ESI
SUPPLEMENTARY MATERIALS

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3-Octyl-1-methylimidazolium bromide, [C₈mim]Br

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- 3-(N-butyl-$N$-methylcarbamoylmethyl)-1,2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_4H_9CH_3NCOCH_2dmim][(CF_3SO_2)N]$ SM8
- $N'$-(N-butyl-$N$-methylcarbamoylmethyl)-$N'$-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide $[C_4H_9CH_3NCOCH_2mpyrrol][(CF_3SO_2)N]$ SM8

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  - Growth of *P. putida* UV4 in shack-flask cultures
  - Growth of micro-organisms on large scale
  - General biotransformation procedure
  - Isolation of the cis-dihydrodiol

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

**Table S1**: Biphasic biotransformation of chlorobenzene in the presence of pyrrolidinium based-ILs with *P. putida* UV4

**Figure S1**: Biotransformation of chlorobenzene by *P. putida* UV4 in the presence of $[C_8mpyrrol][NTf_2]$. 
Figure S2: Biotransformation of chlorobenzene by *P. putida* UV4 in the presence [P\(_{6614}\)][NTf\(_2\)].

Table S2: Biphasic biotransformation of chlorobenzene in the presence of [P\(_{6614}\)][NTf\(_2\)] with *P. putida* UV4

Table S3: Concentration at saturation of hydrophobic ionic liquids in water at 30°C

Table S4: [C\(_n\)mpyrrol][NTf\(_2\)], solubility at saturation in pure water at 30°C.

Table S5: Density and viscosity of novel ILs at 30 °C

Table S6: Biphasic biotransformation of chlorobenzene, 0.98 mmol, in the presence of ester-IL,

Figure S3: Effect of [C\(_8\)mpyrrol]Br & [C\(_8\)dmim]Br on the biotransformation

Figure 3.a to 3.c: Inhibition of oxygen consumption.

Figure E.1 to E.4: Graphical determination of K\(_i\)
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$_4$mim]Br
White crystalline solid is obtained (99% yield).
$^1$H-NMR (300 MHz, $d_1$-Chloroform): $\delta$/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): $\delta$/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$_4$mim]$^+$, 100%), 357 (([C$_4$mim]$_2$Br)$^+$, 10%).

3-Hexyl-1-methylimidazolium bromide, [C$_6$mim]Br
Colourless viscous liquid is obtained (95 % yield).
$^1$H-NMR (300 MHz, $d_1$-Chloroform): $\delta$/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): $\delta$/ppm = 13.3 (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$_6$mim]$^+$, 100%), ES$^-$ m/z (% rel. intensity): 79 (Br, 100%).

3-Octyl-1-methylimidazolium bromide, [C$_8$mim]Br
Colourless viscous liquid is obtained (99.9% yield).
$^1$H-NMR (300 MHz, $d_1$-Chloroform): $\delta$/ppm = 0.79 (t, $J$ = 6.7 Hz, 3H, octyl-CH$_3$); 1.17-1.25 (m, 10H, octyl-(CH$_2$)$_3$); 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): $\delta$/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$_8$mim]$^+$, 100), 471 ([C$_8$mim]$_2$Br)$^+$, 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$_4$dmim]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$_4$dmim]$^+$, 100%). ES$^-$ m/z (% rel. intensity): 79 (Br$^-$, 90%).

3-Hexyl-1,2-dimethylimidazolium bromide, [C$_6$dmim]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$_6$dmim]$^+$, 100%). ES$^-$ m/z (% rel. intensity): 79 (Br$^-$, 90%).

3-Octyl-1,2-dimethylimidazolium bromide, [C$_8$dmim]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$_2$)$_3$); 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\textsuperscript{+}CH\textsubscript{2}); \{7.33 (d, J= 1.2 Hz, 1H); 7.58 (d, J= 1.2 Hz, 1H)\} (4,5-H). \textsuperscript{13}C-NMR (125 MHz, \textit{d}\textsubscript{1}-Chloroform): \textdelta/ppm = 11.1 (C-2-CH\textsubscript{3}); 14.0 (octyl-CH\textsubscript{3}); 22.5, 26.4, 28.9, 29.0, 29.7, 31.6 (octyl-CH\textsubscript{2}); 36.3 (N\textsuperscript{+}CH\textsubscript{3}); 49.1 (N\textsuperscript{+}CH\textsubscript{2}); 120.79, 122.9 (C-4 and C-5); 144.1 (C-2). Electrospray MS: ES\textsuperscript{+} m/z (% rel. intensity): 209 ([C\textsubscript{8}dmim]\textsuperscript{+}, 100%); ES\textsuperscript{-} m/z (% rel. intensity): 79 (Br\textsuperscript{-}, 90%).

3-Decyl-1,2-dimethylimidazolium bromide, [C\textsubscript{10}dmim]Br

White crystalline solid is obtained (96% yield).

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

\textit{N,N}-Butylmethylpyrrolidinium bromide, [C\textsubscript{4}mpyrrol]Br

White crystalline solid is obtained (87% yield).

\textsuperscript{1}H-NMR (300 MHz, \textit{d}\textsubscript{1}-Chloroform): \textdelta/ppm = 0.78 (t, J = 7.3 Hz, 3H, butyl-CH\textsubscript{3}); 1.24 (m, 2H, butyl-CH\textsubscript{2}); 1.57 (m, 2H, butyl-CH\textsubscript{2}); 2.10 (s, 4H, 3-4 CH\textsubscript{2}); 3.08 (s, 3H, N\textsuperscript{+}CH\textsubscript{3}); 3.46 (t, J = 8.4 Hz, 2H, N\textsuperscript{+}CH\textsubscript{2}), 3.63 (s, 4H, 2-5 N\textsuperscript{+}CH\textsubscript{2}). \textsuperscript{13}C-NMR (75 MHz, \textit{d}\textsubscript{1}-Chloroform): \textdelta/ppm = 13.24 (butyl-CH\textsubscript{3}); 19.25 (butyl-CH\textsubscript{2}); 21.2 (4-3 CH\textsubscript{2}), 25.5 (butyl-CH\textsubscript{2}); 48.22 (N\textsuperscript{+}CH\textsubscript{3}); 63.5 (N\textsuperscript{+}CH\textsubscript{2}); 64.0 (5-2 N\textsuperscript{+}CH\textsubscript{2}). Electrospray MS: ES\textsuperscript{+} m/z (% rel. intensity): 142.1 ([C\textsubscript{4}mpyrrol]\textsuperscript{+}, 100%), 365.1 ([[C\textsubscript{4}mpyrrol]\textsubscript{2}Br]\textsuperscript{+}, 10%).

\textit{N,N}-Octylmethylpyrrolidinium bromide, [C\textsubscript{8}mpyrrol]Br

White crystalline solid is obtained (79% yield).

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

Electrospray MS: ES\textsuperscript{+} m/z (% rel. intensity): 198 ([C\textsubscript{8}mpyrrol]\textsuperscript{+}, 100%); ES\textsuperscript{-} m/z (% rel. intensity): 79 (Br\textsuperscript{-}, 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$_4$mim][($\text{CF}_3\text{SO}_2$)$_2$N]

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$_2$); 3.91 (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$_4$mim]$^+$, 100%), 558 ([C$_4$mim]$_2$[($\text{CF}_3\text{SO}_2$)$_2$N]$^+$, 12%).

3-Hexyl-1-methylimidazolium bis(trifluoromethanesulfonyl) imide, [C$_6$mim][($\text{CF}_3\text{SO}_2$)$_2$N]

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$_6$mim]$^+$, 100%), 613.78 ([C$_6$mim]$_2$[($\text{CF}_3\text{SO}_2$)$_2$N]$^+$, 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$_8$mim][($\text{CF}_3\text{SO}_2$)$_2$N]

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$_2$)$_3$); 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 ([C$_8$mim]$^+$, 100%), 670.1 ([C$_8$mim]$_2$[($\text{CF}_3\text{SO}_2$)$_2$N]$^+$, 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\text{10}mim][\text{CF}_3\text{SO}_2\text{N}]

Colourless viscous liquid obtained (90% yield)

$^1$H-NMR (300 MHz, $d_1$-Chloroform): $\delta$/ppm = 0.86 (t, $J = 6.6$ Hz, 3H, decyl-CH$_3$); 1.24-1.30 (m, 14H, decyl-(CH$_2$)$_2$); 1.84 (m, 2H, decyl-CH$_2$); 3.92 (s, 3H, N+CH$_3$); 4.14 (t, $J = 7.5$ Hz, 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): $\delta$/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\text{10}mim]$^+$, 100%), 726.40 ([C\text{10}mim]$_2$[\text{CF}_3\text{SO}_2\text{N}]$^+$, 25%). ES$^-$ $m/z$ (% rel. intensity): 280.11 ([\text{CF}_3\text{SO}_2\text{N}]-, 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\text{2}dmim][\text{CF}_3\text{SO}_2\text{N}]

Colourless viscous liquid obtained (93% yield).

$^1$H-NMR (500 MHz, $d_6$-Acetone): $\delta$/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): $\delta$/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\text{2}dmim]$^+$, 100%), 726.40 ([C\text{2}dmim]$_2$[\text{CF}_3\text{SO}_2\text{N}]$^+$, 25%). ES$^-$ $m/z$ (% rel. intensity): 279.91 ([\text{CF}_3\text{SO}_2\text{N}]-, 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\text{4}dmim][\text{CF}_3\text{SO}_2\text{N}]

Colourless viscous liquid obtained (98% yield).

$^1$H-NMR (300 MHz, $d_1$-Chloroform): $\delta$/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): $\delta$/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\text{4}dmim]$^+$, 100%), 585.9 ([C\text{4}dmim]$_2$[\text{CF}_3\text{SO}_2\text{N}]$^+$, 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, [C₆dmim][CF₃SO₂]N

Colourless viscous liquid obtained (95% yield)

H-NMR (300 MHz, d₇-Chloroform): δ/ppm = 0.85 (t, J = 6.7 Hz, 3H, hexyl-CH₃); 1.29 (m, 6H, hexyl-(CH₂)₃); 1.74 (m, 2H, hexyl-CH₂); 2.55 (s, 3H, 2-CH₃), 3.75 (s, 3H, N⁺CH₃); 4.00 (t, J = 7.5 Hz, 2H, N⁺CH₂); [7.15 (d, J= 2.1 Hz ,1H); 7.17 (d, J= 2.1 Hz, 1H)] (4,5-H). C-NMR (75 MHz, d₇-Chloroform): δ/ppm = 9.4 (hexyl-CH₃); 13.7 (C-2-CH₃); 22.2, 25.8, 29.4, 30.9 (hexyl-CH₂); 35.1 (N⁺CH₃); 48.7 (N⁺CH₂); 121.8-117.7 (CF₃); 120.7, 122.4 (C-4 and C-5); 143.6 (C-2). Electrospray MS: ES⁺ m/z (% rel. intensity): 186.77 ([C₆dmim]⁺, 100%). ES⁻ m/z (% rel. intensity): 280.11 ([CF₃SO₂]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, [C₈dmim][CF₃SO₂]N

Colourless viscous liquid obtained (90.0% yield).

H-NMR (300 MHz, d₇-Chloroform): δ/ppm = 0.87 (t, J = 6.6 Hz, 3H, octyl-CH₃); 1.26-1.32 (m, 10H, octyl-(CH₂)₅); 1.79 (m, 2H, octyl-CH₂); 2.61 (s, 3H, 2-CH₃), 3.81 (s, 3H, N⁺CH₃); 4.04 (t, J = 7.8 Hz, 2H, N⁺CH₂); [7.15 (d, J= 2.1 Hz ,1H); 7.20 (d, J= 2.1 Hz, 1H)] (4,5-H). C-NMR (75 MHz, d₇-Chloroform): δ/ppm = 9.6 (C-2-CH₃); 14.0 (octyl-CH₃); 22.5, 26.3, 28.9, 28.9, 29.5, 31.6 (octyl-CH₂); 35.4 (N⁺CH₃); 48.9 (N⁺CH₂); 121.8-117.7 (CF₃); 120.7, 122.54 (C-4 and C-5); 143.6 (C-2). Electrospray MS: ES⁺ m/z (% rel. intensity): 208.9 ([C₈dmim]⁺, 100%), 279.9 ([CF₃SO₂]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, [C₁₀dmim][CF₃SO₂]N

Colourless viscous liquid obtained (92.0% yield)

H-NMR (300 MHz, d₇-Chloroform): δ/ppm = 0.86 (t, J = 6.7 Hz, 3H, decyl-CH₃); 1.24-1.32 (m, 14H, decyl-(CH₂)₇); 1.51 (m, 2H, decyl-CH₂); 2.61 (s, 3H, 2-CH₃), 3.81 (s, 3H, N⁺CH₃); 4.04 (t, J = 7.5 Hz, 2H, N⁺CH₂); [7.40 (d, J= 2.1 Hz ,1H); 7.70 (d, J= 2.1 Hz, 1H)] (4,5-H). C-NMR (75 MHz, d₇-Chloroform): δ/ppm = 11.1 (decyl-CH₃); 14.1 (decyl-CH₃); 22.6, 26.4, 29.0, 29.2, 29.3, 29.4, 29.8, 31.8 (decyl-CH₂); 36.3 (N⁺CH₃); 49.0 (N⁺CH₂); 121.8-117.7 (CF₃); 120.9, 123.1 (C-4 and C-5); 143.8 (C-2). Electrospray MS: ES⁺ m/z (% rel. intensity): 237.19 ([C₁₀dmim]⁺, 100%). ES⁻ m/z (% rel. intensity): 280.12 ([CF₃SO₂]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, [C₄mpyrrol][CF₃SO₂]N

Colourless viscous liquid obtained (84 % yield).

H-NMR (300 MHz, d₇-Acetone): δ/ppm = 0.99 (t, J = 7.2 Hz, 3H, butyl-CH₃); 1.44 (m, 2H, butyl-CH₂); 1.92 (m, 2H, butyl-CH₂); 2.33 (s, 4H, 3-4 CH₂); 3.28 (s, 3H, N⁺CH₃); 3.56 (t, J = 8.1 Hz, 2H, N⁺CH₂), 3.75
(s, 4H, 2-5 N°CH₂). \(^{13}\)C-NMR (75 MHz, \(d_6\)-Acetone): \(\delta/\text{ppm} = 14.8\) (butyl-CH₃); 21.4 (butyl-CH₂); 23.4 (4-3 CH₂), 27.3 (butyl-CH₂); 50.0 (N°CH₃); 66.0 (N°CH₂); 66.3 (5-2 N°CH₂); 117.6-121.8 (CF₃). Electrospray MS: \(\text{ES}^+ m/z\) (% rel. intensity): 142.1 ([C₄mpyrrol]⁺, 100%). ES⁻ m/z (% rel. intensity): 279.9 ([CF₃SO₂]⁻, 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, [C₈mpyrrol][(CF₃SO₂)₂N]

Colourless viscous liquid obtained (85.0% yield).

\(^1\)H-NMR (300 MHz, \(d_1\)-Chloroform): \(\delta/\text{ppm} = 0.87\) (t, \(J = 6.9\) Hz, 3H, octyl-CH₃); 1.26-1.32 (m, 10H, octyl-(CH₂)₅); 1.73 (m, 2H, octyl-CH₂); 2.24 (s, 4H, 3-4 CH₂); 3.02 (s, 3H, N°CH₃); 3.25 (t, \(J = 8.4\) Hz, 2H, 2-5 N°CH₂).

\(^{13}\)C-NMR (75 MHz, \(d_1\)-Chloroform): \(\delta/\text{ppm} = 13.8\) (octyl-CH₃); 21.3 (4-3 CH₂); 22.4, 23.6, 26.0, 28.8, 28.7, 31.4 (octyl-CH₂); 48.2 (N°CH₃); 64.4 (N°CH₂); 64.7 (5-2 N°CH₂); 117.6-121.8 (CF₃). Electrospray MS: \(\text{ES}^+ m/z\) (% rel. intensity): 198.2 ([C₈mpyrrol]⁺, 100%), 592.0 ([C₈mpyrrol]⁺, 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 [P₆₆₆₁₄][(CF₃SO₂)₂N]

Colourless viscous liquid obtained (95.0% yield).

\(^1\)H-NMR (300 MHz, \(d_1\)-Chloroform): \(\delta/\text{ppm} = 0.86\) (t, \(J = 6.9\) Hz, 3H, tetradecyl-CH₃); 0.88 (t, \(J = 6.4\) Hz, 9H, hexyl-CH₂); 1.18-1.36 (m, 32H), 1.38-1.56 (m, 16H) (hexyl/tetradecyl-CH₂); 1.98-2.19 (m, 8H, P⁺CH₂).

\(^{13}\)C-NMR (75 MHz, \(d_1\)-Chloroform): \(\delta/\text{ppm} = 13.91, 14.19\) (hexyl- and tetradecyl-CH₃); 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-CH₂); 120.00 (q, \(J_{CF} = 320\) Hz, CF₃). \(^{31}\)P-NMR (121 MHz, \(d_1\)-Chloroform): \(\delta/\text{ppm} = 34.97\). Electrospray MS: \(\text{ES}^+ m/z\) (% rel. intensity): 483.5 ([P₆₆₆₁₄]⁺, 100%), 1247.0 ([P₆₆₆₁₄]⁺, 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 cm³) 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 cm³). The organic phase was washed with distilled water (3 x 50 cm³), saturated ammonium chloride (3 x 50 cm³), saturated sodium bicarbonate (3 x 50 cm³) and brine (2 x 50 cm³) 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 cm³) and filtered.

Hexylbromoacetate
Colourless liquid obtained (86.0% yield); Bp(3 mmHg): 90 ºC; ¹H-NMR (300 MHz, d$_2$-Chloroform): δ/ppm = 4.17 (t, J = 6.7 Hz, 2H, CH$_2$O), 3.83 (s, 2H, CH$_2$Br), 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$_3$); ¹³C-NMR (75 MHz, d$_2$-Chloroform): δ/ppm= 167.2(CO), 66.4 (CH$_2$Br), 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; ¹H-NMR (300 MHz, d$_2$-Chloroform): δ/ppm = 4.15 (t, J = 6.7 Hz, 2H, CH$_2$O), 3.81 (s, 2H, CH$_2$Br), 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$_3$); ¹³C-NMR (75 MHz, d$_2$-Chloroform): δ/ppm= 167.3(CO), 66.4 (CH$_2$Br), 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) *Denote both configurations; ¹H-NMR (300 MHz, d$_2$-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$_2$); ¹³C-NMR (75 MHz, d$_2$-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$_2$Br); 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$_6$H$_{13}$OCOCH$_2$dmim]Br
Yellow solid obtained (100% yield)
¹H-NMR (300 MHz, d$_2$-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).
C-NMR (75 MHz, $d_1$-Chloroform): $\delta/$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$_6$H$_{13}$OCOCH$_2$dmim]$^+$, 100%), 559.27 ([C$_6$H$_{13}$OCOCH$_2$dmim]$_2$Br$^+$, 10%). ES$^-$ m/z (% rel. intensity): 80.91 (Br$^-$, 100%).

$N$-Hexoxycarbonylmethyl-$N$-methylpyrrolidinium bromide, [C$_6$H$_{13}$OCOCH$_2$mpyrrol]Br
Yellow solid obtained (99.0% yield)

$^1$H-NMR (300 MHz, $d_1$-Chloroform): $\delta/$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$_2$); 3.80-3.73 (m, 4H, 2-5 N$^+$CH$_2$); 4.29 (s, 2H, N$^+$CH$_2$). $^{13}$C-NMR (75 MHz, $d_1$-Chloroform): $\delta/$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$_6$H$_{13}$OCOCH$_2$mpyrrol]$^+$, 100%).

ES$^-$ m/z (% rel. intensity): 80.91 (Br$^-$, 100%).

3-Octoxycarbonylmethyl-1,2-dimethylimidazolium bromide, [C$_8$H$_{17}$OCOCH$_2$dmim]Br
Yellow solid obtained (73.1%)

$^1$H-NMR (300 MHz, $d_1$-Chloroform): $\delta/$ppm $= 0.87$ (t, $J = 6.0$ Hz, 3H, octyl-CH$_3$); 1.29-1.26 (m, 10H, octyl-(CH$_2$)$_3$); 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)$_2$.

$^{13}$C-NMR (75 MHz, $d_1$-Chloroform): $\delta/$ppm = 11.2 (2-CH$_3$); 14.0 (octyl-CH$_3$); 22.5, 25.8, 28.3, 29.1 (2xC), 31.7 (octyl-CH$_2$); 36.0 (N$^+$CH$_3$); 60.1 (OCH$_2$); 67.0 (N$^+$CH$_2$); 122.2, 122.9 (C-4 and C-5); 145.7 (C-2); 166.2 (CO). Electrospray mass spectrum: ES$^+$ m/z (% rel. intensity): 256.20 ([C$_8$H$_{17}$OCOCH$_2$dmim]$^+$, 100%), 613.36 ([C$_8$H$_{17}$OCOCH$_2$dmim]$_2$Br$^+$, 10%). ES$^-$ m/z (% rel. intensity): 80.91 (Br$^-$, 100%).

$N$-Octoxycarbonylmethyl-$N$-methylpyrrolidinium bromide, [C$_8$H$_{17}$OCOCH$_2$mpyrrol]Br
Yellow solid obtained (99.5% yields)

$^1$H-NMR (300 MHz, $d_1$-Chloroform): $\delta/$ppm $= 0.86$ (t, $J = 6.7$ Hz, 3H, octyl-CH$_3$); 1.24-1.26 (m, 10H, octyl-(CH$_2$)$_3$); 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$_2$); 5.01 (s, 2H, N$^+$CH$_2$). $^{13}$C-NMR (75 MHz, $d_1$-Chloroform): $\delta/$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$_3$); 60.1 (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$_8$H$_{17}$OCOCH$_2$mpyrrol]$^+$, 100%), 613.36 ([C$_8$H$_{17}$OCOCH$_2$mpyrrol]$_2$Br$^+$, 10%). ES$^-$ m/z (% rel. intensity): 80.91 (Br$^-$, 100%).
3-(N-butyl-N-methylcarbamoylmethyl)-1,2-dimethylimidazolium bromide, [C₆H₉CH₃NCOCH₂dmim]Br
Brown viscous liquid obtained (50.0% yield)

*Denote both configurations

$^1$H-NMR (300 MHz, $d_J$-Chloroform): $\delta$/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$^+$CH$_2$); 5.10 (minor, s, 2H, N$^+$CH$_2$), 5.17 (major, s, 2H, N$^+$CH$_2$). $^{13}$C-NMR (75 MHz, $d_J$-Chloroform): $\delta$/ppm = 13.7 (butyl-CH$_3$); 20.0 (NCH$_3$); 29.1 (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 ([C₆H₉CH₃NCOCH₂dmim]$^+$, 100%). ES$^-$ m/z (% rel. intensity): 80.91 (Br$, 100\%$).

$N'$-(N-butyl-N-methylcarbamoylmethyl)-$N'$-methylpyrrolidinium bromide, [C₆H₉CH₃NCOCH₂mpyrrol]Br
Brown viscous liquid obtained (76.0% yield)

$^1$H-NMR (300 MHz, $d_J$-Chloroform): $\delta$/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$^+$CH$_2$); 5.10 (minor, s, 2H, N$^+$CH$_2$), 5.17 (major, s, 2H, N$^+$CH$_2$). $^{13}$C-NMR (75 MHz, $d_J$-Chloroform): $\delta$/ppm = 13.7 (butyl-CH$_3$); 20.0 (NCH$_3$); 29.1 (butyl-CH$_2$); 36.7 (N$^+$CH$_3$); 48.7 (NCH$_2$); 51.2 (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 ([C₆H₉CH₃NCOCH₂mpyrrol]$^+$, 100%). ES$^-$ m/z (% rel. intensity): 80.91 (Br$, 100\%$).

Metathesis of ester and amide precursors, [cation][(CF₃SO$_2$)$_2$N]

3-Hexoxycarbonylmethyl-1,2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, [C₆H₁₃OCOCH₂dmim][(CF₃SO₂)$_2$N]
Yellow viscous liquid obtained (67.0% yield)
1H-NMR (300 MHz, $d_2$-Chloroform): $\delta$/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, $d_2$-Chloroform): $\delta$/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$_6$H$_{13}$OCOCH$_2$ mim]$^+$, 100%). ES$^-$ m/z (% rel. intensity): 758.26 ([C$_6$H$_{13}$OCOCH$_2$ mim]$_2$[(CF$_3$SO$_2$)$_2$N]$^-$, 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$_8$H$_{17}$OCOCH$_2$dmim][(CF$_3$SO$_2$)$_2$N]

Yellow viscous liquid obtained (85.0% yield)

1H-NMR (300 MHz, $d_2$-Chloroform): $\delta$/ppm = 0.87 (t, $J = 6.2$ Hz, 3H, octyl -CH$_3$); 1.26-1.29 (m, 10H, octyl -(CH$_2$)$_3$); 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, $d_2$-Chloroform): $\delta$/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$_8$H$_{17}$OCOCH$_2$ dmim]$^+$, 100%), 814.34 ([C$_8$H$_{17}$OCOCH$_2$ min]$_2$[(CF$_3$SO$_2$)$_2$N]$^+$, 20%). ES$^-$ m/z (% rel. intensity): 279.9 ([CF$_3$SO$_2$]$^-$, 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$_6$H$_{13}$OCOCH$_2$ mpyrrol][(CF$_3$SO$_2$)$_2$N]

Faint yellow viscous liquid obtained (85.0% yield)

1H-NMR (300 MHz, $d_2$-Chloroform): $\delta$/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, $d_2$-Chloroform): $\delta$/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$_6$H$_{13}$OCOCH$_2$ mpyrrol]$^+$, 100%), 736.30 ([C$_6$H$_{13}$OCOCH$_2$ mpyrrol]$_2$[(CF$_3$SO$_2$)$_2$N]$^+$, 20%). ES$^-$ m/z (% rel. intensity): 279.90 ([CF$_3$SO$_2$]$^-$, 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-methylpyrroldinium bis(trifluoromethanesulfonyl) imide,**

[C₈H₁₇OCOCH₃mpyrrol][[(CF₃SO₂)₂N]]

Yellow viscous liquid obtained (80.0% yield)

1H-NMR (300 MHz, d₇-Chloroform): δ/ppm = 0.87 (t, J = 6.7 Hz, 3H, octyl-CH₃); 1.29-1.26 (m, 10H, octyl-(CH₂)₃); 1.65 (m, 2H, octyl-CH₂); 2.25-2.31 (m, 4H, 3-4 CH₂); 3.27 (s, 3H, N⁺CH₃); 3.72-3.83 (m, 4H, 2-5 N⁺CH₂); 4.21 (J = 6.9 Hz, 2H, OCH₂); 4.28 (s, 2H, N⁺CH₂). ¹³C-NMR (75 MHz, d₇-Chloroform): δ/ppm = 14.2 (octyl-CH₃); 21.7 (3-4 CH₂); 22.4, 25.7, 28.3, 29.2 (2xC), 31.9 (octyl-CH₂); 49.7 (N⁺CH₃); 62.4 (OCH₂); 65.9 (5-2 N⁺CH₂); 67.3 (N⁺CH₂); 117.8-122.0 (CF₃); 164.7 (CO). Electrospray mass spectrum: ES⁺ m/z (% rel. intensity): 256.21 ([C₈H₁₇OCOCH₃mpyrrol]⁺, 100%), 792.37 ([C₈H₁₇OCOCH₃mpyrrol][[(CF₃SO₂)₂N]]⁺, 15%). ES⁻ m/z (% rel. intensity): 279.9 ([[(CF₃SO₂)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,

[C₄H₉CH₃NCOCH₃dmim][[(CF₃SO₂)₂N]]

Brown viscous liquid obtained (75.0% yield) *Denote both configurations

1H-NMR (300 MHz, d₇-Chloroform): δ/ppm = 0.92 (major, t, J = 7.3 Hz, 3H, butyl-CH₃) 0.99 (minor, t, J = 7.2 Hz, 3H, butyl-CH₃); 1.23-1.68 (m, 4H*, butyl-CH₂); 2.71 (s*, 3H, 2-CH₃); 3.07 (major, s, 3H, NCH₃); 2.96 (minor, s, 3H, NCH₃); 3.33 (minor, t, J = 7.4 Hz, 2H, NCH₂) 3.38 (major, t, J = 6.5 Hz, 2H, NCH₂); 3.79 (major, s, 3H, N⁺CH₃) 3.80 (minor, s, 3H, N⁺CH₃); 5.06 (major, s, 2H, N⁺CH₂) 5.07 (minor, s, 2H, N⁺CH₂); 7.13 (m*, 1H), 7.19 (m*, 1H) (4,5-H). ¹³C-NMR (75 MHz, d₇-Chloroform): δ/ppm = 10.0 (*N⁺CH₃); 13.7* (butyl-CH₃); 19.8 (minor, NCH₃), 19.9 (major, NCH₃); 29.0(major), 30.3 (minor), 33.8* (butyl-CH₂); 34.3 (minor, N⁺CH₃) 35.4 (major, N⁺CH₃); 49.1 (minor, NCH₂) 48.4 (major, NCH₂); 50.0 (*N⁺CH₂); 117.6-118.6 (CF₃); 121.5-122.7 (C-4* and C-5*); 137.8 (C-2); 164.7 (*CO). Electrospray mass spectrum: ES⁺ m/z (% rel. intensity): 224.17 ([C₄H₉CH₃NCOCH₃dmim]⁺, 100%). ES⁻ m/z (% rel. intensity): 279.91 ([[(CF₃SO₂)₂N]⁻, 100%])

Elemental analysis: Calculated (%): C 33.3, H 4.4, N 11.1; Results (%): C 36.1, H 6.4, N 11.1

**N’-(N-butyl-N-methylcarbamoylmethyl)-N’-methylpyrroldinium bis(trifluoromethanesulfonyl) imide**

[C₄H₉CH₃NCOCH₃mpyrrol][[(CF₃SO₂)₂N]]

Brown viscous liquid obtained (85.0% yield) *Denote both configurations

1H-NMR (300 MHz, d₇-Chloroform): δ/ppm = 0.93 (major, t, J = 7.3 Hz, 3H, butyl-CH₃); 0.95 (minor, t, J = 7.2 Hz, 3H, butyl-CH₃); 1.24-158 (m*, 4H, butyl-(CH₂)₂); 2.17-2.34 (m, 4H*, 3-4 CH₂); 2.94 (minor, 3H, NCH₃); 2.96 (major, 3H, NCH₃); 3.07 (minor, s, 3H, N⁺CH₃), 3.29 (major s, 3H*, N⁺CH₃); 3.23 (major, J = 7.6 Hz, 2H, NCH₂); 3.29 (major s, 3H*, N⁺CH₃); 3.36 (major, t, J = 7.6 Hz, 2H, NCH₂); 3.69-3.91 (m*, 4H,
2-5 N\textsubscript{+}\textsubscript{CH\textsubscript{2}}); 4.27 (minor, s, 2H, N\textsubscript{+}\textsubscript{CH\textsubscript{2}}), 4.35 (major, s, 2H, N\textsubscript{+}\textsubscript{CH\textsubscript{2}}). \textsuperscript{13}C-NMR (75 MHz, \textit{d}\textsubscript{7}\textsuperscript{+}Chloroform): \(\delta/\text{ppm} = 13.7\) (minor, butyl-CH\textsubscript{3}) 13.6 (major, butyl-CH\textsubscript{3}); 19.7 (minor, 4-3 CH\textsubscript{2}), 19.9 (major, 4-3 CH\textsubscript{2}); 21.5 (major, NCH\textsubscript{3}); 21.4 (minor, NCH\textsubscript{3}); 28.9 (major), 30.1 (minor) 33.5 (minor), 34.3 (major) (butyl-CH\textsubscript{2}); 48.1 (minor, N\textsubscript{+}\textsubscript{CH\textsubscript{2}}), 49.6 (major, N\textsubscript{+}\textsubscript{CH\textsubscript{2}}); 63.0 (minor, N\textsubscript{+}\textsubscript{CH\textsubscript{2}}), 63.1 (major, N\textsubscript{+}\textsubscript{CH\textsubscript{2}}); 65.9 (major, 2-5 N\textsubscript{+}\textsubscript{CH\textsubscript{2}}), 66.0 (minor, 2-5N\textsubscript{+}\textsubscript{CH\textsubscript{2}}); 117.6-118.6 (CF\textsubscript{3}); 162.5 (CO). Electrospray mass spectrum: ES\textsuperscript{+} m/z (\% rel. intensity): 213.19 ([C\textsubscript{4}H\textsubscript{9}CH\textsubscript{3}NCOCH\textsubscript{2}mpyrrol]\textsuperscript{+}, 100%). ES\textsuperscript{-} m/z (\% rel. intensity): 279.91 ([(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N]\textsuperscript{-}, 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:

\textit{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 \textit{P. putida} UV4 in shack-flask cultures:

In these experiments the medium used contained 0.96 g L\textsuperscript{-1} KH\textsubscript{2}PO\textsubscript{4}, 1.23 g L\textsuperscript{-1} K\textsubscript{2}HPO\textsubscript{4}, 3.00 g L\textsuperscript{-1} NH\textsubscript{4}Cl, 0.40 g L\textsuperscript{-1} MgSO\textsubscript{4}\textsubscript{7H\textsubscript{2}}O and 1.9 cm\textsuperscript{3} (trace elements solution) L\textsuperscript{-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\textsubscript{2}EDTA, 2.20 g ZnSO\textsubscript{4}7H\textsubscript{2}O, 5.54 g CaCl\textsubscript{2}, 5.06 g MnCl\textsubscript{2}4H\textsubscript{2}O, 5.00 g FeSO\textsubscript{4}7H\textsubscript{2}O, 1.10 g (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}4H\textsubscript{2}O, 1.57 g CuSO\textsubscript{4}5H\textsubscript{2}O and 1.61 g CoCl\textsubscript{2}6H\textsubscript{2}O per litre of distilled water. The Na\textsubscript{2}EDTA 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 \degree C on a L.H.E. vari-speed orbital shaker, at 150 rpm. \textit{P. putida} UV4 was grown on sodium pyruvate (5.0 g L\textsuperscript{-1}) as carbon and energy source.

Growth of micro-organisms on large scale:

\textit{P. putida} UV4 was grown on the same medium. Although, the carbon and energy source used was then D-glucose (5.0 g L\textsuperscript{-1}). The concentration of phosphate was increased to 6.85 g KH\textsubscript{2}PO\textsubscript{4} L\textsuperscript{-1}, for \textit{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 upon the type of organisms. The dry cell concentrations were within a narrow range of 0.5 to 0.8 g L$^{-1}$ dwc. 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:
Biotransformations on halobenzenes (0.50 cm$^3$) were performed in 500 cm$^3$ (x3) shake flasks containing 200 cm$^3$ 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 cm$^3$ x 5). The mother liquor was concentrated and purified by flash chromatography (20%:80% ethyl acetate:hexane) yielding to only the cis-(1S,2S)-1,2-dihydroxy-3-halocyclohexa-3,5-diene.$^a$


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

<table>
<thead>
<tr>
<th></th>
<th>Initial reaction rate – mM h$^{-1}$</th>
<th>Conversion 6 h - %</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>P. putida</em> UV4</td>
<td>0.47 ± 0.01</td>
<td>36.8 ± 0.6</td>
</tr>
<tr>
<td>[C$_8$dmim][NTf$_2$]</td>
<td>2.10 ± 0.06</td>
<td>47.8 ± 0.2</td>
</tr>
<tr>
<td>[C$_4$mpyrrol][NTf$_2$]</td>
<td>N/O</td>
<td>N/O</td>
</tr>
<tr>
<td>[C$_8$mpyrrol][NTf$_2$]</td>
<td>0.56 ± 0.00</td>
<td>15.4 ± 0.0</td>
</tr>
</tbody>
</table>

**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$^{-1}$ dwc. Calculated values show mean of duplicate samples.
Figure S1: Biotransformation of chlorobenzene by *P. putida* UV4 in the presence of [C₈mpyrrol][NTf₂]. Conversion of 0.98 mmol chlorobenzene in a buffer pH 7.2, (▲) without IL and biphasic system volumetric ratio 2.0% (Vᵢl/Vₐq) hydrophobic-IL (●) [C₈mpyrrol][NTf₂] (■) [C₈dmim][NTf₂]. OD₆₀₀ = 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 [P₆₆₆₁₄][NTf₂]. Conversion of 0.98 mmol chlorobenzene in a buffer (pH 7.2), (▲) without IL and biphasic system volumetric ratio 2.0% (Vᵢl/Vₐq) hydrophobic-IL (●) [P₆₆₆₁₄][NTf₂] (■) [C₈dmim][NTf₂]. OD₆₀₀ = 0.9 or 0.35 g L⁻¹ dcw – Data points show mean of duplicate samples.
Table S2: Biphasic biotransformation of chlorobenzene in the presence of [P66614][NTf₂] with *P. putida* UV4, 2.0% (V<sub>IL</sub>/V<sub>aq</sub>) IL, for OD<sub>600</sub> = 0.9 or 0.35 g L<sup>-1</sup> dw. Calculated values show mean of duplicate samples.

<table>
<thead>
<tr>
<th></th>
<th>Initial reaction rate – mM h&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Conversion 6 h - %</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>P. putida</em> UV4</td>
<td>0.47 ± 0.01</td>
<td>36.8 ± 0.6</td>
</tr>
<tr>
<td>[C&lt;sub&gt;8&lt;/sub&gt;dmim][NTf₂]</td>
<td>2.10 ± 0.06</td>
<td>47.8 ± 0.2</td>
</tr>
<tr>
<td>[P&lt;sub&gt;66614&lt;/sub&gt;][NTf₂]</td>
<td>0.54 ± 0.03</td>
<td>35.5 ± 0.7</td>
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Ionic liquids solubility table:

<table>
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<tr>
<th></th>
<th>UV spectroscopy – mmol L&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>IC – mmol L&lt;sup&gt;-1&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>(cation)</td>
<td>(anion)</td>
</tr>
<tr>
<td>[C&lt;sub&gt;2&lt;/sub&gt;mim][NTf₂]</td>
<td>48.22 ± 0.20</td>
<td>51.64 ± 2.53</td>
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<tr>
<td>[C&lt;sub&gt;4&lt;/sub&gt;mim][NTf₂]</td>
<td>16.33 ± 0.18</td>
<td>17.77 ± 0.32</td>
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<tr>
<td>[C&lt;sub&gt;6&lt;/sub&gt;mim][NTf₂]</td>
<td>5.16 ± 0.11</td>
<td>5.57 ± 0.04</td>
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<tr>
<td>[C&lt;sub&gt;8&lt;/sub&gt;mim][NTf₂]</td>
<td>1.38 ± 0.02</td>
<td>1.67 ± 0.02</td>
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<tr>
<td>[C&lt;sub&gt;2&lt;/sub&gt;dmim][NTf₂]</td>
<td>32.18 ± 0.21</td>
<td>32.50 ± 0.41</td>
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<tr>
<td>[C&lt;sub&gt;4&lt;/sub&gt;dmim][NTf₂]</td>
<td>13.42 ± 0.04</td>
<td>12.42 ± 0.20</td>
</tr>
<tr>
<td>[C&lt;sub&gt;6&lt;/sub&gt;dmim][NTf₂]</td>
<td>3.94 ± 0.02</td>
<td>3.47 ± 0.06</td>
</tr>
<tr>
<td>[C&lt;sub&gt;8&lt;/sub&gt;dmim][NTf₂]</td>
<td>1.06 ± 0.01</td>
<td>1.38 ± 0.21</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th></th>
<th>Solubility in water - mmol L&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
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<tr>
<td>[C&lt;sub&gt;4&lt;/sub&gt;mpyrrol][NTf₂]</td>
<td>12.82 ± 0.86</td>
</tr>
<tr>
<td>[C&lt;sub&gt;8&lt;/sub&gt;mpyrrol][NTf₂]</td>
<td>0.92 ± 0.01</td>
</tr>
</tbody>
</table>

Table S4: [C<sub>n</sub>mpyrrol][NTf₂], solubility at saturation in pure water at 30ºC. Quantification method using ion chromatography, [NTf₂]: Calculated values show mean of duplicate samples.
Table S5: Density and viscosity of novel ILs at 30 ºC

<table>
<thead>
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<th>IL Formula</th>
<th>Density – g cm⁻³</th>
<th>Viscosity - cPs</th>
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<tbody>
<tr>
<td>[C₄H₉CH₃NCOCH₂dmim][NTf₂]</td>
<td>1.3906</td>
<td>981.4</td>
</tr>
<tr>
<td>[C₄H₉CH₃NCOCH₂mpyrrol][NTf₂]</td>
<td>1.3714</td>
<td>414.2</td>
</tr>
<tr>
<td>[C₆H₁₃OCOCH₂dmim][NTf₂]</td>
<td>1.3609</td>
<td>299.1</td>
</tr>
<tr>
<td>[C₆H₁₇OCOCH₂dmim][NTf₂]</td>
<td>1.3177</td>
<td>340.7</td>
</tr>
<tr>
<td>[C₆H₁₃OCOCH₂mpyrrol][NTf₂]</td>
<td>1.3349</td>
<td>149.9</td>
</tr>
<tr>
<td>[C₈H₁₇OCOCH₂mpyrrol][NTf₂]</td>
<td>1.2881</td>
<td>252.8</td>
</tr>
<tr>
<td>[C₈dmim][NTf₂]</td>
<td>1.2938</td>
<td>114.2</td>
</tr>
<tr>
<td>[C₈mpyrrol][NTf₂]</td>
<td>1.2796</td>
<td>144</td>
</tr>
</tbody>
</table>

Table S6: Biphasic biotransformation of chlorobenzene, 0.98 mmol, in the presence of ester-IL, 0.15% (V̂_IL/V̂_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.

<table>
<thead>
<tr>
<th>IL Formula</th>
<th>Initial reaction rate – mM h⁻¹</th>
<th>Conversion 6 h - %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P. putida UV4</td>
<td>0.20 ± 0.02</td>
<td>33.4% ± 0.4%</td>
</tr>
<tr>
<td>[C₈dmim][NTf₂]</td>
<td>1.42 ± 0.11</td>
<td>67.6% ± 1.7%</td>
</tr>
<tr>
<td>[C₆H₁₃OCOCH₂dmim][NTf₂]</td>
<td>1.49 ± 0.05</td>
<td>67.2% ± 2.3%</td>
</tr>
<tr>
<td>[C₈H₁₇OCOCH₂dmim][NTf₂]</td>
<td>1.24 ± 0.23</td>
<td>60.1% ± 5.8%</td>
</tr>
</tbody>
</table>
Figure S3: Effect of [C₈mpyrrol]Br & [C₈dmim]Br on the biotransformation of 0.98 mmol of chlorobenzene (pH 7.2) by *P. putida* UV4. Symbols (▲) Without inhibitor, (∆) 4 mM [C₈mpyrrol]Br and (●) 2.4 mM [C₈dmim]Br. OD₆0₀ = 1.8 or 0.70 g L⁻¹ dw. Data points show mean of duplicate samples.

Inhibition of oxygen consumption.

![Figure 3a](image1.png)  
**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, (○) 7.8, (○) 11.9 and (●) 15.5 mM. OD₆0₀ = 1.6 or 0.62 g L⁻¹ dw. Data points show mean of duplicate samples.

![Figure 3b](image2.png)  
**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. OD₆0₀ = 1.7 or 0.66 g L⁻¹ dw. Data points show mean of duplicate samples.

![Figure 3c](image3.png)  
**Figure 3c:** Inhibition of oxygen consumption of *P. putida* UV4 by [C₈dmim]Br & [C₈mpyrrol]Br. Symbol: (▲) Without inhibitor, i) Variation of the concentration of [C₈dmim]Br symbols: (●) 2, (●) 4, (●) 8 and (●) 12 mM. ii) Variation of the concentration of [C₈mpyrrol]Br symbols: (●) 4, (●) 8, (●) 10 and (●) 12 mM. OD₆0₀ = 1.7 or 0.66 g L⁻¹ dw. 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$_8$dmim]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 $[C_8mpyrro]Br$. P. putida UV4, OD$_{600}$: 1.7 or 0.66 g/L dcw. Data points show mean of duplicate samples.