Supplementary Material for Chemical Communications

Supporting Information

Design and synthesis of hydrophobic and chiral anions from amino acids as precursor for functional ionic liquids

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Characterization and physico-chemical properties of trifluoromethanesulfonyl amino acid methyl ester

[I-Ala]: ***N-Trifluoromethanesulfonylalanine methyl ester***

From 3.2g (36 mmol) of L-alanine and equi-molar of trifluoromethanesulfonic anhydride, 5.2g of **I**-Ala was obtained (Yield: 63%).

^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 1.54 (d, *J*=3.8 Hz, 3H), 3.83 (s, 3H), 4.32 (q, *J*=10.8Hz, 1H), 5.68 (s, 1H). ESI–TOF–MS: Calcd. for $C_5H_8NO_4SF_3$ $[M\text{-}1+2Na]^+$: *m/z* = 280.15; Found: 280.06, $[M\text{-}1]^-$: *m/z* = 234.17; Found: 233.82.

$[\alpha]_D^{25}$ = -26.3 (*c* = 1.0 g/ 100 ml MeOH), T_m= 68.0 °C, T_{decomp} = 119.6 °C.

[I-Val]: ***N-Trifluoromethanesulfonylvaline methyl ester***

From 4.2g (36 mmol) of L-valine and equi-molar of trifluoromethanesulfonic anhydride, 4.9g of **I**-Val was obtained (Yield: 53%).

^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 0.93 (d, *J*=3.5 Hz, 3H), 1.05(d, *J*=3.3 Hz, 3H), 2.22(m, *J*=16 Hz, 1H), 3.81 (s, 3H), 4.08 (q, *J*=6.5 Hz, 1H), 5.68 (d, *J*=4Hz, 1H). ESI–TOF–MS: Calcd. for $C_7H_{12}NO_4SF_3$ $[M\text{-}1+2Na]^+$: *m/z* = 308.21; Found: 308.09, $[M\text{-}1]^-$: *m/z* = 262.23; Found : 261.83.

$[\alpha]_D^{25}$ = -9.1 (*c* = 1.0 g/ 100 ml MeOH), T_m= 44.6 °C, T_{decomp} = 137.0 °C.

[I-Leu]: ***N-Trifluoromethanesulfonylleucine methyl ester***

From 4.5g (34 mmol) of L-leucine and equi-molar of trifluoromethanesulfonic anhydride, 6.3 g of **I**-Leu was obtained (Yield: 66%).

^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 0.97 (d, *J*=5.8 Hz, 6H), 1.64 (m, *J*=28 Hz, 2H), 1.80 (m, *J*=16.8 Hz, 1H), 3.80 (s, 3H), 4.23 (q, *J*=7.3, 1H), 5.74 (s, 1H). ESI–TOF–MS: Calcd. for $C_8H_{14}NO_4SF_3$ $[M\text{-}1+2Na]^+$: *m/z* = 322.23; Found: 322.12, $[M\text{-}1]^-$: *m/z* = 276.25; Found: 275.83.

$[\alpha]_D^{25}$ = -28.2 (*c* = 1.0 g/ 100 ml MeOH), T_m= 14.0 °C, T_{decomp}= 132.9 °C.

Characterization of ionic liquids

[bmim][I-Ala]: ***1-butyl-3-methylimidazolium trifluoromethanesulfonylalanine methyl ester salt***
^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 0.95(t, *J*=7.5, 3H), 1.36(m, *J*=16.5Hz, 5H), 1.86(m, *J*=15Hz, 2H), 3.67(s, 3H), 4.01(s, 3H), 4.20(q, *J*=10Hz, 1H), 4.27(m, *J*=11.5Hz, 2H), 7.29(d, *J*=1Hz, 1H), 7.36(d, *J*=1Hz, 1H), 10.3(s, 1H). ESI–TOF–MS: Calcd. for $[C_8H_{15}N_2][C_5H_7NO_4SF_3]$: $[bmim]^+$ *m/z* = 139.22; Found: 139.13, [**I**-Ala]$^-$: *m/z* = 234.17; Found: 233.82.

[bmim][I-Val]: ***1-butyl-3-methylimidazolium trifluoromethanesulfonylvaline methyl ester salt***
^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 0.94(m, *J*=13.75, 9H), 1.37(m, *J*=18.8Hz, 2H), 1.85(m, *J*=15.3Hz, 2H), 1.94(m, *J*=16.8Hz, 1H), 3.65(s, 3H), 3.82(d, *J*=3Hz, 1H), 4.04(s, 3H), 4.28(m, *J*=31.7Hz, 2H), 7.30(d, *J*=0.75Hz, 1H), 7.37(d, *J*=1Hz, 1H), 10.3(s, 1H). ESI–TOF–MS: Calcd. for $[C_8H_{15}N_2][C_7H_{11}NO_4SF_3]$: $[bmim]^+$ *m/z* = 139.22; Found: 139.13, [**I**-Val]$^-$: *m/z* = 262.23; Found: 261.81.

[bmim][I-Leu]: ***1-butyl-3-methylimidazolium trifluoromethanesulfonylleucine methyl ester salt***
^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 0.91(q, *J*=5Hz, 6H), 0.96(t, *J*=7.5 Hz, 6H), 1.37(m, *J*=18.5Hz, 2H), 1.52(t, *J*=7Hz, 2H), 1.82(m, *J*=32.7Hz, 3H), 3.66(s, 3H), 4.02(s, 3H), 4.11(t, *J*=7Hz, 1H), 4.28(m, *J*=29Hz, 2H), 7.27(t, *J*=2.3Hz, 1H), 7.33(t, *J*=1.8Hz, 1H), 10.28(s, 1H). ESI–TOF–MS: Calcd. for $[C_8H_{15}N_2][C_8H_{13}NO_4SF_3]$: $[bmim]^+$ *m/z* = 139.22; Found: 139.13, [**I**-Leu]$^-$: *m/z* = 276.25; Found: 275.83.

[TBP][I-Ala]: ***n-tetrabutylphosphonium trifluoromethanesulfonylalanine methyl ester salt***
^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 0.97(t, *J*=7 Hz, 12H), 1.32(d, *J*=3.5Hz, 3H), 1.52(m, *J*=11.4Hz, 16H), 2.28 (m, *J*=14.5Hz, 8H), 3.74(s, 3H), 4.12(q, *J*=10.5Hz, 1H).
ESI–TOF–MS: Calcd. for $[C_{16}H_{36}P][C_5H_7NO_4SF_3]$: $[TBP]^+$: *m/z* = 259.43; Found: 259.33, [**I**-Ala]$^-$: *m/z* = 234.17; Found: 233.82.

[TBP][I-Val]: ***n-tetrabutylphosphonium trifluoromethanesulfonylvaline methyl ester salt***
^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 0.89 (d, *J*=3.5Hz, 3H), 0.97 (t, *J*=7Hz, 15H), 1.52 (t, *J*=3.5Hz, 16H), 1.91 (m, *J*=17Hz, 1H), 2.27 (m, *J*=13.8Hz, 8H), 3.63 (s, 3H), 3.67 (d, *J*=3.5Hz, 1H).
ESI–TOF–MS: Calcd. for $[C_{16}H_{36}P][C_7H_{11}NO_4SF_3]$: $[TBP]^+$: *m/z* = 259.43; Found: 259.33, [**I**-Val]$^-$: *m/z* = 262.23; Found: 261.83.

[TBP][I-Leu]: ***n-tetrabutylphosphonium trifluoromethanesulfonylleucine methyl ester salt***
^{1}H NMR (500MHz, $CDCl_3$, δ/ppm relative to TMS): 0.90(q, *J*=5.8Hz, 6H), 0.97(t, *J*=7 Hz, 12H),

1.51(m, *J*=6.5Hz, 18H), 1.79(m, *J*=20Hz, 1H), 2.28 (m, *J*=14.5Hz, 8H), 3.63(s, 3H), 4.03(t, *J*=7.3Hz, 1H). ESI–TOF–MS: Calcd. for $[C_{16}H_{36}P][C_8H_{13}NO_4SF_3]$: $[TBP]^+$: *m/z* = 259.43; Found: 259.33, [**I**-Leu]$^-$: *m/z* = 276.25; Found: 275.83.