Electronic Supporting Information for

"The effect of bisimidazolium-based ionic liquids on a bimolecular substitution process. Are two head(group)s better than one?"

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General experimental

Unless otherwise stated all chemicals were purified prior to use as according to standard protocols. Where water is mentioned, Milli-Q™ water was used unless otherwise stated. The terms 'under reduced pressure' and '*in vacuo*' refer to the use of a rotary evaporated fitted with a variable pressure pump and a Schlenk line apparatus, respectively. Before use in the kinetic studies, all ionic liquids were dried *in vacuo* (< 0.1 mbar) at room temperature until a constant, sustained pressure was obtained unless otherwise stated. Under these conditions, the water content of all the ionic liquids considered was < 200 ppm as measured by Karl-Fischer titrimetry.

NMR spectroscopy for the characterisation of the synthesised ionic liquids was conducted on either a Bruker Avance III 300 (300 MHz, ^{1}H) or a Bruker Avance III 400 (400 MHz, ^{1}H) spectrometer. Multiplicities are reported as singlet (s), doublet (d), triplet (t) quartet (q), pentent (p), hextet (h), doublet of triplets (dt) and multiplet (m). ^{1}H NMR spectroscopy used in the kinetic studies were conducted on either a Bruker Avance III 400 (400 MHz, ^{1}H), Bruker Avance III 500 (500 MHz, ^{1}H) or Bruker Avance III 600 (600 MHz, ^{1}H) spectrometer. The results were shown to be reproducible regardless of the NMR spectrometer used.

Pyridine **2** was purified through distillation and stored over 3 Å molecular sieves and sodium hydroxide at -20 °C until use. Benzyl bromide **1** was purified through distillation and stored over 3 Å molecular sieves and in the absence of light at 6 °C until use. The reaction mixtures for the kinetic studies were prepared under pseudo first order conditions such that they contained at least a 10-fold excess of pyridine **2** relative to benzyl bromide **1**. Reaction progress was monitored by ^{1}H NMR spectroscopy following depletion of the signal corresponding benzylic protons of benzyl bromide **1** at approximately 4 ppm. The reactions were monitored until > 95 % completion. Integrals for the calculation of the pseudo first order rate constants were obtained using MestReNova, pseudo first order rate constants were calculated using Equation S1 and the LINEST function in Microsoft Excel, and the second order rate constant was determined using Equation S2.

$$[A] = 1 - e^{-k_{obs}t}$$

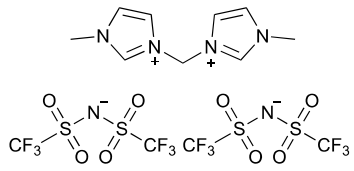
Equation S1: Exponential function used to determine the observed pseudo first order rate constant through monitoring product formation; [A] = the integral of benzyl bromide **1**, k_{obs} = the pseudo first order rate constant and t = time.

$$k_{obs} = k_2[Pyridine\ 2]$$

Equation S2: Relationship used to convert pseudo first order rate constants into the corresponding bimolecular rate constants; k_2 = the bimolecular rate constant, k_{obs} = the pseudo first order rate constant and [Pyridine **2**] = the concentration of pyridine **2** (in excess).

Synthesis of ionic liquids

bis(3-Methylimidazolium-1-yl)methane _bis_(trifluoromethanesulfonyl)imide $[m(mim)_2][N(SO_2CF_3)_2]$ 5a

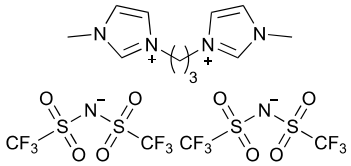


5a

A solution of *N*-methylimidazole (5.88 g, 71.6 mmol) in acetonitrile (10 mL) was added to a solution of diidomethane (8.05 g, 30.1 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from the yellow solution. The volatile components of the mixture were removed *in vacuo*, and the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and was dried *in vacuo* to isolate *bis*(3-methylimidazolium-1-yl)methane iodide as a white solid (12.2 g, 28.2 mmol). m.p. > 240 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (s, 2H, ($NC\underline{H}NCH_2)_2CH_2$)), 7.93 (m, 2H, ($NCHC\underline{H}NCH_2)_2CH_2$), 7.75 (t, 2H, ($NC\underline{H}CHNCH_2)_2CH_2$), 6.61 (s, 2H, $NC\underline{H}_2N$), 3.90 (s, 6H, $NC\underline{H}_3$).

bis(3-Methylimidazolium-1-yl)methane iodide was dissolved in water (15 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (16.8 g, 101 mmol) in water (20 mL) was added and stirred vigorously at room temperature for 24 hours. During this time, a white powder formed. Ethyl acetate (50 mL) was added, and two immiscible layers formed. The yellow bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The collected organic phases were then washed with water (10 x 50 mL). The volatile components of the organic phases were removed *in vacuo* to isolate a yellow crystalline solid. A 1:1 mixture of ethyl acetate and toluene (25 mL) was added to the solid, stirred, and the ethyl acetate was removed *in vacuo*, resulting in a mixture of a pale yellow solid and purple liquid. The liquid was decanted, and the process was repeated five times, and the residue was dried *in vacuo* to yield 1,1-*bis*(3-methylimidazolium-1-yl)methane *bis*(trifluoromethanesulfonyl)imide **5a** (36.1 g, 47.1 mmol, 95%) as a white, crystalline solid (m.p. 92-93 °C), which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 2H, ($NC\underline{H}NCH_2)_2CH_2$)), 7.92 (m, 2H, ($NCHC\underline{H}NCH_2)_2CH_2$), 7.78 (m, 2H, ($NC\underline{H}CHNCH_2)_2CH_2$), 6.60 (s, 2H, $NC\underline{H}_2N$), 3.89 (s, 6H, $NC\underline{H}_3$).

1,3-*bis*(3-Methylimidazolium-1-yl)propane *bis*(trifluoromethanesulfonyl)imide $[p_r(mim)_2][N(SO_2CF_3)_2]$ 5b

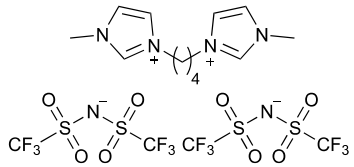


5b

A solution of *N*-methylimidazole (8.65 g, 105 mmol) in acetonitrile (10 mL) was added to a solution of 1,3-dibromopropane (10.0 g, 49.5 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to give the precursor 1,3-*bis*(3-methylimidazolium-1-yl)propane bromide as a white solid (17.6 g, 48.1 mmol, 97%). m.p. 167-169 °C (lit.[1] 172.8 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 2H, NC<u>H</u>N), 7.81 (m, 2H, NCHC<u>H</u>N), 7.75 (m, 2H, NC<u>H</u>CHN), 4.25 (t, J = 7.0 Hz, 4H, NC<u>H</u>$_2$CH$_2$C<u>H</u>$_2$N), 3.88 (s, 6H, NC<u>H</u>$_3$), 2.40 (p, J = 7.0 Hz, 2H, NCH$_2$C<u>H</u>$_2$CH$_2$N).

1,3-*bis*(3-Methylimidazolium-1-yl)propane bromide (17.6 g, 48.1 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (29.0 g, 101 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, a white powder formed. Dichloromethane (50 mL) was added, and three colourless, immiscible layers formed. The bottom two layers were retained, and the top, aqueous layer, was extracted with dichloromethane (3 x 20 mL). The combined organic phases were then washed with water (10 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,3-*bis*(3-methylimidazolium-1-yl)propane *bis*(trifluoromethanesulfonyl)imide **5b** (36.3 g, 47.3 mmol, 98%) as a white, crystalline solid, which was used without any further purification. m.p. 47-48 °C (lit.[2] 49-50 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.73 (m, 4H, (NC<u>H</u>C<u>H</u>N), 4.20 (t, J = 7.0 Hz, 4H, NC<u>H</u>$_2$CH$_2$C<u>H</u>$_2$N), 3.85 (s, 6H, NC<u>H</u>$_3$), 2.37 (p, J = 7.0 Hz, 2H, NCH$_2$C<u>H</u>$_2$CH$_2$N).

1,4-*bis*(3-Methylimidazolium-1-yl)butane *bis*(trifluoromethanesulfonyl)imide [b(mim)$_2$][N(SO$_2$CF$_3$)$_2$] 5c

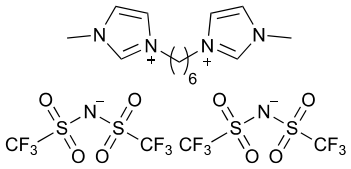


5c

A solution of *N*-methylimidazole (23.1 g, 281 mmol) in acetonitrile (10 mL) was added to a solution of 1,4-dibromobutane (30.3 g, 140 mmol) in acetonitrile (15 mL). The reaction mixture was stirred for 3 days at room temperature, wherein a light beige powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to give the precursor 1,4-*bis*(3-methylimidazolium-1-yl)butane bromide as a light beige solid (52.1 g, 136 mmol 97%). m.p. 150-151 °C (lit.[1] 158.3 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.16 (s, 2H, NC<u>H</u>N), 7.77 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.21 (m, 4H, (NC<u>H</u>$_2$CH$_2$)$_2$), 3.85 (s, 6H, NC<u>H</u>$_3$), 1.78 (m, 4H, (NCH$_2$C<u>H</u>$_2$)$_2$).

1,4-*bis*(3-Methylimidazolium-1-yl)butane bromide (25.8 g, 66.2 mmol) was dissolved in water (50 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (38.9 g, 135 mmol) in water (50 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, a white powder formed. Ethyl acetate (50 mL) was added, and two immiscible layers formed, the bottom of which was a beige colour. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 50 mL). The combined organic phases were then washed with water (10 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,3-*bis*(3-methylimidazolium-1-yl)butane *bis*(trifluoromethanesulfonyl)imide **5c** (52.6 g, 67.4 mmol, 99%) as a white, crystalline solid, which was used without any further purification. m.p. 54-55 °C (lit.[3] 54-56 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 2H, NC<u>H</u>N), 7.74 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.30-4.10 (m, 4H, NC<u>H</u>$_2$(CH$_2$)$_2$C<u>H</u>$_2$N), 3.85 (s, 6H, NC<u>H</u>$_3$), 1.76 (m, 4H, NCH$_2$(C<u>H</u>$_2$)$_2$CH$_2$N).

1,6-*bis*(3-Methylimidazolium-1-yl)hexane *bis*(trifluoromethanesulfonyl)imide $[h_x(mim)_2][N(SO_2CF_3)_2]$ 5e

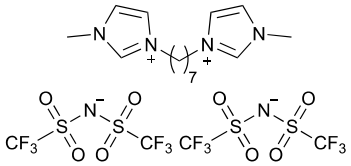


5e

A solution of *N*-methylimidazole (20.1 g, 244 mmol) in acetonitrile (25 mL) was added to a solution of 1,6-dibromohexane (28.2 g, 115 mmol) in acetonitrile (25 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 50 mL), and the residue was dried *in vacuo* to give the precursor 1,6-*bis*(3-methylimidazolium-1-yl)hexane bromide as a white solid (44.0 g, 108 mmol, 94%). m.p. 146-148 °C (lit.[4] 150-151 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (s, 2H, NC<u>H</u>N), 7.76 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.86 (s, 6H, NC<u>H</u>$_3$), 1.84-1.72 (m, 4H, (NCH$_2$C<u>H</u>$_2$CH$_2$)$_2$), 1.39-1.13 (m, 4H, (N(CH$_2$)$_2$C<u>H</u>$_2$)$_2$).

1,6-*bis*(3-Methylimidazolium-1-yl)hexane bromide (24.7 g, 60.5 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (36.0 g, 125 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, a white powder formed. The bottom later was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (10 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,6-*bis*(3-methylimidazolium-1-yl)hexane *bis*(trifluoromethanesulfonyl)imide **5e** (44.6 g, 55.2 mmol, 91%) as a beige liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.14 (t, J = 7.2 Hz, 4H, (NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.84-1.70 (m, 4H, (NCH$_2$C<u>H</u>$_2$CH$_2$)$_2$), 1.33-1.21 (m, 4H, (N(CH$_2$)$_2$C<u>H</u>$_2$)$_2$).

1,7-*bis*(3-Methylimidazolium-1-yl)heptane *bis*(trifluoromethanesulfonyl)imide $[h_p(mim)_2][N(SO_2CF_3)_2]$ 5f

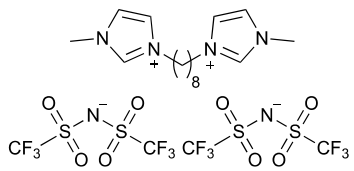


5f

A solution of *N*-methylimidazole (4.89 g, 59.6 mmol) in acetonitrile (10 mL) was added to a solution of 1,7-dibromoheptane (7.03 g, 27.3 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 4 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to give the precursor 1,7-*bis*(3-methylimidazolium-1-yl)heptane as a white solid (11.2 g, 26.5 mmol, 97%). m.p. 132-134 °C (lit.[5] reported as a liquid). ^{1}H NMR (300 MHz, CD_3CN-d_3) δ 9.26 (s, 2H, NC<u>H</u>N), 7.51 (m, 2H, NCHC<u>H</u>N), 7.40 (m, 2H, NC<u>H</u>CHN), 4.23 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.90 (s, 6H, NC<u>H</u>$_3$), 1.88 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$CH$_2$)$_2$CH$_2$), 1.56-1.23 (m, 6H, (NCH$_2$CH$_2$C<u>H</u>$_2$)$_2$C<u>H</u>$_2$).

1,7-*bis*(3-Methylimidazolium-1-yl)heptane bromide (8.97 g, 21.2 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (12.86 g, 101.16 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,7-*bis*(3-methylimidazolium-1-yl)heptane *bis*(trifluoromethanesulfonyl)imide **5f** (16.2 g, 19.6 mmol, 92%) as a white powder, which was used without any further purification. m.p. 59-61 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, (NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$CH$_2$)$_2$CH$_2$), 1.43-1.11 (m, 6H, (NCH$_2$CH$_2$C<u>H</u>$_2$)$_2$C<u>H</u>$_2$).

1,8-*bis*(3-Methylimidazolium-1-yl)octane *bis*(trifluoromethanesulfonyl)imide [o(mim)$_2$][N(SO$_2$CF$_3$)$_2$] 5g

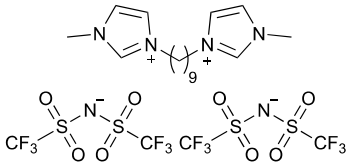


5g

A solution of *N*-methylimidazole (3.03 g, 36.9 mmol) in acetonitrile (10 mL) was added to a solution of 1,8-dibromooctane (4.55 g, 16.7 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and was dried *in vacuo* to give the precursor 1,8-*bis*(3-methylimidazolium-1-yl)octane bromide as a white solid (7.05 g, 16.2 mmol, 97%). m.p. 124-125 °C (lit.[6] 127 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 2H, NCHN), 7.81 (m, 2H, NCHC<u>H</u>N), 7.73 (m, 2H, NC<u>H</u>CHN), 4.17 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.86 (s, 6H, NC<u>H</u>$_3$), 1.77 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_2$)$_2$), 1.38-1.13 (m, 8H, (N(CH$_2$)$_2$(C<u>H</u>$_2$)$_2$)$_2$).

1,8-*bis*(3-Methylimidazolium-1-yl)octane bromide (7.05 g, 16.2 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (12.0 g, 41.9 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,8-*bis*(3-methylimidazolium-1-yl)octane *bis*(trifluoromethanesulfonyl)imide **5g** (13.1 g, 15.7 mmol, 97%) as a colourless liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NCHN), 7.75 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, (NC<u>H</u>$_2$(CH$_2$)$_3$)$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_2$)$_2$), 1.25 (m, 8H, (N(CH$_2$)$_2$(C<u>H</u>$_2$)$_2$)$_2$).

1,9-*bis*(3-Methylimidazolium-1-yl)nonane *bis*(trifluoromethanesulfonyl)imide [n(mim)$_2$][N(SO$_2$CF$_3$)$_2$] 5h

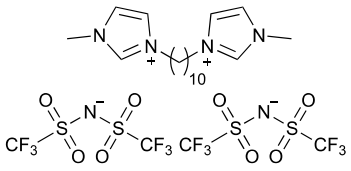


5h

A solution of *N*-methylimidazole (3.62 g, 59.7 mmol) in acetonitrile (10 mL) was added to a solution of 1,9-dibromononane (4.90 g, 12.7 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 7 days at room temperature, wherein the mixture turned light beige. The volatile components of the mixture were removed under reduced pressure, the residue was triturated with ethyl acetate (5 x 30 mL), and the resulting powder was dried *in vacuo* to give the precursor 1,9-*bis*(3-methylimidazolium-1-yl)nonane bromide as a colourless viscous liquid (7.53 g, 16.7 mmol, 98%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.17 (s, 2H, NC<u>H</u>N), 7.78 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.16 (t, J = 7.3 Hz, 4H, NC<u>H</u>$_2$), 3.86 (s, 6H, NC<u>H</u>$_3$), 1.78 (p, J = 7.3 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_2$)$_2$CH$_2$), 1.33-1.18 (m, 10H, (N(C<u>H</u>$_2$)$_2$C<u>H</u>$_2$)$_2$C<u>H</u>$_2$).

1,9-*bis*(3-Methylimidazolium-1-yl)nonane bromide (6.99 g, 15.5 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (10.1 g, 35.3 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phases were removed *in vacuo* to yield 1,9-*bis*(3-methylimidazolium-1-yl)nonane *bis*(trifluoromethanesulfonyl)imide **5h** (12.8 g, 15.1 mmol, 97%) as a light beige liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.69 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.75 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_2$)$_2$CH$_2$), 1.29-1.17 (m, 10H, (N(C<u>H</u>$_2$)$_2$C<u>H</u>$_2$)$_2$C<u>H</u>$_2$).

1,10-*bis*(3-Bethylimidazolium-1-yl)decane *bis*(trifluoromethanesulfonyl)imide [d(mim)$_2$][N(SO$_2$CF$_3$)$_2$] 5i

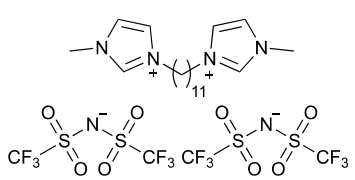


5i

A solution of *N*-methylimidazole (15.1 g, 184 mmol) in acetonitrile (10 mL) was added to a solution of 1,10-dibromodecane (27.4 g, 91.0 mmol) in acetonitrile (30 mL). The reaction mixture was stirred for 7 days at room temperature, wherein the viscosity of the mixture was observed to increase. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to isolate the precursor 1,10-*bis*(3-methylimidazolium-1-yl)decane bromide as a white solid (41.0 g, 88.3 mmol, 97%). m.p. 145-146 °C (lit.[6] 145 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.11 (s, 2H, NC<u>H</u>N), 7.77 (m, 2H, NCHC<u>H</u>N), 7.71 (m, 2H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.85 (s, 6H, NC<u>H</u>$_3$), 1.78 (q, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_3$)$_2$), 1.39-1.09 (m, 12H, (N(CH$_2$)$_2$(C<u>H</u>$_2$)$_3$)$_2$).

1,10-*bis*(3-Methylimidazolium-1-yl)decane bromide (29.2 g, 62.9 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (43.4 g, 151 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,10-*bis*(3-methylimidazolium-1-yl)decane *bis*(trifluoromethanesulfonyl)imide **5i** (51.4 g, 59.4 mmol, 95%) as a light beige liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.69 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_3$)$_2$), 1.33-1.18 (m, 12H, (N(CH$_2$)$_2$(C<u>H</u>$_2$)$_3$)$_2$).

1,11-*bis*(3-Methylimidazolium-1-yl)undecane *bis*(trifluoromethanesulfonyl)imide [ud(mim)$_2$][N(SO$_2$CF$_3$)$_2$] 5j

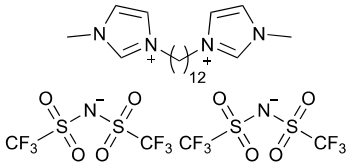


5j

A solution of *N*-methylimidazole (3.69 g, 44.9 mmol) in acetonitrile (5 mL) was added to a solution of 1,11-dibromoundecane (4.76 g, 15.1 mmol) in acetonitrile (5 mL). The reaction mixture was stirred for 3 days at room temperature, wherein the mixture turned a beige colour. The volatile components of the mixture were removed under reduced pressure, and the resulting viscous beige liquid was triturated with ethyl acetate (10 x 20 mL), and the reside was dried *in vacuo* to isolate the precursor 1,11-*bis*(3-methylimidazolium-1-yl)undecane bromide as a colourless viscous liquid (7.23 g, 15.1 mmol, quant.). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.14 (s, 2H, NC<u>H</u>N), 7.78 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.86 (s, 6H, NC<u>H</u>$_3$), 1.77 (p, J = 7.2 Hz, 4H, (N(CH$_2$C<u>H</u>$_2$(CH$_2$)$_3$)$_2$CH$_2$), 1.37-1.10 (m, 14H, (N(CH$_2$CH$_2$(C<u>H</u>$_2$)$_3$)$_2$C<u>H</u>$_2$).

1,11-*bis*(3-Methylimidazolium-1-yl)undecane bromide (7.23 g, 15.1 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (9.37 g, 32.6 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,11-*bis*(3-methylimidazolium-1-yl)undecane *bis*(trifluoromethanesulfonyl)imide **5j** (12.2 g, 13.9 mmol, 92%) as a colourless liquid, which was used without any further purification.^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (N(CH$_2$C<u>H</u>$_2$(CH$_2$)$_3$)$_2$CH$_2$), 1.32-1.18 (m, 14H, (N(CH$_2$CH$_2$(C<u>H</u>$_2$)$_3$)$_2$C<u>H</u>$_2$).

1,12-*bis*(3-Methylimidazolium-1-yl)dodecane *bis*(trifluoromethanesulfonyl)imide [dd(mim)$_2$][N(SO$_2$CF$_3$)$_2$] 5k



5k

A solution of *N*-methylimidazole (11.6 g, 141 mmol) in acetonitrile (10 mL) was added to a solution of 1,12-dibromododecane (21.7 g, 66.1 mmol) in acetonitrile (30 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to isolate the precursor 1,12-*bis*(3-methylimidazolium-1-yl)decane bromide as a white solid (31.6 g, 64.1 mmol, 97%). m.p. 153-154 °C (lit.[1] reported as liquid). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.13 (d, J = 1.8 Hz, 2H, NC<u>H</u>N), 7.78 (m, 2H, NCHC<u>H</u>N), 7.71 (m, 2H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.85 (s, 6H, NC<u>H</u>$_3$), 1.77 (m, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_4$)$_2$), 1.34-1.15 (m, 16H, (NCH$_2$CH$_2$(C<u>H</u>$_2$)$_4$)$_2$).

1,12-*bis*(3-Methylimidazolium-1-yl)decane bromide (24.7 g, 50.2 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (33.6 g, 117 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,12-*bis*(3-methylimidazolium-1-yl)decane *bis*(trifluoromethanesulfonyl)imide **5k** (39.3 g, 44.0 mmol, 88%) as a light beige liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.76 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_4$)$_2$), 1.30-1.17 (m, 16H, (NCH$_2$CH$_2$(C<u>H</u>$_2$)$_4$)$_2$).

Representative stacked plots for the kinetic analyses

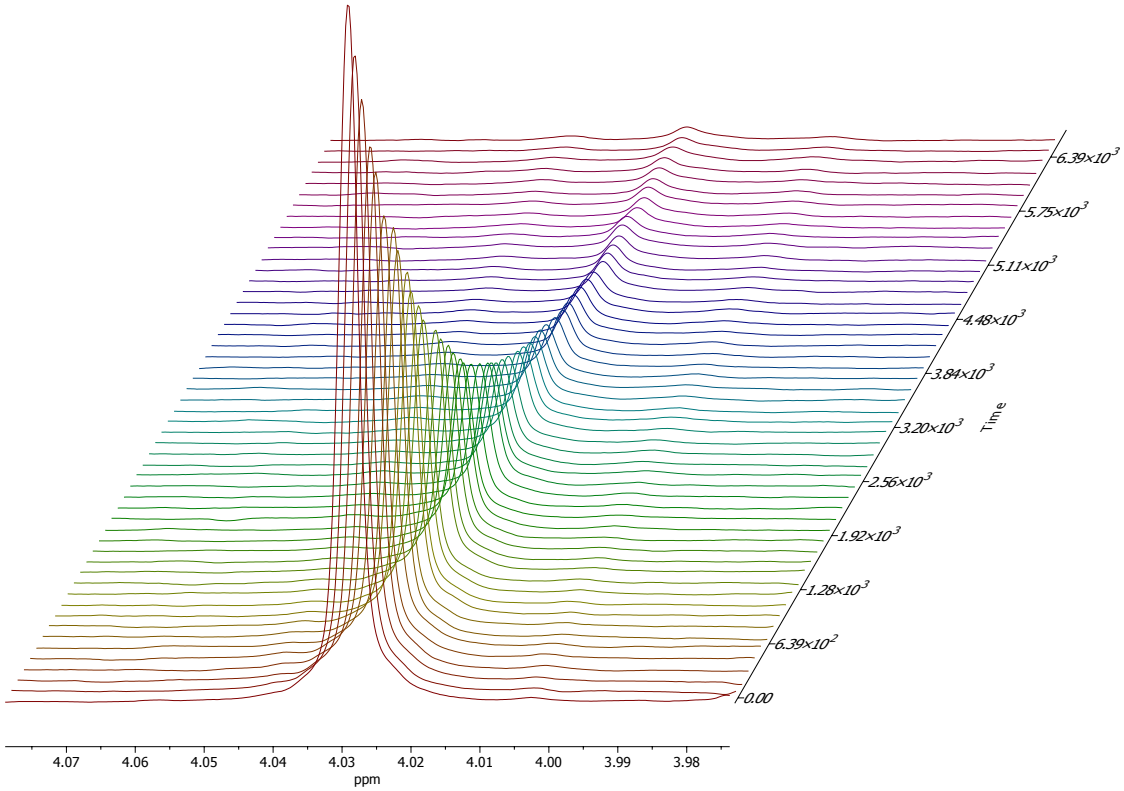


Figure S1. A series of stacked ^{1}H NMR spectra (400 MHz) showing the decrease in integration of the signal due to the starting material **1** (*ca.* 4 ppm) used to determine the extent of reaction. For this series of spectra, the solvent was acetonitrile and the ionic liquid **5b** (χ_{IL} *ca*. 0.2).

Stock solution composition and rate constants for comparisons of ionic liquids at low and high mole fractions

Table S1. Composition of stock solutions by mass, including resultant mole fraction, and concentration of pyridine **2**, in a 2 mL stock solution, used for the kinetic studies of the reaction between pyridine **2** and benzyl bromide **1** in an ionic liquid at mole fractions of *ca*. 0.2, where anhydrous acetonitrile was used as the co-solvent, and with no additional cosolvent.

Ionic liquid (IL)	Mass IL / g	Mass Pyridine **2** / g	[**2**] / mol L^{-1}	χ_{IL}
$[m(mim)_2][N(SO_2CF_3)_2]_2$ **5a**	2.199	0.080	0.51	0.18
$[p_r(mim)_2][N(SO_2CF_3)_2]_2$ **5b**	2.905	0.083	0.53	0.19
$[b(mim)_2][N(SO_2CF_3)_2]_2$ **5c**	2.206	0.082	0.52	0.20
$[h_x(mim)_2][N(SO_2CF_3)_2]_2$ **5e**	2.211	0.085	0.54	0.21
	2.934	0.084	0.53	0.76
$[h_p(mim)_2][N(SO_2CF_3)_2]_2$ **5f**	2.169	0.082	0.52	0.20
$[o(mim)_2][N(SO_2CF_3)_2]_2$ **5g**	2.138	0.081	0.51	0.22
	2.850	0.086	0.54	0.74
$[n(mim)_2][N(SO_2CF_3)_2]_2$ **5h**	2.152	0.083	0.52	0.20
	2.822	0.083	0.53	0.75
$[d(mim)_2][N(SO_2CF_3)_2]_2$ **5i**	2.155	0.082	0.52	0.21
	2.780	0.081	0.51	0.74
$[ud(mim)_2][N(SO_2CF_3)_2]_2$ **5j**	2.138	0.081	0.51	0.21
	2.752	0.083	0.52	0.74
$[dd(mim)_2][N(SO_2CF_3)_2]_2$ **5k**	2.109	0.081	0.51	0.20
	2.703	0.086	0.54	0.72

Table S2. Rate constants determined in the kinetic studies of the reaction between benzyl bromide **1** and pyridine **2** in an ionic liquid at 22.2 ºC. Also included are the corresponding mole fractions and concentrations of pyridine **2** used.

Ionic liquid	χ_{IL}	[Pyridine **2**] / mol L^{-1}	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}
$[m(mim)_2][N(SO_2CF_3)_2]_2$ **5a**	0.18	0.51	18.1	35.8
			16.9	33.5
			17.9	35.4
$[p_r(mim)_2][N(SO_2CF_3)_2]_2$ **5b**	0.19	0.53	14.5	27.7
			14.2	26.9
			14.4	27.4
$[b(mim)_2][N(SO_2CF_3)_2]_2$ **5c**	0.20	0.52	5.28	10.1
			5.36	10.3
			5.44	10.5
$[h_x(mim)_2][N(SO_2CF_3)_2]_2$ **5e**	0.21	0.54	8.17	15.4
			6.77	12.8
			6.73	12.7
	0.76	0.53	8.96	17.4
			10.7	20.9
			10.4	20.5
$[h_p(mim)_2][N(SO_2CF_3)_2]_2$ **5f**	0.20	0.52	8.41	16.2
			8.73	16.8
			8.43	16.4
$[o(mim)_2][N(SO_2CF_3)_2]_2$ **5g**	0.22	0.51	8.67	16.9
			8.75	17.1
			8.55	16.7
	0.74	0.54	8.36	15.4
			8.84	16.3
			7.73	14.2
$n(mim)_2][N(SO_2CF_3)_2]_2$ **5h**	0.20	0.53	8.89	17.0
			8.84	16.9
			8.76	16.7

	0.75	0.53	11.8	23.0
			10.7	20.9
			9.53	18.6
[d(mim)$_2$][N(SO$_2$CF$_3$)$_2$]$_2$ **5i**	0.21	0.52	7.51	14.5
			7.89	15.3
			7.74	14.9
	0.74	0.51	8.96	17.4
			10.7	20.9
			10.4	20.5
[ud(mim)$_2$][N(SO$_2$CF$_3$)$_2$]$_2$ **5j**	0.21	0.51	7.43	14.5
			7.35	14.4
			7.51	14.7
	0.74	0.52	9.39	18.3
			8.22	16.0
			7.44	14.5
[dd(mim)$_2$][N(SO$_2$CF$_3$)$_2$]$_2$ **5k**	0.20	0.51	7.13	13.9
			7.02	13.7
			6.85	13.3
	0.72	0.54	8.39	15.5
			9.35	17.2
		0.51	8.18	15.8

Stock solution composition and rate constants for the comparative mole fraction dependence studies

Table S3. Composition of stock solutions by mass, including resultant mole fraction, and concentration of pyridine **2**, in a 2 mL stock solution, used for the kinetic studies of the reaction between pyridine **2** and benzyl bromide **1** in an ionic liquid at various mole fractions.

Ionic liquid (IL)	Mass IL / g	Mass Pyridine **2** / g	[**2**] / mol L^{-1}	χ_{IL}
$[m(mim)_2][N(SO_2CF_3)_2]_2$ **5a**	0.651	0.081	0.51	0.03
	1.102	0.092	0.58	0.06
	1.701	0.080	0.51	0.11
	2.199	0.080	0.51	0.18
$[p_r(mim)_2][N(SO_2CF_3)_2]_2$ **5b**	0.301	0.080	0.51	0.01
	1.057	0.081	0.51	0.05
	1.628	0.082	0.52	0.10
	2.905	0.083	0.53	0.19
	2.532	0.084	0.53	0.29
	2.714	0.082	0.52	0.38
	2.828	0.080	0.51	0.46
$[b(mim)_2][N(SO_2CF_3)_2]_2$ **5c**	1.051	0.083	0.52	0.05
	1.541	0.081	0.51	0.09
	1.954	0.080	0.51	0.15
	2.206	0.082	0.52	0.20
	2.397	0.080	0.51	0.25
$[h_p(mim)_2][N(SO_2CF_3)_2]_2$ **5f**	1.067	0.081	0.51	0.05
	1.637	0.084	0.53	0.10
	2.169	0.082	0.52	0.20
	2.321	0.081	0.51	0.25
	2.465	0.080	0.51	0.31
$[d(mim)_2][N(SO_2CF_3)_2]_2$ **5i**	1.081	0.084	0.53	0.05
	1.606	0.081	0.51	0.10
	2.155	0.082	0.52	0.21
	2.559	0.083	0.53	0.41
	2.720	0.085	0.53	0.59
	2.780	0.081	0.51	0.74

Table S4. Rate constants determined in the kinetic studies of the reaction between benzyl bromide **1** and pyridine **2** in an ionic liquid at 22.2 ºC. Also included are the corresponding mole fractions and concentrations of pyridine **2** used.

Ionic liquid	χ_{IL}	[Pyridine **2**] / mol L^{-1}	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}
$[m(mim)_2][N(SO_2CF_3)_2]_2$ **5a**	0.03	0.51	6.80	13.3
			6.59	12.9
			6.56	12.8
	0.06	0.58	10.8	18.5
			10.5	18.1
			10.6	18.2
	0.11	0.51	12.7	25.1
			13.3	26.3
			13.3	26.4
	0.18	0.51	18.1	35.8
			16.9	33.4
			17.9	35.4
$[p_r(mim)_2][N(SO_2CF_3)_2]_2$ **5b**	0.01	0.51	4.79	9.47
			4.58	9.05
			4.77	9.42
	0.05	0.51	7.73	15.3
			7.85	15.5
			7.52	14.9
	0.10	0.52	11.0	21.2
			10.7	20.6
			10.9	21.1
	0.19	0.53	14.5	27.7
			14.2	26.9
			14.4	27.4
	0.29	0.53	16.3	30.7
			15.0	28.3
			13.7	25.8

	0.38	0.52	14.9	28.8
			18.2	35.0
			15.9	30.7
	0.46	0.51	19.1	37.5
			17.8	35.0
			17.2	33.8
$[b(mim)_2][N(SO_2CF_3)_2]_2$ **5c**	0.05	0.52	5.35	10.2
			6.24	11.9
			5.98	11.5
	0.09	0.51	5.49	10.7
			4.66	9.11
			4.84	9.45
	0.15	0.51	5.81	11.5
			5.75	11.4
			5.98	11.8
	0.20	0.52	5.28	10.1
			5.36	10.3
			5.44	10.5
	0.25	0.51	5.47	10.8
			5.32	10.5
			5.49	10.9
$[h_p(mim)_2][N(SO_2CF_3)_2]_2$ **5f**	0.05	0.51	5.23	10.2
			6.10	11.9
			6.12	12.0
	0.10	0.53	7.52	14.2
			7.33	13.7
			7.48	14.1
	0.20	0.52	12.6	24.5
			11.6	22.6
			8.48	16.5
	0.25	0.51	8.48	16.5
			8.19	15.9
			8.04	15.6

	0.31	0.51	9.13	18.1
			10.8	21.3
			8.53	16.9
$[d(mim)_2][N(SO_2CF_3)_2]_2$ **5i**	0.05	0.53	5.91	11.1
			5.71	10.8
			5.84	11.0
	0.10	0.51	6.29	12.2
			6.06	11.8
			5.91	11.5
	0.21	0.52	7.51	14.5
			7.89	15.3
			7.74	14.9
	0.41	0.53	7.92	15.1
			8.61	16.4
			9.07	17.3
	0.59	0.53	8.98	16.8
			9.39	17.6
			8.58	16.1
	0.74	0.51	8.96	17.4
			10.7	20.9
			10.4	20.5

Variation of rate constant with chain length for mixtures containing the bisimidazolium salts 5

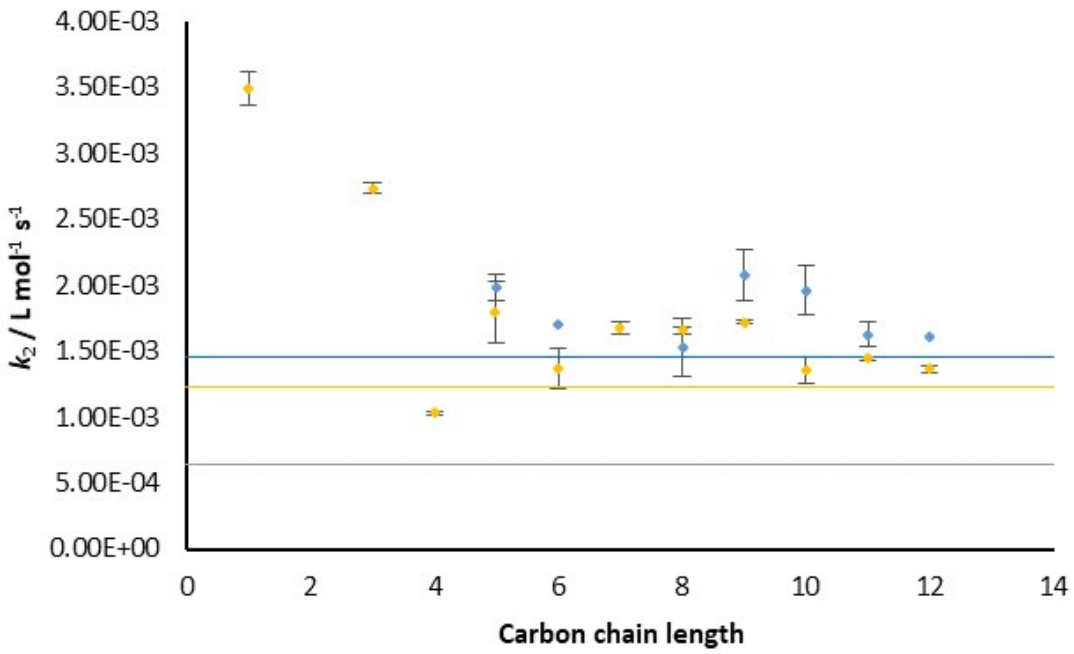


Figure S2. The bimolecular rate constants for the reaction between benzyl bromide **1** and pyridine **2** in acetonitrile (–), different mole fractions of the salt **4** at χ_{IL} *ca*. 0.2 (–) and *ca*. 0.8 (–), and salts **5a** – **k** at χ_{IL} *ca*. 0.2 (♦) and > 0.7 (♦) in acetonitrile, at 295.35 K, across varying alkyl chain length. Uncertainties are reported as the standard deviation of three replicates; some uncertainties fall within the size of the markers used. Data for the salt **4** is reproduced from Schaffarczyk McHale *et al*.[7] Data for the salt **5d** is reproduced from Hawker *et al*.[8]

Normalised mole fraction dependence plots for the bisimidazolium salts 5

In general, the bisimidazolium ionic liquids **5** resulted in greater rate constants for the reaction between benzyl bromide **1** and pyridine **2** across the range of mole fractions. It has been hypothesised that this effect is caused by greater interactions of the cationic component of the bisimidazolium salts with pyridine **2**. However, it must also be noted that as the bisimidazolium salts **5** contain two charged centres, it must be considered whether the charged centres act independently, that is, the bisimidazolium salts effectively act like two corresponding imidazolium salts, or if there is a degree of co-operativity between the two charged sites. Immediately, the fact that observed rate constant at very high mole fractions of either salt **4** or one of the salts **5** are different suggest that there is a degree of cooperativity.

In order to investigate this feature further, normalisation of the mole fraction dependence plots (Figure 2) to compare the effect of increasing the mole fraction of cationic sites in solution, rather than the mole fraction of the salt itself. A proof for the normalisation is as follows:

By definition,

$$\chi_{IL} = \frac{n_{IL}}{n_{IL} + n_{else}} \qquad \textbf{(1)}$$

where $n_{else} = n_{CH_3CN} + n_{pyridine} + n_{benzylbromide}$

Additionally,

$$\chi_{else} = \frac{n_{else}}{n_{IL} + n_{else}} = 1 - \chi_{IL} \qquad \textbf{(2)}$$

From **(2)**,

$n_{else} = (1 - \chi_{IL})(n_{IL} + n_{else})$

$= (1 - \chi_{IL})n_{IL} + (1 - \chi_{IL})n_{else}$

$n_{else}(1 - (1 - \chi_{IL})) = (1 - \chi_{IL})n_{IL}$

$n_{else}\chi_{IL} = (1 - \chi_{IL})n_{IL}$

$$n_{else} = \frac{(1 - \chi_{IL})n_{IL}}{\chi_{IL}} \qquad \textbf{(3)}$$

Now, for [bmim][$N(SO_2CF_3)_2$] **4**, and any other monocationic ionic species,

$n_{cation} = n_{IL}$

and

$$\chi_{cation} = \frac{n_{cation}}{n_{cation} + n_{else}} = \frac{n_{IL}}{n_{IL} + n_{else}}$$

$$\therefore \chi_{cation} = \chi_{IL}$$

However, for any biscationic ionic species,

$$n_{cation} = 2n_{IL}$$

and from **(1)**,

$$\chi_{cation} = \frac{2n_{IL}}{2n_{IL} + n_{else}}$$

From **(3)**,

$$\chi_{cation} = \frac{2n_{IL}}{2n_{IL} + \frac{(1 - \chi_{IL})n_{IL}}{\chi_{IL}}}$$

$$= \frac{2n_{IL}}{\left(\frac{2n_{IL}\chi_{IL} + (1 - \chi_{IL})n_{IL}}{\chi_{IL}}\right)}$$

$$= \frac{2n_{IL}\chi_{IL}}{2n_{IL}\chi_{IL} + n_{IL} - n_{IL}\chi_{IL}}$$

$$= \frac{2n_{IL}\chi_{IL}}{n_{IL}\chi_{IL} + n_{IL}}$$

Therefore, for biscationic species,

$$\chi_{cation} = \frac{2\,\chi_{IL}}{\chi_{IL} + 1}$$

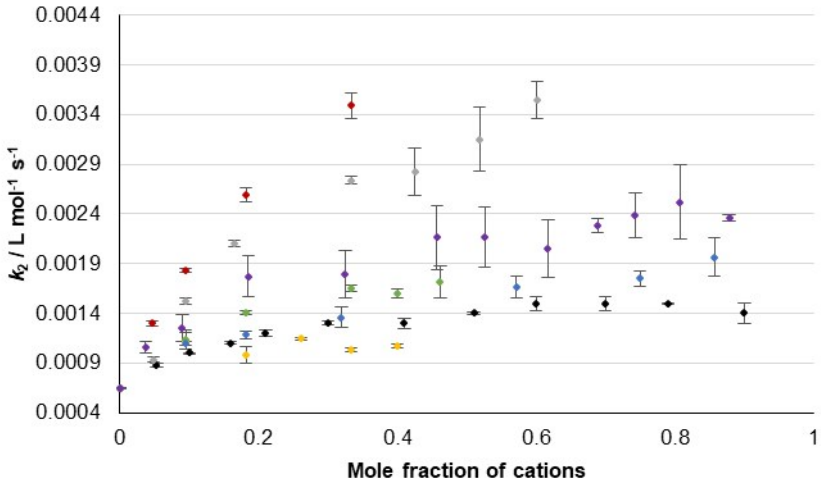


Figure S3. The bimolecular rate constants for the reaction between benzyl bromide **1** and pyridine **2** in different mole fractions of cations for the salts **4** (◆), **5a** (◆), **5b** (◆), **5c** (◆), **5d** (◆), **5f** (◆) and **5i** (◆) in acetonitrile at 295.35 K. Uncertainties are reported as the standard deviation of three replicates; some uncertainties fall with the size of the markers used. Data for the salt **4** is reproduced from Schaffarczyk McHale *et al.*[7] Data for the salt **5d** is reproduced from Hawker *et al.*[8]

Exact stock solution composition and rate constants for the temperature dependent kinetic studies

Table S5. Composition of stock solutions by mass, including resultant mole fraction, and concentration of pyridine **2**, in a 5 mL stock solution, used for the kinetic studies of the reaction between pyridine **2** and benzyl bromide **1** in an ionic liquid at mole fractions of *ca*. 0.2, and with no additional co-solvent.

Ionic liquid (IL)	Mass IL / g	Mass Pyridine **2** / g	[**2**] / mol L^{-1}	χ_{IL}
[bmim][$N(SO_2CF_3)_2$] **4**	4.123	0.211	0.53	0.20
[$m(mim)_2$][$N(SO_2CF_3)_2$]$_2$ **5a**	5.498	0.202	0.51	0.19
[$p_r(mim)_2$][$N(SO_2CF_3)_2$]$_2$ **5b**	5.499	0.201	0.51	0.20
[$b(mim)_2$][$N(SO_2CF_3)_2$]$_2$ **5c**	5.515	0.201	0.51	0.20
[$p_e(mim)_2$][$N(SO_2CF_3)_2$]$_2$ **5d**	5.353	0.200	0.51	0.19
[$d(mim)_2$][$N(SO_2CF_3)_2$]$_2$ **5i**	5.386	0.201	0.51	0.21
	7.099	0.200	0.51	0.76

Table S6. Rate constants determined in the kinetic studies of the reaction between benzyl bromide **1** and pyridine **2** in an ionic liquid at various temperatures. Also included are the corresponding mole fractions and concentrations of pyridine **2** used.

Ionic liquid	χ_{IL}	[Pyridine **2**] / mol L^{-1}	Temperature / K	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}
[bmim][$N(SO_2CF_3)_2$] **4**	0.20	0.53	297.85	7.81	14.6
				7.94	14.9
				7.84	14.7
			300.35	9.58	18.0
				9.67	18.1
				9.55	17.9
			302.85	11.5	21.5
				11.3	21.2
				11.4	21.3
			310.35	18.7	35.0
				19.3	36.2
				19.3	36.1
			317.85	32.2	60.3
				30.6	57.3
[$m(mim)_2$][$N(SO_2CF_3)_2$]$_2$ **5a**	0.19	0.51	302.85	35.0	68.6
				33.1	64.8
				35.6	69.7
			310.35	63.3	124
				66.7	131
				63.3	124
			317.85	112	218
				115	224
				112	219
[$p_r(mim)_2$][$N(SO_2CF_3)_2$]$_2$ **5b**	0.20	0.51	302.85	25.3	49.8
				23.8	46.8
				24.5	48.1

			310.35	39.2	77.1
				41.1	80.8
				40.5	79.7
			317.85	74.8	147
				66.9	132
				67.5	133
$[b(mim)_2][N(SO_2CF_3)_2]_2$ **5c**	0.20	0.51	302.85	10.4	20.5
				10.2	20.1
				9.98	19.6
			310.35	19.4	38.2
				19.4	38.2
				18.8	37.0
			317.85	30.3	59.6
				28.5	56.1
				29.9	58.9
				30.9	60.9
				30.8	60.5
				31.5	61.9
$[p_e(mim)_2][N(SO_2CF_3)_2]_2$ **5d**	0.20	0.51	302.85	16.7	32.9
				16.5	32.7
				16.3	32.2
			310.35	27.8	55.0
				29.1	57.6
				27.4	54.2
			317.85	45.0	89.0
				45.1	89.2
				44.8	88.5
$[d(mim)_2][N(SO_2CF_3)_2]_2$ **5i**	0.21	0.52	302.85	13.1	25.8
				13.0	25.6
				12.9	25.4
			310.35	22.6	44.4
				22.9	45.1
				23.3	45.8

			317.85	35.9	70.6
				36.5	71.8
				37.3	73.5
	0.74	0.51	302.85	13.8	27.3
				14.7	29.1
				15.9	31.4
			310.35	26.5	52.4
				27.7	54.7
				28.3	55.9
			317.85	44.1	87.2
				43.4	85.8
				42.8	84.7
			325.35	72.6	144
				73.6	145
				72.8	144

Eyring plots from which the activation parameters in Table 2 were calculated

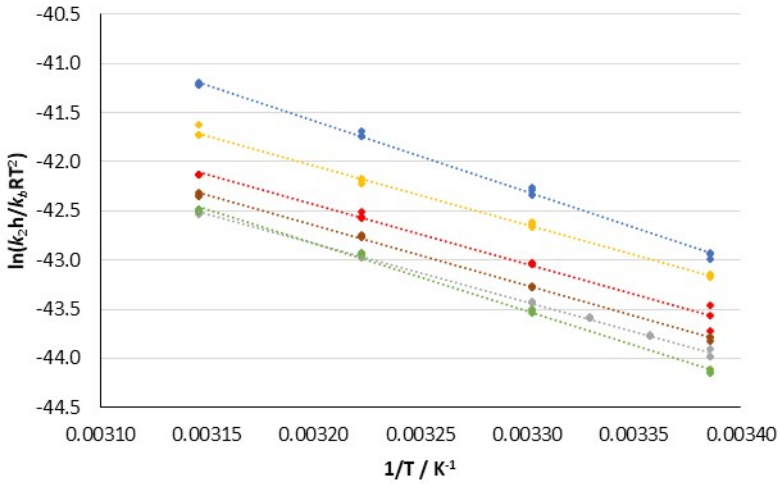


Figure S4. The Eyring plots for the reaction between benzyl bromide **1** and pyridine **2** (Scheme 1) in the presence of salts **4** (♦), **5a** (♦), **5b** (♦), **5c** (♦), **5d** (♦), and **5i** (♦), at χ_{IL} *ca*. 0.2.

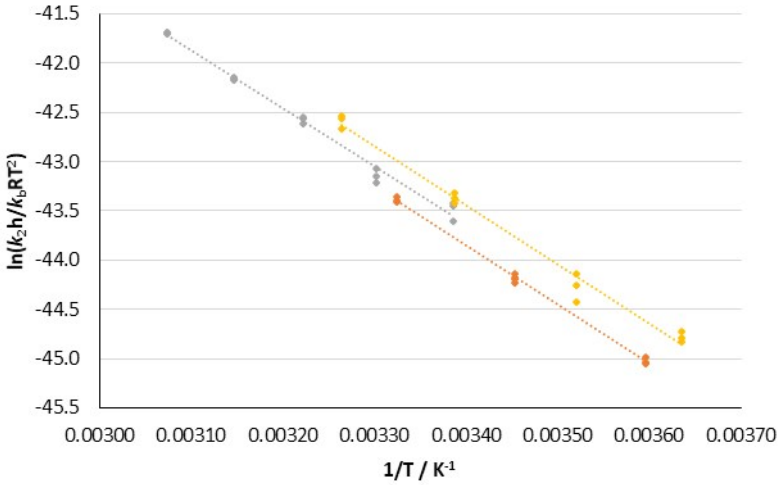


Figure S5. The Eyring plots for the reaction between benzyl bromide **1** and pyridine **2** (Scheme 1) in the presence of salts **4** (♦), **5d** (♦), and **5i** (♦), at $\chi_{IL} > 0.7$, where there is no additional co-solvent present. Data for salt **4** is reproduced from Hawker *et al*.[8]

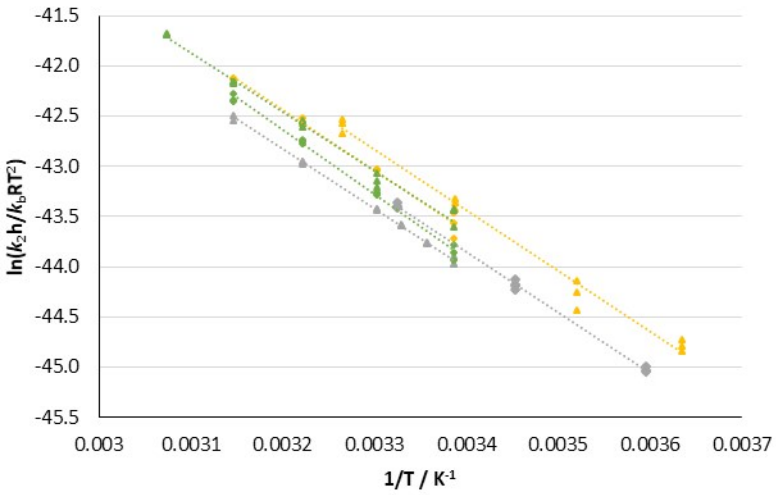


Figure S6. The Eyring plots for the reaction between benzyl bromide **1** and pyridine **2** (Scheme 1) in the presence of salts **4** (♦, ▲),**5d** (♦, ▲), and **5i** (♦, ▲), at χ_{IL} *ca*. 0.2 (♦) and χ_{IL} > 0.7 (▲). Data for salt **4** is reproduced from Hawker *et al*.[8]

Pictorial representation of competing enthalpic and entropic effects χ_{IL} ca. 0.8

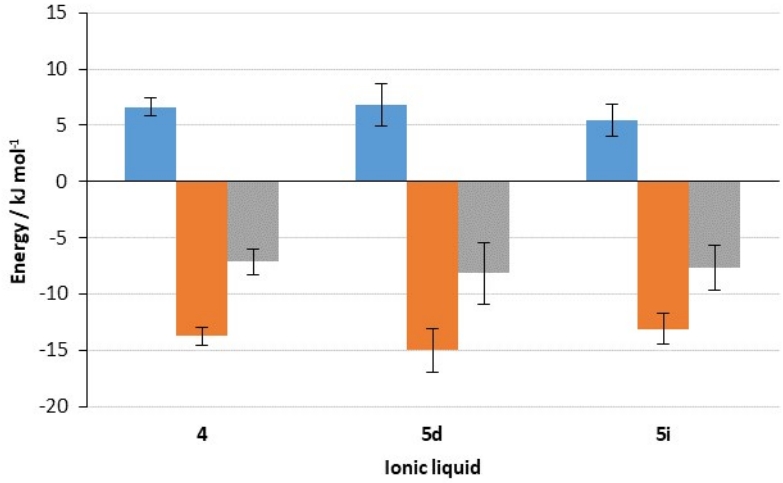


Figure S7. Contributions to the changes in rate constant for the reaction shown in Scheme 1 on moving from acetonitrile to a reaction mixture containing one of the ionic liquids **4** and **5d** and **5i**. Shown (left to right) are the change in activation enthalpy ($\Delta(\Delta H^{\ddagger})$, ■), the change in activation entropy multiplied by the negative temperature ($-\Delta(T\Delta S^{\ddagger})$, ■) and the change in activation energy, which is the sum of the two previous terms ($\Delta(\Delta G^{\ddagger})$, ■). Uncertainties are derived from the uncertainties of the activation parameters described in Table 2.

Dynamic viscosities of neat ionic liquids and mixtures of acetonitrile and ionic liquids at χ_{IL} **ca.** *0.2 at 295.35 K*

Table S7. The dynamic viscosities of ionic liquids **4**, **5d**, **5e**, and **5g-k**, at 295.35 K. Reported uncertainties are derived from standard deviations of replicate measurements.

Ionic liquid (IL)	Dynamic viscosity / mPa·s
[bmim][$N(SO_2CF_3)_2$] **4**	55.70 ± 0.01
[$p_e(mim)_2$][$N(SO_2CF_3)_2]_2$ **5d**	927.0 ± 3.8
[$h_x(mim)_2$][$N(SO_2CF_3)_2]_2$ **5e**	755.7 ± 0.1
[$o(mim)_2$][$N(SO_2CF_3)_2]_2$ **5g**	828.4 ± 5.7
[$n(mim)_2$][$N(SO_2CF_3)_2]_2$ **5h**	791.3 ± 1.4
[$d(mim)_2$][$N(SO_2CF_3)_2]_2$ **5i**	822.2 ± 0.3
[$ud(mim)_2$][$N(SO_2CF_3)_2]_2$ **5j**	944.7 ± 3.6
[$dd(mim)_2$][$N(SO_2CF_3)_2]_2$ **5k**	1032 ± 6

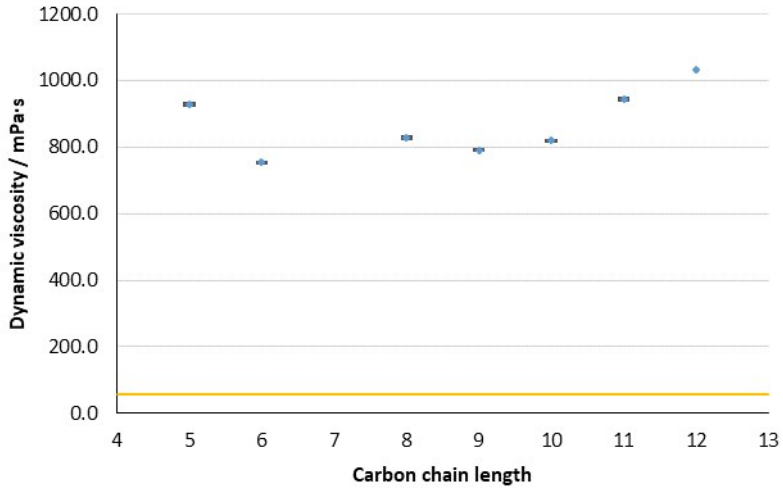


Figure S8. The dynamic viscosities of ionic liquids **4** (–), **5d-e**, **g-k** (♦), at 295.35 K, across varying chain length. Reported uncertainties are derived from standard deviations of replicate measurements. Uncertainties lie within the range of the markers used.

Table S8. Compositions and dynamic viscosities of mixtures of acetonitrile with ionic liquids **4**, **5a-k**, with χ_{IL} *ca*. 0.2, at 295.35 K. Reported uncertainties are derived from standard deviations of replicate measurements.

Ionic liquid (IL)	Mass IL / g	Mass CH_3CN / g	χ_{IL}	Dynamic viscosity / mPa·s
$[bmim][N(SO_2CF_3)_2]$ **4**	2.829	1.102	0.20	2.023 ± 0.001
$[m(mim)_2][N(SO_2CF_3)_2]_2$ **5a**	2.900	0.653	0.20	15.60 ± 0.03
$[p_r(mim)_2][N(SO_2CF_3)_2]_2$ **5b**	2.911	0.632	0.20	12.03 ± 0.02
$[b(mim)_2][N(SO_2CF_3)_2]_2$ **5c**	2.903	0.624	0.20	12.95 ± 0.01
$[p_e(mim)_2][N(SO_2CF_3)_2]_2$ **5d**	2.896	0.605	0.20	11.65 ± 0.01
$[h_x(mim)_2][N(SO_2CF_3)_2]_2$ **5e**	2.893	0.588	0.20	11.90 ± 0.01
$[h_p(mim)_2][N(SO_2CF_3)_2]_2$ **5e**	2.285	0.461	0.20	12.70 ± 0.02
$[o(mim)_2][N(SO_2CF_3)_2]_2$ **5g**	2.838	0.557	0.20	13.58 ± 0.01
$[n(mim)_2][N(SO_2CF_3)_2]_2$ **5h**	2.823	0.547	0.20	14.86 ± 0.01
$[d(mim)_2][N(SO_2CF_3)_2]_2$ **5i**	2.803	0.555	0.20	15.87 ± 0.01
$[ud(mim)_2][N(SO_2CF_3)_2]_2$ **5j**	2.818	0.525	0.20	17.35 ± 0.01
$[dd(mim)_2][N(SO_2CF_3)_2]_2$ **5k**	3.010	0.569	0.20	17.82 ± 0.01

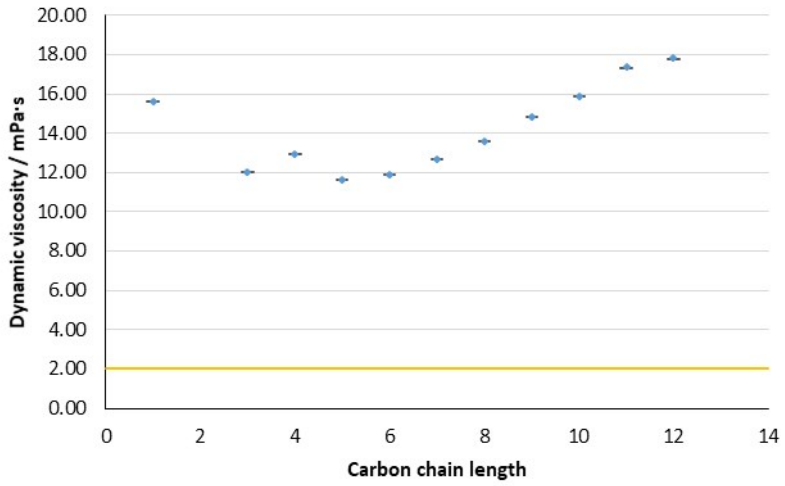


Figure S9. The dynamic viscosities of mixtures of acetonitrile with ionic liquids **4** (–), **5a-k** (♦), with χ_{IL} *ca*. 0.2, at 295.35 K, across varying chain length. Reported uncertainties are derived from standard deviations of replicate measurements. Uncertainties lie within the range of the markers used.

Nucleophile dependence studies

Table S9. Composition of stock solutions by mass, including resultant mole fraction, and concentration of pyridine **2**, in a 1 mL stock solution, used for the kinetic studies of the reaction between pyridine **2** and benzyl bromide **1** in an ionic liquid at mole fractions of *ca*. 0.2, in varying concentrations of pyridine **2**.

Ionic liquid (IL)	Mass IL / g	Mass Pyridine **2** / g	[**2**] / mol L^{-1}	χ_{IL}	k_{obs} / 10^{-4} s^{-1}
$[m(mim)_2][N(SO_2CF_3)_2]_2$ **5a**	1.087	0.018	0.23	0.18	6.32
	1.069	0.058	0.77	0.18	26.3
	1.068	0.080	1.01	0.16	32.0
$[p_r(mim)_2][N(SO_2CF_3)_2]_2$ **5b**	1.087	0.021	0.27	0.19	7.22
	1.071	0.056	0.71	0.19	19.8
	1.095	0.082	1.00	0.20	27.6
$[d(mim)_2][N(SO_2CF_3)_2]_2$ **5i**	1.049	0.022	0.28	0.19	4.32
	1.035	0.057	0.72	0.19	11.3
	1.053	0.080	1.02	0.21	15.6
	1.042	0.084	1.06	0.20	16.3

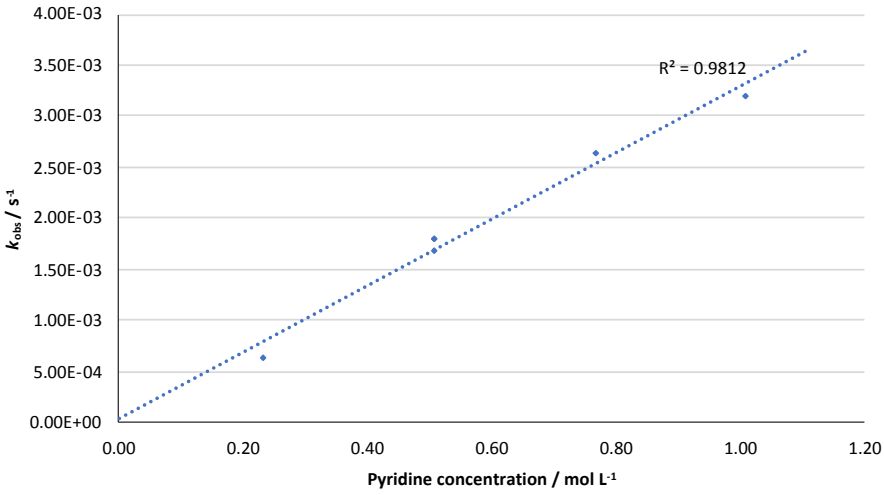


Figure S10. The pseudo first order rate constants for the reaction between benzyl bromide **1** and varying concentrations of pyridine **2** in mixtures of acetonitrile and ionic liquid **5a**, χ_{IL} *ca*. 0.2, at 295.35 K. Slope = (32.7 ± 2.3) × 10^{-4} L mol^{-1} s^{-1}, which is the same as that determined from replicates at [pyridine **2**] *ca.* 0.5 ((34.9 ± 1.2) × 10^{-4} L mol^{-1} s^{-1}). The intercept ((0.4 ± 1.4) × 10^{-4}) indicates no unimolecular component to the rate constant.

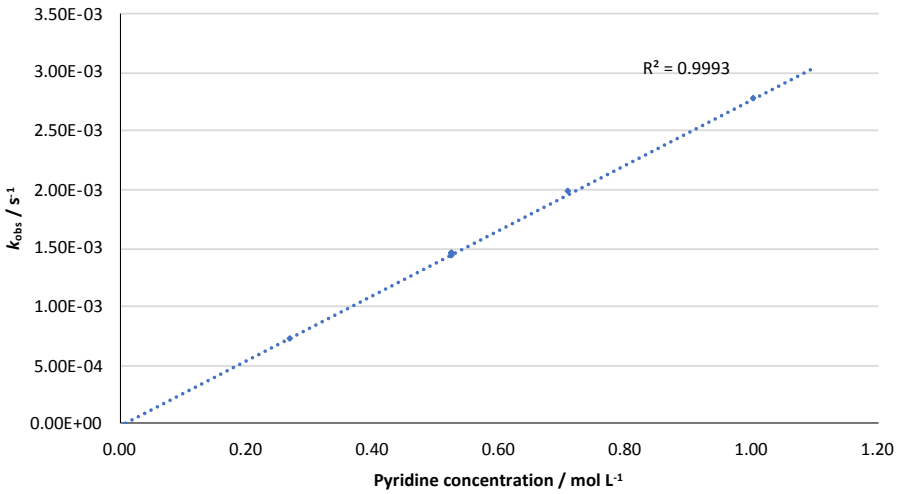


Figure S11. The pseudo first order rate constants for the reaction between benzyl bromide **1** and varying concentrations of pyridine **2** in mixtures of acetonitrile and ionic liquid **5b**, χ_{IL} *ca.* 0.2, at 295.35 K. Slope = (27.9 ± 0.4) × 10^{-4} L mol^{-1} s^{-1}, which is the same as that determined from replicates at [pyridine **2**] *ca.* 0.5 ((27.3 ± 0.4) × 10^{-4} L mol^{-1} s^{-1}). The intercept ((-2.3 ± 2.6) × 10^{-4}) indicates no unimolecular component to the rate constant.

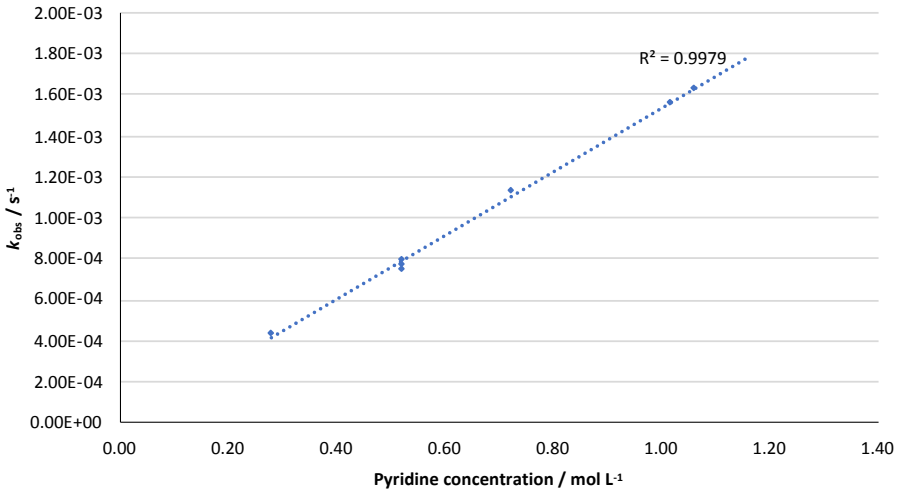
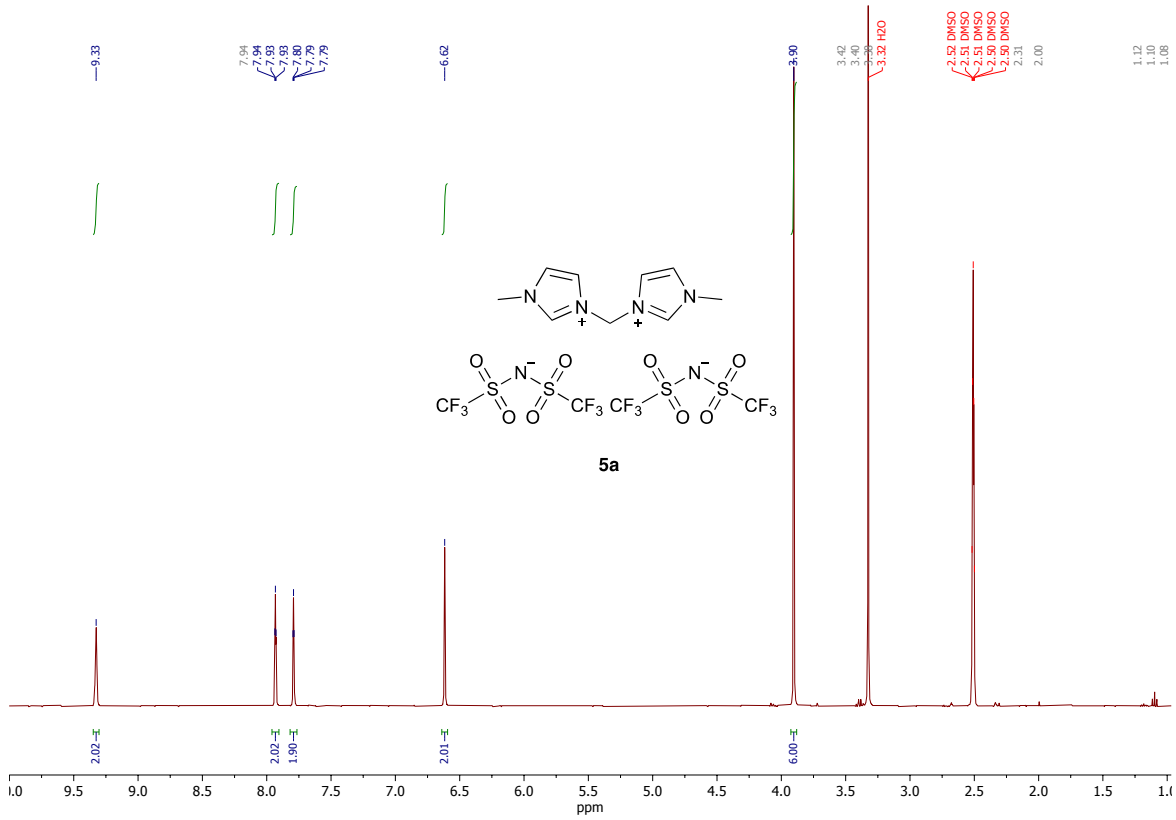


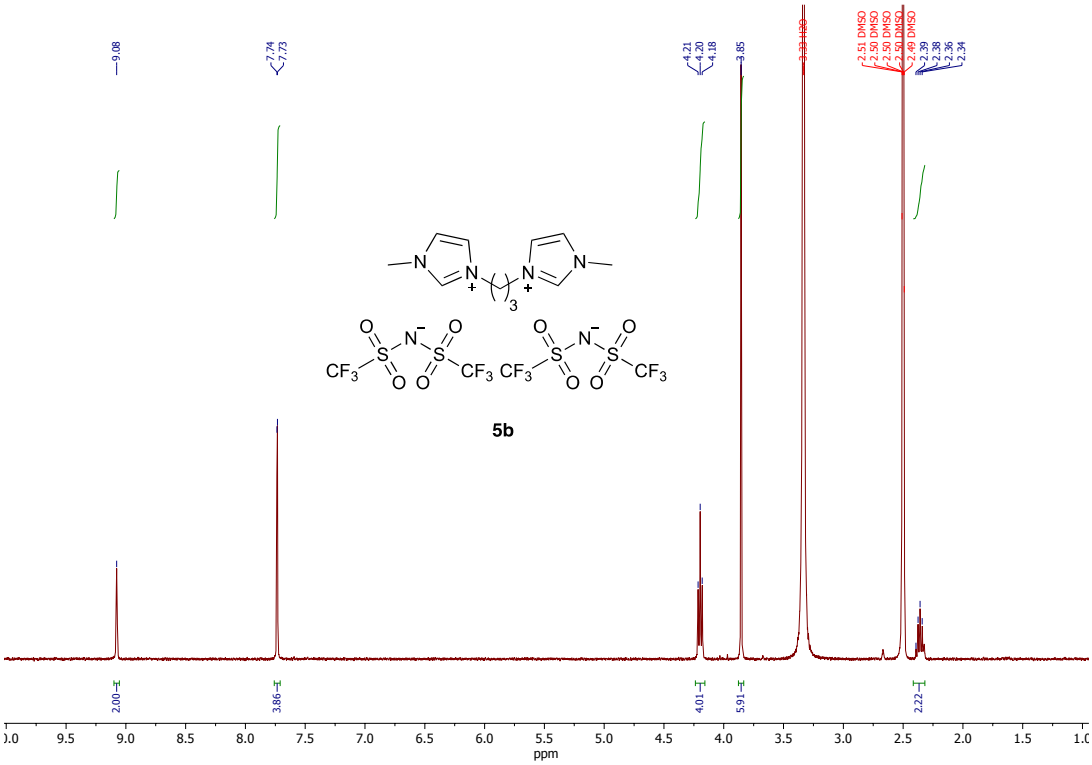
Figure S12. The pseudo first order rate constants for the reaction between benzyl bromide **1** and varying concentrations of pyridine **2** in mixtures of acetonitrile and ionic liquid **5i**, χ_{IL} *ca.* 0.2, at 295.35 K. Slope = (15.6 ± 0.3) × 10^{-4} L mol^{-1} s^{-1}, which is the same as that determined from replicates at [pyridine **2**] *ca.* 0.5 ((14.9 ± 0.4) × 10^{-4} L mol^{-1} s^{-1}). The intercept ((-2.2 ± 2.3) × 10^{-5}) indicates no unimolecular component to the rate constant.

NMR spectra of ionic liquids 5

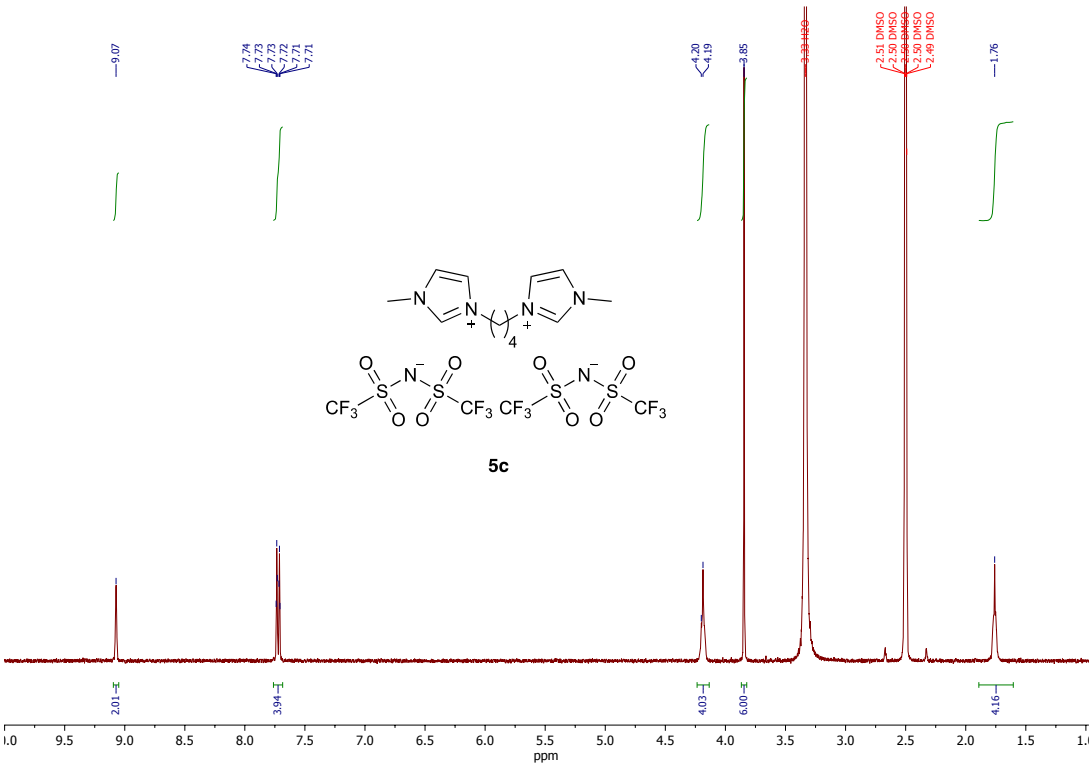
bis(3-Methylimidazolium-1-yl)methane *bis*(trifluoromethanesulfonyl)imide $[m(mim)_2][N(SO_2CF_3)_2]$ **5a**



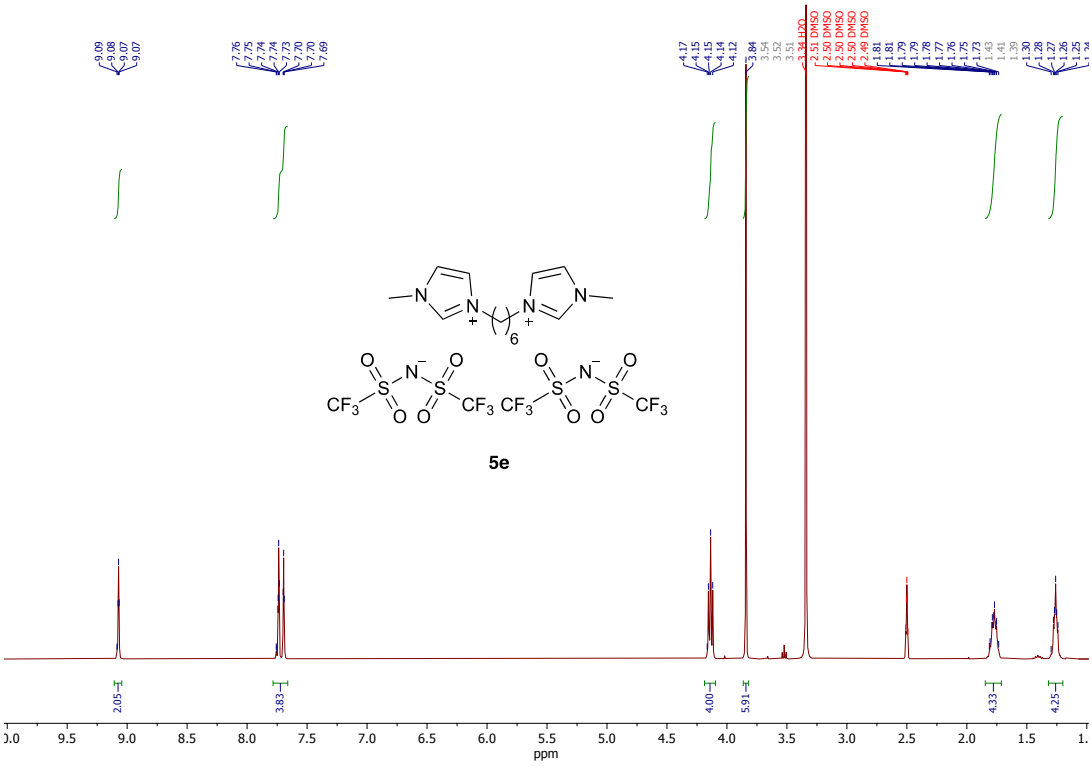
bis(3-Methylimidazolium-1-yl)propane *bis*(trifluoromethanesulfonyl)imide $[p_r(mim)_2][N(SO_2CF_3)_2]$ **5b**



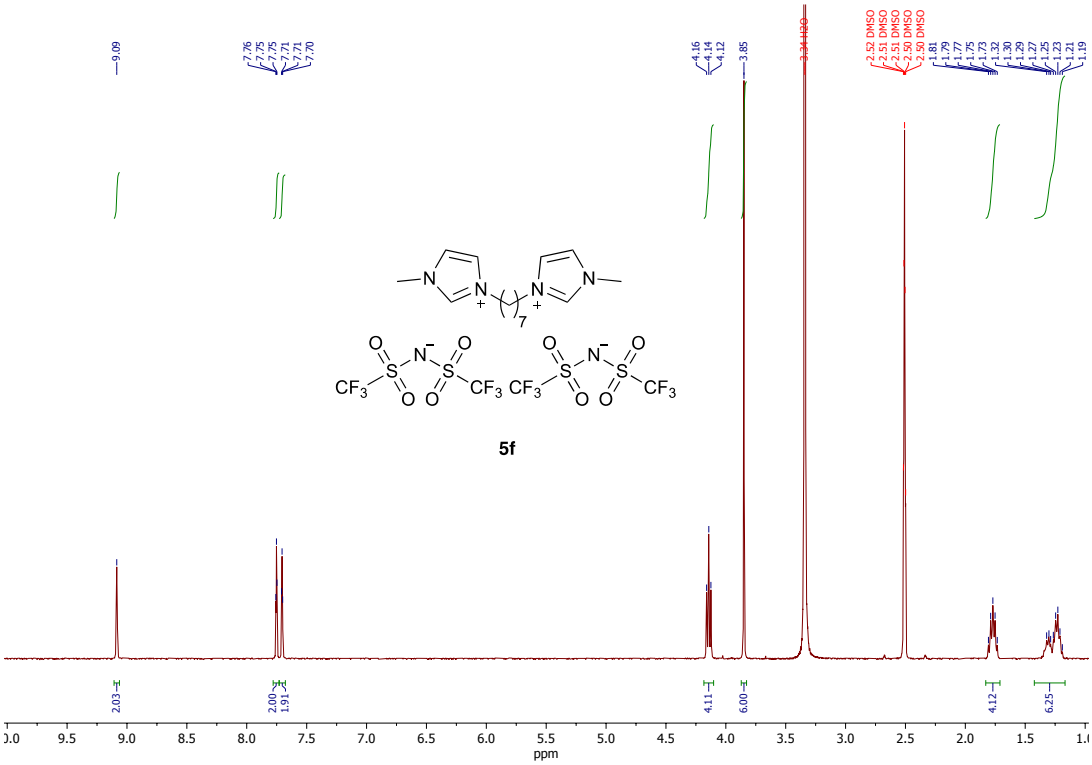
bis(3-Methylimidazolium-1-yl)butane *bis*(trifluoromethanesulfonyl)imide $[b(mim)_2][N(SO_2CF_3)_2]$ **5c**



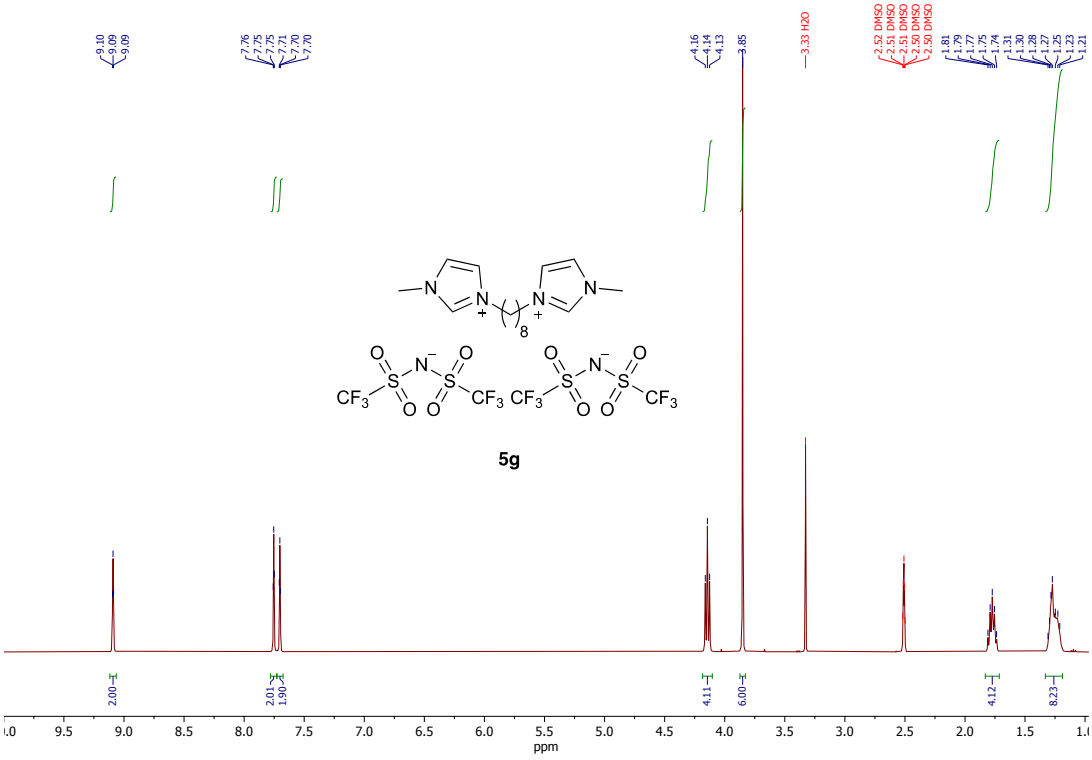
bis(3-Methylimidazolium-1-yl)hexane *bis*(trifluoromethanesulfonyl)imide $[h_x(mim)_2][N(SO_2CF_3)_2]$ **5e**



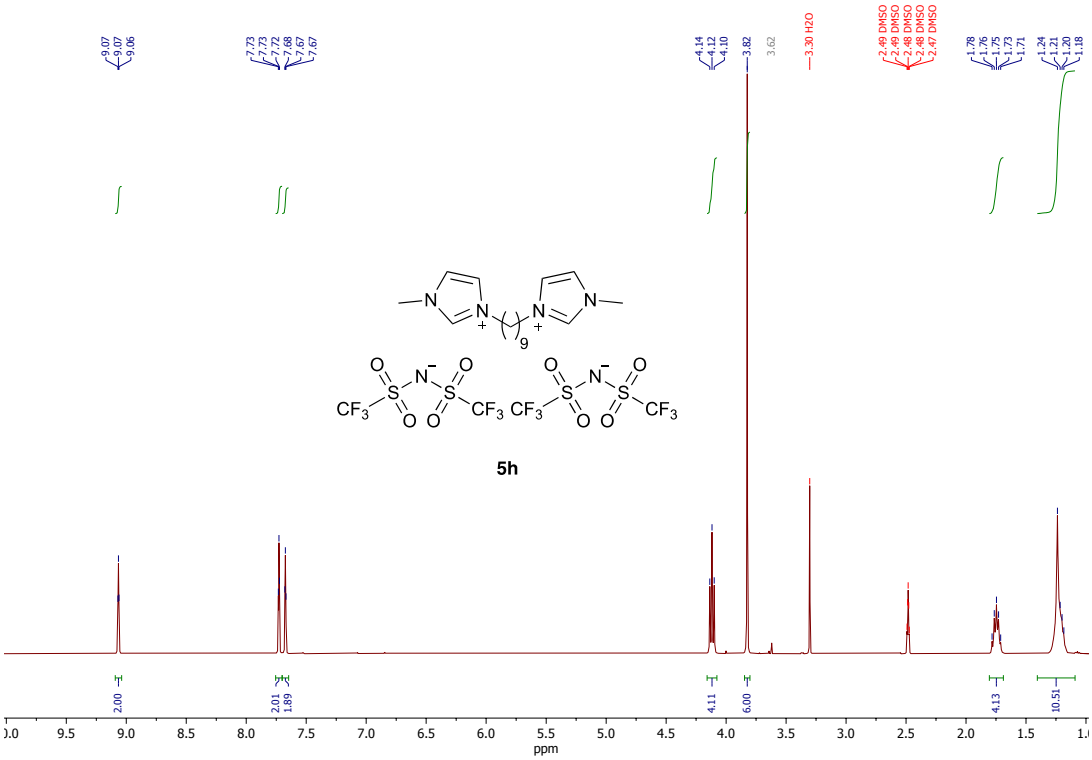
bis(3-Methylimidazolium-1-yl)heptane *bis*(trifluoromethanesulfonyl)imide $[h_p(mim)_2][N(SO_2CF_3)_2]$ **5f**



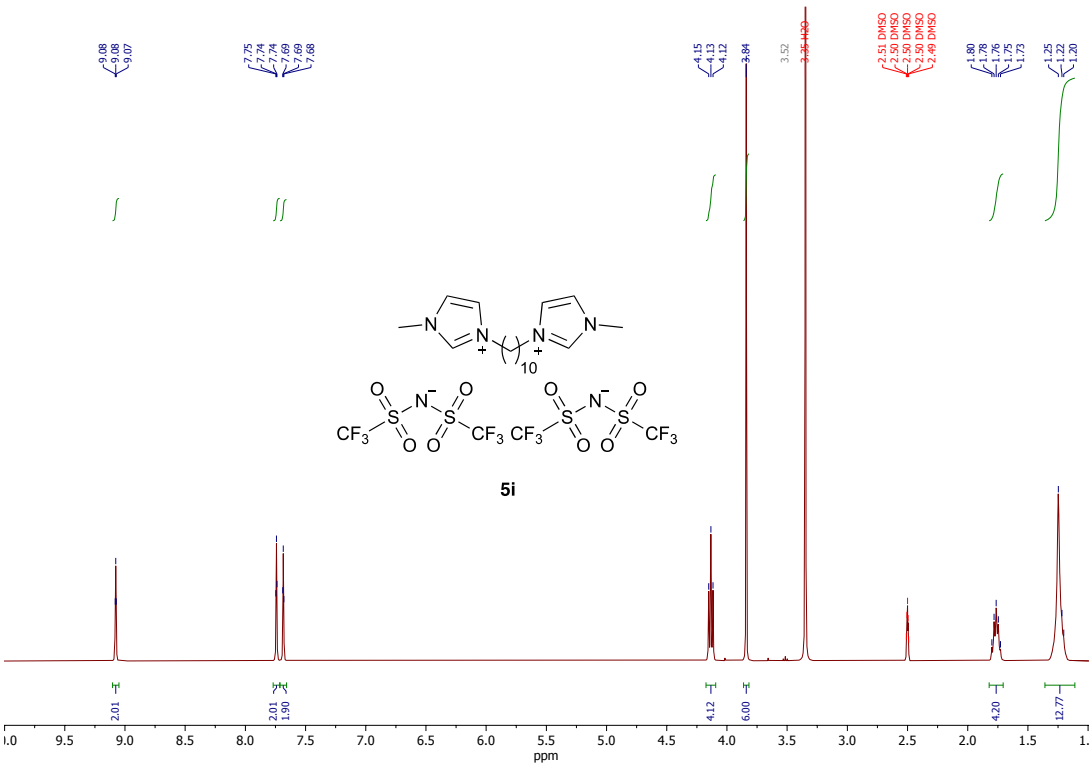
bis(3-Methylimidazolium-1-yl)octane *bis*(trifluoromethanesulfonyl)imide $[o(mim)_2][N(SO_2CF_3)_2]$ **5g**



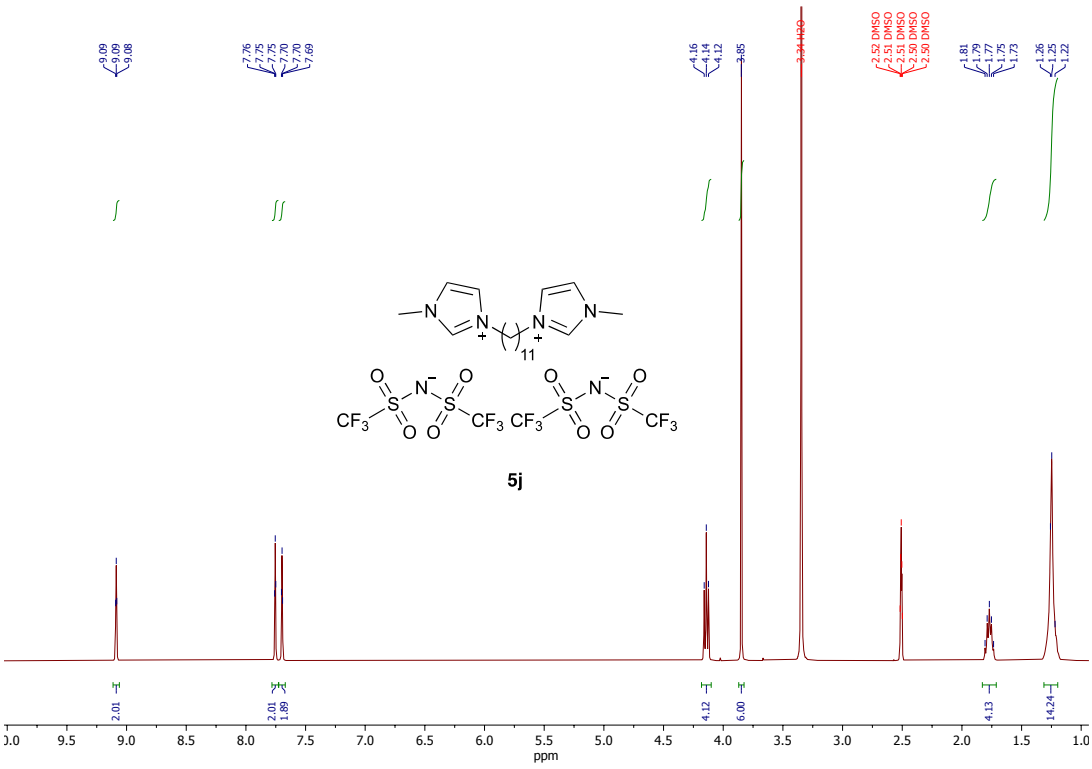
bis(3-Methylimidazolium-1-yl)nonane *bis*(trifluoromethanesulfonyl)imide $[n(mim)_2][N(SO_2CF_3)_2]$ **5h**



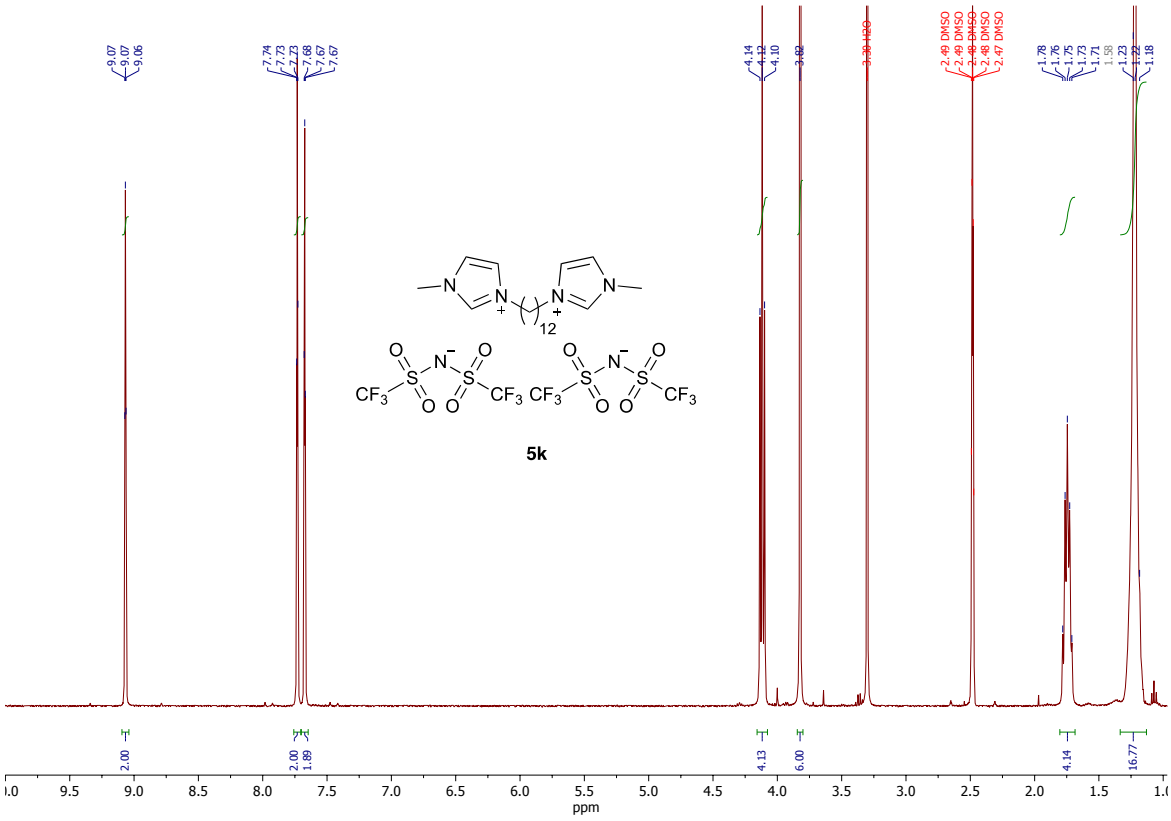
bis(3-Methylimidazolium-1-yl)decane *bis*(trifluoromethanesulfonyl)imide [d(mim)$_2$][N(SO$_2$CF$_3$)$_2$] **5i**



bis(3-Methylimidazolium-1-yl)undecane *bis*(trifluoromethanesulfonyl)imide [ud(mim)$_2$][N(SO$_2$CF$_3$)$_2$] **5j**



bis(3-Methylimidazolium-1-yl)dodecane *bis*(trifluoromethanesulfonyl)imide $[dd(mim)_2][N(SO_2CF_3)_2]$ **5k**



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