

## Electronic supporting information for

### “Probing the importance of ionic liquid structure: A general ionic liquid effect on an S<sub>N</sub>Ar process”

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### General synthetic procedures

Reagents for syntheses of the ionic liquid precursors were purchased from Sigma-Aldrich and distilled *immediately* before use, with the exception of 1,4,5-trimethylimidazole, which was purchased from Star Synthesis Co., Ltd and used without further purification. Lithium bis(trifluoromethylsulfonyl)imide used in metathesis reactions to give the desired ionic liquids **5-9**, was purchased from IoLiTec Ionic Liquids Technologies GmbH.

All other reagents used in synthesis were commercially available, purchased from either Sigma Aldrich or Alfa Aesar and used without further purification.

Organic solvents used in syntheses were either used as received from Ajax Finechem or collected from a Pure Solv MD Solvent Purification System. All organic solvents used in kinetics experiments were either collected from the aforementioned solvent purification system or purified using methods available in the literature.<sup>1</sup> Milli-Q™ water, where mentioned, was collected from a Millipore Milli-Q™ Academic System with a resistivity of 18.2 Ω·cm.

Unless stated otherwise in the text, reduced pressure used in all operations was *ca.* 210 Torr.

## Synthesis of the ionic liquids **8-16**

### *1-Butyl-3-methylimidazolium chloride 11<sup>2</sup>*

1-Methylimidazole (**67**) (32.1 g, 391 mmol) and *n*-chlorobutane (**68**) (39.8 g, 430 mmol) were mixed together and heated to 65°C with vigorous stirring under an inert and dry atmosphere for 8 days. The reaction mixture was allowed to cool to room temperature and the precipitate collected *via* filtration. The solid was washed with ethyl acetate (3 x 100 mL), recrystallized from ethyl acetate and dried under reduced pressure (< 0.5 Torr) at 65°C to give the product as a hygroscopic white solid (63.2 g, 92%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.95 (t, *J* = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.37 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.89 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 4.12 (s, 3H, NCH<sub>3</sub>), 4.32 (t, *J* = 7.4 Hz, 2H, NCH<sub>2</sub>), 7.41 and 7.55 (m, 2H, CHCH), 10.63 (s, 1H, NCHN); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>) δ 13.4 (CH<sub>2</sub>CH<sub>3</sub>), 19.5 (CH<sub>2</sub>CH<sub>3</sub>), 32.2 (NCH<sub>2</sub>CH<sub>2</sub>), 36.6 (NCH<sub>2</sub>CH<sub>2</sub>), 49.8 (NCH<sub>3</sub>), 121.7 and 123.5 (CH<sub>3</sub>NCHCH), 138.2 (NCHN).

### *1-Butyl-3-methylimidazolium dicyanimide 8<sup>2</sup>*

1-Butyl-3-methylimidazolium chloride (40.8 g, 0.233 mol) and sodium dicyanimide (21.6 g, 0.243 mol) was added to acetone (70 mL) and the resulting mixture was stirred at room temperature for 24 h. Sodium chloride was removed *via* filtration and the resulting filtrate was dried to constant weight under reduced pressure at 65°C to yield the ionic liquid **8** as a colourless, viscous liquid (45.8 g, 96%). <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-acetone) δ 0.96 (t, *J* = 7.3 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>),

1.40 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.93 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 4.04 (s, 3H,  $\text{NCH}_3$ ), 4.35 (t,  $J = 7.1$  Hz, 2H,  $\text{NCH}_2$ ), 7.67 and 7.73 (m, 2H,  $\text{CHCH}$ ), 8.97 (s, 1H,  $\text{NCHN}$ ).

*1-Butyl-3-methylimidazolium hexafluorophosphate 9<sup>2</sup>*

1-Butyl-3-methylimidazolium chloride (39.4 g, 0.225 mol) was dissolved in water (75 mL) and combined with a solution of potassium hexafluorophosphate (41.6 g, 0.237 mol) in water (75 mL). Two layers immediately formed, with the desired ionic liquid forming the bottom layer. The mixture was stirred at room temperature for 90 min, after which the top layer was decanted off. The lower layer was washed with water (5 x 100 mL) until the washings tested negative to a silver nitrate test. The organic layer was dried to constant weight under reduced pressure at 65°C to yield the ionic liquid **9** as a colourless, viscous liquid (50.2 g, 78%).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -acetone)  $\delta$  0.95 (t,  $J = 7.3$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.38 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.93 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 4.03 (s, 3H,  $\text{NCH}_3$ ), 4.33 (t,  $J = 7.2$  Hz, 2H,  $\text{NCH}_2$ ), 7.65 and 7.71 (m, 2H,  $\text{CHCH}$ ), 8.88 (s, 1H,  $\text{NCHN}$ ).

*1-Butyl-3-methylimidazolium tetrafluoroborate 10<sup>2</sup>*

1-Butyl-3-methylimidazolium chloride (63.0 g, 0.361 mol) and sodium tetrafluoroborate (43.03 g, 0.392 mol) was added to acetone (200 mL) and the resulting mixture was stirred at room temperature for 24 h. Sodium chloride was removed *via* filtration and the resulting filtrate was dried to constant weight under reduced pressure at 65°C to yield the ionic liquid **10** as a colourless, viscous liquid (58.5 g, 72%).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -acetone)  $\delta$  0.92 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ),

1.35 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.89 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 4.00 (s, 3H,  $\text{NCH}_3$ ), 4.31 (t,  $J = 7.4$  Hz, 2H,  $\text{NCH}_2$ ), 7.66 and 7.71 (m, 2H,  $\text{CHCH}$ ), 8.92 (s, 1H,  $\text{NCHN}$ ).

*1-Butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide 5<sup>2</sup>*

1,2-Dimethylimidazole (50.0 g, 0.520 mol) and *n*-chlorobutane (53.0 g, 0.572 mol) were dissolved in dry toluene (50 mL) and heated under reflux for 40 hours under a nitrogen atmosphere at 80°C; during this time, two layers formed. The vessel was allowed to cool to room temperature before being placed in the freezer at -20°C for 36 hours. The top layer was discarded, whilst the light yellow bottom layer was washed with toluene (3 x 60 mL) and dried under reduced pressure at 65°C to give 1-butyl-2,3-dimethylimidazolium chloride as a cream solid (56.4 g, 58%). <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.98 (t,  $J = 7.3$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.42 (m, 2H,  $\text{CH}_3\text{CH}_2$ ), 1.80 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.82 (s, 3H,  $\text{C}_q\text{CH}_3$ ), 4.04 (s, 3H,  $\text{NCH}_3$ ), 4.21 (t,  $J = 7.2$  Hz, 2H,  $\text{NCH}_2$ ), 7.45 and 7.80 (m, 2H,  $\text{CHCH}$ ).

1-Butyl-2,3-dimethylimidazolium chloride (56.4 g, 0.299 mol) was dissolved in water (50 mL) and combined with a solution of lithium bis(trifluoromethylsulfonyl)imide (95.0 g, 0.331 mol) in water (75 mL). Two layers immediately formed, with the desired ionic liquid forming the bottom layer. The mixture was stirred at room temperature for an hour, after which the top layer was decanted off. The lower layer was washed with water (10 x 50 mL) until the washings tested negative to a silver nitrate test. The organic layer was dried to constant weight under reduced pressure at 65°C to yield the ionic liquid **5** as a colourless, viscous liquid (109 g, 84%). <sup>1</sup>H NMR (300 MHz,  $d_6$ -acetone)  $\delta$  0.97 (t,  $J = 7.3$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.42 (m, 2H,  $\text{CH}_3\text{CH}_2$ ), 1.87 (m, 2H,

NCH<sub>2</sub>CH<sub>2</sub>), 2.83 (s, 3H, C<sub>q</sub>CH<sub>3</sub>), 3.99 (s, 3H, NCH<sub>3</sub>), 4.31 (t, *J* = 7.2 Hz, 2H, NCH<sub>2</sub>), 7.64 and 7.67 (m, 2H, CHCH).

*1-Butyl-3,4,5-trimethylimidazolium bis(trifluoromethylsulfonyl)imide 13<sup>3</sup>*

1,4,5-Trimethylimidazole (15.1 g, 0.137 mol) and *n*-chlorobutane (39.0 g, 0.421 mol) were heated at 70°C for 13 days. The reaction mixture was allowed to cool to room temperature and the precipitate collected *via* filtration and suspended in ethyl acetate (200 ml). After stirring for 2 h the ethyl acetate was decanted and process repeated twice. The remaining cream solid was dried under reduced pressure at 90°C to give 1-butyl-3,4,5-trimethylimidazolium chloride (20.1 g, 72%), m.p. 60-61°C. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-acetone) δ 0.97 (t, *J* = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.42 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>), 1.79-1.95 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 2.34 (s, 3H, NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 2.36 (s, 3H, NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 3.95 (s, 3H, NCH<sub>3</sub>), 4.29 (t, *J* = 7.4 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 10.5 (s, 1H, NCHN). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-acetone) δ 7.22 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 7.42 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 12.95 (CH<sub>2</sub>CH<sub>3</sub>), 19.19 (CH<sub>2</sub>CH<sub>3</sub>), 31.53 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 32.88 (NCH<sub>3</sub>), 46.23 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 125.98 ((NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 127.07 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 136.74 (NCHN).

1-Butyl-3,4,5-trimethylimidazolium chloride (20.0 g, 0.099 mol) was dissolved in water (20 ml) and combined with a solution of lithium *bis*(trifluoromethylsulfonyl)imide (31.4 g, 0.109 mol) in water (30 ml). Two layers immediately formed, with the desired ionic liquid forming the bottom layer. The mixture was stirred for an hour at room temperature. The top layer was discarded while the lower layer was collected and was washed with water (10 x 30 ml) until the washings tested negative to the silver nitrate test. The organic layer was decolourised using charcoal in dichloromethane, then dried under reduced pressure at 90°C to yield the ionic liquid as a yellow,

viscous liquid (26.4 g, 60%).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -acetone)  $\delta$  0.97 (t,  $J = 7.3$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.42 (m, 2H,  $\text{CH}_3\text{CH}_2$ ), 1.79-1.92 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.34 (s, 3H,  $\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}$ ), 2.36 (s, 3H,  $\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}$ ), 3.89 (s, 3H,  $\text{NCH}_3$ ), 4.22 (t,  $J = 7.4$  Hz, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 8.81 (s, 1H,  $\text{NCHN}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -acetone)  $\delta$  7.20 ( $\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}$ ), 7.39 ( $\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}$ ), 12.80 ( $\text{CH}_2\text{CH}_3$ ), 19.15 ( $\text{CH}_2\text{CH}_3$ ), 31.34 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 33.08 ( $\text{NCH}_3$ ), 46.57 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 120.06 (q,  $J_{\text{HF}} = 321$  Hz,  $\text{NSO}_2((\text{CF}_3)_2)$ ), 126.85 ( $\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}$ ), 127.83 ( $\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}$ ), 134.20 ( $\text{NCHN}$ ).

*1-Butyl-2,3,4,5-tetramethylimidazolium bis(trifluoromethylsulfonyl)imide 7<sup>2</sup>*

1,2,4,5-Tetramethylimidazole (10.0 g, 0.0806 mol) and *n*-chlorobutane (13.6 g, 0.147 mol) were combined and heated under reflux for 24 hours under a nitrogen atmosphere at 80°C; during this time two layers formed. The vessel was allowed to cool to room temperature before being placed in the freezer at -20°C for 36 hours. The top layer was discarded, whilst the bottom layer was dried under reduced pressure at 140°C. This yielded a dark brown viscous oil (14.2 g) containing *ca.* 5% of the imidazole starting material by  $^1\text{H}$  NMR spectroscopy, which was used without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.90 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.39 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.73 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.21 (s, 3H,  $\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}$ ), 2.23 (s, 3H,  $\text{NC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}$ ), 2.86 (s, 3H,  $\text{NC}(\text{CH}_3)\text{N}$ ), 3.55 (s, 3H,  $\text{NCH}_3$ ), 3.83 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).

1-Butyl-2,3,4,5-tetramethylimidazolium chloride (14.2 g, from above) was dissolved in water (50 mL) and acetone (40 mL) and combined with a solution of lithium bis(trifluoromethylsulfonyl)imide (20.9 g, 0.0727 mol) in water (60 mL). The mixture was

stirred at room temperature for 12 hours, at which point the top layer was decanted off. The lower layer was washed with water (3 x 100 mL) until the washings tested negative to a silver nitrate test. The organic layer was decolourised using charcoal in dichloromethane, which was removed *in vacuo*, and dried to constant weight under reduced pressure at 90°C to yield the ionic liquid **7** as light yellow crystals (20.09 g, 66% over two steps) which contained none of imidazole starting material, m.p. 31-32°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.94 (t, *J* = 7.3 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.36 (h, *J* = 7.3 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.64 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.17 (m, 6H, NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 2.53 (s, 3H, NC(CH<sub>3</sub>)N), 3.57 (s, 3H, NCH<sub>3</sub>), 3.91 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 8.35 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 8.36 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 9.95 (NC(CH<sub>3</sub>)N), 13.33 (CH<sub>2</sub>CH<sub>3</sub>), 19.66 (CH<sub>2</sub>CH<sub>3</sub>), 31.41 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.77 (NCH<sub>3</sub>), 45.31 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 119.60 (q, *J*<sub>HF</sub> = 320 Hz, NSO<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>), 124.94 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 126.12 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)N), 141.7 (NC(CH<sub>3</sub>)N).

#### *1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide 8<sup>4</sup>*

1-Methylpyrrolidine (50.0 g, 0.587 mol) and *n*-chlorobutane (60.0 g, 0.763 mol) were dissolved in dry acetonitrile (50 mL) and heated under reflux for 18 hours under a nitrogen atmosphere at 70°C. The solvent was removed under reduced pressure and the remaining solid was washed in petroleum ether (3 x 150 mL) and the residue dried under reduced pressure at 65°C for 6 hours to give 1-butyl-1-methylpyrrolidinium chloride as a pale yellow solid (100 g, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.01 (t, *J* = 7.5 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>); 1.41 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.80 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.23 (m, 4H, CH<sub>3</sub>NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 3.06 (s, 3H, NCH<sub>3</sub>), 3.35 (m, 2H, NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 3.52 (m, 4H, CH<sub>3</sub>NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>).



1-Butyl-1-methylpyrrolidinium chloride (100 g, 0.565 mol) was dissolved in water (300 mL) and combined with a solution of lithium bis(trifluoromethylsulfonyl)imide (162 g, 0.565 mol) in water (300 mL). Two layers immediately formed, with the desired ionic liquid forming in the bottom layer. The mixture was stirred at room temperature for 17 hours, after which the top layer was decanted off. The lower layer was washed with water (7 x 50 mL) until the washings tested negative to a silver nitrate test. The bright yellow organic layer was decolourised twice using charcoal in dichloromethane, the solvent was removed *in vacuo* and the residue was dried to constant weight under reduced pressure at 65°C to give the title compound **8** as a pale yellow viscous liquid (207 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.02 (t, *J* = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.45 (h, *J* = 7.4 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.77 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.30 (m, 4H, CH<sub>3</sub>NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 3.08 (s, 3H, NCH<sub>3</sub>), 3.34 (m, 2H, NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 3.58 (m, 4H, CH<sub>3</sub>NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>).

*Tetraoctylammonium bis(trifluoromethylsulfonyl)imide 9<sup>5</sup>*

To a solution of tetraoctylammonium bromide (24.9 g, 0.0455 mol) in acetone (100 mL) and water (50 mL) was added a solution of lithium bis(trifluoromethylsulfonyl)imide (15.0 g, 0.0519 mol) in water (50 mL) and stirred at room temperature for 12 hours. The top water layer was decanted off and the bottom layer containing the ionic liquid was washed with water (3 x 100 mL) until the washings tested negative to silver nitrate. The organic layer was dried to constant weight under reduced pressure at 65°C to give the title compound **9** which was isolated as colourless crystals on standing (22.1 g, 96%), m.p. 30-31°C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 6.5$  Hz, 12H,  $\text{N}(\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3)_4$ ), 1.13-1.44 (m, 40H,  $\text{N}(\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3)_4$ ), 3.10 (m, 8H,  $\text{NCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ), 4.52-4.91 (m, 8H,  $\text{NCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ).  $^{19}\text{F}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.75 (s,  $\text{NSO}_2(\text{CF}_3)_2$ ).

### General procedures for kinetic analyses

A series of 10 mL stock solutions was prepared containing triethylamine (350 mg, 0.418 mol) and ethanol (950 mg, 2.06 mol) dissolved in one of the ILs **8-9,12-16**. The probe in the NMR spectrometer was equilibrated to the desired temperature ( $\pm 0.1$  K) using a thermocouple fixed in a 5 mm NMR tube containing either ethanol (for temperatures  $< 45$  °C) or ethylene glycol (for temperatures  $> 45$  °C). A portion of the stock solution (0.6 mL for a 5 mm NMR tube) was added to an NMR tube followed by 1-fluoro-2,4-dinitrobenzene **5** (15 mg, 0.06 mol). The NMR tube was placed in the NMR spectrometer and the temperature of the sample was allowed to equilibrate. The reaction progress was followed using  $^{19}\text{F}$  NMR spectroscopy to observe the depletion of the starting material signal at  $\delta -109$ . This allowed calculation of the observed pseudo first order rate constant and, from the ethanol concentration, the second order rate constant for the process. This was repeated at least in triplicate for each solvent over each of four temperatures. The results are summarized in Tables S2-S11.

In the case of the preparations of mixtures of ionic liquids **10** and **11** with ionic liquid **4**, a mass of the primary ionic liquid (**10** or **11**) that corresponded to a mole fraction of at least 0.4 was combined with *ca.* 950 mg of ethanol and 395 mg triethylamine and was brought to volume with ionic liquid **4** in a 10 mL volumetric flask (see Table S1 for exact masses).

**Table S1.** Masses for the components of the stock solutions made up for ionic liquids **10** and **11** in the cases where they could not be studied as solvents for the reaction shown in Scheme 2.

ionic liquid	mass of <b>10</b> or <b>11</b> / g	mass of <b>4</b> / g	ethanol / mg	triethylamine / g	mole fraction <b>10</b> or <b>11</b>
<b>10</b>	4.189	6.989	956.2	392.0	0.53
<b>11</b>	2.712	8.310	950.9	393.1	0.43

Rate data for the Eyring plot shown in Figure 1, main text

**Table S2.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in ethanol at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 12.62 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-5} \text{ s}^{-1}$	$k_2 / 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$
304.0	7.80	0.619
304.0	9.50	0.754
304.0	10.2	0.810
314.0	17.2	1.36
314.0	14.9	1.18
314.0	17.4	1.38
324.0	33.8	2.68
324.0	34.7	2.74
324.0	32.7	2.59
334.0	58.7	4.65
334.0	44.6	3.53
334.0	57.8	4.58

**Table S3.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **8** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.07 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
303.0	1.47	0.712
303.0	1.01	0.486
303.0	0.85	0.410
313.0	2.38	1.15
313.0	1.96	0.95
313.0	2.34	1.13
323.0	5.10	2.46
323.0	4.56	2.20
323.0	4.76	2.30
333.0	10.5	5.06
333.0	10.3	4.98
333.0	10.3	4.97

**Table S4.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **9** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.06 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
303.0	1.31	0.635
303.0	1.34	0.650
303.0	1.17	0.570
313.0	3.14	1.52
313.0	3.04	1.47
313.0	3.63	1.76
323.0	6.83	3.32
323.0	6.48	3.15
323.0	6.20	3.01
333.0	11.9	5.80
333.0	12.4	6.01
333.0	12.1	5.89

**Table S5.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **10** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.10 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
313.0	1.64	0.793
313.0	1.89	0.914
313.0	1.86	0.900
323.0	3.41	1.65
323.0	3.24	1.57
323.0	3.93	1.90
333.0	8.26	3.99
333.0	6.45	3.12
333.0	6.44	3.11
343.0	10.1	4.86
343.0	9.70	4.68
343.0	10.7	5.14



**Table S6.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **11** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.16 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
303.0	3.31	1.61
303.0	3.32	1.61
303.0	3.18	1.54
313.0	5.49	2.66
313.0	6.92	3.36
313.0	4.09	1.98
323.0	12.5	6.05
323.0	11.8	5.75
323.0	8.19	3.97
333.0	18.0	8.72
333.0	20.8	10.1
333.0	20.4	9.92

**Table S7.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **12** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.05 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
314.0	3.23	1.58
314.0	4.17	2.02
314.0	4.53	3.27
324.0	6.71	3.50
324.0	7.39	3.59
324.0	8.00	3.88
334.0	11.5	5.59
334.0	11.9	5.78
334.0	14.1	6.84
344.0	20.4	9.93
344.0	17.5	8.49
344.0	16.1	7.83

**Table S8.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **13** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.15 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
304.8	1.70	1.44
304.6	2.14	1.23
304.6	1.92	0.82
314.0	3.36	2.50
314.1	3.14	2.05
314.1	4.61	2.72
324.1	7.98	3.71
324.1	7.02	3.47
324.1	5.59	3.08
333.7	14.5	6.74
333.3	13.8	7.28
333.4	12.5	6.88

**Table S9.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **14** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.22 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
314.0	3.19	1.44
314.0	2.85	1.28
314.0	2.63	1.19
324.0	5.99	2.70
324.0	5.68	2.56
324.0	5.25	2.36
334.0	8.80	3.97
334.0	10.6	4.79
334.0	10.4	4.69
344.0	15.8	7.13
344.0	15.3	6.91
344.0	16.4	7.39



**Table S10.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **15** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.16 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
304.0	2.11	0.976
304.0	1.93	0.895
304.0	1.88	0.870
314.0	3.74	1.73
314.0	4.02	1.86
314.0	4.02	1.86
324.0	7.74	3.58
324.0	6.50	3.01
324.0	8.15	3.77
334.0	10.1	4.66
334.0	10.1	4.68
334.0	9.37	4.34

**Table S11.** Observed rate constants and second-order rate constants for the ethanolysis of 1-fluoro-2,4-dinitrobenzene (**5**) in the ionic liquid **16** at different temperatures. The latter was calculated using the known concentration of ethanol. [Ethanol] = 2.10 mol L<sup>-1</sup>

Temperature / K	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \cdot \text{s}^{-1}$
304.0	2.30	1.09
304.0	1.82	0.866
304.0	1.89	0.883
314.0	4.06	1.97
314.0	3.97	1.93
314.0	4.43	2.11
324.0	7.75	3.69
324.0	6.85	3.32
324.0	7.75	3.76
334.0	14.6	6.96
334.0	15.3	7.44
334.0	13.7	6.64

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