

Supporting information

Solubility and Diffusivity of Oxygen in Ionic Liquids

Tangqiumei Song ^a, Oscar Morales-Collazo ^b, and Joan F. Brennecke ^{b,*}

^a*Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana, 46556, USA*

^b*McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, USA*

**Tel: (512) 471-5092. Fax: (512) 471-1760. E-mail: jfb@che.utexas.edu.*

Table S1. Densities of ILs investigated in this work at pressure $p=0.1$ MPa^a.

| T (K) | Density, ρ (g/cm ³) | | | | | | | |
|-------|--------------------------------------|----------------------------------|--------------------------------|------------------|------------------|-----------------|-----------------|-----------------|
| | [PP ₁₄] [TFSI] | [Pyrro ₁₄] [TFSI] | [N ₁₂₂₄] [TFSI] | [MTBD] [TFSI] | [MTBD] [beti] | [TMG] [beti] | [MTBD] [TSE] | [bmim] [TSE] |
| 283 | | | | 1.527 | | 1.588 | 1.503 | 1.430 |
| 293 | 1.384 | 1.398 | 1.362 | 1.518 | 1.587 | 1.577 | 1.493 | 1.420 |
| 295 | 1.382 | 1.396 | 1.361 | 1.516 | 1.584 | 1.575 | 1.491 | 1.418 |
| 298 | 1.380 | 1.394 | 1.358 | 1.513 | 1.582 | 1.571 | 1.488 | 1.415 |
| 303 | 1.375 | 1.389 | 1.354 | 1.508 | 1.577 | 1.566 | 1.483 | 1.410 |
| 313 | 1.367 | 1.380 | 1.345 | 1.498 | 1.566 | 1.555 | 1.472 | 1.399 |
| 323 | 1.358 | 1.372 | 1.336 | 1.489 | 1.556 | 1.544 | 1.462 | 1.389 |
| 333 | 1.350 | 1.363 | 1.328 | 1.479 | 1.545 | 1.533 | 1.452 | 1.379 |
| 343 | 1.341 | 1.355 | 1.319 | 1.470 | 1.535 | 1.522 | 1.443 | 1.370 |
| 353 | 1.333 | 1.346 | 1.311 | 1.461 | 1.525 | 1.512 | 1.433 | 1.360 |

^a Standard uncertainties are $u(T) = 0.1$ K, $u_r(\rho) = 0.002$.

Table S2. Viscosities of ILs investigated in this work at pressure $p=0.1$ MPa^a

| T (K) | Viscosity, η (mPa•s) | | | | | | | |
|-------|-------------------------------|----------------------------------|--------------------------------|------------------|------------------|-----------------|-----------------|-----------------|
| | [PP ₁₄] [TFSI] | [Pyrro ₁₄] [TFSI] | [N ₁₂₂₄] [TFSI] | [MTBD] [TFSI] | [MTBD] [beti] | [TMG] [beti] | [MTBD] [TSE] | [bmim] [TSE] |
| 283 | 512 | 159 | 306 | 297 | 1342 | | 348 | 112 |
| 293 | 240 | 90 | 156 | 151 | 538 | 341 | 169 | 66 |
| 295 | | | | 133 | 463 | 295 | 149 | 60 |
| 298 | 173 | 70 | 114 | 112 | 363 | 240 | 125 | 52 |
| 303 | 131 | 57 | 89 | 89 | 264 | 174 | 97 | 43 |
| 313 | 78 | 39 | 57 | 57 | 144 | 96 | 61 | 30 |
| 323 | 51 | 28 | 39 | 39 | 87 | 59 | 42 | 23 |
| 333 | 37 | 22 | 29 | 30 | 58 | 43 | 31 | 19 |
| 343 | 27 | 17 | 23 | 24 | 41 | 30 | 25 | 16 |
| 353 | 22 | 14 | 18 | 19 | 30 | 20 | 20 | 15 |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(\eta)_r = 0.05$.

Table S3. Solubility of O₂ in [hmim][TFSI], [hmpy][TFSI], [P₂₂₂₈][TFSI], [PP₁₃][TFSI], [PP₁₄][TFSI], [bthiol][TFSI], [bmim][TSE], and [MTBD][TSE] at 293 K^a

| [hmim][TFSI] | | [hmpy][TFSI] | | [P ₂₂₂₈][TFSI] | | [PP ₁₃][TFSI] | |
|---------------------------|------------------------------|----------------|------------------------------|----------------------------|------------------------------|---------------------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1.01 | 0.036 | 1.00 | 0.031 | 1.00 | 0.034 | 1.01 | 0.022 |
| 1.99 | 0.069 | 2.99 | 0.091 | 1.49 | 0.048 | 2.02 | 0.045 |
| 3.01 | 0.103 | 4.98 | 0.142 | 2.03 | 0.069 | 3.01 | 0.066 |
| 3.99 | 0.130 | 6.97 | 0.189 | 3.00 | 0.096 | 4.00 | 0.090 |
| 4.98 | 0.158 | 6.06 | 0.167 | 4.00 | 0.124 | 5.01 | 0.110 |
| 5.99 | 0.184 | 4.03 | 0.118 | 4.49 | 0.132 | 6.01 | 0.127 |
| 6.97 | 0.205 | | | | | 7.00 | 0.145 |
| [PP ₁₄][TFSI] | | [bthiol][TFSI] | | [bmim][TSE] | | [MTBD][TSE] | |
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1.03 | 0.032 | 0.50 | 0.012 | 1.00 | 0.030 | 1.01 | 0.031 |
| 2.00 | 0.055 | 1.50 | 0.037 | 2.01 | 0.062 | 2.00 | 0.056 |
| 3.00 | 0.080 | 2.49 | 0.057 | 3.00 | 0.090 | 3.00 | 0.084 |
| 3.99 | 0.101 | 5.49 | 0.115 | 3.98 | 0.113 | 3.99 | 0.105 |
| 5.00 | 0.124 | 6.51 | 0.134 | 4.99 | 0.137 | 4.99 | 0.130 |
| 5.99 | 0.142 | 6.03 | 0.127 | 5.99 | 0.159 | 7.97 | 0.187 |
| 7.04 | 0.162 | | | 7.96 | 0.196 | 7.04 | 0.172 |
| 8.11 | 0.180 | | | 7.06 | 0.179 | 6.03 | 0.154 |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa

Table S4. Solubility of O₂ in [MTBD][beti] at 293 K, 313 K, and 333 K^a

| 293 K | | 313 K | | 333 K | |
|----------------|------------------------------|----------------|------------------------------|----------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 2.52 | 0.083 | 1.05 | 0.025 | 1.07 | 0.025 |
| 5.51 | 0.164 | 3.00 | 0.075 | 3.00 | 0.057 |
| 8.00 | 0.215 | 4.99 | 0.113 | 4.99 | 0.100 |
| 7.02 | 0.195 | | | | |
| 6.02 | 0.171 | | | | |
| 4.51 | 0.135 | | | | |
| 3.52 | 0.106 | | | | |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa

Table S5. Solubility of O₂ in [MTBD][TFSI] at 293 K, 313 K, and 333 K^a

| 293 K | | 313 K | | 333 K | |
|----------------|------------------------------|----------------|------------------------------|----------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 1.02 | 0.029 | 1.02 | 0.019 | 1.01 | 0.013 |
| 3.01 | 0.074 | 3.00 | 0.054 | 3.02 | 0.046 |
| 4.98 | 0.116 | | | | |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa

Table S6. Solubility of O₂ in [TMG][beti] at 293 K, 313 K, and 333 K^a

| 293 K | | 313 K | | 333 K | |
|----------------|------------------------------|----------------|------------------------------|----------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 0.11 | 0.011 | 1.04 | 0.028 | 3.03 | 0.073 |
| 1.08 | 0.048 | 3.01 | 0.077 | 5.01 | 0.119 |
| 3.02 | 0.113 | 4.98 | 0.129 | 5.97 | 0.140 |
| 4.99 | 0.171 | 5.98 | 0.154 | 4.09 | 0.101 |
| 7.98 | 0.243 | | | 2.01 | 0.047 |
| 6.54 | 0.214 | | | 0.99 | 0.024 |
| 4.01 | 0.144 | | | | |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa.

Table S7. Solubility of O₂ in [N₁₂₂₄][TFSI] at 293 K, 313 K, and 333 K^a

| 293 K | | 313 K | | 333 K | |
|----------------|------------------------------|----------------|------------------------------|----------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 1.01 | 0.034 | 1.00 | 0.022 | 1.26 | 0.021 |
| 2.00 | 0.062 | 2.00 | 0.045 | 2.00 | 0.034 |
| 3.00 | 0.088 | 3.00 | 0.068 | 3.01 | 0.057 |
| 4.01 | 0.117 | 6.01 | 0.138 | 7.00 | 0.141 |
| 4.99 | 0.138 | 7.02 | 0.159 | 6.01 | 0.124 |
| 5.99 | 0.159 | 5.01 | 0.116 | 4.99 | 0.102 |
| 7.98 | 0.203 | 4.02 | 0.094 | 3.99 | 0.080 |
| 7.02 | 0.183 | | | 3.01 | 0.058 |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa.

Table S8. Solubility of O₂ in [DEME][TFSI] at 293 K, 313 K, and 333 K^a

| 293 K | | 313 K | | 333 K | |
|----------------|------------------------------|----------------|------------------------------|----------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 1.02 | 0.026 | 1.00 | 0.023 | 1.02 | 0.014 |
| 2.01 | 0.050 | 2.00 | 0.045 | 2.01 | 0.031 |
| 3.01 | 0.074 | 3.01 | 0.064 | 4.01 | 0.070 |
| 4.01 | 0.097 | 3.99 | 0.085 | 2.96 | 0.051 |
| 5.01 | 0.117 | 4.99 | 0.103 | 9.32 | 0.155 |
| 6.01 | 0.137 | 7.02 | 0.144 | 6.01 | 0.103 |
| 7.00 | 0.157 | | | | |
| 8.00 | 0.175 | | | | |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa.

Table S9. Solubility of O₂ in [PP₁₂₀₁][TFSI] at 293 K, 313 K, and 333 K^a

| 293 K | | 313 K | | 333 K | |
|----------------|------------------------------|----------------|------------------------------|----------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 2.32 | 0.048 | 1.02 | 0.018 | 1.00 | 0.026 |
| 3.01 | 0.061 | 3.01 | 0.058 | 3.11 | 0.057 |
| 4.03 | 0.079 | 5.00 | 0.099 | 4.99 | 0.087 |
| 5.01 | 0.097 | | | | |
| 6.00 | 0.110 | | | | |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa.

Table S10. Solubility of O₂ in [Pyrro₁₂₀₁][TFSI] at 293 K, 313 K, and 333 K^a

| 293 K | | 313 K | | 333 K | |
|----------------|------------------------------|----------------|------------------------------|----------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 1.02 | 0.027 | 1.00 | 0.021 | 1.04 | 0.016 |
| 2.06 | 0.049 | 2.98 | 0.063 | 3.33 | 0.060 |
| 3.01 | 0.070 | 4.99 | 0.105 | 4.97 | 0.088 |
| 4.02 | 0.094 | | | | |
| 5.00 | 0.111 | | | | |
| 5.99 | 0.127 | | | | |
| 7.00 | 0.146 | | | | |
| 8.01 | 0.164 | | | | |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa.

Table S11. Solubility of O₂ in [Pyrro₁₄][TFSI] at 293 K, 313 K, and 333 K^a

| 293 K | | 313 K | | 333 K | |
|----------------|------------------------------|----------------|------------------------------|----------------|------------------------------|
| Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction | Pressure (MPa) | O ₂ mole fraction |
| 1.00 | 0.037 | 1.02 | 0.026 | 1.03 | 0.025 |
| 1.99 | 0.068 | 3.00 | 0.072 | 3.02 | 0.060 |
| 2.99 | 0.099 | 5.00 | 0.102 | 4.98 | 0.089 |
| 3.99 | 0.127 | 5.98 | 0.116 | 3.99 | 0.072 |
| 4.99 | 0.154 | 3.99 | 0.086 | 1.98 | 0.047 |
| 5.98 | 0.176 | 1.98 | 0.049 | | |
| 7.98 | 0.221 | | | | |
| 7.03 | 0.200 | | | | |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(x_{O_2}) = 0.001$ mole fraction, $u(p) = 0.01$ MPa.

Table S12. Diffusion coefficients of O₂ at 313 K and 333 K, 3 MPa and 5 MPa

| Ionic Liquids | At 313 K | | | | At 333 K | | | |
|--------------------------------|--|-------|-------|-------|--|-------|-------|-------|
| | Diffusion coefficients of O ₂ , $D_{O_2} \times 10^6 / \text{cm}^2 \text{ s}^{-1}$ | | | | Diffusion coefficients of O ₂ , $D_{O_2} \times 10^6 / \text{cm}^2 \text{ s}^{-1}$ | | | |
| | 3 MPa | | 5 MPa | | 3 MPa | | 5 MPa | |
| [Pyrro ₁₂₀₁][TFSI] | 4.9 | ± 0.3 | 6.0 | ± 0.5 | 6.0 | ± 2.0 | 8.0 | ± 2.0 |
| [Pyrro ₁₄][TFSI] | 4.4 | ± 0.3 | 4.6 | ± 0.2 | 6.4 | ± 0.2 | 6.7 | ± 0.7 |
| [DEME][TFSI] | 6.0 | ± 1.0 | - | - | 7.0 | ± 1.0 | - | - |
| [MTBD][TFSI] | 4.1 | ± 0.3 | - | - | 3.0 | ± 2.0 | - | - |
| [N ₁₂₂₄][TFSI] | 4.4 | ± 0.2 | 4.6 | ± 0.2 | 6.5 | ± 0.4 | 6.5 | ± 0.6 |
| [PP ₁₂₀₁][TFSI] | 3.5 | ± 0.6 | 2.5 | ± 1.0 | 4.3 | ± 0.7 | 5.4 | ± 1.0 |
| [TMG][beti] | 3.0 | ± 0.2 | 3.2 | ± 0.2 | 5.3 | ± 0.2 | - | - |
| [MTBD][beti] | 2.0 | ± 1.0 | 2.0 | ± 0.5 | - | - | - | - |

^a Standard uncertainties are $u(T) = 0.1$ K, $u(p) = 0.01$ MPa, and the standard uncertainties in the diffusion coefficients are listed in the table.

Synthesis Methods

Triethyl(octyl)phosphonium bromide, [P₂₂₂₈][Br]

Under inert atmosphere, in a flame dried round bottom flask (500 mL) a solution of triethylphosphine (25 g, 212 mmol) in anhydrous toluene (200 mL) was treated with 1-bromooctane (43 g, 222 mmol) via cannula. The reaction was stirred at room temperature for 20 minutes and 343 K for 5 h. After completion the reaction was concentrated, dissolved in acetonitrile and recrystallized from acetonitrile/ethyl acetate (1:2) to obtain triethyl(octyl) phosphonium bromide ([P₂₂₂₈][Br]) as a white solid. ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.30 (m, 8H), 1.48 (m, 2H), 1.37 (m, 2H), 1.26 (m, 8H), 1.12 (dt, *J* = 18.0, 7.7 Hz, 9H), 0.84 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 31.70, 30.71, 30.59, 28.92, 28.72, 22.53, 21.08, 21.05, 17.28, 16.90, 14.41, 11.40, 11.02, 5.83, 5.79.

Triethyl(octyl)phosphonium bis(trifluoromethanesulfonyl)imide, [P₂₂₂₈][TFSI]

In a round bottom flask (500 mL) a solution of triethyl(octyl)phosphonium bromide ([P₂₂₂₈][Br]) (10.00 g, 42.00 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (12.66 g, 44.10 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO₃ test. ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.21 (m, 8H), 1.48 (m, 2H), 1.40 (quint, *J* = 6.6 Hz, 2H), 1.28 (m, 8H), 1.13 (dt, *J* = 18.0, 7.7 Hz, 9H), 0.87 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 123.79, 121.23, 118.67, 116.11, 31.67, 30.66, 30.54, 28.86, 28.67, 22.50, 20.95, 20.91, 17.05, 16.67, 14.35, 11.17, 10.78, 5.60, 5.56. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.77

1-Hexyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide, [hmim][TFSI]

In a round bottom flask (500 mL) a solution of 1-hexyl-3-methyl-imidazolium bromide ([hmim][Br]) (10.00 g, 40.50 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (11.61 g, 40.50 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO₃ test. ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.10 (s, 1H), 7.75 (dd, *J* = 1.8 Hz, 1H), 7.68 (dd, *J* = 1.8 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.79 (p, *J* = 7.4 Hz, 2H), 1.28 (m, 6H), 0.87 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 136.93, 124.01, 123.78, 122.66, 121.22, 118.66, 116.11, 49.25, 36.11, 30.97, 29.78, 25.57, 22.28, 14.11. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.89.

1-Hexyl-3-methylpyridinium bromide, [hmpy][Br]

Under inert atmosphere, in a flame dried round bottom flask (250 mL) a solution of 3- picoline (12.00 g, 129.0 mmol) in anhydrous toluene (60 mL) was treated with 1-bromohexane (22.33 g, 135.0 mmol) via cannula. The reaction was stirred at room temperature for 20 minutes and 343 K for 5 h. After completion the reaction was concentrated, dissolved in acetonitrile and recrystallized from acetonitrile/ethyl acetate (1:2) to obtain 1-hexyl-3-methylpyrrolidinium bromide ([hmpy][Br]) as a white solid. ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.21 (s, 1H), 9.07 (d, *J* = 6.0 Hz, 1H), 8.48 (d, *J* = 7.9 Hz, 1H), 8.08 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.63 (t, *J* = 7.5 Hz, 2H), 2.50 (s, 3H), 1.92 (quint, *J* = 7.4 Hz, 2H), 1.26 (d, *J* = 4.3 Hz, 6H), 0.83 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 146.21, 144.77, 142.45, 139.11, 127.76, 60.83, 31.11, 31.02, 25.50, 22.30, 18.30, 14.28.

1-Hexyl-3-methylpyridinium bis(trifluoromethanesulfonyl)imide, [hmpy][TFSI]

In a round bottom flask (500 mL) a solution of 1-hexyl-3-methylpyridinium bromide ([hmpy][Br]) (10.00 g, 38.70 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (11.12 g, 38.70 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO₃ test. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.99 (s, 1H), 8.91 (d, *J* = 6.0 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.04 (t, *J* = 6.1 Hz, 1H), 4.54 (t, *J* = 7.5 Hz, 2H), 1.92 (quint, *J* = 7.4 Hz, 2H), 1.29 (m, 6H), 0.86 (t, *J* = 6.3 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 146.15, 144.64, 142.38, 139.28, 127.76, 123.78, 121.22, 118.66, 116.10, 61.15, 31.04, 30.98, 25.51, 22.25, 18.24, 14.16. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.81.

N-Butyl-N-methylpyrrolidinium bromide, [Pyrro₁₄][Br]

Under inert atmosphere, in a flame dried round bottom flask (250 mL) a solution of 1-methylpyrrolidine (12.00 g, 141.0 mmol) in anhydrous toluene (70 mL) was treated with 1-bromobutane (20.28 g, 148.0 mmol) via cannula. The reaction was stirred at room temperature for 20 minutes and 343 K for 5 h. After completion the reaction was concentrated, dissolved in acetonitrile and recrystallized from acetonitrile/ethyl acetate (1:2) to obtain N-butyl-N-methylpyrrolidinium bromide ([Pyrro₁₄][Br]) as a white solid. ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.52 (m, 4H), 3.41 (m, 2H), 3.03 (s, 3H), 2.07 (q, *J* = 5.6, 4.8 Hz, 4H), 1.67 (ddt, *J* = 12.1, 8.0, 6.1 Hz, 2H), 1.29 (h, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 63.74, 63.06, 47.91, 25.44, 21.51, 19.76, 14.00.

N-Butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, [Pyrro₁₄][TFSI]

In a round bottom flask (500 mL) a solution of N-butyl-N-methylpyrrolidinium bromide ([Pyrr₁₄][Br]) (10.00 g, 45.00 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (13.57 g, 47.30 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO₃ test. ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.44 (m, 4H), 3.29 (m, 2H), 2.98 (s, 3H), 2.09 (p, *J* = 3.6 Hz, 4H), 1.68 (quint, *J* = 8.1 Hz, 2H), 1.33 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 123.78, 121.23, 118.67, 116.11, 63.90, 63.87, 63.85, 63.42, 63.40, 63.38, 47.97, 47.94, 47.90, 25.37, 21.51, 19.74, 13.84. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.79

N-Butyl-N-methylpiperidinium bromide, [PP₁₄][Br]

Under inert atmosphere, in a flame dried round bottom flask (500 mL) a solution of 1-methylpiperidine (18.00 g, 181.0 mmol) in anhydrous toluene (150 mL) was treated with 1-bromobutane (27.40 g, 200.0 mmol) via cannula. The reaction was stirred at room temperature for 20 minutes and 343 K for 5 h. After completion the reaction was concentrated, dissolved in acetonitrile and recrystallized from acetonitrile/ethyl acetate (1:2) to obtain N-butyl-N-methylpiperidinium bromide ([PP₁₄][Br]) as a white solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 3.39 (m, 6H), 3.06 (s, 3H), 1.79 (m, 4H), 1.65 (dq, *J* = 12.0, 7.8 Hz, 2H), 1.54 (m, 2H), 1.32 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

N-Butyl-N-methylpiperidinium bis(trifluoromethanesulfonyl)imide, [PP₁₄][TFSI]

In a round bottom flask (500 mL) a solution of N-butyl-N-methylpiperidinium bromide ([PP₁₄][Br]) (10.00 g, 42.30 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (12.28 g, 42.80 mmol) and stirred for 8 h. The mixture was

washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO₃ test. ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.30 (m, 6H), 2.99 (s, 3H), 1.79 (bs, 4H), 1.66 (quint, 7.3 Hz, 2H), 1.56 (m, 2H), 1.34 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 123.79, 121.23, 118.67, 116.11, 60.48, 60.46, 60.44, 23.40, 21.12, 19.70, 19.68, 13.82. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.84.

1-(2-methoxyethyl)-1-methylpyrrolidinium bromide, [Pyrro₁₂₀₁][Br]

Under inert atmosphere, in a flame dried round bottom flask (500 mL) a solution of N-methylpyrrolidine (15.00 g, 176.0 mmol) in anhydrous toluene (150 mL) was treated with 2-bromoethyl methyl ether (23.26 g, 167.0 mmol) via cannula. The reaction was stirred at room temperature for 20 minutes and 343 K for 5 h. After completion the reaction was concentrated, dissolved in acetonitrile and recrystallized from acetonitrile/ethyl acetate (1:2) to obtain 1-(2-methoxyethyl)-1-methylpyrrolidinium bromide ([Pyrro₁₂₀₁][Br]) as a white solid.

1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, [Pyrro₁₂₀₁][TFSI]

In a round bottom flask (500 mL) a solution of 1-(2-methoxyethyl)-1-methylpyrrolidinium bromide ([Pyrro₁₂₀₁][Br]) (10.00 g, 44.60 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (12.93 g, 45.10 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO₃ test. ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.76 (m, 2H), 3.57 (m, 2H), 3.51 (m, 4H), 3.32 (s, 3H), 3.04 (s, 3H), 2.11 (quint, *J* = 3.4 Hz, 4H). ¹³C NMR (126 MHz, DMSO-*d*₆)

δ 123.78, 121.22, 118.67, 116.11, 66.40, 64.69, 64.67, 64.65, 62.60, 62.58, 62.55, 58.41, 48.47, 48.44, 48.41, 21.24. ^{19}F NMR (471 MHz, DMSO- d_6) δ -78.99.

1-(2-methoxyethyl)-1-methylpiperidinium bromide, [PP₁₂₀₁][Br]

Under inert atmosphere, in a flame dried round bottom flask (500 mL) a solution of 1-methylpiperidine (15.00 g, 181.0 mmol) in anhydrous toluene (150 mL) was treated with 2-bromoethyl methyl ether (19.97 g, 144.0 mmol) via cannula. The reaction was stirred at room temperature for 20 minutes and 343 K for 5 h. After completion the reaction was concentrated, dissolved in acetonitrile and recrystallized from acetonitrile/ethyl acetate (1:2) to obtain 1-(2-methoxyethyl)-1-methylpiperidinium bromide ([PP₁₂₀₁][Br]) as a white solid. ^1H NMR (400 MHz, DMSO- d_6) δ 3.73 (t, J = 4.7 Hz, 2H), 3.57 (m, 2H), 3.3.35 (m, 4H), 3.26 (s, 3H), 3.05 (s, 3H), 1.75 (h, J = 5.9 Hz, 4H), 1.50 (m, 2H).

1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethanesulfonyl)imide, [PP₁₂₀₁][TFSI]

In a round bottom flask (500 mL) a solution of 1-(2-methoxyethyl)-1-methylpiperidinium bromide ([PP₁₂₀₁][Br]) (10.00 g, 42.00 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (12.66 g, 44.10 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO_3 test. ^1H NMR (500 MHz, DMSO- d_6) δ 3.76 (m, 2H), 3.56 (m, 2H), 3.36 (m, 4H), 3.30 (s, 3H), 3.06 (s, 3H), 1.79 (quint, J = 6.0 Hz, 4H), 1.54 (m, 2H). ^{13}C NMR (126 MHz, DMSO- d_6) δ 123.78, 121.23, 118.67, 116.11, 65.47, 62.17, 61.30, 58.53, 48.40, 21.00, 19.74. ^{19}F NMR (471 MHz, DMSO- d_6) δ -78.79.

1-Butyltetrahydrothiophenium iodide, [bthiol][I]

Under inert atmosphere, in a flame dried pressure tube round (100 mL) tetrahydrothiophene (12.00 g, 136.0 mmol) was treated with 1-iodobutane (26.30 g, 143.0 mmol) via cannula. The reaction was stirred at room temperature for 20 minutes and 343 K for 5 h. After completion the reaction was concentrated, dissolved in acetonitrile and recrystallized from acetonitrile/ethyl acetate (1:2) to obtain 1-butyltetrahydrothiophenium iodide ([bthiol][I]) as a white solid. ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.51 (m, 2H), 3.41 (m, 2H), 3.21 (t, *J* = 7.8 Hz, 2H), 2.22 (m, 2H), 2.15 (m, 2H), 1.68 (quint, *J* = 7.5 Hz, 2H), 1.42 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 43.26, 41.32, 28.56, 26.93, 21.46, 13.80.

1-Butyltetrahydrothiophenium bis(trifluoromethanesulfonyl)imide, [bthiol][TFSI]

In a round bottom flask (500 mL) a solution of 1-butyltetrahydrothiophenium iodide ([bthiol][I]) (10.00 g, 36.70 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (10.65 g, 37.10 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO₃ test. ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.49 (dt, *J* = 13.3, 6.7 Hz, 2H), 3.38 (dt, *J* = 12.5, 6.0 Hz, 2H), 3.18 (t, *J* = 7.6 Hz, 2H), 2.22 (m, 2H), 2.14 (m, 2H), 1.68 (p, *J* = 7.5 Hz, 2H), 1.42 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 123.79, 121.23, 118.67, 116.11, 43.18, 41.40, 28.45, 26.89, 21.41, 13.60. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.82.

Tetra-methyl-guanidinium bis(perfluoroethylsulfonyl)imide, [TMG][beti]

In a round bottom flask (500 mL) a solution of tetra-methyl-guanidine ([TMG]) (1.50 g, 13.0 mmol) in water (80 mL) was treated with the slow addition of nitric acid (0.82 g, 13.0 mmol) and lithium bis(perfluoroethylsulfonyl)imide (5.09 g, 13.2 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.77 (s, 2H), 2.89 (s, 12H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 161.44, 121.65 (t, $J = 33.4$ Hz), 119.37, 117.08, 114.80 (t, $J = 33.6$ Hz), 113.92 (q, $J = 37.8$ Hz), 111.74, 111.43, 109.26 (q, $J = 37.8$ Hz), 39.72. ^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) δ -78.68, -117.46.

N-Butyl-N,N-diethyl-N-methylammonium bis(trifluoromethanesulfonyl)imide,
[N₁₂₂₄][TFSI]

In a round bottom flask (500 mL) a solution of N-butyl-N,N-diethyl-N-methylammonium bromide ([N₁₂₂₄][Br]) (7.00 g, 31.2 mmol) in water (200 mL) was treated with lithium bis(trifluoromethanesulfonyl)imide (9.05 g, 31.5 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO_3 test. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 3.32 (q, $J = 7.3$ Hz, 4H), 3.21 (m, 2H), 2.95 (s, 3H), 1.64 (quint, $J = 7.6$ Hz, 2H), 1.36 (h, $J = 7.4$ Hz, 2H), 1.25 (t, $J = 7.4$ Hz, 6H), 0.98 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 123.79, 121.23, 118.67, 116.11, 63.90, 63.87, 63.85, 63.40, 59.78, 59.76, 59.74, 55.98, 55.96, 55.93, 46.95, 46.92, 46.88, 25.37, 23.74, 21.50, 19.74, 19.64, 13.83, 7.83. ^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) δ -78.80.

1,3,4,6,7,8-hexahydro-1-methyl-2H-pyrimido[1,2-a]pyrimidinium
bis(trifluoromethanesulfonyl)imide, [MTBD][TFSI]

In a round bottom flask (500 mL) a solution of 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine ([MTBD]) (3.00 g, 19.6 mmol) in water (100 mL) was treated with the slow addition of nitric acid (1.23 g, 19.6 mmol) and lithium bis(trifluoromethanesulfonyl)imide (5.90 g, 20.6 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.61 (s, 1H), 3.27 (m, 8H), 2.91 (s, 3H), 1.91 (dq, *J* = 29.5, 6.0 Hz, 4H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 151.16, 123.79, 121.23, 118.67, 116.11, 47.99, 47.45, 46.98, 38.83, 37.41, 20.81, 20.66. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.78.

1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidinium

bis(perfluoroethylsulfonyl)imide, [MTBD][beti]

In a round bottom flask (500 mL) a solution of 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine ([MTBD]) (3.00 g, 19.6 mmol) in water (100 mL) was treated with the slow addition of nitric acid (1.23 g, 19.6 mmol) and lithium bis(perfluoroethylsulfonyl)imide (7.65 g, 19.8 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.63 (s, 1H), 3.28 (m, 8H), 2.92 (s, 3H), 1.94 (quint, *J* = 6.0 Hz, 2H), 1.89 (quint, *J* = 6.0 Hz, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 151.18, 121.65, 119.63, 119.37, 119.10, 117.35, 117.08, 116.81, 114.80, 114.09, 113.79, 112.07, 111.76, 111.46, 111.16, 109.43, 109.13, 47.93, 47.40, 46.92, 38.78, 37.28, 20.73, 20.57. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.90, -117.58.

Potassium perfluoropropanoyl(trifluoromethylsulfonyl)imide, K[TSE]

In a 1 L three-necked flask fitted a cylindrical funnel and a thermometer, trifluoromethanesulfonamide (10 g, 0.067 mol) was placed in 67 mL of dry methanol. After

addition of (7.53 g, 0.0671 mol) of potassium *t*-butoxide the mixture was stirred at 333 K for 3 h under nitrogen atmosphere. The reaction mixture was concentrated under reduced pressure to give the white solid. After addition of 30 mL of dry diethyl ether, a solution of 20.8 g (0.0671 mol) of pentafluoropropanoic anhydride in 30 mL of dry diethyl ether was added dropwise at 273 K and stirred at 273 K for 2 h and then at room temperature for 4 h. The reaction mixture was filtered and washed with dry diethyl ether. The crystals were dried under reduced pressure to give of K[TSE] as a colorless crystal. ^{13}C NMR (101 MHz, DMSO- d_6) δ 161.01 (t, $J = 24.5$ Hz), 121.93, 120.45 (t, $J = 35.7$ Hz), 117.61 (t, $J = 35.7$ Hz). ^{19}F NMR (376 MHz, DMSO- d_6) δ -81.73, -84.91, -122.78

1-Butyl-3-methyl-imidazolium perfluoropropanoyl(trifluoromethylsulfonyl)imide, [bmim][TSE]

In a round bottom flask (500 mL) a solution of 1-butyl-3-methyl-imidazolium bromide ([bmim][Br]) (10.00 g, 45.60 mmol) in water (200 mL) was treated with potassium perfluoropropanoyl(trifluoromethylsulfonyl)imide (15.97 g, 47.90 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane until no residual halide precipitation was observed by AgNO_3 test. ^1H NMR (500 MHz, DMSO- d_6) δ 9.11 (s, 1H), 7.76 (d, $J = 1.7$ Hz, 1H), 7.69 (d, $J = 1.8$ Hz, 1H), 4.17 (t, $J = 7.2$ Hz, 2H), 3.86 (s, 3H), 1.77 (quint, $J = 7.3$ Hz, 2H), 1.27 (h, $J = 7.4$ Hz, 2H), 0.90 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (126 MHz, DMSO- d_6) δ 160.98, 160.78, 160.59, 136.96, 124.03, 123.96, 122.68, 121.39, 119.94, 118.82, 117.95, 117.67, 116.26, 107.41, 107.11, 48.97, 36.11, 31.80, 19.18, 13.55. ^{19}F NMR (471 MHz, DMSO- d_6) δ -78.63, -81.84, -119.69.

**1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidinium
perfluoropropanoyl(trifluoromethylsulfonyl)imide, [MTBD][TSE]**

In a round bottom flask (500 mL) a solution of 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine ([MTBD]) (3.00 g, 19.6 mmol) in water (100 mL) was treated with the slow addition of nitric acid (1.23 g, 19.6 mmol) and potassium perfluoropropanoyl(trifluoromethylsulfonyl)imide (5.95 g, 19.8 mmol) and stirred for 8 h. The mixture was washed with water (3x) and extracted with dichloromethane. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.62 (s, 1H), 3.28 (m, 8H), 2.92 (s, 3H), 1.94 (quint, *J* = 6.0 Hz, 2H), 1.88 (quint, *J* = 6.0 Hz, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 160.97, 160.77, 160.58, 151.19, 123.97, 121.40, 120.23, 119.95, 118.84, 117.68, 116.27, 107.42, 107.13, 47.95, 47.42, 46.94, 38.80, 37.32, 20.76, 20.60. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -78.71, -81.96, -119.77

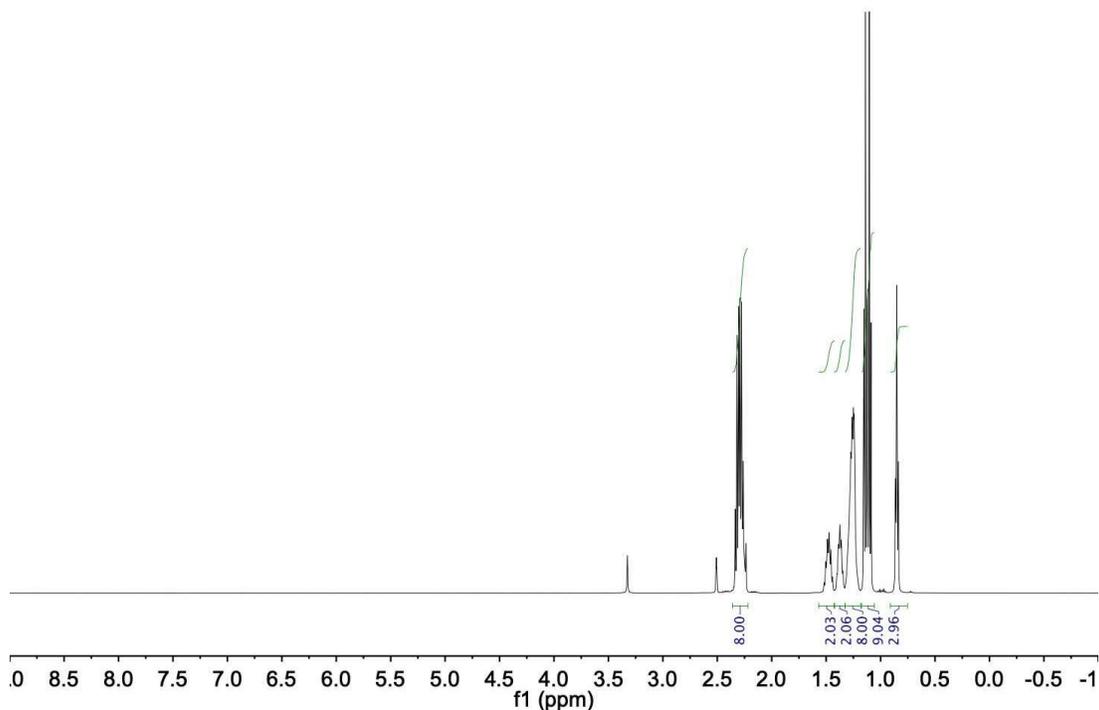


Figure S1. ¹H NMR of [P₂₂₂₈][Br]

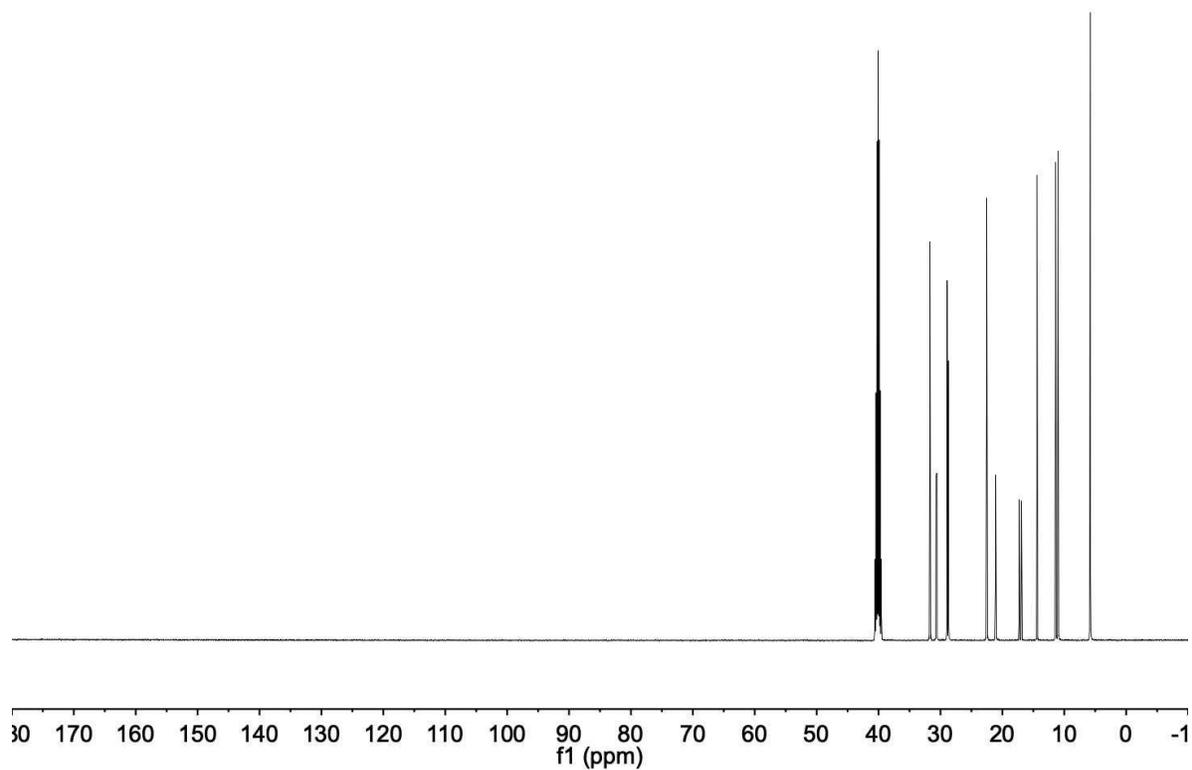


Figure S2. ^{13}C NMR of $[\text{P}_{2228}][\text{Br}]$

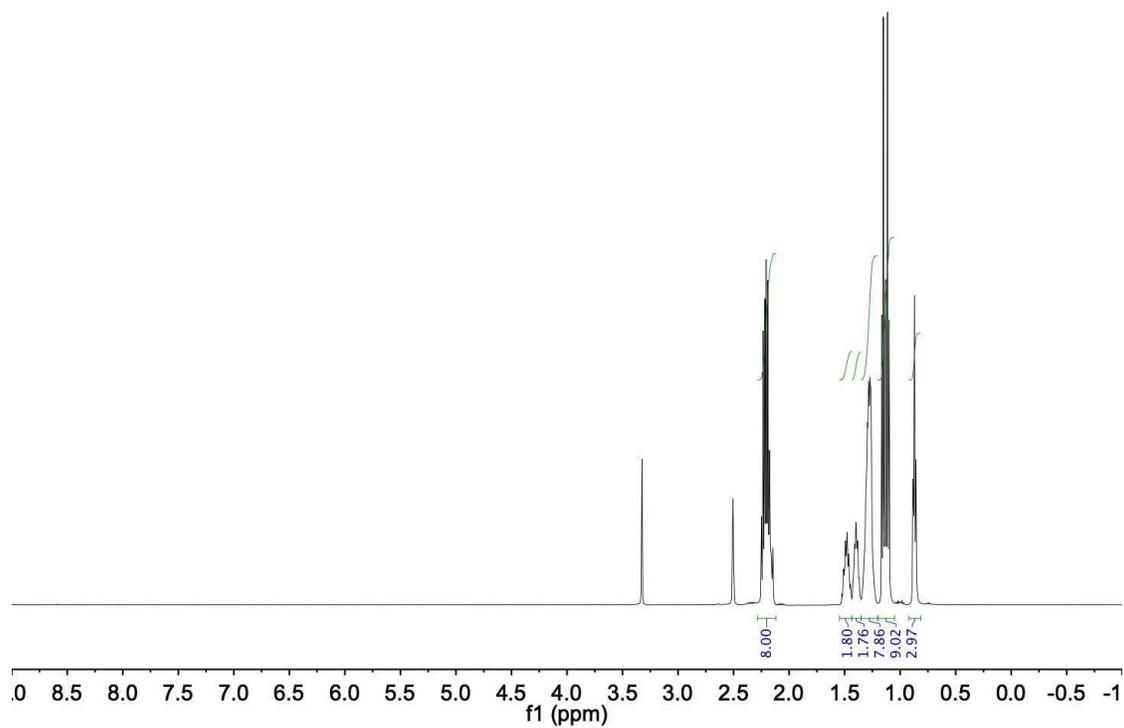


Figure S3. ^1H NMR of $[\text{P}_{2228}][\text{TFSI}]$

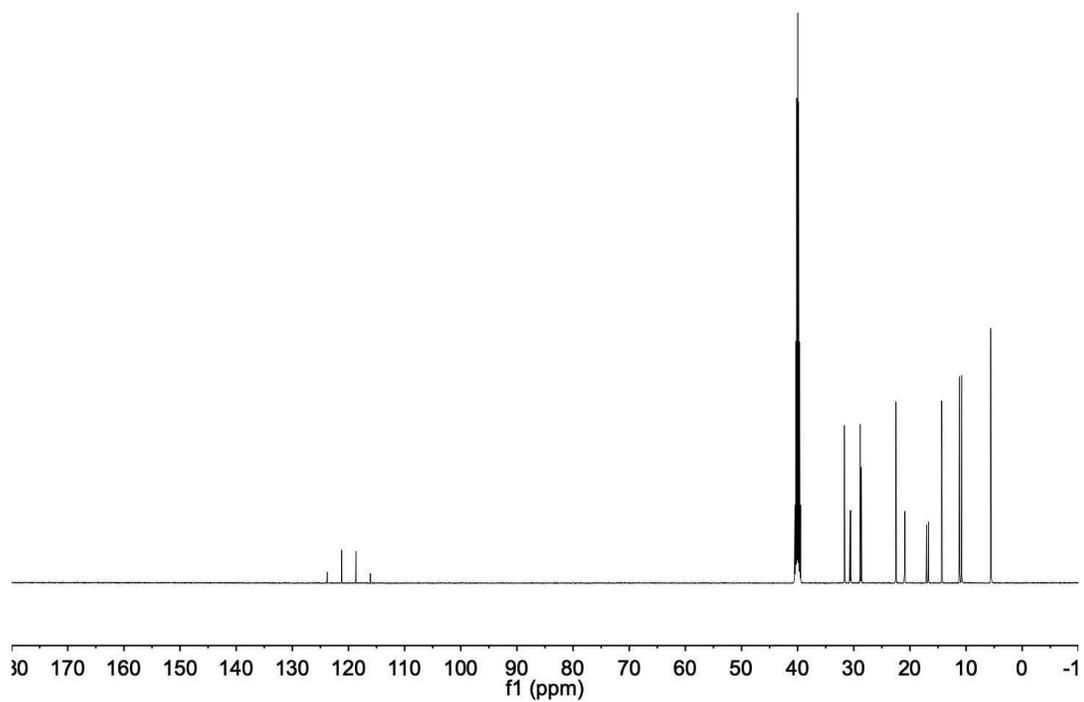


Figure S4. ^{13}C NMR of $[\text{P}_{2228}][\text{TFSI}]$

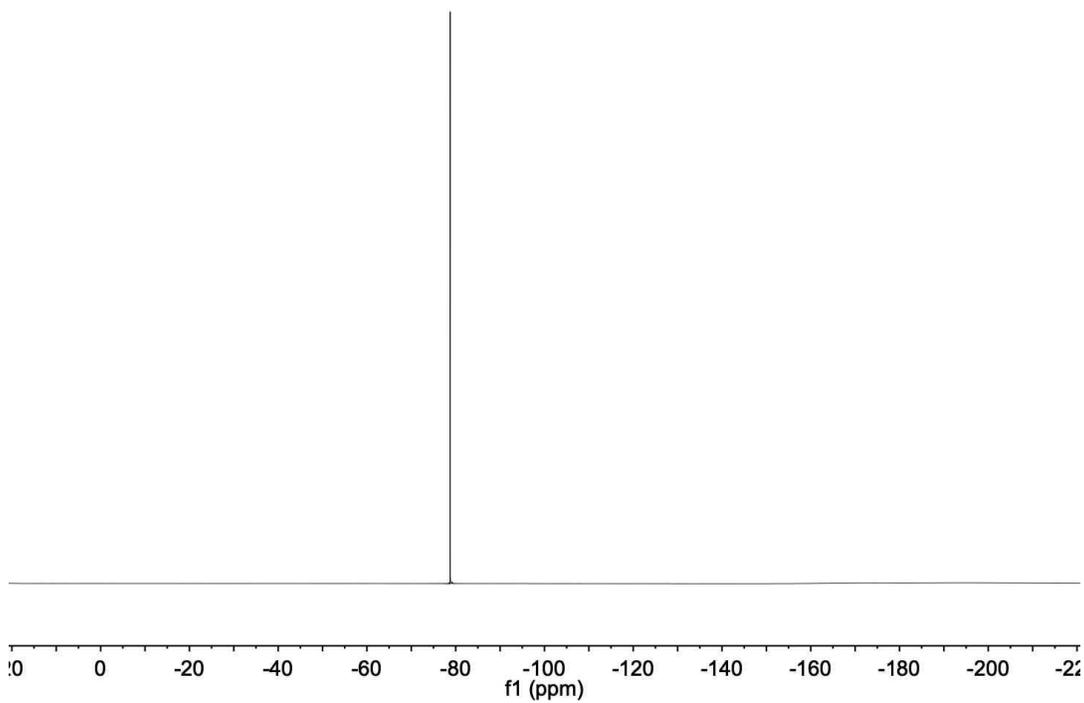


Figure S5. ^{19}F NMR of $[\text{P}_{2228}][\text{TFSI}]$

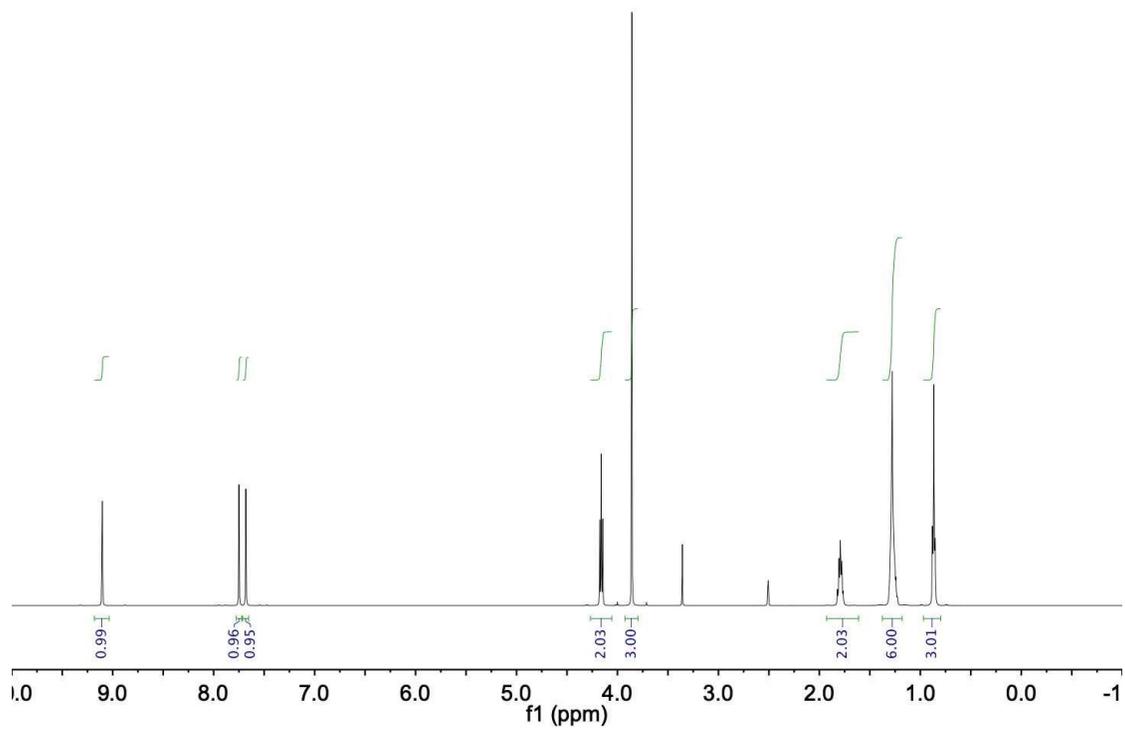


Figure S6. ^1H NMR of [hmim][TFSI]

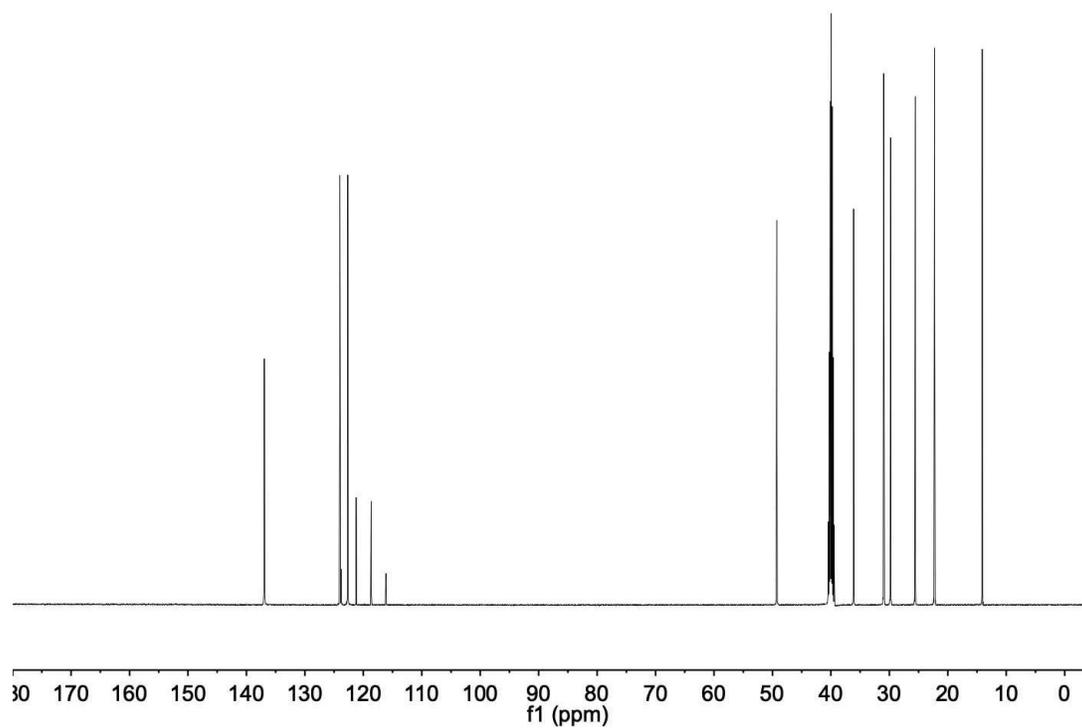


Figure S7. ^{13}C NMR of [hmim][TFSI]

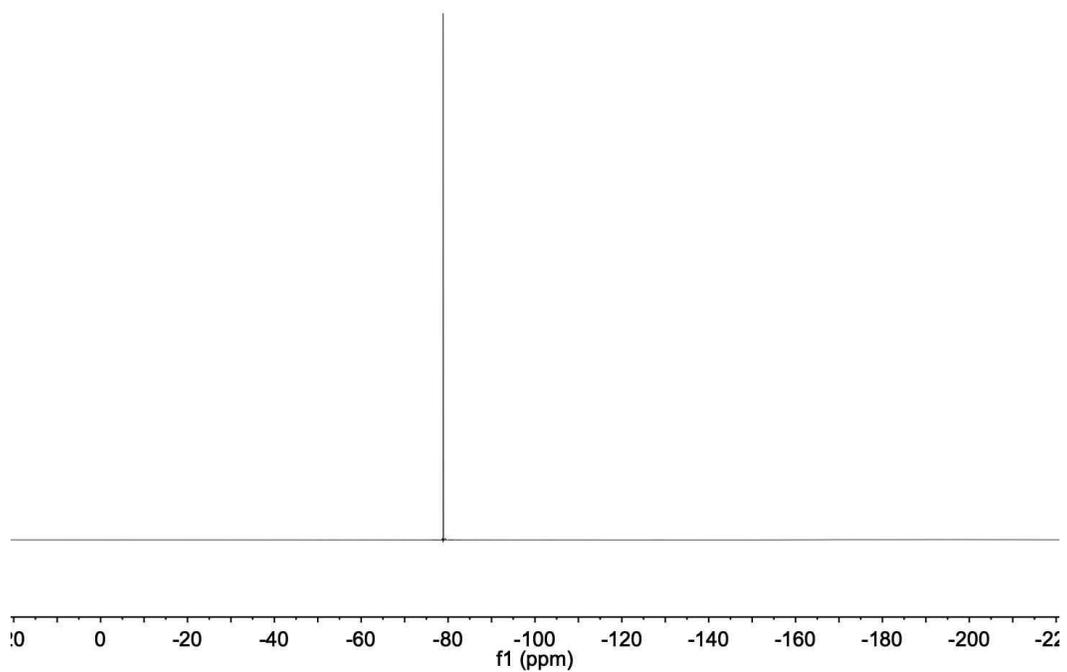


Figure S8. ^{19}F NMR of [hmim][TFSI]

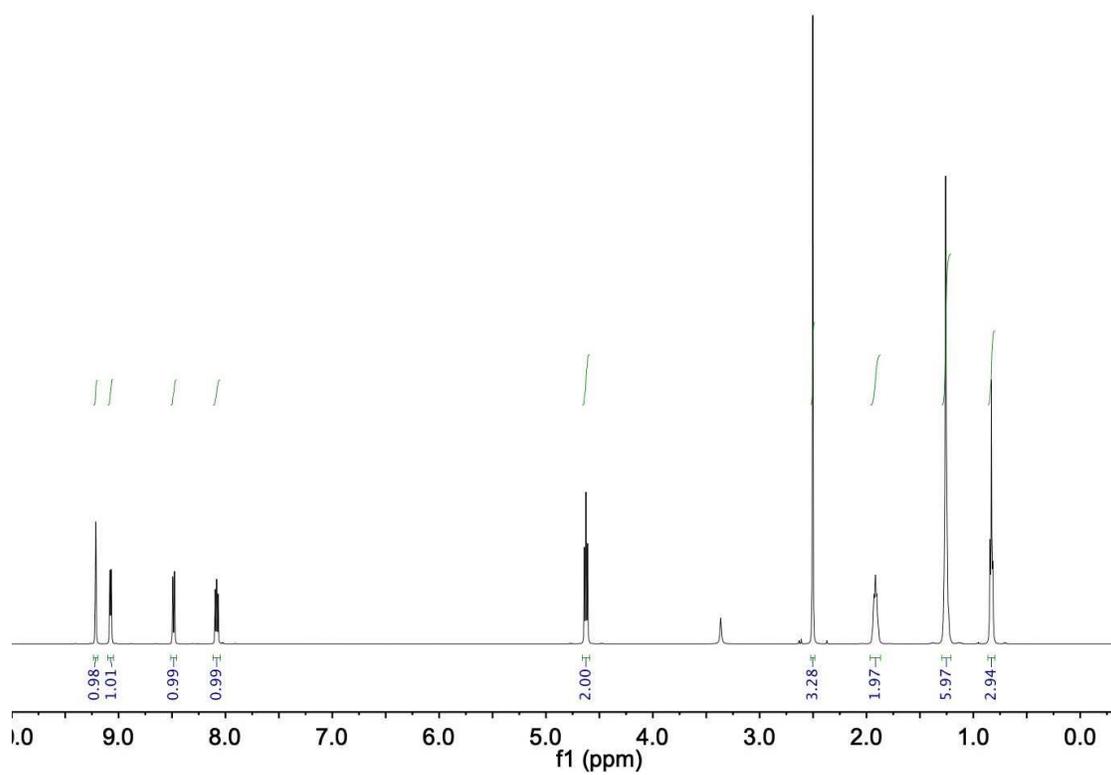


Figure S9. ^1H NMR of [hmpy][Br]

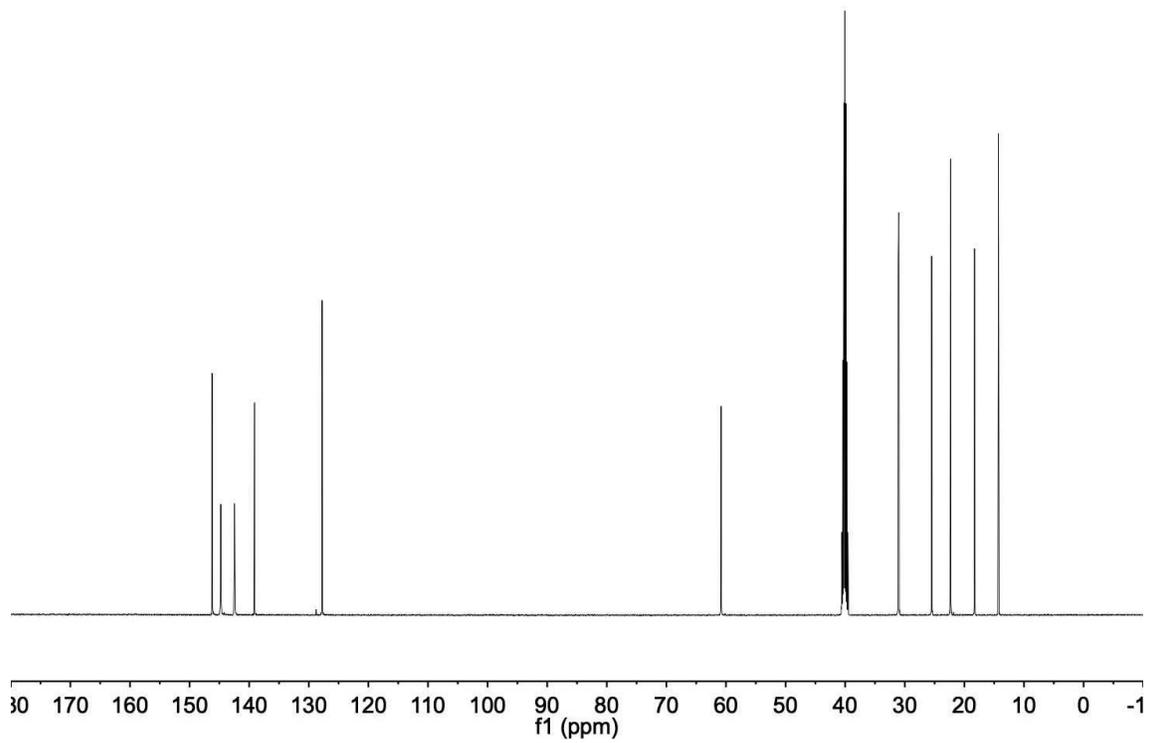


Figure S10. ¹³C NMR of [hmpy][Br]

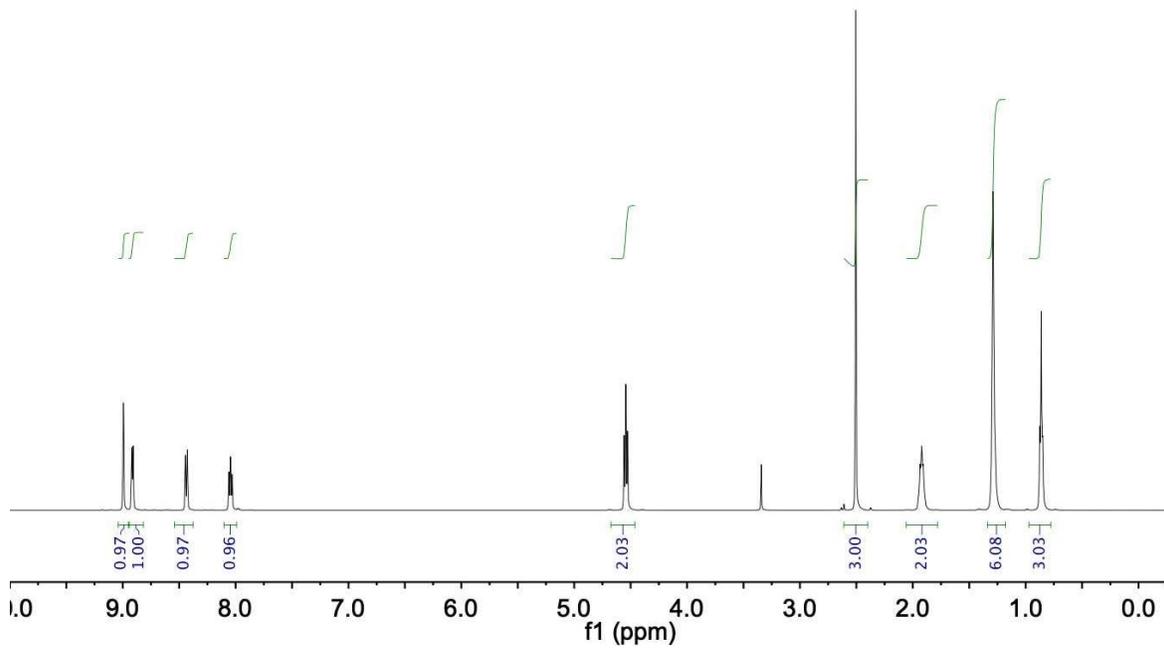


Figure S11. ¹H NMR of [hmpy][TFSI]

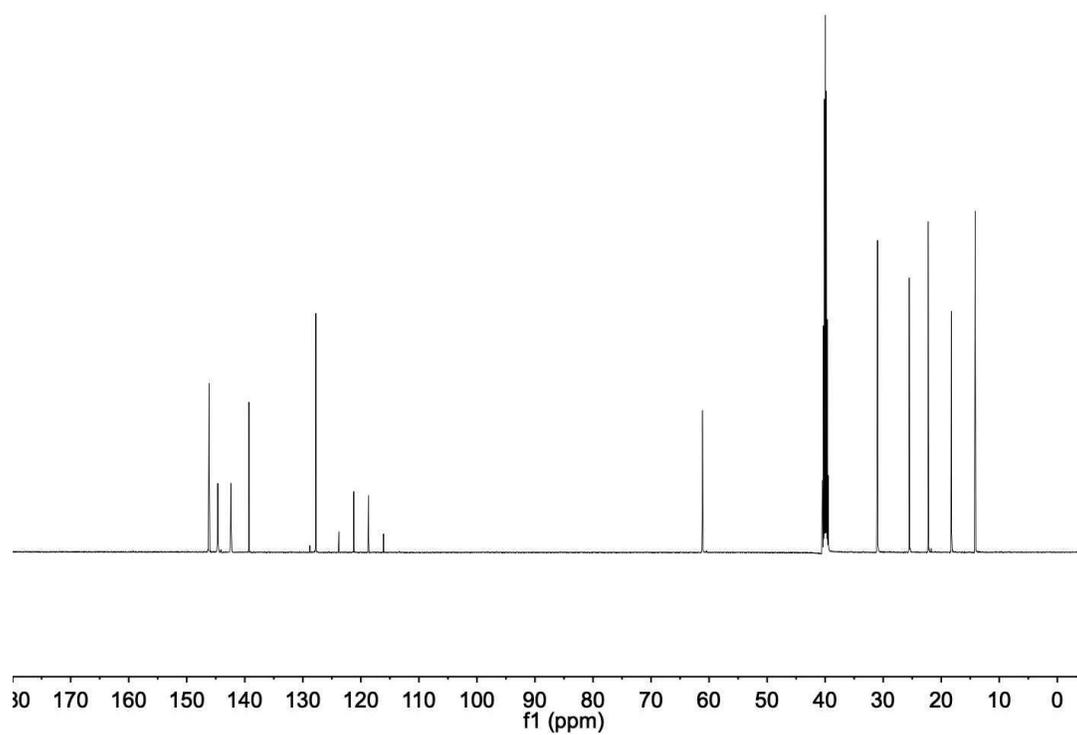


Figure S12. ^{13}C NMR of [hmpy][TFSI]

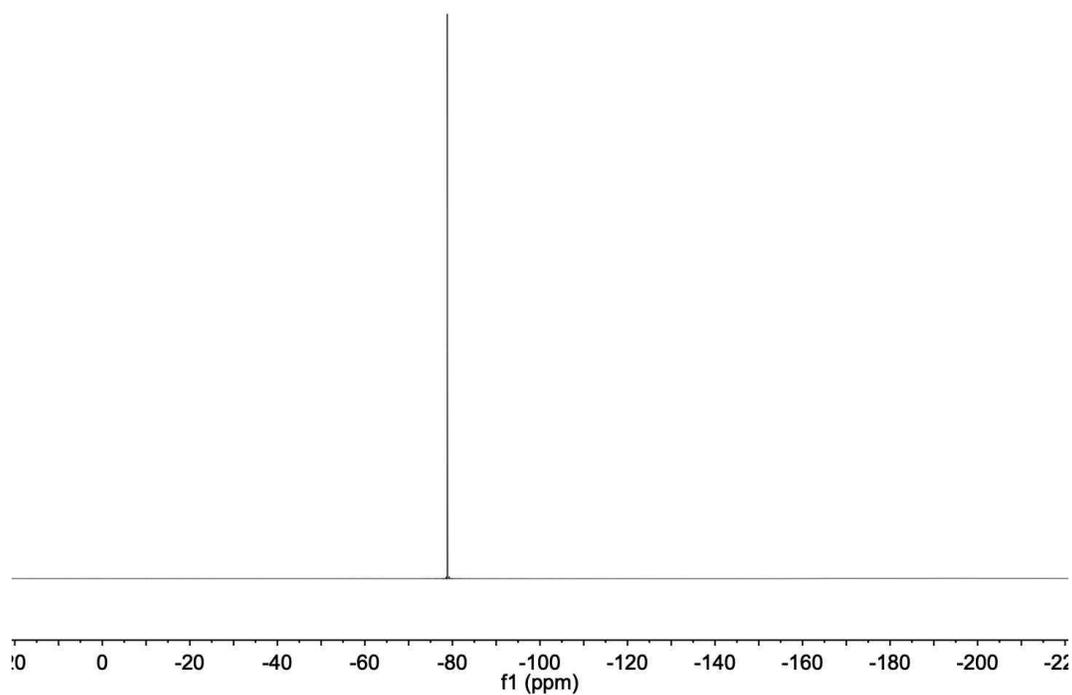


Figure S13. ^{19}F NMR of [hmpy][TFSI]

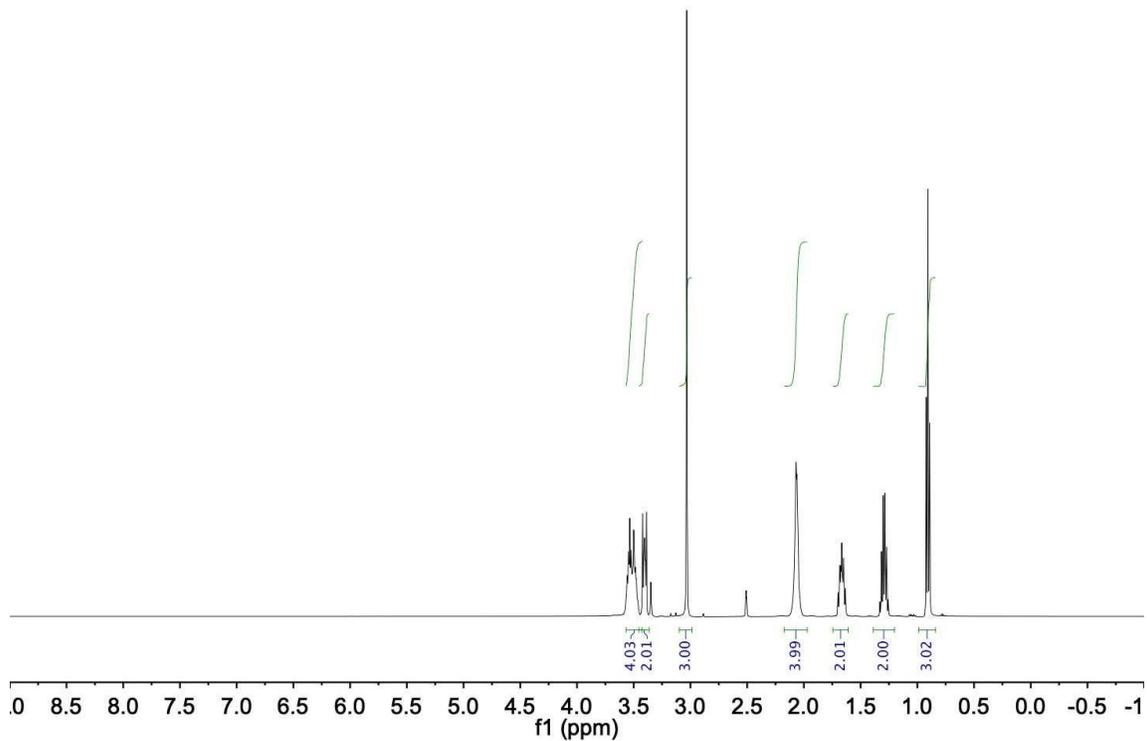


Figure S14. ¹H NMR of [Pyrro₁₄][Br]

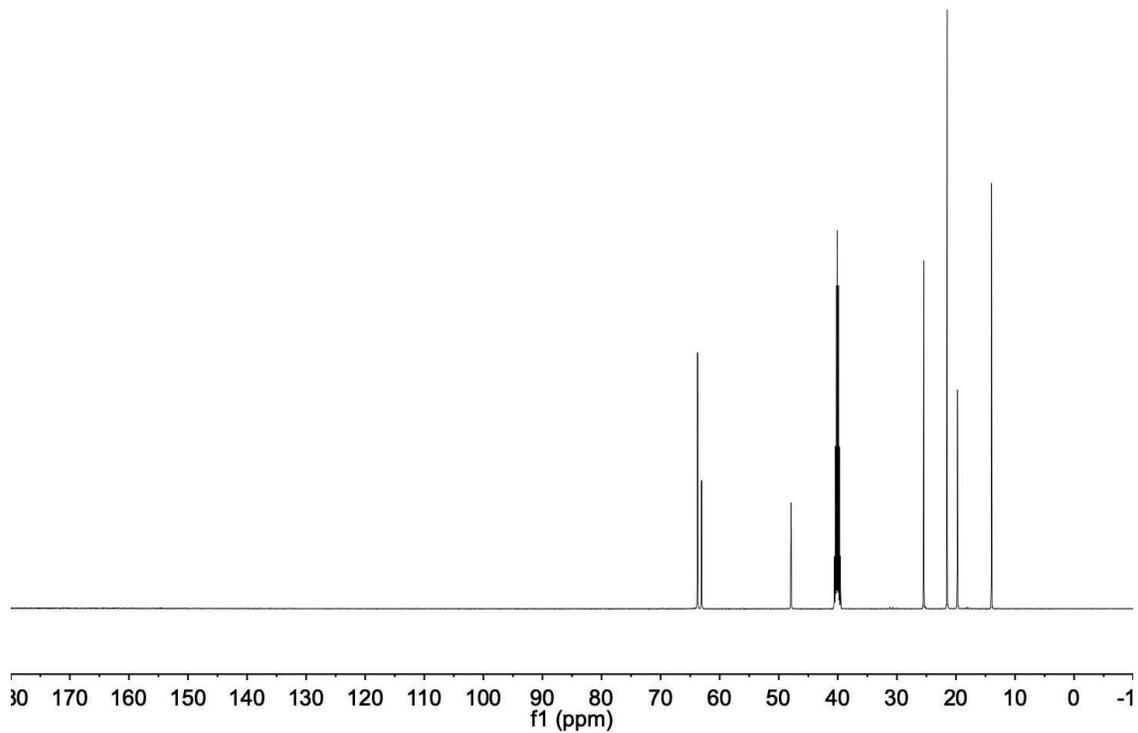


Figure S15. ¹³C NMR of [Pyrro₁₄][Br]

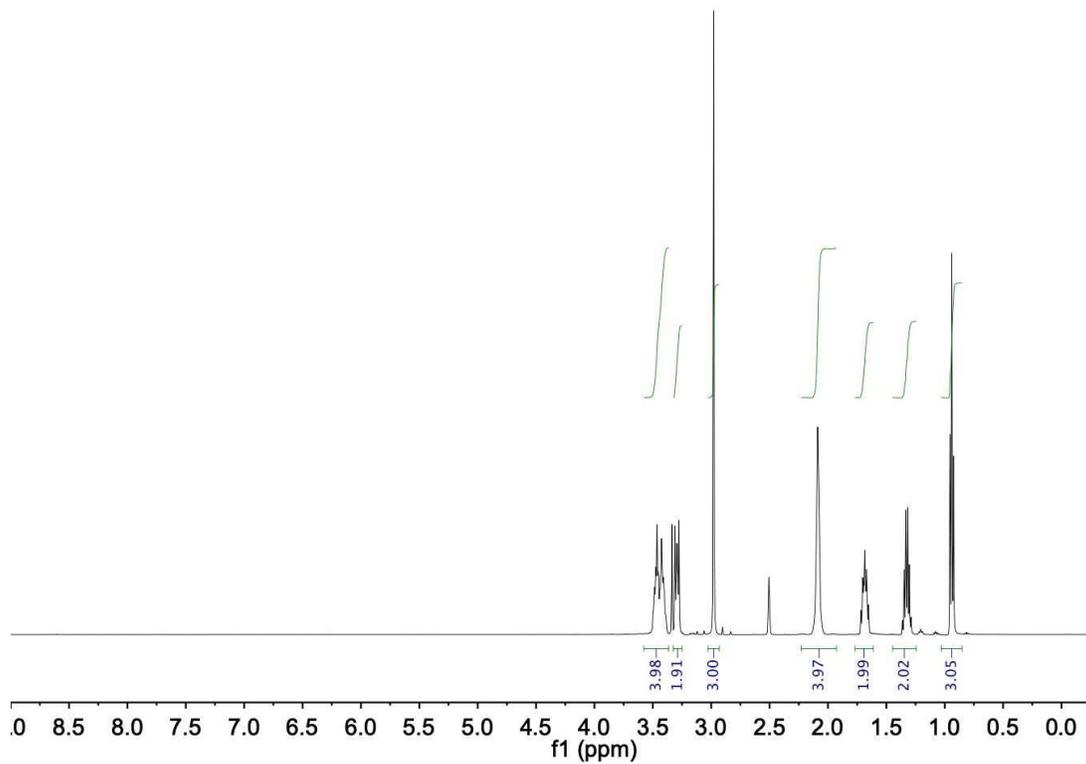


Figure S16. ¹H NMR of [Pyrro₁₄][TFSI]

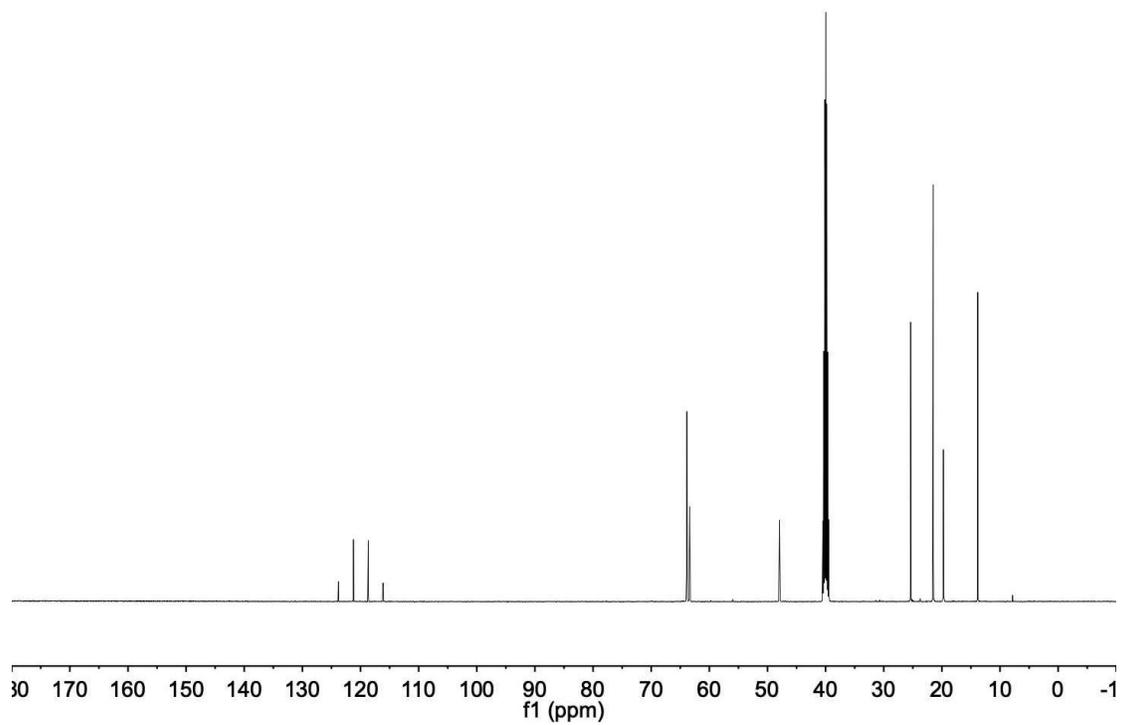


Figure S17. ¹³C NMR of [Pyrro₁₄][TFSI]

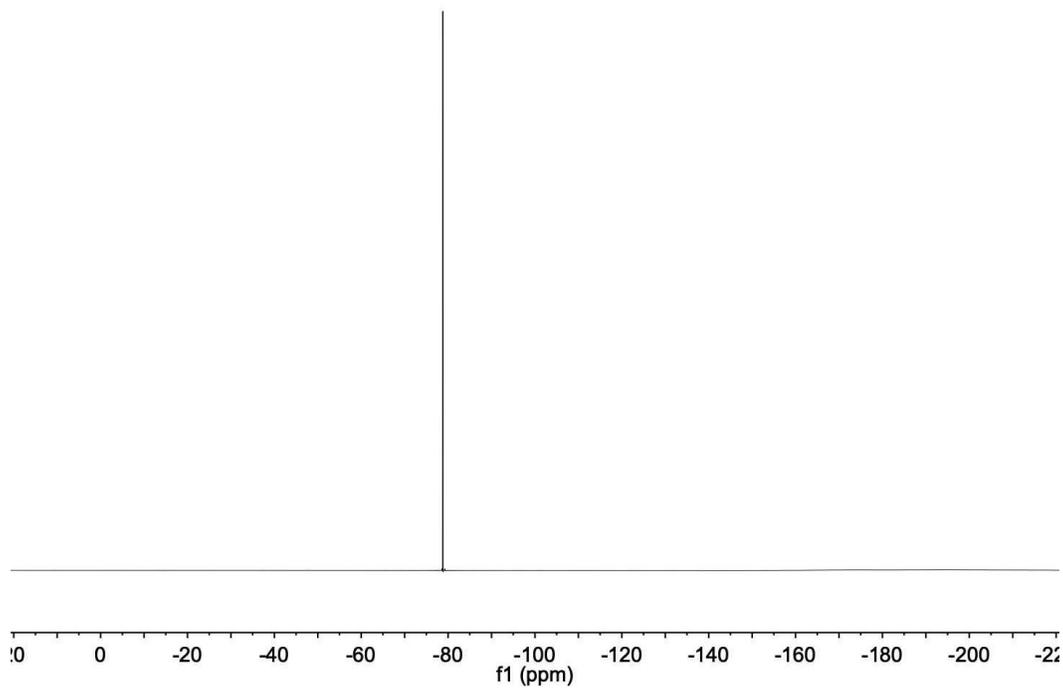


Figure S18. ^{19}F NMR of $[\text{PyrrO}_{14}][\text{TFSI}]$

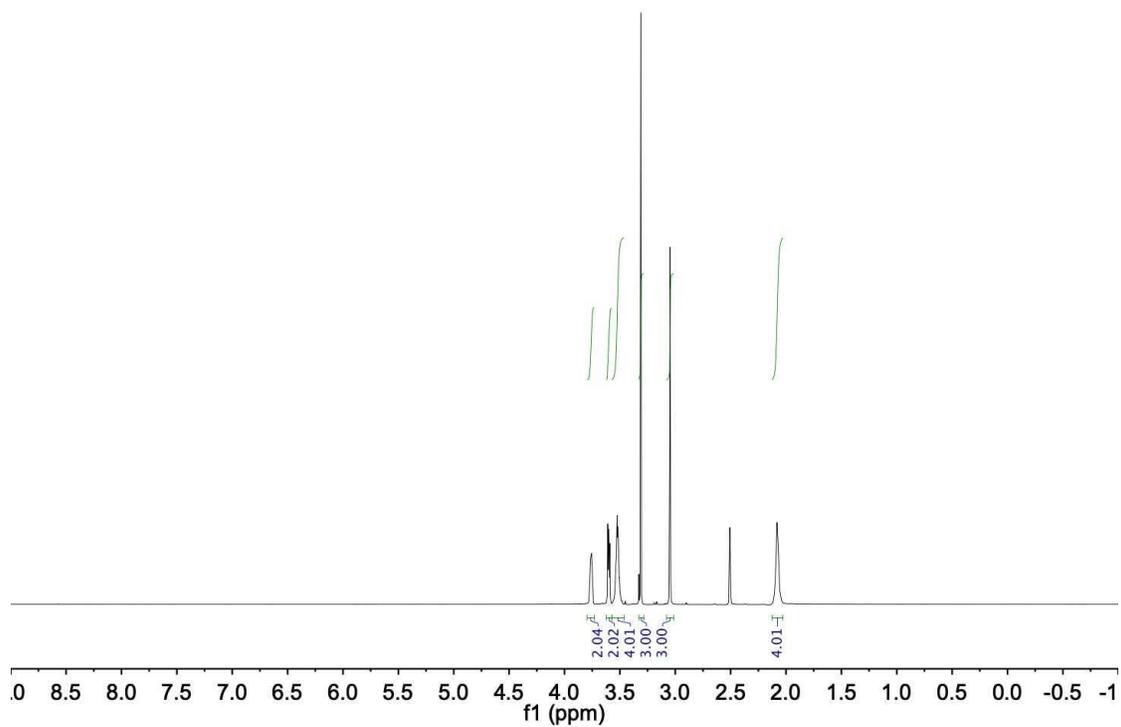


Figure S19. ^1H NMR of $[\text{PyrrO}_{12}\text{O}_1][\text{Br}]$

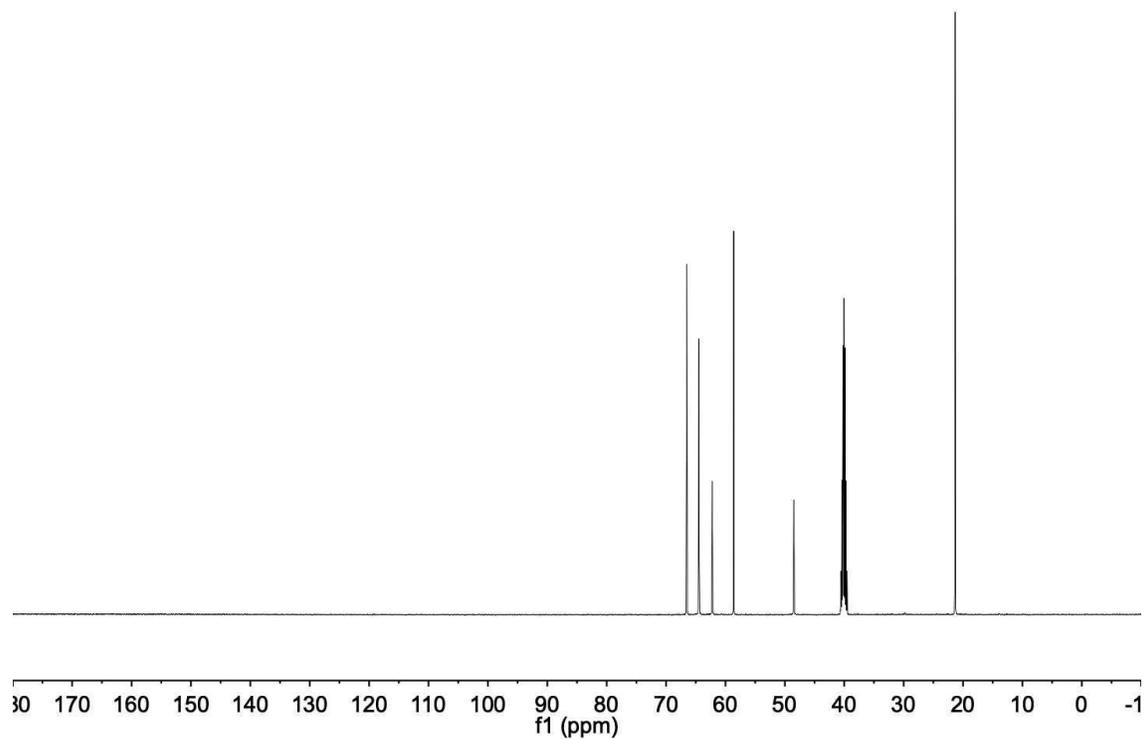


Figure S20. ^{13}C NMR of [Pyrro₁₂₀₁][Br]

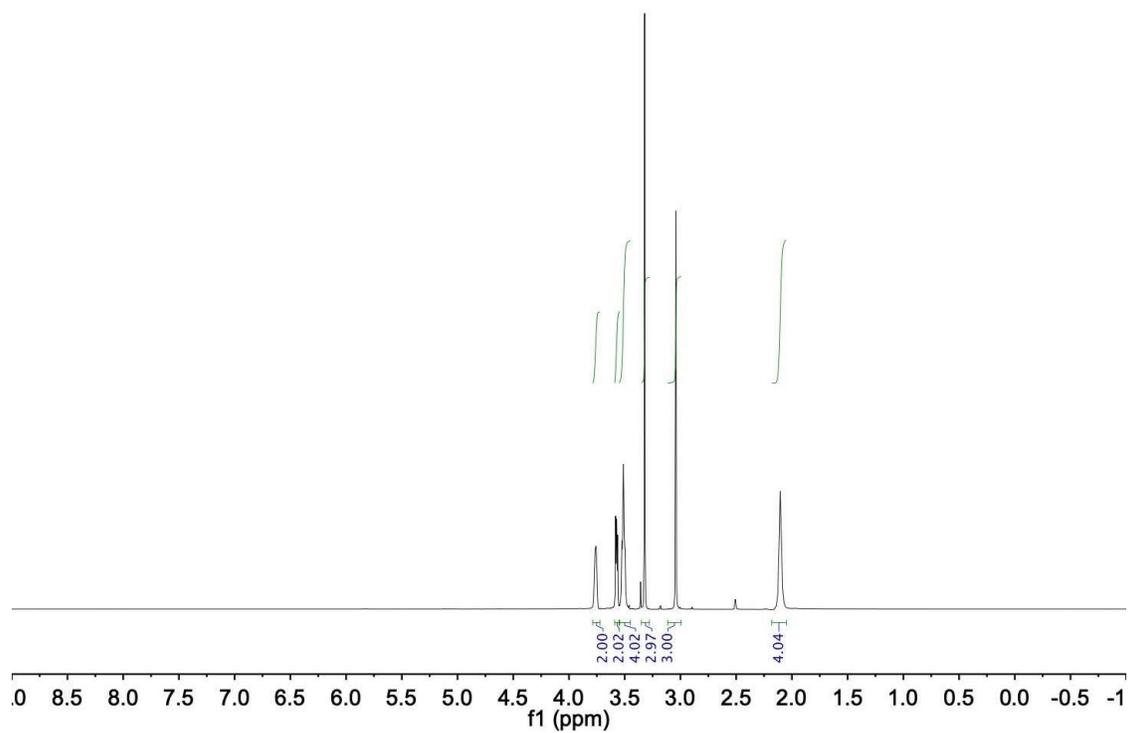


Figure S21. ^1H NMR of [Pyrro₁₂₀₁][TFSI]

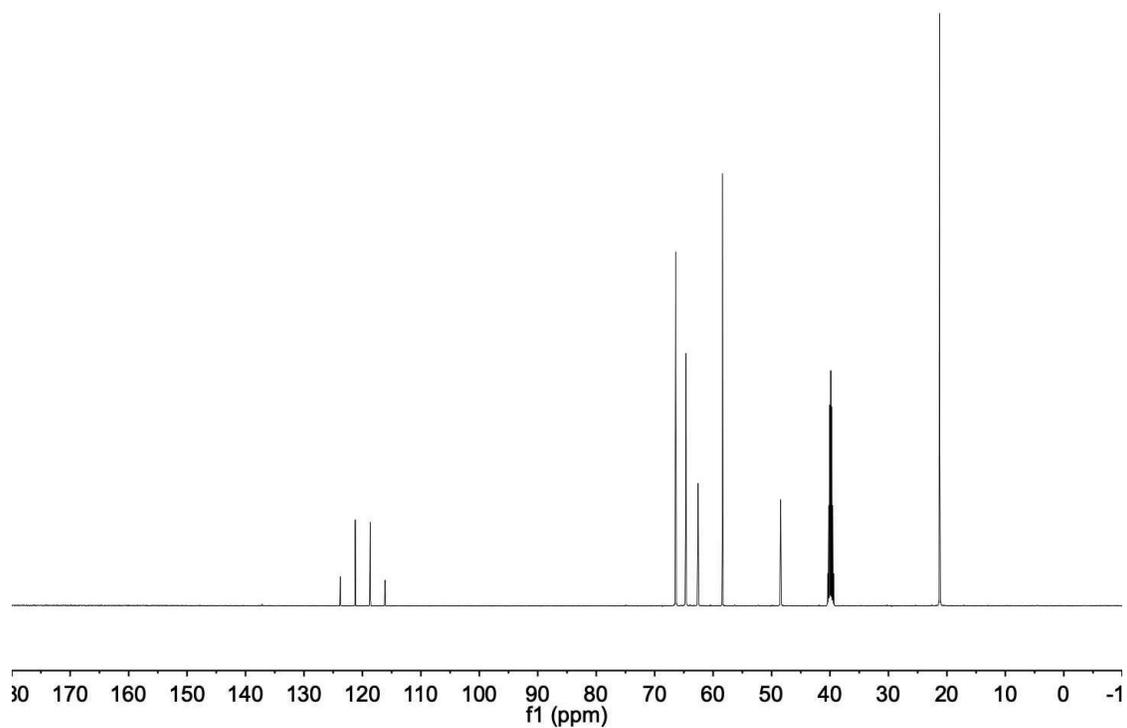


Figure S22. ^{13}C NMR of [Pyrro₁₂O₁][TFSI]

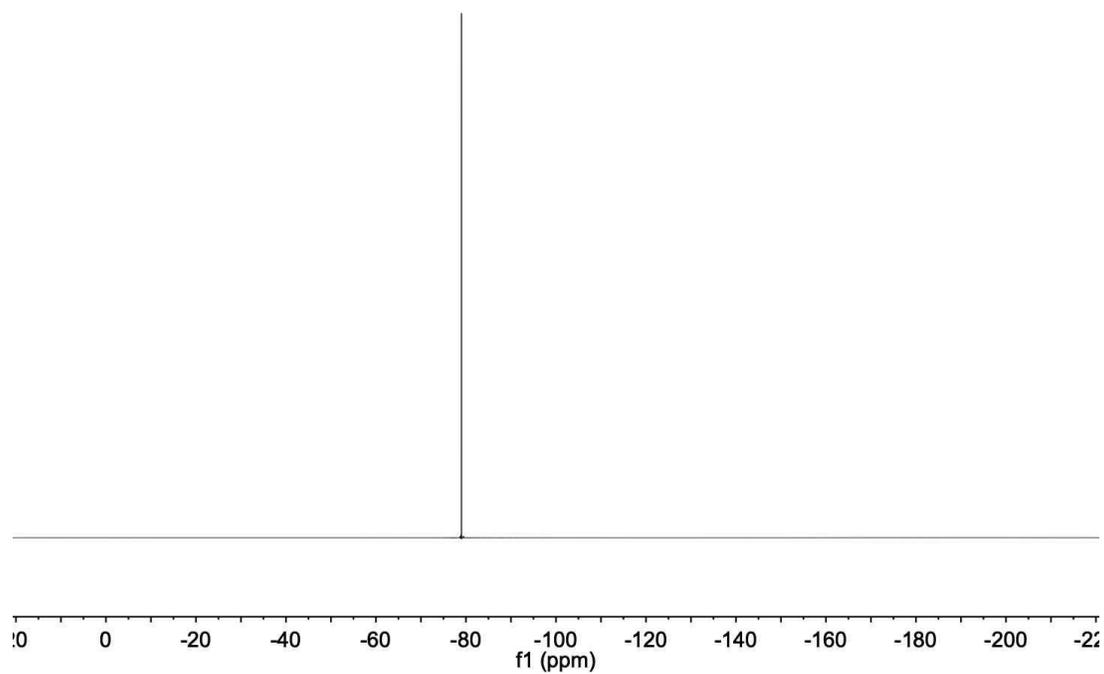


Figure S23. ^{19}F NMR of [Pyrro₁₂O₁][TFSI]

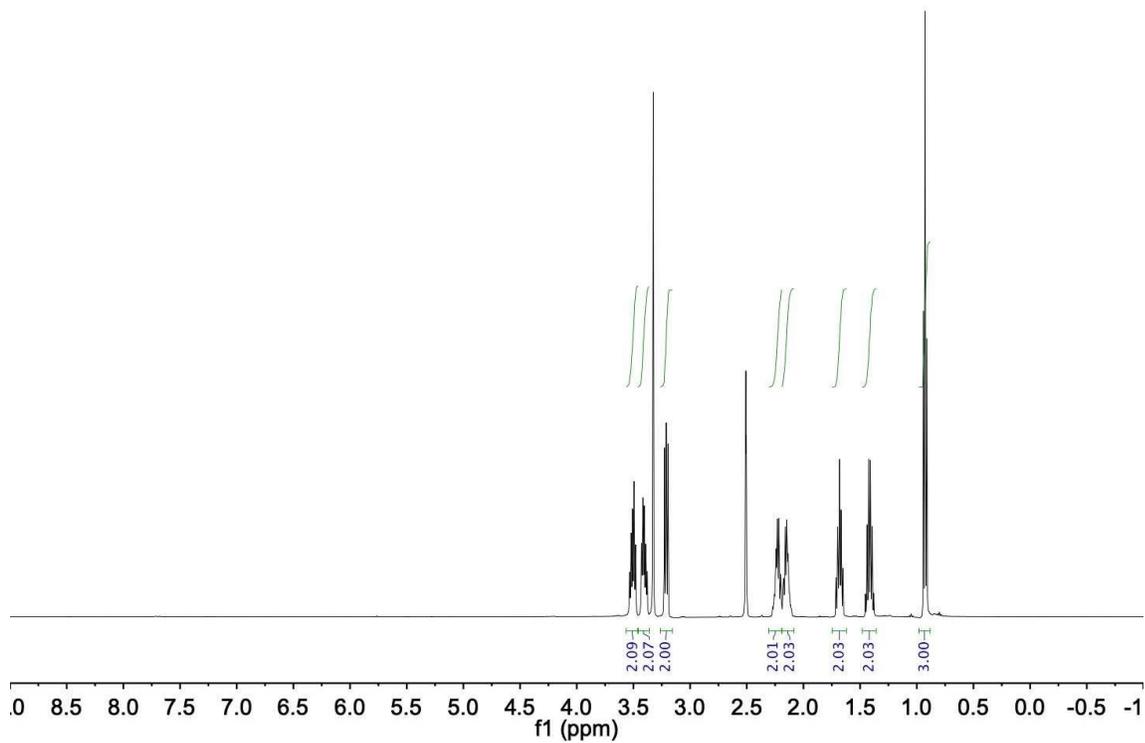


Figure S24. ^1H NMR of [bthiol][I]

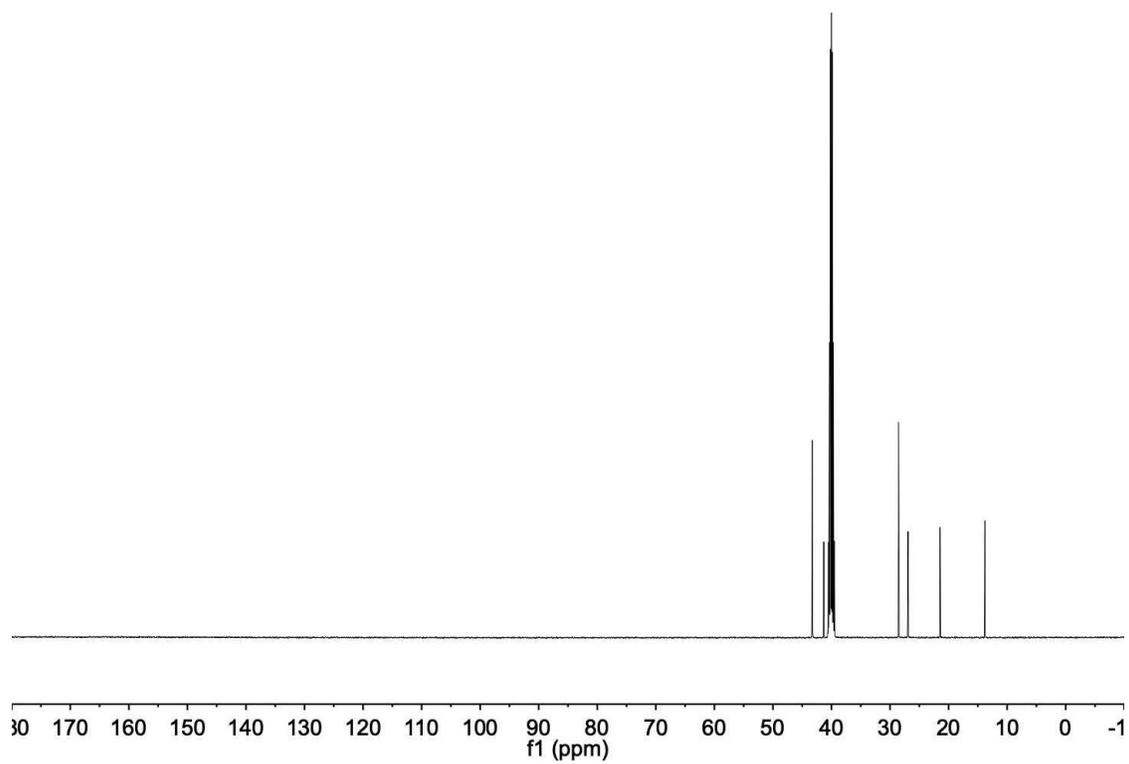


Figure S25. ^{13}C NMR of [bthiol][I]

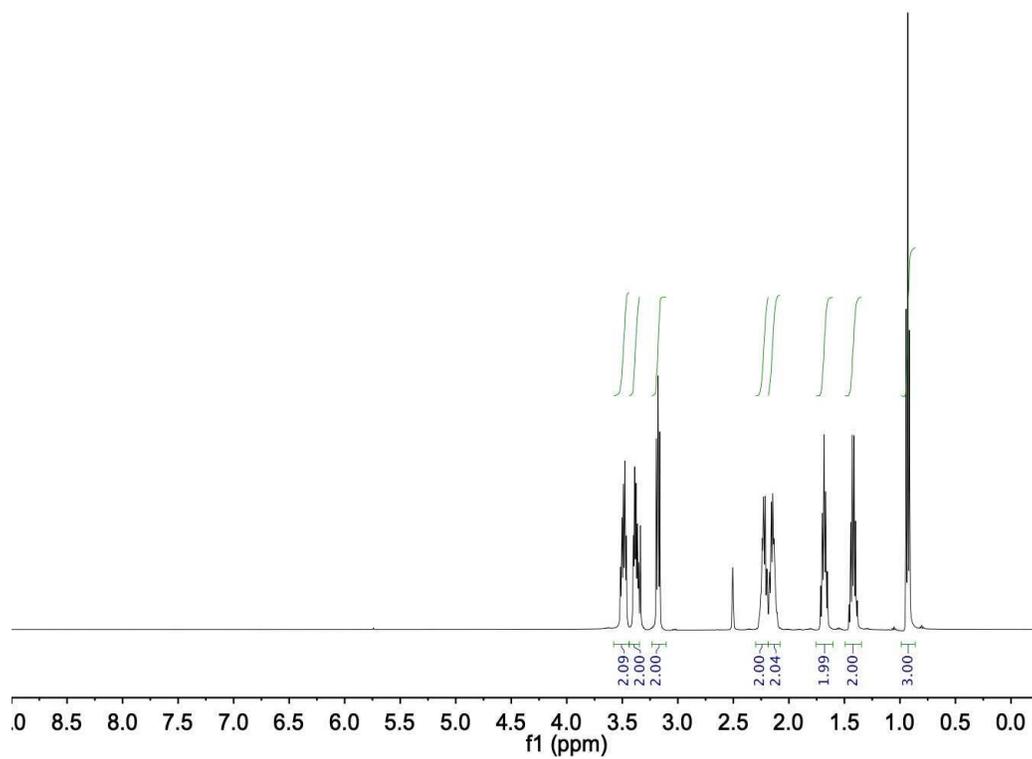


Figure S26. ^1H NMR of [bthiol][TFSI]

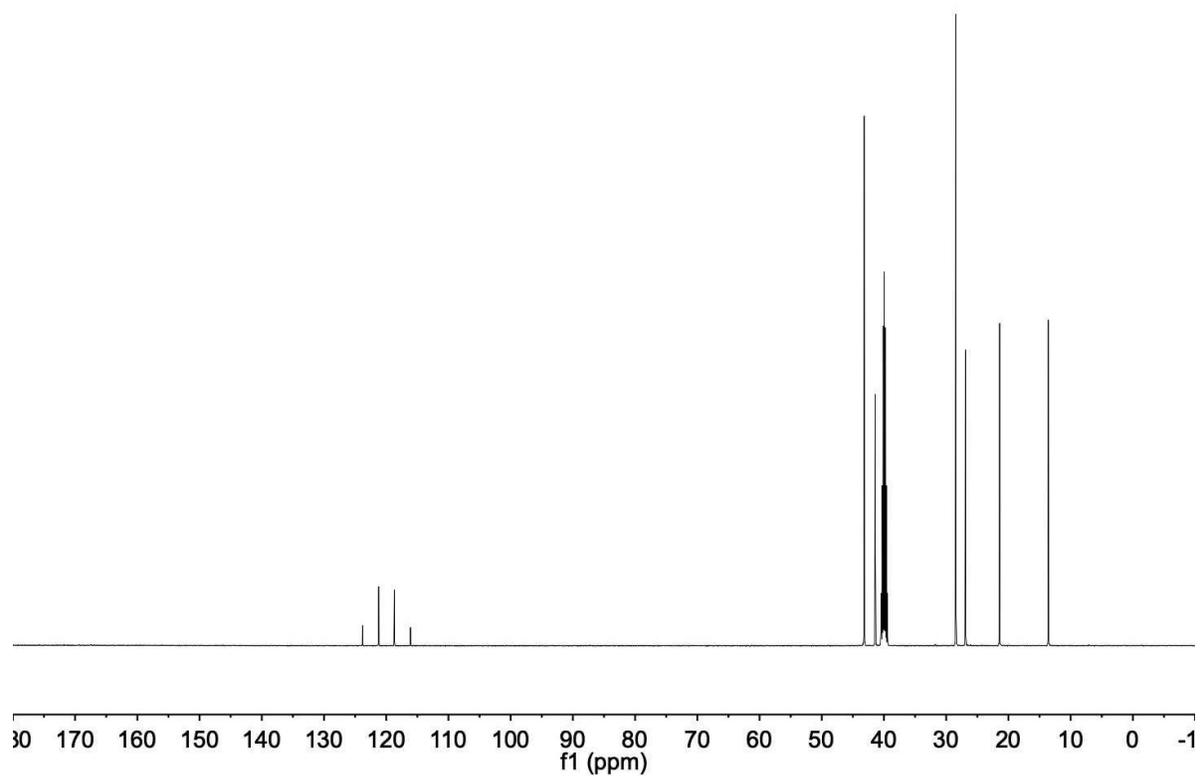


Figure S27. ^{13}C NMR of [bthiol][TFSI]

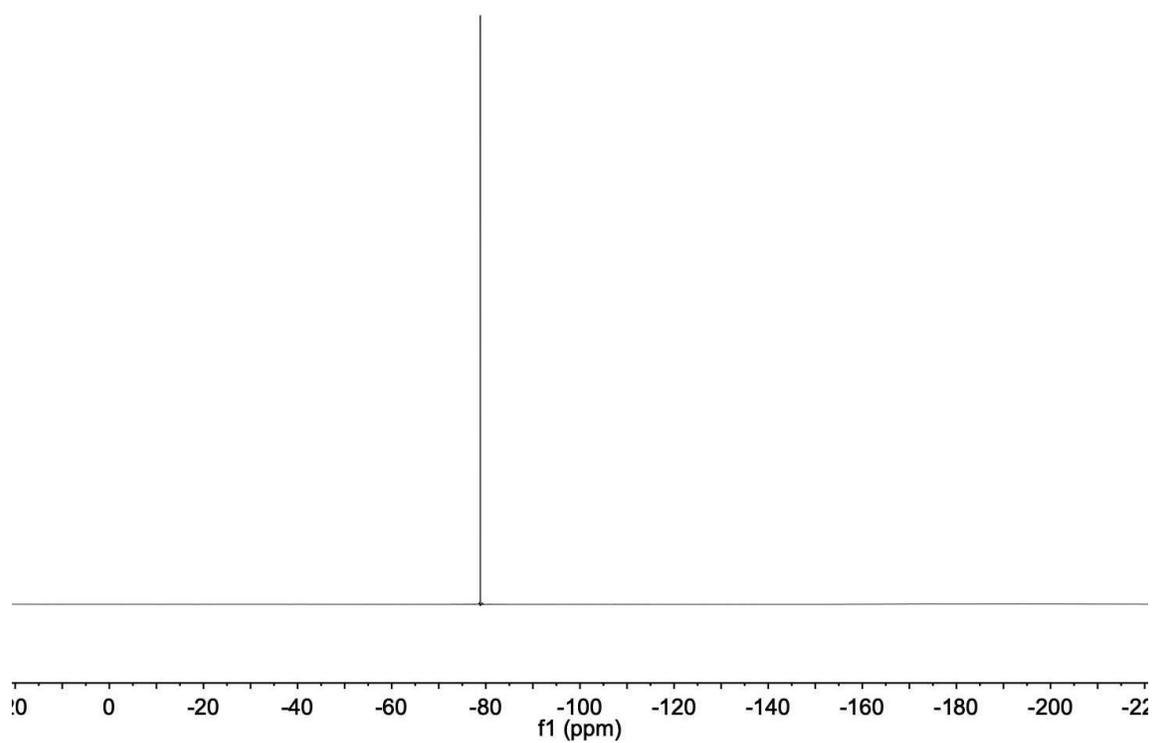


Figure S28. ^{19}F NMR of [bthiol][TFSI]

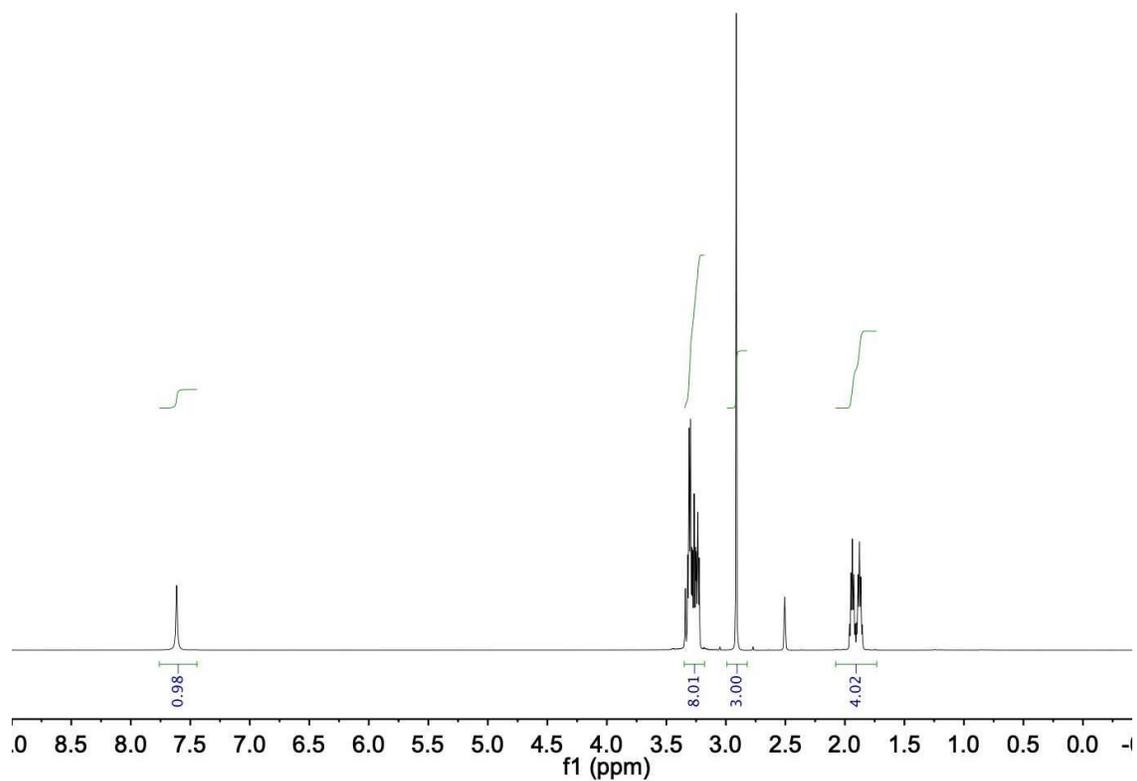


Figure S29. ¹H NMR of [MTBD][TFSI]

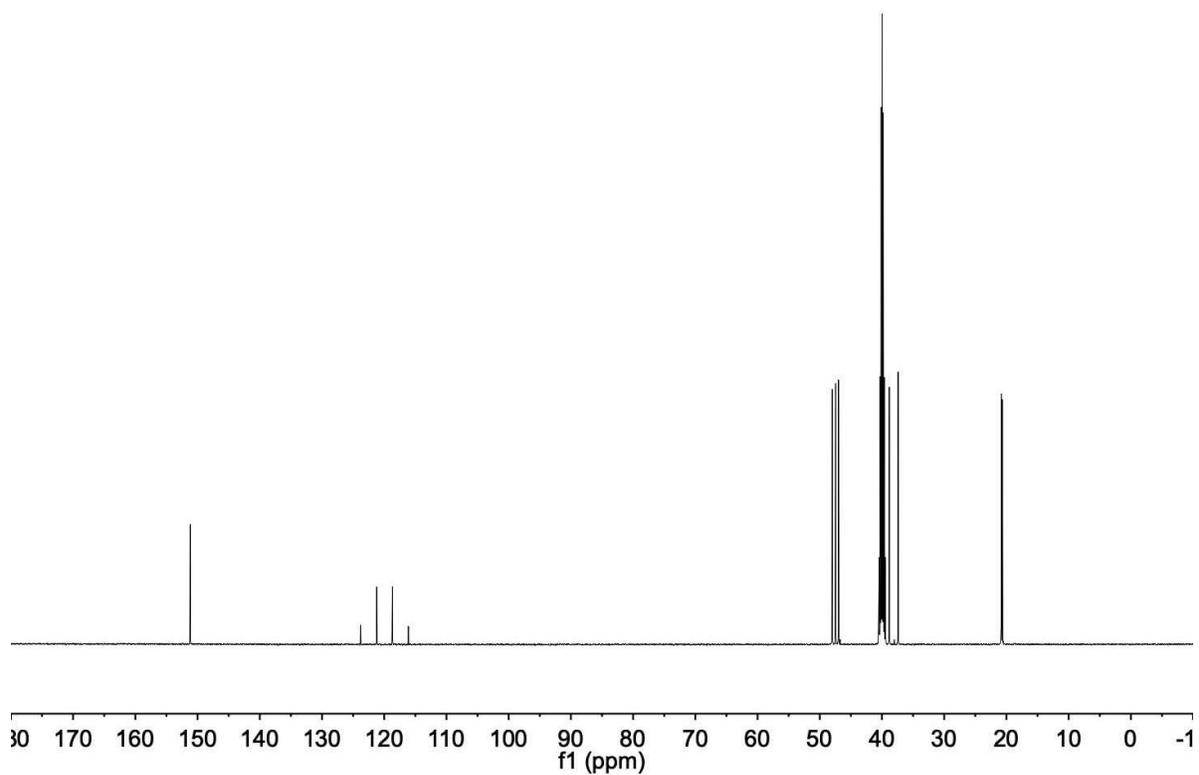


Figure S30. ¹³C NMR of [MTBD][TFSI]

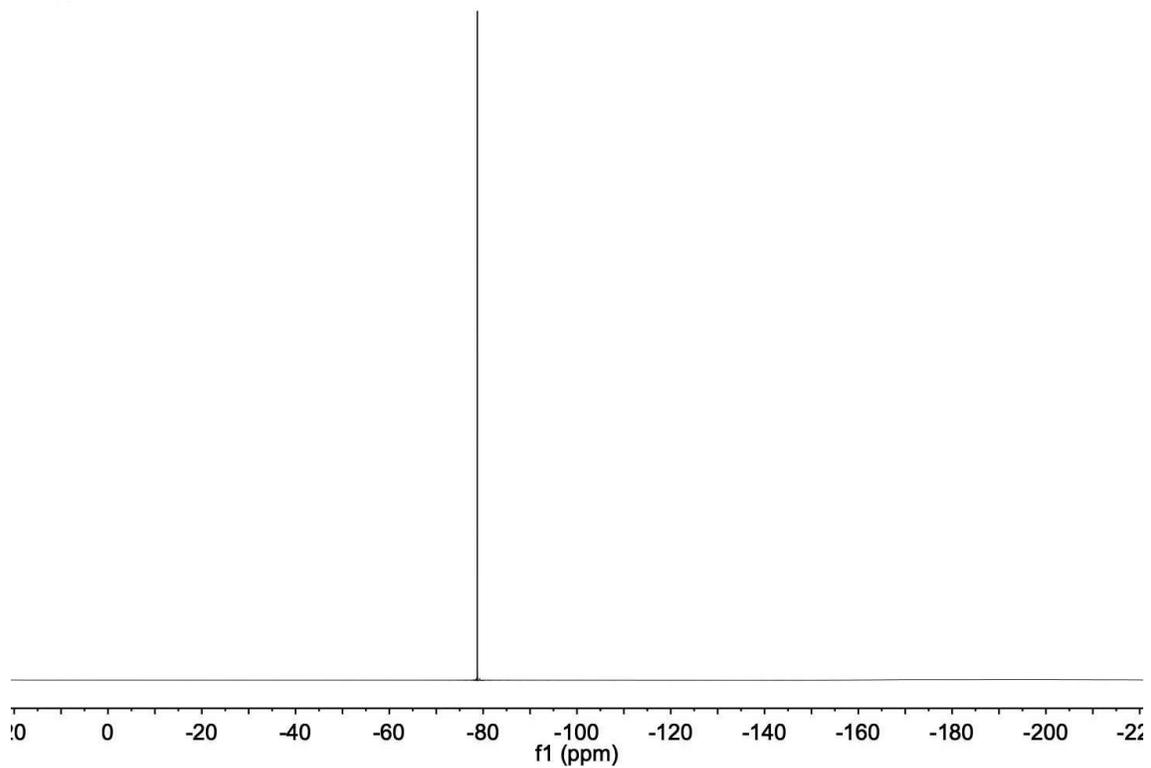


Figure S31. ^{19}F NMR of [MTBD][TFSI]