

## Physicochemical characterisation of novel tetrabutylammonium aryltrifluoroborate ionic liquids

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### General Experimental

<sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 MHz NMR operating at a probe temperature of 25 °C.

### General method for the synthesis of tetrabutylammonium aryltrifluoroborates

The following method for the synthesis of tetrabutylammonium (4-methoxyphenyl)trifluoroborate (**f1**) is considered typical for the transformation of arylboronic acids to their tetrabutylammonium aryltrifluoroborate derivatives:

A 500 mL round-bottomed flask was charged with 4-methoxyphenylboronic acid (10.00 g, 22.7 mmol, 1.0 eq.), HF<sub>2</sub>K (20.56 g, 263 mmol, 4.0 eq.), TBAF·3H<sub>2</sub>O (91.6% w/w, 24.93 g, 72.4 mmol, 1.1 eq.), CH<sub>2</sub>Cl<sub>2</sub> (50 mL), CH<sub>3</sub>OH (50 mL), then H<sub>2</sub>O (100 mL). A large stir bar was then introduced and the biphasic mixture stirred vigorously (690 rpm) for 3 hours. Stirring was halted and an aliquot of the bottom layer taken and concentrated for <sup>1</sup>H NMR analysis, which showed clean conversion to the product and a small amount of excess TBAF (ca. 8:1 ratio). The mixture was transferred to a 500 mL separating funnel and the organic phase collected and washed with H<sub>2</sub>O (2 x 100 mL). The organic phase was then dried (MgSO<sub>4</sub>) and concentrated by rotary evaporation to give the crude trifluoroborate as a caramel solid (26.16 g). The solid was triturated with Et<sub>2</sub>O (ca. 1 mL/g) and filtered on a Buchner funnel before drying in a vacuum oven at 30 °C for 2 hours to give tetrabutylammonium (4-methoxyphenyl)trifluoroborate as a beige solid (25.90 g, 99 %); **mp** 101.1–102.1 °C; **<sup>1</sup>H NMR** (400 MHz, DMSO) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 7.7 Hz, 2H), 3.69 (s, 3H), 3.21–3.12 (m, 8H), 1.63–1.51 (m, 8H), 1.32 (tq, *J* = 7.3, 7.3 Hz, 8H), 0.95 (t, *J* = 7.3 Hz, 12H); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 8.3 Hz, 2H), 6.73 (d, *J* = 8.3 Hz, 2H), 3.73 (s, 3H), 2.95 – 2.87 (m, 8H), 1.44–1.34 (m, 8H), 1.34–1.21 (m, 8H), 0.92 (t, *J* = 7.2 Hz, 12H).

#### **Tetrabutylammonium phenyltrifluoroborate (a)**

Colourless solid (0.820 mol scale, 52%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d, 2H), 7.12 (t, 2H), 7.05 (t, 1H), 2.83 (t, 8H), 1.2-1.4 (m, 16H), 0.90 (t, 12H).

#### **Tetrabutylammonium (4-fluorophenyl) trifluoroborate (b1)**

Colourless solid (0.143 mol scale, 75%);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.25 (t, 2H), 6.80 (t, 2H), 3.10 (t, 8H), 1.35-1.5 (m, 8H), 1.25-1.35 (m, 8H), 0.95 (t, 12H).

#### **Tetrabutylammonium (3-fluorophenyl) trifluoroborate (b2)**

Colourless solid (0.143 mol scale, 94%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (d, 1H), 7.18(d, 1H), 7.10 (q, 1H), 6.75(t, 1H), 2.9 (t, 8H), 1.3-1.42 (m, 8H), 1.2-1.3 (m, 8H), 0.90 (t, 12H).

#### **Tetrabutylammonium (4-chlorophenyl) trifluoroborate (c1)**

Colourless solid (0.128 mol scale, 81%);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.25 (d, 2H), 7.05 (d, 2H), 3.10 (t, 8H), 1.35-1.5 (m, 8H), 1.25-1.35 (m, 8H), 0.95 (t, 12H).

#### **Tetrabutylammonium (3-chlorophenyl) trifluoroborate (c2)**

Colourless solid (0.153 mol scale, 68%);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.46 (s, 1H), 7.40 (d, 1H), 7.08 (t, 1H), 7.04 (d, 1H), 2.95 (t, 8H), 1.35-1.5 (m, 8H), 1.25-1.35 (m, 8H), 0.95 (t, 12H).

#### **Tetrabutylammonium (4-bromophenyl) trifluoroborate (d1)**

Colourless solid (0.10 mol scale, 90%);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.2 (t, 4H), 3.10 (t, 8H), 1.45-1.55 (m, 8H), 1.2-1.35 (m, 8H), 0.9 (t, 12H).

#### **Tetrabutylammonium (3-bromophenyl) trifluoroborate (d2)**

Colourless solid (0.10 mol scale, 67%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (s, 1H), 7.50 (d, 1H), 7.23 (d, 1H), 7.05 (t, 1H), 2.95 (t, 8H), 1.40-1.50 (m, 8H), 1.25-1.40 (m, 8H), 0.9 (t, 12H).

#### **Tetrabutylammonium (4-iodophenyl) trifluoroborate (e1)**

Colourless solid (0.081 mol scale, 93%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d, 2H), 7.35 (d, 2H), 3.00 (t, 8H), 1.40-1.50 (m, 8H), 1.30-1.40 (m, 8H), 0.95 (t, 12H).

#### **Tetrabutylammonium (3-iodophenyl) trifluoroborate (e2)**

Colourless solid (0.081 mol scale, 85%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.95 (t, 12H), 1.30-1.40 (m, 8H), 1.45-1.55 (m, 8H), 3.05 (t, 8H), 6.96 (t, 1H), 7.23 (d, 1H), 7.45 (d, 1H), 7.57 (d, 1H), 7.92(s, 1H).

### **Tetrabutylammonium (4-methoxyphenyl)trifluoroborate**

Beige solid (25.90 g, 99 %); **mp** 101.1–102.1 °C;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.24 (d,  $J = 8.4$  Hz, 2H), 6.67 (d,  $J = 7.7$  Hz, 2H), 3.69 (s, 3H), 3.21–3.12 (m, 8H), 1.63–1.51 (m, 8H), 1.32 (tq,  $J = 7.3, 7.3$  Hz, 8H), 0.95 (t,  $J = 7.3$  Hz, 12H);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.3$  Hz, 2H), 6.73 (d,  $J = 8.3$  Hz, 2H), 3.73 (s, 3H), 2.95 – 2.87 (m, 8H), 1.44–1.34 (m, 8H), 1.34–1.21 (m, 8H), 0.92 (t,  $J = 7.2$  Hz, 12H).

### **Tetrabutylammonium(3-methoxyphenyl)trifluoroborate (f2)**

Colourless solid (0.132 mol scale, 80%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.15 (s, 2H), 7.11-7.05 (t, 1H), 6.65 (d, 1H), 3.73 (s, 3H), 2.99-2.88 (m, 8H), 1.48-1.22 (m, 16H), 0.98-0.88 (m, 12H).

### **Tetrabutylammonium (4-*n*-butylphenyl) trifluoroborate (g)**

Colourless solid (0.132 mol scale, 76%); **mp** 65-68 °C;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.15 (d, 2H) 6.83 (d, 2H), 3.10 (t, 8H), 2.4 (m, 2H), 1.4-1.6 (m, 11H), 1.2-1.3 (m, 11H), 0.8-0.9 (m, 15H).

### **Tetrabutylammonium 1,4-phenylenebis(trifluoroborate) (h1)**

(30.2 mmol scale, 2.2 eq. TBAF.H<sub>2</sub>O, 8.0 eq. HF<sub>2</sub>K, 90%); **mp** 171.8–174.3 °C;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.04 (s, 4H), 3.18–3.10 (m, 16H), 1.61–1.49 (m, 16H), 1.30 (h,  $J = 7.4$  Hz, 16H), 0.93 (t,  $J = 7.4$  Hz, 24H).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (s, 4H), 2.75–2.66 (m, 16H), 1.38–1.23 (dd,  $J = 7.4, 6.1$  Hz, 32H), 0.95–0.87 (m, 24H).

### **Tetrabutylammonium 1,3-phenylenebis(trifluoroborate) (h2)**

(0.152 mol scale, 73%);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.75 (s, 1H), 7.35 (d, 2H), 6.99 (t, 1H), 2.70-2.75 (t, 16H), 1.22-1.40 (m, 32H), 0.95 (t, 24H).

### **Tetrabutylammonium 9,9-dimethyl-9H-fluoren-2,7-diyl-2,7-ditrifluoroborate (i)**

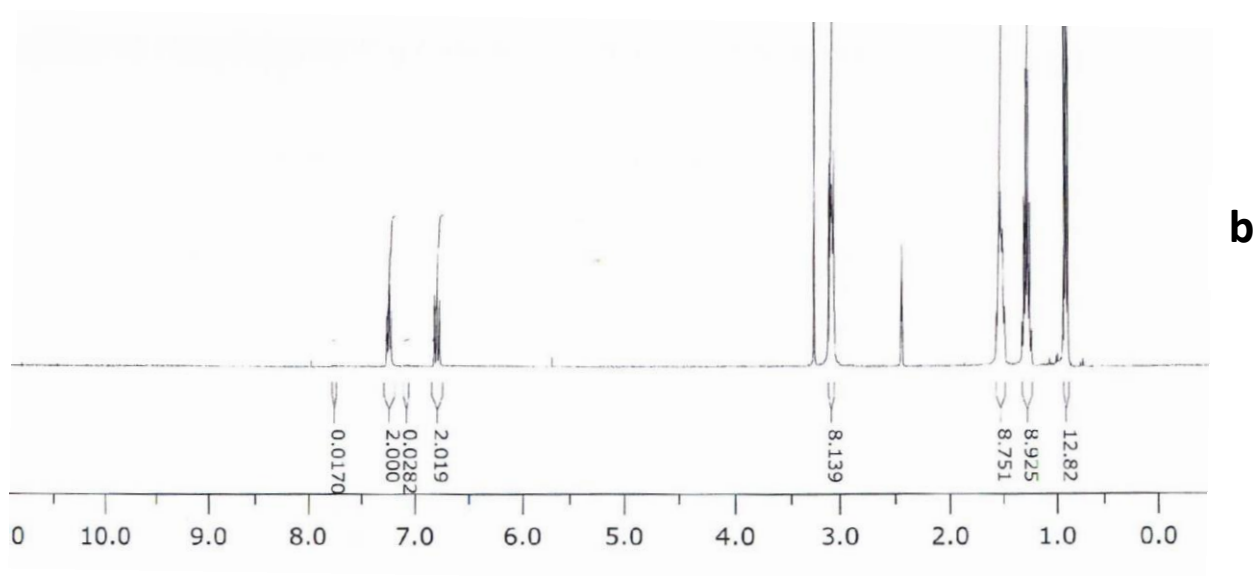
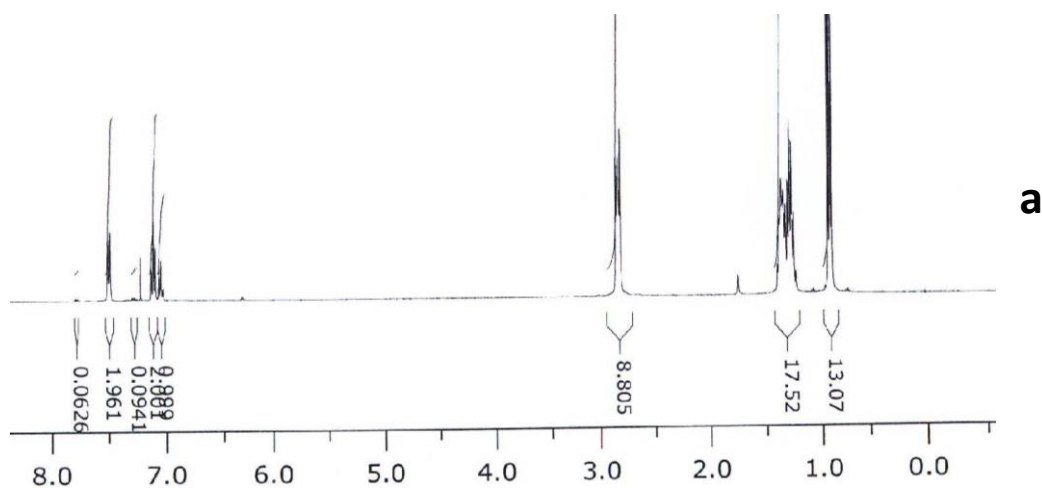
Colourless solid (0.177 mol scale, 2.4 eq. TBAF.H<sub>2</sub>O, 8.0 eq. HF<sub>2</sub>K, 98%);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.35 (d, 4H), 7.2 (d, 2H), 3.10 (t, 16H), 1.45-1.55 (m, 16H), 1.2-1.35 (m, 22H), 0.9 (t, 24H).

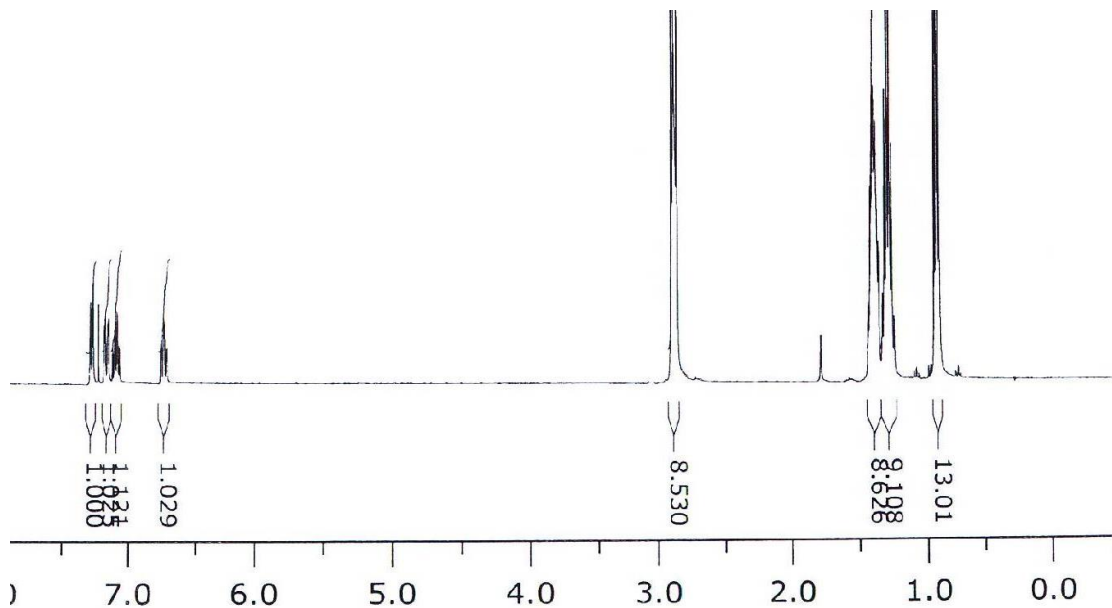
### **Potassium 4-methoxyphenyltrifluoroborate (j)**

To a mixture of 4-methoxyphenylboronic acid (100.00 g, 0.66 mol, 1.0 eq.) and potassium hydrogenfluoride (116.34 g, 1.49 mol, 2.26 eq.) in a 2 L plastic beaker was added CH<sub>3</sub>OH (200 mL) then water (400 mL), and the thick slurry stirred vigorously overnight. The mixture was filtered through a Buchner funnel and the solid washed with a small amount of H<sub>2</sub>O. The solid was then transferred to a 1 L conical flask and triturated with hot water (400 mL) for 20 minutes before cooling to 4 °C for an hour. Filtration of the solid and drying in a vacuum oven overnight at 100 °C gave potassium 4-

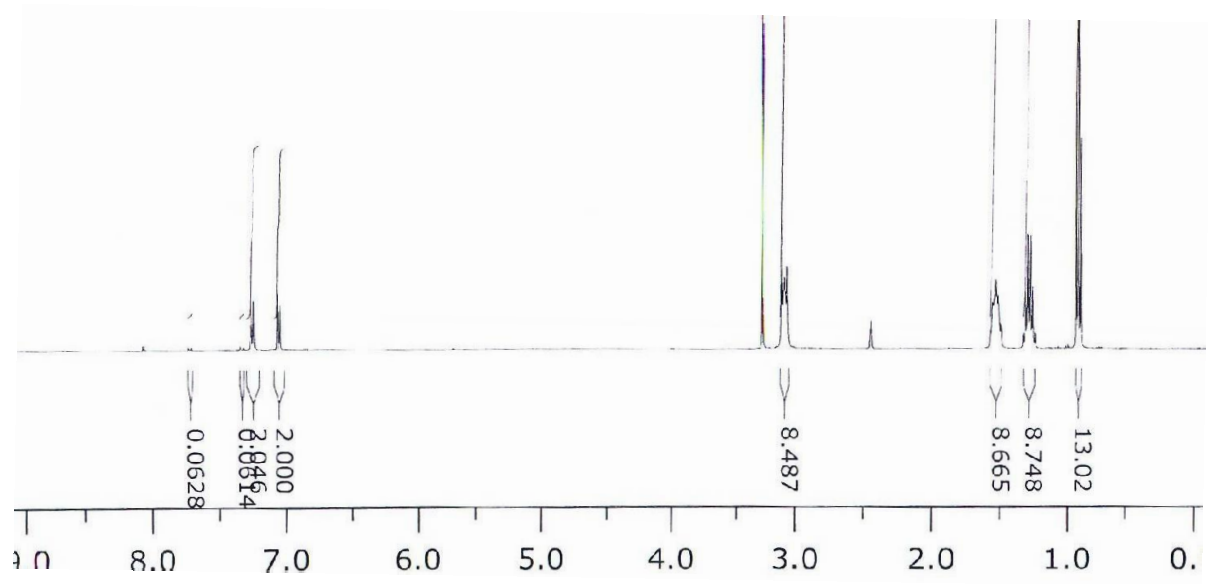
methoxytetrafluoroborate as a lustrous colourless solid (110.56 g, 78 %);  $^1\text{H NMR}$  (DMSO- $d_6$ , 400MHz)  
 $\delta$  7.20 (d,  $J = 8.2$  Hz, 2H), 6.65 (d,  $J = 8.2$  Hz, 2H), 3.78 (s, 3H).

### $^1\text{H NMR}$ Spectra

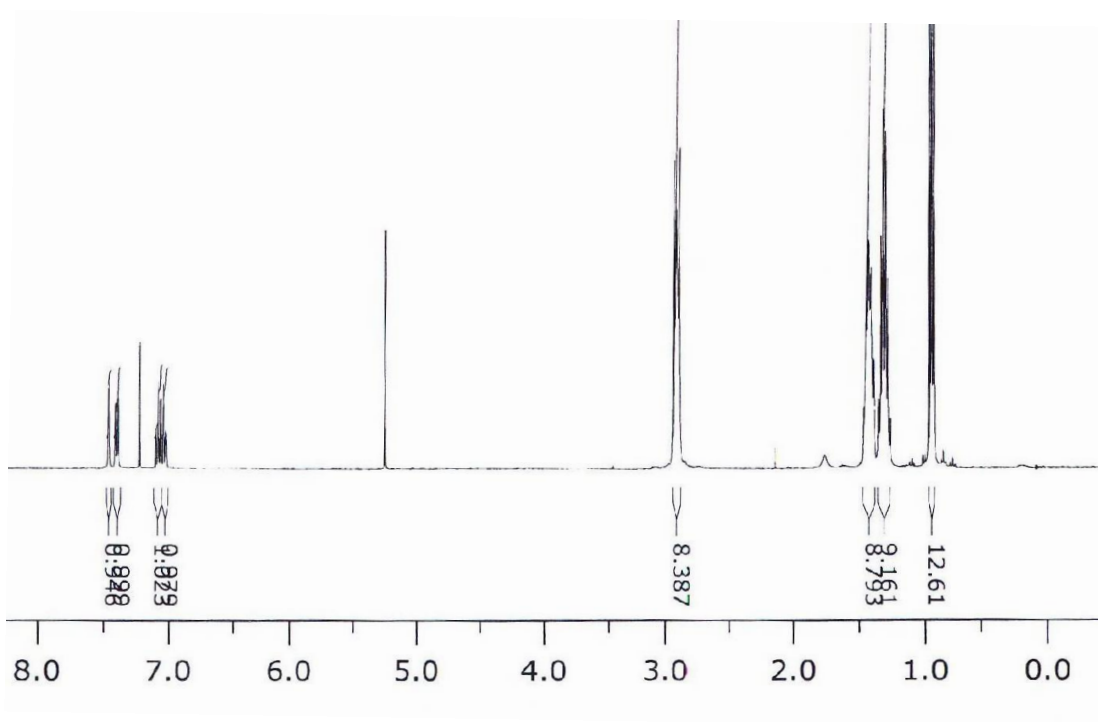




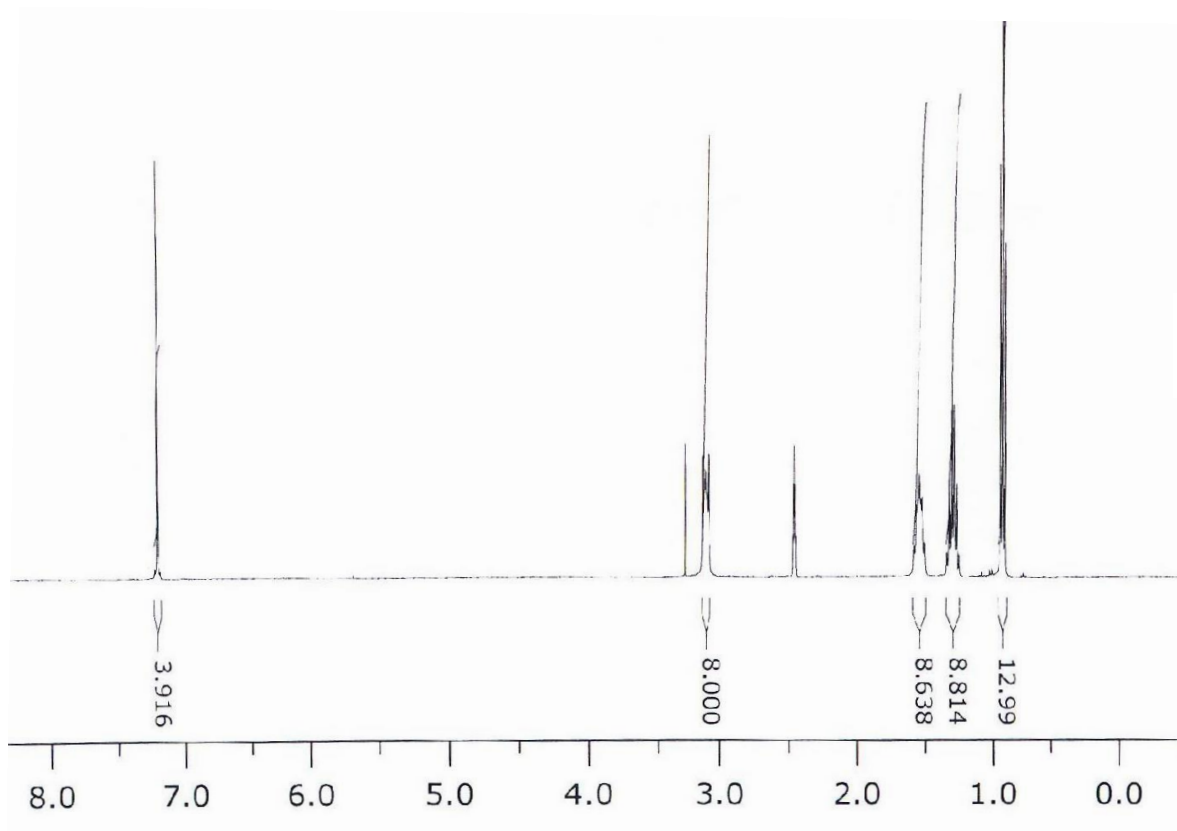
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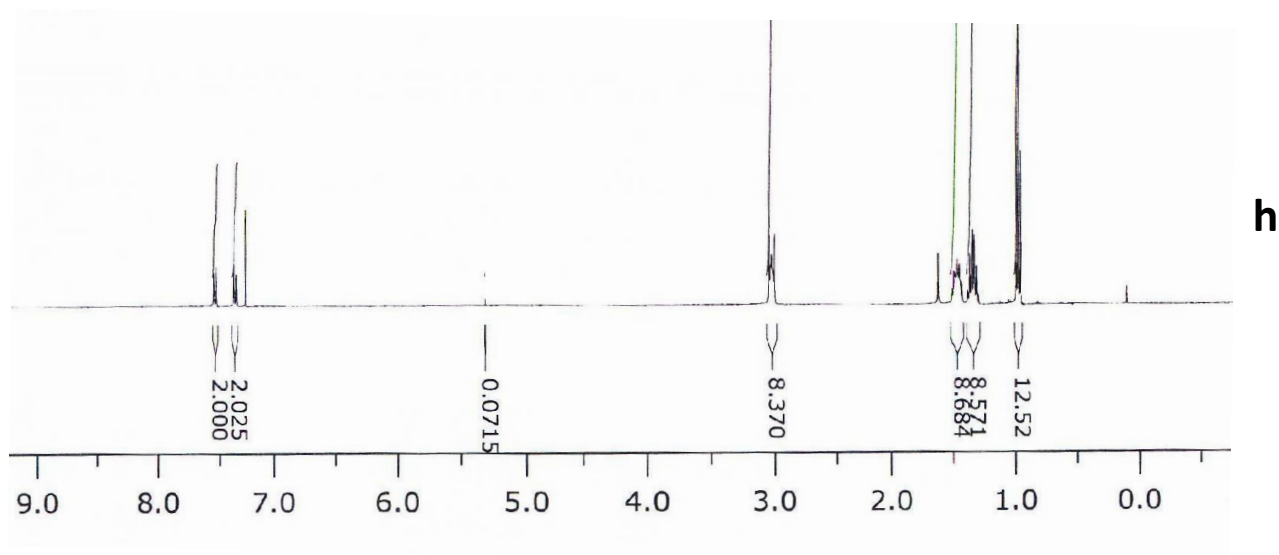
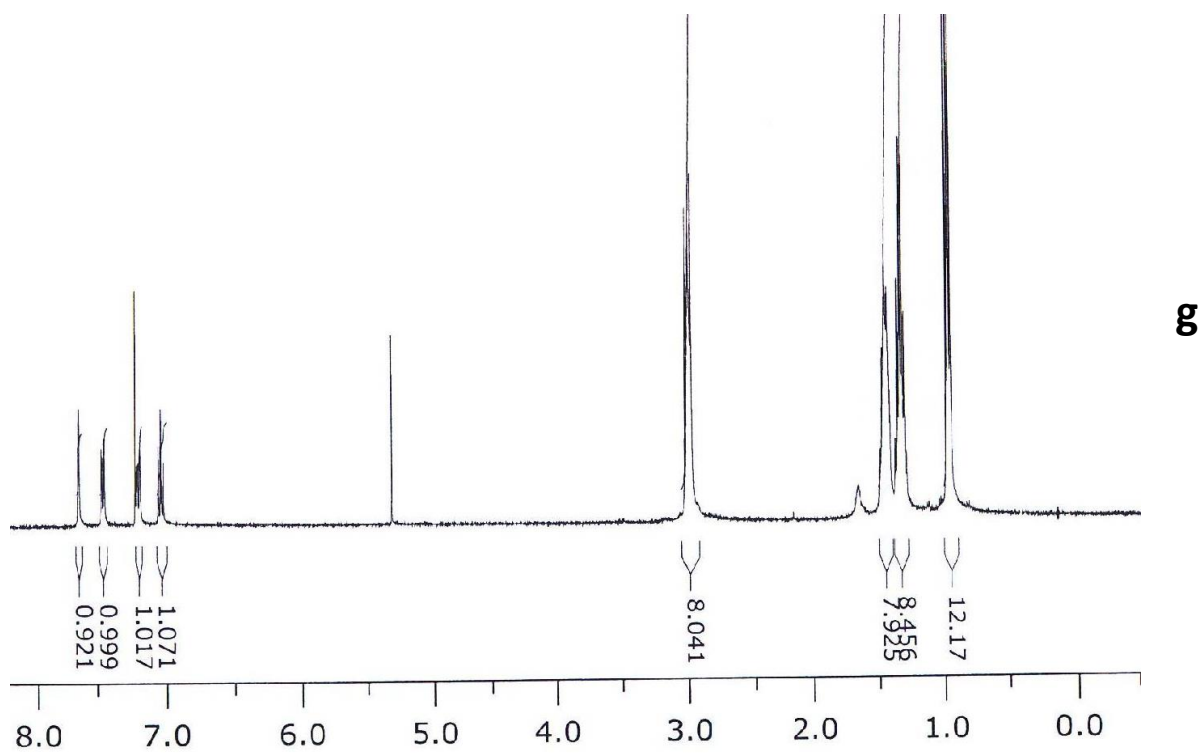
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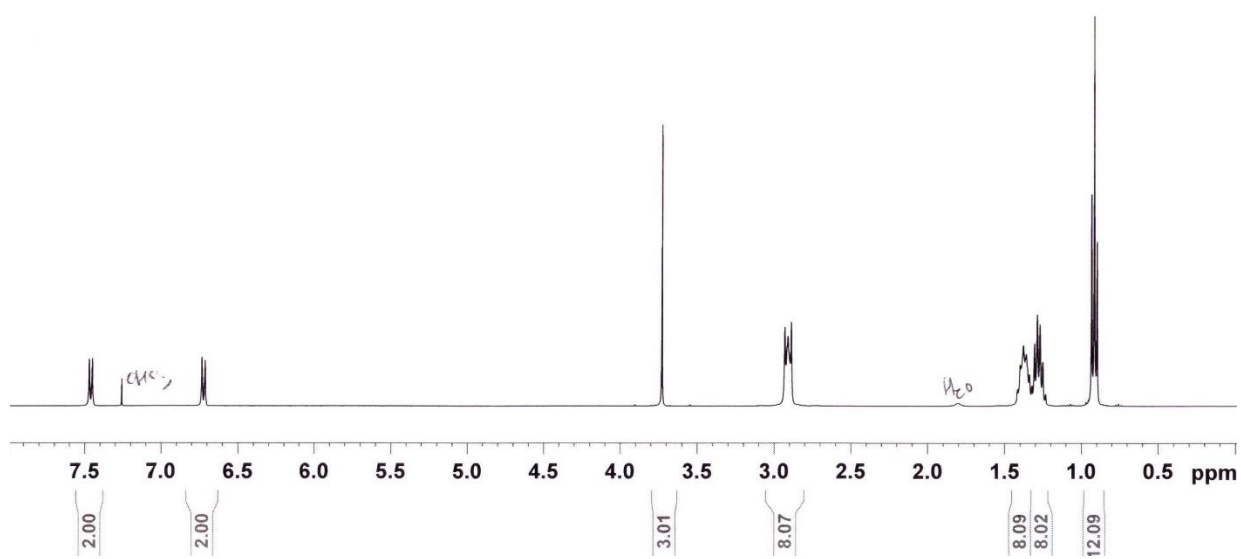
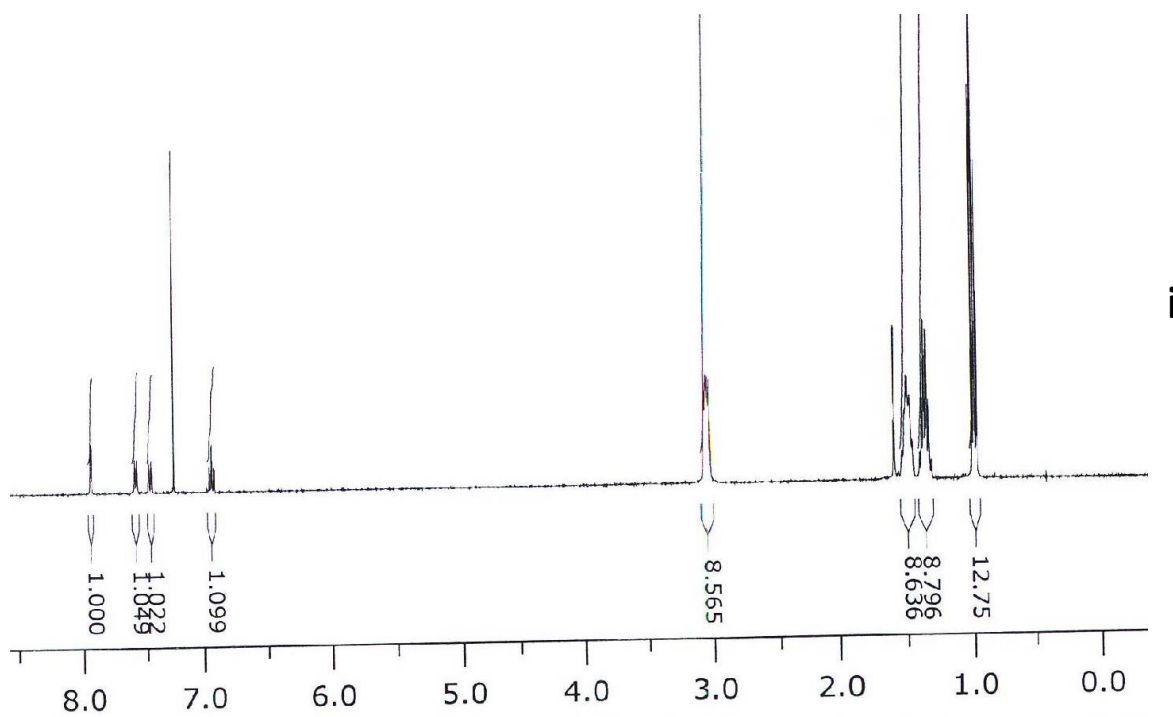


e

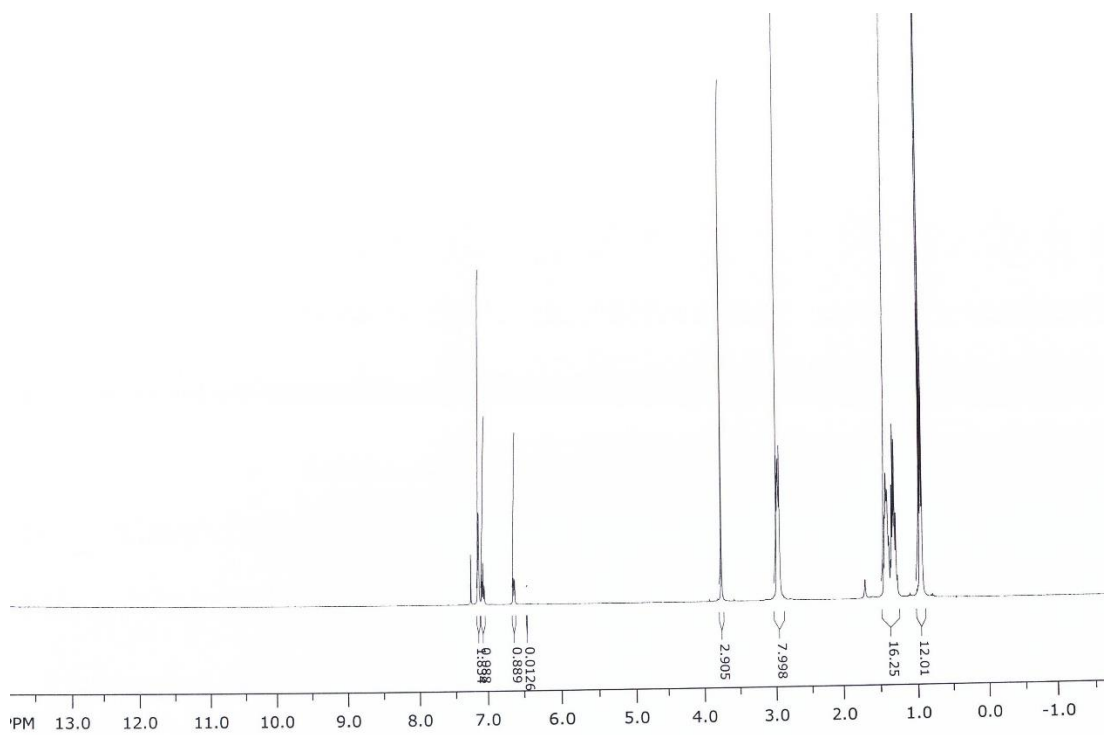


f

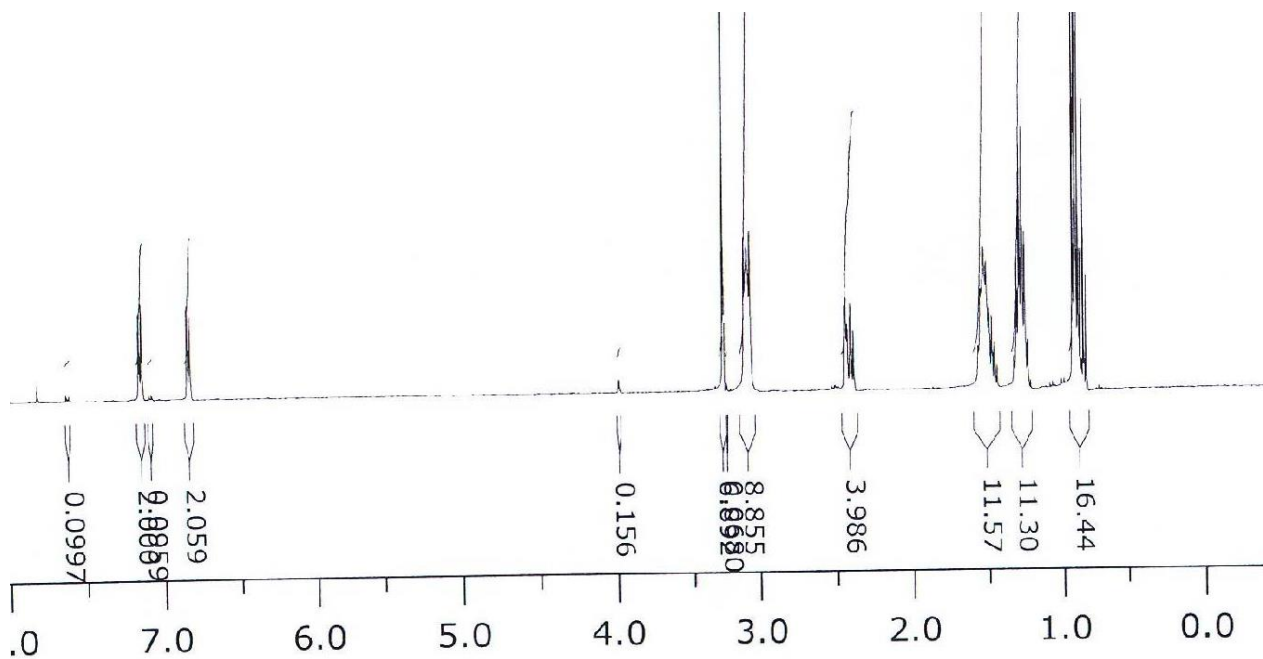




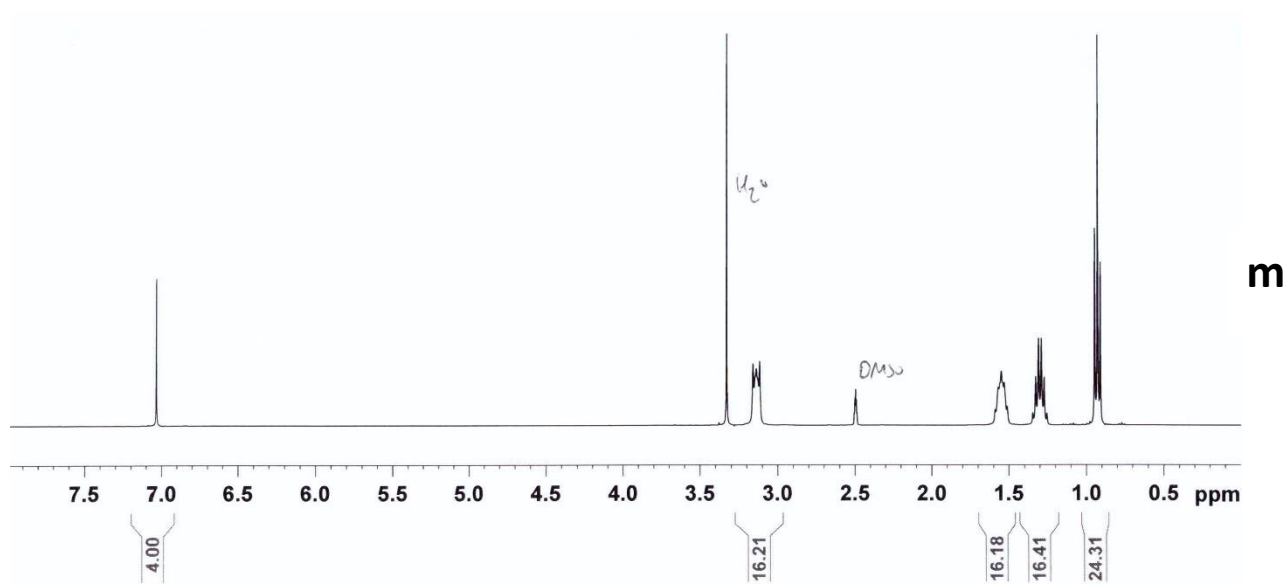




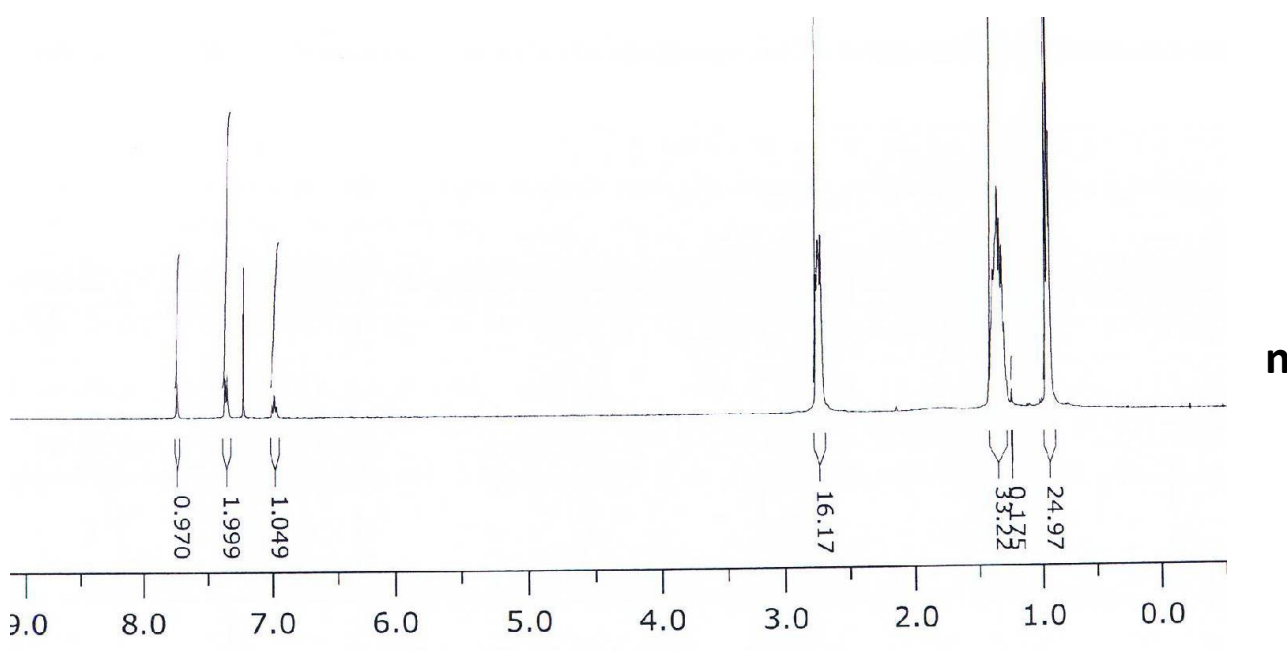
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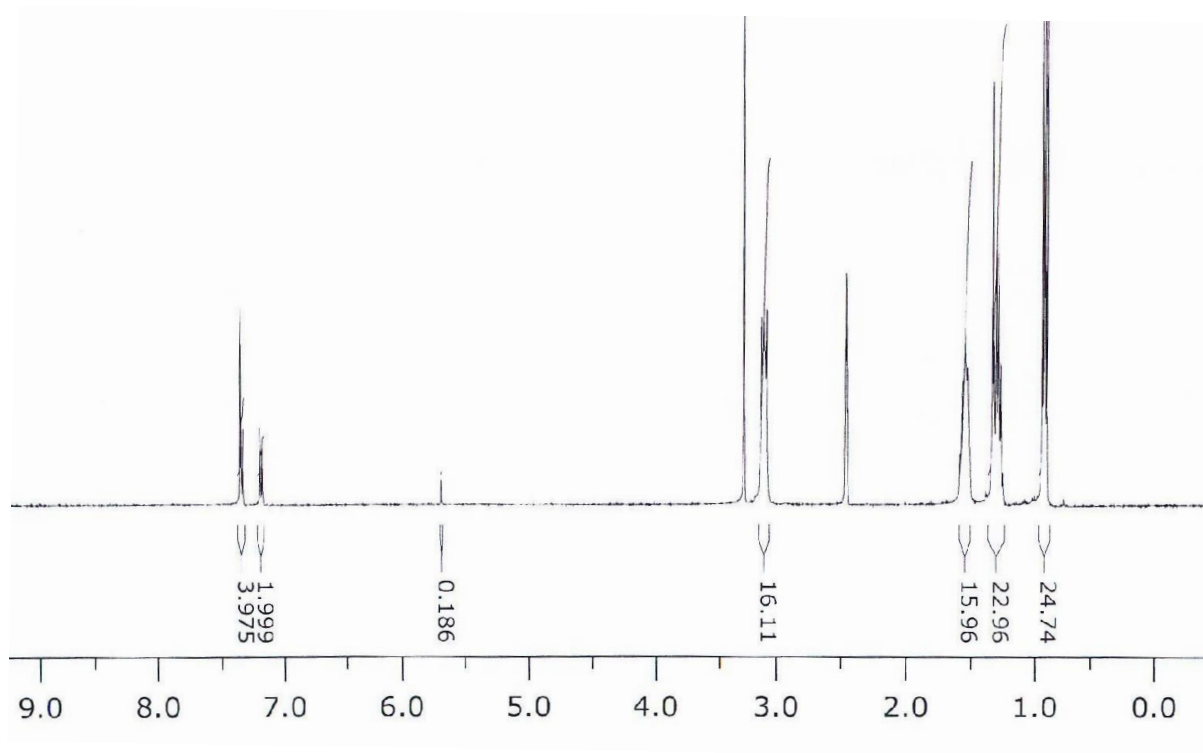
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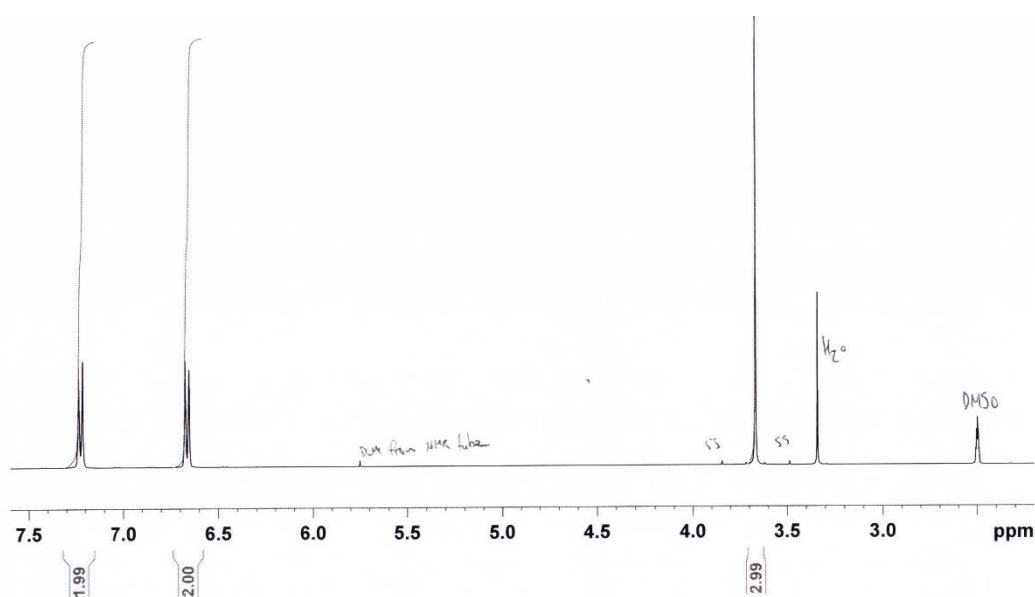
m



n

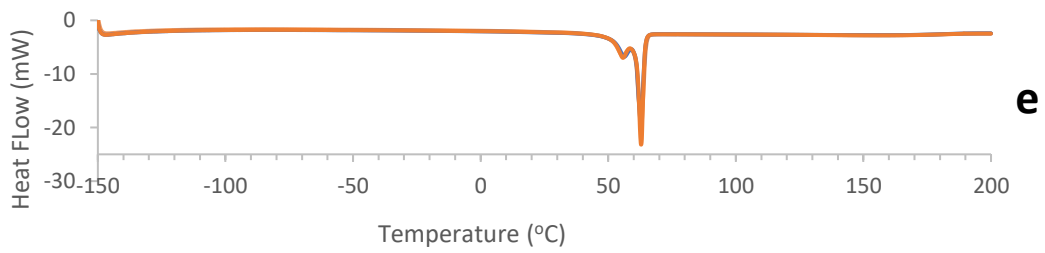
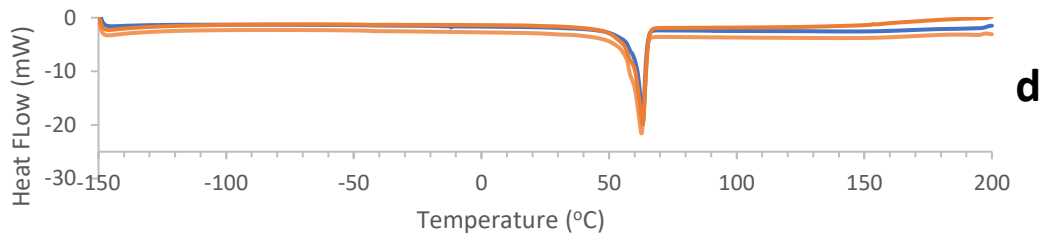
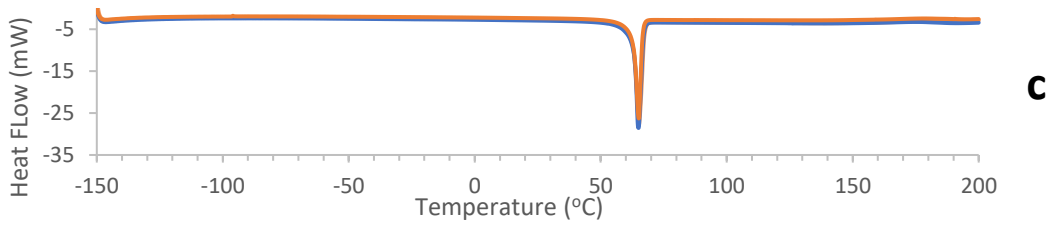
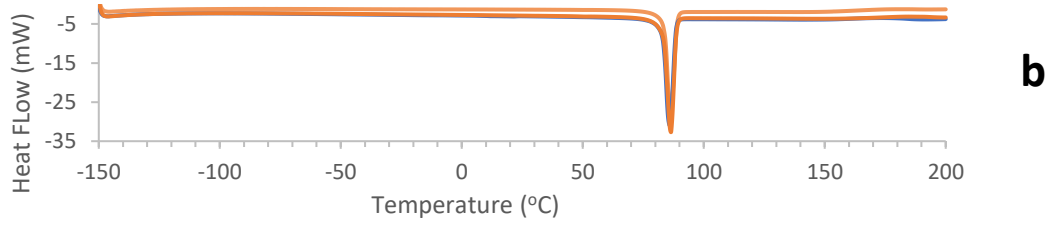
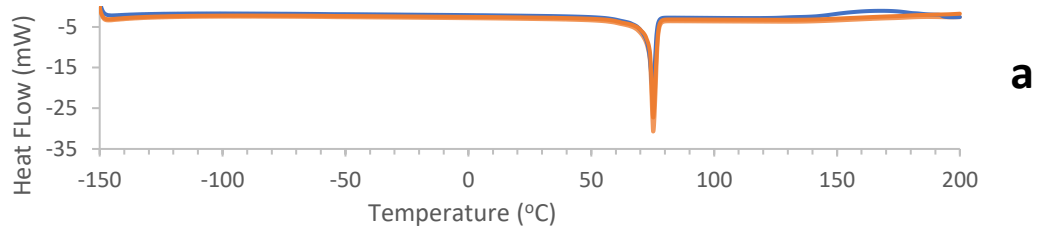


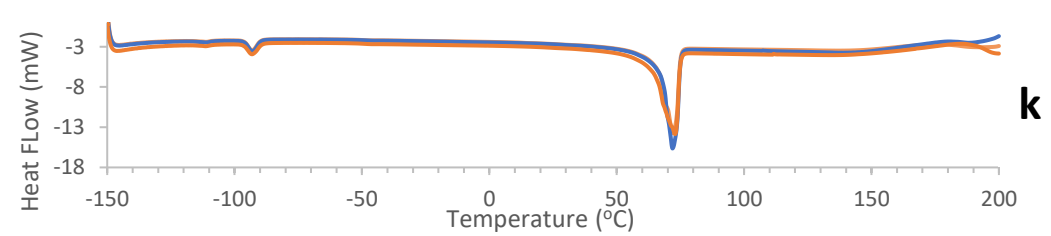
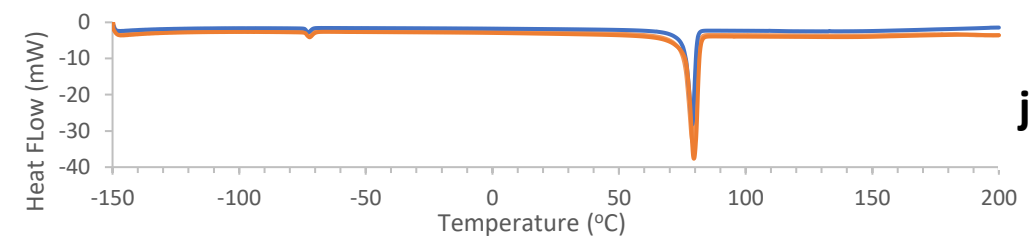
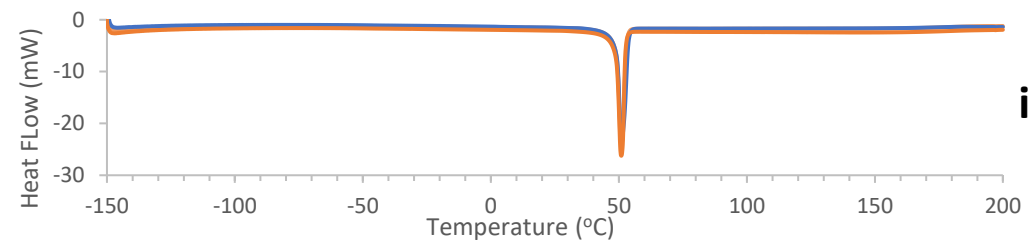
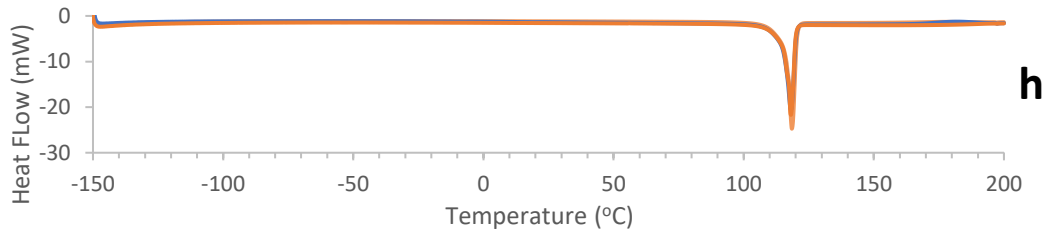
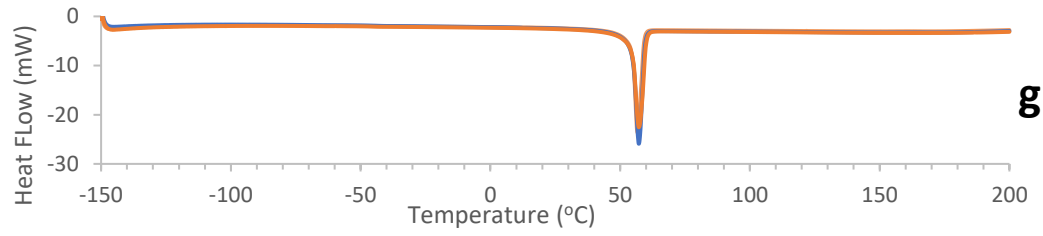
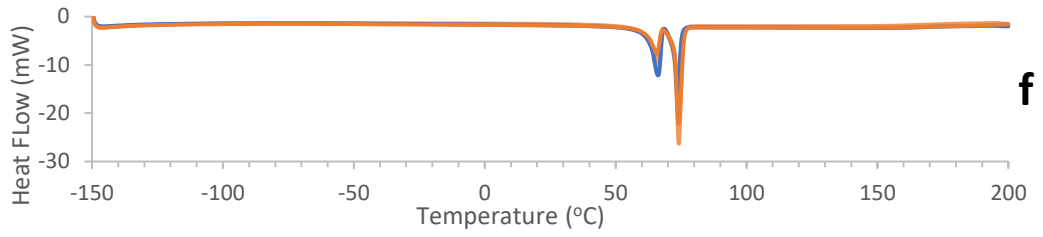
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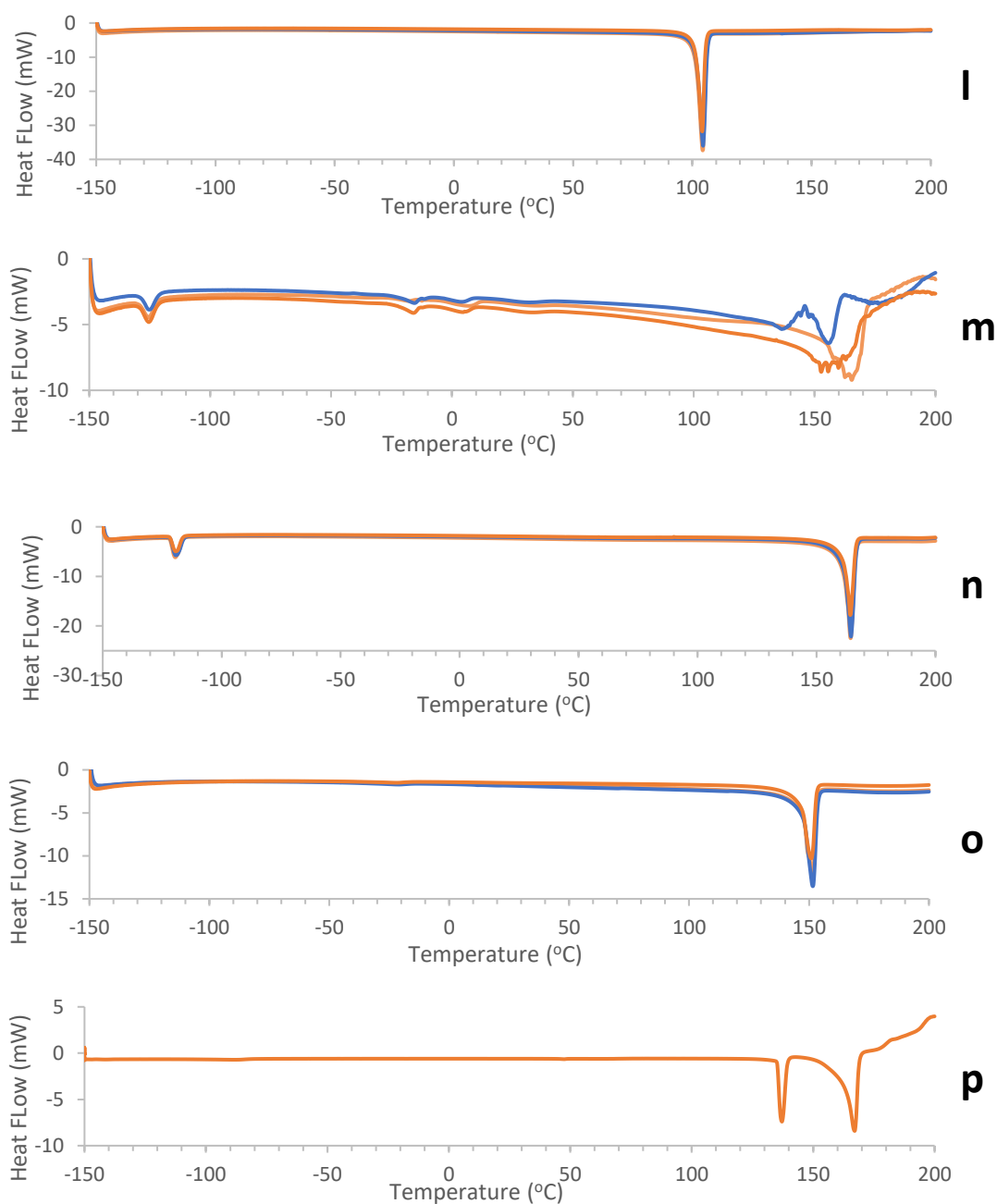


**p**

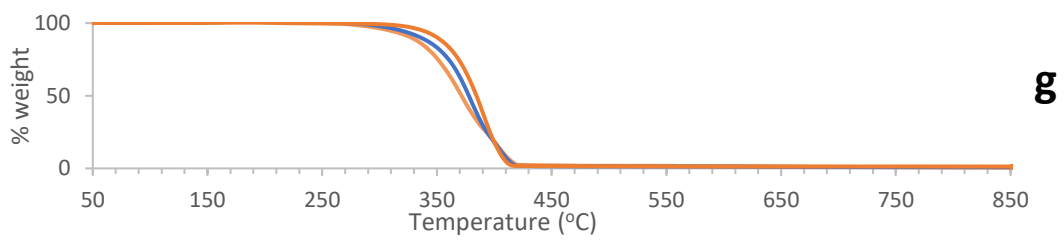
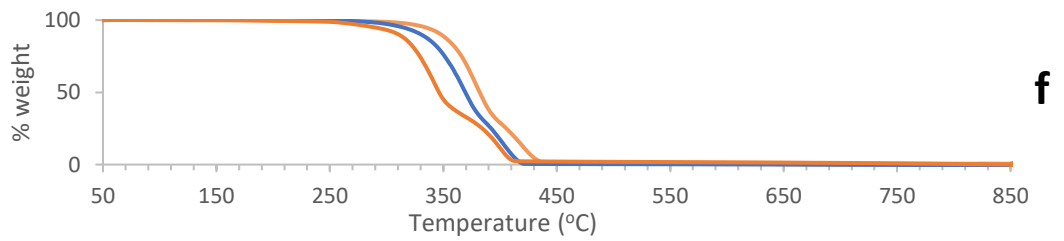
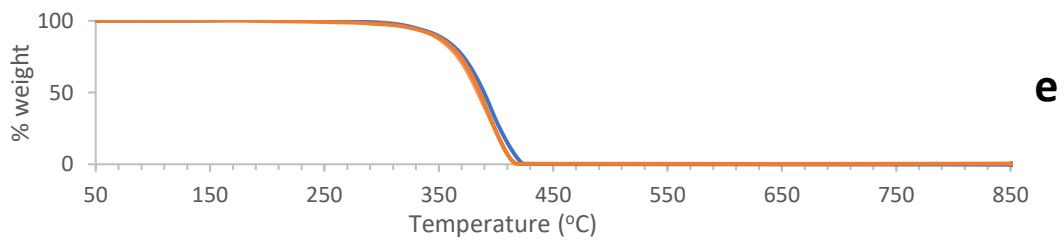
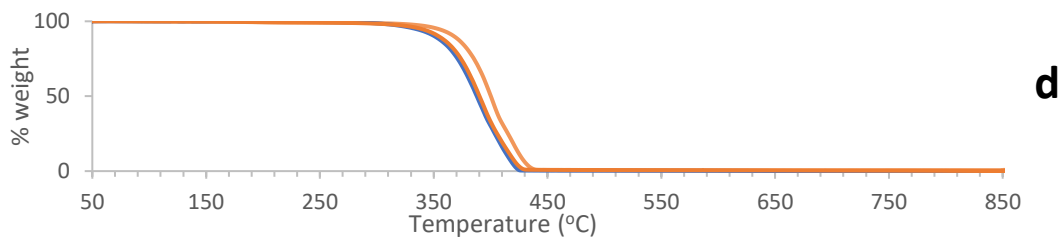
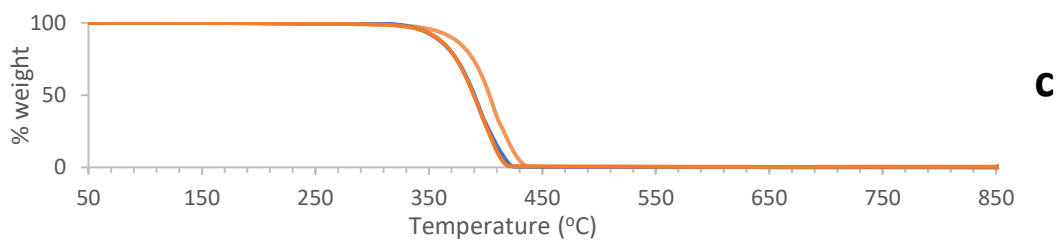
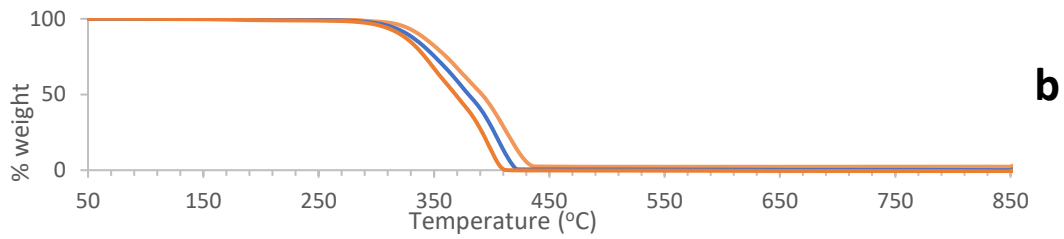
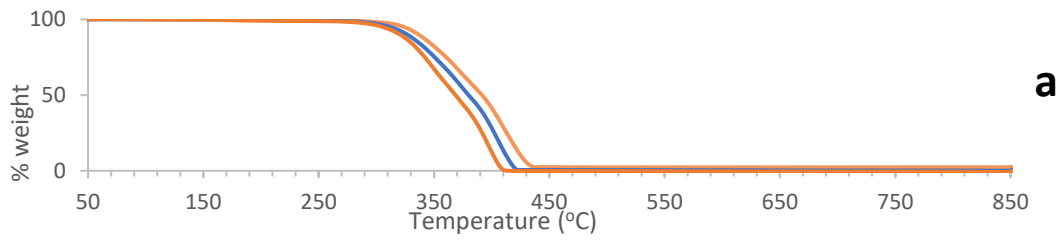
**Figure S1:** The <sup>1</sup>H NMR spectra for samples (a) tetrabutylammonium phenyltrifluoroborate, (b) tetrabutylammonium 4-fluorophenyltrifluoroborate, (c) tetrabutylammonium 3-fluorophenyltrifluoroborate, (d) tetrabutylammonium 4-chlorophenyltrifluoroborate, (e) tetrabutylammonium 3-chlorophenyltrifluoroborate, (f) tetrabutylammonium 4-bromophenyltrifluoroborate, (g) tetrabutylammonium 3-bromophenyltrifluoroborate, (h) tetrabutylammonium 4-iodophenyltrifluoroborate, (i) tetrabutylammonium 3-iodophenyltrifluoroborate, (j) tetrabutylammonium 4-methoxyphenyltrifluoroborate, (k) tetrabutylammonium 3-methoxyphenyltrifluoroborate, (l) tetrabutylammonium 4-n-butylphenyltrifluoroborate, (m) tetrabutylammonium 1,4-phenylenebistrifluoroborate, (n) tetrabutylammonium 1,3-phenylenebistrifluoroborate, (o) tetrabutylammonium 9,9-dimethyl-9H-fluoren-2,7-diyl-2,7-difluoroborate, (p) potassium 4-methoxyphenyltrifluoroborate.

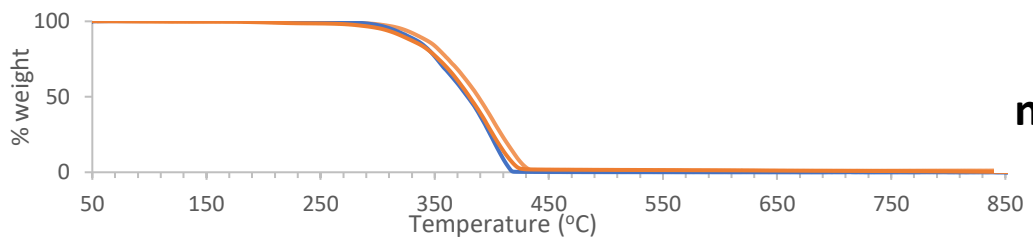
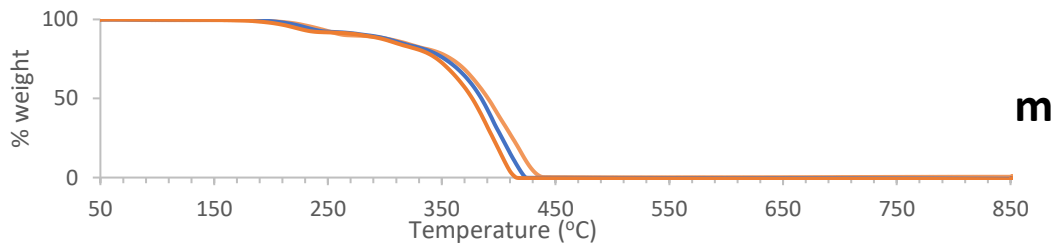
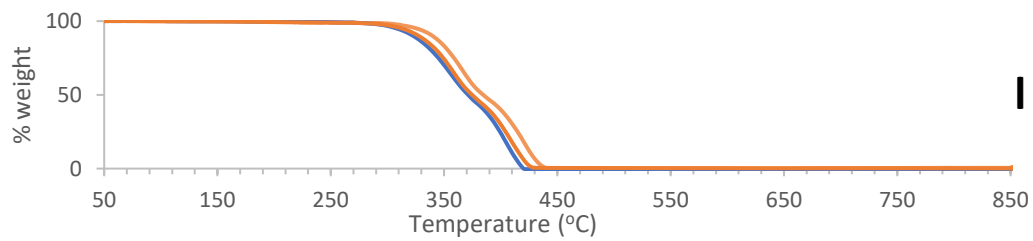
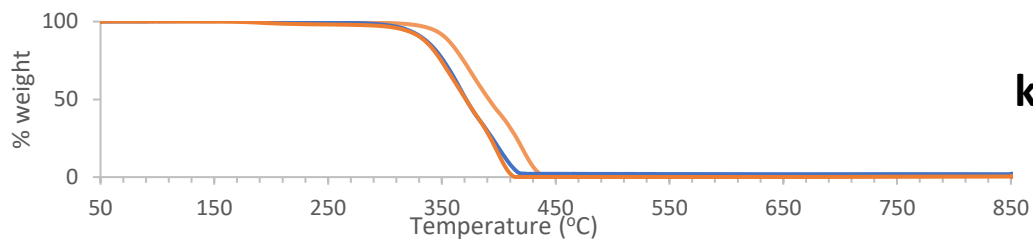
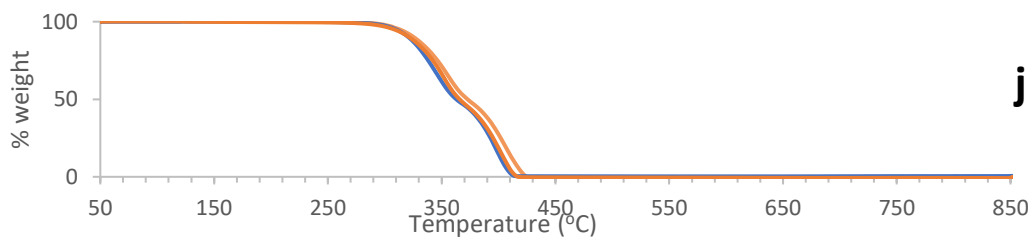
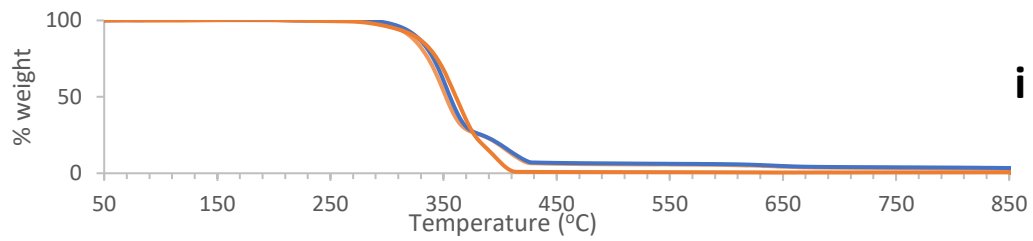
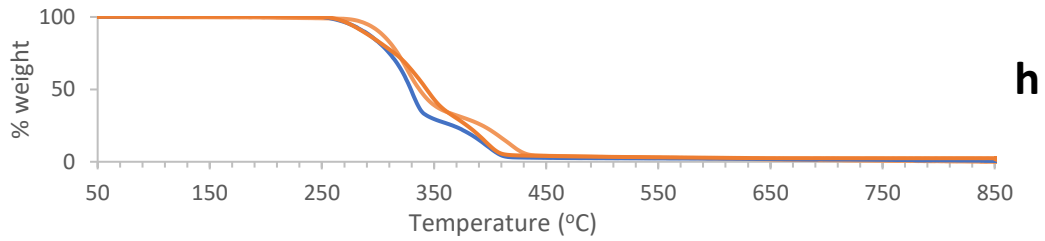




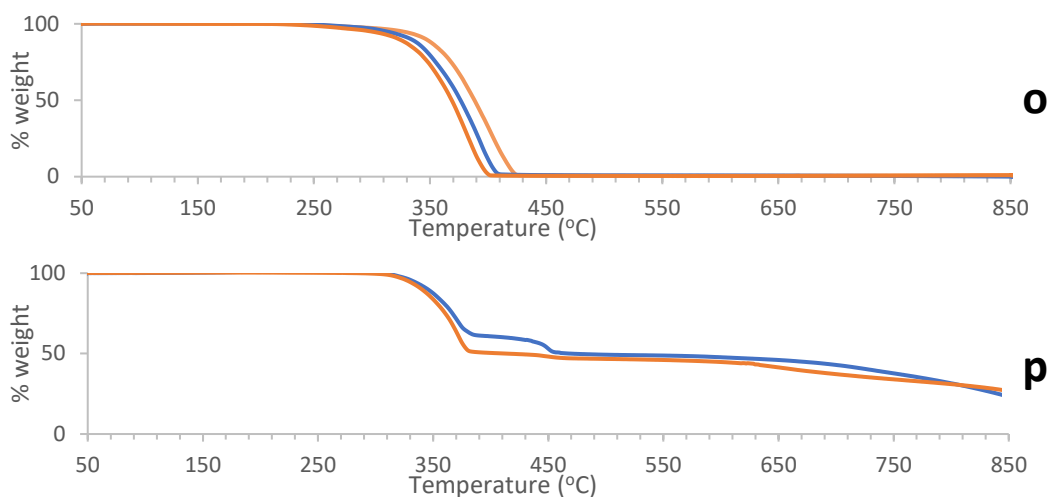


**Figure S2:** The triplicate DSC traces for samples (a) tetrabutylammonium phenyltrifluoroborate, (b) tetrabutylammonium 4-fluorophenyltrifluoroborate, (c) tetrabutylammonium 3-fluorophenyltrifluoroborate, (d) tetrabutylammonium 4-chlorophenyltrifluoroborate, (e) tetrabutylammonium 3-chlorophenyltrifluoroborate, (f) tetrabutylammonium 4-bromophenyltrifluoroborate, (g) tetrabutylammonium 3-bromophenyltrifluoroborate, (h) tetrabutylammonium 4-iodophenyltrifluoroborate, (i) tetrabutylammonium 3-iodophenyltrifluoroborate, (j) tetrabutylammonium 4-methoxyphenyltrifluoroborate, (k) tetrabutylammonium 3-methoxyphenyltrifluoroborate, (l) tetrabutylammonium 4-n-butylphenyltrifluoroborate, (m) tetrabutylammonium 1,4-phenylenebistrifluoroborate, (n) tetrabutylammonium 1,3-phenylenebistrifluoroborate, (o) tetrabutylammonium 9,9-dimethyl-9H-fluoren-2,7-diyl-2,7-ditrifluoroborate, (p) potassium 4-methoxyphenyltrifluoroborate. (a single DSC trace).

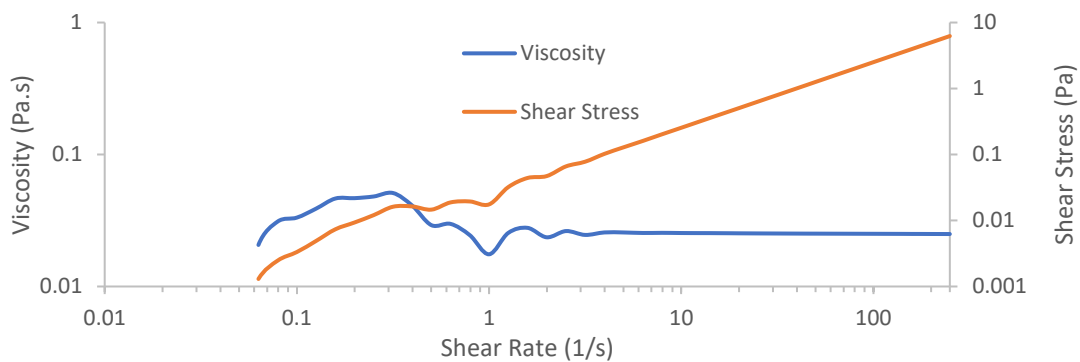




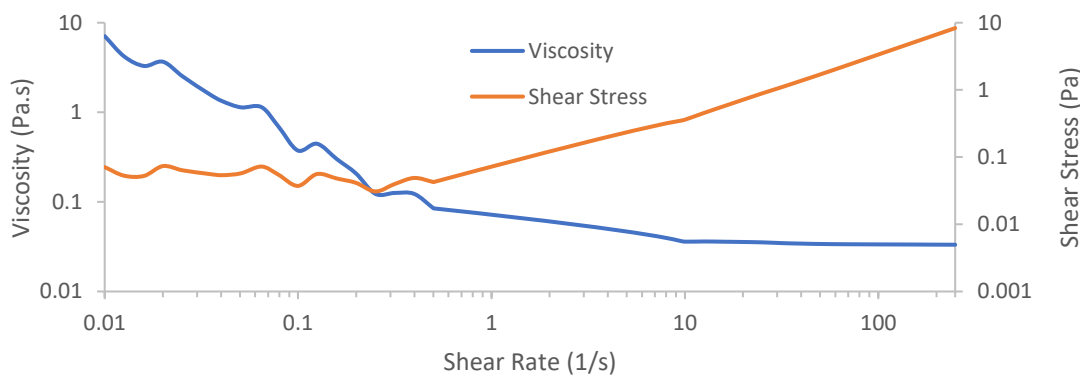




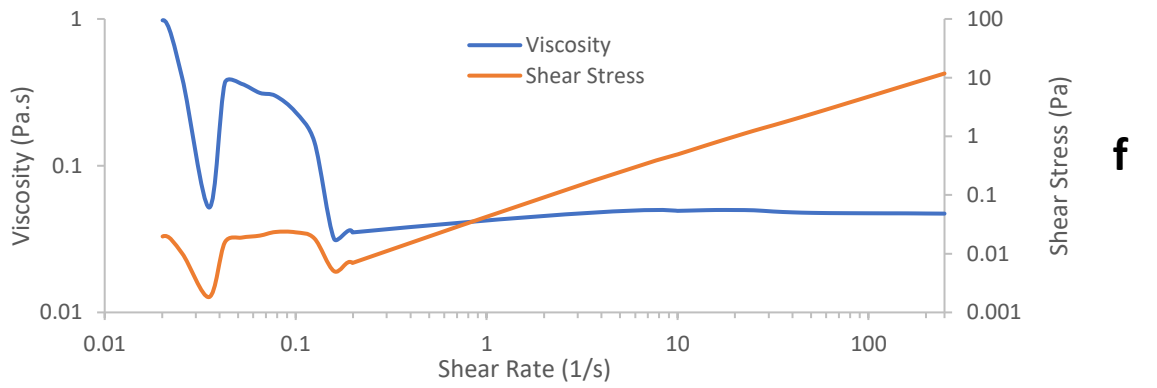
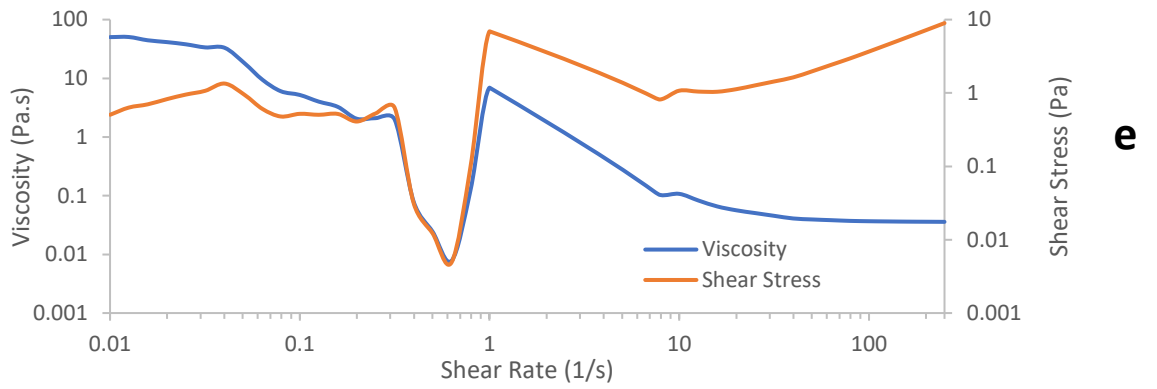
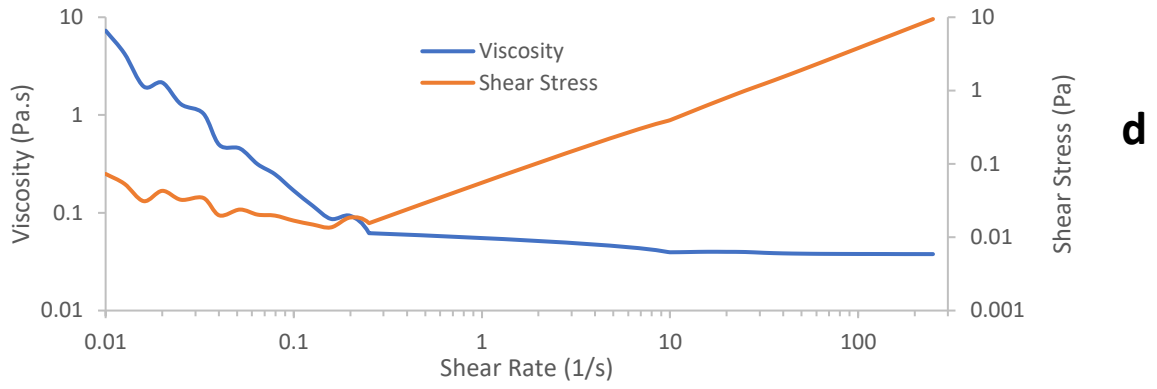
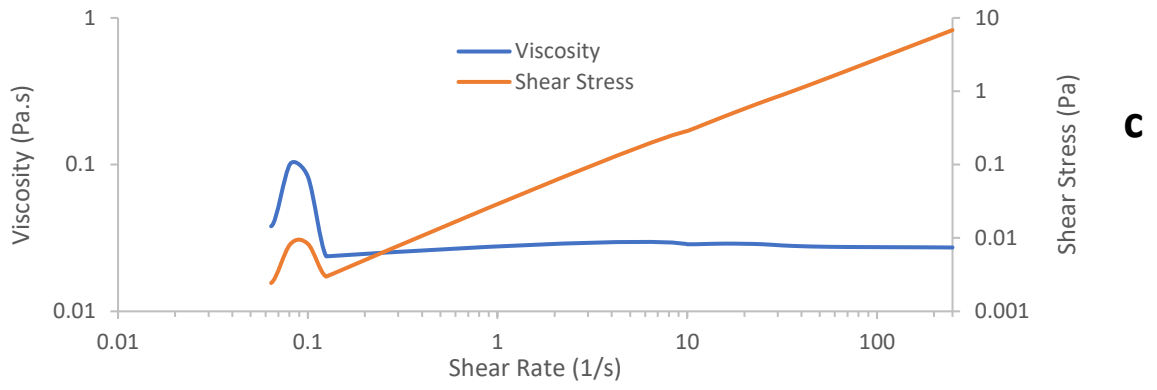
**Figure S3:** The triplicate TGA traces for samples **(a)** tetrabutylammonium phenyltrifluoroborate, **(b)** tetrabutylammonium 4-fluorophenyltrifluoroborate, **(c)** tetrabutylammonium 3-fluorophenyltrifluoroborate, **(d)** tetrabutylammonium 4-chlorophenyltrifluoroborate, **(e)** tetrabutylammonium 3-chlorophenyltrifluoroborate, **(f)** tetrabutylammonium 4-bromophenyltrifluoroborate, **(g)** tetrabutylammonium 3-bromophenyltrifluoroborate, **(h)** tetrabutylammonium 4-iodophenyltrifluoroborate, **(i)** tetrabutylammonium 3-iodophenyltrifluoroborate, **(j)** tetrabutylammonium 4-methoxyphenyltrifluoroborate, **(k)** tetrabutylammonium 3-methoxyphenyltrifluoroborate, **(l)** tetrabutylammonium 4-n-butylphenyltrifluoroborate, **(m)** tetrabutylammonium 1,4-phenylenebistrifluoroborate, **(n)** tetrabutylammonium 1,3-phenylenebistrifluoroborate, **(o)** tetrabutylammonium 9,9-dimethyl-9H-fluoren-2,7-diyl-2,7-ditrifluoroborate, **(p)** potassium 4-methoxyphenyltrifluoroborate. (duplicate TGA traces).

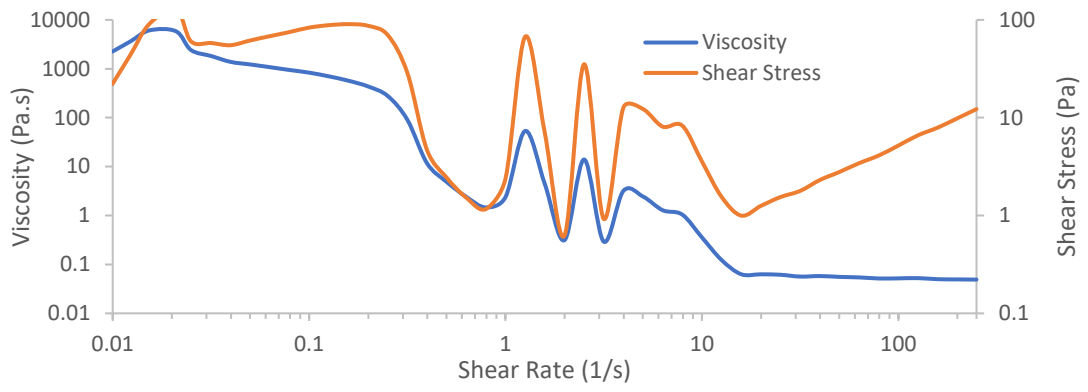


**a**

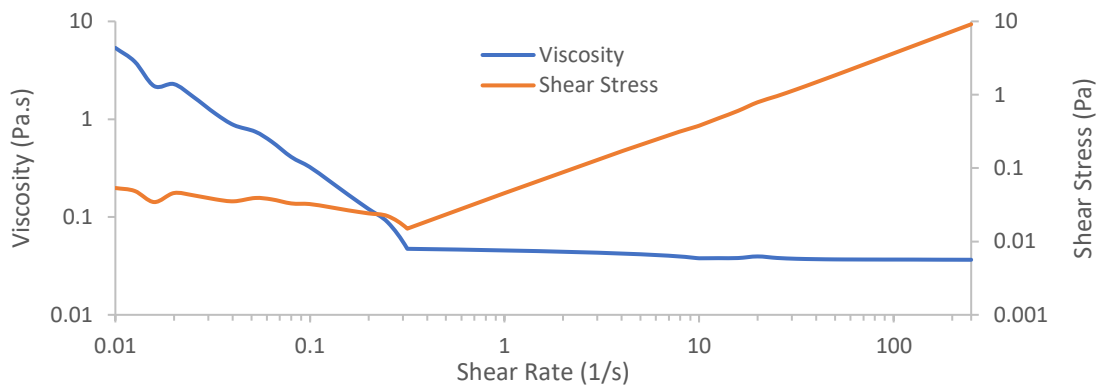


**b**

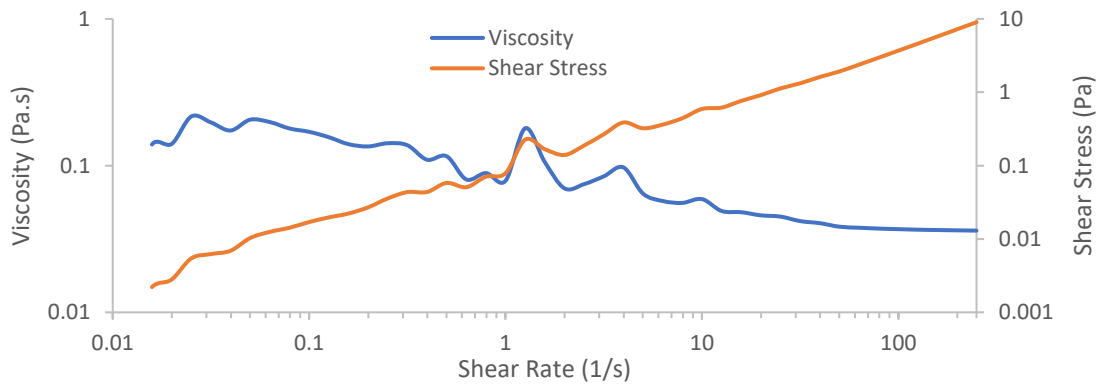




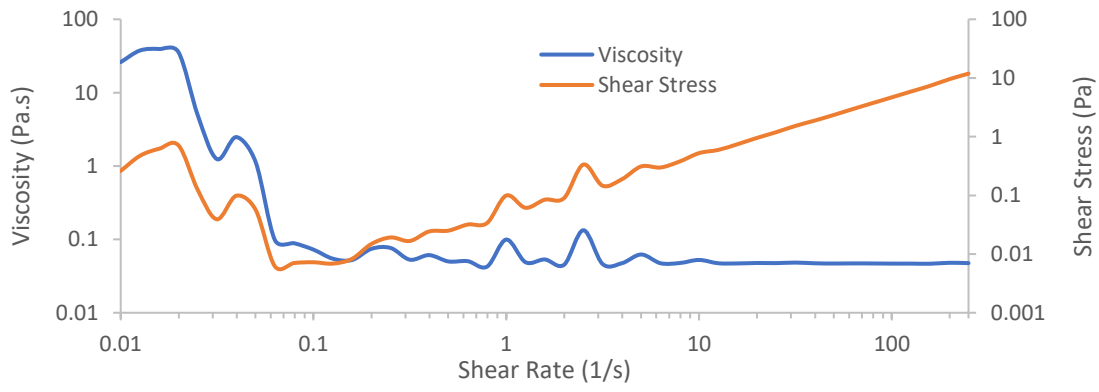
**g**



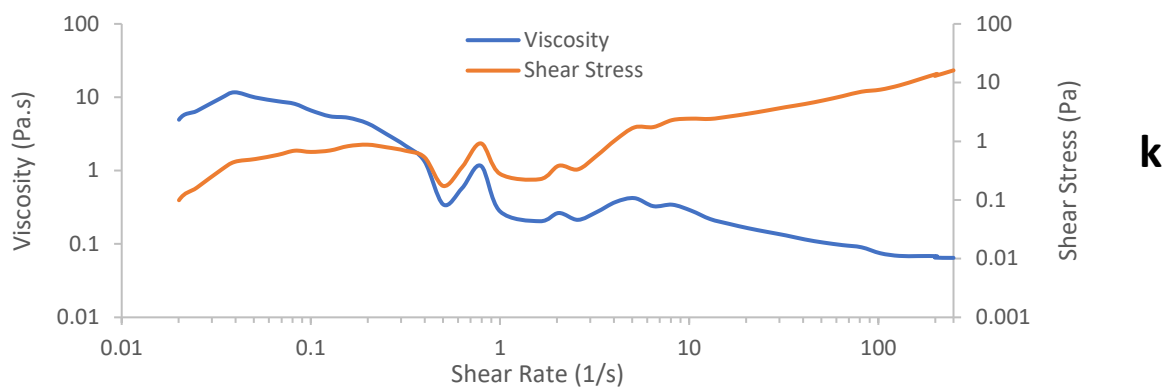
**h**



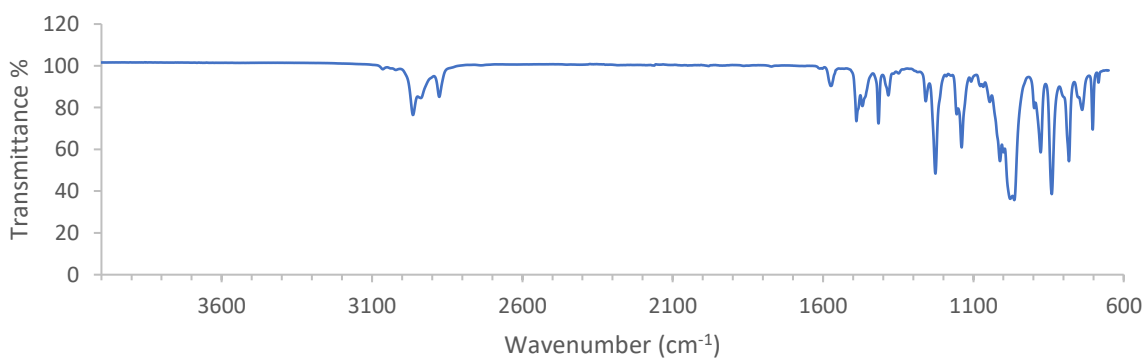
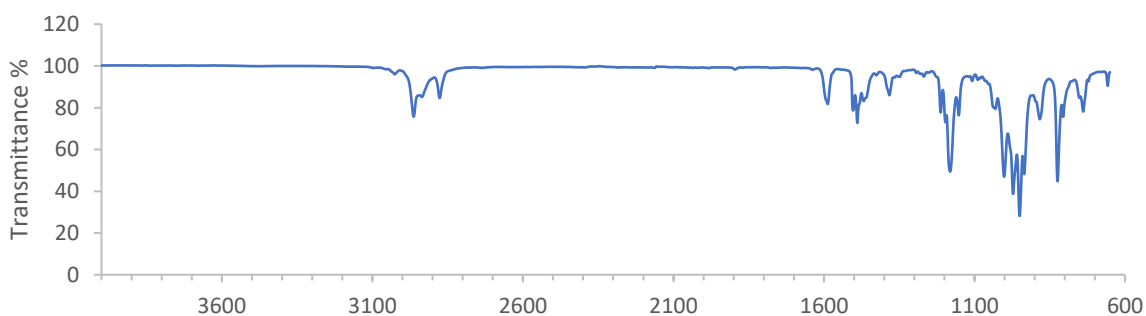
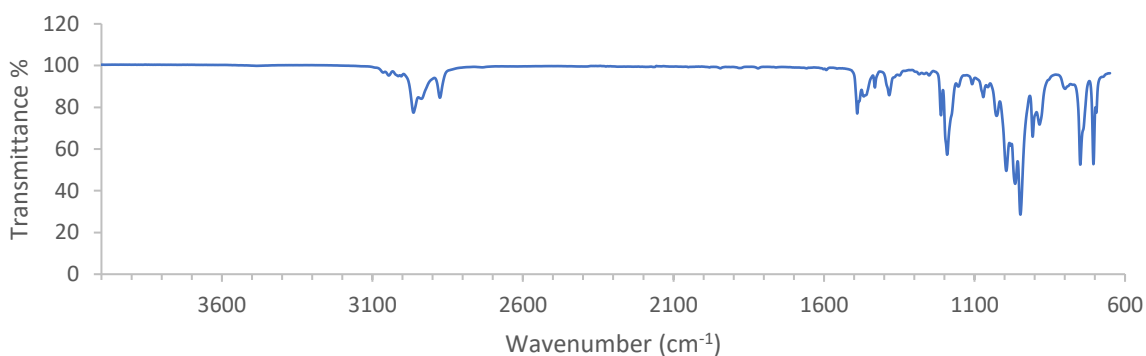
**i**

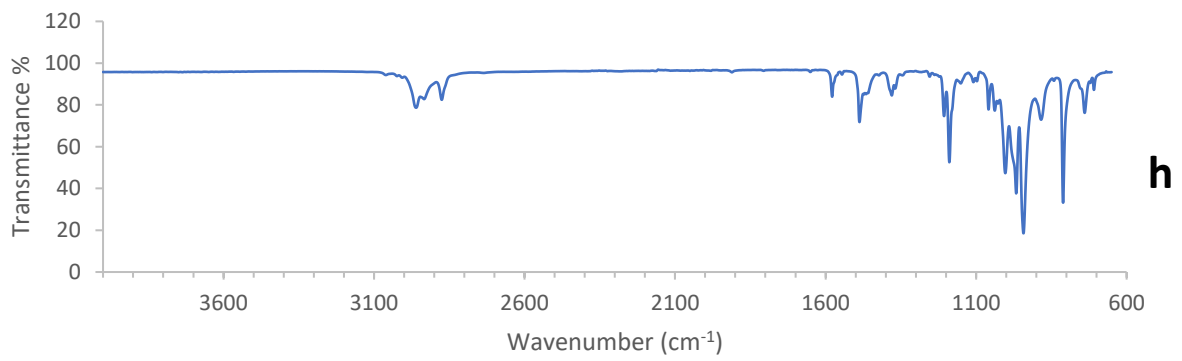
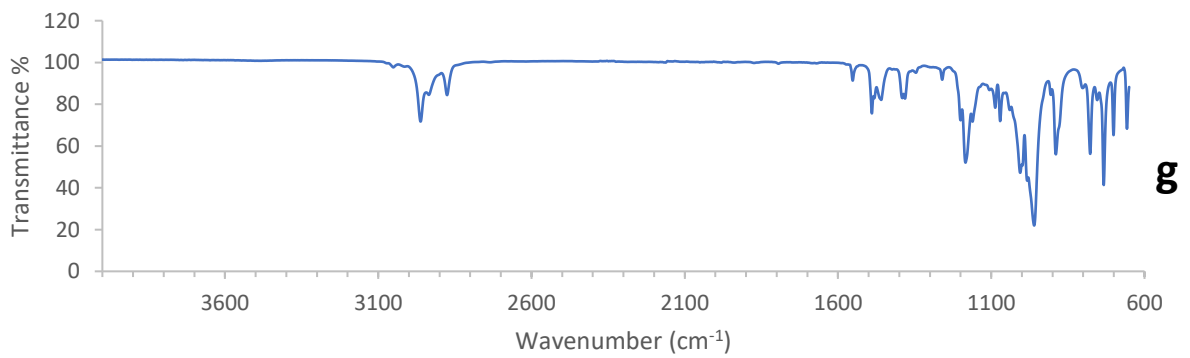
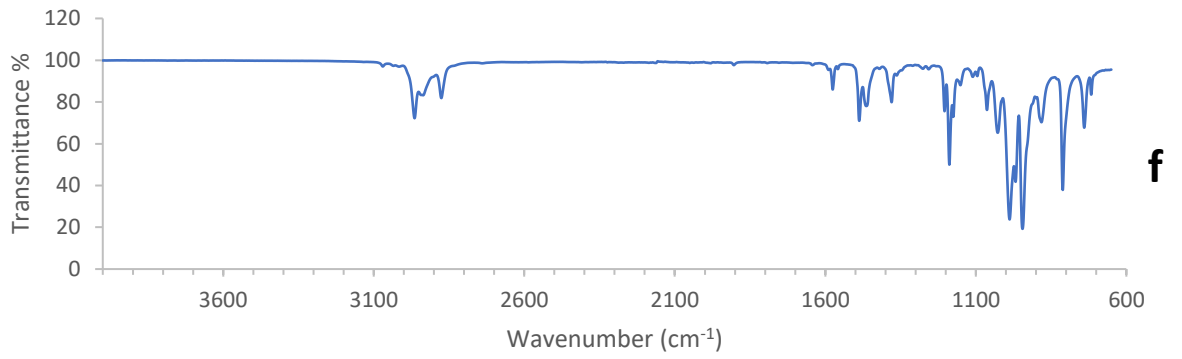
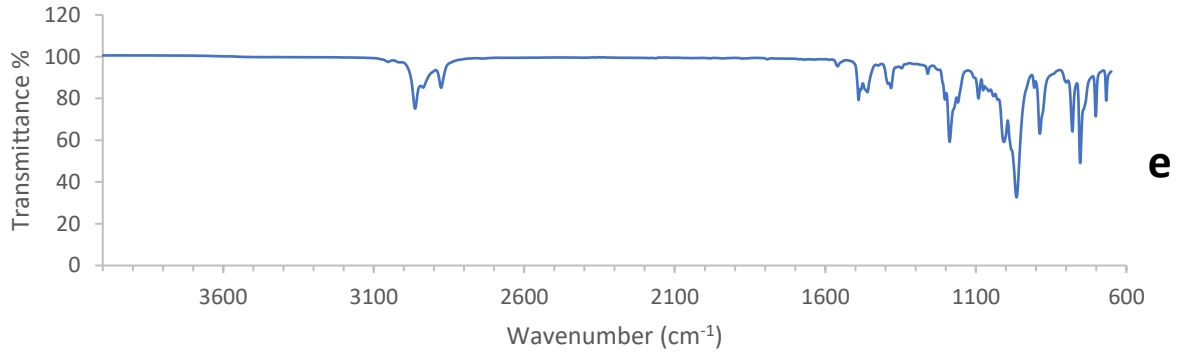
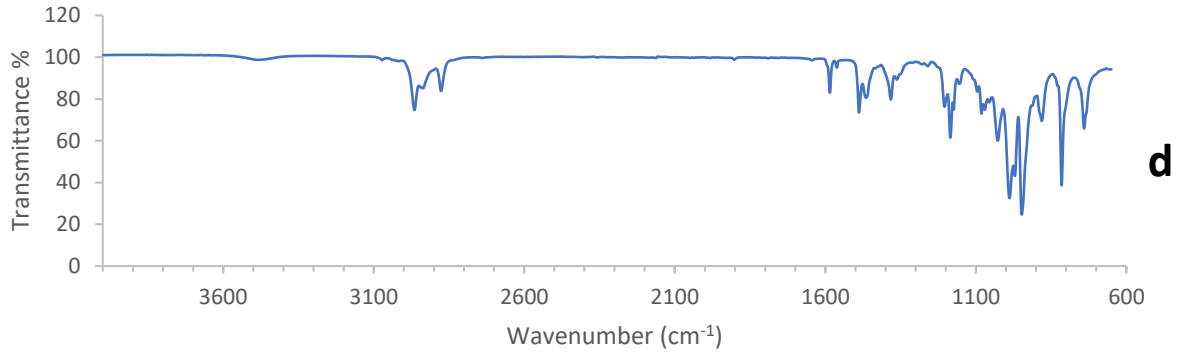


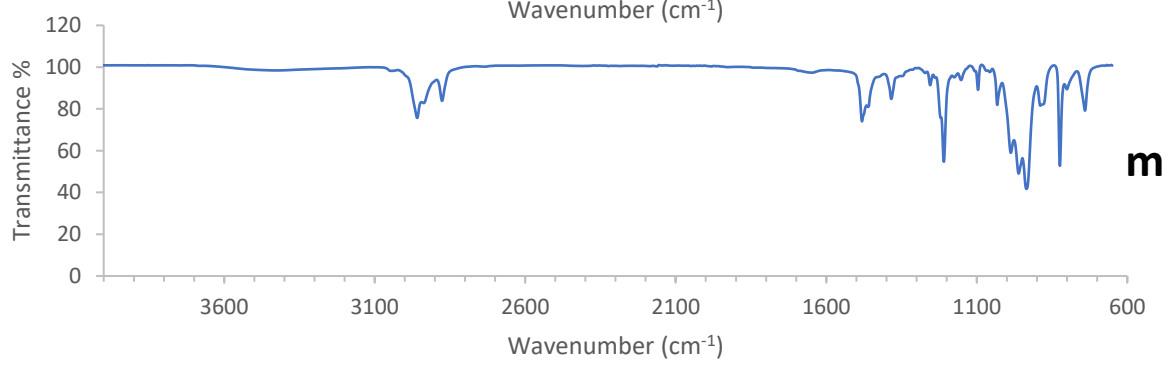
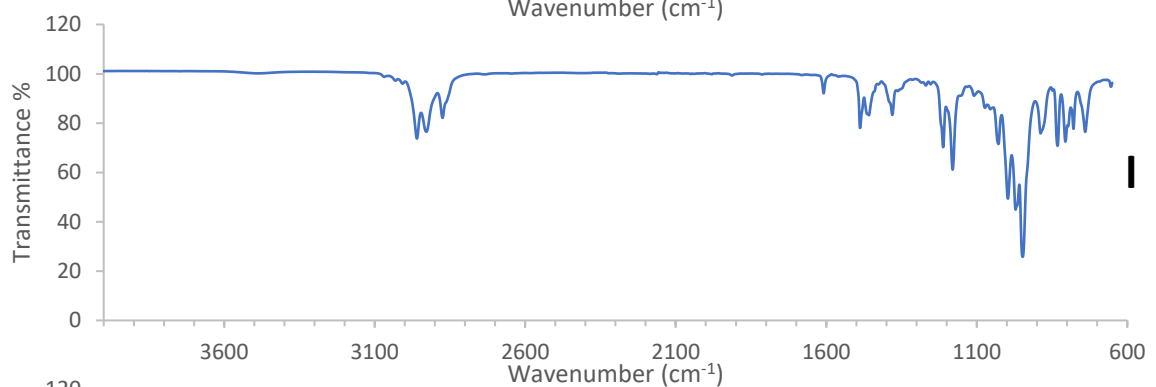
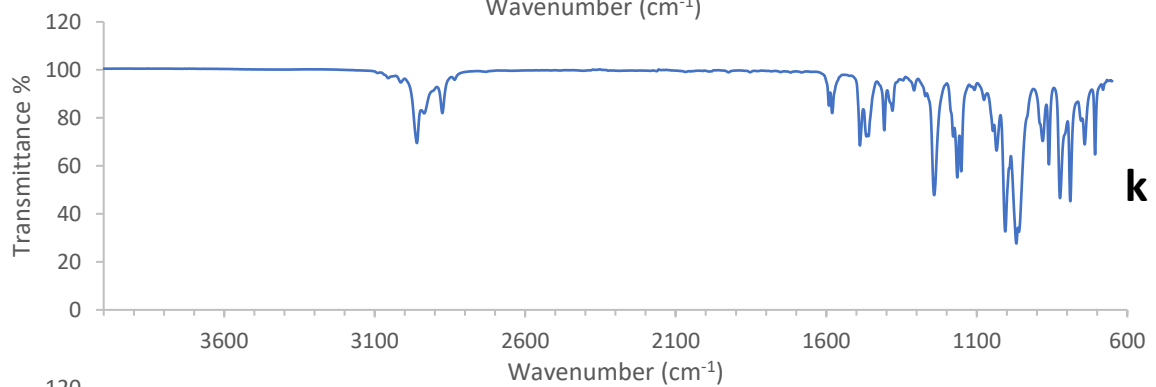
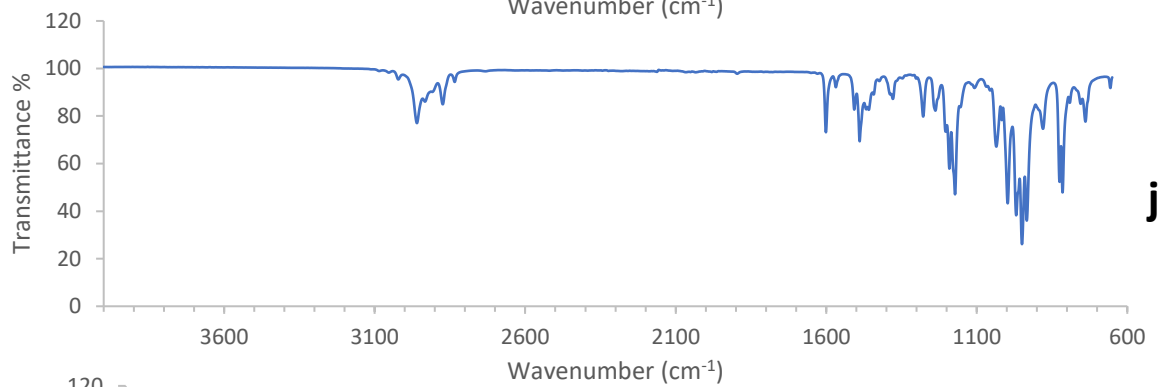
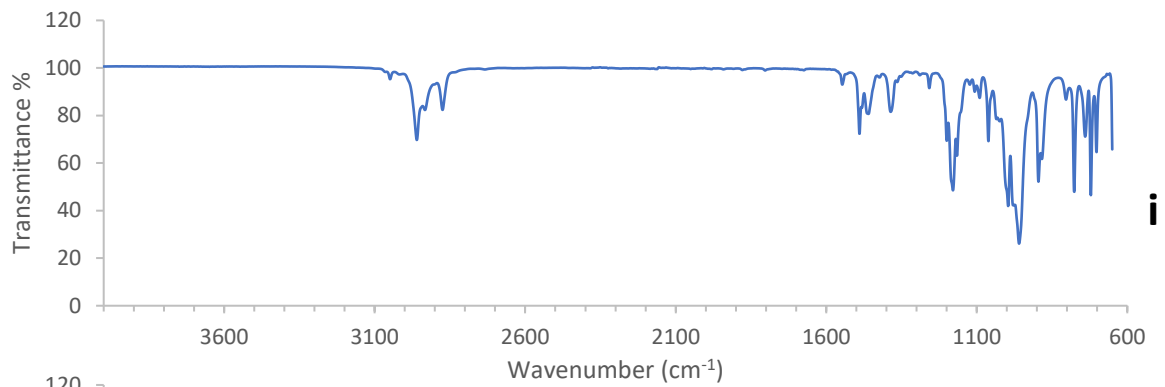
**j**

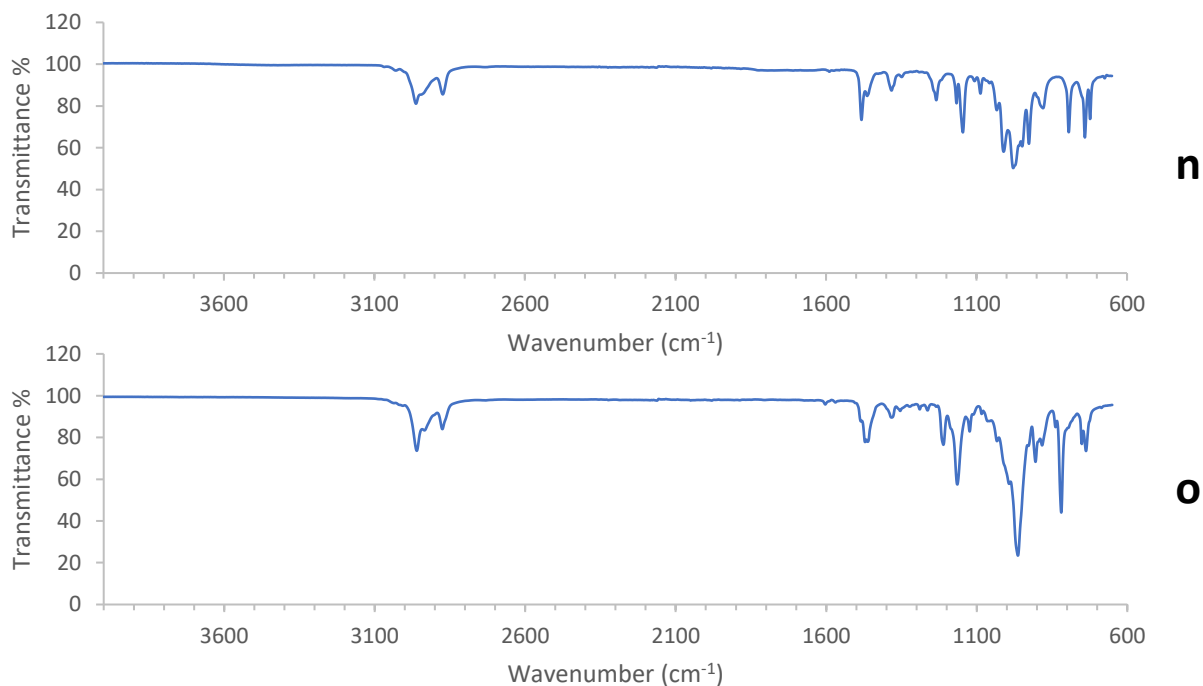


**Figure S4:** The averaged duplicate viscosity and shear stress traces for samples at 100°C, **(a)** tetrabutylammonium phenyltrifluoroborate, **(b)** tetrabutylammonium 4-fluorophenyltrifluoroborate, **(c)** tetrabutylammonium 3-fluorophenyltrifluoroborate, **(d)** tetrabutylammonium 4-chlorophenyltrifluoroborate, **(e)** tetrabutylammonium 3-chlorophenyltrifluoroborate, **(f)** tetrabutylammonium 4-bromophenyltrifluoroborate (single trace), **(g)** tetrabutylammonium 3-bromophenyltrifluoroborate, **(h)** tetrabutylammonium 3-iodophenyltrifluoroborate, **(i)** tetrabutylammonium 4-methoxyphenyltrifluoroborate (at 105°C), **(j)** tetrabutylammonium 3-methoxyphenyltrifluoroborate, **(k)** tetrabutylammonium 4-n-butylphenyltrifluoroborate.

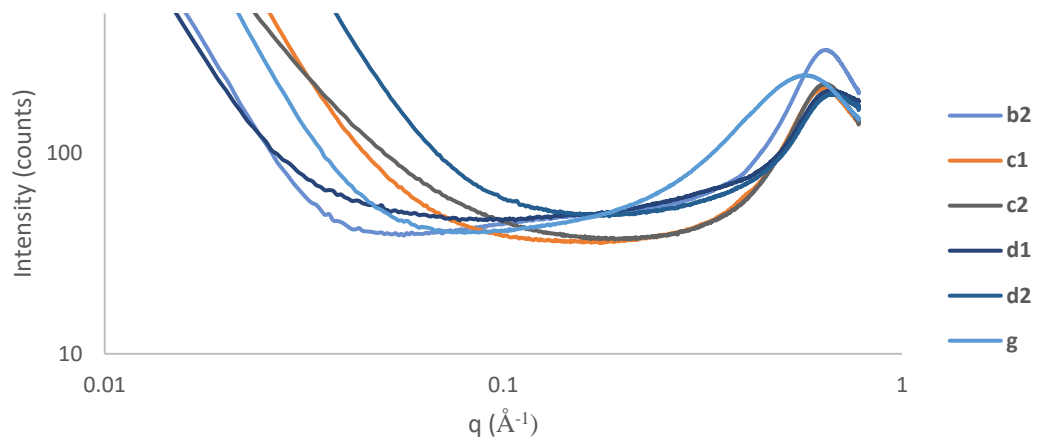








**Figure S5:** The FTIR spectra for samples (a) tetrabutylammonium phenyltrifluoroborate, (b) tetrabutylammonium 4-fluorophenyltrifluoroborate, (c) tetrabutylammonium 3-fluorophenyltrifluoroborate, (d) tetrabutylammonium 4-chlorophenyltrifluoroborate, (e) tetrabutylammonium 3-chlorophenyltrifluoroborate, (f) tetrabutylammonium 4-bromophenyltrifluoroborate, (g) tetrabutylammonium 3-bromophenyltrifluoroborate, (h) tetrabutylammonium 4-iodophenyltrifluoroborate, (i) tetrabutylammonium 3-iodophenyltrifluoroborate, (j) tetrabutylammonium 4-methoxyphenyltrifluoroborate, (k) tetrabutylammonium 3-methoxyphenyltrifluoroborate, (l) tetrabutylammonium 4-n-butylphenyltrifluoroborate, (m) tetrabutylammonium 1,4-phenylenebistrifluoroborate, (n) tetrabutylammonium 1,3-phenylenebistrifluoroborate, (o) tetrabutylammonium 9,9-dimethyl-9H-fluoren-2,7-diyl-2,7-ditrifluoroborate.



**Figure S6:** The SAXS spectra of samples **(b2)** tetrabutylammonium 3-fluorophenyltrifluoroborate, **(c1)** tetrabutylammonium 4-chlorophenyltrifluoroborate, **(c2)** tetrabutylammonium 3-chlorophenyltrifluoroborate, **(d1)** tetrabutylammonium 4-bromophenyltrifluoroborate, **(d2)** tetrabutylammonium 3-bromophenyltrifluoroborate, **(g)** tetrabutylammonium 4-n-butylphenyltrifluoroborate.