Electronic Supplementary Material (ESI) for Chemical Communications.


# Supporting Information

**Efficient continuous synthesis of high purity deep eutectic solvents by twin screw extrusion**

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## 1. Experimental Details

All materials were purchased from Sigma Aldrich UK with >98% purity and were used as received, unless indicated. Ball mill experiments were carried out using a Retsch MM400 mixer mill or a Retsch PM100 planetary ball mill. Extrusion was carried out using a Three-Tec 12 mm, 40:1 L:D co-rotating twin screw extruder with six heating zones. NMR analysis was carried out with a Brüker Advance DPX 300 with $CH_3OD$-TMS as solvent. Digital Scanning Calorimetry (DSC) was carried out with a Flash DSC 1 Mettler Toledo instrument and data were analysed with STAR$^e$SW 9.10 software. A heating rate of $20^0$C was employed in an atmosphere of air. DSC experiments were carried out in a sealed aluminium pan. Refractive Index experiments were carried out with a Bellingham and Stanley Refractometer, RFM732.

Pre-mixing of choline chloride and urea was carried out using a planetary ball mill. Choline chloride (41.89 g, 0.3 mol) and urea (36.07 g, 0.6 mol) were rotated in a 250 mL stainless steel jar at 400 rpm for 8 minutes in the absence of grinding balls to give a homogeneous powder.

Mixer mill experiments: Choline chloride (0.28 g, 2 mmol), urea (0.24 g, 4 mmol) and a grinding ball (13.6 g) were added to a 25 $cm^3$ stainless steel jar which was shaken at 30 Hz for 30 minutes to produce a colourless liquid.

Planetary ball mill experiments: Choline chloride (41.89 g, 0.3 mol), urea (36.07 g, 0.6 mol) and 25 4.0 g grinding balls were added to a 250 $cm^3$ stainless steel jar which was rotated at 400 rpm for 2 hours to produce a colourless liquid.

Extrusion experiments: were carried out by pre-mixing choline chloride (27.92 g, 0.2 mol) and either urea (24.02 g, 0.4 mol), zinc(II) chloride (54.67 g, 0.4 mol) or D-fructose (23.42 g, 0.13 mol), either by hand for *ca.* 30 seconds or by using a planetary ball mill as described above. The six heating zones of the barrel were all pre-heated to the required temperature and the screws rotated at the required speed (Table 1). Optionally a 2 mm die was attached to the exit of the extruder. The reagents were fed manually into the extruder over 8-9 minutes. After several minutes, a colourless viscous liquid was extruded and collected.

## 2. Characterisation of Reline 200

Reline 200 (entries 8,9, and 10 in Table 1 of the manuscript) was analysed by $^{1}$H NMR spectroscopy, Differential Scanning Calorimetry and the refractive index was determined.

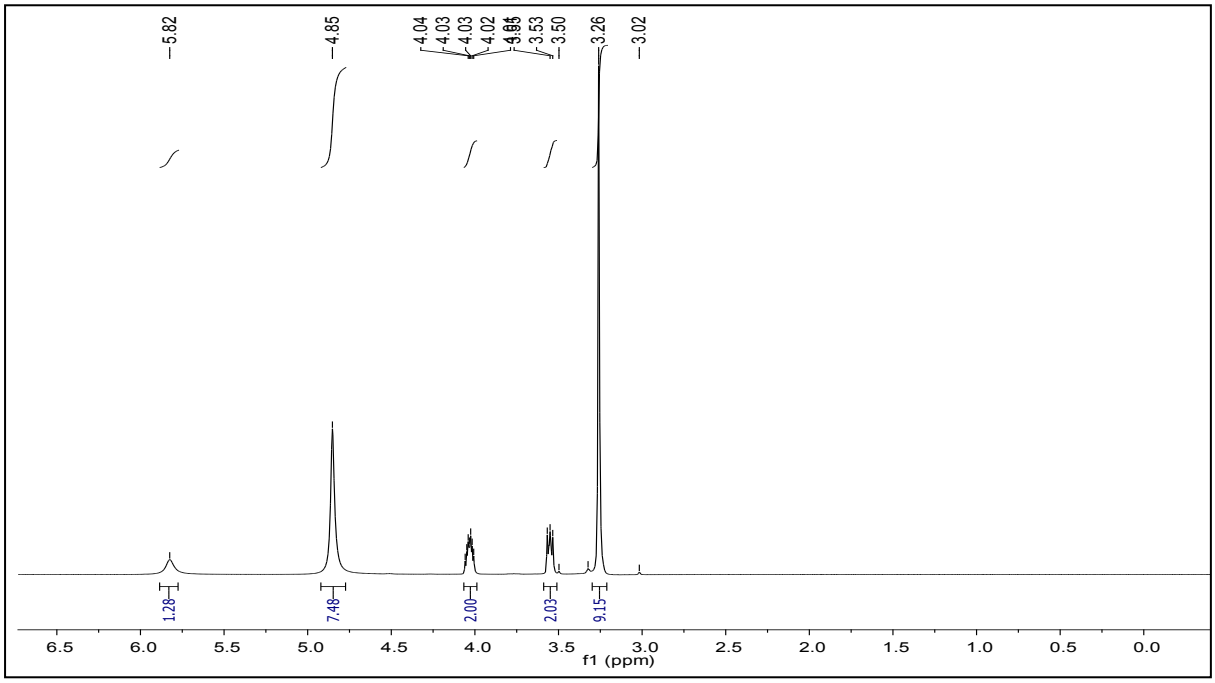


**Figure S1.** $^{1}$H NMR spectrum of Reline 200 ($CH_3OD$) prepared by conventional heating.

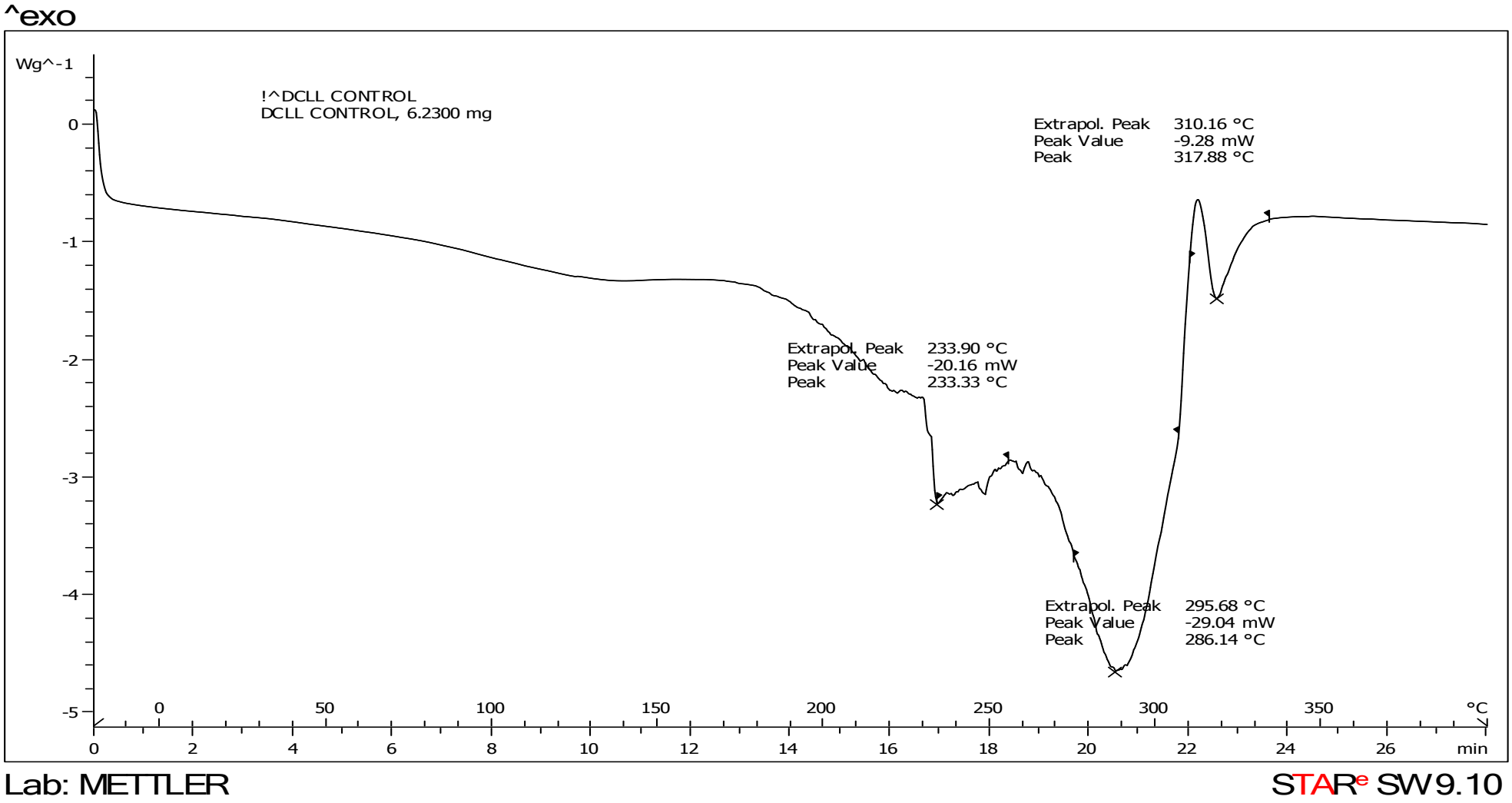


**Figure S2.** DSC scan of Reline 200 prepared by conventional heating.

**Reline 200 - Entry 8 from Table 1 in main text**

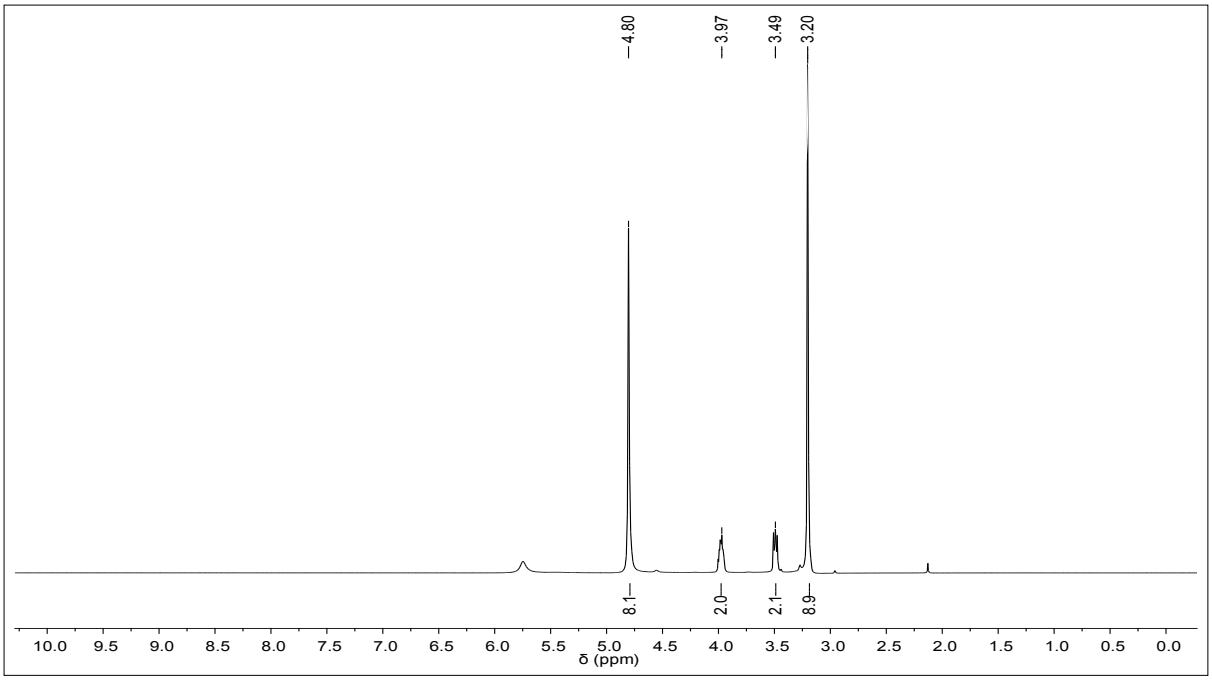


**Figure S3.** $^{1}H$ NMR spectrum of Reline 200 ($CH_3OD$).

Refractive Index: 1.502 at 17 °C.

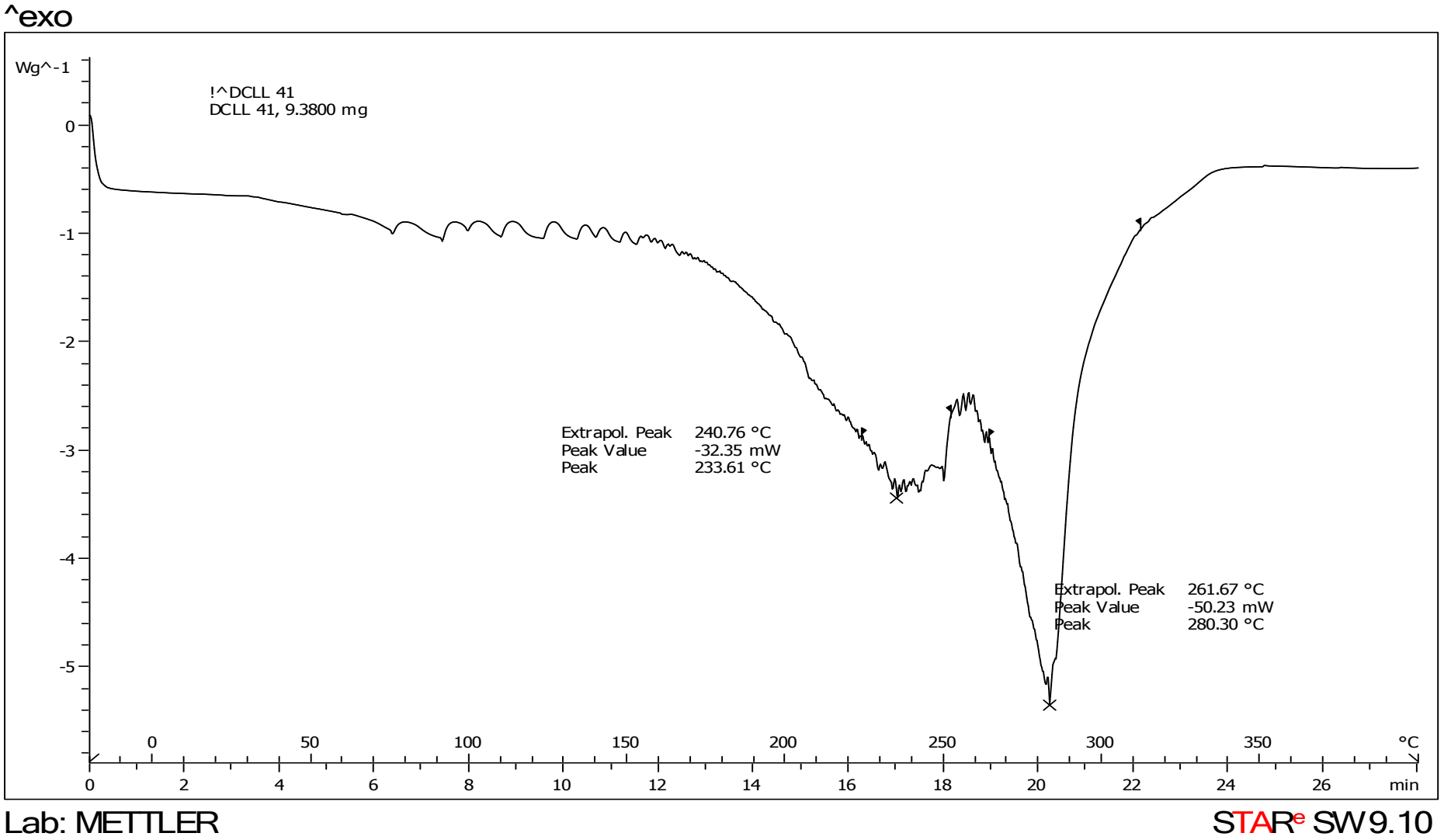


**Figure S4.** DSC scan of Reline 200. Oscillations between 60°C and 150°C are artefacts associated with incidental vibration.

**Reline 200 - Entry 9 from Table 1 in main text**

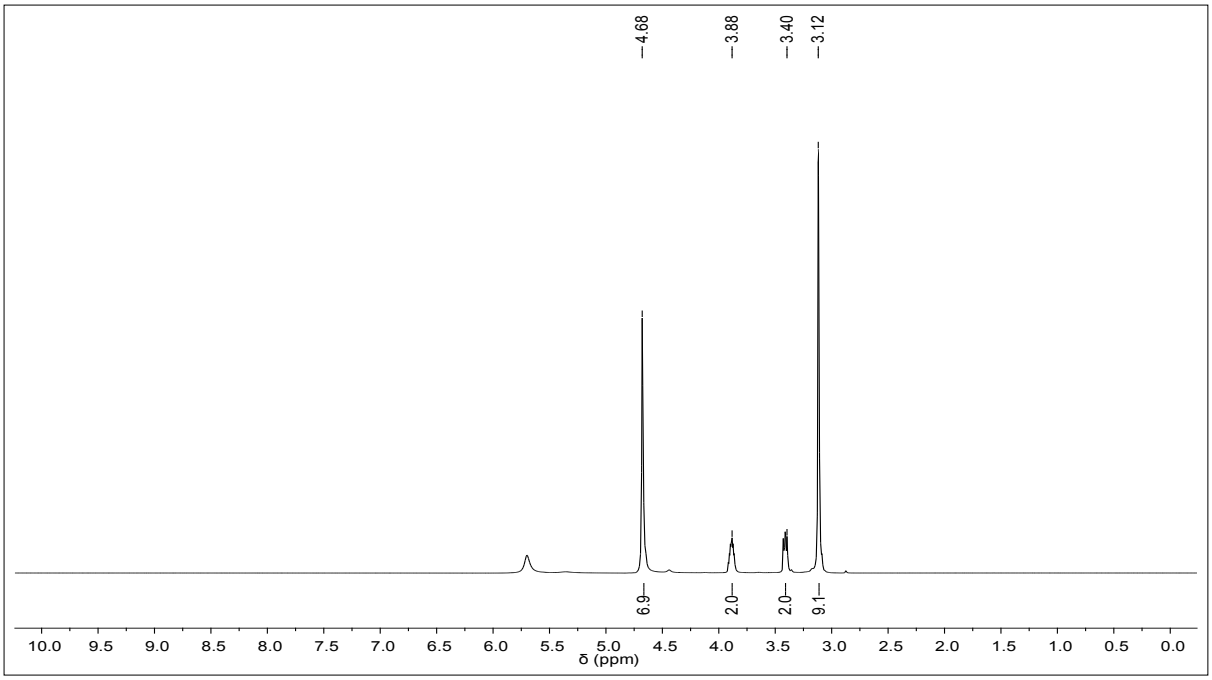


**Figure S5.** $^{1}H$ NMR spectrum of Reline 200 ($CH_3OD$).

Refractive Index: 1.504 at 17 °C.

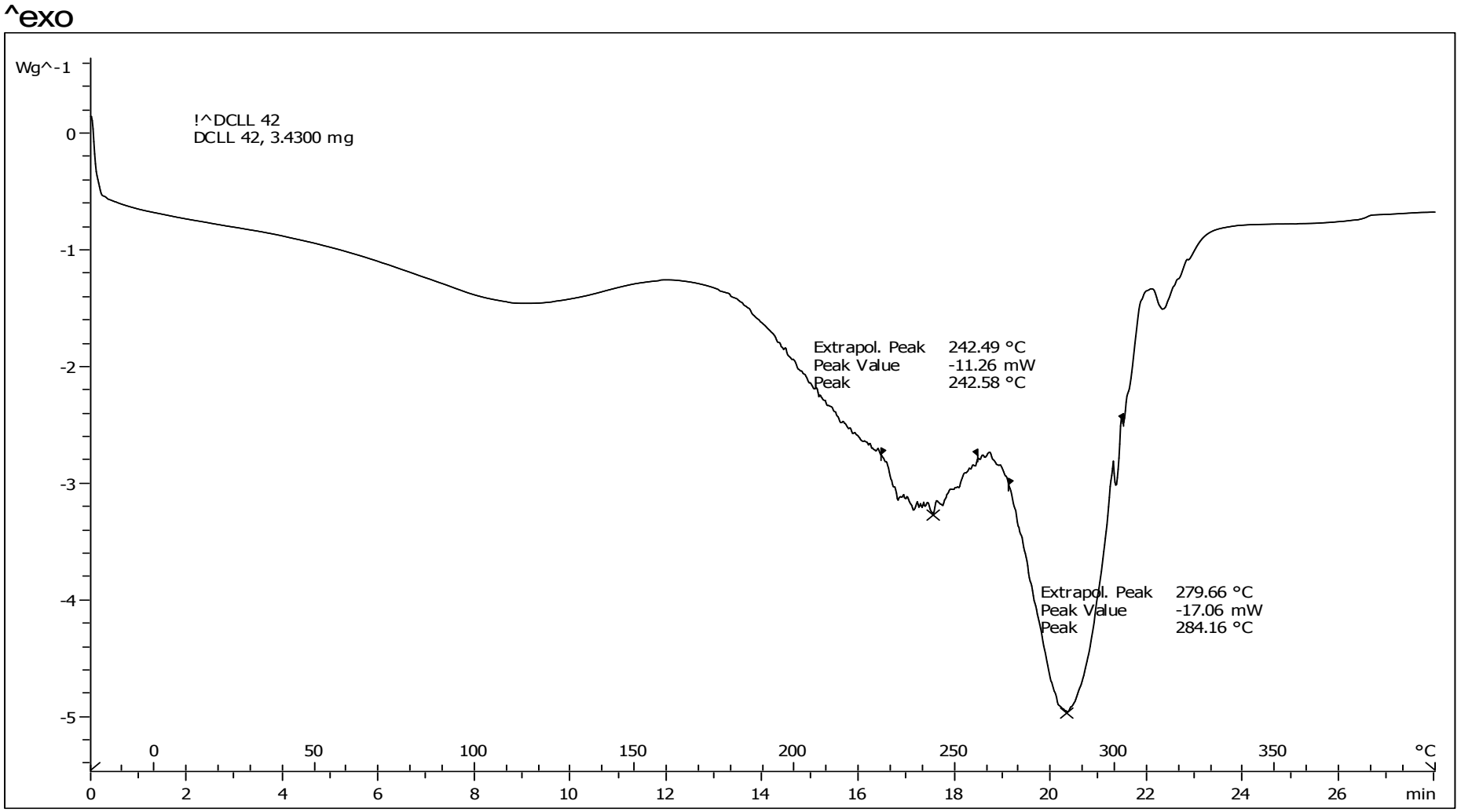


**Figure S6.** DSC scan of Reline 200.

**Reline 200 - Entry 10 from Table 1 in main text**

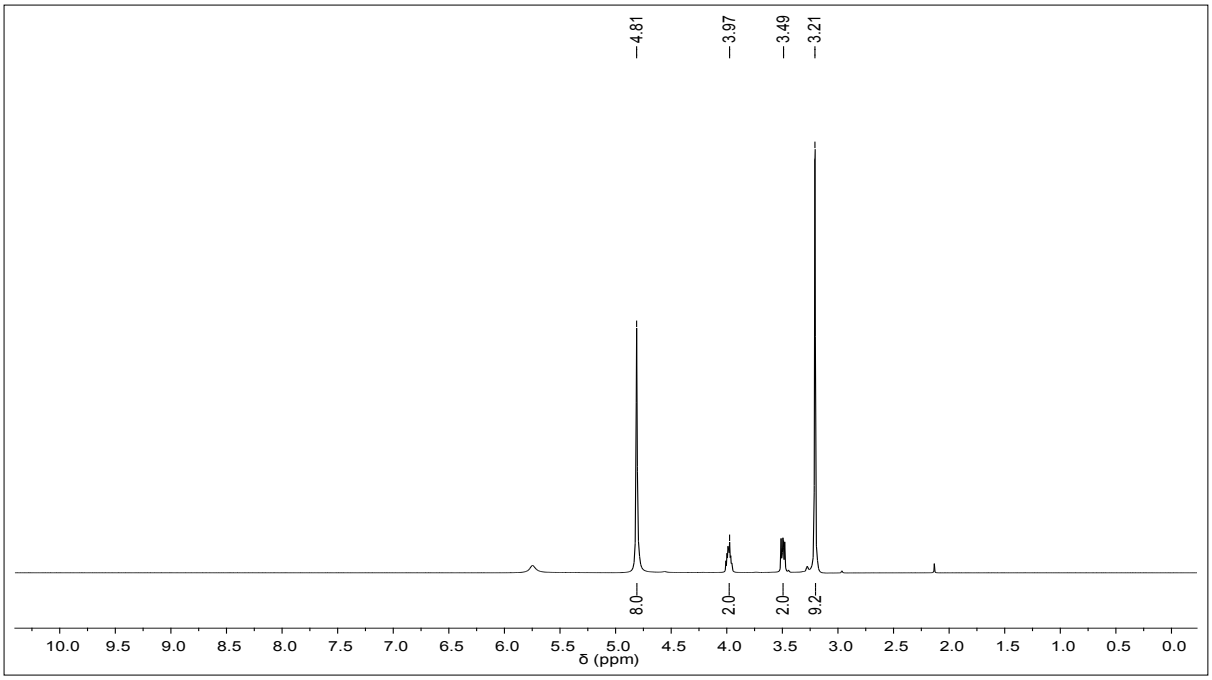


**Figure S7.** $^{1}H$ NMR spectrum of Reline 200 ($CH_3OD$).

Refractive Index: 1.505 at 17 °C.

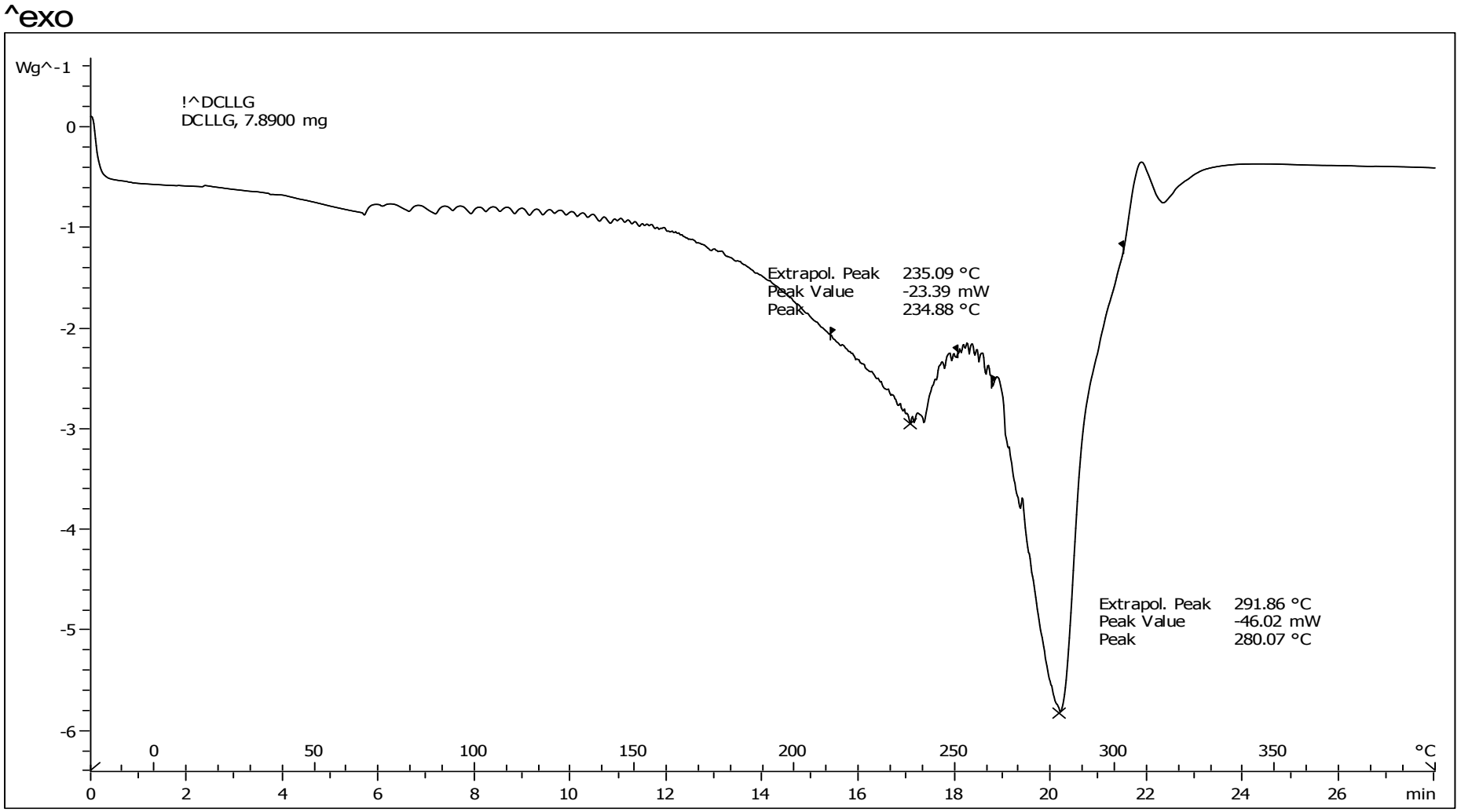


**Figure S8.** DSC scan of Reline 200 (entry 10).

## 3. Characterisation of choline chloride: D-fructose

Choline chloride: D-fructose was analysed by $^{1}$H NMR spectroscopy, UV-visible spectroscopy and Differential Scanning Calorimetry and the refractive index was determined.

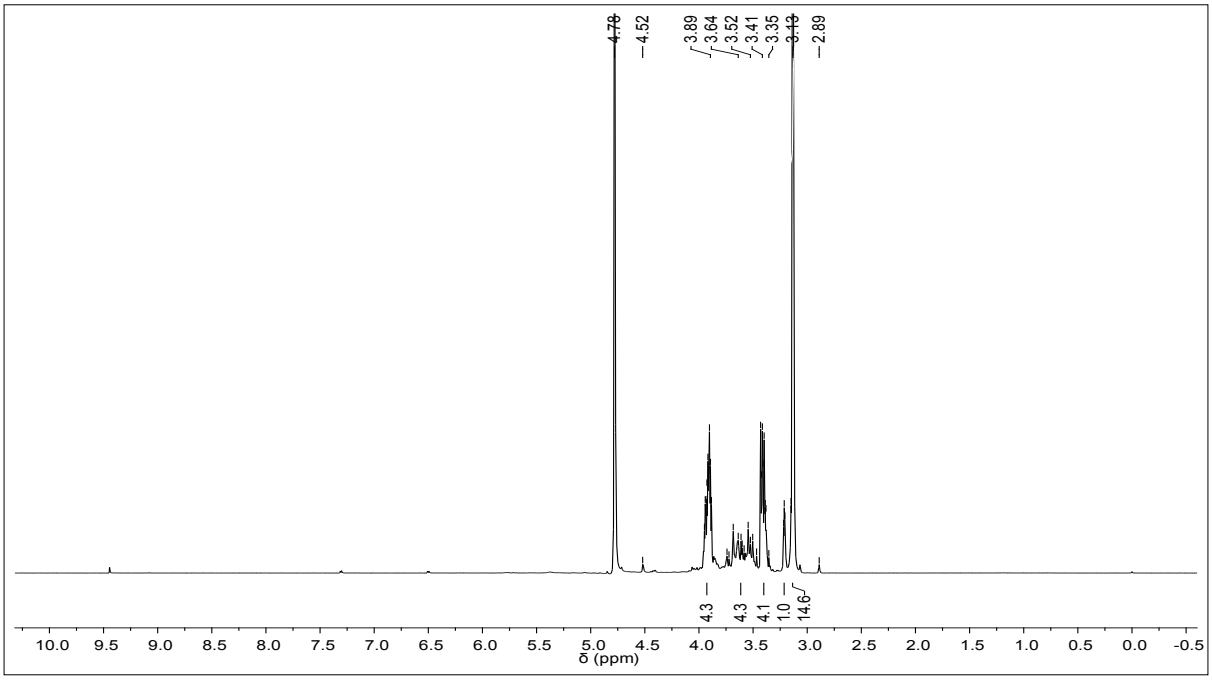


**Figure S9.** $^{1}$H NMR spectrum of choline chloride:D-fructose 200 ($CH_3OD$) prepared by conventional heating.

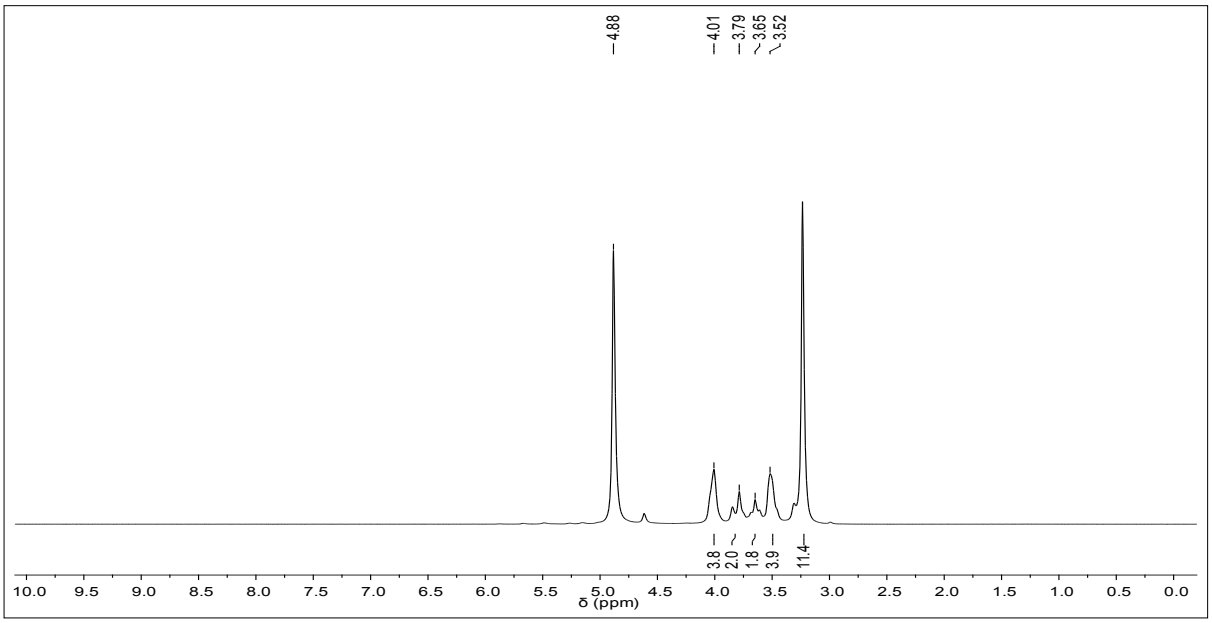


**Figure S10.** $^{1}$H NMR spectrum of choline chloride:D-fructose 200 ($CH_3OD$) prepared by TSE.

Refractive Index: 1.51250 at 22.5 °C.

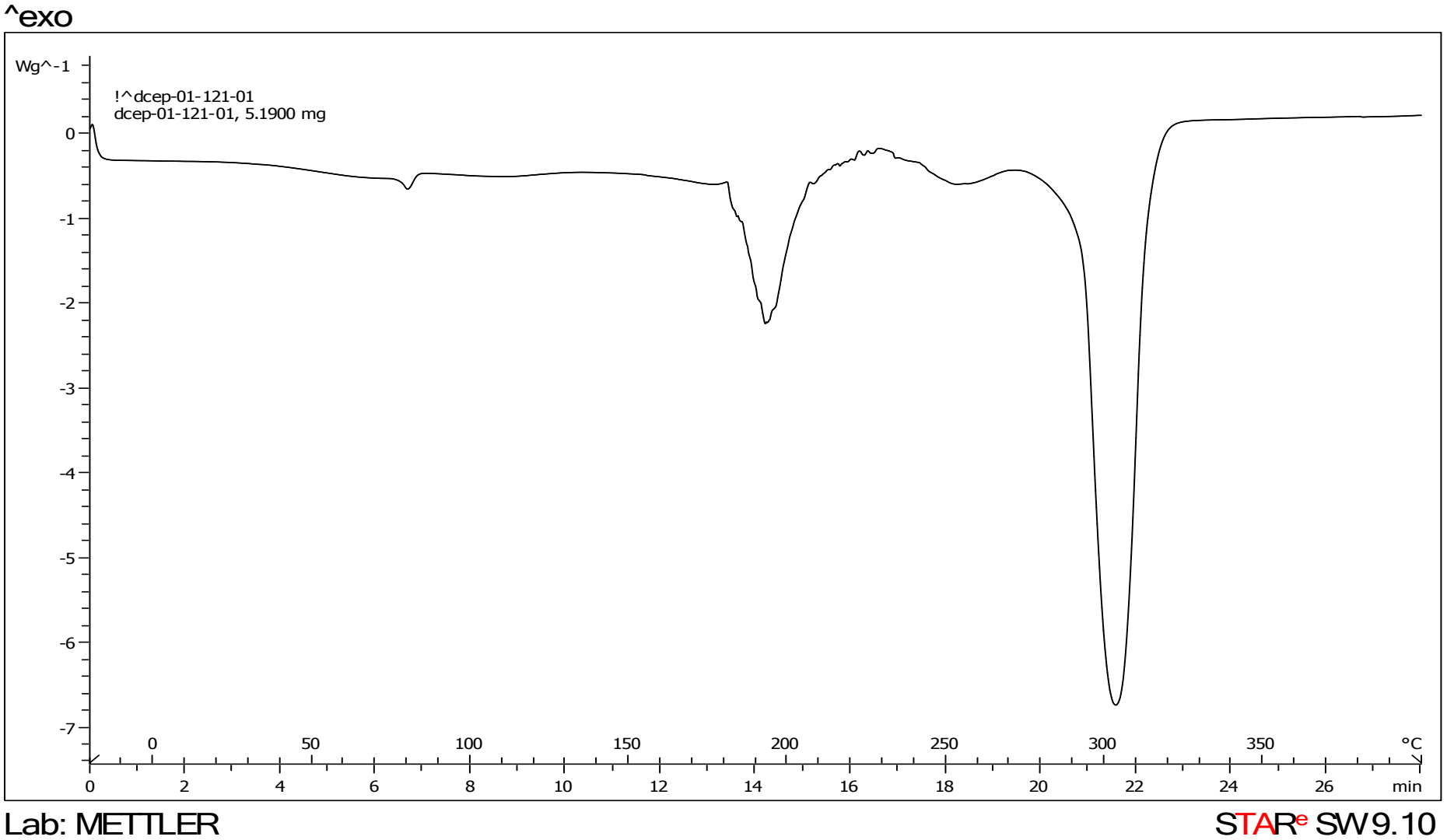


**Figure S11.** DSC scan of DES choline chloride: D-fructose.

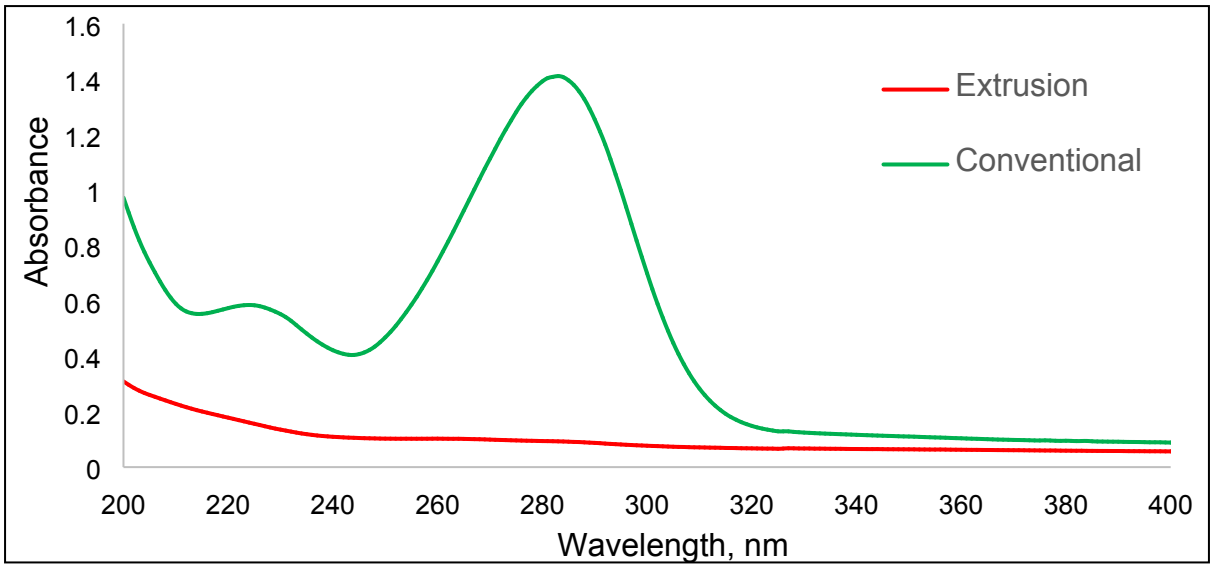


**Figure S12.** UV-Vis spectra of DES choline chloride: D-fructose made by TSE (red) and conventional heating (green).

Conventional heating: molar extinction coefficient: 3513.17 $dm^3mol^{-1}cm^{-1}$ at 283 nm.

Extrusion: molar extinction coefficient: 256.74 $dm^3mol^{-1}cm^{-1}$ at 280 nm.

## 4. Characterisation of choline chloride: zinc chloride

The product was analysed by $^1$H NMR spectroscopy, Refractive Index Determination and Digital Scanning Calorimetry.

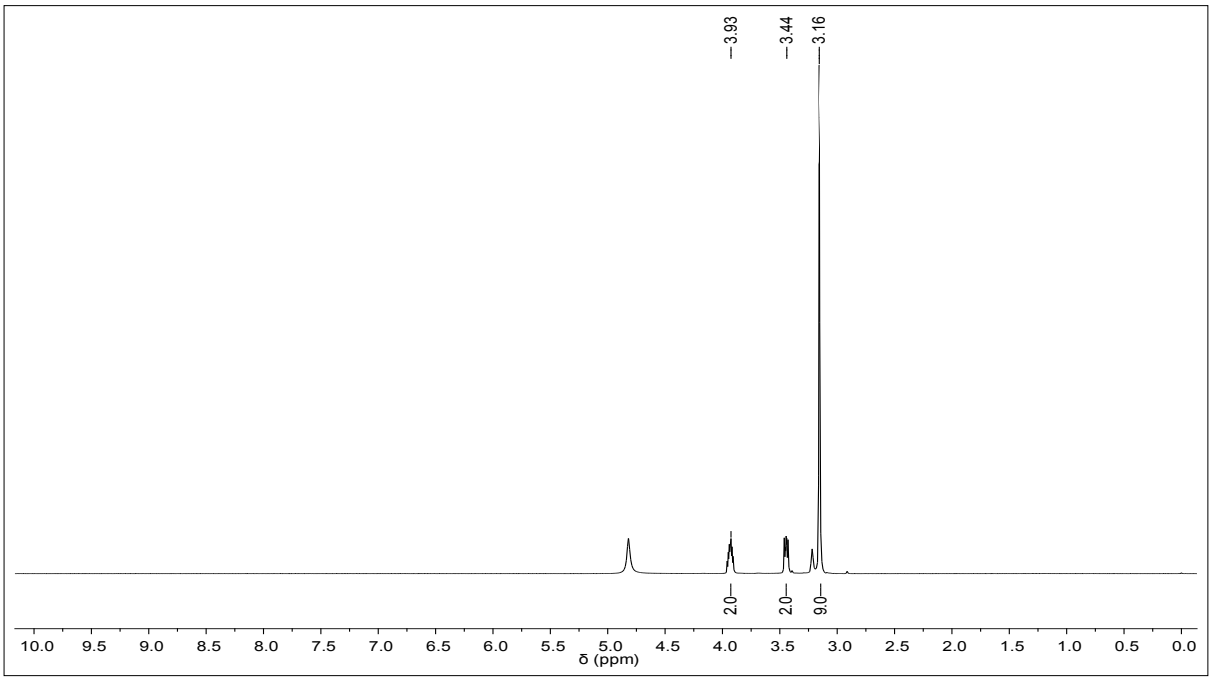


**Figure S13.** $^1$H NMR spectrum of choline chloride:zinc chloride ($CH_3OD$) prepared by heating.

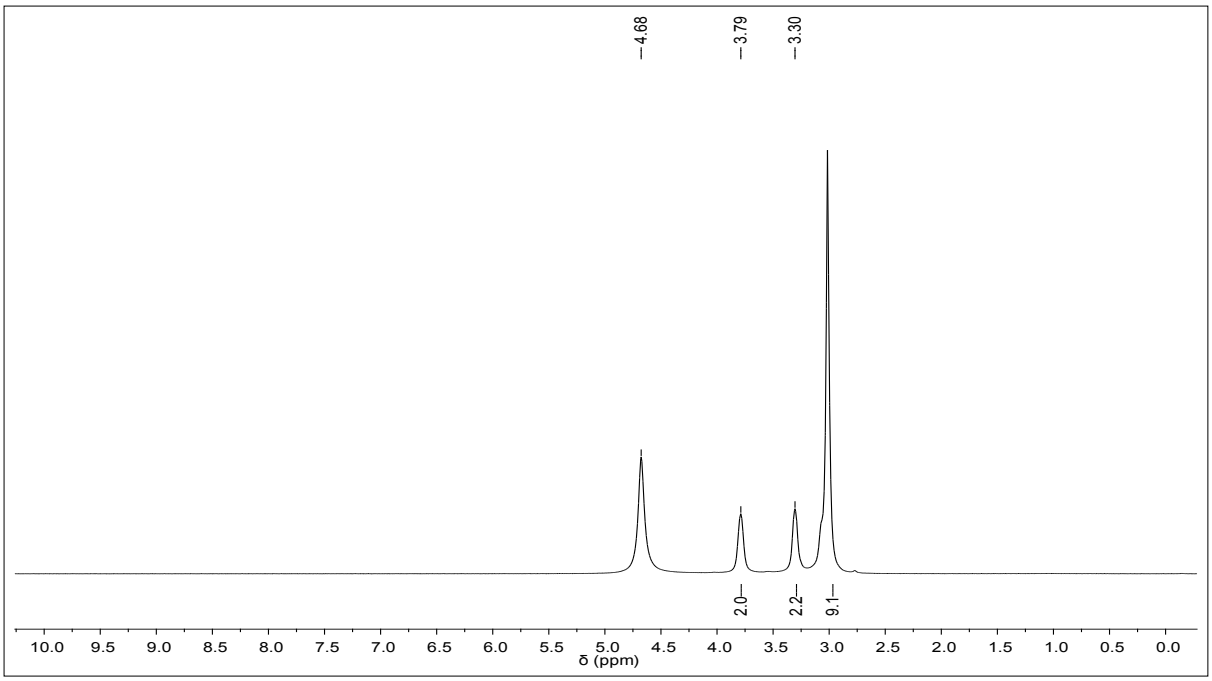


**Figure S14.** $^{1}$H NMR spectrum of choline chloride:zinc chloride ($CH_3OD$) prepared by TSE.

Refractive Index: 1.54450 at 23.8 °C.

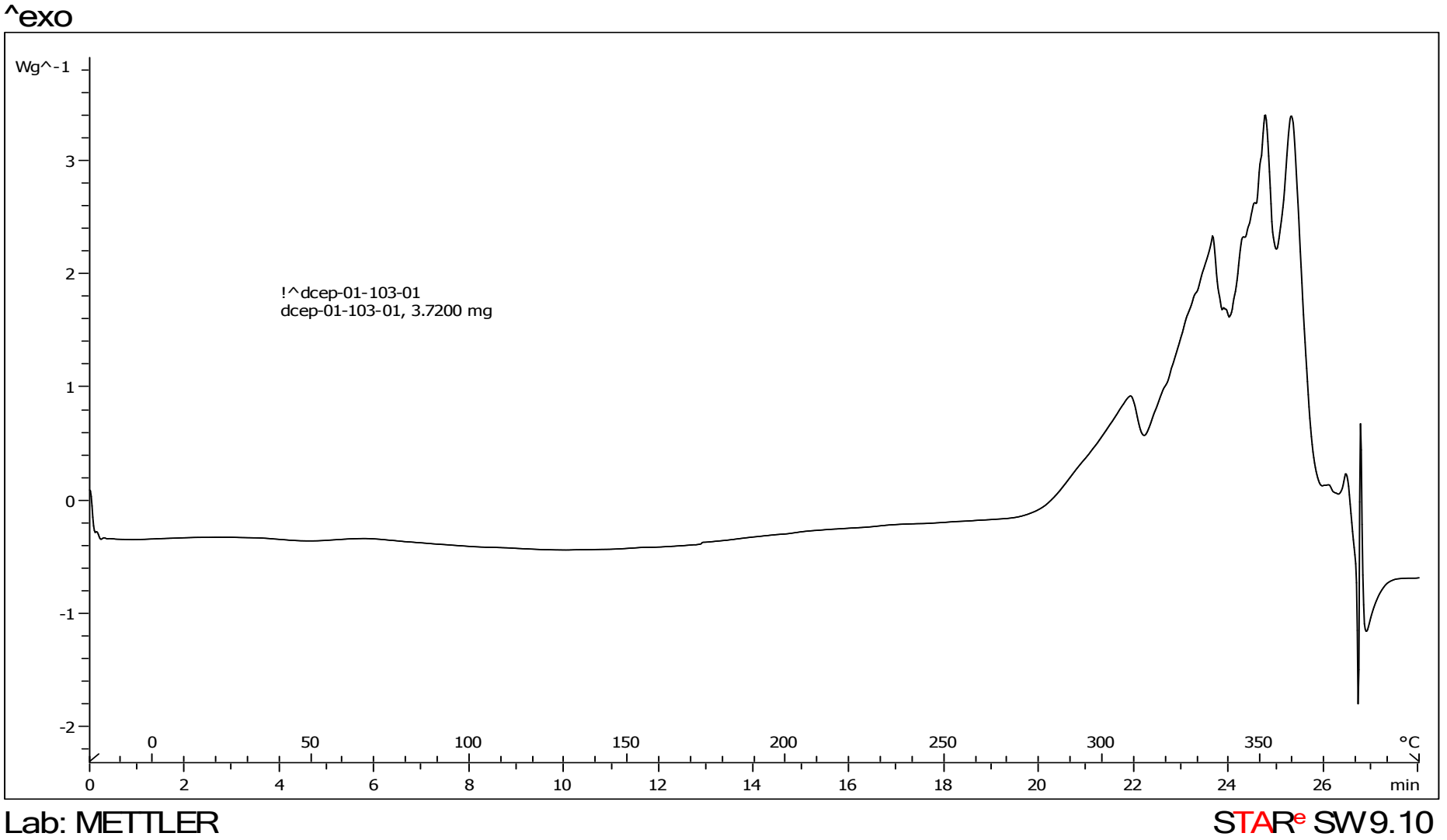


**Figure S15.** DSC scan of DES choline chloride: zinc chloride.