

Green synthesis of 5-hydroxymethylfurfural and 5-acetoxymetilfurfural using deep eutectic solvent in a biphasic system assisted for microwaves

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GENERAL TECHNIQUES

Analytical grade commercial solvents and reagents were purchased from Sigma-Aldrich, and used as received. Infrared spectra were recorded as neat using a FT-IR Varian 660 Fourier transform infrared spectrometer. Values are expressed in wavenumbers (cm^{-1}) and recorded in a range of 4000–400 cm^{-1} . NMR spectra were recorded at 25 °C in CDCl_3 and $\text{DMSO-}d_6$ on a Varian Mercury 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C . All chemical shifts are reported in parts per million (ppm) and were measured relative to the solvent in which the sample was analyzed (CDCl_3 $\delta = 7.26$ and $\text{DMSO-}d_6$ $\delta = 2.49$ for ^1H NMR and CDCl_3 $\delta = 77.0$ and $\text{DMSO-}d_6$ $\delta = 39.5$ for ^{13}C NMR). Coupling constants (J) are reported in hertz (Hz). The chromatograms were obtained by gas chromatography coupled to a mass spectrometer, using a SHIMADZU GCMS-QP2010C Ultra mass spectrometer and the method with the following specifications: column Ultra Alloy 5, 30 m, DI 0.25 mm; helium carrier gas; injector temperature: 290 °C; the oven temperature was: 40 °C (2.0 min), with a ramp from 30 °C min^{-1} to 250 °C (maintained for 1.0 min). The percentage of HMF yield (%) was calculated based on the calibration curve, using TMB as an internal standard.

EXPERIMENTAL PROCEDURES

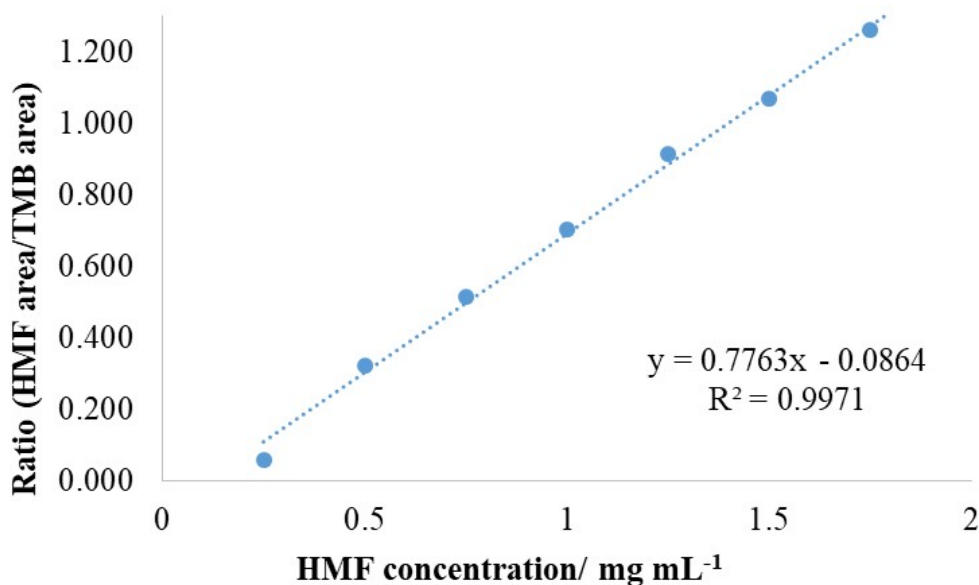


Fig. S1 calibration curve of HMF with internal standard (TMB) in ethyl acetate.

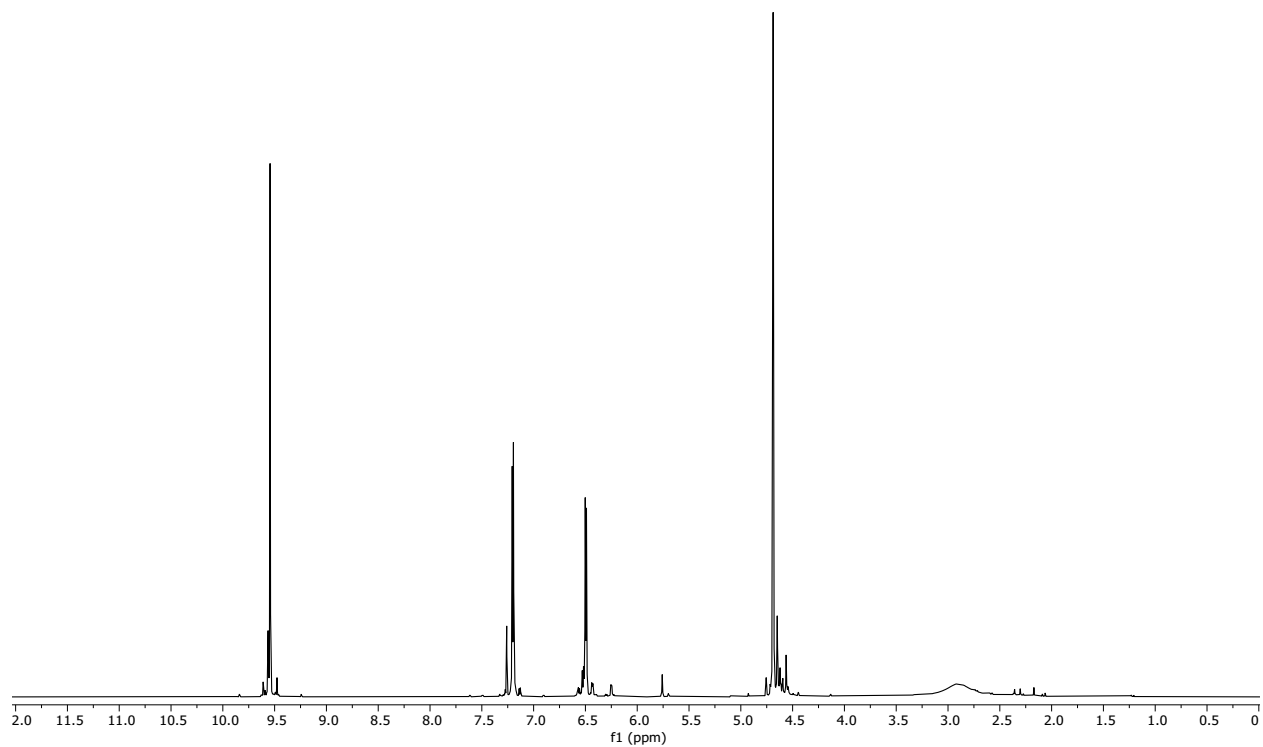


Fig. S2 ¹H NMR (300 MHz; CDCl₃, δ_{CHCl₃} 7.26) of 5-hydroxymethylfurfural produced in DES+CX4SO₃H/Ethyl acetate system.

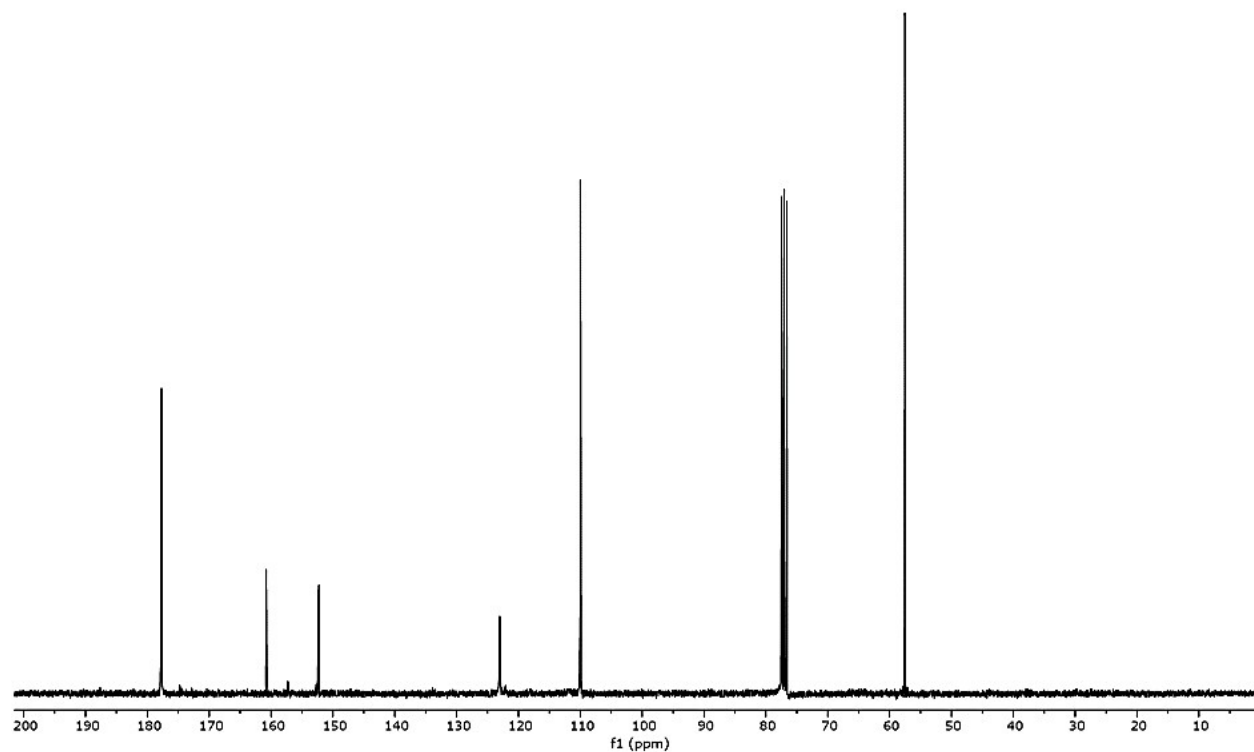


Fig. S3 ^{13}C NMR (75 MHz; CDCl_3 , δ_{CHCl_3} 77.00) of 5-hydroxymethylfurfural.

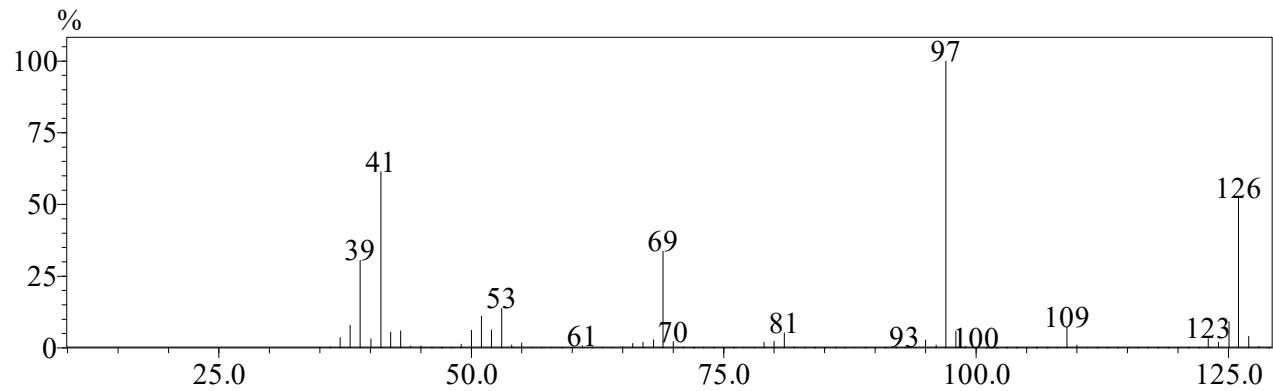


Fig. S4 5-hydroxymethylfurfural mass spectrum.

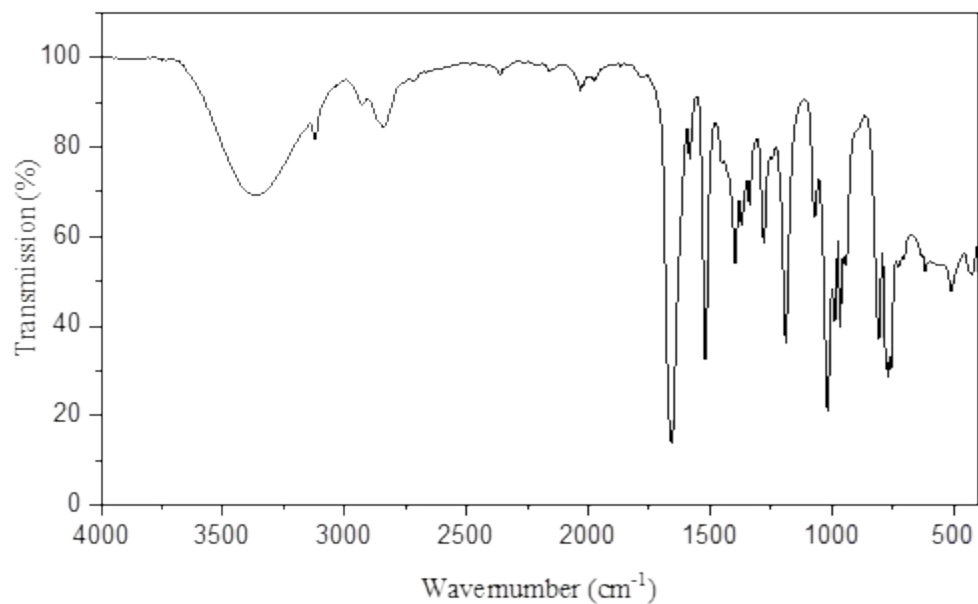


Fig. S5 5-hydroxymethylfurfural infrared spectrum.

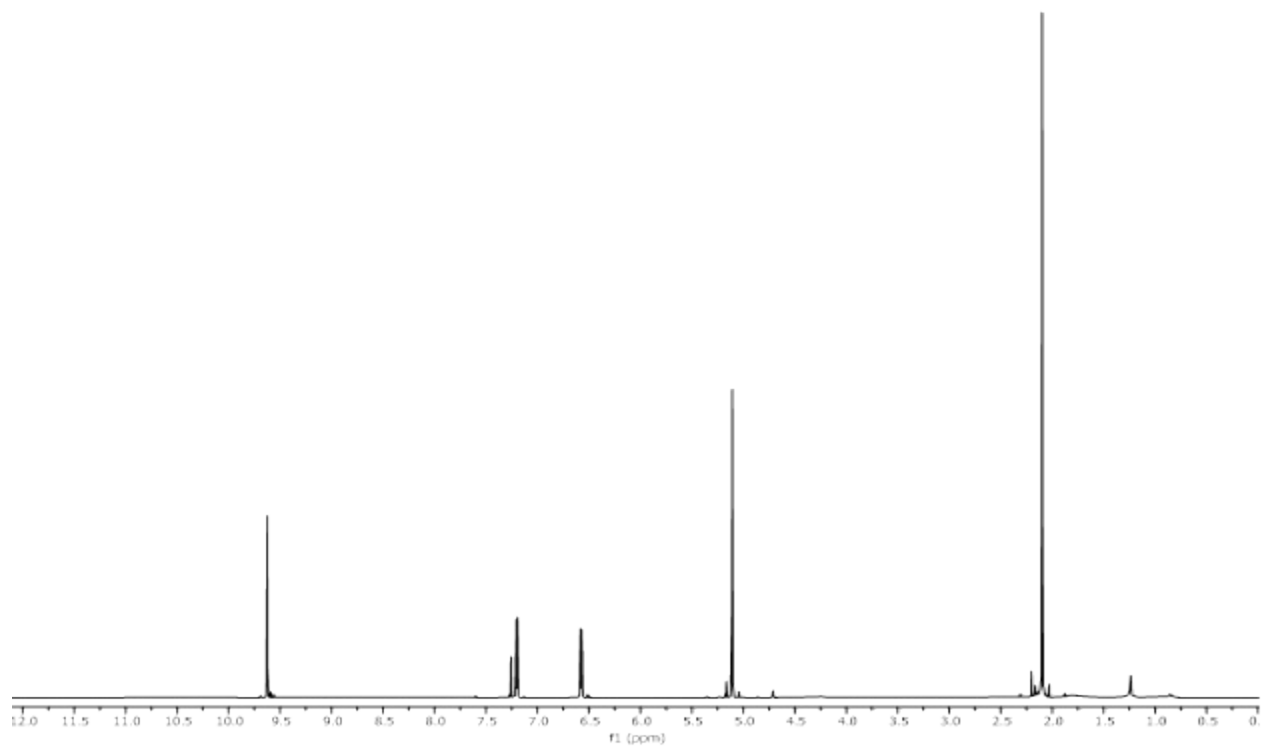


Fig. S6 ^1H NMR (300 MHz; CDCl_3 , δ_{CHCl_3} 7.26) of 5-acetoxymethylfurfural.

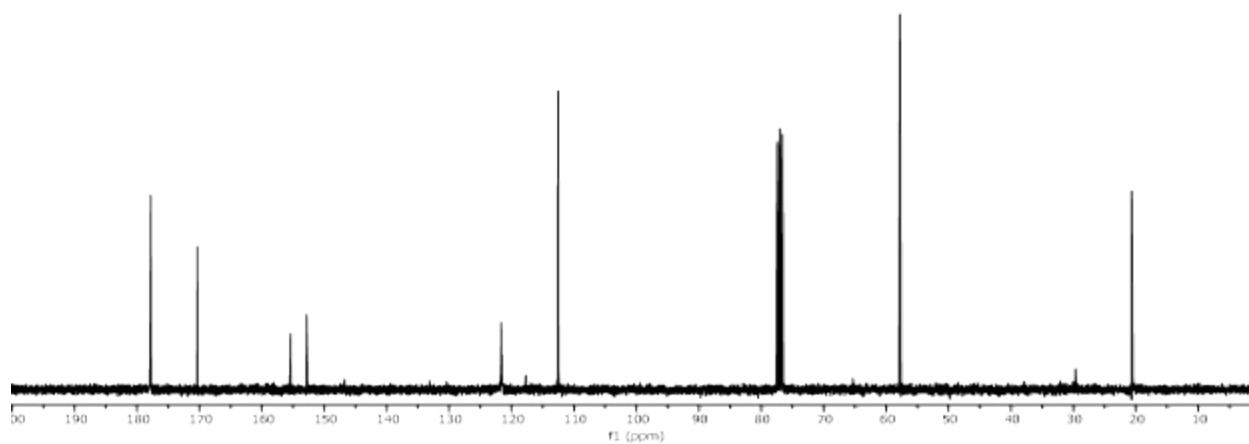


Fig. S7 ^{13}C NMR (75 MHz; CDCl_3 , δ_{CHCl_3} 77.00) of 5-acetoxymethylfurfural.

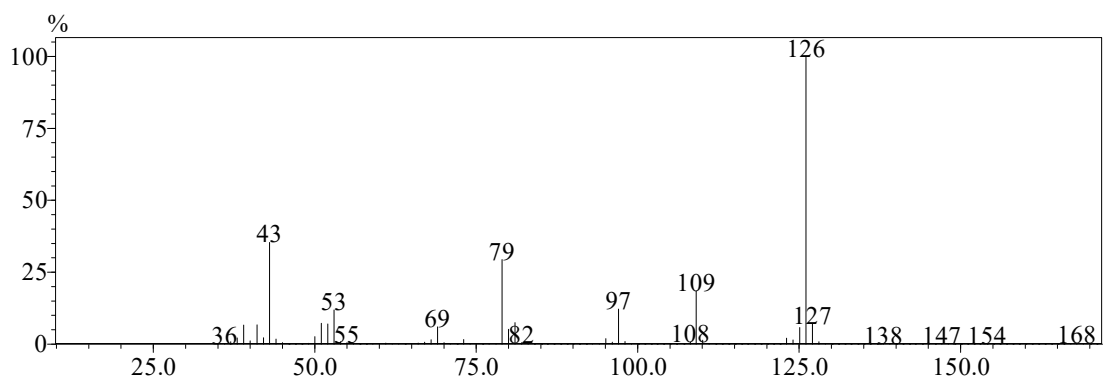


Fig. S8 5-acetoxymethylfurfural mass spectrum.

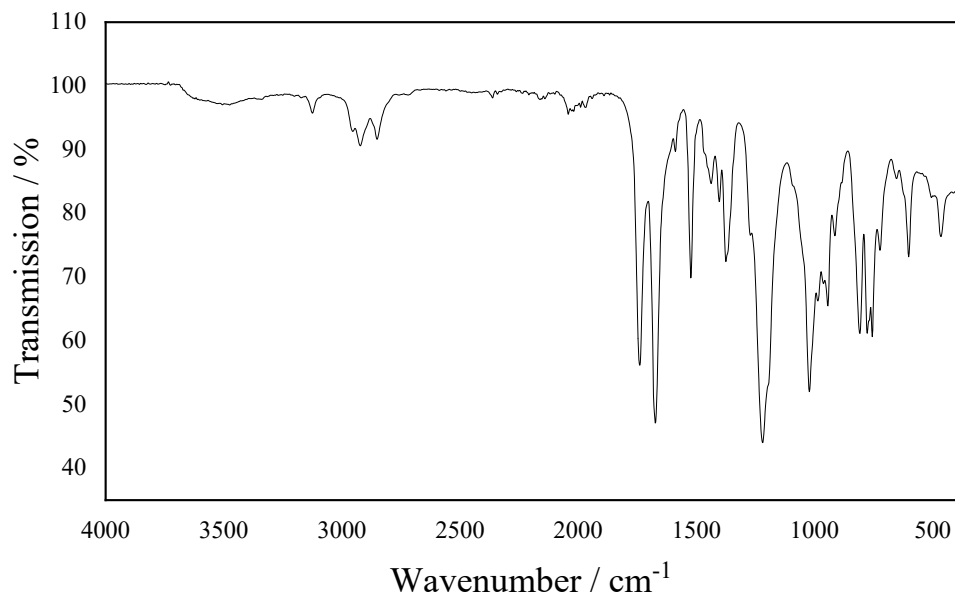


Fig. S9 5-acetoxymethylfurfural infrared spectrum.

DES characterization

The infrared spectra of fructose, ChCl and DES formed by these were investigated (Fig. 4). The strong OH-linked stretch band, present in all spectra, was shifted in DES (3303 cm^{-1}) to higher wavenumber compared to ChCl (3220 cm^{-1}) and to lower wavenumber compared to fructose (3397 cm^{-1}). The C-N binding stretch band (1082 cm^{-1}) present in the ChCl spectrum and the fructose C-O binding stretch band (1048 cm^{-1}) overlapped in the DES infrared spectrum.

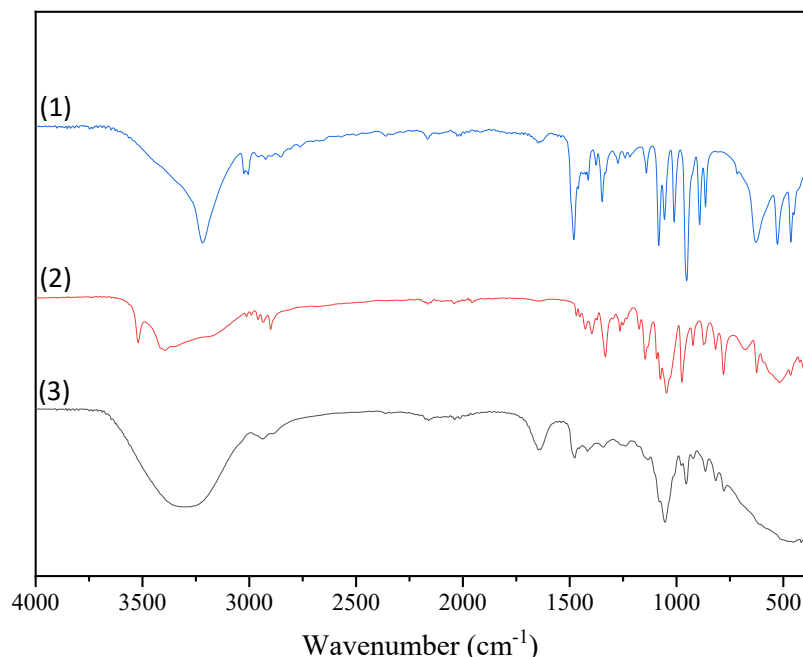


Fig. S10 Infrared spectra of ChCl (1), fructose (2) and DES (3).

On the other hand, when comparing the ^1H NMR spectra of fructose, ChCl and prepared DES (Fig. 5), a change in the chemical shifts of all DES constituent signals was observed, when compared with those of pure substances. When comparing the ^1H NMR spectra of DES prepared in the conventional heating in bench and DES prepared in the microwave reactor, no differences were noted (Fig. 5 c and d). In general, the signals for fructose were for greater chemical shifts when it is constituting DES (Table 5). It is mainly noticed that the signals referring to the fructose hydroxyls (H6, H8, H9, H10, H12) had the greatest changes in chemical shifts ($\Delta\delta \geq 0.10\text{ ppm}$). This observation was also noted for the hydroxyl referent signal of ChCl, which had a shift change of 0.19 ppm . This effect can be explained by the hydrogen bond-type interactions between these hydroxyls, which lead to the unshielding/shielding of their hydrogens and altering their chemical environment.

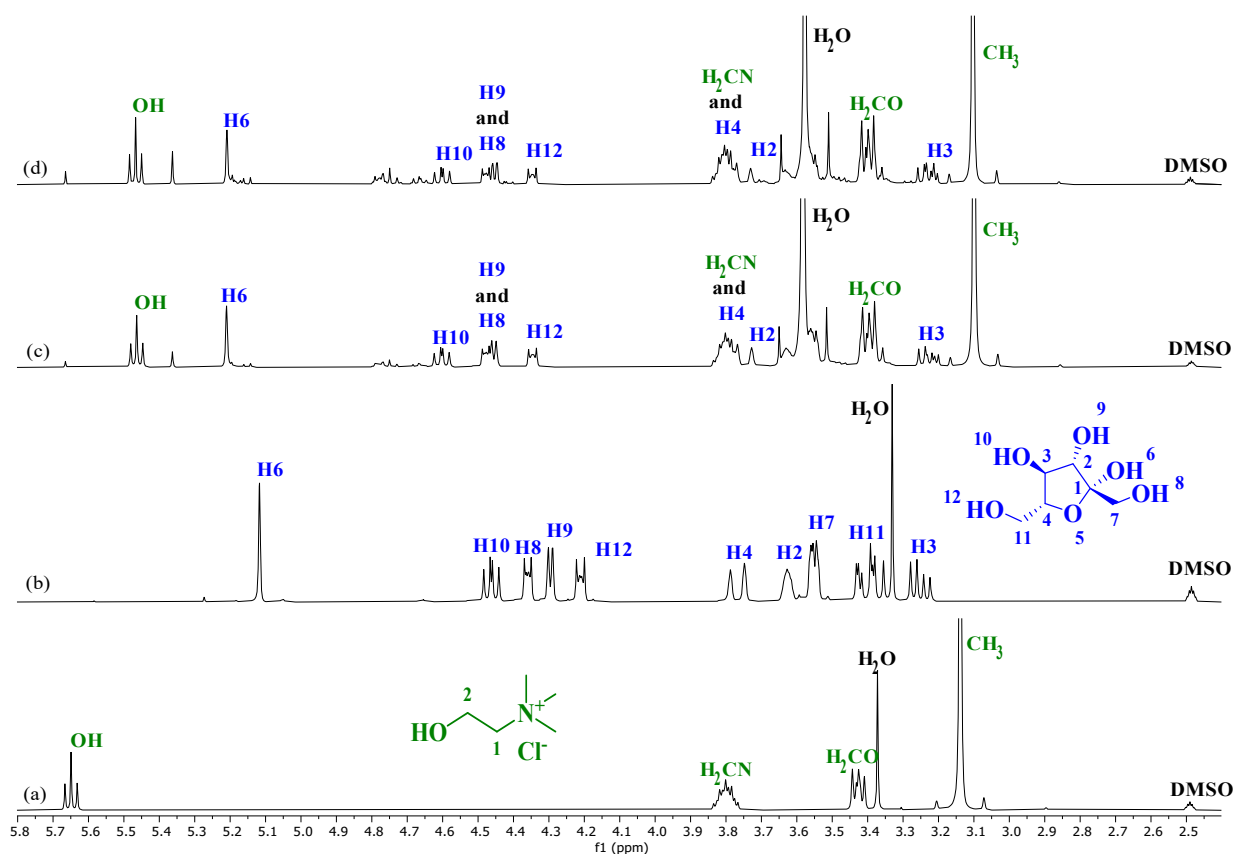


Fig. S11 ^1H NMR spectrum (300 MHz, $\text{DMSO-}d_6$, $\delta_{\text{DMSO}} = 2.49$ ppm) of (a) ChCl, (b) fructose, (c) DES prepared with heating via MW and (d) DES prepared with bench-top oil bath heating.

Table S1 Chemical shifts in ^1H NMR of isolated ChCl and fructose signals and in DES.

Hydrogens	δ Isolated (ppm)	δ in DES (ppm)	$ \Delta\delta $ (ppm) = $ \delta_{\text{DES}} - \delta_{\text{isolated}} $
ChCl- CH_3	3.14	3.11	-0.03
ChCl- H_2CO	3.43	3.40	-0.03
ChCl-OH	5.65	5.46	-0.19
Fructose-H2	3.63	3.73	0.10
Fructose-H3	3.25	3.23	0.02
Fructose-H6	5.11	5.21	0.10
Fructose-H8	4.36	4.48	0.12
Fructose-H9	4.30	4.45	0.15
Fructose-H10	4.47	4.60	0.13
Fructose-H12	4.21	4.35	0.14

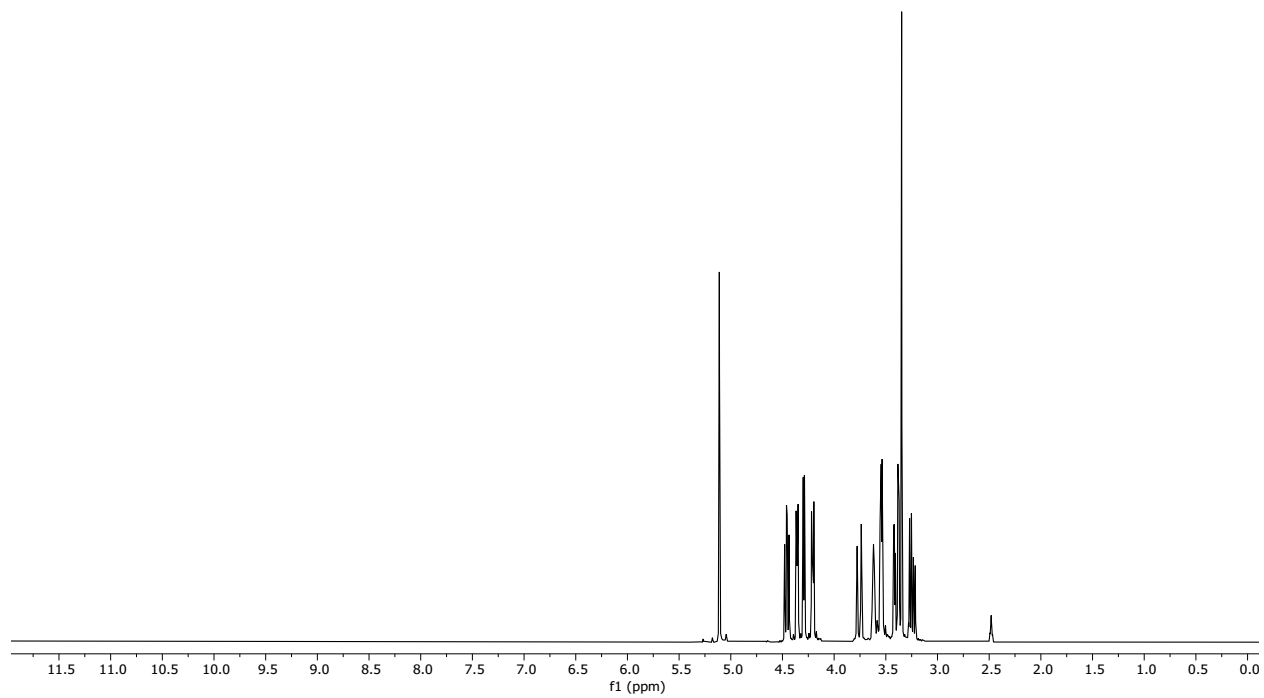


Fig. S12 ¹H NMR (300 MHz; DMSO-*d*₆, δ_{DMSO} 2.49) of *D*-fructose.

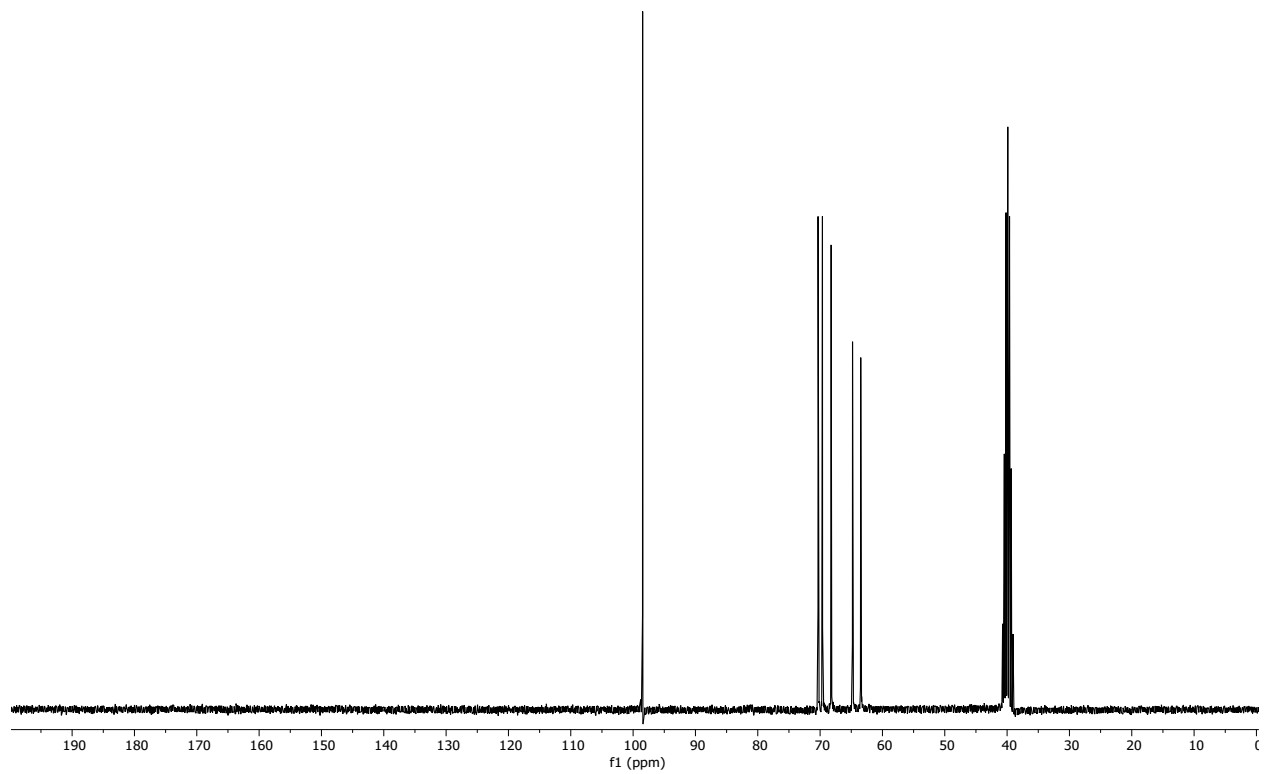


Fig. S13 ¹³C NMR (75 MHz; DMSO-*d*₆, δ_{DMSO} 39.5) of *D*-fructose.

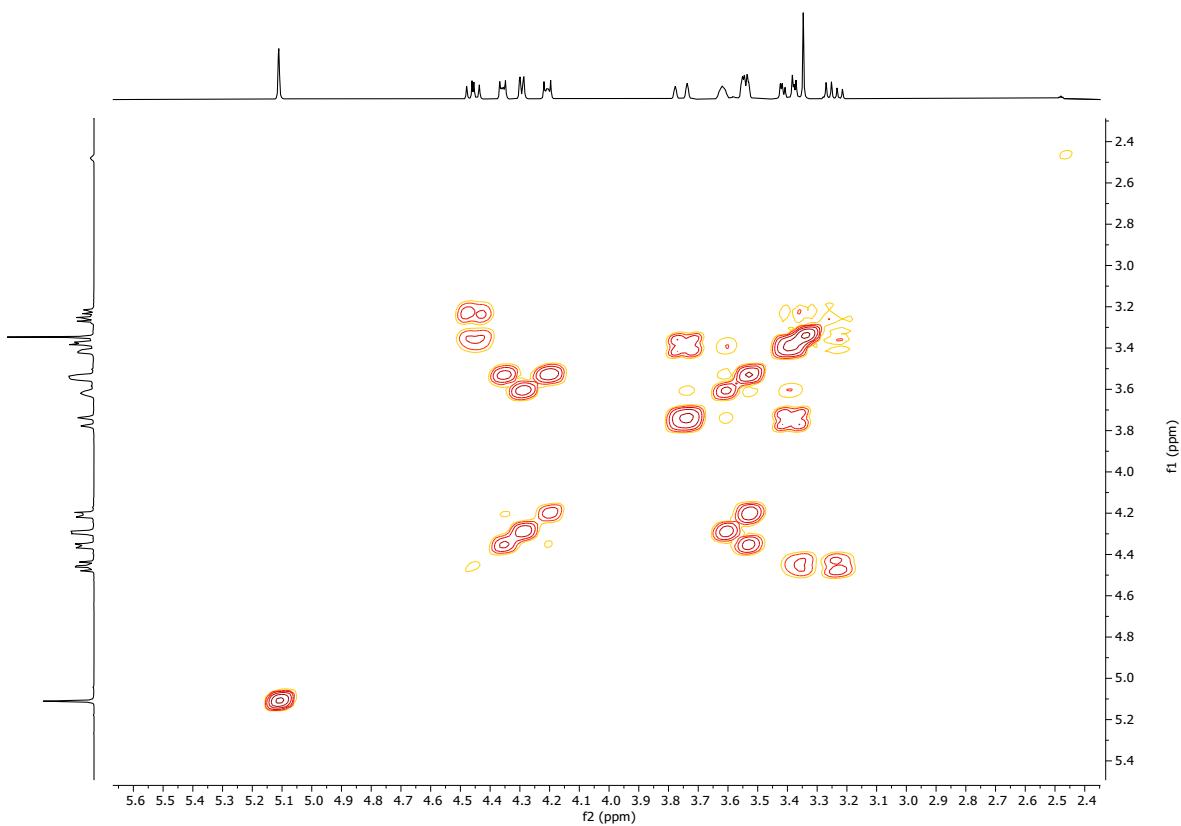


Fig. S14 COSY NMR spectrum (300 MHz; DMSO- d_6 , δ_{DMSO} 2.49) of *D*-fructose.

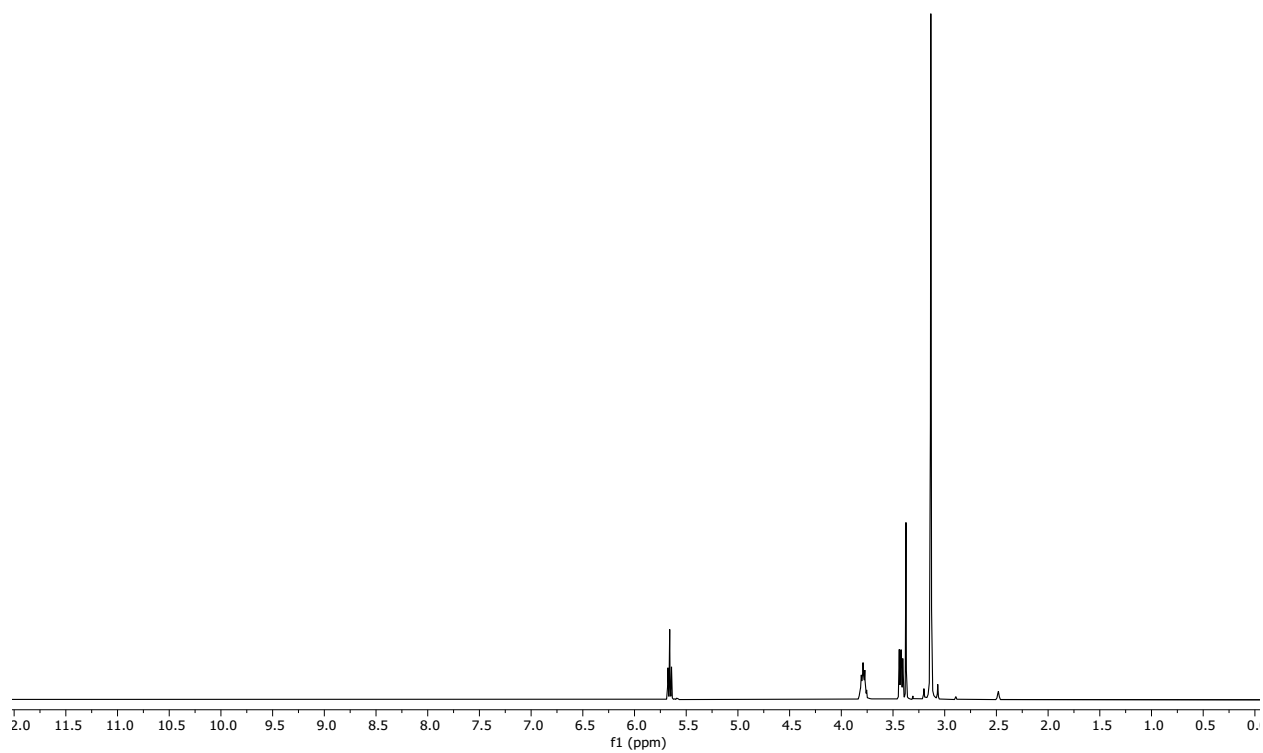


Fig. S15 ^1H NMR (300 MHz; DMSO- d_6 , δ_{DMSO} 2.49) of chloride coline.

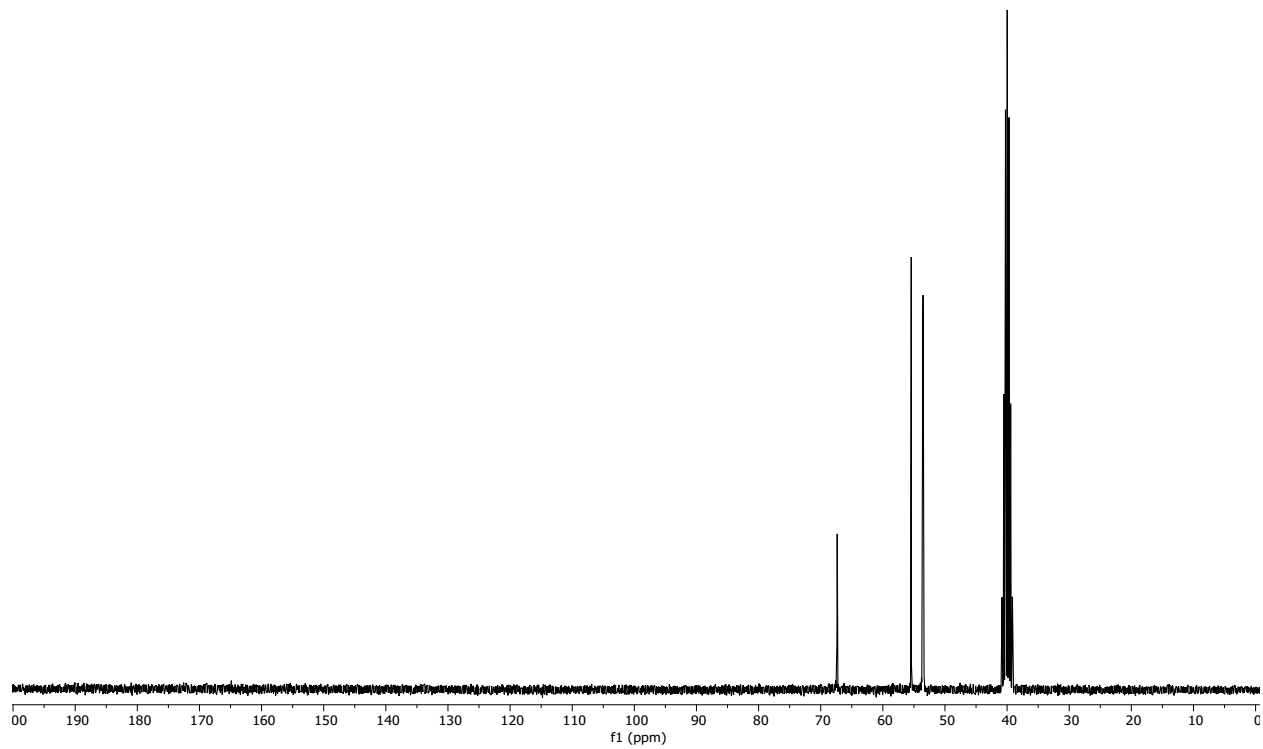


Fig. S16 ^{13}C NMR (75 MHz; $\text{DMSO-}d_6$, δ_{DMSO} 39.5) of chloride coline.

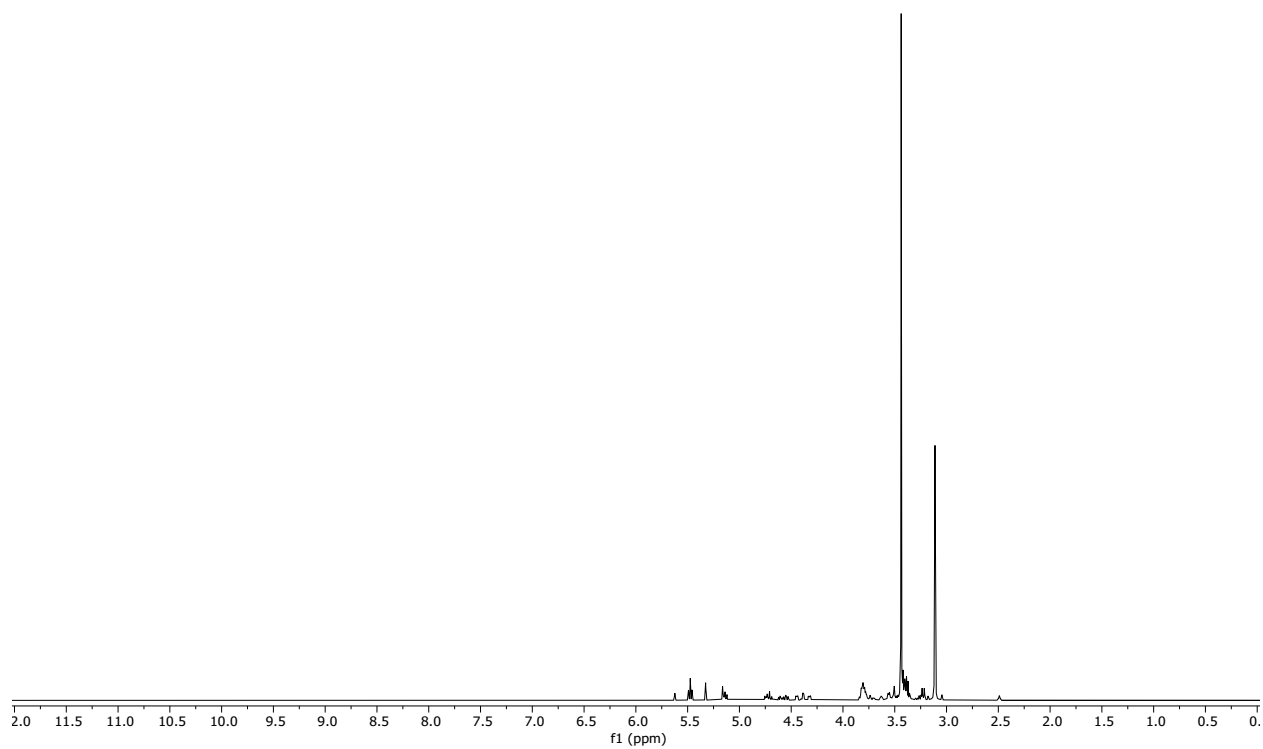


Fig. S17 ^1H NMR (300 MHz; $\text{DMSO-}d_6$, δ_{DMSO} 2.49) of DES.