New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing

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Electronic Supplementary Information

ESI 1. Materials and Methods

ESI 1.1 Screening of LTTMs

DL malic acid, was provided by Merck Chemicals (≥99%), lactic acid was obtained at pharmaceutical grade from PURAC Biochem bv, and the other chemicals were obtained from Sigma-Aldrich (≥98%). Choline chloride and lactic acid (both hygroscopic) were dried under vacuum before use.

The required preparation temperature for the LTTMs depends on the lowest melting point of the constituents. Both hydrogen bond donor and acceptor starting materials were added to a closed 25 ml flask provided with magnetic stirring, and which temperature was controlled by using a thermostatic oil bath set to 60-130C.

Both starting components where homogeneously mixed into the flask and set into the heating bath until the melting of the mixture provides enough liquid to initiate the magnetic stirring. The melting point of the mixture is always found to be much lower than the melting point of the starting materials. The better the mixing of the solid starting materials the less heating is required for melting.

Once the mixture forms a transparent liquid, it is cooled down and a TGA analysis was carried out to check the thermal stability. The water content was measured with Karl-Fisher titration method on a Metrohm 870 KF Titrino plus.

The glass transitions and melting points were analysed by a Q20 TA instruments differential scanning calorimeter (DSC).

ESI 1.2 Screening of biopolymer solubilities

Lignin (96%, Alkali lignin, low sulfonate content), cellulose (90%) and starch (practical grade) were purchased from Sigma-Aldrich. More details about the lignin used in these experiments are provided in Table ESI 1.2. The Solubility of the biopolymers was determined by cloud point method. Vials containing 2 g of solvent were placed into an oil bath at constant temperature: 60 ºC for less viscous mixtures and 80 or 100 ºC for the ones showing higher viscosities. Consecutive additions of 0.2 - 1 mg of solute were made while keeping vigorous stirring. Once turbidity was noticeable, the samples were equilibrated for 24 hours. If the sample did not become clear, cloud point was registered; below 0.1 wt% no solubility was considered.

Table ESI 1.2. Product information of the lignin used in the solubility experiments

Name	Alkali Lignin, low sulfonate content
Sigma-Aldrich product nr.	471003
average M_w	~10,000
total impurities	4% sulfur
pH	10.5 (3 wt. %)

ESI 1.3 Lignin and LTTM regeneration screening

Recoverability of the solvent after lignin subtraction is desirable; therefore a screening for suitable anti-solvents was done. Water and ethanol are likely to precipitate the lignin from the LTTMs[11]. First, the miscibility of LTTM with water and ethanol (mixtures) was tested, finding complete miscibility. Then ethanol, water and their combinations (3:7, 1:1, 7:3 [v:v]) were added to saturated solutions of LC2:1 and lignin. Precipitation occurred and after centrifuging the supernatant became coloured but transparent. In order to get an overview of which antisolvent is working the best for each LTTM and in which ratios, more experiments need to be done. Solvents with strong hydrogen bonding are likely to separate from non hydrogen bonding solvents. For this reason LC2:1 and acetone were mixed. Direct precipitation of the LTTM occurred when adding LC2:1 to acetone, while a two liquid phase system appeared when adding acetone to pure LC2:1. This implies that the pure LTTM or its starting materials in principle are able to be (partially) recovered.

ESI 2 FT-IR Analysis

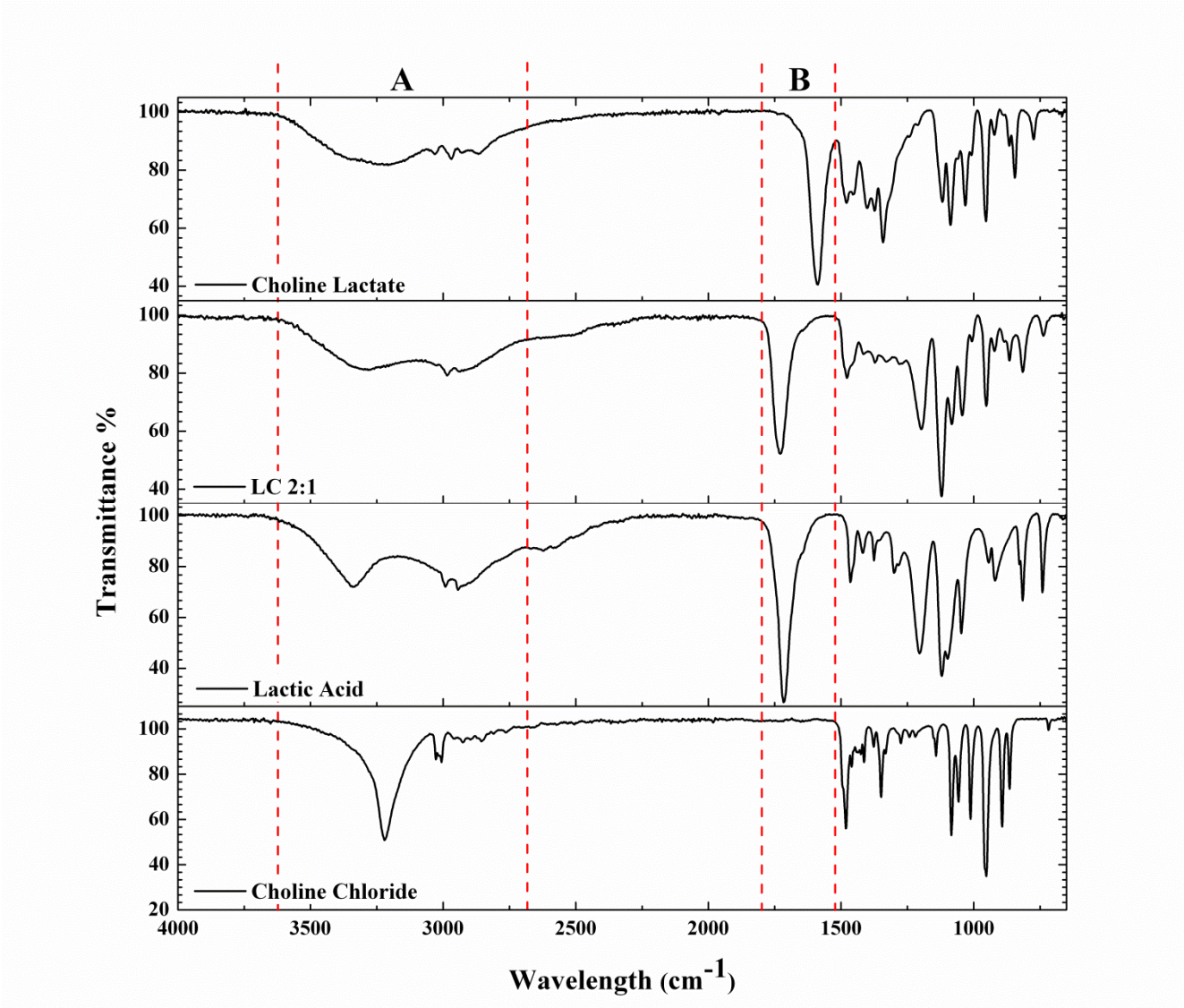

Fig. ESI 1 FT- IR spectra for Choline chloride, Lactic Acid, LC2:1 and Choline Lactate.

The representative peak of carboxylic acid group of Lactic Acid (1710 cm^{-1} for the C=O group) can be also observed in the LC2:1. In the FT-IR spectra of the IL Choline Lactate only the representative peak of lactate (1550cm^{-1} for the C=O group) can be observed while the carboxylic acid is not present. In LC2:1 no evidence of lactate presence can be found. The peaks involved in the H-bonding responsible for the formation of the LTTM are shifted and broader in the LC2:1 (2900-3600 cm^{-1} for the O-H groups for carboxylic acid and alcohol). The main bands for the peak shifts and lactic acid/lactate peaks are delimited by dashed red lines in the figures.

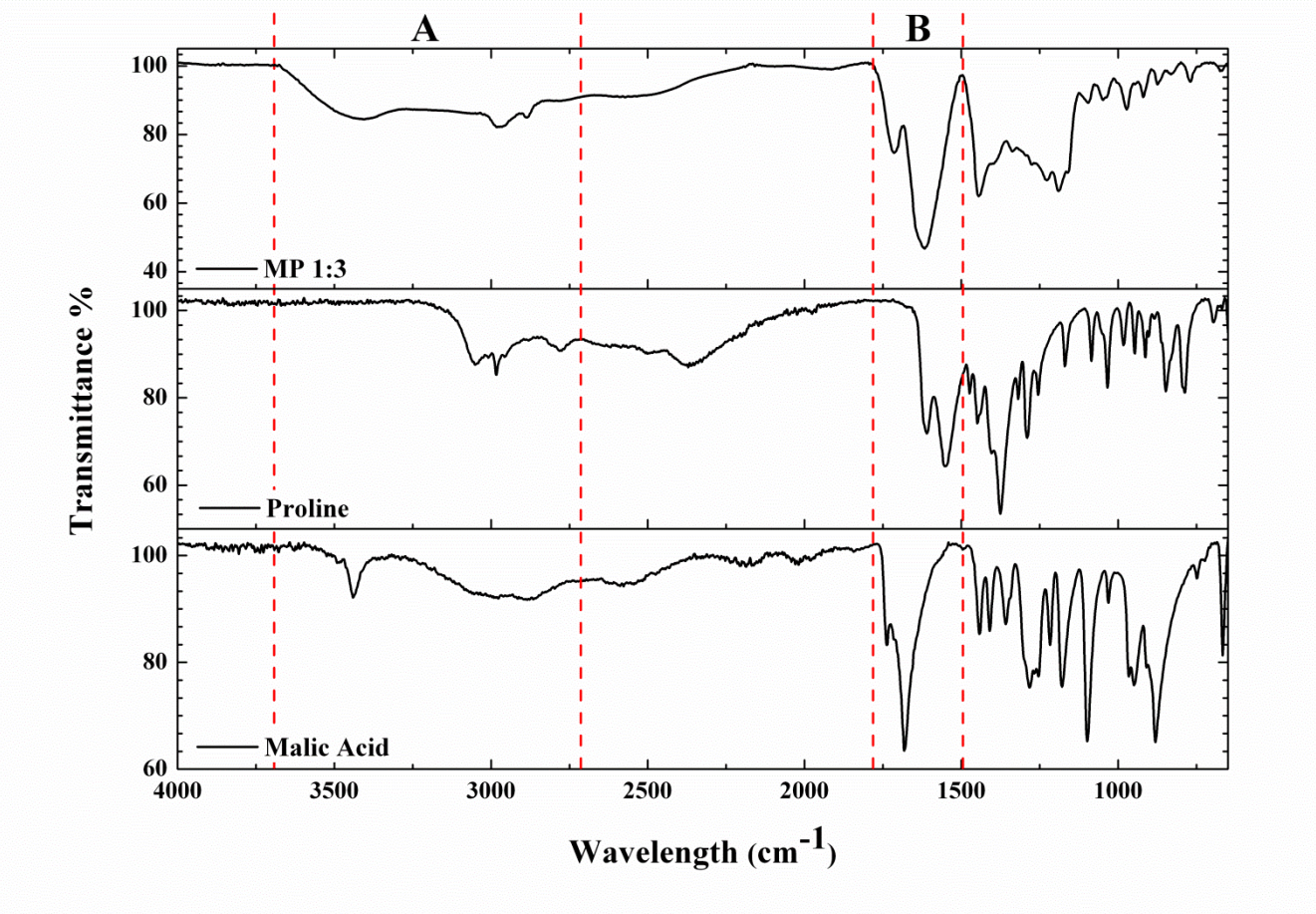

Fig. ESI 2 FT- IR spectra for Proline, Mactic Acid and MC1:3.

The representative peak of carboxylic acid group of Malic Acid (1710 cm^{-1} for the C=O group) can be also observed in the MC1:3, broaded and overlapped with the peak of proline because of the hydrogen bonding. No representative peak of malate can be observed in MC1:3 (1550cm^{-1} for the C=O group). The peaks involved in the H-bonding responsible for the formation of the LTTM are shifted and broader in the MC1:3 (2900-3600 cm^{-1} for the O-H groups for carboxylic acid and alcohol). The main bands for the peak shifts and lactic acid/lactate peaks are delimitated by dashed red lines in the figures.

ESI 3 ^{1}H-NMR Analysis

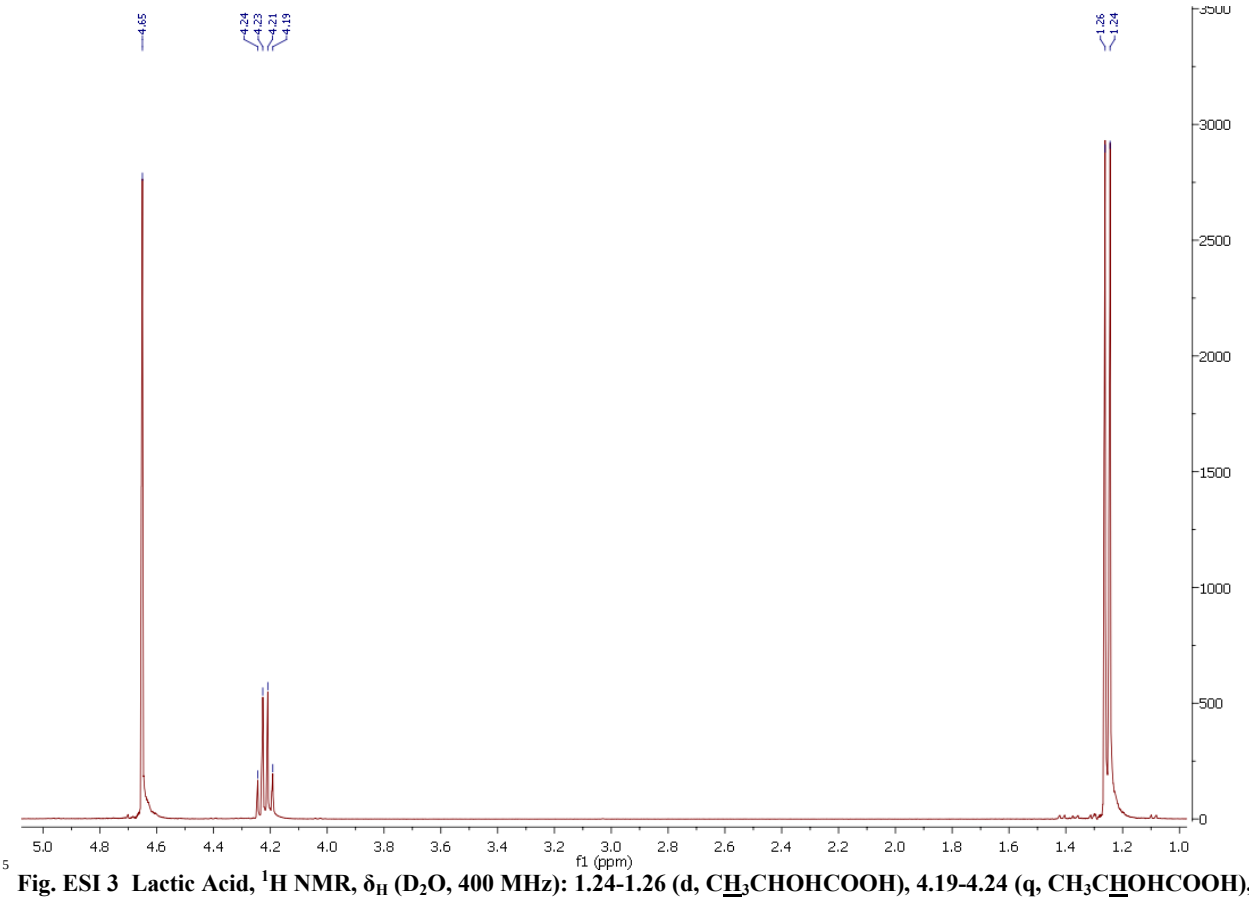

Fig. ESI 3 Lactic Acid, ^{1}H NMR, δ_H (D_2O, 400 MHz): 1.24-1.26 (d, $C\underline{H}_3CHOHCOOH$), 4.19-4.24 (q, $CH_3C\underline{H}OHCOOH$), 4.65 (s, $CH_3CHO\underline{H}COO\underline{H}$, $\underline{H}DO$)

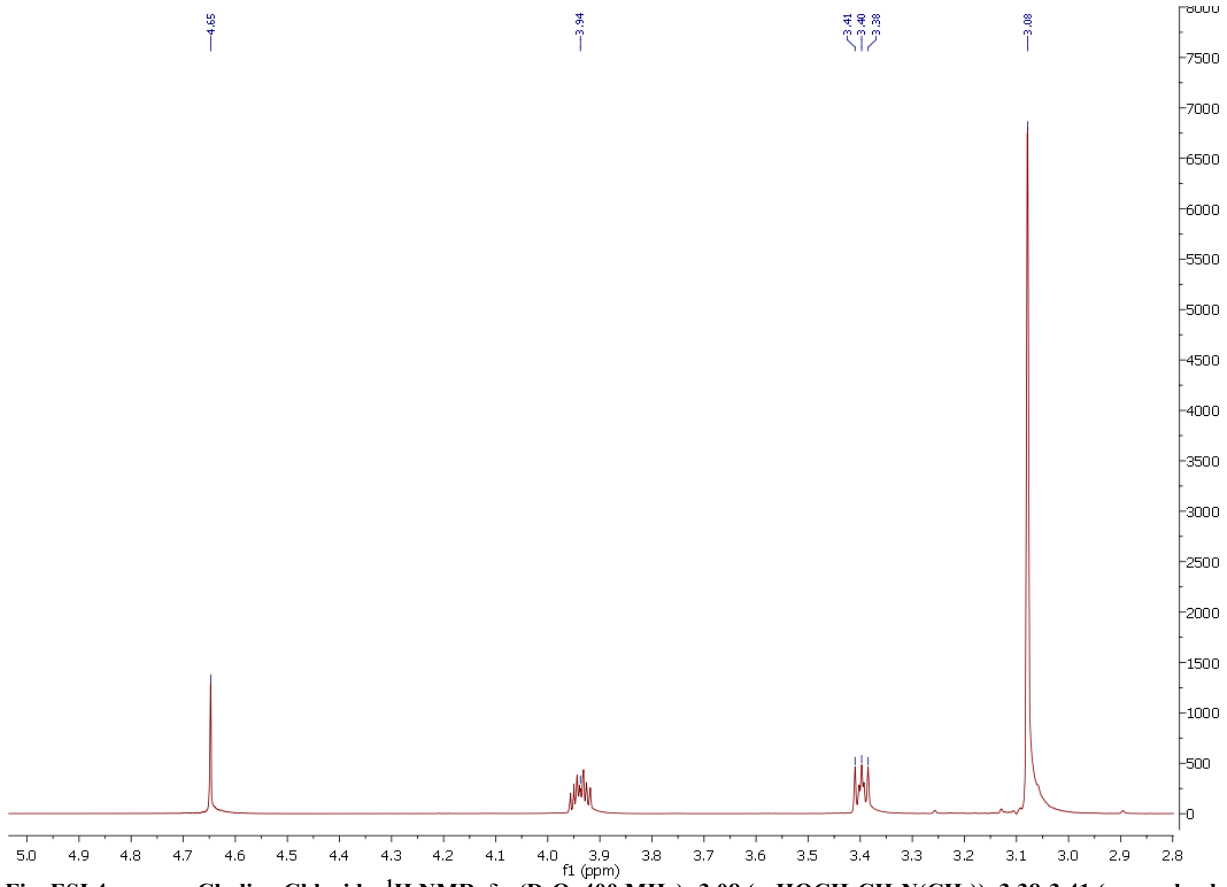

Fig. ESI 4 **Choline Chloride, ^{1}H NMR, δ_H (D_2O, 400 MHz): 3.08 (s, $HOCH_2CH_2N(C\underline{H}_3)$), 3.38-3.41 (unresolved, $HOCH_2C\underline{H}_2N(CH_3)$), 3.92-3.96 (unresolved, $HOC\underline{H}_2CH_2N(CH_3)$), 4.65 (s, $\underline{H}OCH_2CH_2N(CH_3)$, $\underline{H}DO$)**

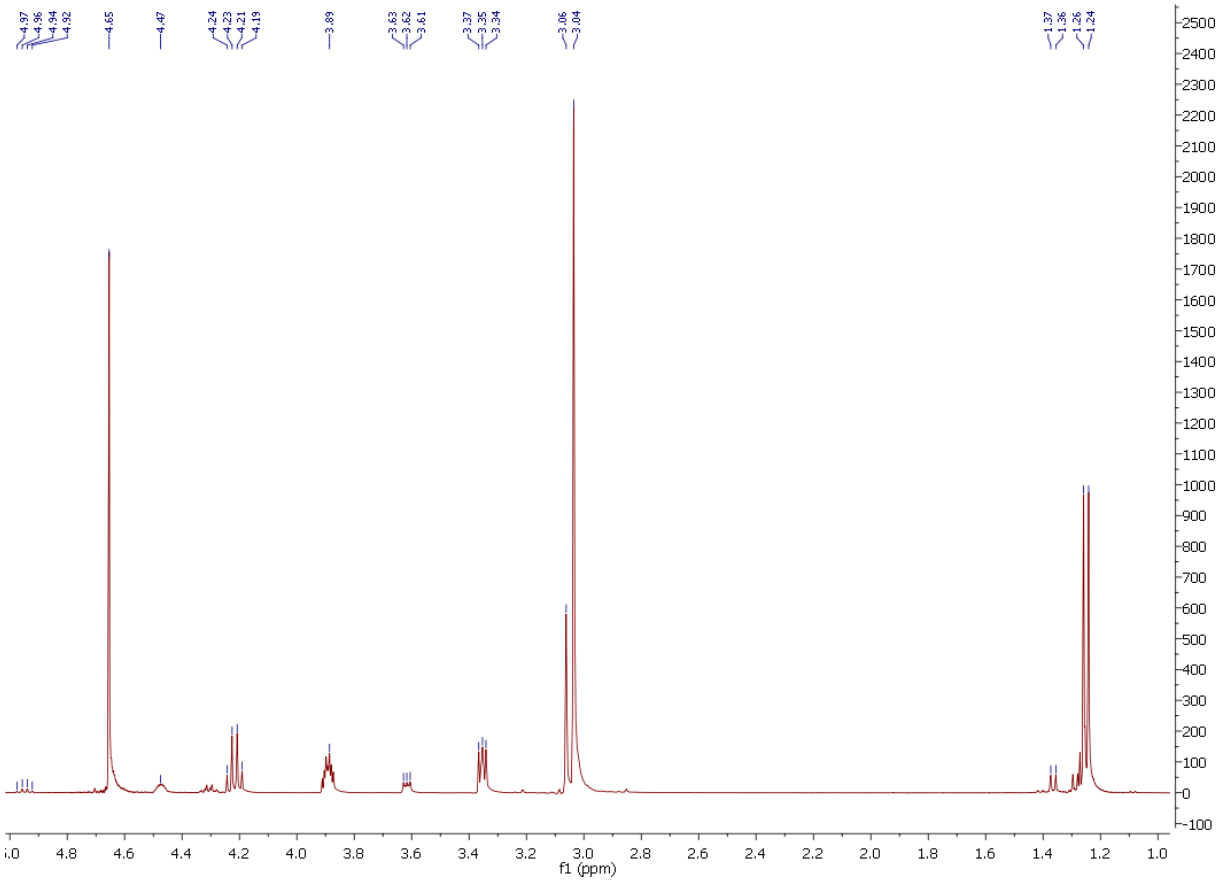

Fig. ESI 5 **10 wt% LC 2:1 in D_2O , ^1H NMR, δ_H (D_2O, 400 MHz): 1.24-1.26 (d, $C\underline{H}_3CHOHCOOH$), 1.36-1.37 (d, $C\underline{H}_3CHOHCOOH$, shifted), 3.04 (s, $HOCH_2CH_2N(C\underline{H}_3)$), 3.06 (s, $HOCH_2CH_2N(C\underline{H}_3)$, shifted), 3.34-3.37 (unresolved, $HOCH_2C\underline{H}_2N(CH_3)$), 3.61-3.63 (unresolved, $HOCH_2C\underline{H}_2N(CH_3)$, shifted), 3.87-3.92 (unresolved, $HOC\underline{H}_2CH_2N(CH_3)$), 4.19-4.24 (q, $CH_3C\underline{H}OHCOOH$), 4.27-4.34 (unresolved), 4.45-4.49 (unresolved, $HOC\underline{H}_2CH_2N(CH_3)$, shifted), 4.65 (s, $CH_3CHO\underline{H}COO\underline{H}$, $\underline{H}DO$), 4.92-4.97 (q, $CH_3C\underline{H}OHCOOH$, shifted)**

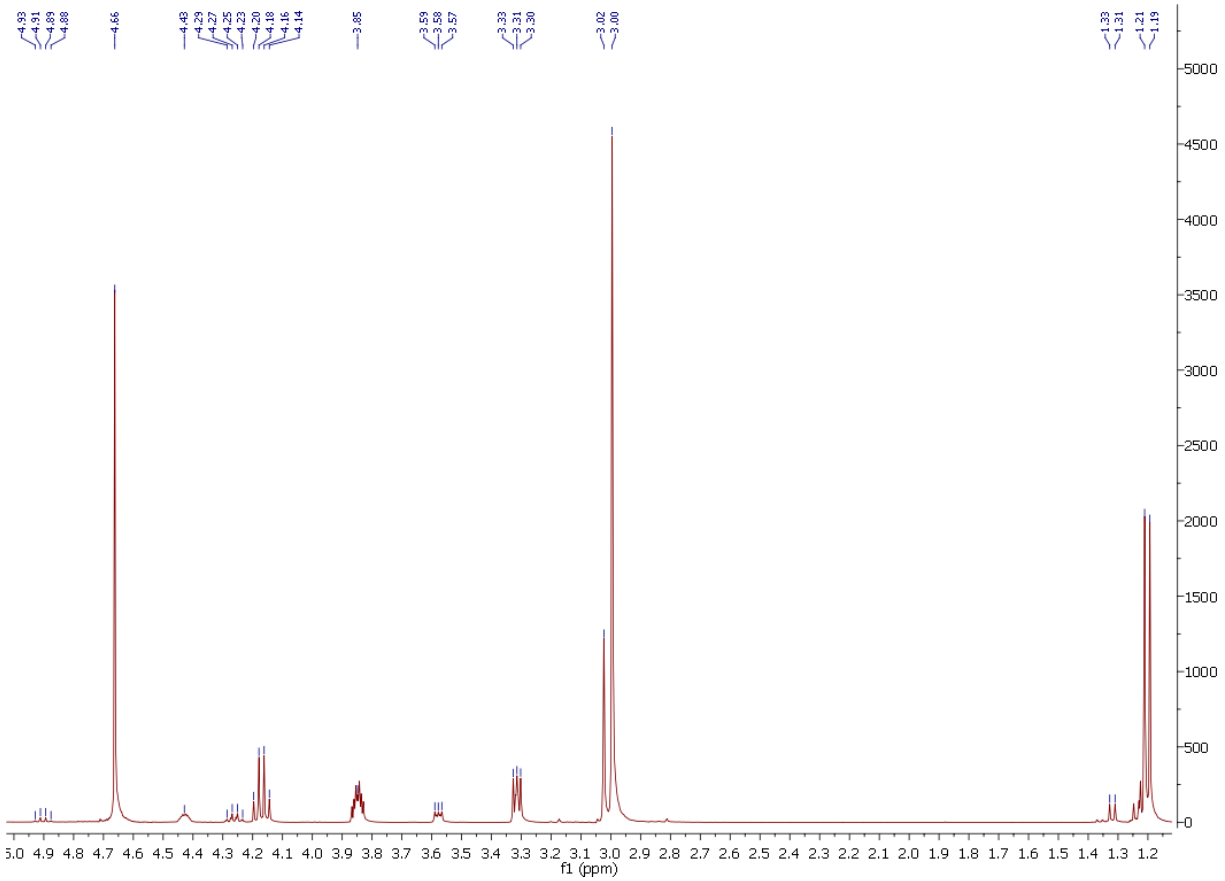

Fig. ESI 6. **20 wt% LC 2:1 in D_2O , ^1H NMR, δ_H (D_2O, 400 MHz): 1.19-1.21 (d, $C\underline{H}_3CHOHCOOH$), 1.31-1.33 (d, $C\underline{H}_3CHOHCOOH$, shifted), 3.00 (s, $HOCH_2CH_2N(C\underline{H}_3)$), 3.02 (s, $HOCH_2CH_2N(C\underline{H}_3)$, shifted), 3.30-3.33 (unresolved, $HOCH_2C\underline{H}_2N(CH_3)$), 3.57-3.59 (unresolved, $HOCH_2C\underline{H}_2N(CH_3)$, shifted), 3.83-3.89 (unresolved, $HOC\underline{H}_2CH_2N(CH_3)$), 4.14-4.29 (q, $CH_3C\underline{H}OHCOOH$), 4.23-4.29 (unresolved), 4.41-4.45 (unresolved, $HOC\underline{H}_2CH_2N(CH_3)$, shifted), 4.66 (s, $CH_3CHO\underline{H}COO\underline{H}$, $\underline{H}DO$), 4.88-4.93 (q, $CH_3C\underline{H}OHCOOH$, shifted)**

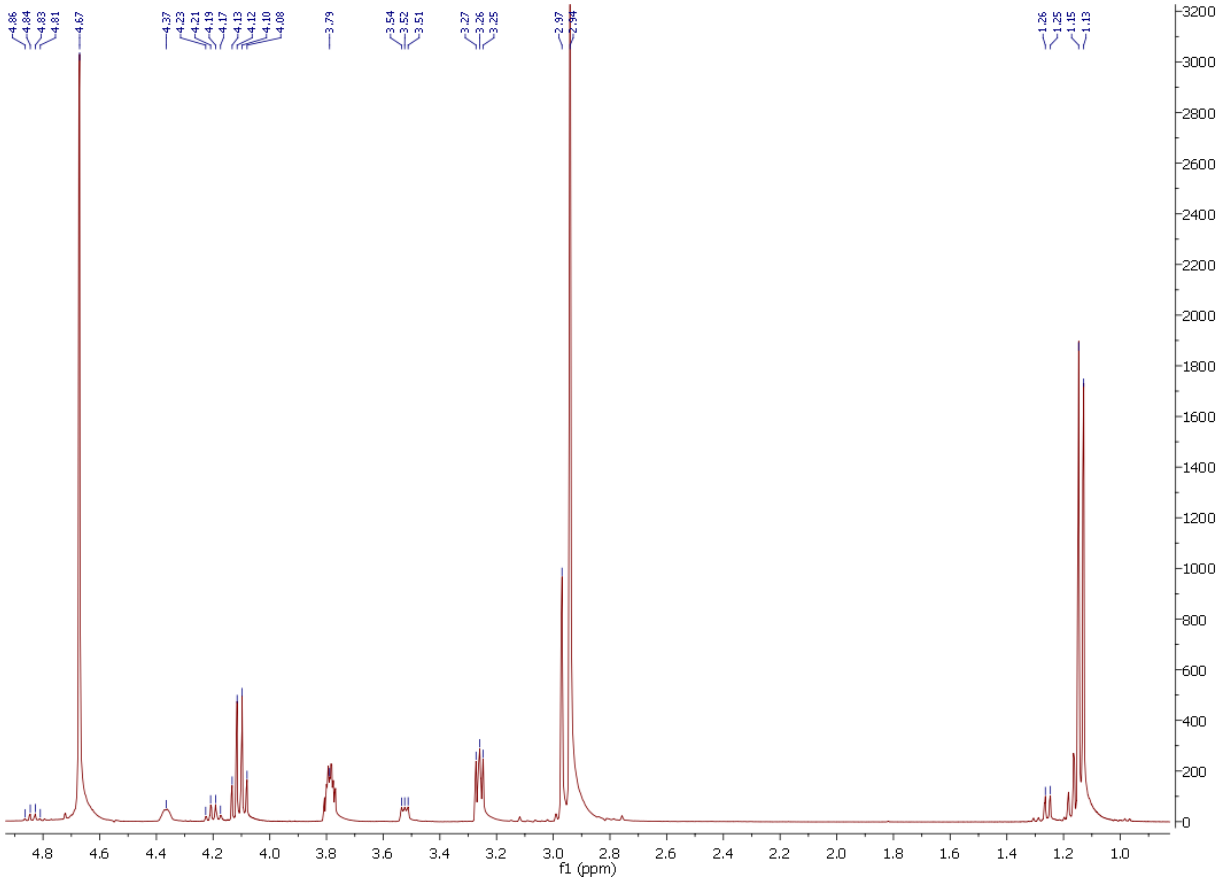

Fig. ESI 7 30 wt% LC 2:1 in D_2O , ^1H NMR, δ_H (D_2O, 400 MHz): 1.13-1.15 (d, $C\underline{H}_3CHOHCOOH$), 1.25-1.26 (d, $C\underline{H}_3CHOHCOOH$, shifted), 2.94 (s, $HOCH_2CH_2N(C\underline{H}_3)$), 2.97 (s, $HOCH_2CH_2N(C\underline{H}_3)$, shifted), 3.25-3.27 (unresolved, $HOCH_2C\underline{H}_2N(CH_3)$), 3.51-3.54 (unresolved, $HOCH_2C\underline{H}_2N(CH_3)$, shifted), 3.77-3.82 (unresolved, $HOC\underline{H}_2CH_2N(CH_3)$), 4.08-4.13 (q, $CH_3C\underline{H}OHCOOH$), 4.17-4.23 (unresolved), 4.35-4.39 (unresolved, $HOC\underline{H}_2CH_2N(CH_3)$, shifted), 4.67 (s, $CH_3CHO\underline{H}COO\underline{H}$, $\underline{H}DO$), 4.81-4.86 ($CH_3C\underline{H}OHCOOH$, shifted)