SUPPORTING INFORMATION

From Experimental Data to Thermophysical Insight: Characterizing Choline-Based Ionic Liquids Using Advanced Data Analysis

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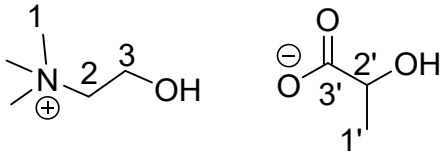
General synthesis process of cholinium-based ILs (CHILs)

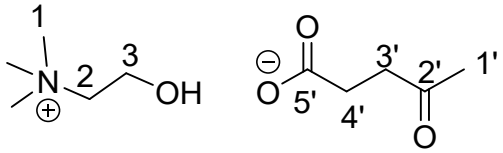
In a 250 mL two-necked flask, the corresponding carboxylic acid (levulinic or lactic, 1 eq., 61.09 mmol) was added dropwise to the cholinium hydroxide solution (1 eq., 46 % in H_2O, 61.09 mmol, 15 mL) and water (20 mL). After 24 h of stirring at room temperature under nitrogen atmosphere, the excess of water was evaporated under reduced pressure at 50°C. The final product was a light or dark yellow orange oil, respectively, and was dried under vacuum for 48 h at 45°C.

Cholinium Lactate 1 (abbrev. Chol Lac)



Light yellow orange oil. Quantitative Yield.
IR: ν (cm^{-1}) 3500-2800 (CH_2-OH, N^+-$(CH_3)_3$), 1587 (COO^-), 1478-1343 (CH_2), 1118, 1087 (C-O). ^{1}H NMR (500 MHz, DMSO) δ 3.8 (t, *J* = 7.0, 2H, H3), 3.54 (q, *J* = 6.7 Hz, 1H, H2‘), 3.41 (~~m~~ t, *J* = 7.0, 2H, H2), 3.12 (s, 9H, H1), 1.08 (d, *J* = 6.7 Hz, 3H, H1‘). ^{13}C NMR (126 MHz, DMSO) δ 177.6 (C3’), 67.4 (C2’), 67.2 (C2), 55.3 (C3), 53.2 (C1), 21.5 (C1’). Elemental Analysis: % Calc. for $C_8H_{19}NO_4$.1.3 H_2O: C 44.35, H 10.05, N 6.46. % Found: C 44.40, H 9.720, N 6.42.

Cholinium Levulinate 2 (abbrev. Chol Lev)



Dark yellow orange oil. Quantitative Yield.
IR: ν (cm^{-1}) 3500-2800 (CH_2-OH, N^+-$(CH_3)_3$), 1704 (C=O), 1567 (COO^-), 1478-1368 (CH_2), 1165, 1087, 1057 (C-O). ^{1}H NMR (500 MHz, DMSO) δ 3.82 (t, *J* = 5.7, 2H, H3), 3.40 (t, *J* = 5.7, 2H, H2), 3.12 (s, 9H, H1), 2.45 (t, *J* = 7.0 Hz, 2H, H3’), 2.07 (t, *J* = 6.9 Hz, 2H, H4’), 2.04 (s, 3H, H1’).^{13}C NMR (126 MHz, DMSO) δ 209.7 (C2’), 175.9 (C5’), 67.8 (C2), 55.7 (C3), 53.5, 53.5, 53.4 (C1), 40.5 (C4’), 32.7 (C3’), 29.9 (C1’). Elemental Analysis: % Calc. for $C_{10}H_{21}NO_4$.1.6 H_2O: C 48.41, H 9.83, N 5.65. % Found: C 48.24, H 9.70, N 5.74.

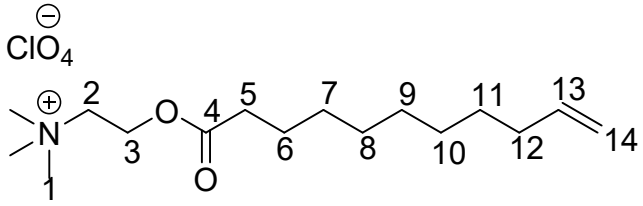
General synthesis process of cholinium ester-based ILs

Chol-C_{11}-Cl 3

In a 500 mL three-necked flask choline (1 eq, 89.53 mmol, 12.5 g) and methane sulfonic acid (2 eq, 179.06 mmol, 11.63 mL) with 10-undecenoic acid (2 eq., 179.06 mmol, 36.2 mL) were placed along with molecular sieves. The reaction medium was then heated to 115°C under reduced pressure (50-100 mbar) and maintained at these conditions for 19 h, yielding a brown solution. The obtained solution was then cooled to room temperature and filtered to remove the molecular sieves. The compound was used without purification for the second step, assuming that the conversion in the current step is 100%.

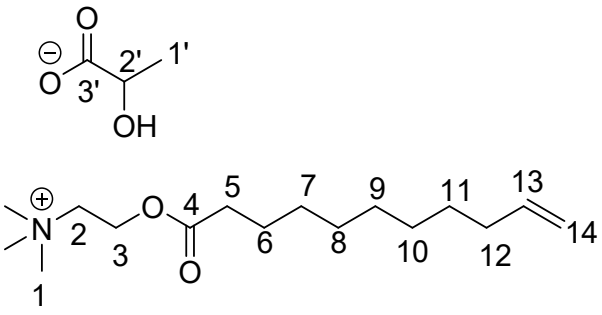
Chol-C11-ClO_4 4

A solution of Cho-C11-Cl **3** (in 15 mL of water) obtained in the previous step was introduced into a 250 mL Erlenmeyer flask. An excess of sodium perchlorate monohydrate (4 eq., 358.12 mmol, 51.76 g), previously dissolved in a small amount of water (100 mL), was then added. A white precipitate formed immediately, and the reaction medium was then stirred for 24 h to optimize the anionic metathesis between the chloride and perchlorate ions. After the addition of dichloromethane (50 mL) and washing with water (5 x 100 mL) to remove unreacted choline chloride and excess of sodium perchlorate and methane sulfonic acid, the organic phase was evaporated under reduced pressure. Finally, diethyl ether (4 x 100 mL) was added to the reaction medium to help precipitate the perchlorate salt and to remove the unreacted fatty acid. Finally, after filtration and drying under vacuum, a yellow powder was obtained (24 g, 73% yield).



mp: 68.90°C. IR: ν (cm^{-1}) 2921, 2852 (CH_2, N^+-$(CH_3)_{3)}$, 1744 (COOR), 1480-1450 (-CH_2-), 1166 (C-O-C), 1075 (ClO_4^-). ^{1}H NMR (500 MHz, DMSO) δ 5.79 (qt, J = 16.9, 1H, H13), 5.03-4.89 (dd, 2H, H14), 4.44 (m, 2H, H3), 3.67-3.61 (m, 2H, H2), 3.11 (s, 9H, H1), 2.33 (t, J = 7.5 Hz, 2H, H5), 2.00 (q, J = 7.1 Hz, 2H, H12), 1.53 (m, 2H, H6), 1.35 – 1.24 (m, 10H, H7, H8, H9, H10, H11). ^{13}C NMR (126 MHz, DMSO) δ 172.3 (C4), 138.8 (C13), 114.65 (C14), 63.8 (C2), 57.6 (C3), 52.9, 52.9, 52.9 (C1), 33.3 (C5), 33.2 (C12), 28.7, 28.7, 28.5, 28.4, 28.2 (C7, C8, C9, C10, C11), 24.2 (C6). Elemental Analysis: % Calc. for $C_{16}H_{32}ClNO_6$ C 51.96, H 8.97, N 3.79. % Found C 52.07, H 9.06 N 3.74.

Choline-C11-Lac 5 (abbrev. Chol-C11 Lac)

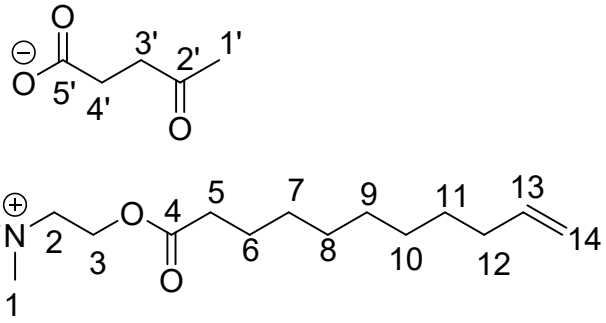


4 (1 eq., 13.54 mmol, 5 g) was dissolved in 100 mL of ethanol in a 250 mL Erlenmeyer flask. An aqueous solution of potassium lactate (60 %) (1 eq., 13.54 mmol, 2.870 g) was added to the mixture that was then stirred at room temperature for 24 h. A white precipitate was obtained and filtered. Finally, after evaporation of the solvents under reduced pressure, a yellow–brown oil was obtained (4.58 g, 94%).

IR: ν (cm^{-1}) 3371 (OH), 2924, 2853 (CH_2, N^+-$(CH_3)_3$), 1736 (COO),1596 (COO^-), 1480-1450 (CH_2), 909 ($HC=CH_2$). ^{1}H NMR (500 MHz, DMSO): δ 5.78 (m, 1H, H13), 5.03-4.90 (dd, *J* = 10.5, 7.4 Hz, 2H, H14), 4.44 (t, *J* = 4.9 Hz, 2H, H3), 3.71-3.65 (t, *J* = 4.9 Hz, 2H, H2), 3.44 (q, *J* = 6.7 Hz, 1H, H2'), 3.13 (s, 9H, H1), 2.33 (t, *J* = 7.5 Hz, 2H, H5), 2.04-1.95 (m, 2H, H12), 1.58-1.48 (m, 2H, H6), 1.26 (d, *J* = 6.2 Hz, 10H, H7, H8, H9, H10, H11), 1.05 (d, *J* = 6.7 Hz, 3H, H1'). ^{13}C NMR (126 MHz, DMSO) δ 177.0 (C3'), 172.8 (C4), 139.3 (C13), 115.1 (C14), 67.4 (C2'), 64.1 (C3), 58.2 (C2), 53.4, 53.3, 53.2 (C1), 33.80 (C6), 33.64 (C12), 29.2, 29.1, 29.0, 28.9, 28.7 (C7, C8, C9, C10, C11), 24.6 (C5), 22.1 (C1'). Elemental Analysis: % Calc. for $C_{19}H_{37}NO_5$: C 63.48, H 10.37 N 3.90. % Found C 63.72, H 10.82 N 3.46.

Choline-C11-Levulinate 6 (Chol-C11 Lev)

Similar procedure as for **5** was used with **4** (1 eq., 13.54 mmol, 5 g) dissolved in 100 mL of ethanol and a solution of potassium levulinate (1 eq., 13.54 mmol, 2.08 g) in ethanol (20 mL). A yellow-brown oil was obtained (5.40 g, > 95 %).



IR: ν (cm^{-1}) 2925, 2854 (CH_2, N^+-$(CH_3)_3$), 1738 (COO), 1711 (CO),1580 (COO^-), 1480-1450 (CH_2), 909 ($HC=CH_2$). ^{1}H NMR (500 MHz, DMSO): δ 5.79 (m, 1H, H13), 4.95 (dd, *J* = 10.9, 7.3 Hz, 2H, H14), 4.44 (t, *J* = 5.2, 4.8 Hz, 2H, H3), 3.67 (t, *J* = 5.2, 4.8 Hz, 2H, H2), 3.13 (s, 9H, H1), 2.47 (t, *J* = 6.9 Hz, 2H, H3'), 2.33 (t, *J* = 7.5 Hz, 2H, H5), 2.15 (t, *J* = 6.9 Hz, 2H, H4'), 2.05 (s, 3H, H1'), 2.03 – 1.97 (m, 2H, H12), 1.55 – 1.51 (m, 2H, H6), 1.37 – 1.20 (m, 10H, H7, H8, H9, H10, H11). ^{13}C NMR (126 MHz, DMSO): δ 208.5 (C2'), 172.4 (C4), 174.2 (C5'), 138.8 (C13), 114.6 (C14), 63.7 (C3), 57.7 (C2), 52.9, 52.8, 52.8 (C1), 39.7 (C3'), 33.3 (C5), 33.2 (C12), 31.3 (C4'), 29.8, 28.7, 28.6 (C9, C10, C11), 28.5, 28.4, 28.3 (C6, C7, C8) 24.2 (C1'). Elemental Analysis: % Calc. for $C_{21}H_{39}NO_5S$: C 65.42, H 10.20, N 3.65%. Found C 65.12, H 10.18, N 3.99.

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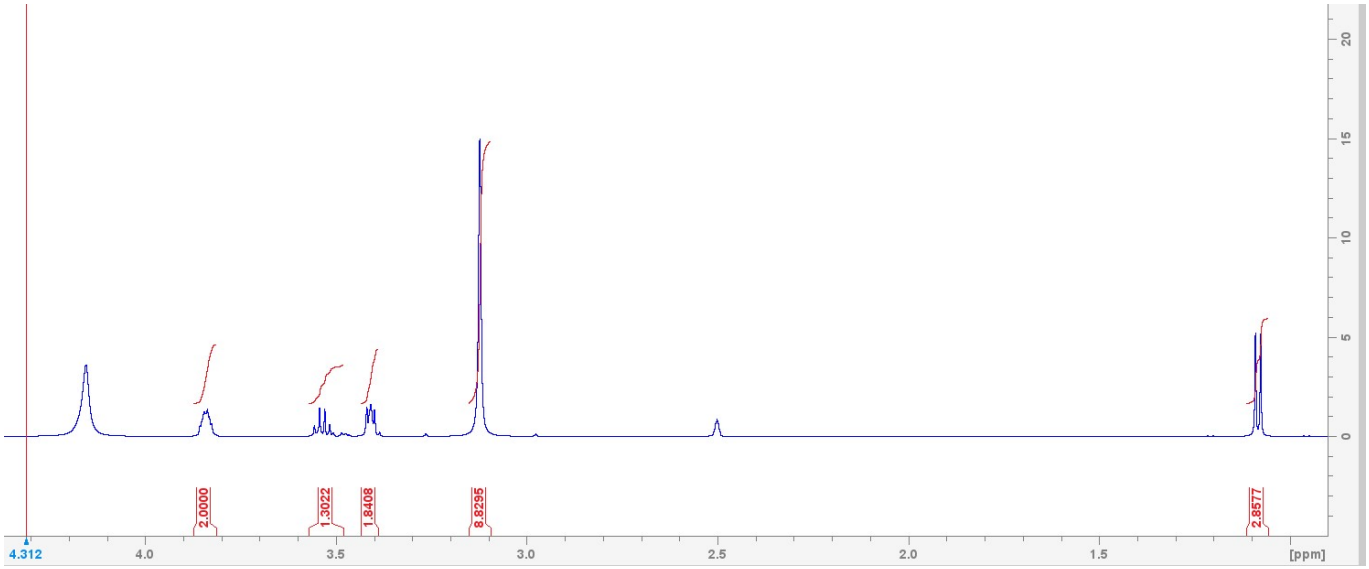
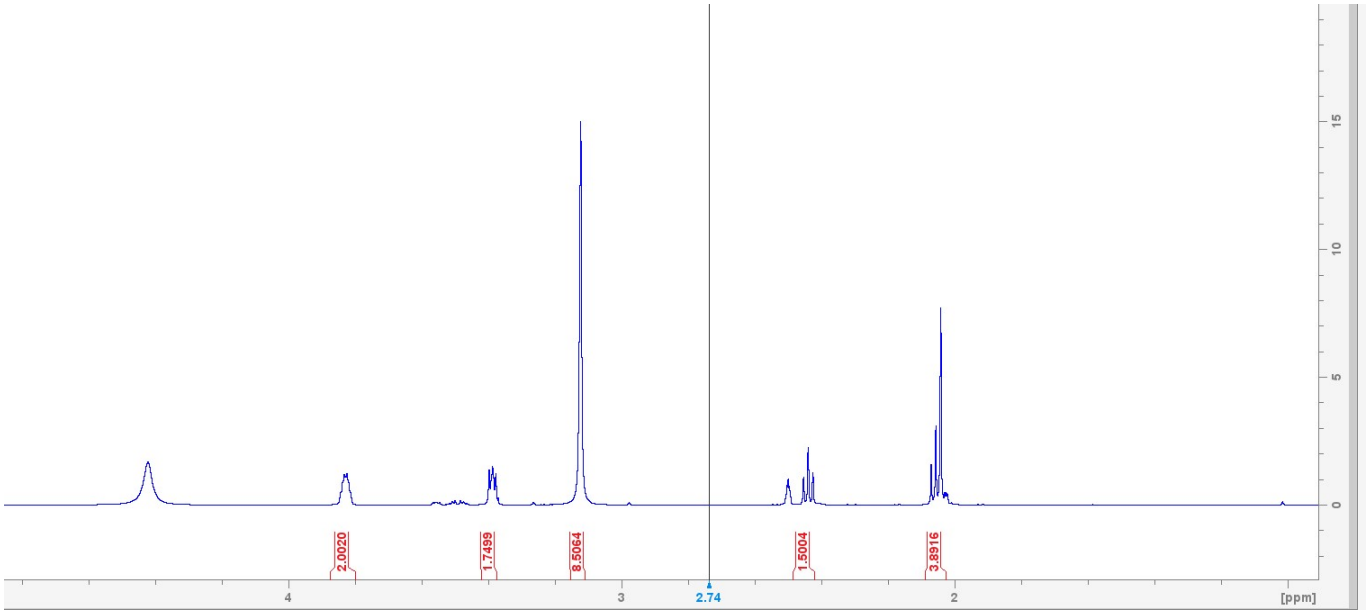
^{1}H spectra of the studied CHILs after synthesis

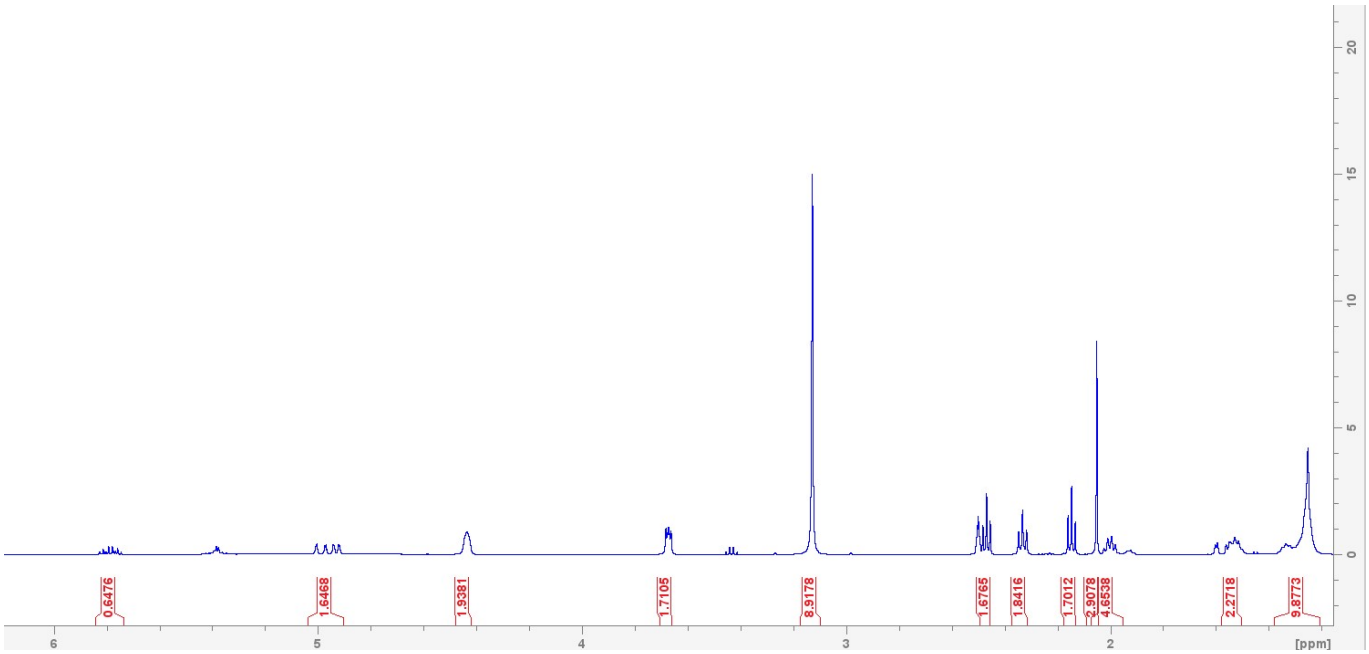
Chol Lac



Chol Lev



Chol-C11 Lev



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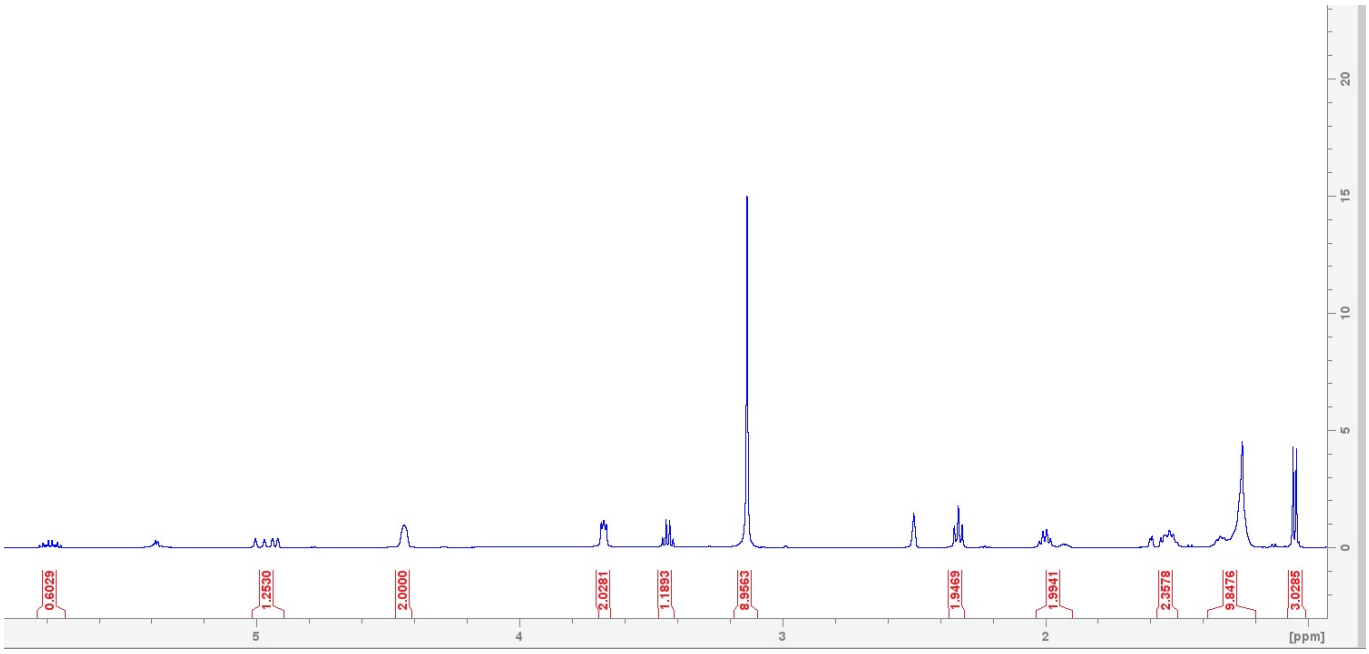
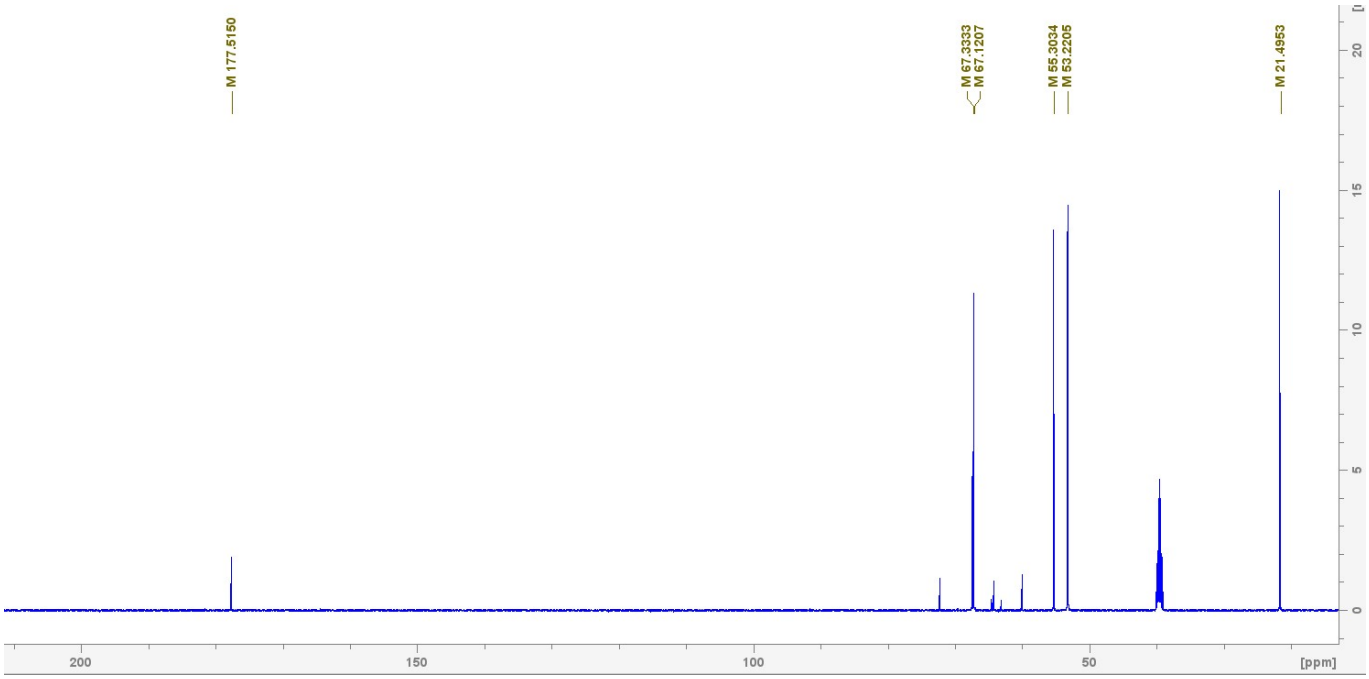
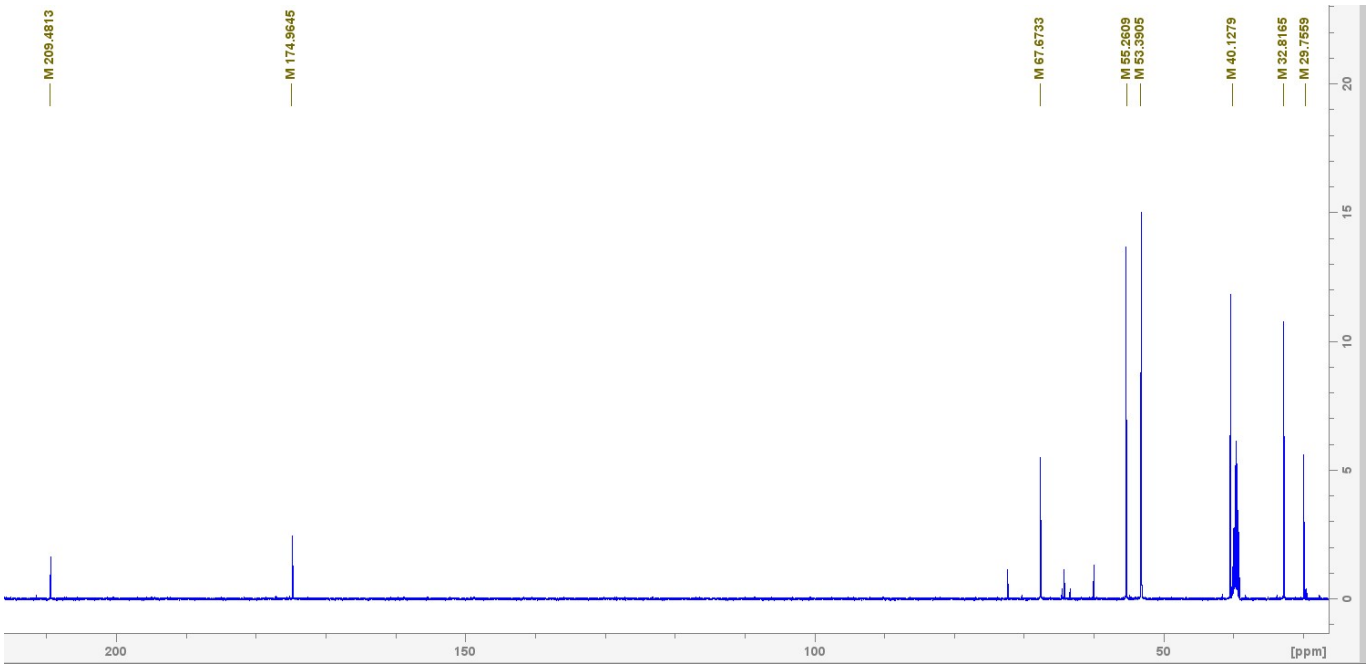


^{13}C NMR spectra of the studied CHILs after synthesis

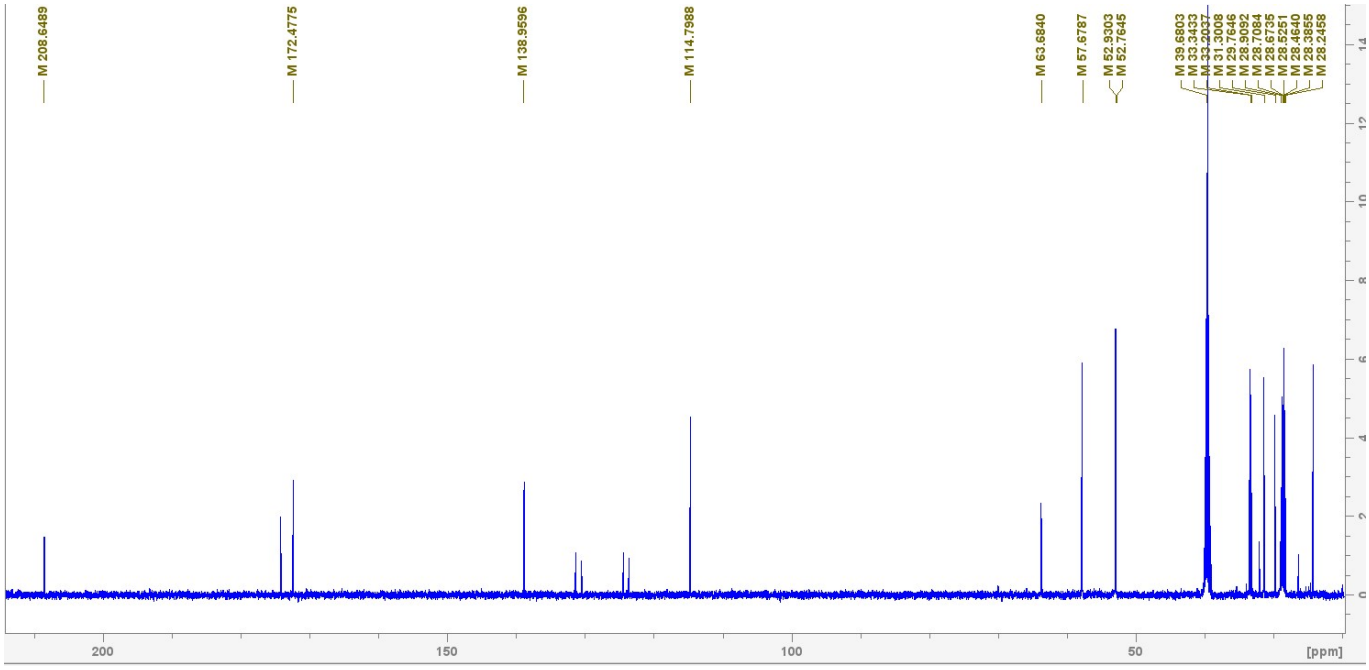
Chol Lac



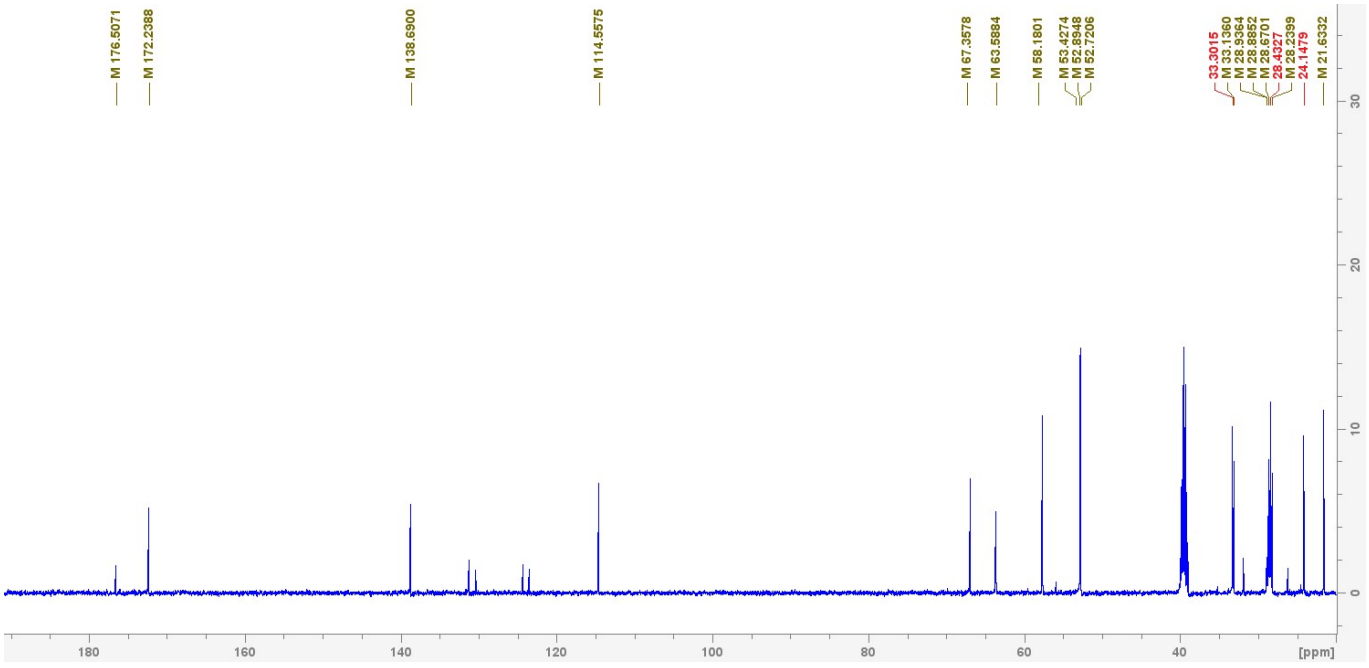
Chol Lev



Chol-C11 Lev

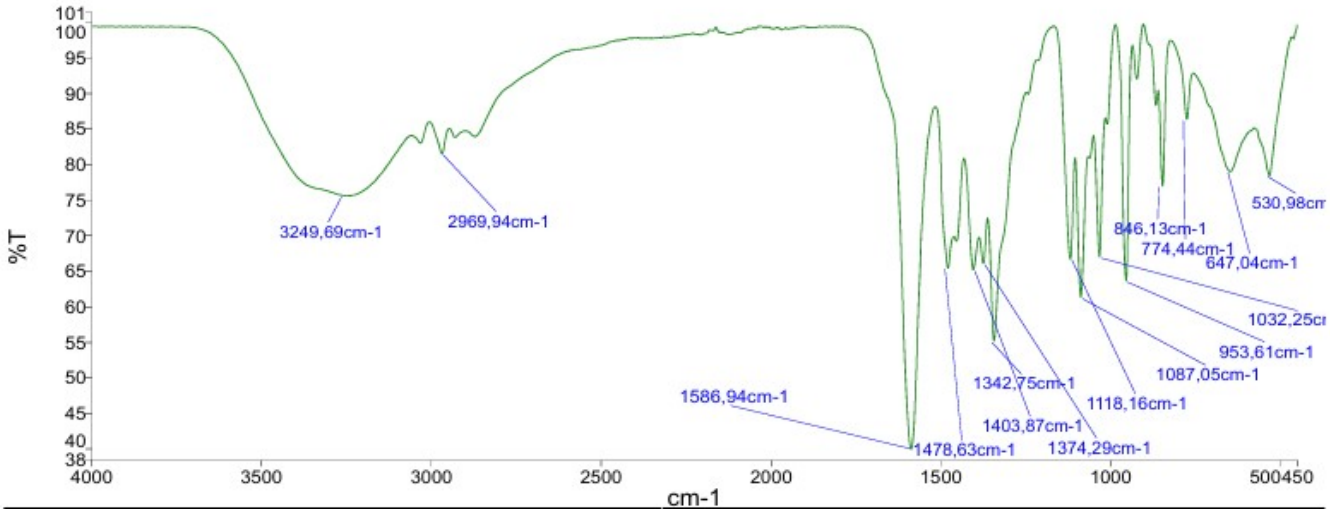


Chol-C11 Lac

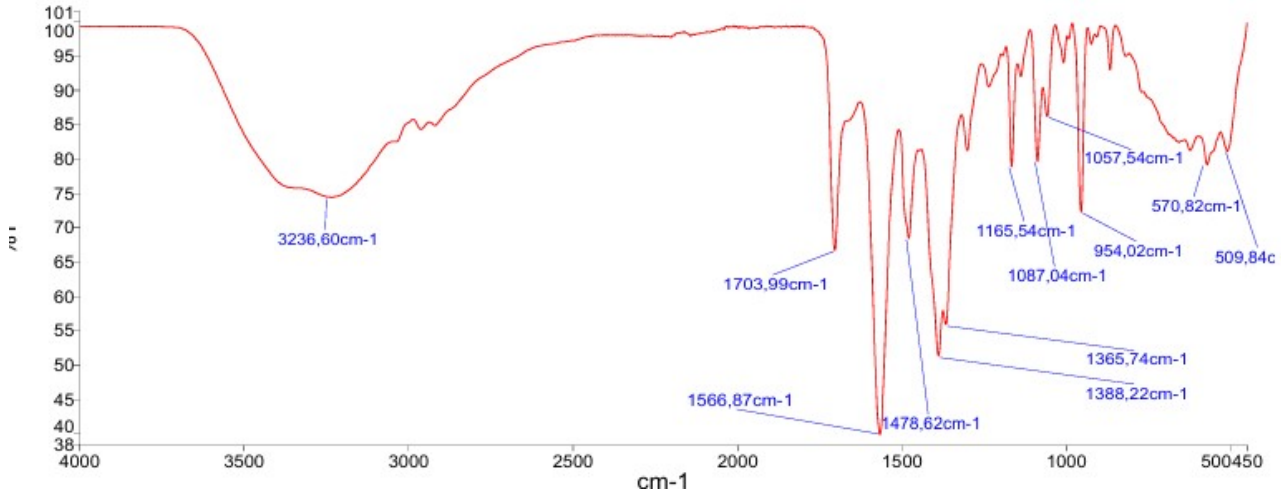


FTIR spectra of the studied CHILs after synthesis

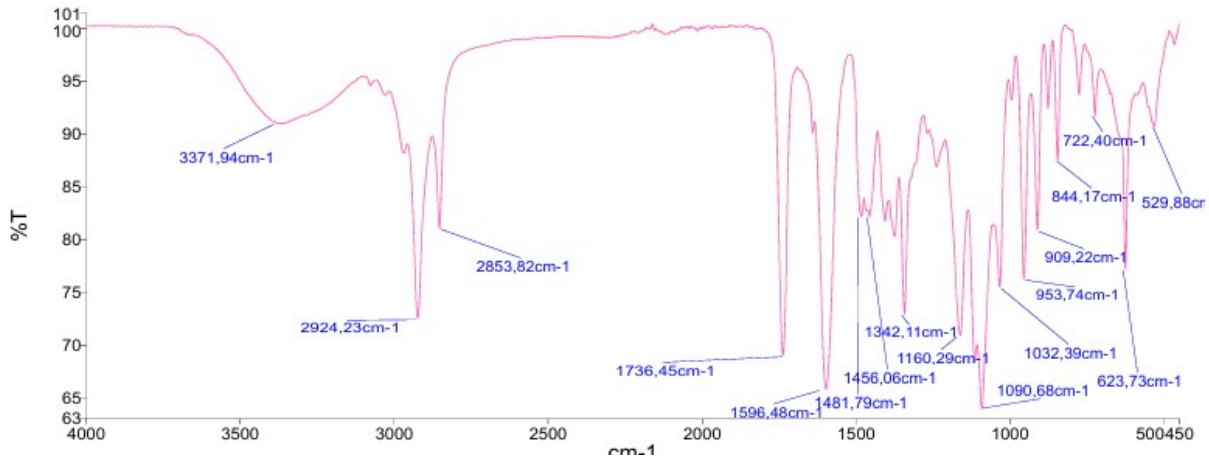
Chol Lac



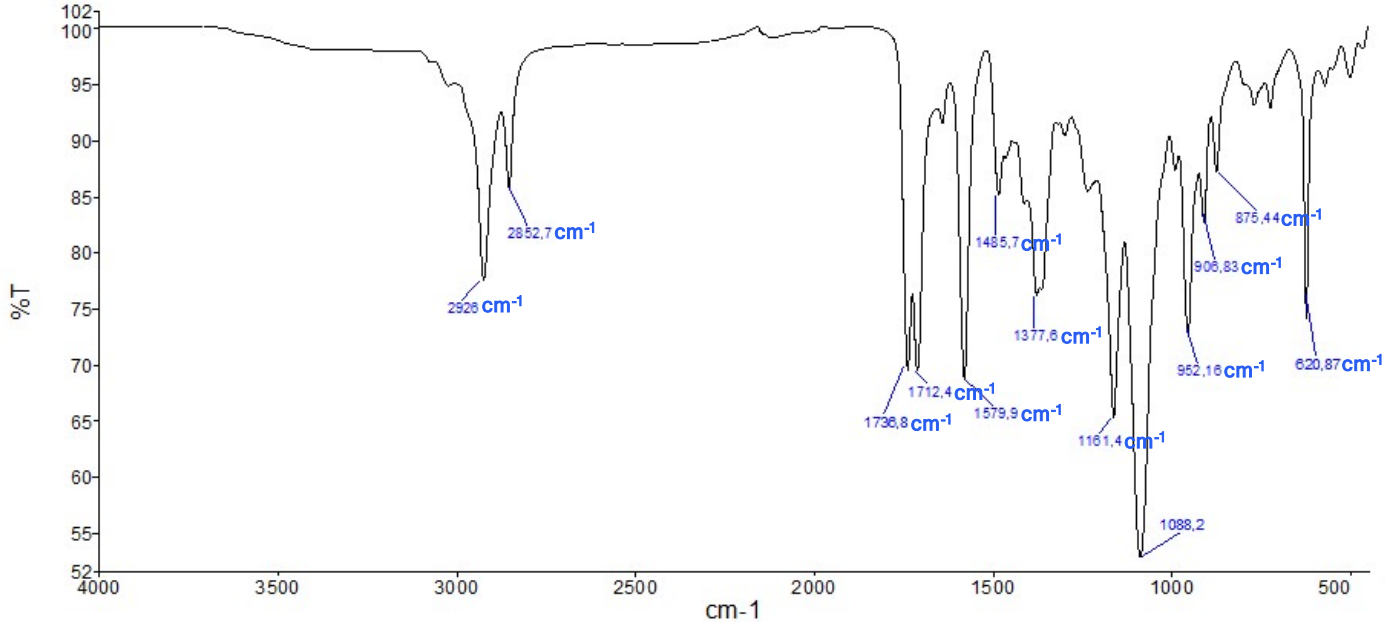
Chol Lev



Chol-C11 Lac



Chol-C11 Lev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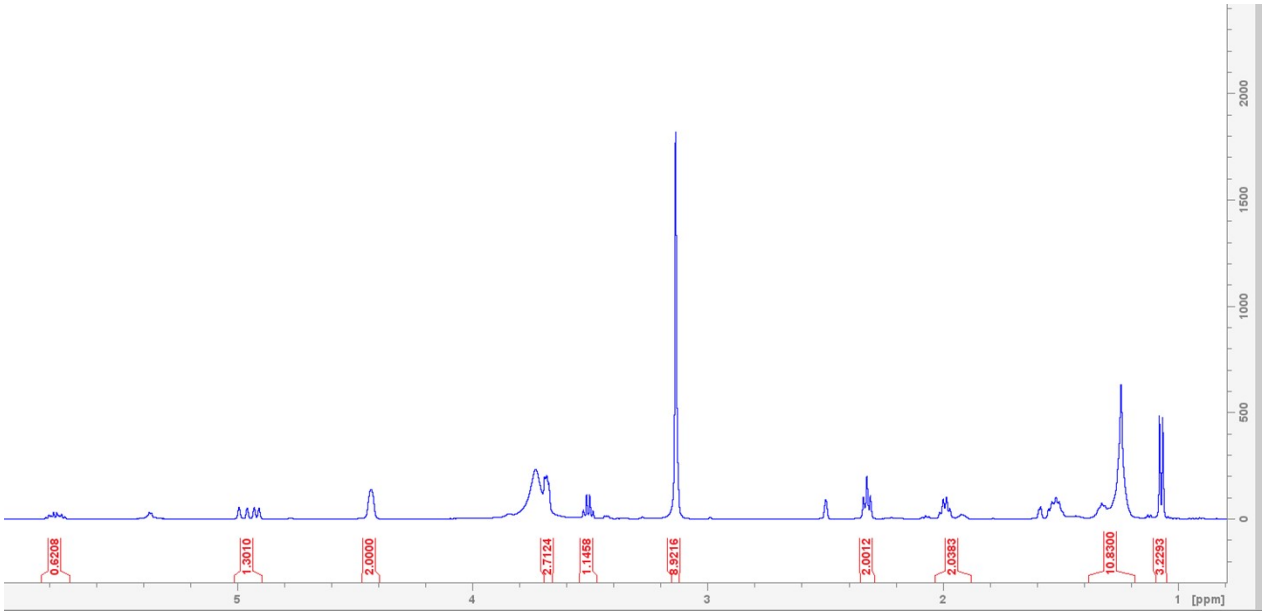
^{1}H NMR spectra of ester based choline ionic liquids after heat capacity measurements

Chol-C11 Lac



Chol-C11 Lev