

**ELECTRONIC SUPPLEMENTARY INFORMATION:**

**Cholinium-Amino Acid based Ionic Liquids: a new method of synthesis and physico-chemical characterization.**

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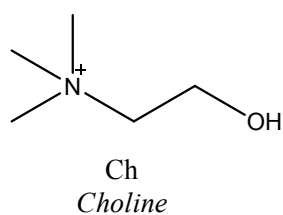
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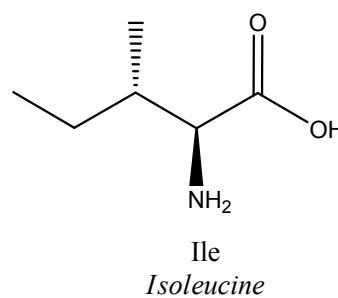
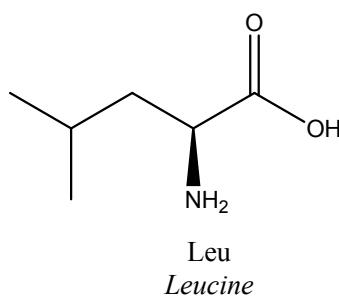
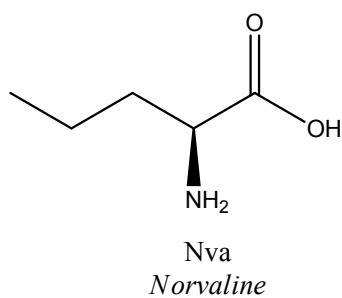
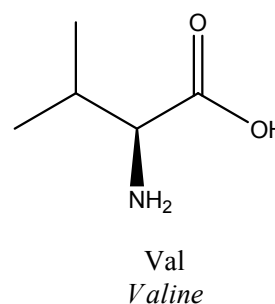
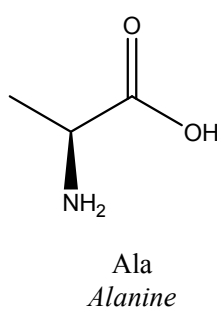
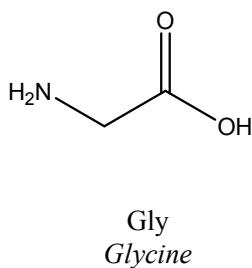
1. Structure of the cation and anions of [Ch][AA]ILs
2. <sup>1</sup>H NMR spectra for amino acid ionic liquids
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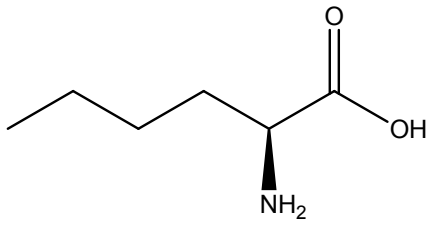
**1. Structure of the cation and anions of [Ch][AA]ILs**

**Cation**

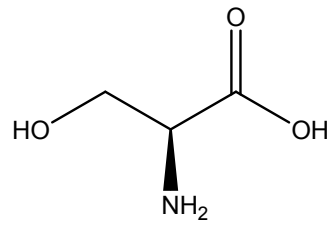


**Anions**

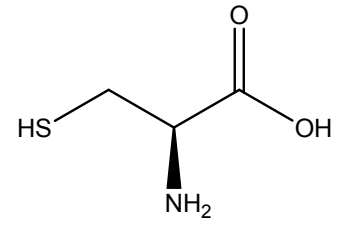




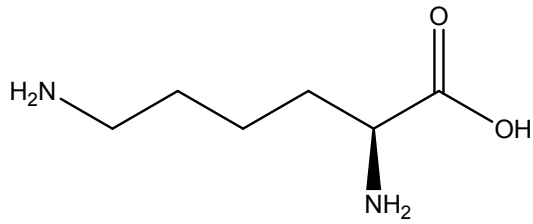
Nle  
*Norleucine*



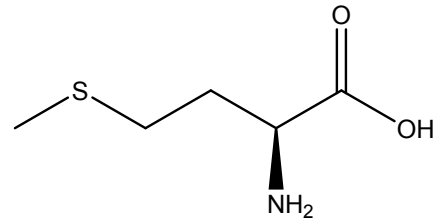
Ser  
*Serine*



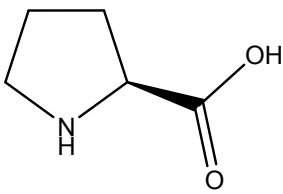
Cys  
*Cysteine*



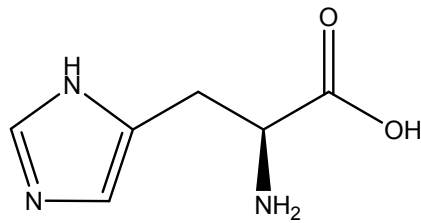
Lys  
*Lysine*



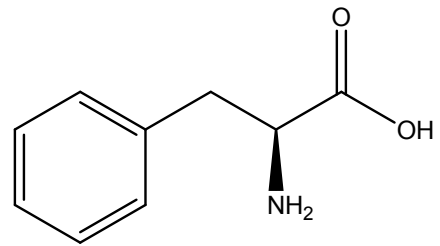
Met  
*Methionine*



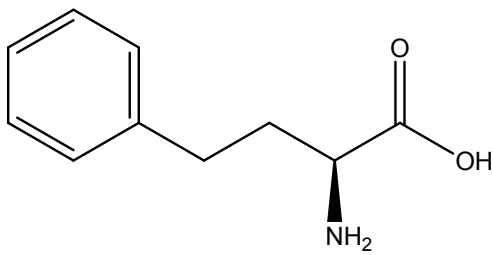
Pro  
*Proline*



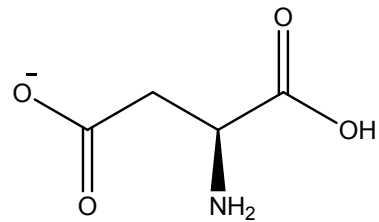
His  
*Histidine*



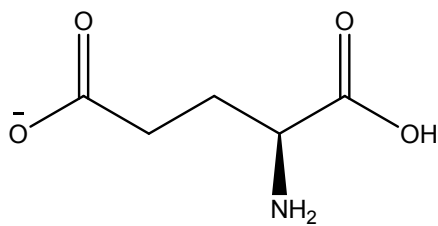
Phe  
*Phenylalanine*



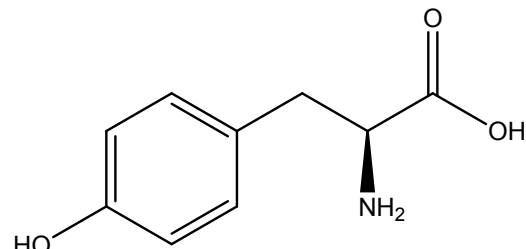
Hph  
*Homophenylalanine*



Asp  
*Aspartic Acid*

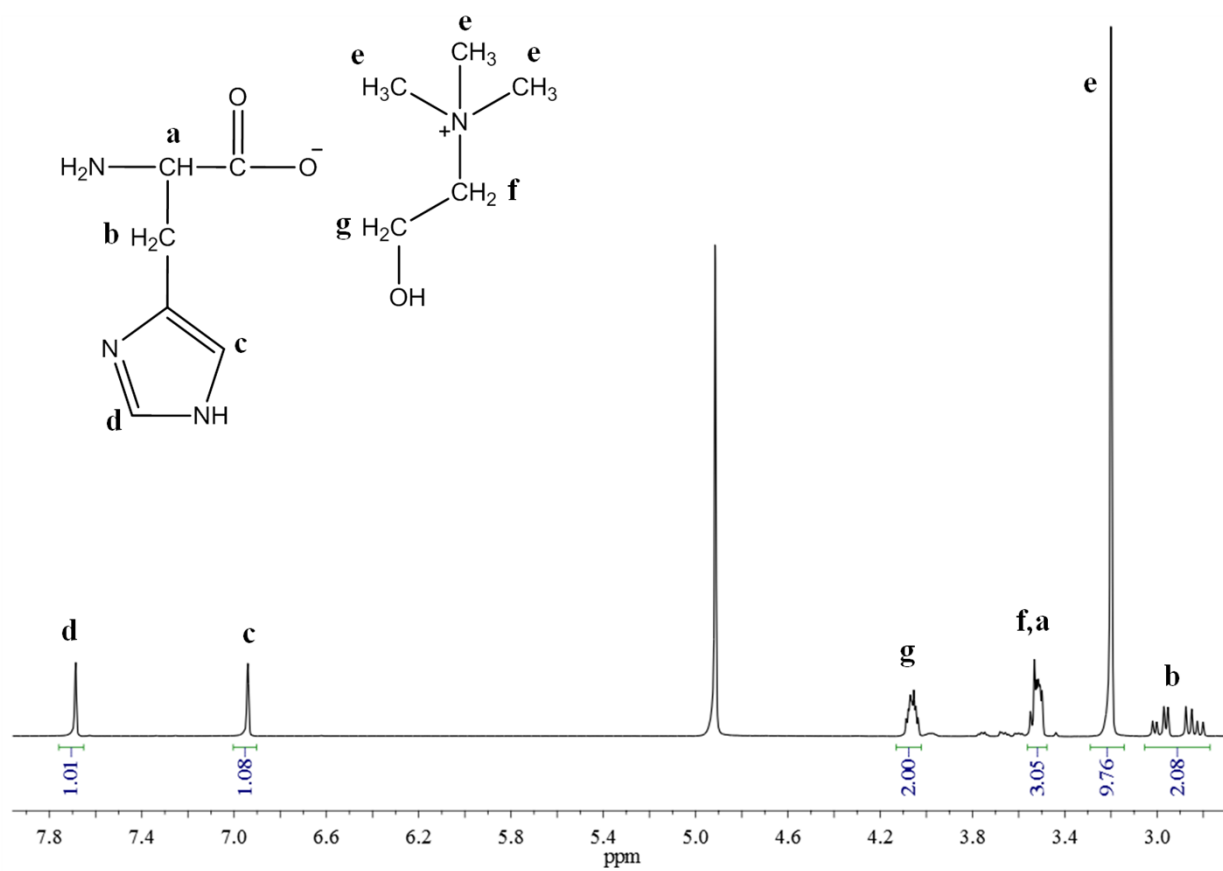


Glu  
*Glutamic Acid*

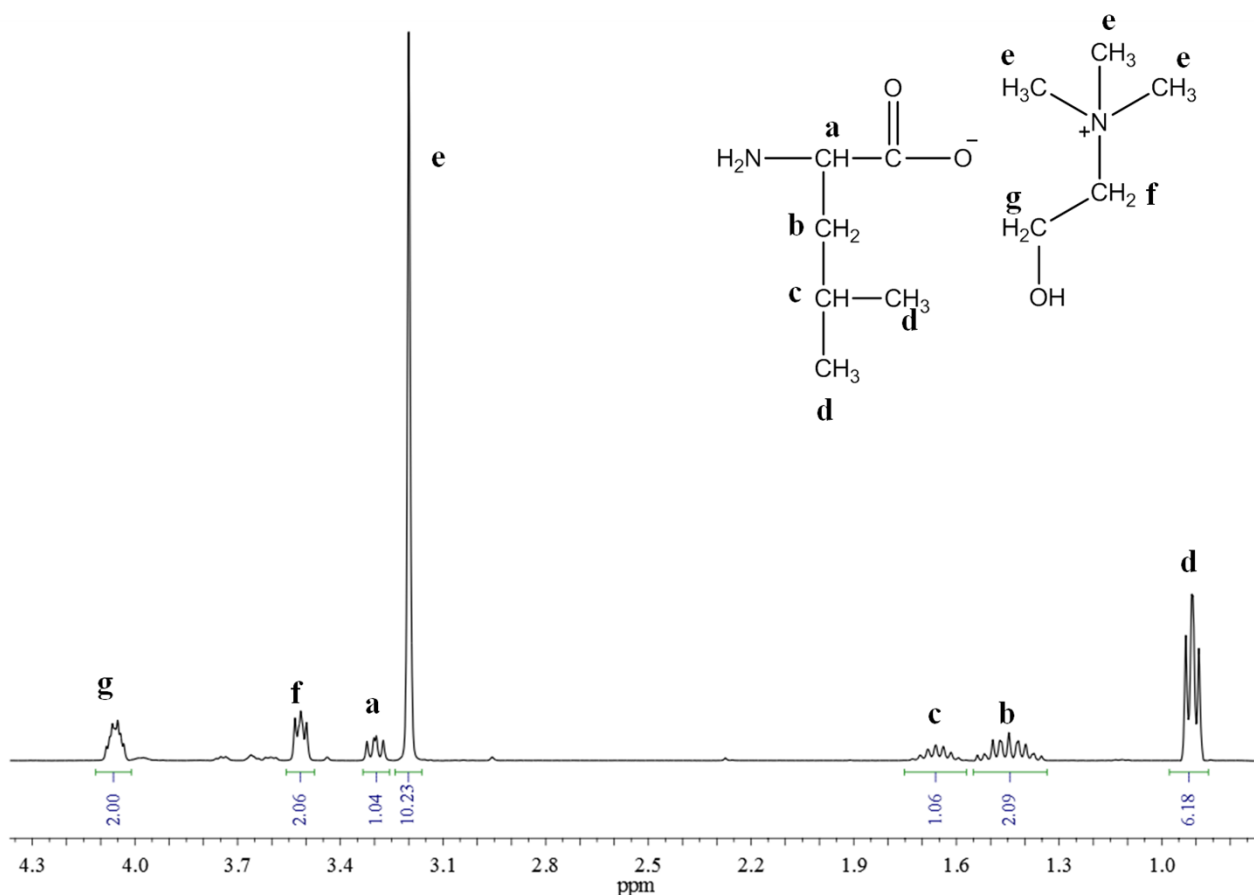


Tyr  
*Tyrosine*

## 2. $^1\text{H}$ NMR spectra for amino acid ionic liquids



**S 1**  $^1\text{H}$  NMR spectra for  $[\text{Ch}][\text{His}]$  in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ . The 1:1 stoichiometry of the IL is confirmed by the integrals ratio.



**S 2**  $^1\text{H}$  NMR spectra for [Ch][Leu] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ . Even if the excess of amino acid above the equivalence point has to be reduced due to solubility problems, 1:1 stoichiometry can be achieved.

**[Ch][Gly].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 3.19 (s, 2H,  $\text{CH}_2\text{-N}$ ), 3.22 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.52 – 3.55 (m, 2H,  $\text{CH}_2$ ), 4.06 – 4.10 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Ala].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 1.23 (d, 3H,  $\text{CH}_3$ ), 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.31 (q, 1H,  $\text{CH-N}$ ), 3.47 – 3.56 (m, 2H,  $\text{CH}_2$ ), 4.01 – 4.08 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Nva].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.91 (t, 3H,  $\text{CH}_3$ ), 1.24 – 1.40 (m, 2H,  $\text{CH}_2$ ), 1.49 – 1.57 (m, 2H,  $\text{CH}_2$ ), 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.26 (m, 1H,  $\text{CH-N}$ ), 3.51 (apparent t, 2H,  $\text{CH}_2$ ), 4.02 – 4.09 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Leu].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.92 (t, 6H,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 1.32 – 1.56 (m, 2H,  $\text{CH}_2$ ), 1.57 – 1.72 (m, 1H,  $\text{CH}$ ), 3.21 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.30 (q, 1H,  $\text{CH-N}$ ), 3.48 – 3.56 (apparent t, 2H,  $\text{CH}_2$ ), 4.05 – 4.09 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Ile].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.86 – 0.92 (t, 3H,  $\text{CH}_3$ ; d, 3H,  $\text{CH}_3$ , overlap), 1.09 – 1.18 (m, 1H,  $\text{CH}_2$ ), 1.38 – 1.44 (m, 1H,  $\text{CH}_2$ ), 1.64 – 1.70 (m, 1H,  $\text{CH}$ ), 3.10 (d, 1H,  $\text{CH-N}$ ), 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.51 (apparent t, 2H,  $\text{CH}_2$ ), 4.03 – 4.07 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Nle].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.88 (t, 3H,  $\text{CH}_3$ ), 1.20 – 1.38 (m, 4H,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 1.51 – 1.66 (m, 2H,  $\text{CH}_2$ ), 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.27 (m, 1H,  $\text{CH-N}$ ), 3.51 (apparent t, 2H,  $\text{CH}_2$ ), 4.02 – 4.09 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Ser].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.34 (t, 1H,  $\text{CH-N}$ ), 3.53 (apparent t, 2H,  $\text{CH}_2$ ), 3.72 (dd, 2H,  $\text{CH}_2$ ), 4.02 – 4.09 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Lys].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 1.27 – 1.42 (m, 2H,  $\text{CH}_2$ ), 1.42 – 1.54 (m, 2H,  $\text{CH}_2$ ), 1.55 – 1.67 (m, 2H,  $\text{CH}_2$ ), 2.69 (t, 2H,  $\text{CH}_2$ ), 3.22 (s, 10H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH-N}$ ), 3.52 (apparent t, 2H,  $\text{CH}_2$ ), 3.87 – 4.13 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Cys].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 2.73 – 2.91 (dd, 2H,  $\text{CH}_2$ ), 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.50 – 3.55 (t, 1H,  $\text{CH-N}$ ), 3.52 (apparent t, 2H,  $\text{CH}_2$ ), 4.03 – 4.09 (m, 2H,  $\text{CH}_2$ ).

**[Ch][Met].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 1.72 – 1.99 (m, 1H,  $\text{CH}_2$ ), 2.11 (s, 3H,  $\text{CH}_3$ ), 2.56 (t, 2H,  $\text{CH}_2$ ), 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.34 (t, 1H,  $\text{CH-N}$ ), 3.48 – 3.55 (apparent t, 2H,  $\text{CH}_2$ ), 4.05 – 4.10 (m, 2H,  $\text{CH}_2$ ).

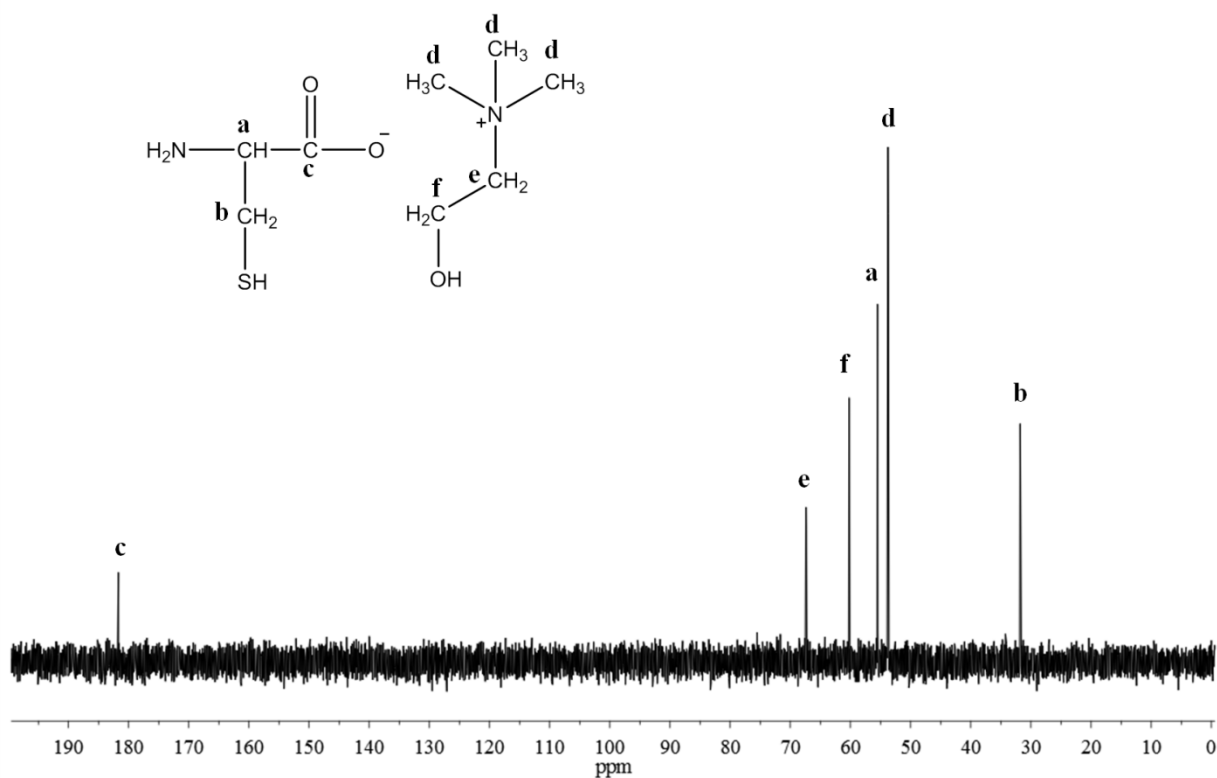
**[Ch][Pro].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 1.69 – 1.80 (m, 3H,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 2.06 – 2.18 (m, 1H,  $\text{CH}_2$ ), 2.74 – 2.87 (m, 1H,  $\text{CH}_2\text{-N}$ ), 3.01 – 3.14 (m, 1H,  $\text{CH}_2\text{-N}$ ), 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.47 – 4.47 (m, 3H,  $\text{CH-N}$ ,  $\text{CH}_2$ ), 4.03 – 4.08 (m, 2H,  $\text{CH}_2$ ).

**[Ch][His].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 2.79– 2.84 (m, 1H,  $\text{CH}_2$ ), 2.94– 2.99 (m, 1H,  $\text{CH}_2$ ), 3.18 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.46– 3.55 (m, 3H,  $\text{CH}_2$ ,  $\text{CH-N}$ ), 4.02– 4.06 (m, 2H,  $\text{CH}_2$ ), 6.94 (s, 1H,  $=\text{CH}$ ), 7.69 (s, 1H,  $=\text{CH}$ ).

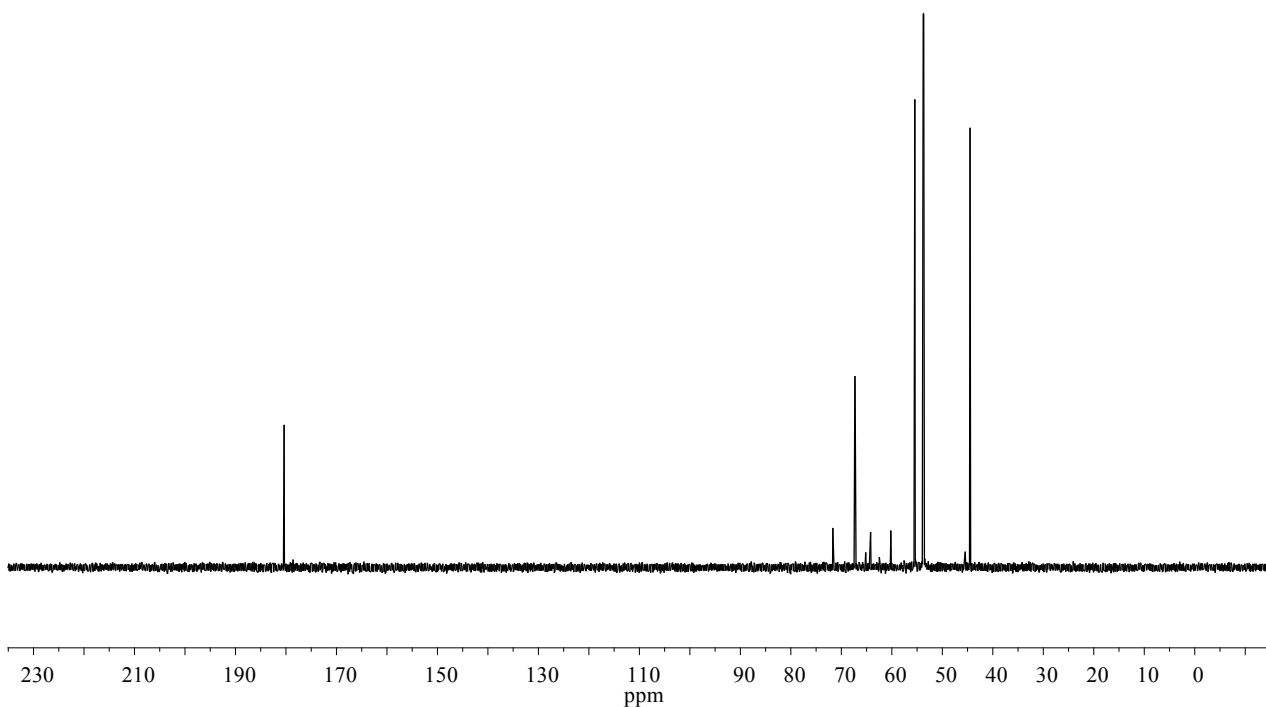
**[Ch][Phe].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 2.85 – 2.99 (m, 1H,  $\text{CH}_2$ ), 3.02 – 3.14 (m, 1H,  $\text{CH}_2$ ), 3.21 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.51 (m, 2H,  $\text{CH}_2$ ), 3.56 (t, 1H,  $\text{CH-N}$ ), 4.05 – 4.09 (m, 2H,  $\text{CH}_2$ ), 7.32 – 7.50 (m, 5H,  $\text{C}_6\text{H}_5$ ).

**[Ch][Hph].**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 1.80 – 2.00 (m, 2H,  $\text{CH}_2$ ), 2.61 – 2.76 (m, 2H,  $\text{CH}_2$ ), 3.21 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.31(t, 1H,  $\text{CH-N}$ ), 3.50 (m, 2H,  $\text{CH}_2$ ), 4.01 – 4.09 (m, 2H,  $\text{CH}_2$ ), 7.26 – 7.50 (m, 5H,  $\text{C}_6\text{H}_5$ ).

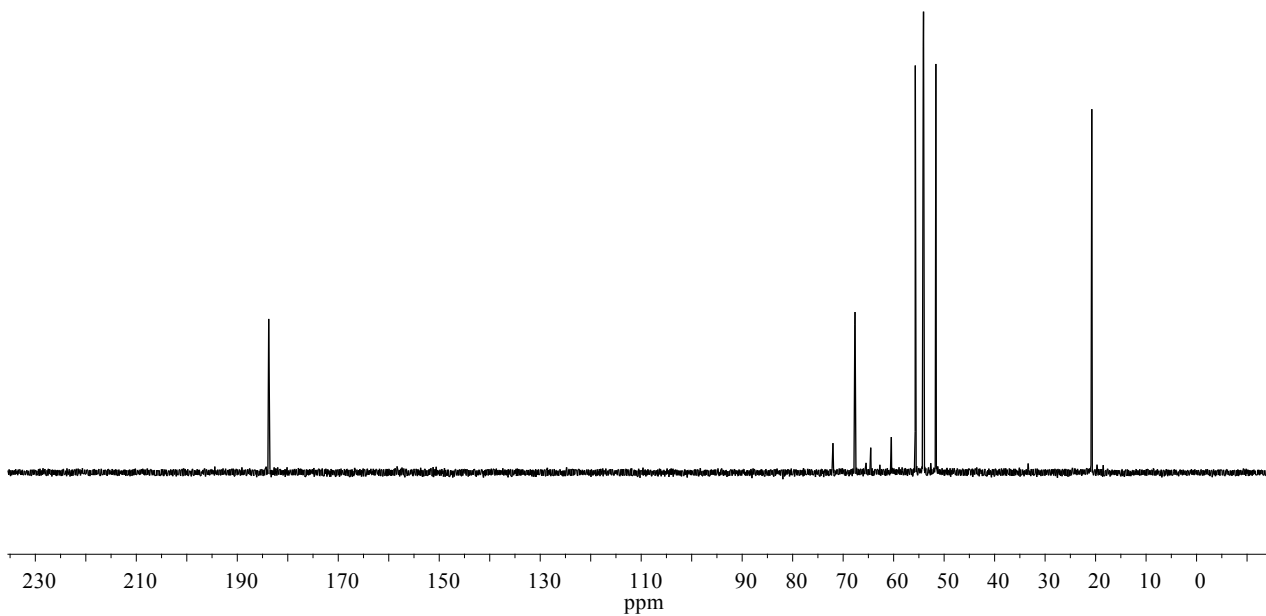
### 3. $^{13}\text{C}$ NMR spectra for amino acid ionic liquids



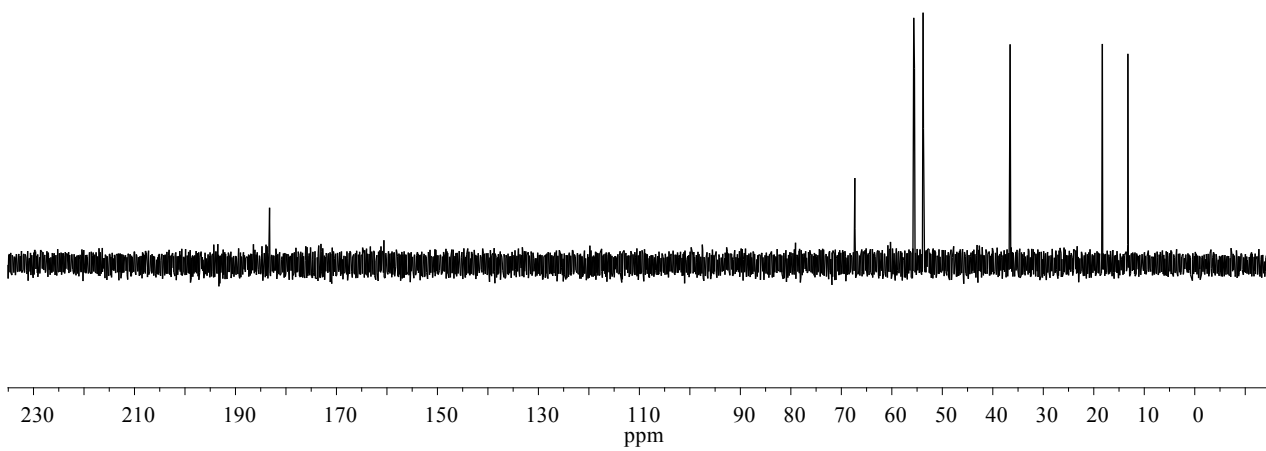
**S 3**  $^{13}\text{C}$  NMR spectra for [Ch][Cys] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ . The absence of a signal for a C bound to S-S demonstrates that no reductions of Cysteine occurred during the [Ch][Cys] preparation process.



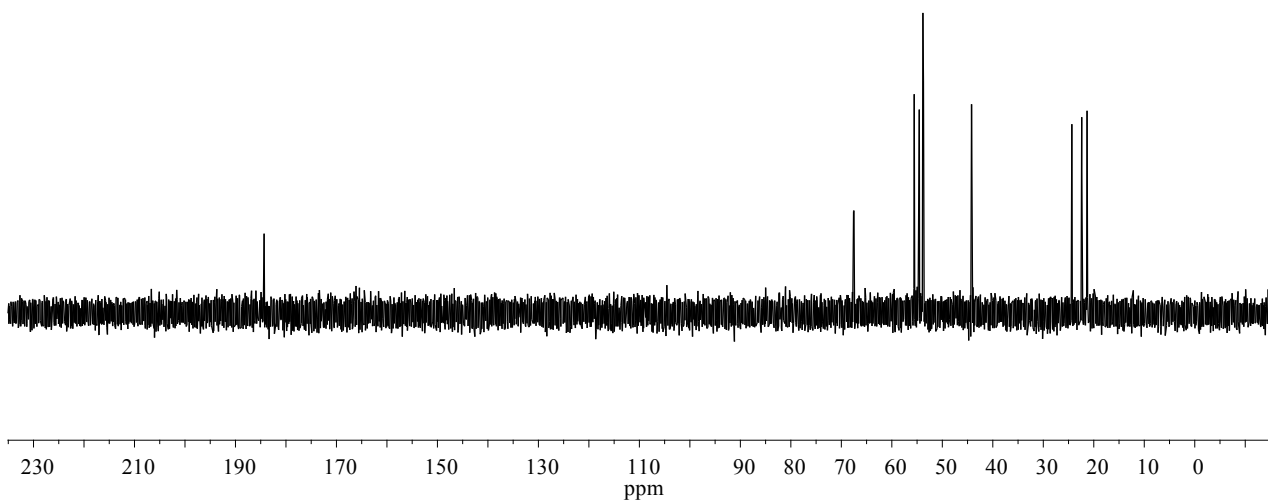
**S4**  $^{13}\text{C}$  NMR spectra for [Ch][Gly] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



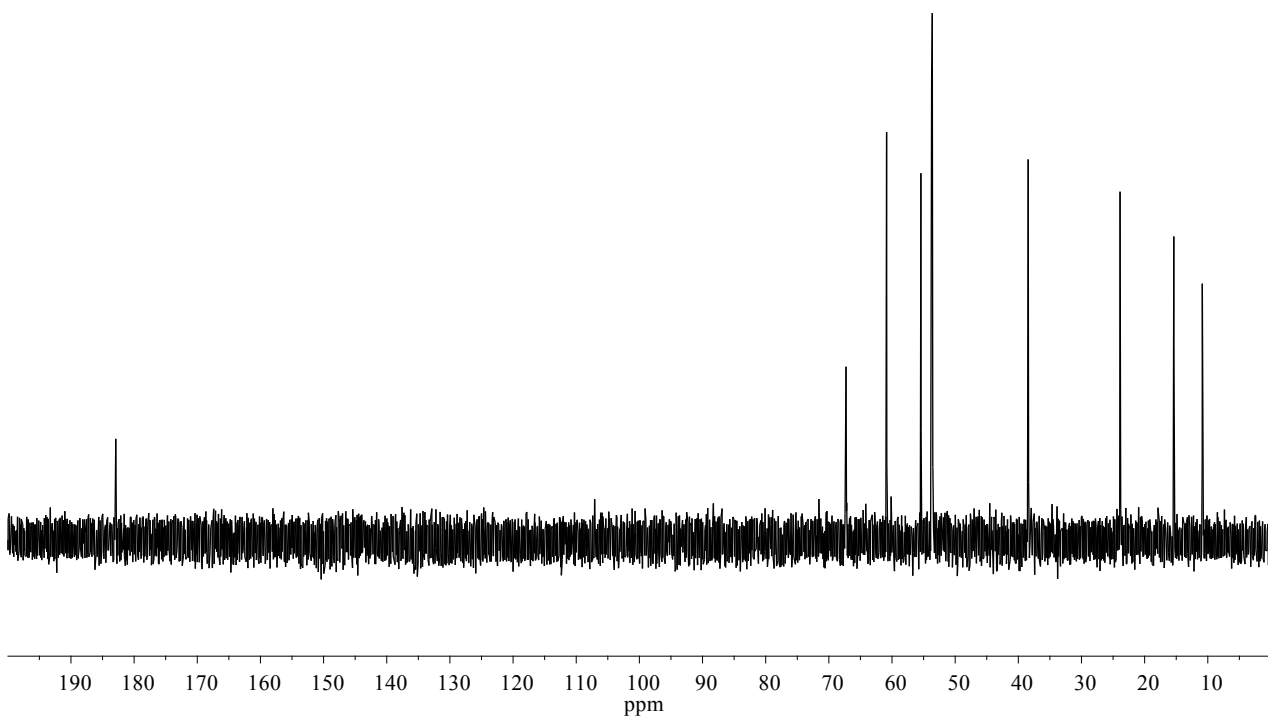
**S5**  $^{13}\text{C}$  NMR spectra for [Ch][Ala] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



**S6**  $^{13}\text{C}$  NMR spectra for [Ch][Nva] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .

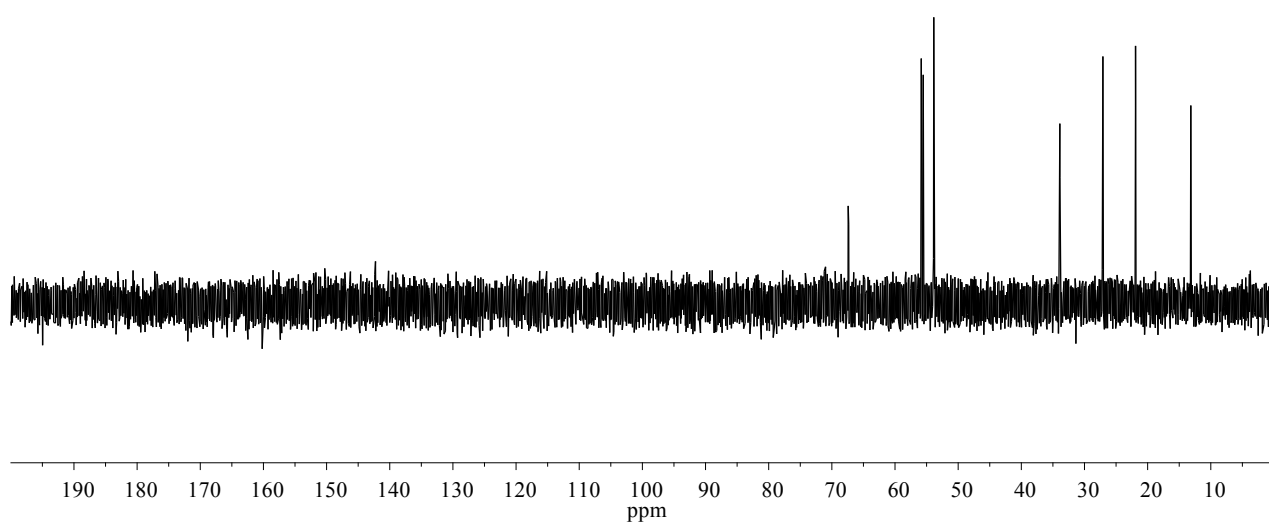


**S7**  $^{13}\text{C}$  NMR spectra for [Ch][Leu] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .

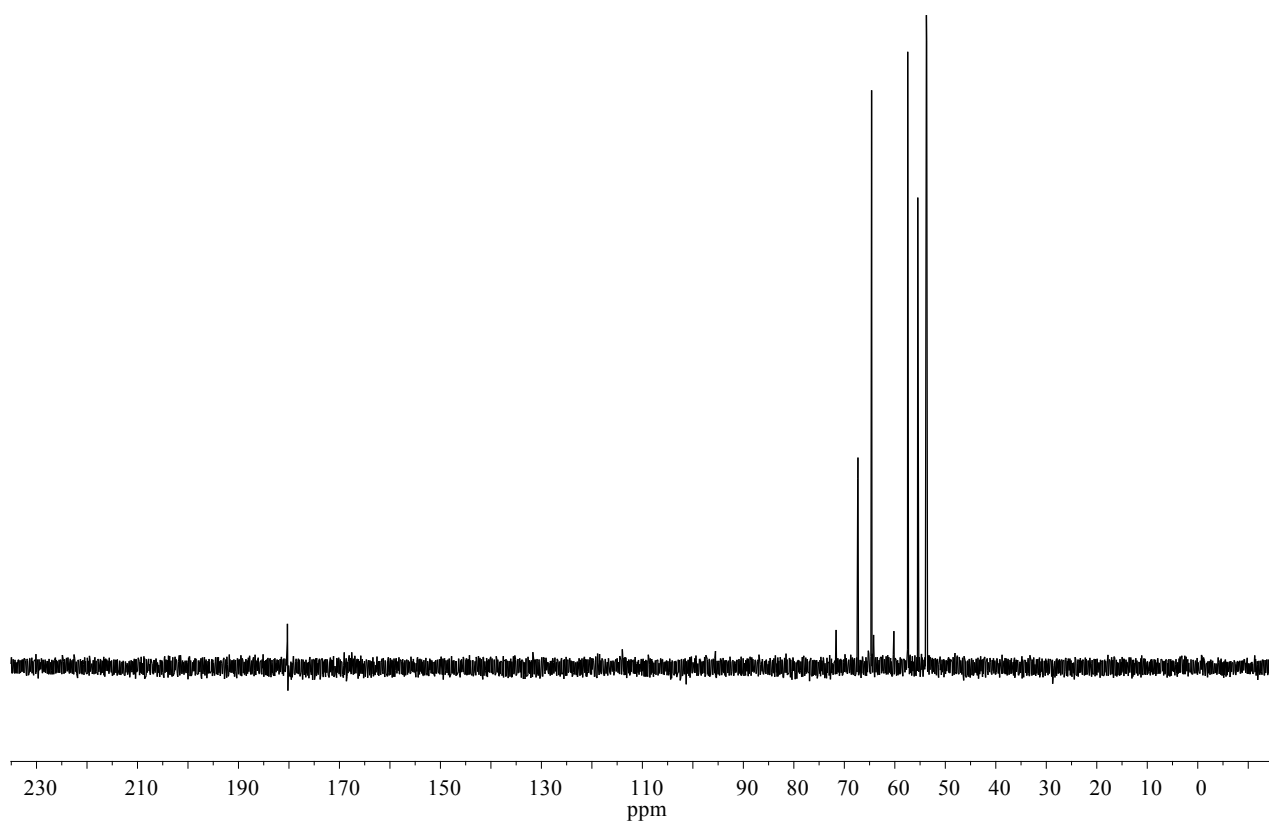


**S8**  $^{13}\text{C}$  NMR spectra for [Ch][Ile] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .

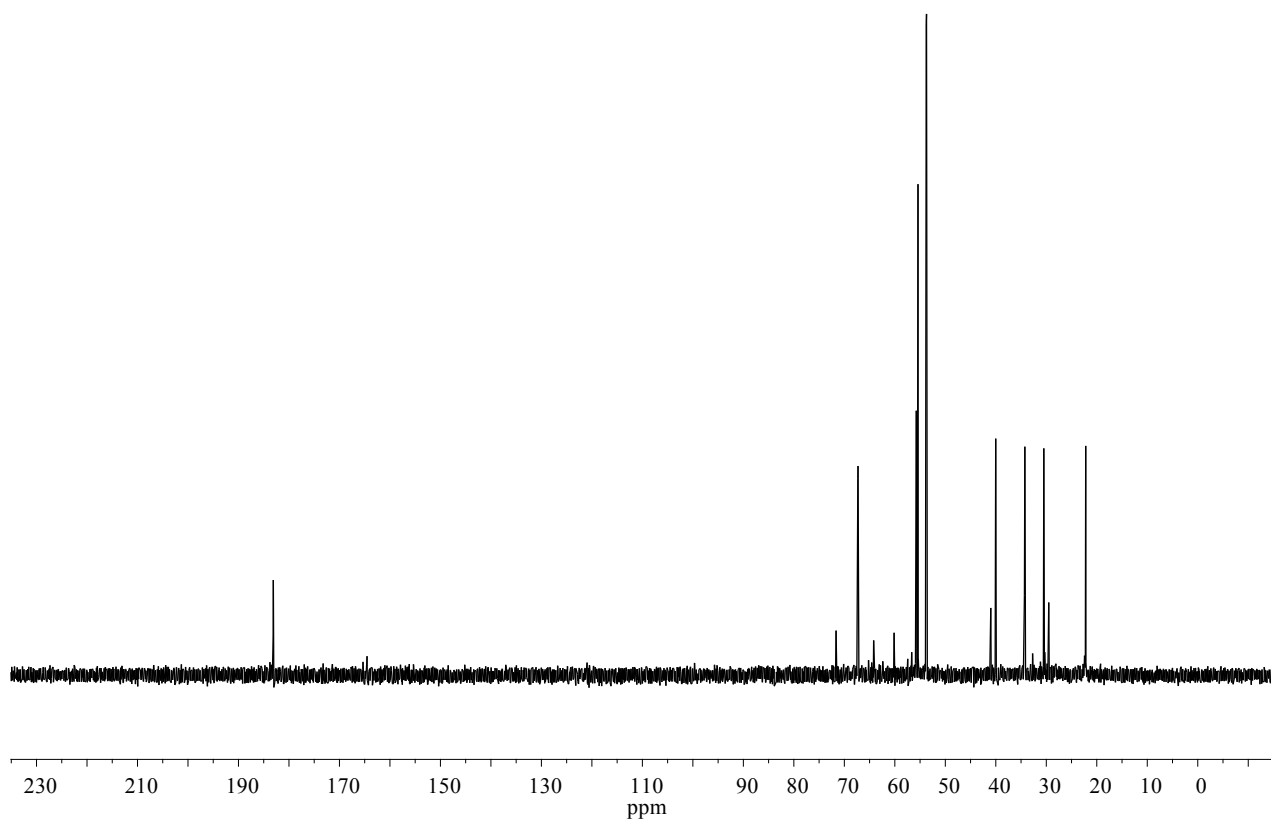




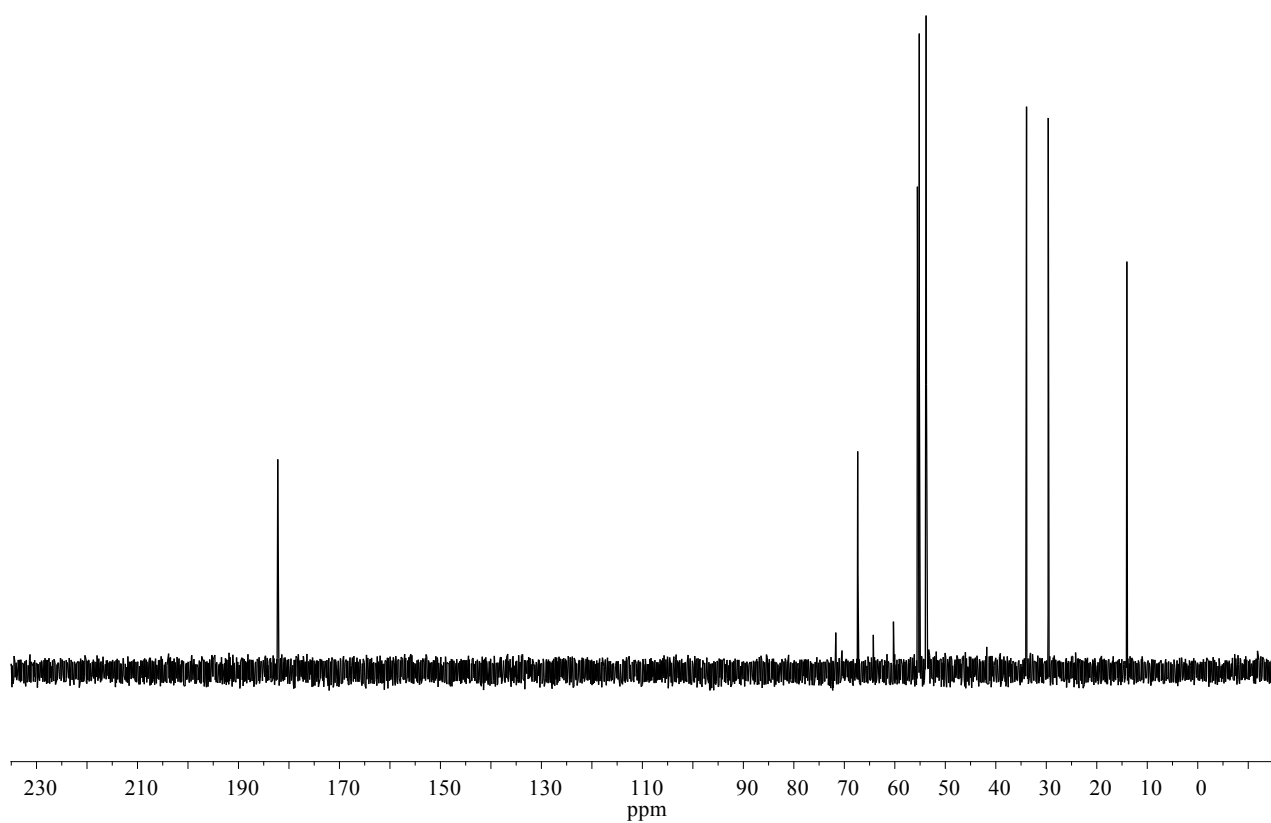
**S9**  $^{13}\text{C}$  NMR spectra for [Ch][Nle] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



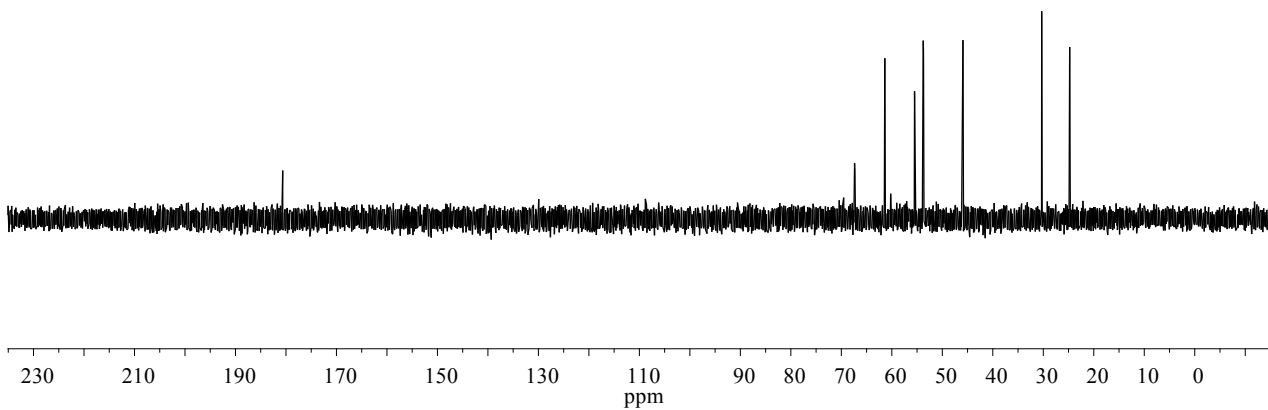
**S10**  $^{13}\text{C}$  NMR spectra for [Ch][Ser] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



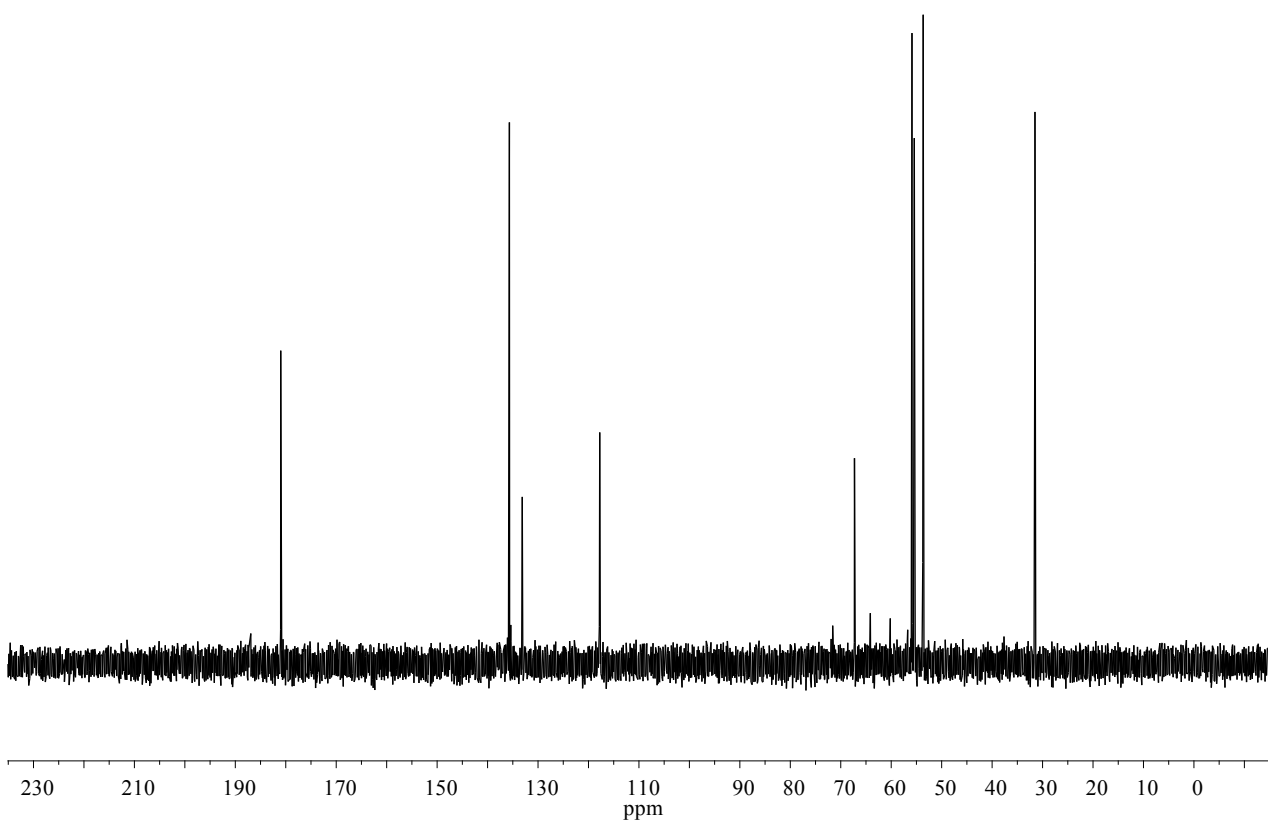
**S11**  $^{13}\text{C}$  NMR spectra for [Ch][Lys] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



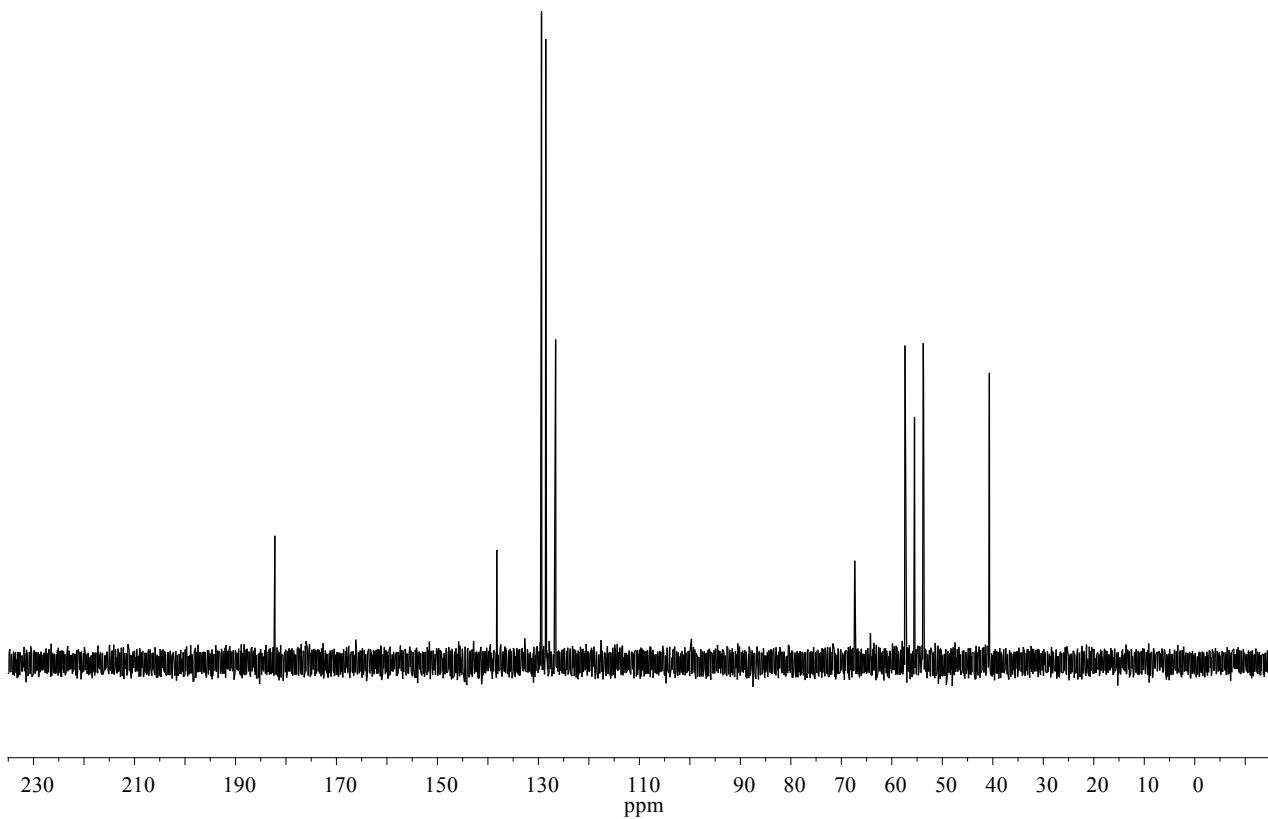
**S12**  $^{13}\text{C}$  NMR spectra for [Ch][Met] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



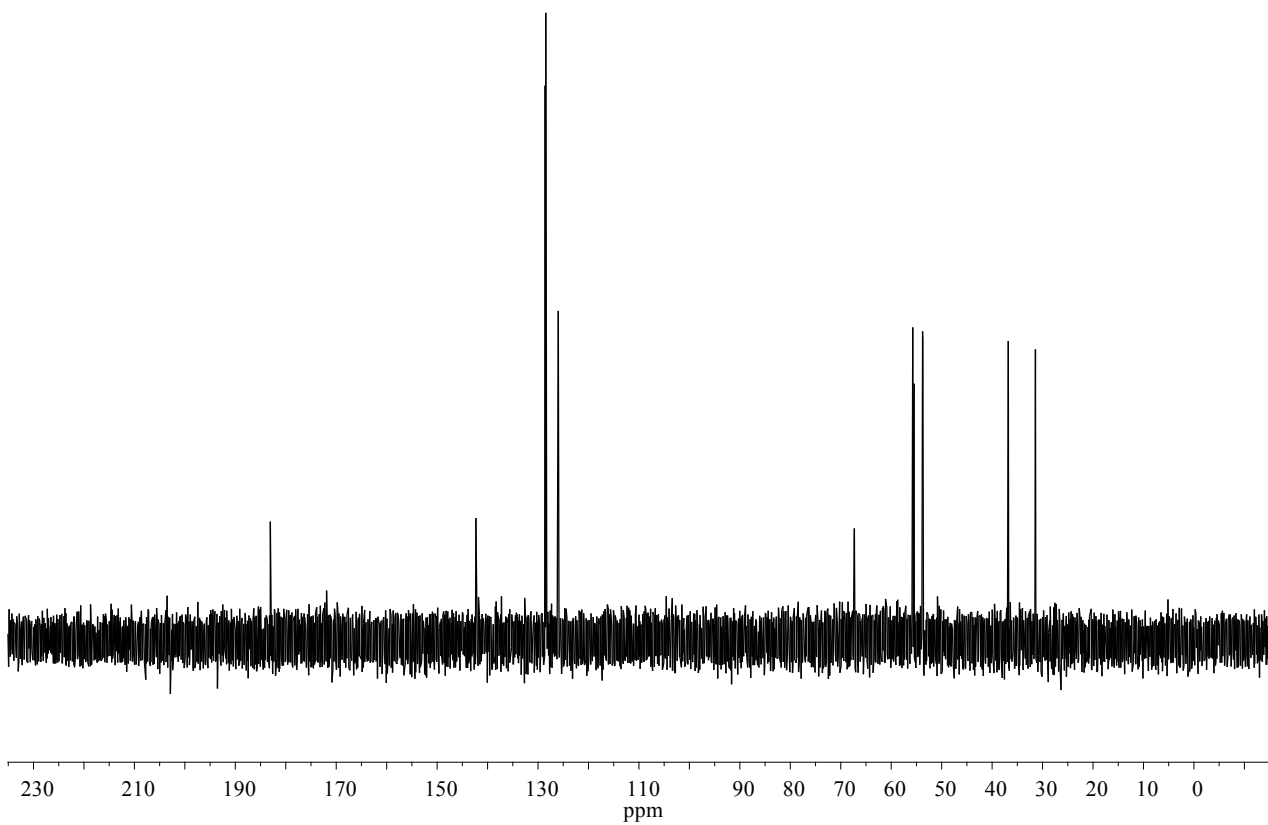
**S12**  $^{13}\text{C}$  NMR spectra for [Ch][Pro] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



**S12**  $^{13}\text{C}$  NMR spectra for [Ch][His] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



**S12**  $^{13}\text{C}$  NMR spectra for [Ch][Phe] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .



**S12**  $^{13}\text{C}$  NMR spectra for [Ch][Hph] in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ .

#### 4. Fitting parameters

**Table S1** Fitting Parameters Values of eq. 4 and standard deviations  $\sigma_r$

	$A_2$	$A_3$	R	$\sigma_r$
<b>ChGly</b>	1.56747	-0.000221	0.994671	0.000264
<b>ChAla</b>	1.57642	-0.0002705	0.998269	0.000184
<b>ChNva</b>	1.56079	-0.0002392	0.998244	0.000164
<b>ChLeu</b>	1.56469	-0.0002564	0.999021	0.000132
<b>ChIle</b>	1.52551	-0.0001224	0.992725	0.000172
<b>ChNle</b>	1.56057	-0.0002488	0.999725	6.78E-05
<b>ChSer</b>	1.57008	-0.0002143	0.997656	0.000168
<b>ChLys</b>	1.56365	-0.0001642	0.983666	0.000342
<b>ChCys</b>	1.59782	-0.0002345	0.999253	0.000103
<b>ChMet</b>	1.60871	-0.0002914	0.997793	0.000220
<b>ChPro</b>	1.60905	-0.0003406	0.984309	0.000700
<b>ChHis</b>	1.60550	-0.0002238	0.999695	6.20E-05
<b>ChPhe</b>	1.61804	-0.0002583	0.992489	0.000363
<b>ChHph</b>	1.61975	-0.0002741	0.999671	7.90E-05

$$\sigma_r = \sqrt{\frac{\sum_i [(n_D^{exp} - n_D^{cal})/n_D^{cal}]^2}{n - v}}$$

where  $n$  and  $v$  are the number of experimental points and adjustable parameters, respectively.

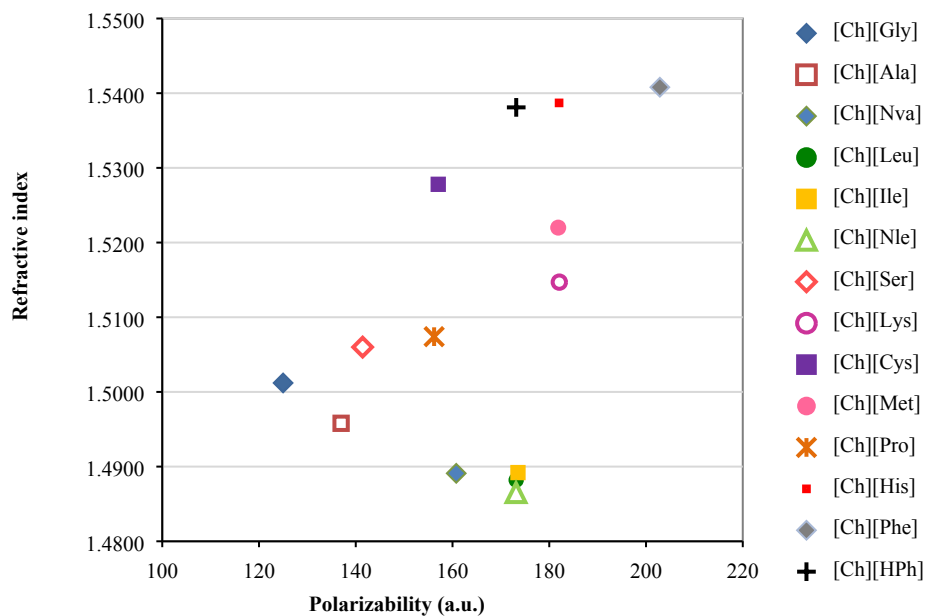
**Table S2** Fitting Parameters Values of eq. 5 and standard deviations  $\sigma_r$ 

	<b>A<sub>4</sub></b>	<b>A<sub>5</sub></b>	<b>A<sub>6</sub></b>	<b>R</b>	<b><math>\sigma_r</math></b>
[Ch][Gly]	4.28E+06	1383.7	169.99	0.99995	0.02076
[Ch][Ala]	3.89E+06	1359.3	173.39	0.99995	0.02238
[Ch][Ser]	1.40E+06	1238.9	188.91	0.99997	0.04134
[Ch][Lys]	3.17E+07	2398.9	160.23	0.99999	0.04013
[Ch][Pro]	1.41E+06	1300.9	191.70	0.99997	0.05884
[Ch][Met]	3.17E+07	2278.2	129.13	0.99994	0.04125
[Ch][Cys]	2.69E+04	954.71	197.25	0.99926	0.08028
[Ch][Phe]	9.97E+05	1128.3	207.43	0.99999	0.11121
[Ch][His]	7.10E+05	1396.0	206.88	0.99962	0.23676
[Ch][Leu]	2.67E+06	1472.6	178.15	0.99999	0.01399
[Ch][Ile]	1.55E+06	1387.8	181.97	0.99997	0.07411
[Ch][Nle]	3.29E+05	910.09	201.92	0.99990	0.14091
[Ch][Nva]	2.26E+06	1389.3	174.18	0.99999	0.02196
[Ch][Hph]	2.15E+06	1395.5	190.06	0.99997	0.10141

$$\sigma_r = \sqrt{\frac{\sum_i [(\sigma_i^{exp} - \sigma_i^{cal}) / \sigma_i^{cal}]^2}{n - \nu}}$$

where  $n$  and  $\nu$  are the number of experimental points and adjustable parameters, respectively.

## 5. Refractive index



**S13** Refractive indices  $n_D$  at 25°C of [Ch][AA] ILs as a function of the molecular polarizability of the amino acid per molar volume. We determined the [Ch][AA]ILs polarizability according to the method proposed by Kassimi et al. (N. E. Kassimi, A. J. Thakkar, *Chem. Phys. Lett.*, 2009, **472**, 232–236.)