Relationship between lignocellulosic biomass dissolution and physicochemical properties of ionic liquids composed of 3-methylimidazolium cations and carboxylate anions

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SUPPLEMENTARY INFORMATION

S1 Differential Thermogravimetric (DTG) curves of ionic liquids

S2 Temperature-dependent viscosity of ionic liquids

S3 Measurement of Kamlet-Taft parameters

S4 ^{13}C NMR characterization of all four ionic liquids used in this study

S1. Differential Thermogravimetric (DTG) curves of ionic liquids

Thermograms obtained from the thermogravimetric analysis (TGA) of ionic liquids were differentiated into weight loss rate or differential TG (DTG) to observe the temperature at which each ionic liquid decomposes. These differential peaks are shown in the figure below. The procedures for conducting TGA are presented in the manuscript.

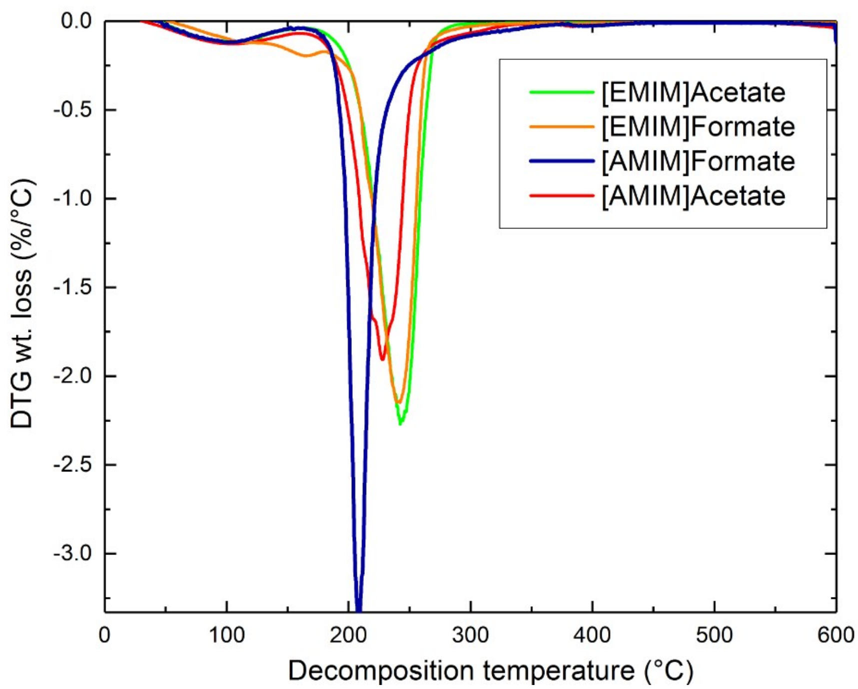

Fig. S1 DTG curves for all four ionic liquids. The global maxima of each curve shows Td.

S2. Temperature dependent viscosity of ionic liquids used in this study

The viscosity of each ionic liquid ([EMIM]Acetate, [EMIM]Formate, [AMIM]Formate, and [AMIM]Acetate) was measured using a rheometer according to the procedures described in the manuscript. Although 80 °C was our temperature of interest, temperature dependent viscosity was measured from 25-100 °C for all ILs except [EMIM]Formate, for which a range of 45-100 °C was used.

Table S2 Averaged temperature-dependent viscosity of [EMIM]Acetate, [EMIM]Formate, [AMIM]Formate, and [AMIM]Acetate measured using a rheometer

Temperature (°C)	Viscosity (mPa-s)			
	[EMIM]Acetate	[EMIM]Formate	[AMIM]Formate	[AMIM]Acetate
25	218.8	ND	49.3	42.5
30	180.5	ND	40.5	38.5
35	188.5	ND	33.4	35.0
40	135.7	ND	27.9	27.8
45	80.5	23.4	23.6	23.6
50	63.7	21.4	20.1	20.3
55	51.0	18.9	17.4	17.5
60	42.6	16.8	15.2	15.3
65	36.2	14.8	13.4	13.7
70	32.5	12.9	11.9	12.9
75	28.7	12.8	10.6	12.0
80	25.1	12.3	9.7	11.2
85	21.4	12.2	8.7	11.2
90	18.5	12.0	8.0	11.1
95	16.0	11.8	7.3	10.9
100	14.1	11.7	6.7	10.9

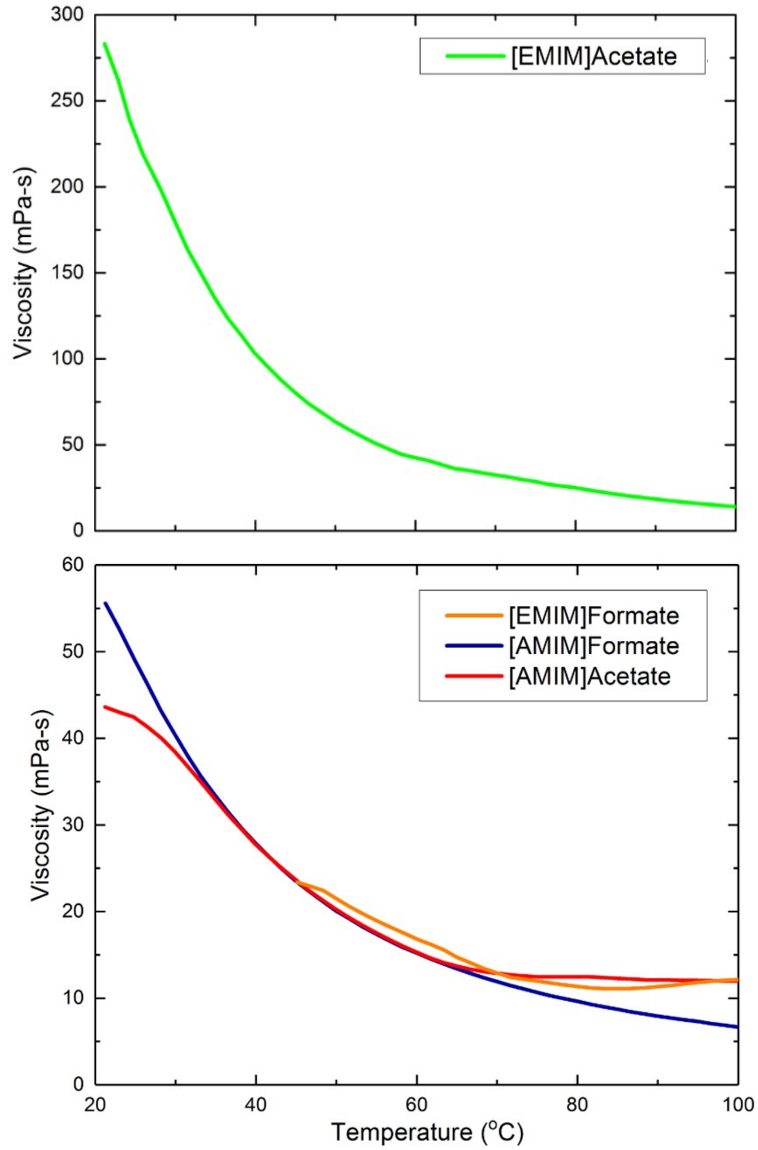

Fig. S2 (a) Temperature-dependent viscosity of [EMIM]Acetate. **(b)** Temperature-dependent viscosity of [EMIM]Formate, [AMIM]Formate and [AMIM]Acetate. The plots below are split into two because of the large difference in scales used on the y-axis.

S3. Measurement of Kamlet-Taft parameters

All ionic liquid samples were prepared in a similar manner. The visible spectra of the dye-IL mixtures containing either Reichardt's dye (RD), N, N-diethyl-4-nitroaniline (DENA), or 4-nitroaniline (NA) were adjusted to produce an Abs_{max} of <1.0. The visible spectra of all three dyes in [EMIM]Acetate was combined and shown in the figure below.

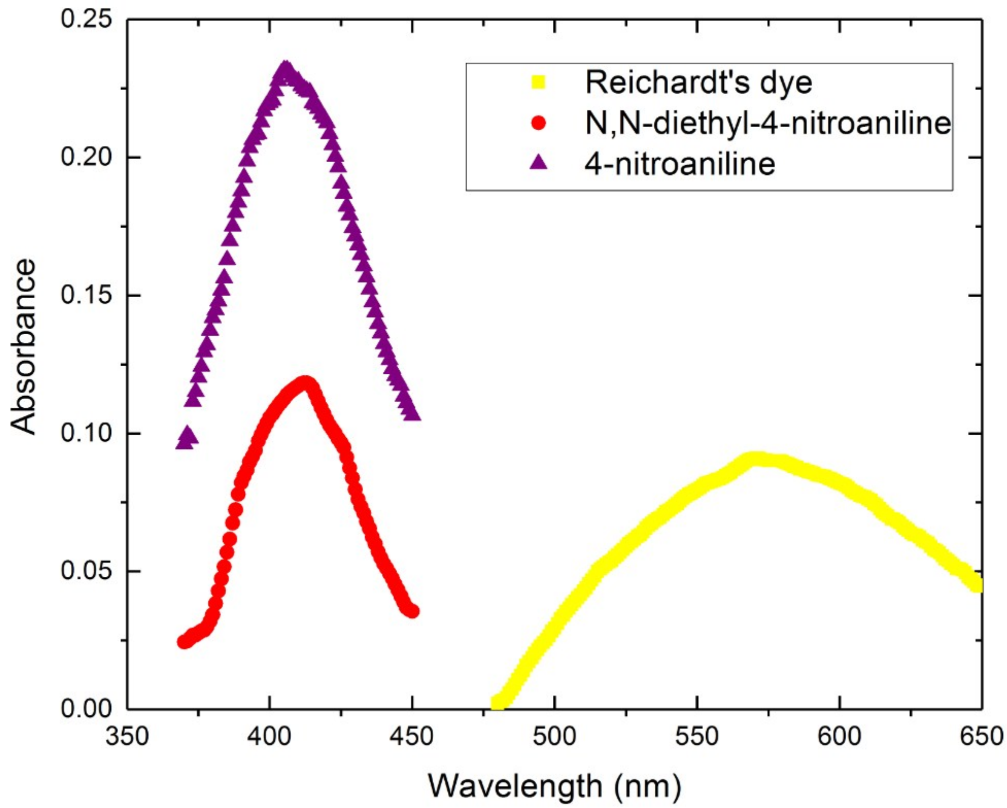

Fig. S3 UV Spectra of [EMIM]Acetate containing either 4-nitroaniline, N,N-diethyl-4-nitroaniline, or Reichardt's dye.

Table S3. Summary of Kamlet-Taft parameters reported in the literature for [EMIM]Acetate, [AMIM]Formate, and [AMIM]Acetate.

<table>
<tr><th>IL</th><th>α</th><th>β</th><th>π*</th><th>Reference</th></tr>
<tr><td rowspan="2">[EMIM]Acetate</td><td>0.57</td><td>1.06</td><td>0.97</td><td>Ab Rani, M. A., Brant, A., Crowhurst, L., Dolan, A., Lui, M., Hassan, N. H., ... & Schrems, M. (2011). Physical Chemistry Chemical Physics, 13(37), 16831-16840.</td></tr>
<tr><td>0.49</td><td>1.09</td><td>1.01</td><td>Hauru, L. K., Hummel, M., King, A. W., Kilpeläinen, I., & Sixta, H. (2012). Biomacromolecules, 13(9), 2896-2905.</td></tr>
<tr><td rowspan="2">[AMIM]Formate</td><td>0.48</td><td>0.99</td><td>1.08</td><td>Fukaya, Y., Sugimoto, A., & Ohno, H. (2006). Biomacromolecules, 7(12), 3295-3297.</td></tr>
<tr><td>ND</td><td>0.99</td><td>ND</td><td rowspan="2">Zhang, Y., Xu, A., Lu, B., Li, Z., & Wang, J. (2015). Carbohydrate polymers, 117, 666-672.</td></tr>
<tr><td>[AMIM]Acetate</td><td>ND</td><td>1.11</td><td>ND</td></tr>
</table>

Standard deviations were not reported by authors.

S4. ^{13}C NMR characterization of all four ionic liquids used in this study.

A 400 MHz Varian Liquid-state NMR spectrometer was used to collect the data.

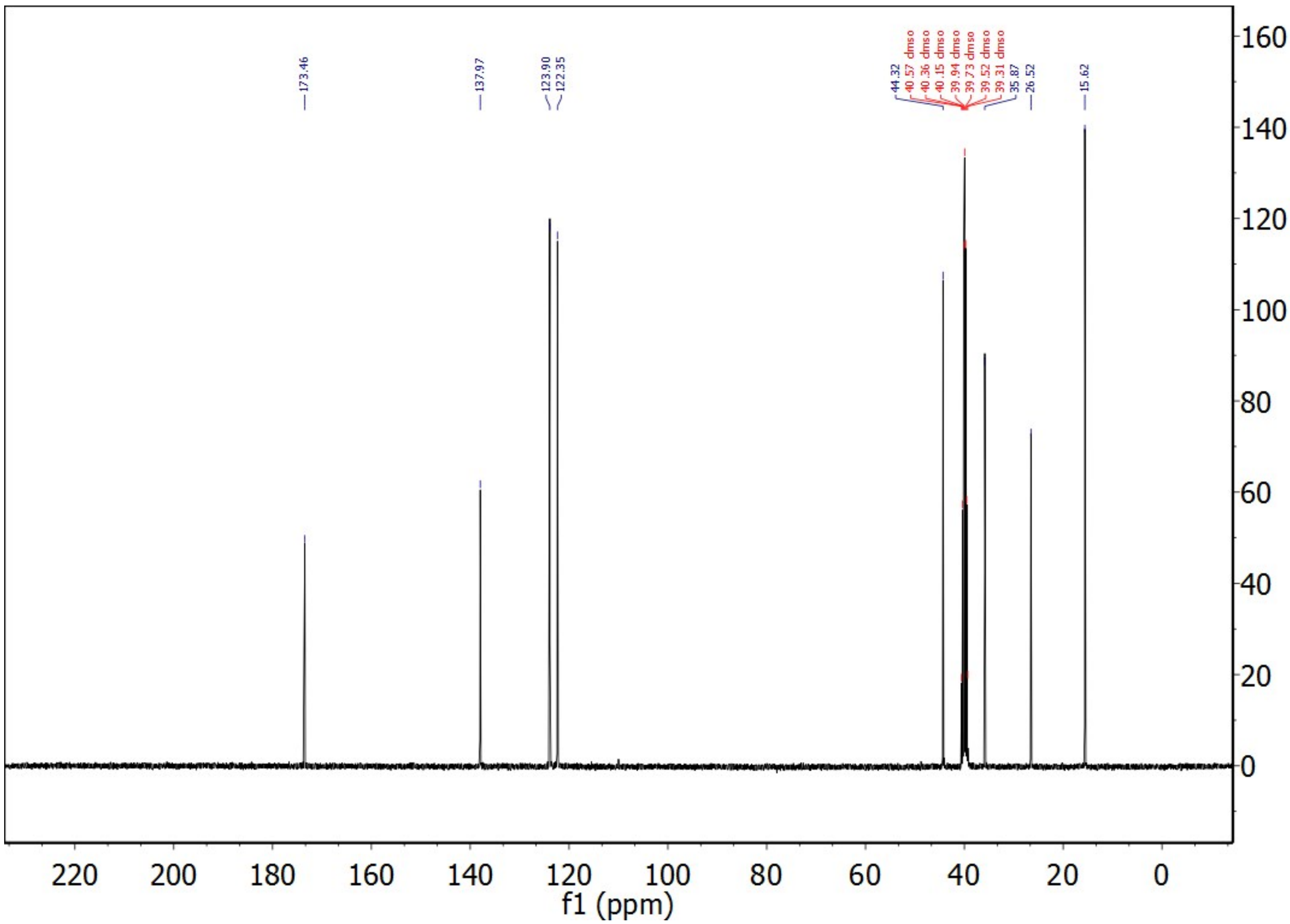

Fig. S4 (a) ^{13}C NMR of 1-ethyl-3-methylimidazolium acetate ([EMIM]Acetate).

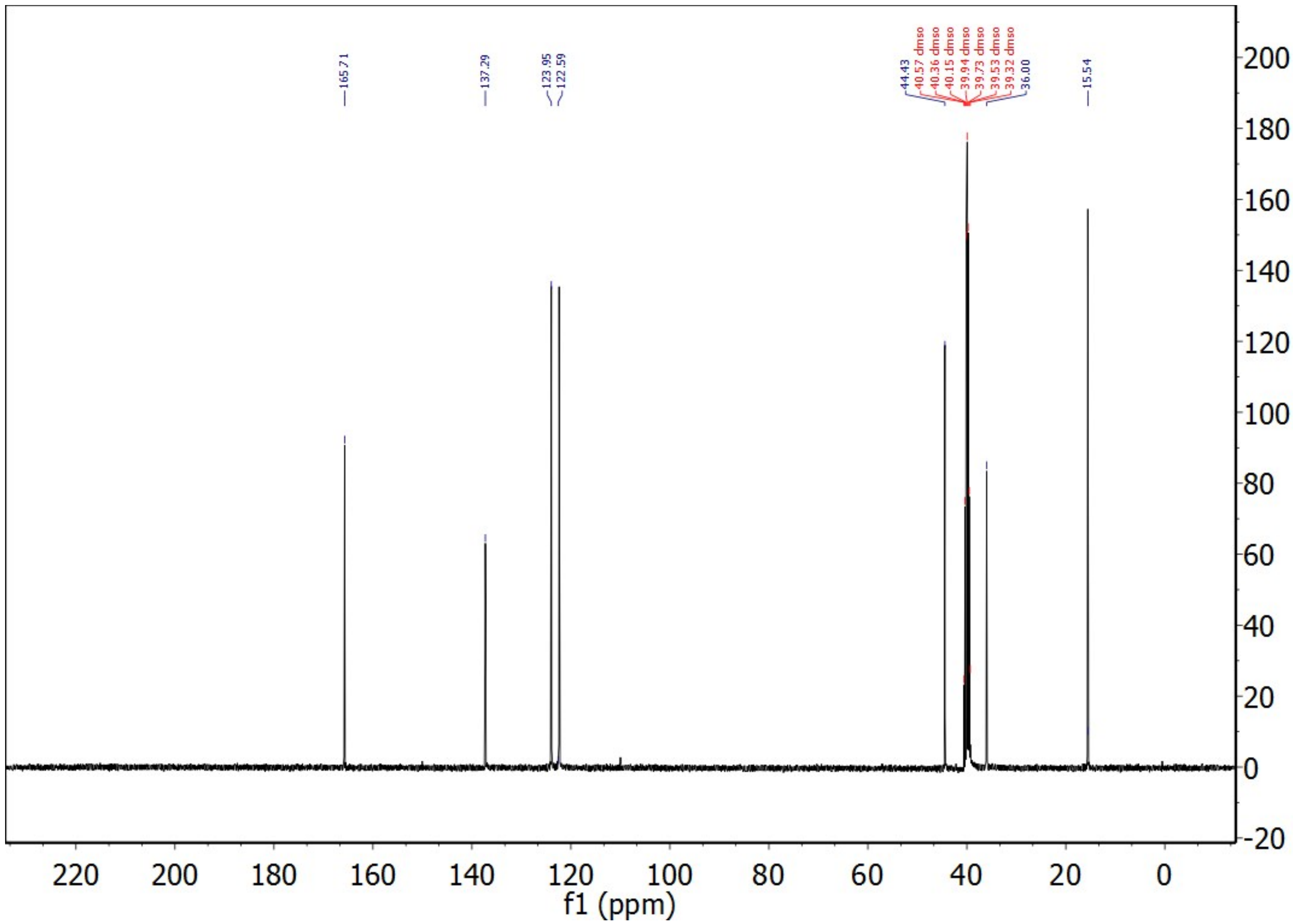

Fig. S4 (b) ^{13}C NMR of 1-ethyl-3-methylimidazolium formate ([EMIM]Formate).

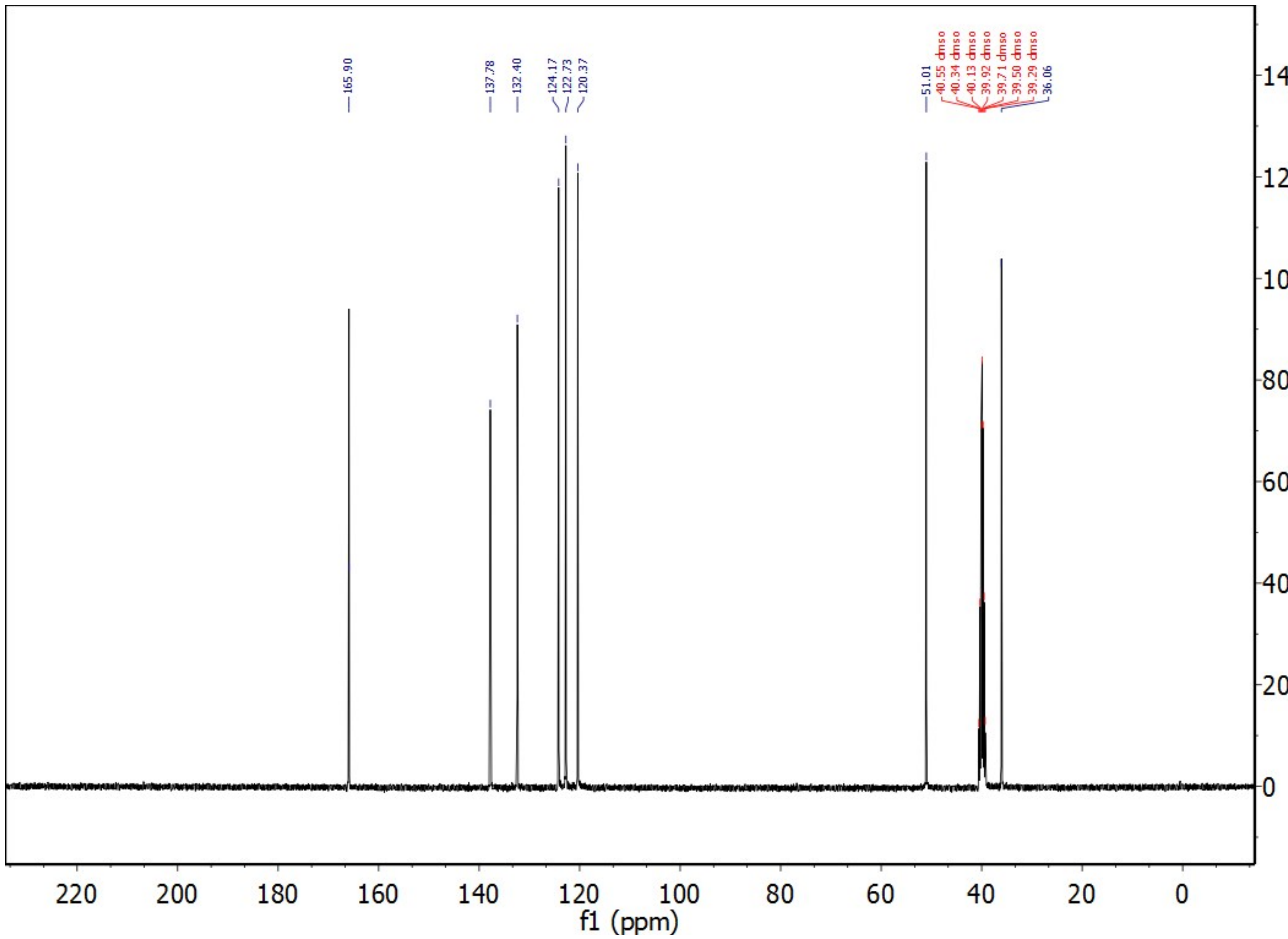

Fig. S4 (c) ^{13}C NMR of 1-allyl-3-methylimidazolium formate ([AMIM]Formate).

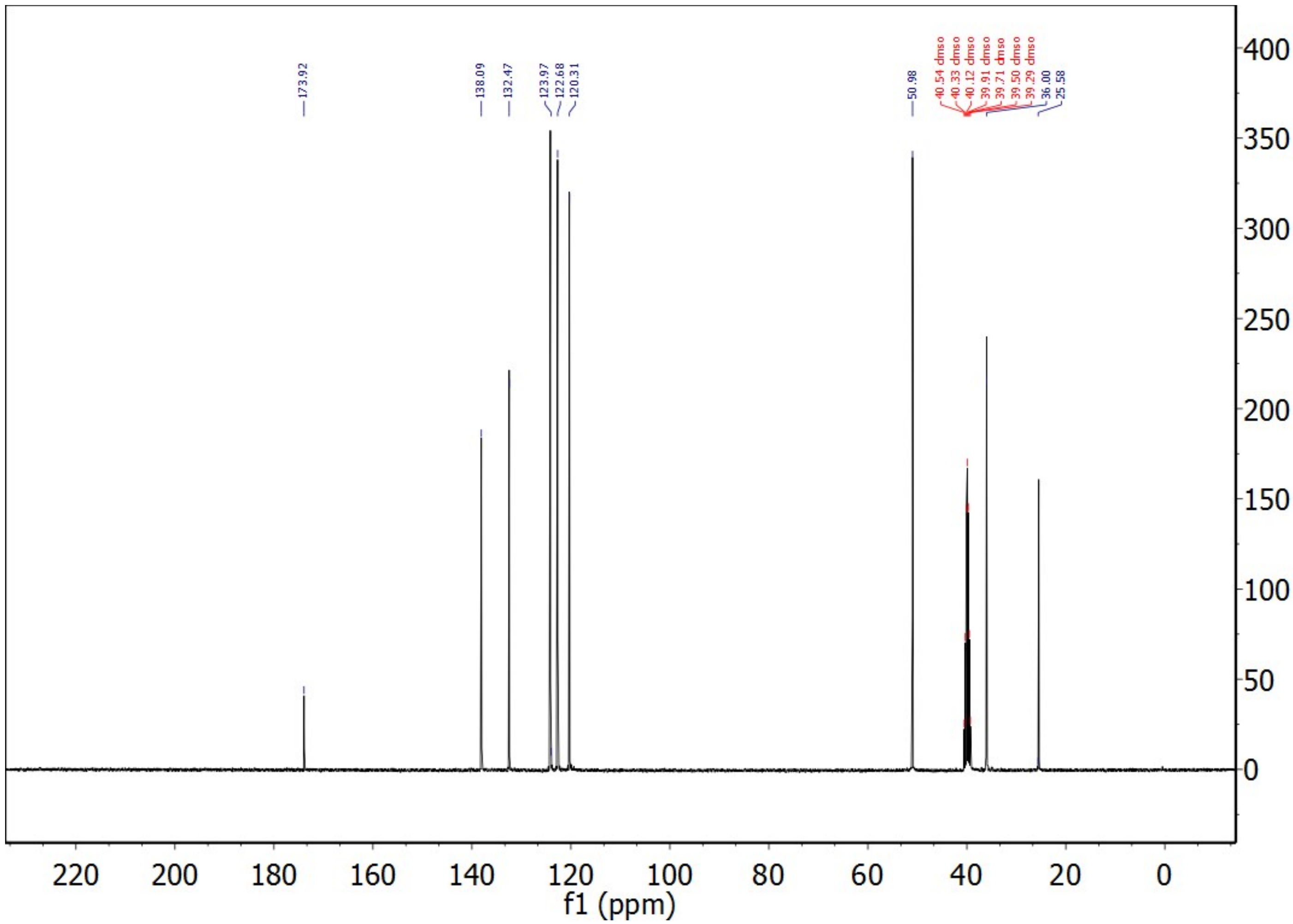

Fig. S4 (d) ^{13}C NMR of 1-allyl-3-methylimidazolium acetate ([AMIM]Acetate).