Electronic supporting information for

"The effect of changing the components of an ionic liquid upon the solubility of lignin"

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Contents

General experimental

Reagents for syntheses of the ionic liquid precursors were purchased from Sigma-Aldrich and distilled *immediately* before use, with the exception of 1-butyl-3-methyl imidazolium chloride, which was donated by Dr Janjira Panchompoo and used without further purification. 1-Ethyl-3-methylimidazolium based ionic liquids were purchased from IoLiTec Ionic Liquids Technologies GmbH and used without further purification. The wood flour used as the source of lignin was Radiata Pine milled to an average particle diameter of 530 μm, donated by Micro Milling Pty. Ltd. (NSW, Australia).

All other reagents used in synthesis were commercially available, purchased from either Sigma-Aldrich or Alfa Aesar and used without further purification. All hazardous materials were kept from the environment and effectively handled following UNSW guidelines (document HS321), and following the plans and policies outlined in UNSW's Green Lab Environmental Compliance Program.

Water, where mentioned, refers to water obtained from a Millipore Milli-Q™ Academic System and had a resistivity of 18.2 Ω cm.

Mass spectrometric analysis for this work was carried out at the Bioanalytical Mass Spectrometry Facility, UNSW. Samples were run on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer using a nanospray (nano-electrospray) ionization source to generate ions from the analyte in solution. The instrument was calibrated with a standard calibration solution (as outlined in the instrument manual) on the day of analysis using direct infusion into the ESI source. The instrument conditions were optimized forsensitivity of the compounds using LC tune software. The analysis was carried out in positive ion mode using the orbitrap FTMS analyser at a resolution of 60000. Samples, at a concentration of *ca*. 1 μg mL^{-1} in methanol, were injected into a glass needle and inserted into the nanospray source. Ions generated were measured over the mass range 150 to 2000 Da window. Data wasacquired in full scan mode over 30 seconds. Data was analysed using the Qual Browser feature in Xcaliber 2.1 (Thermo Fisher Scientific, San Jose, CA, USA).

All NMR spectra were obtained using either a BrukerAvance III 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) a BrukerAvance III 400 spectrometer (400 MHz, ^{1}H; 125 MHz, ^{13}C, 156 MHz ^{7}Li), or a BrukerAvance III 600 spectrometer (600 MHz, ^{1}H; 150 MHz, ^{13}C). Multiplicities are reported as singlet (s), doublet (d), triplet (t) and multiplet (m). Unless otherwise noted, all coupling constants (*J*) refer to proton-proton coupling and all ^{13}C NMR resonances are singlets. NMR spectra were processed using either the Bruker TOPSPIN 3.1 software, or the MestReNova 9.0.0 software with the qNMR plugin (used for lithium quantification).

The phrase "*in vacuo*" refers to use of a Heidolph "Hei-Vap Precision" rotary evaporator with a Vacuubrand PC500 series pump unit. This has a variable pressure control, so the pressure was varied in order to remove solvent at a suitable rate.

The term "UV-Vis spectrometry" refers to the use of a Varian Cary 50 Bio UV-Visible spectrophotomer, using 2 nm s^{-1} scan rate and a 1 cm ES-quartz cuvette. Data was processed in Varian UV Scan Application v3.00.

Infra-red absorbance spectra were obtained on an Agilent Technologies Cary 630 FTIR.

Procedure for the extraction of lignin from wood flour

A modification of a previously reported method[1] was employed. Wood flour (12.71 g) was dried in a vacuum oven (<10 mbar, 100°C) for 15 h. The dried wood flour (11.89 g) was extracted using dichloromethane (200 mL) in a Soxhlet apparatus for 24 h. This process was repeated using acetone (200 mL) for 7 h. The wood flour was then dried in a vacuum oven (<10 mbar, 100°C) for 15 h. The dried wood flour (11.60 g) was then stirred at reflux in a 9:1 dioxane:0.1 M hydrochloric acid mixture for 15 h. The mixture was filtered and the dark red filtrate collected. This was then reduced to *ca.* 20% of its original volume *in vacuo*[*] and water (140 mL) was then added to the concentrate causing the precipitation of a brown powder. The mixture was then acidified to pH ~2 using concentrated hydrochloric acid (32%) and the mixture was left overnight. Filtration of the mixture gave lignin (0.91 g) as a brown powder after drying.

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[*] This dioxane solution was recycled >5 times after removal by re-acidifying with hydrochloric acid (32%)

UV-Vis spectra of lignin extracted from wood flour using [Emim][CF_3SO_3]

The UV-Visible spectrum was obtained for lignin extracted by ionic liquid as well. To do this, wood flour (~100 mg) was stirred in [Emim][CF_3SO_3] (~1 g) at 60°C for 1 h. The supernatant was then diluted (by *ca.* 40 fold) in aqueous sodium hydroxide (pH 12.5) and the UV-Visible spectrum was obtained (Figure S1).

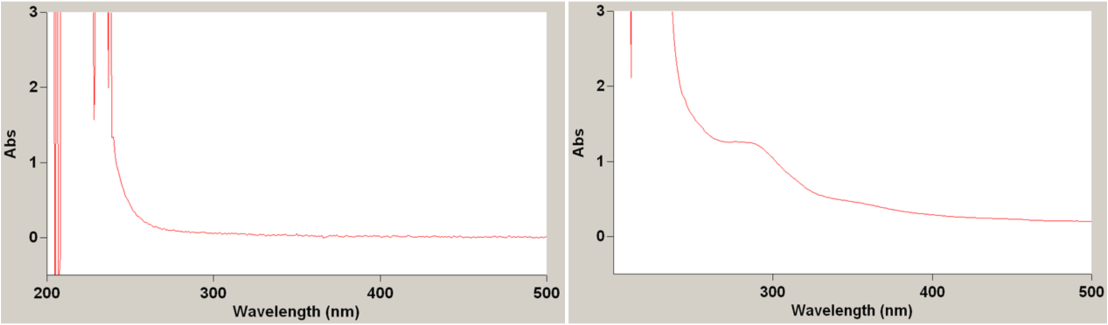


Figure S1 UV-Vis spectra of 26 g L^{-1} [Emim][CF_3SO_3] in aqueous sodium hydroxide (pH 12.5), highlighting a clear spectrum between 250 – 300 nm (left) and 1.5 g L^{-1} [Emim][CF_3SO_3] in aqueous sodium hydroxide (pH 12.5) after being used to extract lignin from wood flour, highlighting the presence of extracted lignin

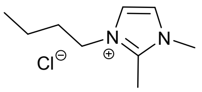
Lithium NMR spectroscopy for quantification of lithium impurities in ionic liquids

In each applicable case, the trifluoromethanesulfonate ionic liquids were tested to see if there were any lithium ions in the sample. (This was done to indicate if any lithium trifluoromethanesulfonate remained in the sample after metathesis.) To do this, the ^{7}Li NMR spectrum of a solution of the ionic liquid at known concentration was obtained and the integration of signal due to the lithium ion at δ *ca*. 0.10 was compared to the integration of the equivalent signal in the spectrum of a standard solution of known concentration. The MestReNova 9.0.0 software with the qNMR plugin was then used to correlate these integrations to concentrations. Outcomes are detailed in the following section on the synthesis of ionic liquids and their precursors.

Synthesis of ionic liquids and their precursors

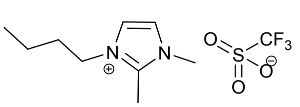
The ionic liquids tributyloctylammonium iodide,[2] tributyloctylammonium trifluoromethanesulfonate,[2] 1-butyl-2,3-dimethylimidazolium chloride,[3] 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonate,[3] 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate[4] and butylpyridinium trifluoromethanesulfonate[5] were prepared according to standard procedures and had physical and spectral properties consistent with those reported. A representative synthesis is included below. Note that in all cases no signal was observed in the ^{7}Li NMR spectrum indicating a concentration of lithium of less than 0.1 mol%.

1-Butyl-2,3-dimethylimidazolium chloride



1,2-Dimethylimidazole (6.34 g, 66.0 mmol) was dissolved in 1-chlorobutane (8.68 g, 93.8 mmol) and stirred overnight under a nitrogen atmosphere at reflux. The remaining chlorobutane was removed *in vacuo* and acetone (20 mL) was added to the resulting viscous orange liquid, causing a white precipitate to form. This mixture was then filtered and the residue was washed with acetone until the washings were colourless to give [Bm$_2$im][Cl] as a hygroscopic white powder (6.14 g, 49%). ^{1}H NMR (300 MHz, CD$_3$CN) δ 7.45 (d, J = 2.1 Hz, 1H, N$\underline{\mathrm{CH}}$CHN), 7.42 (d, J = 2.1 Hz, 1H, NCH$\underline{\mathrm{CH}}$N), 4.10 (t, J = 7.5 Hz, 2H, N$\underline{\mathrm{CH_2}}$(CH$_2$)$_2CH_3$), 3.76 (s, 3H, C$_q$$\underline{\mathrm{CH_3}}$), 2.55 (s, 3H, N$\underline{\mathrm{CH_3}}$), 1.84 – 1.68 (m, 2H, CH$_2$$\underline{\mathrm{CH_2}}CH_2$), 1.44 – 1.29 (m, 2H, CH$_2$$\underline{\mathrm{CH_2}}CH_3$), 0.96 (t, J = 7.4 Hz, 3H, CH$_2$$\underline{\mathrm{CH_3}}$); ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN) δ 122.35, 120.88, 64.06, 47.94, 34.78, 31.33, 19.10, 12.78, 9.21.

1-Butyl-2,3-dimethylimidazolium trifluoromethanesulfonate



1-Butyl-2,3-dimethylimidazolium chloride (5.79 g, 30.7mmol) was dissolved in dichloromethane (30 mL)[†]. Lithium trifluoromethanesulfonate (5.26 g, 33.7 mmol) dissolved in acetone (10 mL) was added dropwise over 10 min. The reaction mixture was then stirred at room temperature

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[†] Volatile organic solvents such as dichloromethane were always removed *in-vacuo* and have the potential to be recycled.

for 2 days. The solvent was reduced to half its original volume *in vacuo* and dichloromethane (20 mL) was added. The mixture was filtered and the filtrate was stored at -22°C overnight. Once again, the mixture was filtered and the filtrate collected. The solvent was removed from the combined filtrates *in vacuo* to give the title compound as a pale yellow liquid which crystallised on standing to white crystals (6.69 g, 72%). m.p. 38°C; ^{1}H NMR (400 MHz, $\mathrm{CD_3CN}$) δ 7.31 (d, J = 2.1 Hz, 1H, $\mathrm{N\underline{CH}CHN}$), 7.30 (d, J = 2.1 Hz, 1H, $\mathrm{NCH\underline{CH}N}$), 4.06 (t, J = 7.5 Hz, 2H, $\mathrm{N\underline{CH_2}(CH_2)_2CH_3}$), 3.72 (s, 3H, $\mathrm{C_q\underline{CH_3}}$), 2.53 (s, 3H, $\mathrm{N\underline{CH_3}}$), 1.82 – 1.70 (m, 2H, $\mathrm{CH_2\underline{CH_2}CH_2}$), 1.37 (m, 2H, $\mathrm{\underline{CH_2}CH_3}$), 0.97 (t, J = 7.4 Hz, 3H, $\mathrm{\underline{CH_2}CH_3}$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (151 MHz, $\mathrm{CD_3CN}$) δ 144.58, 122.35, 121.02, 120.99 (q, $^{1}J_{\mathrm{CF}}$ = 321 Hz, $\mathrm{\underline{CF_3}SO_3}$), 47.95, 34.66, 31.54, 19.09, 13.03, 9.04; $^{19}\mathrm{F}\{^{1}\mathrm{H}\}$NMR (282 MHz, $\mathrm{CDCl_3}$) δ -78.62; ^{7}Li NMR (156 MHz, $\mathrm{H_2O/D_2O}$) δ 0.12 (0.48%).

Derivation of the relationship between observed extinction coefficient and lignin concentration

At the concentrations used in this study, none of the chosen ionic liquids absorb in the UV-Visible region. Hence the absorbance of an ionic liquid-lignin mixture in dilute solutions of alkaline water is due to only the lignin present in the sample.

$$A_{mix} = A_{Lignin}$$

According to the Beer-Lambert law, this means;

$$\varepsilon_{Total}[Total]l = \varepsilon_{Lignin}[Lignin]l$$

$$\varepsilon_{Total} = \frac{\varepsilon_{Lignin}[Lignin]l}{[Total]l}$$

Since the mole fraction of lignin is;

$$\frac{[Lignin]}{[Total]}$$

Then;

$$\varepsilon_{Total} = \varepsilon_{Lignin}\chi$$

This shows that a comparison of the extinction coefficient of the mixture should change linearly with the mol fraction of the mixture. However this assumes that the extinction coefficient of lignin remains constant with a varying amount of ionic liquid present. This is not the case, in reality the following equation holds.

$$\varepsilon_{Lignin(IL)} = \varepsilon_{Lignin} + k[IL]_{initial}$$

This indicates that the measured extinction coefficient of lignin is equal to the extinction coefficient of a pure lignin sample plus the initial IL concentration (prior to dilution for extinction coefficient measurement) multiplied by some factor *k*.

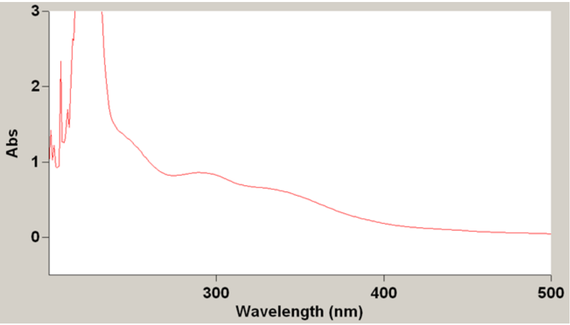


Figure S2 UV-Vis spectra of dioxane extracted lignin (*ca.* 100mg L^{-1}) dissolved in aqueous sodium hydroxide (pH 12.5).

Figure S2 above displays the UV-Vis spectra of *ca.* 100 mg L^{-1} lignin when dissolved in aqueous sodium hydroxide (pH 12.5). The absorbance was monitored at 286 nm, and ionic liquid [Emim][CH_3CO_2] added to the solution in order to monitor the effect that large excesses of the ionic liquid might have on the spectra. No major changes were observed except for minor increases in the relative extinction coefficient at 286 nm, as discussed below.

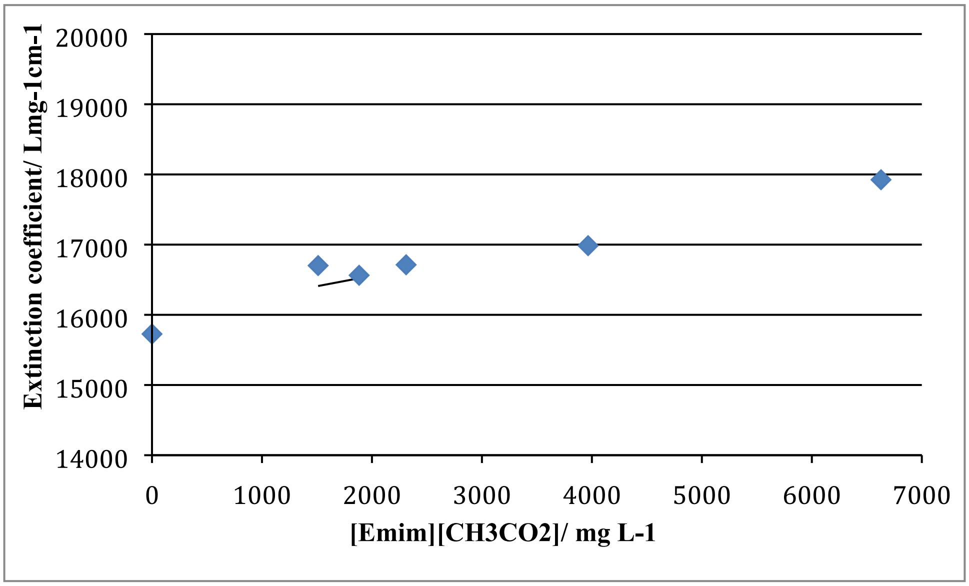


Figure S3 The change in extinction coefficient at 286 nm due to lignin at a constant concentrationin mixtures of lignin and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate diluted in aqueous sodium hydroxide (pH 12.5) at *ca.* 298 K.

Figure S3 shows that there is only a *ca.* 20% increase in the extinction coefficient when the ionic liquid concentration is increased above *ca.* 2000 mg ionic liquid per L (while keeping lignin concentration constant). For this reason it was ensured that the ionic liquid content never exceeded 100 mg L^{-1} such that any ionic liquid induced changes were essentially negligible. By ensuring that these experiments are only performed at low concentrations (due to the dilution of the sample prior to UV absorbance measurement), we can approximate the above formula where k[IL] is approximately 0.

$$\varepsilon_{Lignin(IL)} = \varepsilon_{Lignin}$$

This allows for the determination of mixture composition by measurement of the extinction coefficient of the mixture from the use of a simple calibration curve based off the percentage composition by weight.

Raw data for figures presented in the main text

Lignin concentration/ wt%	Extinction coefficient relative to pure lignin
1.55	0.0177
2.57	0.0277
4.33	0.0460
5.26	0.0554
6.47	0.0687
10.85	0.1337
10.86	0.0803
13.41	0.1563
18.14	0.2064
22.37	0.2080
23.51	0.2609
32.09	0.3416
34.94	0.4066
38.26	0.3635
49.6	0.5478
50.59	0.5860
50.7	0.5666
50.88	0.5099
55.17	0.5935
58.25	0.5594
58.78	0.5699
65.06	0.6768
79.42	0.7633
96.43	0.9947
100	1.0000

TableS1 Extinction coefficient of lignin / ionic liquid mixtures at 286 nm relative to pure lignin for solutions in aqueous sodium hydroxide (pH 12.5) at 298 K (presented in Fig. 1, main text).

Ionic Liquid [Emim][X]	Proportion of lignin at saturation at 298 K / wt%	Proportion of lignin at saturation at 253 K / wt%
$[O_2P(OCH_2CH_3)_2]^-$	52.18	3.46 ± 2.16
$[CH_3SO_3]^-$	45.11	6.09 ± 1.46
$[CH_3CO_2]^-$	53.68	6.76 ± .091
$[NCS]^-$	46.20 ± 2.27	12.06
$[CF_3SO_3]^-$	55.00	19.02 ± 3.10
$[CF_3CO_2]^-$	53.08	20.24 ± 11.19
$[BF_4]^-$	5.00 ± 5.00	
$[(SO_2CF_3)_2N]^-$	5.00 ± 5.00	

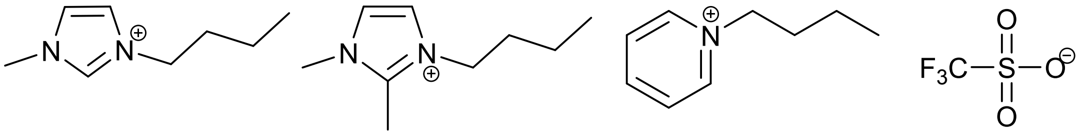
Table S2 The proportion of lignin (wt%) in saturated solutions of lignin in a range of $[Emim]^+$-based ionic liquids at either 298 K (presented in Fig. 3, main text) or 253 K. Uncertainties, where reported, are half the range of duplicate measurements. Other datum represent a single experiment.

Ionic Liquid $[X][CF_3SO_3]$	Proportion of lignin at saturation at 298 K / wt%
$[Bmim]^+$	40.1 ± 2.3
$[Bm_2im]^+$	19.9 ± 2.8
$[Bpyr]^+$	32.7 ± 0.2
$[Emim]^+$	31.4 ± 0.5
$[N_{4448}]^+$	11.2 ± 2.4

Table S3 The proportion of lignin (wt%) in saturated solutions of lignin in a range of $[CF_3SO_3]^-$-based ionic liquids at 318 K (presented in Fig. 4, main text). Uncertainties are half the range of duplicate measurements.

NMR studies to investigate interactions in lignin-ionic liquid solutions

Analyses were carried out using 500 µL of the appropriate ionic liquid in a 5mm NMR tube with deuterated acetonitrile in an internal capillary. NMR spectra were then obtained (^{1}H and ^{13}C{^{1}H}). Lignin was then dissolved in each sample until viscosity halted mixing. Spectra were then rerun and any change in chemical shift was noted by calibrating both spectra to the same chemical shift for the CH_3 group on the butyl chain.



[Bmim]$^+$ [Bm$_2$im]$^+$ [Bpyr]$^+$ [CF_3SO_3]$^-$

Figure S4 The components of the three ionic liquids examined for changes in NMR chemical shift upon the dissolution of lignin. Each ionic liquid had the trifluoromethanesulfonate anion.

		Change in chemical shift (Hz) when lignin is dissolved in either $[Bpyr][CF_3SO_3]$ by atom position					
Ionic liquid cation (wt% lignin dissolved)		$CH_3\underline{CH_2}$	$CH_3CH_2\underline{CH_2}$	$N\underline{CH_2}CH_2$	$N\underline{CH}$	$NCH\underline{CH}$	$NCHCH\underline{CH}$
$[Bpyr]^+$ (6.5)	^1H	-4	-17	-23	-33	-27	-27
	$^{13}C\{^1H\}$	-3	-3	-4	-14	-6	-10

Table S4 Chemical shift change (Hz) of the signals due to $[Bpyr][CF_3SO_3]$ on the addition of lignin. Spectra were calibrated by setting the signals due to the methyl group on the butyl chain to the same chemical shift.

		Change in chemical shift (Hz) when lignin is dissolved in either $[Bmim][CF_3SO_3]$ or $[Bm_2im][CF_3SO_3]$by atom position							
Ionic liquidcation (wt% lignin dissolved)		$CH_3C\underline{H_2}$	$CH_3CH_2\underline{CH_2}$	$N\underline{CH_2}CH_2$	$N\underline{CH_3}$	$C_q\underline{CH_3}$	$\underline{C_q}CH_3$	$N\underline{CH}N$	$2xN\underline{CH}CHN$‡
$[Bmim]^+$ (4.5)	^1H	0	-9	-9	-9	N/A	N/A	-15	-17
	$^{13}C\{^1H\}$	-3	-4	-4	-1	N/A	N/A	-18	-12
$[Bm_2im]^+$ (1.6)	^1H	-1	-2	-5	-5	-5	N/A	N/A	-9
	$^{13}C\{^1H\}$	0	0	0	0	-2	-1	N/A	-2

Table S5 Chemical shift change (Hz) of the signals corresponding to the two imidazolium-based ionic liquids on the addition of lignin. Spectra were calibrated by setting the signals due to the methyl group on the butyl chain to the same chemical shift.

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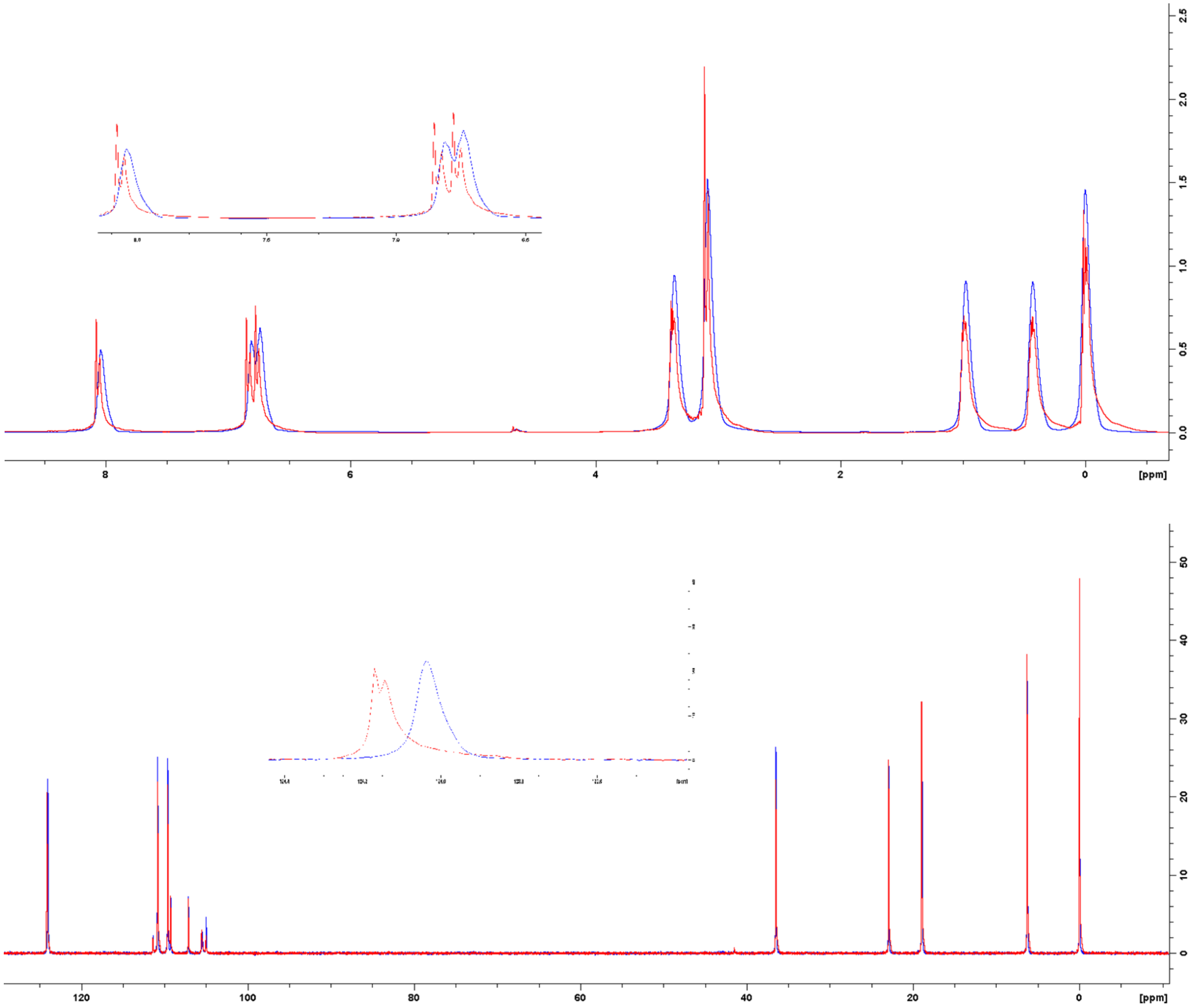
‡Average of the two signals due to the C4 and C5 positions on the imidazolium ring.



FigureS5 Representative spectra for the analysis of signal movement when lignin is dissolved in a trifluoromethanesulfonate ionic liquid. Seen here is [Bmim][CF_3SO_3] before (red) and after (blue) lignin dissolution, ^1H NMR (top),$^{13}C\{^1H\}$ NMR (bottom).

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