Electronic Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information

On the solubility of wood in non-derivatising ionic liquids

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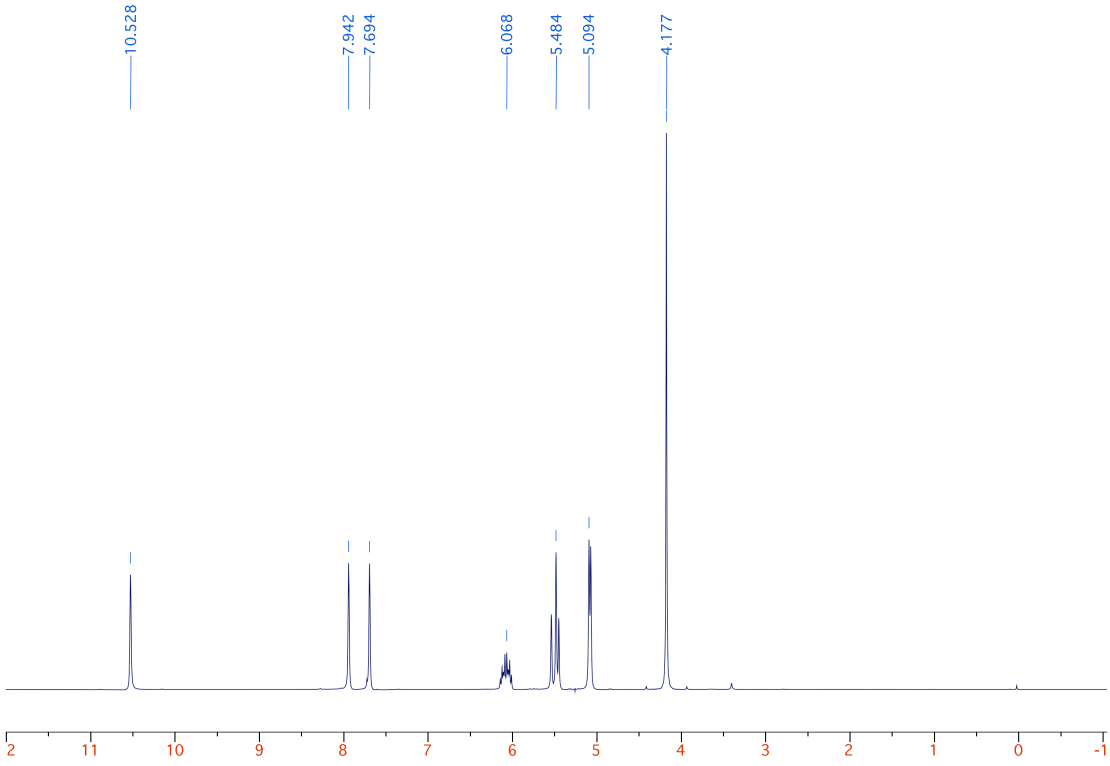
S1. Commercial Materials

1-Ethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ([emim][NTf_2], 99 %) was provided by Solvent Innovation GmbH (now Merck KGaA). 4-Nitroaniline was purchased from Fluka AG. *N*,*N*-diethyl-4-nitroaniline was purchased from Fluorochem. Reichardt's dye was purchased from Sigma-Aldrich. All other reagents used below were purchased from Sigma-Aldrich and all reagents were used without further purification.

S2. Synthesis of [amim]Cl

1-Methylimidazole (125 ml, 1.57 mol) was added slowly (over 1 h) to neat allyl chloride (160 ml, 1.97 mol) at room temperature, with stirring under argon. The mixture was then refluxed at 55 ^{o}C for 18 h under argon. Excess allyl chloride was removed by rotary evaporation, in a fume-hood. The mixture was then rotary evaporated at 70 ^{o}C under high vacuum (vacuum pump) for 6 h, to yield a clear orange liquid (15.80 g, 100%). It is critical to avoid the introduction of moisture into the mixture before all traces of allyl chloride are removed. ^{1}H NMR (300 MHz; $CDCl_3$): δ 10.39 (1H, s), 7.94 (1H, s), 7.69 (1H, s), 6.07 (1H, ddt, J = 16.9, 10.3, 6.5 Hz), 5.48 (2H, m), 5.09 (2H, d, J = 6.4 Hz), 4.18 (3H, s). Water content was determined to be less than 0.4 % w/w by Karl-Fischer titration. The mixture was stored in a tightly sealed bottle to avoid moisture uptake.

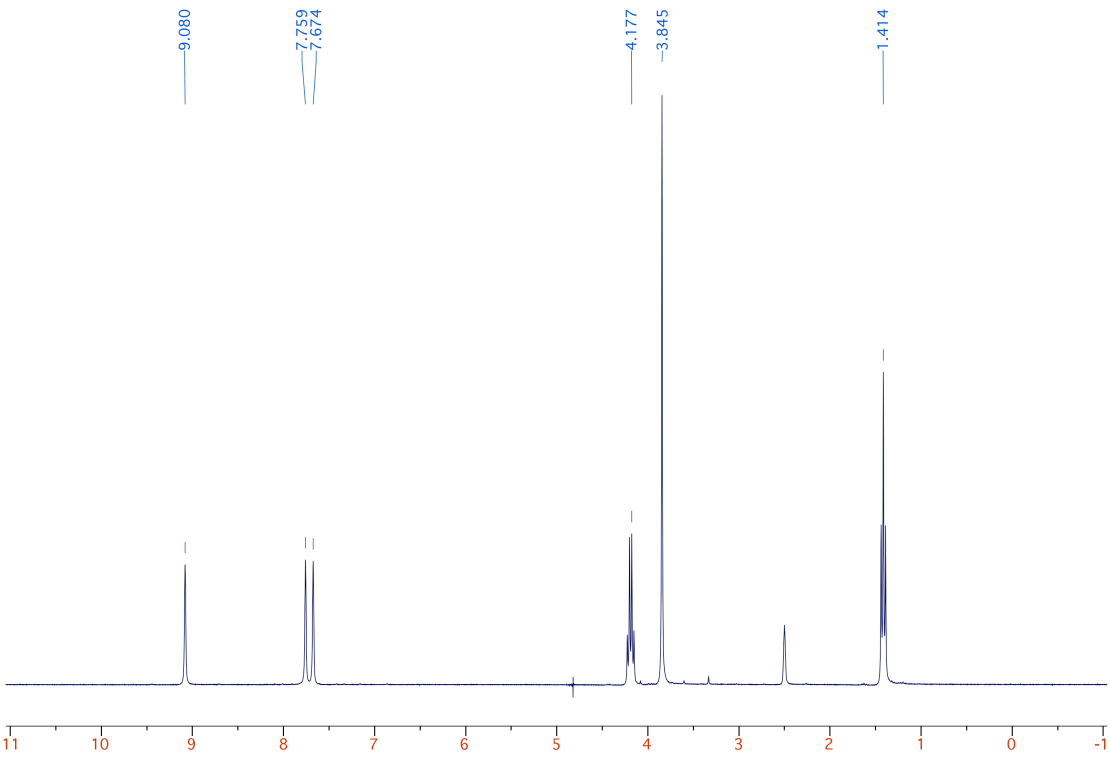
^{1}H NMR Spectra:



S3. Synthesis of [emim][OTf]

1-Ethylimidazole (5.86 g, 0.0609 mol) was added dropwise (over 1 h) to neat methyl trifluoromethylsulphonate (10 g, 0.0609 mol) in an ice bath. The reaction was very exothermic and the solution was allowed to stir for a further 18 h at room temperature. The mixture was rotary evaporated at 65 ^{o}C under high vacuum for 18 h. Trace acid was removed by stirring the product in water (10 ml) with the addition of $NaHCO_3$ (1 g). The salt was reprecipitated with acetonitrile and filtered through celite. Solvents were evaporated under high vacuum yielding the product, as a clear pale yellow oil. (15.80 g, 100%). ^{1}H NMR (300 MHz, DMSO-d6): δ 1.41 (3H, t, *J*=7.2 Hz), 3.85 (3H, s), 4.18 (2H, q, *J*=7.3 Hz), 7.67 (1H, s), 7.76 (1H, s), 9.08 (1H, s); IR (ATR, cm^{-1}) 3159 (CH_3), 3120 (CH_2), 2982 (CH_3), 1578 (C=N, C=C), 1454 (CH_3), 1251 (CF_3), 1145 (CF_3), 640 (CF_3).

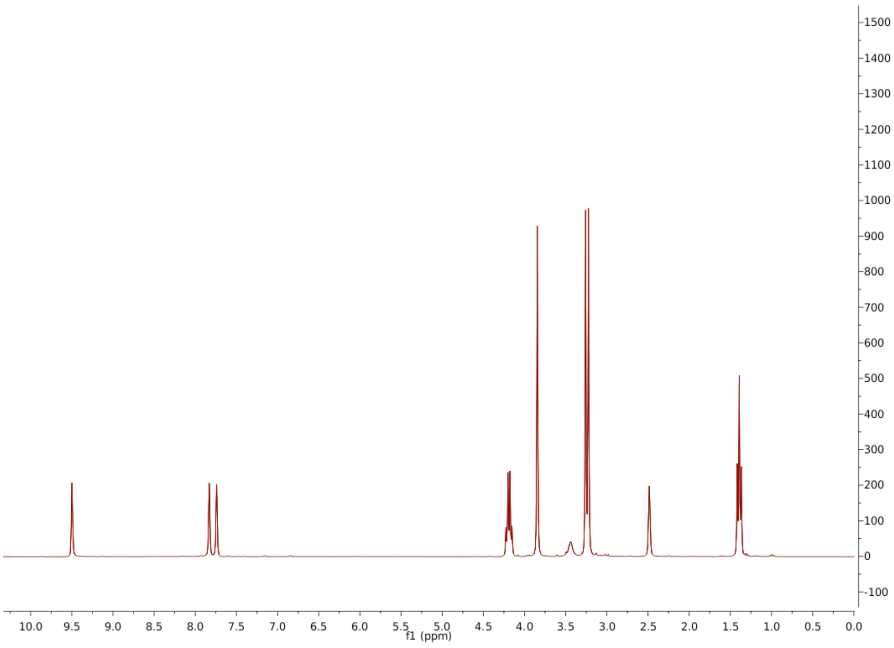
^{1}H NMR Spectra:

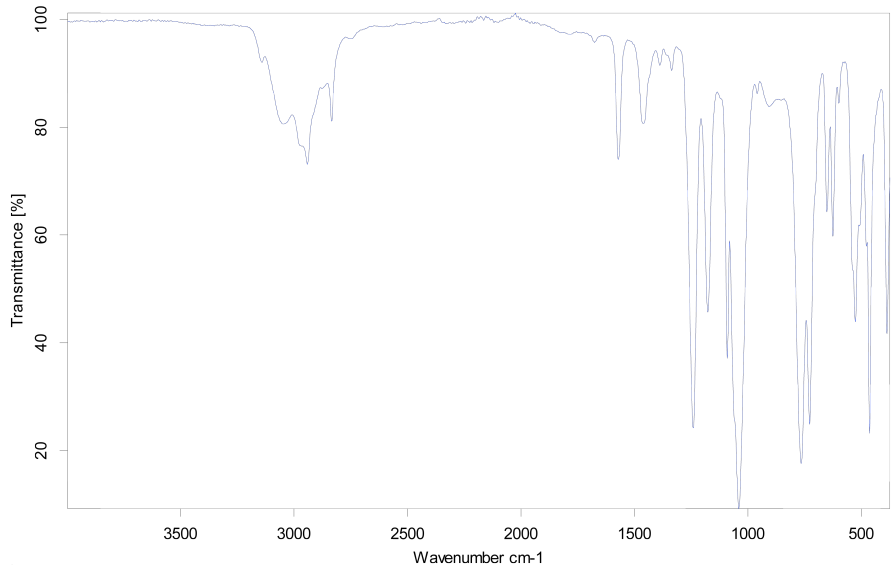


S4. Synthesis of [emim][Me_2PO_4]

1-Ethylimidazole (48.0 g, 0.500 mol) was added dropwise (over 1 h) to neat trimethylphosphate (70.0 g, 0.500 mol) at 100 °C. The reaction was allowed to stir for a further 18 h at 80 °C. The mixture was rotary evaporated at 65 °C under high vacuum for 18 h, to yield a clear pale yellow oil (118.0 g, 100%). ^{1}H NMR (300 MHz, DMSO-d6): δ 1.39 (3H, t, *J*=7.3 Hz), 3.24 (6H, d, *J*=10.3 Hz), 3.85 (3H, s), 4.19 (2H, q, *J*=7.3 Hz), 7.74 (1H, s), 7.83 (1H, s), 9.50 (1H, s); IR (ATR, cm^{-1}) 3139 (CH_3), 3055 (CH_2), 2936 (CH_3), 1565 (C=N, C=C), 1460 (CH_3), 1231 (CH_3), 1034 (Me_2PO_4), 765 (Me_2PO_4).

^{1}H NMR Spectra:

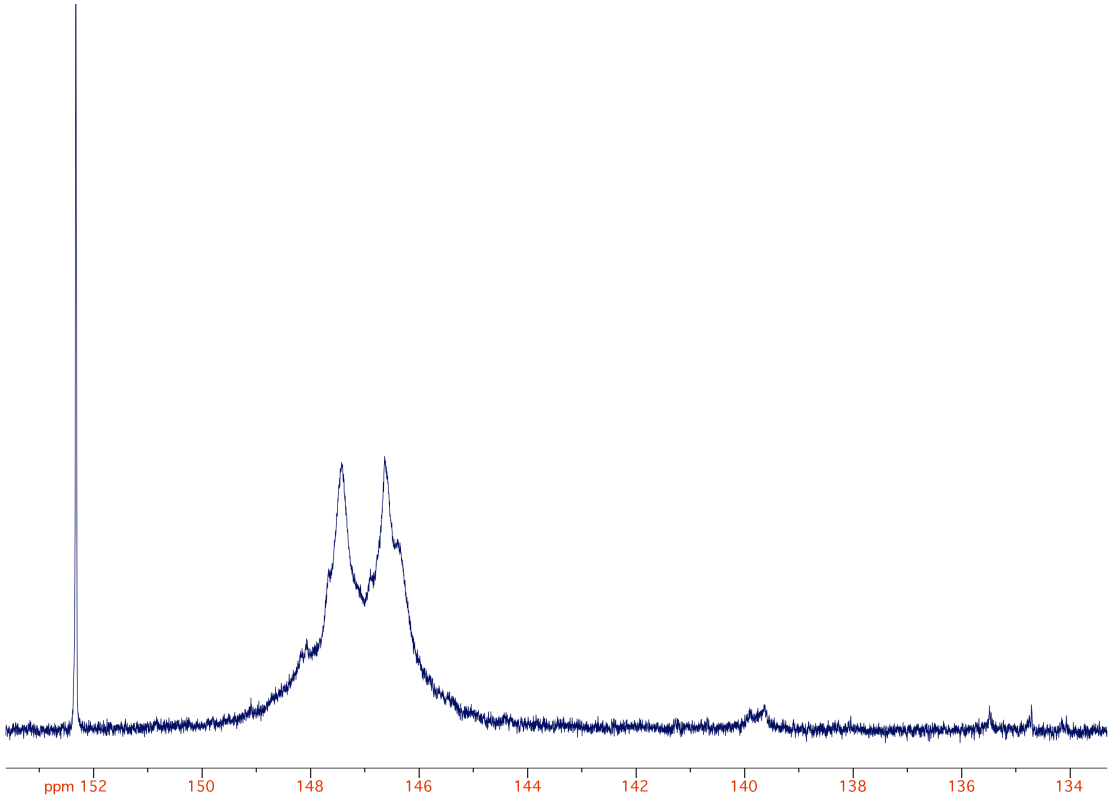




S5. ^{31}P NMR Analysis Procedure

Milled wood samples were phosphitylated and analysed using the following procedure: Ionic liquid (~0.40 ml, 475 mg) was added, by syringe, to pulverized wood (25 mg) in in a 8 ml sample vial The mixture was manually mixed with a needle, until homogeneous, flushed with argon and sealed. The sample was heated at 90 ^{o}C until clear (or a maximum time of 18 hr was reached). Pyridine (150 µl, 1.88 mmol) was added in one portion and the sample vortexed, at 2500 rpm, using an Janke & Kunkel Vibrofix VF1 Electronic orbital shaker, until visibly homogeneous (~20 s). The sample was allowed to cool to room temperature, whereby 2-Cl-TMDP (200 µl, 1.26 mmol) was added in one portion and vortexed until visibly homogeneous (~30 s), as a cream paste. A stock solution of $Cr(acac)_3/CDCl_3$ (0.04 M, 500 µl) was added in 4*125 µl portions with vortexing (~30 s) between each addition. *e*-HNDI solution (121.5 mM in 3:2 pyridine:$CDCl_3$, 125 µl) was added in one portion and the solution vortexed (~30 s). Further $Cr(acac)_3/CDCl_3$ (0.04 M, 3.5 ml) was added in a 500 µl and 3*1 ml portions, with vortexing (~30 s) between each addition. ^{31}P NMR spectra (243 MHz) were recorded with 700 µl samples, in a 5 mm o.d. NMR tube. Spectral width was 20000 Hz. The transmitter offset was centered on 150 ppm. The pulse flip angle was 80 ^{o}. The pre-relaxation delay was 5 s and acquisition time was 1 s. The samples were measured using a Varian Inova 600 MHz spectrometer equipped with a direct detection probe for broadband nuclei such as ^{31}P. $CDCl_3$ was used as locking solvent, and standard transients of 700 were collected. The experiment temperature was maintained at 27 ^{o}C for all experiments. This data was processed routinely, without baseline correction, using VNMRJ version 2.1b by Varian Inc. A 0 Hz (fourier transformed) exponential line-broadening factor was used in all cases. Drift correction was performed between 160 and 130 ppm. The anhydride peak, derived from reaction of 2-Cl-TMDP with water, was used as the calibration peak at 132.2 ppm. The ‘total hydroxyl’ integration region was 133 - 151.5 ppm. The guaiacyl hydroxyl integration region was defined as 138.75 - 140.5 ppm. The internal standard was at ~152.3 ppm.

NMR Spectra for 98 hr planetary milled spruce, phosphitylated from [amim]Cl:



S6. Kamlet-Taft Parameterisation Procedure

All samples were prepared in similar fashion. The absorbance of the dye compounds was adjusted so that Abs_{max} <1.5.This was achieved with following concentrations, nitroaniline 24 µl/ml, diethylnitroaniline 24 µl/ml and Reichardt's dye 100 µl/ml.

Samples were recorded on Varian Cary 50 conc. UV Vis spectrometer with a Varian Cary Single Cell Peltier accessory. The UV spectrometer creates the spectra using 1000 data points, changing the wavelength as a function of absorbance. From a closer view the distance between adjacent data points is few nanometers and the A_{max} value, given by the software, is the data point at the highest A value. To improve accuracy, we transferred the data points to ORIGIN 7.5. We selected only the data representing the A_{max} peak (~200 nm) from each measurement and fitted a polynomial function to these data points, to get more accurate view of the peak shape. The polynomial function that was used was as follows:

$$Y=A+B_1X+B_2X^2+B_3X^3+B_4X^4+B_5X^5 , \qquad \text{(eq.1)}$$

where Y and X are the relative axes, B is slope and A is constant. The A_{max} value was extracted from the plot data simply sorting the plot data points in decreasing order. From the extracted data KT parameters were calculated using equations from Hauru *et al*.[5]