Electronic supplementary information (ESI)

Soaking of Pine Wood Chips with Ionic Liquids for Reduced Energy Input During Grinding

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Synthesis of 1-butyl-3-methylimidazolium acetate

200 ml (1.52 mol) N-butylimidazole, 168 ml dimethyl carbonate (1.98 mol) and 200 ml methanol were heated in a stirred stainless steel pressure reactor (Parr Instruments) at 140°C for 24 h. The methanol was evaporated and the viscous liquid washed 3 times with 150 ml dry toluene under a nitrogen atmosphere. The washed product was dried *in vacuo* until crystals appeared. The product was dissolved in 100 ml acetonitrile at 80°C. 100 ml ethyl acetate was added and the liquid slowly cooled to room temperature. The crystals were washed twice with 200 ml ethyl acetate. The off-white solid was dried under vacuum and mild heating. The ^{1}H-NMR spectrum showed that the product was a mixture of 1-butyl-3-methylimidazolium carboxylates (carboxylated at position 2,4, and 5 of the ring). 90.0 g (494 mmol) of 1-butyl-3-methylimidazolium carboxylate mixture was transferred into a Schlenk flask in the glove box. 100 ml methanol was added under a nitrogen atmosphere. 29.7 g acetic acid (494 mmol) was added drop wise. The mixture was stirred at room temperature overnight to allow the evolution of carbon dioxide go to completion. The liquid was dried *in vacuo* at 60°C, yielding a brown oily liquid with a water content of 6.1 wt% or 34 mol%.

δ_H (400 MHz; DMSO-d_6) 10.2 (1H, s, C*H*-2), 7.96 (1H, s, C*H*-5), 7.83 (1H, s, C*H*-4), 4.21 (2H, t, N-CH_2-), 3.89 (3H, s, N-CH_3), 1.75 (2H, m, N-CH_2-CH_2-), 1.61 (3H, s, H_3C-CO_2), 1.22 (2H, m, N-$(CH_2)_2$-CH_2-) and 0.86 (3H, t, N-$(CH_2)_3$-CH_3).

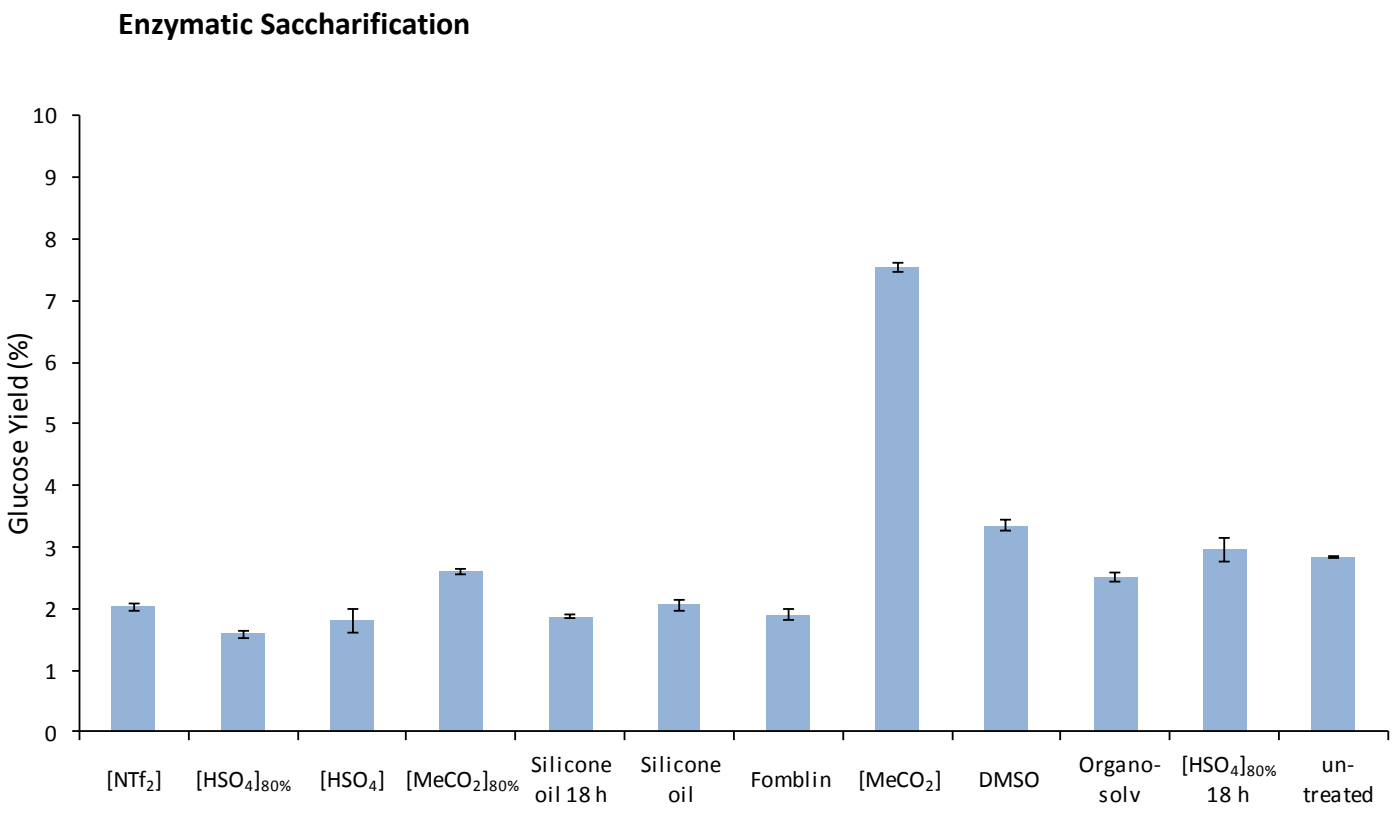

Figure 1: Glucose yields (percentage of sample dried-weight) from enzymatically treated ground wood chips treated with various liquids. Particle size range: 180 – 850 µm, treatment conditions: 90°C, 1 h unless otherwise stated. Cation of all ionic liquids is $[C_4C_1im]$.

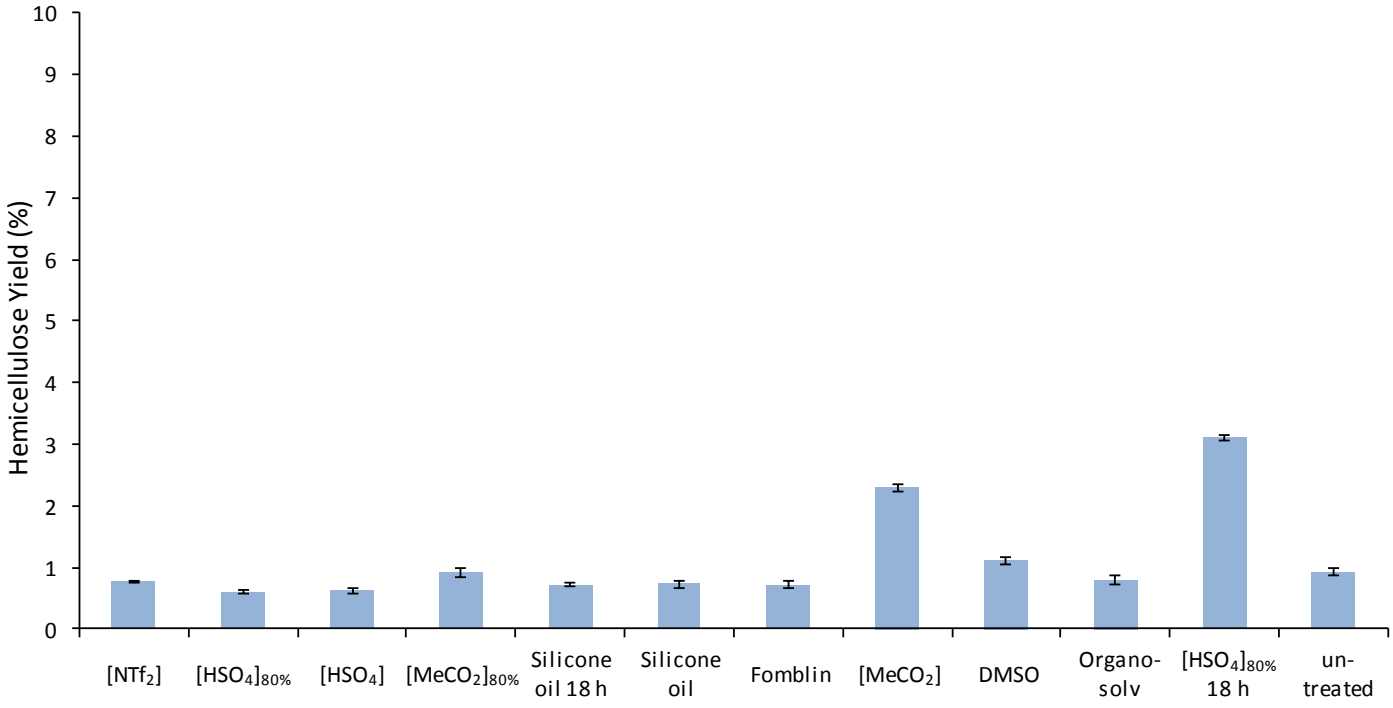

Figure 2: Hemicellulose yields (percentage of sample dried-weight) from enzymatically treated ground wood chips treated with various liquids. Particle size range: 180 – 850 µm, treatment conditions: 90°C, 1 h unless otherwise stated. Cation of all ionic liquids is $[C_4C_1im]$.

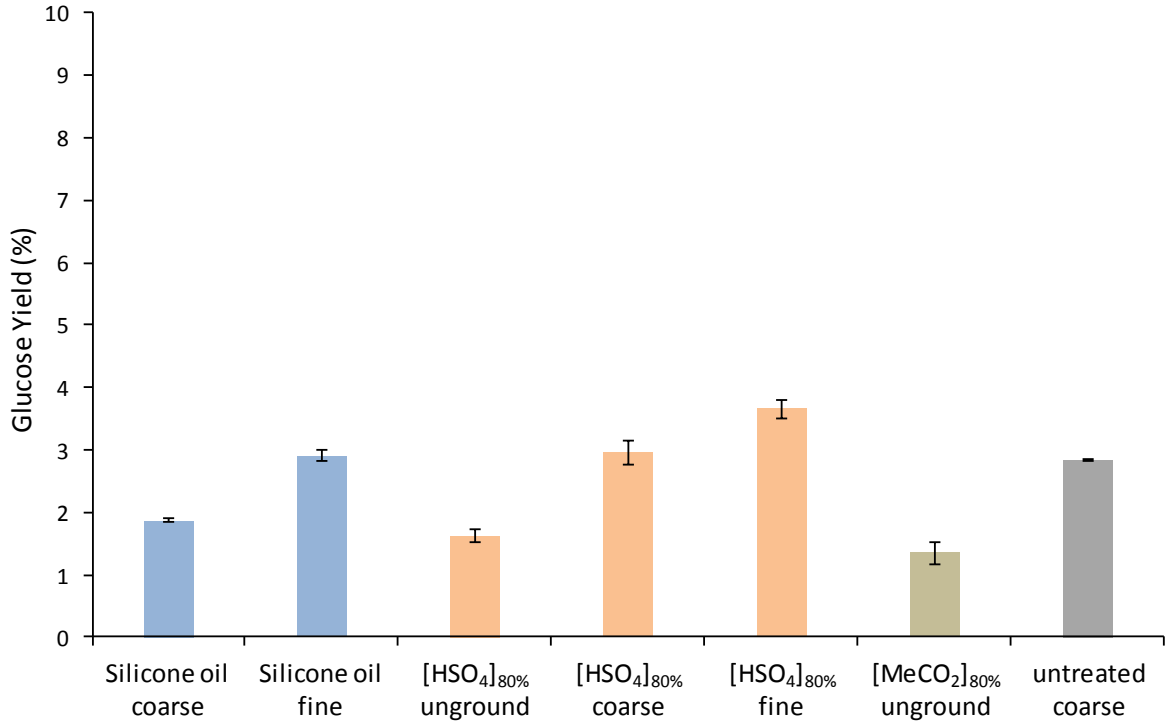

Figure 3: Influence of particle size on glucose yields (percentage of sample dried-weight) from enzymatically treated ground wood chips treated with various liquids. Coarse particle size: 180 – 850 µm, fine: 53 – 150 µm, treatment conditions: 90°C, 18 h. Cation of all ionic liquids is $[C_4C_1im]$.

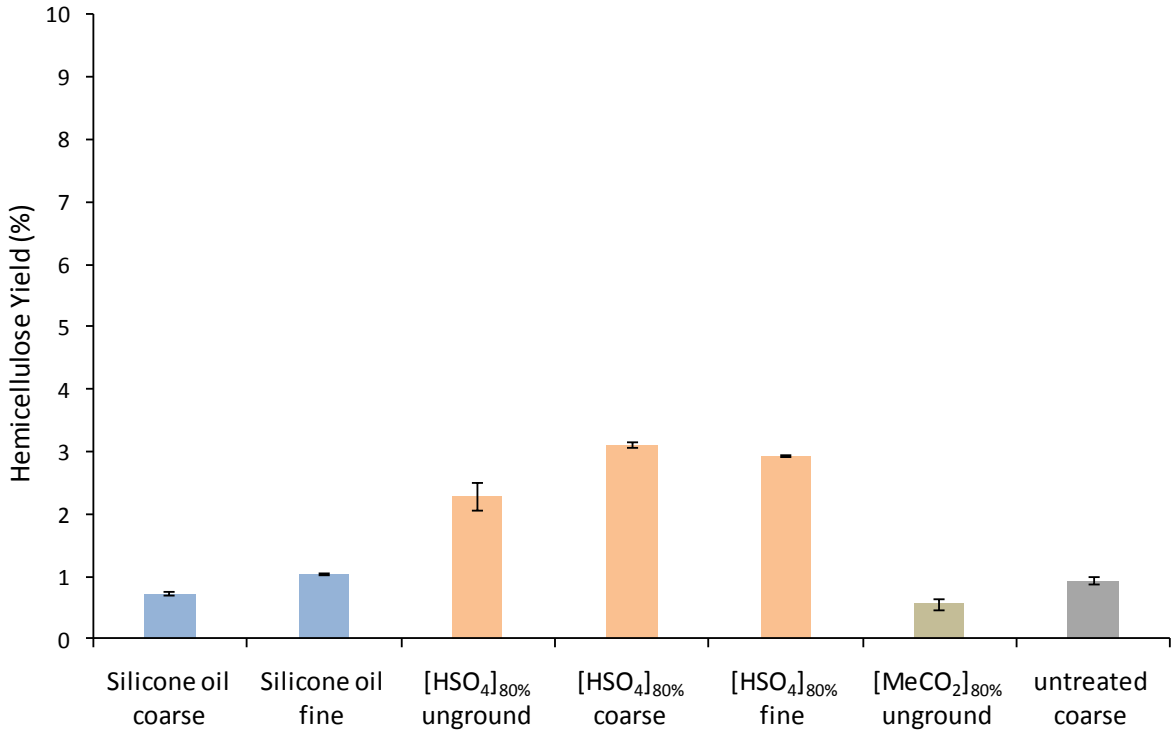

Figure 4: Influence of particle size on hemicellulose yields (percentage of sample dried-weight) from enzymatically treated ground wood chips treated with various liquids. Coarse particle size: 180 – 850 µm, fine: 53 – 150 µm, treatment conditions: 90°C, 18 h. Cation of all ionic liquids is $[C_4C_1im]$.

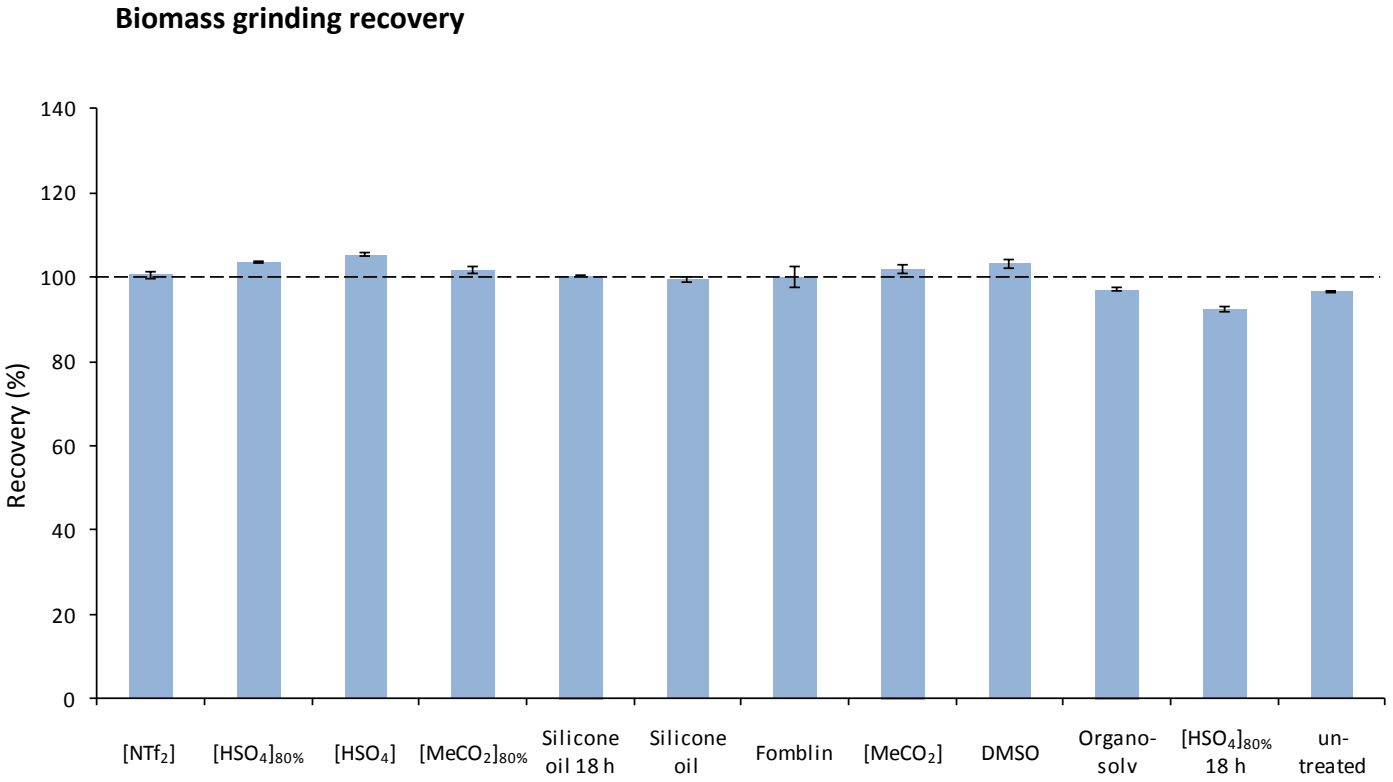

Figure 5: Percentage weight of wood chips recovered as powder after grinding and washing (oven-dried basis) after treatment with various liquids. Cation of all ionic liquids is [C_4C_1im]. Recoveries over 100% are most likely due to residual treatment liquid in the dried wood powder.

Ionic Liquid ^{1}H NMR Spectra

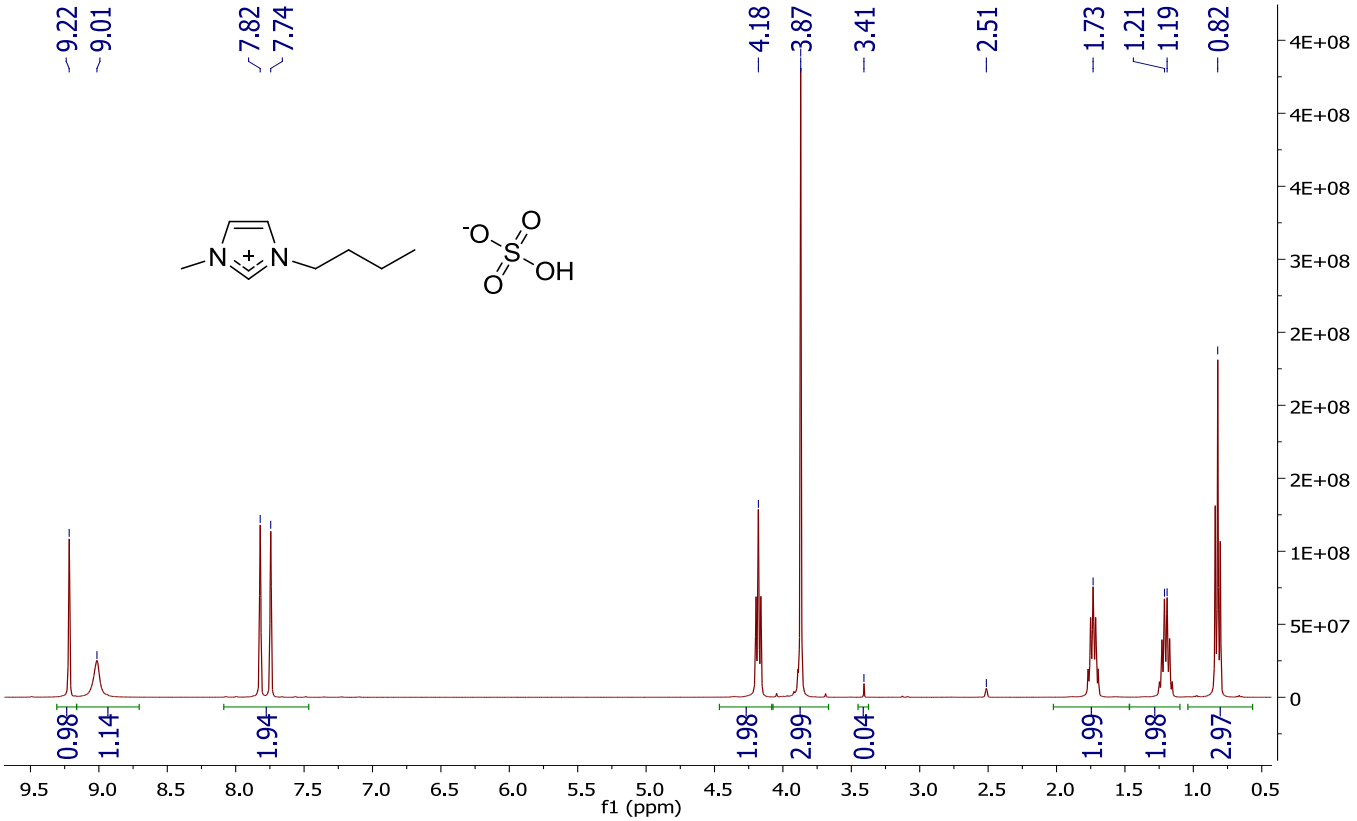

Figure 6: ^{1}H NMR spectrum of [C_4C_1im][HSO_4] in DMSO d_6.

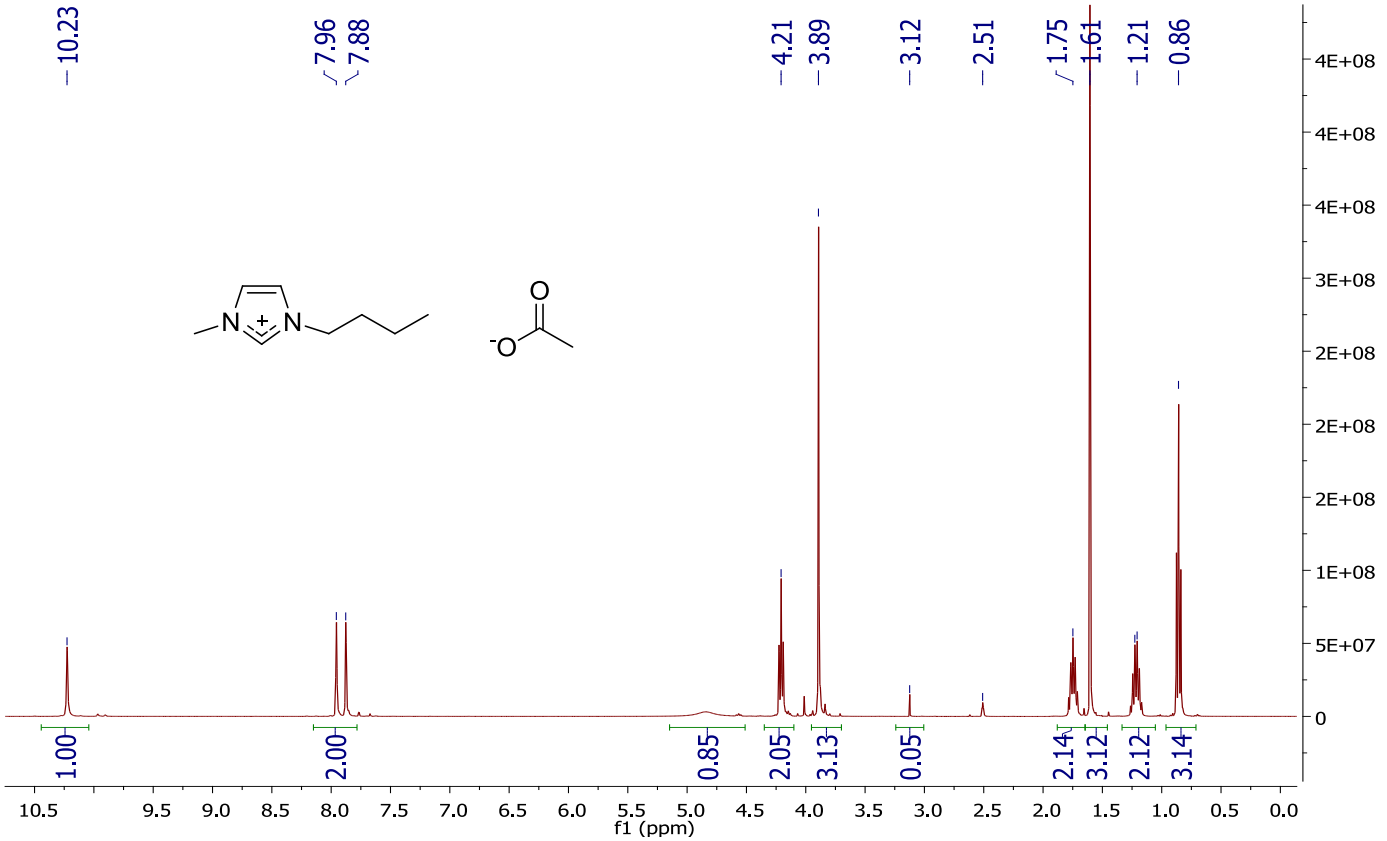

Figure 7: ^{1}H NMR spectrum of $[C_4C_1im][MeCO_2]$ in DMSO d_6.

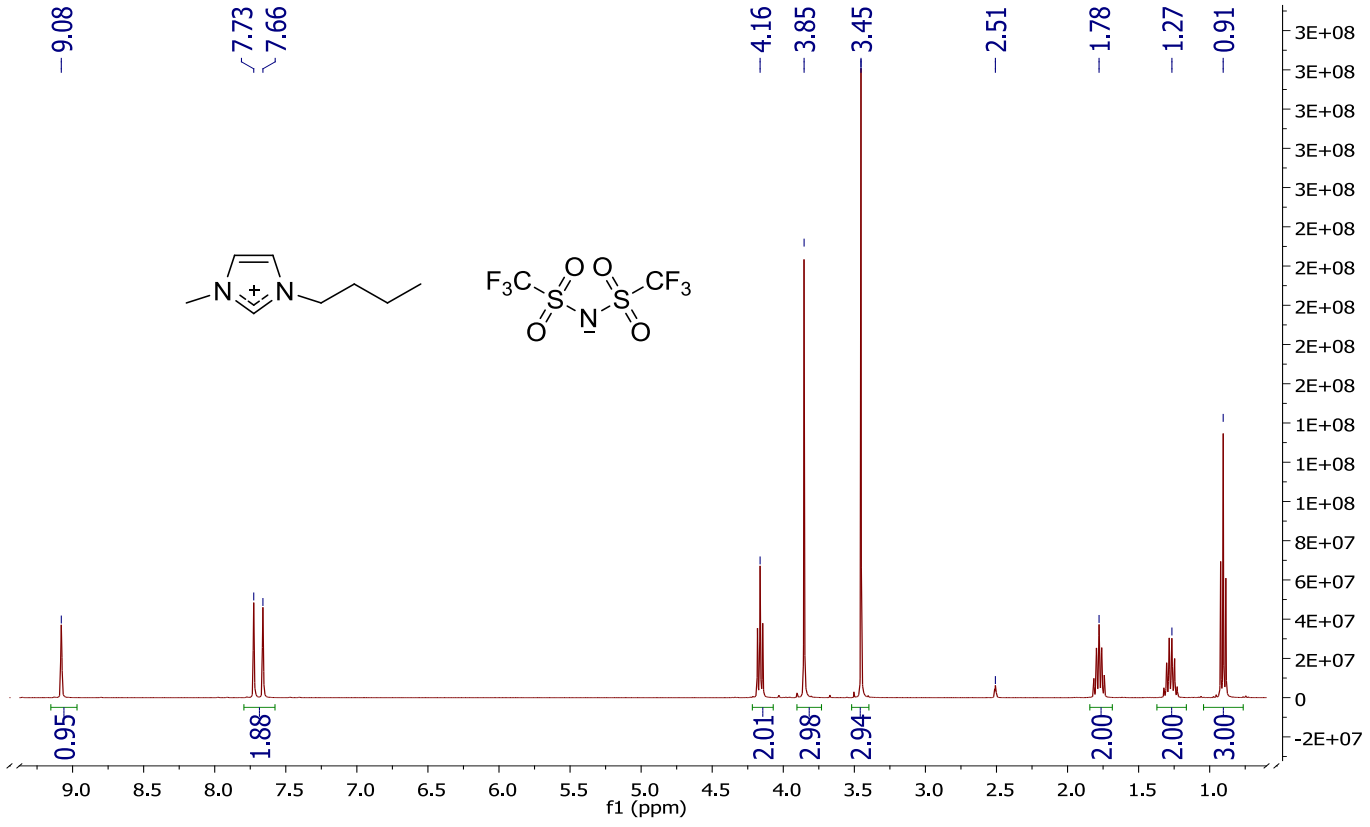

Figure 8: ^{1}H NMR spectrum of $[C_4C_1im][NTf_2]$ in DMSO d_6.