Supplementary Material (ESI) for Green Chemistry

Electronic Supporting Information

Effects of acidity and immiscibility of lactam-based Brønsted-acidic ionic liquids on their catalytic performance for esterification

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S1. NMR Characterization of the Lactam-Based Brønsted Acidic Ionic Liquids

ϵ-caprolactam tetrafluoroborate ([CP][BF_4]): ^{1}H NMR ($CDCl_3$): 1.55-1.65 (m, 6H), 2.63 (q, J) 5.2, 2H), 3.35 (q, J) 5.6, 2H), 7.89 (s, 1H), 8.52 (s, 1H). ^{13}C NMR ($CDCl_3$): 21.48, 25.96, 29.20, 32.12, 44.32, 183.73.

ϵ-caprolactam nitrate ([CP][NO_3]): ^{1}H NMR (CDCl3): 1.64-1.75 (m, 6H), 2.58 (q, J) 5.2, 2H), 3.36 (q, J) 5.6, 2H), 8.60 (s, 1H), 15.20 (s, 1H). ^{13}C NMR ($CDCl_3$): 22.21, 27.52, 29.88, 33.97, 43.70, 182.68.

ϵ-caprolactam trifluoroacetate ([CP][TFA]): ^{1}H NMR ($CDCl_3$) 1.67-1.79 (m, 6H), 2.50 (q, J) 5.2, 2H), 3.28 (q, J) 5.6, 2H), 8.43 (s, 1H), 14.81 (s, 1H). ^{13}C NMR ($CDCl_3$): 22.38, 28.07, 29.94, 34.83, 43.13, 110.83-119.39 (q, CF_3, J) 288.0), 160.80, 181.57.

ϵ-caprolactam methyl sulfonate ([CP][CH_3SO_3]): ^{1}H NMR ($CDCl_3$): 1.66-1.78 (m, 6H), 2.64 (q, J) 5.2, 2H), 3.39 (q, J) 5.6, 2H), 7.29 (s, 1H), 10.14 (s, 1H), 12.06. ^{13}C NMR ($CDCl_3$): 22.02, 27.03, 29.77, 33.35, 39.38, 43.98, 76.90, 182.55.

N-methyl-2-pyrrolidone nitrate ([NMP][NO_3]): ^{1}H NMR ($CDCl_3$): 1.91, 2.40, 2.72 (3H, NCH_3), 3.37, 14.91. ^{13}C NMR ($CDCl_3$): 17.18, 30.11, 30.20, 50.86, 177.58.

N-methyl-2-pyrrolidone trifluoroacetate ([NMP][TFA]): ^{1}H NMR ($CDCl_3$): 1.97, 2.42, 2.77(3H, NCH_3), 3.38, 15.40. ^{13}C NMR ($CDCl_3$): 17.17, 30.07, 50.12, 77.19, 110.79-119.35(q, CF_3, J) 288.0), 158.79, 177.27.

N-methyl-2-pyrrolidone methyl sulfonate ([NMP][CH_3SO_3]): ^{1}H NMR ($CDCl_3$): 2.05, 2.72 (3H, NCH_3), 2.88, 3.54, 13.92. ^{13}C NMR ($CDCl_3$): 17.34, 30.19, 30.99, 51.66, 77.32, 178.02.

S2. TG-DTA Characterization of the Lactam-Based Brønsted Acidic Ionic Liquids

Thermal gravimetric analysis (TGA) was performed with Simultaneous Thermal Analysis-STA 409EP. The samples for TGA were placed in an aluminium crucible, thermal analysis and temperature-dependent mass changes were examined in the range of 30 to 600 ºC. The thermal decomposition temperature (T_d) was recorded with 10% of mass loss of lactam-based Brønsted acidic ILs with scan rate of 10 ºC/min under N_2 atmosphere.

S3. Acidity Characterization of the Lactam-Based Brønsted Acidic Ionic Liquids

The measurement of acidic scale of these lactam-based Brønsted acidic ILs was conducted on an Shimadzu 2100 UV-visible spectrophotometer with a basic indicator according to the procedures previously reported in literatures. [1,2] Based on the Eq 1, where H_0 is the Hammett acidity function which stands for the relative acidity of ILs, [I] and [IH^+] are the molar concentrations of, respectively, the unprotonated and protonated forms of the indicator in the solvents, the value of H_0 was calculated by determining the ratio of [I]/[IH^+]. Based on the Lambert-Beer law that absorption is proportional to the concentration of absorbing species in the material on condition of the same light path length, the ratio of [I]/[IH^+] can be calculated by the absorbance difference of basic indicator measured after addition of lactam-based Brønsted acidic ILs.

$$H_0=pK(I)+\log([I]/[IH^+]) \qquad \text{(Eq 1)}$$

Methyl yellow (MY) (15 mg/l, p*K*a = 3.3), 4-phenylazodi- phenylamine (PADA) (10 mg/l, p*K*a = 1.5) and 2-nitrophenyl- amine (NPA) (5 mg/l, p*K*a = -0.2) in ethanol were chosen as basic indicators to characterize the acidity of different lactam-based Brønsted acidic ILs and the concentration of lactam-based Brønsted acidic ILs was set at 80 mmol/l in ethanol, we determined the H_0 of these ILs.

S4. Solubility Characterization of Ionic Liquid [CP][CH_3SO_3] in Different Esters

The measurement of solubility of [CP][CH_3SO_3] in different esters was conducted on an Shimadzu 2100 UV-visible spectrophotometer according to the procedures previously reported in literature.[3] A nearly linear relationship of absorbency and concentration was established by measuring the absorption values of different concentration [CP][CH_3SO_3] in *n*-butyl acetate at 288 nm.

To measure the solubility of [CP][CH_3SO_3], excess amounts of [CP][CH_3SO_3] were added in the corresponding esters and vigorously stirred for 24 h at 30 ºC. After phase separation, an aliquot of the ester phase was removed by pipette and diluted by a facter of 5-20 (to reach a concentration range where the UV-visible response is nearly linear, above). Then the absorption values of this diluted solution were analylized by using the corresponding ester as reference solution, and the concentration of this diluted solution can be obtained by combining the absorption values and the linear relationship of absorbancy and concentration. The solubility of [CP][CH_3SO_3] in esters can be calculated according to the diluted factor.

1 C.Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts and B. Gilbert, *J. Am. Chem. Soc.,* 2003, **125,** 5264.

2 Z.Y. Du, Z. P. Li, S. Guo, J. Zhang, L. Y. Zhu and Y. Q. Deng, *J. Phys. Chem. B.,* 2005, **109,** 19542.

3. A. Beyaz, W. S. Oh, V. P. Reddy, *Colloids and Surfaces B: Biointerfaces*., 2004, **35,**

119.

S5. NMR Spectra of Lactam -Based Brønsted Acidic ILs in $CDCl_3$

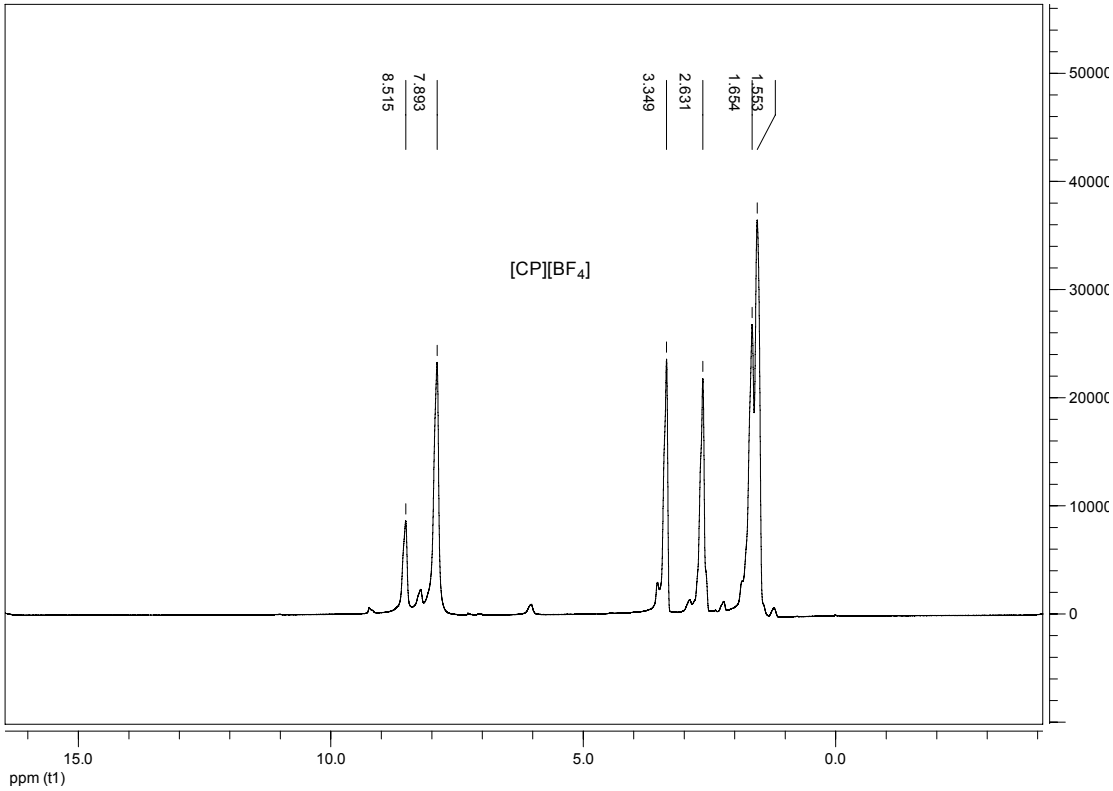

Fig. S1 ^{1}H spectra of $[CP][BF_4]$.

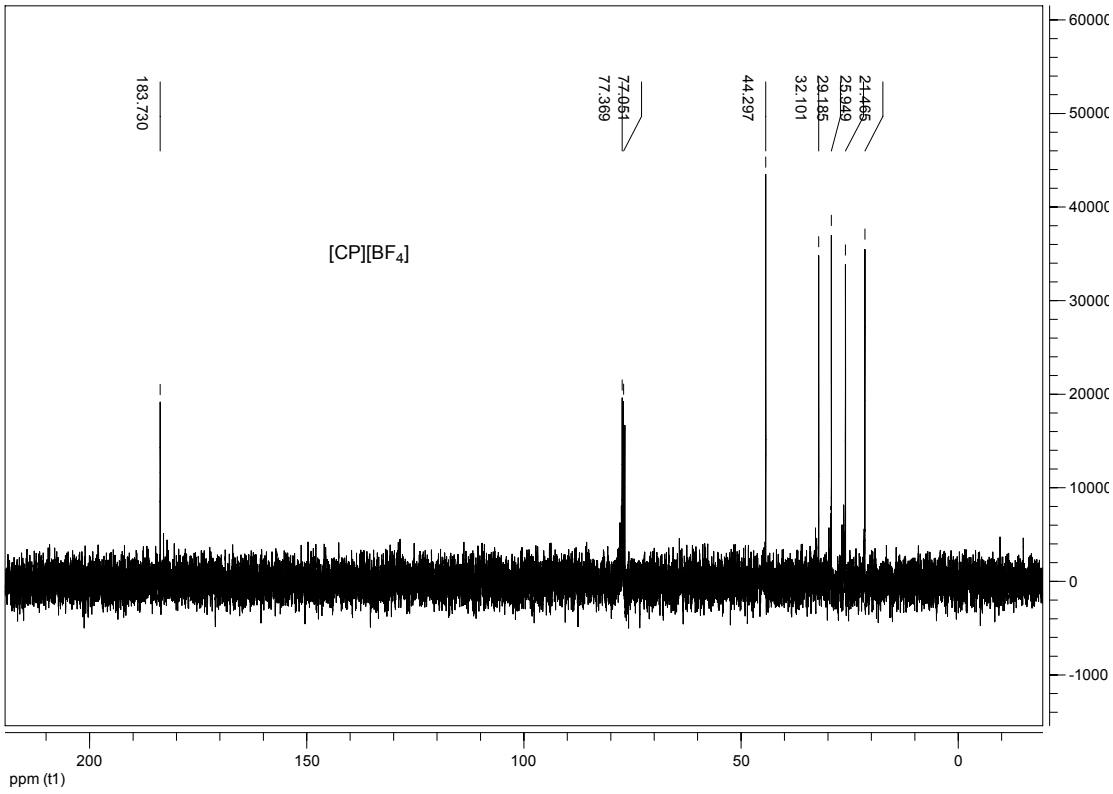

Fig. S2 ^{13}C spectra of $[CP][BF_4]$.

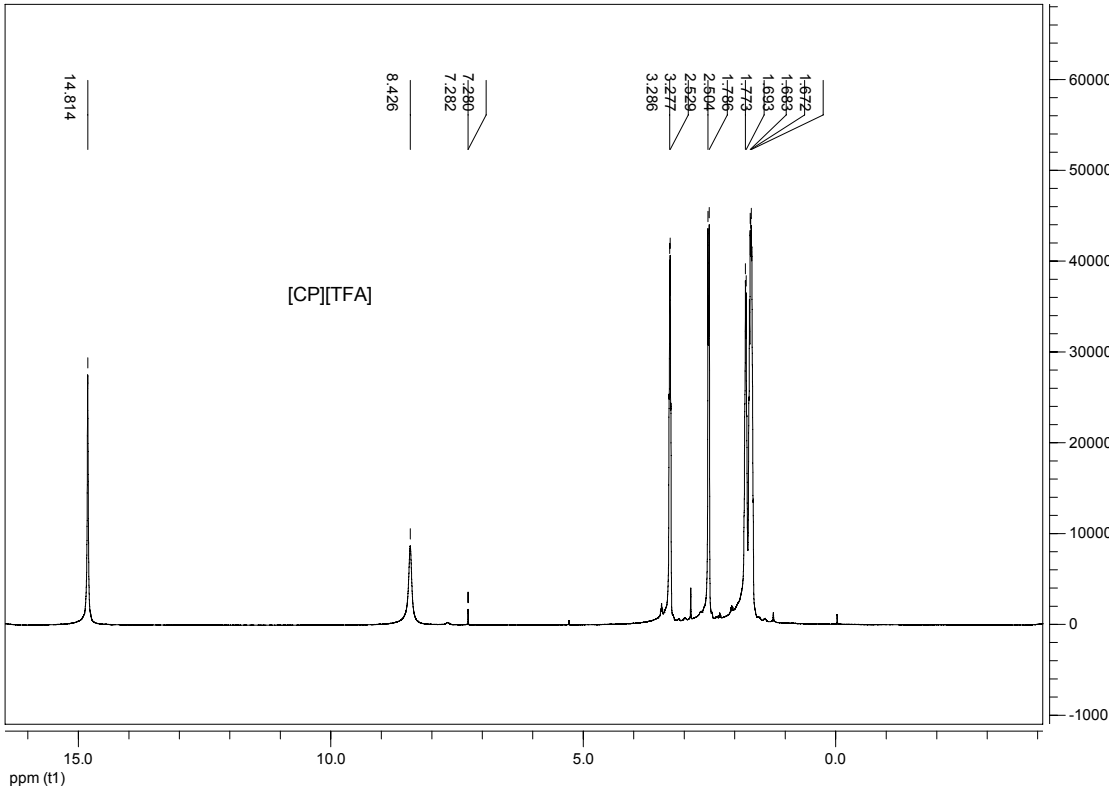

Fig. S3 ^{1}H spectra of [CP][TFA].

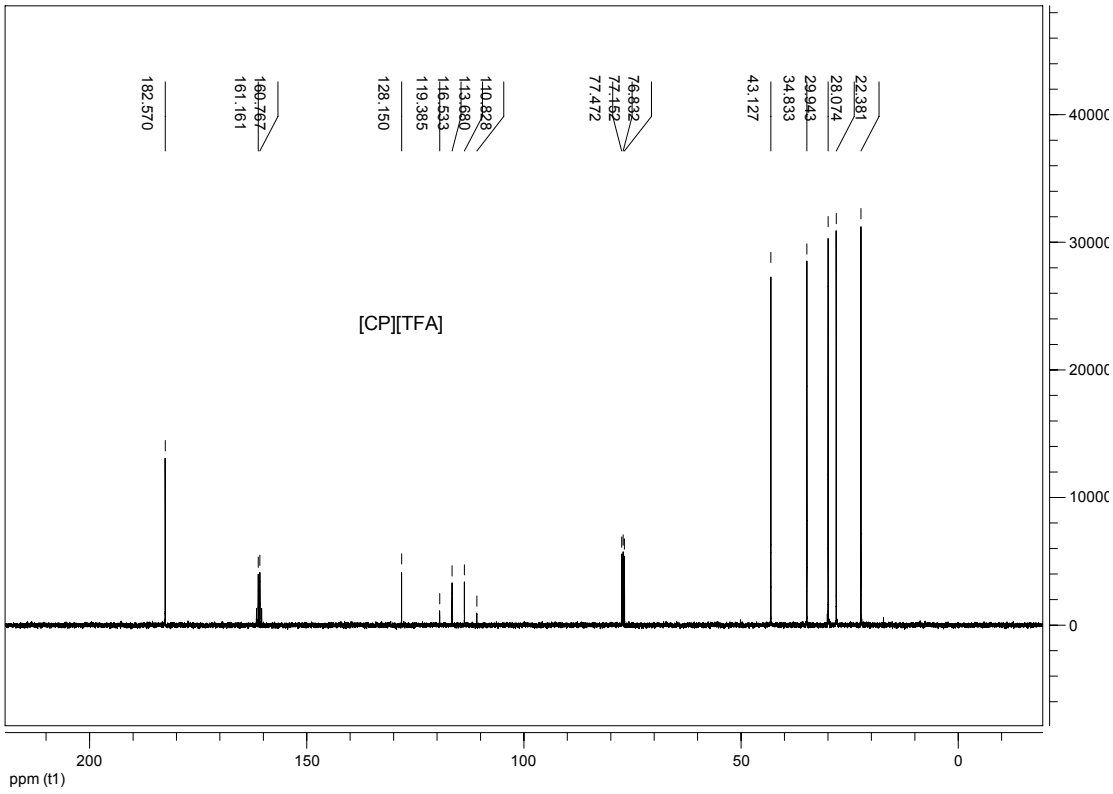

Fig. S4 ^{13}C spectra of [CP][TFA].

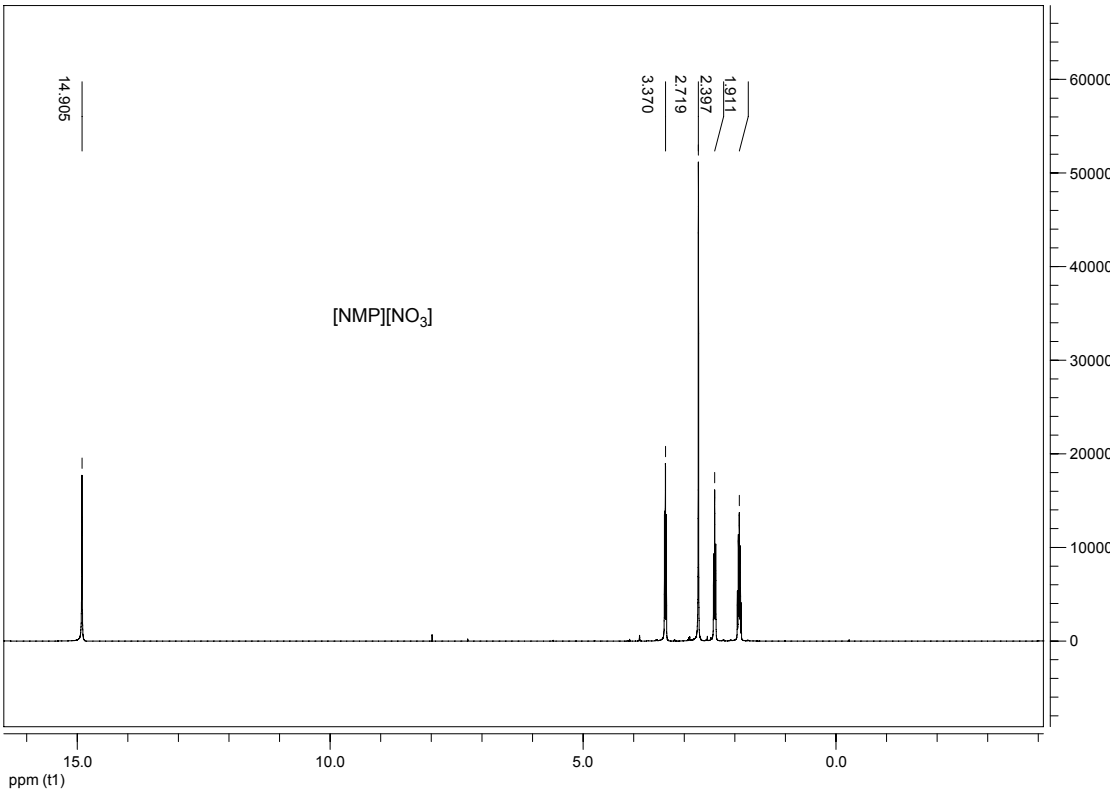

Fig. S5 ^{1}H spectra of [NMP][NO_3].

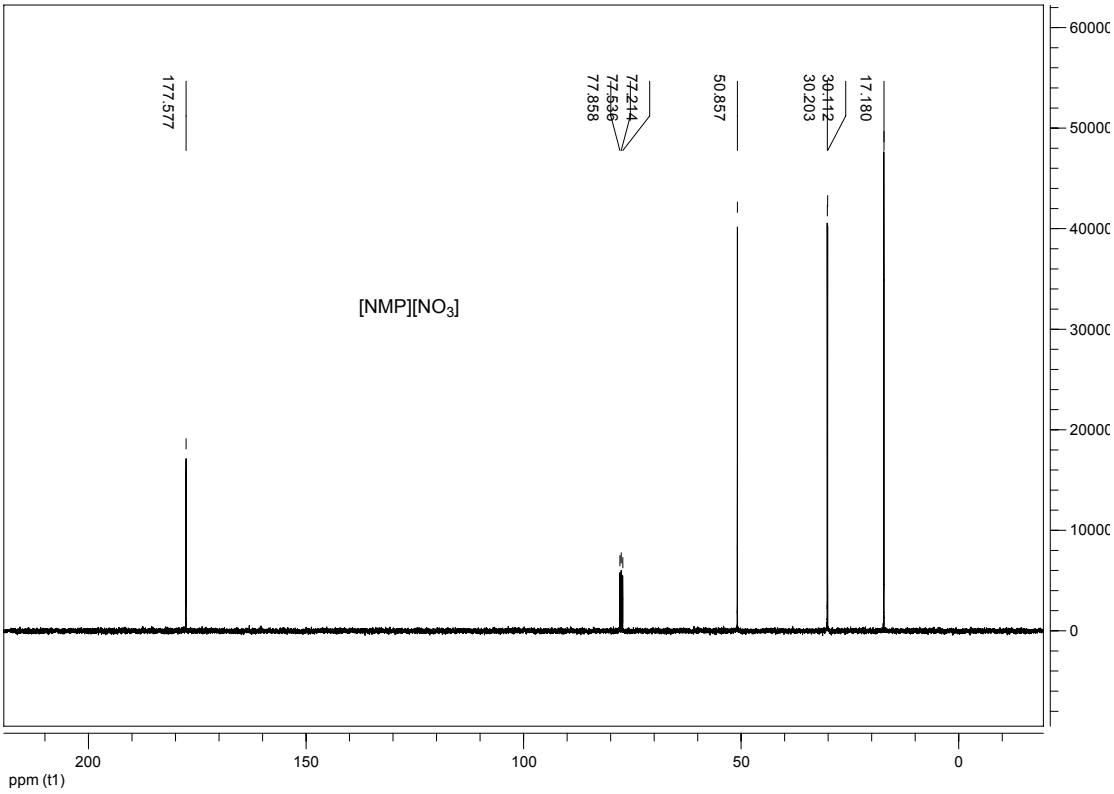

Fig. S6 ^{13}C spectra of [NMP][NO_3].

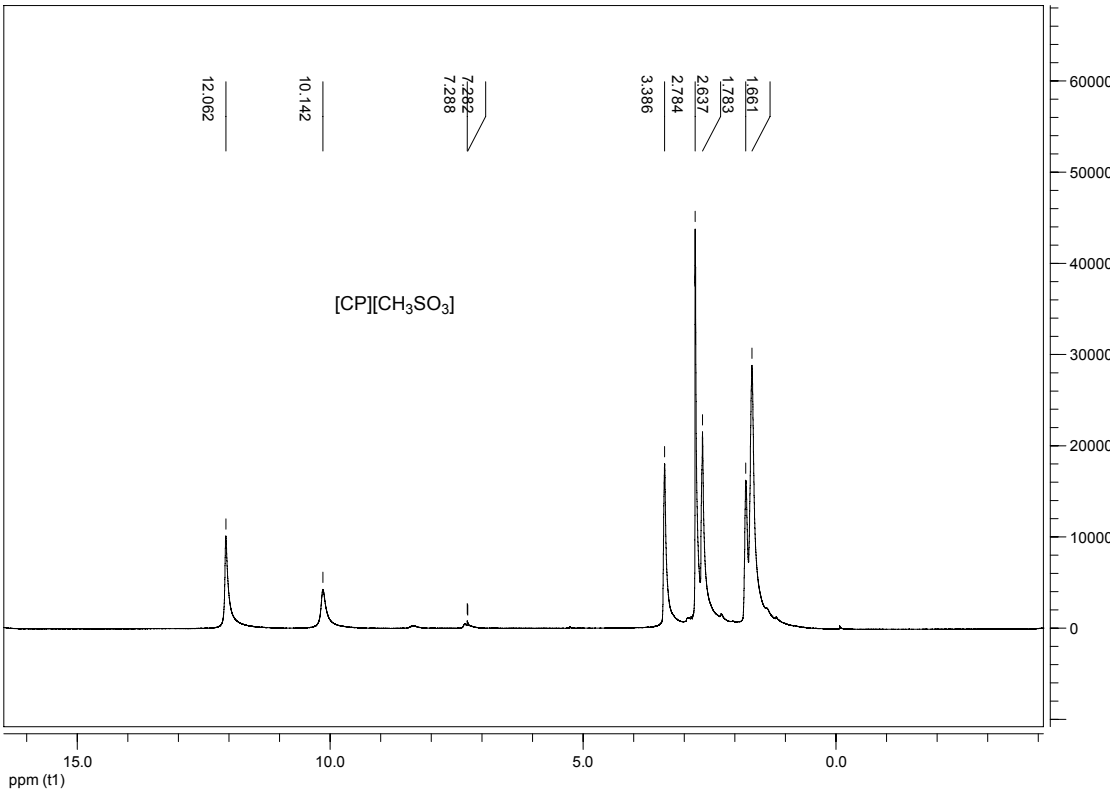

Fig. S7 ^{1}H spectra of $[CP][CH_3SO_3]$.

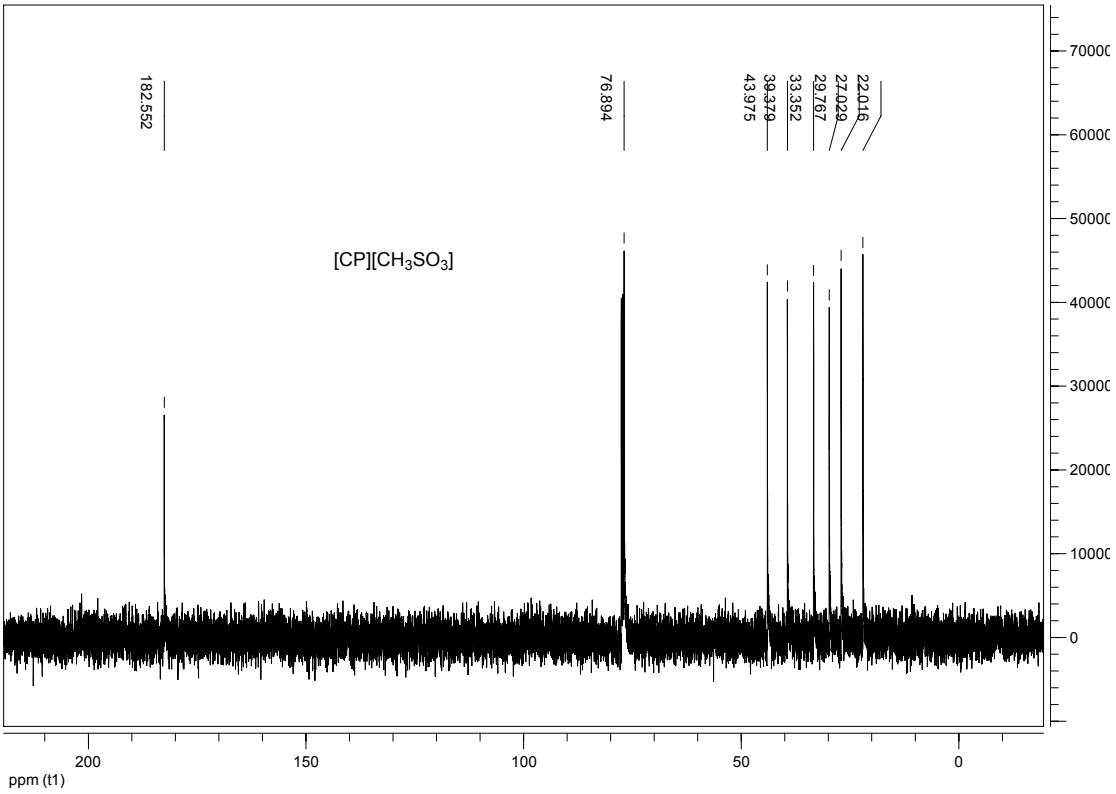

Fig. S8 ^{13}C spectra of $[CP][CH_3SO_3]$.

S5. Thermal Gravimetric Analysis Plot of Lactam -Based Brønsted Acidic ILs

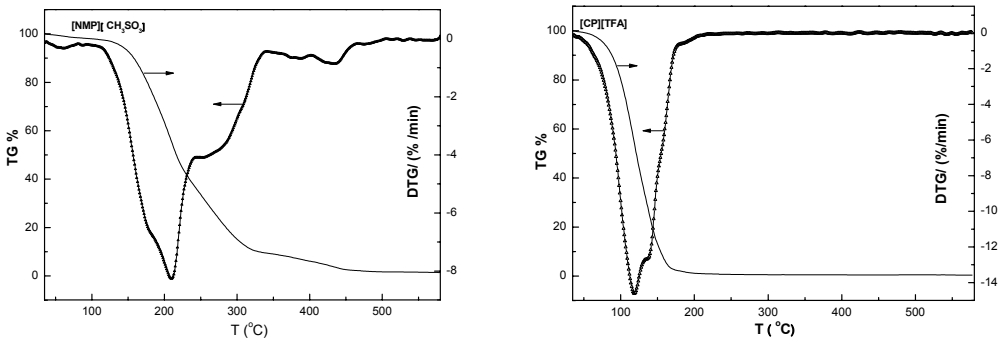

Fig. S9 TG-DTA profiles of [NMP][CH_3SO_3] and [CP][TFA].

S6. UV-Vis Absorbance Spectra of Four Lactam-Based Brønsted Acidic ILs

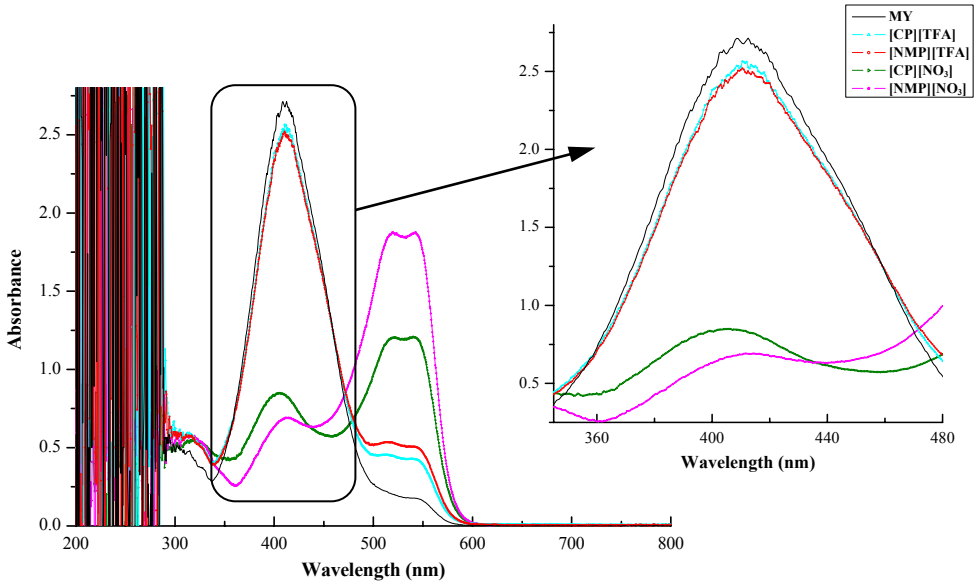

Fig. S10 UV-Vis Spectra of MY basic indicators and several lactam-based Brønsted acidic ILs.