

Supporting Information

Brønsted acidic ionic liquids catalyzed conversion of hemicellulose into sugars

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1. Synthesis of ionic liquids (ILs):

a) 1-methyl-3-(3-sulfopropyl)-imidazolium para-toluenesulfonate, [C₃SO₃HMIM][PTS]:

1-methyl imidazole, 7.625 mmol and 1,3-propane sultone, 7.625 mmol were dissolved in 10 mL toluene and refluxed at 110 °C for 16 h in a round bottom flask under stirring. The product; the zwitter ion was formed in quantitative yield and was precipitated out as a white solid. The white precipitate formed was isolated by filtration, and dried and used as such for the next step. Synthesis of IL was accomplished by mixing equimolar quantities of *p*-toluenesulfonic acid (PTSA) and zwitter ion. The resulting solution was stirred at 70 °C for 24h. During this time the solids react, resulting in the formation of the BAIL. The color of the BAIL was pale yellow.

b) 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate, [C₃SO₃HMIM][HSO₄]:

The synthesis procedure is same as mentioned above. However, in place of PTSA equimolar quantities of sulphuric acid and zwitter ions were mixed together. Rest procedure is same to yield BAIL.

c) 1-methyl-3-(3-sulfopropyl)-imidazolium chloride, [C₃SO₃HMIM][Cl]:

1-Methyl imidazole and 1,3-propanesultone (7.625 mmol each) were dissolved in 10mL toluene and refluxed at 110 °C in a RB flask for 24 h under constant stirring. The product; the zwitter ion was formed in quantitative yield and was precipitated out as a solid. The precipitate formed was isolated by filtration, and dried and used as such for the next step. Equimolar quantities of HCl was added to this precipitate and heated at 85 °C for 24 h. This results in the formation of the BAIL.

d) 1-butyl-3-methyl imidazolium chloride, [BMIM][Cl]:

1-butyl-3-methylimidazolium chloride was prepared according to literature procedure¹. In a typical synthesis a solution of 1-chlorobutane (108 mmol) and N-methyl imidazole (108 mmol) was refluxed in round bottom flask at 343K for 24 h under inert atmosphere. After 24 h the reaction mixture showed two distinct layers. The upper layer containing unreacted starting material was decanted and bottom layer was extracted with ethyl acetate (a volume approximately equal to half that of

bottom layer). This procedure was repeated thrice. Washing with ethyl acetate should suffice to remove any untreated starting material from bottom phase. The remaining solvent from crude ionic liquid was distilled off on rotavac and the product was dried under high vacuum. Dried IL showed slightly yellow appearance.

2 Characterization results

2.1. 1-methyl-3-(3-sulfopropyl)-imidazolium para-toluenesulfonate, [C₃SO₃HMIM][PTS]:

¹H NMR (D₂O, 200 MHz): δ 8.60 (s, 1H), 7.53 (d, 2H), 7.39 (s, 1H), 7.37 (s, 1H), 7.24 (d, 2H), 4.21 (t, 2H), 3.74 (s, 3H), 2.78 (t, 2H) 2.25 (s, 3H), 1.90 (m, 2H);

¹³C NMR (D₂O, 50 MHz): δ (ppm): 142.42, 139.43, 136.09, 129.40, 125.31, 123.72, 122.14, 47.69, 47.17, 35.66, 25.05, 20.44.

Microanalysis: the approximate % element by microanalysis is C (43), H (5.3), N (7.5) and S (15).

Calculated element % C (60.4), H (5.2), O (17.2), P (5.5), and S (11.5).

2.2. 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate, [C₃SO₃HMIM][HSO₄]:

¹H NMR (D₂O, 200 MHz): δ 8.66 (s, 1H), 7.42(s, 1H), 7.35 (s, 1H), 4.26 (t, 2H), 3.79 (s, 3H), 2.82 (t, 2H), 2.21 (m, 2H);

¹³C NMR (D₂O, 50 MHz), δ 13.16, 123.74, 122.16, 47.7, 47.16, 35.66, 25.04.

Microanalysis: the approximate % element by microanalysis is C (24.2), H (6.5), N (7.2) and S (20.7).

Calculated element % C (27.8), H (4.6); N (9.3), O (37), and S (21.2).

2.3. 1-methyl-3-(3-sulfopropyl)-imidazolium chloride, [C₃SO₃HMIM][Cl]:

¹H NMR (D₂O, 200 MHz) δ 8.63 (s, 1H), 7.40 (s, 1H), 7.32 (s, 1H), 4.24 (t, 2H), 3.77 (s, 3H), 2.80 (t, 2H), 2.19 (m, 2H);

¹³C NMR (D₂O, 50 MHz), δ 136.2, 123.7, 122.2, 47.73, 47.2, 35.7, 25.1.

Microanalysis: the approximate % element by microanalysis is C (31.75), H (6.2), N (11.5) and S (12.6).

Calculated element % C (34.9), H (5.44), Cl (14.7), N (11.6), O (19.9) and S (13.3).

2.4. 1-butyl-3-methyl imidazolium chloride, [BMIM][Cl]:

^1H NMR (D_2O , 200 MHz) δ 8.6 (s, 1H), 7.37 (s, 1H), 7.33 (s, 1H), 4.10 (t, 2H), 3.8 (s, 3H), 1.75 (m, 2H), 1.2 (m, 2H) 0.82 (t, 3H);

^{13}C NMR (D_2O , 50 MHz), δ 123.5, 122.2, 49, 35.7, 31.3, 18.8, 12.7.

Microanalysis: the approximate % element by microanalysis is C (50.3), H (9) and N (15).

Calculated element % C (55), H (8.6), Cl (20.3) and N (16).

3. Thermal stability study of ILs:

TGA profiles of ILs under air atmosphere.

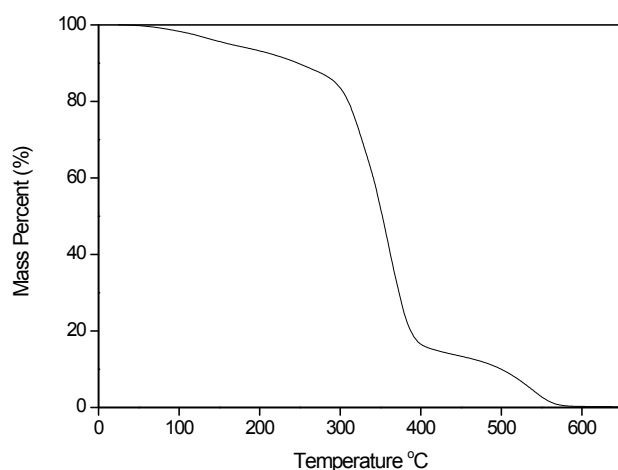


Figure S1.1. TGA profile of [C₃SO₃HMIM][HSO₄].

The thermal degradation of [C₃SO₃HMIM][HSO₄] started at 300 °C, it is stable up to 300 °C and total degradation happens at 560 °C.

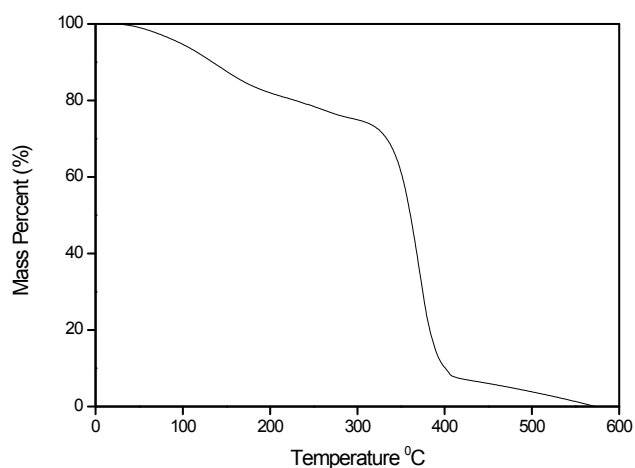


Figure S1.2. The TGA profile of [C₃SO₃HMIM][Cl].

The thermal degradation of [C₃SO₃HMIM][Cl] started at 350 °C, it is stable up to 350 °C and total degradation happens at 580 °C.

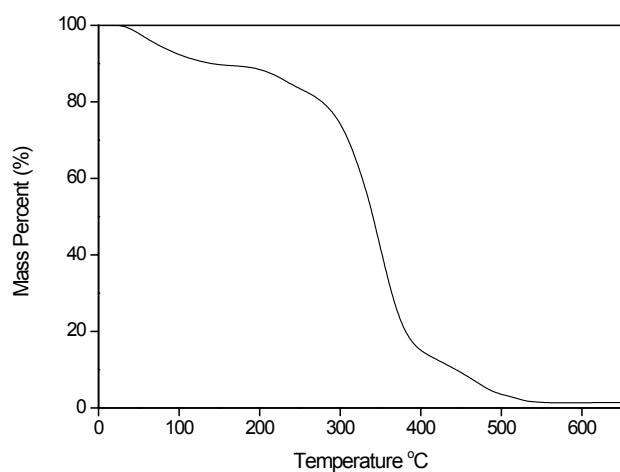


Figure S1.3. The TGA profile of [C₃SO₃HMIM][PTS].

The thermal degradation of [C₃SO₃HMIM][PTS] started at 300 °C, it is stable up to 300 °C and total degradation happens at 550 °C.

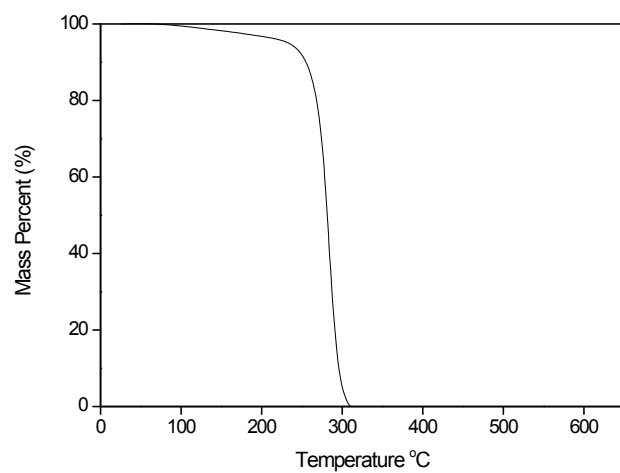


Figure S1.4. The TGA profile of [BMIM][Cl].

The thermal degradation of [BMIM][Cl] started at 250 °C, it is stable up to 250 °C and total degradation happens at 300 °C.

4. HPLC profile of reaction mixture and standards

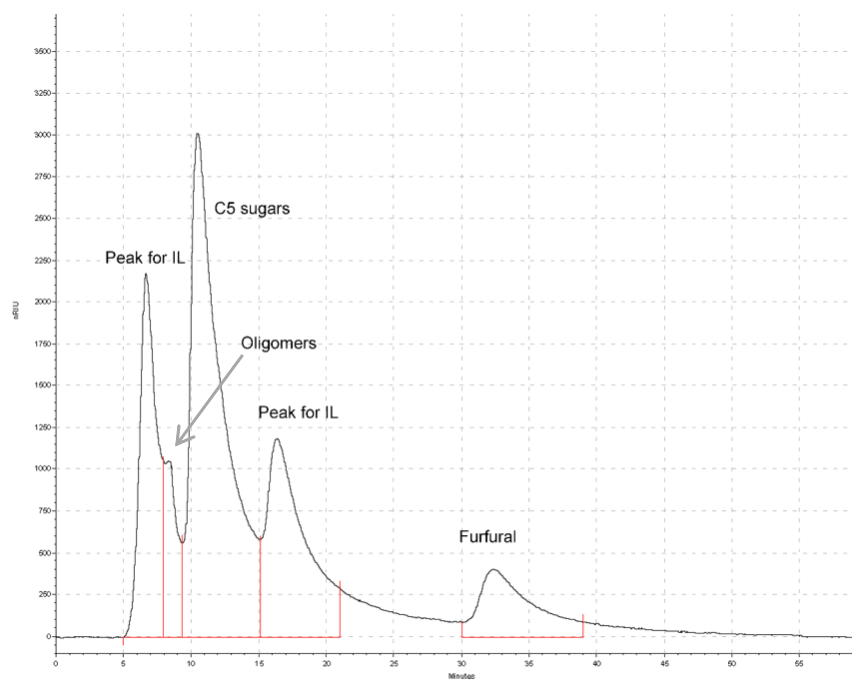


Fig. S2.1. HPLC profile of reaction mixture.

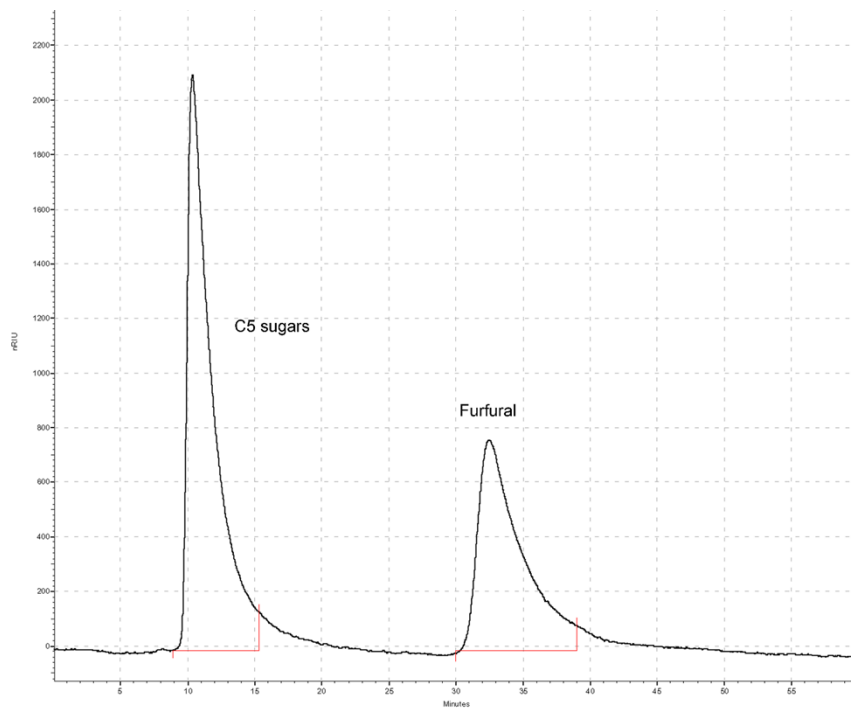


Fig. S2.2. HPLC profile of standards C5 sugar (xylose + arabinose) and furfural

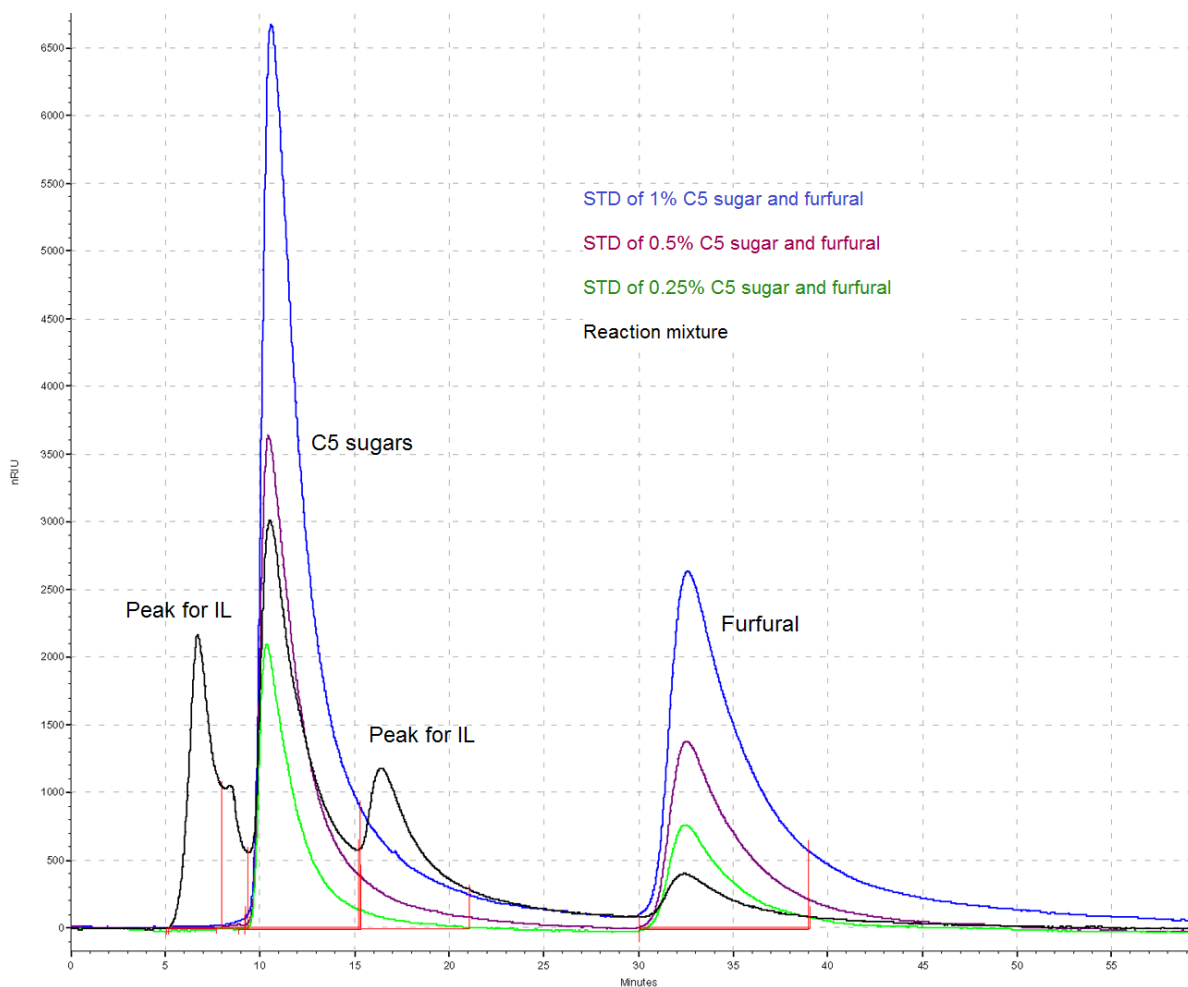


Fig. S2.3 HPLC Profile of reaction mixture and standards of C5 sugar and furfural.

In the analysis, we have considered same starting point of peaks and end point of peaks for calibration curve and for the peaks obtained from reaction mixture.

Also we have used HPLC (Shimadzu Japan) equipped with H⁺ column and 0.1% orthophosphoric acid used as mobile phase with flow rate 0.6 mL/min. A refractive index detector (RID, 6 A, Shimadzu, Japan) with a cell temperature 40 °C. The results of analysis shows that we have observed same results with both the HPLC Fig. S2.4.

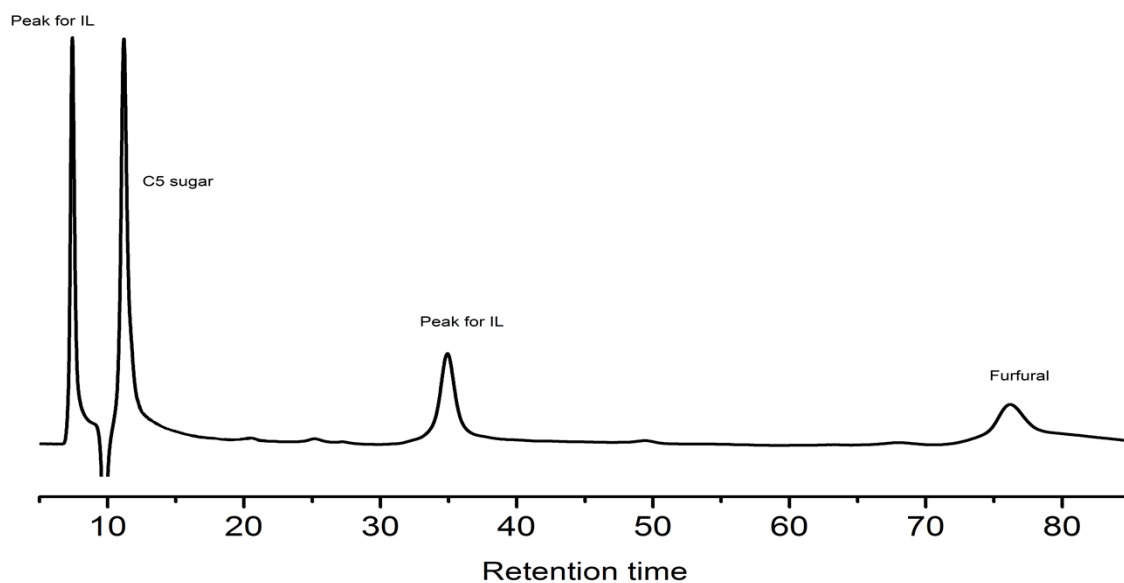


Fig. S2.4 HPLC Profile of reaction mixture using $[C_3SO_3HMIM][PTS]$ ILs.

5. TPD-NH₃ profiles of solid acid catalysts:

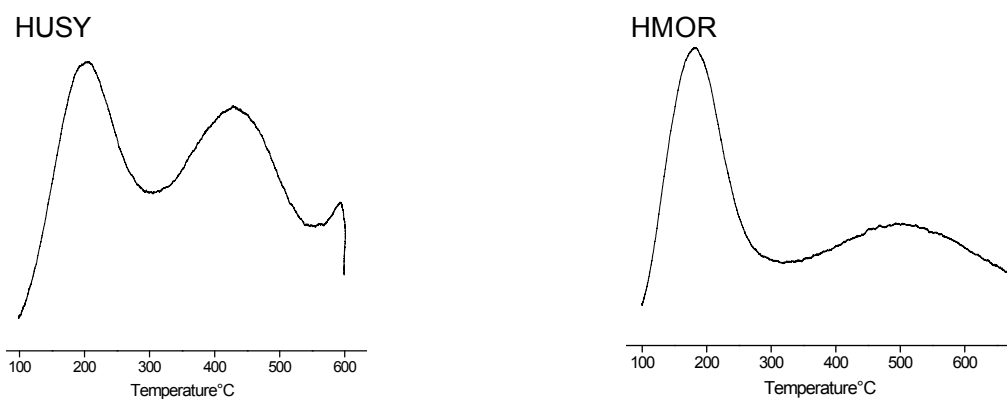


Fig. S3. The TPD-NH₃ profile of HUSY and HMOR catalysts.

The acid amount of solid acids was measured by TPD-NH₃ analysis. Temperature programmed desorption (TPD) of NH₃ was carried out in Micromeritics AutoChem-2920 instrument. Generally, catalyst was activated at 600 °C in helium flow (30 mL/min) for 1 h. The temperature was decreased to 50 °C and NH₃ was adsorbed by exposing the samples to 10% NH₃ in helium for 1 h. It was then flushed with helium for another 1 h at 100 °C to remove all the physisorbed NH₃. Desorption of NH₃ was carried out in helium flow (30 mL/min) by increasing the temperature from 100 to 600 °C at the rate of 10 °C/min.

The HUSY (Si/Al=15) has acid amount of 0.55 mmol/g and HMOR (Si/Al=10) has acid amount of 1.20 mmol/g.

6. Catalyst recycle study:

Two catalyst $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ and $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAILs were recovered and characterized by ^1H NMR and also recycle study were carried out after carrying out typical reaction under following reaction conditions: Substrate (beechwood), 0.6 g; $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$, 0.24 g; water 60 mL; 160 °C; 1 h. After completion of a reaction, water is removed by rotavap and after that 2 mL of water is added in to it and then slowly acetone (30 mL) was added to give light white color solution. Up on excess addition of acetone, light white color disappears. The solution was kept under static condition for a while. Afterwards, the acetone layer is decanted leaving viscous liquid at the bottom of a container. This liquid contains ionic liquid which was used in recycle study. The acetone layer contains sugars. By this method we could recover ca. 65% ionic liquid and the remaining 35% ionic liquid is present in acetone layer because of its partial solubility, the sugar yield decrease by 20% recovered from acetone layer. The separation of ionic liquids from sugar solution or vice versa is challenging problem that requires further study. In the recycle study, recovered BAIL was subjected to next reaction with following charge: hemicellulose (beechwood) 0.6 g; IL, 0.16 g; water, 60 mL; the reaction was done for 1 h at 160 °C.

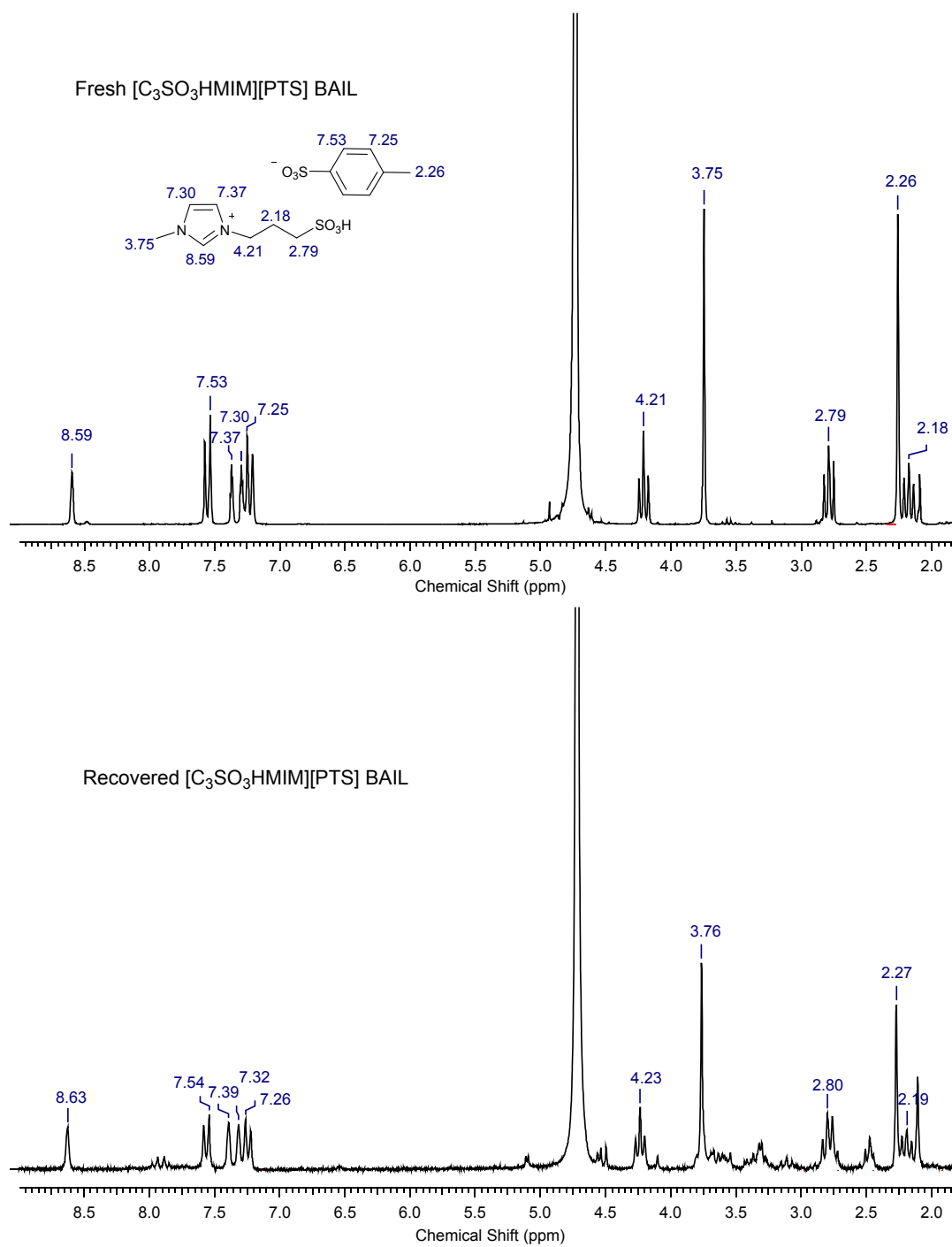


Fig. S4. ¹H NMR of Fresh $[C_3SO_3HMIM][PTS]$ and recovered $[C_3SO_3HMIM][PTS]$ BAILs

7. ^1H NMR of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ and $[\text{BMIM}][\text{Cl}]$ in DMSO-d_6 solvent

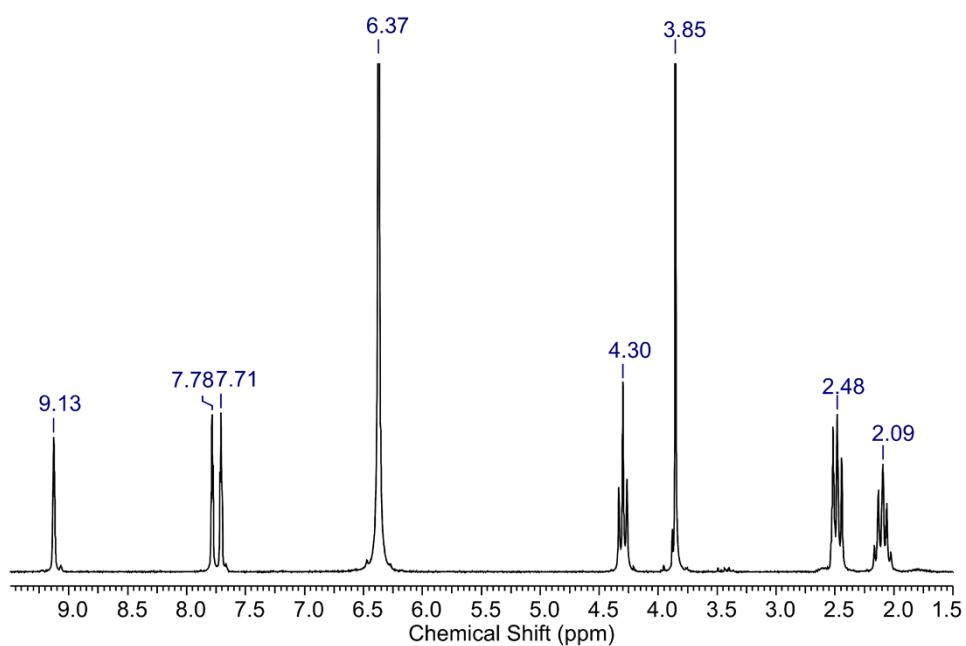


Fig. S5. ^1H NMR of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL in DMSO-d_6

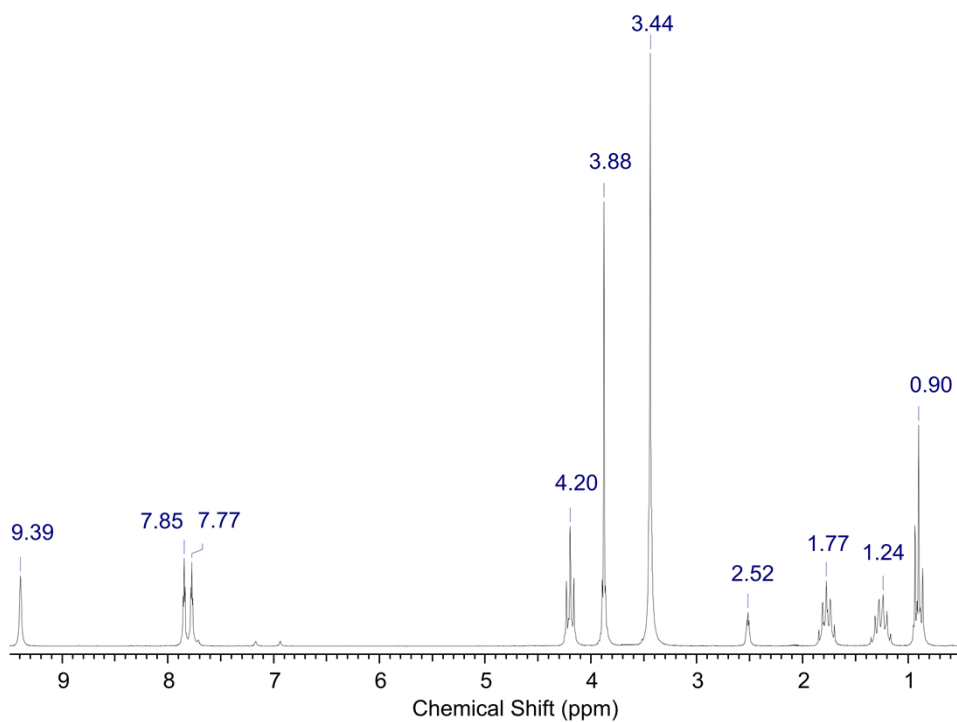


Fig. S6. ^1H NMR of $[\text{BMIM}][\text{Cl}]$ ionic liquid in DMSO-d_6

References

- 1 A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, J. H. Davis, *J. Am. Chem. Soc.* **2002**, 124, 5962.