

Supporting Information

Solid acid and ionic liquid catalyzed one-Pot transformation of Biorenewable substrates into platform chemical and promising biofuel

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Full experimental procedure for the best condition of HMF and EMF synthesis:

Synthesis of HMF from foxtail weed under microwave assisted heating

A microwave tube was charged with 25 mg Foxtail weed, 2.5 mg $[\text{DMA}]^+[\text{CH}_3\text{SO}_3]^-$ catalyst and 0.5 g DMA-LiCl solvent. The loaded tube was then inserted into the microwave reactor pre-set at 120 °C for 2 min reaction time. Upon completion of reaction for 2 min, the reactor was opened. The temperature of the reaction mass was cooled down to room temperature. HMF was extracted with diethyl ether and further purified with column chromatography (4 times) by using diethyl ether as a mobile phase and silica gel of 200-400 mesh as a stationary phase. The yield of crude HMF was determined by HPLC analysis.

Synthesis of HMF from foxtail weed under conventional heating

A 100 mL round-bottom flask was charged with 500 mg Foxtail weed, 50 mg $[\text{DMA}]^+[\text{CH}_3\text{SO}_3]^-$ catalyst and 10 g DMA-LiCl solvent containing 10 wt% LiCl. The reaction mixture was refluxed with continuous stirring at 140 °C for 4 h. After 4 h, the temperature of the

reaction mass was cooled down to room temperature. The yield of crude HMF was determined by HPLC analysis.

Synthesis of EMF from Foxtail weed

A 100 mL round-bottom flask was charged with 1g Foxtail weed, 0.1 g $[\text{DMA}]^+[\text{CH}_3\text{SO}_3]^-$ catalyst and 20 mL ethanol. The mixture was refluxed with continuous stirring at 120 °C for 15 h using a long condenser and chilled water so that ethanol vapor can be easily condensed back to liquid phase. The aliquots were collected at different time intervals (3 h, 10 h and 15 h) to monitor the progression of the conversion. After 15 h reaction, Upon completion of reaction for 15 h, the reaction mixture was cooled down to room temperature, ethanol was evaporated under vacuum and the oily residue was run through a column chromatograph made with silica gel of 200-400 mesh as a stationary phase and a mixed dichloromethane/diethyl ether solvent (2:1 volume ratio) as a mobile phase. After separating $[\text{DMA}]^+[\text{CH}_3\text{SO}_3]^-$ component by column chromatography, the oily liquid product was characterized by ^1H NMR spectroscopy. ^1H NMR spectrum of the isolated product revealed the presence of both EMF and EL in 7:1 ratio (Fig. S7).

Table S1. Results of direct conversion of cellulose into HMF using 10-40 wt% Brønsted acidic IL as catalyst.

Entry	Substrate, 5 wt%	IL, wt%	HMF Yield (%) ^a
1	MCC	[NMP] ⁺ [CH ₃ SO ₃] ⁻ 10	17
2	MCC	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 10	21
3	MCC	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 40	24
4	Fiber	[NMP] ⁺ [CH ₃ SO ₃] ⁻ 10	26
5	Fiber	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 10	32
6	Fiber	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 40	35
7	Sigmacell	[NMP] ⁺ [CH ₃ SO ₃] ⁻ 10	28
8	Sigmacell	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 10	34
9	Sigmacell	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 40	42
10	α-Cellulose	[NMP] ⁺ [CH ₃ SO ₃] ⁻ 10	34
11	α-Cellulose	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 10	36
12	α-Cellulose	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 40	42
13	Starch	[NMP] ⁺ [CH ₃ SO ₃] ⁻ 10	41
14	Starch	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 10	52
15	Starch	[DMA] ⁺ [CH ₃ SO ₃] ⁻ 40	56

Solvent = DMA-LiCl (0.5 g, 10 wt% LiCl), *T* = 120 °C, *t* = 2 min,
^aHMF yields were obtained from HPLC measurement.

Fig. S1 UV/Vis spectra *p*-nitroaniline, *p*-nitroaniline-DMA⁺ and *p*-nitroaniline-NMP⁺ solutions.

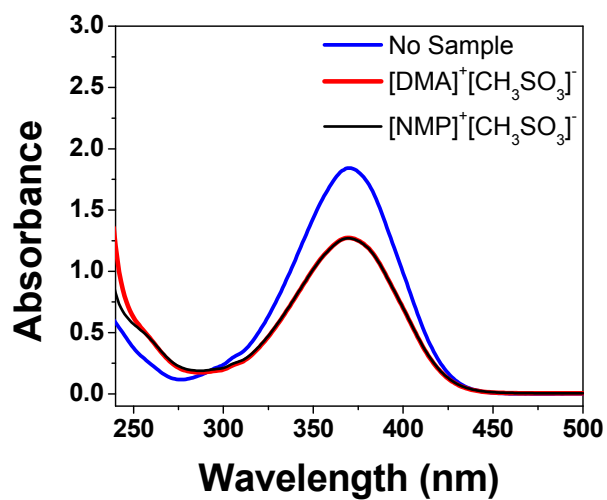


Fig. S2 ^1H NMR spectrum of $[\text{DMA}]^+[\text{CH}_3\text{SO}_3]^-$ in $\text{DMSO-}d_6$.

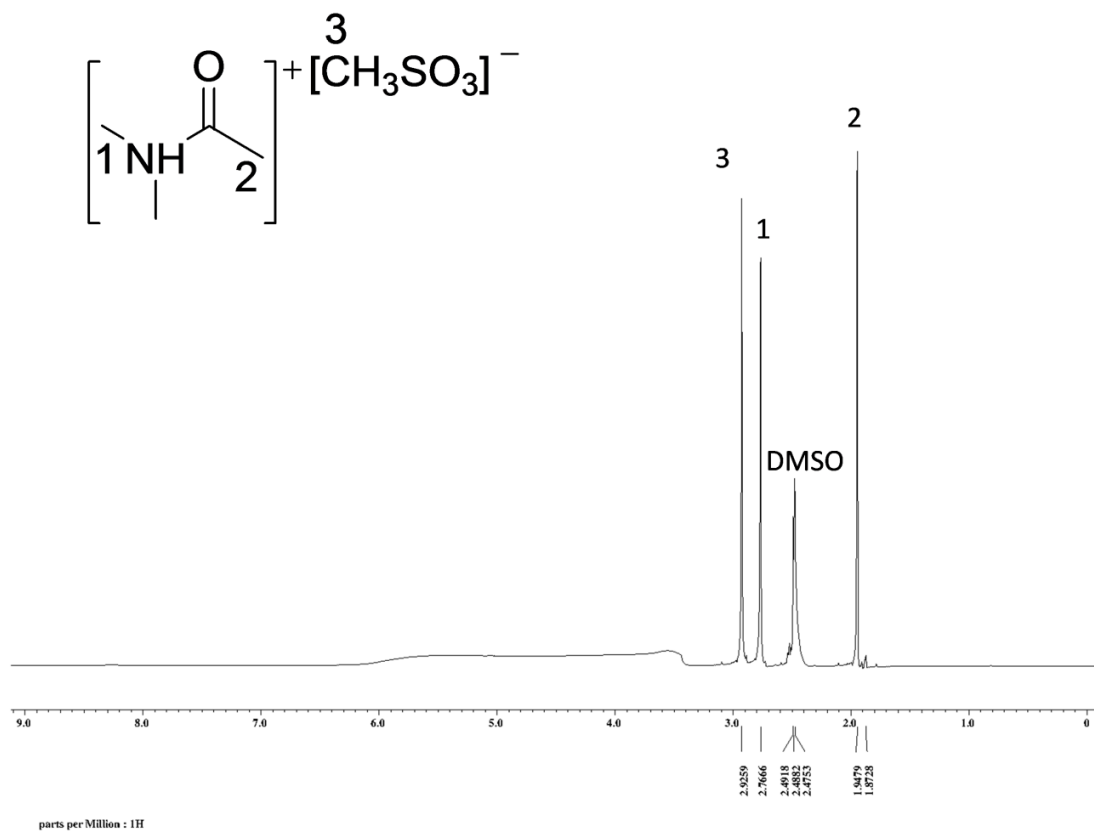


Fig. S3 ^{13}C NMR spectrum of $[\text{DMA}]^+[\text{CH}_3\text{SO}_3]^-$ in $\text{DMSO-}d_6$.

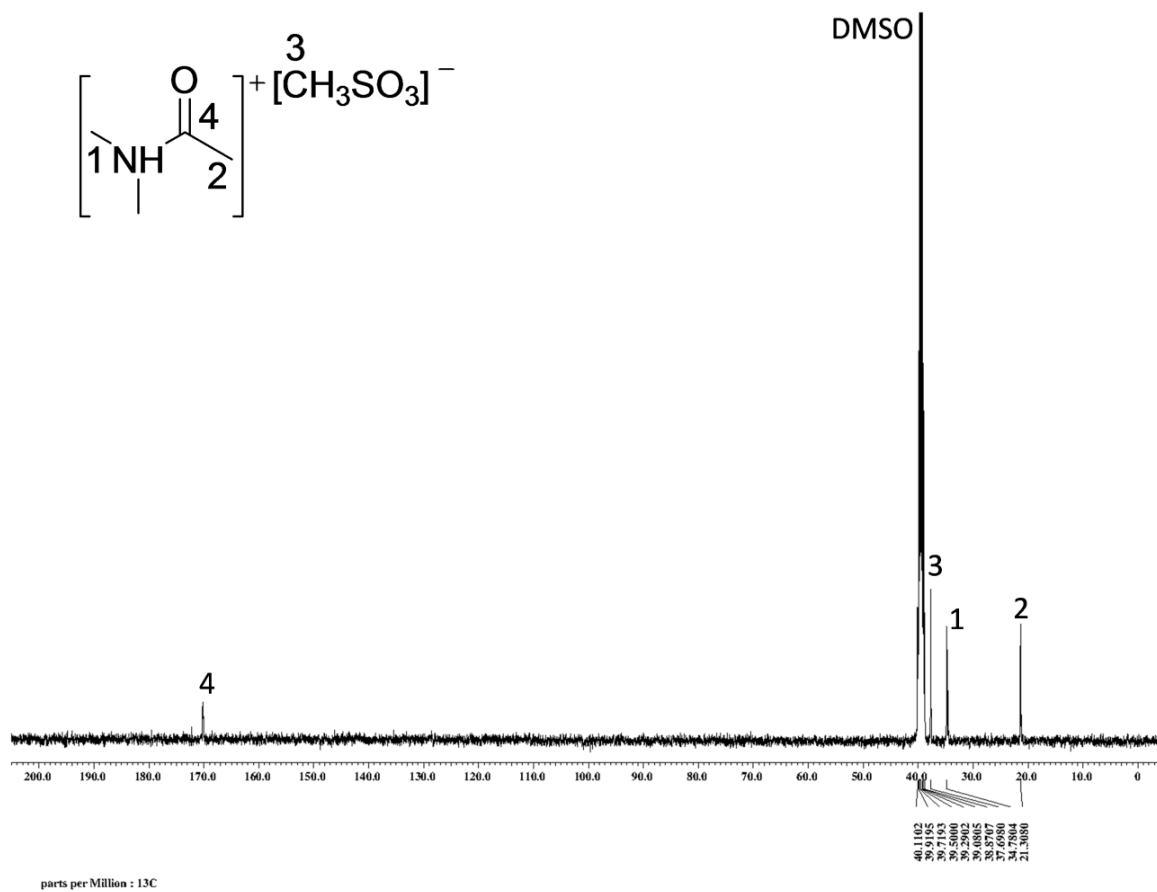


Fig. S4 ^1H NMR spectrum of $[\text{NMP}]^+[\text{CH}_3\text{SO}_3]^-$ in $\text{DMSO-}d_6$.

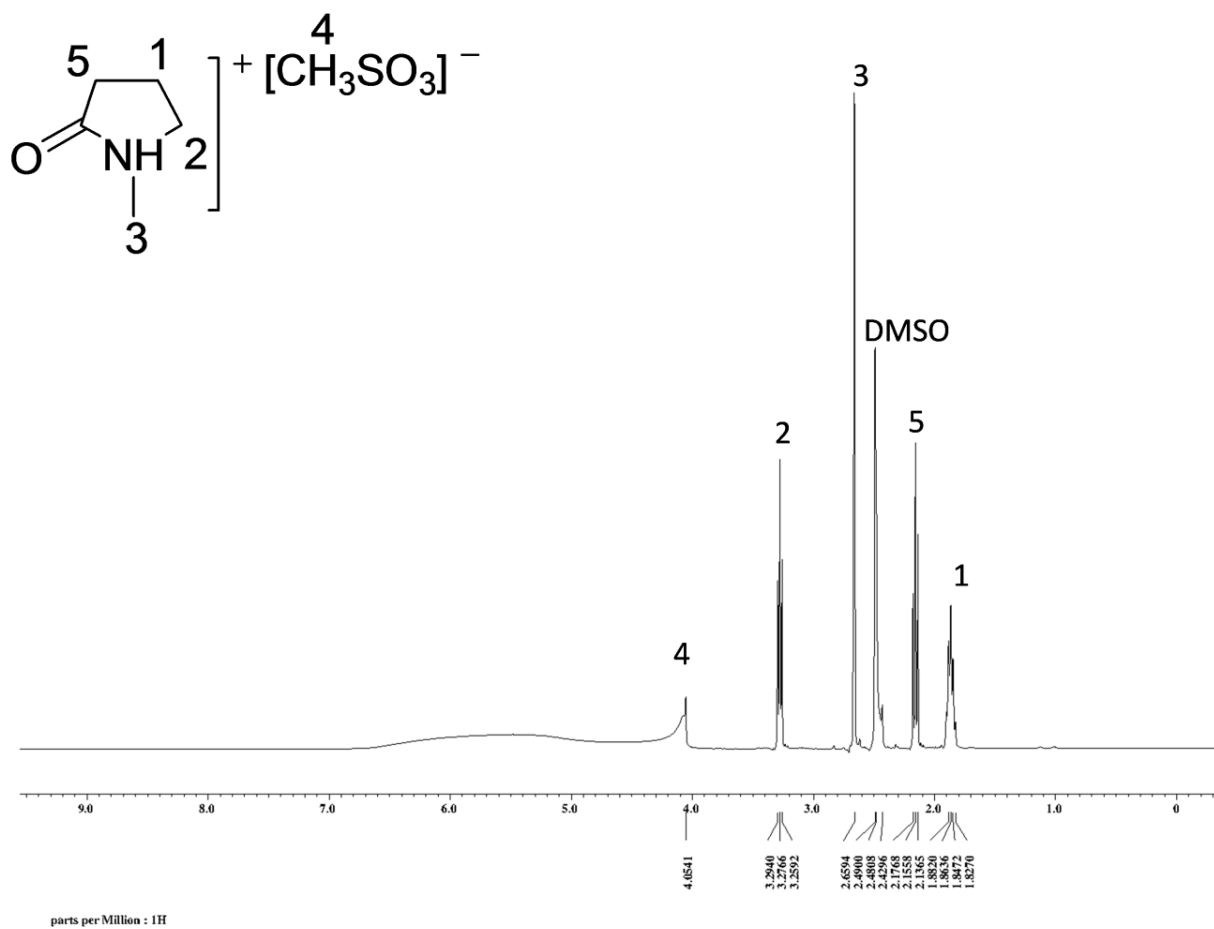


Fig. S5 ^{13}C NMR spectrum of $[\text{NMP}]^+[\text{CH}_3\text{SO}_3]^-$ in $\text{DMSO-}d_6$.

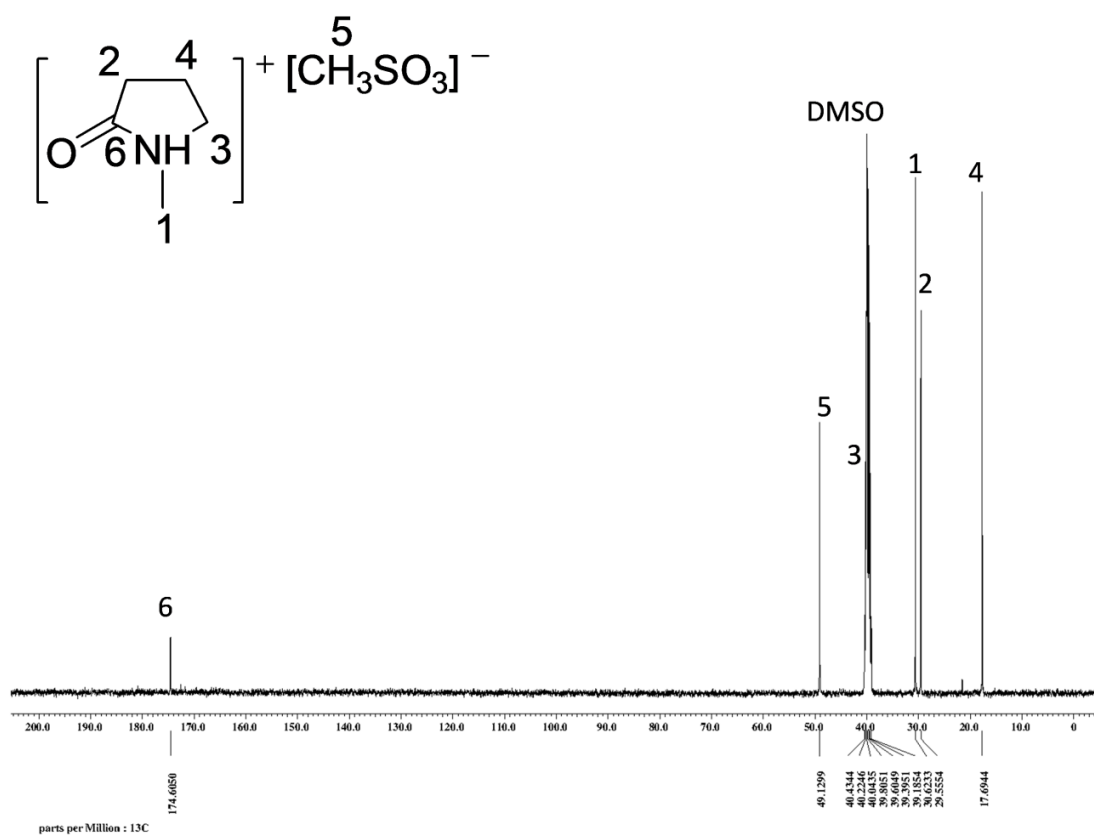


Fig. S6 (a) ^1H NMR spectra (CDCl_3) of the HMF product (A) obtained by diethyl ether extraction followed by repeated purification (4 times) by column chromatography made with silica gel as a stationary phase and diethyl ether as a mobile phase and (B) Diethyl ether extracted HMF product without further purification by column chromatography.

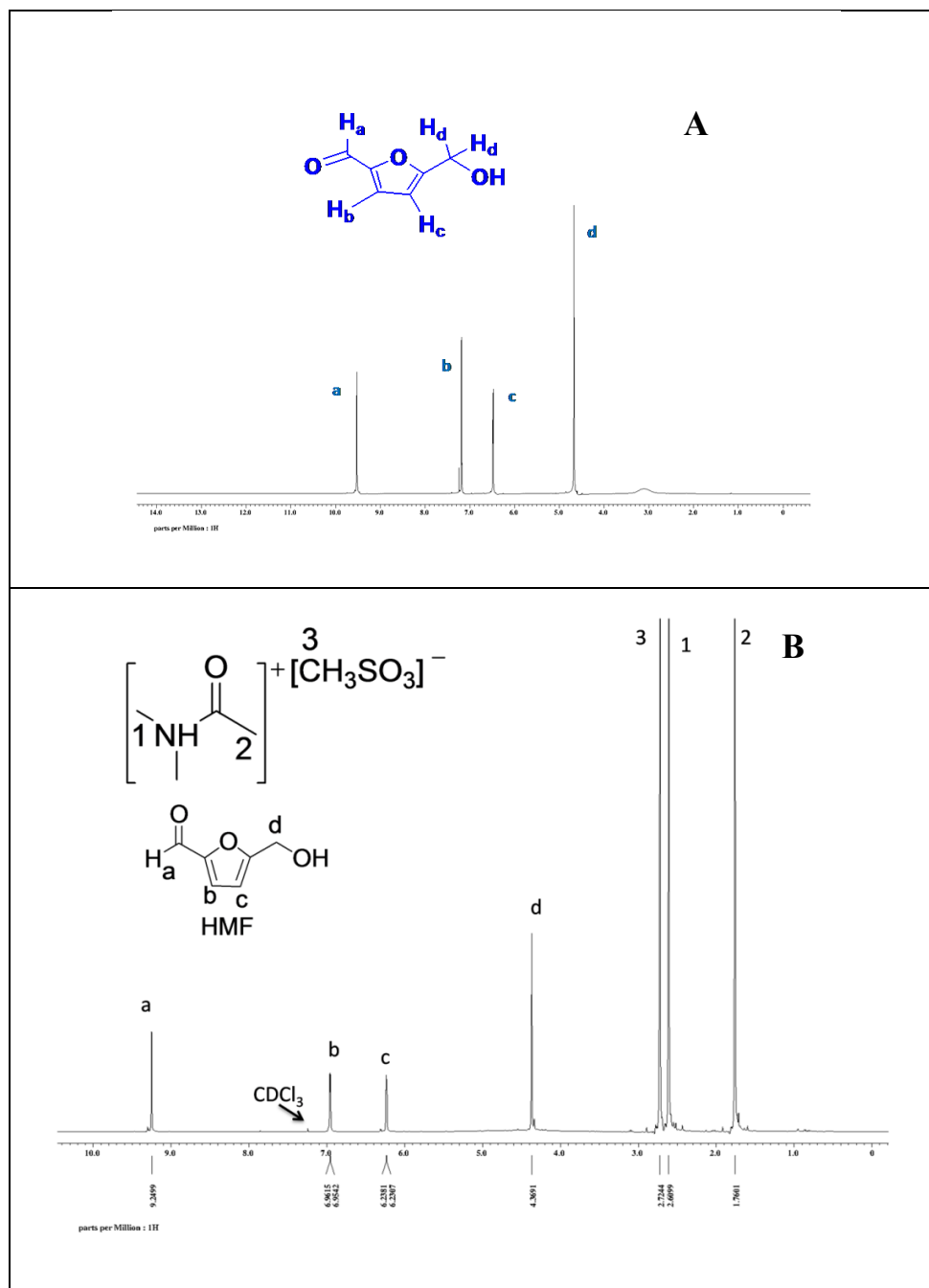


Fig. S7 ^{13}C NMR spectrum (CDCl_3) of the isolated HMF product extracted with diethyl ether from the reaction mixture.

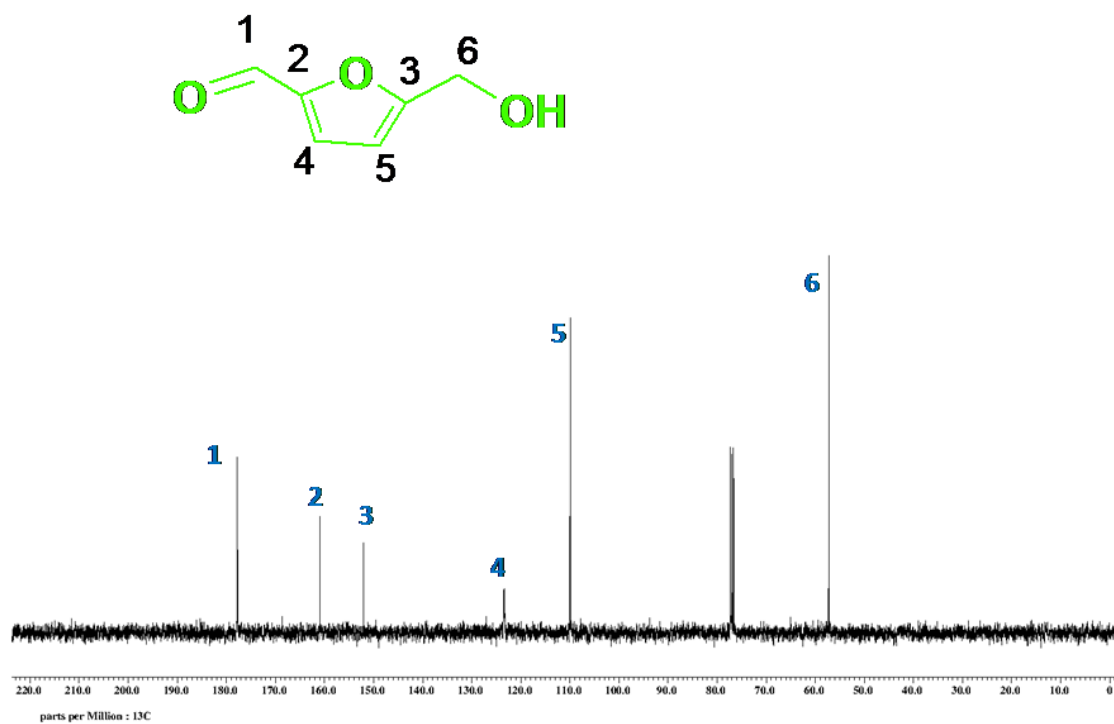


Fig. S8 ^1H NMR spectrum (CDCl_3) of the purified oily liquid product obtained from a reaction between weeds (Foxtail, 1g) and $[\text{DMA}]^+[\text{CH}_3\text{SO}_3]^-$ (0.1 g) in ethanol at $120\text{ }^\circ\text{C}$ for 15 h. IL catalyst was separated from the product by column chromatography as described in the experimental section. Spectrum shows the product contains EMF and EL in 7:1 ratio.

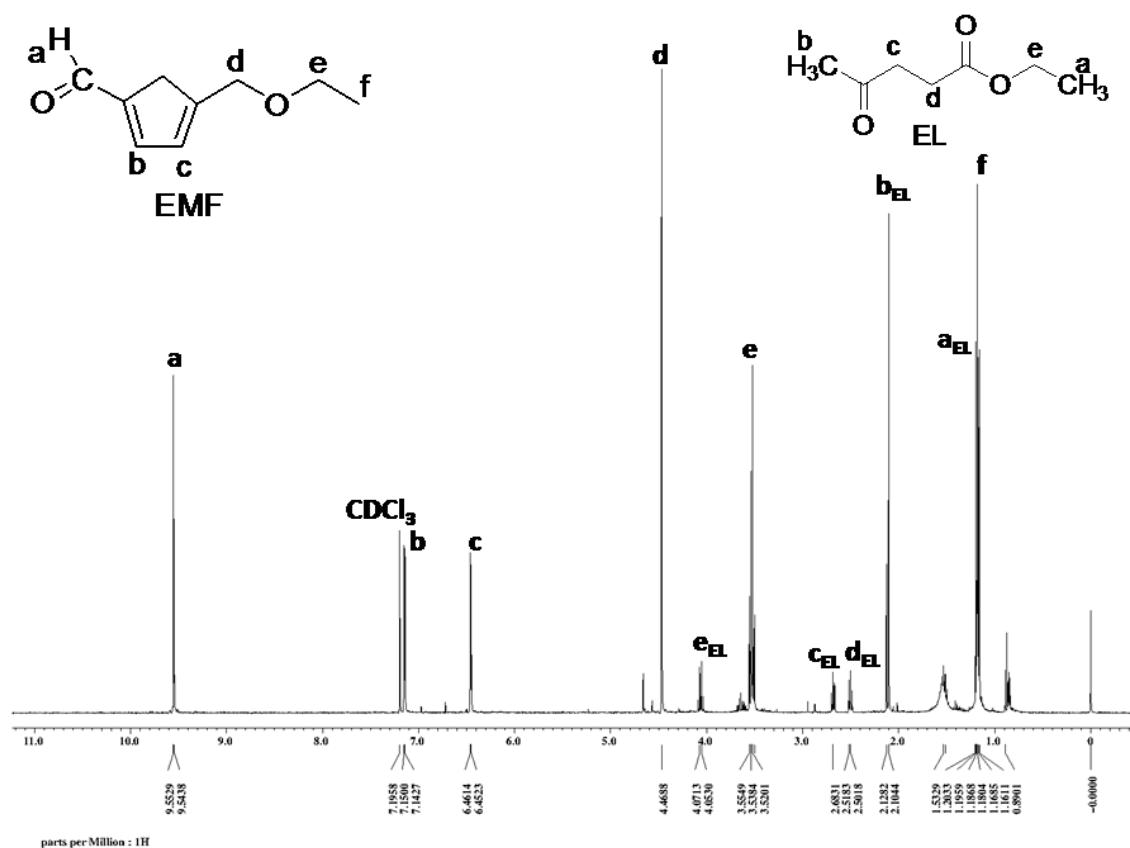


Fig. S9 (a) The HPLC chromatograms of (a) authentic HMF sample, and (b) purified HMF product obtained from weed substrate.

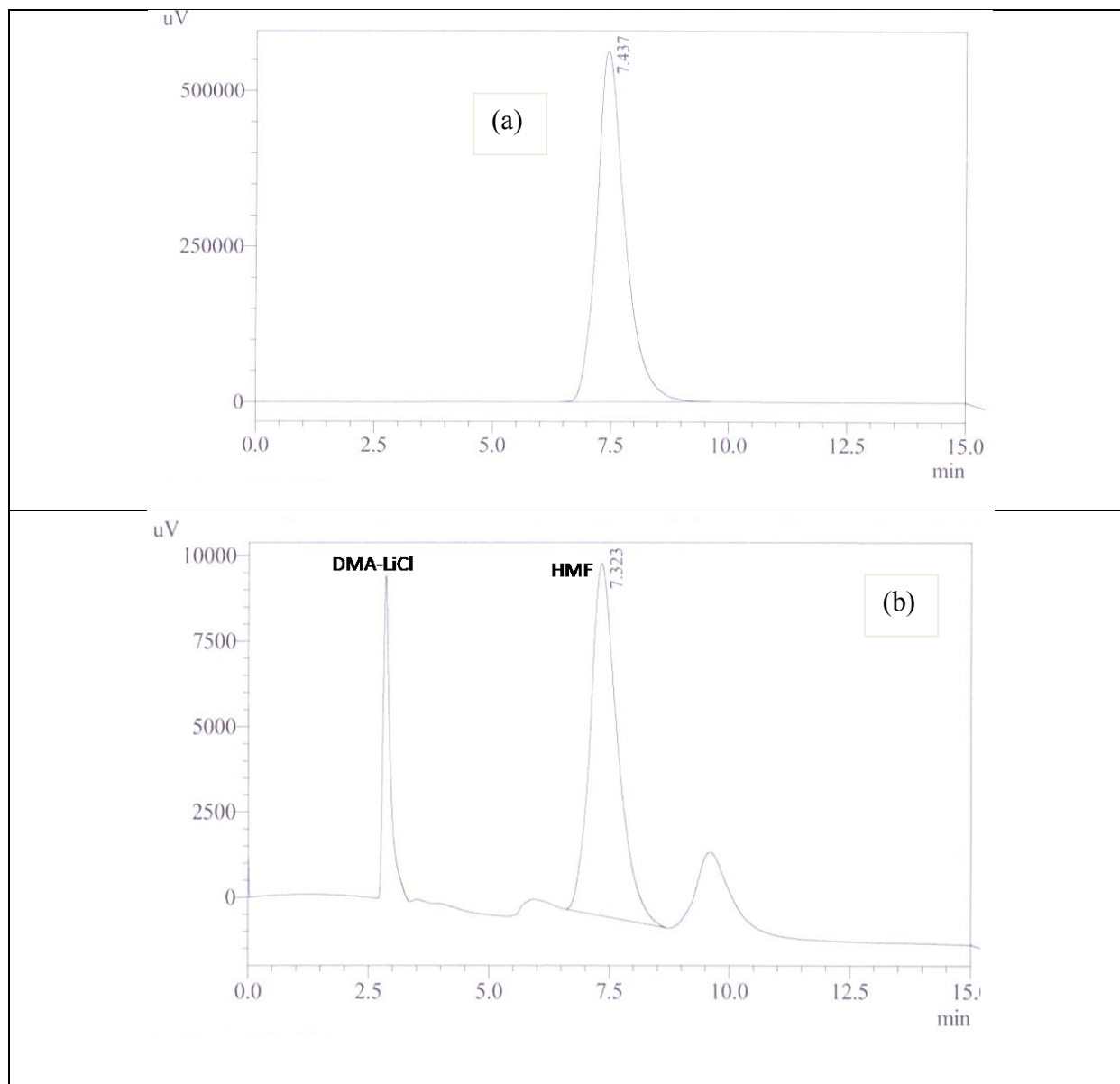


Fig. S10. ^1H NMR spectra of the reaction media containing the catalyst (A) before and (B) after the reaction.

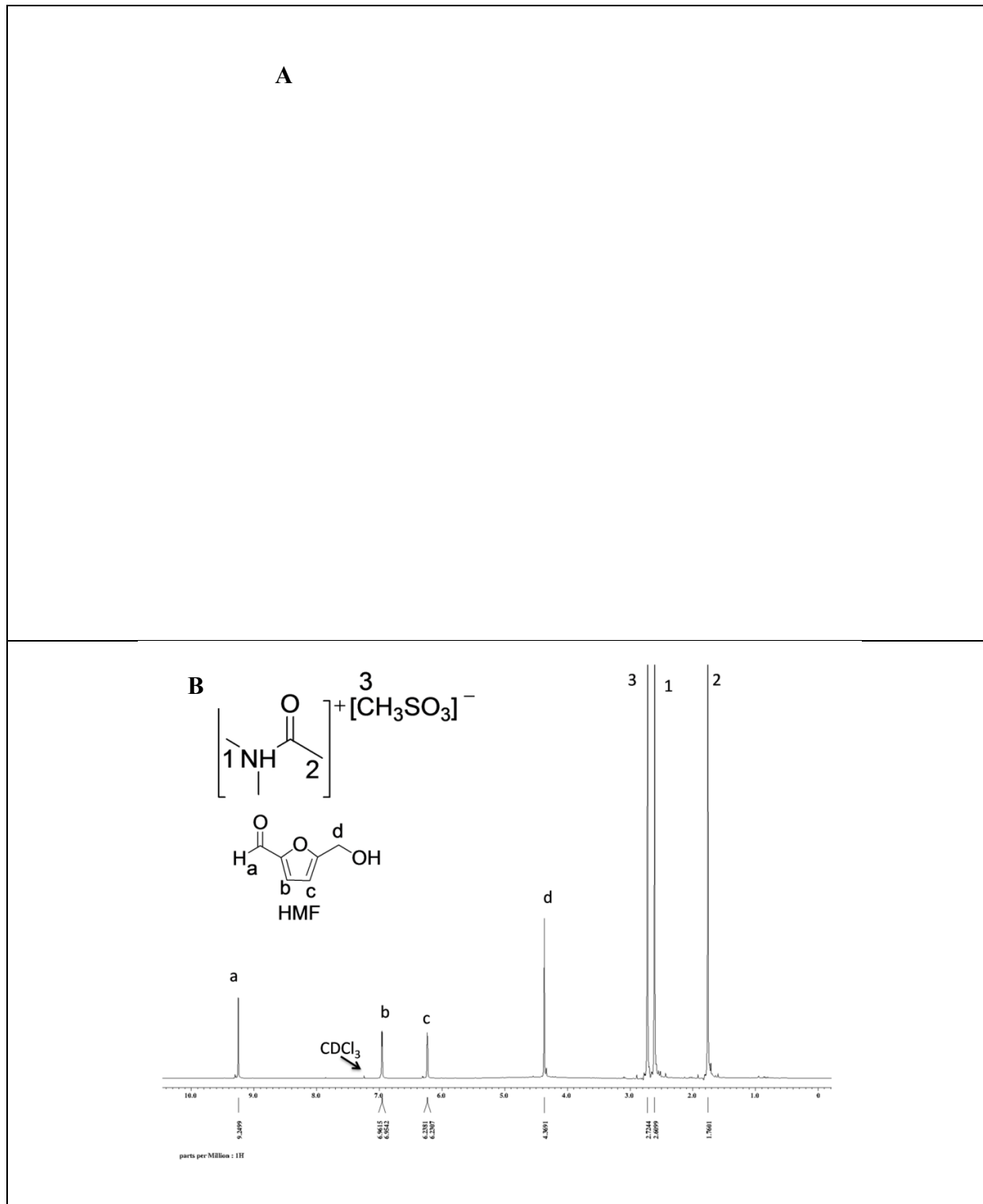


Fig. S11. Temperature programmed desorption (TPD) of ammonia over HPA-SiO₂ material.

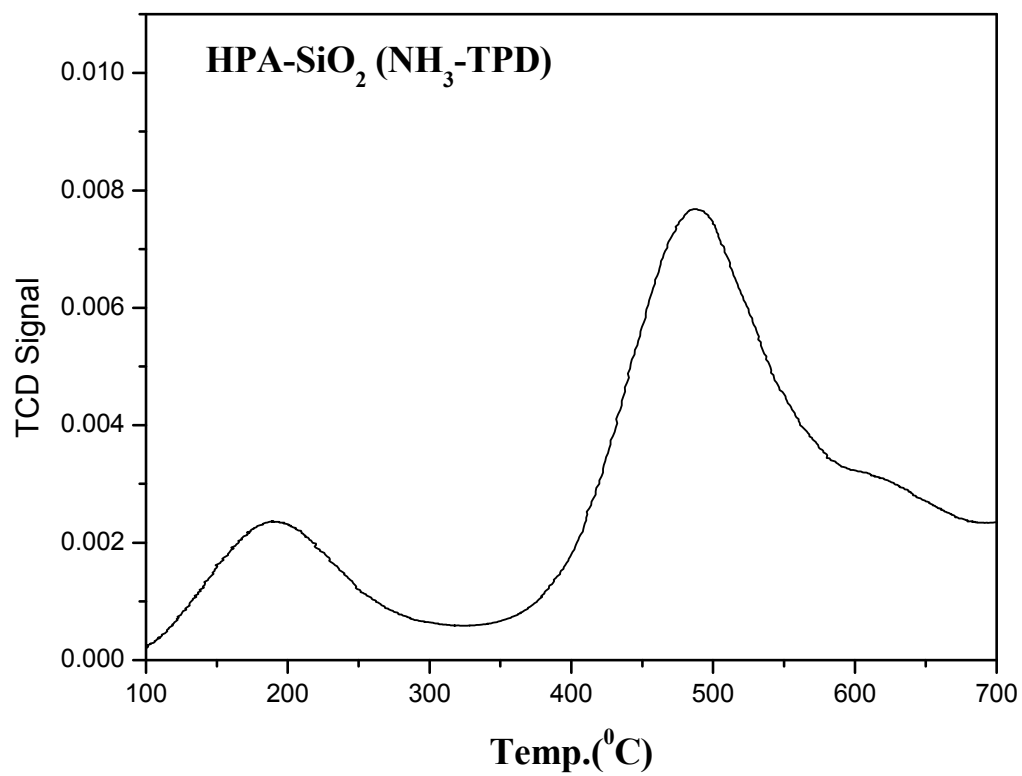


Fig. S12 XRD analysis of the HPA-SiO₂.

