Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.


**Supplementary Information**

# Highly selective hydrogenation of biomass-derived 5-hydroxymethylfurfural into 2,5-bis(hydroxymethyl)furan over an acid-base bifunctional hafnium-based coordination polymer catalyst

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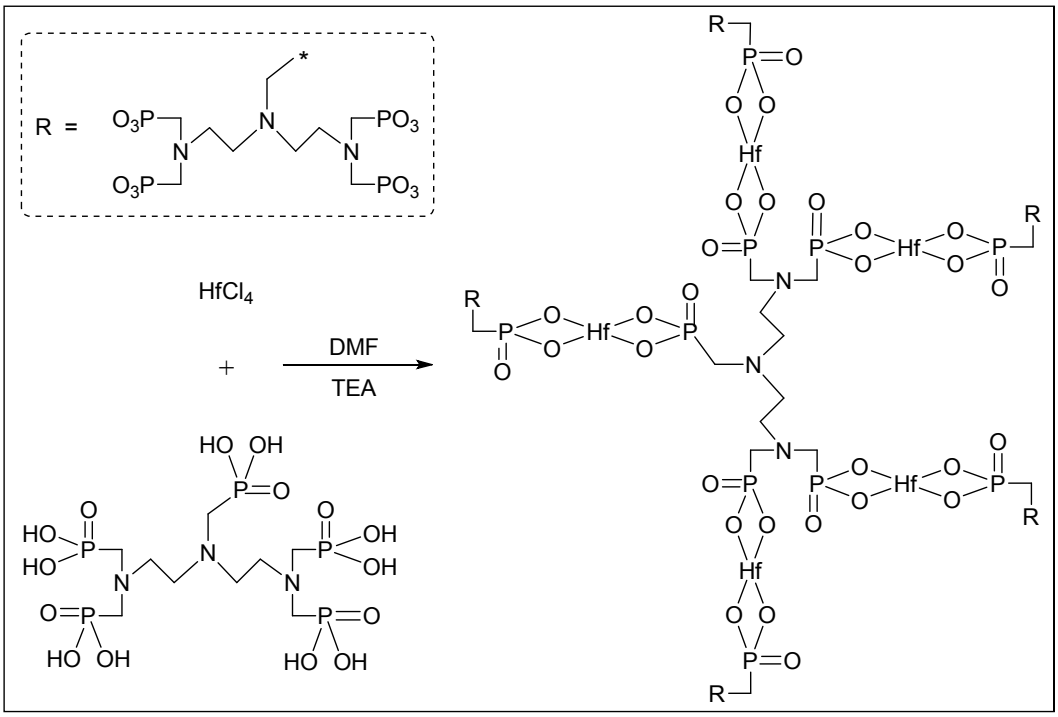


**Fig. S1** Synthetic process and most possible structure of Hf-DTMP.

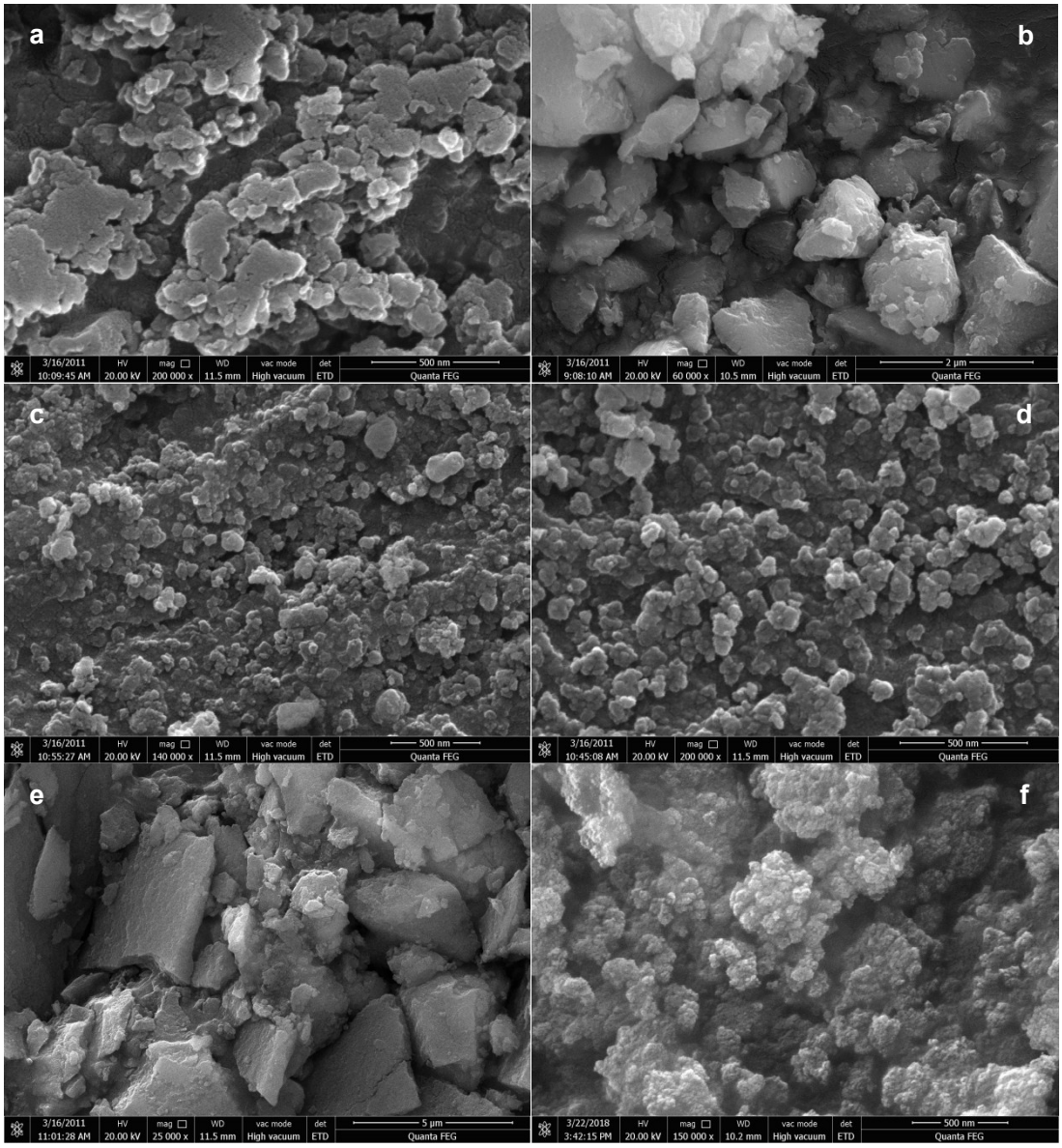


**Fig. S2** SEM images of Hf-BTC (a), Hf-ICA (b), Hf-IHP (c), Hf-ATMP (d), Sn-DTMP (e) and Nb-DTMP (f).

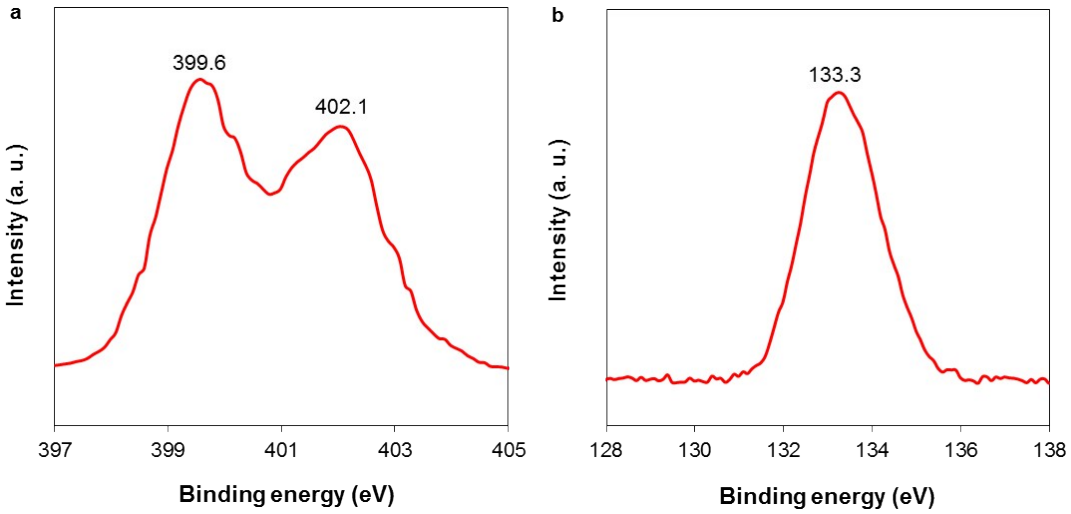


**Fig. S3** XPS spectra of N 1*s* (a) and P 2*p* (b) of Hf-DTMP.

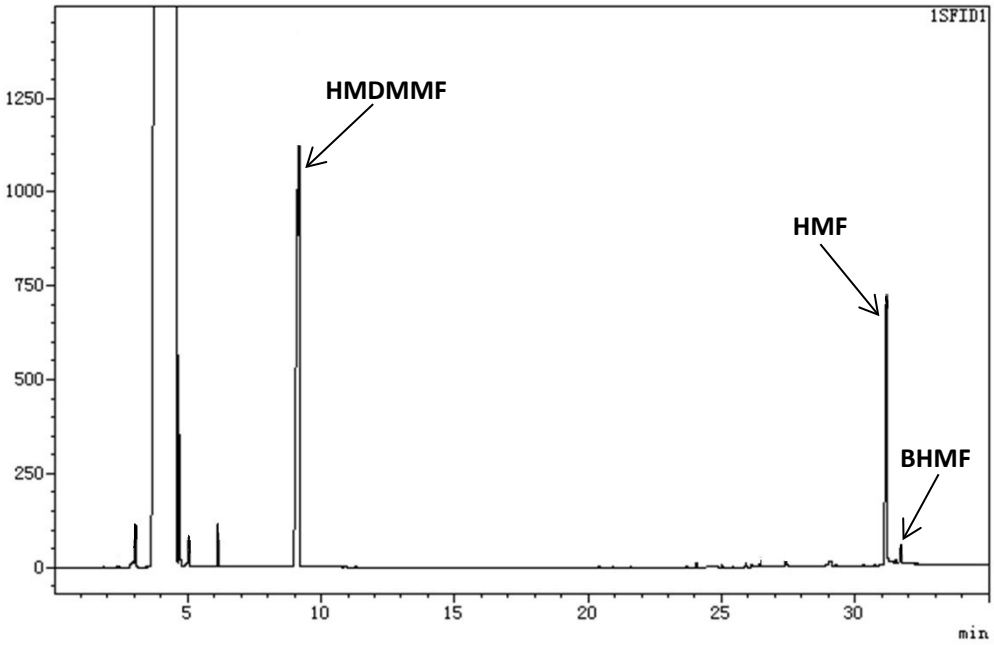


**Fig. S4** GC chromatogram for the CTH of HMF in MeOH over Hf-DTMP.

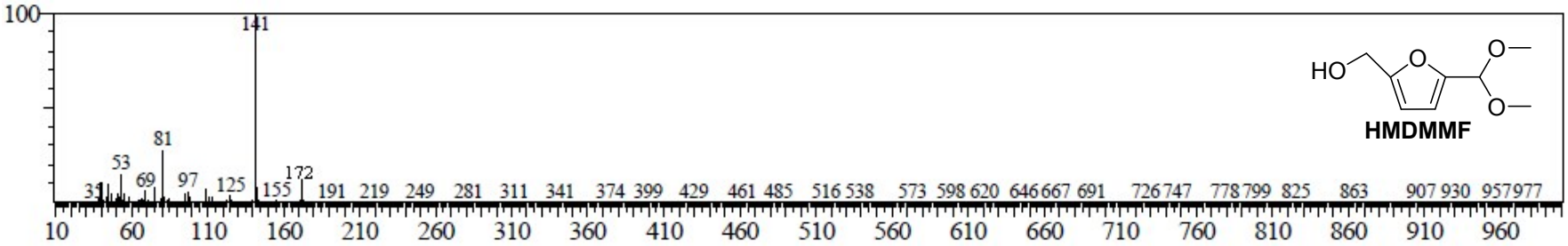


**Fig. S5** MS spectrum of HMDMMF.

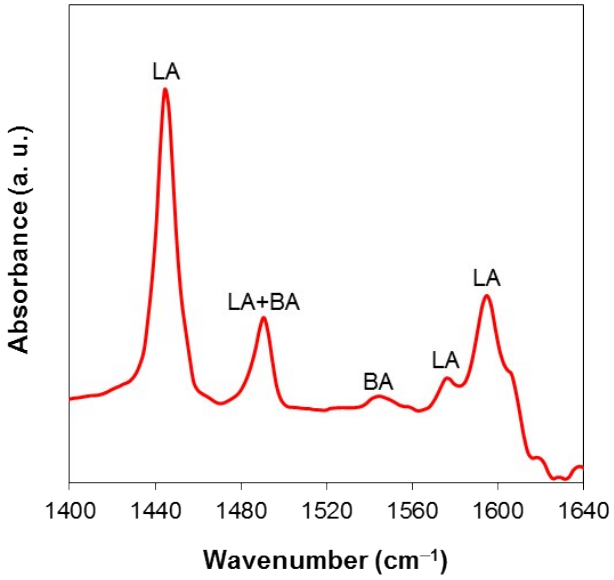


**Fig. S6** Pyridine-adsorbed FT-IR spectrum of Hf-DTMP.

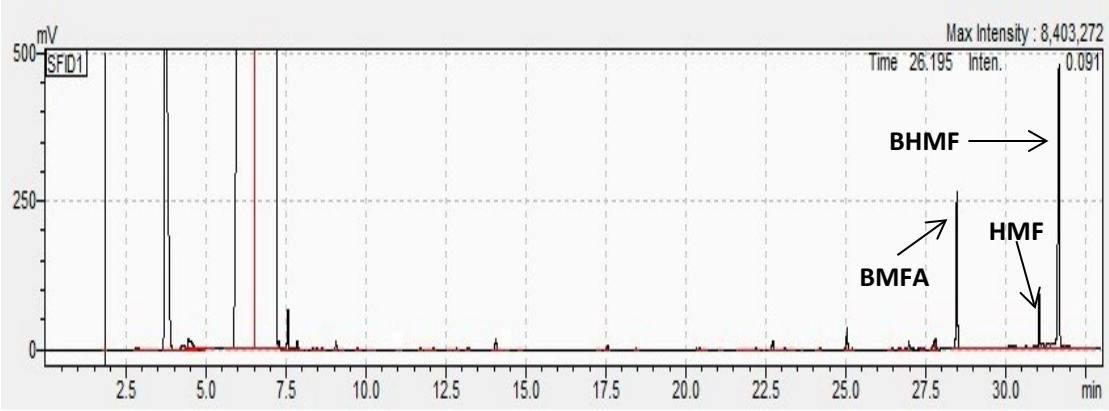


**Fig. S7** GC chromatogram for the CTH of HMF in *s*BuOH over Hf-DTMP.

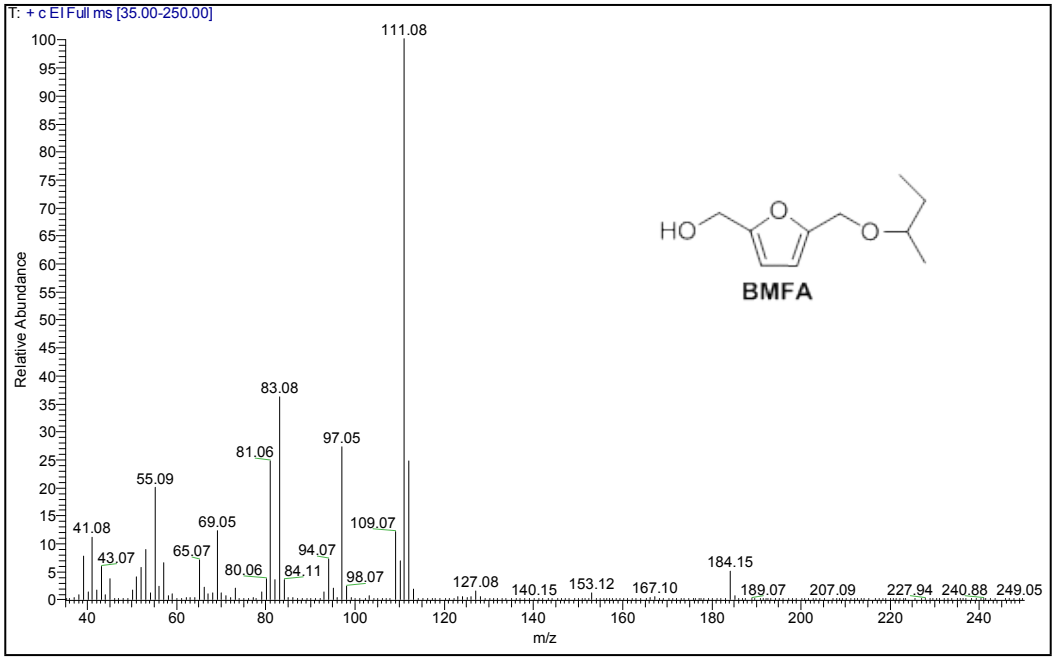


**Fig. S8** MS spectrum of BMFA.

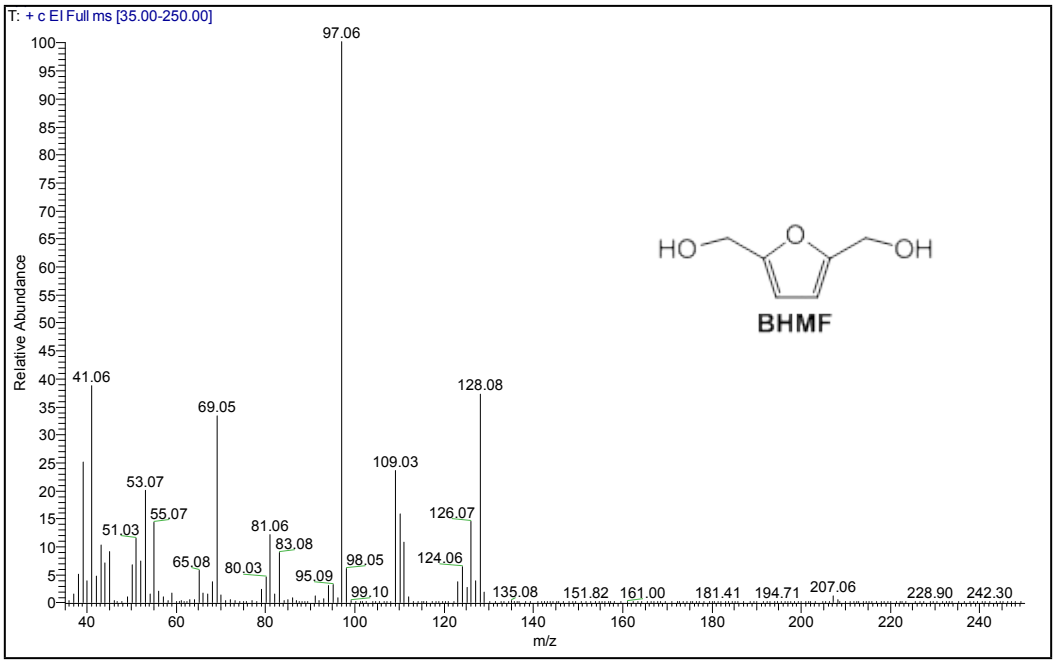


**Fig. S9** MS spectrum of BHMF.

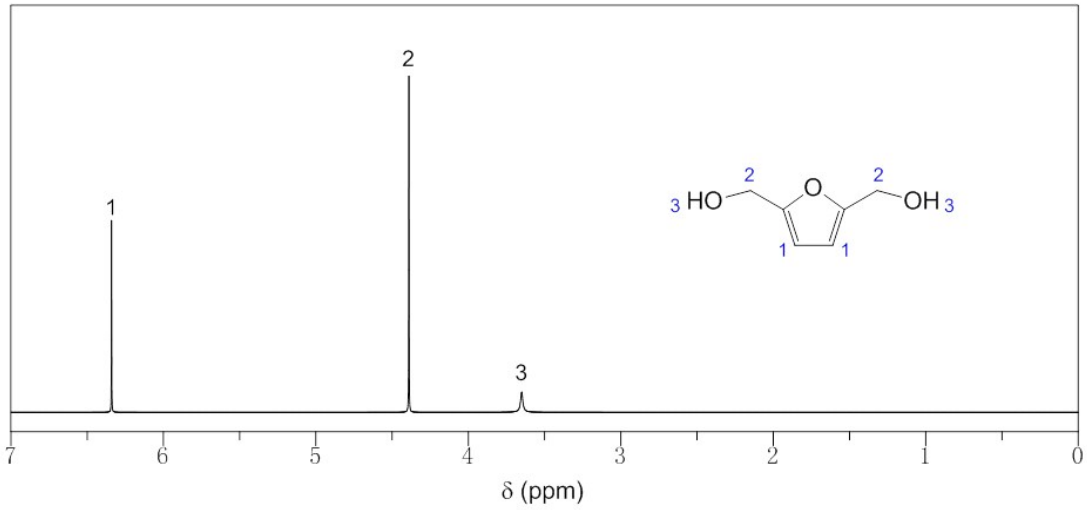


**Fig. S10** $^{1}$H NMR spectrum of purified BHMF.

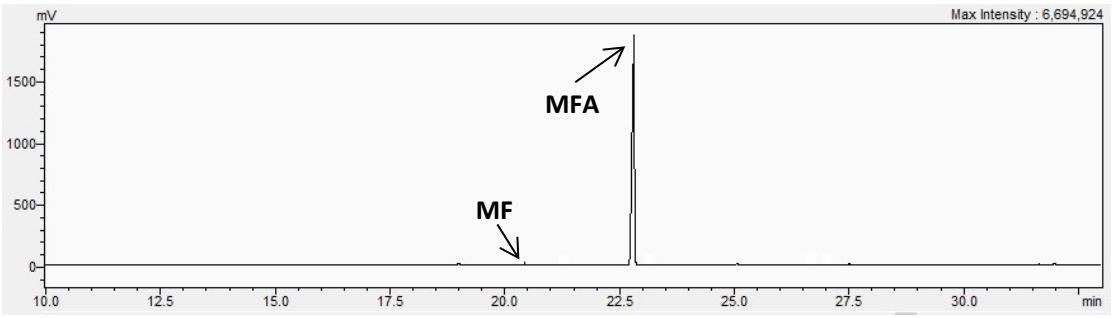


**Fig. S11** GC chromatogram for the CTH of MF in *s*BuOH over Hf-DTMP.

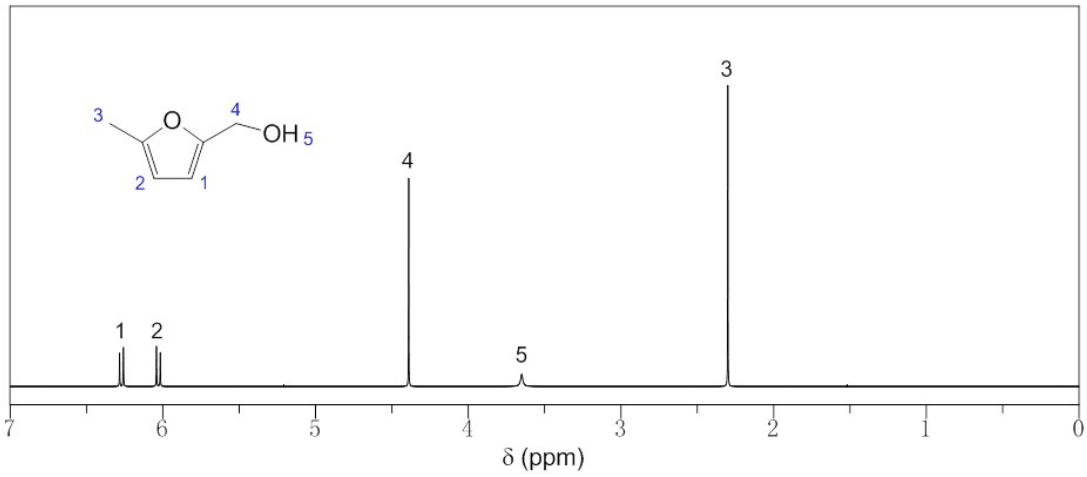


**Fig. S12** $^{1}$H NMR spectrum of purified MFA.

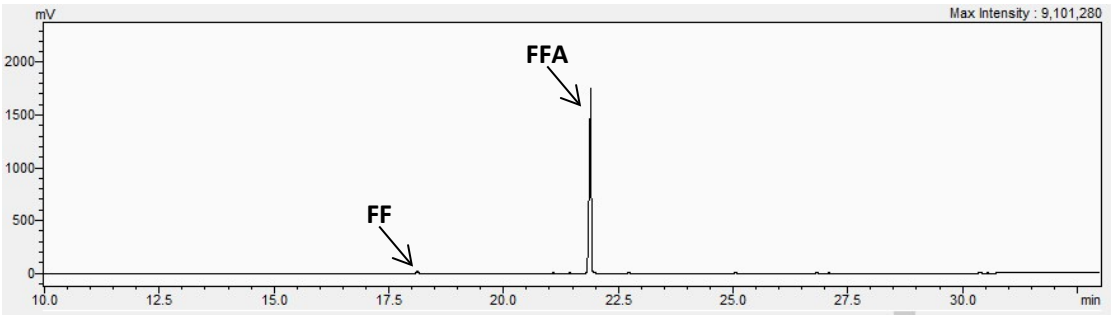


**Fig. S13** GC chromatogram for the CTH of FF in *s*BuOH over Hf-DTMP.

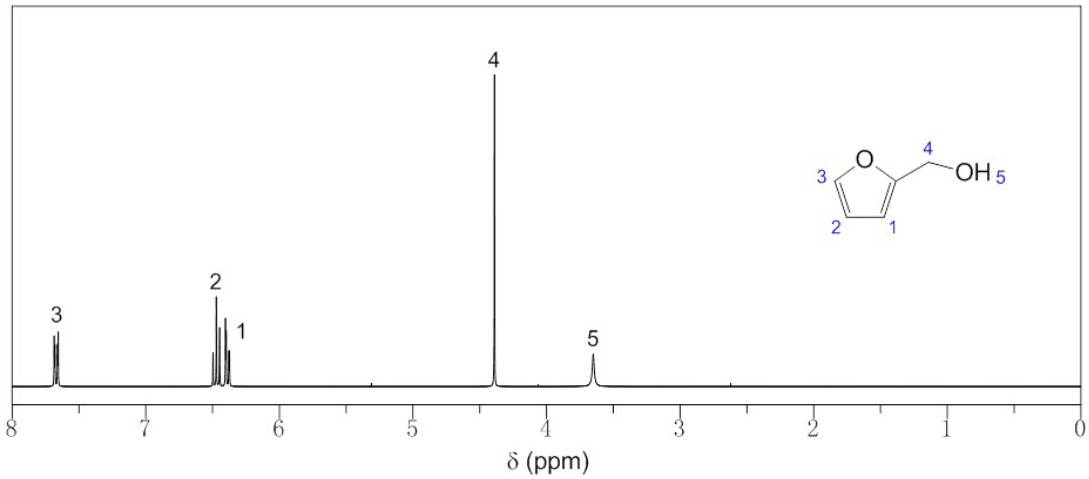


**Fig. S14** $^{1}$H NMR spectrum of purified FFA.

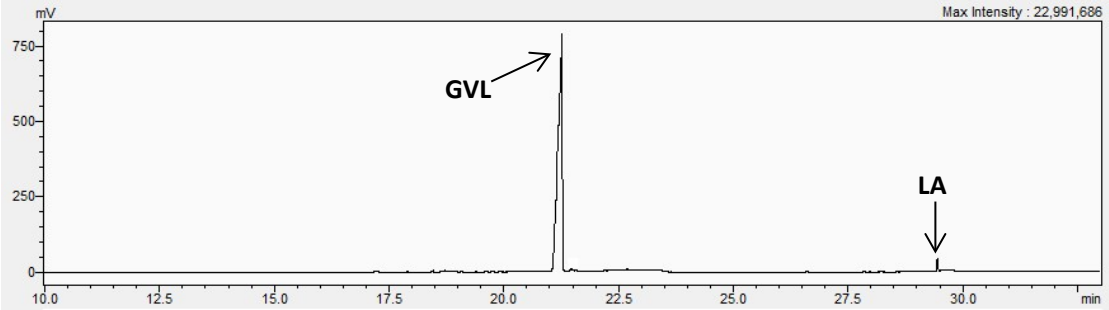


**Fig. S15** GC chromatogram for the CTH of LA in *s*BuOH over Hf-DTMP.

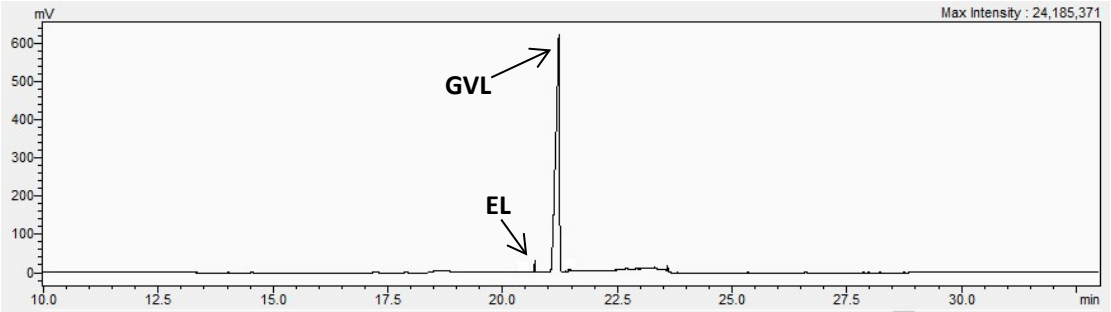


**Fig. S16** GC chromatogram for the CTH of EL in *s*BuOH over Hf-DTMP.

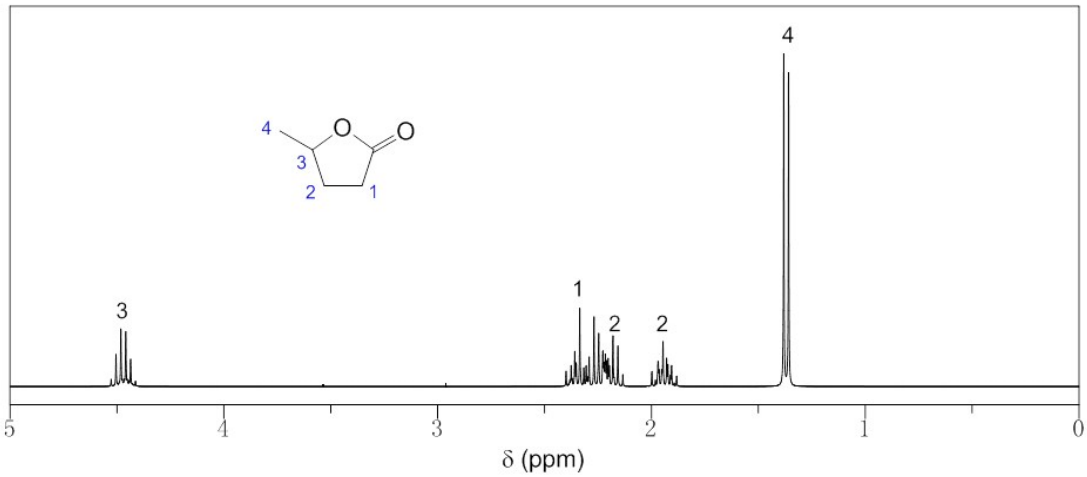


**Fig. S17** $^{1}$H NMR spectrum of purified GVL.

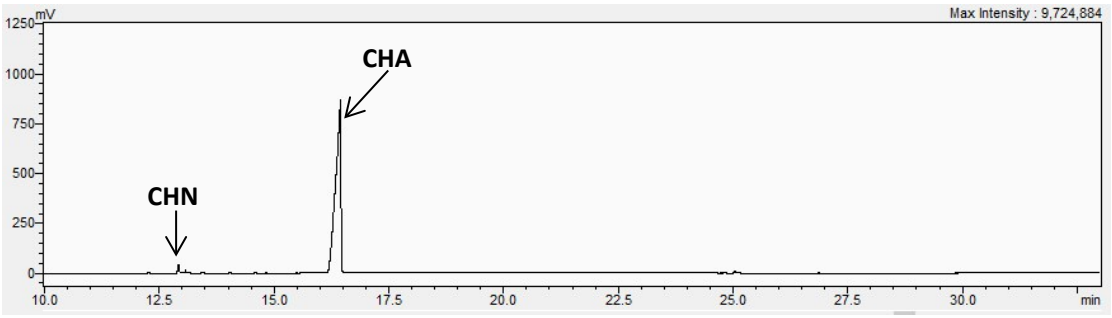


**Fig. S18** GC chromatogram for the CTH of CHN in *s*BuOH over Hf-DTMP.

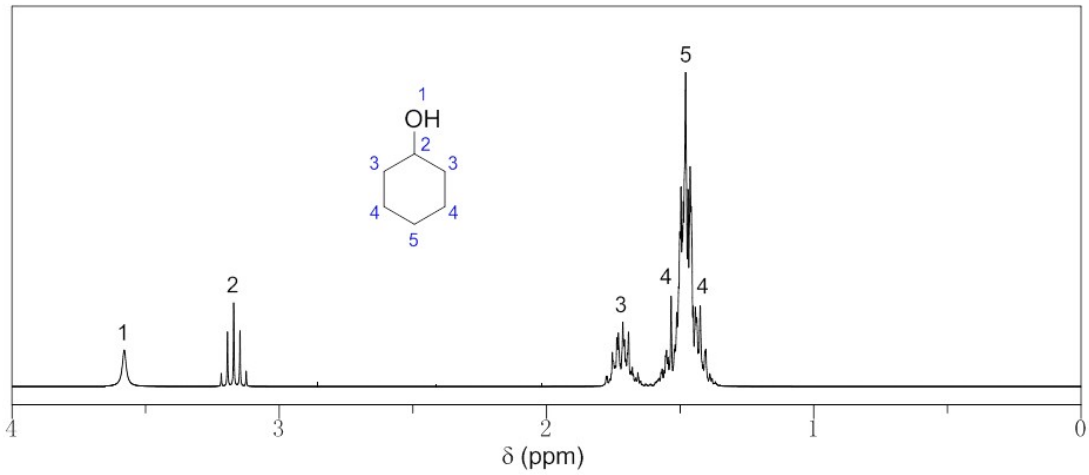


**Fig. S19** $^{1}$H NMR spectrum of purified CHA.

**Table S1** Element contents of Hf-DTMP.

| Element | Analyzed content (wt%) | Calculated content (wt%) | Formula |
|---|---|---|---|
| Hf | 45.23[a] | 44.22 | $Hf_5P_{10}C_{18}N_6O_{30}H_{36}$ |
| P | 15.07[a] | 15.36 | |
| C | 11.02[b] | 10.71 | |
| N | 4.54[b] | 4.16 | |

[a] Hf and P were determined by ICP. [b] C and N were measured by EA.

**Table S2** CTH of HMF into BHMF over various catalysts.[a]

| Catalyst | HMF conversion (%) | BHMF yield (%) |
|---|---|---|
| $HfCl_4$ | 50.3 | 6.5 |
| DTMP | 31.7 | 0.8 |

[a] Reaction conditions: 0.2 g catalyst, 0.5 g HMF, 24.5 g *s*BuOH, 130 °C, 3 h.

**Table S3** Reduction potentials (RPs) of various alcohols.

| Alcohol | Reduction potential (kJ/mol) |
|---|---|
| MeOH | 130.1[a] |
| EtOH | 85.4[a] |
| *n*PrOH | 87.3[b] |
| *i*PrOH | 70.0[b] |
| *n*BuOH | 79.7[b] |
| *s*BuOH | 69.3[b] |

[a] The numerical values of RPs were calculated according to the definition of RP. [b] The numerical values of RP were obtained from van der Waal et al. (J. Catal. 173 (1998) 74-83).