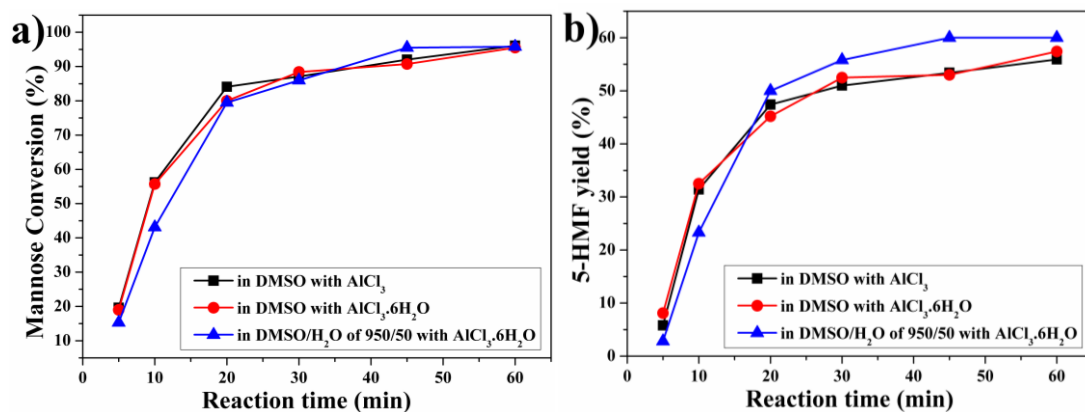
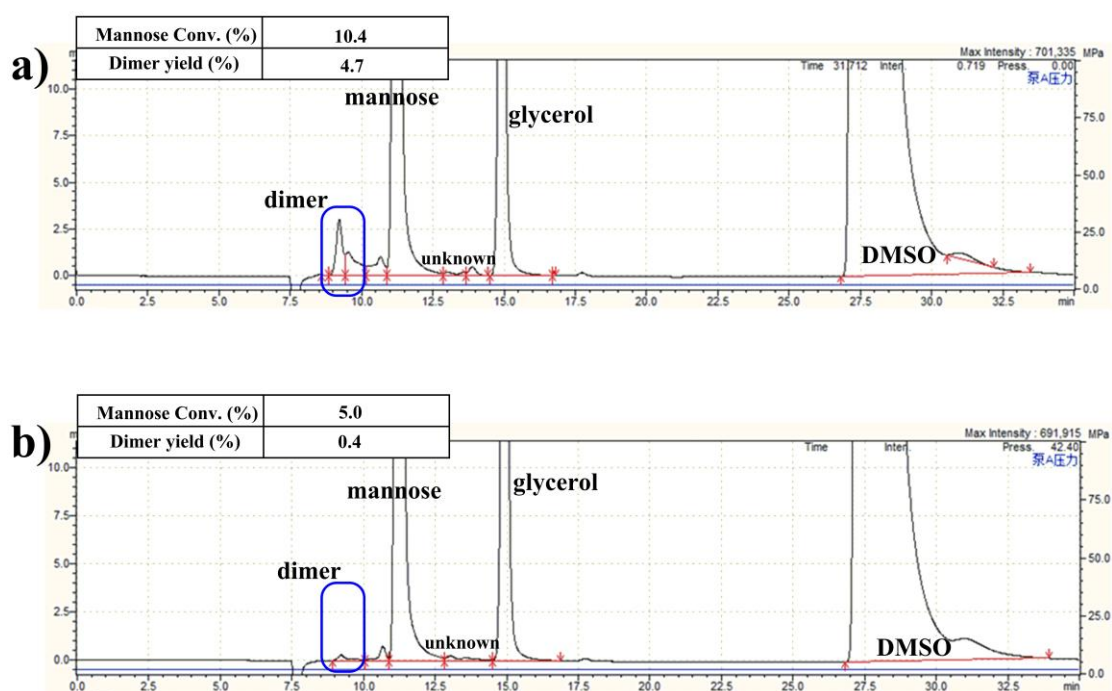


**Fig. S1** Appearances of reaction mixture in DMSO (left) and DMSO/H<sub>2</sub>O of 950/50 (μL/μL) (right) after 10 min at 130 °C.

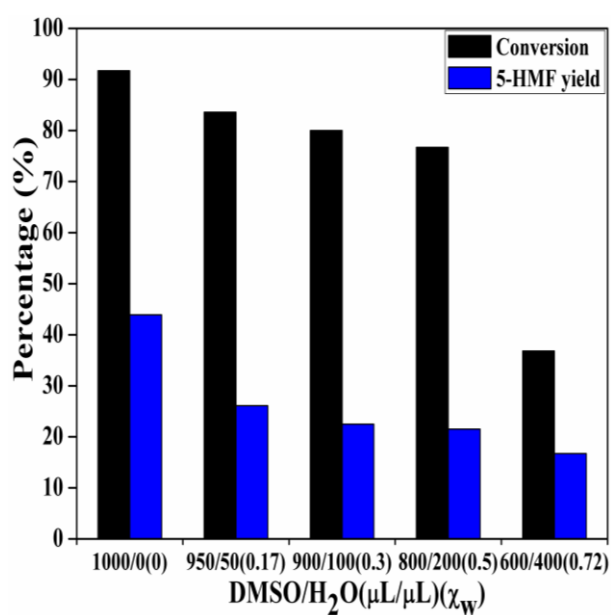


**Fig. S2** Results on the conversion of mannose into 5-HMF in DMSO and DMSO/H<sub>2</sub>O of 950/50 (μL/μL) with different catalysts at 130 °C.

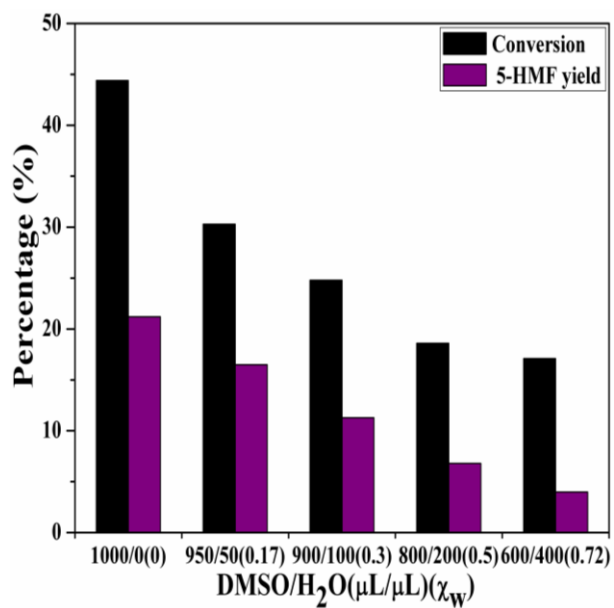


**Fig. S3** Chromatograms on the conversion of mannose in DMSO (a) and DMSO/H<sub>2</sub>O (b) of 950/50 (μL/μL) without catalyst at 130 °C for 1 h.

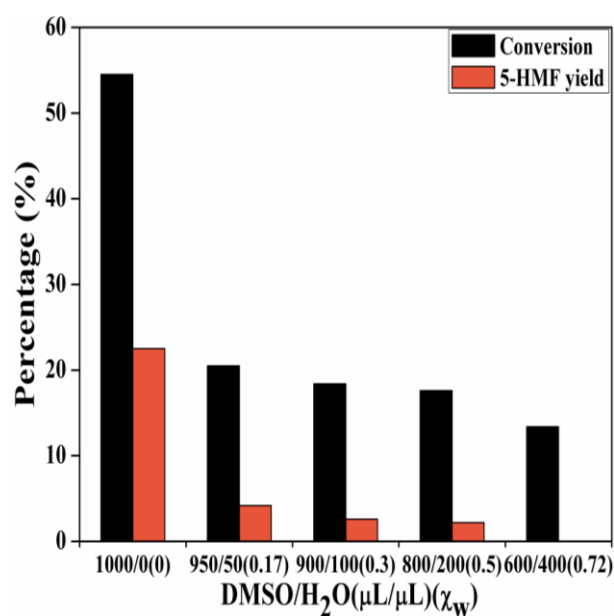
(Note: Cellobiose, a dimer of glucose, has a retention time of about 9.0 min in the HPLC. The compounds with retention times around 9.0 min from mannose are proposed to be the dimers. The dimer yield is calculated based on the assumption that the dimer has an equal response value to cellobiose in the HPLC.)



**Fig. S4** Conversion of mannose in varied DMSO/H<sub>2</sub>O mixed solvents with SnCl<sub>4</sub>•5H<sub>2</sub>O catalyst at 130 °C for 30 min.



**Fig. S5** Conversion of mannose in varied DMSO/H<sub>2</sub>O mixed solvents with CrCl<sub>3</sub>•6H<sub>2</sub>O catalyst at 130 °C for 30 min. at 130 °C for 30 min.



**Fig. S6** Conversion of mannose in varied DMSO/H<sub>2</sub>O mixed solvents with InCl<sub>3</sub>•4H<sub>2</sub>O catalyst at 130 °C for 30 min.