Electronic supplementary information

Efficient conversion of chitin into 5-hydroxymethylfurfural via a simple formylation step under mild conditions

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Details of DFT calculations

In the M06-2X-D3 method, the D3 term represents a dispersion correlation.[1] The vibrational frequencies calculated with the same level were also used to verify whether the structure is stationary points (no imaginary frequency) or TSs (only one imaginary frequency). To check the relative saddle point links connecting each TS to reactant and product of the proposed mechanism, the intrinsic reaction coordinate (IRC) pathways[2] had been traced using the second order González-Schlegel integration method.[3] All reported Gibbs free energies were the sum of electronic energy at M06-2X/def2TZVP and thermal correction to Gibbs free energy at M06-2X-D3/def2SVP level.

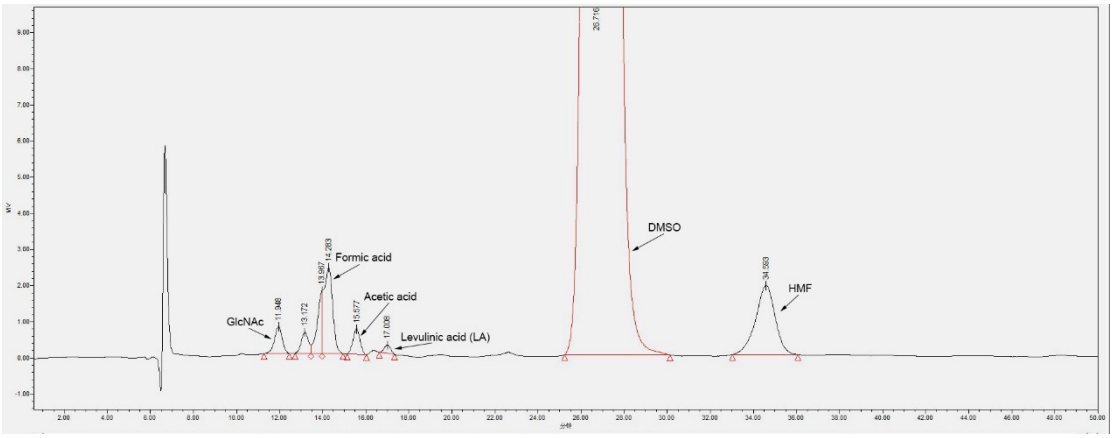

Fig. S1. HPLC results of FC's reaction system of at 160°C for 1 min.

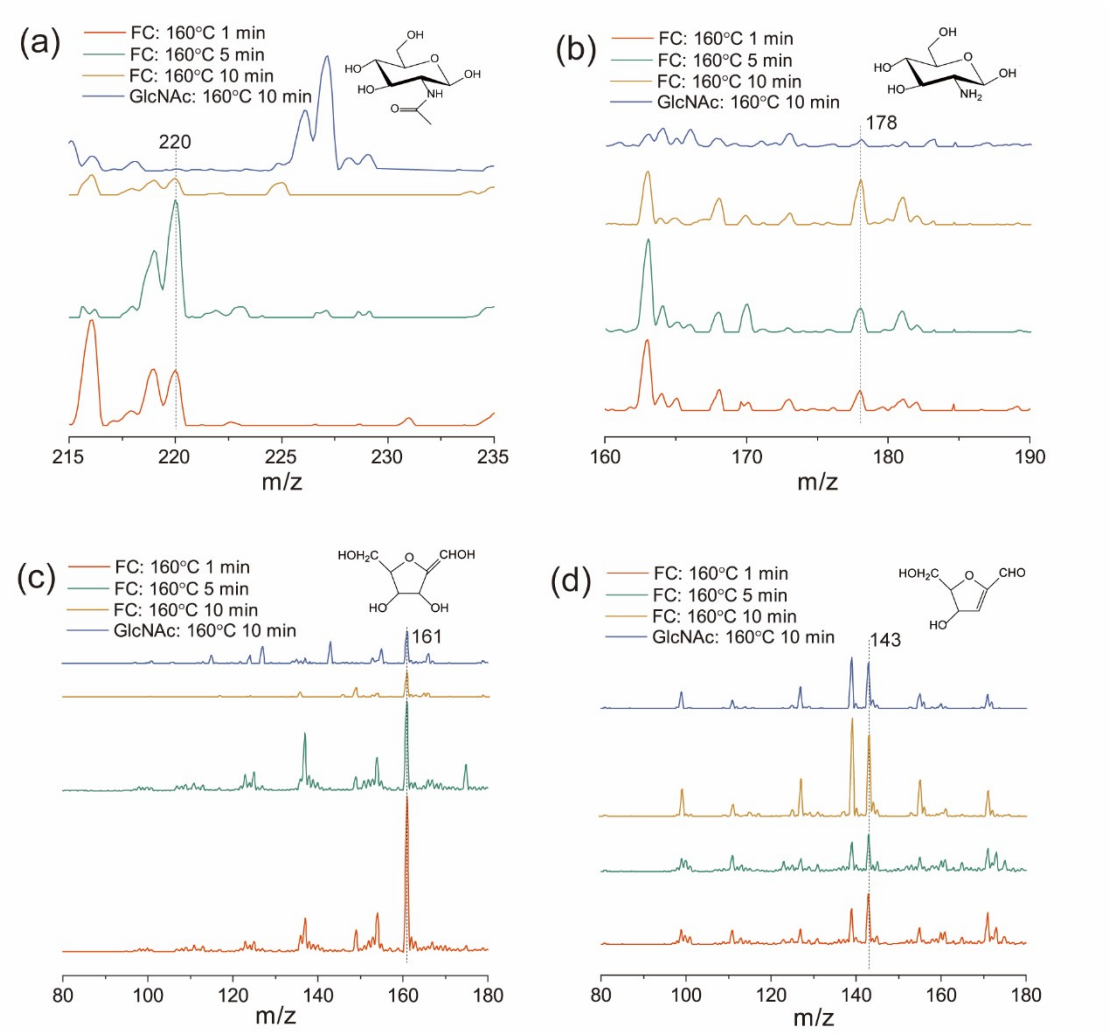

Fig. S2. HPLC-MS results of samples.

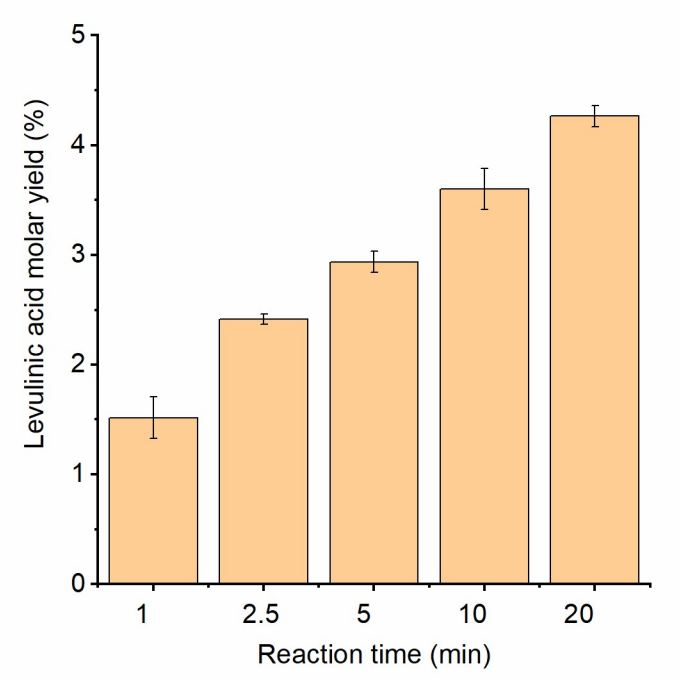

Fig. S3. The molar yield of LA of samples with different reaction times at 160°C (reaction condition in the DMSO-H_2O (4:1 v/v) mixture).

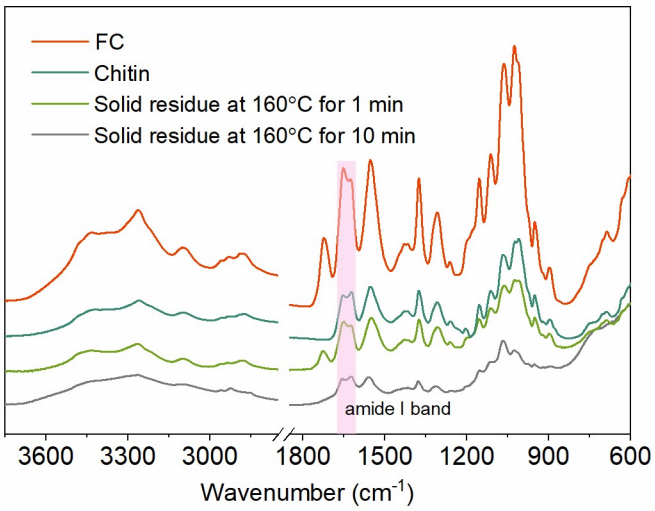

Fig. S4. ATR-FTIR results of chitin, FC, and the solid residues of reactions (FC to HMF) at 160°C for 1 and 10 min, respectively.

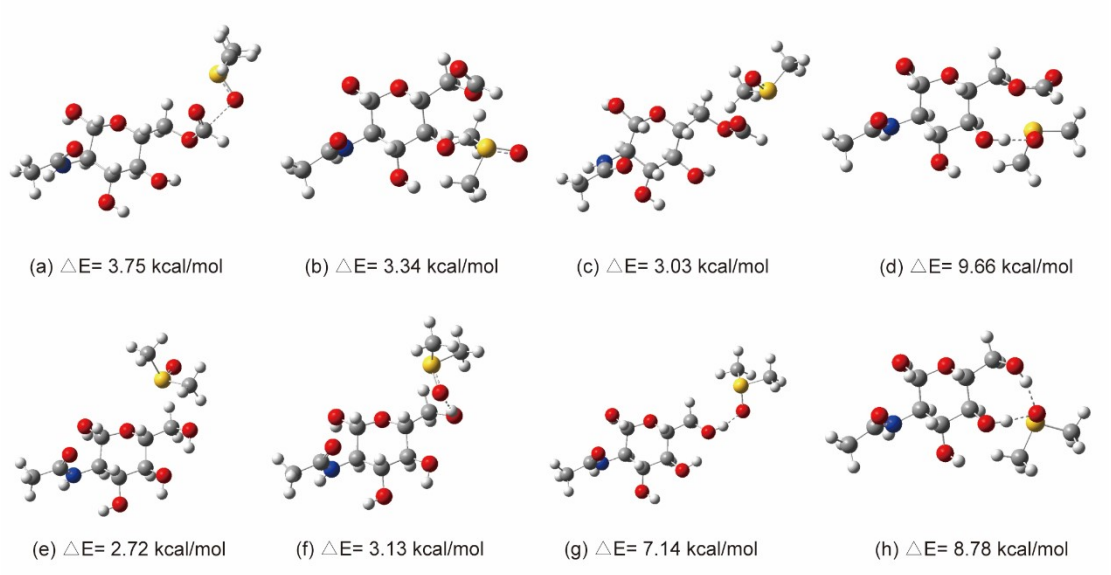

Fig. S5. The optimized structures and interaction energies of (a-d) FC-DMSO around formyl group of FC and (e-h) chitin-DMSO around O1H1 and O2H2 of chitin at M06-2X/def2TZVP//M06-2X-D3/def2SVP level.

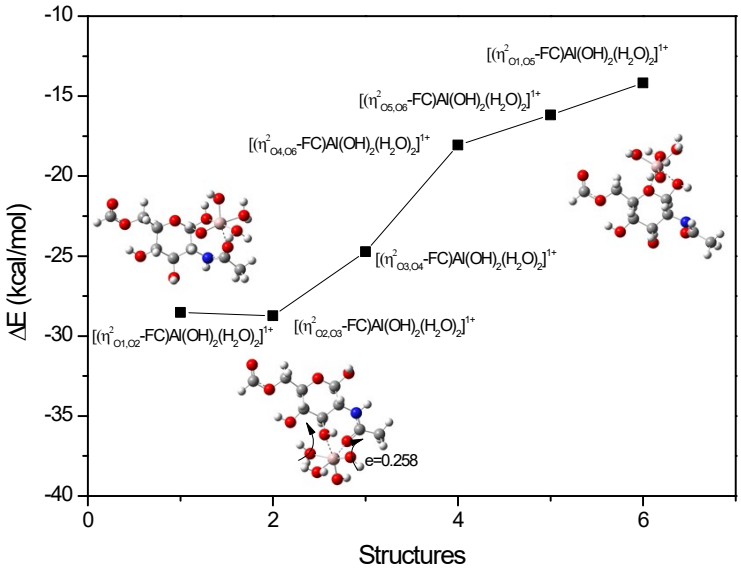

Fig. S6. The binding energies of double-O-ligands of the coordination of FC to $[Al(OH)_2(H_2O)_2]^{1+}$ ion.

1. S. Grimme, S. Ehrlich and L. Goerigk, *Journal of Computational Chemistry*, 2011, **32**, 1456-1465.
2. K. Fukui, *The Journal of Physical Chemistry*, 1970, **74**, 4161-4163.
3. C. Gonzalez and H. B. Schlegel, *The Journal of Chemical Physics*, 1991, **95**, 5853-5860.