Supporting information

Post-Synthetic Sulfonation of MIL-101(Cr) Enabling High-Performance Fructose Conversion to HMF

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S1. Materials and instrumentation

All reagents and solvents were procured from Sigma-Aldrich, Biochem, and Chem-Lab and were employed as received without any additional purification. High-purity grades were selected whenever available to ensure the reliability and reproducibility of the experimental studies. A detailed description of all analytical techniques, instrumentation settings, and measurement procedures including structural, spectroscopic, and thermal analyses can be found in the Supporting Information. These include the methodologies used for phase identification, functional-group analysis, morphology assessment, surface-area measurements, and thermal stability evaluation, along with the corresponding operational parameters.

S2. Synthesis of MIL-101(Cr)

MIL-101(Cr) was obtained through an HF-free hydrothermal route analogous to that reported by the Jiang group. In this approach, chromium(III) nitrate nonahydrate (0.80 g) and 1,4-benzenedicarboxylic acid (0.33 g) were combined in distilled water (10 mL) and subjected to controlled heating to 210 °C at a rate of approximately 1.5 °C min^{-1}, where the system remained for 8 h. After cooling to room temperature, the resulting green solid underwent purification through sequential exposure to distilled water, acetone, and subsequently dimethylformamide for 24 h to ensure removal of residual BDC ligands. Final solvent exchange was accomplished with ethanol

under Soxhlet treatment, after which the material was activated under vacuum at 150 °C overnight to generate accessible chromium centers.

S3. Acidity measurement

The acidity of the functionalized MIL-101(Cr) was quantified through an acid-base titration approach designed to evaluate the concentration of $–SO_3H$ groups. In this method, the modified material (50 mg) was brought into contact with a 2 M NaCl solution (10 mL) for 24 h at room temperature, enabling ion-exchange between the protonated sulfonic acid groups and Na^+ ions, thereby generating the $–SO_3^-Na^+$ form in the solid phase. Following removal of the solid, the acidity released into the supernatant solution was assessed via titration with 0.01 M NaOH, employing phenolphthalein (two drops) as the visual indicator. This procedure allowed for quantitative determination of the Brønsted acid density associated with the grafted sulfonic functionalities.

S4. Calibration curve

To establish the calibration curve for 5-hydroxymethylfurfural (HMF), a primary standard solution was prepared by dissolving 0.100 g of HMF in deionized water and adjusting the volume to 100 mL, resulting in a stock solution with a concentration of 1000 $mg \cdot L^{-1}$. An intermediate standard solution (500 $mg \cdot L^{-1}$) was then obtained by transferring 50 mL of the stock solution into a 100 mL volumetric flask followed by dilution to volume with deionized water. A series of working standard solutions with concentrations between 1 and 5 $mg \cdot L^{-1}$ were subsequently prepared through appropriate dilution of the intermediate solution using deionized water.

The absorbance of each standard solution was recorded at the maximum absorption wavelength of HMF (λ_{max} = 284 nm) employing a SPECORD 210 PLUS double-beam UV-Vis

spectrophotometer. The calibration plot was constructed by correlating the measured absorbance values with the corresponding HMF concentrations, as illustrated in Figure 1.

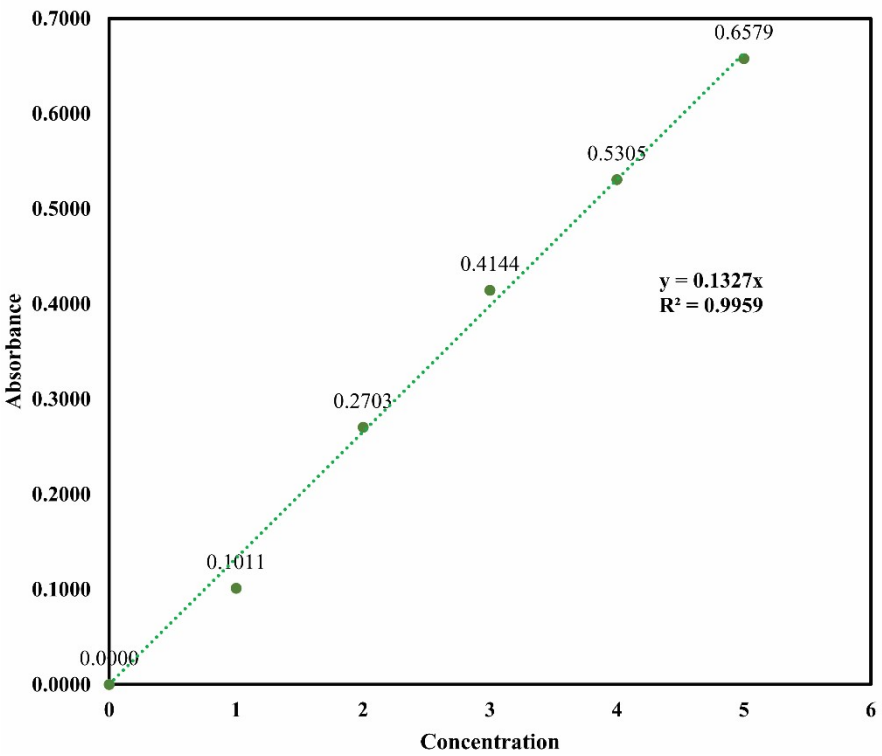


Figure S1. UV-Vis calibration curve for HMF obtained at λ_{max} = 284 nm over the concentration range of 1-5.5 mg·L^{-1}.

S5. UV-Vis absorption spectra of the investigated samples recorded in the 200-400 nm wavelength region.

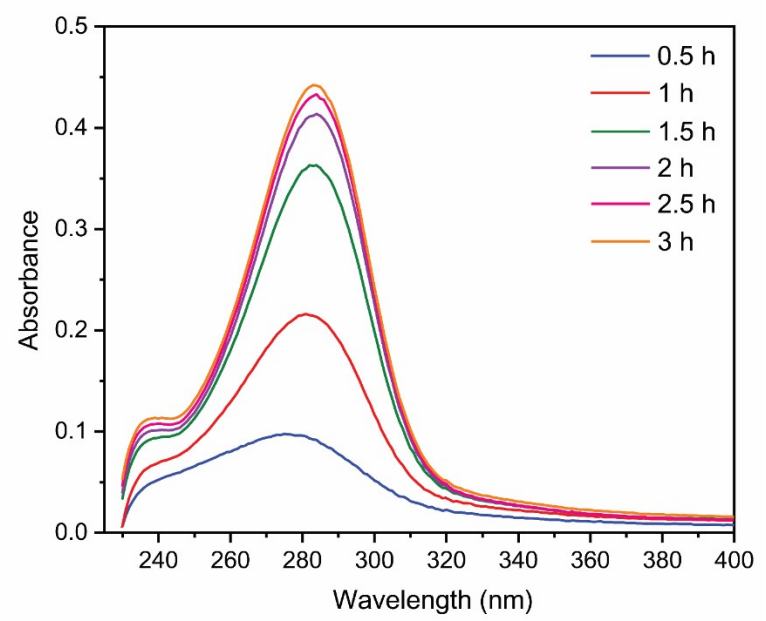


Figure S2. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in DMSO (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (100 mg) at 120 °C.

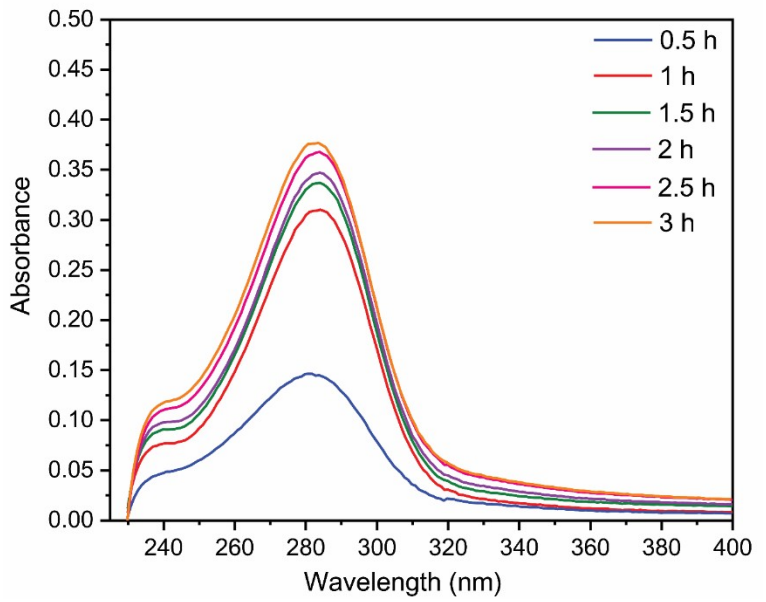


Figure S3. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in DMSO (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (100 mg) at 100 °C.

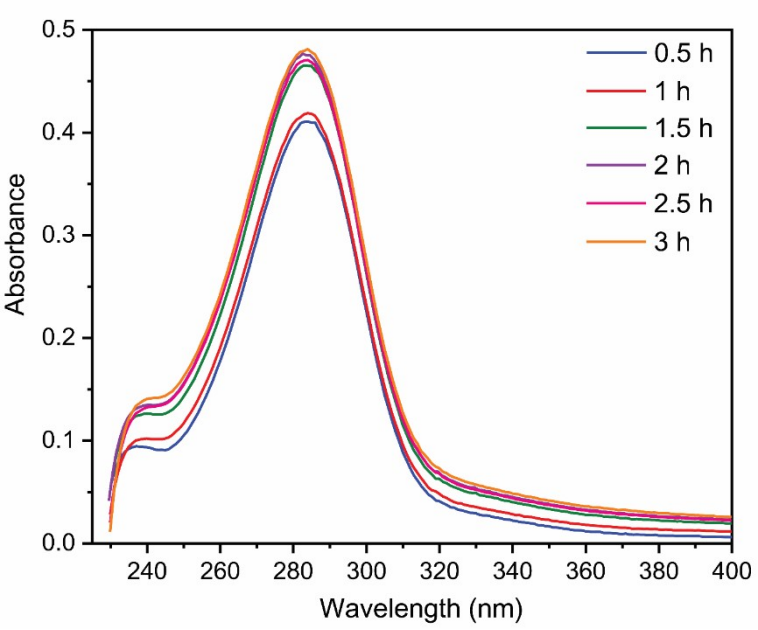


Figure S4. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in DMSO (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (100 mg) at 140 °C.

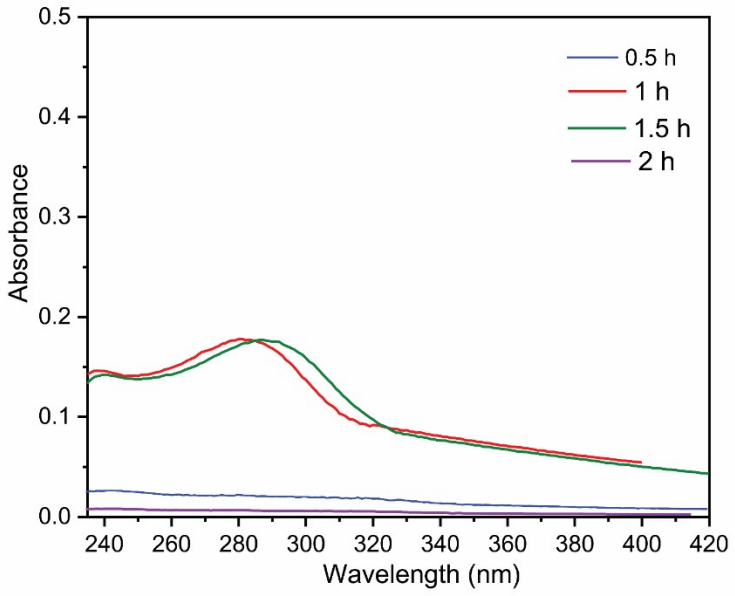


Figure S5. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in DMSO (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (100 mg) at 160 °C.

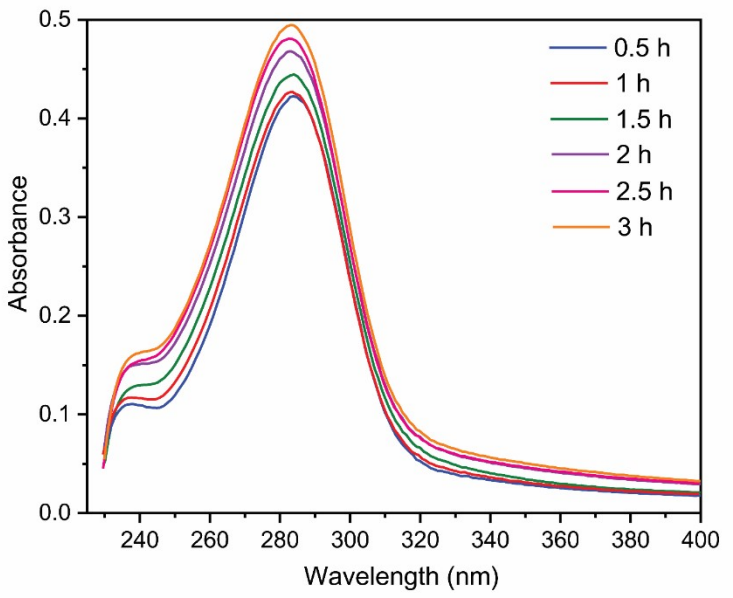


Figure S6. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in DMSO (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (50 mg) at 140 °C.

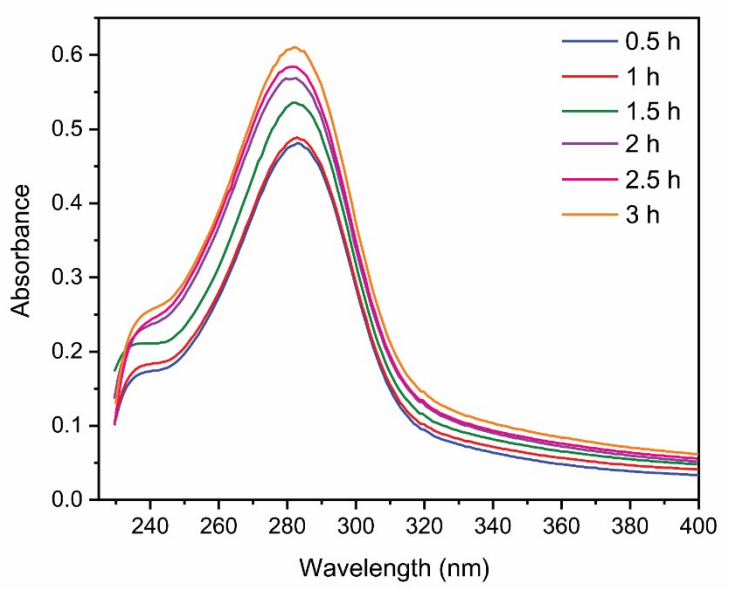


Figure S7. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in DMSO (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (150 mg) at 140 °C.

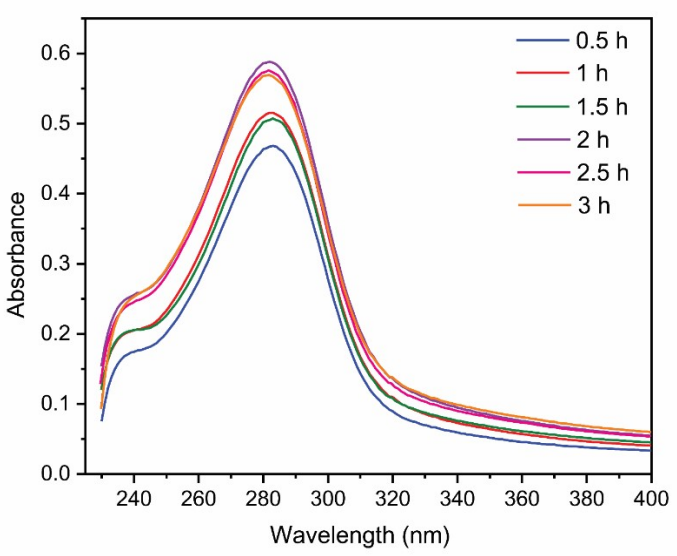


Figure S8. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in DMSO (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (200 mg) at 140 °C.

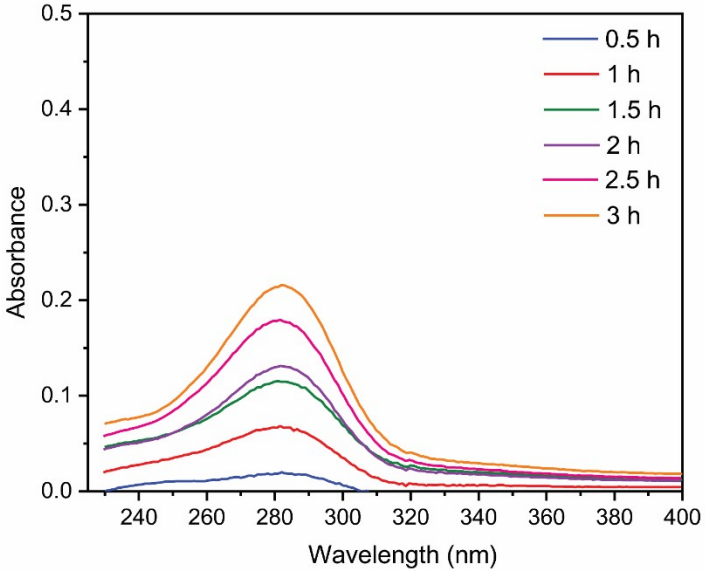


Figure S9. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in Isopropanol (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (150 mg) at 140 °C.

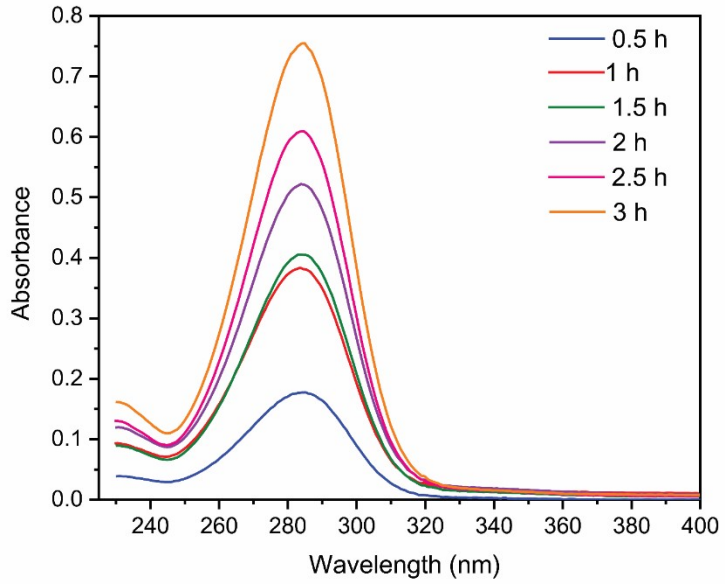


Figure S10. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in 1,4-dioxane (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (150 mg) at 140 °C.

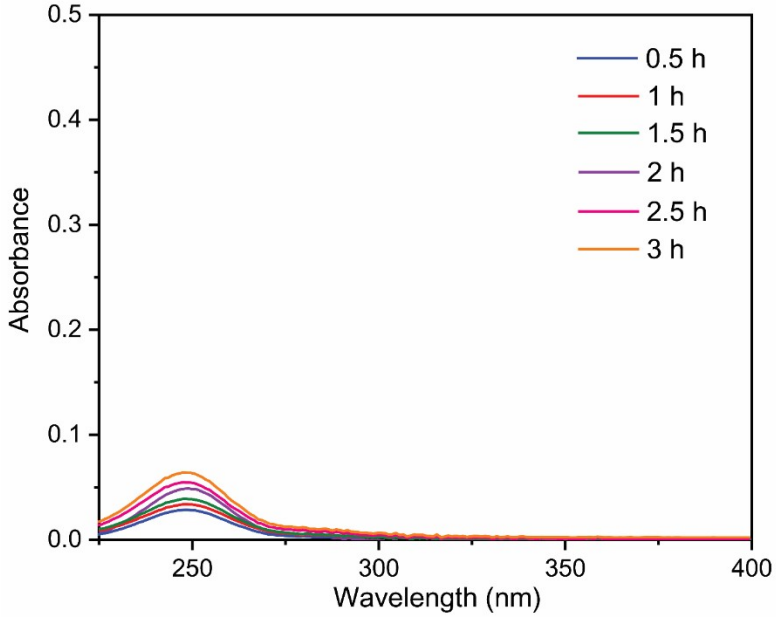


Figure S11. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in Ethanol (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (150 mg) at 140 °C.

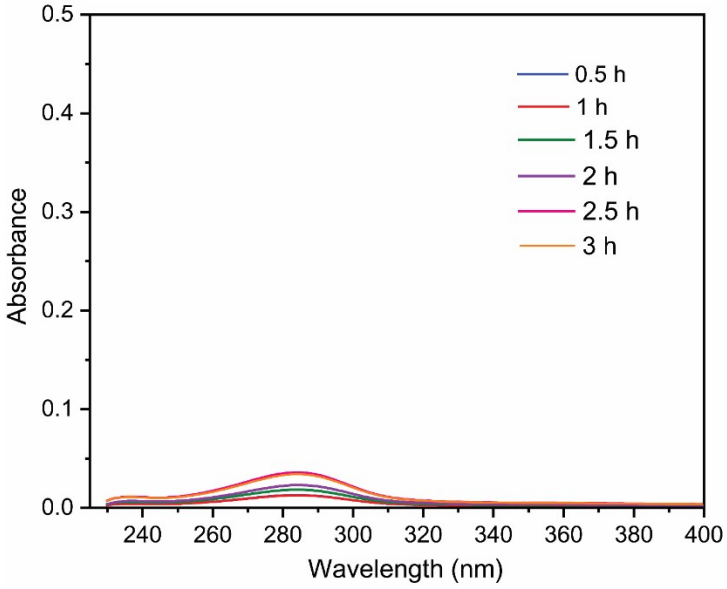


Figure S12. UV-Vis absorption spectra of samples obtained from the fructose conversion reaction carried out in Water (3 mL) using fructose (100 mg), ChCl (0.1 g), and catalyst (150 mg) at 140 °C.

S6. Zero-Order, (b) Pseudo-First-Order, and (c) Pseudo-Second-Order Kinetic Plots for Fructose to HMF Conversion.

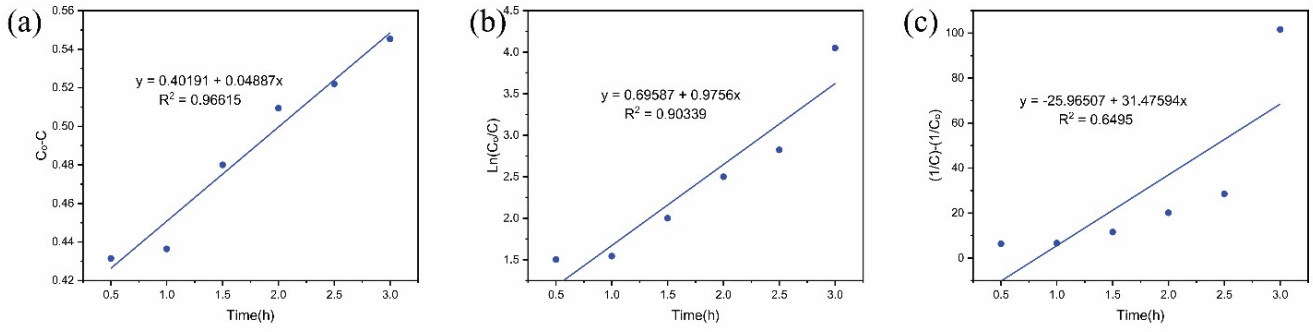


Figure S13. Zero-Order, (b) Pseudo-First-Order, and (c) Pseudo-Second-Order Kinetic Plots for Fructose to HMF Conversion.

S7. (a) FT-IR spectra, (b) XRD patterns of fresh and recovered catalyst, (c) SEM image of recovered catalyst, and (d) result of hot filtration experiment.

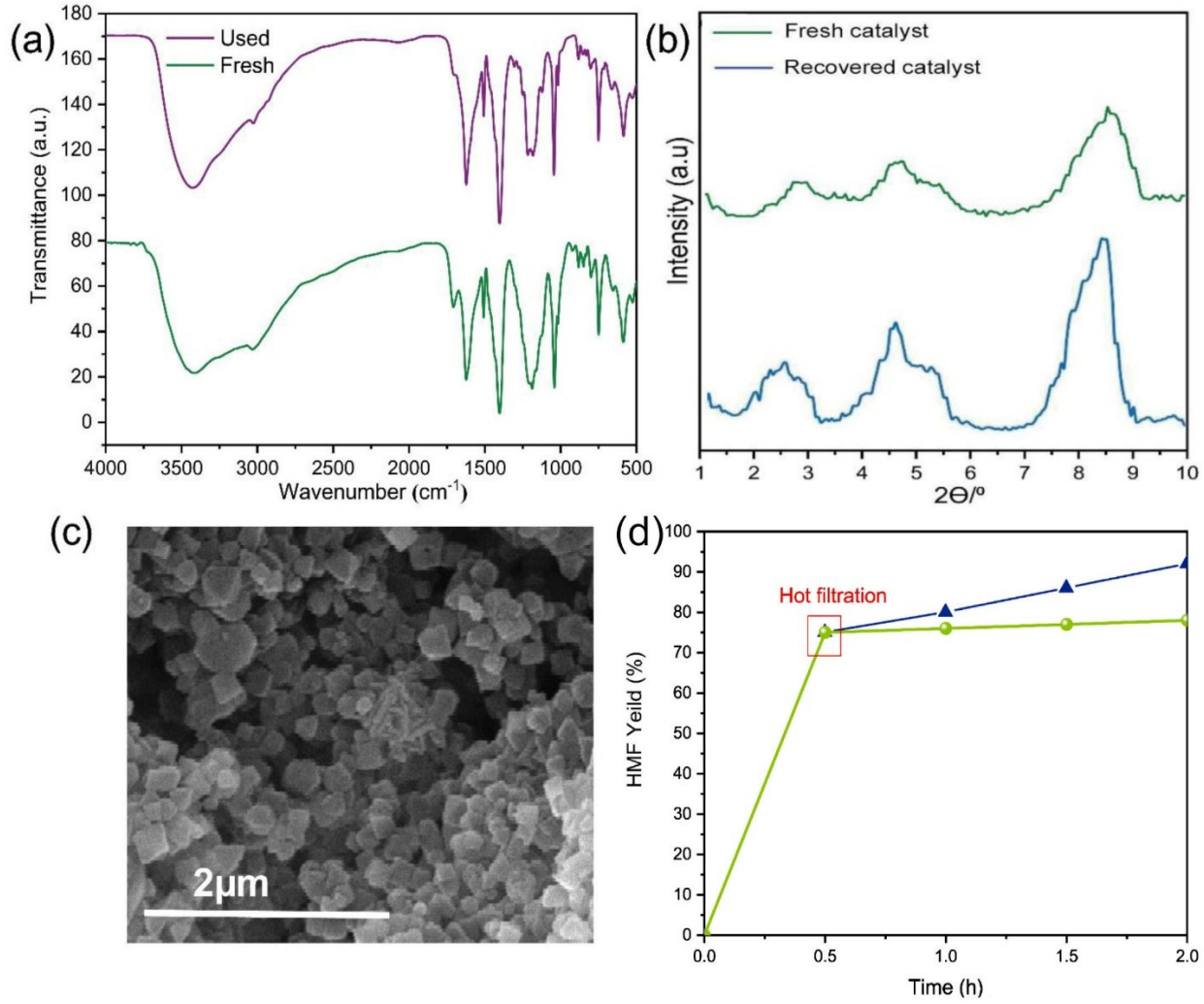


Figure S14. (a) FT-IR spectra, (b) XRD patterns of fresh and recovered catalyst, (c) SEM image of recovered catalyst, and (d) results of hot filtration experiment.

S8. NMR spectra of the isolated HMF in DMSO

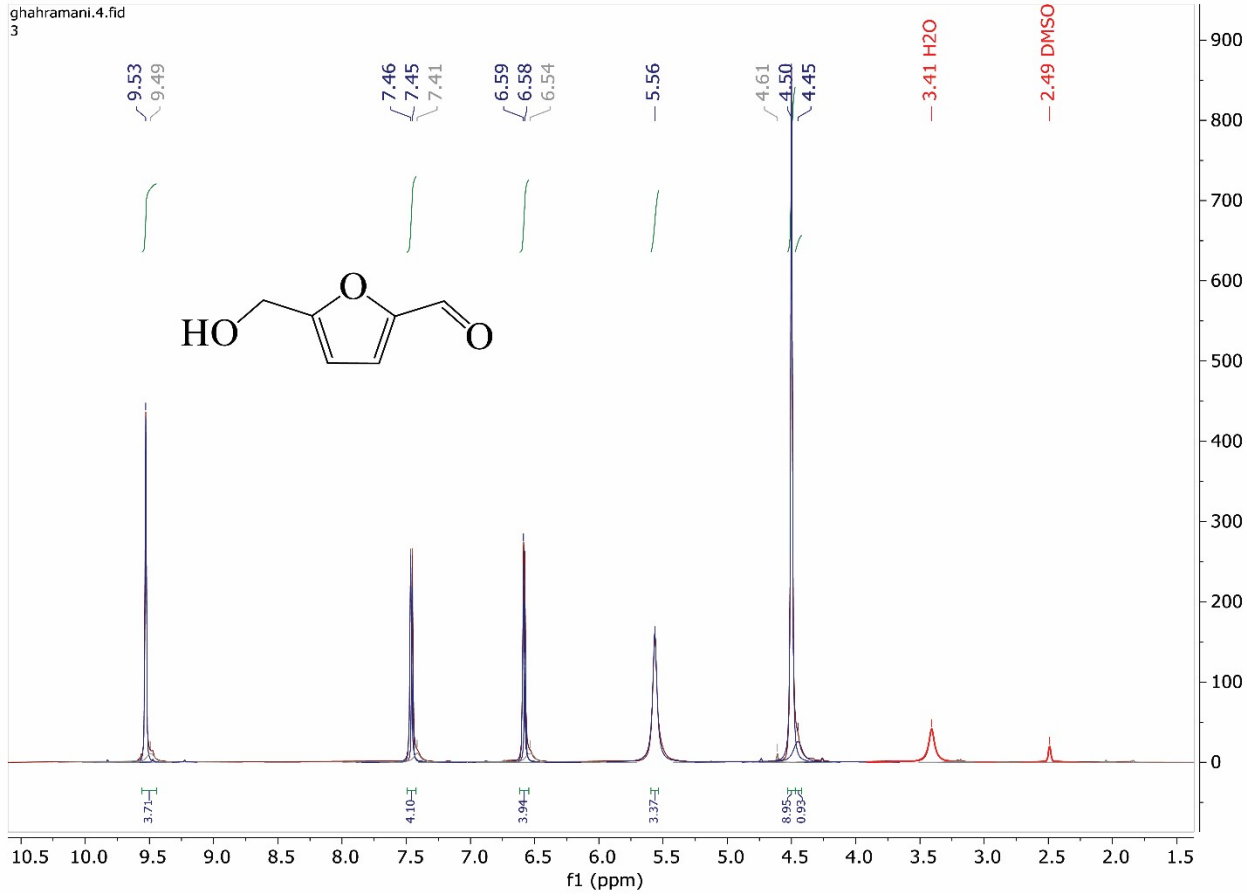


Figure S15. [1]H-NMR spectrum of the isolated HMF in DMSO.

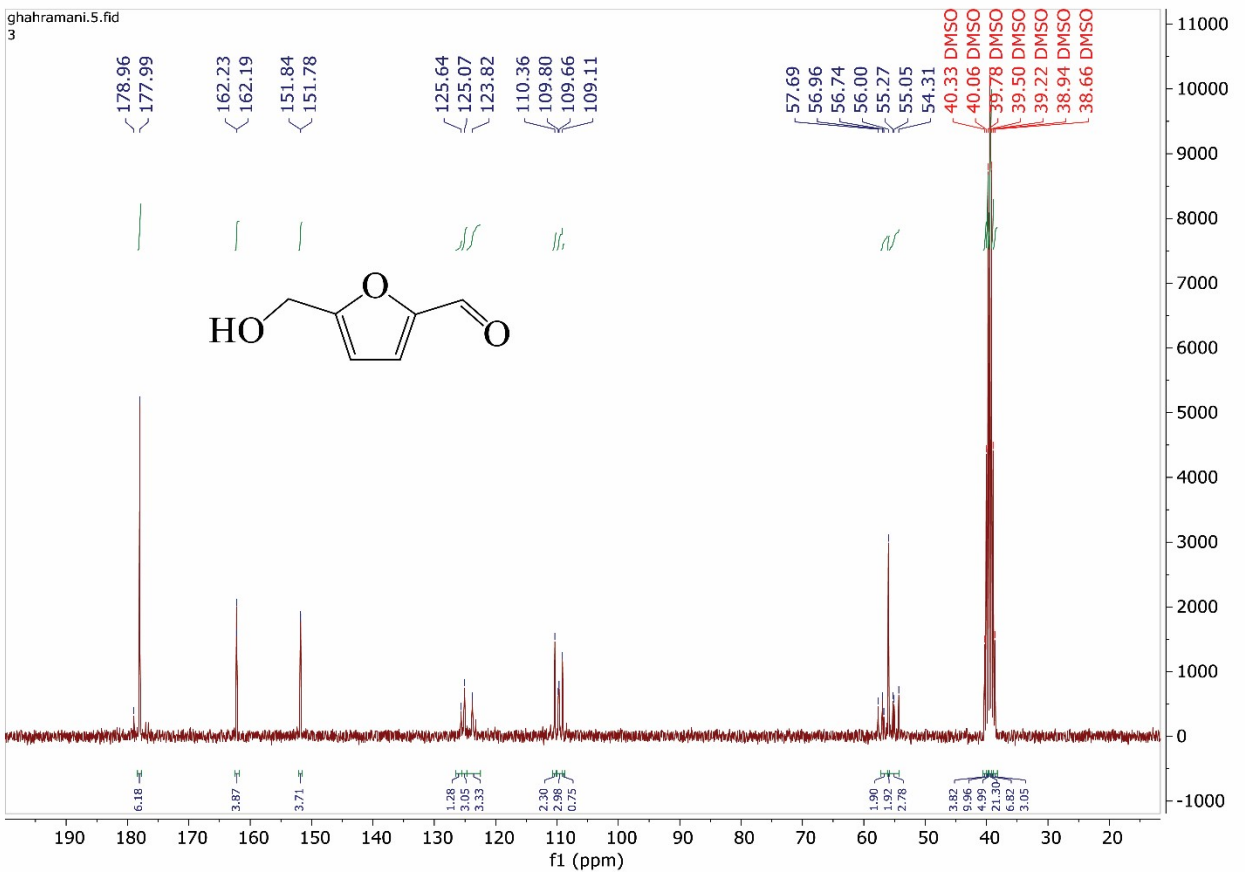
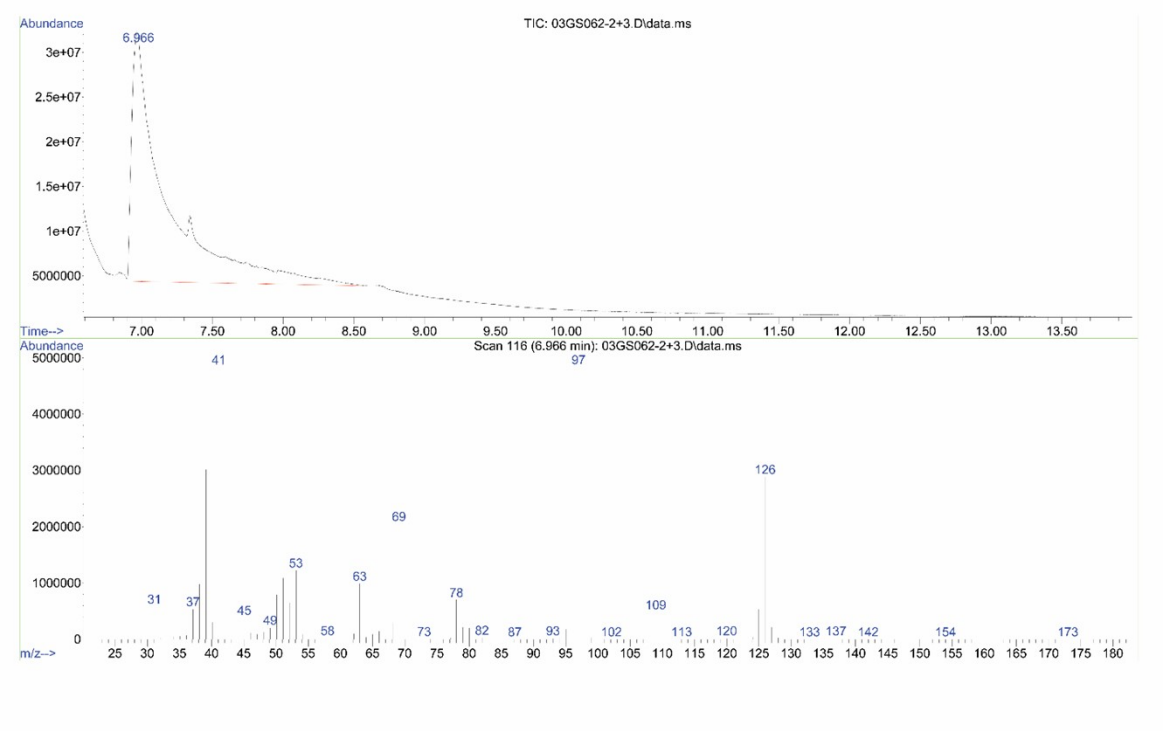


Figure S16. ^{13}C-NMR spectrum of the isolated HMF in DMSO.

S9. Identification of HMF by Gas Chromatography-Mass Spectrometry (GC–MS)



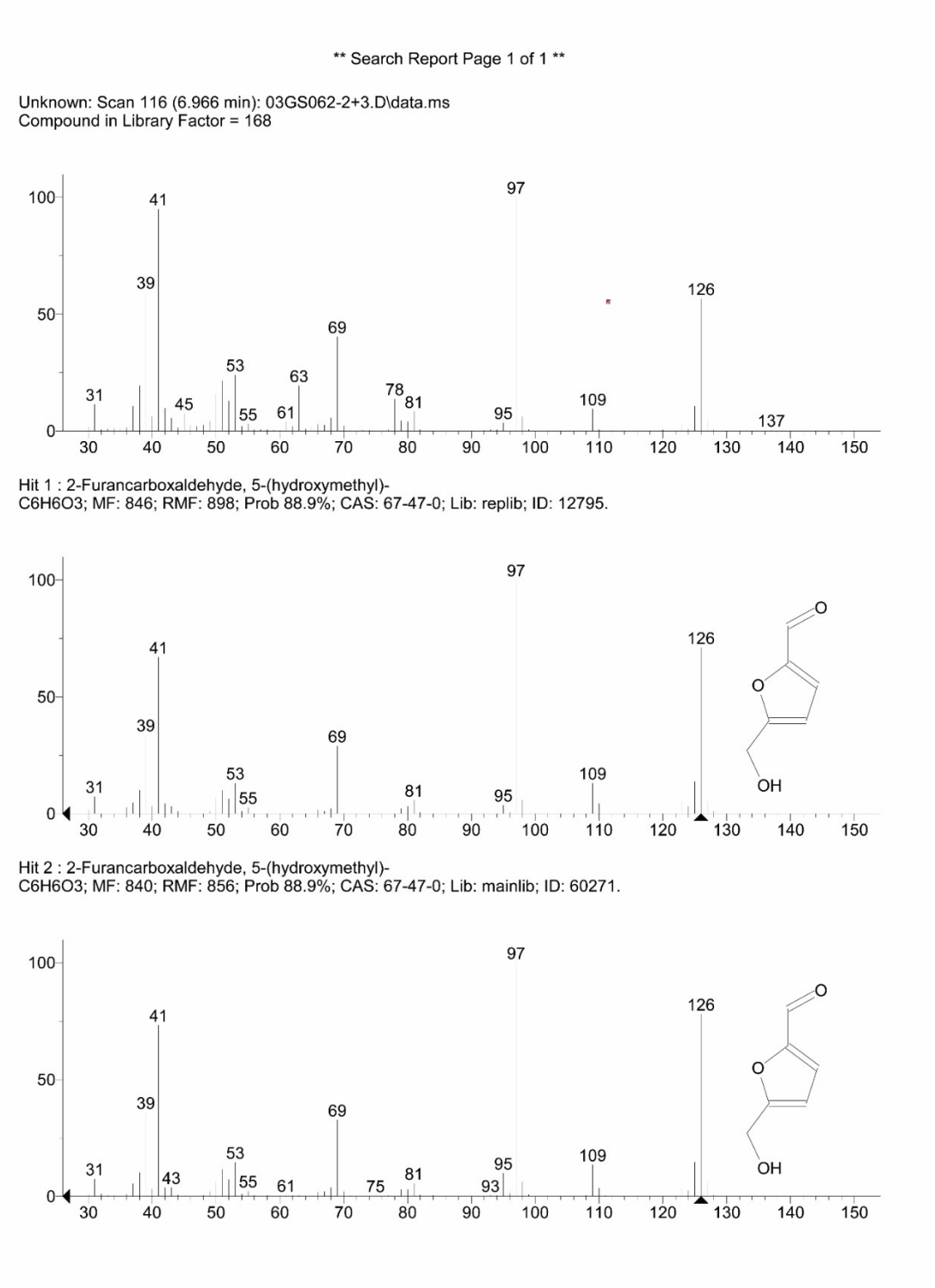


Figure S17. Gas chromatography-Mass spectrometry (GC-MS) analysis of the catalytic experiment.

S10. HPLC chromatographs of the catalytic experiment

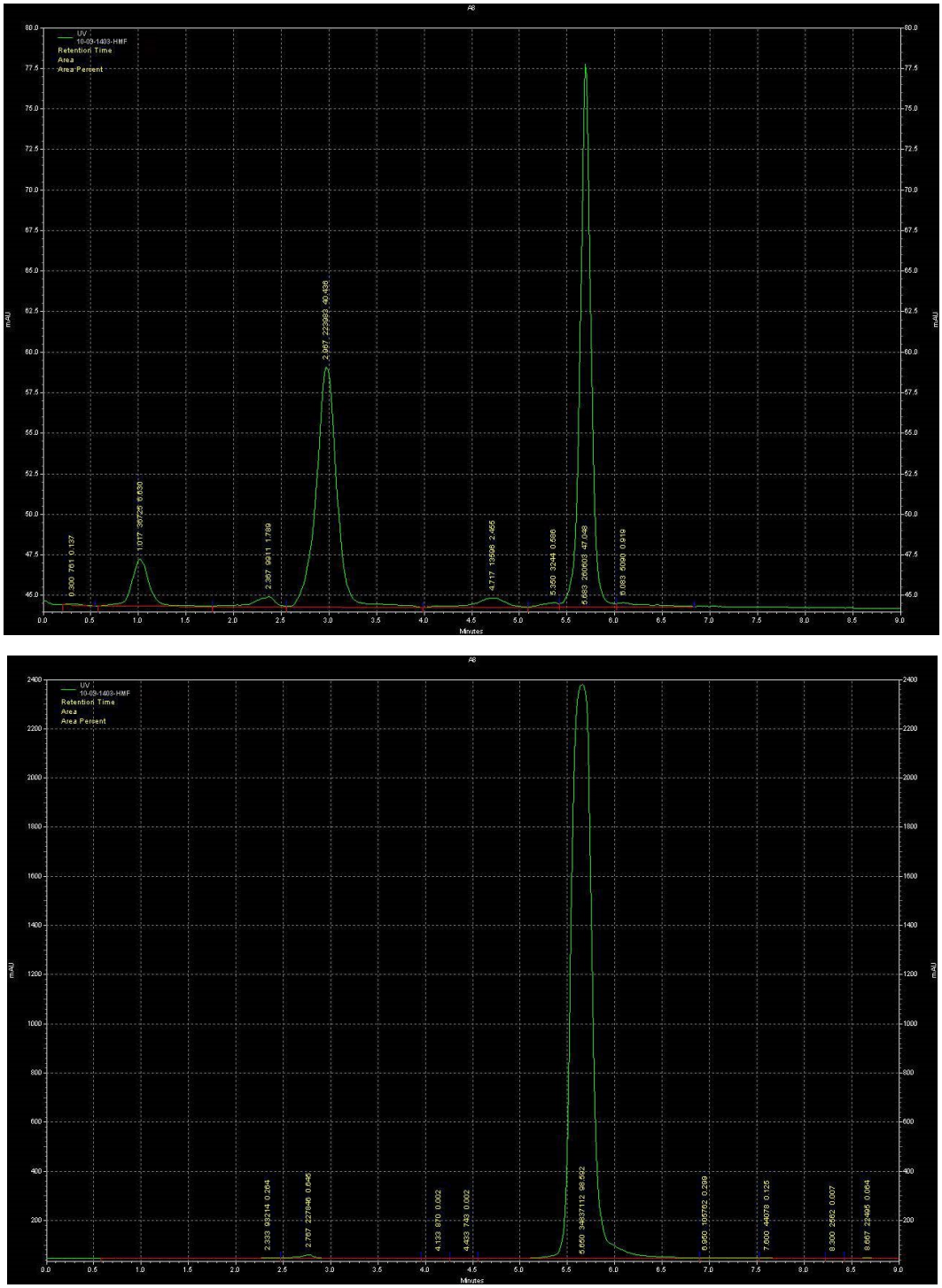


Figure S18. HPLC chromatograms of the catalytic experiment after (a) 0.5 h and (b) 3 h. Reaction conditions: DMSO: 3 mL, ChCl: 1 g, fructose: 0.1g, catalyst: 150 mg, 140 °C.