

Electronic Supplementary Information

Ruthenium Complex Immobilized on Poly(4-vinylpyridine)-Functionalized Carbon-Nanotube for Selective Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran

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1. Experimental

1.1. Materials

Unless otherwise stated, all chemicals in this work were commercial available and used without further purification. 5-hydroxymethylfurfural (HMF), 2,5-diformylfuran (DFF), *N,N*-dimethylformamide, dimethylsulfoxide, isopropyl alcohol, ethanol, toluene, 1,4-dioxane, acetonitrile, *o*-cresol, sulfuric acid were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, P.R. China). 4-vinylpyridine, 1-vinylimidazole and azobis(isobutyronitrile) (AIBN) were purchased from Aladdin Industrial Inc. (Shanghai, P. R. China). Ruthenium (III) chloride hydrate (RuCl₃·xH₂O) was provided by Kunming Boren Precious Metals Co. Ltd (Kunming, P.R. China). High-purity multi-walled carbon nanotubes (CNT, OD: 10~20 nm, Length: 10~30 μm) were supplied by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (Chengdu, P. R. China). Oxygen gas (>99.999%) was obtained from Huate Co. Ltd (Foshan, P.R. China). De-ionized pure water from Millipore-Milli Q Plus System.

1.2. Preparation of composite material PVP/CNT

The poly(4-vinylpyridine) functionalized CNT was prepared according to literature.^{1,2} Typically, a 200 mL dried Schlenk flask was charged with a magnetic stirrer, CNT (600 mg), and DMF (100 mL). After stirring for 6 h at room temperature, 4-vinylpyridine (10.52 g, 100 mmol) and AIBN (105.2 mg) were added, and the mixture was degassed by four freeze-pump-thaw cycles. Then the flask was placed in a thermostated oil bath at 70 °C under nitrogen atmosphere and stirred for 48 h. After polymerization, the mixture was cooled to room temperature and centrifuged. After removal of the homogeneous black supernatant, the black sediment was washed thoroughly with anhydrous ethanol (50 mL) twice, and vacuum-filtered through nylon membrane. The solid was finally dried overnight at 80 °C under vacuum.

1.3. Preparation of composite material PVI/CNT

The poly(1-vinylimidazole) functionalized CNT was prepared according to literature.^{3,4} Typically, a 200 mL dried Schlenk flask was charged with a magnetic stirrer, CNT (600 mg), and DMF (100 mL). After stirring for 6 h at room temperature, 1-vinylimidazole (12.3 mL) and AIBN (180 mg) were added, and the mixture was degassed by four freeze-pump-thaw cycles. Then the flask was placed in a thermostated oil bath at 65 °C under nitrogen atmosphere and stirred for 48 h. After polymerization, the mixture was cooled to room temperature and centrifuged. After removal of the homogeneous black supernatant, the black sediment was washed thoroughly with anhydrous ethanol (50 mL) twice, and vacuum-filtered through nylon membrane. The solid was finally dried overnight at 80 °C under vacuum.

1.4. Preparation of polymer PVP

The polymer poly(4-vinylpyridine) was prepared according to literature.^{1,2} Typically, a 200 mL dried Schlenk flask was charged with a magnetic stirrer and DMF (100 mL). After adding the 4-vinylpyridine (10.52 g, 100 mmol) and AIBN (105.2 mg), the mixture was degassed by four freeze-pump-thaw cycles. Then the flask was placed in a thermostated oil bath at 70 °C under nitrogen atmosphere and stirred for 48 h. After polymerization, the mixture was cooled to room temperature and vacuum-filtered through nylon membrane. The sediment was washed thoroughly with cyclohexane and anhydrous ethanol twice. The solid was finally dried overnight at 80 °C under vacuum.

2. Catalyst Characterization

Inductively coupled plasma-Optical Emission Spectroscopy (ICP-OES) analysis was performed by means of a Perkin-Elmer Optima 8000 instrument. The sample was dissolved with 30% HCl and HNO₃ mixture (3:1).

Thermal gravimetric-differential thermal analysis (TG-DTA) was performed using TA Q50 from room temperature to 780 °C with a scan rate of 10 K/min under a stream of nitrogen gas.

Fourier transform infrared (FT-IR) spectra of KBr pellets were recorded at room temperature in the 1200-3000 cm⁻¹ region with a Bruker Tensor 27 spectrometer,

equipped with a Data Station, at a spectral resolution of 4 cm^{-1} and accumulations of 32 scans.

Raman spectra were employed at ambient temperature in LabRAM HR800-LS55 with an argon-ion laser at an excitation wavelength of 532 nm.

Ultraviolet visible (UV-vis) absorption spectra were recorded in the wavelength range of 200 - 300 nm with a Shimadzu UV-1750 spectrometer. The apparatus was calibrated using ethanol.

Brunauer-Emmett-Teller (BET) surface area measurements were performed with N_2 adsorption-desorption isotherms at 77 K (SI-MP-10/PoreMaster 33, Quantachrome), after degassed under vacuum at 423 K for 24 h. The specific BET surface areas were evaluated using the method in the p/p_0 range 0.05 to 0.3.

Powder X-ray diffraction (XRD) analysis was carried out with a PANalytical X'pert Pro multipurpose diffractometer at 40 KV and 40 mA, using Ni-filtered Cu-K α radiation with a scan speed of 0.3 sec/step, a step size of 0.02° in 2θ , and a 2θ range of 0-80.

Transmission electron microscopy (TEM) was performed by JEM-2100HR. TEM studies were prepared by placing a drop of the suspension of sample in ethanol onto a carbon-coated copper grid, followed by evaporating the solvent.

X-ray photoelectron spectroscopy (XPS) data was obtained with a Kratos Axis Ultra (DLD) photoelectron spectrometer operated at 15 kV and 5 mA at a pressure of about 5×10^{-9} torr using Al K α as the exciting source (1486.6 eV). The binding energies were referenced to the C 1s photoelectron peak (Binding energy = 284.2 eV).

Temperature-programmed reduction (TPR) was carried out with Micromeritics AutoChem II 2920 equipped with a thermal conductivity detector. Samples were heated up to 1073 K at 10 K min^{-1} in a gas stream of 5% hydrogen in argon.

3. The quantitative analysis of substrate and product

The quantitative analysis of HMF was determined by high performance liquid chromatography (HPLC, Shimadzu LC-20AT) equipped with a Shodex Sugar SH-1011 column ($300 \times 8\text{ mm}$) and UV/refractive index detectors. H_2SO_4 (HPLC grade, 0.005 M) aqueous solution was used as the mobile phase at a flow rate of 0.5 mL min^{-1} , and the column temperature was maintained at $50\text{ }^\circ\text{C}$. The amounts of HMF were calculated based on external standard curves constructed with authentic standards.

The quantitative analysis of DFF was performed by gas chromatograph-mass spectrometer (GC-MS, Agilent 5973 Network 6890N) and gas chromatograph (GC, Agilent 6890) with a KB-5 capillary column ($30.0\text{ m} \times 0.32\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$) and a hydrogen flame-ionization detector (FID). Product separation was achieved using the following conditions: injector temperature $260\text{ }^\circ\text{C}$, detector temperature $280\text{ }^\circ\text{C}$, oven temperature $100\text{ }^\circ\text{C}$ held for 1 min, $25\text{ }^\circ\text{C min}^{-1}$ to $220\text{ }^\circ\text{C}$, and held at $220\text{ }^\circ\text{C}$ for 1.5 min using *o*-cresol as internal standard.

The HMF conversion and DFF yield were calculated as follows.

$$\text{HMF conversion (\%)} = \frac{[(\text{Initial amount of HMF}) - (\text{Amount of residual HMF})]}{(\text{Initial amount of HMF})} \times 100$$

$$\text{DFF yield (\%)} = \frac{(\text{Amount of produced DFF})}{(\text{Initial amount of HMF})} \times 100$$

1. S. H. Qin, D. Q. Qin, W. T. Ford, J. E. Herrera and D. E. Resasco, *Macromolecules*, 2004, **37**, 9963-9967.
2. A. B. Chen, Y. L. Li, J. Z. Chen, G. Y. Zhao, L. L. Ma and Y. F. Yu, *ChemPlusChem*, 2013, **78**, 1370-1378.
3. M. Takafuji, S. Ide, H. Ihara and Z. H. Xu, *Chem. Mater.*, 2004, **16**, 1977-1983.
4. J. Z. Chen, W. Zhang, L. M. Chen, L. L. Ma, H. Gao and T. J. Wang, *ChemPlusChem*, 2013, **78**, 142-148.

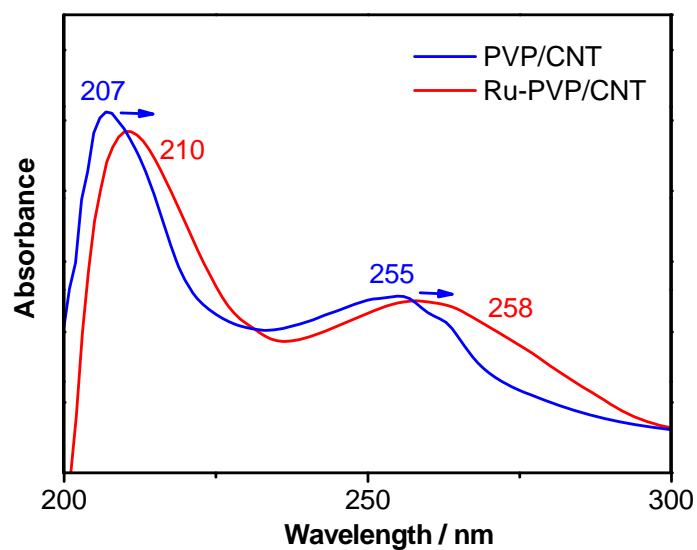


Figure S1 UV-vis spectra of PVP/CNT and Ru-PVP/CNT.

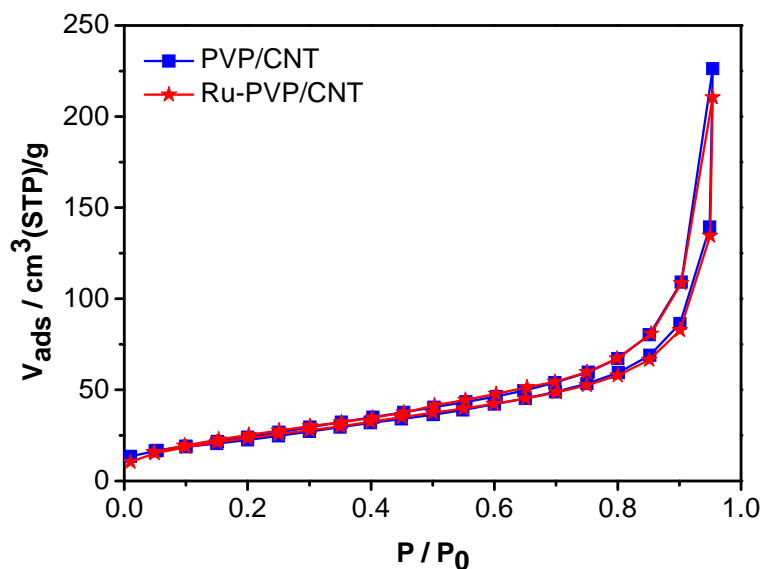


Figure S2 N₂ adsorption/desorption isotherms of PVP/CNT and Ru-PVP/CNT.

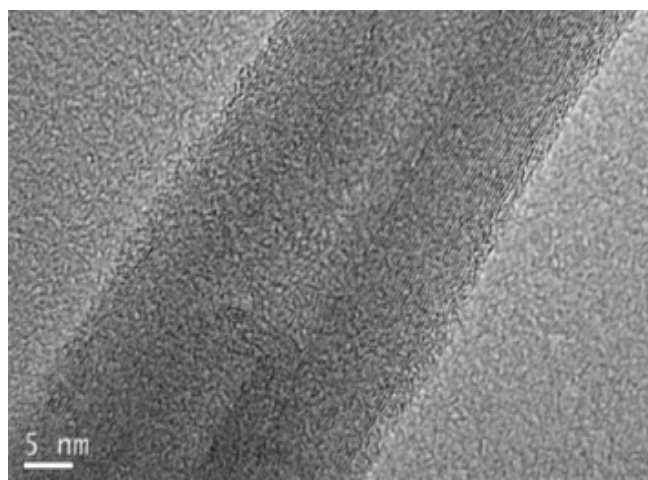


Figure S3. TEM images of CNT.

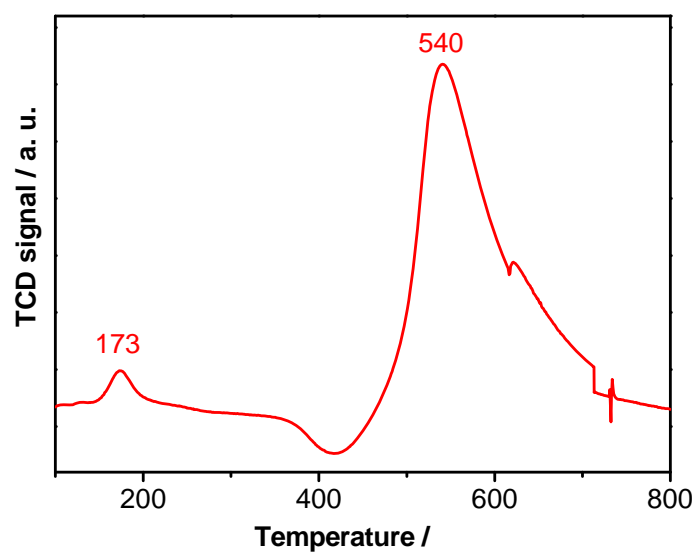


Figure S4. H₂-TPR profile for Ru-PVP/CNT

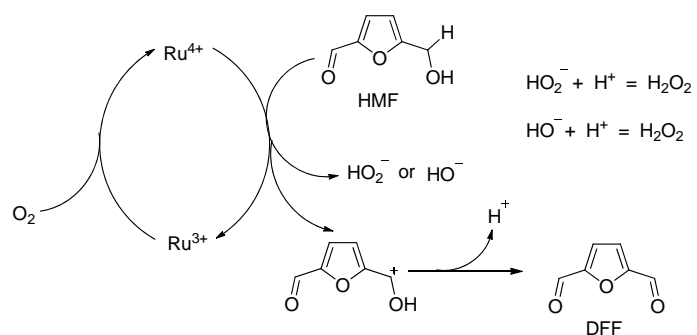


Figure S5. Proposed mechanism of Ru-PVP/CNT catalyzed aerobic oxidation of HMF to DFF.

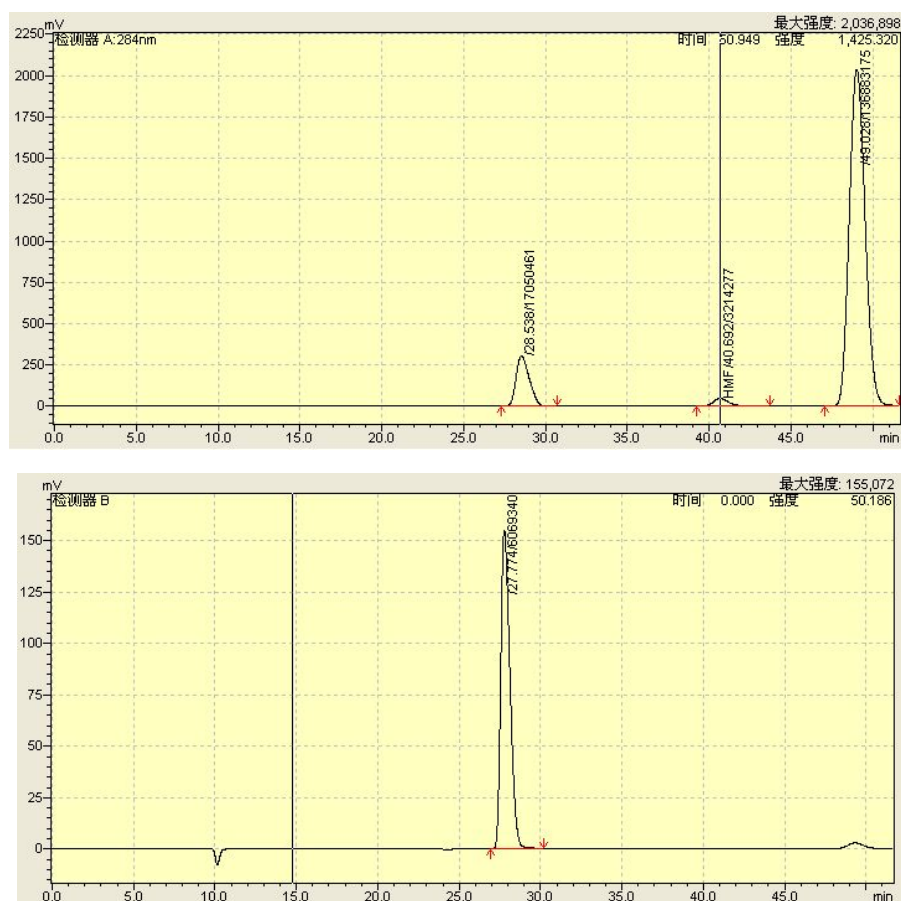


Figure S6. Typical HPLC analysis of Ru-PVP/CNT catalyzed aerobic oxidation of HMF to DFF.

Reaction conditions: HMF (63 mg, 0.5 mmol), Ru-PVP/CNT (60 mg, Ru 2.2 wt%), DMF (5 mL), temperature (120 °C), time (12 h), O₂ (2 MPa). Retention time (min): t 28.54 for FFCA, t 40.69 for HMF, t 49.03 for DFF (UV detector, above); t 27.77 for DMF (Refractive index detector, below).

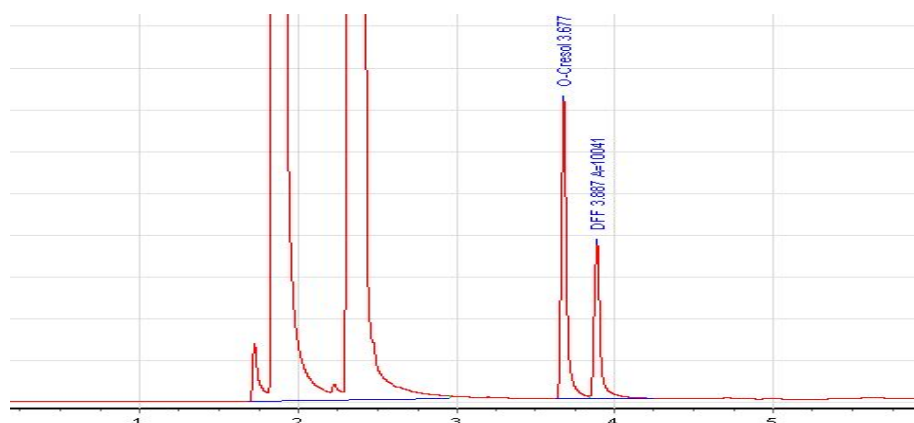


Figure S7. Typical GC analysis of Ru-PVP/CNT catalyzed aerobic oxidation of HMF to DFF.

Reaction condition: HMF (63 mg, 0.5 mmol), Ru-PVP/CNT (60 mg, Ru 2.2 wt%), DMF (5 mL), temperature (120 °C), time (12 h), O₂ (2 MPa). Retention time (min): t

1.83 for ethanol, t 2.36 for DMF, t 3.68 for *o*-cresol (internal standard), t 3.89 for DFF.

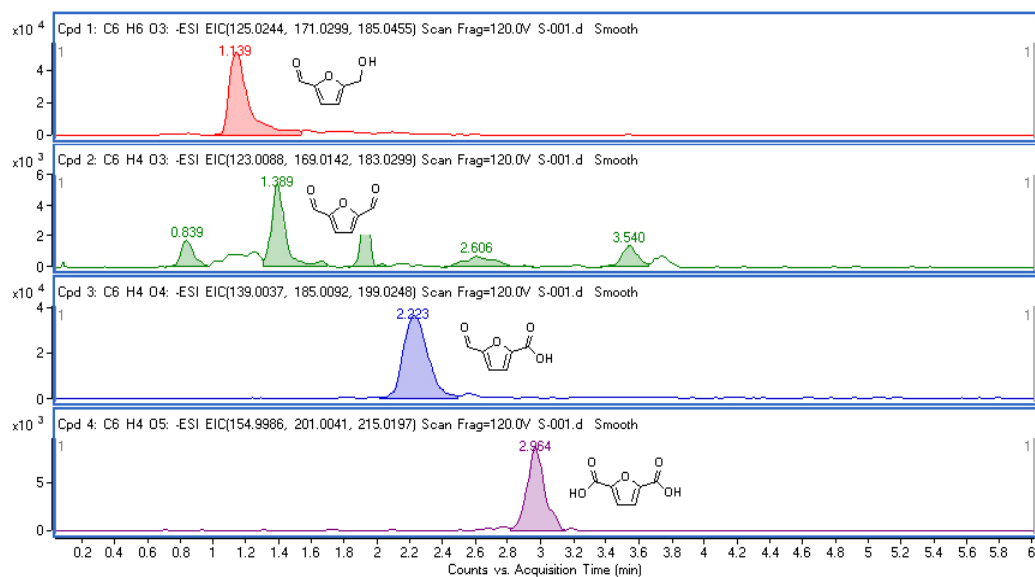


Figure S8. HPLC-MS analysis for aerobic oxidation of HMF.

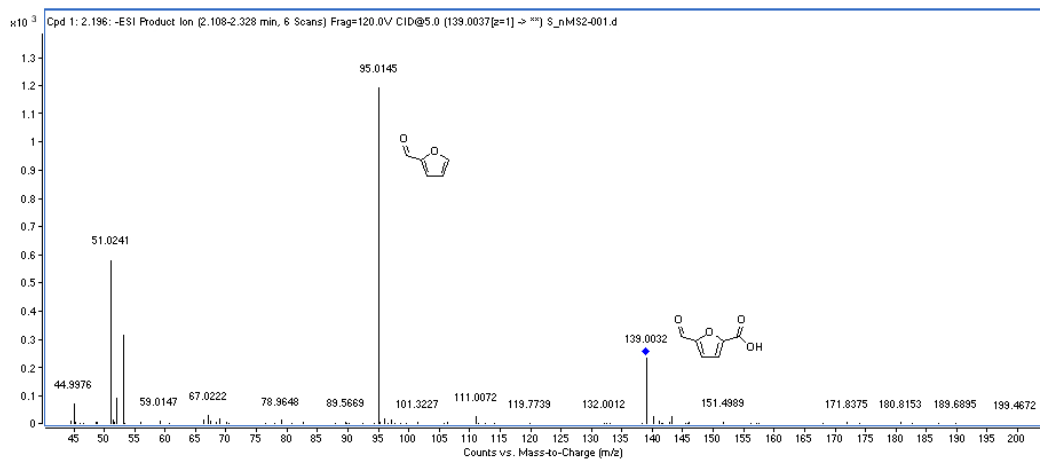
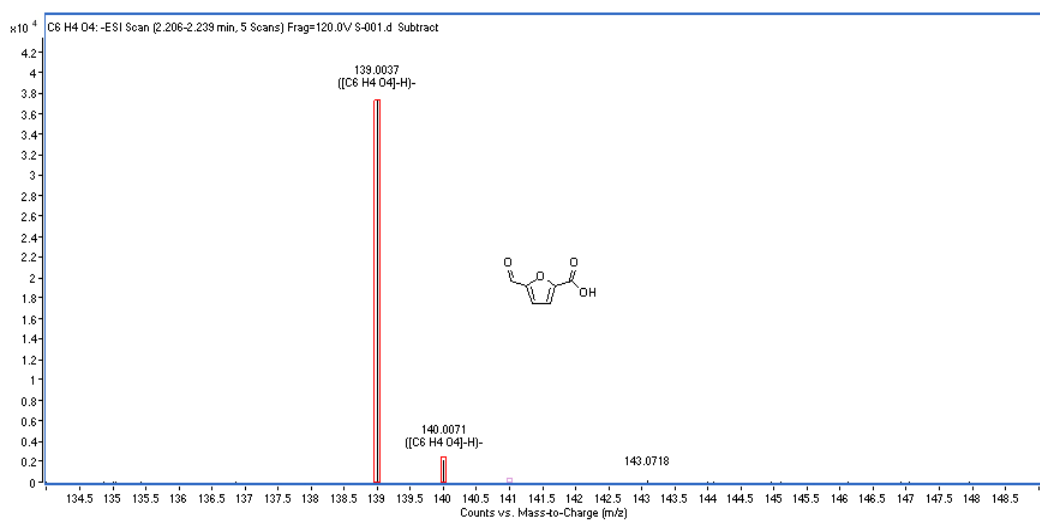


Figure S9. HPLC-MS analysis of 5-formyl-2-furancarboxylic acid

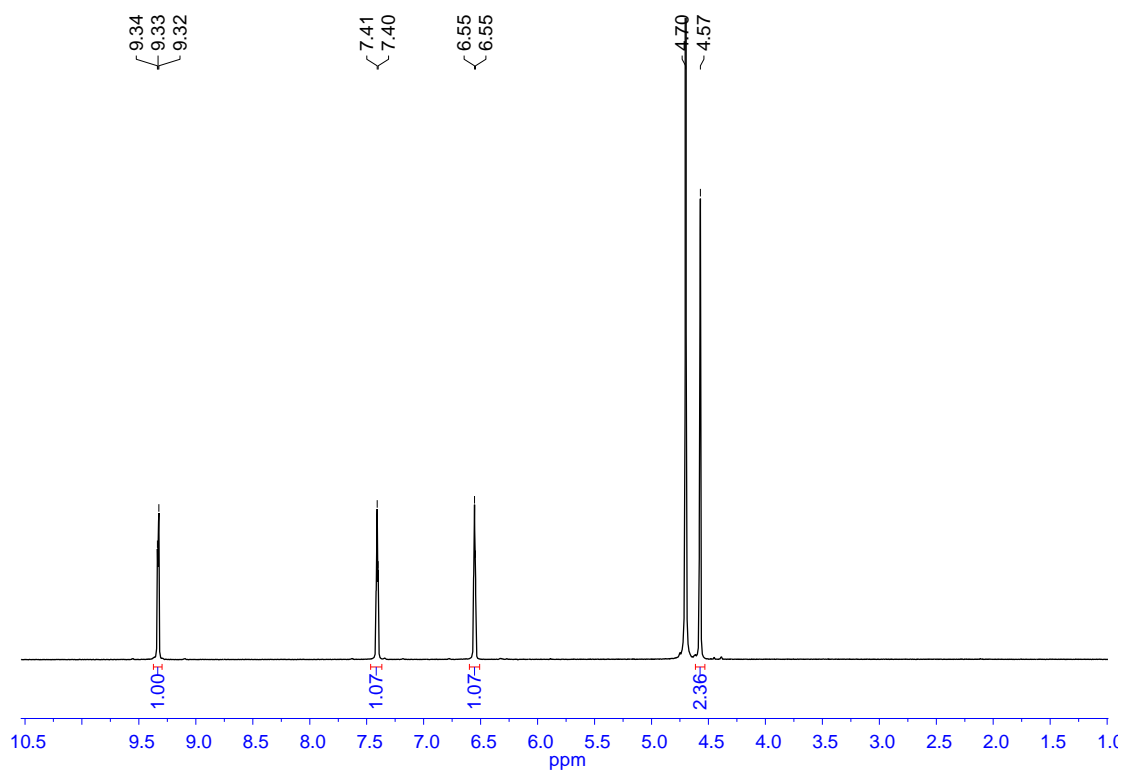


Figure S10. ¹H NMR of 5-hydroxymethylfurfural in D₂O.

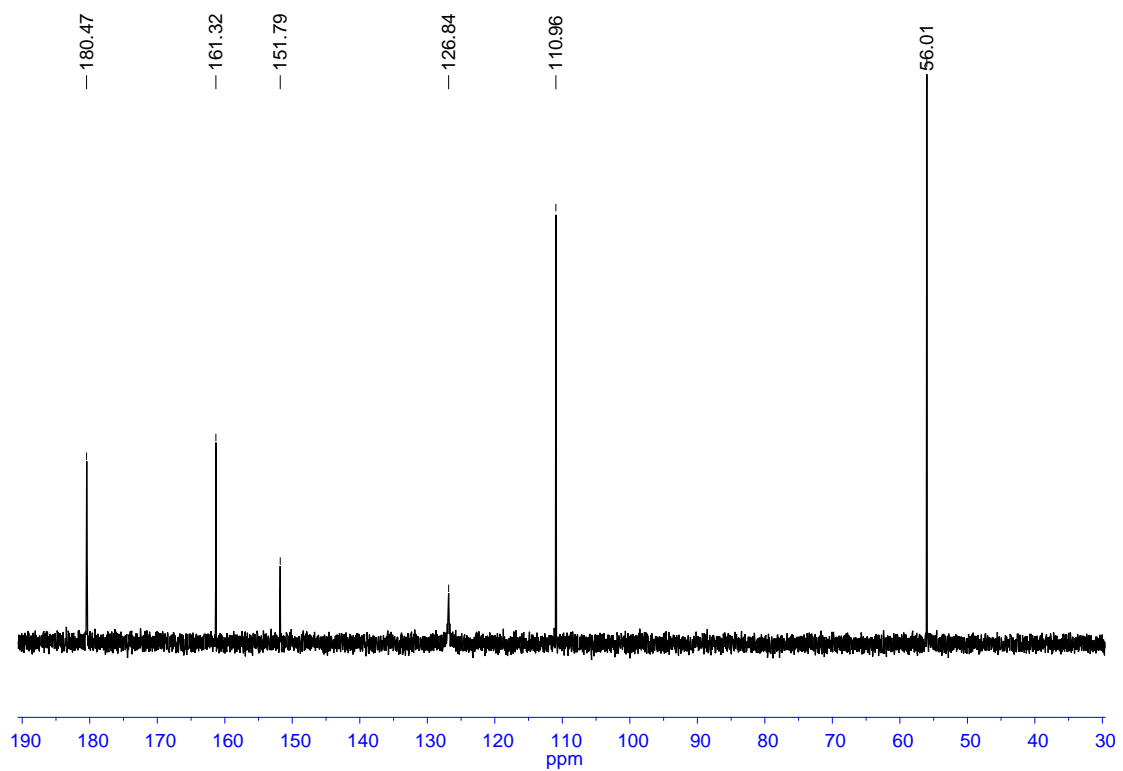


Figure S11. ¹³C {¹H} NMR of 5-hydroxymethylfurfural in D₂O.

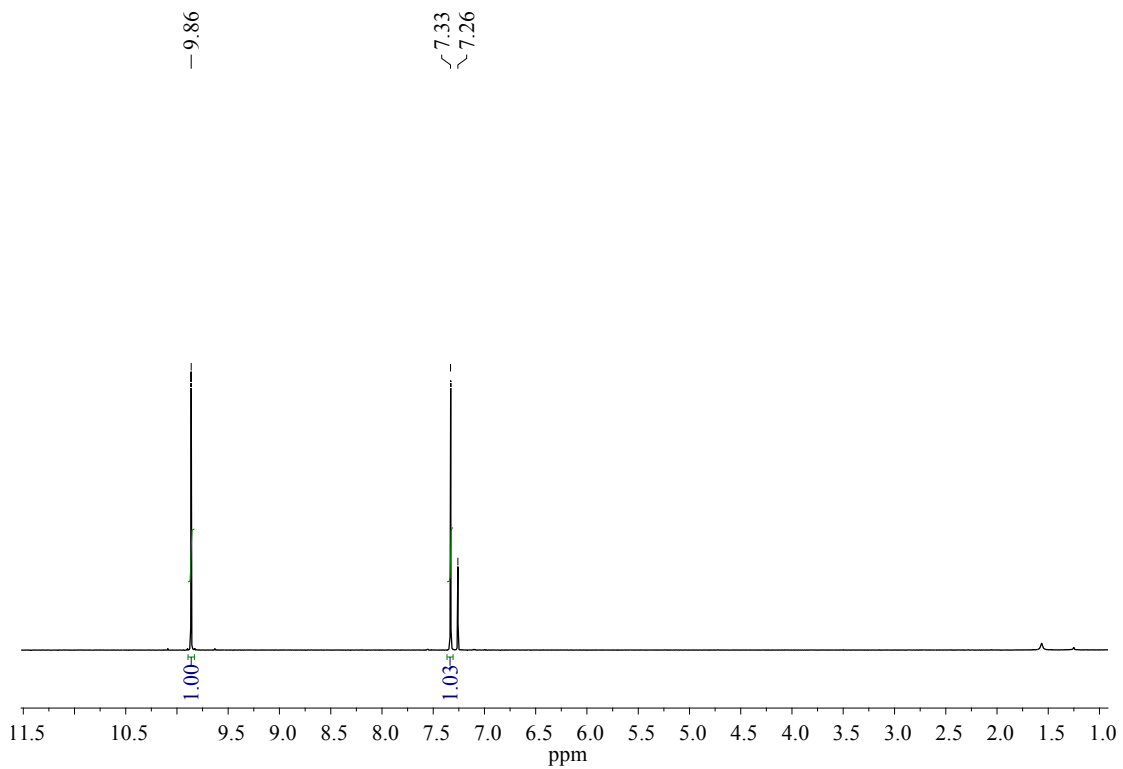


Figure S12. ¹H NMR of 2,5-diformylfuran in CDCl₃.

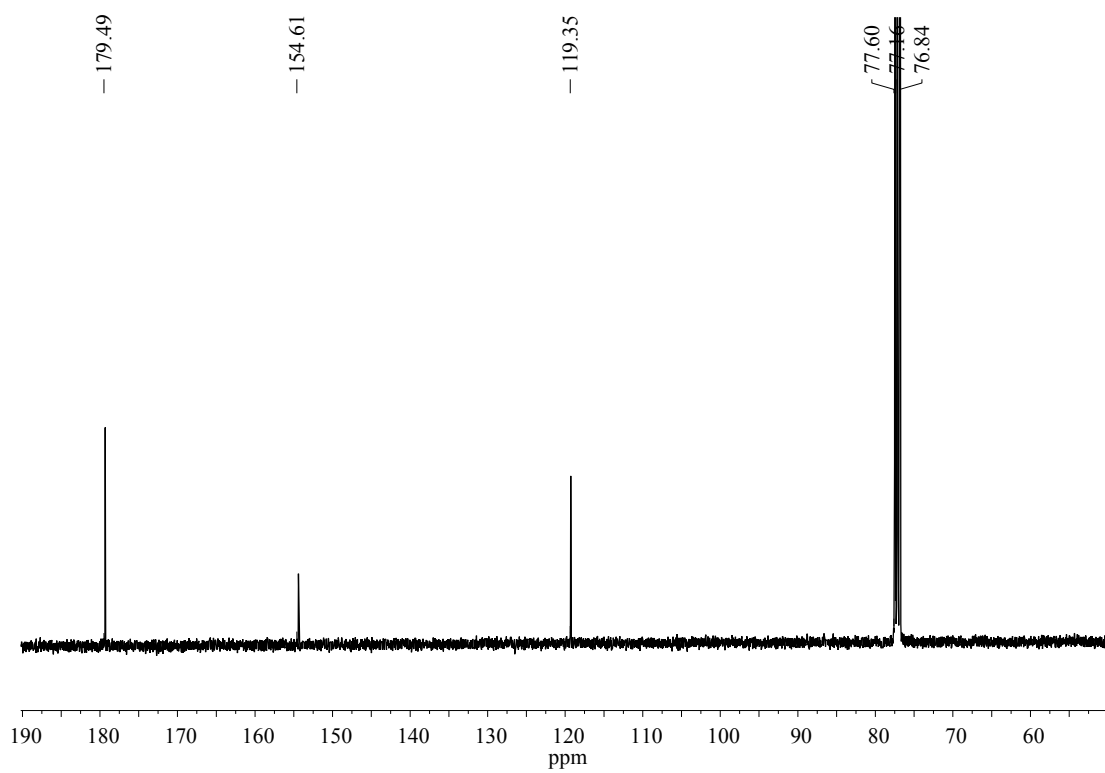


Figure S13. ¹³C {¹H} NMR of 2,5-diformylfuran in CDCl₃.