Supporting information

Synthesis of 5-hydroxymethylfurfural from monosaccharides catalyzed by superacid VNU-11-SO_4 in [Emim]Cl ionic liquid

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Table of Contents

Section S1: Materials and General Methods

Materials

1,3,5-benzenetricarboxylic acid (H_3BTC, purity > 95%), hafnium chloride ($HfCl_4$, purity >98%), hydrofluoric acid (HF, 48 wt% in water), anhydrous chloroform a with amylenes as stabilizer ($CHCl_3$, purity > 99%), were obtained from Sigma-Aldrich Chemical Company. *N,N*-dimethylformamide (DMF, purity > 99%), choline chloride (97%), [EMIM]Cl (99%), ethylene glycol (99%), phenol (99%), zinc chloride (99%) were obtained from Acros Organics. Formic acid (HCOOH, purity > 98 and silica gel 230–400 mesh for flash chromatography, TLC plates (silica gel 60 F254), anhydrous dichloromethane (CH_2Cl_2, 99%), anhydrous ethyl acetate (EtOAc, purity ≥ 99%), acetone, and n-hexane (purity ≥ 99.5%) were obtained from Merck. Deuterated solvents, $CDCl_3$, acetone-d_6 and DMSO-d_6, were purchased from Cambridge Isotope Laboratories (Andover, MA). Ethyl acetate (99%), hexane (98%), D-glucose (99%, D-fructose (99%) were obtained from Fisher. All chemicals were used without further purification.

Methanol, acetonitrile from J.T.Baker (HPLC grade). Sulfuric acid (95-97 %) from Merck. HMF (99 %) was obtained from Aldrich. The water was purified with a water purification system (Smart2pure – Thermo Scientific).

General methods

Powder X-ray diffraction (PXRD) patterns were recorded using a D8 Advance diffractometer equipped with a LYNXEYE detector (Bragg-Brentano geometry, Cu Kα radiation λ = 1.54056 Å. Fourier transform infrared (FT-IR) spectra were measured on a Bruker E400 FT-IR spectrometer using potassium bromide pellets. Low-pressure N_2 adsorption measurements were carried out on a Quantachrome Autosorb iQ volumetric gas adsorption analyzer. A liquid N_2 bath was used for measurements at 77 K. Helium was used as an estimation of dead space. Ultrahigh-purity-grade N_2, and He (99.999% purity) were used throughout adsorption experiments. Solution NMR spectra were acquired on a Bruker Advance-500 MHz NMR spectrometer. ICP-MS analyses were performed on a PerkinElmer NexION 350X. HPLC analyses of HMF were recorded on Agilent Technologies 1260 Infinity high-performance liquid chromatography InertSustain C18 (4.6 x 150 mm) column, the size of particles is 5 μm, equipped with a UV photodiode array detector. Fructose conversion was analyzed by Shimadzu LC-20ADXR high-performance liquid chromatography with InertSustain NH2 (4.6 × 250 mm) column, the size of particles is 5 μm,

equipped with an evaporative light scattering detector – ELSD Alltech 3300: temperature 90 °C, air flow 2.5 L/min, gain 2. A combination of CH_3CN (80%) and H_2O (20%) was used as the mobile phase at a flow rate of 1.0 mL min^{-1}. HRMS (ESI) data were collected using Sciex X500R QTOF.

Section S2. Preparation of MOF

MOFs were synthesized using literature methods and characterization data were in good agreement with those previously reported.

Microcrystalline powder sample of VNU-11: A mixture of H_3BTC (2.50 mmol, 537 mg) and $HfOCl_2 \cdot 8H_2O$ (7.50 mmol, 3.10 g) were dissolved in DMF/formic acid (160 mL/160 mL) and placed in a 500 mL screw-capped glass jar, which was heated to 120 °C for three days. A white precipitate was collected by filtration and washed three times with 100 mL of fresh DMF and immersed in 100 mL DMF for three days, during which time the DMF was replaced three times per day. The DMF-exchanged compound was filtrated off and immersed in 100 mL of water for three days, during which time the water was replaced three times per day. Water exchanged material was then immersed in 100 mL of anhydrous acetone for three days, during which time the acetone was replaced three times per day. The acetone-exchanged sample was then evacuated at room temperature for 24 h and at 150 °C for 24 h to yield activated sample (Yield: 2.30 g, 74% based on $HfOCl_2 \cdot 8H_2O$).

Microcrystalline powder sample of VNU-11-SO_4: Activated VNU-11 microcrystalline powder (200 mg, 0.109 mmol) was immersed in 20 mL of 0.1 M sulfuric acid (2.00 mmol) for 24 h during which time the mixture was stirred about once every two hours. The solid material was thoroughly washed with deionized water (3 x 20 mL per day for three days total), quickly exchanged with 5 x 20 mL anhydrous acetone. To obtain guest-free material, VNU-11-SO_4 was immersed in anhydrous chloroform (3 x 20 mL per day over a total of three days). The solvent exchanged sample was activated under vacuum for 24 h at room temperature and 24 h at 150 °C to get activated VNU-11-SO_4 (Yield 195 mg).

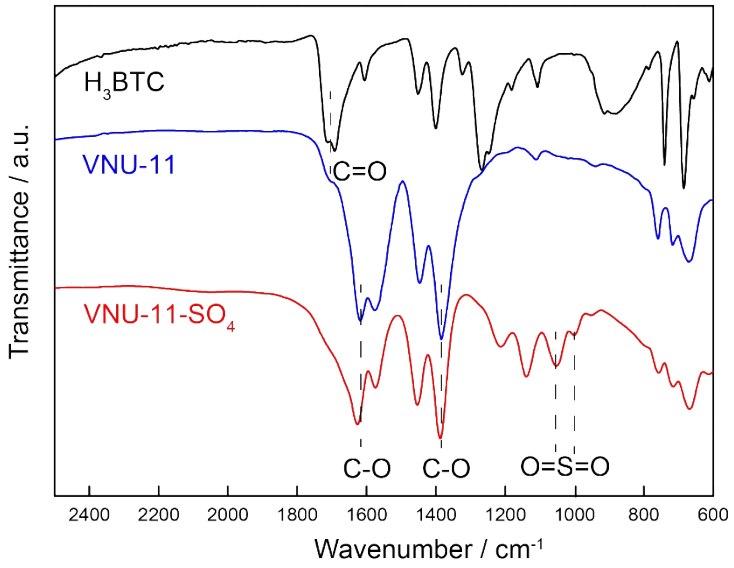

Figure S1. FT-IR spectra of the activated of VNU-11 and VNU-11-SO_4 compound

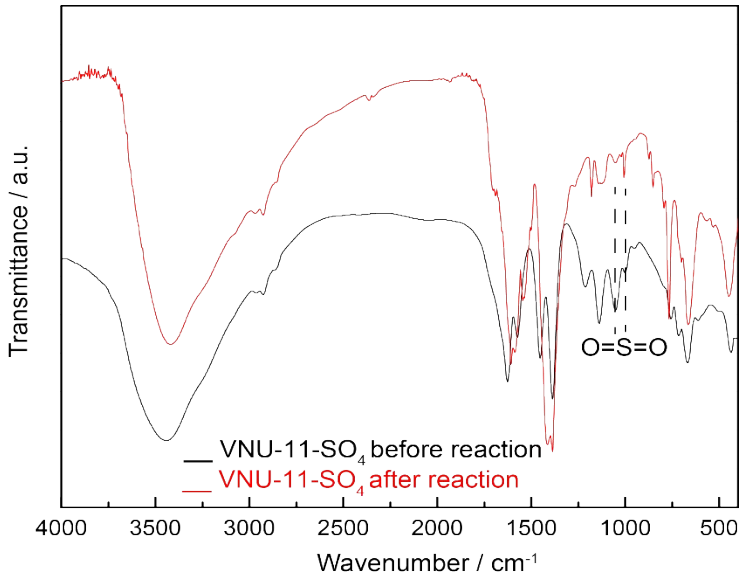

Figure S2. Infrared spectra of VNU-11-P-SO_4 before (black) and after (red) synthesis of HMF

Section S3. Preparation of deep eutectic solvent

Deep eutectic solvent between choline chloride and phenol

The amount of choline chloride and phenol was carried out at a 1:4 ratio. The reaction was heated by a magnetic stirrer at 110 ^{o}C for 2 h until a homogeneous colorless liquid was formed, which was used directly for the reactions without purification.

Deep eutectic solvent between choline chloride and ethylene glycol

The amount of choline chloride and ethylene glycol was carried out at a 1:2 ratio. The reaction was heated by magnetic stirrer at 110 ^{o}C for 2 h until a homogeneous colorless liquid was formed, which was used directly for the reactions without purification.

Section S4. Catalytic study

Building a standard curve of HMF

30 mg of HMF was dissolved in 3 mL of water to obtain the solution having 10000 ppm concentration. The obtained solution was diluted to the standard solution having 1000 ppm and 50 ppm concentration. Determining the concentration of HMF in experimental samples: 2 mL of distilled water was added to dissolve the sample in the vial. The sample was filtered by 0.45 µm membrane then the obtained solution was moved to 1.5 mL HPLC vial and analyzed by HPLC system at λ_{max} = 210 nm, λ_{max} = 285 nm. After that, standard samples were analyzed by HPLC system at λ_{max} = 210 nm, λ_{max} = 285 nm.

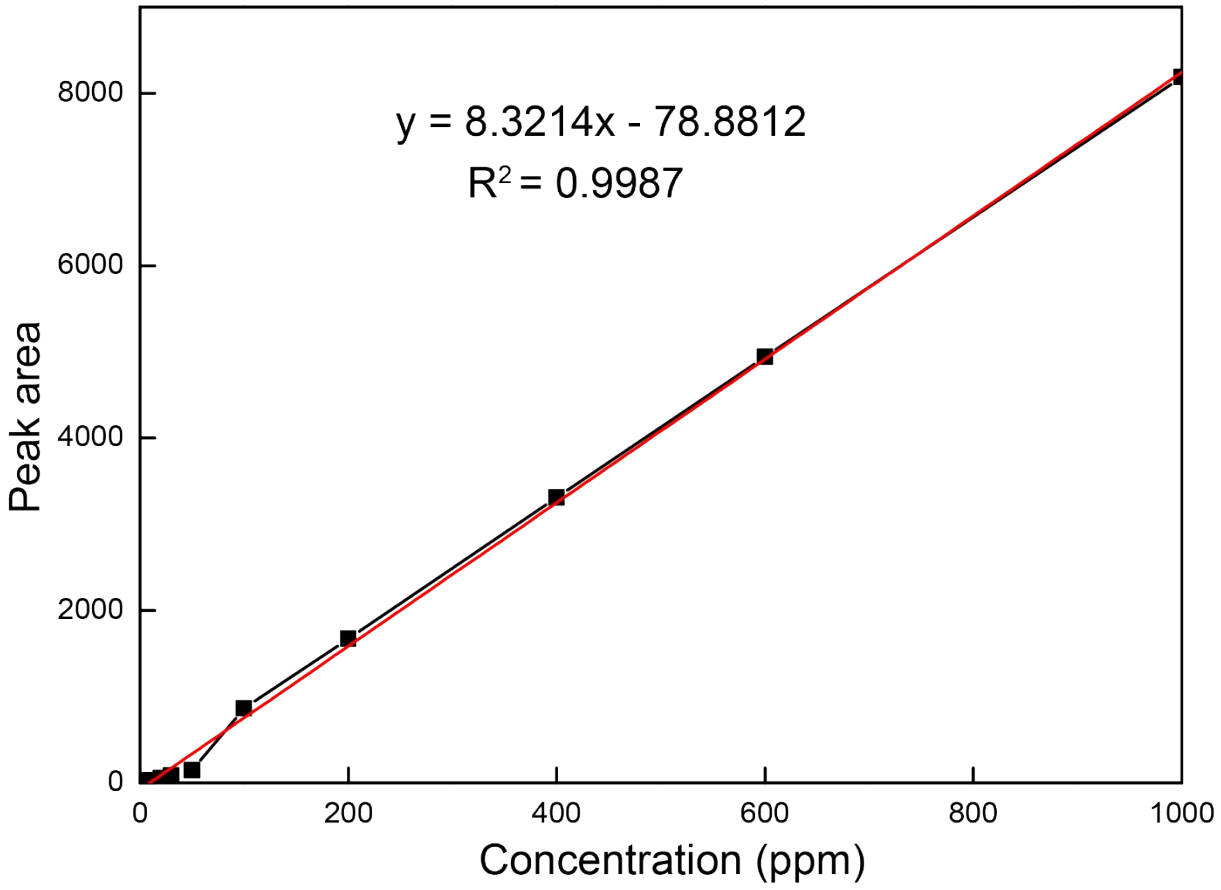

Figure S3. Standard concentration of HMF

Building a standard curve of glucose conversion

30 mg of glucose was dissolved in 3 mL of water to obtain the solution having 10000 ppm concentration. The obtained solution was diluted to a standard solution having 1000 ppm and 50 ppm concentration. It is the same as the method of building standard curve of HMF. Determining the glucose conversion in experimental samples: 5 mL of distilled water was added to dissolve sample. Next, distilled water was added to 10 mL of solution. The sample was filtered by 0.45 µm membrane then the obtained solution was moved to 1.5 mL HPLC vial.

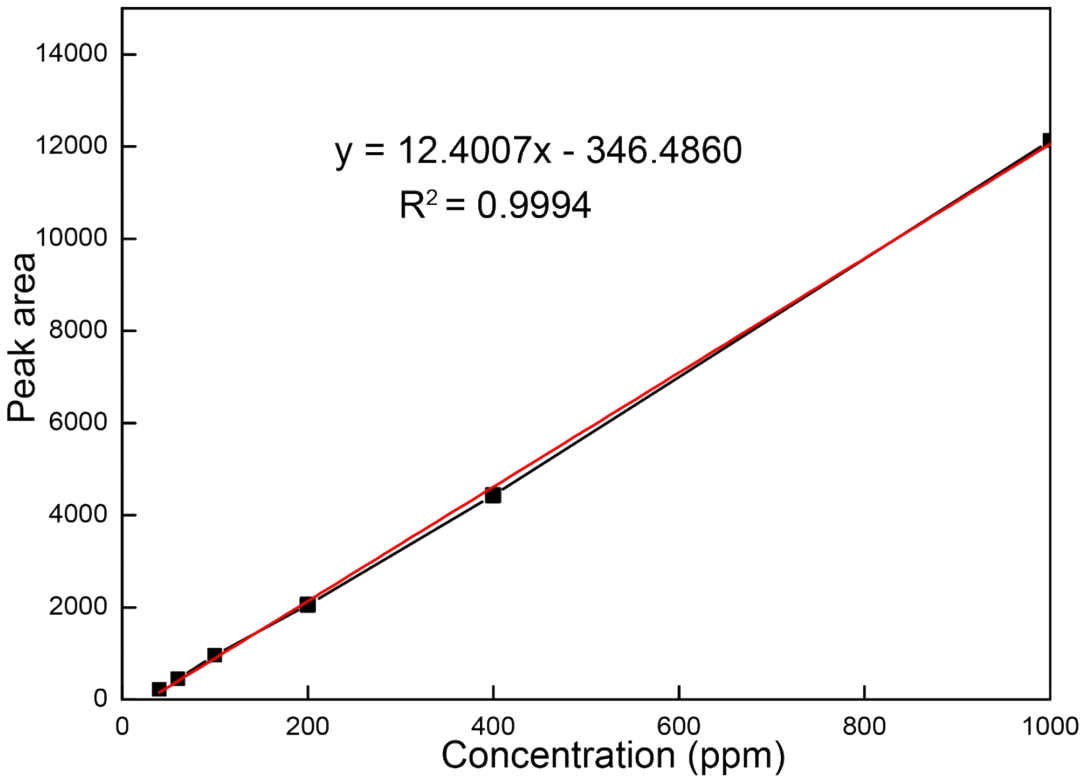

Figure S4. Standard concentration of standard glucose solutions

Building a standard curve of Fructose conversion

It is the same as the method of building standard curve of glucose conversion. Determining the fructose conversion in experimental samples: 5 mL of distilled water was added to dissolve

sample. Next, distilled water was added to 10 mL of solution. The sample was filtered by 0.45 μm membrane; then the obtained solution was moved to 1.5 mL HPLC vial.

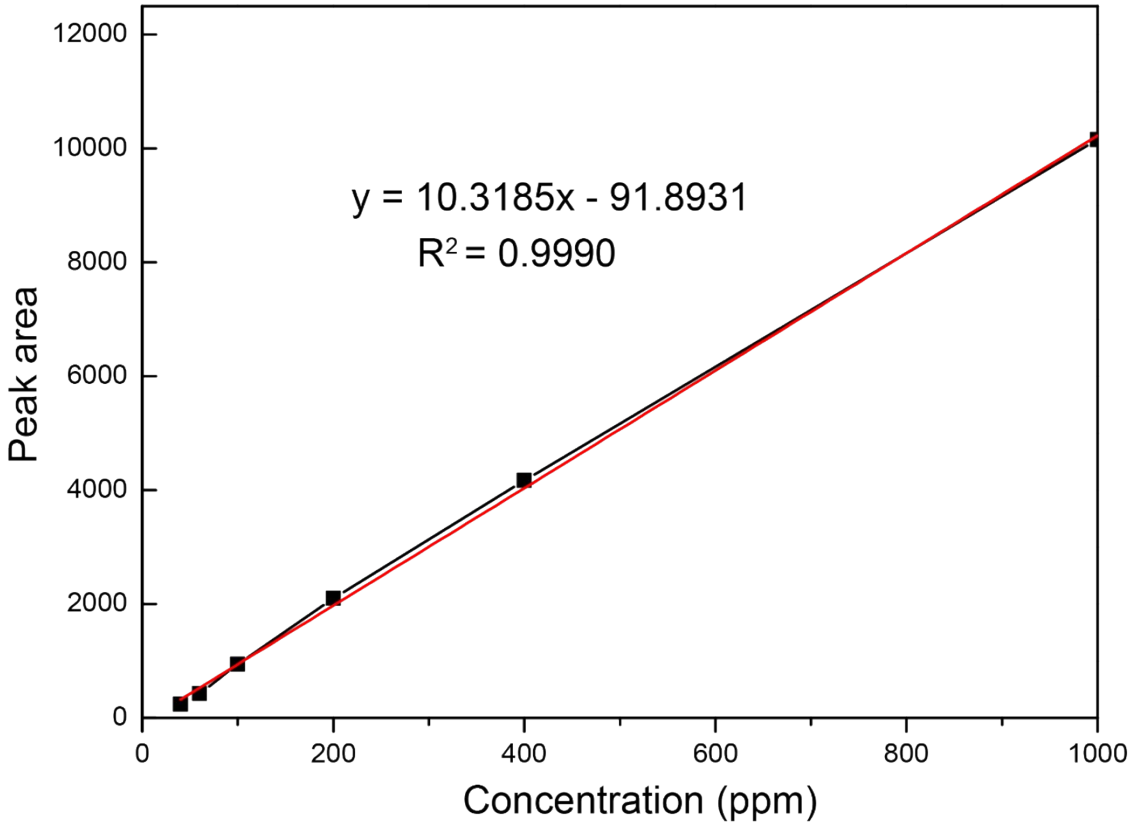

Figure S5. Standard concentration of standard Fructose solutions

Procedure for the synthesis of HMF

In a typical experiment, Glucose or Fructose (1 mmol) was dissolved in [EMIM]Cl (6 mmol) and then VNU-11-P-SO_4 catalyst (20 mg) was added. The flask was heated to 110 ^oC in a magnetic stirrer with an oil bath, and conditions were maintained for 24 h. Samples were taken from the reaction mixture at specified times for HPLC analysis to determine HMF yield and fructose conversion.

After finishing the reaction, a mixture including HMF was extracted from the reaction mixture with ethyl acetate. HMF can be highly soluble in both water and organic solvents so it is moved absolutely into the water phase, while the remaining impurities are kept in an organic solvent. Next, HMF was extracted again from the reaction mixture with ethyl acetate. HMF will be

transferred into ethyl acetate so that excessive fructose is retained in the water. Pure HMF is achieved after evaporating Ethyl acetate. HMF obtained were characterized by ^{1}H NMR method and have been identified by the comparison of the spectral data with those reported.

Distilled water was added to the flask after extracting HMF. Shaking the flask to dissolve the remaining mixture. Next, the insoluble material was filtered to separate the catalyst. The catalyst was washed with distilled water and reactivated in the vacuum at 150 ^{o}C in 12 h. The obtained catalyst was characterized by PXRD, IR spectroscopy and identified by the comparison of the spectral data with those reported.

Analysis of the products

The yield of HMF were determined by using an Agilent Technologies 1260 Infinity high performance liquid chromatography with photodiode array detector (HPLC – PAD). The analytical column applied is InertSustain C18 (5 μm, 4.6 x 150 mm). The mobile phase was a mixture of A methanol and B 2.5 mM sulfuric acid aqueous solution at 0.7 mL min -1 in a 25 min, gradient as follows: 0 – 2.50 min, 100 - 100% B; 2.50 - 2.51 min, 100 - 85% B; 2.51 – 17.00 min, 85 - 85% B; 17.00 – 17.01 min, 85 -100 % B; 17.01 – 25.00 min, 100 -100 % B. For the analysis of fructose and glucose conversion, a Shimadzu LC-20ADXR high performance liquid chromatography with evaporative light scattering detector – ELSD Alltech 3300 (HPLC–ELSD) and an InertSustain NH_2 (5 μm, 4.6 x 250 mm) column. Operating conditions: Pump: isocratic, flowrate = 1.0 mL/min; Injection volume: 10 μL; Mobile Phase: ACN (80%) and H2O (20%); ELSD: temperature 90 ^{o}C, air flow 2.5 L/min, gain 2). The fructose conversion and HMF yield were calculated based on external standard curves constructed with authentic standards.

HRMS (ESI) analysis was used to confirm the exact mass of HMF. The system conditions were set as follows: Ion source gas 1: 40 psi; Ion source gas 2: 60 psi; Curtain gas: 30 psi; CAD gas: 7 psi; Source temperature: 500oC; Experiment: IDA (Information Dependent Acquisition Scanning); Spray voltage: 500 V (Positive) and -500 V (Negative); Declustering potential (DP): 80 V; Collison energy (CE): 10 V. The LC paramaters: inject volume: 5 μL; The mobile phase was A conc.: 40% (MeOH) and B conc.: 60% (HCOOH 0.1%, HCOONH4 5mM); Flow: 0.3 ml/min.

Section S5: NMR, HRMS, HPLC data and spectra

5- Hydroxylmethylfurfural

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 6.51 (d, *J* = 3.5 Hz 1H), 4.71 (s, 2H).

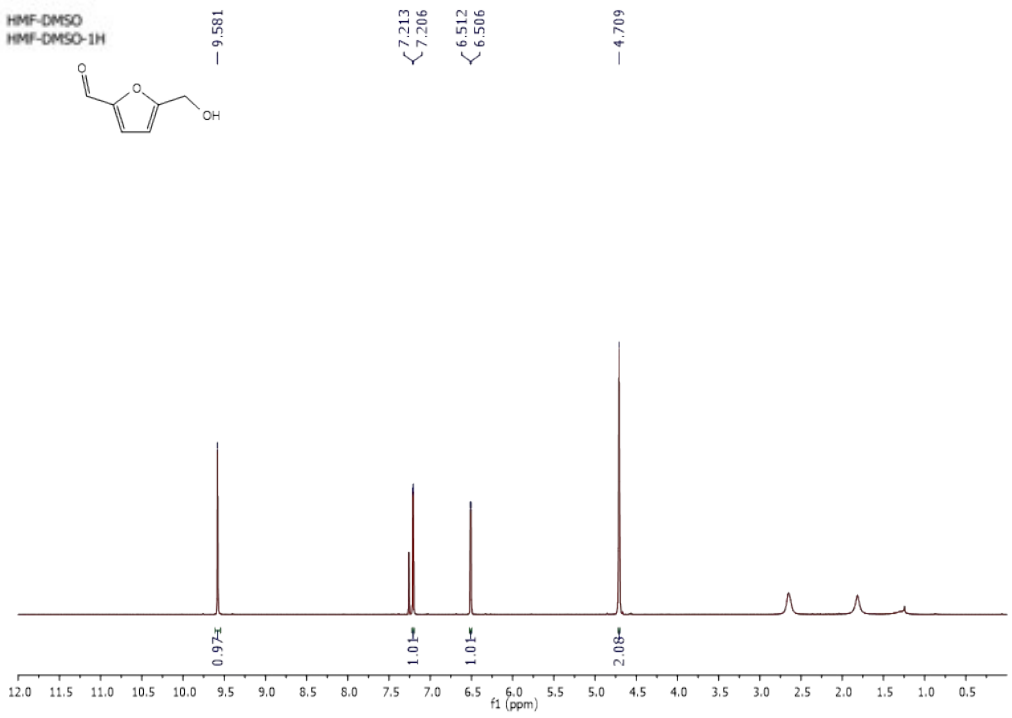

Figure S6. ^{1}H spectrum of 5-HMF

HRMS (ESI) m/z calcd for [M]+ C6H7O3 127.0395, found 127.0379.

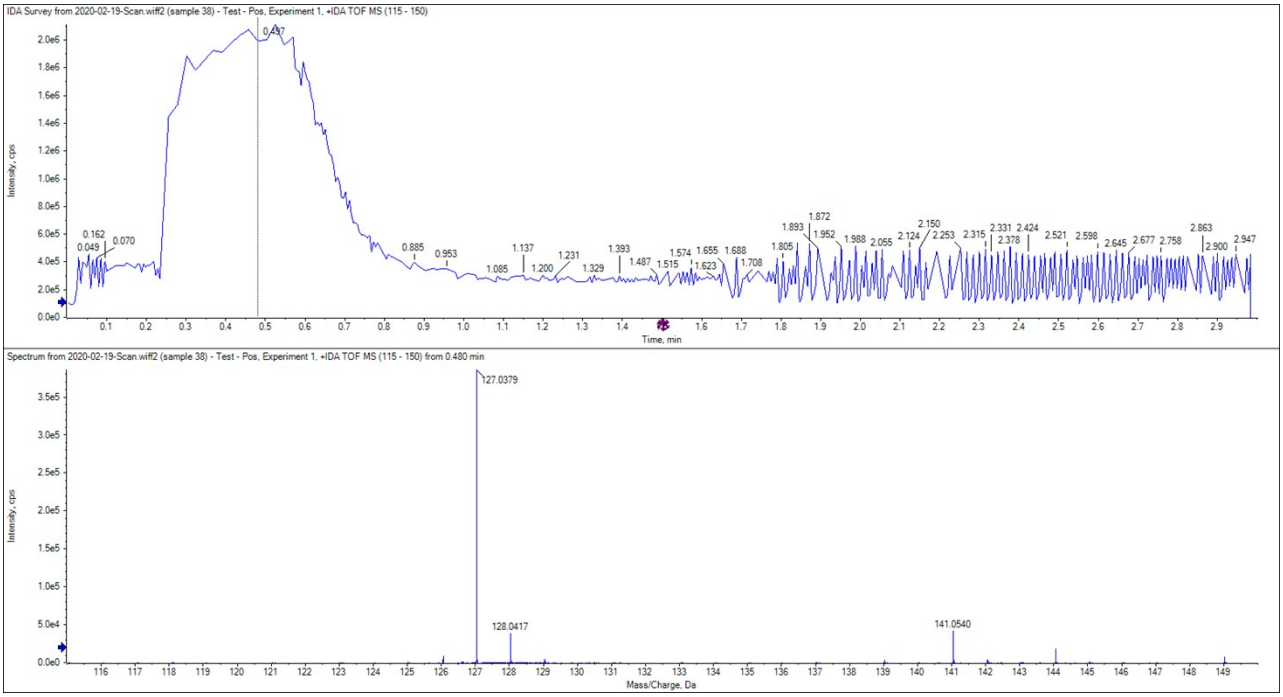

Figure S7.HRMS (ESI) of 5-HMF

Chromatography of HMF

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                                                    Inj Volume : 5.000 µl
    Different Inj Volume from Sequence !     Actual Inj Volume : 10.000 µl
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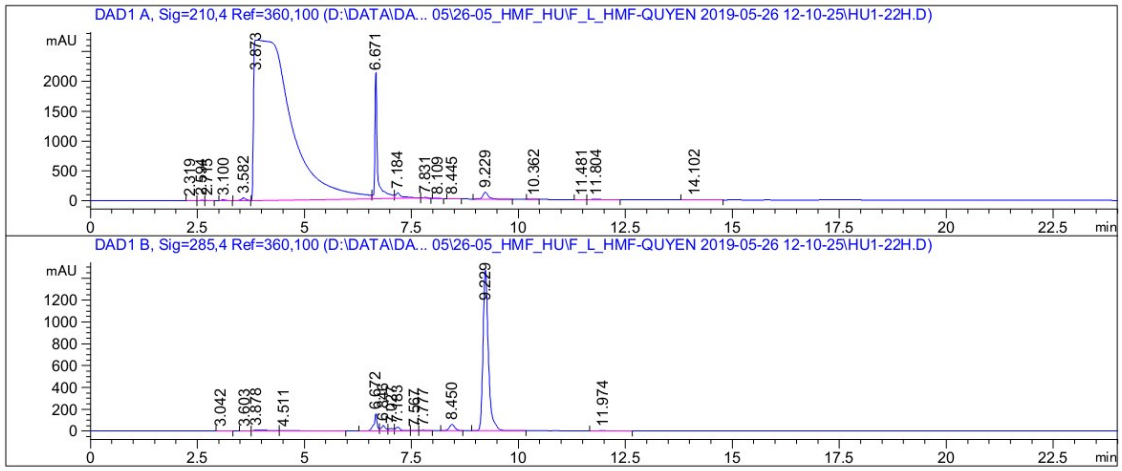


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    Dilution:                     :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

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    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [mAU*s]                [ppm]
    -------|------|----------|----------|----------|--|------------------
      9.229 BB     1105.60864 1.27825e-1  141.32465    HMF

    Totals :                              141.32465


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Chromatography of Glucose

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Acquired by : Long - Huong
Sample Name : Hu20-6h
Vail # : 22
Injection Volume : 10 uL
Data File Name : Hu20-6h__10.lcd
Method File Name : Duong ruou-Duong tu nhien.lcm
Data Acquired : 6/24/2019

Chromatogram
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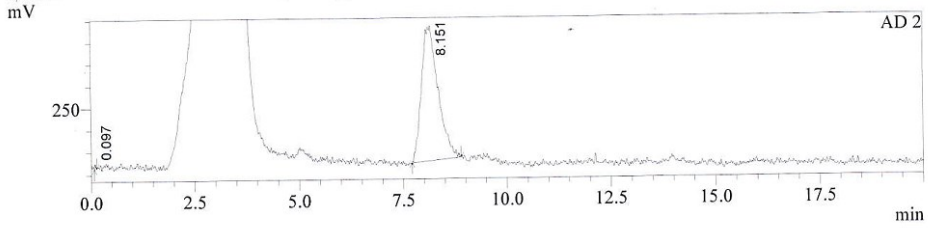
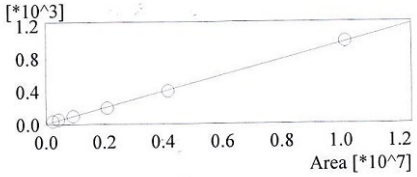


1 AD 2/

Quantitative Results
AD2

Name	Ret. Time	Area	Conc.
Fructose	0.000	0	0.000
Glucose	8.151	8549373	717.135

Name : Fructose
Function : f(x)=9.68401e-005*x+9.12482
Rr1=0.9996235 Rr2=0.9992471
MeanRF:0.000117744 RFSD:3.05249e-005 RFRSD:25.9249



#	Conc. (Ratio)	MeanArea	Area
1	40.000	236027.8	236028
2	60.000	427127.4	427127
3	100.000	937680.1	937680
4	200.000	2096006.7	2096007
5	400.000	4165866.8	4165867
7	1000.000	10159282.8	10159283

Name : Glucose
Function : f(x)=8.05958e-005*x+28.0907
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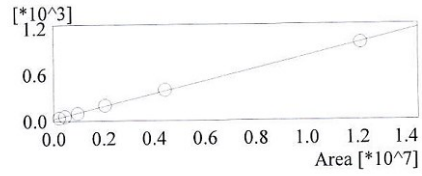

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3	100.000	958276.7	958277
4	200.000	2053186.9	2053187
5	400.000	4431582.8	4431583
7	1000.000	12130896.4	12130896

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Chromatography of Fructose

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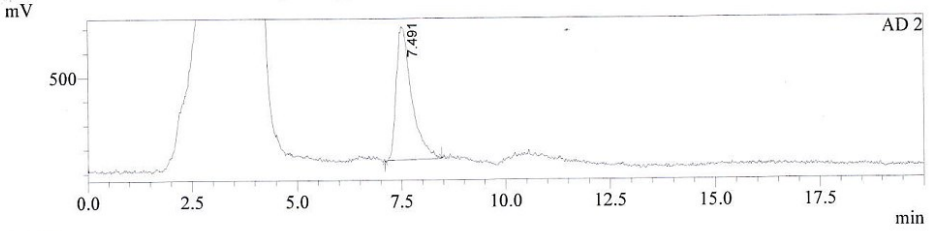
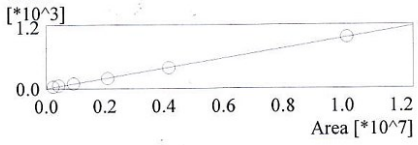


1 AD 2/

Quantitative Results
AD2

Name	Ret. Time	Area	Conc.
Fructose	7.491	14164565	1380.822
Glucose	0.000	0	0.000

Name : Fructose
Function : f(x)=9.68401e-005*x+9.12482
Rr1=0.9996235 Rr2=0.9992471
MeanRF:0.000117744 RFSD:3.05249e-005 RFRSD:25.9249



#	Conc. (Ratio)	MeanArea	Area
1	40.000	236027.8	236028
2	60.000	427127.4	427127
3	100.000	937680.1	937680
4	200.000	2096006.7	2096007
5	400.000	4165866.8	4165867

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