

Direct Transformation of Cellulose into 5-Hydroxymethyl-2-furfural using a Combination of Metal Chlorides in Imidazolium Ionic Liquid

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Supplementary Information

1. Experimental Procedures

Materials and instruments: All chemicals including cellulose (microcrystalline), 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), all metal chlorides, 5-hydroxymethyl-2-furfural (HMF, for authentic reagent) were purchased from Sigma-Aldrich (USA). All reagents were directly used without further purification. Leed (*Phragmites communis*, Trin.) was generously presented as a gift from Rural Development Administration of Korea. CH₃CN for HPLC solvents and general solvents such as methanol, diethyl ether, dichloromethane were obtained from Fisher Scientific (USA) and Samchun chemicals (Korea), respectively. Parallel reactions were carried out under identical conditions using Carousel 12 Plus Reaction Station (Radley).

Reactions were analyzed by HPLC (Pro Star 310, Varian) equipped with auto sampler (Model No. 410, Varian), detector (Model No. 310 for UV, Varian), C₁₈ reverse-phase column (Allure C18 5 μm 250×4.6 mm) and processed by Galaxie Chromatography Data

System software. Also, reactions were monitored by HPLC (Agilent 1200 series) equipped with auto sampler (G1329A, Agilent), column temperature controller (G1316A, Agilent), detector (G1315D for UV and G1362A for RID, Agilent) using ion-exclusion column (Bio-Rad Aminex HPX-87H 300×7.8 mm) and processed by ChemStation software. Synthetic HMF was characterized by HPLC and confirmed by ¹H and ¹³C FT-NMR (400 MHz, JNM-AL400, Jeol) processed by Delta program (ver. 4.3.6) and GC-MS (GCMS-QP5050, Shimadzu) processed by CLASS-5000 software. Quantification was done with standard curves generated from commercially available authentic standards.

Parallel reaction of HMF synthesis from cellulose for metal chloride screening: In the 12 tubular reactors for Carousel 12 Plus Reaction Station were individually placed metal chloride(s) to be screened (10 mol% of cellulose) and [EMIM]Cl (500 mg). After all reactors were installed into Carousel 12 Plus Reaction Station, the mixtures were heated to 90 °C and stirred at 700 rpm for 20 min. Then they were cooled to room temperature and cellulose (50 mg) was added to each reactor. The reaction mixtures were heated to the designated temperature and stirred for the designated time. Finally, all reaction mixtures were cooled to room temperature, diluted with deionized water for HPLC analysis.

Time course experiment of HMF synthesis from cellulose: In the 250 mL round-bottomed flask were placed CrCl₂ and RuCl₃ (10 mol % of cellulose, 8 mol% of CrCl₂ + 2 mol% of RuCl₃) and [EMIM]Cl (40 g), the mixture was heated to 90 °C and stirred for 40 min. The mixture was cooled to room temperature and cellulose (4 g) was added to the mixture. Then it was re-heated to 120 °C and stirred in a temperature-controlled oil bath with magnetic stirring. An aliquot of reaction mixture was pipetted out at intervals (20 min, 1 h, 2 h, 3 h, 4 h) and diluted with deionized water (×10). The solution was centrifuged at 10,000 rpm for 5 min and the upper clear liquid was pipetted off and diluted with deionized water (×10). The samples were analyzed using HPLC.

HMF and furfural synthesis from lignocellulosic raw material (reed): In the 6 mL vials were placed CrCl₂ and RuCl₃ (10 mol % of cellulose, 8 mol% of CrCl₂ + 2 mol% of RuCl₃) and [EMIM]Cl (500 mg) and the mixture was heated to 90 °C and stirred for 20 min. The mixture was cooled to room temperature and reed (50 mg) was added to the mixture. Then it was re-heated to 120 °C and stirred in a temperature-controlled oil bath with magnetic stirring (700 rpm) for 2 h. The resulting mixture were cooled to room temperature, diluted with deionized water for HPLC analysis.

2. HMF Quantification Procedure

Resulting reaction mixture (*ca* 0.5 mL) was diluted with 5 mL of deionized water and the solution was centrifuged at 10,000 rpm for 5 min. Then 100 µL of the upper clear liquid was pipetted off and diluted with deionized water to 1.0 mL for analysis. HMF concentration was measured on a HPLC (Pro Star 310, Varian) (Fig. S1) at 280 nm using standard curve method (HMF concentration *vs* HPCL area) (Fig. S2).

M_{HMF} was calculated as follows,

$$M_{HMF} (\text{mg}) = \text{HMF concentration} (\text{mg/mL}) \times [V_{RM} (\text{mL}) + V_D (\text{mL})] \times DF$$

In which,

V_{RM} is the volume of reaction mixture = *ca* 0.5 mL

V_D is the dilution volume = 5 mL

DF is the dilution factor in second dilution = (1 mL ÷ 100 µL) × 10³ = 10

HMF yield was calculated as follows,

$$\text{HMF Yield (\%)} = [M_{HMF} (\text{mg}) \div MW_{HMF}] \div [M_{CL} (\text{mg}) \div [MW_{GL} - MW_{WT}]] \times 100\%$$

In which,

M_{HMF} is the mass of HMF

M_{CL} is the mass of cellulose

MW_{HMF} is the molecular weight of HMF = 126.11

MW_{GL} is the molecular weight of glucose (monomer of cellulose) = 180.16

MW_{WT} is the molecular weight of water = 18.02

3. Total Reducing Sugar (TRS) Analysis

Into deionized water (500 mL) were added potassium sodium tartrate (182 g), 3, 5-dinitrosalicylic acid (DNS, 6.3 g) and 2 N NaOH (262 mL). After dissolved at 50 °C, phenol (5 g) and sodium sulfite (5 g) were added in the solution and stirred until homogeneous solution. Then the solution was cooled to room temperature and diluted with deionized water to 1000 mL to give the DNS reagent.

A mixture of DNS reagent (0.5 mL) and reaction sample (*ca* 0.5 mL) diluted ($\times 11$) with deionized water (0.5 mL) was stayed at 100 °C for 5 min and then cooled to room temperature. The resulting mixture was diluted with 4 mL of deionized water and absorbance of the mixture was measured by UV spectrophotometer (UVIKONxs, bio-Tek) at 540 nm. The concentration of total reducing sugars was calculated based on a standard curve obtained with glucose (Fig. S7).

The mass of TRS (M_{TRS}) and the yield of TRS were calculated as follows,

$$M_{TRS} \text{ (mg)} = \text{TRS concentration (mg/mL)} \times V_{RM} \text{ (mL)} \times DF$$

$$\text{TRS Yield} = M_{TRS} \div [100 \div [MW_{GL} - MW_{WT}] \div MW_{GL}] \times 100\%$$

In which,

M_{TRS} is the mass of TRS,

V_{RM} is the volume of reaction mixture = *ca* 0.5 mL

DF is the dilution factor = 11

MW_{GL} is the molecular weight of glucose (as monomer of cellulose) = 180.16

MW_{WT} is the molecular weight of water = 18.02

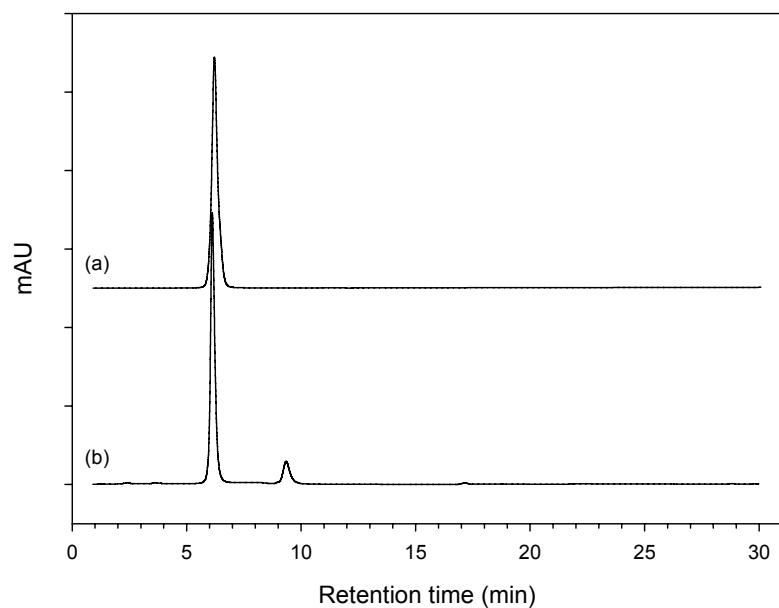


Fig. S1. HPLC chromatograms of (a) authentic sample of HMF and (b) representative reaction mixture of HMF synthesis from cellulose at 280 nm (Allure C18 5 μ m 250 \times 4.6 mm, 0.1% TFA in water/CH₃CN = 100:0 to 0:100 from 5 min to 20 min, 1.0 mL/min, 35 °C).

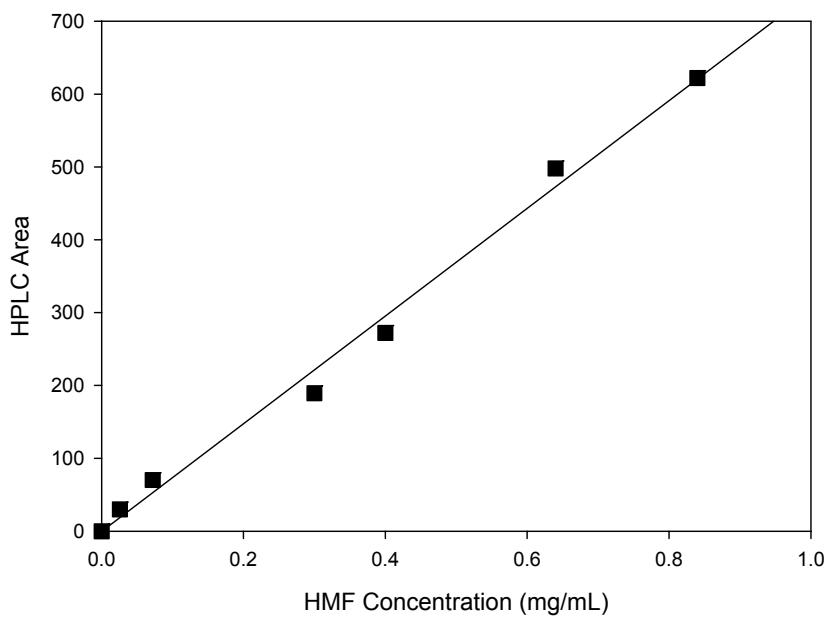


Fig. S2. Standard curve of authentic HMF in H₂O (HPLC area = 738.61 \times HMF concentration (mg/mL), R² = 0.9924).

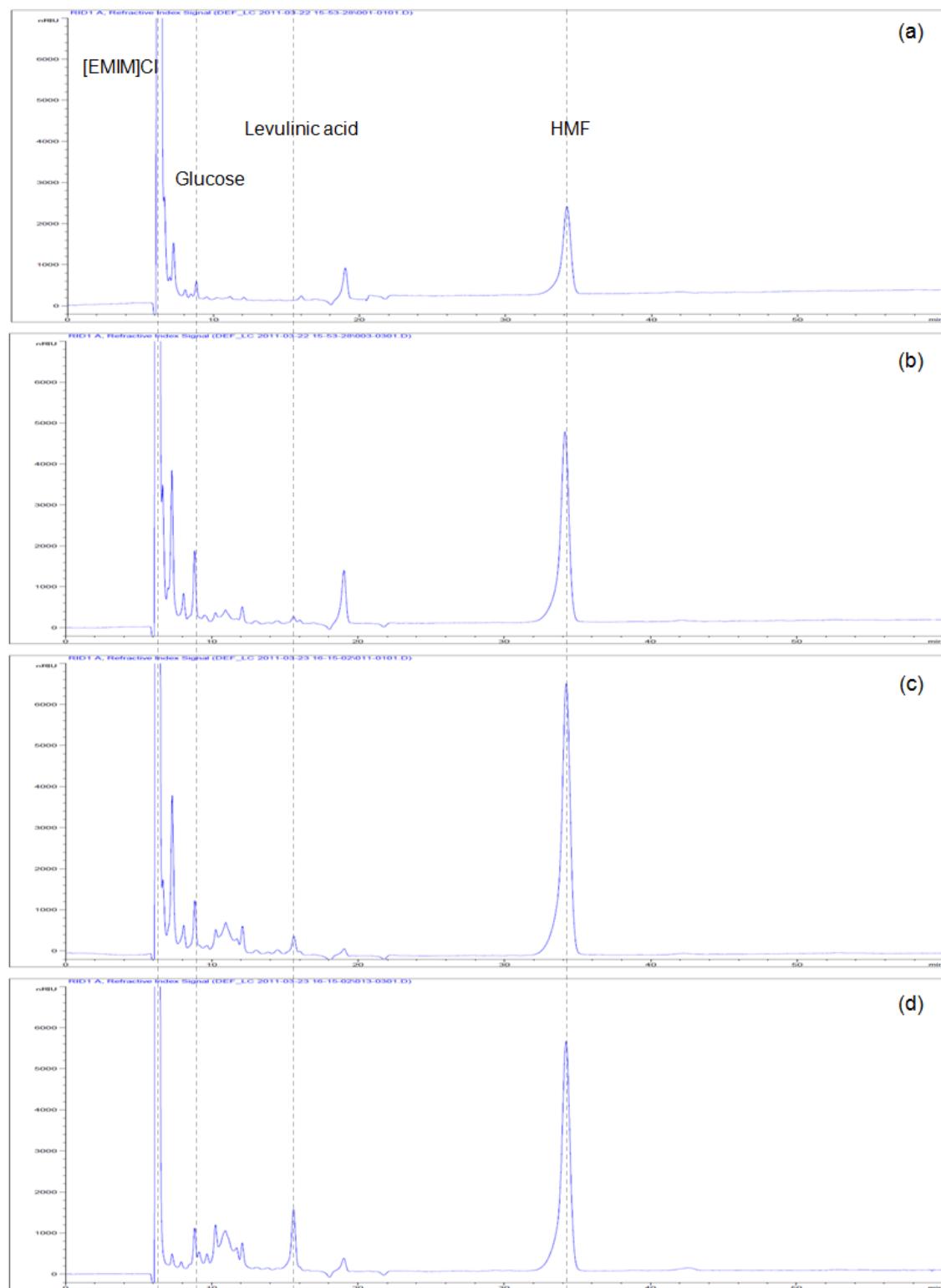


Fig. S3. RI-HPCL traces from direct transformation of cellulose into HMF using Cr/Ru (4:1) in [EMIM]Cl after (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h (Bio-Rad Aminex HPX-87H 300×7.8 mm, 0.05% H₂SO₄ in water, 0.6 mL/min, 65 °C).

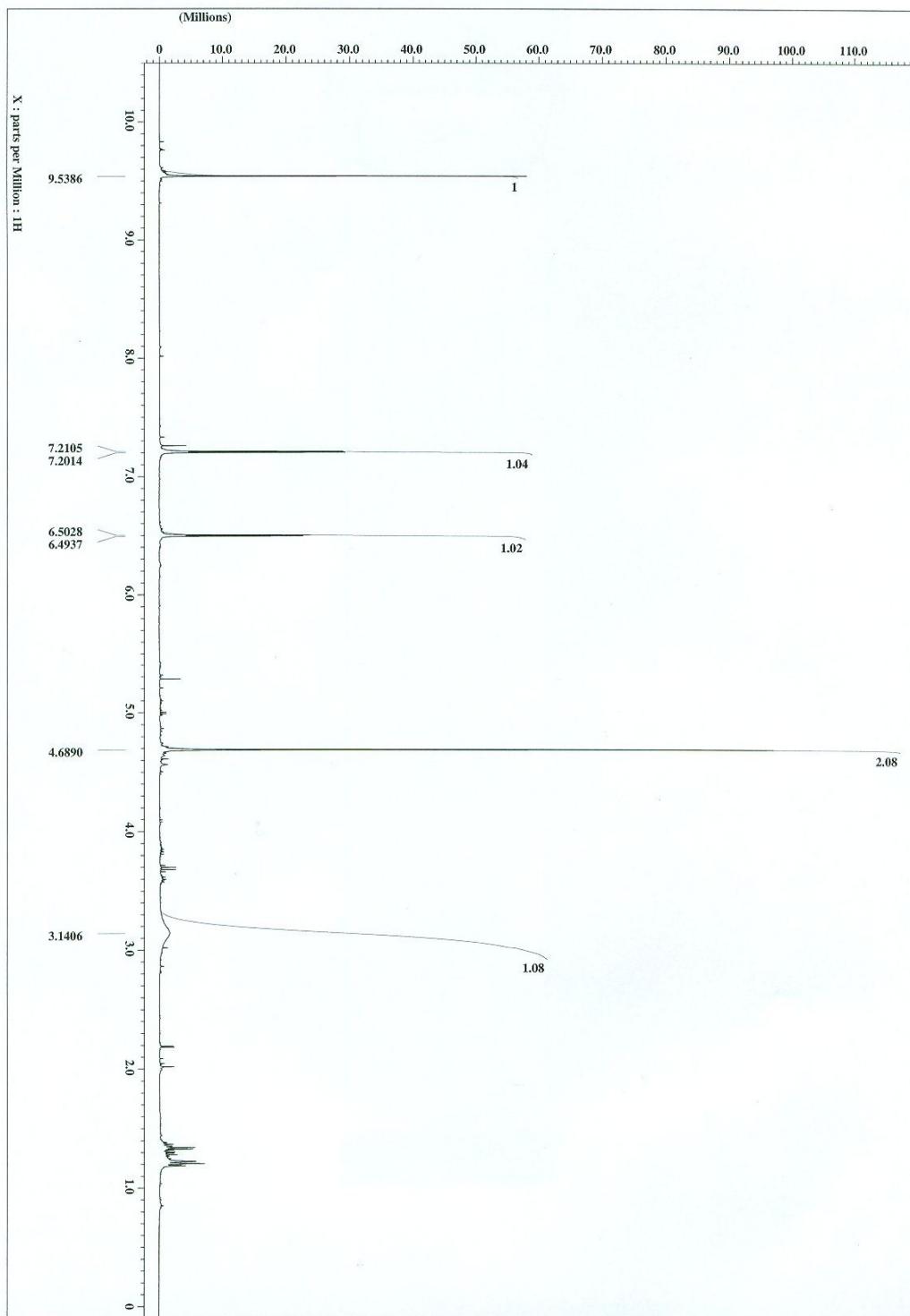


Fig. S4. ¹H NMR spectra of synthetic HMF.

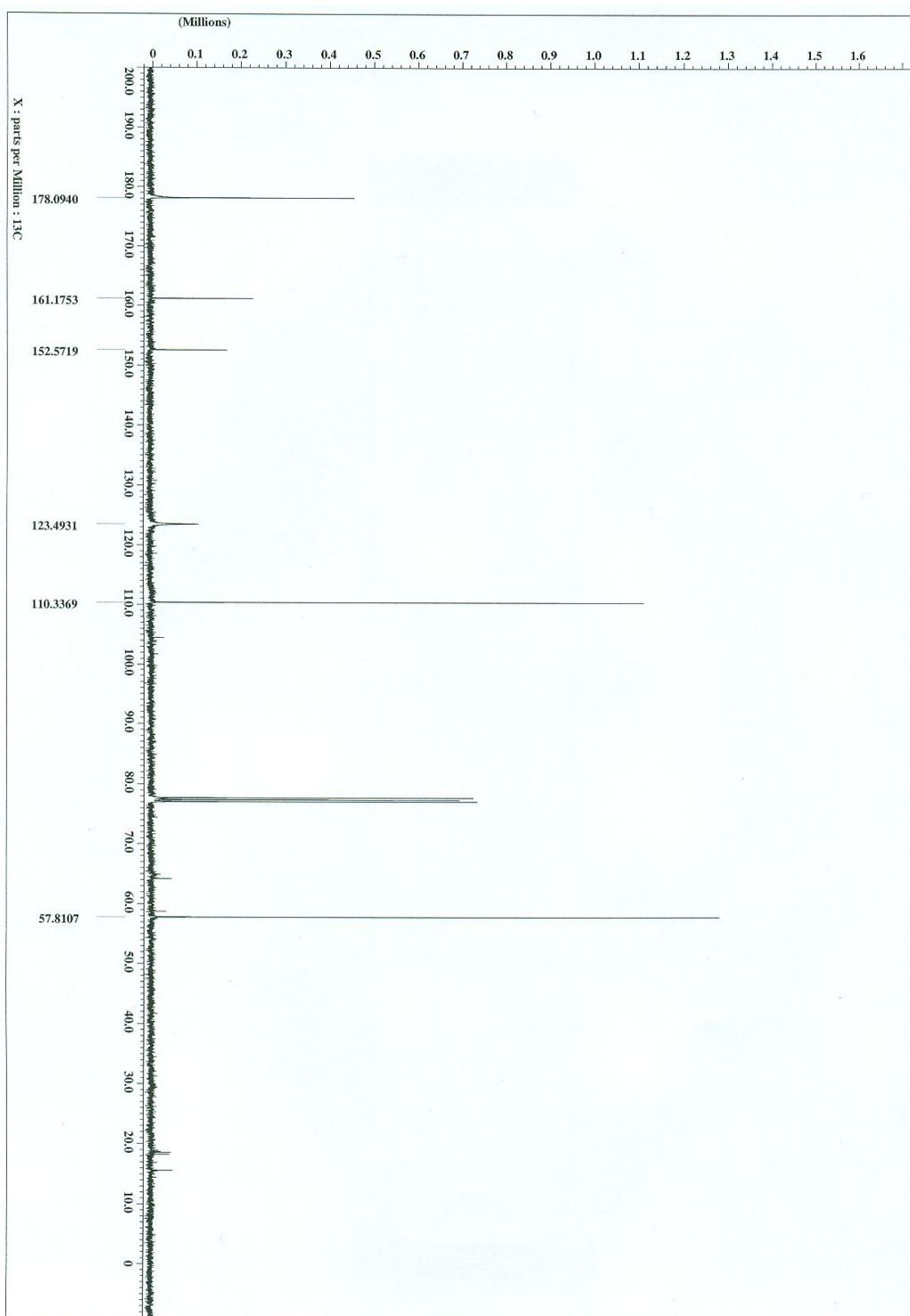
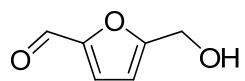


Fig. S5. ¹³C NMR spectra of synthetic HMF.



Chemical Formula: C₆H₆O₃
Molecular Weight: 126.11

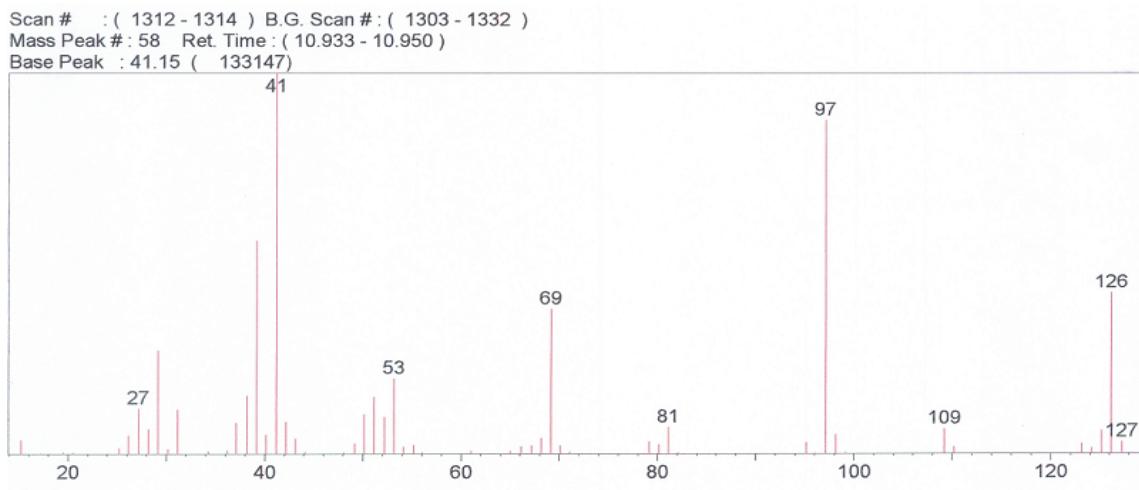


Fig. S6. ESI-MS spectra of synthetic HMF.

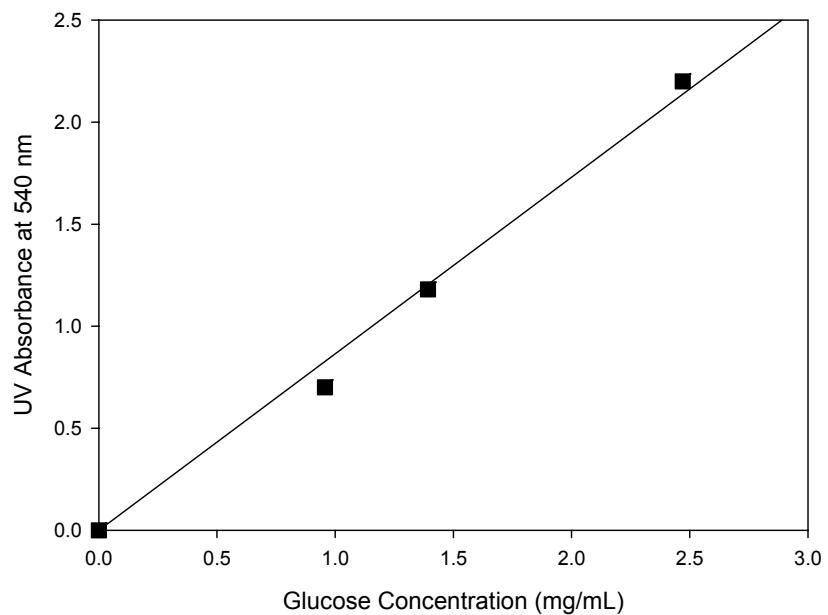


Fig. S7. Standard curve of Glucose in H₂O (UV absorbance at 540 nm = 0.865 × Glucose concentration (mg/mL), R² = 0.9918).