Electronic Supplementary Information

Conversion of Fructose into 5-Hydroxymethylfurfural and Alkyl Levulinates Catalyzed by Sulfonic Acid-Functionalized Carbon Materials

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1. Experimental

Materials:

Unless otherwise stated, all chemicals in this work were commercially available and used without further purification. High-purity multi-walled carbon nanotubes (MWCNTs, OD: 10~20 nm, Length: 10~30 um) were supplied by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (Chengdu, PR China). Carbon nanofibers (CNFs, OD: 150~200 nm, Length: 10~30 um) were purchased from Beijing DK nano technology Co. Ltd. (Beijing, PR China). Sodium *p*-styrenesulfonate was purchased from Fluka. Potassium persulfate, *p*-sulfanilic acid, methyl palmitate, hydrochloric acid, fructose, sucrose, glucose, inulin, furfuryl alcohol, P123 (EO20PO70EO20, M_a = 5800), tetraethylorthosilicate (TEOS), $AlCl_3$, $NaNO_2$, H_3PO_2, were purchased from Aladdin Industrial Inc. and Sinopharm Chemical Reagent Co. Ltd. (Shanghai, PR China).

Characterization techniques:

The HPLC analysis was performed on Shimadzu LC-20AT equipped with an UV/refractive index detector and a Shodex Sugar SH-1011 column (ø8×300 mm). Aqueous solution of H_2SO_4 (0.005 M) was used as the mobile phase at a flow rate of 0.5 mL min^{-1}, and the column temperature was maintained at 50 °C. The amounts of fructose and HMF were calculated based on external standard curves constructed with authentic standards. The GC analysis was performed by Agilent 6890 or Shimadzu 2010 equipped with a flame ionization detector (FID) and a KB-5 capillary column (internal diameter 0.32 mm, 30.0 m×0.32 μm×0.25 μm length 30 m) using nitrogen as the carry gas. The GC-MS analysis was performed by Trace GC-MS 2000 as well as by comparing the retention times to respective standards in GC traces. The operating conditions for GC and GC-MS were as follows: Injector Port Temperature, 260 °C; Column Temperature, Initial temperature 50 °C (2 min), Gradient Rate 30°C min (7 min), Final Temperature 260 °C (3 min), Flow Rate 75 mL min^{-1}. The amounts of products were calculated based on internal standard curves (methyl palmitate) constructed with authentic standards. IR spectra were measured by using a Bruker Tensor 27 FTIR spectrometer as KBr pellets. Acid–base titration was performed by using a Metrohm 877 Titrino plus instrument. The density of SO_3H groups, as well as the leaching of SO_3H groups during the reaction, was determined by the ion chromatography (881 Compact IC pro).

Preparation of BSA-15:[1]

SBA-15 was prepared from a mixture with starting composition of 0.02 P123 : 1 TEOS : 1.5 KCl : 6 HCl : 166 H_2O (in molar ratio). Briefly, 12 g of P123 was dissolved in a mixture of 74.4 g of concentrated HCl and 375.6 g of distilled water at 38 °C, followed by the addition of 16.5 g of KCl. To the solution, 31.5 g of TEOS was added with vigorous stirring for 8 min. The mixture was kept statically at the same temperature for 24 h, and the mixture was transferred to Teflon lined autoclaves and put in an oven at 130 °C for another 24 h. The solid was recovered by filtration,

washed by water, and calcined at 550 °C in air for 5 h.

Preparation of CMK-5:[2,3]

Templated synthesis of CMK-5 followed a reported procedure using furfuryl alcohol (FA) as carbon precursor. Al was incorporated into SBA-15 (molar ratio Si/Al = 20) by well dispersion of calcined SBA-15 into an aqueous solution of $AlCl_3$, followed by removal of H_2O by rotavapor and calcination in air. Impregnation of FA into Al-SBA-15 was achieved by incipient wetness infiltration at room temperature. The mixture was then heated up at 80 °C for 16 h for Al-catalyzed polymerization of FA. The obtained composite was recovered by filtration to remove excess and unpolymerized FA, and washed by EtOH and acetone. The composite was heated to 850 °C under vacuum at a ramp of 10 °C/min, and the carbonization was carried out at the same temperature for 3 h under vacuum. Ordered mesoporous carbon (CMK-5) was obtained by removal of silica template by HF (10 % in 1 : 1 EtOH–H_2O), washed with copious water and EtOH, and finally dried at 100 °C.

Preparation of 4-Benzenediazoniumsulfonate:[4]

4-Benzenediazoniumsulfonate was synthesized by diazotization of *p*-sulfanilic acid. In a three-necked ground flask, 12.99 g (0.075 mol) of *p*-sulfanilic acid was dispersed in 1 M HCl, resulting a 0.1 M suspension. To the well-stirred suspension in an ice-water bath (3-5 °C), was dropwise added a 10 % excess of 1 M aqueous solution of $NaNO_2$ (82.5 mL). The solid *p*-sulfanilic acid was slowly dissolved during of the addition of $NaNO_2$ and a clear solution was obtained after all of $NaNO_2$ solution was added. The mixture was stirred for another 45 min at the same temperature. The white precipitate formed was filtered off, washed by small amount of cold water, and dried under reduced pressure.

References

[1] C. Yu, J. Fan, B. Tian, D. Zhao, G. D. Stucky, *Adv. Mater.* **2002**, *14*, 1742–1745.
[2] S. H. Joo, J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* **2001**, *412*, 169–172.
[3] M. Kurk, M. Jaroniec, T.-W. Kim, R. Ryoo, *Chem. Mater.* **2003**, *15*, 2815–2823.
[4] M.-J. Bouchet, A. Rendon, C. G. Wermuth, M. Goeldner, C. Hirth, *J. Med. Chem.* **1987**, *30*, 2222–2227.

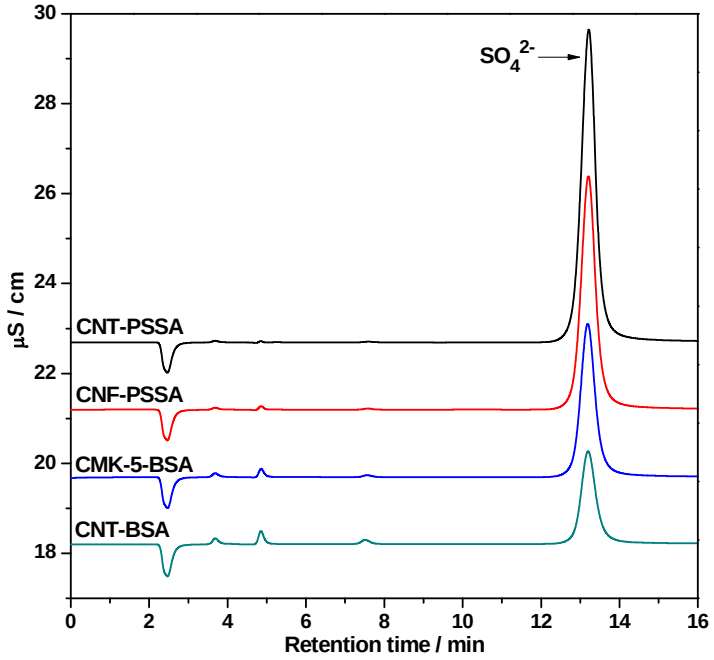

Figure S1-1. The ion chromatography of digested C-SO_3H.

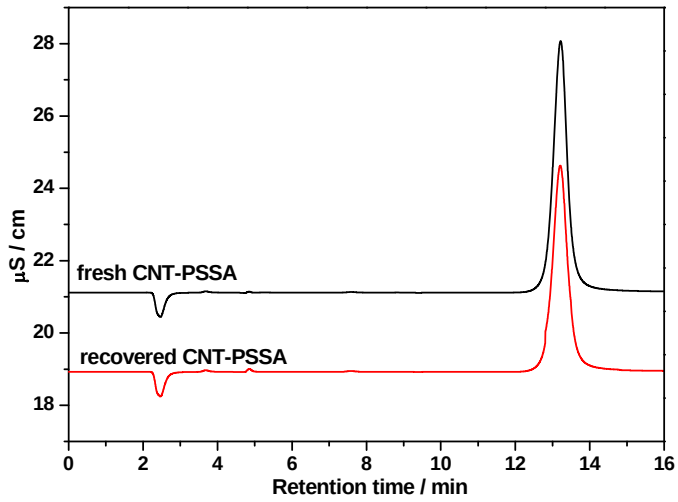

Figure S1-2. The ion chromatography of fresh and recovered CNT-PSSA.

Figure S2. HPLC analysis for the data listed in table 2.

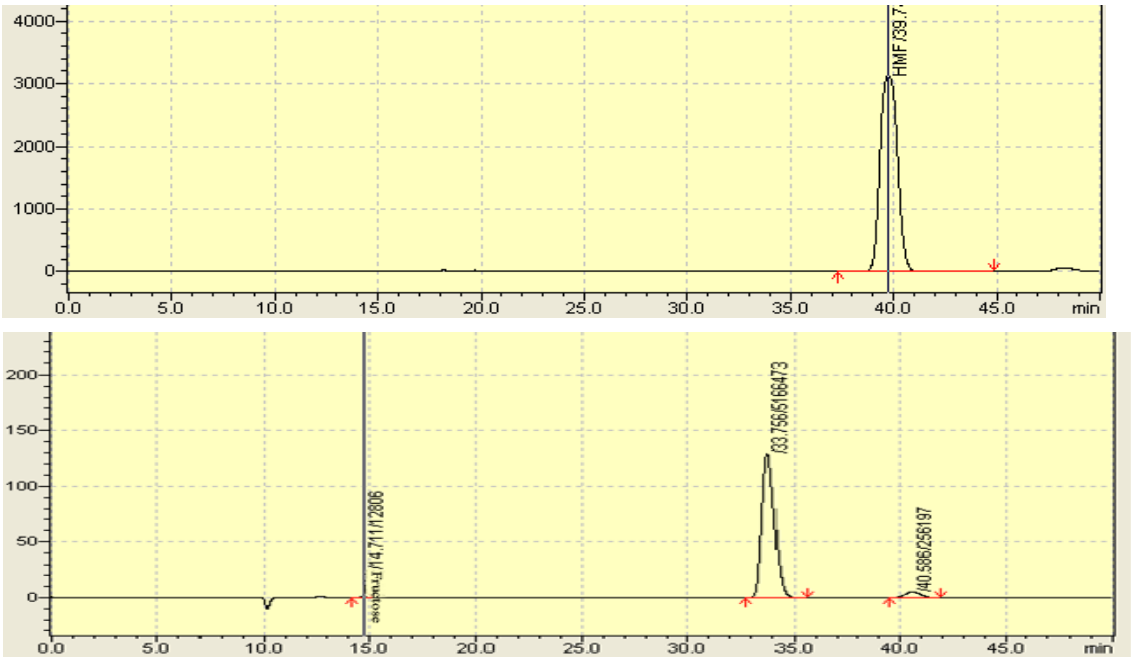

Figure S2-1 HPLC of CNT-PSSA-catalyzed fructose dehydration [UV (above)/refractive index (below) detector]. Reaction condition: fructose 150 mg, CNT-PSSA 15 mg, DMSO 1.5 mL, 100 °C, 90 min.

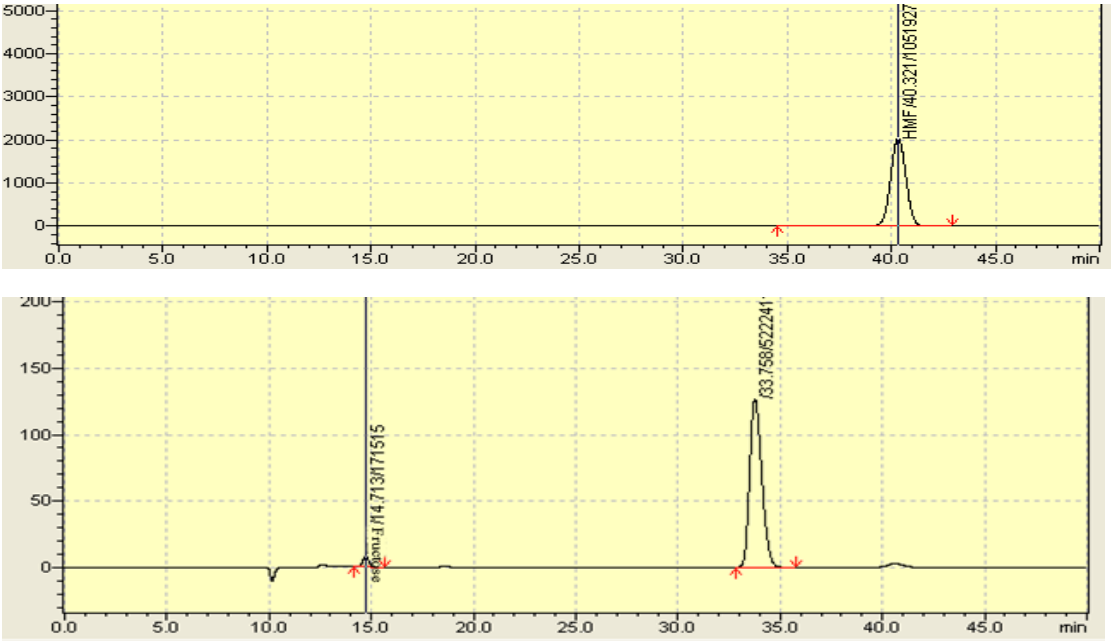

Figure S2-2 HPLC of CNT-PSSA-catalyzed fructose dehydration [UV (above)/refractive index (below) detector]. Reaction condition: fructose 150 mg, CNT-PSSA 15 mg, DMSO 1.5 mL, 100 °C, 10 min.

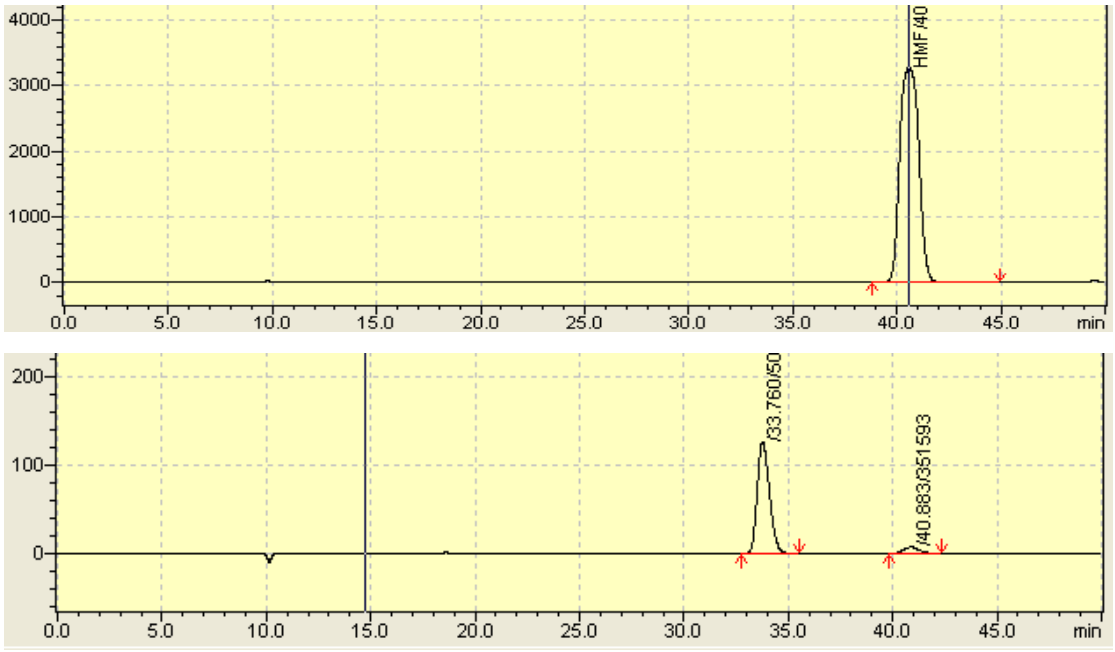

Figure S2-3 HPLC of CNT-PSSA-catalyzed fructose dehydration [UV (above)/refractive index (below) detector]. Reaction condition: fructose 150 mg, CNT-PSSA 15 mg, DMSO 1.5 mL, 120 °C, 90 min.

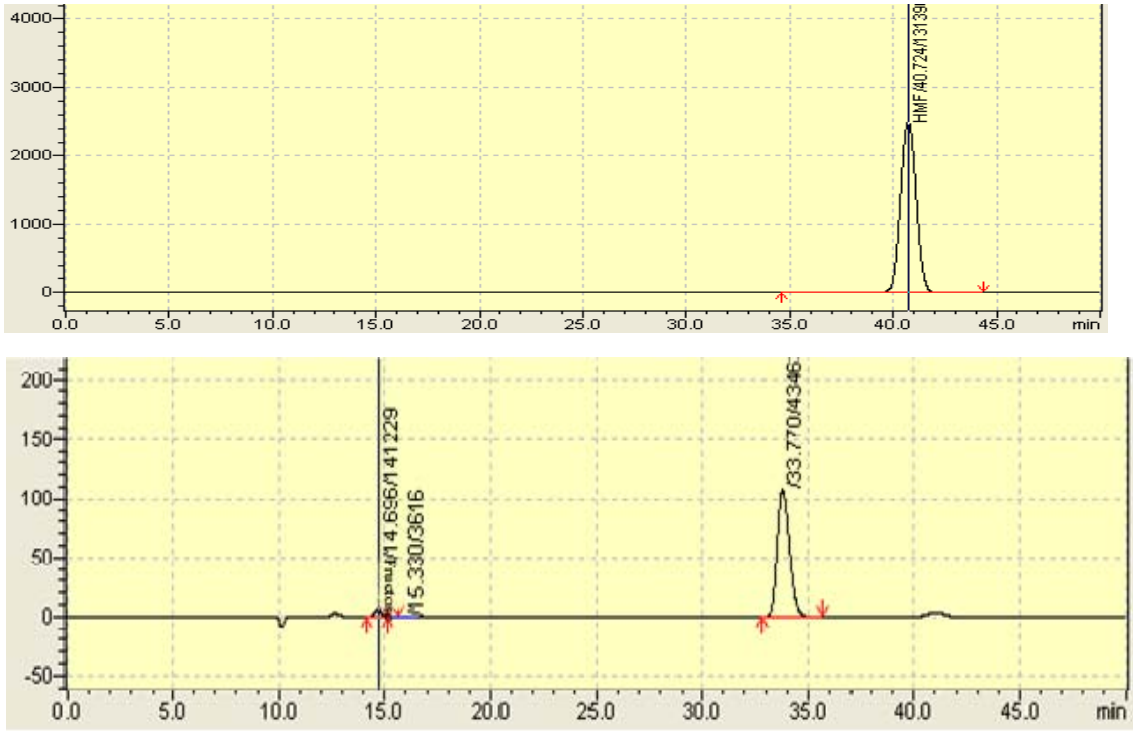

Figure S2-4 HPLC of CNT-PSSA-catalyzed fructose dehydration [UV (above)/refractive index (below) detector]. Reaction condition: fructose 150 mg, CNT-PSSA 15 mg, DMSO 1.5 mL, 80 °C, 90 min.

Figure S2-5 HPLC of CNT-PSSA-catalyzed inulin conversion into HMF [UV (above)/refractive index (below) detector]. Reaction condition: inulin 100 mg, CNT-PSSA 15 mg, DMSO 1.5 mL, 120 °C, 90 min.

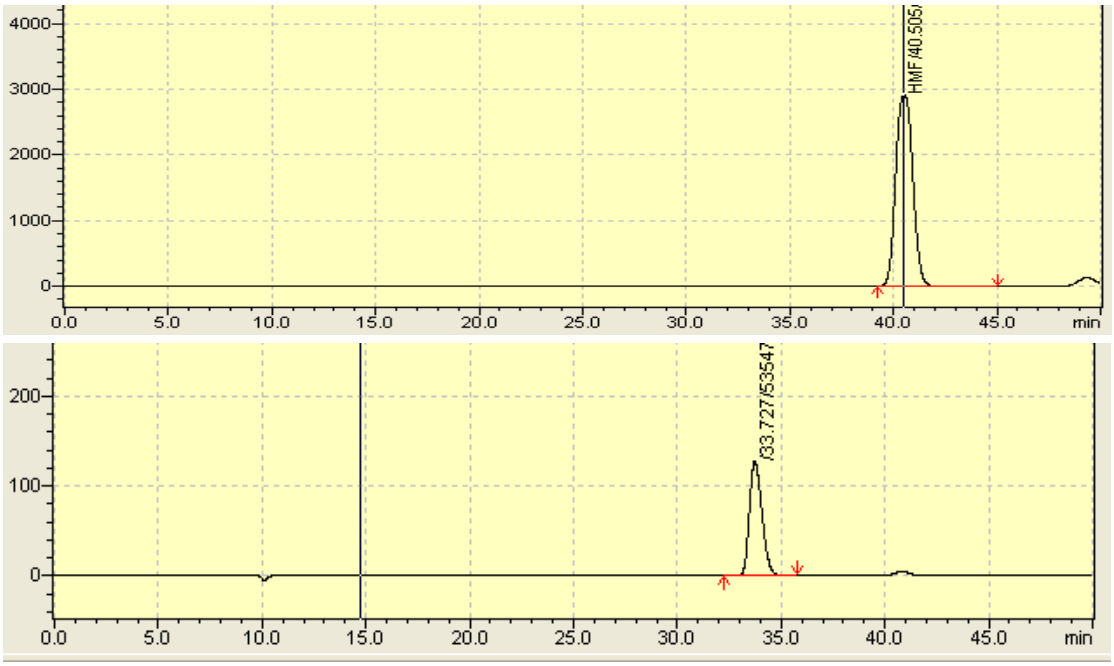

Figure S2-6 HPLC of CNT-PSSA-catalyzed sucrose conversion into HMF [UV (above)/refractive index (below) detector]. Reaction condition: sucrose 100 mg, CNT-PSSA 15 mg, DMSO 1.5 mL, 140 °C, 90 min.

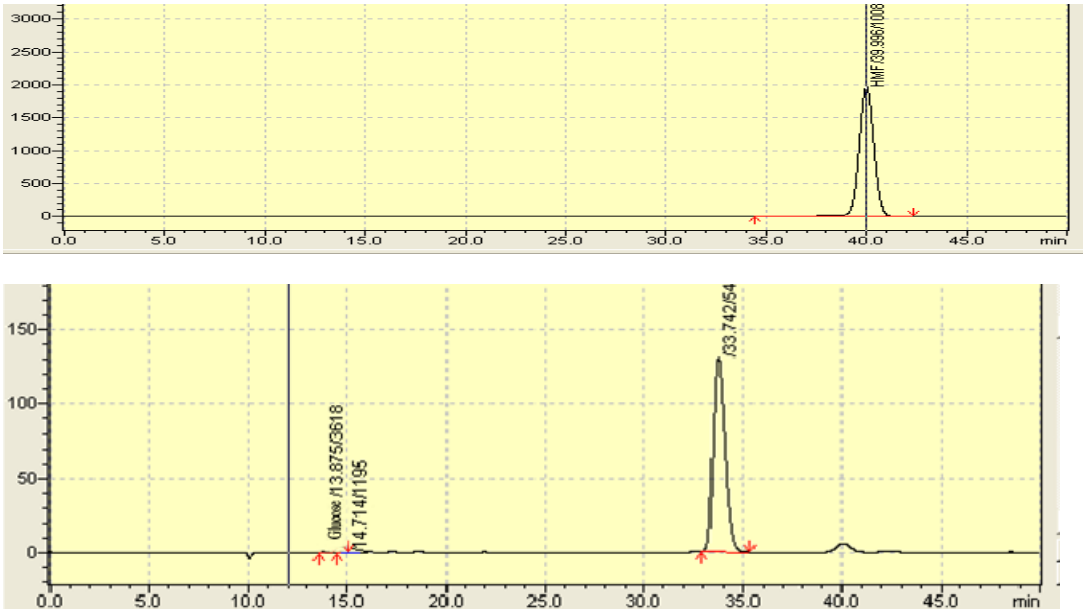

Figure S2-7 HPLC of CNT-PSSA-catalyzed glucose conversion into HMF [UV (above)/refractive index (below) detector]. Reaction condition: glucose 50 mg, CNT-PSSA 15 mg, DMSO 1.5 mL, 140 °C, 60 min.

Figure S3. GC analysis for the data listed in Table 3.

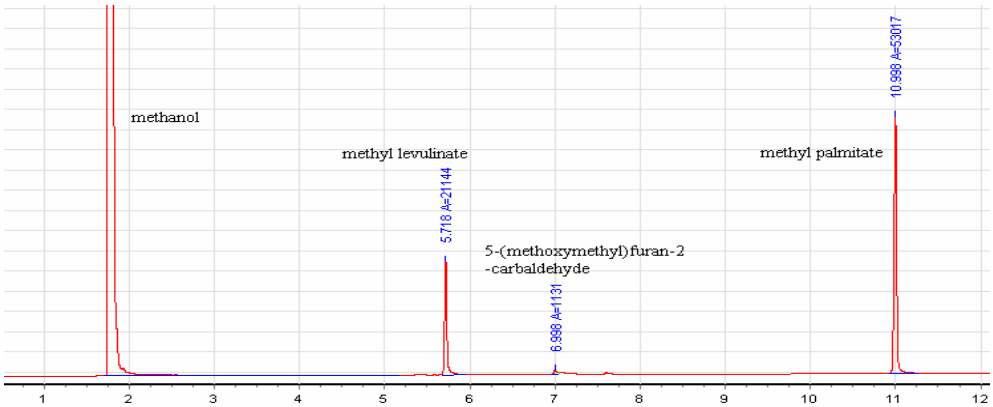

Figure S3-1. GC of CNT-PSSA-catalyzed fructose conversion into methyl levulinate (Reaction condition: fructose 50 mg, CNT-PSSA 20 mg, methanol 4 mL, 100 °C, 24 h)

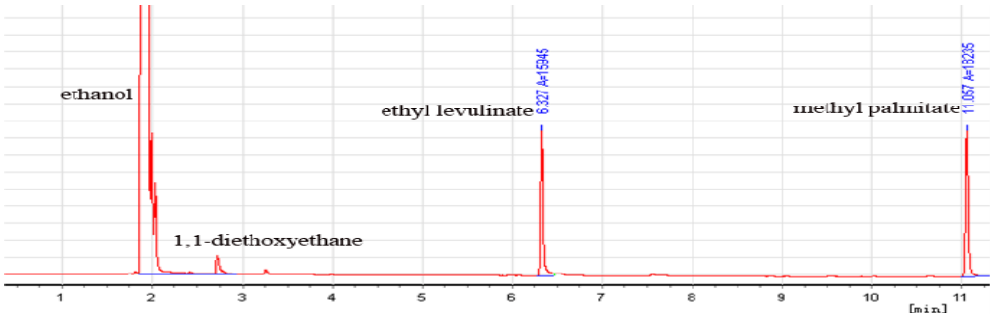

Figure S3-2. GC of CNT-PSSA-catalyzed fructose conversion into ethyl levulinate (Reaction condition: fructose 50 mg, CNT-PSSA 20 mg, ethanol 4 mL, 120 °C, 24 h)

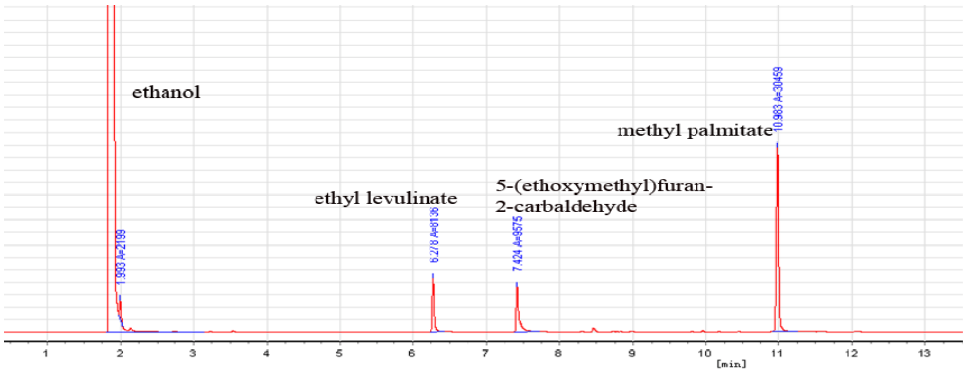

Figure S3-3. GC of CNT-PSSA-catalyzed fructose conversion into ethyl levulinate (Reaction condition: fructose 50 mg, CNT-PSSA 20 mg, ethanol 4 mL, 100 °C, 12 h)

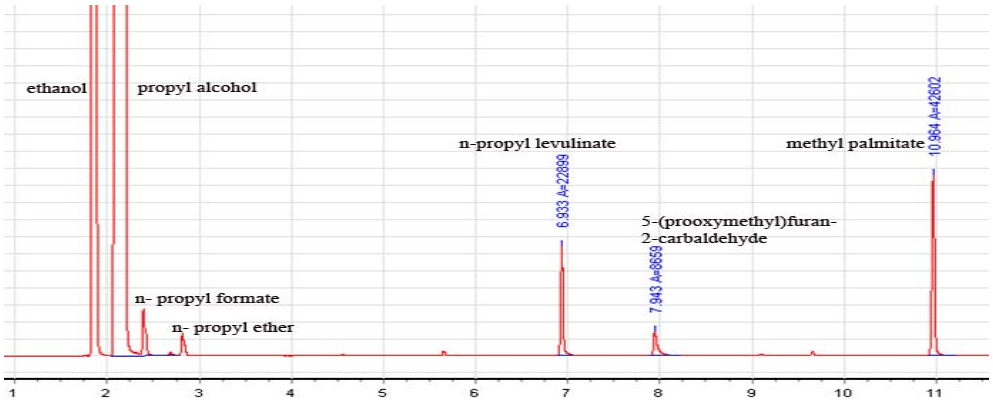

Figure S3-4. GC of CNT-PSSA-catalyzed fructose conversion into *n*-propyl levulinate (Reaction condition: fructose 50 mg, CNT-PSSA 20 mg, *n*-propyl alcohol 4 mL, 120 °C, 24 h)

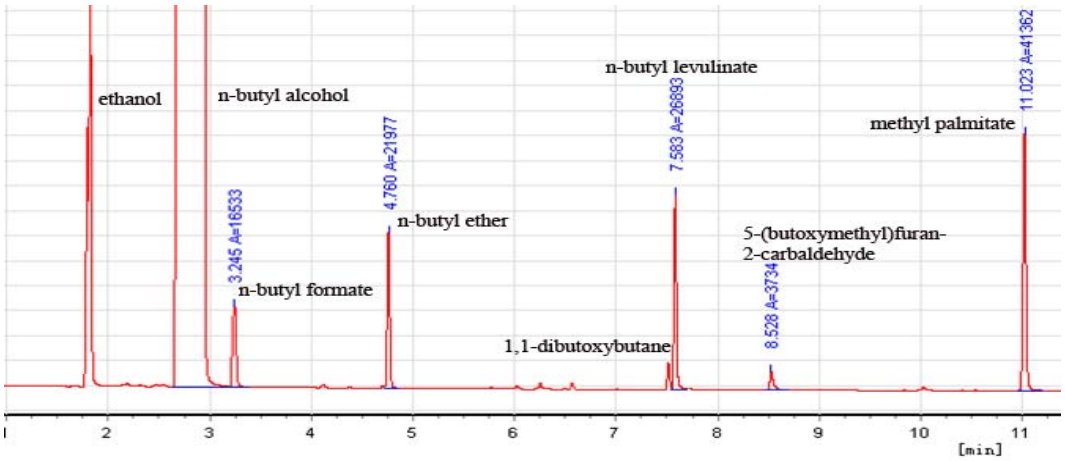

Figure S3-5. GC of CNT-PSSA-catalyzed fructose conversion into *n*-butyl levulinate (Reaction condition: fructose 50 mg, CNT-PSSA 20 mg, *n*-butyl alcohol 4 mL, 120 °C, 24 h)

Figure S4. GC-MS analysis

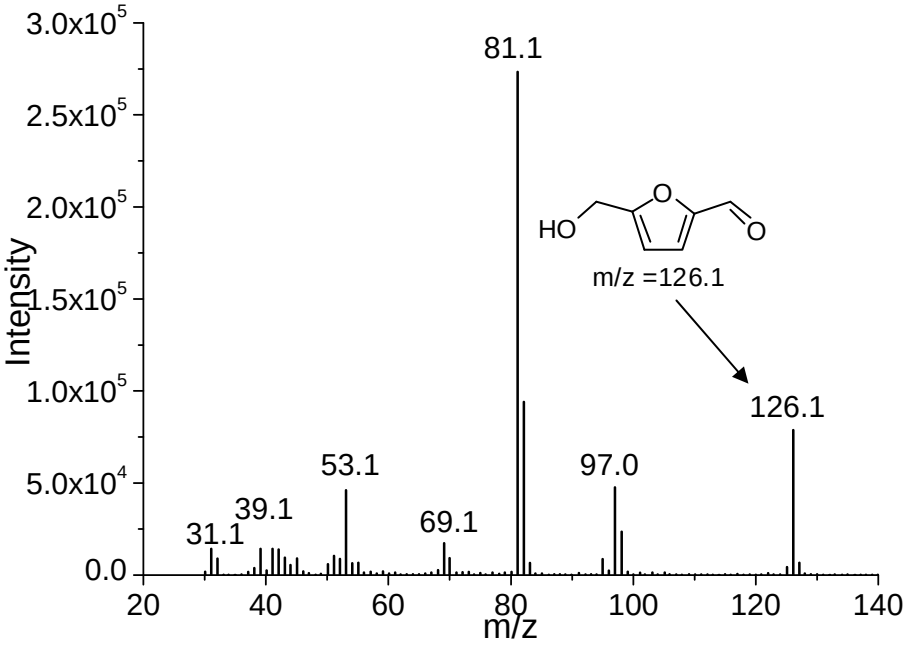

Figure S4-1. MS of 5-hydroxymethylfurfural

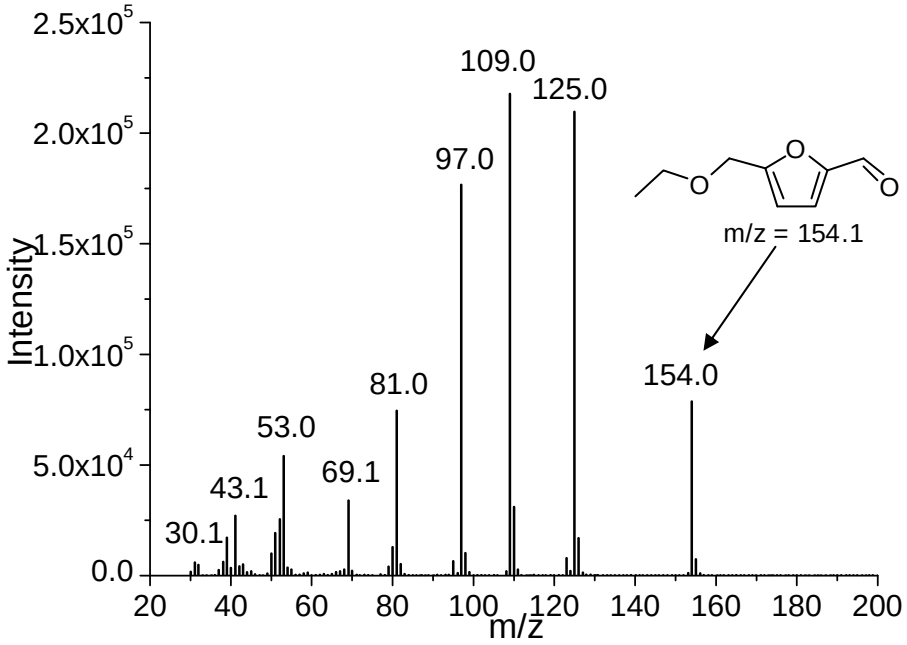

Figure S4-2. MS of 5-ethoxymethylfurfural

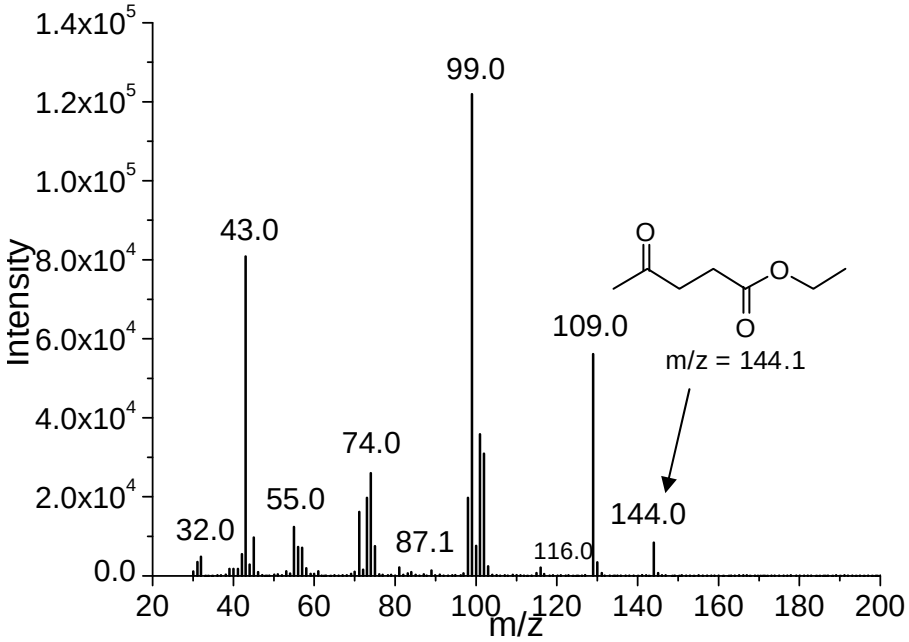

Figure S4-3. MS of ethyl levulinate

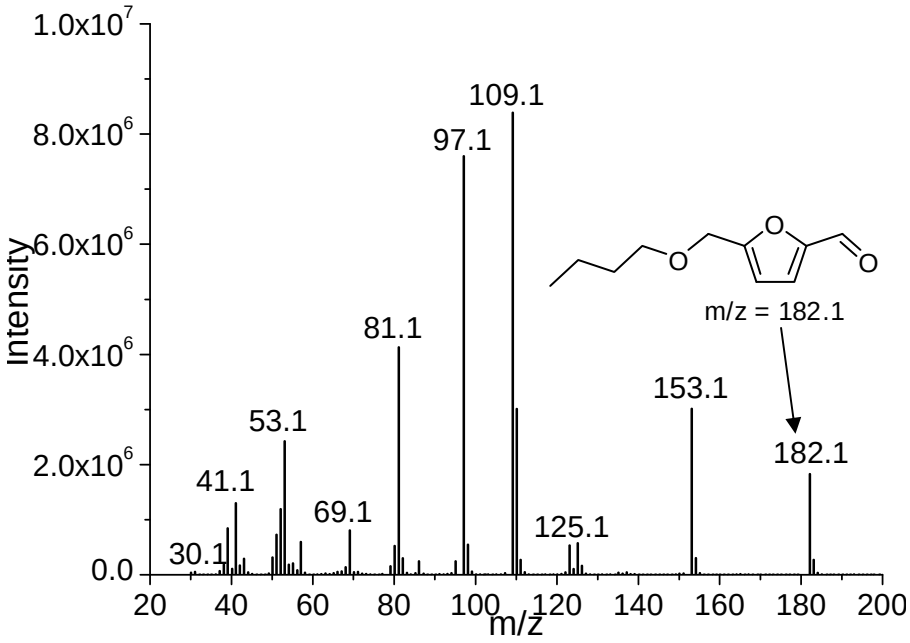

Figure S4-4. MS of 5-butoxymethylfurfural

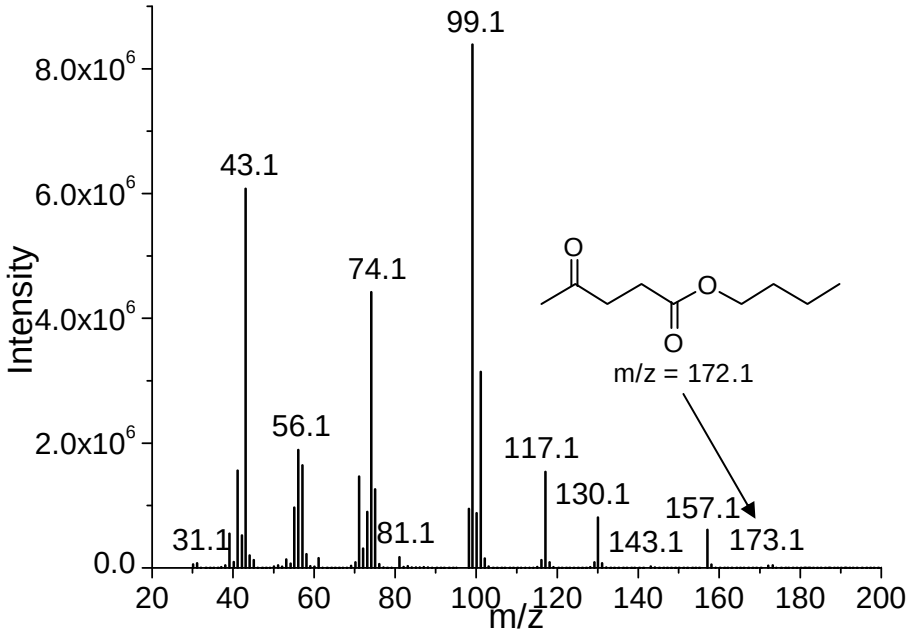

Figure S4-5. MS of butyl levulinate