Supporting Information

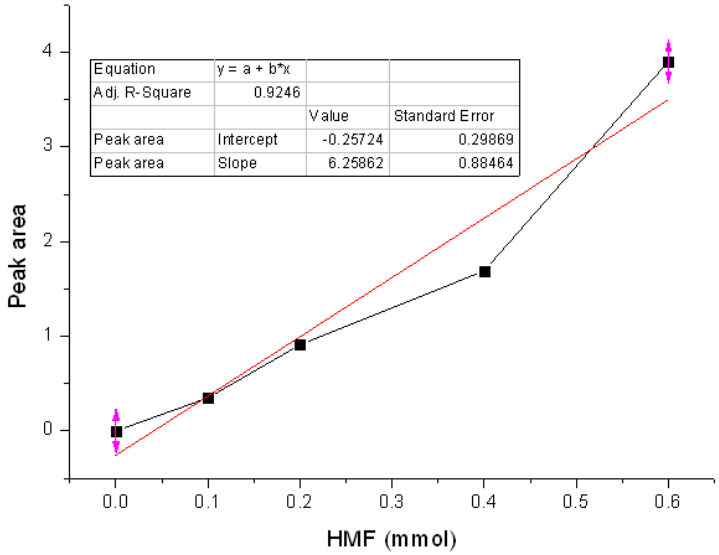
Conversion of carbohydrates into 5-hydroxymethylfurfural using Polymer bound sulfonic acids as efficient and recyclable catalysts

1. General information.

All reactions were carried out under air in oven-dried glassware with magnetic stirring. All materials were obtained from commercial suppliers and were used without further purification, Corn stover was obtained from our test field.

Unless otherwise noted, HMF was extracted with diethyl ether absolute or ethyl acetate, concentrated with a rotary evaporator, and dried under vacuum at 50 °C. NMR spectra were recorded at 400 (^{1}H) and 101 (^{13}C) MHz, respectively, on a Varian Mercury plus-400 instrument using $CDCl_3$ as solvent and TMS as internal standard. Mass-spectra were recorded on a Bruker APEX Ⅱ instrument. The products was analyzed by HPLC with Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45:90) were used as the mobile phase at a flow rate of 0.8 mL min^{-1}. The following abbreviations were used to describe peak patterns where appropriate: singlet (s), doublet (d), triplet (t), multiplet (m).

HMF was quantified with calibration curves generated from commercially available standards.



The concentrations of products were calculated from HPLC-peak integrations and used to calculate molar yield.

The yields of HMF were defined as follows:

Conversion = moles of carbohydrates reacted/moles of starting carbohydrates

HMF yield = moles of HMF produced/moles of starting glucose or fructose

For disaccharides and polysaccharides, HMF yields were defined as follows:

HMF yield = moles of HMF produced/moles of hexose units in polysaccharides

2. Structural and textural characterization

The structure of PEG-OSO_3H has been confirmed in our previous jobs,[1] while the qualities of PS-PEG-OSO_3H was measured by TG-DTA, XRD, SEM and XPS analysis. The thermal stability of the materials was checked by the DTA technique and their TG curves are shown in

Figure S1. We can see from Figure S1 that chloromethylated bead (PS) was decomposed in the range 320-410°C. The thermal stability was reduced through polyethylene glycol modified chloromethylated bead (PS-PEG_{400}). PS-PEG_s-OSO_3H showed main peaks for loss of weight in the range 80-110 °C, Sulfonic acid decomposition temperature in the range 120-280 °C, the results showed that PEG_s-OSO_3H was successful grafted on chloromethylated bead.

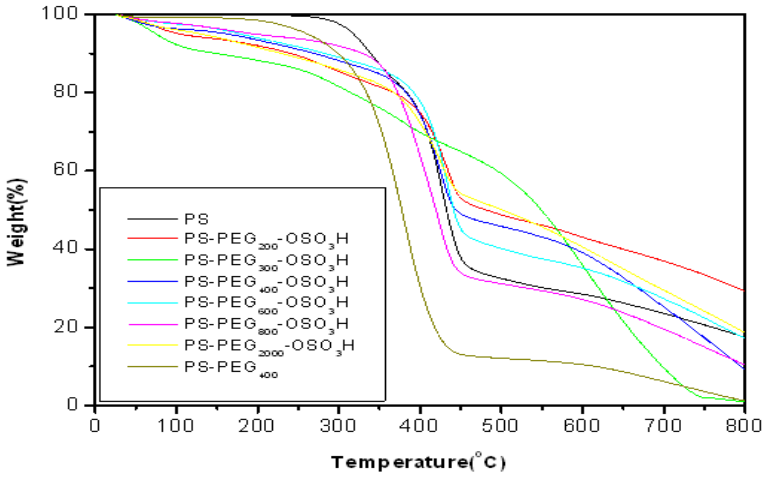
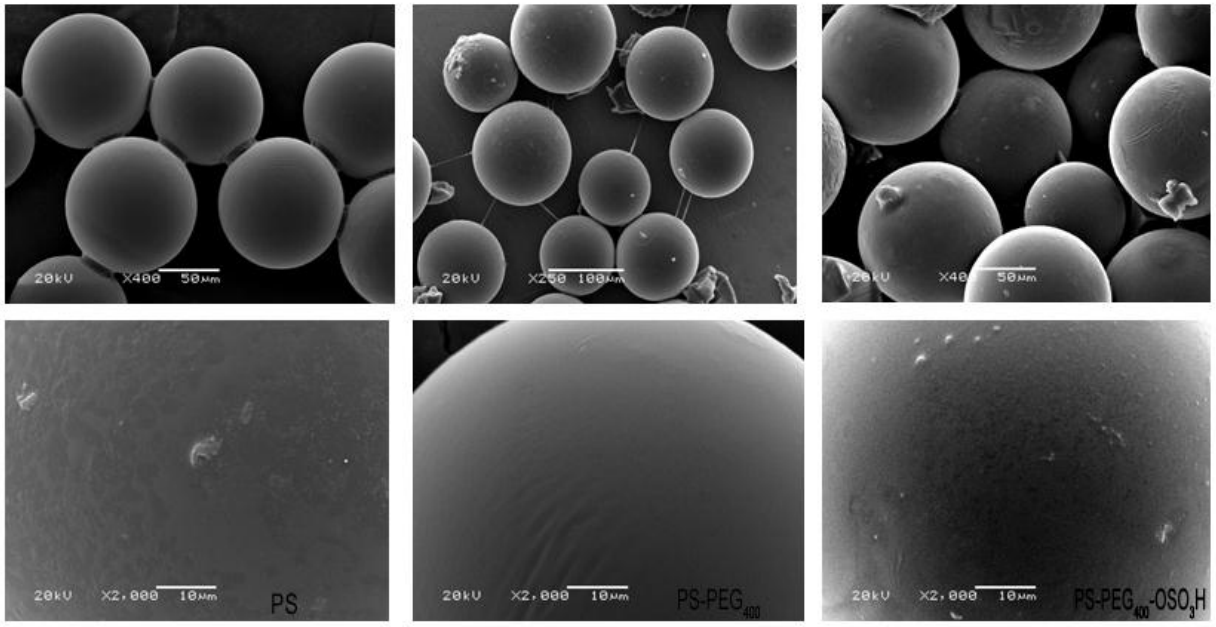


Figure S1. TG curves of PS, PS-$PEG_{200\text{-}2000}$-OSO_3H and PS-PEG_{400} samples

The X-ray powder diffraction (XRD) patterns confirmed that the structure of PS, PS-PEG_{400}, PS-PEG_{400}-OSO_3H were amorphous crystal, these peak strength and & position were different in Figure S2. The SEM image indicates that functionalization of PS-PEG_{400} using sulfonic acid groups does not cause a significant change in structure. PS surface is smooth, while PS-PEG_{400} and PS-PEG_{400}-OSO_3H surface is rough.



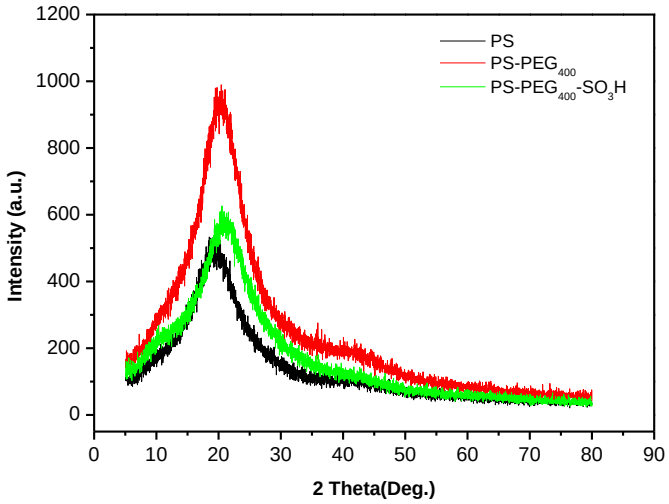


Figure S2. SEM micrographs and XRD patterns of PS, PS-PEG_{400} and PS-PEG_{400}-OSO_3H

Figure S3 shows the XPS spectra of the PS-PEG_{400}-OSO_3H. Only three peaks were observed at binding energies of around 163, 285 and 541 eV, the characteristic peaks of S, C and O for PS-PEG_{400}-OSO_3H, respectively, which indicates that sulfonic acid groups were grafted on the surface PS-PEG_{400} species.

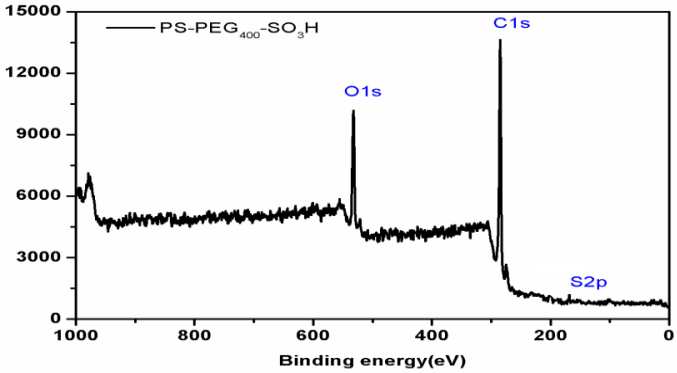


Figure S3. XPS spectra of PS-PEG_{400}-OSO_3H

3. Typical Procedure for the Catalysis

Carbohydrates (2 mmol), PEG-OSO_3H (0.7 g) or PS-PEG-OSO_3H (0.2 g), LiCl (0.3 g), DMSO (4 mL) and distilled water (2 mL) were added to 50 mL round bottom flask; the reaction was heated to 120 °C for 0.3 to 5 h. In a typical experiment for the transformation of corn stover in DMSO/H_2O system, a 50 mL round bottom flask was charged with corn stover (0.5 g), PEG-OSO_3H (0.7 g) or PS-PEG-OSO_3H (0.2 g), LiCl (0.3 g), DMSO (4 mL) and distilled water (2 mL); the reaction was heated to 130 °C for 6 to 7 h.

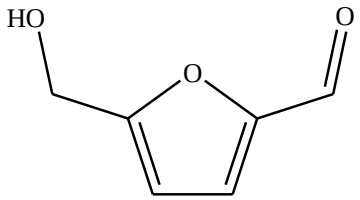
Dehydration of glucose to HMF using PEG-OSO_3H as catalyst. A mixture of glucose (2 mmol), LiCl (0.3 g) and PEG-OSO_3H (0.7 g, 0.23 mmol -SO_3H) in DMSO aqueous solution was stirred at 120 °C for 1.5 h. After completion monitored by TLC, the resulting mixture was cooled to room temperature immediately, distilled water was added into the reaction system, The mixture was

extracted 3 times with 10 mL of diethyl ether absolute. The combined organic phase was dried over Na_2SO_4. After evaporating the solvent a yellowish oily matter, HMF (76% isolated yield, 100% purity by HPLC) obtained and dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$): 3.00 (s, 1H, OH), 4.72 (s, 2H, CH_2), 6.52 (d, *J* = 3.6 Hz, 1H, Furan-H-4), 7.23 (d, *J* = 3.6 Hz, 1H, Furan-H-3), 9.58 (s, 1H, CHO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): 57.39 (CH_2), 109.93, 123.18 (Ar), 152.15 (Ar), 160.83 (Ar), 177.69 (CHO) ppm. FTIR (KBr) (ν, cm-1): 1026 (C-O-C), 1520 (C=C), 1674 (-CHO), 2992, 2908 (-CH_2), 3412 (-OH). HRMS (ESI): calculated for $C_6H_6O_3$: $[M+H]^+$ 127.0390; found: 127.0392.

Dehydration of glucose to HMF using PS-PEG-OSO_3H as catalyst. A mixture of glucose (2 mmol), LiCl (0.3 g) and PS-PEG-OSO_3H (0.2 g, 0.66 mmol -SO_3H) in DMSO aqueous solution was stirred at 120 °C for 1 h. After completion monitored by TLC, the resulting mixture was cooled to room temperature immediately, distilled water was added into the reaction system, the mixture was filtered and the resin was washed with EtOH (3×10 mL). Then the filtrate was extracted with 3×10 mL of ethyl acetate and the combined organic phase were dried over Na_2SO_4 and concentrated. The HMF was dried under vacuum.

All the products were confirmed by ^{1}H NMR, ^{13}C NMR, HRMS (ESI) and HPLC analysis.

5-hydroxymethylfurfural



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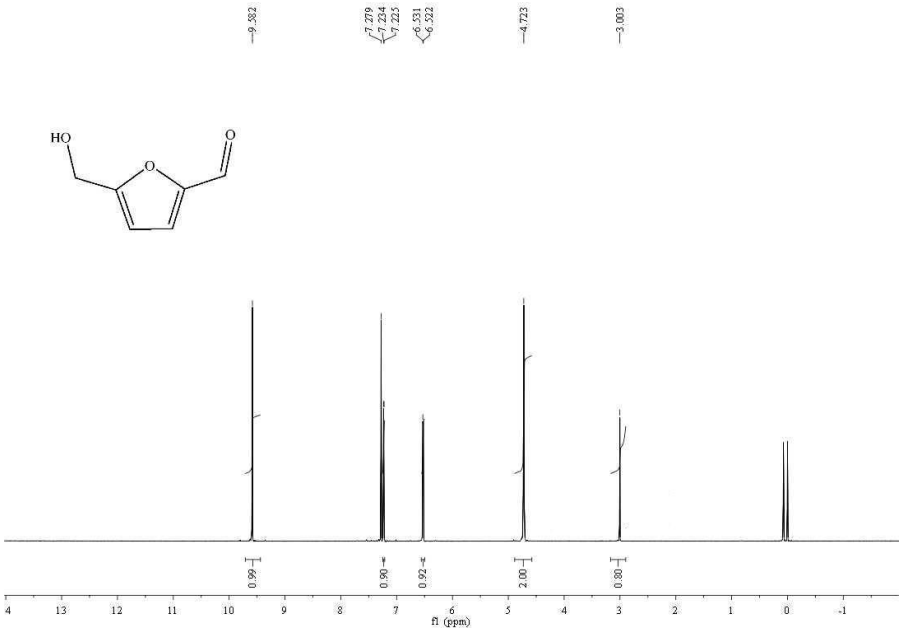
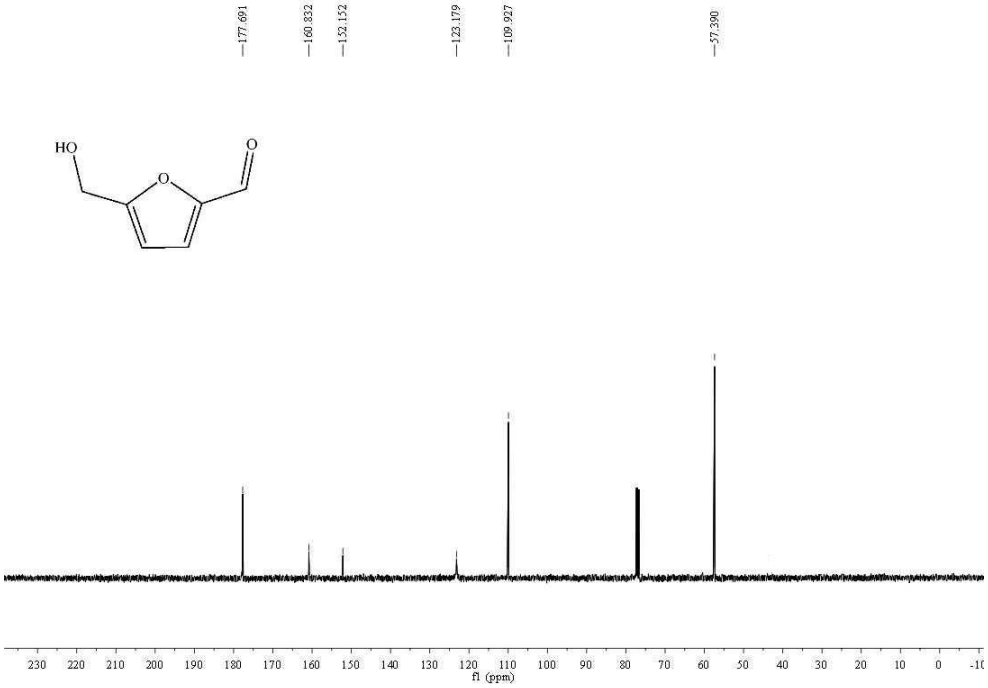
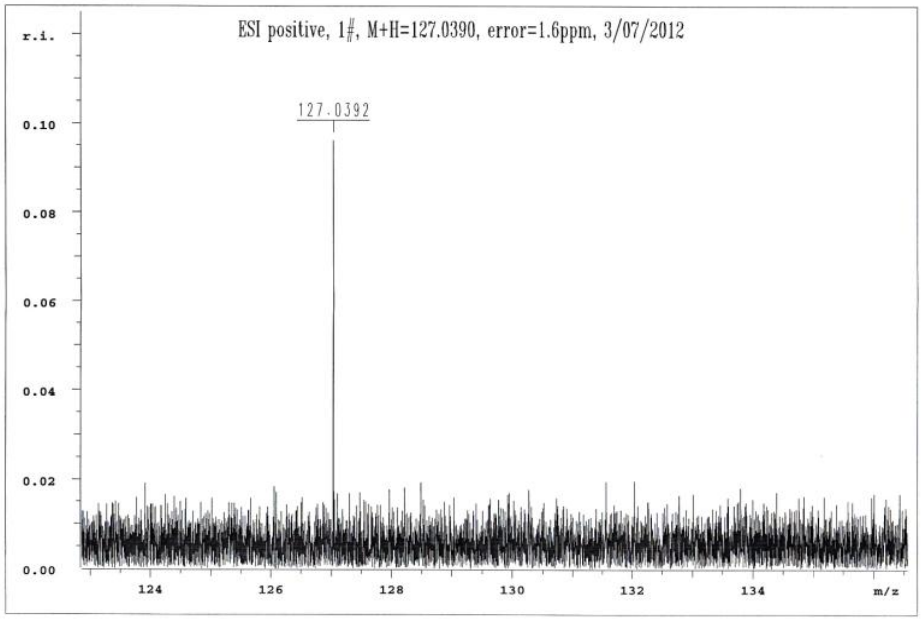






Dehydration of raw biomass variant to HMF using PS-PEG-OSO_3H as catalyst. Finally, we applied the polymer bound sulfonic acids catalysts to raw biomass variant. A 50 mL round bottom flask was charged with corn stover (0.5 g), PS-PEG-OSO_3H (0.2 g), LiCl (0.3 g), DMSO (4 mL) and distilled water (2 mL); the reaction was heated to 130 °C for 6. After completion monitored by TLC, the resulting mixture was filtered and washed with distilled water. Then the filtrate was extracted with 3×10 mL of ethyl acetate and the organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Then the amount of HMF was analyzed by HPLC with Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. N-hexane and isopropanol (95:5) were used as the mobile phase at a flow rate of 1.0 mL min^{-1}, 36% (wt/wt) of isolated HMF (the crude product contained HMF and furfural in a ratio of 15:82 with 3% of other side products) was obtained.

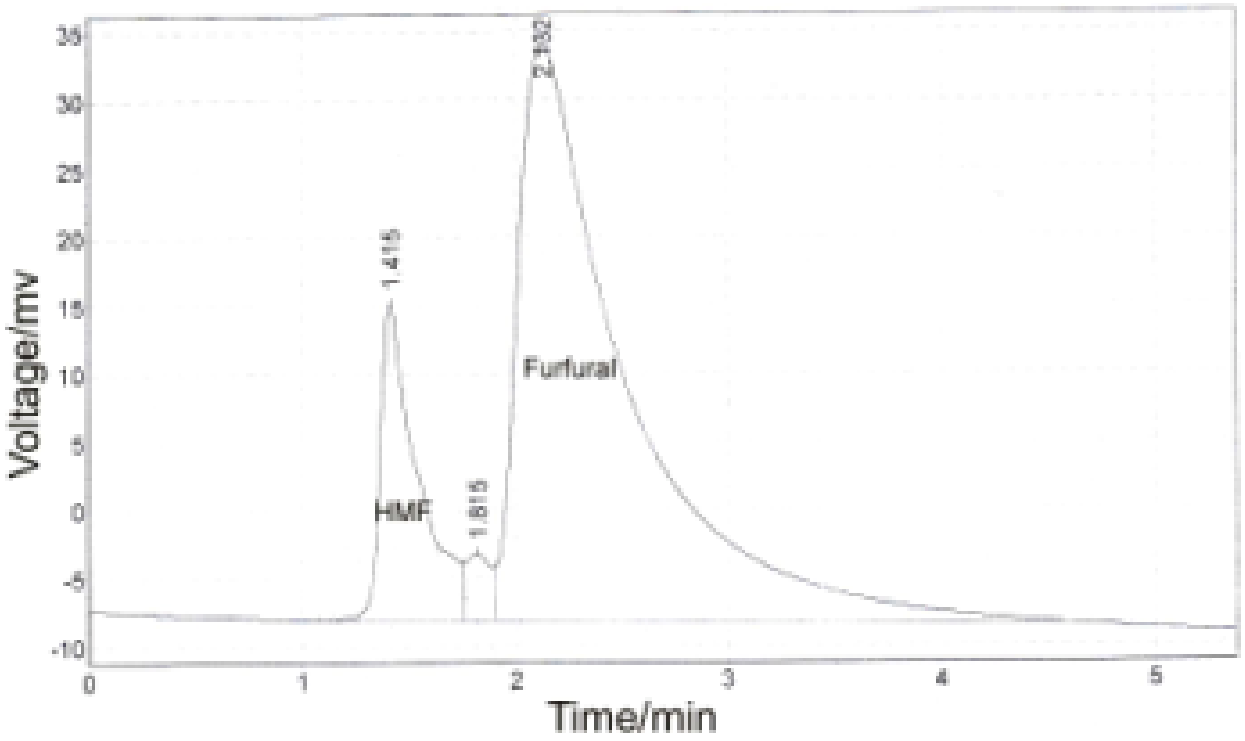


Figure S4. Refractive index HPLC trace of corn stover reaction mixture. Analyses were Performed with a Kromasil-C_{18}-5µ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. N-hexane and isopropanol (95:5) were used as the mobile phase at a flow rate of 1.0 mL min^{-1}. Major components are indicated.

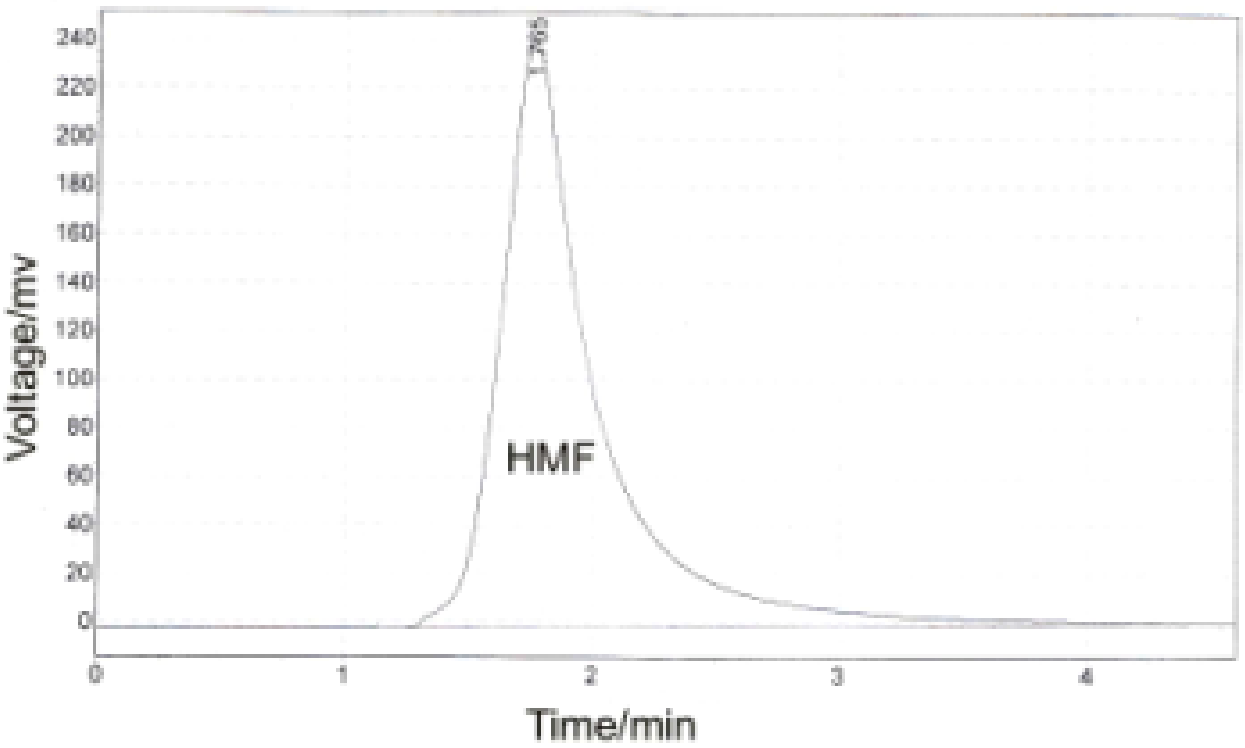
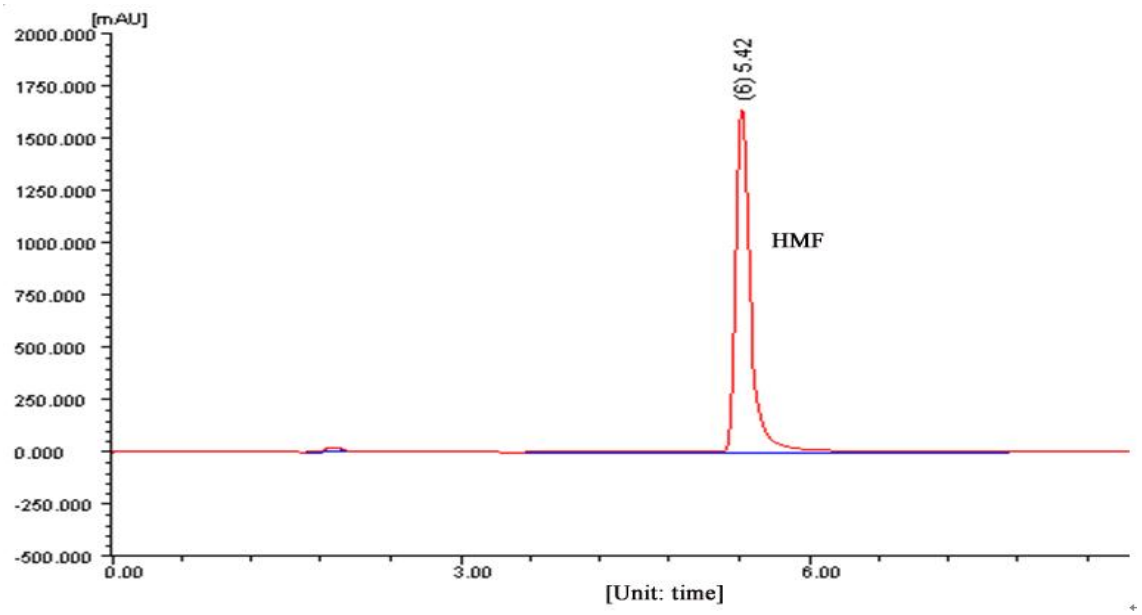
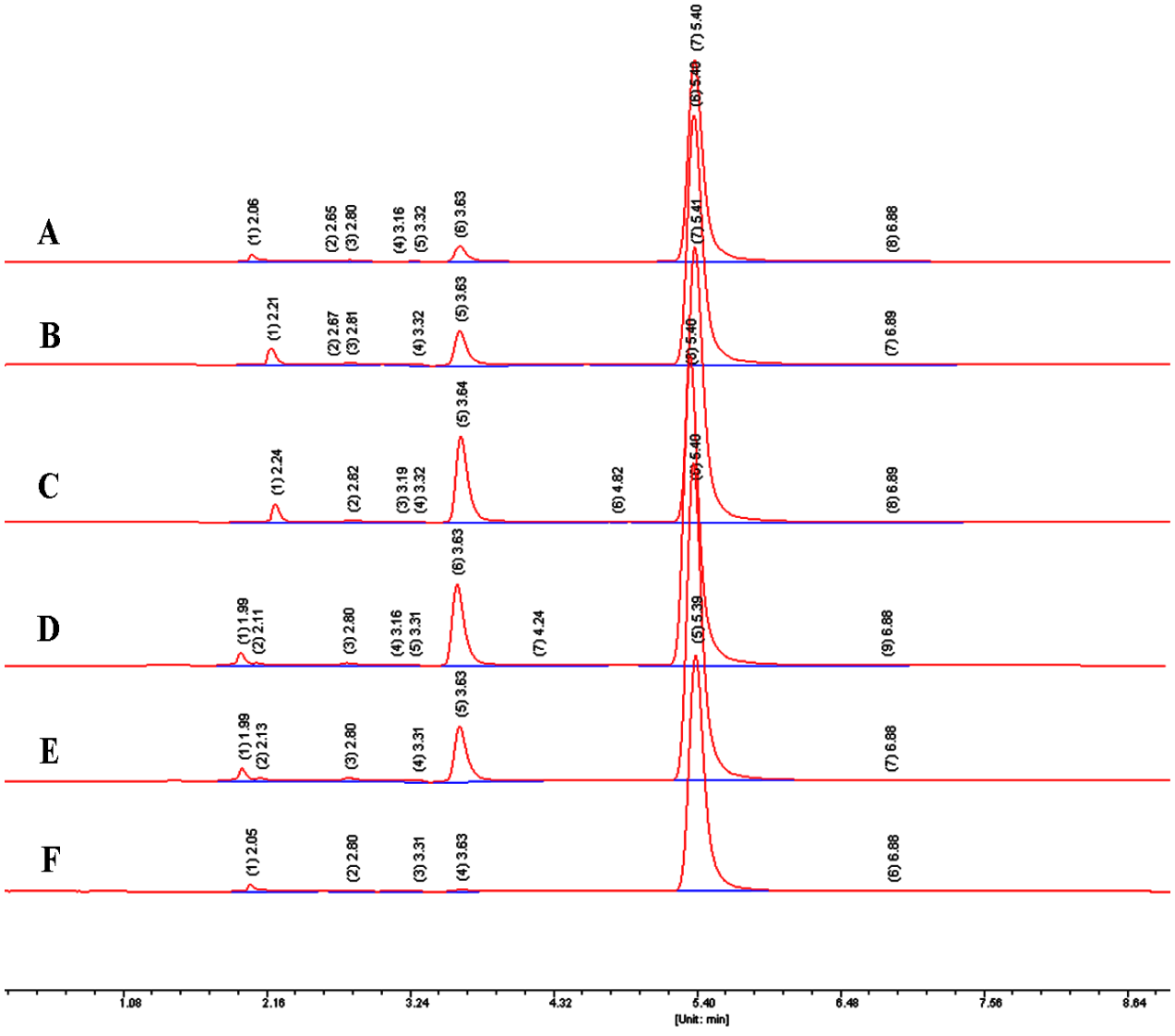


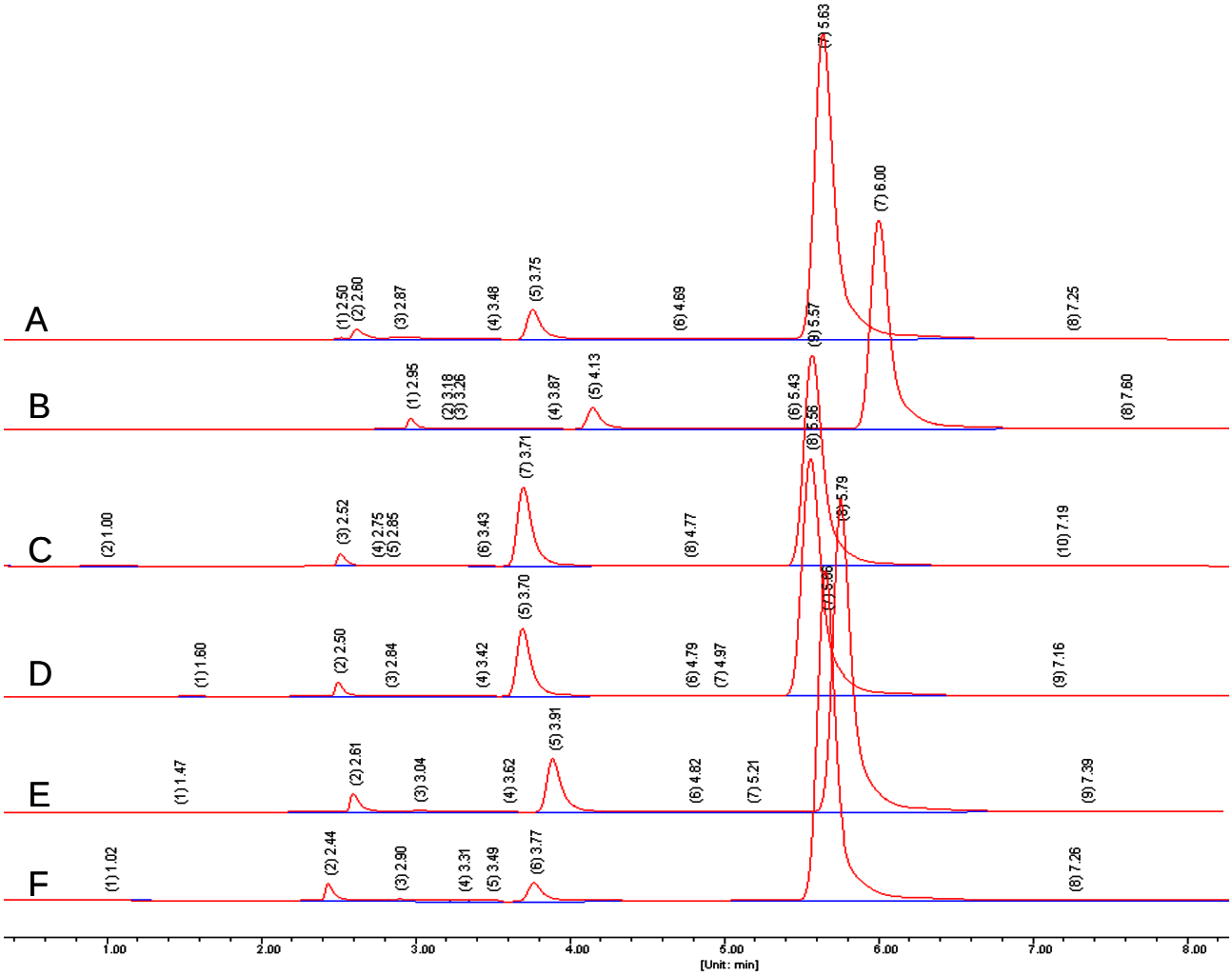
Figure S5. Refractive index HPLC trace of HMF. Analyses were Performed with a Kromasil-C_{18}-5µ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. N-hexane and isopropanol (95:5) were used as the mobile phase at a flow rate of 1.0 mL min^{-1}.



Figurre S6. Refractive index HPLC traces of HMF. Analyses were performed with a Kromasil-C_{18}-5µ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45:90) were used as the mobile phase at a flow rate of 0.8 mL min^{-1}.



Figurre S7. Refractive index HPLC traces of representative reaction mixtures. Analyses were performed with a Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45:90) were used as the mobile phase at a flow rate of 0.8 mL min^{-1}. (A) Synthesis of HMF from glucose with PEG-OSO_3H in DMSO/H_2O reaction system. (B) Synthesis of HMF from fructose with PEG-OSO_3H in DMSO/H_2O reaction system. (C) Synthesis of HMF from sucrose with PEG-OSO_3H in DMSO/H_2O reaction system. (D) Synthesis of HMF from maltose with PEG-OSO_3H in DMSO/H_2O reaction system. (E) Synthesis of HMF from starch with PEG-OSO_3H in DMSO/H_2O reaction system. (F) Synthesis of HMF from cellulose with PEG-OSO_3H in DMSO/H_2O reaction system.



Figurre S8. Refractive index HPLC traces of representative reaction mixtures. Analyses were performed with a Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45:90) were used as the mobile phase at a flow rate of 0.8 mL min^{-1}. (A) Synthesis of HMF from glucose with PS-PEG-OSO_3H in DMSO/H_2O reaction system. (B) Synthesis of HMF from fructose with PS-PEG-OSO_3H in DMSO/H_2O reaction system. (C) Synthesis of HMF from sucrose with PS-PEG-OSO_3H in DMSO/H_2O reaction system. (D) Synthesis of HMF from maltose with PS-PEG-OSO_3H in DMSO/H_2O reaction system. (E) Synthesis of HMF from starch with PS-PEG-OSO_3H in DMSO/H_2O reaction system. (F) Synthesis of HMF from cellulose with PS-PEG-OSO_3H in DMSO/H_2O reaction system.

References

1 (a) X. C. Wang, Z. J. Quan, F. Wang, M. G. Wang, Z. Zhang, Z. Li, *Synth. Commun*., 2006, **36**, 451–456; (b) Z. J. Quan, Y. X. Da, Z. Zhang, X. C. Wang, *Catal*. *Commun*., 2009**, 10**, 1146–1148.