Electronic Supplementary Information

Highly effective synthesis of biomass-derived furanic diethers over a sulfonated zirconium-carbon coordination catalyst in alcohol systems

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Experimental materials

5-Hydroxymethylfurfural (HMF, 98%), 5-methylfurfural (MF, 98%), 5-methylfurfuryl alcohol (MFA, 97%), 5-methoxymethylfurfural (MMF, 97%), 2,5-bis(hydroxymethyl)furan (BHMF, 98%), 2,5-bis(methoxymethyl)furan (BMMF, 97%), furfural (FF, 99%), furfuryl alcohol (FFA, 98%), benzaldehyde (BAL, 99%), benzyl alcohol (BAO, 99%), levulinic acid (LvA, 98%), methyl levulinate (ML, 99%), ethyl levulinate (EL, 98%), propyl levulinate (PL, 97%), butyl levulinate (BL, 98%) and γ-valerolactone (GVL, 98%) were purchased from Saen Chemical Technology Co., Ltd. (Shanghai, China). CT269DR, a macroporous sulfonated resin, was provided by Purolite Co., Ltd. (Huzhou, China). Zirconium tetrachloride ($ZrCl_4$, 99%) and p-toluenesulfonic acid (TsOH, 99%) were obtained from Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). Glucose, methanol (MeOH), ethanol (EtOH), n-propanol (nPrOH), isopropanol (iPrOH), n-butanol (nBuOH), sec-butanol (sBuOH), dimethylformamide (DMF) and other chemicals were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without any purification.

Catalyst characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrometer. X-ray diffraction (XRD) patterns were performed on a Bruker D8 Advance diffractometer with a Cu Kα radiation source (λ=0.15418 nm). Scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were carried out on a Zeiss Supra55 microscope, a JEM-2100f

microscope and a FEI Titan Themis G2 F30 microscope, respectively. Element contents were determined by a VISTA-MPX inductively coupled plasma atomic emission spectrometer (ICP-AES) and a Vario EL III elemental analyzer (EA), respectively. Nitrogen adsorption-desorption (NAD) isotherms were measured on a ASAP 2020 physisorption analyzer at 77 K. Temperature-programmed desorption (TPD) profiles, X-ray photoelectron spectroscopy (XPS) spectra and pyridine-adsorbed FT-IR spectra were collected on an AutoChem II 2920 chemisorption analyzer, an Escalab 250Xi spectrometer with an Al Kα excitation source (*hv* = 1486.6 eV) and a Bruker Tensor 27 spectrometer in the range of 1300 to 1700 cm^{-1}, respectively.

2,5-Bis(alkoxymethyl)furans (BAMFs) synthesis

Take the standard 2,5-bis(isopropoxymethyl)furan (BIPMF) as an example (Scheme S1), the detailed synthesis procedures were as follows: 1 g of BHMF, 0.25 g of CT269DR and 49 g of iPrOH were mixed and added into a 100 mL of stainless steel autoclave, which was sealed and heated to 50 °C under a stirring rate of 400 rpm. After 24 h, the autoclave was rapidly quenched to room temperature (RT). Note that BHMF conversion and BIPMF selectivity were greater than 99% (Fig. S1). Next, CT269DR was separated from the reaction mixture by filtration, and then, the filtrate was distilled to remove the low-boiling iPrOH and H_2O at 60 °C for 1 h under the reduced pressure. Subsequently, the remnant was renewedly dissolved into 25 mL ethyl acetate (EtOAc), which was followed by adding 0.5 g of activated carbon (AC). After 10 min under vigorous agitation, the mixture was further filtered and distilled to obtain the pure BIPMF. Finally, the pure BIPMF was confirmed by nuclear magnetic resonance (NMR)

spectrometer (Bruker ADVANCE II) (Fig. S2). Moreover, other BAMFs, including 2,5-bis(ethoxymethyl)furan (BEMF), 2,5-bis(propoxymethyl)furan (BPMF), 2,5-bis(butoxymethyl)furan (BBMF) and 2,5-bis(sec-butoxymethyl)furan (BSBMF), were also synthesized by using the above method in the corresponding alcohols (Fig. S3-S6) and confirmed by NMR (Fig. S7-S10).

5-(Isopropoxymethyl)furfural (IPMF) synthesis

In order to synthesize the standard IPMF (Scheme S2), 1 g of HMF, 0.25 g of CT269DR and 49 g of iPrOH were mixed and added into a 100 mL of stainless steel autoclave, which was sealed and heated to 60 °C under a stirring rate of 400 rpm. After 24 h, the autoclave was rapidly quenched to RT. Note that HMF conversion and IPMF selectivity were greater than 98% (Fig. S11). Next, other procedures were the same to those of BIPMF. Finally, the pure IPMF was confirmed by NMR (Fig. S12).

5-Methyl-2-(isopropoxymethyl)furan (MIPMF) synthesis

For the standard MIPMF (Scheme S3), 1 g of MFA, 0.25 g of CT269DR and 49 g of iPrOH were mixed and added into a 100 mL of stainless steel autoclave, which was sealed and heated to 50 °C under a stirring rate of 400 rpm. After 20 h, the autoclave was rapidly quenched to RT. Note that MFA conversion and MIPMF selectivity were greater than 99% (Fig. S13). Next, other procedures were the same to those of BIPMF. Finally, the pure MIPMF was confirmed by NMR (Fig. S14).

Isopropyl furfuryl ether (IPFE) synthesis

For the standard IPFE (Scheme S4), 1 g of FFA, 0.25 g of CT269DR and 49 g of iPrOH were mixed and added into a 100 mL of stainless steel autoclave, which was

sealed and heated to 50 °C under a stirring rate of 400 rpm. After 20 h, the autoclave was rapidly quenched to RT. Note that FFA conversion and IPFE selectivity were greater than 98% (Fig. S15). Next, other procedures were the same to those of BIPMF. Finally, the pure IPFE was confirmed by NMR (Fig. S16).

Product analysis

The liquid samples were analyzed by gas chromatograph (GC, Shimadzu GC-2014), which were equipped with a flame ionization detector (FID) and a SK-WAX capillary column (30 m × 0.32 mm × 0.25 μm). For analysis, the injector temperature and detector temperature were set to 300 °C. Meanwhile, the initial column temperature was set to 40 °C and maintained for 2 min, and then, the column temperature was increased to 100 °C with a heating rate of 5 °C/min and maintained for 2 min, after that, the column temperature was further increased to 250 °C with a heating rate of 10 °C/min and maintained for 1 min. Moreover, HMF, BHMF, IPMF, HIPMF, BIPMF and other BAMFs were based on the following equations:

$$\text{HMF conversion (\%)} = (1-\frac{\text{Mole of HMF in products}}{\text{Initial mole of HMF}}) \times 100 \quad (1)$$

$$\text{BHMF yield (\%)} = \frac{\text{Mole of BHMF in products}}{\text{Initial mole of HMF}} \times 100 \quad (2)$$

$$\text{IPMF yield (\%)} = \frac{\text{Mole of IPMF in products}}{\text{Initial mole of HMF}} \times 100 \quad (3)$$

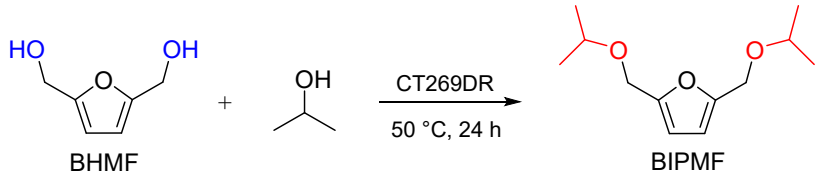
$$\text{HIPMF yield (\%)} = \frac{\text{Mole of HIPMF in products}}{\text{Initial mole of HMF}} \times 100 \quad (4)$$

$$\text{BIPMF yield (\%)} = \frac{\text{Mole of BIPMF in products}}{\text{Initial mole of HMF}} \times 100 \quad (5)$$

$$\text{BAMF yield (\%)} = \frac{\text{Mole of BAMF in products}}{\text{Initial mole of HMF}} \times 100 \quad (6)$$

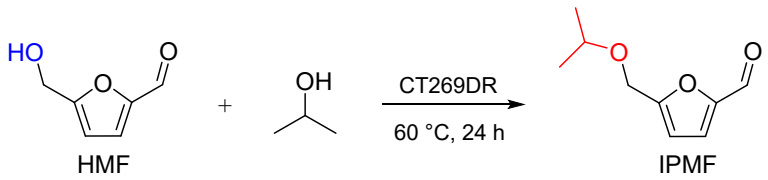
Catalyst recovery

To investigate the reusability of Zr-GC-SO_3H-1.0, when each reaction cycle was completed, the catalyst was removed by centrifugation from the reaction mixture, and washed with EtOH and ultrapure water (UPW) for five times, respectively. After drying at 80 °C for 12 h in a vacuum oven, the recovered catalyst was directly used for the next reaction cycle under the same reaction conditions.



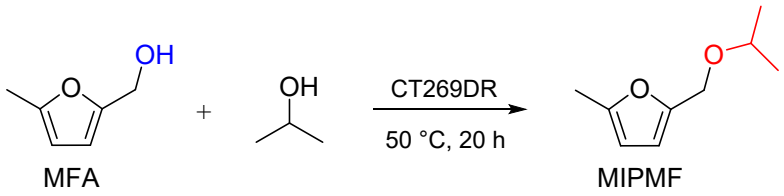
Scheme S1 Synthesis of BIPMF over CT269DR in iPrOH.

Reaction conditions: 1 g BHMF, 0.25 g CT269DR, 49 g iPrOH, 50 °C, 24 h.



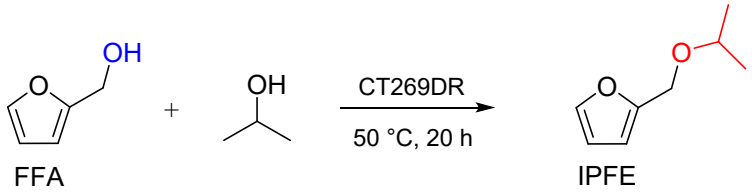
Scheme S2 Synthesis of IPMF over CT269DR in iPrOH.

Reaction conditions: 1 g HMF, 0.25 g CT269DR, 49 g iPrOH, 60 °C, 24 h.



Scheme S3 Synthesis of MIPMF over CT269DR in iPrOH.

Reaction conditions: 1 g MFA, 0.25 g CT269DR, 49 g iPrOH, 50 °C, 20 h.



Scheme S4 Synthesis of IPFE over CT269DR in iPrOH.

Reaction conditions: 1 g FFA, 0.25 g CT269DR, 49 g iPrOH, 50 °C, 20 h.

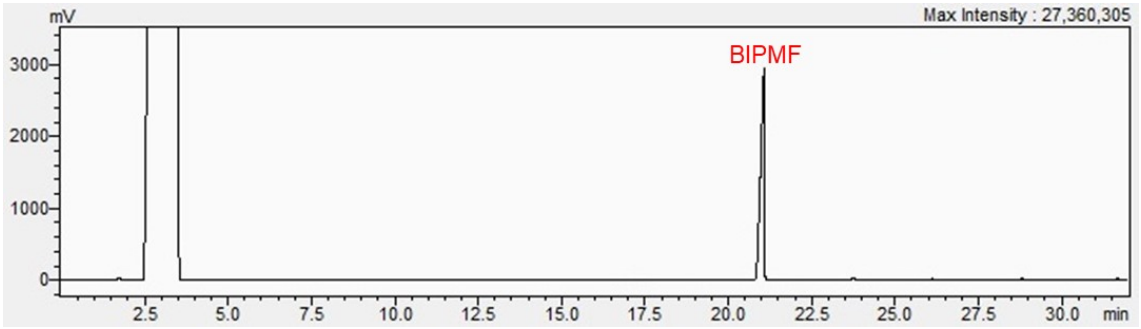


Fig. S1 GC chromatogram for the etherification of BHMF to BIPMF over CT269DR.

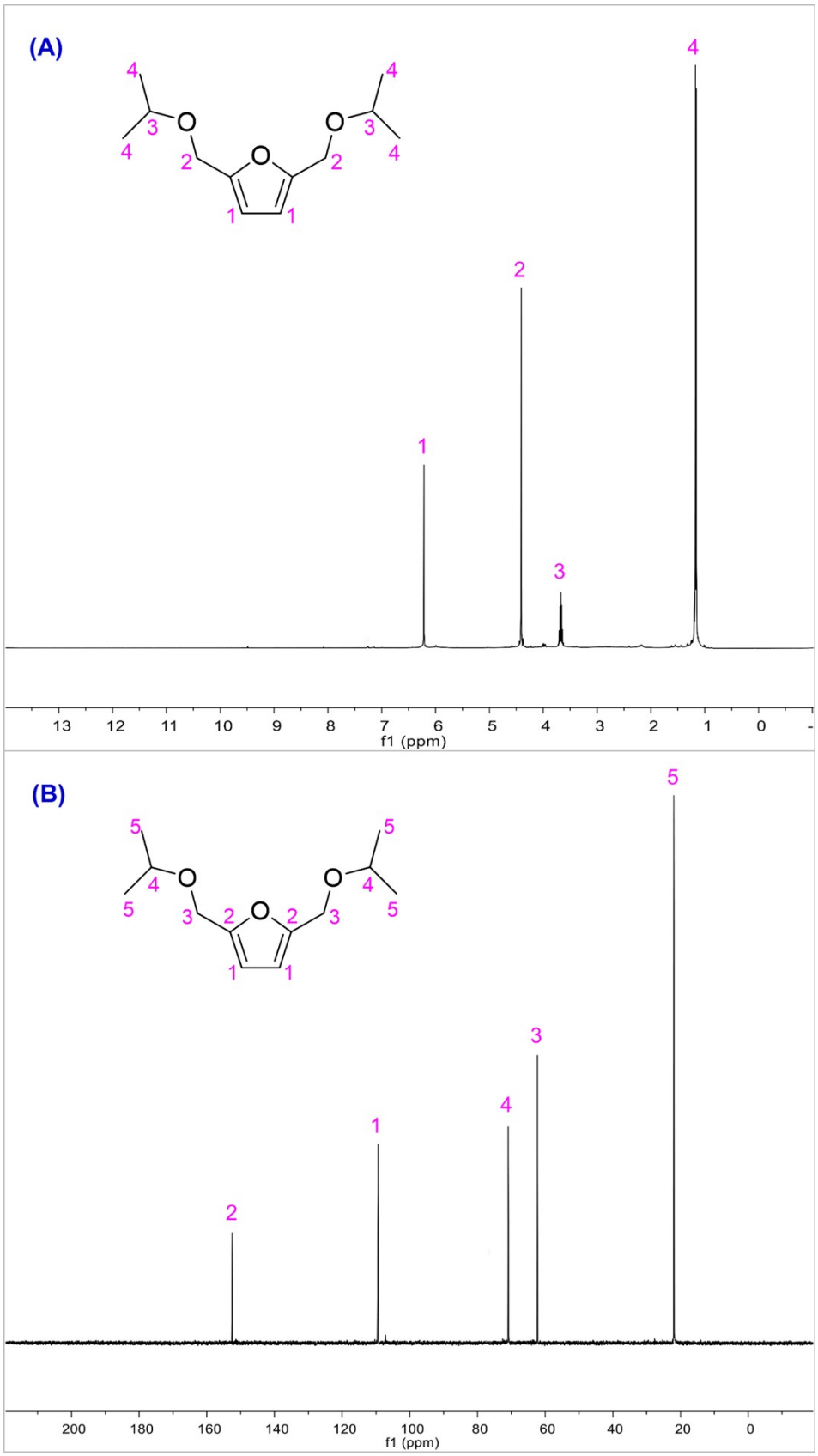


Fig. S2 ^{1}H NMR (A) and ^{13}C NMR (B) of BIPMF in $CDCl_3$.

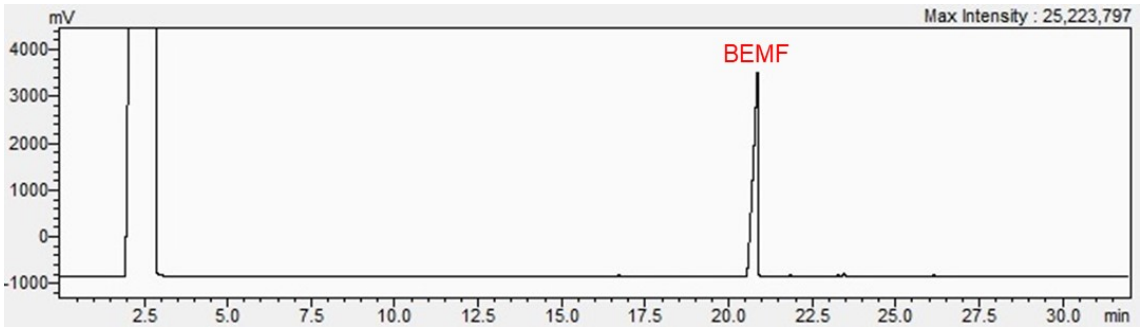


Fig. S3 GC chromatogram for the etherification of BHMF to BEMF over CT269DR.

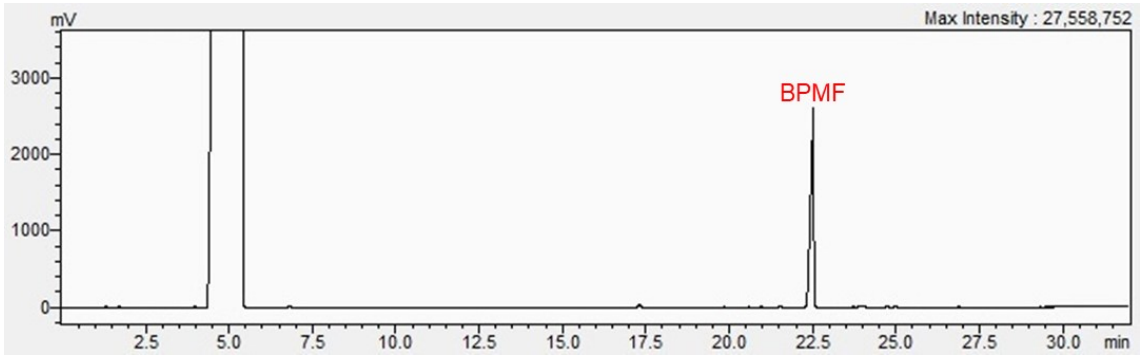


Fig. S4 GC chromatogram for the etherification of BHMF to BPMF over CT269DR.

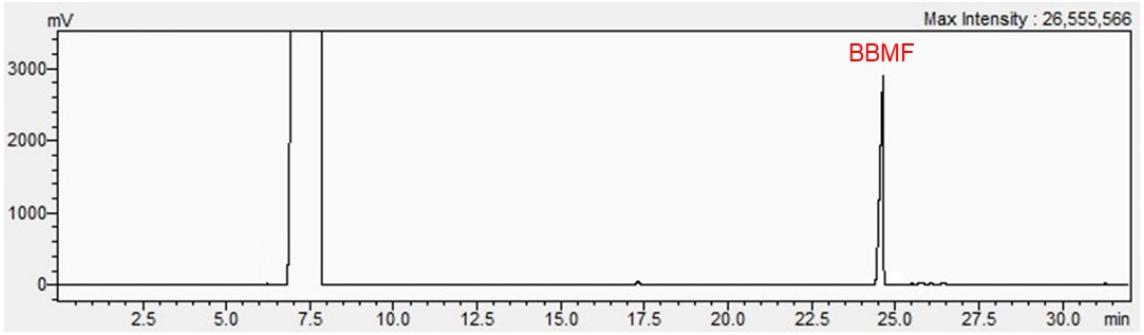


Fig. S5 GC chromatogram for the etherification of BHMF to BBMF over CT269DR.

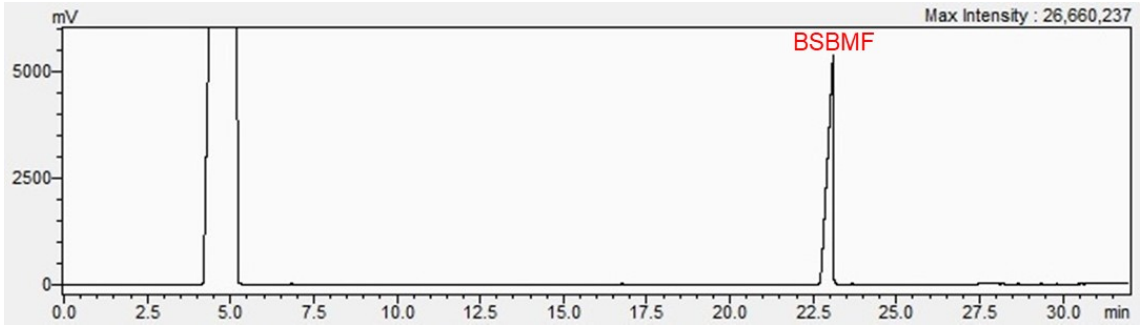


Fig. S6 GC chromatogram for the etherification of BHMF to BSBMF over CT269DR.

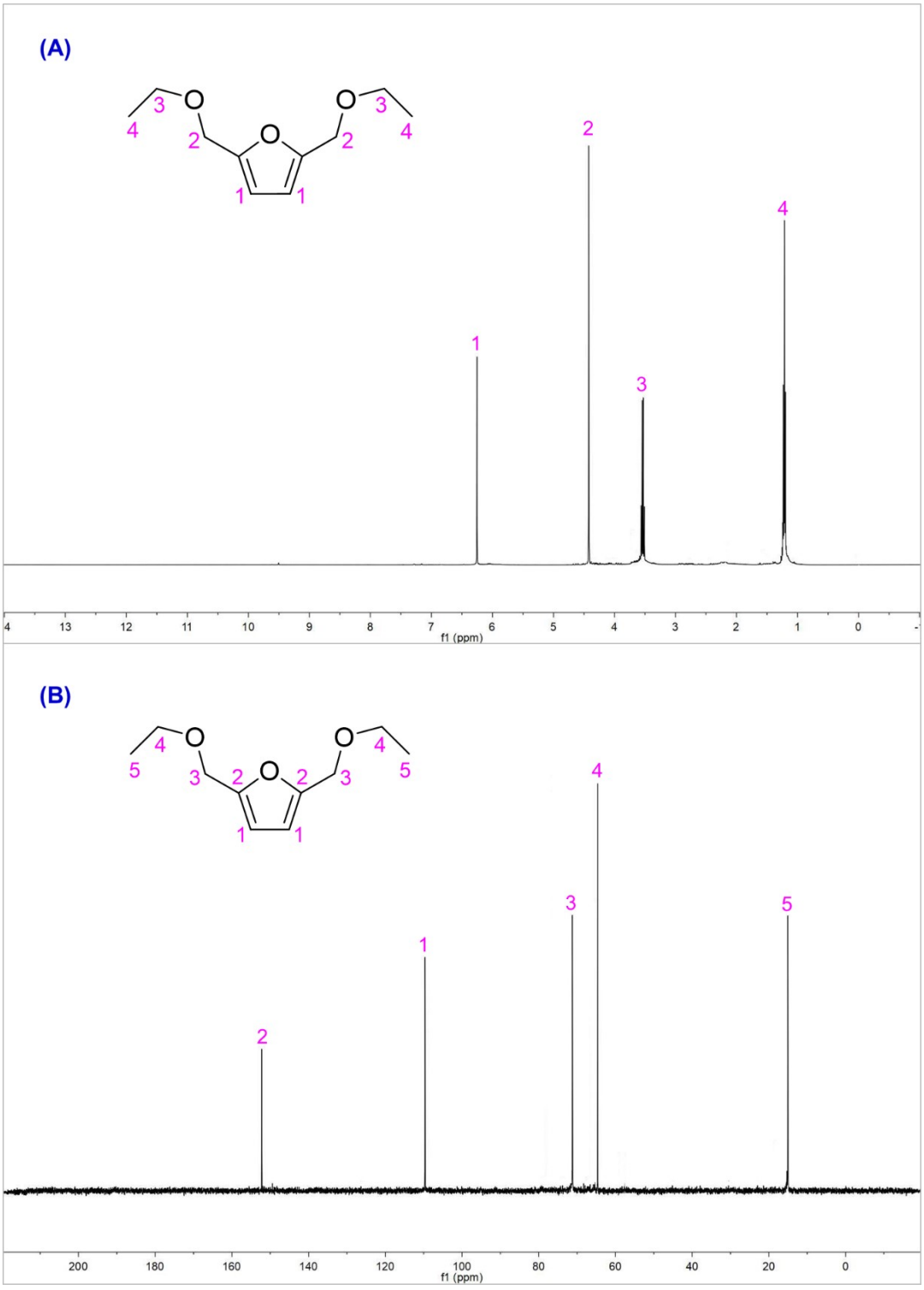


Fig. S7 ^{1}H NMR (A) and ^{13}C NMR (B) of BEMF in $CDCl_3$.

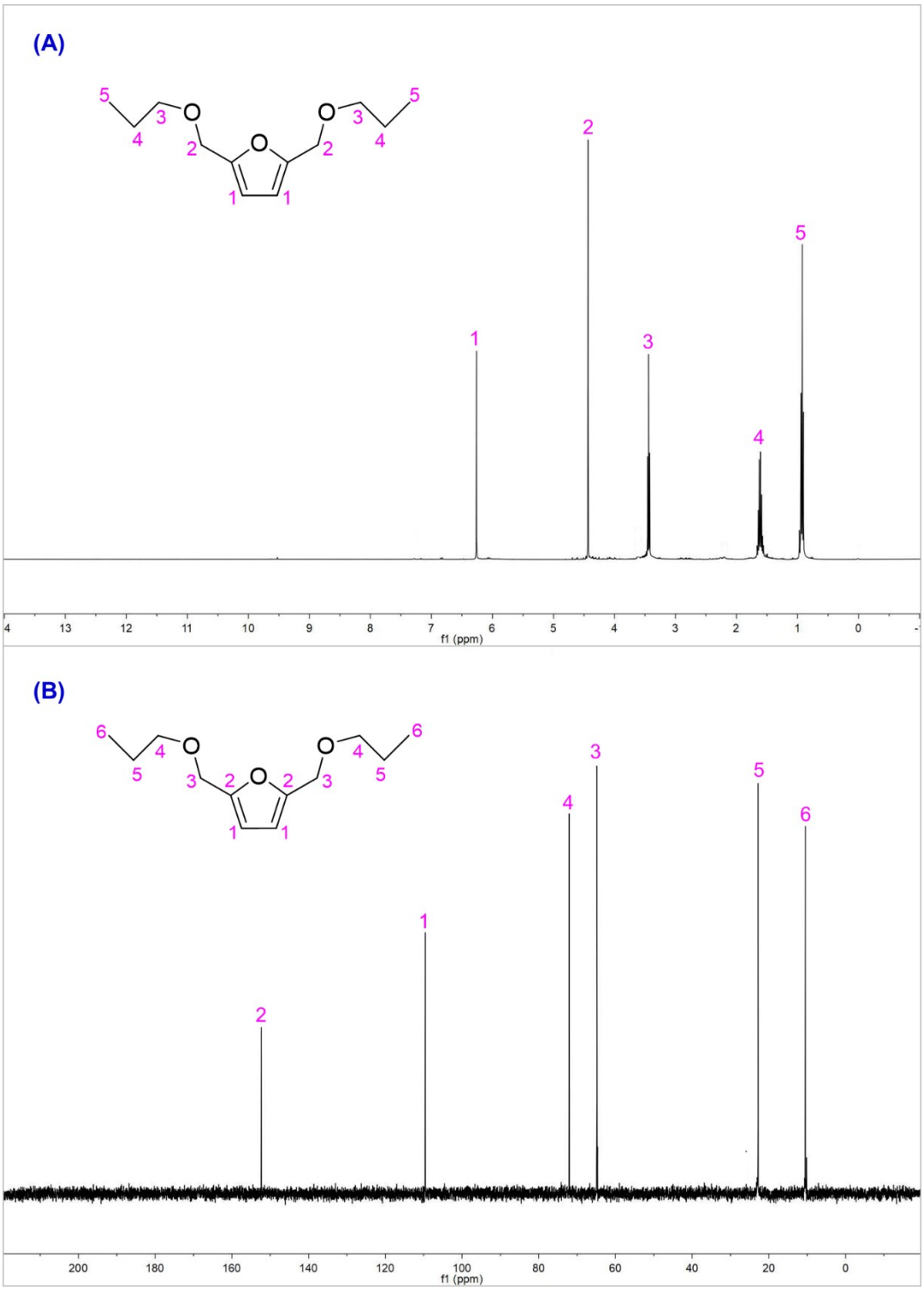


Fig. S8 ^{1}H NMR (A) and ^{13}C NMR (B) of BPMF in $CDCl_3$.

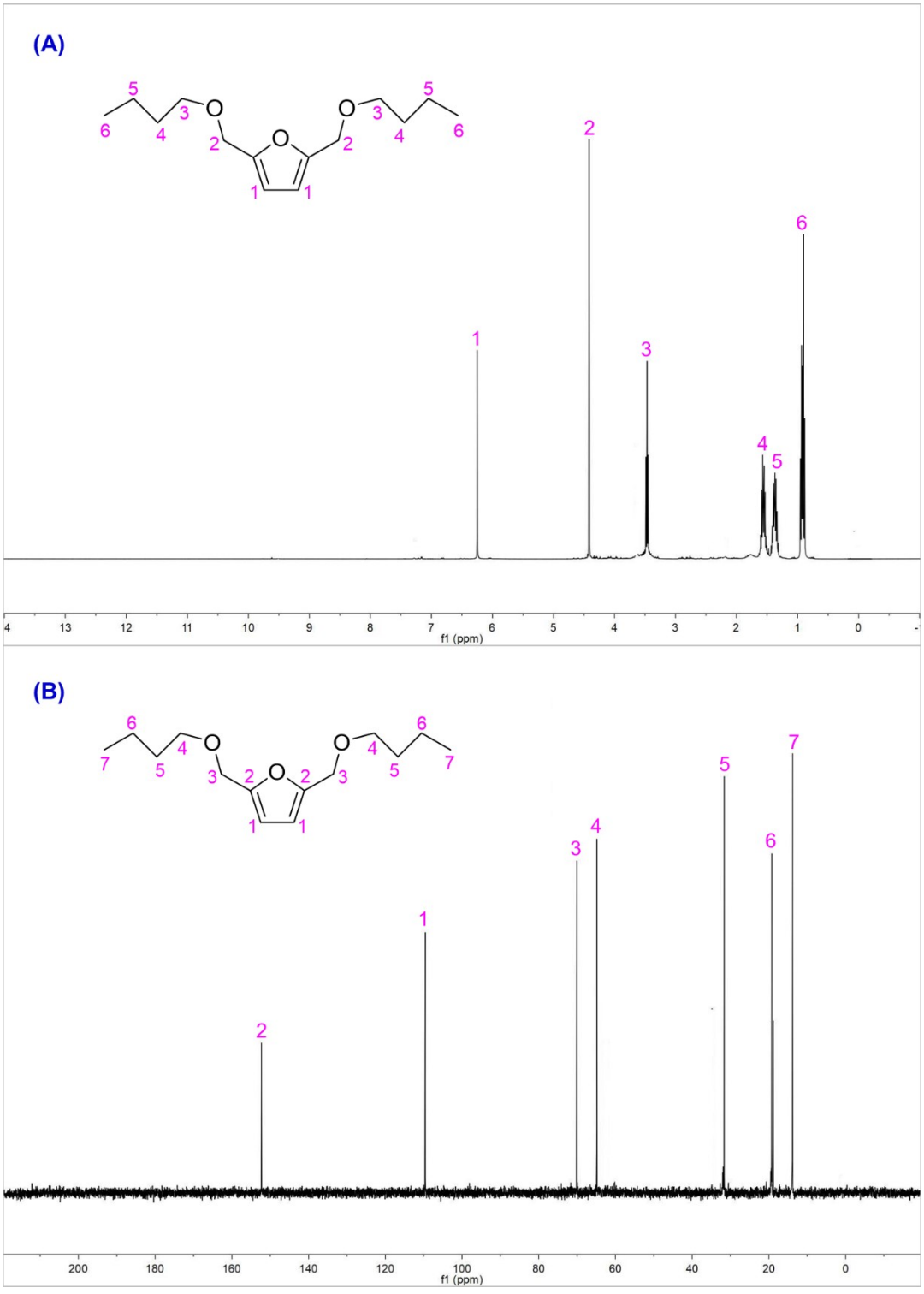


Fig. S9 ^{1}H NMR (A) and ^{13}C NMR (B) of BBMF in $CDCl_3$.

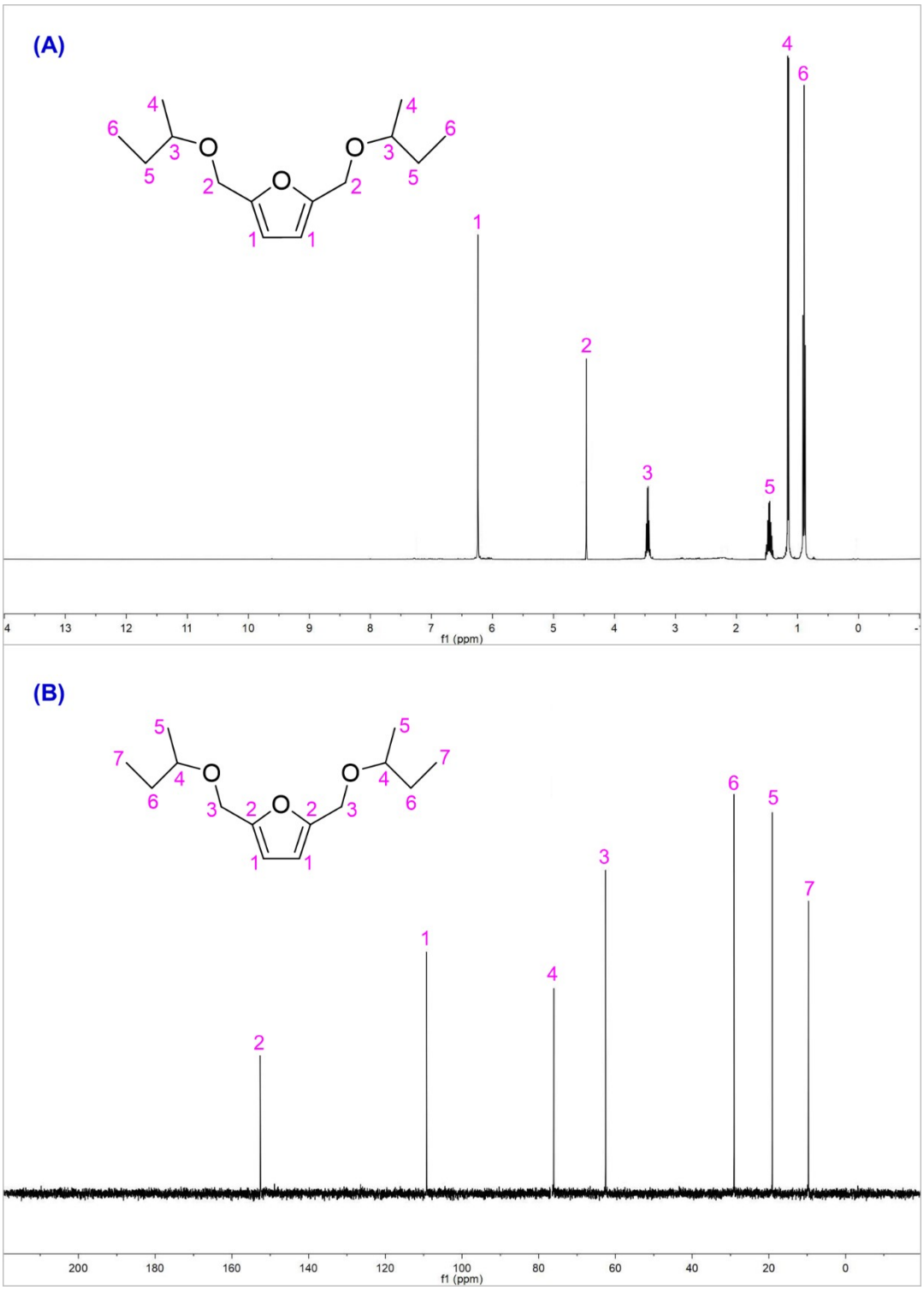


Fig. S10 ^{1}H NMR (A) and ^{13}C NMR (B) of BSBMF in $CDCl_3$.

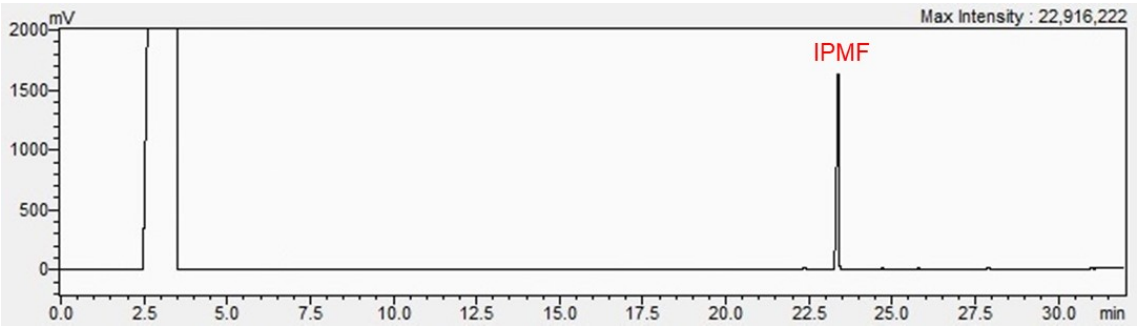


Fig. S11 GC chromatogram for the etherification of HMF to IPMF over CT269DR.

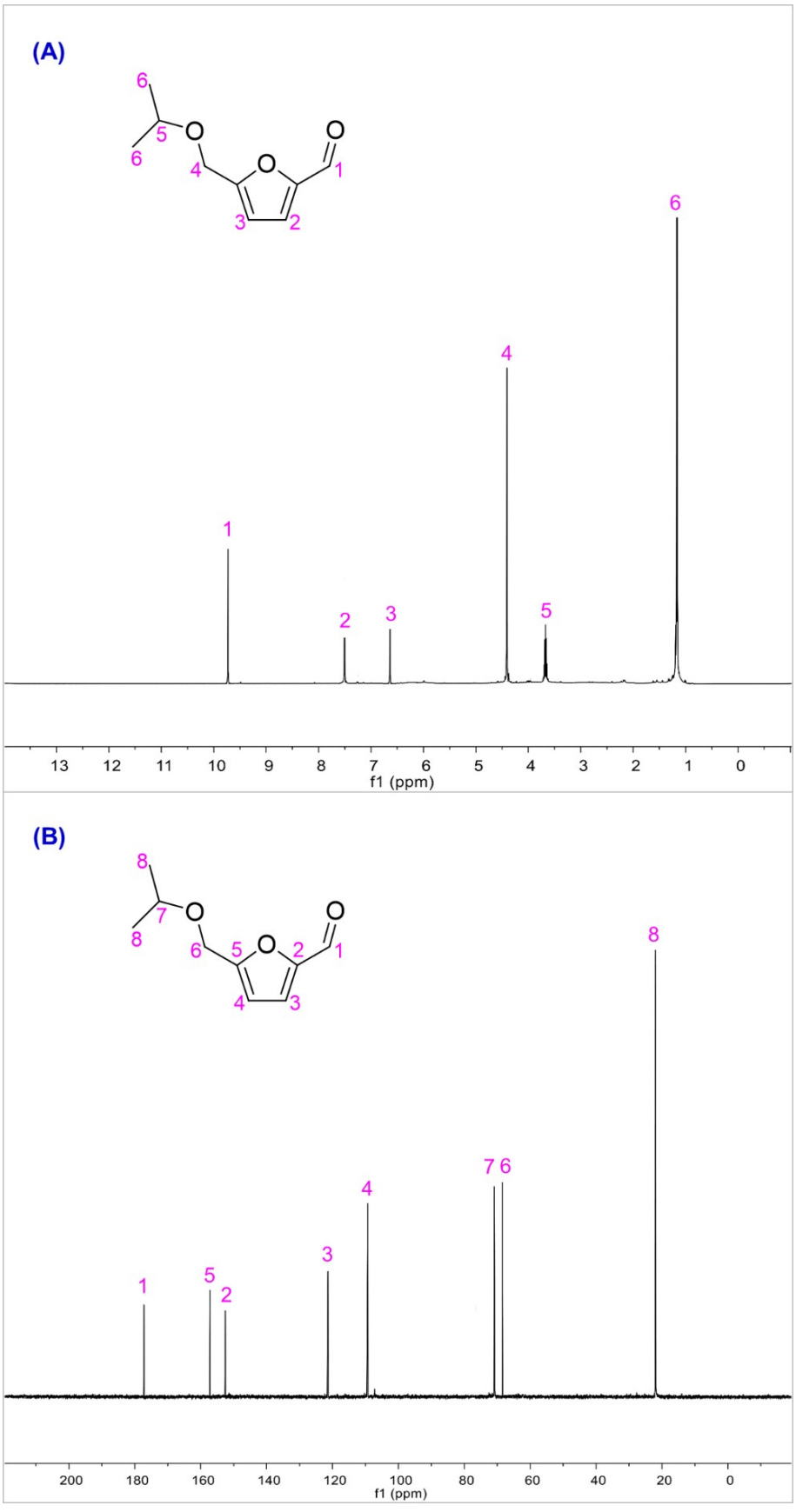


Fig. S12 ^{1}H NMR (a) and ^{13}C NMR (b) of IPMF in $CDCl_3$.

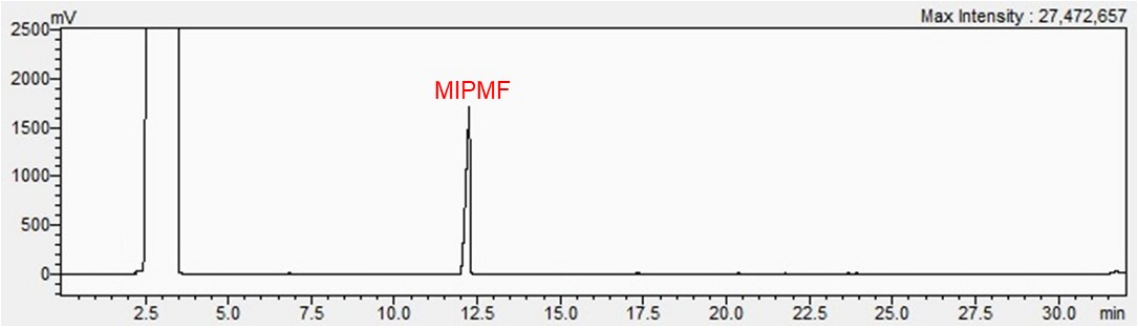


Fig. S13 GC chromatogram for the etherification of MFA to MIPMF over CT269DR.

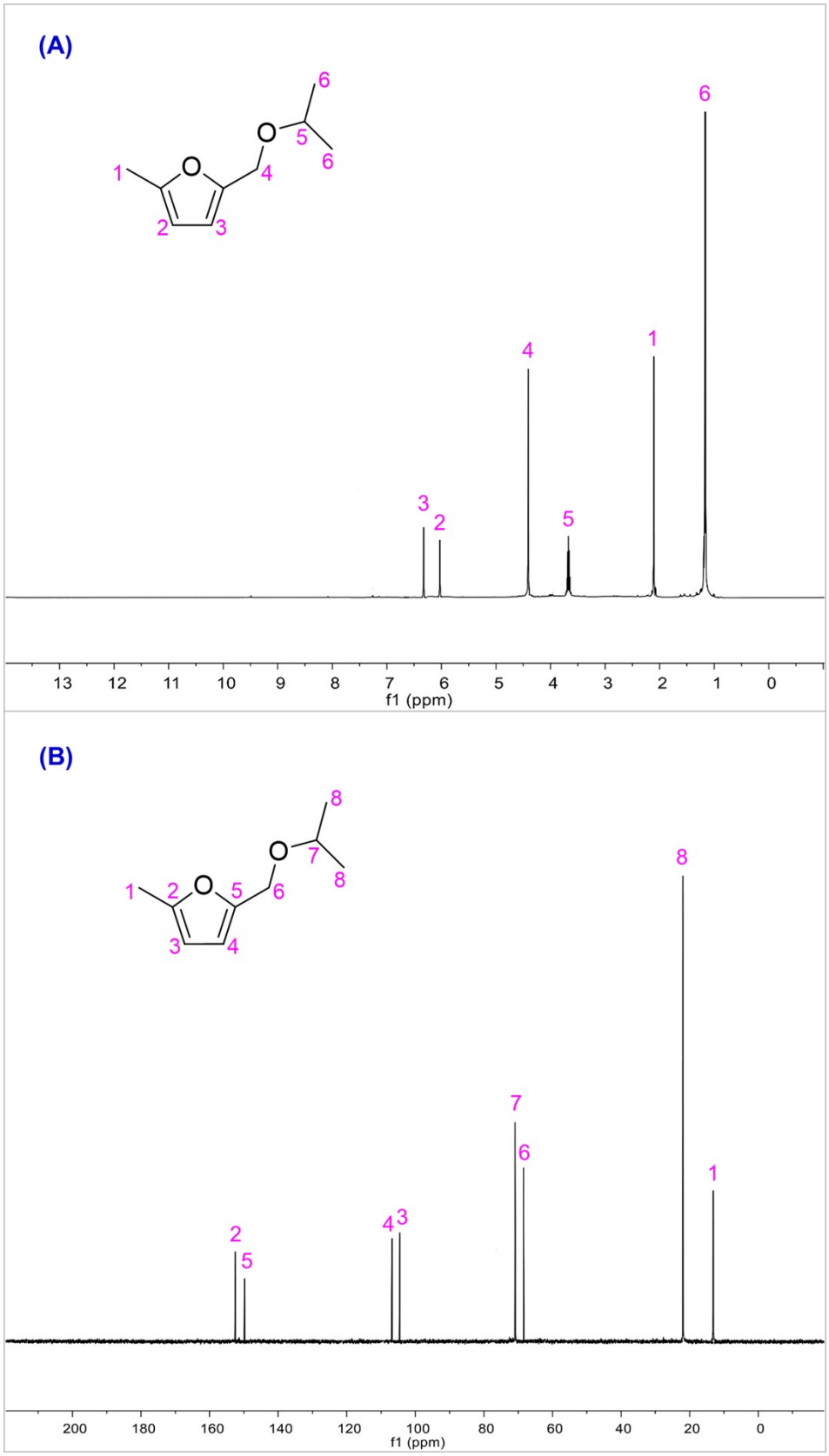


Fig. S14 ^{1}H NMR (a) and ^{13}C NMR (b) of MIPMF in $CDCl_3$.

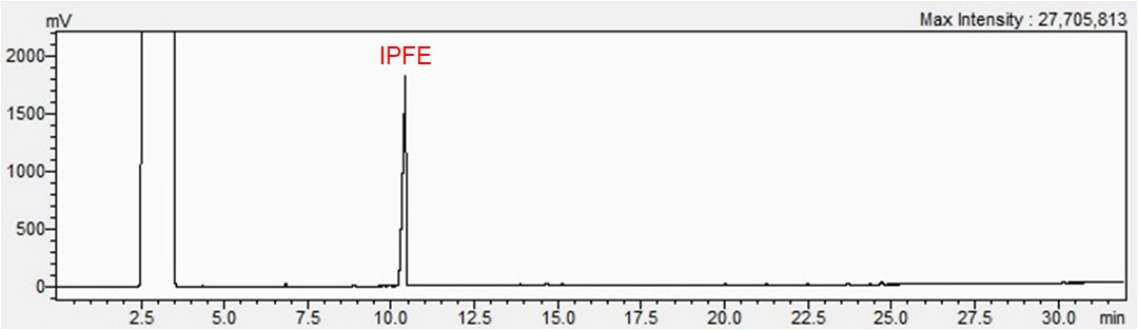


Fig. S15 GC chromatogram for the etherification of FFA to IPFE over CT269DR.

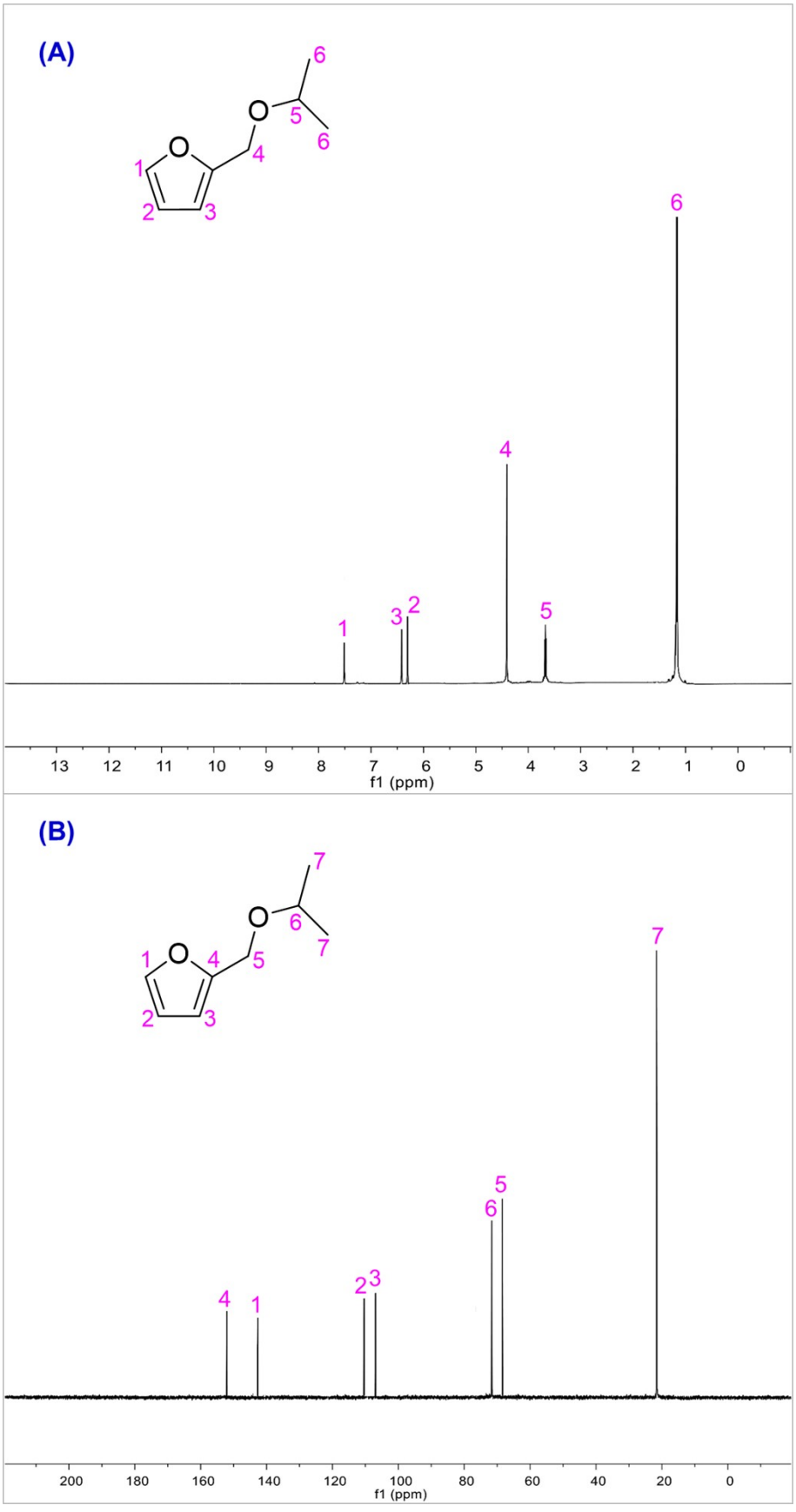


Fig. S16 ^{1}H NMR (a) and ^{13}C NMR (b) of IPFE in $CDCl_3$.

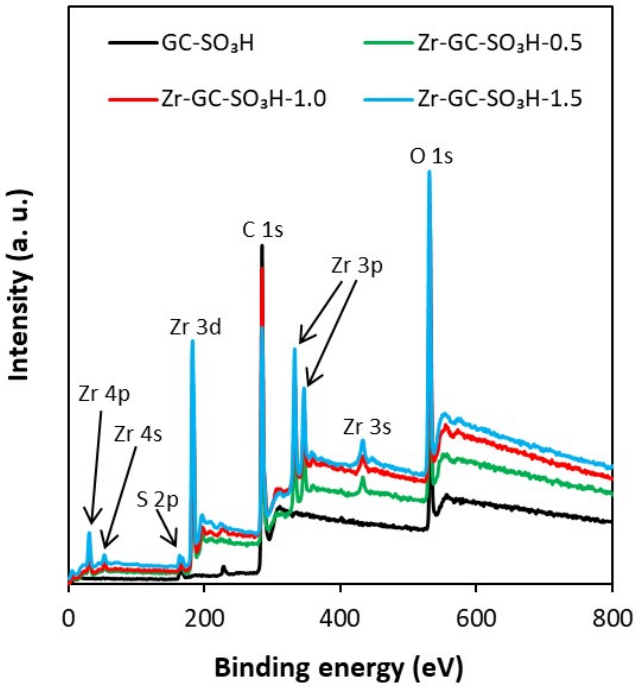


Fig. S17 XPS survey scan spectra of GC-SO_3H and Zr-GC-SO_3H-X.

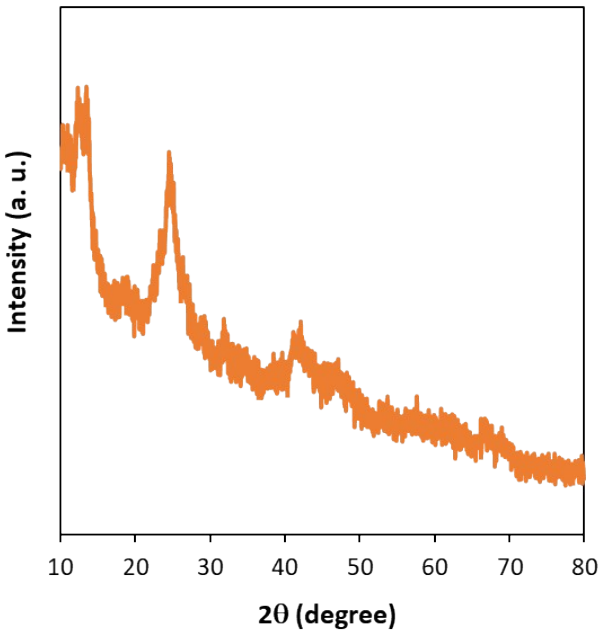


Fig. S18 XRD pattern of $ZrCl_4$.

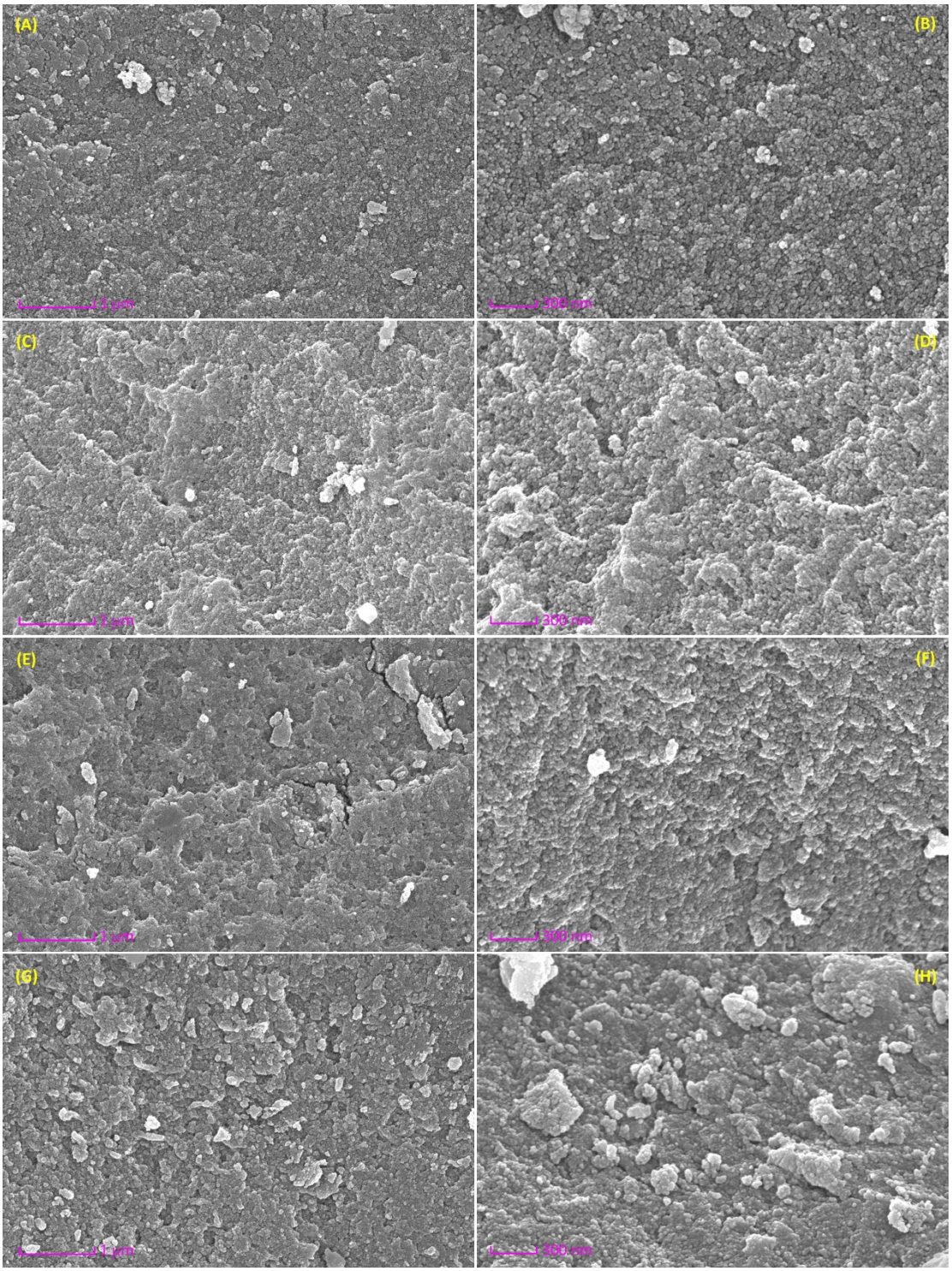


Fig. S19 SEM images of GC-SO_3H (A and B), Zr-GC-SO_3H-0.5 (C and D), Zr-GC-SO_3H-1.0 (E and F) and Zr-GC-SO_3H-1.5 (G and H).

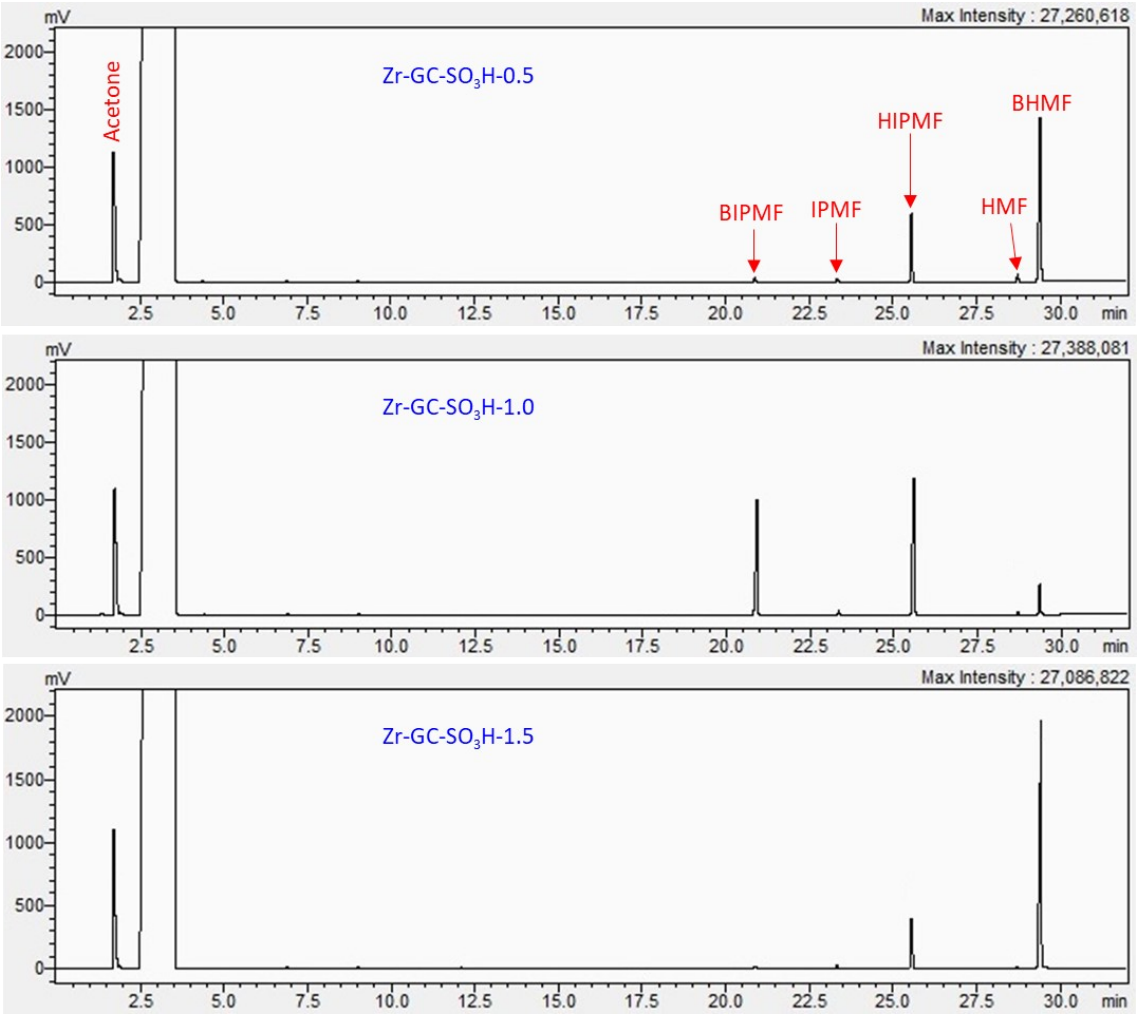


Fig. S20 GC chromatograms for the OPRE of HMF to BIPMF over Zr-GC-SO_3H-X.

Reaction conditions: 0.25 g HMF, 19.75 g iPrOH, 0.1 g Zr-GC-SO_3H-X, 140 °C, 4 h.

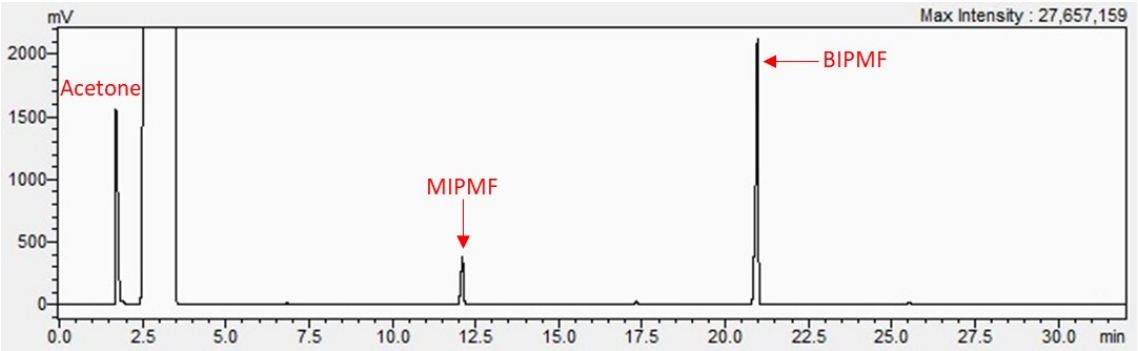


Fig. S21 GC chromatogram for the OPRE of HMF to BIPMF over Zr-GC-SO_3H-1.0.

Reaction conditions: 0.25 g HMF, 19.75 g iPrOH, 0.1 g Zr-GC-SO_3H-1.0, 180 °C, 7 h.

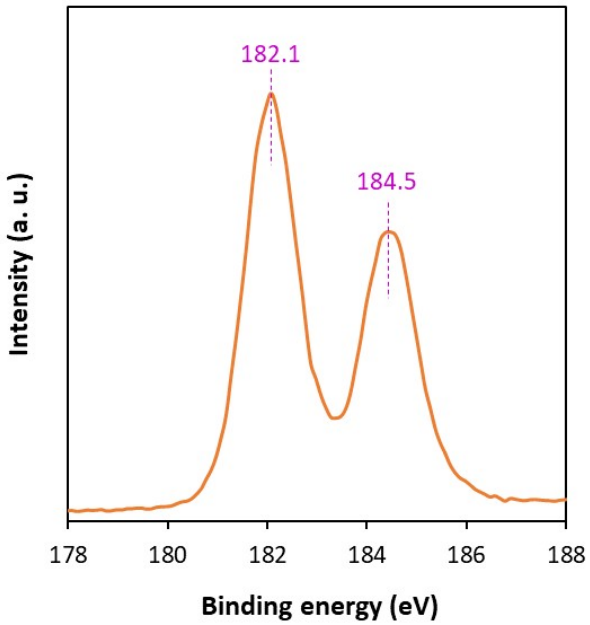


Fig. S22 Zr 3d XPS spectrum of ZrO_2.

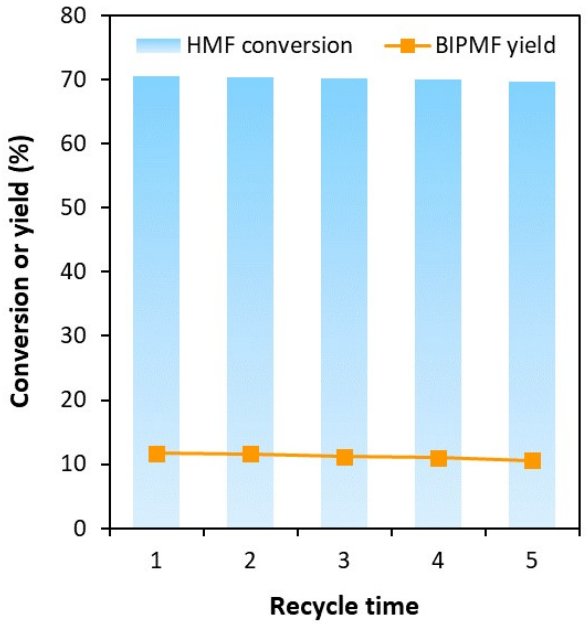


Fig. S23 Reusability of Zr-GC-SO_3H-1.0 in the OPRE of HMF to BIPMF.

Reaction conditions: 0.25 g HMF, 19.75 g iPrOH, 0.1 g Zr-GC-SO_3H-1.0, 130 °C, 4 h.

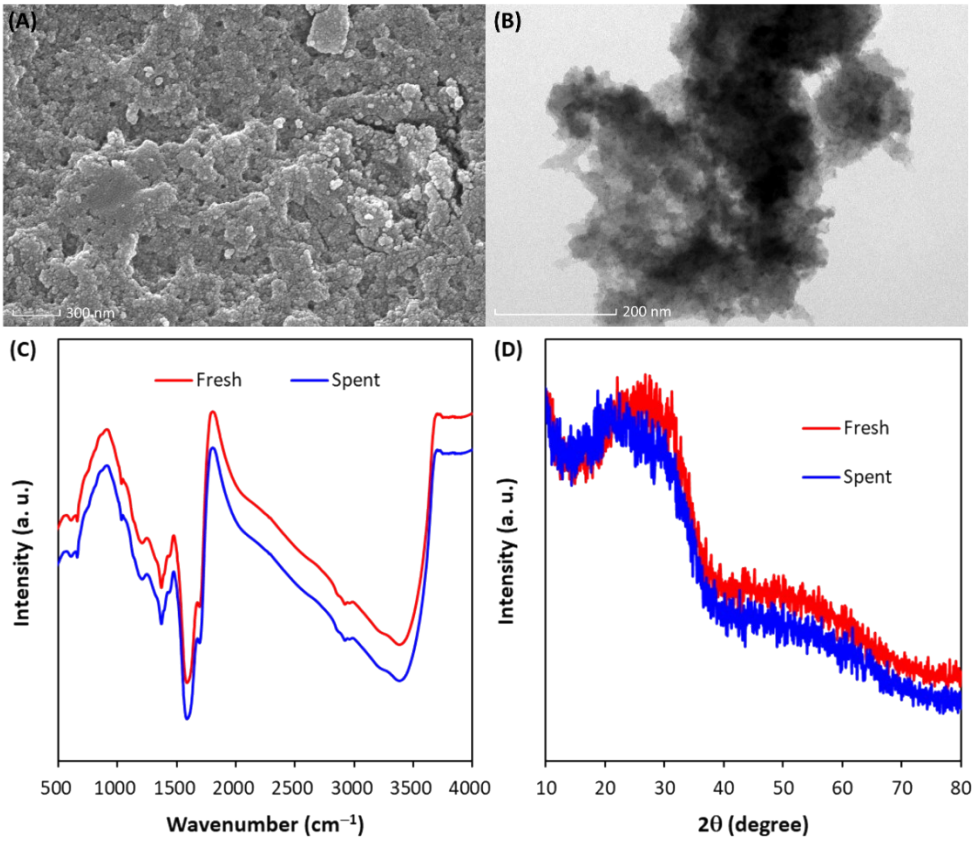


Fig. S24 SEM images (A), TEM images (B), FT-IR spectra (C) and XRD patterns (D) of the fresh and spent Zr-GC-SO_3H-1.0.

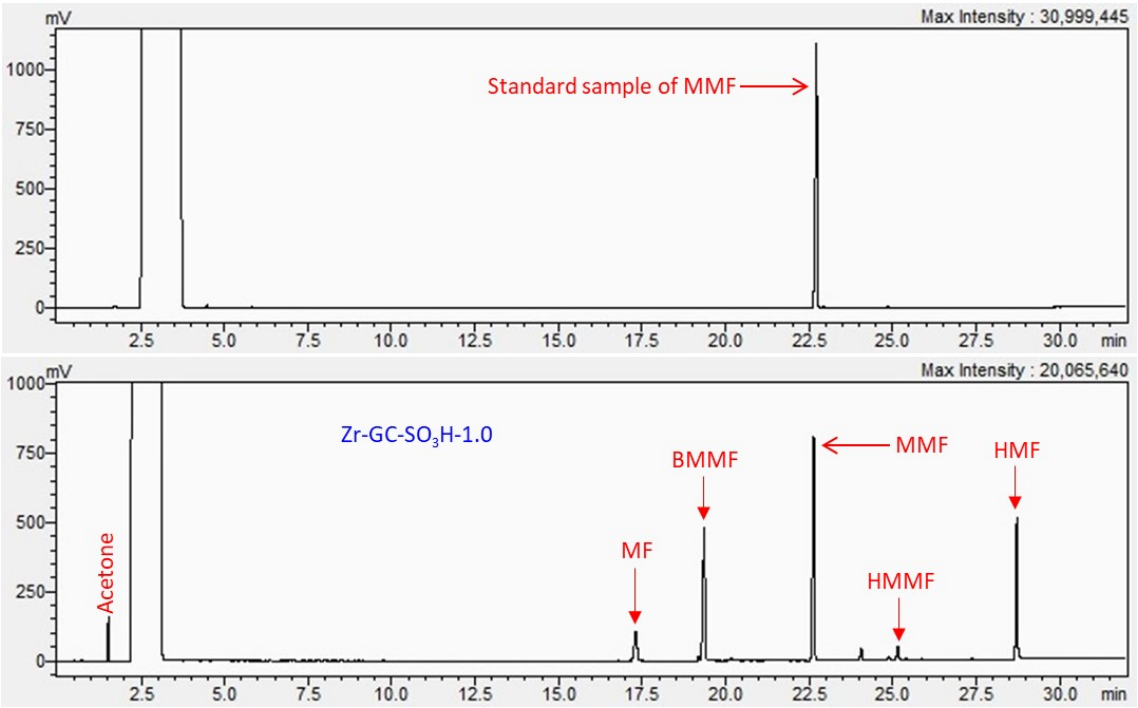


Fig. S25 GC chromatograms for the OPRE of HMF in MeOH over Zr-GC-SO_3H-1.0. Reaction conditions: 0.25 g HMF, 19.75 g MeOH, 0.1 g Zr-GC-SO_3H-1.0, 180 °C, 6 h.

Table S1 Physicochemical properties of various catalysts

Catalyst	Surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]	Pore size (nm)[b]	Acid content (mmol/g)[c]	Base content (mmol/g)[d]	L/B ratio[e]
ZrO_2	26.5	0.062	9.2	0.08	0.11	—
TsOH	—	—	—	—	—	—
GHTC	57.12	0.058	5.44	1.78	0.28	—
GC-SO_3H	260.23	0.115	3.37	2.27	0.49	—
Zr-GHTC	313.54	0.149	4.78	1.19	1.72	40.62
Zr-GC-SO_3H-0.5	235.46	0.107	3.11	1.84	0.96	5.37
Zr-GC-SO_3H-1.0	199.32	0.088	2.81	2.08	1.39	7.12
Zr-GC-SO_3H-1.5	135.86	0.052	2.62	2.34	1.67	8.81
Zr-GC-SO_3H-1.0[f]	190.65	0.081	2.67	1.96	1.28	7.01

[a] Surface areas were obtained by the method of BET. [b] Pore volumes and pore sizes were estimated by the method of BJH. [c] Acid contents were determined by the profiles of NH_3-TPD. [d] Base contents were determined by the profiles of CO_2-TPD. [e] L/B ratios were measured by the profiles of pyridine-adsorbed FT-IR at 110 °C. [f] The catalyst was reused for five reaction cycles.

Table S2 OPRE of HMF to BIPMF over Zr-GC-SO_3H-1.0 at the lower reaction temperatures

Entry	Temperature (°C)	Conversion (%)	Yield (%)			
			BHMF	IPMF	HIPMF	BIPMF
1	80	19.1	6.8	0.0	5.6	0.0
2	90	25.7	10.4	0.0	9.9	0.0
3	100	34.8	12.9	0.0	16.7	0.0
4	120	57.6	14.1	2.1	20.2	7.9

Reaction conditions: 0.25 g HMF, 19.75 g iPrOH, 0.1 g Zr-GC-SO_3H-1.0, 4 h.

Table S3 EA and ICP-AES of the fresh and spent Zr-GC-SO_3H-1.0

Catalyst	Element content (%)			
	C[a]	S[a]	H[a]	Zr[b]
Fresh	59.85	2.05	2.38	5.97
Spent	64.78	1.96	2.41	5.82

[a] C, S and H were measured by EA. [b] Zr was measured by ICP-AES.