

Supporting information for

# Scale-up Preparation, Column Chromatography-Free Purification of Protected Carbonyl Containing Biomass Molecules and Their Derivatizations

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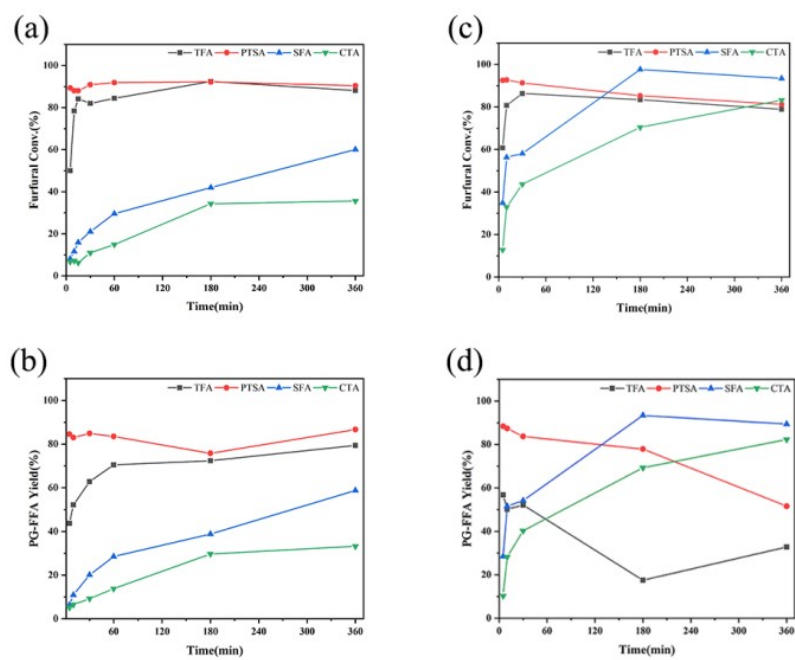
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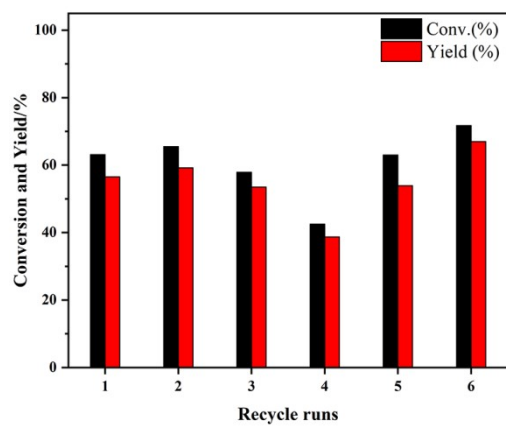
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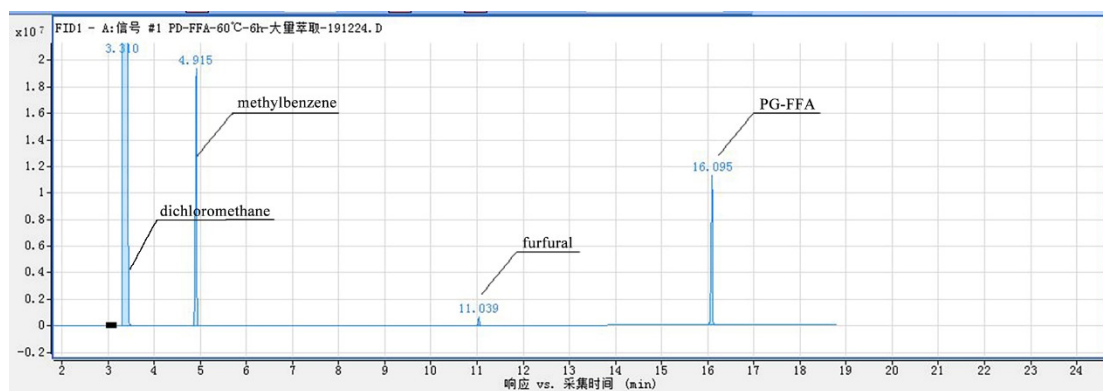
† These authors contributed equally.



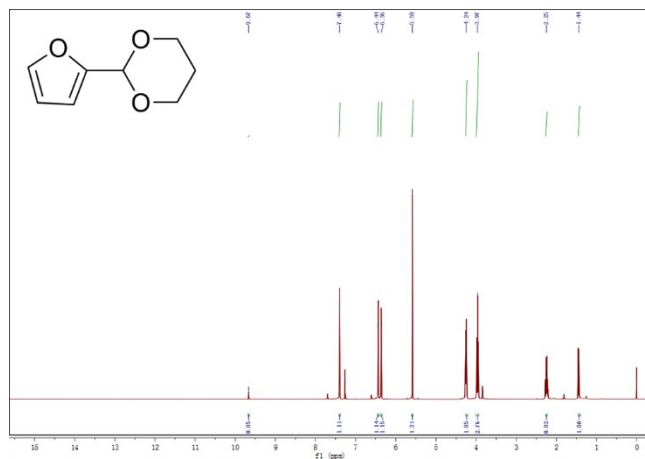
**Figure S1.** Effect of reaction time on furfural acetalization over sulfamic acid (SFA) catalyst. a) furfural conversion at 30 °C. b) PG-FFA yield at 30 °C. c) furfural conversion at 60 °C. d) PG-FFA yield at 60 °C. Reaction conditions: 1 mmol furfural, 4 mmol 1,3-propylene glycol, 1 mmol catalyst, 3 mL dichloromethane solvent.



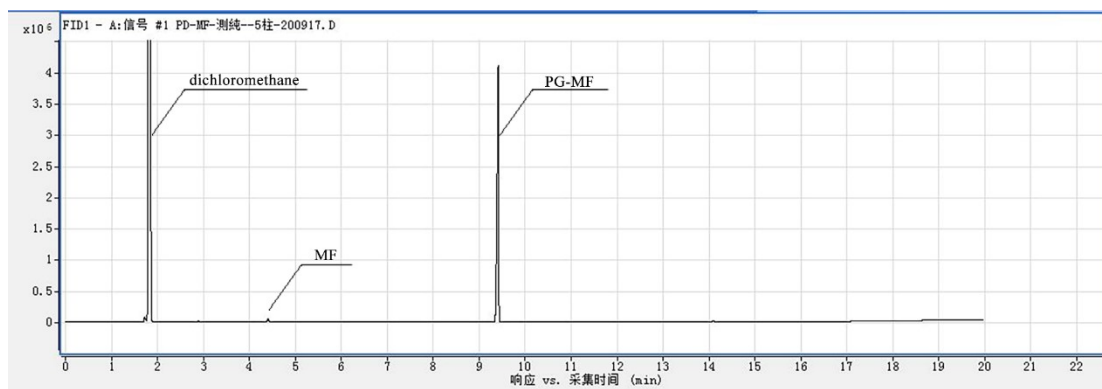
**Figure S2.** Recycling tests at a higher SFA loading. Reaction conditions: 1 mmol HMF, 4 mmol 1,3-propylene glycol, 1mmol SFA catalyst, 60 °C, 10 min, 3 mL dichloromethane solvent.



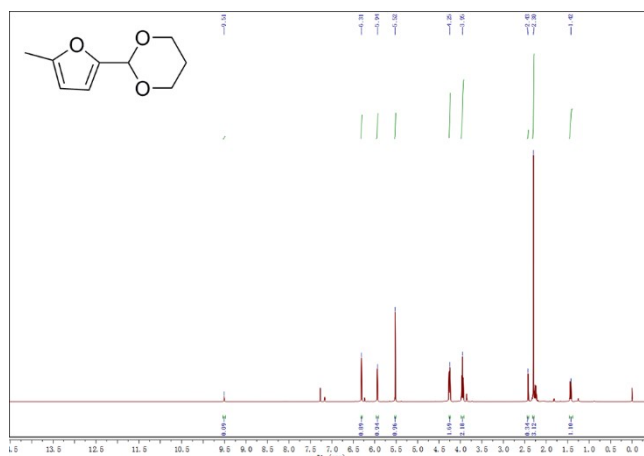
**Figure S3.** GC spectra of PG-FFA after purification. Reaction conditions: 10 mmol furfural, 40 mmol 1,3-propylene glycol, 1 mmol SFA catalyst, 60 °C, 6 h, 60 mL dichloromethane.



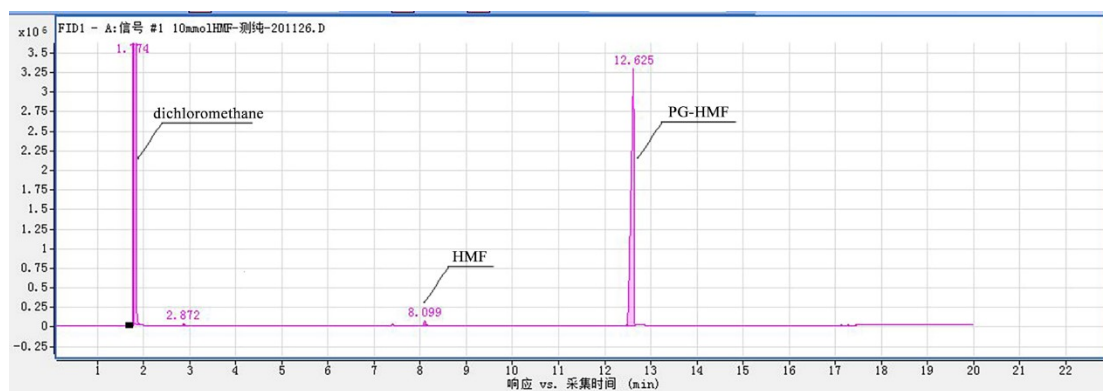
**Figure S4.** <sup>1</sup>H NMR spectra of PG-FFA after purification. Reaction conditions: 10 mmol furfural, 40 mmol 1,3-propylene glycol, 1 mmol SFA catalyst, 60 °C, 6 h, 60 mL dichloromethane. 2-(furan-2-yl)-1,3-dioxane (PG-FFA): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) 6.44 (d, 1H), 6.36 (d, 1H), 5.59 (s, 1H), 4.24 (m, 2H), 3.97 (m, 3H), 2.25 (m, 1H), 1.44 (m, 1H).



**Figure S5.** GC spectra of PG-MF after purification. Reaction conditions: 10 mmol MF, 60 mmol 1,3-propylene glycol, 1 mmol SFA catalyst, 80 °C, 6 h, 60 mL dichloromethane.

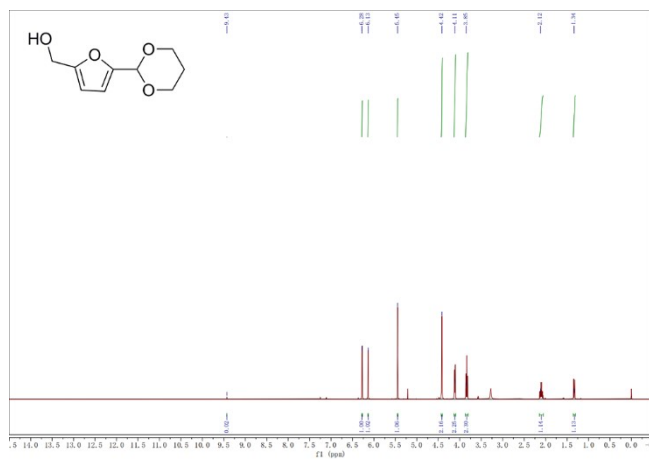


**Figure S6.** <sup>1</sup>H NMR spectra of PG-MF after purification. Reaction conditions: 10 mmol MF, 60 mmol 1,3-propylene glycol, 1 mmol SFA catalyst, 80 °C, 6 h, 60 mL dichloromethane. 2-(5-methylfuran-2-yl)-1,3-dioxane (PG-MF): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) 6.31 (d, 1H), 5.94 (d, 1H), 5.52 (s, 1H), 4.25 (s, 2H), 3.95 (m, 2H), 2.43 (m, 1H), 2.30 (m, 3H), 1.42 (m, 1H).

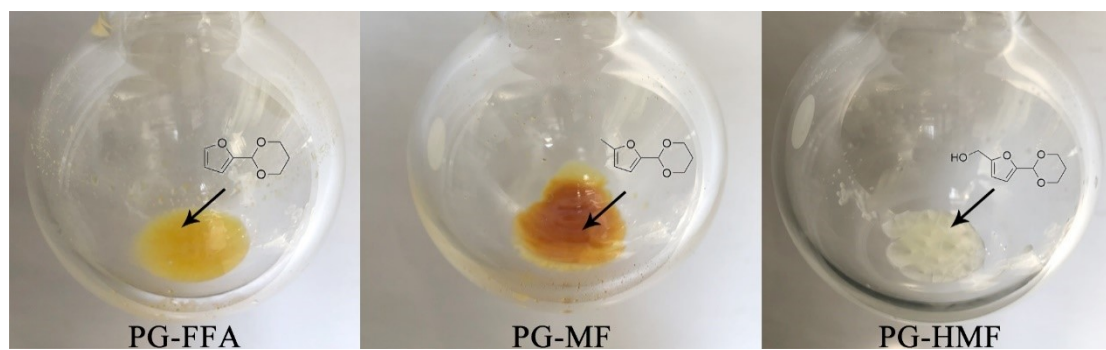


**Figure S7.** GC spectra of PG-HMF after purification. Reaction conditions: 10 mmol HMF, 70 mmol 1,3-propylene glycol, 3 mmol SFA catalyst, 25 °C, 0.5 h, 60 mL dichloromethane.

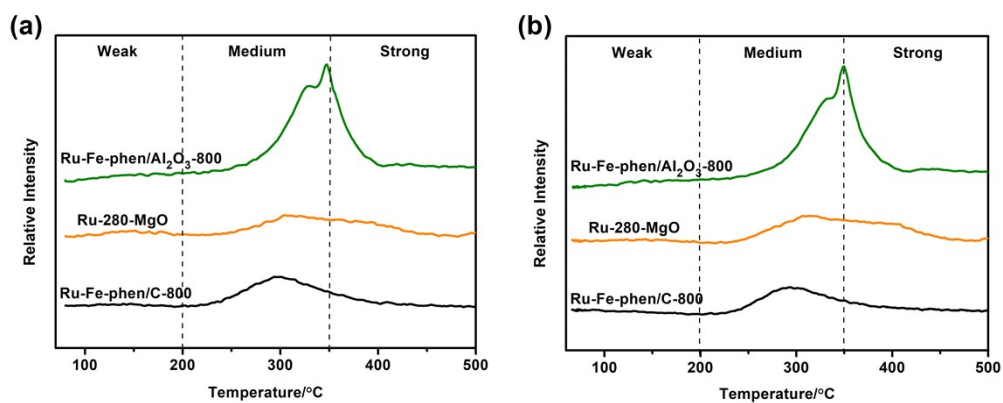




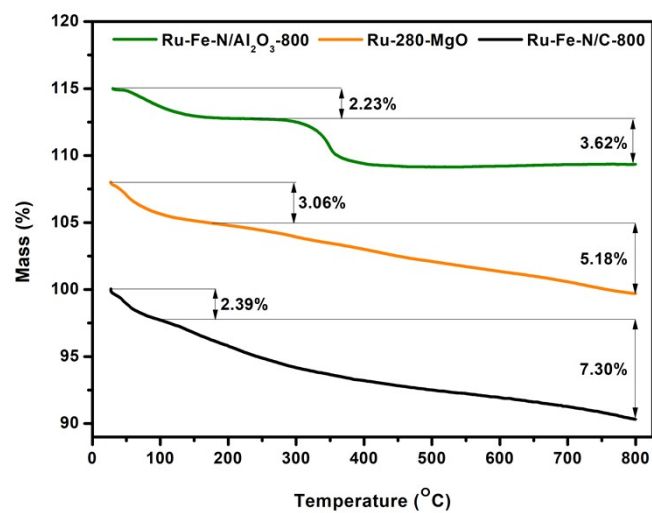
**Figure S8.**  $^1\text{H}$  NMR spectra of PG-HMF after purification. Reaction conditions: 10 mmol HMF, 70 mmol 1,3-propylene glycol, 3 mmol SFA catalyst, 25 °C, 0.5 h, 60 mL dichloromethane. (5-(1,3-dioxan-2-yl)furan-2-yl)methanol (PG-HMF):  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ), 6.25 (d, 1H), 6.12 (d, 1H), 5.43 (s, 1H), 4.38 (s, 2H), 4.08 (m, 2H), 3.81 (m, 2H), 2.06 (m, 1H), 1.30 (m, 1H).



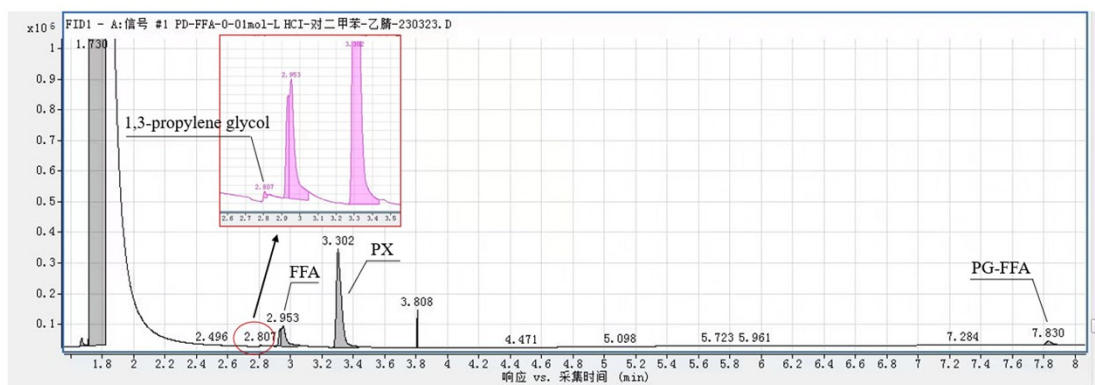
**Figure S9.** Purified acetals of FFA, MF, and HMF. Reaction conditions: PG-FFA:10 mmol furfural, 40 mmol 1,3-propylene glycol, 1 mmol SFA catalyst, 60 °C, 6 h, 60 mL dichloromethane. PG-MF:10 mmol MF, 60 mmol 1,3-propylene glycol, 1 mmol SFA catalyst, 80 °C, 6 h, 60 mL dichloromethane. PG-HMF:10 mmol HMF, 70 mmol 1,3-propylene glycol, 3 mmol SFA catalyst, 25 °C, 0.5 h, 60 mL dichloromethane.



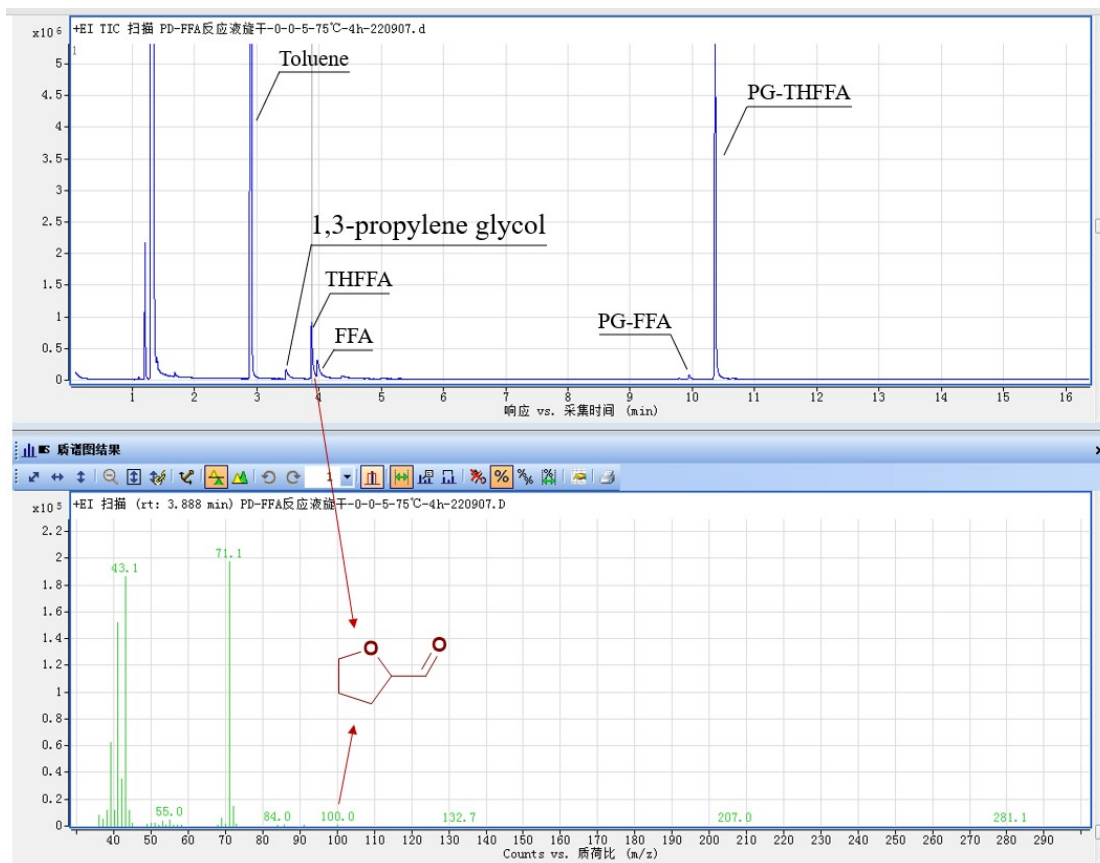
**Figure S10.**  $\text{NH}_3$ - (a) and  $\text{CO}_2$ -TPD (b) profiles of the Ru-Fe-phen/ $\text{Al}_2\text{O}_3$ -800, Ru-280-MgO and Ru-Fe-phen/C-800 catalysts.



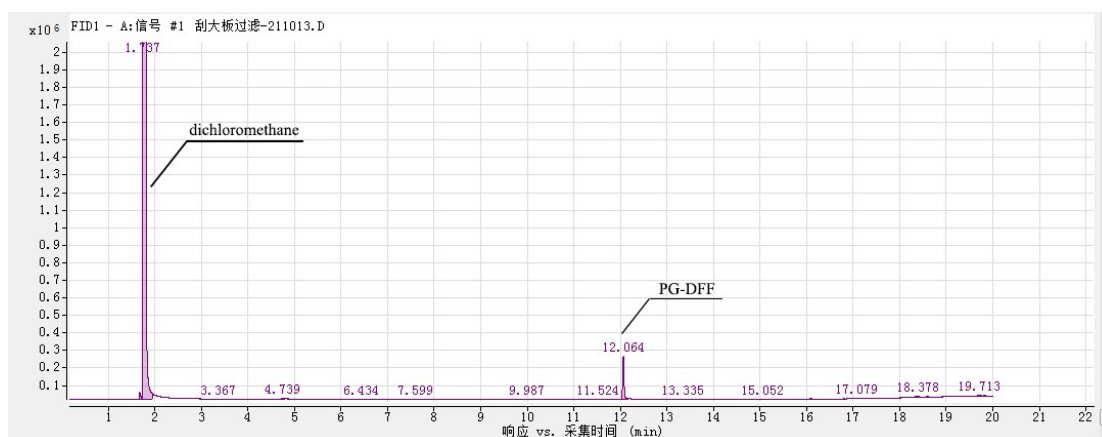
**Figure S11.** TGA profiles of Ru-Fe-phen/Al<sub>2</sub>O<sub>3</sub>-800, Ru-280-MgO and Ru-Fe-phen/C-800 catalysts.



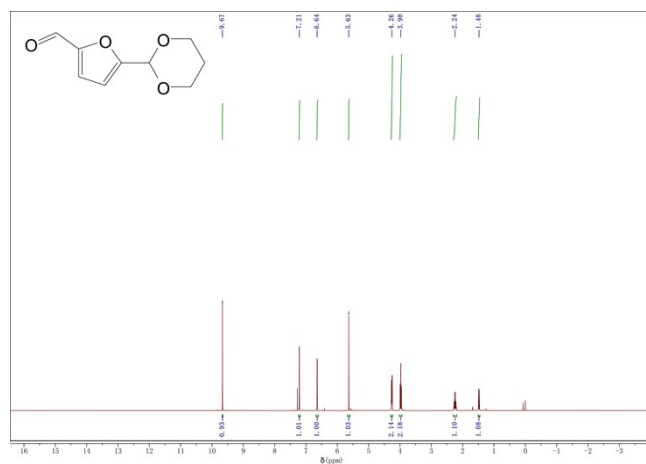
**Figure S12.** GC spectrum of the product solution after deprotection of PG-FFA. Deprotection conditions: 0.25 mmol PG-FFA, 2 mL 0.01 mol/L HCl aqueous solution, room temperature, 30 s. After deprotection, the solution is neutralized by 0.05 mol/L NaOH aqueous solution, and then diluted 10 fold with  $\text{CH}_3\text{CN}$  to collect the GC spectrum.



**Figure S13.** GC-MS spectra of the extracted solution after deprotection of PG-THFFA. PG-THFFA is first obtained by ring hydrogenation of PG-FFA. After removal of heterogeneous catalyst, 2 mL 0.05 mol/L HCl aqueous solution is added, and the deprotection is operated at 75 °C for 4 h. Then the solution is neutralized by NaOH followed by extraction by dichloromethane for three times.

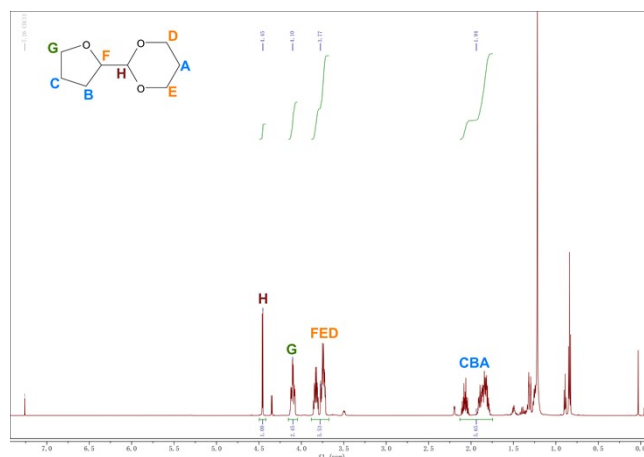


**Figure S14.** GC spectrum of PG-DFF after purification. Reaction conditions: 1 mmol DFF, 2 mmol 1,3-propylene glycol, 0.3 mmol SFA catalyst, 25 °C, 8 h, 6 mL dichloromethane. After reaction, PG-DFF is purified via preparative thin-layer chromatography (PTLC) using dichloromethane and ethyl acetate as elution solvents. The colored product under UV light was scraped off and transferred into a glass flask. Dichloromethane was then used to dissolve PG-DFF, and solid silica gel was removed by filtration. The rotary evaporation of liquid fraction afforded pure PG-DFF sample.



**Figure S15.** <sup>1</sup>H NMR spectra of purified PG-DFF. 5-(1,3-dioxan-2-yl)furan-2-carbaldehyde (PG-DFF): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), 9.67 (s, 1H), 7.21 (d, 1H), 6.64 (d, 1H), 5.63 (s, 1H), 4.26 (m, 2H), 3.98 (m, 2H), 2.24 (m, 1H), 1.48 (m, 1H).





**Figure S16.** <sup>1</sup>H NMR spectra of crude sample of acetal of tetrahydrofurfural (PG-THFFA). PG-THFFA was obtained from ring hydrogenation of furfural. Reaction conditions: 0.5 mmol furfural, 160 °C, 2 h, 4 MPa H<sub>2</sub>, 100 mg catalyst, 20 mL THF. After reaction, heterogeneous Ru-280-MgO catalyst was removed via filtration, and then the solvent in percolate was removed by rotating evaporation at 40 °C.

**Table S1.** Protection group effect in HDO reactions over 1%Ru-Fe-phen/C-800 using 5-20 mmol substrates.<sup>a</sup>

Entry	Substrate	Mol. /mmol	Conv. /%	Selectivity /%			
				DMF	MF	PG-MF	PG-M
1	MF	5	99	85.4	-	-	-
2		20	88.9	56.9	-	-	-
3	PG-MF	5	98.1	80.0	1.7	-	-
4		20	91.4	38.7	12.8	-	-
5	HMF	5	>99.9	64.6	-	-	-
6	PG-HMF	5	>99.9	36.9	-	-	-

<sup>a</sup> Reaction conditions: 240 °C, 12 h, 4 MPa H<sub>2</sub>, 100 mg catalyst, 10 mL THF in reactions using 5-20 mmol substrates.

**Table S2.** Photo-oxidation of HMF and its acetals over TiO<sub>2</sub> and Cd<sub>1.5</sub>In<sub>2</sub>S<sub>4.5</sub>.<sup>a</sup>

Entry	Catalyst	Substrate	Conc./ mmol	Incident light/nm	t	Conv./%	Yield/%		Sel./ %	
							DFF	PG-DFF		
1	TiO <sub>2</sub> , anatase	HMF	0.1	467	4	19.46	3.76	-	19.3	
2		PG-HMF				7.5	-	4.1	54.7	
3		HMF	0.02	White light <sup>b</sup>		>99.9	5.53	-	5.53	
4		PG-HMF				>99.9	-	3.86	3.86	
5	P25	HMF	0.1	467	12	16.56	2.68	-	6.2	
6		PG-HMF				30.6	-	3.63	11.7	
7	Cd <sub>1.5</sub> In <sub>2</sub> S <sub>4.5</sub>	HMF	0.1	467		6	93.9	4.7	-	5.0
8		PG-HMF					91.9	-	6.7	7.3

<sup>a</sup> Reaction conditions: 0.02-0.1 mmol substrate, 20 mg photocatalyst,  $\lambda = 467$  nm, room temperature, O<sub>2</sub> balloon, 3 mL CH<sub>3</sub>CN. <sup>b</sup>Xe lamp.  $\lambda = 320$ -780 nm.