Supporting information

Synthesis procedures

Synthesis of IPL

The synthesis of i-propyl levulinate was according to previous literature.[1] 0.1 mL H_2SO_4 was added into a mixture of levulinic acid (0.58 g, 5 mmol), and i-propanol (0.75 g, 12.5 mmol) in toluene (15 mL) under reflux. After refluxing the mixture for 4 h, the mixture was cooled to room temperature. Subsequently, the mixture was added into 20 mL dichloromethane and washed twice with 10 mL water. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated with vacuum distillation at 70 ^oC to yield 2-propyl levulinate as a yellowish liquid. The yield was determined by using H-NMR method with DMSO as internal standard. The purity of the product was analyzed by H-NMR analysis and used to calculate the correction factor with reaction standard for GC analysis (Figure S4).

Synthesis of IPMF.

1 mmol 5-hydroxymethylfurfural and 5 mL 2-propanol were charged into a 35 mL glass reaction tube with 0.2 mmol H_2SO_4. The mixture was stirred and heated to 110 ^oC for 2 h. After that, the mixture was evaporated at 60 ^oC and residues was extracted with dichloromethane (2 ×10 mL). The extract was then concentrated at 40 ^oC to yield AMF as a brown liquid (64.1%). The purity of the product was analyzed by H-NMR analysis and used to calculate the correction factor with reaction standard for GC analysis (Figure S5).

[1] C. H. Kuo et al., Heterogeneous acidic TiO_2 nanoparticles for efficient conversion of biomass derived carbohydrates. *Green Chemistry.,* **2014**, 16, 785.

Table S1 Conversion of methyl levulinate via different CTH catalysts

Entry	Catalyst	Conversion (%)	GVL (%)
1	5% Ru/Al_2O_3	100	94.3
2	5% Ru/TiO_2	100	98.9
3	5% Ru/ZrO_2	100	98.5
4	5% Ru/CeO_2	95.1	91.4
5	5% Ru/AC	100	96.6
6	5% Ni/ZrO_2	25.6	21.7
7	5% Pt/ZrO_2	100	94.1
8	5% Pd/ZrO_2	95.7	89.5

Reaction conditions: methyl levulinate 3 mmol, 100 mg Ru/ZrO_2, 14 mL i-PrOH, 800 W, 180 ^oC, 40 min.

Table S2 Conversion of methyl levulinate with extra H_2SO_4.

Entry	Catalyst	Conversion (%)	GVL (%)
1	5% Ru/Al_2O_3	60.0	34.1
2	5% Ru/TiO_2	93.7	91.0
3	5% Ru/ZrO_2	94.9	93.1
4	5% Ru/CeO_2	55.3	33.9
5	5% Ru/AC	47.2	27.5
6	5% Ni/ZrO_2	25.6	21.7
7	5% Pt/ZrO_2	95.9	92.1
8	5% Pd/ZrO_2	92.8	85.6

Reaction conditions: methyl levulinate 3 mmol, 100 mg Ru/ZrO_2, 0.8mmol H_2SO_4, 14 mL i-PrOH, 800 W, 180 ^oC, 40 min.

Table S3 Conversion of methyl levulinate with extra H_2O

Entry	Catalyst	Conversion (%)	GVL (%)
1	5% Ru/Al_2O_3	100	92.7
2	5% Ru/TiO_2	100	96.6
3	5% Ru/ZrO_2	100	97.1
4	5% Ru/CeO_2	100	88.9
5	5% Ru/AC	100	92.5
6	5% Ni/ZrO_2	21.6	15.2
7	5% Pt/ZrO_2	73.9	43.4
8	5% Pd/ZrO_2	32.8	15.6

Reaction condition: 3 mmol Methyl levulinate, 100 mg Ru/ZrO_2, 14 mL i-PrOH, 0.6 mL H_2O, 800 W, 180 ^oC,.

Table S4 Influence of reaction temperature on the product distribution.

Temp. (^oC)	Time (min)	Conv. (%)	Product yields (%)				
			GVL	IPL	IPMF	Glucose	IPGP
170	20	7.3	0.2	0.7	0.8	3.4	1.8
	40	34.3	3.9	4.5	2.5	11.7	6.4
	60	74.1	11.8	8.7	4.2	22.1	11.9
	80	99.7	20.8	9.1	3.9	23.2	11.4
	100	100	38.5	4.8	3.0	6.8	3.4
	120	100	45.9	0.4	0.2	0	0
	130	100	43.7	0	0	0	0
180	10	45.3	3.4	4.1	2.8	16.2	9.7
	20	73.1	12.9	7.2	3.8	22.4	11.5
	30	95.1	22.4	9.5	4.7	24.1	14.2
	40	100	34.7	10.4	3.0	16.2	9.2
	50	100	42.1	7.4	1.5	7.5	4.5
	60	100	48.4	4.5	0.4	1.4	1.2

	70	100	51.2	0.2	0	0.1	0.6
	80	100	49.7	0	0	0	0
190	10	65.2	14.2	5.1	2.8	17.2	8.4
	20	93.1	25.1	6.2	3.7	18.1	7.4
	30	100	31.9	4.9	1.4	5.4	2.6
	40	100	39.5	2.1	1.1	0.5	0.9
	50	100	41.9	0.2	0	0	0
	60	100	33.7	0	0	0	0

Reaction condition: 3 mmol cellulose, 0.8 mmol $Al_2(SO_4)_3$, 100 mg Ru/ZrO_2, 0.6 mL H_2O, 14 mL 2-PrOH, 800 W. IPGP was calculated by using methyl α-D-glucopyranoside as substitute.

Table S5. Influence of water content on GVL production from cellulose[a]

Entry	Water content (mL)	IPL (%)	GVL (%)
1	0	0	29.7
2	0.2	0	40.4
3	0.4	0.2	47.9
4	0.6	0.2	51.2
5	0.8	1.3	46.1

[a]Reaction Conditions: cellulose 3 mmol, $Al_2(SO_4)_3$ 0.8 mmol, Ru/ZrO_2 100 mg, i-PrOH 14 mL, 800 W, 180 ^oC, 70 min.

Table S6. GVL production from xylan[a]

Entry	substrate	IPL (%)	GVL (%)
1	xylan	0	13.3
2	xylan	0	15.2

[a]Reaction Conditions: xylan 3 mmol, $Al_2(SO_4)_3$ 0.8 mmol, Ru/ZrO_2 100 mg, i-PrOH 14 mL, 0.6 mL H_2O, 800 W, 180 ^oC, 70 min.

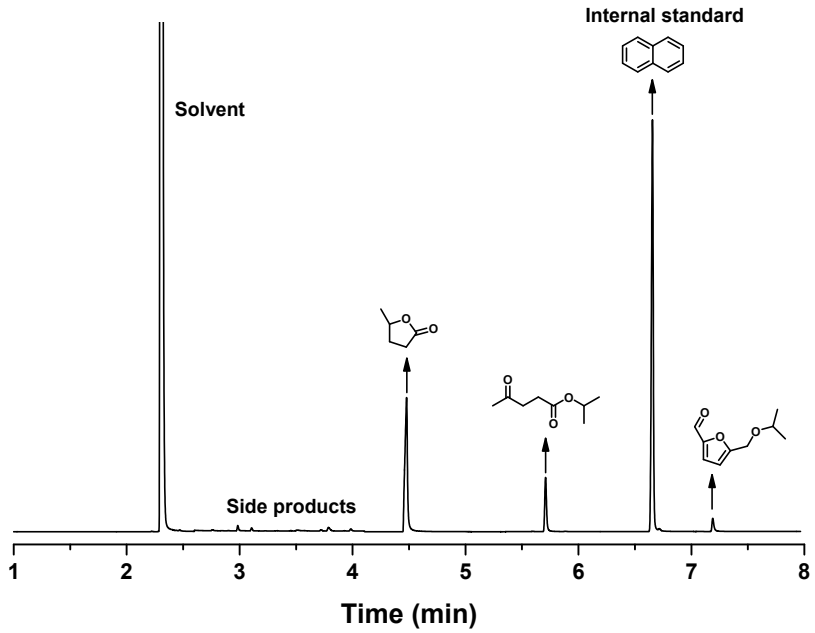

Figure S1. GC analysis of the cellulose conversion at 40 min reaction time. Condition: 3 mmol cellulose, 0.8 mmol $Al_2(SO_4)_3$, 100 mg Ru/ZrO_2, 0.6 mL H_2O, 14 mL 2-PrOH, 800 W, 180 ^oC, 40 min.

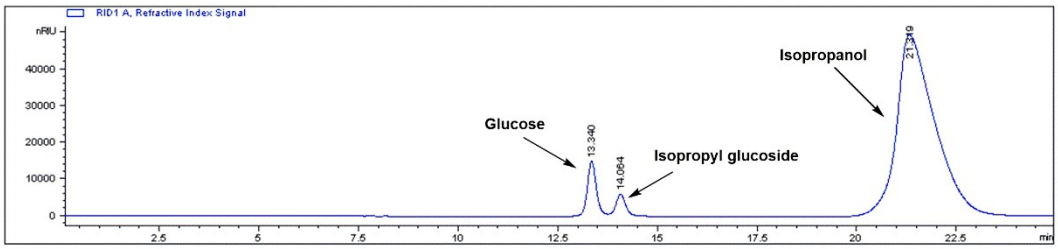

Figure S2. Typical HPLC chromatogram of the reaction mixture of cellulose conversion. Condition: 3 mmol cellulose, 0.8 mmol $Al_2(SO_4)_3$, 100 mg Ru/ZrO_2, 0.6 mL H_2O, 14 mL 2-PrOH, 800 W, 180 ^oC, 40 min.

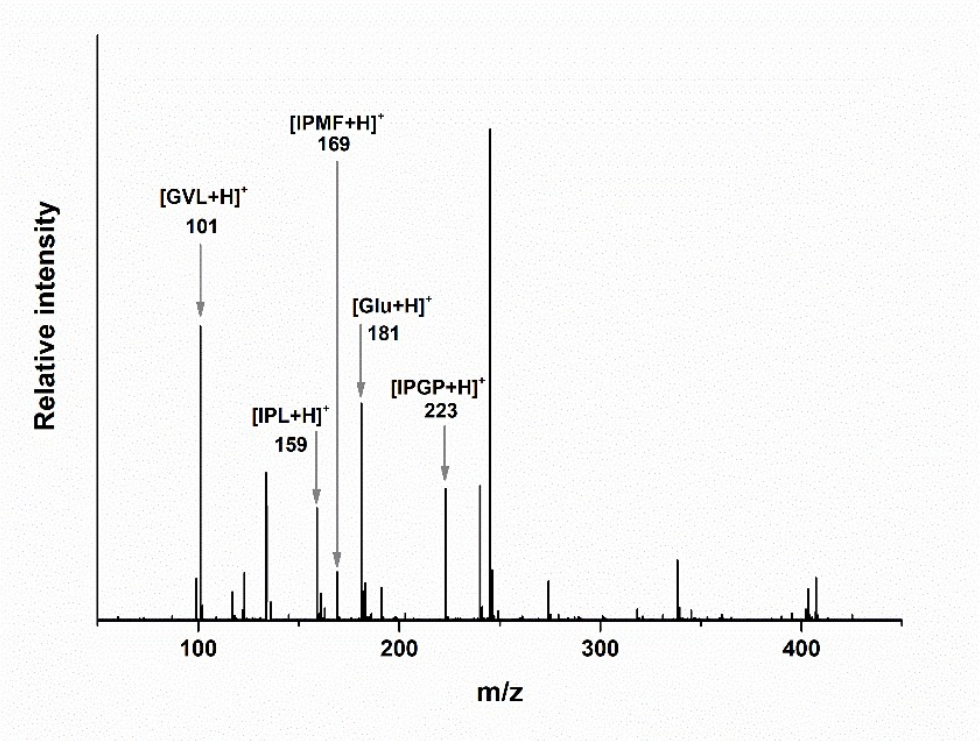

Figure S3. Electron spin ionization−mass spectroscopy (ESI-MS) spectra of reaction mixture in positive mode. Condition: 3 mmol cellulose, 0.8 mmol $Al_2(SO_4)_3$, 100 mg Ru/ZrO_2, 0.6 mL H_2O, 14 mL i-PrOH, 800 W, 180 ^oC, 40 min. The reaction mixture was diluted with 50 mL water before analysis.

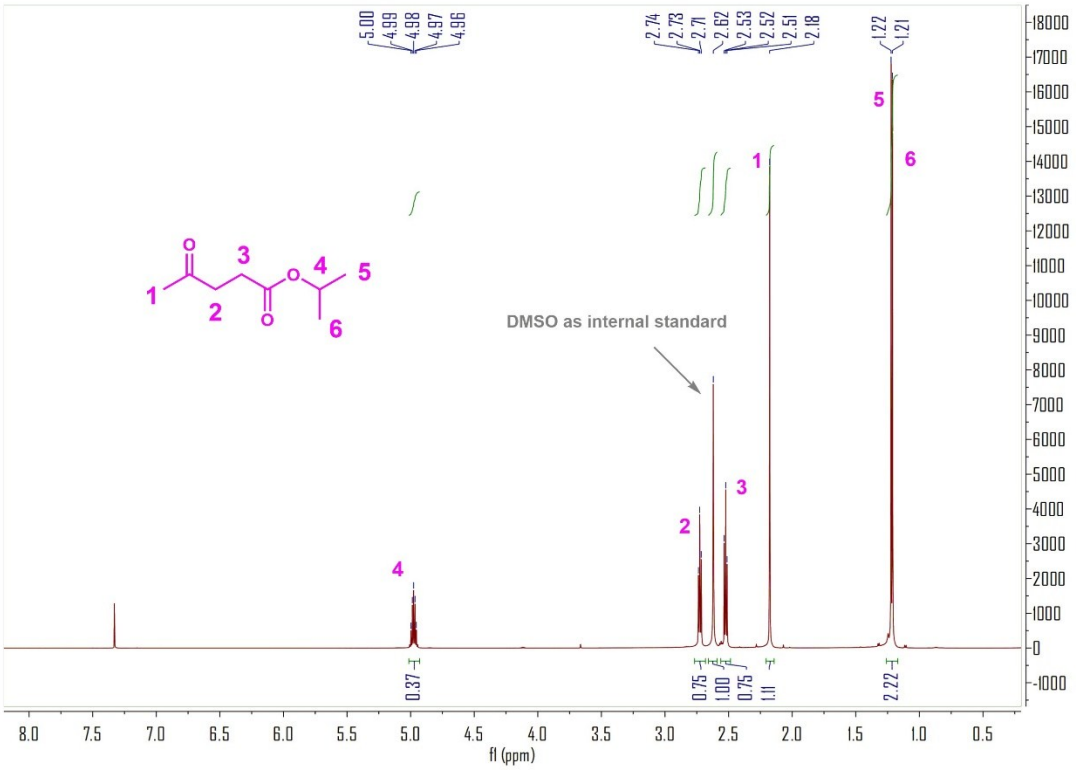

Figure S4. Representative ^{1}H-NMR spectrum of intermediates IPL in chloroform-d.

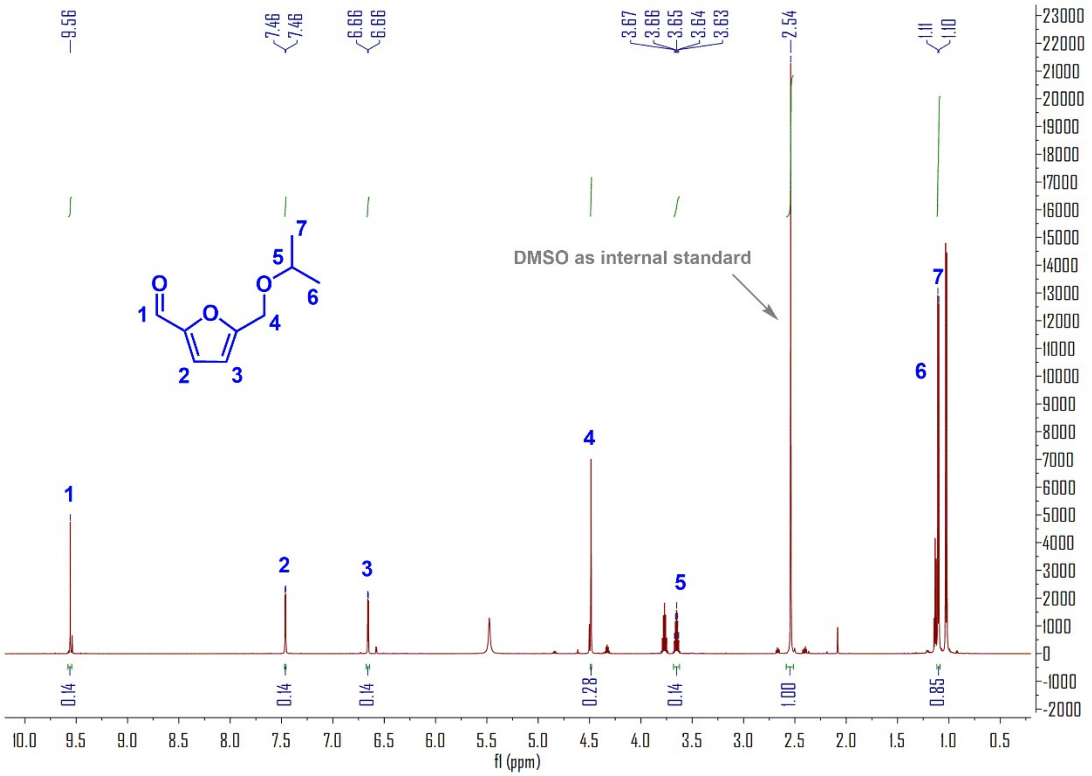

Figure S5. Representative ^{1}H-NMR spectrum of intermediates IPMF in dimethyl sulfoxide-d6.

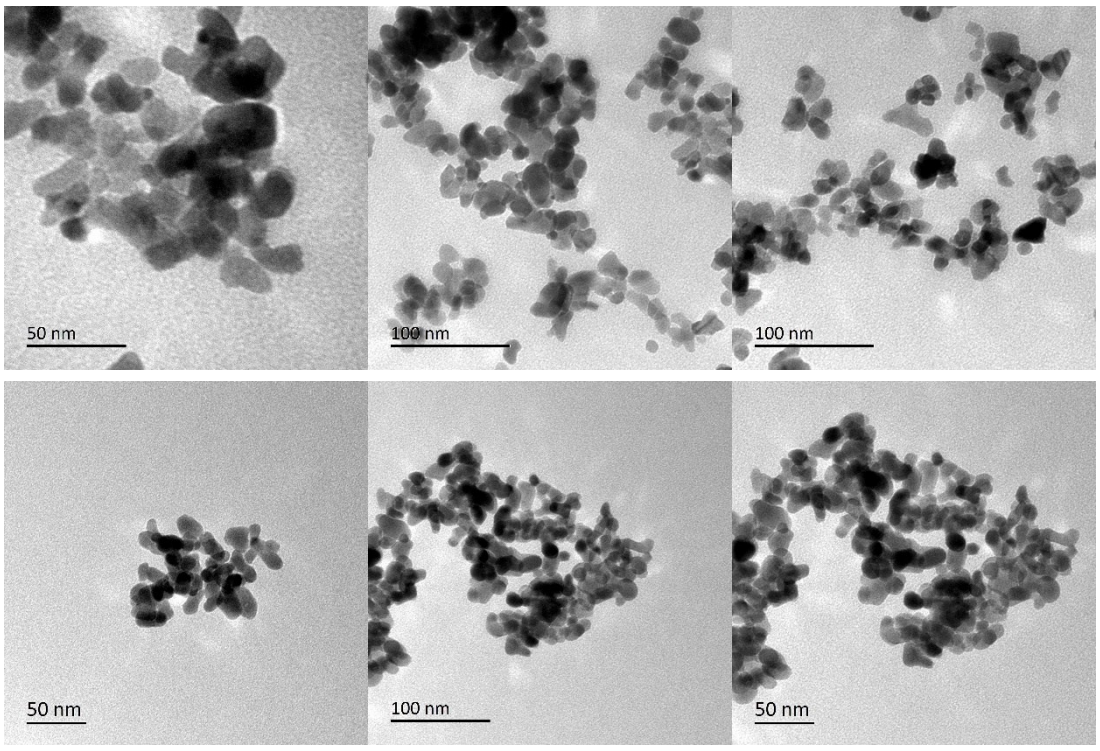

Figure S6 TEM of the fresh (above) and spent Ru/ZrO_2 catalyst (bottom).

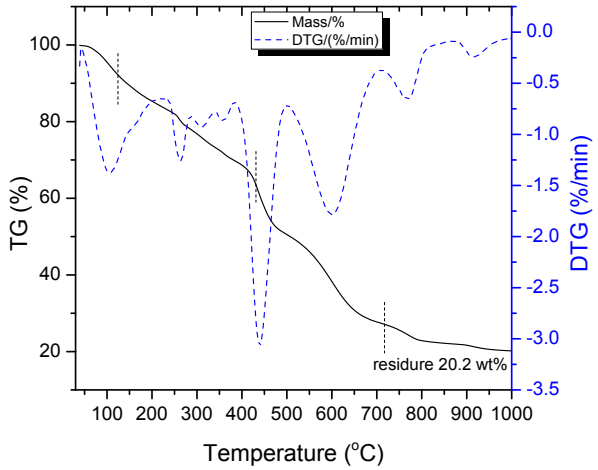

Figure S7. TGA curves of the recovered metal salt catalyst. The remaining weight percentage was 20.2%. Proposed catalyst formulas were $2Al(OH)_2(H_2O)_4 + 3H_2SO_4$ (Mw=533) and the final reside was Al_2O_3(Mw=102). Theoretical residue weight percentage was 102/533*100%=19.1%.