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Supporting Information

The preparation method of 2-iodomethylfuran

In a 25 mL round bottom flask furfuryl alcohol, acetonitrile, NaI and P_2O_5 were added, we obtained 80.1% 2-iodomethylfuran (Scheme 3). The prepared 2-iodomethylfuran solution was passed through 0.22 μm filter (the solid matter was removed) into 50 ml reactor lining and heated to 100°C reaction for 30 min by passing through a 300 psi H_2/N_2 seal.

Table S1 Metal ion concentration table in the reaction solution

Elem	Avg	Units
Al1670	0.07574	ppm
As1890	0.2570	ppm
B 2497	0.1223	ppm
Ba4554	0.000996	ppm
Be3130	0.5299	ppm
Bi2230	0.01746	ppm
Cd2288	0.02754	ppm
Co2286	0.1926	ppm
Cr2835	0.06133	ppm
Cu3247	0.06133	ppm
Fe2599	0.7966	ppm
Ga2943	-0.01578	ppm
Ir2242	0.001183	ppm
Li6707	0.004131	ppm
Mg2795	0.2939	ppm

Mn2576	0.02474	ppm
Ni2216	0.8167	ppm
Pd3404	0.003764	ppm
Pt2144	0.001518	ppm
Rh3434	-0.09333	ppm
Ru2678	0.1481	ppm
Sb2068	0.05287	ppm
Sn1899	1.23	ppm
Sr4077	0.01644	ppm
Zn2138	0.1565	ppm

Table S2 Adding $SnCl_2$ to catalyze starch conversion

Catalyst	2-MF (%)	Furfural (%)	5-MF (%)	Total yield (%)
$SnCl_2$	1.8	1.0	29.7	32.5

Reaction Condition: 100 mg starch, 2 mmol NaI, 0.18 mmol HCl, 3.5% eq $SnCl_2$ (4.2 mg), 2 mL H_2O, 3 mL MTHF, 500 r/min, 2 h, 300 psi H_2, 160℃.

Table S3 Effect of different iodized salts

Entry	Salt	2-MF%	Furfural%	5-MF%	Total yield%
1	KI	3.5	1.7	30.1	35.3
2	NaI	3.6	1.5	31.1	36.2
3	LiI	4.2	1.6	33.0	38.8

Reaction Condition: 100 mg starch, 2 mmol salt, 0.18 mmol HCl, 2 mL H_2O, 3 mL MTHF, 500 r/min, 2 h, 300 psi H_2, 160℃

Table S4 5-MF recovery experiment

Substrate	Conversion (%)	Yield (%)	
		2-MF	Furfural
5-MF	41.0	34.6	N. D.

Reaction Condition: 0.5 mmol HMF, 2 mmol NaI, 0.18 mmol HCl, 2 mL H_2O 3 mL MTHF, 500 r/min, 2 h, 300 psi H_2, 160℃.

Table S5 Optimal conditions

Entry	2-MF/%	Furfural/%	5-MF/%	Levulinic acid /%	Humins wt.%
1	5.6	2.0	38.0	22.5	45.6

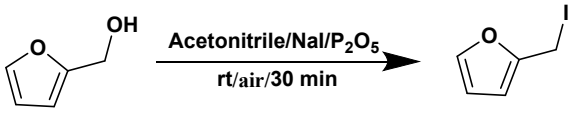
Reaction Condition:100 mg starch, 2 mmol NaI, 0.18 mmol HCl, 2 mL H_2O, 6 mL MTHF, 500 r/min, 2 h, 300 psi H_2, 160℃.

Table S6 Product analysis

Entry	glucose /%	fructose /%	HMF/%	Levulinic acid /%	2-MF/%	Furfural/ %	5-MF/%	Humins wt.%
1[a]	4.6	4.2	3.6	20.2	3.6	1.5	32.1	13.9
2[b]	26.0	15.0	20.2	15.6	N. D.	N. D.	1.7	5.6

[a]Reaction Condition:100 mg starch, 2 mmol NaI, 0.18 mmol HCl, 2 mL H_2O, 3 mL MTHF, 500 r/min, 2 h, 300 psi H_2, 160℃. [b] 140℃.

Table S7 Preparation of 2-iodomethylfuran



Conversion 100 % **Yield 80.1 %**

Substrate	Conversion (%)	2-iodomethylfuran (%)
Furfuryl alcohol	100	80.1

Reaction Condition: 1.0 mmol furfuryl alcohol, 2 mmol NaI, 1.5 mmol P_2O_5, 5 mL acetonitrile, 1500 r/min, 30 min, rt.

Table S8 Starch amplification experiment

Entry	2-MF (%)	Furfural (%)	5-MF (%)	Total yield (%)
1	1.5	1.6	31.3	34.4

Reaction Condition: 1 g starch, 20 mmol NaI, 1.8 mmol HCl, 10 mL H_2O, 15 mL MTHF, 500 r/min, 3 h, 300 psi H_2, 160℃.

Table S9 Metal-free catalytic verification

Entry	Metal salt	2-MF%	Furfural%	5-MF%	Total yield%
1	/	3.4	1.2	33.5	38.1
2	$PdCl_2$	4.0	0.7	33.1	37.8
3	$RhCl_3$	4.3	1.0	34.1	39.4

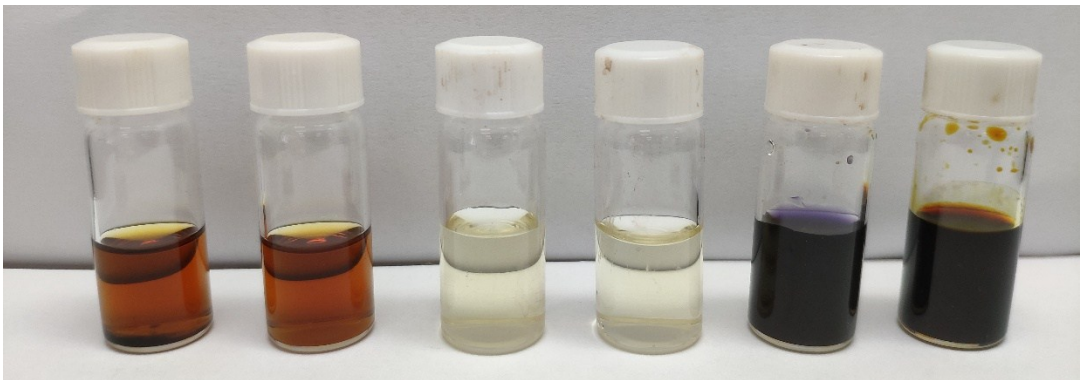
Reaction Condition: 100 mg starch, 2 mmol NaI, 0.18 mmol HCl, 2 mL H_2O, 3 mL MTHF, 500 r/min, 2 h, 300 psi H_2, 160℃. 1.8 % eq $RhCl_3 \cdot 3H_2O$ (2.6 mg), 2.0 % eq $PdCl_2$ (1.9 mg).

Both THF, MTHF, and 1,4-dioxane contain trace amounts of butylated hydroxytoluene (BHT) and may interfere with experimental results. The results were the same using the solvent after re-distilled under the standard condition as shown in entries 1, 2, &3. Then we reduced the reaction time to 0.5 hours, and re-distilled MTHF as a solvent showed a better result as shown in entries 4 and 5. Thus BHT present indeed has an effect on the initial reaction rate, which proves that it is indeed a radical reaction.

Table S10 Effect of re-distilling solvent

Entry	Solvent	2-MF%	Furfural%	5-MF%	Total yield%
1	MTHF	2.8	1.0	30.5	34.3
2	1,4-dioxane	1.3	N. D.	30.7	32.0
3	THF	2.7	N. D.	28.3	31.0
4	0.5 h MTHF	3.9	N. D.	18.6	22.5
5	0.5 h un-distilling MTHF	3.7	N. D.	9.9	13.6

Reaction Condition: 100 mg starch, 2 mmol NaI, 0.18 mmol HCl (0.015 mL), 2 mL H_2O, 3 mL re-distilling Solvent, 500 r/min, 2 h, 300 psi H_2, 160℃



1 2 3 4 5 6

Fig. S1 Detecting the iodine content in the reaction solution. 1. Organic phase. 2. Organic phase and starch potassium iodide. 3. aqueous phase 4. aqueous phase and starch potassium iodide. 5. Water, I_2 and starch potassium iodide. 6. MTHF, I_2 and starch potassium iodide.

Determination of the starch conversion

First, different concentrations of starch solution was prepared with potassium iodide added. Then, the absorbance was measured with an ultraviolet-visible spectrophotometer. And the result was used to draw a standard curve of obsorbance to the starch concentration. Specific steps are as follows: Starch, or a fraction thereof (20, 40, 60, 80, 100, 120 mg), was accurately weighed and dissolved in 10 mL water. 1.00 ml of a solution of iodine (0.0025mol/L) in potassium iodide (0.0065mol/L) was added with mixing. Then the sample was put in a 1cm path length quartz cell, and he absorbance of the sample was read at 600nm using a UV/Visible spectrophotometer.

The starch content in the aqueous phase was determined under typical reaction conditions (100 mg starch, 2 mmol NaI, 0.18 mmol HCl, 2 mL H2O, 3 mL MTHF, 500 r/min, 2 h, 300 psi H2, 160℃) And the thermogravimetric curves of starch and humins were also determined. The residual starch in the aqueous phase was 0.26%, so the starch conversion rate was 99.74%.

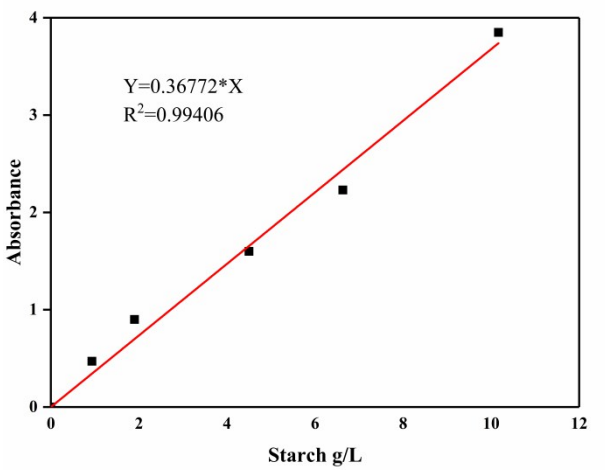


Fig. S2 Standard absorption curve of starch-iodine solution.

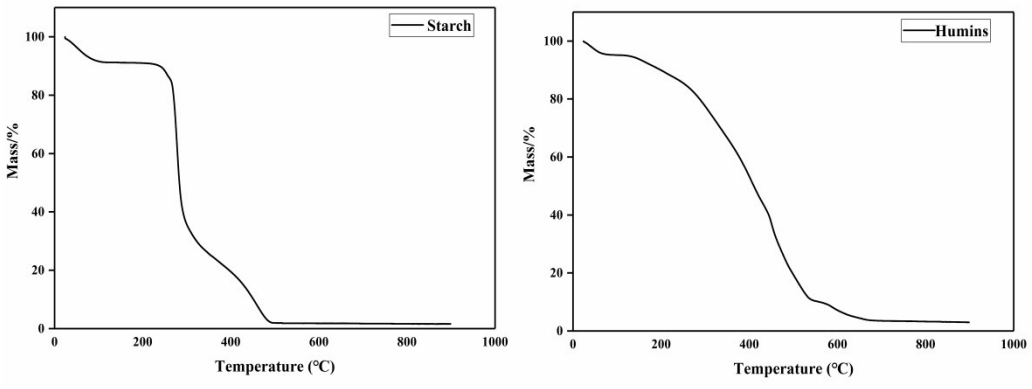


Fig. S3 Starch and Humins thermogravimetric images.

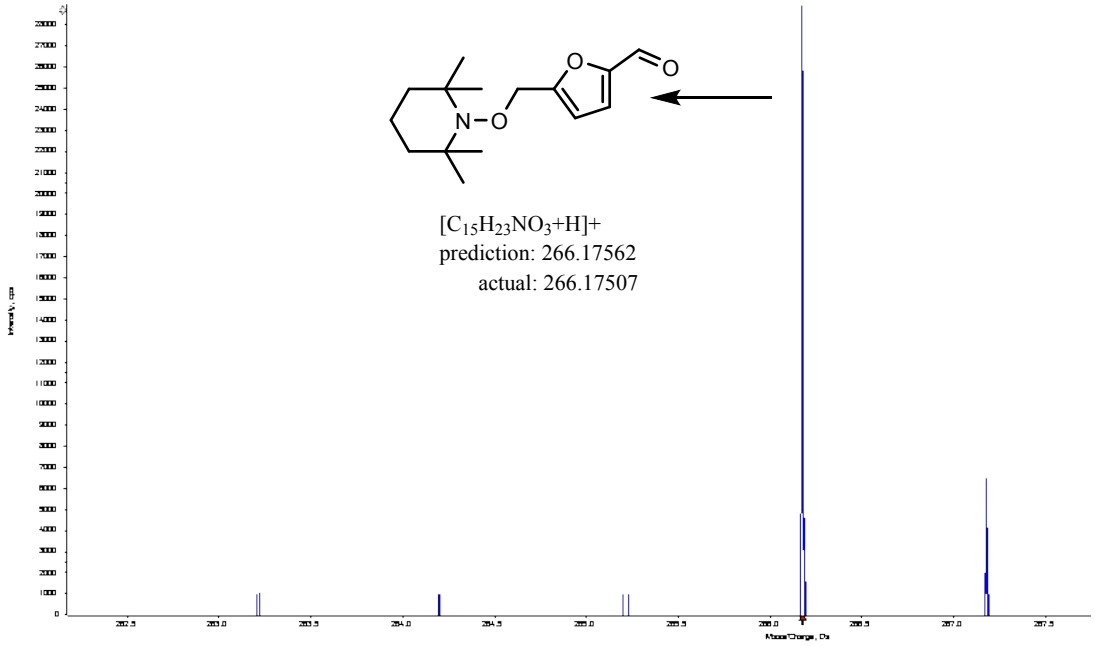


Fig. S4 $C_{15}H_{23}NO_3$ (Tempo captured the 5-MF radical to form a new compound) Q-TOF graph. $C_{15}H_{23}NO_3$ hydrogenation ($[C_{15}H_{23}NO_3+H]+$) prediction quality 266.17562 under Q-TOF positive ion scan, actual measurement quality 266.17507.

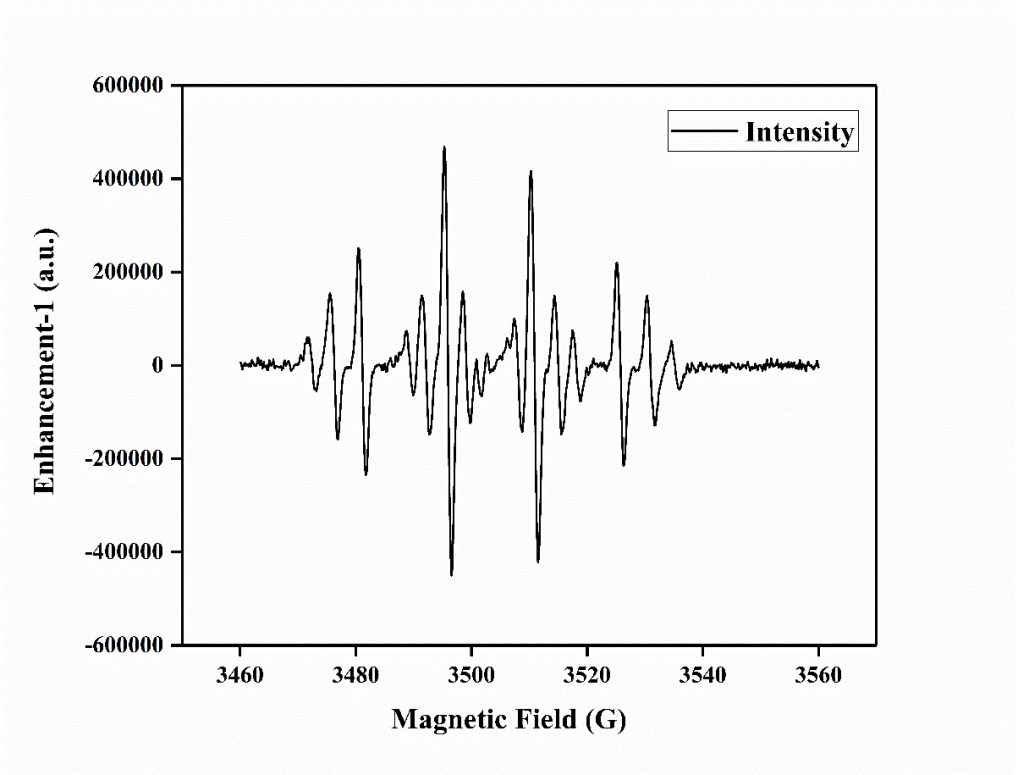


Figure. S5 Continuous-wave EPR signal at typical condition. Reaction Condition: 1 mmol HMF, 4 mmol NaI, 0.36 mmol H_2SO_4, 6 mL MTHF, 60 μL DMPO, 500 rpm, 20 min, 300 psi H_2, 180℃.

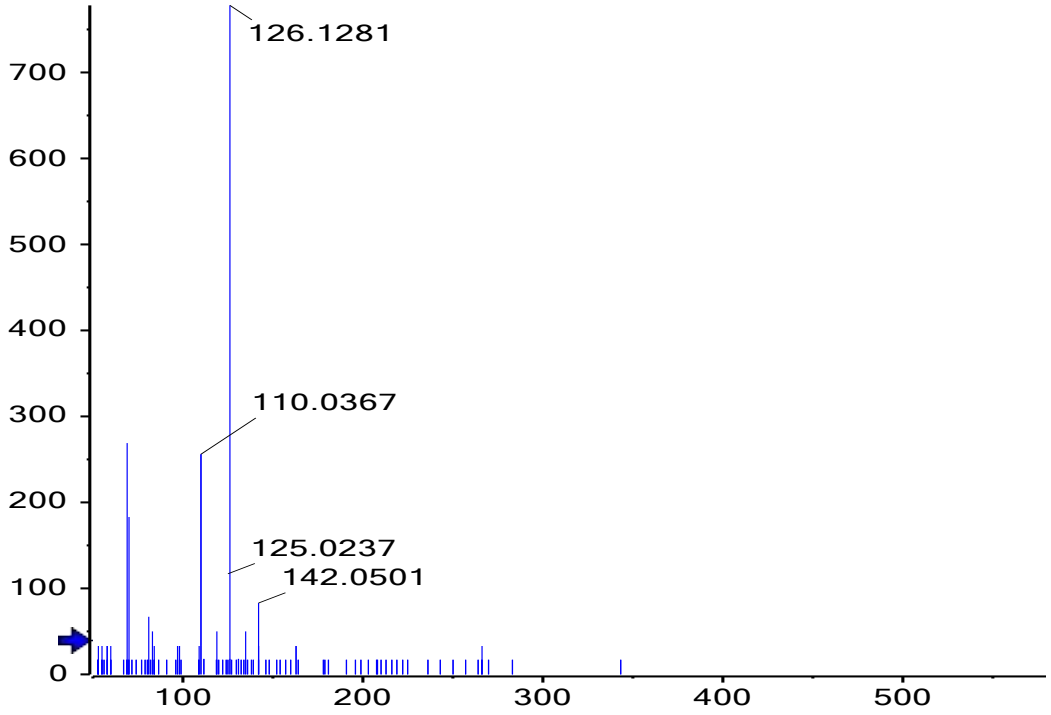


Fig. S6 $C_{15}H_{23}NO_3$ (Tempo captured the 5-MF radical to form a new compound) Q-TOF fragment peak graph.

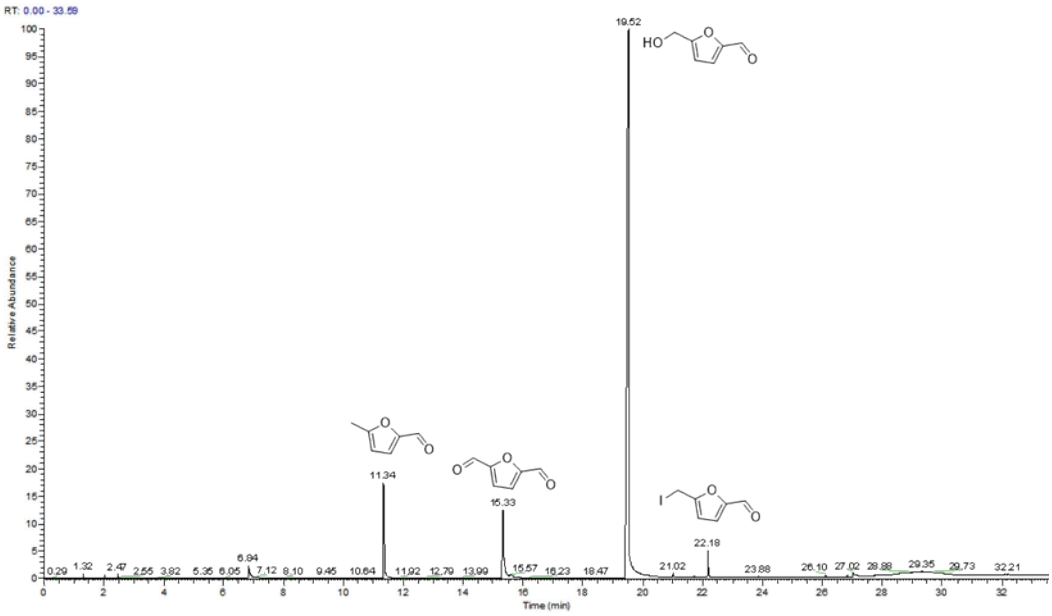


Fig. S7 5-iodomethylfuran-2-carbaldehyde GCMS graph. Ethyl acetate is GCMS washing needle solvent, chloroform by-product. At 2.1-3.5 min is the solvent MTHF peak, cut off on GCMS.

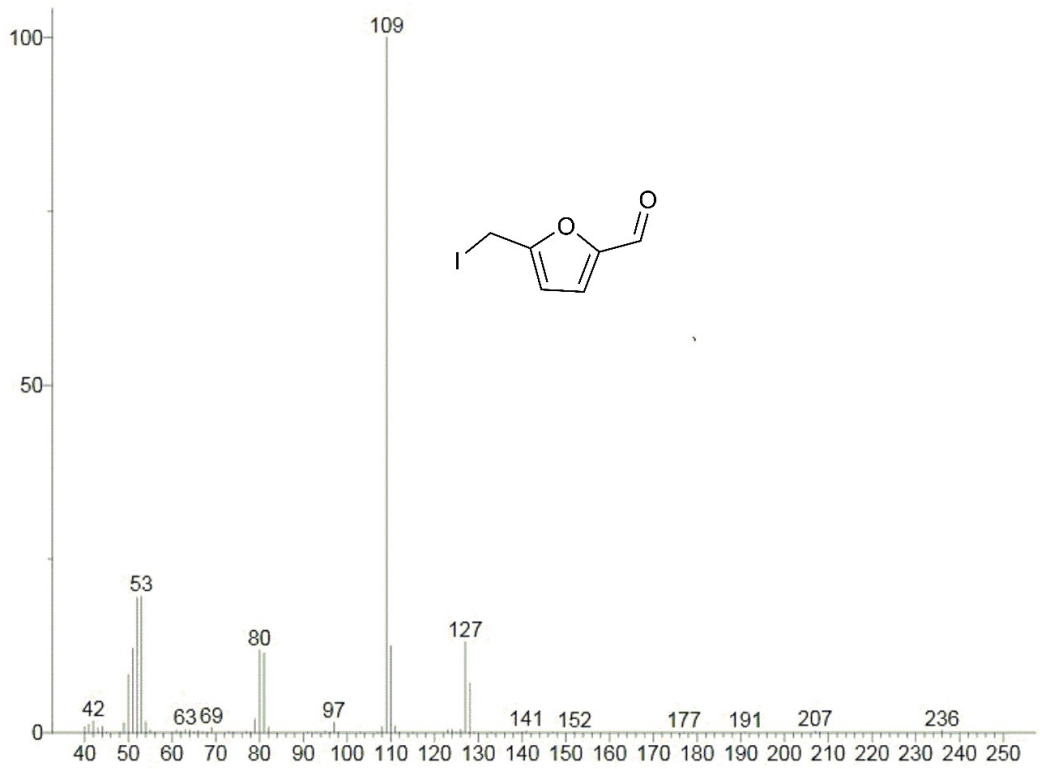


Fig. S8 5-iodomethylfuran-2-carbaldehyde GCMS fragment peak graph.