

Supporting Information

I. General

If not stated otherwise, the reaction was carried out in an autoclave sponsored by Anhui Kemi Machinery Technology Co., Ltd. Usually the initial temperature was 30 °C, then the reaction was heated to the required temperature through an intelligent temperature controller in 30 min. After that the reaction was carried out in a heating preservation period with a certain time.

^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. NMR spectra were analysed with MestReNova software.

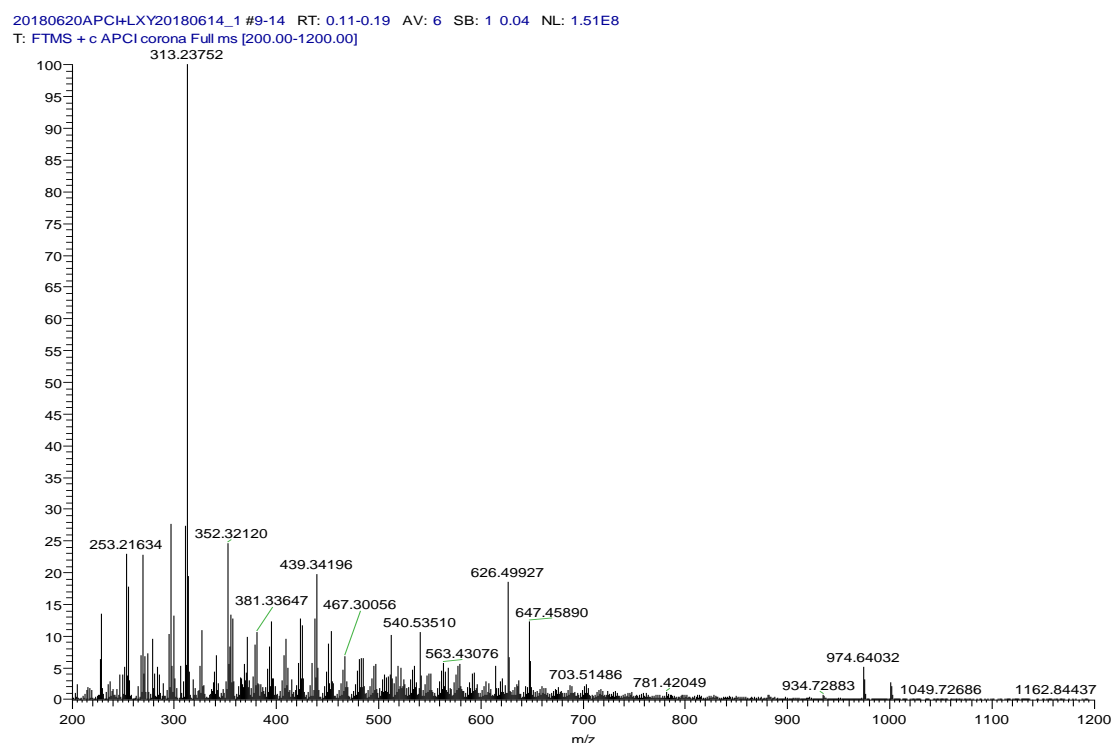
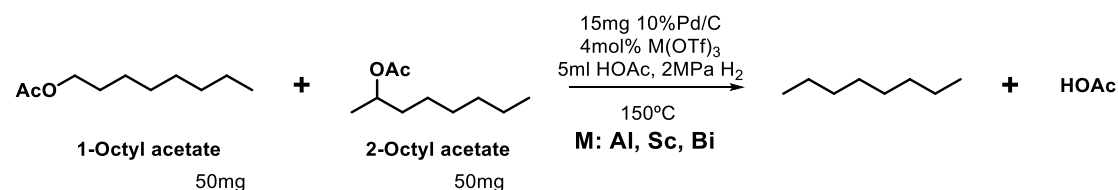


Figure S1. The ESI of product

In order to prove that the raw materials can be polymerized in the reaction process, ESI was used to detect the reaction products. The reaction of FFA to OA was carried out under low hydrogen pressure. We found in FigureS1 that 253, 313, 439 and 563 characteristic peaks appeared in the products. This indicates that the raw materials was polymerized in the process of reaction.

II. Model Reaction Test

In order to verify the relationship between the ability of remove ester groups and the radius of the central metal ion, we chose the following method:



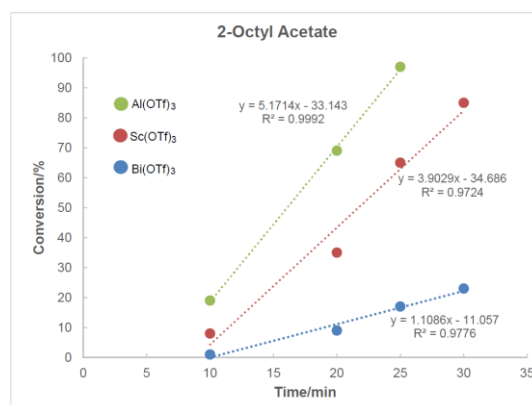
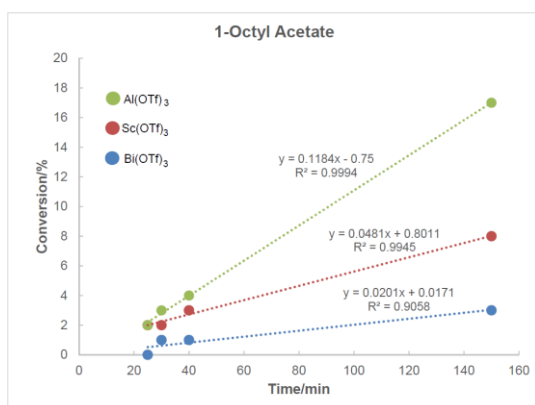
Reaction conditions: 50 mg 1-octyl acetate, 50 mg 2-octyl acetate, 15 mg 10% Pd/C, 4 mol% metal triflate, 2 MPa H₂, 5 mL acetic acid, 150°C.

$$\text{Conversion: } c = \left(1 - \frac{n}{n_{\text{initial}}}\right) \times 100\%$$

$$\text{Charge density: } d = \frac{\text{valence}}{\text{ionic radii}}$$

$$\text{Conversion rate: } k = \left(\frac{\partial c}{\partial t}\right)_{T, P}$$

Reaction Time / min	Conversion of 1-Octyl acetate / %			Conversion of 2-Octyl acetate / %		
	Al(OTf) ₃	Sc(OTf) ₃	Bi(OTf) ₃	Al(OTf) ₃	Sc(OTf) ₃	Bi(OTf) ₃
0	0	0	0	0	0	0
10	0	1	0	19	8	1
20	1	1	0	69	35	9
25	2	2	0	97	65	17
30	3	2	1	100	85	23
40	4	3	1	100	100	32
150	17	8	3	100	100	78



M(OTf) ₃	Ionic radii / Å	charge density	k_{pri} for 1-OctOAc	k_{sec} for 2-OctOAc	k_{sec} / k_{pri}
Al(OTf) ₃	0.535	5.61	0.1184	5.1714	44
Sc(OTf) ₃	0.745	4.03	0.0481	3.9029	81
Bi(OTf) ₃	1.030	2.91	0.0201	1.1086	55

III. Reaction Test

In order to verify the effect of catalyst dosage, we obtained a series of products and intermediates by modifying the amount of Pd/C under the same reaction conditions (FFA (0.75mmol), H₂ (2MPa), 120min, 10% Pd/C (2 mol %), acetic acid (5 mL) and 150°C). We found that when the dosage of Pd/C was 2% mol, the yield of product OA reached the maximum (90%).

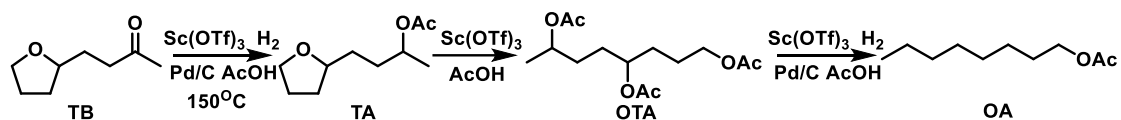
Table S1. Effect of catalyst dosage on product yield

Reaction scheme: 4-(furan-2-yl)butan-2-one + Pd/C, M(OTf)_n, AcOH → TA + OTA + OA + OT

Entry	Pd/C	Conversion/%	Yield/%				
			TA	OTA	OA	Octane	Others
1	5mg	100	19	37	34	0	10
2	10mg	100	0	21	70	3	5
3	15mg	100	0	1	90	8	1
4	20mg	100	0	1	84	11	4
5	25mg	100	0	0	80	15	5

Reaction conditions: FFA (0.75mmol), H₂ (2MPa), 120min, acetic acid (5 mL) and 150°C. TA: 4-(tetrahydrofuran-2-yl)butan-2-yl acetate; OA: 1-octyl acetate; OTA: octane-1,4,7-triyl triacetate; Others including products that cannot be detected.

In order to verify the reaction mechanism, we added a blank TB experiment with the following results:



Reaction conditions: TB (0.75mmol), 10% Pd/C (2 mol%), Sc(OTf)₃ (4 mol%), acetic acid (5mL), 150 °C, and 2 MPa H₂.

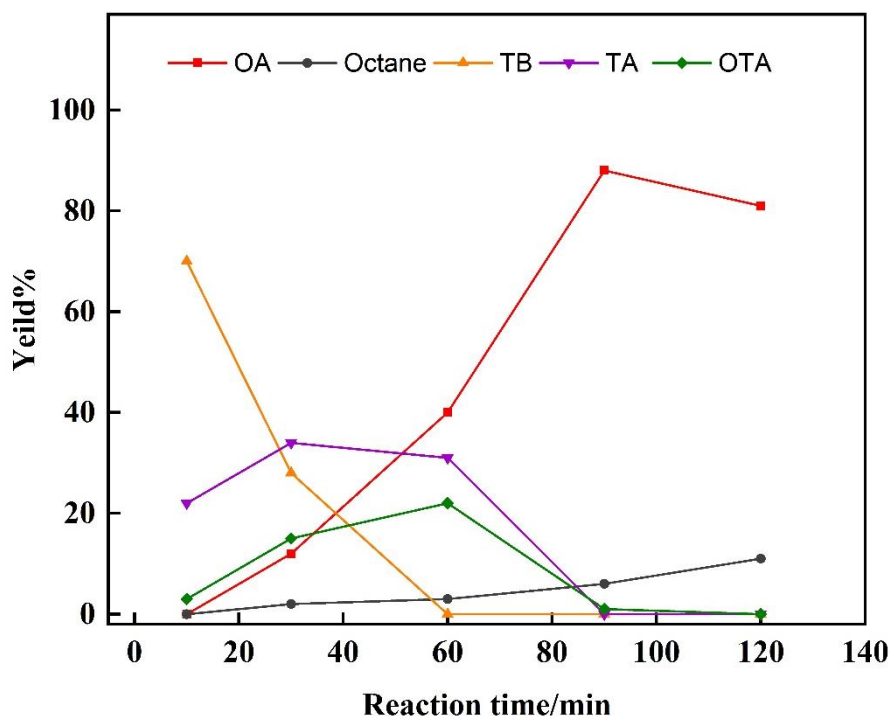
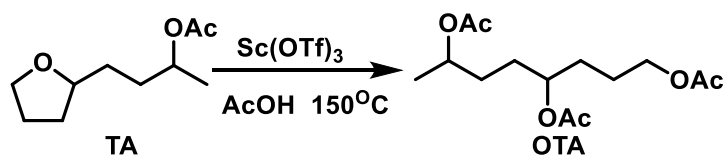


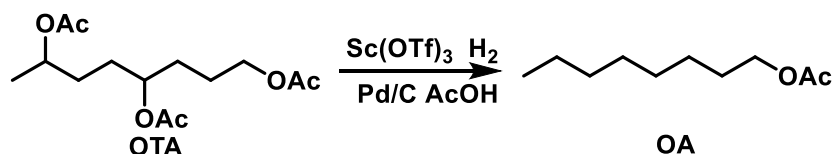
Figure S2. Effect of reaction time under blank TB. Reaction conditions: TB (0.75mmol), 10% Pd/C (2 mol%), Sc(OTf)₃ (4 mol%), acetic acid (5mL), 150 °C, and 2 MPa H₂

In order to verify the reaction mechanism, we added a blank TA experiment with the following results:



The reaction of intermediate TA was also carried out. We found that Sc(OTf)₃ catalyzes the ring opening of tetrahydrofuran ring at high temperature (150°C) without hydrogen, and TA can be converted into OTA.

In order to verify the reaction mechanism, we added a blank OTA experiment with the following results:



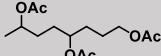
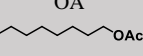


The intermediate OTA reaction was also carried out, and we found that the product was OA. According to the theory obtained by SI-III, Sc(OTf)₃ can promote hydrogenolysis of secondary

alcohol esters while retaining primary alcohol esters, thereby achieving selective hydrodeoxygenation (Sel-DHO).

In order to verify the effects of the one-component catalyst, we added a one-component catalyst experiment, we separately use one catalyst to carry on the reaction:

Table S2. Effect of one-component catalyst on product yield

Entry	Metal triflate	Hydrogenation catalyst	Yield/%				Others
			TB 	TA 	OTA 	OA 	
1	4% Sc(OTf) ₃	-	0	0	0	0	100
2	-	2% Pd/C	37	58	0	0	5
3	4% Sc(OTf) ₃	2% Pd/C	0	0	1	90	9

Reaction conditions: FFA (0.75mmol), H₂ (2MPa), 120min, acetic acid (5 mL) and 150°C.

IV. Characterization of Pd/C

Catalysts were characterized by X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD). 2θ range was $20\text{--}80^\circ$

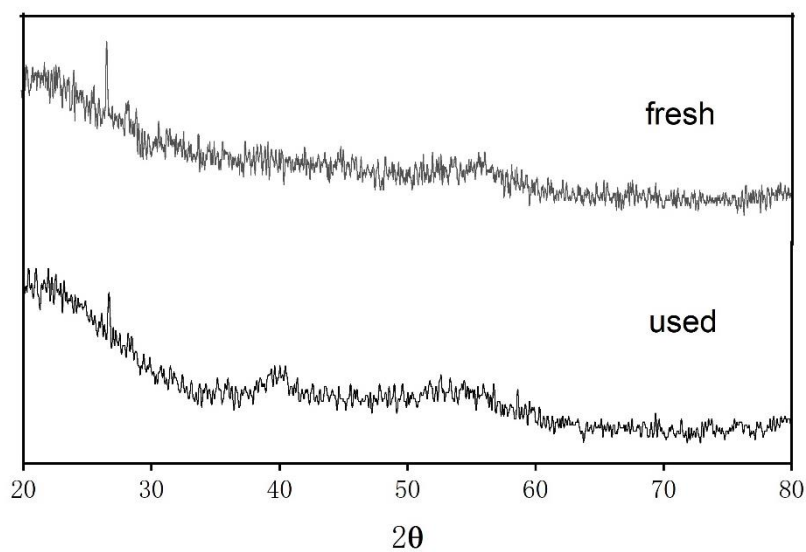


Figure S3. XRD spectra of fresh Pd/C catalyst and the used catalyst.

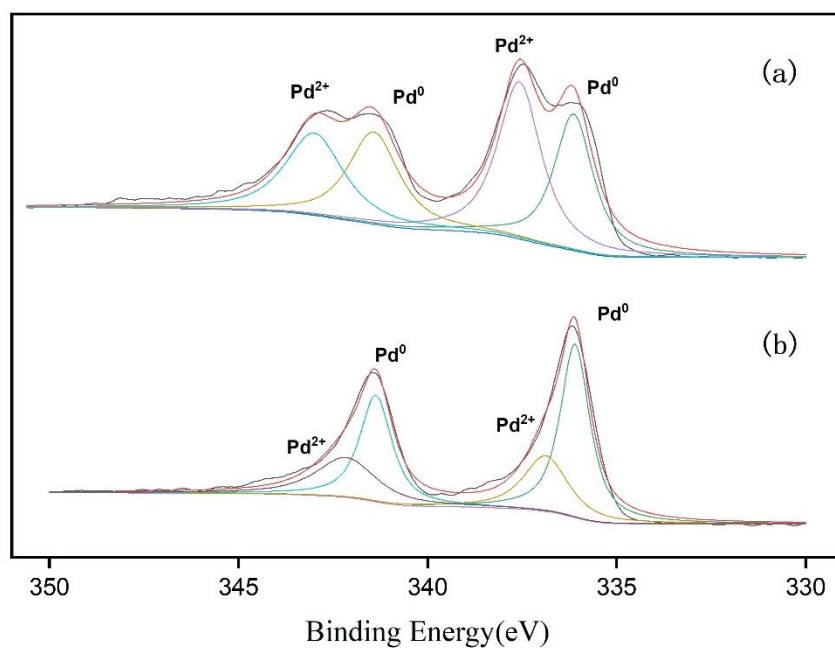


Figure S4. XPS Pd3d spectra for Pd/C catalysts a) Pd/C catalyst after recycling eight times. b) Fresh Pd/C catalyst.

Catalysts were characterized by Transmission electron microscope (TEM).

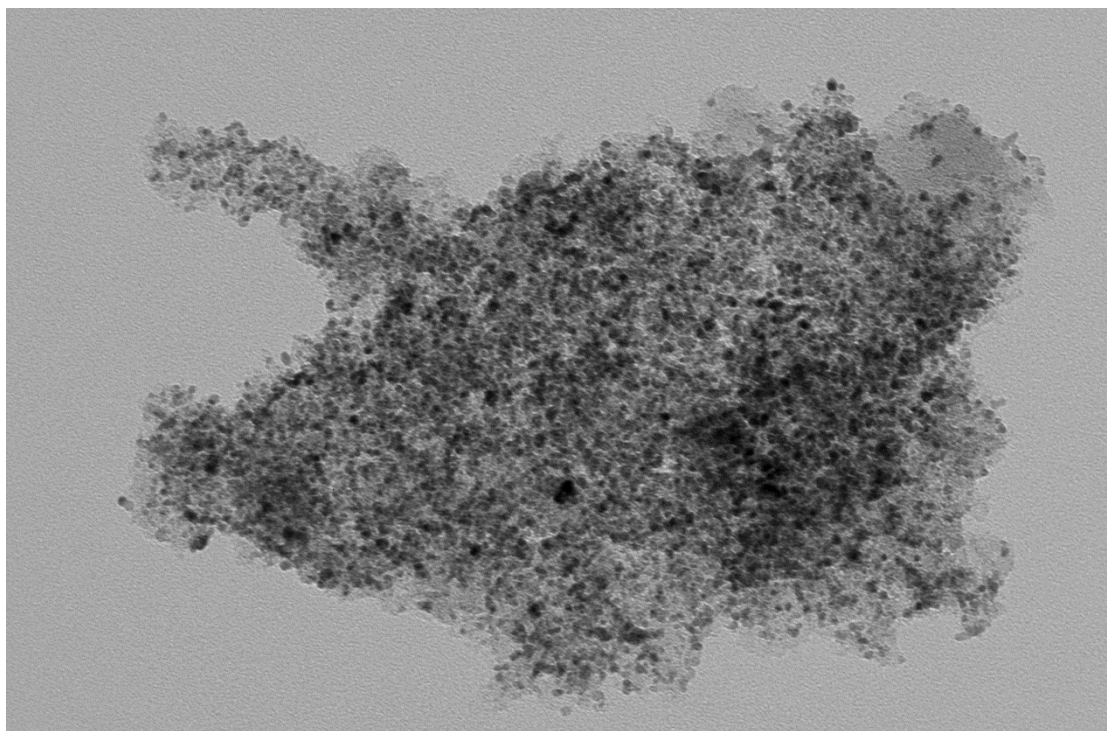


Figure S5-1. The TEM of Pd/C catalyst before reaction

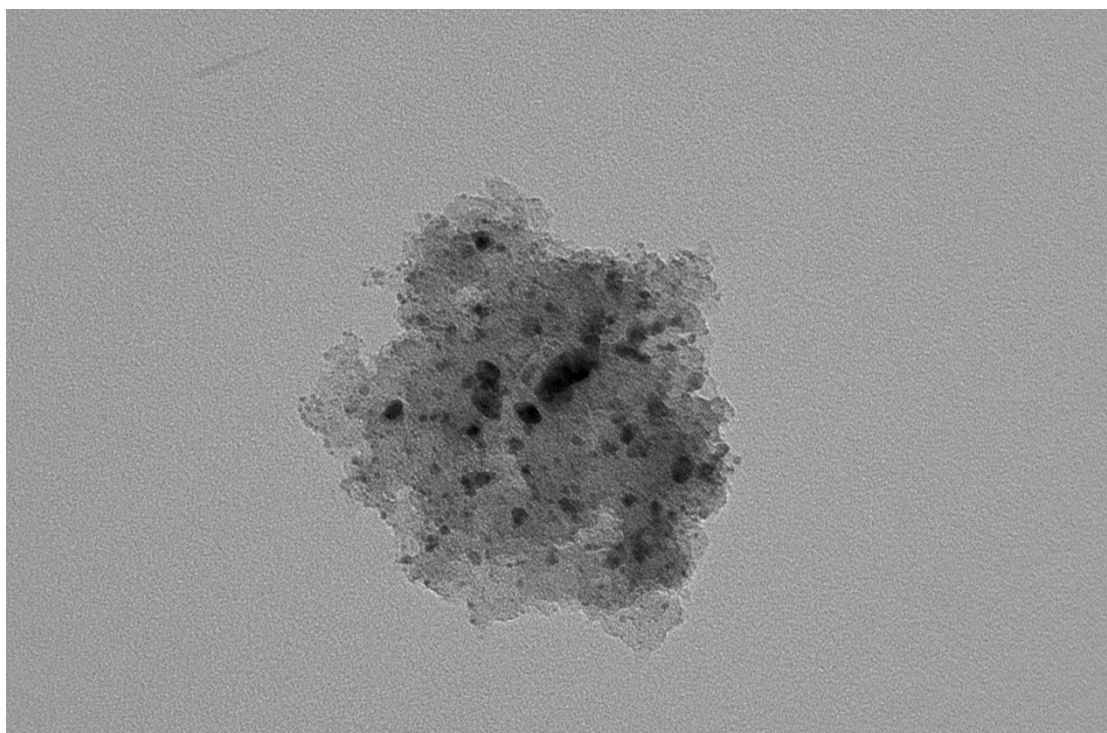


Figure S5-2. The TEM of Pd/C catalyst after reaction

V ^1H -NMR Tracking Monitoring

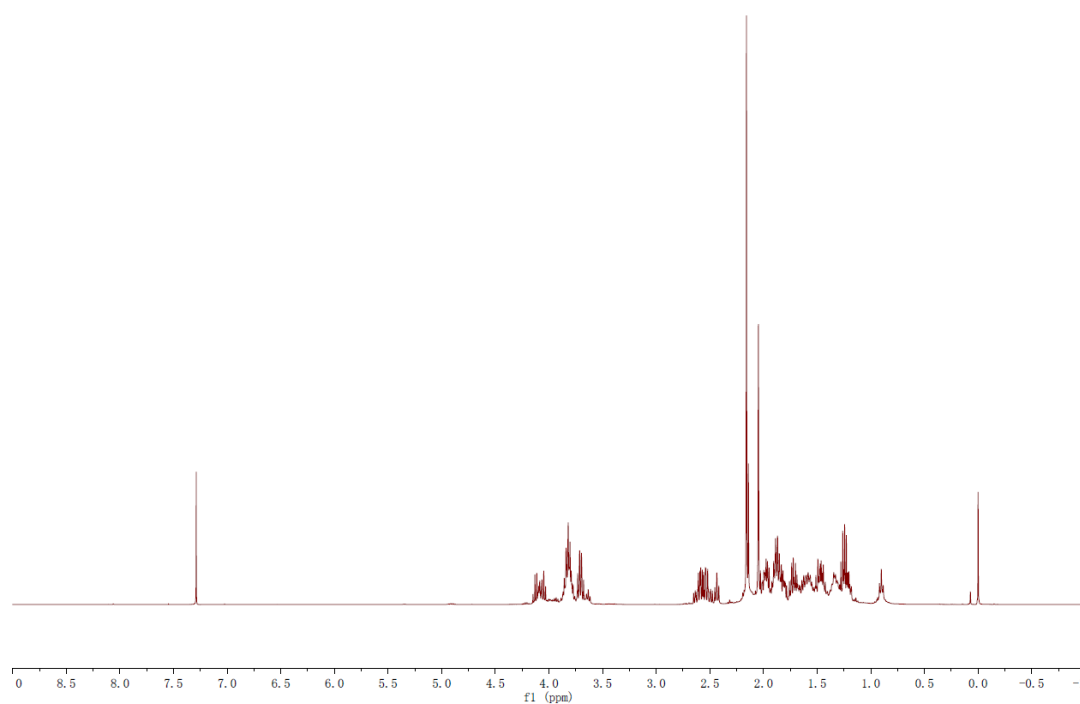


Figure S6. The ^1H -NMR spectrum of reaction heated for 10 min

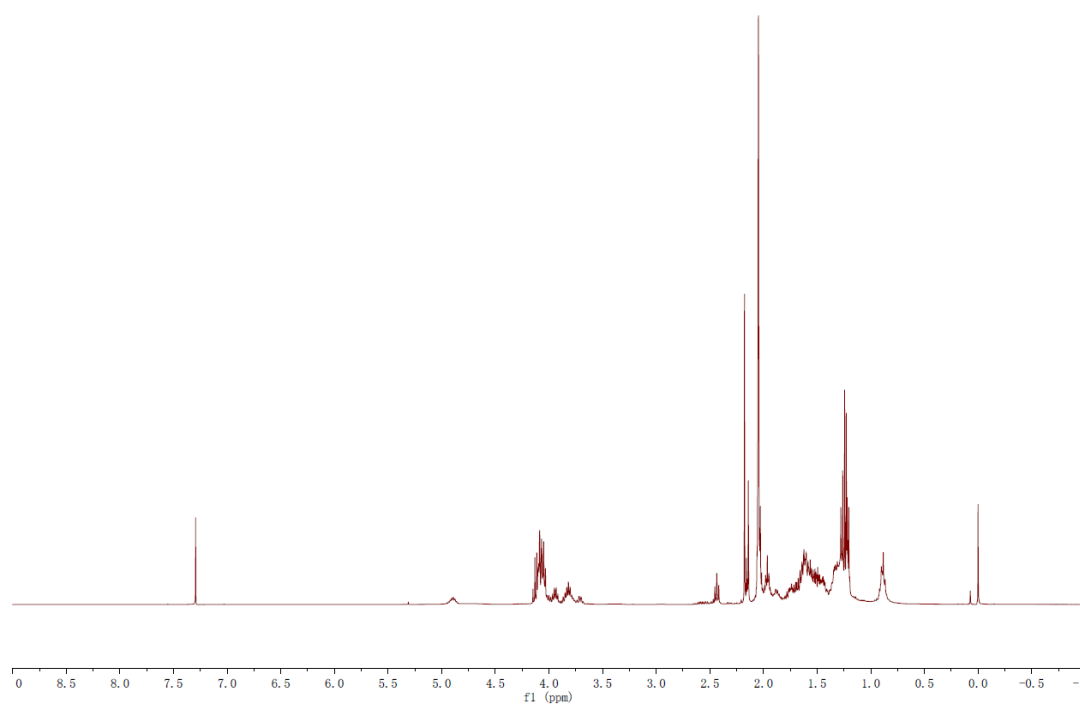


Figure S7. The ^1H -NMR spectrum of reaction heated for 20 min

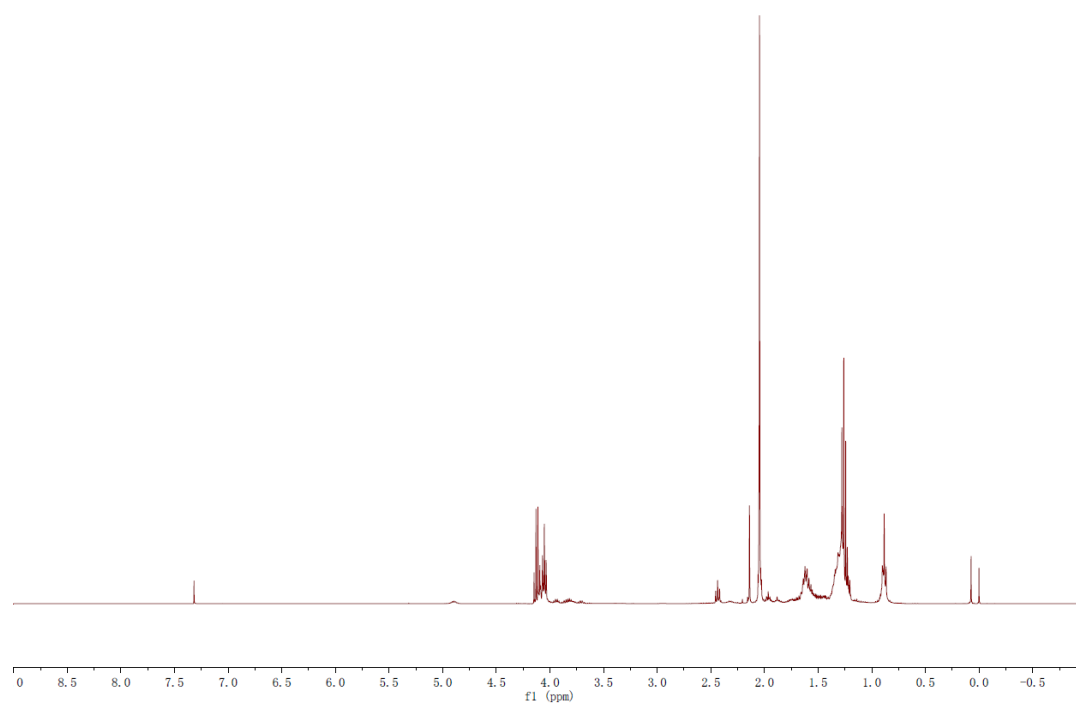


Figure S8. The ^1H -NMR spectrum of reaction heated for 30 min

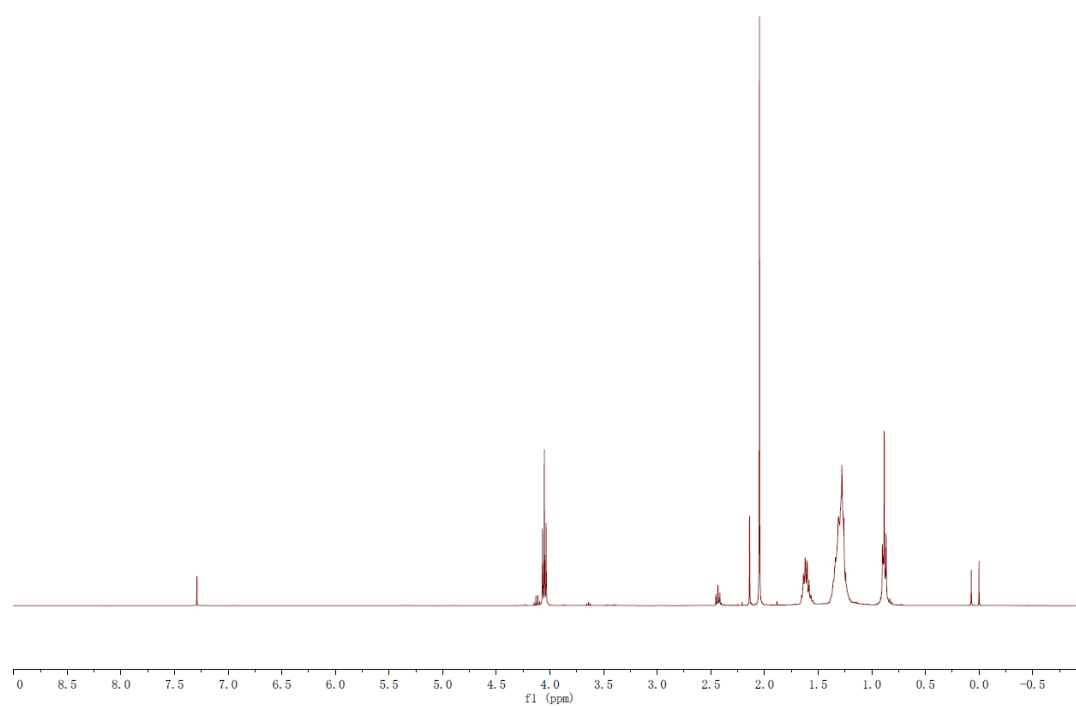


Figure S9. The ^1H -NMR spectrum of reaction heated for 30 min and constant heating for 60 min

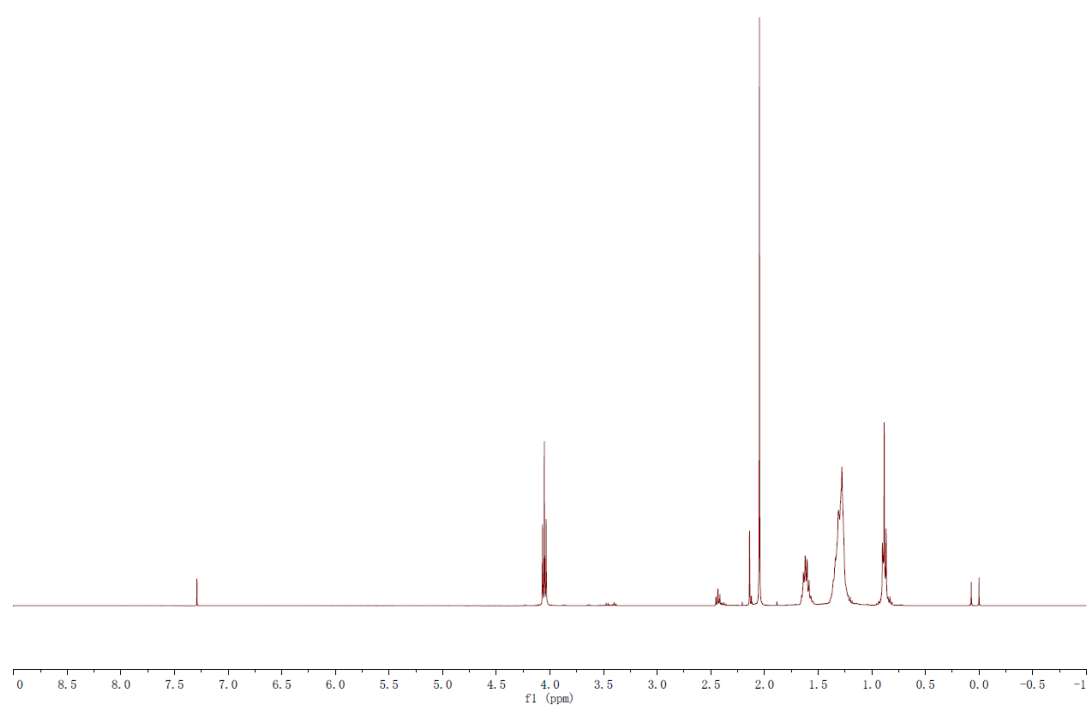


Figure S10. The ^1H -NMR spectrum of reaction heated for 30 min and constant heating for 120 min

VI. NMR spectrum

