

Electronic Supplementary Information (ESI)
for
One-pot two-step process directly converting biomass-derived
carbohydrate to lactide

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Experimental Section

Preparation of Sn-DeAl-Beta. Sn-DeAl-Beta was prepared by solid-state ion-exchange method according to the procedure reported in the literature. At first, commercial H-Beta ($n_{\text{Si}}/n_{\text{Al}}=12.5$, Nankai University Catalyst Co. Ltd.) was dealuminated with $13 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 solution (20 mL g^{-1}) at $100 \text{ }^\circ\text{C}$ for 20 h. The dealuminated Beta (marked as DeAl-Beta) was filtered, washed with deionized water and dried at $160 \text{ }^\circ\text{C}$ overnight. Then, 1g DeAl-Beta was grinded with the appropriate amount of $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ in agate mortar for 30 min at room temperature. Samples were calcined in an air flow at $550 \text{ }^\circ\text{C}$ and denoted as Sn-DeAl-Beta-x, where x represents the $n_{\text{Si}}/n_{\text{Sn}}$ ratio.

Characterization. The X-ray powder diffraction (XRD) patterns were obtained with the Bruker D8 ADVANCE diffractometer (Cu-K α radiation, 40 kV and 40 mA). Temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out in a Micrometrics AutoChem 2920 instrument. The FT-IR studies of pyridine adsorption were conducted via the Nicolet 6700 spectrometer equipped with an analysis platform (a CRCP-7070 supplied by Tianjin Xianquan Industry and Trade Development Co., Ltd, China.) designed for in situ FTIR spectroscopy. Self-supported wafer of sample was placed in the IR cell and evacuated at $450 \text{ }^\circ\text{C}$ for 2 h with a vacuum system. Reference spectrums at different temperatures ($300 \text{ }^\circ\text{C}$, $450 \text{ }^\circ\text{C}$) were recorded (64 scans at a 4 cm^{-1} resolution). After cooling to room temperature, the sample was subjected to pyridine vapor for enough time and IR spectra were recorded repeatedly until the evolution of adsorbed species indicated that pyridine saturation of the surface was reached. Afterwards, the sample was evacuated under vacuum at $300 \text{ }^\circ\text{C}$, $450 \text{ }^\circ\text{C}$ for 30 min and spectra were collected. Scanning transmission electron micrographs (STEM) in high-angle annular darkfield (HAADF) modes, as well as energy dispersive X-ray spectroscopy (EDS) element maps were acquired on a Tecnai G2 F20 S-Twin operated at 200 kV. The specific rotation was measured in dichloromethane solutions at concentrations of 1.0% (w/v) using a wavelength of 589 nm cell with Anton Paar MCP5500.

Conversion of carbohydrate toward lactic acid. All reactions were performed in a microwave reactor. A mixture of carbohydrate (100 mg), H_2O (5 mL) and catalyst (100 mg) was placed in a 30 mL microwave reaction tube and then put into a microwave instrument (PreeKem Nova-2S) and heated to the specified temperature in 3 ~ 5 min. At different intervals, the reaction solution was collected and analysed by HPLC (Shimadzu Corporation) equipped with an Aminex HPX-87H ($7.8 \text{ mm} \times 300 \text{ mm}$) sugar column and refractive index detector (RID). The quantification analysis of products mixture was based on calibration curves obtained by analyzing standard solutions.

Conversion of lactic acid toward lactide. When starting from DHA, 100 mg of H-Beta catalyst, 5 mL of lactic acid solution from DHA and 5 mL toluene were added to a 25 mL round bottom flask under magnetic stirring (Figure S7). On top of the setup, a phase settler filled beforehand with toluene was placed, allowing reflux of the solvent with trapping of the water. The flask was put into a preheated oil bath whose setting temperature was $140 \text{ }^\circ\text{C}$ to assure reflux. After reaction, 10 mL of acetonitrile was added to the flask and left to set for overnight. The addition of acetonitrile turns the liquid phase into a homogeneous one. Then, 4 mL of the mixture was filtered with a syringe filter to remove the solid catalyst. The filtered solution was dried in a

flowing Ar-atmosphere to remove toluene and acetonitrile solvents. Dry sample was dissolved in 0.6 mL DMSO-d₆ or CDCl₃ and ¹H NMR characterization was measured on BRUKER AVANCE III HD 400MHz. The lactide yield was estimated according to the following formula from ¹H NMR spectra: Lactide yield = (A+B)/(A+B+C+D+E+F)×100% (seen in Figure 2). When starting from monosaccharides or disaccharides, some additional operations were performed. After the first step, small amount of activated carbon was added to the reaction mixture and then centrifuged and filtered for decoloring. HPLC analysis proves that the composition of reaction mixture is consistent before and after decolorization.

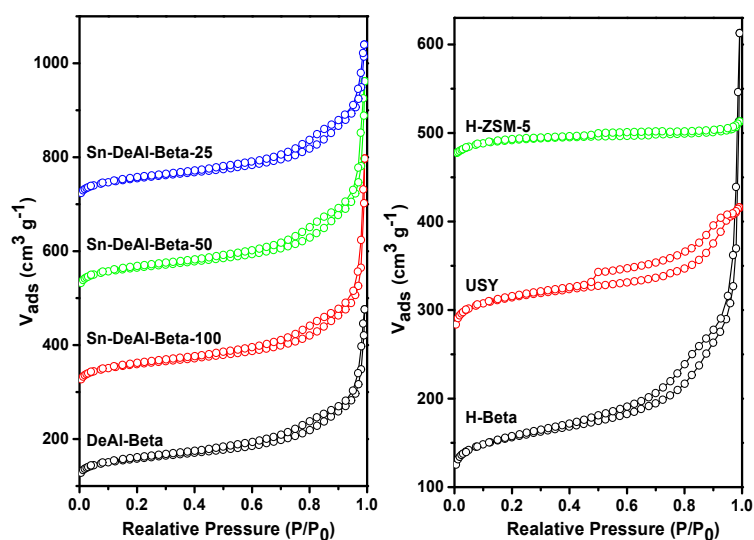


Figure S1. N₂ adsorption and desorption isotherms of various samples. Curves artificially offset by 200 cm³ g⁻¹ (left) and 100 cm³ g⁻¹ (right) for clarity.

Table S1. Physical parameters of various zeolites.

Sample	V _{total} ^a (cm ³ g ⁻¹)	V _{micro} ^b (cm ³ g ⁻¹)	S _{BET} ^c (m ² g ⁻¹)	S _{ext} ^b (m ² g ⁻¹)
DeAl-Beta	0.50	0.19	625	149
Sn-DeAl-Beta-100	0.47	0.18	592	135
Sn-DeAl-Beta-50	0.47	0.18	601	146
Sn-DeAl-Beta-25	0.47	0.18	583	141
H-Beta	0.46	0.18	601	140
USY	0.49	0.29	843	96
H-ZSM-5	0.17	0.13	352	29

^a Volume adsorbed at P/P₀ = 0.96. ^b t-plot method. ^c BET method

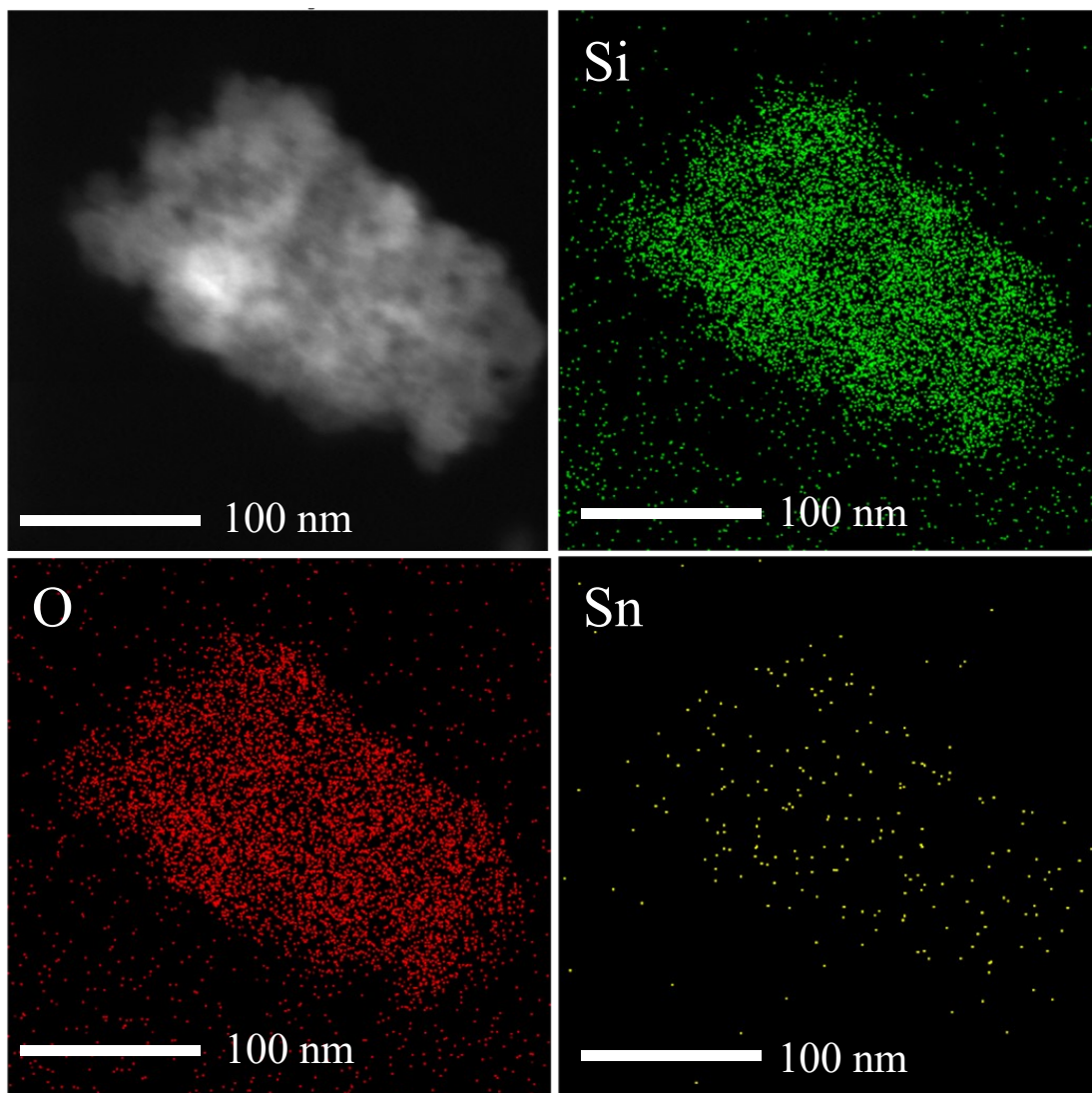


Figure S2. STEM images of Sn-DeAl-Beta-50 and its corresponding element mapping

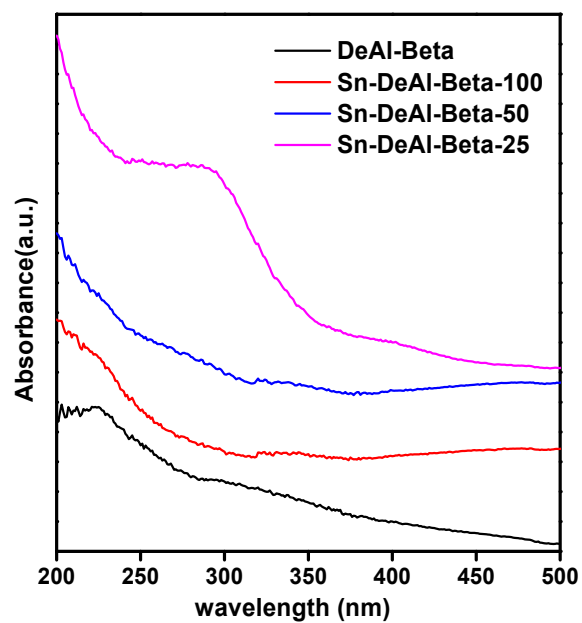


Figure S3. DR UV-vis spectra of DeAl-Beta, Sn-DeAl-Beta-100, Sn-DeAl-Beta-50, Sn-DeAl-Beta-25.

A broad band at around 300 nm in Sn-DeAl-Beta-25 indicates the presence of the extraframework SnO_2 species owing to excessive Sn loading.

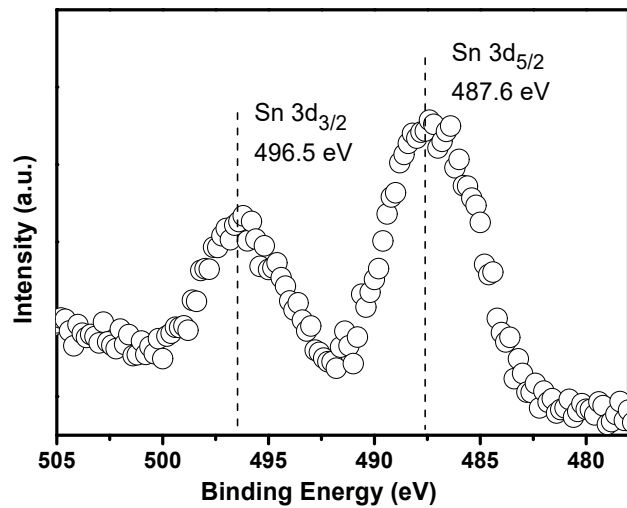


Figure S4. XPS spectrum of Sn 3d in Sn-DeAl-Beta-50.

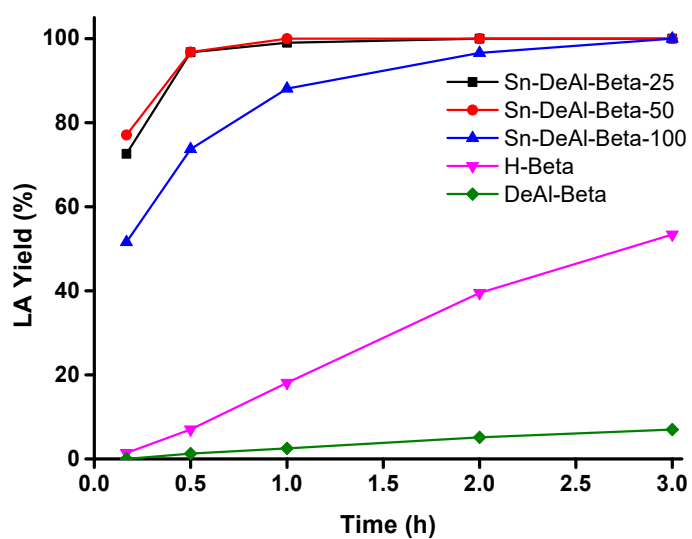


Figure S5. Catalytic conversion of 1,3-dihydroxyacetone (DHA) to lactic acid (LA) over various catalysts. Reaction condition: 100 mg DHA, 5 g H₂O, 100 mg catalyst, 130 °C, microwave.

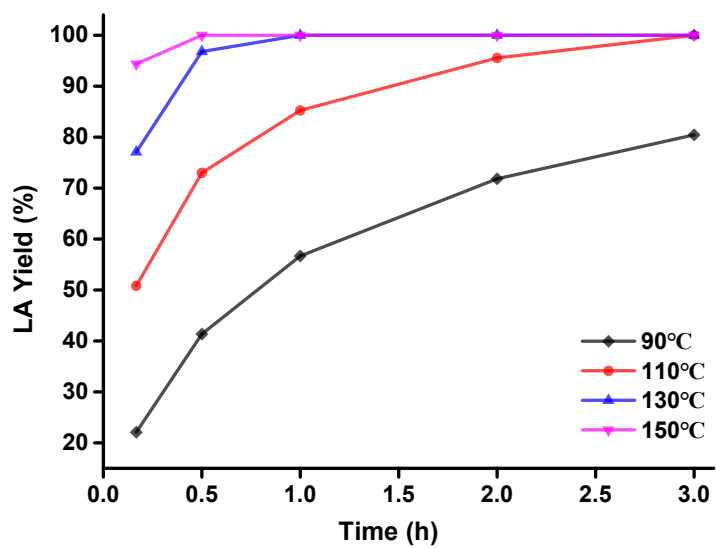


Figure S6. The yield of LA over Sn-DeAl-Beta-50 under different temperatures. Reaction condition: 100 mg DHA, 5 g H₂O, 100 mg Sn-DeAl-Beta-50, 90 °C-150 °C.

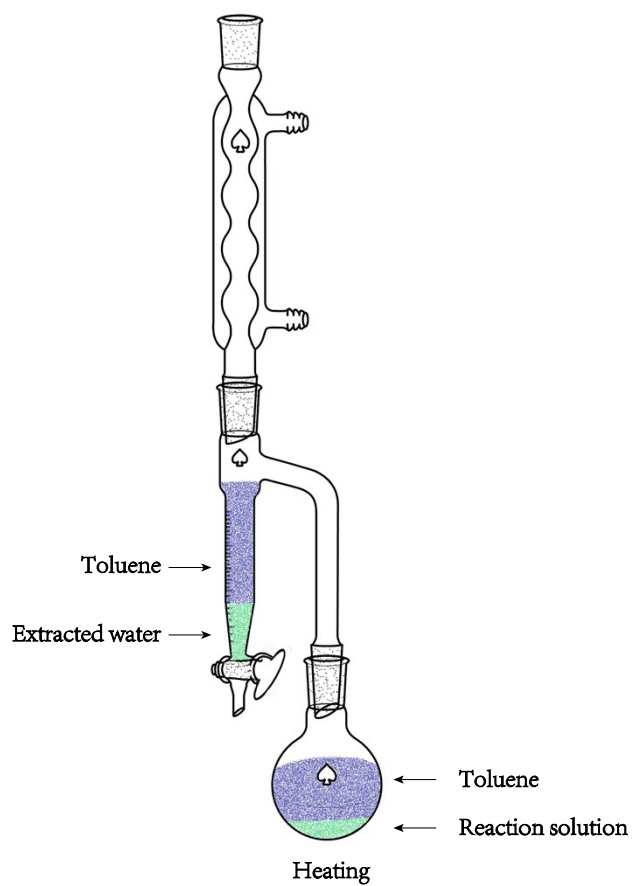


Figure S7. The experimental setup for LD production.

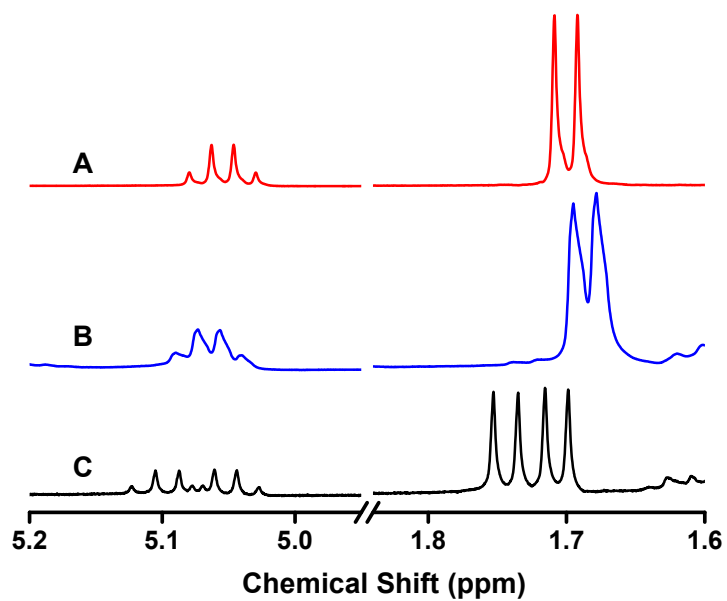


Figure S8. ¹H NMR spectra (in CDCl₃) of L-LD reference (**A**), LD directly from LA (**B**) and LD from DHA (**C**). Reaction conditions: **B**: 1.18 g 85 wt% LA, 100 mg H-Beta, 5 mL toluene, 140 °C reflux, 5 h; **C**: step 1: 100 mg DHA, 5 g H₂O, 100 mg Sn-DeAl-Beta-50, 130 °C, 3 h; step 2: 100 mg H-Beta, 5 mL toluene, 140 °C reflux, 5 h.

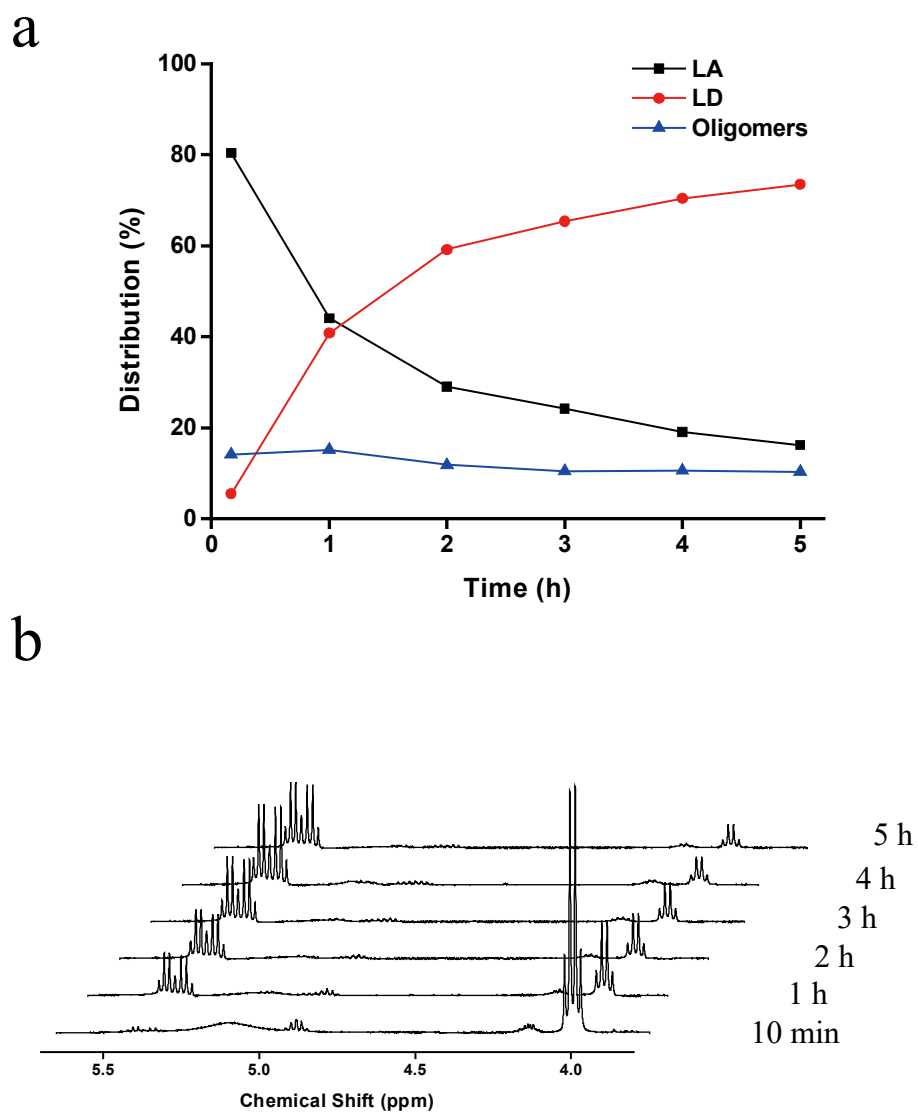


Figure S9. (a) Additional time profiles of catalytic reaction of step 2. (b) ^1H NMR spectra (in DMSO-d_6) of reaction solution of step 2 at different reaction time. Reaction conditions: step 1: 100 mg DHA, 5 g H_2O , 100 mg Sn-DeAl-Beta-50, 130 $^\circ\text{C}$, 3 h; step 2: 100 mg H-Beta, 5 mL toluene, 140 $^\circ\text{C}$ reflux, 10min - 5h.

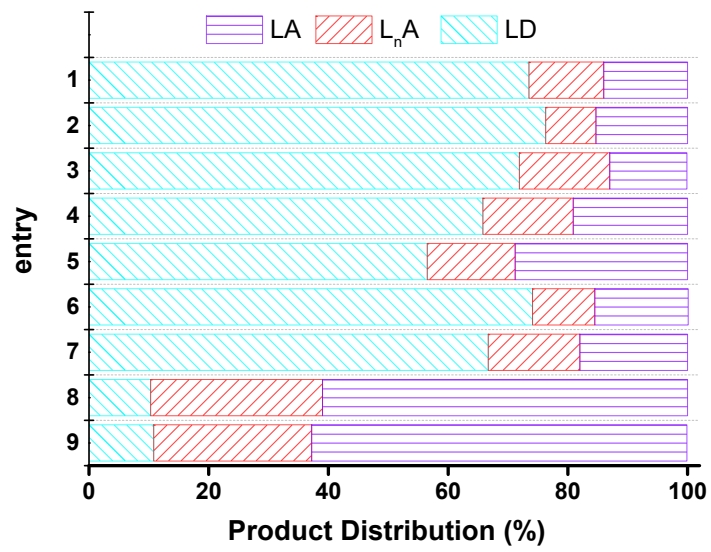


Figure S10. The product distributions of different conditions in same order as the Table 1 in the manuscript.