

## Experiment

### Raney nickel characterization and evaluation

The Raney nickel is provided by Hangzhou Fangsheng Chemical Co., Ltd. The XRD patterns of the catalyst is recorded with a Philips PW 3040/00 X'Pert MPD/MRD diffractometer using Cu K $\alpha$  radiation operated at 45 kV and 40 mA. N<sub>2</sub> adsorption-desorption isotherms are determined at 77K on a Micromeritics TriStar 3000 instrument. The catalyst is first degassed under vacuum at 353K for 8 h. Scanning Electron Microscopy (SEM) is measured on a JSM-7001F microscope. The TEM (Transmission electron microscope) is conducted on a JEM-2100F microscope. Temperature programmed reduction (H<sub>2</sub>-TPR) is carried out in an automatic equipment (Chemisorb 2750, Micromeritics). The sample (0.25g) is submitted to a heat treatment (from room temperature to 900 °C with 10 °C/min) in a gas flow (20 mL/min) of the mixture N<sub>2</sub>:H<sub>2</sub> (volume ratio = 95:5). XPS is performed under an ultrahigh vacuum on a Kratos AXIS ULTRA DLD spectrometer with Al K radiation and a multichannel detector. The collected binding energies were calibrated by the C1s peak at 285.1 eV as reference. The MALDI-TOF-MS spectra were performed on a Biflex III reflectron time-of-flight (TOF) mass spectrometer (Bruker Daltonics, USA) equipped with a nitrogen laser as the excitation source and N-(1-naphthyl)ethylenediamine dihydrochloride (NEDC) as a matrix. Angelica lactone was analyzed by GC (Shimadzu, GC-2010Plus) equipped with a flame ionization detector and an Rtx-1 PONA (100m×0.25mm×0.5 $\mu$ m) capillary column. The yield of angelica lactone self-aggregations was determined by using a Shimadzu high-pressure liquid chromatograph (LC-10AT) equipped with a UV-VIS detector (SPD-10A) at a wavelength of 215nm. A 4.6 mm id×250 mm Kromstar C 18 reverse-phase column was used. The mobile phase was 50% acetonitrile and 50% deionized water at a flow rate of 0.1 mL min<sup>-1</sup>. The column temperature was maintained at 308K.

Levulinic acid (99 wt%) is purchased from langfang haoke technology co, LTD.; Alpha angelica lactone 97% (GC grade) is purchased from Sahn chemical technology (Shanghai) co, LTD.; Anhydrous potassium carbonate, anhydrous ethanol, cyclohexane, decahydronaphthalene, petroleum ether, ethyl acetate and phosphate acid are purchased from Tianjin Kemiou Chemical Reagent Co, LTD.

### Levulinic acid dehydration

Synthesis of levulinic acid from biomass sources has been industrialized so far, but levulinic acid downstream products' further development and utilization are reported rarely. Of the levulinic acid downstream products, angelica lactone is a kind of potential platform compound. In present work, angelica lactone is synthesized from levulinic acid via intramolecular esterification reaction: 200.00g levulinic acid and a small amount of phosphoric acid are introduced into 250mL round-bottomed flask and heated to the set temperature in an oil bath. The flask is attached to a distillation column and the pressure in this system is controlled by an oil vacuum pump. The temperature of the heating jacket is set at 343K. The reaction lasts for 5 hours. After the reaction system separates into two phases spontaneously, products are washed 3-4 times with distilled water to remove the catalyst. The final products are analyzed by a Shimadzu GC-2010 plus.

### Angelica lactone self-aggregation

Because of C=C bond present in the molecular structure of angelica lactone, the angelica lactone self-aggregation reaction could take place and premium C10 dimer could be obtained by C-C bond coupling. In present work, 10.00g angelica lactone is added to 100mL round-bottomed flask and heated by oil bath. When it is heated to 353K, anhydrous K<sub>2</sub>CO<sub>3</sub> is put into the flask and stirred for 1 hour. Products are washed 1-2 times with distilled water to remove K<sub>2</sub>CO<sub>3</sub> catalyst. The final products are analyzed by a Shimadzu GC-2010 plus. Next, the final products are analyzed by HPLC, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, and MALDI-TOF-MS techniques. The chemical structures of products are characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MALDI-TOF-MS techniques. The <sup>1</sup>H NMR and <sup>13</sup>C NMR and dept135-<sup>13</sup>C NMR spectra of angelica lactone di/trimers are recorded in DMSO with DSS as internal standard on a Bruker AV-III 400 for frequency at 400.13 and 100.61 MHz, respectively. The MALDI-TOF-MS spectra are performed on a Biflex III reflectron time-of-flight (TOF) mass spectrometer (Bruker Daltonics, USA) equipped with a nitrogen laser as the excitation source.

### Hydrodeoxygenation

0.5g Angelica lactone self-aggregated intermediates, 0.1g Raney nickel catalyst, 30mL solvent and a magnetic stir bar are

introduced into a 100mL tetrafluoroethylene lining, which is put into the high pressure reaction kettle. The reactor is sealed, flushed 3-5 times with hydrogen and finally pressurized to 5 MPa. Temperature is programmed-heated to 483K and stirring (500rpm) is initiated when the pressure kettle reaches 483K. Then the reaction lasts for 5 hours. After the reaction, heating and stirring are stopped and the kettle is cooled to room temperature by cooling water. After opening the kettle, there are two phases: liquid phase and solid phase. The liquid products are extracted and analyzed by GC after centrifugalization. We used area normalization method to calculate each of the generated alkane in GC analysis.

LA-AL conversation (%) = (1-the liquid chromatographic peak area of levulinic acid after the reaction /the liquid chromatographic peak area of levulinic acid before the reaction) x 100%

yield(%) = the mass of the angelica lactone/ the mass of levulinic acid

Angelica lactone aggregation conversation (%) = (1-the liquid chromatographic peak area of angelica lactone after the reaction /the liquid chromatographic peak area of angelica lactone before the reaction) x 100%

yield (%) = the mass of the angelica lactone aggregation/ the mass of angelica lactone

HDO conversation (%) = (1-the liquid chromatographic peak area of angelica lactone aggregation after the reaction /the liquid chromatographic peak area of angelica lactone aggregation before the reaction) x 100%

yield (%) =the HDO conversation\* the HDO selectivity (%)

Fig. S1 HPLC chromatograms of isomerization of angelica lactone di/trimers.

Fig. S2 Mass spectra of di/trimerization products.

Fig. S3 <sup>13</sup>C NMR spectra of angelica lactone di/trimers.

Fig. S4 DEPT-<sup>13</sup>C NMR spectra of angelica lactone di/trimers.

Fig. S5 <sup>13</sup>C NMR spectra of angelica lactone.

Fig. S6 <sup>1</sup>H NMR spectra of angelica lactone.

Fig. S7 (a) GC/MS chromatogram of the products after angelica lactone dimer hydrodeoxygenation.

(b) GC-MS oven temperature profile for the analysis of the hydrodeoxygenation products.

Fig. S8 Pictures of products of each step.

Fig. S9 Angelica lactone preparation experiment device.

Fig. S10 Angelica lactone self-aggregated reaction device.

Fig. S11 Angelica lactone self-aggregation HDO device.

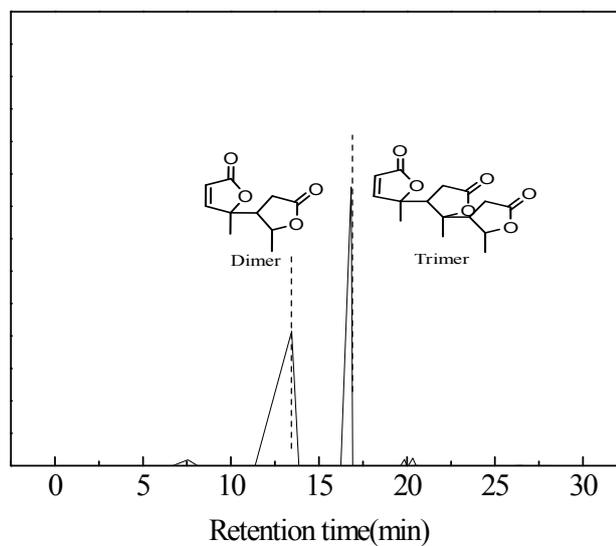


Fig. S1 HPLC chromatograms of isomerization of angelica lactone di/trimers.

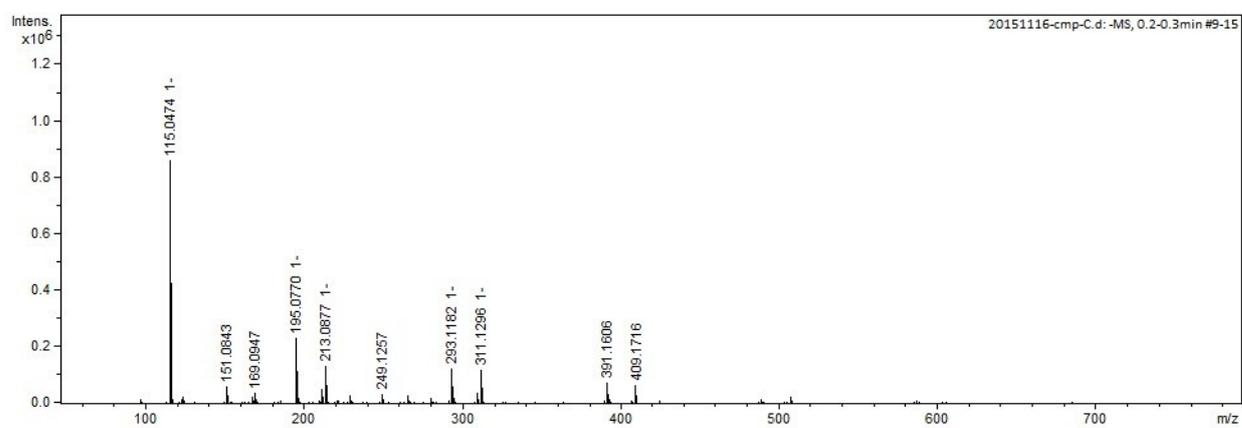


Fig. S2 Mass spectra of di/trimerization products

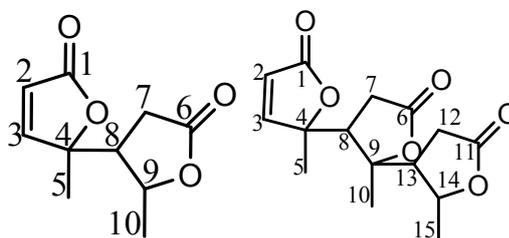
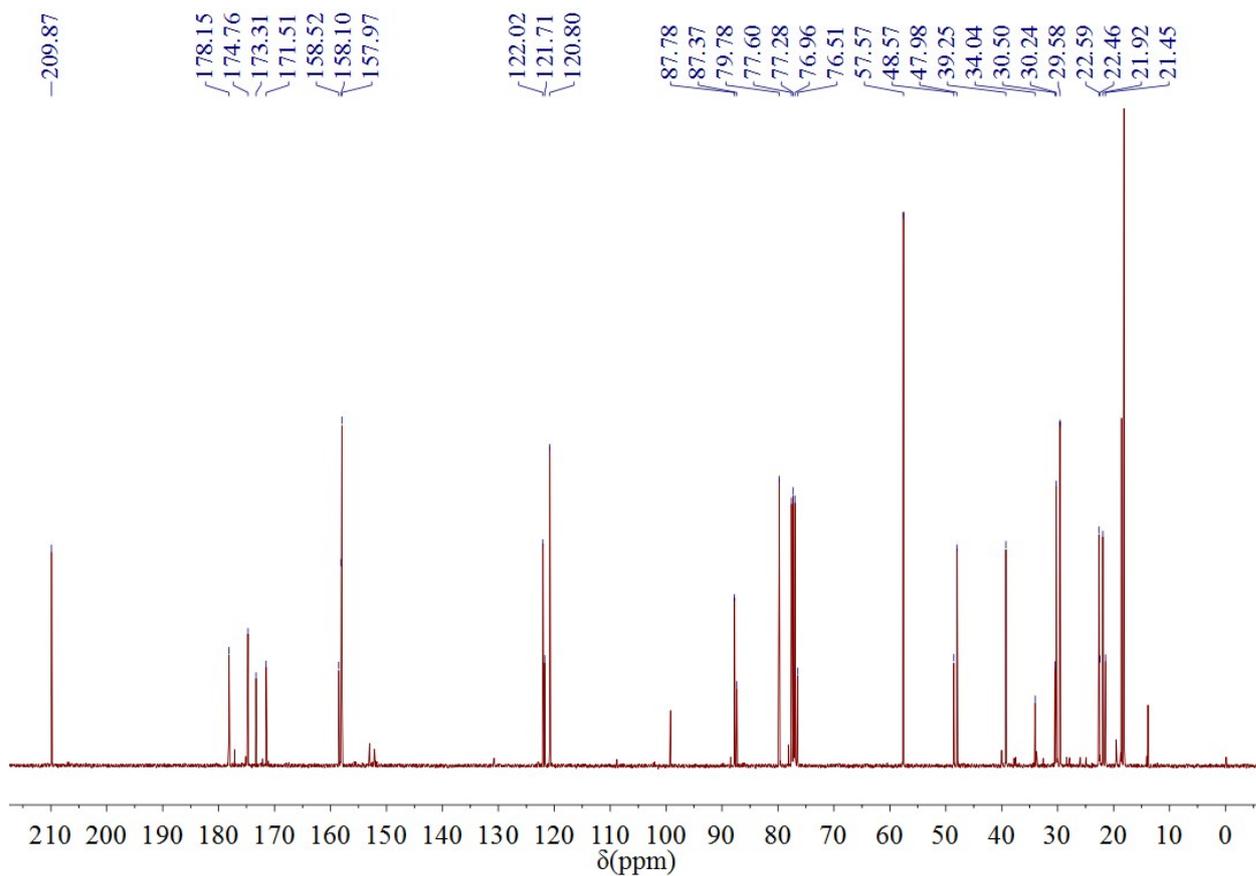


Fig. S3  $^{13}\text{C}$  NMR spectra of angelica lactone dimer.

Angelica lactone dimer 1C&6C 177ppm; 2C 158ppm; 3C 122ppm; Quaternary carbon 4C 87ppm;

5C&10C 22ppm; Secondary carbon 7C 30ppm; 8C 47ppm; 9C 77ppm.

Angelica lactone trimer C1 175.5ppm; C2 120.1ppm; C3 163.9ppm; C4 87.9ppm; C5 25.7ppm; C6 176.1ppm; C7 25.0ppm; C8 44.9ppm; C9 89.9ppm; C10 27.0ppm; C11 176.1ppm; C12 34.5ppm; C13 39.9ppm; C14 74.6ppm; C15 19.3ppm.

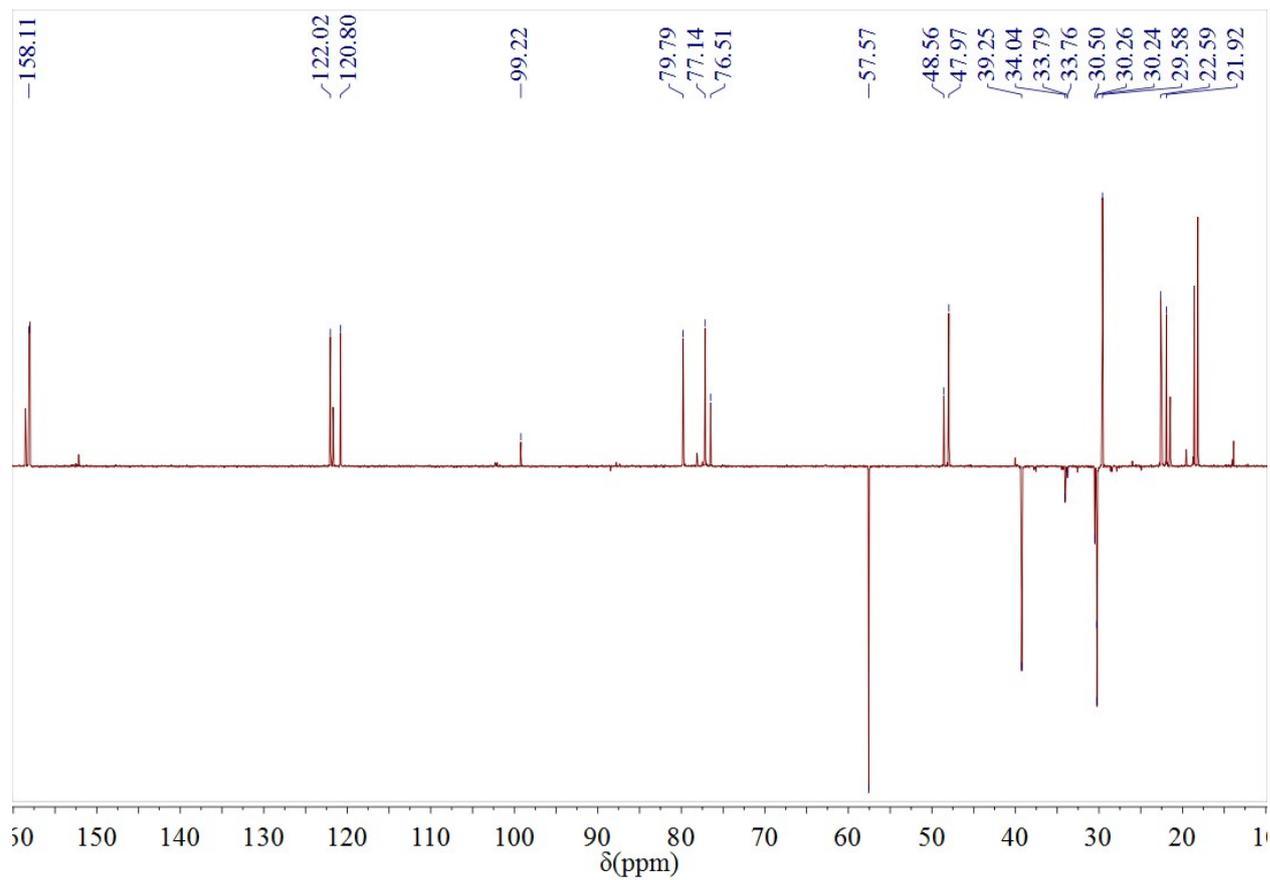


Fig. S4 DEPT-<sup>13</sup>C NMR spectra of angelica lactone dimer.  
 1C&6C 177ppm; 2C 158ppm; 3C 122ppm; Quaternary carbon 4C 87ppm;  
 5C&10C 22ppm; Secondary carbon 7C 30ppm; 8C 47ppm; 9C 77ppm.

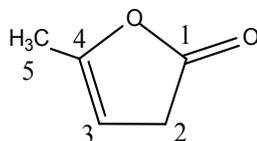
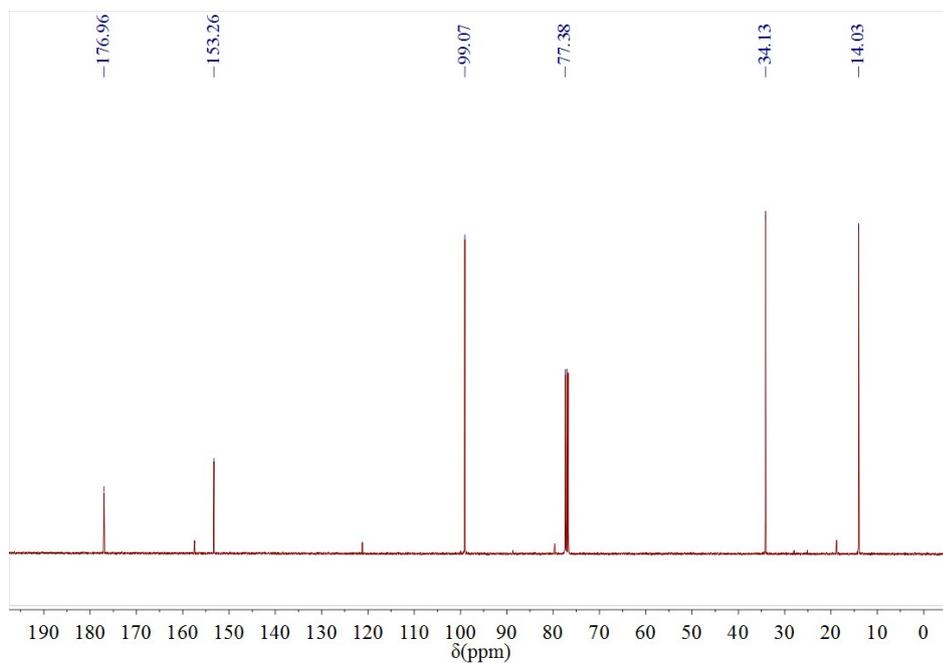


Fig. S5  $^{13}\text{C}$  NMR spectra of angelica lactone.

Angelica lactone 1C 176ppm; 2C 34.05ppm; 3C 99.25ppm; 4C 153.02ppm; 5C 15.86ppm.  
 $\text{CDCl}_3$  77.38ppm.

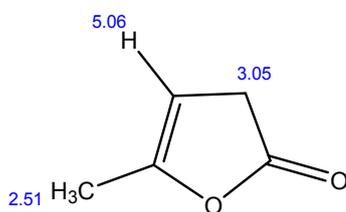
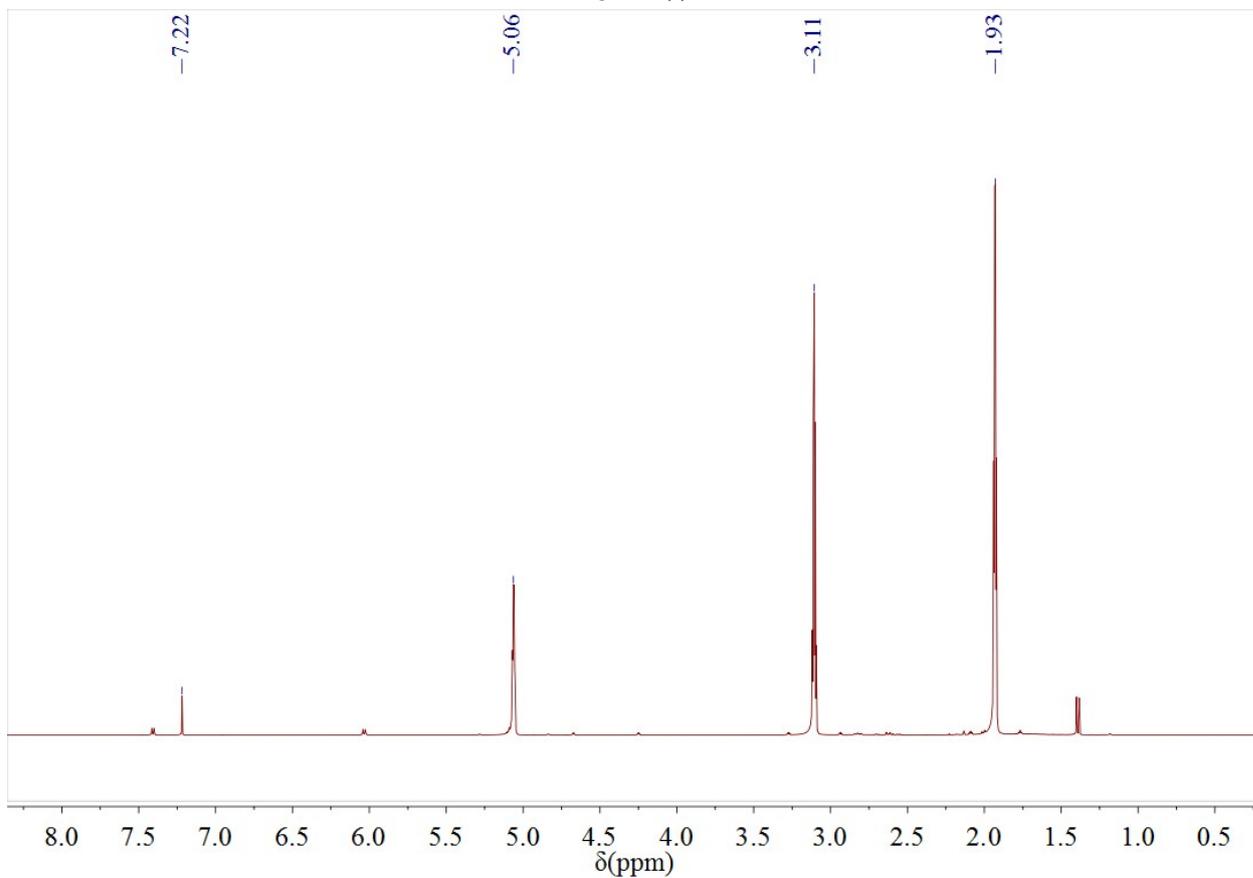
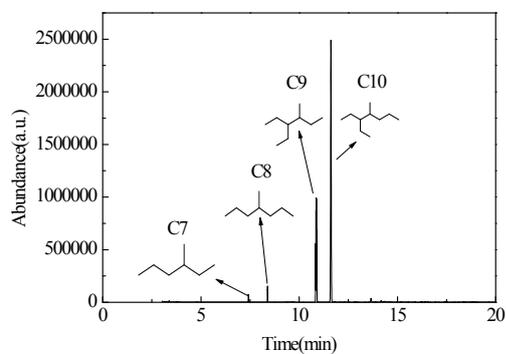


Fig. S6  $^1\text{H}$  NMR spectra of angelica lactone.

Angelica lactone C2-H 3.05ppm; C3-H 5.06ppm; C5-H 2.51ppm;  $\text{CDCl}_3$  7.22ppm.



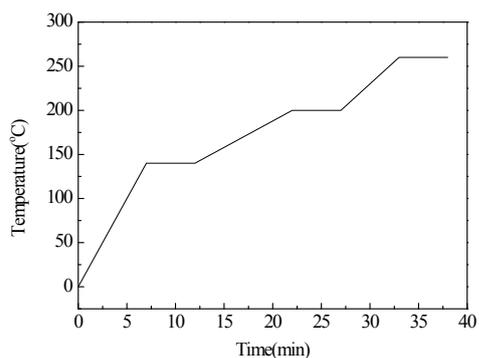


Fig. S7 (a) GC/MS chromatogram of the products after angelica lactone dimer hydrodeoxygenation.  
 (b) GC-MS oven temperature profile for the analysis of the hydrodeoxygenation products.



Angelica lactone                      Angelica lactone di/trimers                      Bio-alkanes

Fig. S8 Pictures of products of each step

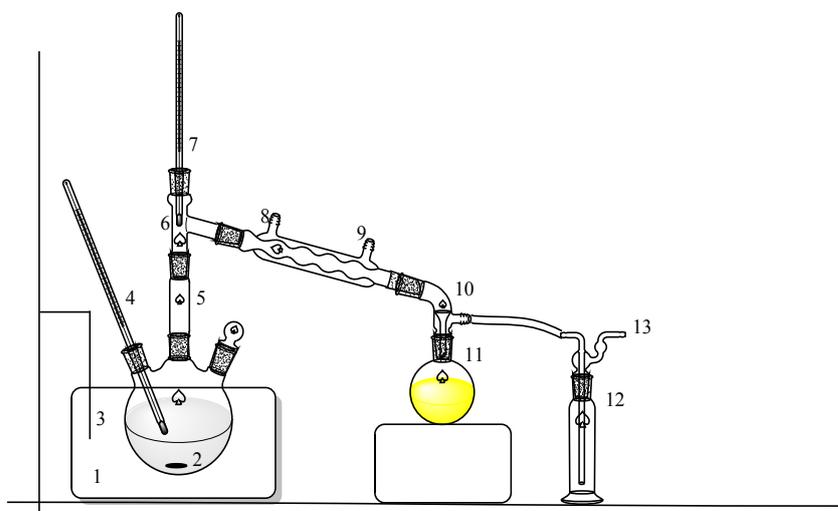


Fig. S9 AL-LA preparation experiment device

- 1 oil bath pot 2 magneton 3 thermocouple 4 thermometer 5 distillation column 6 distilling head
- 7 thermometer 8 condensed water outlet 9 condensate water inlet 10 the tail to take over 11 receives the bottle 12 color silicone column 13 vacuum device (pressure gauge, vacuum pump)

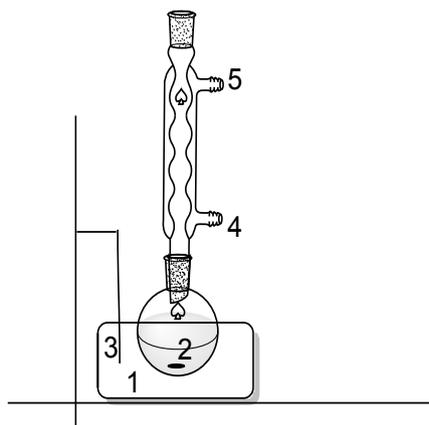


Fig. S10 Angelica lactone self-aggregated reaction device

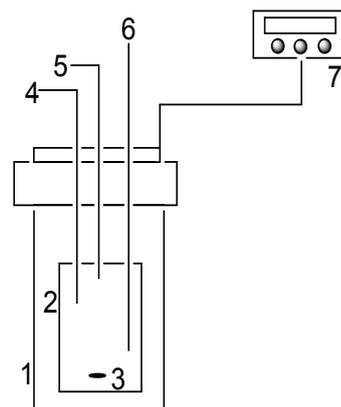


Fig. S11 Hydrodeoxygenation device

(9)1 oil bath pot 2 magneton 3 thermocouple 4 condensate water inlet 5 condensate water outlet

(10)1 high pressure reaction kettle 2 PTFE lining 3 magneton 4 air inlet 5 the outlet 6 thermocoupl