Electronic Supplementary Material (ESI) for Green Chemistry.

Synthesis of renewable diesel with 2-methylfuran and angelica lactone derived from carbohydrates

Wei Wang,[a,b] Ning Li,*[a,c] Shanshan Li,[a,d] Guangyi Li,[a] Fang Chen,[a,d] Xueru Sheng,[a,d] Aiqin Wang,[a,c] Xiaodong Wang,[a] Yu Cong[a] and Tao Zhang*[a,c]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, No. 457 Zhongshan Road, Dalian 116023, China.

[b] School of Chemical & Environment Science, Shaanxi University of Technology, Hanzhong 723001, China

[c] Collaborative Innovation Center of Chemistry for Energy Materials (*iChEM*)

[d] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding authors:

Prof. Tao Zhang; E-mail: taozhang@dicp.ac.cn; Tel.: +86 411 84379015; Fax: +86 411 84691570.

Dr. Ning Li; E-mail: lining@dicp.ac.cn; Tel.: +86 411 84379738; Fax: +86 411 84685940.

1 Experimental Section

1.1 Catalysts

Nafion-212 resin was supplied by Dupont. Amberlyst-15 and Amberlyst-36 resin were purchased from Sigma Aldrich. $FeCl_3$, $SnCl_4$, $ZnCl_2$ and $TiCl_4$ were bought from Sigma-Aldrich.

The Pd/C catalyst used for low-temperature hydrogenation and hydrodeoxygenation was prepared by the incipient wetness impregnation of the HNO_3 treated active carbon with an aqueous solution of $PdCl_2$. The Pt/C catalyst used for hydrodeoxygenation was prepared by the incipient wetness impregnation of the HNO_3 treated active carbon with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$. The Ru/C catalyst used for hydrodeoxygenation was prepared by the incipient wetness impregnation of the HNO_3 treated active carbon with an aqueous solution of $RuCl_3 \cdot 3H_2O$. The catalyst precursors as-obtained were dried at 353 K for 24 h and then reduced by H_2 (160 mL min^{-1} g_{cat}^{-1}) at 773 K for 2 h. After cooling in H_2 to room temperature, the catalysts were passivated with 1 vol.% O_2 in N_2. To facilitate comparison, the metal content in each catalyst was fixed at 5% by weight (denoted as 5wt.%).

1.2 Preparation of angelica lactone

Angelica lactone (a mixture of α-angelica lactone and β-angelica lactone) was prepared by the dehydration of levulinic acid according to the method described in the literature.[1] Typically, 25.0 g levulinic acid and 1.0 g H-ZSM-5 (SiO_2/Al_2O_3 molar ratio = 25, supplied by Nankai University) were loaded in a distillation flask and stirred at 453 K in an oil bath. The outlet of the flask was connected to a fractionation column (20cm) and a vacuum pump which was set at 60 mmHg. The dehydration products (*i.e.* angelica lactones and water) vaporized from the distillation flask, passed through a water-cooled condenser and became two phases in another flask. The ^1H and ^{13}C NMR spectra of the angelica lactones as obtained were illustrated in Figure S8. According to our analysis, up to 90% isolated carbon yield of angelica lactone was achieved by the dehydration of levulinic acid over the H-ZSM-5 catalyst under the investigated conditions. Before being used for the hydroalkylation/alkylation (HAA) test, the angelica lactone was dried by anhydrous sodium sulfate for 2 h.

1.3 Hydroxyalkylation/alkylation (HAA)

The HAA of 2-methylfuran (2-MF) and angelica lactone was carried out in a round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. The reaction temperature was controlled with a water bath. Typically, a mixture of catalyst, 2-MF, and angelica lactone was stirred at the set temperature for 1 h. The product was extracted with dichloromethane and analyzed by an Agilent GC 7890A equipped with HP-5 column (30 m, 0.25 mm ID, 0.5 mm film) and a flame ionization detector (FID).

1.4 Low-temperature hydrogenation

The low-temperature hydrogenation of the HAA product was carried out in a 316 L stainless steel tubular flow reactor described in our previous work.[2] For this process, 1.8 g 5wt.% Pd/C catalyst was used. A 30wt.% methanol solution of HAA product (purified by the vacuum distillation) was fed into the reactor using a HPLC pump (at the rate of 0.16 mL min^{-1}) from the bottom along with H_2 at a flow rate of 120 mL min^{-1}. The system pressure was controlled at 6 MPa by a back pressure regulator. The reaction temperature was controlled at 433 K. After hydrogenation, the methanol was removed by vacuum distillation. The product as obtained was directly used as the feedstock for the following solvent-free hydrodeoxygenation. From the results of GC-MS, the HAA product of 2-MF and angelica lactone was completely converted to 4,4-bis(5-methyl-tetrahydrofuran-2-yl)pentan-1-ol, 5,5'-(ethane-1,1-diyl)-bis- (2-methyltetrahydrofuran) and bis(5-methyltetrahydrofuran-2-yl)methane under the investigated conditions. According to the elemental analysis, the weight percentages of C, H, O in the hydrogenated HAA product were measured as 67.1%, 8.9% and 24.0%, respectively.

1.5 Hydrodeoxygenation (HDO)

The solvent-free HDO of the hydrogenated HAA product was carried out by the same reactor as we used for low-temperature hydrogenation. For each test, 1.8 g of active carbon loaded noble metal catalyst was used. The hydrogenated HAA product of (*i.e.* a mixture of 4,4-bis(5-methyl-tetrahydrofuran-2-yl)pentan-1-ol, 1,1-bis(5-methyltetrahydrofuran-2-yl)ethane and bis(5-methyl -tetrahydrofuran-2-yl)methane) was fed into the reactor (at the rate of 0.04 mL min^{-1}) by a HPLC pump from the bottom along with H_2 at a flow rate of 120 mL min^{-1}. The HDO process was carried out at 623 K. The products from the outlet of the reactor tube passed through a gas-liquid separator and became two phases. The gaseous products flowed through a back pressure regulator to maintain the pressure in the reaction system at 6 MPa and were analyzed online by an Agilent 6890N GC. The CO_2 in the gaseous product was measured by a thermal conductivity detector (TCD) equipped with an Alltech

HAYESEP DB 100/120 column (30 feet, 1/8 inch outer diameter, 2.0 mm inner diameter). The alkanes in the gaseous product were analyzed by a flame ionization detector (FID) equipped with an Rt-Q-BOND capillary column (30 m, 0.32 mm ID, 10 μm film). Liquid products were drained periodically from the gas-liquid separator and analyzed by an Agilent 7890A GC equipped with a HP-INNOWAX capillary column (30 m, 0.25 mm ID, 0.5 mm film) and FID detector.

The carbon yields of different alkanes in the HDO process were calculated according to the following formulas:

Carbon yield of C_9-C_{15} diesel and jet fuel range alkanes (%) = Total carbon of C_9-C_{15} alkanes in the liquid products/Total carbon of feedstock pumped into the reactor × 100%

Carbon yield of C_5-C_8 gasoline range alkanes (%) = Total carbon of C_5-C_8 alkanes in the gas products per unit time/Total carbon of feedstock pumped into the reactor per unit time × 100% + Total carbon of the C_5-C_8 alkanes in liquid phase products/Total carbon of feedstock pumped into the reactor × 100%

Carbon yield of C_1-C_4 light alkanes (%) = Total carbon of the C_1-C_4 alkanes in the gas products per unit time/Total carbon of feedstock pumped into the reactor per unit time × 100%

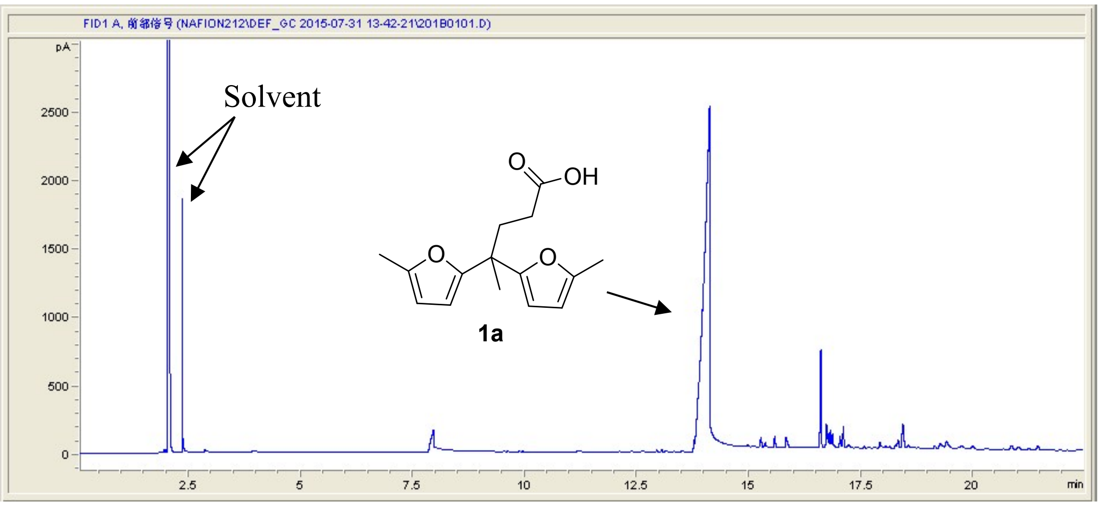


Figure S1. GC chromatogram of the liquid products from the HAA of 2-methylfuran (2-MF) and angelica lactone. Reaction conditions: 323 K, 1 h; 0.98 g (10 mmol) angelica lactone, 1.68 g (20 mmol) 2-methylfuran (2-MF), 0.1 g Nafion-212 resin.

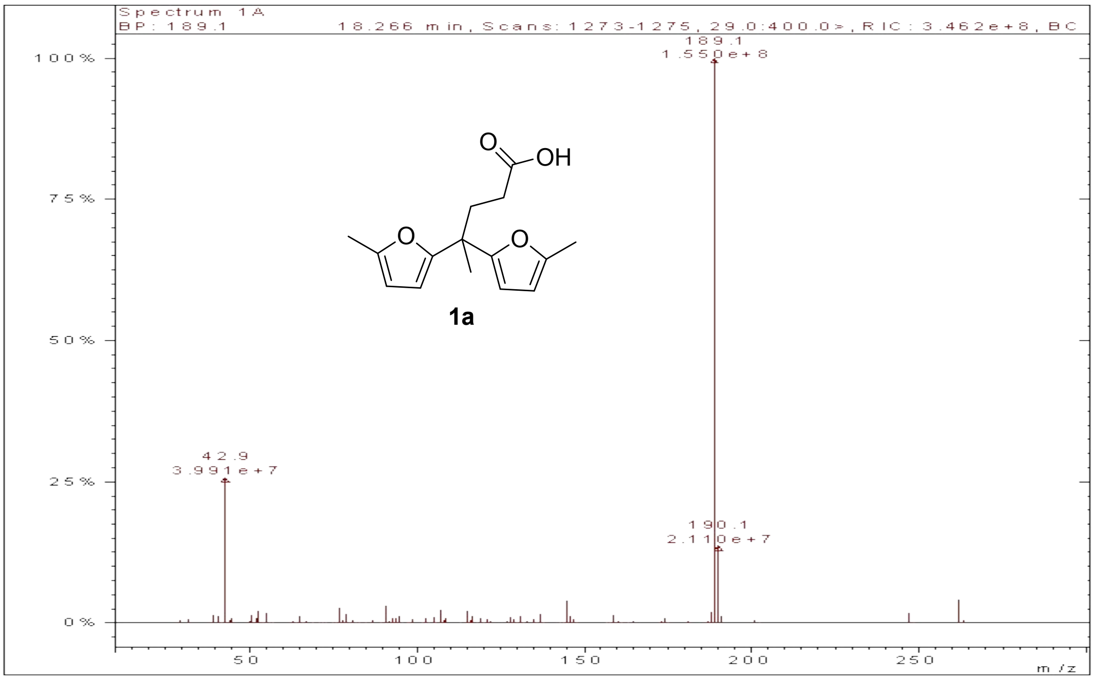


Figure S2. Mass spectrogram of the **1a** produced by the HAA of 2-MF and angelica lactone. Reaction conditions: 323 K, 1 h; 0.98 g (10 mmol) angelica lactone, 1.68 g (20 mmol) 2-MF, 0.1 g Nafion-212 resin.

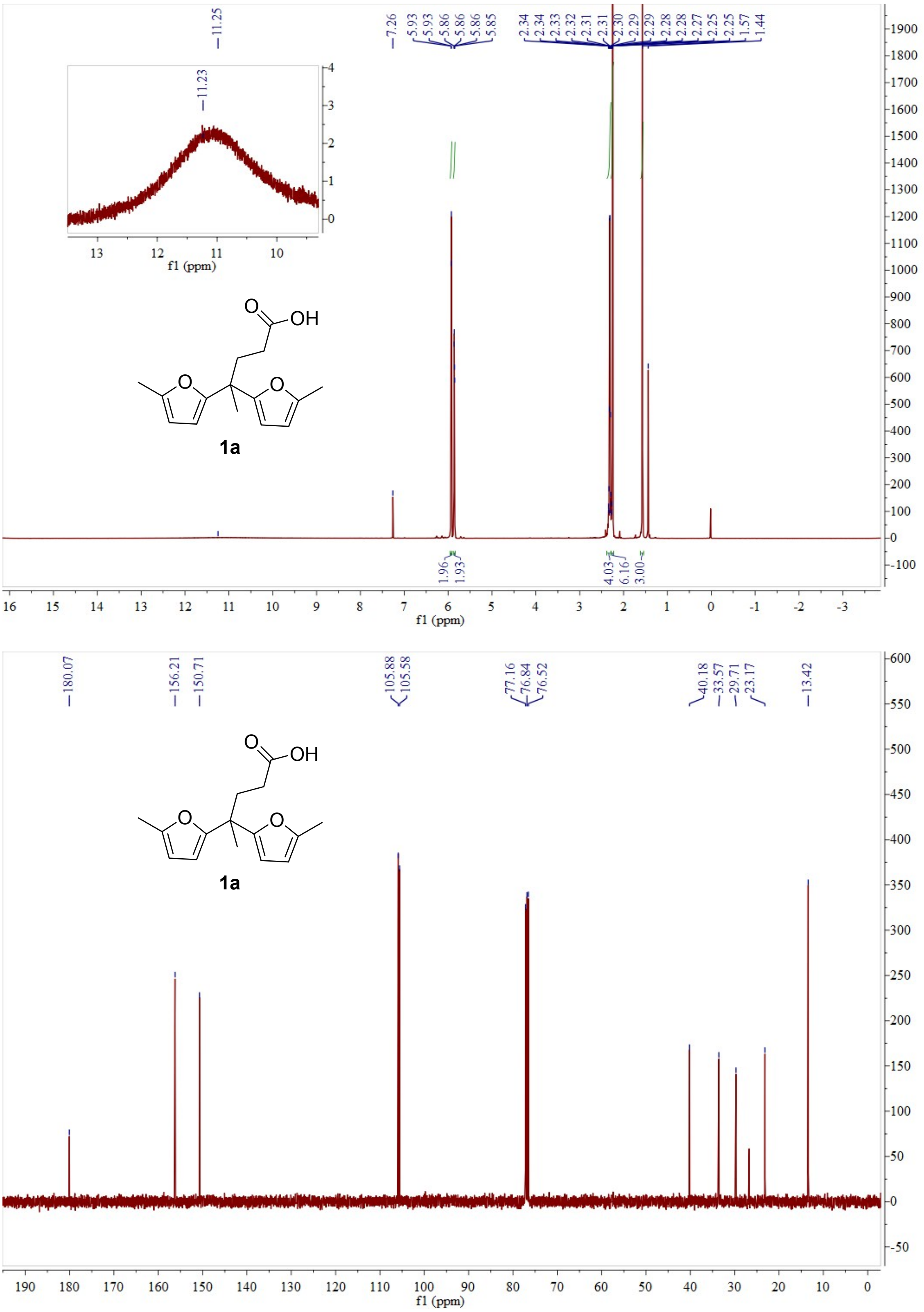


Figure S3. ^{1}H and ^{13}C NMR spectra of the **1a** from the HAA of 2-MF and angelica lactone.

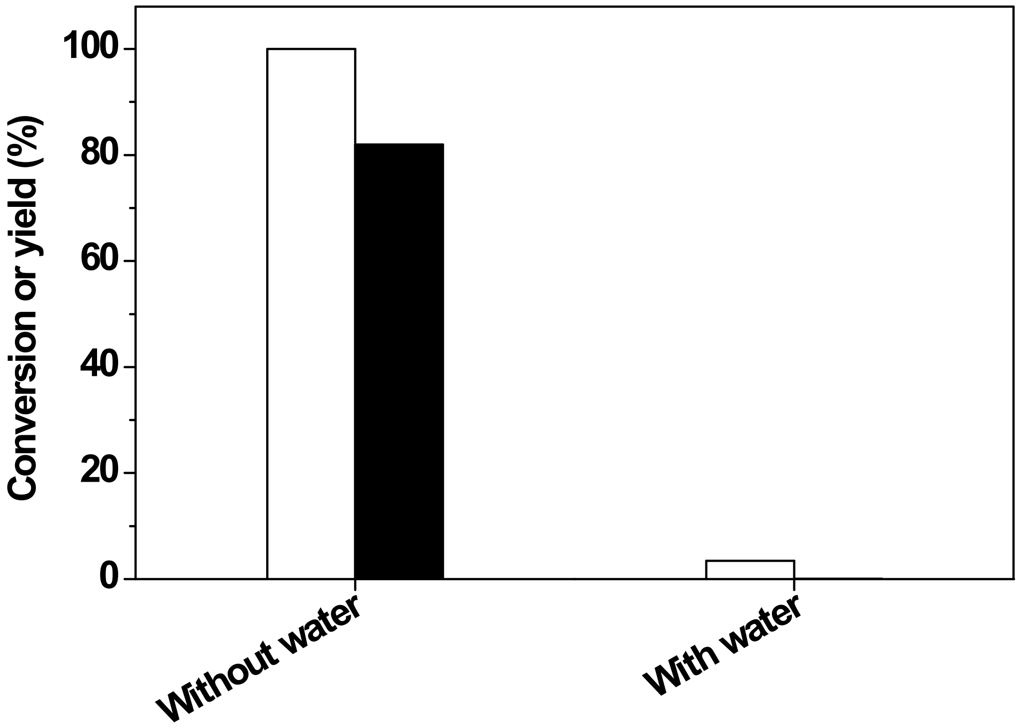


Figure S4. Effect of stoichiometric water on the conversion of angelica lactone (white bars) and the carbon yield of **1a** (black bars) over the Nafion-212 resin. Reaction conditions: 323 K, 1 h; 0.98 g angelica lactone, 1.68 g 2-MF, 0 (or 0.18) g H_2O, and 0.1 g Nafion-212 resin.

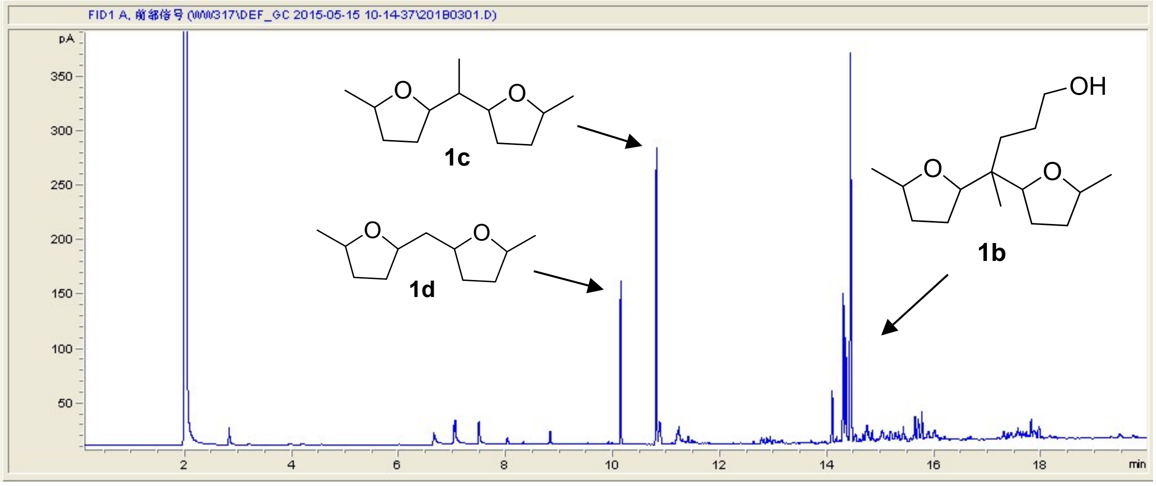


Figure. S5. GC chromatogram of the liquid products from the hydrogenation of **1a** over the 5wt.% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H_2, 1.8 g catalyst; liquid feedstock (30wt.% **1a** in methanol) flow rate of 0.16 mL min^{-1}; H_2 flow rate of 120 mL min^{-1}.

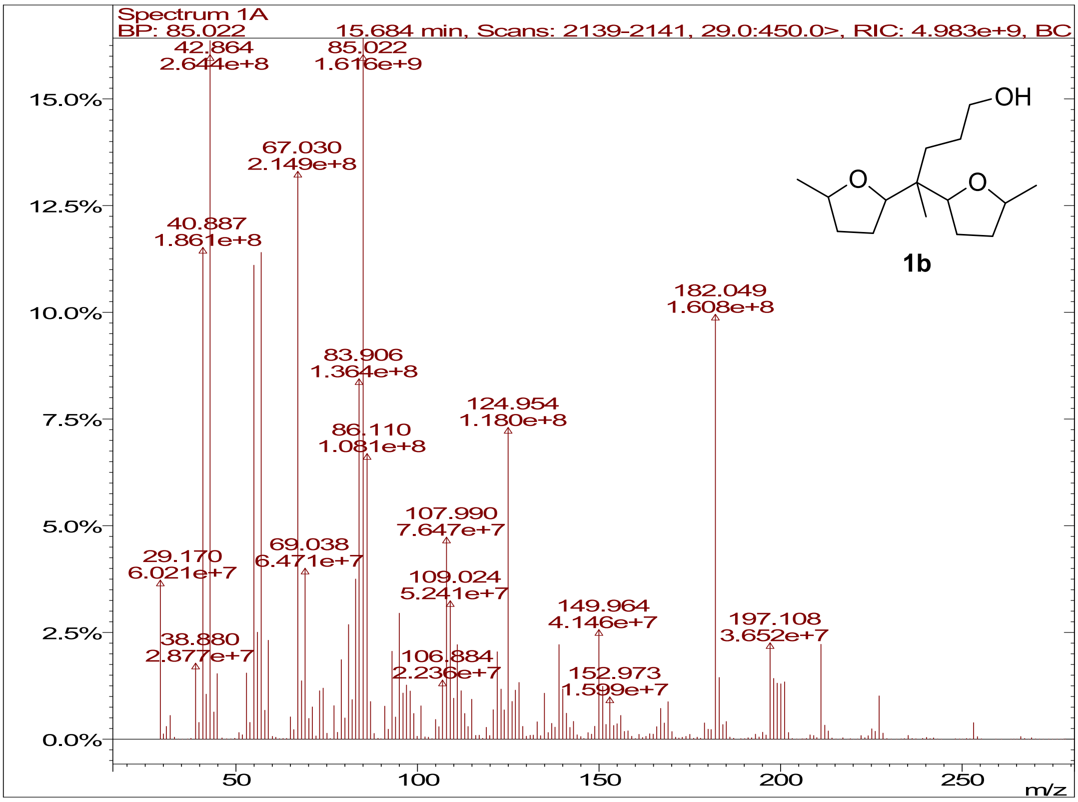


Figure S6. Mass spectrogram of the **1b** from the hydrogenation of **1a** over the 5wt.% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H_2, 1.8 g catalyst; liquid feedstock (30wt.% **1a** in methanol) flow rate of 0.16 mL min^{-1}; H_2 flow rate of 120 mL min^{-1}.

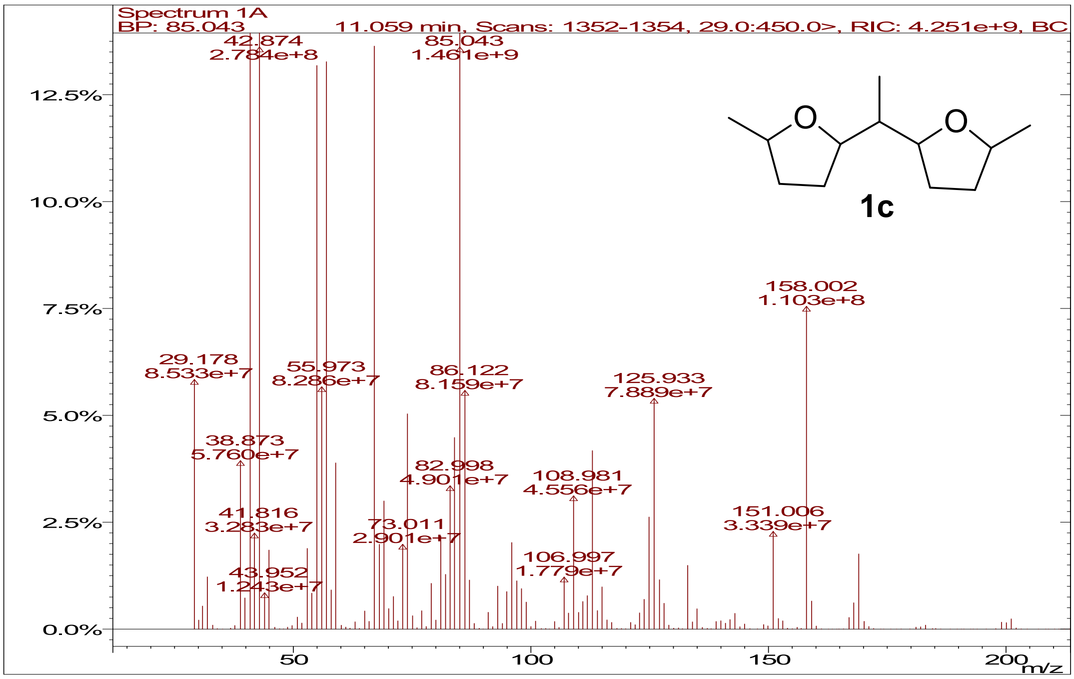


Figure S7. Mass spectrogram of the **1c** generated during the hydrogenation of **1a** over the 5wt.% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H_2, 1.8 g catalyst; liquid feedstock (30wt.% **1a** in methanol) flow rate of 0.16 mL min^{-1}; H_2 flow rate of 120 mL min^{-1}.

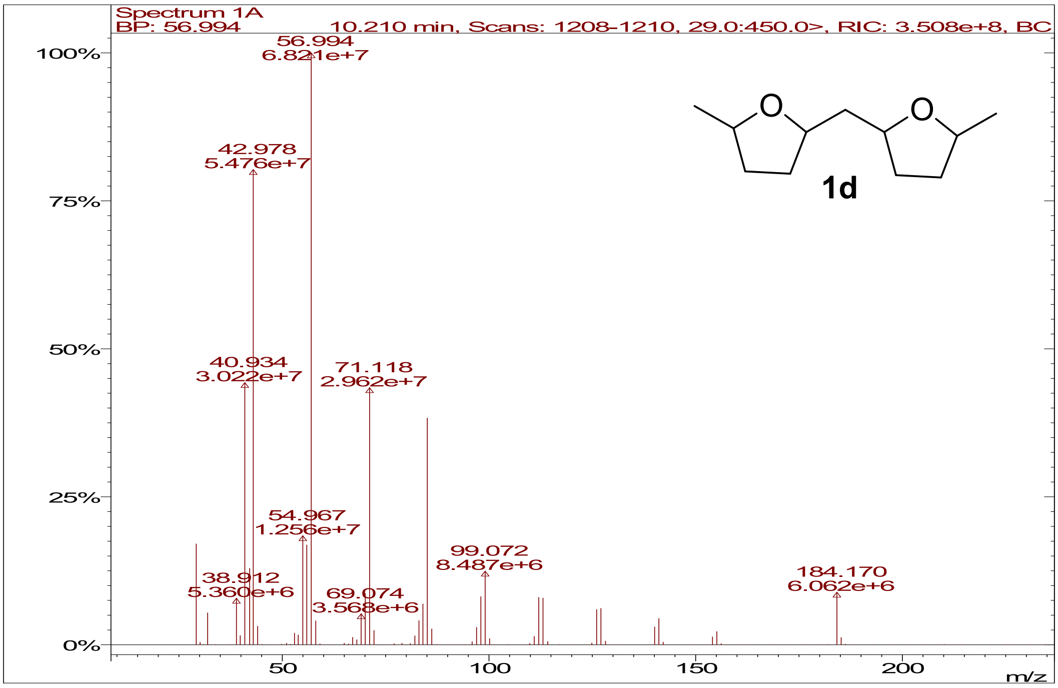
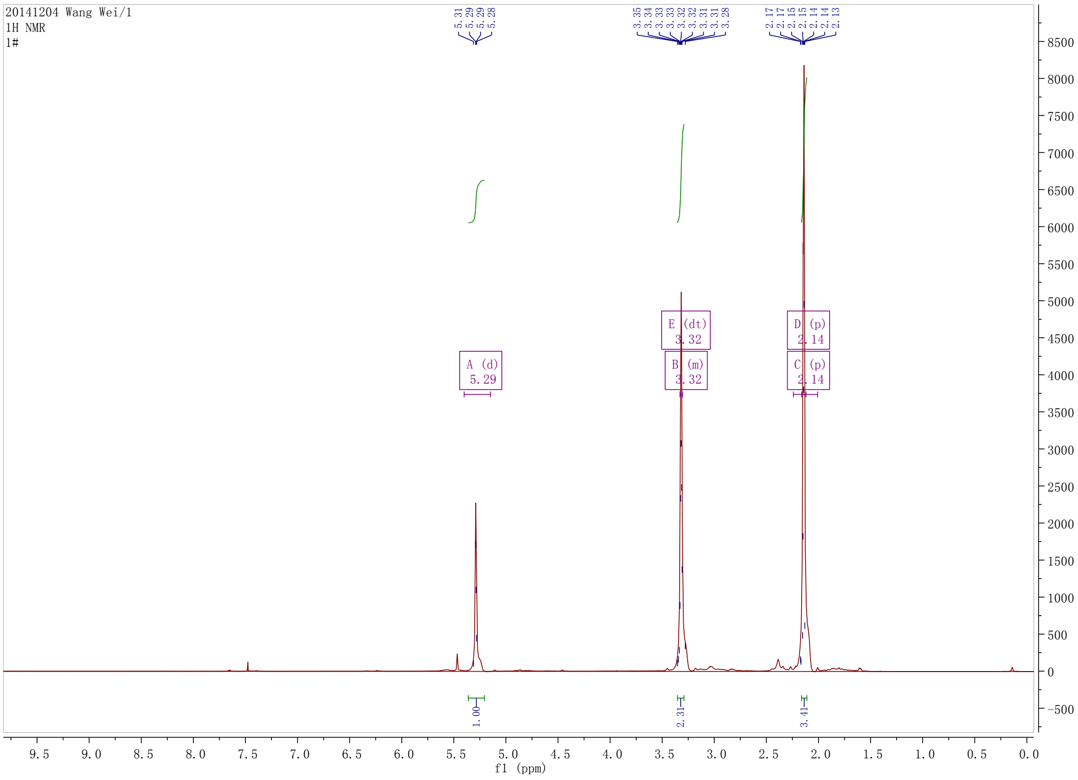


Figure S8. Mass spectrogram of the **1d** generated during the hydrogenation of **1a** over the 5wt.% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H_2, 1.8 g catalyst; liquid feedstock (30wt.% **1a** in methanol) flow rate of 0.16 mL min^{-1}; H_2 flow rate of 120 mL min^{-1}.



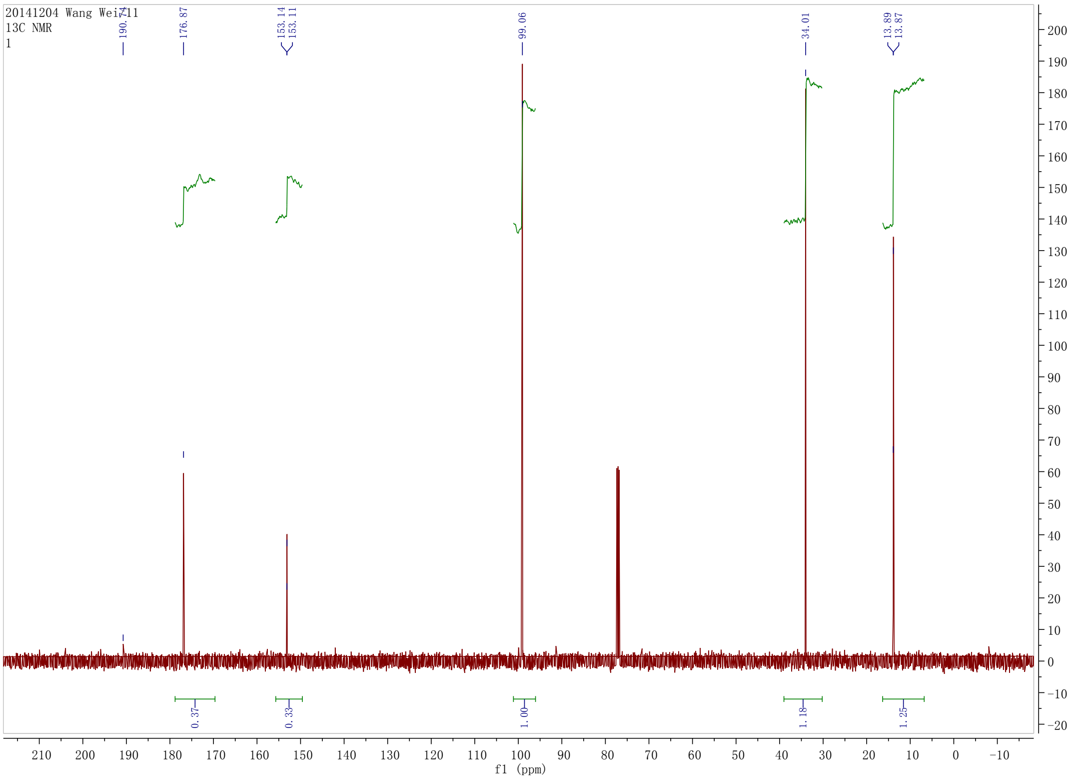


Figure S9. ^{1}H and ^{13}C NMR spectra of angelica lactone from the dehydration of levulinic acid.

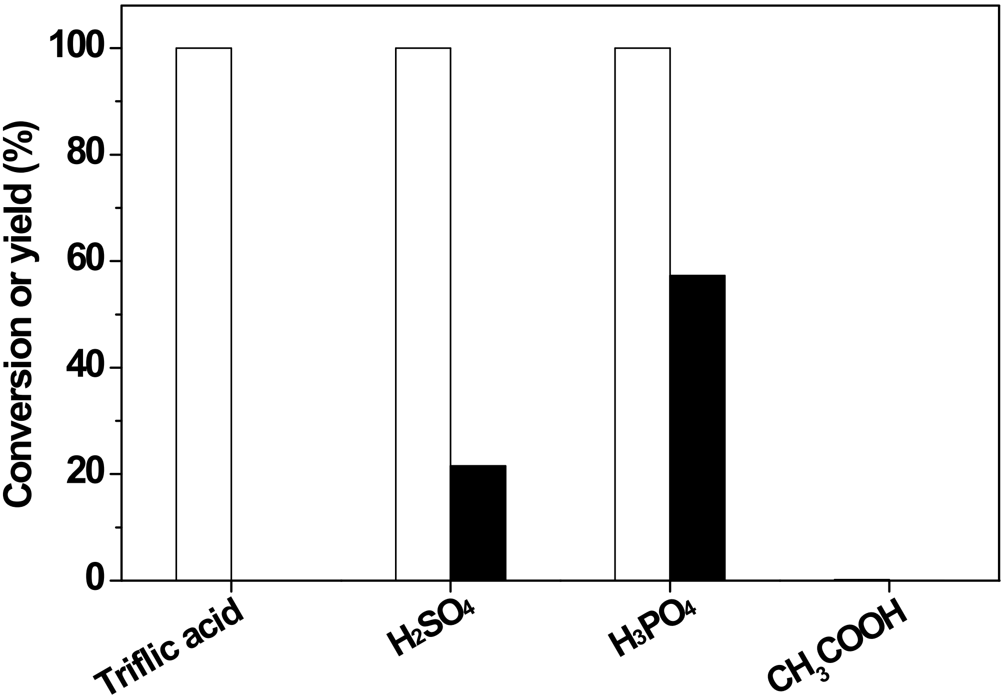


Figure S10. Conversions of angelica lactone (white bars) and the carbon yields of **1a** (black bars) under the catalysis of different Brønsted acids. Reaction conditions: 323 K, 1 h; 0.98 g (10 mmol) angelica lactone, 1.68 g (20 mmol) 2-MF and 0.1 g catalyst.

In this work, we also found that the too high dosage of Brønsted acid catalyst has negative effect on the HAA of 2-MF and angelica lactone. For example, when we used 0.1 g Brønsted acid catalysts, some solid product was generated, which led to the lower carbon yield of HAA product (*i.e.* **1a**) and some confusing results. According to literature,[3] this phenomenon can be explained because the utilization of excessive Brϕnsted acid catalysts will lead to the polymerization of angelica lactone and the decrease of **1a** selectivity.

References

1. M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem. Int. Ed.*, 2014, **53**, 1854-1857; J. Xin, S. Zhang, D. Yan, O. Ayodele, X. Lu and J. Wang, *Green Chem.*, 2014, **16**, 3589-3595.
2. G. Li, N. Li, Z. Wang, C. Li, A. Wang, X. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2012, **5**, 1958-1966; G. Li, N. Li, J. Yang, A. Wang, X. Wang, Y. Cong and T. Zhang, *Bioresour. Technol.*, 2013, **134**, 66-72; G. Li, N. Li, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Chem. Commun.*, 2013, **49**, 5727-5729.
3. J.C. Serrano-Ruiz, R.M. West and J.A. Dumesic, *Annu. Rev. Chem. Biomol.*, 2010, **1**, 79-100; M.J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516-547.