

Supporting Information

Synthesis jet fuel range polycyclic alkanes and aromatics from furfuryl alcohol and isoprene

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Materials

Furfuryl alcohol, isoprene and Ru/C catalyst were purchased from Aladdin Chemistry Co. Ltd. According the information form supplier, the Ru content in the Ru/C catalyst was 5% by weight (denoted as 5wt.%). The H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 80) and H- β ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 62.3) used in the HDO tests was purchased from the Nankai University. Preparation of 4-hydroxy-cyclopent-2-enone:

4-Hydroxy-cyclopent-2-enone (*i.e.* HCP) was made according to our previous work¹ by the aqueous phase rearrangement of furfuryl alcohol which was carried out in a semi-continuous reaction system. Typically, 0.65 g CaO and 2 L deionized water were loaded into a 1-gallon batch reactor (Parr Instrument Co.). After being purged with Ar for six times, the reactor was heated to 503 K, then 500 mL aqueous solution (20 wt%) of furfuryl alcohol (Sinopharm Chemical Reagent Co. Ltd) was injected into the reactor with a HPLC pump (Elite P270, injection time: 6 min). The reactant solution was stirred at a rate of 800 rpm for 2 min and quickly cooled down to room temperature by water. The liquid product was taken out from the batch reactor, centrifuged to remove the catalyst (and polymerization product), and analyzed by a GC. The carbon yield of HCP was calculated as 77.6%. After removing the water (used as a solvent) by vacuum distillation, HCP was obtained. According to our analysis, the HCP prepared by this method has high purity (~97%) and can be used for the hydrogenation reaction without further purification.

SiO_2 supported noble metal (Pd, Ru and Rh) catalysts were prepared by the incipient wetness impregnation of SiO_2 (Qingdao Ocean Chemical Ltd.) with the aqueous solutions of PdCl_2 , $\text{RuCl}_3 \cdot 3 \text{H}_2\text{O}$ and $\text{RhCl}_3 \cdot 6 \text{H}_2\text{O}$, respectively. The products were dried at 393 K for 12 h. To facilitate the comparison, the noble metal contents in all catalysts were controlled at 4wt.%. Mo modified Pd/ SiO_2

catalysts (denoted as Pd-MoO_x/SiO₂) were prepared by the successive incipient wetness impregnation of noble metal loaded SiO₂ catalysts with the aqueous solution of (NH₄)₆Mo₇O₂₄. For comparison, MoO_x/SiO₂ was also prepared by the incipient wetness impregnation of SiO₂ with the aqueous solution of (NH₄)₆Mo₇O₂₄. The Mo content was the same as that of 4% Pd-MoO_x/SiO₂ (Mo/Pd atomic ratio = 0.13). All of the SiO₂ supported catalysts were dried at 393 K overnight then calcined in air at 773 K for 3 h. Before being used for the transfer hydrogenation or transfer hydrodeoxygenation of D-A products, the SiO₂ supported catalysts were reduced by hydrogen flow at 773 K for 3 h, cooled down to room temperature in hydrogen flow, then passivated at room temperature for 3 h.

Activity tests

Diels-Alder (D-A) reaction. the D-A reaction of HCP and isoprene was carried out in a stainless-steel batch reactor under solvent-free conditions without using any catalyst. Typically, 20 mmol HCP, 50 mmol isoprene were stirred at 423 K for 24 h. The reactions were stopped by rapidly quenching the stainless batch reactor with cool water. Subsequently, dodecane was added into the reaction system as an internal standard. The mixture was diluted by tetrahydrofuran (THF) and analyzed by an Agilent 7890A gas chromatograph (GC) that was equipped with a HP-5 capillary column (30 m, 0.32 mm ID, 0.25 μm film) and a flame ionization detector (FID). Injection port temperature and split flow ratio were set as 523 K and 50:1, respectively. The temperature of column was controlled by the oven that was kept at 323 K for 2 min, heated up to 523 K at a rate of 10 K min⁻¹ and stayed at that temperature for 5 min. The conversions of HCP and the yields of D-A product were calculated according to following equations:

Conversion of HCP (%) = (moles of HCP in the feedstock - moles of HCP in the product)/(moles of HCP in the feedstock) × 100%

Yield of specific D-A product (%) = (moles of specific D-A product generated during the reaction)/(moles of HCP in the feedstock) × 100%.

Hydrodeoxygenation (HDO). After being purified by vacuum distillation and silica gel column chromatography (using ether/ethyl acetate = 10/1 as solvent) to remove excess isoprene and other impurities, the D-A product was used for the HDO process that was carried out by a 50 mL stainless-steel batch reactor (Parr Instrument Co.) without using any solvent. Typically, 1 g purified D-A product, 0.1 g Ru/C catalyst and 0.2 g acidic zeolite were employed for each test. The HDO reaction was conducted under 6 MPa H₂ at 433 K for 3 h and terminated by putting the reactor in cool water. After releasing of unreacted hydrogen, dodecane (used as an internal standard) was added into the reaction system. The mixture was filtered and analysed by the GC (used for D-A reaction of HCP and isoprene) and GC-MS. The conversion of bicyclic/tricyclic D-A products and the yields of specific products from HDO tests were calculated according to following equations:

Conversion of bicyclic/tricyclic product (%) = (molar of bicyclic/tricyclic D-A product consumed during the HDO test)/(molar of bicyclic/tricyclic D-A product in the feedstock) × 100%

Yield of specific bicyclic/tricyclic product in HDO test (%) = (molar of specific bicyclic/tricyclic product obtained in HDO test)/(molar of bicyclic/tricyclic D-A product in the feedstock) × 100%

The heat value of the polycoalkane mixture obtained in the HDO step was measured by a KA921D Automatic Calorimeter.

Transfer hydrogenation (or hydrodeoxygenation): The transfer hydrogenation or hydrodeoxygenation of the D-A product was carried out by a stainless-steel batch reactor. Typically, 0.4 g D-A product, 80 mg catalyst and 40 mL EA were employed for each test. The reaction was

conducted under 0.1 MPa N₂ at 533 K for 8 h and terminated by putting the reactor in cool water. The mixture was filtered and analyzed by the GC (used for D-A reaction of HCP and isoprene) and GC-MS. The methods of calculating the conversion of D-A product and the yields of specific product from transfer hydrogenation (or hydrodeoxygenation) test were calculated according to following equations:

Conversion of bicyclic/tricyclic product (%) = (molar of bicyclic/tricyclic D-A product consumed during the HDO test)/(molar of bicyclic/tricyclic D-A product in the feedstock) × 100%

Yield of specific bicyclic/tricyclic product in transfer hydrogenation (or hydrodeoxygenation) (%) = (molar of specific bicyclic/tricyclic product obtained in transfer hydrogenation (or hydrodeoxygenation))/(molar of bicyclic/tricyclic D-A product in the feedstock) × 100%

Characterization of catalyst

Nitrogen adsorption was carried out at 77 K with an ASAP 2010 apparatus to determine the specific Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) of the catalysts. Before each measurement, the acidic zeolites were evacuated at 373 K for 6 h.

NH₃-chemisorption and NH₃-TPD: The acid amounts and acid strengths of the catalysts characterized by NH₃-chemisorption and NH₃-TPD. Before each test, 0.1 g sample was placed in a quartz reactor, pretreated in He flow at 773 K for 0.5 h and cooled down in He flow to 373 K. After the stabilization of base line, pulses of NH₃ (1 mL) were dosed in the reactor until saturation. The amount of acid sites on the catalyst was calculated by the adsorptions of NH₃ during the test. Subsequently, the desorption of NH₃ was conducted in He flow from 373 K to 773 K at a heating rate of 10 K min⁻¹. The desorbed NH₃ molecules were detected by a TCD detector.

The Pd dispersions in Pd/SiO₂ and Pd-MoO_x/SiO₂ (Mo/Pd atomic ratio = 0.13) catalysts were measured with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System by

CO chemisorption. These values correspond to the ratio of surface metal atoms to total metal atoms assuming that the stoichiometry of adsorbed CO to surface metal atom is one. Before the tests, the samples were dried in helium flow at 393 K for 0.5 h and cooled down to 323 K. After the stabilization of baseline, the CO adsorption was carried out at 323 K by the pulse adsorption of 5% CO in He.

The high-resolution transmission electron microscopy (HRTEM) images of the Pd/SiO₂ and Pd-MoO_x/SiO₂ (Mo/Pd atomic ratio = 0.13) catalysts were collected by a JEM-2100F field emission electronic microscope. Prior to characterization, the catalysts were pretreated in hydrogen flow at 573 K for 3 h. Before the tests, the samples were first suspended in ethanol by an ultrasonic method then loaded onto a holey carbon film supported by a nickel TEM grid.

The XRD patterns of Ru-based catalysts were obtained with a PW3040/60X' Pert PRO (PANalytical) diffractometer equipped with Cu K α radiation source ($\lambda = 0.15432$ nm) at 40 kV and 40 mA.

The types of acid sites over the H-ZSM-5 and H- β zeolites were characterized by a XF808-04 FT-IR using pyridine as the probing molecule. Prior to the tests, the zeolites were pressed into self-supporting discs (at a radius of 13 mm), pretreated in situ in an IR cell at 573 K under vacuum conditions for 0.5 h and cooled down to room temperature. At this stage, the spectrum was collected as the background reference. Subsequently, pyridine was introduced for the adsorption for 5 min at room temperature followed by evacuation for 0.5 h. Finally, we elevated the temperature to 373 K, 473 K, 573 K and evacuated at those temperatures for 0.5 h. All the spectra were collected at room temperature and extracted with the background reference. The ratios of Brønsted to Lewis acid sites over the surfaces of H-ZSM-5 and H- β zeolites were calculated based on the FT-IR result using pyridine as the probing molecule according to the method described in literature.²



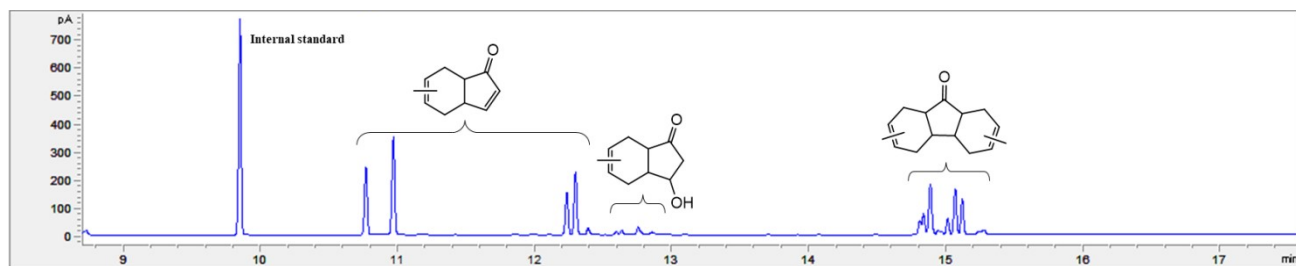


Figure S1. Gas chromatogram of the product from the D-A reaction of HCP and isoprene. Reaction conditions: 423 K, 36 h; 40 mmol HCP, 50 mmol isoprene.

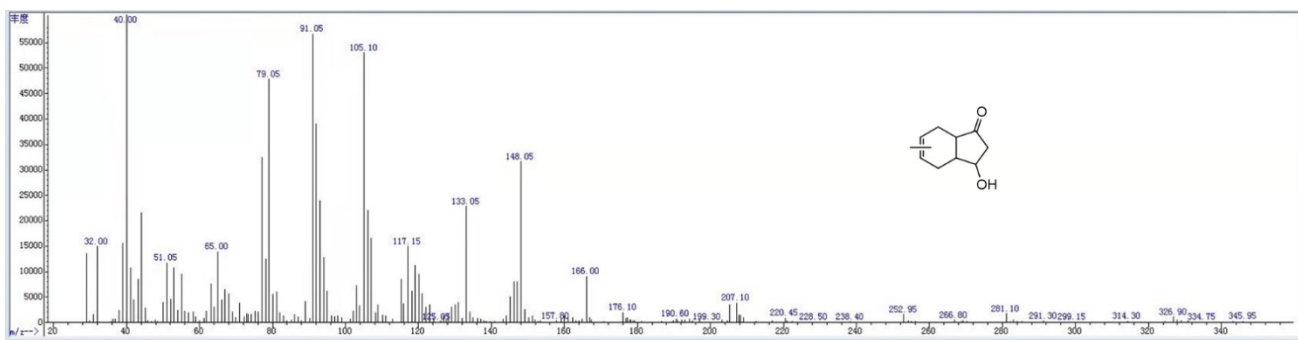


Figure S2. Mass spectrum of the compound **1** from the D-A reaction of HCP and isoprene.

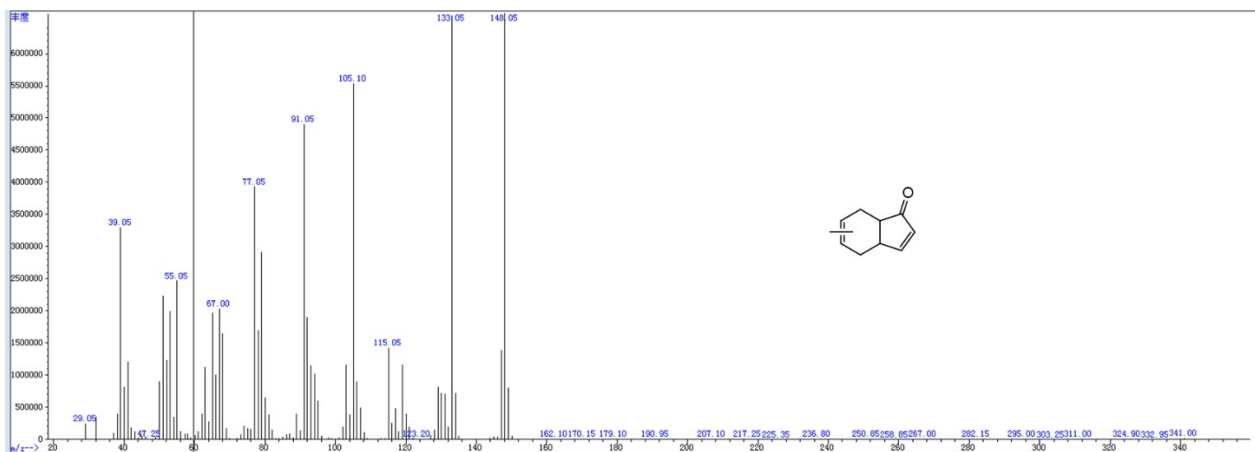


Figure S3. Mass spectrum of the compound **2** from the D-A reaction of HCP and isoprene.

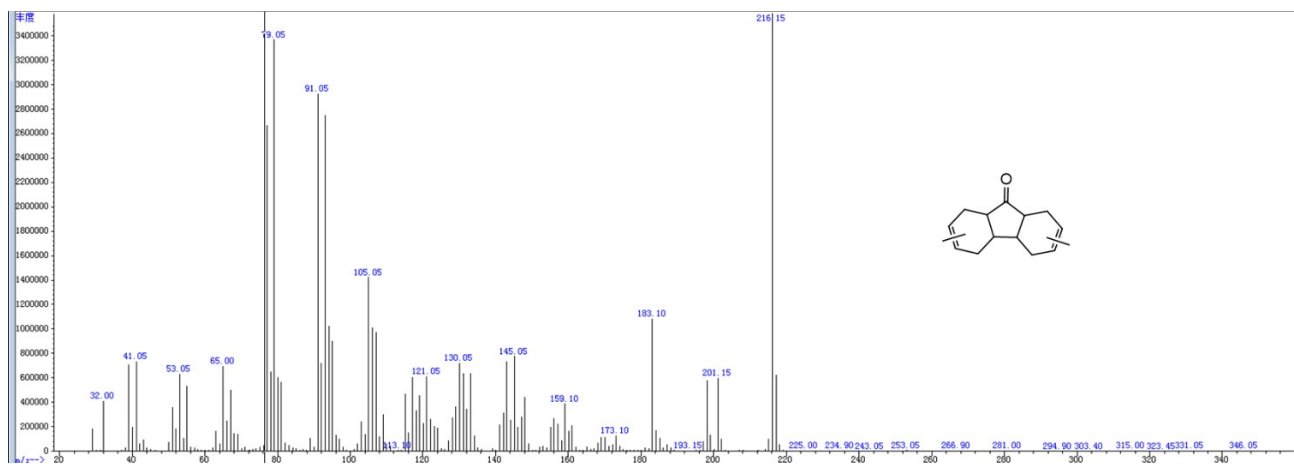


Figure S4. Mass spectrogram of the compound **3** from the D-A reaction of HCP and isoprene.

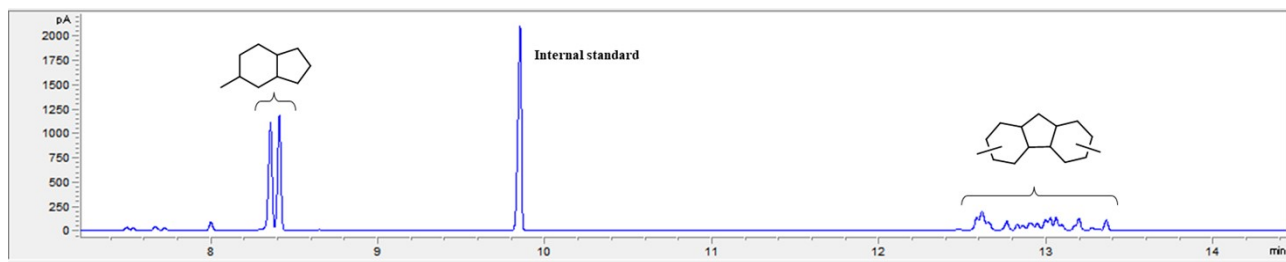


Figure S5. Gas chromatogram of the HDO product. Reaction conditions: 433 K, 6 MPa H₂, 6 h; 1 g D-A product, 0.1 g Ru/C, 0.2 g H- β were used in the test.

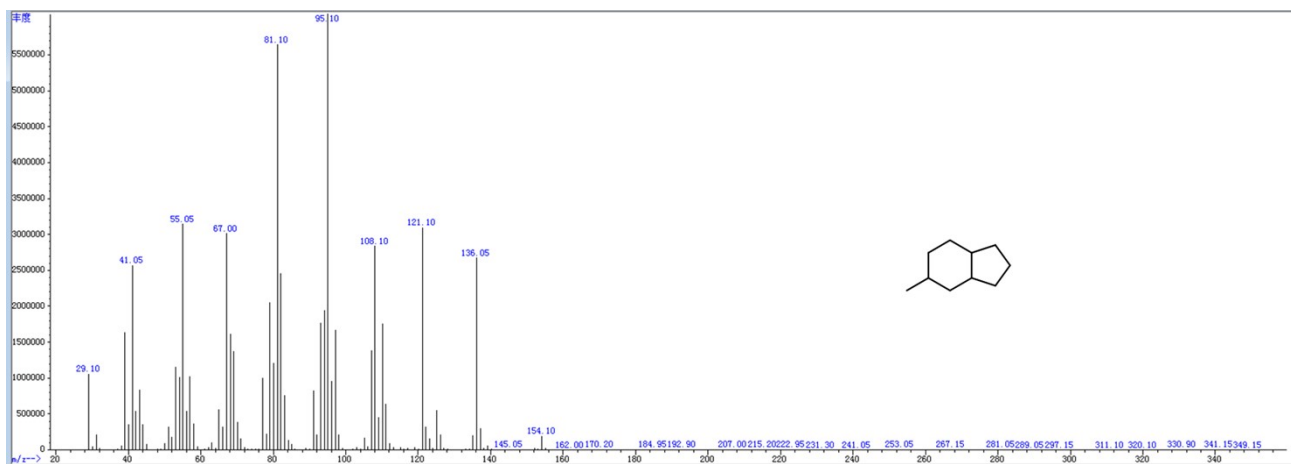


Figure S6. Mass spectrogram of the compound **4** from the HDO of the D-A product.

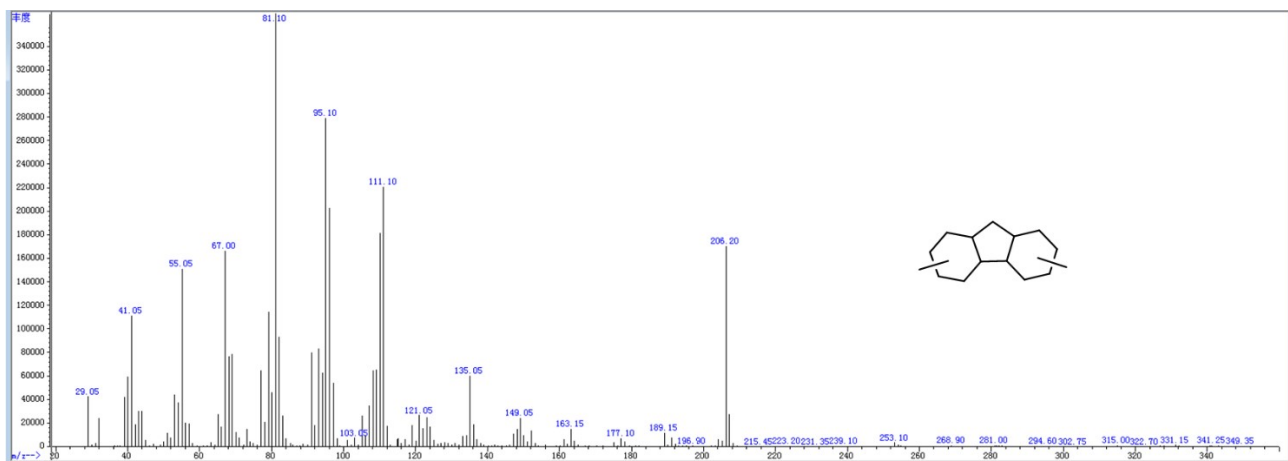


Figure S7. Mass spectrogram of the compound **5** from the HDO of the D-A product.

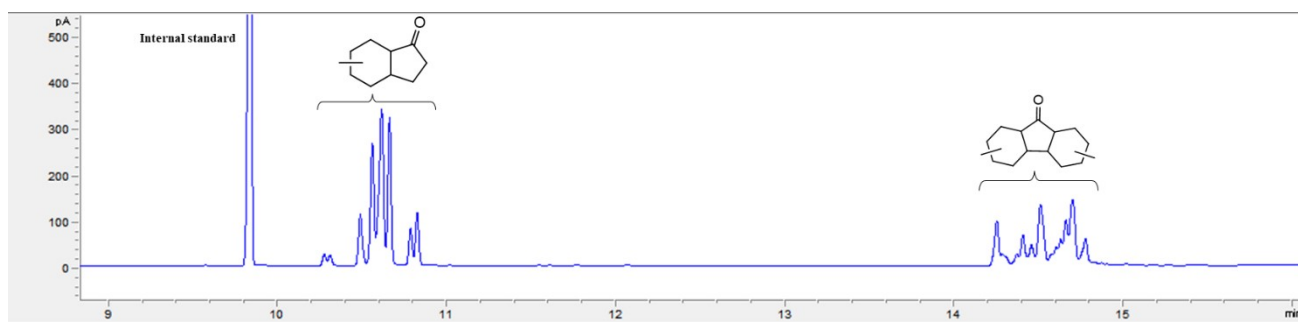


Figure S8. Gas chromatogram of the hydrogenation product over the Ru/C catalyst. Reaction conditions: 433 K, 6 MPa H₂, 6 h; 1 g D-A product and 0.1 g Ru/C were used in the test.

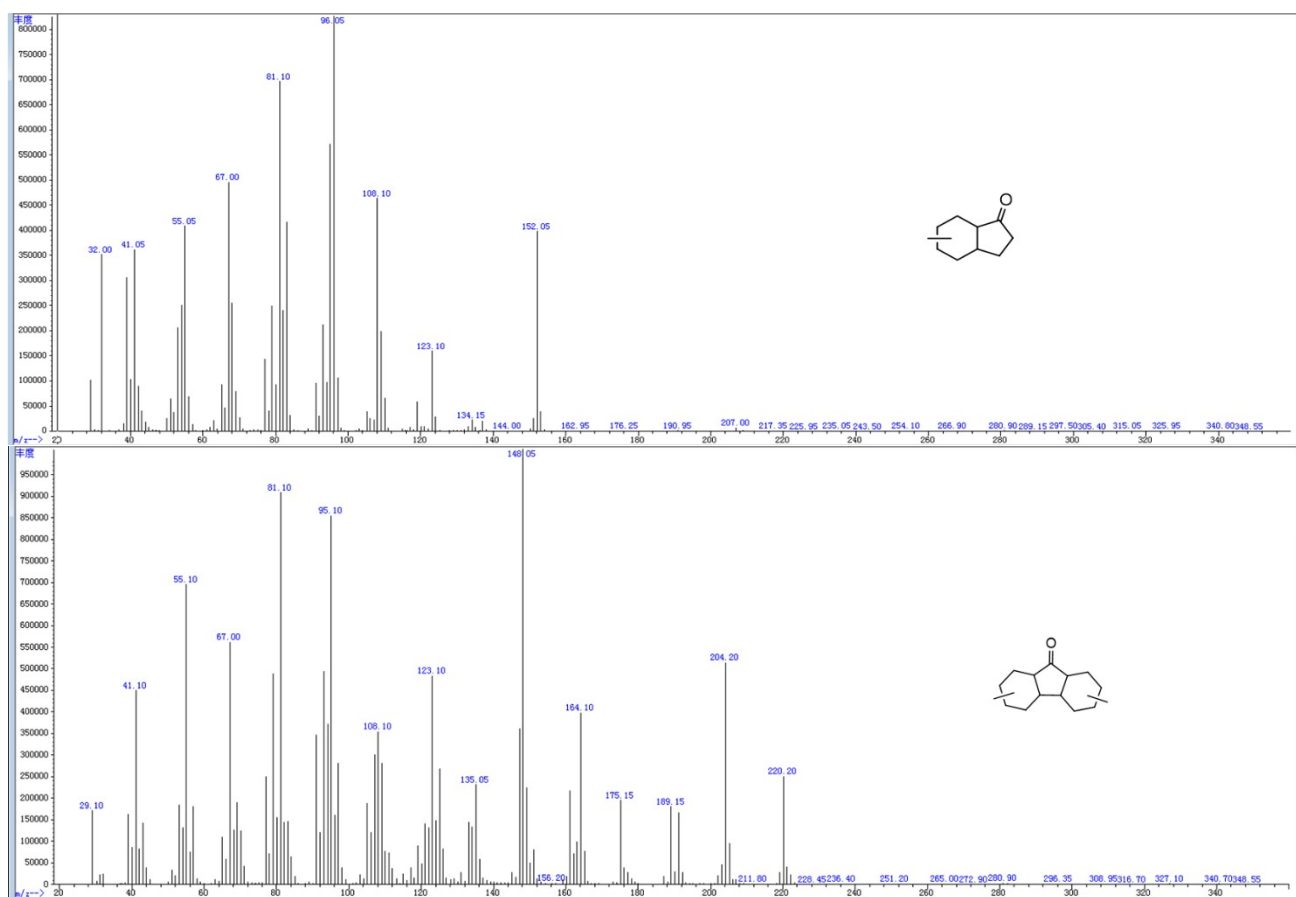


Figure S9. Mass spectrogram of the C₁₀ and C₁₅ oxygenates generated from the hydrogenation of D-A product over the Ru/C catalyst.

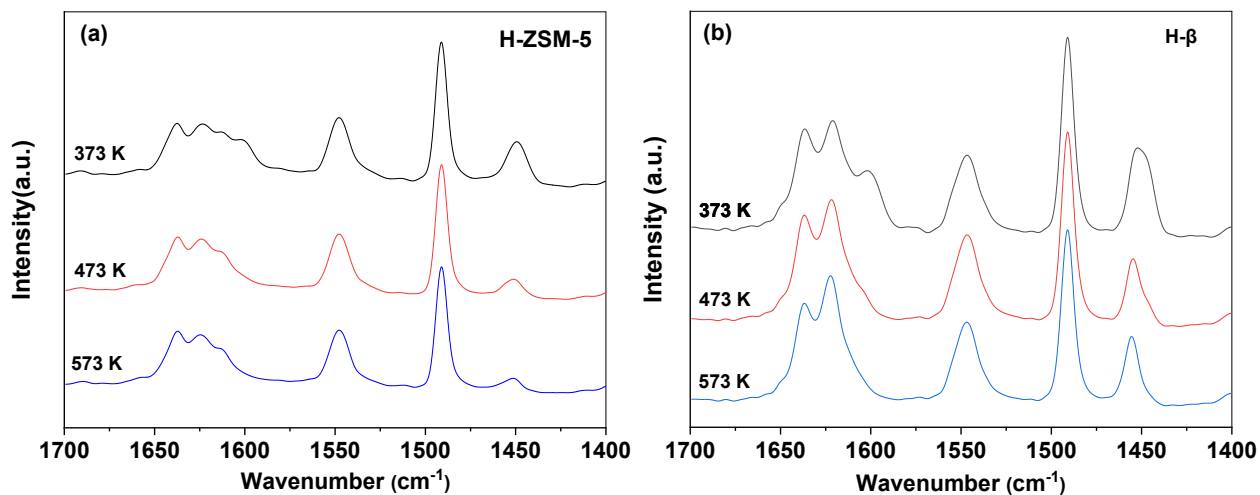


Figure S10. FT-IR spectra of H-ZSM-5 (a) and H-β (b) zeolites after the adsorption of pyridine and vacuumation at different temperatures.

Table S1. Ratios of Brønsted to Lewis acid sites on the surfaces of H-ZSM-5 and H- β zeolites after the adsorption of pyridine and vacuation at different temperatures.

Zeolite	Temperature (K)	Ratio of Brønsted to Lewis acid sites
H-ZSM-5	373	1.93
	473	5.59
	573	9.66
H- β	373	1.44
	473	2.51
	573	2.65

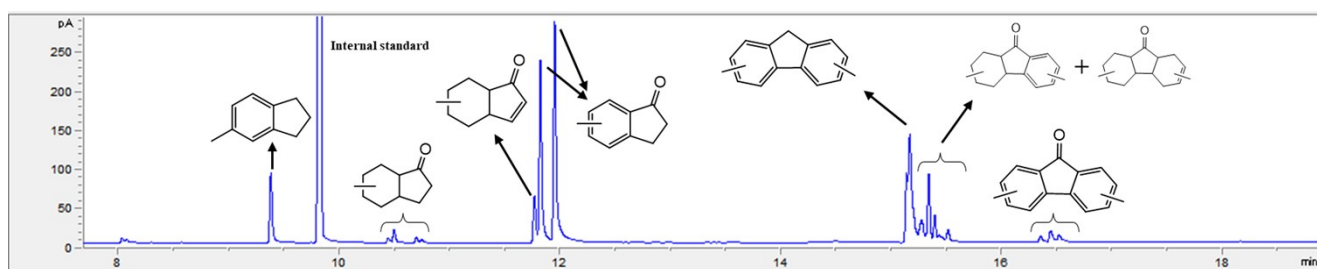


Figure S11. Gas chromatogram of the transfer hydrodeoxygenation product over the Pd/SiO₂ catalyst. Reaction conditions: 533 K, 0.1 MPa N₂, 4 h; 0.4 g D-A product and 40 mg Pd/SiO₂ catalyst were used in the test.

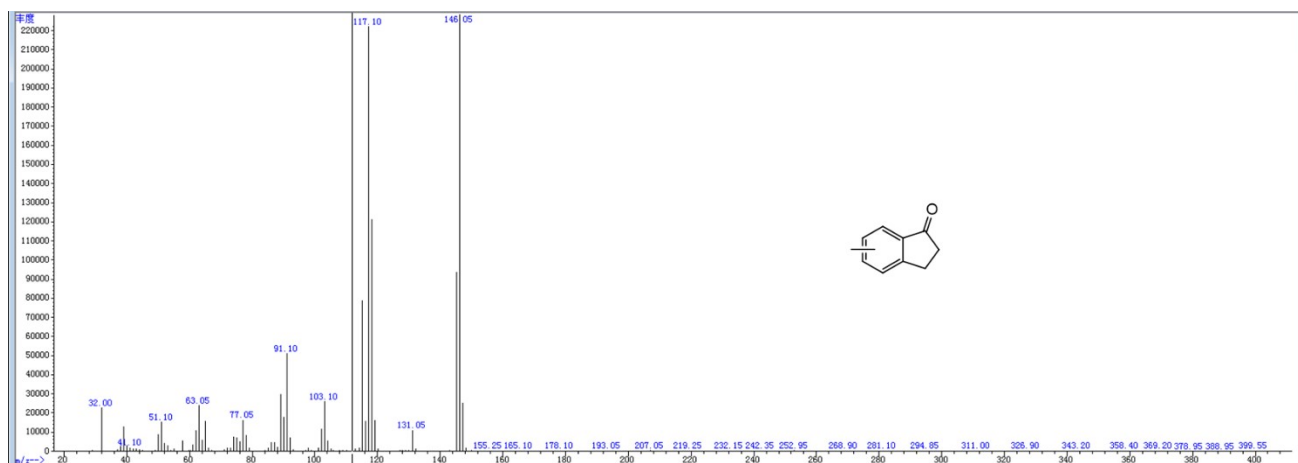


Figure S12. Mass spectrum of the **1a** generated from the transfer hydrogenation of the D-A product.

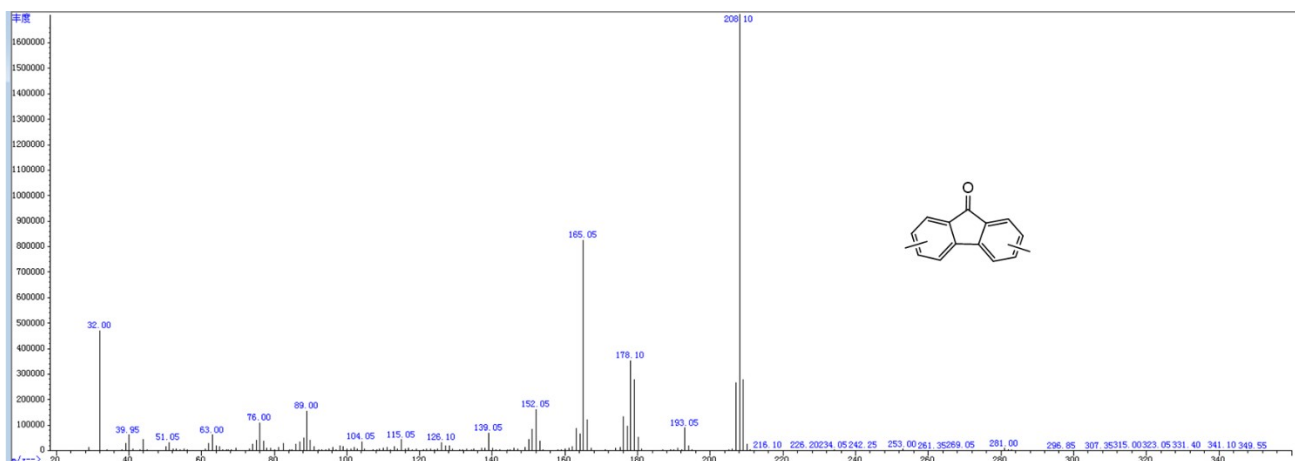


Figure S13. Mass spectrogram of the **2a** generated from the transfer hydrogenation of the D-A product.

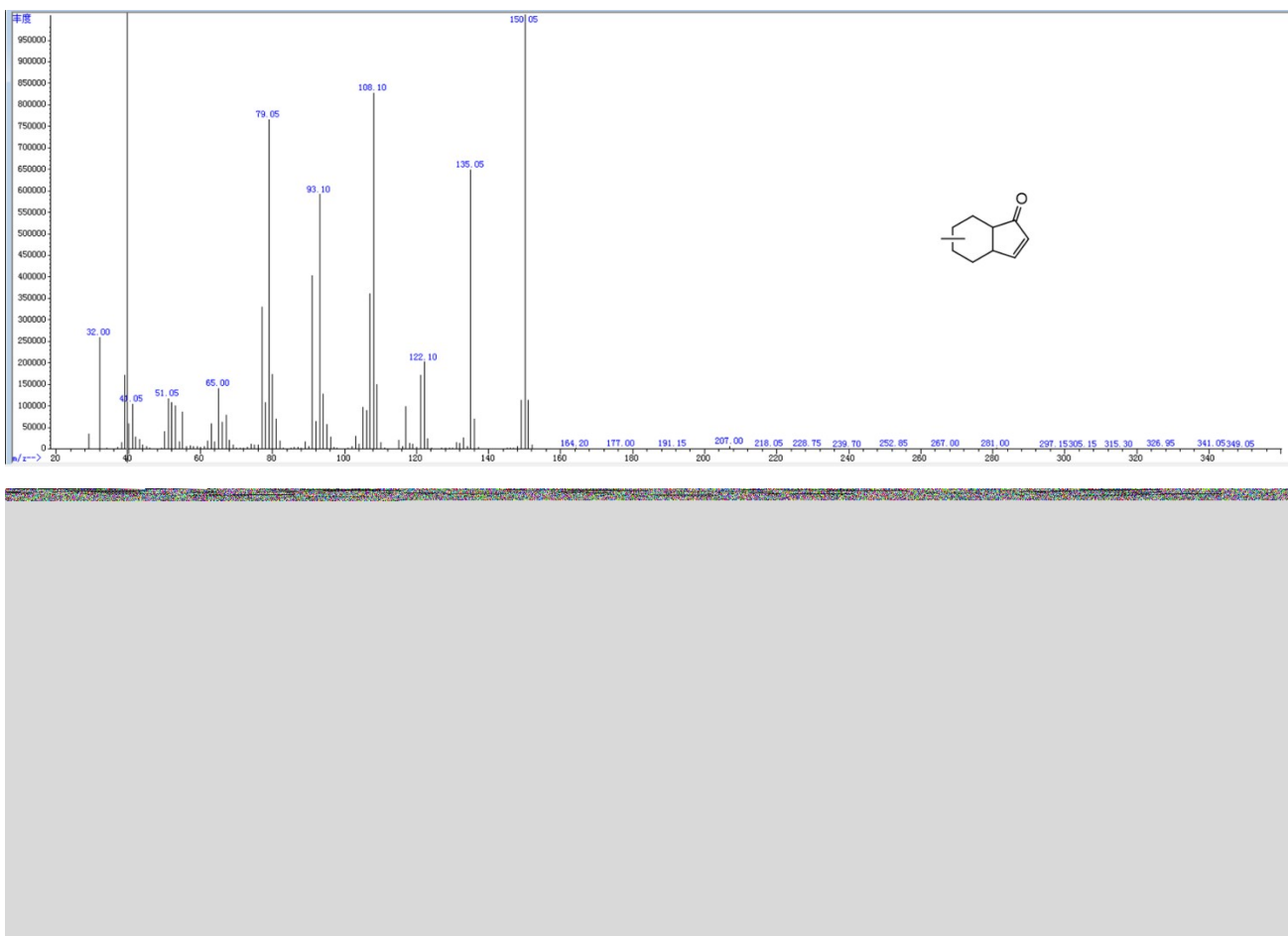


Figure S14. Mass spectrograms of other hydrogenated C₁₀ oxygenates generated from the transfer hydrogenation of the D-A product.

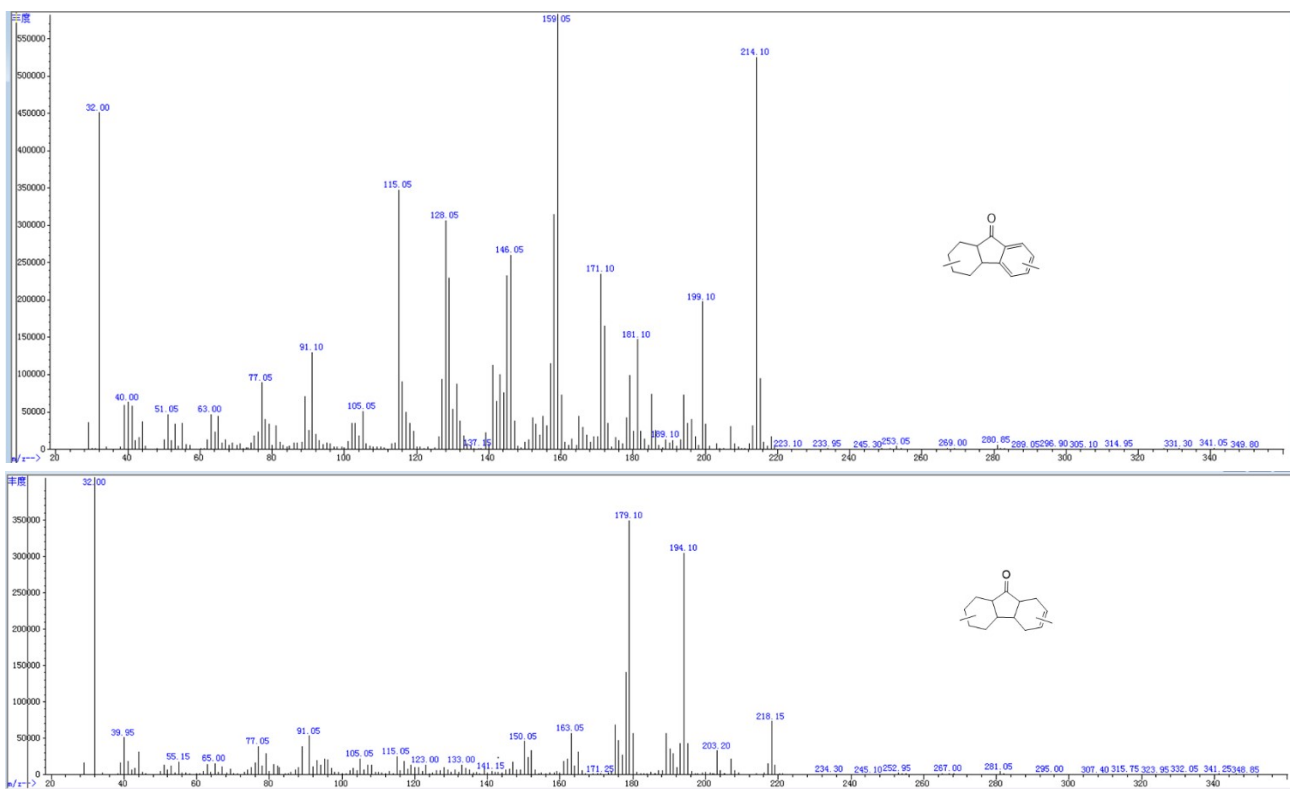


Figure S15. Mass spectrogram of other hydrogenated C_{15} oxygenates generated from the transfer hydrogenation of the D-A product.

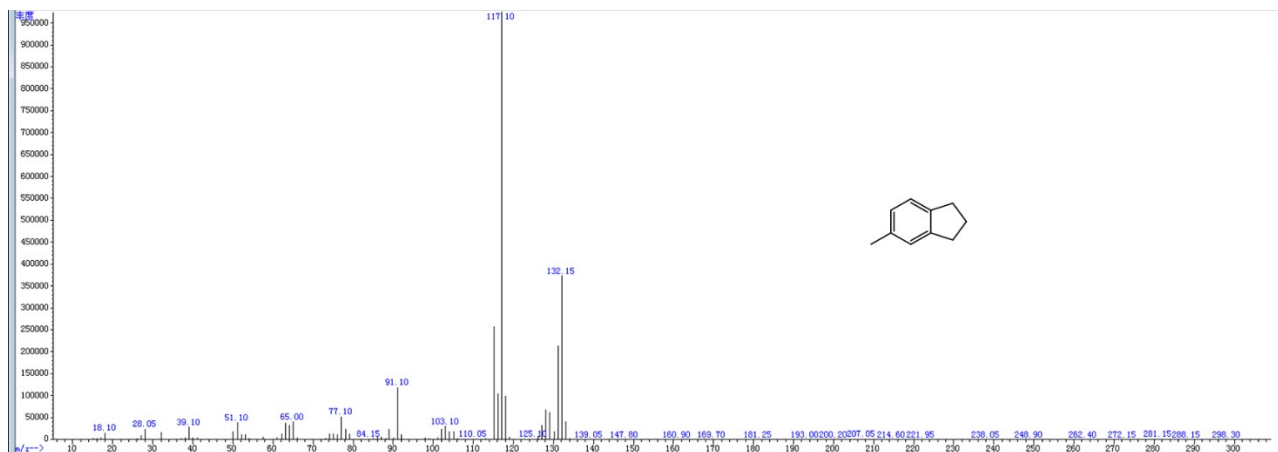


Figure S16. Mass spectrogram of the compound **6** generated from the transfer hydrodeoxygenation of D-A product.

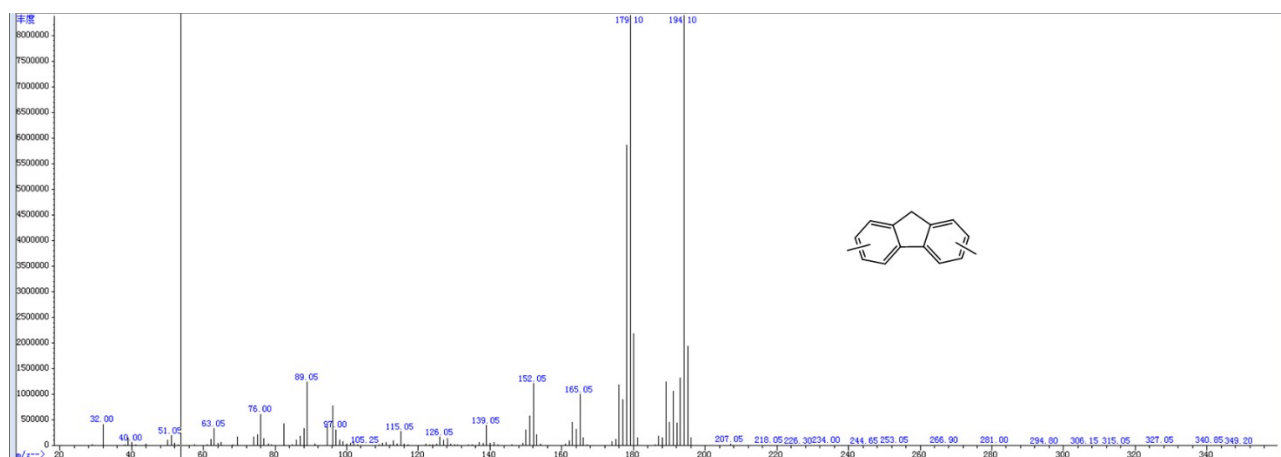


Figure S17. Mass spectrogram of the compound **7** generated from the transfer hydrodeoxygenation of the D-A product.

References

1. G. Li, N. Li, M. Zheng, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Green Chem.*, 2016, **18**, 3607-3613; G. Li, B. Hou, A. Wang, X. Xin, Y. Cong, X. Wang, N. Li and T. Zhang, *Angew. Chem., Int. Ed.*, 2019, **58**, 12154-12158.
2. T. Barzetti, E. Selli, D. Moscotti and L. Forni, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1401-1407.