

Supporting Information

Synthesis of jet fuel range high-density polycycloalkanes with polycarbonate waste

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1. Materials

In this work, pure PC pellets (2 mm length × 2 mm diameter) from Luxi Chemical Group Co., Ltd. were used as a model of waste PC. In hydrodeoxygenation (HDO) tests, the bisphenol A (*i.e.* **1A**) was bought from Aladdin company, while the 4,4'-(ethane-1,1-diyl)diphenol (*i.e.* **2A**) and 4,4'-methylenediphenol (*i.e.* **3A**) were purchased from Tokyo Chemical Industry (TCI) Co., Ltd.. The activated carbon loaded noble metal (denoted as M/C, M = Pt, Pd or Ru) catalysts were obtained from Aladdin company. We chose Pt, Pd and Ru as active metals because they are often used catalysts in many hydrogenation reactions. The H-ZSM-5, H- β and H-MOR zeolite were purchased from Nankai University. According to the information from the supplier, the SiO₂/Al₂O₃ molar ratios of these zeolites were 25, 160 and 24, respectively.

2. Characterization

The specific BET surface areas of the activated carbon loaded noble metal (denoted as M/C, M = Pt, Ru or Pd) and zeolite catalysts (see Table S1) used in the HDO of bisphenols were determined by N₂-physisorption at 77 K using a Micromeritics ASAP 2010 apparatus.

The XRD patterns of M/C 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. Based on the XRD results, the average particle sizes of catalysts (see Table S1) were estimated by Debye-Scherrer equation.

The metal dispersions in M/C catalysts (see Table S1) were measured with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System based on the molar ratios of CO chemisorption and noble metals in the catalysts. These values correspond to the ratios 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 acid amounts and acid strengths of the zeolites were characterized by NH_3 -chemisorption and NH_3 -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 NH_3 (1 mL) were dosed in the reactor until saturation. The amount of acid sites on the catalyst was calculated by the adsorptions of NH_3 during the test. Subsequently, the desorption of NH_3 was conducted in He flow from 373 K to 1073 K at a heating rate of 10 K min^{-1} . The desorbed NH_3 molecules were detected by a mass spectrometry (MS) OminiStar equipped with the software quadstar.

3. Activity test

3.1 Alcoholysis and glycolysis of PC waste

The alcoholysis and glycolysis reactions of PC waste were carried out in a batch reactor in a 100 mL stainless steel batch reactor (Parr 4848) under nitrogen atmosphere. For each test, 1 g PC waste and 40 mL alcohol (or polyol) were used. After purging the reactor with nitrogen for three times, the mixture was stirred at 413-473 K for 3 h, then quenched to room temperature with cool water. Subsequently, an excess amount of methanol was added to into the reaction system. According to the saturated solutions of bisphenol A (*i.e.* **1A** in Scheme 2) and carbonates at room temperature, the amount of methanol used in this work was more than enough to dissolve them even when they were produced at 100% yield. The residual PC

waste is unsolvable in methanol. Therefore, it was easily separated from the alcoholysis product by filtration, dried at 343 K overnight and weighted to calculate the conversion of PC waste. The **1A** generated during the alcoholysis (or glycolysis) of PC waste was solved in methanol and quantitatively analyzed by an Agilent 7890A GC. The PC waste conversions and the **1A** yields in the alcoholysis (or glycolysis) tests were calculated according to following equations.

Conversion of PC waste (%) = $(\text{Initial weight of PC waste} - \text{the weight of residual PC waste}) / (\text{Initial weight of PC waste}) \times 100\%$

Yield of **1A** (%) = $(\text{Mole of } \mathbf{1A} \text{ generated during the alcoholysis (or glycolysis) test}) / (\text{Theoretical mole of } \mathbf{1A} \text{ which should be produced from the complete conversion of the PC waste}) \times 100\%$

3.2 Hydrodeoxygenation (HDO) of bisphenols

The HDO of bisphenols was carried out in a 100 mL stainless steel batch reactor (Parr 4848). For each test, 5 mmol bisphenol, 40 mL cyclohexane, 0.04 g M/C catalyst and 0-0.6 g zeolite were used. After purging the reactor and filling it with hydrogen, the reaction system was heated to 353-453 K and vigorously stirred at that temperature for certain time. During the reaction, hydrogen was added from time to time to keep the system pressure at 3 MPa. After the test, the reactor was quenched to room temperature with cool water. The unreacted hydrogen was released. The liquid product was separated with catalyst by filtration, diluted and analyzed by an Agilent 7890A GC. The bisphenol conversions and yields of specific products during the HDO tests were calculated according following equations.

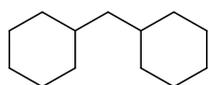
Conversion of bisphenol (%) = $(\text{Initial mole of bisphenol in the feedstock} - \text{mole of$

unreacted bisphenol in the product)/(Initial mole of bisphenol in the feedstock) \times 100%

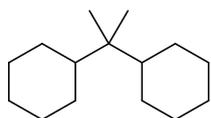
Yield of specific product (%) = (Mole of carbon atoms in the specific HDO product/Mole of carbon atoms in the bisphenol feedstock) \times 100%

General experimental details for NMR and GC-MS analysis

^1H NMR and ^{13}C NMR spectra were recorded at room temperature in CDCl_3 on Bruker AVANCE III 400 MHz instrument. The chemical shifts for ^1H NMR were recorded in ppm downfield using the peak of CDCl_3 (7.26 ppm) as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of CDCl_3 (77.16 ppm) as the internal standard. GC-MS analysis of the samples was carried out by Varian Corp 450GC/320MS which was equipped with a HP-5 capillary column.



^1H NMR (400 MHz, CDCl_3) δ 1.75–1.58 (m, 10H), 1.39–1.08 (m, 8H), 1.02 (t, $J = 7.0$ Hz, 2H), 0.91–0.74 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 45.8, 34.5, 33.9, 27.0, 26.6.



^1H NMR (400 MHz, CDCl_3) δ 1.81–1.65 (m, 10H), 1.30–1.13 (m, 8H), 1.00–0.89 (m, 4H), 0.70 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 44.0, 27.6, 27.3, 27.2, 20.6.

Table S1. Specific BET surface areas (S_{BET}), actual metal contents, average metal particle sizes and metal dispersions of activated carbon loaded noble metal catalysts.

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a	Actual metal content (wt.%) ^b	Metal dispersion (%) ^c	Average metal particle size (nm) ^d
Pt/C	882	3.7	7.7	0.9
Pd/C	1108	4.0	14.0	4.9
Ru/C	659	4.6	0.2	2.7

^a Measured by N₂-physisorption. ^b Measured by ICP analysis. ^c Calculated based on the CO-chemisorption results. ^d Estimated from the XRD results by Debye-Scherrer equation.

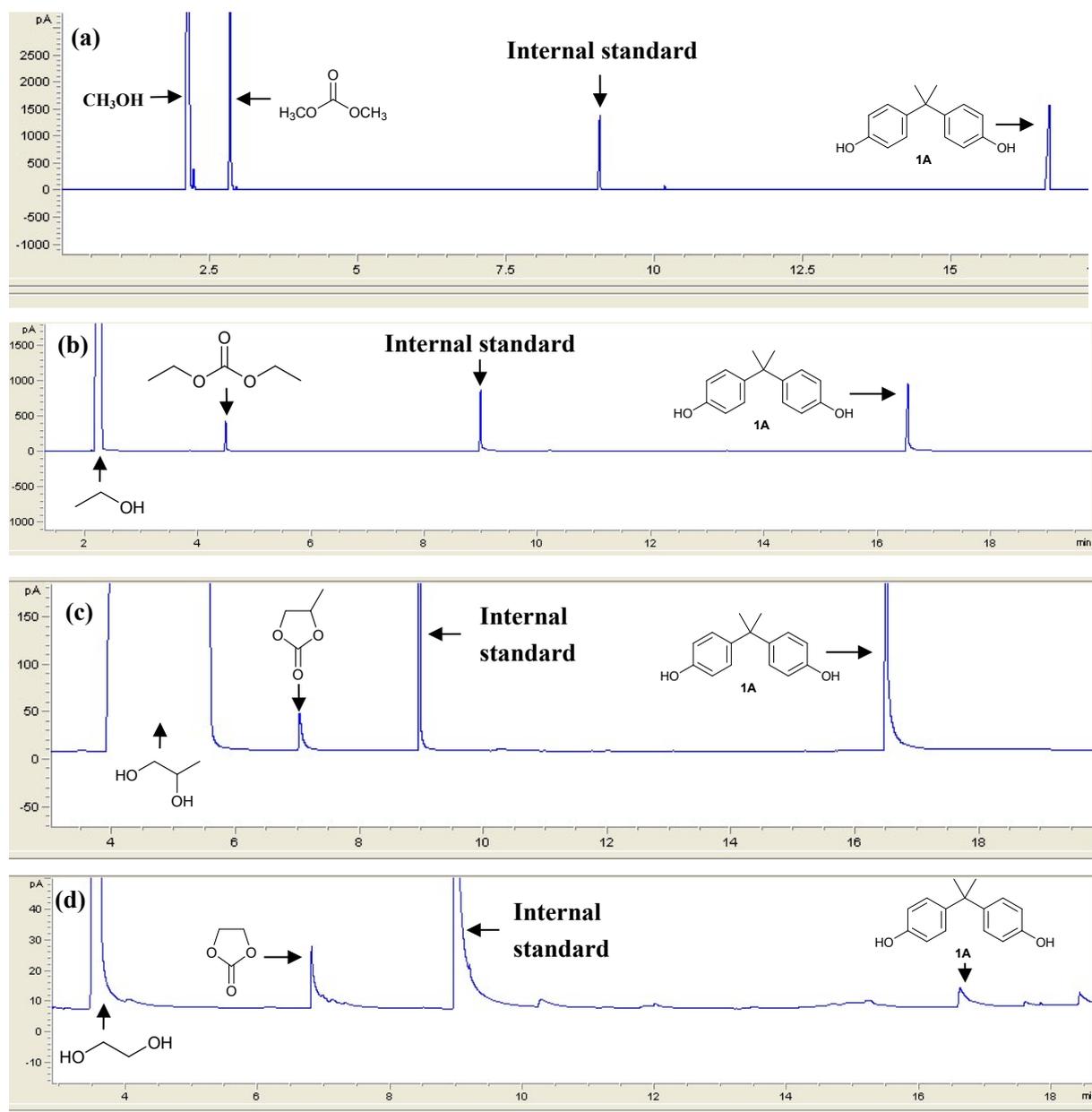


Figure S1. GC chromatograms of the products from the reaction of PC waste with methanol (a), ethanol (b), 1,2-propylene glycol (c) and ethylene glycol (d). Reaction conditions: 453 K, 3 h; 1 g PC waste and 40 mL alcohol (or polyol) were used in the tests.

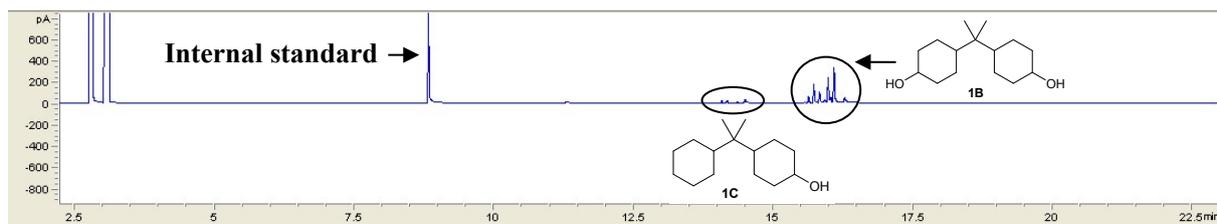


Figure S2. GC chromatograms of the products from the HDO of **1A** over the Pt/C catalyst.

Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol **1A**, 40 mL cyclohexane and 0.04 g Pt/C catalyst were used for the test.

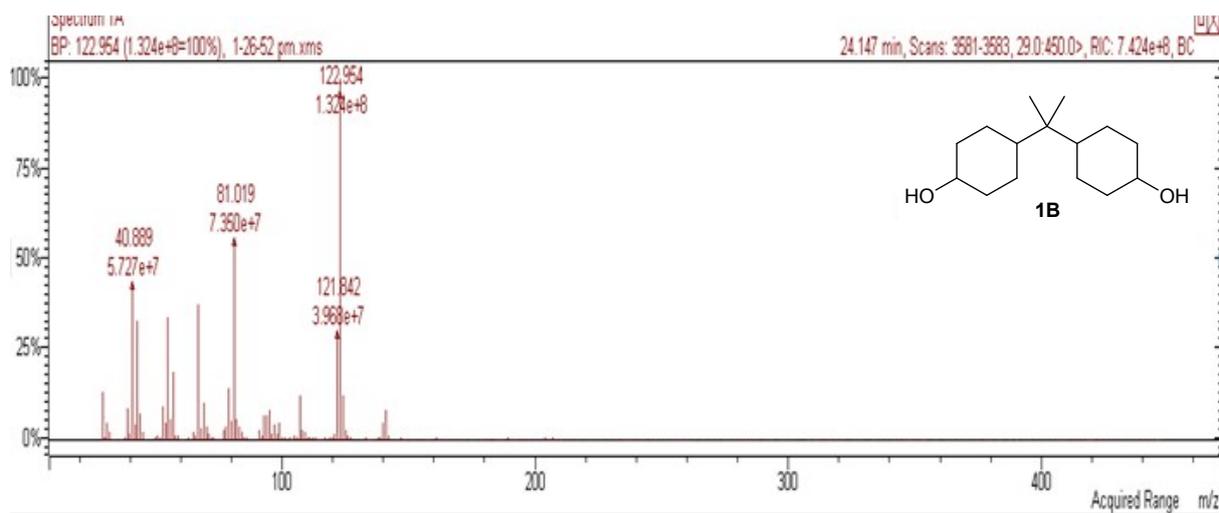


Figure S3. Mass spectrogram of the **1B** from the HDO of **1A** over the Pt/C catalyst. Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol **1A**, 40 mL cyclohexane and 0.04 g Pt/C catalyst were used for the test.

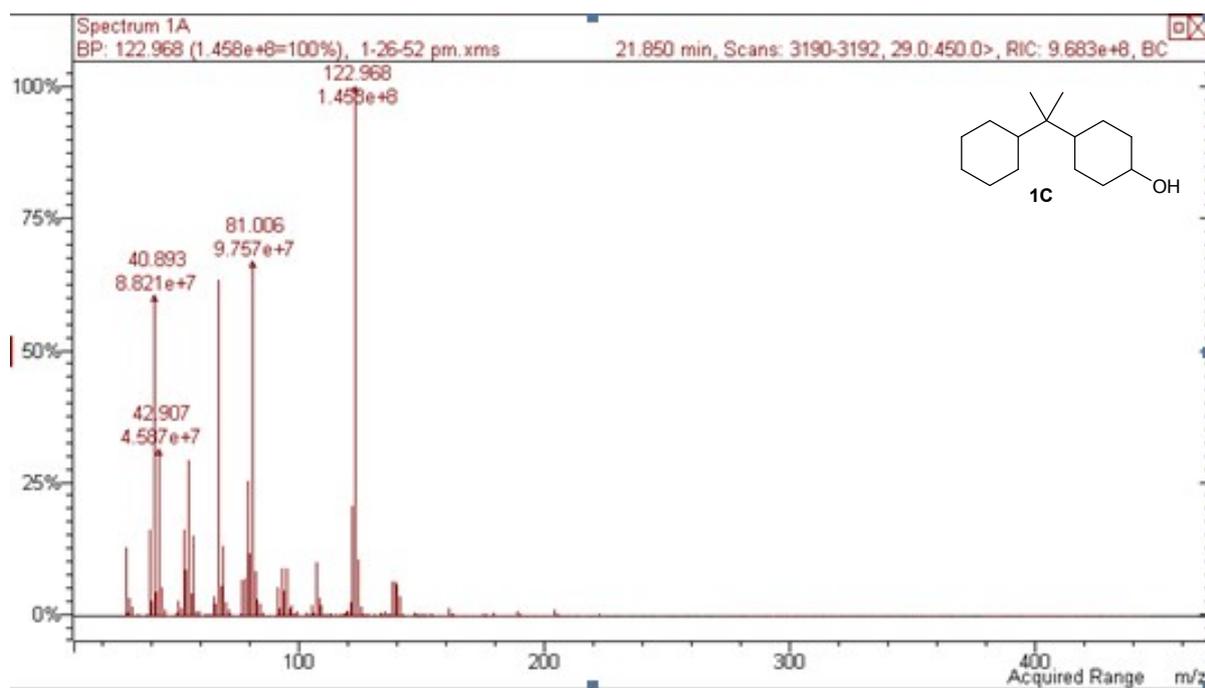


Figure S4. Mass spectrogram of the **1C** from the HDO of **1A** over the Pt/C catalyst. Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol **1A**, 40 mL cyclohexane and 0.04 g Pt/C catalyst were used for the test.

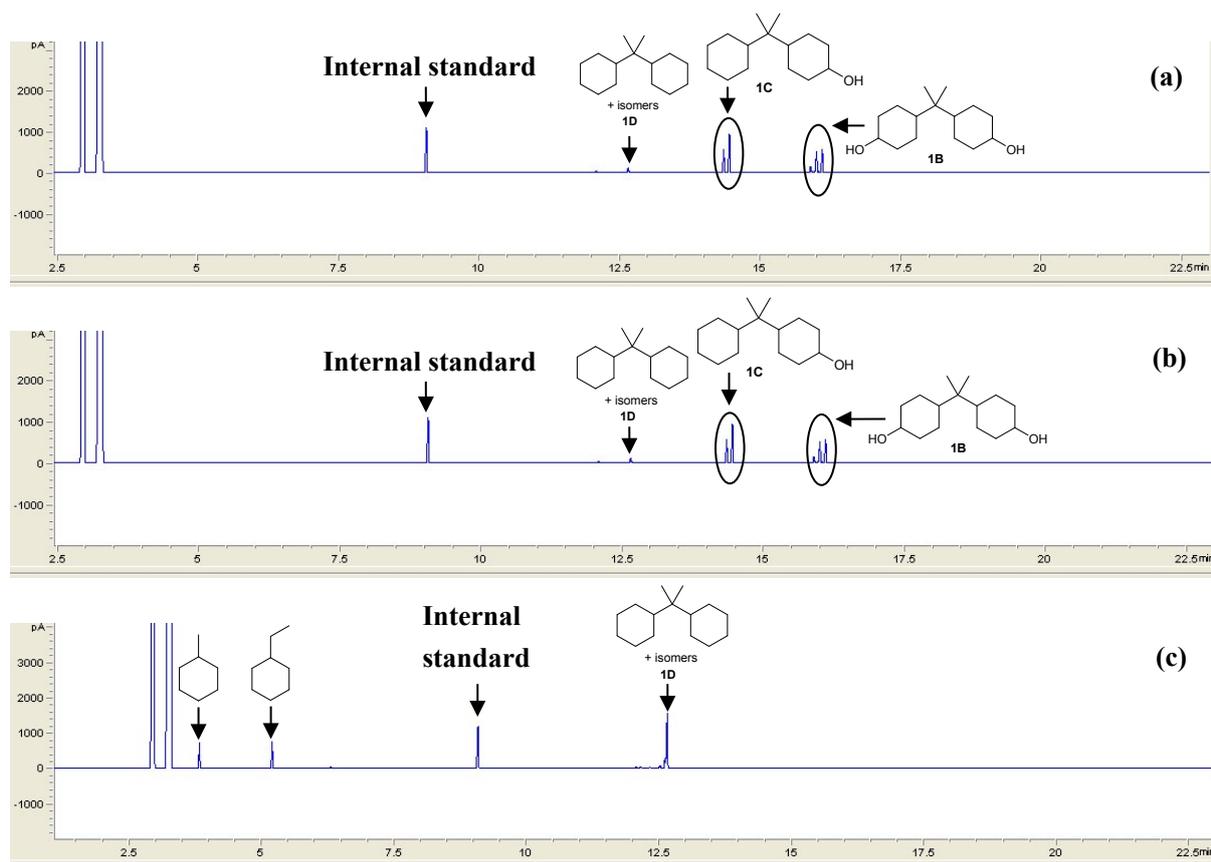


Figure S5. GC chromatograms of the products from the HDO of **1A** over the Pt/C + H-MOR (a), Pt/C + H-ZSM-5 (b) and Pt/C + H-β (c) catalysts. Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol **1A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g zeolite were used for the tests.

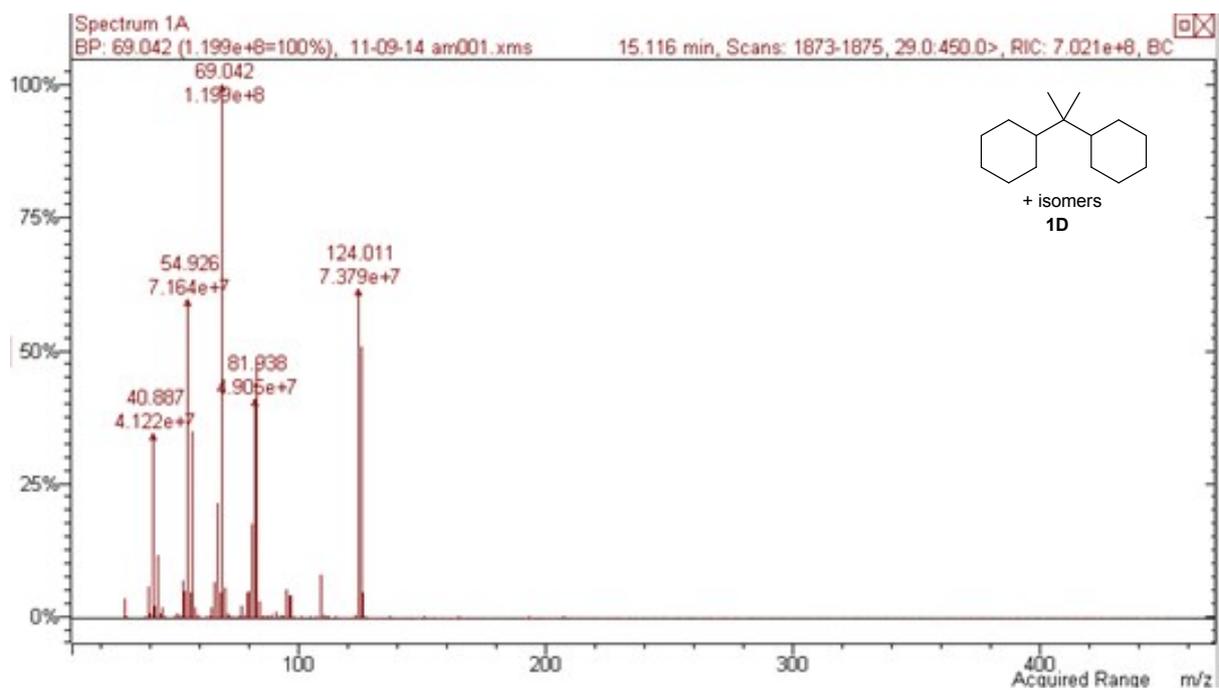


Figure S6. Mass spectrogram of the **1D** from the HDO of **1A** over the Pt/C + H- β catalyst.

Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol **1A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H- β zeolite were used for the test.

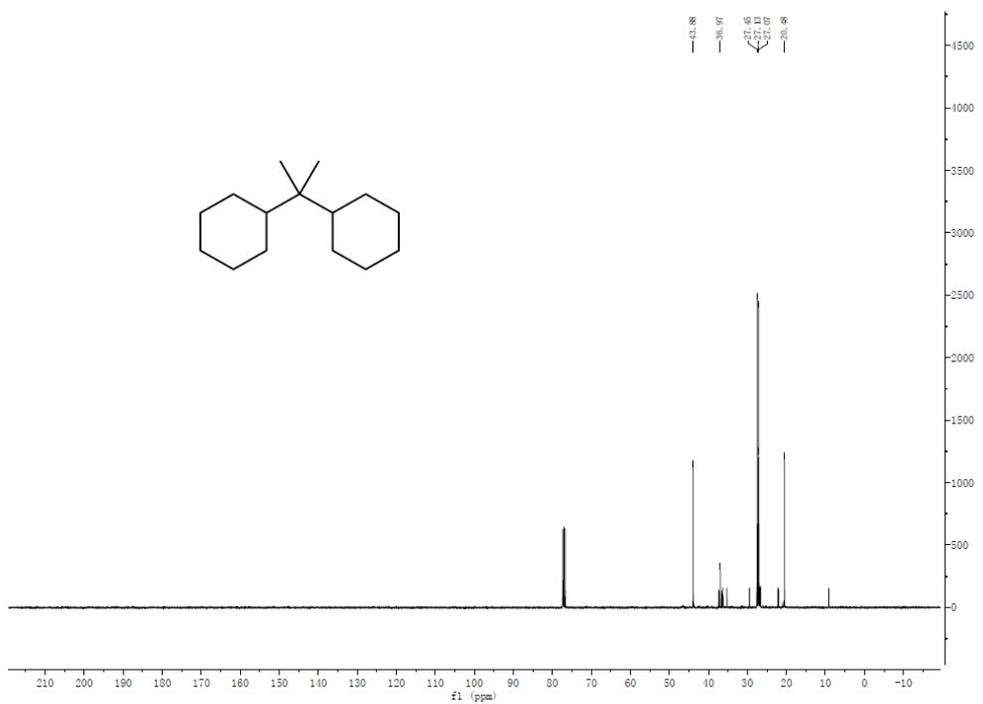
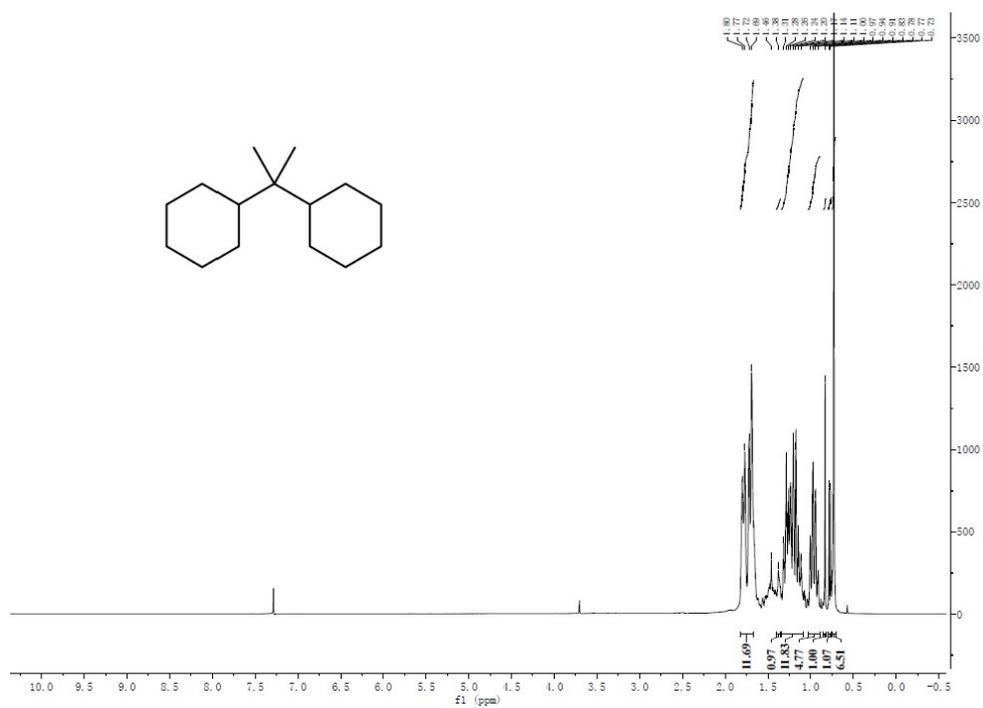


Figure S7. ^{13}C and ^1H NMR spectra of the **1D** from the HDO of **1A** over the Pt/C + H- β catalyst. Reaction conditions: 413 K, 3 MPa H_2 , 4 h; 5 mmol **1A**, 40 mL cyclohexane, 0.04 g Pt/C and 0.5 g H- β zeolite were used for the test.

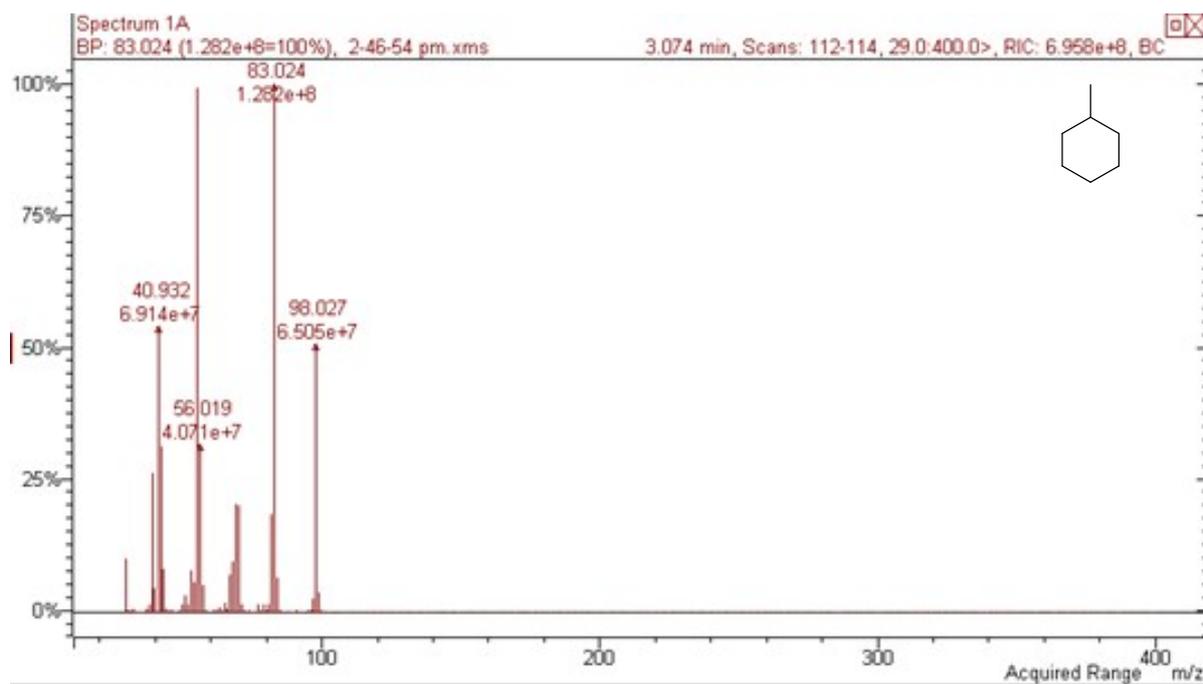


Figure S8. Mass spectrogram of the methylcyclohexane from the HDO of **1A** over the Pt/C + H- β catalyst. Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol **1A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H- β zeolite were used for the test.

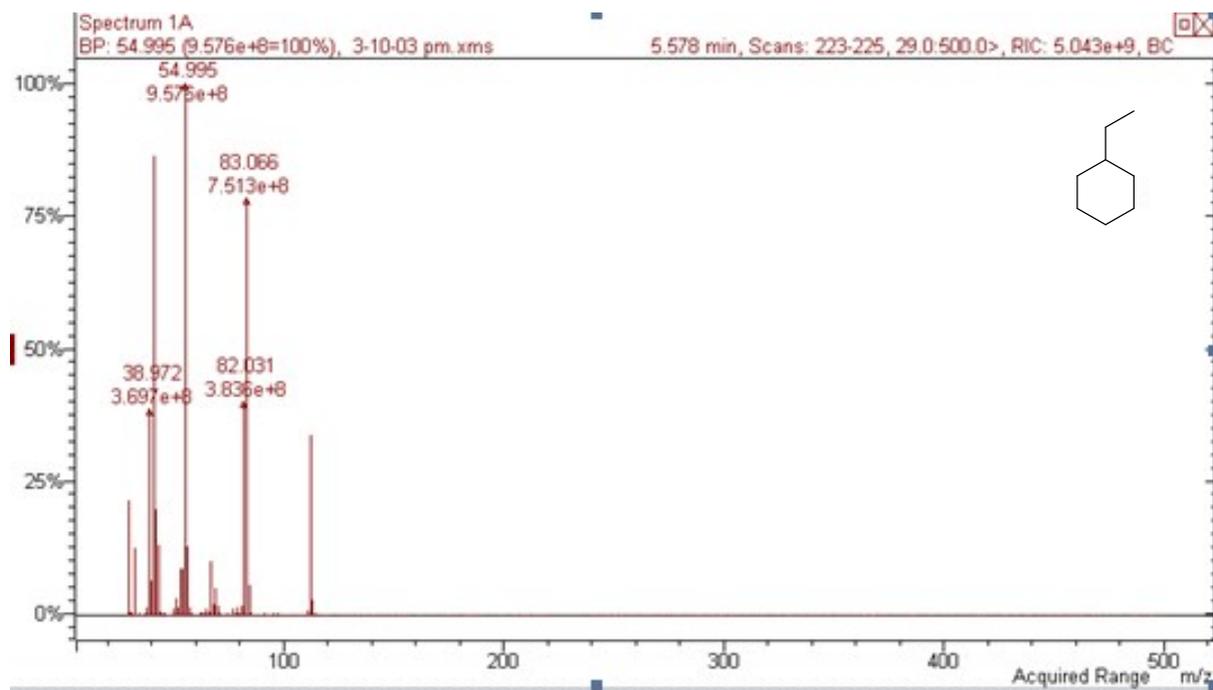


Figure S9. Mass spectrogram of the ethylcyclohexane from the HDO of **1A** over the Pt/C + H- β catalyst. Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol **1A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H- β zeolite were used for the test.

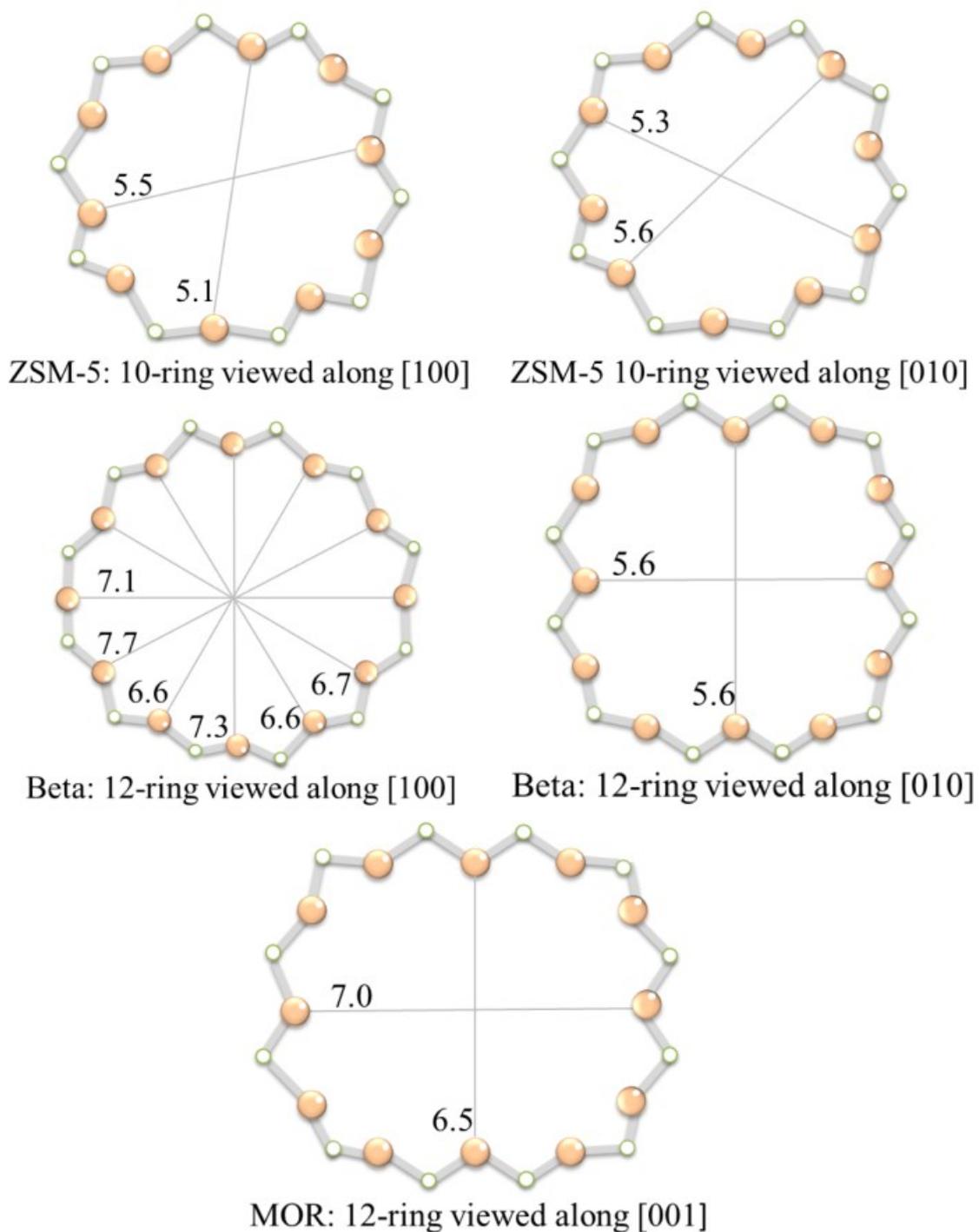


Figure S10. The pore diameters of H-ZSM-5, H-Beta (H- β) and H-MOR zeolites according to reference.¹

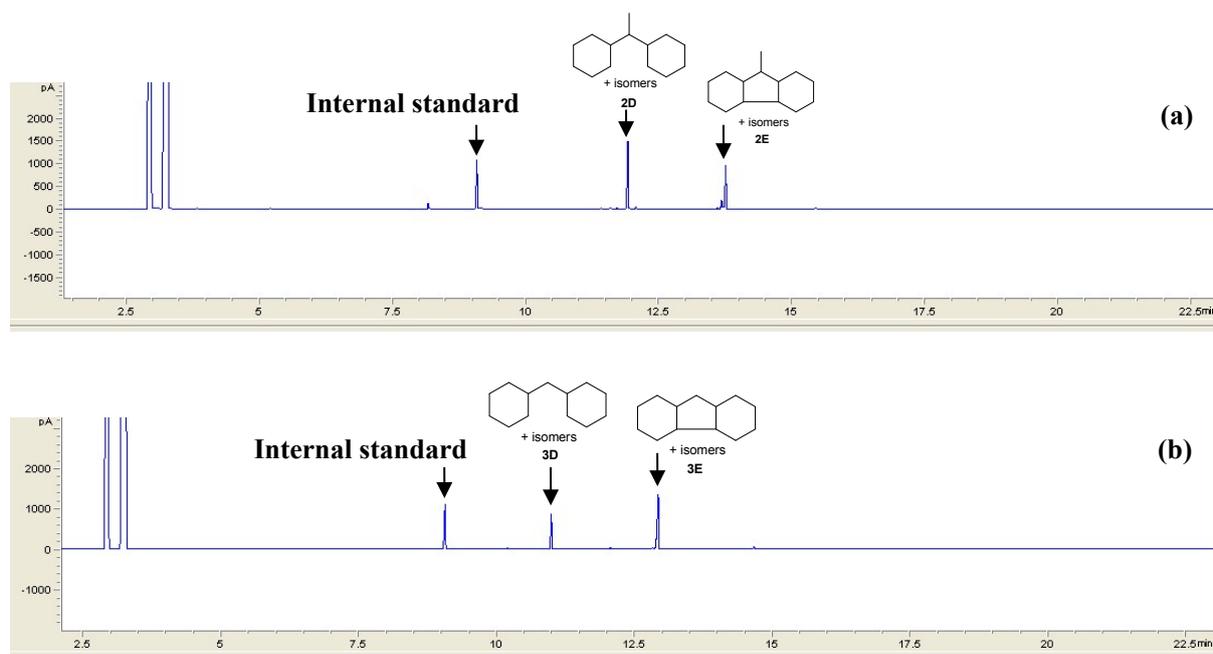


Figure S11. GC chromatograms of the products from the HDO of **2A** (a) and **3A** (b) over the Pt/C + H- β catalyst. Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol **2A** or **3A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H- β zeolite were used for each test.

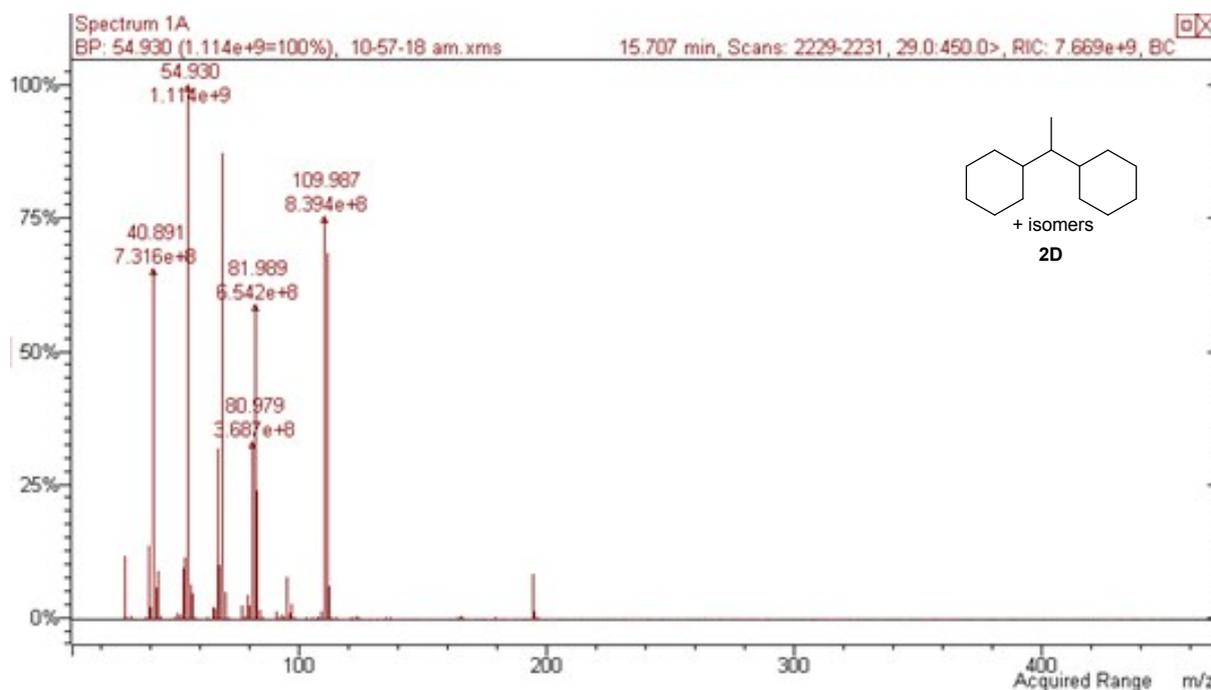


Figure S12. Mass spectrogram of the **2D** from the HDO of **2A** over the Pt/C + H- β catalyst. Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol **2A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H- β zeolite were used for the test.

In this work, we could not selectively produce **2D** and **2E** under the investigated conditions. **2D** and **2E** always produced at the same time. It is difficult to separate them. That is the reason why we did not give the ¹³C and ¹H NMR spectra of the **2D** and **2E**.

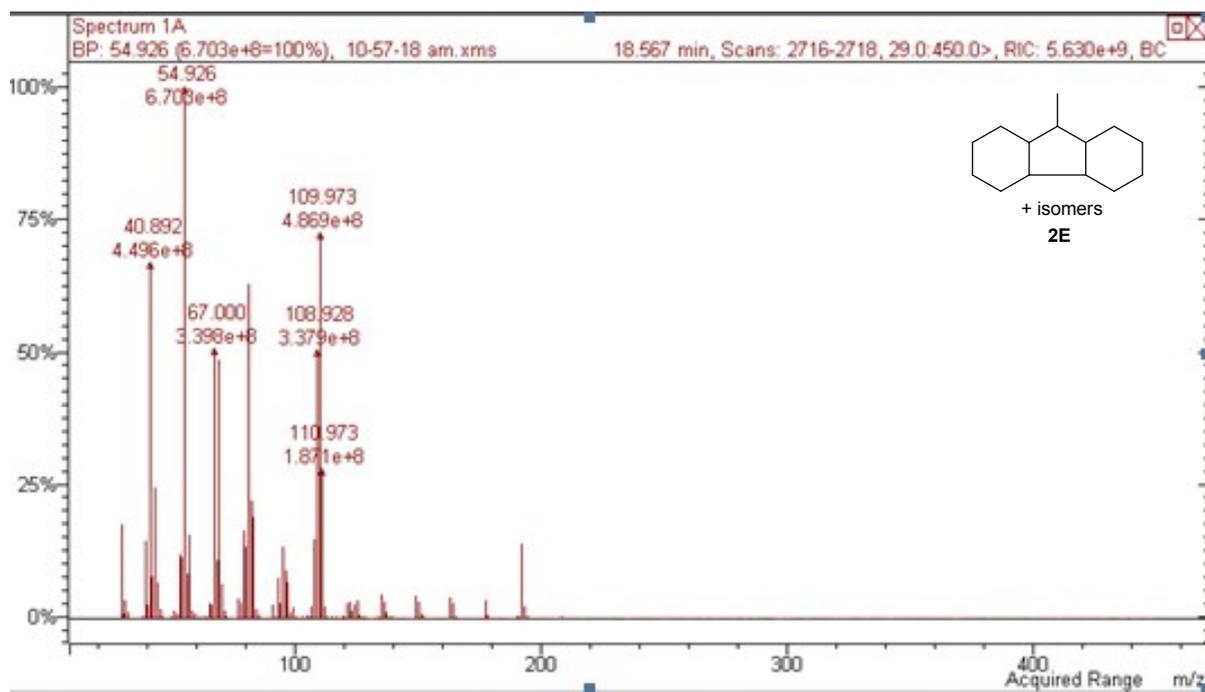


Figure S13. Mass spectrogram of the **2E** from the HDO of **2A** over the Pt/C + H- β catalyst.

Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol **2A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H- β zeolite were used for the test.

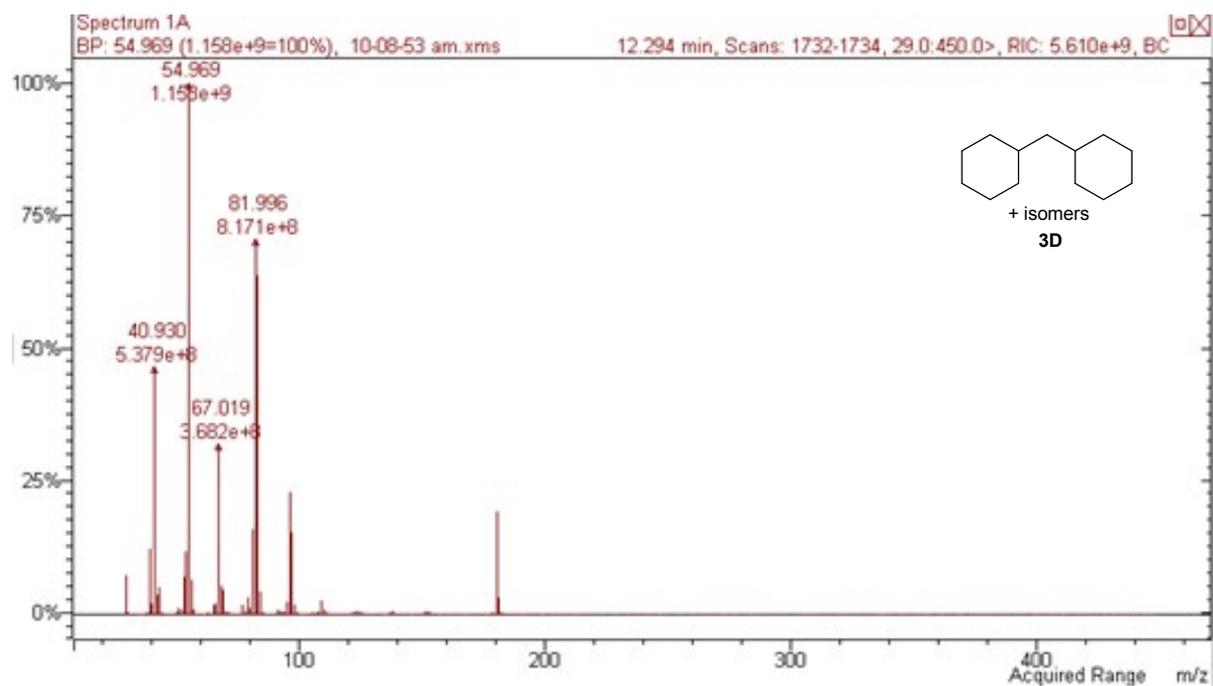


Figure S14. Mass spectrogram of the **3D** from the HDO of **3A** over the Pt/C + H- β catalyst.

Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol **3A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g zeolite were used for the test.

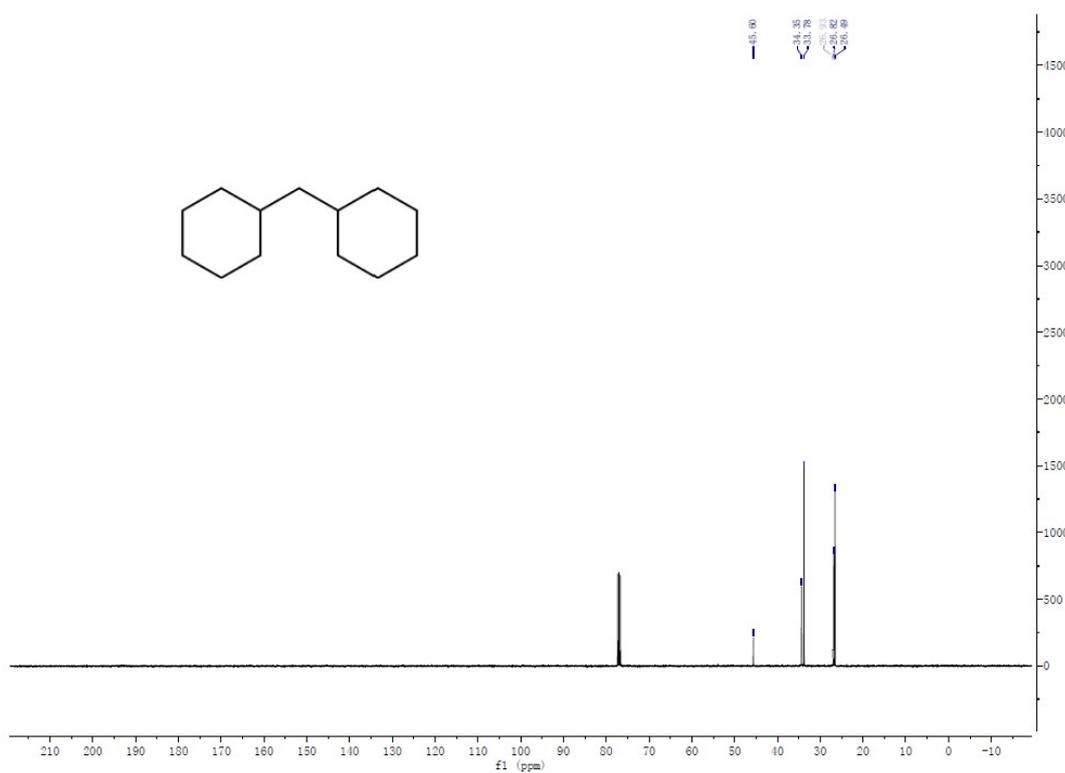
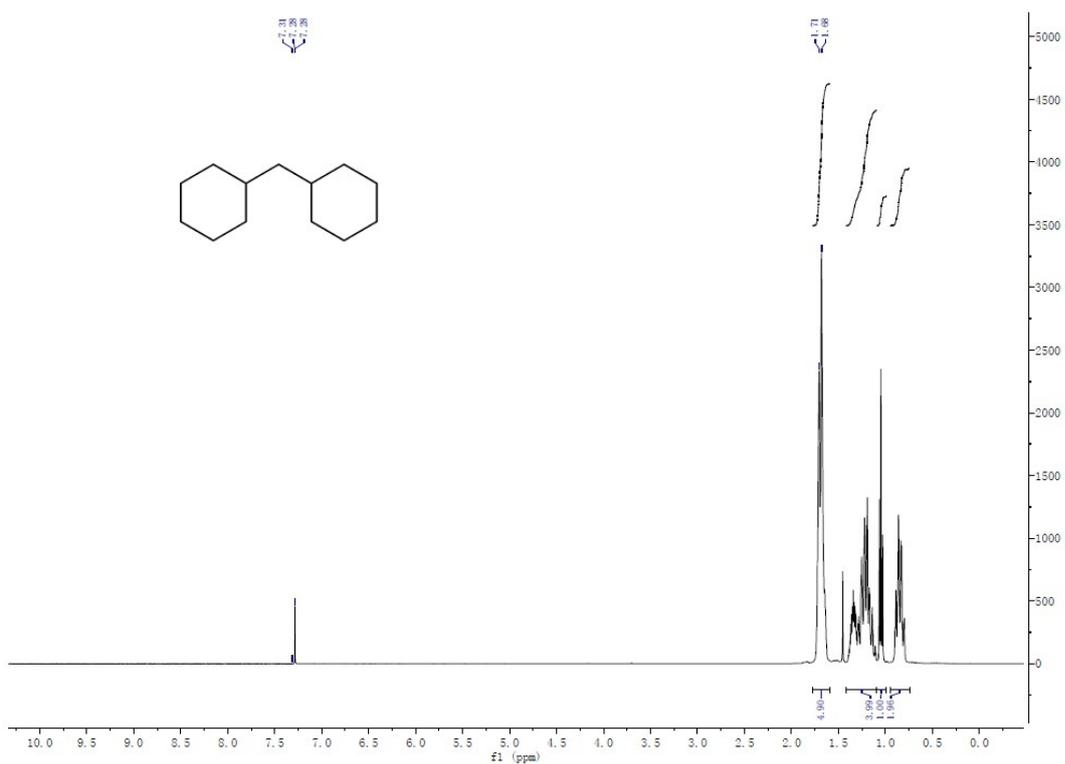


Figure S15. ^{13}C and ^1H NMR spectra of the **3D** from the HDO of **3A** over the Pt/C + H- β catalyst. Reaction conditions: 413 K, 3 MPa H_2 , 4 h; 5 mmol **3A**, 40 mL cyclohexane, 0.04 g Pt/C and 0.6 g H- β zeolite were used for each test.

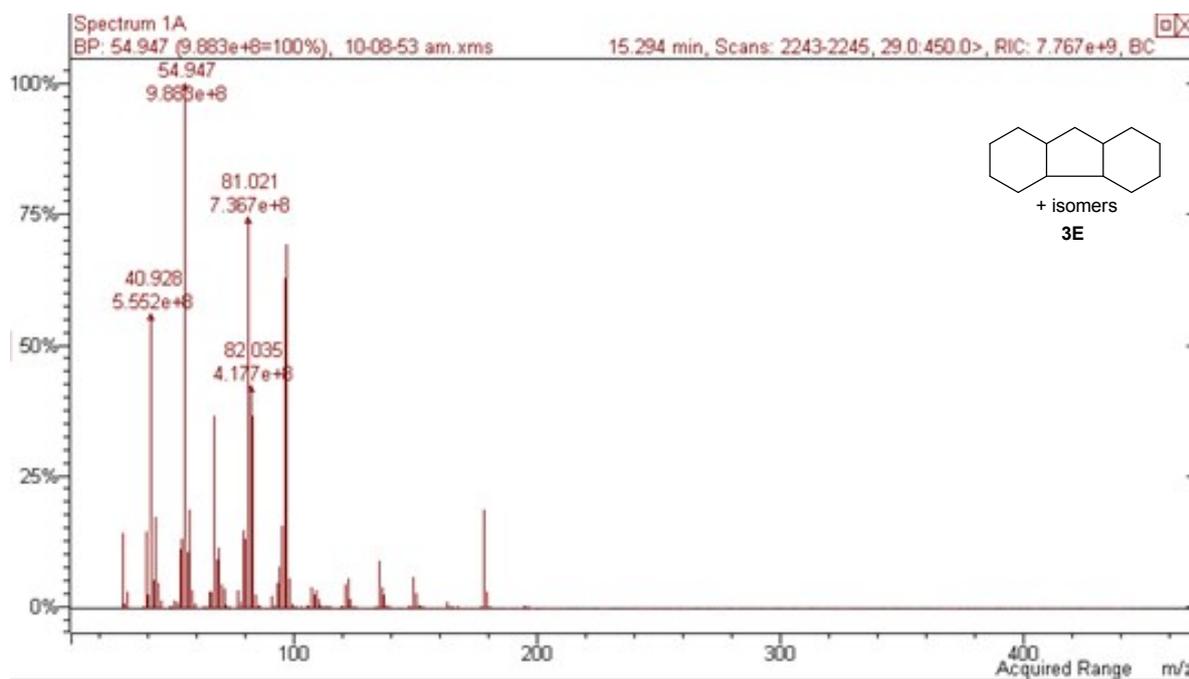


Figure S16. Mass spectrogram of the **3E** from the HDO of **3A** over the Pt/C + H- β catalyst. Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol **3A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H- β zeolite were used for the test.

In this work, we could not selectively produce **3E** under the investigated conditions. **3D** and **3E** always produced at the same time. It is difficult to separate them. That is the reason why we did not give the ¹³C and ¹H NMR spectra of the **3E**.

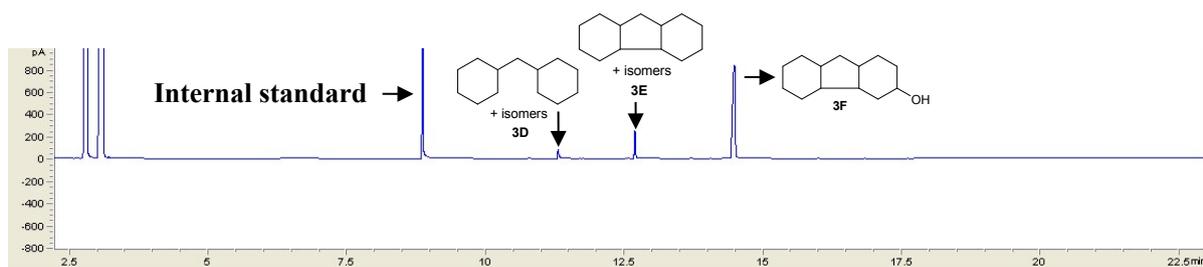


Figure S17. GC chromatogram of the products from the HDO of **3A** over the Pt/C catalyst.

Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol **3A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst were used for the test.

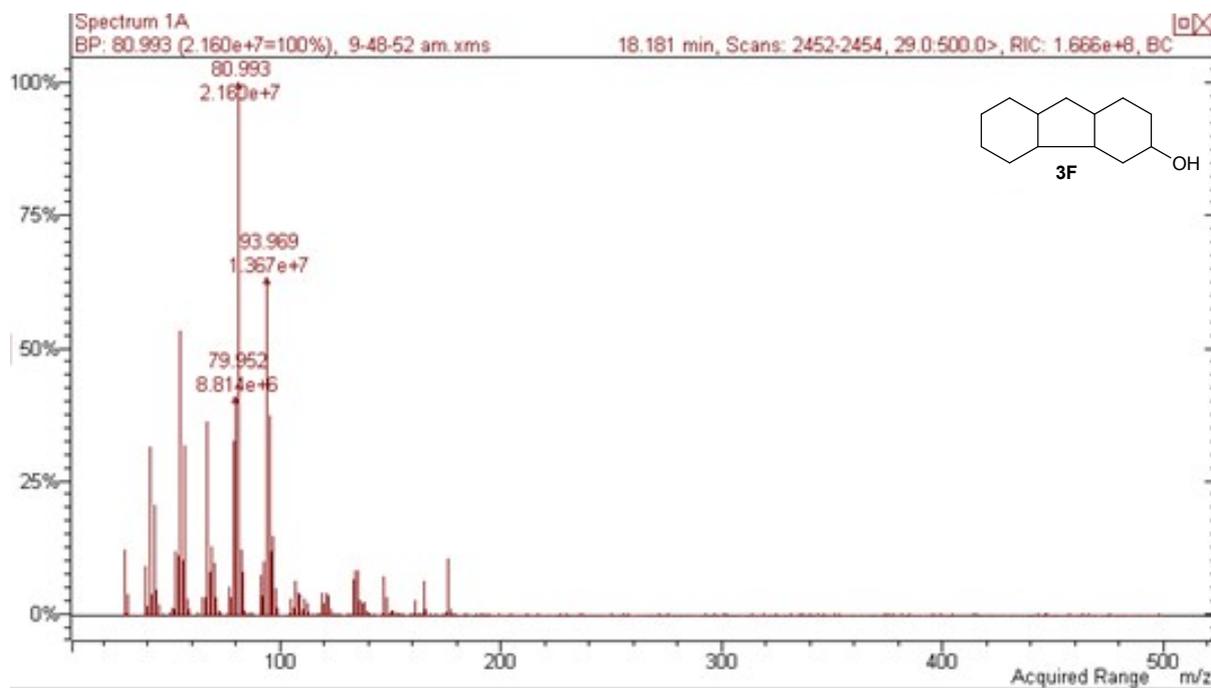


Figure S18. Mass spectrogram of the **3F** from the HDO of **3A** over the Pt/C catalyst. Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol **3A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst were used for the test.

Reference

- 1 Ch. Baerlocher, L.B. McCusker, D.H. Olson, Atlas of Zeolite Framework Types, sixth ed., Elsevier Science B.V., Amsterdam, 2007.