

Supporting Information

## **Synthesis of renewable alkyl decalins with *p*-quinone and 2-methyl-2,4-pentanediol**

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### **Detail information for the analysis of products:**

In this work, the products were analyzed using an Agilent 7890A GC equipped with HP-5 column (30 m, 0.32 mm ID, 0.25  $\mu\text{m}$  film) and a flame ionization detector (FID). In split injection, samples were introduced with a split ratio of 50:1. The injector temperature was 523 K. The temperature program involved holding the initial temperature at 323 K for 2 min after injection and then programming at 15 K  $\text{min}^{-1}$  to 553 K, which was held for 22.3 min.

### **Characterization of ChCl-based acidic DESs by Kamlet-Taft solvatochromic method**

As we know, Kamlet-Taft solvatochromic method served as a quantitative tool to estimate the chemical properties of the ionic liquids (ILs) since some solution properties can be determined by the solvatochromism of dye molecules in ILs.<sup>1,2</sup> The properties of ILs, including the hydrogen bond donating (HBD) ability ( $\alpha$ ), hydrogen bond accepting (HBA) ability ( $\beta$ ) and dipolarity/polarizability ( $\pi^*$ ), can be investigated using solvatochromism of UV/Vis probes. By measuring of the Kamlet-Taft solvatochromic parameters, Xia *et al.* studied the relationship among the acidic strength, H-bond accepting ability and the lignin extraction efficiency during biomass pretreatment in ChCl-based DESs.<sup>3</sup>

To gain an insight into their acidity, we measured the Kamlet-Taft solvatochromic parameters ( $\alpha$  and  $\pi^*$ ) of ChCl-based DESs, Nile red (NR) was used as a solvatochromic indicator to determine  $\alpha$ . 4-Nitroanisole (OMe) was used to determine  $\pi^*$ .<sup>2,3</sup> Taking ChCl/MSA (10:1) for example, a concentrated anhydrous methanol solution of dye was added to 1 g of ChCl/MSA (10:1). Then methanol was carefully removed by vacuum at 313 K for 12 h. The mixture of ChCl/MSA (10:1) and dye was transferred into quartz cell. The absorption spectrum of the mixture was checked using UV-visible spectrophotometer (LAMBDA A950) in the wavelength range of 300-700 nm. The Kamlet-Taft parameters ( $\alpha$  and  $\pi^*$ ) were calculated according to literature<sup>3,4</sup> using the following equations:

$$\pi^* = 14.57 - 4270/\lambda_{max,OMe}$$

$$\alpha = (19.9657 - 1.0241\pi^* - 10^4/\lambda_{max,NR})/1.6078$$

### **Method for the purification of 2A+2B and 2B**

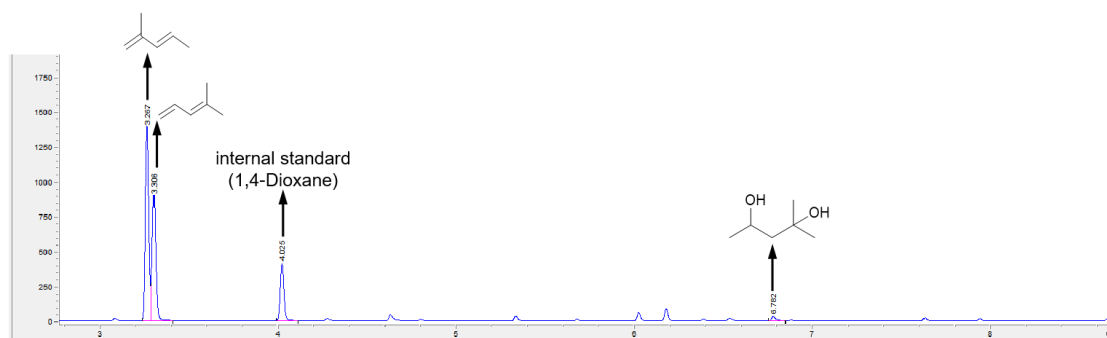
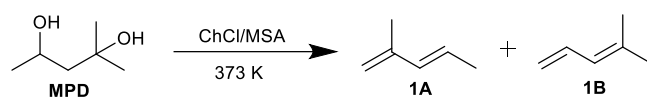
The Diels-Alder reaction product was a mixture of target compounds (**2A+2B**), unreacted **1A+1B** and 1:2 addition product. After removing the unreacted **1A+1B** by vacuum distillation, the content of the 1:2 addition product **2C** was ~1%. The resulting mixture of **2A+2B** was then purified by recrystallization from absolute methanol for the subsequent hydrodeoxygenation step. The compound **2B** was further isolated by column chromatogram for qualitative analysis using a Bruker AVANCE III HD 700MHz Spectrometer.

### **Preparation of Ni/H- $\beta$ and Pd/NbOPO<sub>4</sub> catalysts**

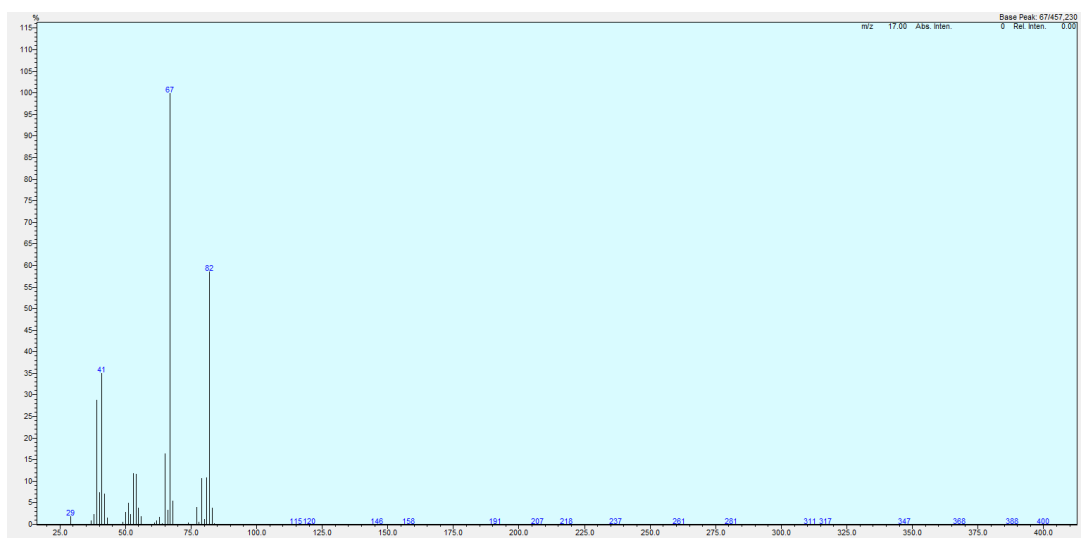
The Ni/H- $\beta$  catalyst used in hydrodeoxygenation step was prepared by the incipient wetness impregnation of a commercial H- $\beta$  zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio = 25, purchased from Nankai University) with an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O according to the method described in our previous work.<sup>5</sup> The theoretical Ni content in the catalyst was fixed as 5% by weight and the product was kept at room temperature for 12 h, dried at 393 K for 6 h, and then calcined in air at 773 K for 2 h. Finally, the Ni/H- $\beta$  was reduced by hydrogen flow for 2 h at 673 K. After being cooled down to room temperature in hydrogen, the catalysts were passivated by 1% O<sub>2</sub> in N<sub>2</sub>.

The Pd/NbOPO<sub>4</sub> was prepared by the method described in literature.<sup>6</sup> In a typical synthesis, 1.32 g (0.01 mol) of diammonium hydrogen phosphate was dissolved in 20 mL water and then adjusted to pH = 2 using phosphoric acid. Under vigorous stirring, 20 mL of 0.5 mol L<sup>-1</sup> niobium tartrate (pH = 2) was added to the above solution. Then the mixed solution was dropped into the aqueous solution of cetyltrimethyl ammonium bromide (CTAB), which was previously prepared by dissolving 1.0 g of CTAB in 13 mL of water. The pH value of the final solution was about 2. Afterwards,

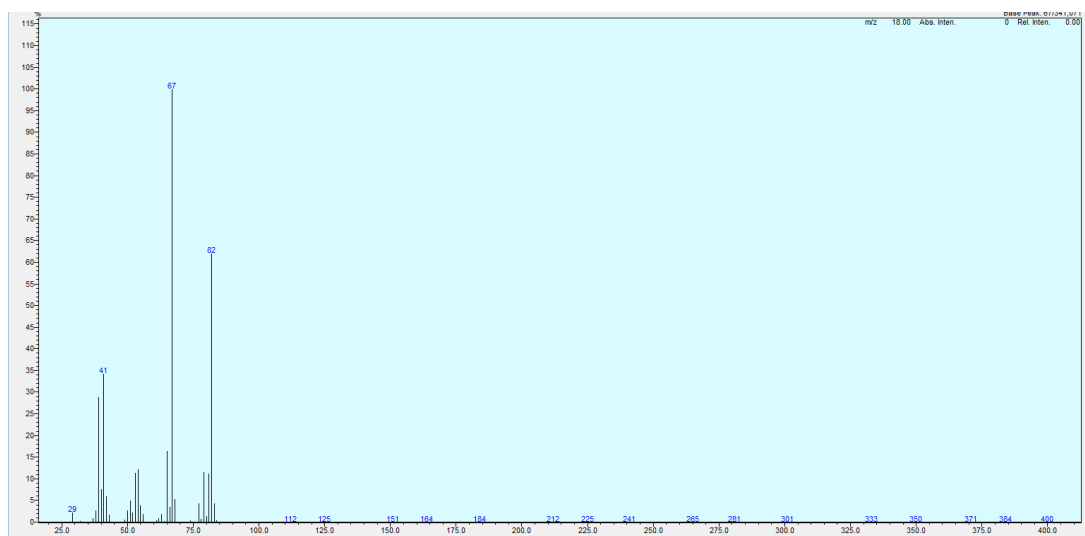
this mixture was stirred for additional 60 min at 308 K. The solution was aged in a Teflon-lined autoclave for 24 h at 433 K. After being cooled down, the solid was filtrated, washed with distilled water and then dried at 323 K. Finally, NbOPO<sub>4</sub>-pH<sub>2</sub> sample was obtained by calcination at 773 K for 5 h in air to remove organic species. The Pd/NbOPO<sub>4</sub> catalyst was prepared by incipient wetness impregnation of the NbOPO<sub>4</sub>-pH<sub>2</sub> support with calculated amount of aqueous solution of PdCl<sub>2</sub> (to keep the theoretical Pd content in the Pd/NbOPO<sub>4</sub> catalyst as 5% by weight). After being dried in air overnight, the obtained sample was reduced with pure hydrogen (30 mL min<sup>-1</sup>) at 673 K for 2 h. After being cooled down to room temperature in hydrogen, the Pd/NbOPO<sub>4</sub> catalyst was passivated by 1% O<sub>2</sub> in N<sub>2</sub>.



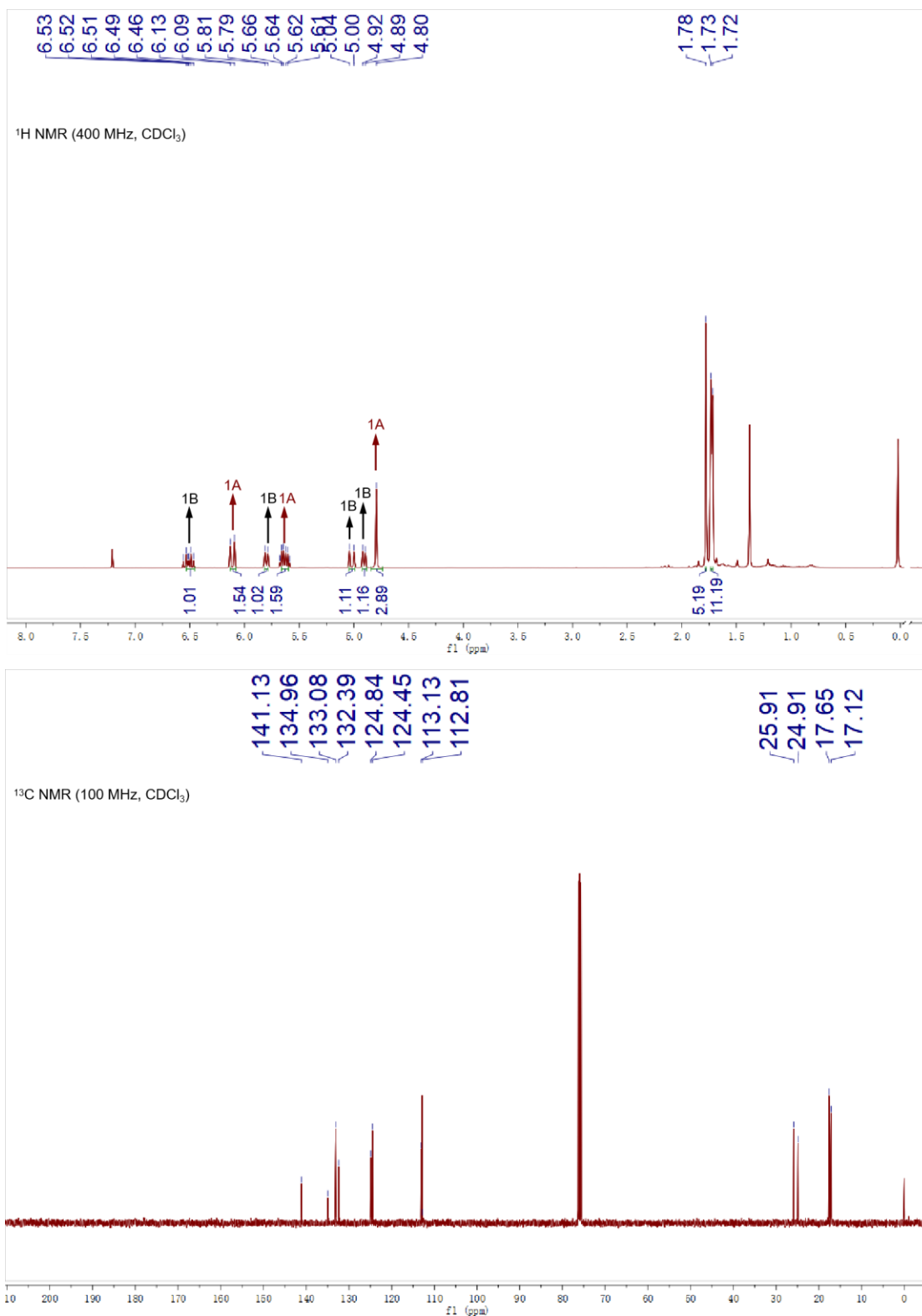
**Figure S1.** GC chromatogram of the dehydration of MPD over ChCl/MSA DES (the molar ratio of ChCl/MSA = 10:1). Reaction conditions: 373 K, 2 h; 0.5 g MPD and 2 g ChCl/MSA DES were used in the test.



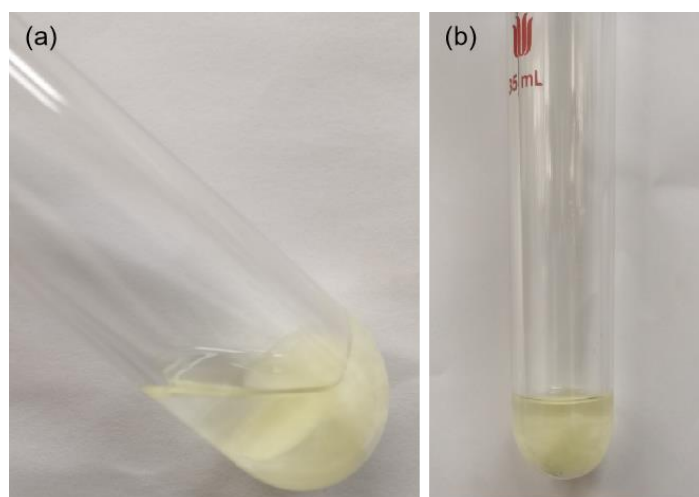
**Figure S2.** Mass spectrogram of compound **1A** from the dehydration of MPD under the catalysis of ChCl/MSA DES (the molar ratio of ChCl/MSA = 10:1).



**Figure S3.** Mass spectrogram of compound **1B** from the dehydration of MPD under the catalysis of ChCl/MSA DES (the molar ratio of ChCl/MSA = 10:1).

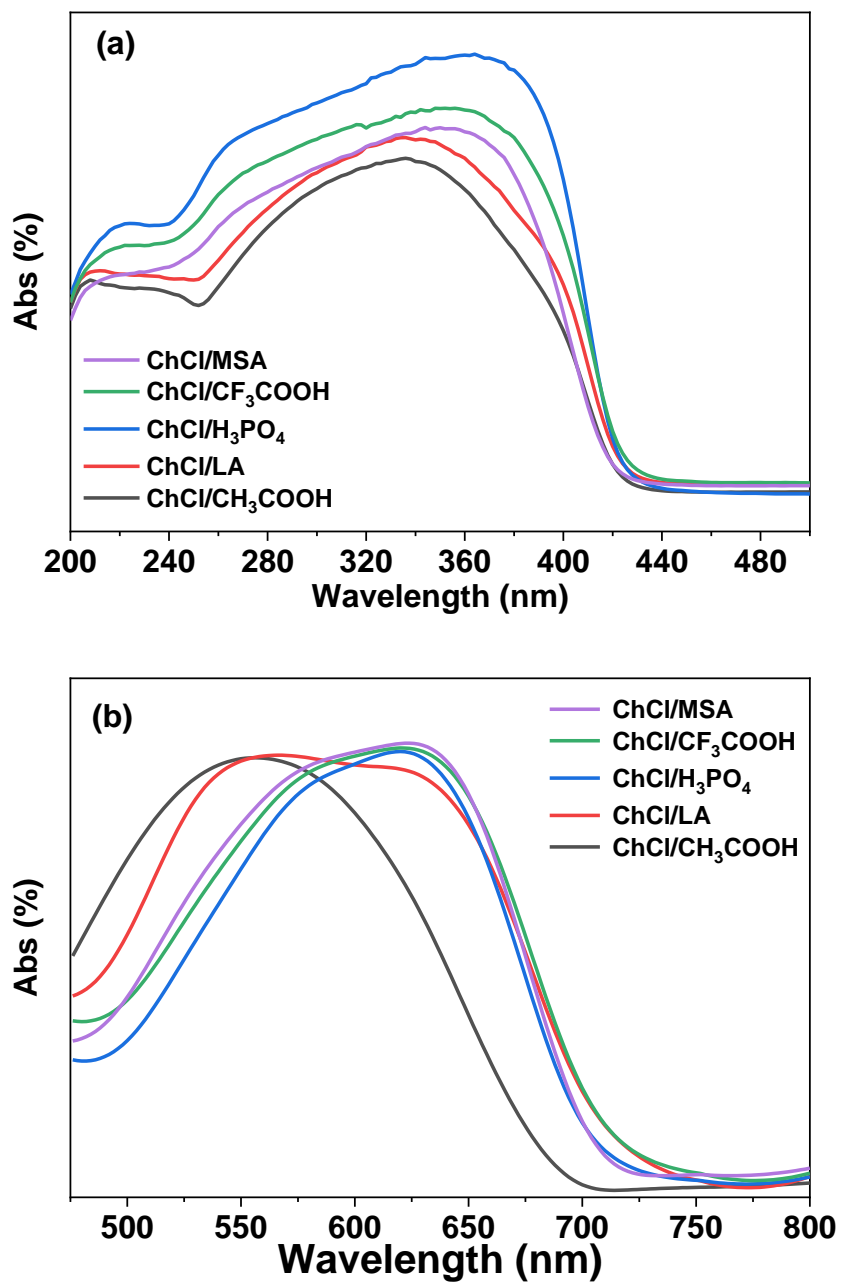


**Figure S4.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the dehydration products (*i.e.* **1A+1B**) from the dehydration of MPD under the catalysis of ChCl/MSA DES (the molar ratio of ChCl/MSA = 10:1).

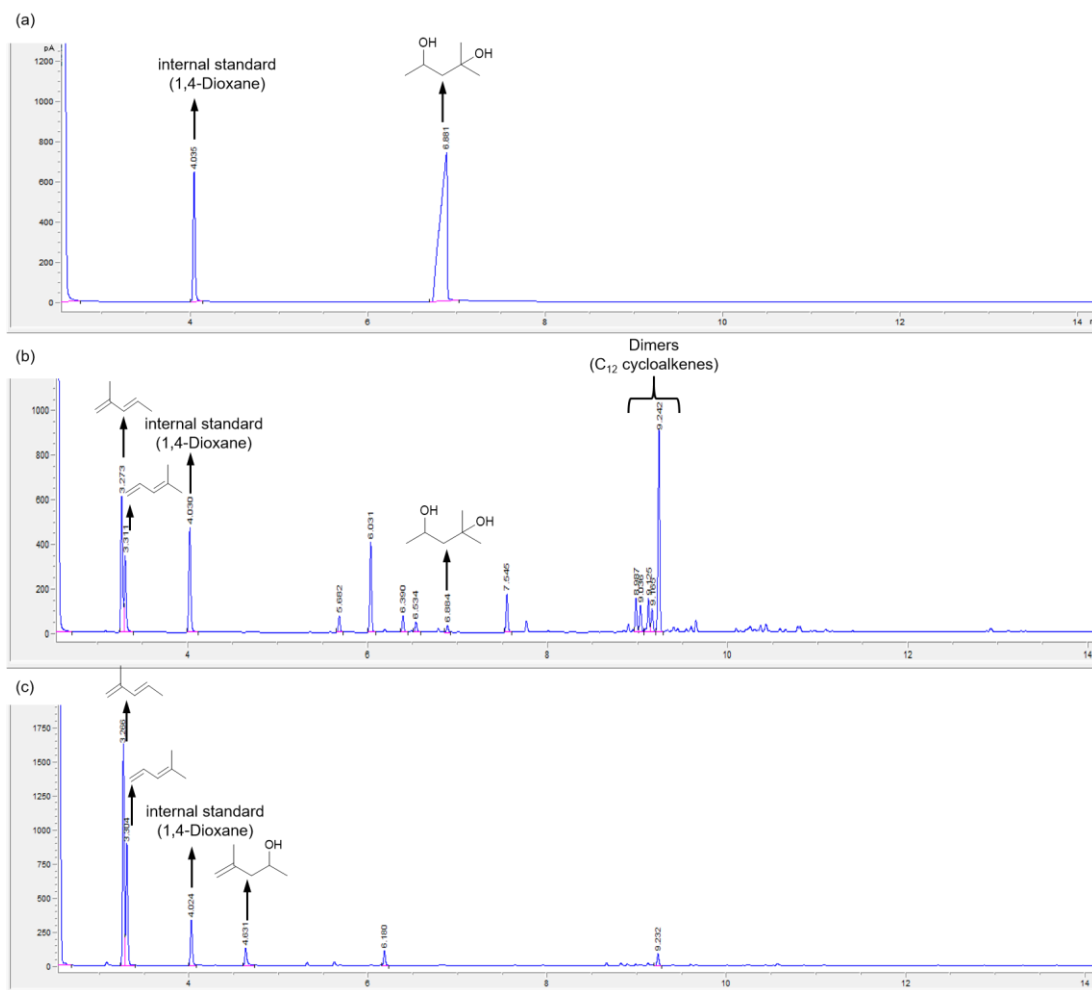


**Figure S5.** Photographs of the reaction system after being stirred at 373 K for 2 h and cooled down to room temperature completion in ChCl/MSA (the molar ratio of ChCl/MSA = 10:1).

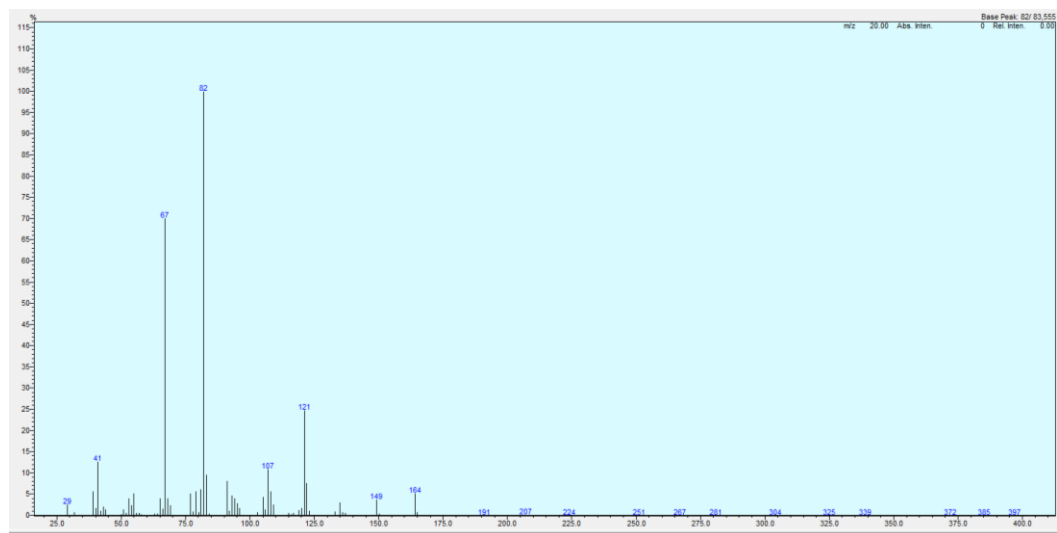




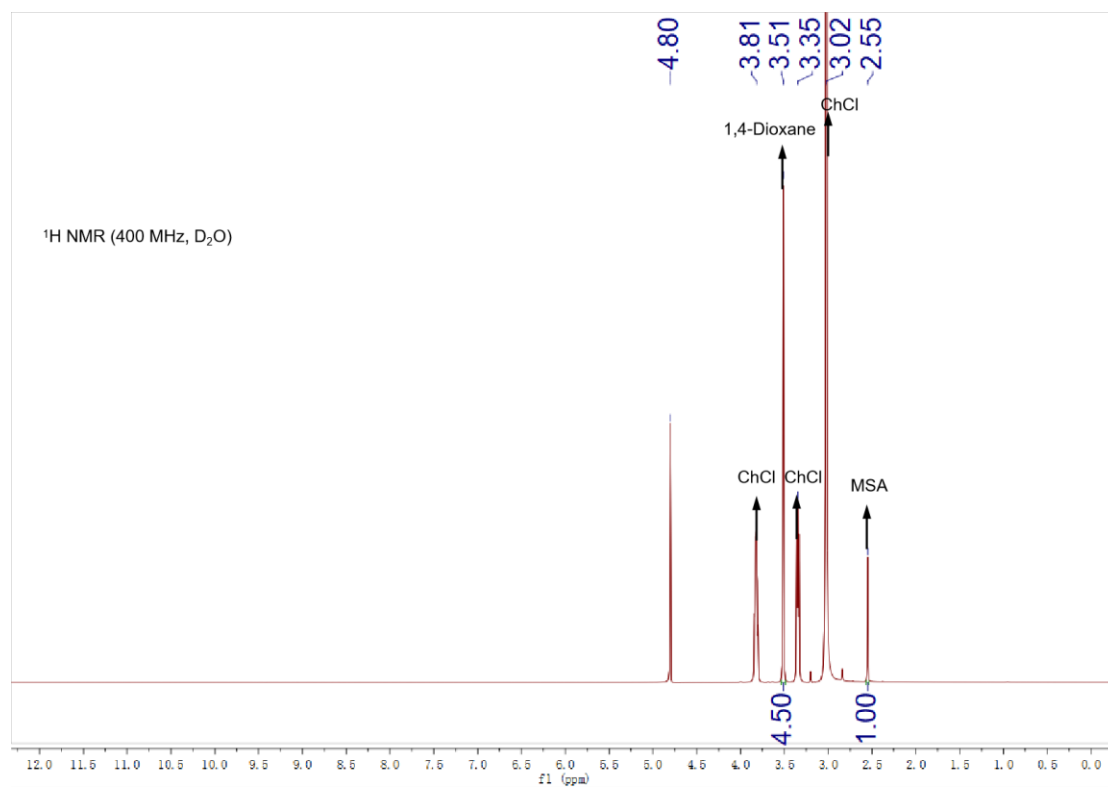
**Figure S6.** UV/Vis absorption spectra ChCl-based acidic DESs using (a) 4-nitroanisole (OMe) or (b) Nile red (NR) as solvatochromic probe.



**Figure S7.** GC chromatograms of the dehydration products of MPD in the presence of (a) ChCl (14 mmol), (b) MSA (0.35 mmol) and (c) ChCl/MSA (40:1, 2 g). Reaction conditions: 373 K, 2 h; 0.5 g MPD were used in the test.

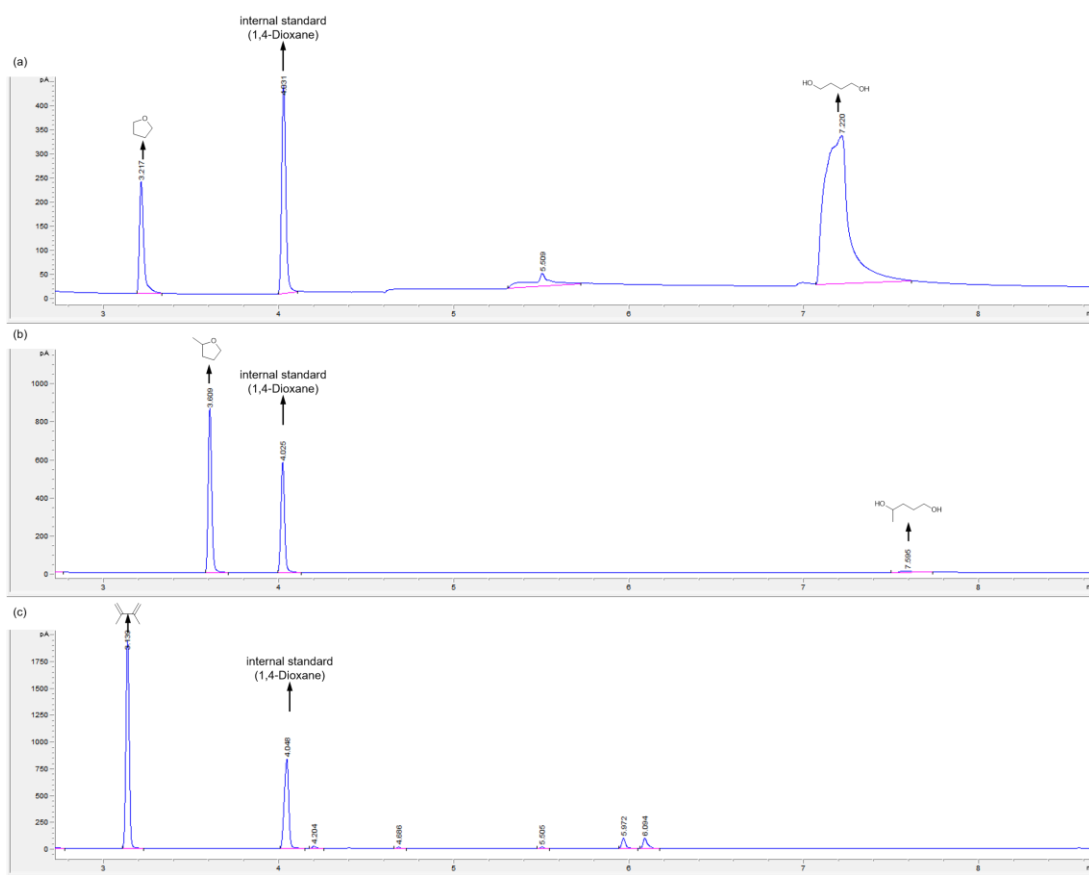


**Figure S8.** Mass spectrogram of the C<sub>12</sub> cycloalkenes generated from the further self Diels-Alder reaction of **1A** and **1B**.

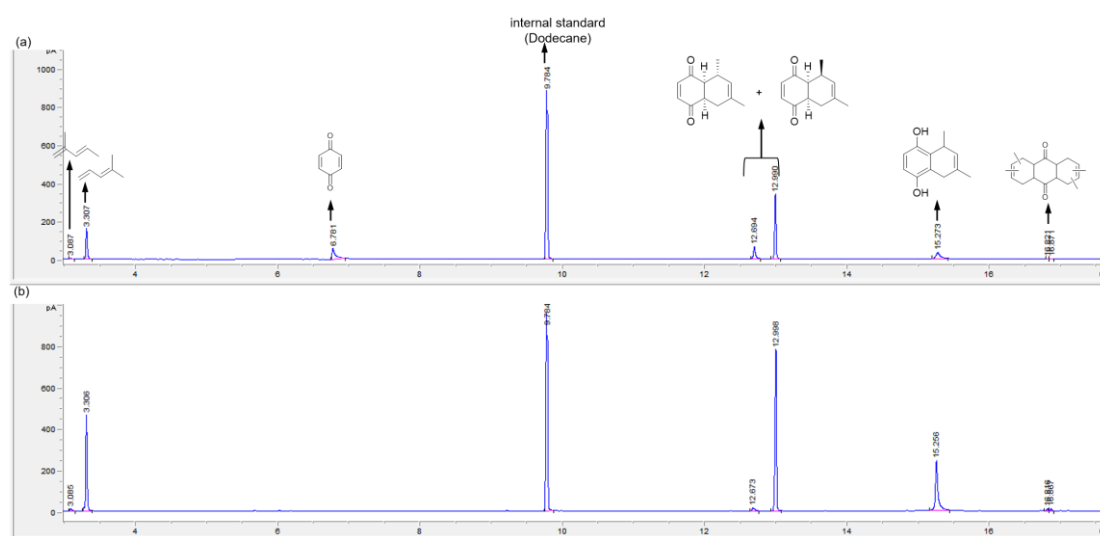
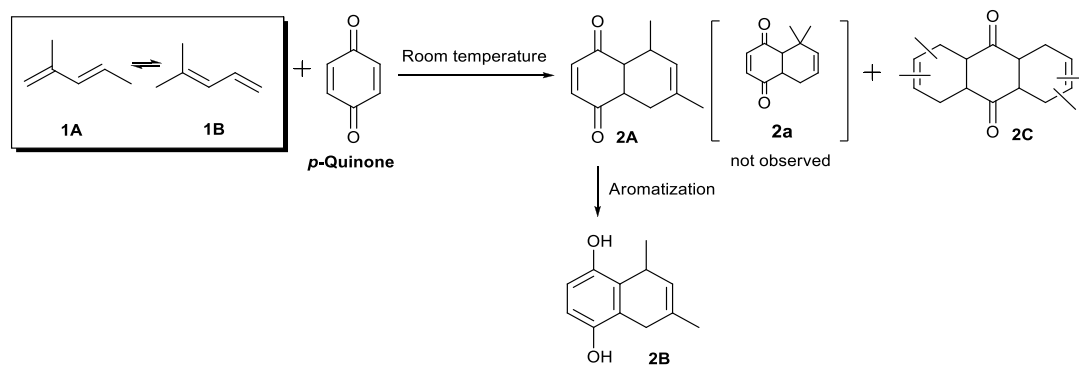


**Figure S9.** <sup>1</sup>H NMR of the used ChCl/MSA DES (molar ratio of ChCl to MSA = 40:1) containing internal standard 1,4-dioxane.

To further confirm the stability of ChCl/MSA DES, an internal standard 1,4-dioxane (0.0590 g) was added to the remaining lower layer (*i.e.* used ChCl/MSA DES) and diluted with 10 mL of D<sub>2</sub>O to give a homogeneous liquid. About 0.5 mL of the mixture was transferred into a NMR tube. The identical <sup>1</sup>H NMR spectra of the used ChCl/MSA DES indicated that the ChCl/MSA DES was stable under the investigated conditions. The theoretical mass of remaining MSA was calculated as 0.40 mmol, which was consistent with the initial amount of MSA in the ChCl/MSA DES (0.41 mmol). Based on the above results, ChCl/MSA DES was believed to be stable under the investigated conditions.



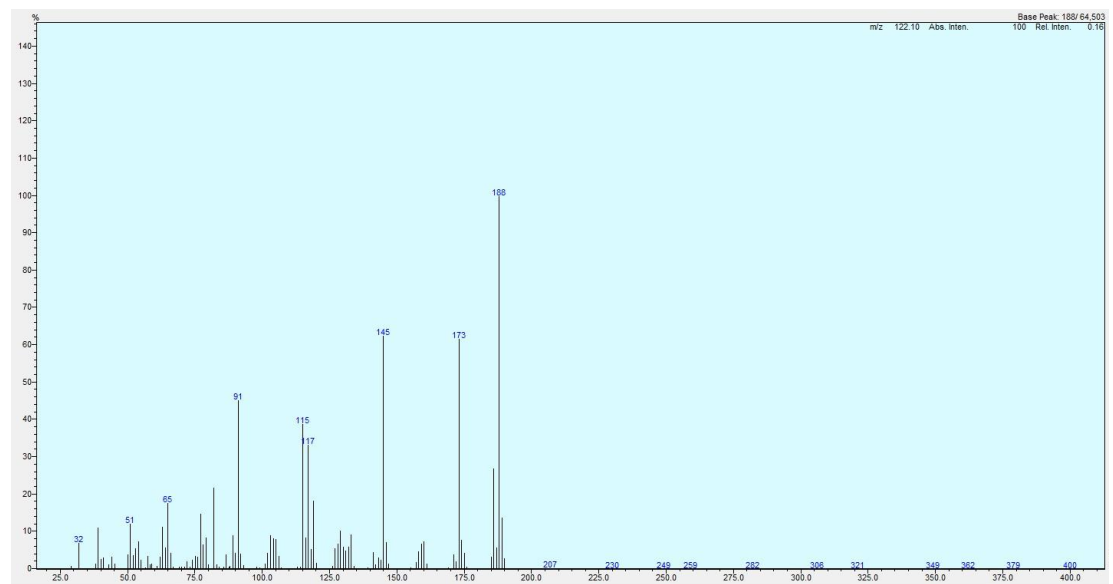
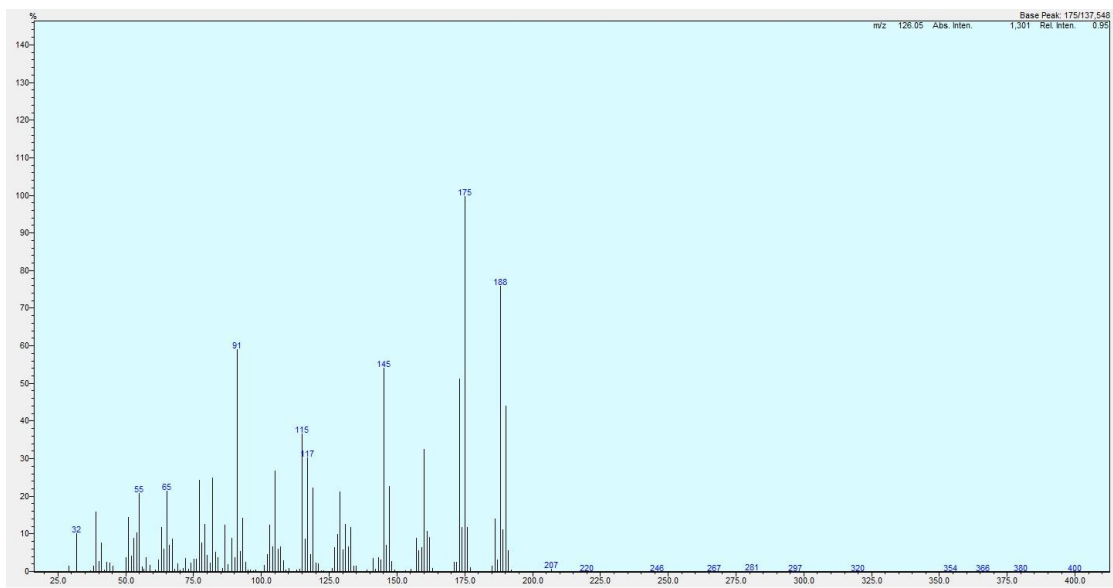
**Figure S10.** GC chromatograms of the dehydration products of (a) 1,4-butanediol, (b) pentane-1,4-diol and (c) pinacol. Reaction conditions: 373 K, 1 h; 0.5 g diol and 2 g ChCl/MSA DES were used in each test. The molar ratios of ChCl to MSA in the ChCl/MSA DES were 40:1.



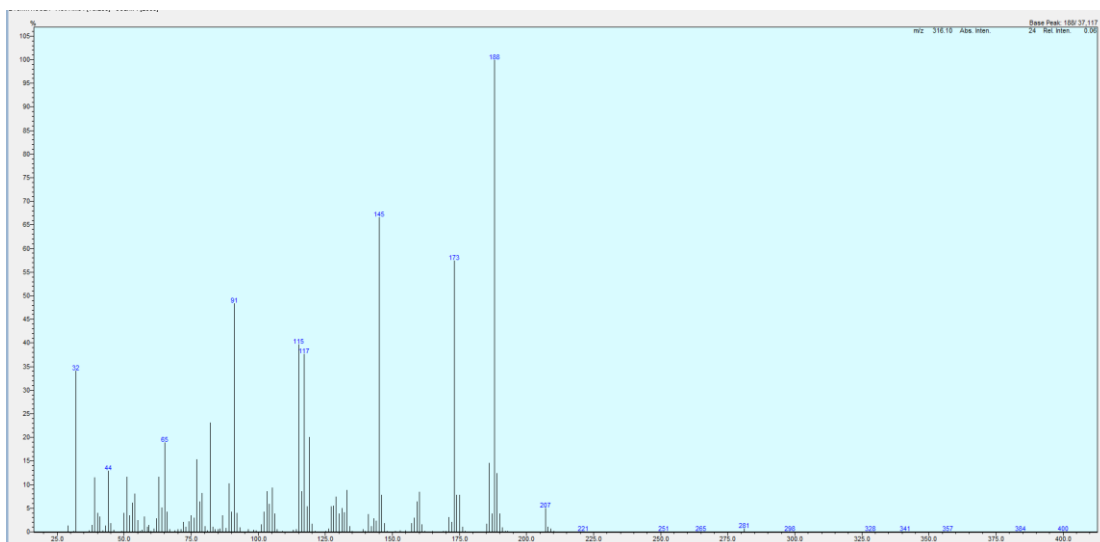
**Figure S11.** GC chromatograms of the products from the Diels-Alder reaction of dehydration products

(*i.e.* **1A+1B**) with *p*-quinone at an initial **1A+1B** to *p*-quinone molar ratio of (a) 1:1 and (b) 2:1.

Reaction conditions: room temperature, 24 h; 1 mmol *p*-quinone was used in each test.

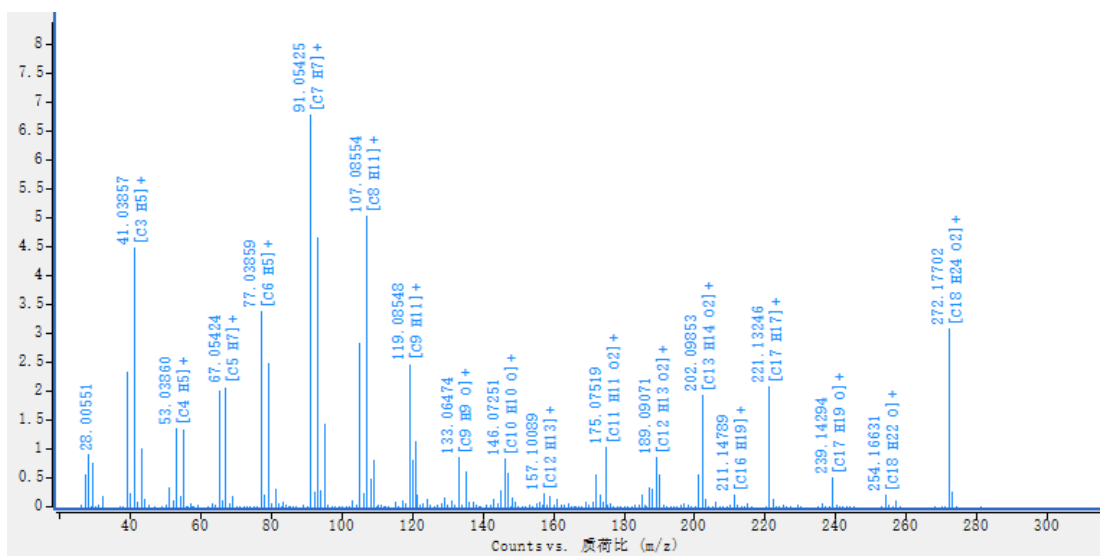


**Figure S12.** Mass spectrogram of two isomers of compound **2A** (cis and trans isomers) from the Diels-Alder reaction of dehydration products (*i.e.* **1A**+**1B**) with *p*-quinone.

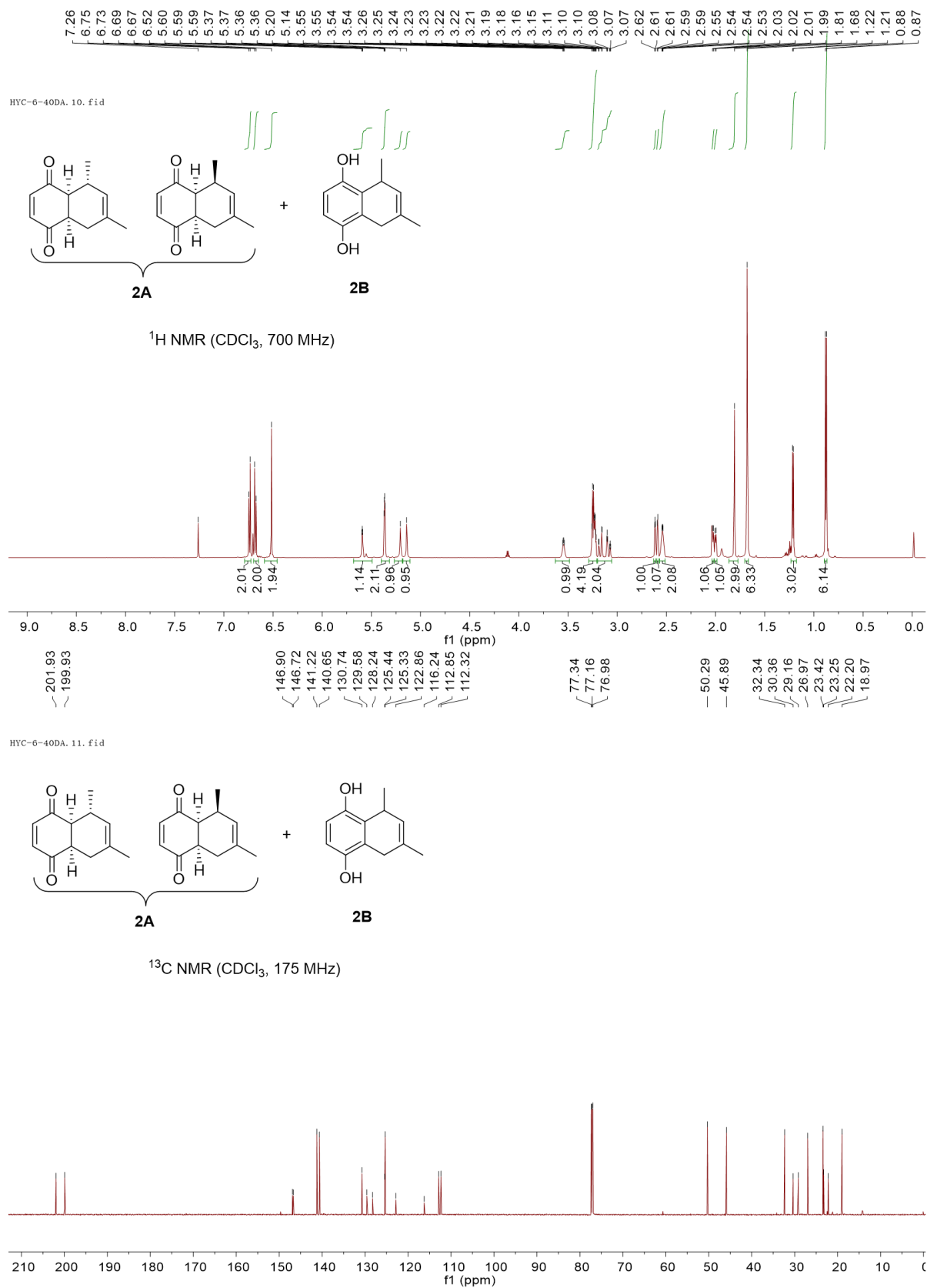


**Figure S13.** Mass spectrogram of the compound **2B** from the Diels-Alder/aromatization reaction of dehydration products (*i.e.* **1A+1B**) with *p*-quinone.

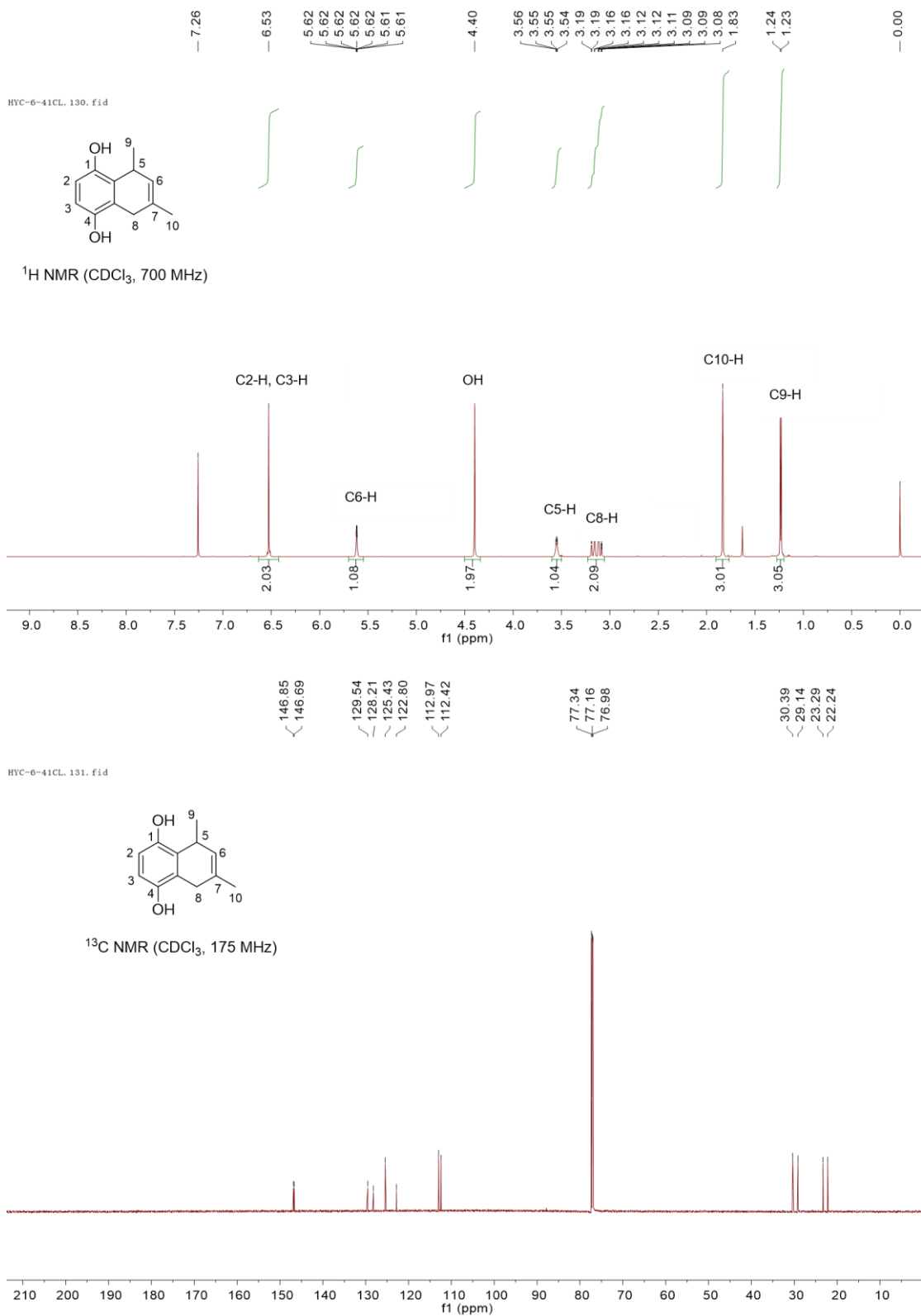




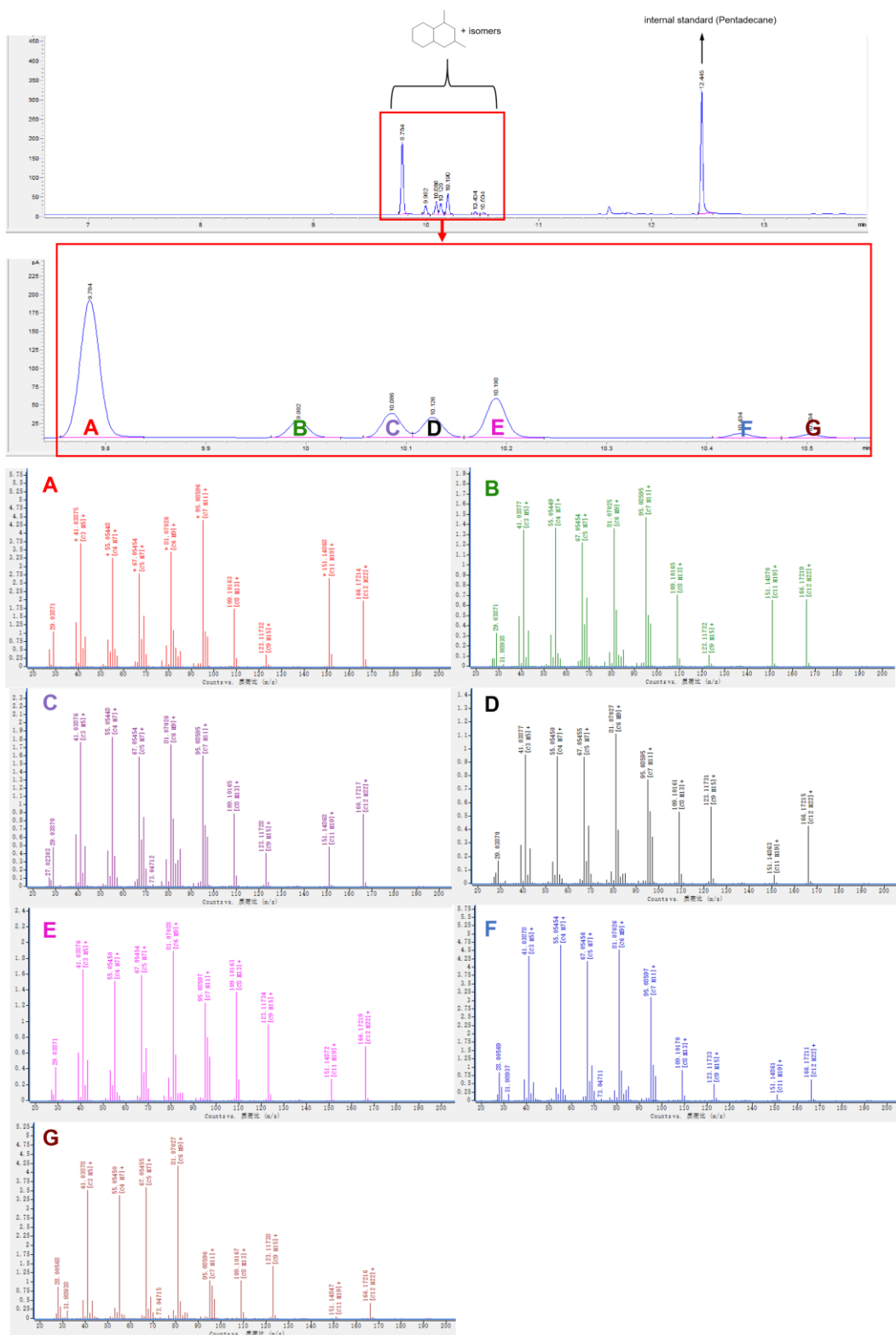
**Figure S14.** Mass spectrogram of the 1:2 addition product **2C** from the further Diels-Alder reaction of **2A** and C<sub>6</sub> dienes (*i.e.* **1A** and **1B**).



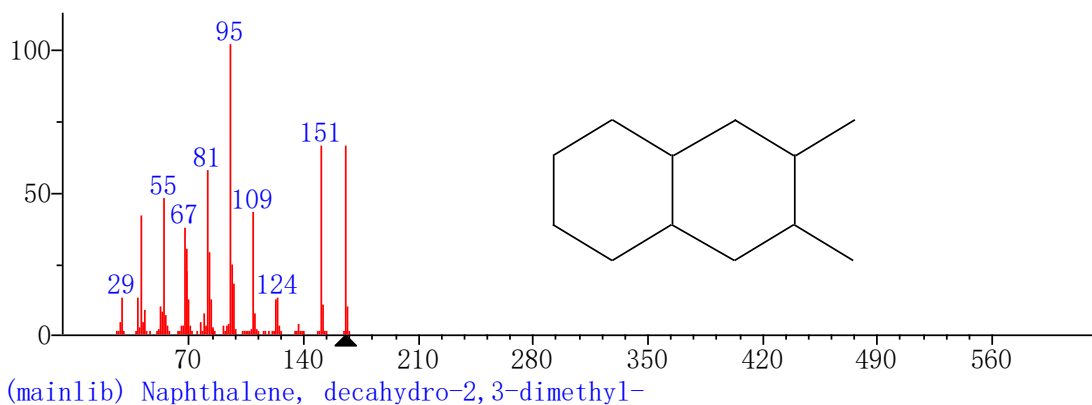
**Figure S15.**  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  spectra of the mixture of products (**2A+2B**) from the Diels-Alder reaction of  $\text{C}_6$  dienes (*i.e.* **1A** and **1B**) and *p*-quinone.



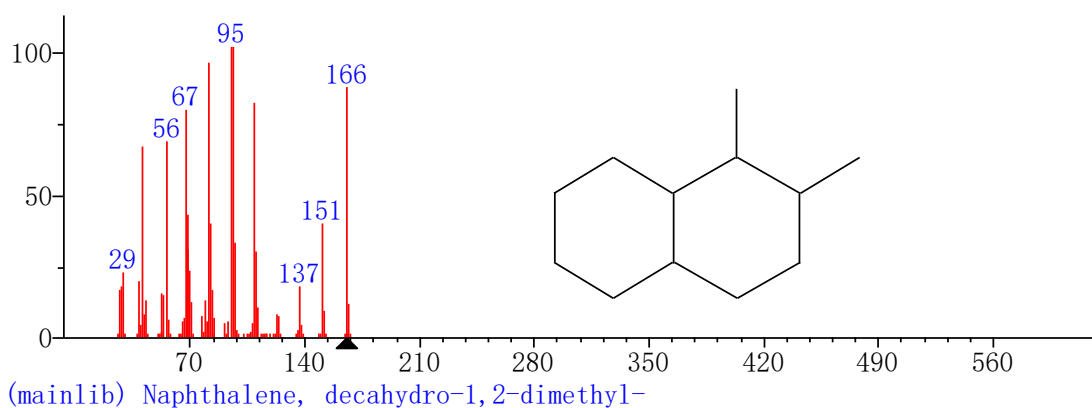
**Figure S16.**  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  spectra of the compound **2B** from the Diels-Alder/aromatization reaction of  $\text{C}_6$  dienes (*i.e.* **1A** and **1B**) and *p*-quinone.



**Figure S17.** Gas chromatogram and mass spectrometry of compound **3A** from the hydrodeoxygenation of Diels-Alder reaction products (*i.e.* **2A+2B**). Reaction conditions: 433 K, 4 MPa H<sub>2</sub>, 12 h; 0.1 g Diels-Alder reaction products (*i.e.* **2A+2B**), 3 mL 1,4-dioxane, 0.02 g Pd/C and 0.02 g H-Y zeolite were used in the test.

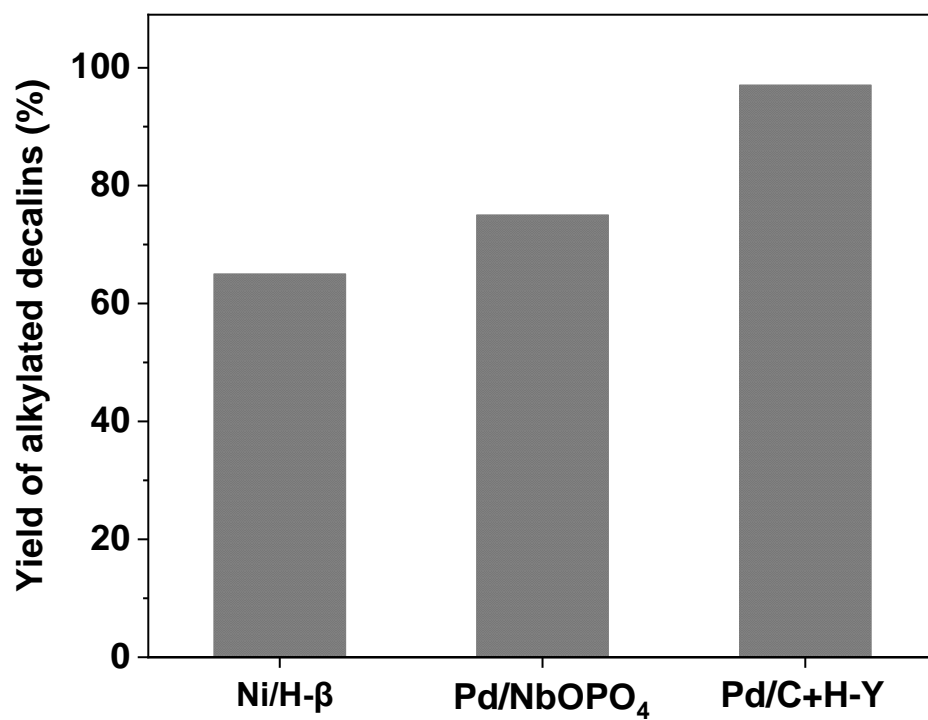


**Figure S18.** Mass spectrogram of 2,3-dimethyldecahydronaphthalene (CAS 1008-80-6).

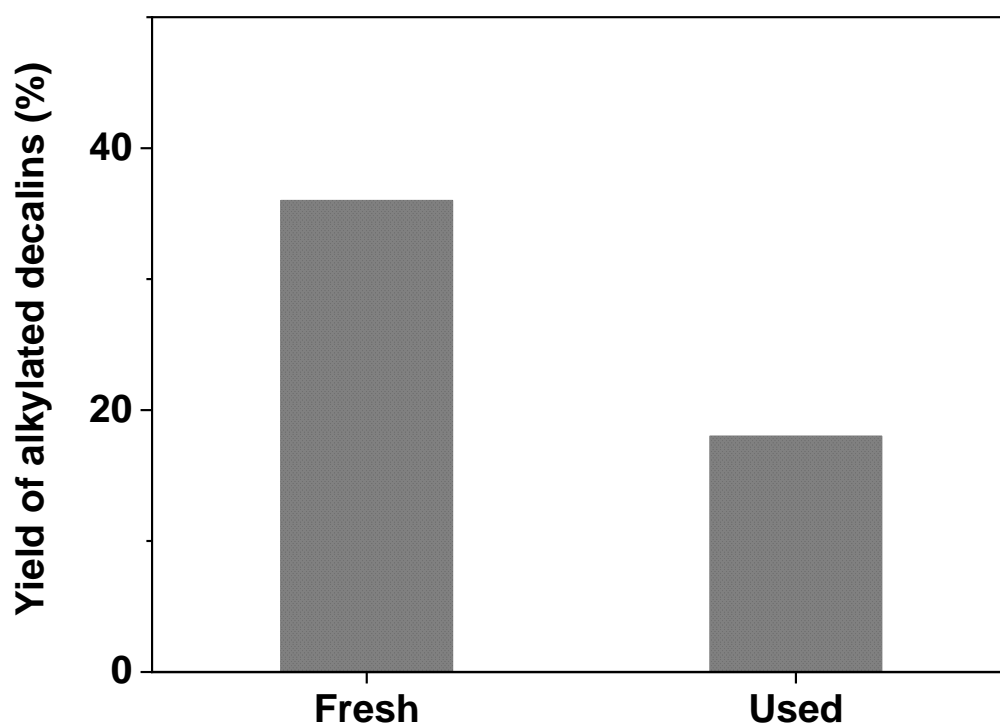


**Figure S19.** Mass spectrogram of 1,2-dimethyldecahydronaphthalene (CAS 3604-14-6).

The chemical structure of hydrodeoxygenation products were distinguished one by one by TIC (Total Ions Chromatograph) using an Agilent 8890-7250 gas chromatograph-mass spectrometer (GC-MS) (see Figure S17). The compounds A-G as shown in GC chromatogram exhibited the same fragment peaks but had different abundance at  $m/z = 151$  based on the analysis of GC-MS. There is no MS spectrum of the compound **3A** in the NIST database currently, while the 2,3-dimethyldecahydronaphthalene (CAS 1008-80-6) and 1,2-dimethyldecahydronaphthalene (CAS 3604-14-6) with two methyl groups on the decalin structure are found as the closest match in the NIST database. The comparative analysis of MS spectrum of the 2,3-dimethyldecahydronaphthalene and 1,2-dimethyldecahydronaphthalene (see Figures S18-S19) shows different abundance at  $m/z = 151$ . We think that the abundance at  $m/z = 151$  depends mostly on the position of two methyl groups on the decalin structure. In addition, there was cis-trans isomerism on compound **3A** (as the result of decalin structure). Based on what has been discussed above, we may reasonably draw the conclusion that compounds A-G are the isomers of compound **3A**.



**Figure S20.** Yield of alkylated decalins from the HDO of the Diels-Alder reaction products over different catalysts. Reaction conditions: 433 K, 4 MPa H<sub>2</sub>, 12 h; 0.1 g Diels-Alder reaction products (**2A+2B**), 3 mL 1,4-dioxane, 0.02 g catalyst were used in each test.



**Figure S21.** Yield of alkylated decalins over the fresh and used Pd/C+H-ZSM-5 catalyst. Reaction conditions: 433 K, 4 MPa H<sub>2</sub>, 12 h; 0.1 g Diels-Alder reaction products (**2A+2B**), 3 mL 1,4-dioxane, 0.02 g Pd/C and 0.02 g H-ZSM-5 were used in each test.

## References

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