

Supporting Information

Synthesis of jet fuel and diesel range cycloalkanes with 2-methylfuran and benzaldehyde

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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 measurements, the acidic resins were evacuated at 373 K for 6 h, metal catalysts were evacuated at 573 K for 6 h .

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

The metal dispersions in Ru-based 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 Ru-based 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 3h. 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.

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.

HDO of hydrogenated 1A

To better interpret the reason for the better HDO catalytic performance of the Ru/HAP + H-ZSM-5 catalyst, we hydrogenated the HAA product (*i.e.* **1A**) over a commercial 5wt.% Pd/C catalyst and used the hydrogenated **1A** as the feedstock in the HDO process. The hydrogenation of **1A** was carried out in a stainless-steel batch reactor using ethyl acetate as the solvent. During the reaction, hydrogen was continuously added into the batch reactor to maintain the system pressure around 4 MPa. After being hydrogenated at 393 K for 24 h, the furan rings and one benzene ring in **1A** molecule were completely saturated (see Figures S24-S25). Subsequently, we used the hydrogenated **1A** (purified from the hydrogenation product by vacuum distillation) for the hydrodeoxygenation under the same reaction conditions as we used for **1A** (see Figure S26). As we expected, evidently higher total carbon yield (93.3% vs. 82.8%) of C_{12} and C_{17} cycloalkanes were achieved from the HDO of the hydrogenated **1A** over the Ru/HAP + H-ZSM-5 catalyst. Meanwhile, it was noticed that the molar ratio of C_{17} cycloalkane/ C_{12} cycloalkane also increased from 4.5 to 5.6 after using the hydrogenated **1A** as the feedstock for the hydrodeoxygenation step.

Table S1. Actual Ru contents in the Ru-based catalysts used in HDO process.

Catalyst	Actual Ru content measured by ICP (wt.%)
Ru/HAP	1.89
Ru/Al ₂ O ₃	2.02
Ru/C	1.86
Ru/SiO ₂	1.87

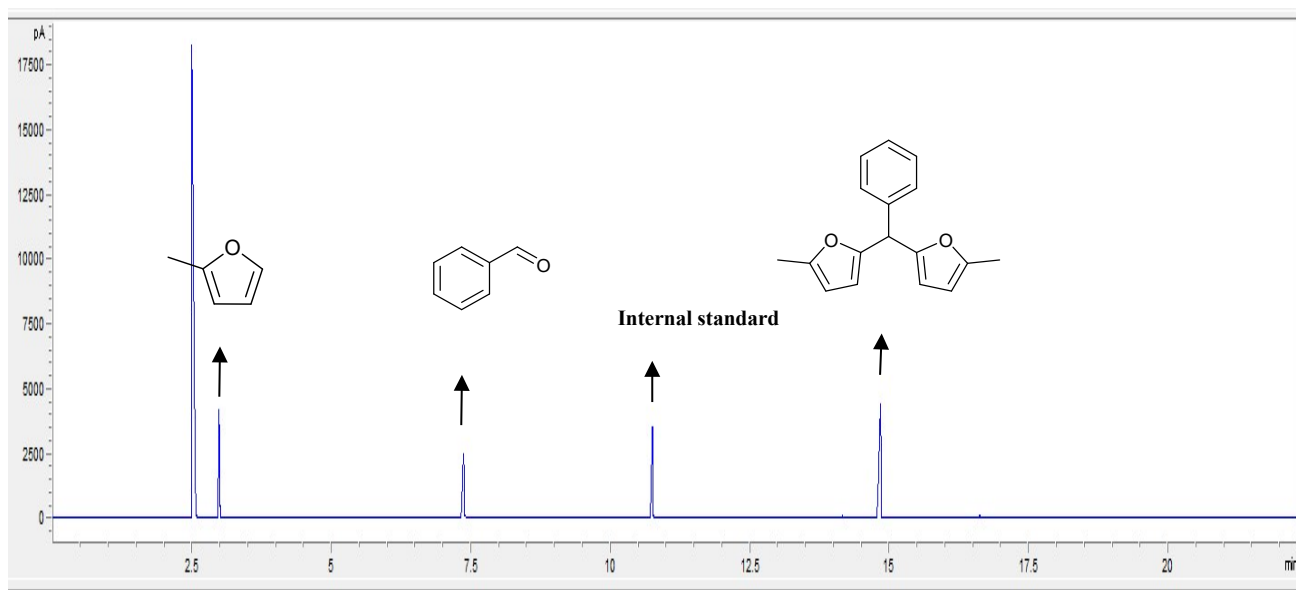


Figure S1. Gas chromatogram of the HAA product of 2-methylfuran and benzaldehyde. Reaction conditions: 323 K, 2 h; 40 mmol 2-methylfuran, 20 mmol benzaldehyde, 0.2 g Nafion resin were used in the test.

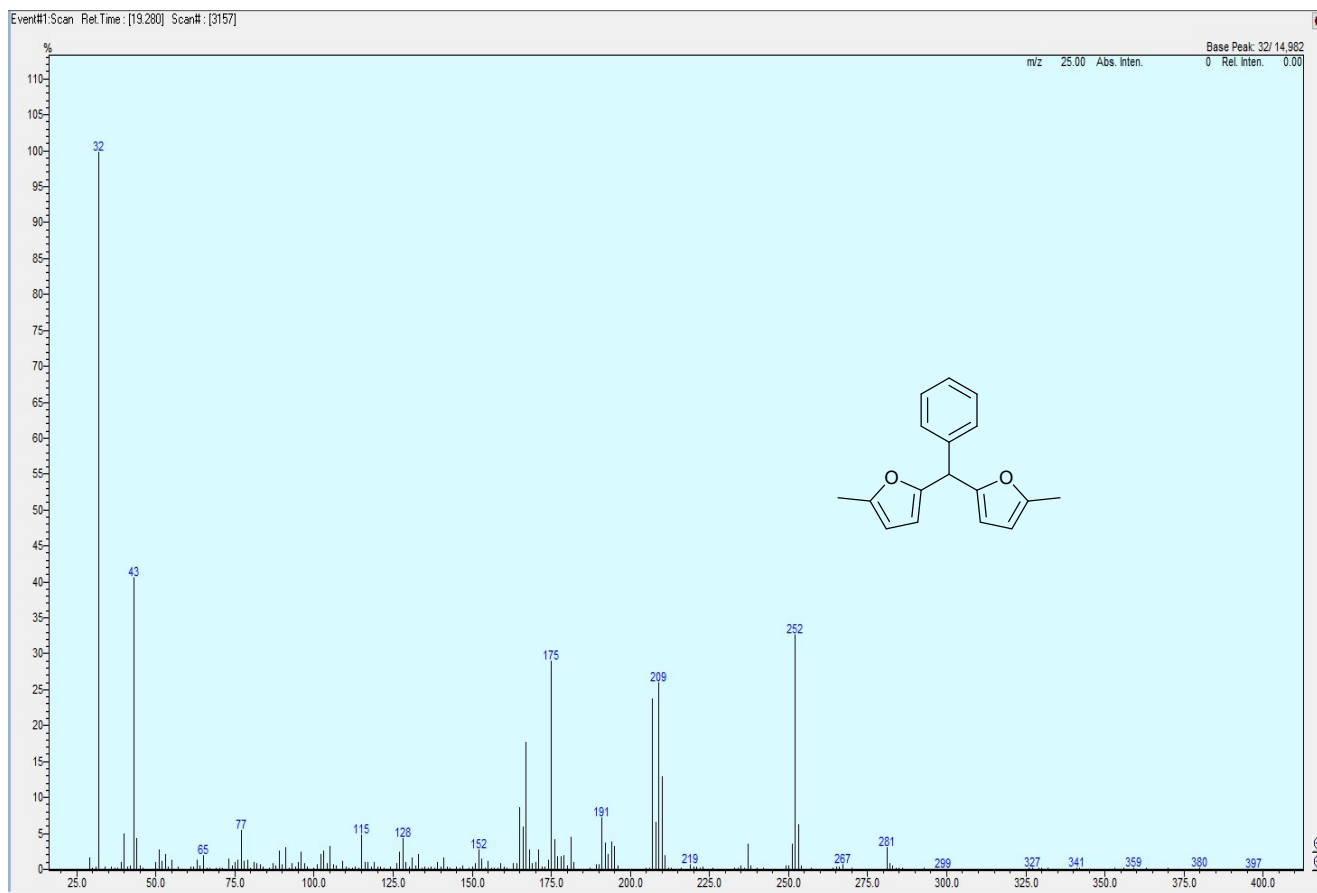


Figure S2. Mass spectrogram of the HAA product of 2-methylfuran and benzaldehyde.

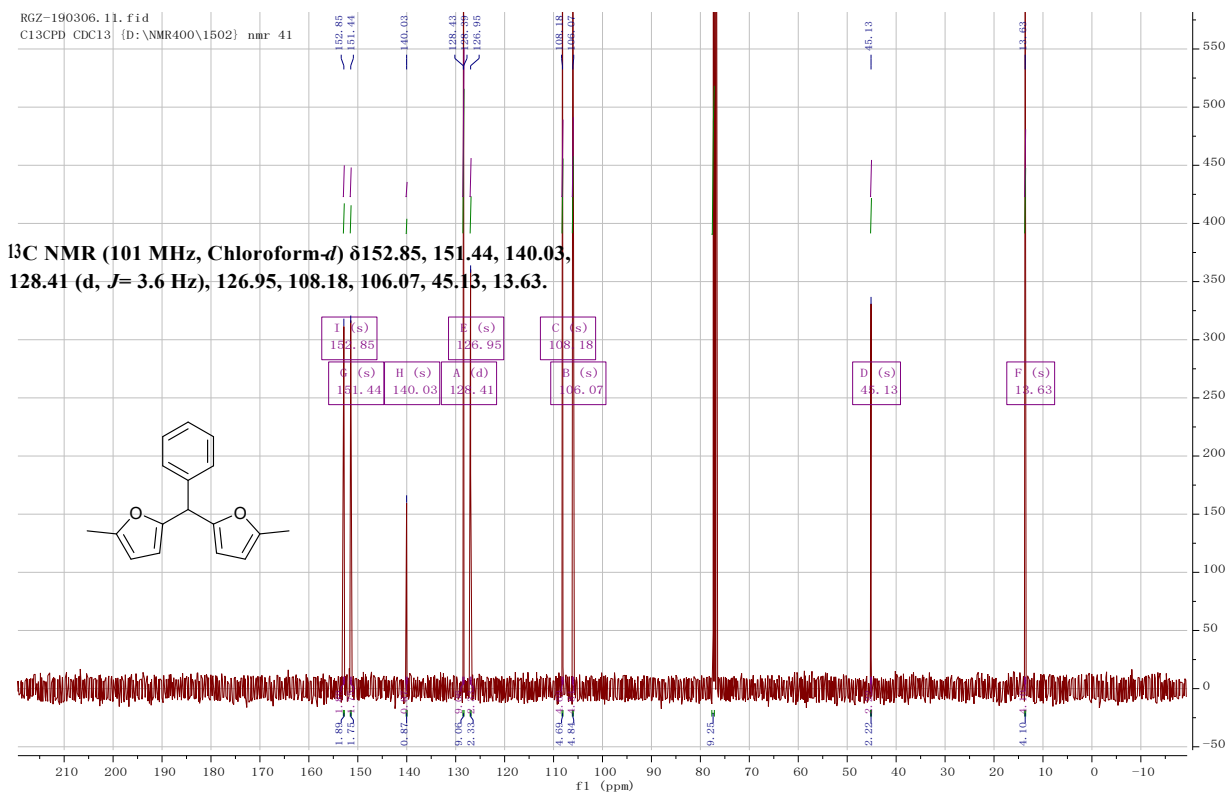
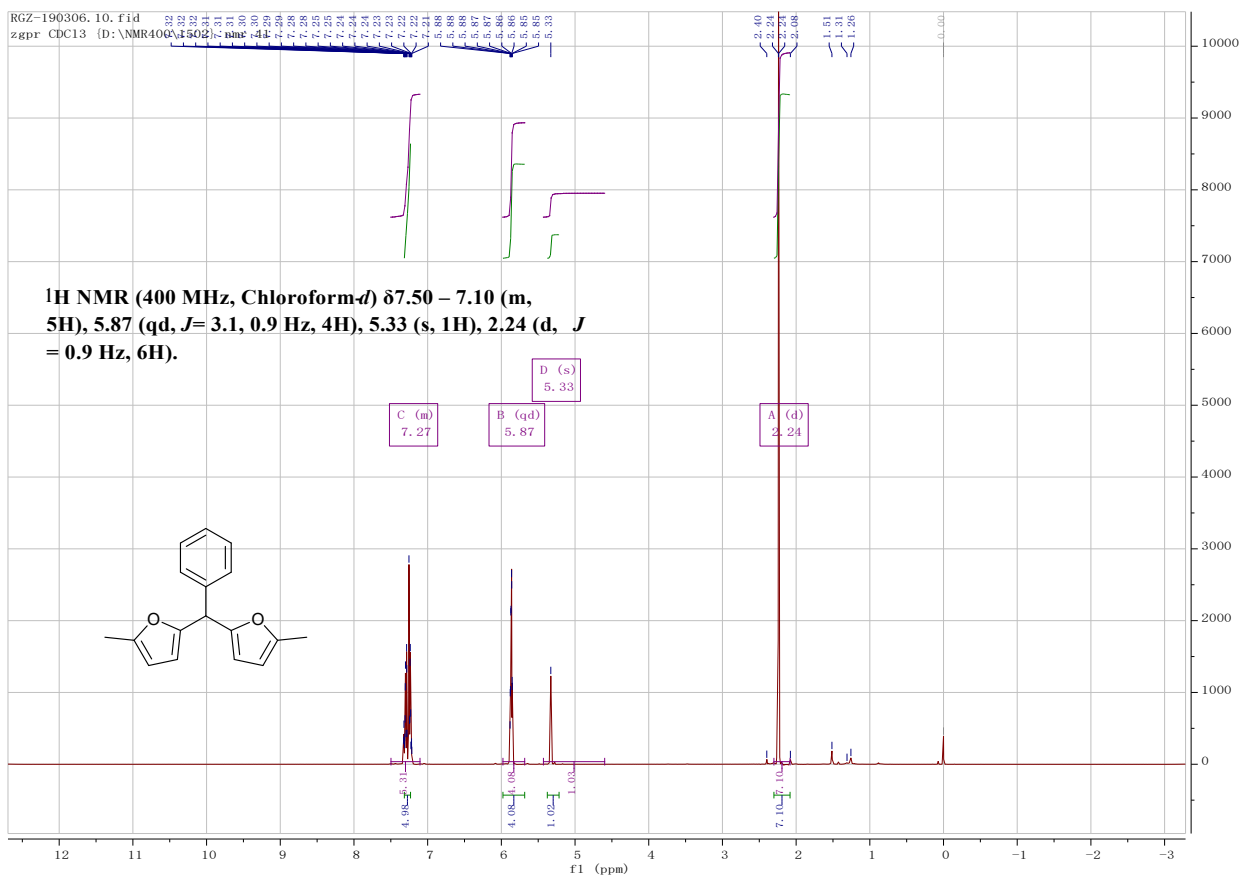


Figure S3. ¹H-NMR and ¹³C-NMR spectra of the HAA product of 2-methylfuran and benzaldehyde.

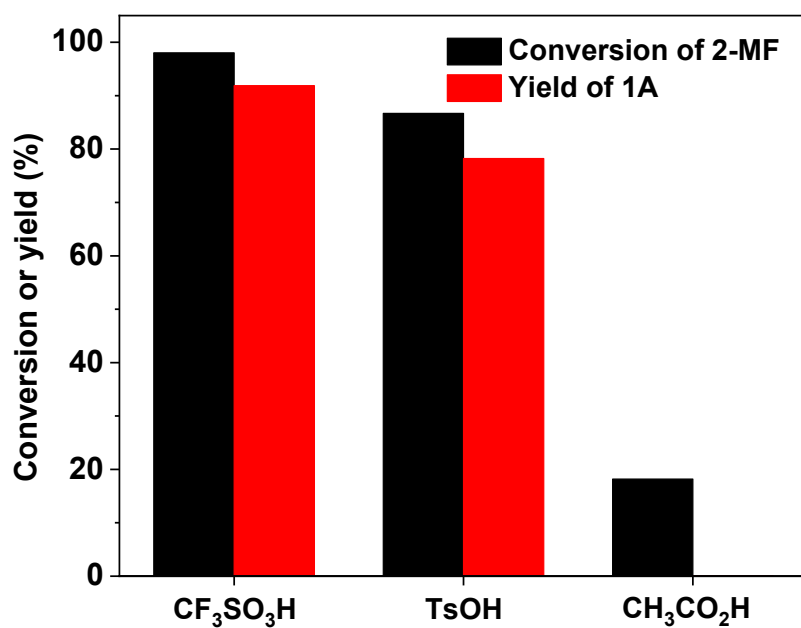


Figure S4. Conversion of 2-MF and the yields of **1A** under the catalysis of different acids. Reaction conditions: 333 K, 5 h; 40 mmol 2-methylfuran, 20 mmol benzaldehyde and 1 mmol acid were used in each test.

Table S2. Effect of water on the catalytic performance of Nafion resin.

Catalyst	Water	Conversions of 2-MF (%)	Yields of 1A (%)
Nafion	-	73.3	53.3
Nafion	0.5 g	50.0	15.5

Reaction conditions: 323 K for 2 h; 40 mmol 2-methylfuran, 20 mmol benzaldehyde, 0.2 g Nafion resin, 0 or 0.5 g water were used in each test.

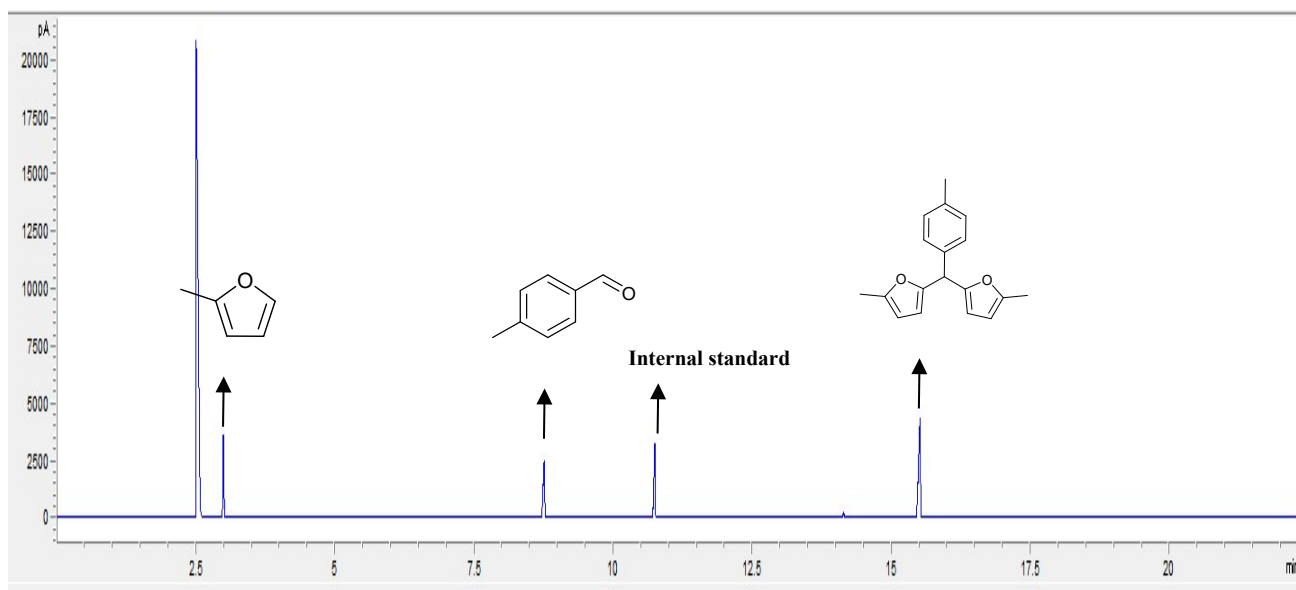


Figure S5. Gas chromatogram of the HAA product of 2-methylfuran and 4-methyl benzaldehyde. Reaction conditions: 323 K, 2 h; 40 mmol 2-methylfuran, 20 mmol 4-methyl benzaldehyde and 0.2 g Nafion resin were used in the test.

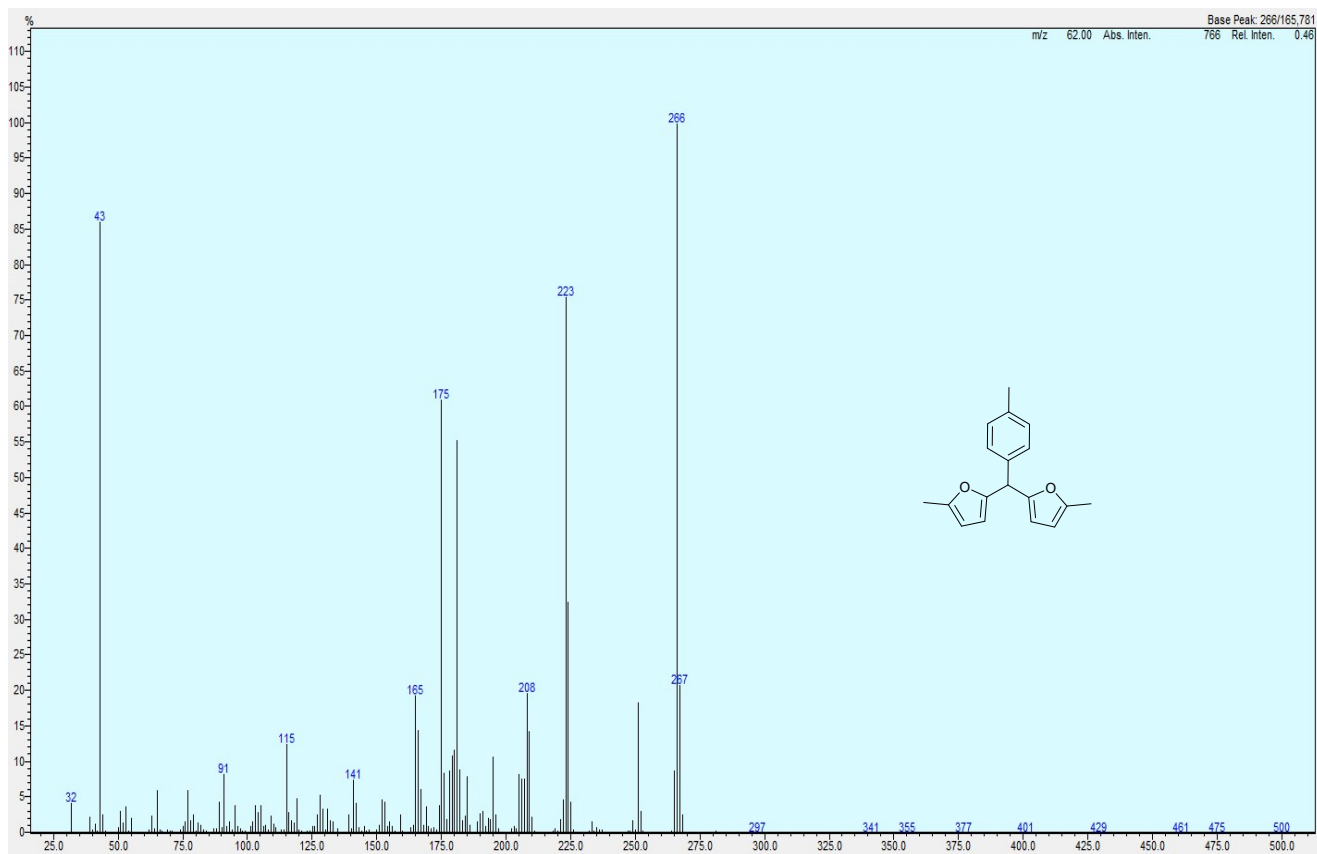


Figure S6. Mass spectrogram of the HAA product of 2-methylfuran and 4-methyl benzaldehyde.

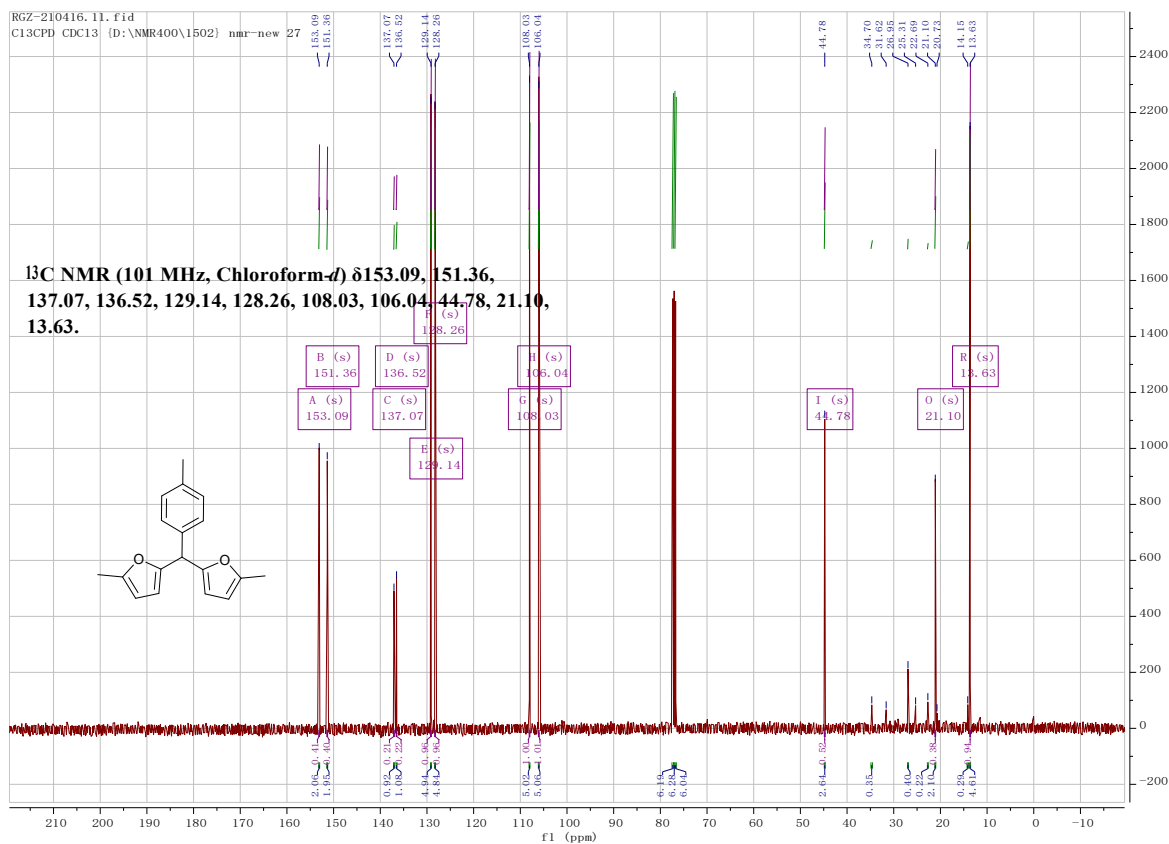
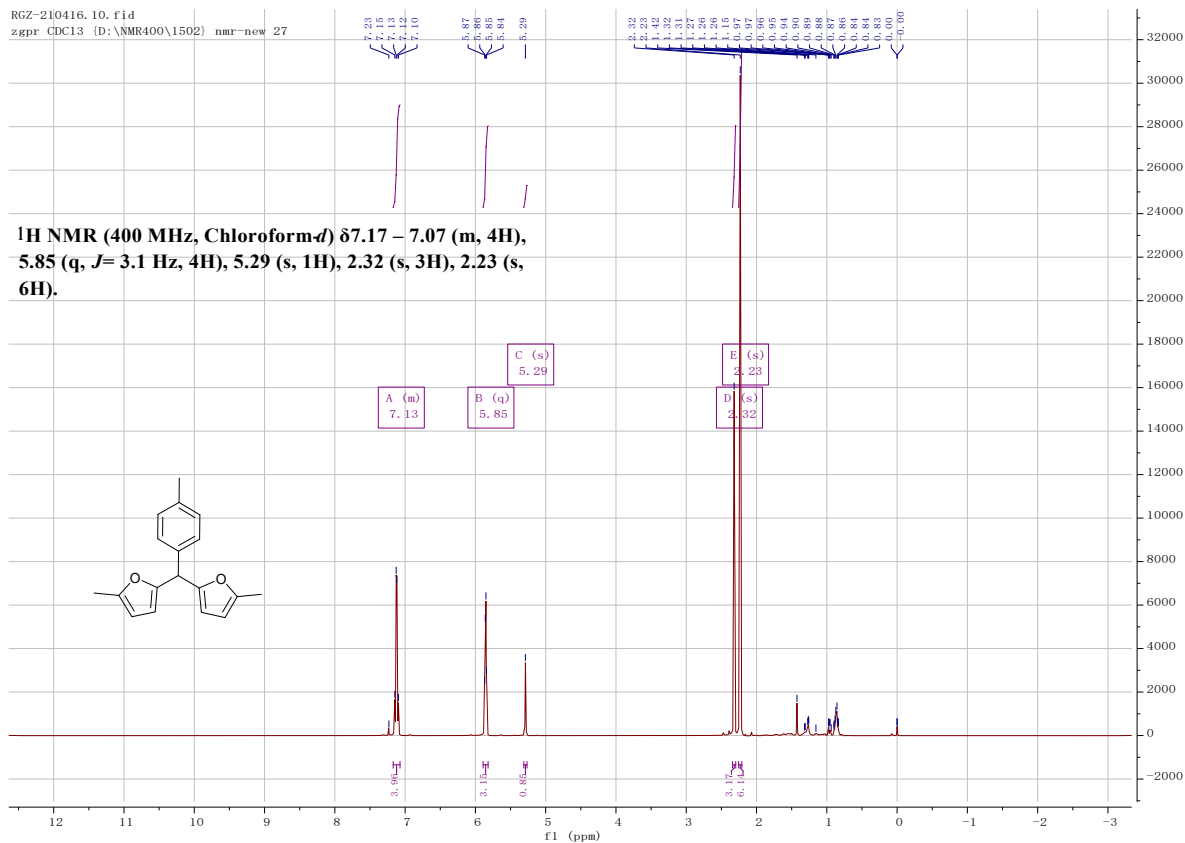


Figure S7. ¹H-NMR and ¹³C-NMR spectra of the HAA product of 2-methylfuran and 4-methyl benzaldehyde.

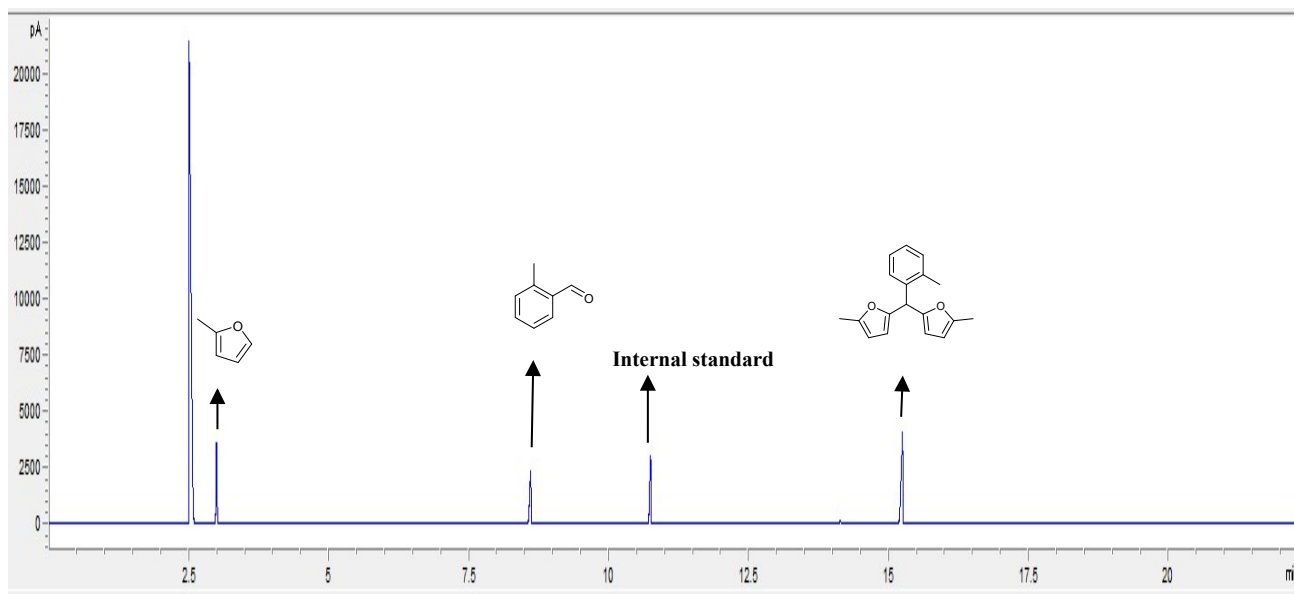


Figure S8. Gas chromatogram of the HAA product of 2-methylfuran and 2-methyl benzaldehyde. Reaction conditions: 323 K, 2 h; 40 mmol 2-methylfuran, 20 mmol 2-methyl benzaldehyde and 0.2 g Nafion resin were used in the test.

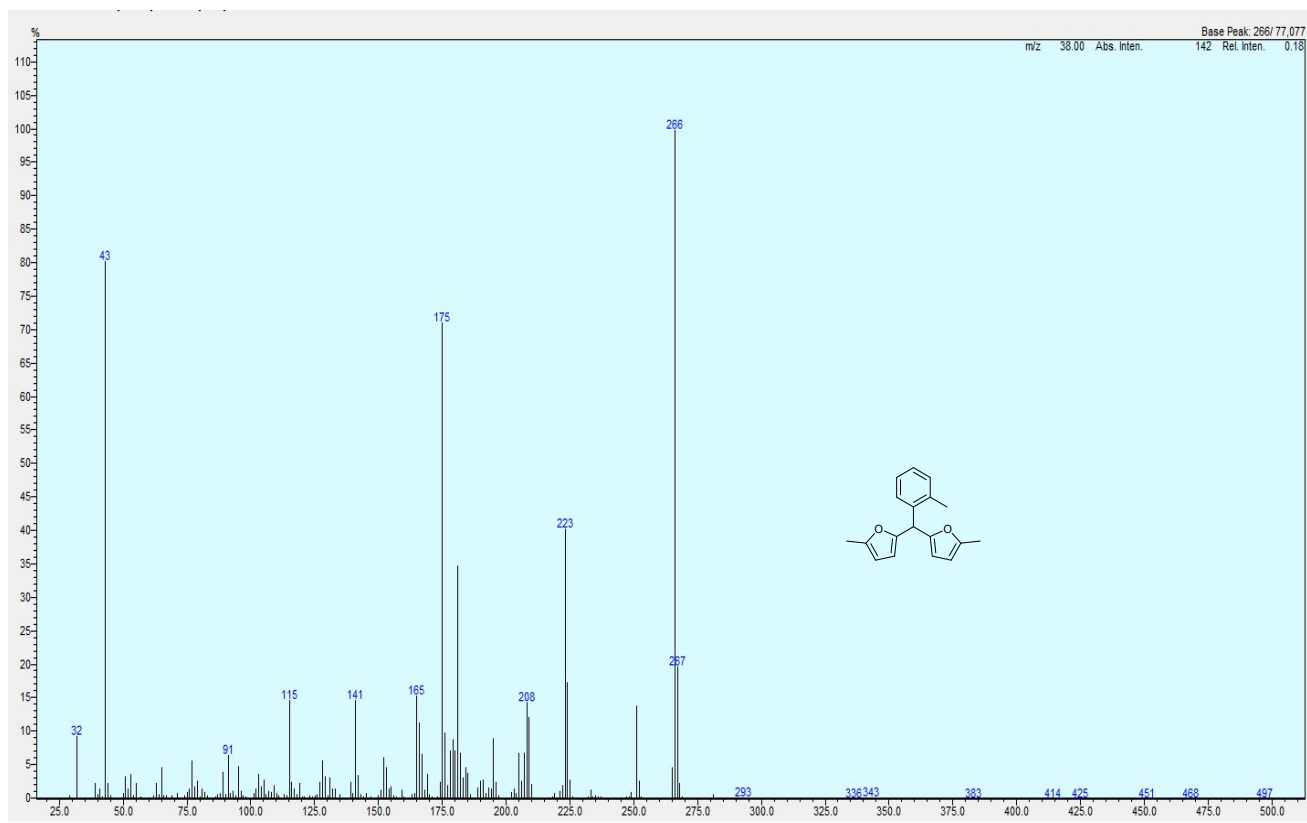


Figure S9. Mass spectrogram of the HAA product of 2-methylfuran and 2-methyl benzaldehyde.

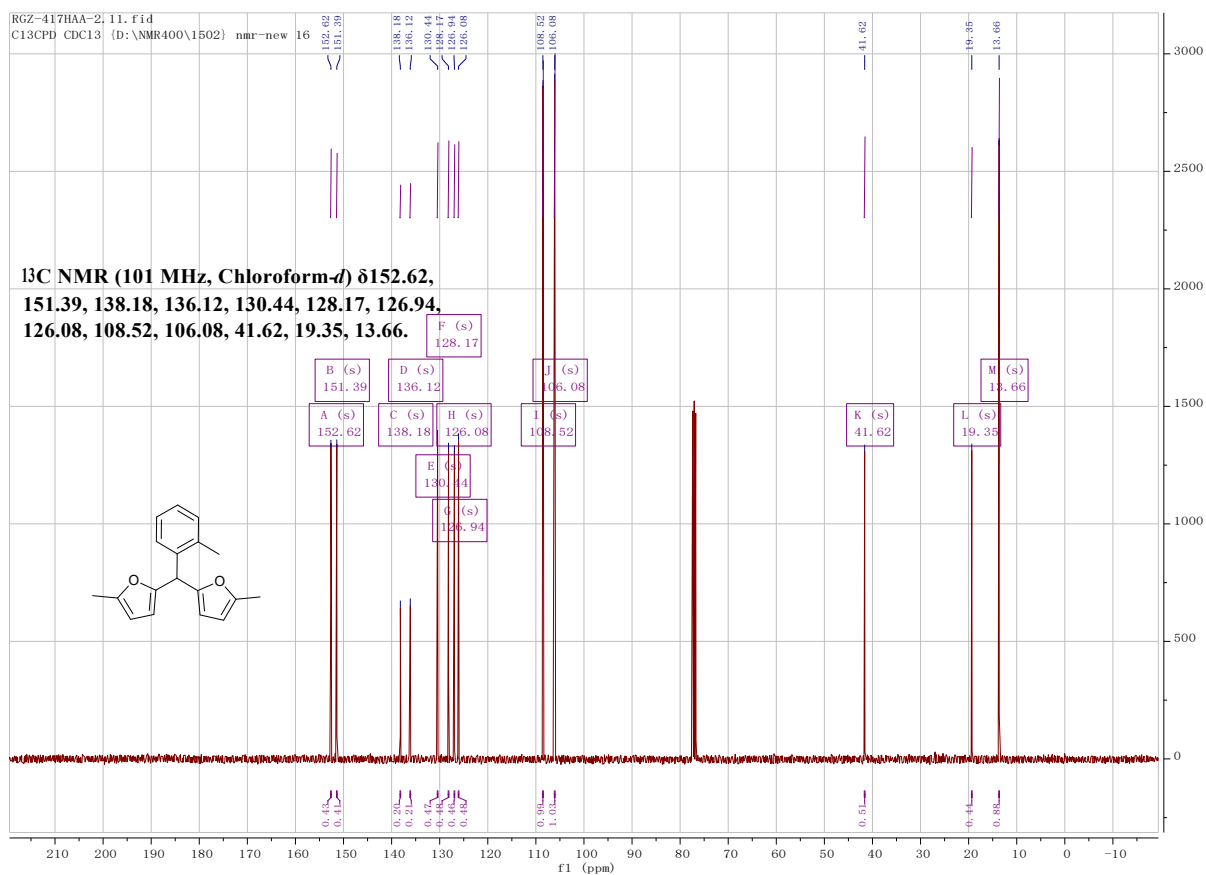
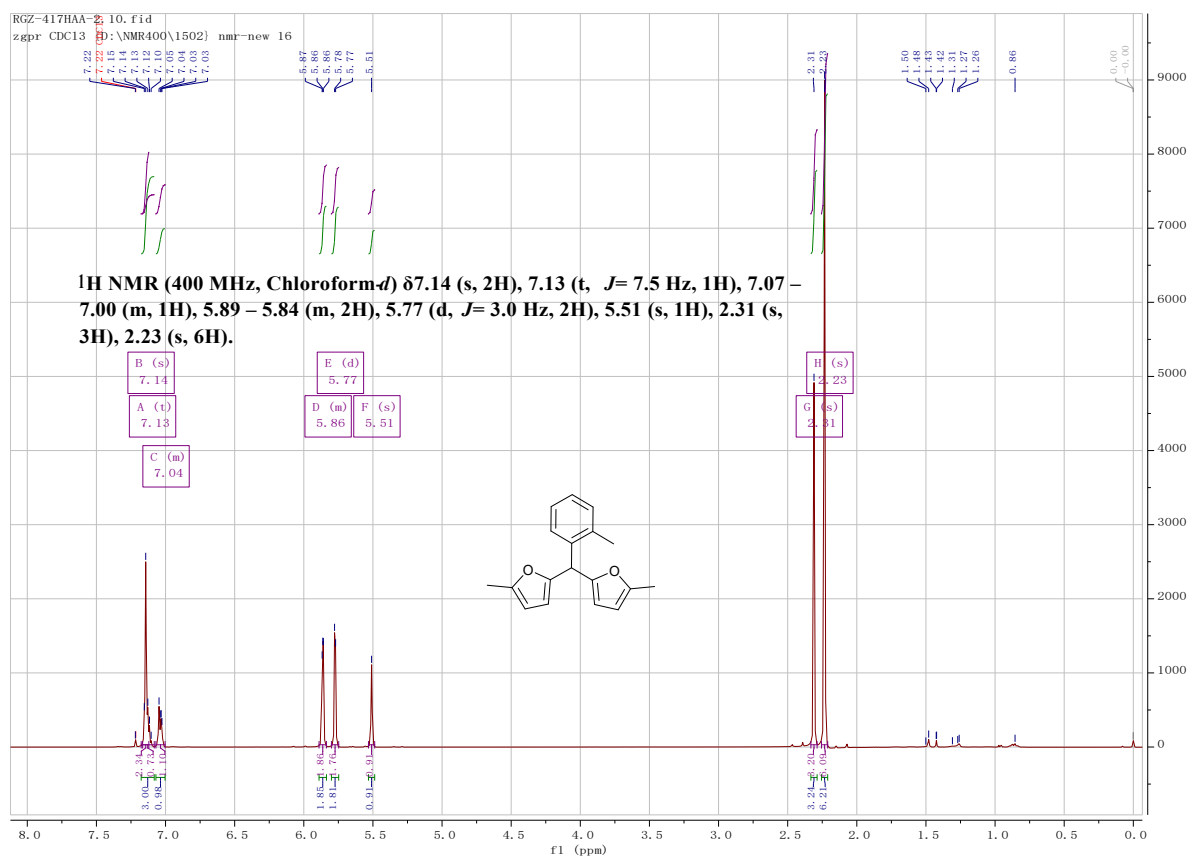


Figure S10. ¹H-NMR and ¹³C-NMR spectra of the HAA product of 2-methylfuran and 2-methyl benzaldehyde.

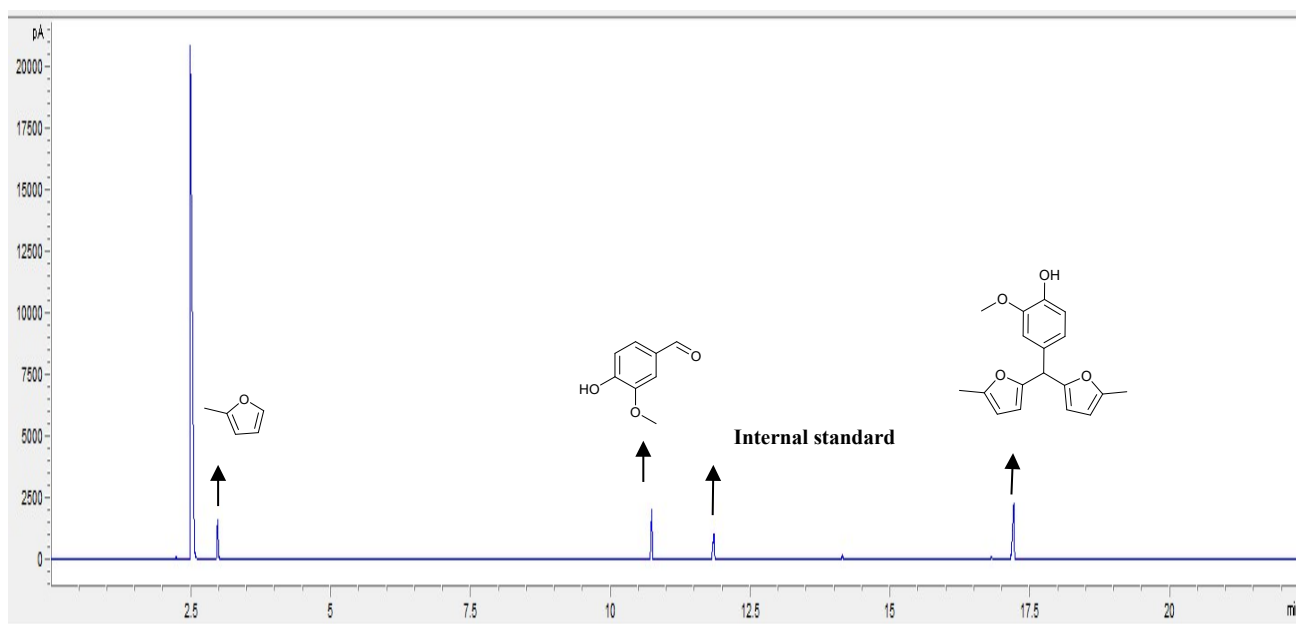


Figure S11. Gas chromatogram of the HAA product of 2-methylfuran and vanillina. Reaction conditions: 323 K, 2 h; 40 mmol 2-methylfuran, 20 mmol vanillina and 0.2 g Nafion resin were used in the test.

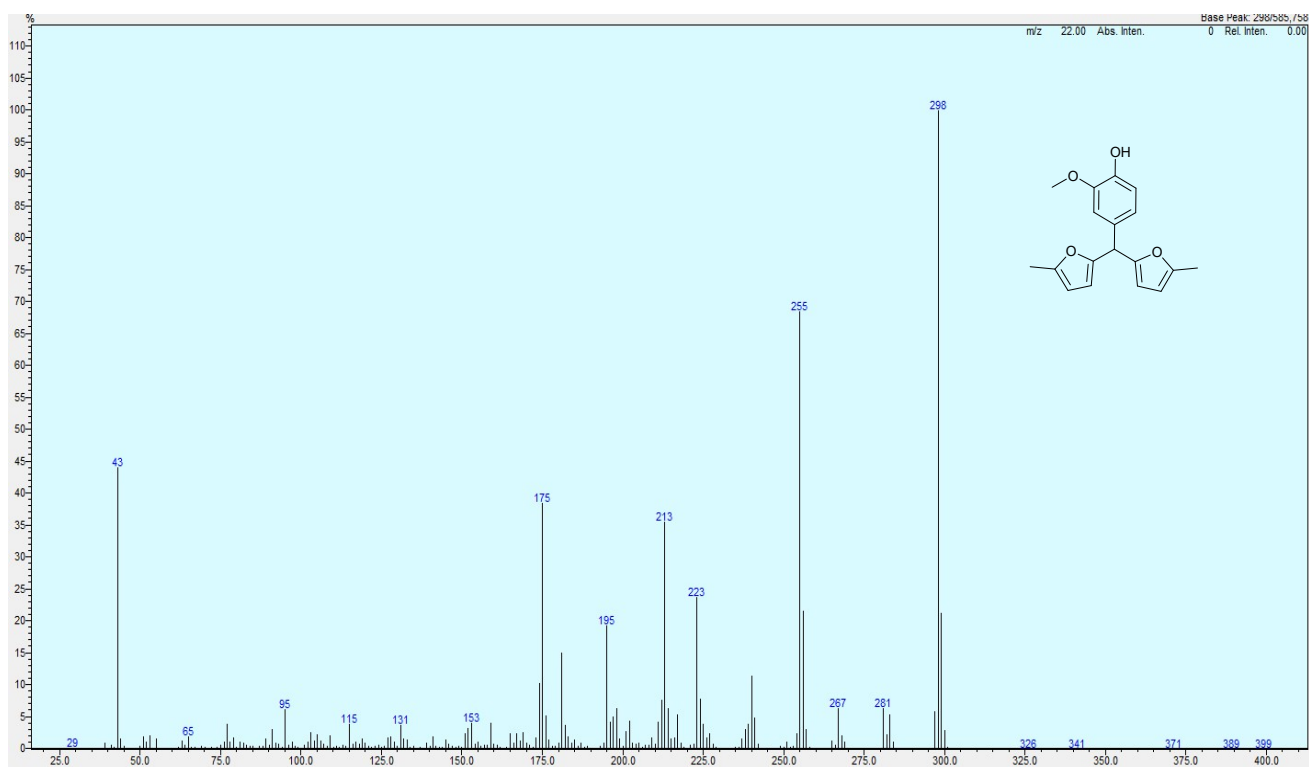


Figure S12. Mass spectrogram of the the HAA product of 2-methylfuran and vanillina.

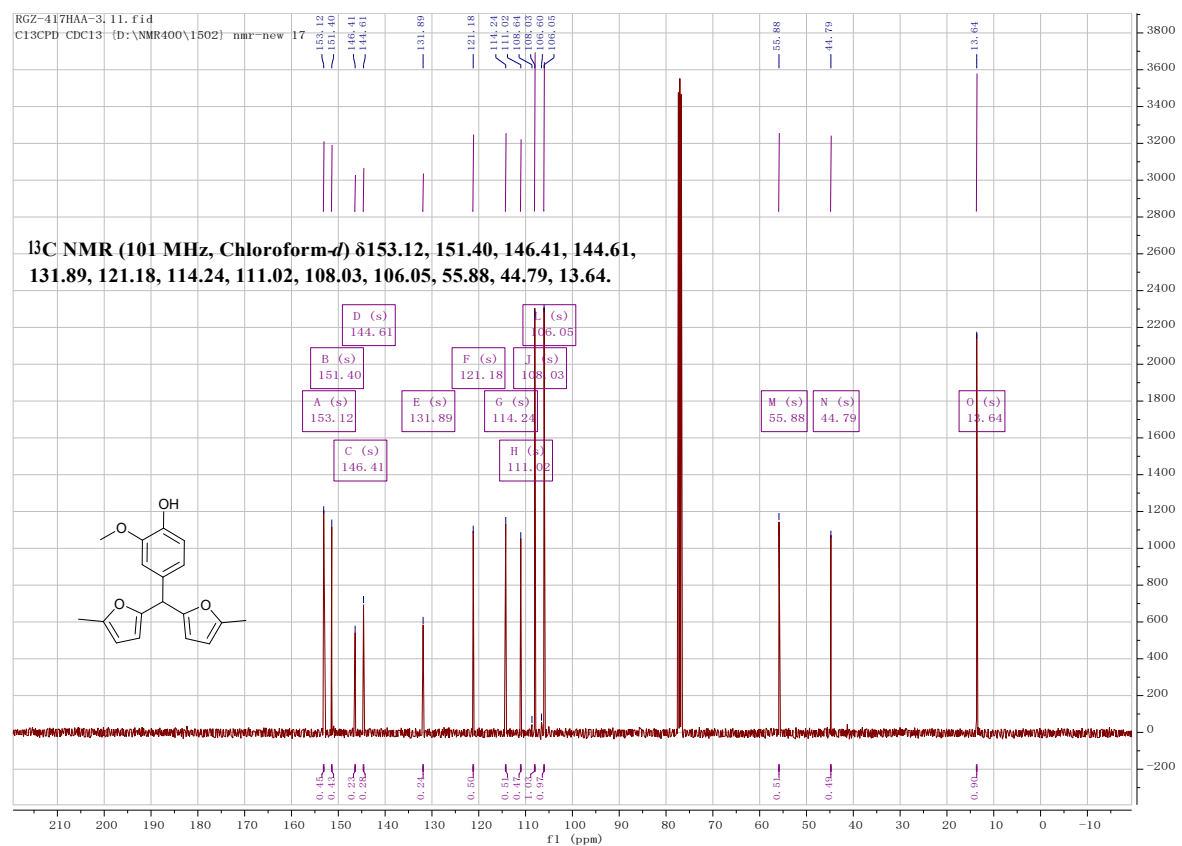
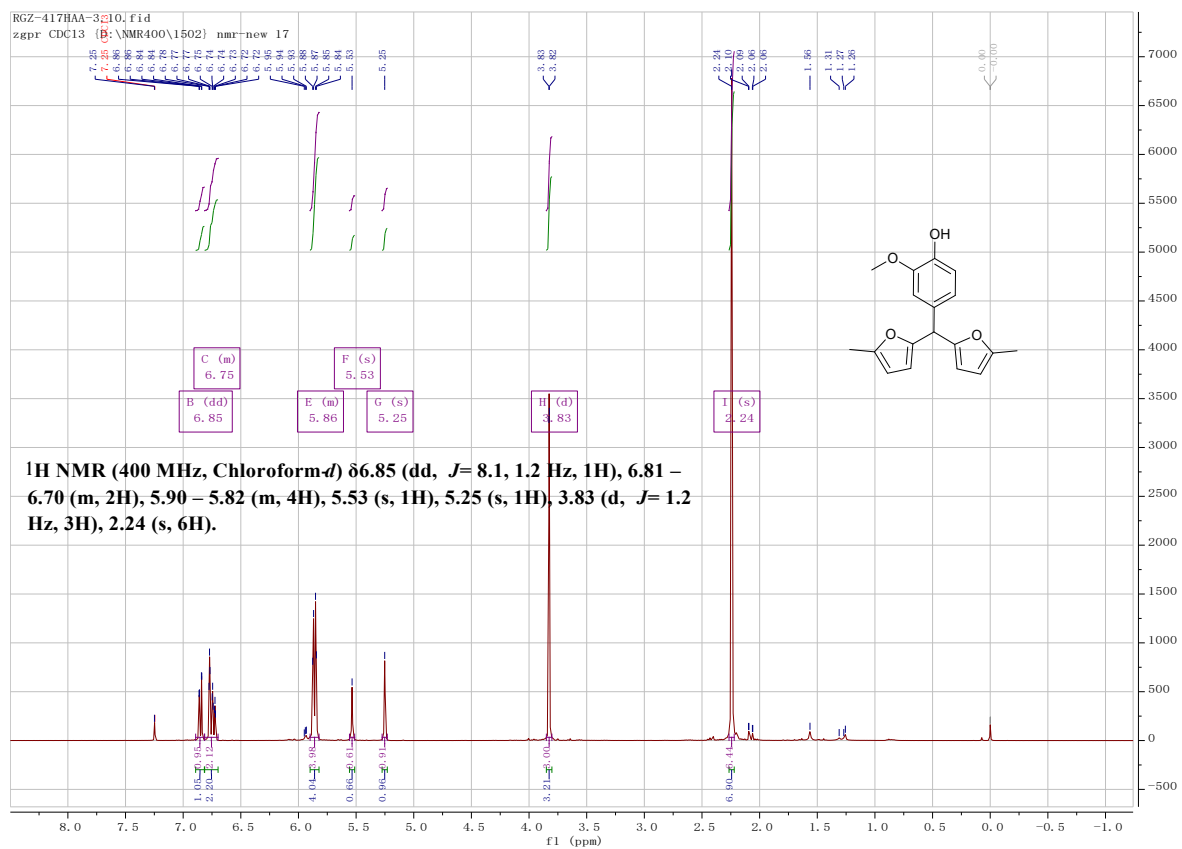


Figure S13. ¹H-NMR and ¹³C-NMR spectra of the HAA product of 2-methylfuran and vanilla

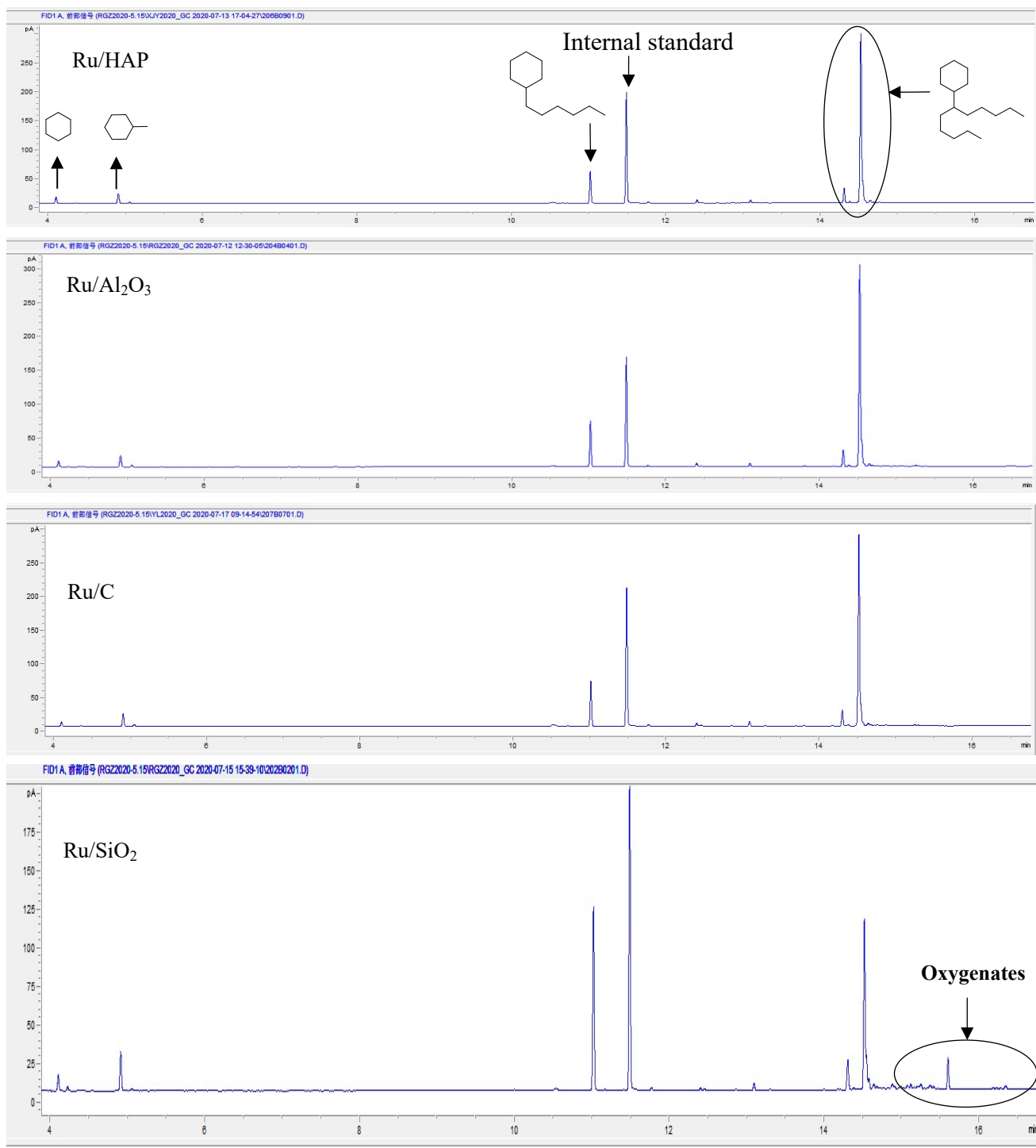


Figure S14. Gas chromatogram of the HDO products of 1A under the different Ru-based catalyst. Reaction conditions:

453 K, 4 MPa H₂, 24 h; 0.1 g 1A, 0.1 g Ru-based catalyst and 0.1 g H-ZSM-5, 50 mL cyclopentane were used in the test.

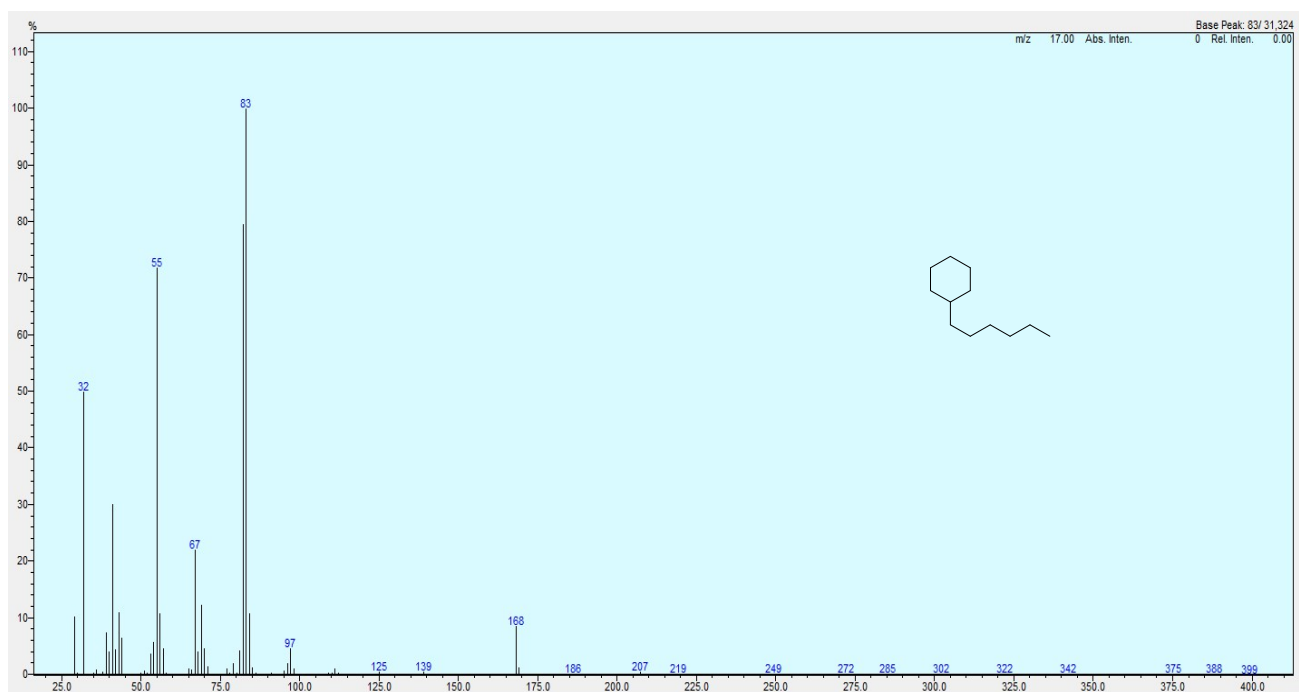
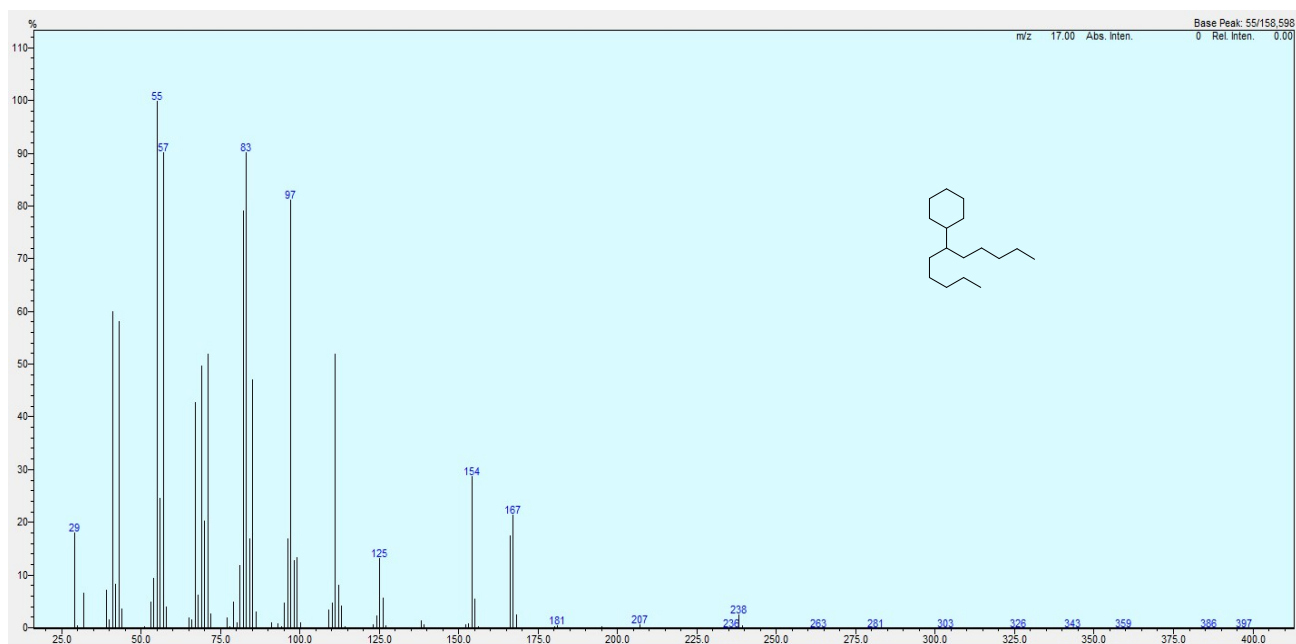


Figure S15. Mass spectrogram of the C₁₇ and C₁₂ cycloalkanes from the HDO of 1A.

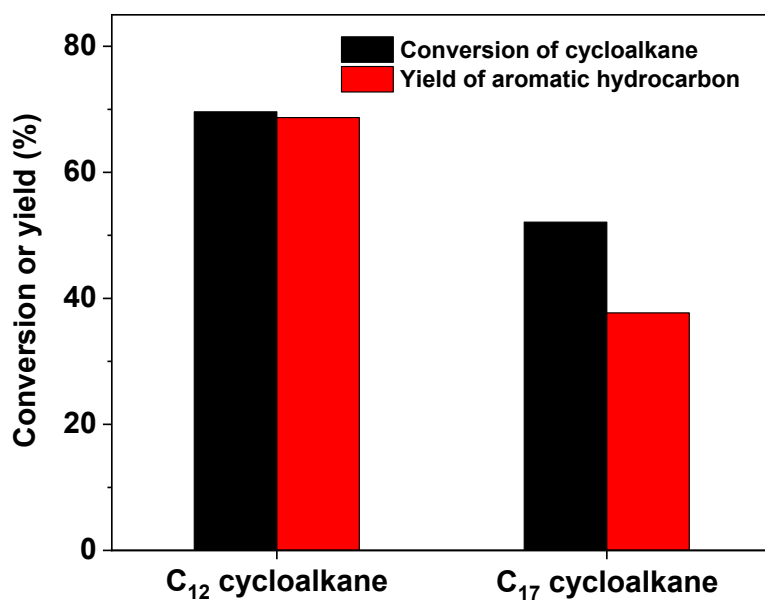


Figure S16. Conversions of cycloalkanes and the yields of aromatic hydrocarbons over the Pd/C catalyst. Reaction conditions: 533 K, 12 h; 0.3 g C₁₂ or C₁₇ cycloalkane produced during the HDO step, 0.1 g Pd/ C, 30 mL heptane were used in the test.

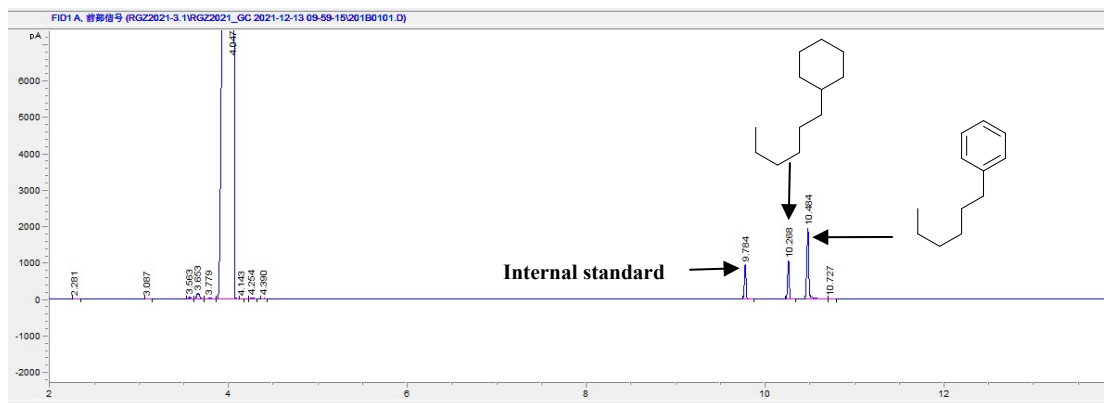


Figure S17. Gas chromatogram of the product from the dehydrogenation of C₁₂ cycloalkane over the Pd/C catalyst.

Reaction conditions: 533 K, 12 h; 0.3 g C₁₂ cycloalkane, 0.1 g Pd/ C, 30 mL heptane were used in the test.

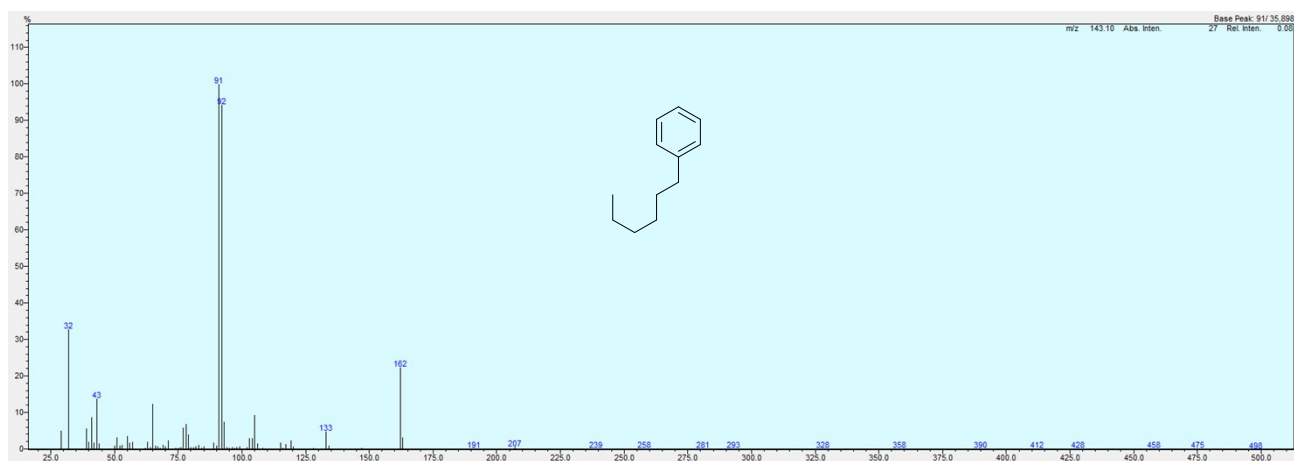


Figure S18. Mass spectrogram of the C₁₂ aromatic hydrocarbon generated from the dehydrogenation of C₁₂ cycloalkane from the HDO of **1A**.

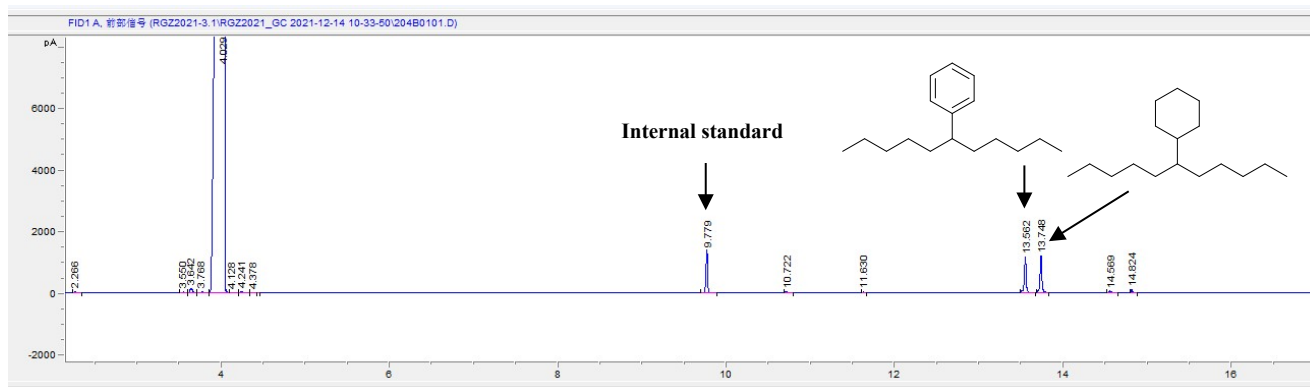


Figure S19. Gas chromatogram of the product from the dehydrogenation of C₁₇ cycloalkane over the Pd/C catalyst.

Reaction conditions: 533 K, 12 h; 0.3 g C₁₂ cycloalkane, 0.1 g Pd/ C, 30 mL heptane were used in the test.

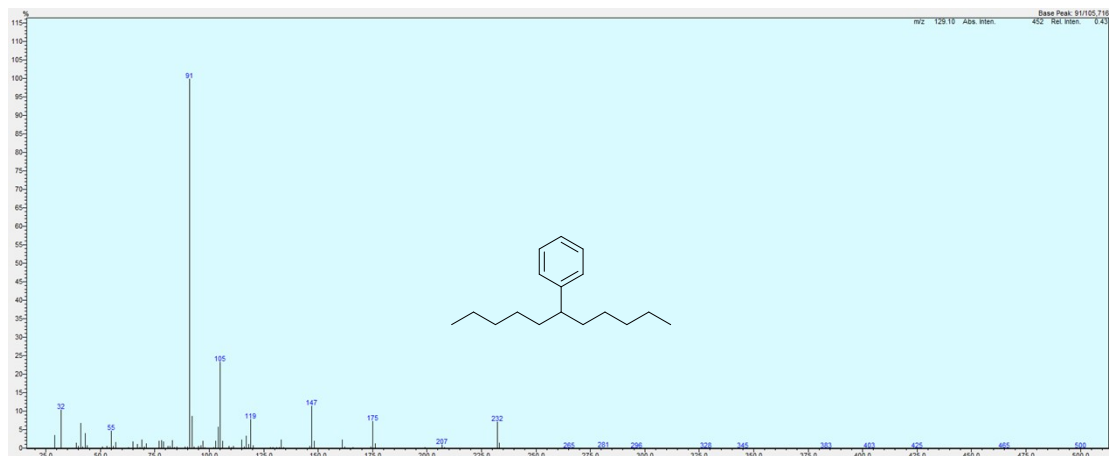


Figure S20. Mass spectrogram of the C₁₇ aromatic hydrocarbon generated from the dehydrogenation of C₁₇ cycloalkane from the HDO of **1A**.

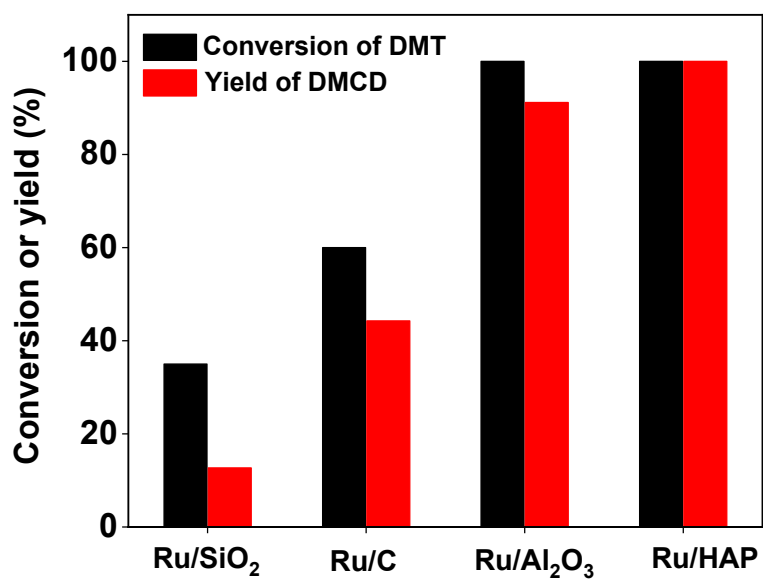


Figure S21. Conversions of dimethyl terephthalate (DMT) and the yields of dimethyl cyclohexane dicarboxylate (DMCD) over different Ru-based metal catalysts. Reaction conditions: 373 K, 5 MPa H₂, 7 h; 30 g DMT and 1 g catalyst were used in each test.

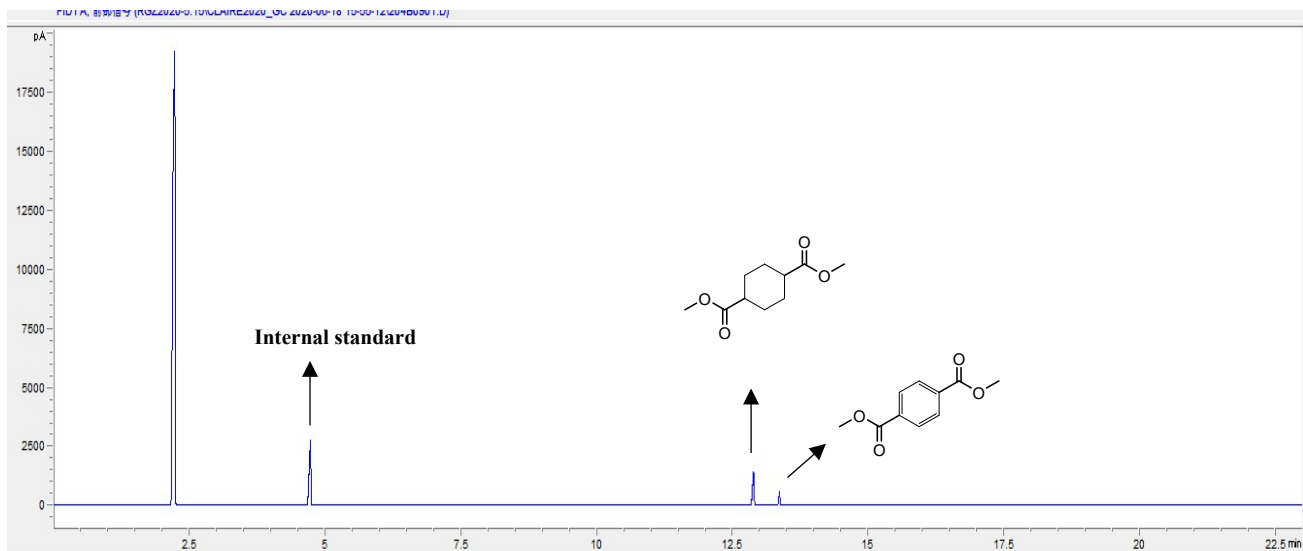


Figure S22. Gas chromatogram of DMCD from the hydrogenation of DMT over Ru/SiO₂ catalysts. Reaction conditions: 373 K, 5 MPa H₂, 7 h; 30 g DMT and 1 g catalyst were used in the test.

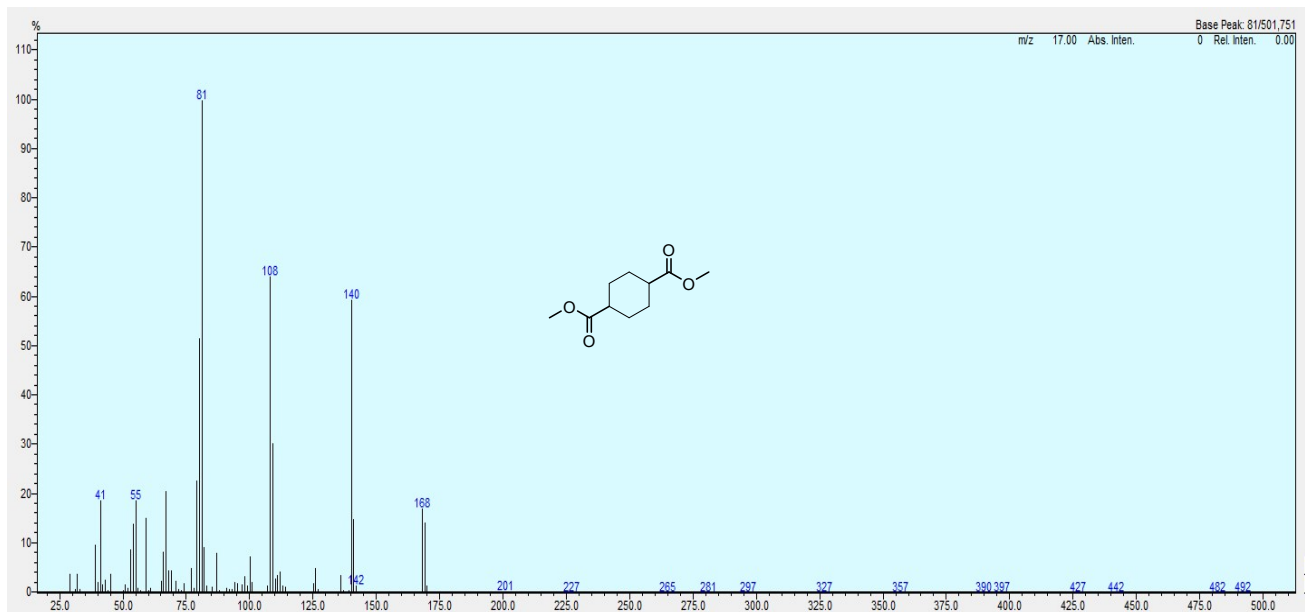


Figure S23. Mass spectrogram of DMCD from the hydrogenation of DMT.

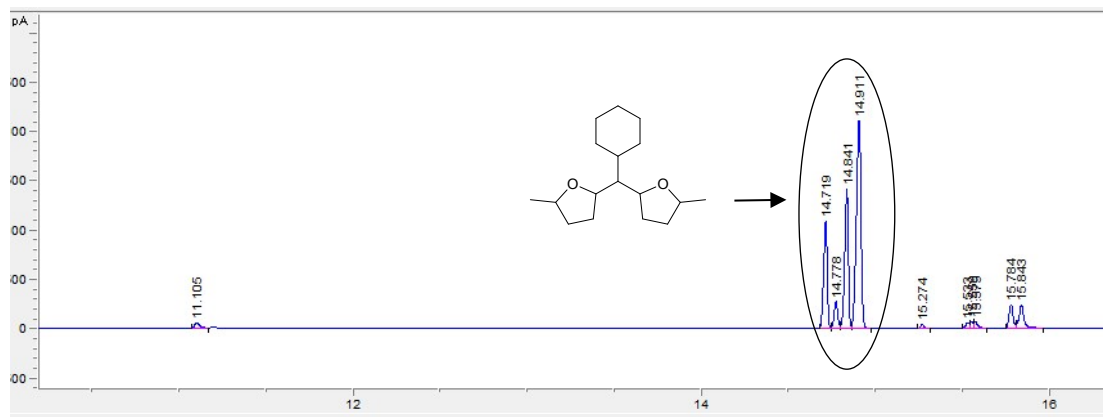


Figure S24. Gas chromatogram of the hydrogenation product of **1A** over the Pd/C catalyst. Reaction conditions: 393 K, 4 MPa H₂, 24 h; 5 g **1A**, 0.25 g Pd/C and 40 mL ethyl acetate were used in the test.

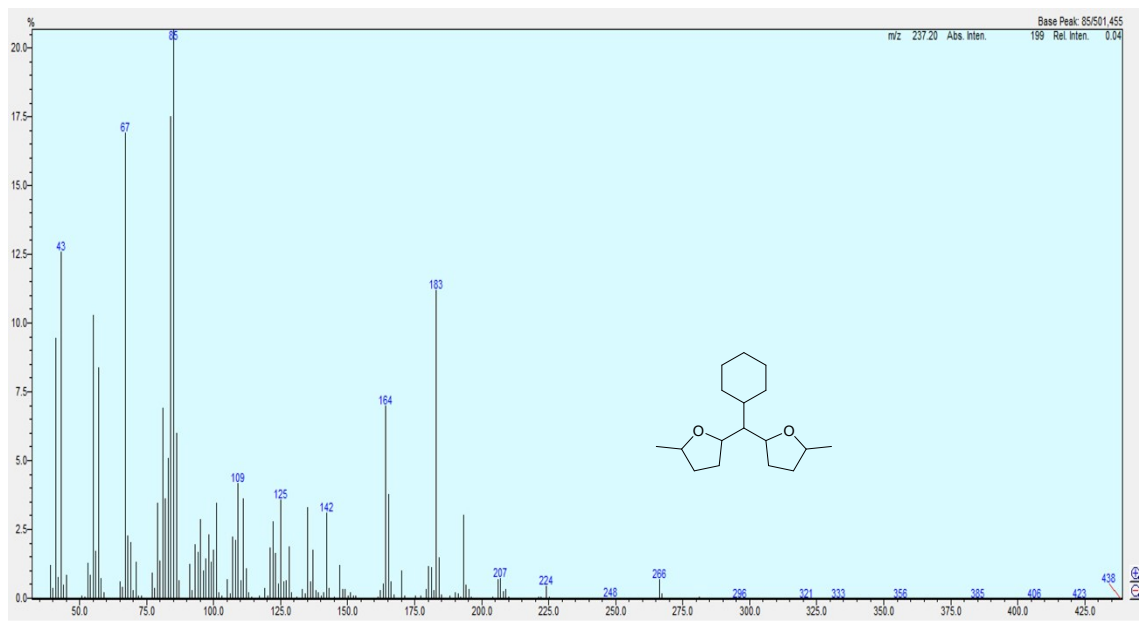


Figure S25. Mass spectrogram of the hydrogenated 1A.

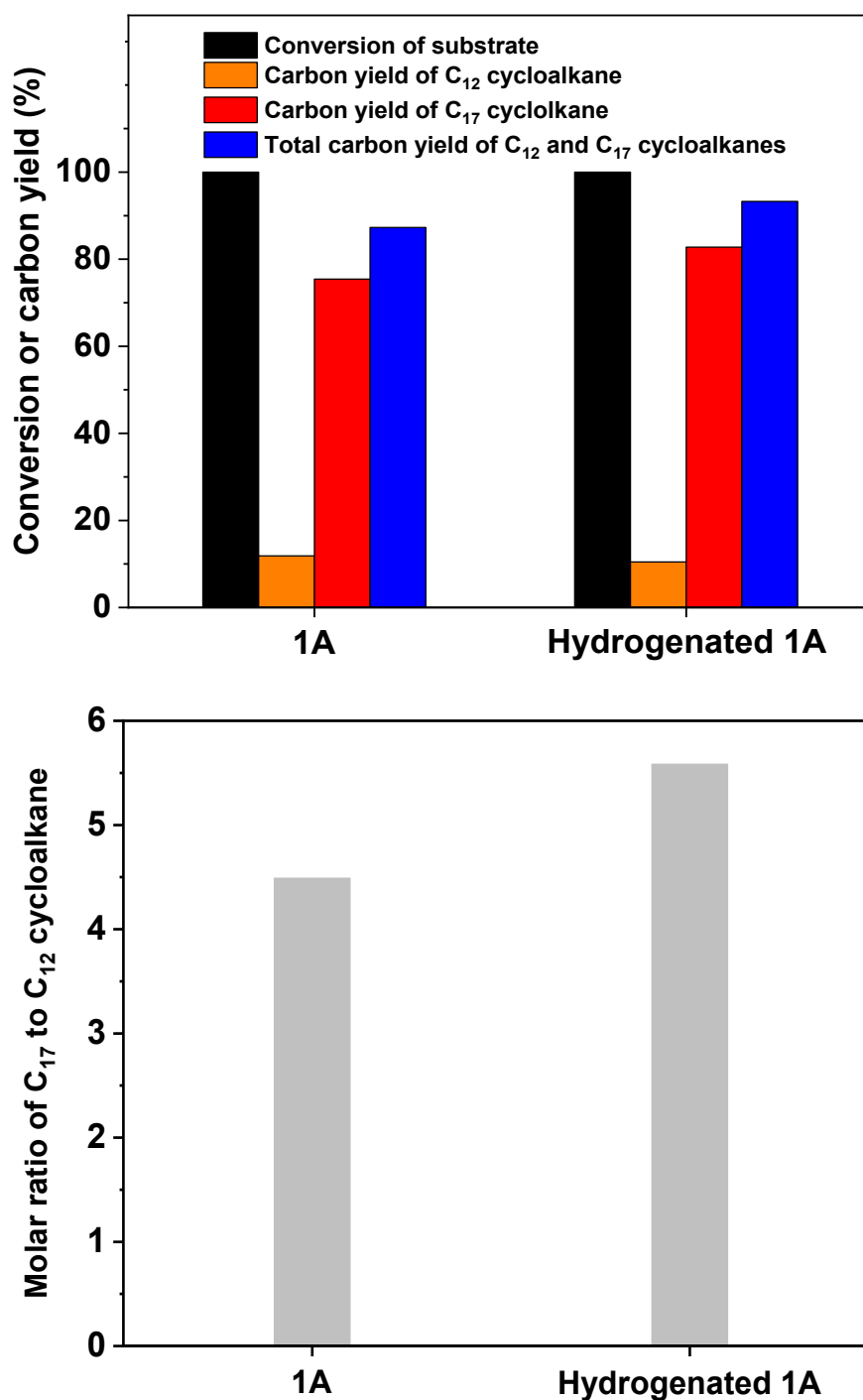


Figure S26. Carbon yields of different products and the molar ratio of C₁₇ to C₁₂ cycloalkane from the HDO of **1A** (or hydrogenated **1A**) under the co-catalysis of Ru/HAP + H-ZSM-5 catalyst. Reaction conditions: 453 K, 4 MPa H₂, 24 h; 0.1 g **1A**, 0.1 g Ru/HAP and 0.1 g H-ZSM-5, 50 mL cyclopentane were used in each test.