Supporting Information

Synthesis of jet fuel range high-density dicycloalkanes with methyl benzaldehyde and acetone

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The number of Figures: 28

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1. Characterization

1.1. Transmission electron microscope (TEM)

The TEM images of the titanate catalysts were obtained with a TECNAI G^2 Spirit FEI Transmission Electron Microscopy operated at an accelerating voltage of 120 kV. Before the tests, the Ni catalysts were reduced by H_2 at 773 K for 2 h.

1.2. X-ray diffraction (XRD)

XRD patterns of the titanate catalysts were recorded with a PW3040/60X' Pert PRO (PANalytical) diffractometer using a Cu K_α radiation source ($\lambda = 0.15432$ nm) operated at 40 kV and 40 mA.

1.3. N_2−physical adsorption

The N_2-physical adsorption was carried out at 77 K by ASAP 2010 (Micromeritics). The specific surface areas of different titanate samples were measured by Brunauer–Emmett–Teller (BET) method. Before each measurement, the sample was evacuated at 573 K to eliminate the adsorbents.

1.4. NH_3 chemisorption

The amounts of acid sites on the surfaces of different titanate catalysts were measured by NH_3 chemisorption according to the method described in our previous work.[3] The measurements were carried out by a Micrometeritics Autochem 2920 Automated Catalyst Characterization System. Typically, 0.1 g of catalyst was loaded into a quartz reactor, purged at 393 K for 2 h and cooled down to 373 K in He flow. Subsequently, pulses of NH_3 (1 mL) were dosed in the reactor until saturation. The amounts of acid sites on different catalysts were calculated by the adsorptions of NH_3 during the tests.

1.5. NH_3 temperature programmed desorption (NH_3−TPD)

The acid strengths of titanate catalysts were characterized by NH_3-TPD which was carried out on a Micrometeritics AutoChem II 2920 Automated Catalyst Characterization System. For each test, 0.1 g sample was used. Before the measurement, the sample was purged with He flow at 393 K for 2 h. After saturated adsorption of NH_3 at 373 K, the sample was heated at 373 K in He flow for 45 min to remove the physically adsorbed ammonia. 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 an OminiStar mass spectrometry (MS) equipped with the software quadstar 32-bit.

1.6. Pyridine infrared (IR)

Different types of acid sites on solid catalyst surface (TiO_2 P25-and PTNT) were analysed by pyridine IR to get deeper insight the acidity change during preparation of PTNT. The analyses were conducted by Bruker Vertex 70 spectrometer equipped with a mercury cadmium telluride (MCT) detector. Generally, samples were grounded, pressed to form 1cm-diameter wafers, and installed on supports. The sample cell was heated to 423 K for 1 h in order to remove the physically absorbed water and then cooled to room temperature. The spectrum of sample was recorded using a mercury–cadmium–telluride (MCT) infrared detector as background. Subsequently, Pyridine was introduced into the cell, and the adsorption was performed. The excess and physically adsorbed pyridine was evacuated under vacuum at room temperature. Finally, the IR spectrum of sample was recorded at room temperature by the subtraction of background.

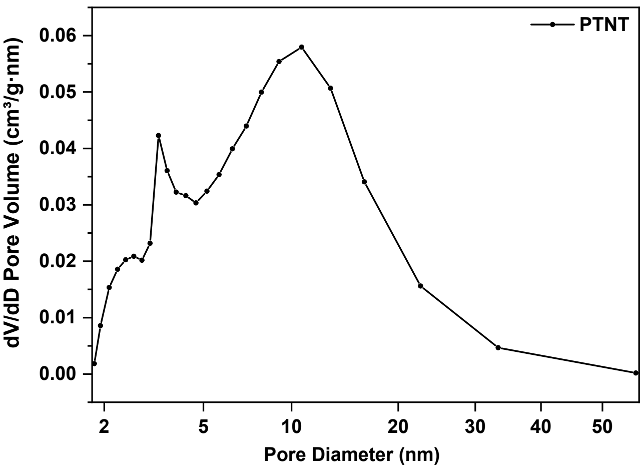

Fig. S1 The pore-size distributions for PTNT.

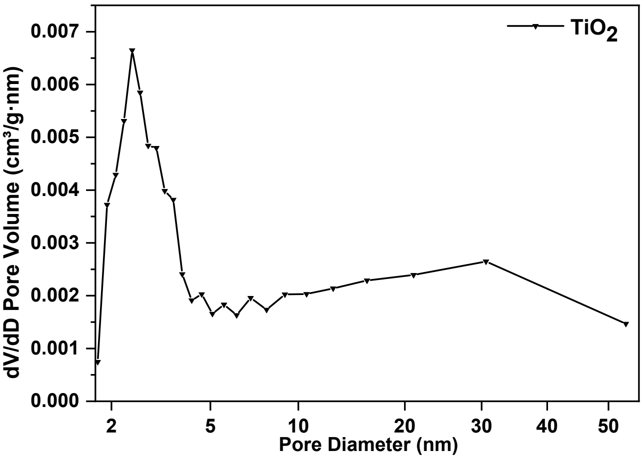

Fig. S2 The pore-size distributions for TiO_2.

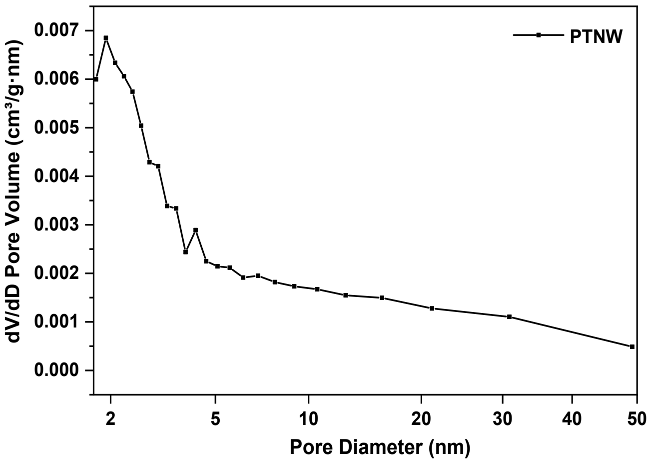

Fig. S3 The pore-size distributions for PTNW.

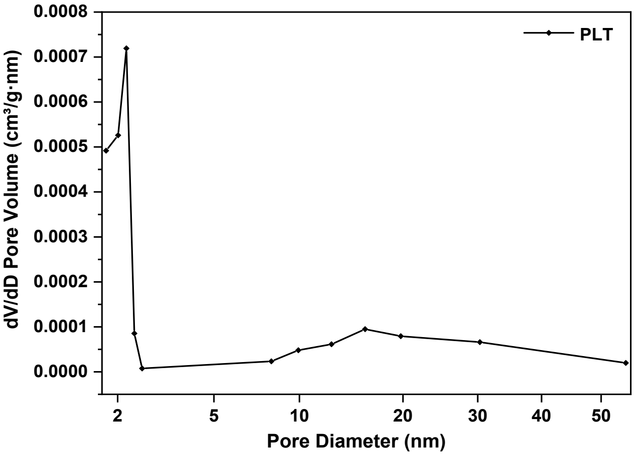

Fig. S4 The pore-size distributions for PLT.

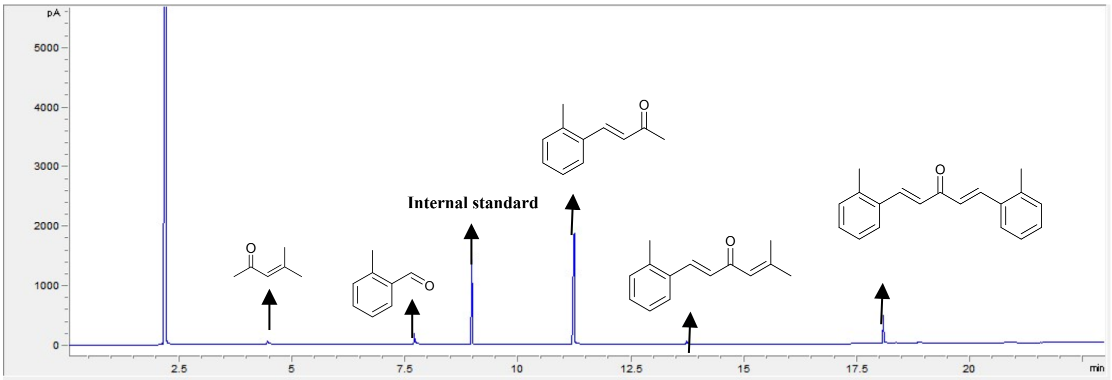

Fig. S5 Gas chromatogram of the reaction product of 2-methyl benzaldehyde and acetone. Reaction conditions: 10 mL acetone, 5 mmol 2-methyl benzaldehyde, 0.15 g PTNT; 343 K for 8 h.

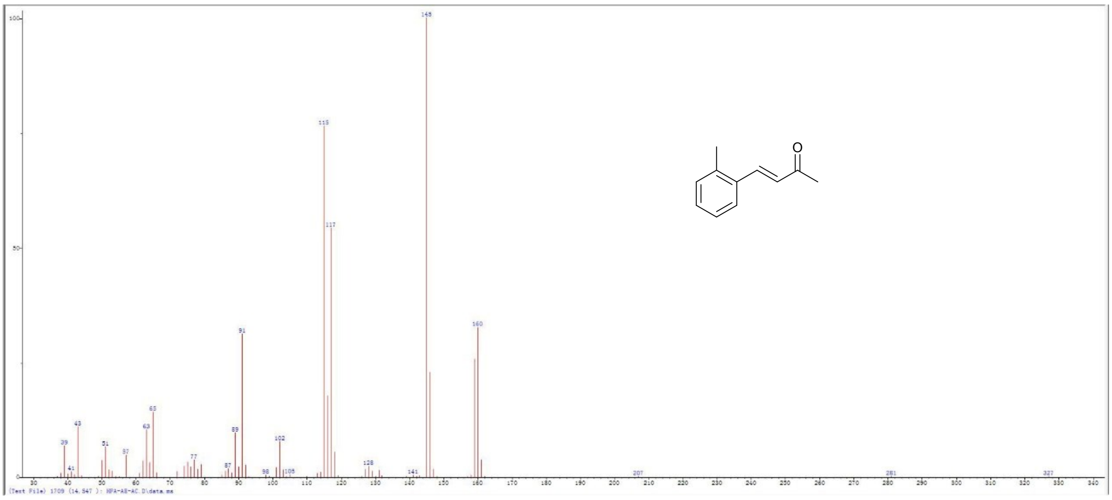

Fig. S6 Mass spectrogram of the **1A** from the aldol condensation of 2-methyl benzaldehyde and acetone.

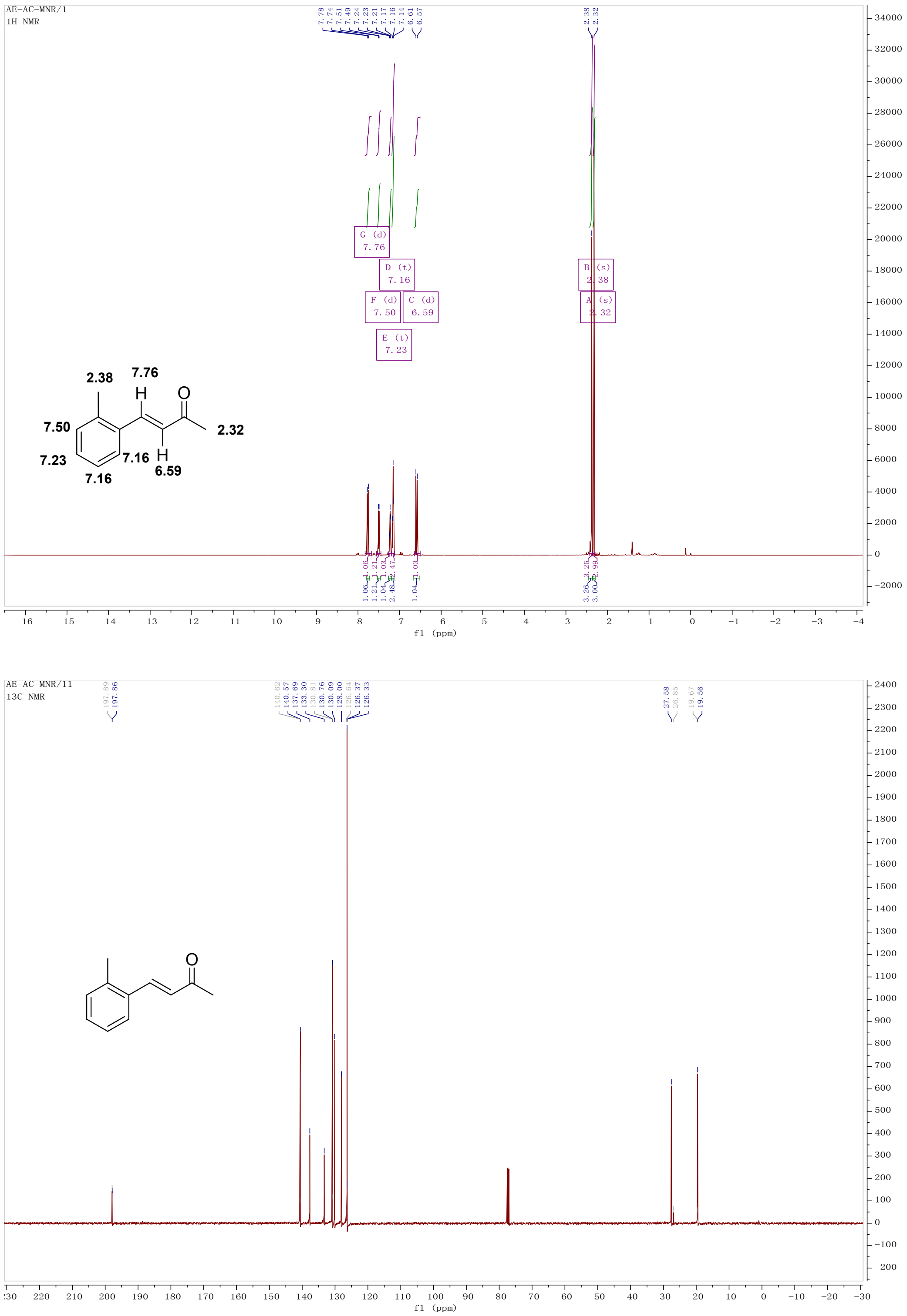

Fig. S7 ^{1}H-NMR and ^{13}C-NMR spectra of the **1A** from the aldol condensation of 2-methyl benzaldehyde and acetone.

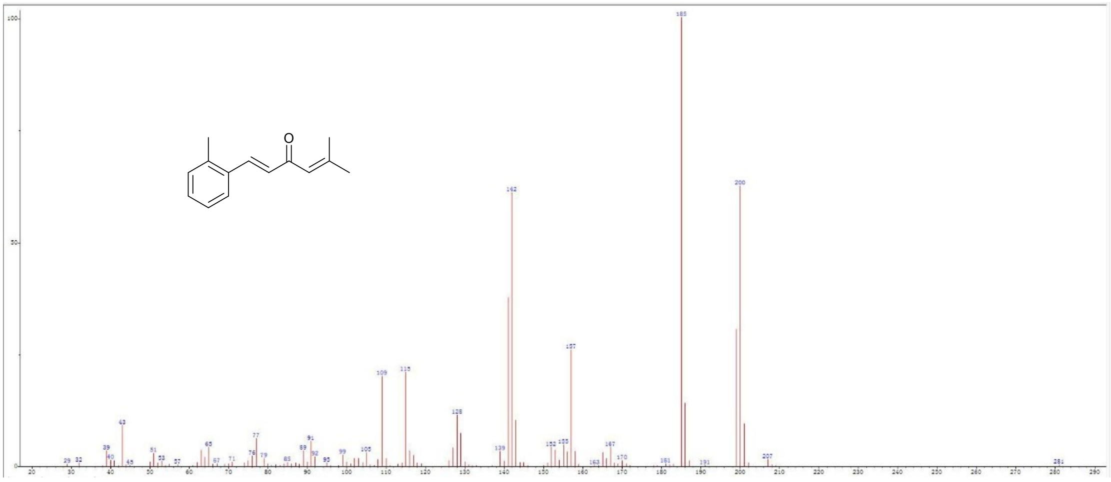

Fig. S8 Mass spectrogram of the **1AII** from the aldol condensation of 2-methyl benzaldehyde and acetone.

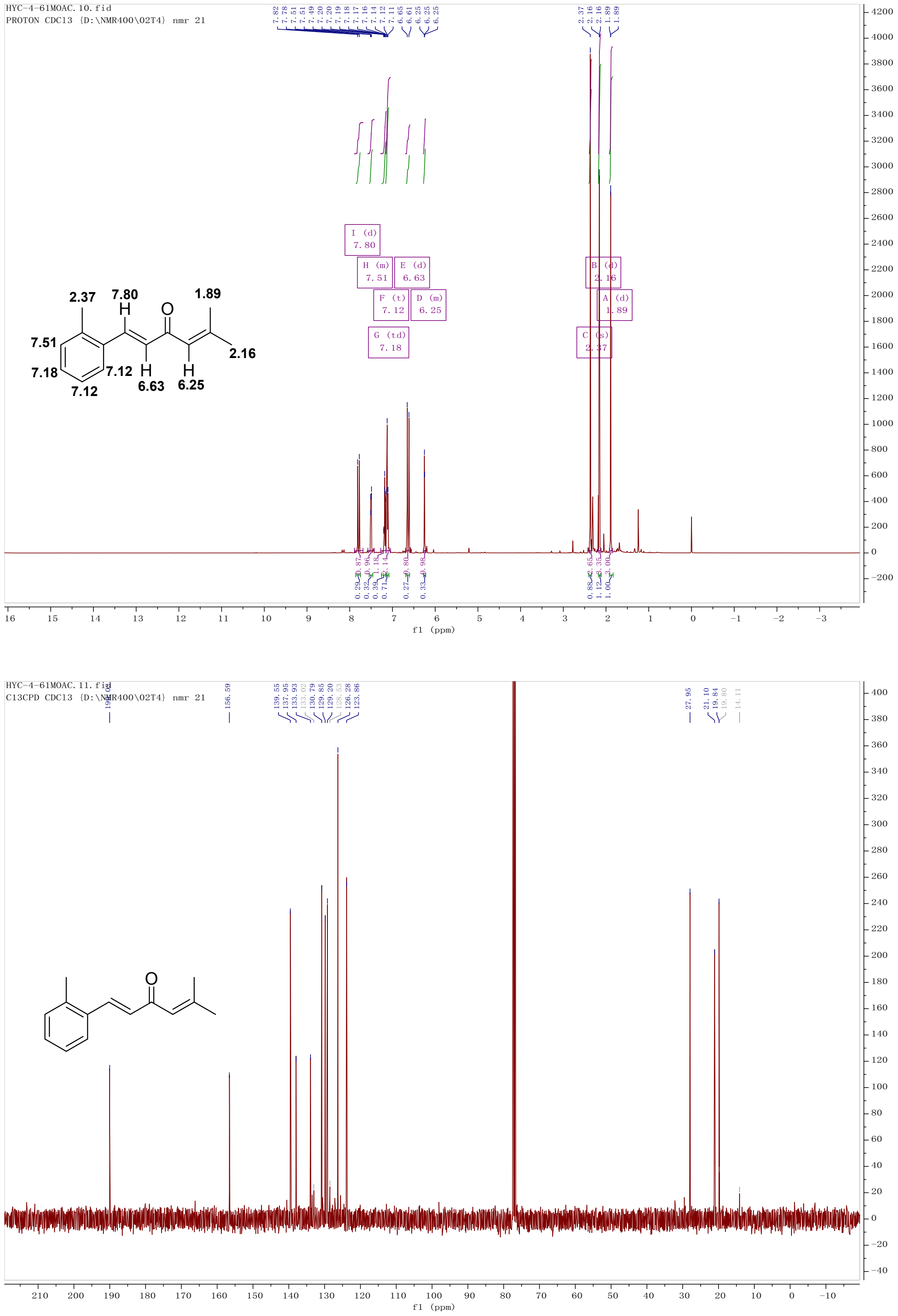

Fig. S9 ^{1}H-NMR and ^{13}C-NMR spectra of the **1AII** from the aldol condensation of 2-methyl benzaldehyde and acetone.

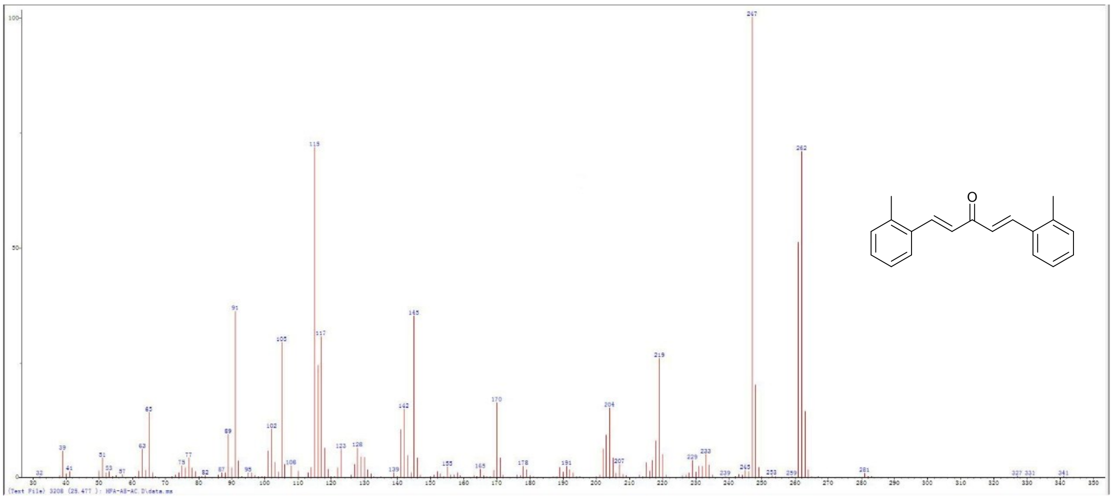

Fig. S10 Mass spectrogram of the **1AIII** from the aldol condensation of 2-methyl benzaldehyde and acetone.

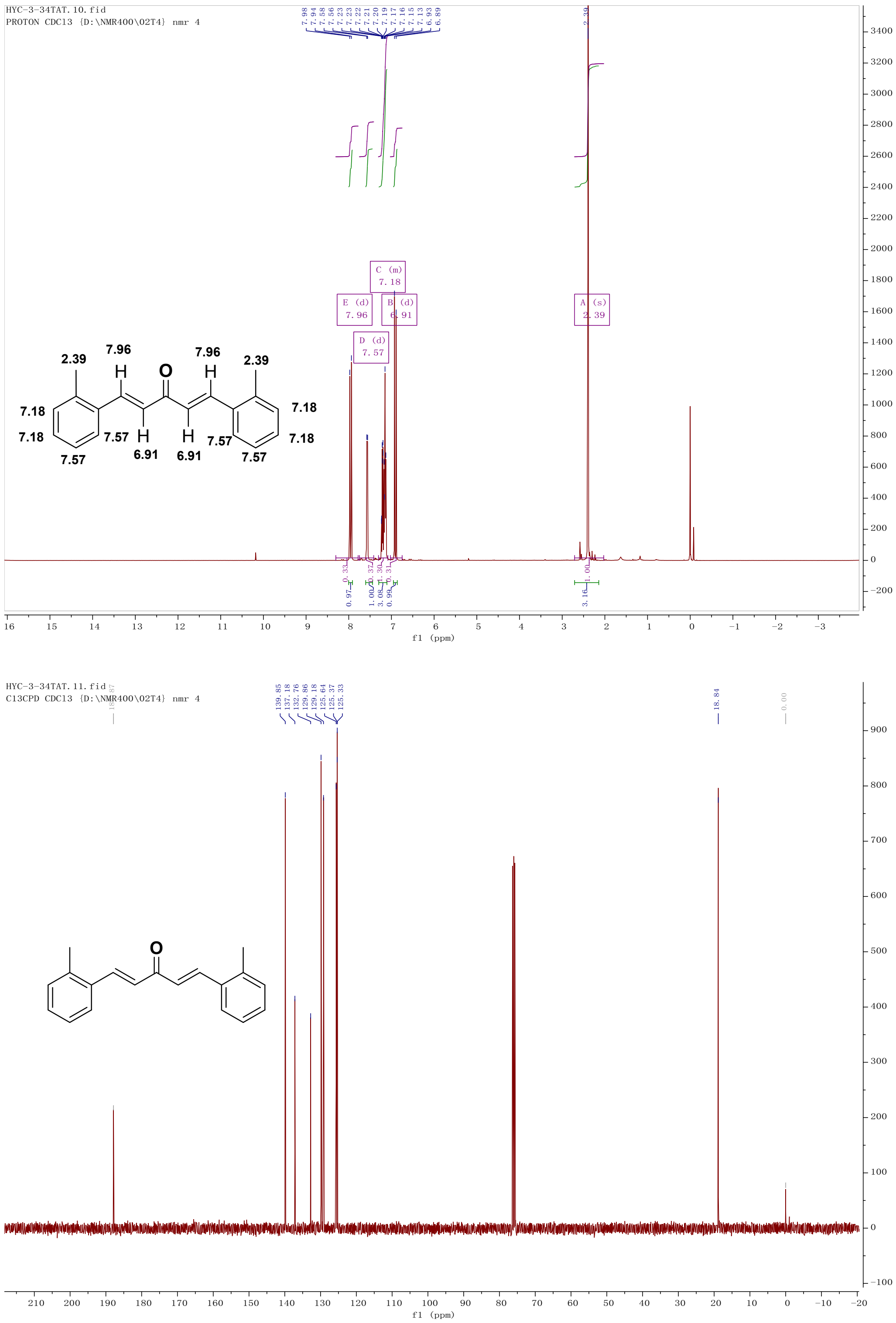

Fig. S11 ^{1}H-NMR and ^{13}C-NMR spectra of the **1AIII** from the aldol condensation of 2-methyl benzaldehyde and acetone.

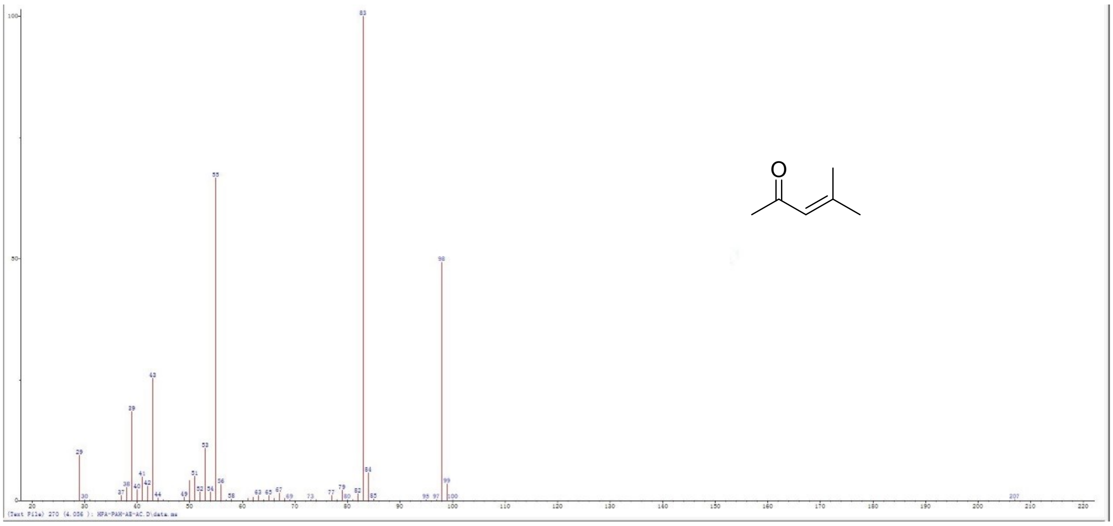

Fig. S12 Mass spectrogram of the methyl isobutenyl ketone from the self aldol-condensation of acetone

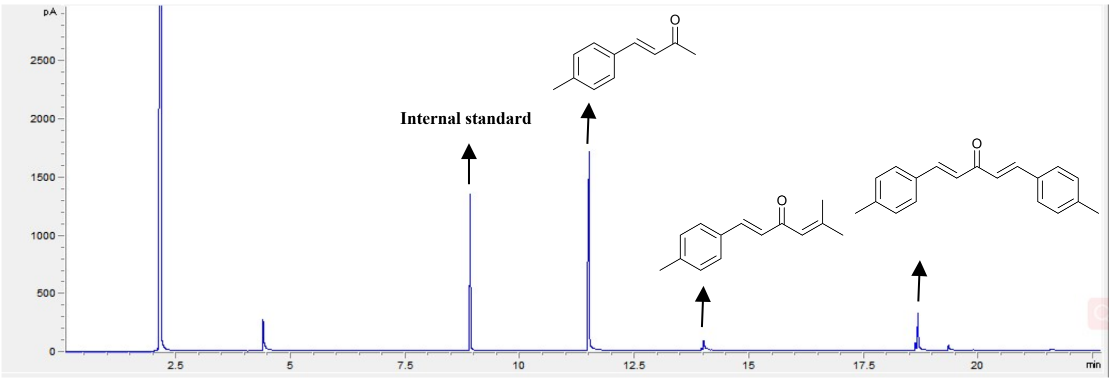

Fig. S13 Gas chromatogram of the reaction product of 4-methyl benzaldehyde and acetone. Reaction conditions: 10 mL acetone, 5 mmol 4-methyl benzaldehyde, 0.15 g PTNT, 353 K for 6 h.

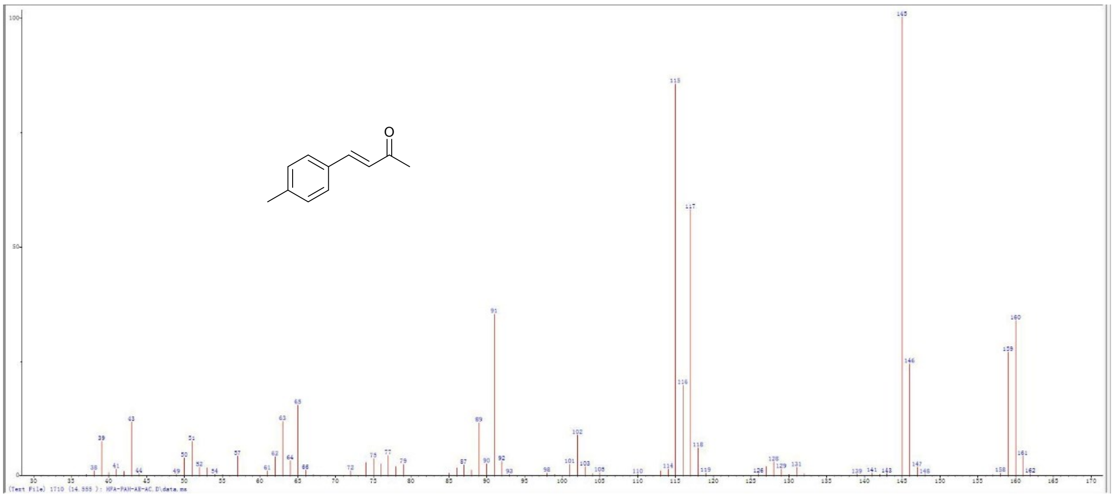

Fig. S14 Mass spectrogram of the **2A** from the aldol condensation of 4-methyl benzaldehyde and acetone.

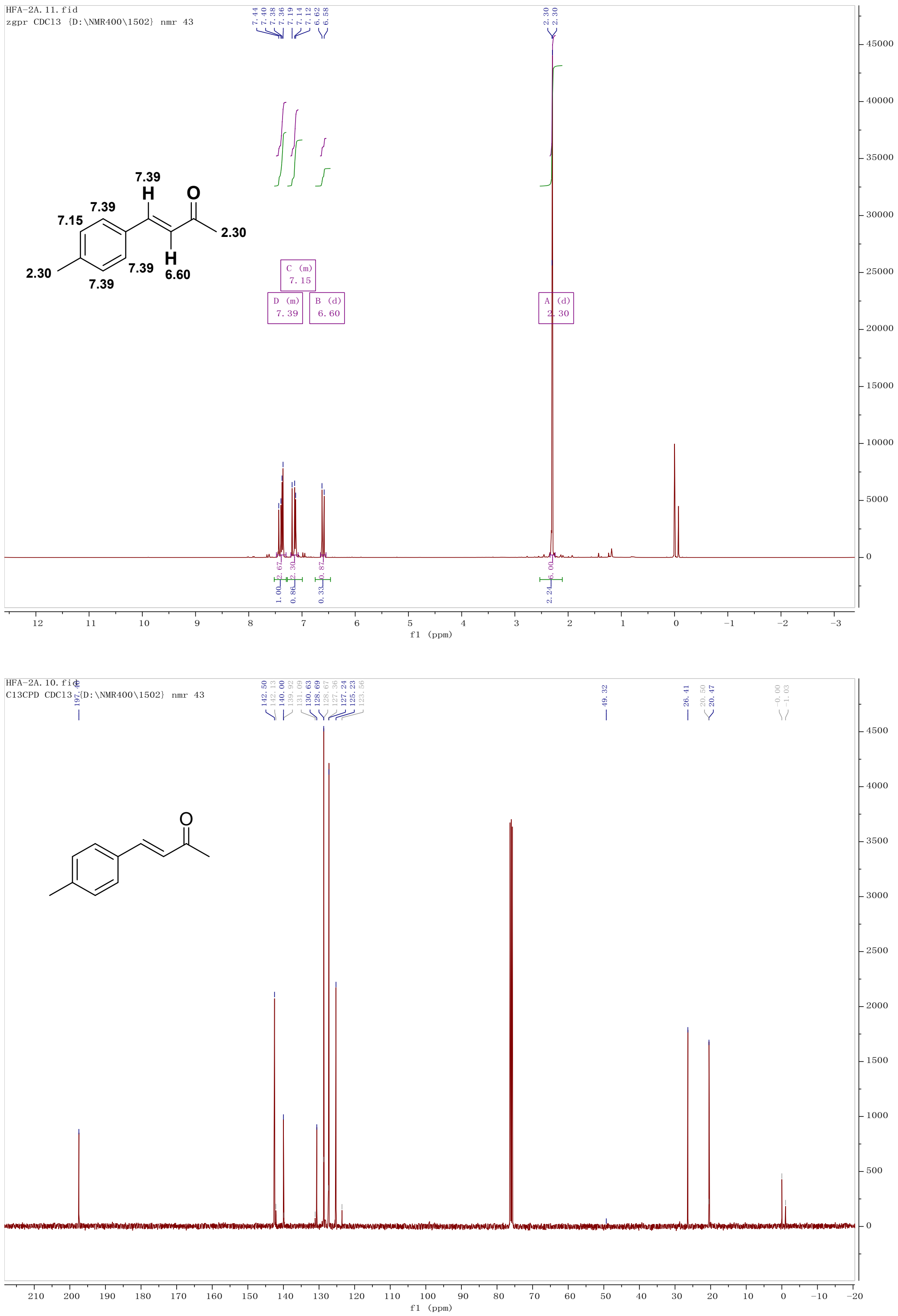

Fig. S15 ^{1}H-NMR and ^{13}C-NMR spectra of the **2A** from the aldol condensation of 4-methyl benzaldehyde and acetone.

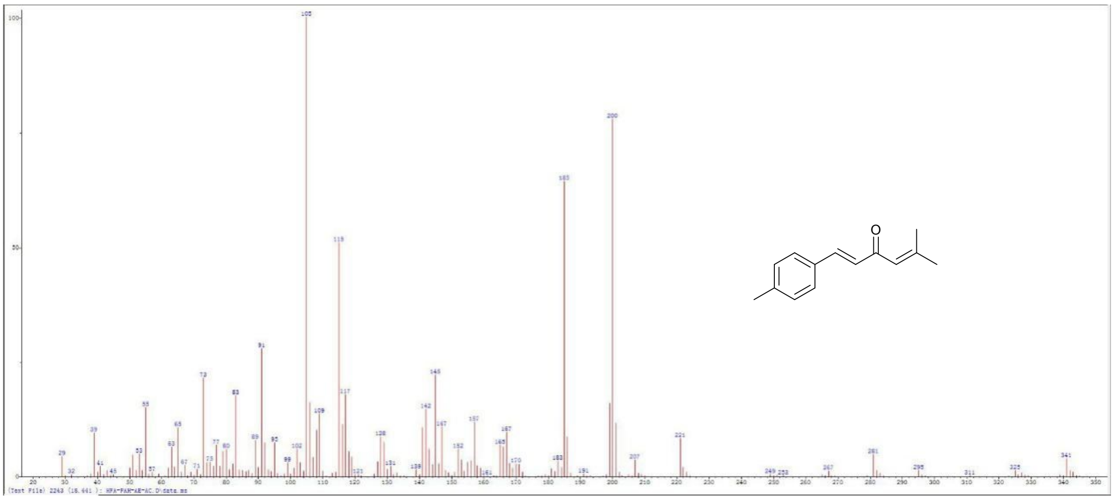

Fig. S16 Mass spectrogram of the **2AII** from the aldol condensation of 4-methyl benzaldehyde and acetone.

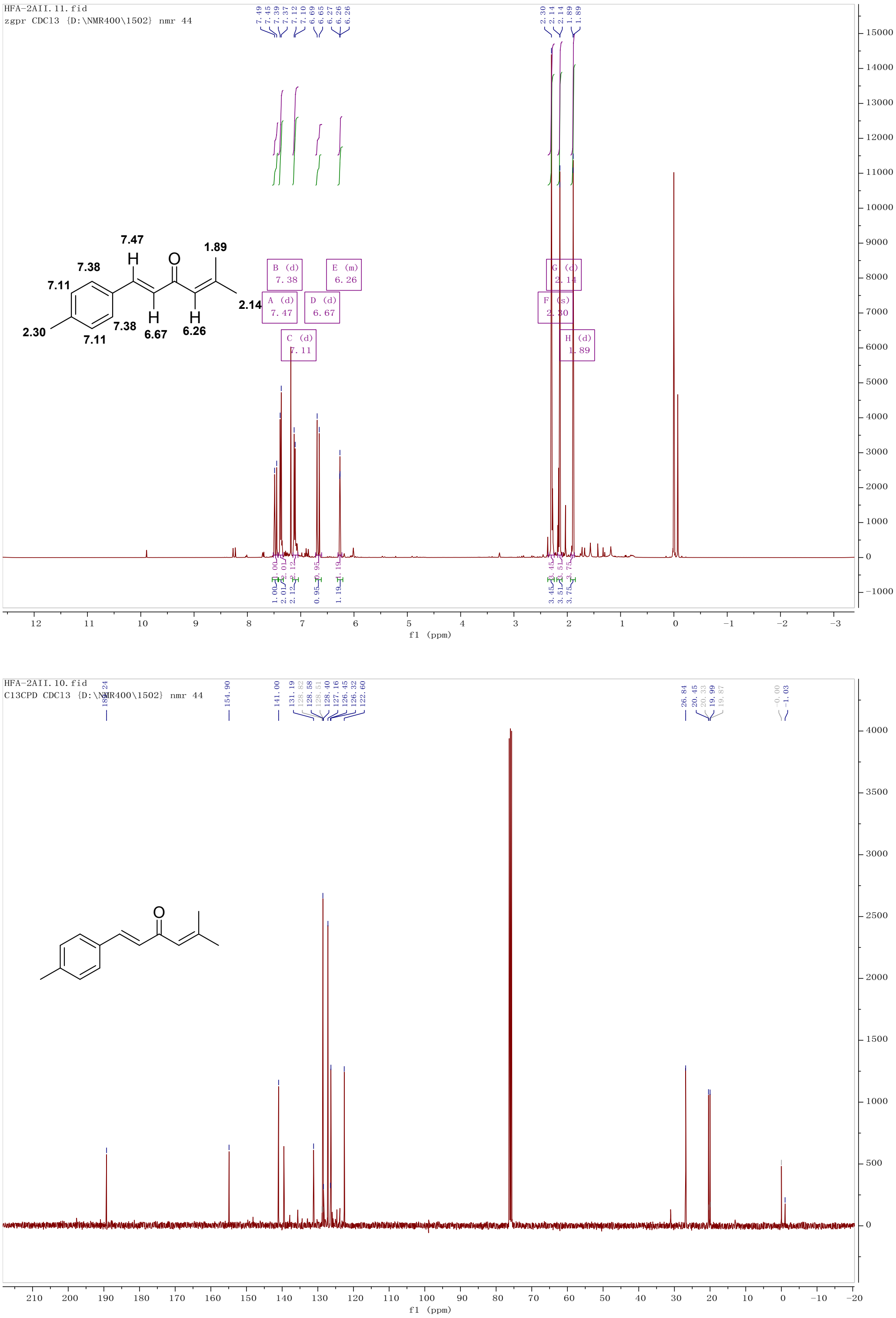

Fig. S17 ^{1}H-NMR and ^{13}C-NMR spectra of the **2AII** from the aldol condensation of 4-methyl benzaldehyde and acetone.

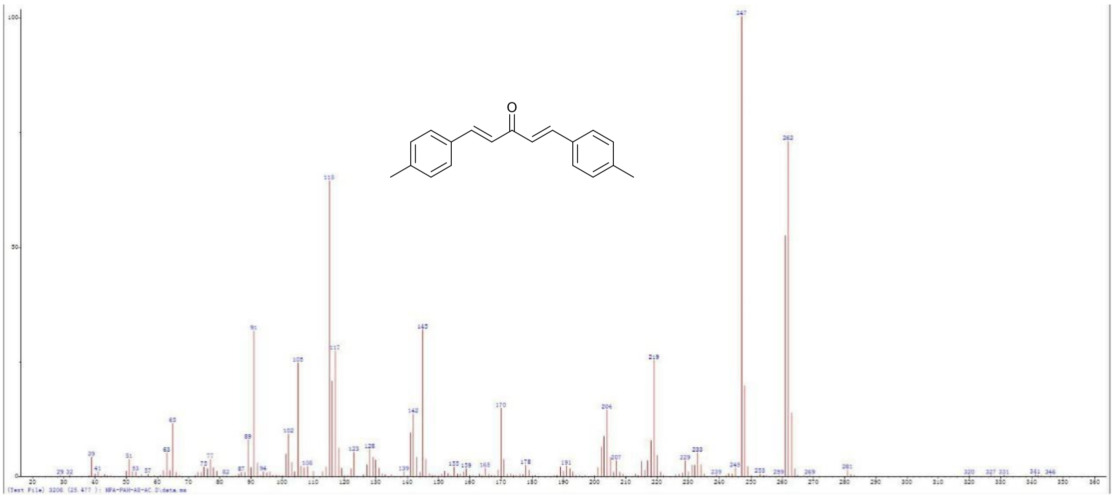

Fig. S18 Mass spectrogram of the **2AIII** from the aldol condensation of 4-methyl benzaldehyde and acetone.

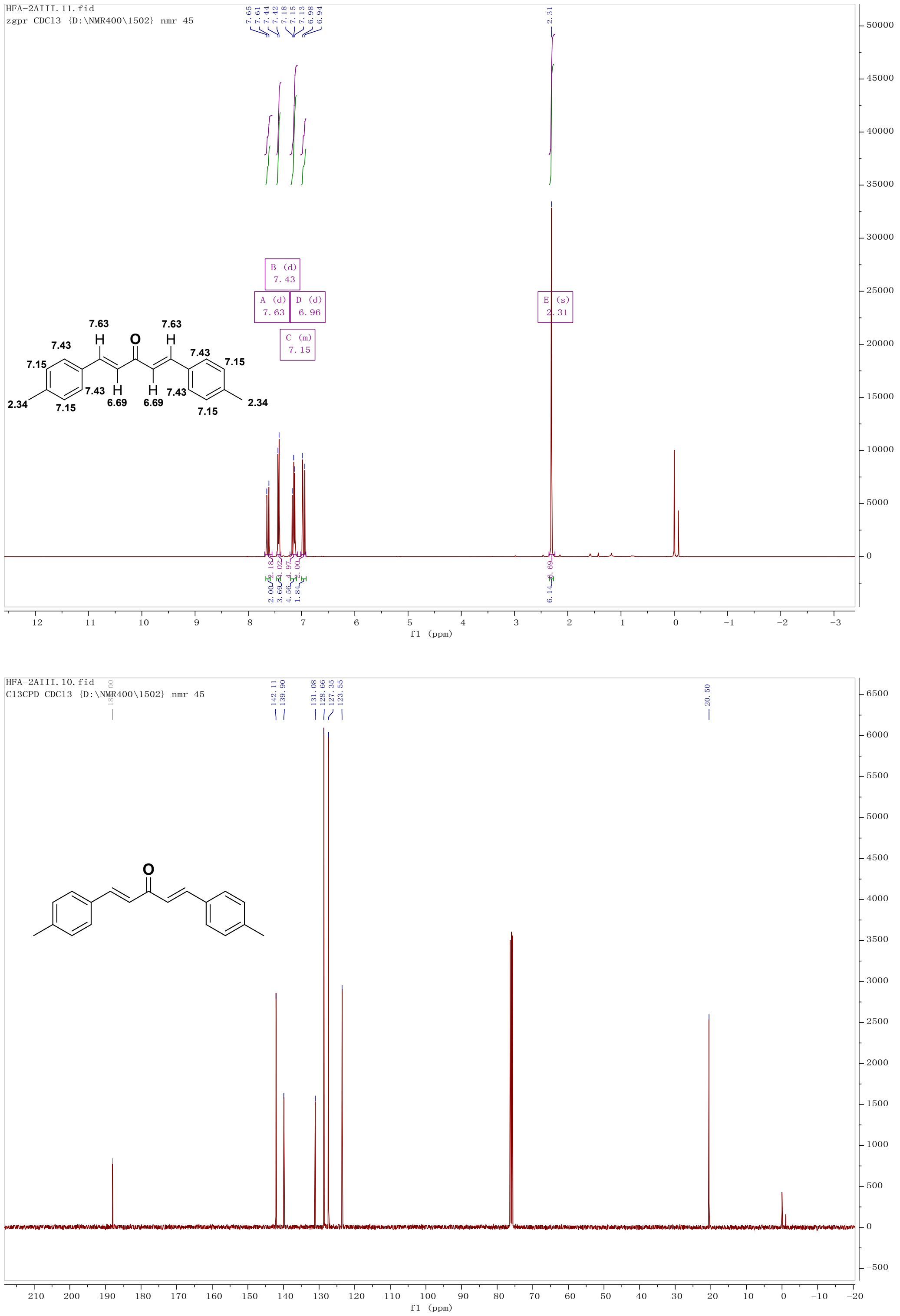

Fig. S19 ^{1}H-NMR and ^{13}C-NMR spectra of the **2AIII** from the aldol condensation of 4-methyl benzaldehyde and acetone.

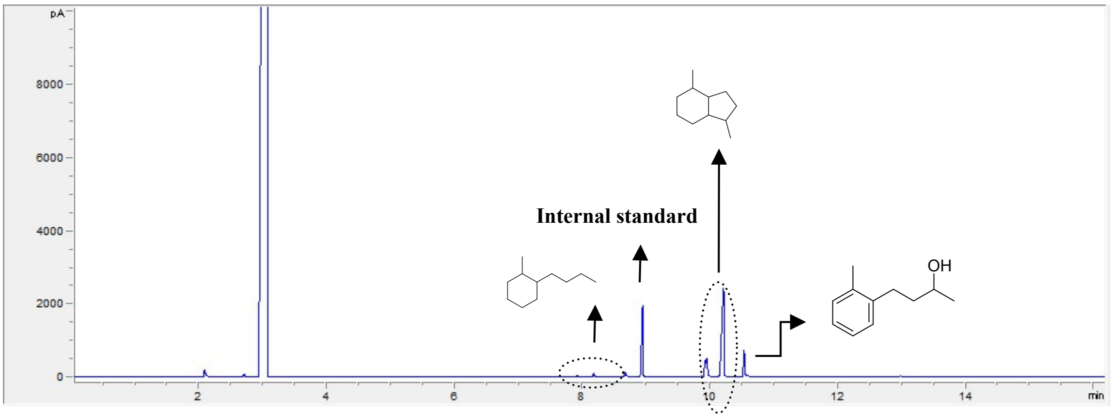

Fig. S20 Gas chromatogram of the HDO products of **1A** over the Pt/C catalyst. Reaction conditions: 10 mmol **1A**, 40 mL cyclohexane, 0.1 g Pt/C, 6 MPa H_2; 393 K for 4 h.

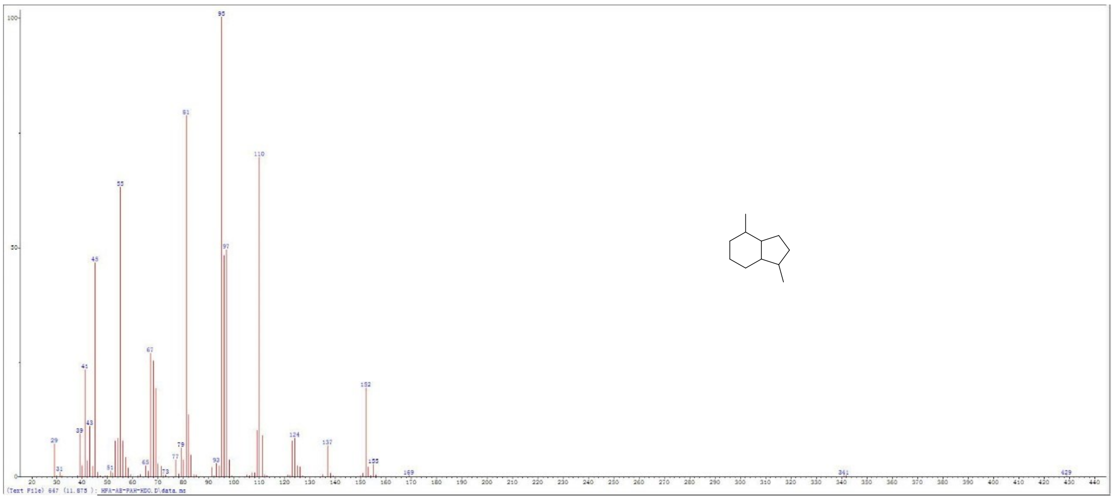

Fig. S21 Mass spectrogram of **1B** from the HDO of **1A**.

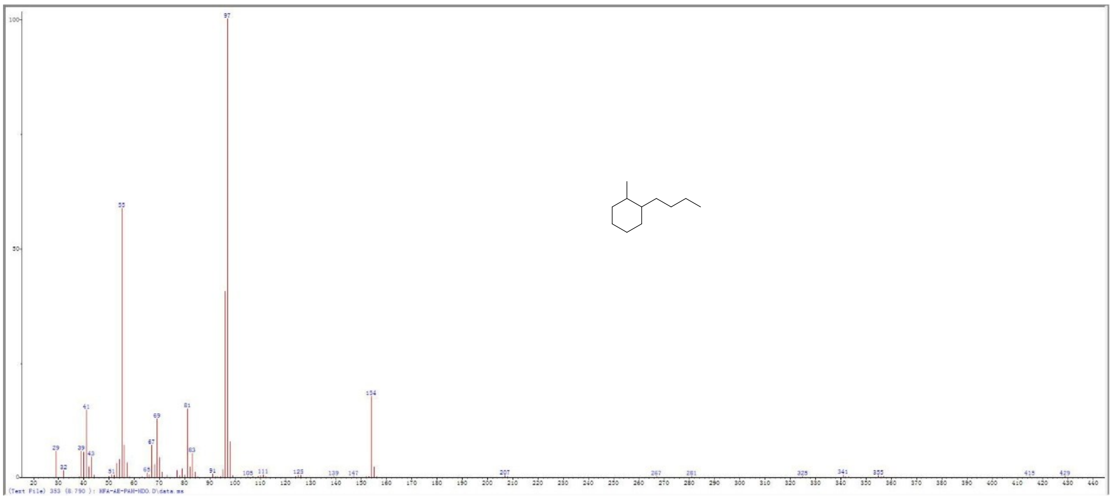

Fig. S22 Mass spectrogram of **1C** from the HDO of **1A**.

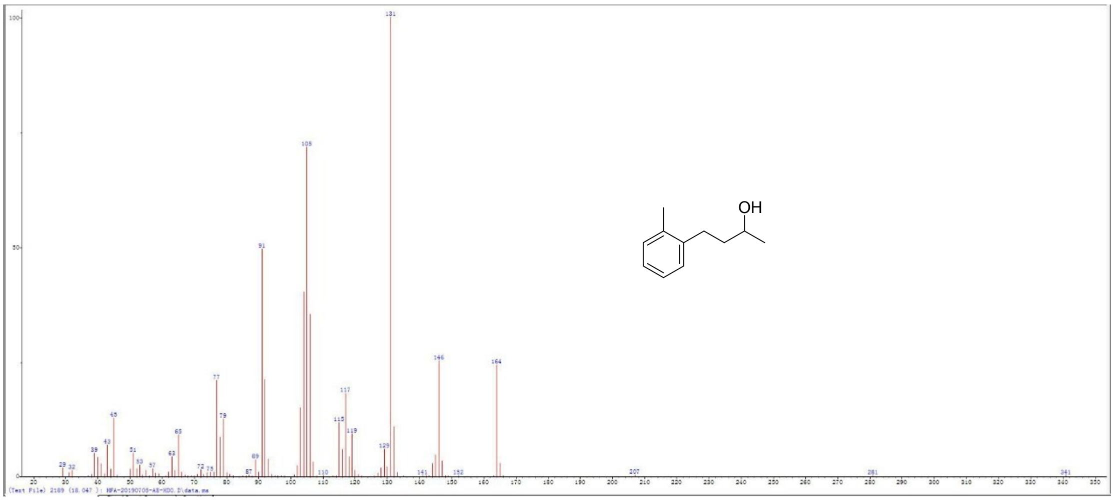

Fig. S23 Mass spectrogram of **1D** from the HDO of **1A**.

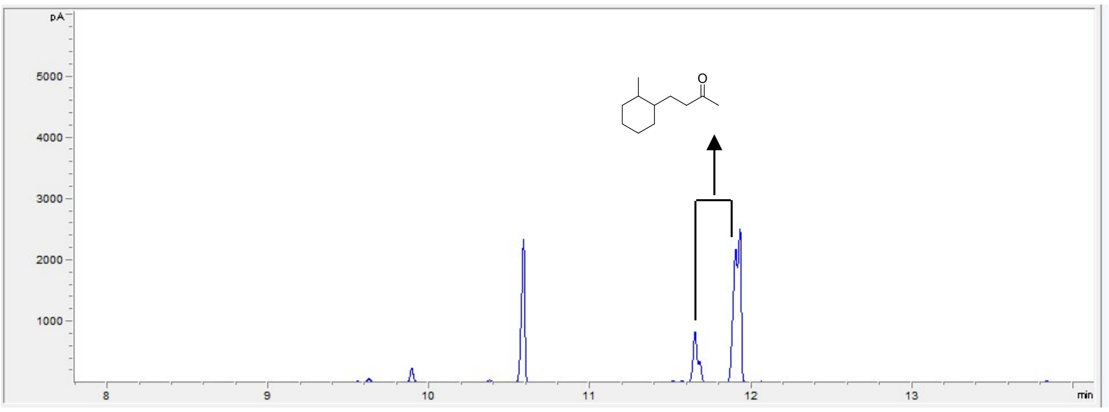

Fig. S24 Gas chromatogram of the HDO products of **1A** over Pt/C catalyst. Reaction conditions: 10 mmol **1A**, 40 mL cyclohexane, 0.1 g Pt/C, 2 MPa H_2; 403 K for 4 h.

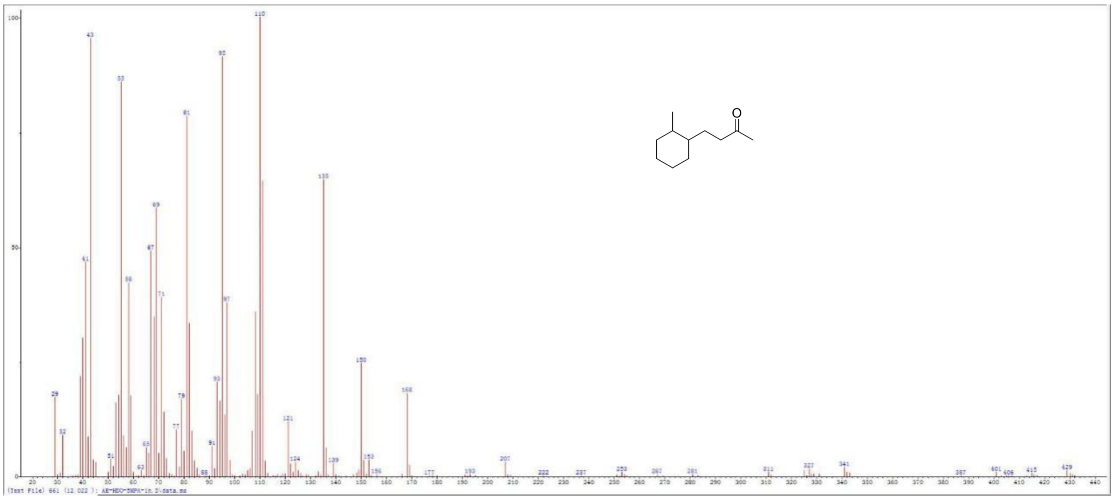

Fig. S25 Mass spectrogram of **1E** from the HDO of **1A**.

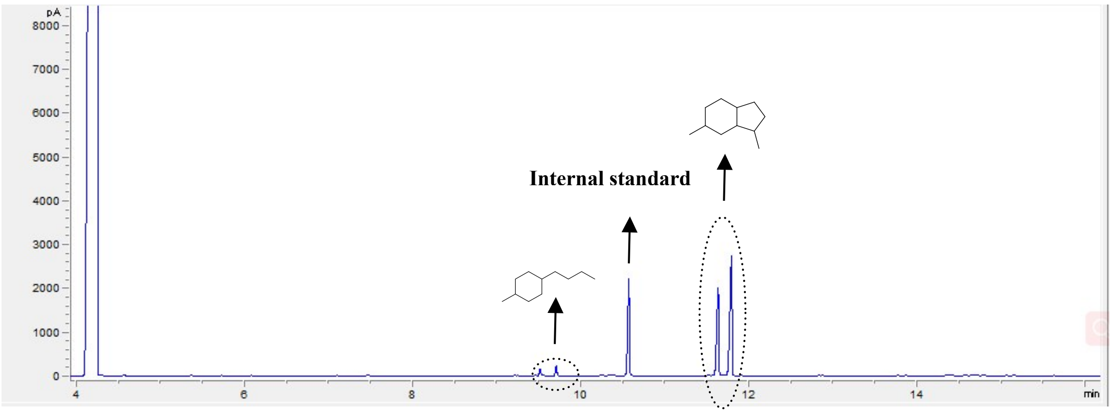

Fig. S26 Gas chromatogram of the HDO products of **2A** over Pt/C catalyst. Reaction conditions: 10 mmol **2A**, 40 mL cyclohexane, 0.1 g Pt/C, 5 MPa H_2; 403 K for 2 h.

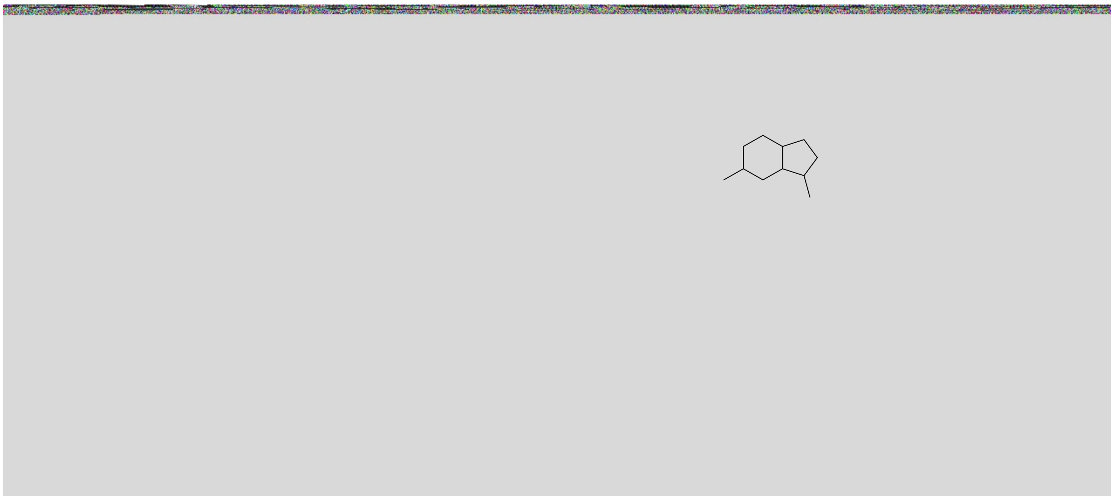

Fig. S27 Mass spectrogram of **2B** from the HDO of **2A**.

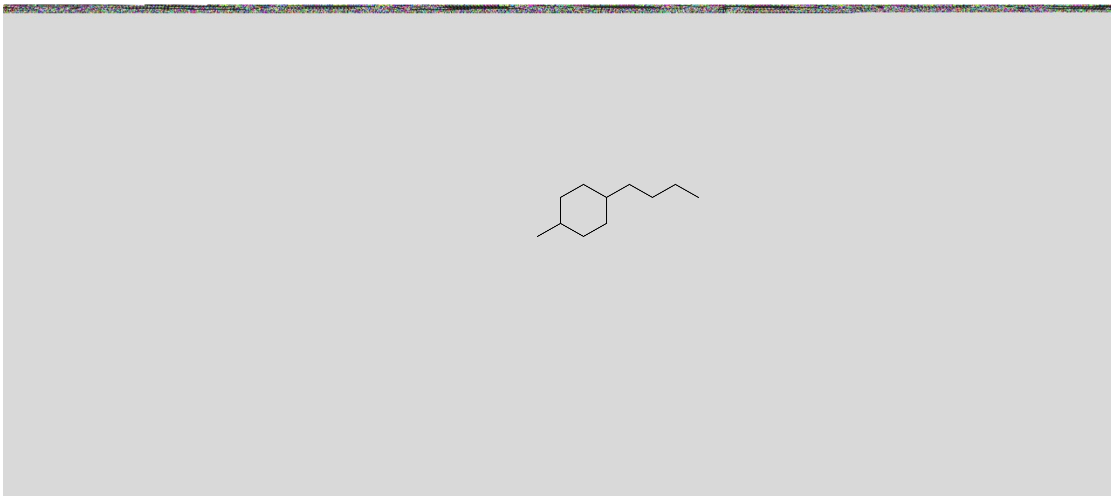

Fig. S28 Mass spectrogram of **2C** from the HDO of **2A**.

References

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2 W. Dong, A. Cogbill, T. Zhang, S. Ghosh, Z. R. Tian, *J. Phys. Chem. B,* 2006, **110**, 16819.

3 J. Pang, A. Wang, M. Zheng, T. Zhang, *Chem. Commun.,* 2010, **46**, 6935.