

## Supporting Information

### **Production of Cyclopentanone from Furfural over Ru/C with Al<sub>11.6</sub>PO<sub>23.7</sub> and Applied to the Synthesis of Diesel Range Alkanes**

Tao Shen<sup>a,b</sup>, Ruijia Hu<sup>a,b</sup>, Chenjie Zhu<sup>\*a,b,c</sup>, Ming Li<sup>a,b</sup>, Wei Zhuang<sup>a,b</sup>, Chenglun  
Tang<sup>a,b</sup> and Hanjie Ying<sup>\*a,b,c</sup>

<sup>a</sup> College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University,  
Nanjing, China

<sup>b</sup> National Engineering Technique Research Center for Biotechnology, Nanjing, China

<sup>c</sup> Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM)

Fax: (+86)-25-58139389; phone: (+86)-25-86990001; E-mail: zhucj@njtech.edu.cn

## Materials

All of the substrates consist of furfural and furfuryl alcohol were purchased from Aladdin Company, all of the standard sample to be detected consists of cyclopentanone, cyclopentaol and tetrahydrofurfuryl alcohol were purchased from Sigma-Aldrich.

Pd/C (5 wt%), Pt/C (5 wt%), Ru/C (5 wt%) and Raney Ni catalysts used in hydrogenation step were purchased from Aladdin company. Zeolite catalysts (H-Beta) used in the hydrodeoxygenation steps were purchased from The Catalyst Plant of Nankai University. *para*-toluene sulfonic acid and TBD ((1,5,7-triazabicyclo[4.4.0]-dec-5-ene) used in the C-C coupling reactions were purchased from Aladdin company

Other reagents were ACS reagent grade and used without further purification. All reagents and solvents were commercial quality and used without further purification unless stated otherwise.

## General Method

NMR spectra were recorded on a Bruker Ascend 400 MHz NMR spectrometer at 400 MHz ( $^1\text{H}$  NMR) and 100 MHz ( $^{13}\text{C}$  NMR). Chemical shifts are reported in parts per million (ppm).  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are referenced relative to the tetramethylsilane.

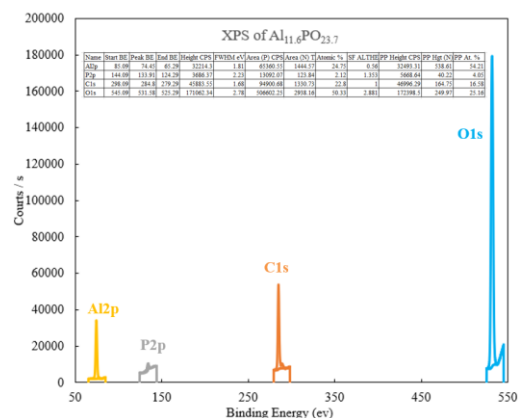
GC-MS instrument (Agilent 7890B GC/5977A MS detector) was equipped with a HP-5 MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). The injection volume was

1.0  $\mu\text{L}$  with an autosampler and helium was used as a carrier gas with column flow rate of  $1.5 \text{ mL min}^{-1}$ . The temperature program was carried out as follows: initial temperature  $50 \text{ }^\circ\text{C}$  for 4 min, then to  $250 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C min}^{-1}$ , and maintained at  $250 \text{ }^\circ\text{C}$  for 2 min. Initial temperature  $40 \text{ }^\circ\text{C}$  for 4 min, then to  $60 \text{ }^\circ\text{C}$  at  $2 \text{ }^\circ\text{C min}^{-1}$ , and maintained at  $60 \text{ }^\circ\text{C}$  for 2 min, then to  $150 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C min}^{-1}$ , and maintained at  $150 \text{ }^\circ\text{C}$  for 2 min. (For Figure 4). The electron ionization (EI) mass spectra in the range of 35 -700 (m/z) were recorded in the full-scan mode. The detected compounds were identified based on NIST database.

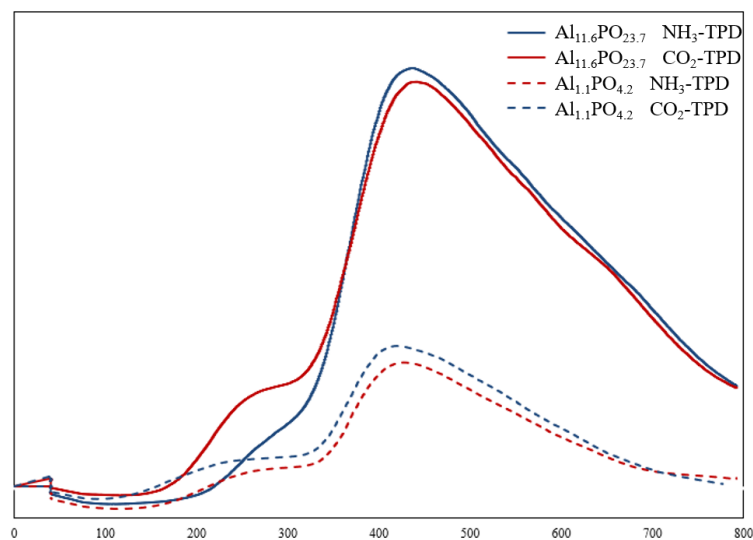
HPLC instrument (Waters 1525-2414, RID (Refractive Index Detector) detector) was equipped with Carbomix H-NPI column ( $300 \text{ mm} \times 7.8 \text{ mm} \times 10.0 \text{ }\mu\text{m}$ ), 5mM  $\text{H}_2\text{SO}_4$  as the mobile phase and the flow rate was  $0.6 \text{ mL min}^{-1}$ , column temperature controlled at  $55 \text{ }^\circ\text{C}$ .

XRD patterns of different catalyst were obtained on a Rigaku D MAX III VC diffractometer equipped with a Cu-K $\alpha$  radiation source ( $\lambda = 0.15432 \text{ nm}$ ). The BET surface area, total pore volume, and average pore diameter were measured by  $\text{N}_2$  adsorption-desorption method by Micromeritics Instrument TriStar II 3020. Before each measurement, the sample was evacuated at 473 K for 3 h.  $\text{NH}_3$ -TPD and  $\text{CO}_2$ -TPD were carried out by a micromeritics Autochem 2920 Automated Catalyst Characterization System. Typically, 0.1 g of catalyst was loaded into a quartz reactor purged in He flow at 473K for 2 h and cooled down to 372 K. Pulses of  $\text{NH}_3$  were dosed in until saturation. The amount of acid sites on catalysts were calculated by the uptakes of  $\text{NH}_3$  during the tests. In situ pyridine adsorption was carried out by FT-IR





**Figure S1.** XPS P 2p, O 1s and Al 2p spectra of different mole ratio of Al and P aluminum phosphate catalysts. (catalyst prepared 0.5, 1, 2, 5, 20 portion  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 1 portion  $(\text{NH}_4)_2\text{HPO}_4$ , respectively)

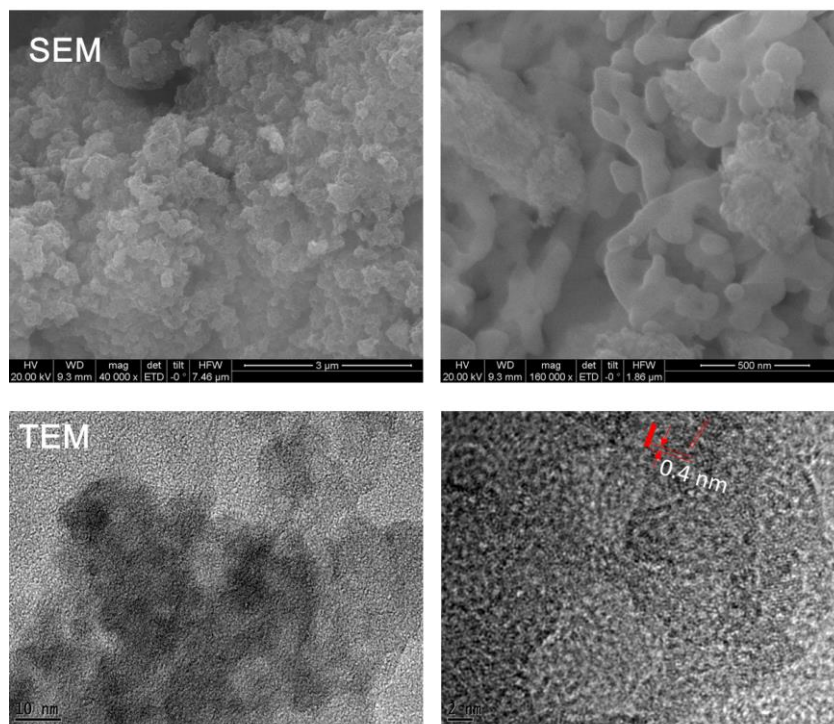


**Figure S2.**  $\text{NH}_3$  TPD and  $\text{CO}_2$  TPD spectra of  $\text{Al}_{11.6}\text{PO}_{23.7}$  and  $\text{Al}_{1.1}\text{PO}_{4.2}$

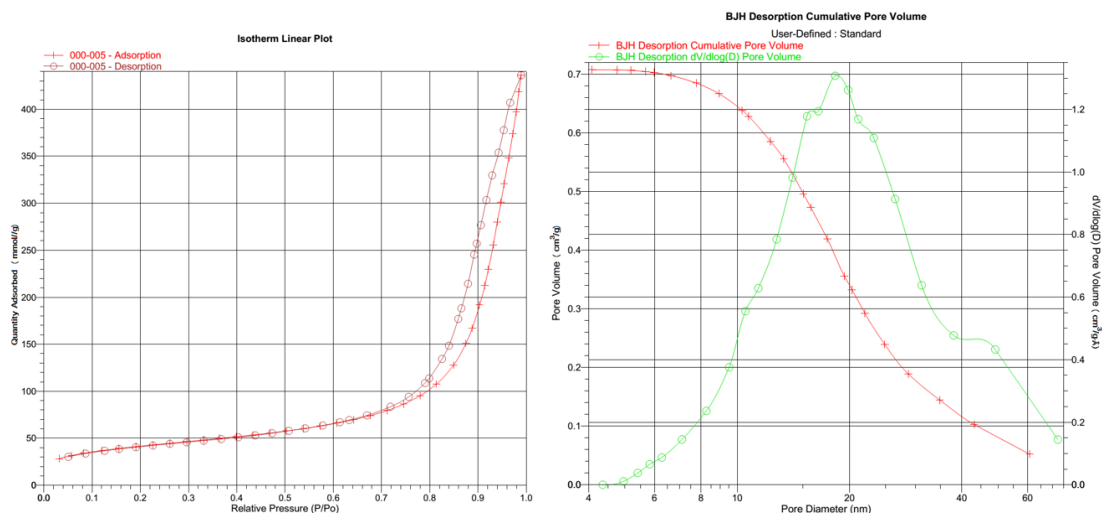
(The acid amount of  $\text{Al}_{11.6}\text{PO}_{23.7}$  and  $\text{Al}_{1.1}\text{PO}_{4.2}$  are 1.211 mmol/g and 0.295 mmol/g respectively; The base amount of  $\text{Al}_{11.6}\text{PO}_{23.7}$  and  $\text{Al}_{1.1}\text{PO}_{4.2}$  are 0.705 mmol/g and 0.2444 mmol/g respectively)

**Table S1.** The ratio of L and B acid amount results of different mole ratio of Al and P Aluminum phosphate catalyst

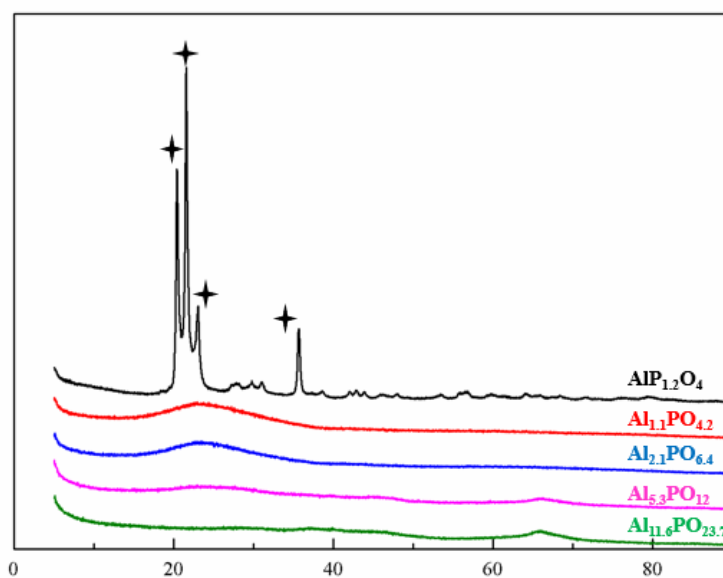
Catalyst	Temperature (K)	Acid amount ( $\mu\text{mol/g}$ )	L/B
$\text{AlP}_{1.2}\text{O}_4$	313	114.77	13.55
	433	18.577	1.97
$\text{Al}_{1.1}\text{PO}_{4.2}$	313	425.86	34.87
	433	233.01	9.01
$\text{Al}_{2.1}\text{PO}_{6.4}$	313	489.69	200.32
	433	104.99	32.28
$\text{Al}_{11.6}\text{PO}_{23.7}$	313	707.30	82.84
	433	123.71	56.49



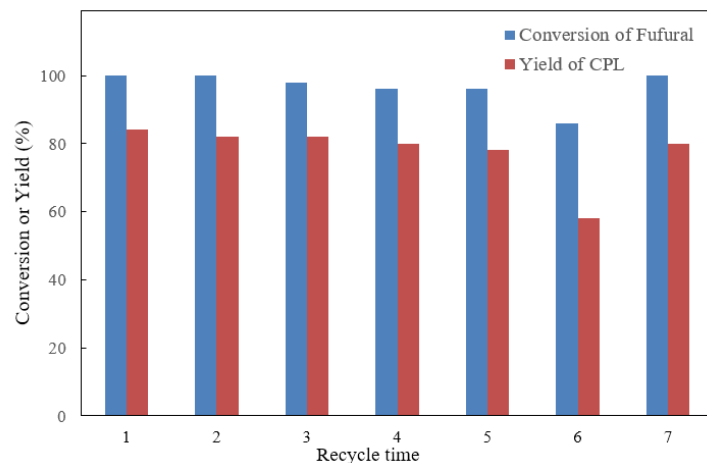
**Figure S3.** Scanning electron micrograph of  $\text{Al}_{11.6}\text{PO}_{23.7}$  and transmission electron micrograph of  $\text{Al}_{11.6}\text{PO}_{23.7}$ .



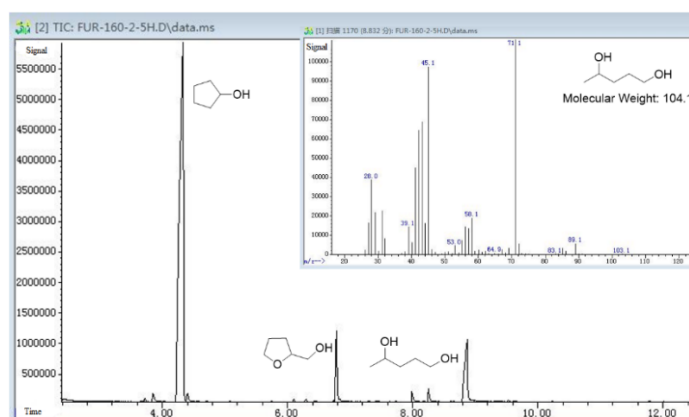
**Figure S4.** (Left)  $N_2$  adsorption isotherm of  $Al_{11.6}PO_{23.7}$ ; (Right) BJH pore size distribution of  $Al_{11.6}PO_{23.7}$ . The BET surface area, average pore size and total pore volume of  $Al_{11.6}PO_{23.7}$  were  $146.7 \text{ m}^2/\text{g}$ ,  $14.7 \text{ nm}$ ,  $0.539 \text{ cm}^3/\text{g}$  respectively.



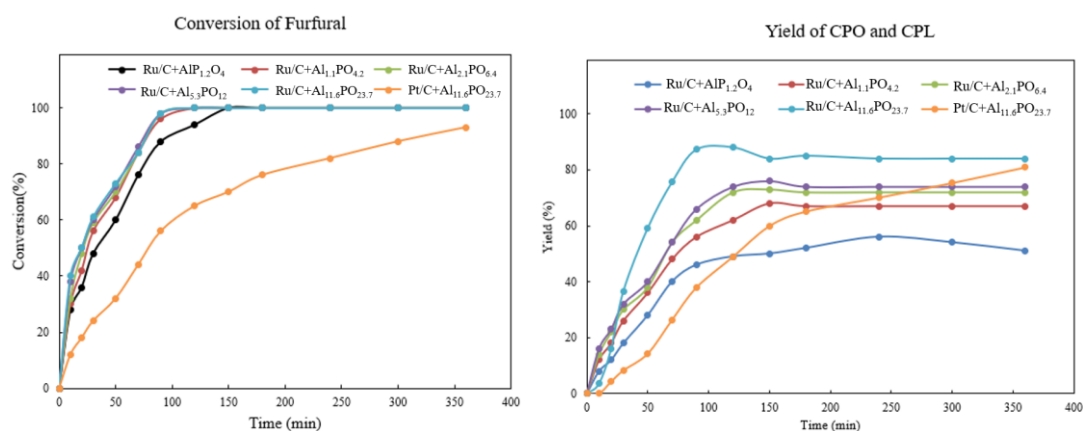
**Figure S5.** XRD pattern of different mole ratio of Al and P aluminum phosphate catalysts. The XRD of  $AIP_{1.2}O_4$  has the crystal morphology, and the length of a, b, c was  $9.638 \text{ \AA}$ ,  $8.664 \text{ \AA}$ ,  $18.280 \text{ \AA}$ . The XRD of  $Al_{1.1}PO_{4.2}$ ,  $Al_{2.1}PO_{6.4}$ ,  $Al_{5.3}PO_{12}$ ,  $Al_{11.6}PO_{23.7}$  were amorphous.



**Figure S6.** Recycling of the Ru/C and  $\text{Al}_{11.6}\text{PO}_{23.7}$  catalyst for the hydrogenation reaction. Reaction conditions: furfural (20 mmol), Ru/C (0.25 g) and  $\text{Al}_{11.6}\text{PO}_{23.7}$  (0.25g) as the catalyst, 50 mL water as the solvent, 4 MPa  $\text{H}_2$ , reacted at 433 K for 4 h.

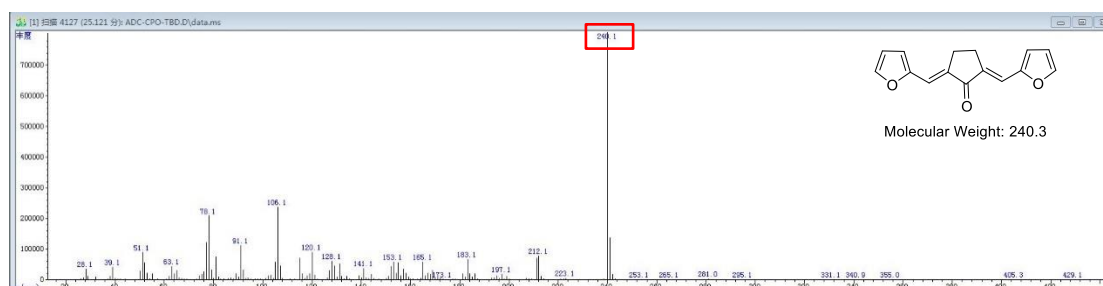
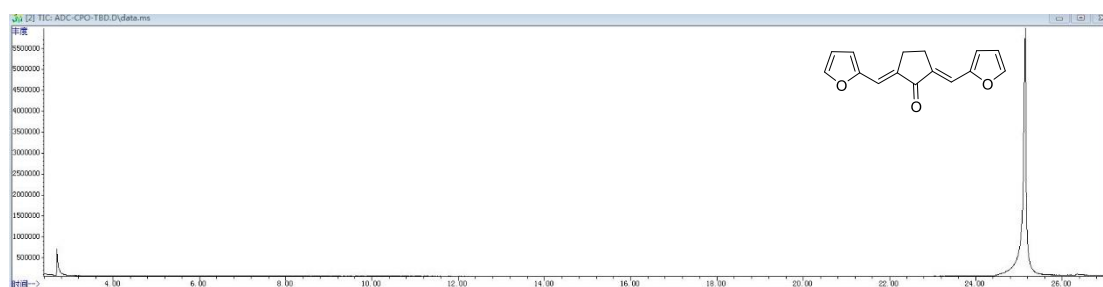


**Figure S7.** GC-MS result of furfural converted to CPO at the 6 MPa hydrogen pressure

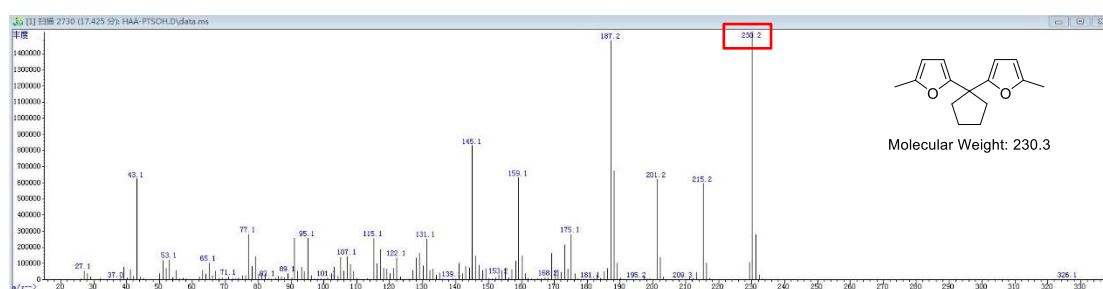
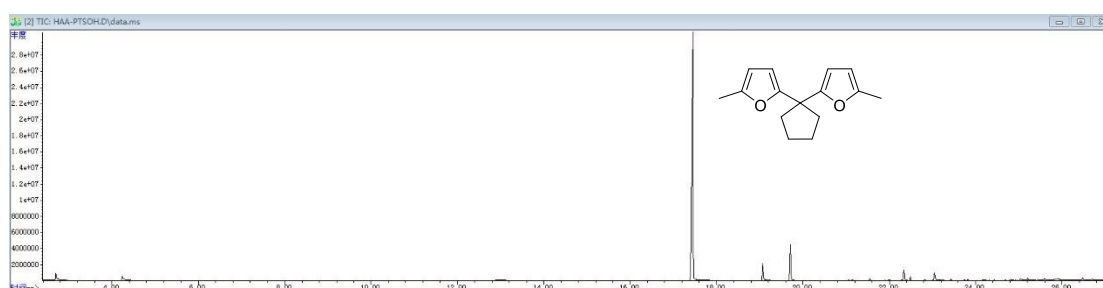


**Figure S8.** Kinetics results of different catalysts by the conversion of furfural and yield of CPO and CPL.

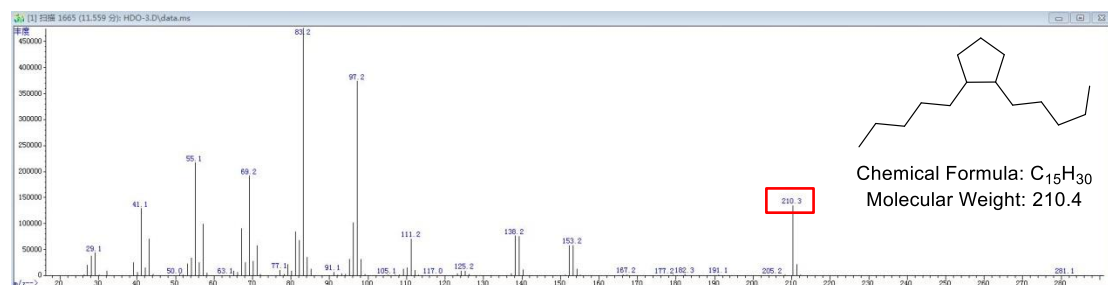
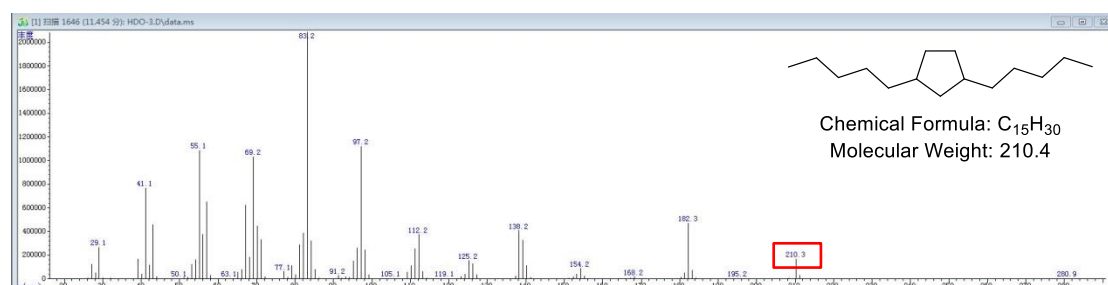
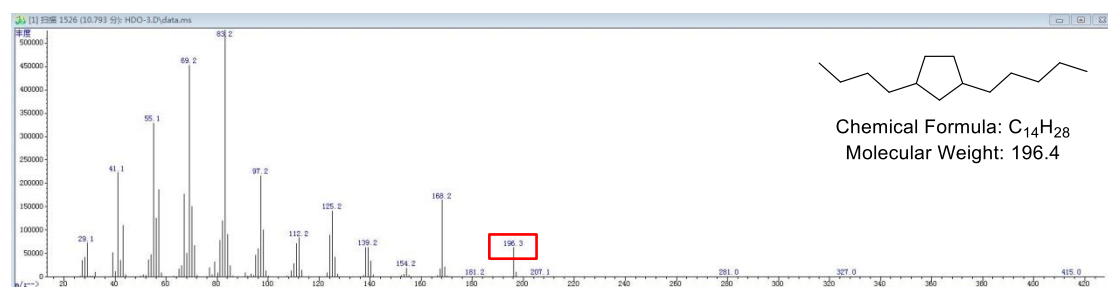
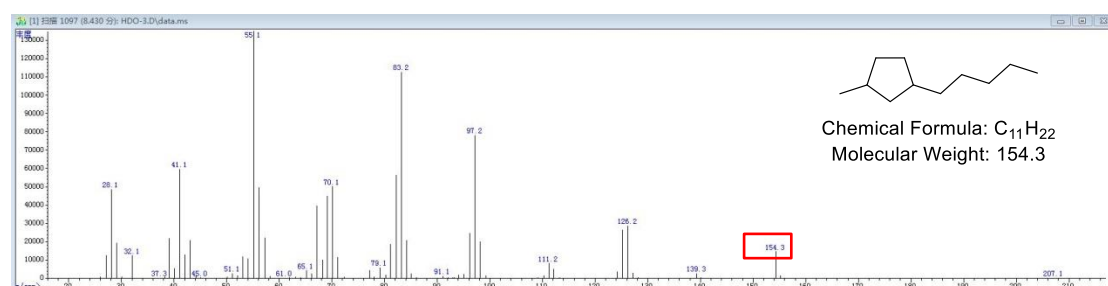
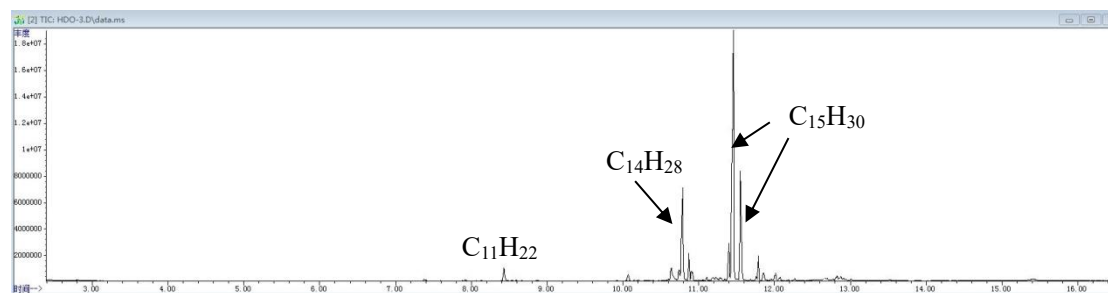




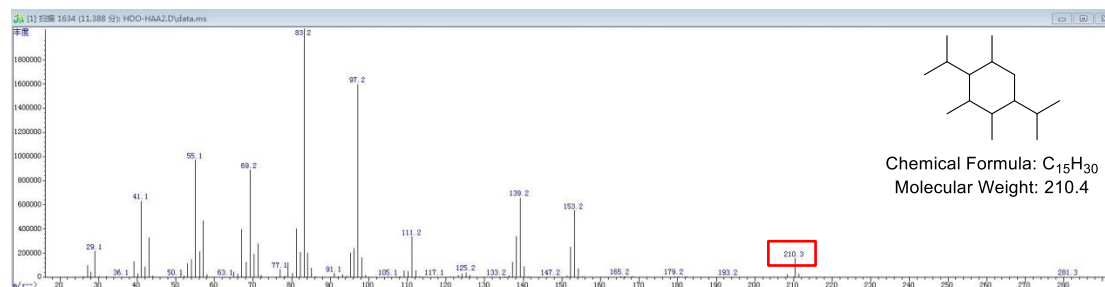
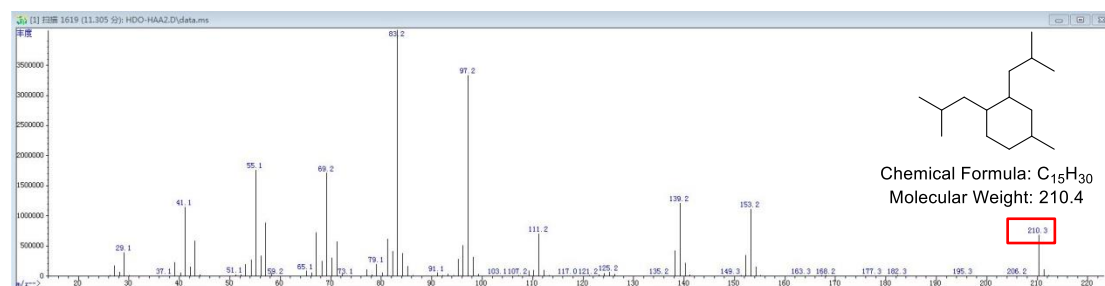
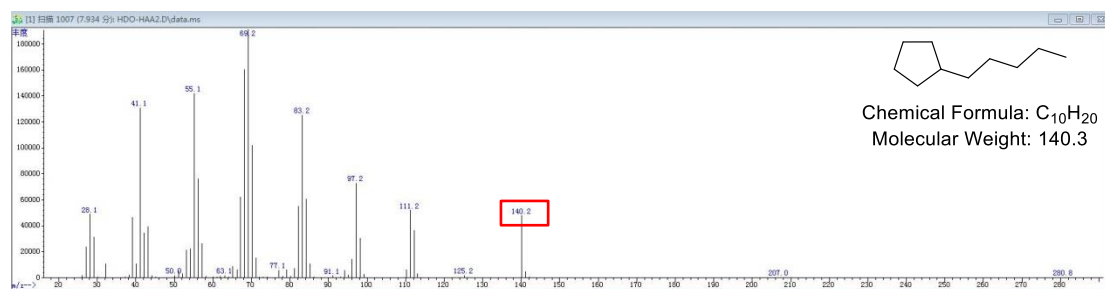
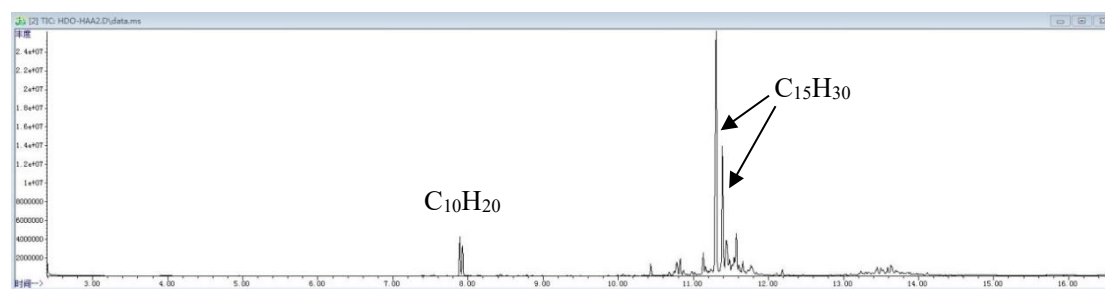
**Figure S9.** GC-MS Spectrum of the products identified from the reaction of furfural with CPO catalyzed by TBD.



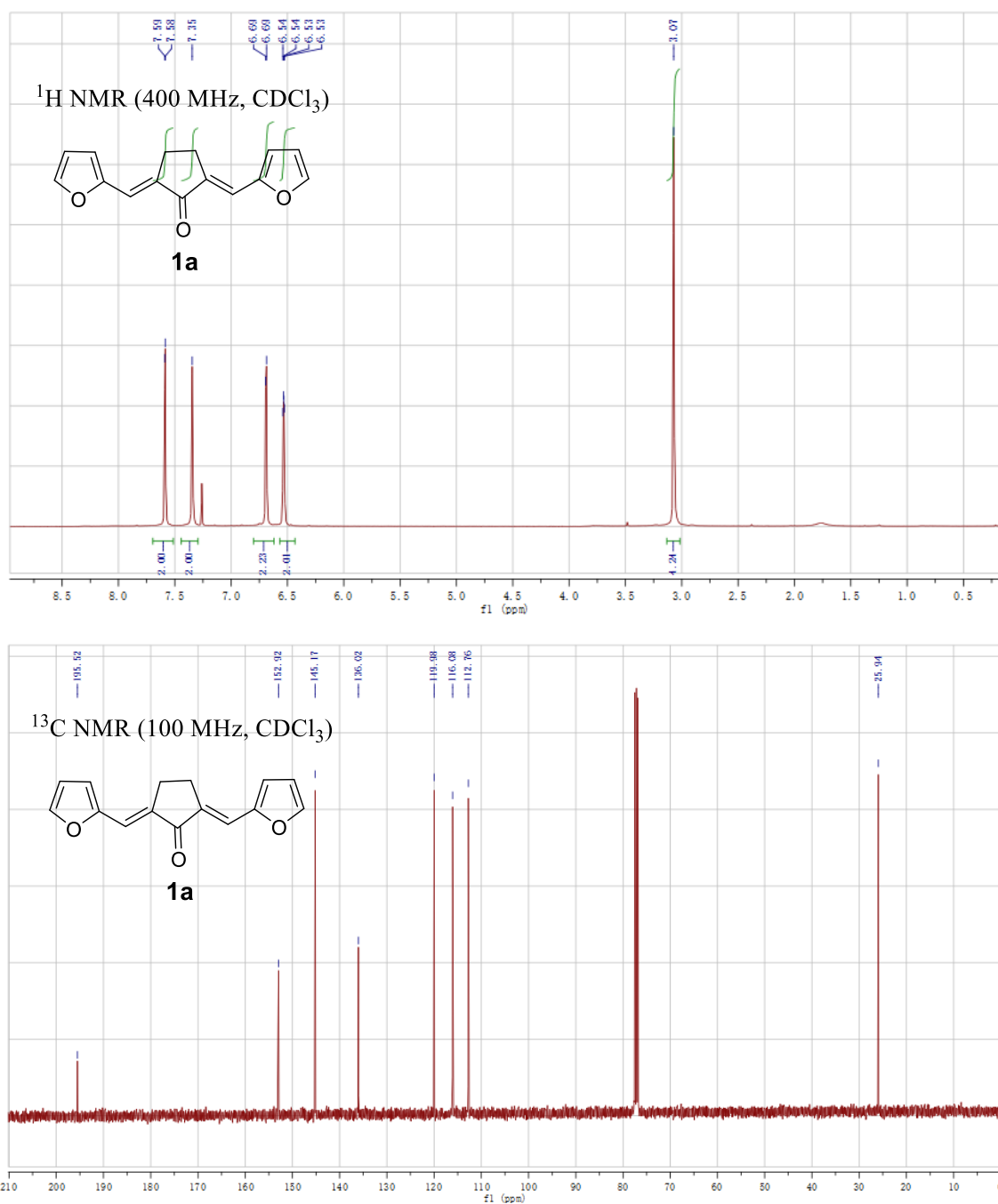
**Figure S10.** GC-MS Spectrum of the products identified from the reaction of CPO with 2-methyl furan catalyzed by *para*-toluene-sulfonic acid.



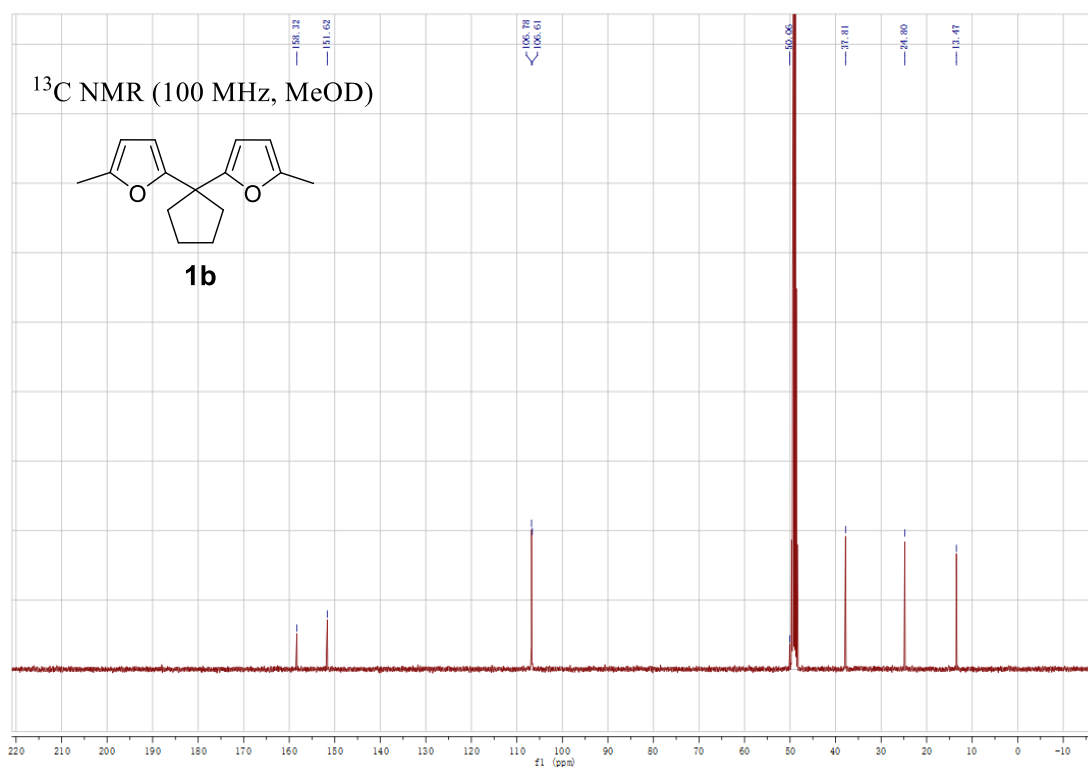
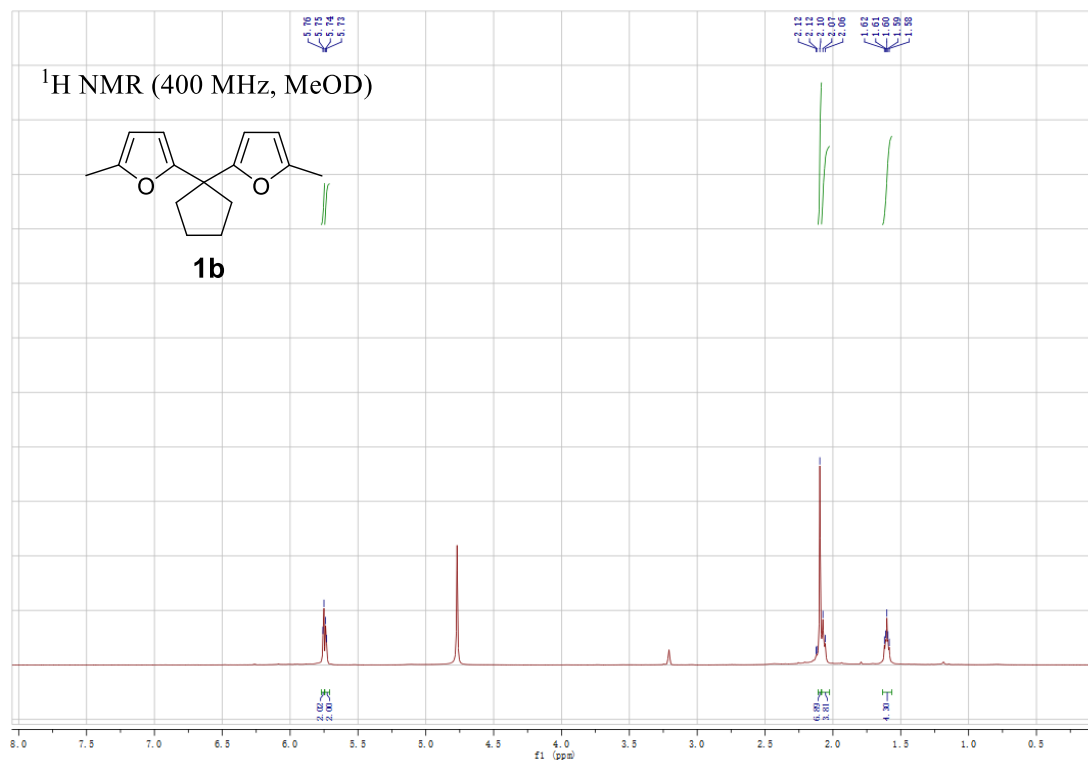
**Figure S11.** GC-MS spectrum of the products identified from the organic-phase products produced by HDO of **1a**. Inset graphics depict the structures of detected compounds based on NIST database.



**Figure S12.** GC-MS spectrum of the products identified from the organic-phase products produced by HDO of **1b**. Inset graphics depict the structures of detected compounds based on NIST database.



**Figure S13.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the aldol condensation product **1a** produced from CPO and furfural.



**Figure S14.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the hydroxyalkylation and alkylation product **1a** produced from CPO and 2-methyl furan.