

## Supporting Information

### **Production of liquid hydrocarbon fuels with 3-pentanone and platform molecules derived from lignocellulose**

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## 1. General methods

### 1.1 Characterization

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 mL  $\text{min}^{-1}$ . The temperature program was carried out as follows: initial temperature 50 $^\circ\text{C}$  for 5 min, then to 250 $^\circ\text{C}$  at 10 $^\circ\text{C}$   $\text{min}^{-1}$ , and maintained at 250 $^\circ\text{C}$  for 2 min. 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.

### 1.2 Materials

Zeolite catalysts (H-Beta) were purchased from The Catalyst Plant of Nankai University. Ionic liquid  $[\text{H}_3\text{N}^+-\text{CH}_2-\text{CH}_2-\text{OH}][\text{CH}_3\text{COO}^-]$  (EAIL) and  $[\text{H}_3\text{N}^+-\text{CH}_2-\text{CH}_2-\text{OH}][\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]$  (LAIL) were prepared using our previous method.<sup>1</sup> Amorphous aluminium phosphate (ALPO) was prepared according to a reported procedure.<sup>2</sup> Pd/C (5 wt%) and Pt/C (5 wt%) catalysts used in HDO step were purchased from Aladdin company. NbOPO<sub>4</sub>, TaOPO<sub>4</sub>, and ZrP were prepared according to reported procedures.<sup>3,4,5</sup> Other reagents were ACS reagent grade and used without further purification unless stated otherwise.

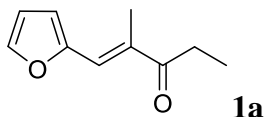
## 2. Experimental

### 2.1 Aldol condensation of 3-pentanone with furfural, HMF or 5-MF

Generally, to a solution of 3-pentanone (10 mmol, 0.86 g) and furan aldehyde (10~30 mmol) was added catalyst (3 mmol for organic base, 1.8 g for NaOH, and 0.15 g for ionic liquid). The mixture was stirred at 80 $^\circ\text{C}$  or room temperature for several hours while checking the reaction progress by using gas or thin-layer chromatography. After

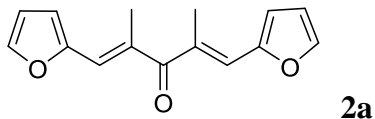
completion, the mixture was diluted with EtOAc, the obtained organic layer was evaporated and purified by column chromatography to provide the analytically pure product for further characterization.

### 1-(furan-2-yl)-2-methylpent-1-en-3-one



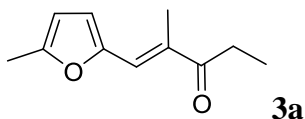
Reaction of 3-pentanone (10 mmol, 0.86 g) and furfural (10 mmol, 0.96 g) at room temperature under solvent-free condition catalyzed by DBU (1 mmol, 0.15 g) according to the general procedure afforded 1.49 g (92%) of product **1a**, isolated as pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.64 (d,  $J = 1.4$  Hz, 1H), 7.32 (s, 1H), 6.73 (d,  $J = 3.5$  Hz, 1H), 6.55 (dd,  $J = 3.4, 1.8$  Hz, 1H), 2.74 (q,  $J = 7.3$  Hz, 2H), 2.07 (s, 3H), 1.07 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  203.7, 153.2, 146.0, 134.0, 127.0, 116.8, 113.5, 31.3, 13.4, 9.4.

### 1,5-di(furan-2-yl)-2,4-dimethylpenta-1,4-dien-3-one



Reaction of 3-pentanone (10 mmol, 0.86 g) and furfural (25 mmol, 2.4 g) at  $80^\circ\text{C}$  under solvent-free condition catalyzed by DBU (3 mmol, 0.45 g). After reaction, the mixture were purified by column chromatography to provide the analytically pure product for further characterization afforded 2.20 g (91%) of product **2a**, isolated as pale yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.71 (t,  $J = 4.6$  Hz, 2H), 7.00 (s, 2H), 6.77 (d,  $J = 3.4$  Hz, 2H), 6.61 (dd,  $J = 3.3, 1.8$  Hz, 2H), 2.27 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  202.7, 152.9, 145.7, 134.1, 127.8, 116.0, 113.3, 15.3.

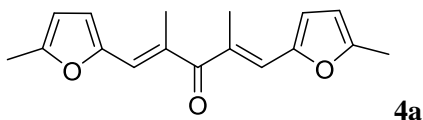
### 2-methyl-1-(5-methylfuran-2-yl)pent-1-en-3-one



Reaction of 3-pentanone (10 mmol, 0.86 g) and 5-methylfurfural (10 mmol, 1.10g) at

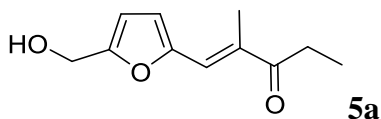
room temperature under solvent-free condition catalyzed by DBU (1 mmol, 0.15 g) according to the general procedure afforded 1.60 g (90%) of product **3a**, isolated as pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 (s, 1H), 6.46 (d,  $J = 3.3$  Hz, 1H), 6.02 (d,  $J = 3.2$  Hz, 1H), 2.64 (q,  $J = 7.3$  Hz, 2H), 2.24 (s, 3H), 2.01 (s, 3H), 1.03 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.8, 154.8, 150.6, 131.9, 125.7, 116.8, 109.0, 30.4, 13.9, 13.1, 9.1.

#### 2,4-dimethyl-1,5-bis(5-methylfuran-2-yl)penta-1,4-dien-3-one



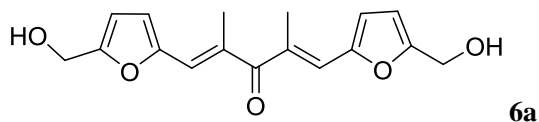
Reaction of 3-pentanone (10 mmol, 0.86 g) and 5-methylfurfural (25 mmol, 2.75 g) at  $80^\circ\text{C}$  under solvent-free condition catalyzed by DBU (3 mmol, 0.45 g), After reaction, the mixture were purified by column chromatography to provide the analytically pure product for further characterization afforded 2.29 g (85%) of product **4a**, isolated as yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  6.87 (s, 2H), 6.60 (d,  $J = 3.2$  Hz, 2H), 6.17 (d,  $J = 2.7$  Hz, 2H), 2.33 (s, 6H), 2.17 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  202.9, 156.1, 151.5, 132.6, 128.1, 117.6, 109.8, 32.7, 23.7.

#### 1-(5-(hydroxymethyl)furan-2-yl)-2-methylpent-1-en-3-one



Reaction of 3-pentanone (10 mmol, 0.86 g) and 5-hydroxymethylfurfural (10 mmol, 1.26 g) at room temperature under solvent-free condition catalyzed by DBU (1 mmol, 0.15 g) according to the general procedure afforded 1.68 g (87 %) of product **5a**, isolated as pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.40 (s, 1H), 6.77 (d,  $J = 3.4$  Hz, 1H), 6.49 (d,  $J = 3.4$  Hz, 1H), 4.58 (s, 3H), 2.83 (q,  $J = 7.3$  Hz, 2H), 2.14 (d,  $J = 0.9$  Hz, 3H), 1.11 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  204.7, 158.7, 152.9, 133.8, 127.5, 118.2, 111.2, 57.7, 31.5, 13.4, 9.5.

### 1,5-bis(5-(hydroxymethyl)furan-2-yl)-2,4-dimethylpenta-1,4-dien-3-one

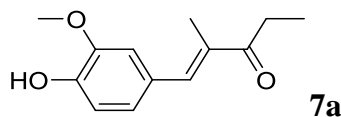


Reaction of 3-pentanone (10 mmol, 0.86 g) and 5-hydroxymethylfurfural (25 mmol, 3.15 g) at 80 °C under solvent-free condition catalyzed by DBU (3mmol, 0.45 g), After reaction, the mixture were purified by column chromatography to provide the analytically pure product for further characterization afforded 2.22 g (73%) of product **6a**, isolated as yellow solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 6.95 (s, 2H), 6.70 (d, *J* = 3.3 Hz, 2H), 6.47 (d, *J* = 3.3 Hz, 2H), 4.58 (s, 4H), 2.23 (s, 6H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 202.7, 158.2, 152.5, 133.1, 128.0, 117.1, 110.0, 57.6, 15.5.

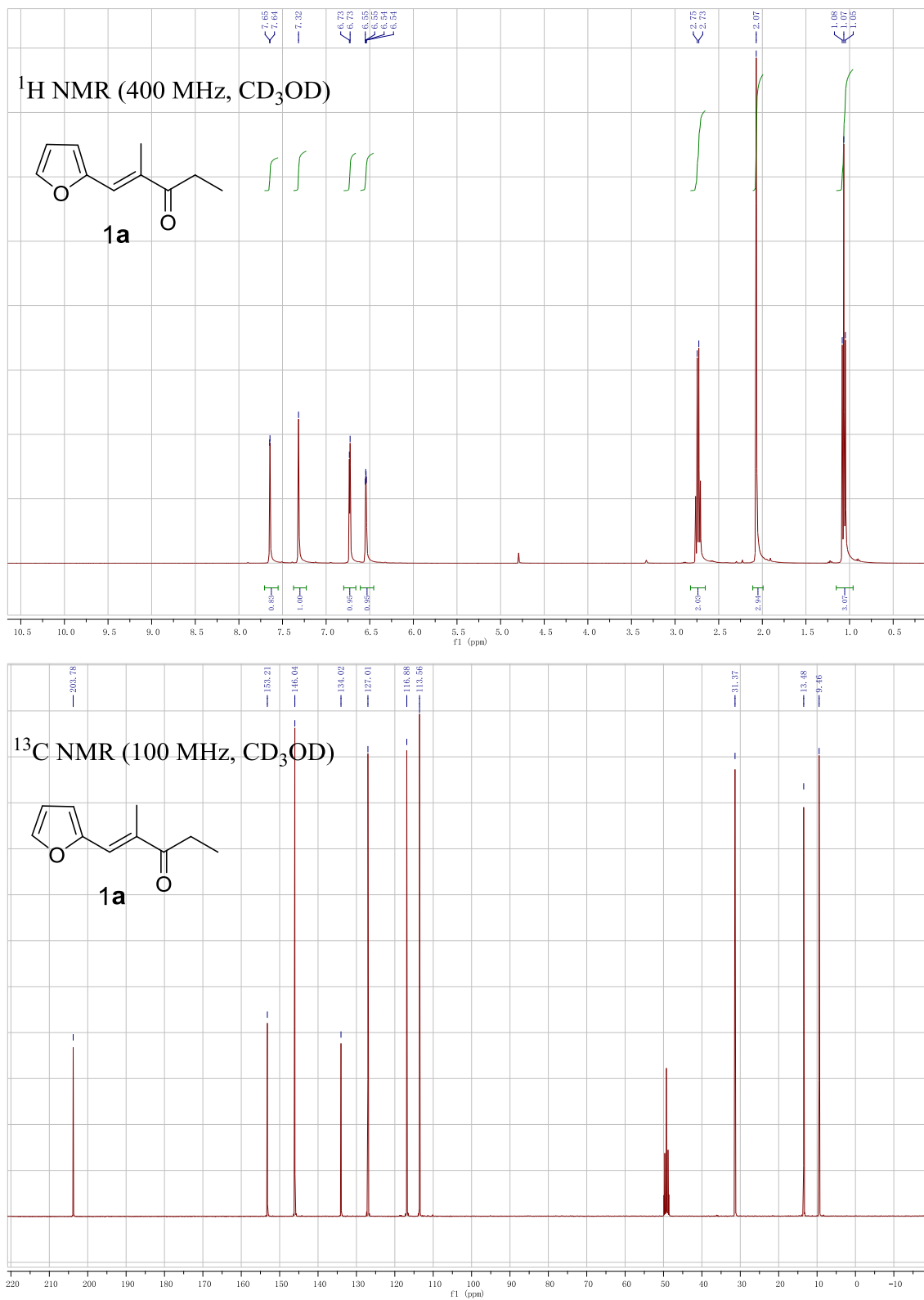
### 2.2 Aldol condensation of 3-pentanone with vanillin

To a solution of 3-pentanone (20 mmol, 1.72 g) and vanillin (20 mmol, 3.1 g) was added amorphous aluminium phosphate (ALPO) (0.4 g) at 120 °C under solvent-free condition. After completion, the mixture was diluted with EtOAc and ALPO was removed by filtration. The obtained organic layer was evaporated and purified by column chromatography to afforded 2.82 g (64%) of product **7a**, isolated as white solid.

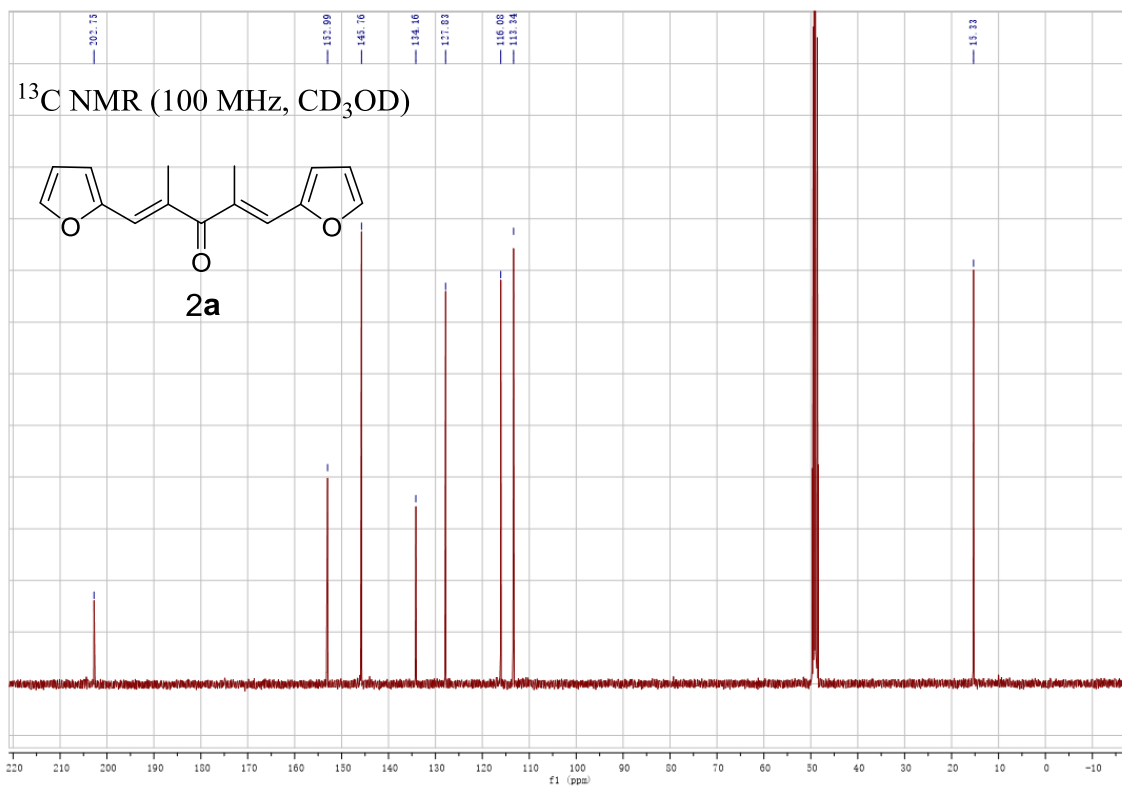
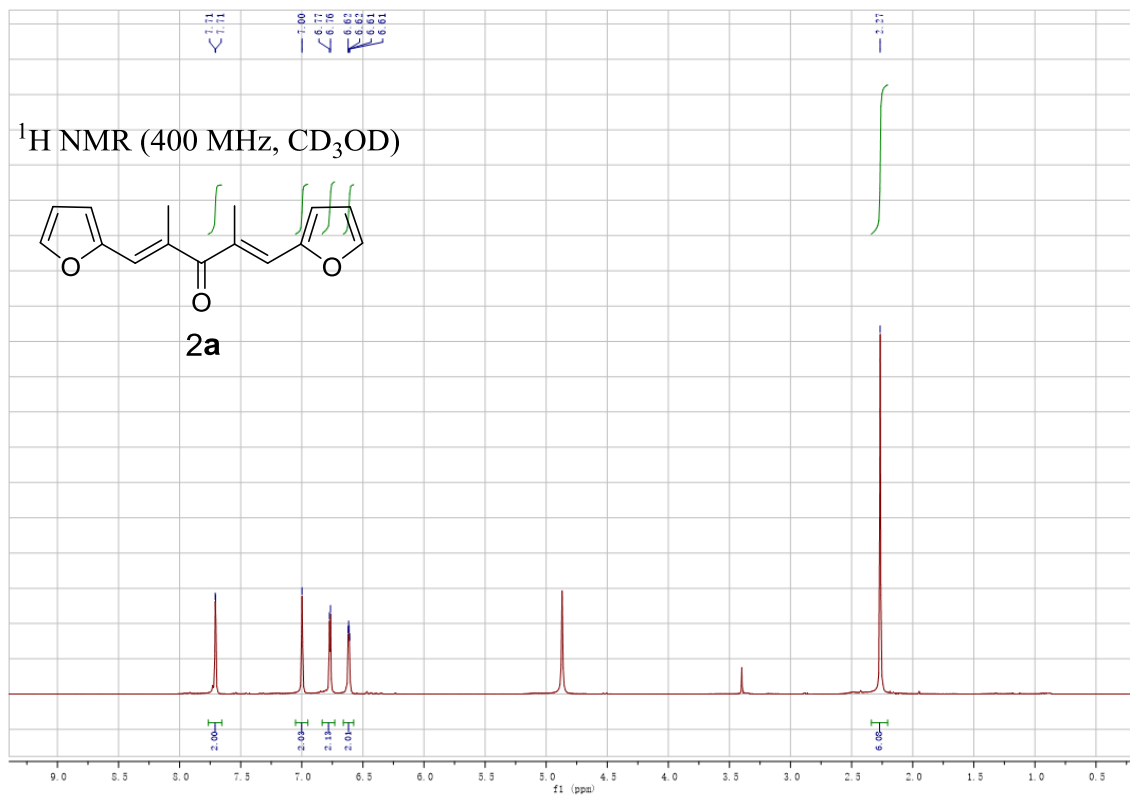
### 1-(4-hydroxy-3-methoxyphenyl)-2-methylpent-1-en-3-one



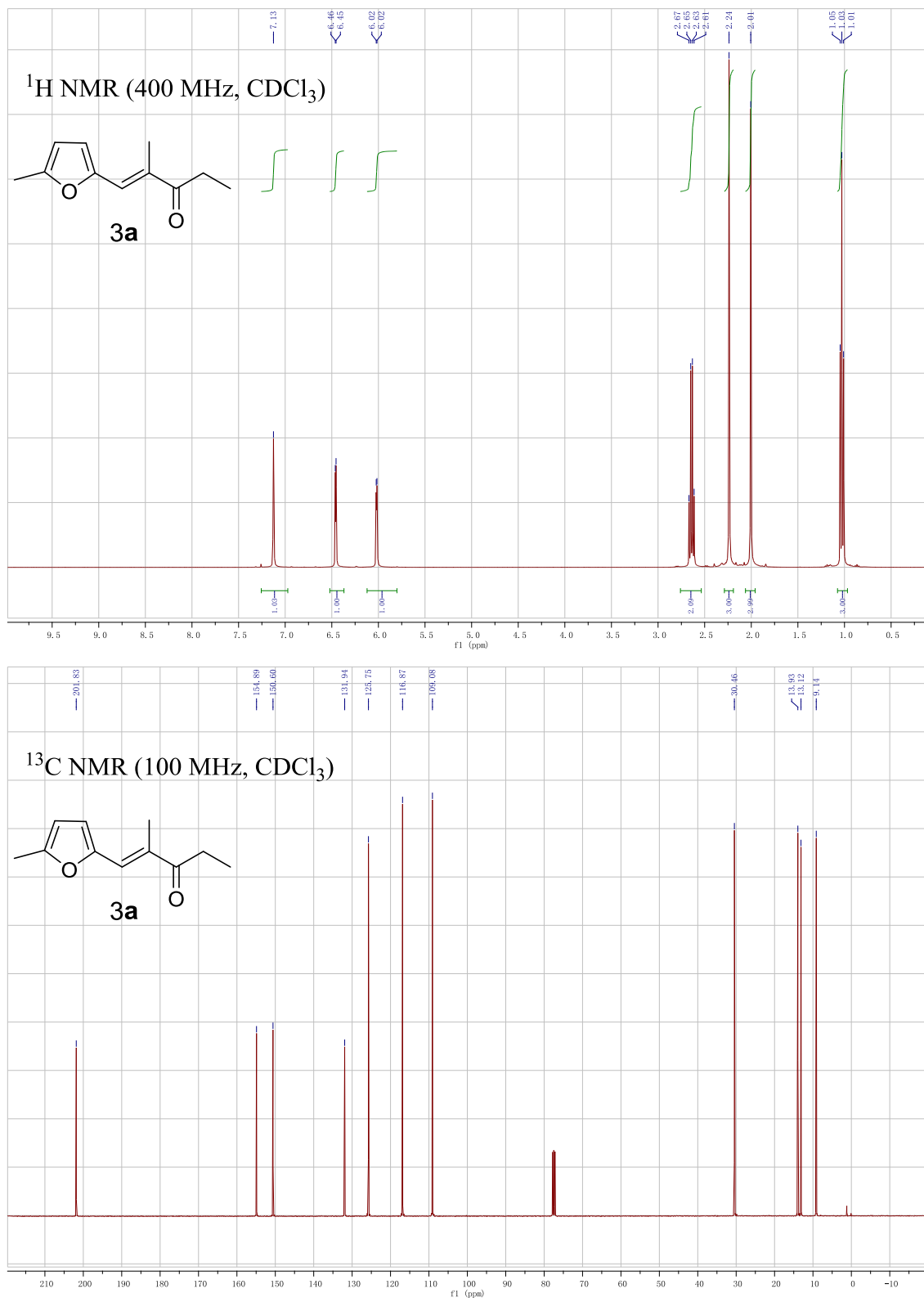
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (s, 1H), 6.91 (ddd, *J* = 8.2, 6.6, 2.5 Hz, 3H), 5.83 (s, 1H), 3.85 (s, 3H), 2.75 (q, *J* = 7.3 Hz, 2H), 2.02 (d, *J* = 1.3 Hz, 3H), 1.09 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.0, 146.4, 146.3, 138.6, 135.3, 128.4, 124.1, 114.6, 112.4, 56.0, 30.8, 13.3, 9.1.



**Fig. S1.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the single condensation product **1a** produced from furfural and 3-pentanone.

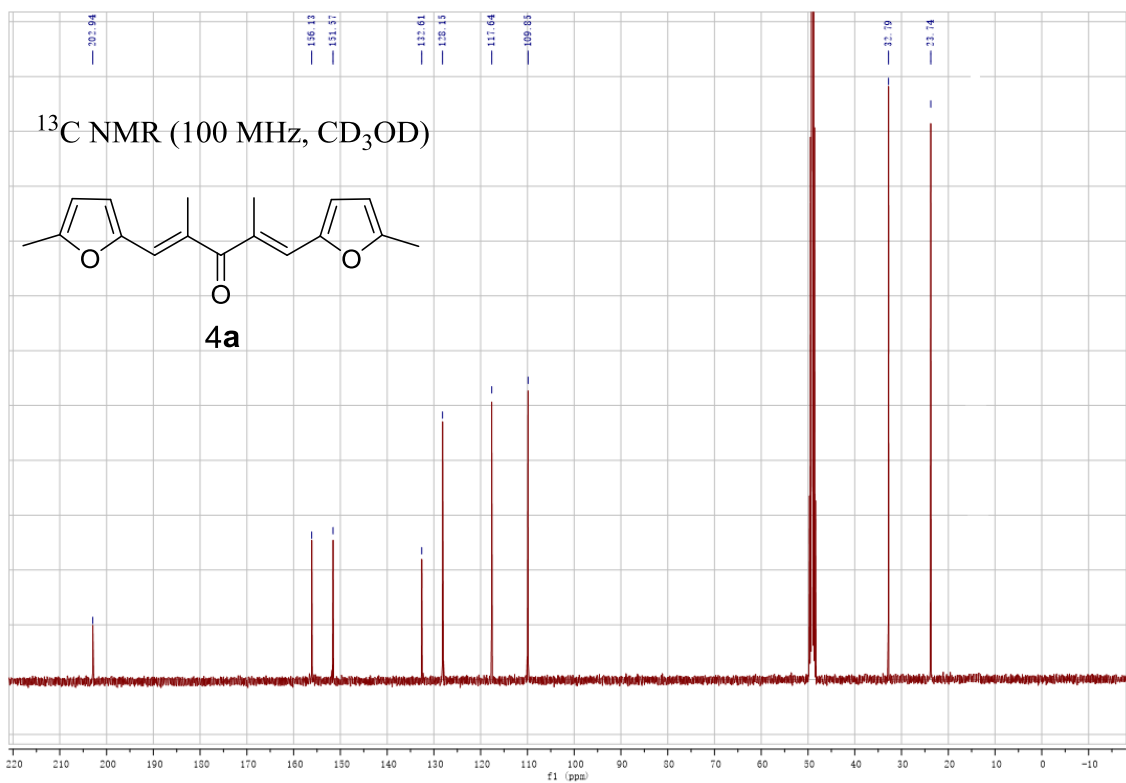
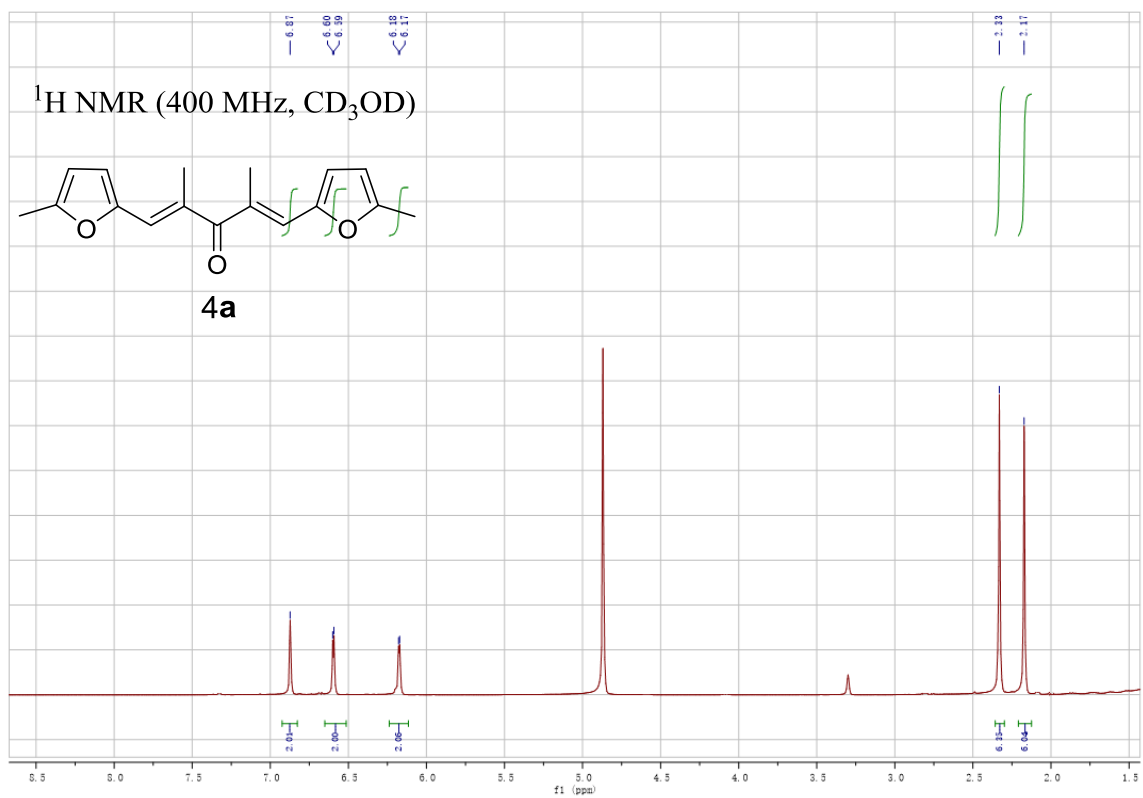


**Fig. S2.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the double condensation product **2a** produced from furfural and 3-pentanone.

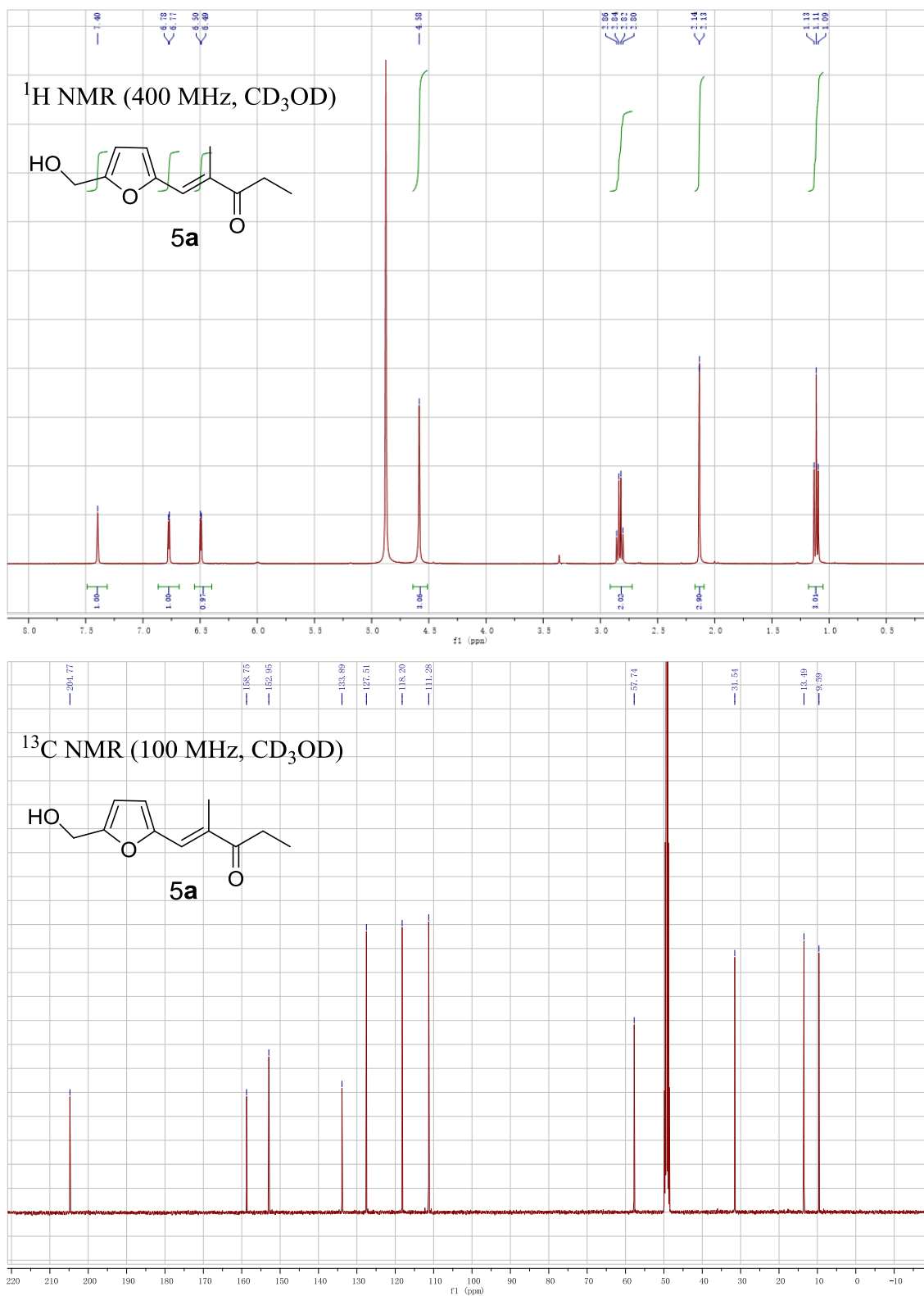


**Fig. S3.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the single condensation product **3a** produced from 5-MF and 3-pentanone.

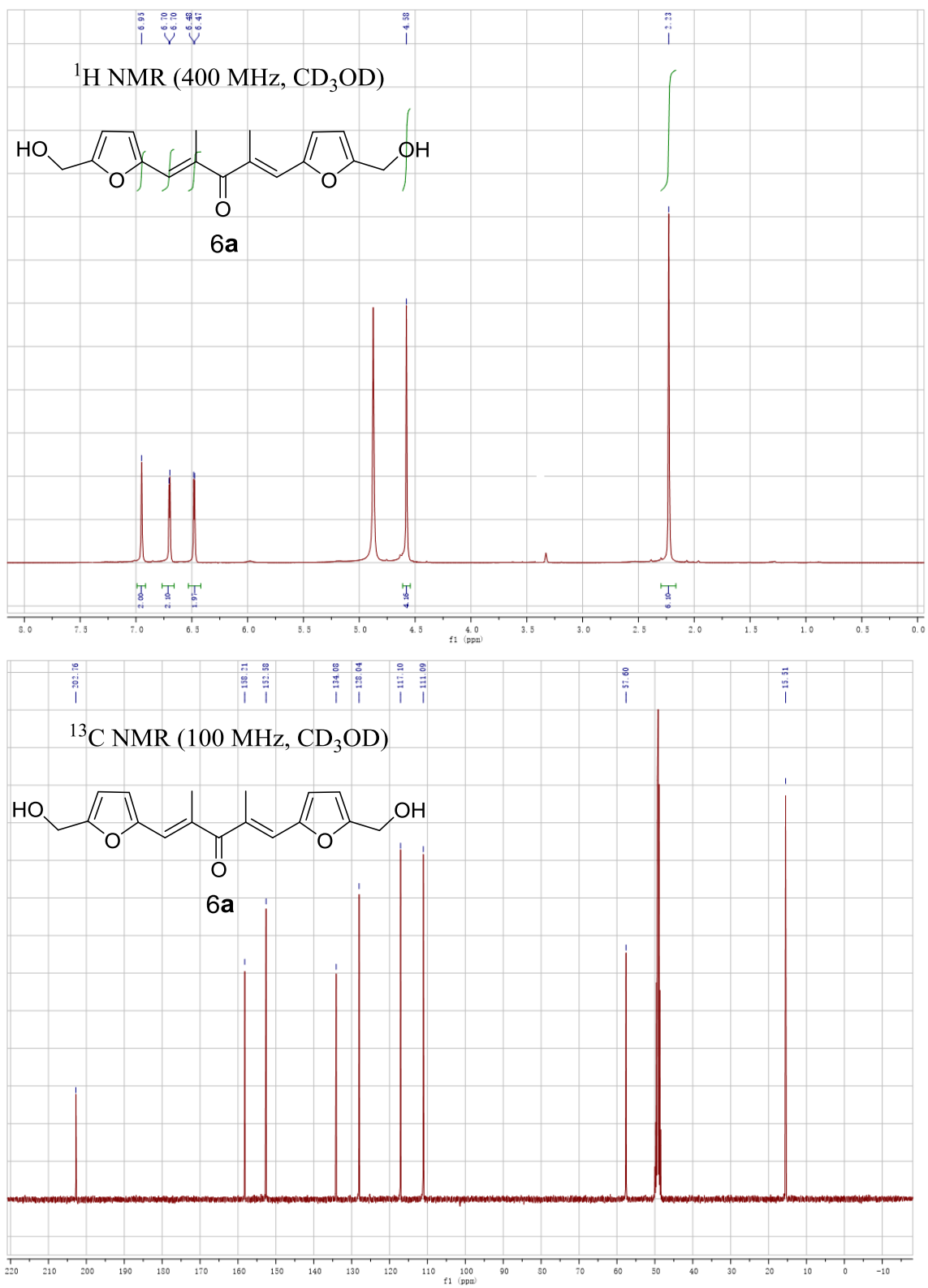




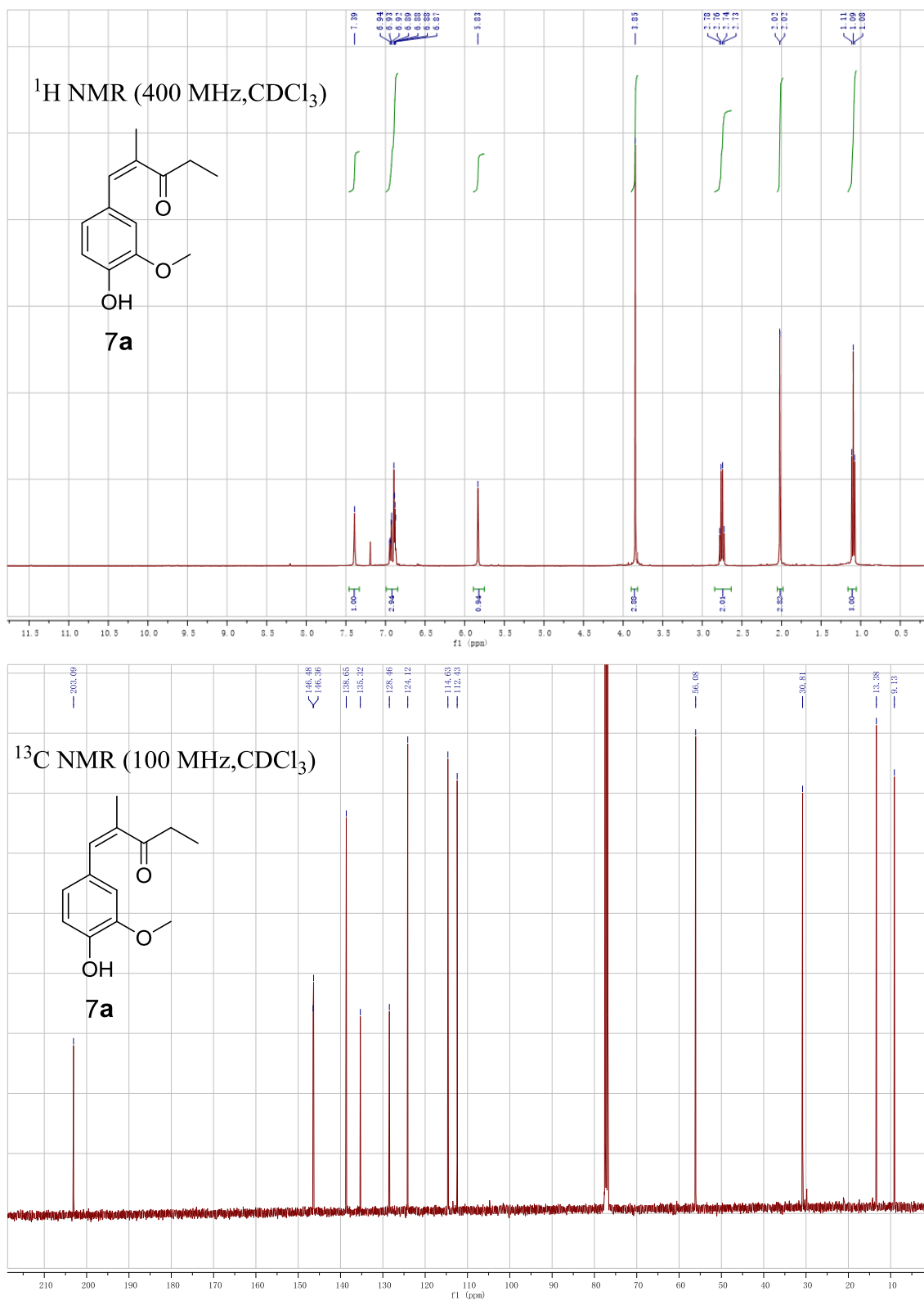
**Fig. S4.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the double condensation product **4a** produced from 5-MF and 3-pentanone.



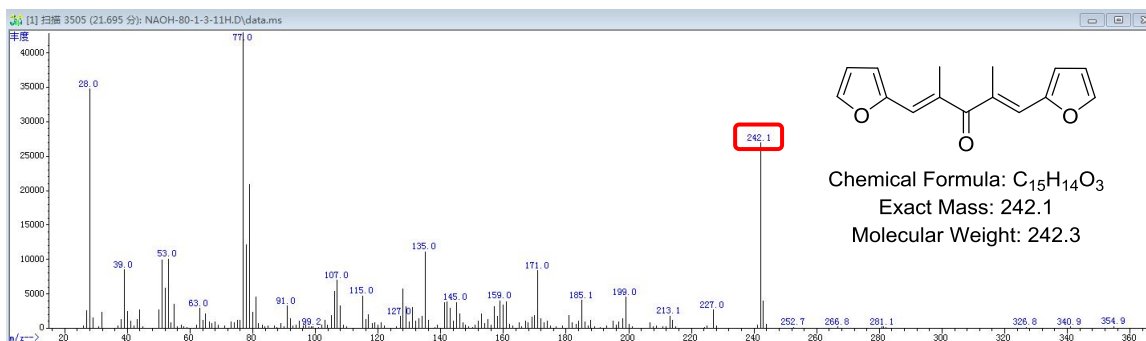
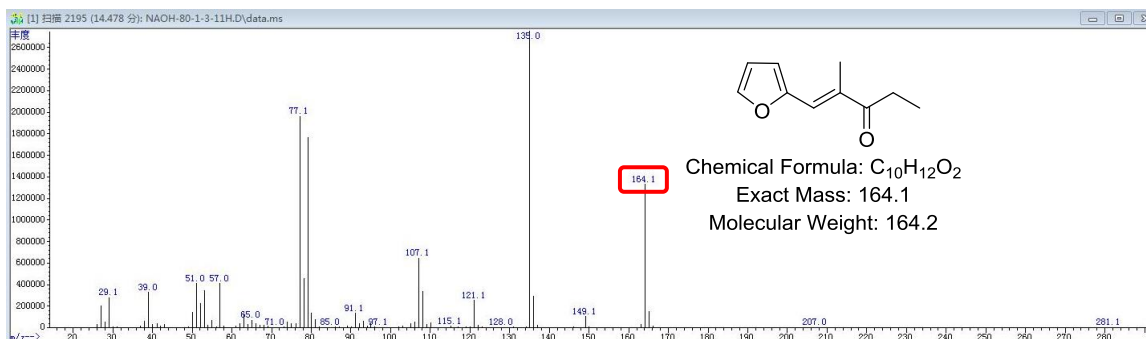
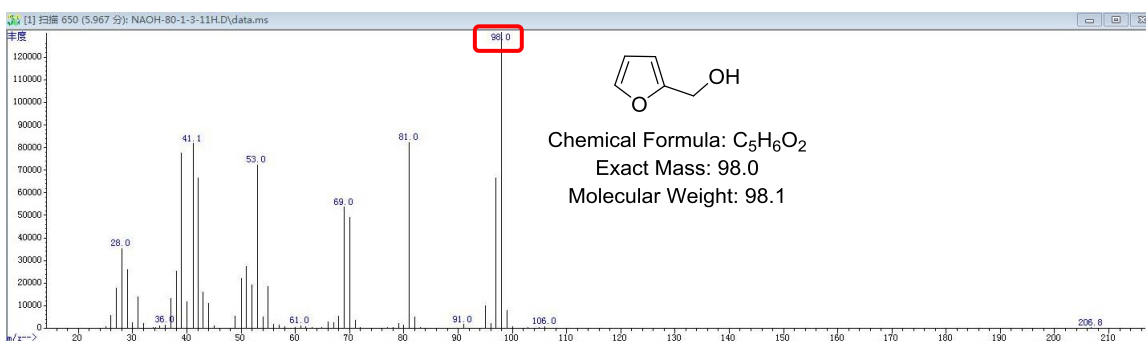
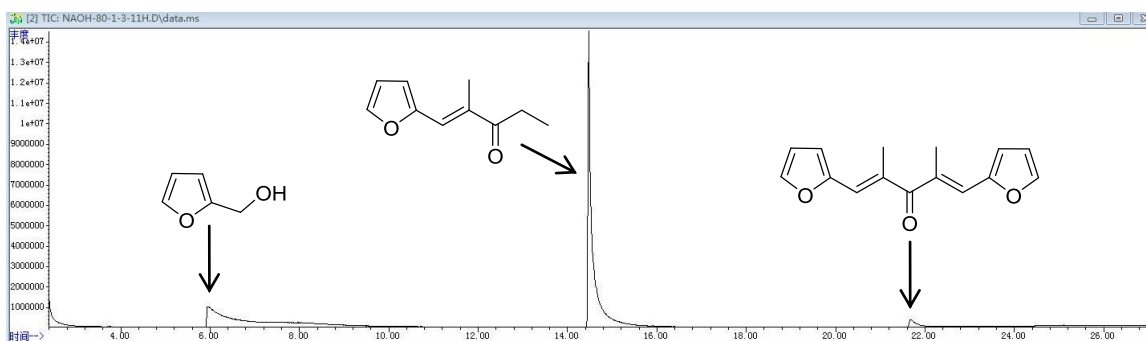
**Fig. S5.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the single condensation product **5a** produced from HMF and 3-pentanone.



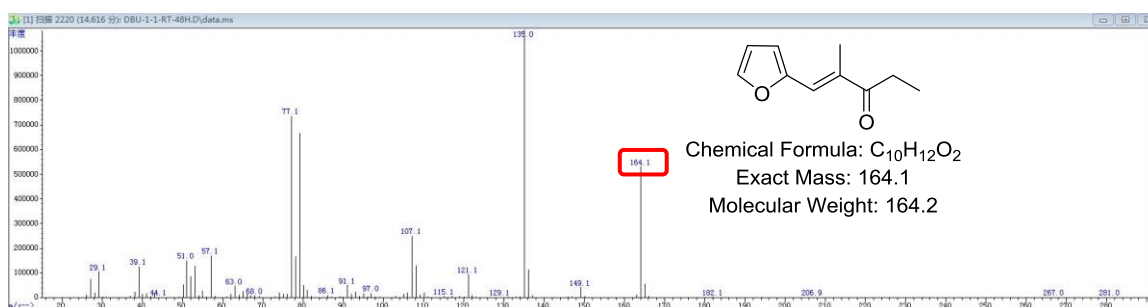
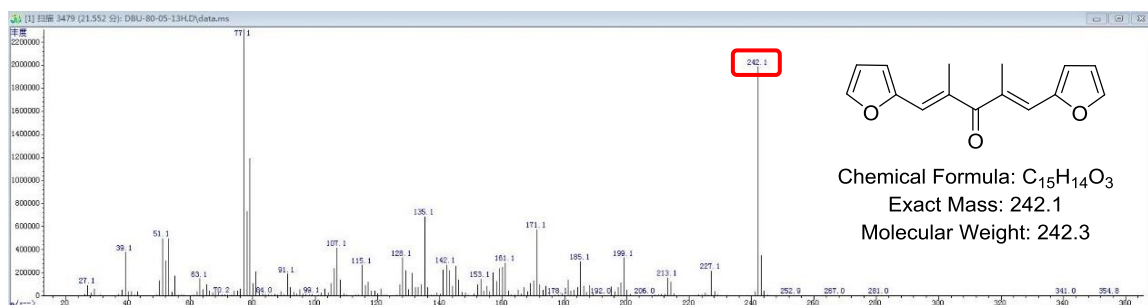
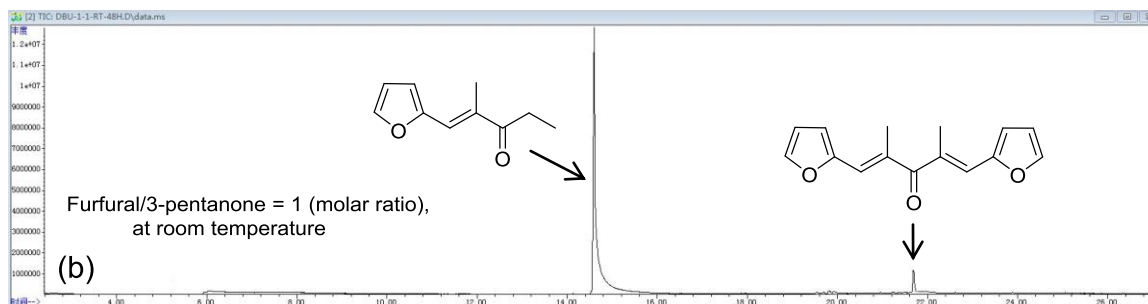
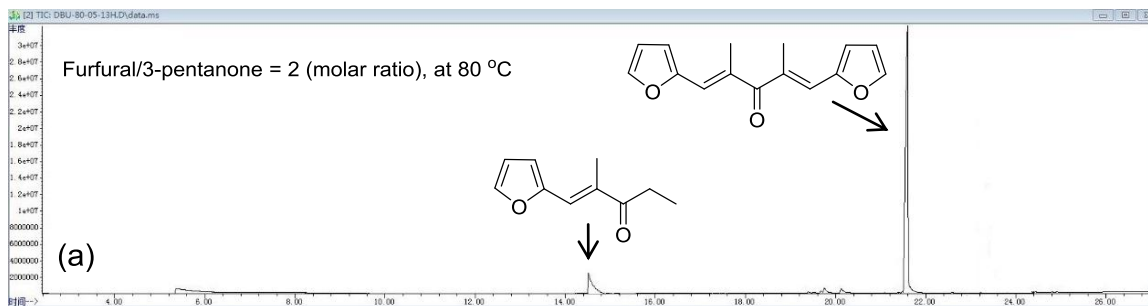
**Fig. S6.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the double condensation product **6a** produced from HMF and 3-pentanone.



**Fig. S7.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the single condensation product **7a** produced from vanillin and 3-pentanone.



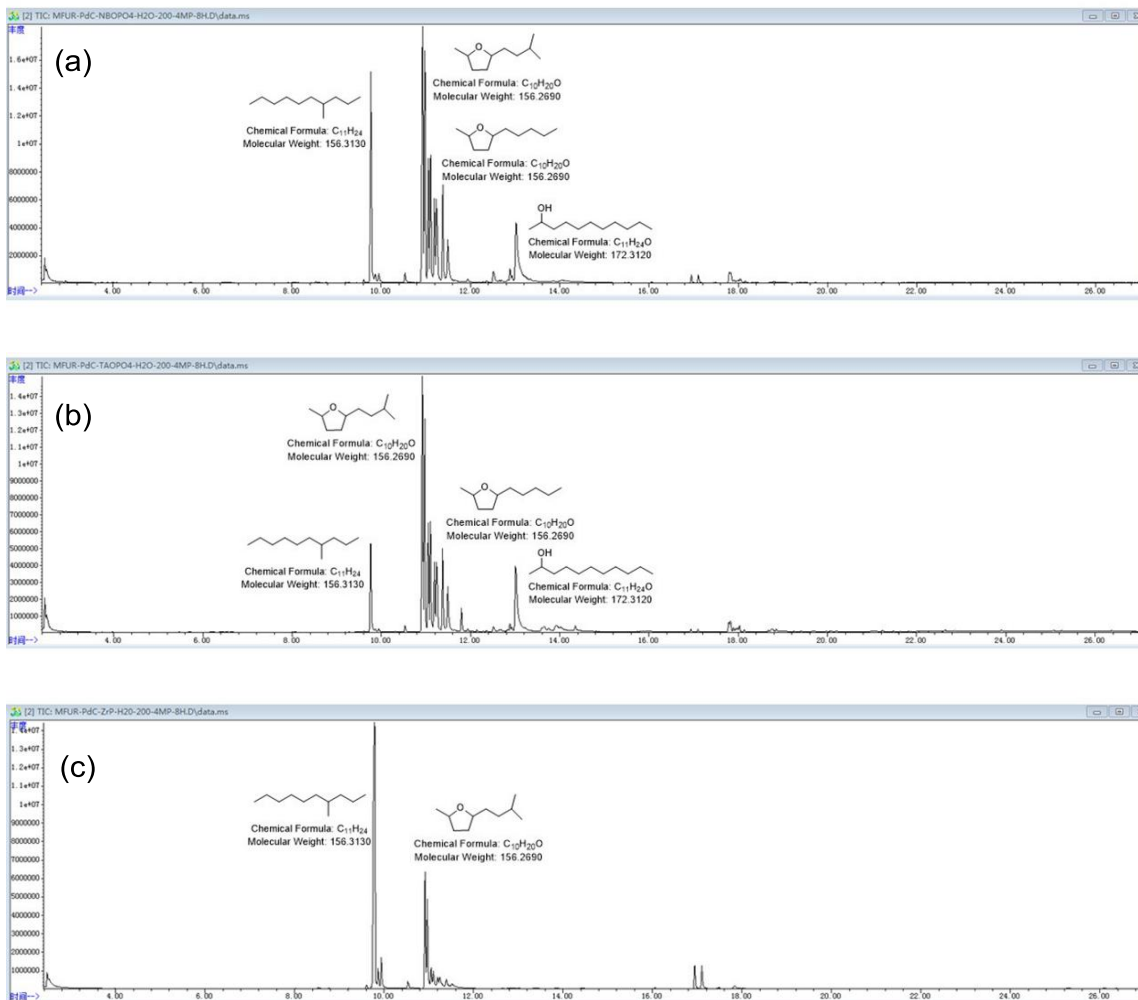
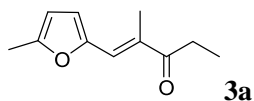
**Fig. S8.** GC-MS Spectrum of the products identified from the reaction of furfural with 3-pentanone catalyzed by NaOH.



**Fig. S9.** GC-MS Spectrum of the products identified from the reaction of furfural with 3-pentanone catalyzed by DBU.

## 2.3 Hydrodeoxygenation

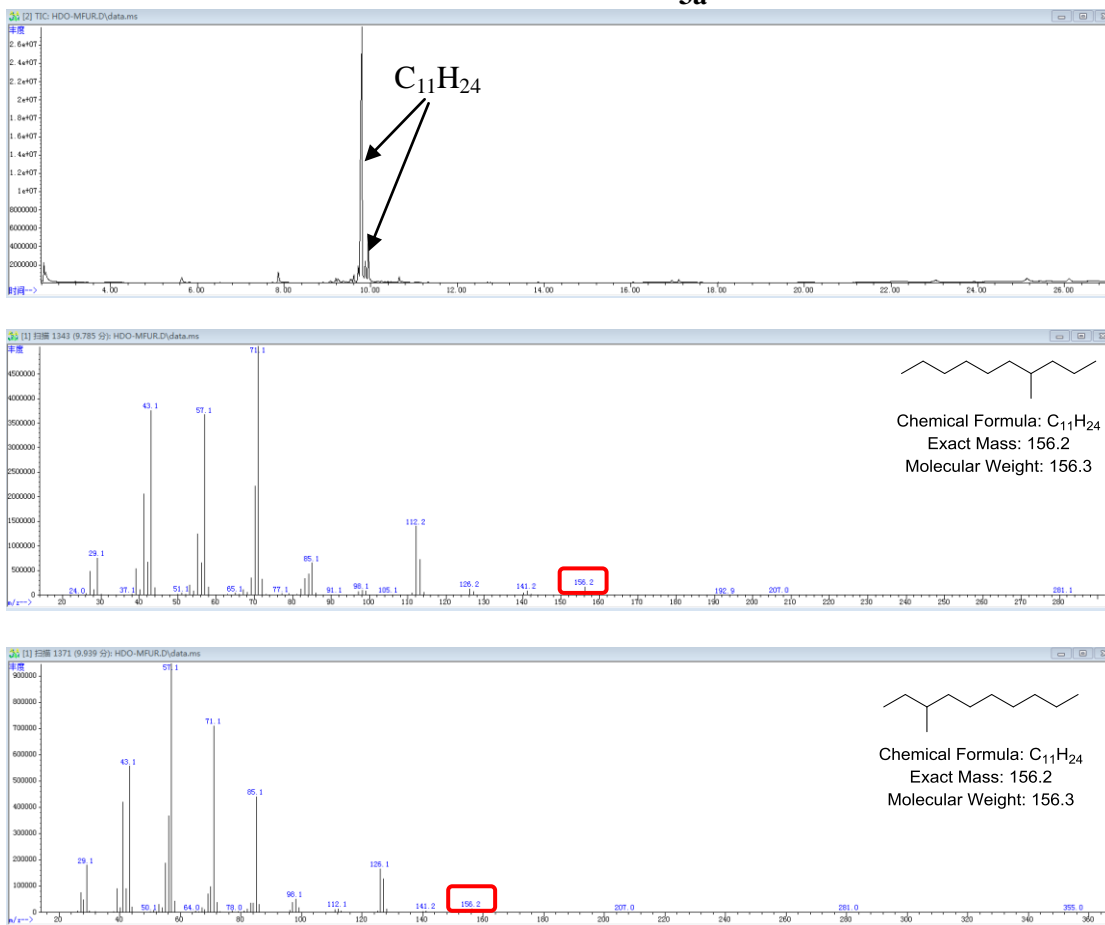
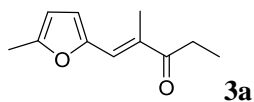
GC-MS spectrum of using NbOPO<sub>4</sub>, TaOPO<sub>4</sub>, and ZrP for the HDO of **3a**.



**Fig. S10.** GC-MS spectrum of the products identified from the organic-phase products produced by HDO of **3a**. Inset graphics depict the structures of detected compounds based on NIST database.

- (a) NbOPO<sub>4</sub> + Pd/C system;
- (b) TaOPO<sub>4</sub> + Pd/C system
- (c) ZrP + Pd/C system.

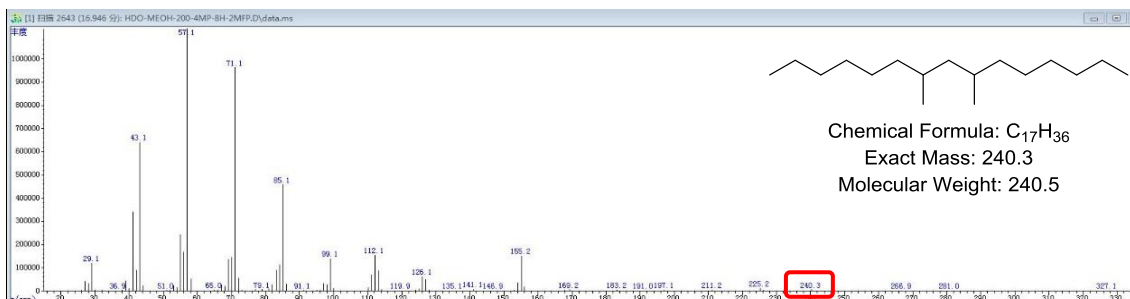
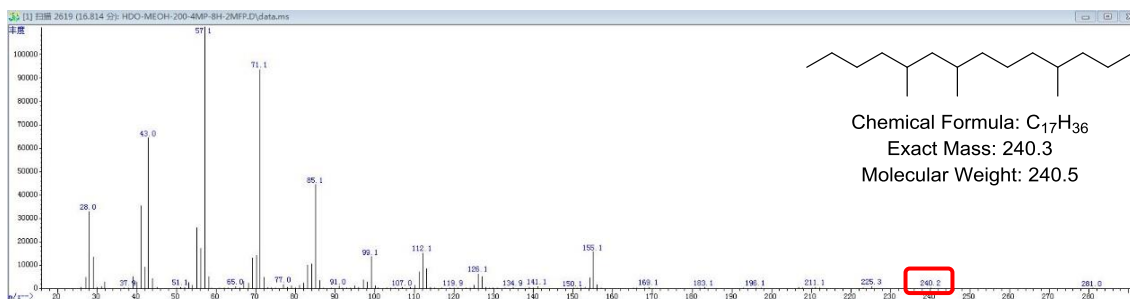
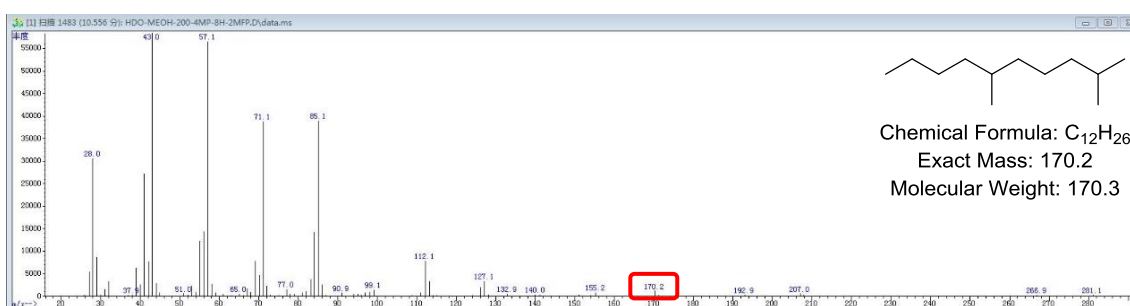
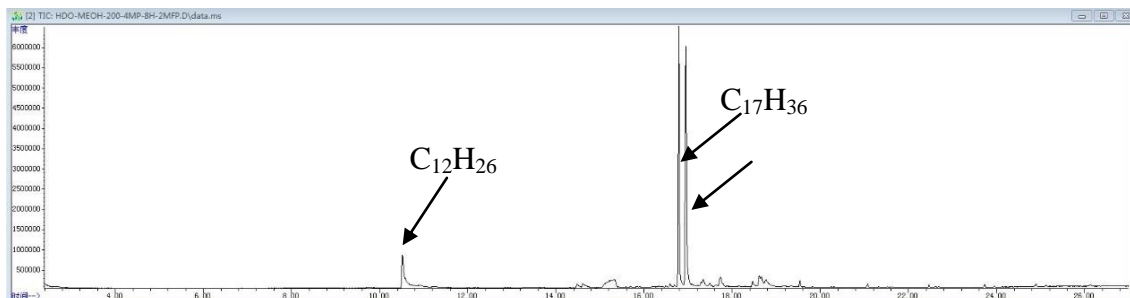
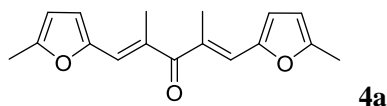
GC-MS spectrum of using H-beta zeolite + Pd/C system for the HDO of **3a**.



**Fig. S11.** GC-MS spectrum of the products identified from the organic-phase products produced by HDO of **3a** catalyzed by H-beta zeolite + Pd/C system. Inset graphics depict the structures of detected compounds based on NIST database.

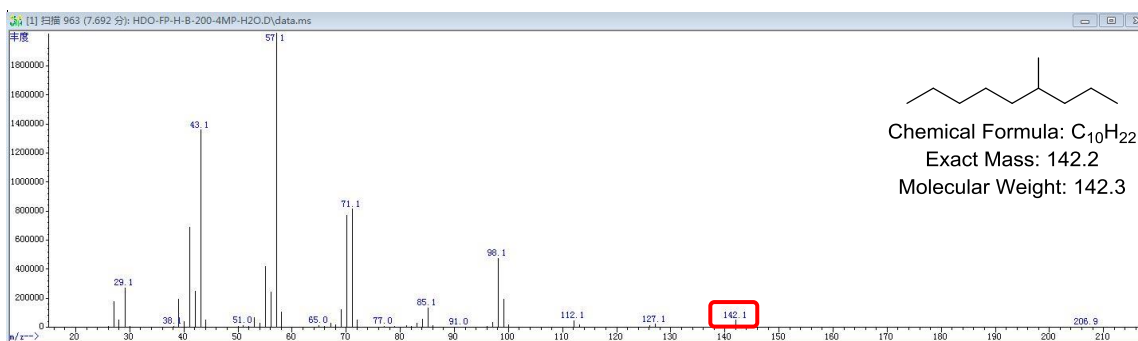
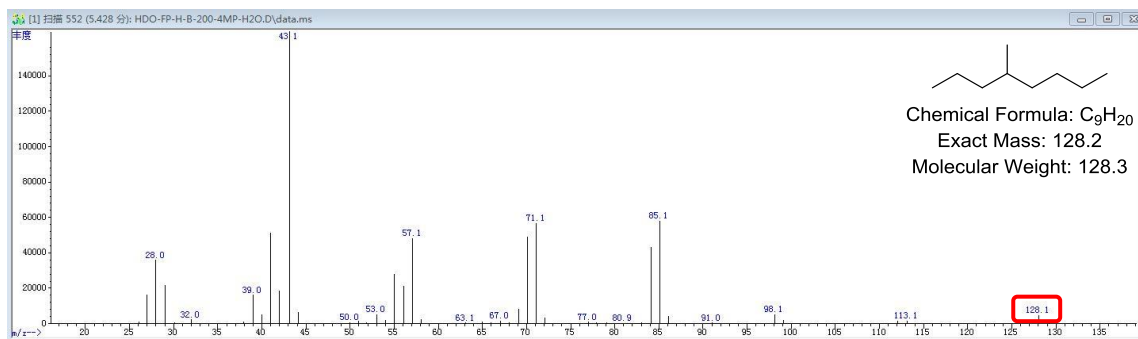
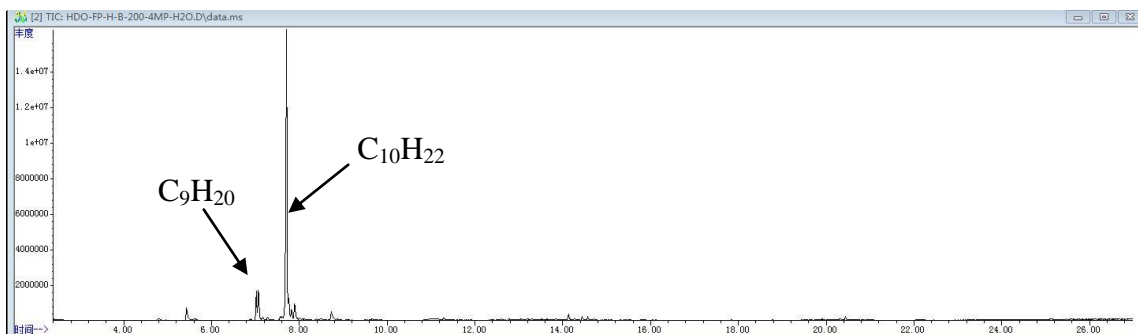
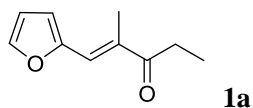


GC-MS spectrum of using H-beta zeolite + Pd/C system for the HDO of **4a**.



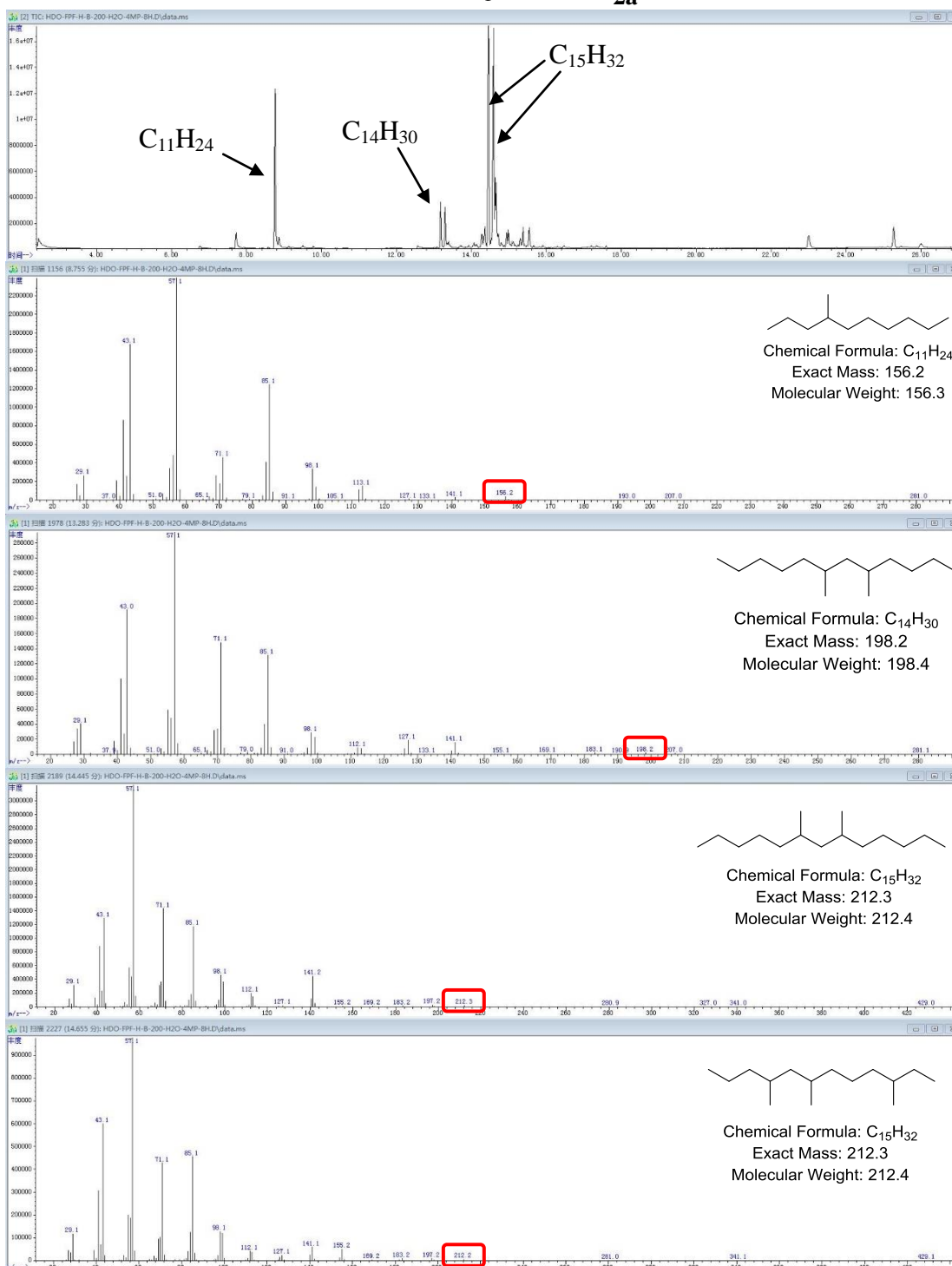
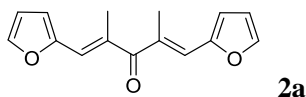
**Fig. S12.** GC-MS spectrum of the products identified from the organic-phase products produced by HDO of **4a** catalyzed by H-beta zeolite + Pd/C system. Inset graphics depict the structures of detected compounds based on NIST database.

GC-MS spectrum of using H-beta zeolite + Pd/C system for the HDO of **1a**.



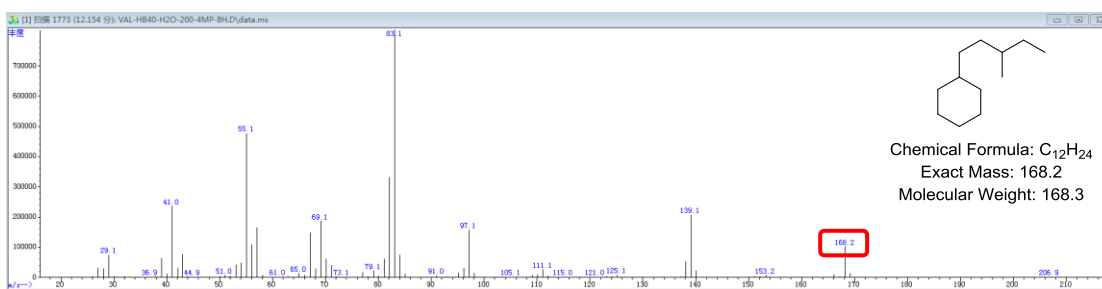
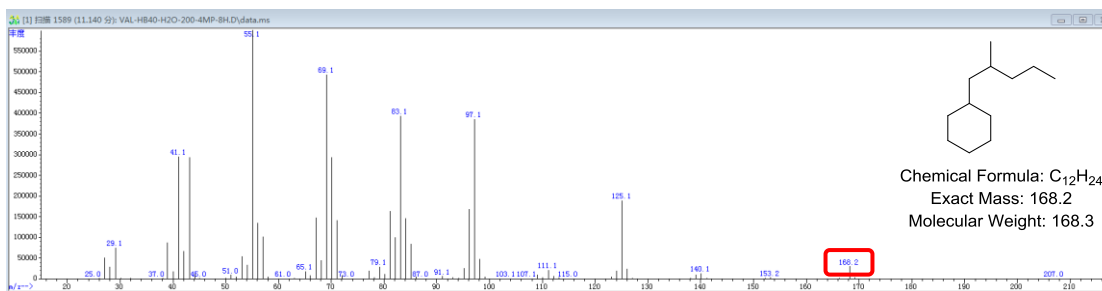
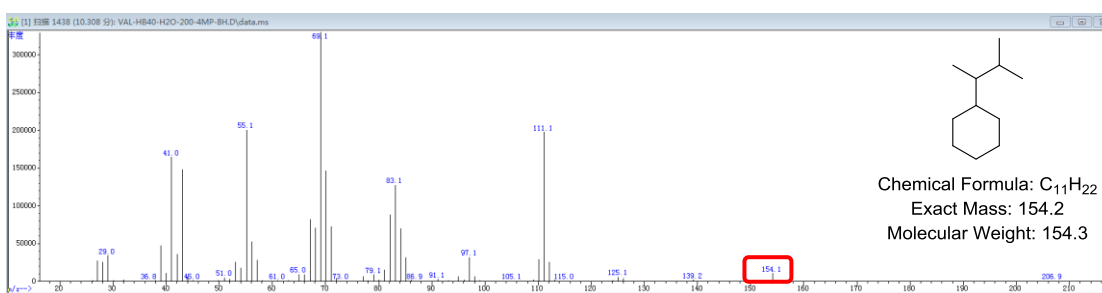
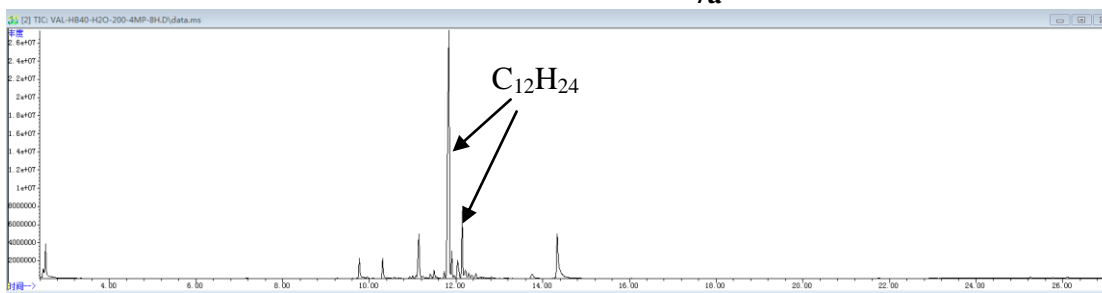
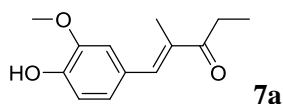
**Fig. S13.** GC-MS spectrum of the products identified from the organic-phase products produced by HDO of **1a** catalyzed by H-beta zeolite + Pd/C system. Inset graphics depict the structures of detected compounds based on NIST database.

GC-MS spectrum of using H-beta zeolite + Pd/C system for the HDO of **2a**.



**Fig. S14.** GC-MS spectrum of the products identified from the organic-phase products produced by HDO of **2a** catalyzed by H-beta zeolite + Pd/C system. Inset graphics depict the structures of detected compounds based on NIST database.

GC-MS spectrum of using H-beta zeolite + Pd/C system for the HDO of **7a**.



**Fig. S15.** GC-MS spectrum of the products identified from the organic-phase products produced by HDO of **7a** catalyzed by H-beta zeolite + Pd/C system. Inset graphics depict the structures of detected compounds based on NIST database.

## References

- 1) C. Zhu, L. Ji and Y. Wei, *Catal. Commun.*, 2010, **11**, 1017-1020.
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