Supporting Information

Production of liquid hydrocarbon fuels with acetoin 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}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}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×0.25 mm×0.25 μm). The injection volume was 1.0 μL with an autosampler and helium was used as a carrier gas with column flow rate of 1.5 mL min^{-1}. The temperature program was carried out as follows: initial temperature 45℃ for 5 min, then to 280℃ at 10℃ min^{-1}, and maintained at 280℃ for 10 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. HRMS spectra were obtained from a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an Infinity cell, a 7.0 T superconducting magnet, an RF-only hexapole ion guide, and an external electrospray ion source (off axis spray) and with ESI(+)-MS and tandem ESI(+)-MS/MS using a hybrid high-resolution and high accuracy MicrOTOF-Q II mass spectrometer. Preparative chromatography was equipped with a peristaltic pump and a 254 nm UV Optics Module. XRD patterns of different catalyst were obtained on a Riguku D MAX III VC diffractometer equipped with a Cu-Kα radiation source (λ = 0.15432 nm). The BET surface area, total pore volume, and average pore diameter were measured by N_2 adsorption-desorption method by Micromeritics Instrument TriStar II 3020. Before each measurement, the sample was evacuated at 473 K for 3 h. NH_3-TPD were carried out by a micrometeritics Autochem 2920 Automated Catalyst Characterization System. Typically, 0.1 g of catalyst was loaded into a quartz reactork purged in He flow at 473K for 2 h and cooled down to 372 K. Pulses of NH_3 were dosed in until saturation. The amount of acid sites on catalysts were calculated by the uptakes of NH_3 during the tests. In situ pyridine adsorption was carried out by FT-IR spectroscopy (Nikolet 560, USA). The sample was first degassed (1×10^{-4} Pa, 473 K for 4 h) in an IR cell and then the spectra of adsorbed pyridine were recorded. The SEM micrographs were taken by FEI Nova NanoSEM 450 scanningmicroscopy, and TEM was performed on a FEI Tecnai 20 instrument.

1.2 Materials

Zeolite catalysts (H-Beta, H-Y, H-ZSM-5) were purchased from The Catalyst Plant of Nankai University. H-Y (Si/Al = 20) zeolite was purchased from Zibo Xinhong Chemical Co. Ltd. Amberlyst-15 resin was purchased from Sigma-Aldrich. Nafion-212 resin (average pore size about 4 nm, 51 μm thick) was supplied by Dupont Company. Zirconia supported trifluoromethanesulfonic acid were prepared according to a reported procedure with minor modification.[1] $Cs_2H_2PMo_{11}VO_{40}$ was prepared according to literature procedure.[2] Sulfated zirconia was prepared according to the method[3] and activated at 773 K for 8 h in static air prior to the catalytic run.

Amberlite IRA-900 resin was purchased from Sigma-Aldrich. Hydrotalcites (calcined or rehydrated) were prepared according to reported procedures.[4,5] $MgO\text{-}ZrO_2$ was prepared according to a reported procedure.[6] Amorphous aluminium phosphate (ALPO) was prepared according to a reported procedure.[7] CaO sample were prepared by the thermal decomposition of $Ca(OH)_2$ at 973 K in nitrogen flow for 10 h. Ionic liquid $[H_3N^+\text{-}CH_2\text{-}CH_2\text{-}OH][CH_3COO^-]$ (EAIL) and $[H_3N^+\text{-}CH_2\text{-}CH_2\text{-}OH][CH_3CH(OH)COO^-]$ (LAIL) were prepared using our previous method.[8]

Pd/C (5 wt%) and Pt/C (5 wt%) catalysts used in HDO step were purchased from Aladdin company. $NbOPO_4$ and $TaOPO_4$ were prepared according to reported procedures.[9,10]

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.

2. Experimental

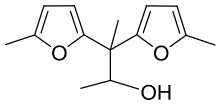
2.1 Fermentation and separation method.

C. acetobutylicum fermentations were performed anaerobically in P2 medium as described in our previously report.[11] Batch fermentations were performed in 500-mL Duran bottles with 300 mL of working volume. Each bottle was inoculated with 30 mL of a 12-h old seed culture. The cell density (OD600 nm), as well as concentrations of residual sugars and metabolites (acids and solvents), were determined using our previous method.[12] The removal and separation of ABE products (Acetoin-Butanol-Ethanol) from the fermentation broth were performed according to our previous method.[13,14]

2.2 Hydroxyalkylation and alkylation of acetoin with 2-methylfuran

Generally, to a solution of 2-methylfuran (22 mmol, 1.81 g) and acetoin (10 mmol, 0.88 g) was added catalyst (5 mol% for *para*-toluenesulfonic acid and H_2SO_4, or 0.1 g for solid acid) at 333 K under solvent-free condition. After reaction, the mixture was diluted with water. The aqueous portion was extracted with EtOAc, the combined organic extracts were concentrated under vacuum and purified by column chromatography to provide the analytically pure product for further characterization

3,3-bis(5-methylfuran-2-yl)butan-2-ol



1b

Reaction of acetoin (10 mmol, 0.88 g) and 2-methylfuran (22 mmol, 1.81 g) catalyzed by TFA-ZrO_2 (0.1 g) according to the general procedure afforded 2.18 g (93 %) of product **1b**, isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (d, *J* = 3.1 Hz, 1H), 5.97 (d, *J* = 3.1 Hz, 1H), 5.93-5.89 (m, 1H), 5.89-5.84 (m, 1H), 4.37 (d, *J* = 6.4 Hz, 1H), 2.27 (dd, *J* = 5.6, 0.7 Hz, 6H), 1.56 (s, 3H), 1.08 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.41, 154.35, 150.14, 149.90, 106.42, 106.04, 105.00, 104.86, 71.11, 45.78, 16.85, 16.65, 12.61, 12.58.

2.3 Aldol condensation of acetoin with lignocellulose derived aldehydes

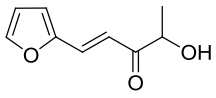
2.3.1 Aldol condensation of acetoin with furfural, HMF or 5-MF

Generally, to a solution of acetoin (20 mmol, 1.76 g) and furan aldehyde (20 mmol) in H_2O (15 mL) was added catalyst (0.1 g for NaOH, 2 mmol for organocatalyst, 0.2 g for ionic liquid). The mixture was stirred at 323 K for several hours while checking the reaction progress by using gas or thin-layer chromatography. For solid base catalyst (0.2 g used in the reaction), the reaction was performed under solvent-free condition at 393 K. After completion, the mixture was extracted with EtOAc, the obtained organic layer was evaporated and purified by column chromatography to provide the analytically pure product for further characterization.

2.3.2 Recycling of the ionic liquid catalyst for the Aldol reaction.

After the reaction, extraction of the mixture with EtOAc led to the separation between the catalyst EAIL and products due to the ionic liquid catalyst EAIL is completely soluble in water, but insoluble in EtOAc. Fresh substrates were then recharged to the residual water layer which contains the catalyst EAIL and the mixture was heated to react once again.

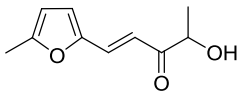
1-(furan-2-yl)-4-hydroxypent-1-en-3-one



2b

Reaction of acetoin (20 mmol, 1.76 g) and furfural (20 mmol, 1.92 g) in H_2O (15 mL) catalyzed by EAIL (0.2 g) according to the general procedure afforded 2.49 g (75 %) of product **2b**, isolated as pale yellow oil; ^{1}H NMR (400 MHz, MeOD): δ 7.65 (d, *J* = 1.4 Hz, 1H), 7.49 (d, *J* = 15.8 Hz, 1H), 6.93 (d, *J* = 15.8 Hz, 1H), 6.84 (d, *J* = 3.4 Hz, 1H), 6.56 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 1H), 1.35 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, MeOD): δ 203.24, 152.69, 146.97, 131.18, 119.36, 117.90, 113.85, 73.39, 20.35.

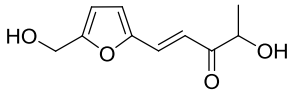
4-hydroxy-1-(5-methylfuran-2-yl)pent-1-en-3-one



2d

Reaction of acetoin (20 mmol, 1.76 g) and 5-methylfurfural (20 mmol, 2.21 g) in H_2O (15 mL) catalyzed by EAIL (0.2 g) according to the general procedure afforded 3.13 g (87 %) of product **2d**, isolated as pale yellow oil; ^{1}H NMR (400 MHz, MeOD): δ 7.42 (d, *J* = 15.7 Hz, 1H), 6.83 (d, *J* = 15.7 Hz, 1H), 6.74 (d, *J* = 3.3 Hz, 1H), 6.23-6.17 (m, 1H), 4.40 (q, *J* = 6.9 Hz, 1H), 2.35 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, MeOD): δ 203.33, 157.83, 151.37, 131.32, 119.95, 117.58, 110.51, 73.34, 20.45, 13.77.

4-hydroxy-1-(5-(hydroxymethyl)furan-2-yl)pent-1-en-3-one



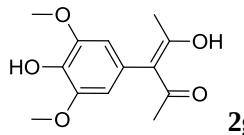
2e

Reaction of acetoin (20 mmol, 1.76 g) and 5-hydroxymethylfurfural (20 mmol, 2.52 g) in H_2O (15 mL) catalyzed by EAIL (0.2 g) according to the general procedure afforded 1.33 g (34 %) of product **2e**, isolated as pale yellow oil; ^{1}H NMR (400 MHz, MeOD): δ 7.46 (d, *J* = 15.7 Hz, 1H), 6.91 (d, *J* = 15.7 Hz, 1H), 6.80 (d, *J* = 3.4 Hz, 1H), 6.45 (d, *J* = 3.4 Hz, 1H), 4.55 (s, 2H), 4.42 (q, *J* = 6.9 Hz, 1H), 1.35 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, MeOD): δ 203.31, 159.66, 152.31, 131.22, 119.05, 118.99, 111.32, 73.36, 57.57, 20.37.

2.3.3 Aldol condensation of acetoin with p-hydroxy benzaldehyde, vanillin or syringaldehyde

Generally, to a solution of acetoin (20 mmol, 1.76 g) and lignin model compound (15 mmol), was added amorphous aluminium phosphate (ALPO) (0.2 g) at 393 K 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 provide the analytically pure product for further characterization.

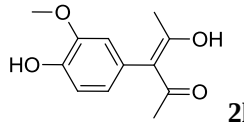
4-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)pent-3-en-2-one



2g

Reaction of acetoin (20 mmol, 1.76 g) and syringaldehyde (15 mmol, 2.73 g) catalyzed by ALPO (0.2 g) according to the general procedure afforded 2.95 g (78 %) of product **2g**, isolated as aubergine solid; ^{1}H NMR (400 MHz, MeOD): δ 6.43 (s, 2H), 3.79 (s, 6H), 1.85 (s, 6H). ^{13}C NMR (100 MHz, MeOD): δ 192.18, 149.55, 136.27, 128.75, 116.57, 109.42, 56.89, 24.15.

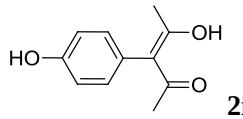
4-hydroxy-3-(4-hydroxy-3-methoxyphenyl)pent-3-en-2-one



2h

Reaction of acetoin (20 mmol, 1.76 g) and vanillin (15 mmol, 2.28 g) catalyzed by ALPO (0.2 g) according to the general procedure afforded 2.73 g (82 %) of product **2h**, isolated as white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, *J* = 8.5 Hz, 1H), 6.59 (dd, *J* = 6.8, 1.8 Hz, 2H), 3.82 (s, 3H), 1.84 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.27, 145.69, 144.07, 127.74, 123.12, 114.02, 113.76, 112.31, 54.96, 23.06.

4-hydroxy-3-(4-hydroxyphenyl)pent-3-en-2-one



2i

Reaction of acetoin (20 mmol, 1.76 g) and *p*-hydroxy benzaldehyde (15 mmol, 1.83 g) catalyzed by ALPO (0.2 g) according to the general procedure afforded 2.54 g (88 %) of product **2i**, isolated as white solid; ^{1}H NMR (400 MHz, MeOD): δ 6.99 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, MeOD): δ 192.25, 158.12, 133.30, 129.10, 116.69, 116.01, 29.75, 24.25.

2.4 Hydrodeoxygenation

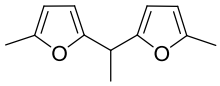
2.4.1 HDO of fuel precursors

Typically, **2d** (2.5 mmol, 0.45 g) was dissolved in 20 mL distilled water and transferred to a 100 mL Parr pressure reactor. To this reactor was added Pd/C (5 wt%, 0.25 g, 4.7 mol% Pd relative to **2d**) and H-beta zeolite (0.25 g). The reactor was purged thrice with nitrogen and charged to 3 MPa H_2. After that, the reactor was heated to 473 K under vigorous stirring for 8 h. After the system reached to room temperature, the gas was collected in a gas cylinder of known volume and the pressure of the gas cylinder was adjusted to 1 atm using high purity nitrogen as a makeup gas. The gaseous products were analyzed by GC using methanizer (for CO and CO_2) and TCD analyzer (for other gaseous hydrocarbons), and the gas overall yield was determined. Then, the catalysts were removed by centrifugation, and the liquid solution was extracted with EtOAc and analyzed by GC-MS. Alkane selectivity was reported based on the percentage of peak areas measured by GC. Total organic carbon (TOC) analysis was performed on final concentrated liquid organic products to quantify the total carbon present and calibrate the GC for reaction products.

*2.4.2 Control experiment of fragmentation of **1b** catalyzed by H-beta zeolite*

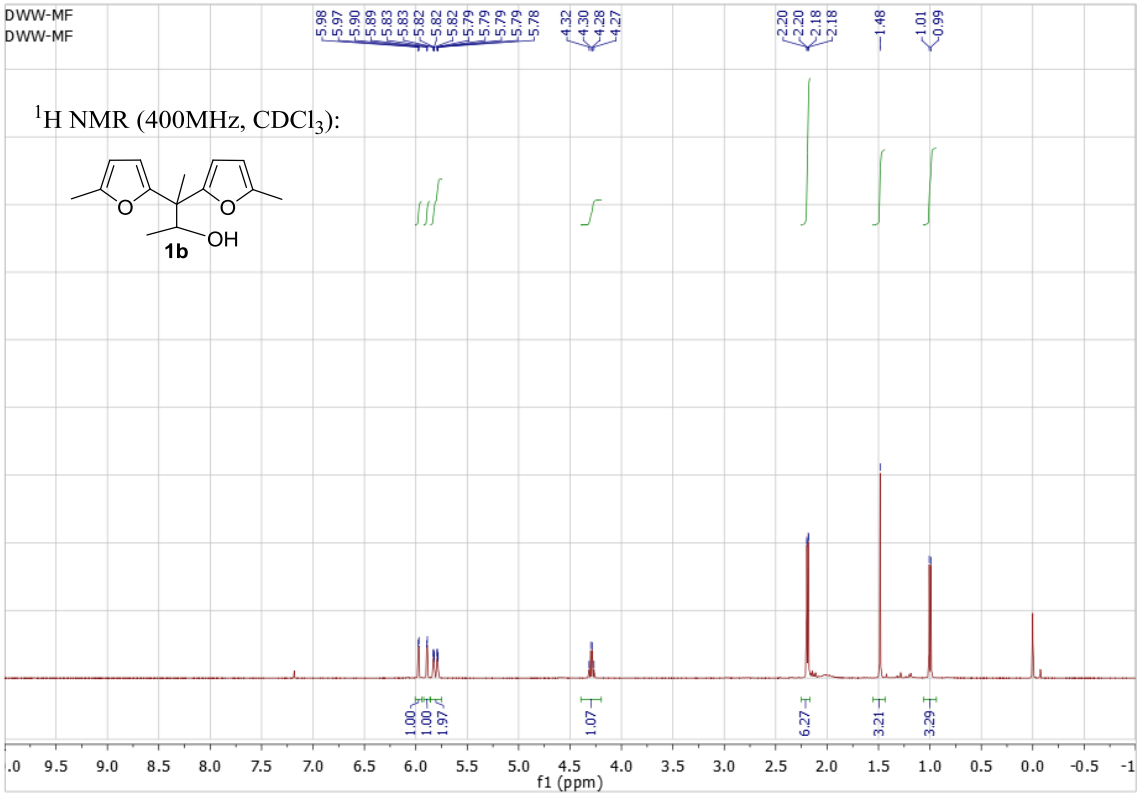
Typically, to a solution of **1b** (2.5 mmol, 0.59 g) in H_2O (15 mL) was added H-beta zeolite catalyst (Si/Al = 40, 0.25 g). The reactor was purged thrice with nitrogen and heated to 473 K under vigorous stirring for 8 h. After completion, the mixture was extracted with EtOAc, the obtained organic layer was evaporated and purified by column chromatography to provide the analytically pure product for further characterization.

5,5'-(ethane-1,1-diyl)bis(2-methylfuran)



3h

Reaction of **1b** (2.5 mmol, 0.59 g) catalyzed by H-beta zeolite catalyst (0.25 g) according to the above procedure afforded **3h** (0.28 g, 61 %) as the mian product, isolated as pale yellow oil; ^{1}H NMR (400 MHz, MeOD): δ 5.87-5.85 (m, 4H), 4.03 (q, *J* = 7.3 Hz, 1H), 2.20 (s, 6H), 1.50 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, MeOD): δ 156.34, 151.70, 106.93, 106.48, 34.34, 18.71, 13.48.



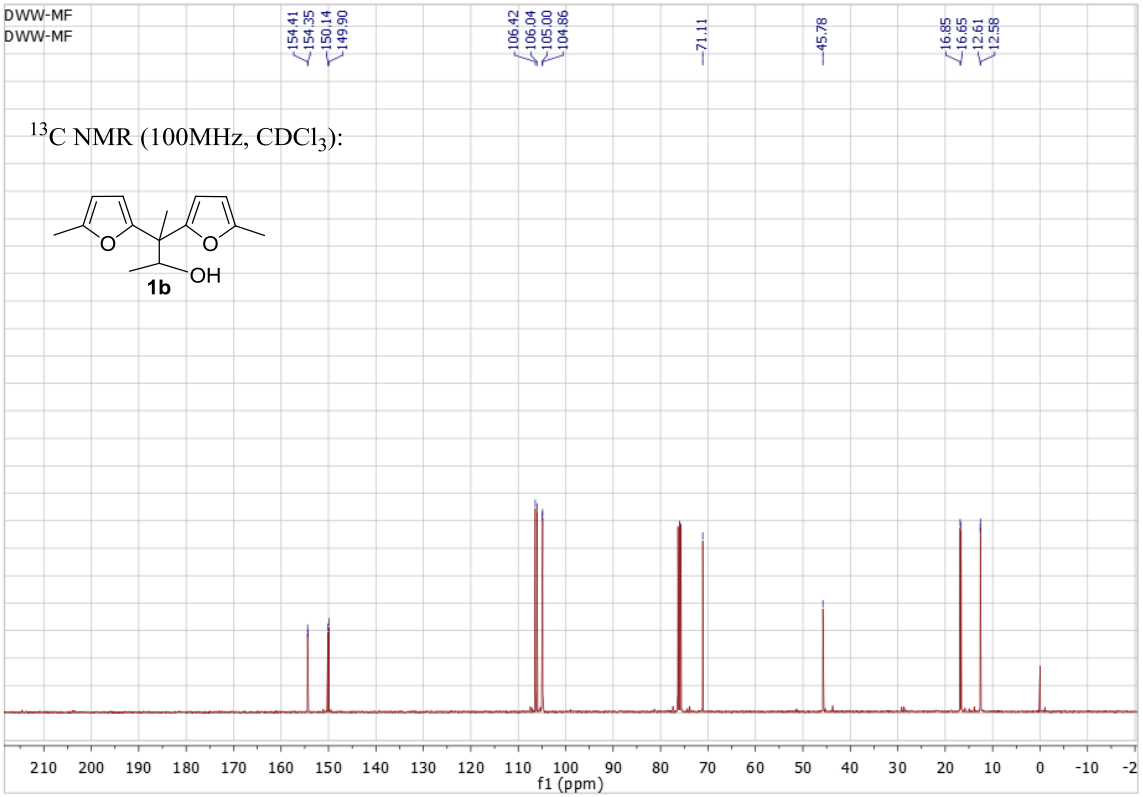


Figure S1. ^{1}H and ^{13}C NMR spectra of the product **1b** produced from 2-MF and acetoin.

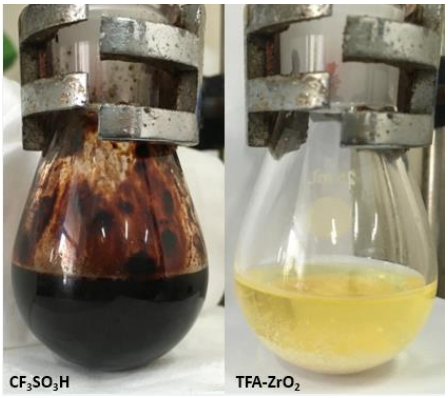


Figure S2. The comparative photos of the HAA reaction using TFA and TFA-ZrO_2 as a catalyst. (*Left*) Using of TFA as a homogeneous liquid acid catalyst for the reaction; (*Right*) Using TFA-ZrO_2 as a heterogeneous solid acid catalyst for the reaction.

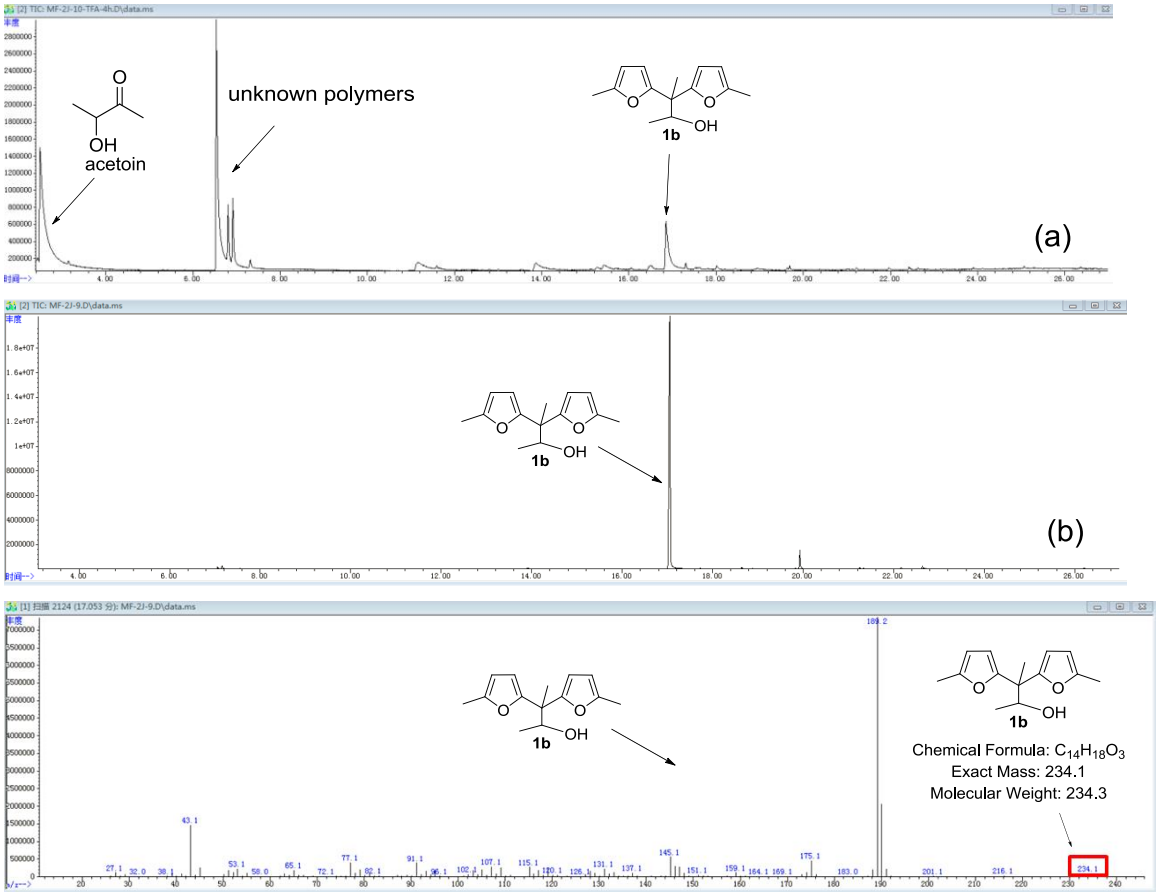


Figure S3. The comparative GC-MS spectrum of the HAA reaction. (a) Using TFA as a homogeneous catalyst; (b) Using TFA-ZrO_2 as a heterogeneous catalyst.

Table S1 Optimization study for the HAA of 2-MF with acetoin catalyzed by TFA-ZrO_2

Entry	Catalyst [a]	Tem.(K)	Time (h)	Con.(%)[b]	Yield of **1b**[c]
1	TFA_5-ZrO_2, 0.1g	333	2	76	69
2	TFA_{10}-ZrO_2, 0.1g	333	2	88	82
3	TFA_{20}-ZrO_2, 0.1g	333	2	100	93
4	TFA_{30}-ZrO_2, 0.1g	333	2	100	90
5	TFA_{20}-ZrO_2, 0.05g	333	2	86	78
6	TFA_{20}-ZrO_2, 0.15g	333	2	100	87
7	TFA_{20}-ZrO_2, 0.1g	323	2	100	93
8	TFA_{20}-ZrO_2, 0.1g	313	2	100	91
9	TFA_{20}-ZrO_2, 0.1g	323	1	100	96
10	TFA_{20}-ZrO_2, 0.1g	r.t.	6	96	91

[a] Different loading of TFA over ZrO_2 (5 to 30 wt%) were carried out by varying the molar ratios of zirconium propoxide, water, and TFA, and designated as $TFA_{5\sim30}$-ZrO_2. [b] Conversion with respect to the limiting reactant acetoin. [c] Isolation yield.

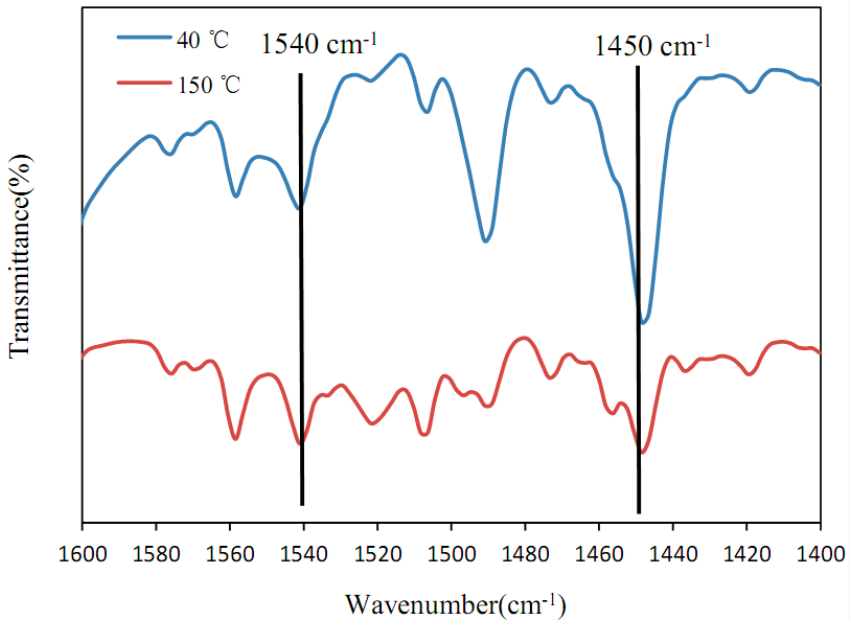


Figure S4. Pyridine-FTIR spectra of TFA-ZrO_2 obtained after evacuation at different temperature. The ratio of Lewis/Brønsted acid in TFA-ZrO_2 is about 1.4, which is calcluated accroding to literature.[16]

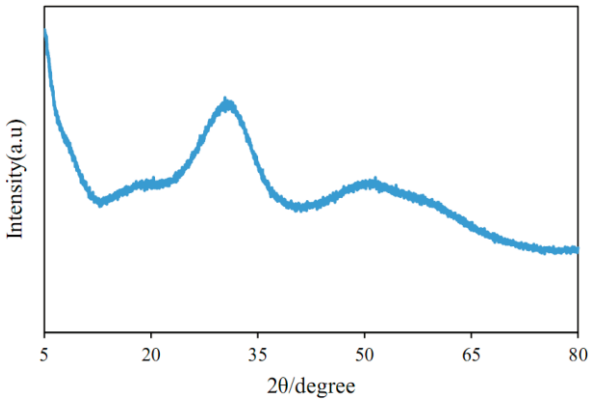


Figure S5. XRD pattern of TFA-ZrO_2. The reflections observed at about 31^o (broad) and 50^o (small) in the catalyst are attributed to the tetragonal, monoclinic, and cubic phases of ZrO_2.

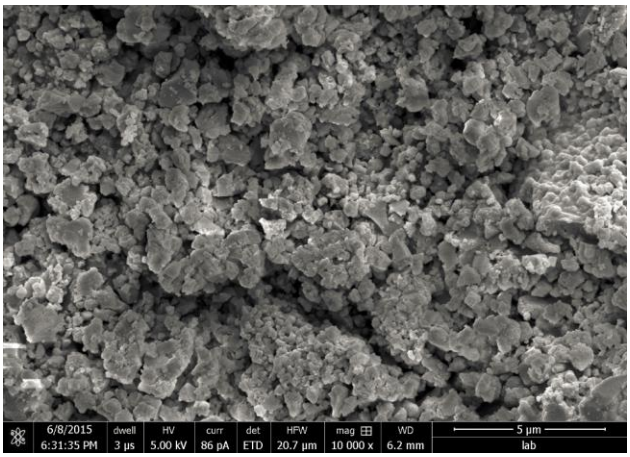


Figure S6. Scanning electron micrograph of TFA-ZrO_2.

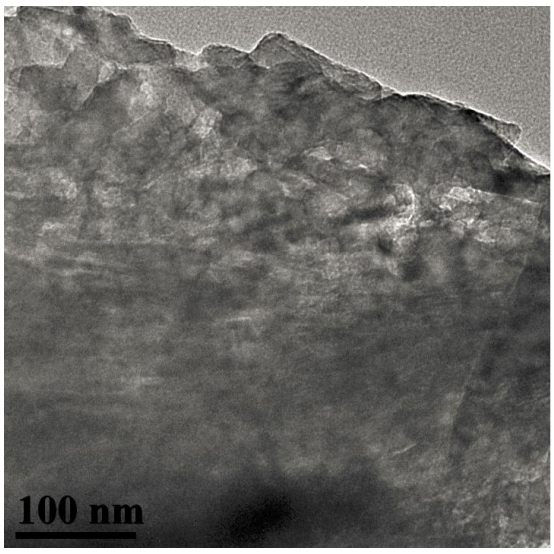


Figure S7. Transmission electron micrograph of TFA-ZrO_2.

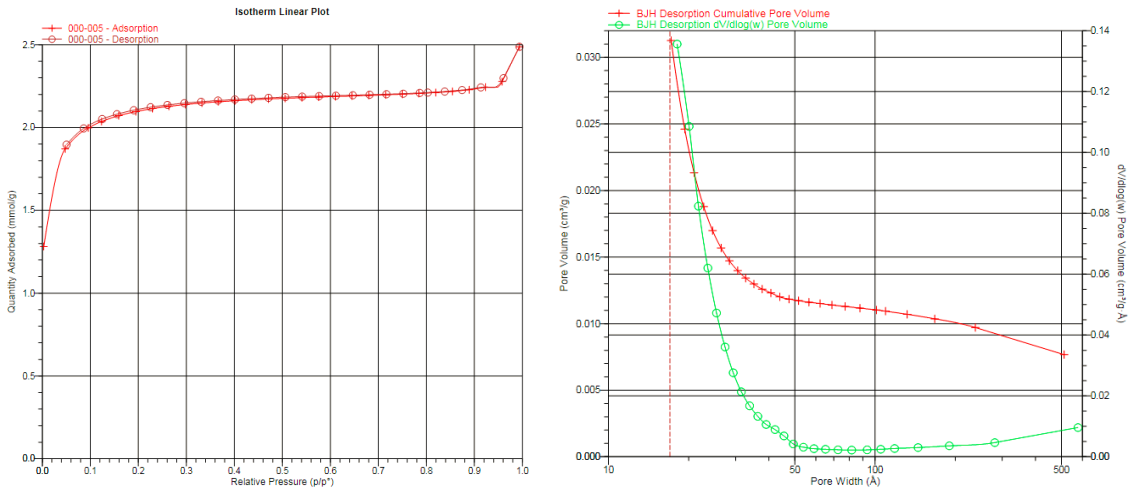


Figure S8. (Left) N_2 adsorption isotherm of TFA-ZrO_2; (Right) BJH pore size distribution of TFA-ZrO_2. The BET surface aera, average pore diameter, and total pore volume of TFA-ZrO_2 were 149.8 m^2 g^{-1}, 33.4 Å, and 0.03 cm^3 g^{-1}, respectively.

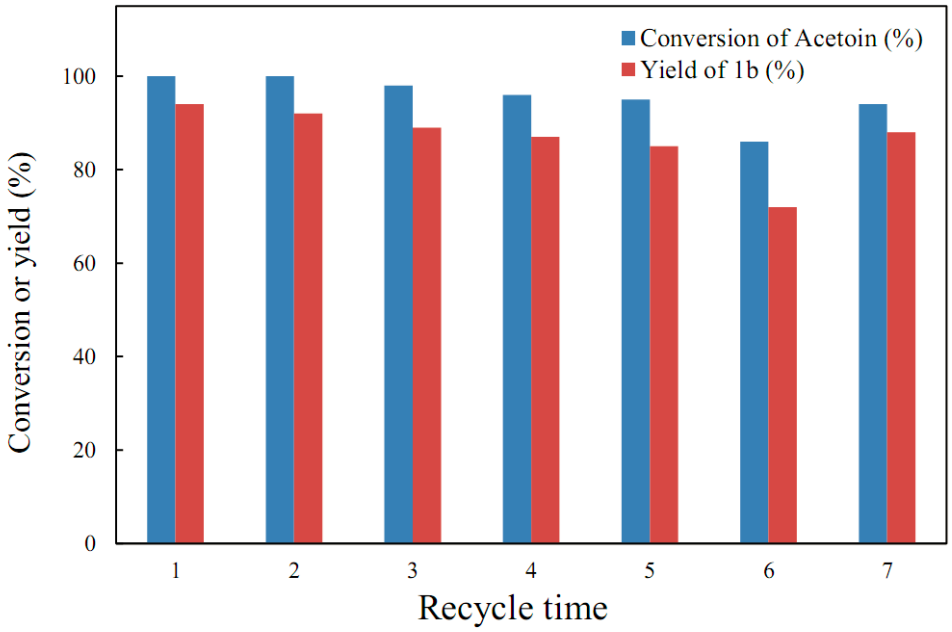
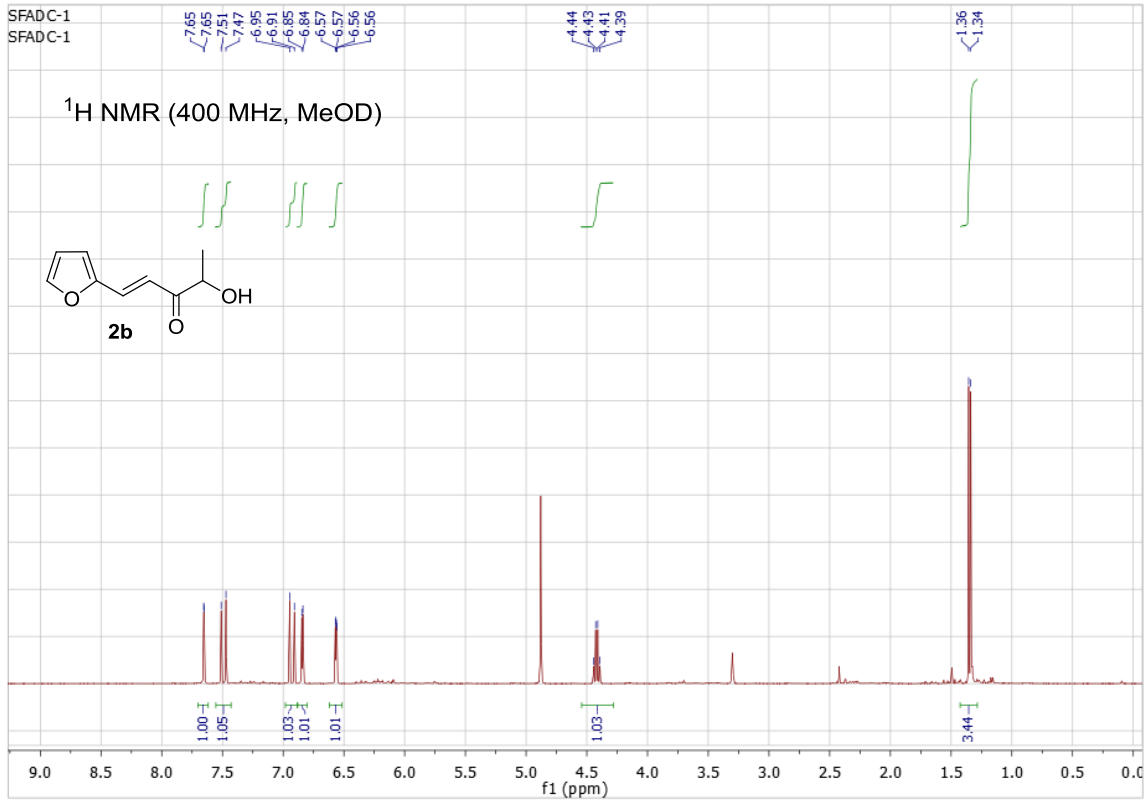


Figure S9. Recycling of the TFA-ZrO_2 catalyst for the HAA reaction. reaction conditions: 2-MF (22 mmol), acetoin (10 mmol), catalyst (0.15 g) under solvent-free condition at 323K for 1 h.



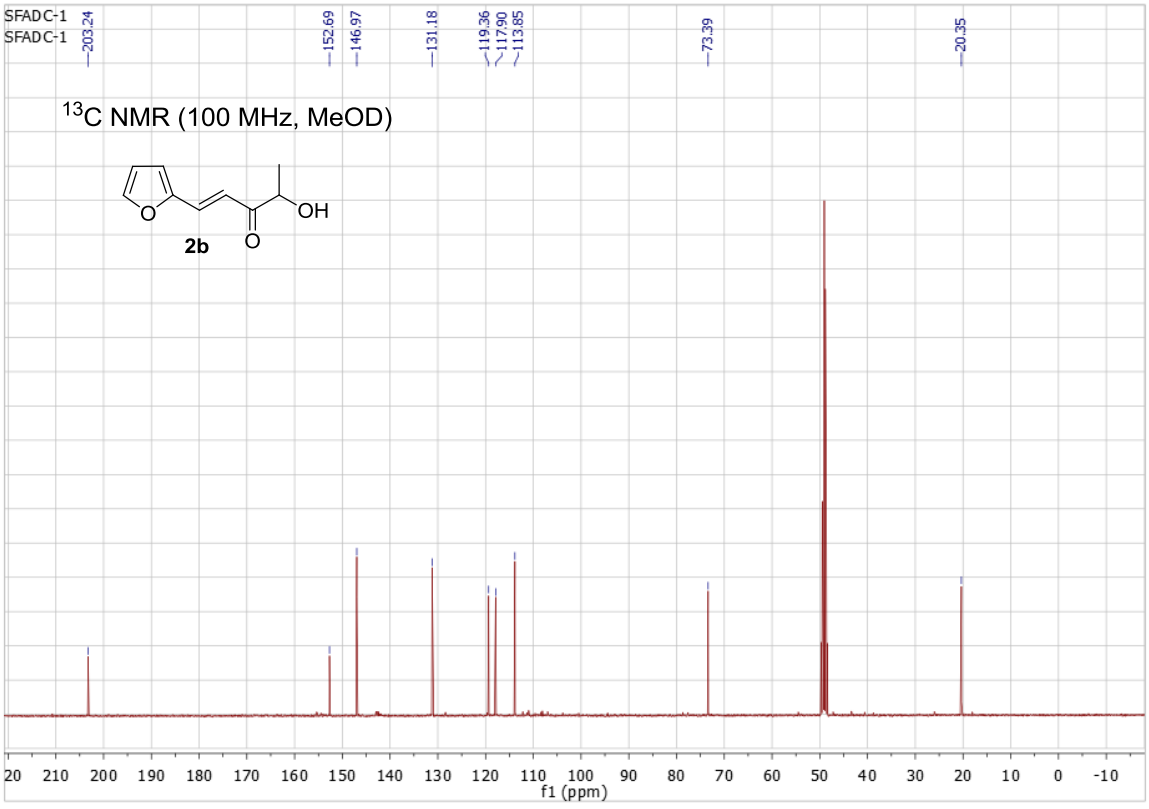


Figure S10. ^{1}H and ^{13}C NMR spectra of product **2b** produced from furfural and acetoin.

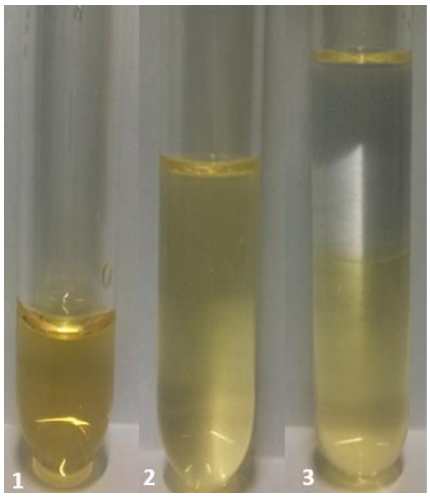


Figure S11. Solubility of ionic liquid [H_3N^+-CH_2-CH_2-OH][CH_3COO^-] (EAIL) in different solvent.

(1) [H_3N^+-CH_2-CH_2-OH][CH_3COO^-]: 2 mL;

(2) [H_3N^+-CH_2-CH_2-OH][CH_3COO^-]/H_2O = 2 mL/2 mL;

(3) [H_3N^+-CH_2-CH_2-OH][CH_3COO^-]/H_2O/EtOAc = 2 mL/2 mL/4 mL, the upper layer was EtOAc.

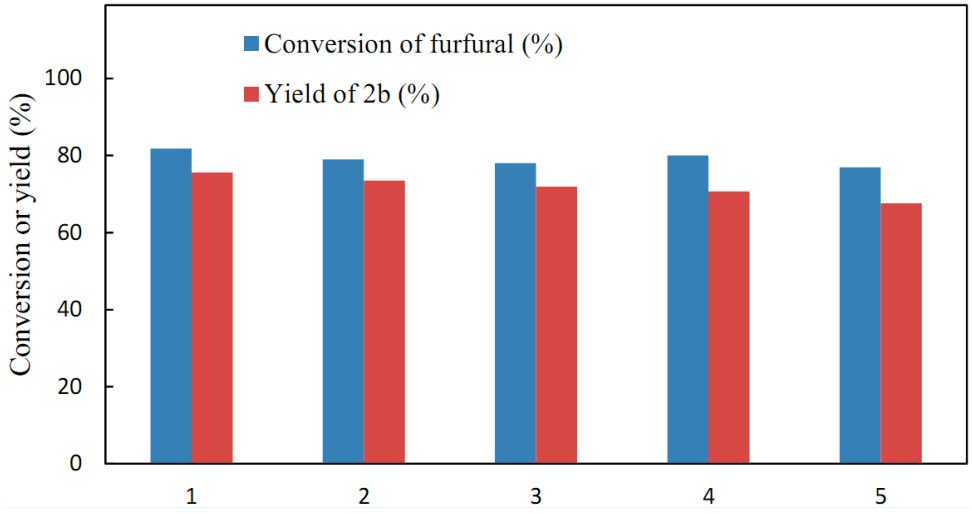
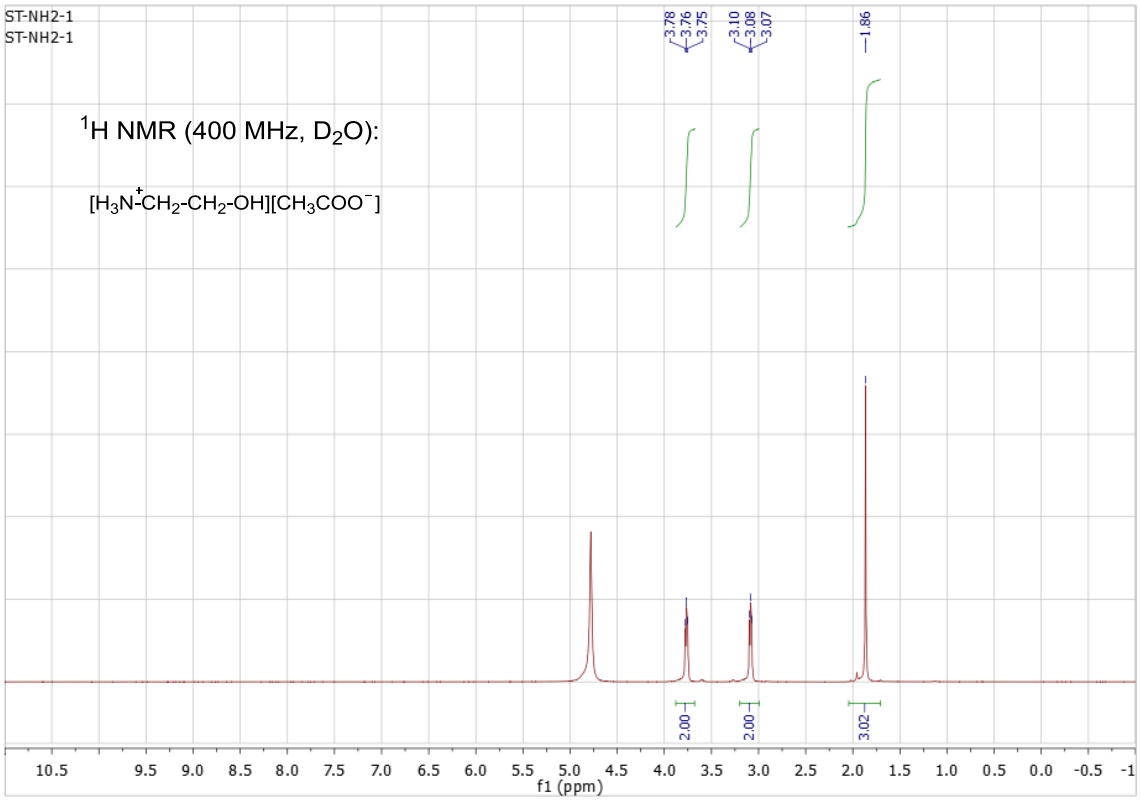


Figure S12. Recycling of the EAIL catalyst for the aldol reaction of furfural with acetoin. reaction conditions: furfural (20 mmol), acetoin (20 mmol), H_2O (15 mL), EAIL (0.2 g) at 323K for 6 h.



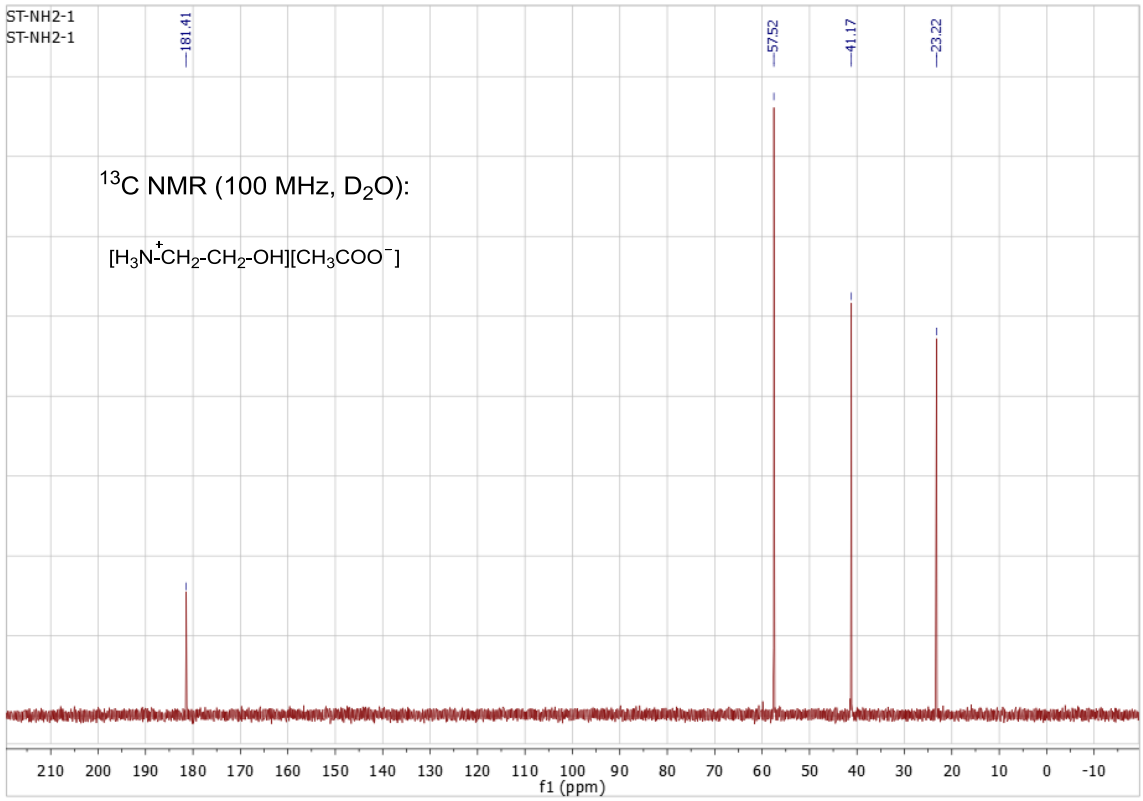
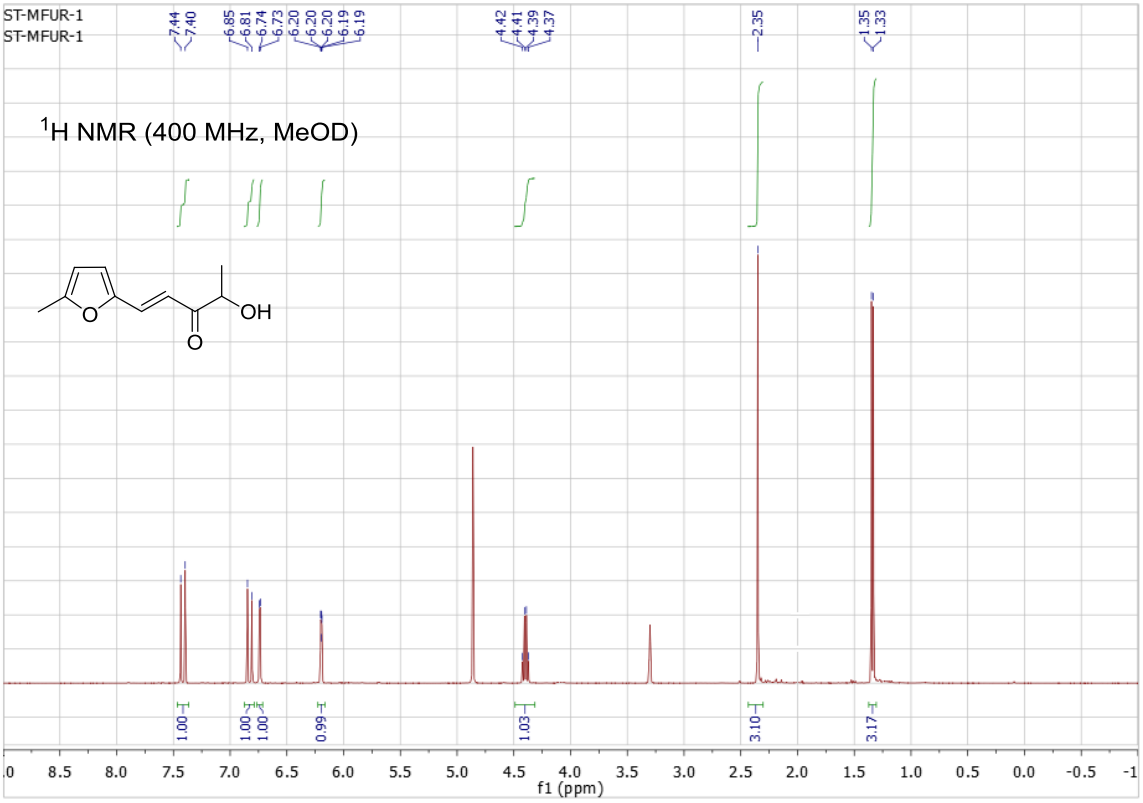


Figure S13. ^{1}H and ^{13}C NMR spectra of ionic liquid $[H_3N^+-CH_2-CH_2-OH][CH_3COO^-]$



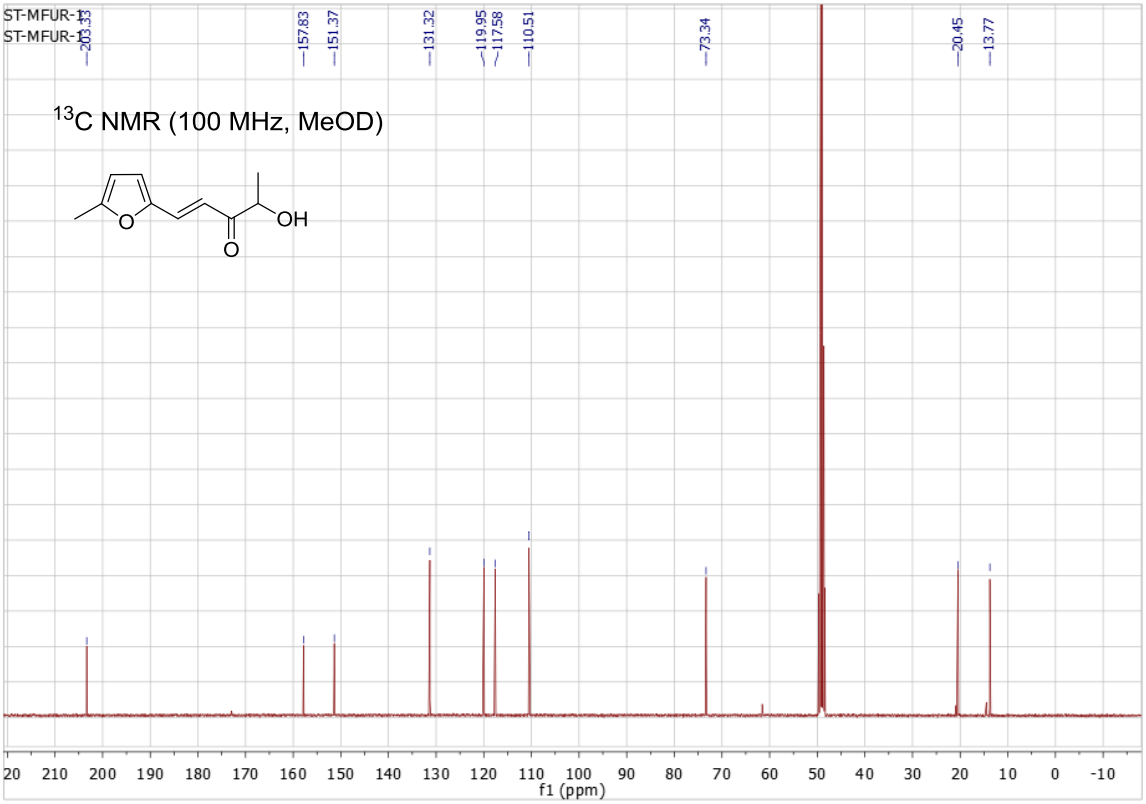


Figure S14. ^{1}H and ^{13}C NMR spectra of product **2d** produced from 5-MF and acetoin.

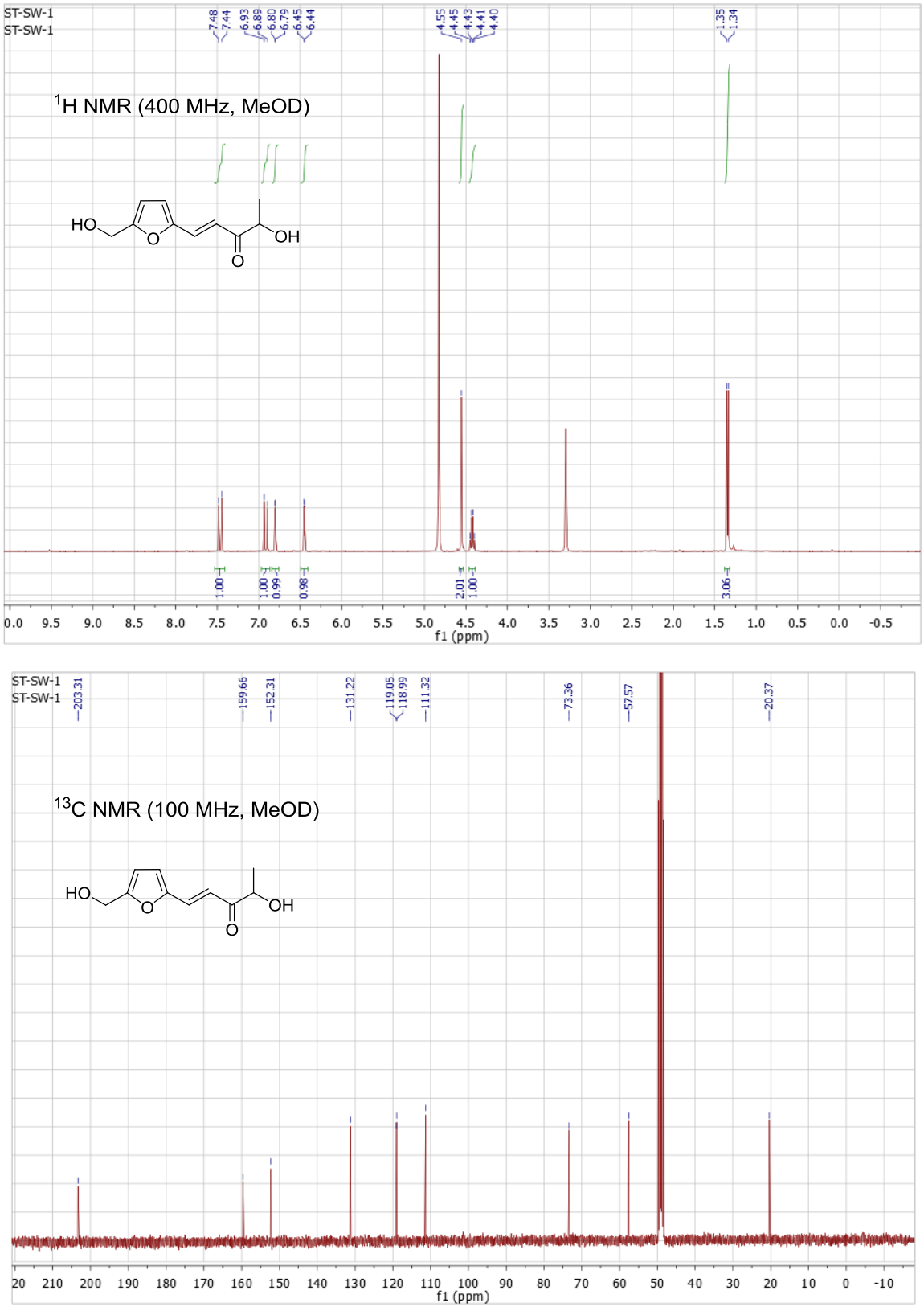


Figure S15. ^{1}H and ^{13}C NMR spectra of product **2e** produced from HMF and acetoin.

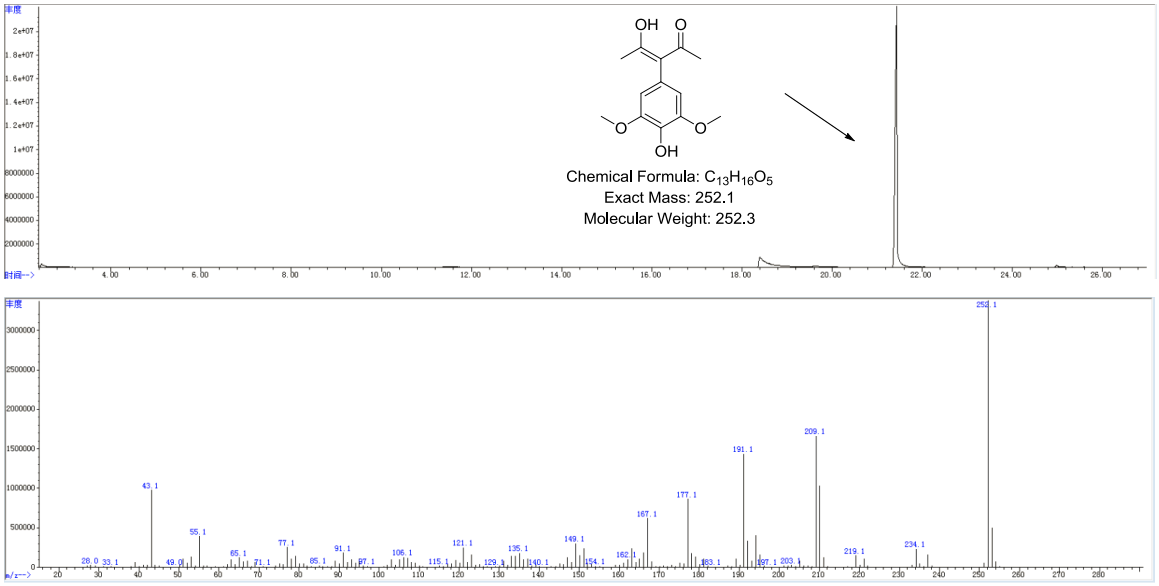
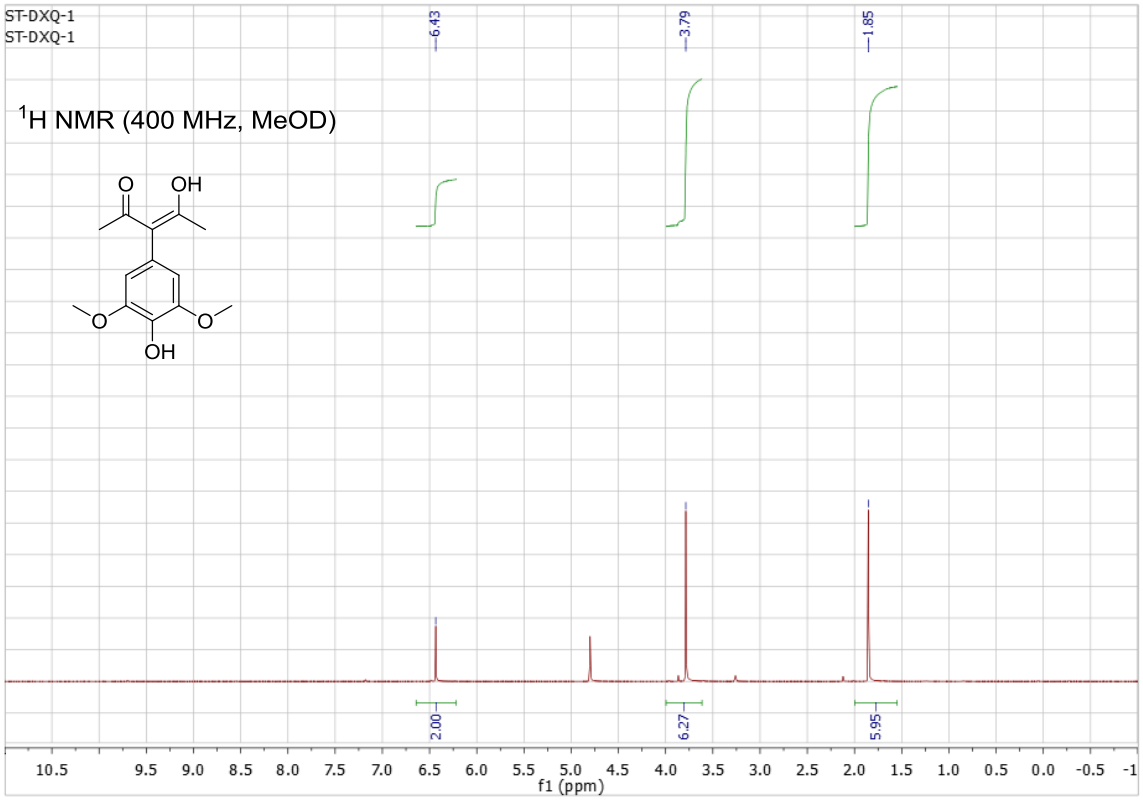


Figure S16. GC-MS spectra of the reaction of acetoin with syringaldehyde.



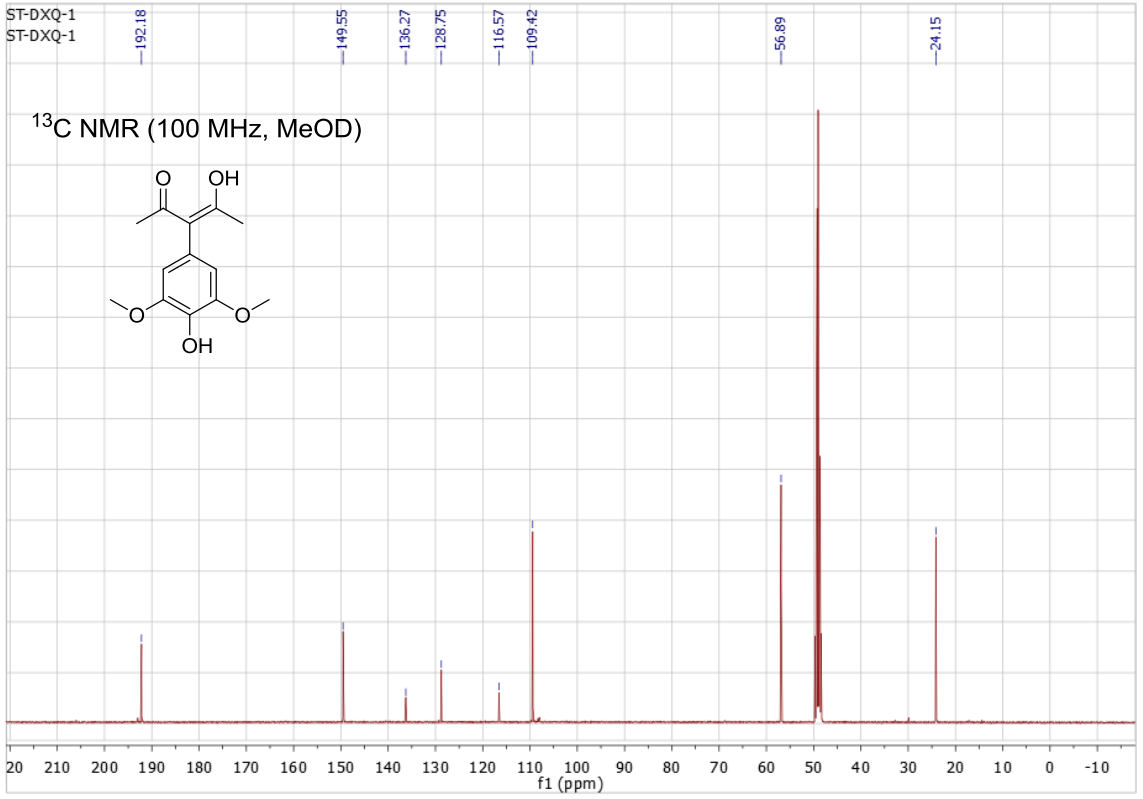
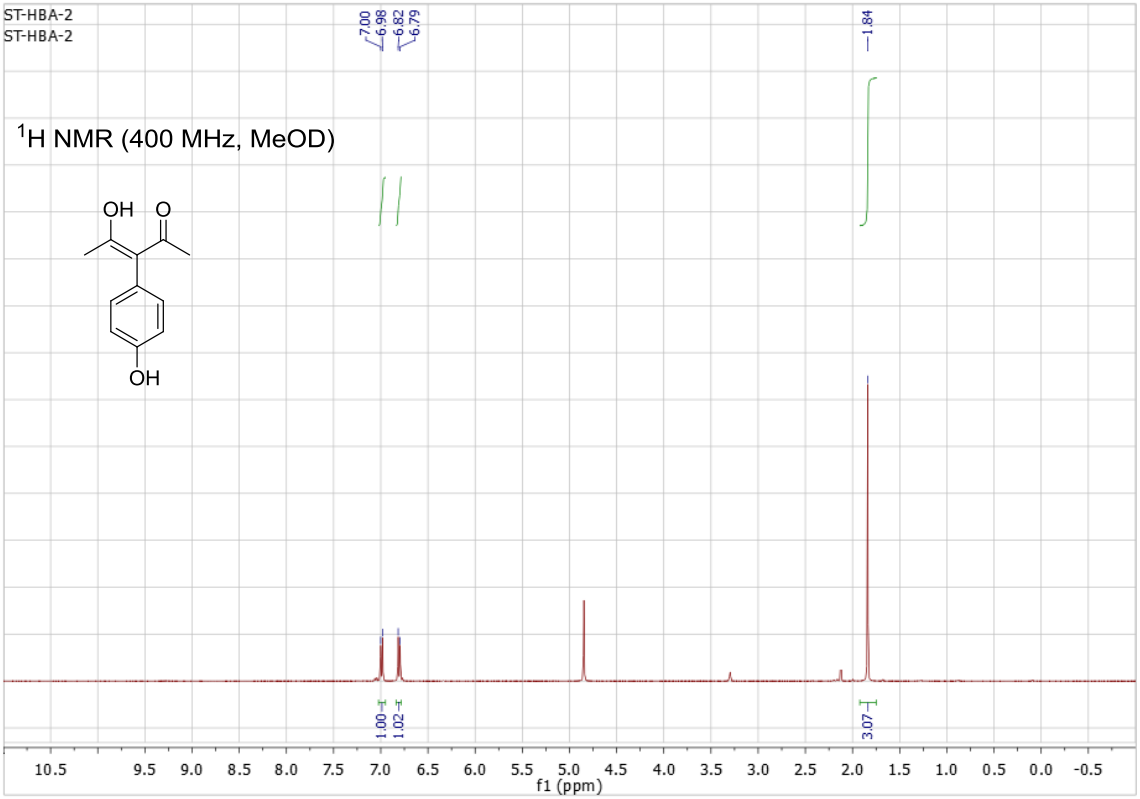


Figure S17. ^{1}H and ^{13}C NMR spectra of product **2g** produced from and acetoin with syringaldehyde.



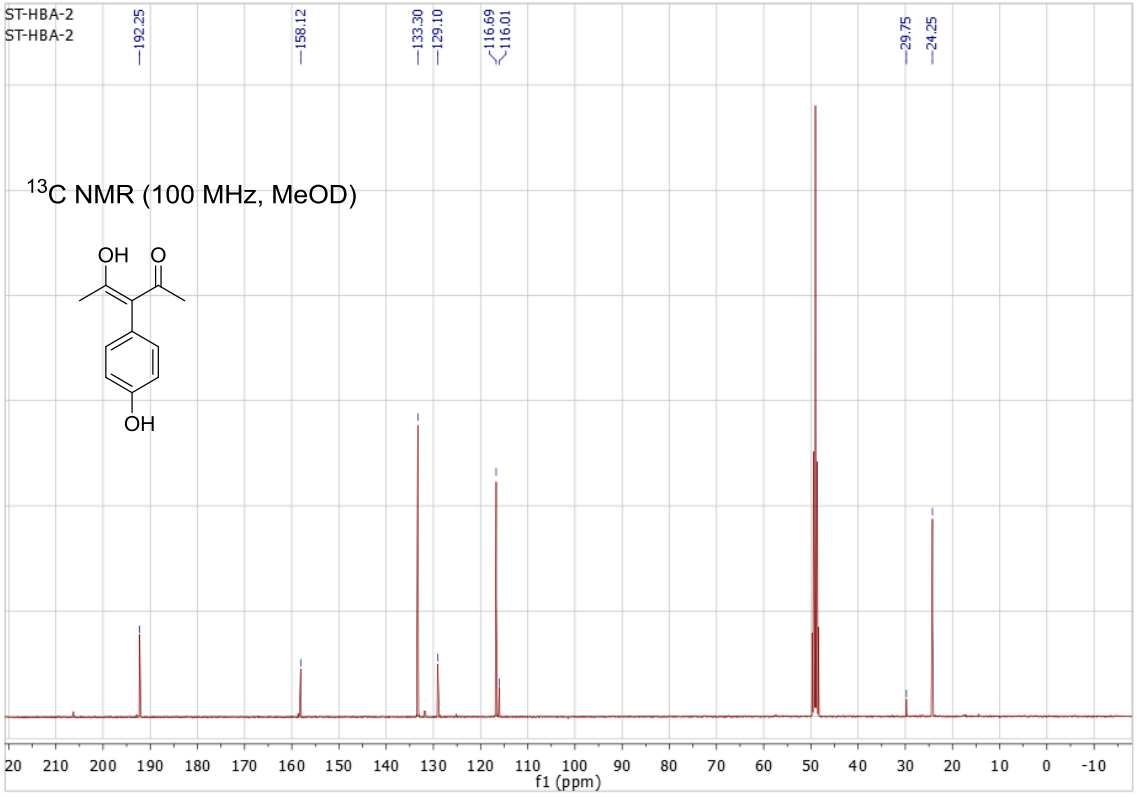
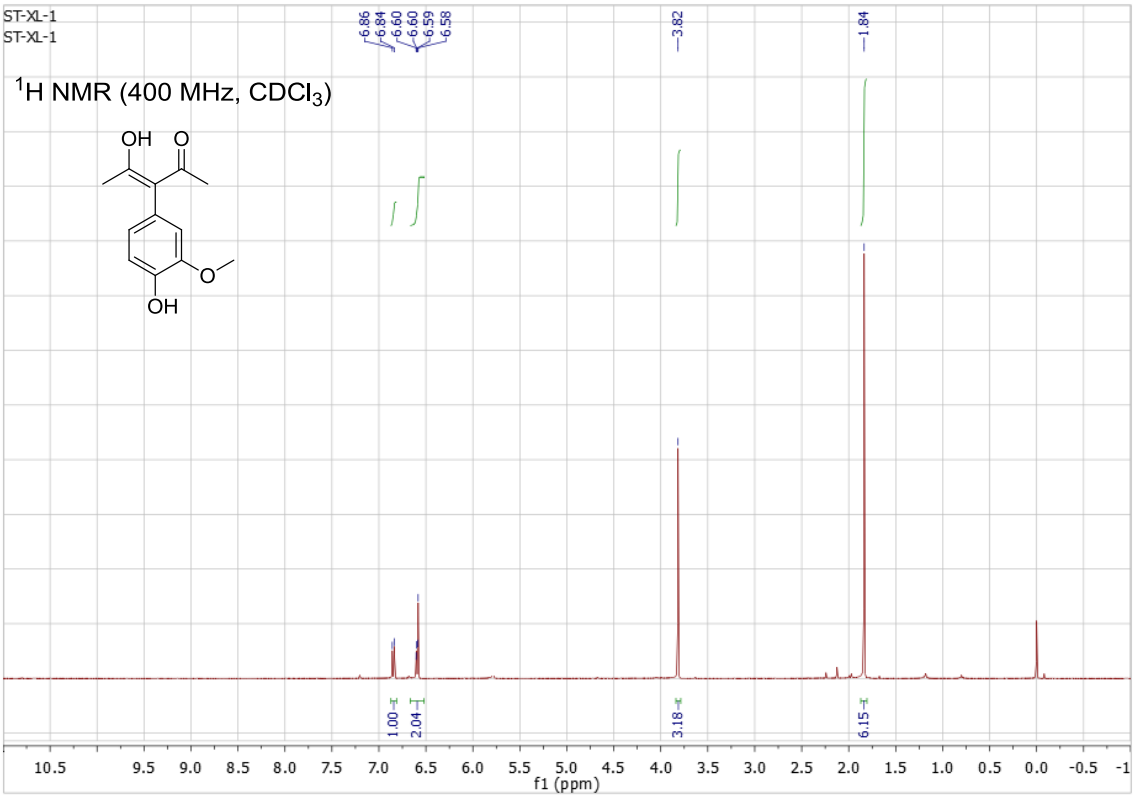


Figure S18. ^{1}H and ^{13}C NMR spectra of product **2i** from and acetoin with *p*-hydroxy benzaldehyde.



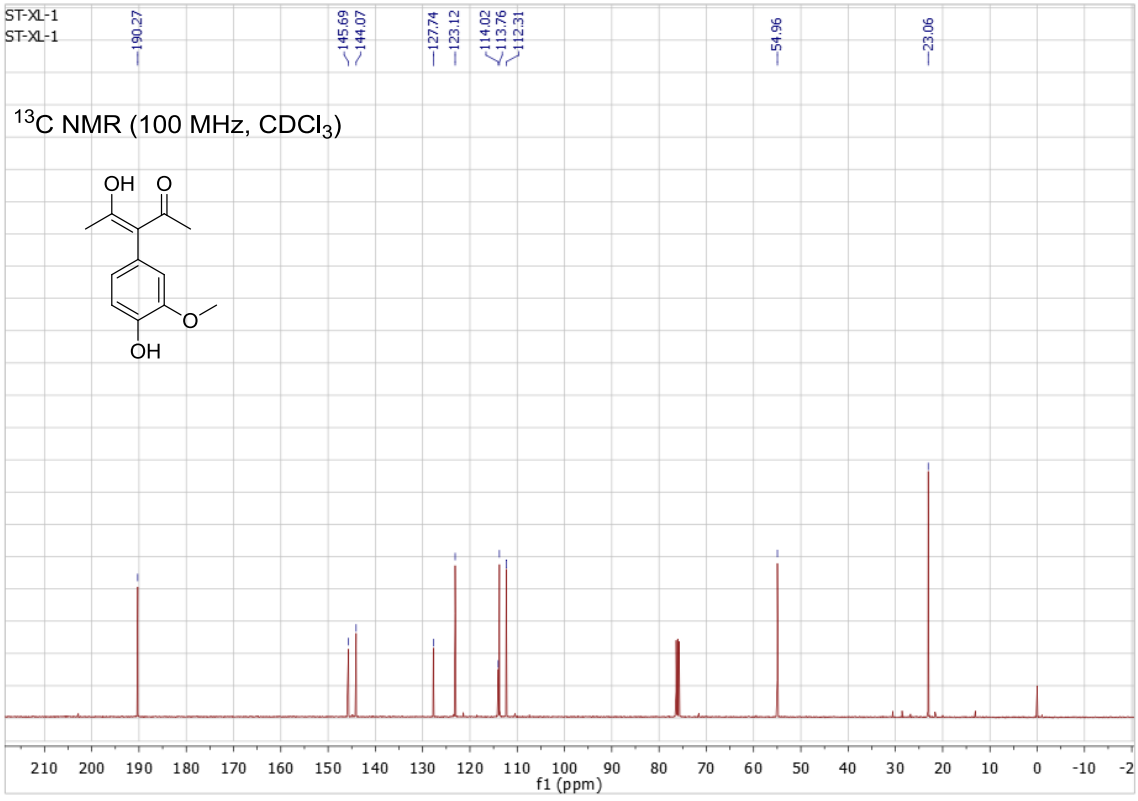
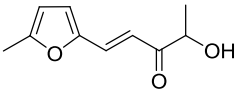


Figure S19. ^{1}H and ^{13}C NMR spectra of product **2h** produced from and acetoin with vanillin.

GC-MS identification of the products identified from HDO of **2d**.



2d

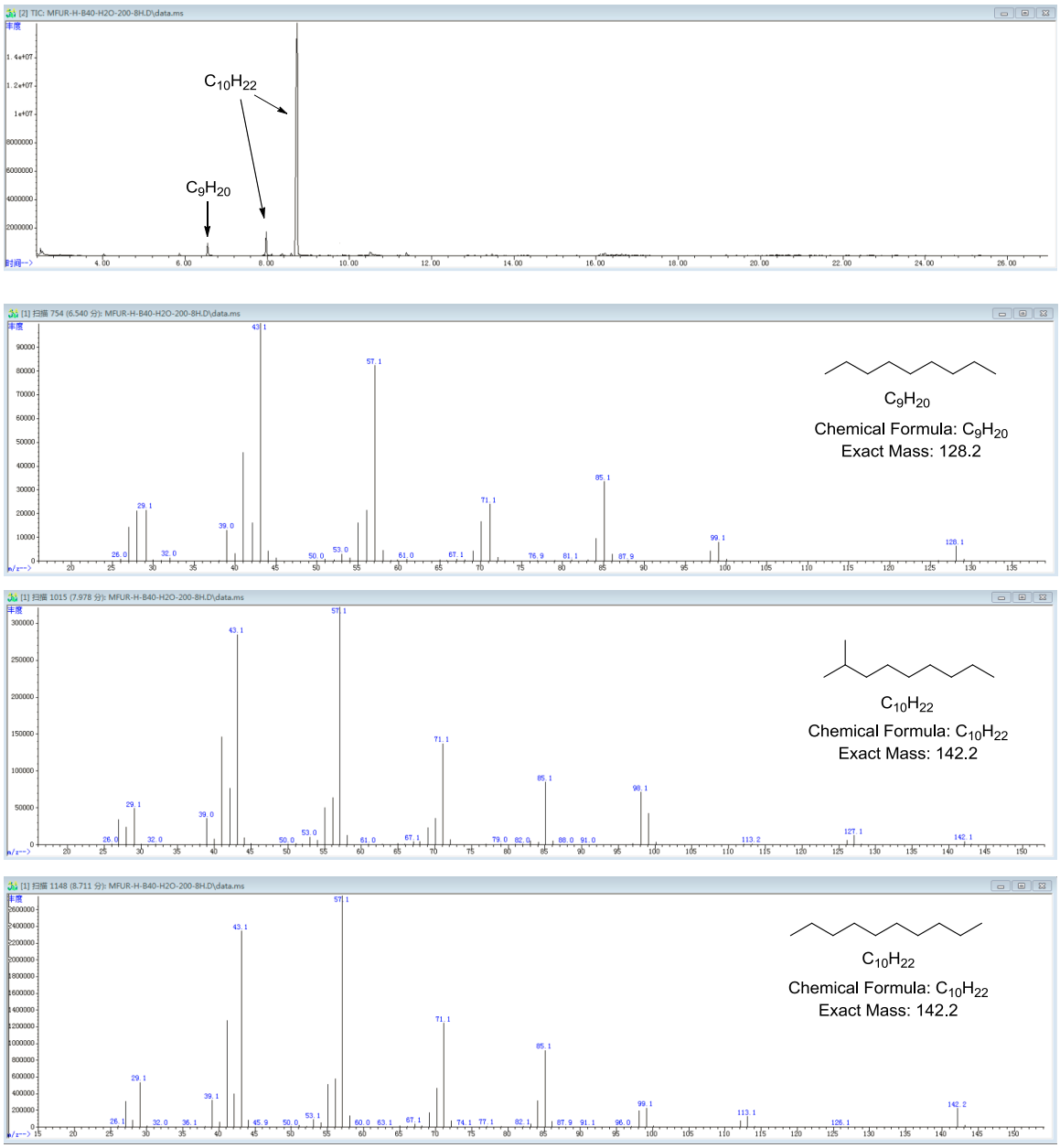
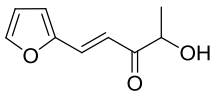


Figure S20. GC-MS Spectrum of the products identified from the organic-phase products produced by HDO of **2d** catalysed by Pd/C + H-beta zeolite system. Inset graphics depict the structures of detected compounds based on NIST database.

GC-MS identification of the products identified from HDO of **2b**.



2b

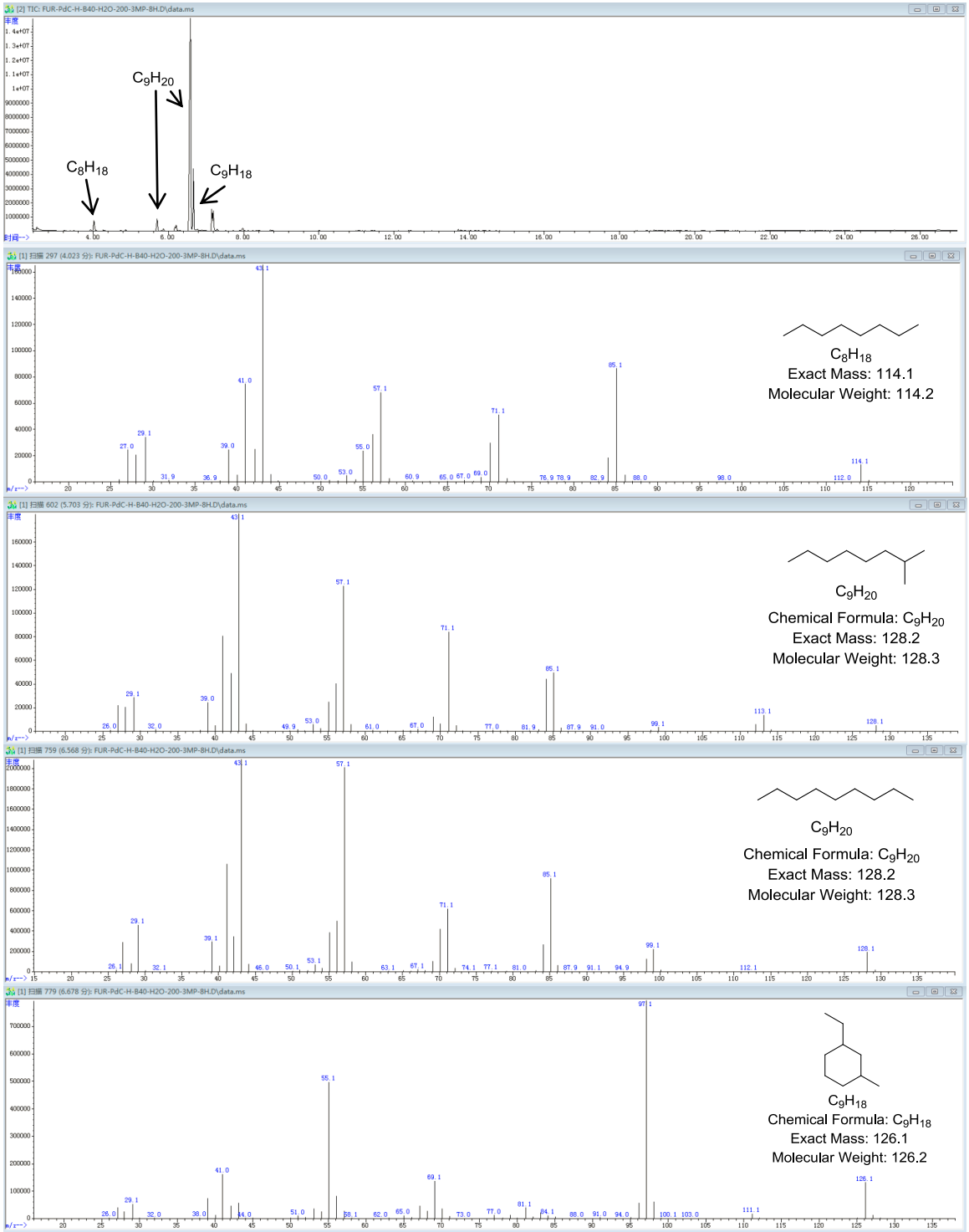
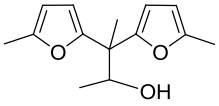


Figure S21. GC-MS Spectrum of the products identified from the organic-phase products produced by HDO of **2b**. Inset graphics depict the structures of detected compounds based on NIST database.

GC-MS identification of the products identified from HDO of **1b**.



1b

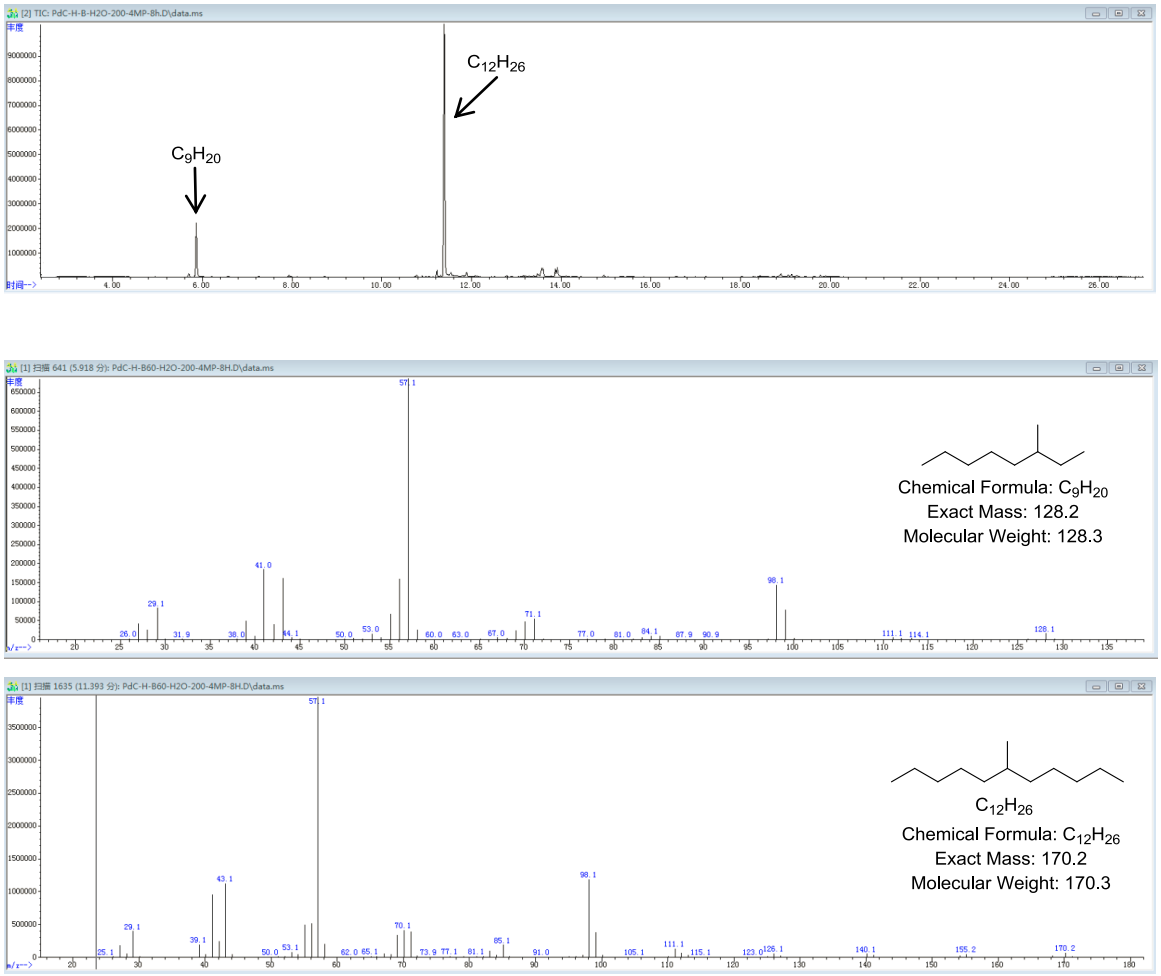
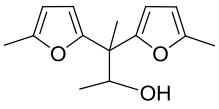


Figure S22. GC-MS Spectrum of the products identified from the organic-phase products produced by HDO of **1b**. Inset graphics depict the structures of detected compounds based on NIST database.

Comparative GC-MS spectrum of using $NbOPO_4$, $TaOPO_4$, and H-Beta zeolite for the HDO of **1b**.



1b

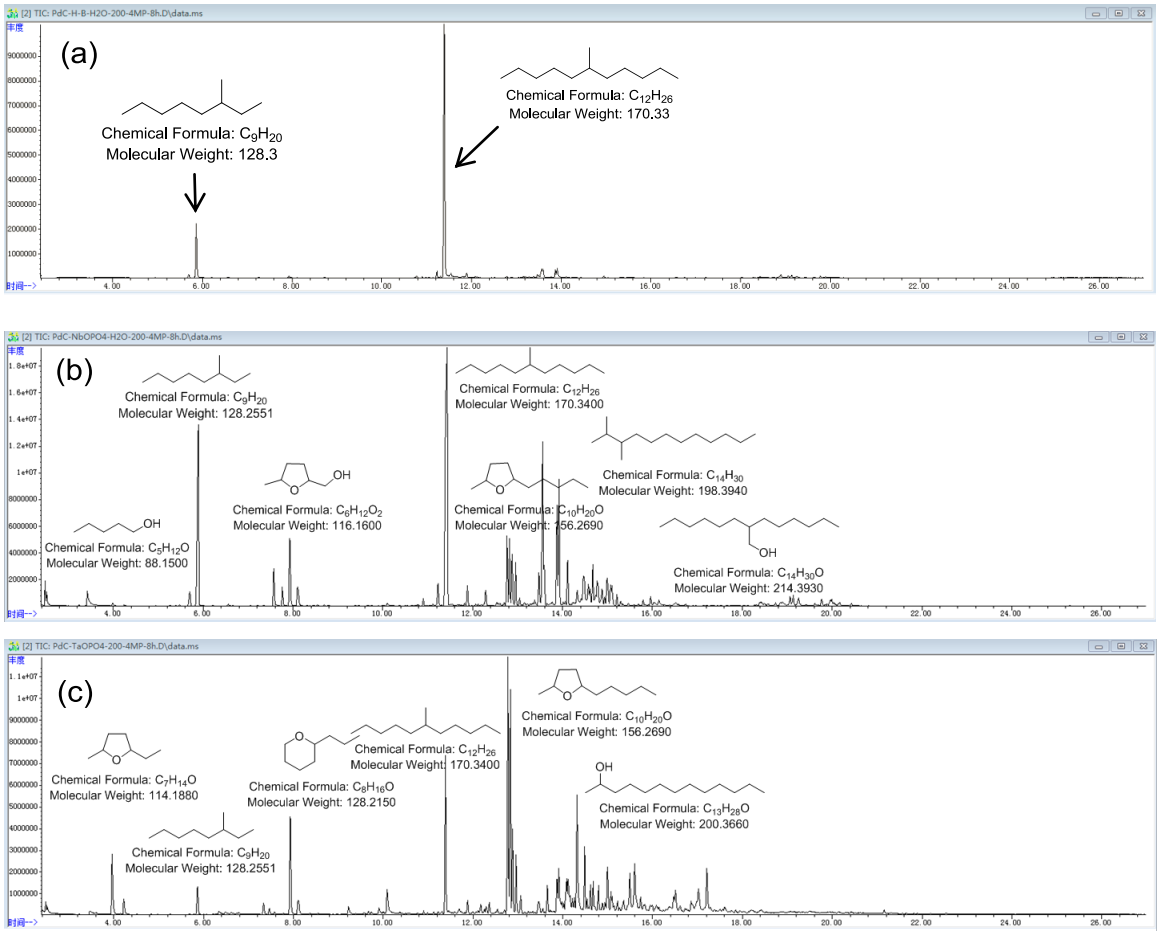
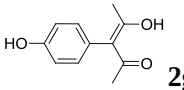


Figure S23. Comparative GC-MS spectrum of the HDO of **1b**. (a) Pd/C-H-Beta system; (b) Pd/C-$NbOPO_4$ system; (c) Pd/C-$TaOPO_4$ system. Inset graphics depict the structures of detected compounds based on NIST database.

GC-MS identification of the products identified from HDO of **2g**.



2g

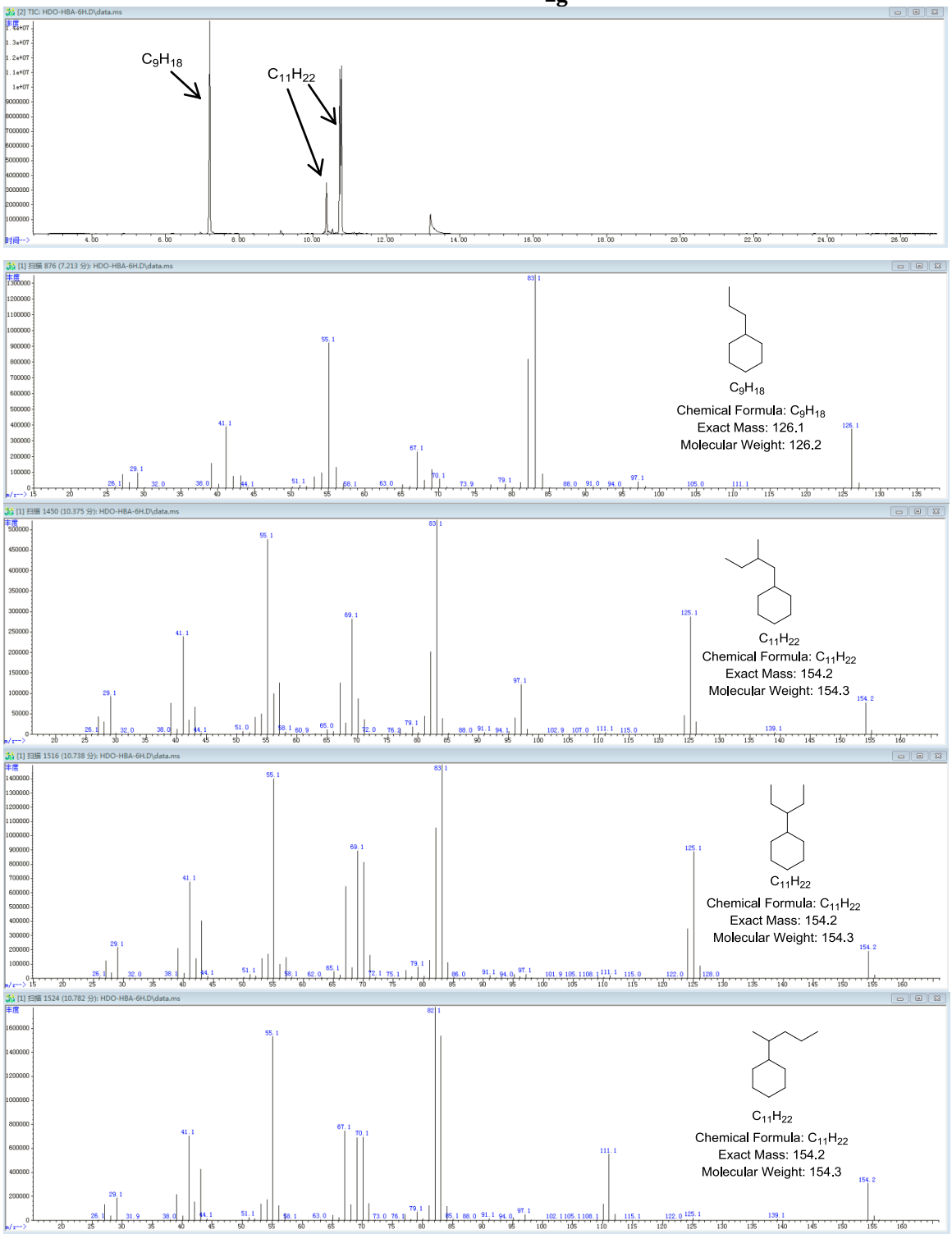


Figure S24. GC-MS Spectrum of the products identified from the organic-phase products produced by HDO of **2g**. Inset graphics depict the structures of detected compounds based on NIST database.

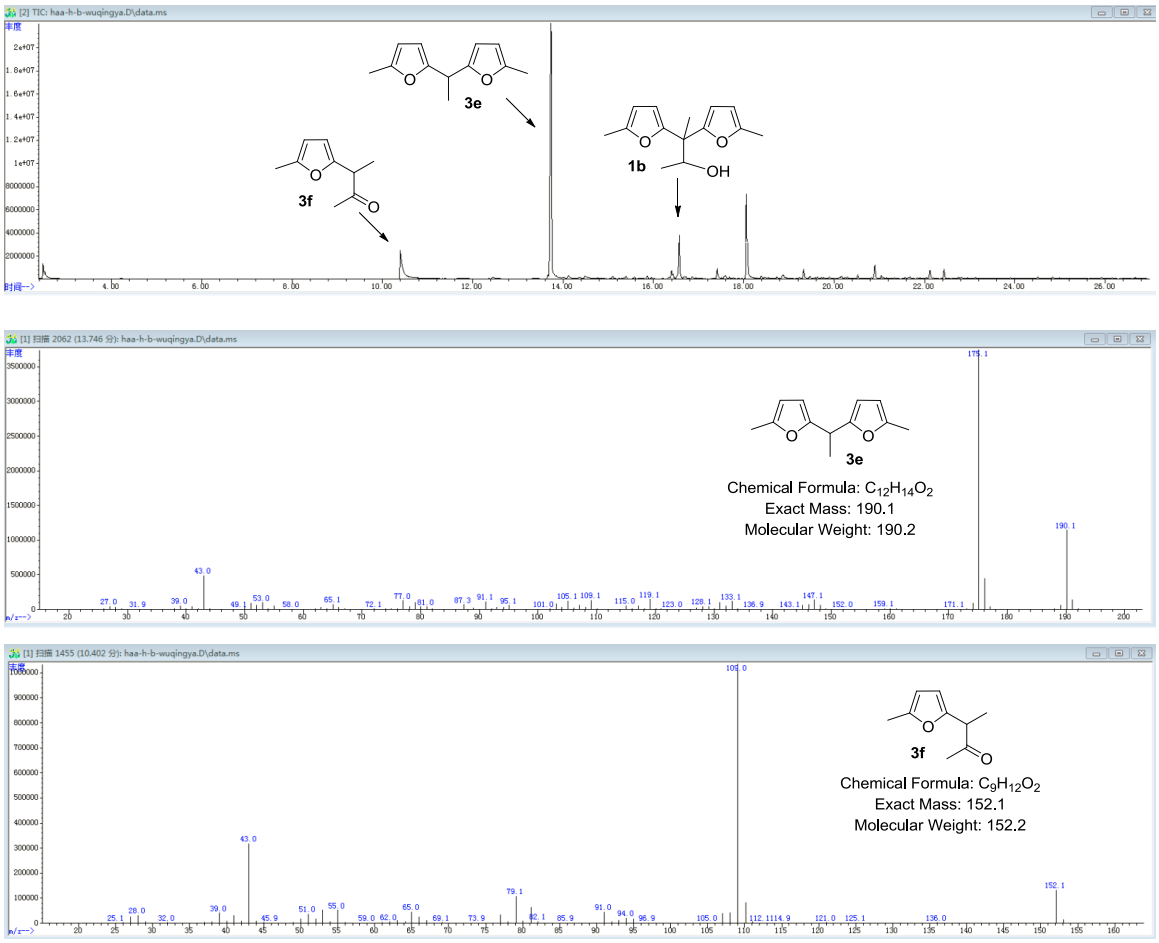


Figure S25. GC-MS spectrum of the reaction mixture of **1b** using only H-beta zeolite as a catalyst.

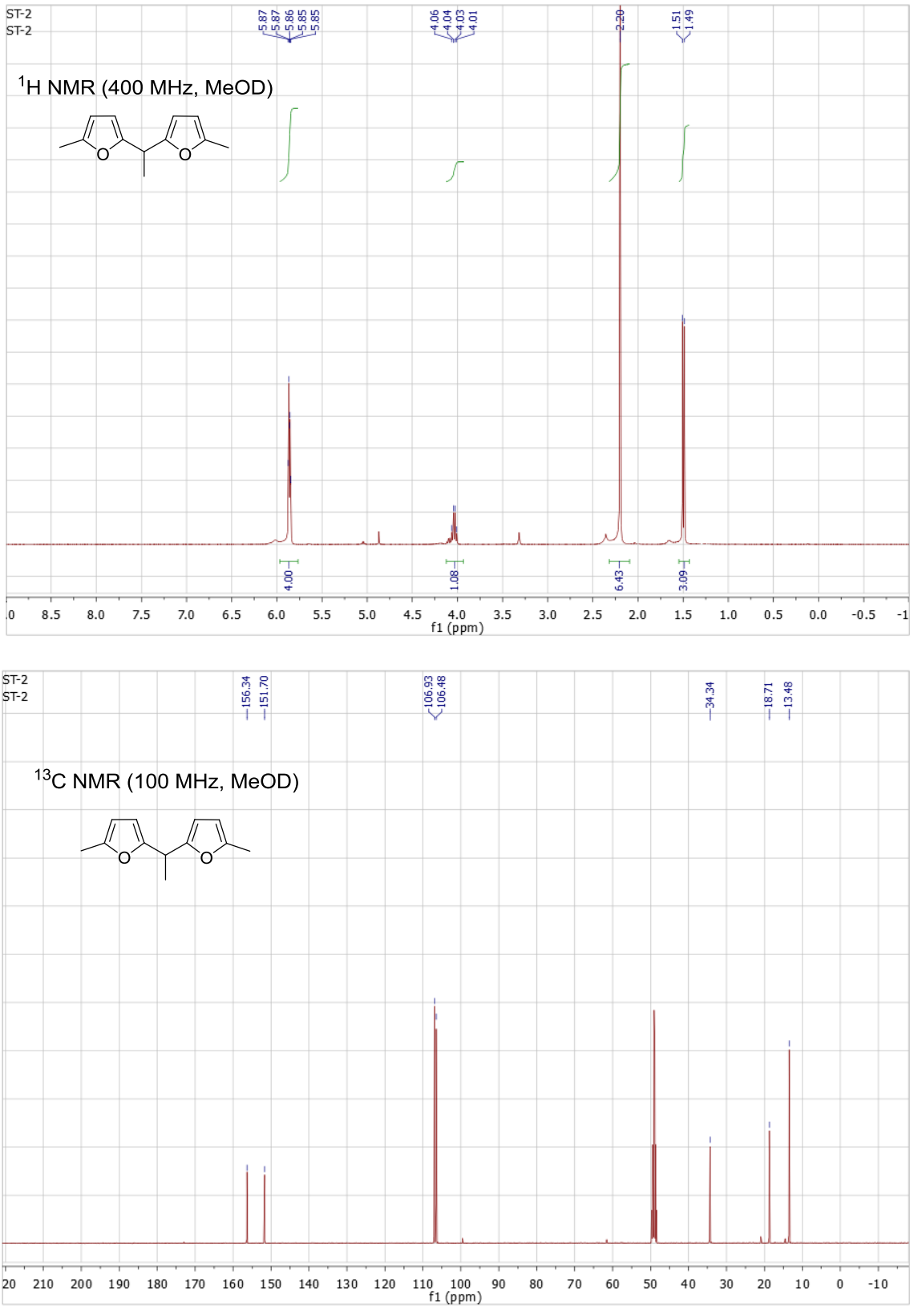


Figure S26. ^{1}H and ^{13}C NMR spectra of product **3h**.

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