Supporting Information

Catalyst-free Synthesis of Biodiesel Precursors from Biomass-based Furfuryl Alcohols in the Presence of H_2O and Air

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† S. Qin and T. Li contributed equally to this work.

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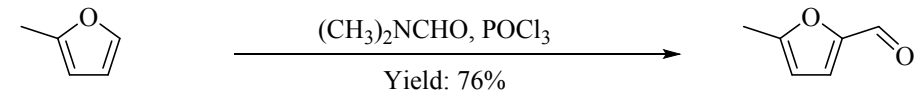
1. Methods for preparing 5-methylfurfural (5-MF)

Scheme S-1. 5-MF preparation methods

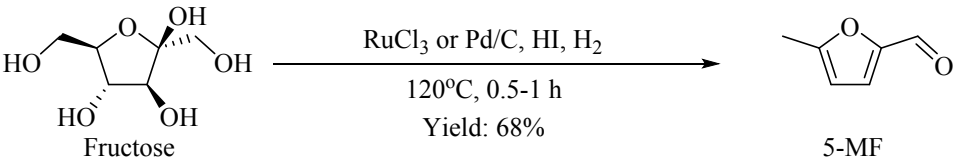
(**a**). Industrial process for 5-MF production



2-methylfuran 5-MF

J. Org. Chem. 1957, **22**, 1268 - 1269.

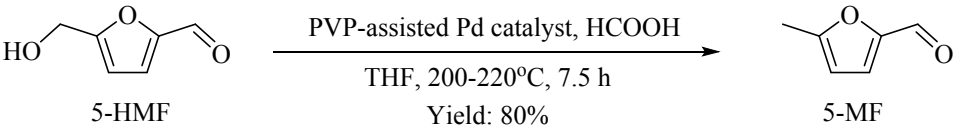
(**b**). Direct catalytic synthesis of 5-MF from fructose



Fructose 5-MF

ChemSusChem., 2011, **4**, 349 - 352.

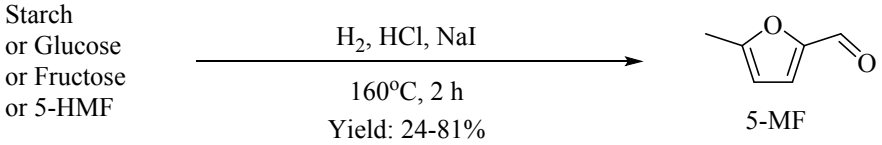
(**c**). Conversion of 5-HMF into 5-MF by using a PVP-assisted Pd catalyst



5-HMF 5-MF

Catal. Sci. Technol., 2019, **9**, 1238 - 1244.

(**d**). One step preparation of 5-MF from starch by iodide mediated hydrogenolysis

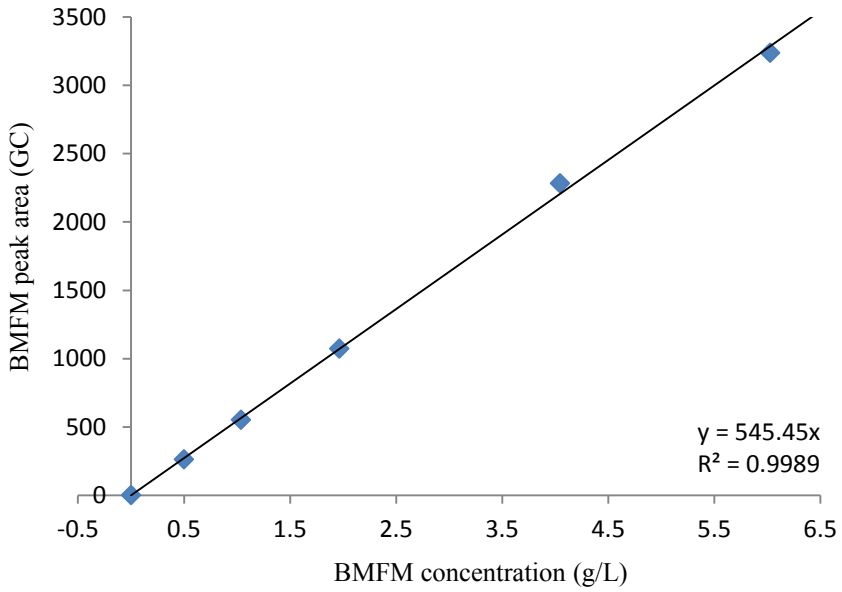


5-MF

Green Chem., 2019, **21**, 4169 - 4177.

2. Calibration curves for the product

Make a series of cyclohexane solutions with different product concentrations by using a 25 ml volumetric flask, and then perform the GC-FID measurement to draw the standard curve.



3. ICP-AES analysis and control experiments

3.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis

After the typical reaction, cyclohexane was removed from the reaction mixture by vacuum distillation. 0.5 mL the resulting solution was digested by using plasma-pure nitric acid and then diluted to 25.0 mL with double distilled H_2O. ICP-AES analysis was performed on thermo scientific 7000 series.

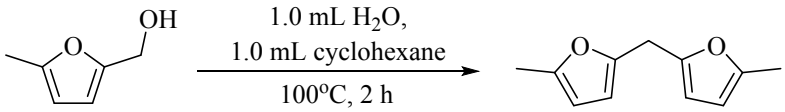
The concentration of metals in reaction liquid was listed in the following **Table S-1**:

Elem.	**Conc. (ppm)**
Al	0.004313
Bi	0.04755
Cd	0.003818
Co	0.0005510
Cr	0.05767
Cu	0.003466
Fe	0.1001
Mg	0.03485
Mn	0.003081
Ni	0.004018
Ir	-0.005900
Pd	-0.001308

Pt	-0.0002870
Rh	-0.05071
Ru	0.04197
Sn	0.04795
Sr	0.005078
Zn	0.005782

3.2 Control experiments

Table S-2. Different brands of 5-methylfurfuryl alcohol (5-MFA) and purified 5-MFA experiments[a]

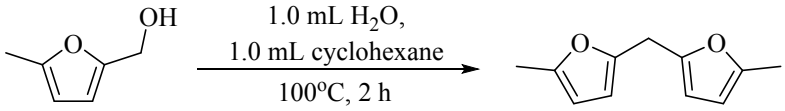


5-MFA BMFM

Entry	5-MFA brand	Yield (%)
1	Ark	74
2	9-dingchem	68
3	Energy Chemical	71
4[b]	Energy Chemical	75

[a] 5-MFA (0.2 mmol), [b] 5-MFA is purified by vacuum distillation.

Table S-3. Different sources of cyclohexane and H_2O experiments[a]



5-MFA BMFM

Entry	Cyclohexane brand	Different sources of H_2O	Yield (%)
1	Inno-chem	Running H_2O	64
2	Inno-chem	Distilled H_2O	68
3	Inno-chem	Ultra-pure H_2O	70
4	Xilong scientific	Ultra-pure H_2O	71
5	Tokyo chemical industry	Ultra-pure H_2O	73

[a] 5-MFA obtained from Energy chemical (0.2 mmol).

4. Kinetic study

The kinetic curves were drawn in **Figure S-1** to study the reaction process. In just 10 minutes, both the conversion and the yield are more than half, showing that this reaction occurs very quickly. As the increase of time, the yield gradually increases with the conversion rate, and 92% of 5-MFA was converted and 79% yield of BMFM were obtained in 2 h. Some intermediates might existence in this process, but they were not detected by NMR, GC-MS and UPLC-MS.

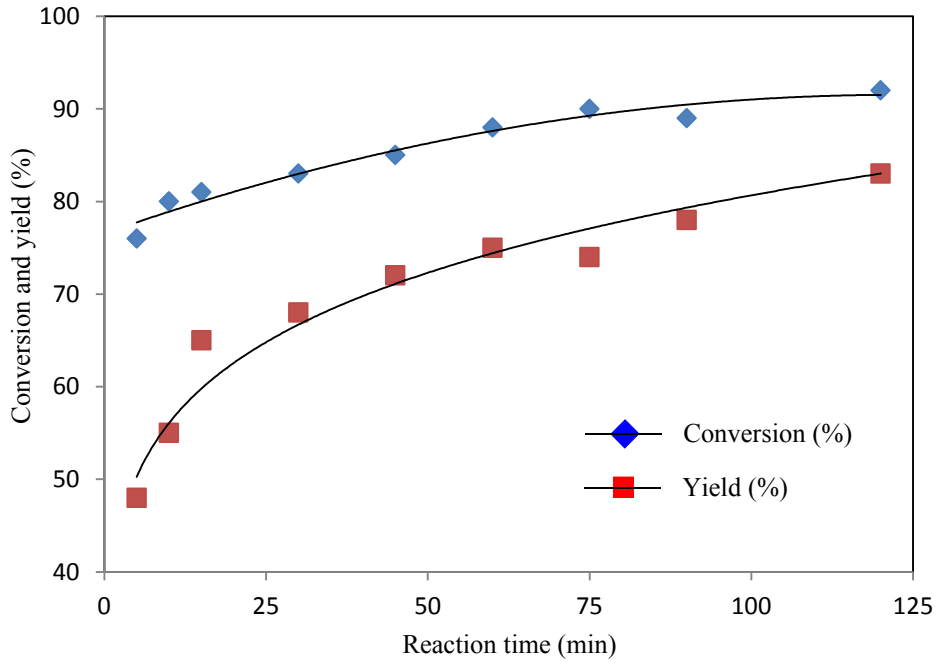


Figure S-1. Kinetic study on the BMFM production from 5-MFA

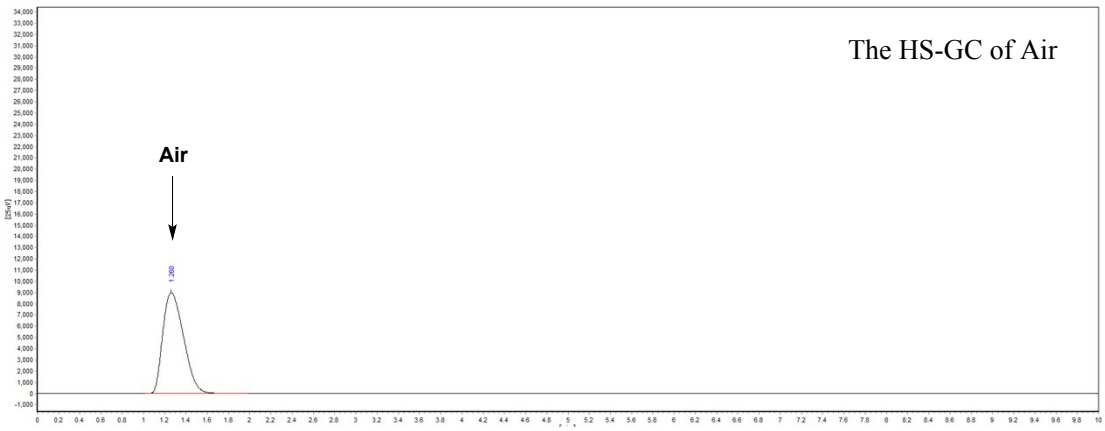
5. CO_2 detection experiments

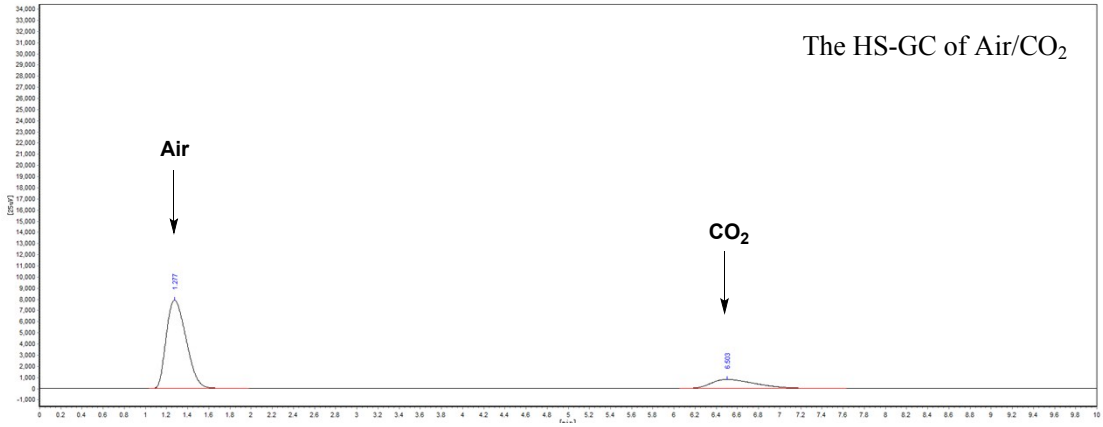
A typical reaction in 10 mL stainless reactor was carried out and the gaseous products were analyzed by HS-GC.

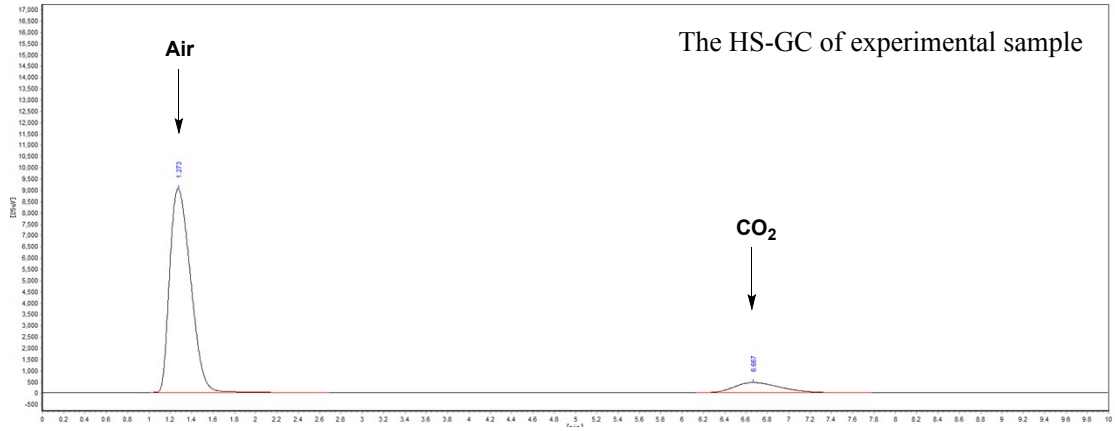
Scheme S-2. CO_2 detection experiments

raw material
0.4 mmol
→ (2.0 mL H_2O, 2.0 mL cyclohexane; 100°C, 2 h, 50 psi air) → CO_2

None	N. D.
5-MFA	D.
HCHO	N. D.



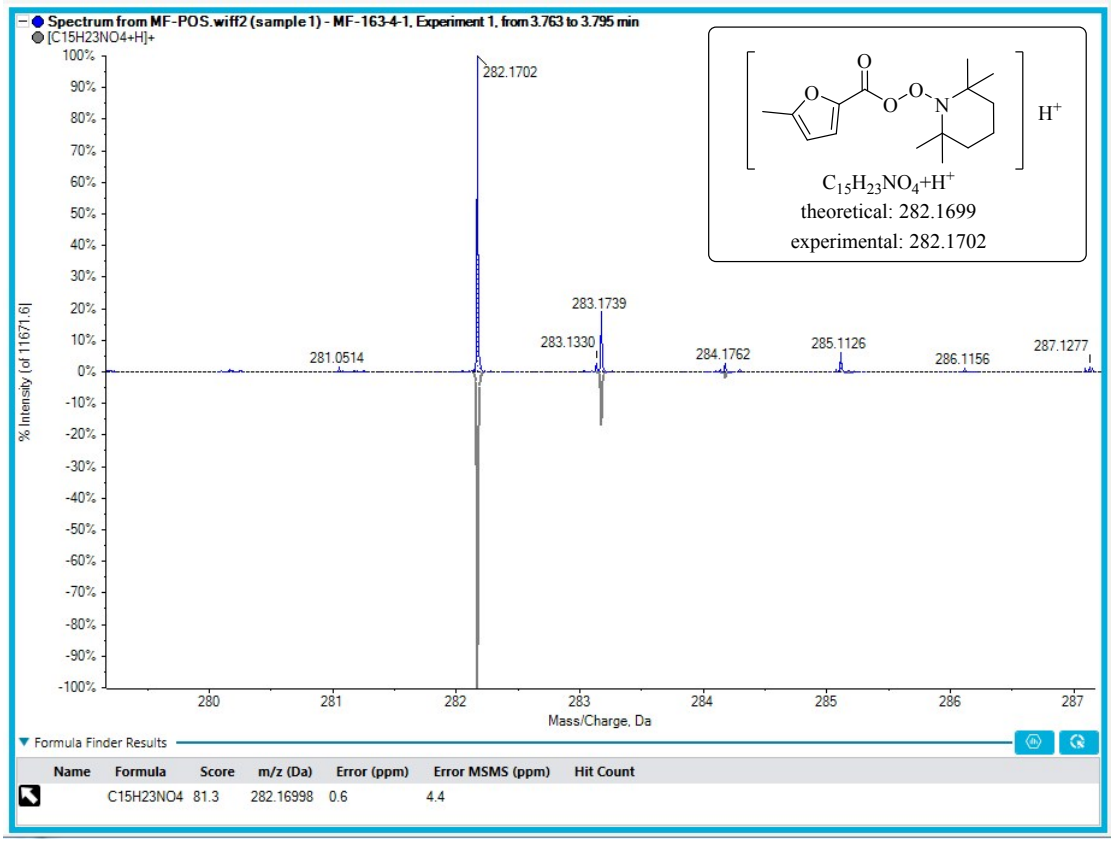

The HS-GC of Air/CO_2
Air
CO_2
1.277
6.603

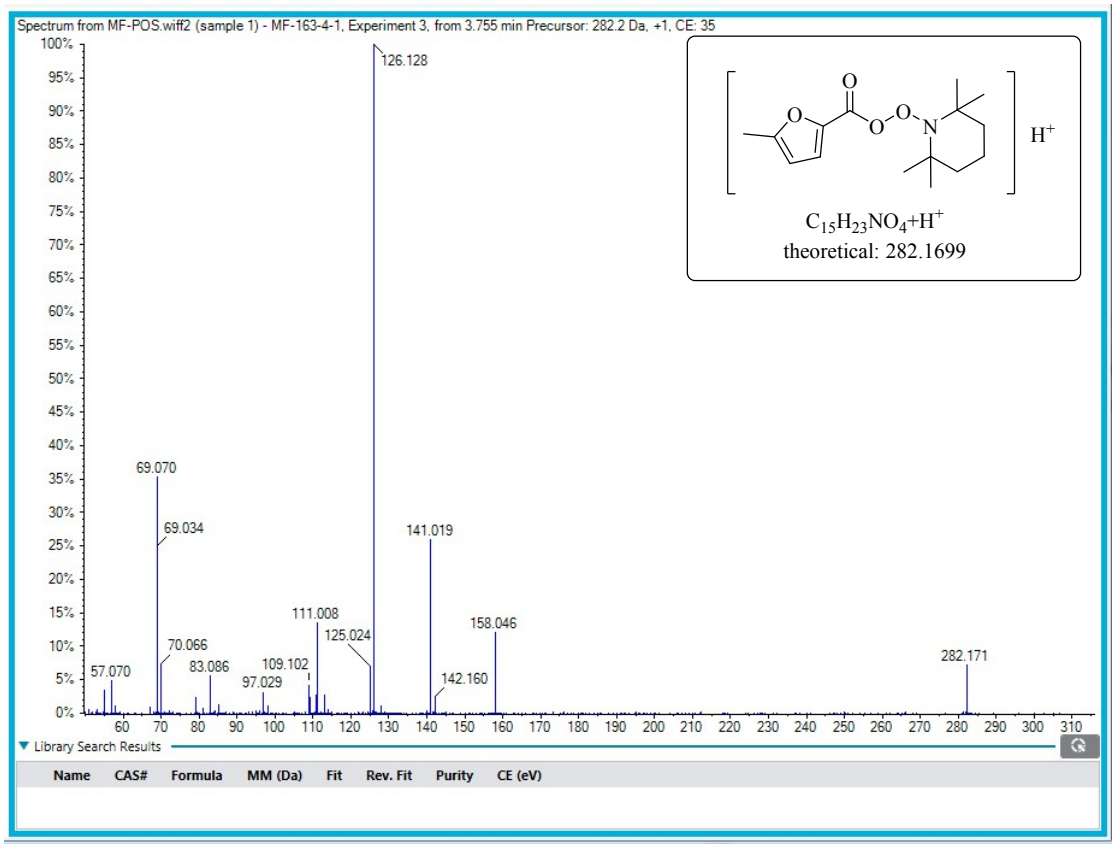

The HS-GC of experimental sample
Air
CO_2
1.273
6.667

6. Ultra Performance Liquid Chromatography Quadrupole Time-of-flight Mass Spectrometry (UPLC-QTOF-MS) analysis

A typical reaction with TEMPO (3.0 equivalents) was performed for free radical trapping experiments. After this reaction, cyclohexane phase was concentrated and tested with UPLC-QTOF-MS equipment. The result is as follows

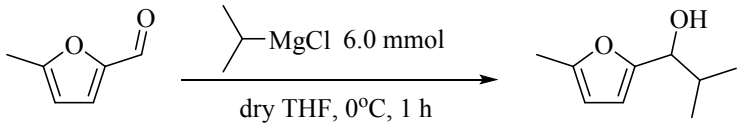
Figure S-2. Free radical trapping experiments




Spectrum from MF-POS.wiff2 (sample 1) - MF-163-4-1, Experiment 3, from 3.755 min Precursor: 282.2 Da, +1, CE: 35
126.128
69.070
69.034
141.019
111.008
125.024
158.046
70.066
83.086
109.102
97.029
57.070
142.160
282.171
Library Search Results
Name CAS# Formula MM (Da) Fit Rev. Fit Purity CE (eV)
O
O
O
O
N
H+
C15H23NO4+H+
theoretical: 282.1699

7. Synthesis of substrates

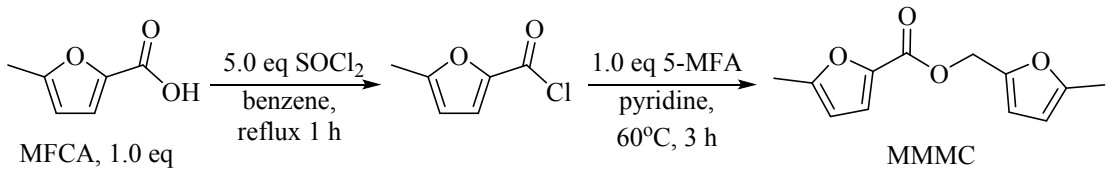
Synthesis of 2-methyl-1-(5-methylfuran-2-yl)propan-1-ol (MFPL)



5-MF, 5.4 mmol MFPL, Yield: 97%

A solution of 5-MF (0.536 mL, 5.4 mmol) in dry THF (5.0 mL) was added to a solution of isopropylmagnesium chloride in Et_2O (2.0 M, 3.0 mL, 6.0 mmol). The mixture was stirred at 0°C for 1 hour. After the reaction, saturated aqueous NH_4Cl (10.0 mL) was added, and the mixture was extracted with diethyl ether (3 × 10 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. 2-methyl-1-(5-methylfuran-2-yl)propan-1-ol (MFPL) was isolated as a yellow oil (0.8081 g, 97%) and used without further purification.

Synthesis of (5-methylfuran-2-yl)methyl 5-methylfuran-2-carboxylate (MMMC)



MFCA, 1.0 eq MMMC

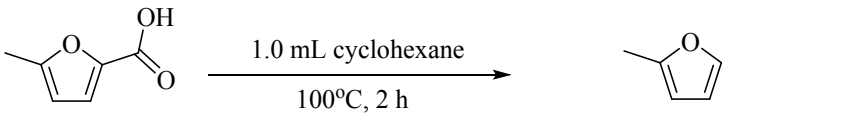
A solution of MFCA (0.378 g, 3.0 mmol) and $SOCl_2$ (1.1 mL, 15.0 mmol) in benzene (15.0 mL) was refluxed for 1 h. Removal of the solvent under reduced pressure afforded crude 5-methylfuran-2-carbonyl chloride in a quantitative yield. After added pyridine (10.0 mL), 5-methylfurfuryl alcohol (5-MFA) (0.336 g, 3.0 mmol), the mixture was stirred at 60°C for 3 h under N_2. The reaction liquid was cooled down and extracted with ethyl acetate and the extractive liquid was dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure. The residue was separated by flash column chromatography over silica gel eluting with petroleum

ether and ethyl acetate to obtain the product (5-methylfuran-2-yl)methyl 5-methylfuran-2-carboxylate (MMMC) as light yellow liquid.

8. Mechanism verification experiments

Scheme S-3. Mechanism verification experiments

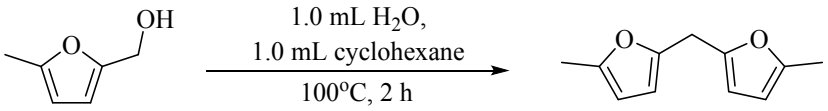
(**a**). Study on the effect of H_2O on the system



0.2 mmol

with 1.0 mL H_2O, 10%
without 1.0 mL H_2O, trace

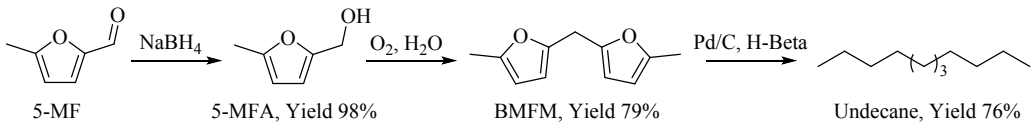
(**b**). The effect of acid-base environment on the reaction



0.2 mmol — 79%
Added 0.1 mL Et_3N — 0%
0.1 mL CH_3COOH — 73%

9. Application for C_{11} biodiesel synthesis from 5-MF

Scheme S-4. Synthetic of biodiesel application from 5-MF



5-MF 5-MFA, Yield 98% BMFM, Yield 79% Undecane, Yield 76%

Synthesis of 5-MFA by hydrogenation of 5-MF

5-MF (1.0 g, 9.08 mmol) was dissolved in anhydrous CH_3OH (10.0 mL) in a 50 mL round bottom flask under nitrogen. $NaBH_4$ (0.678 g, 18.2 mmol) was added, and the mixture was stirred for 16 h at room temperature. H_2O was added, and the aqueous phase was extracted with dichloromethane. The organic layer was dried with Na_2SO_4 and filtered. Evaporation of the solvent afforded a 98% yield 5-MFA as orange liquid.

Synthesis of BMFM from 5-MFA through our method

5-MFA (0.5606 g, 5.0 mmol), 20.0 mL H_2O and 20.0 mL cyclohexane were added to a 50 mL round bottom flask, under 100°C heating for 2 h with the condenser tube reflux. The the reaction was cooled to room temperature and the aqueous phase was extracted with EA. The combined organic layer was dried over Na_2SO_4 and filtered. Evaporation of the solvent afforded a 79% yield BMFM as light yellow oil.

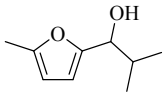
Synthesis of C_{11} biodiesel via the hydrodeoxygenation of BMFM

BMFM (0.5 mmol, 88.0 mg), Pd/C (5.0 wt%, 25 mg), H-beta zeolite (25.0 mg) and 4.0 mL cyclohexane were added to a 10 mL high pressure reactor. The reactor was purged three times with nitrogen and then charged with 3.5 MPa H_2. Then the reactor was heated to 240°C under vigorous stirring for 10 h. After the system cooled down to room temperature, the catalyst was

removed by filter and the liquid solution was analyzed by GC-MS, 76% yield C_{11} biodiesel was obtained by GC.

10. Analytical data and NMR spectra of compounds

2-methyl-1-(5-methylfuran-2-yl)propan-1-ol (MFPL)

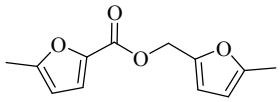


Yellow liquid,

^{1}H NMR (400 MHz; CD_3OD): δ = 6.08-6.07 (d, 1H), 5.91-5.90 (d, 1H), 4.19-4.17 (d, 1H), 2.25 (s, 3H), 2.10-2.00 (t, 1H), 1.01-0.99 (d, 3H), 0.82-0.81 (d, 3H);

^{13}C NMR (100 MHz; CD_3OD): δ = 154.70, 150.74, 106.85, 105.41, 72.88, 32.90, 17.98, 17.71, 12.09.

(5-methylfuran-2-yl)methyl 5-methylfuran-2-carboxylate (MMMC)

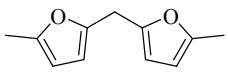


Light yellow liquid,

^{1}H NMR (400 MHz; DMSO-D_6): δ = 7.22-7.21 (d, 1H), 6.46-6.45 (d, 1H), 6.32-6.31 (d, 1H), 6.08-6.07 (d, 1H), 5.18 (s, 2H), 2.34 (s, 3H), 2.26 (s, 3H);

^{13}C NMR (100 MHz; DMSO-D_6): δ = 157.91, 157.88, 153.18, 147.81, 142.42, 120.70, 112.83, 109.42, 107.33, 58.20, 13.97, 13.74.

bis(5-methylfuran-2-yl)methane (BMFM)

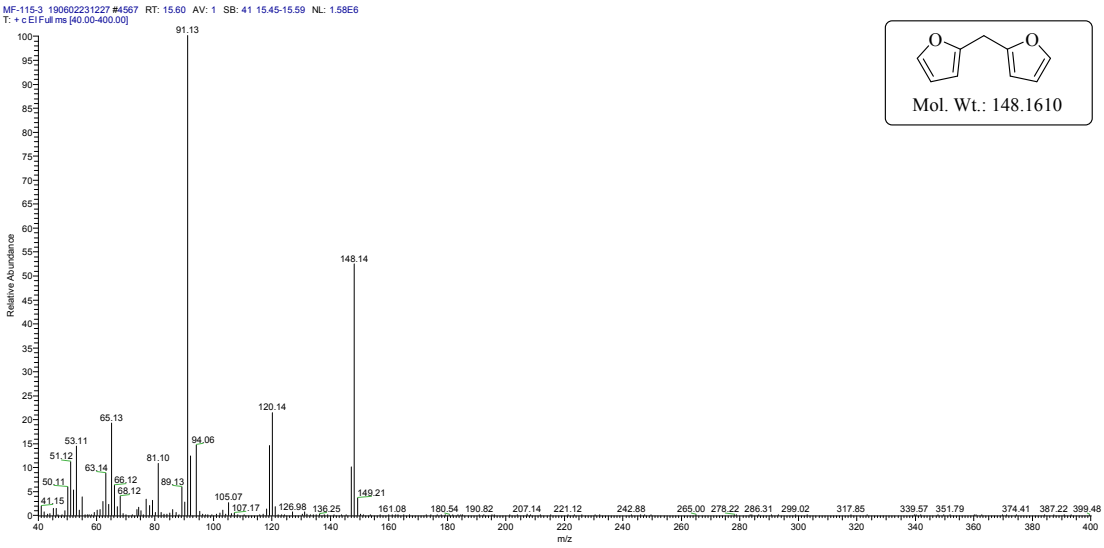


Light yellow liquid,

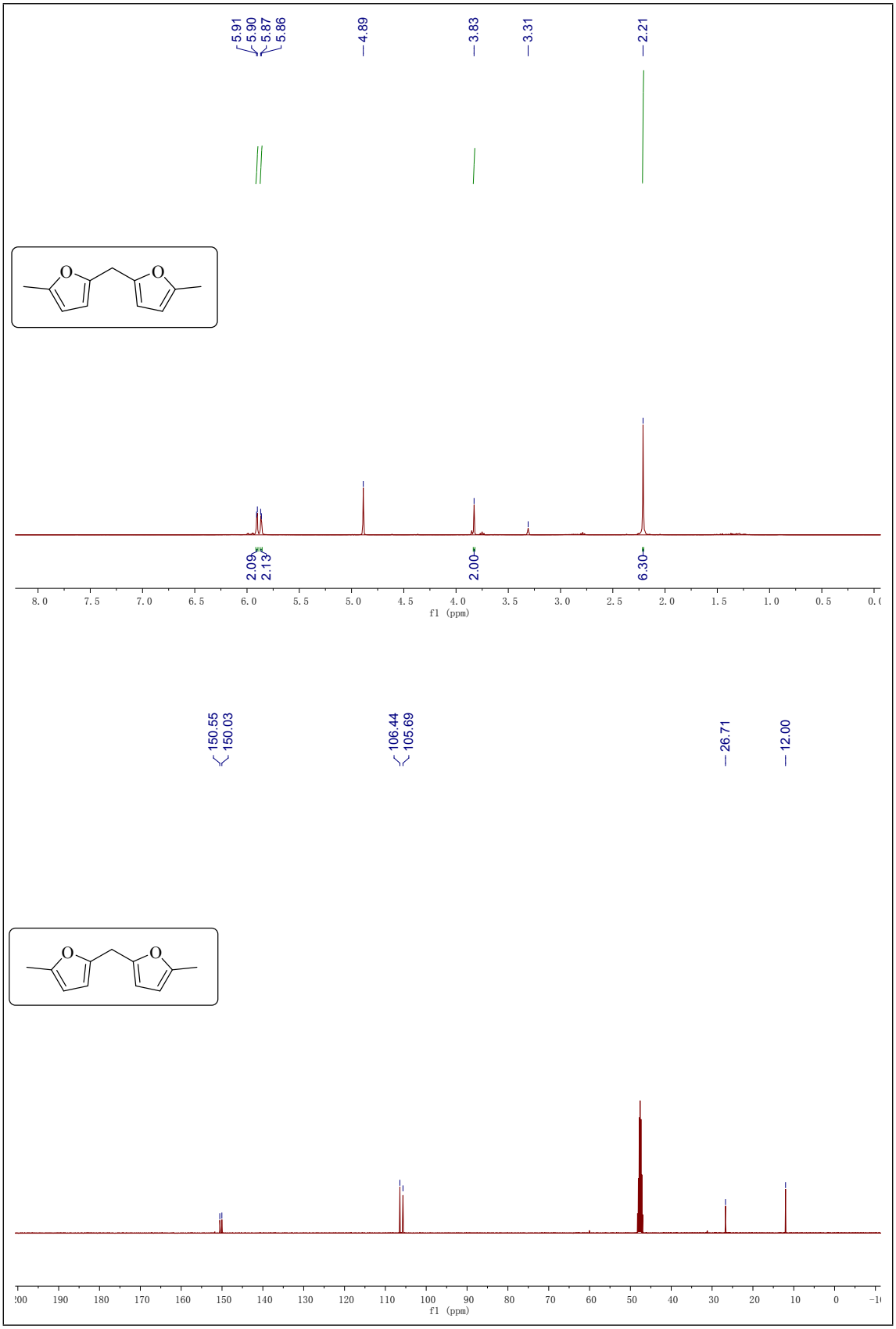
^{1}H NMR (600 MHz; CD_3OD): δ = 5.91-5.90 (dd, 2H), 5.87-5.86 (dd, 2H), 3.83 (s, 2H), 2.21 (s, 6H);

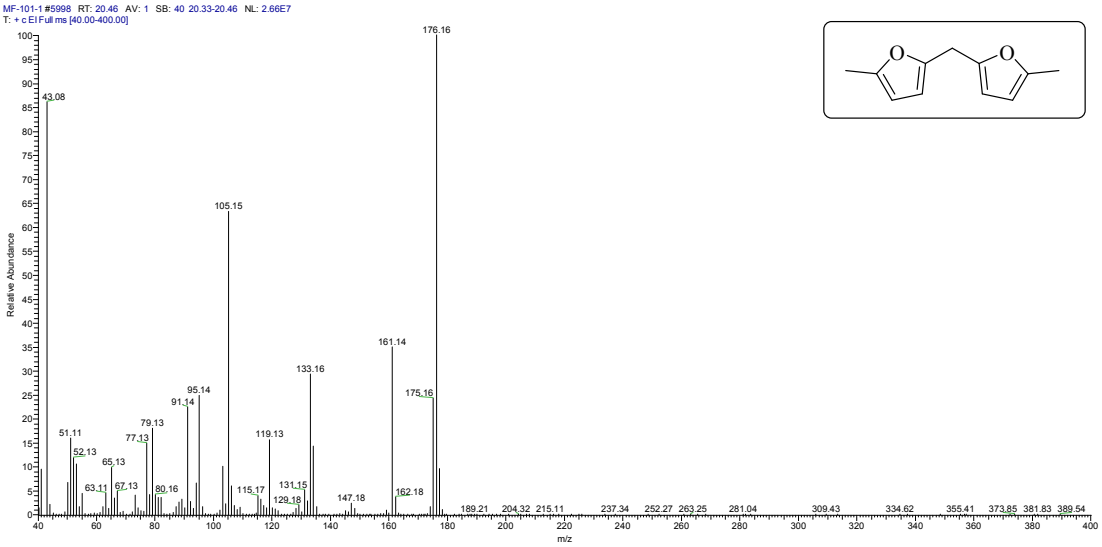
^{13}C NMR (100 MHz; CD_3OD): δ = 150.55, 150.03, 106.44, 105.69, 26.71, 12.00.

HRMS (ESI-TOF) (m/z): Calcd for $C_{11}H_{12}O_2$, $[M+H]^+$: 177.0910, Found : 177.0914.

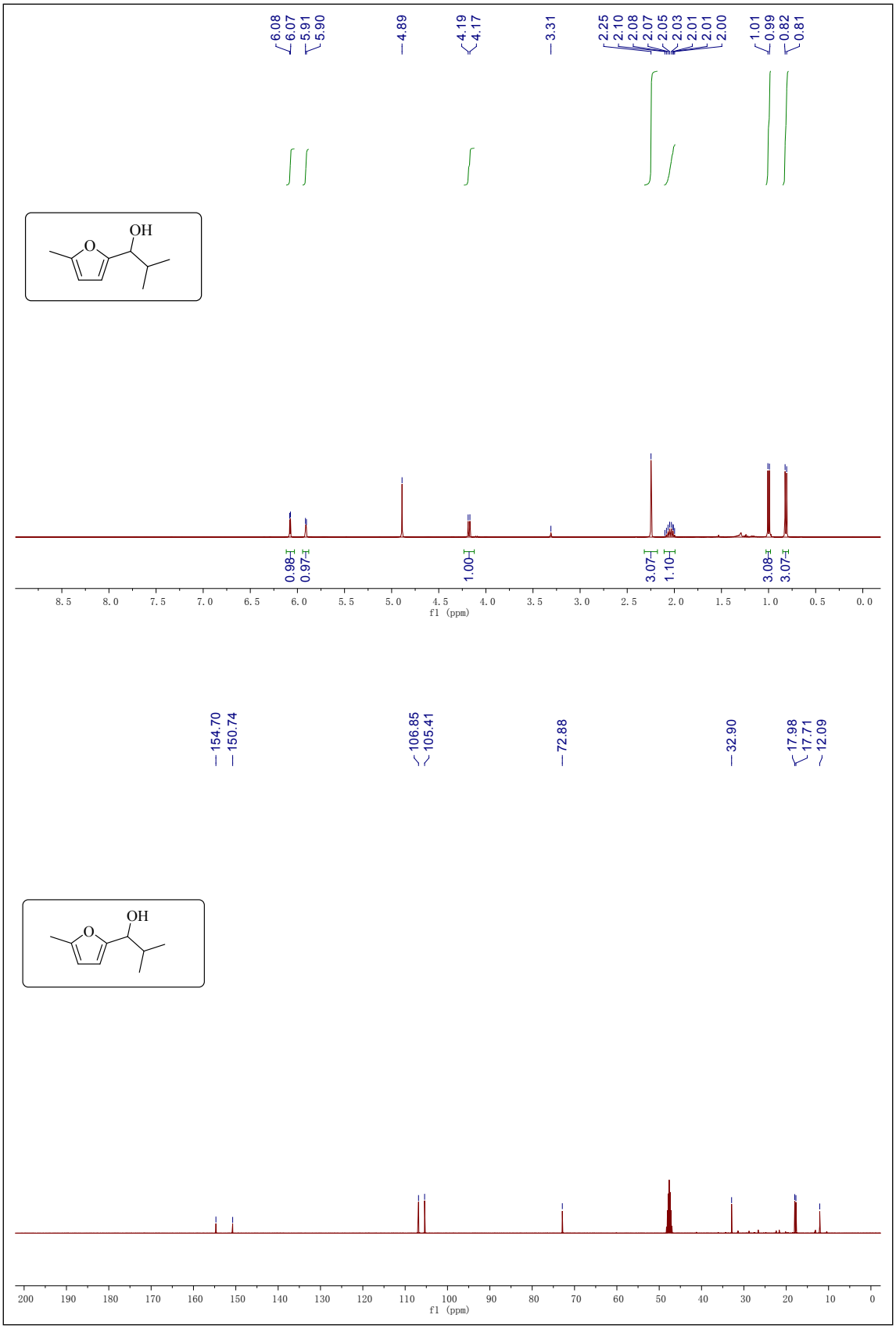


Mass spectrogram of the component of BFM with retention time of 15.60 min. Inset shows the suggested molecular formula.

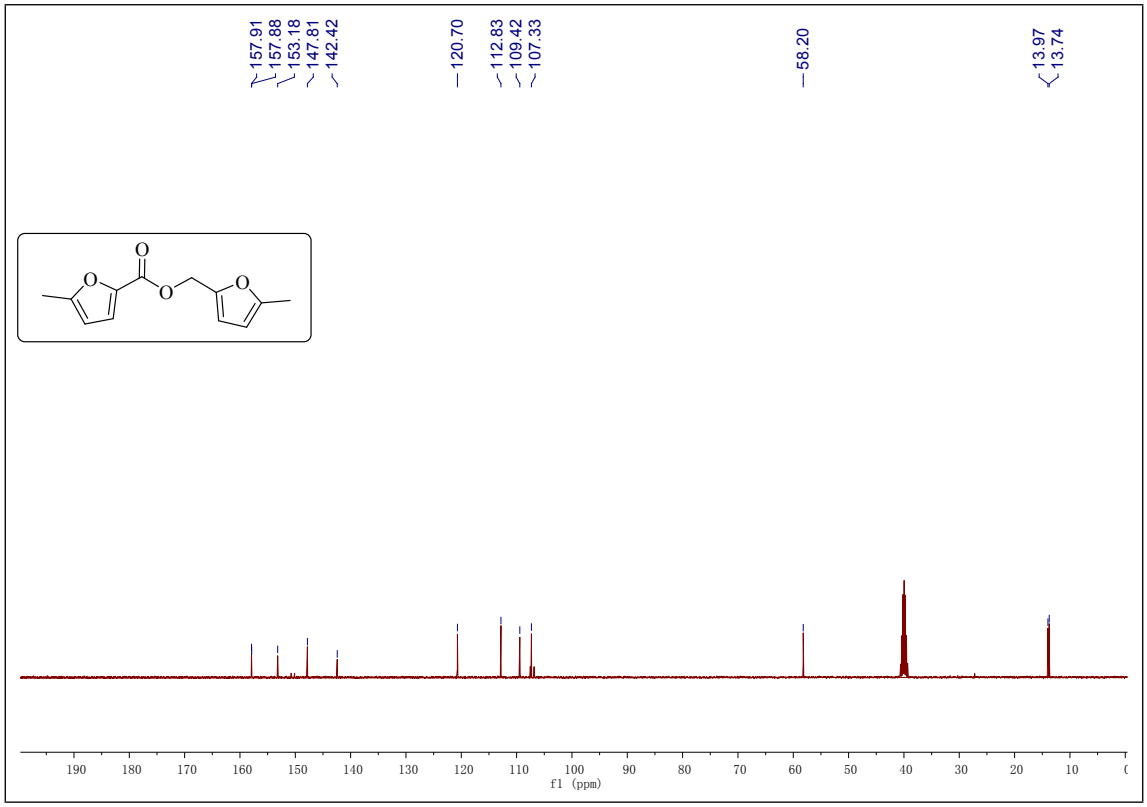

5.91
5.90
5.87
5.86
4.89
3.83
3.31
2.21
2.09
2.13
2.00
6.30
f1 (ppm)
150.55
150.03
106.44
105.69
26.71
12.00
f1 (ppm)



Mass spectrogram of the component of BMFM with retention time of 20.46 min. Inset shows the suggested molecular formula.


6.08
6.07
5.91
5.90
4.89
4.19
4.17
3.31
2.25
2.10
2.08
2.07
2.05
2.03
2.01
2.01
2.00
1.01
0.99
0.82
0.81
OH
O
0.98
0.97
1.00
3.07
1.10
3.08
3.07
f1 (ppm)
154.70
150.74
106.85
105.41
72.88
32.90
17.98
17.71
12.09
OH
O
f1 (ppm)


7.22
7.21
6.46
6.45
6.32
6.31
6.08
6.07
5.18
3.35
2.50
2.34
2.26
O
O
O
O
1.02
1.01
1.01
0.98
2.00
3.05
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


157.91
157.88
153.18
147.81
142.42
120.70
112.83
109.42
107.33
58.20
13.97
13.74
O
O
O
O
190
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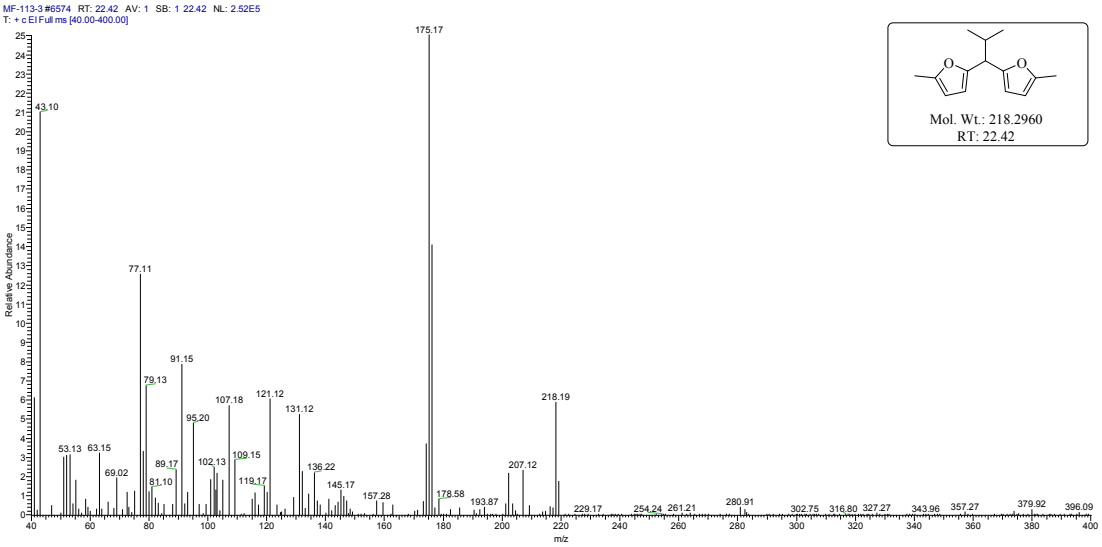
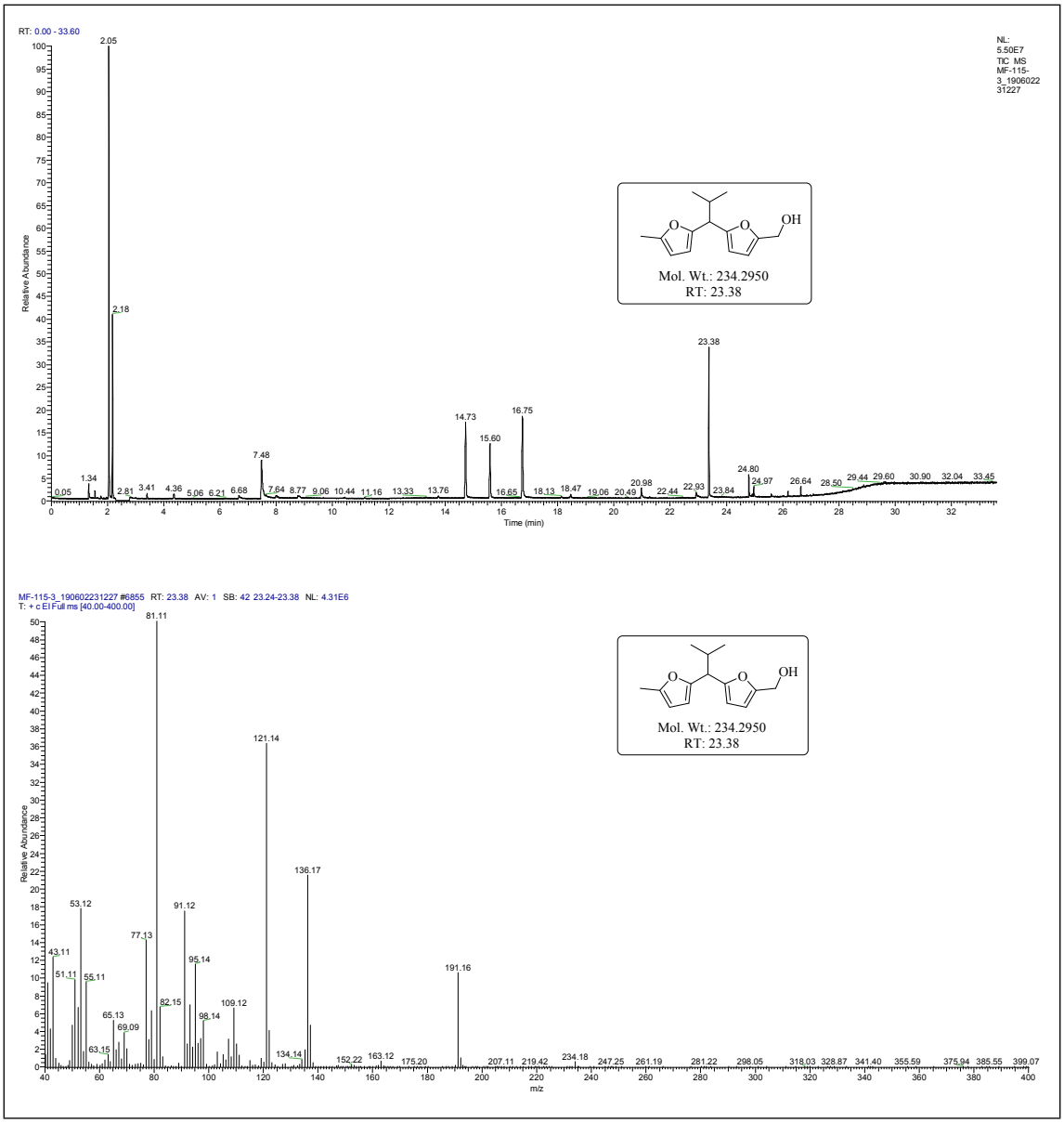
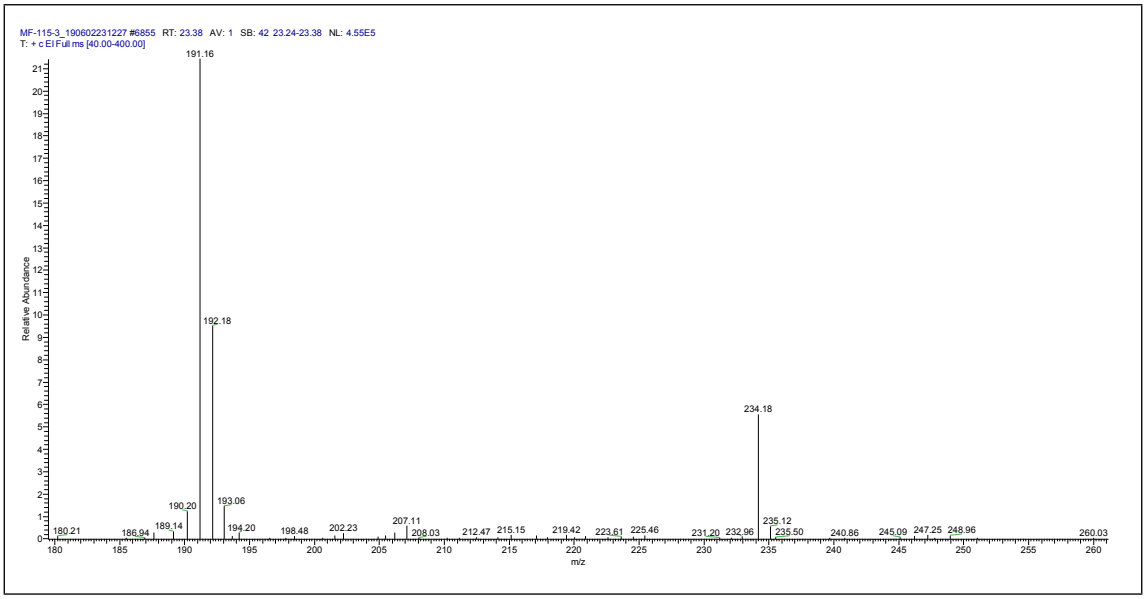
70
60
50
40
30
20
10
f1 (ppm)

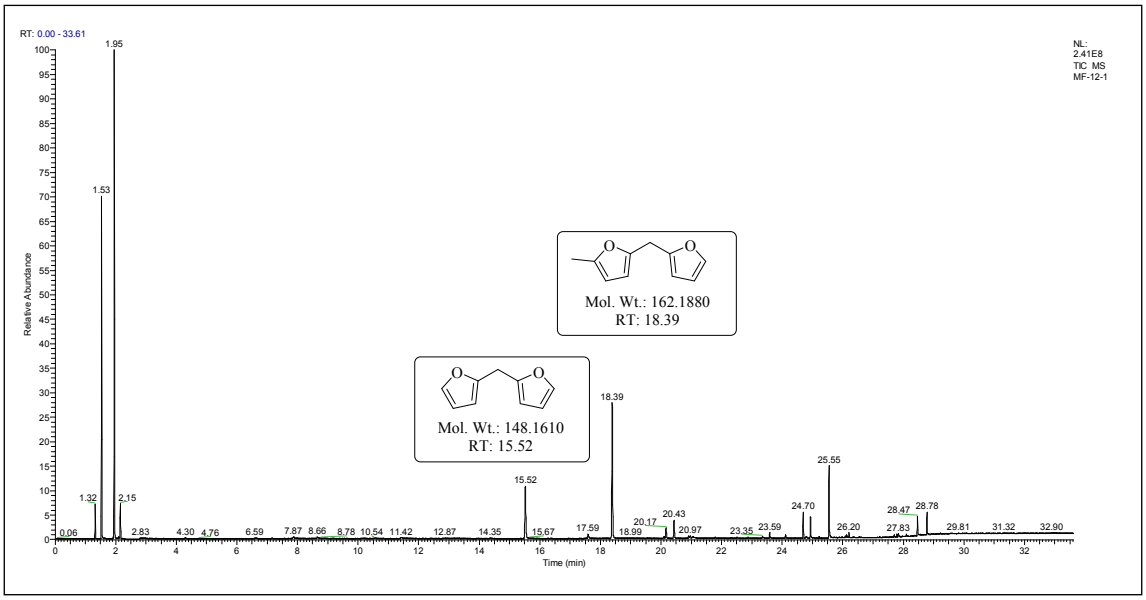


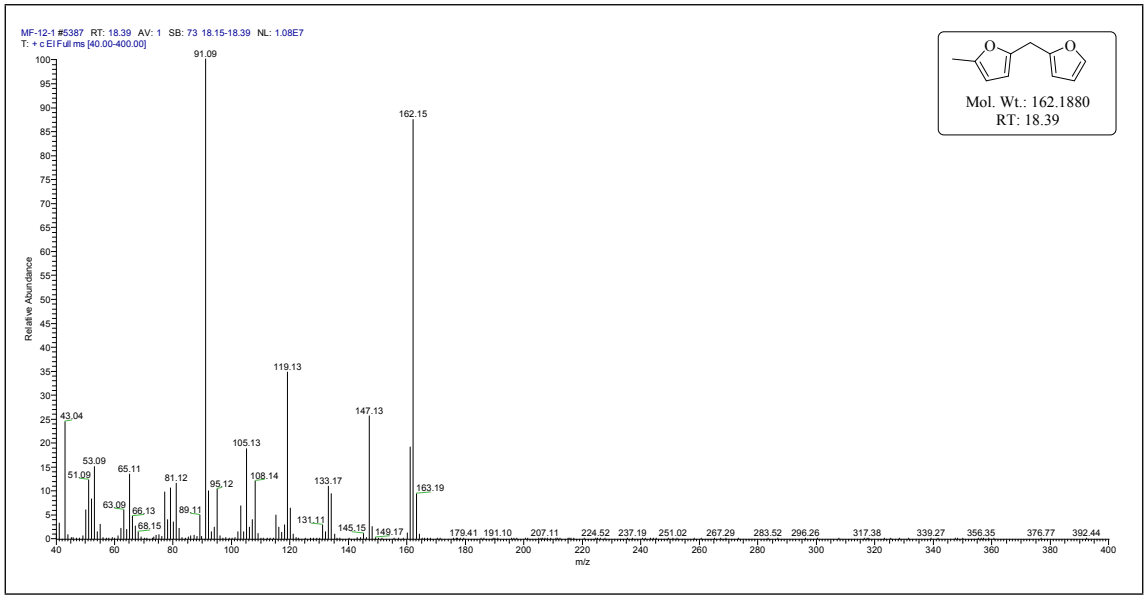
Mass spectrogram of the component of MDBF with retention time of 22.42 min. Inset shows the suggested molecular formula.


RT: 0.00 - 33.60
NL:
5.50E7
TIC MS
MF-115-
3_1906022
3T227
Relative Abundance
Time (min)
Mol. Wt.: 234.2950
RT: 23.38
MF-115-3_190602231227 #6855 RT: 23.38 AV: 1 SB: 42 23.24-23.38 NL: 4.31E6
T: + c EI Full ms [40.00-400.00]
Relative Abundance
m/z
Mol. Wt.: 234.2950
RT: 23.38

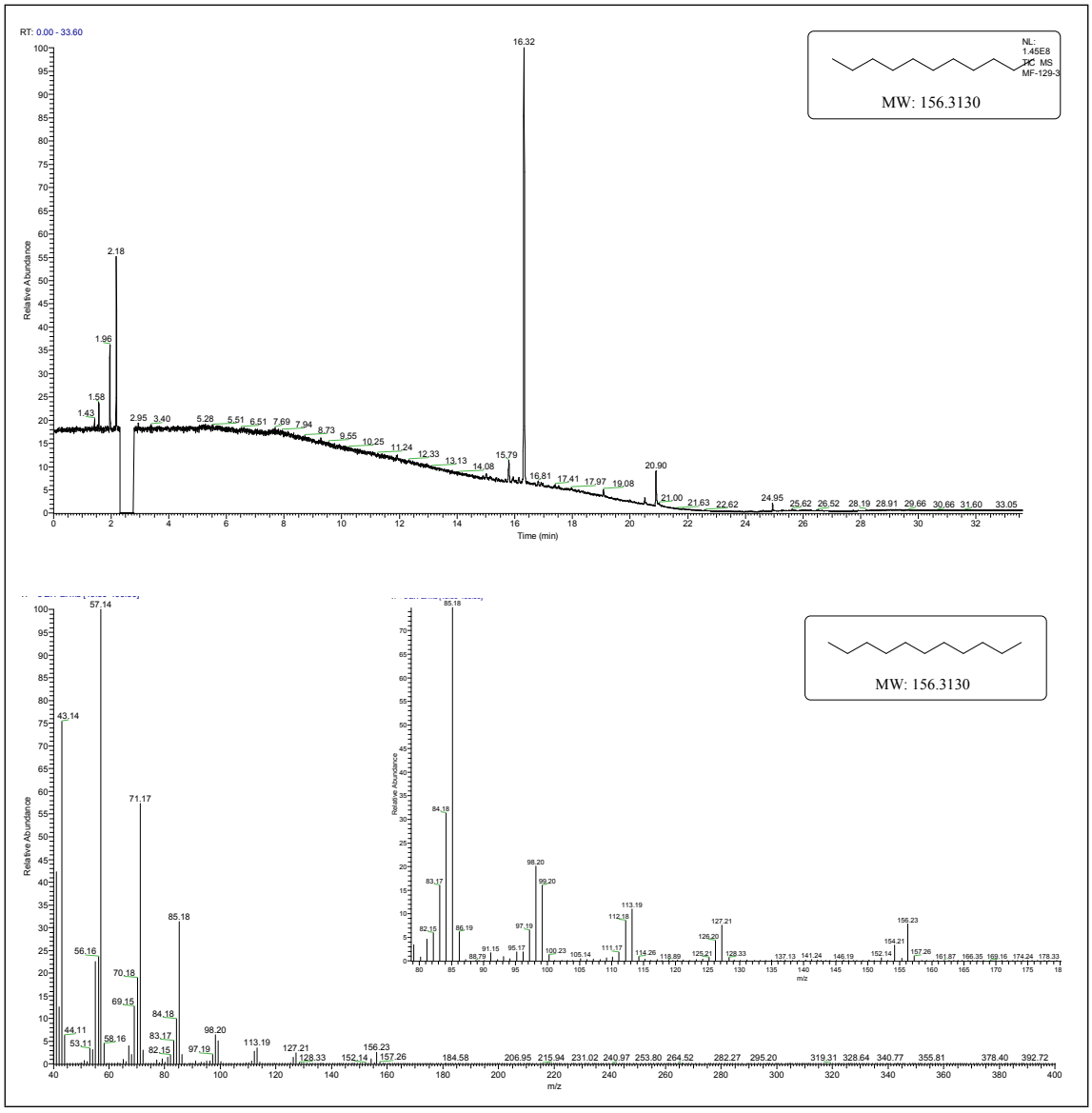


Mass spectrogram of the component of (5-(2-methyl-1-(5-methylfuran-2-yl)propyl)furan-2-yl)methanol (MPFM) with retention time of 23.38 min. Inset shows the suggested molecular formula.





Mass spectrogram of the component of FMMF with retention time of 18.39 min. Inset shows the suggested molecular formula.



Mass spectrogram of the component of undecane with retention time of 16.32 min. Inset shows the suggested molecular formula.