Supporting Information

Near Quantitative Conversion of Xylose to Bisfuran

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1. Experimental procedures

1.1 Materials

D-Xylose, Acetylacetone (acac), Furfural, $ZrCl_4$, ZrF_4, $TaCl_5$, $HfCl_4$, $CrCl_3\cdot6H_2O$, $CuCl_2$, $CoCl_2$, $MnCl_2$, $SnCl_2$, H_3PO_4, formic acid, acetic acid, oxalic acid and citric acid were purchased from Sigma-Aldrich. Acetophenone, $ZrOCl_2\cdot8H_2O$, $NiCl_2\cdot6H_2O$, $AlCl_3\cdot6H_2O$, $CuCl_2$ and $CoCl_2$ were obtained from Merck. NaCl, NaBr, NaI, Na_2SO_4, KCl, KI and $MgCl_2\cdot6H_2O$ were obtained from Fisher chemical. $Zr(SO_4)_2$, $La(OTf)_3$, $Nd(OTf)_3$, $Y(OTf)_3$, $Sc(OTf)_3$, $Hf(OTf)_4$, $Al(OTf)_3$, $Fe(OTf)_3$ and $Yb(OTf)_3$ were supplied by Alpha Asia. N,N-Diisopropylethylamine (DIPEA) was obtained from Tokyo Chemical Industry. Dichloromethane and Ethyl acetate were purchased from Honeywell. NMR solvents, including Deuterium oxide (D_2O), Methanol-d4 (MeOD) and Chloroform-d were supplied by Eurisotop. All chemicals and solvents were obtained from commercial suppliers and used as received.

1.2 General reaction procedure

For a typical run, 2 mmol xylose, 5 mol% $ZrCl_4$ catalyst, 5 mL H_2O (with 25 mmol NaCl) and 5 mL acetylacetone were added together into a 30 mL reaction tube. For furfural production experiment, 5 mL of acac was replaced by 5 mL of toluene. The experiment was conducted by a Microwave equipment at target temperature for desired reaction time. The stirring rate was 600 r/min. When completed, the reaction mixture was collected for further analysis. Parallel experiments were conducted and the average value were presented (error within ± 5%).

For furfural production experiments, 2 mmol xylose, 5 mol% $ZrCl_4$ or 10 mol% $AlCl_3\cdot6H_2O$ catalyst, 5 mL H_2O (with 30 wt% NaCl) and 5 mL toluene were added together into a 30 mL microwave reaction tube.

The NMR (Nuclear magnetic resonance) study was conducted at different reaction temperature. For a typical reaction set-up, 2 mmol xylose, 20 mol% $ZrCl_4$ catalyst, 2 mL D_2O, 2 mL acac (when needed) were added into a vial and stirred at 600 r/min for 60 min. For elevated temperature experiments, vials with reaction mixture were immersed in a preheated 90 °C oil-bath for desired time and cooled down immediately with flowing tap water. The aqueous phase was subjected to NMR measurement directly for ^1H and ^{13}C NMR. The organic phase was first evaporated and dissolved in MeOD for NMR measurement.

1.3 Product analysis

Reaction mixture was diluted with ethyl acetate and filtered with silicon prior to the injection to gas chromatography mass spectrometer (GC-MS, Agilent 5973-6890N) and two distinguish peaks with m/z = 178 and m/z = 260 were observed during catalyst screening. The reaction mixture was then purified by silica-gel column chromatography (eluent:

Dichloromethane/ethyl acetate = 30/1) to give isolated products. The products were then identified by ^{1}H, ^{13}C, 2D HSQC and HMBC NMR analysis, recorded on a Bruker Avance III 400-MHz spectrometer. The calibration and analysis of spectra was conducted by using MestReNova. High-resolution electrospray-ionization mass spectra (HRESI-MS) were recorded with a Bruker microTOF mass spectrometer in a positive ion mode using sodium formate as a calibrant. Infrared Spectroscopy (IR) spectra were recorded on a Bruker Alpha-P Fourier transform infrared spectrometer in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans.

For GC-MS analysis, HP-5 MS Ultra Inert column (30 m × 250 µm × 0.25 µm) was employed and He as a carrier gas at a flow rate of 0.9 mL/min. The initial oven temperature 60 °C was held for 0.5 min and then increased to 90 °C at a rate of 10 °C /min followed by a temperature ramp of 20 °C/min to 300 °C, and held for 6 min. The detector temperature was 300 °C. The products were analyzed quantitatively by Agilent 7890B GC system equipped with a flame ionization detector (FID). The initial oven temperature 60 °C was held for 0.5 min and then increased to 100 °C at a rate of 10 °C /min followed by a temperature ramp of 15 °C/min to 200 °C (held for 2 min), and then to 300 °C (20 °C/min, held for 2 min). The relatively pure isolated products were used as standards for quantification and acetophenone was employed as internal standard. The yield of products was calculated as follow: Yield (%) = mol of product / mol of starting xylose × 100%.

The conversion of xylose was quantitative analysed by HPLC (1200 Infinite series, Agilent) equipped with a refractive index detector (G1362A RID) and a Phenomenex column (Rezex™ ROA-Organic Acid H+ (8%), 300 x 7.8 mm). The eluent was dilute H_2SO_4 (5 mM) flowing at a rate of 0.5 mL min^{-1} while the column temperature maintained at 40 °C. The RI detector was maintained at 35 °C. Samples were filtered (0.2 µm) before injection. Data were elaborated according to calibration curve with standard xylose. The conversion of xylose was calculated as follow: Conversion (%) = (mol of starting xylose - moles of xylose after reaction) / mol of starting xylose × 100%.

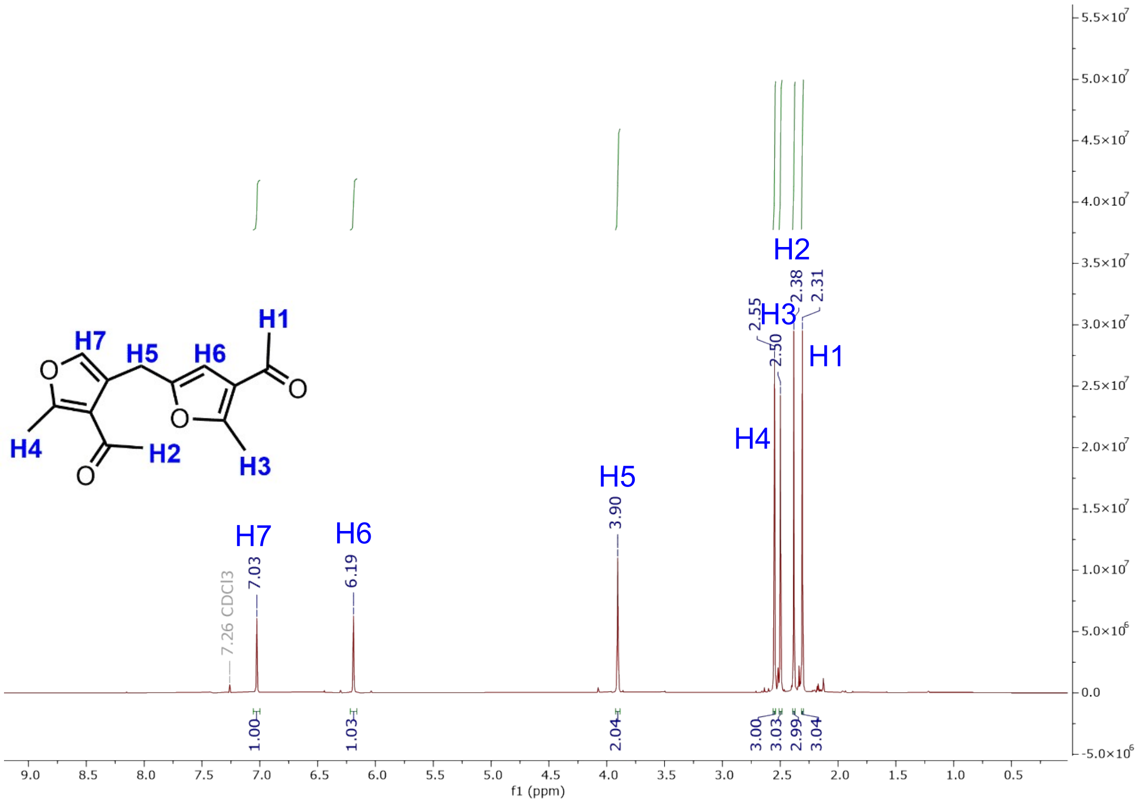


Fig. S1 ^1H NMR spectrum of 1-(4-((4-acetyl-5-methylfuran-2-yl)methyl)-2-methylfuran-3-yl)ethanone (MFE) (400 MHz, $CDCl_3$): δ 7.03 (s, 1H), 6.19 (s, 1H), 3.90 (s, 2H), 2.55 (s, 3H), 2.50 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H).

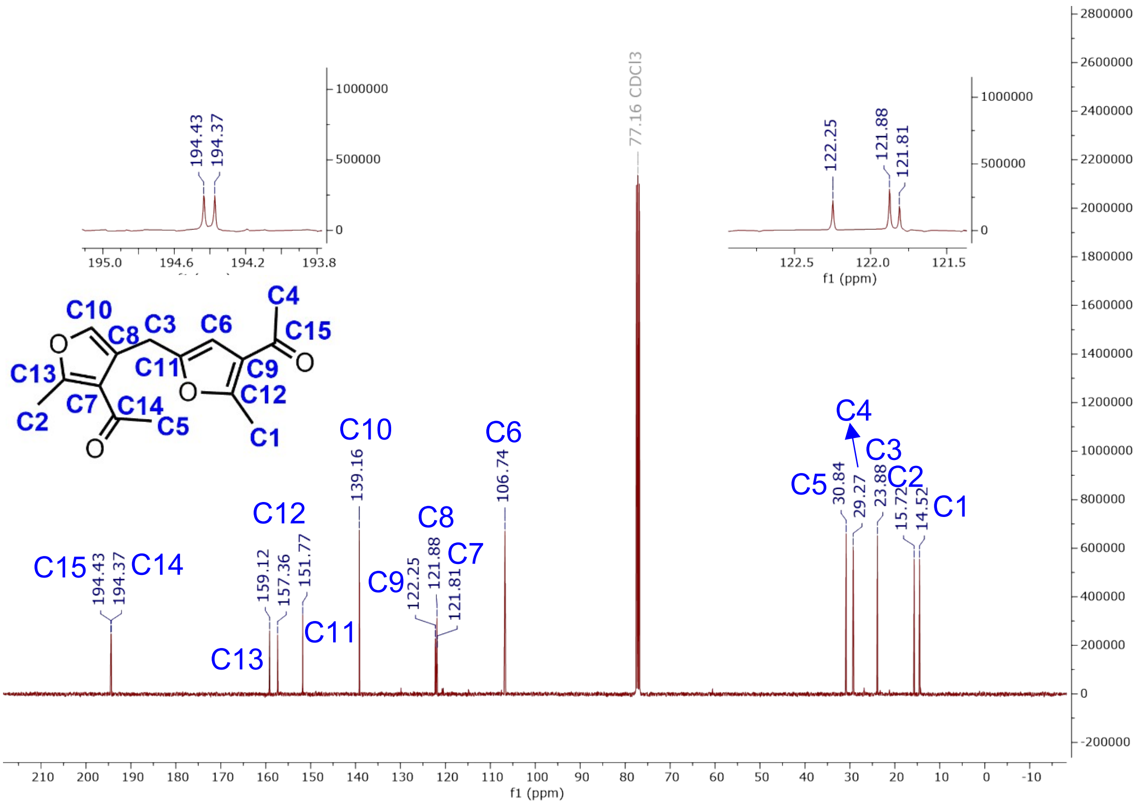
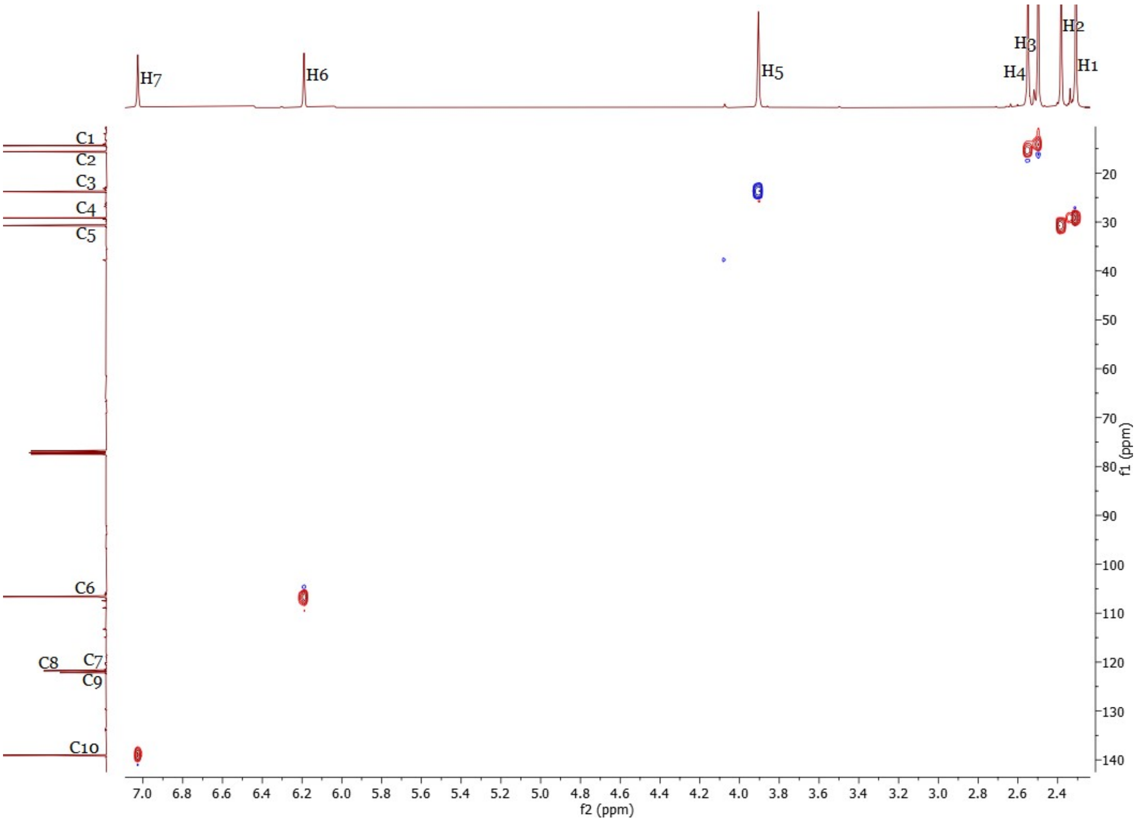


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of MFE (100 MHz, $CDCl_3$): δ 194.43, 194.37, 159.12, 157.36, 151.77, 139.16, 122.25, 121.88, 121.81, 106.74, 30.84, 29.27, 23.88, 15.72, 14.52.



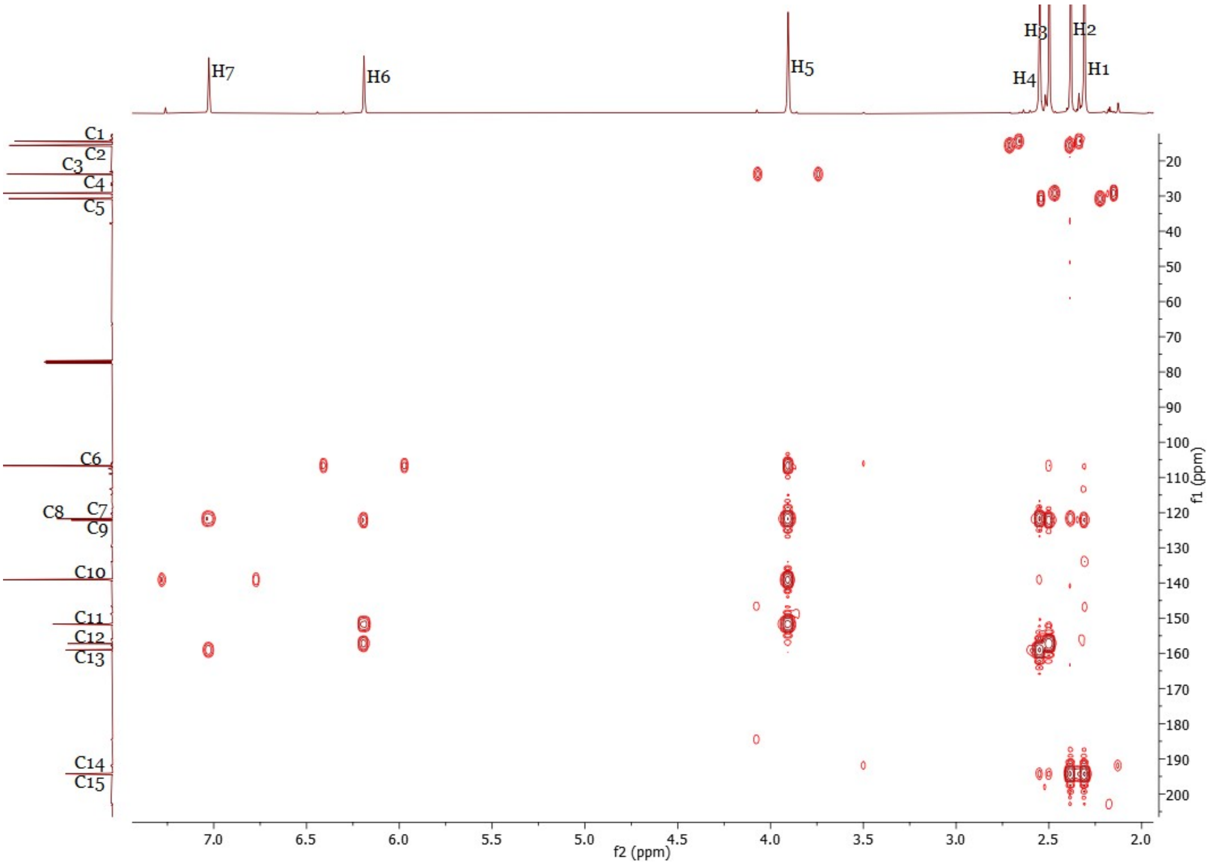
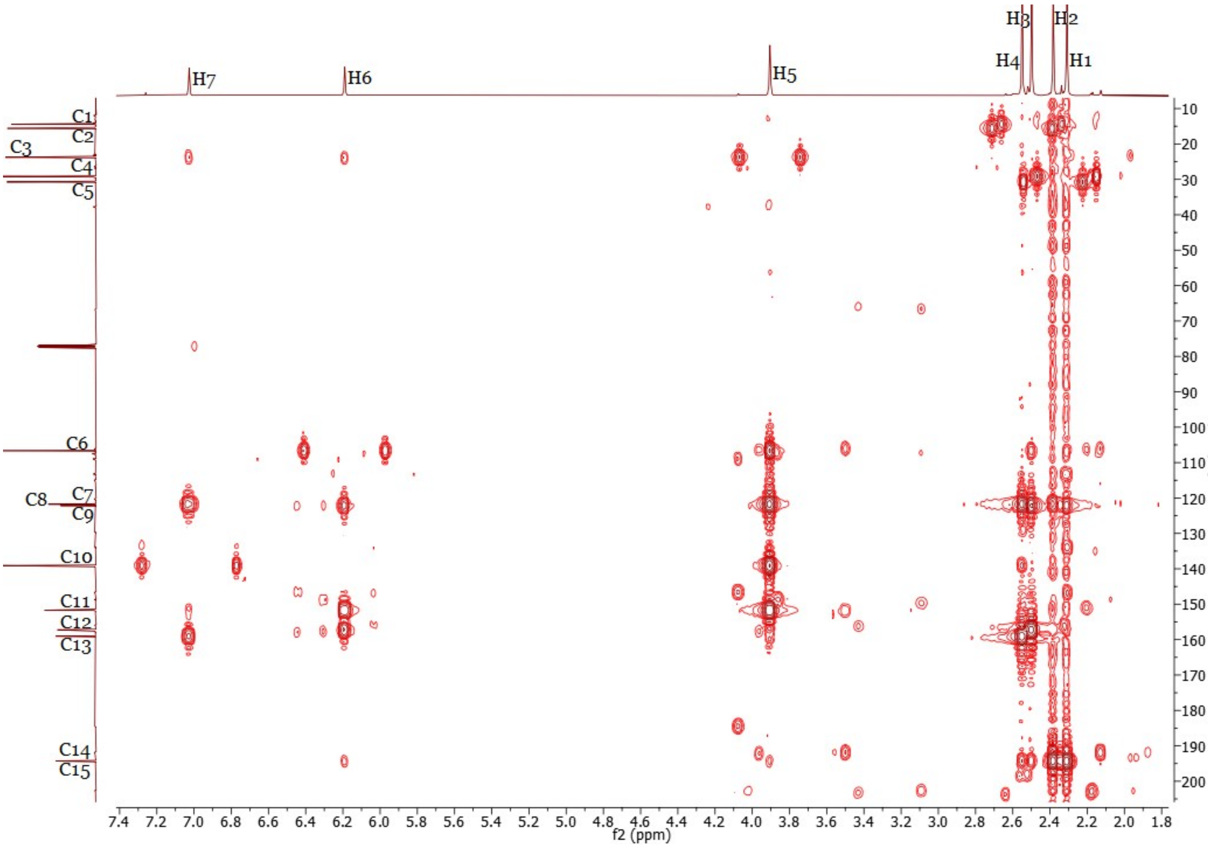
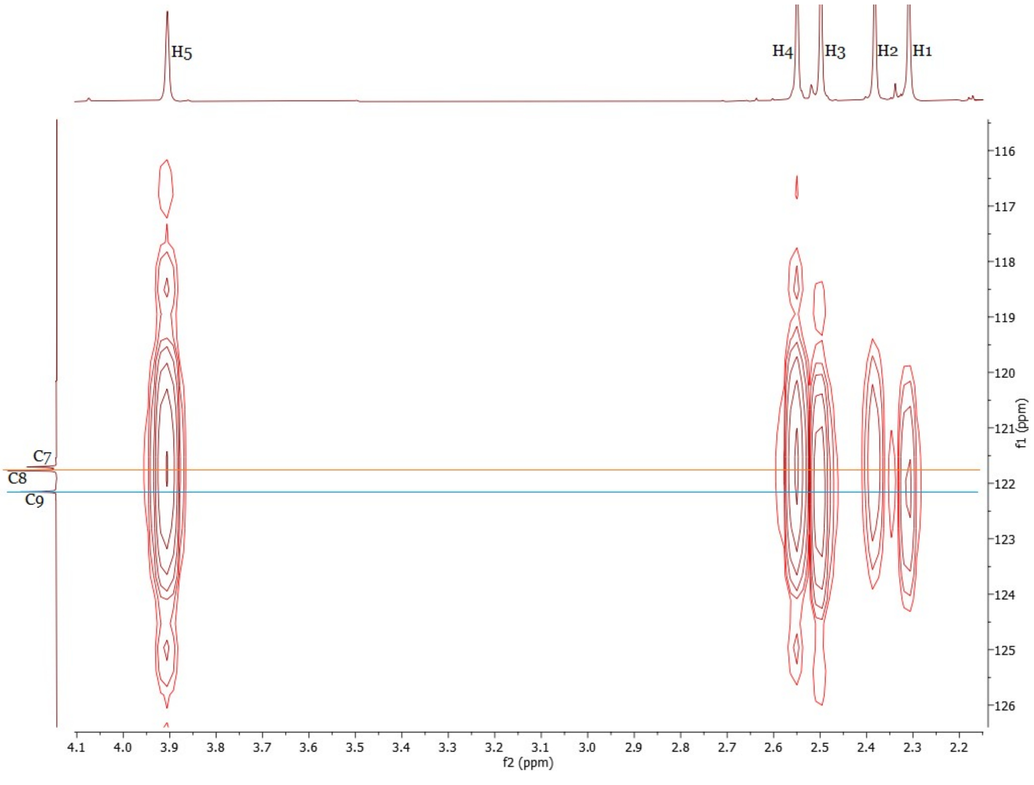


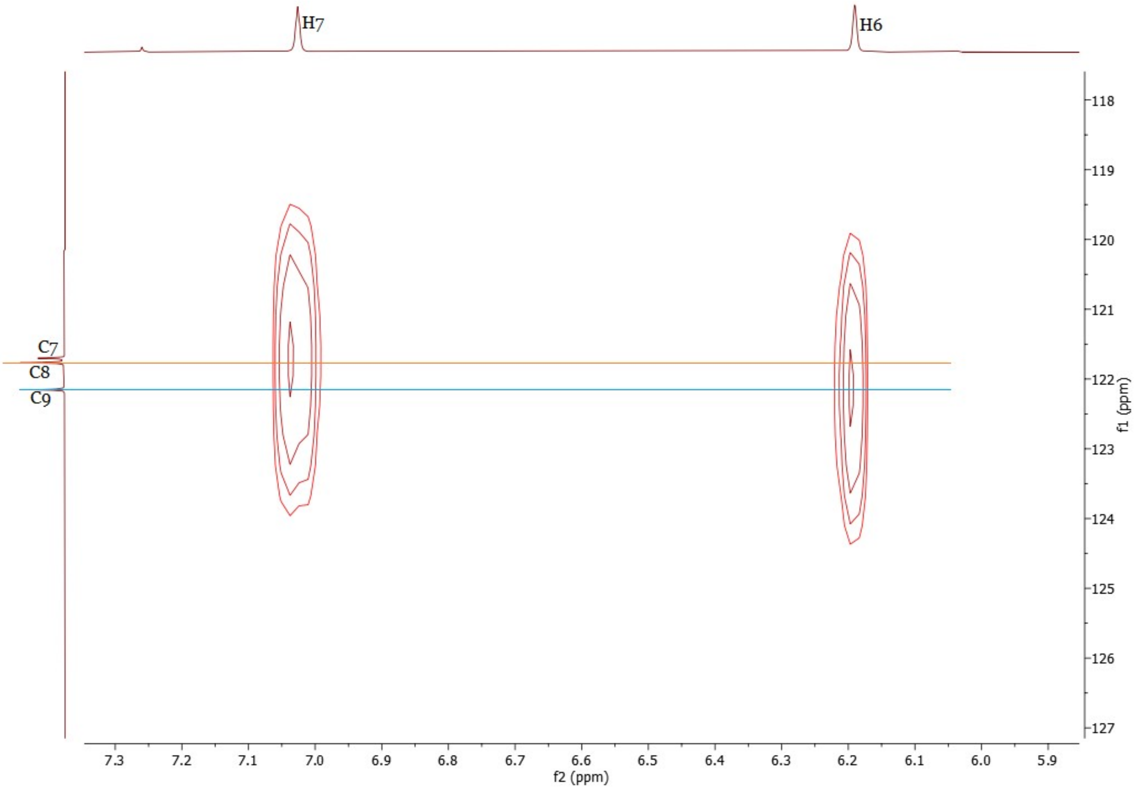
Fig. S3 HSQC spectrum of MFE ($CDCl_3$).



a) HMBC spectrum of MFE ($CDCl_3$) extra zoomed to show interaction of H6 and H7 with C3.



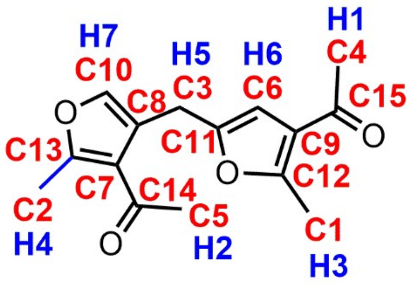
b) HMBC spectrum of MFE ($CDCl_3$) detailed zoom in to carbons C9, C8 and C7. Blue line shows correlation between C9, H1 and H3. Similarly, C8 is correlating with H2, H4 and H5 (orange line).



c) HMBC spectrum for MFE ($CDCl_3$) detailed zoom in to carbons C9, C8 and C7 with H6 and H7. Carbon C9 is correlating with H6 (blue line). C7 and C8 is correlating with H7 (orange line).

Fig. S4 HMBC spectrum of MFE ($CDCl_3$).

2D NMR measurement observations for MFE:



Protons H1 are attached to carbon C4 forming CH_3 group. The group has connectivity to carbons C9 (weak) and C15.

Protons H2 are attached to carbon C5 forming CH_3 group. The group has connectivity to carbons C7 (weak) and C14.

Protons H3 are attached to carbon C1 forming CH_3 group. The group has connectivity to carbons C9 and C12.

Protons H4 are attached to carbon C2 forming CH_3 group. The group has connectivity to carbons C7 and C13.

Protons H5 are attached to carbon C3 forming CH_2 group. The group has connectivity to carbons C6, C8, (possibly C7), C10 and C11.

Proton H6 is attached to carbon C6 forming CH group. The group has connectivity to carbons C3 (weak), C9, C11 and C12.

Proton H7 is attached to carbon C10 forming CH group. The group has connectivity to carbons C3 (weak), C8, (possibly C7) and C13.

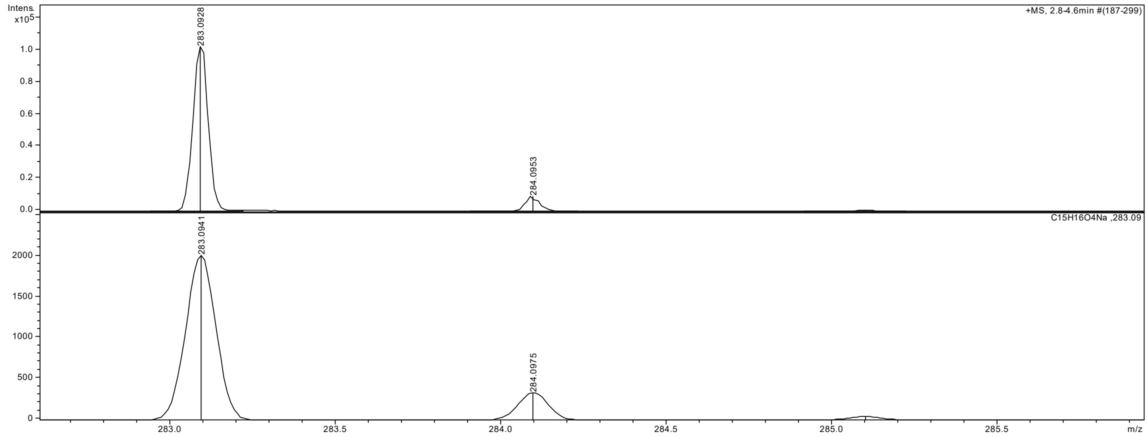


Fig. S5 HRESI-MS experimental (above) and calculated (below) isotopic patterns of MFE. $[C_{15}H_{16}O_4+Na]^+$ calculated m/z 283.0941, found m/z 283.0928, error 4.407 ppm.

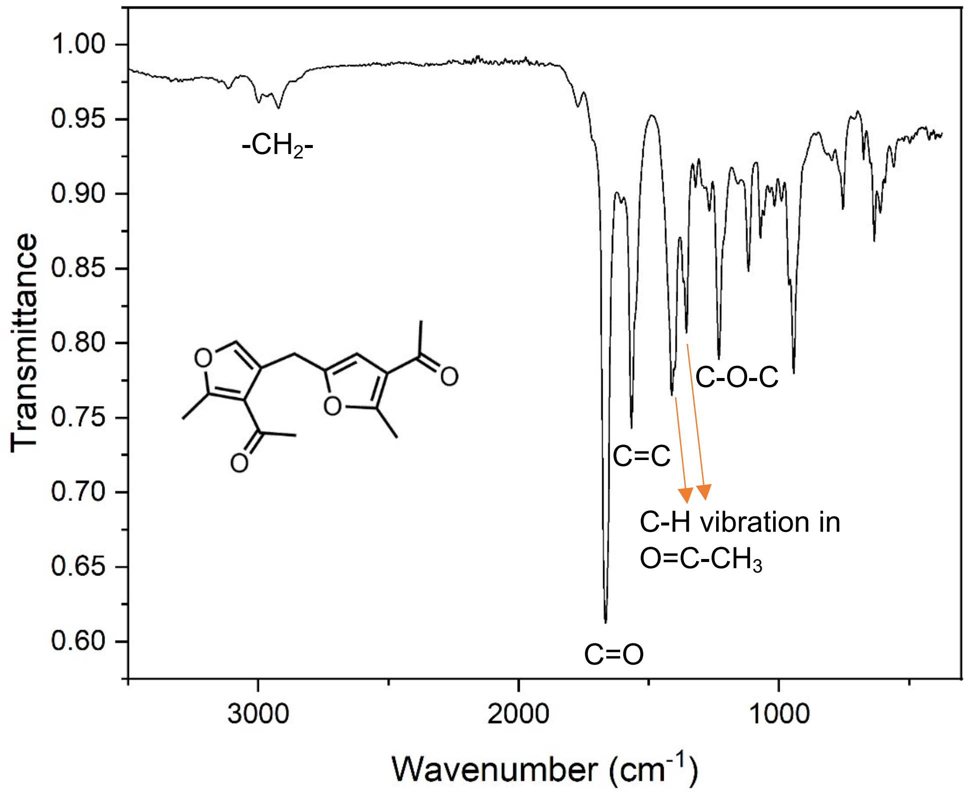


Fig. S6 IR spectra of MFE.

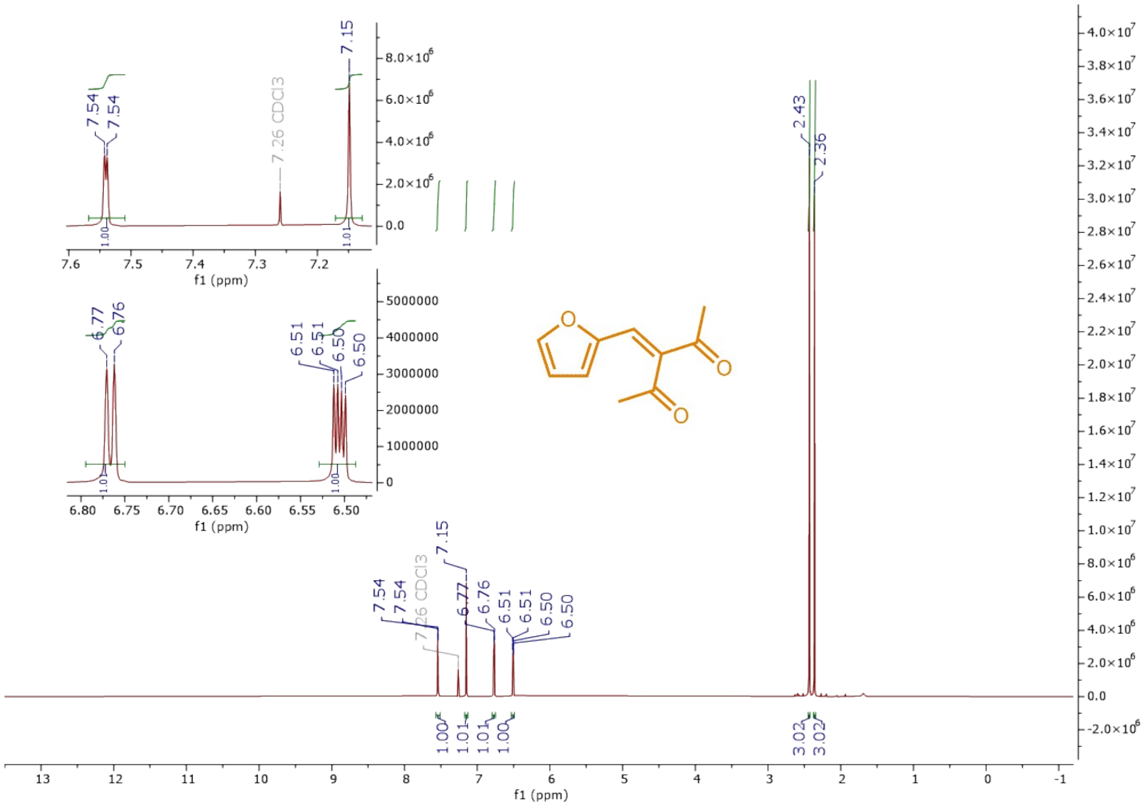


Fig. S7 ^{1}H NMR of 3-(furan-2-ylmethylene)pentane-2,4-dione (FMPD) (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.8 Hz, 1H), 7.15 (s, 1H), 6.77 (d, *J* = 3.5 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.8 Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H).

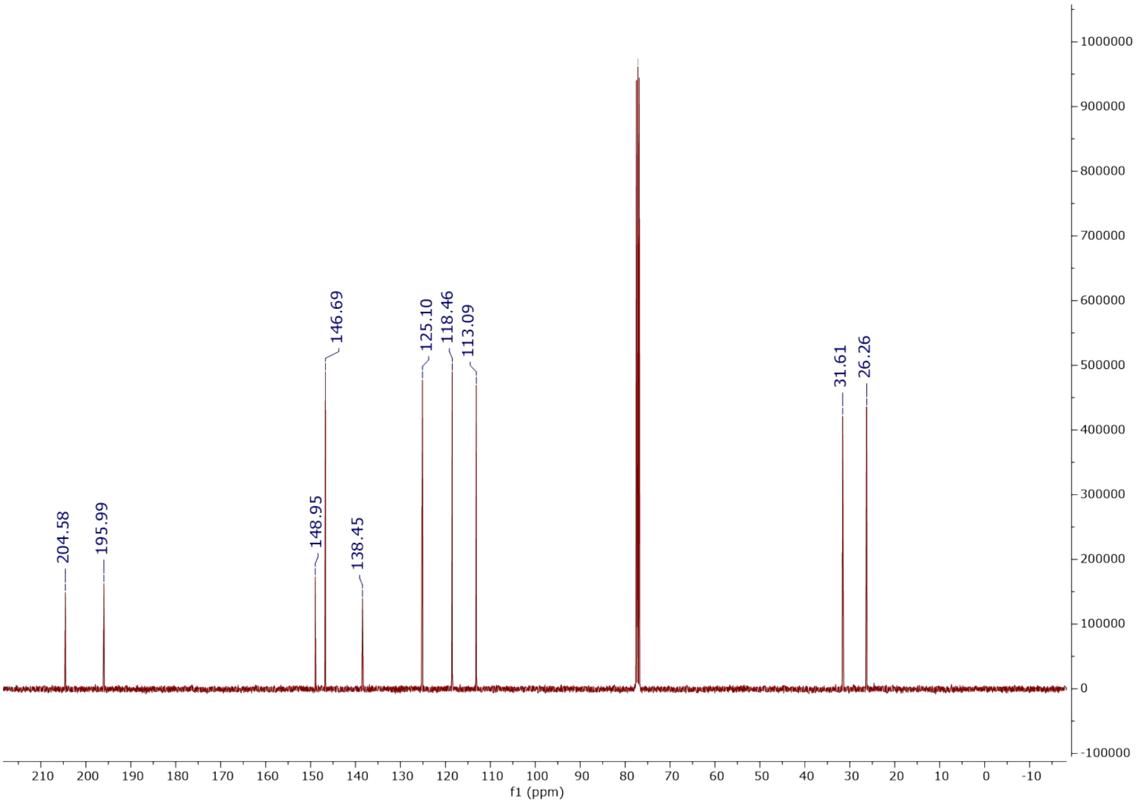


Fig. S8 ^{13}C{^{1}H} NMR spectrum of FMPD (100 MHz, $CDCl_3$): δ 204.58, 195.99, 148.95, 146.69, 138.45, 125.10, 118.46, 113.09, 31.61, 26.26.

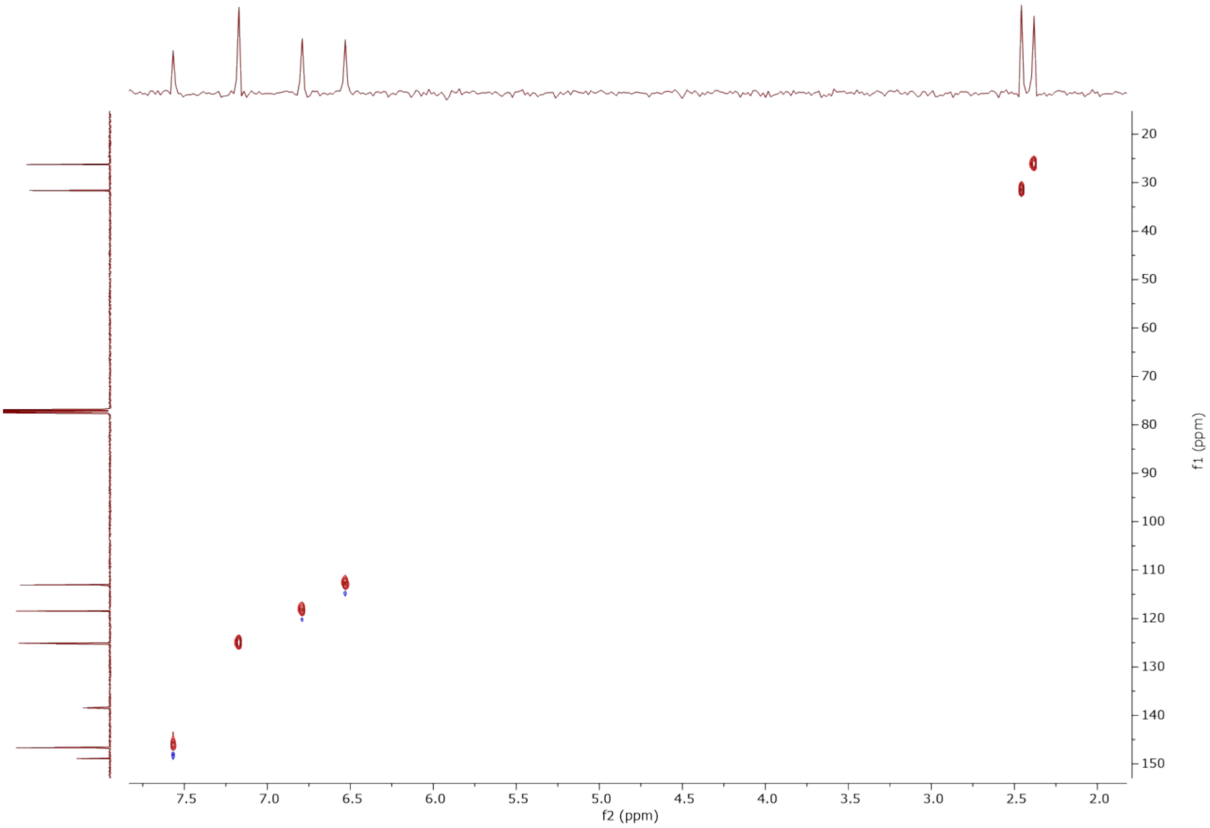


Fig. S9 HSQC spectrum of FMPD ($CDCl_3$).

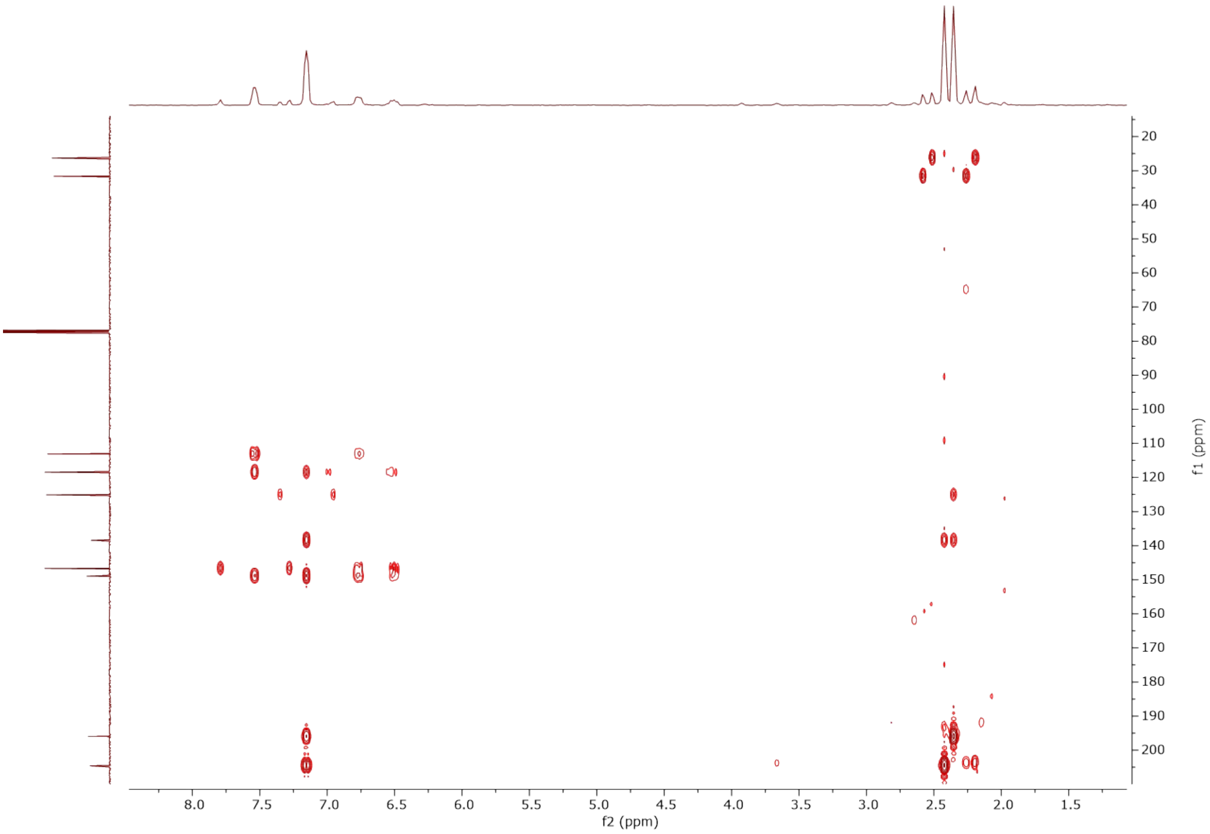


Fig. S10 HMBC spectrum of FMPD ($CDCl_3$).

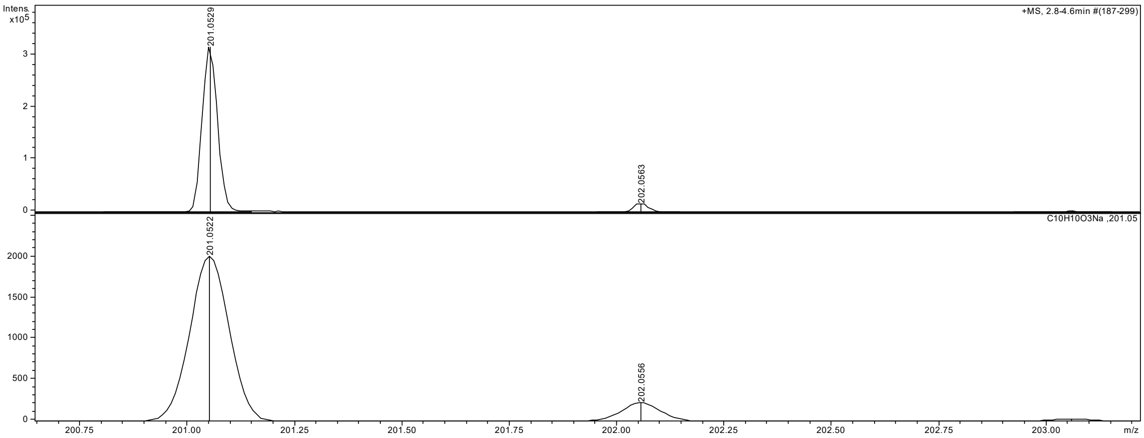


Fig. S11 HRESI-MS experimental (above) and calculated (below) isotopic patterns of FMPD. $[C_{10}H_{10}O_3+Na]^+$ calculated m/z 201.0522, found m/z 201.0529, error 3.524 ppm.

Table S1 The yield of FMPD and MFE with different catalysts.[a]

Entry	Catalyst	FMPD Yield (%)[b]	MFE Yield (%)[b]	Total carbon yield (%)[c]
1	$CuCl_2$	2.6		2.6
2	$SnCl_2$	2.7		2.7
3	$MnCl_2$	7.4		7.4
4	$CrCl_3 \cdot O_2H6$	9.6	-	9.6
5	$Fe(OTf)_3$	11.5		11.5
6	$CoCl_2$	13.6		13.6
7	$TaCl_5$	14.5		14.5
8	$NiCl_2 \cdot 6H_2O$	27.7	-	27.7
9	$AlCl_3 \cdot O_2H6$	38.4	-	38.4
10	$Al(OTf)_3$	34.7	-	34.7
11	$AlCl_3$_Oxalic acid	24.3	-	24.3
12	$AlCl_3$_Acetic acid	35.1	-	35.1
13	$AlCl_3$_Formic acid	35.9	-	35.9
14	$AlCl_3$_Citric acid	36.9	-	36.9
15	$AlCl_3 \cdot O_2H6$_H_3PO_4	43.2	-	43.2
16	$La(OTf)_3$	14.8	3.5	18.3
17	$Nd(OTf)_3$	27.6	9.9	37.5
18	$Y(OTf)_3$	33.9	14.2	48.1
19	$Yb(OTf)_3$	37.8	20.8	58.6
20	$Sc(OTf)_3$	42.6	32.6	75.2
21	$Hf(OTf)_4$	38.9	30.4	69.3
22	$HfCl_4$	47.2	32.3	79.5
23	ZrF_4	48.1	25.9	74.0
24	$ZrCl_4$	45.5	33.1	78.6

[a] Reaction conditions: 2 mmol xylose, 10 mol% catalyst, 5 mL H_2O (with 25 mmol NaCl), 5 mL acac, microwave heating, 150 °C, 14 min, 600 r/min. [b] The products yield is determined by GC using acetophenone as an internal standard. Yield (%) = mol of product / mol of xylose × 100%. [c] Total carbon yield is a sum of the yield of FMPD and MFE.

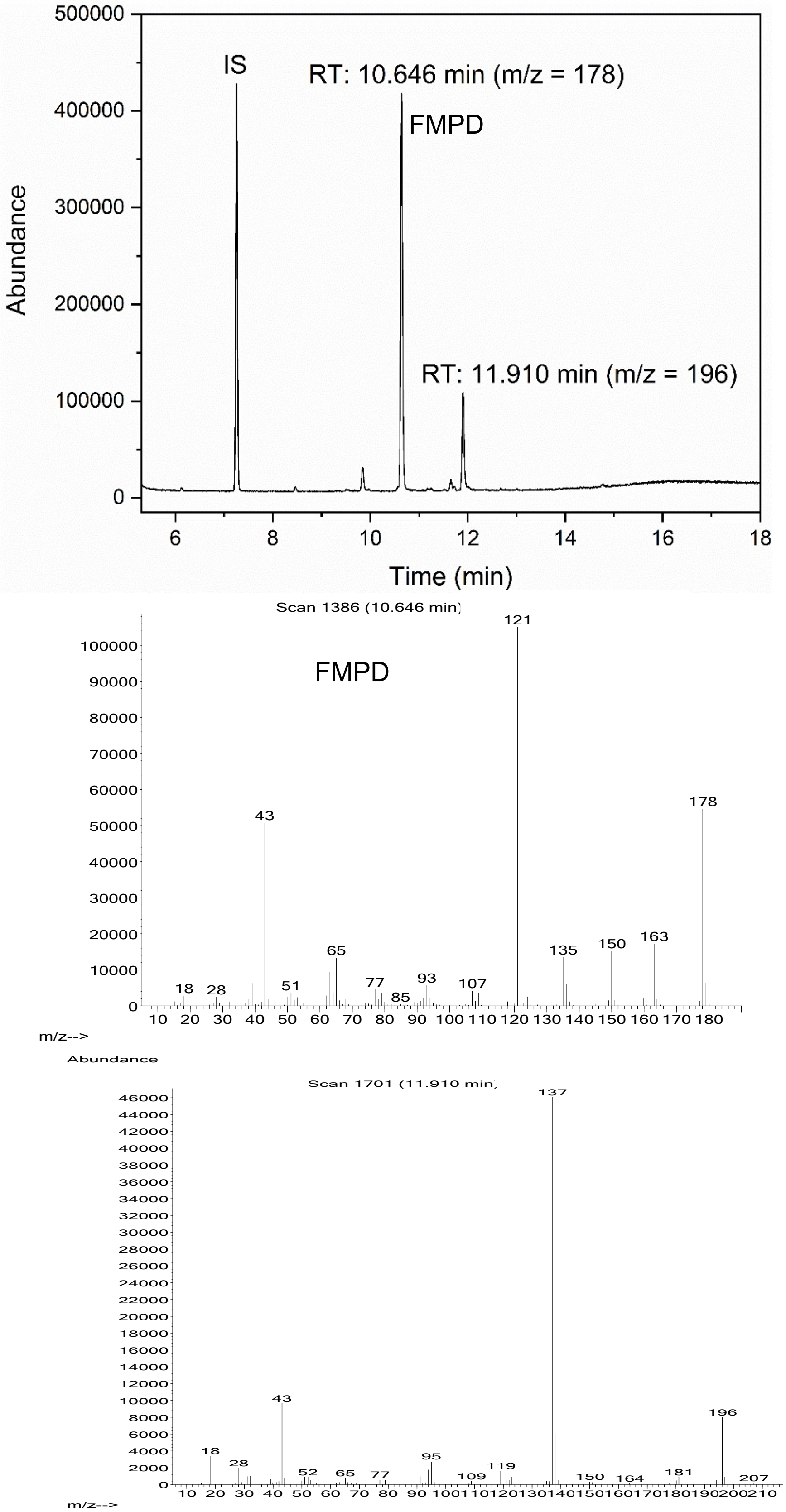


Fig. S12 A typical GC-MS spectrum of $AlCl_3{\cdot}6H_2O$ catalysed reaction mixture and the MS data of FMPD (reaction conditions: 2 mmol xylose, 10 mol% $AlCl_3{\cdot}6H_2O$, 5 mL acac, 5 mL H_2O with 25 mmol NaCl, microwave heating, 150 °C, 14 min).

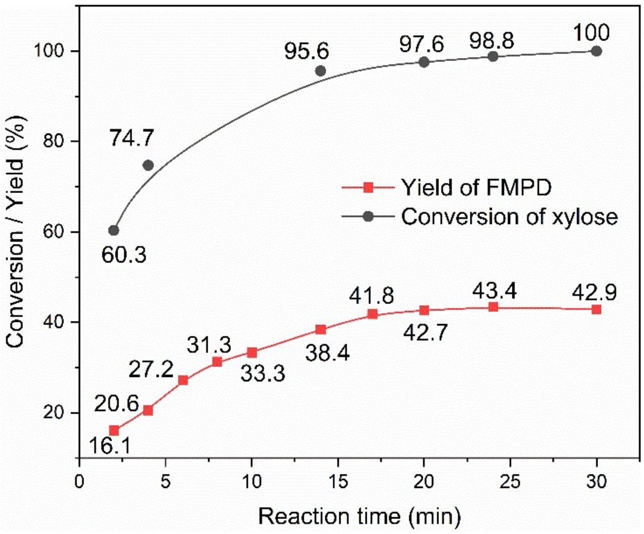


Fig. S13. The yield of FMPD and the conversion of xylose using $AlCl_3 \cdot 6H_2O$ as a catalyst. Reaction conditions: 2 mmol xylose, 10 mol% $AlCl_3 \cdot 6H_2O$, 5 mL H_2O (with 25 mmol NaCl), 5 mL acac, microwave heating, 150 °C, 600 r/min.

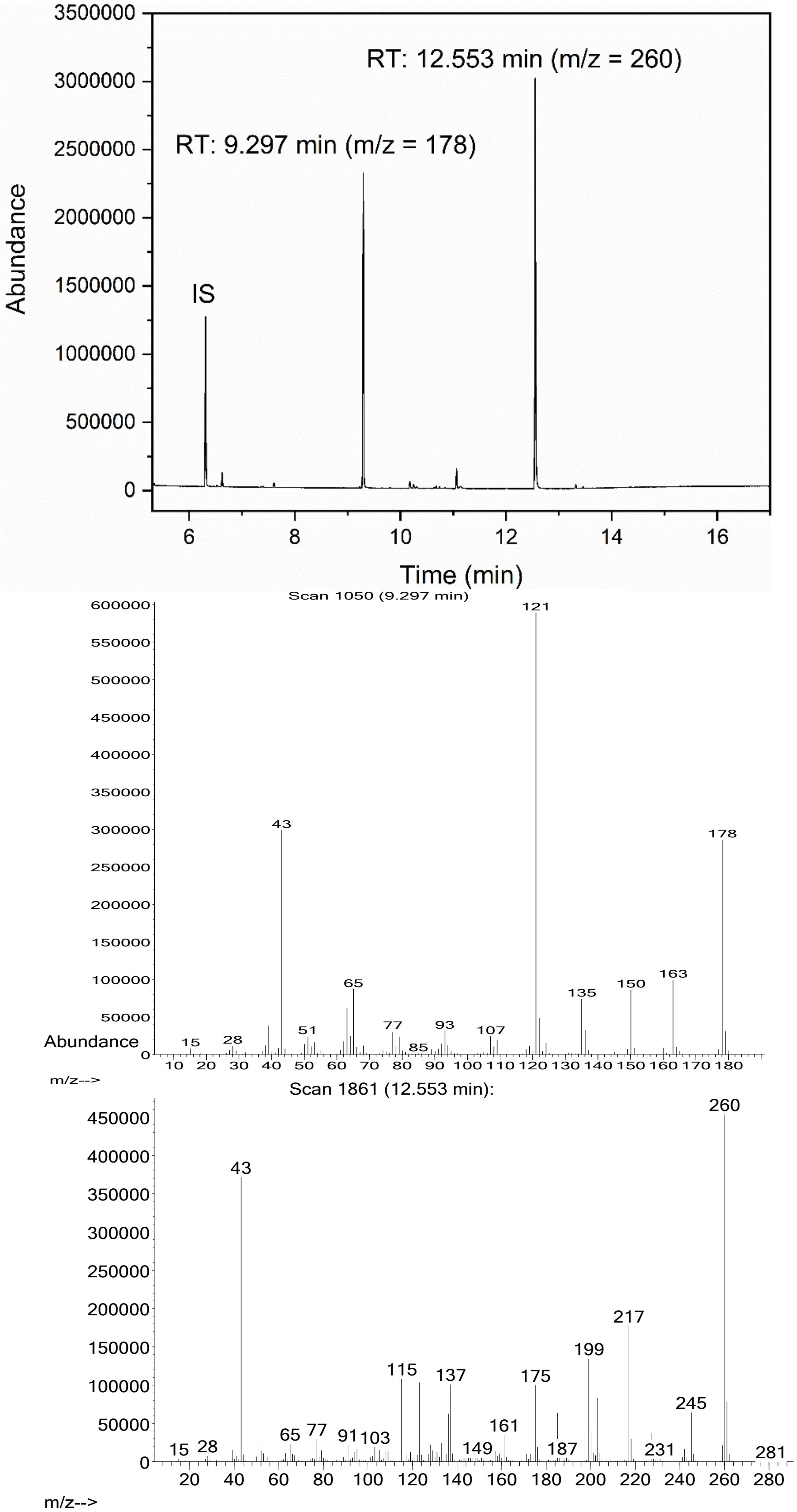


Fig. S14. A typical GC-MS spectrum of $ZrCl_4$ catalysed reaction mixture and the MS data of FMPD and MFE. Reaction conditions: 2 mmol xylose, 10 mol% $ZrCl_4$, 5 mL H_2O (with 25 mmol NaCl), 5 mL acac, microwave heating, 150 °C, 14 min, 600 r/min.

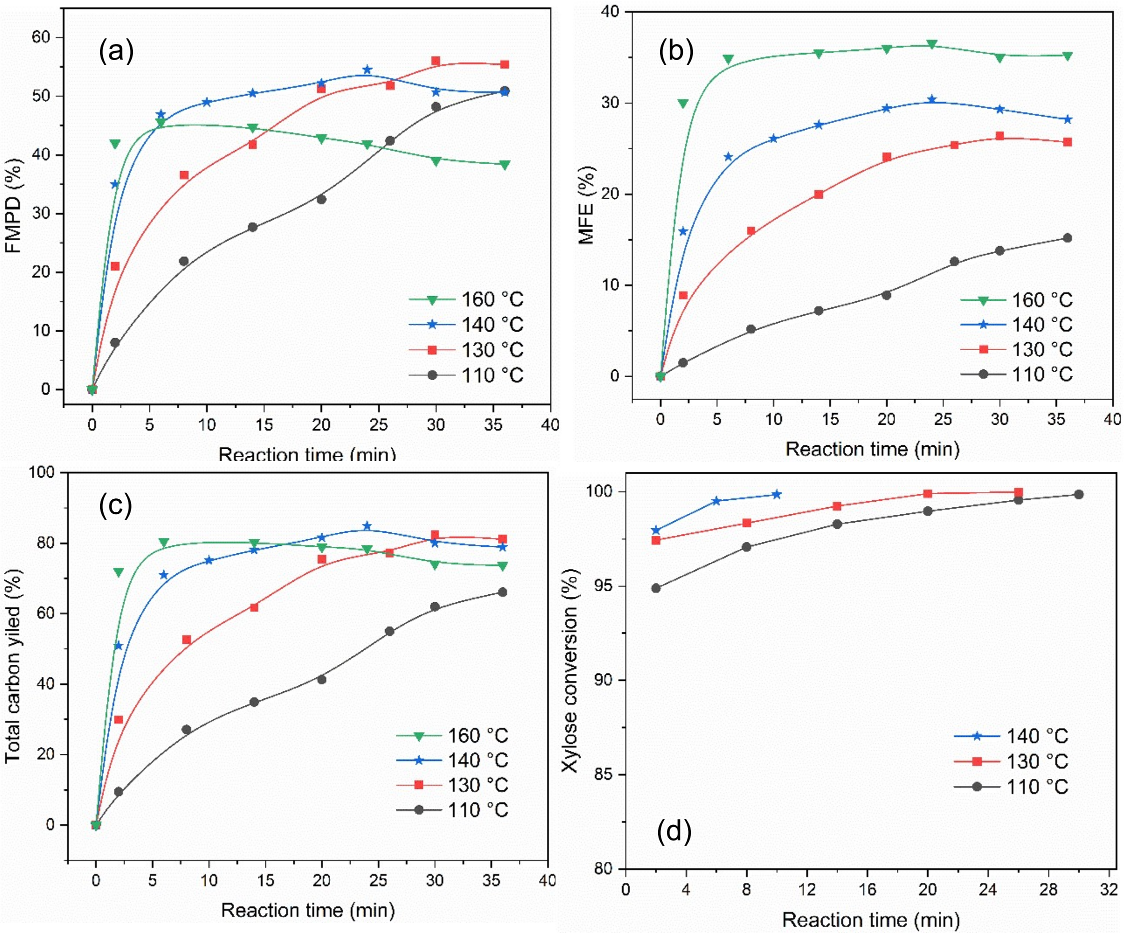


Fig. S15 (a) The yield of FMPD; (b) the yield of MFE; (c) the total carbon yield; (d) the conversion of xylose as a function of reaction time at different temperature (°C). Reaction conditions: 2 mmol xylose, 5 mol% $ZrCl_4$, 5 mL H_2O (with 25 mmol NaCl), 5 mL acac, microwave heating, 600 r/min.

Table S2 Yield of FMPD and MFE at 70 °C.[a]

Entry	Time(h)	FMPD (%)	MFE (%)	Total carbon yield (%)
1	3	33.8	7.4	41.2
2	8	53.5	10.7	64.2
3	14	65.3	12.7	78.0
4	18	66.1	13.0	79.1
5	20	66.8	13.1	79.9
6	24	66.5	13.2	79.7
7	30	66.2	13.0	79.2

[a] Reaction conditions: 2 mmol xylose, 5 mol% $ZrCl_4$, 5 mL H_2O (with 25 mmol NaCl), 5 mL acac, oil bath heating, 70 °C, 600 r/min. The product yield is determined by GC using acetophenone as an internal standard.

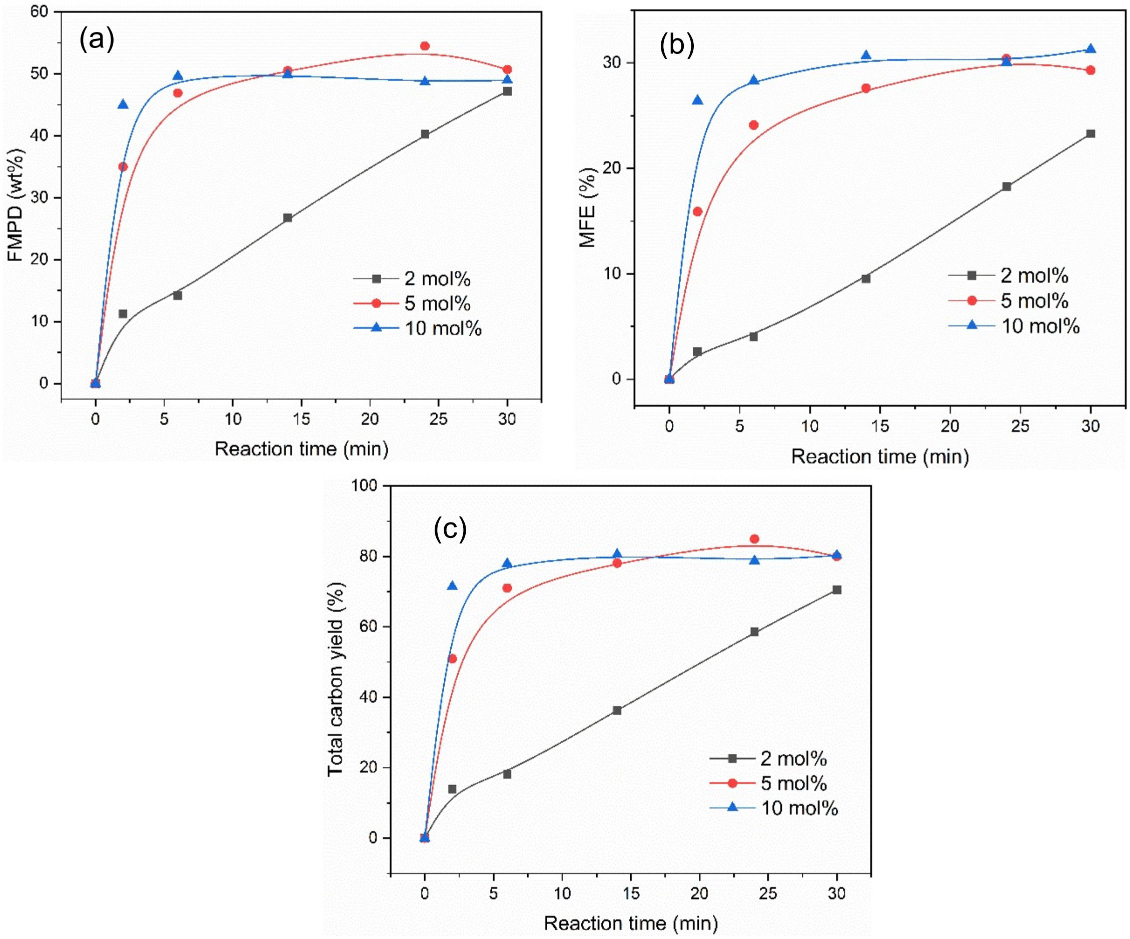


Fig. S16 (a) The yield of FMPD; (b) the yield of MFE; (c) the total carbon yield as a function of reaction time at different $ZrCl_4$ catalyst loading (mol%). Reaction conditions: 2 mmol xylose, 5 mL H_2O (with 25 mmol NaCl), 5 mL acac, microwave heating, 600 r/min, 140 °C.

Table S3 The effect of xylose loading on the total carbon yield.[a]

Time (min)	Xylose (mmol)	FMPD (%)	MFE (%)	Total carbon yield (%)
1	2.0	50.5	27.6	78.1
2	3.3	49.7	28.1	77.8
3	4.7	46.5	29.5	76.0
4	6.0	42.0	28.0	70.0
5	7.3	38.7	26.4	65.1

[a] Reaction conditions: 5 mol% $ZrCl_4$, 5 mL H_2O (with 25 mmol NaCl), 5 mL acac, microwave heating, 140 °C, 14 min, 600 r/min.

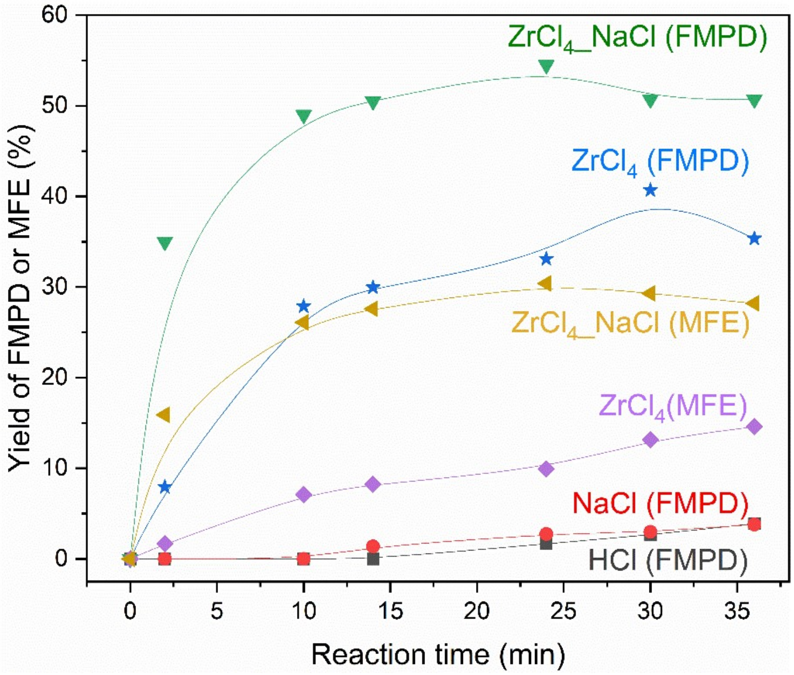


Fig. S17 The yield of FMPD and MFE with HCl, NaCl or $ZrCl_4$ as a catalyst (reaction conditions: 5 mL H_2O with 25 mmol NaCl, 10 mol% HCl or 5 mol% $ZrCl_4$ when needed, microwave heating, 140 °C, 600 r/min).

Table S4 The yield of FMPD and MFE with different catalysts and the addition of base.[a]

Entry	Catalyst	Conditions	FMPD Yield (%)	MFE Yield (%)	Total carbon yield (%)
1	10 mol% $ZrCl_4$	150 °C, 14 min	45.5	33.1	78.6
2	10 mol% $ZrOCl_2\cdot 8H_2O$	150 °C, 14 min	46.5	29.3	75.8
3	5 mol% $ZrCl_4$	140 °C, 24 min	54.5	30.4	84.9
4	5 mol% $ZrOCl_2\cdot 8H_2O$	140 °C, 24 min	51.5	28.9	80.4
5[b]	5 mol% $ZrCl_4$	140 °C, 24 min	51.0	26.6	77.6

[a] Reaction conditions: 2 mmol xylose, 5 mL H_2O (with 25 mmol NaCl), 5 mL acac, microwave heating, 600 r/min. [b] 0.2 mmol N,N-Diisopropylethylamine (DIPEA) was added to trap HCl.

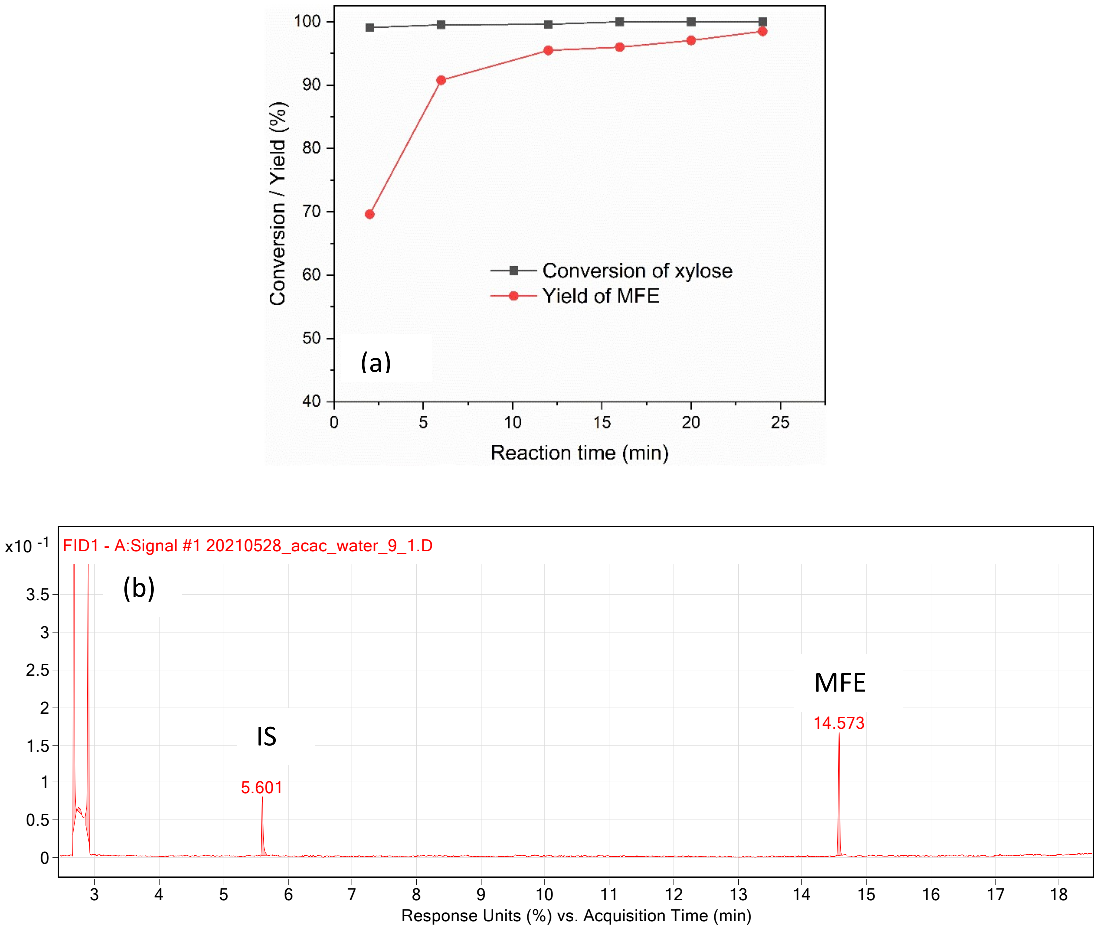


Fig. S18 (a) Time courses of xylose conversion into MFE; (b) GC-FID spectrum of reaction mixture of 24 min. Reaction conditions: 2 mmol xylose, 5 mol% $ZrCl_4$, 1 mL H_2O (with 25 mmol NaI), 9 mL acac, microwave heating, 140 °C, 600 r/min.

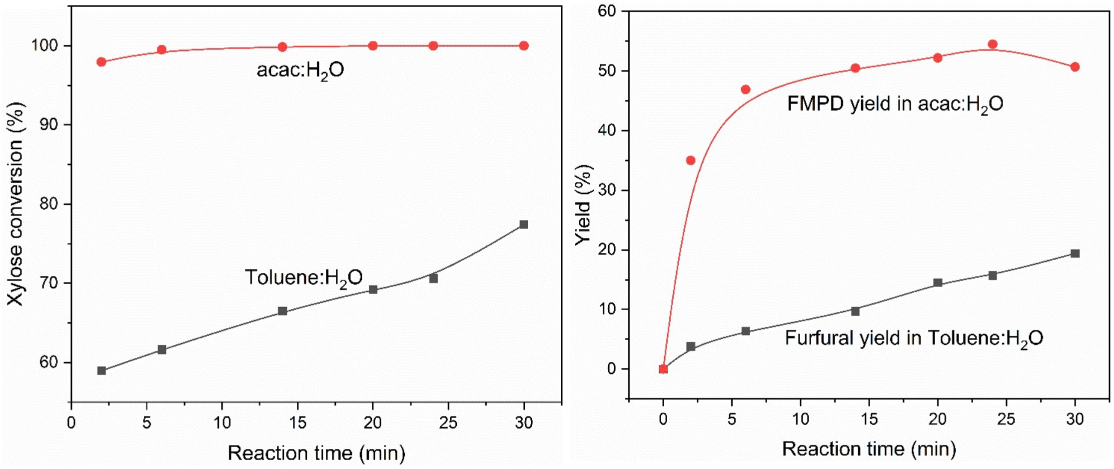


Fig. S19 The conversion of xylose and the yield of FMPD and furfural using $ZrCl_4$ as a catalyst. Reaction conditions: 2 mmol xylose, 5 mol% $ZrCl_4$, 5 mL H_2O (with 25 mmol NaCl), 5 mL organic solvent (acac or toluene), microwave heating, 140 °C, 600 r/min.

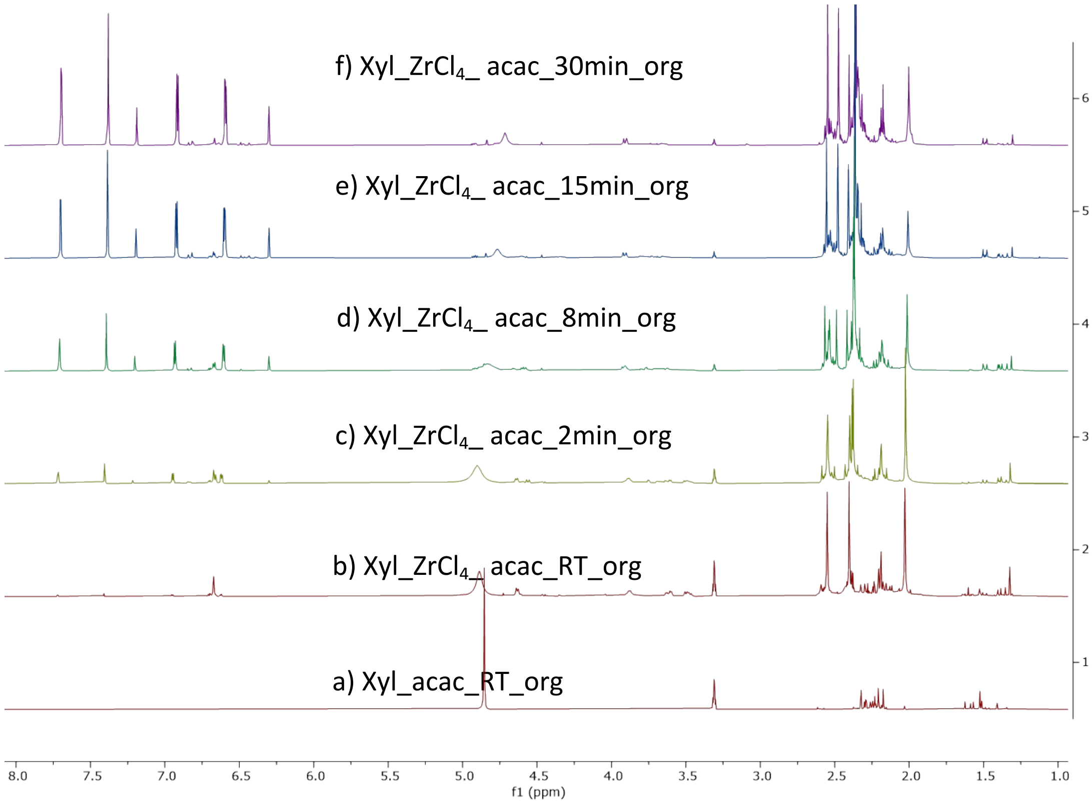


Fig. S20 ^{1}H NMR spectra of organic phase (a) xylose_acac at room temperature (RT); (b) xylsoe_ZrCl$_4$_acac at RT for 60 min; (c) at 90 °C for 2 min; (d) at 90 °C for 8 min; (e) at 90 °C for 15 min; (f) at 90 °C for 30 min. Reaction conditions: 2 mmol xylose, 20 mol% ZrCl$_4$ catalyst, 2 mL D_2O (with 10 mmol NaCl), 2 mL acac were added into a vial and reacted at 90 °C in oil bath for certain minutes.

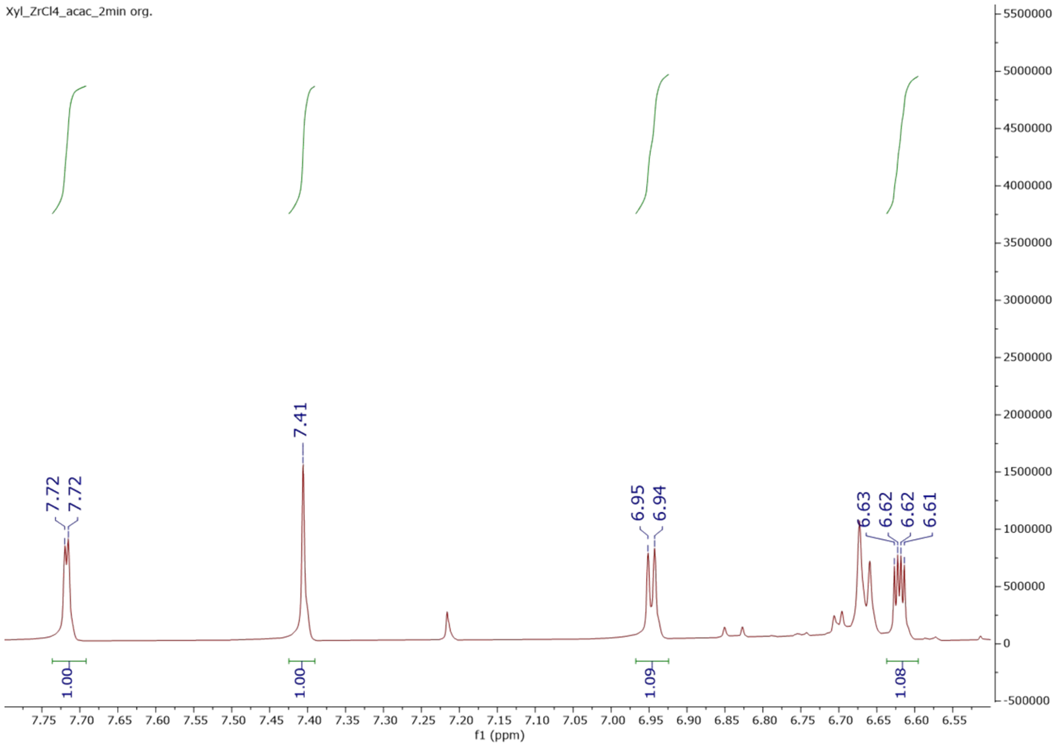


Fig. S21 ^{1}H NMR spectra of reaction mixture in organic phase, the observation of FMPD signals at 90 °C for 2 min from **Fig. S20c**.

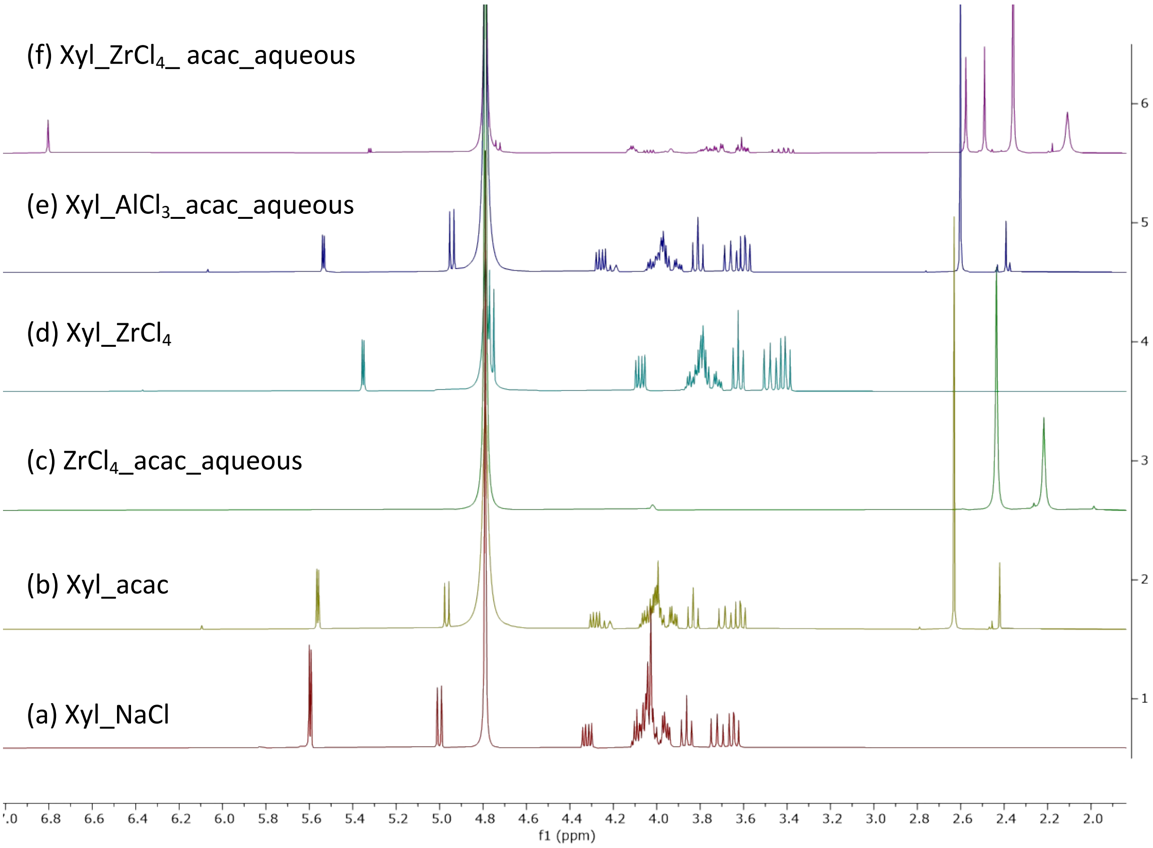


Fig. S22 ^{1}H NMR spectrum of aqueous phase (a) xylose in D_2O; (b) xylose in D_2O with acac; (c) $ZrCl_4$ in D_2O with acac; (d) xylose in D_2O with $ZrCl_4$; (e) xylose in D_2O with $AlCl_3 \cdot 6H_2O$ and acac; (f) xylose in D_2O with $ZrCl_4$ and acac. Reaction conditions: 2 mmol xylose, 20 mol% $ZrCl_4$ or $AlCl_3 \cdot 6H_2O$ catalyst, 2 mL D_2O (with 10 mmol NaCl), 2 mL acac (when needed) were added into a vial and stirred at 600 r/min at RT for 60 min.

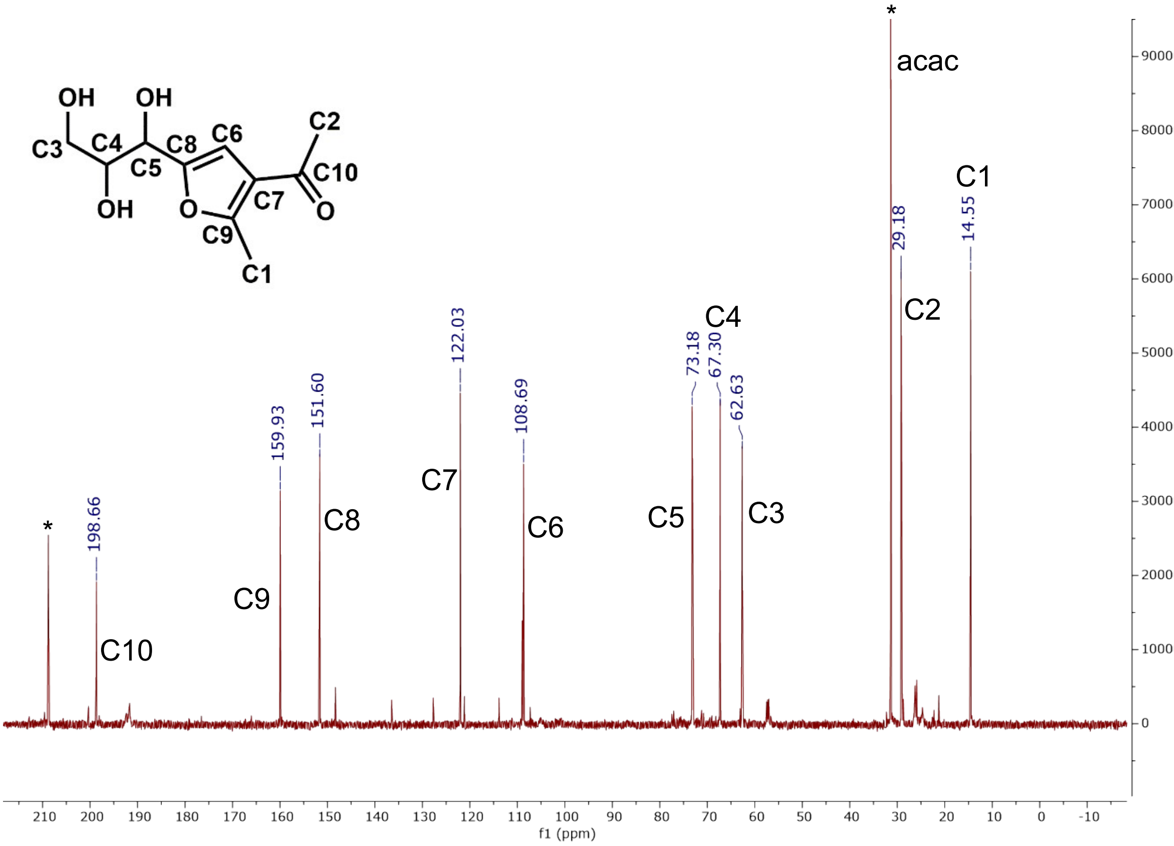
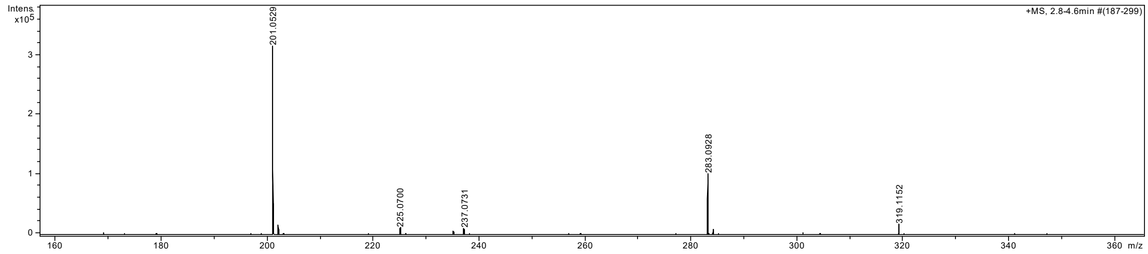
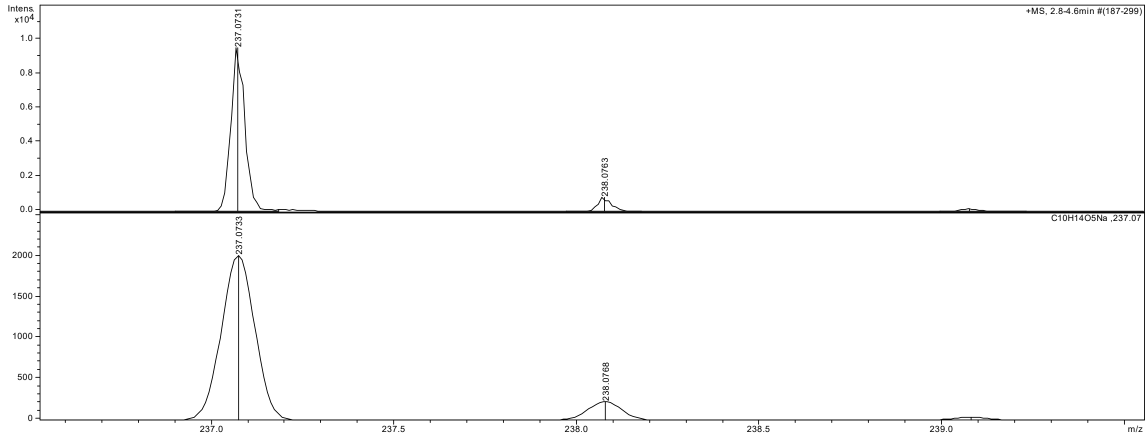
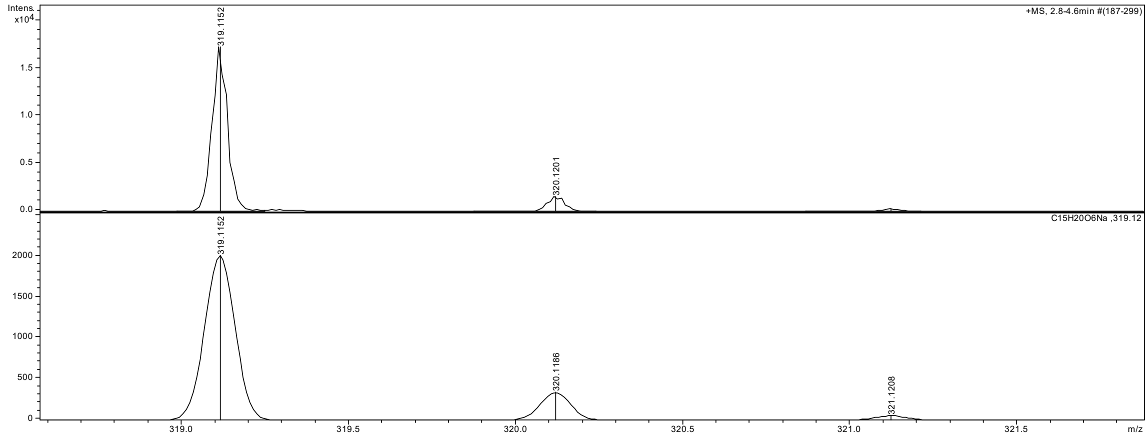


Fig. S23 Recognition of intermediate **B** from ^{13}C NMR spectra (400 MHz, D_2O).





Experimental (above) and calculated (below) isotopic patterns of intermediate **B**. $[C_{10}H_{14}O_5+Na]^+$ calculated m/z 237.0733, found m/z 237.0731, error 0.968 ppm.



Experimental (above) and calculated (below) isotopic patterns of intermediate **E**. $[C_{15}H_{20}O_6+Na]^+$ calculated m/z 319.1152, found m/z 319.1152, error 0.015 ppm.

Fig. S24 HRESI-MS spectra of reaction mixture at 140 °C for 2 min and recognized species.

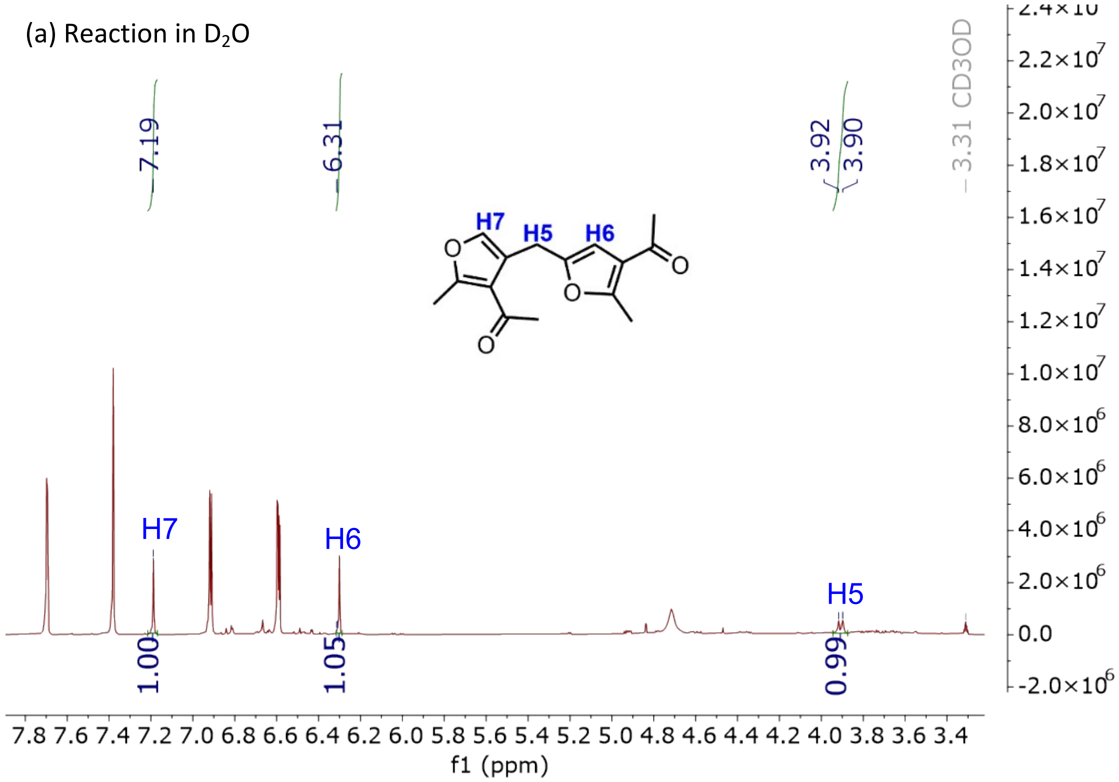
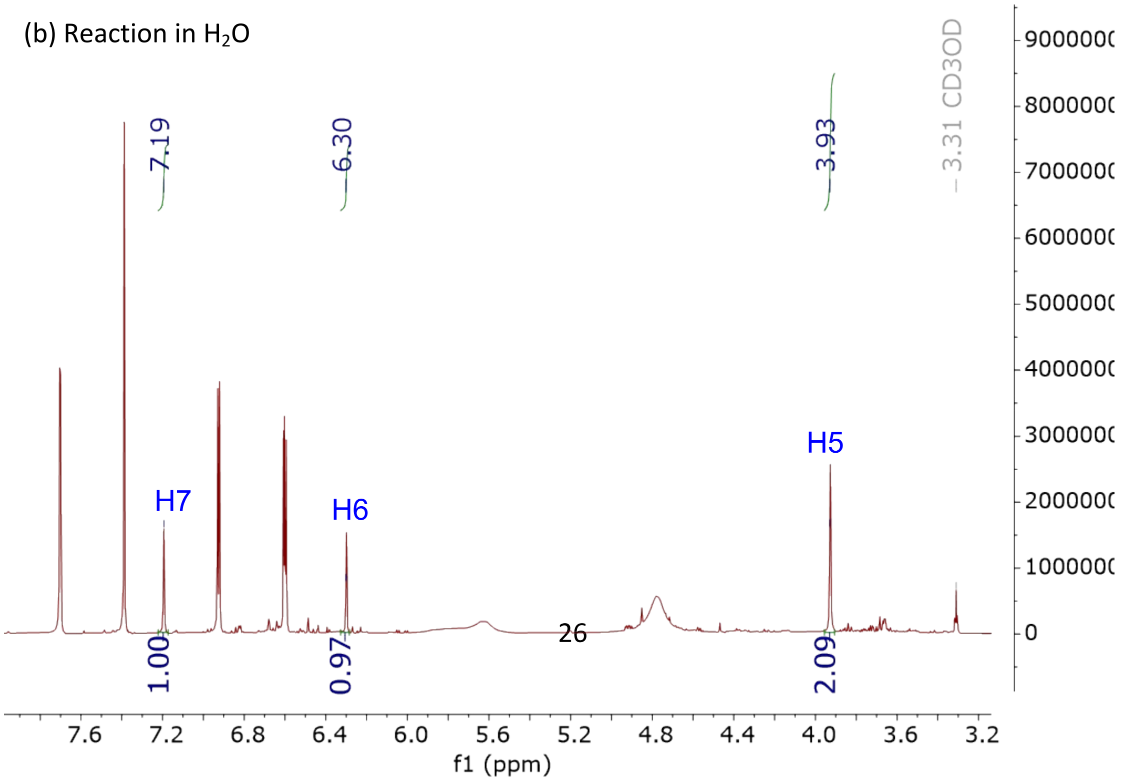


Fig. S25 ^{1}H NMR spectra of reaction mixture in organic phase, the observation of MFE signals at 90 °C for 30 min in oil bath from (a) **Fig. S20f** as an example and (b) reaction performed in H_2O.

1.4 Computational details

All DFT calculations were performed using Gaussian16 (Rev. C.01)[1] program package. The geometry optimizations were conducted using PBE1PBE hybrid exchange-functional[2,3] in



combination with Def2-SVP basis set.[4,5] Grimme's empirical dispersion correction with Becke-Johnson damping (GD3BJ)[6] was utilized to treat the effects of dispersion as well as an ultrafine integration grid. Optimized structures of B and C+H_2O were confirmed to be true minima on the potential energy surface (no imaginary frequencies) and the transition state connecting structures **B** and **C** has one imaginary frequency. The energies reported here represent the Gibbs free energies (given in kJ/mol) in the gas phase.

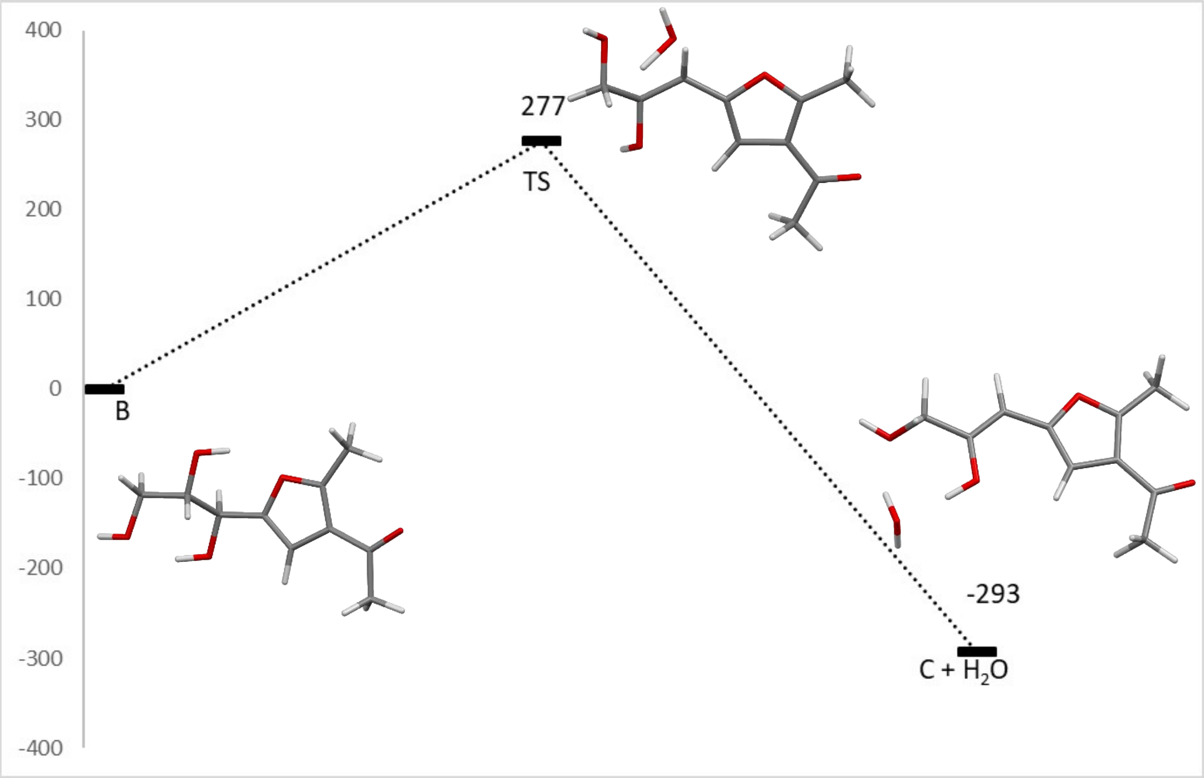


Fig. S26 Energy diagram for the dehydration reaction from **B** to **C**. Gibbs free energies are given in kJ/mol.

xyz-coordinates of the optimized structures

B

29

O	0.31020	1.17109	-0.42693
C	-0.18378	-0.10334	-0.41042
C	0.82164	-0.97943	-0.16925
C	2.02152	-0.19229	-0.03214
C	1.64268	1.12098	-0.19588
C	2.37652	2.40188	-0.16891
C	3.39452	-0.66992	0.22872

H	0.70279	-2.05703	-0.10747
C	-1.64937	-0.28666	-0.62825
H	3.43754	2.19161	0.00664
H	2.25880	2.94117	-1.12221
H	1.99736	3.05666	0.63244
O	4.33891	0.08855	0.32876
C	3.57114	-2.16132	0.36705
H	4.62765	-2.38421	0.55789
H	2.95372	-2.54773	1.19303
H	3.24144	-2.67504	-0.54954
O	-1.88078	-1.66068	-0.66489
C	-2.47402	0.42219	0.46898
H	-1.92318	0.21127	-1.58650
C	-3.96881	0.23762	0.26935
H	-2.19314	-0.04291	1.43723
O	-2.27399	1.80517	0.46236
H	-4.48711	0.84667	1.03111
H	-4.23923	0.64025	-0.72522
O	-4.28799	-1.13272	0.38863
H	-2.80216	-1.80359	-0.38969
H	-1.32741	1.98032	0.39275
H	-5.21012	-1.26705	0.15067

TS B to C

29

O	0.46711	-1.51456	-0.19542
C	-0.21529	-0.33511	-0.06379
C	0.68391	0.69263	0.02887
C	1.98447	0.10605	-0.05010
C	1.77715	-1.25711	-0.18526
C	2.70073	-2.40163	-0.31767
C	3.29199	0.79029	-0.00655
H	0.40973	1.73793	0.12478
C	-1.64907	-0.41850	-0.05704
H	3.73118	-2.03036	-0.30230
H	2.55011	-3.11486	0.50808
H	2.51339	-2.94226	-1.25886
O	4.34365	0.18679	-0.08647
C	3.25969	2.29079	0.14369
H	4.28692	2.67399	0.15978
H	2.70347	2.75066	-0.68803
H	2.74274	2.57358	1.07398
O	-2.10041	-0.98629	1.71465
C	-2.52493	0.72287	0.05242
H	-2.06045	-1.31323	-0.53174
C	-3.82514	0.63388	-0.71306

H	-2.62295	0.07669	1.28855
O	-1.94394	1.99626	-0.01228
H	-4.48792	1.44935	-0.36068
H	-3.65736	0.80808	-1.79814
O	-4.38256	-0.63857	-0.48126
H	-2.78798	-1.65897	1.58907
H	-2.18502	2.46846	0.79010
H	-5.10768	-0.77300	-1.09741

C + H_2O

29

O	1.14703	-1.75301	0.01813
C	0.19106	-0.77983	-0.09986
C	0.80340	0.44487	-0.11529
C	2.21245	0.19830	0.00061
C	2.35560	-1.17315	0.07906
C	3.53161	-2.05763	0.20991
C	3.30377	1.18806	0.03126
H	0.28657	1.39503	-0.20176
C	-1.16905	-1.23664	-0.17707
H	4.43497	-1.43869	0.24751
H	3.46277	-2.66651	1.12577
H	3.59521	-2.75228	-0.64314
O	4.47420	0.87267	0.13520
C	2.89625	2.63784	-0.07431
H	3.79259	3.26874	-0.04040
H	2.34892	2.81675	-1.01294
H	2.21813	2.90819	0.75012
O	-4.47422	1.99739	0.17584
C	-2.25220	-0.43254	-0.28858
H	-1.31536	-2.31668	-0.14721
C	-3.62307	-1.01921	-0.42985
H	-4.32208	2.55300	0.94858
O	-2.11899	0.89638	-0.34744
H	-4.06789	-0.67138	-1.38374
H	-3.53068	-2.11512	-0.47365
O	-4.45723	-0.63413	0.66245
H	-4.69396	1.11405	0.54006
H	-2.98647	1.36705	-0.26572
H	-5.28795	-1.11699	0.58783

Table S5 The yield of FMPD and MFE with the addition of base.[a]

Entry	$ZrCl_4$ (mmol)	DIPEA (mmol)	FMPD Yield (%)	MFE Yield (%)	Total carbon yield (%)
1	0.1	-	-	98.5	98.5
2	0.1	0.2	-	70.5	70.5

[a] Reaction conditions: 2 mmol xylose, 5 mol% $ZrCl_4$, 1 mL H_2O (with 25 mmol NaI), 9 mL acac, microwave heating, 140 °C, 24 min, 600 r/min.

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