Support Information for

Continuous flow Meerwein-Ponndorf-Verley reduction of HMF and Furfural using basic zirconium carbonate

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General Procedures

Commercially available reagents and solvents were used without further purification, unless otherwise stated. Basic zirconium carbonate was acquired from Sigma-Aldrich, product SKU 14616, lot BCBW5143. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 and Avance III 500 MHz spectrometers. Chemical shifts (δ) are given in parts per million, referenced to the residual peak of $CDCl_3$, $\delta = 7.26$ (^{1}H NMR) and $\delta = 77.0$ (^{13}C NMR) as internal references. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. GC-MS analysis was performed on a 9870A Agilent GC system. The chromatographic column was an Agilent HP-5MS (60 m length, 0.25 mm diameter, and 0.25 μm film). The injector and MS source temperatures were 280 and 230 °C, respectively. The MS ionization impact was set at 70 eV and the mass spectrometer was operated with a mass scan range of 30–400 m/z. All microwave experiments were carried out using a Biotage Initiator+ Microwave Synthesizer using a 5 mL pressurized vial. All continuous flow experiments were carried out using the Vapourtec R2/R4 modules. The FTIR in-line monitoring data were recorded using the DS Micro Flow Cell connected to the ReactIR 45 from Mettler Toledo. Continuous flow reactions were statistically evaluated by Design Expert software version 10 (Stat-Ease).

Thermal analysis of the catalyst

When trying to perform reactions under continuous flow at 150 °C, we observed the formation of channels in the catalyst column and gas evolution. For further comprehension of the catalyst behaviour, thermogravimetric analysis (TGA – TA Instruments model 2950, r.t. to 500 °C, 10 °C/min, inert atmosphere) and differential scanning calorimetry (DSC) of the material were performed (Figure S1). Hence, we constrained our evaluation to 120 °C as an upper limit to avoid catalyst decomposition and change of properties. Additionally, we performed a TGA for the catalysts after the scale up experiments with furfural and HMF. The different thermal profiles indicate change in the catalyst structure. Additionally, the weight loss above 200 °C is greater for the used catalyst, indicating decomposition of organic compounds.

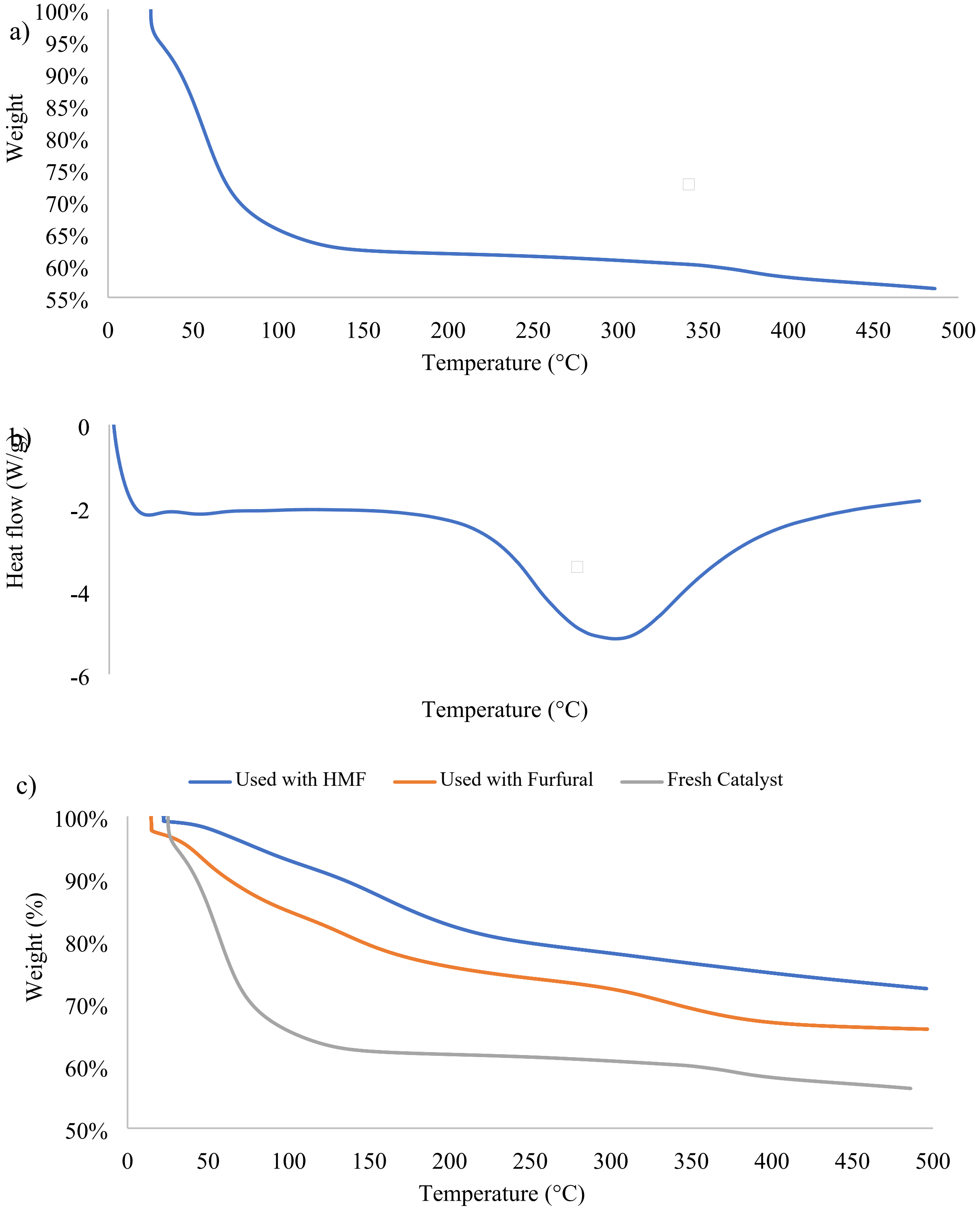


Figure S1. (**a**) TGA of the commercial BZC. (**b**) DSC of the BZC. (**c**)TGA of fresh BZC and after scale-up experiments with furfural and HMF. [i]The important mass loss around 100 °C can be associated with water removal while the loss at 380 °C may indicate the decomposition of the carbonate. [ii] shows an important thermal event at around 130 °C

Catalyst evolution and evaluation of additives with HMF

A visual comparison can be done of the catalyst after processing furfural and HMF (Figure S2). The darker colour after processing HMF (**6**) is an indicative that large quantities of side-products are adsorbed in the column, probably humins.

a) b) c)

Figure S2. Comparison of the catalyst (a) before use, (b) after processing ~55 mmol of furfural and (c) after processing ~55 mmol of HMF.

Aldol products between acetone and furfural were detected using GC-MS while running the system at high aldehyde concentrations (1 mol L^{-1}). Although highly coloured, these side-products were not problematic for the reaction development.

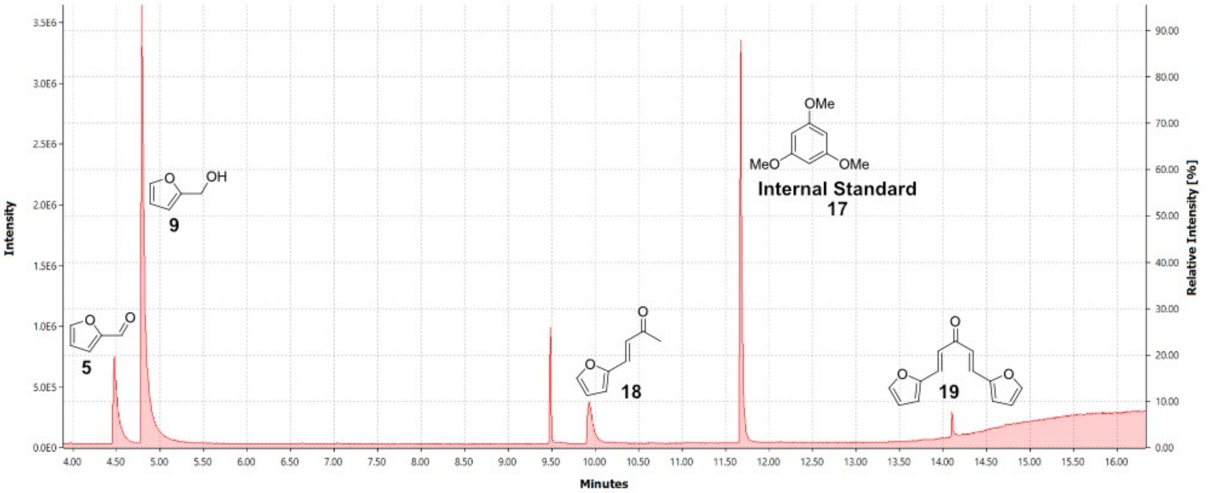
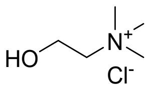
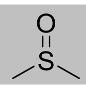
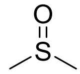
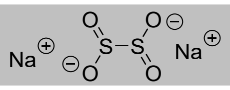
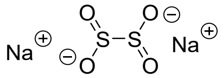
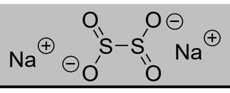


Figure S3. GC-MS with identified side-products from the reduction of furfural in continuous flow.

The use of additives for further improvement on HMF transformation was evaluated. Previously, Gomes and co-workers used choline chloride (ChCl), DMSO and sodium dithionite ($Na_2S_2O_4$) as additives to mitigate side-reactions involving HMF.[1] We first evaluated them under batch conditions at 150 °C for 30 min (Table S1). While choline chloride and DMSO have significantly inhibited the reaction (entries 2-4), sodium dithionite at low concentrations did not influence the reaction (entry 5). We speculate that this is a result of the low solubility in *iso*-propanol. Adding higher quantities of $Na_2S_2O_4$ also resulted in reduced yields (entries 6-7). Hence, none of the evaluated additives were deemed suitable for the transformation of interest.

Table S1. Additive evaluation for stabilizing HMF towards reduction over BZC.

#	Additive	Structure	Loading (m/m)	Conversion (%)	Yield (%)
1	-	-	-	88	82
2	ChCl		1.3%	76	70
3	DMSO		1.3%	74	67
4*	DMSO		1650%	37	31
5	$Na_2S_2O_4$		1.3%	87	82
6	$Na_2S_2O_4$		2.6%	83	79
7	$Na_2S_2O_4$		5.2%	78	75

*It corresponds to 15% v/v in *iso*-propanol, previously used for the fructose dehydration.[2]

**Reactions were performed in the same conditions as the general procedure in batch: 4mL scale, 0.25 M at 150 °C for 30 min under microwave heating.

Procedure for collection and analysis of reduction over BZC under continuous flow

First the system was followed using the infrared detector, following the wavenumbers 1713 cm^{-1} and 1680 cm^{-1}. When the signals stabilized, aliquots of ~5 mL – around 4 column void-volumes – were collected and samples of 100 µL were diluted with 900 µL solution of internal standard trimethoxybenzene of known concentration (around 1.0 g/L). The reaction crudes were analysed using GC-MS. Multiple fractions were collected and analysed per condition to ensure that the samples correspond to steady-state operation. Samples were seldom collected before a stable concentration was achieved, for these cases the last fractions were used for the analysis as they correspond to the actual chemical information of the system (steady-state operation). Yields were calculated as previously described. Productivity was calculated using the reactor void-volume ($V_{reactor}[mL] = 1.2\ mL$, determined through weight difference between the dry packed column and the column after filled with *iso*-propanol. $V_{reactor} = \dfrac{m_{reactor,\ with\ solvent} - m_{reactor,\ dry}}{\rho_{solvent}}$), yield ($Yield[\%]$), concentration ($C[mol\ L^{-1}]$), product molecular weight ($MW[g\ mol^{-1}]$), and residence time ($t_R[s]$) according to the following equation:

$$Productivity = \frac{V_{reactor} \cdot C \cdot MW \cdot Yield}{\left(\frac{t_R[s]}{60}\right)}$$

Response factors and yields measurements

Response factors for each component (furfural, furfuryl alcohol, HMF and DHMF) to the internal standard were updated at least 14 days before usage to ensure reliability of the results. They were calculated from 3-6 different solutions prepared before injection. Masses of the compounds of interest, alongside with the internal standard, were weighted and further diluted to proper concentrations. The response factor was calculated according to the following equation.

$$R_i = \frac{A_i \cdot m_{IS}}{A_{IS} \cdot m_i}$$

Yields were calculated using the following equation:

$$Yield = \frac{A_{product} \cdot m_{IS}}{R_{product} \cdot A_{IS} \cdot m^0_{product}}$$

Where, $A_{product}$ is the area of the product signal after baseline correction, m_{IS} is the mass of internal standard in the vial calculated from the dilution, $R_{product}$ is the response factor, A_{IS} is the area of the internal standard signal and $m^0_{product}$ is the expected mass of product if reaction yield was quantitative.

Statistics results for the productivity DoE of furfuryl alcohol and DHMF

The statistical results were done using the Design-Expert version 10.0.6.0 from Stat-Ease Inc.

1. Furfuryl alcohol productivity model

Table S2. ANOVA for the log-transformed reduced cubic model for the reduction of furfural.

Transform: Base 10 Log Constant: 0
ANOVA for Response Surface Reduced Cubic model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1.53	8	0.19	69.46	< 0.0001	significant
A-Temperature	*0.021*	*1*	*0.021*	*7.60*	*0.0187*	
B-Time	*0.31*	*1*	*0.31*	*113.55*	*< 0.0001*	
C-Concentration	*0.60*	*1*	*0.60*	*217.98*	*< 0.0001*	
AB	*0.052*	*1*	*0.052*	*18.89*	*0.0012*	
A^2	*4.268E-004*	*1*	*4.268E-004*	*0.16*	*0.7013*	
B^2	*1.110E-004*	*1*	*1.110E-004*	*0.040*	*0.8445*	
A^2B	*0.030*	*1*	*0.030*	*11.04*	*0.0068*	
AB^2	*0.033*	*1*	*0.033*	*11.82*	*0.0055*	
Residual	0.030	11	2.753E-003			
Lack of Fit	*0.013*	*6*	*2.206E-003*	*0.65*	*0.6961*	*not significant*
Pure Error	*0.017*	*5*	*3.408E-003*			
Cor Total	1.56	19				

Table S3. R-squared and deviations for furfuryl alcohol productivity reduced cubic model.

Std. Dev.	0.052	R-Squared	0.9806
Mean	1.43	Adj R-Squared	0.9665
C.V. %	3.66	Pred R-Squared	0.9439
PRESS	0.088	Adeq Precision	33.136
-2 Log Likelihood	-73.10	BIC	-46.14
		AICc	-37.10

Table S4. Furfuryl alcohol productivity model coefficients and their error.

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	1.43	1	0.018	1.40	1.47	
A-Temperature	-0.10	1	0.037	-0.18	-0.021	5.00
B-Time	-0.40	1	0.037	-0.48	-0.31	5.00
C-Concentration	0.24	1	0.017	0.21	0.28	1.00
AB	-0.081	1	0.019	-0.12	-0.040	1.00
A^2	-0.012	1	0.029	-0.076	0.053	1.56
B^2	5.889E-003	1	0.029	-0.059	0.070	1.56
A^2B	0.14	1	0.041	0.047	0.23	5.00
AB^2	0.14	1	0.041	0.051	0.23	5.00

Table S5. Furfuryl alcohol productivity reduced cubic model equations in coded (A, B and C) and real variables (T, t_R and C).

$\mathrm{Log}_{10(\mathrm{Productivity})}$ =		$\mathrm{Log}_{10(\mathrm{Productivity})}$ =	
+1.43		-6.46998	
-0.10	* A	+0.14202	* T
-0.40	* B	+0.077469	* t_R
+0.24	* C	+0.65323	* Concentration
-0.081	* AB	-1.28935E-003	* T * t_R
-0.012	* A^2	-6.03042E-004	* T^2
+5.889E-003	* B^2	-1.25723E-004	* t_R^2
+0.14	* A^2B	+4.59337E-006	* T^2* t_R
+0.14	* AB^2	+1.26770E-006	* T * t_R^2

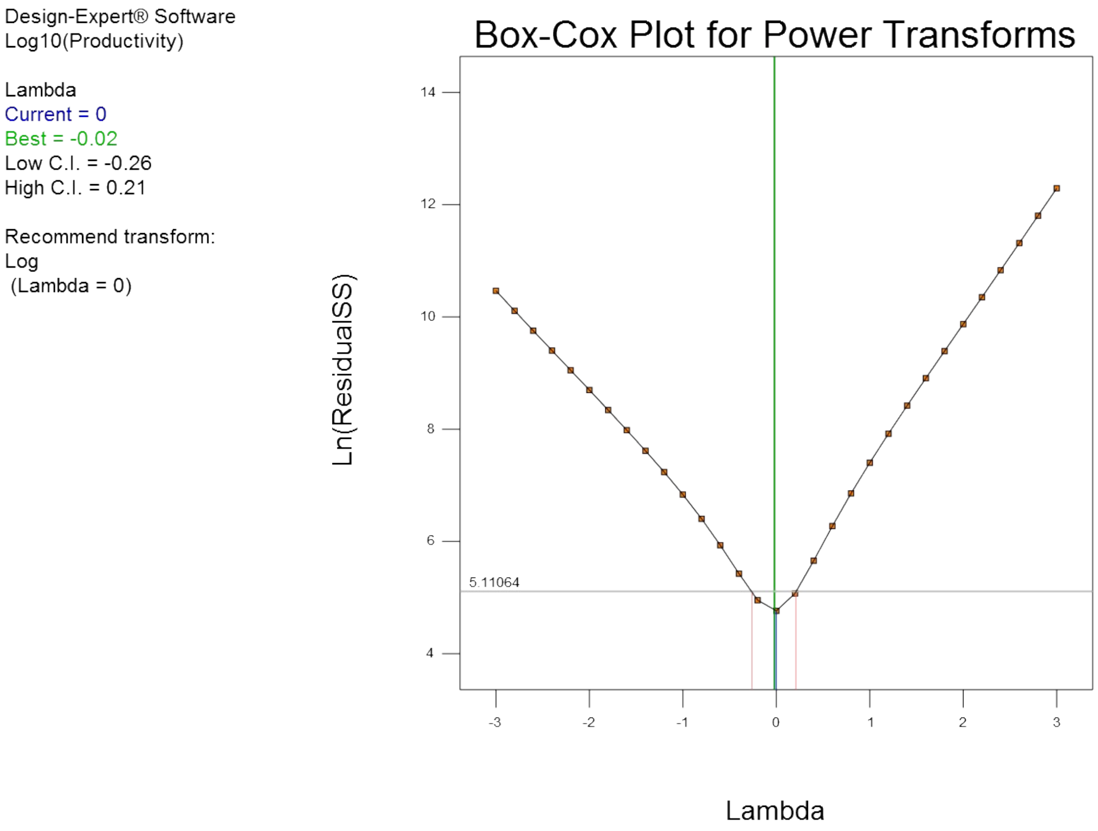


Figure S3. Box-Cox plot for furfuryl alcohol productivity model.

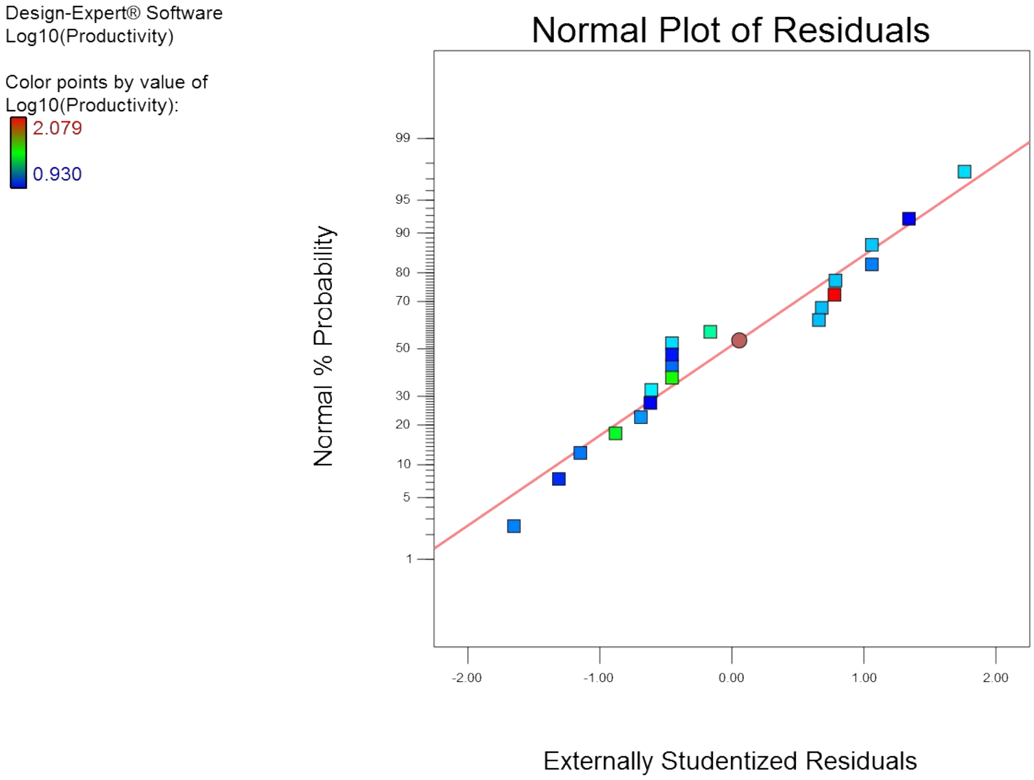


Figure S4. Normal plot of residuals for furfuryl alcohol productivity model.

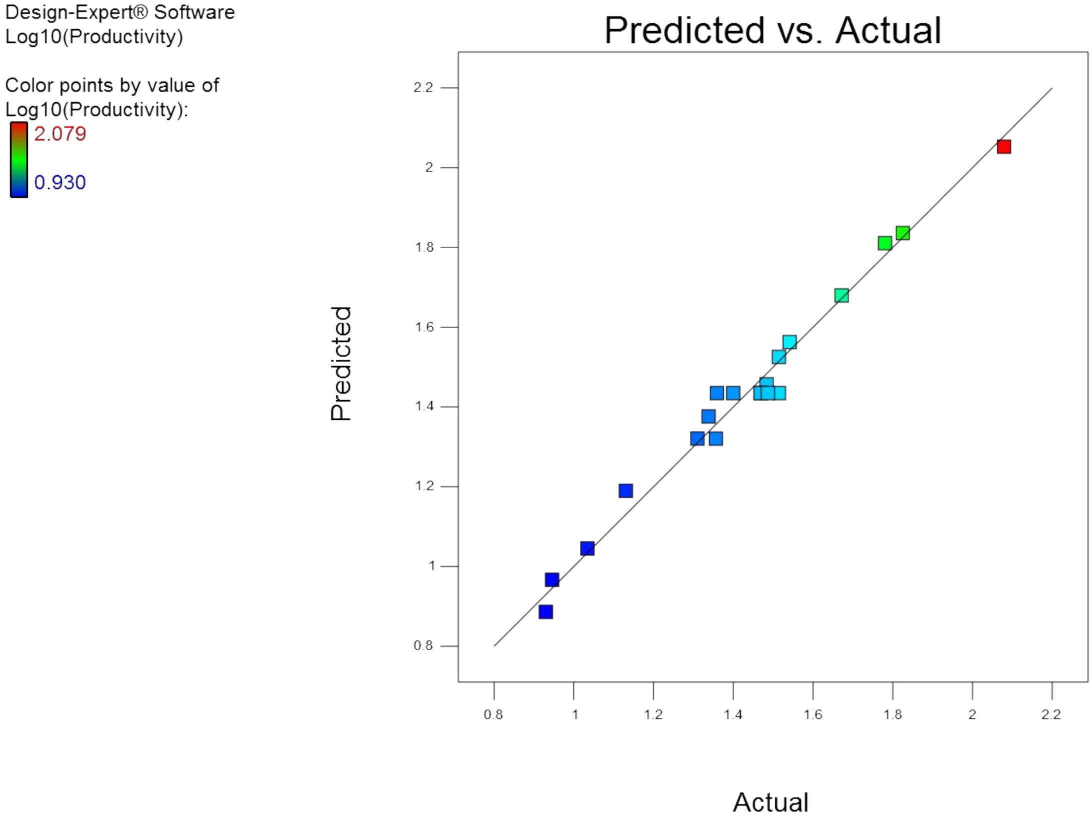


Figure S5. Plot of predicted versus actual values for furfuryl alcohol productivity.

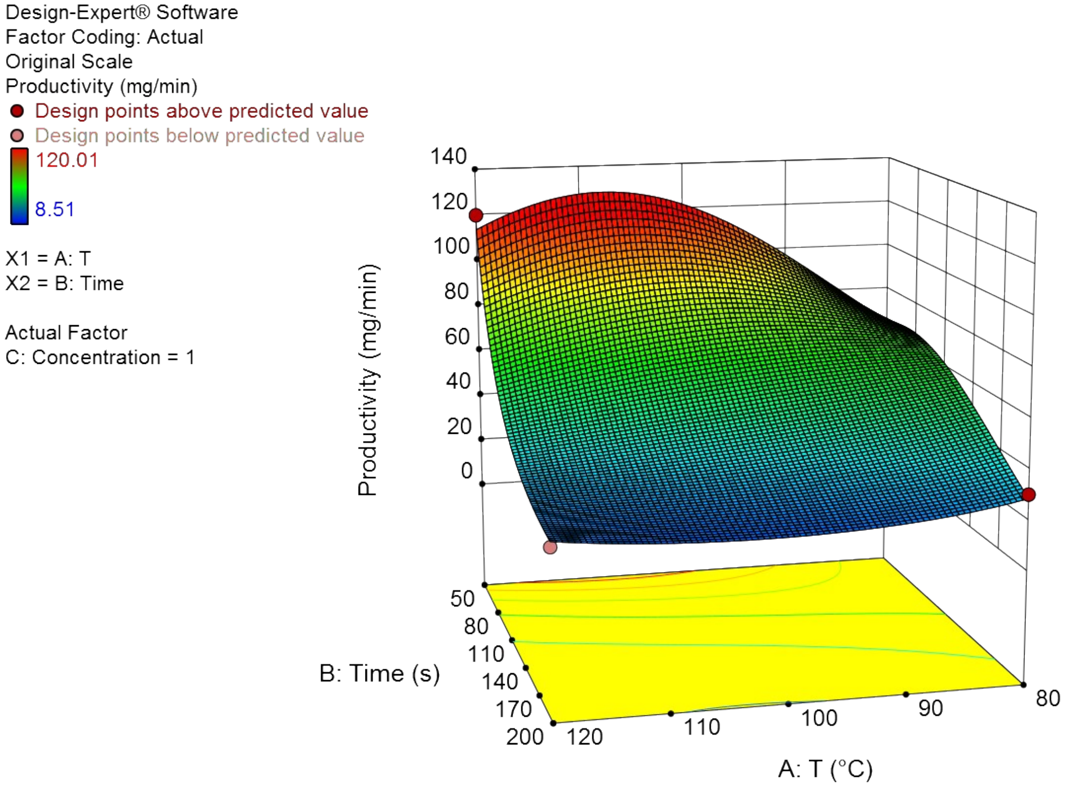


Figure S6. Productivity response surface at high furfural concentrations.

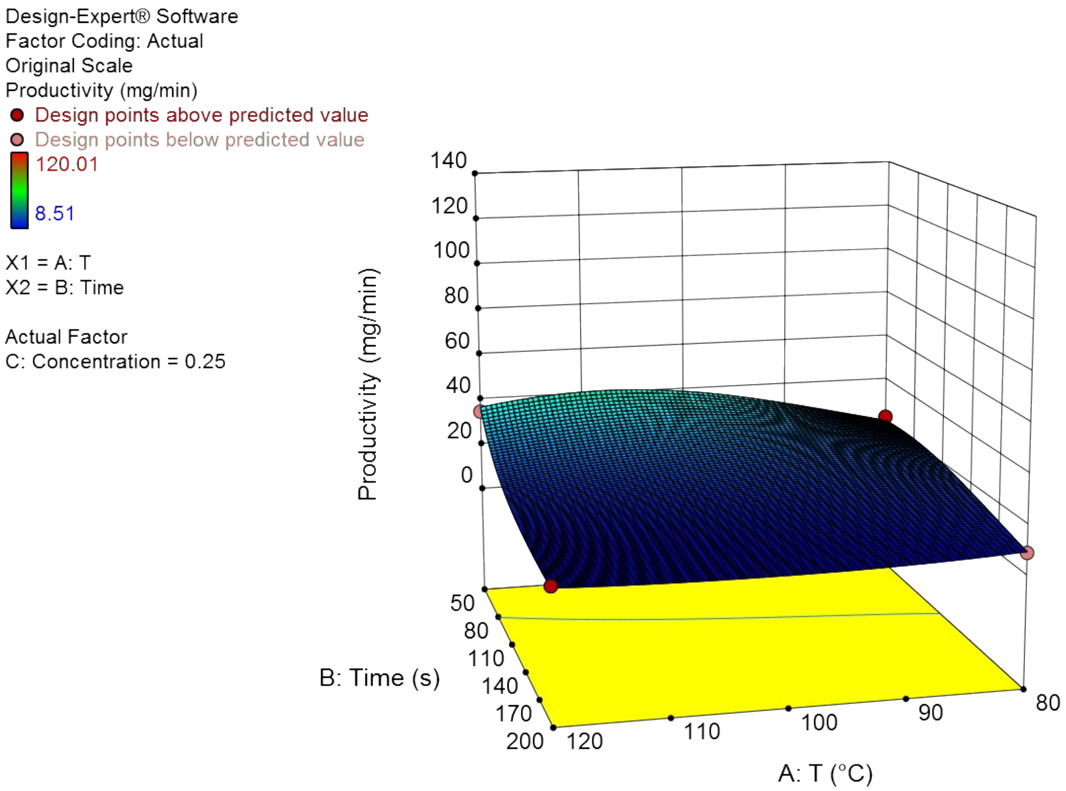


Figure S7. Productivity response surface at low furfural concentrations.

2. DHMF productivity model

Table S6. ANOVA for the reduced cubic model for the reduction of HMF.

ANOVA for Response Surface Reduced Cubic model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1824.22	5	364.84	61.69	0.0002	significant
A-Temperature	*67.06*	*1*	*67.06*	*11.34*	*0.0199*	
B-Time	*1285.90*	*1*	*1285.90*	*217.41*	*< 0.0001*	
AB	*200.49*	*1*	*200.49*	*33.90*	*0.0021*	
B^2	*93.37*	*1*	*93.37*	*15.79*	*0.0106*	
AB^2	*206.67*	*1*	*206.67*	*34.94*	*0.0020*	
Residual	29.57	5	5.91			
Lack of Fit	*25.96*	*3*	*8.65*	*4.79*	*0.1775*	*not significant*
Pure Error	*3.61*	*2*	*1.81*			
Cor Total	1853.79	10				

Table S7. R-squared and deviations for DHMF productivity reduced cubic model.

Std. Dev.	2.43	R-Squared	0.9840
Mean	19.22	Adj R-Squared	0.9681
C.V. %	12.65	Pred R-Squared	0.8874
PRESS	208.71	Adeq Precision	24.184
-2 Log Likelihood	42.10	BIC	56.48
		AICc	75.10

Table S8. DHMF productivity model coefficients and their error.

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	16.03	1	1.09	13.23	18.82	
A-Temperature	-5.79	1	1.72	-10.21	-1.37	3.00
B-Time	-14.64	1	0.99	-17.19	-12.09	1.00
AB	-7.08	1	1.22	-10.21	-3.95	1.00
B^2	5.85	1	1.47	2.07	9.64	1.00
AB^2	12.45	1	2.11	7.04	17.86	3.00

Table S9. DHMF productivity model reduced cubic equations in coded (A-B) and real variables (t_R-T).

Productivity =	Productivity	=
+16.03	-113.05446	
-5.79 * A	+1.64207	* T
-14.64 * B	+1.89955	* t_R
-7.08 * AB	-0.022215	* t_R * T
+5.85 * B^2	-5.63988E-003	* t_R^2
+12.45 * AB^2	+6.22500E-005	* t_R^2* T

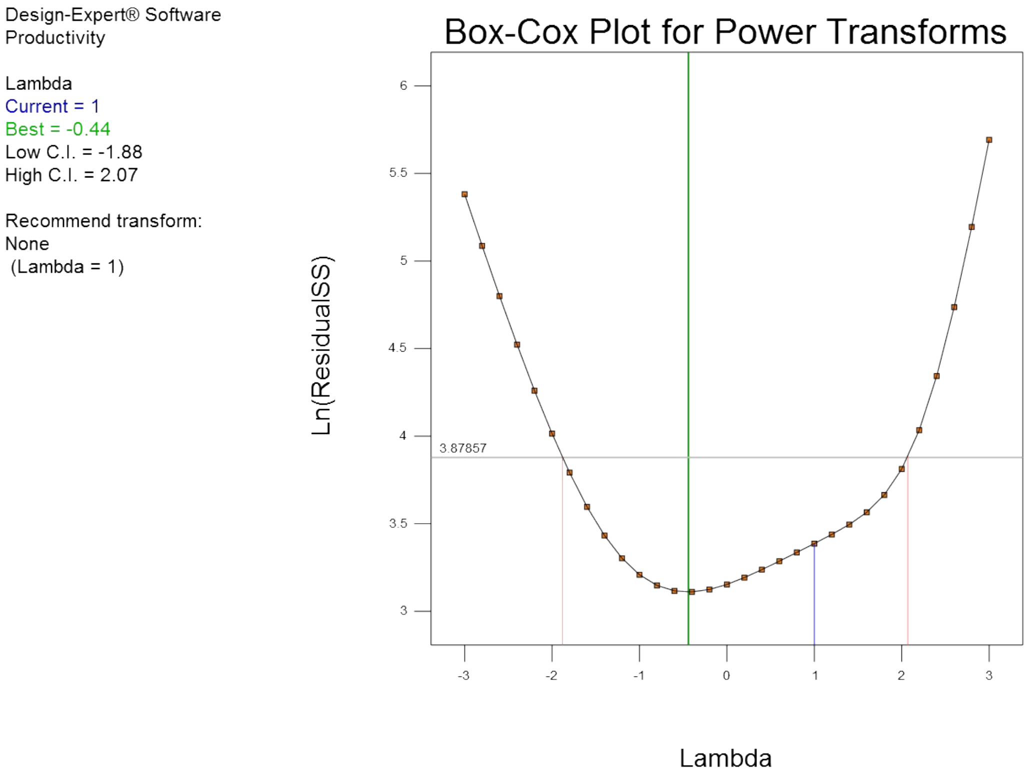


Figure S8. Box-Cox plot for DHMF productivity model.

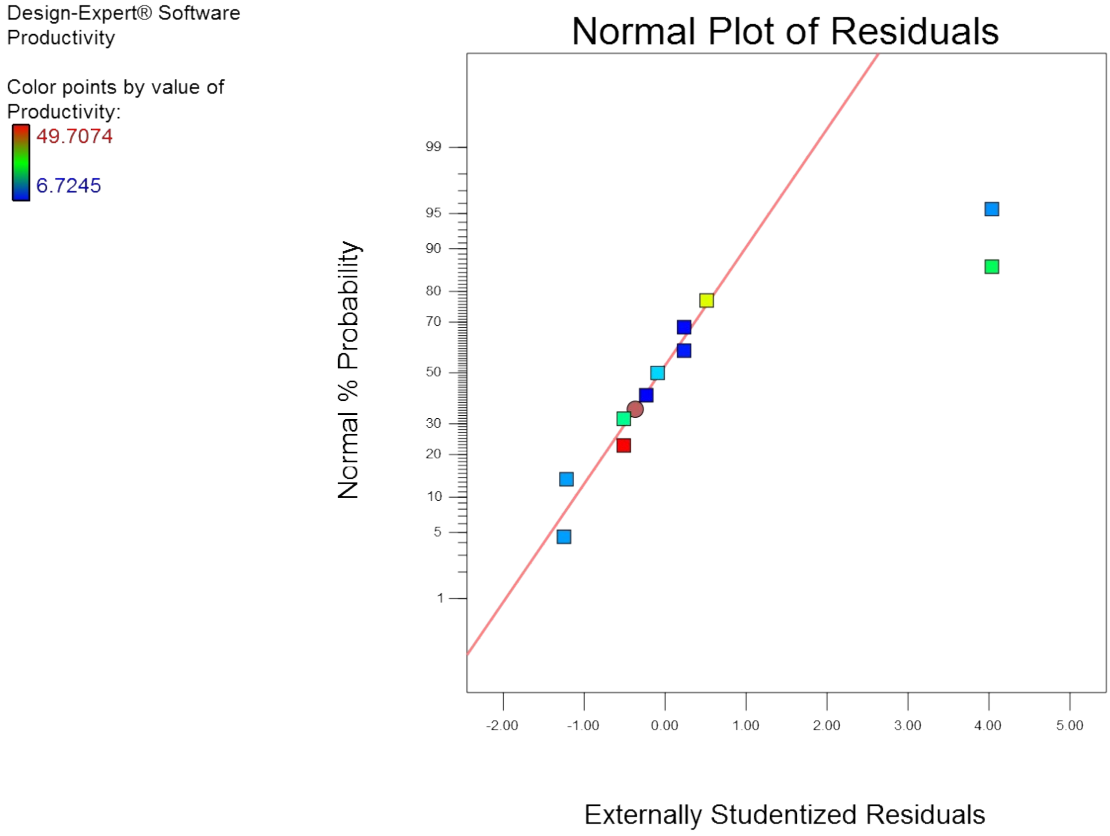


Figure S9. Normal plot of residuals for DHMF productivity model.

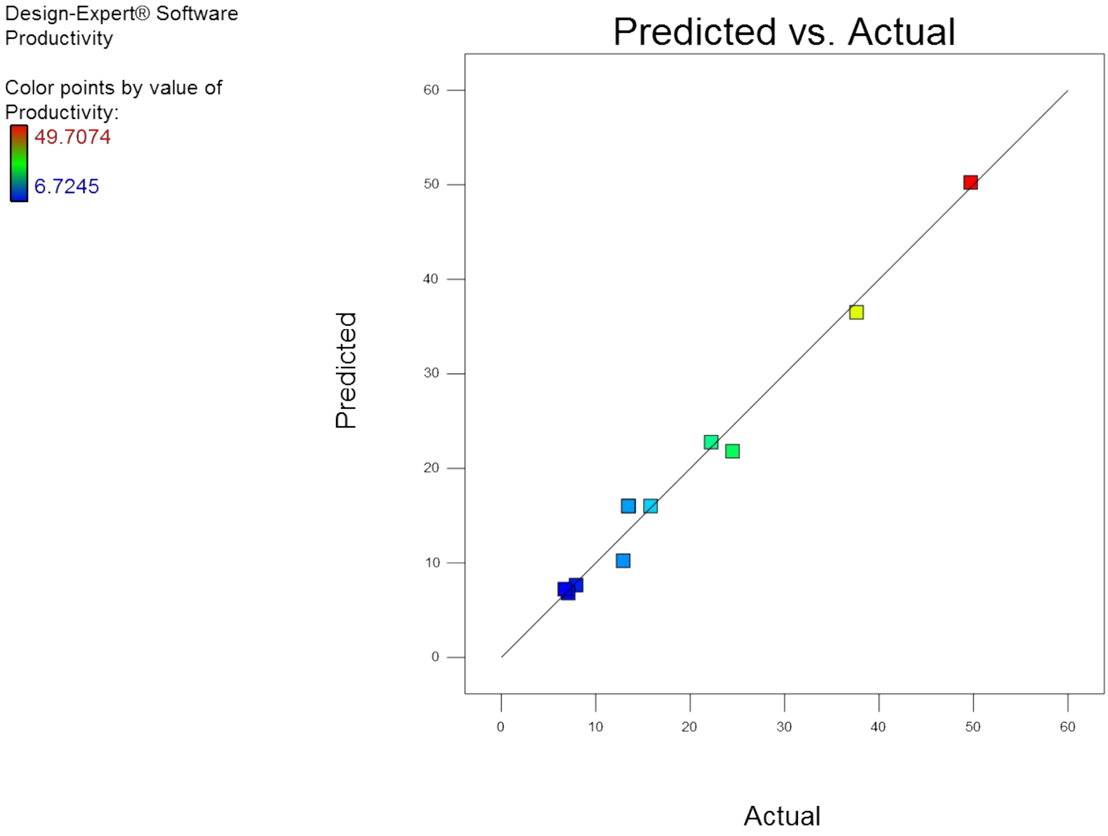


Figure S10. Plot of predicted versus actual values for DHMF productivity.

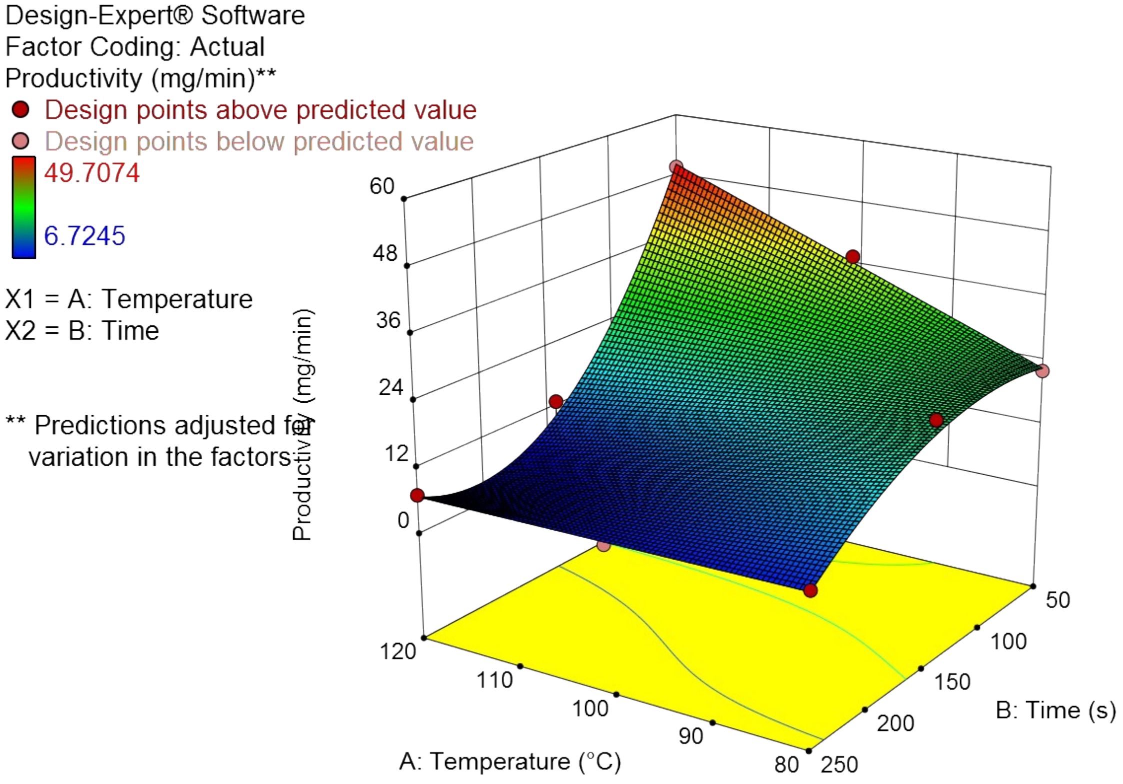


Figure S11. DHMF productivity response surface.

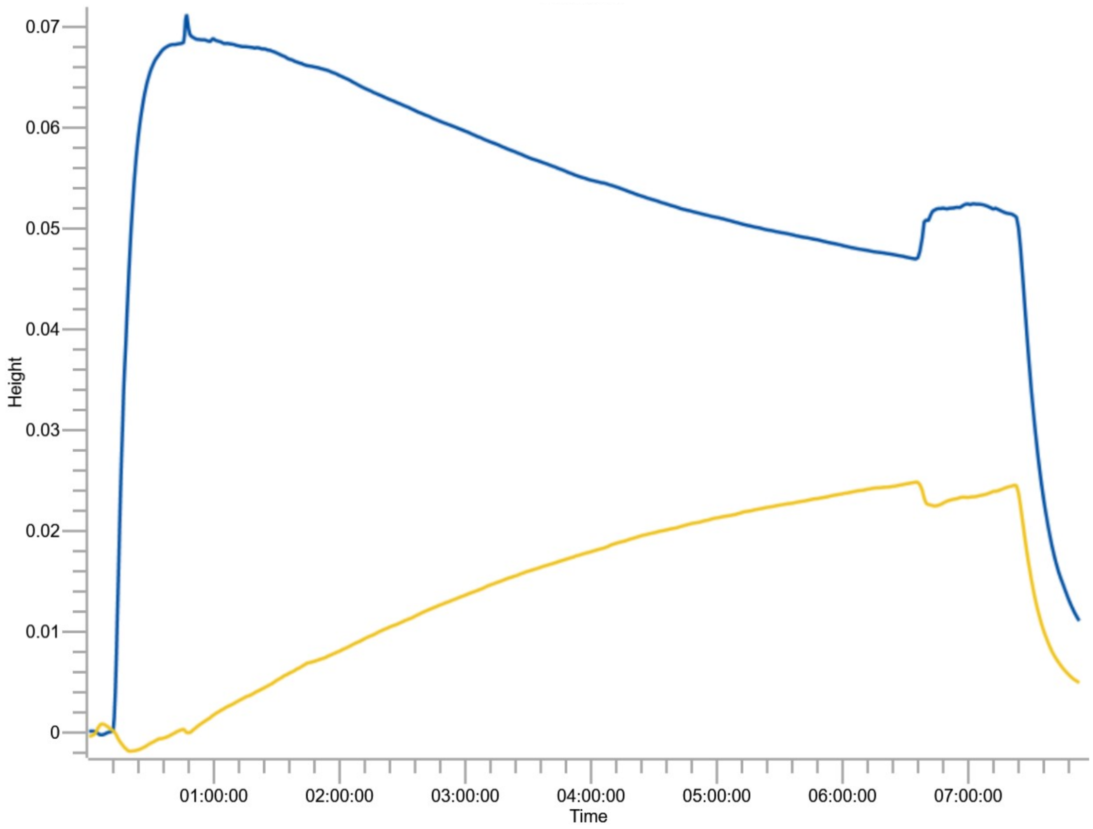


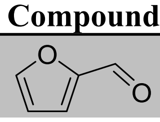
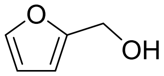
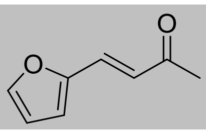
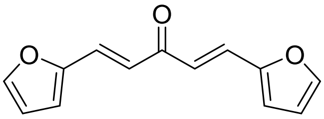
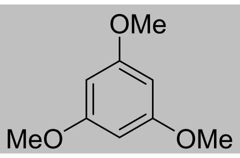
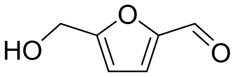
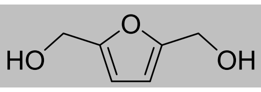
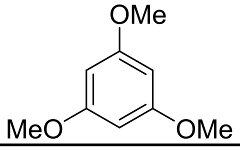
Figure S12. Trend analysis of HMF reduction for the scale-up reduction at 120 °C, 50 s residence time. Wavenumbers selected: 1713 cm^{-1} (blue) to acetone and 1680 cm^{-1} (yellow) for the aldehyde.

Selected GC-MS analysis of scale-up experiments

Furfural Method: Temperature ramp started at 40 °C for 1 min, and it was increased to 90 °C at a rate of 10 °C min^{-1} and then increased to 280 °C at 30 °C min^{-1}, finally it was kept at 280 °C for 1 min.

HMF Method: Temperature ramp started at 80 °C for 1 min, and it was increased to 180 °C at a rate of 10 °C min^{-1} and then increased to 280 °C at 30 °C min^{-1}, finally it was kept at 280 °C for 1 min.

Table 10. GC-MS retention time of standards in the methods used

Compound	Method	Retention time (min)
	Furfural	4.468
	Furfural	4.789
	Furfural	9.929
	Furfural	14.101
	Furfural	11.668
	HMF	6.060
	HMF	6.676
	HMF	9.218

1. Furfural reduction to furfuryl alcohol

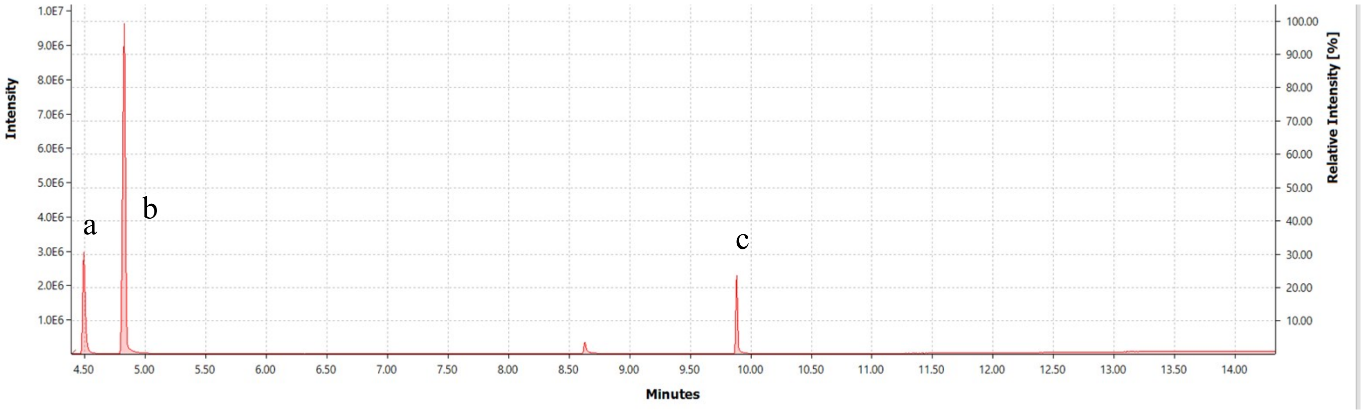


Figure S13. GC-MS of furfural reduction after 1 hours of column use (a = furfural, b = furfuryl alcohol, c = trimethoxymenzene internal standard).

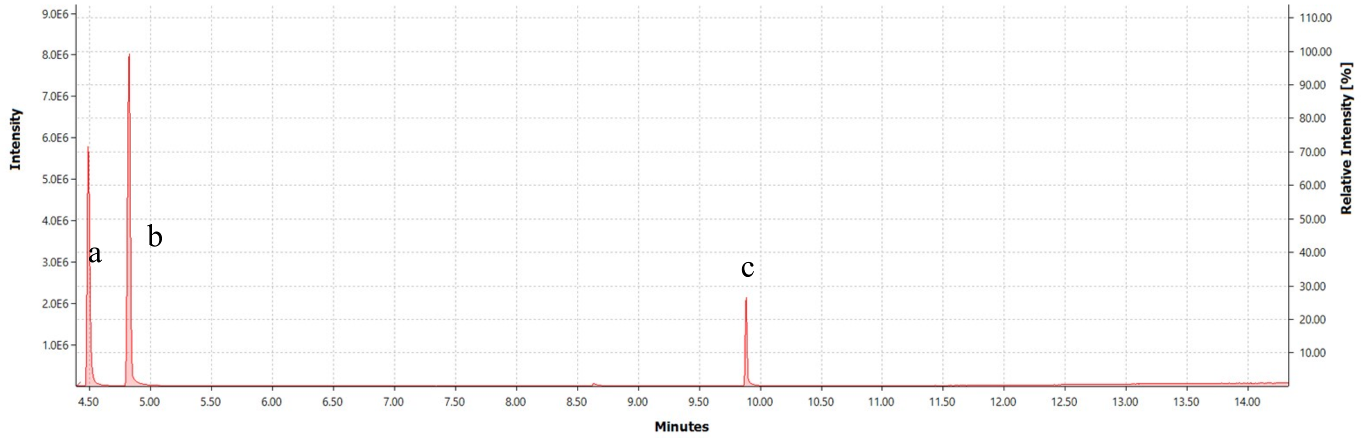


Figure S14. GC-MS of furfural reduction after 6 h 30 min of column use (a = furfural, b = furfuryl alcohol, c = trimethoxymenzene internal standard).

2. HMF reduction to DHMF

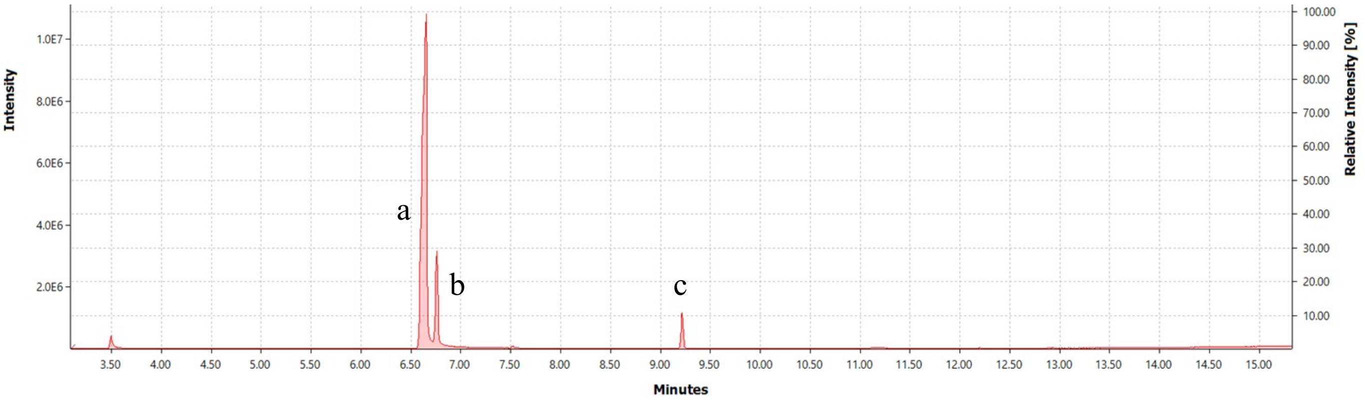


Figure S15. GC-MS of HMF reduction under continuous flow after 1h of column use (a = DHMF, b = HMF, c = trimethoxybenzene internal standard).

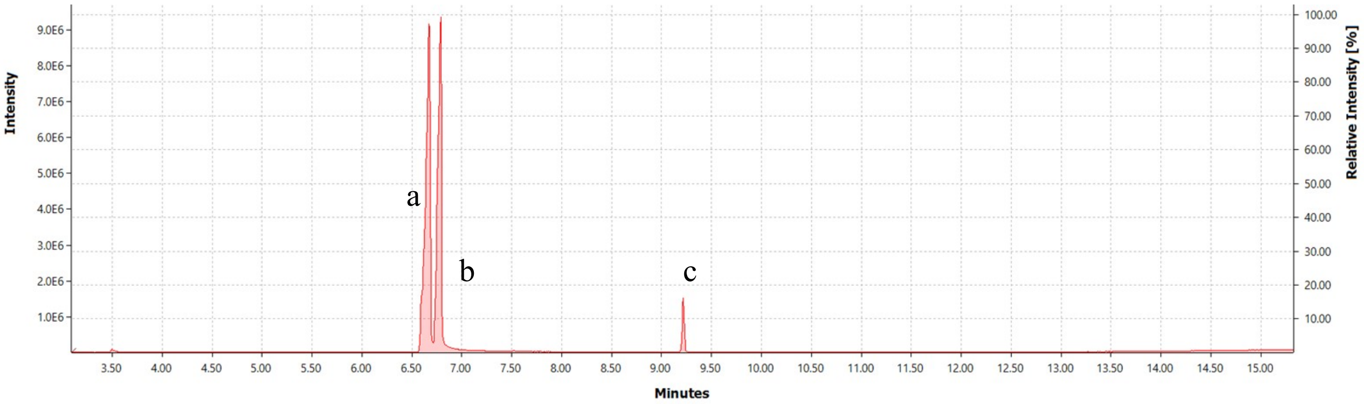


Figure S16. GC-MS of HMF reduction under continuous flow after 6h30 of column use (a = DHMF, b = HMF, c = trimethoxybenzene internal standard).

Preparation and characterization of model substrates

DHMF (10)

^{1}H NMR (250 MHz, DMSO-d6): δ 6.20 (s, 2H), 5.18 (t, *J* = 5.8 Hz, 2H), 4.36 (d, *J* = 5.8 Hz, 4H).

^{13}C NMR (63 MHz, DMSO-d6): δ 155.1 (C_0), 107.9 (CH), 56.2 (CH_2).

Furfuryl Alcohol (9)

Furfuryl alcohol standard was purified by distilling the commercially available furfuryl alcohol under reduced pressure over Na_2SO_4 and Na_2CO_3.

^{1}H NMR (250 MHz, DMSO-d6): δ 7.57 (dd, *J* = 1.8, 0.8 Hz 1H), 6.39 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.29 (d, *J* = 0.8 Hz, 1H), 5.22 (t, *J* = 5.7 Hz, 1H), 4.41 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (63 MHz, DMSO-d6): δ 155.9 (C_0), 142.5 (CH), 110.7 (CH), 107.3 (CH), 56.1 (CH_2).

4-(furan-2-yl)but-3-en-2-one (18)

Furfural (1 g) and acetone (6 g) were charged into a 50 mL round-bottom flask, followed by the addition of a water–methanol solution (20 g, 1:1 in m/m) containing 0.1 g of NaOH. After stirring at 30 °C for 2 h, the mixture was neutralized with dilute HCl and extracted with CH_2Cl_2, followed by the removal of the solvent and purification through column chromatography (hexanes:EtOAc gradient). Fractions were analysed by GC-MS, only the mono-aldol product was collected for NMR analysis.

^{1}H NMR (250 MHz, DMSO-d6): δ7.83 (d, *J* = 1.4 Hz, 1H), 7.42 (d, *J* = 16.1 Hz, 1H), 6.95 (d, *J* = 3.5 Hz, 1H), 6.63 (dd, *J* = 3.5, 1.6 Hz, 1H), 6.48 (d, *J* = 16.1 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (63 MHz, DMSO-d6): δ 197.8 (C_0), 150.9 (C_0), 146.4 (CH), 130.1 (CH), 124.5 (CH), 116.7 (CH), 113.3 (CH), 27.6 (CH_3).

1,5-di(furan-2-yl)penta-1,4-dien-3-one (19)

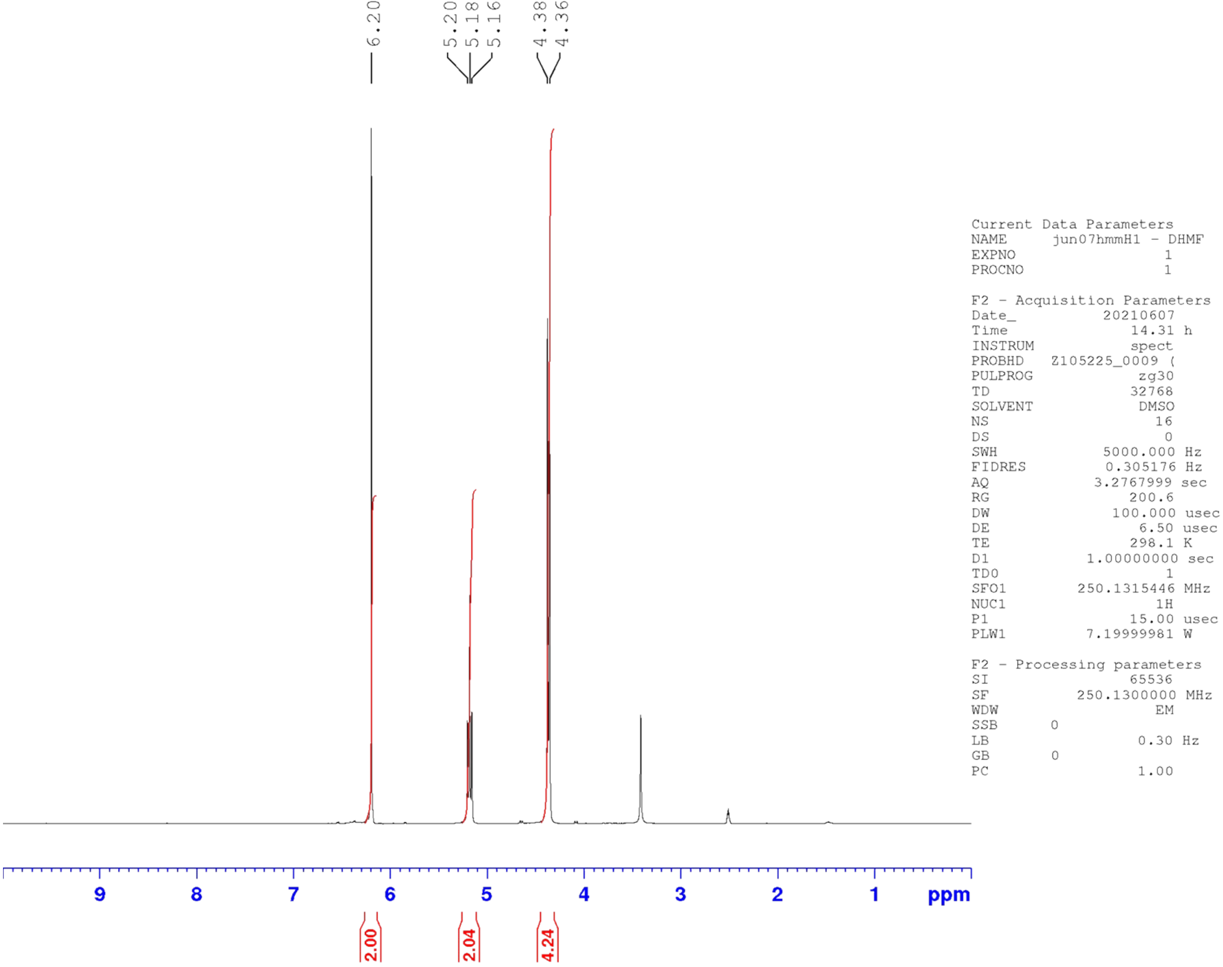
Furfural (1 g) and acetone (3 g) were charged into a 50 mL round-bottom flask, followed by the addition of a water–methanol solution (20 g, 1:1 in m/m) containing 0.1 g of NaOH. After stirring at 30 °C for 2 h, the mixture was neutralized with dilute HCl and extracted with CH_2Cl_2, followed by the removal of the solvent and purification through column chromatography (hexanes:EtOAc gradient).

^{1}H NMR (250 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.47 (d, *J* = 15.6 Hz, 1H), 6.90 (d, *J* = 15.6 Hz, 2H), 6.67 (d, *J* = 3.4 Hz, 2H), 6.47 (dd, *J* = 3.4, 1.8, 2H).

^{13}C NMR (63 MHz, $CDCl_3$): δ 188.1 (C_0), 151.5 (C_0), 145.0 (CH), 129.2 (CH), 123.2 (CH), 115.9 (CH), 112.7 (CH).

NMR spectra of model substrates

DHMF (**10**)



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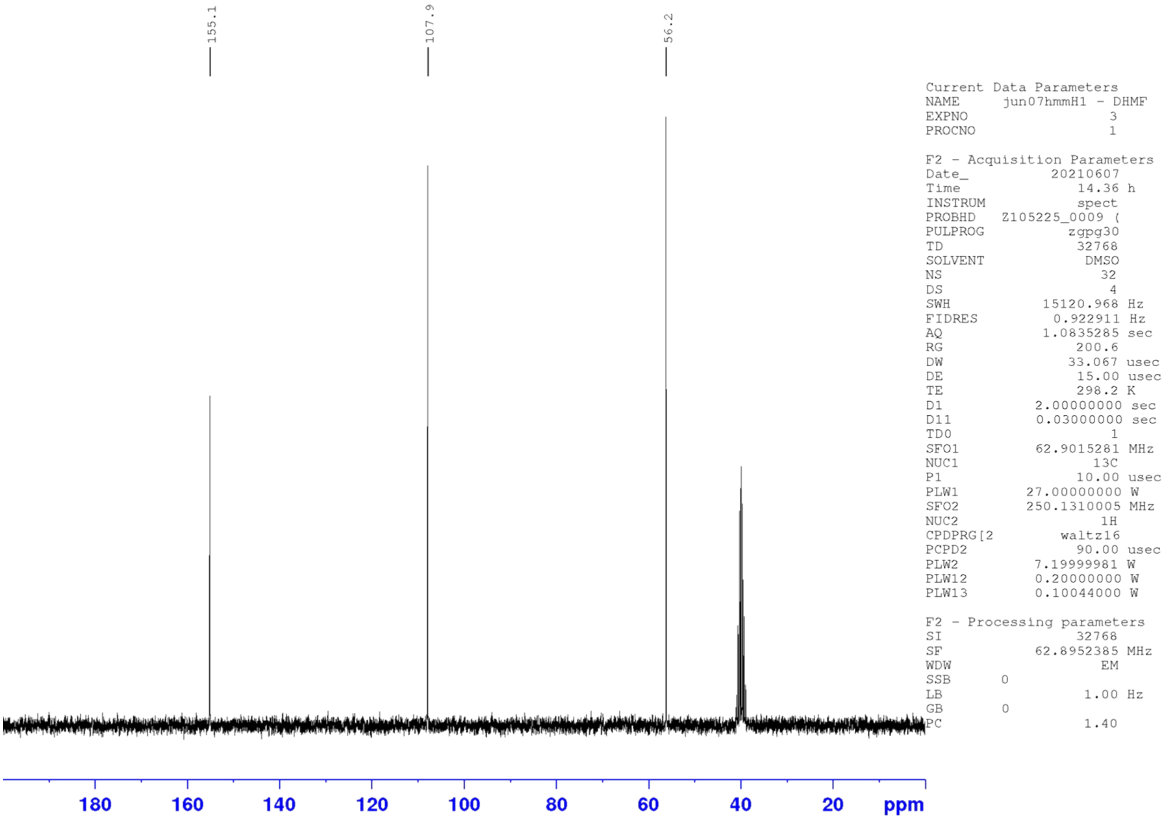
Current Data Parameters
NAME       jun07hmmH1 - DHMF
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_            20210607
Time              14.31 h
INSTRUM           spect
PROBHD   Z105225_0009 (
PULPROG            zg30
TD                32768
SOLVENT            DMSO
NS                   16
DS                    0
SWH            5000.000 Hz
FIDRES         0.305176 Hz
AQ            3.2767999 sec
RG                200.6
DW              100.000 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                   1
SFO1        250.1315446 MHz
NUC1                 1H
P1                15.00 usec
PLW1         7.19999981 W

F2 - Processing parameters
SI                65536
SF          250.1300000 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

Figure S17. ^{1}H NMR spectrum (DMSO-d6, 250 MHz) of DHMF (**10**).



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Current Data Parameters
NAME       jun07hmmH1 - DHMF
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_            20210607
Time                14.36 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG           zgpg30
TD                 32768
SOLVENT             DMSO
NS                    32
DS                     4
SWH          15120.968 Hz
FIDRES        0.922911 Hz
AQ           1.0835285 sec
RG                200.6
DW               33.067 usec
DE                15.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         62.9015281 MHz
NUC1                 13C
P1                10.00 usec
PLW1        27.00000000 W
SFO2        250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         7.19999981 W
PLW12        0.20000000 W
PLW13        0.10044000 W

F2 - Processing parameters
SI                 32768
SF           62.8952385 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```
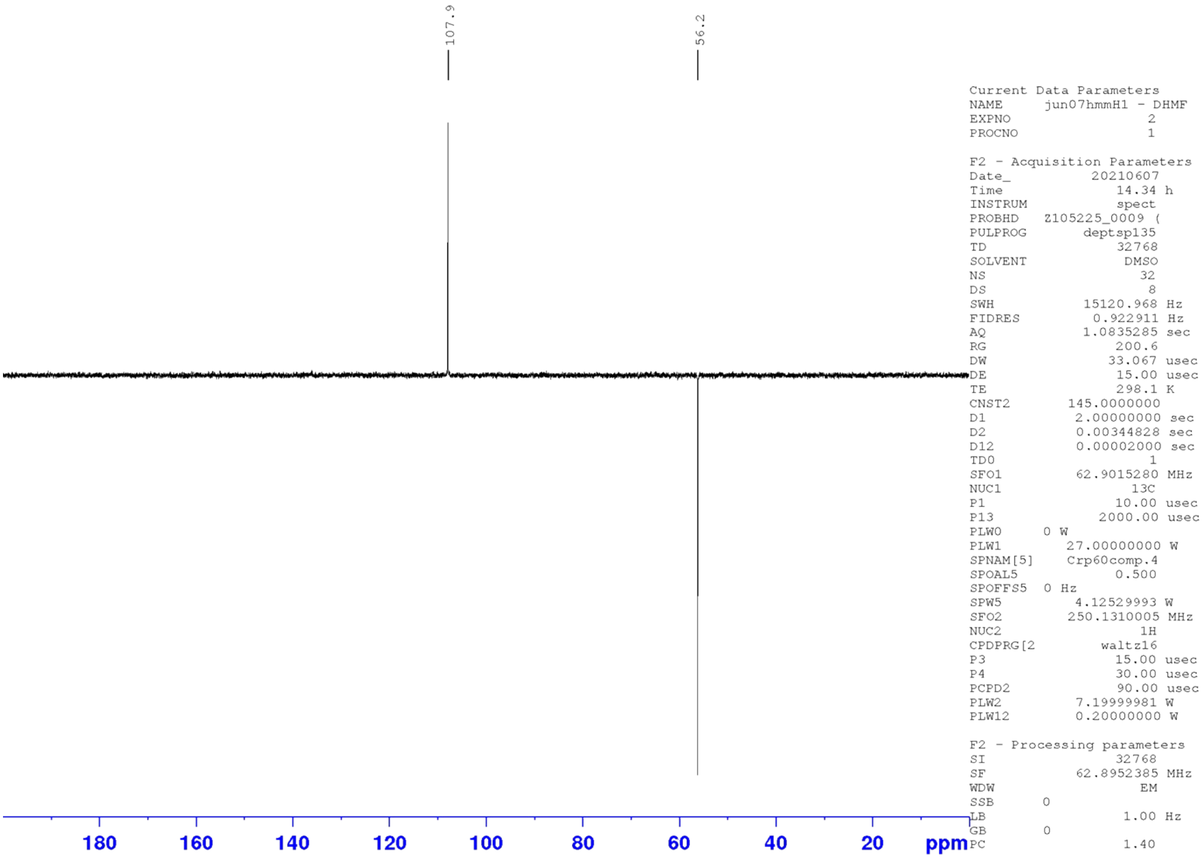

Figure S18. ^{13}C NMR spectrum (DMSO-d6, 63 MHz) of DHMF (**10**).



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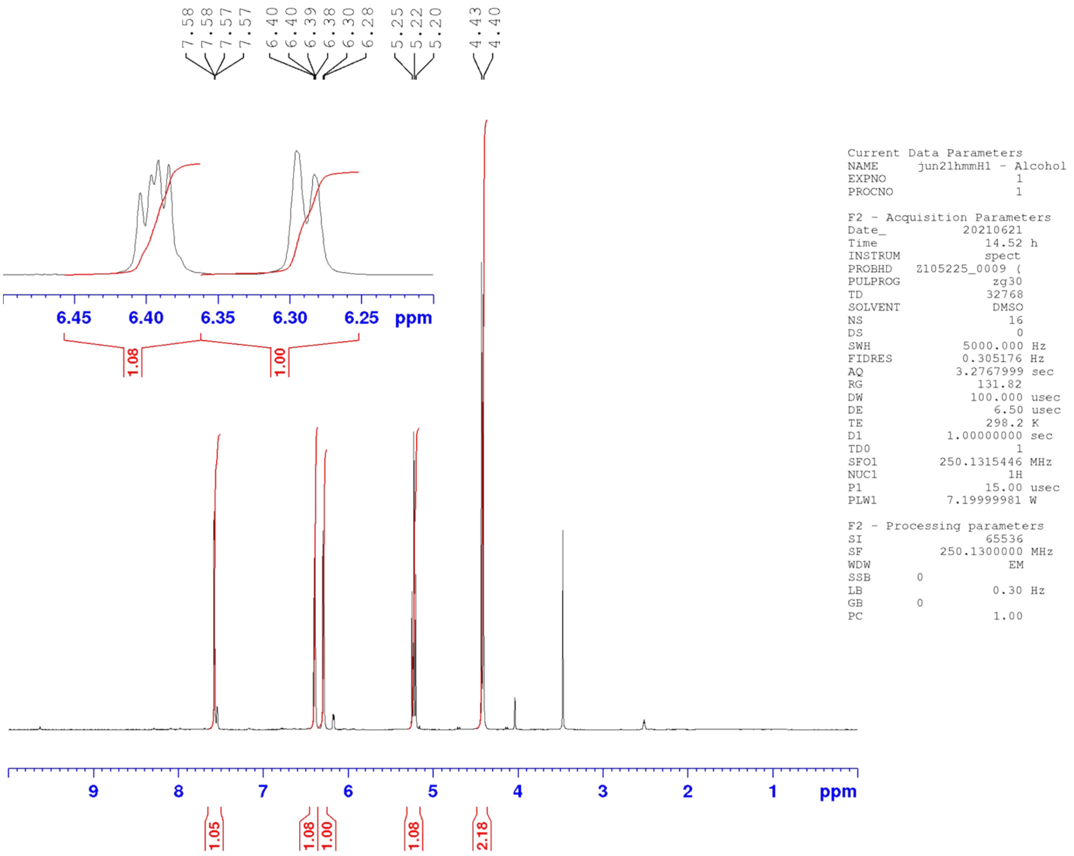
Current Data Parameters
NAME       jun07hmmH1 - DHMF
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_            20210607
Time                14.34 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG        deptsp135
TD                 32768
SOLVENT             DMSO
NS                    32
DS                     8
SWH          15120.968 Hz
FIDRES        0.922911 Hz
AQ           1.0835285 sec
RG                200.6
DW               33.067 usec
DE                15.00 usec
TE                298.1 K
CNST2        145.0000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                    1
SFO1         62.9015280 MHz
NUC1                 13C
P1                10.00 usec
P13             2000.00 usec
PLW0       0 W
PLW1        27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5    0 Hz
SPW5         4.12529993 W
SFO2        250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                15.00 usec
P4                30.00 usec
PCPD2             90.00 usec
PLW2         7.19999981 W
PLW12        0.20000000 W

F2 - Processing parameters
SI                 32768
SF           62.8952385 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

Figure S19. DEPT135 NMR spectrum (DMSO-d6, 63 MHz) of DHMF (**10**).

Furfuryl Alcohol (9)



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Current Data Parameters
NAME      jun21hmmH1 - Alcohol
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210621
Time                 14.52 h
INSTRUM              spect
PROBHD   Z105225_0009 (
PULPROG               zg30
TD                   32768
SOLVENT               DMSO
NS                      16
DS                       0
SWH               5000.000 Hz
FIDRES            0.305176 Hz
AQ               3.2767999 sec
RG                  131.82
DW                 100.000 usec
DE                    6.50 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                      1
SFO1           250.1315446 MHz
NUC1                    1H
P1                   15.00 usec
PLW1            7.19999981 W

F2 - Processing parameters
SI                   65536
SF             250.1300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```
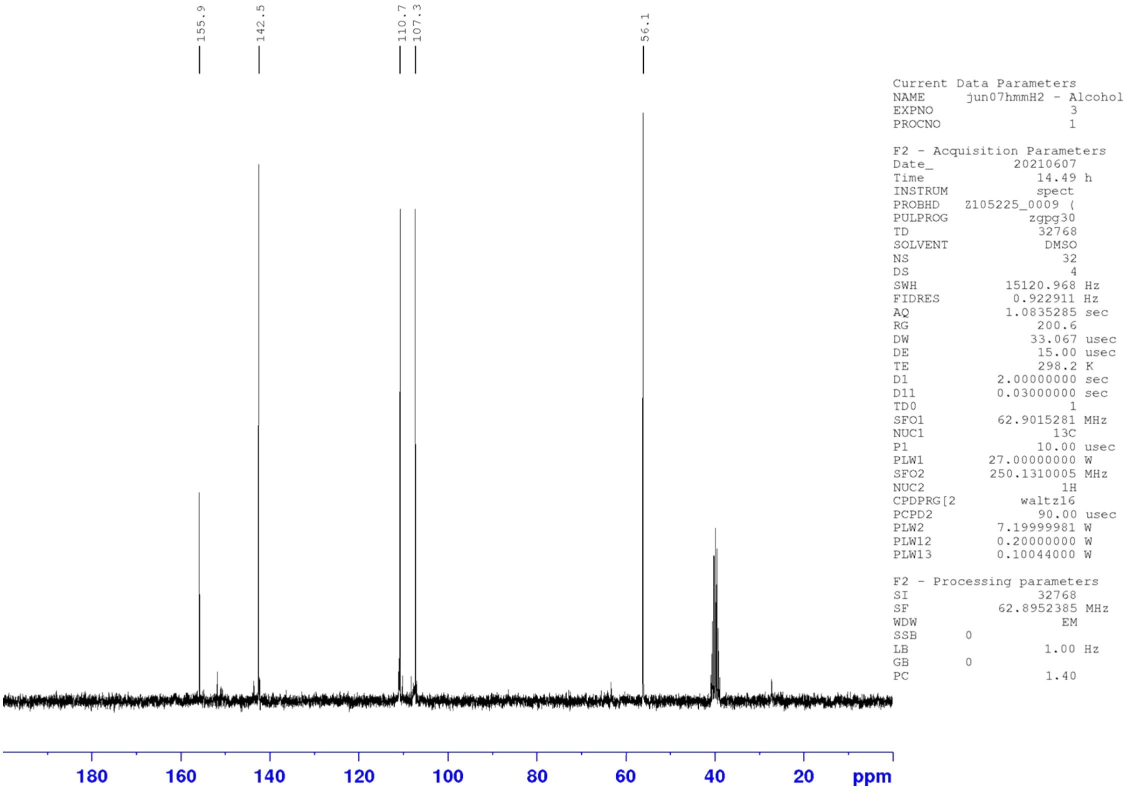
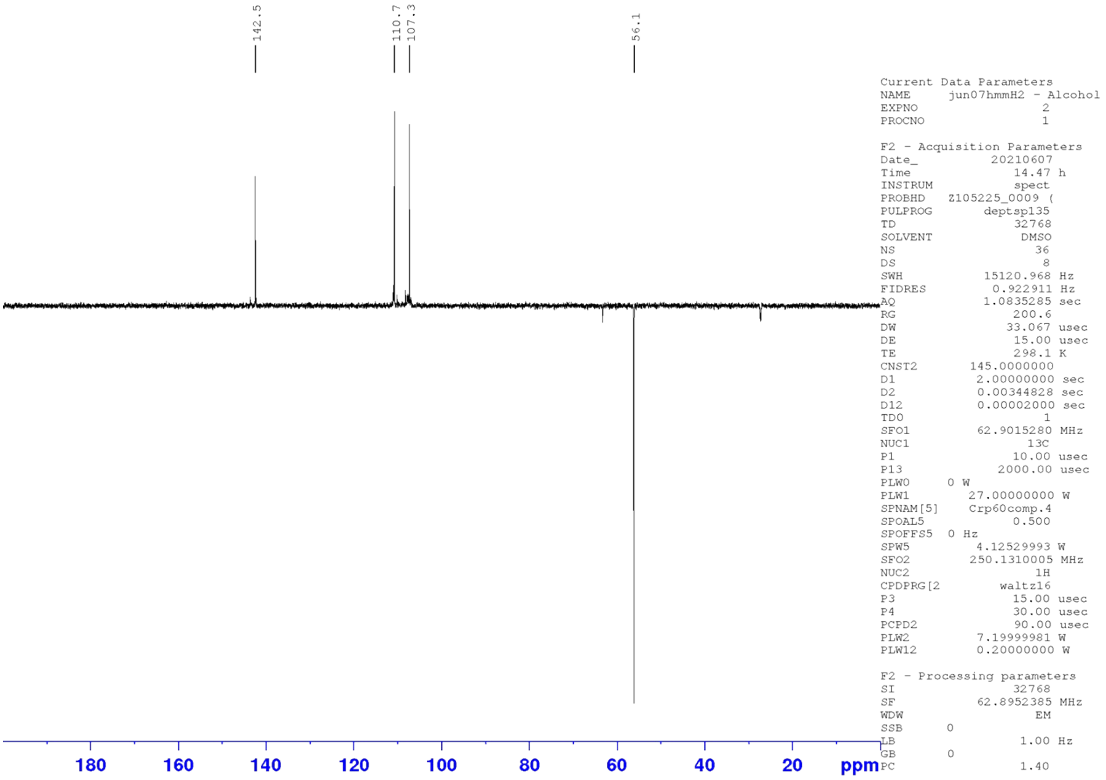

Figure S20. ^{1}H NMR spectrum (DMSO-d6, 250 MHz) of Furfuryl Alcohol (**9**).



```
Current Data Parameters
NAME      jun07hmmH2 - Alcohol
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210607
Time                 14.49 h
INSTRUM              spect
PROBHD   Z105225_0009 (
PULPROG             zgpg30
TD                   32768
SOLVENT               DMSO
NS                      32
DS                       4
SWH              15120.968 Hz
FIDRES            0.922911 Hz
AQ               1.0835285 sec
RG                   200.6
DW                  33.067 usec
DE                   15.00 usec
TE                   298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1            62.9015281 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           27.00000000 W
SFO2           250.1310005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2            7.19999981 W
PLW12           0.20000000 W
PLW13           0.10044000 W

F2 - Processing parameters
SI                   32768
SF              62.8952385 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

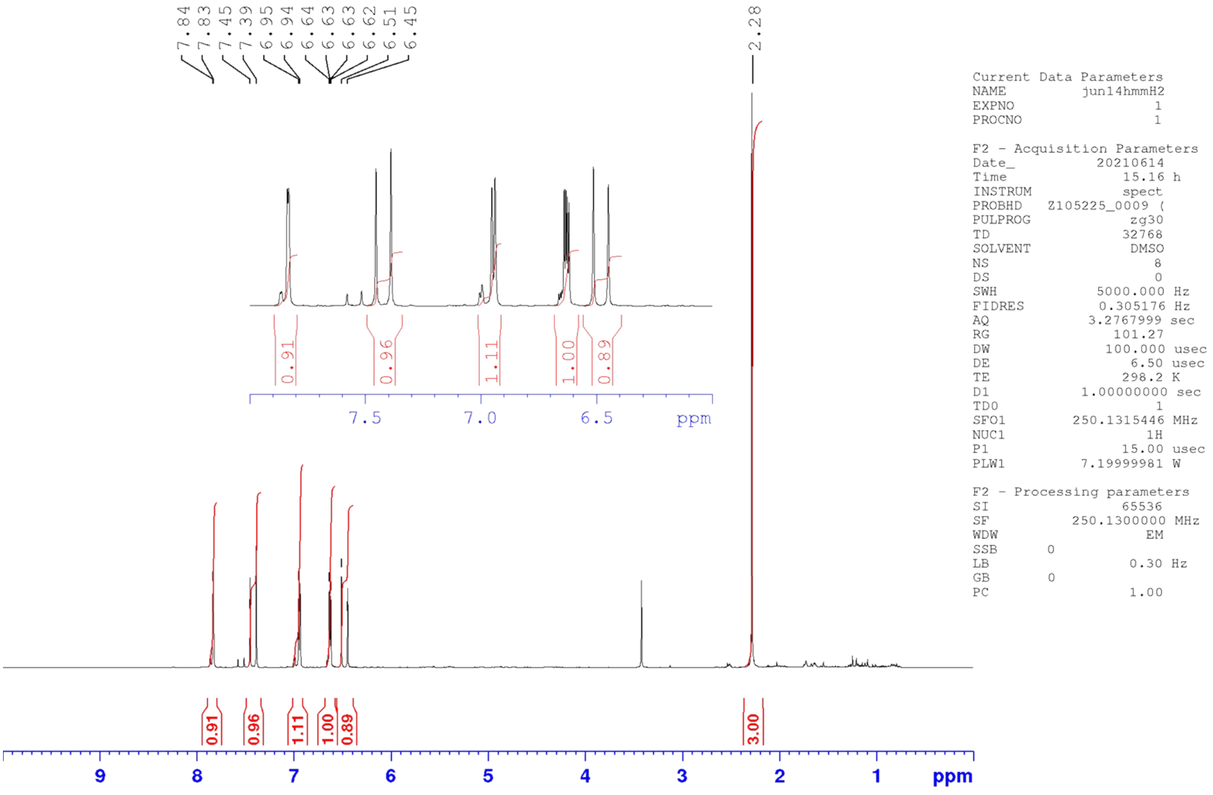
Figure S21. ^{13}C NMR spectrum (DMSO-d6, 63 MHz) of Furfuryl Alcohol (**9**).



```
Current Data Parameters
NAME      jun07hmmH2 - Alcohol
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_            20210607
Time                14.47 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG         deptsp135
TD                  32768
SOLVENT              DMSO
NS                     36
DS                      8
SWH             15120.968 Hz
FIDRES           0.922911 Hz
AQ              1.0835285 sec
RG                  200.6
DW                 33.067 usec
DE                  15.00 usec
TE                  298.1 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                     1
SFO1           62.9015280 MHz
NUC1                  13C
P1                  10.00 usec
P13               2000.00 usec
PLW0      0 W
PLW1          27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5              0.500
SPOFFS5   0 Hz
SPW5           4.12529993 W
SFO2          250.1310005 MHz
NUC2                   1H
CPDPRG[2          waltz16
P3                  15.00 usec
P4                  30.00 usec
PCPD2               90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W

F2 - Processing parameters
SI                  32768
SF             62.8952385 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

Figure S22. DEPT135 NMR spectrum (DMSO-d6, 63 MHz) of Furfuryl Alcohol (**9**).

4-(furan-2-yl)but-3-en-2-one (18)



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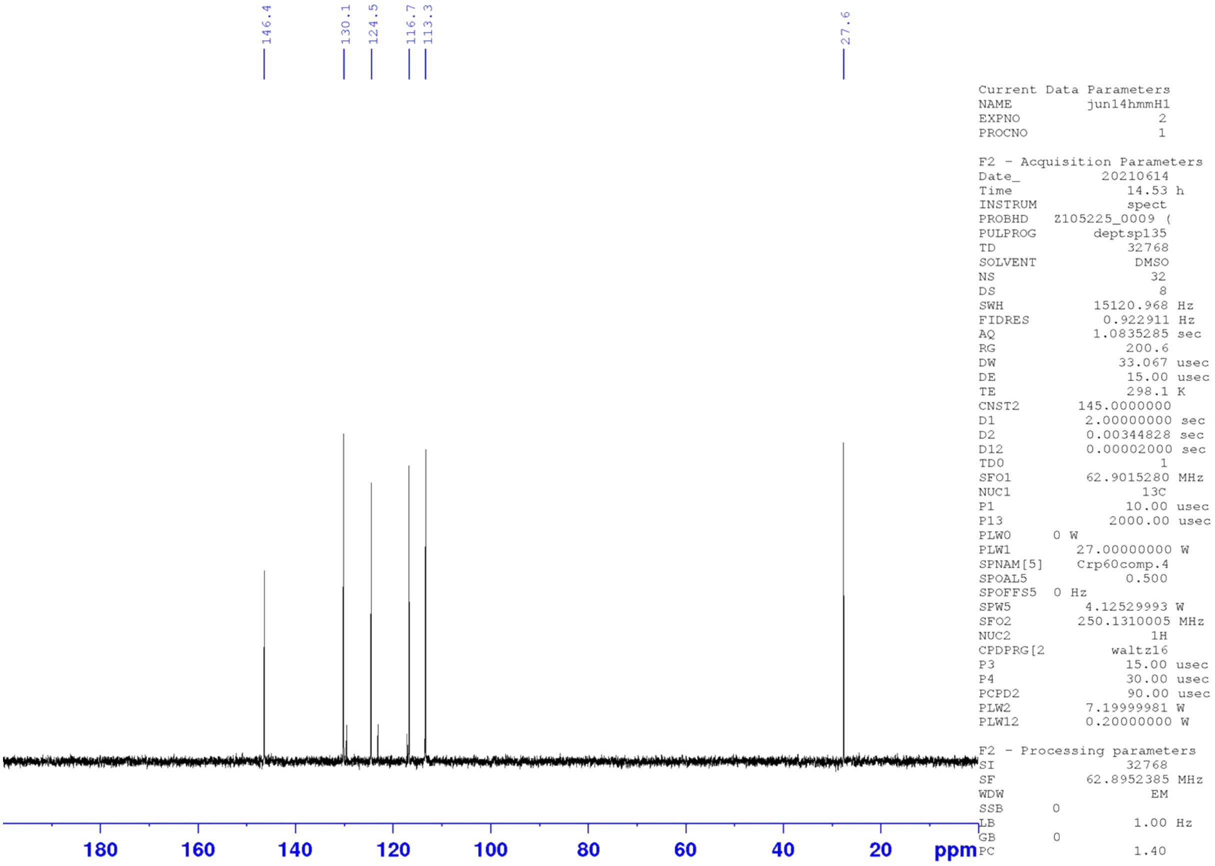
Current Data Parameters
NAME             jun14hmmH2
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20210614
Time                  15.16 h
INSTRUM               spect
PROBHD      Z105225_0009 (
PULPROG                zg30
TD                    32768
SOLVENT                DMSO
NS                        8
DS                        0
SWH                5000.000 Hz
FIDRES             0.305176 Hz
AQ                3.2767999 sec
RG                   101.27
DW                  100.000 usec
DE                     6.50 usec
TE                    298.2 K
D1               1.00000000 sec
TD0                       1
SFO1            250.1315446 MHz
NUC1                     1H
P1                    15.00 usec
PLW1             7.19999981 W

F2 - Processing parameters
SI                    65536
SF              250.1300000 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

Figure S23. ^{1}H NMR spectrum (DMSO-d6, 250 MHz) of compound **18**.

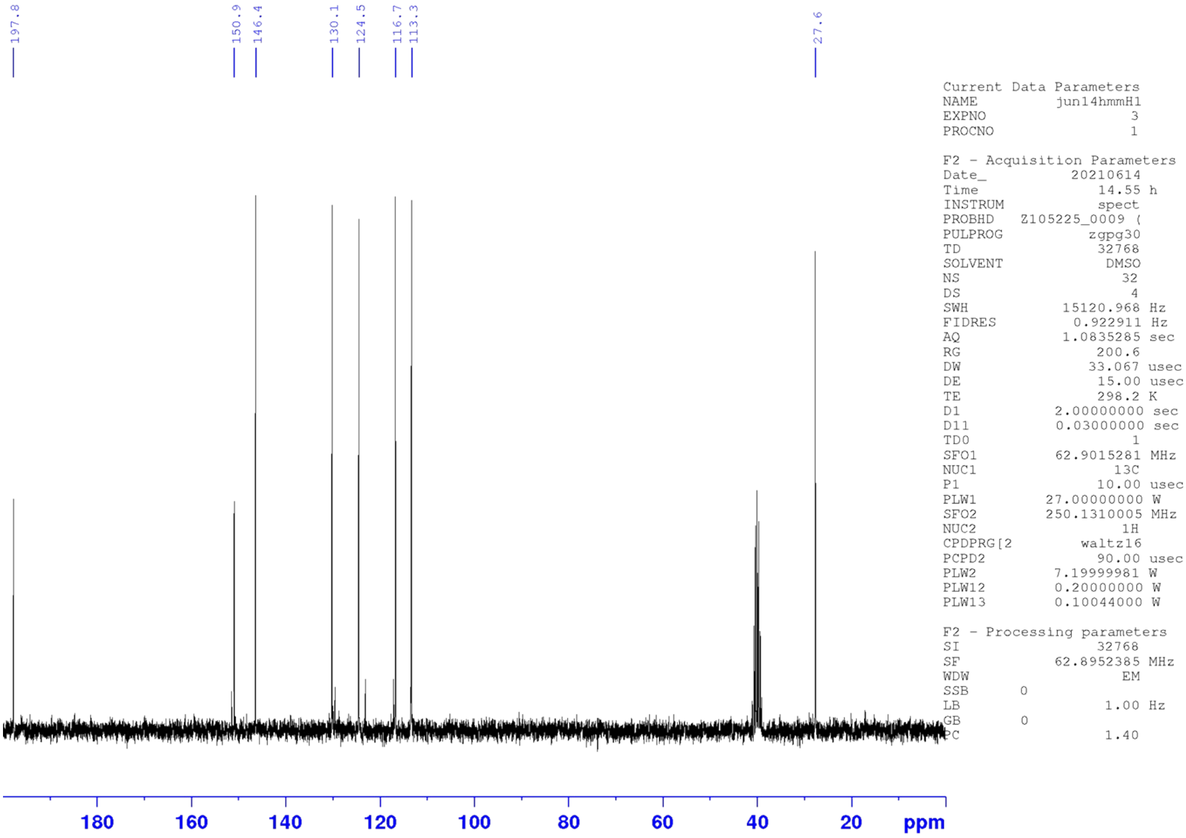


```
Current Data Parameters
NAME          jun14hmmH1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210614
Time               14.53 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG        deptsp135
TD                 32768
SOLVENT             DMSO
NS                    32
DS                     8
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                 15.00 usec
TE                 298.1 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1
SFO1          62.9015280 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
PLW0      0 W
PLW1         27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5          4.12529993 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2         waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Figure S24. DEPT135 NMR spectrum (DMSO-d6, 63 MHz) of compound **18**.



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Current Data Parameters
NAME          jun14hmmH1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210614
Time               14.55 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG          zgpg30
TD                 32768
SOLVENT             DMSO
NS                    32
DS                     4
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                 15.00 usec
TE                 298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1          62.9015281 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         27.00000000 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W
PLW13         0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```
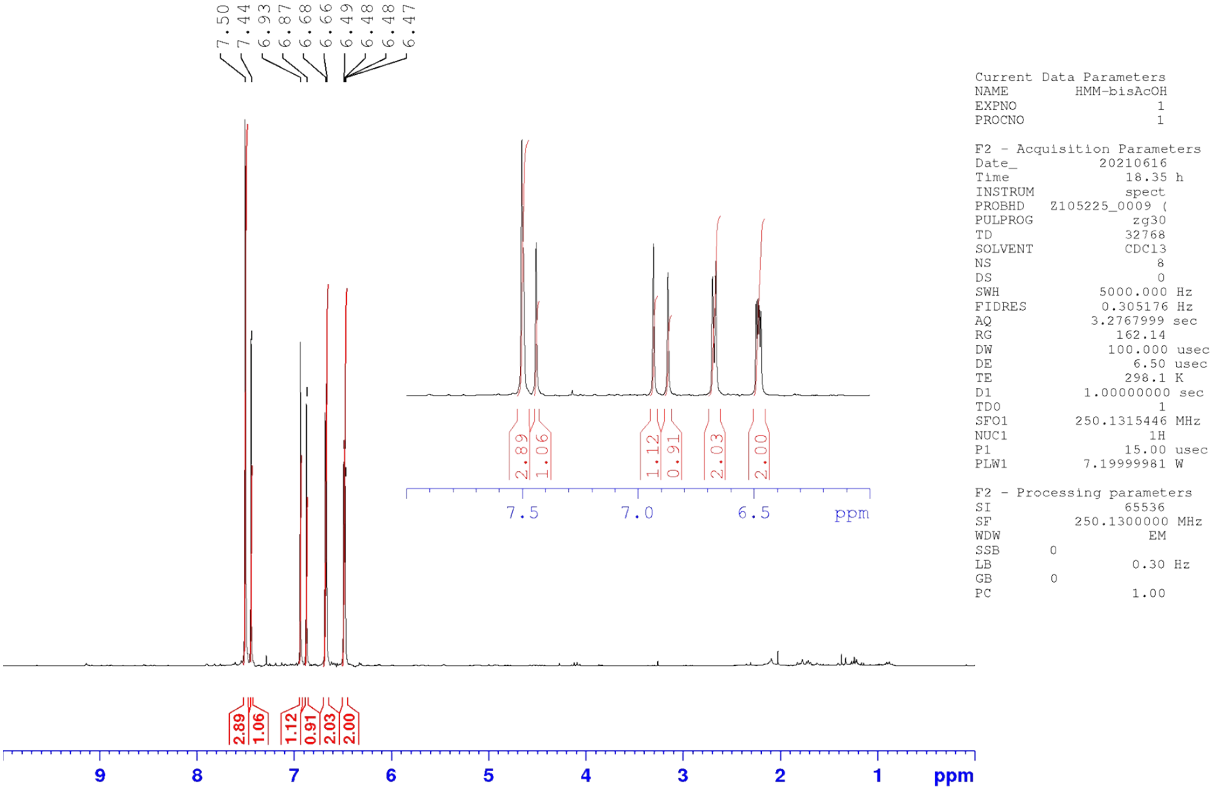

Figure S25. ^{13}C NMR spectrum (DMSO-d6, 63 MHz) of compound **18**.

1,5-di(furan-2-yl)penta-1,4-dien-3-one (19)



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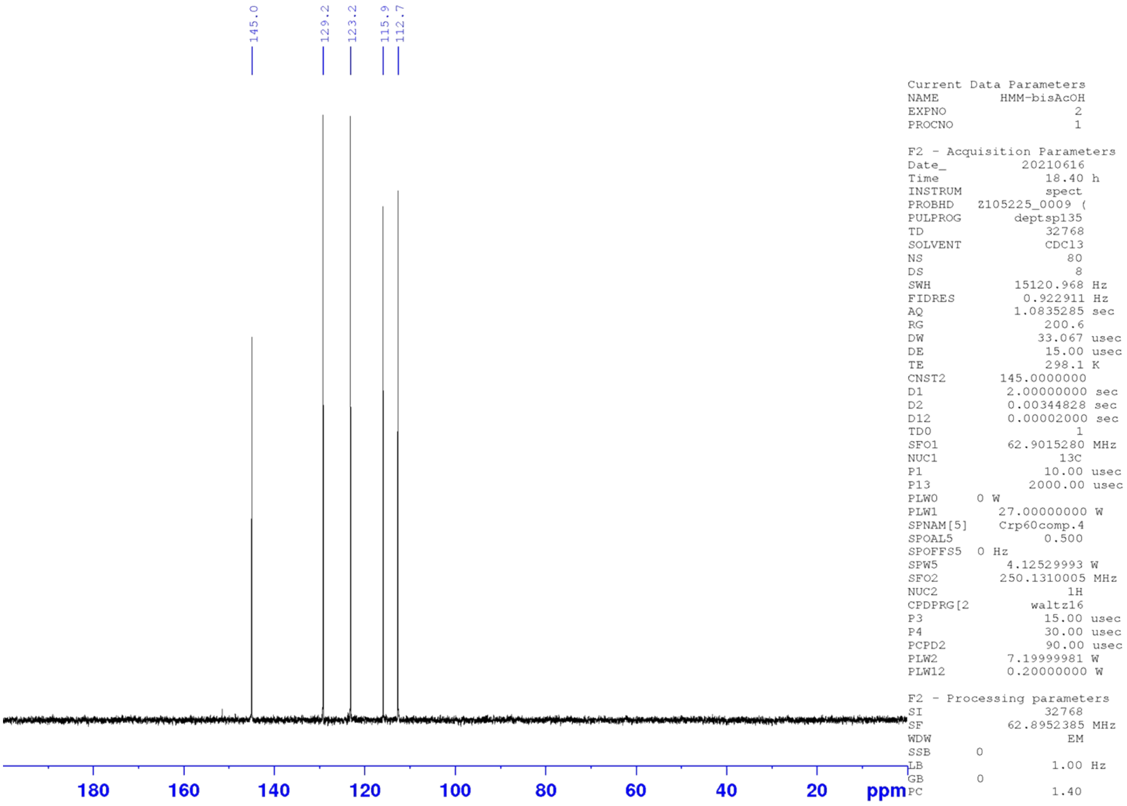
Current Data Parameters
NAME          HMM-bisAcOH
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210616
Time                18.35 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              5000.000 Hz
FIDRES           0.305176 Hz
AQ              3.2767999 sec
RG                 162.14
DW                100.000 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1
SFO1          250.1315446 MHz
NUC1                   1H
P1                  15.00 usec
PLW1           7.19999981 W

F2 - Processing parameters
SI                  65536
SF            250.1300000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

Figure S26. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of compound **19**.



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Current Data Parameters
NAME          HMM-bisAcOH
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210616
Time                18.40 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG         deptsp135
TD                  32768
SOLVENT             CDCl3
NS                     80
DS                      8
SWH             15120.968 Hz
FIDRES           0.922911 Hz
AQ              1.0835285 sec
RG                  200.6
DW                 33.067 usec
DE                  15.00 usec
TE                  298.1 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                     1
SFO1           62.9015280 MHz
NUC1                  13C
P1                  10.00 usec
P13               2000.00 usec
PLW0      0 W
PLW1          27.00000000 W
SPNAM[5]      Crp60comp.4
SPOAL5              0.500
SPOFFS5   0 Hz
SPW5           4.12529993 W
SFO2          250.1310005 MHz
NUC2                   1H
CPDPRG[2          waltz16
P3                  15.00 usec
P4                  30.00 usec
PCPD2               90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W

F2 - Processing parameters
SI                  32768
SF             62.8952385 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```
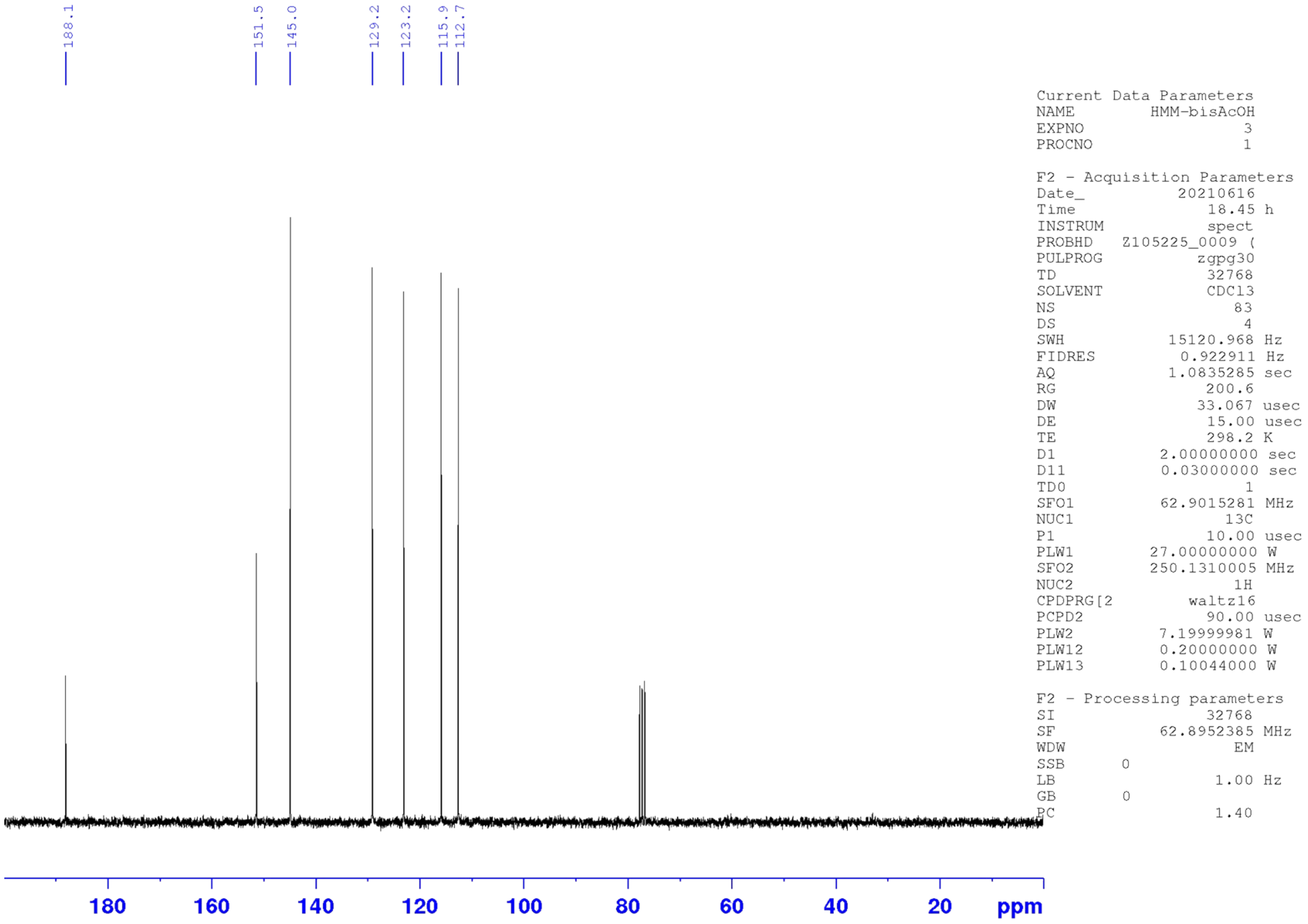

Figure S27. DEPT135 NMR spectrum ($CDCl_3$, 63 MHz) of compound **19**.



```
Current Data Parameters
NAME         HMM-bisAcOH
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210616
Time               18.45 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                    83
DS                     4
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                 15.00 usec
TE                 298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1          62.9015281 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         27.00000000 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W
PLW13         0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

Figure S28. ^{13}C NMR spectrum (CDCl$_3$, 63 MHz) of compound **19**.

References

1 R. F. A. Gomes, Y. N. Mitrev, S. P. Simeonov and C. A. M. Afonso, *ChemSusChem*, 2018, **11**, 1612–1616.

2 R. Galaverna, M. C. Breitkreitz and J. C. Pastre, *ACS Sustainable Chem. Eng.*, 2018, **6**, 4220–4230.