

Supplementary materials

Conversion of D-fructose to 5-acetoxymethyl-2-furfural using immobilized lipase and cation exchange resin

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1. Characterization methods:

1.1 Nuclear Magnetic Resonance (NMR):

NMR analysis was performed on a Bruker Spectrospin 300 (Bruker Corporation, Germany). Figure S1 shows ¹H NMR of DAF (300 MHz, CDCl₃): 4.44-4.33 (m, 1H on C2), 4.30-4.23 (m, 2H of C5-CH₂), 4.21-4.13 (m, 2H on C3 and C4), 4.05-4.00 (m, 2H of C2-CH₂), 2.17-2.12 (m, 6H of 2 -COOCH₃; major anomer: 2.14 and 2.13; minor anomer: 2.17 and 2.12). ¹³C NMR of DAF (300 MHz, DMSO-d₆): 170.83-170.47 (d, 2C in -COO- groups), 100.86 (s, C5 in the ring), 78.85 (s, C2 in the ring), 76.49 (s, C4 in the ring), 75.57 (s, C3 in the ring), 66.16 (s, C6 in -CH₂ group), 64.62 (s, C1 in -CH₂ group), 21.04 (m, 2C in -CH₃ groups) (Figure S2).

AMF was also analyzed with NMR and Figure S4 shows ¹H NMR of AMF (300 MHz, THF-d₈): 9.62 (s, 1H on -CHO), 7.31-7.30 (d, 1H of C4 on furan ring), 6.68-6.67 (d, 1H of C3 on furan ring), 5.13 (s, 2H of -CH₂), 2.06 (s, 3H of -CH₃). ¹³C NMR of AMF (300 MHz, THF-d₈): 176.91 (s, C in -CHO group), 169.23 (s, C in -COO- group), 155.57 (s, C2 in the furan ring), 155.37 (s, C5 in the furan ring), 120.62 (s, C4 in the furan ring), 112.06 (s, C3 in the furan ring), 57.27 (s, C in -CH₂ group), 19.32 (s, C in -CH₃ group) (Figure S5).

1.2 High performance liquid chromatography (HPLC):

HPLC analysis of the dehydration products was performed on an Agilent 1200 series equipped with a Bio-Rad Animex HPX-87P column and an RID detector (at 254 nm). H₂O was used as mobile phase and the flow rate was adjusted at 0.6 mL/min. The retention times for AMF and HMF are 54.2 min. and 29.3 min. respectively (shown in figure S7).

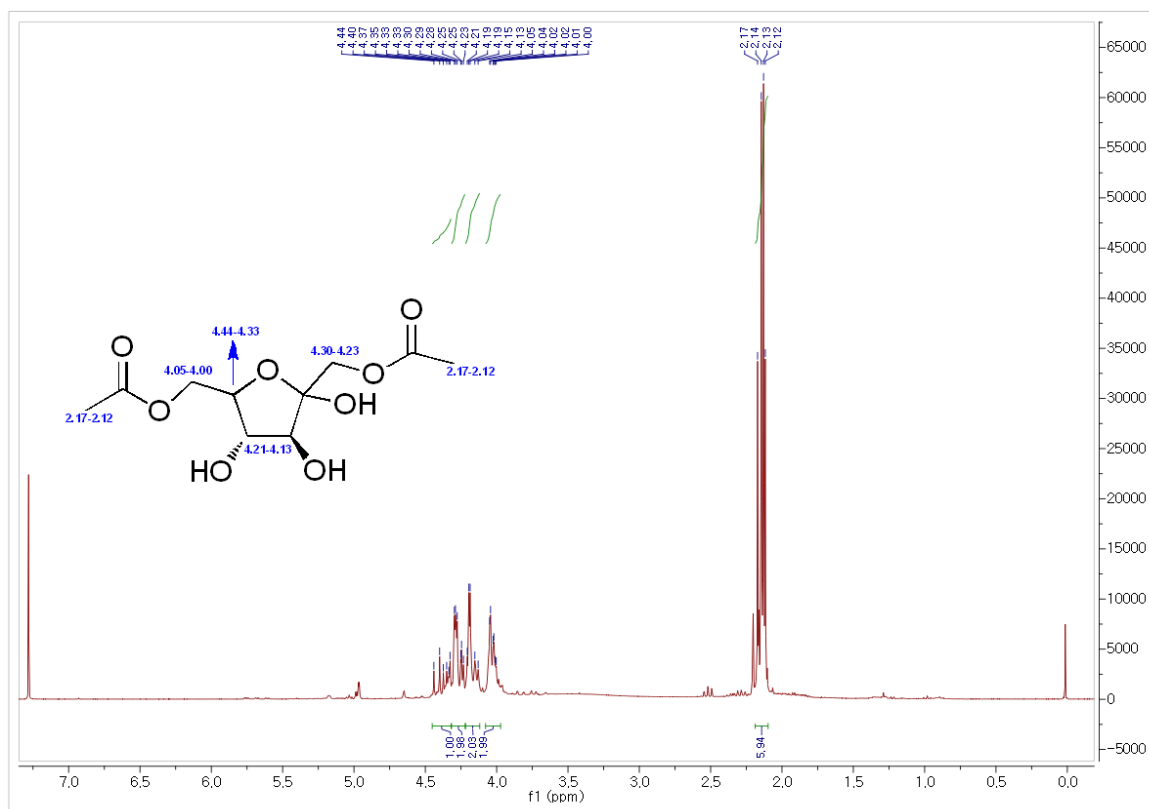
1.3 Liquid chromatography combined with mass spectroscopy (LC-MS):

LC-MS analysis of the DAF was performed on an Agilent 1260 Infinity II series equipped with an InfinityLab LC/MSD mass spectrometer detector. HCOOH 0.001 M in H₂O was used as mobile phase and the flow rate was adjusted at 0.5 mL/min. DAF was ionized in API-ES positive mode and the mass spectrum was shown in Figure S3.

1.4 Gas chromatography combined with mass spectroscopy (GC-MS):

41 GC-MS analysis of the dehydration products was performed on a Shimadzu GC-2010 Plus
42 system equipped with QP2010 Ultra mass spectrometer detector. AMF and HMF formation (Figure
43 S8) is verified by comparing spectrum with GC-MS NIST 2011 database.

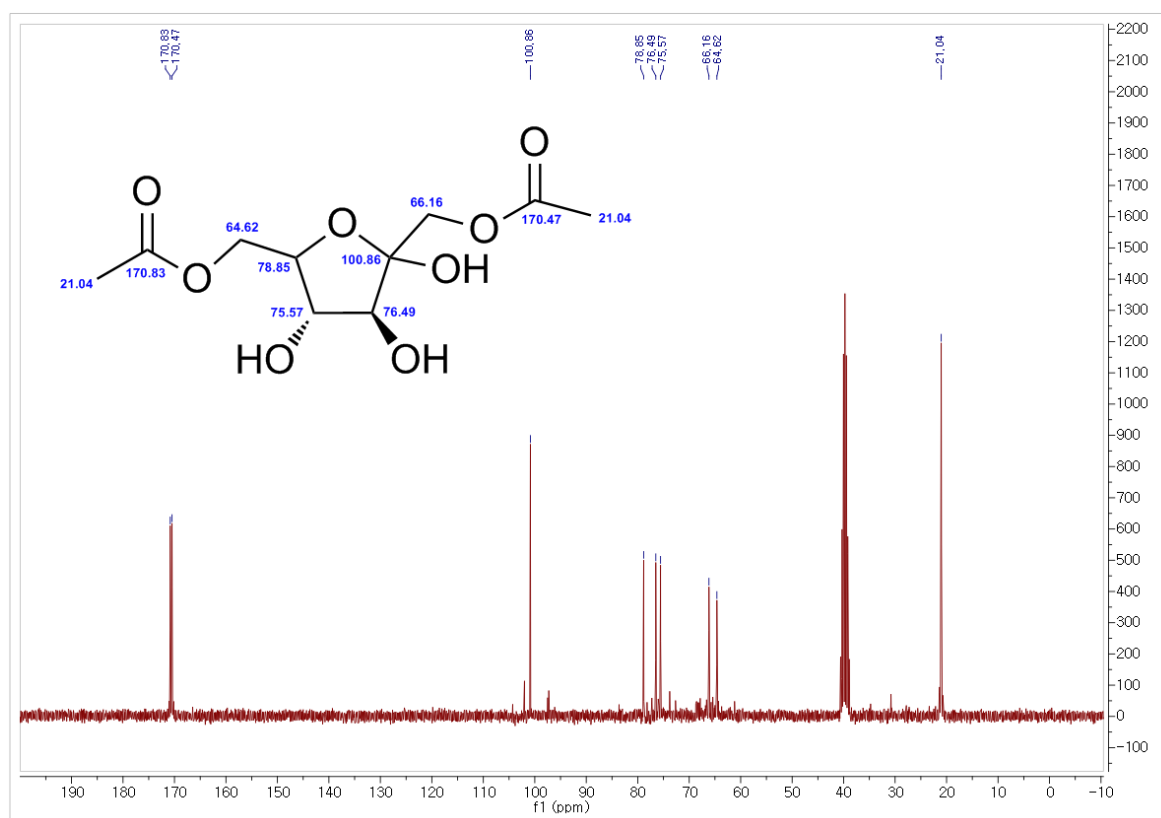
44 2. Analysis results:



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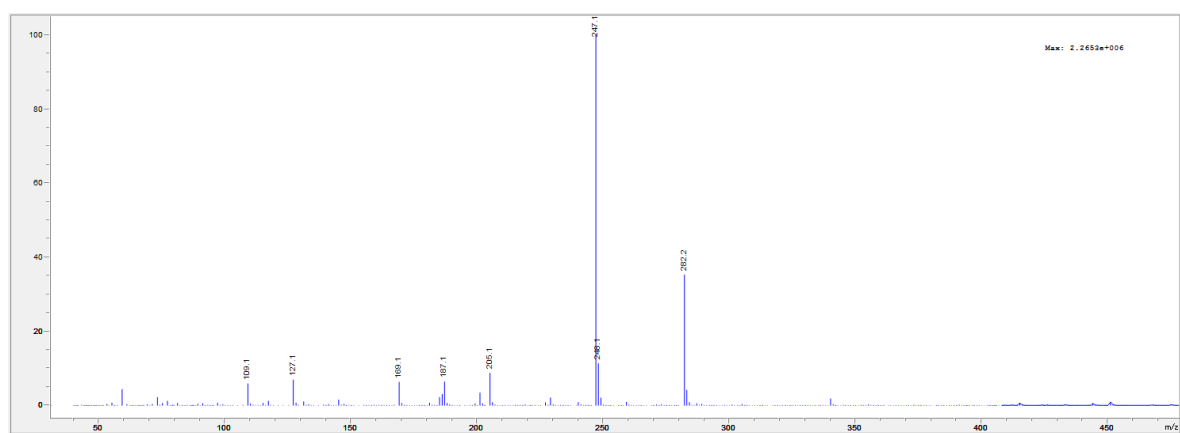
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Figure S1. ¹H NMR analysis of DAF



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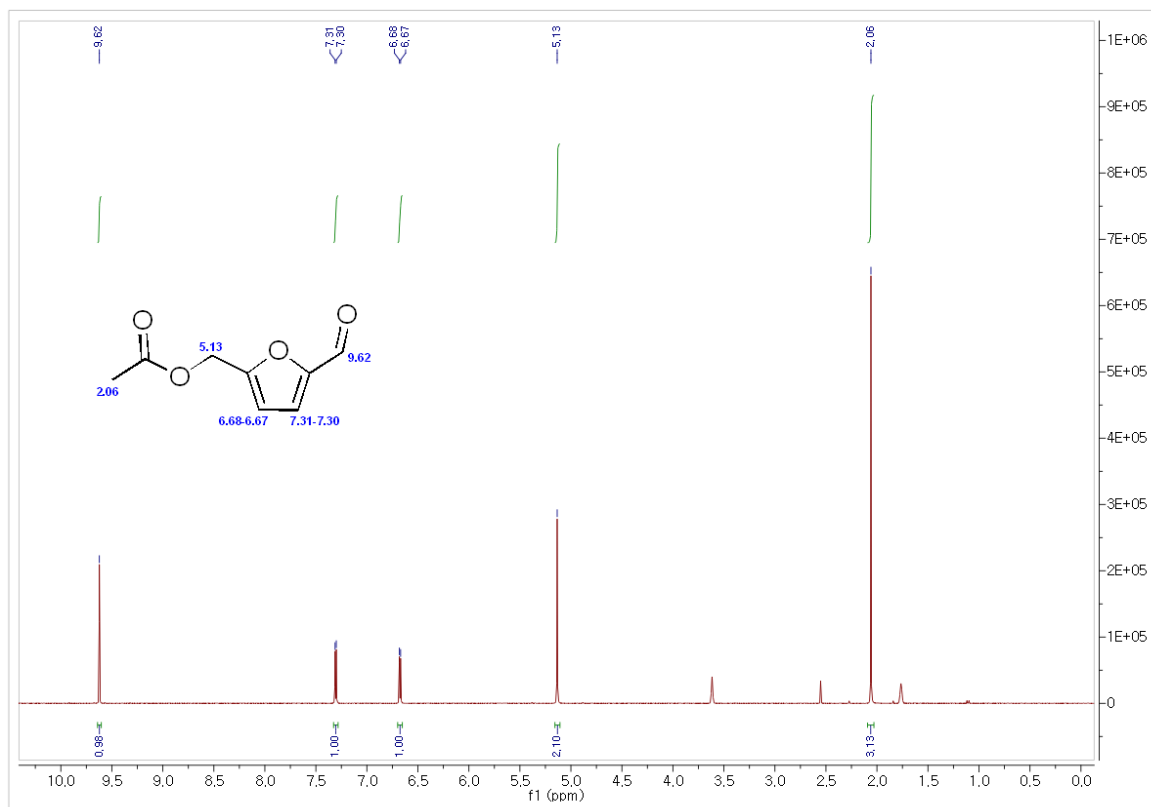
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Figure S2. ¹³C NMR analysis of DAF

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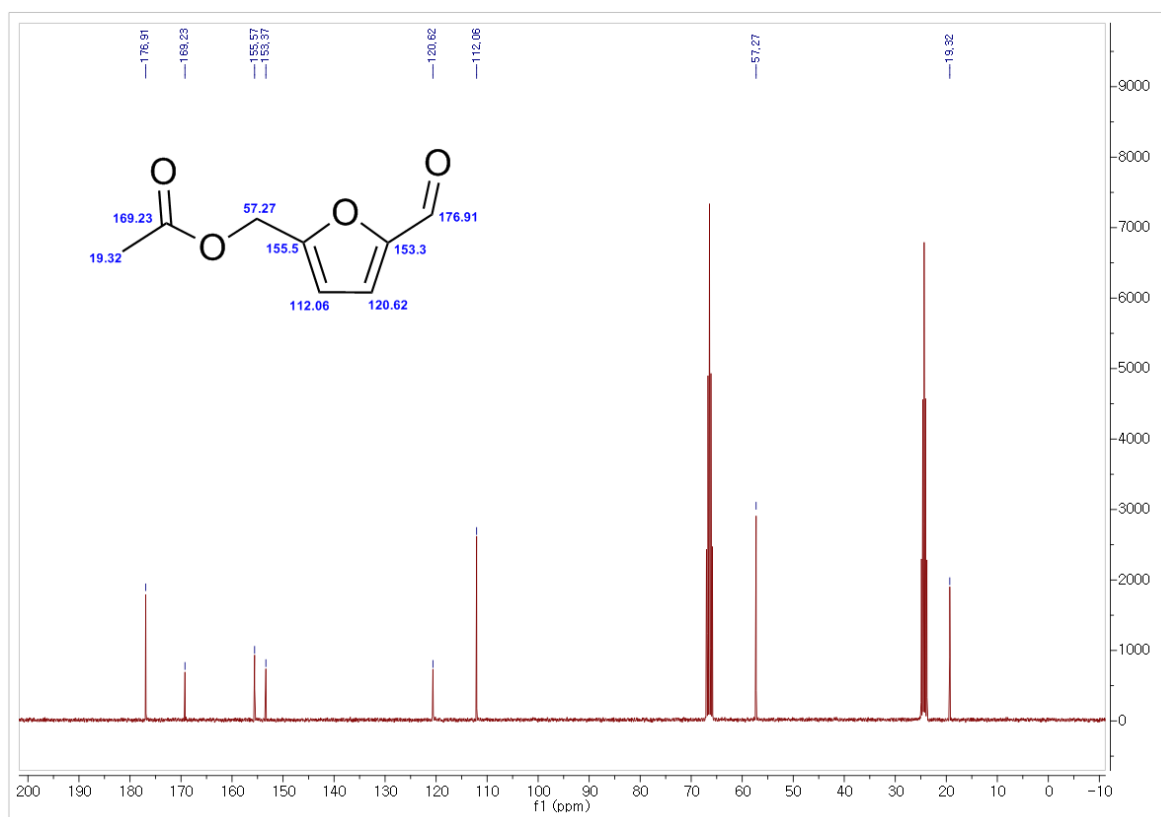
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Figure S3. Mass spectrum of DAF



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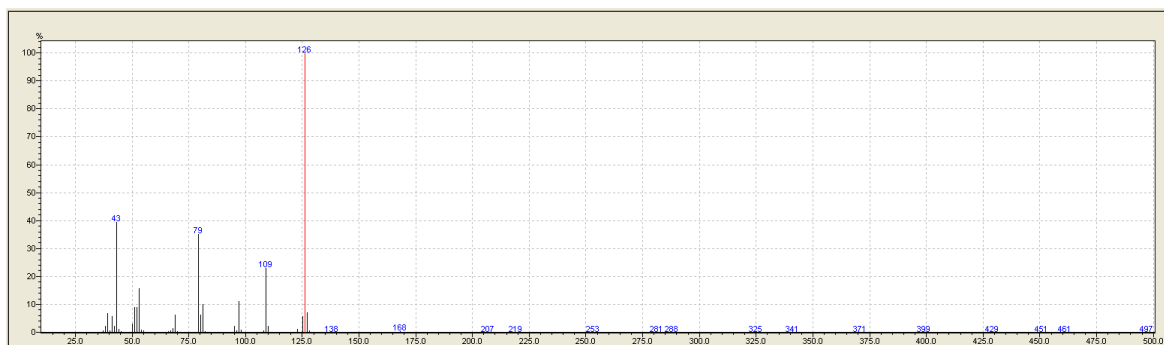
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Figure S4. ¹H NMR analysis of AMF

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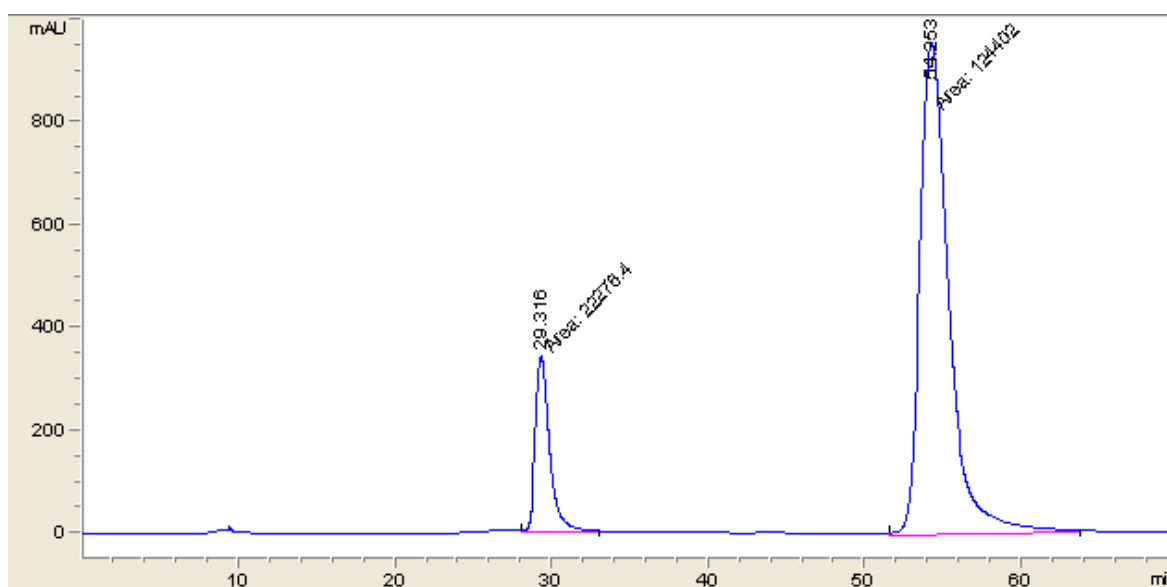
Figure S5. ¹³C NMR analysis of AMF



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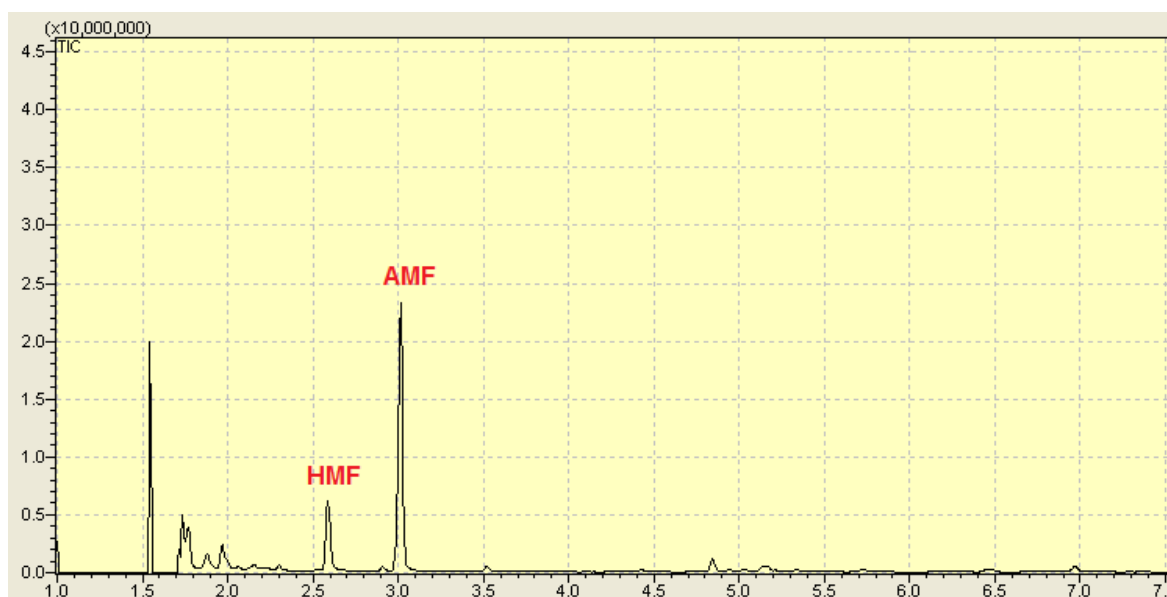
Figure S6. Mass spectrum of AMF



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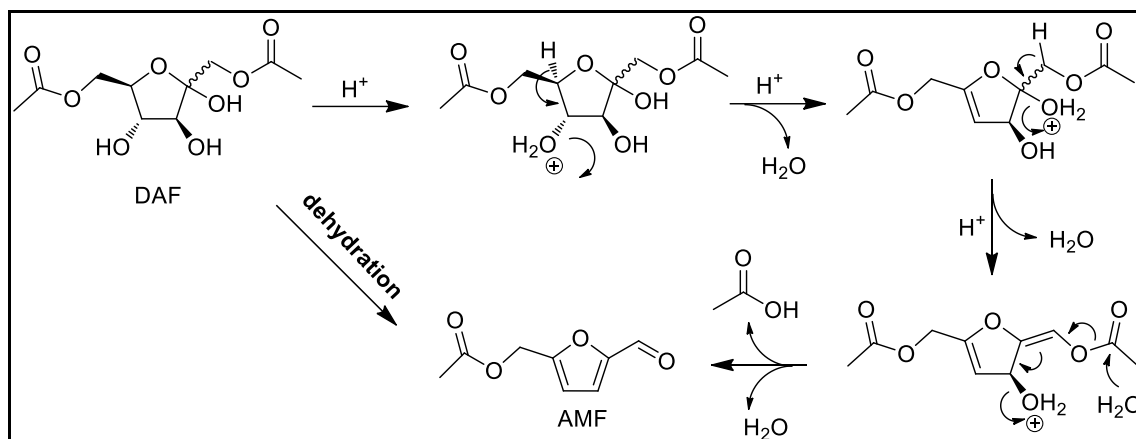
Figure S7. HPLC analysis of AMF and HMF



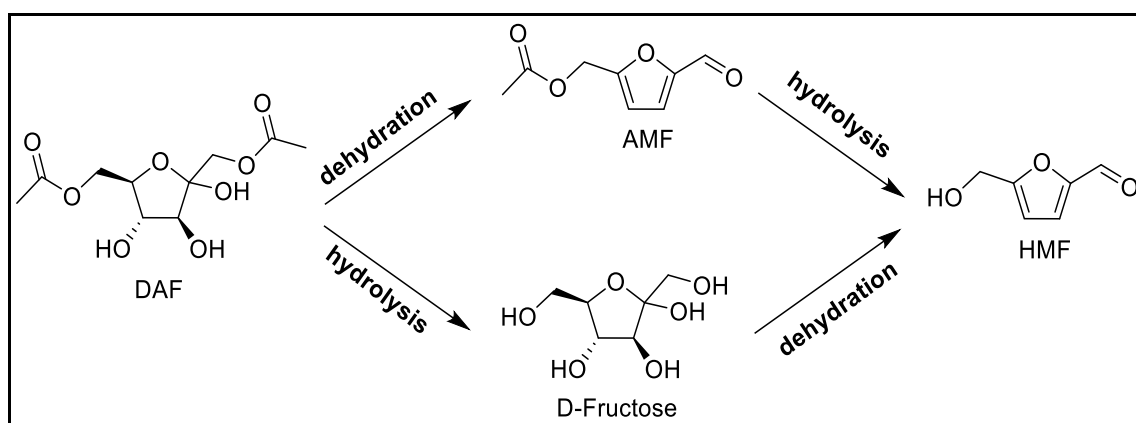
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Figure S8. GC-MS analysis of AMF and HMF



Scheme S1. Plausible mechanism for the dehydration of DAF to AMF under acidic conditions



Scheme S2. Suggested pathway for the formation of AMF and HMF in the dehydration of DAF