

## Supporting information

For

# One-step synthesis of 2,5-diformylfuran from monosaccharides by lanthanum(III) triflate, sulfur, and DMSO

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## Section S1. Chemicals, analytical techniques and procedure

Sulfur, lanthanum(III) trifluoromethanesulfonate (99%), bismuth trifluoromethanesulfonate (99%), holmium trifluoromethanesulfonate (99%), HMF (99%), levulinic acid (98 %), furfural (99.5 %), glucose (99.0 %), and fructose (99%) were from Sigma-Aldrich. Methanol, acetonitrile, ethyl acetate from J.T.Baker (HPLC grade). Formic acid (>98%), thin-layer chromatography (TLC), and sulfuric acid (>95%) from Merck. DFF (98%) was supplied from the J&K chemical (China). The water was purified with a water purification system (Smart2pure – Thermo Scientific). Diethyl ether (purity  $\geq$  99.5%) and *n*-hexane were obtained from Xilong Chemical (China).

HPLC-PDA data were carried out on an Agilent Technologies 1260 Infinity HPLC instrument with an InertSustain C<sub>18</sub> column (5  $\mu$ m, 4.6 x 150 mm) and photodiode array detector. LC-MS/MS data were analyzed on an AB SCIEX QTRAP® 5500. HRMS (ESI) data were collected using Sciex X500R QTOF. The NMR spectra were performed by a Bruker Advance 500 instruments using CDCl<sub>3</sub> as a solvent.

**General procedure for the direct synthesis of DFF.** One-flask transformation of fructose to DFF was carried out as follow: To a 10 mL round-bottom flask containing fructose (180 mg, 1 mmol), sulfur (192 mg, 6 mmol), and La(OTf)<sub>3</sub> (15 mg, 2.5 mol%) was added DMSO (3 mL). The mixture was heated at 150 °C with vigorous stirring in a thermostatic oil bath. Samples were taken from the reaction mixture at specified times for HPLC analysis to determine DFF yield and fructose conversion. The conversion of substrate and yield of the product was determined by the following equations.

Conversion of fructose (%) = (molar amount of fructose reacted)/(molar amount of fructose originally charged)  $\times$  100%

Conversion of glucose (%) = (molar amount of glucose reacted)/(molar amount of glucose originally charged) × 100%

Yield of HMF (%) = (molar amount of HMF produced)/(molar amount of substrate originally charged) × 100%

Yield of DFF (%) = (molar amount of DFF produced)/(molar amount of substrate originally charged) × 100%

## **Section S2. Analysis of the products**

At varying time points, the aliquots of the reaction mixture were taken, followed by dilution in ethyl acetate, and then centrifugation at 4000 rpm for 5 min. Filtration of the resulting supernatant was conducted through a 0.45 μm membrane, and the filtrate was stored in a vial.

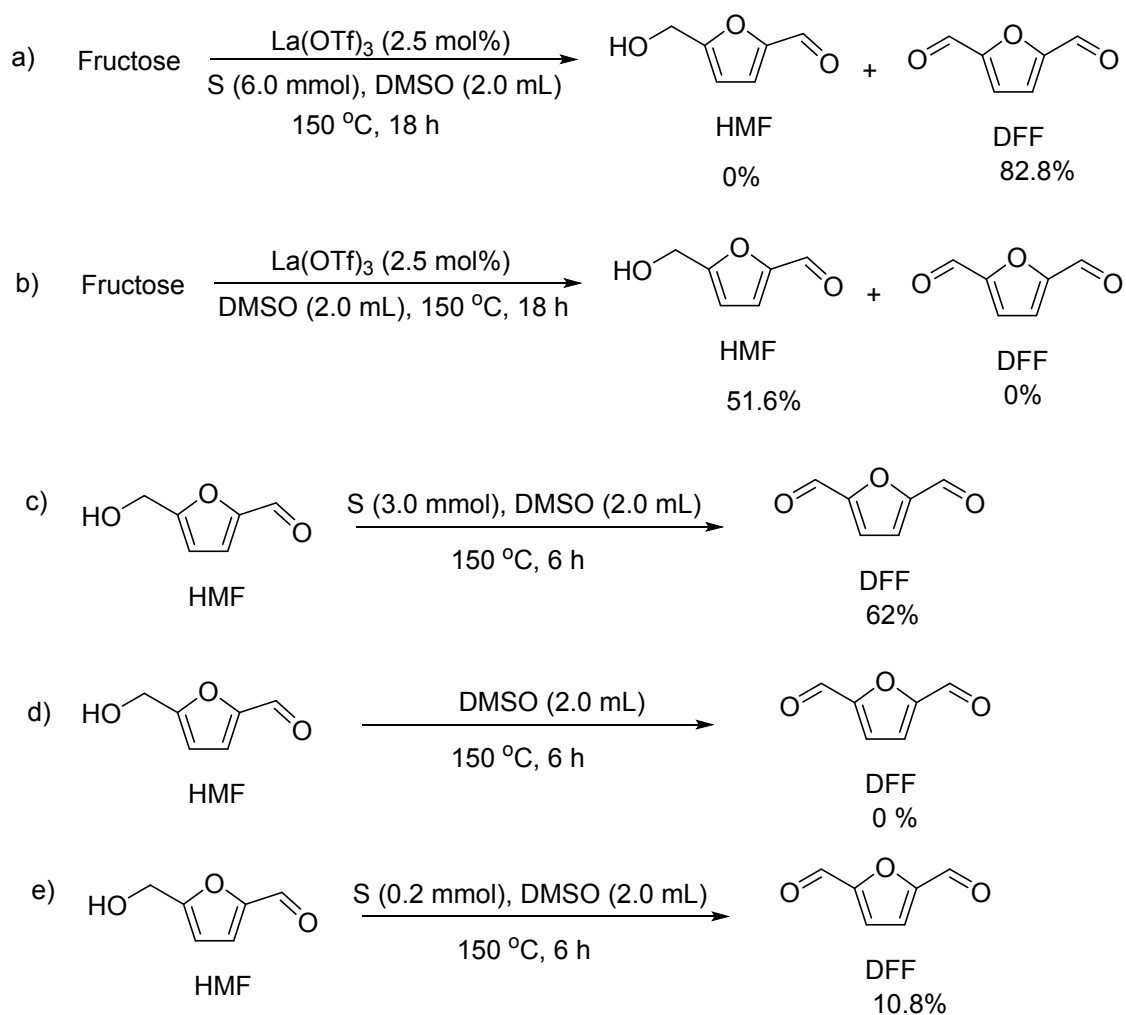
The yield of HMF and DFF was determined by using a HPLC–PAD (Agilent Technologies 1260 Infinity) with an InertSustain C<sub>18</sub> column (5 μm, 4.6 x 150 mm). The mobile phase was a mixture of methanol (A) and 2.5 mM sulfuric acid aqueous solution (B) with a flow rate at 0.5 mL min<sup>-1</sup> in a 25 min, gradient as follows: 0 – 2.50 min, 100% B; 2.50 - 2.51 min, 100% - 85% B; 2.51 – 17.00 min, 85% B; 17.00 – 17.01 min, 85% -100 % B; 17.01 – 25.00 min, 100 % B.

Fructose and glucose conversions were analyzed using a AB SCIEX QTRAP® 5500 LC-MS/MS System with electrospray ionization in negative ion mode was used 90% and an InertSustain NH<sub>2</sub> column. The mobile phase was used acetonitrile-10% H<sub>2</sub>O with a flow rate at 1.0 mL min<sup>-1</sup> and the column temperature was kept at 35 °C. The mass spectrometer detector conditions were set as follows: Ion Source Gas 1: 40 psi, Temperature: 500°C, Ion Spray Voltage: -4500 V, Curtain Gas: 35, Ion Source Gas 2: 40 psi, CAD: Medium. The fructose conversion and HMF, DFF yield were determined on the basis of the external standard curves plotted with authentic standards.

HRMS (ESI) analysis was used to confirm the correct structure of HMF and DFF. The system conditions were set as follows: Source temperature: 500°C; Curtain gas:

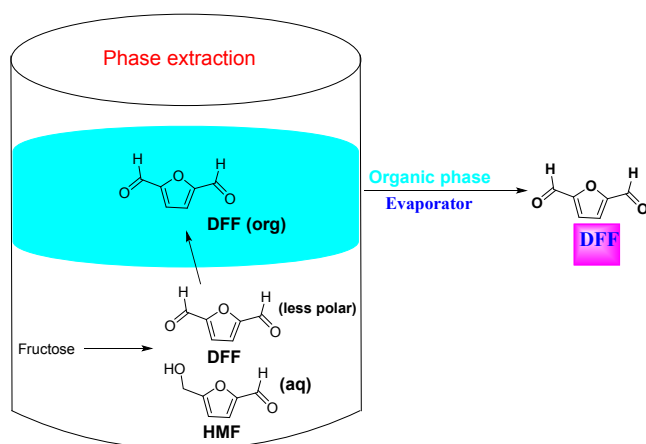
30 psi; CAD gas: 7 psi; Ion source gas 1: 40 psi; Ion source gas 2: 60 psi; Experiment: IDA (*Information Dependent Acquisition Scanning*); Spray voltage: 500 V (Positive); Declustering potential (DP): 80 V; Collision energy (CE): 10 V. The LC parameters: inject volume: 5  $\mu$ L; The mobile phase was A conc.: 40% (MeOH) and B conc.: 60% (HCOOH 0.1%); Flow: 0.3 ml/min.

### Section S3. Control experiments

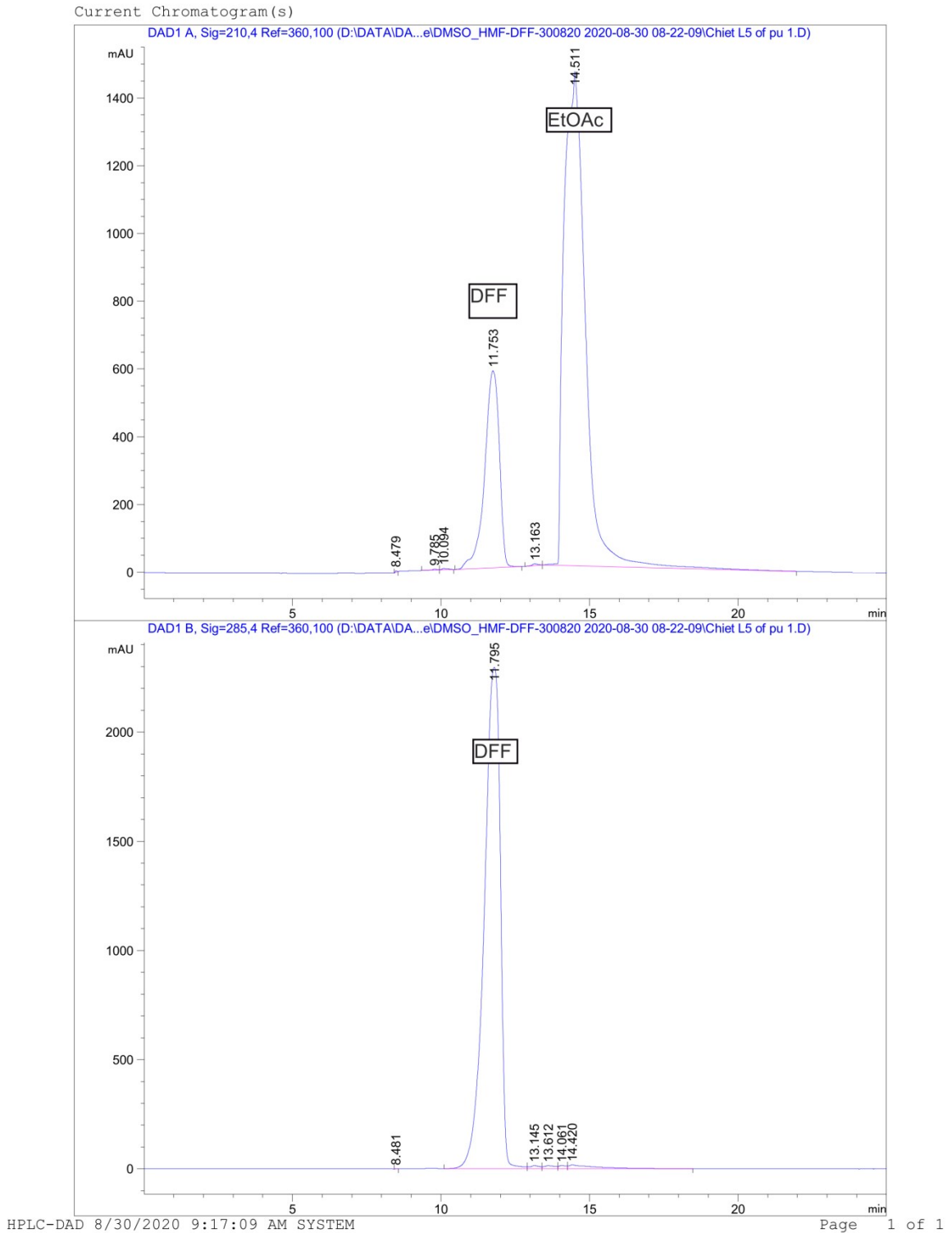


**Fig. S1** Control experiments

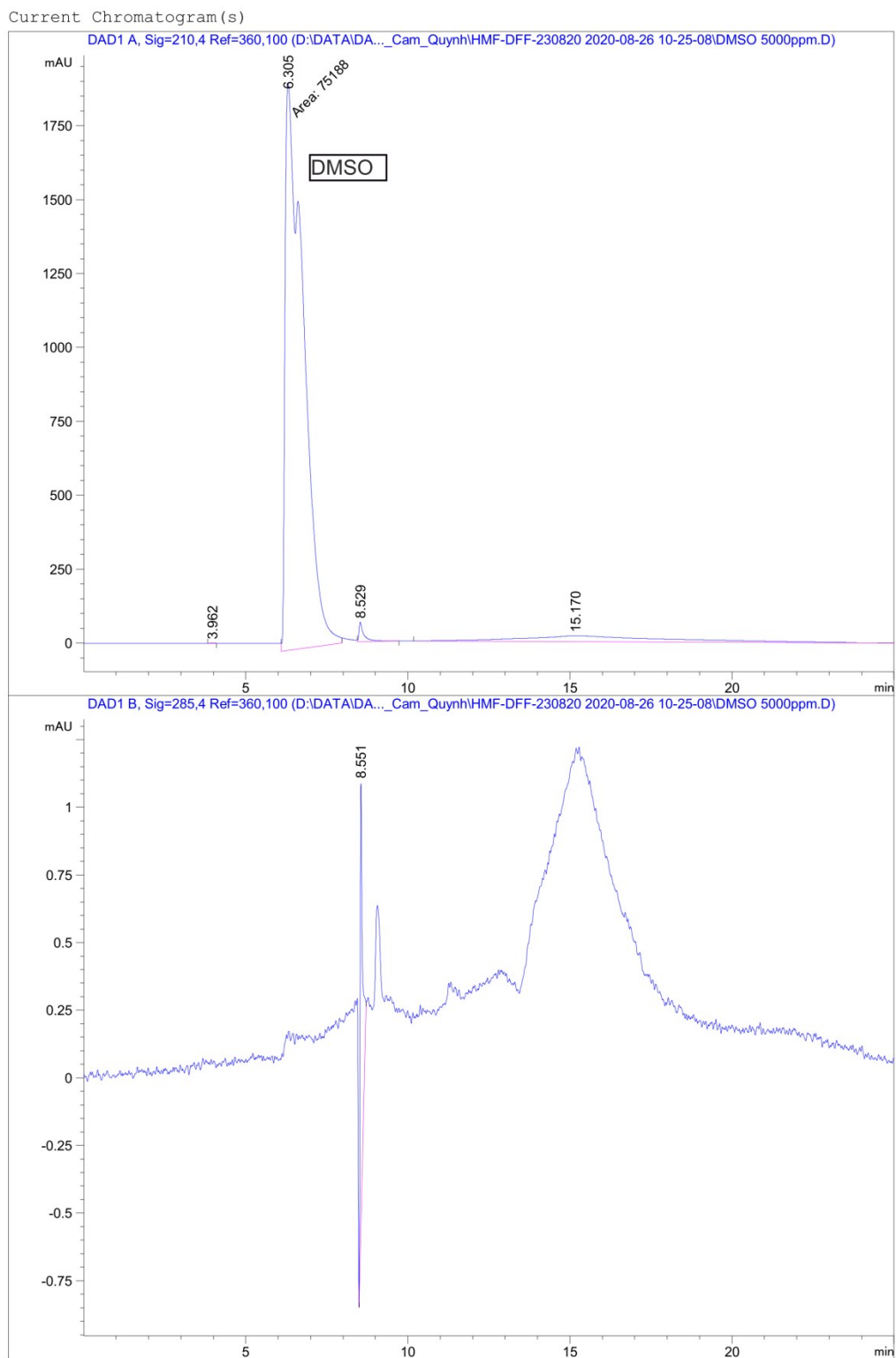
## Section S4. Phase extraction of product



**Fig. S2** Phase extraction for the DFF production: The aqueous phase (white) contains  $\text{H}_2\text{O}$ , DMSO,  $\text{La}(\text{OTf})_3$  and the organic phase (light blue) contains DFF and ethyl acetate/diethyl ether.



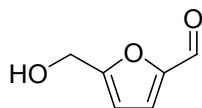
**Fig. S3** The HPLC chromatography of organic solvent extraction



**Fig. S4** HPLC chromatography of DMSO

## Section S5. Spectral data

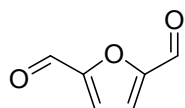
### 5-Hydroxymethylfurfural (HMF)<sup>1, 2</sup>



**<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 9.58 (s, 1H), 7.21 (d, J = 3.2 Hz, 1H), 6.51 (d, J = 3.2 Hz, 1H), 4.71 (s, 2H).

**HRMS (ESI)** *m/z* calcd for [M]<sup>+</sup> C<sub>6</sub>H<sub>7</sub>O<sub>3</sub> 127.0395, found 127.0379.

### 2,5-Diformylfuran (DFF)<sup>2, 3</sup>



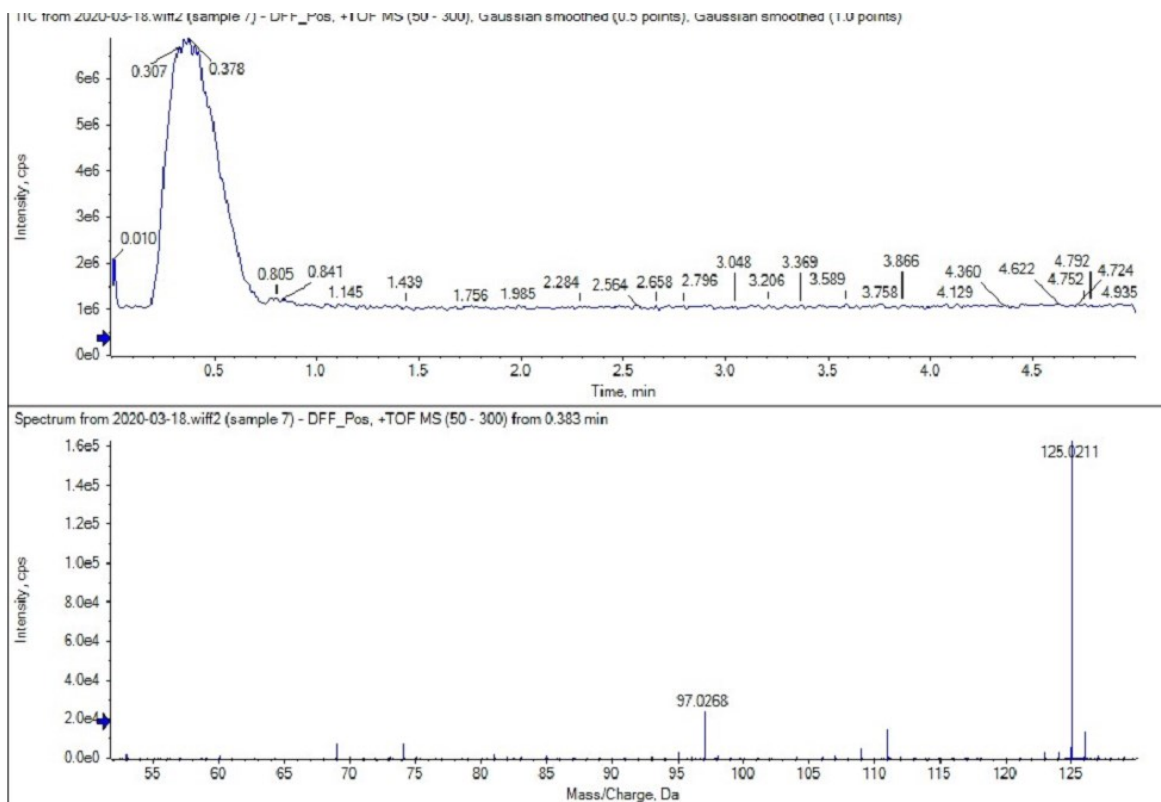
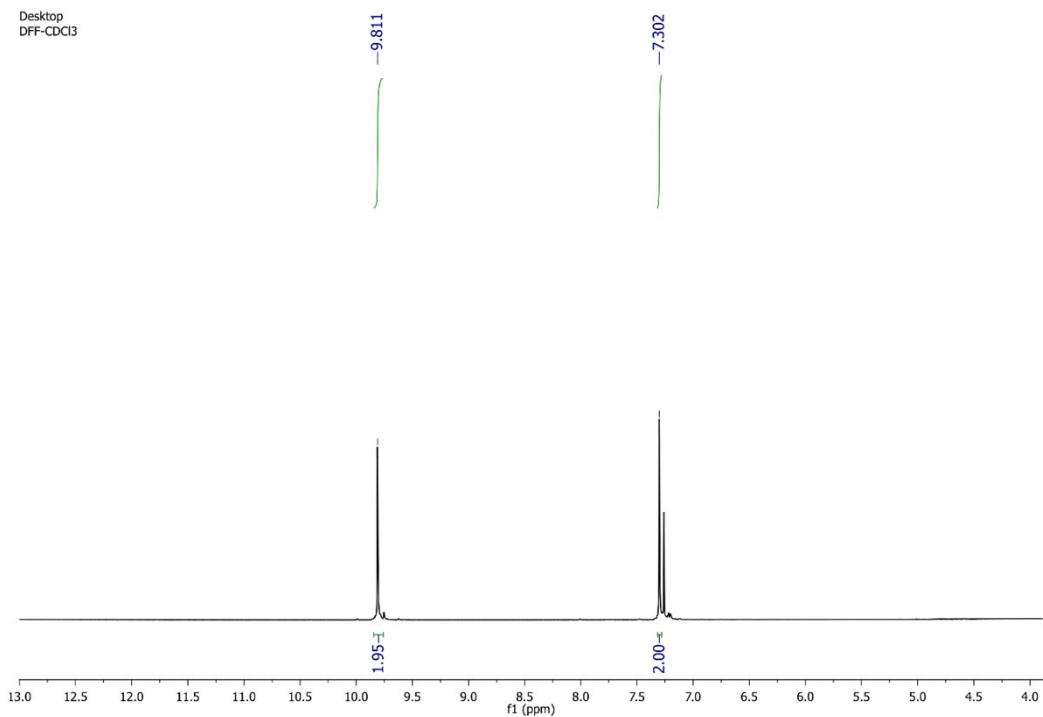
**<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 9.8 (s, 2H), 7.3 (s, 2H).

**HRMS (ESI)** *m/z* calcd for [M]<sup>+</sup> C<sub>6</sub>H<sub>7</sub>O<sub>3</sub> 125.0239, found 125.0211.



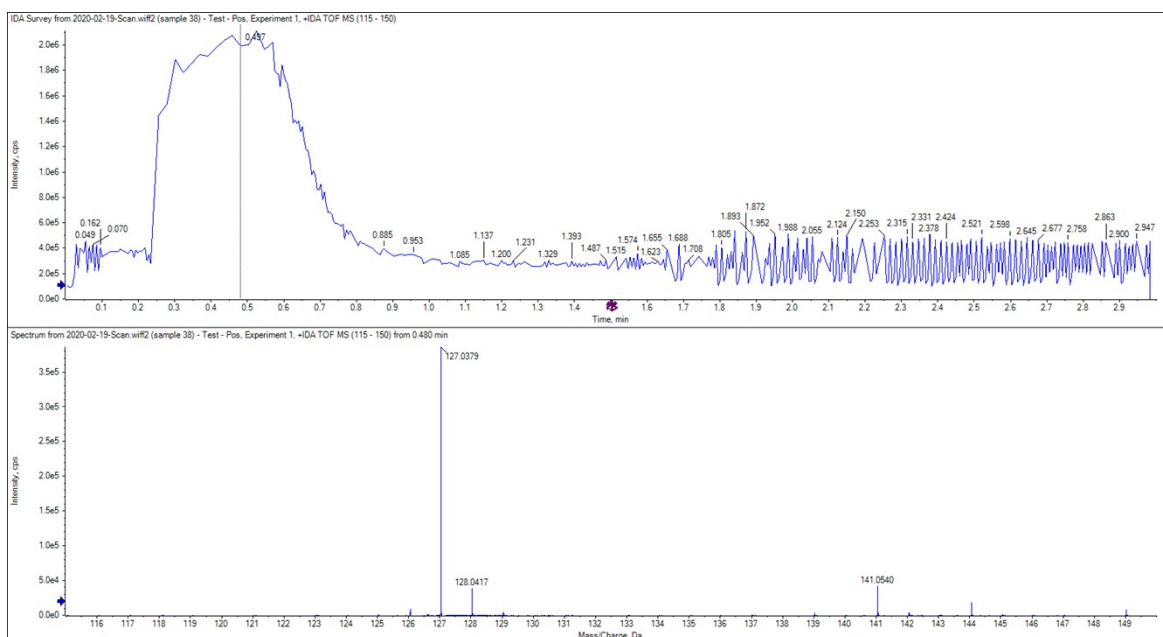
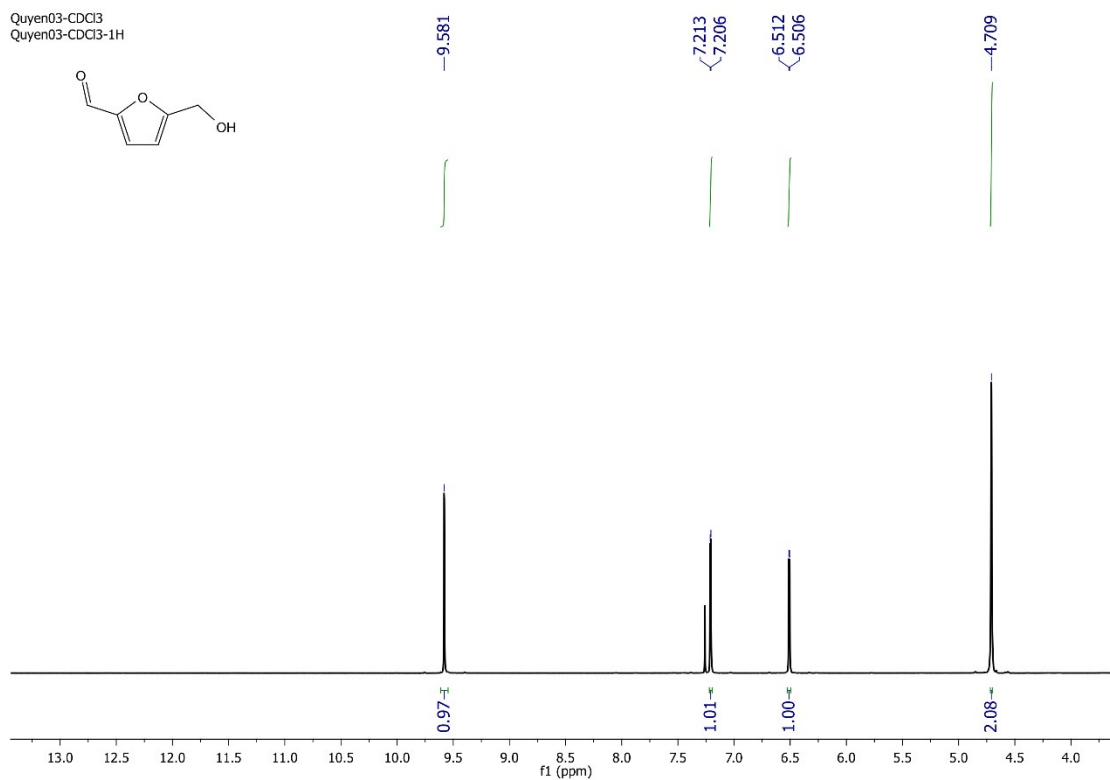
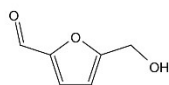
## Section S6. $^1\text{H}$ NMR, HRMS, HPLC spectra

### $^1\text{H}$ NMR and HRMS of DFF



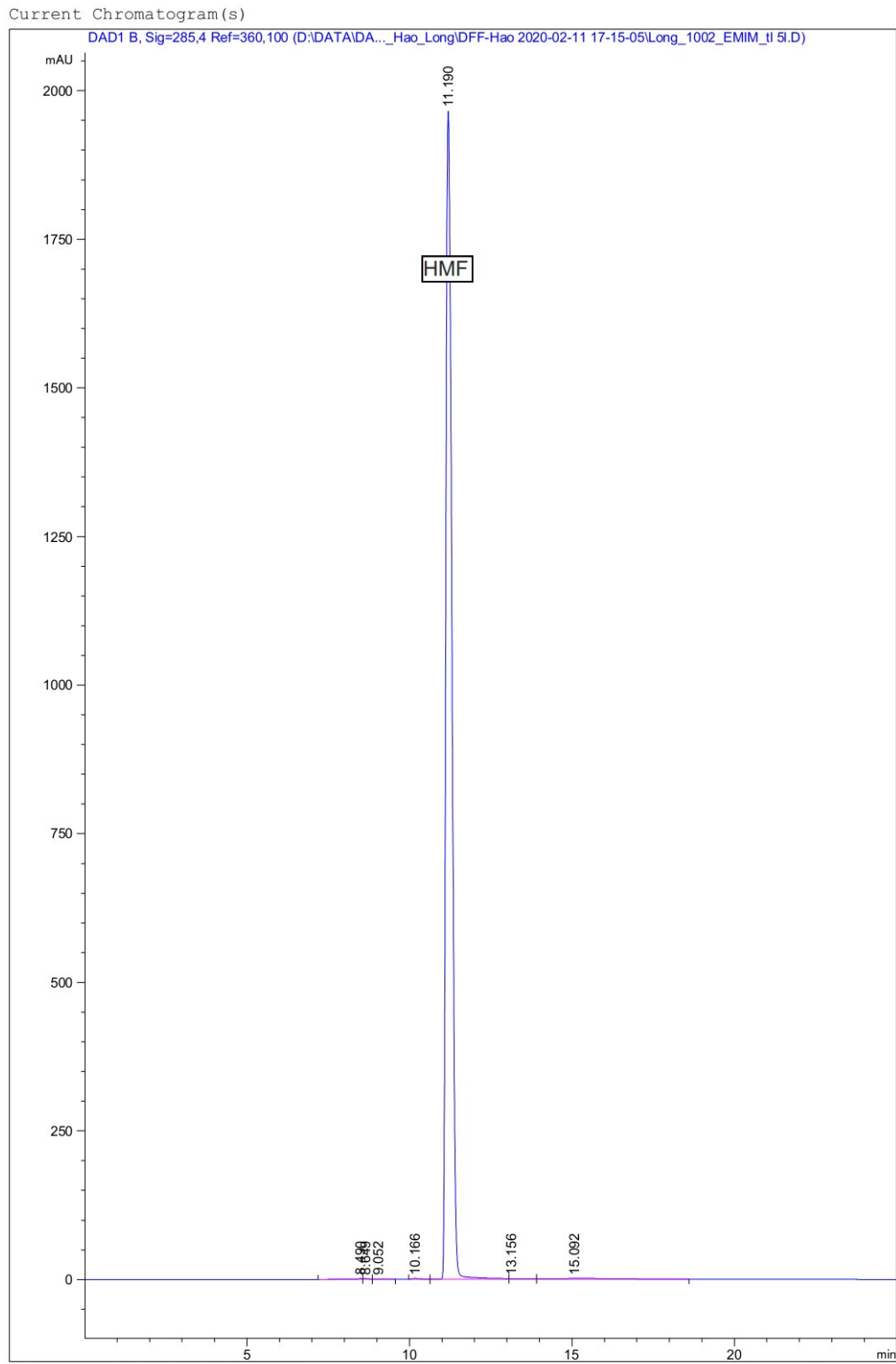
# <sup>1</sup>H NMR and HRMS of HMF

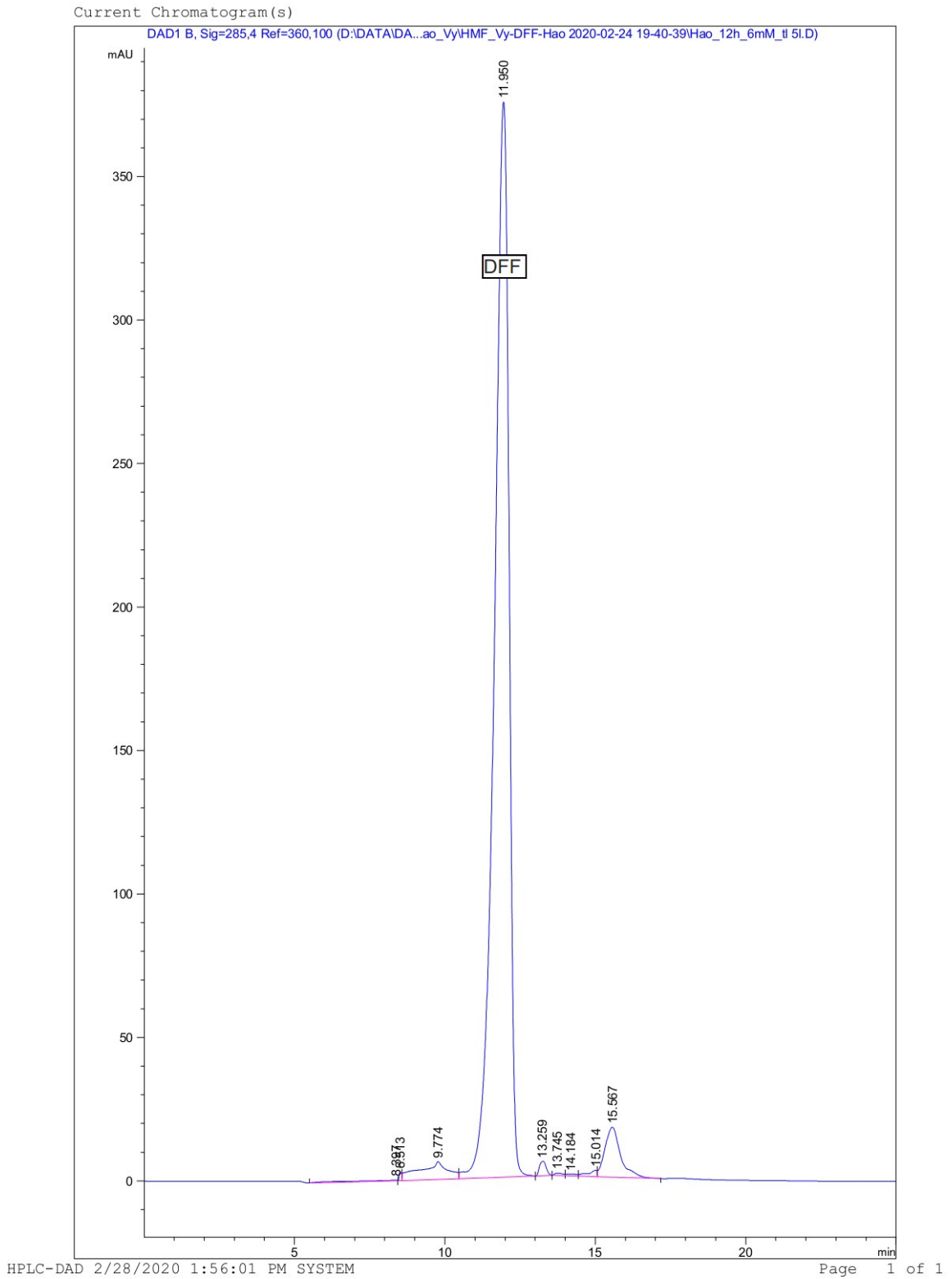
Quien03-CDCl3  
Quien03-CDCl3-1H

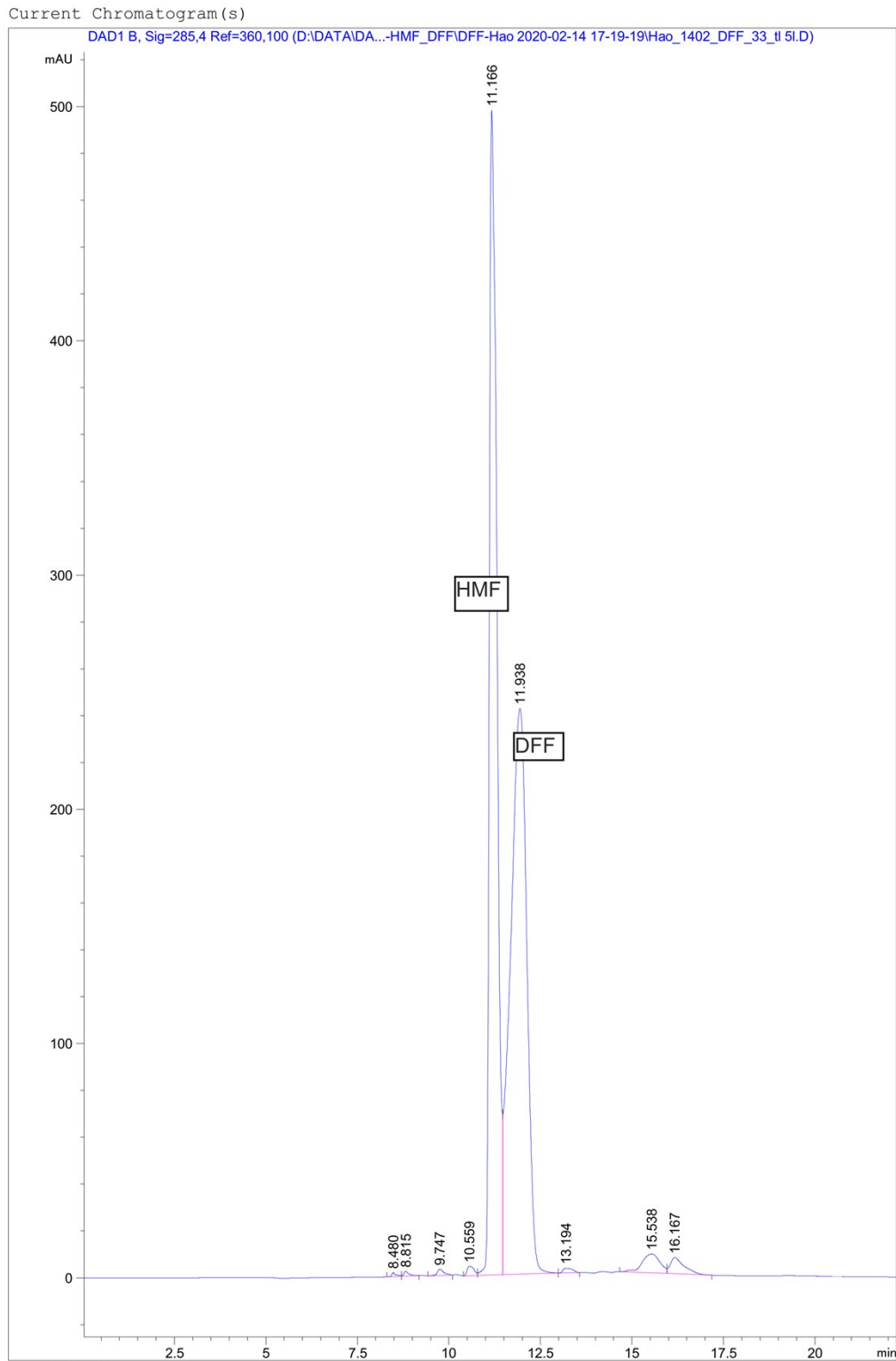


# Chromatography of HMF and DFF

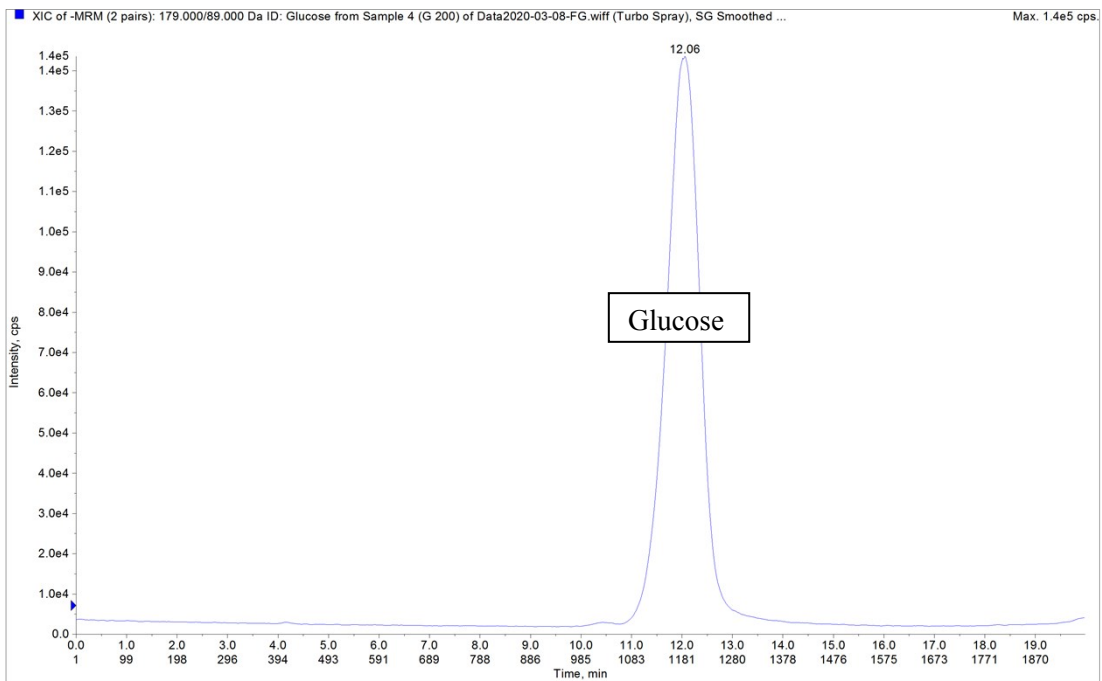
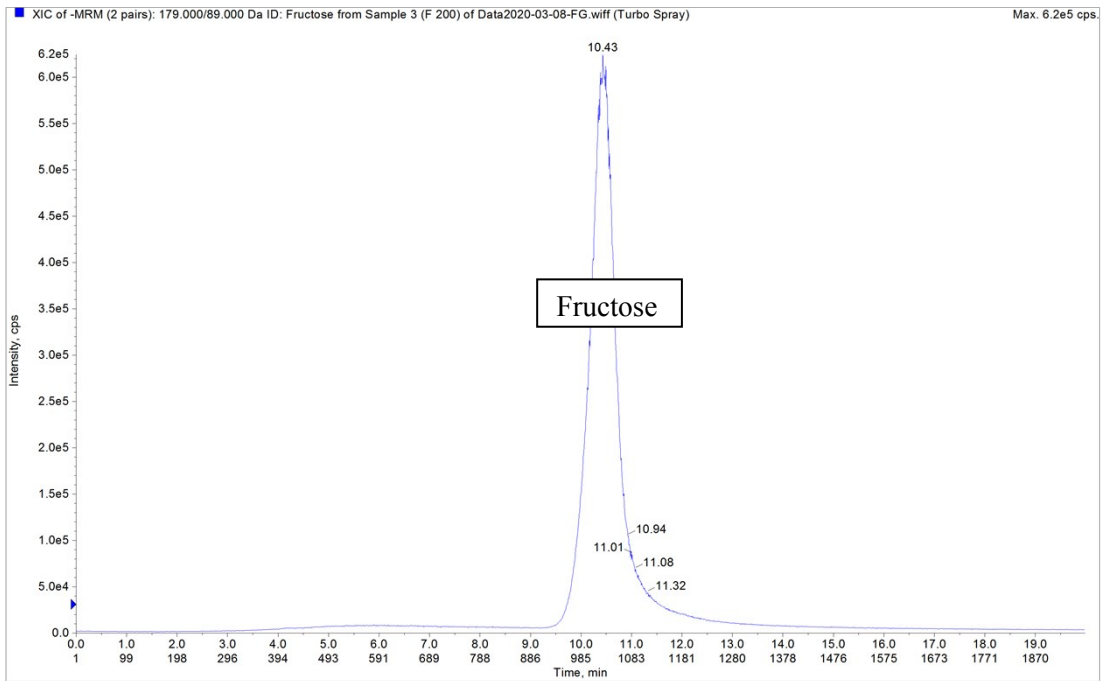
Print of window 38: Current Chromatogram(s)







# Chromatography of fructose and glucose.



## Section S7. References

1. Yang, L.; Tsilomelekis, G.; Caratzoulas, S.; Vlachos, D. G., Mechanism of Bronsted acid-catalyzed glucose dehydration. *ChemSusChem* 2015, 8, 1334-1341.
2. Hong, M.; Wu, S.; Li, J.; Wang, J.; Wei, L.; Li, K., Aerobic oxidation of 5-(hydroxymethyl)furfural into 2,5-diformylfuran catalyzed by starch supported aluminum nitrate. *Catal. Commun.* 2020, 136, 105909-105313.
3. Yang, Z.-Z.; Deng, J.; Pan, T.; Guo, Q.-X.; Fu, Y., A one-pot approach for conversion of fructose to 2,5-diformylfuran by combination of Fe<sub>3</sub>O<sub>4</sub>-SBA-SO<sub>3</sub>H and K-OMS-2. *Green Chem.* 2012, 14, 2986-2989.