Electronic Supplementary Material (ESI) for Green Chemistry.

Conversion of Saccharides into Formic Acid using Hydrogen Peroxide and a Recyclable Palladium(II) Catalyst in Aqueous Alkaline Media at Ambient Temperatures

Supporting Information

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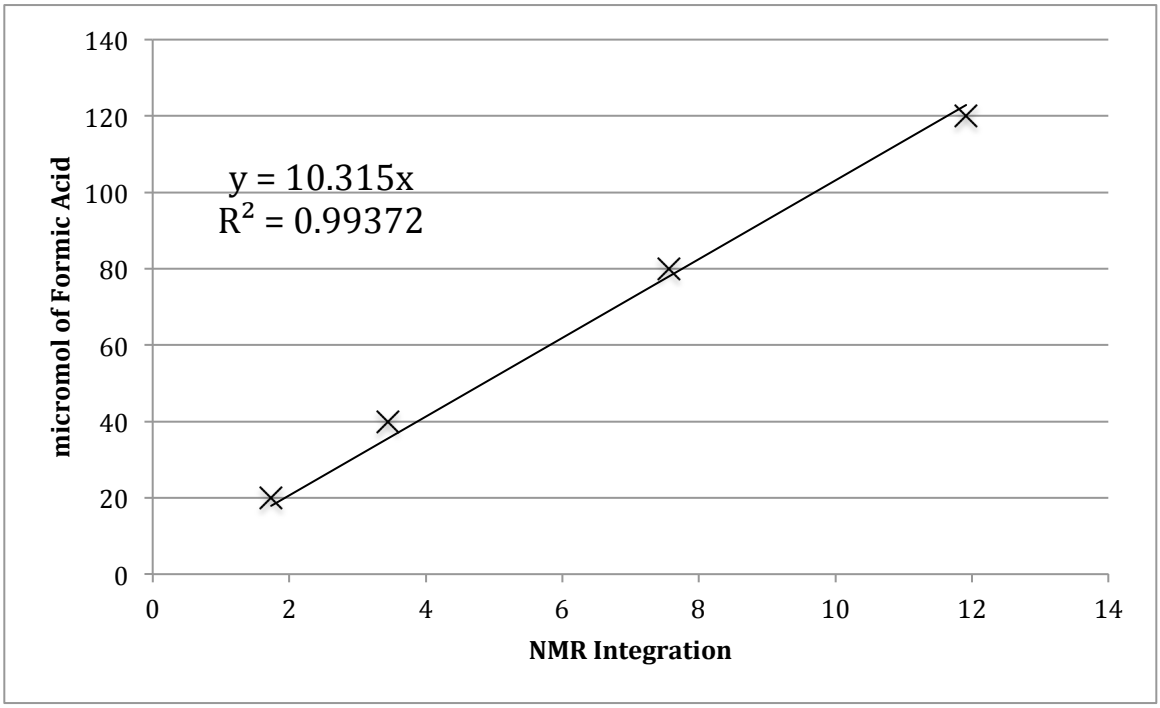
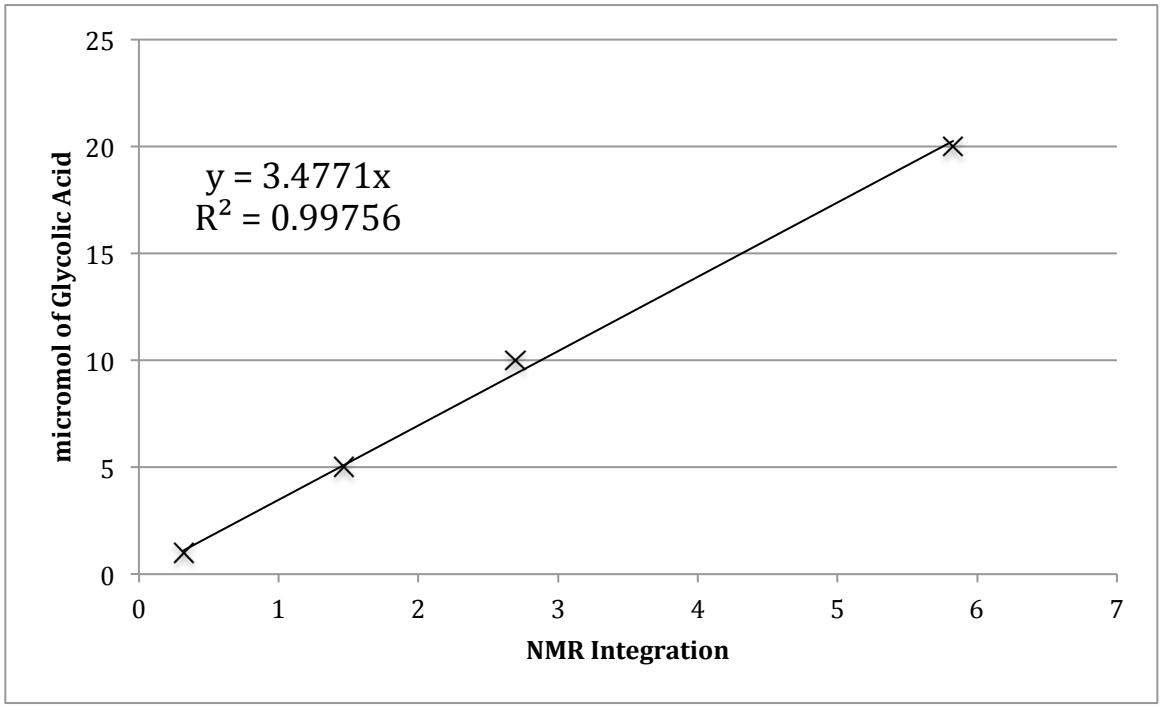
S1



The calibration curve of a DMSO standard was taken with known amounts of formic acid. The ^{1}H NMR of 20, 40, 80, and 120 μmol of formic acid was taken in 0.75 mL of D_2O with a sealed capillary DMSO standard.

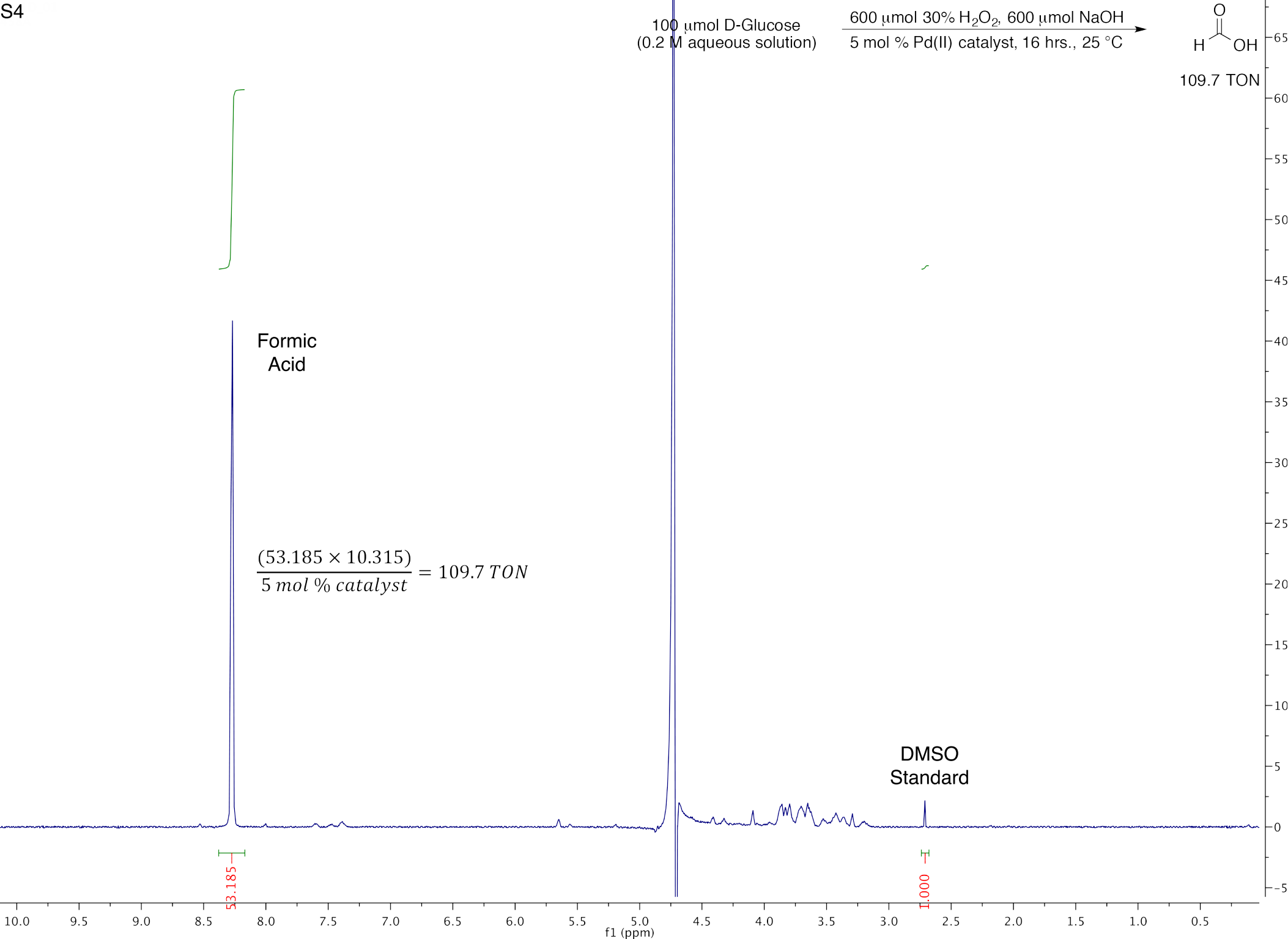


The calibration curve of a DMSO standard was taken with known amounts of glycolic acid. The ^{1}H NMR of 1, 5, 10, and 20 μmol of glycolic acid was taken in 0.75 mL of D_2O with a sealed capillary DMSO standard.

Lewis Acid Additive Results

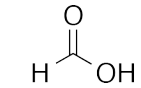
Lewis Acid	TON
$AlCl_3$	34.6
$CrCl_3$	79.9
$ZnCl_2$	64.9
$SnCl_2$	51.5

Reaction conditions: 100 µmol of substrate, 5 µmol of Lewis acid, and 600 µmol NaOH were dissolved in 0.44 mL H_2O. 60 µL 30% H_2O_2 was added and the mixture stirred at 25 °C for 16 hours. 0.25 mL of D_2O was then added to the reaction mixture with a sealed capillary DMSO standard. The solution was then analyzed using wet1D NMR.


100 µmol D-Glucose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C
109.7 TON
Formic Acid
$\frac{(53.185 \times 10.315)}{5\ mol\ \%\ catalyst} = 109.7\ TON$
DMSO Standard
53.185
1.000
f1 (ppm)

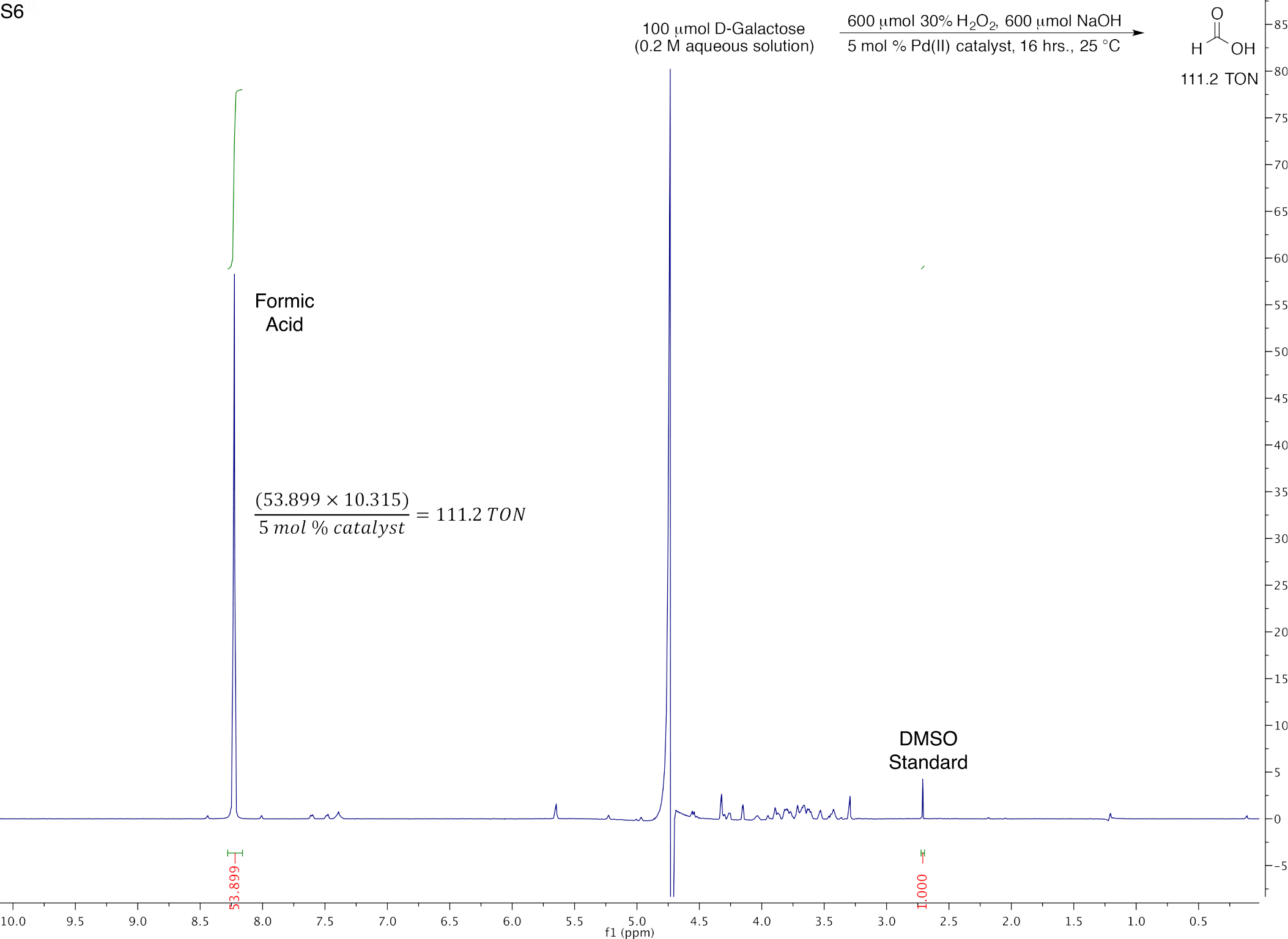
100 μmol D-Glucose
(0.2 M aqueous solution)

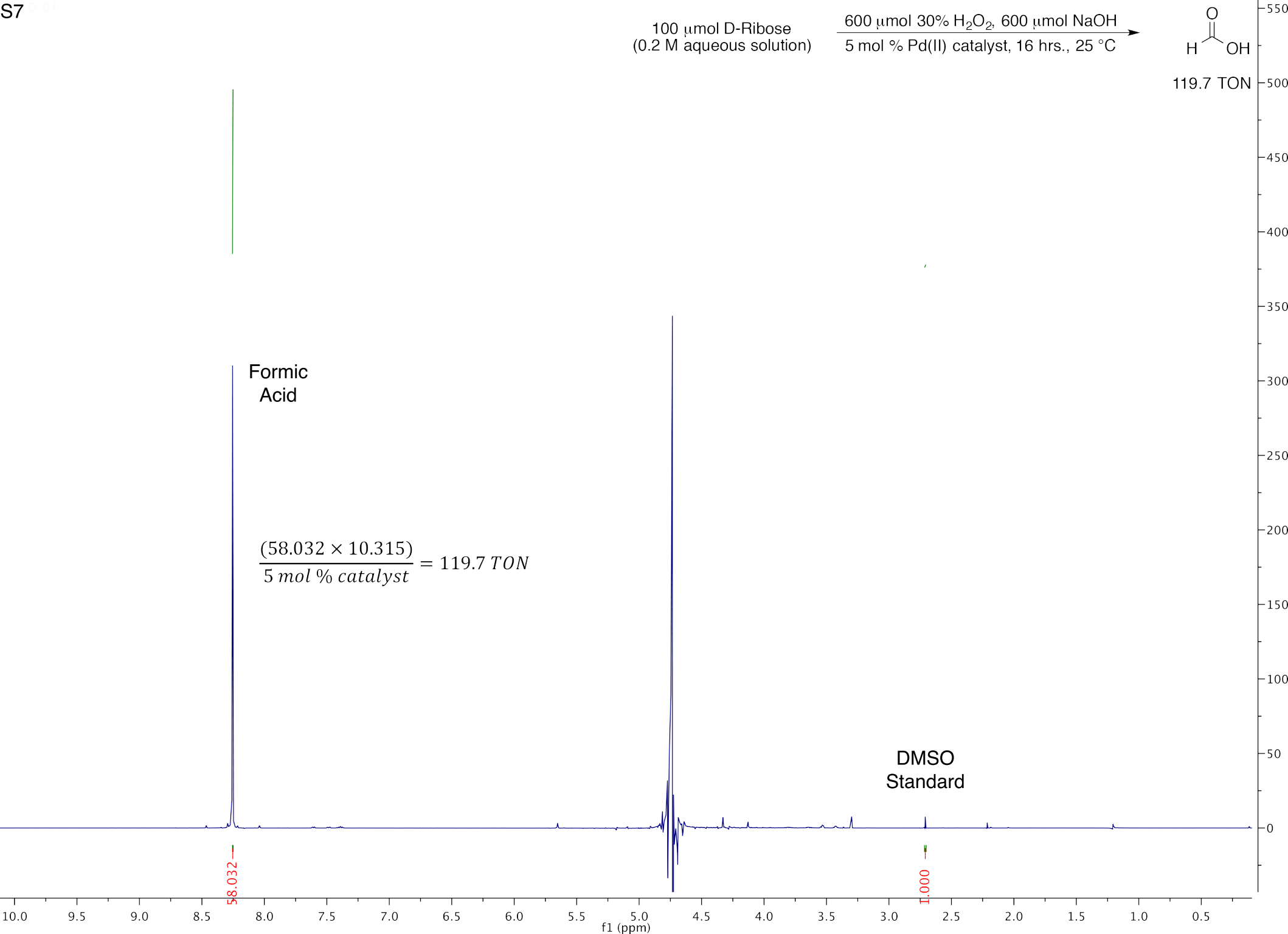
600 μmol 30% H_2O_2, 600 μmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C

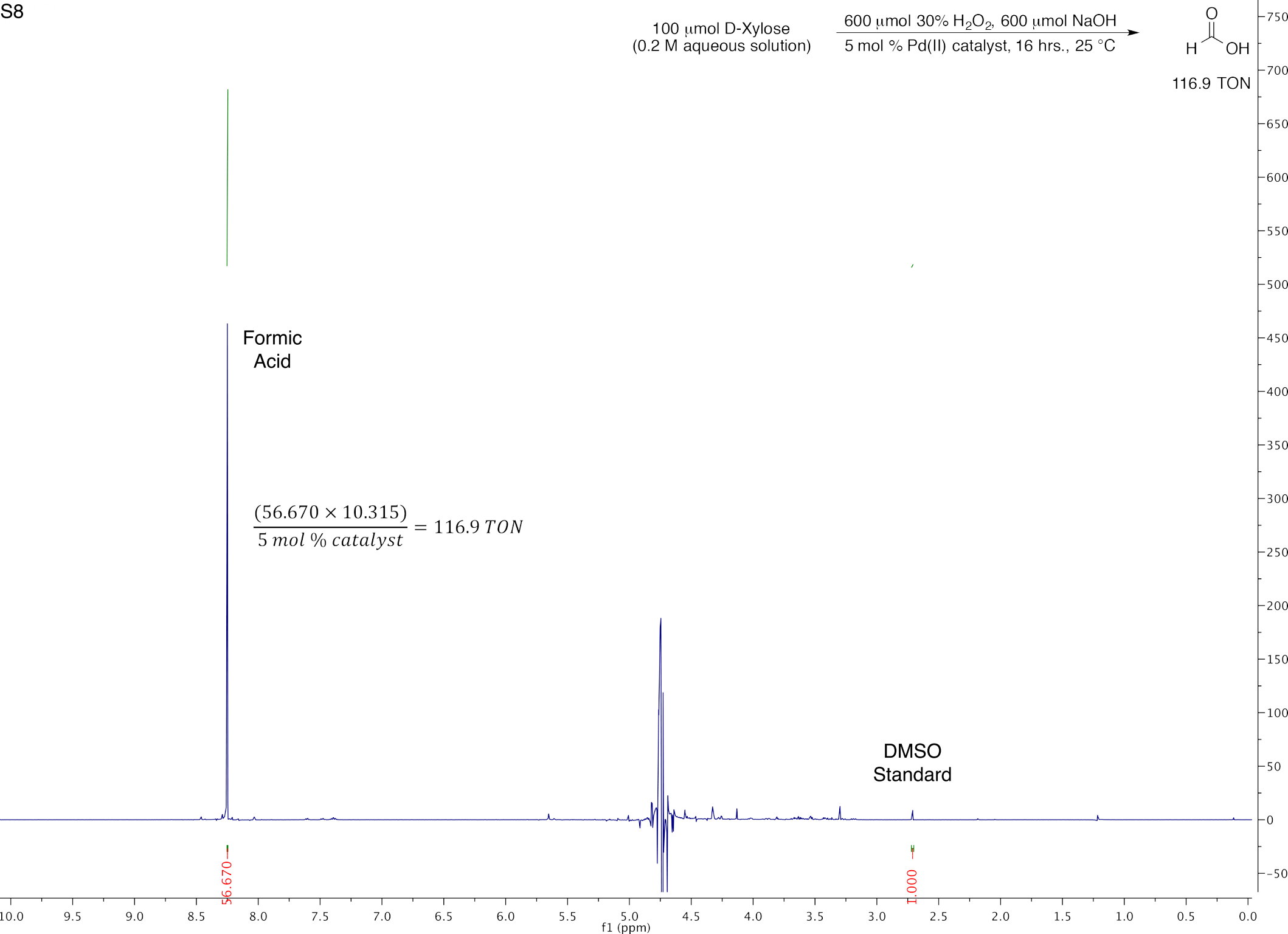


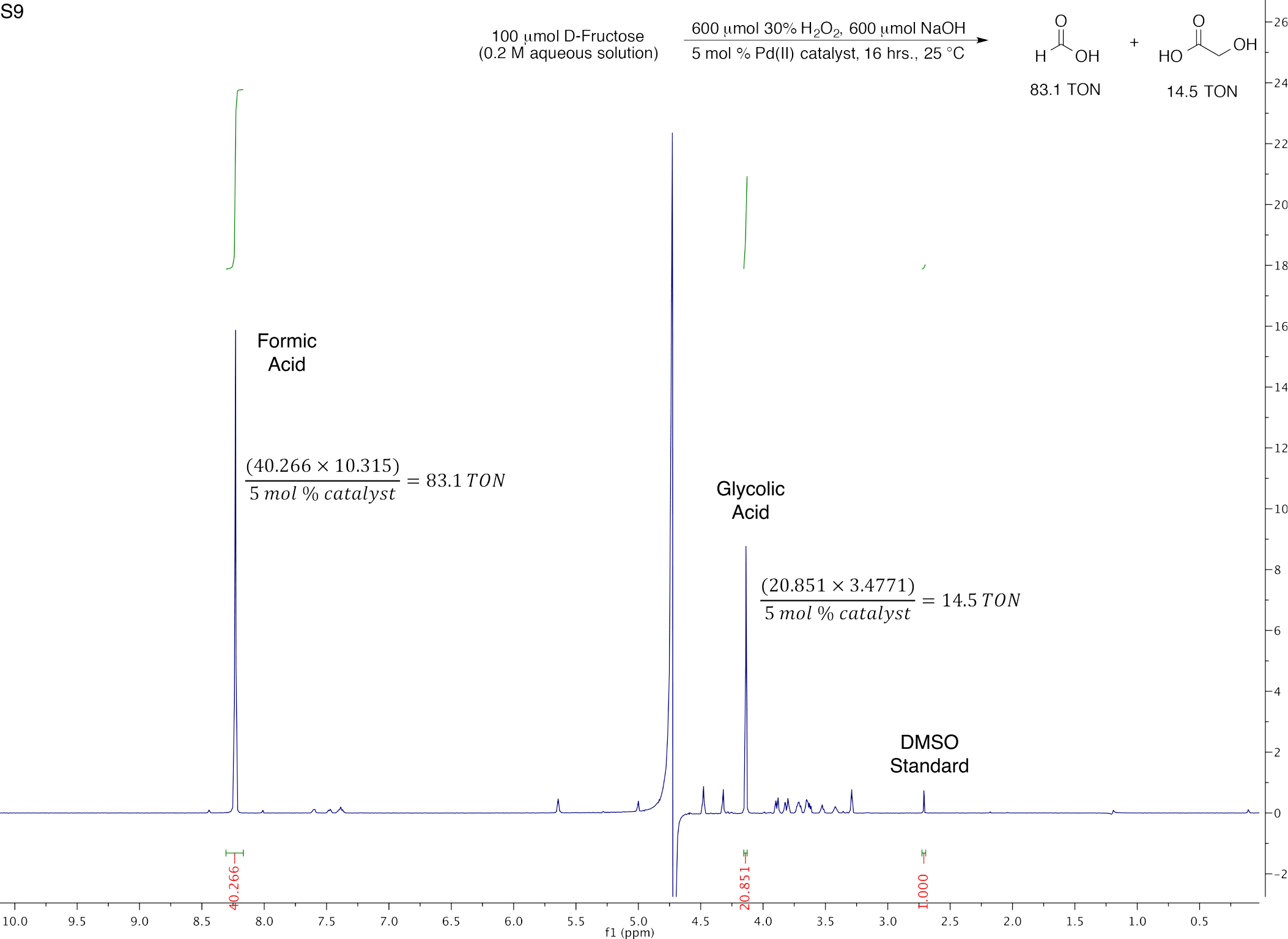
109.7 TON

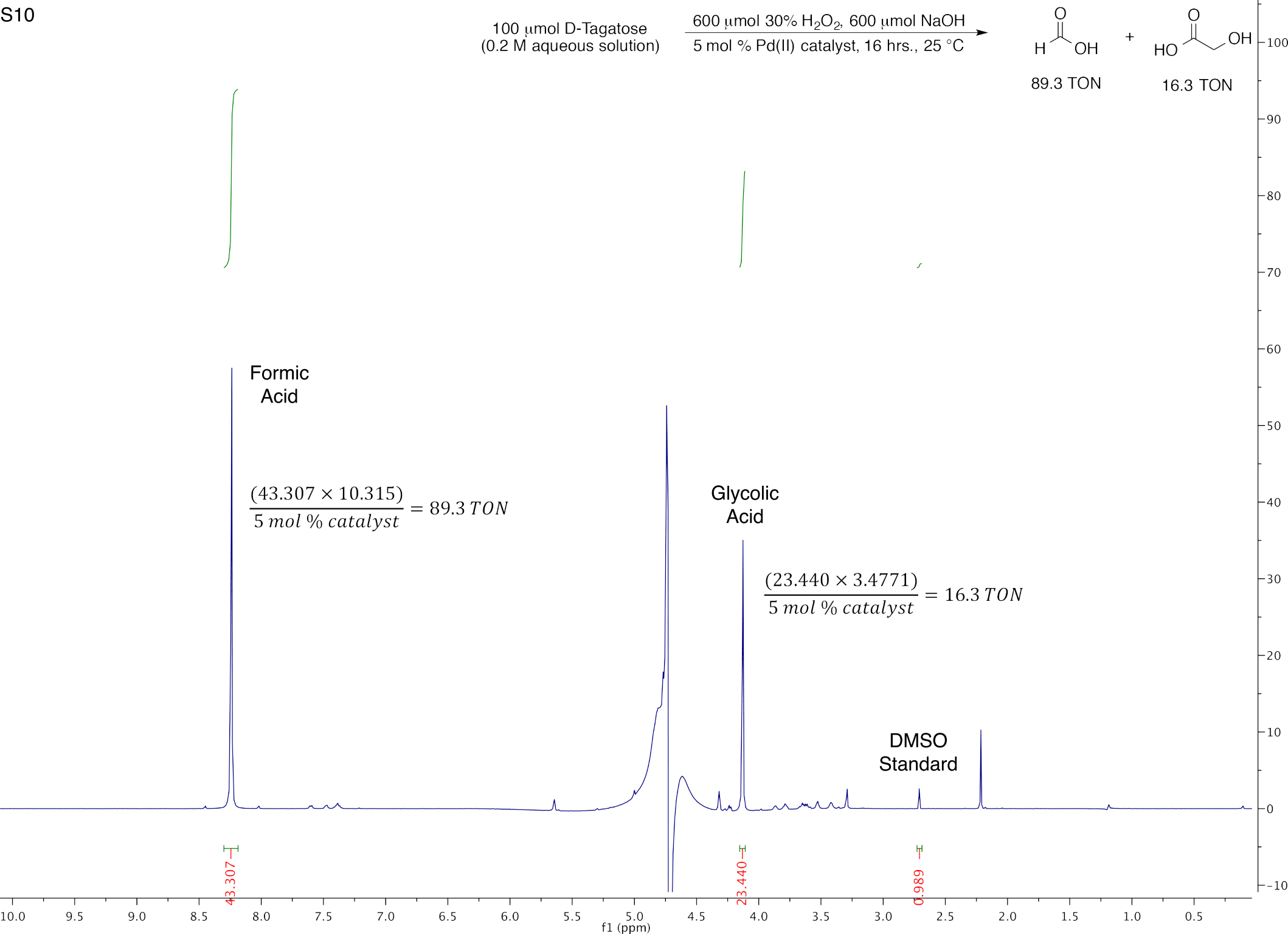
Formic Acid
Carbonyl Carbon

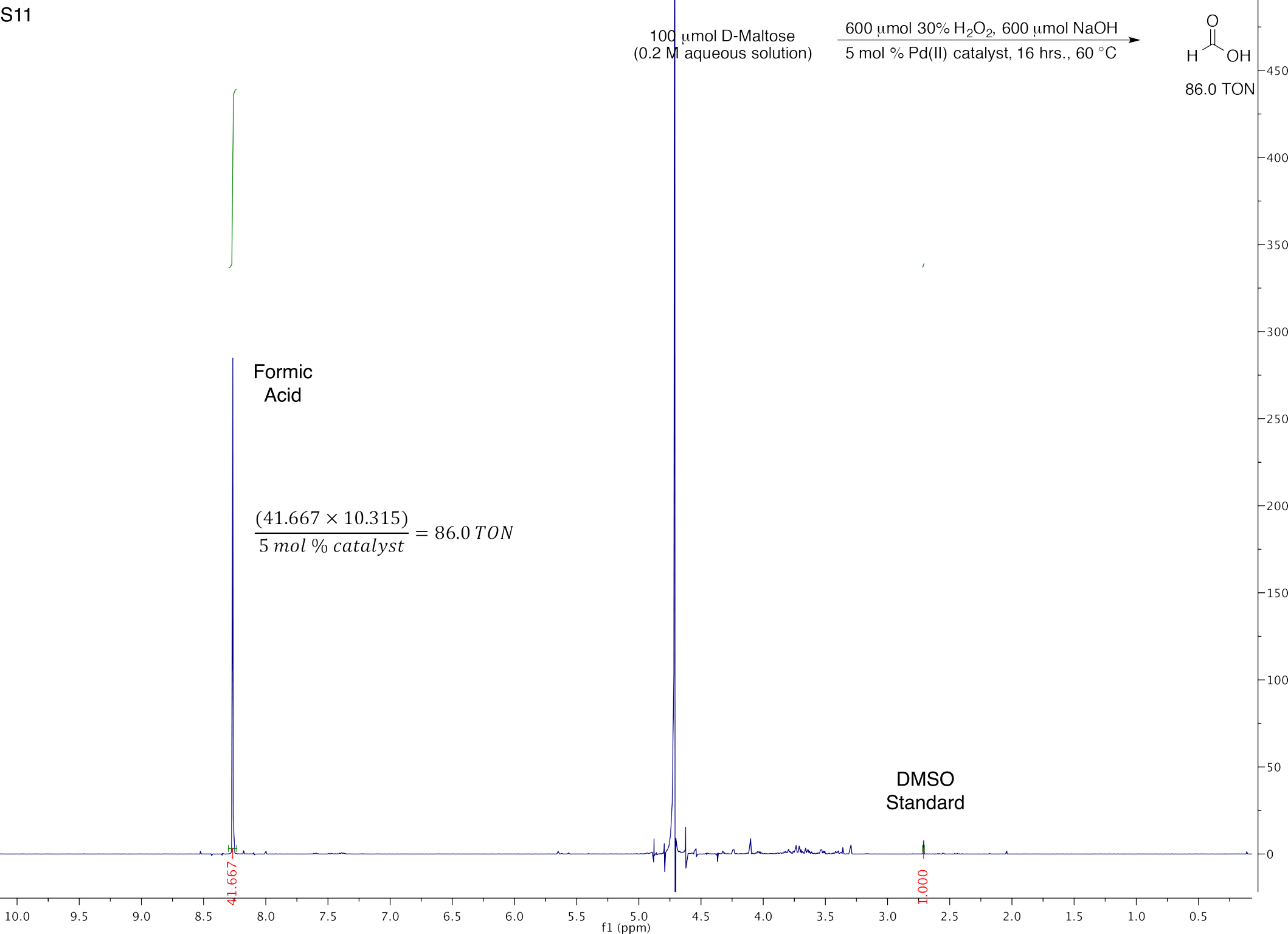

100 μmol D-Galactose
(0.2 M aqueous solution)
600 μmol 30% H_2O_2, 600 μmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C
111.2 TON
Formic
Acid
$\frac{(53.899 \times 10.315)}{5\ mol\ \%\ catalyst} = 111.2\ TON$
DMSO
Standard
53.899
1.000
f1 (ppm)

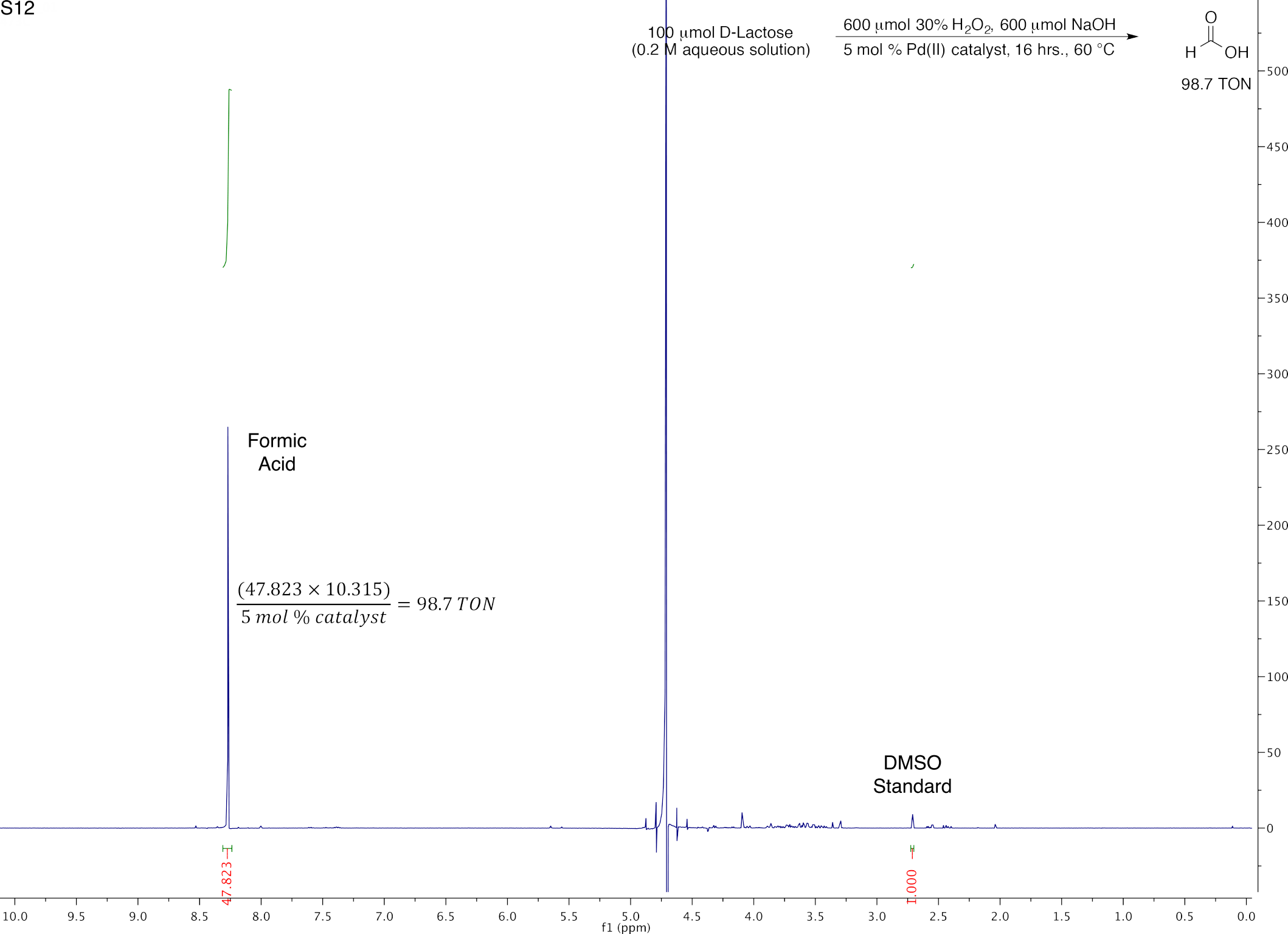

100 µmol D-Ribose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C
O
H
OH
119.7 TON
Formic
Acid
$\frac{(58.032 \times 10.315)}{5\ mol\ \%\ catalyst} = 119.7\ TON$
DMSO
Standard
58.032
1.000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0

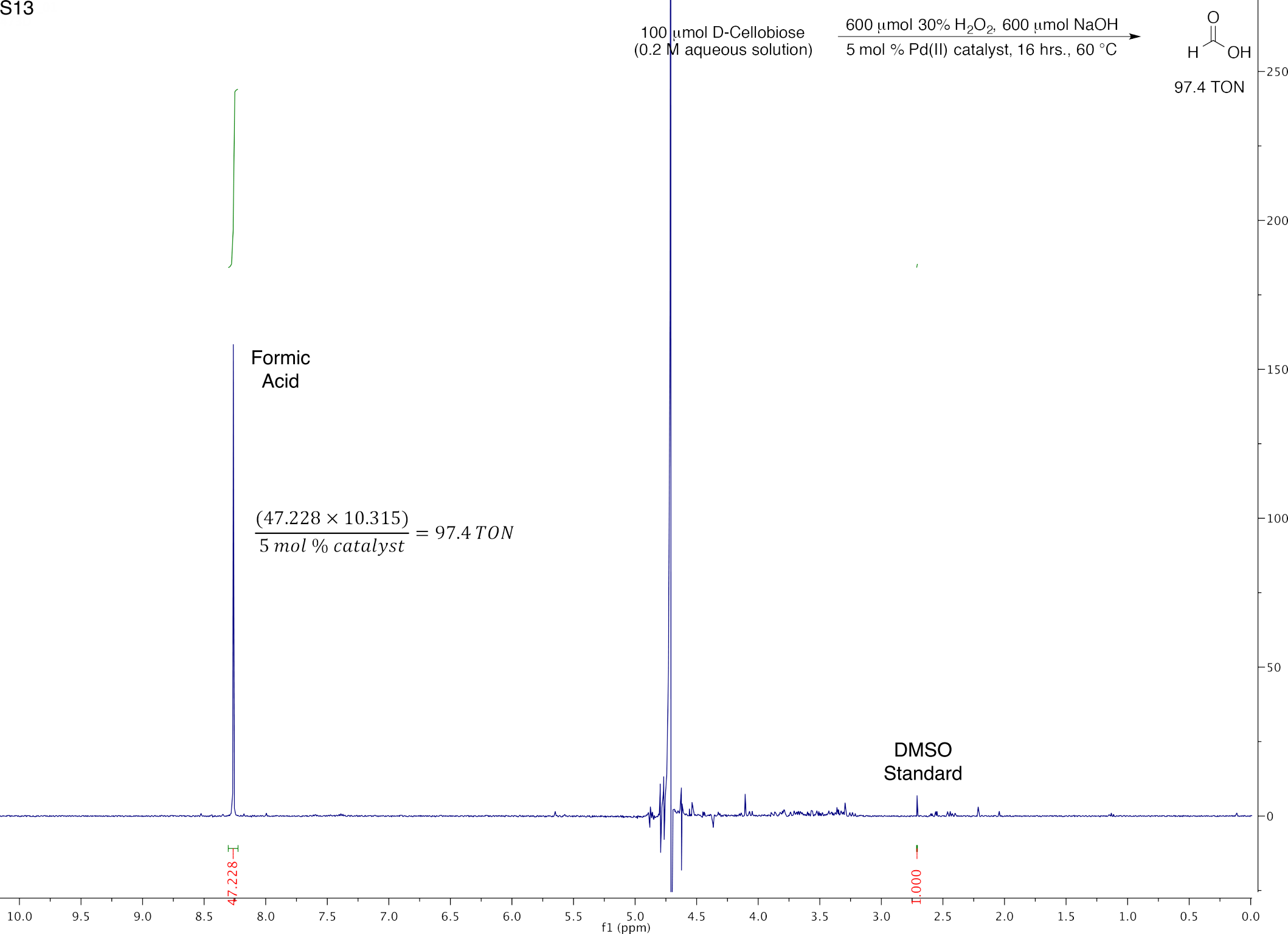

100 µmol D-Xylose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C
H
O
OH
116.9 TON
Formic
Acid
$\frac{(56.670 \times 10.315)}{5\ mol\ \%\ catalyst} = 116.9\ TON$
DMSO
Standard
56.670
1.000
f1 (ppm)

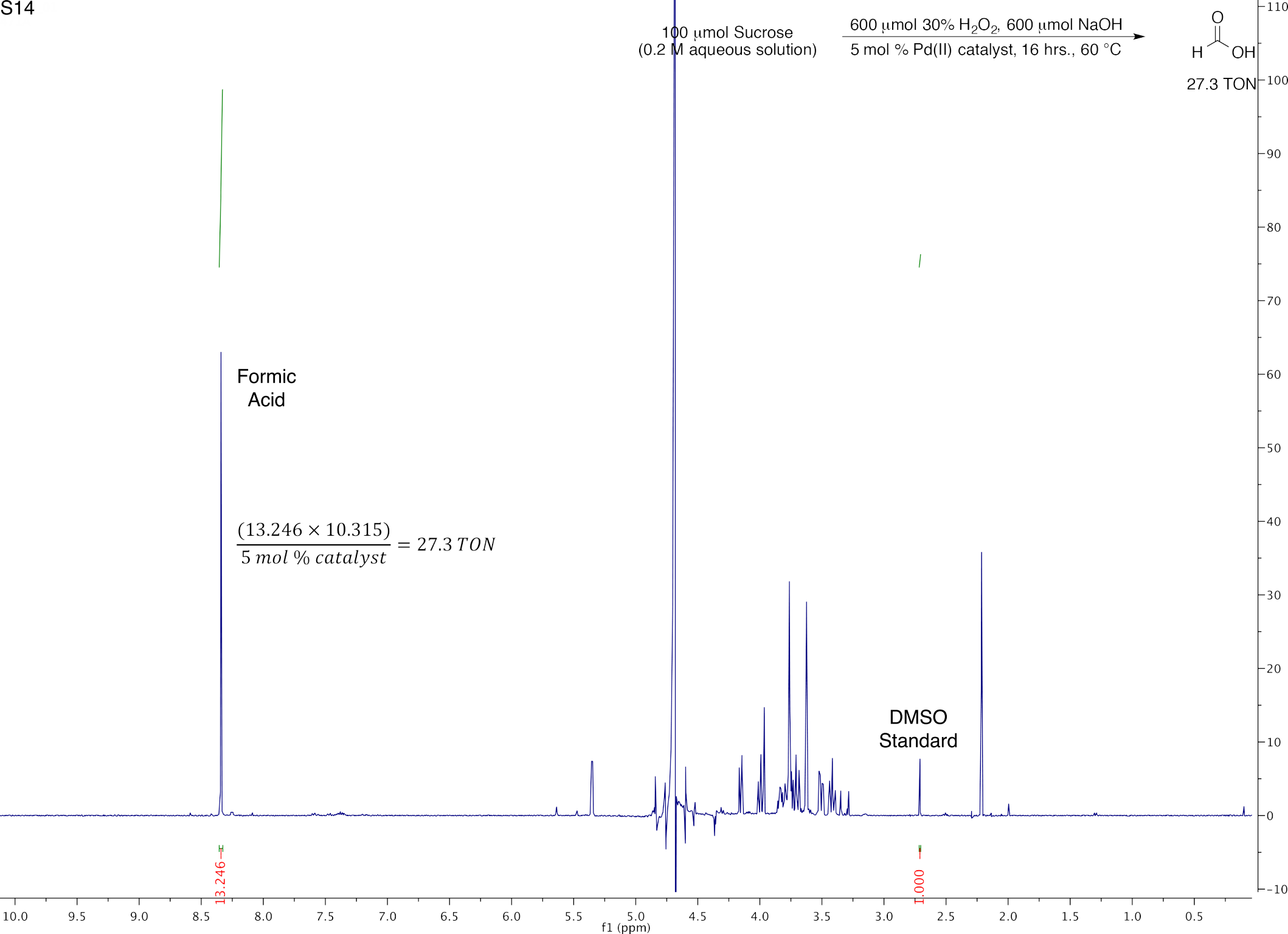

100 µmol D-Fructose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C
83.1 TON
14.5 TON
Formic Acid
$\frac{(40.266 \times 10.315)}{5\ mol\ \%\ catalyst} = 83.1\ TON$
Glycolic Acid
$\frac{(20.851 \times 3.4771)}{5\ mol\ \%\ catalyst} = 14.5\ TON$
DMSO Standard
40.266
20.851
1.000
f1 (ppm)

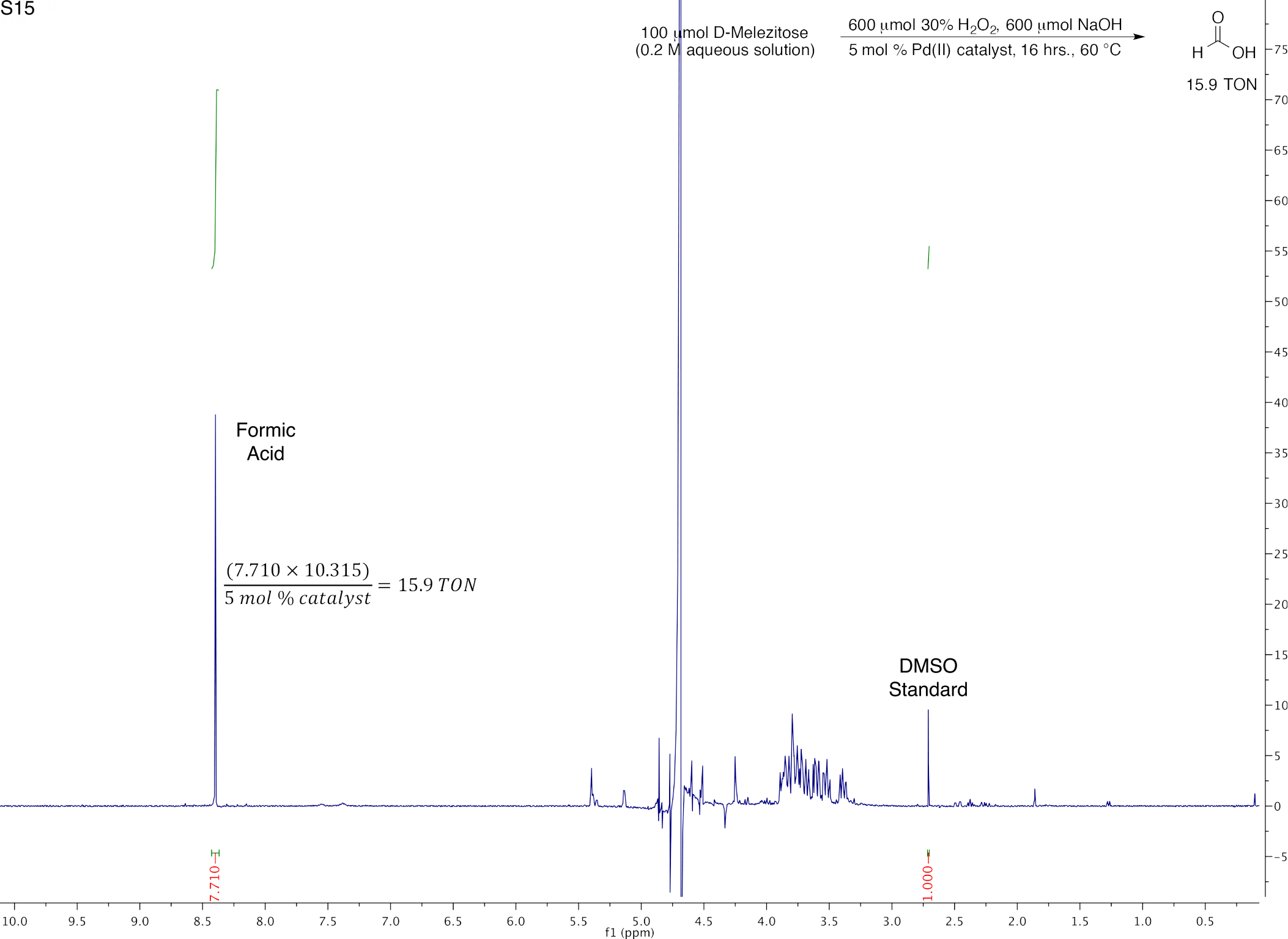

100 µmol D-Tagatose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C
89.3 TON
16.3 TON
Formic Acid
$\frac{(43.307 \times 10.315)}{5\ mol\ \%\ catalyst} = 89.3\ TON$
Glycolic Acid
$\frac{(23.440 \times 3.4771)}{5\ mol\ \%\ catalyst} = 16.3\ TON$
DMSO Standard
43.307
23.440
0.989
f1 (ppm)

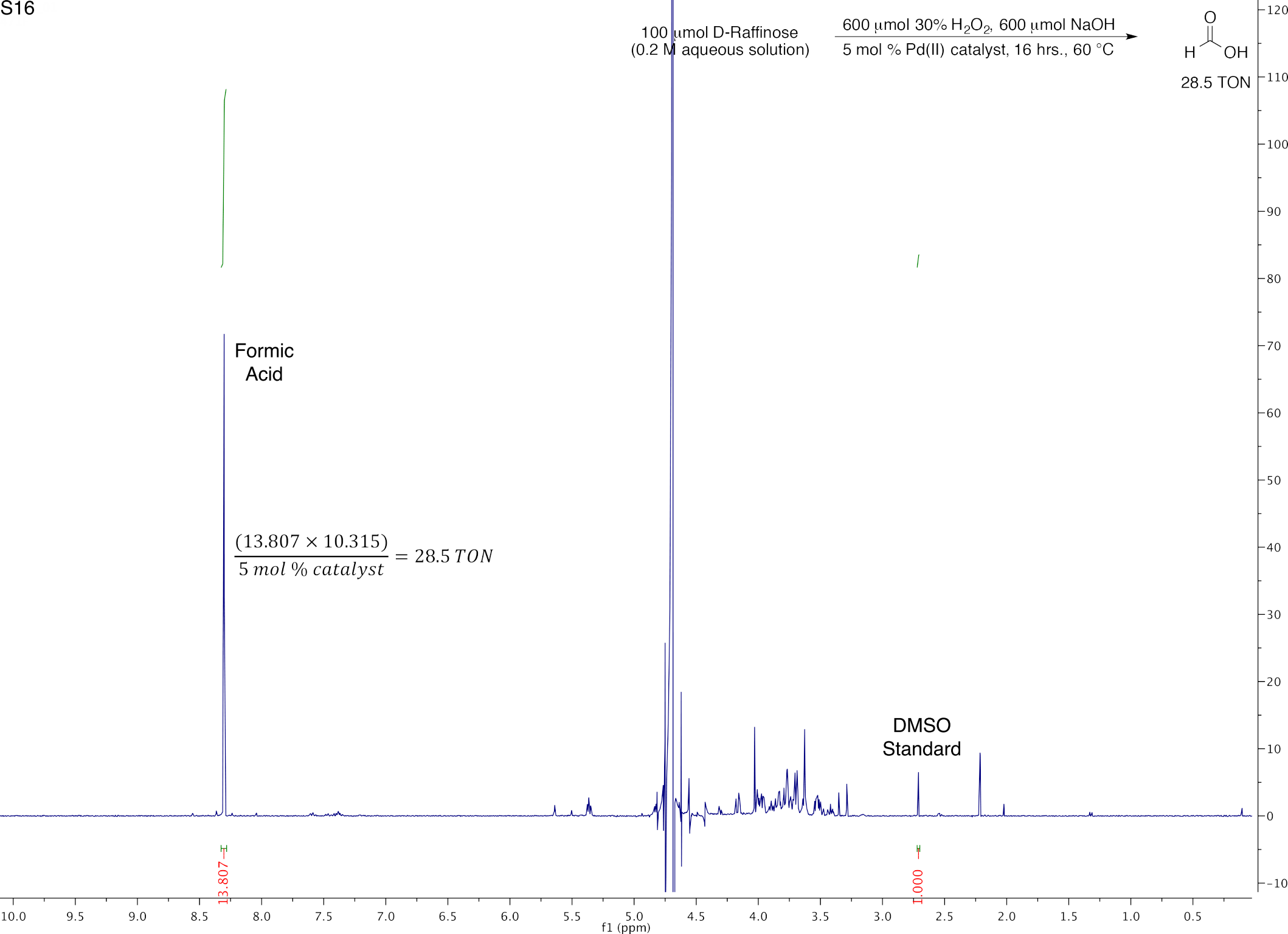

100 µmol D-Maltose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 60 °C
86.0 TON
Formic Acid
$\frac{(41.667 \times 10.315)}{5\ mol\ \%\ catalyst} = 86.0\ TON$
DMSO Standard
41.667
1.000
f1 (ppm)

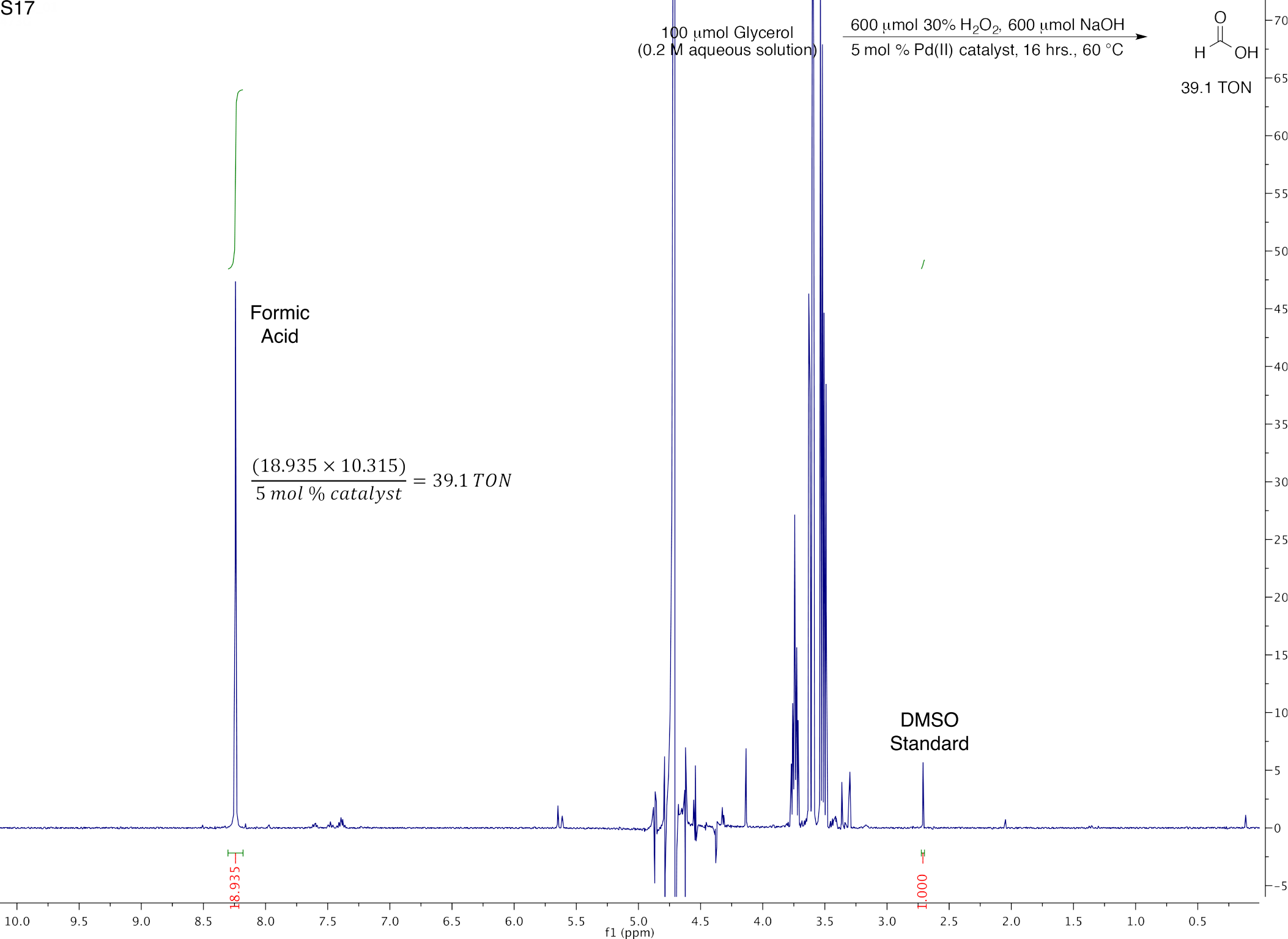

100 μmol D-Lactose
(0.2 M aqueous solution)
600 μmol 30% H_2O_2, 600 μmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 60 °C
98.7 TON
Formic Acid
$\frac{(47.823 \times 10.315)}{5\ mol\ \%\ catalyst} = 98.7\ TON$
DMSO Standard
47.823
1.000
f1 (ppm)


100 µmol D-Cellobiose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 60 °C
O
H
OH
97.4 TON
Formic
Acid
$\frac{(47.228 \times 10.315)}{5\ mol\ \%\ catalyst} = 97.4\ TON$
DMSO
Standard
47.228
1.000
f1 (ppm)


100 µmol Sucrose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 60 °C
27.3 TON
Formic Acid
$\frac{(13.246 \times 10.315)}{5\ mol\ \%\ catalyst} = 27.3\ TON$
DMSO Standard
13.246
1.000
f1 (ppm)


100 µmol D-Melezitose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 60 °C
O
H
OH
15.9 TON
Formic
Acid
$\frac{(7.710 \times 10.315)}{5\ mol\ \%\ catalyst} = 15.9\ TON$
DMSO
Standard
7.710
1.000
f1 (ppm)


100 µmol D-Raffinose
(0.2 M aqueous solution)
600 µmol 30% H_2O_2, 600 µmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 60 °C
28.5 TON
Formic Acid
$\frac{(13.807 \times 10.315)}{5\ mol\ \%\ catalyst} = 28.5\ TON$
DMSO Standard
13.807
1.000
f1 (ppm)


100 μmol Glycerol
(0.2 M aqueous solution)
600 μmol 30% H_2O_2, 600 μmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 60 °C
O
H
OH
39.1 TON
Formic
Acid
$\frac{(18.935 \times 10.315)}{5\ mol\ \%\ catalyst} = 39.1\ TON$
DMSO
Standard
18.935
1.000
f1 (ppm)