

Supplementary Material for Tetrahedron Letters.

Oxidative Degradation of Reducing Carbohydrates to Ammonium Formate with H₂O₂ and NH₄OH

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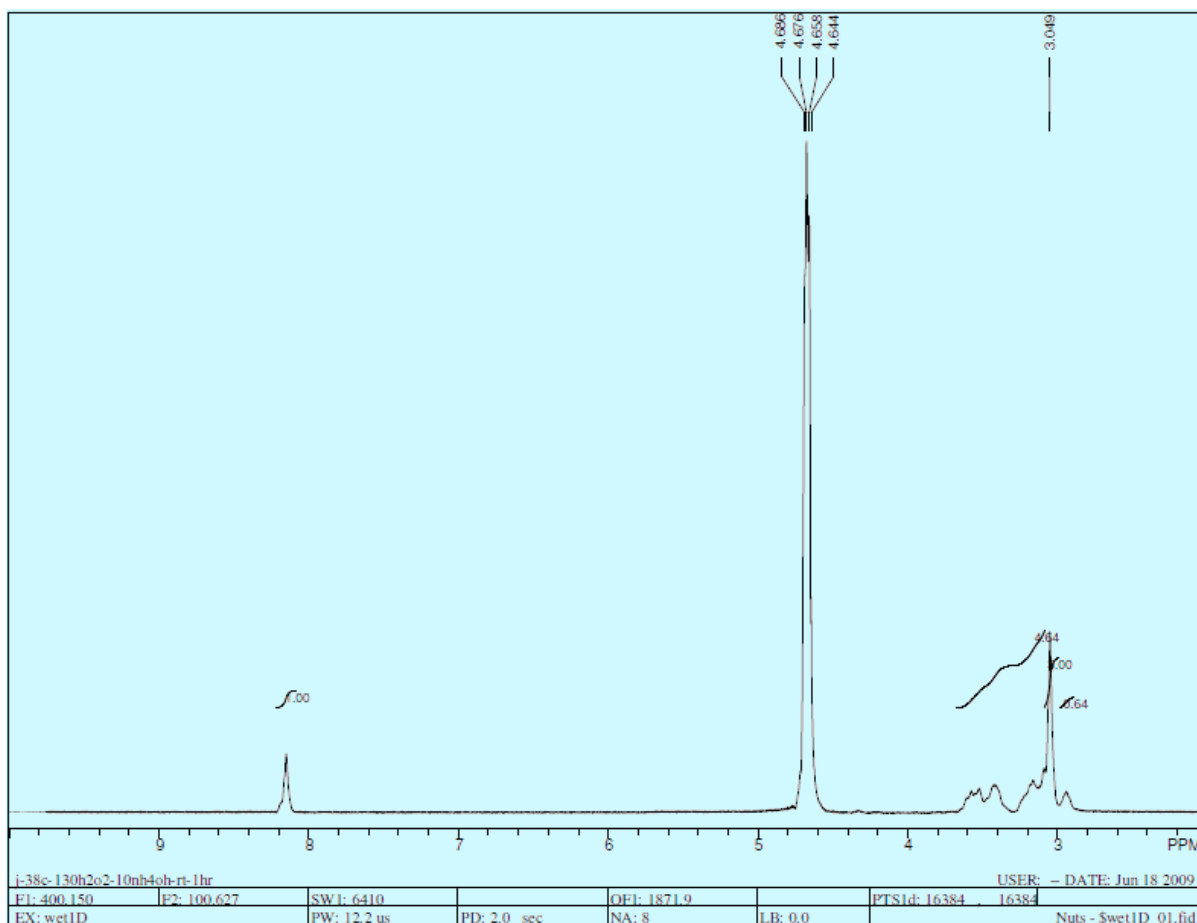
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Details of experiment, NMR spectra.

All the experiments were run in 10 mL vials. Aqueous H₂O₂ (30%) solution was purchased from Mallinckrodt Chemicals and aqueous NH₄OH (25%) solution used was from EMD. MeOH was used as standard to calculate percentage yields. 1,3-Dihydroxyacetone dimer, D-(+)-galactose, D-(+)-cellobiose, D-(+)-xylose, α -D-lactose, D-(+)-maltose monohydrate, D-erythrose, D-(+)-melezitose, D-(+)-raffinose were purchased from Alfa Aesar, D-glucose was from Mallinckrodt chemicals and sucrose was purchased from JT Baker. Wet NMR spectra were recorded on Varian Mercury 400 NMR spectroscopy using water and D₂O mixture as solvent. Known mixture of methanol (1 or 2 μ L) in water was prepared and used for formic acid percentage calculations. Finnpiquette or Hamilton chromatography syringe was used to measure the solvents.

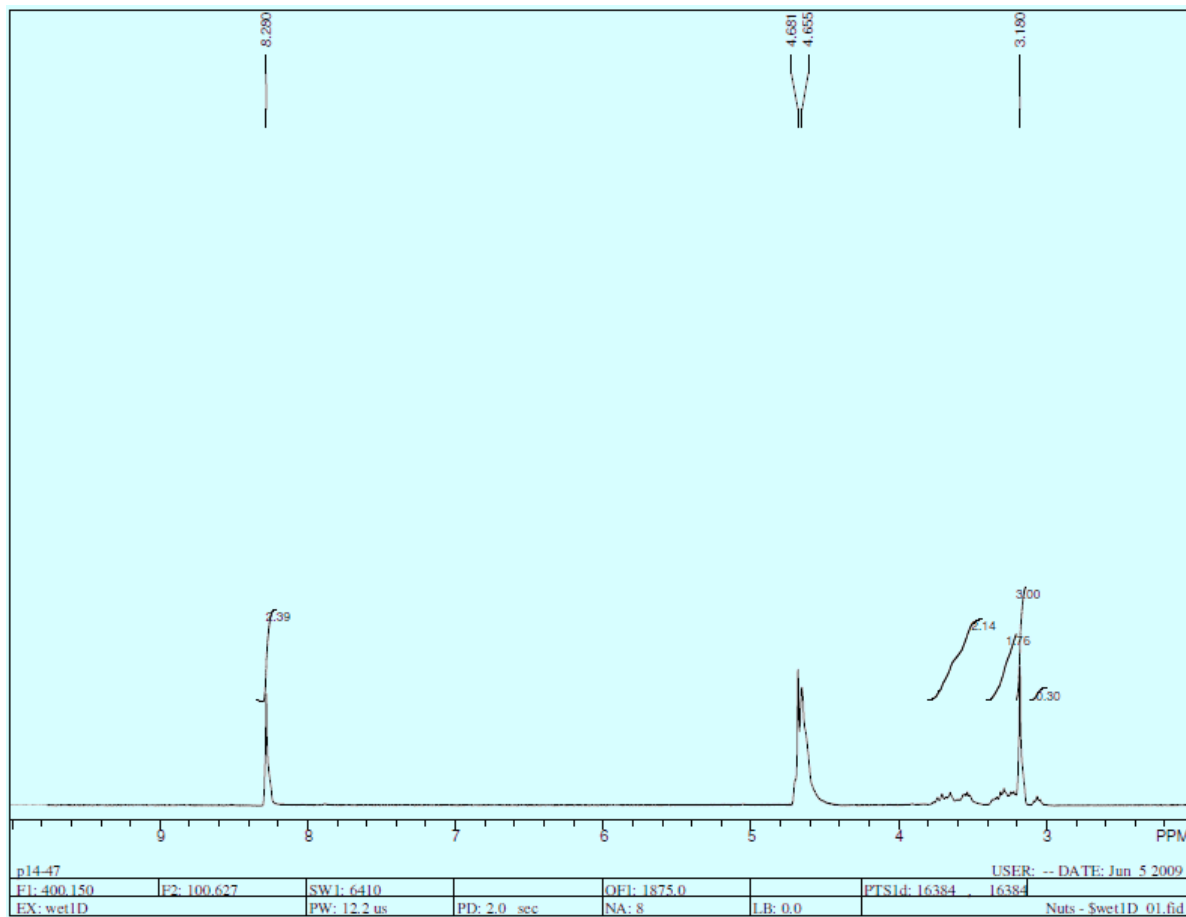
¹H wet 1D NMR of entry 1, Table 1

Glucose (5mg, 0.028 mmole), 130 μ L H₂O₂ and 10 μ L NH₄OH at rt for 1 hr; 1 μ L of MeOH as standard was used for NMR. Formic acid observed was 17 %.



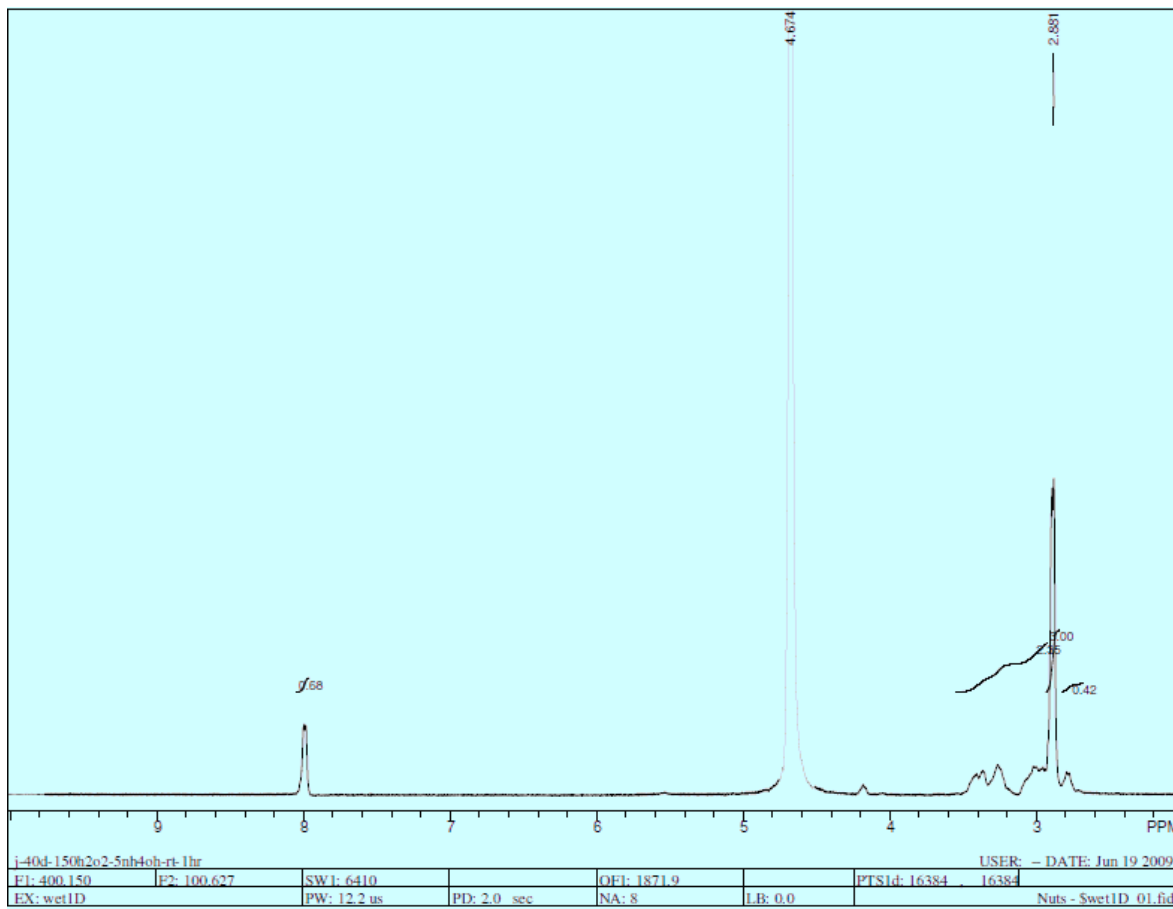
¹H wet 1D NMR of entry 2, Table 1

Glucose (5mg, 0.028 mmole), 130 μL H₂O₂ and 30 μL NH₄OH at rt for 1 hr; 1 μL of MeOH as standard was used for NMR. Formic acid observed was 41 %.



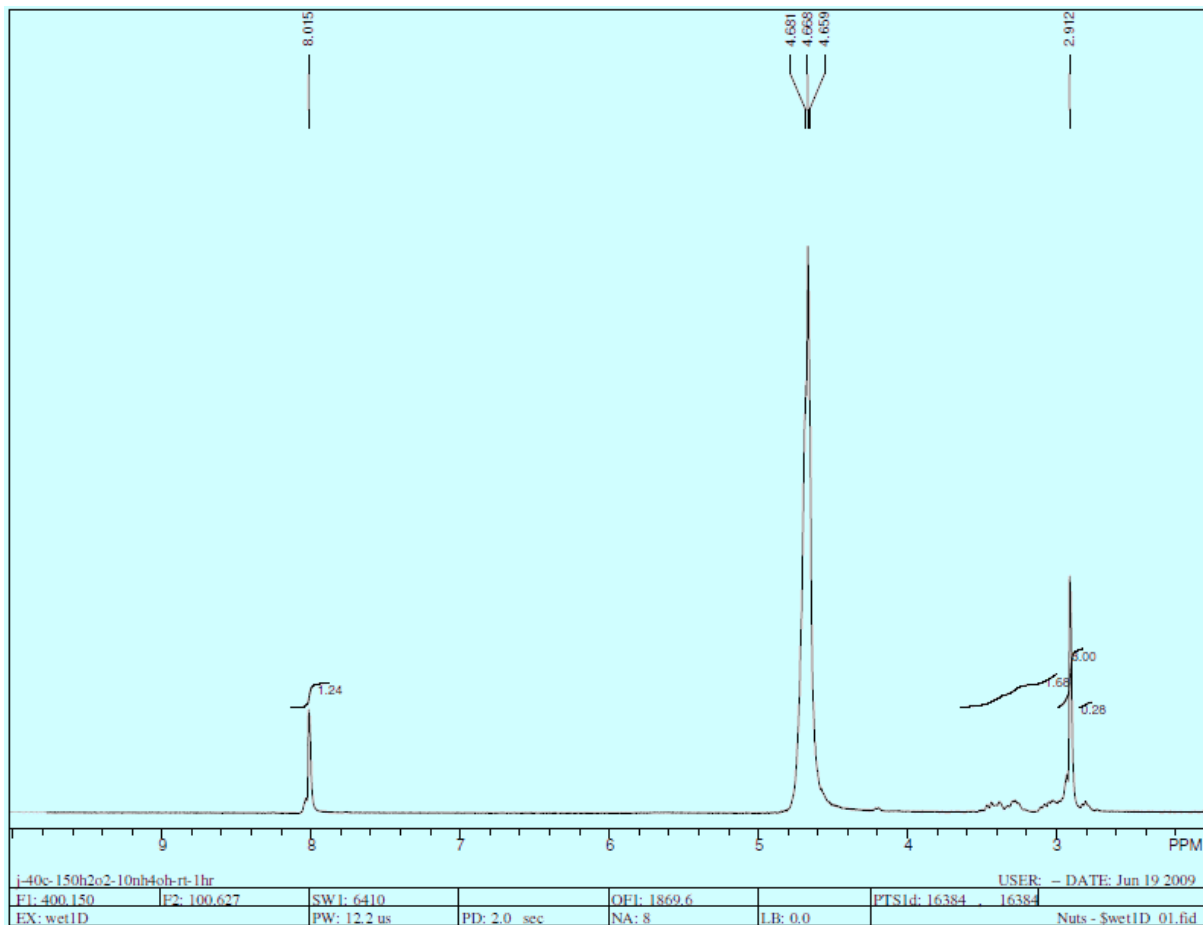
¹H wet 1D NMR of entry 3, Table 1

Glucose (5mg, 0.028 mmole), 150 μ L H₂O₂ and 5 μ L NH₄OH at rt for 1 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 23 %.



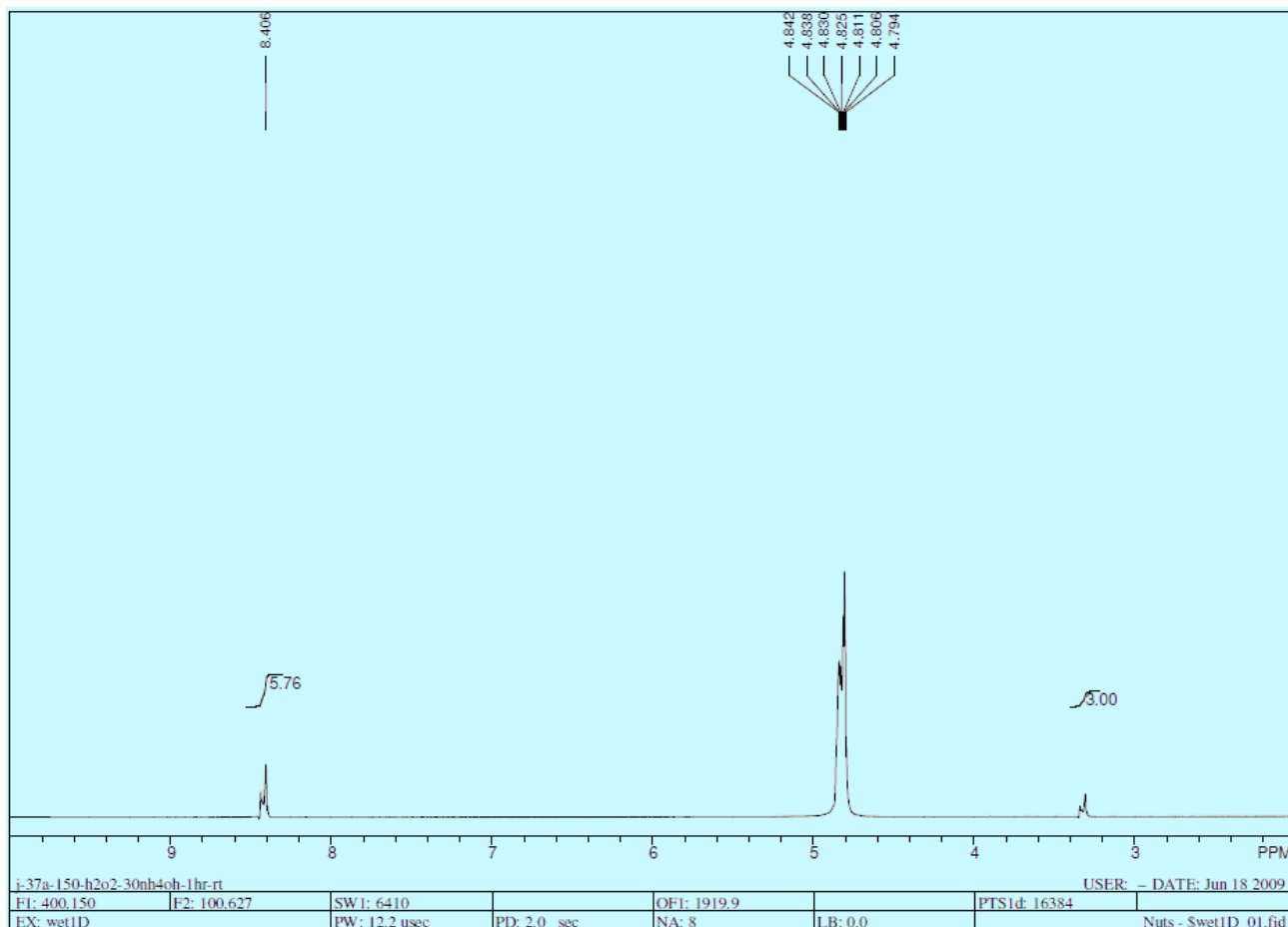
¹H wet 1D NMR of entry 4, Table 1.

Glucose (5mg, 0.028 mmole), 150 μ L H₂O₂ and 10 μ L NH₄OH at rt for 1 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 44 %.



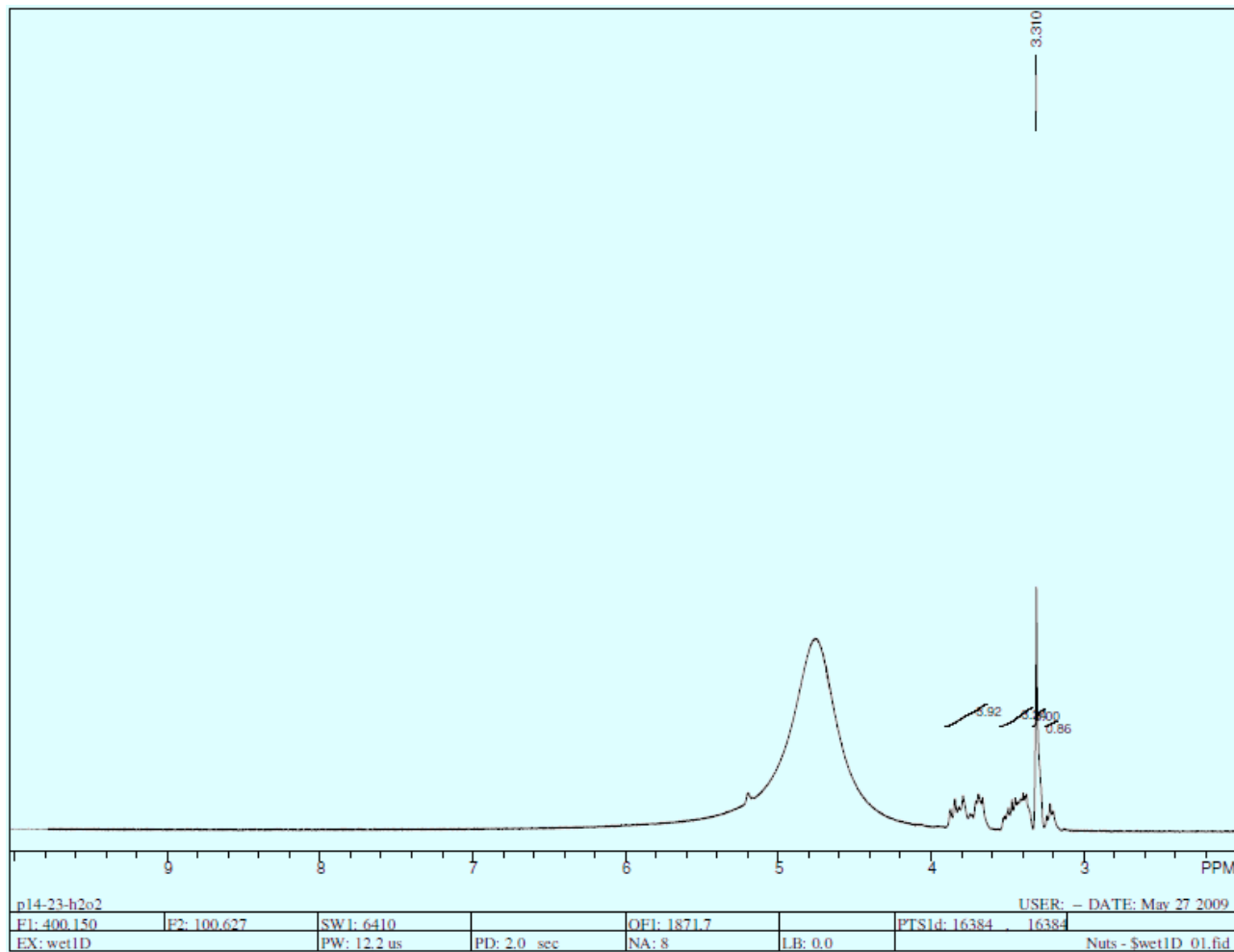
¹H wet 1D NMR of entry 5, Table 1 and entry 4, Table 2

Glucose (5mg, 0.028 mmole), 150 μ L H₂O₂ and 30 μ L NH₄OH at rt for 1 hr; 1 μ L of MeOH as standard was used for NMR. Formic acid observed was 99 %.



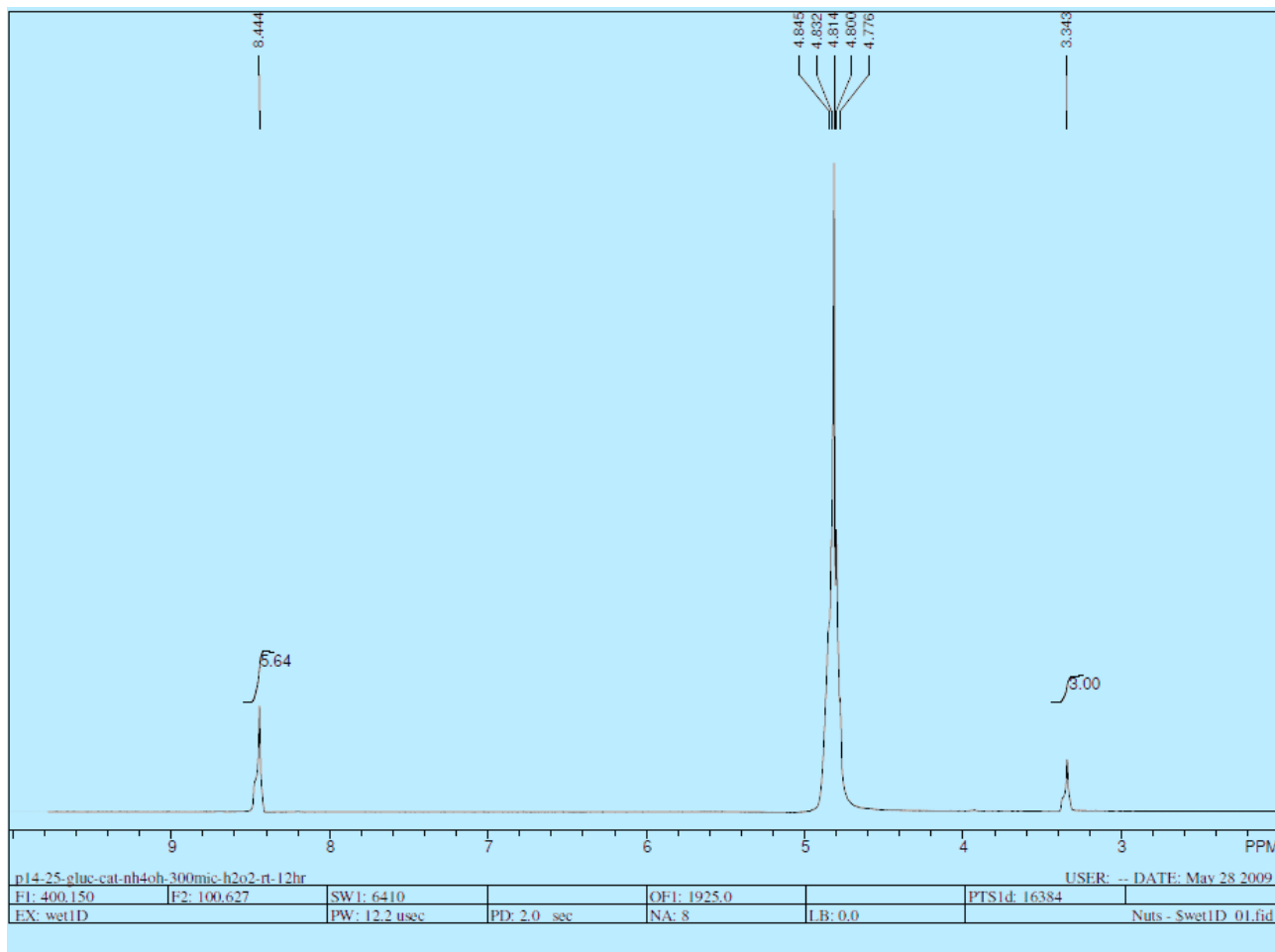
¹H wet 1D NMR of entry 6, Table 1

Glucose (5mg, 0.028 mmole), 300 μ L H₂O₂ and without NH₄OH at rt for 1 hr; 1 μ L of MeOH as standard was used for NMR. Formic acid observed was 0%.

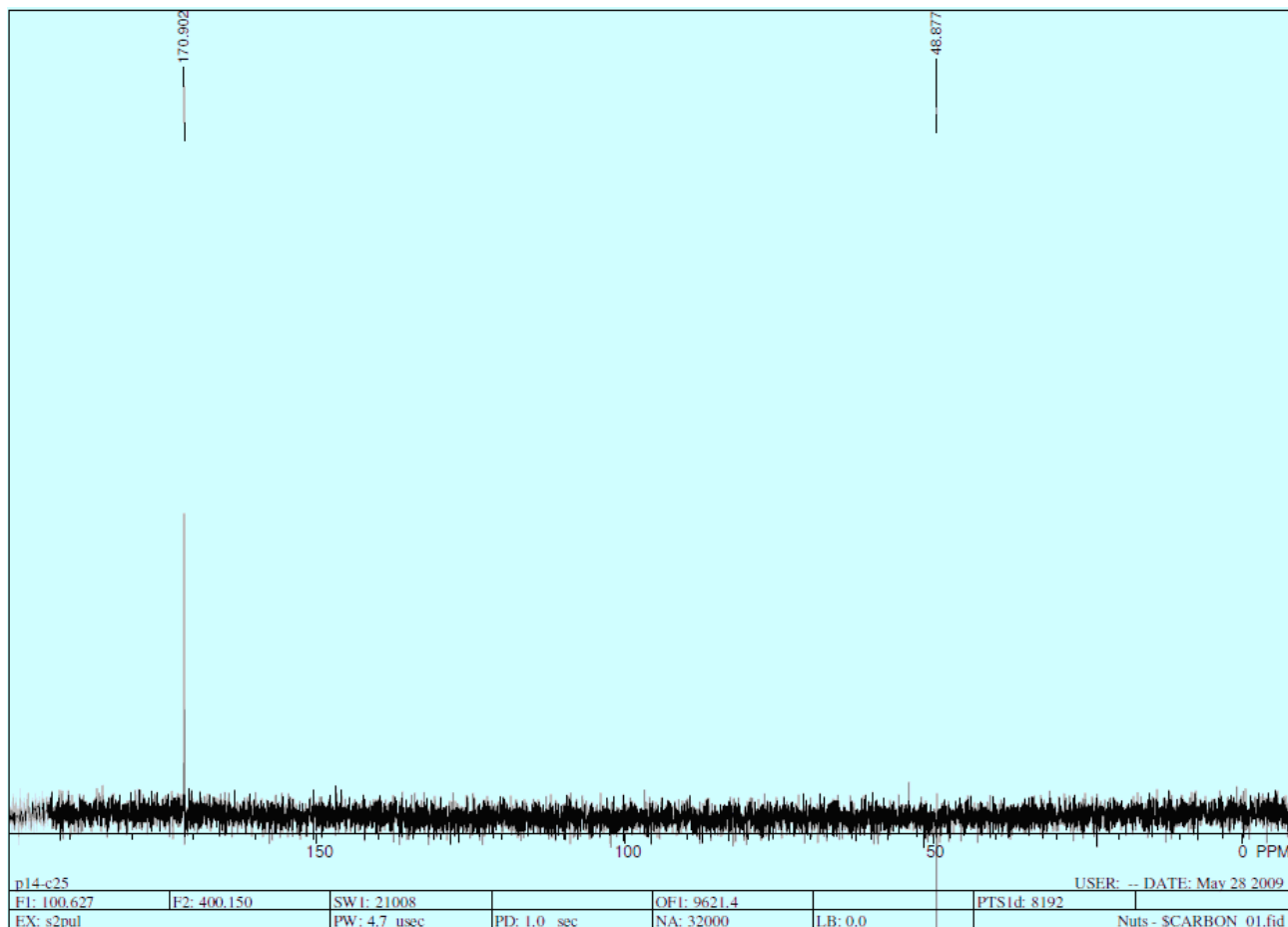


¹H wet 1D NMR of entry 7, Table 1

Glucose (5mg, 0.028 mmole), 300 μ L H₂O₂ and 30 μ L NH₄OH at rt for 24 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 99%.

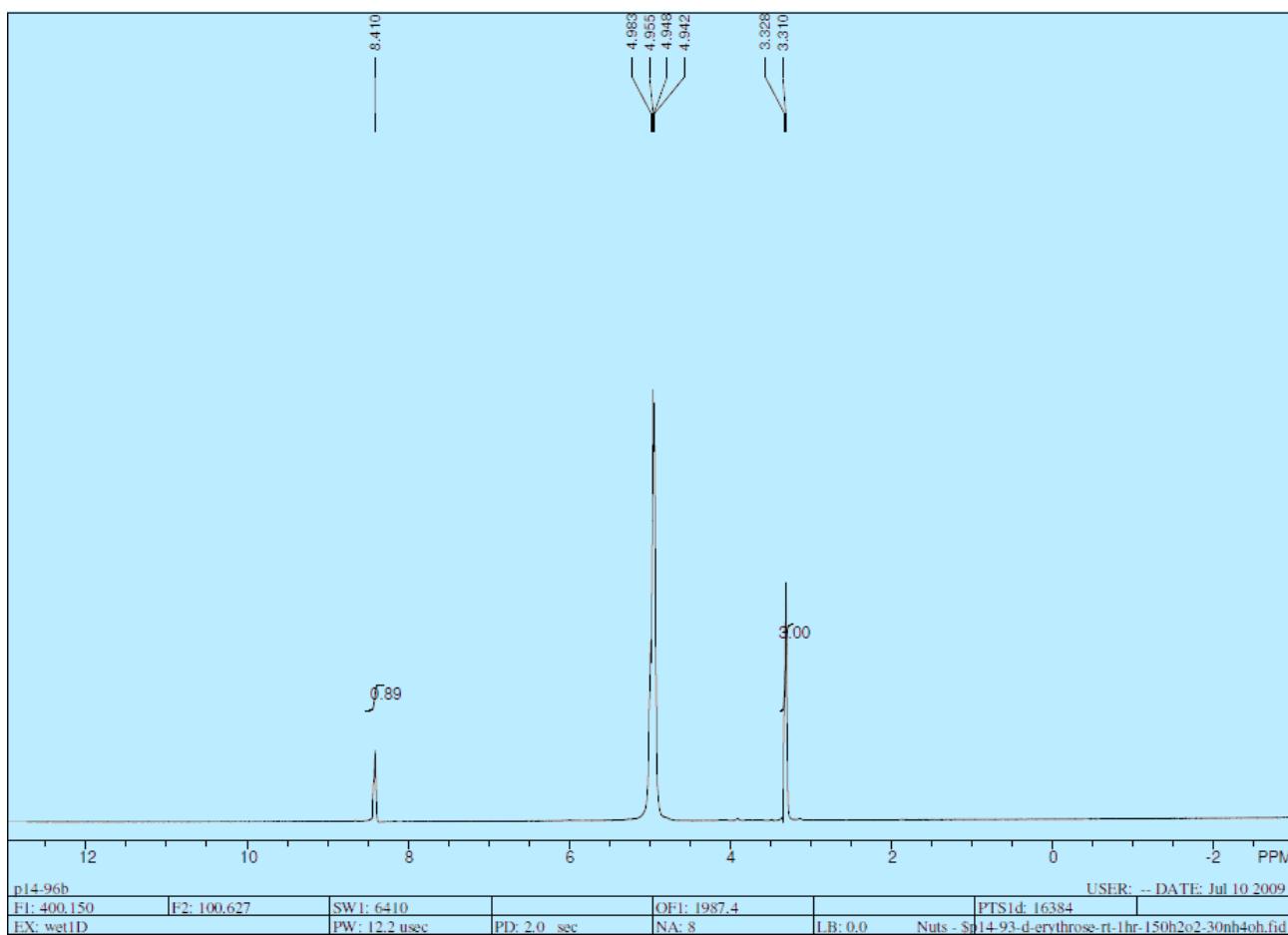


¹³C NMR of entry 7, Table 1



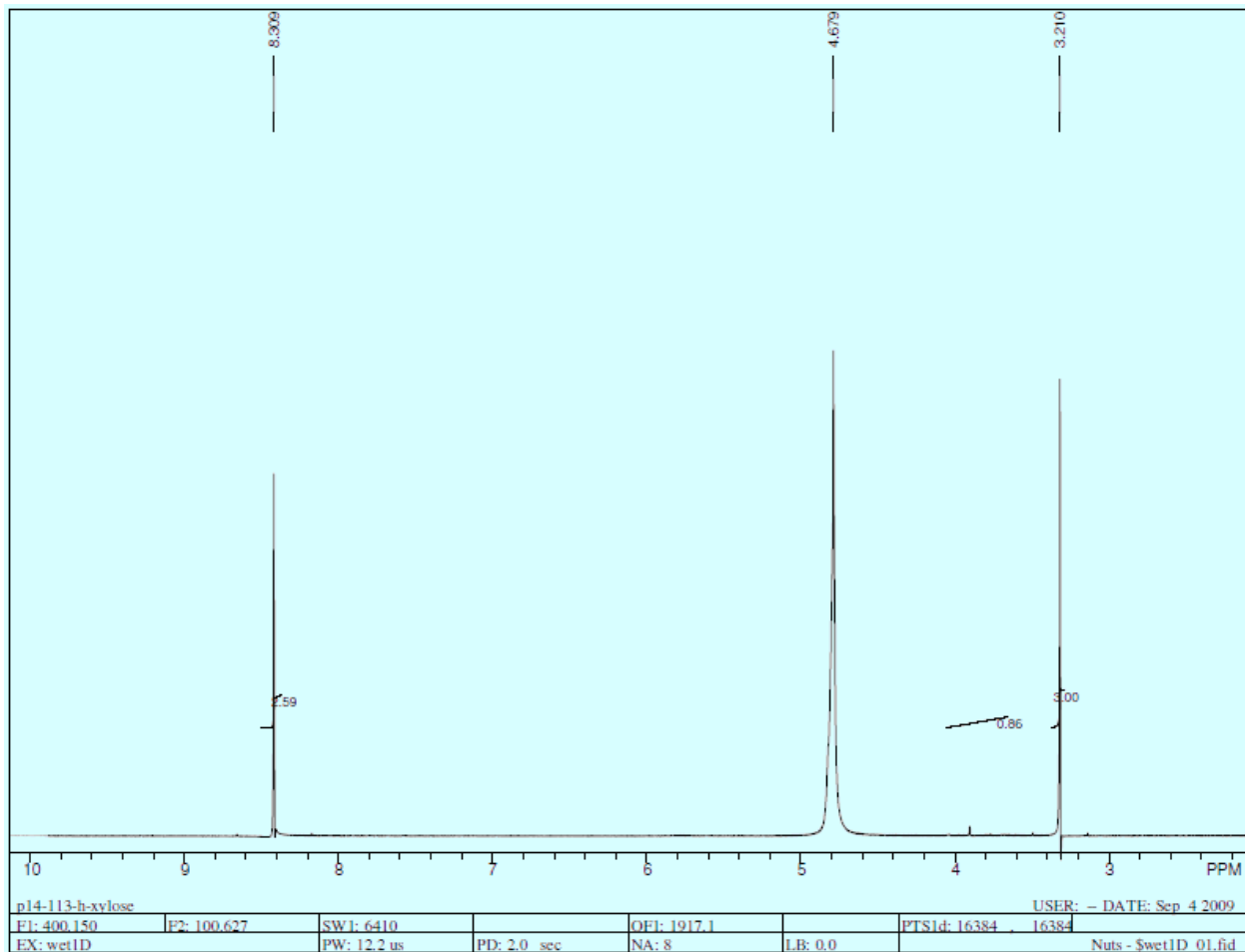
¹H wet 1D NMR of entry 1, Table 2

Erythrose (0.042 mmol), 150 μ L H₂O₂ and 30 μ L NH₄OH at rt for 1 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 32%.



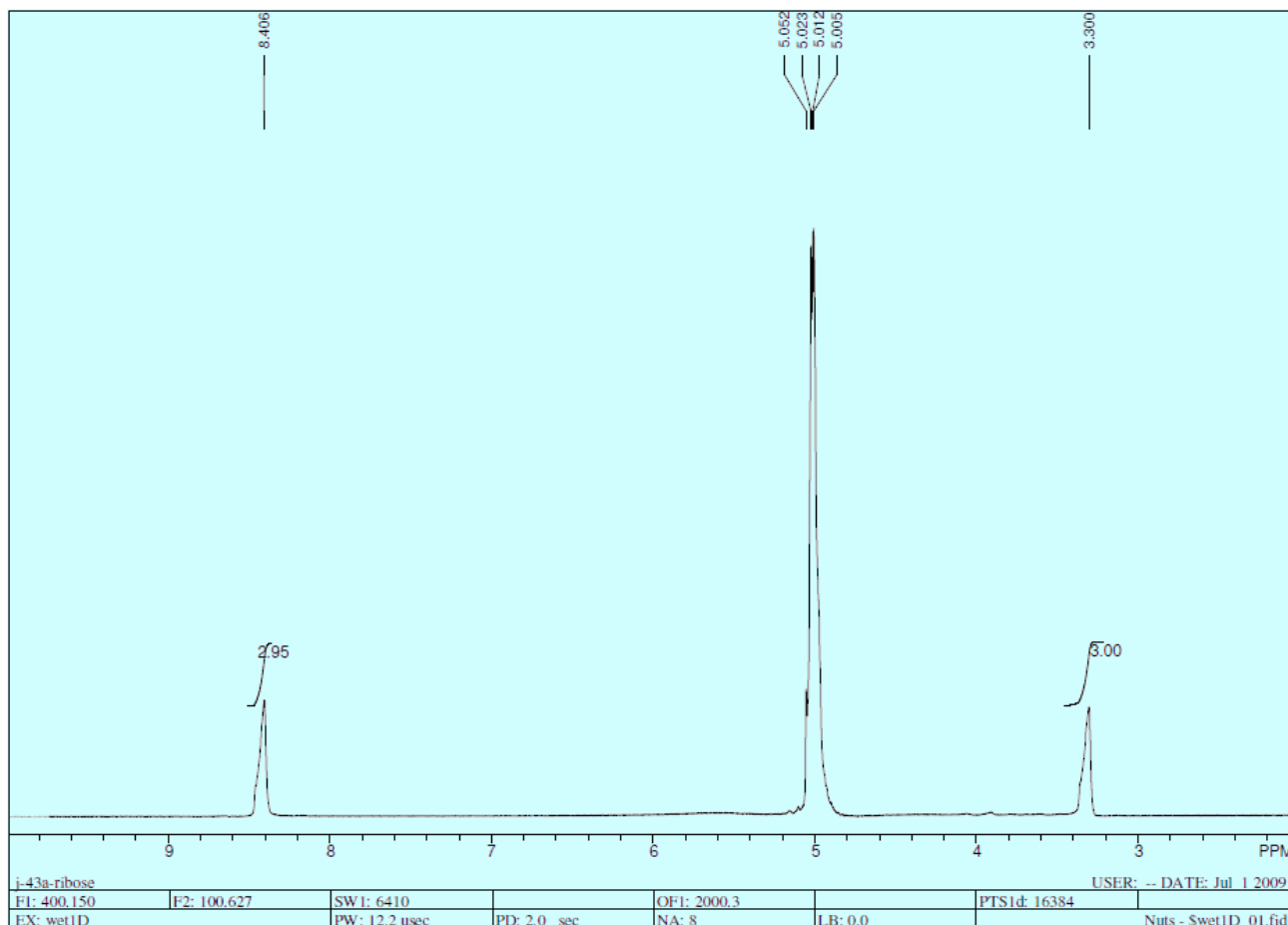
¹H wet 1D NMR of entry 2, Table 2.

Xylose (0.013 mmole (1hr) 150 μ L H₂O₂ and 30 μ L NH₄OH at RT for 1 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 92%.



¹H wet 1D NMR of entry 3, Table 2.

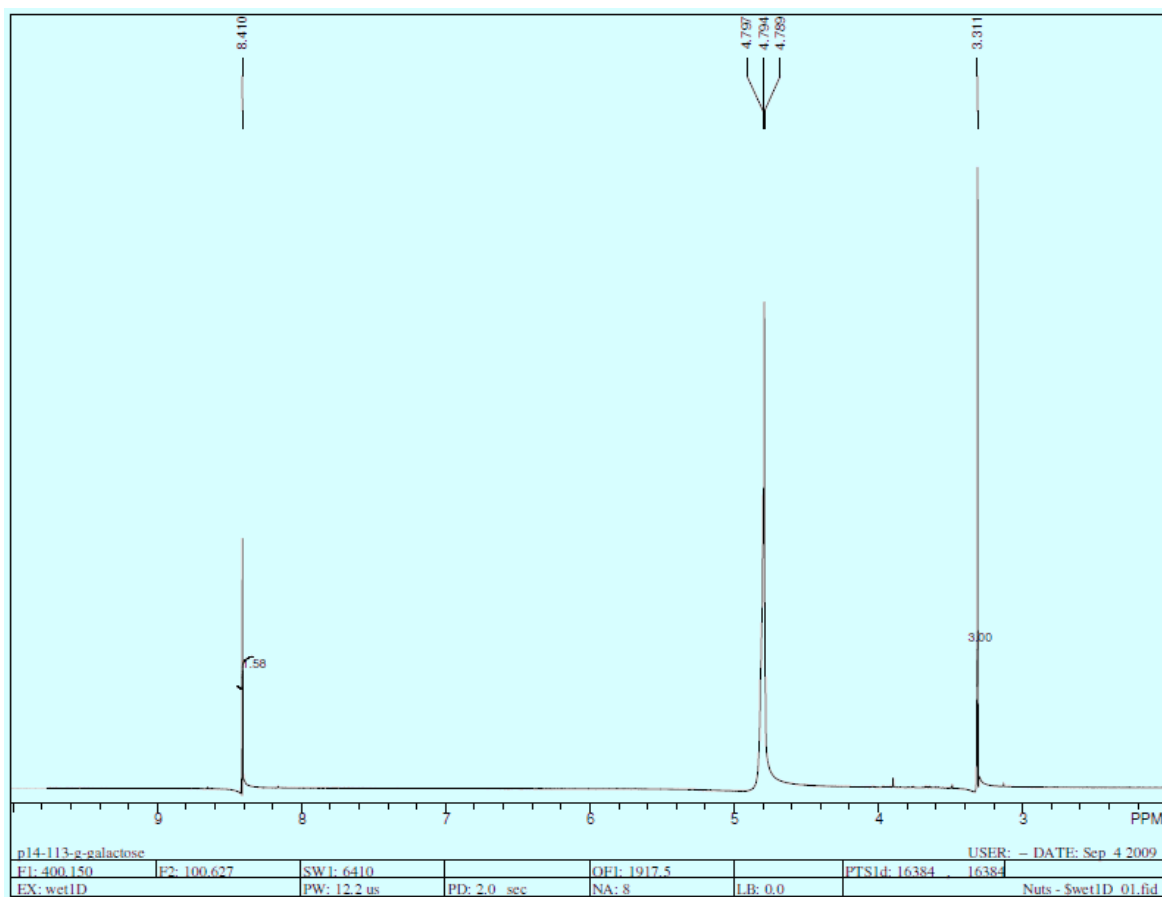
Ribose (0.033 mmole) 150 μ L H₂O₂ and 30 μ L NH₄OH at RT for 1 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was ~99%.



¹H wet 1D NMR of entry 4, Table 2 is same as the entry 5, Table 1

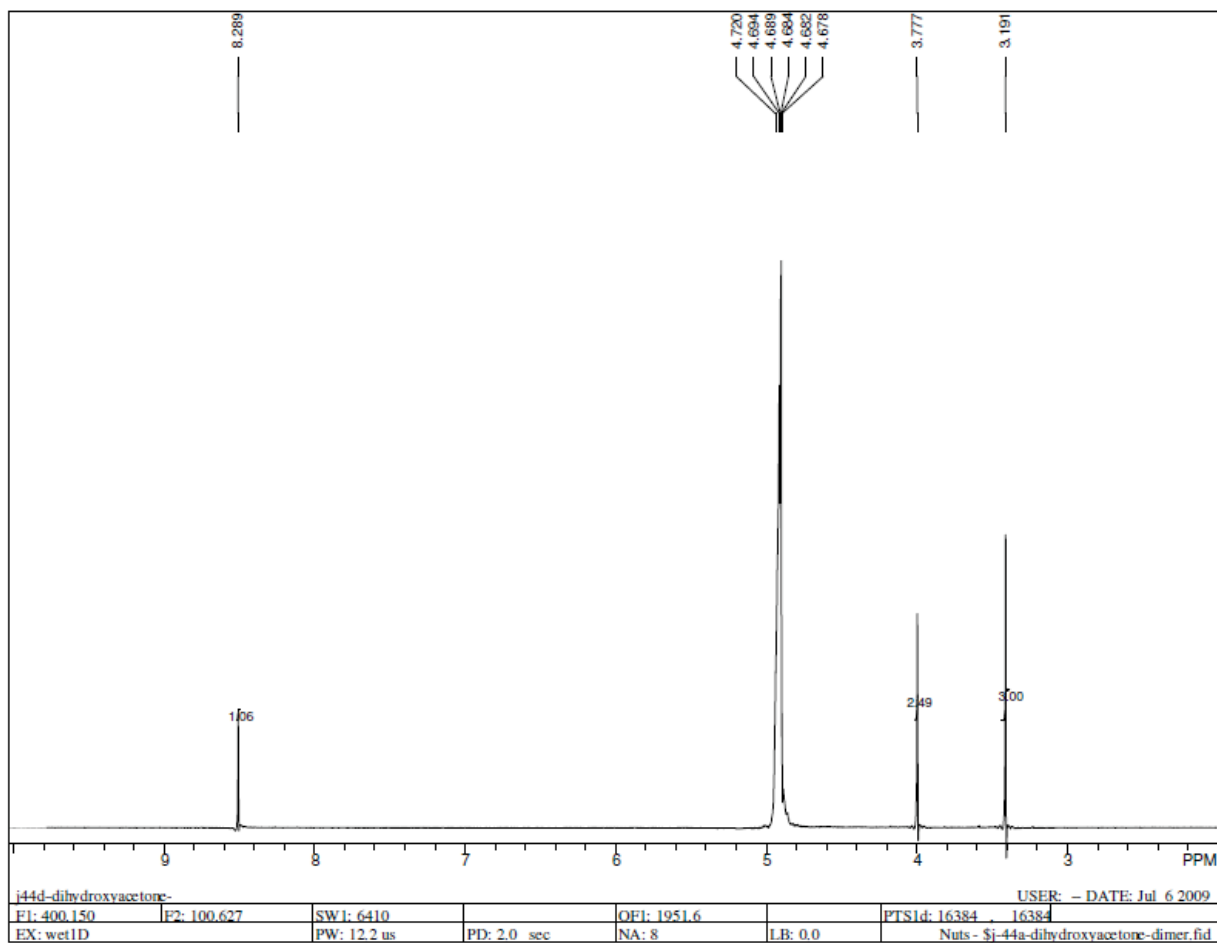
¹H wet 1D NMR of entry 5, Table 2

Galactose (0.005gm, 0.028 mmol), 150 μ L H₂O₂ and 30 μ L NH₄OH at RT for 1 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 93%



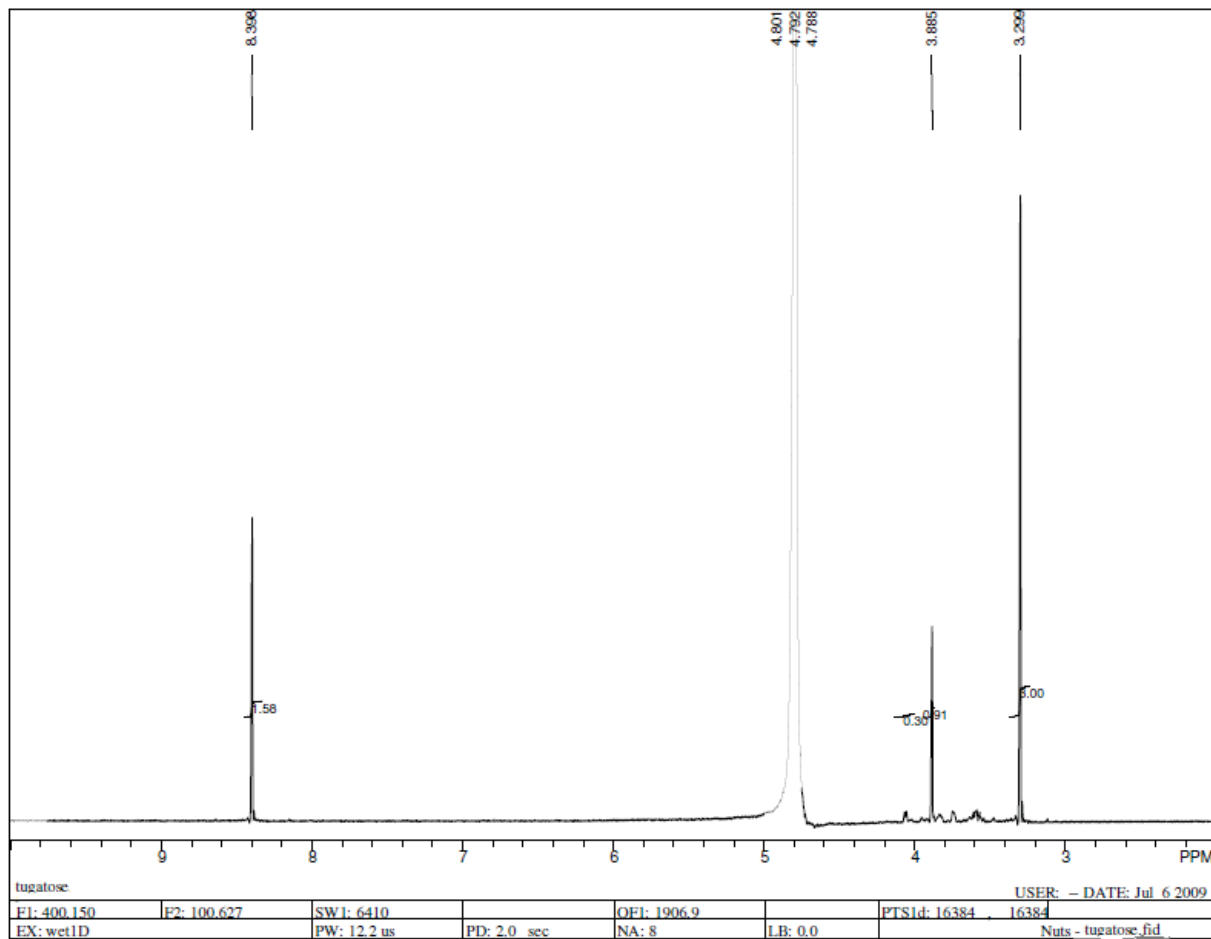
¹H wet 1D NMR of entry 6, Table 2

Dihydroxyacetone (0.005 gm, 0.056 mmol), 150 μL H₂O₂ and 30 μL NH₄OH at RT for 1 hr; 2 μL of MeOH as standard was used for NMR. Formic acid observed was ~99%

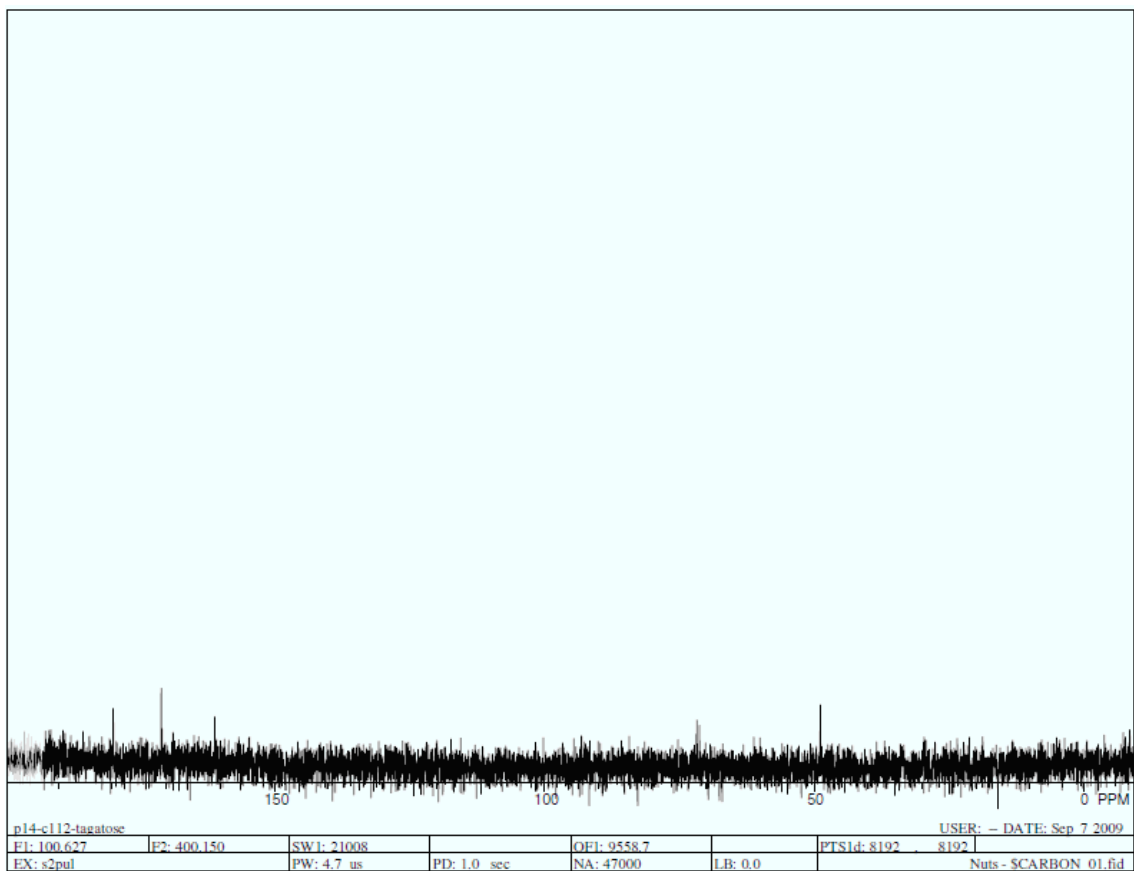


¹H wet 1D NMR of entry 7, Table 2

Tagatose (0.005 gm, 0.028 mmol) 150 μL H₂O₂ and 30 μL NH₄OH at RT for 1 hr; 2 μL of MeOH as standard was used for NMR. Formic acid observed was 83%.

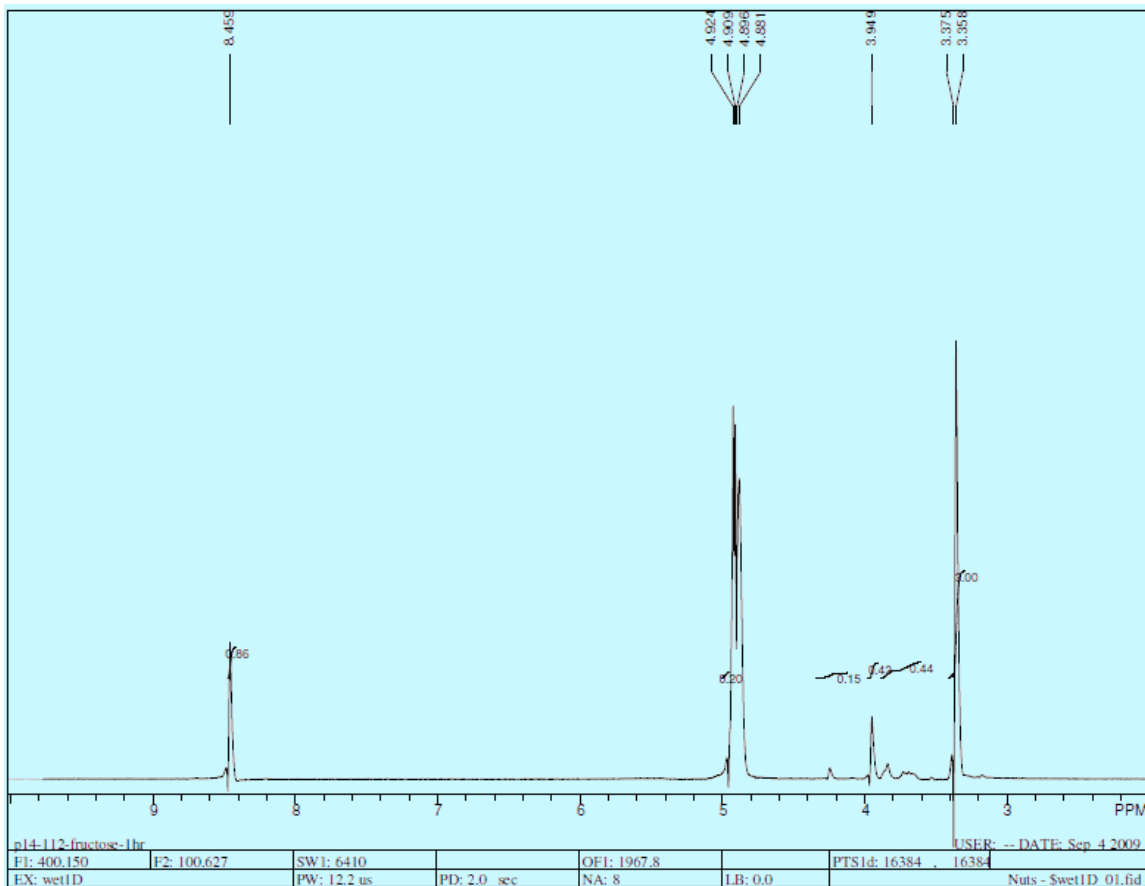


¹³C NMR of entry 7, Table 2

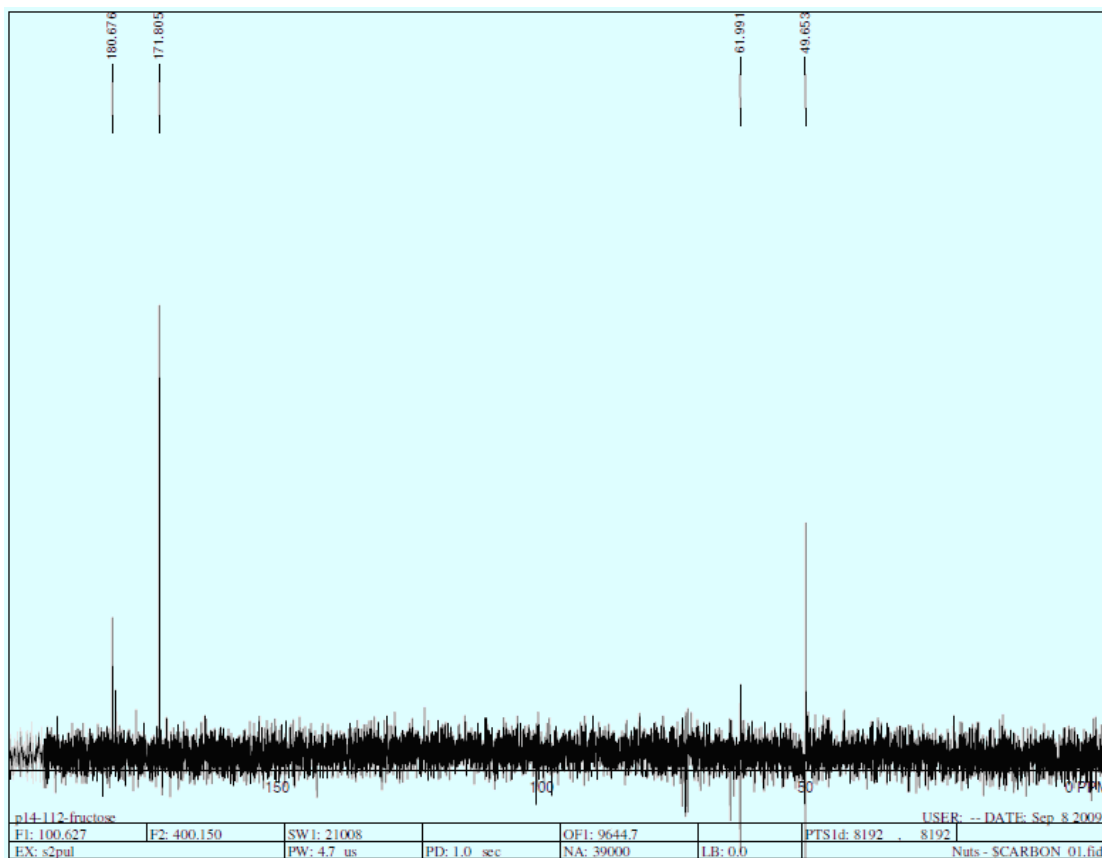


¹H wet 1D NMR of entry 8, Table 2

Fructose (0.005 gm, 0.28 mmol) 150 μL H₂O₂ and 30 μL NH₄OH at RT for 1 hr; 2 μL of MeOH as standard was used for NMR. Formic acid observed was 46%.

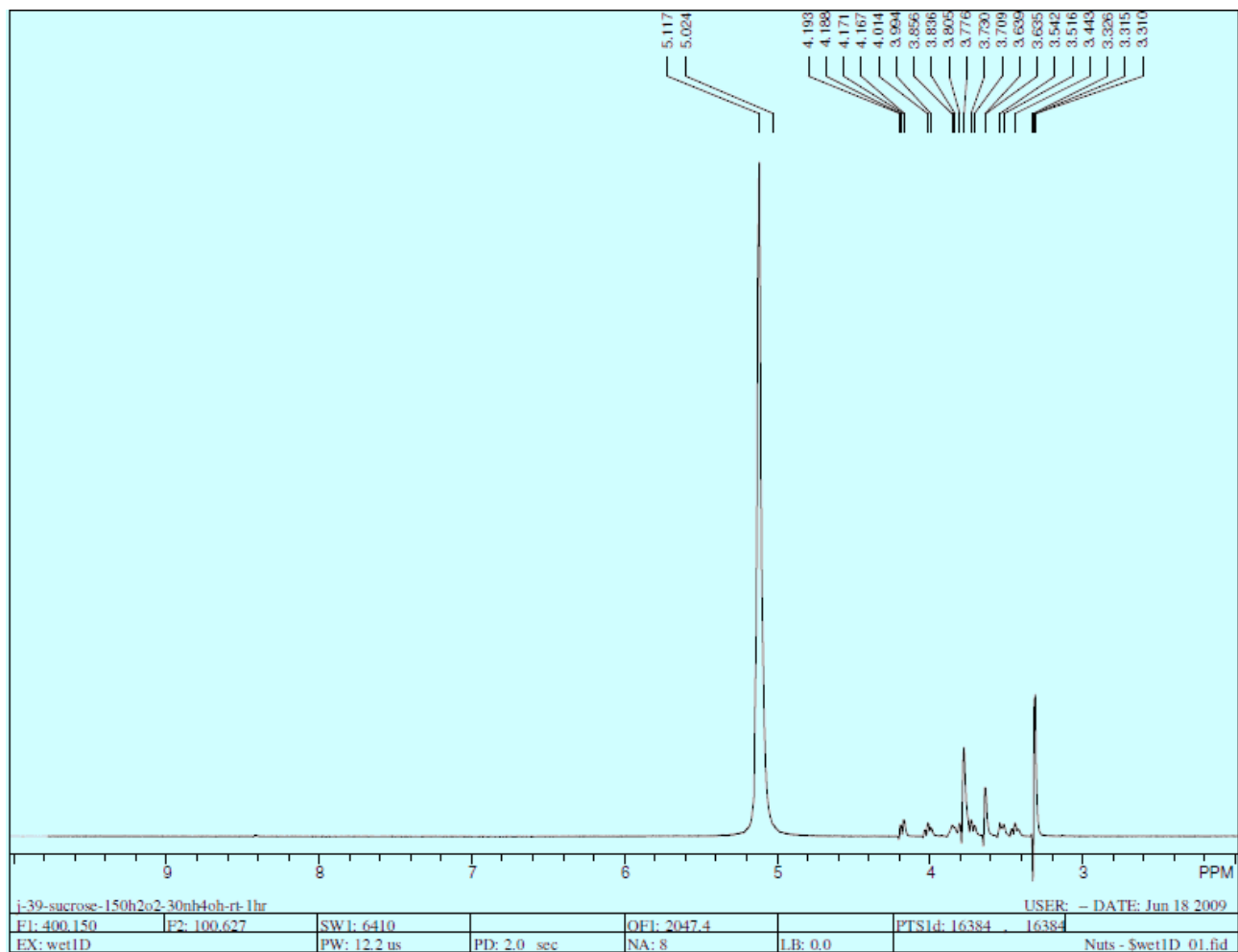


¹³C NMR of entry 8, Table 2.



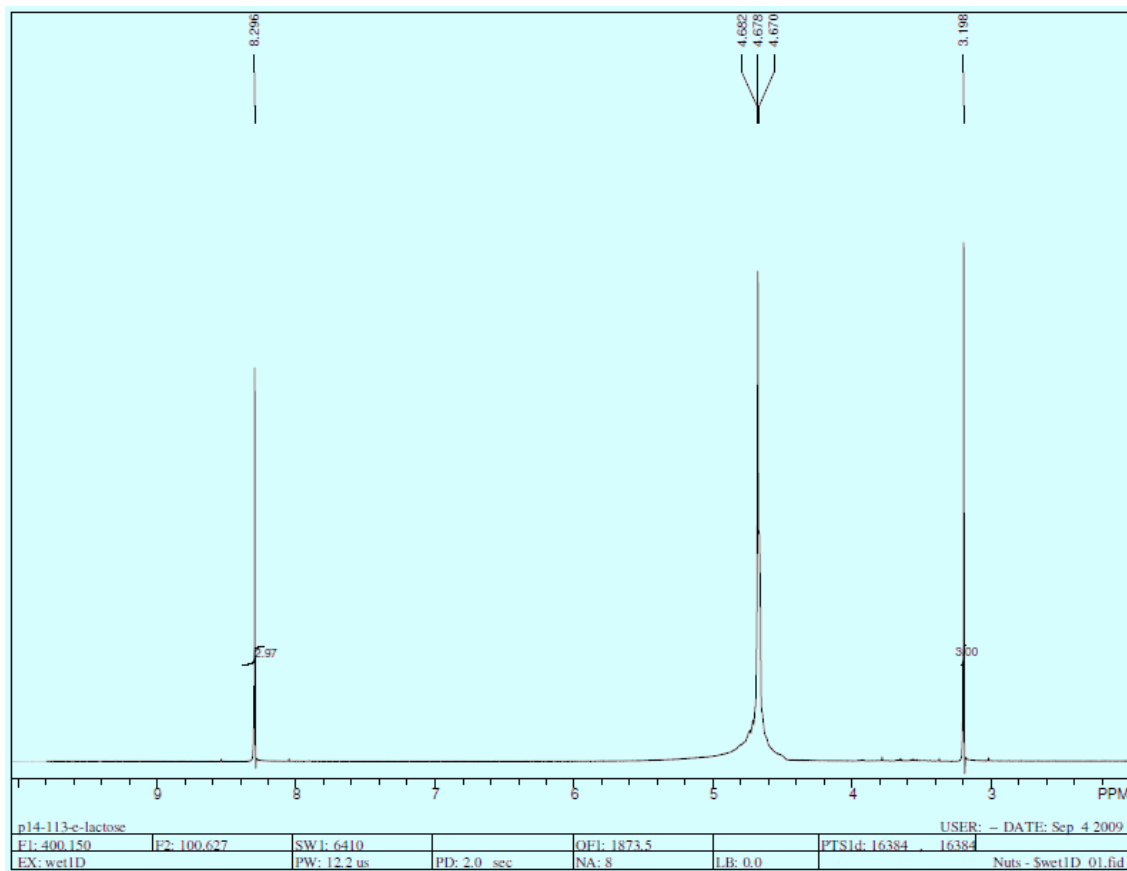
¹H wet 1D NMR of entry 9, Table 2

Sucrose (0.005gm, *mmol*), 150 μ L H₂O₂ and 30 μ L NH₄OH at RT for 1 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 0%.



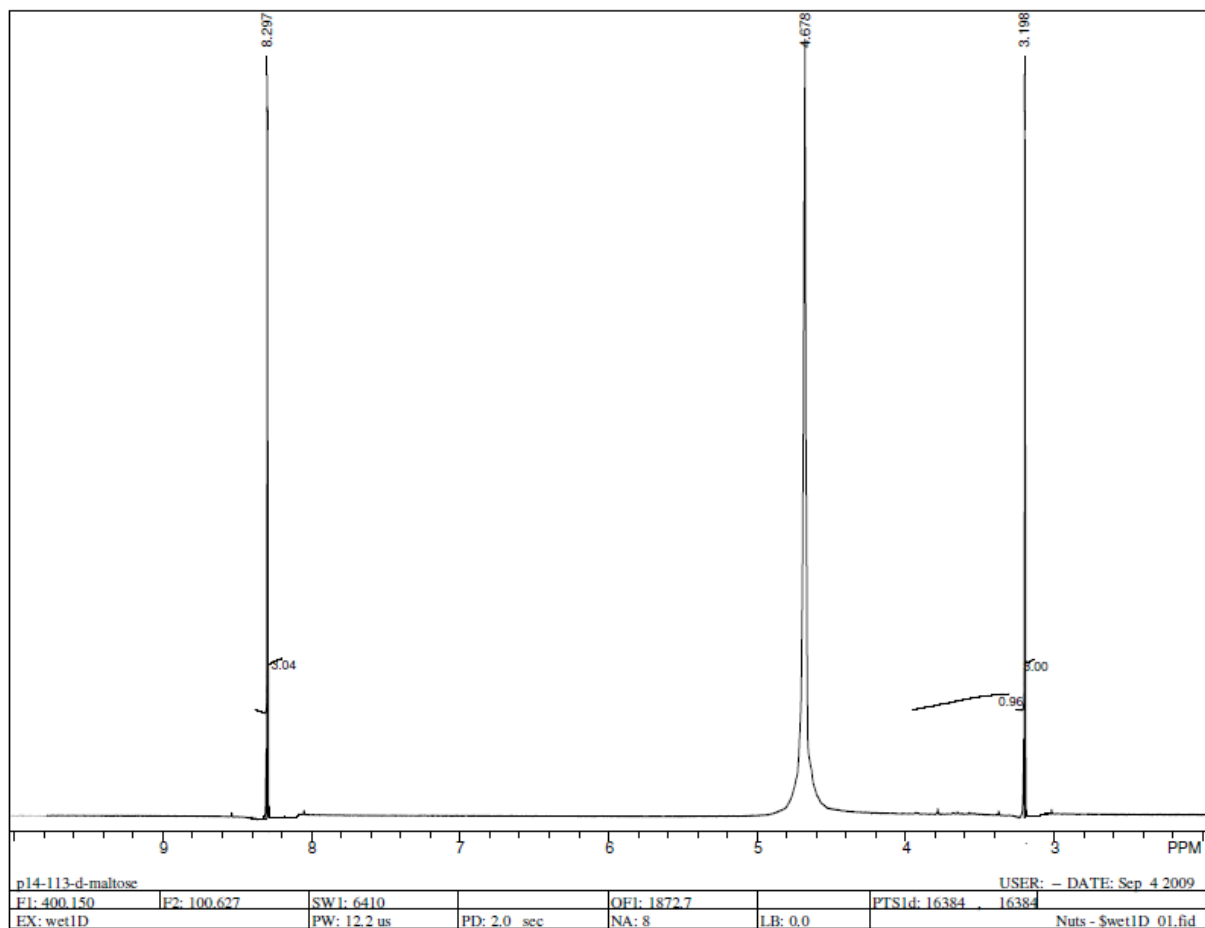
¹H wet 1D NMR of entry 10, Table 2.

α -D-Lactose (0.005 gm, 0.015 mmol), 150 μ L H₂O₂ and 30 μ L NH₄OH at RT for 24 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 99%



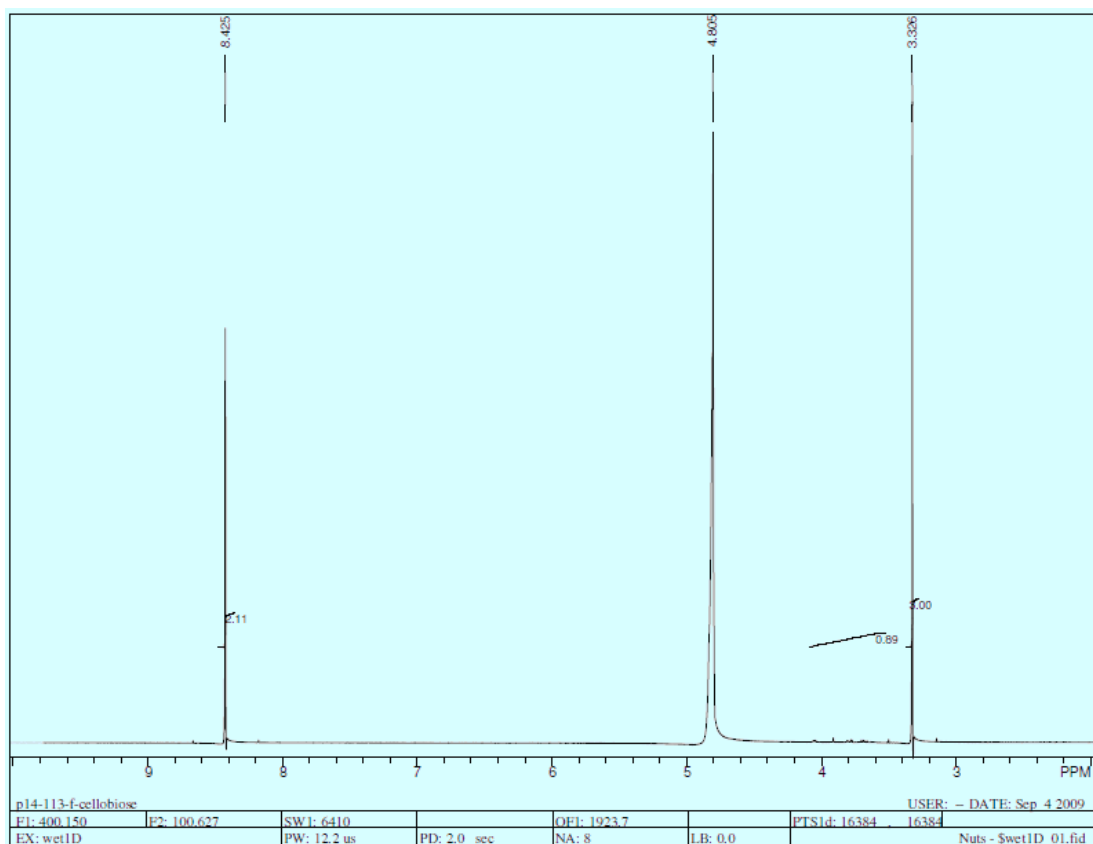
¹H wet 1D NMR of entry 11, Table 2.

Maltose (0.005 gm, 0.015 mmol), 150 μL H₂O₂ and 30 μL NH₄OH at RT for 24 hr; 2 μL of MeOH as standard was used for NMR. Formic acid observed was 99%.



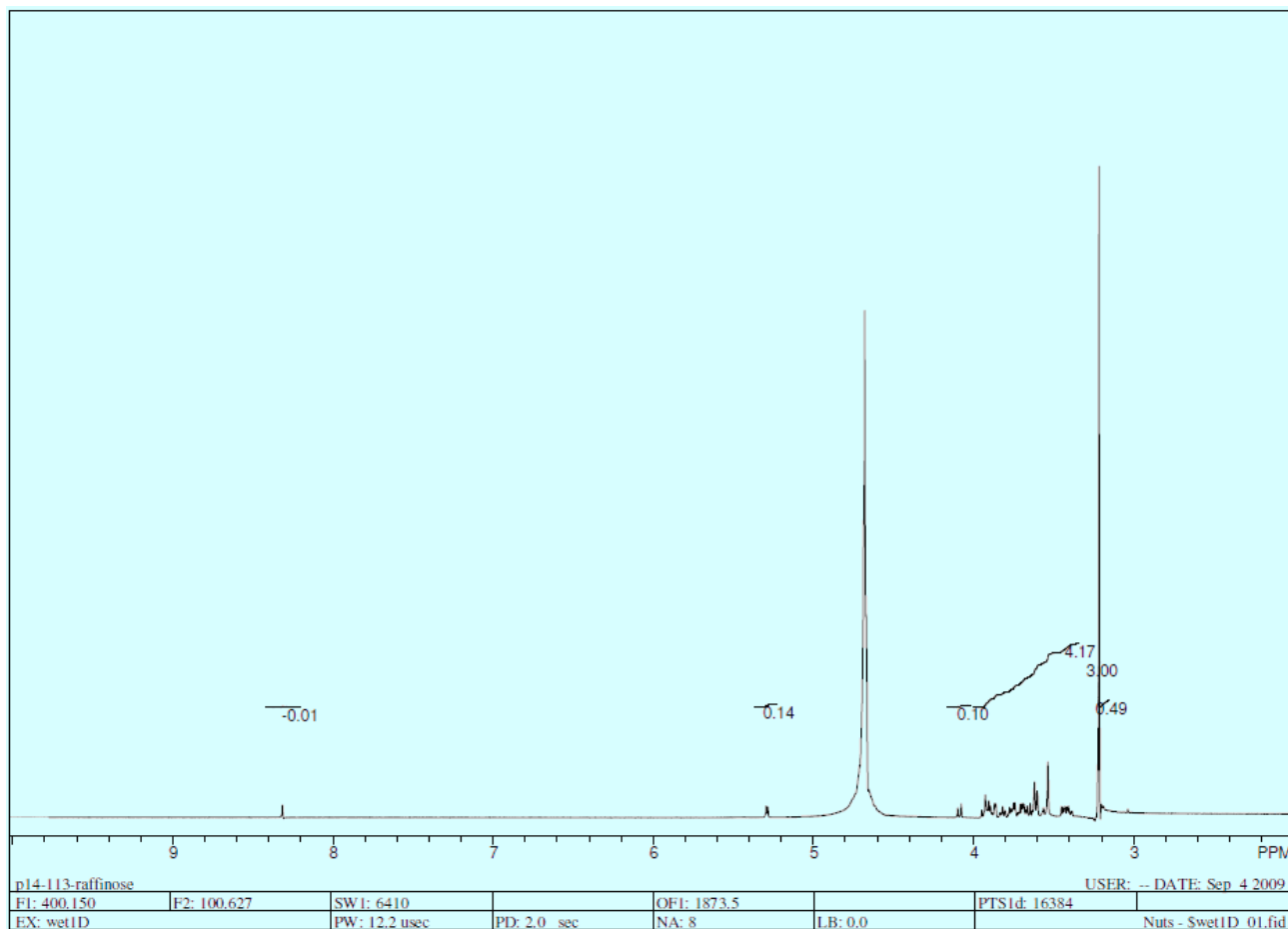
¹H wet 1D NMR of entry 12, Table 2.

Cellobiose (0.005 gm, 0.015 mmol), 150 μL H₂O₂ and 30 μL NH₄OH at RT for 24 hr; 2 μL of MeOH as standard was used for NMR. Formic acid observed was 70%.



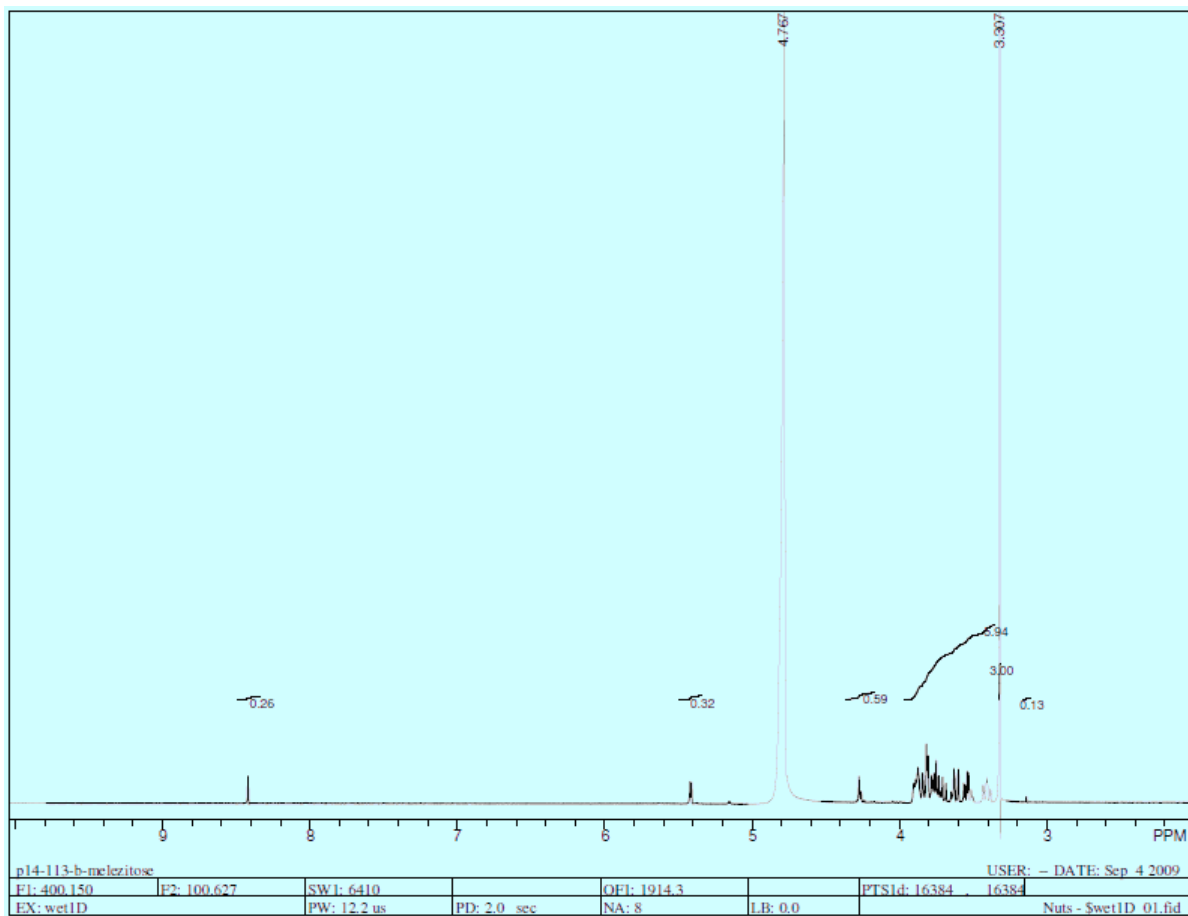
¹H wet 1D NMR of entry 13, Table 2

Raffinose (0.005 gm, 0.01 mmol) 150 μL H₂O₂ and 30 μL NH₄OH at RT for 24 hr; 2 μL of MeOH as standard was used for NMR. Formic acid observed was 0%.

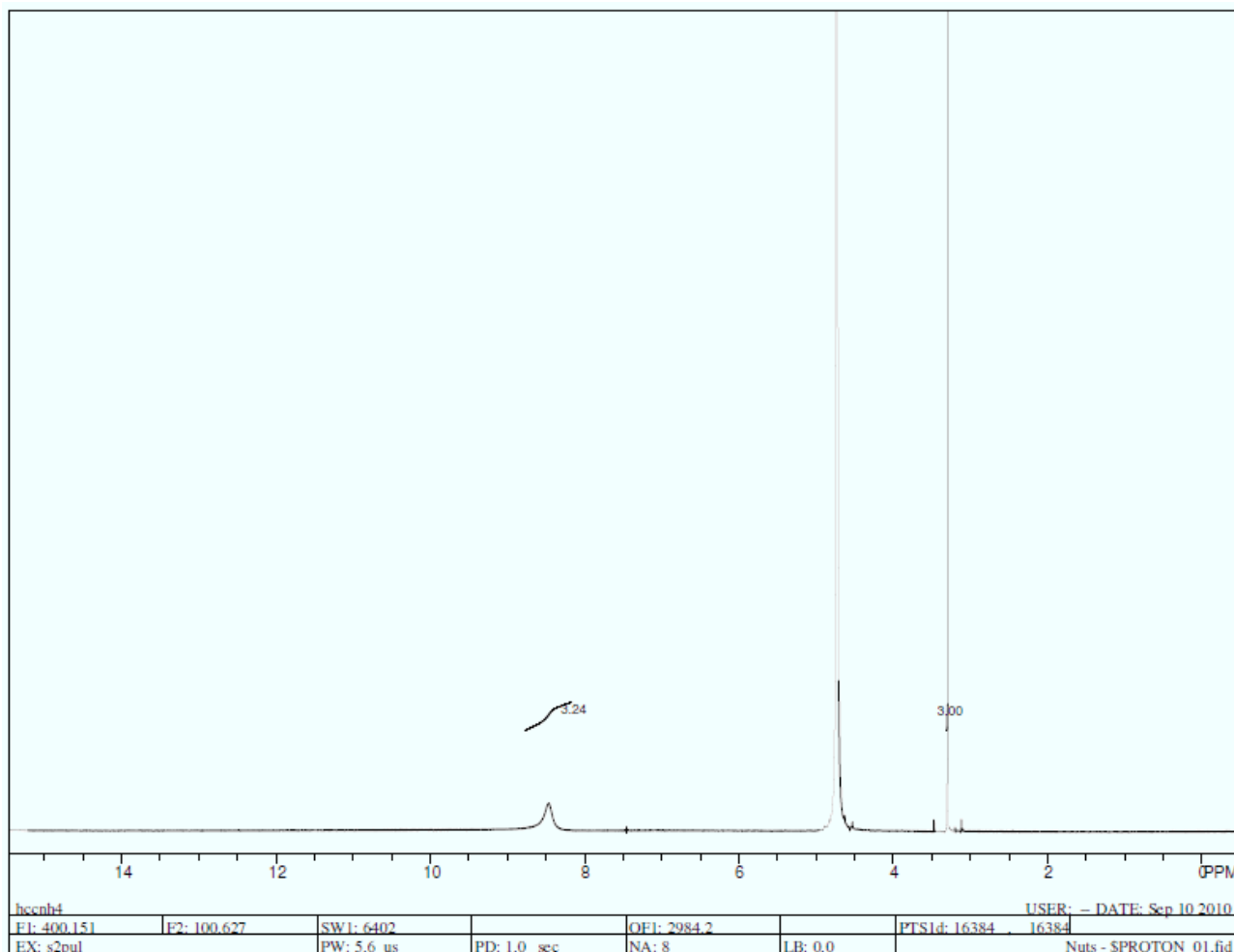


¹H wet 1D NMR of entry 14, Table 2

Melezitose (0.005 gm, 0.01 mmol) 150 μ L H₂O₂ and 30 μ L NH₄OH at RT for 24 hr; 2 μ L of MeOH as standard was used for NMR. Formic acid observed was 26%.



¹H wet 1D NMR of ammonium formate (10 mg, 1.59x10⁻⁴ moles) (20 μL of solution was used for NMR as a methanol standard corresponding to 2μL MeOH from a solution of 20 μL methanol in 180 μL D₂O mixture)



^1H NMR of mixture of formic acid (10 μL) and ammonium formate (6.9 mg, 1.09×10^{-3} moles)

