

Supplementary Information

An enzyme-initiated Smiles rearrangement enables the development of an assay of MshB, the GlcNAc-Ins deacetylase of mycothiol biosynthesis

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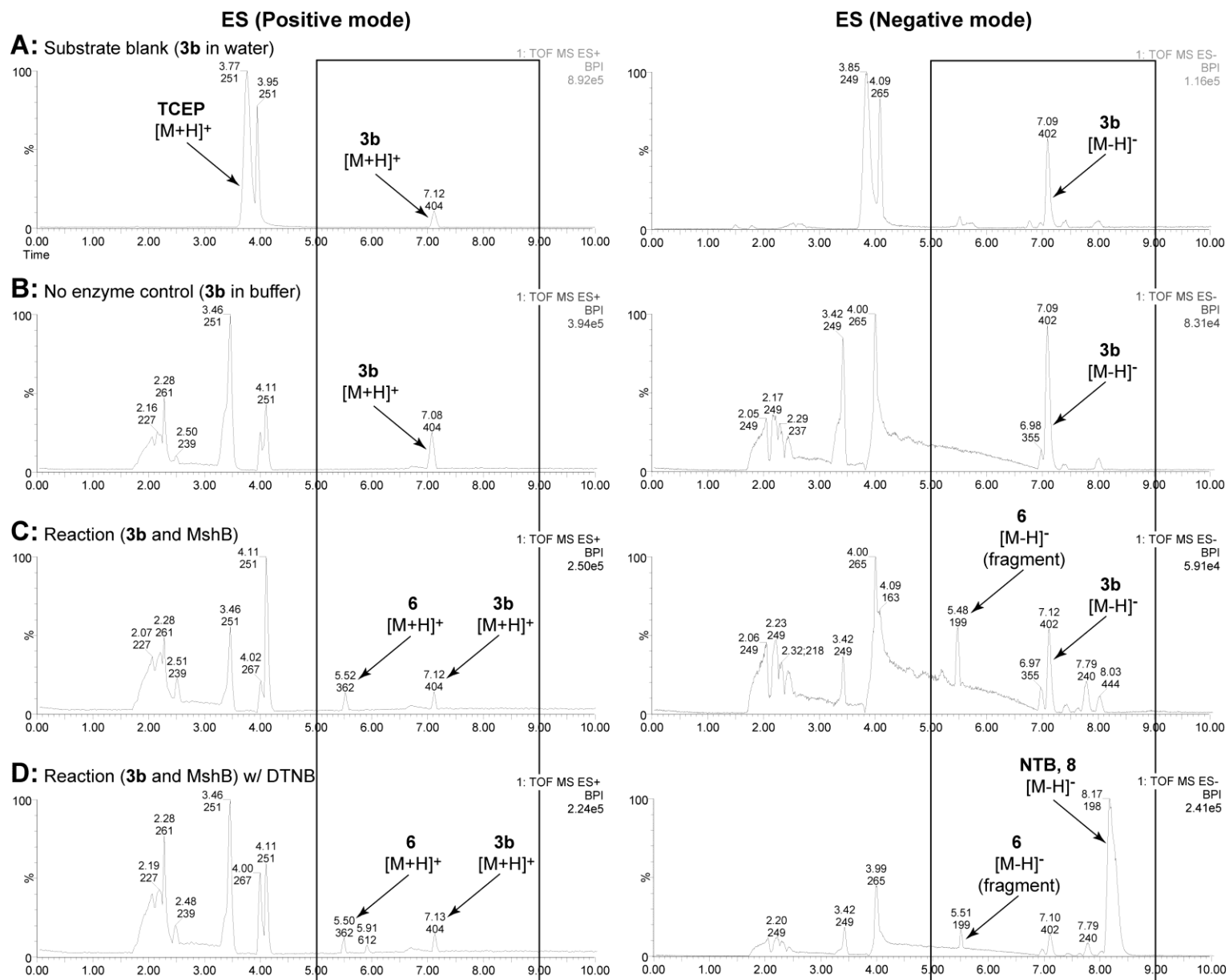
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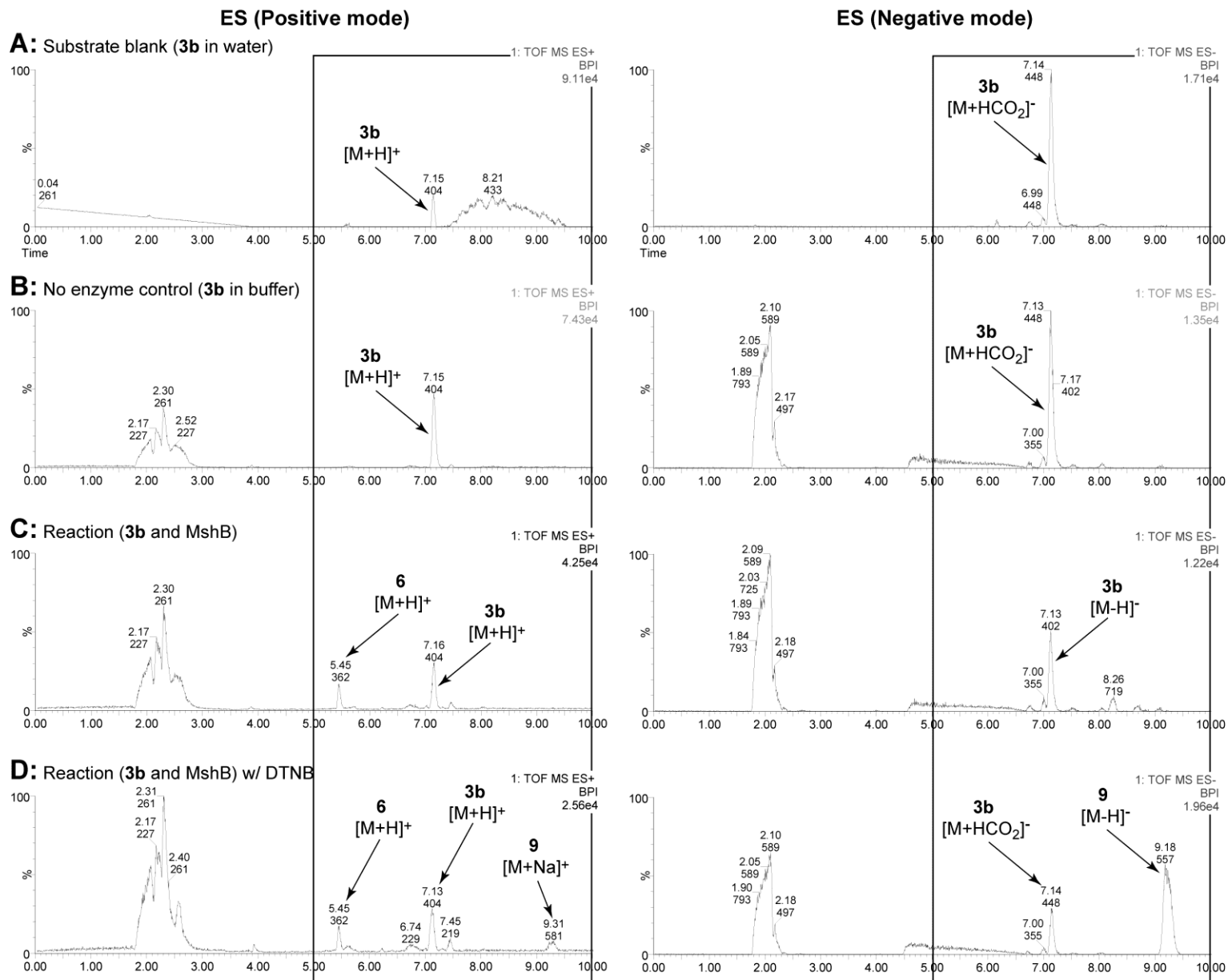
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LC-HRMS: Base peak ion chromatograms

For samples prepared with TCEP added:

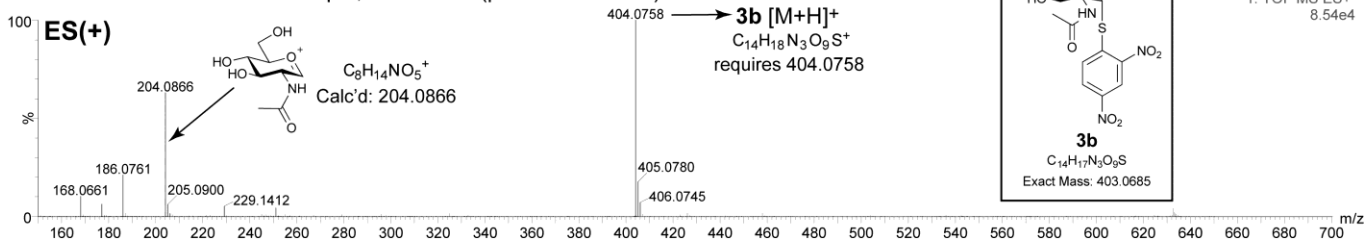


For samples prepared without added TCEP:

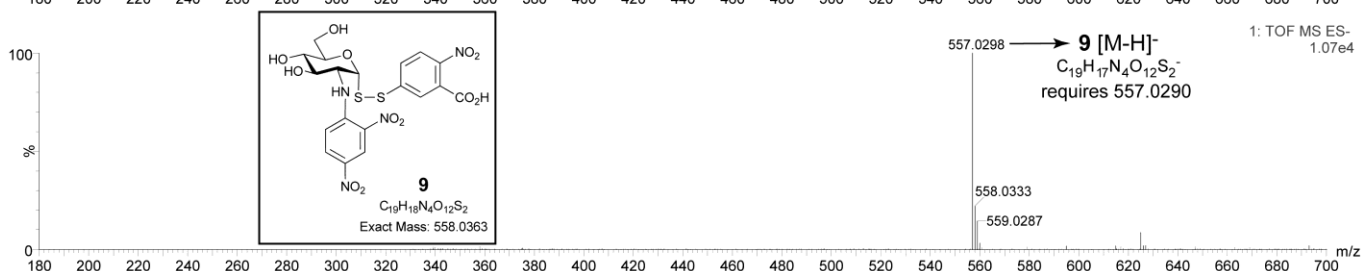
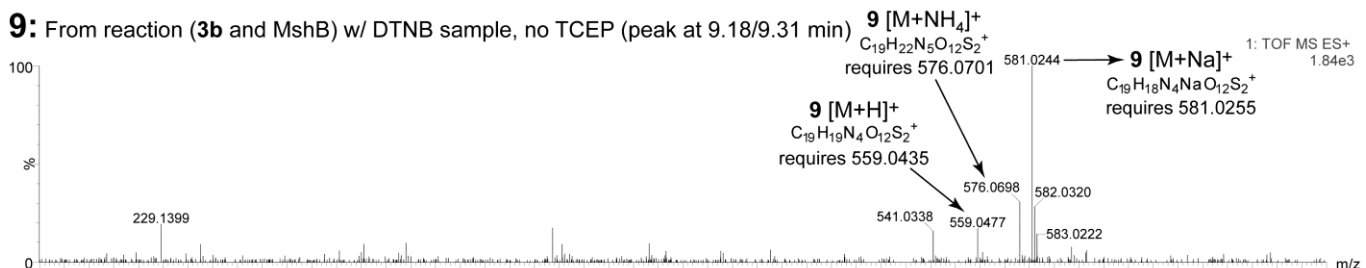
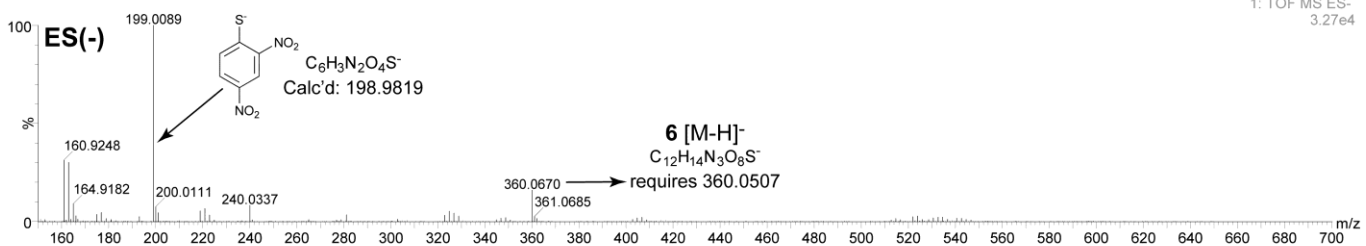
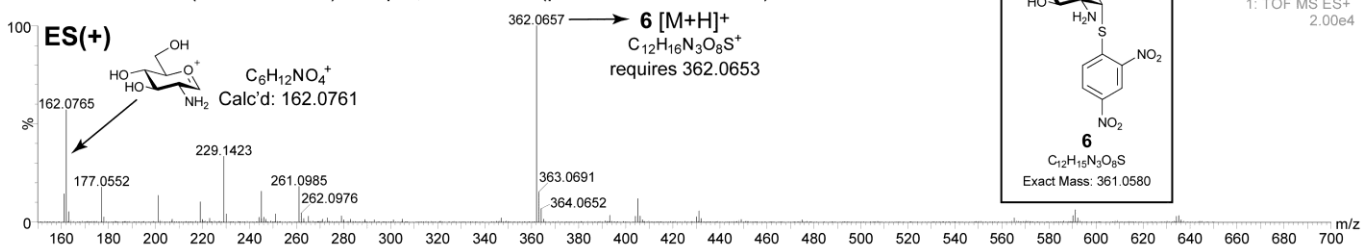


Mass spectra extracted from chromatograms:

3b: From substrate blank sample, with TCEP (peak at 7.08 min)



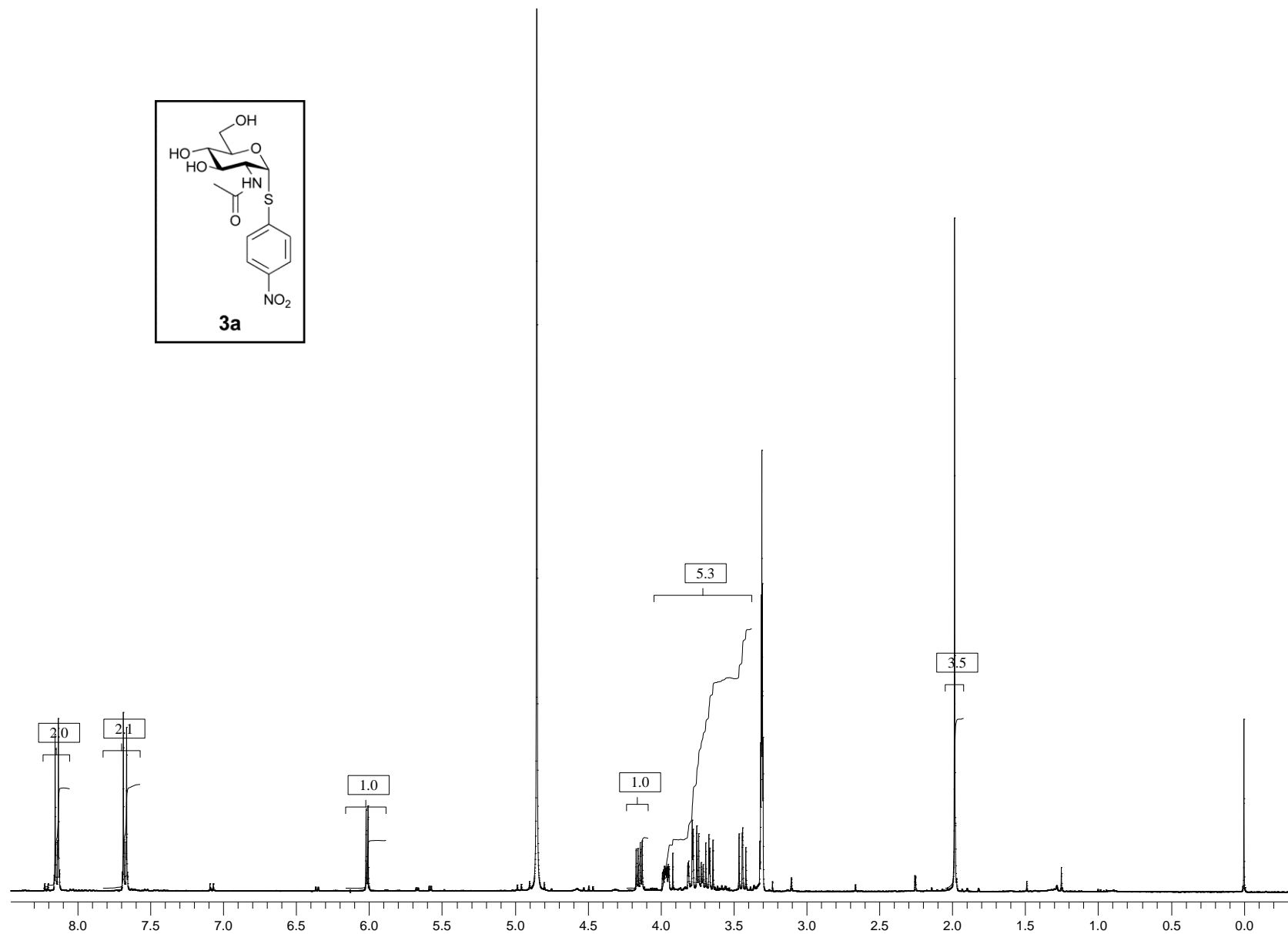
6: From reaction (3b and MshB) sample, with TCEP (peak at 5.48/5.52 min)



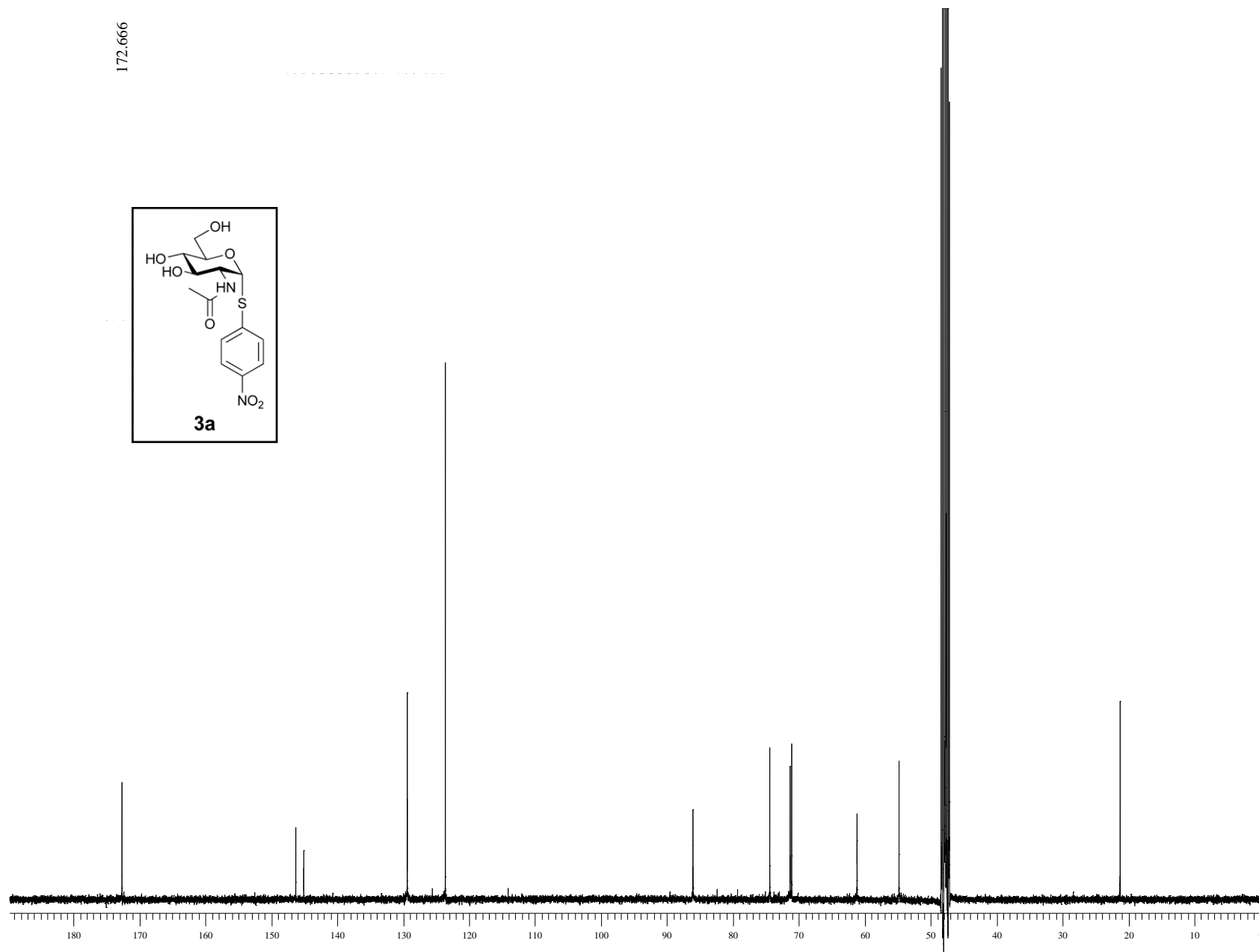
NMR Spectra:

4-Nitrophenyl 2-acetamido-2-deoxy-1-thio- α -D-glucopyranose (3a)

^1H NMR (300 MHz, CD_3OD):

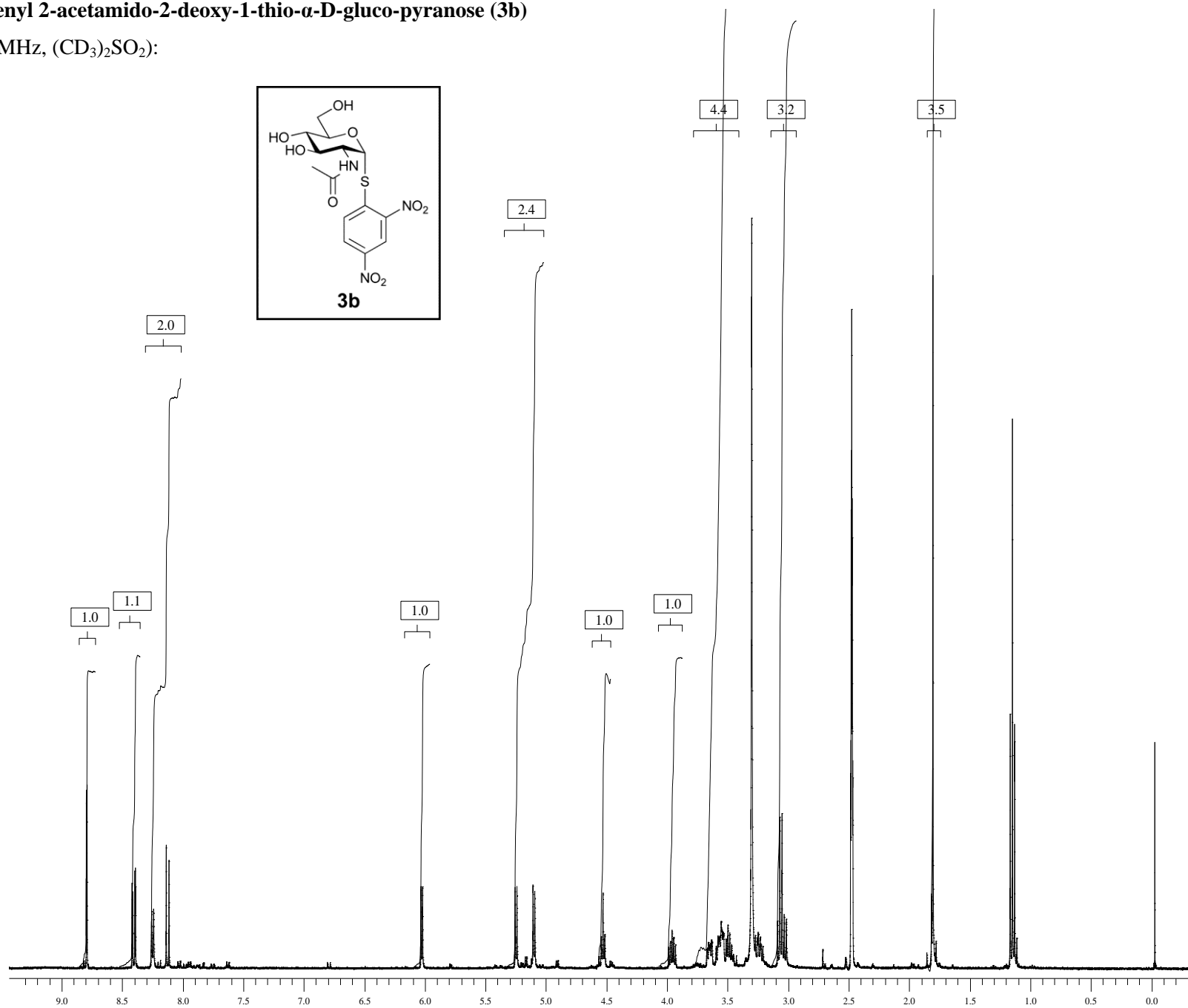


^{13}C NMR (75 MHz, CD_3OD):



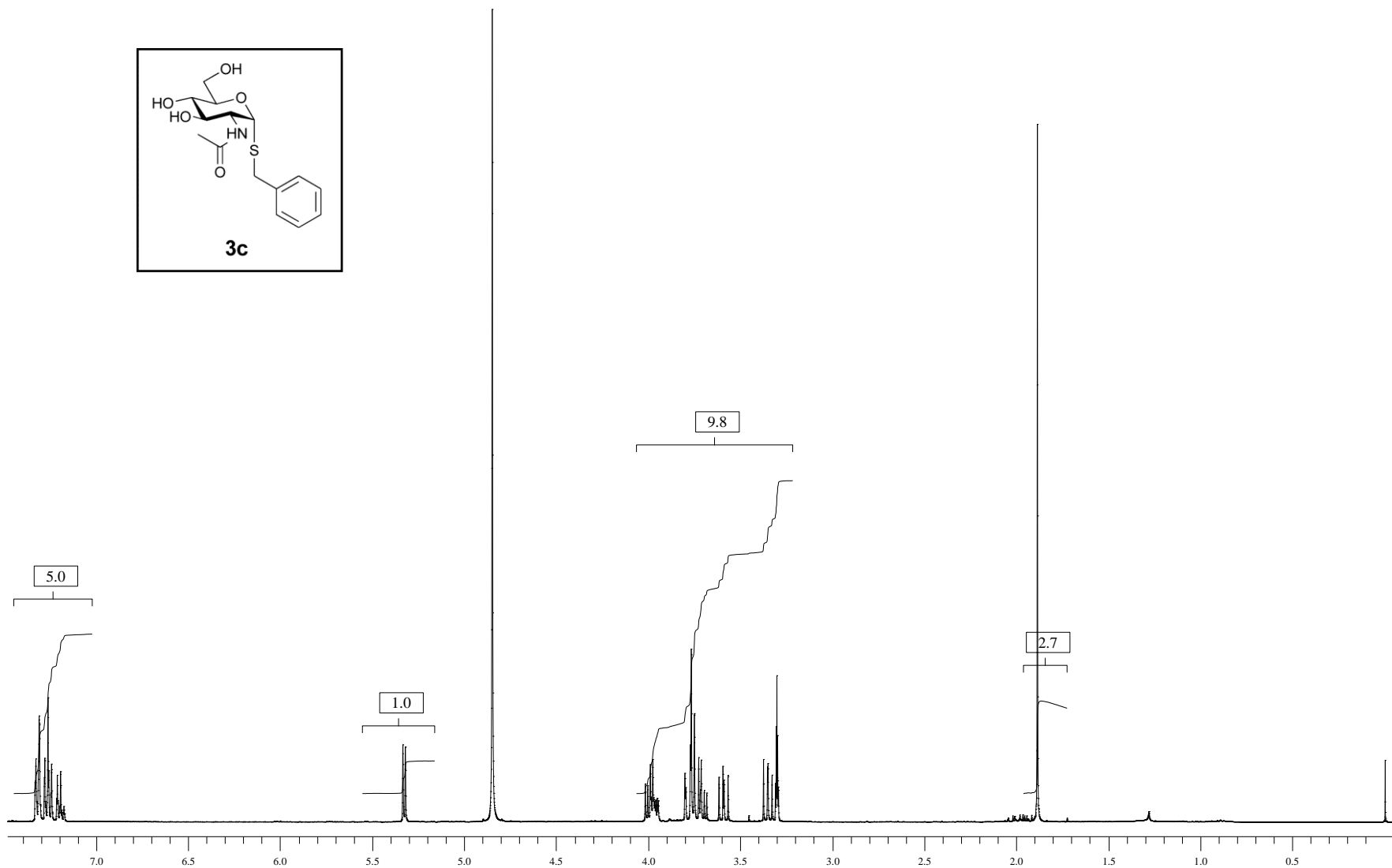
2,4-Dinitrophenyl 2-acetamido-2-deoxy-1-thio- α -D-gluco-pyranose (**3b**)

^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}_2$):



Benzyl 2-acetamido-2-deoxy-1-thio- α -D-glucopyranose (3c)

^1H NMR (300 MHz, CD_3OD):



^{13}C NMR (75 MHz, CD_3OD):

172.289

