

Electronic Supplementary Material

Broadening the reaction scope of unprotected aldoses via their corresponding nitrones: 1,3-dipolar cycloadditions with alkenes.

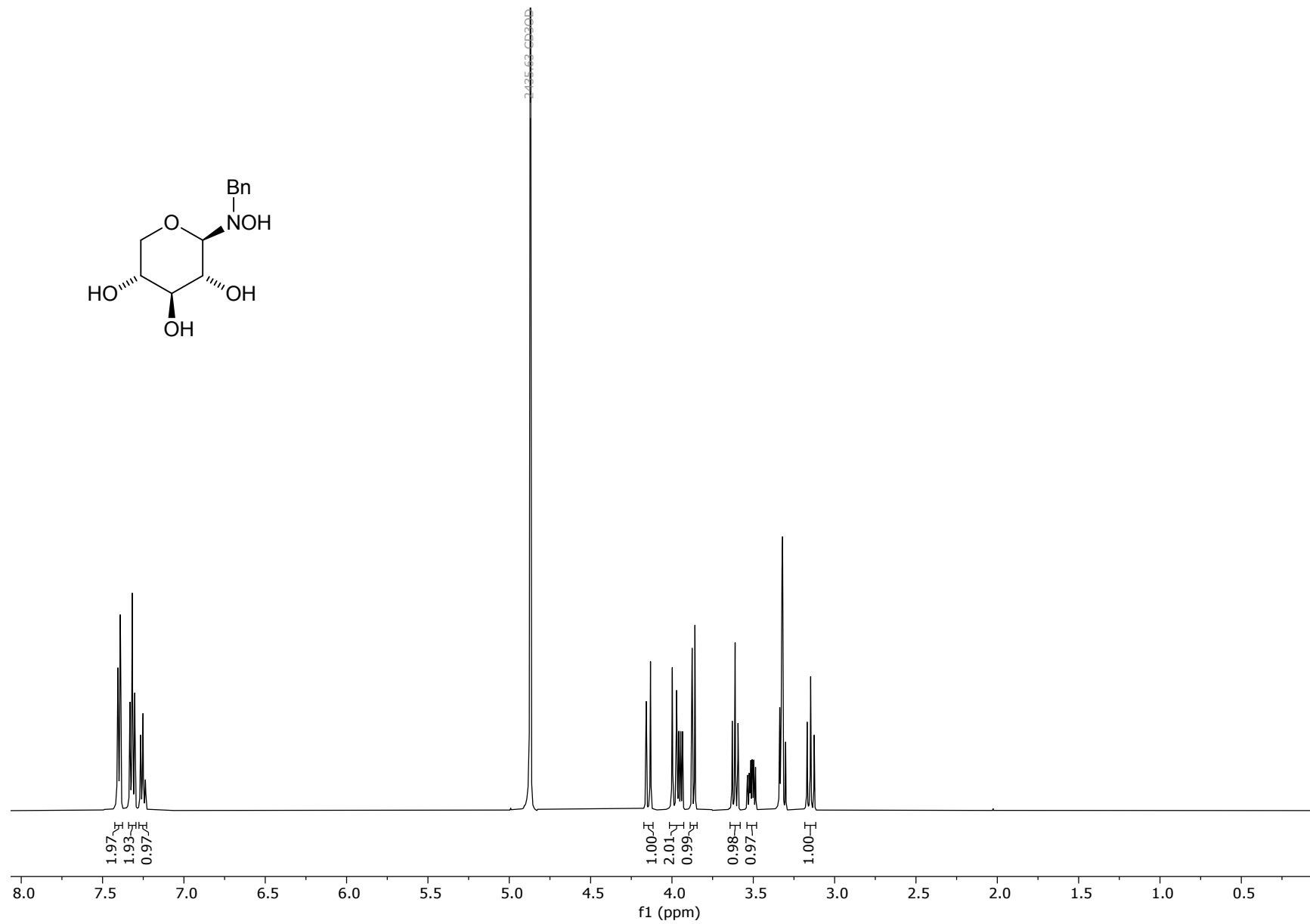
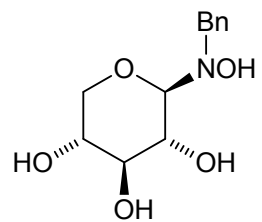
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^a Univ. Reims Champagne-Ardenne, ICMR, CNRS UMR 7312, FR Condorcet CNRS 3417, 51687 Reims Cedex 2, France.
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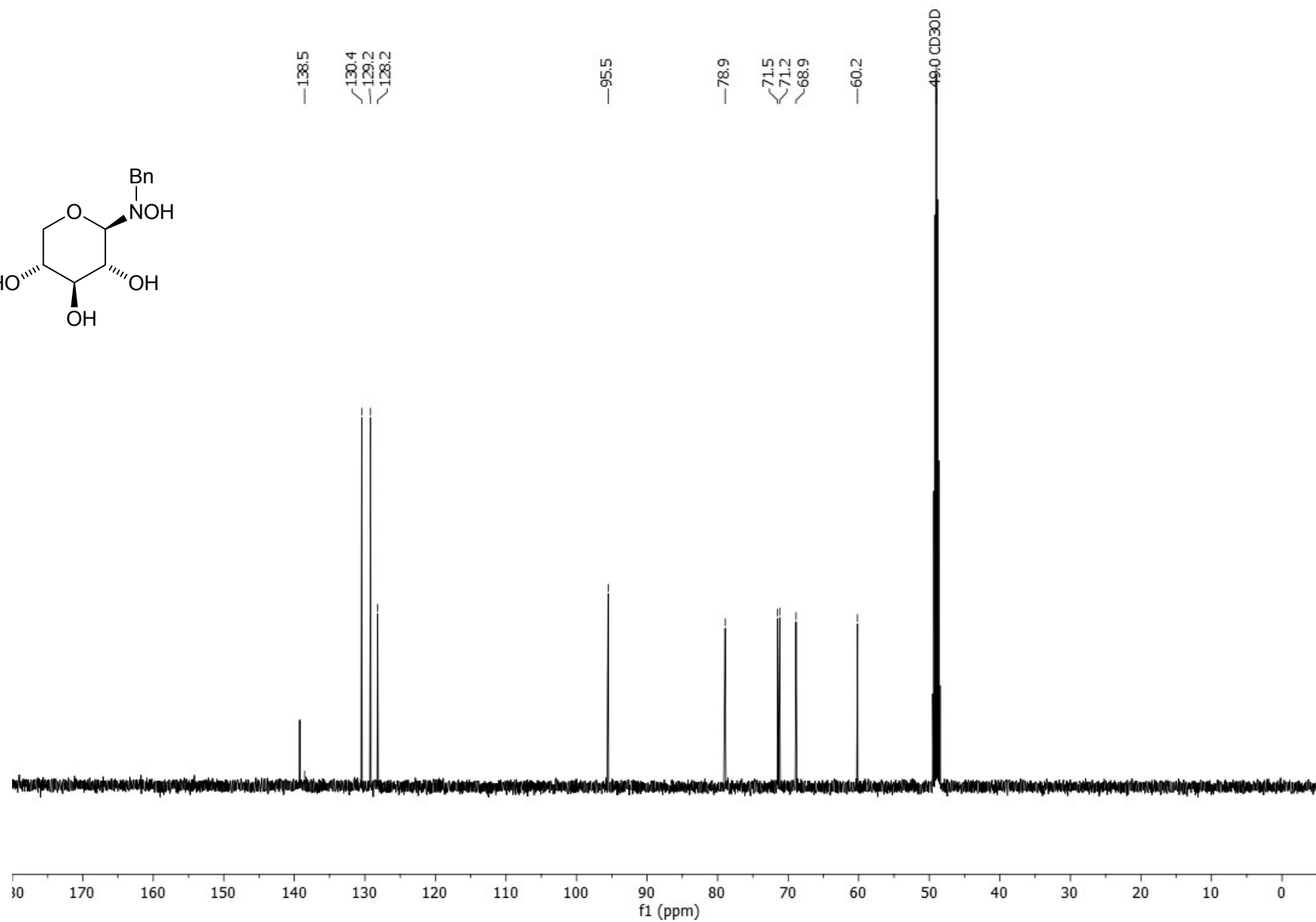
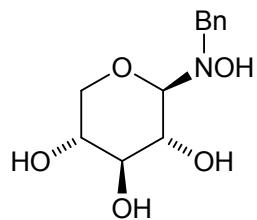
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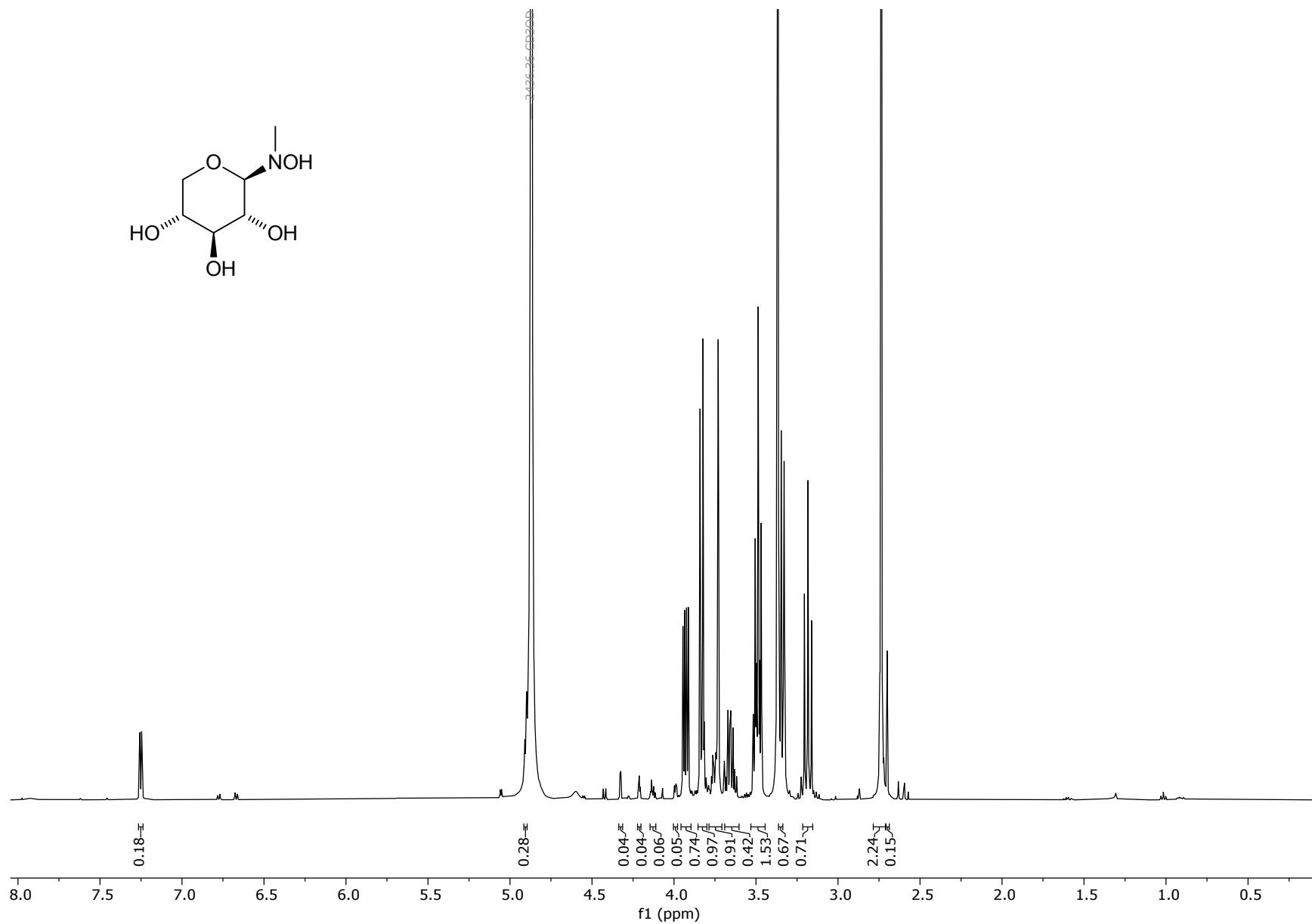
¹H-NMR spectrum of 4a (CD₃OD)



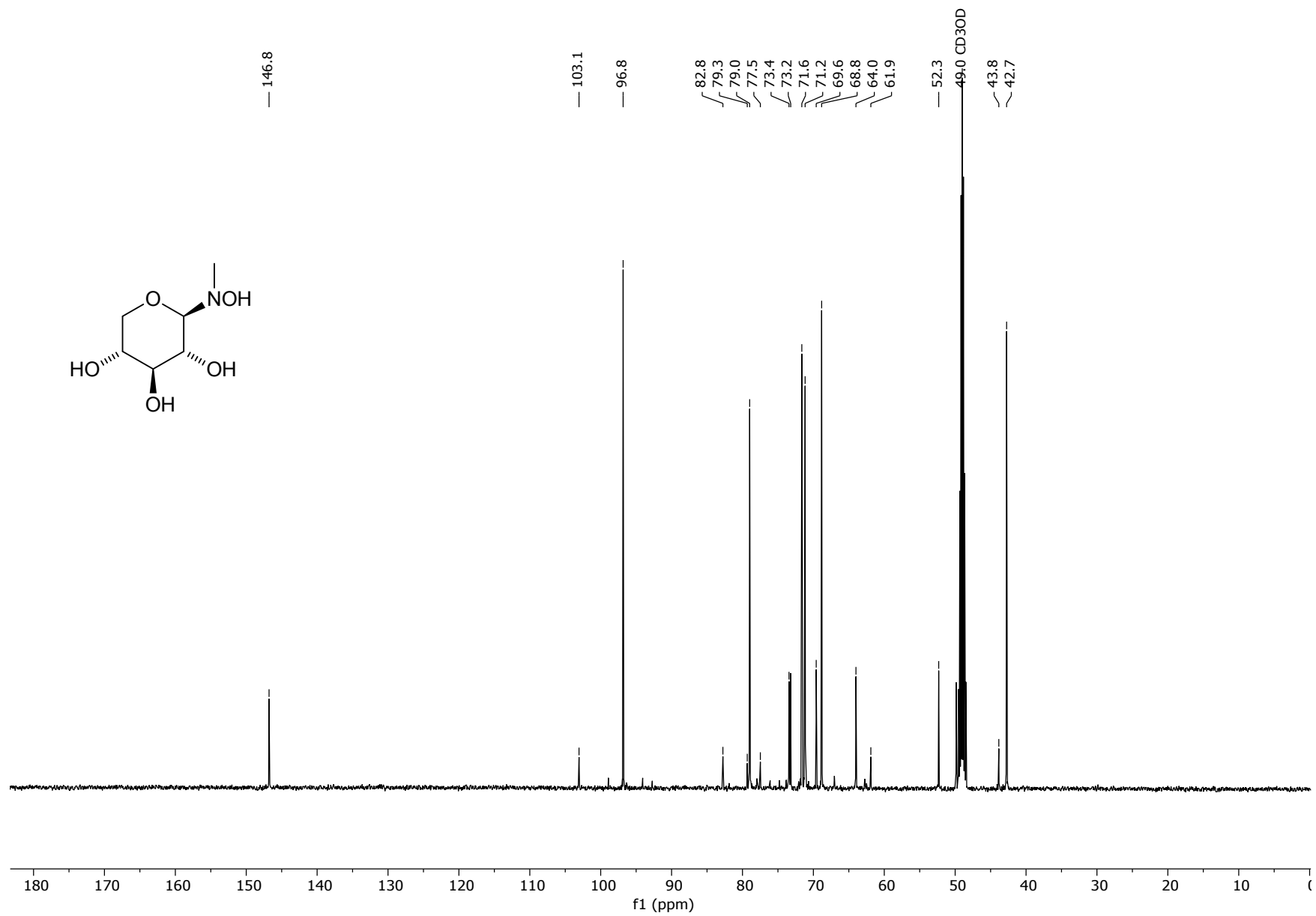
¹³C-NMR spectrum of 4a (CD₃OD)



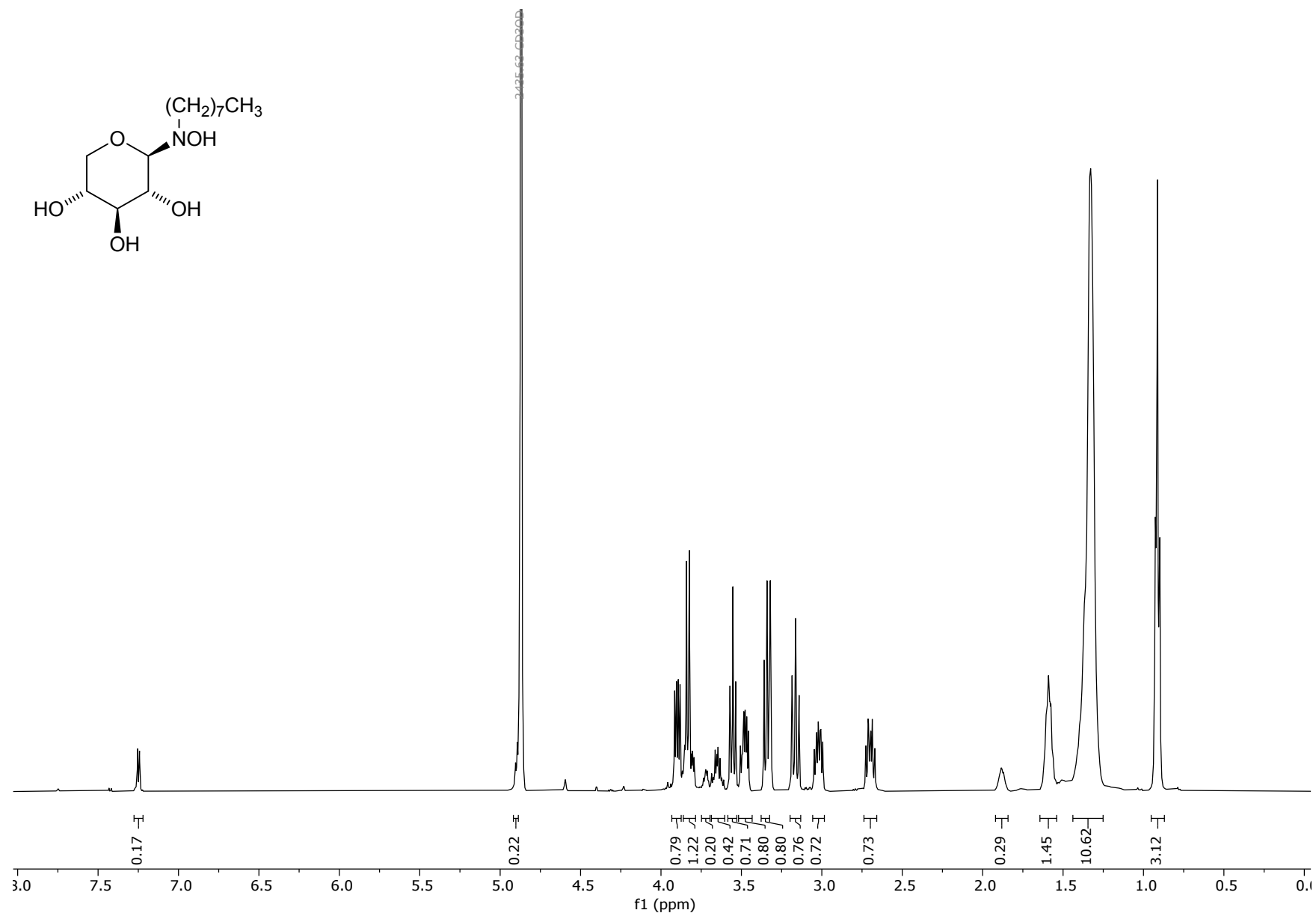
¹H-NMR spectrum of 4b (CD₃OD)



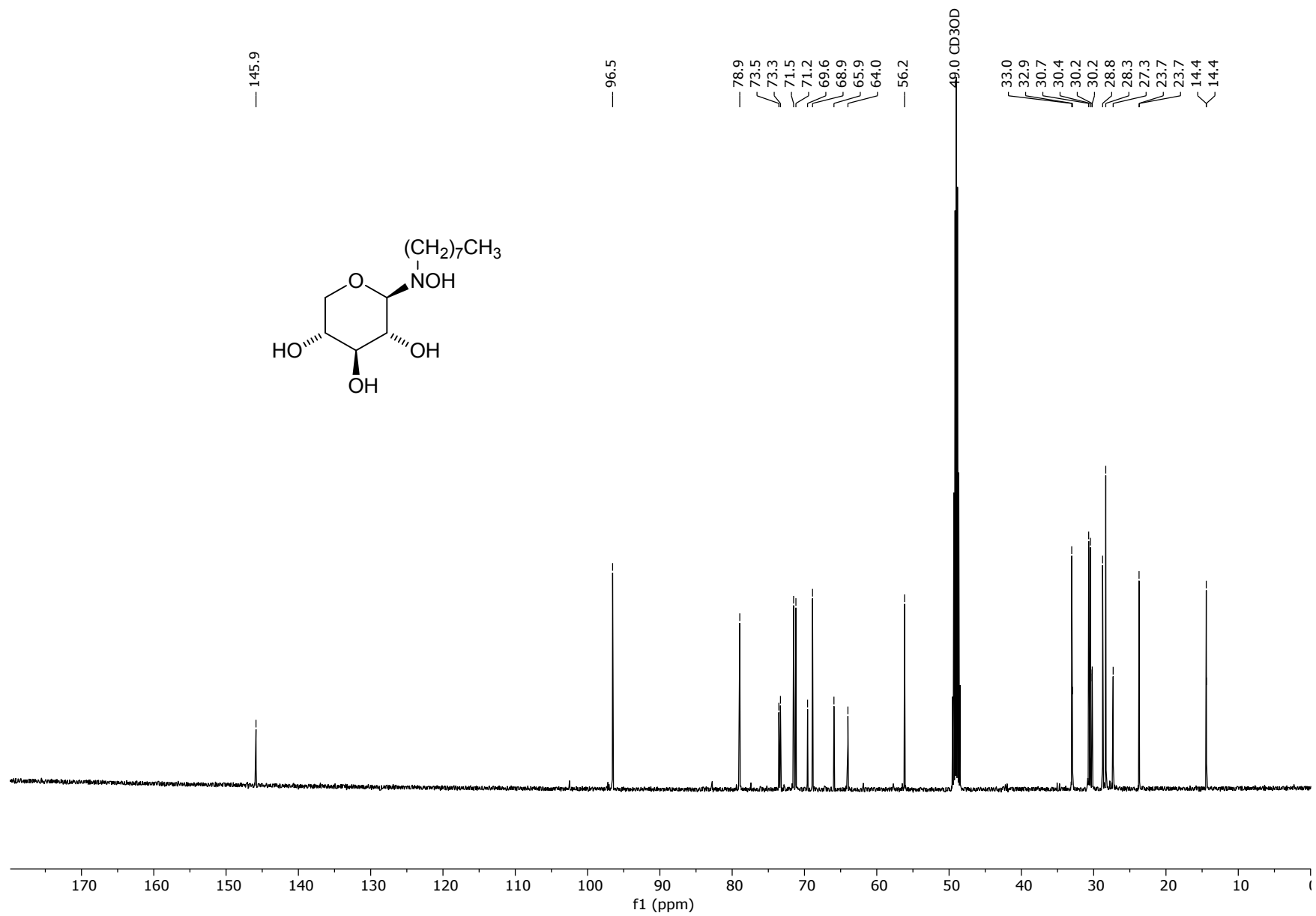
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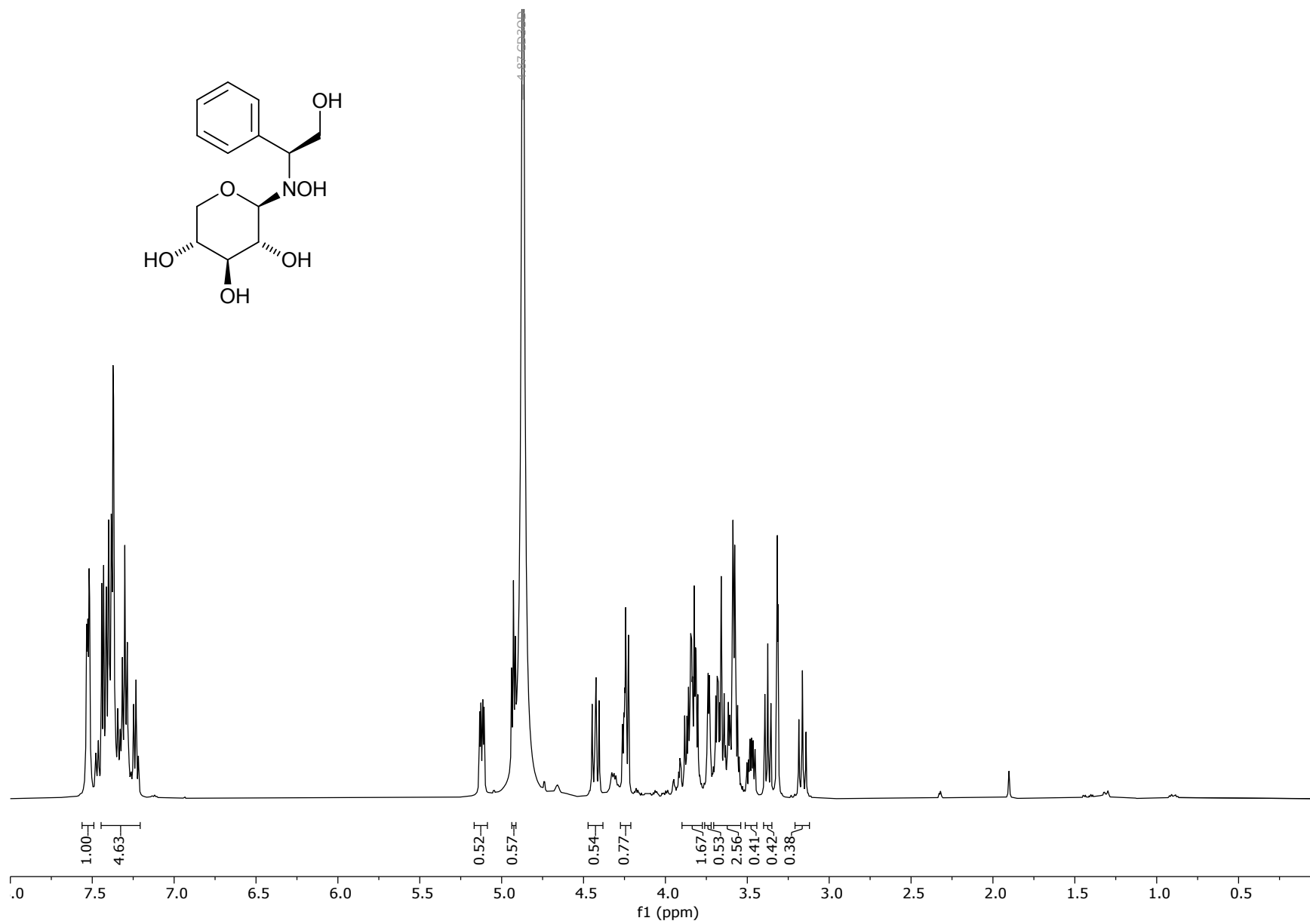
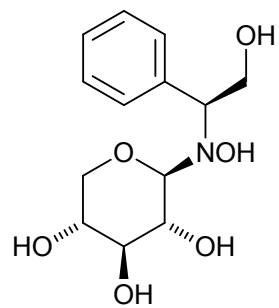
¹H-NMR spectrum of 4c (CD₃OD)



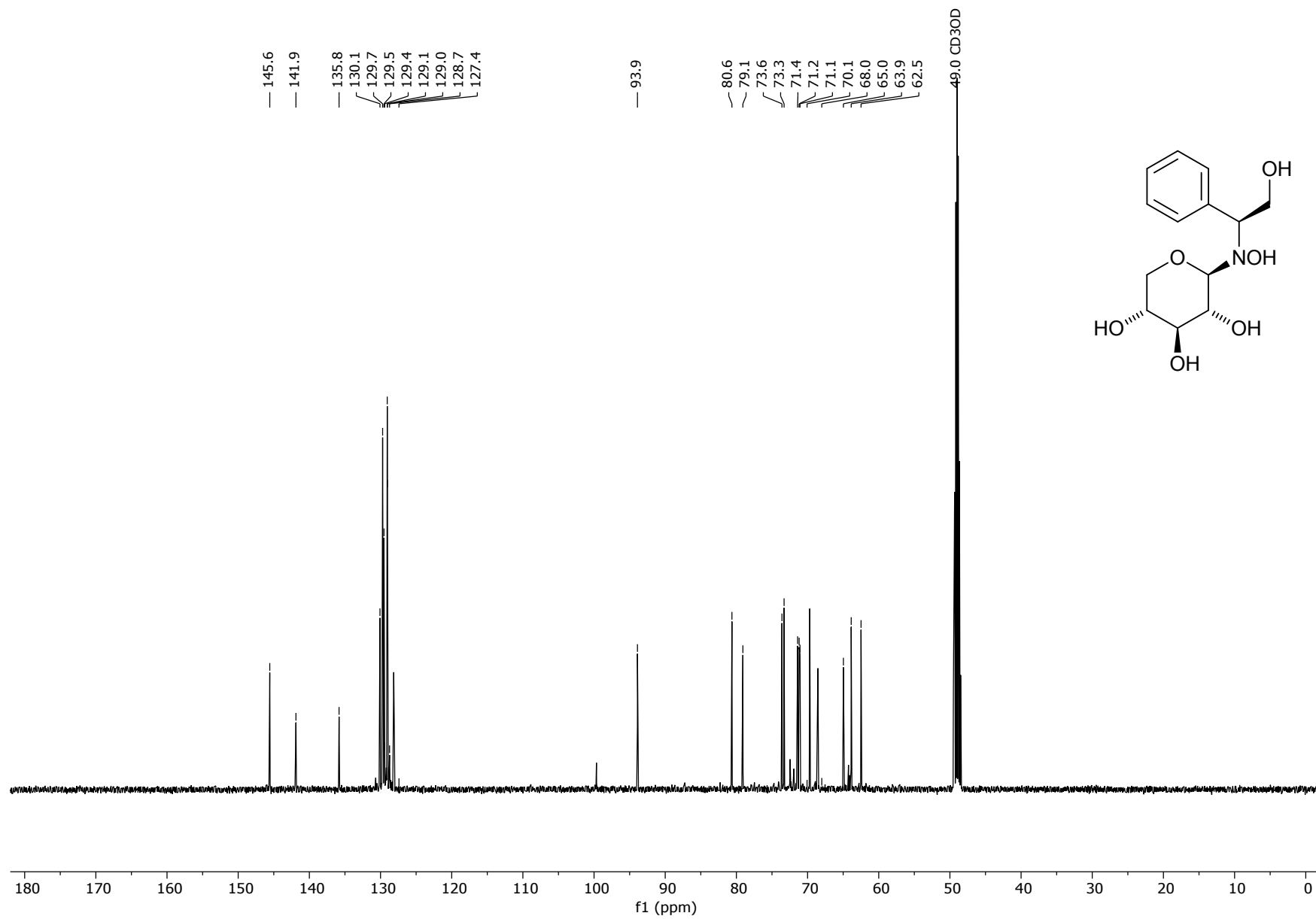
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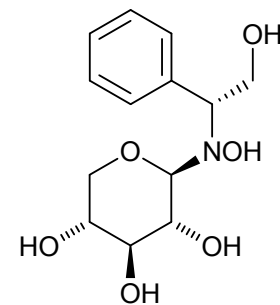
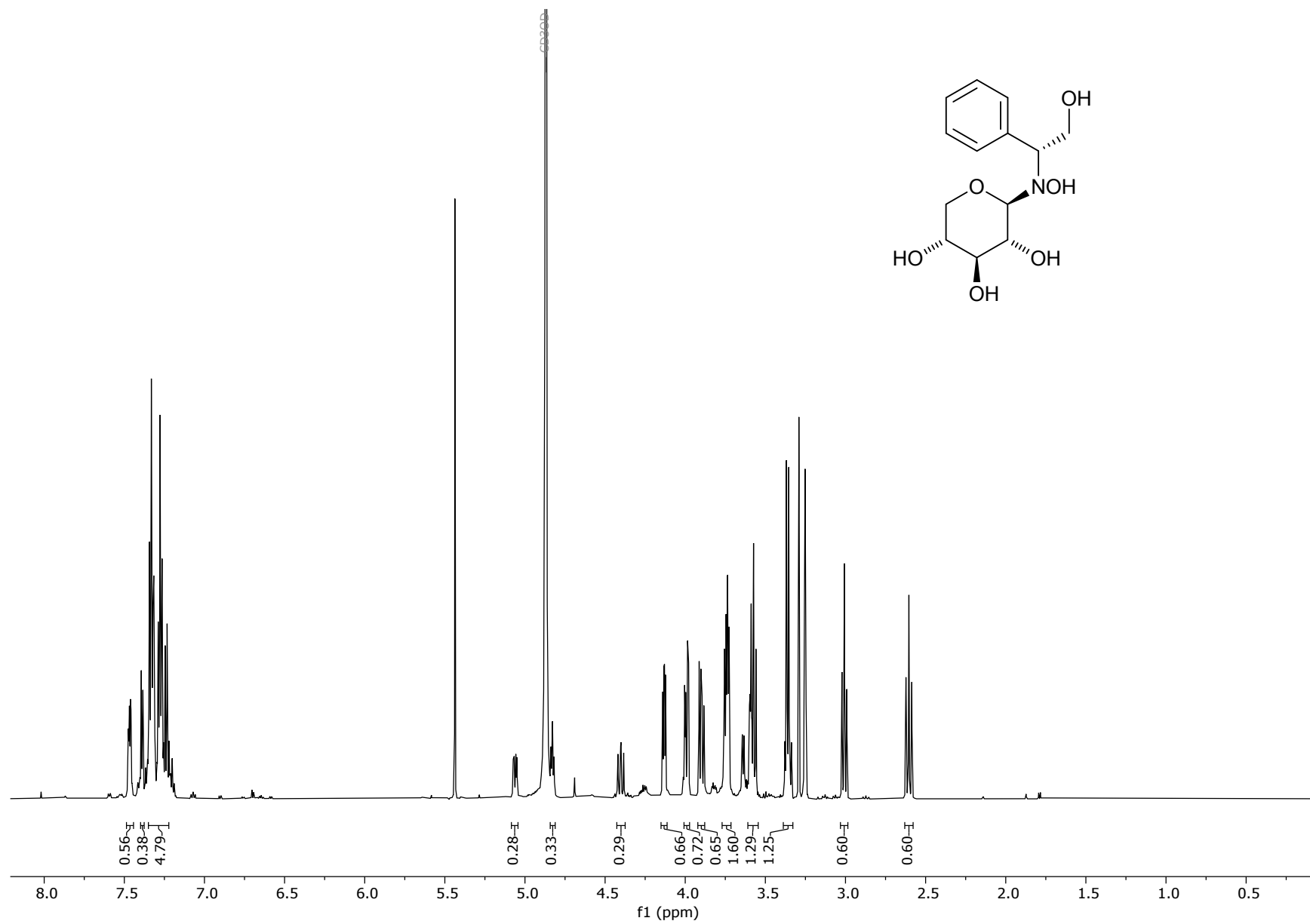
¹H-NMR spectrum of 4d (CD₃OD)



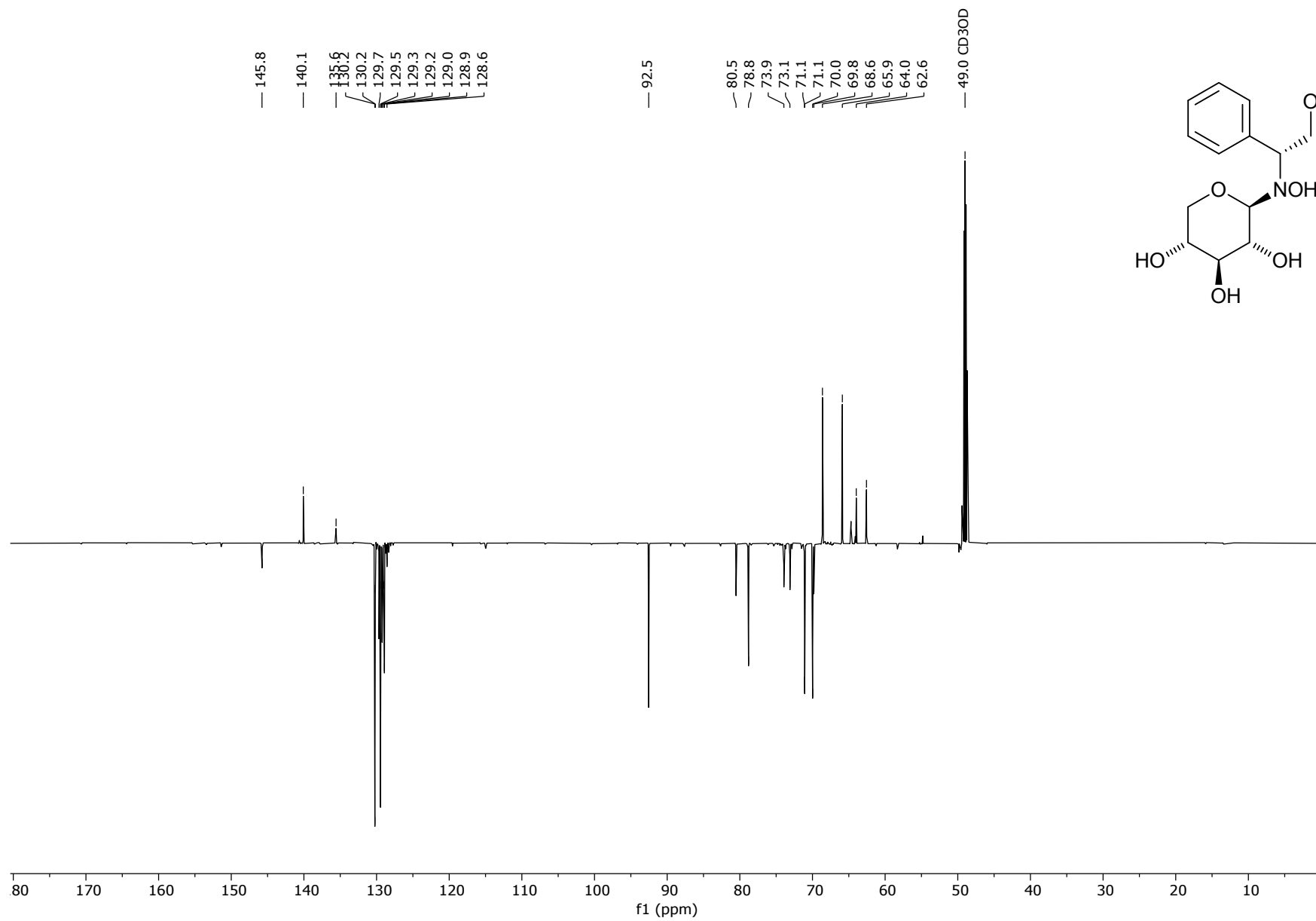
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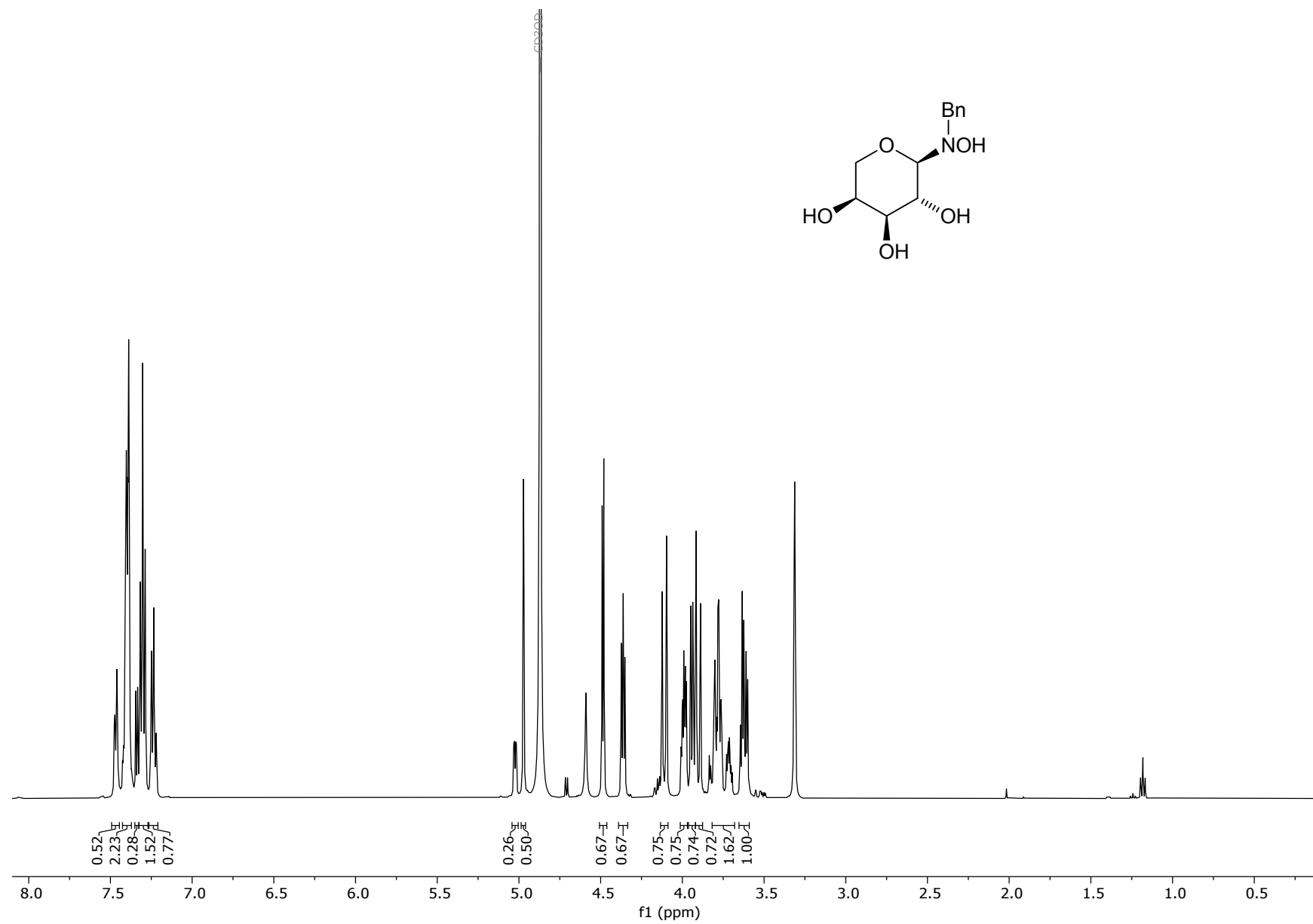
¹H-NMR spectrum of 4e (CD₃OD)



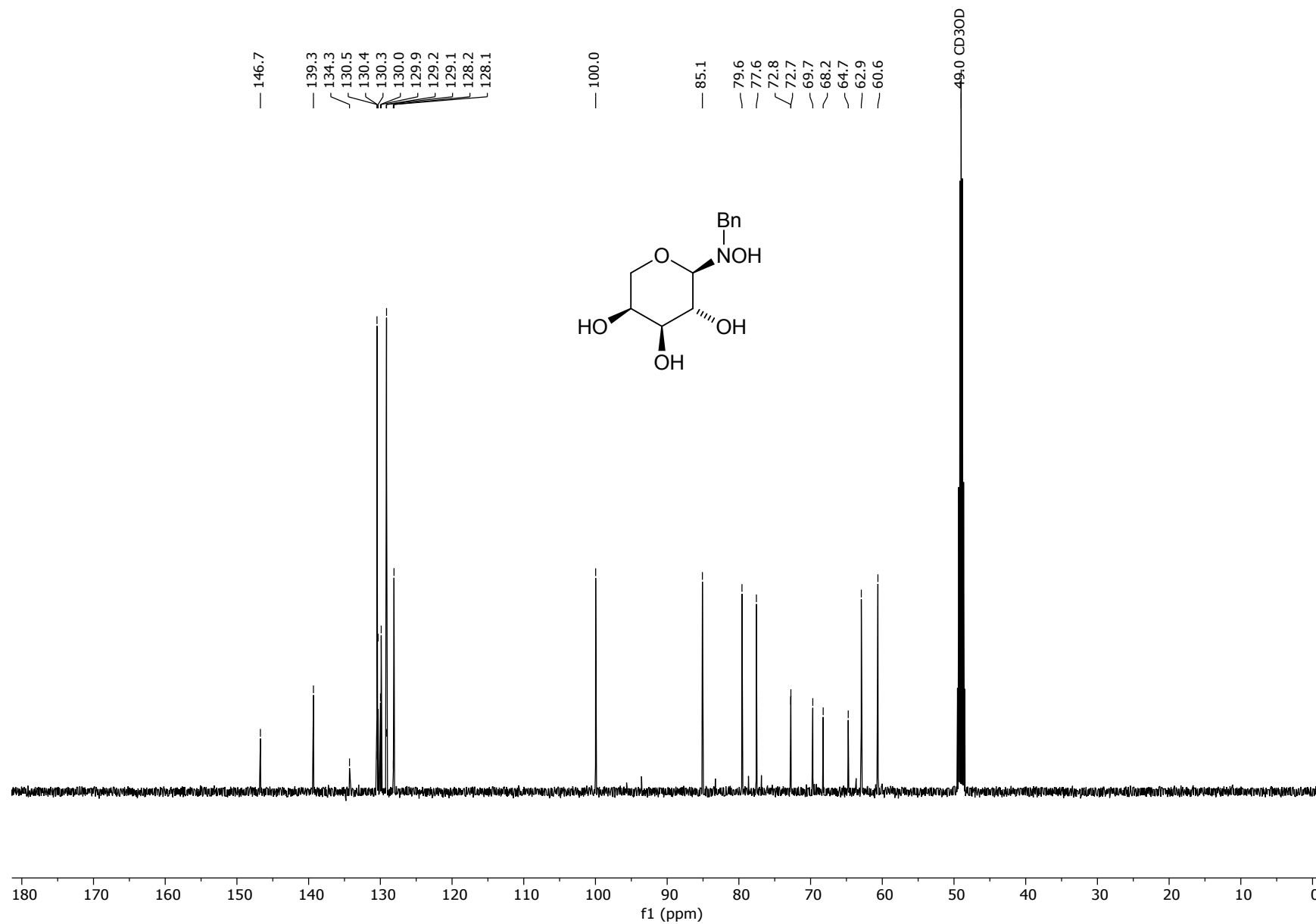
¹³C-NMR spectrum (J-MOD) of 4e (CD₃OD)



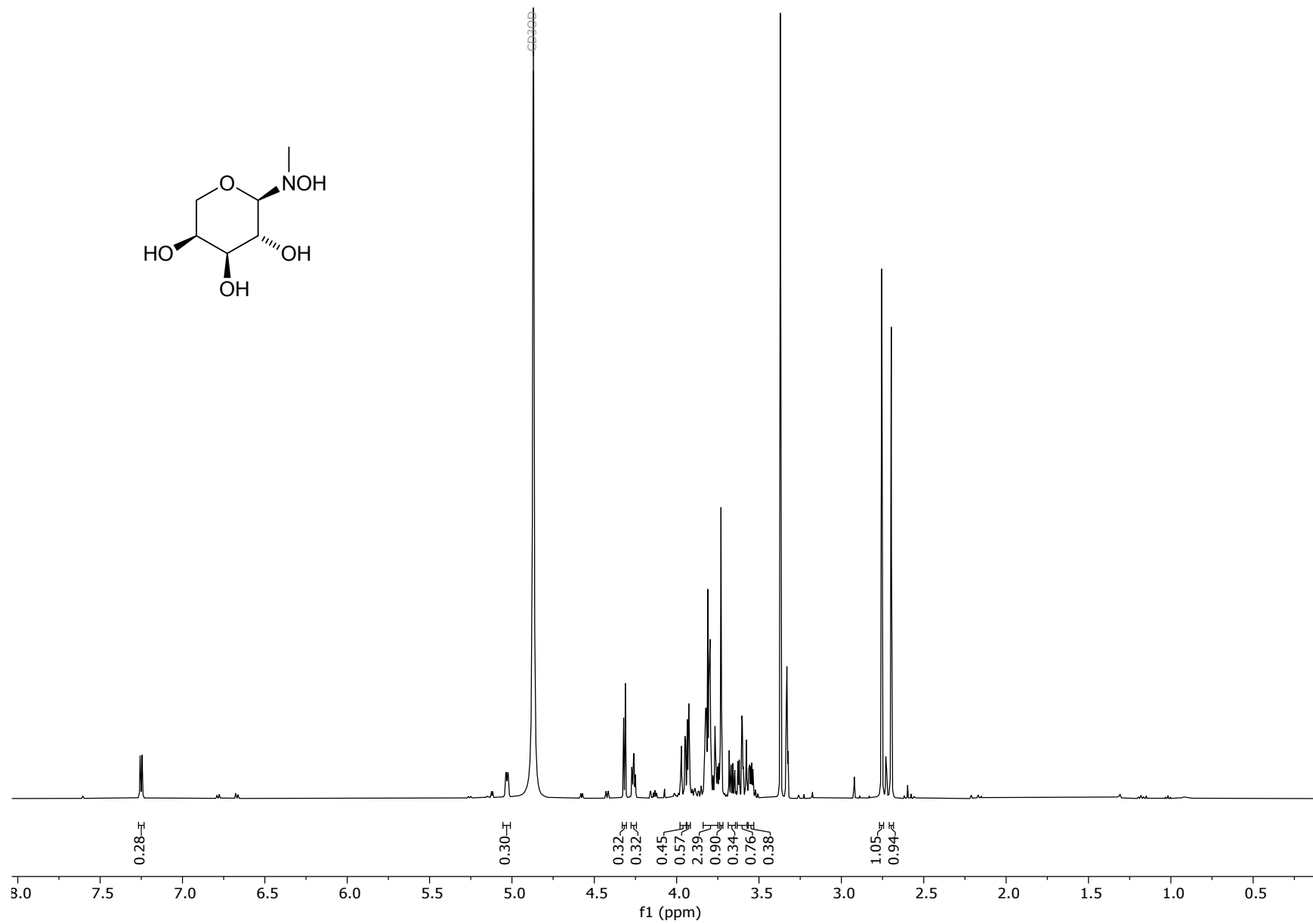
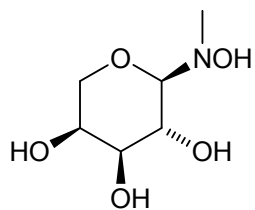
¹H-NMR spectrum of 5a (CD₃OD)



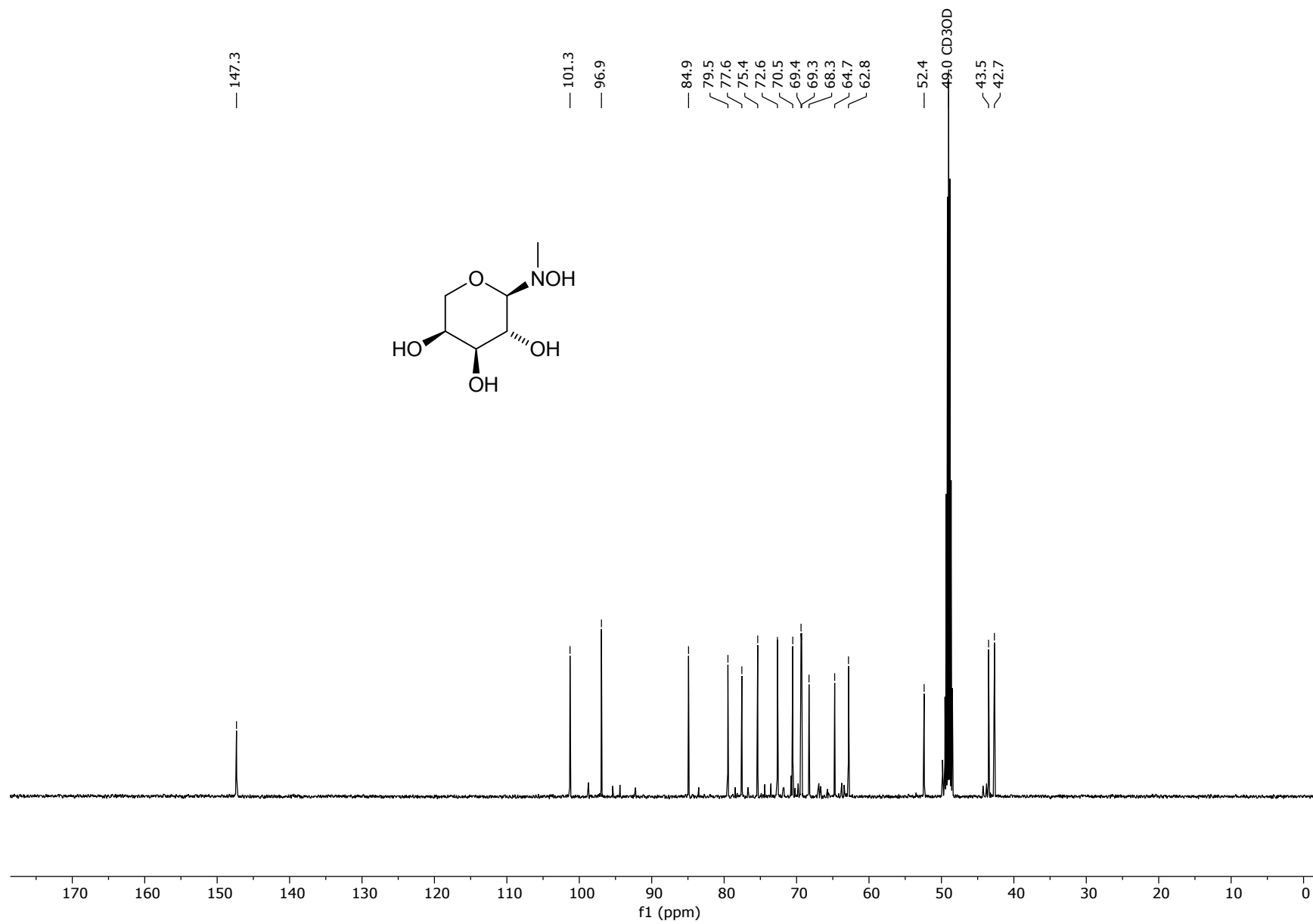
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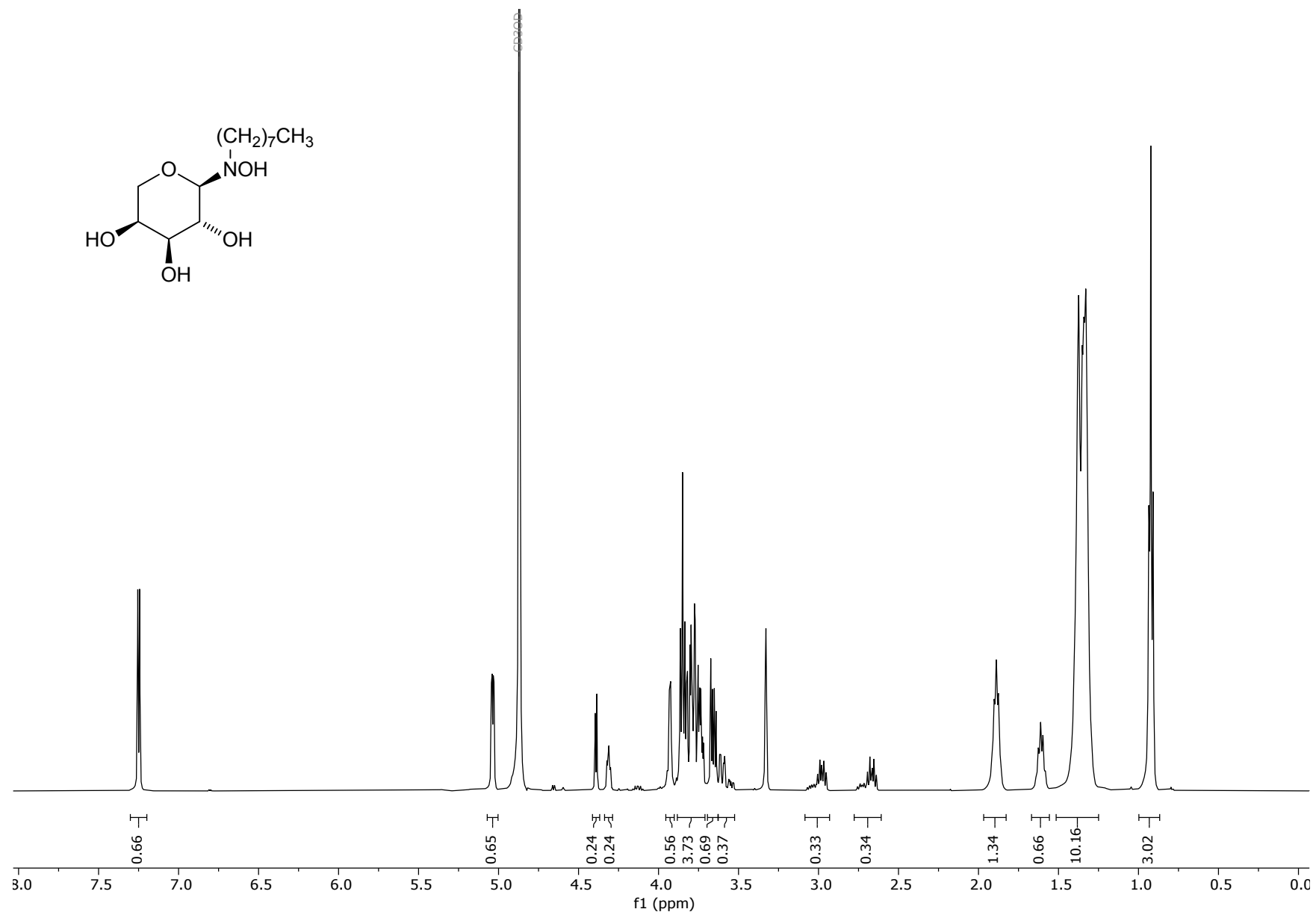
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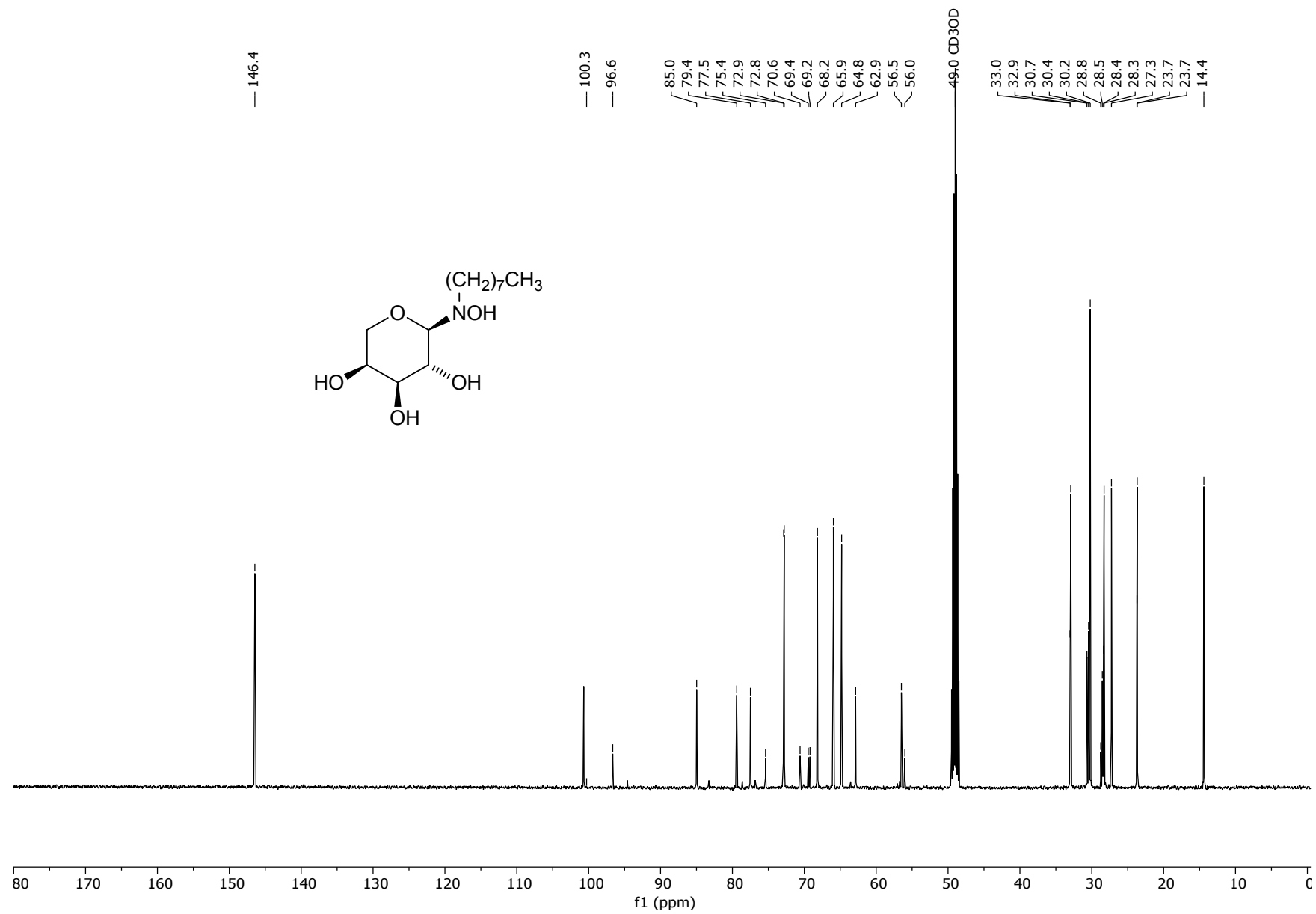
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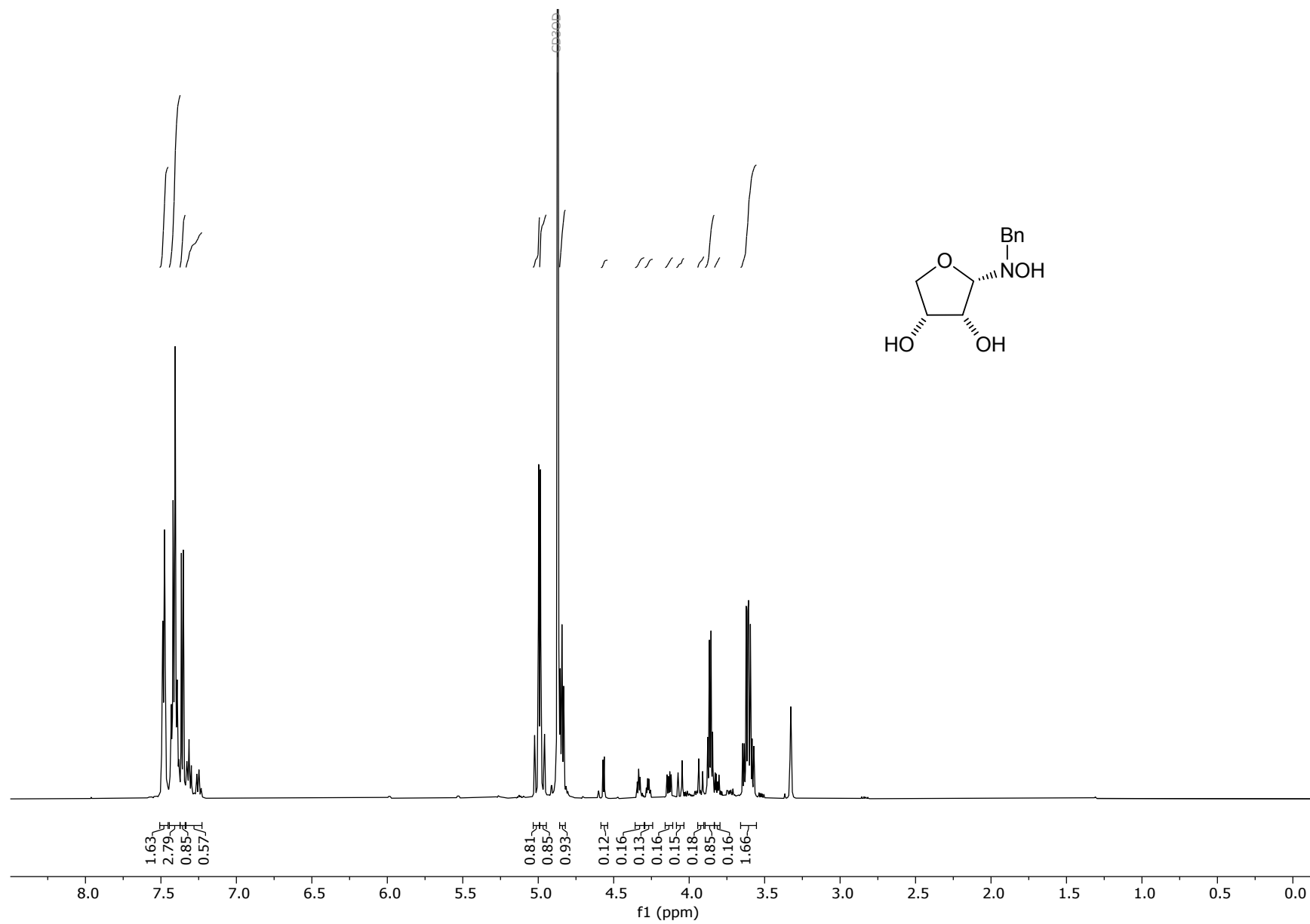
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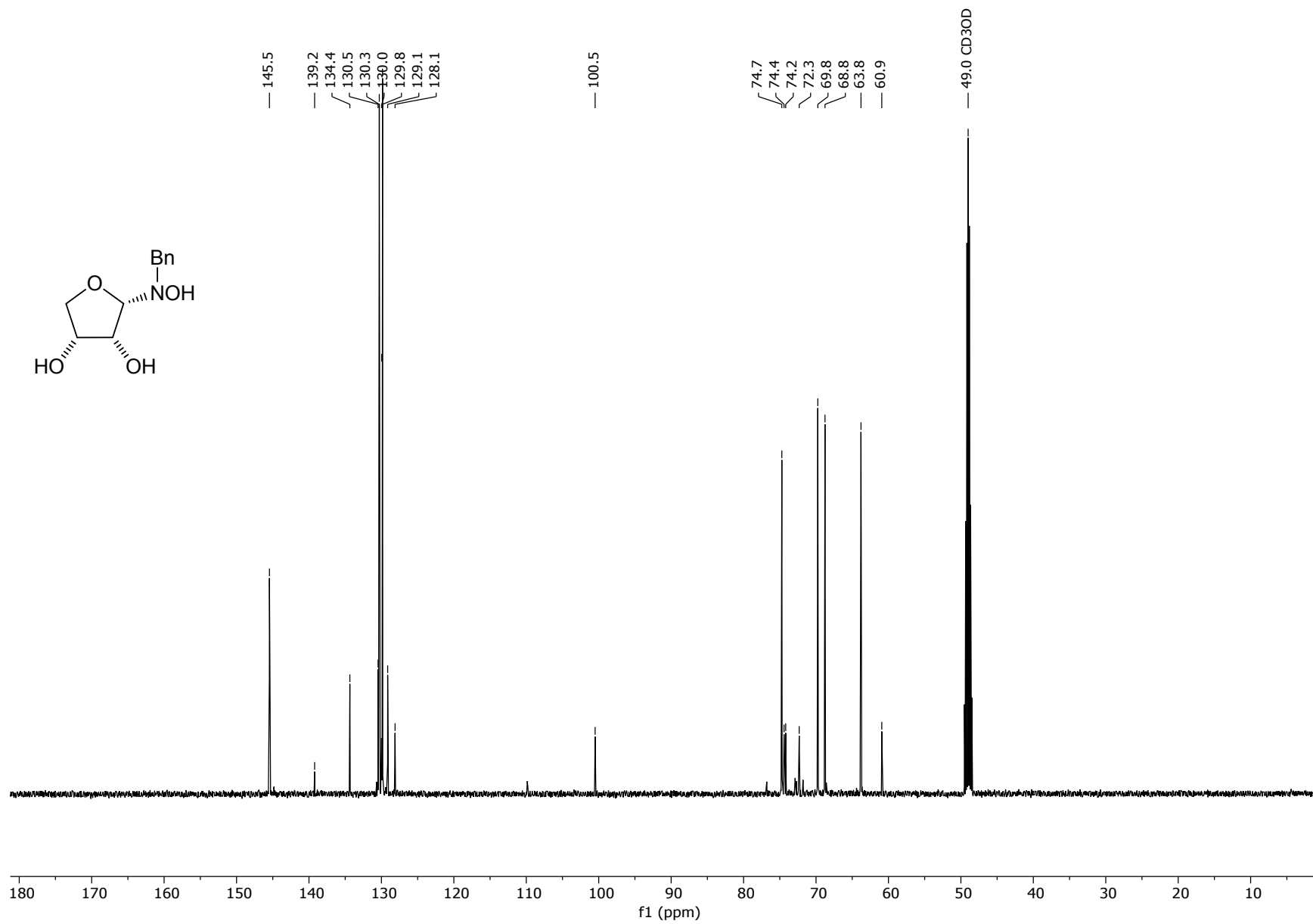
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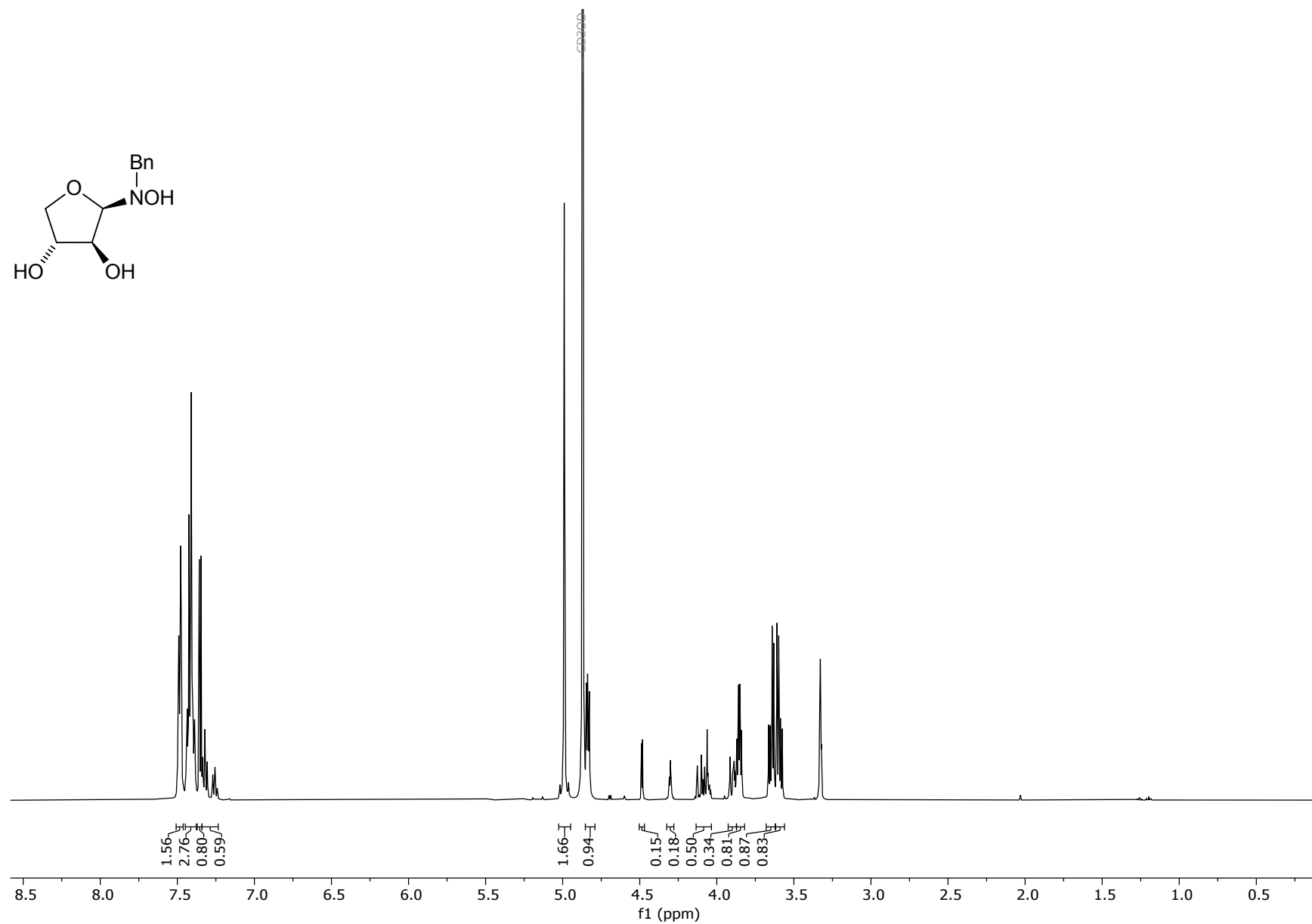
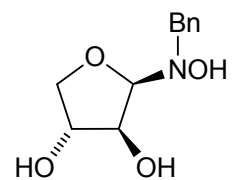
¹H-NMR spectrum of 6a (CD₃OD)



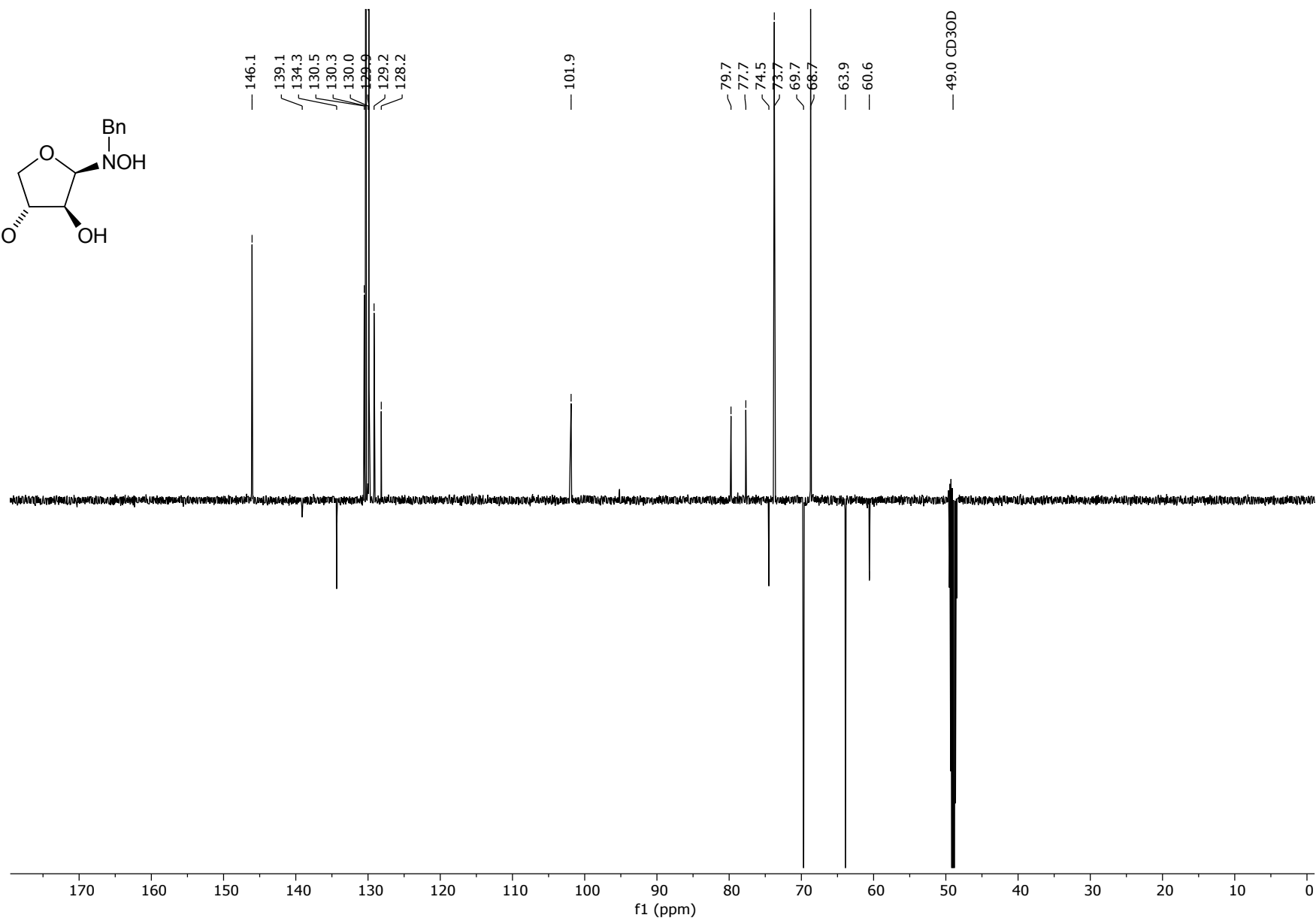
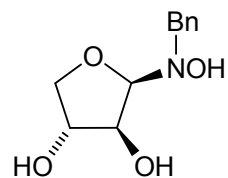
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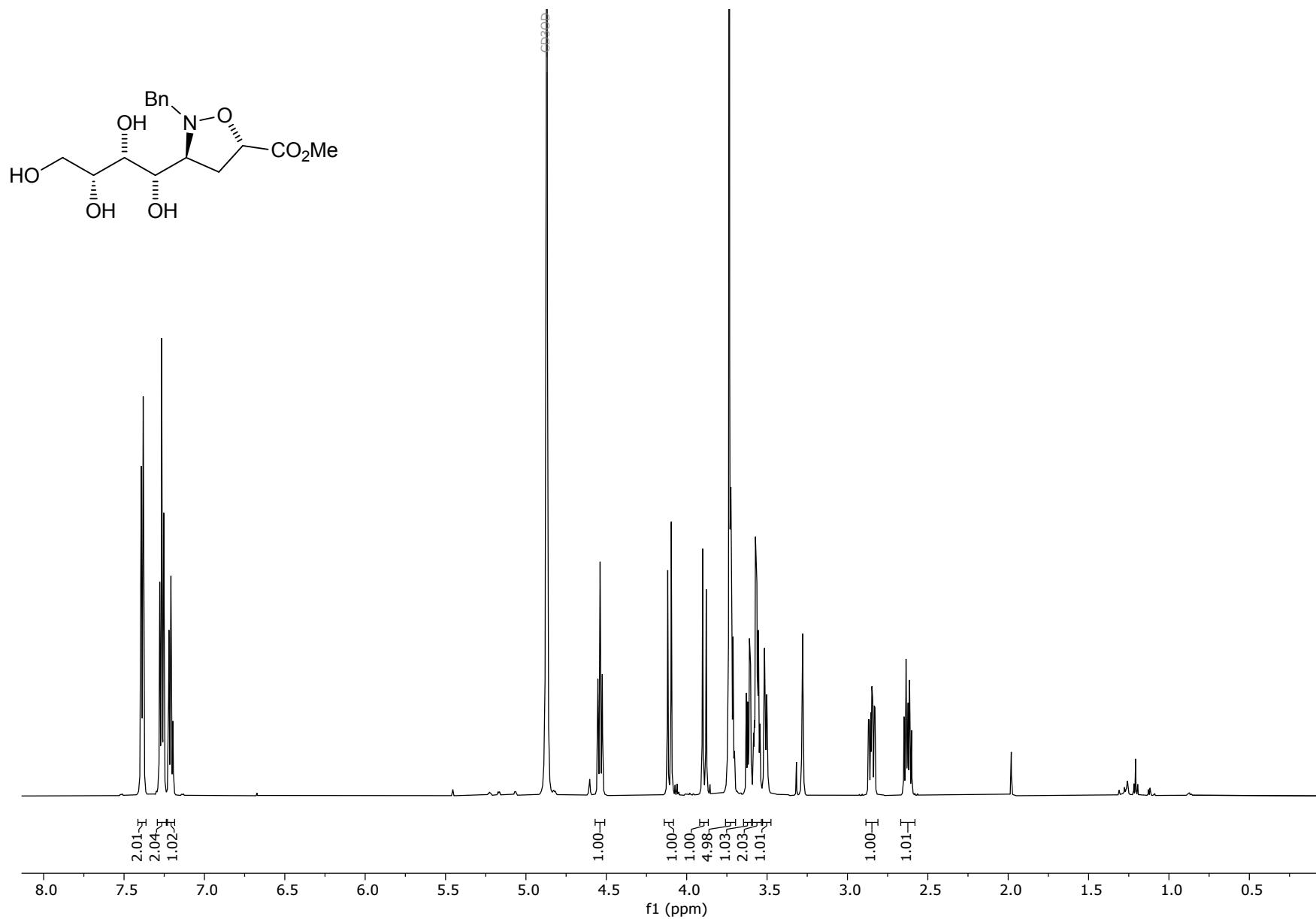
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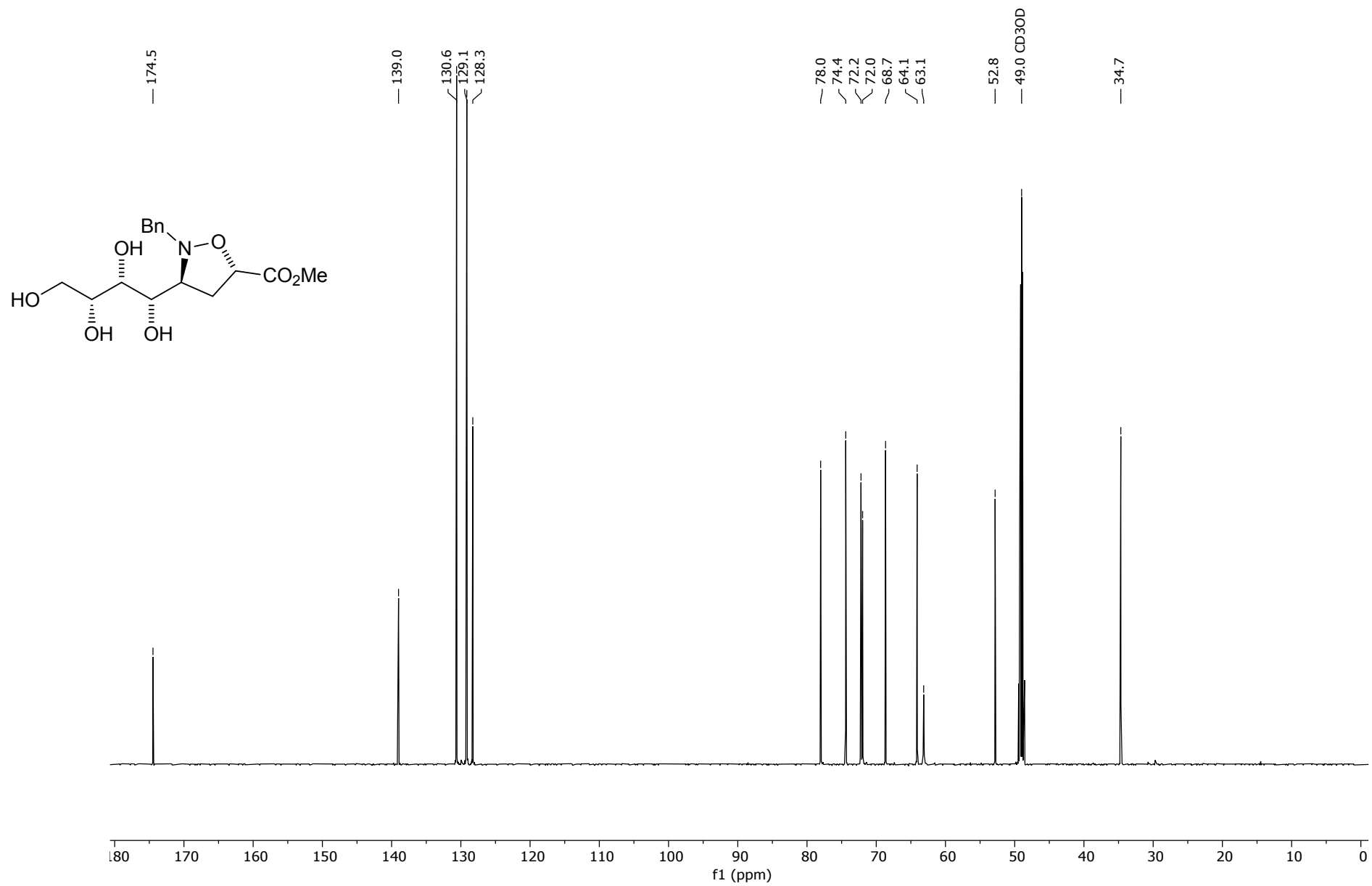
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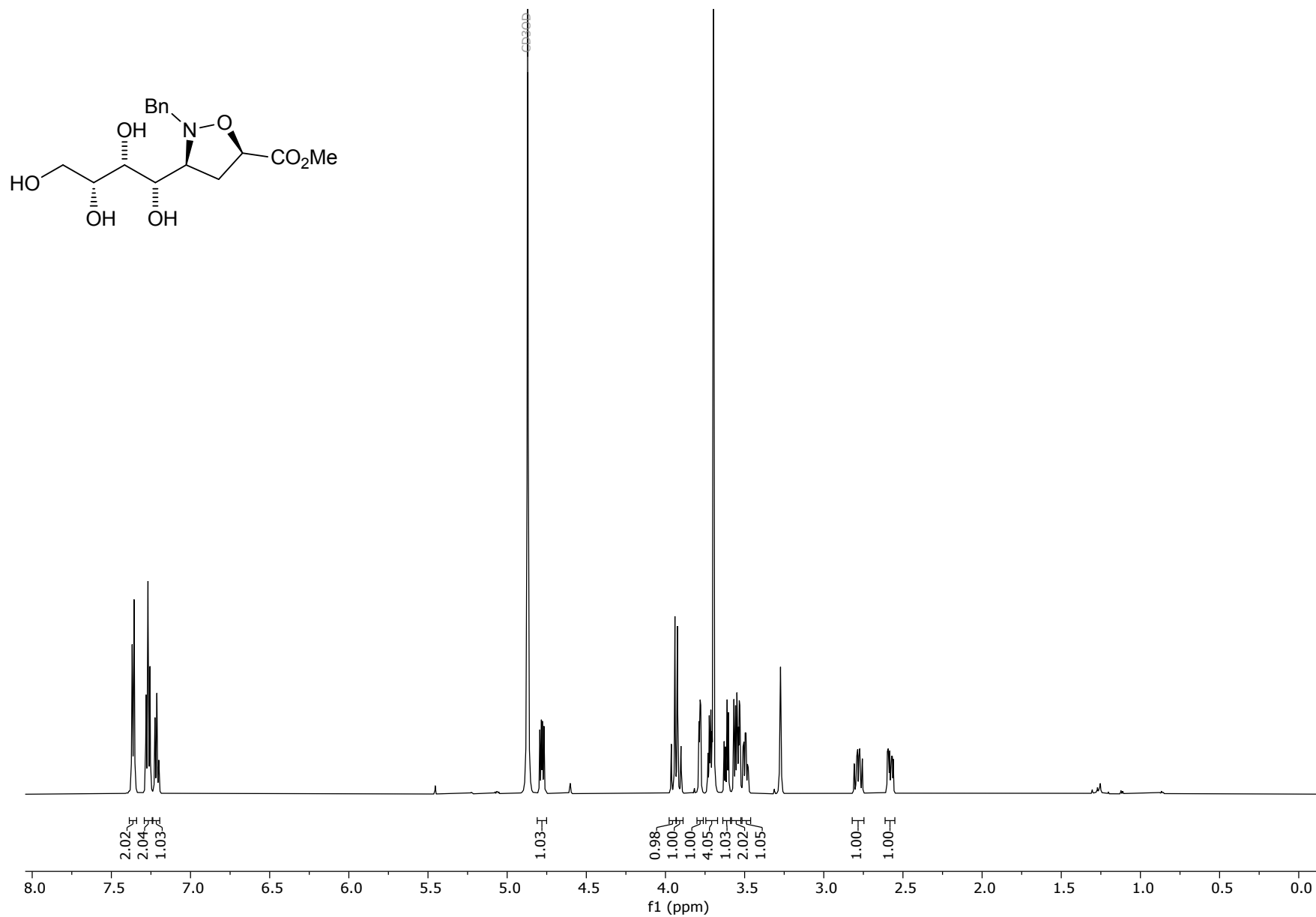
¹H-NMR spectrum of (3S,5S)-10 (CD₃OD)



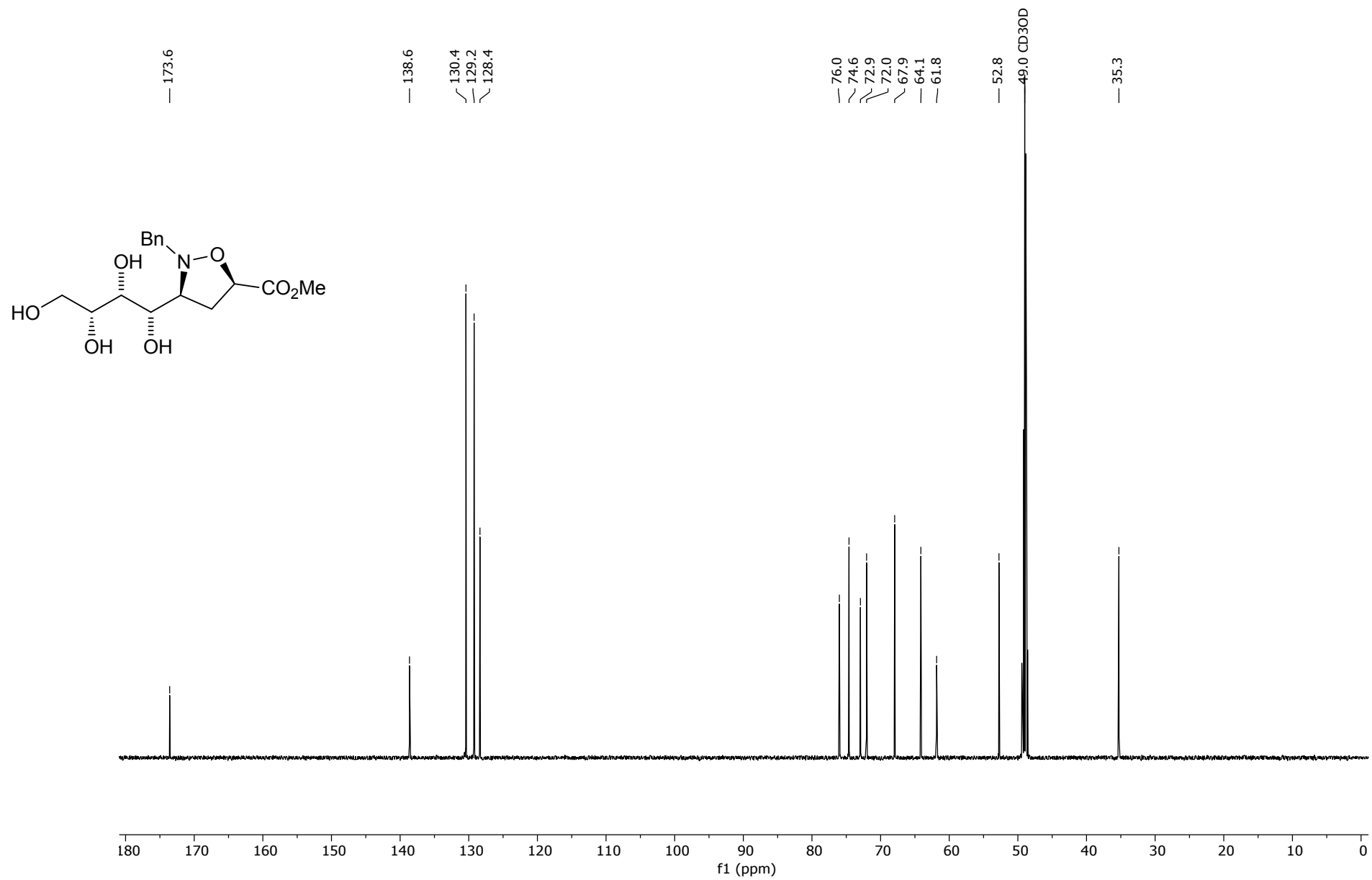
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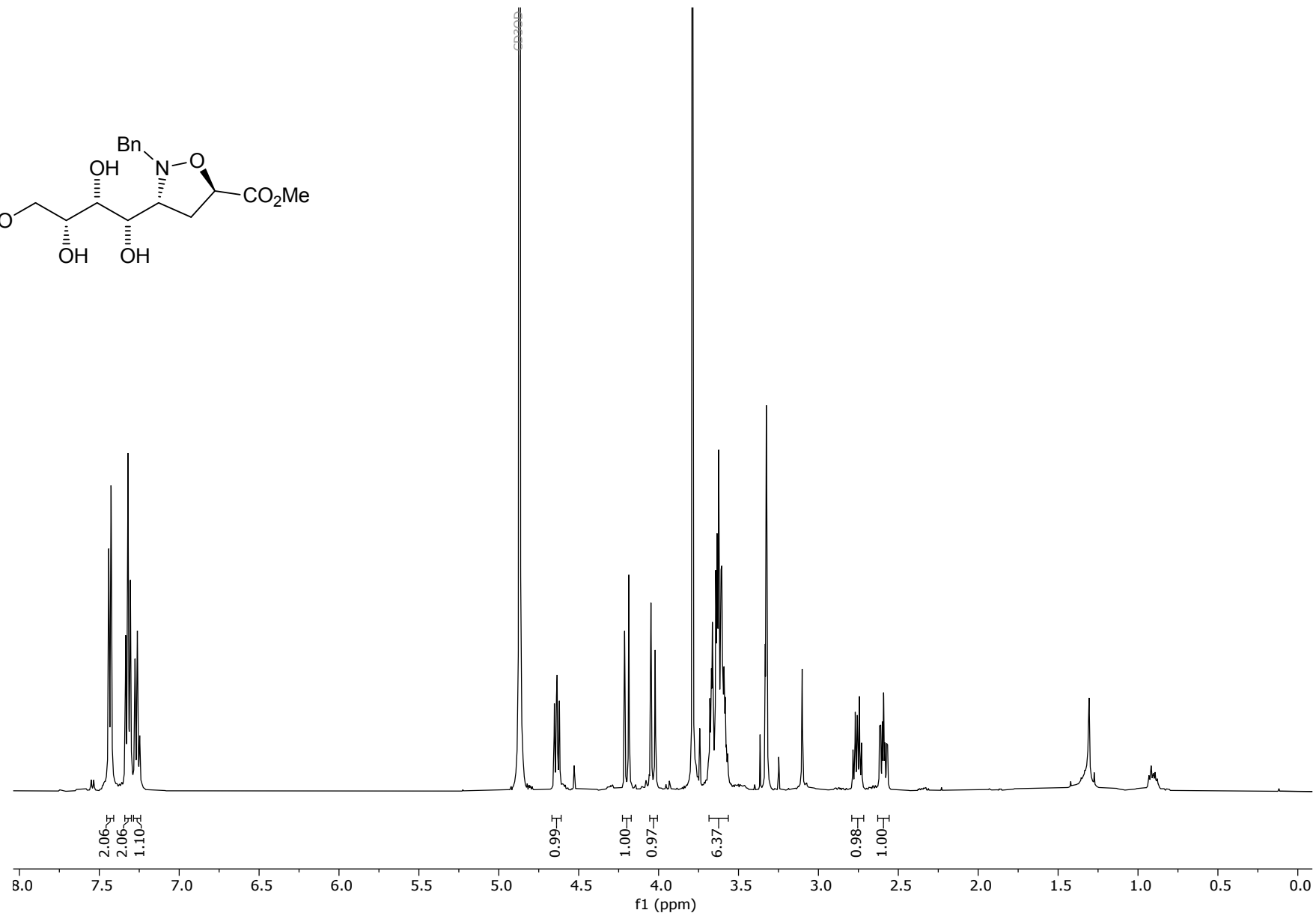
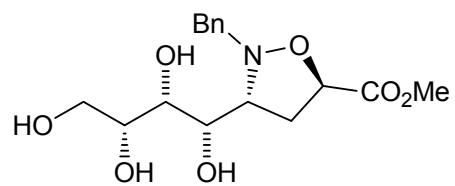
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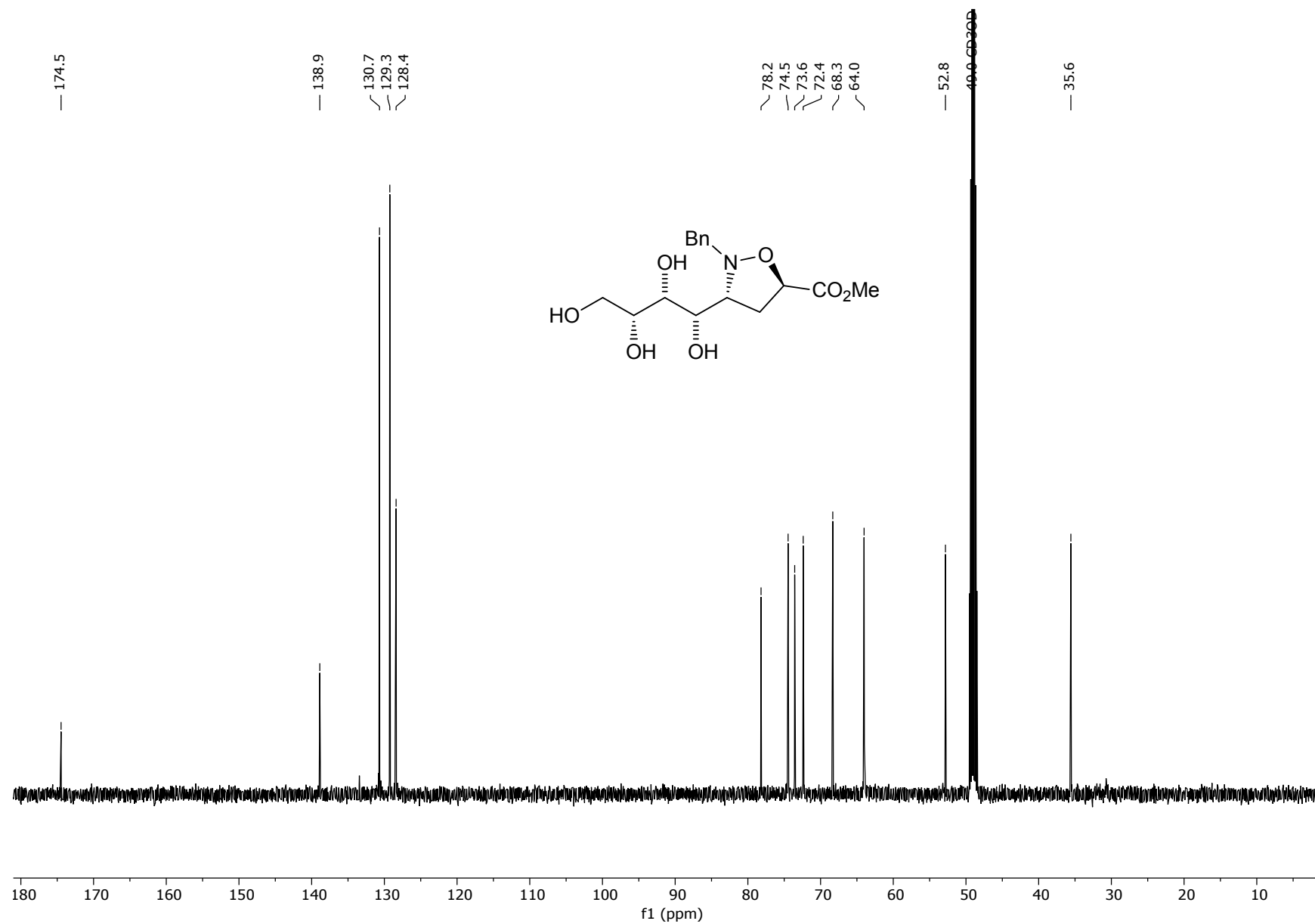
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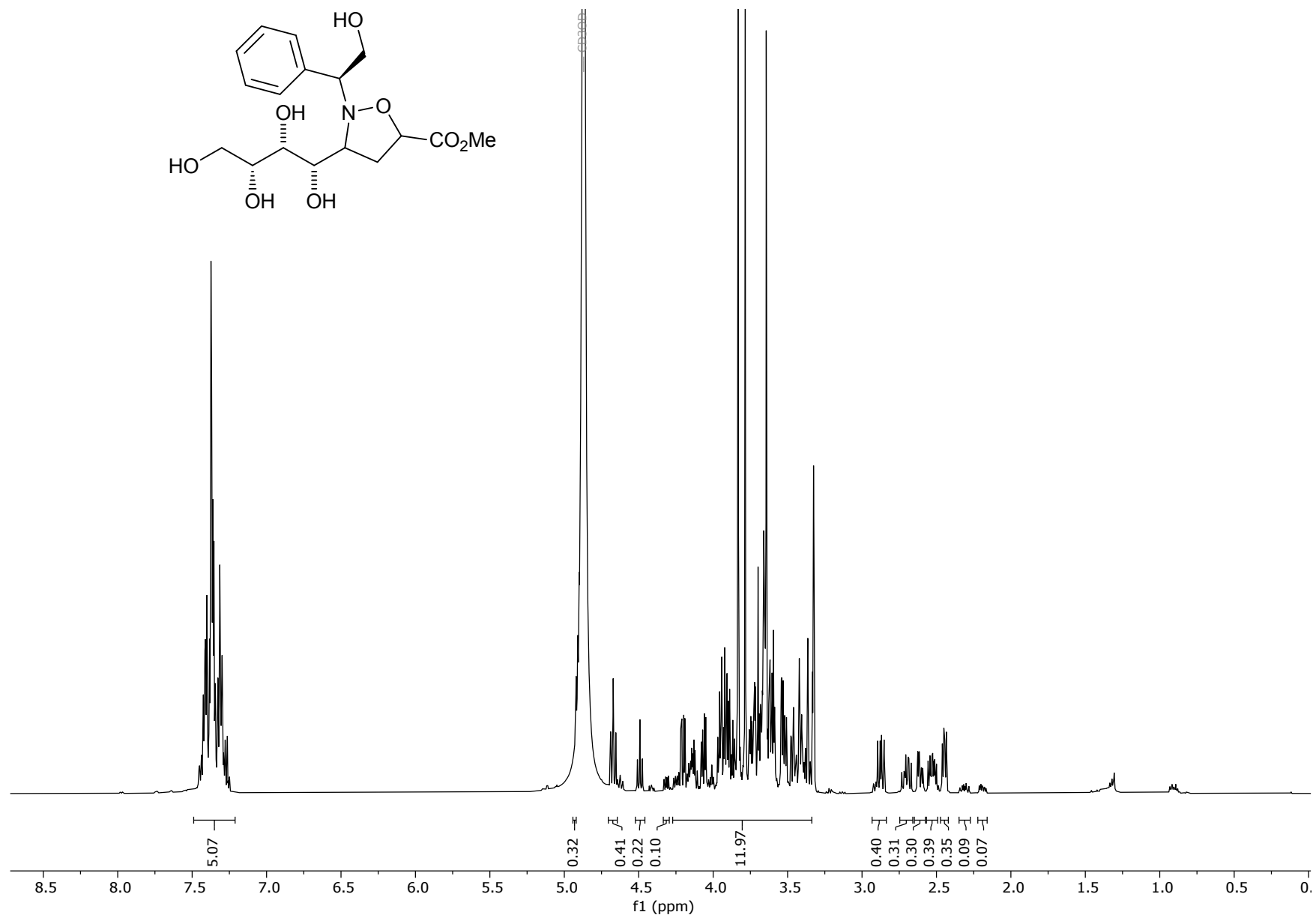
¹H-NMR spectrum of (3*R*,5*R*)-10 (CD₃OD)



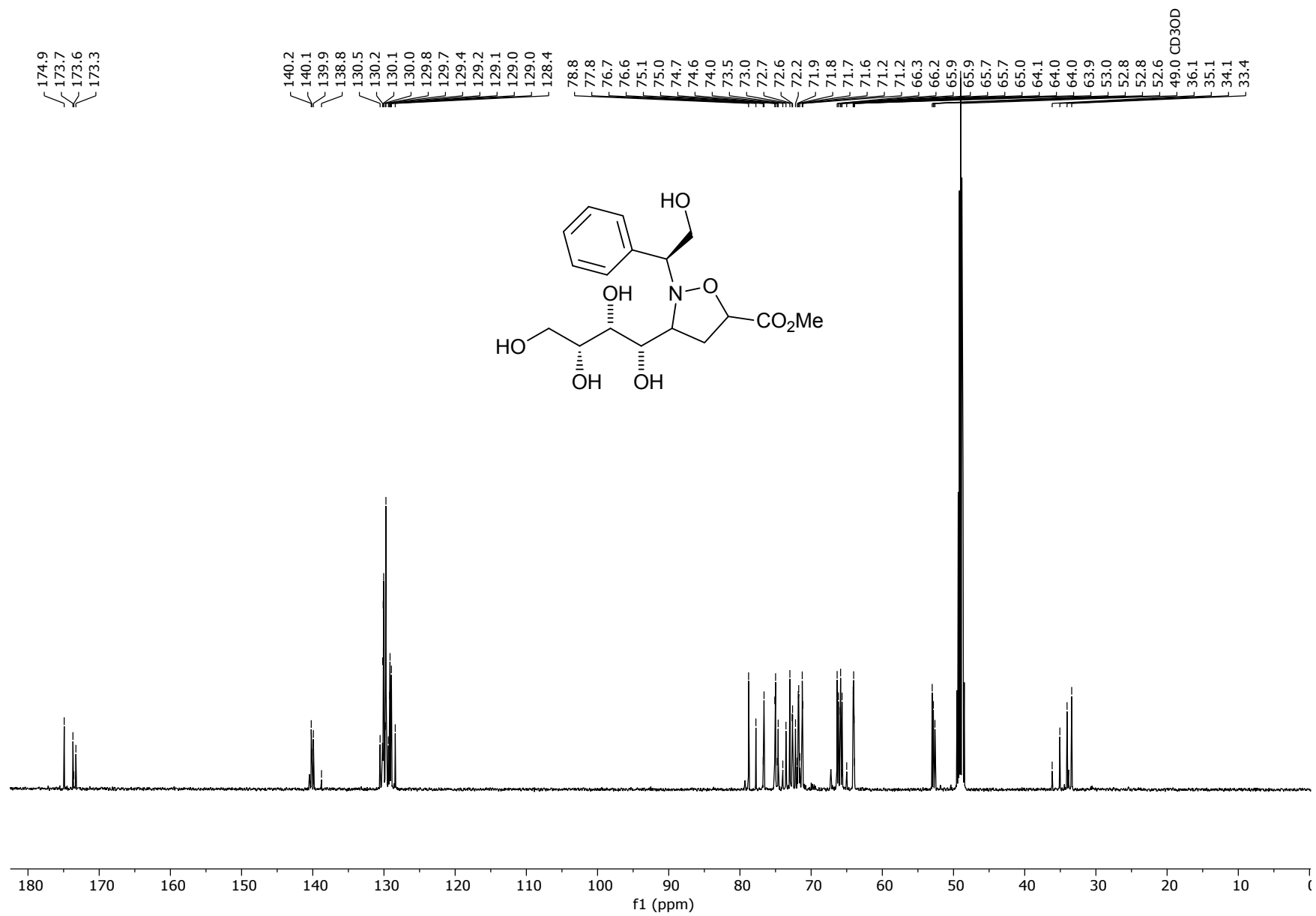
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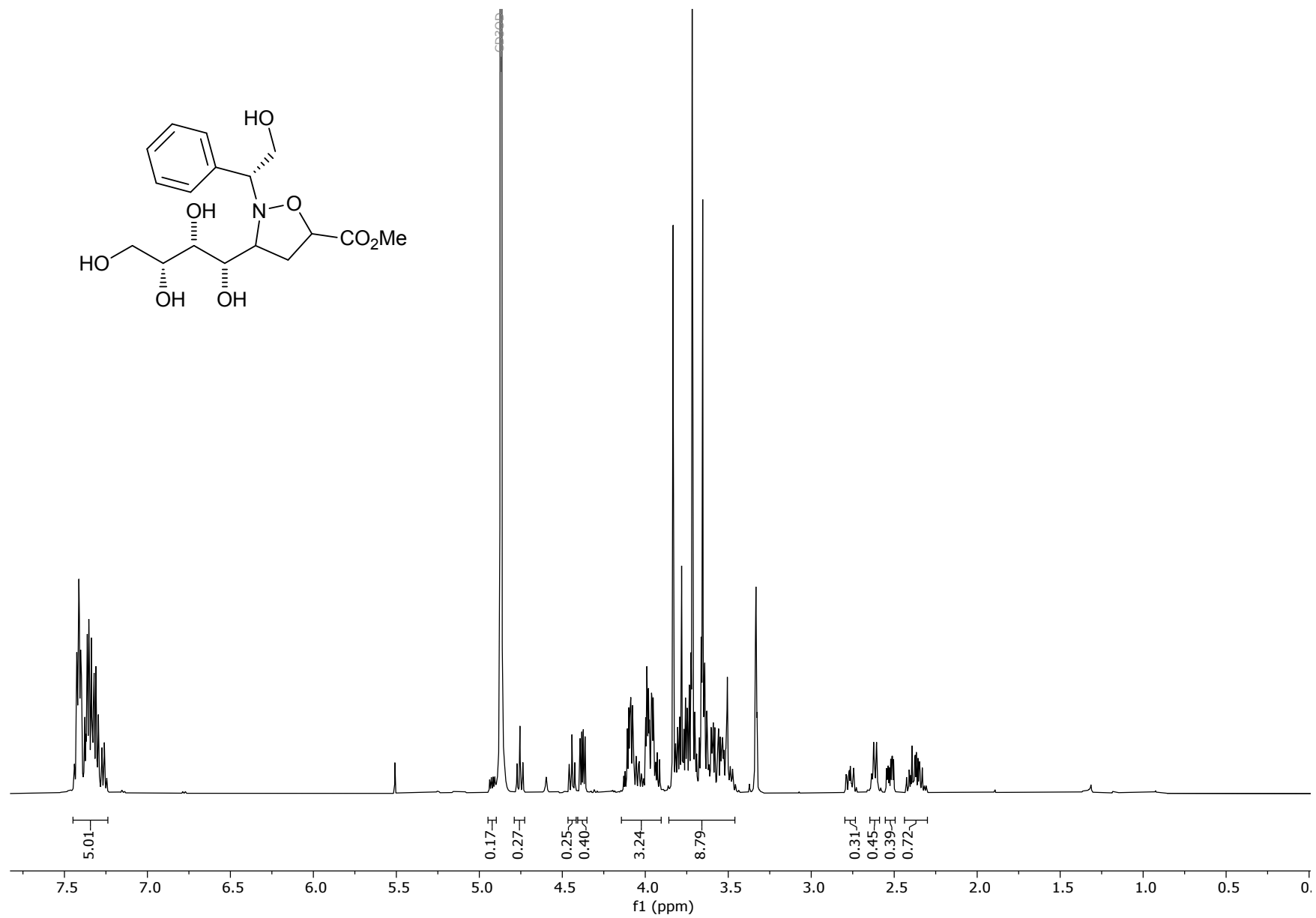
¹H-NMR spectrum of 10' (CD₃OD)



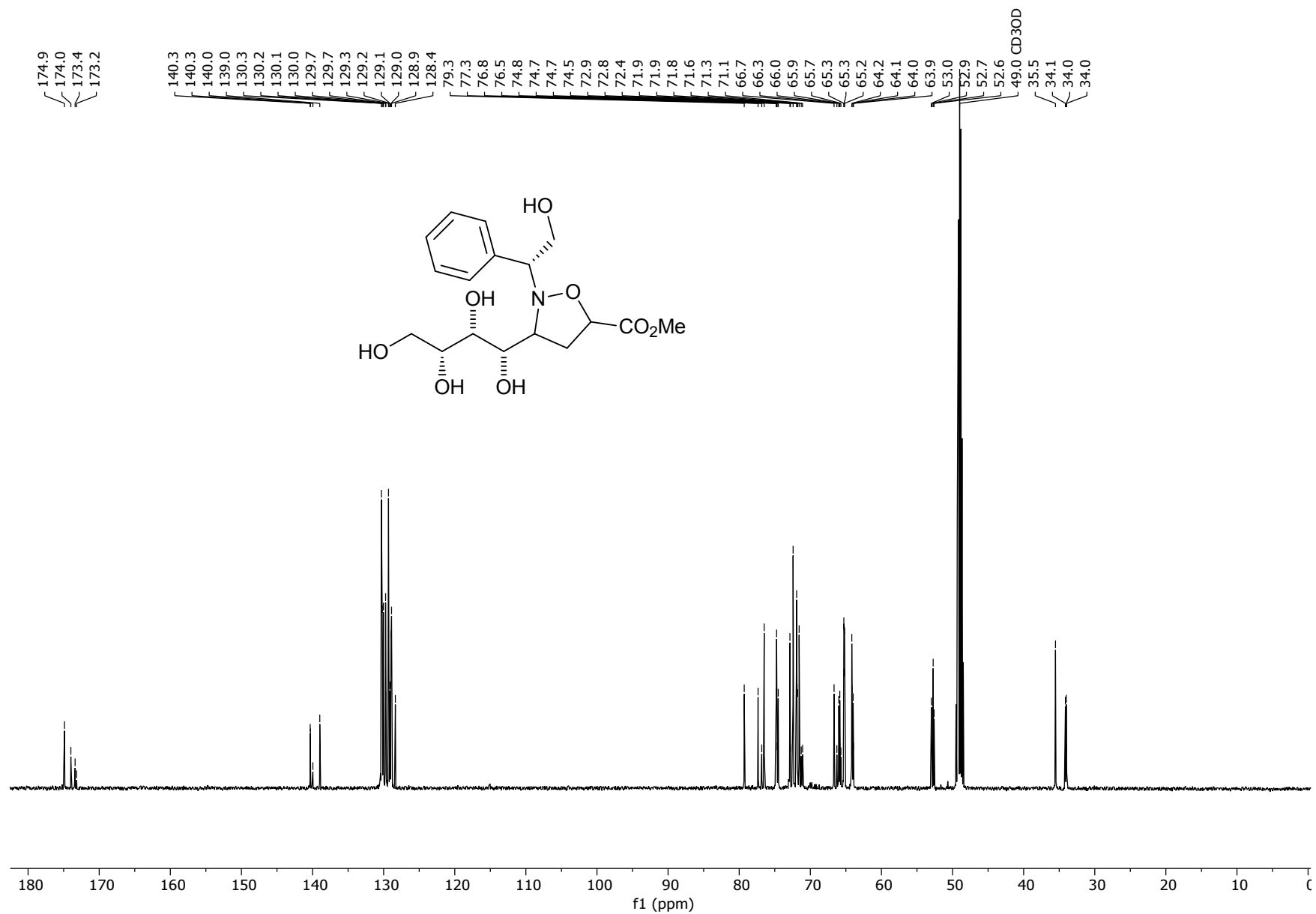
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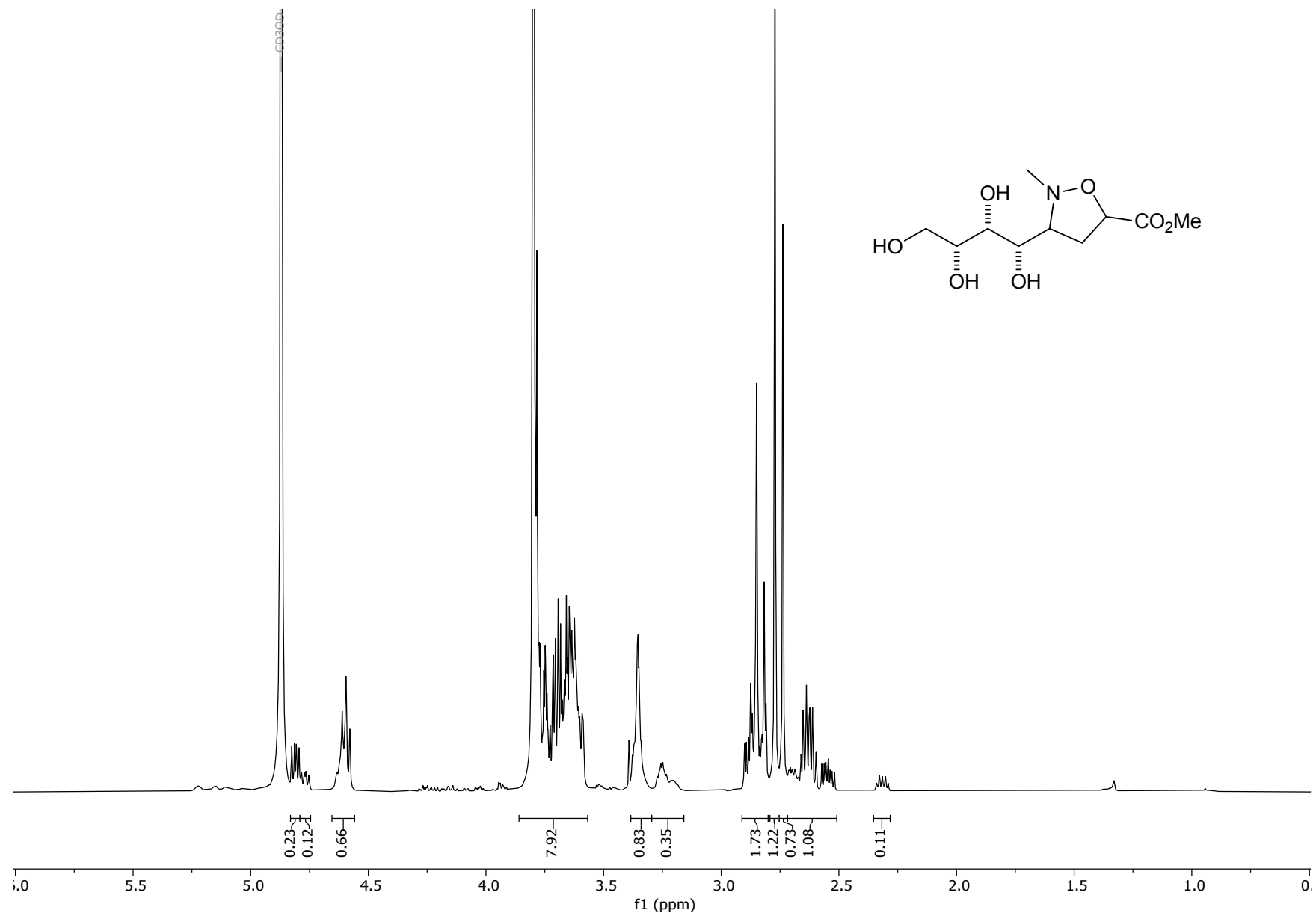
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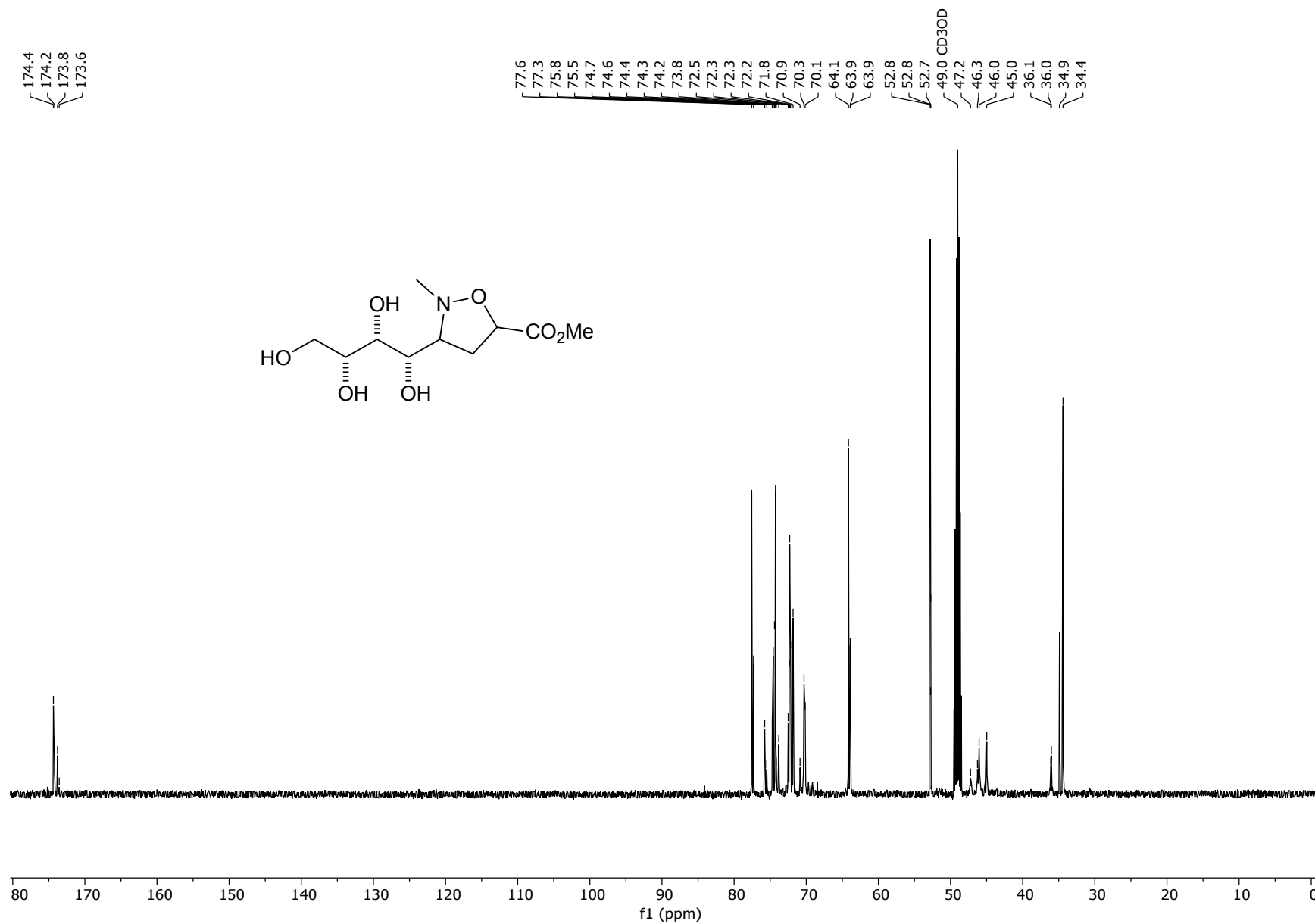
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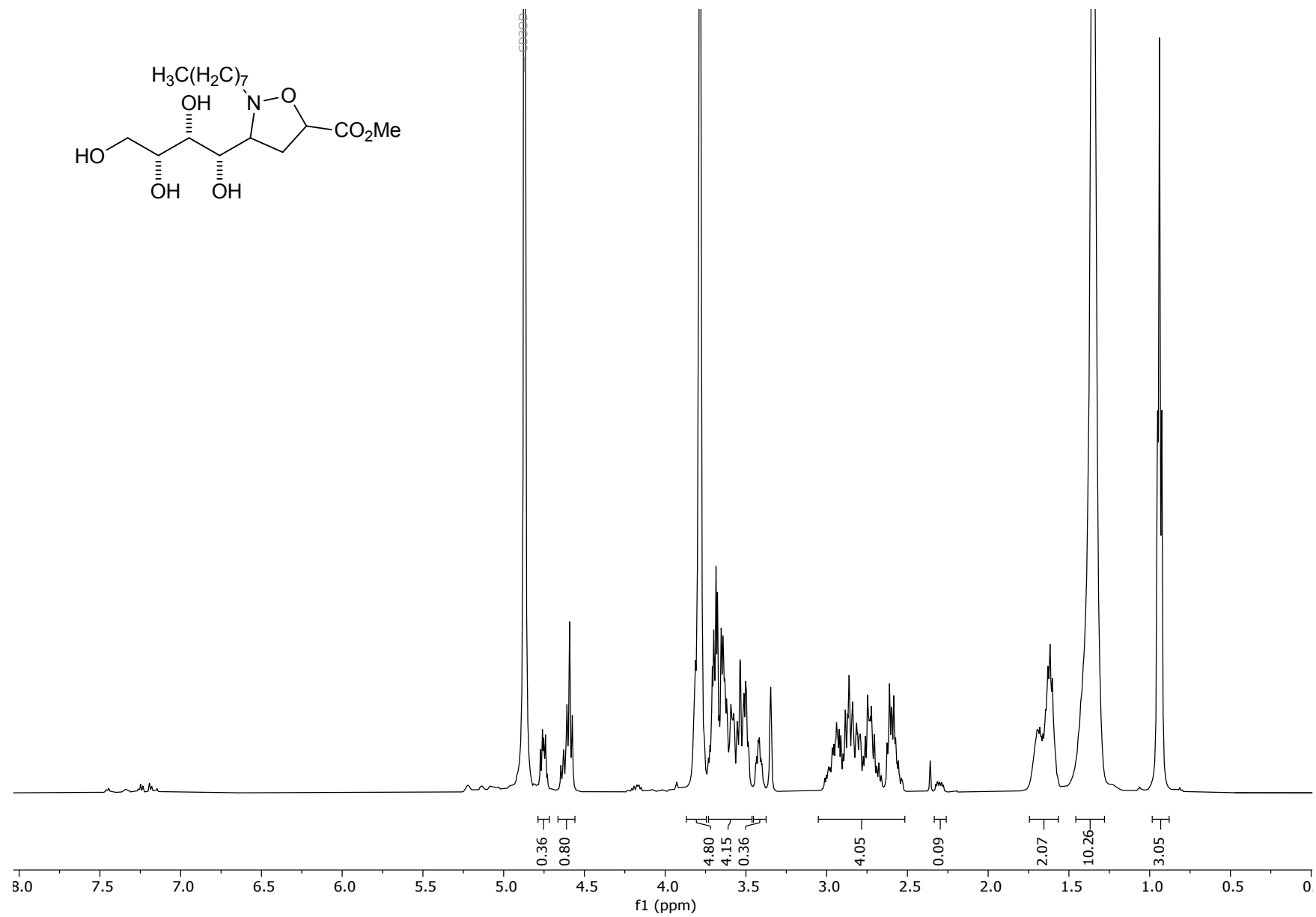
¹H-NMR spectrum of 14 (CD₃OD)



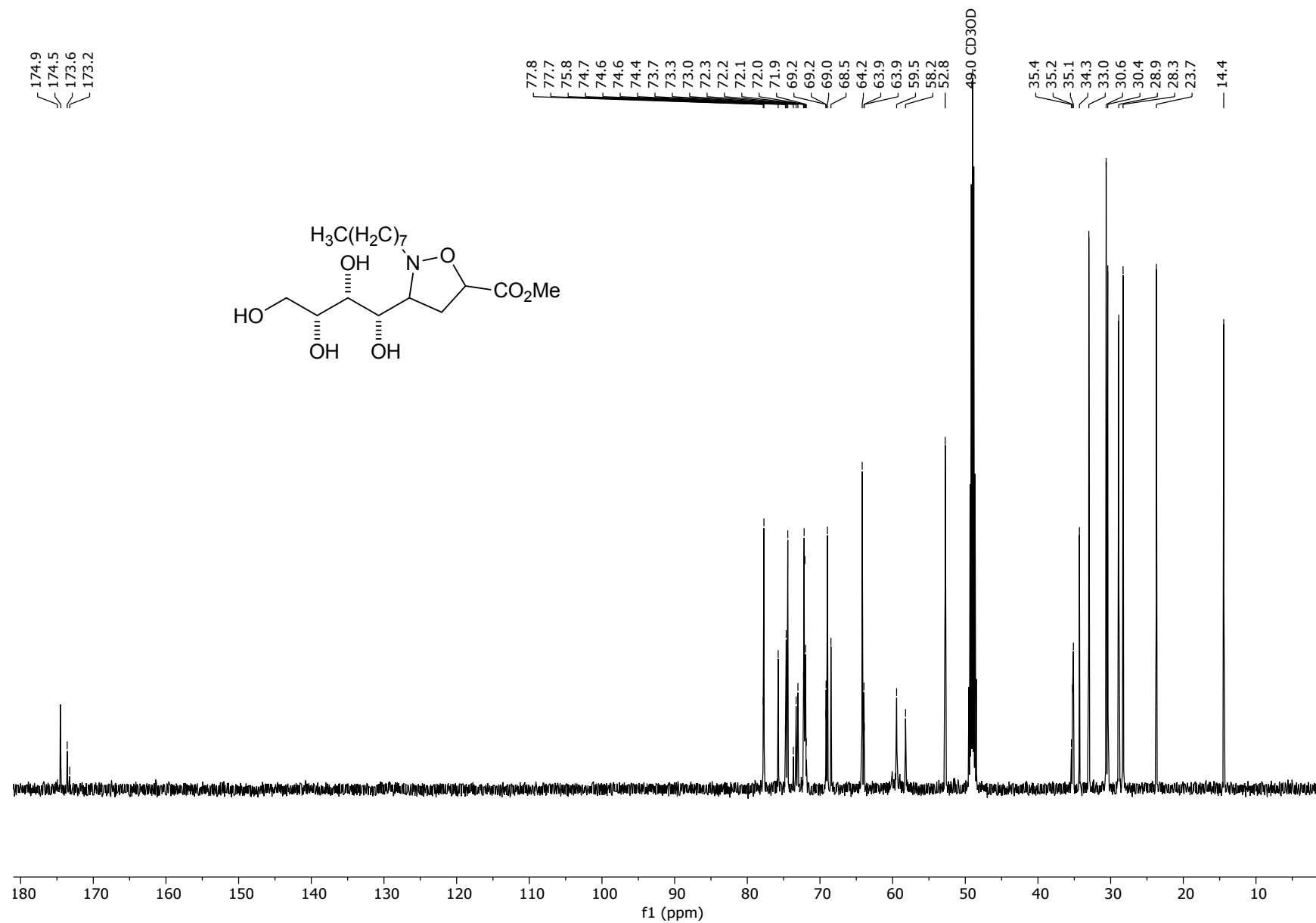
¹³C-NMR spectrum of 14 (CD₃OD)



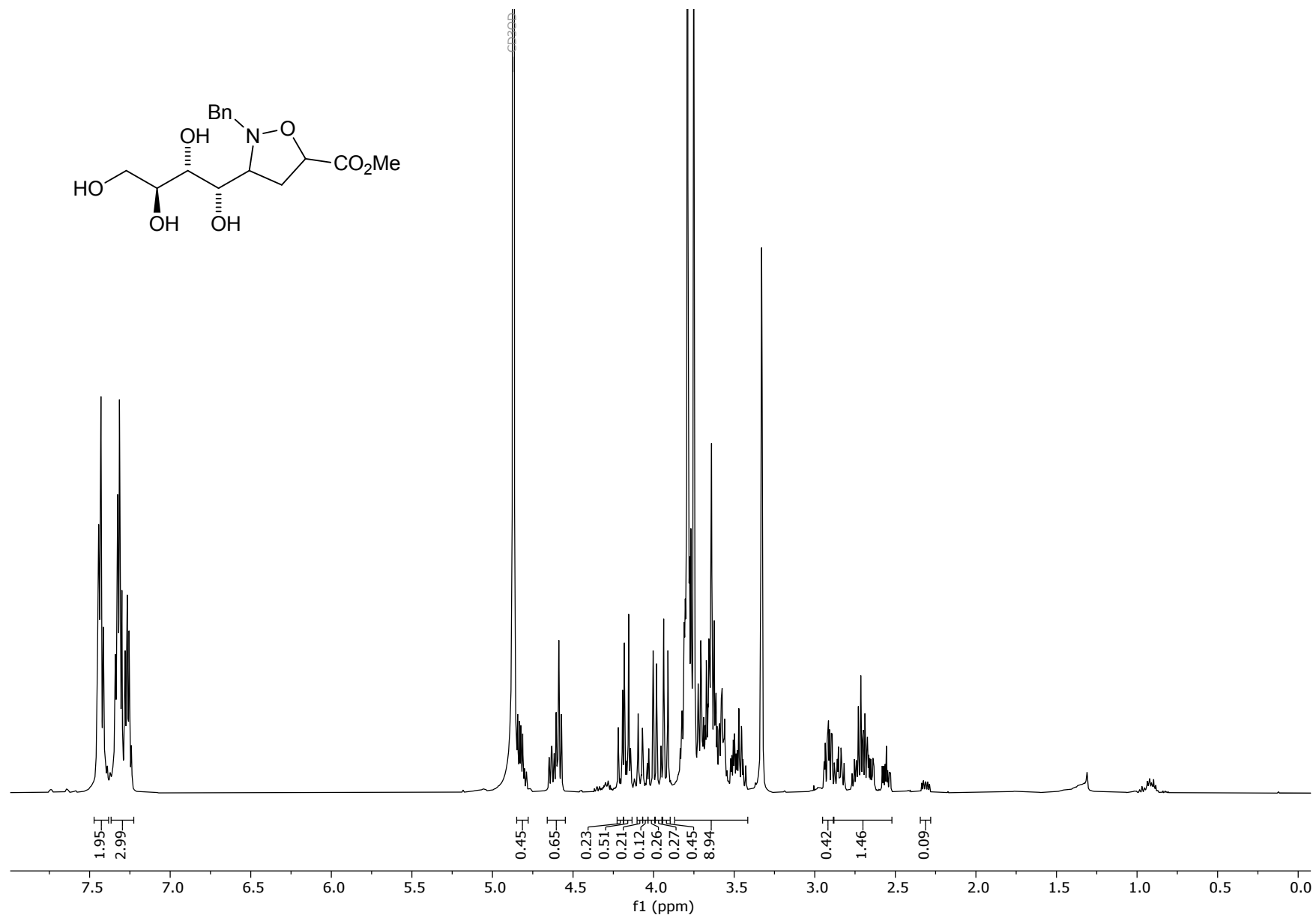
¹H-NMR spectrum of 15 (CD₃OD)



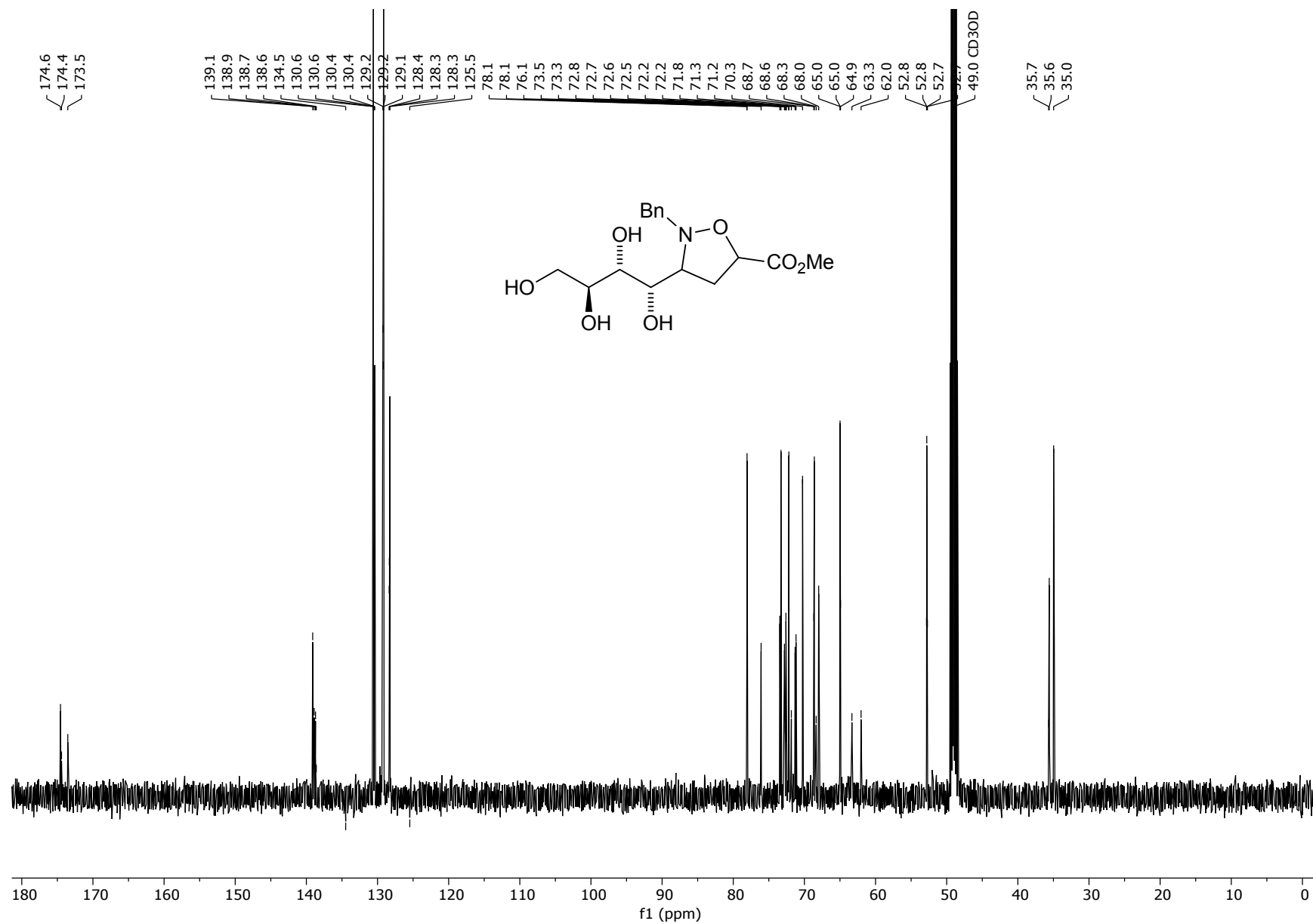
¹³C-NMR spectrum of 15 (CD₃OD)



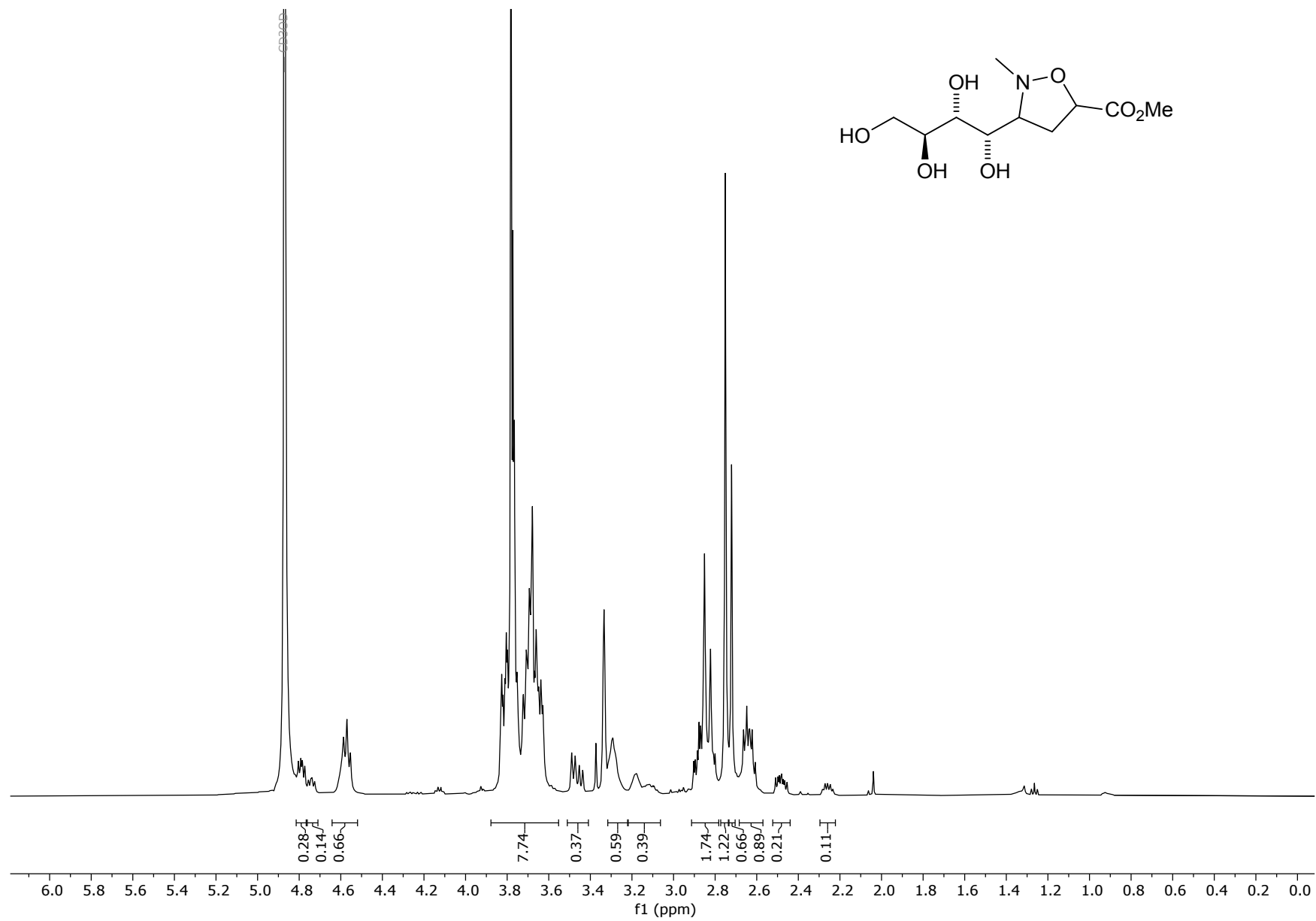
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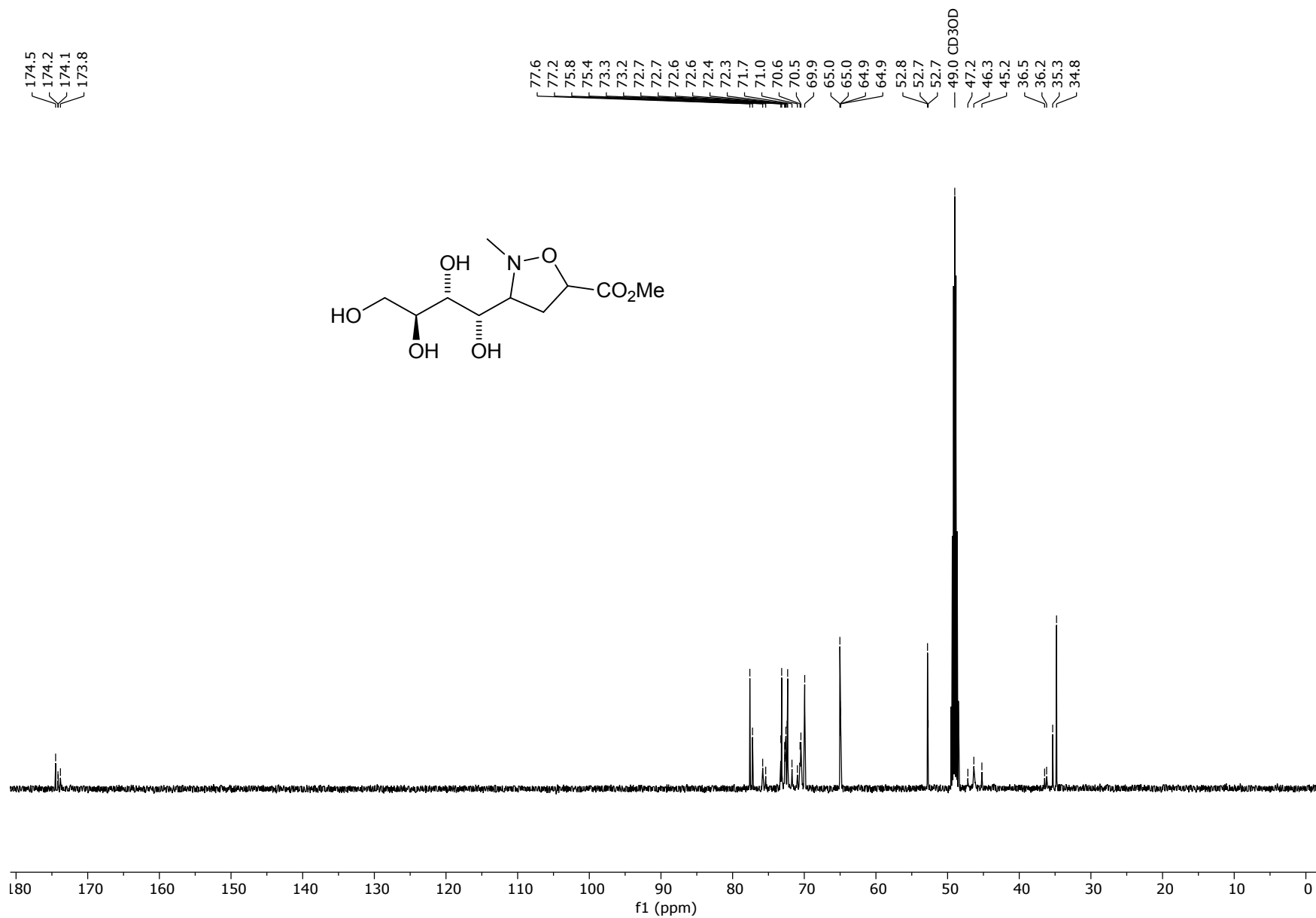
¹³C-NMR spectrum of 16 (CD₃OD)



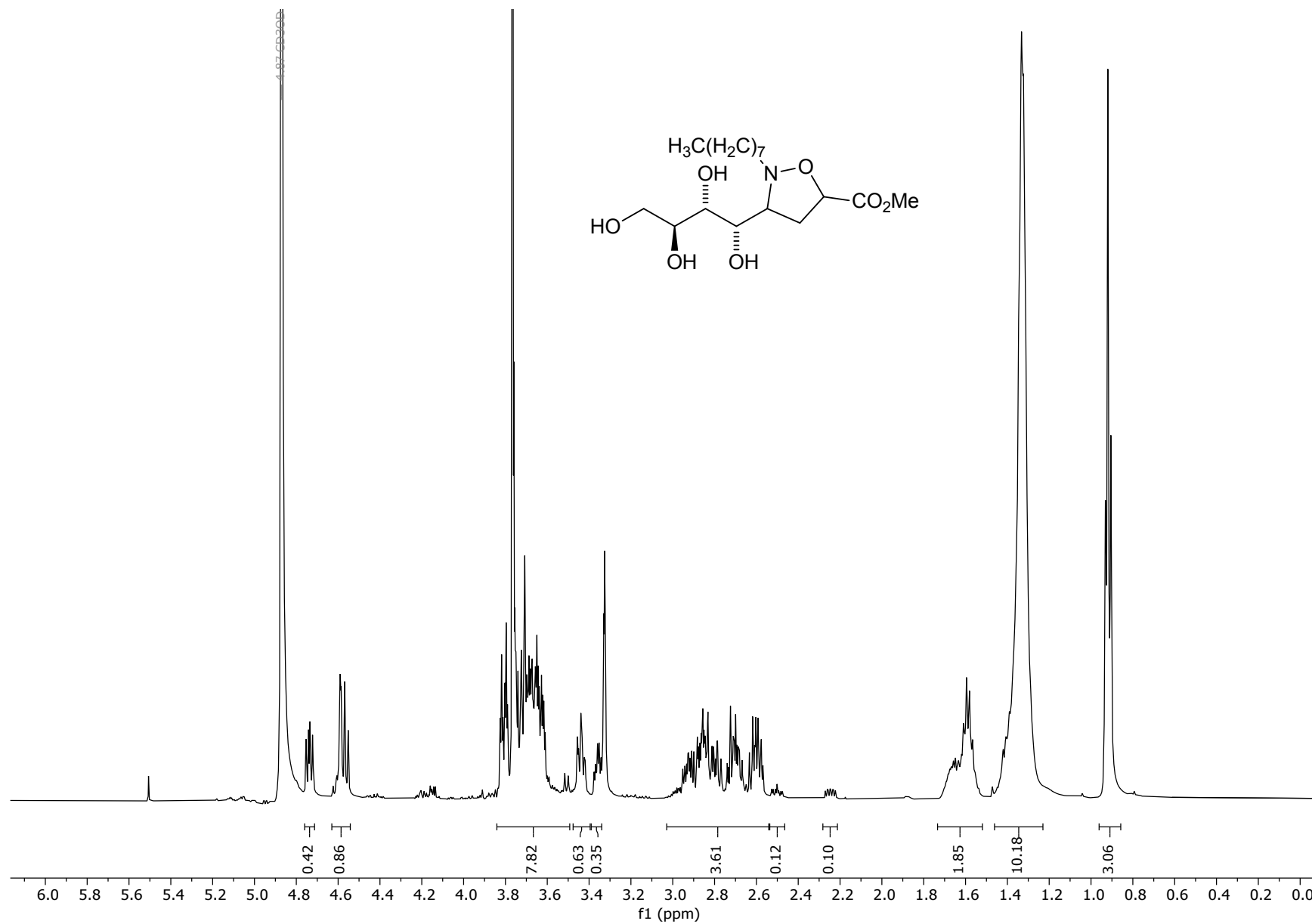
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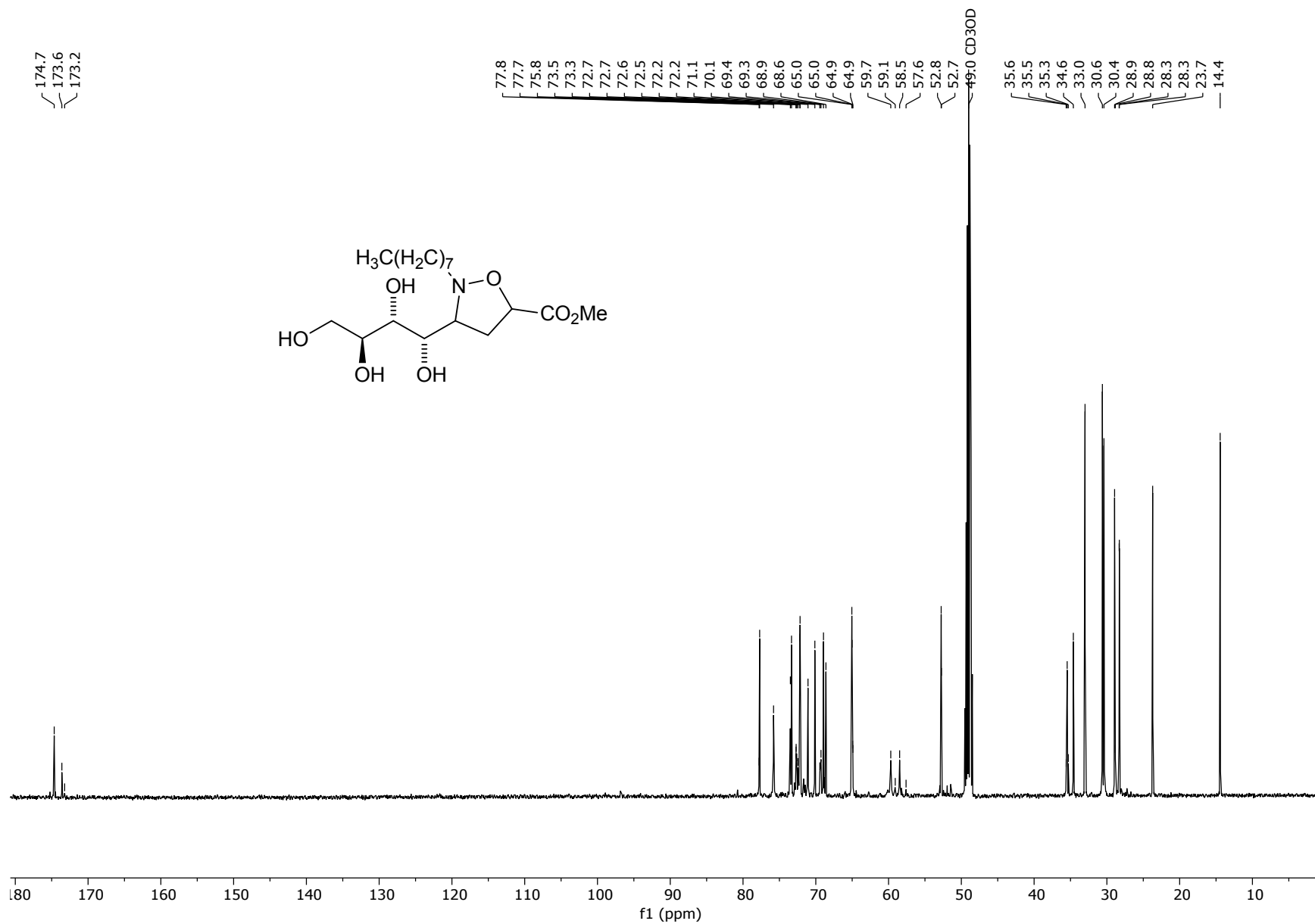
¹³C-NMR spectrum of 17 (CD₃OD)



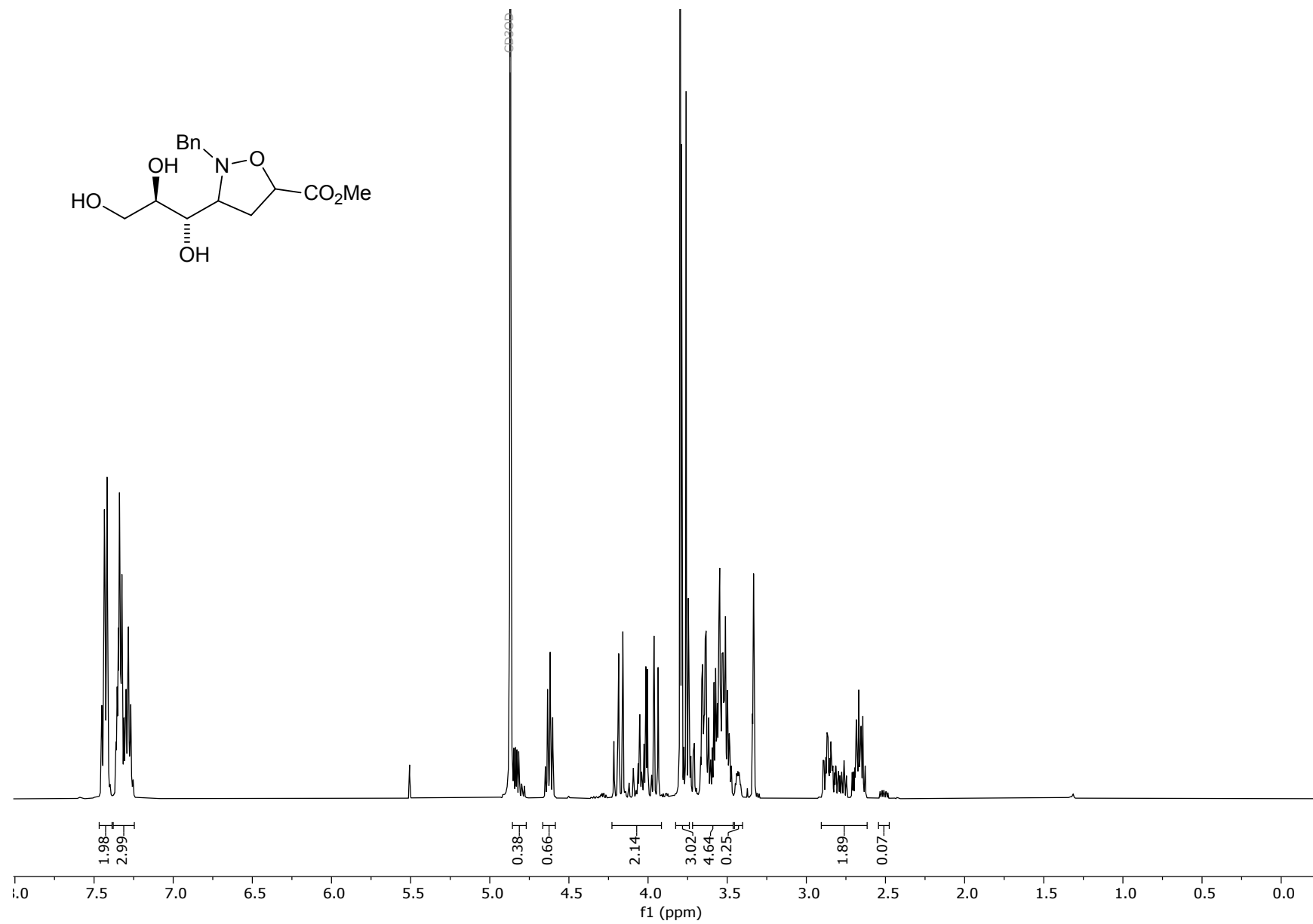
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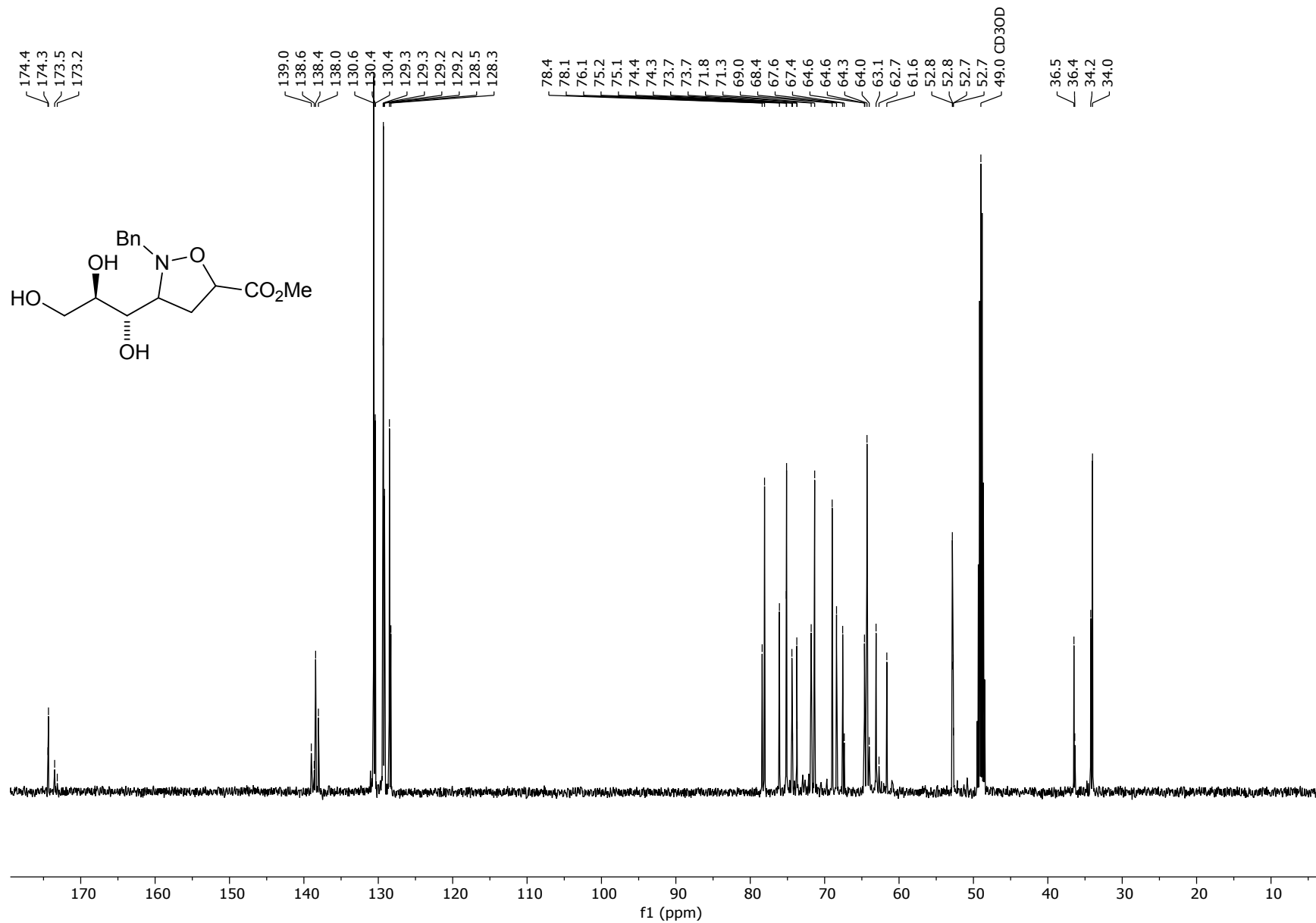
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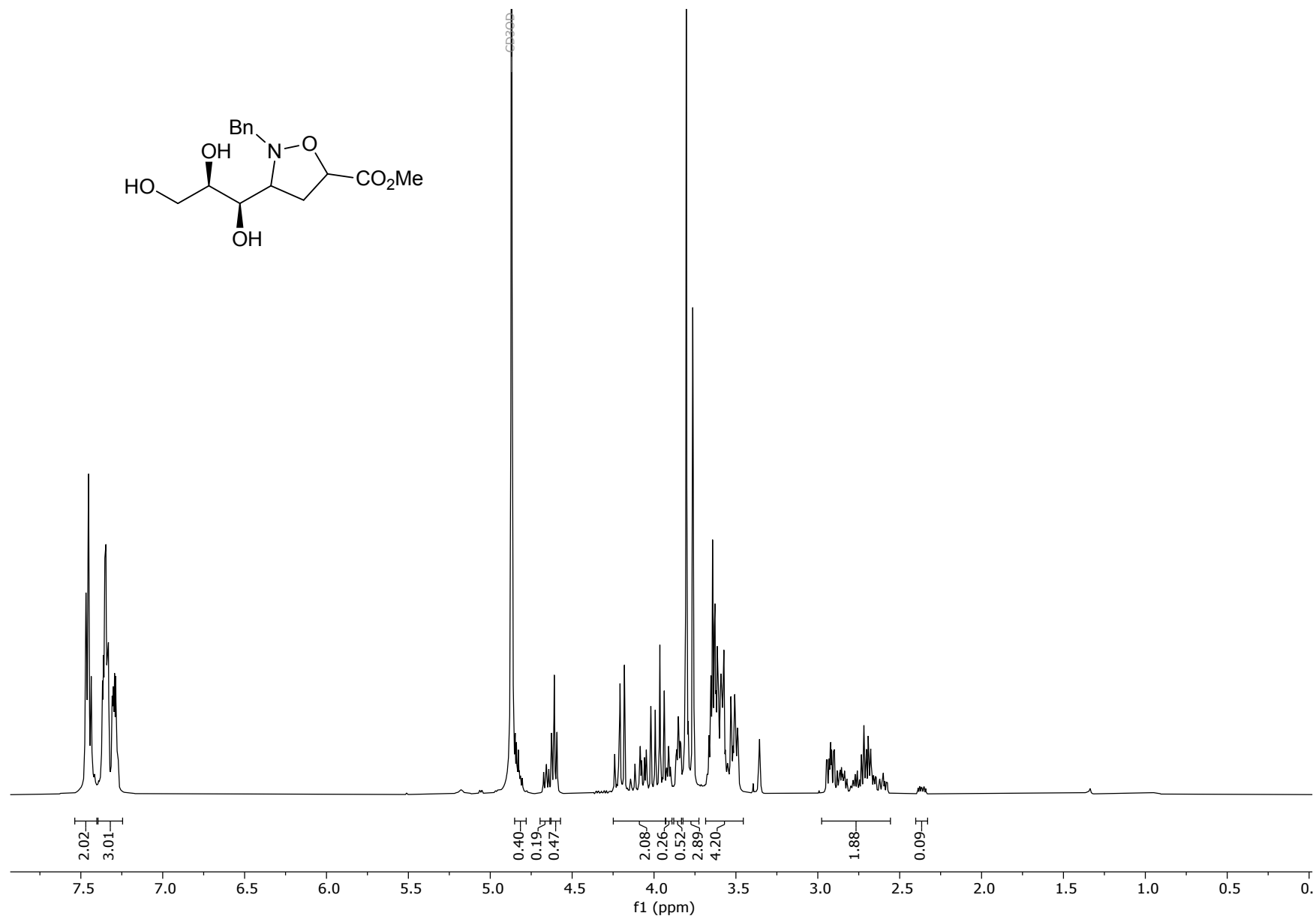
¹H-NMR spectrum of 19 (CD₃OD)



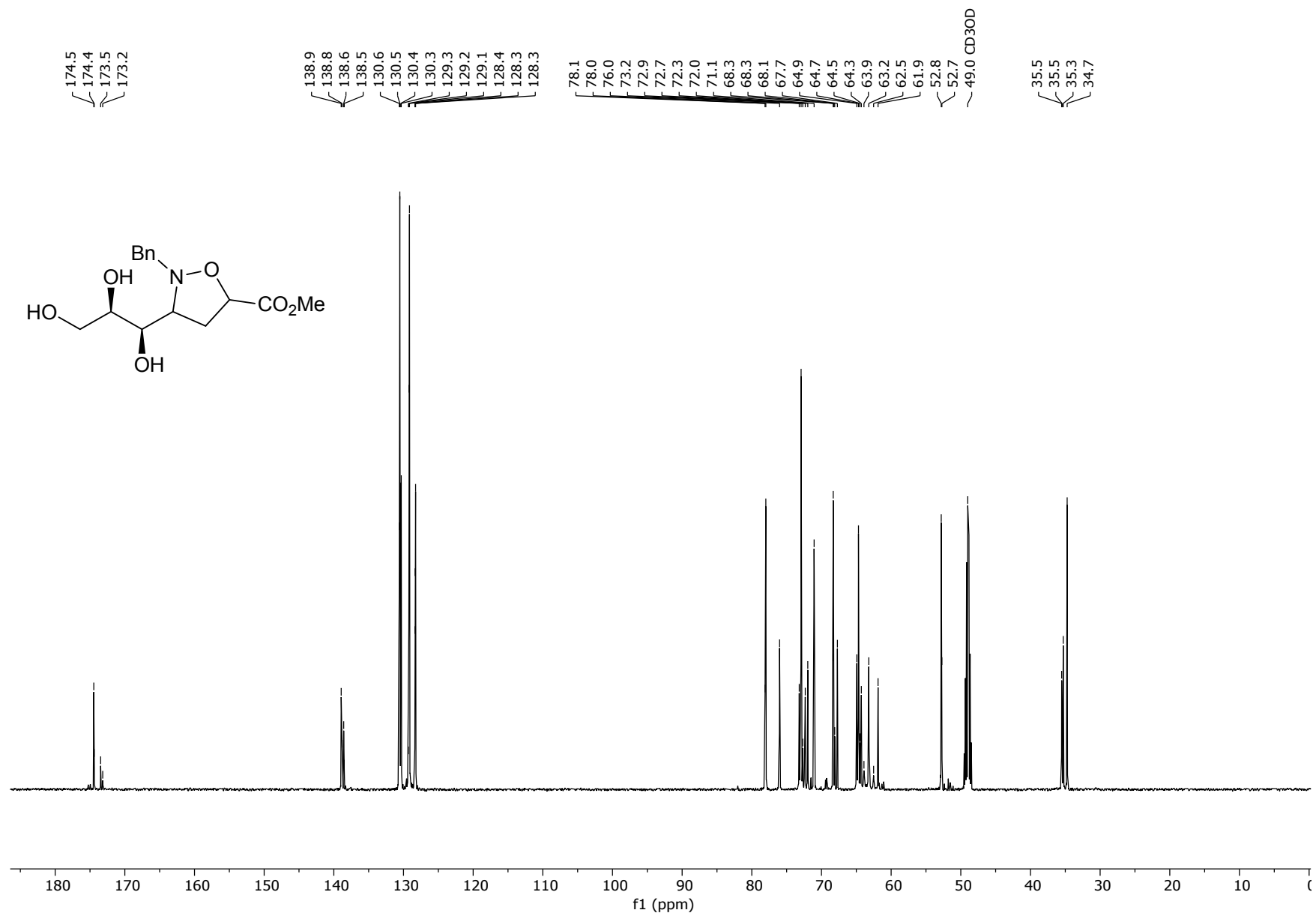
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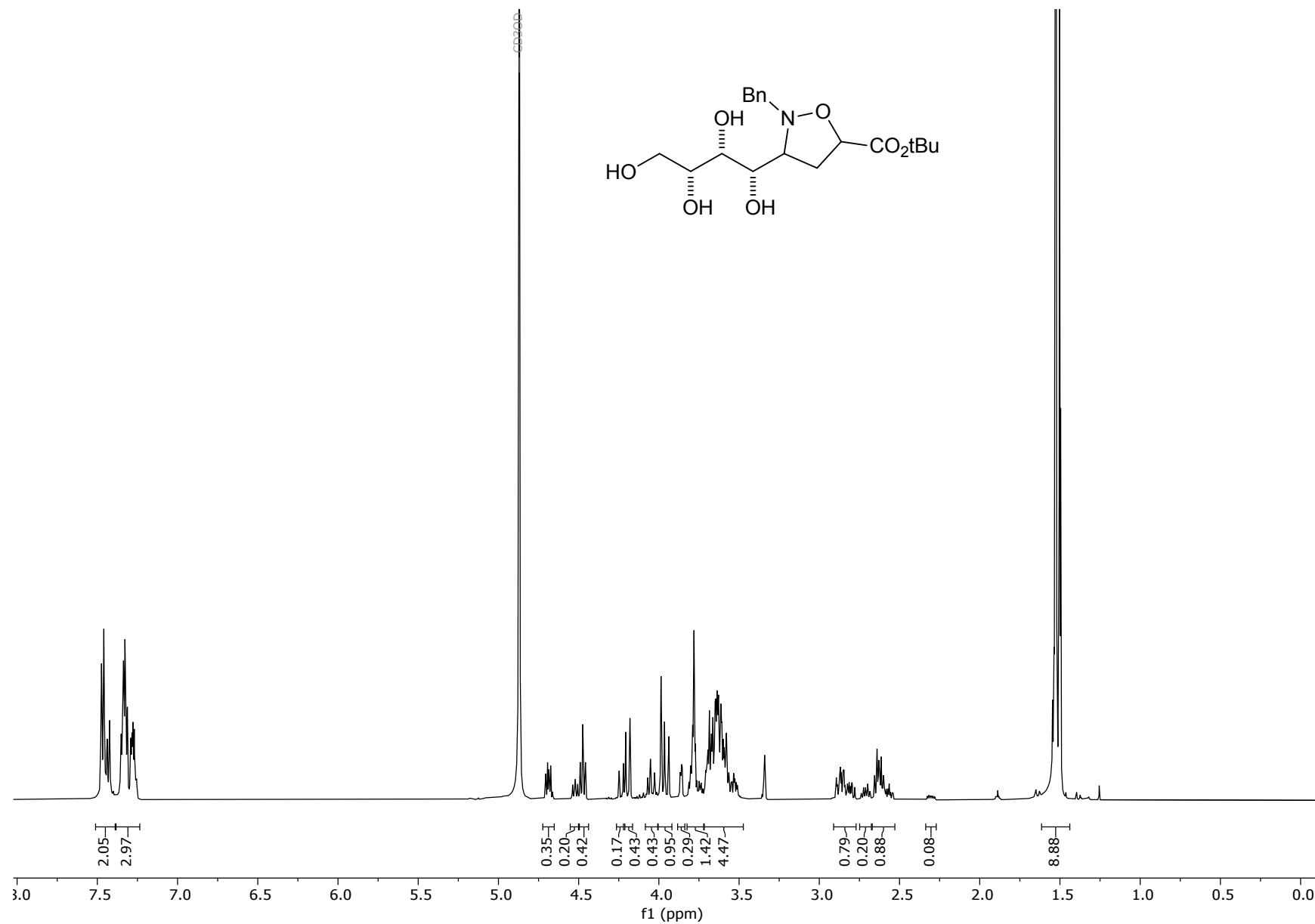
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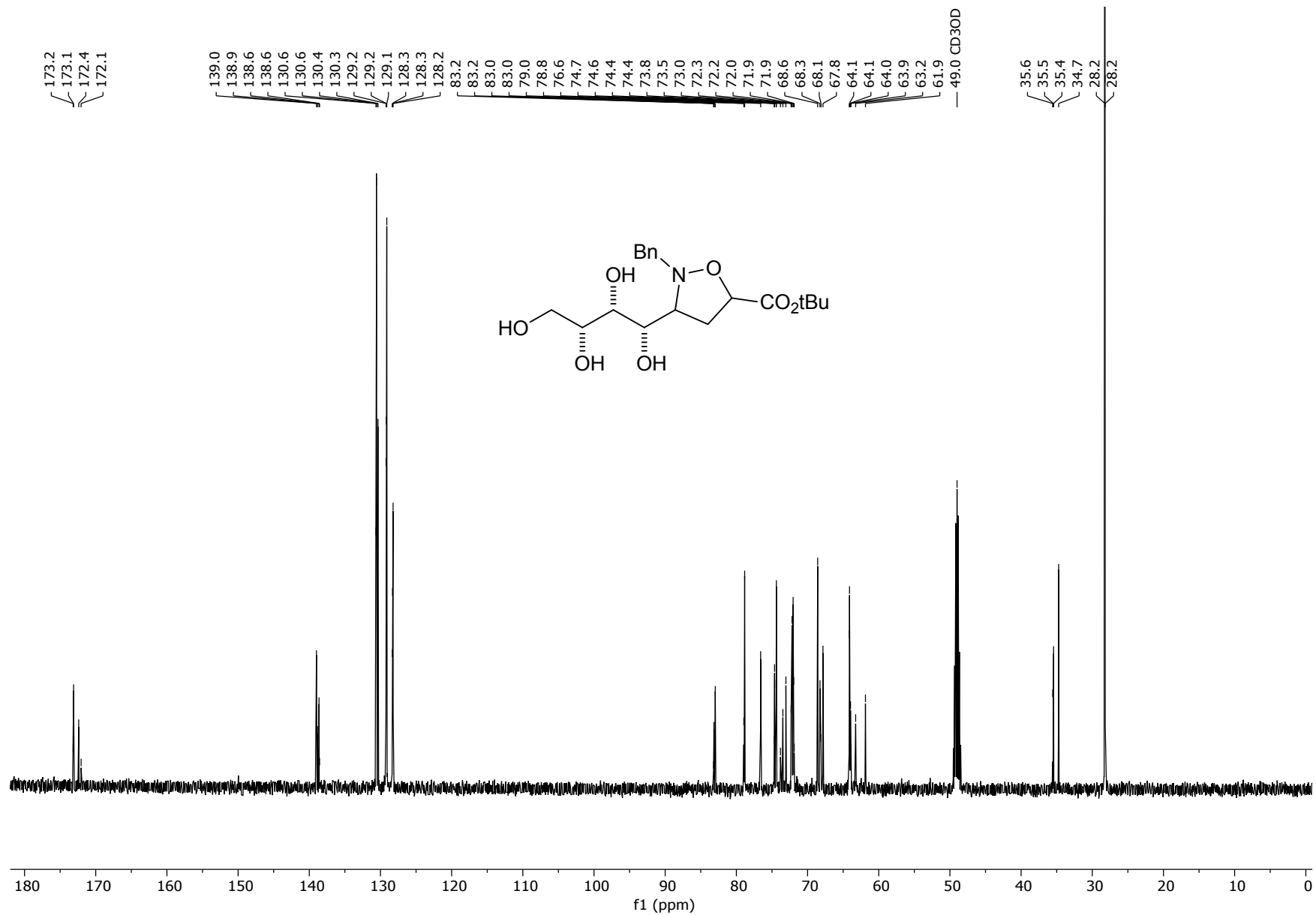
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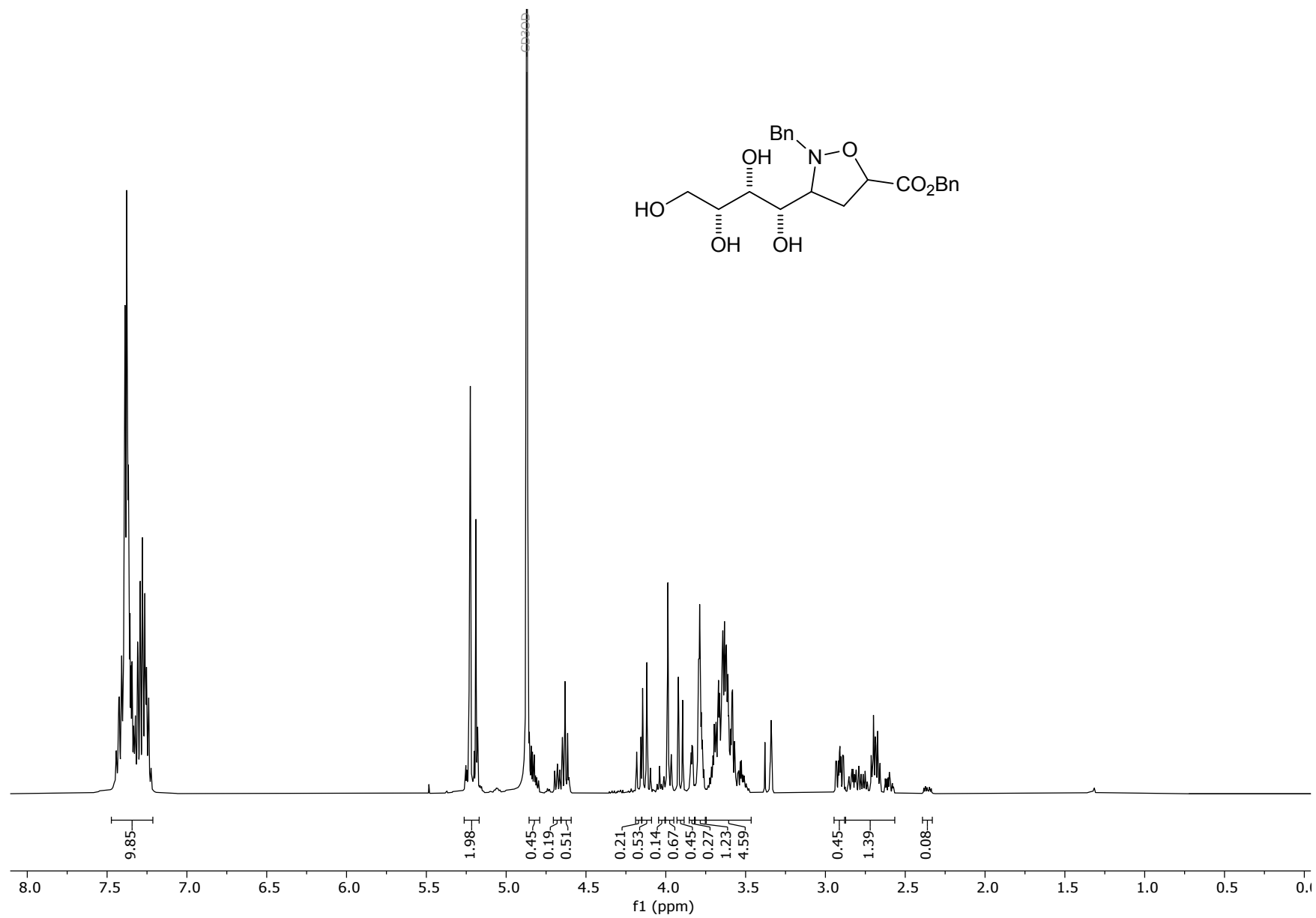
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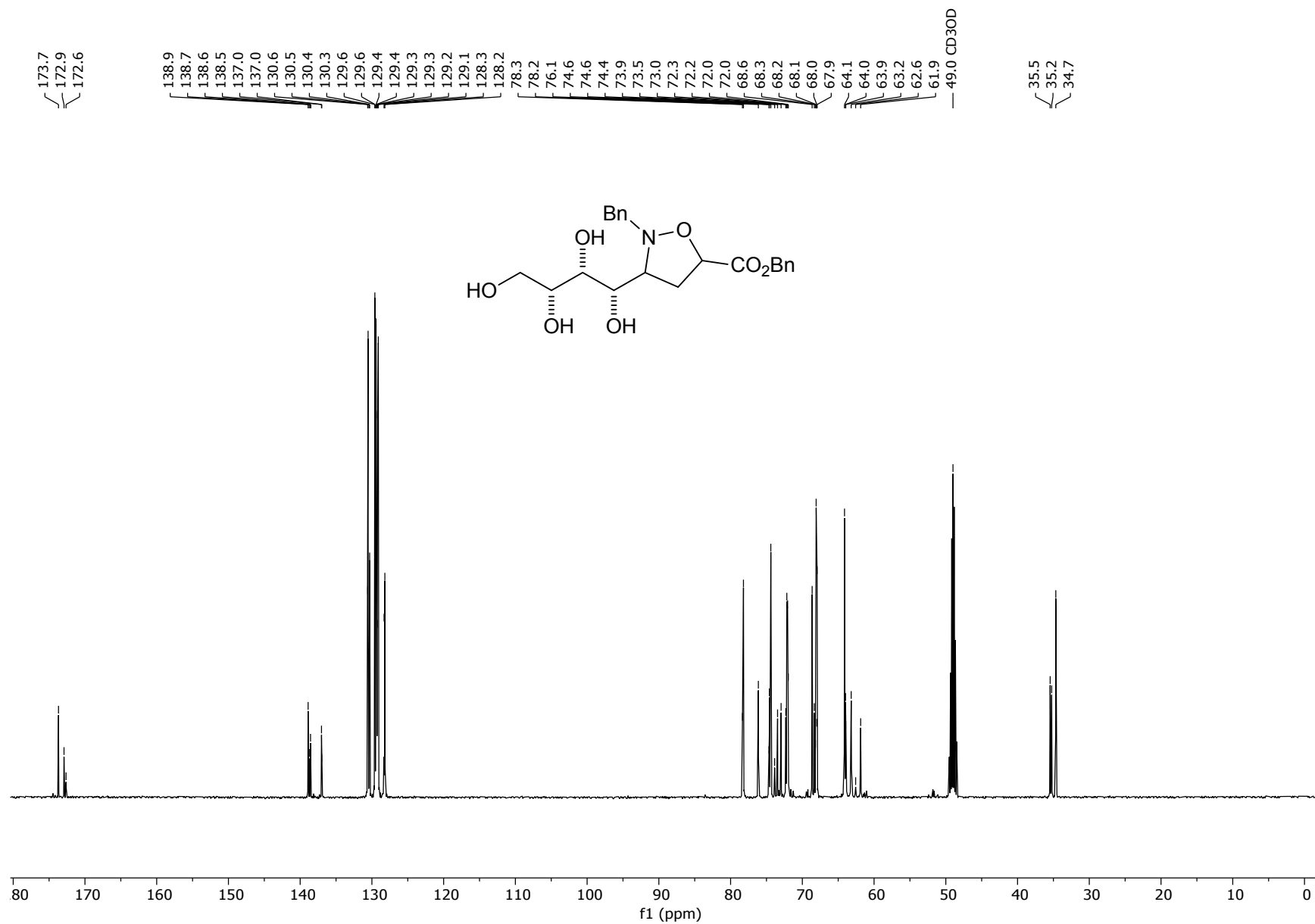
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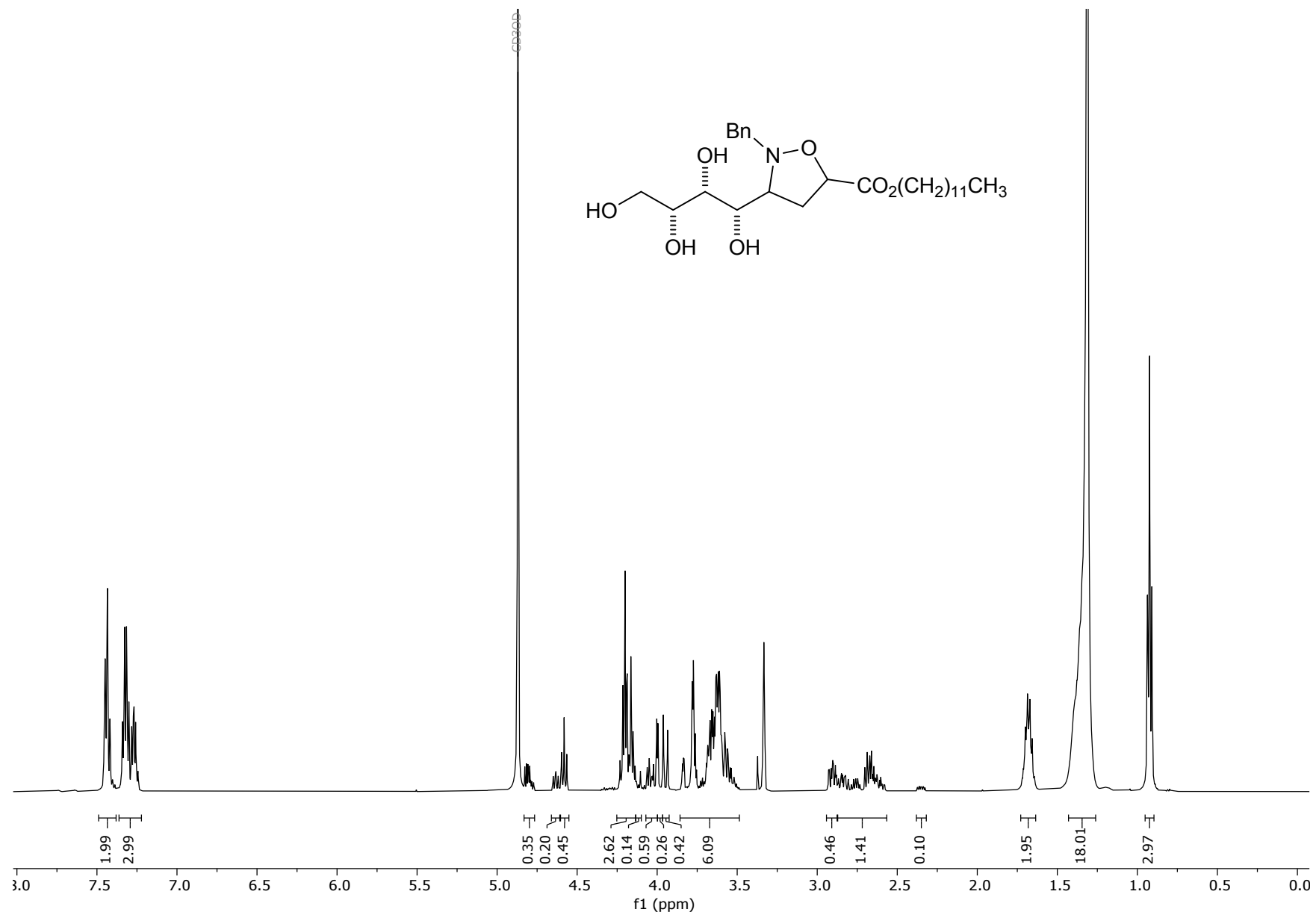
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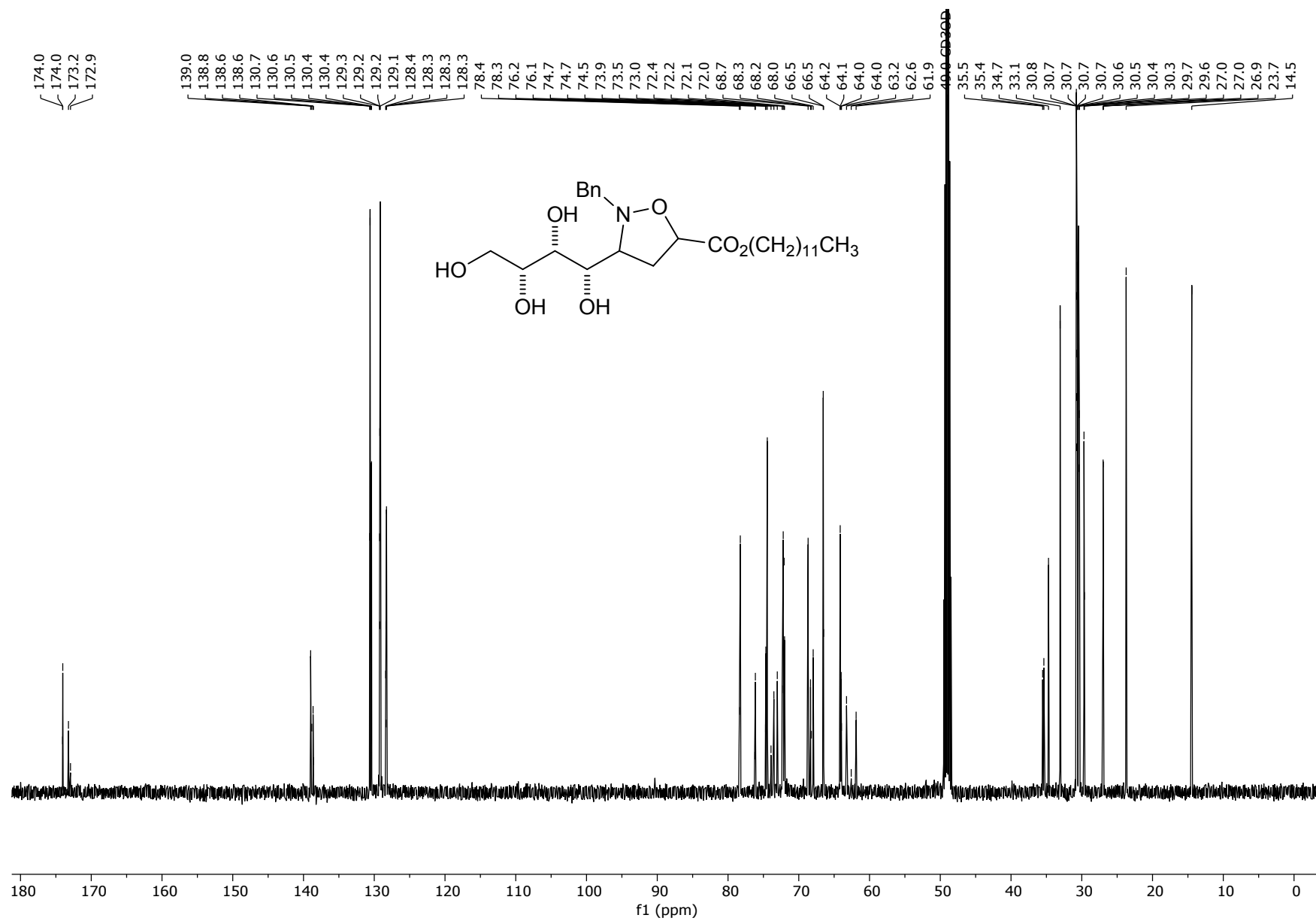
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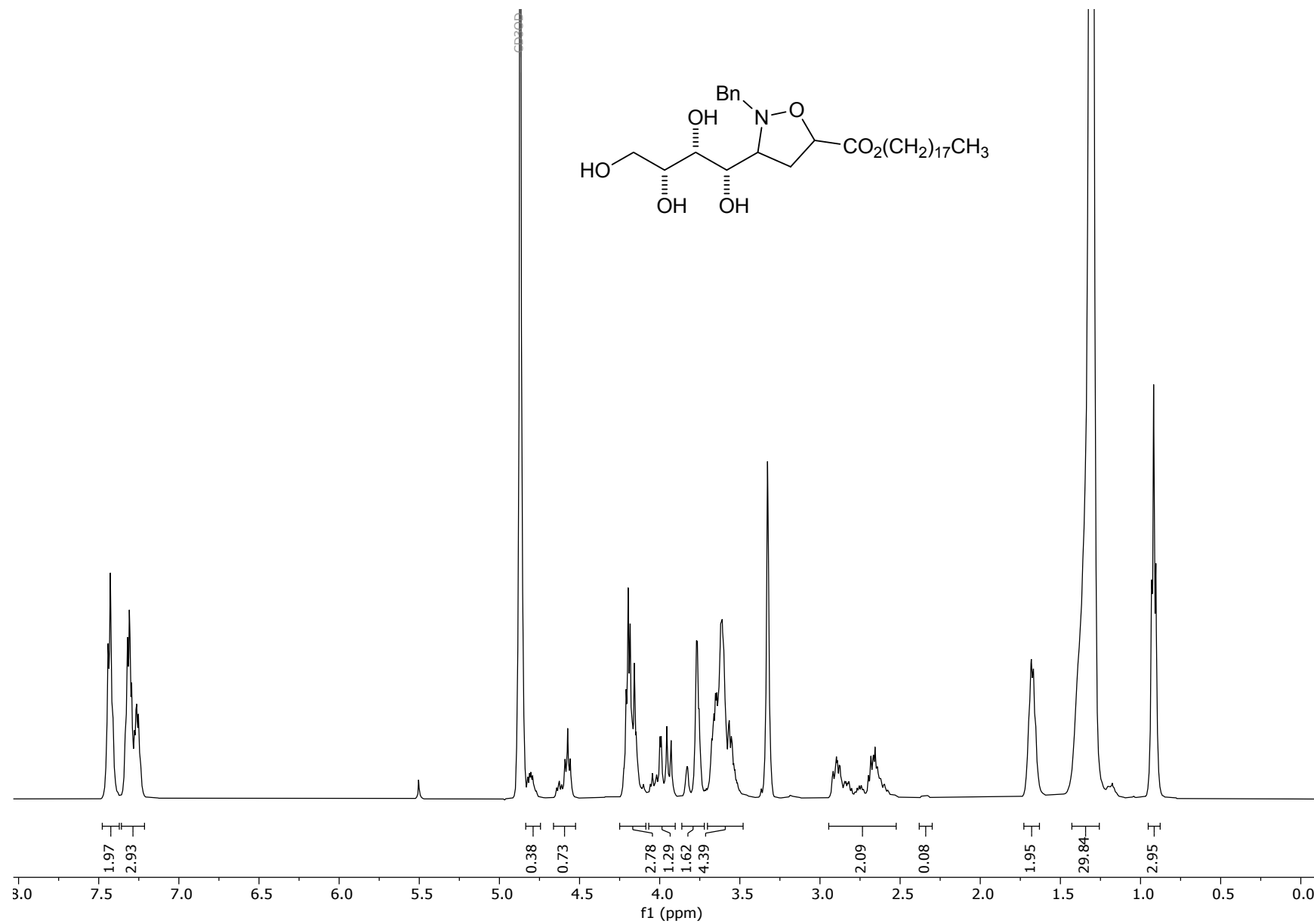
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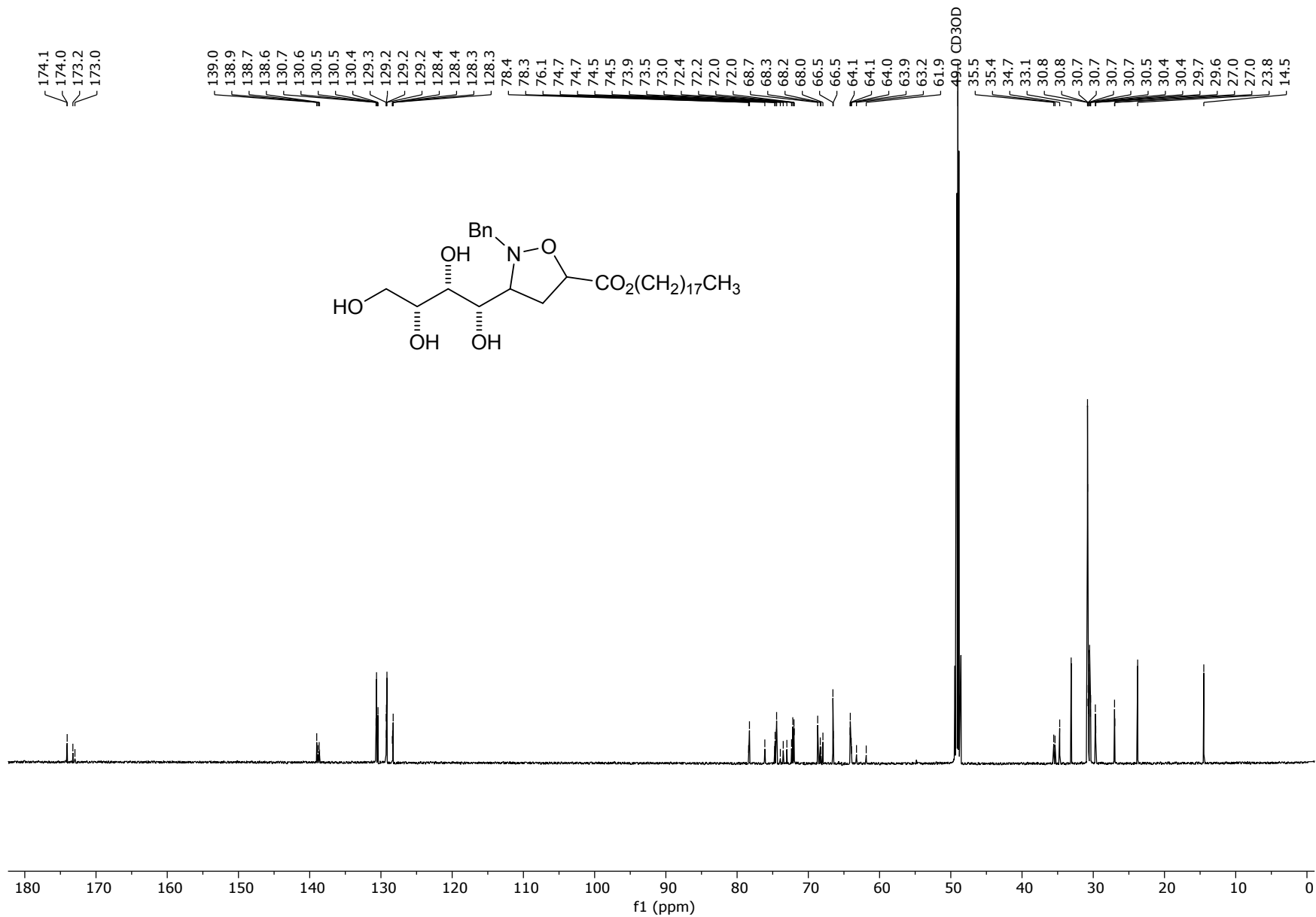
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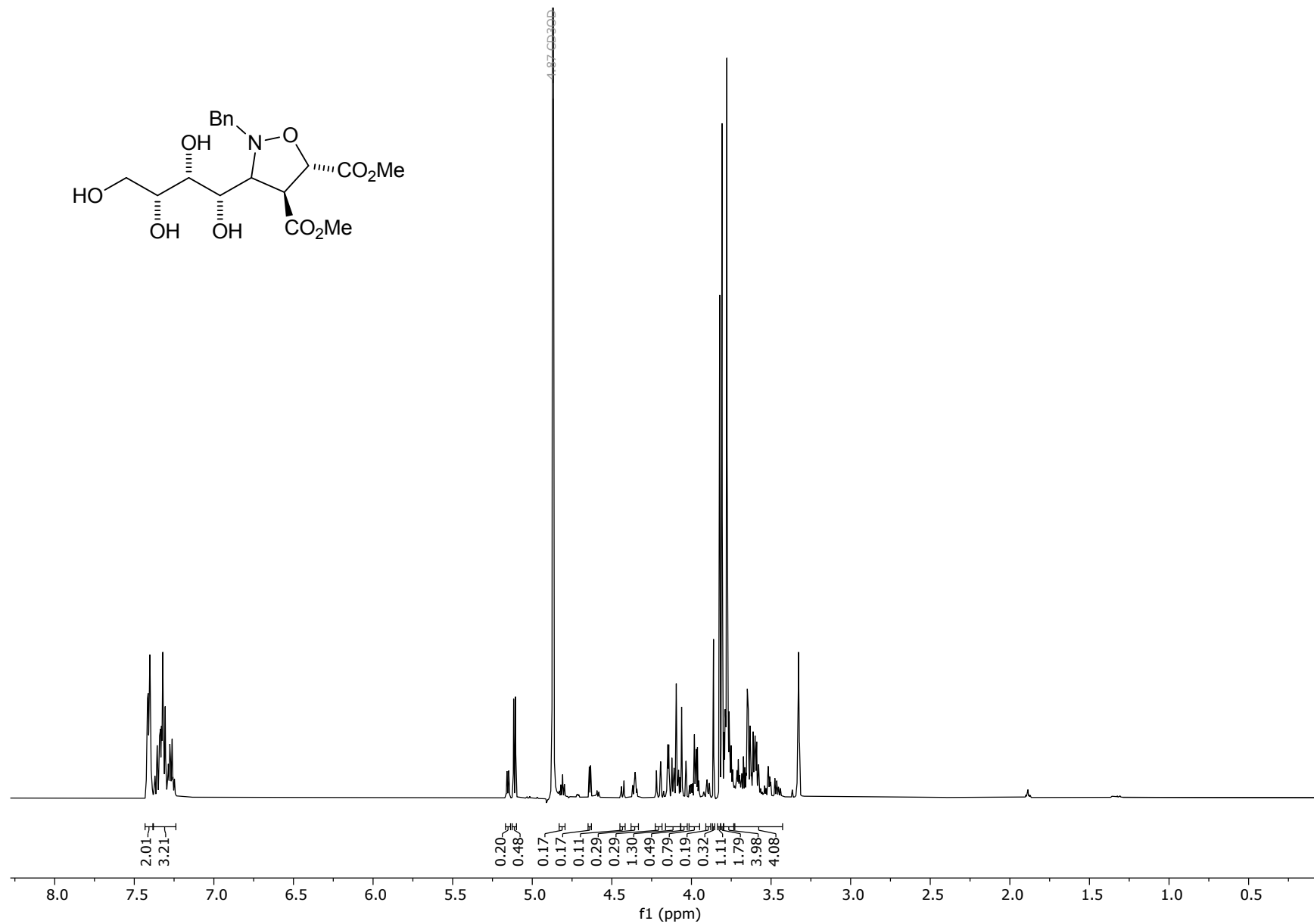
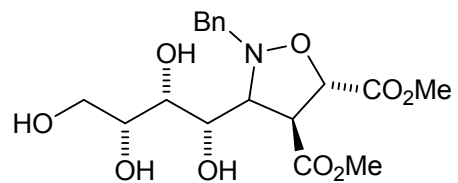
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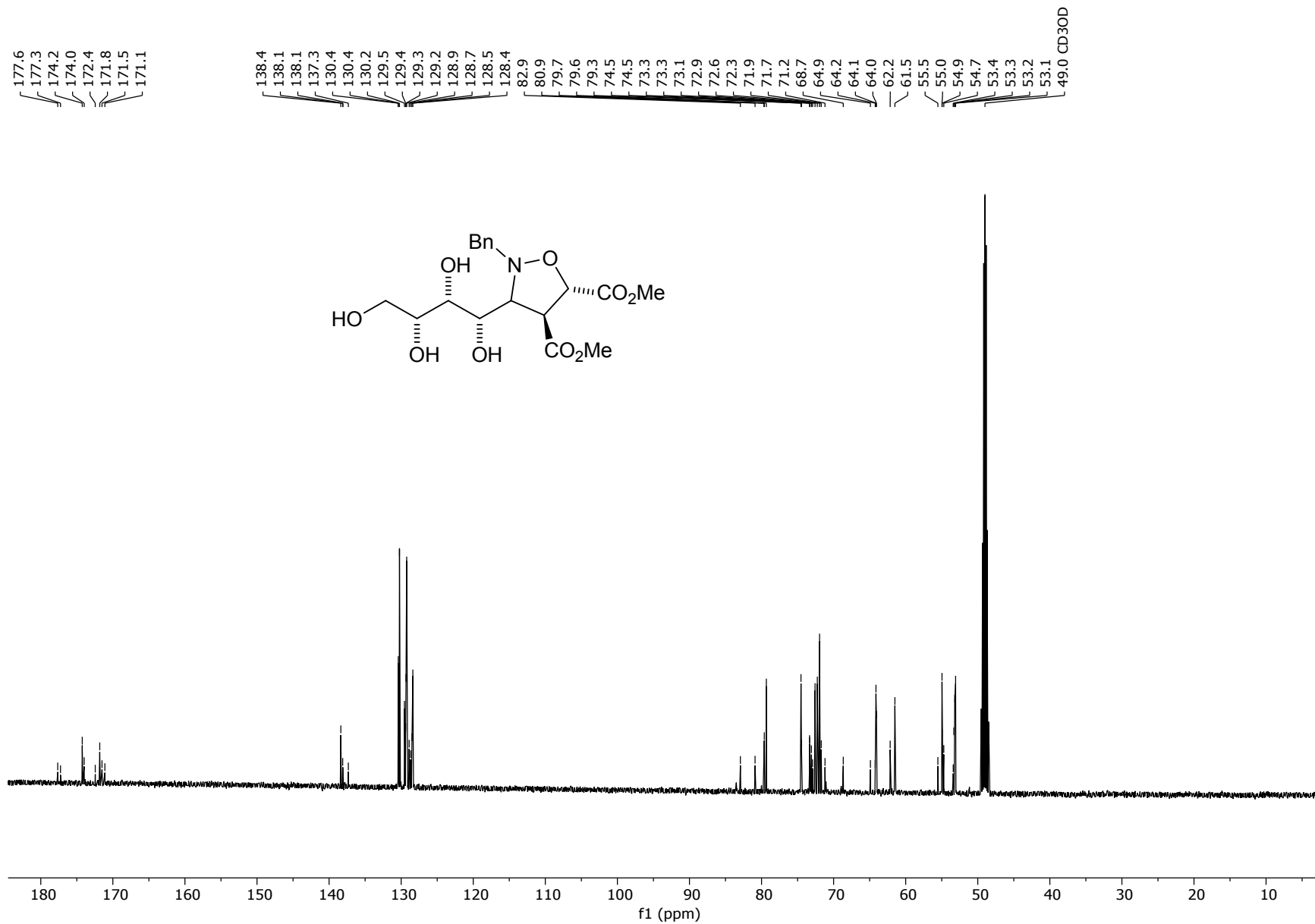
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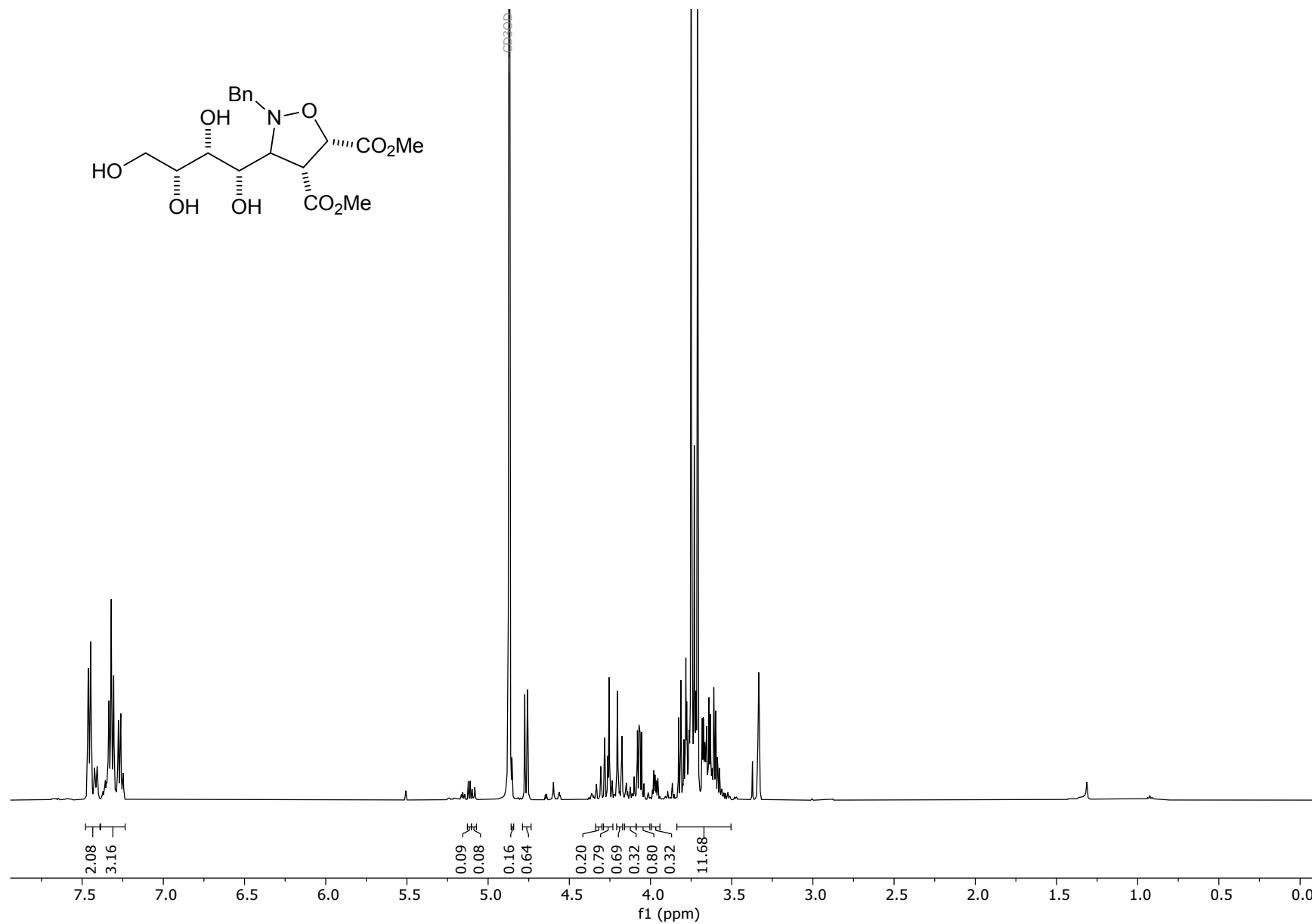
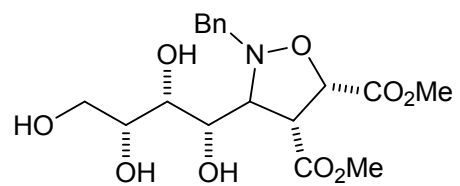
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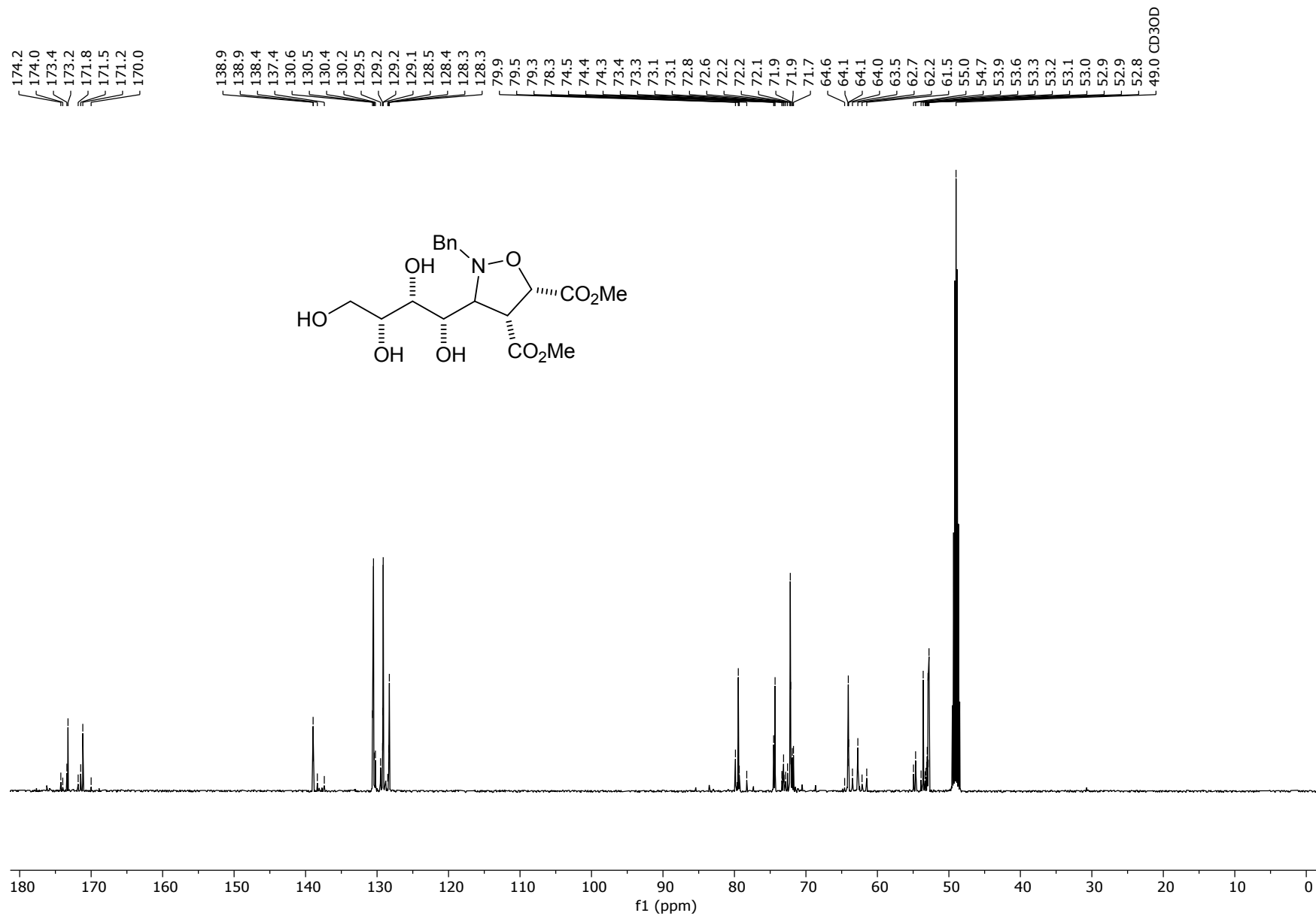
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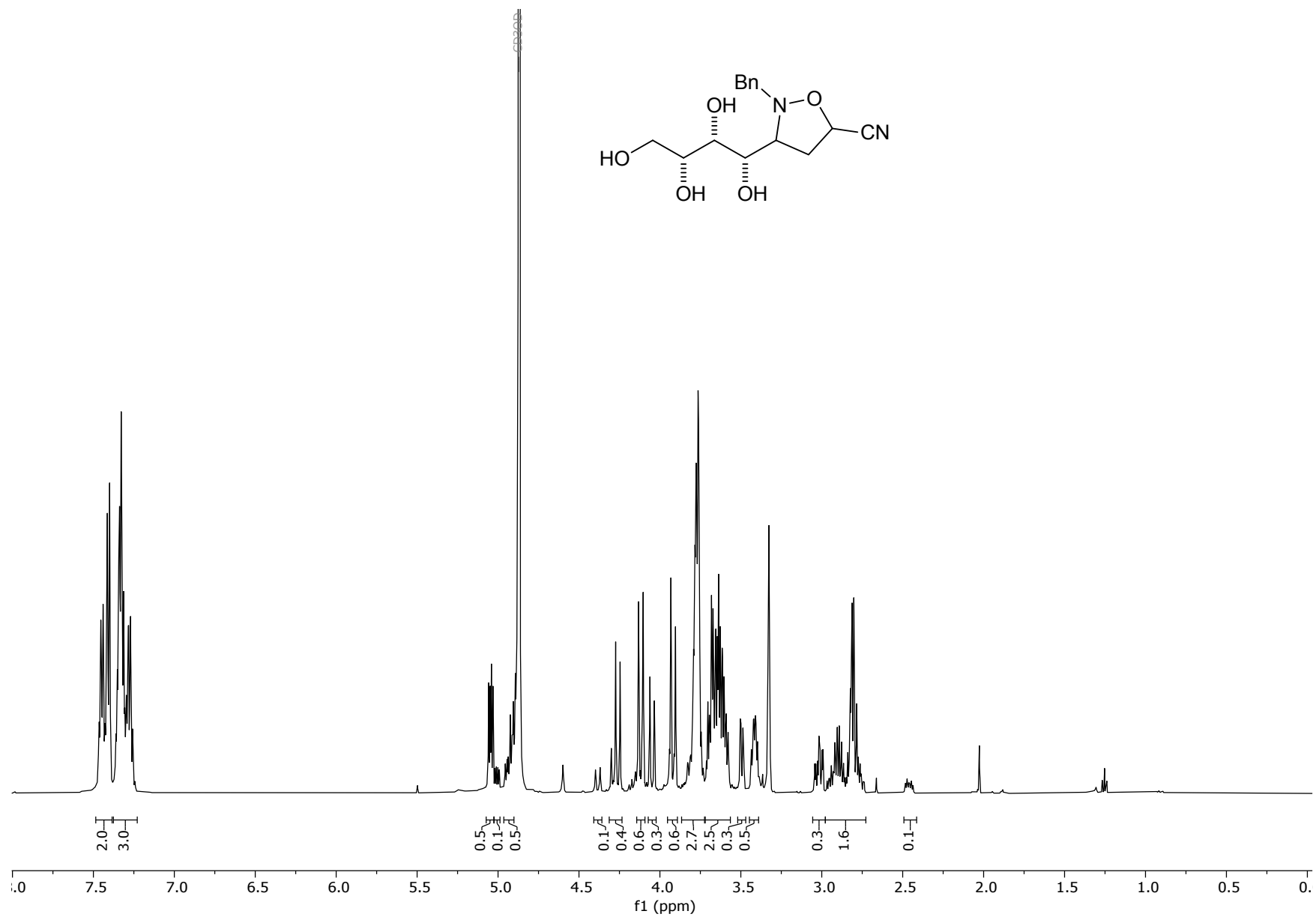
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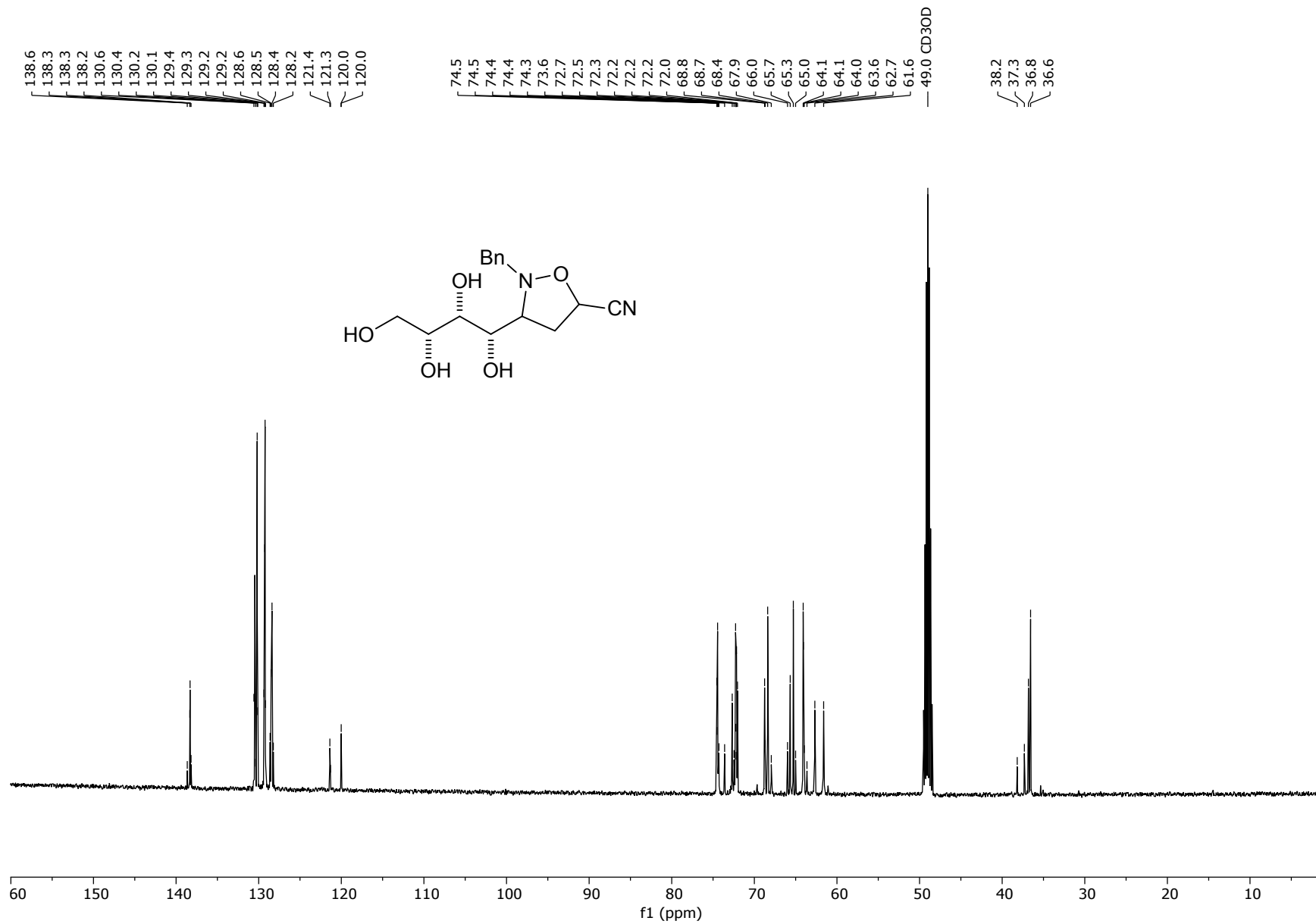
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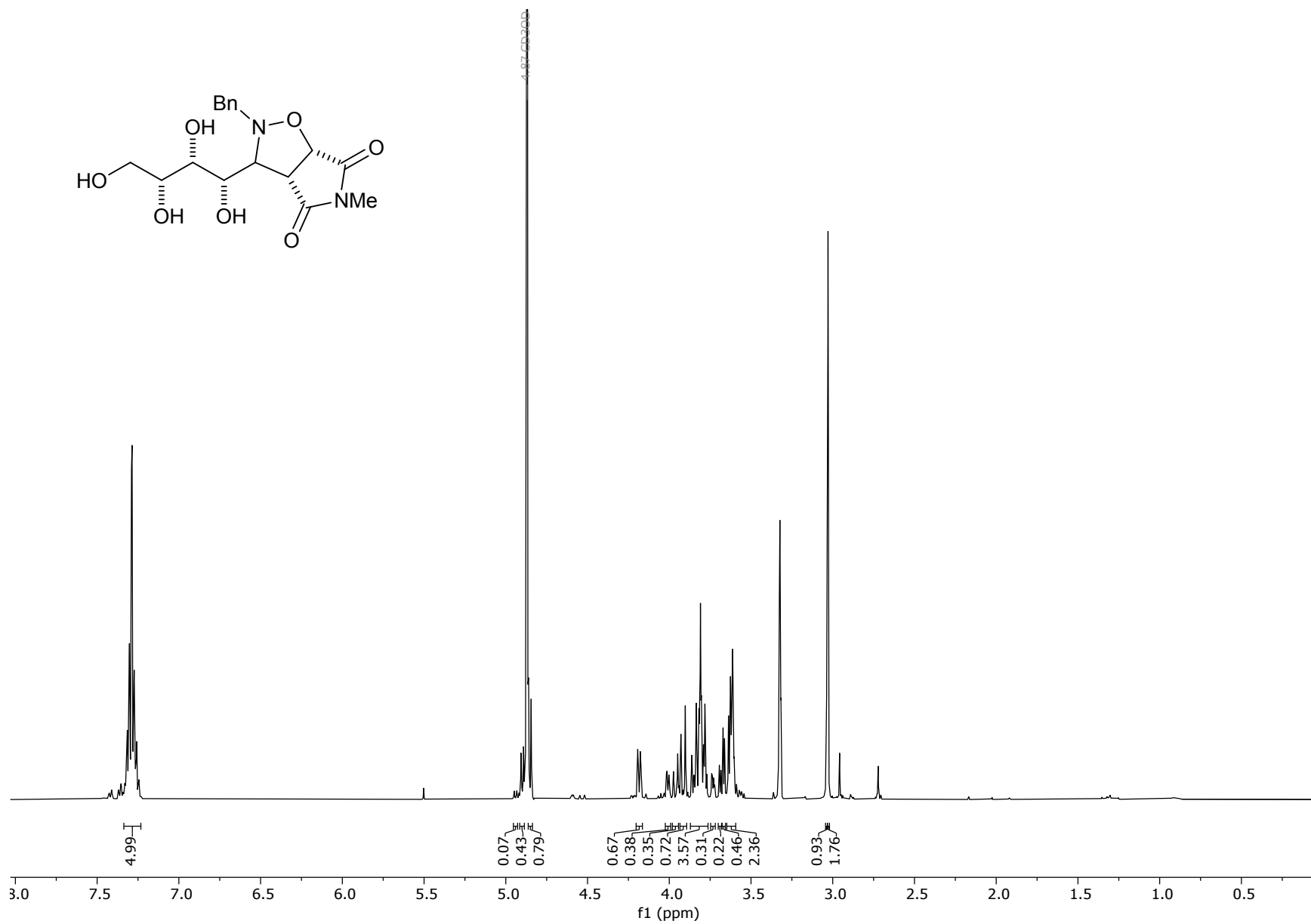
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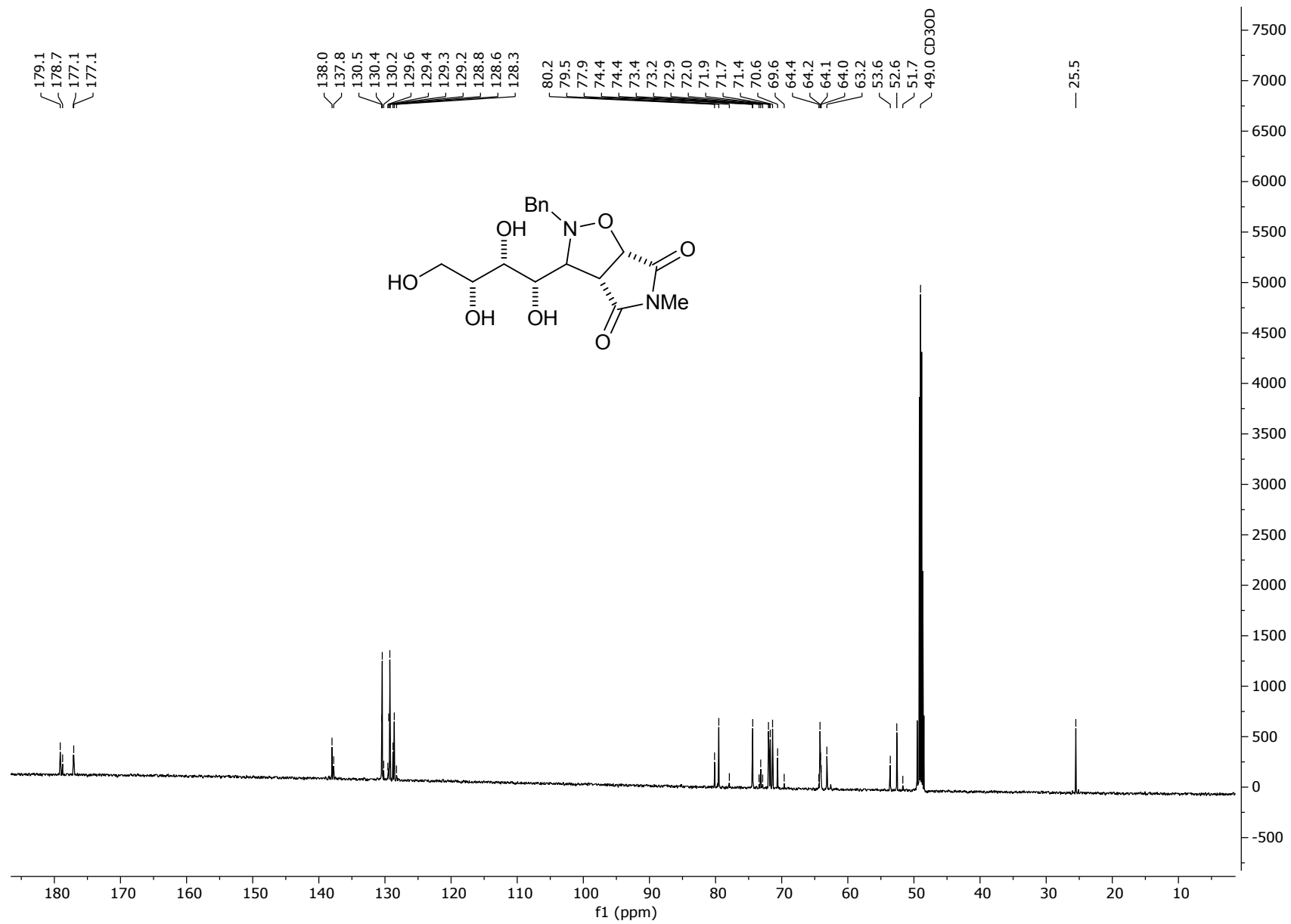
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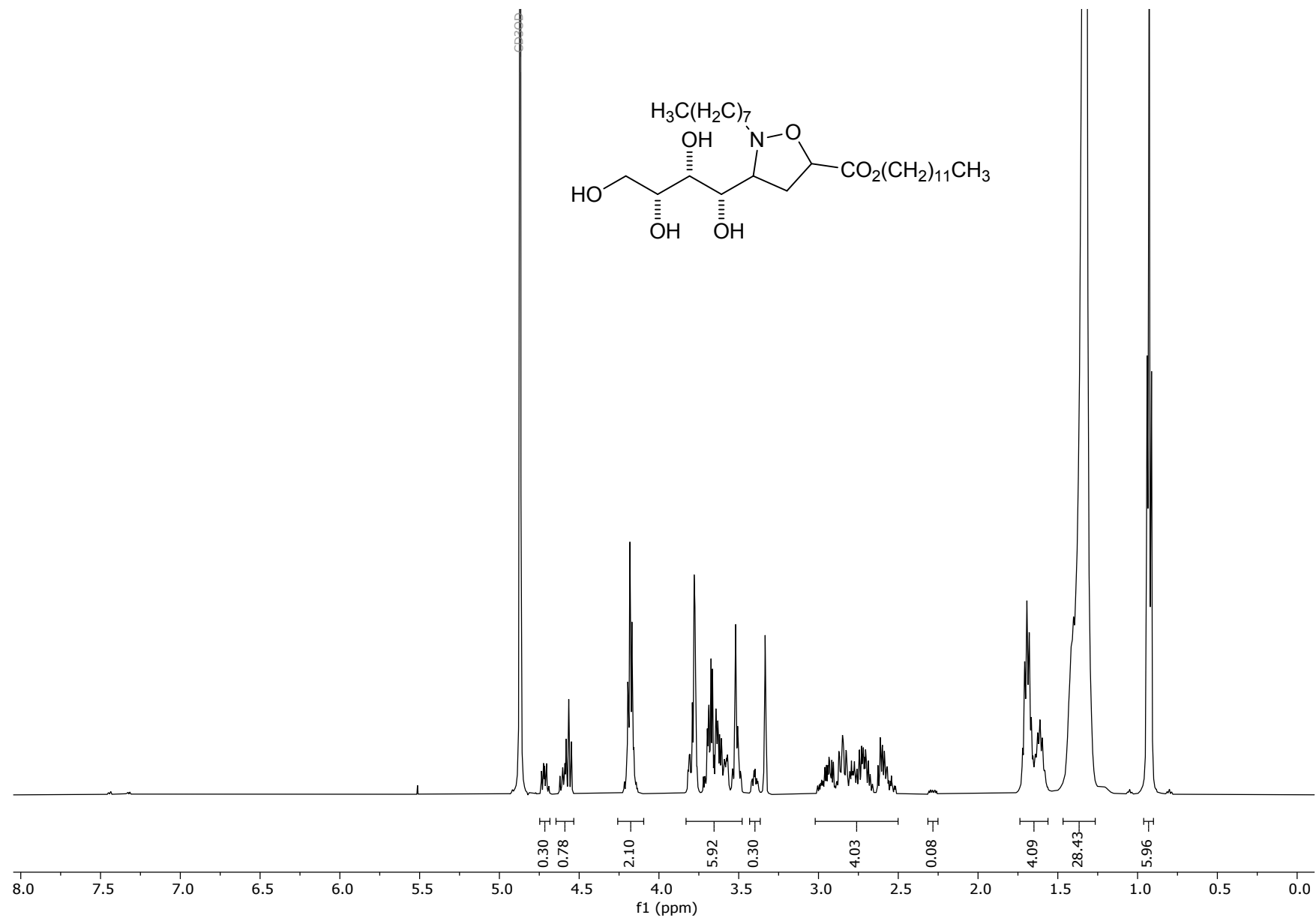
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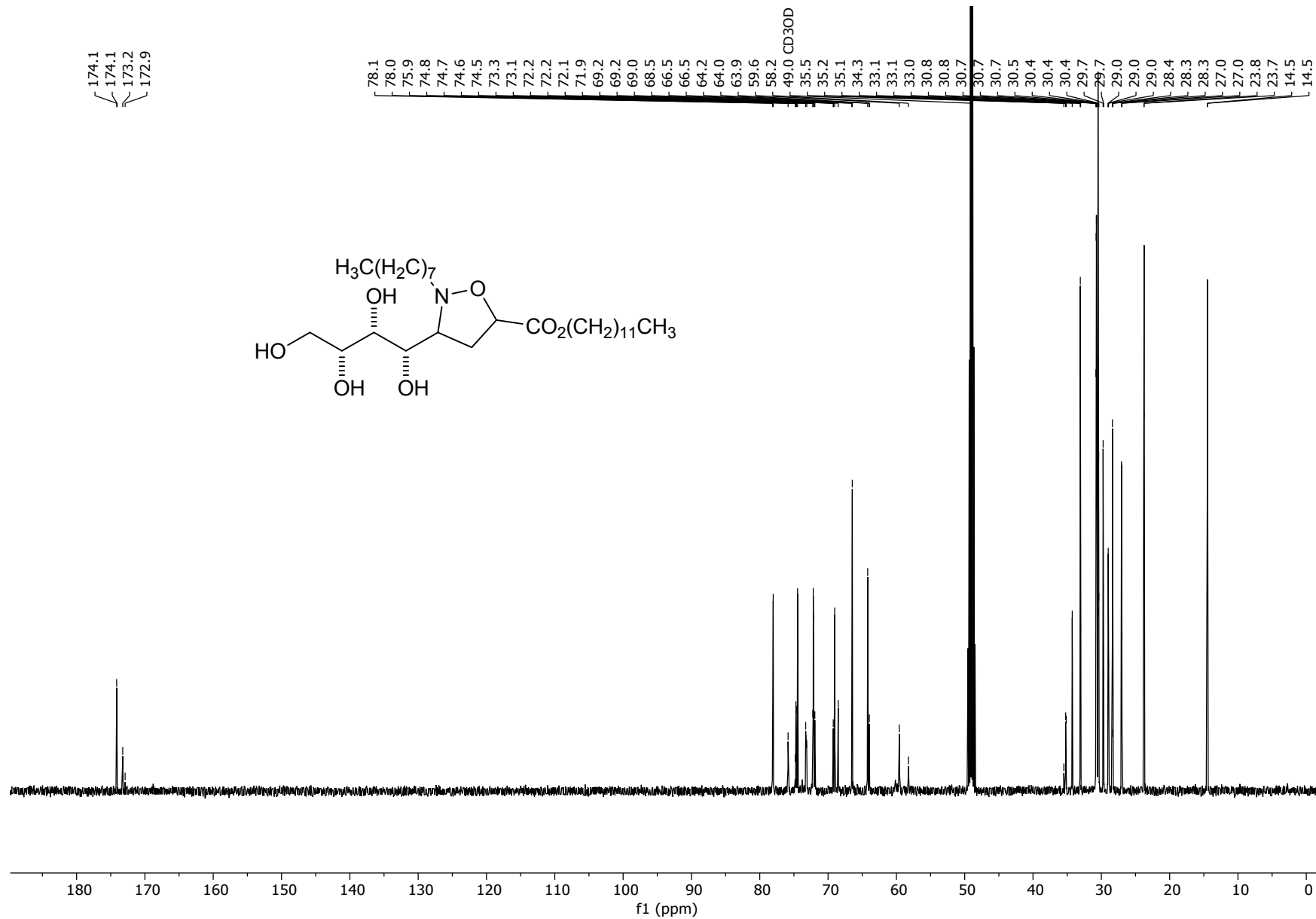
¹³C-NMR spectrum of 28 (CD₃OD)



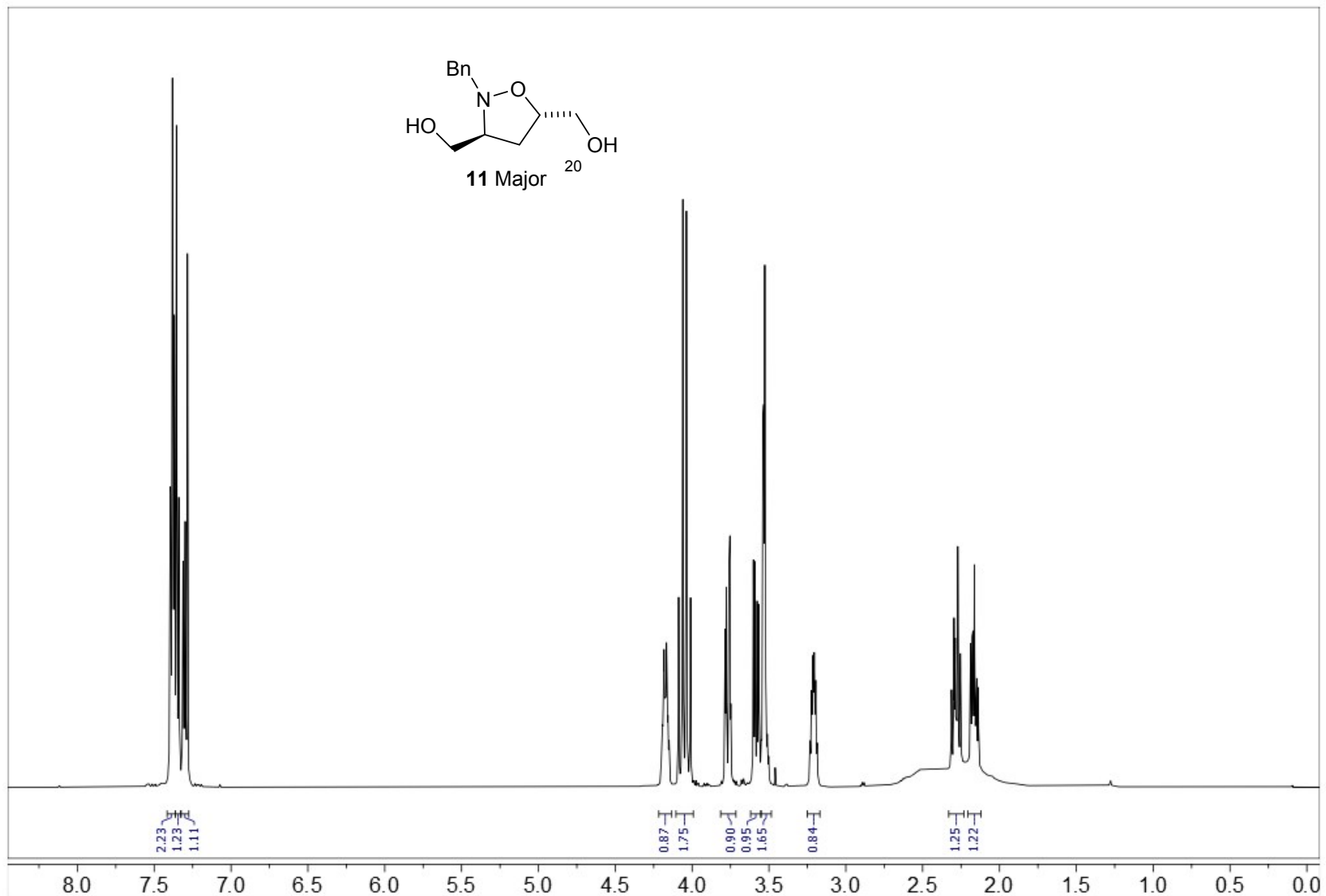
¹H-NMR spectrum of 29 (CD₃OD)



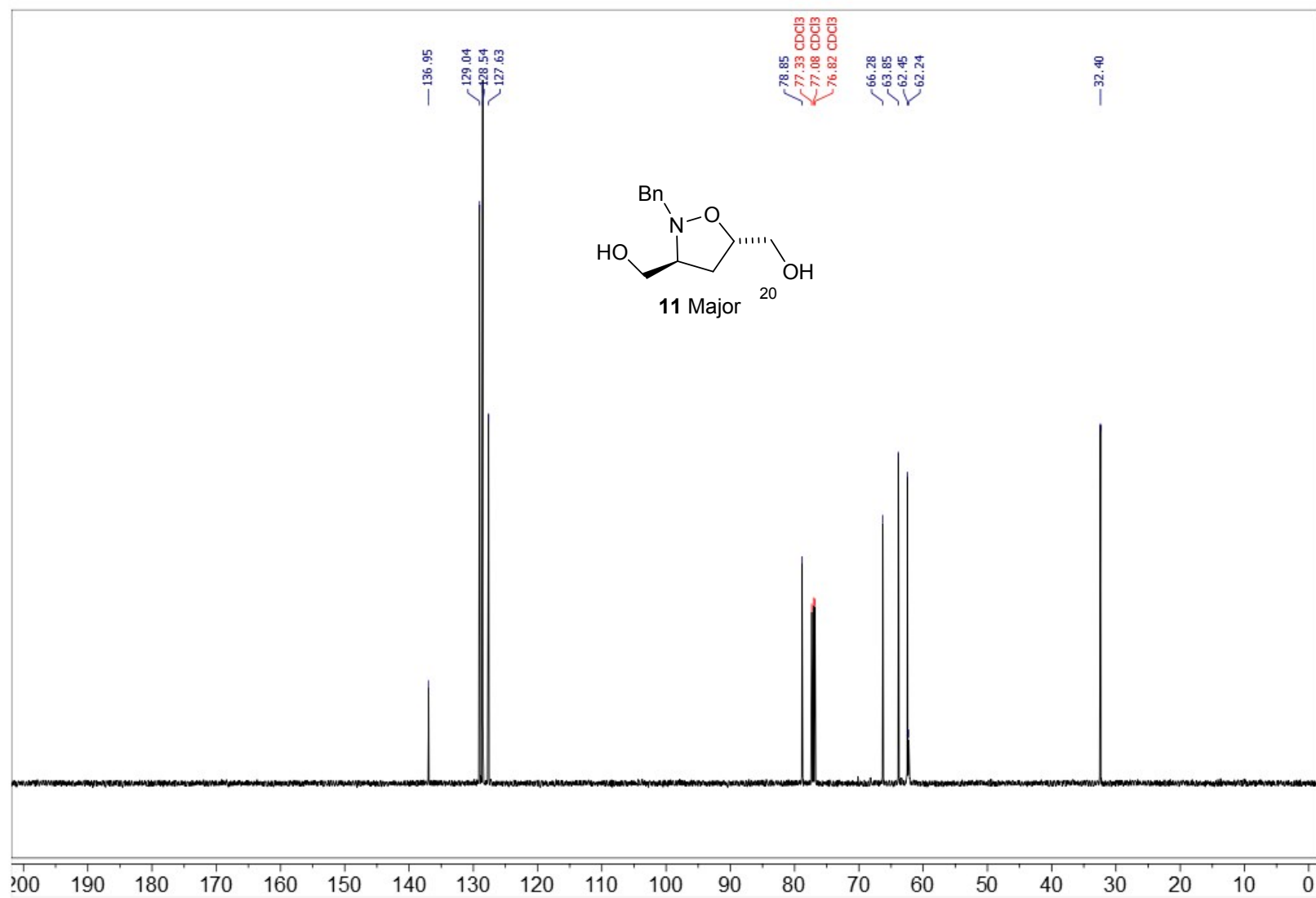
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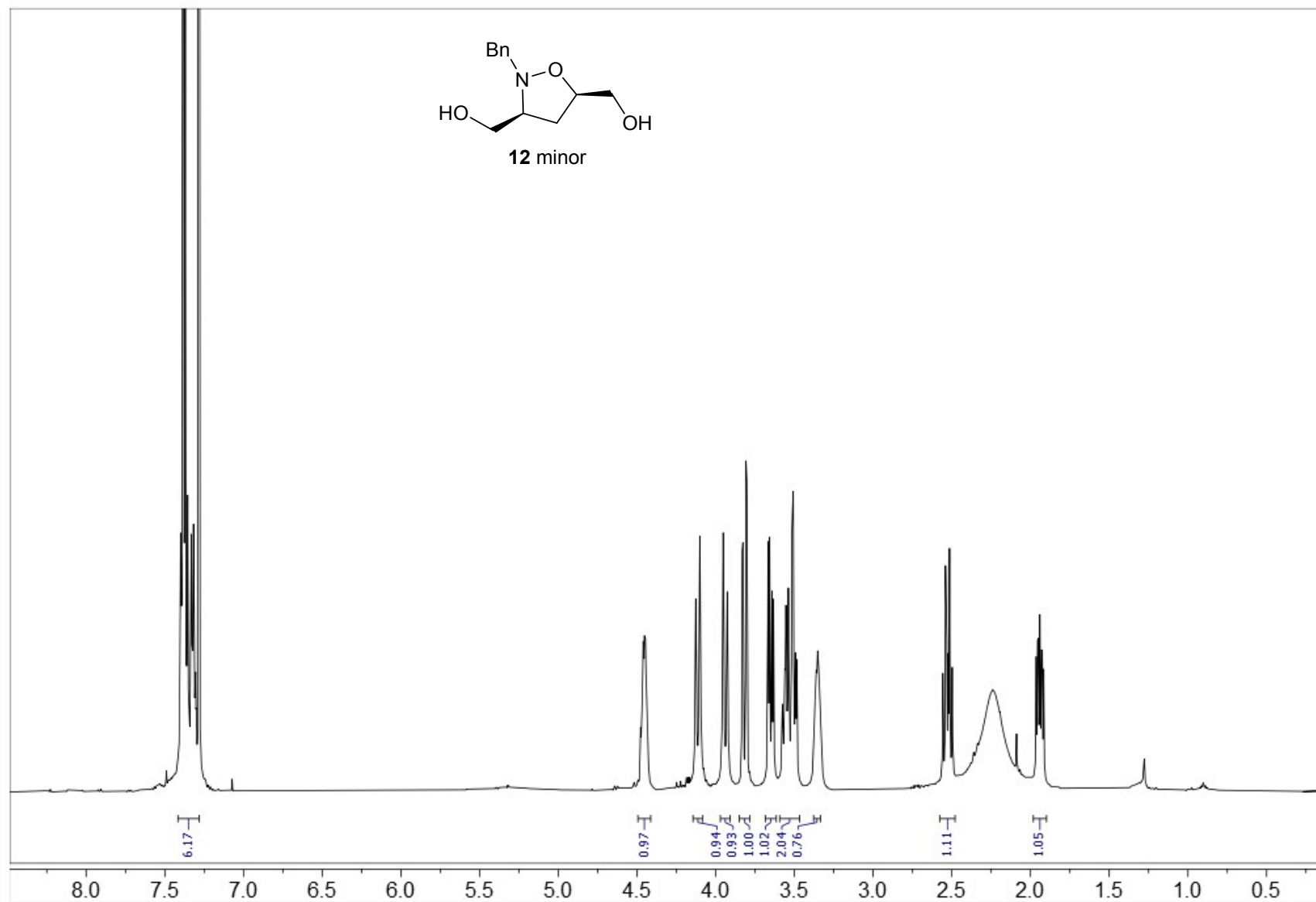
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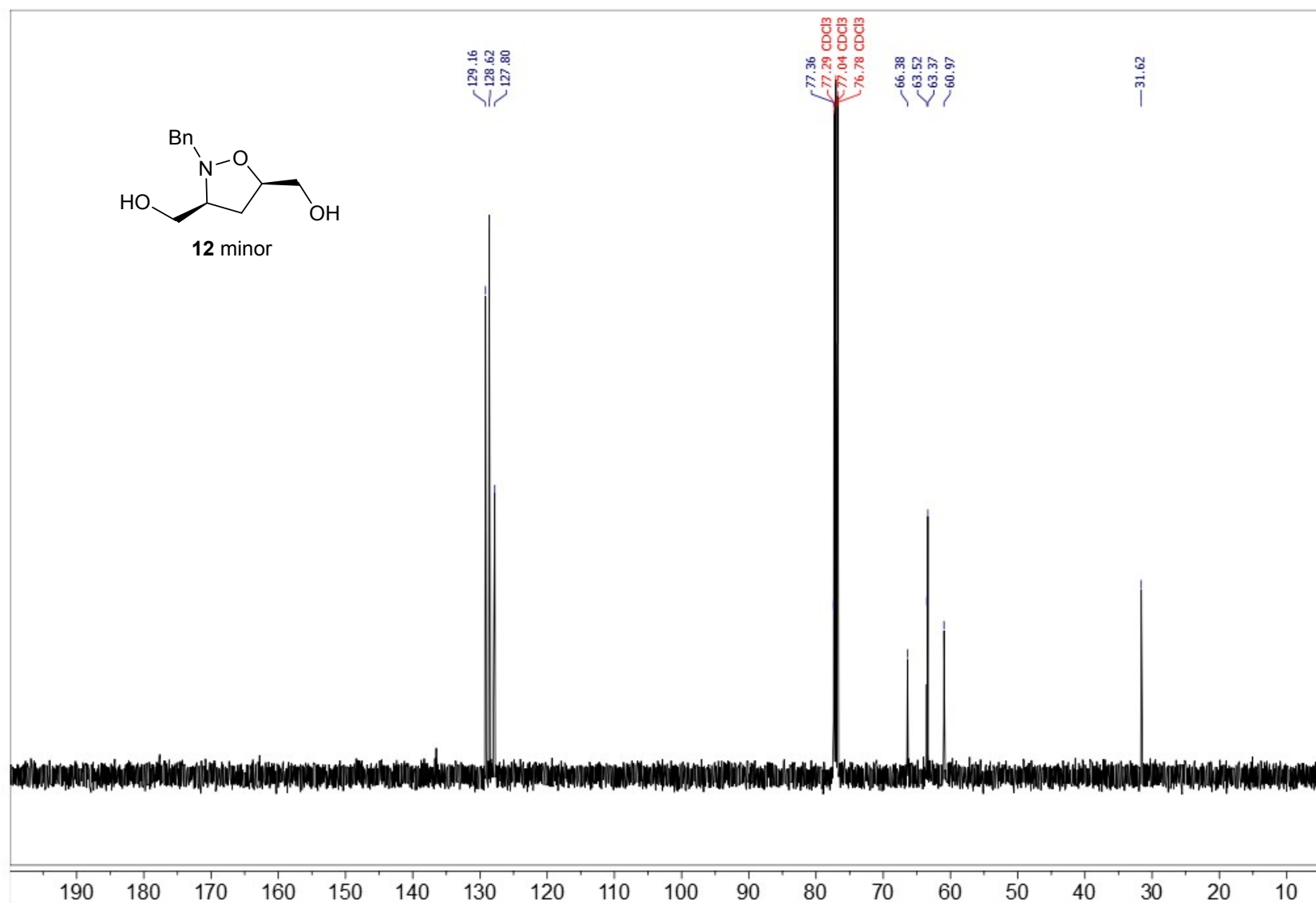
¹³C-NMR spectrum of 11 (CDCl₃)



¹H-NMR spectrum of 12 (CDCl₃)



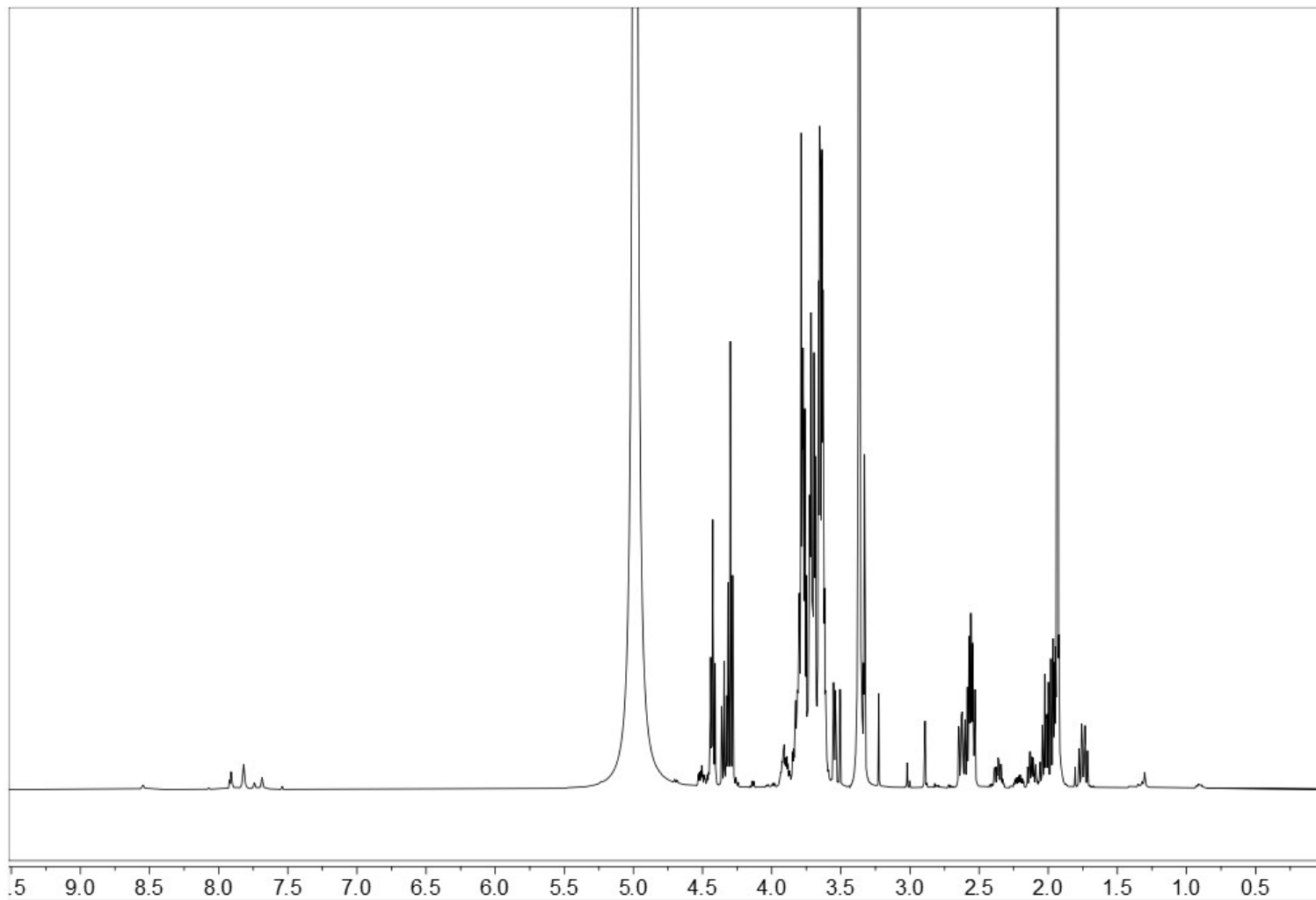
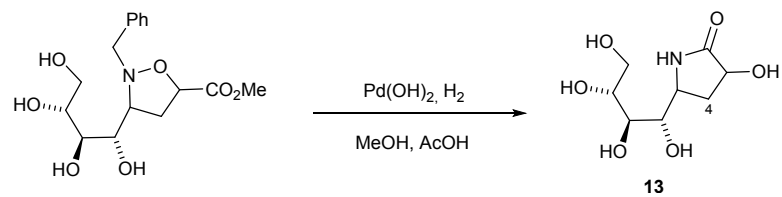
¹³C-NMR spectrum of 12 (CDCl₃)



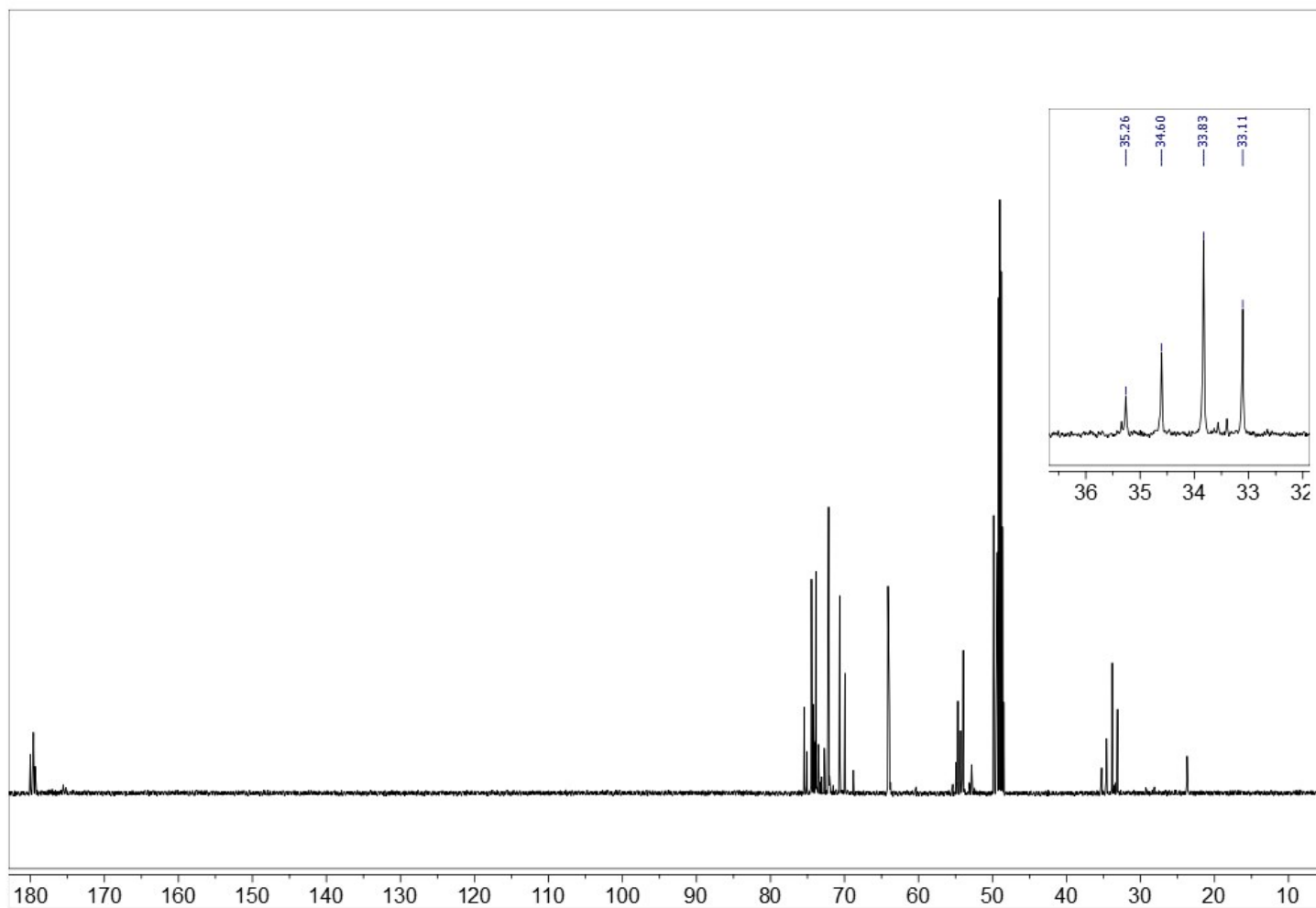
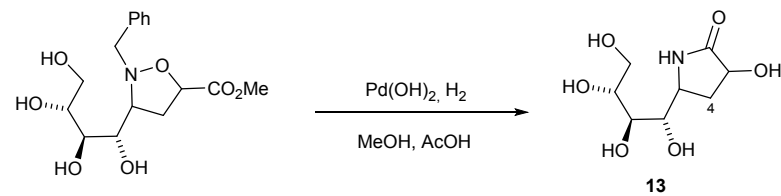
Hydrogenation of compounds **10**, **10'** and **10''** for chemical correlation

Procedure : compound **10**, **10'** or **10''** (0.53 mmol) in MeOH (14 mL) and AcOH (1.6 mL) were stirred under H₂ atmosphere for 24 h in the presence of Pearlman's catalyst (Pd(OH)₂/C, 74 mg). Filtration of the solution over a small pad of silica followed by evaporation of the solvents afforded a yellow oil, which was purified by chromatography on silical gel (CHCl₃/MeOH/NH₄OH, 6/4/1; R_f = 0.2) to afford pyrrolidone **13** in quantitative yield.

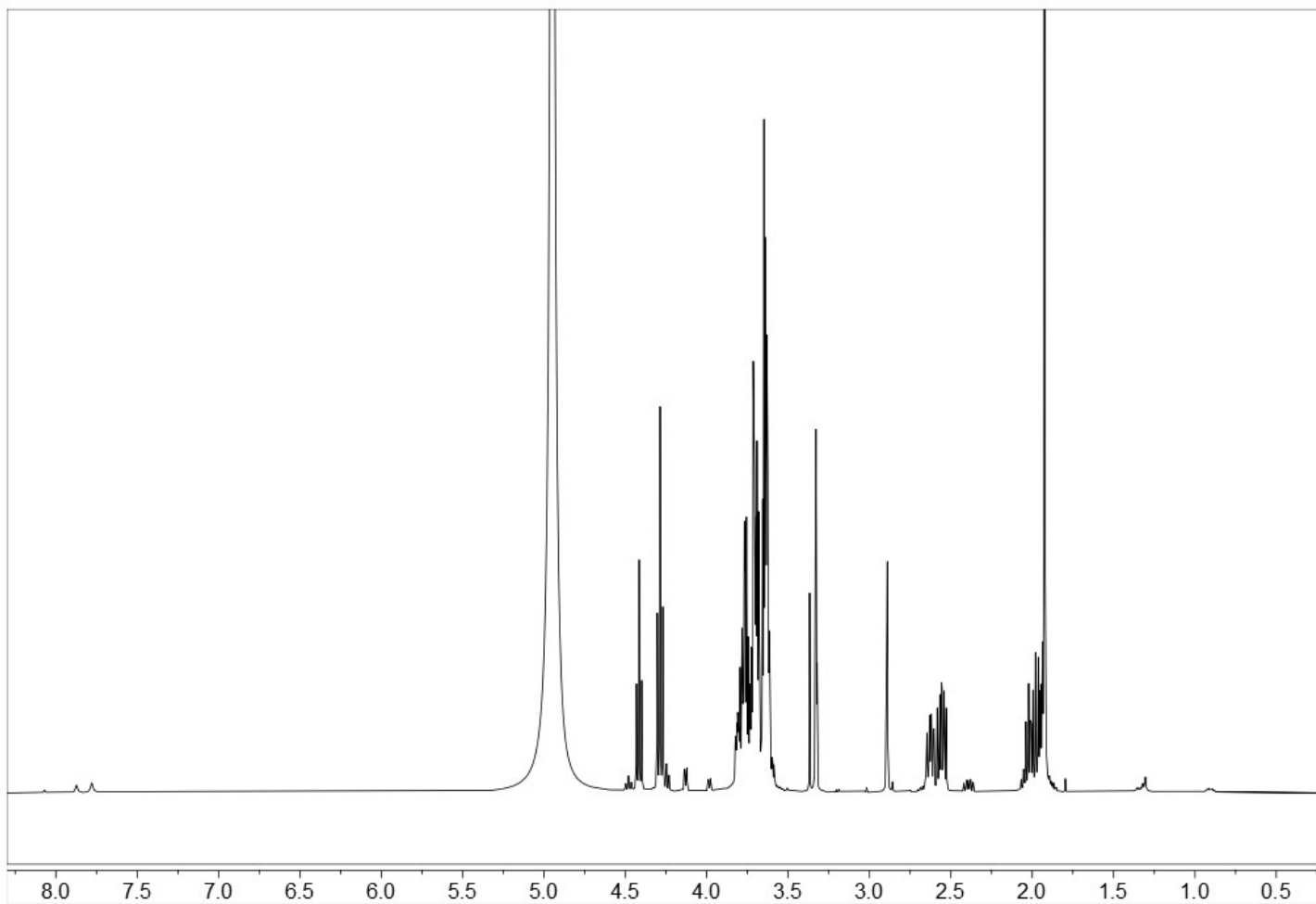
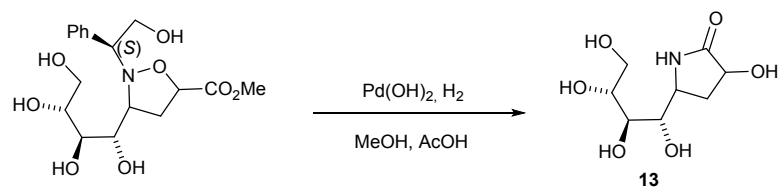
¹H-NMR spectrum of 2-pyrrolidinones isolated after hydrogenation of 10 (4 diastereoisomers)



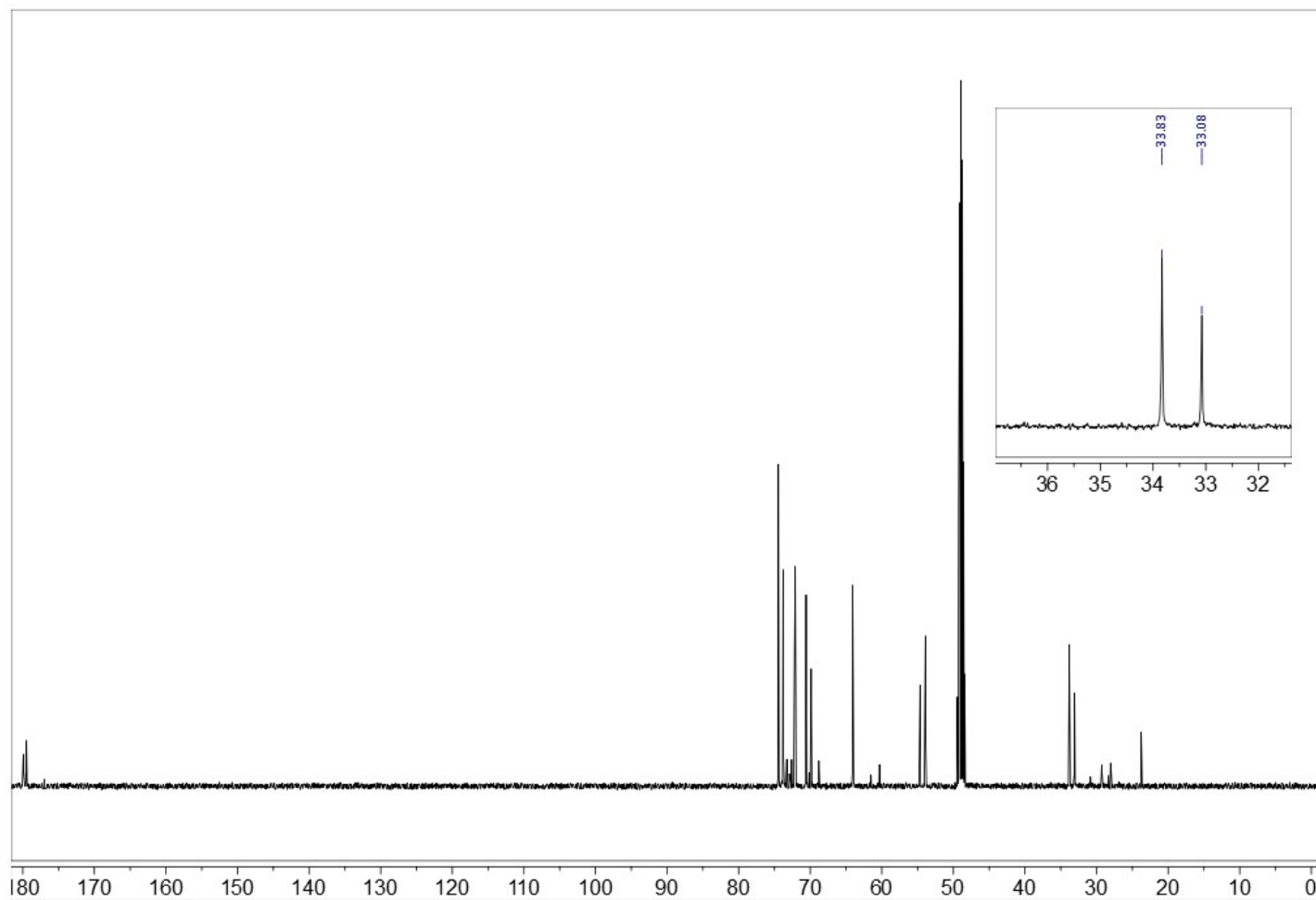
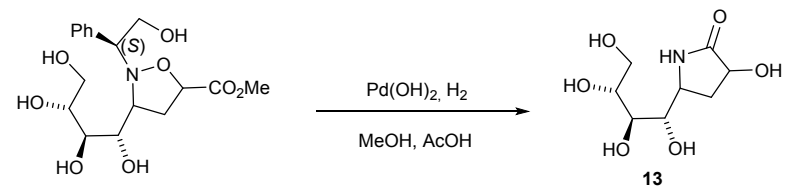
¹³C-NMR spectrum of 2-pyrrolidinones isolated after hydrogenation of 10 (4 diastereoisomers) – extension shows C-4



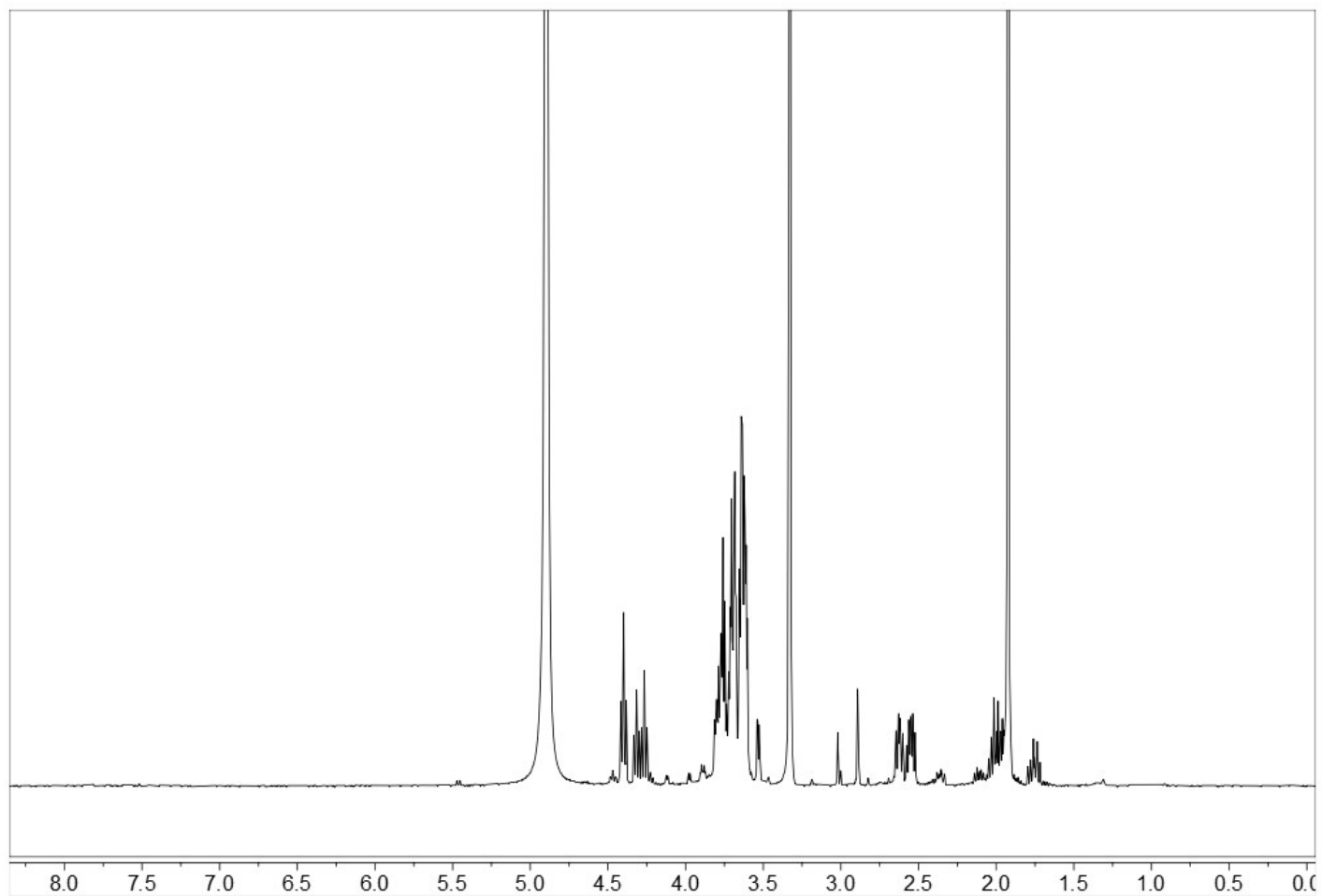
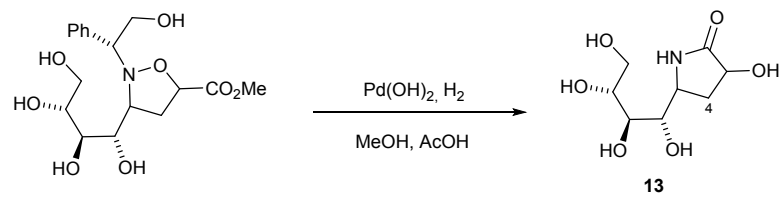
¹H-NMR spectrum of 2-pyrrolidinones isolated after hydrogenation of 10' (reaction was performed on a fraction which contained the 2 major diastereoisomers)



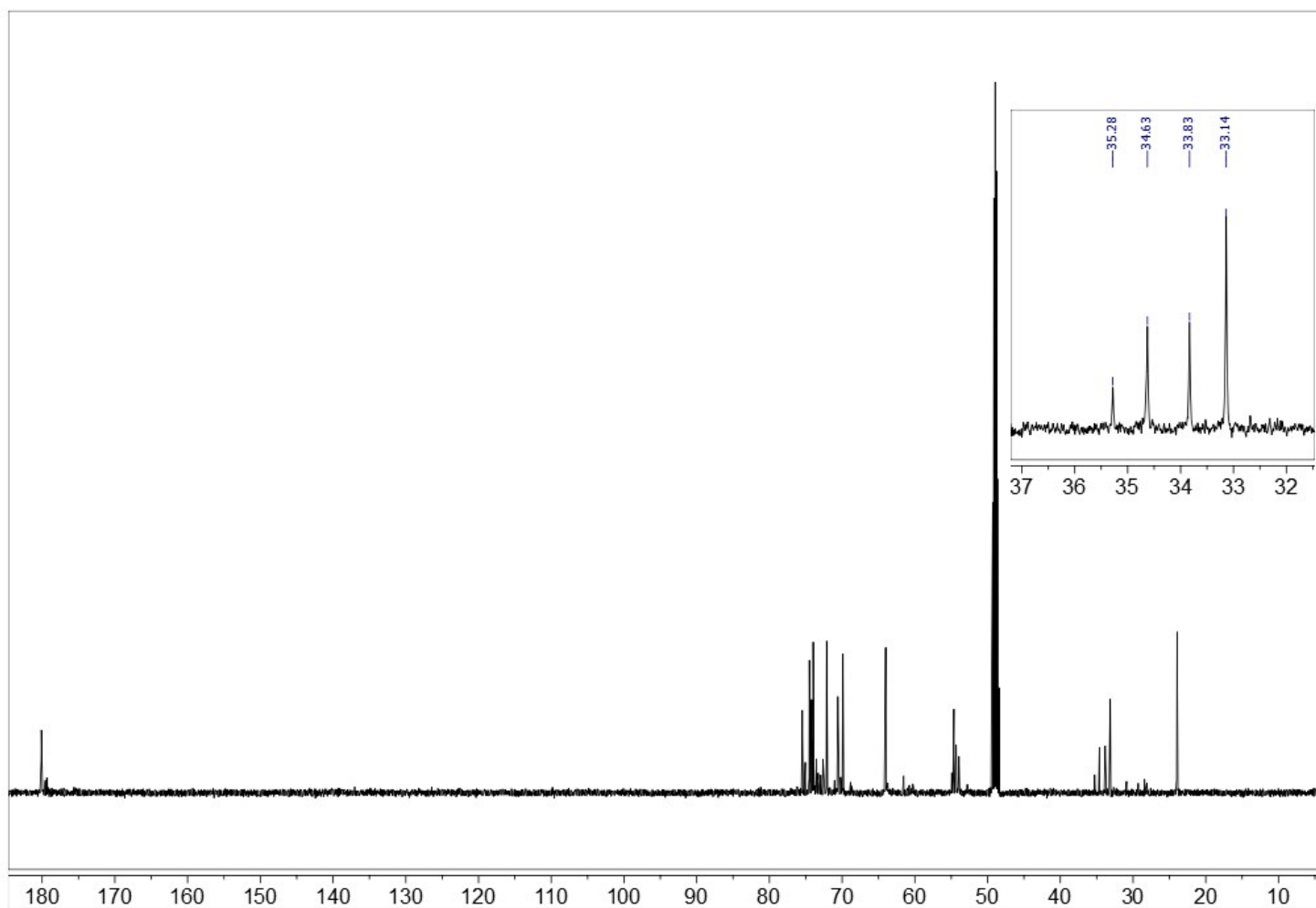
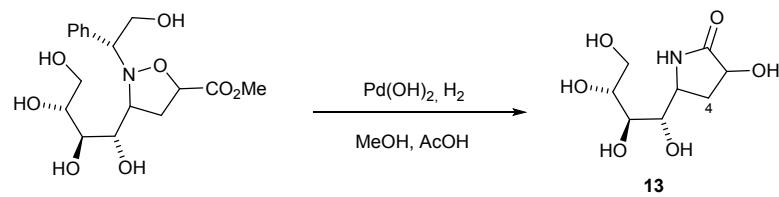
¹³C-NMR spectrum of 2-pyrrolidinones isolated after hydrogenation of 10' (reaction was performed on a fraction which contained the 2 major diastereoisomers) – extension shows C-4



¹H-NMR spectrum of 2-pyrrolidinones isolated after hydrogenation of 10'' (4 diastereoisomers)



¹³C-NMR spectrum of 2-pyrrolidinones isolated after hydrogenation of 10'' (4 diastereoisomers) – extension shows C-4



Enzyme assay: all enzymes were purchased from Sigma Chemical Co. In a typical experiment, the glycosidase (0.013 U/mL) was pre-incubated at 33 °C for 5 min in the presence of the **13** in 50 mM acetate buffer (pH 5.6, except for rice α -glucosidase pH 5.1 and yeast α -glucosidase pH 6.2). The reaction was started by addition of the appropriate substrate (*p*-nitrophenyl glycoside, 1 mM concentration) to a final volume of 250 μ l. The reaction was stopped after 10-15 min (depending on the enzyme) by addition of 300 μ L of 0.4 M Na₂CO₃. The released *p*-nitrophenolate was quantified spectrophotometrically at 415 nm with a microplate reader (300 μ L of the reaction mixture in a well, OD *ca* 0.7 for the control, without inhibitor). All the assays were done in duplicate (less than 10% variability in each case). Absorbance was corrected by subtracting the blank. The blank was measured in an additional experiment, conducted in the absence of enzyme. The control experiment contained no inhibitor.

Percentage of inhibition was calculated as follows:

$$\%I = \left(1 - \frac{A_{\text{sample}}}{A_{\text{control}}} \right) * 100$$