

Supporting Information

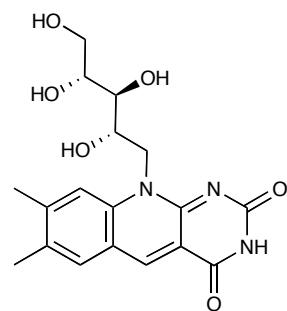
Improved Chemical Synthesis of 1- and 5-Deazariboflavin.

Erin E. Carlson and Laura L. Kiessling

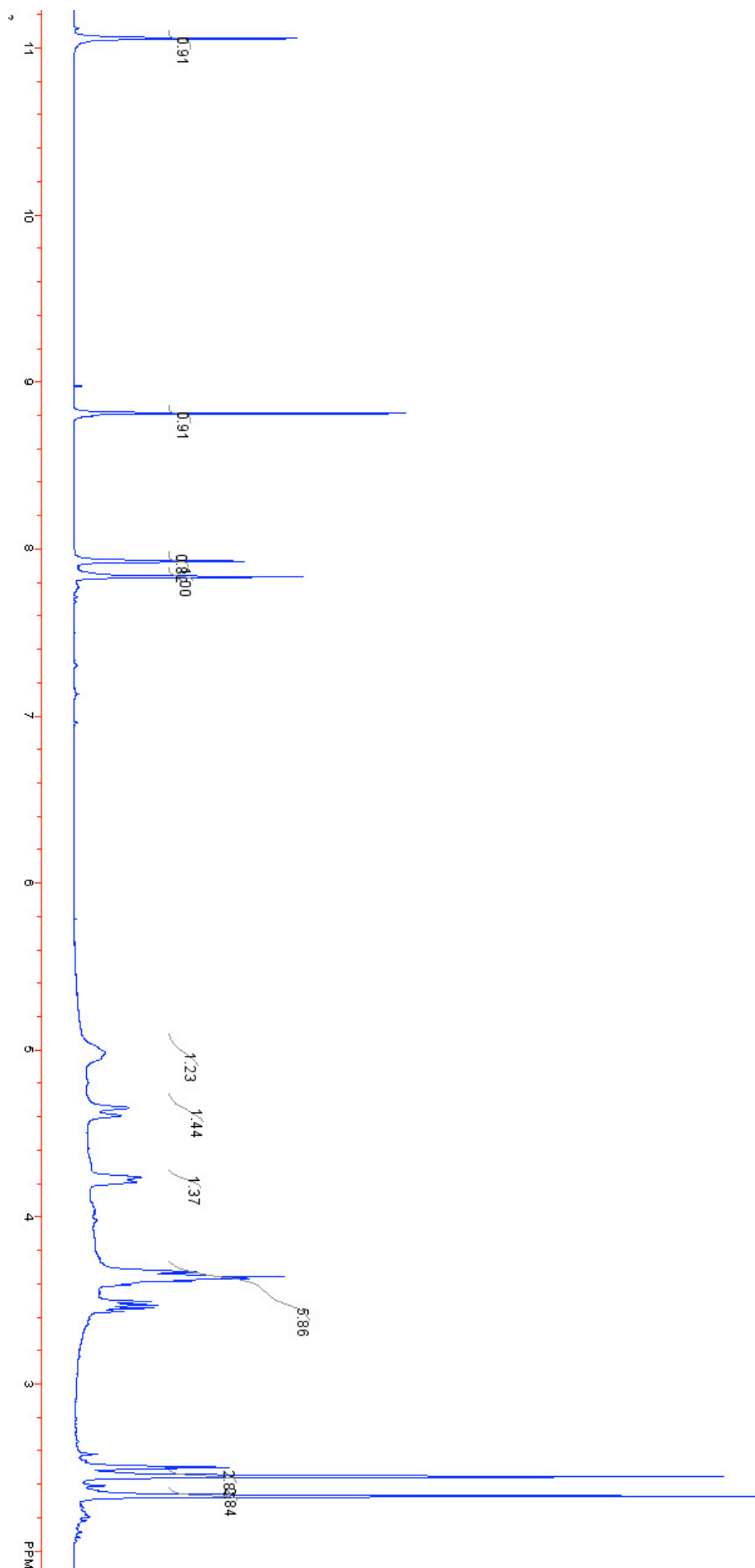
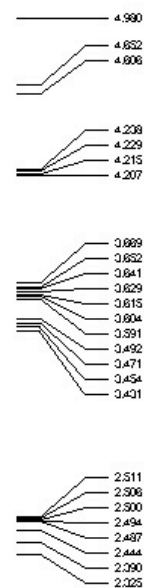
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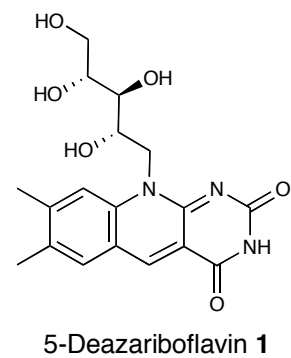
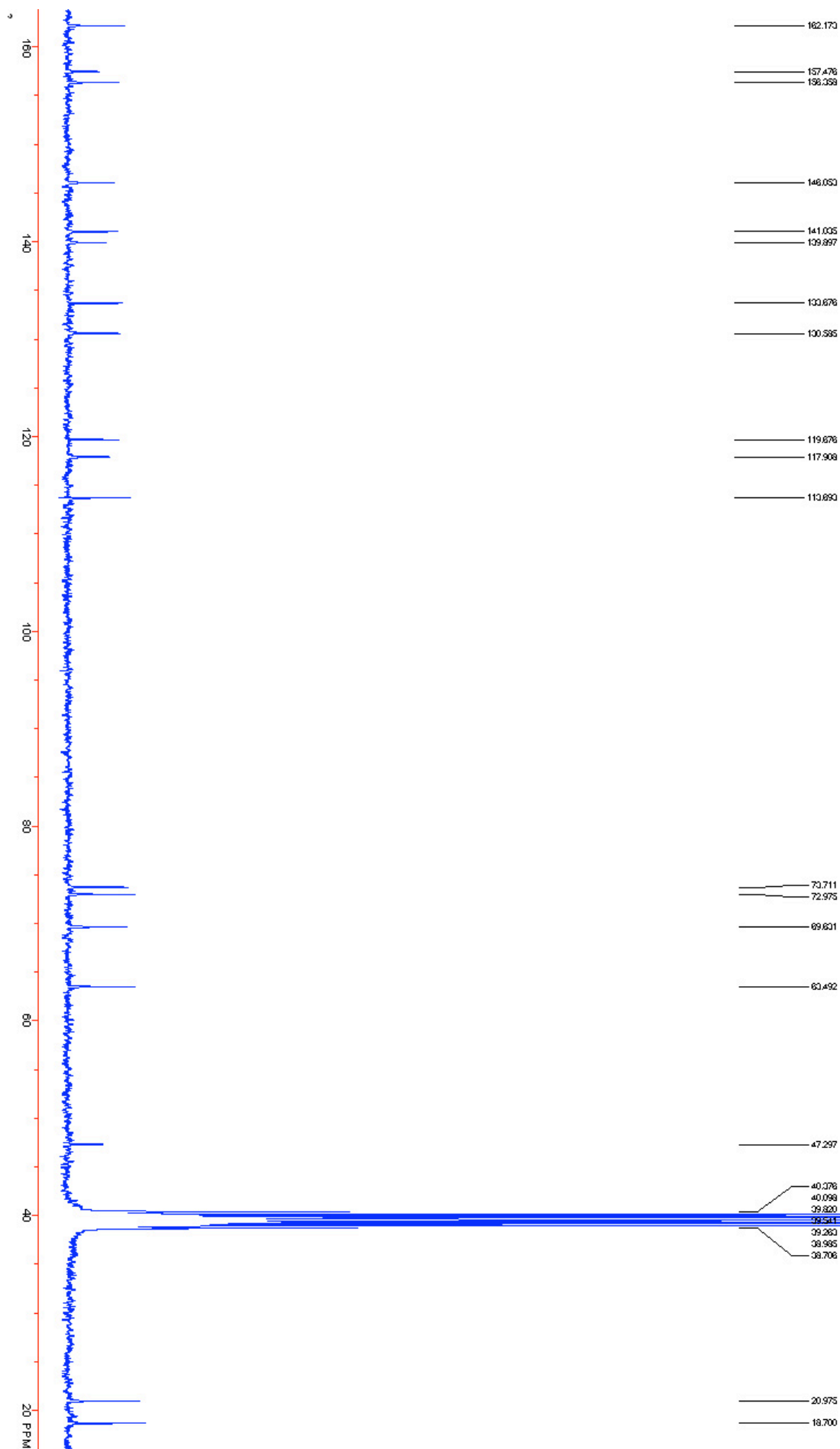
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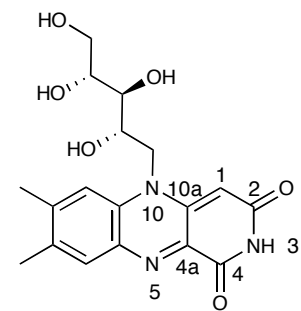
All moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware under nitrogen atmosphere. All materials were purchased and used without further purification, unless otherwise noted. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride, methanol was distilled from magnesium and pyridine was distilled from sodium and anthracene. Dimethylformamide (DMF) was rendered amine-free by treatment with Dowex 50WX8-200 cation exchange resin, H^+ form, 1 g/L. Analytical thin layer chromatography (TLC) was carried out on TLC plates pre-coated with silica gel 60 F_{254} (250 μm layer thickness). Analyte visualization was accomplished using a UV lamp, and charring with at least one of the following solutions: a *p*-anisaldehyde stain (18 mL *p*-anisaldehyde, 7.5 mL glacial acetic acid, 25 mL concentrated H_2SO_4 , 675 mL absolute EtOH), ninhydrin stain (200 mg ninhydrin, 95 mL *n*-butanol, 5 mL 10% AcOH), or potassium permanganate stain (3 g KMnO_4 , 20 g K_2CO_3 , 5 mL 5% aqueous NaOH, 300 mL H_2O). Flash chromatography was performed on silica gel (32-63 μM , 60 Å pore size) using distilled reagent grade hexanes and ACS grade ethyl acetate (EtOAc) or methanol and chloroform. The term, “concentrated under reduced pressure” refers to the removal of solvents and other volatile materials using a rotary evaporator at water aspirator pressure (< 20 torr) while maintaining the water bath temperature below 40 °C, followed by residual solvent removal at high vacuum (< 0.1 torr). The term, “high vacuum,” refers to vacuum achieved by a mechanical belt-drive oil pump. High performance liquid chromatography (HPLC) was performed on a C_{18} reverse phase column using water (A) and acetonitrile (B) buffered with 1% trifluoroacetic acid as the elution solvent. Compound elution was detected by UV at 254 and 280 nm. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AC-300 and chemical shifts are reported relative to tetramethylsilane or residual solvent peaks in parts per million (CHCl_3 : ^1H : δ 7.26, ^{13}C : δ 77.0; CH_3OH : ^1H : δ 3.31, ^{13}C : δ 49.15, DMSO: ^1H δ 2.50, ^{13}C : δ 39.51) ^1H NMR data are assumed to be first order. Peak multiplicity is reported as: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Mass spectrometry was performed on Micromass LCT Electrospray ionization (ESI).



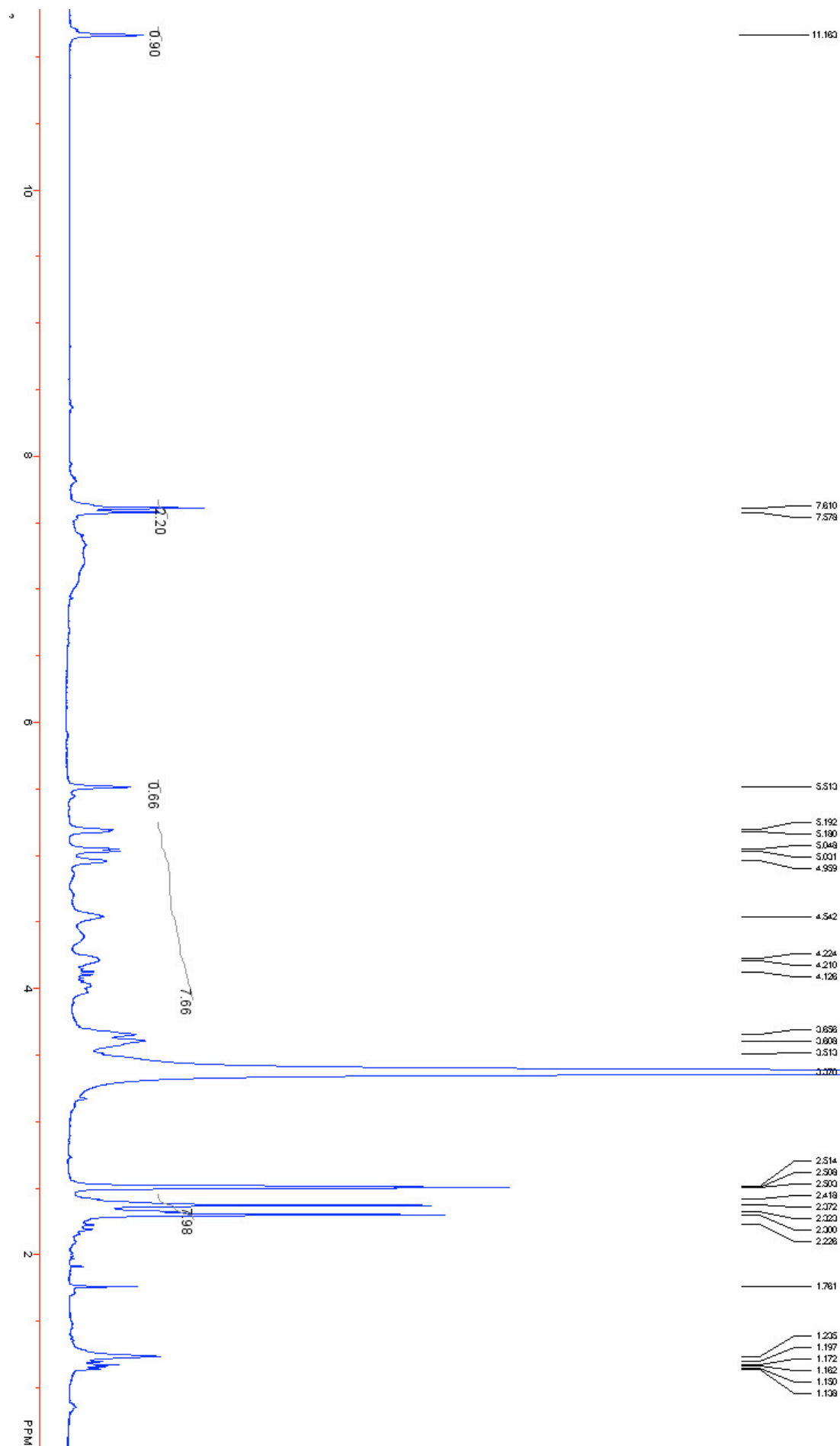
5-Deazariboflavin 1

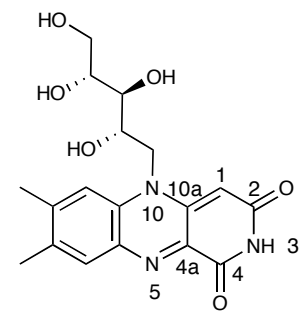
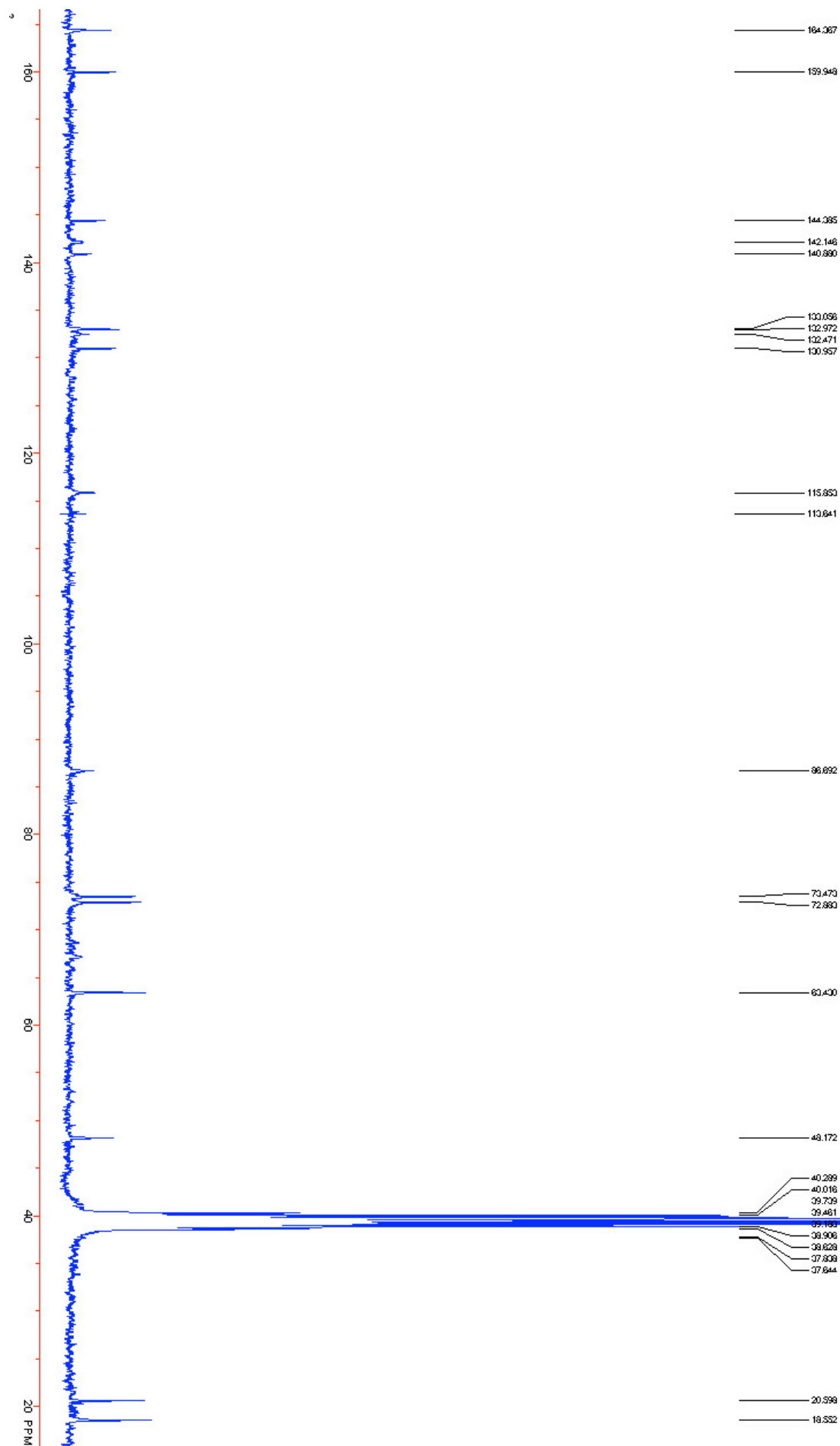




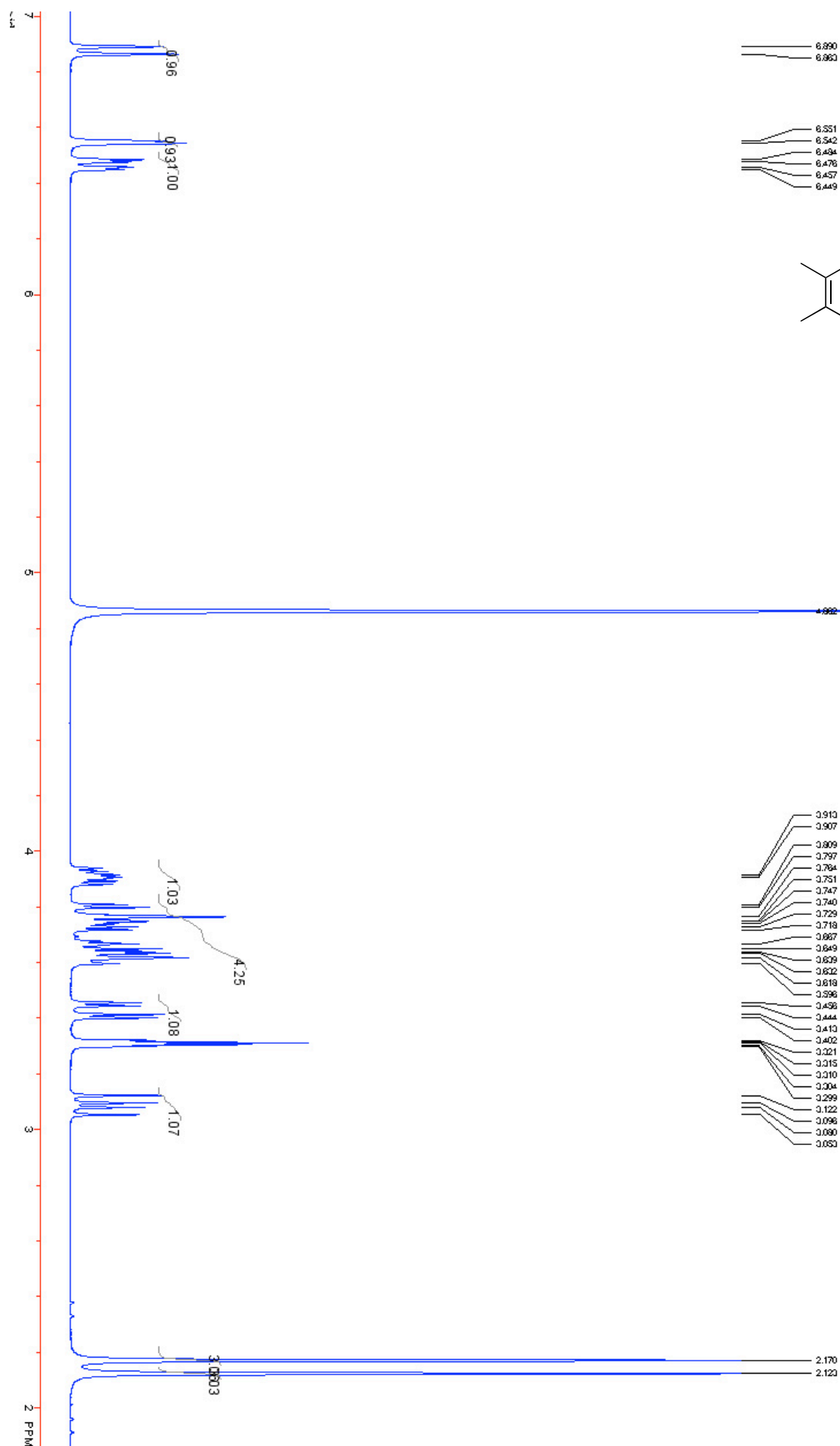
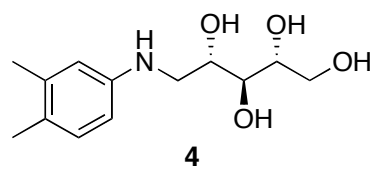


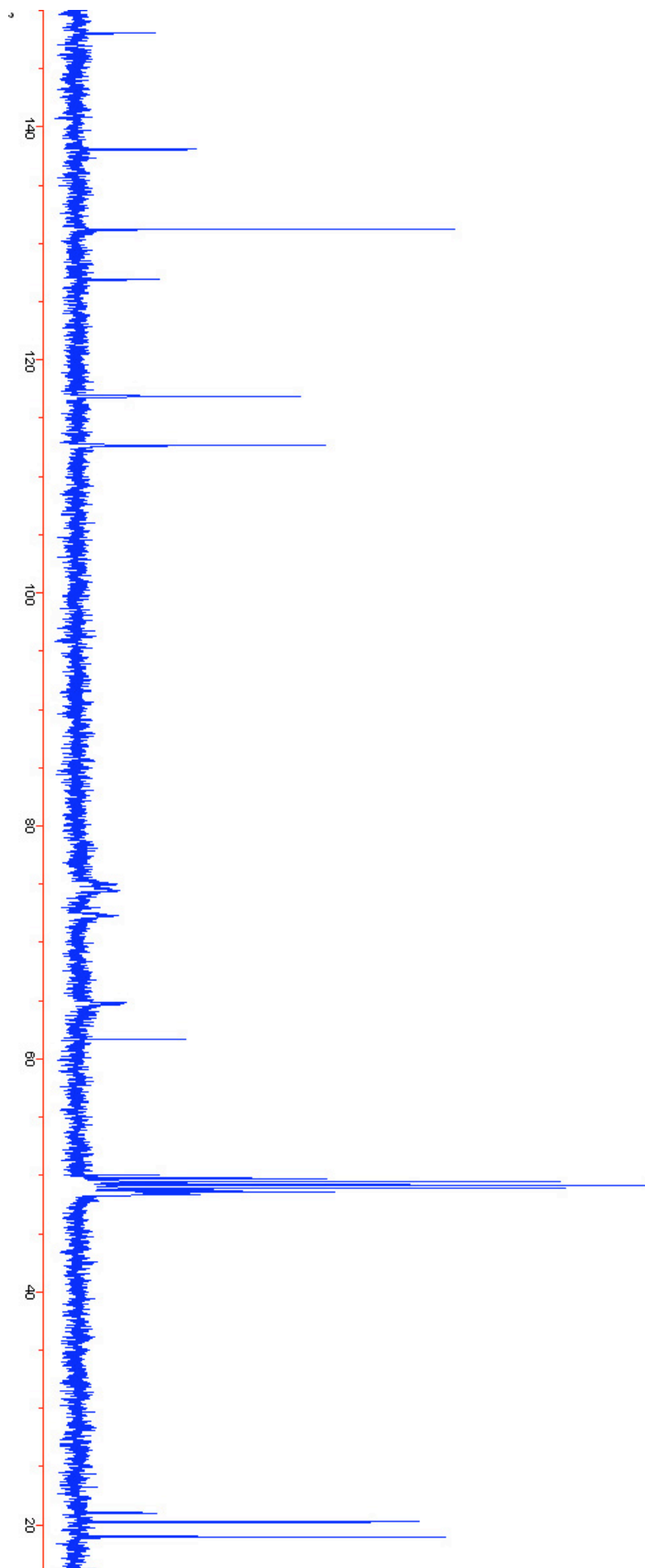
1-Deazariboflavin **2**





1-Deazariboflavin 2





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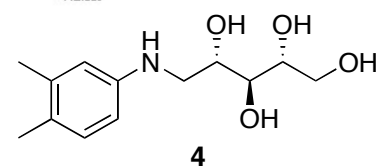
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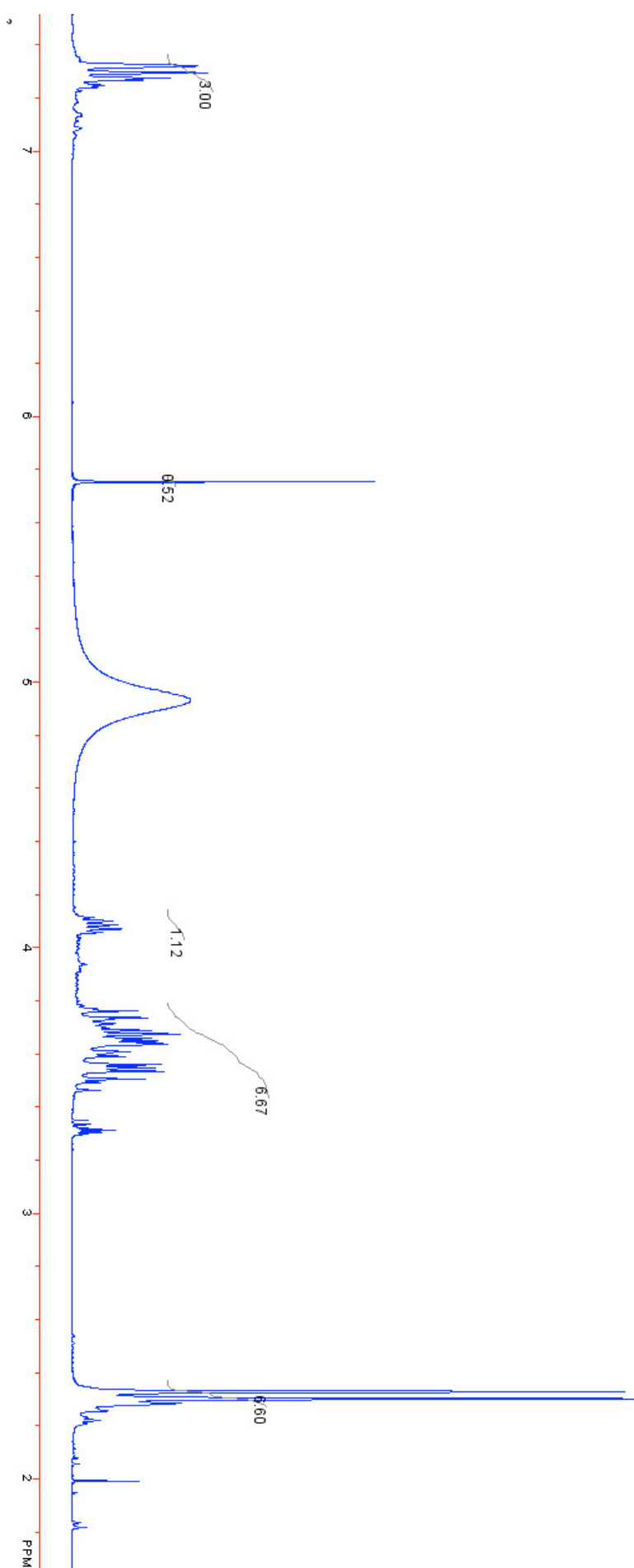
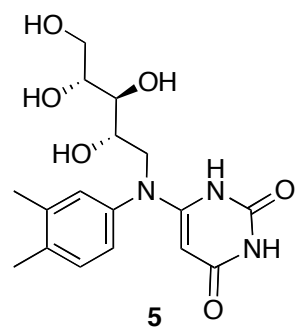
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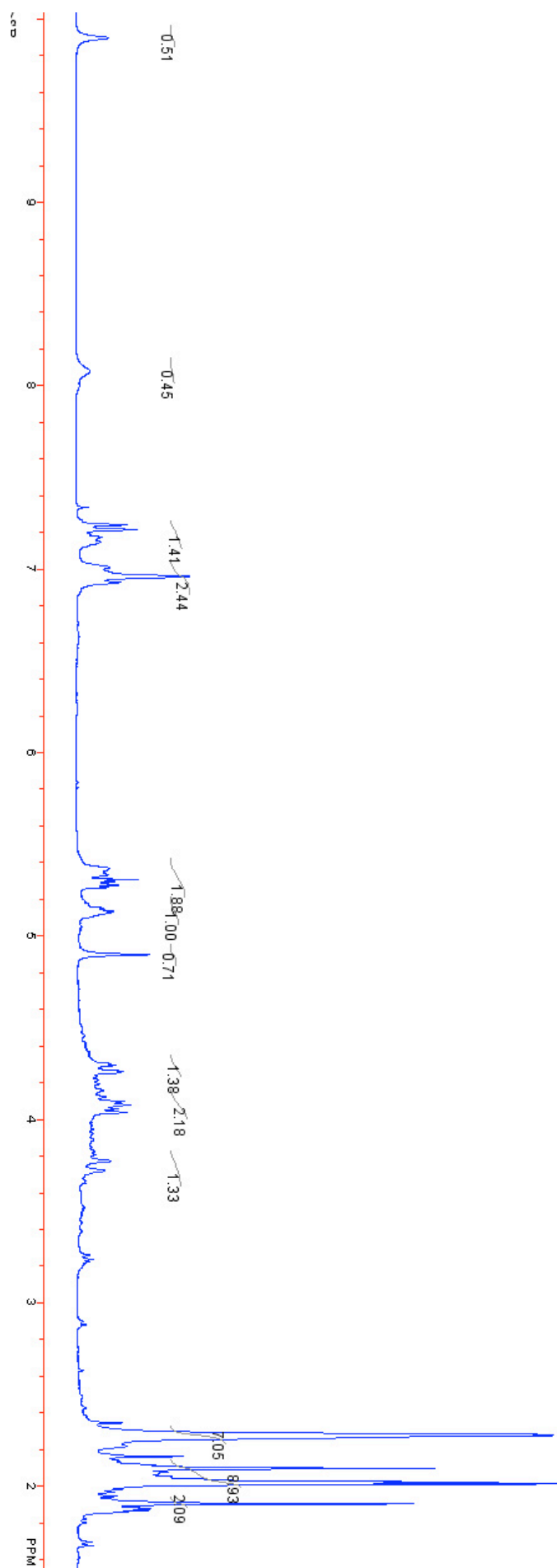
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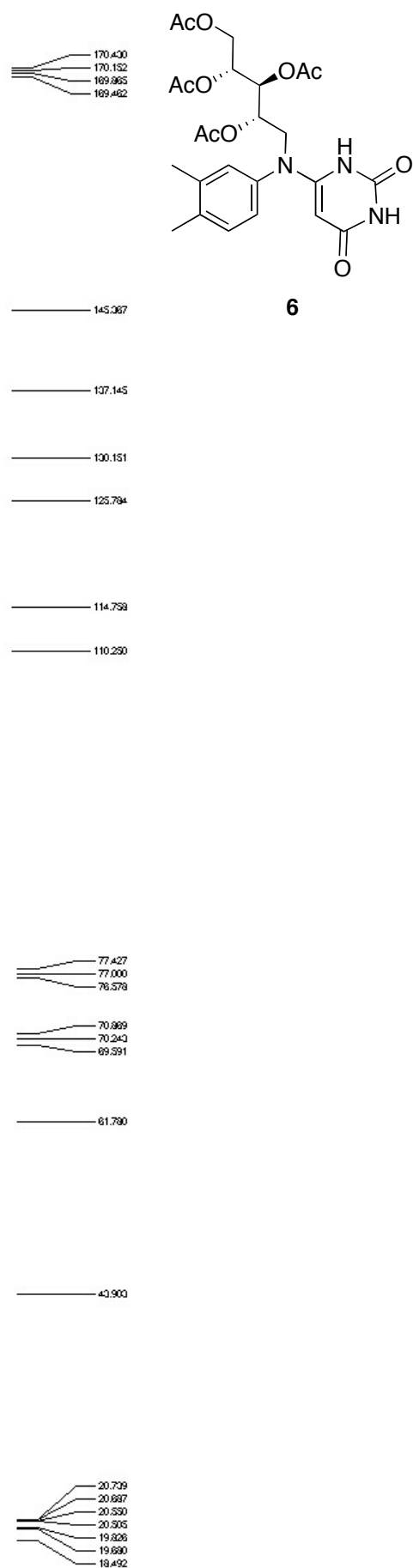
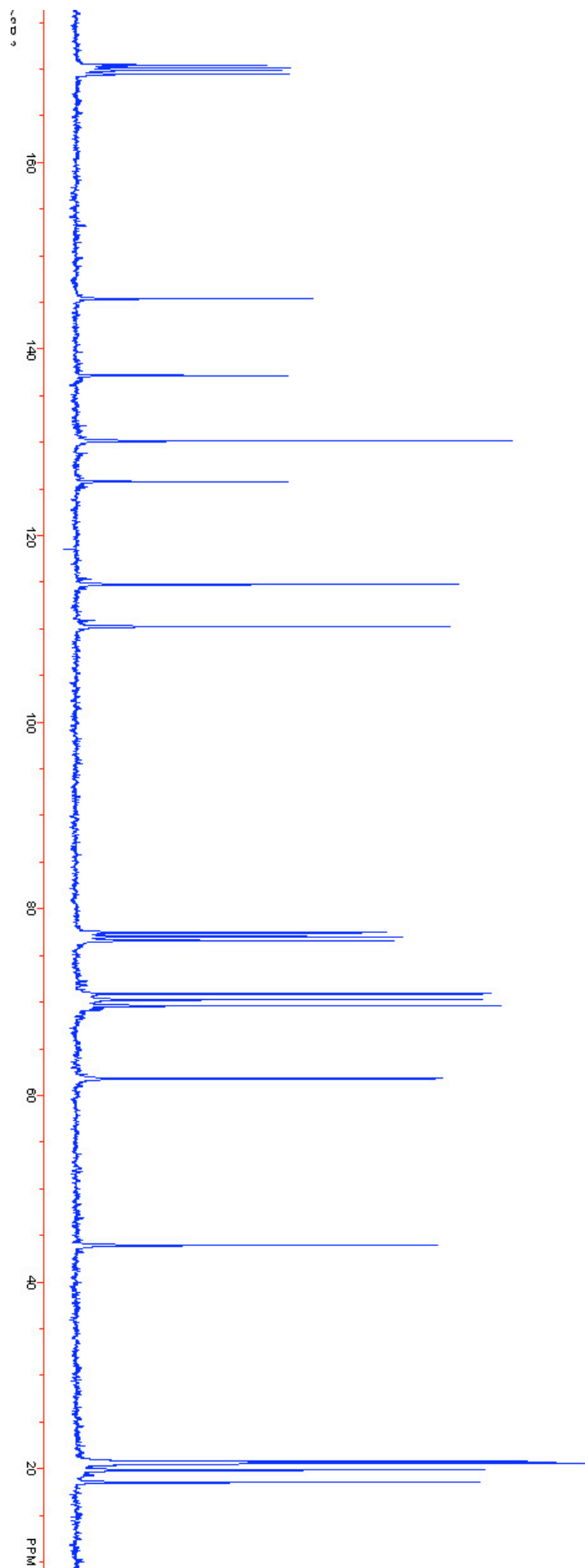
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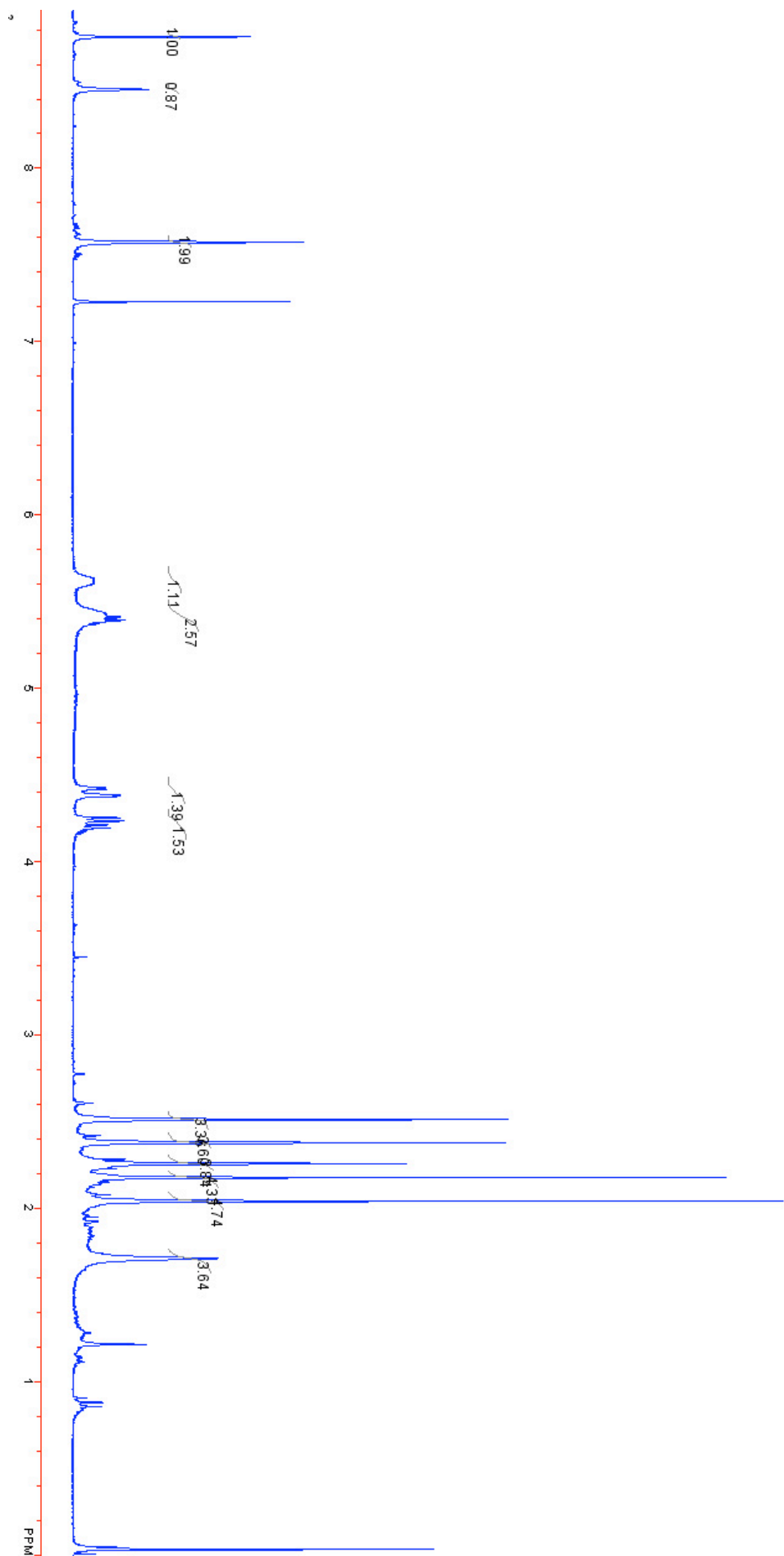
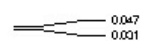
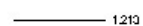
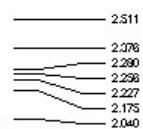
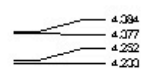
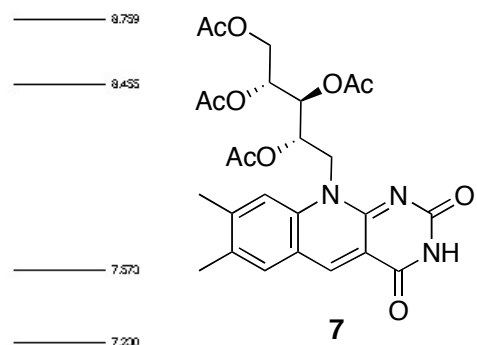
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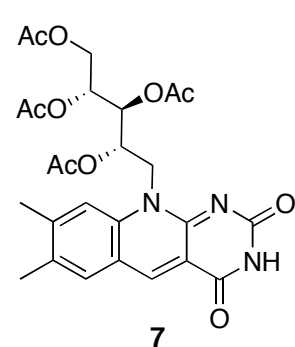
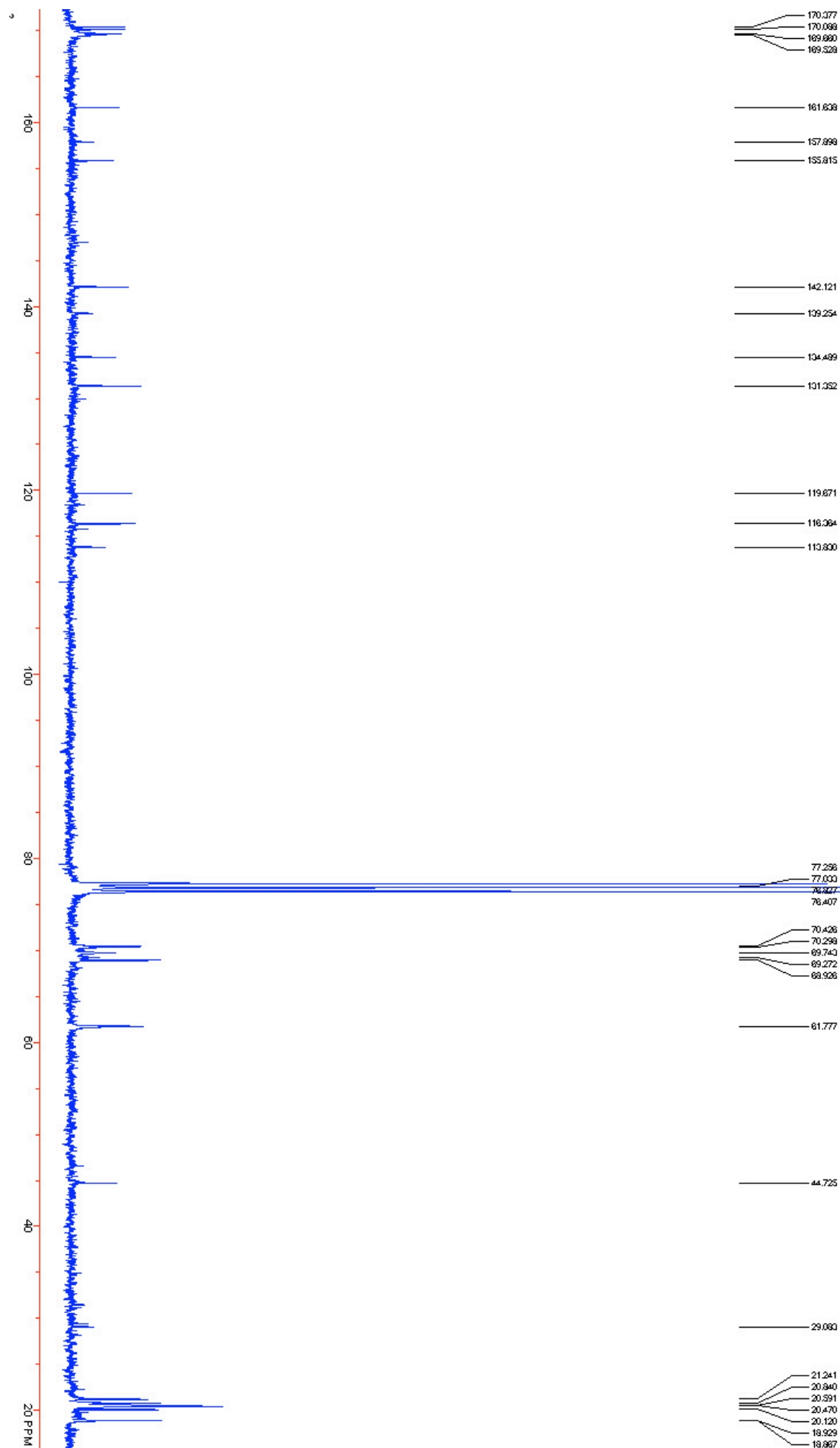
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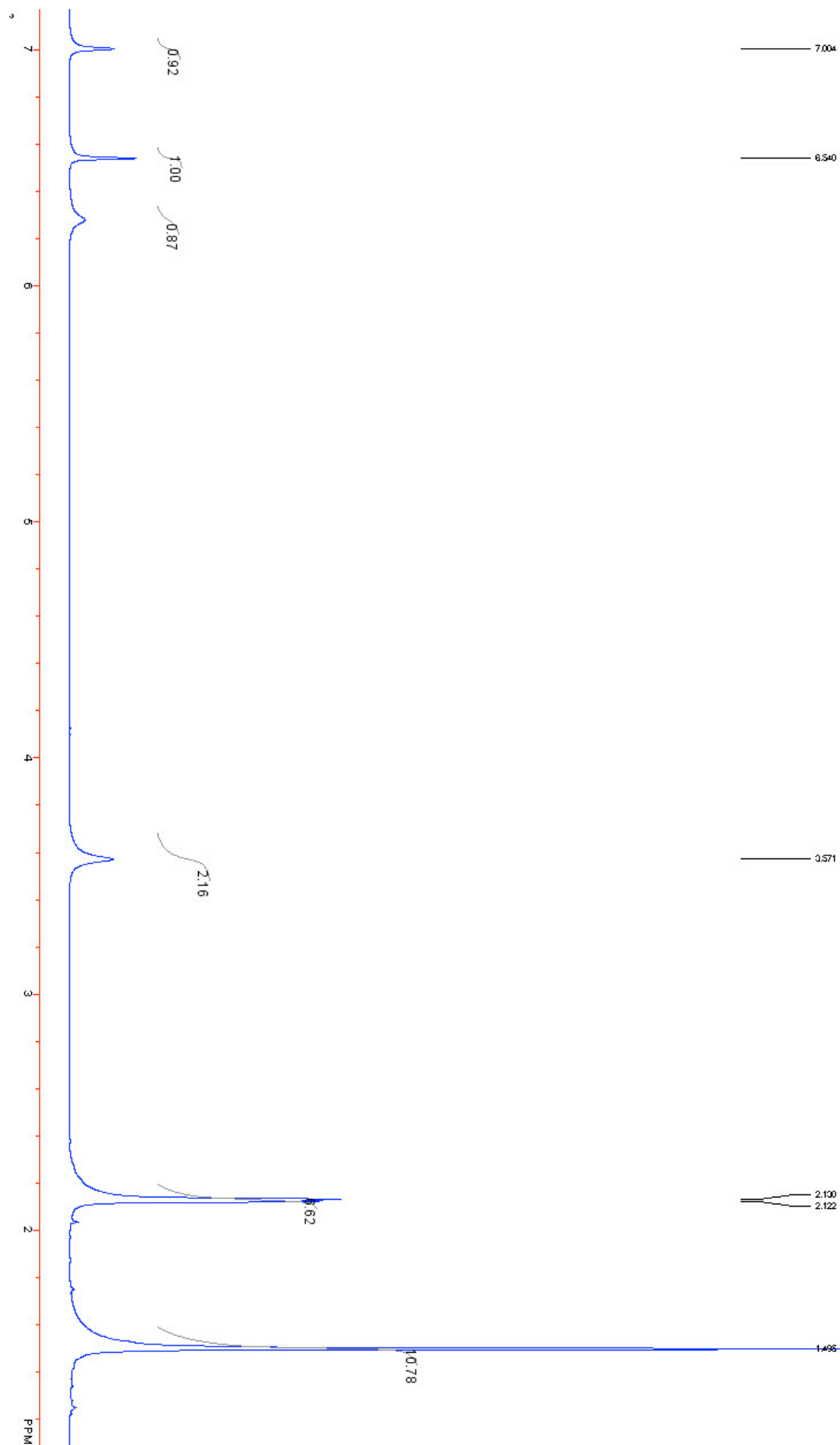
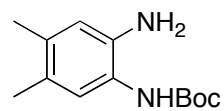


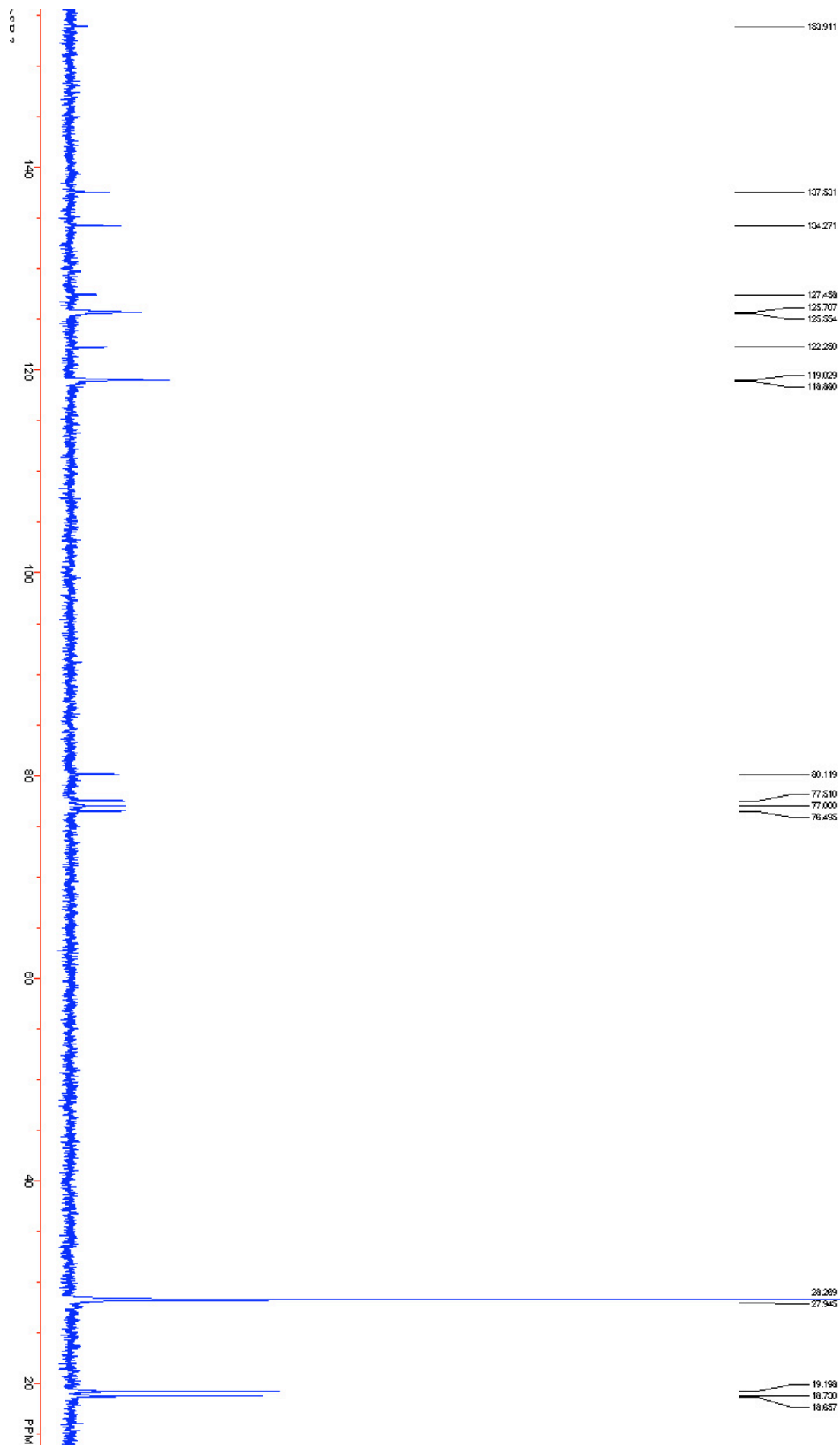
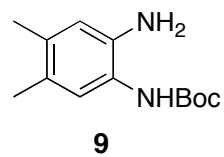


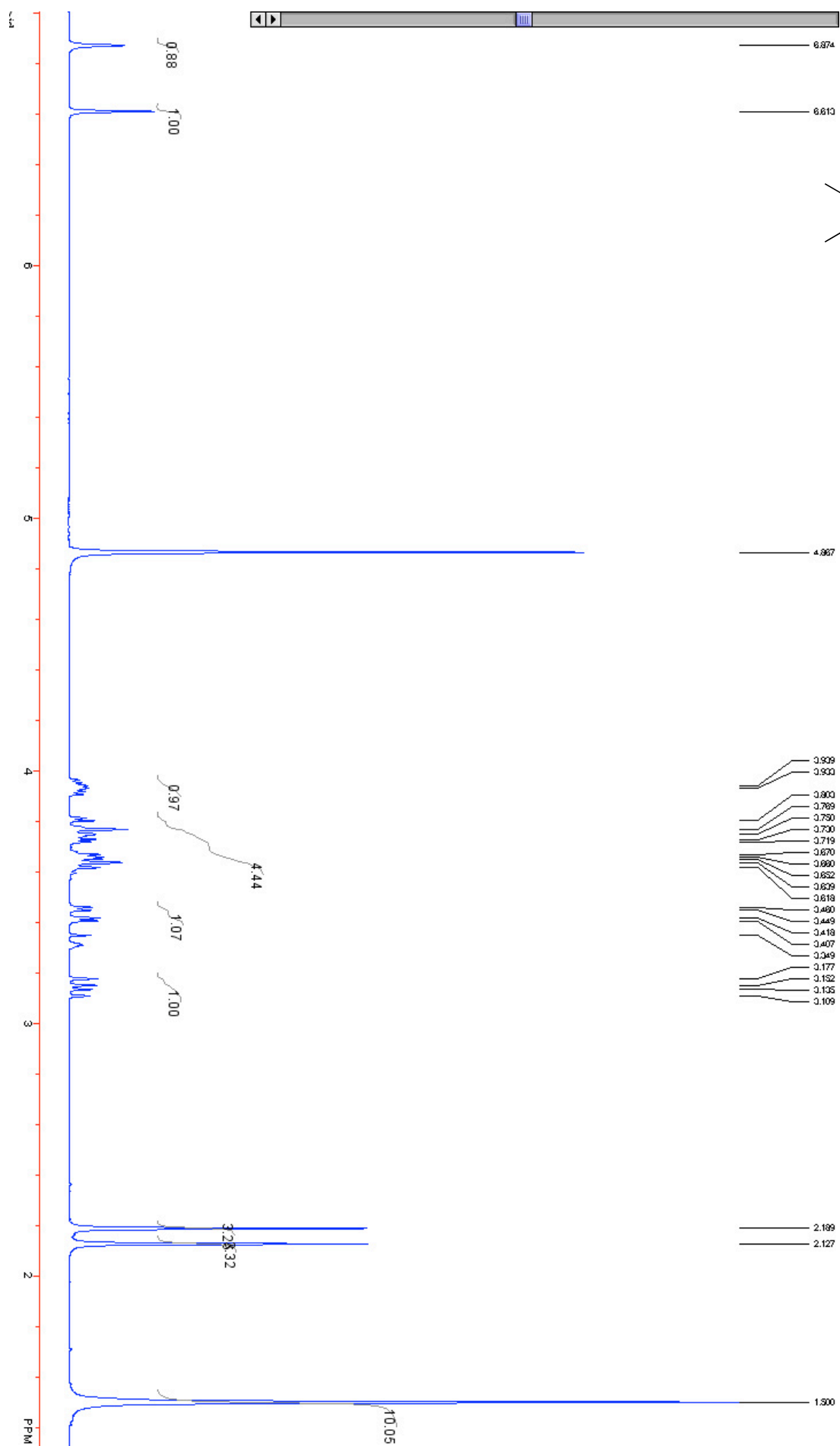




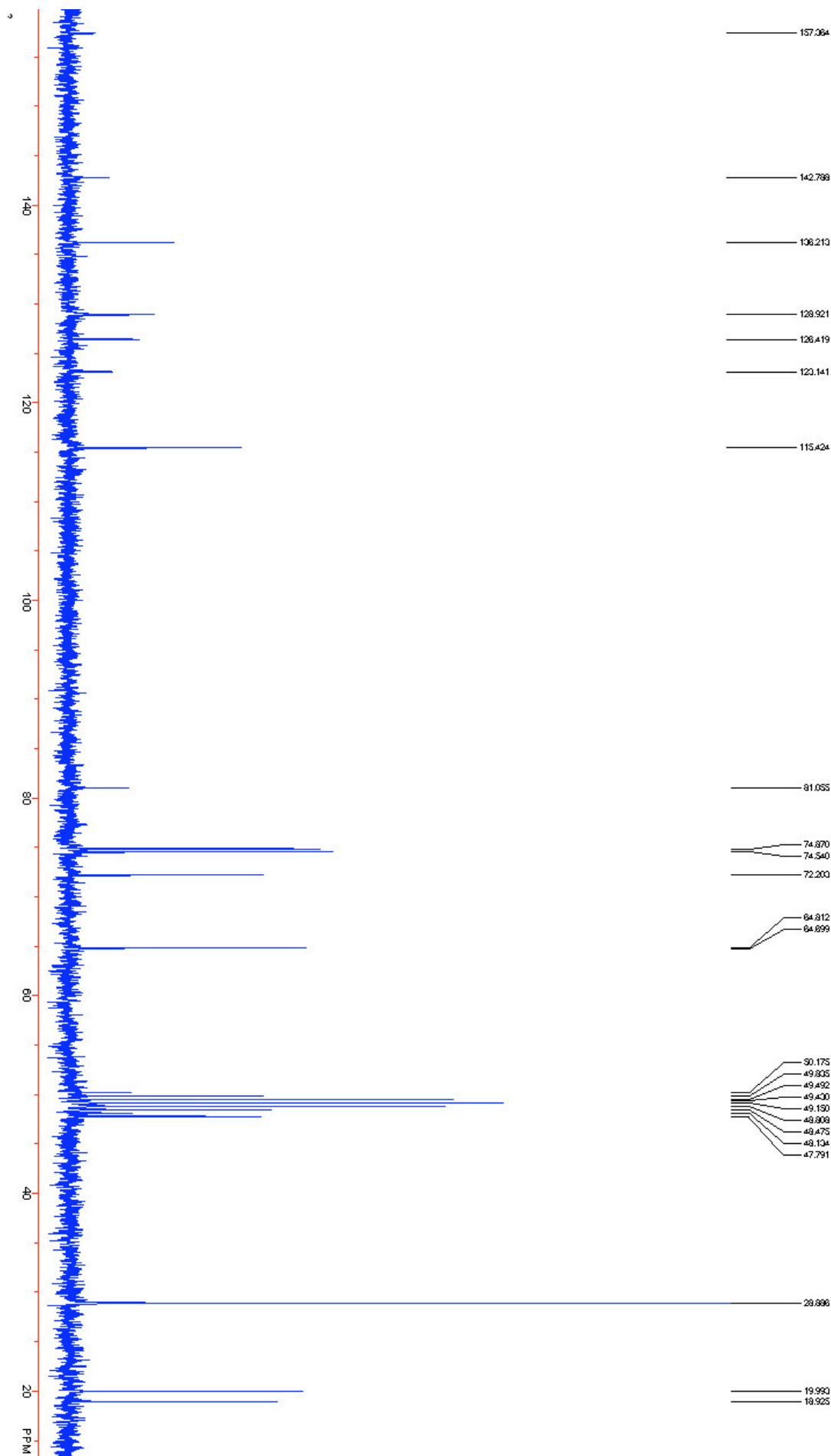


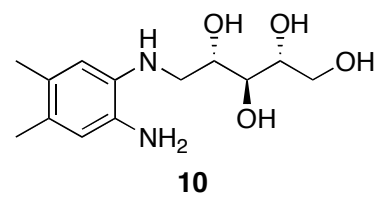
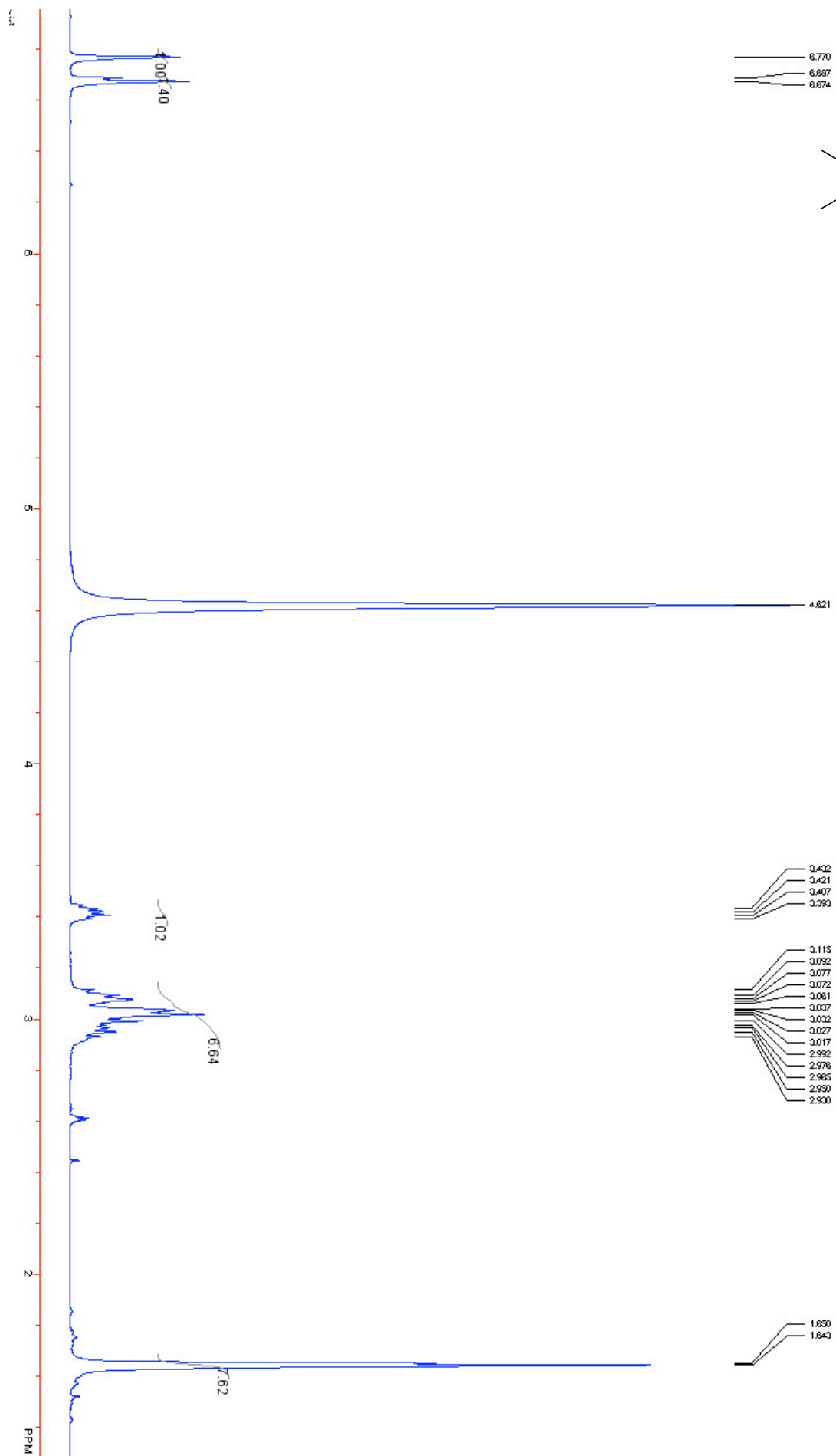


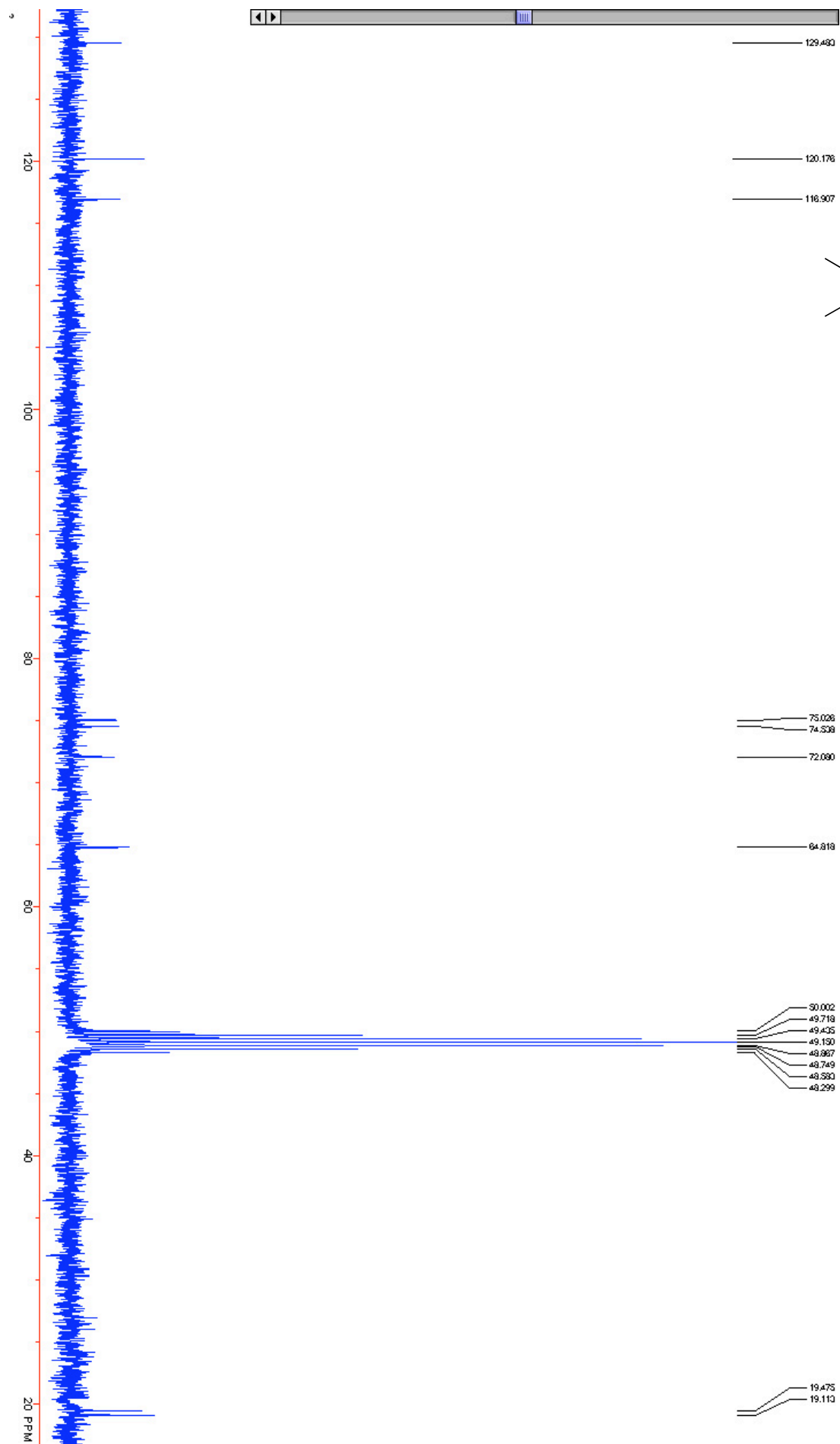


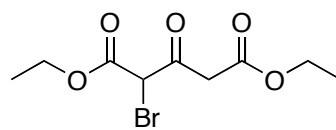


9 intermediate









11

