

SUPPORTING INFORMATION

Cycloadditions of 2-Azaallyllithium Species with Conjugated Polyenes

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Supporting Information

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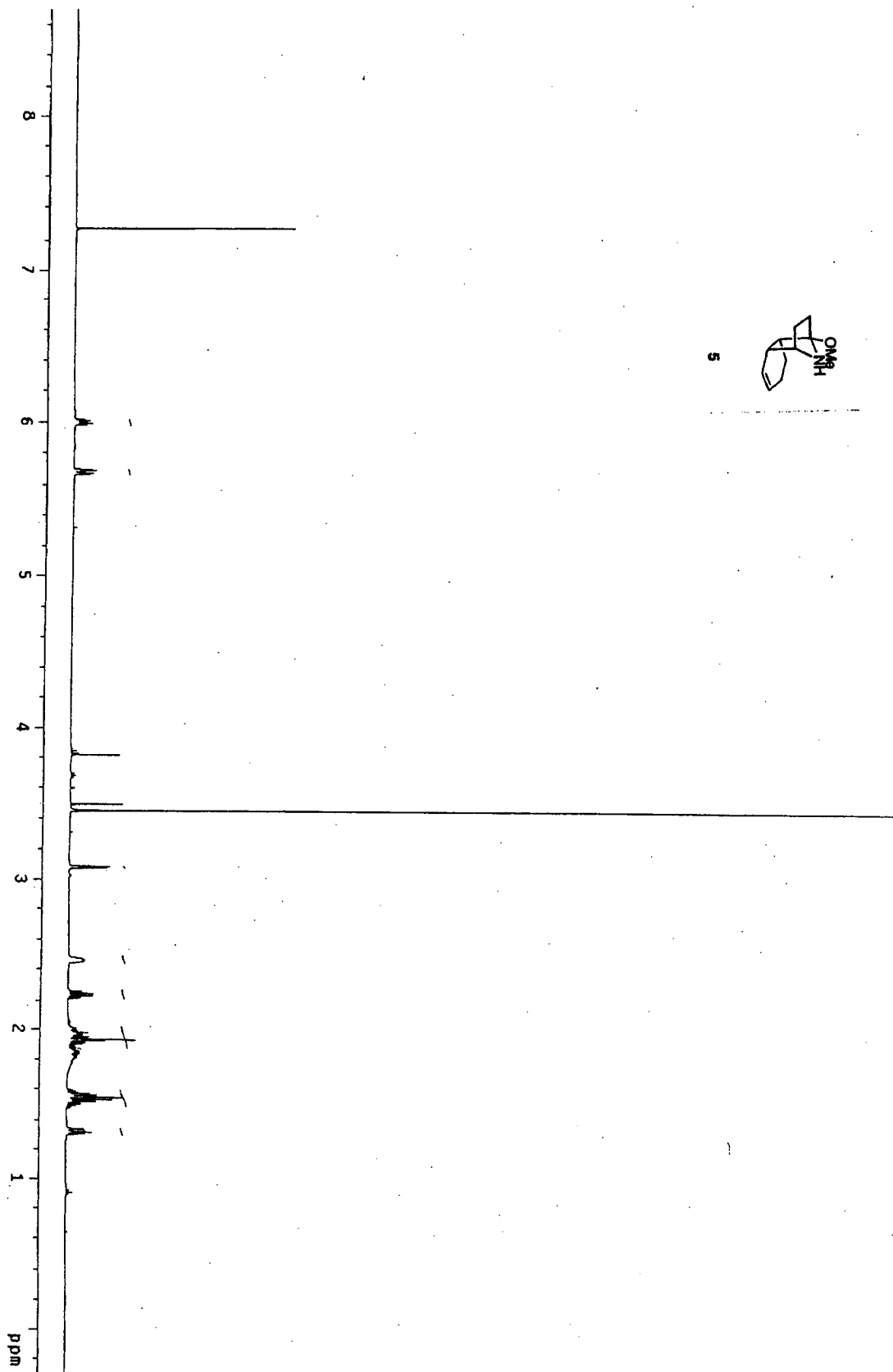
General Methods. All reactions were performed under an atmosphere of dry nitrogen or argon in flame-dried glassware equipped with tightly fitting rubber septa. All syringes and needles were oven-dried and cooled in a dessicator prior to use. Reactions at 0 °C were carried out in an ice/water bath. Reactions at -78 °C were carried out in a dry ice/acetone bath. Solvents were freshly prepared before use. Benzene, toluene, methylene chloride (CH_2Cl_2), pyridine, triethylamine and diisopropylamine were distilled from calcium hydride. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone ketyl. Dimethylformamide (DMF) was distilled from barium oxide under reduced pressure. *n*-Butyllithium was purchased from Aldrich Chemical Company, and titrated with diphenylacetic acid prior to use.

All reactions were monitored by gas chromatography/mass spectroscopy (GC/MS) and /or analytical thin layer chromatography (TLC). Routine mass spectral data were obtained using a Hewlett Packard 6890 Gas Chromatograph equipped with an HP 5973 mass selective detector via electron impact (EI) at 70 eV. TLC was conducted on pre-coated silica gel plates (Kieselgel 60 F₂₅₄, 0.25 mm thickness, manufactured by E. Merck & Co., Germany) or pre-coated aluminum oxide plates (aluminum oxide 60 F₂₅₄, manufactured by E. Merck & Co., Germany). For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine or phosphomolybdic acid solution. Chromatography refers to flash chromatography, which was performed according to the general procedure by Still using ICN (Sili-Tech 32-60, 60 Å) silica gel purchased from Bodman Chemicals or aluminum oxide (activated neutral, Brockman I, standard grade, ~150 mesh, 58Å) purchased from Aldrich. Unless noted, chromatography refers to that using silica gel.

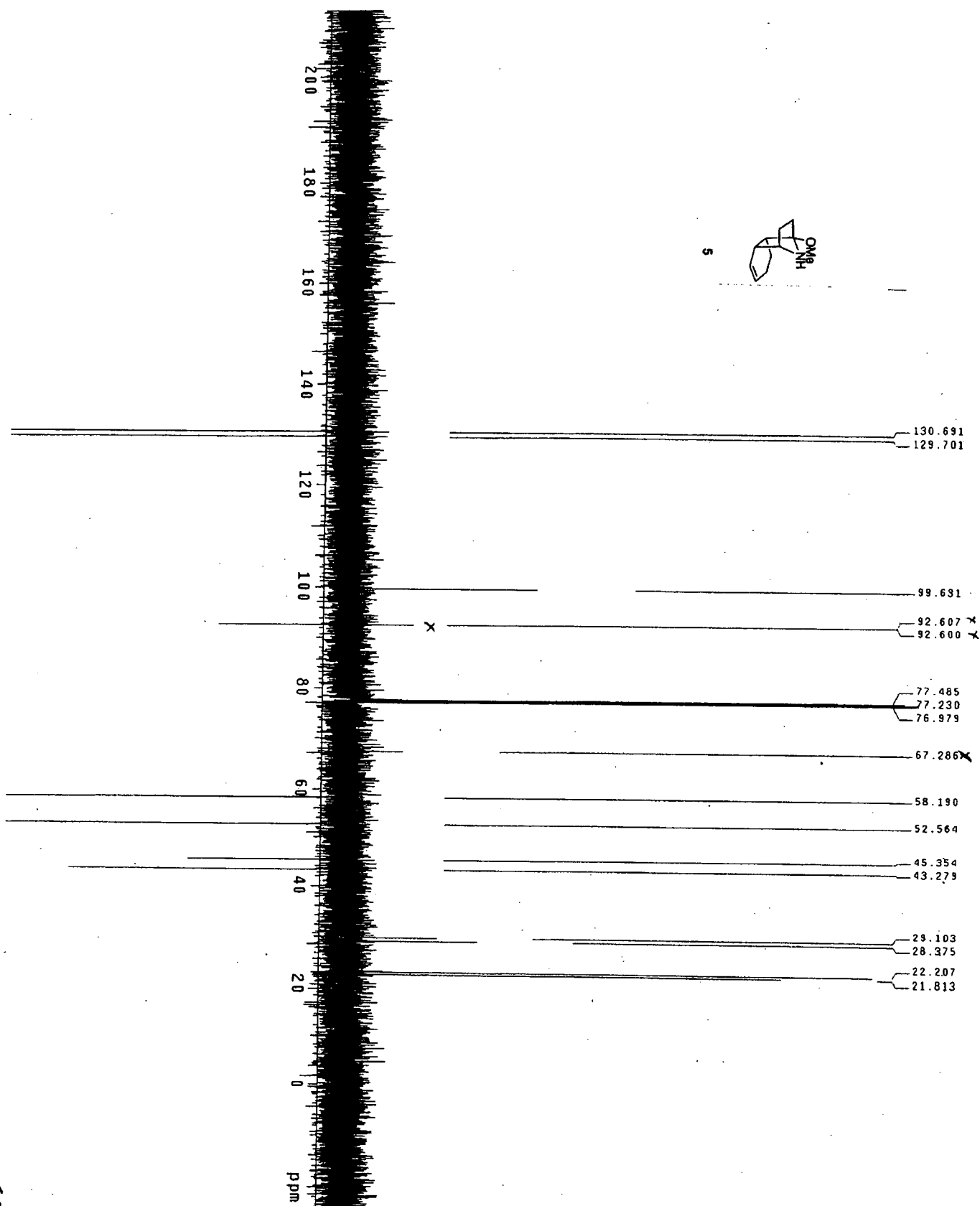
Proton nuclear magnetic resonance spectra (^1H NMR) were obtained on either a Varian Gemini 300 MHz, Varian Inova 400 MHz, or a Varian Inova 500 MHz spectrometer. The chemical shifts are reported as δ values, in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard, or relative to residual chloroform (7.26 ppm) or benzene (7.16 ppm). Data are reported in the following manner: chemical shift (multiplicity, integrated intensity, coupling constant (*J*) in hertz (Hz), assignment (when possible)). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad; app, apparent. For proton resonances that exhibit satellite peaks due to coupling with ^{117}Sn and ^{119}Sn , the average of the two couplings is reported when measurable. Assignments and stereochemical determinations were made on the basis of two-dimensional

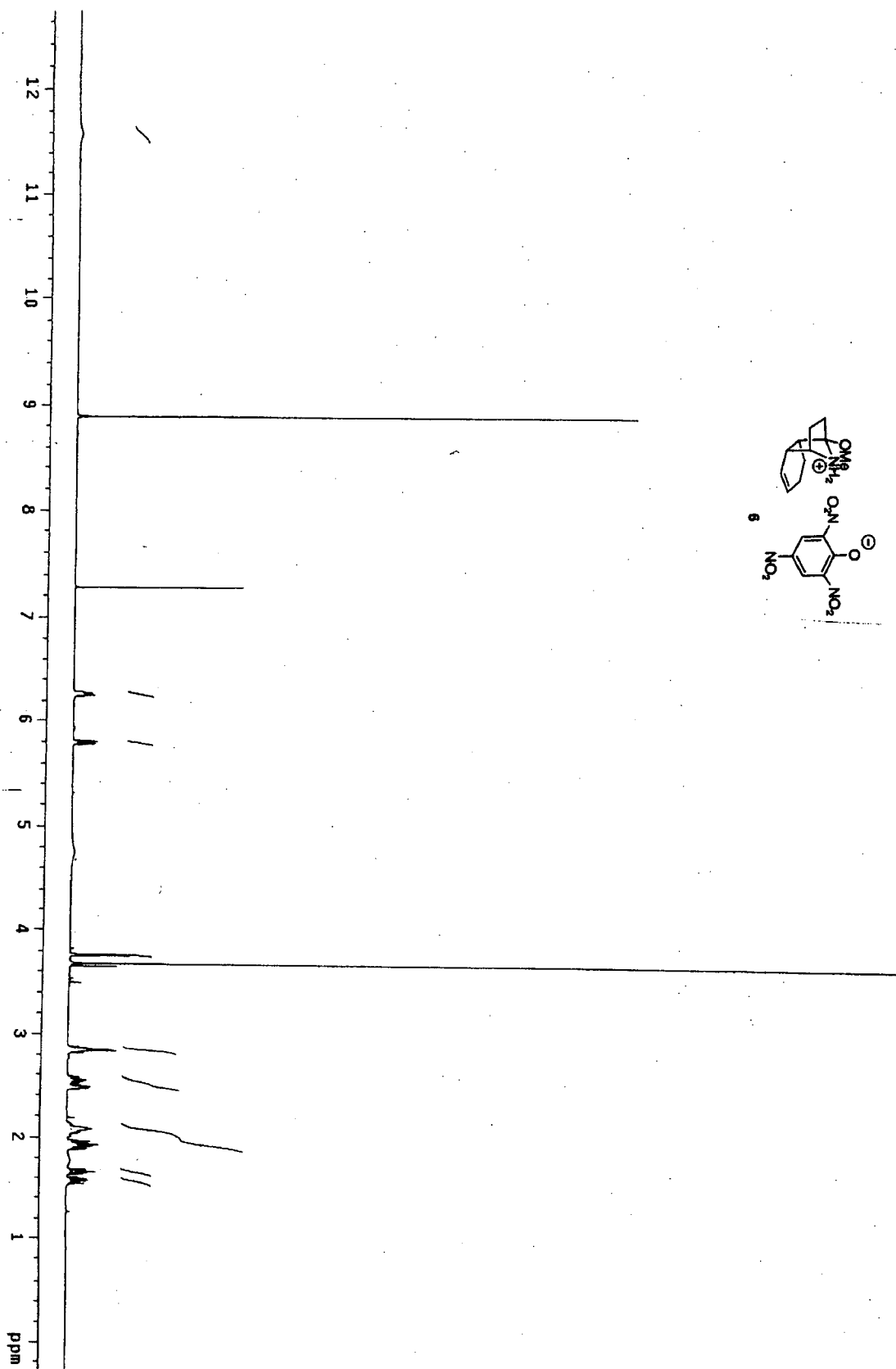
correlated off-resonance spectroscopy (COSY) experiments as well as one-dimensional Nuclear Overhauser effect spectroscopy (1D-NOE). ^{13}C nuclear magnetic resonance spectra (^{13}C NMR) were recorded using the spectrometers mentioned above, at 75, 100, and 125 MHz respectively. Chemical shifts in the ^{13}C spectra are reported as δ values in ppm relative to either deuteriochloroform (CDCl_3 , 77.23 ppm) or hexadeuteriobenzene (C_6D_6 , 128.0 ppm).

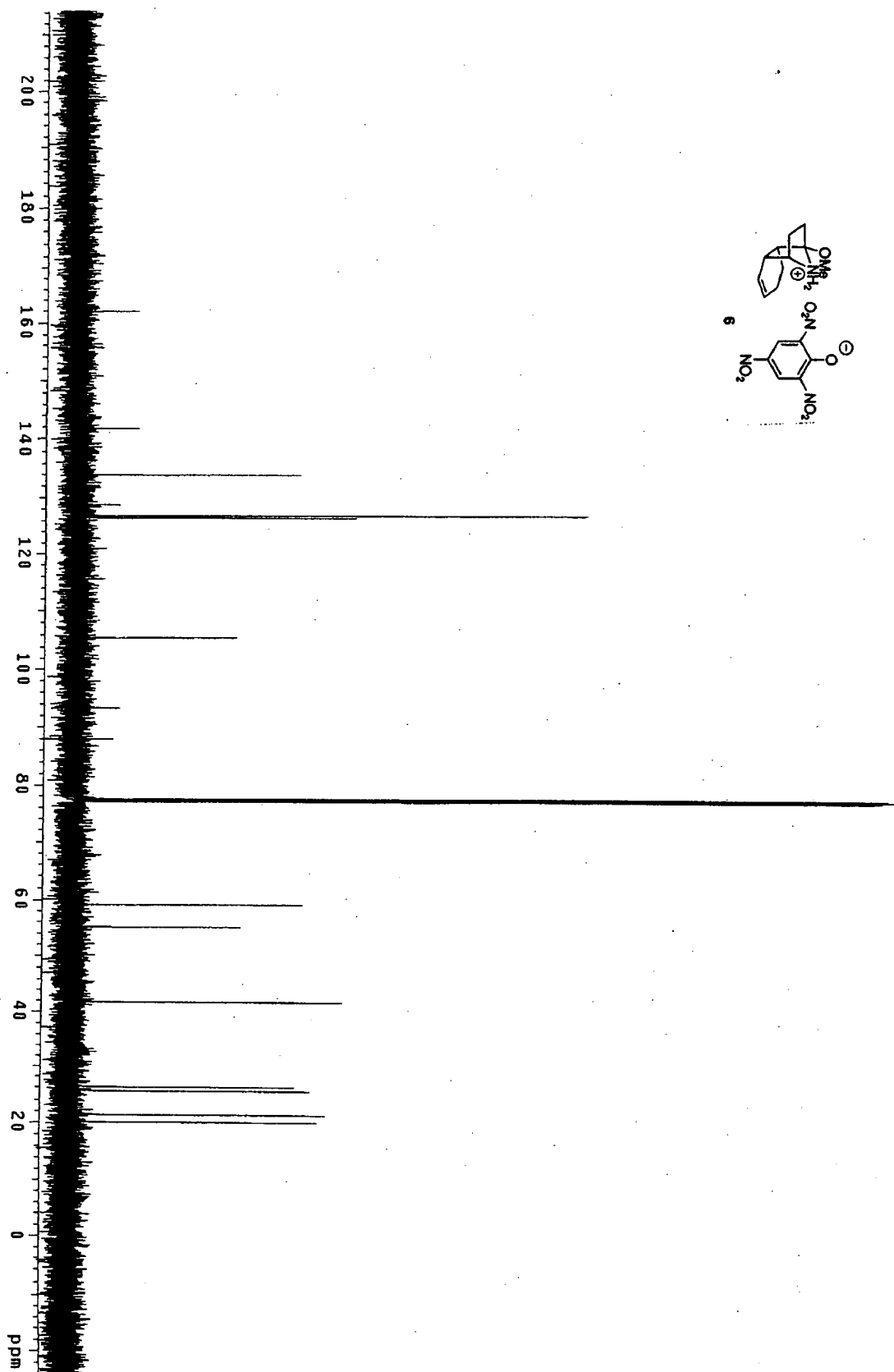
Infrared (IR) spectra were obtained using a Perkin-Elmer BX FT-IR spectrometer. IR data are reported in wavenumbers (cm^{-1}). Abbreviations used to describe the intensity and shape of the peaks are: w, weak; m, medium; s, strong; and br, broad. Mass spectra (MS) were obtained on a VF 70-250S mass spectrometer. Data are reported as m/z (%). High resolution mass spectroscopy (HRMS) was performed on the same instrument. All mass spectra were obtained by Jim Wyndak or Paul Lennon, Department of Chemistry, University of Michigan at Ann Arbor, MI. Elemental analyses were performed by Carol Carter, Department of Chemistry, University of Michigan at Ann Arbor, MI. X-ray analyses were performed by Jeff Kampf, Department of Chemistry, University of Michigan at Ann Arbor, MI.

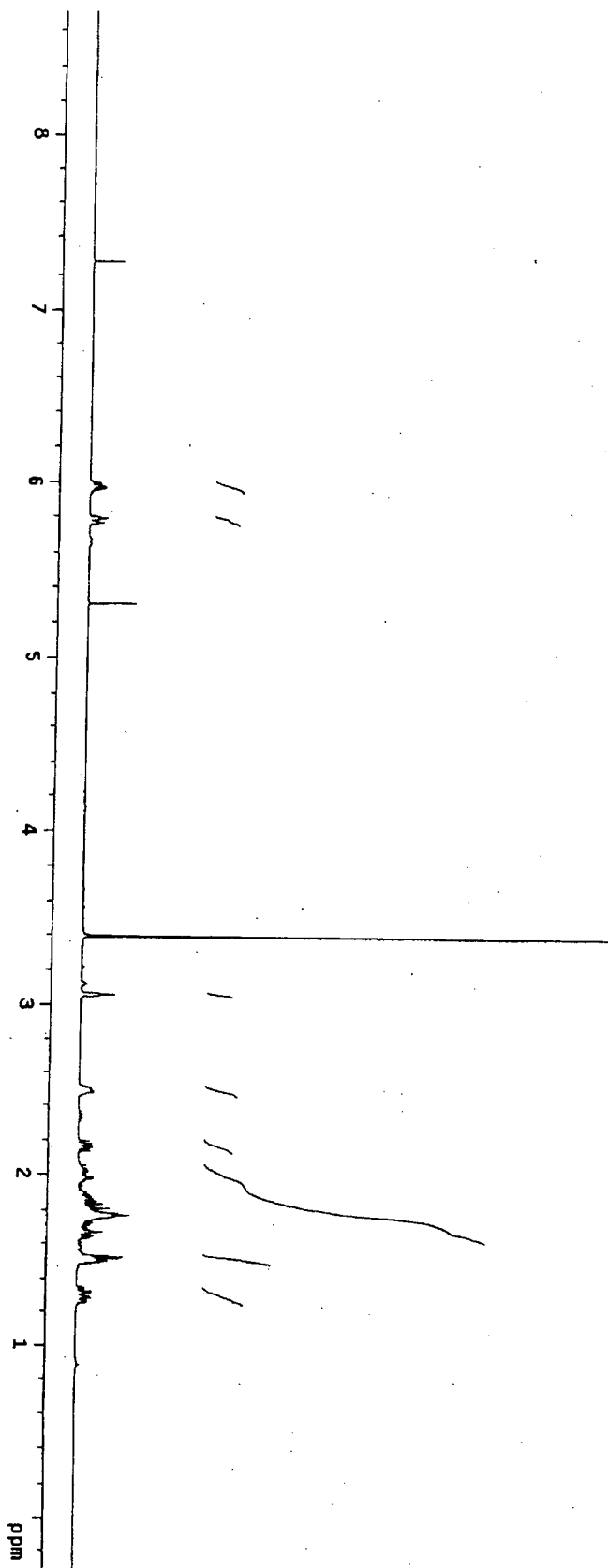


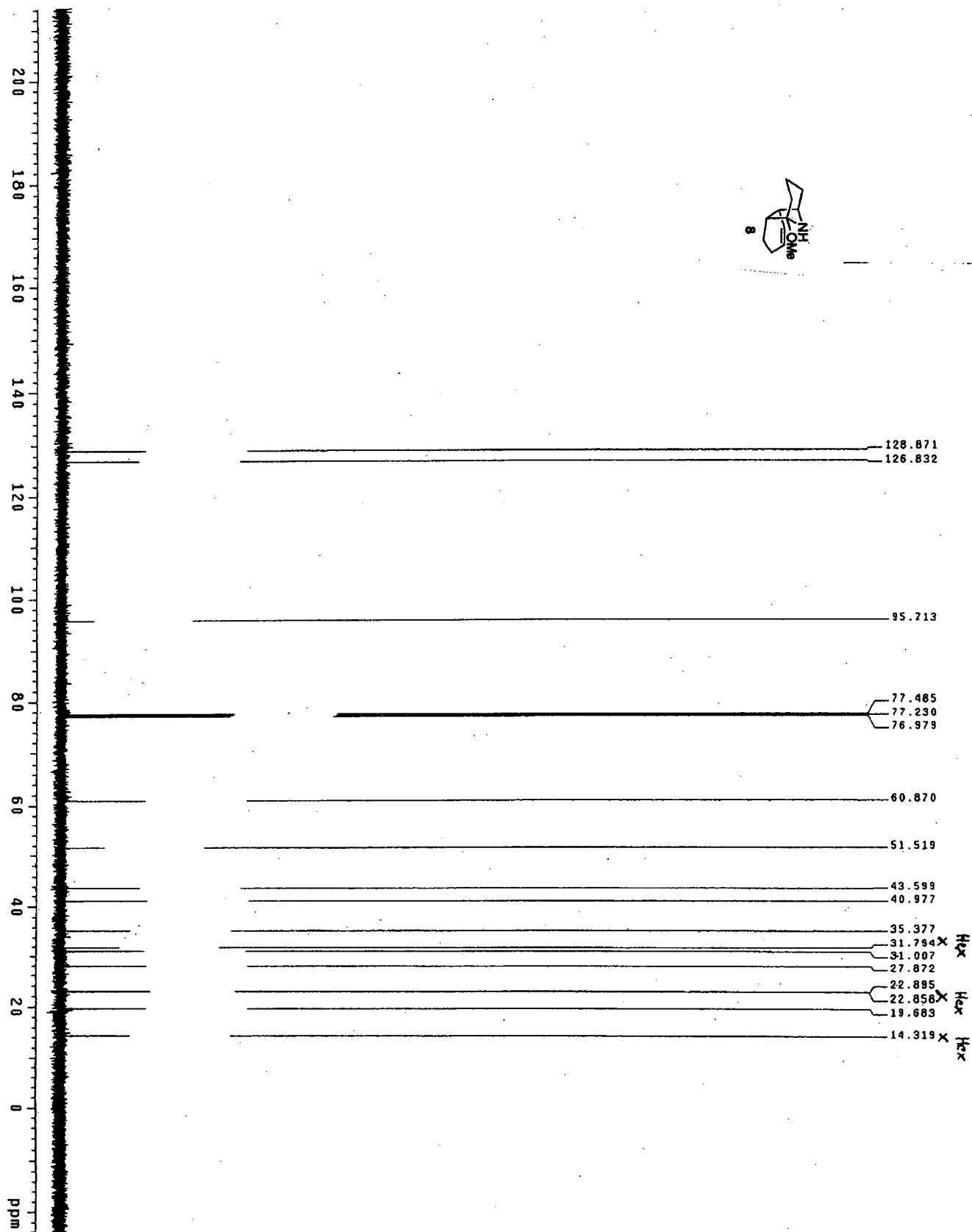
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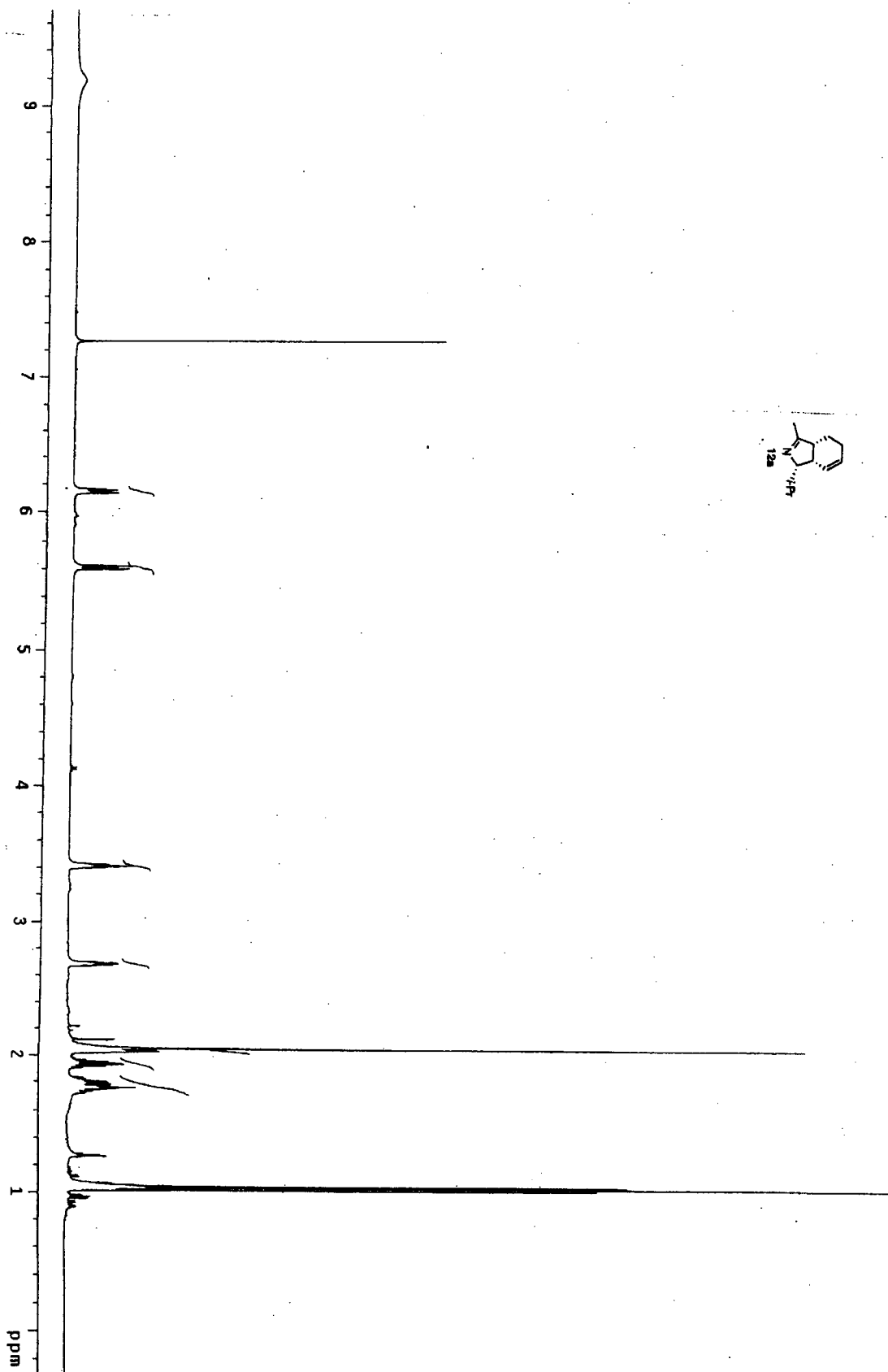


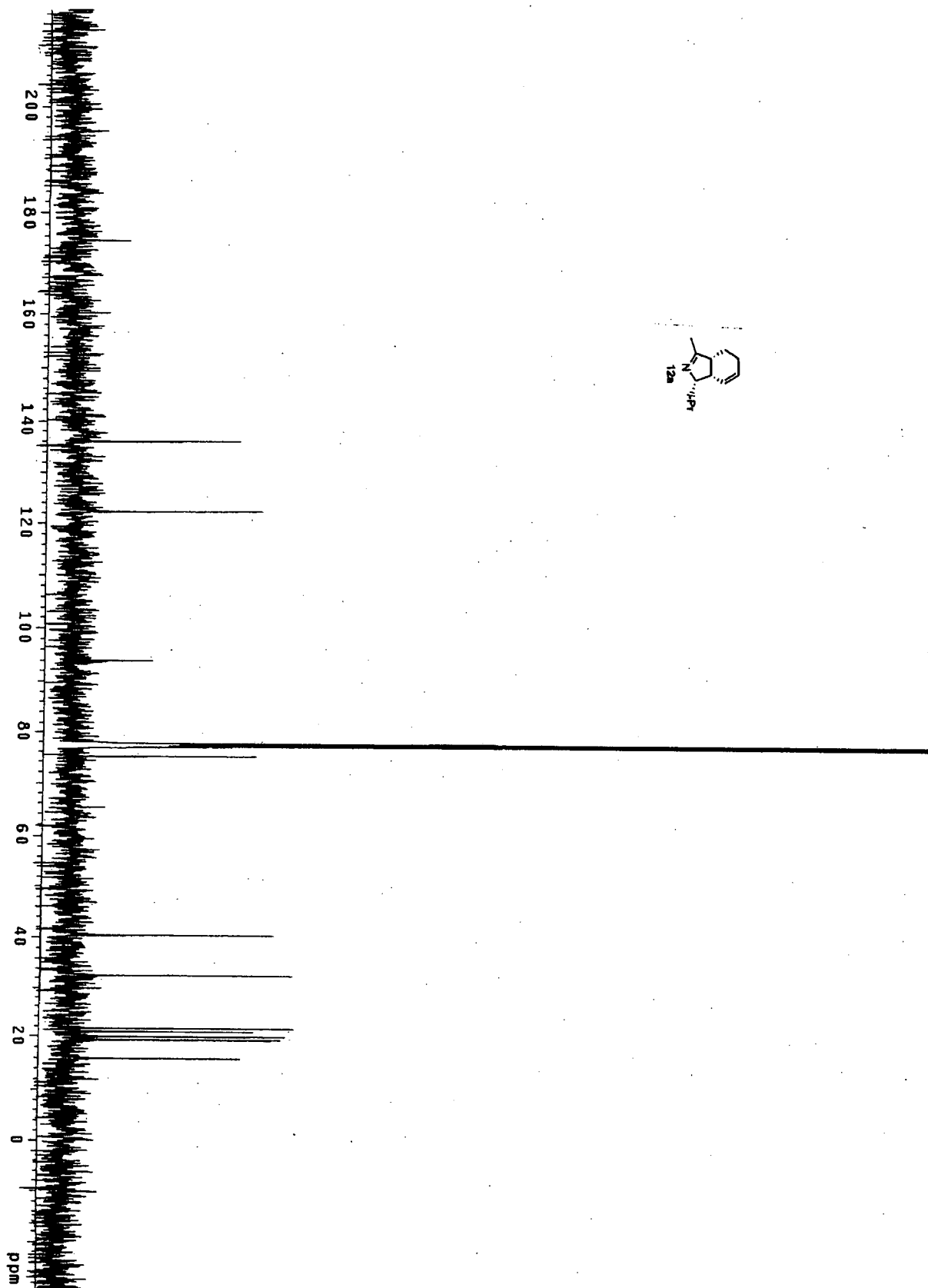


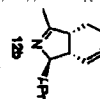
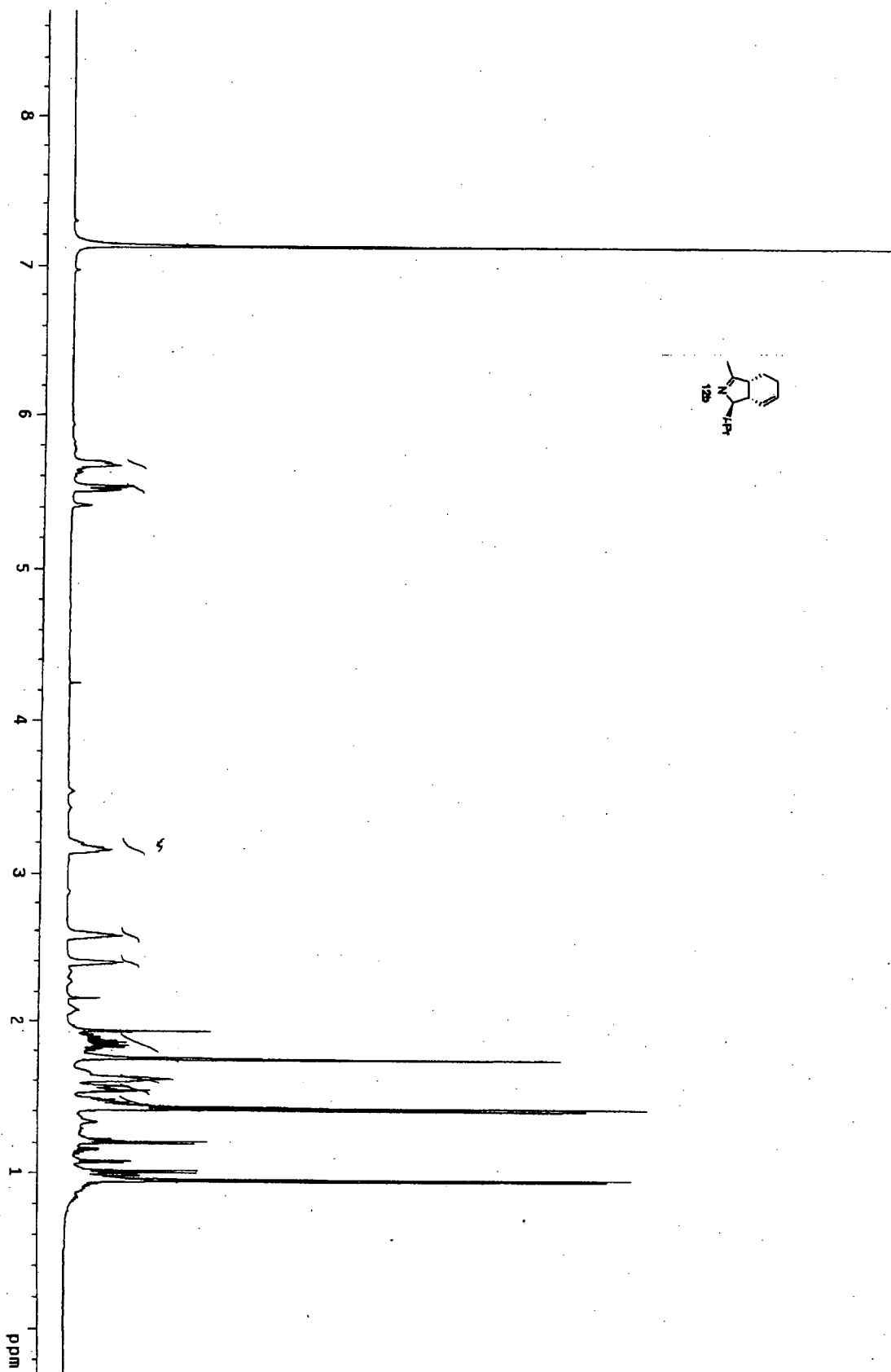


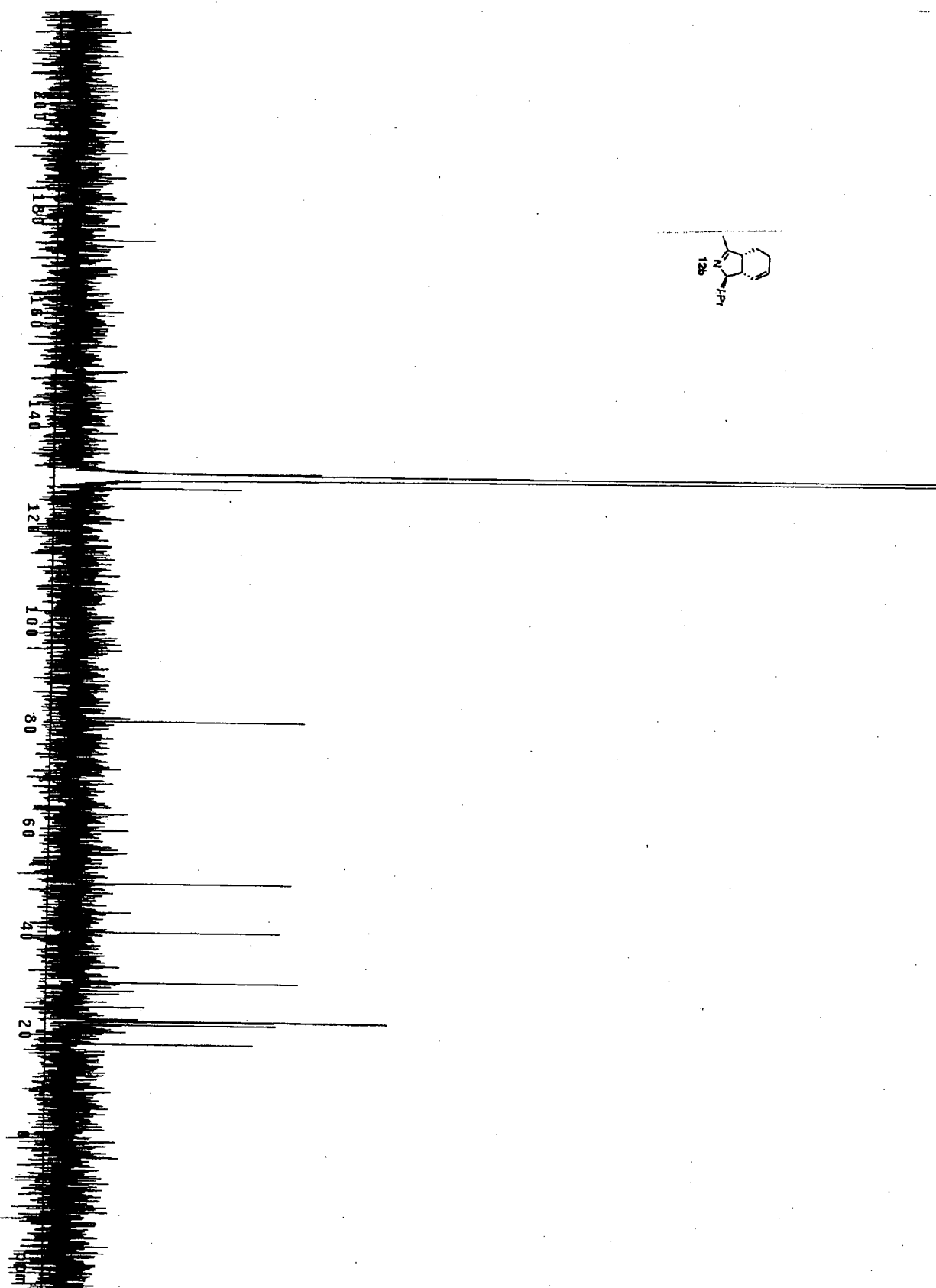


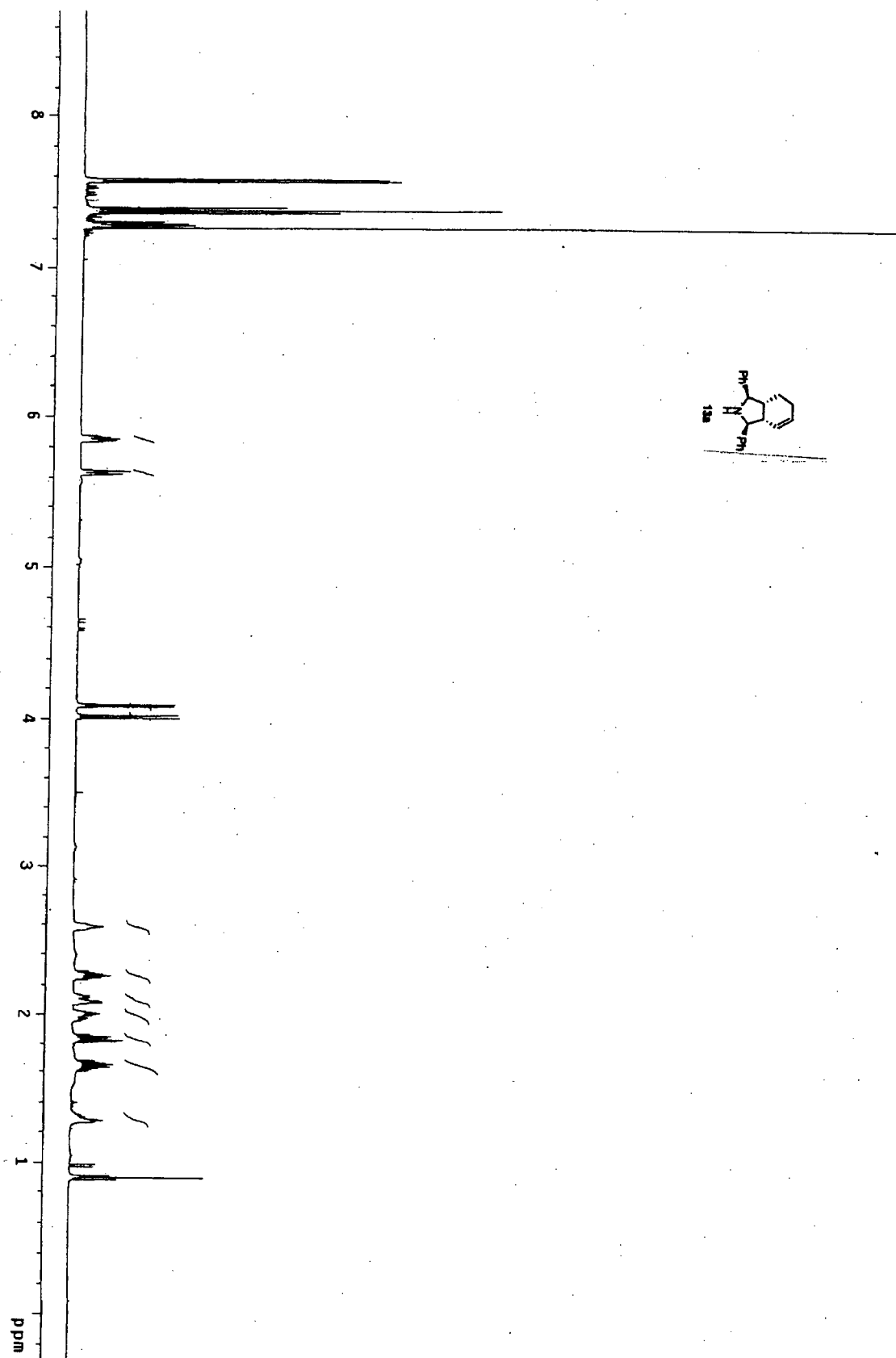
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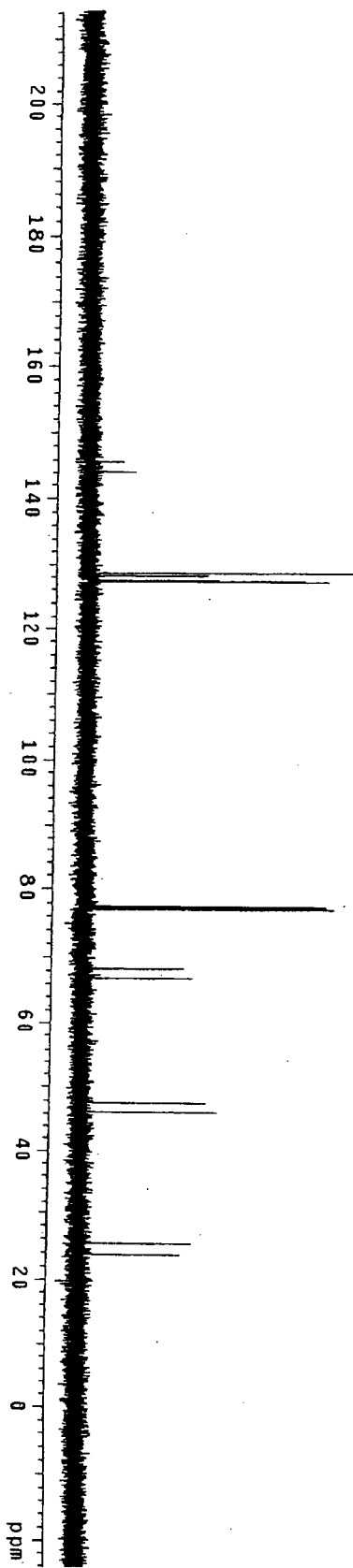
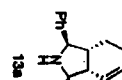




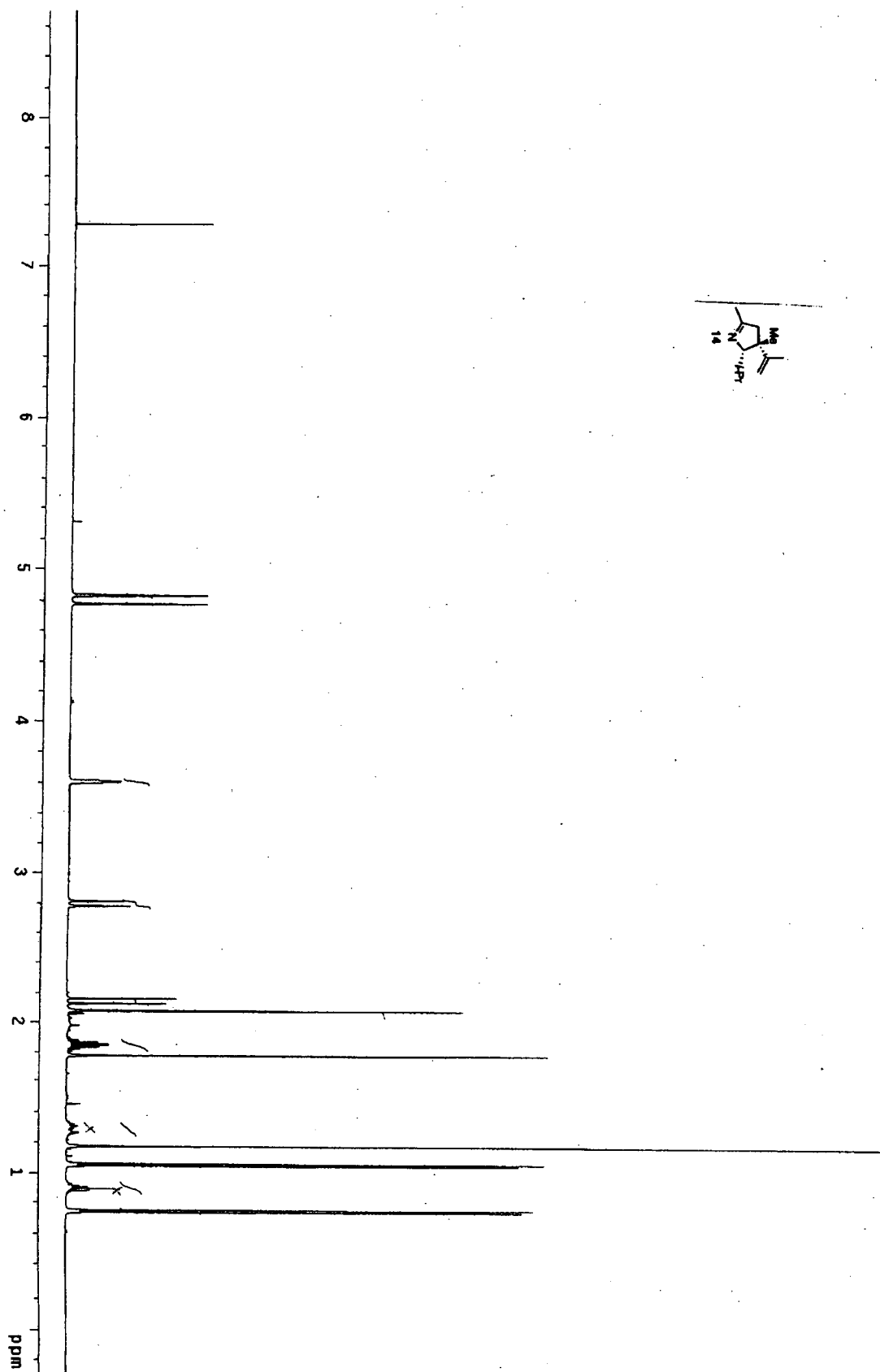


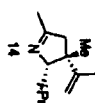
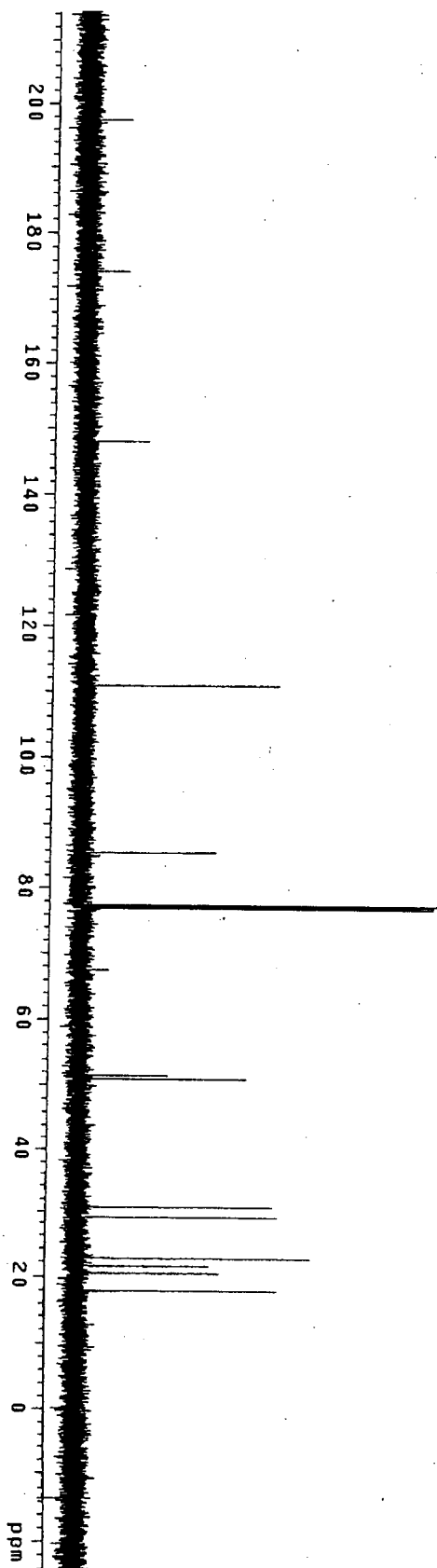


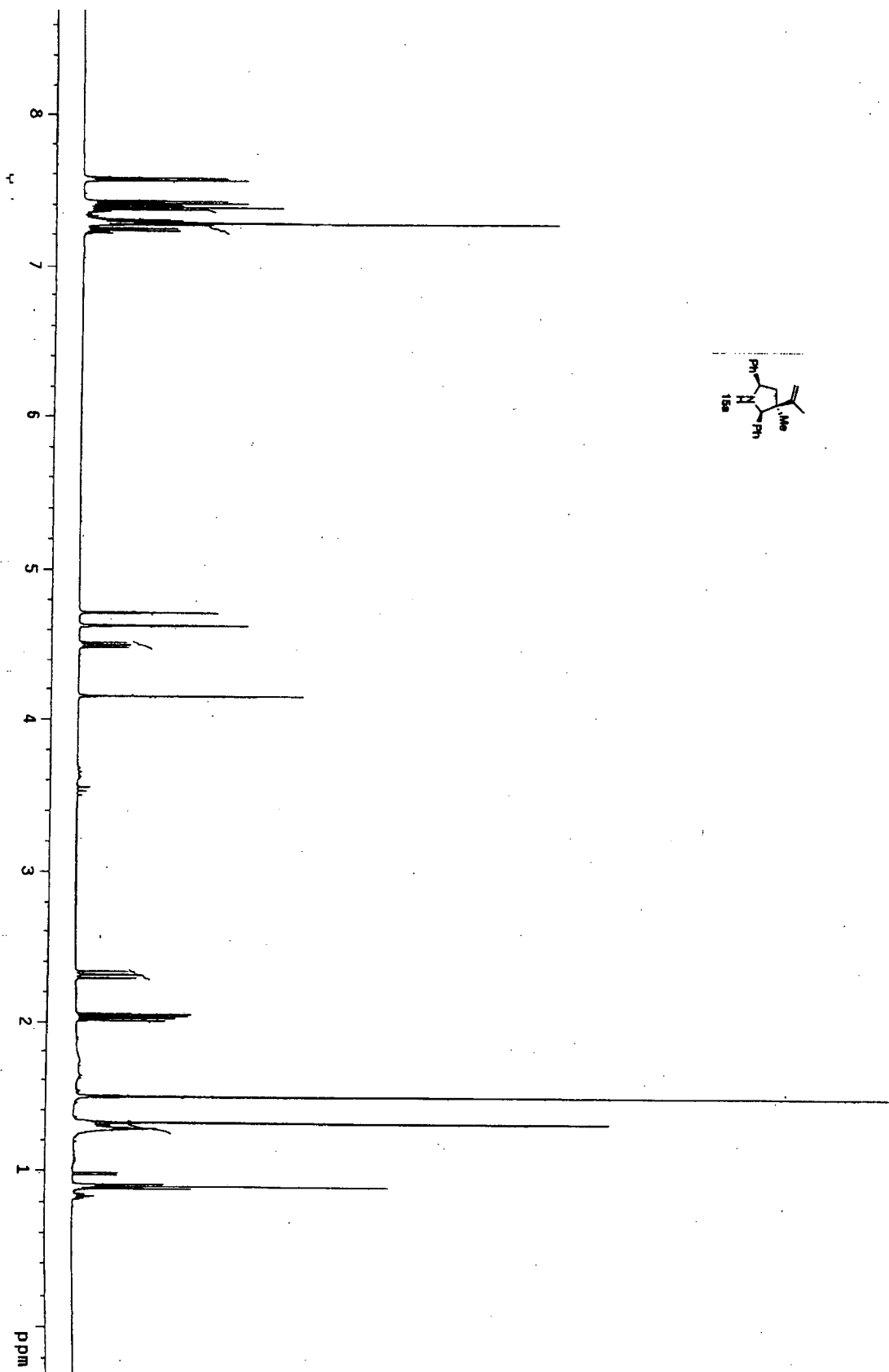
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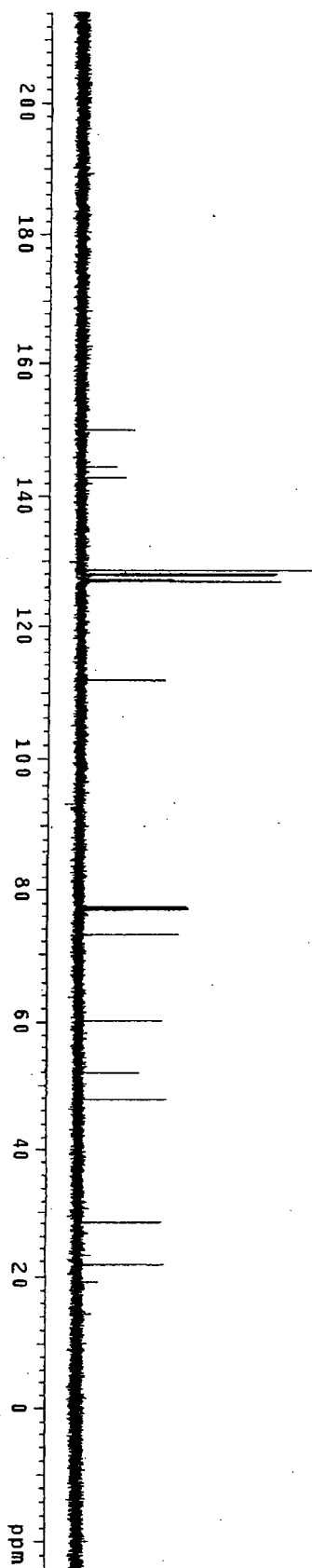
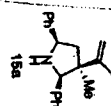


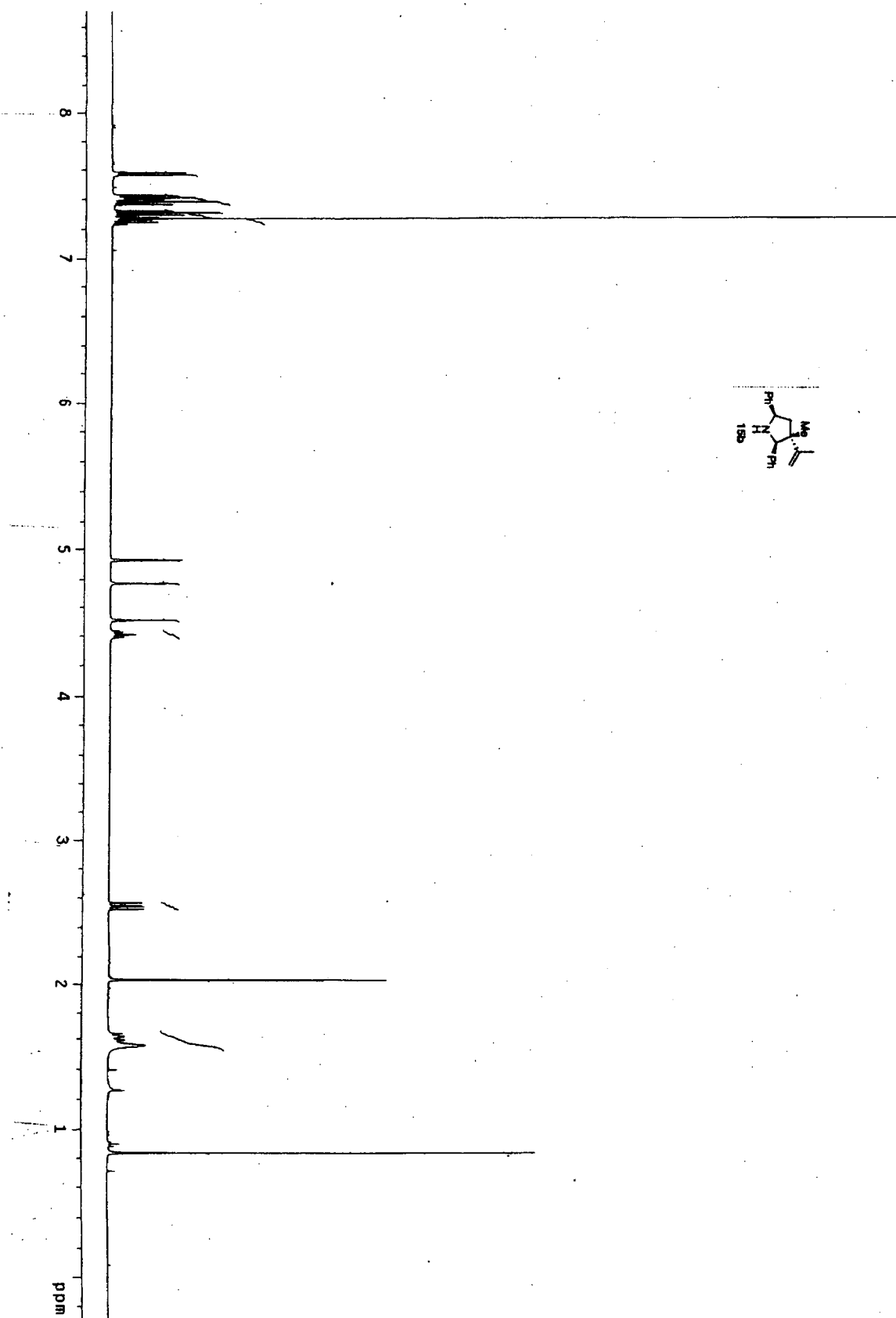
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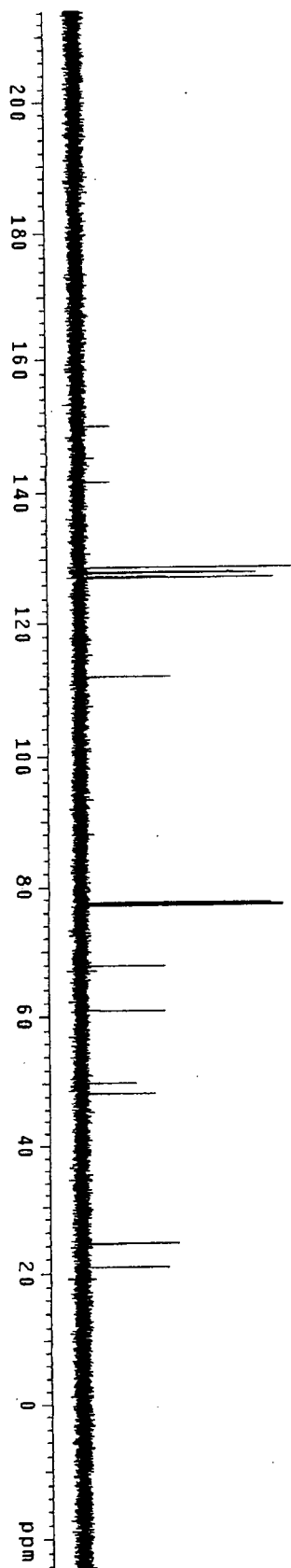
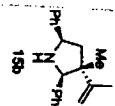


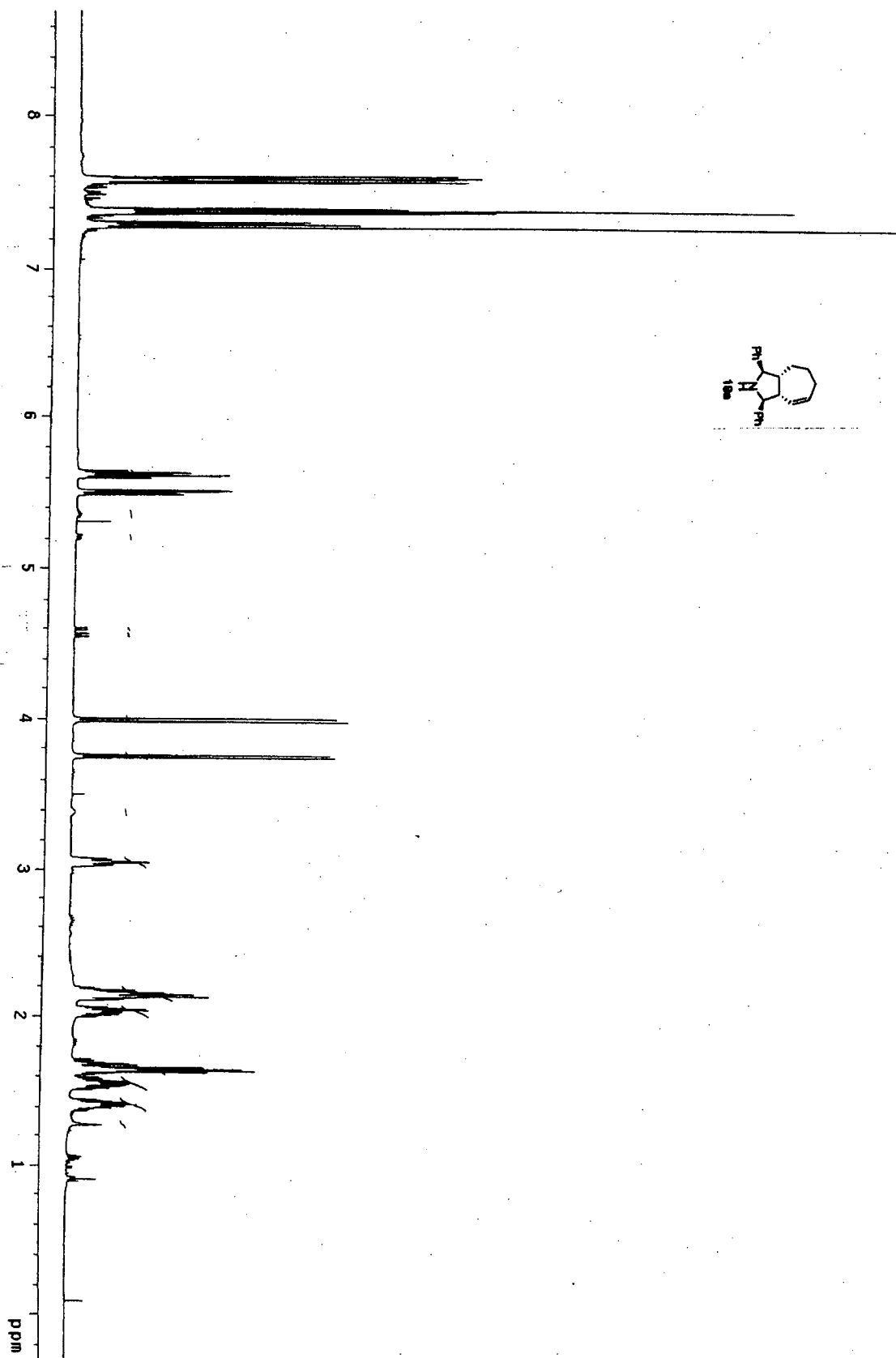


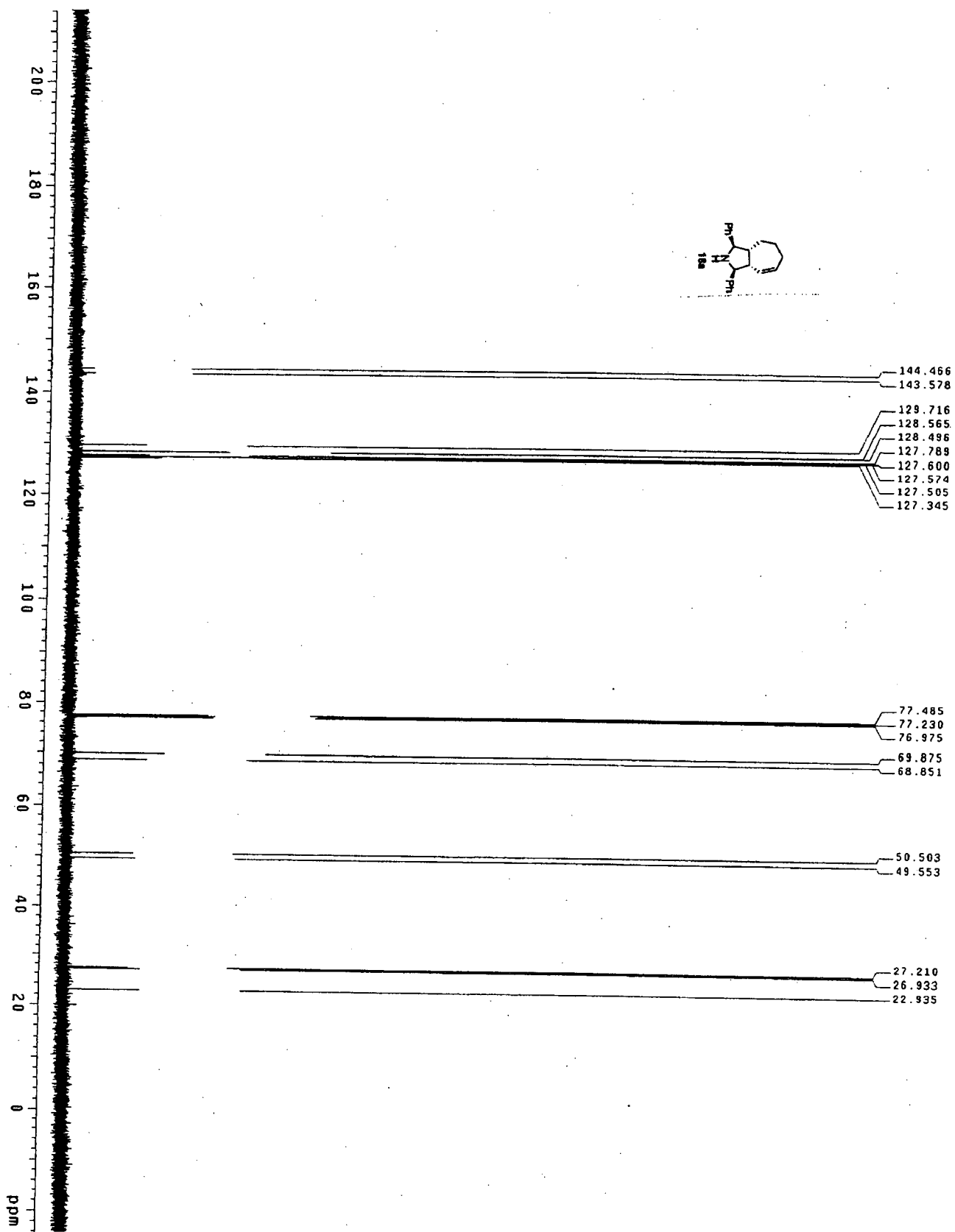


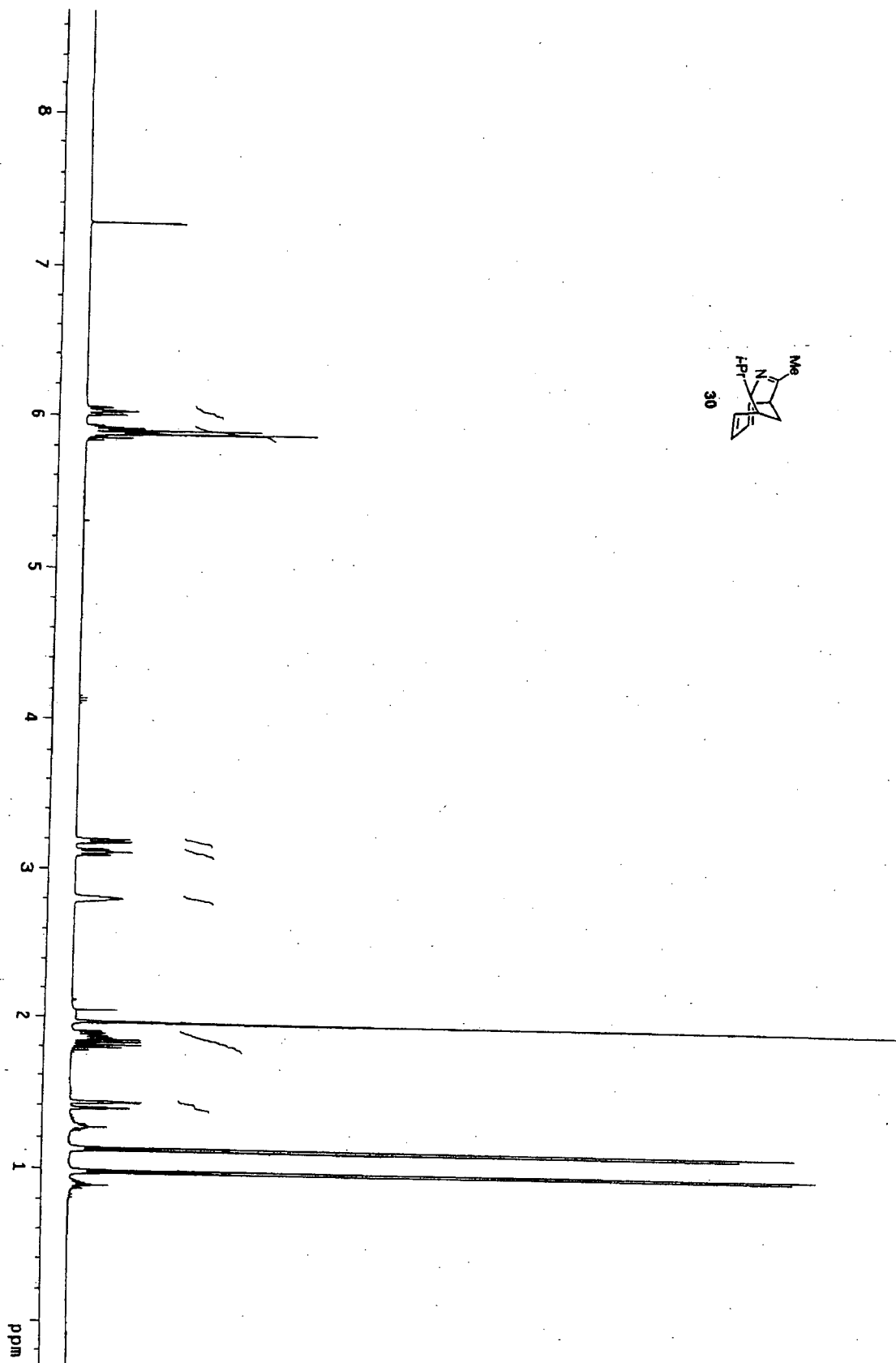
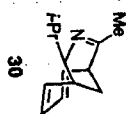












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