

Trifluoromethide as a strong base: $[\text{CF}_3^-]$ mediates dichloromethylation of nitrones by proton abstraction from the solvent.

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General considerations.

Nitrone **1** was purchased from commercial sources. The other nitrones were prepared, according to previously reported procedures.⁵ Dichloromethane was purified by simple distillation before use. All reactions were performed under argon. Silica gel F₂₅₄ (0.2 mm) was used for TLC plates, detection being carried out by spraying with an alcoholic solution of phosphomolybdic acid, followed by heating. Flash column chromatography was performed over silica gel M 9385 (40-63 μ m) Kieselgel 60. NMR spectra were recorded at 250 MHz for ¹H, 62.5 MHz for ¹³C or 500 MHz for ¹H, 125 MHz for ¹³C. Chemical shifts are expressed in parts per million (ppm) and were calibrated to the residual solvent peak. Coupling constants are in Hz and splitting pattern abbreviations are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Optical rotations were determined at 20 °C in the specified solvents. High Resolution Mass Spectra (HRMS) were performed on Q-TOF (ESI).

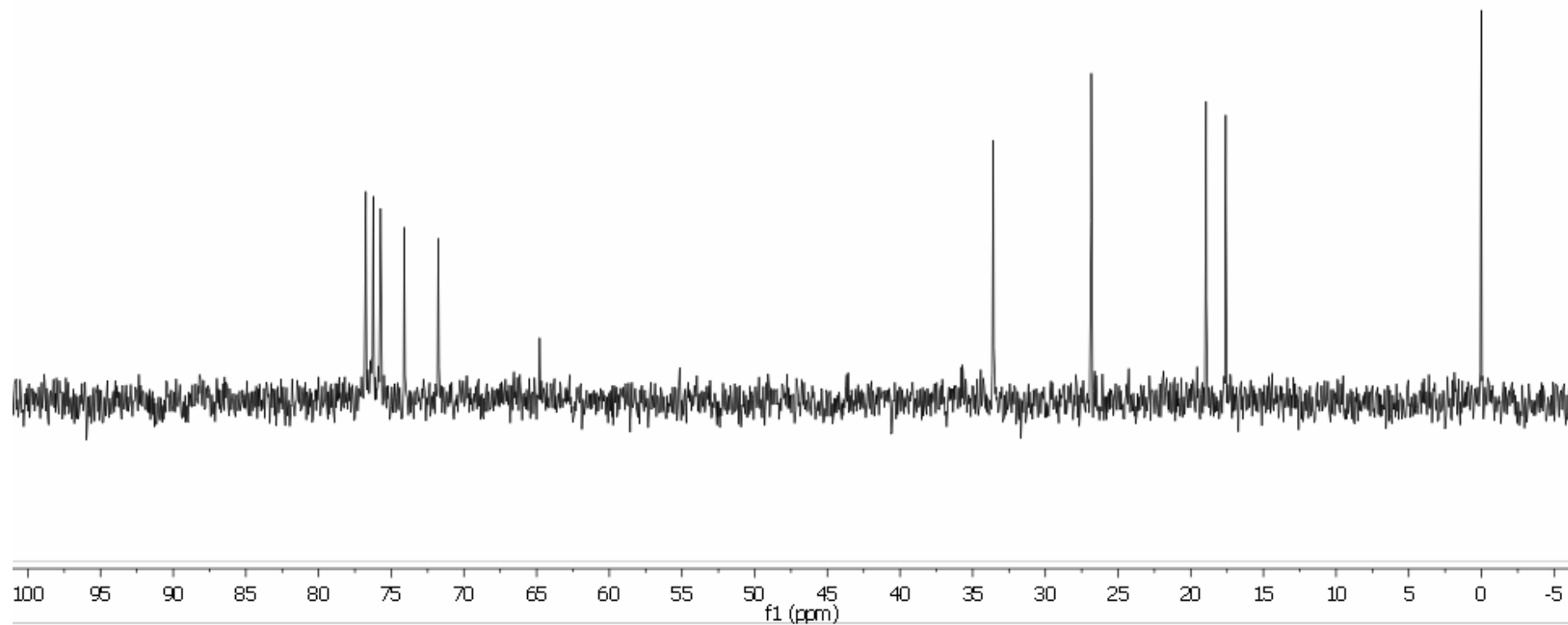
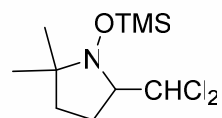
⁵ (a) Evans, D. A.; Song, H.-J.; Fandrick, K. R. *Org. Lett.* **2006**, *8*, 3351; (b) Murahashi, S.-H.; Mitsui, H.; Shiota, T.; Tsuda, T.; Watanabe, S. *J. Org. Chem.* **1990**, *55*, 1736; (c) Colacino, E.; Nun, P.; Colacino, F. M.; Martinez, J.; Lamaty, F. *Tetrahedron* **2008**, *64*, 5569.

CC1(C)CC(C1)N(OC)CCl

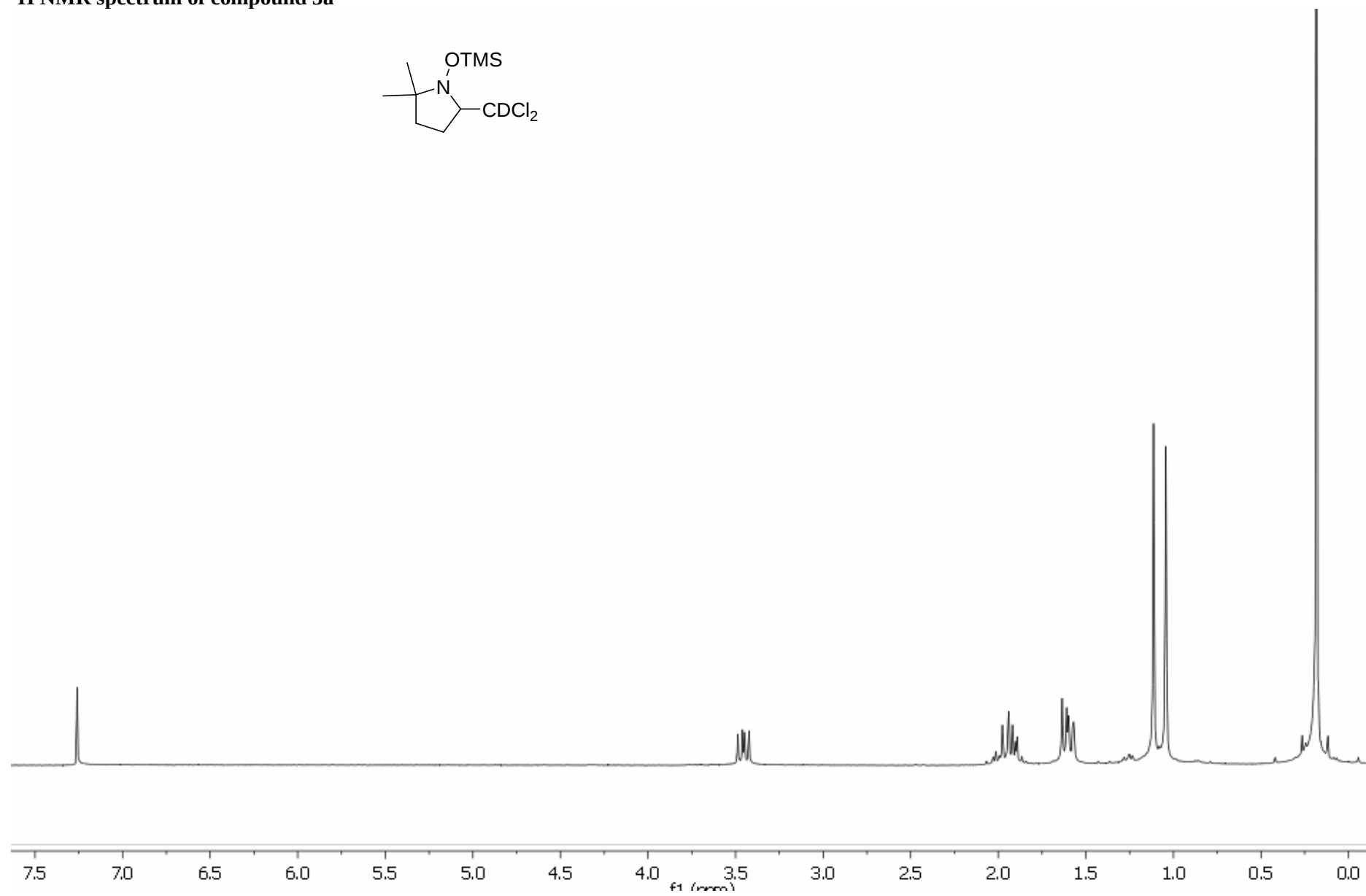
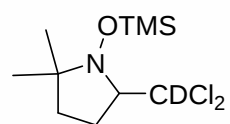
1H NMR spectrum (400 MHz, CDCl₃) of 1-(chloromethyl)-2-(trimethylsilyloxy)-2-methylpyrrolidine. The spectrum shows several peaks corresponding to the structure:

- ~7.2 ppm: Solvent peak (H₂O).
- ~5.8 ppm: CHCl₂ solvent peak.
- 3.4-3.6 ppm: Multiplet (CH₂Cl and N-CH₂).
- 1.8-2.2 ppm: Multiplet (CH₂ groups).
- ~1.5 ppm: Multiplet (CH₂ groups).
- ~1.1 and ~1.0 ppm: Two very tall sharp peaks (OTMS methyl groups).
- ~0.2 ppm: Small peak (N-CH₂).

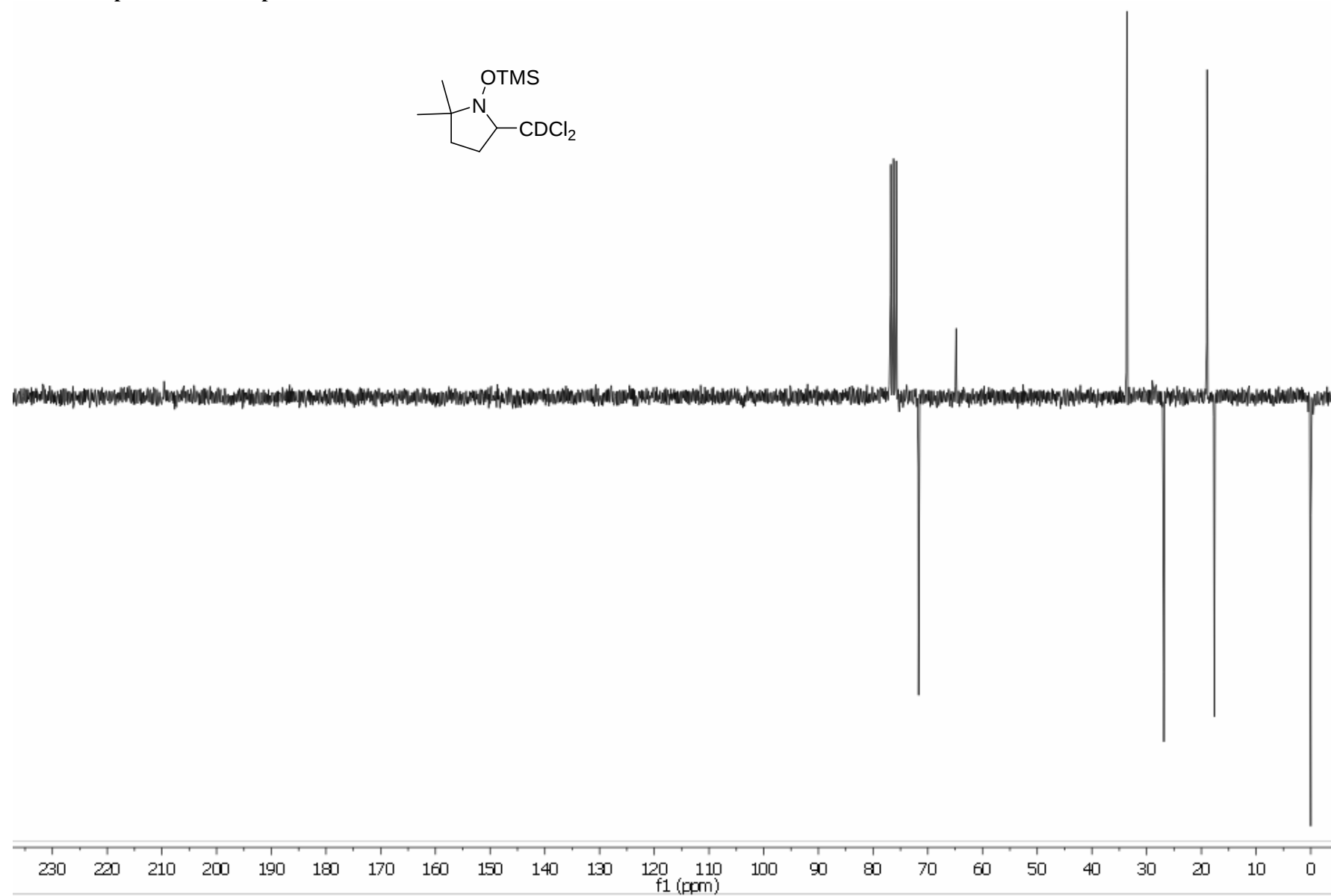
¹³C NMR spectrum of compound 2a



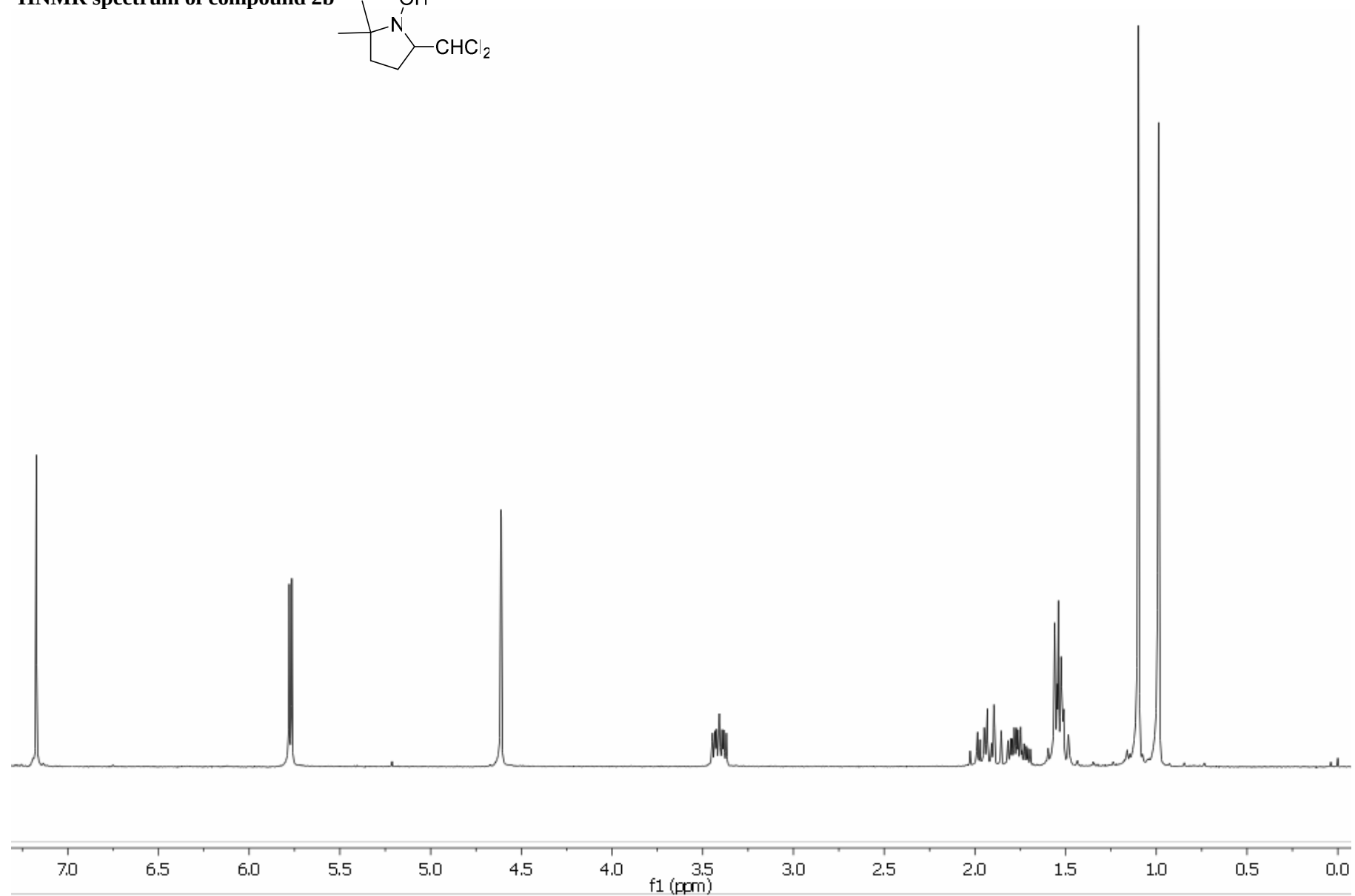
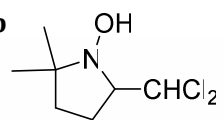
¹H NMR spectrum of compound 3a



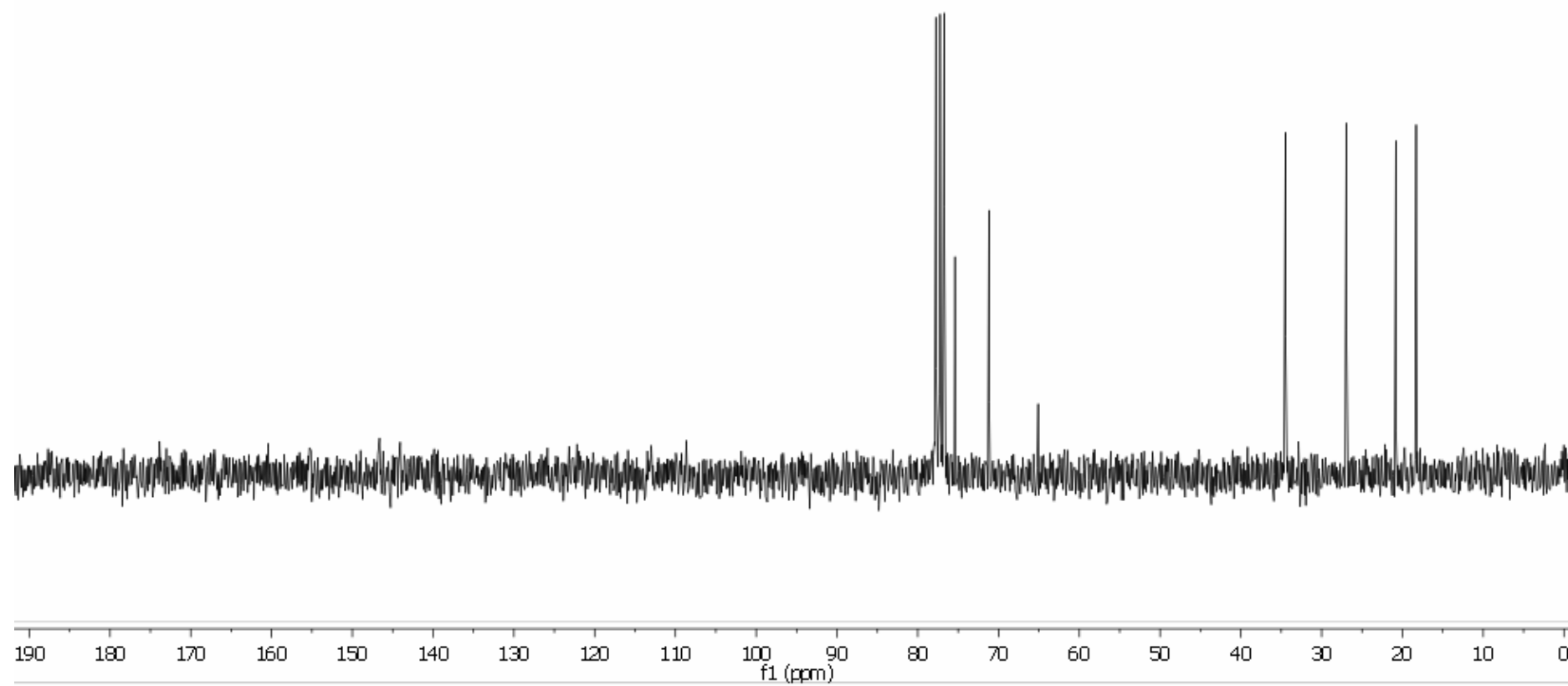
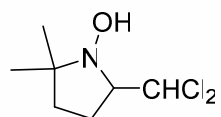
¹³C NMR spectrum of compound 3a



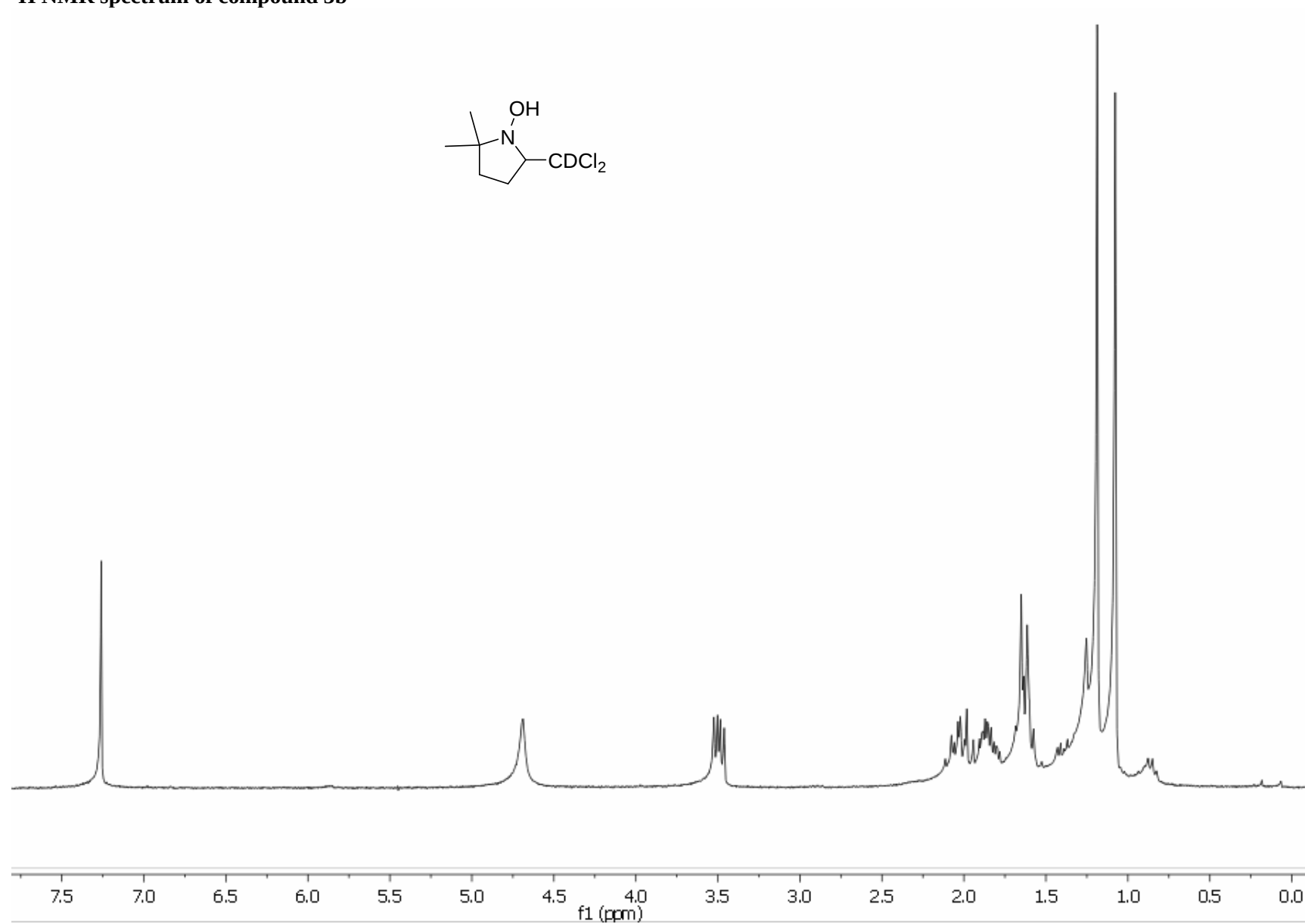
¹H NMR spectrum of compound 2b



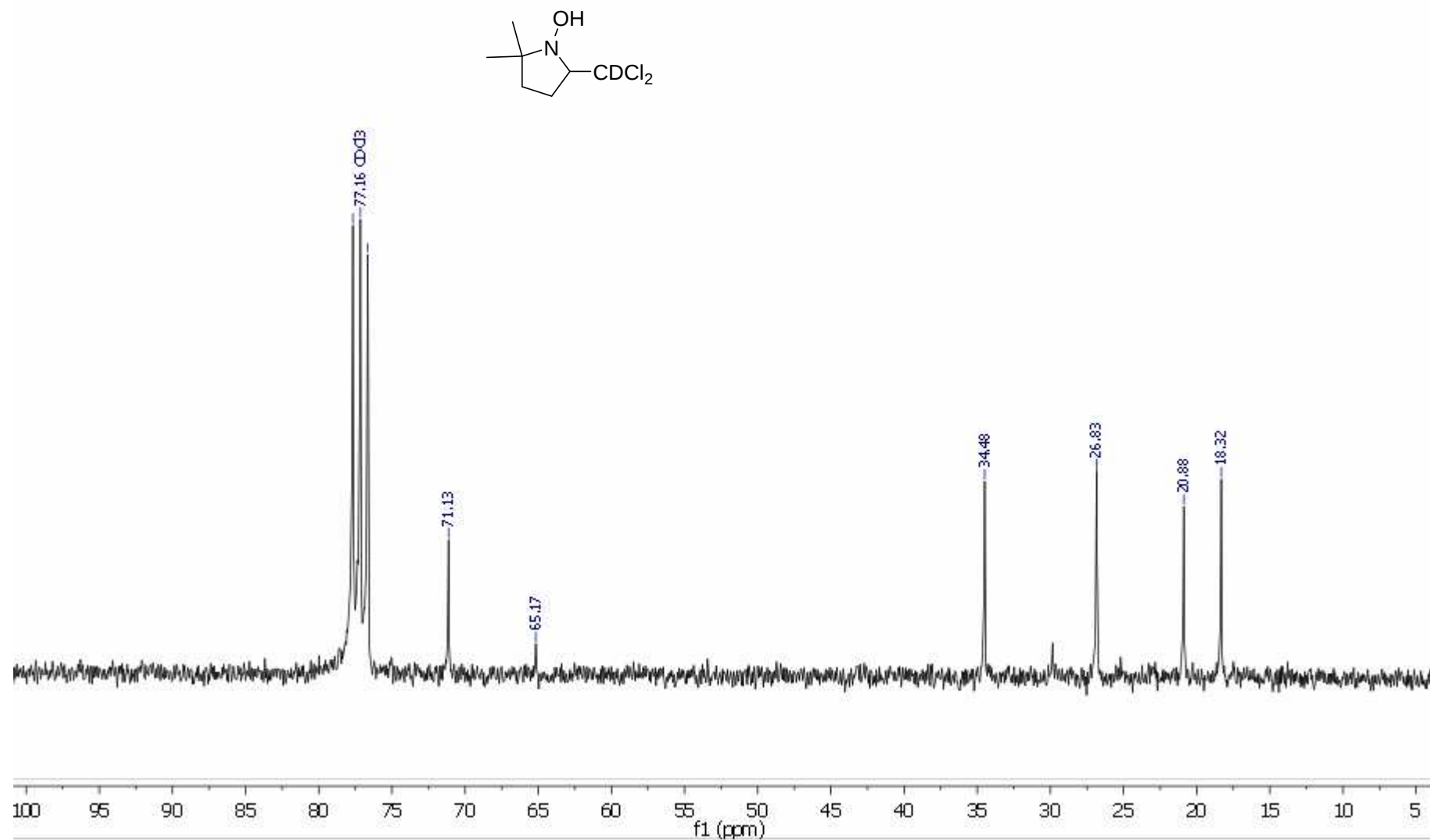
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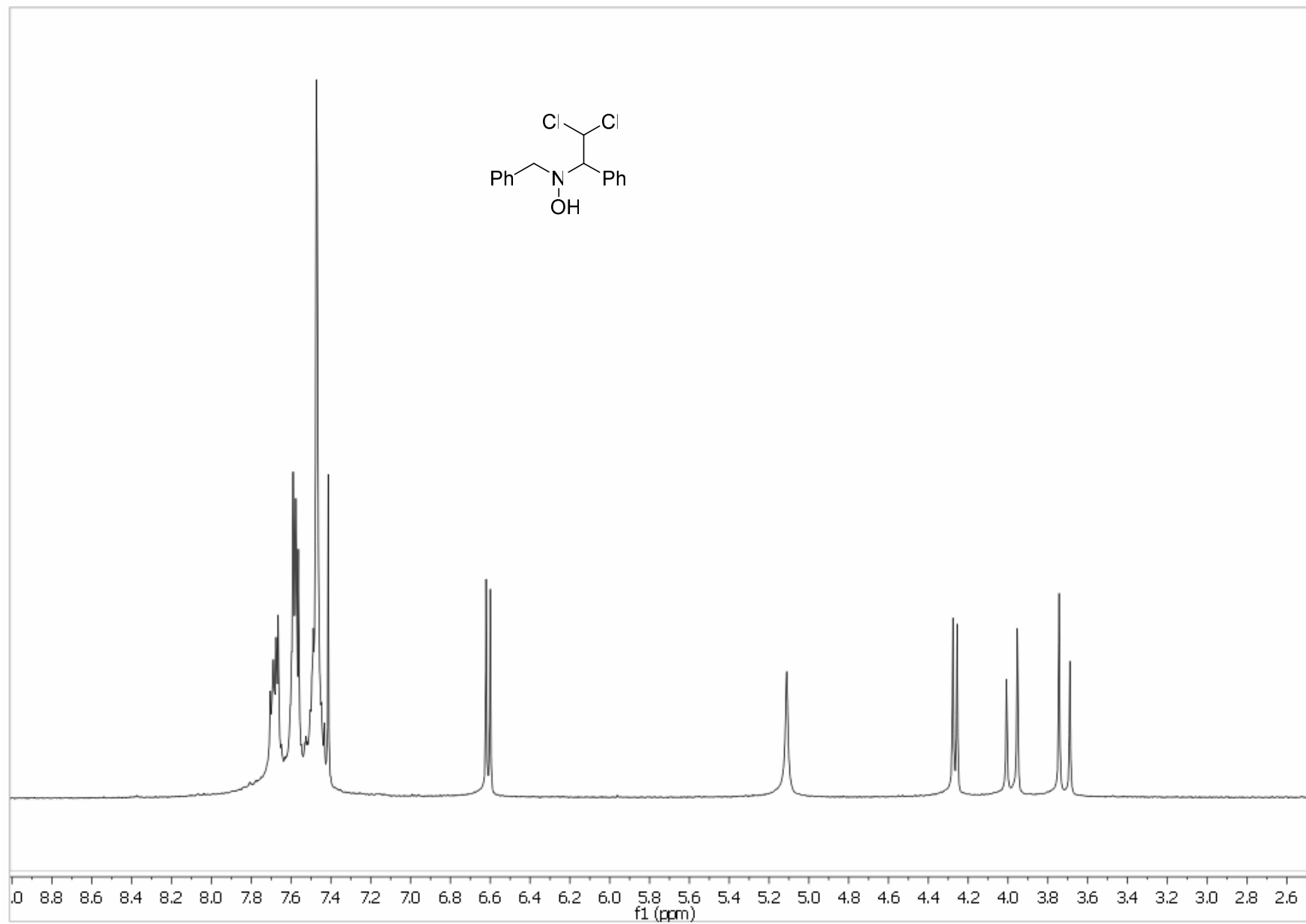
¹H NMR spectrum of compound 3b



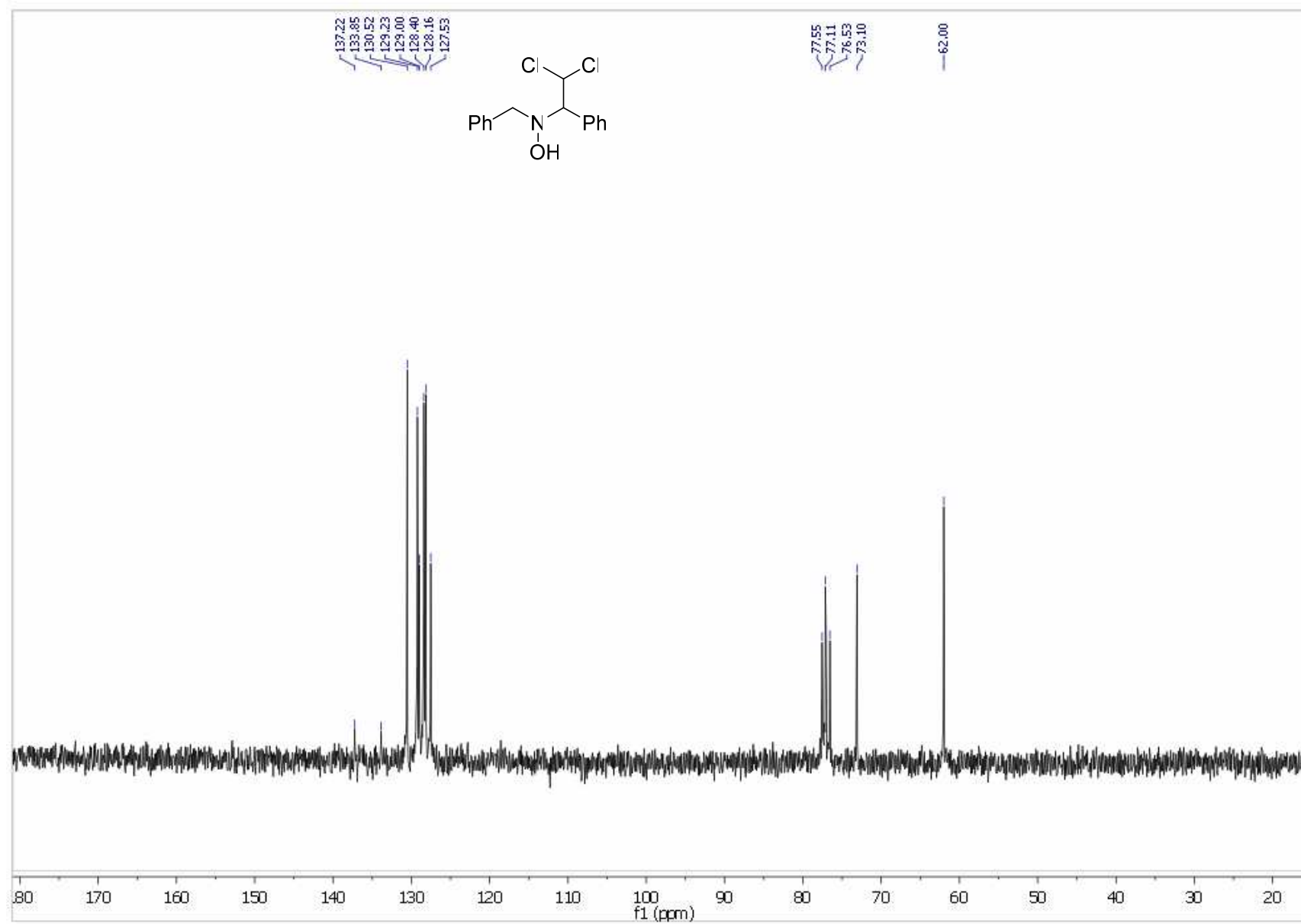
¹³C NMR spectrum of compound 3b



¹H NMR spectrum of compound 4

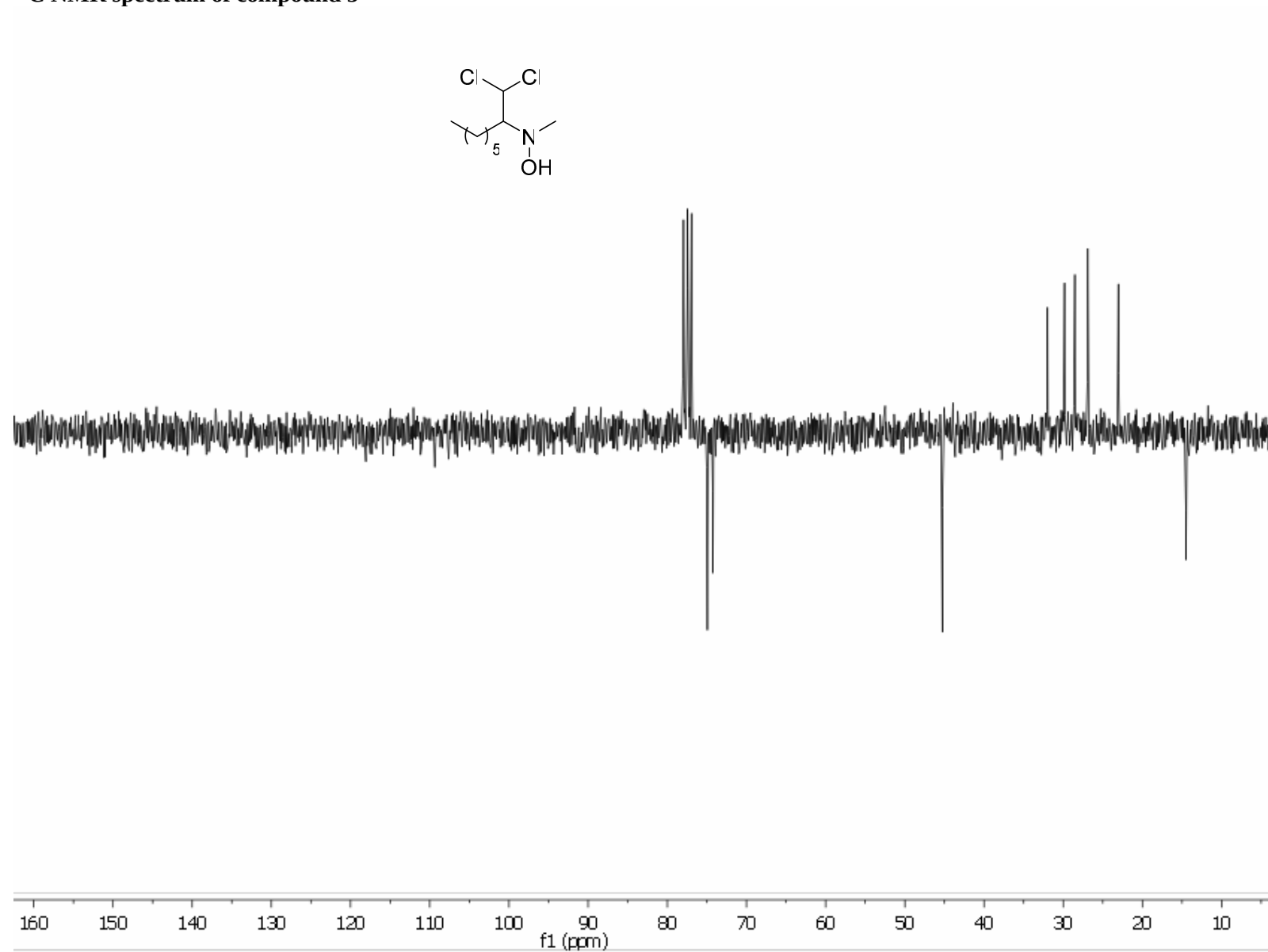


¹³C NMR spectrum of compound 4

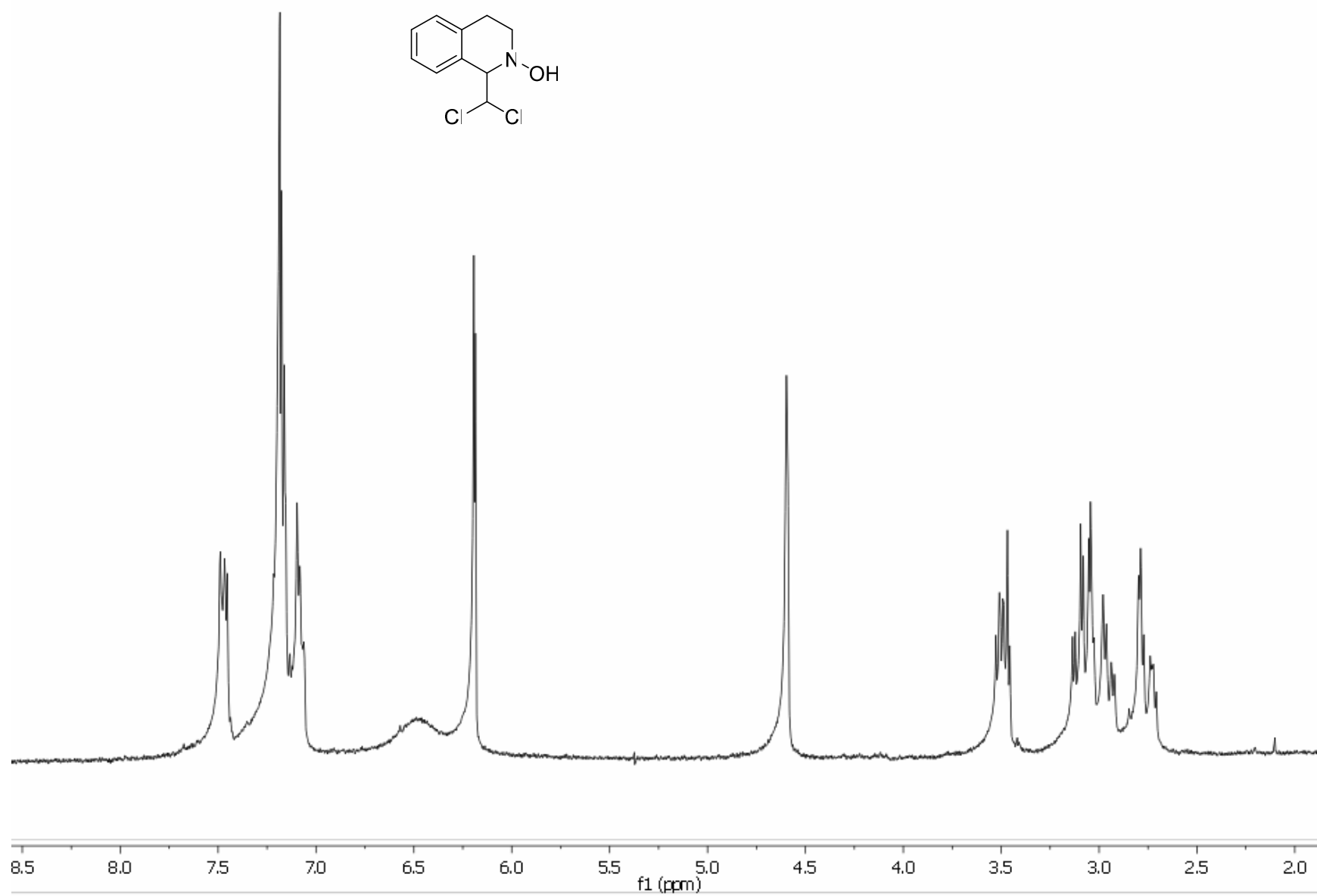


[illegible]

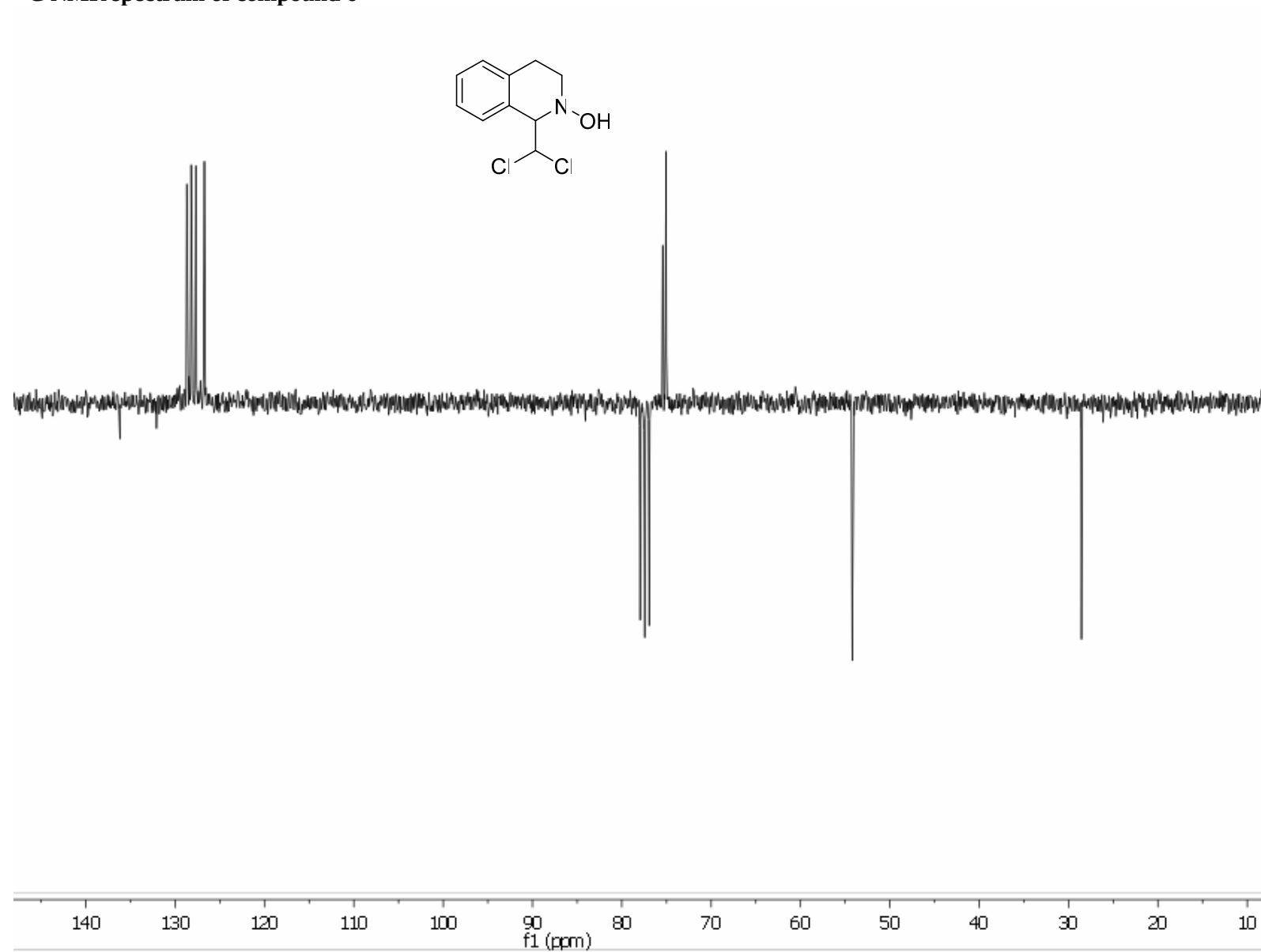
¹³C NMR spectrum of compound 5



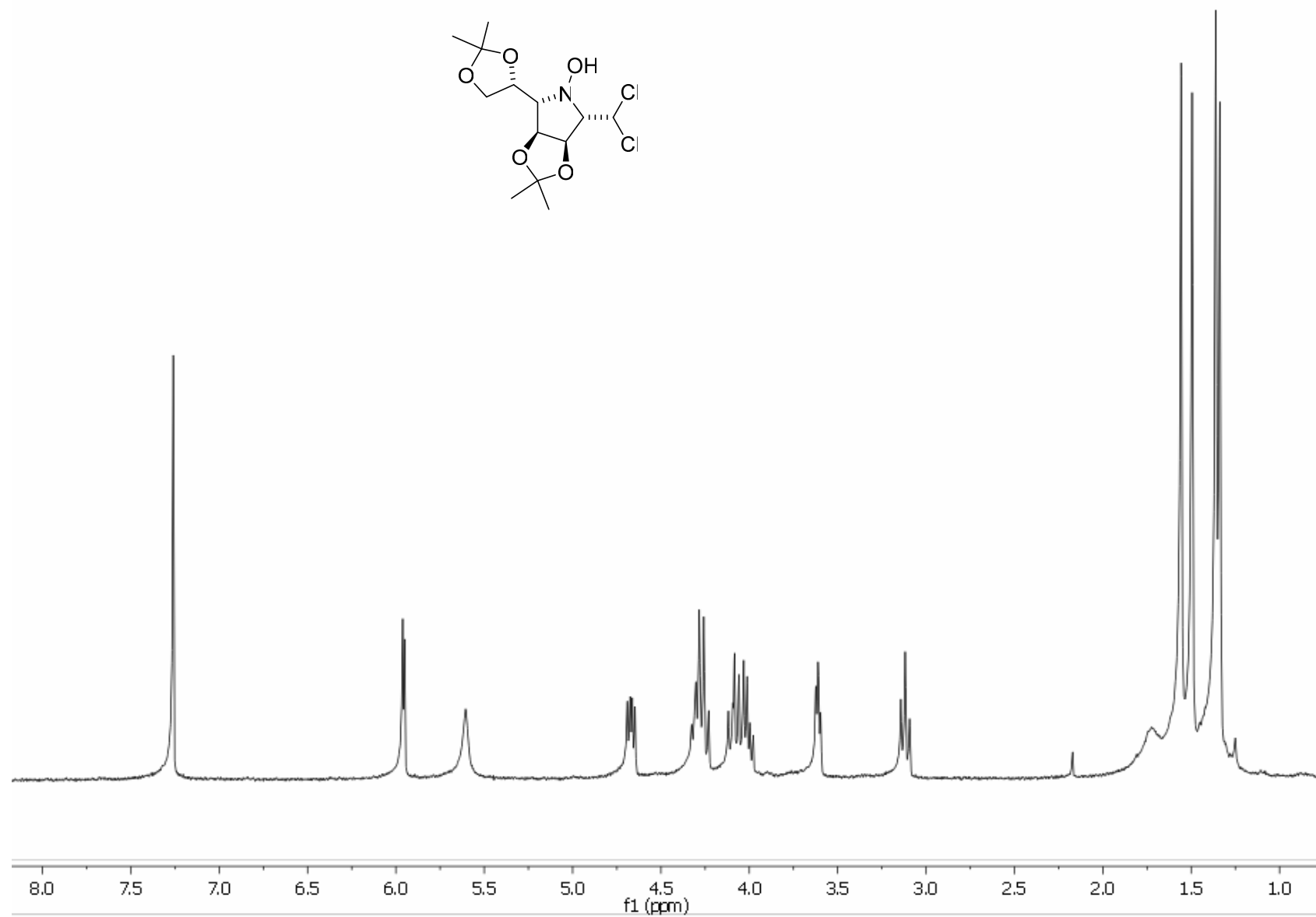
¹H NMR spectrum of compound 6



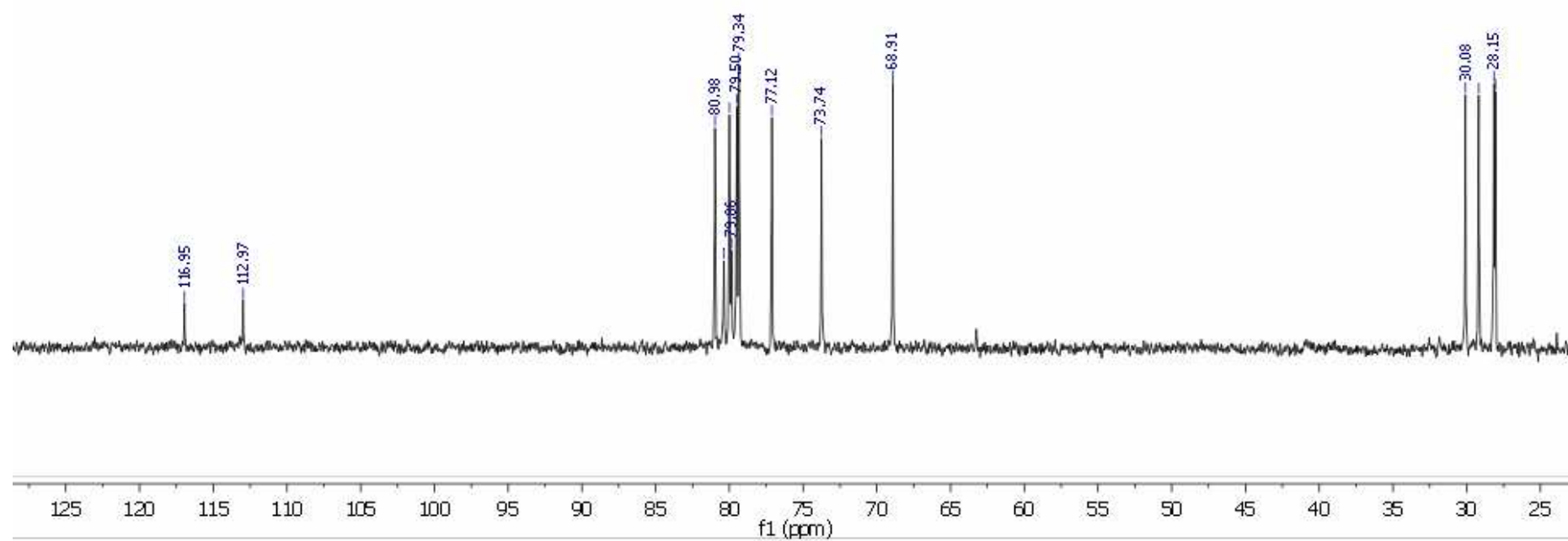
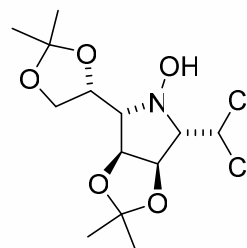
¹³C NMR spectrum of compound 6



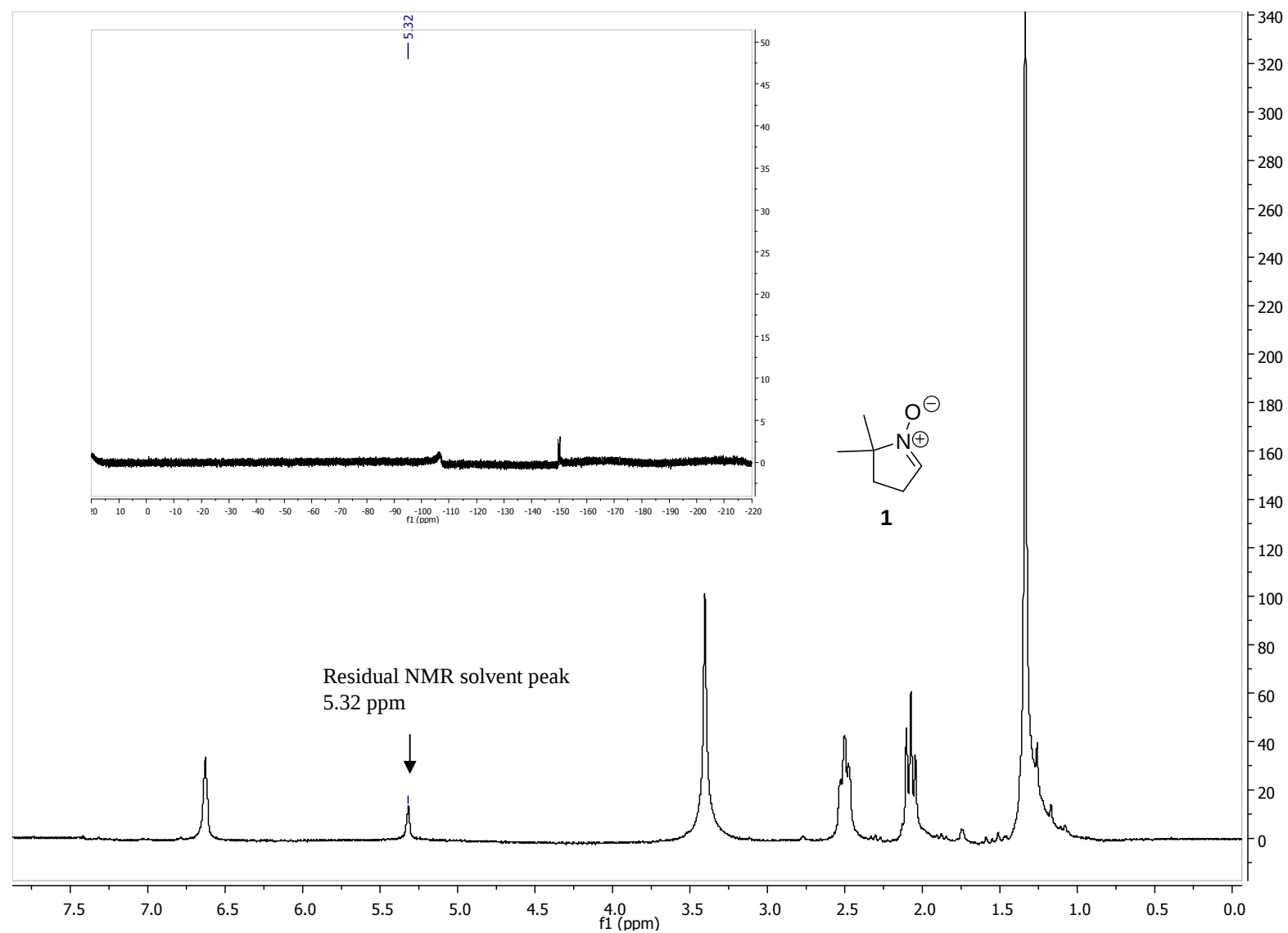
¹H NMR spectrum of compound 7a



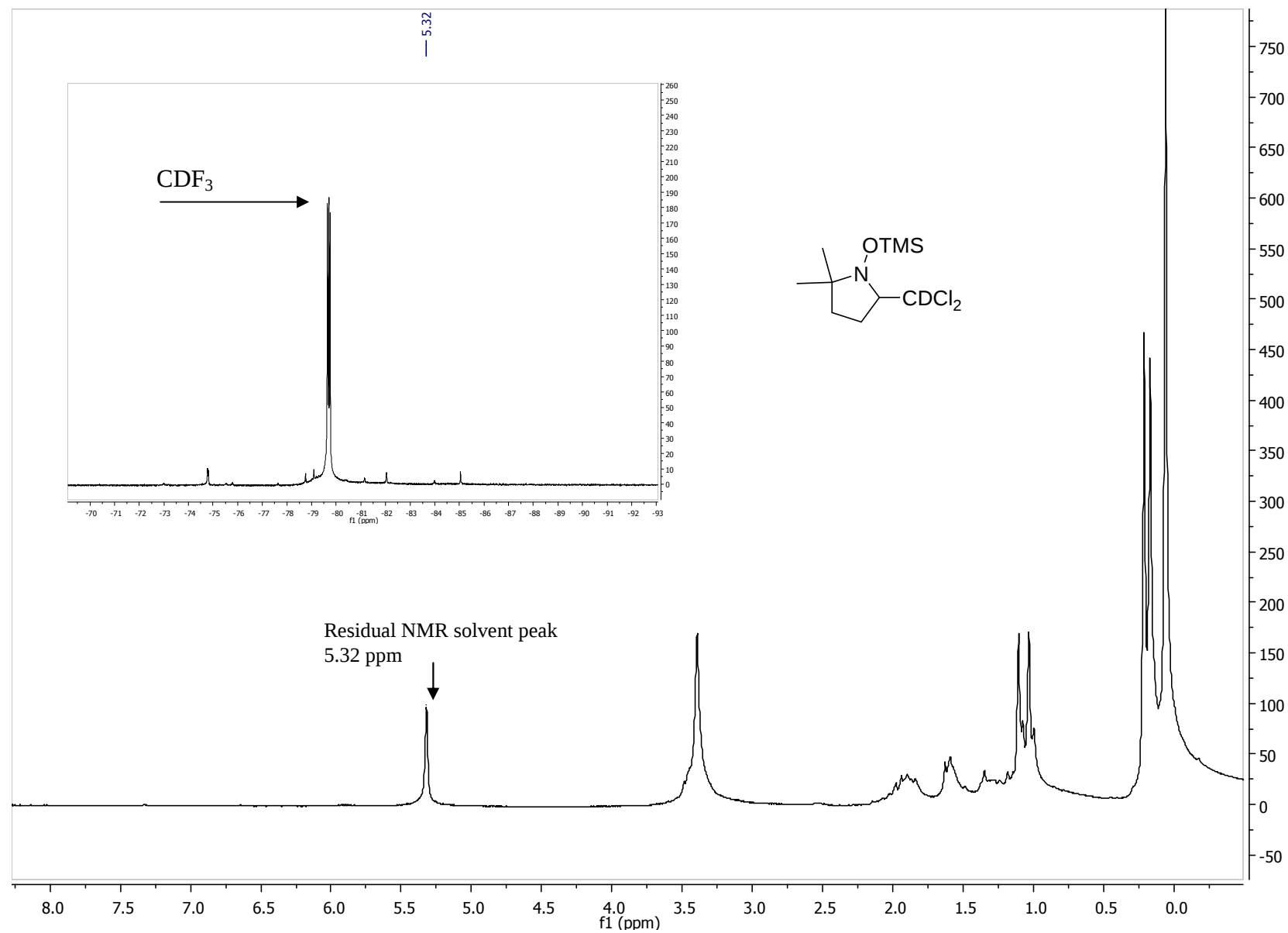
¹³C NMR spectrum of compound 7a



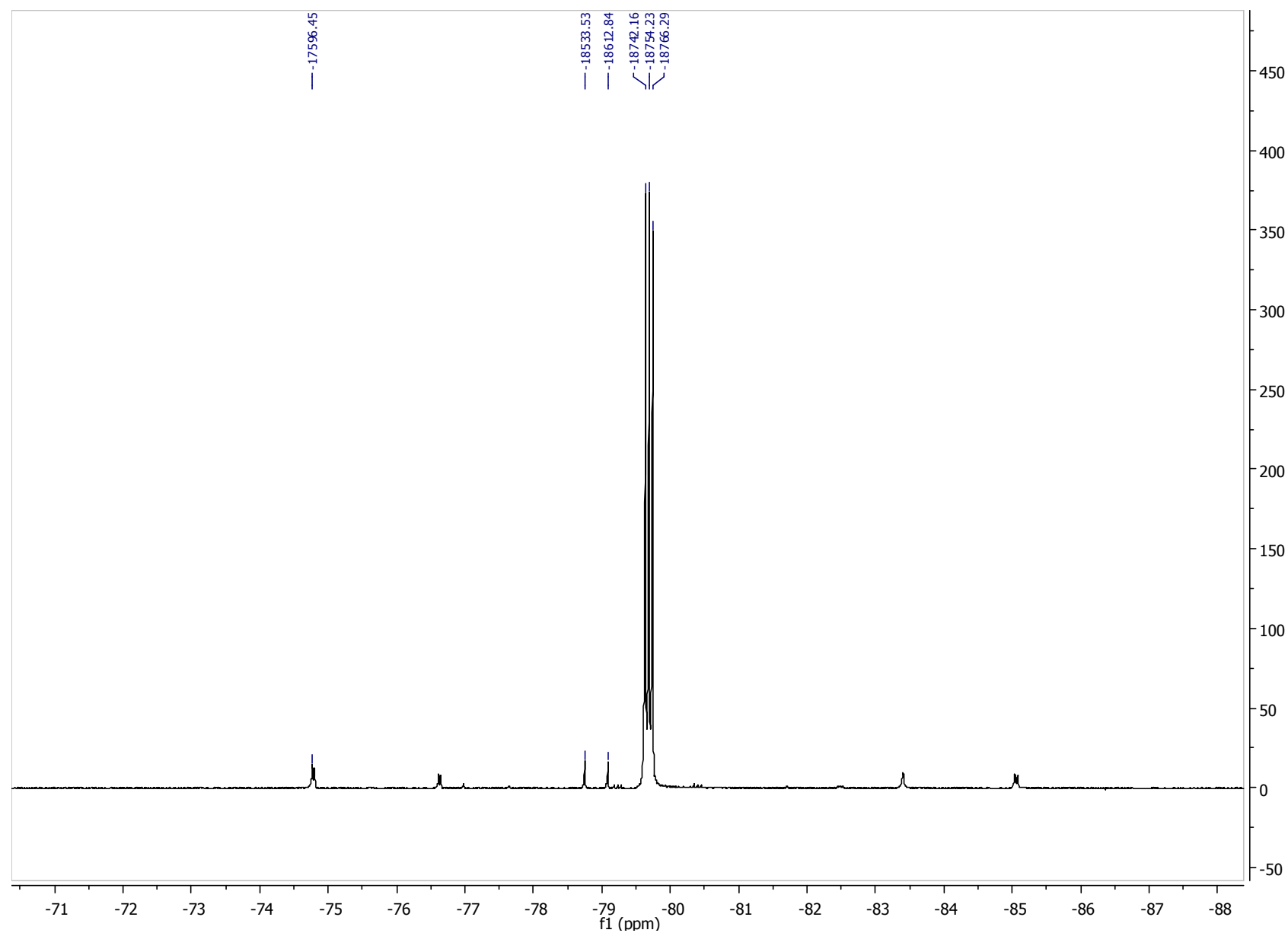
^1H NMR and ^{19}F NMR spectra of the reaction mixture (nitron + TMAF in CD_2Cl_2) before addition of $\text{CF}_3\text{-TMS}$



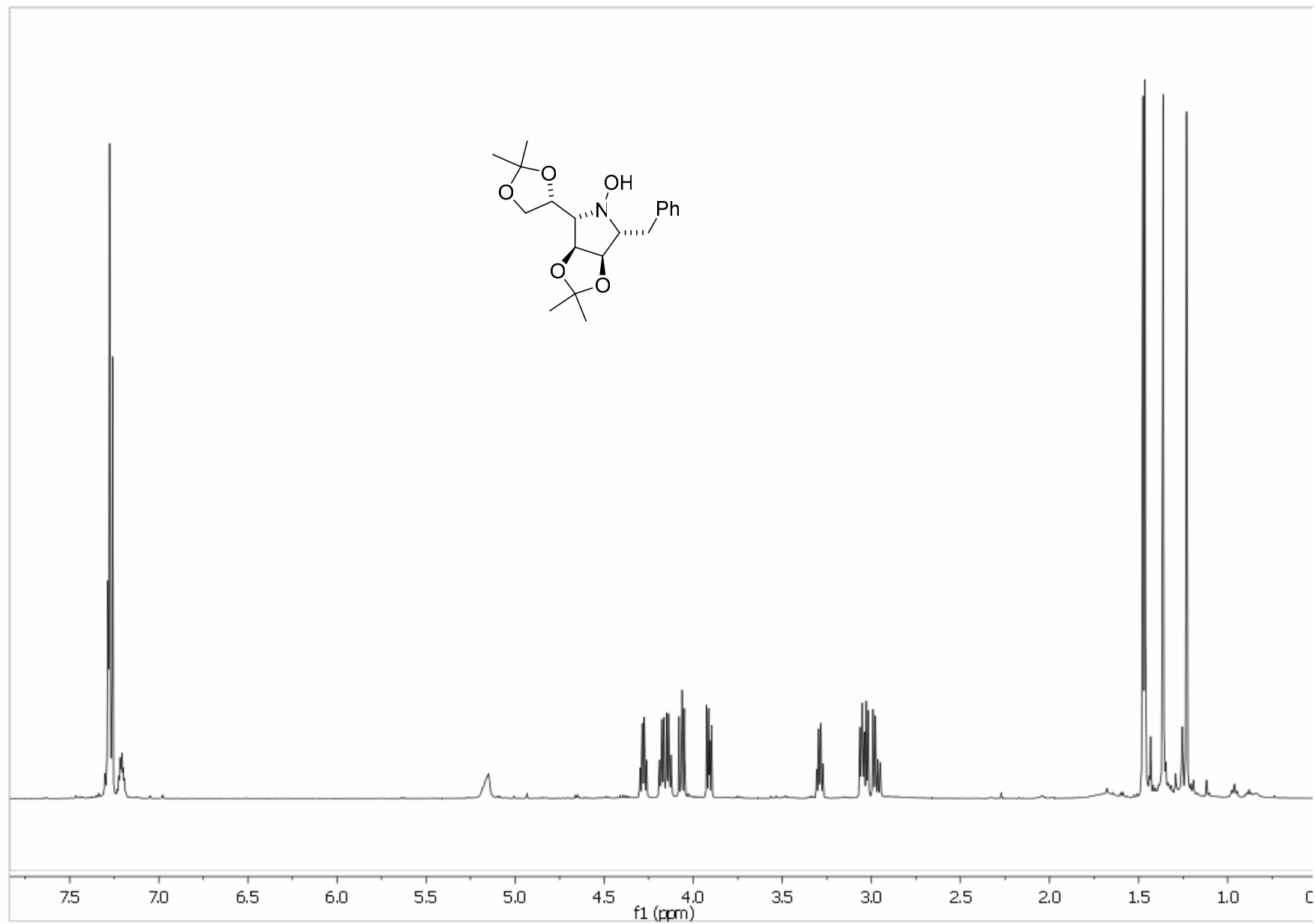
^1H NMR and ^{19}F NMR spectra of the reaction mixture 5 min after addition of $\text{CF}_3\text{-TMS}$



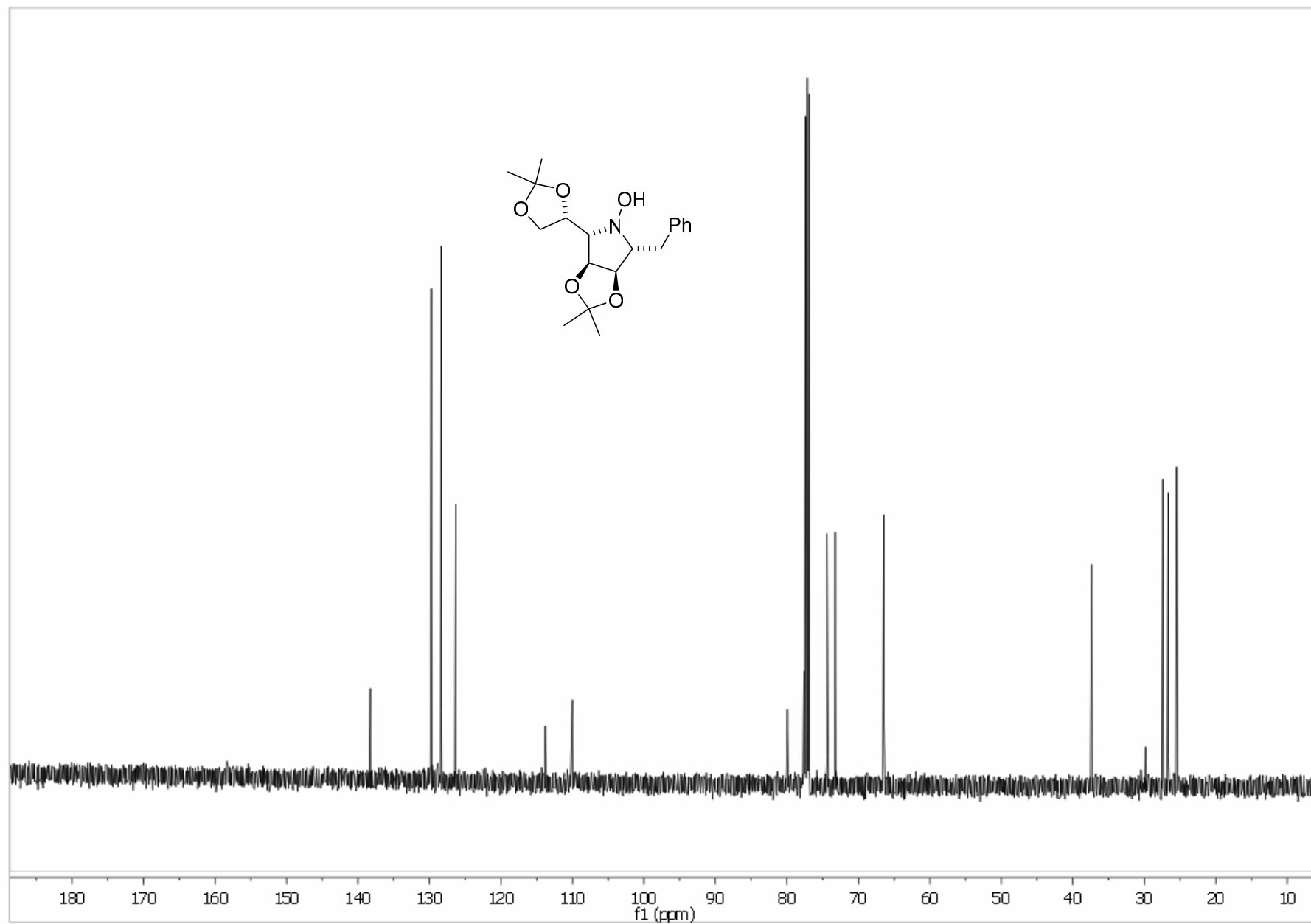
¹⁹F NMR spectra of the reaction mixture after 30 min



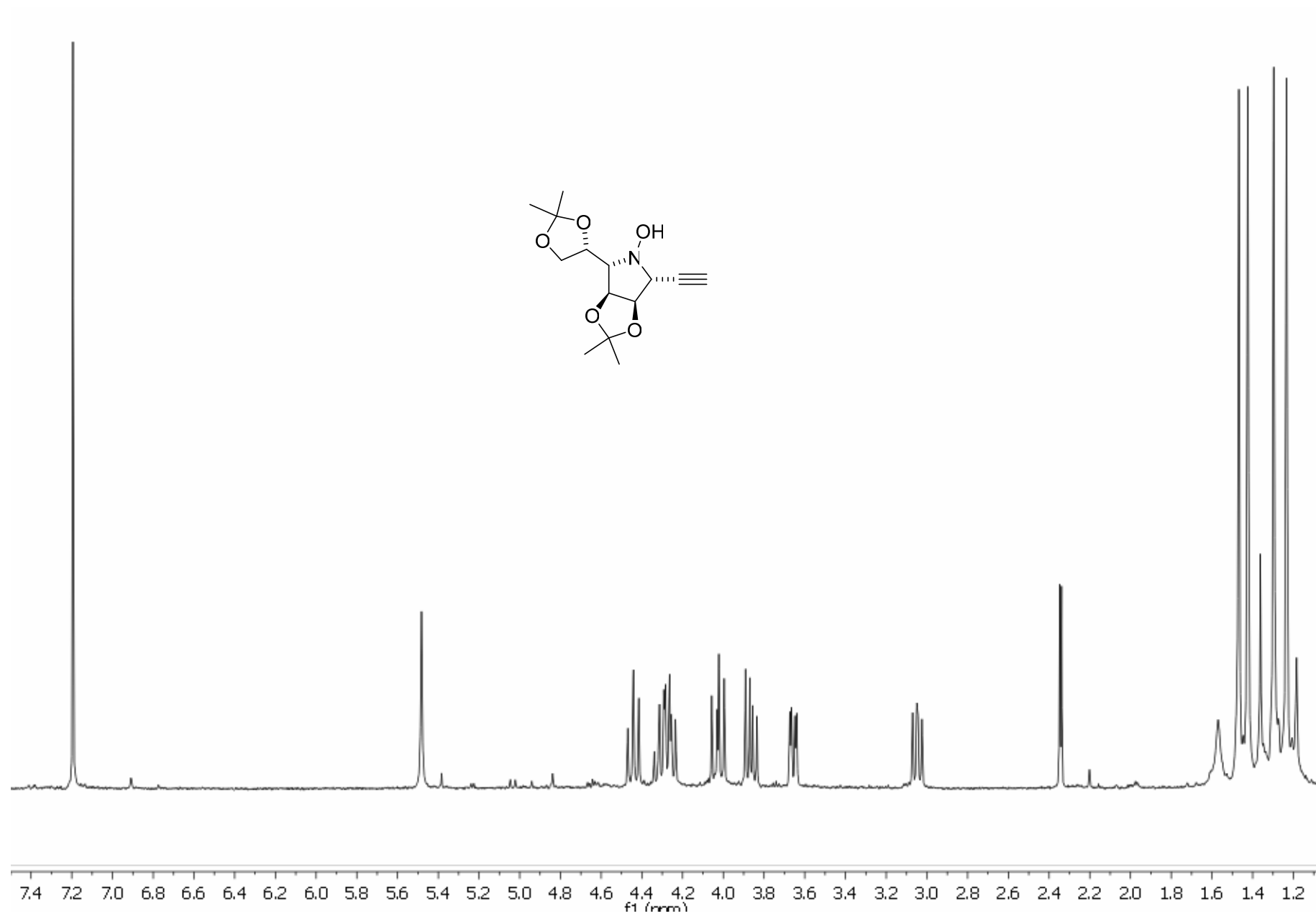
¹H NMR spectrum of compound 7b



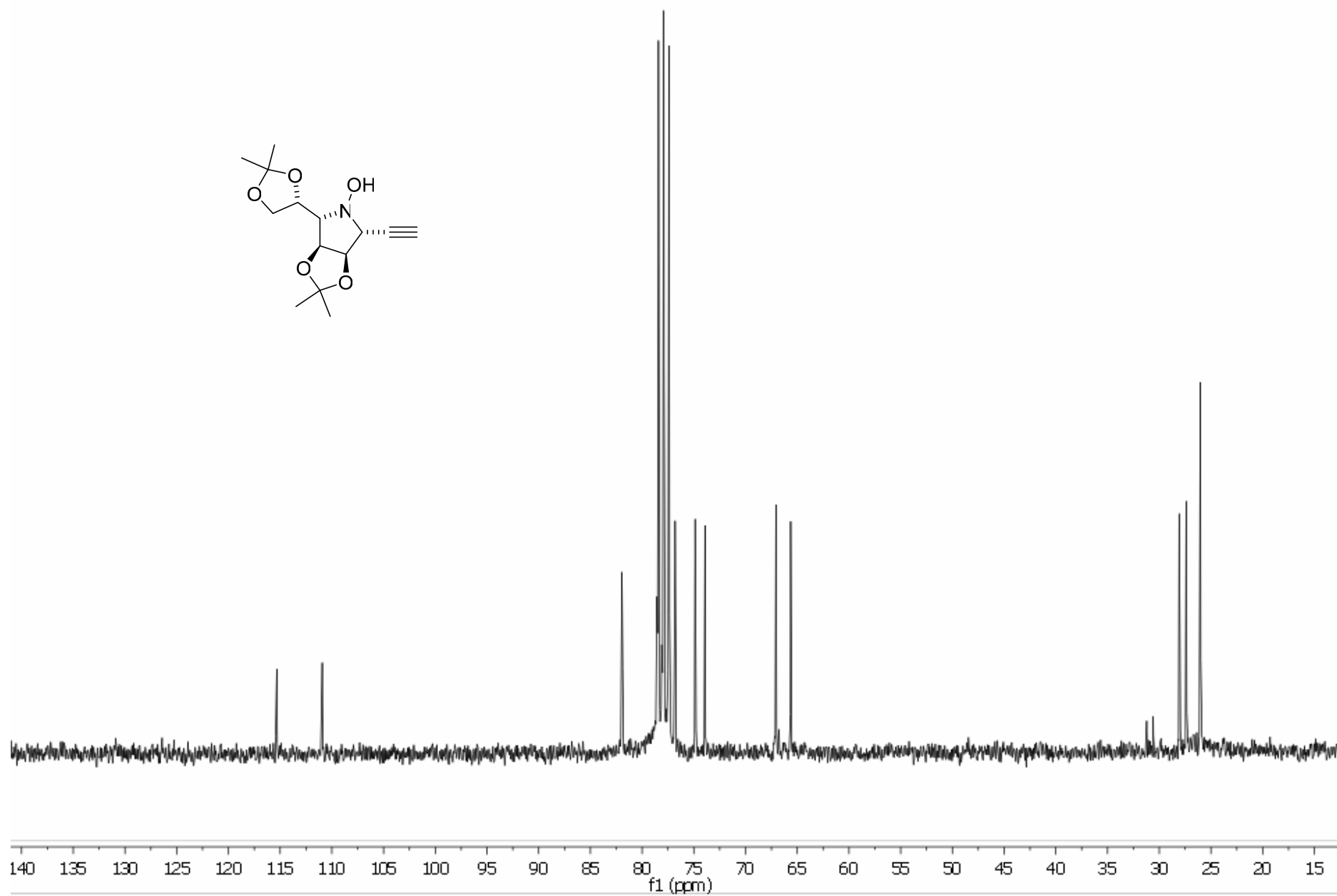
^{13}C NMR spectrum of compound 7b



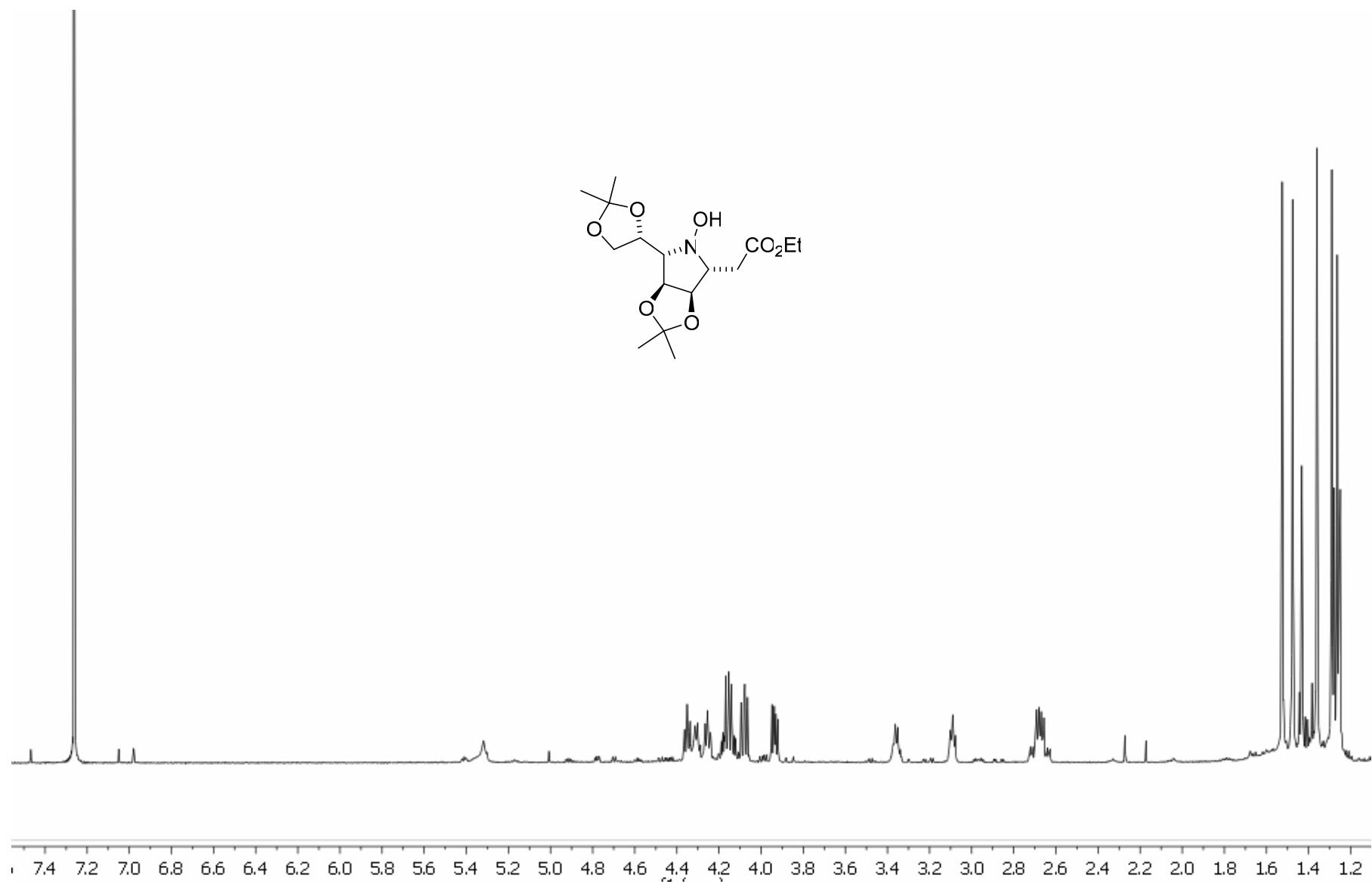
¹H NMR spectrum of compound 7c



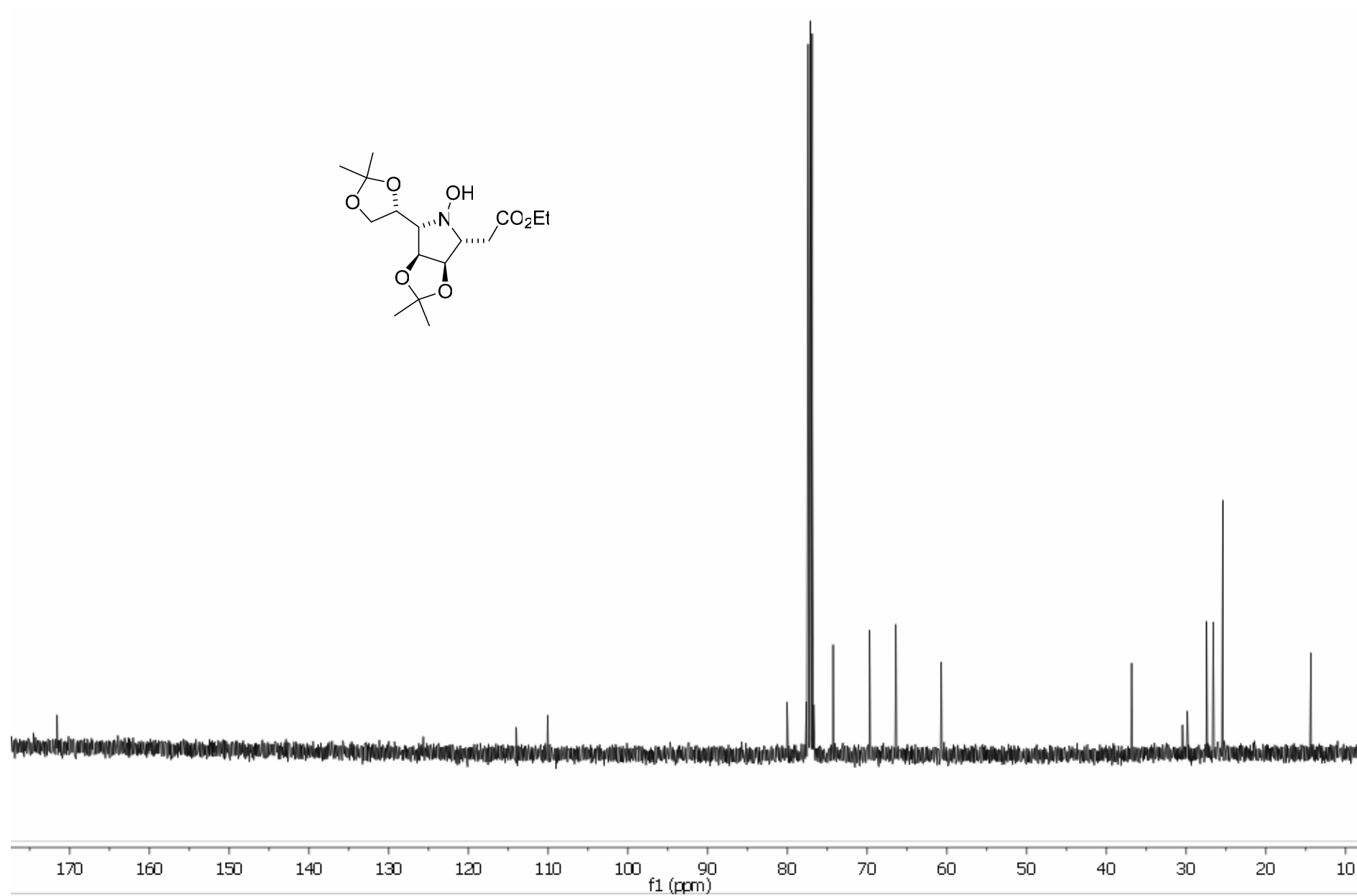
¹³C NMR spectrum of compound 7c



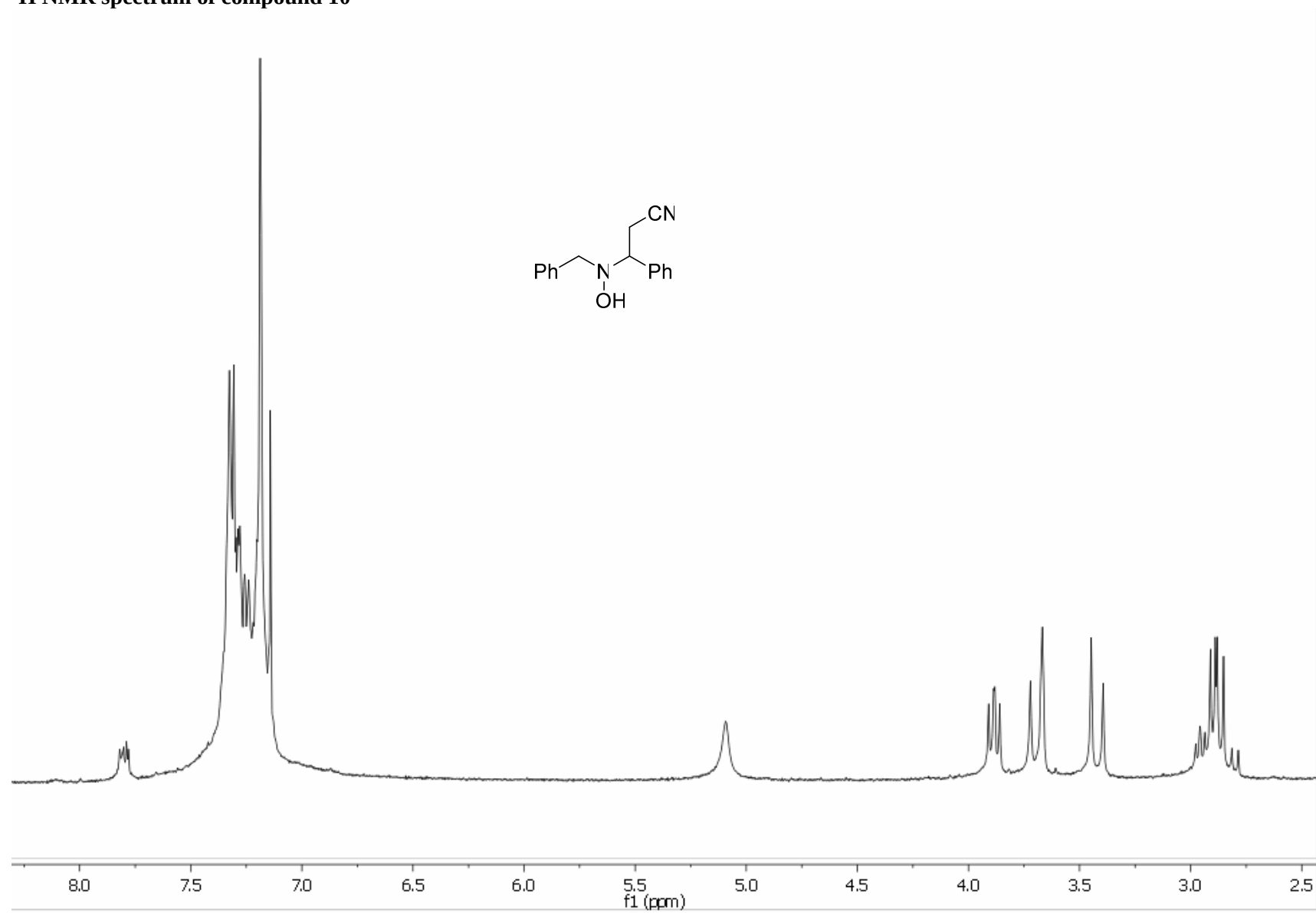
¹H NMR spectrum of compound 7d



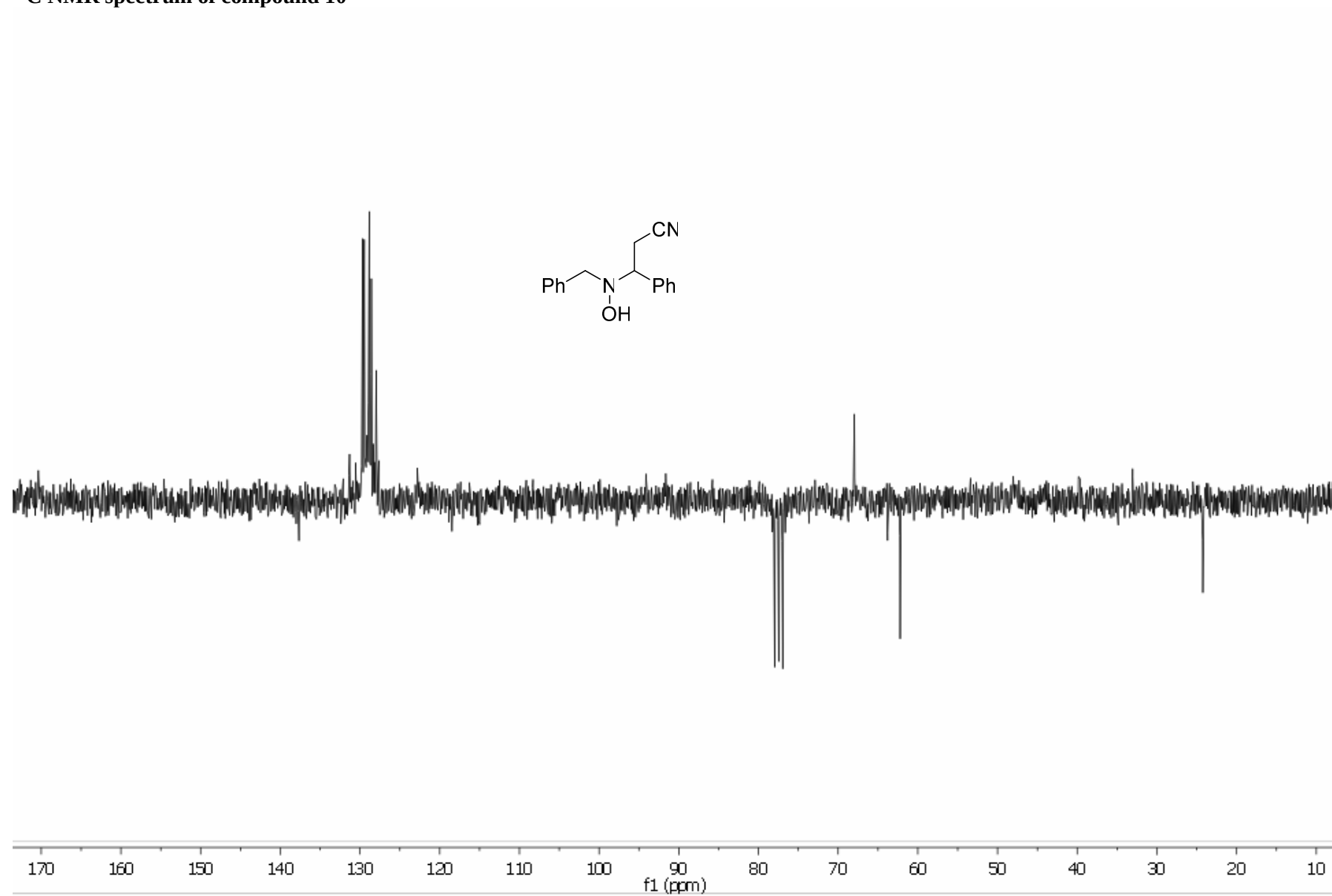
¹³C NMR spectrum of compound 7d



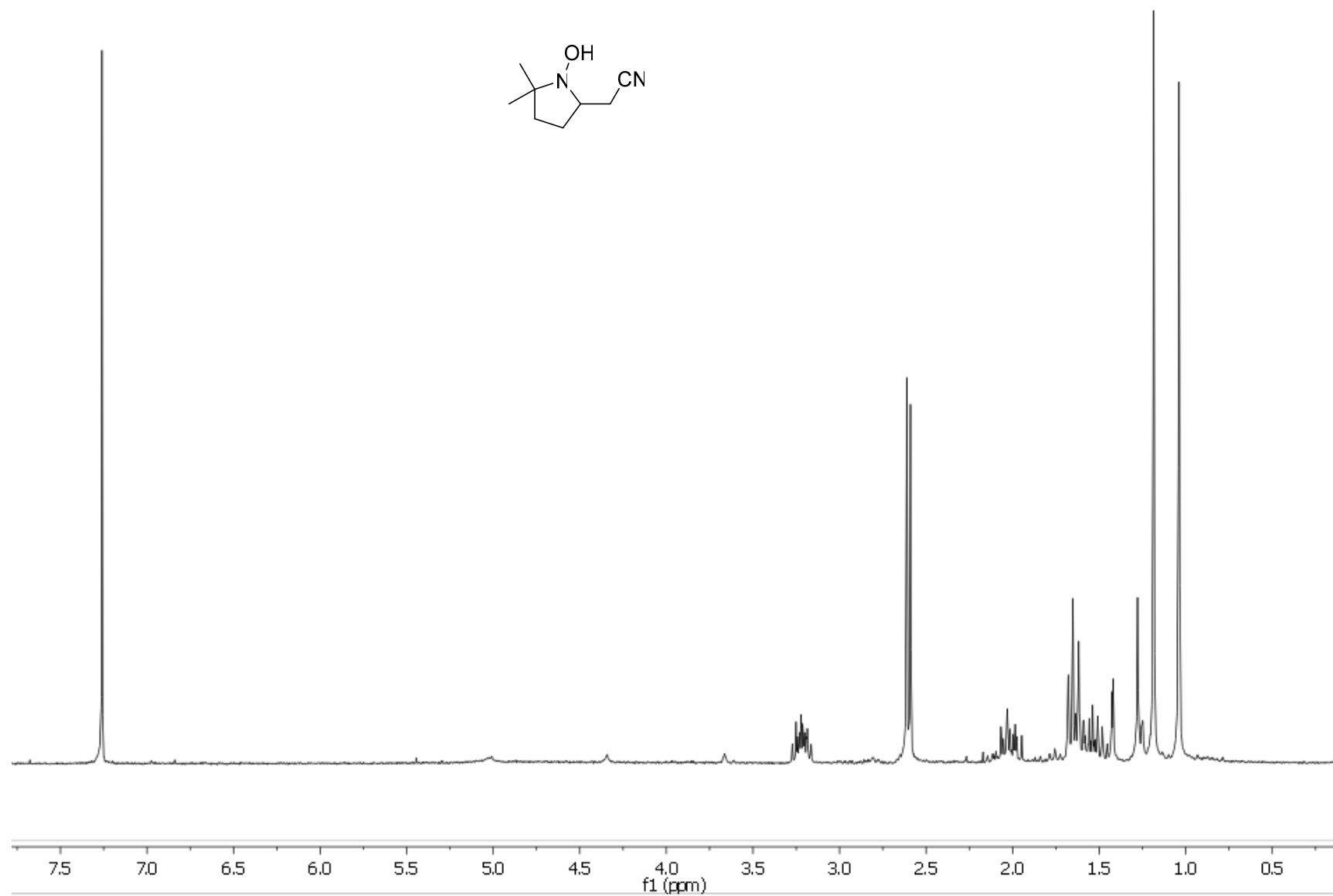
¹H NMR spectrum of compound 10



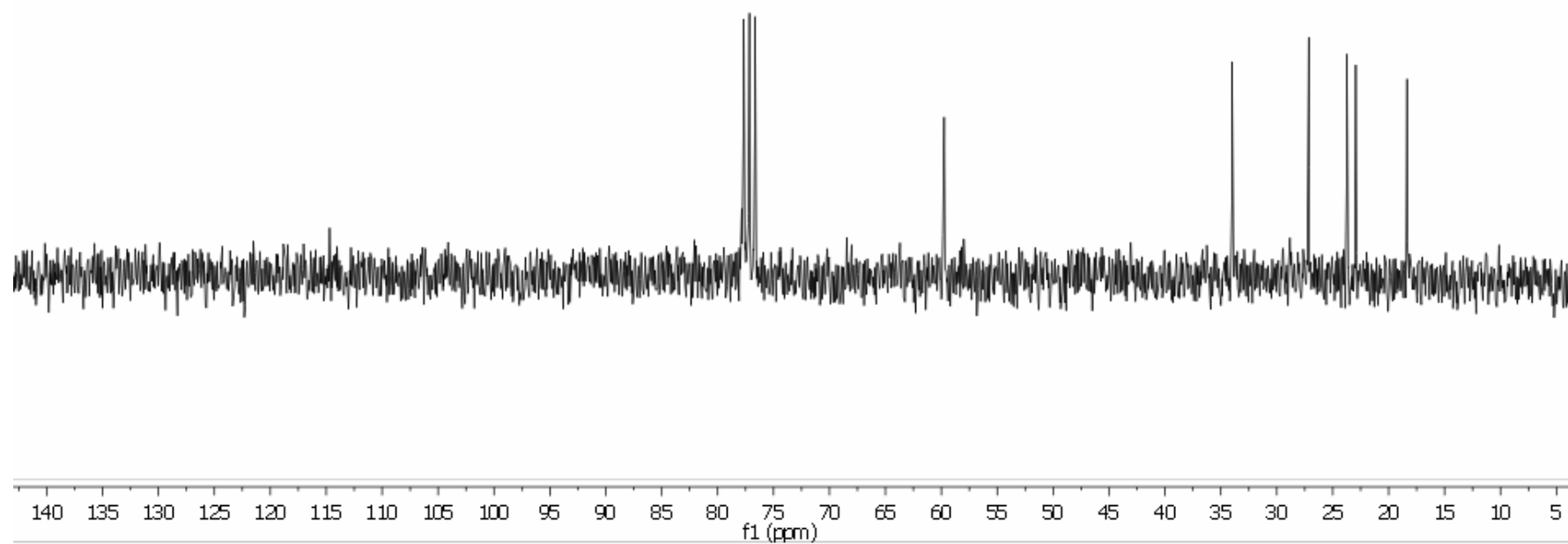
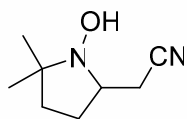
¹³C NMR spectrum of compound 10



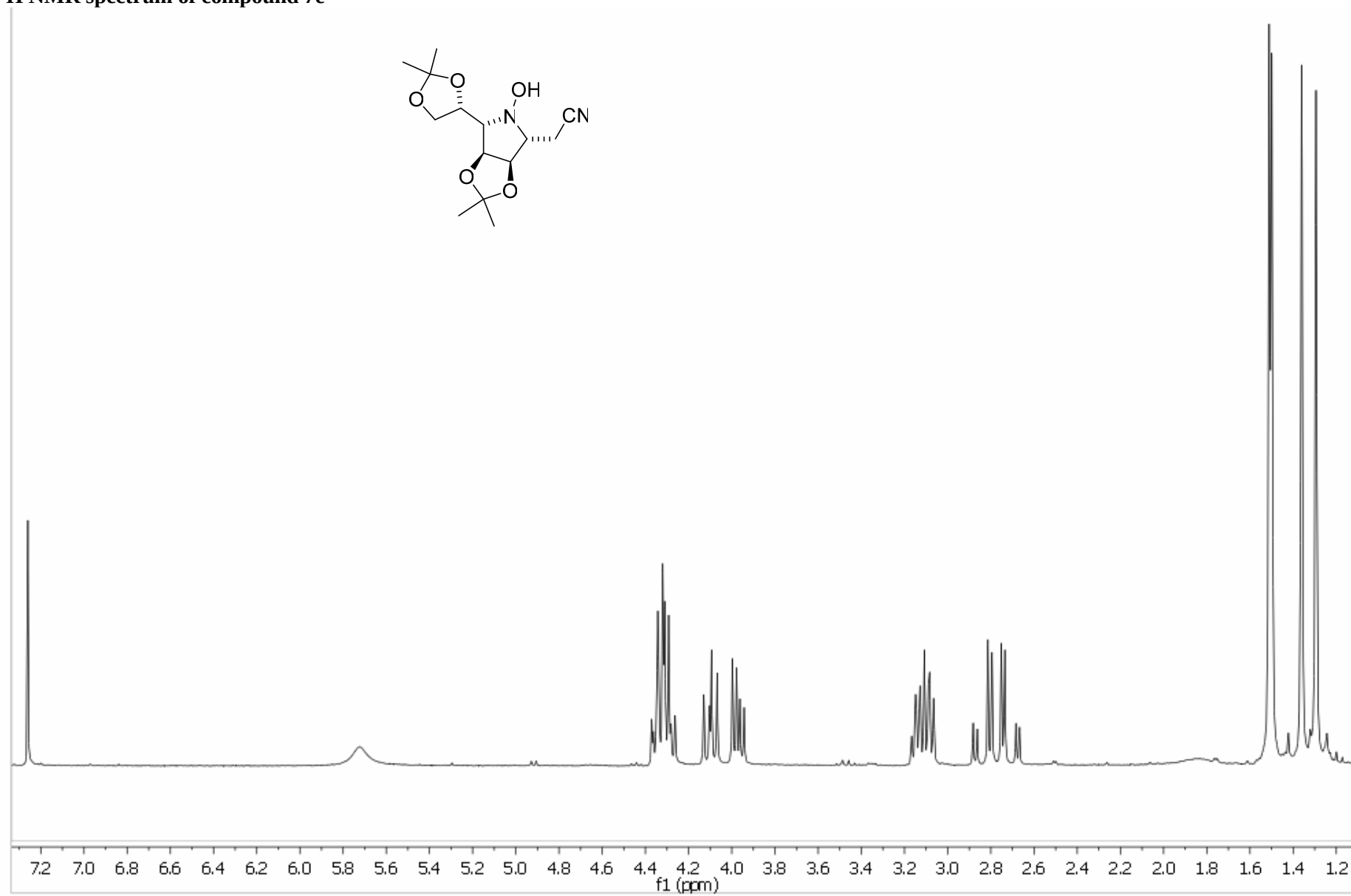
¹H NMR spectrum of compound 11



^{13}C NMR spectrum of compound 11



¹H NMR spectrum of compound 7e



¹³C NMR spectrum of compound 7e

