

Total synthesis of dendrobate alkaloid (+)-241D, isosolenopsin and isosolenopsin A: application of a gold-catalyzed cyclization

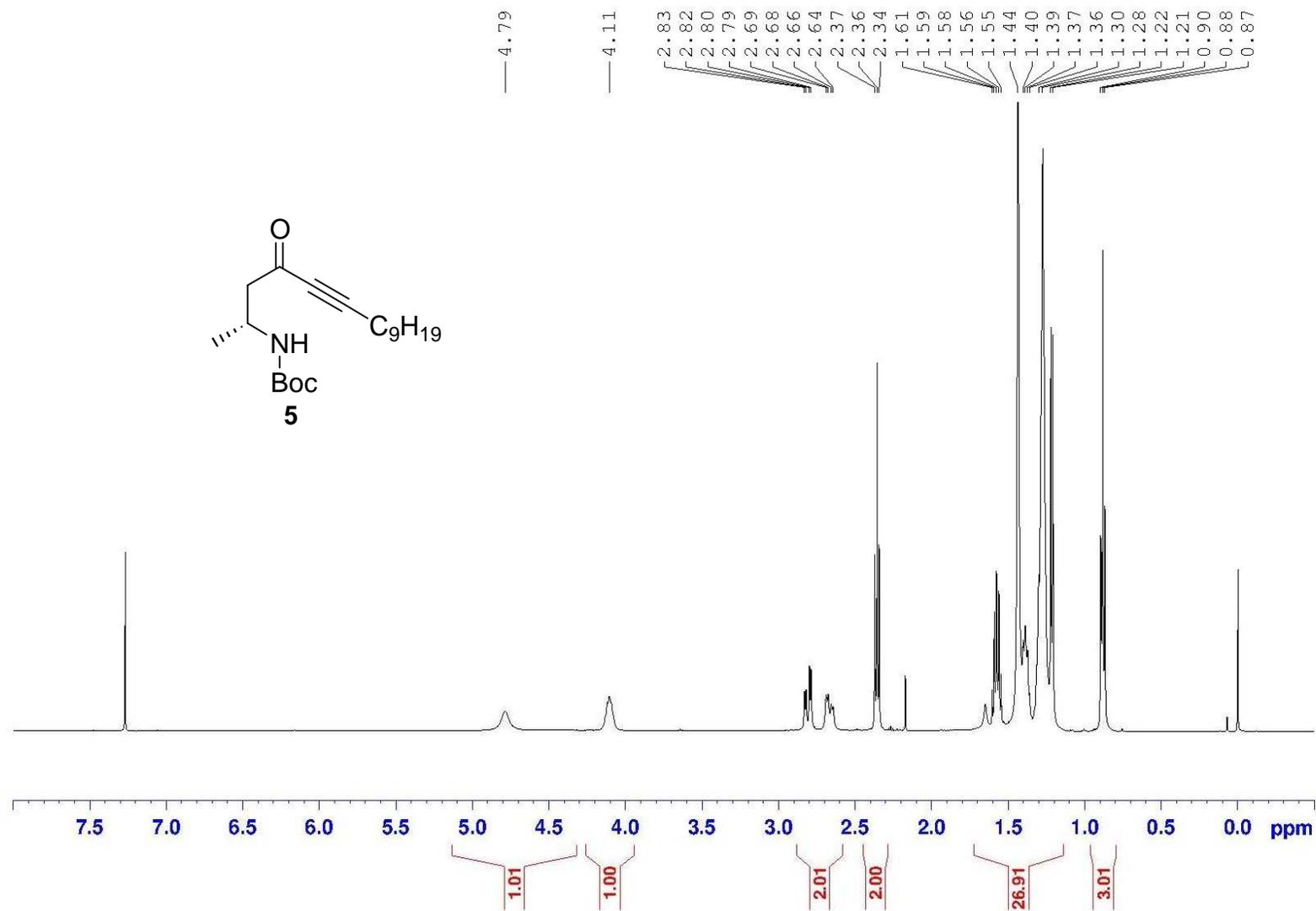
Nicolas Gouault,* Myriam Le Roch, Gisele de Campos Pinto and Michèle David

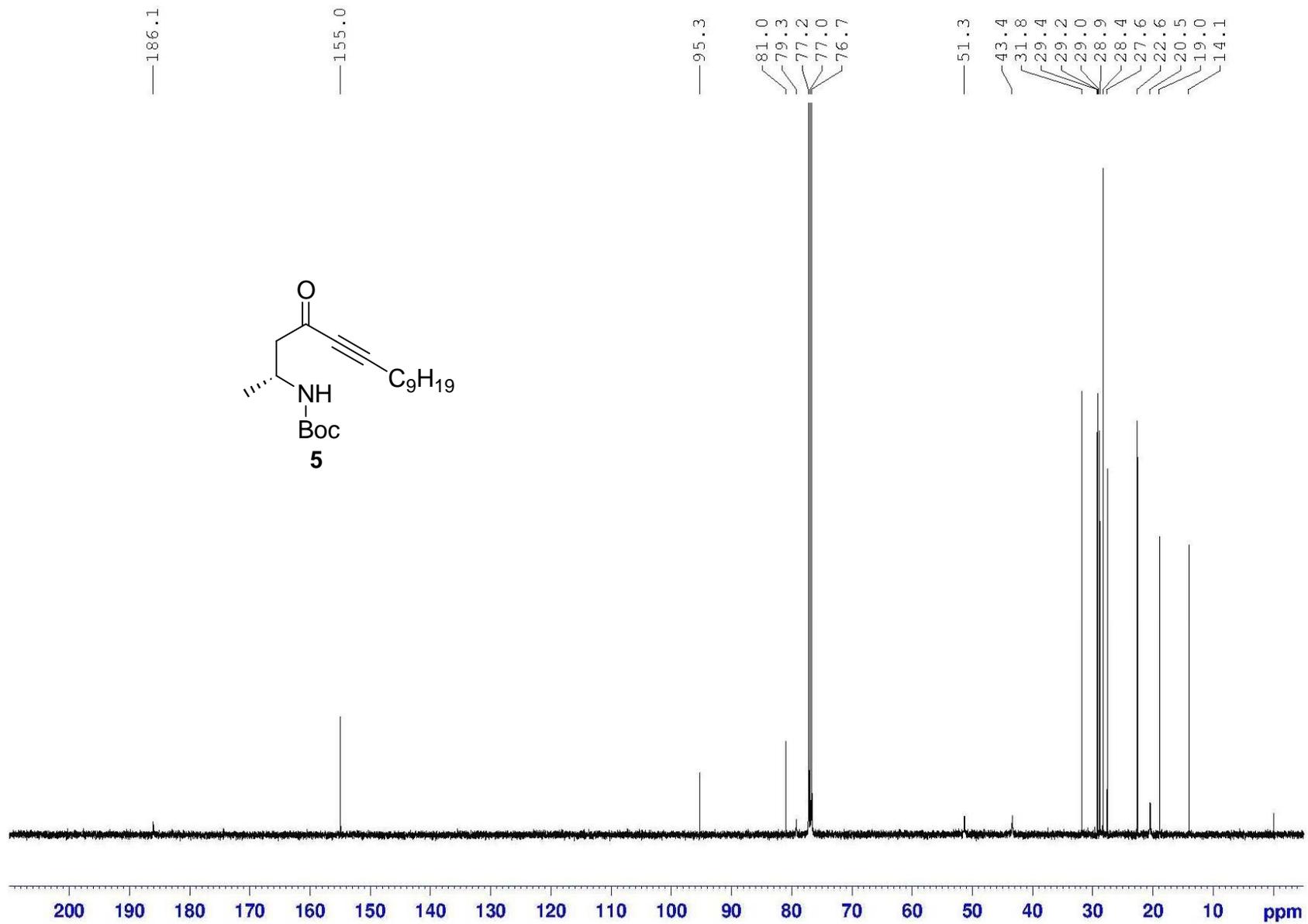
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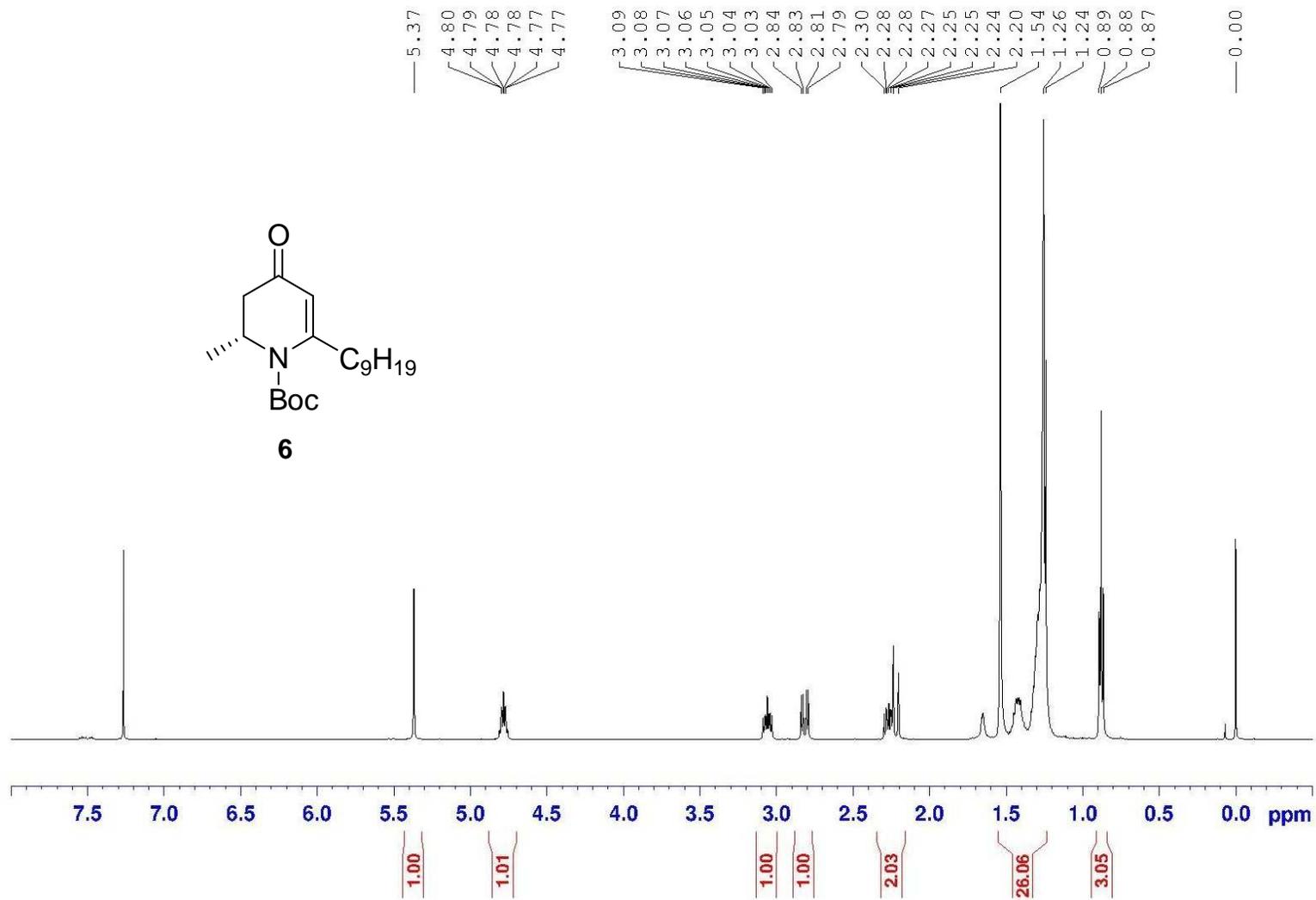
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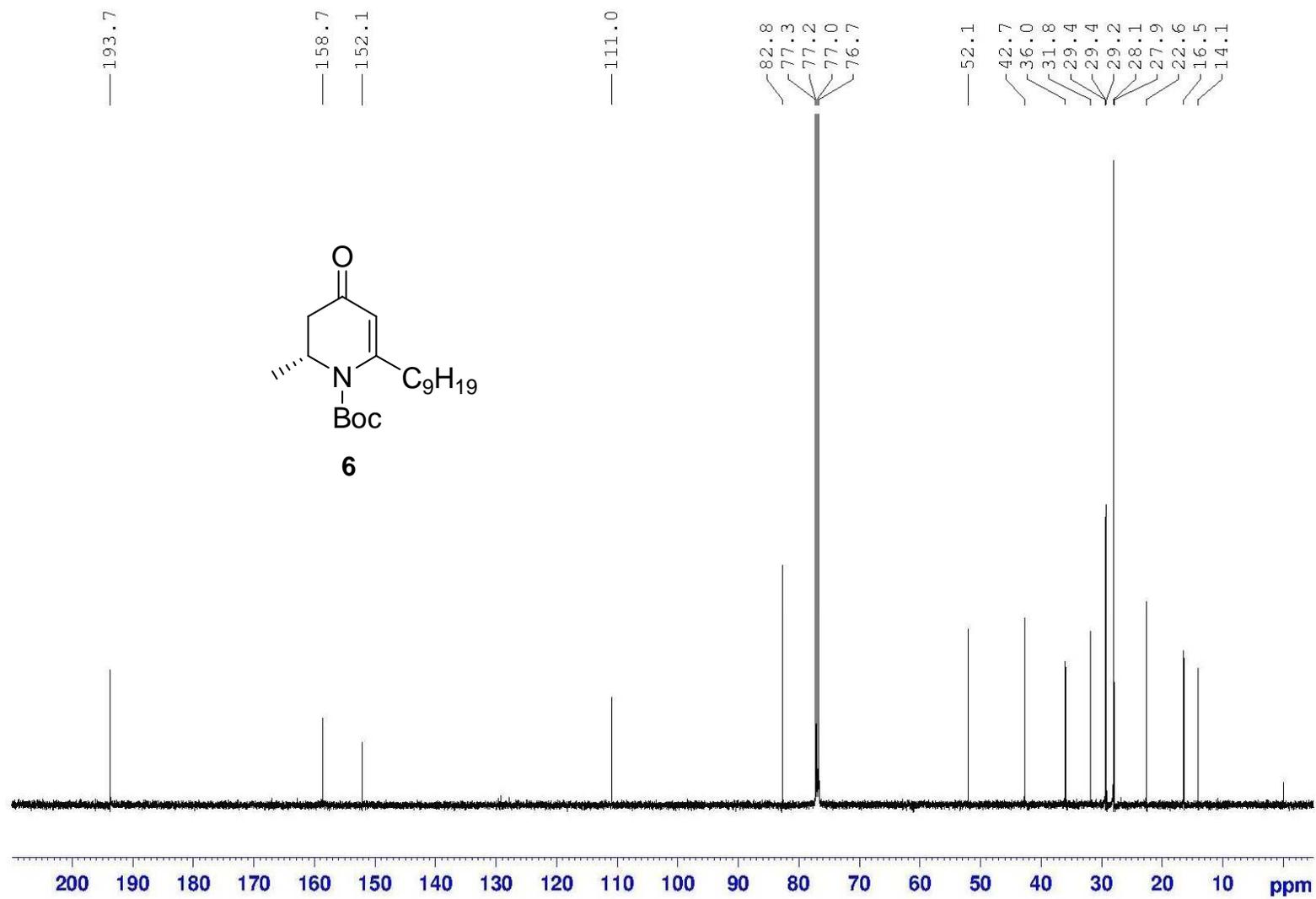
¹H & ¹³C NMR Data

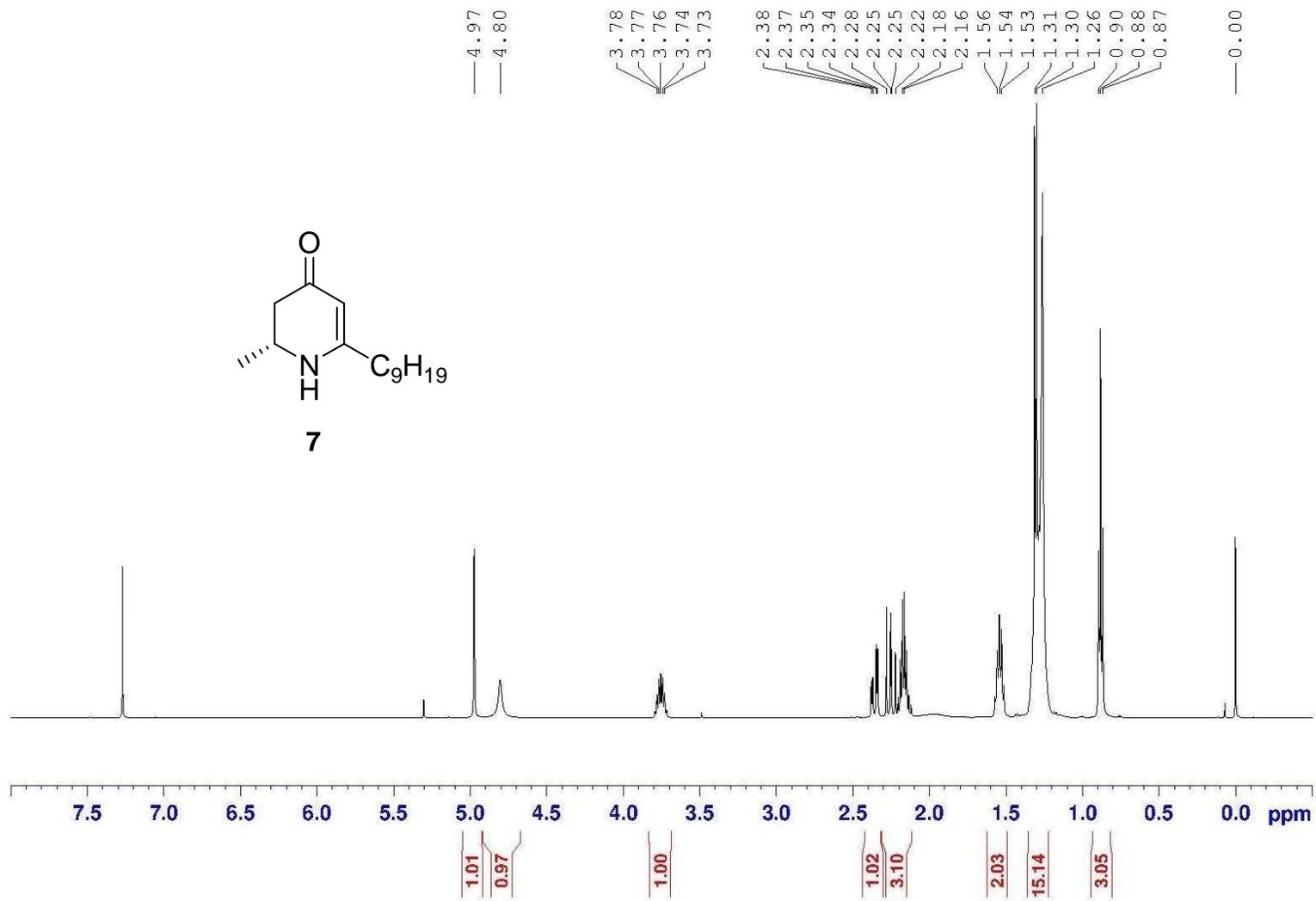
(37 Pages)

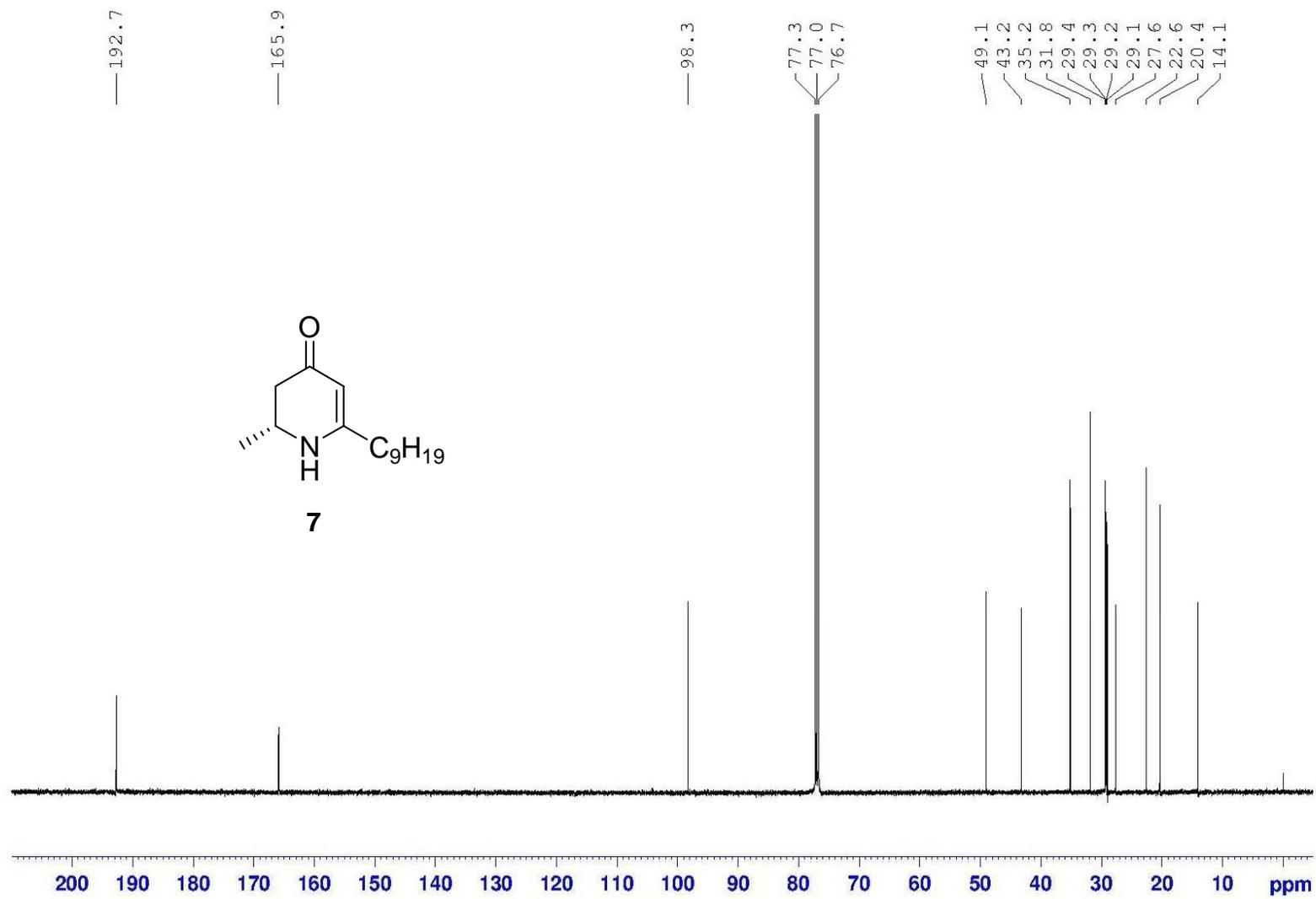


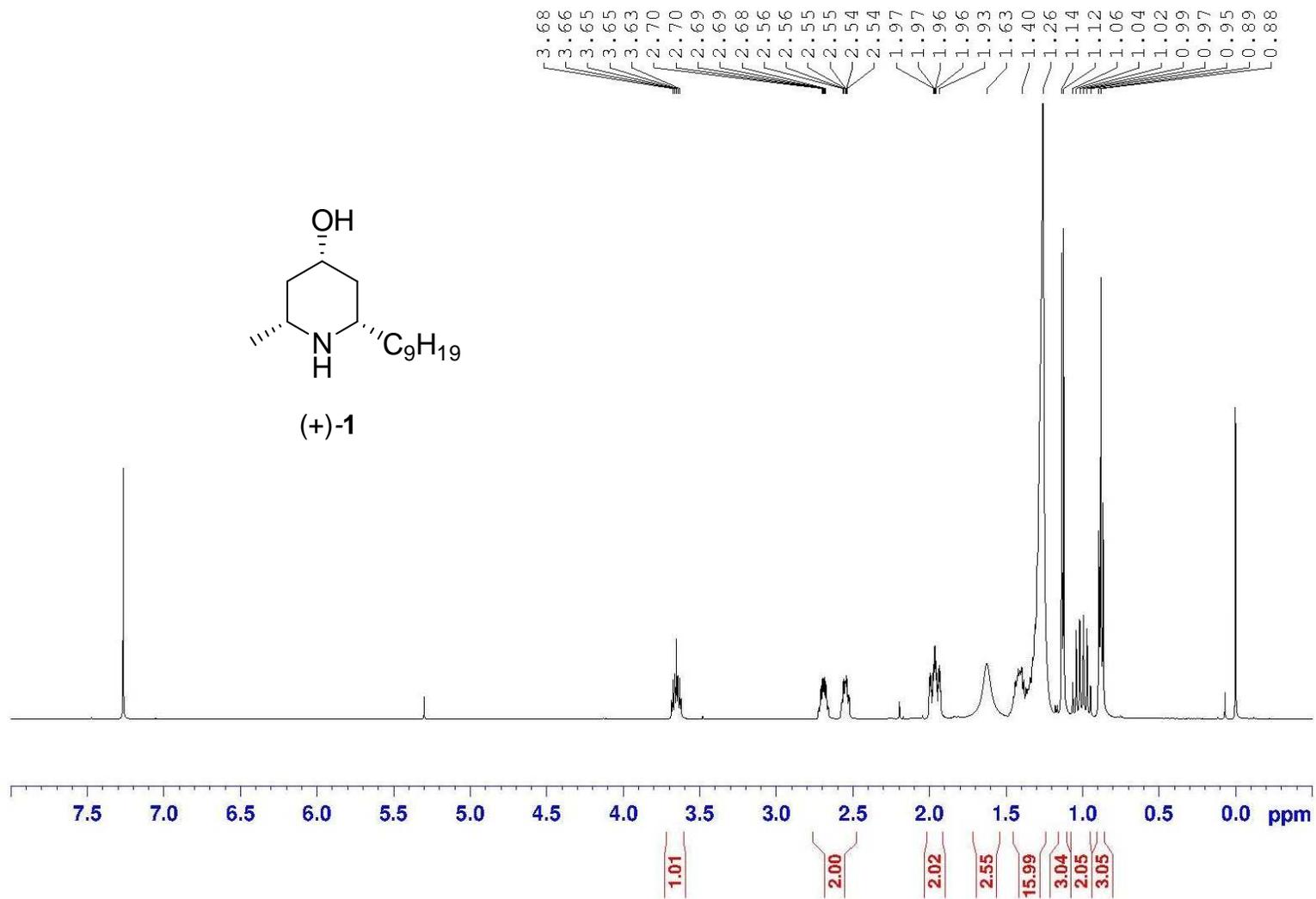


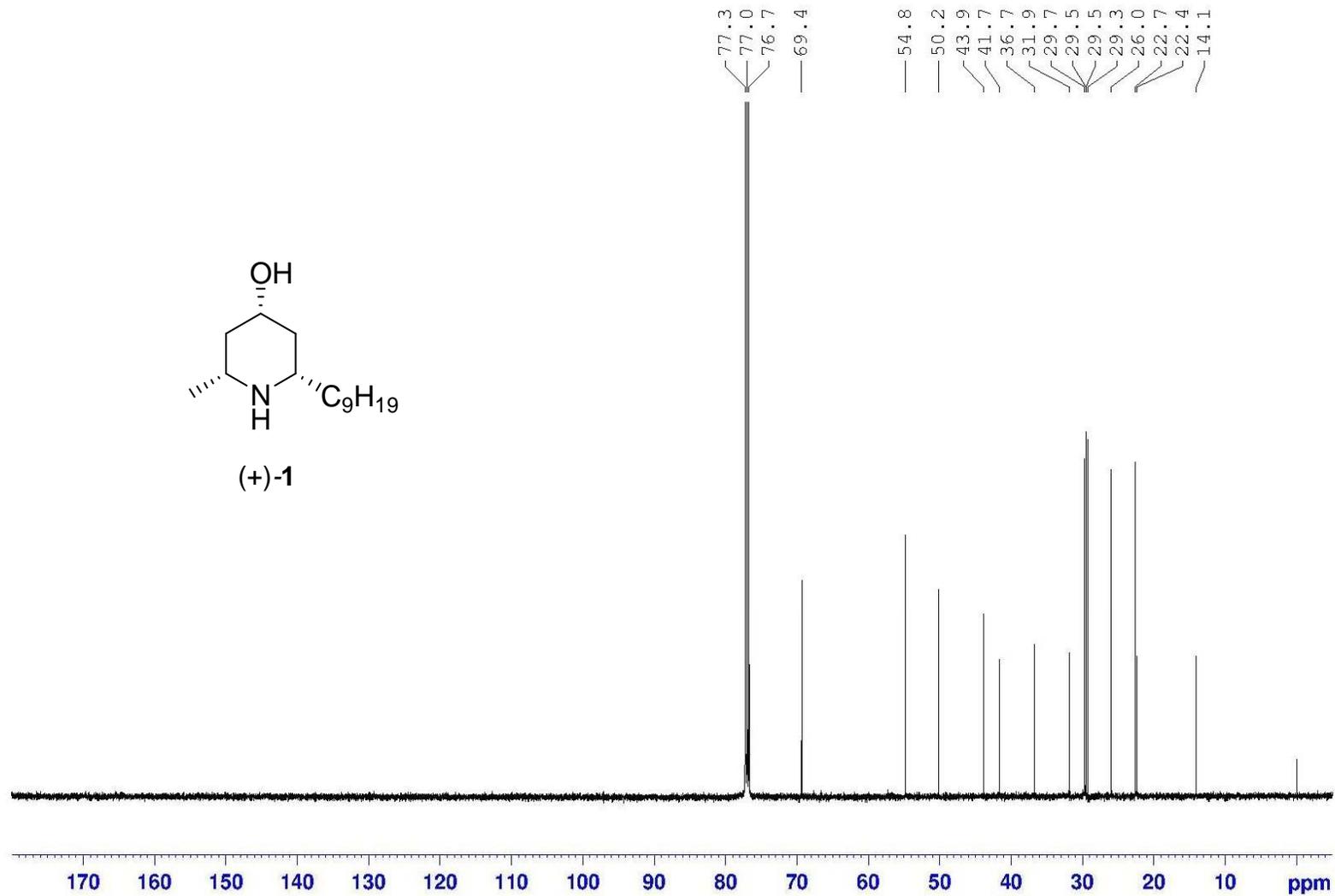


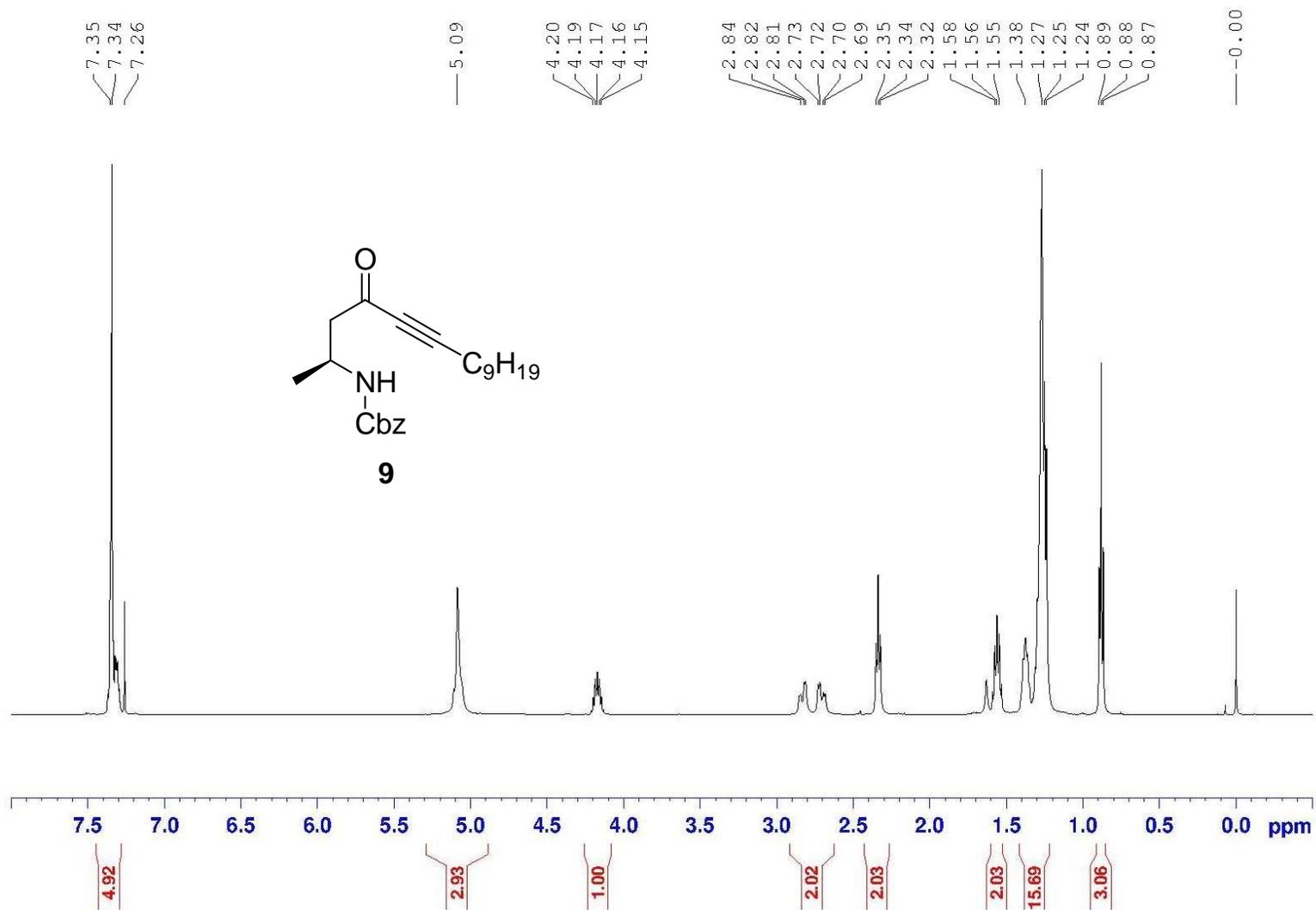


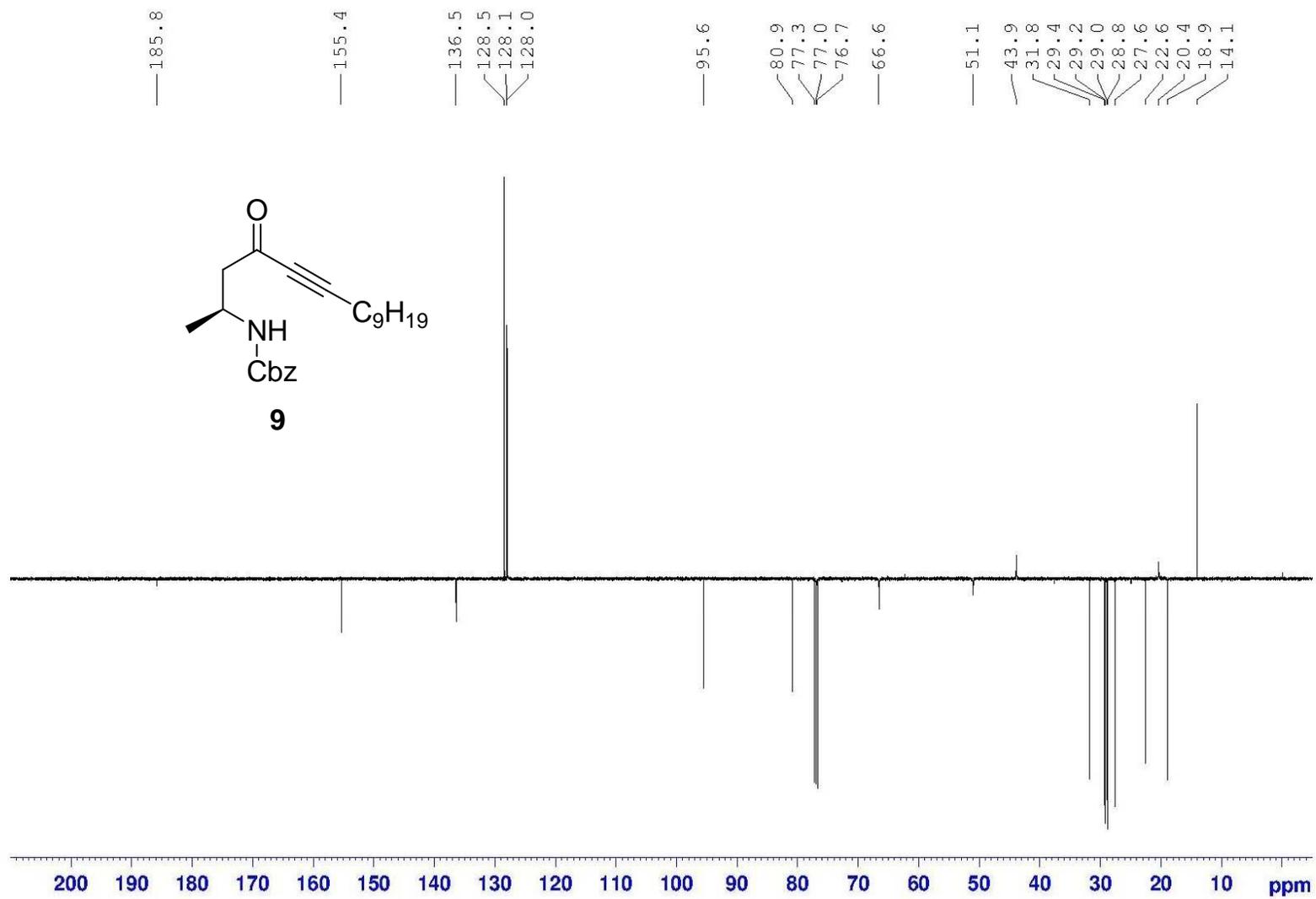


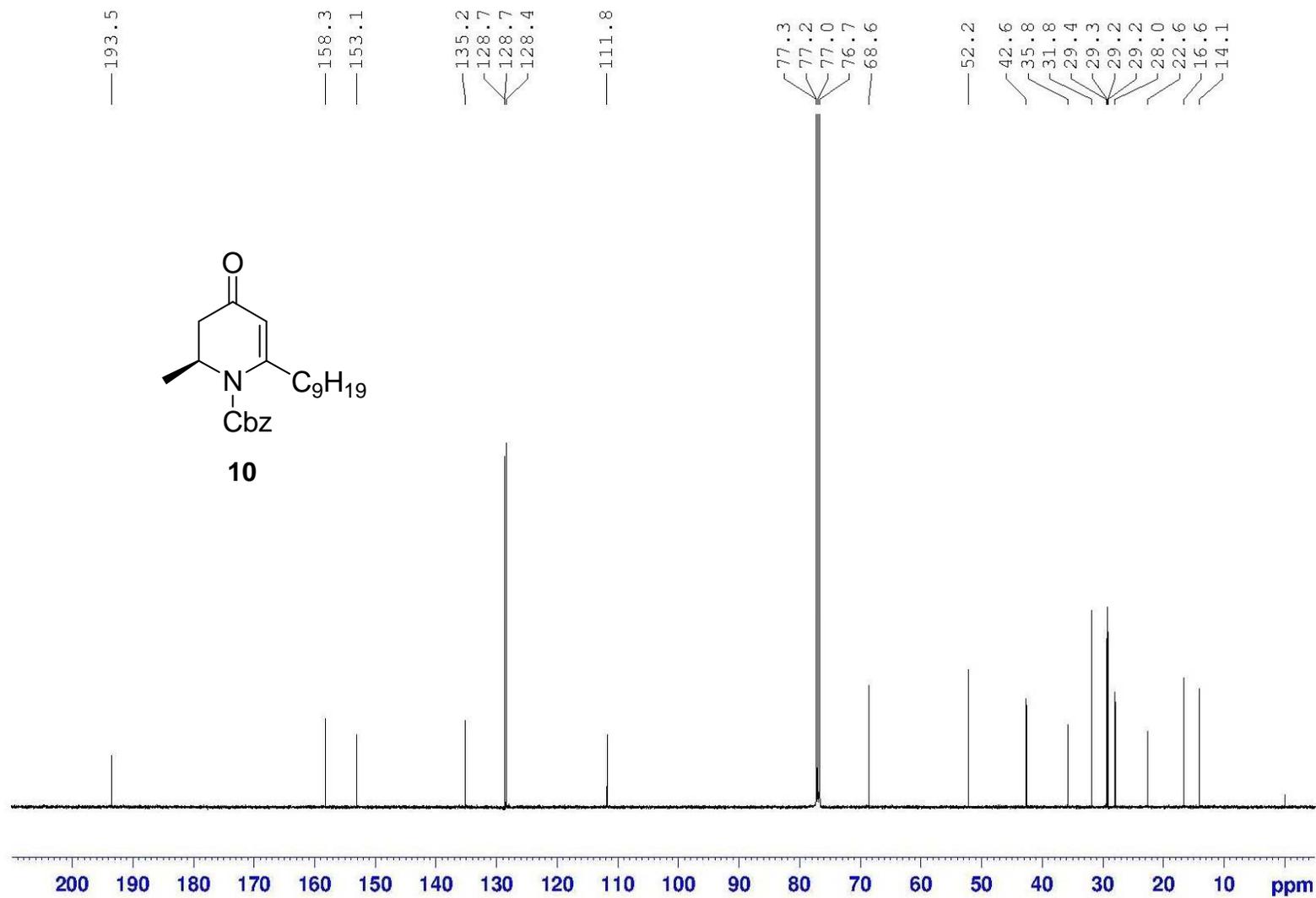


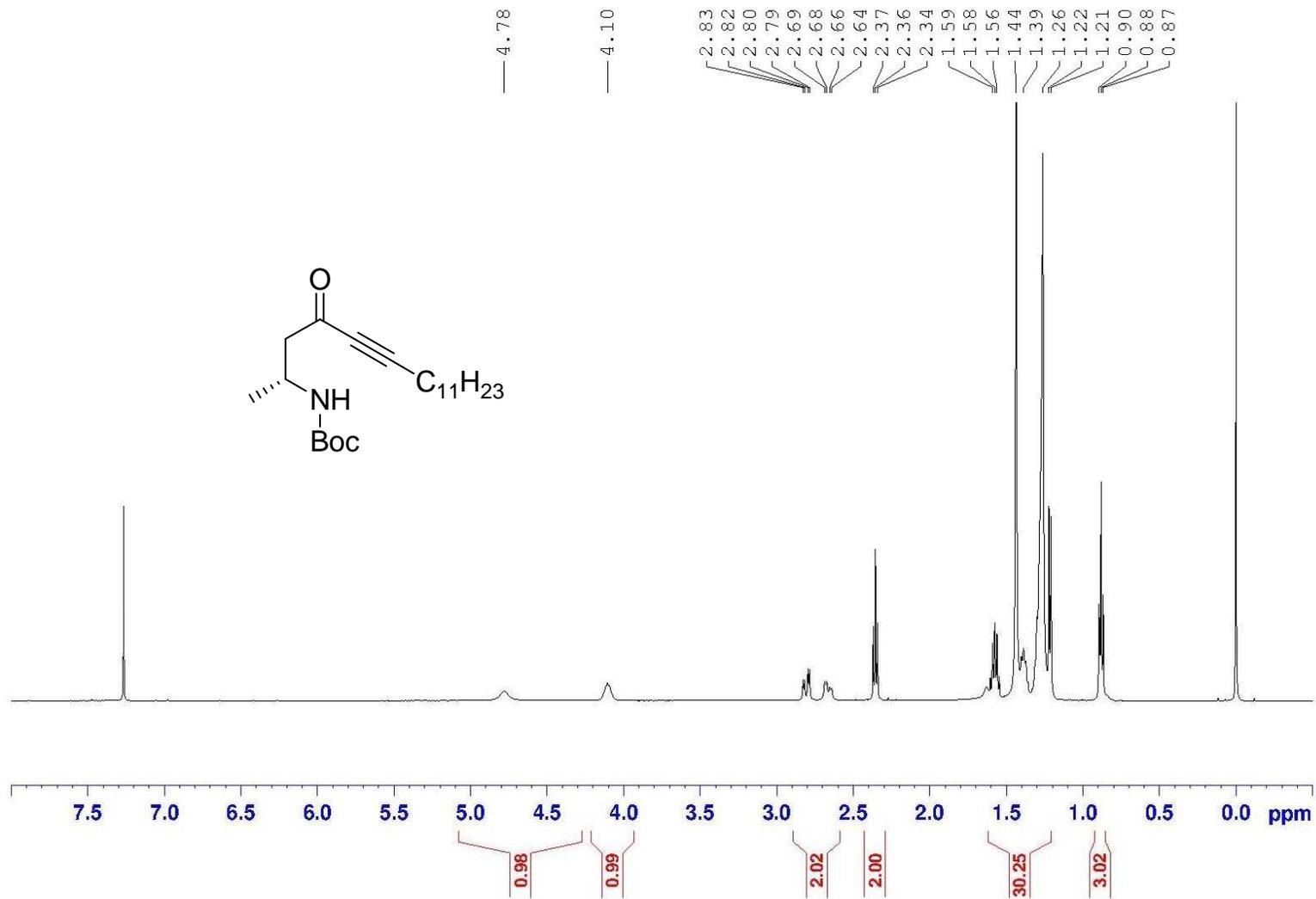


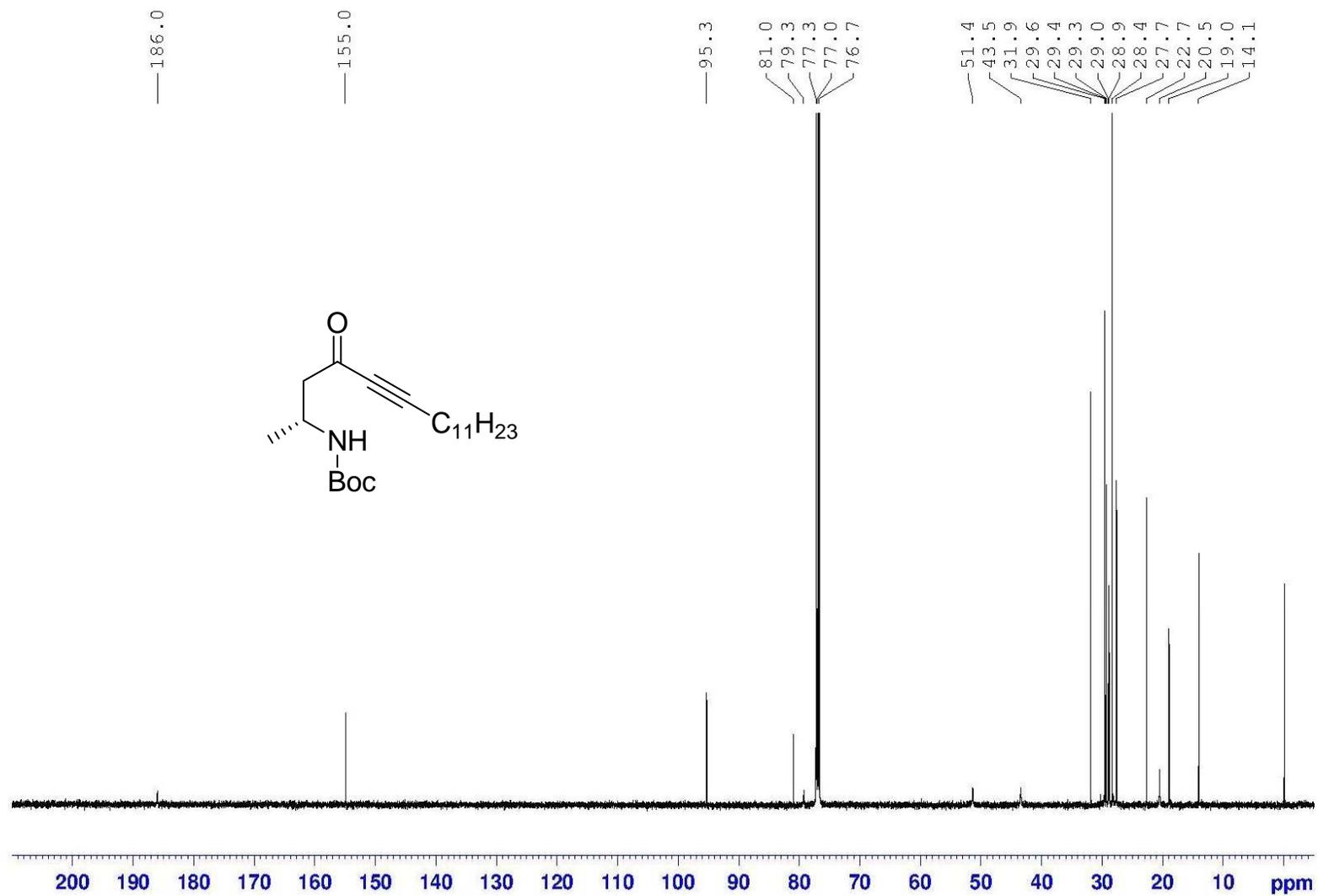


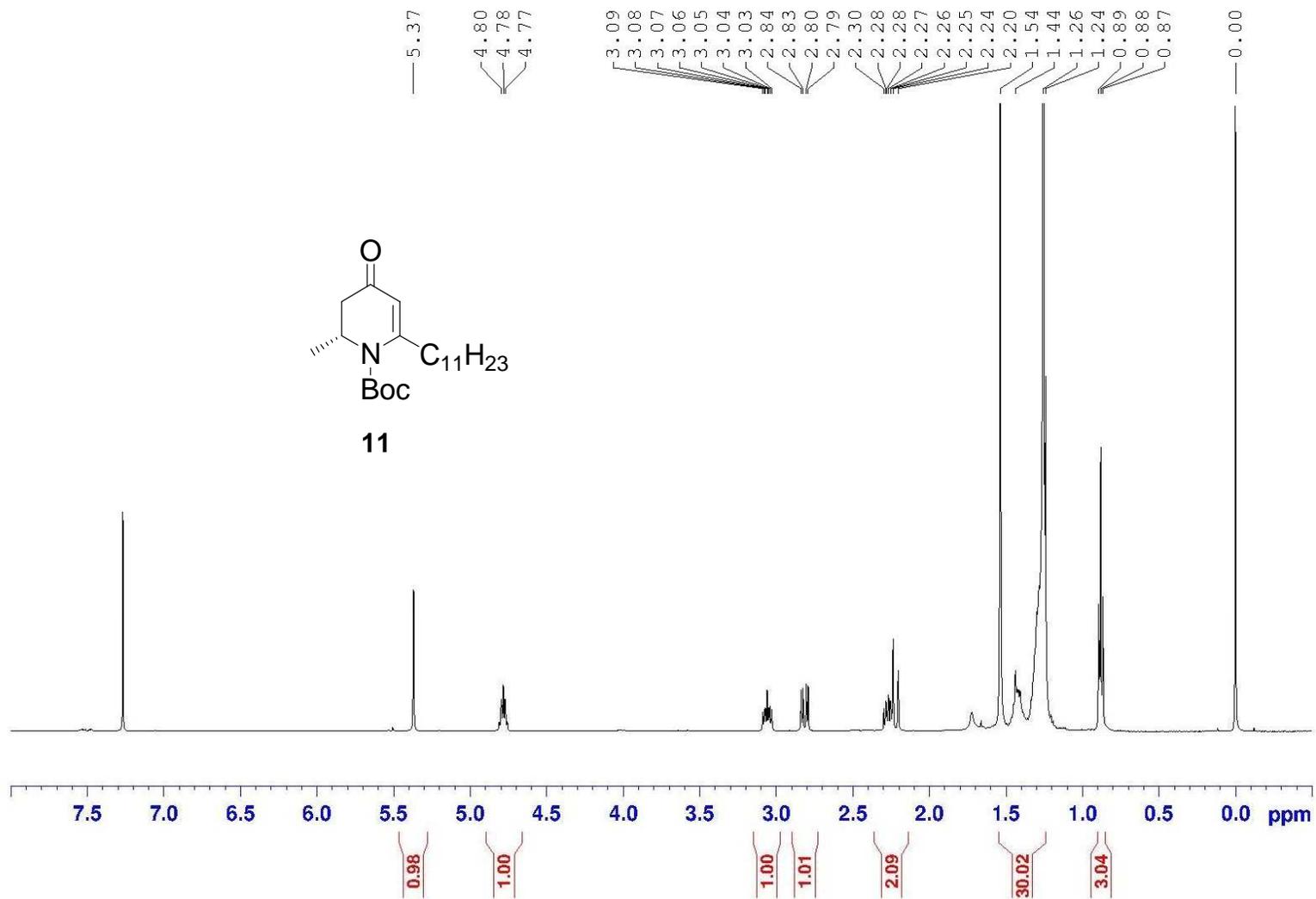


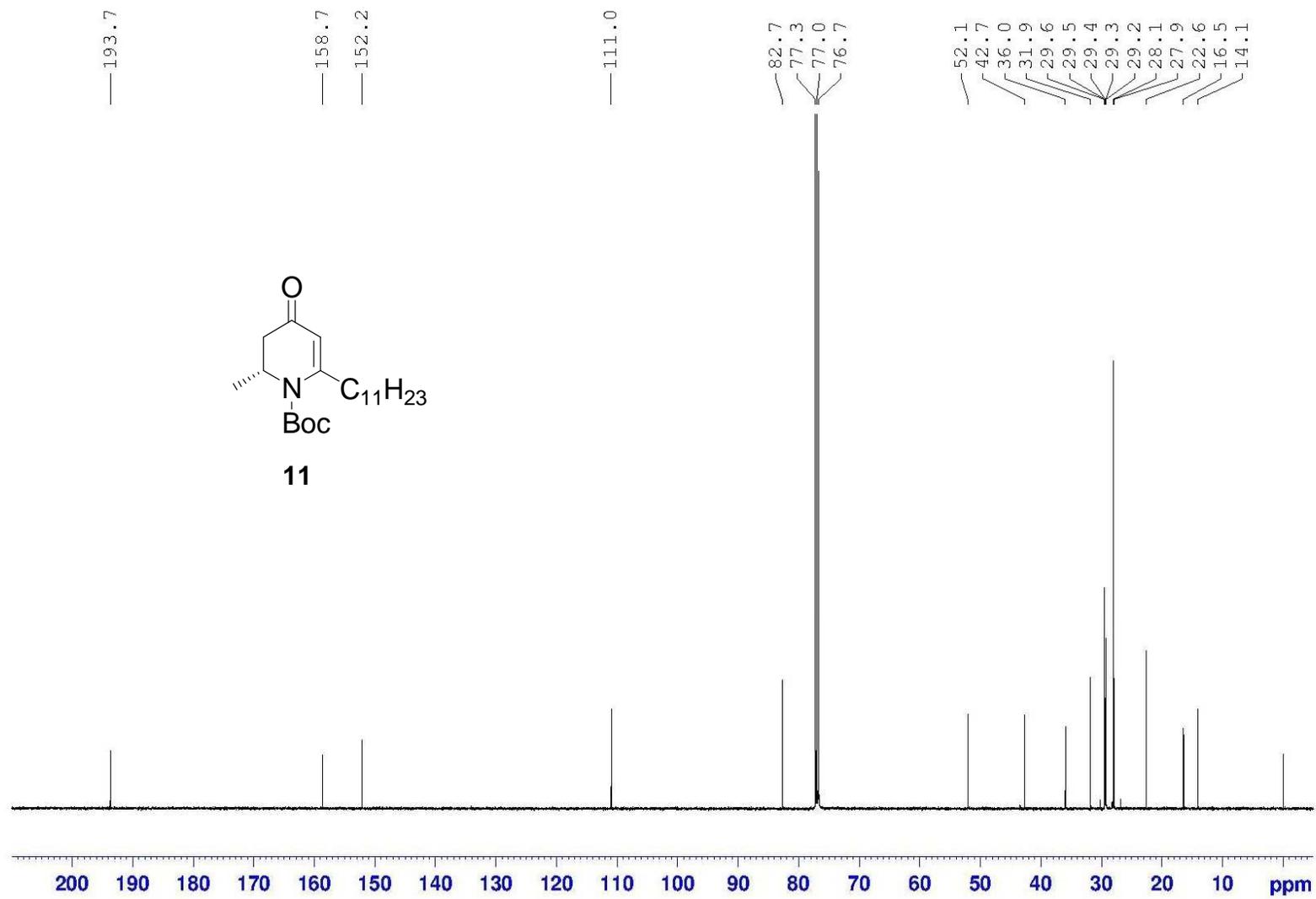


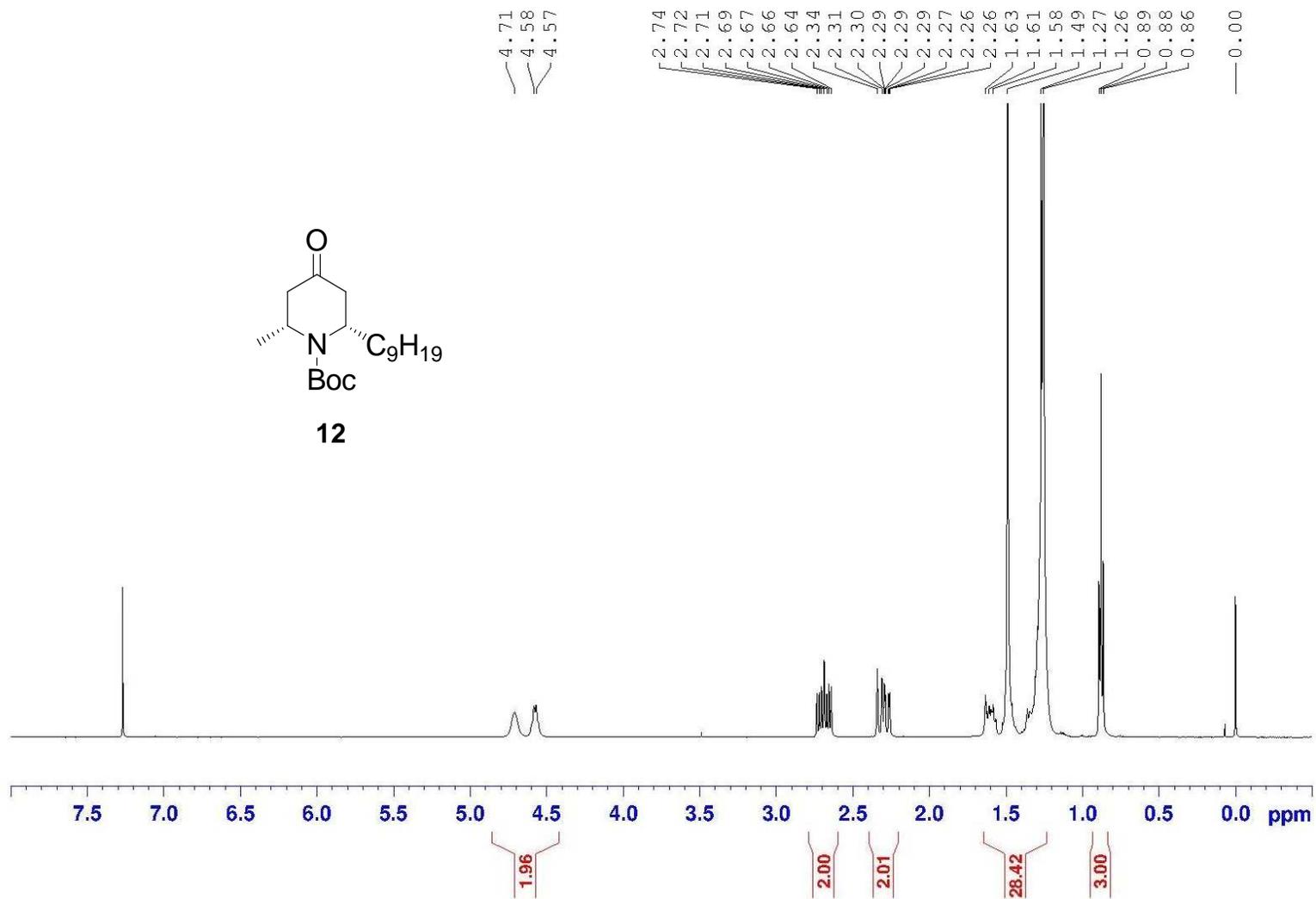


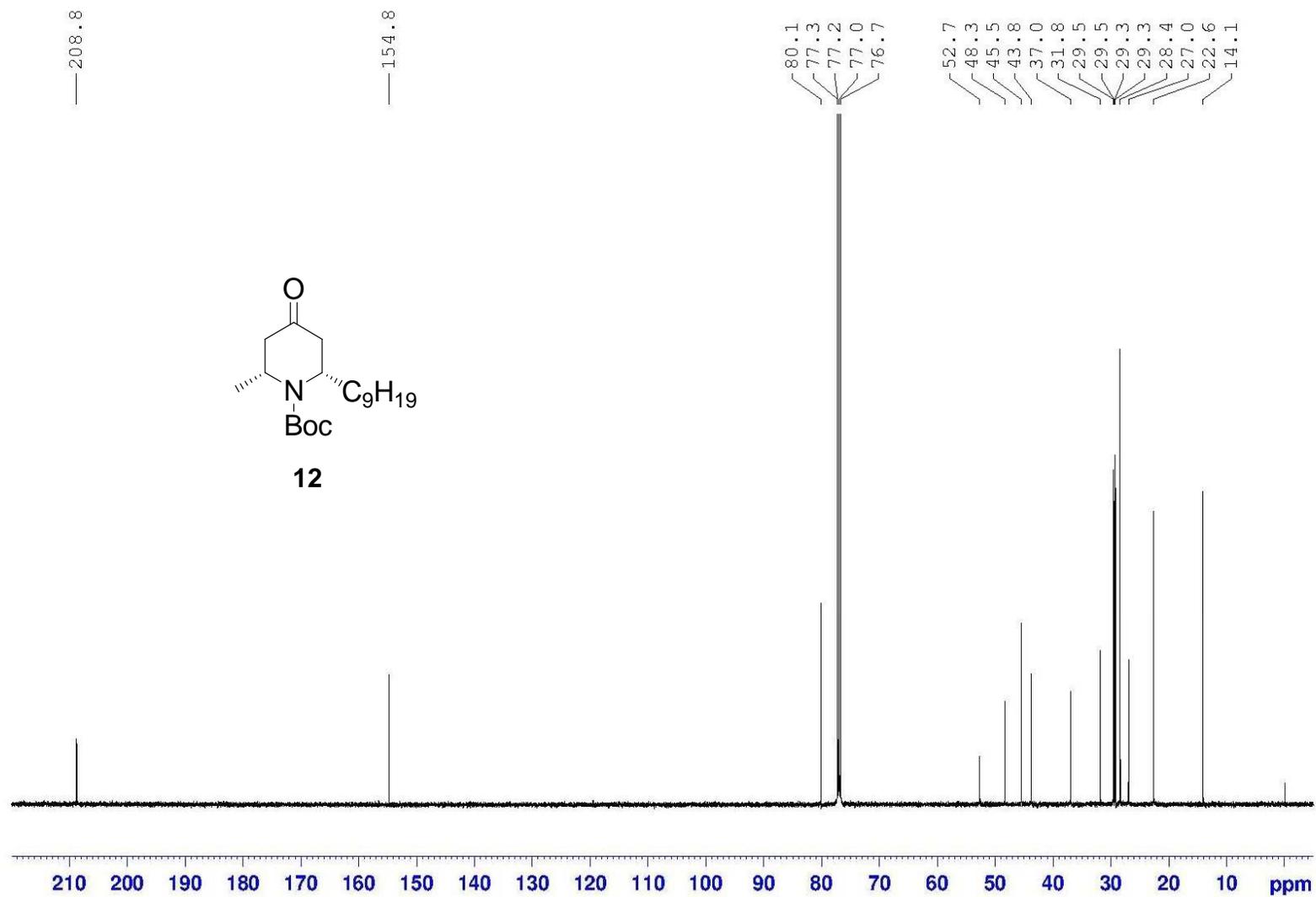


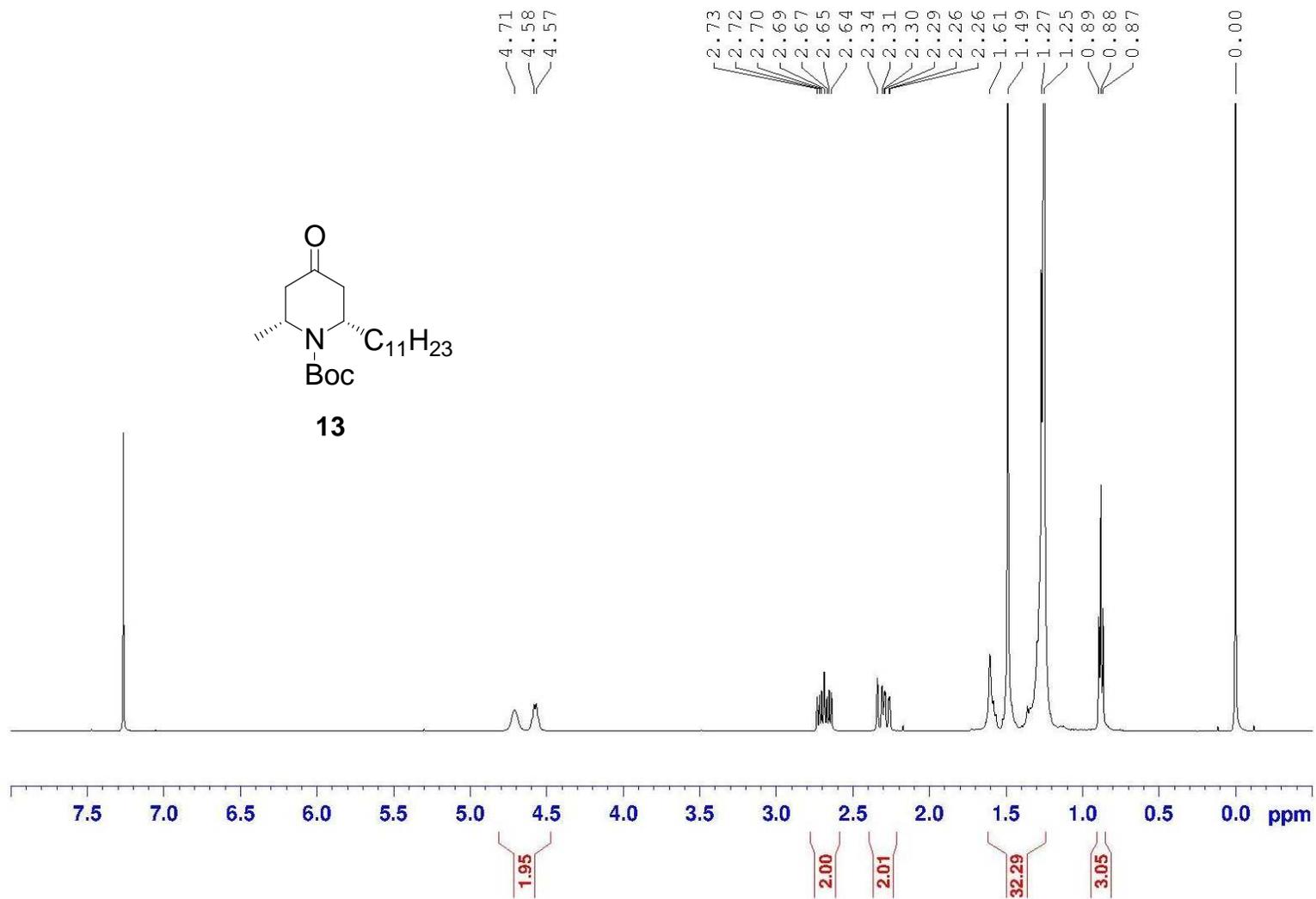


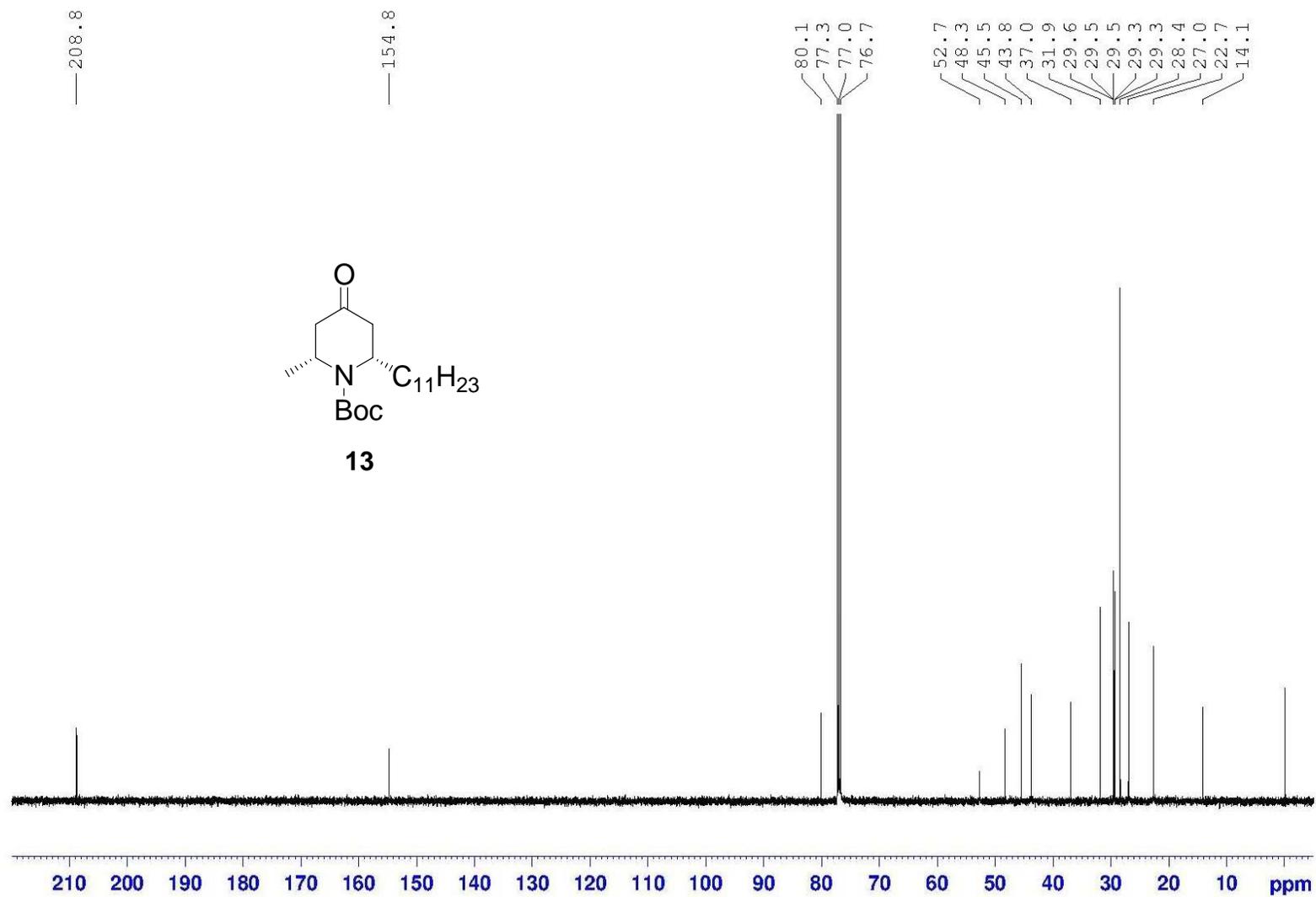


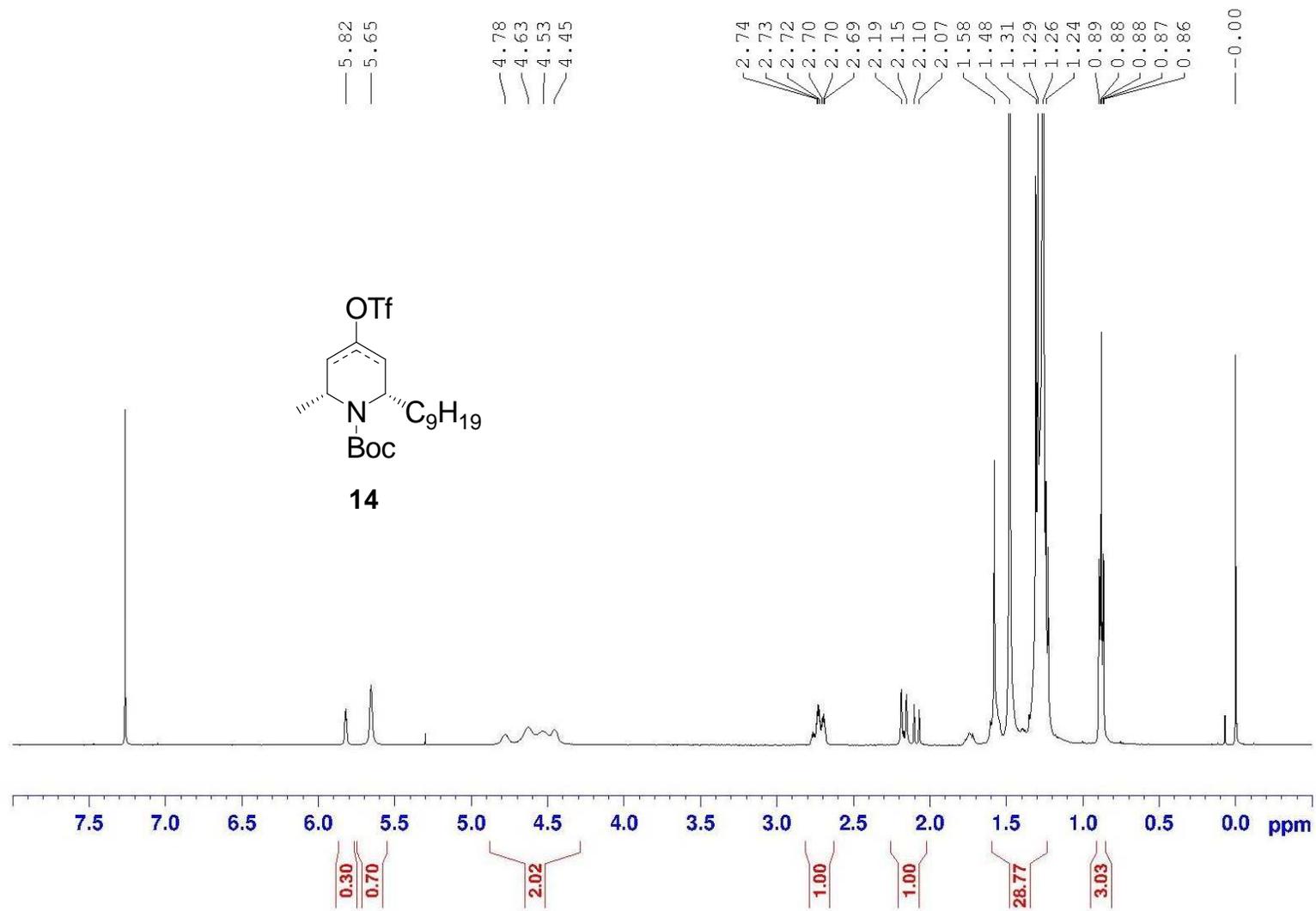


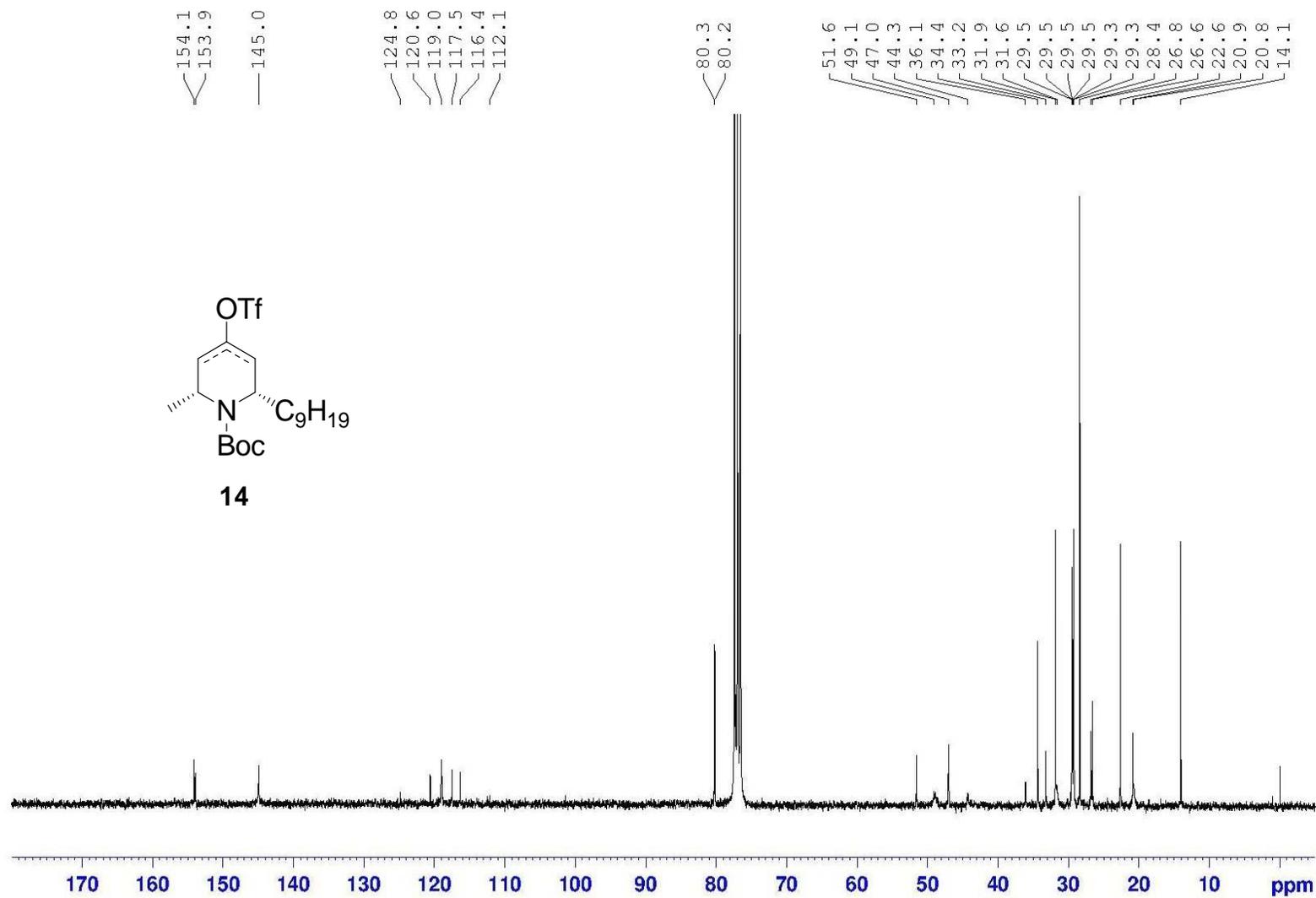


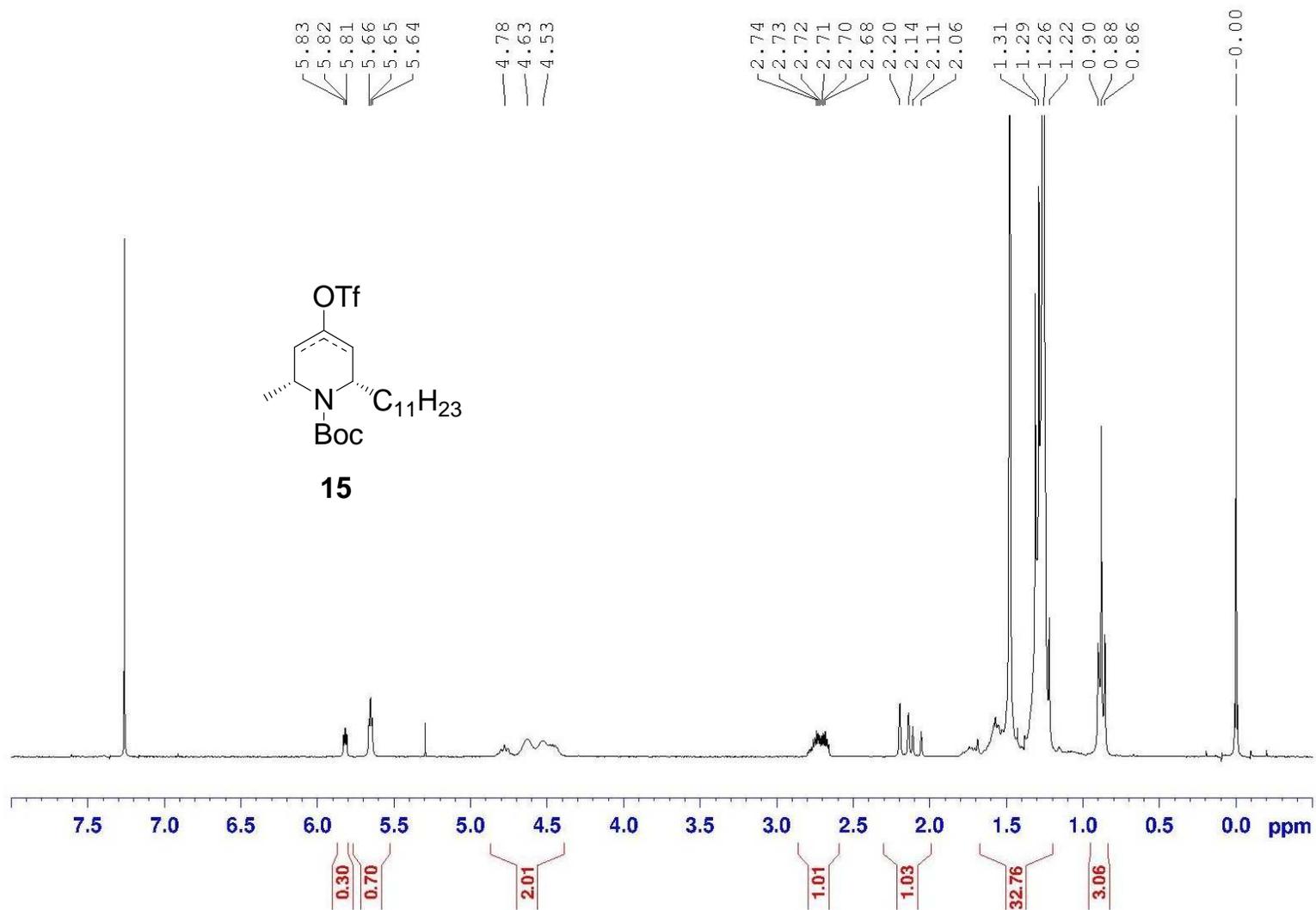


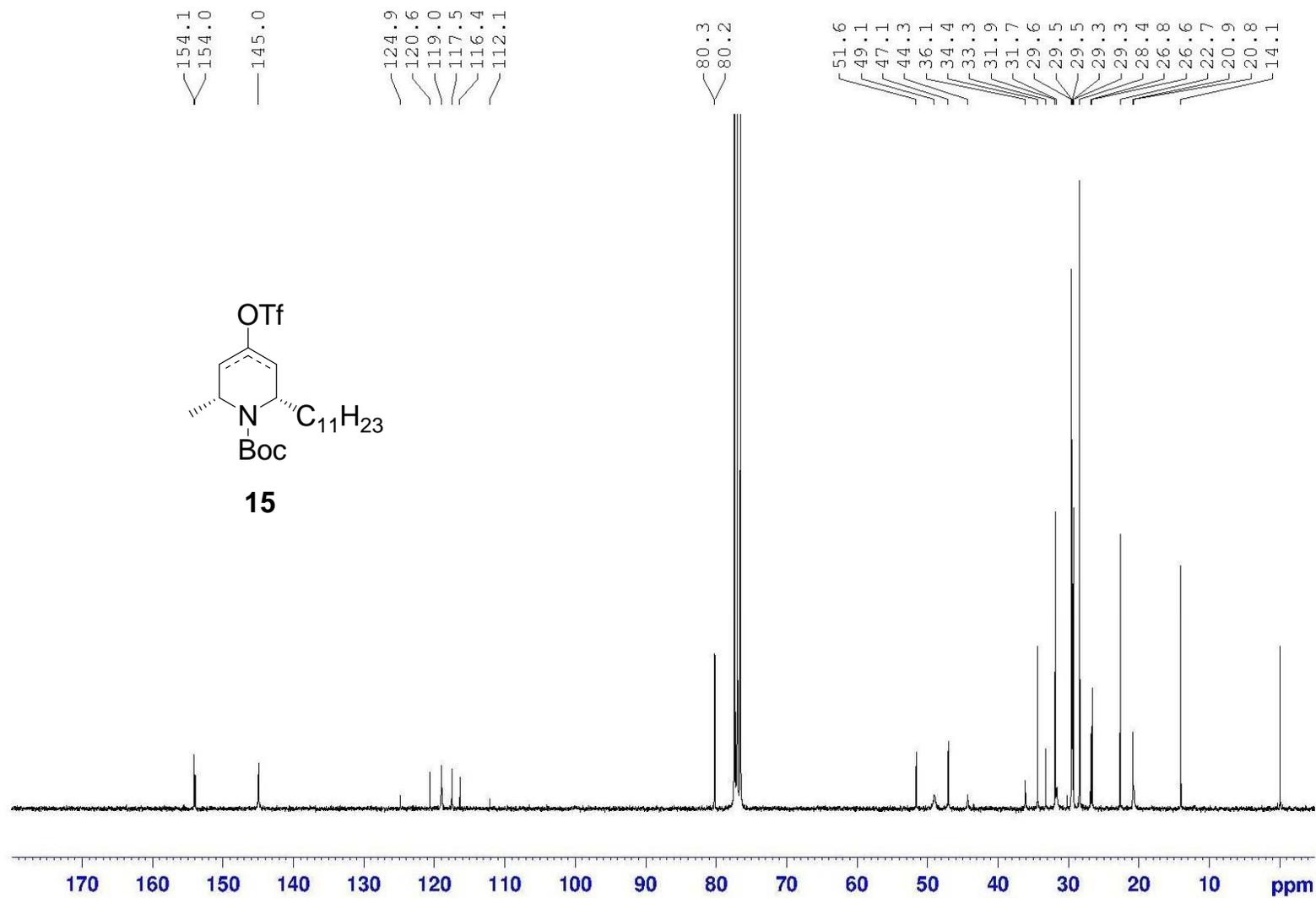


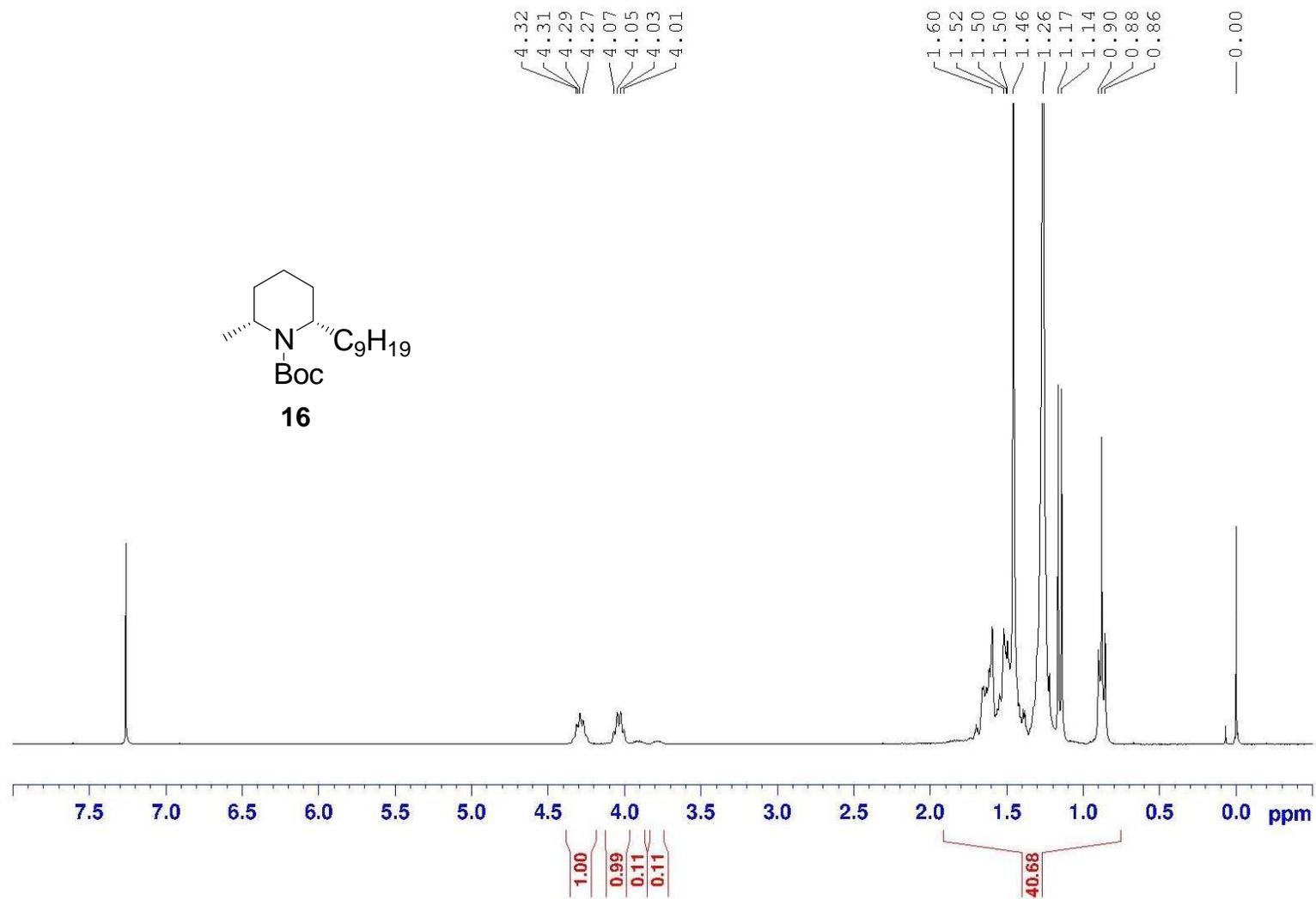


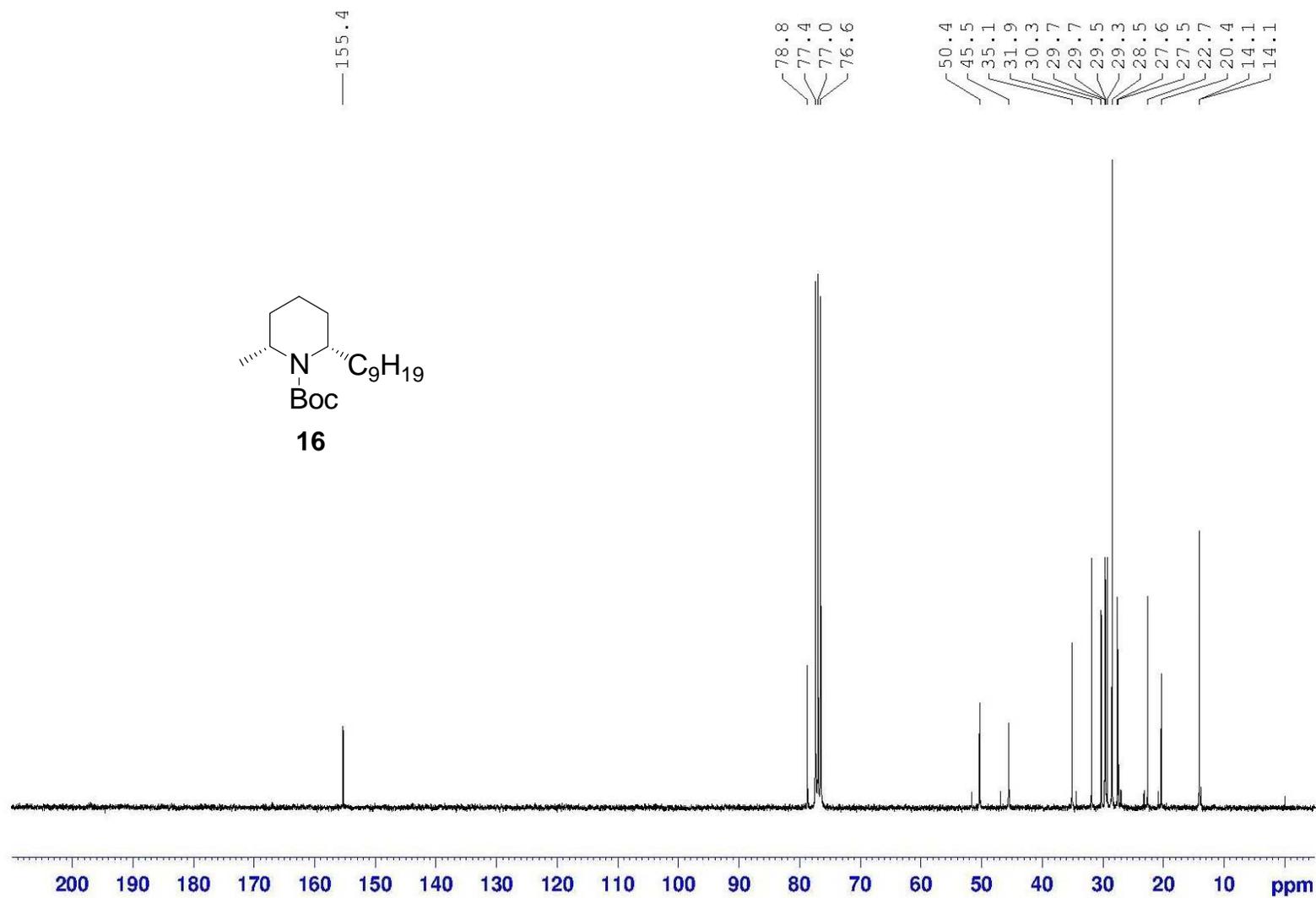


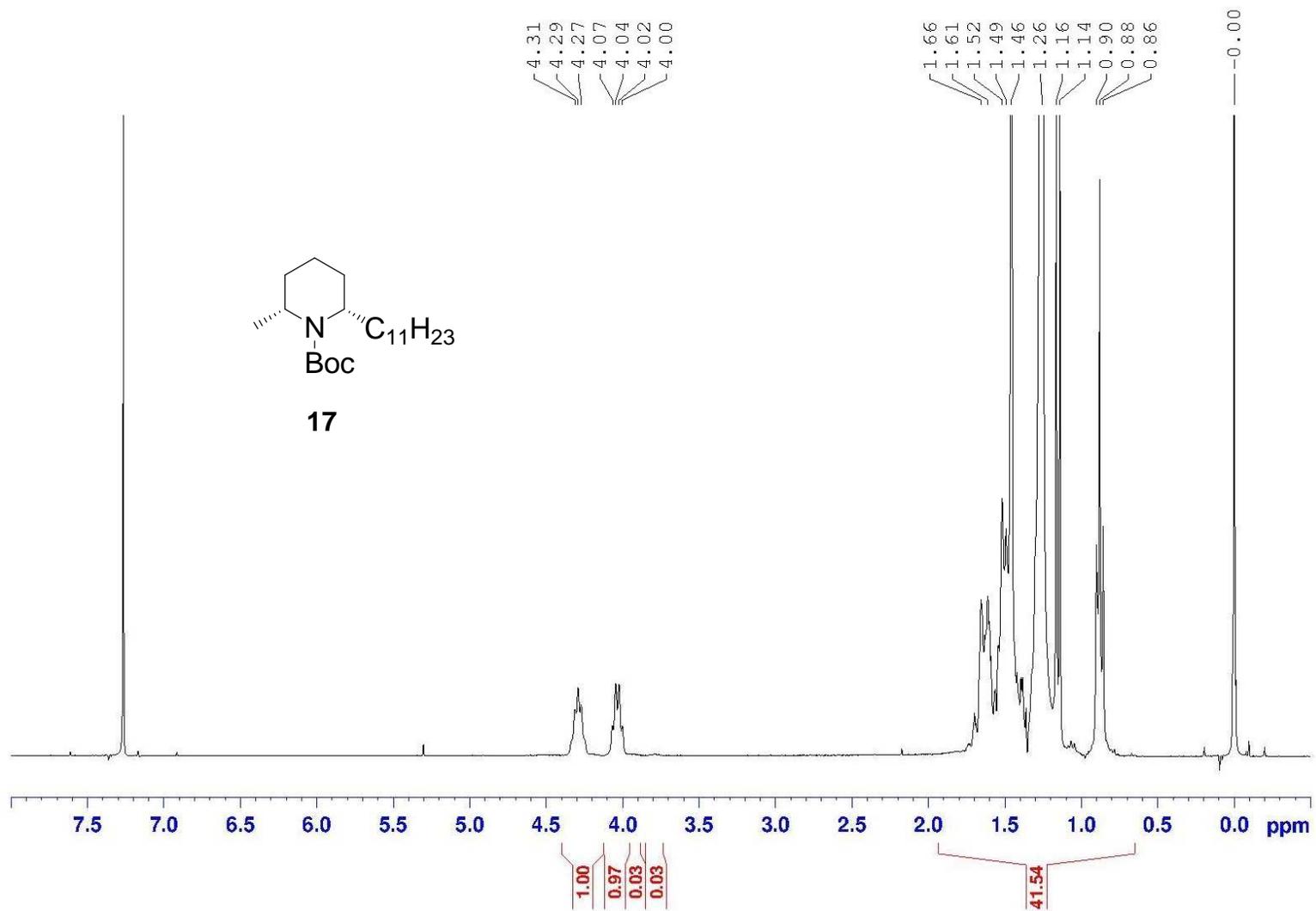


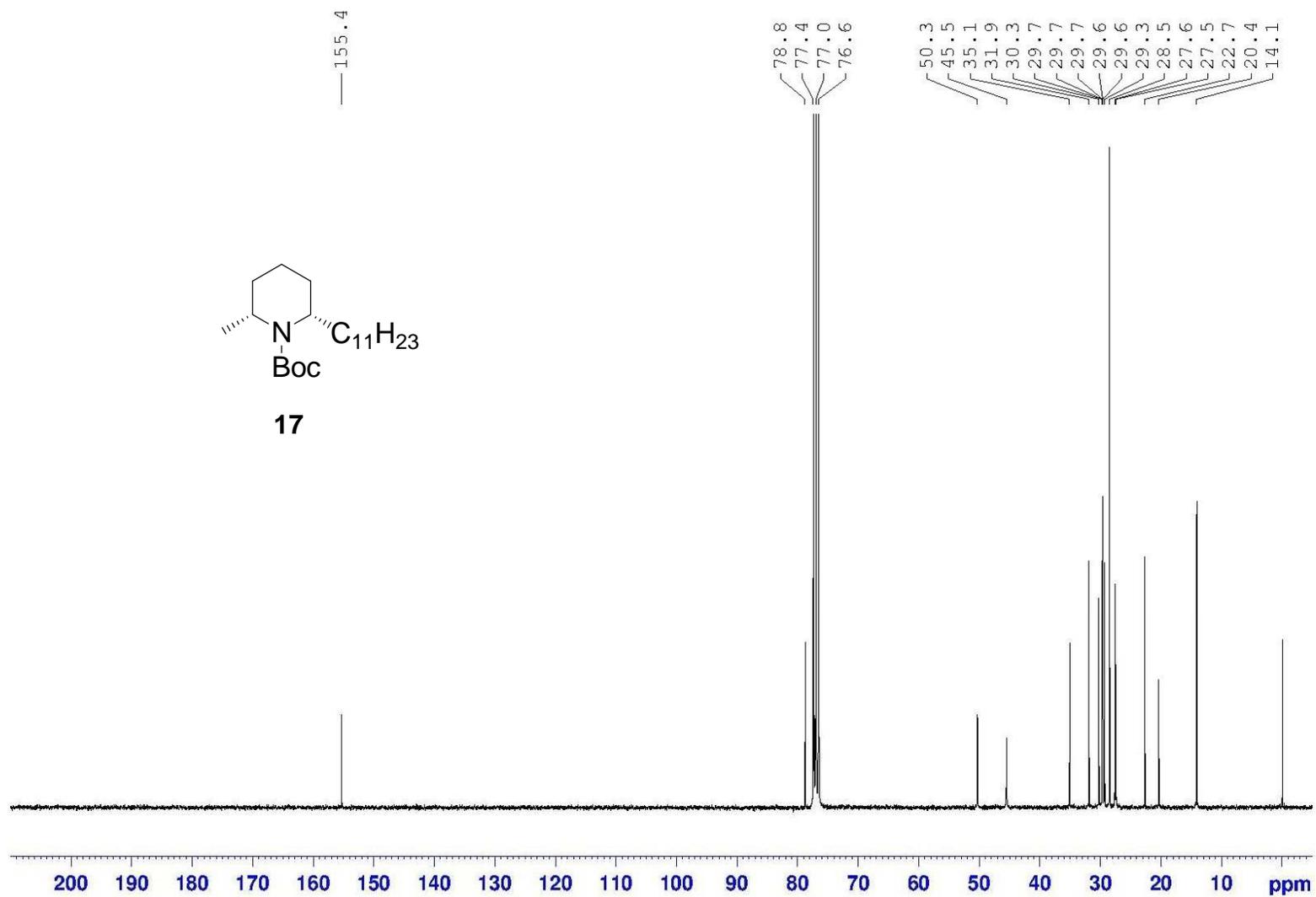


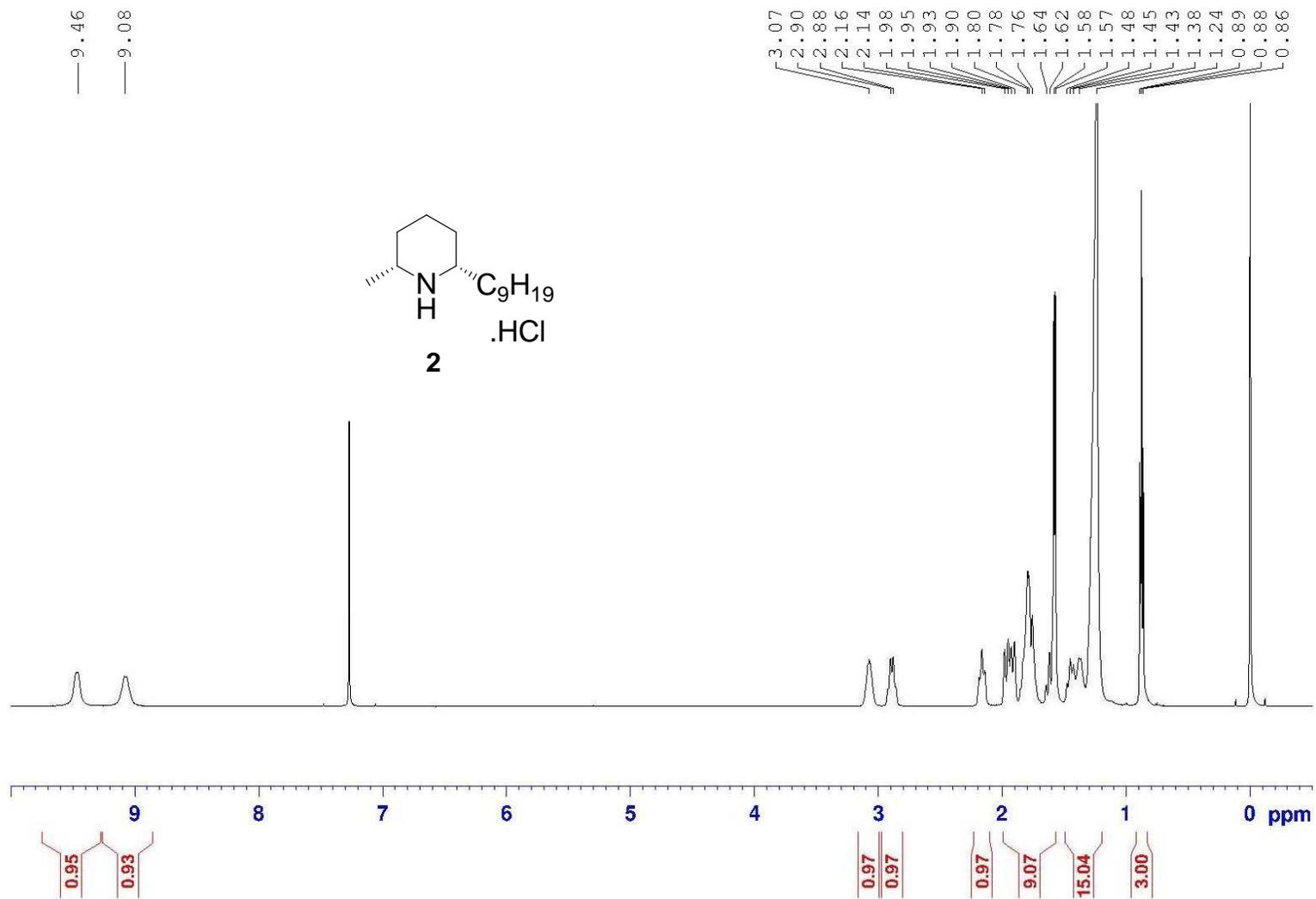


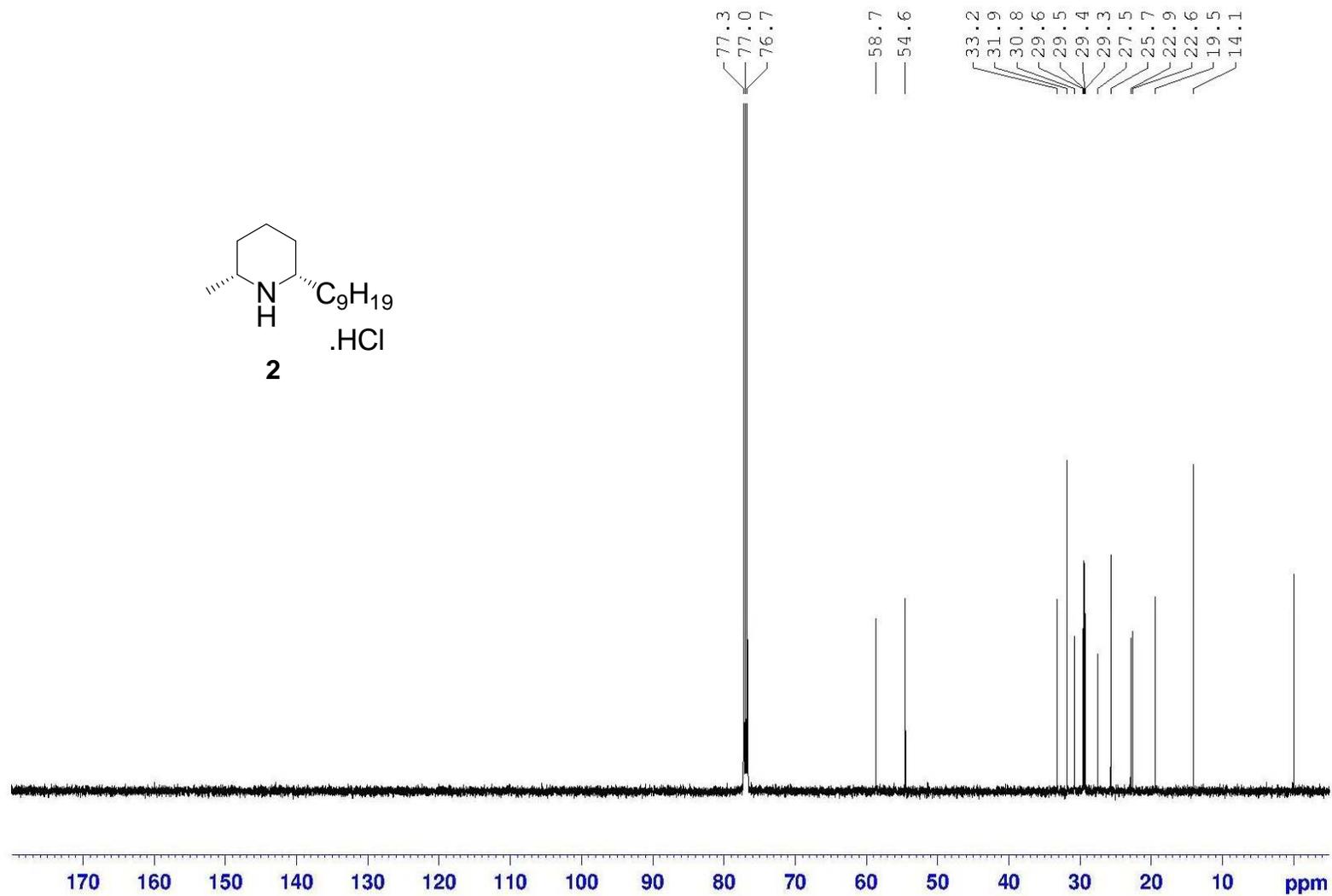


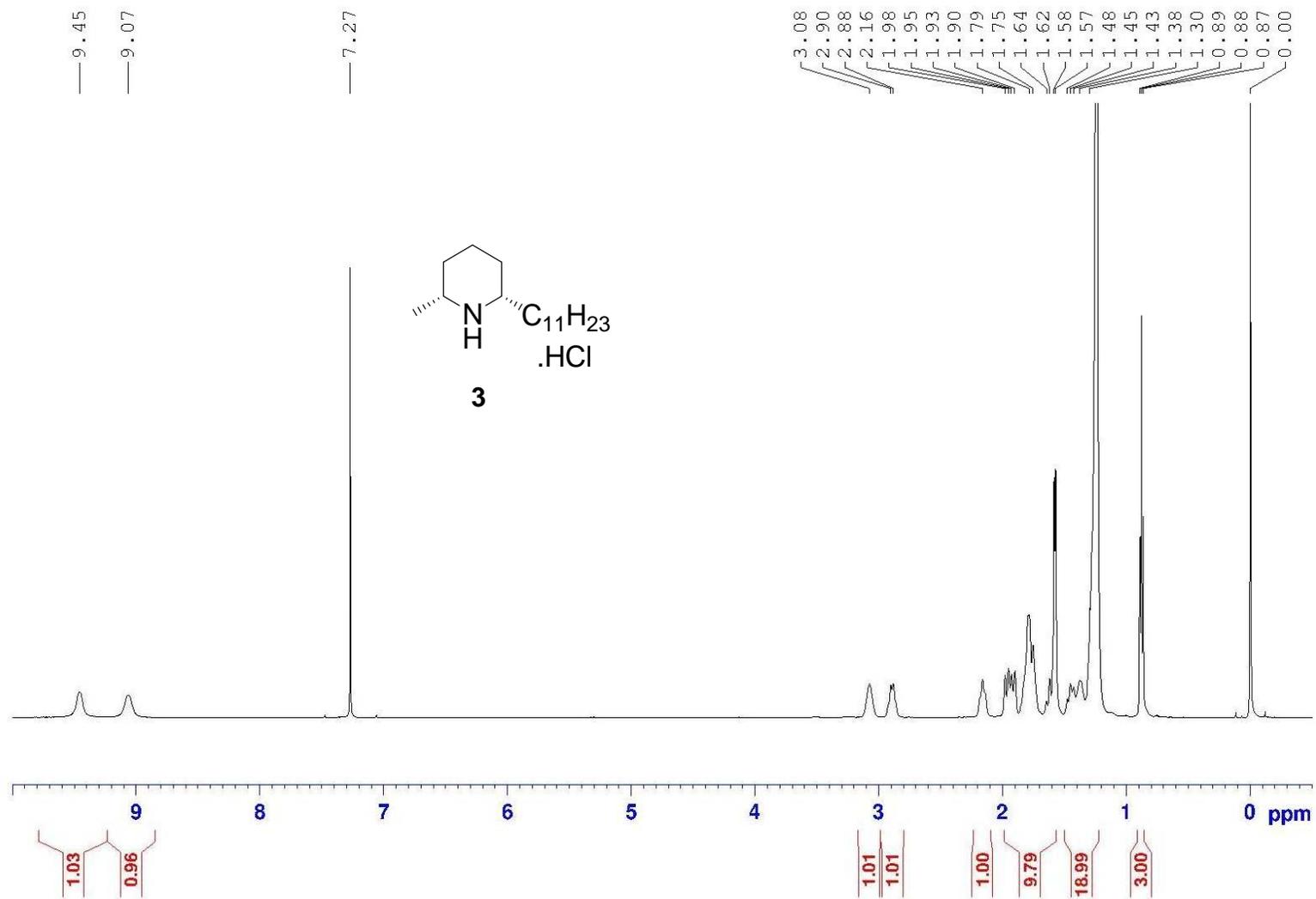


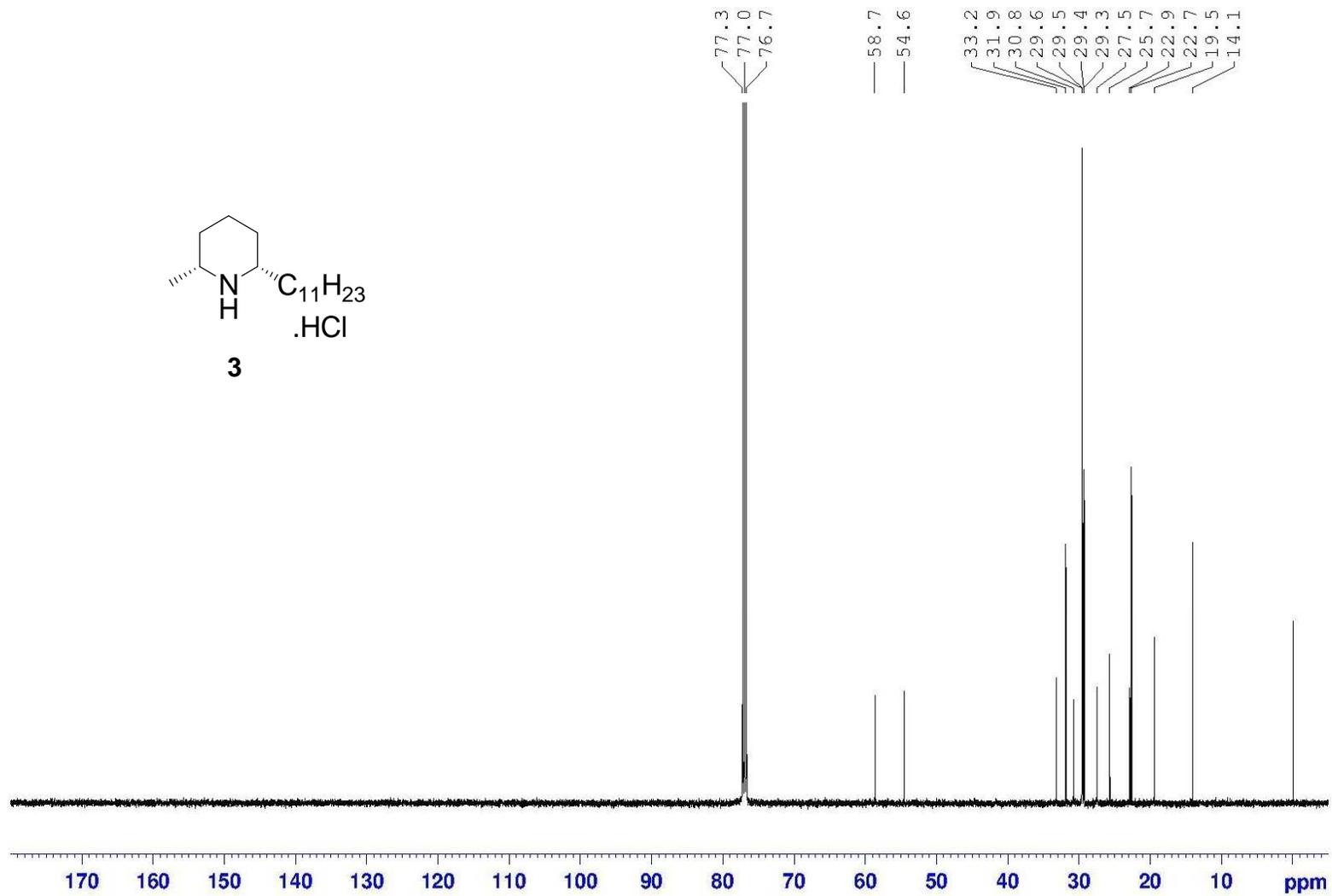




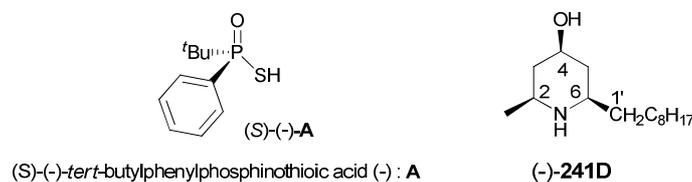








^{13}C NMR spectroscopy confirms the existence of a single enantiomer by using (*S*)-(-)-*tert*-butylphenylphosphinothioic acid (-)-**A** as a chiral solvating agent¹⁵.



The ^{13}C NMR spectra of (-)-241D, and its salt (-)-241D•(-)-A [44 μmol of (-)-241D in the presence of 1.05 molar equivalent of (-)-A] were recorded in CDCl_3 . (Table below)

Table : ^{13}C NMR data for (-)-241D and (-)-241D•(-)-A in CDCl_3 .

N°	δ (-)-241D	δ (-)-241D•(-)-A
2	50.2	51.5
3	43.9	40.1
4	69.4	66.7
5	41.7	37.2
6	54.8	55.8
C1'	36.7	33
C2' to C8'	31.9 ; 29.7 ; 29.5 ; 29.5 ; 29.3 ; 26 ; 22.7	31.9 ; 29.5 ; 29.4 ; 29.2 ; 29.1 ; 25.5 ; 22.7
Me-C2	22.4	19.1
C9'	14.1	14.1

* δ CSA (**A**): *t*-Bu group (δ :25.1; 36.2, $^1J_{\text{CP}} = 73.8$ Hz) and aromatics C (δ :127.0; $^2J_{\text{CP}} = 11.2$ Hz ; 129.8; $^2J_{\text{CP}} = 2.1$ Hz; 132.7; $^3J_{\text{CP}} = 9.3$ Hz; 137.9 ; $^1J_{\text{CP}} = 90.7$ Hz)

A characteristic downfield shift is observed for the carbons α to the nitrogen (C-2, C-6) and C-3, C-4 and C-5 (β -carbons) became shielded upon protonation of nitrogen (Spectrum page 34).

Then the ^{13}C NMR spectrum of two samples of enantioenriched with (+)-241-D (8:2 er - Spectrum in red) and (6:4 er - Spectrum in green) were recorded in the presence of 1.05 equivalent of (-)-A. As shown in figure page 37, the magnetic nonequivalence was particularly visible for C6, C2, C3, C5 and C1'.

