Electronic Supporting Information

Chemoselective and stereoselective lithium carbenoid mediated cyclopropanation of acyclic allylic alcohols

M. J. Durán-Peña,[a,†] M. E. Flores-Giubi,[a,†] J. M. Botubol-Ares,[a] L. M. Harwood,[b] I. G. Collado,[a] A. J. Macías-Sánchez[a] and R. Hernández-Galán[a]

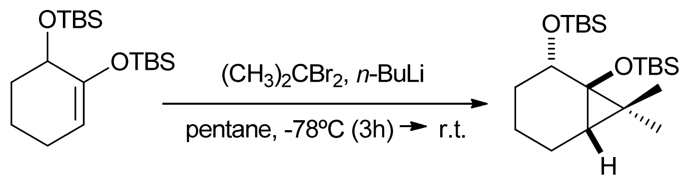
[a]*Departamento de Química Orgánica, Facultad de Ciencias, Campus Universitario Río San Pedro s/n, Torre sur, 4º planta, Universidad de Cádiz, 11510, Puerto Real, Cádiz, Spain. E-mail: rosario.hernandez@uca.es, antoniojose.macias@uca.es*

[b]*Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, United Kingdom*

Table of contents:

PART A: TABLE S1

Table S1. Optimization of cyclopropanation of compound 1 with 2,2-dibromopropane



1 **2**

	Concentration (nº equiv.)		
Entry	**2,2-dibromopropane**	***n*-BuLi**	**Yield (%)**
1	1	2	12
2	2	4	21
3	4	6	40
4	4	8	50

PART B : Discussion of spectroscopic observations for compounds 10 and 11

Dichlorocyclopropanation compound **10** showed ions in its HRMS (APGC$^+$) at *m/z*= 237.0809, 219.0710, 201.1050 and 183.0941, consistent with formulae $C_{11}H_{19}OCl_2$, $C_{11}H_{17}Cl_2$, $C_{11}H_8OCl$ and $C_{11}H_{16}Cl$ respectively, that correspond to the protonated molecular ion, the loss of one molecule of water, the loss of a molecule of HCl and the loss of a molecule of water and another of HCl from a protonated ion of molecular formula $C_{11}H_{19}OCl_2$. The presence of two chlorine atoms in the compound **10** was confirmed by a quaternary carbon resonance at δ_C 72.0 (C-2') ppm in its ^{13}C NMR spectrum. On the other hand, spectroscopic data for compound **10** showed a homonuclear gCOSY correlation between signals at δ_H 5.45 (H-2) and 4.16 (C$\underline{H_2}$-1) ppm and gHMBC correlations between signal at δ_C 72.0 (C-2') ppm and *gem*-dimethyl group signals at δ_H 1.33 and 1.15 ppm. These data are consistent with a dichlorocyclopropanation on the distal double bond of geraniol, leading to (*E*)-5-(2,2-dichloro-3,3-dimethylcyclopropyl)-3-methylpent-2-en-1-ol (**10**).

Double cyclopropanation compound **11** showed ions in its HRMS (APGC$^+$) at *m/z*= 265.0302 [M+H-H$_2$O-HCl]$^+$, 247.0611 [M+H-2HCl]$^+$ and 229.0539 [M+H-H$_2$O-2HCl]$^+$, consistent with formulae $C_{12}H_{16}Cl_3$, $C_{12}H_{17}OCl_2$ and $C_{12}H_{15}Cl_2$ respectively, that correspond to the loss of one molecule of water and another of HCl, the loss of two molecules of HCl and the loss of one molecule of water and two of HCl from a protonated ion of molecular formula $C_{12}H_{19}Cl_4O$. Furthermore, compound **11** presented signals in its ^{13}C-NMR spectrum at δ_C 70.1 and 71.7 ppm, corresponding to quaternary carbons substituted with chlorine atoms, consistent with a double cyclopropanation. NOESY 2D effects (Fig. S.1) between signals, at δ_H 3.78 (C$\underline{H_2}$-1) and 1.23 ((C$\underline{H_3}$)C-3') ppm and δ_H 1.54 (H-1') ppm, were consistent with stereochemistry for this compound as (1'*R**,3'*S**,1'''*S**).

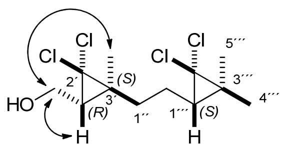
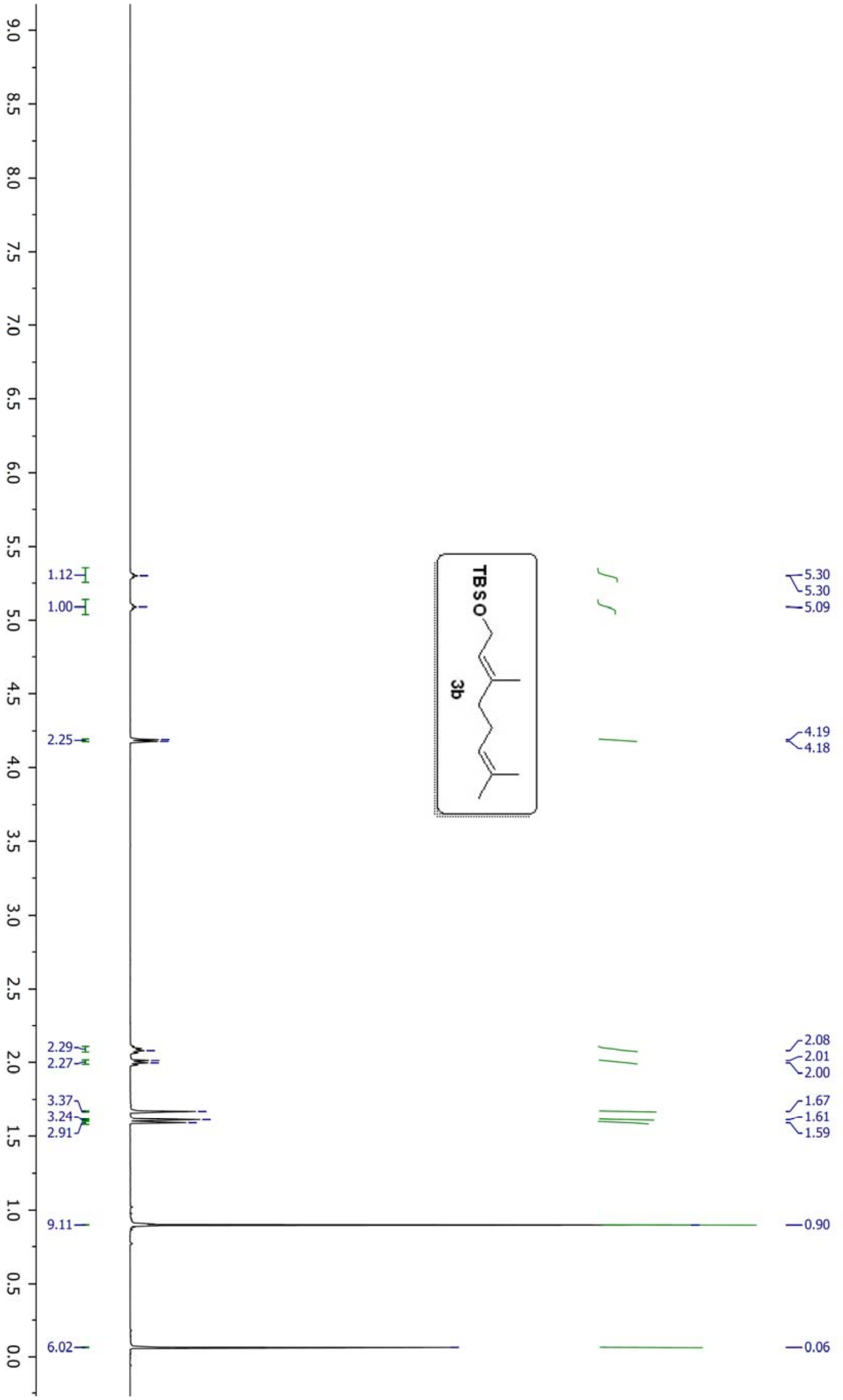
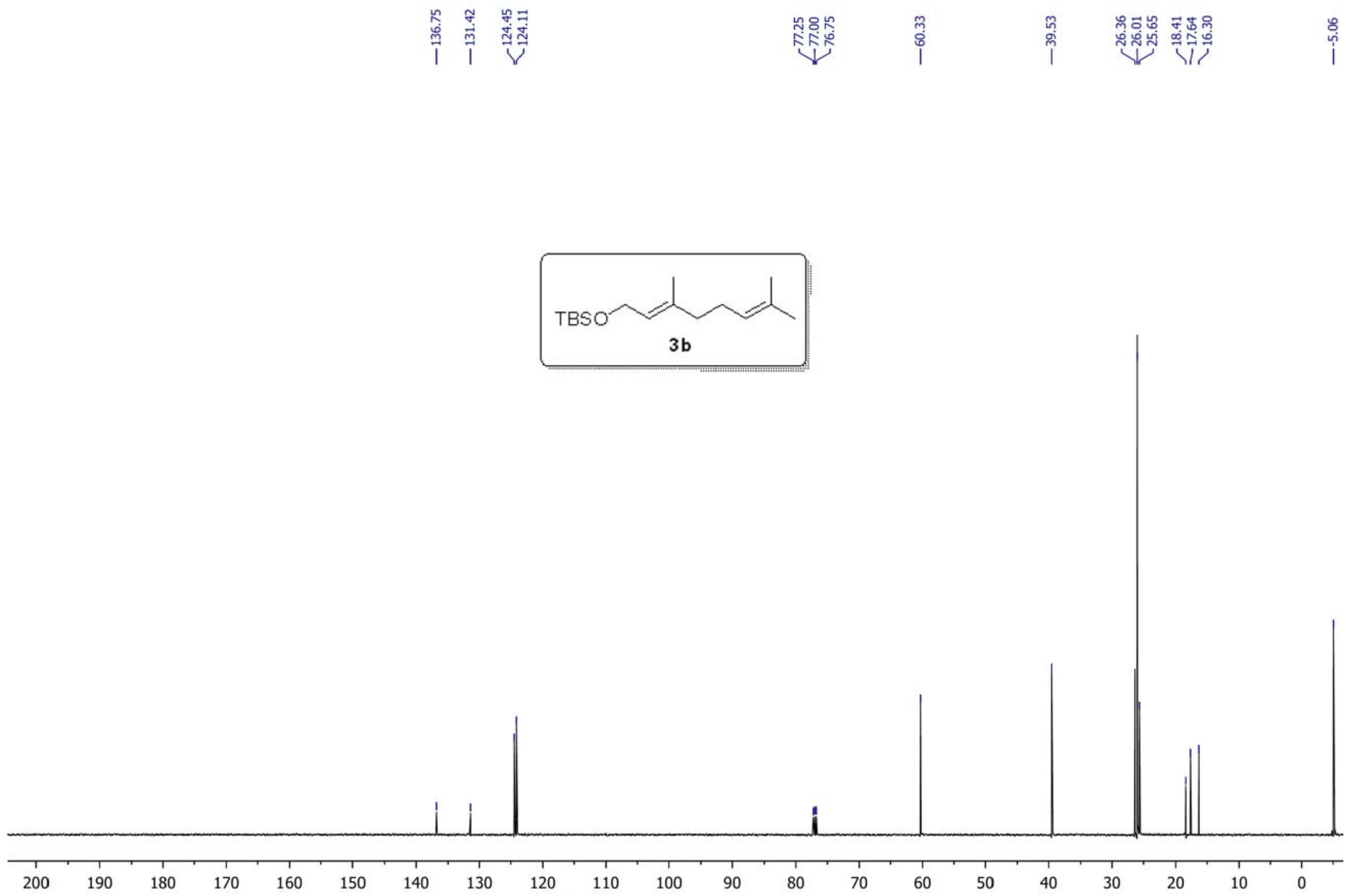


Fig. S1 Selected NOESY 2D correlations for compound **11**.

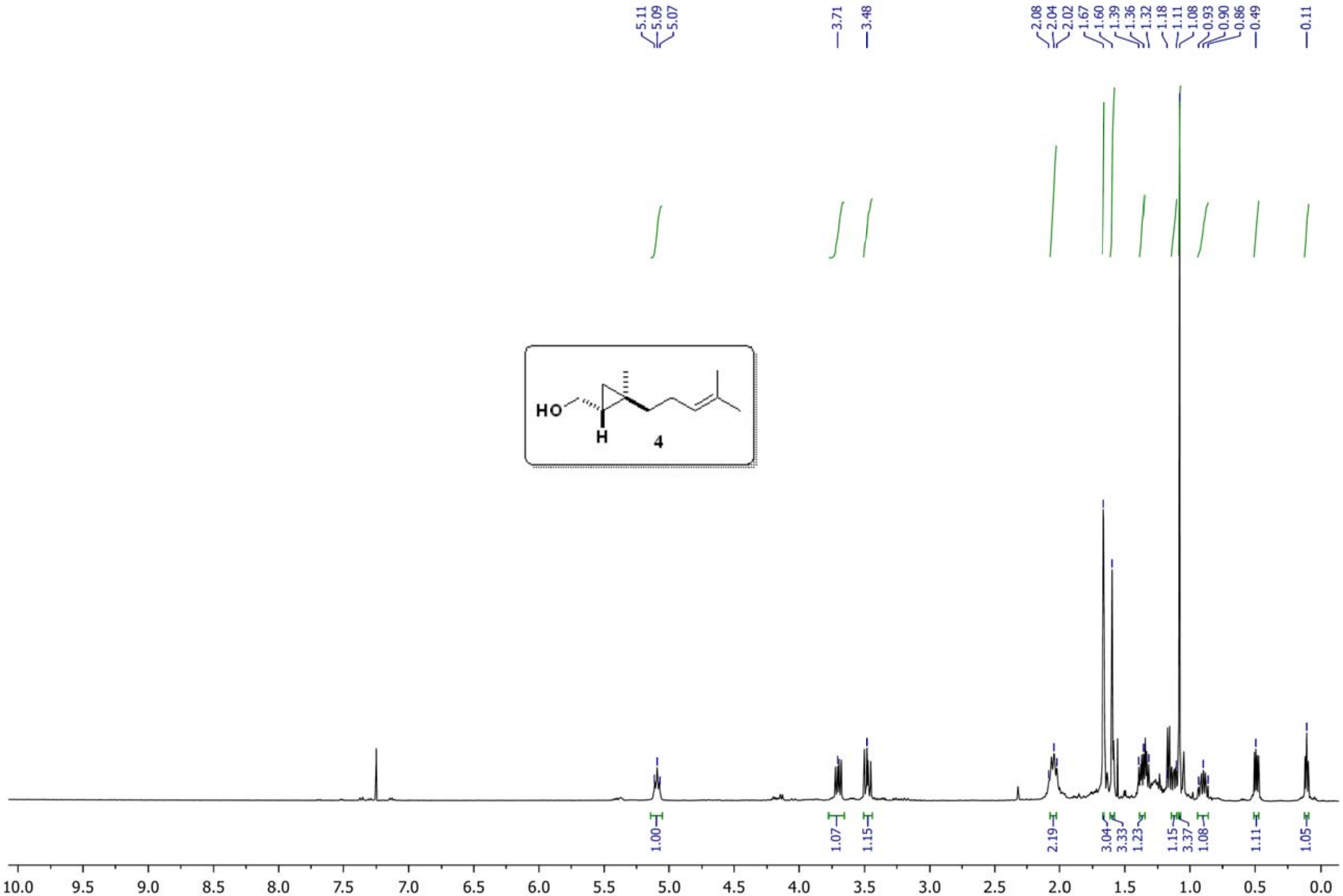
PART C : ^{1}H,^{13}C-NMR and selected 2D NMR spectra



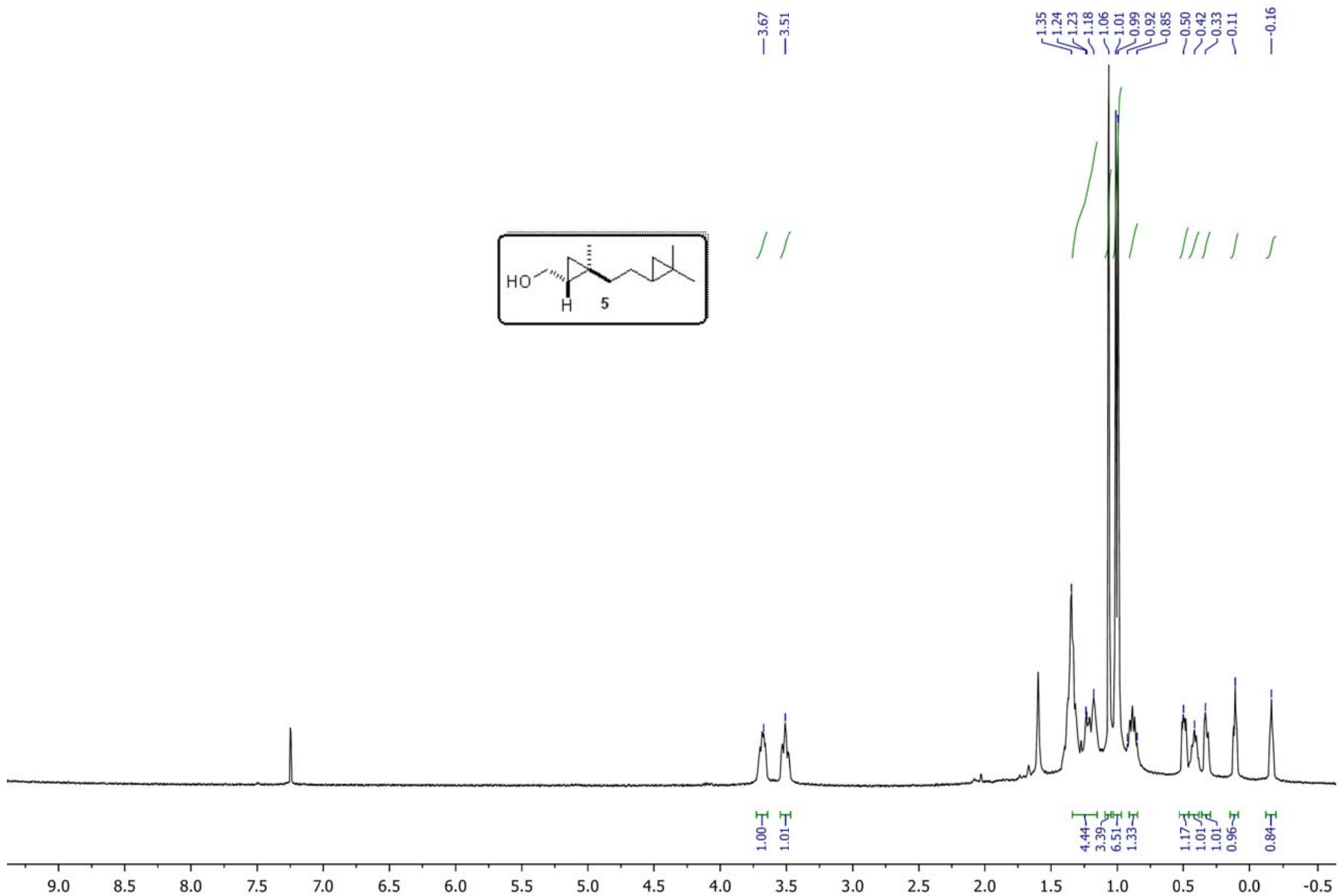
400 MHz ^{1}H NMR of compound **3b** in $CDCl_3$



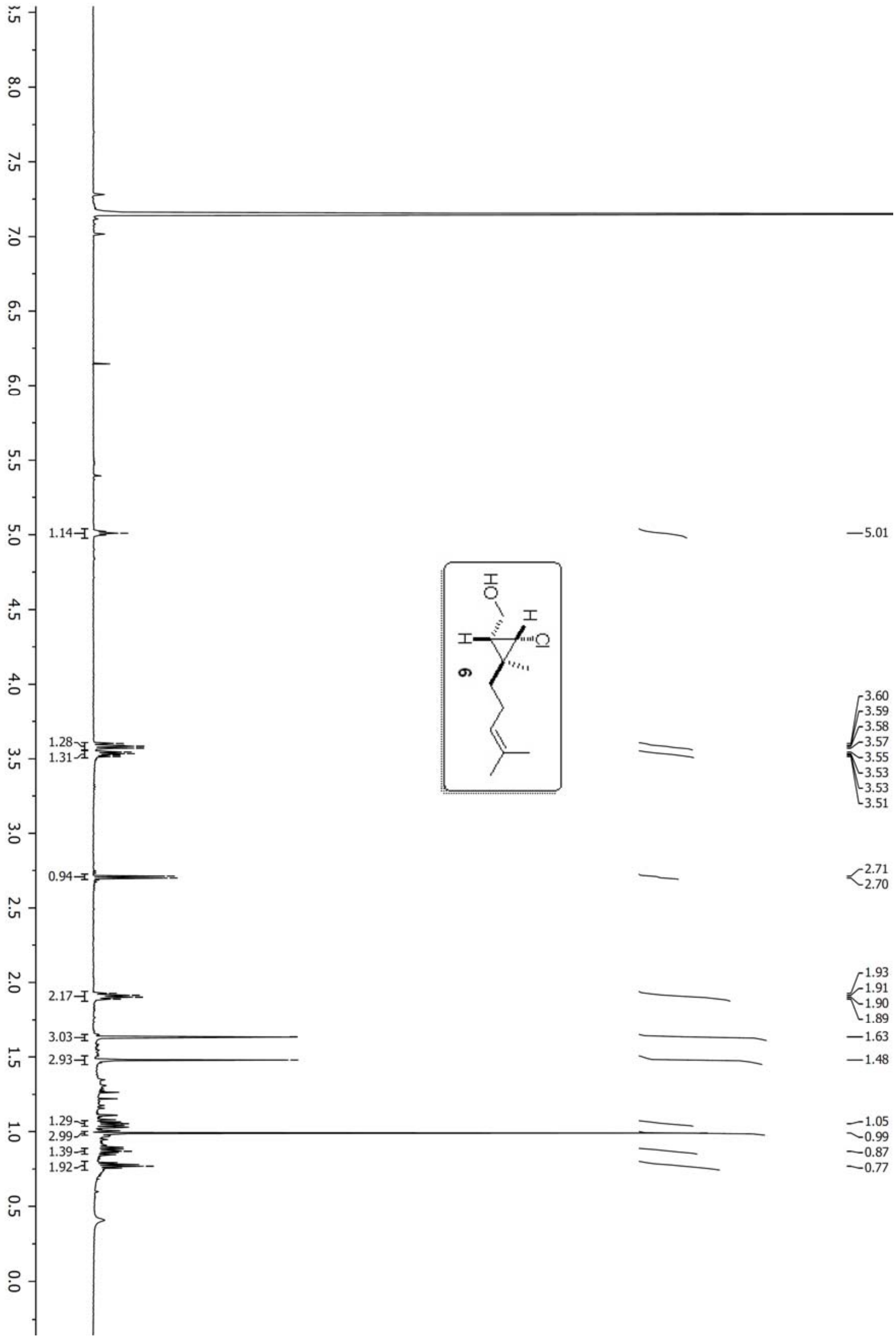
100 MHz ^{13}C NMR of compound **3b** in $CDCl_3$



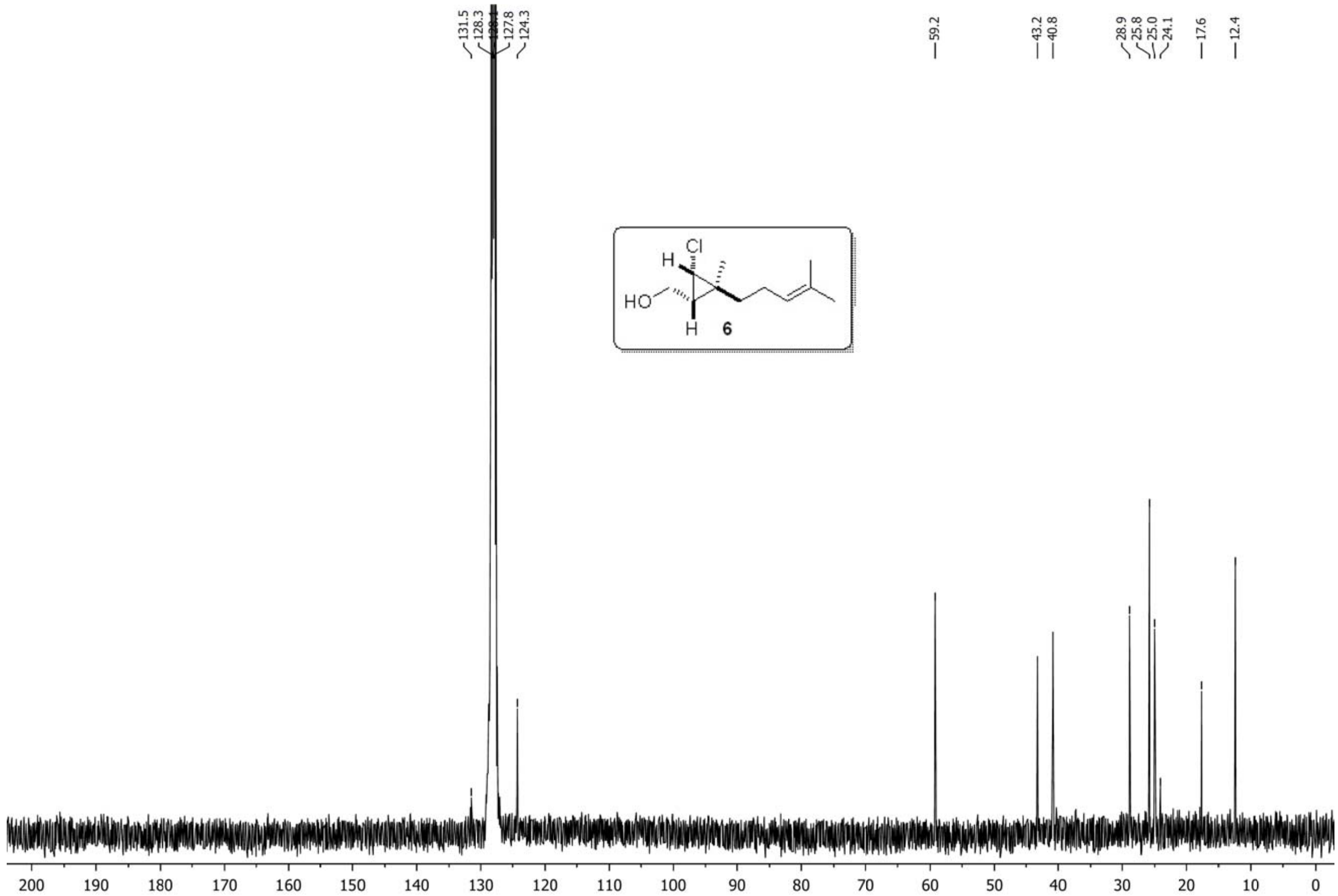
400 MHz ^{1}H NMR of compound **4** in $CDCl_3$



400 MHz ^{1}H NMR of compound **5** in $CDCl_3$

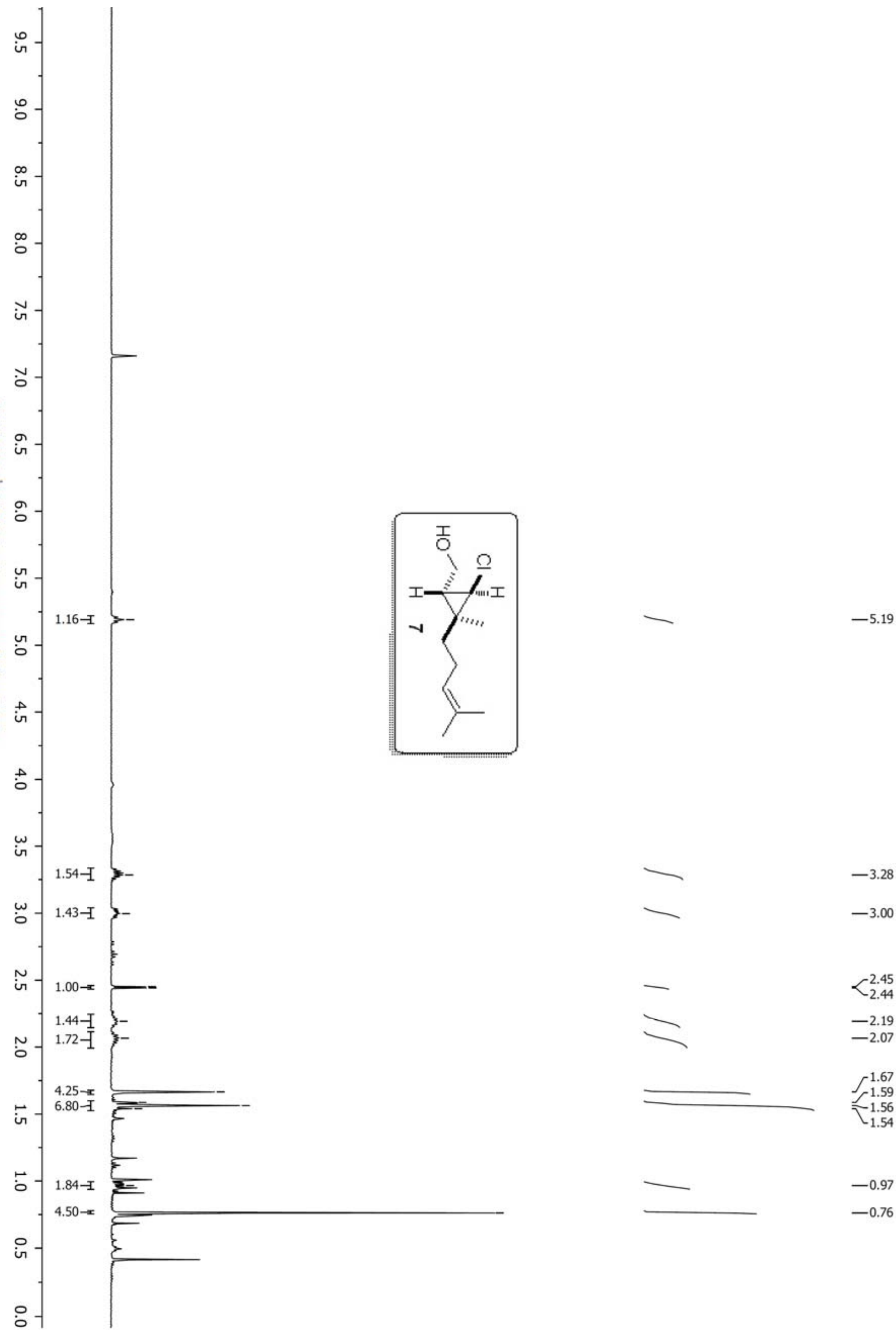


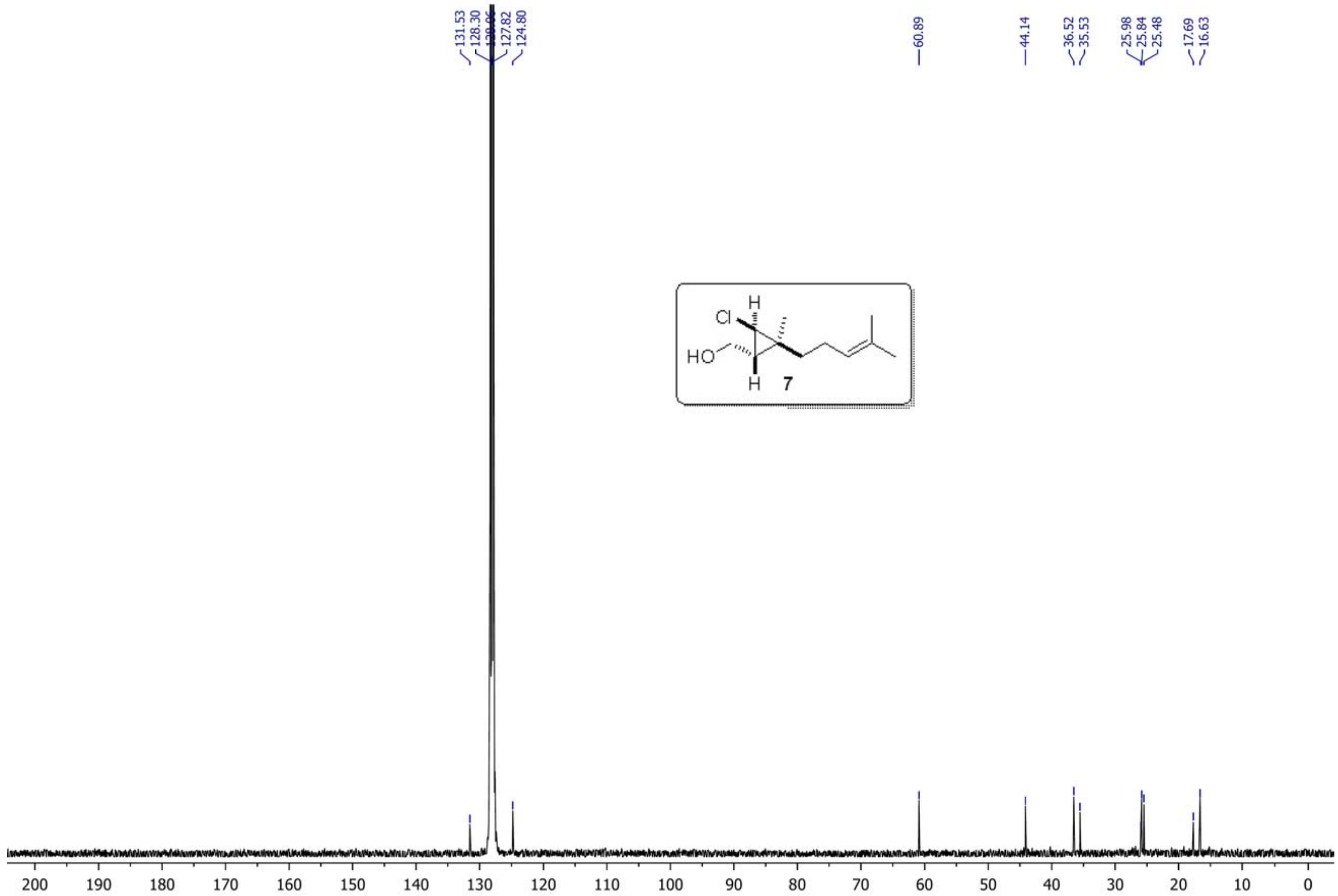
600 MHz ^1H NMR of compound **6** in C_6D_6



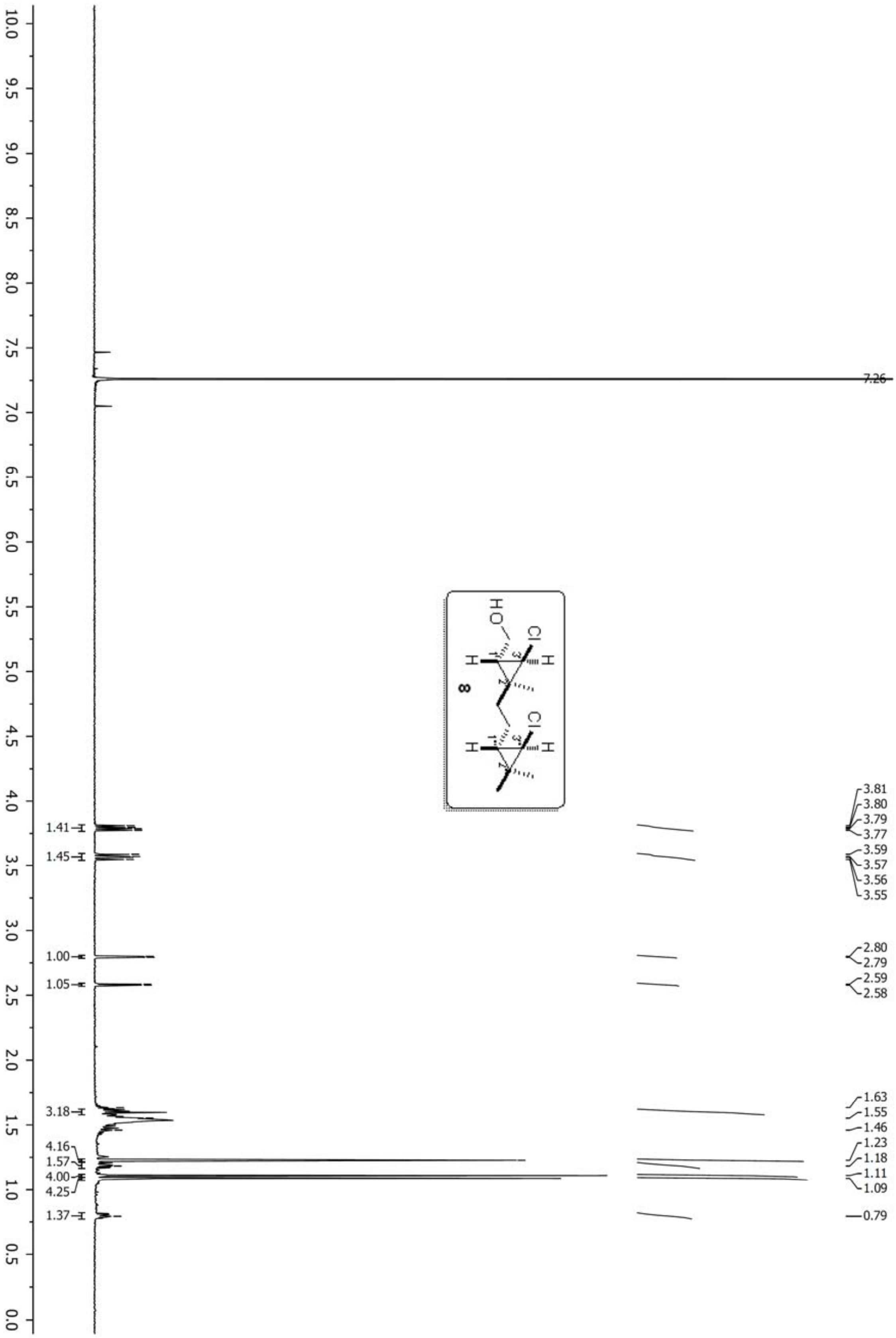
100 MHz ^{13}C NMR of compound **6** in C_6D_6

400 MHz ^{1}H NMR of compound 7 in C_6D_6

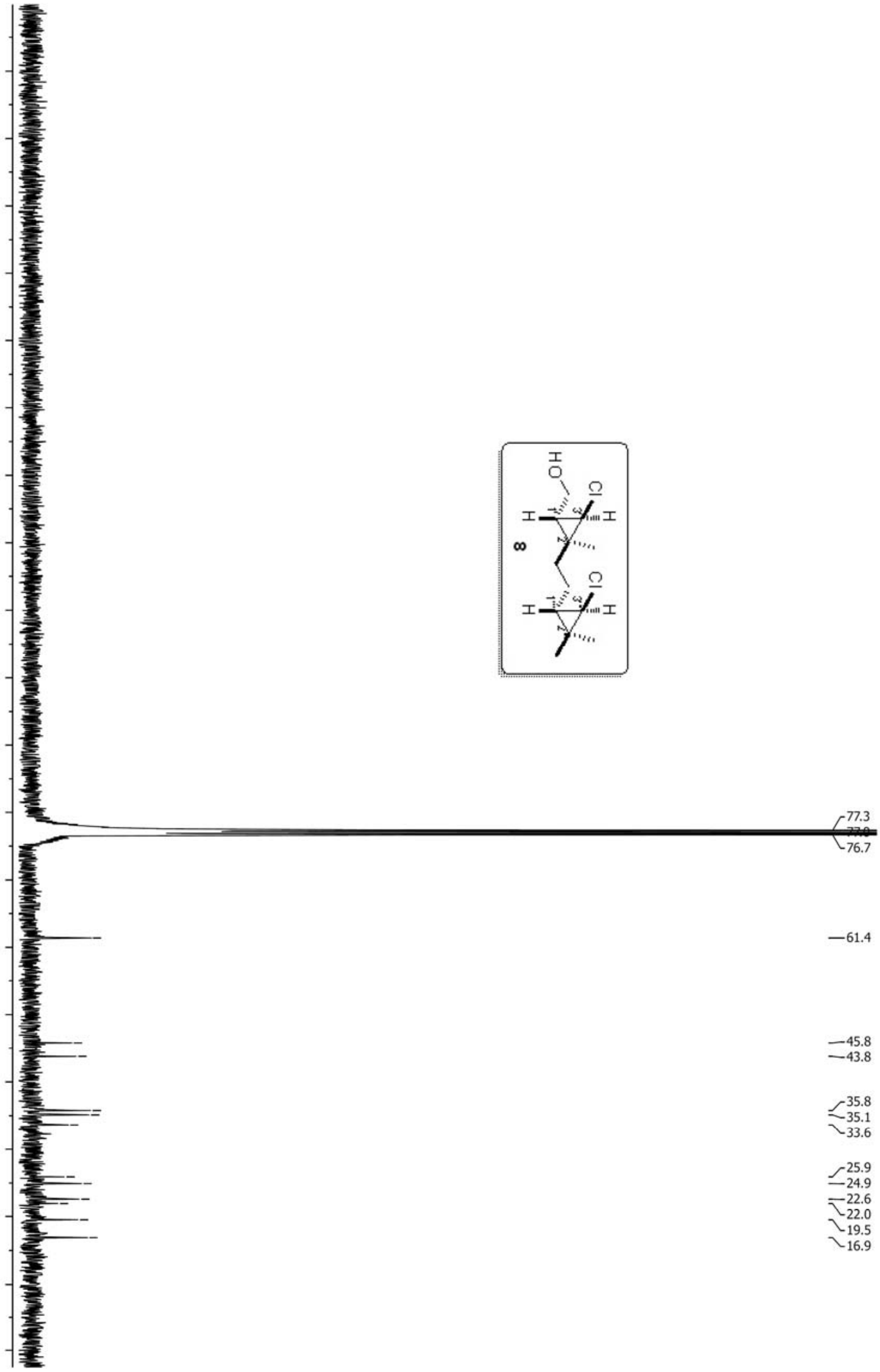




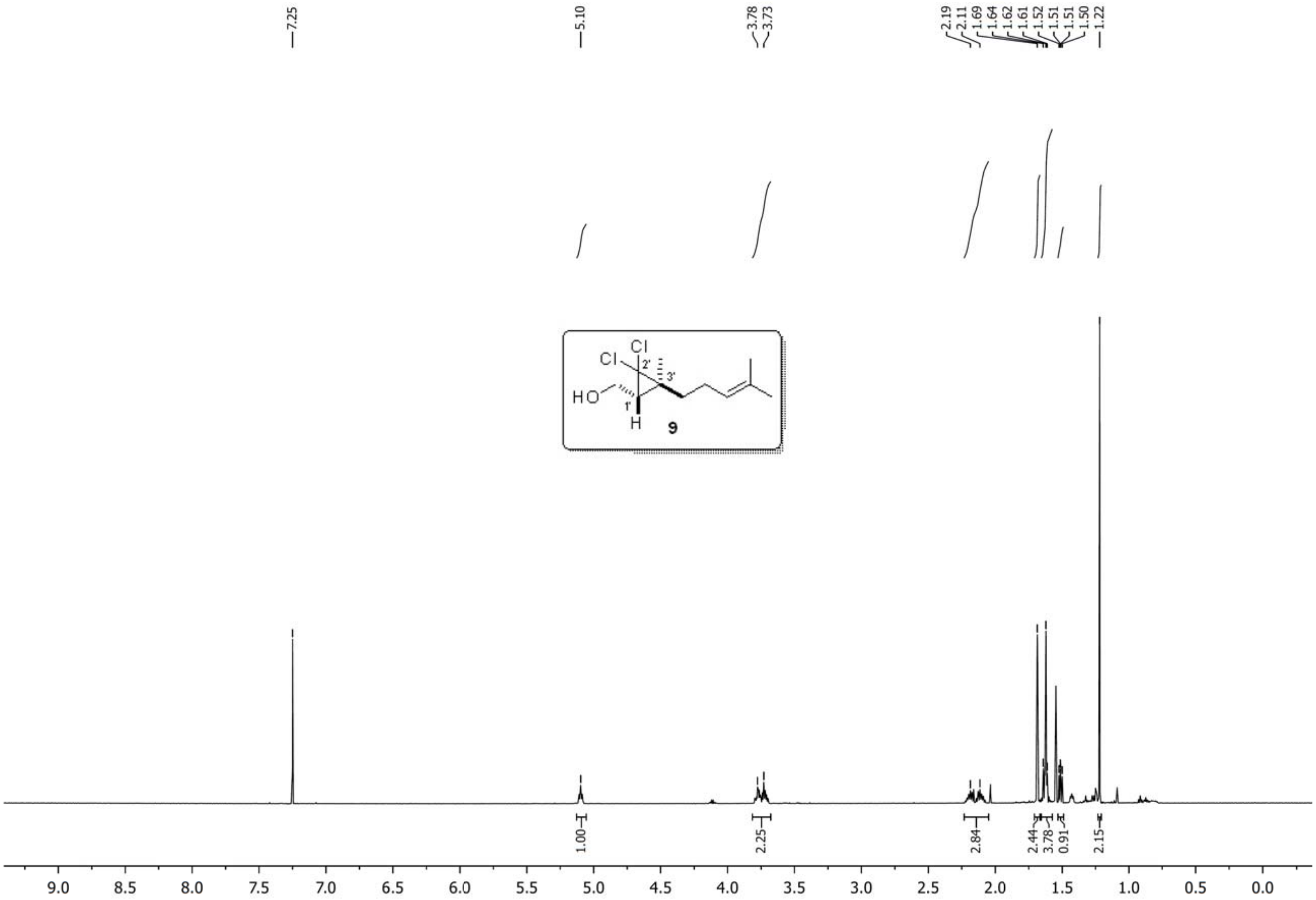
100 MHz ^{13}C NMR of compound **7** in C_6D_6



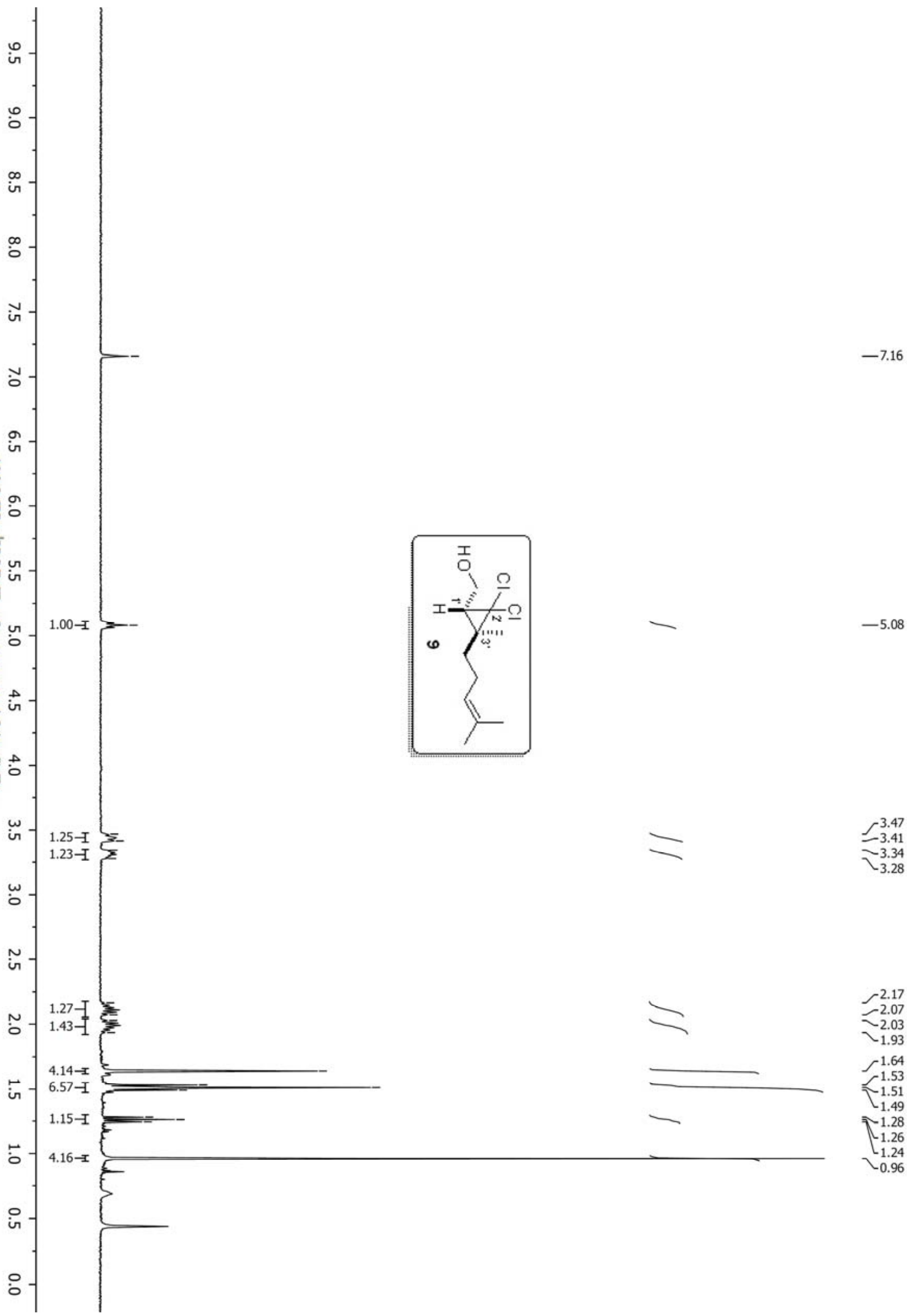
500 MHz ^{1}H NMR of compound **8** in $CDCl_3$



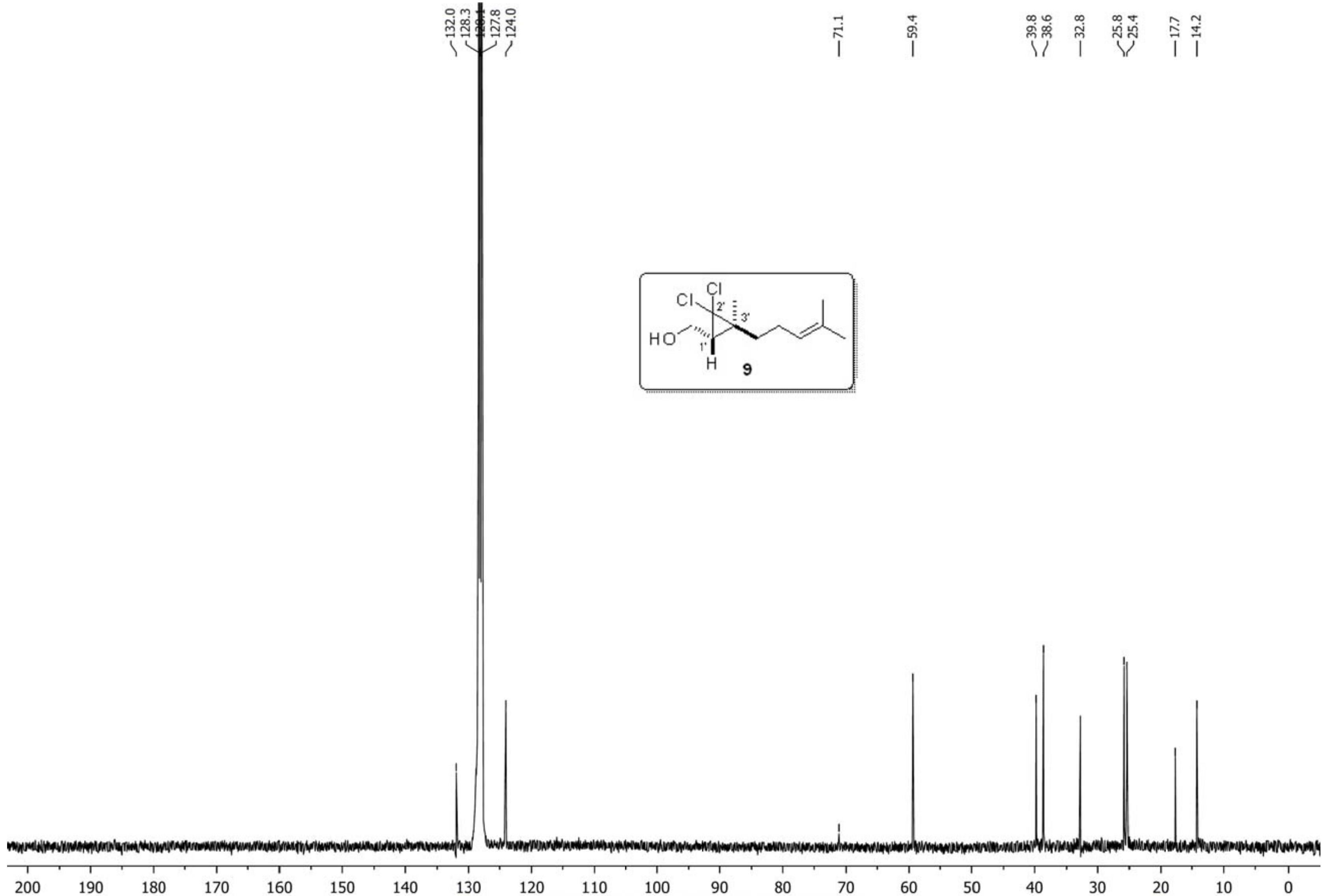
125 MHz ^{13}C NMR of compound **8** in $CDCl_3$



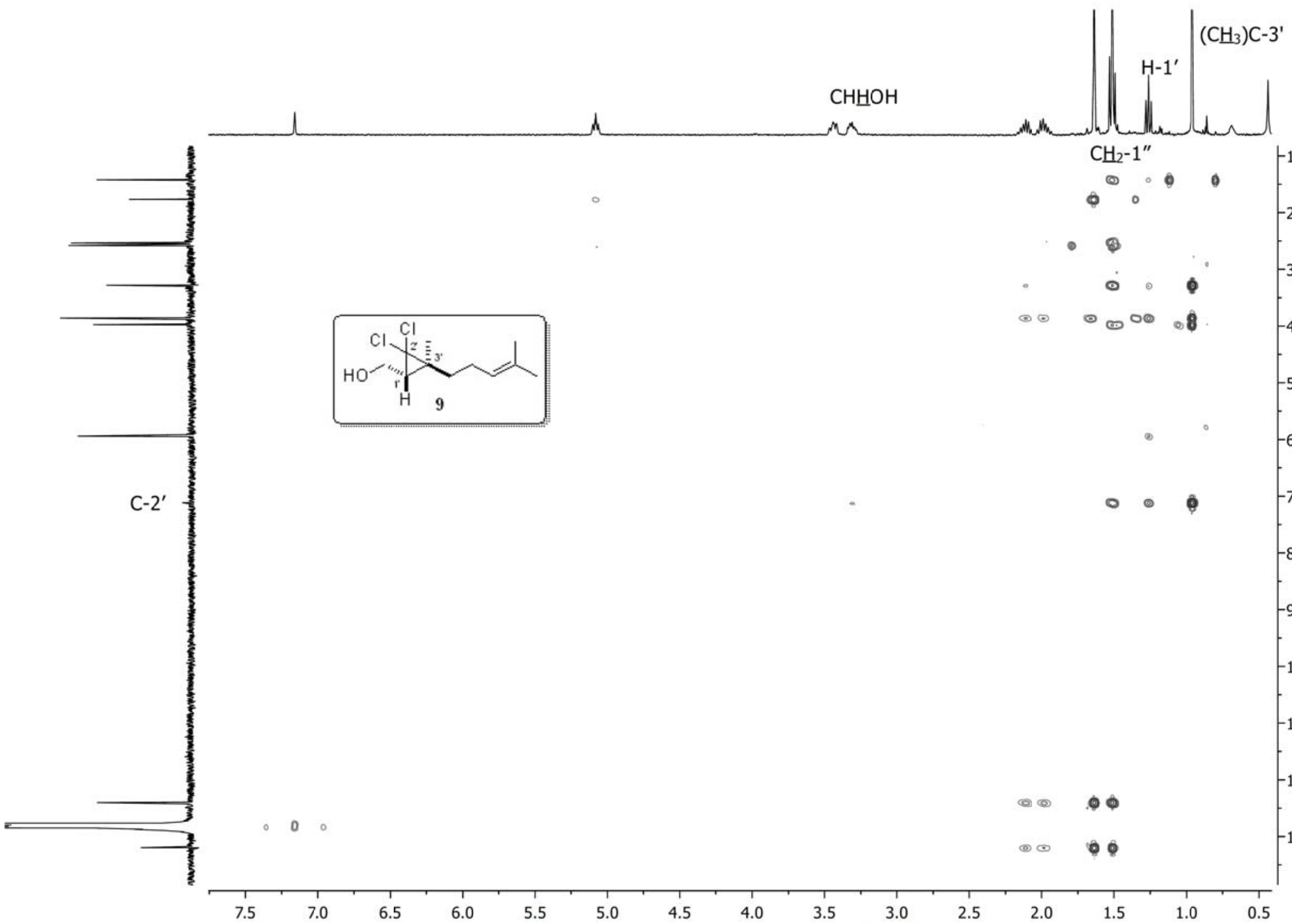
600 MHz ^{1}H NMR of compound **9** in $CDCl_3$



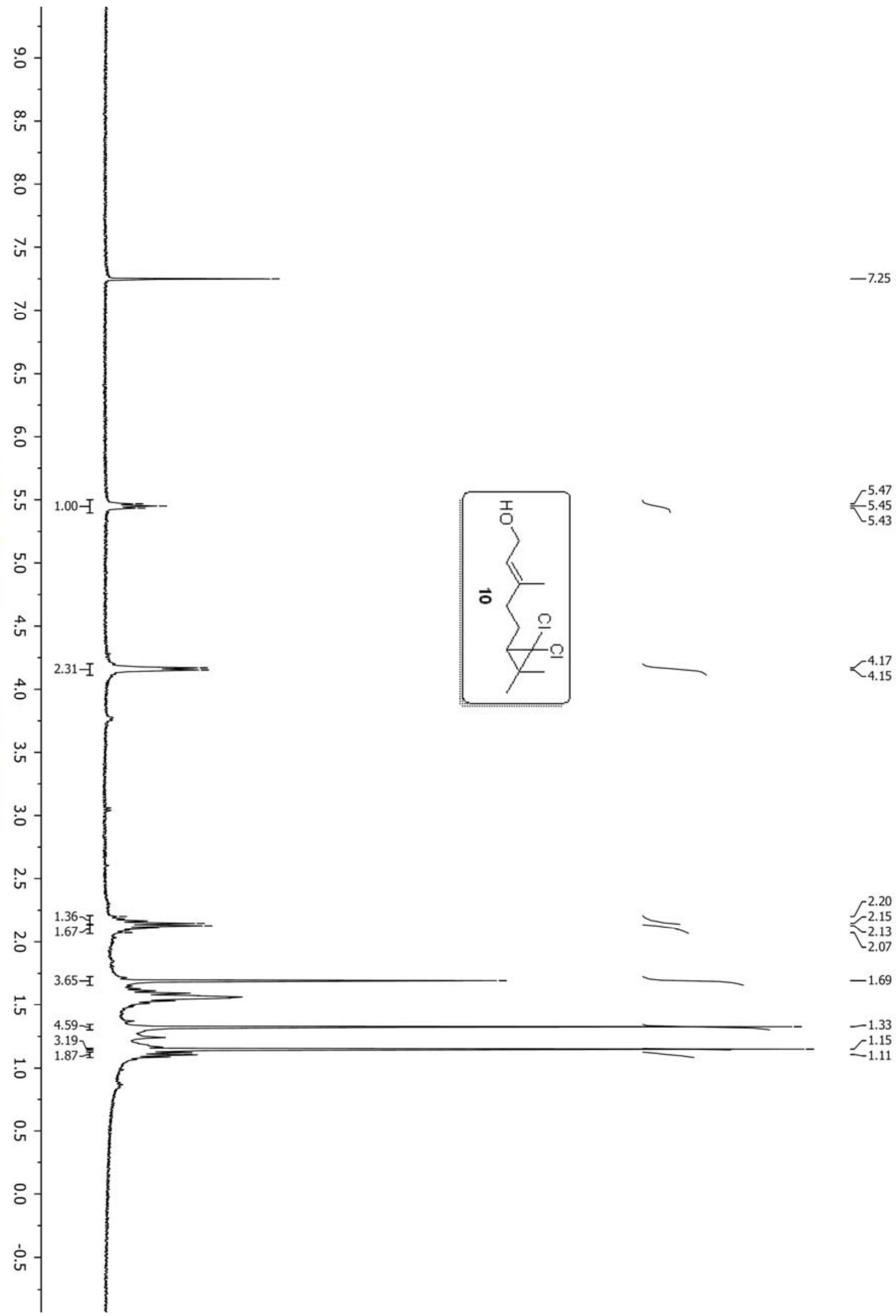
400 MHz ^1H NMR of compound **9** in C_6D_6



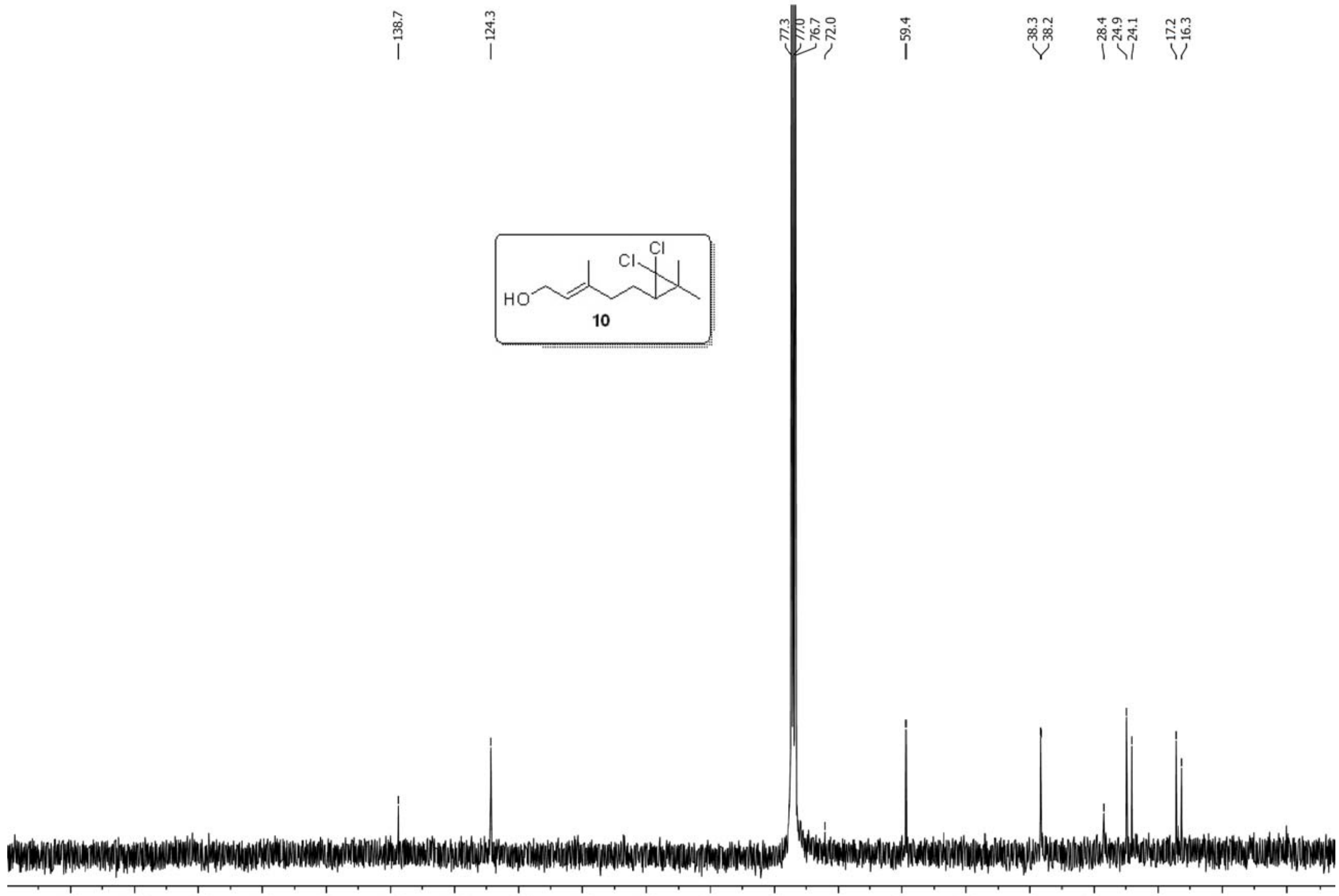
100 MHz ^{13}C NMR of compound **9** in C_6D_6



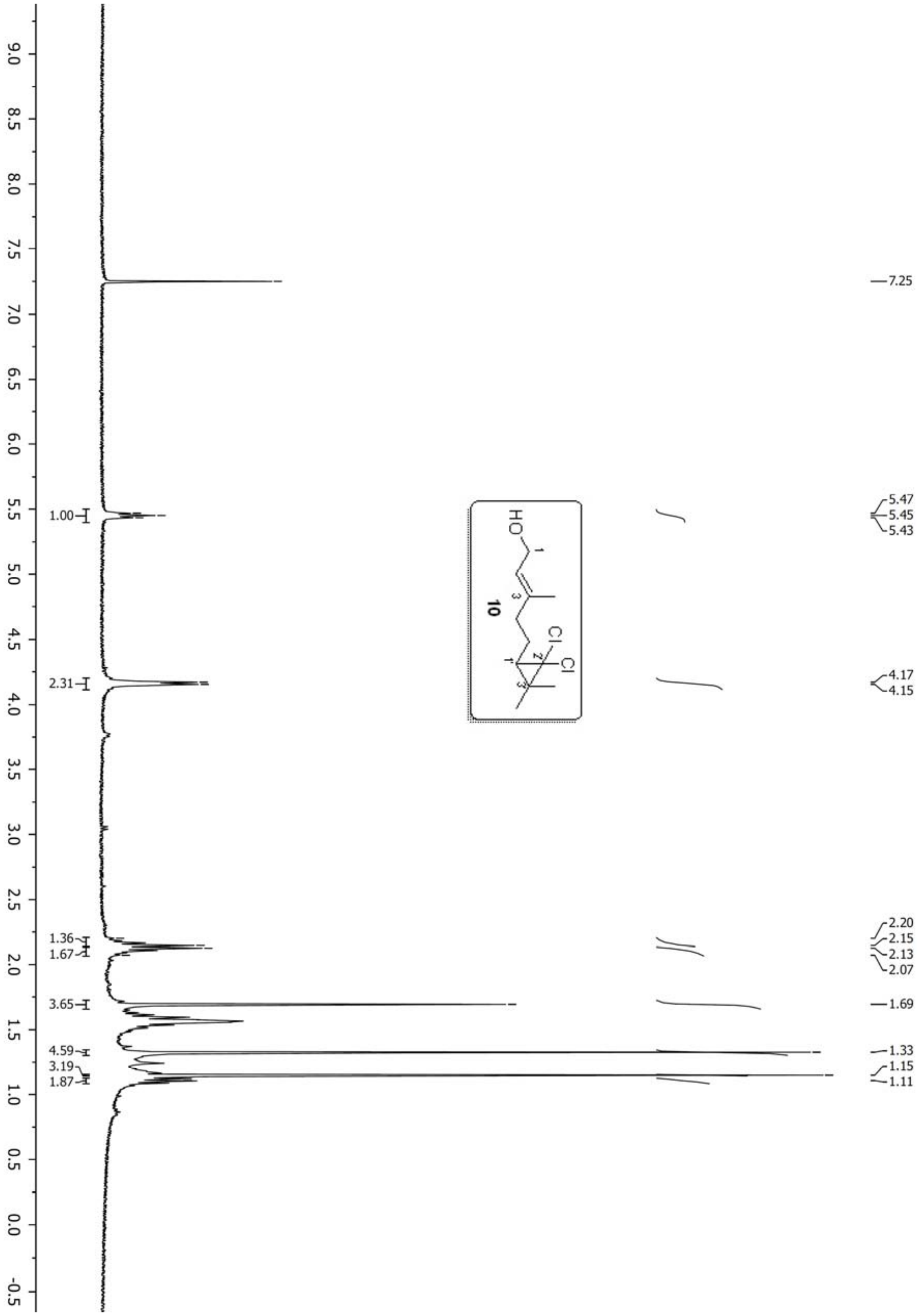
gHMBC correlation spectrum for compound **9** in C_6D_6



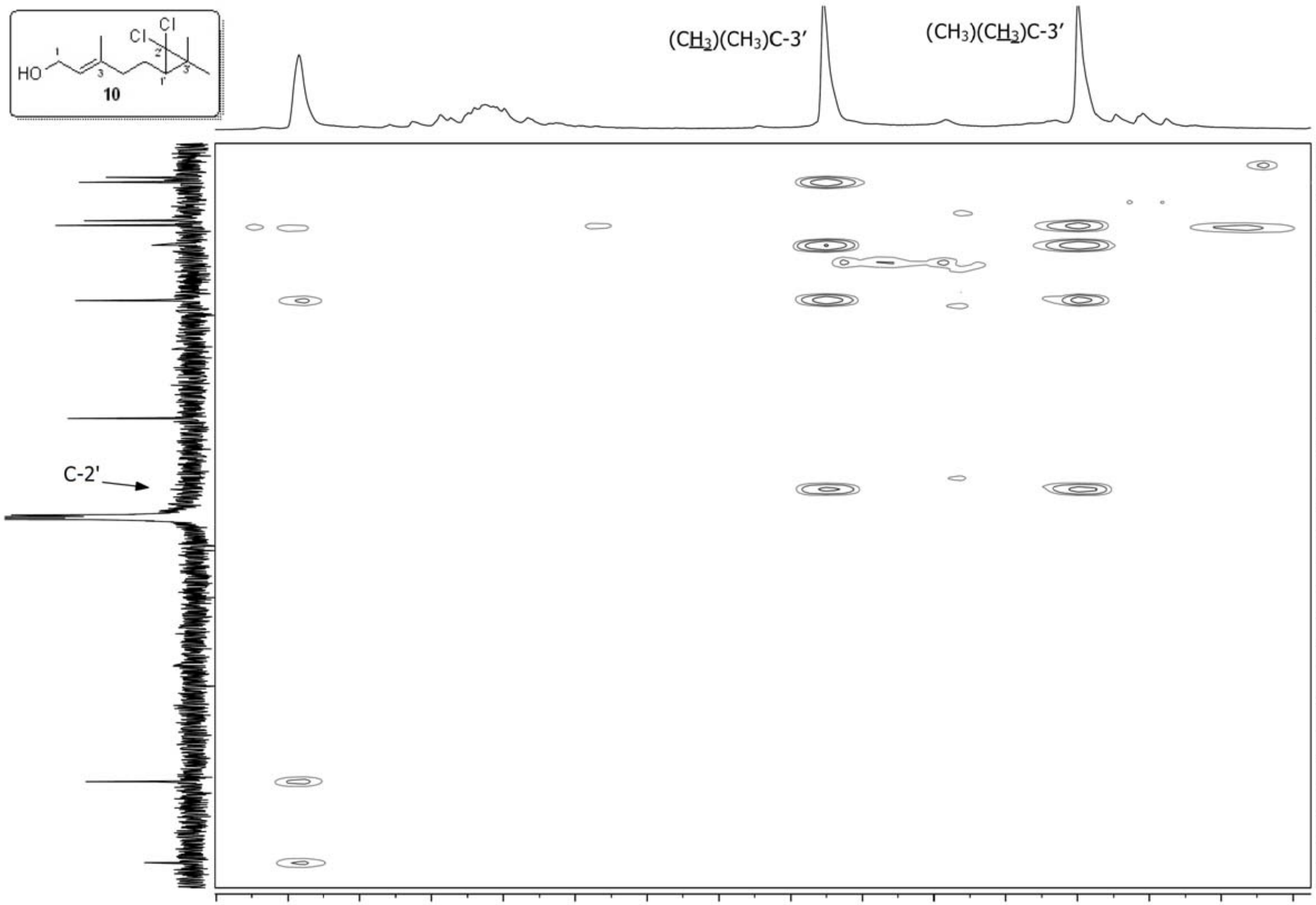
400 MHz ^{1}H NMR of compound **10** in $CDCl_3$



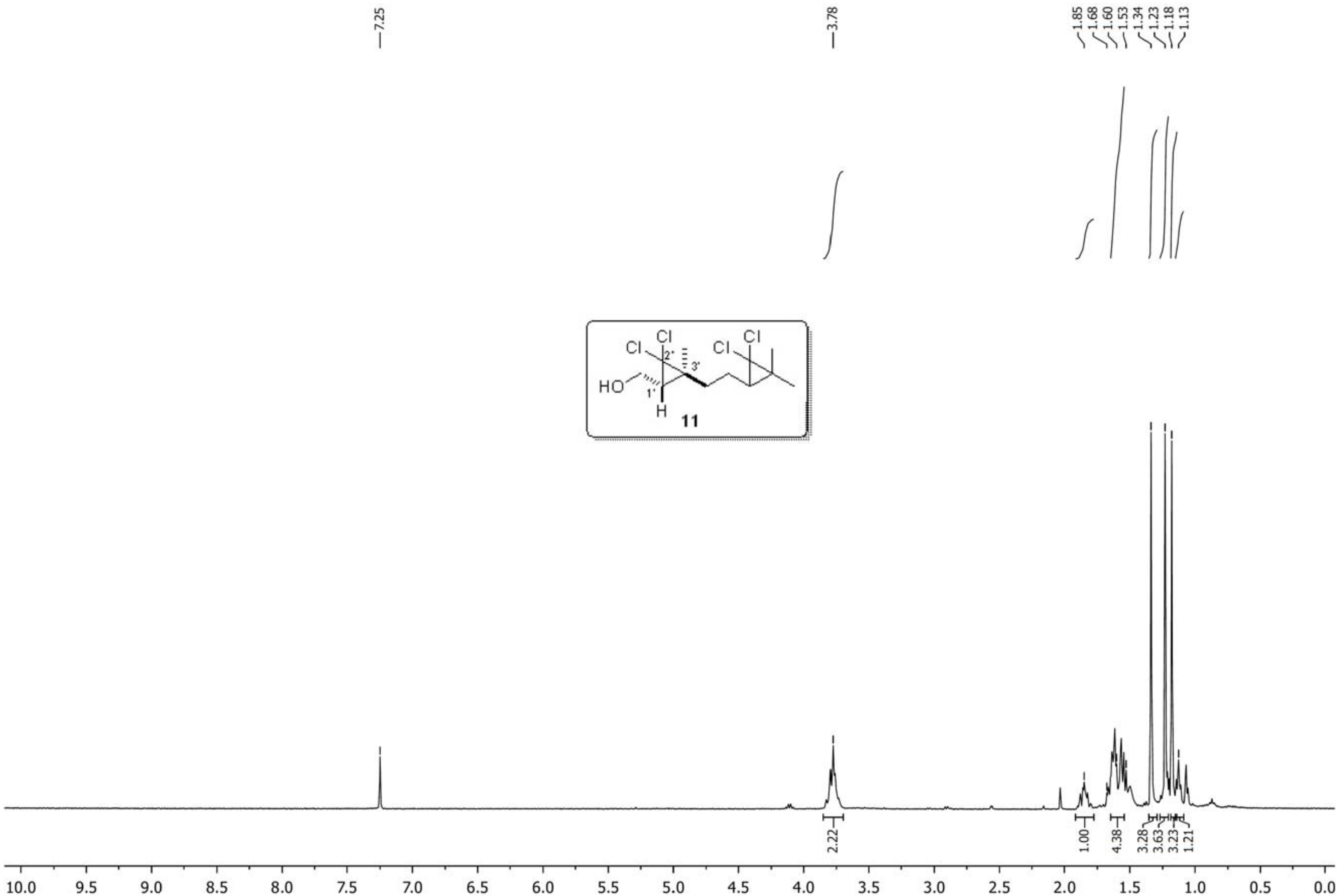
100 MHz ^{13}C NMR of compound **10** in $CDCl_3$



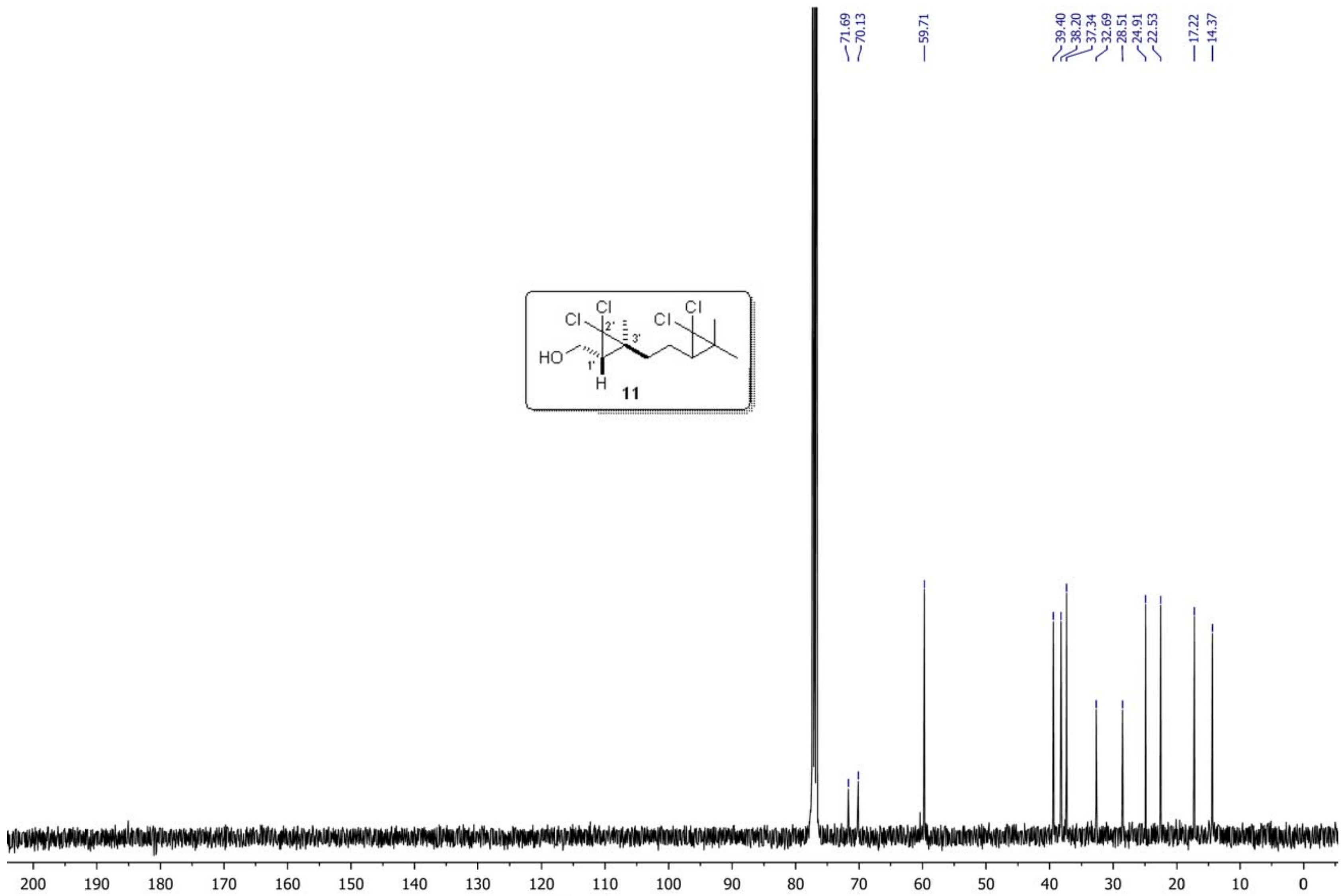
400 MHz ^{1}H NMR of compound **10** in $CDCl_3$



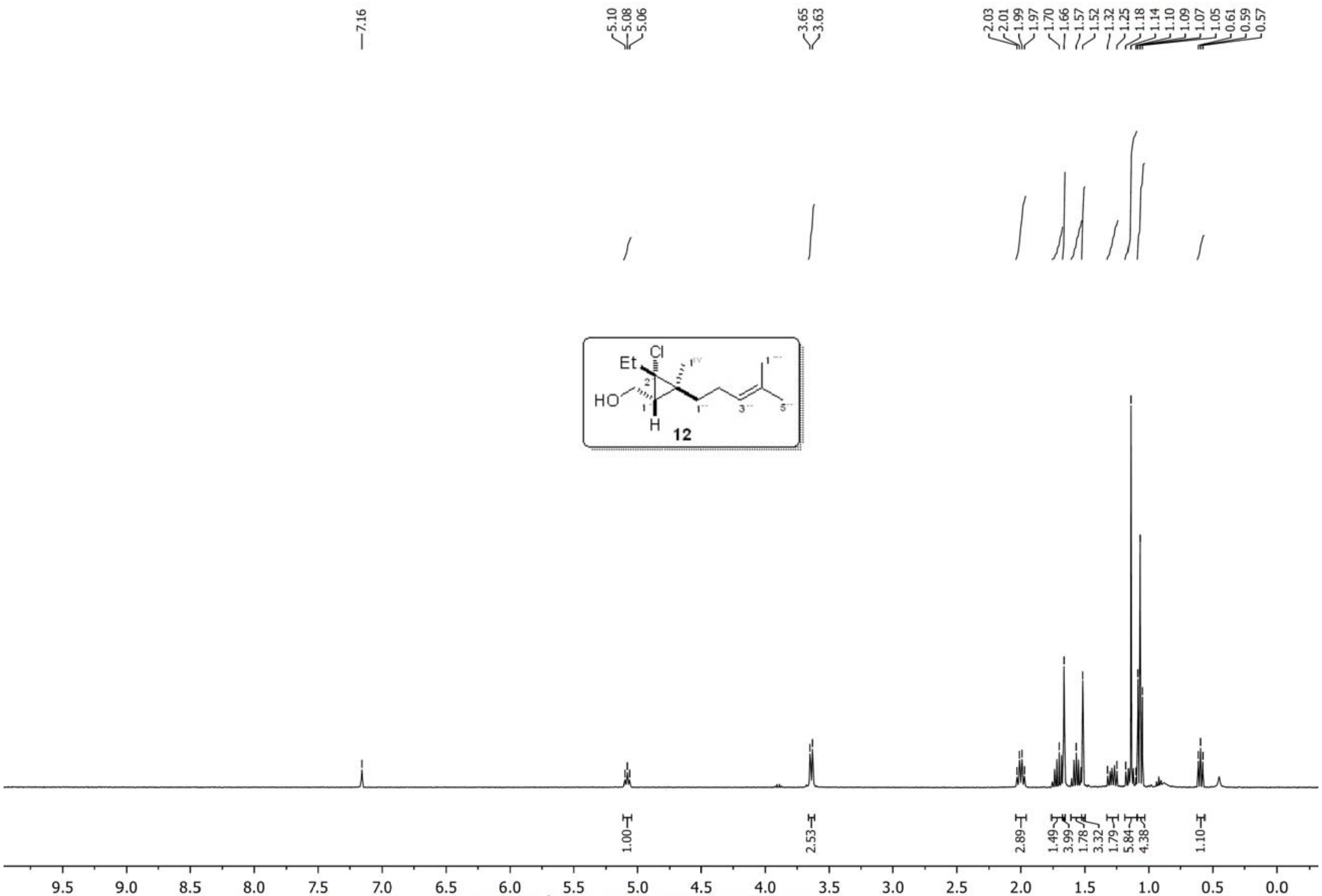
400 MHz gHMBC correlation spectrum for compound **10** in $CDCl_3$



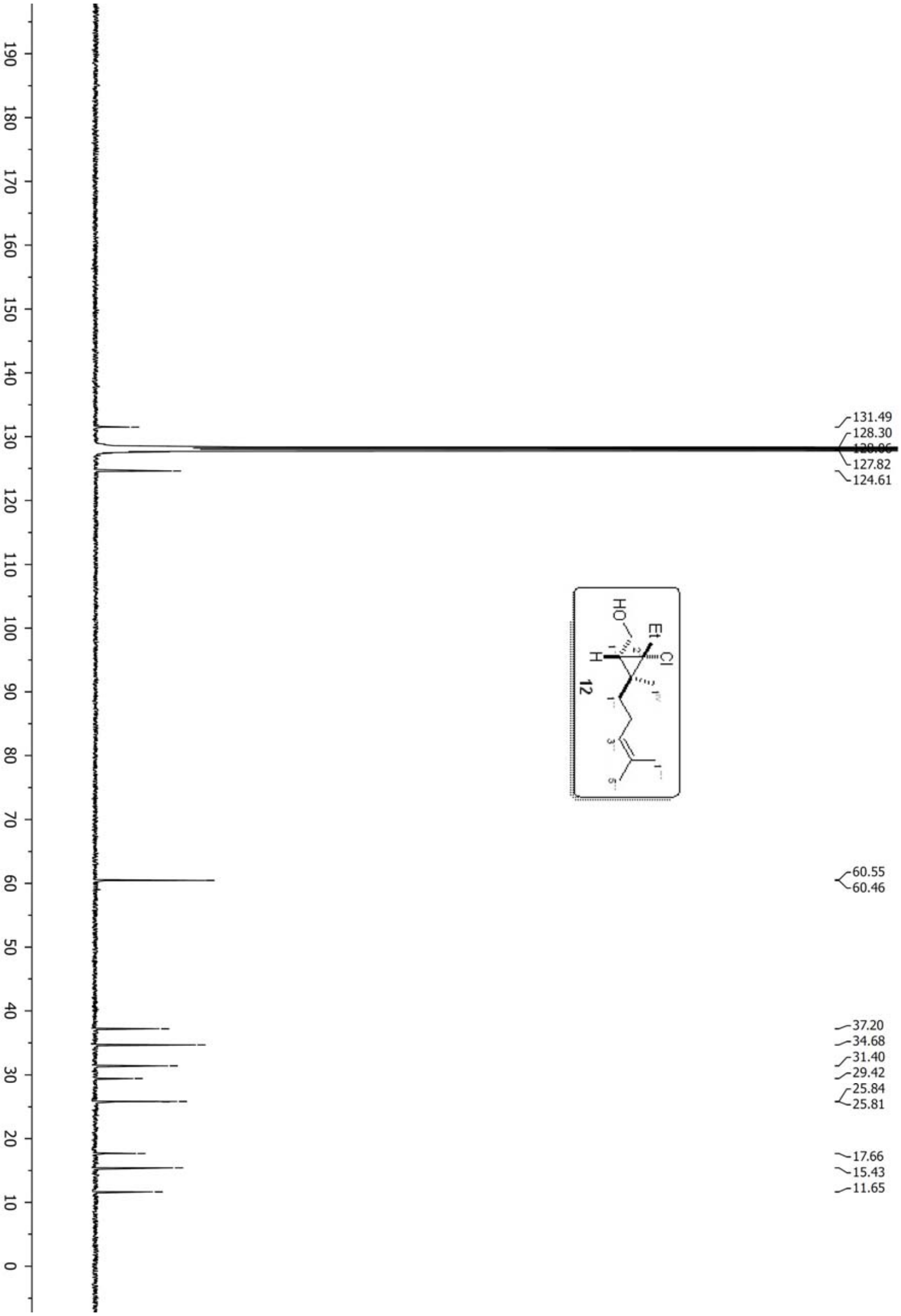
400 MHz ^{1}H NMR of compound **11** in $CDCl_3$



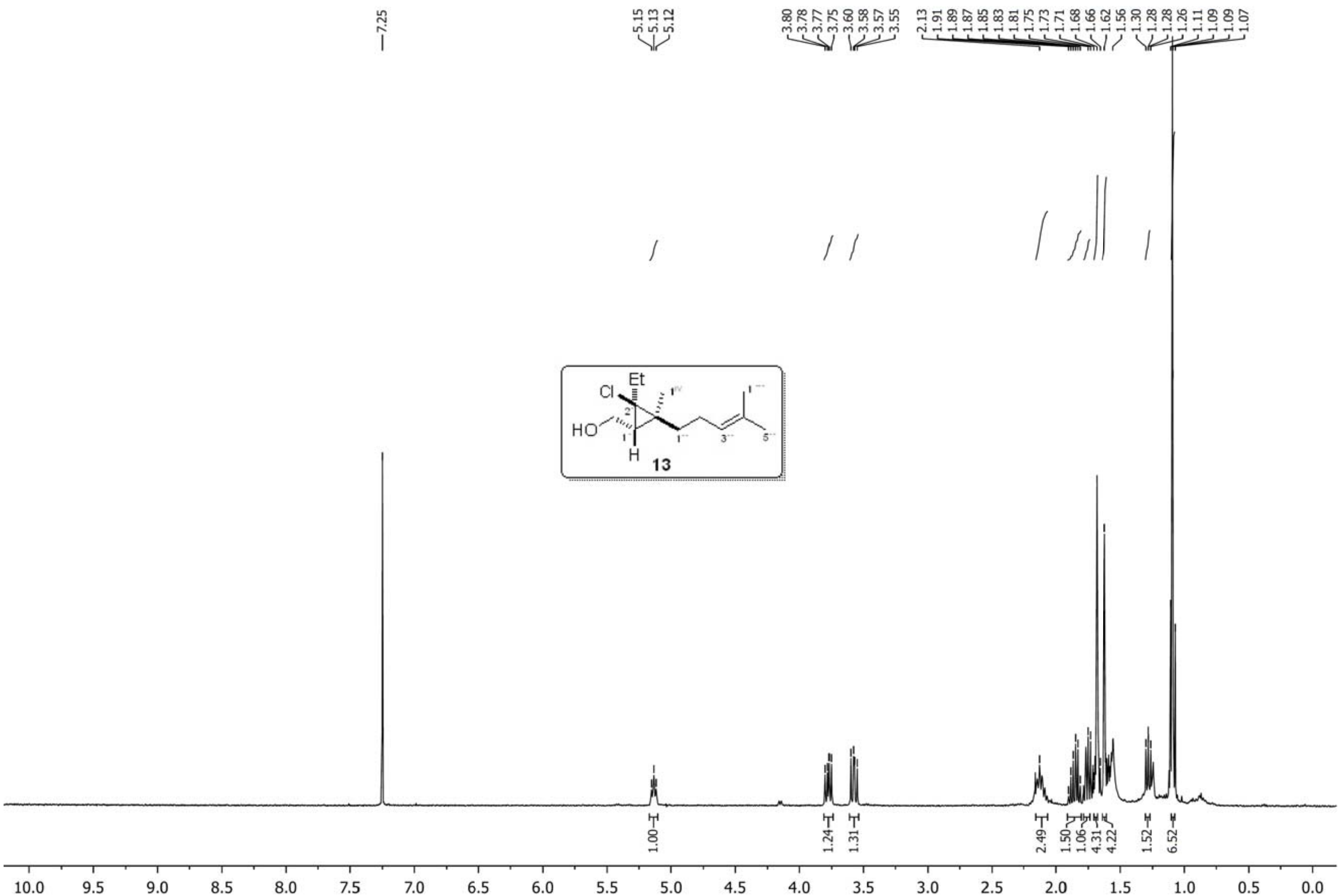
100 MHz ^{13}C NMR of compound **11** in $CDCl_3$



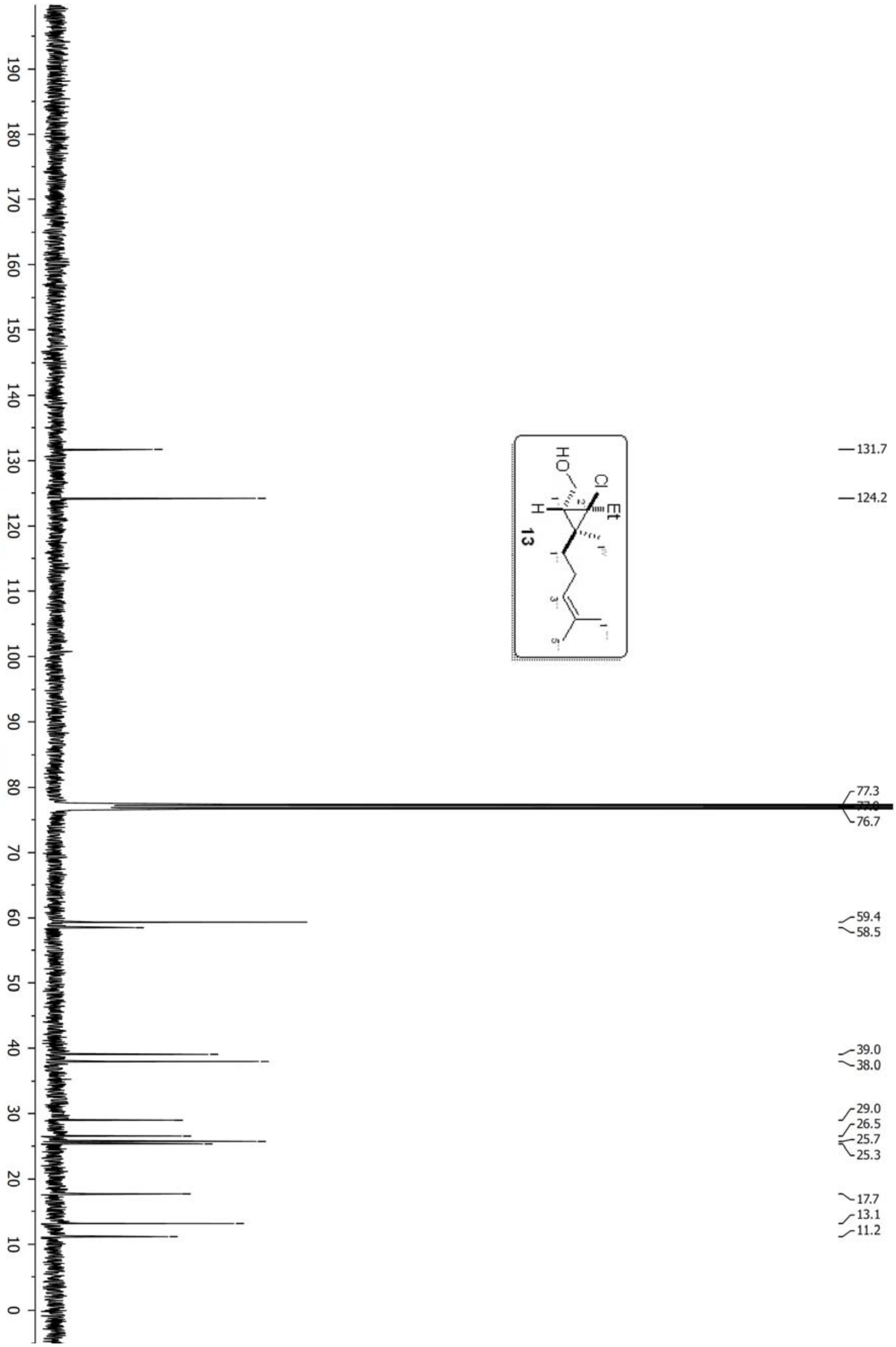
400 MHz ^{1}H NMR of compound **12** in C_6D_6



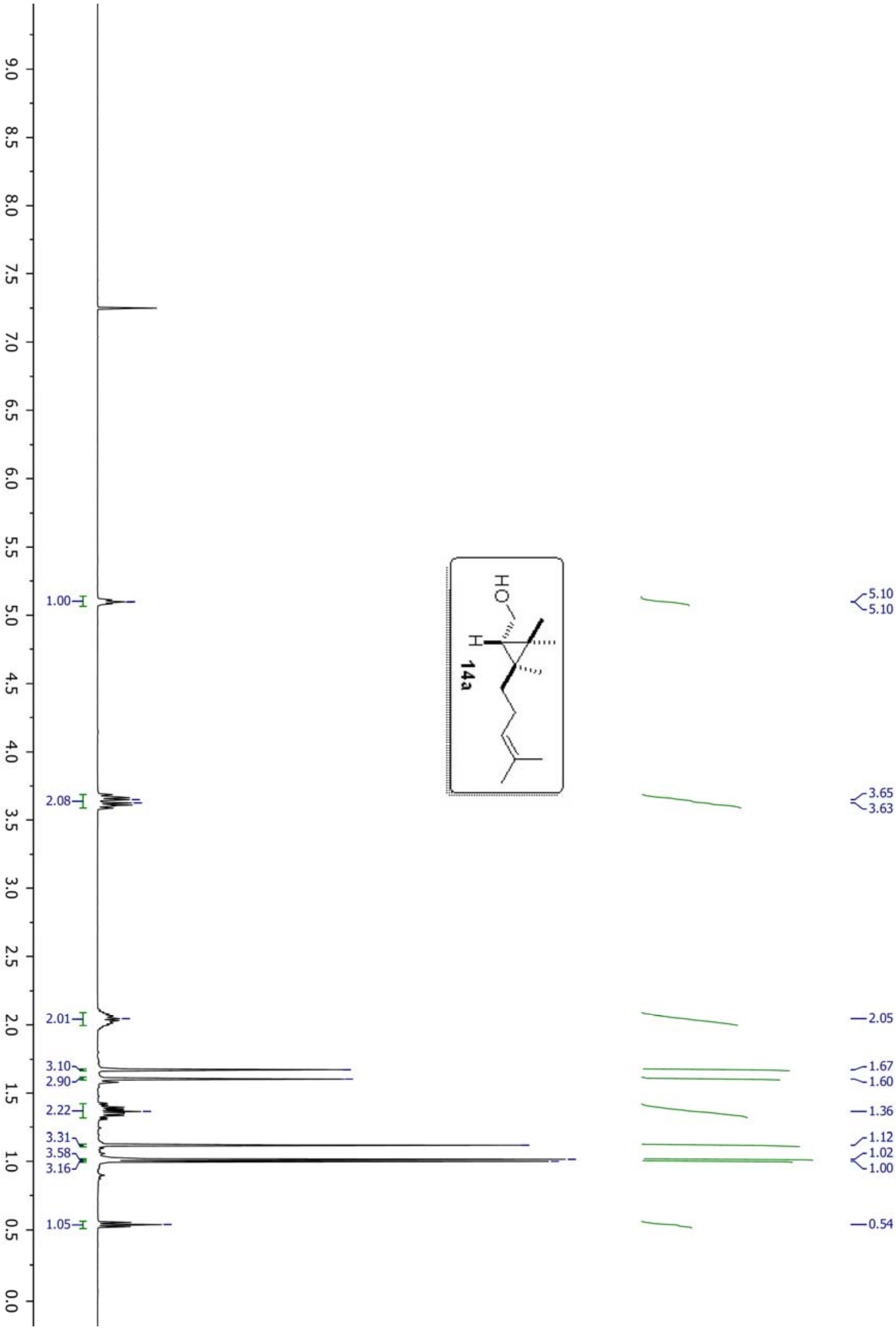
100 MHz ^{13}C NMR of compound **12** in C_6D_6



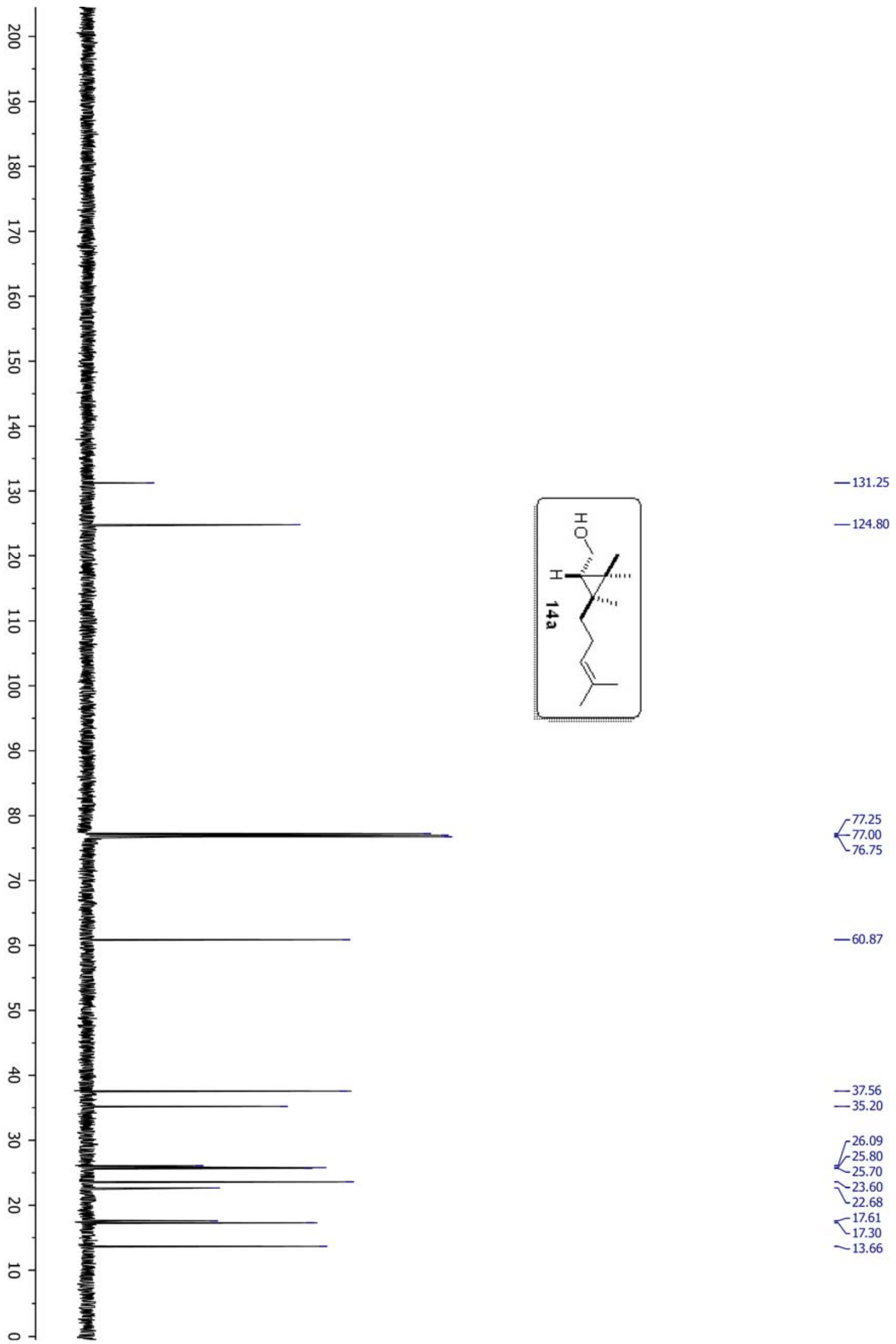
400 MHz ^{1}H NMR of compound **13** in $CDCl_3$



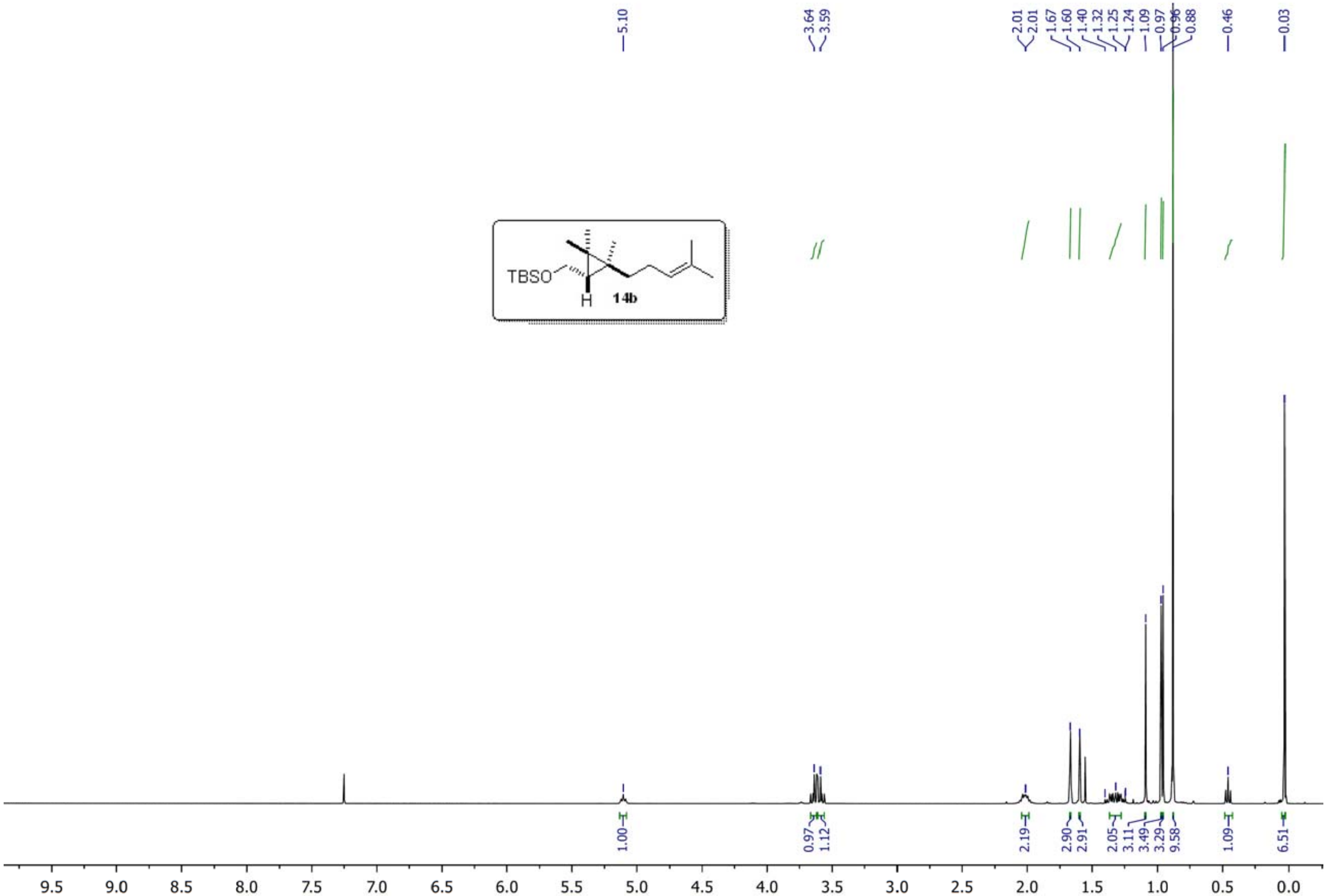
100 MHz ^{13}C NMR of compound **13** in $CDCl_3$



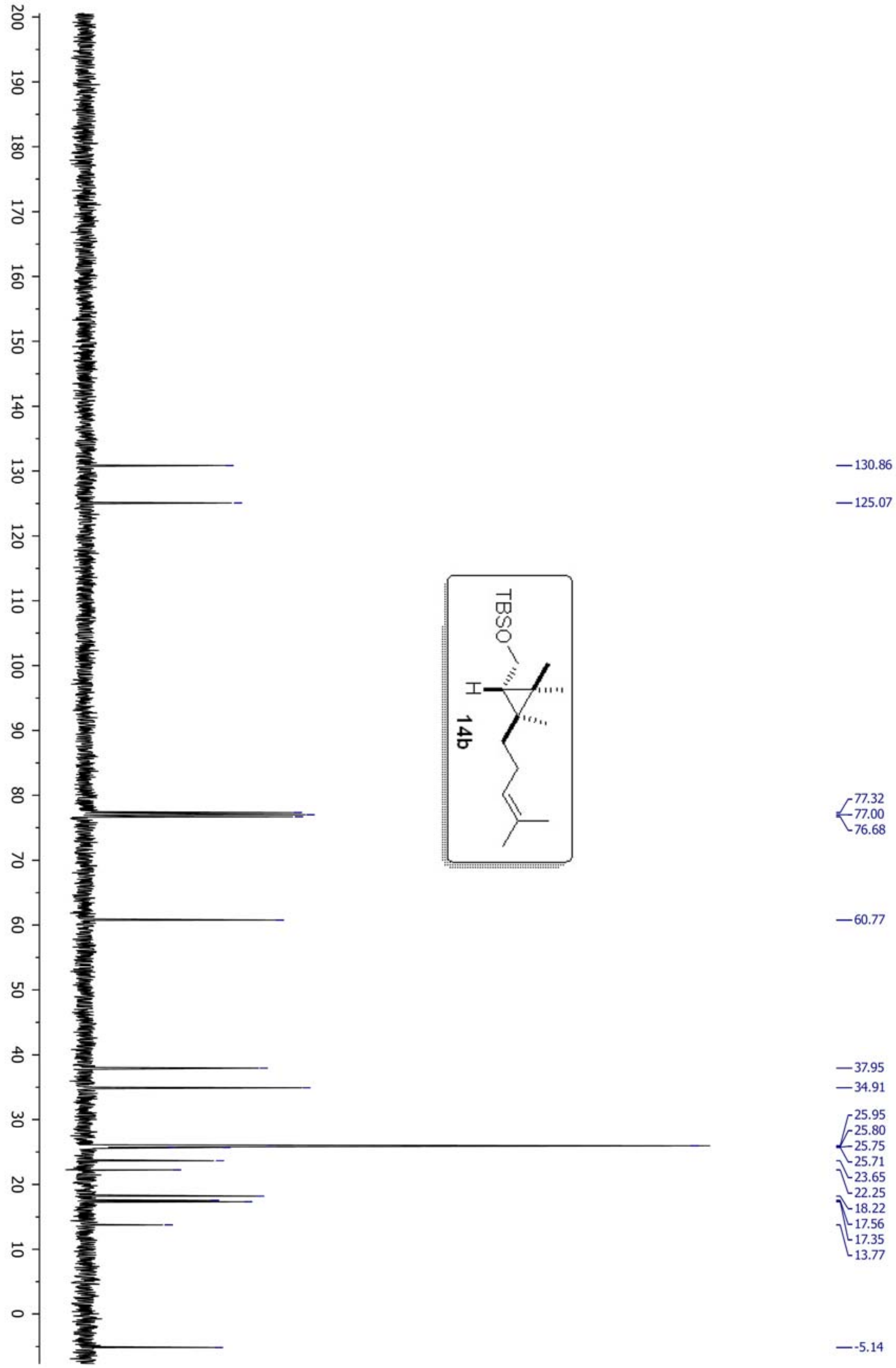
400 MHz ^{1}H NMR of compound **14a** in $CDCl_3$



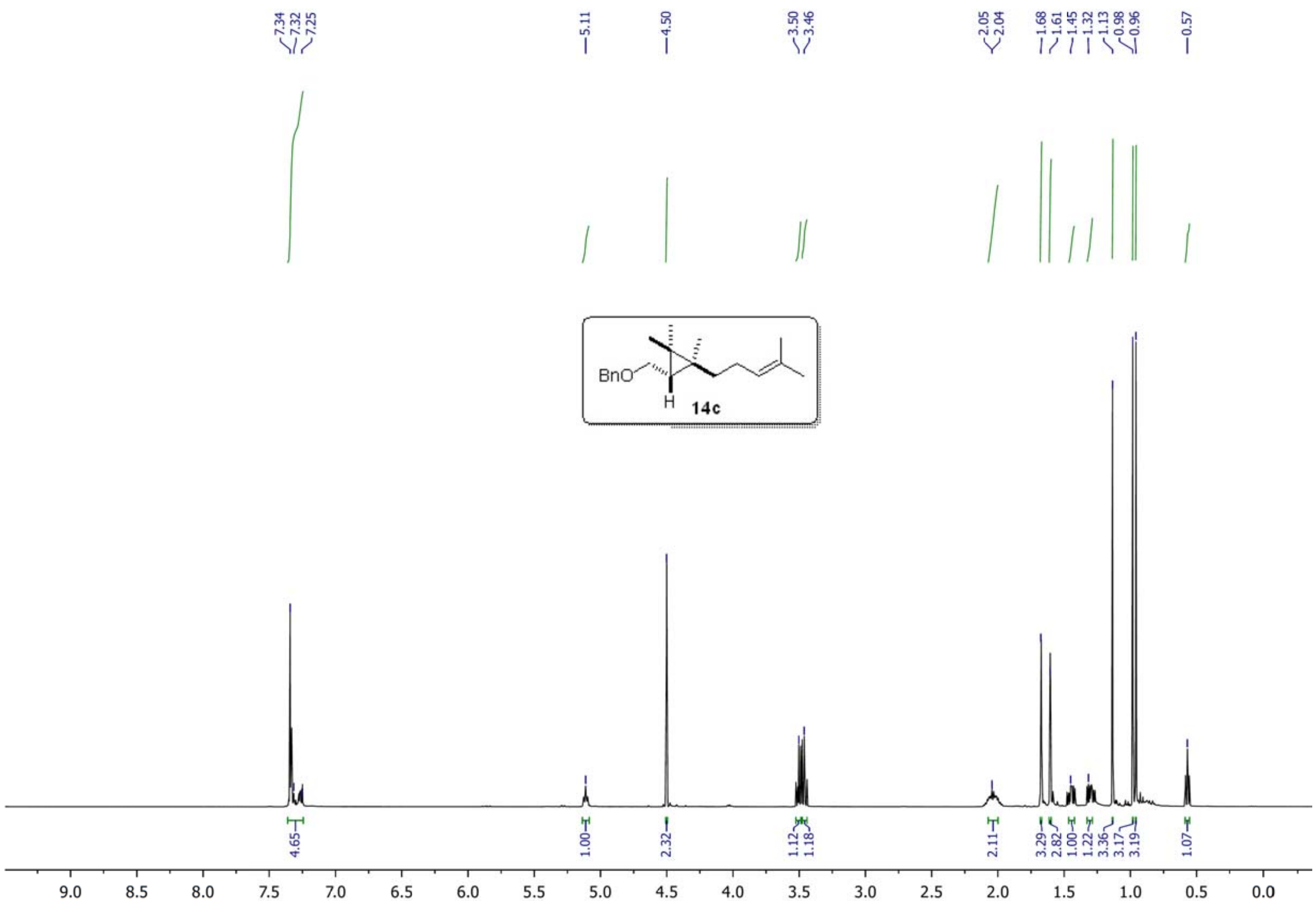
100 MHz ^{13}C NMR of compound **14a** in $CDCl_3$



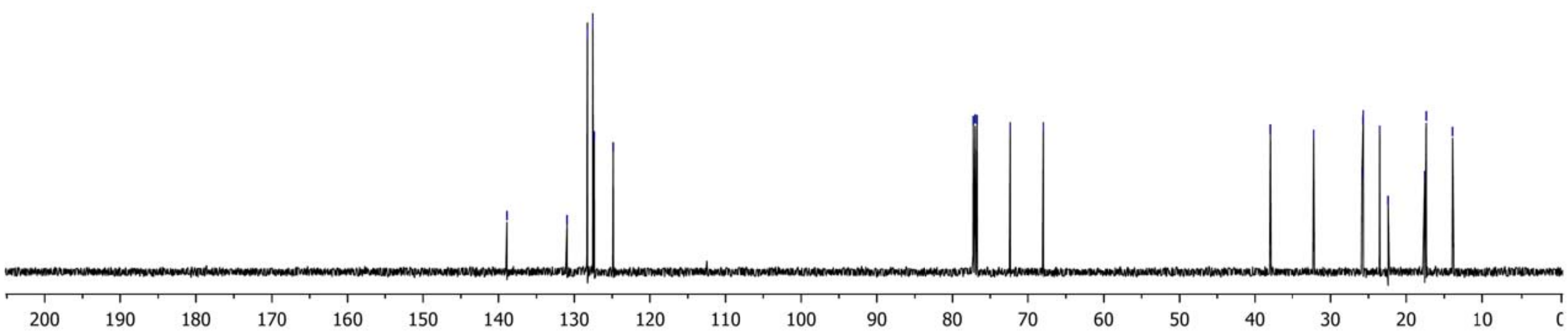
400 MHz ^{1}H NMR of compound **14b** in $CDCl_3$

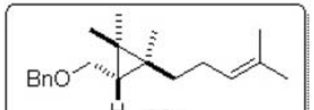


100 MHz ^{13}C NMR of compound **14b** in $CDCl_3$



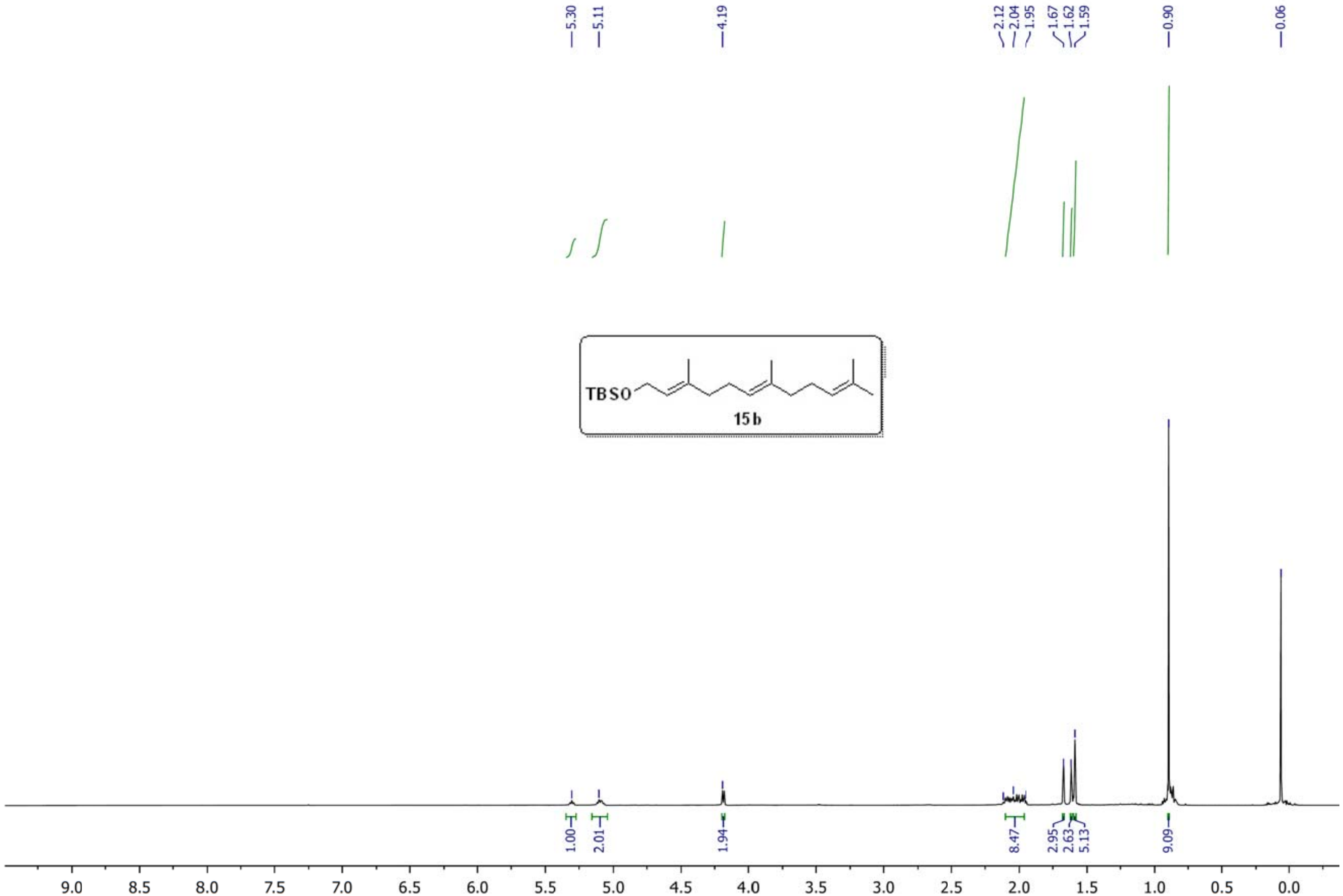
400 MHz ^{1}H NMR of compound **14c** in $CDCl_3$



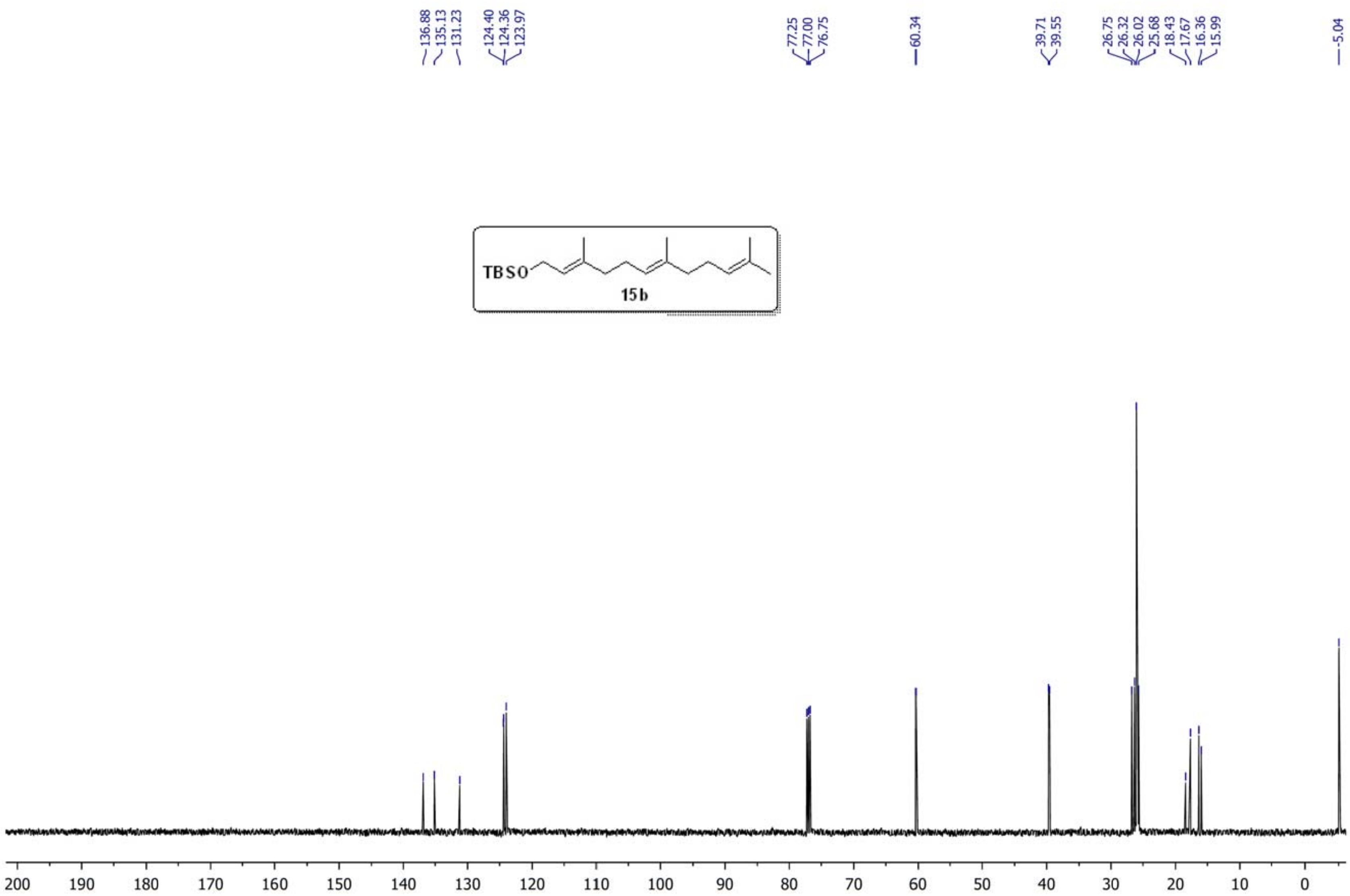


14c

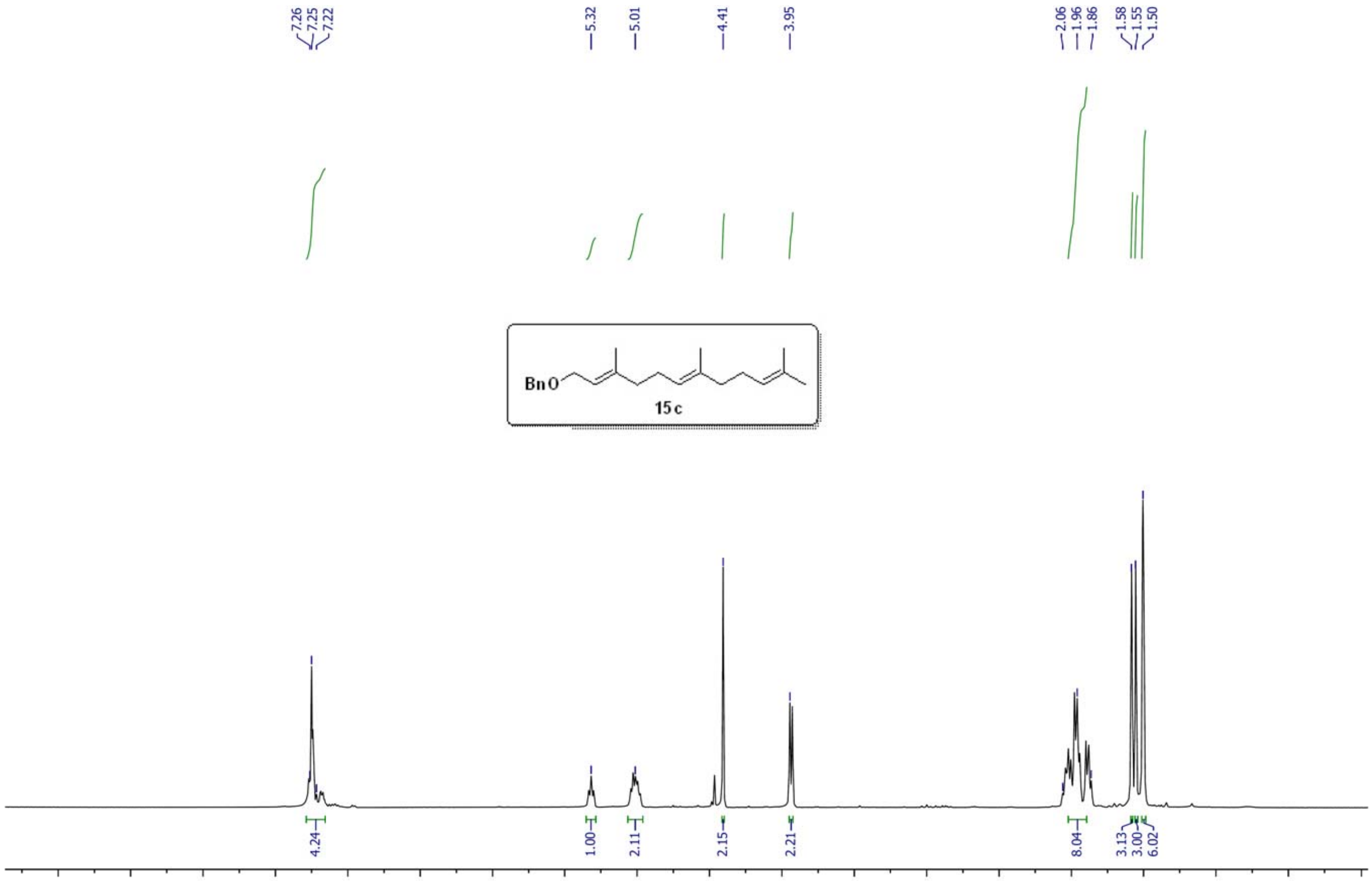
100 MHz ^{13}C NMR of compound **14c** in $CDCl_3$



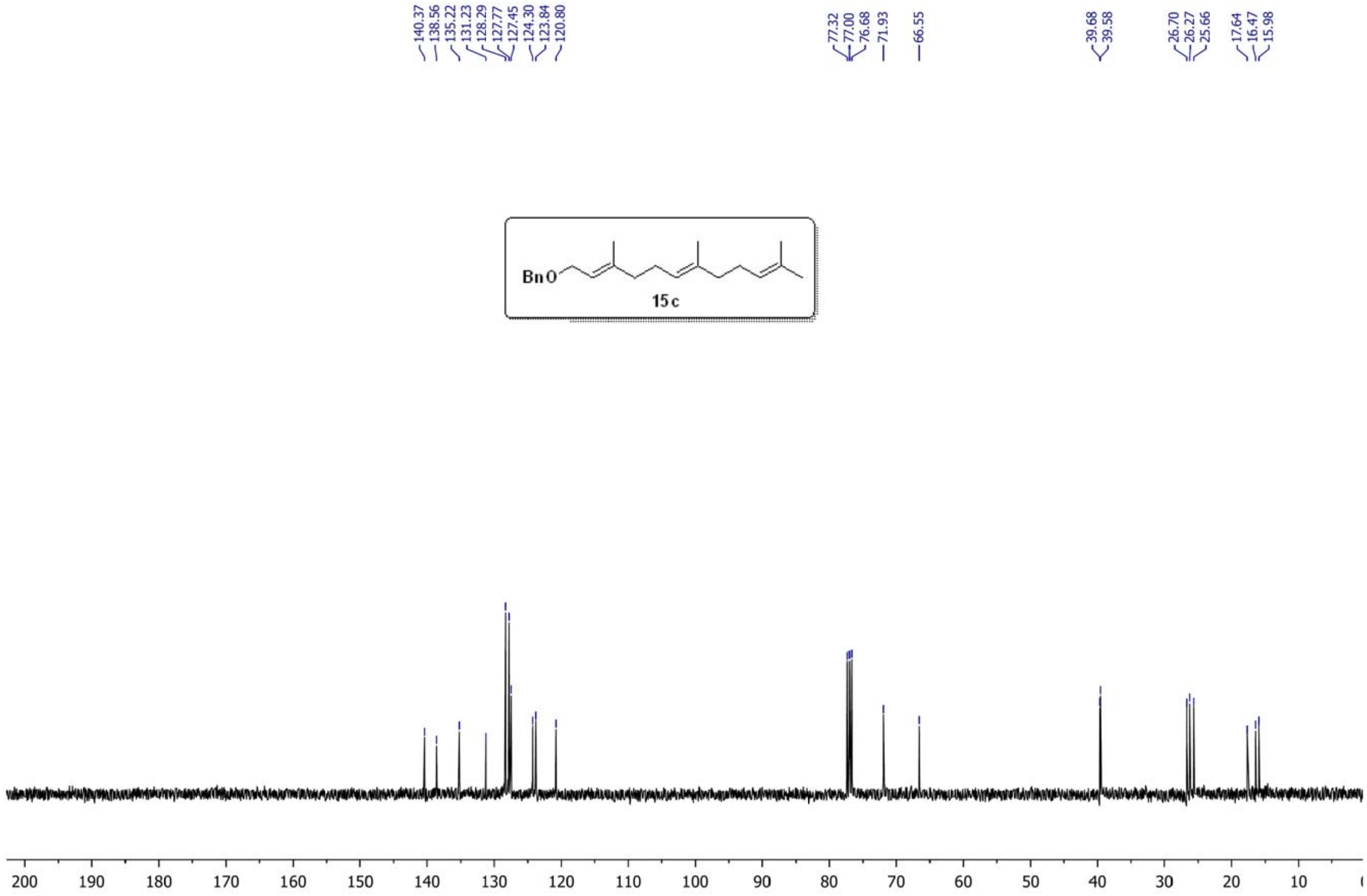
400 MHz ^{1}H NMR of compound **15b** in $CDCl_3$



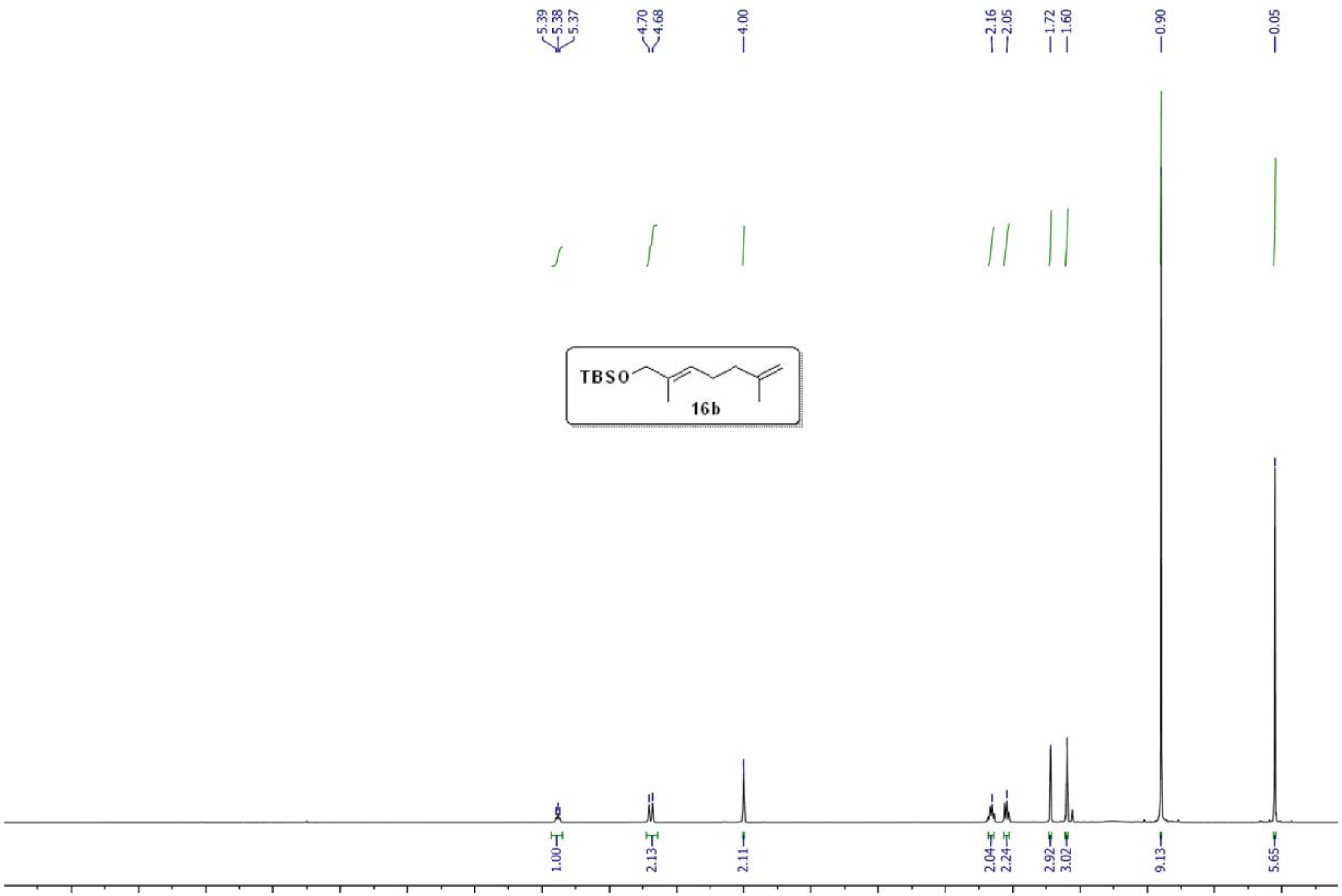
100 MHz ^{13}C NMR of compound **15b** in $CDCl_3$



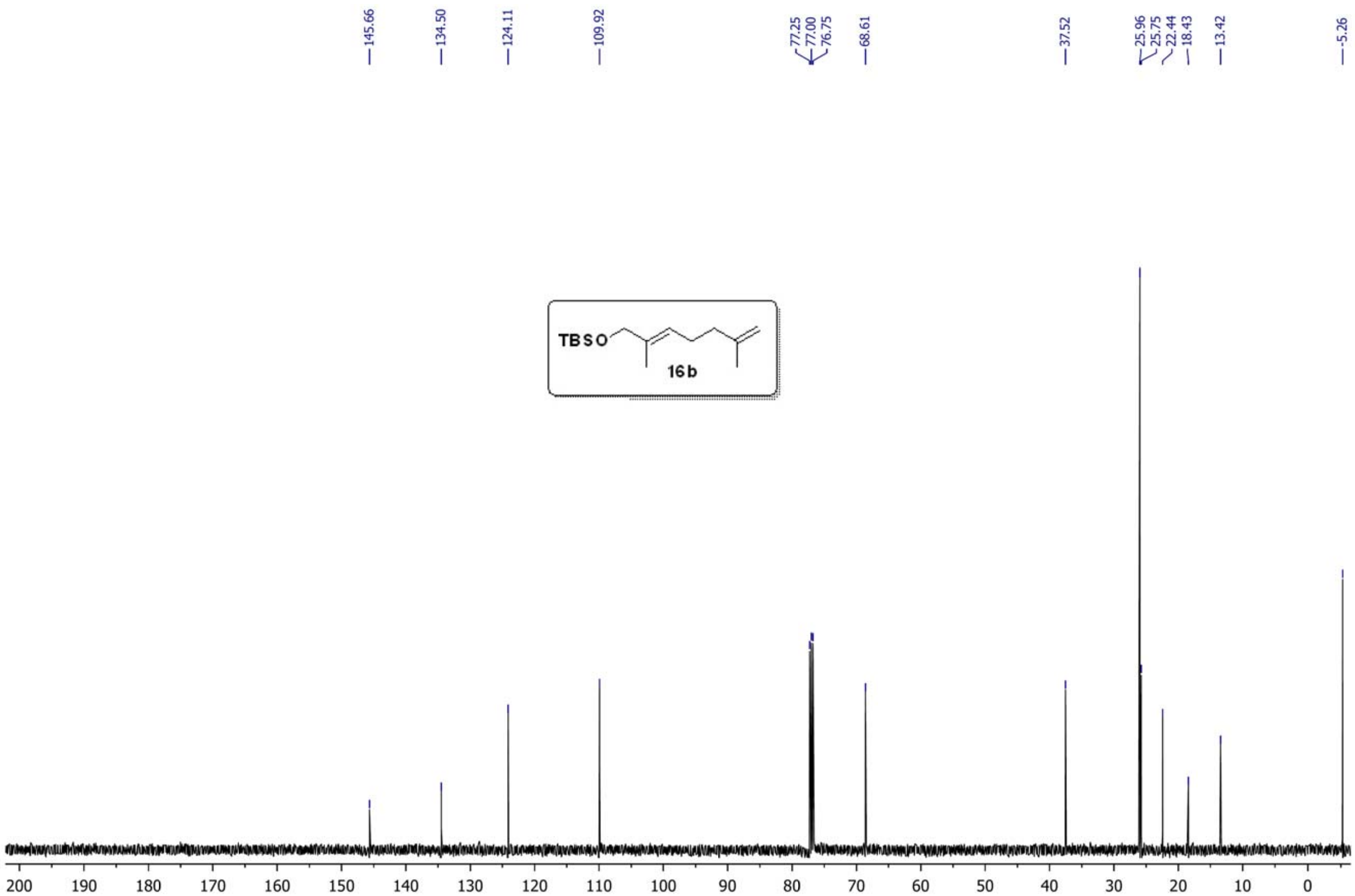
400 MHz ^{1}H NMR of compound **15c** in $CDCl_3$



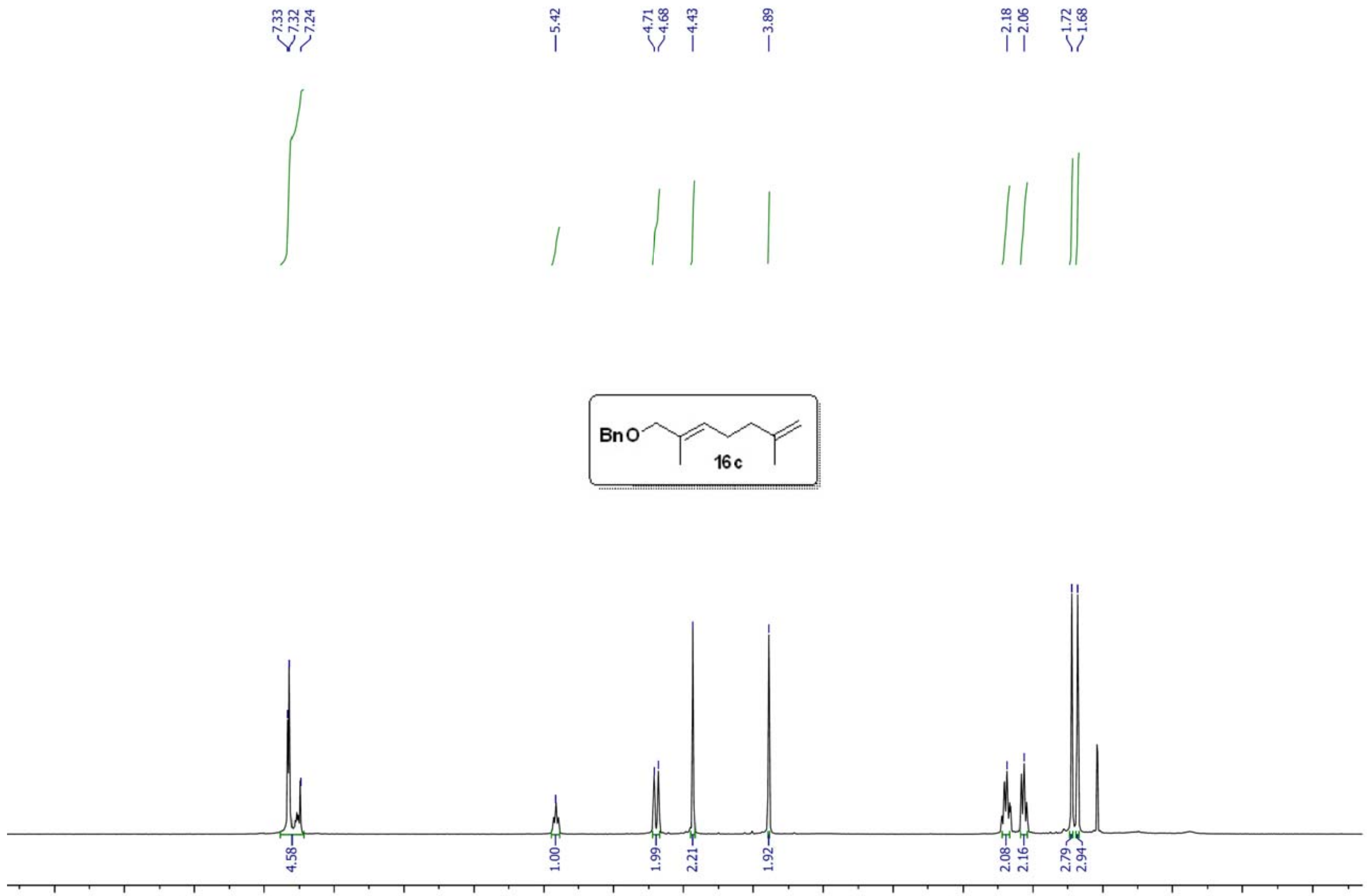
100 MHz ^{13}C NMR of compound **15c** in $CDCl_3$



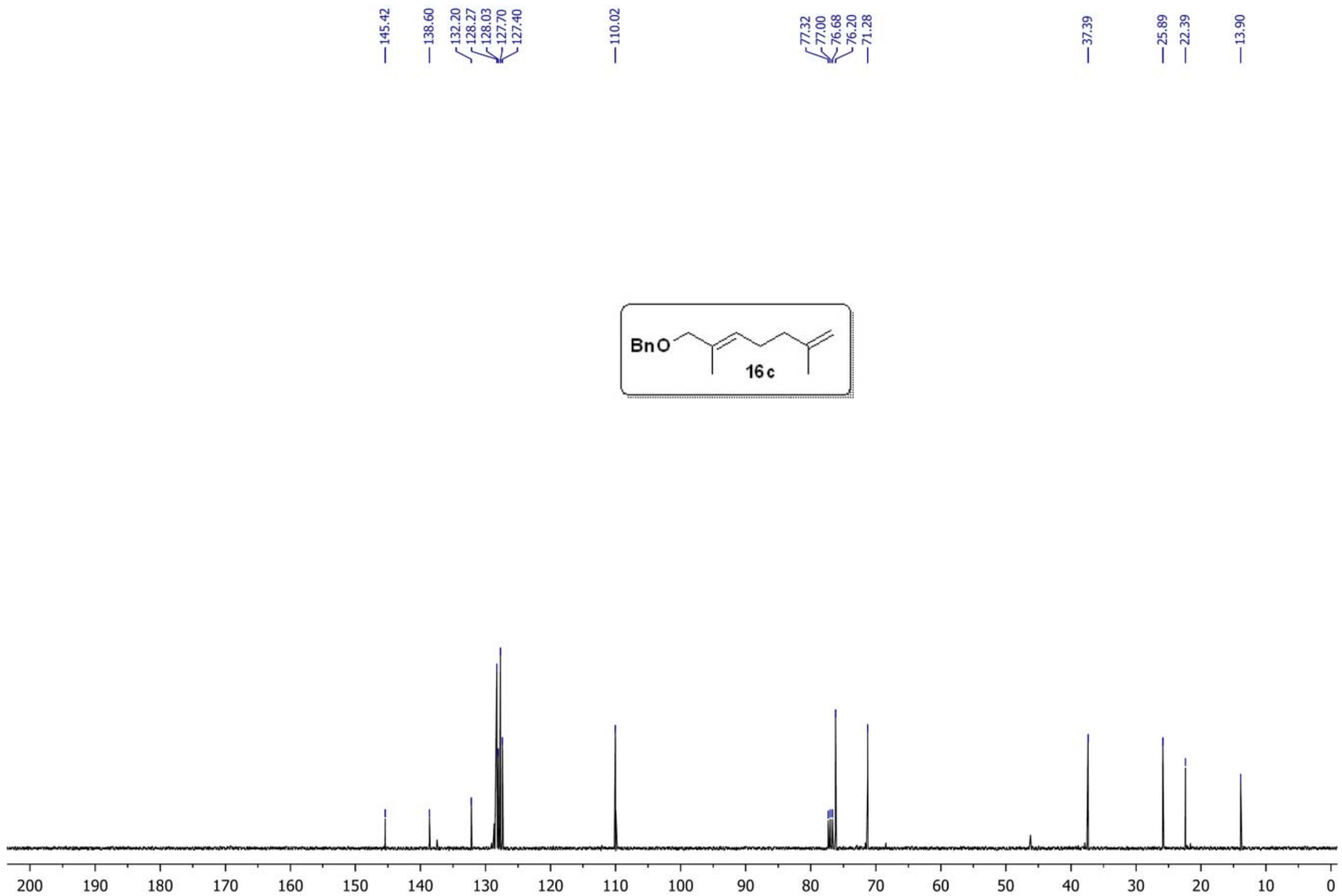
400 MHz ^{1}H NMR of compound **16b** in $CDCl_3$



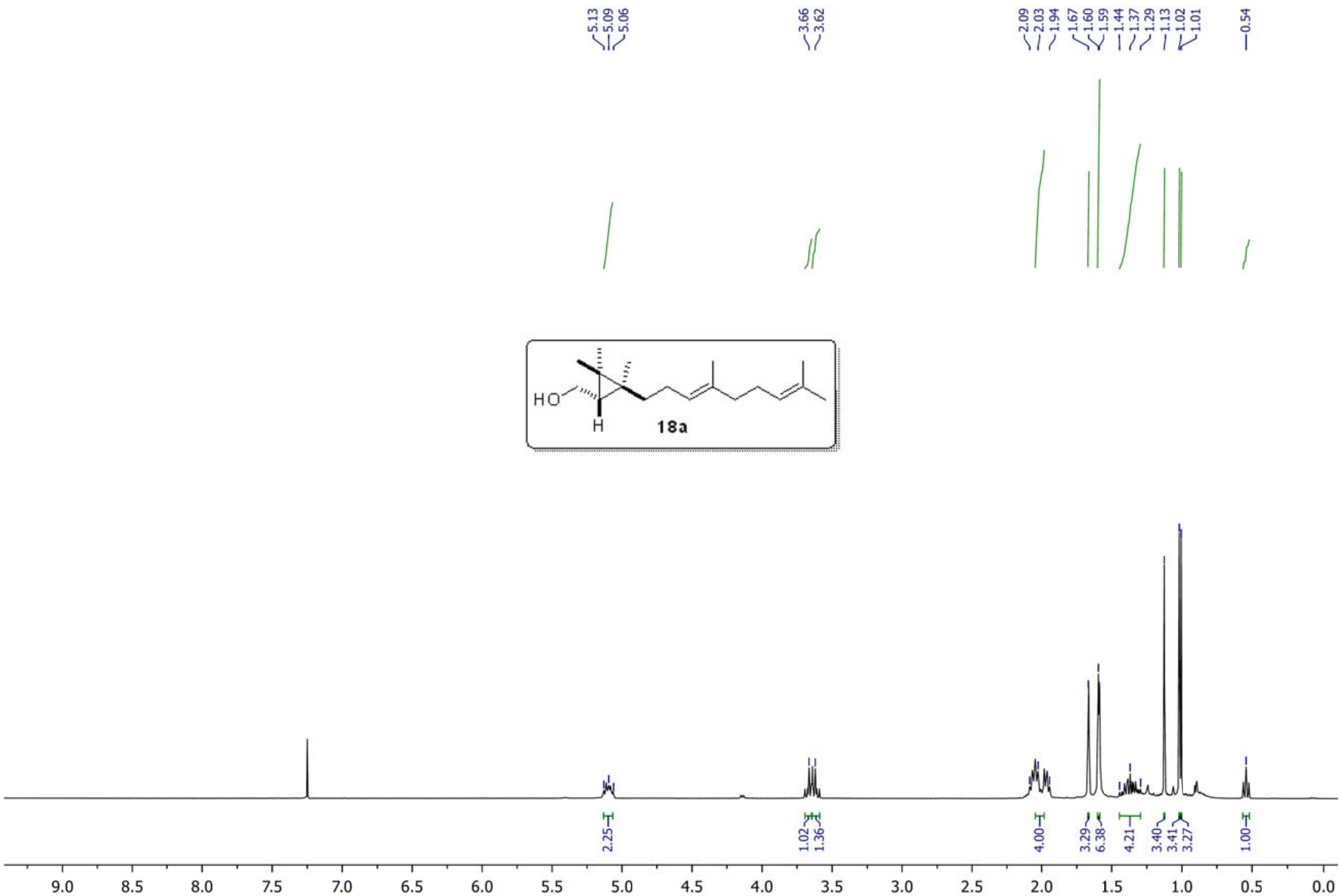
100 MHz ^{13}C NMR of compound **16b** in $CDCl_3$



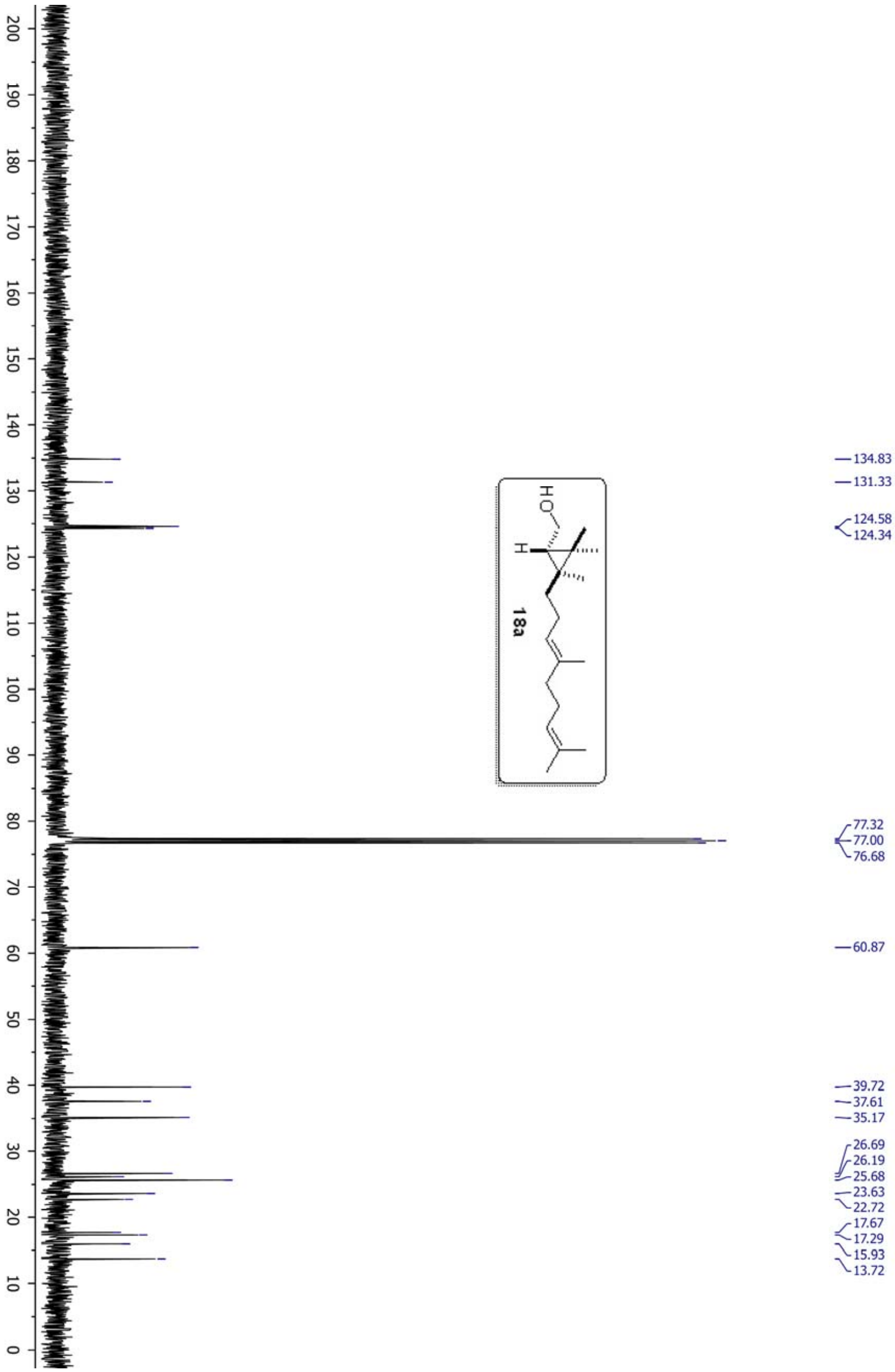
400 MHz ^{1}H NMR of compound **16c** in $CDCl_3$



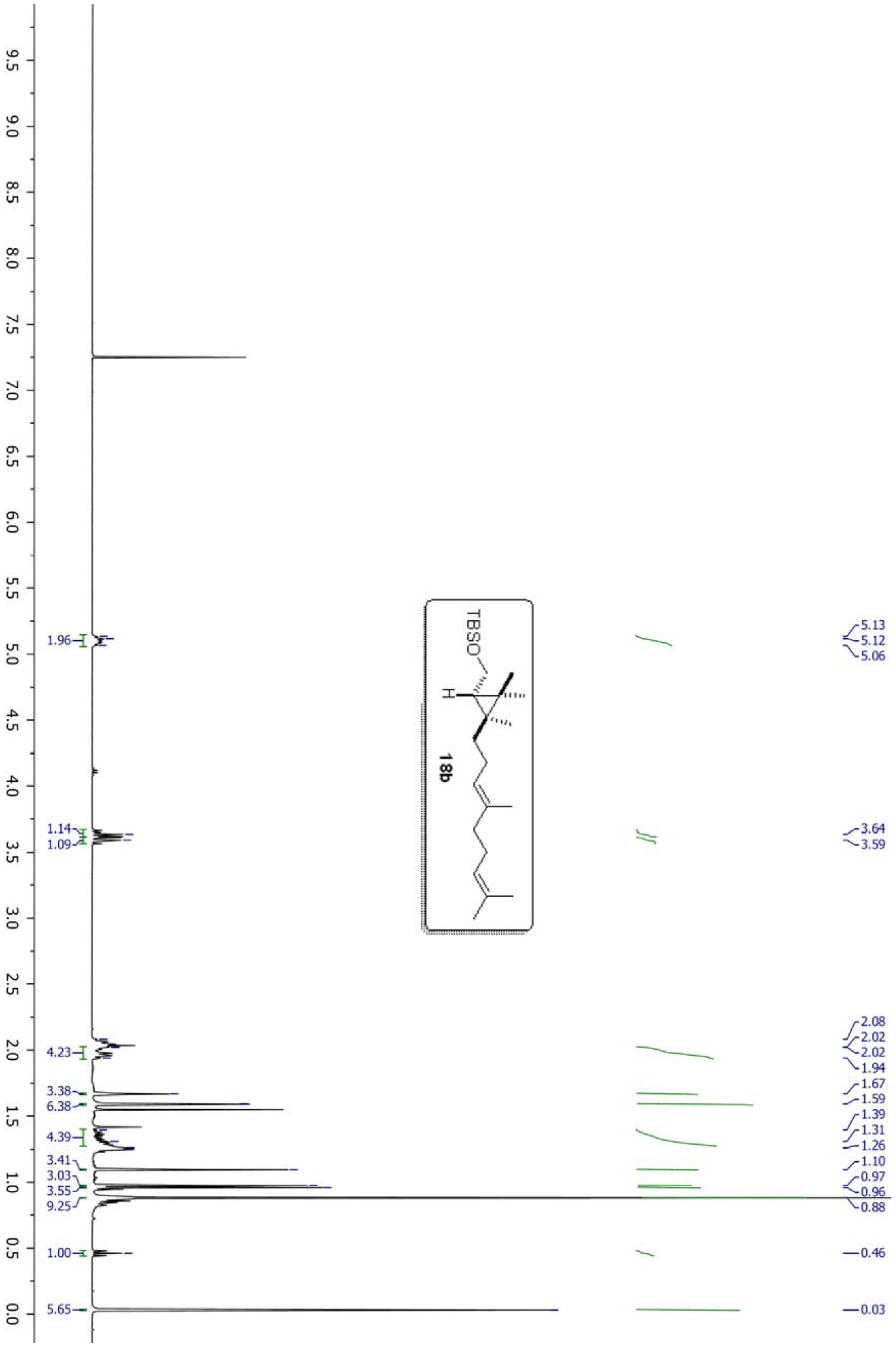
100 MHz ^{13}C NMR of compound **16c** in $CDCl_3$



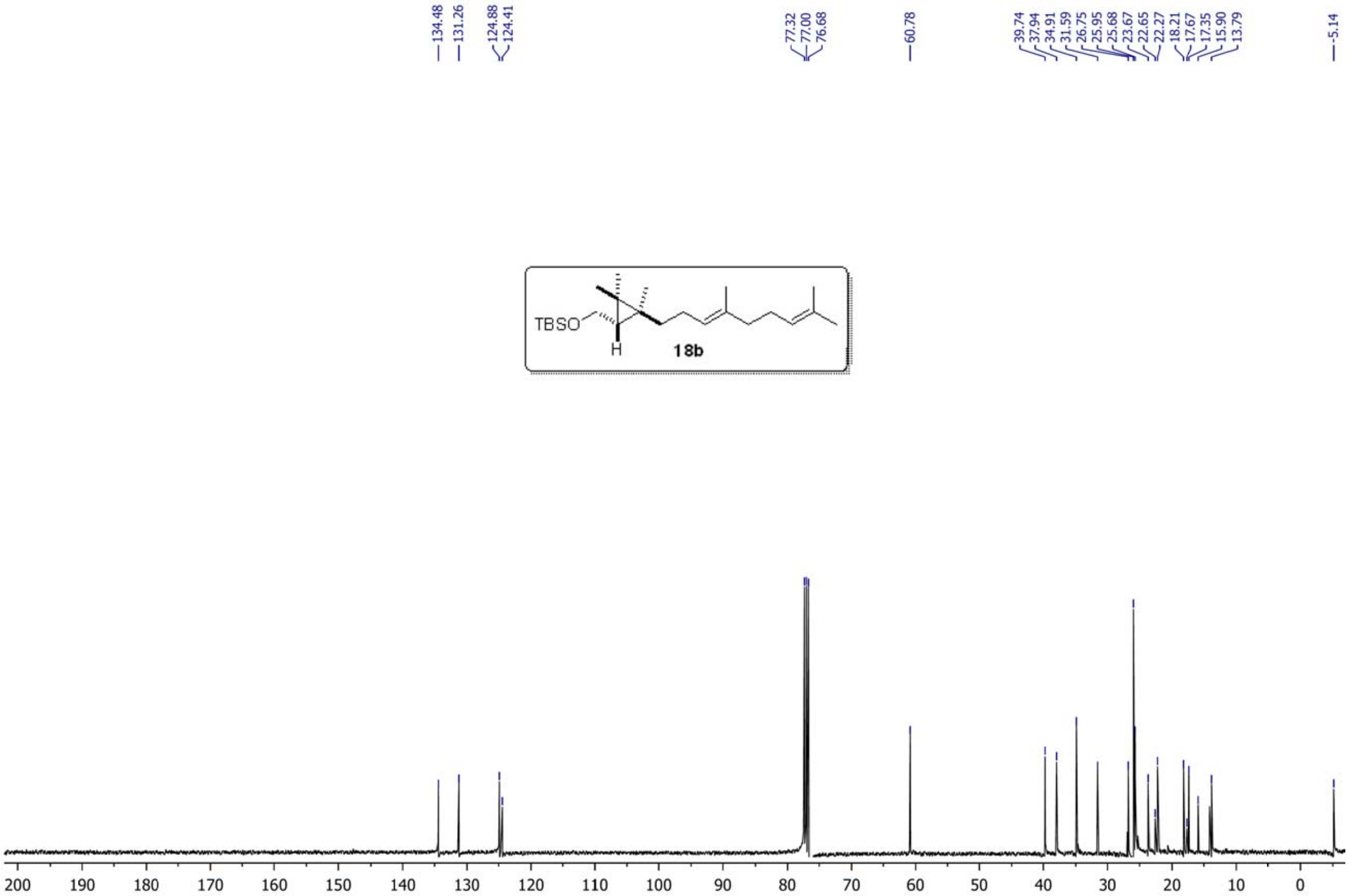
400 MHz ^{1}H NMR of compound **18a** in $CDCl_3$



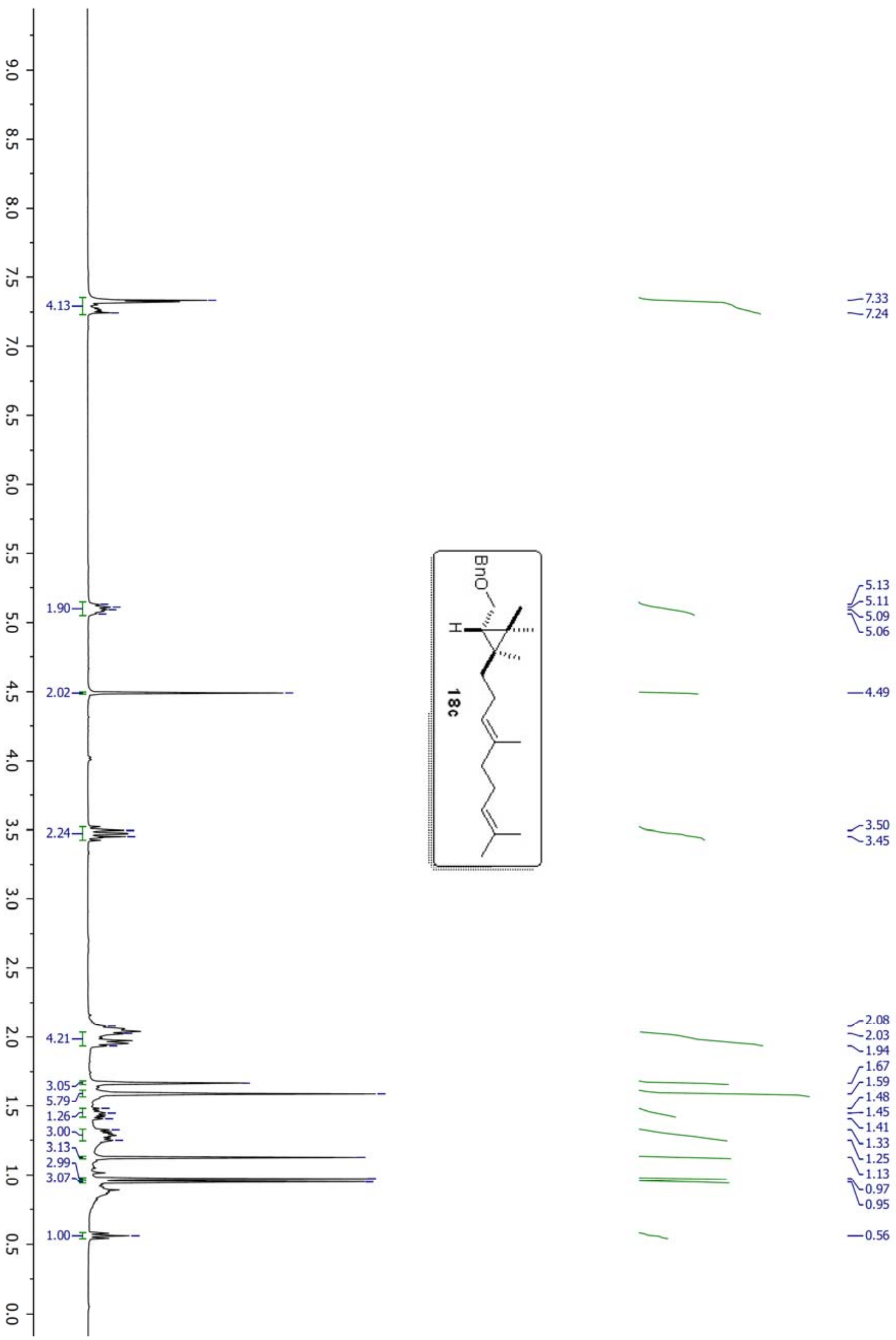
100 MHz ^{13}C NMR of compound **18a** in $CDCl_3$



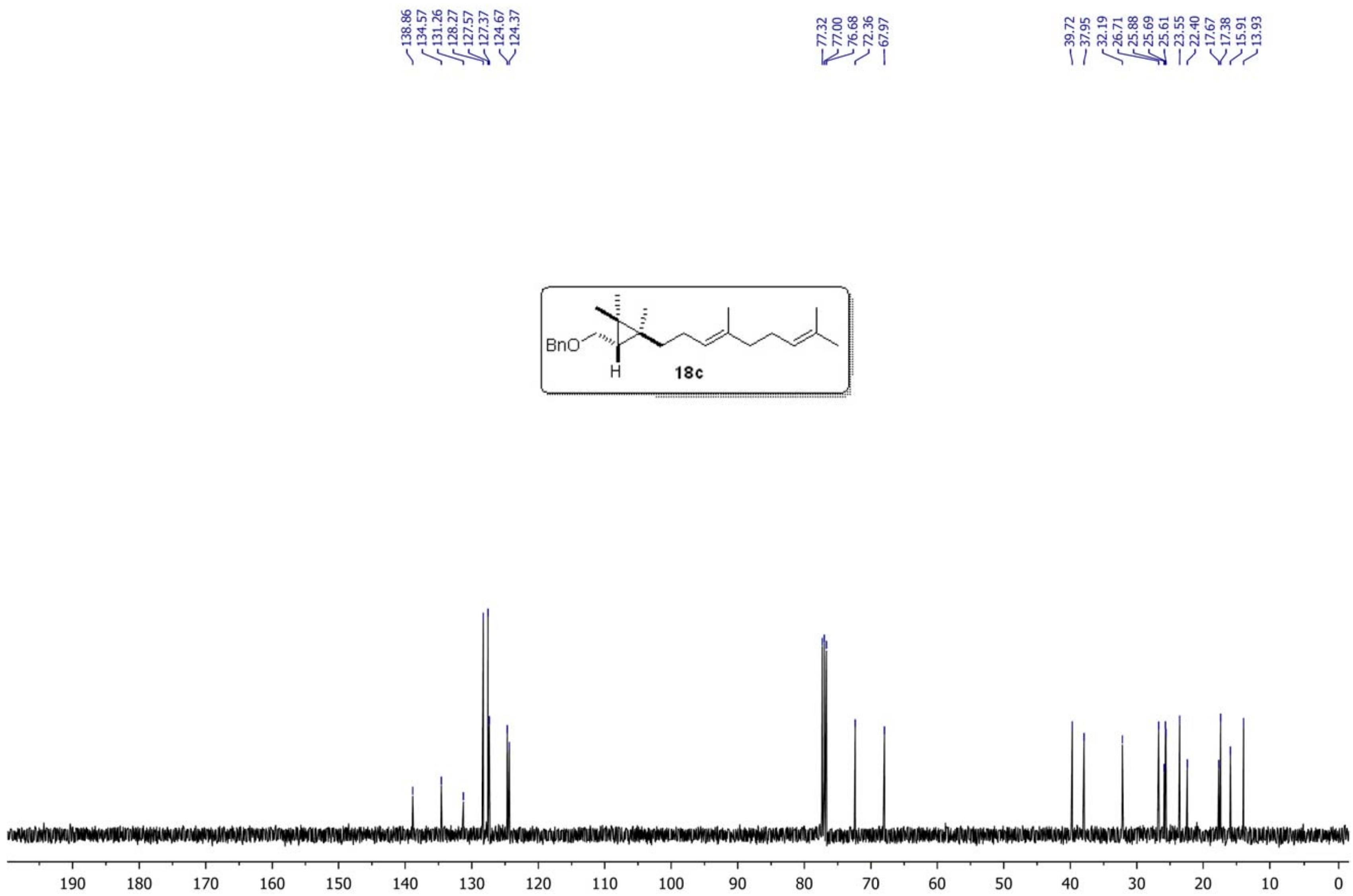
400 MHz ^{1}H NMR of compound **18b** in $CDCl_3$



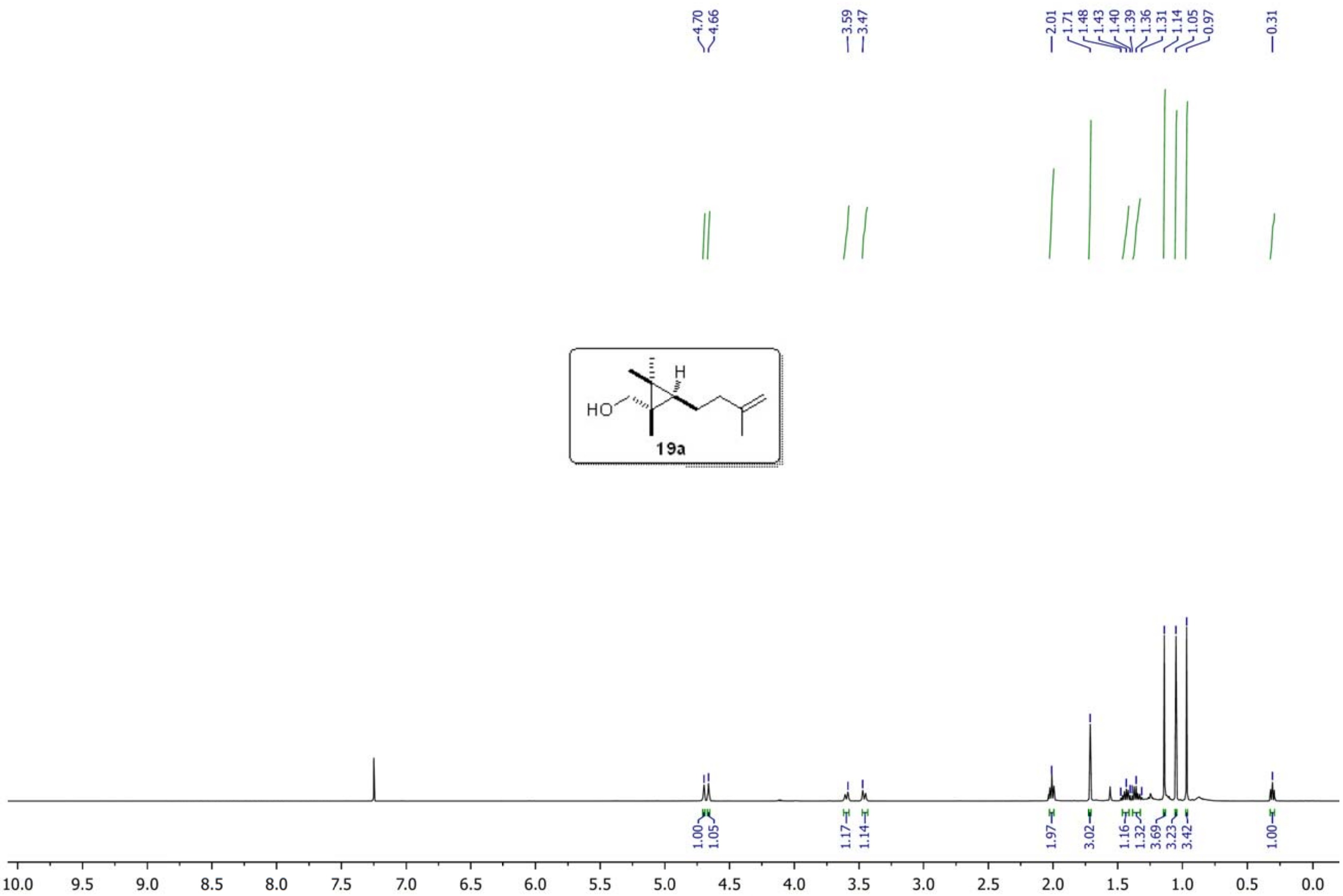
100 MHz ^{13}C NMR of compound **18b** in $CDCl_3$



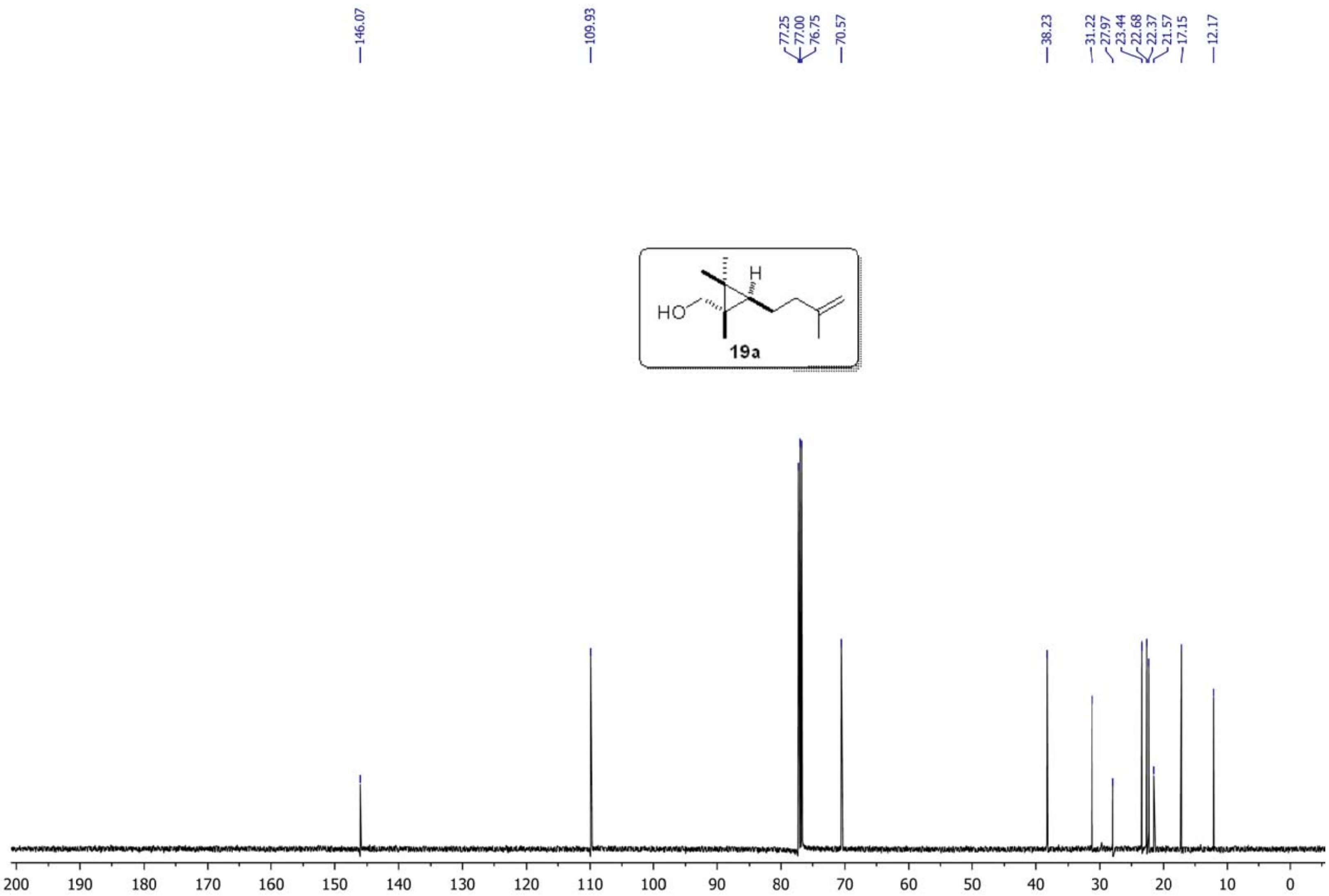
400 MHz ¹H NMR of compound **18c** in $CDCl_3$



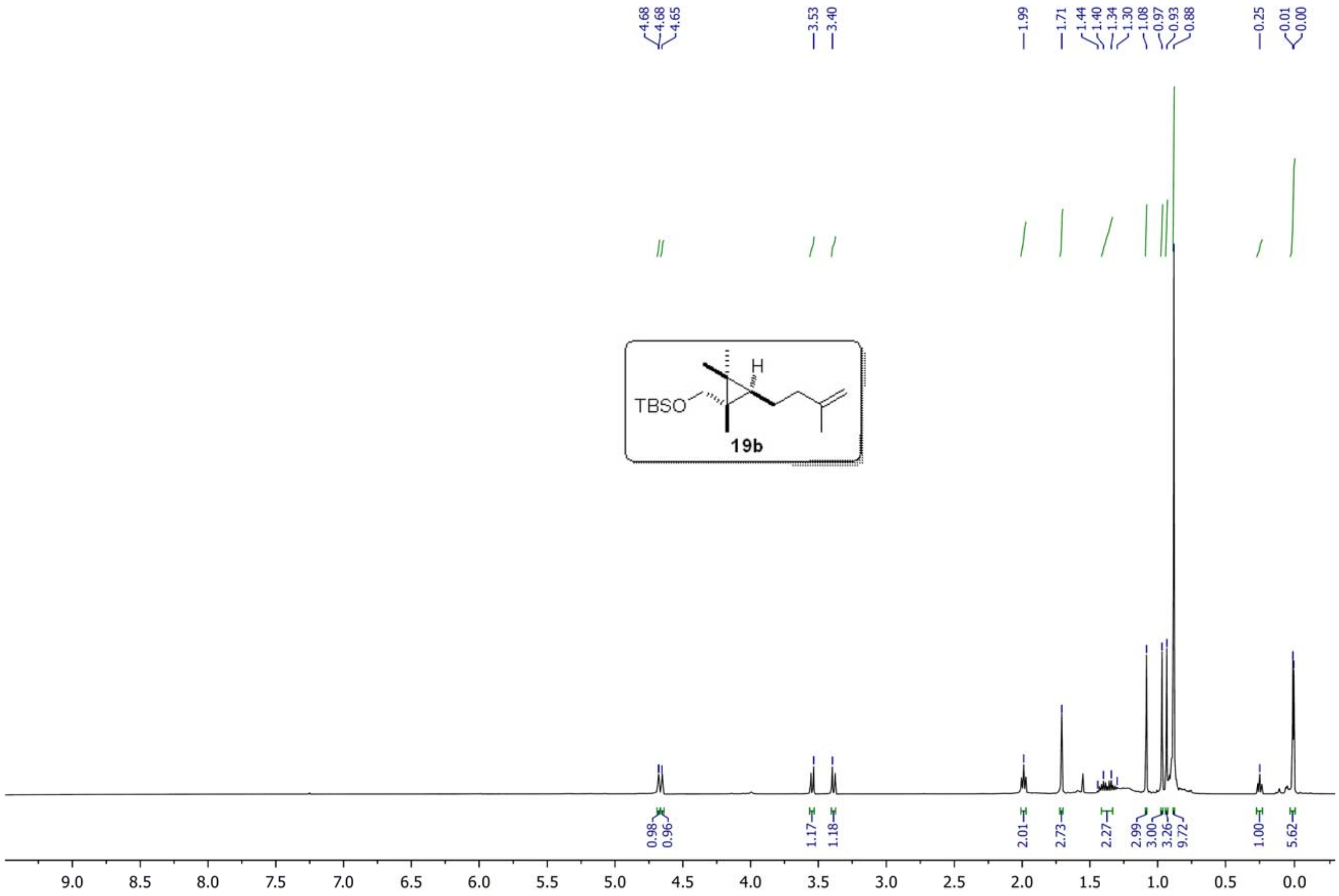
100 MHz ^{13}C NMR of compound **18c** in $CDCl_3$



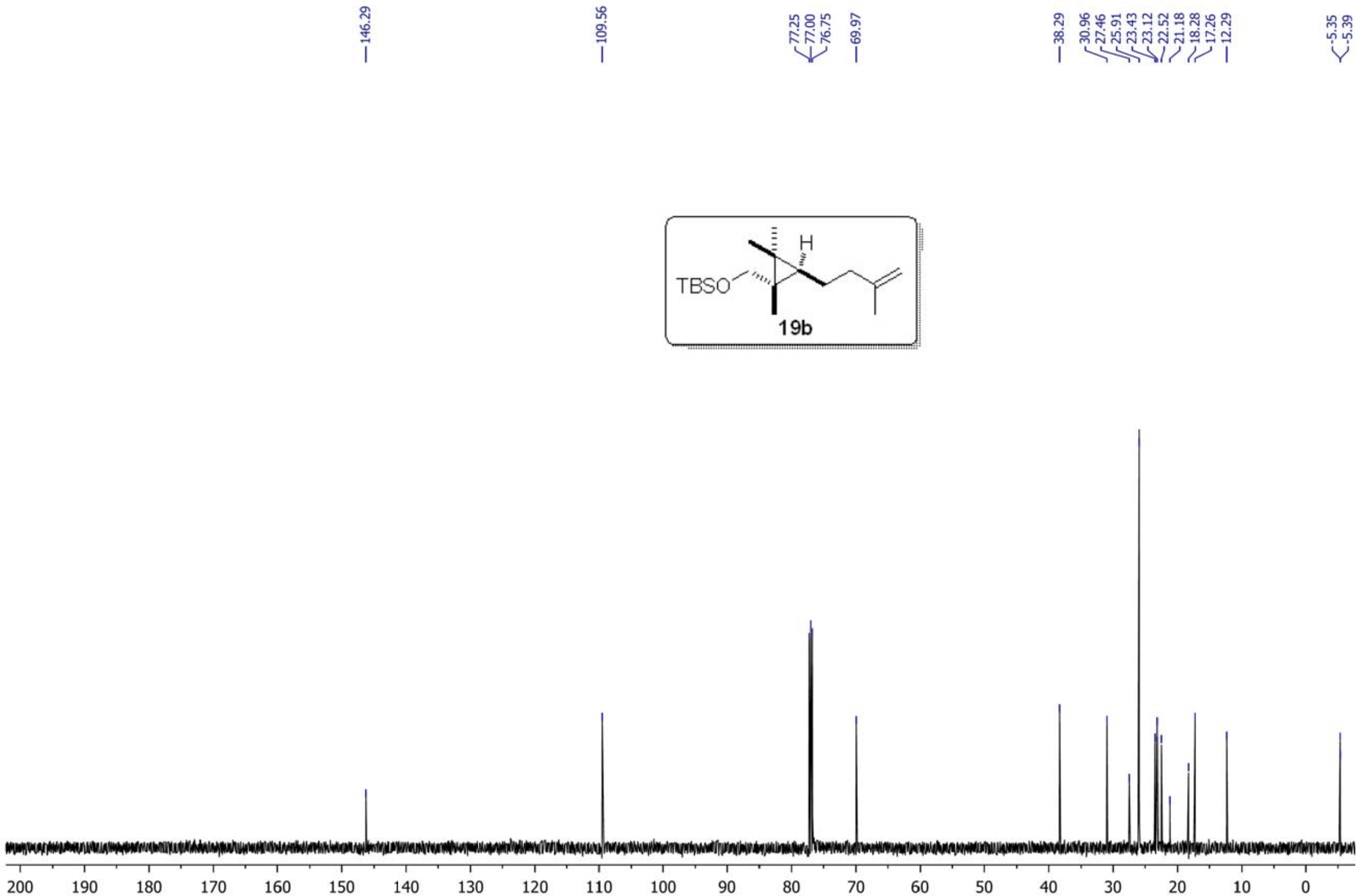
400 MHz ^{1}H NMR of compound **19a** in $CDCl_3$



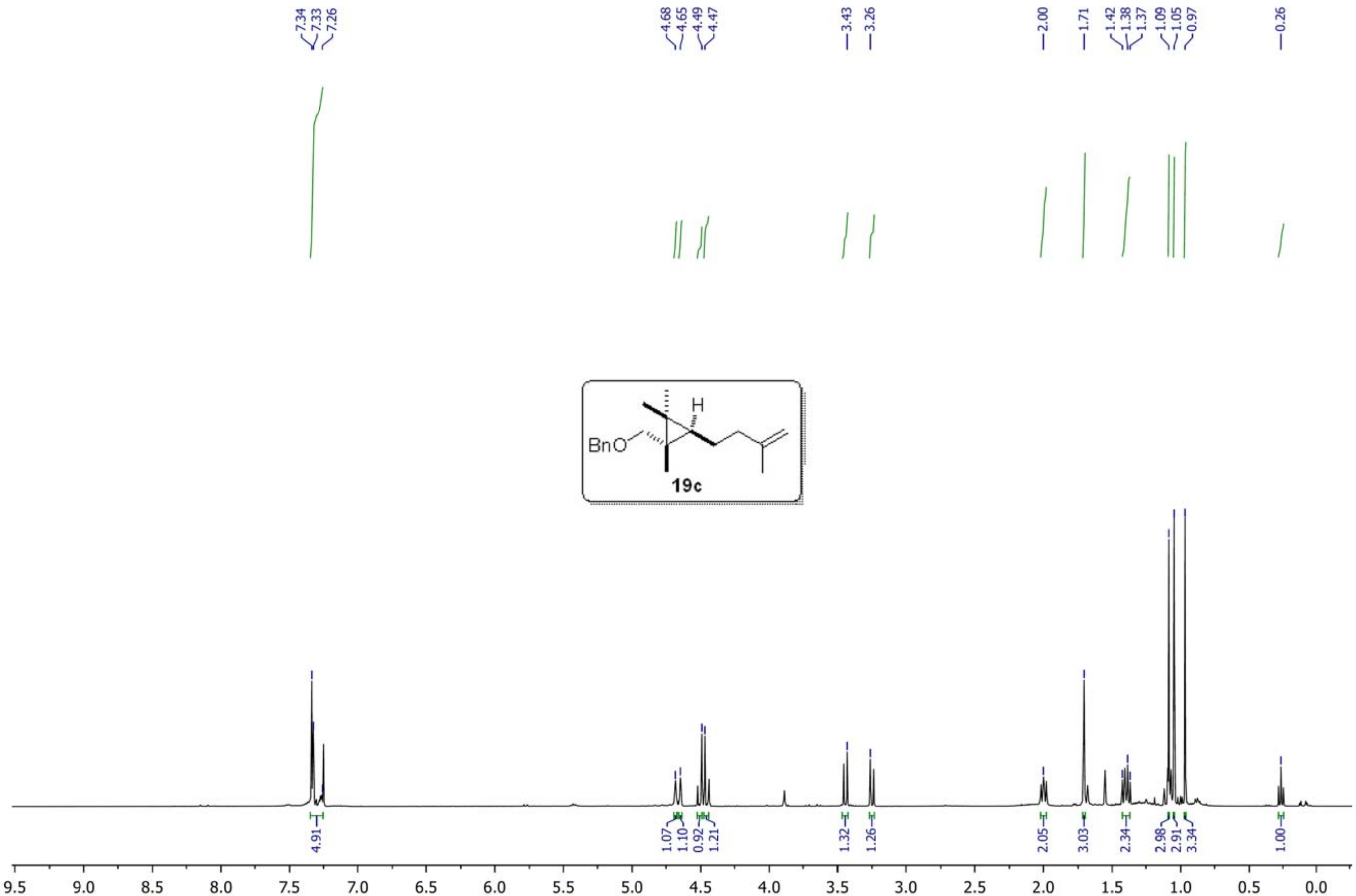
100 MHz ^{13}C NMR of compound **19a** in $CDCl_3$



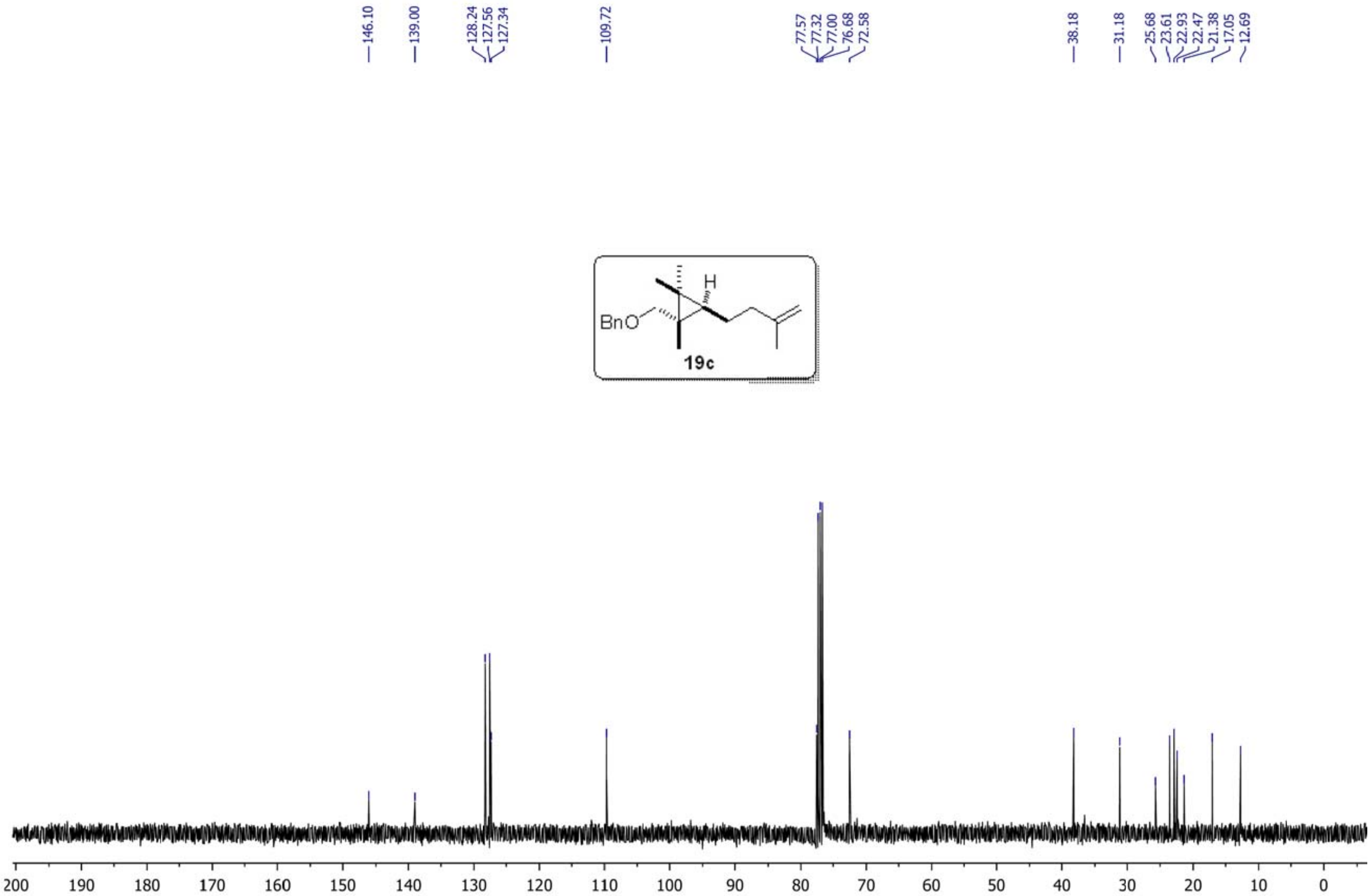
400 MHz ^{1}H NMR of compound **19b** in $CDCl_3$



100 MHz ^{13}C NMR of compound **19b** in $CDCl_3$

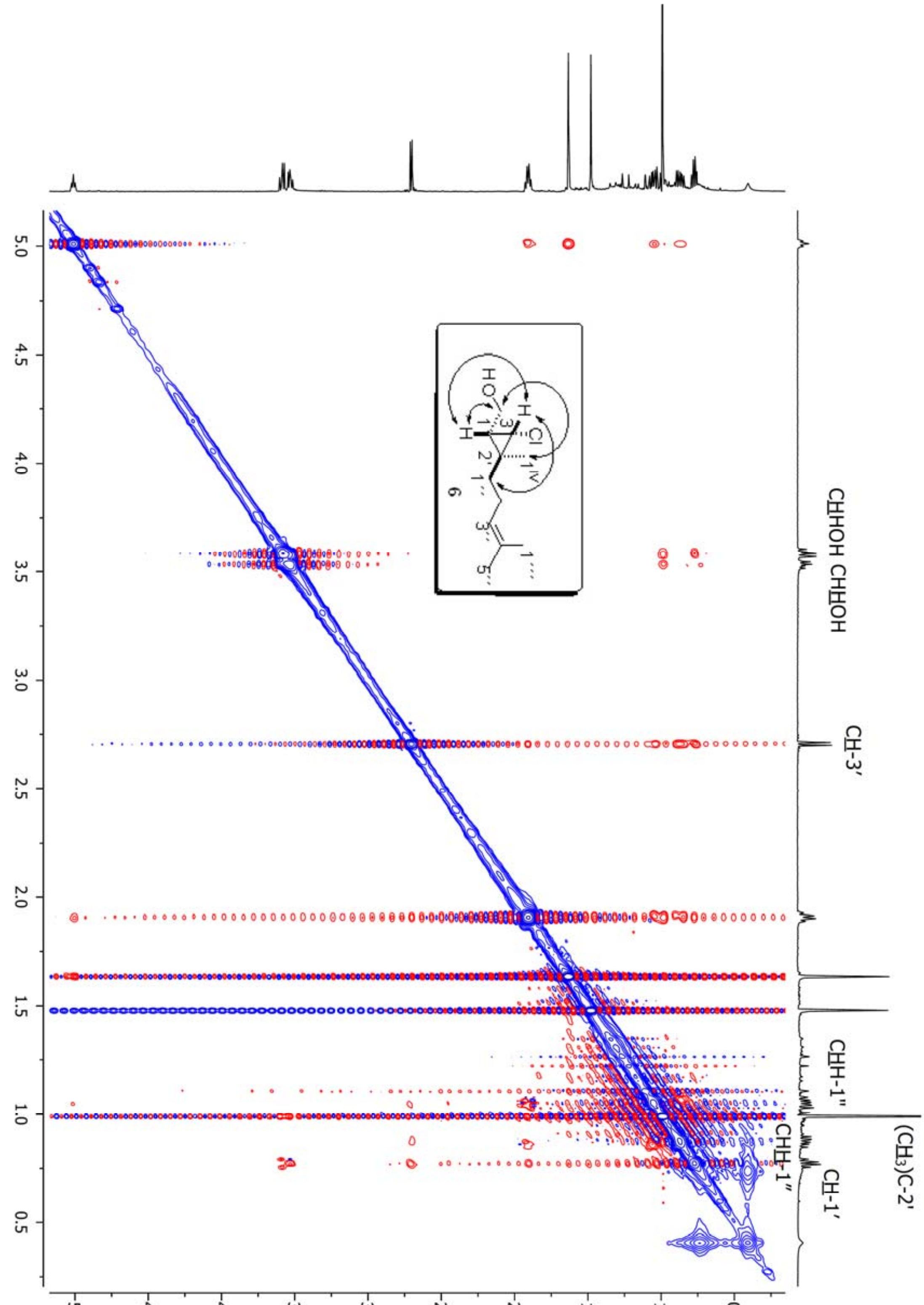


400 MHz ^{1}H NMR of compound **19c** in $CDCl_3$

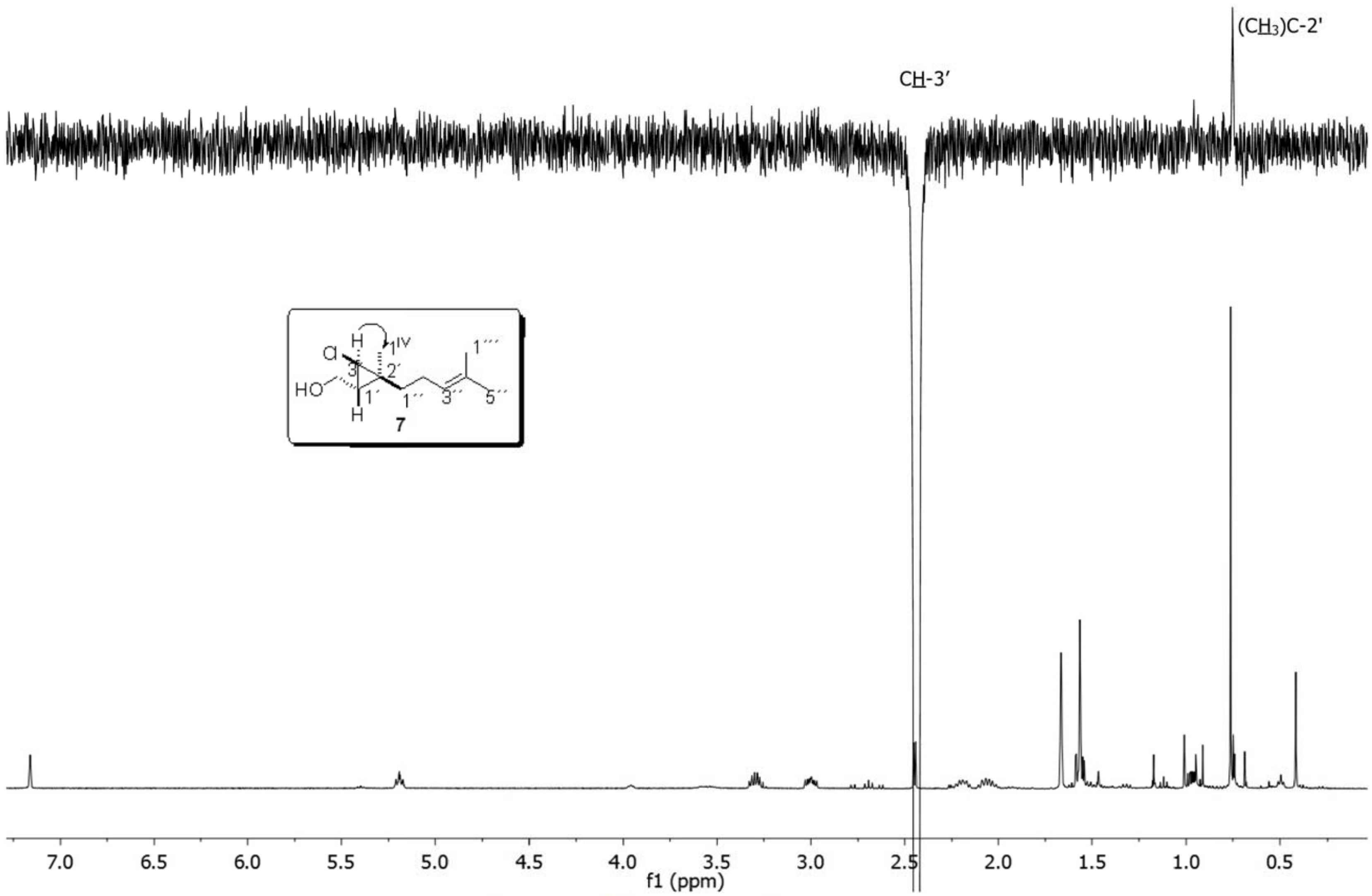


100 MHz ^{13}C NMR of compound **19c** in $CDCl_3$

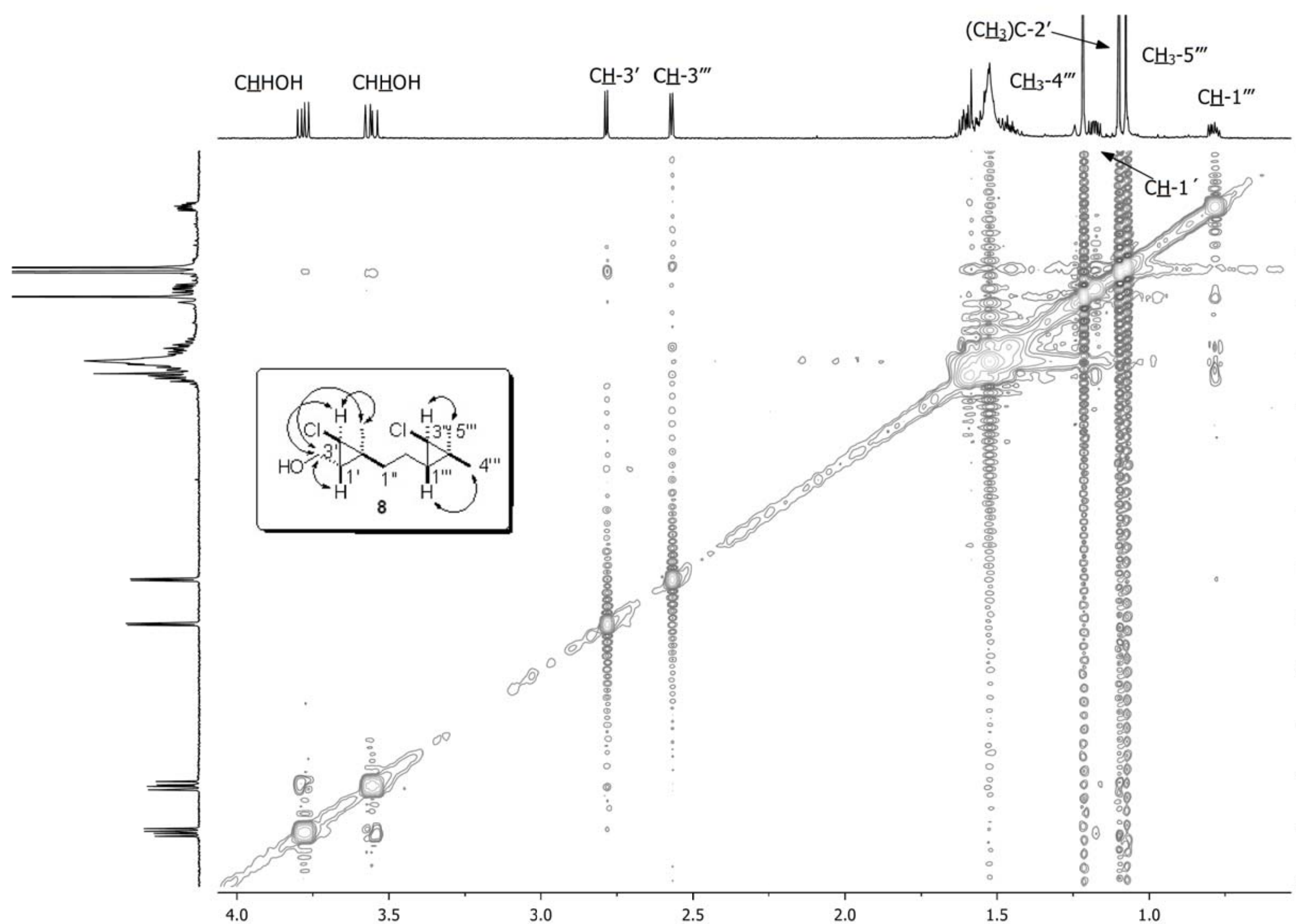
PART D : SELECTED NOESY SPECTRA



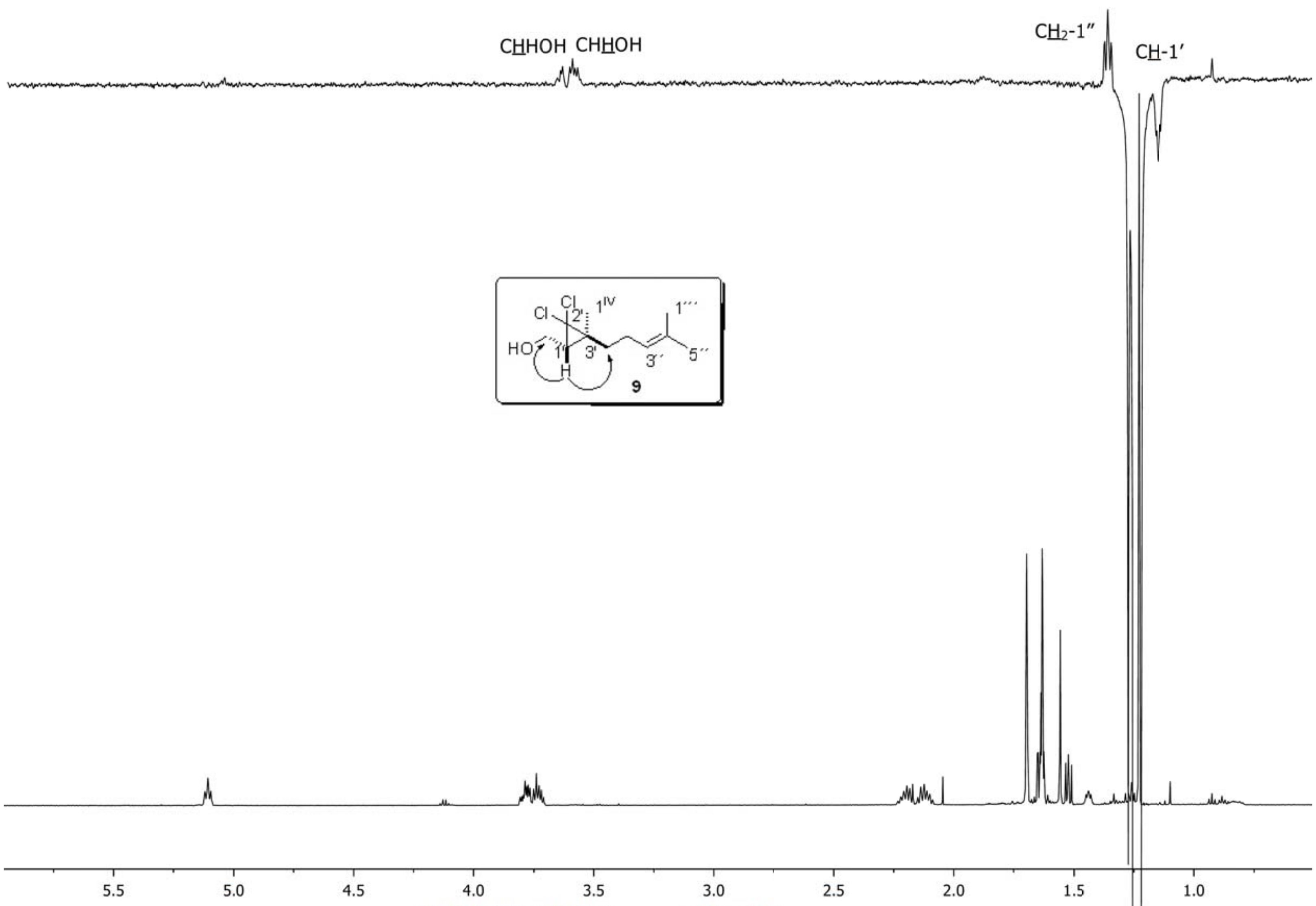
600 MHz NOESY 2D correlation spectrum for compound **6** in C_6D_6



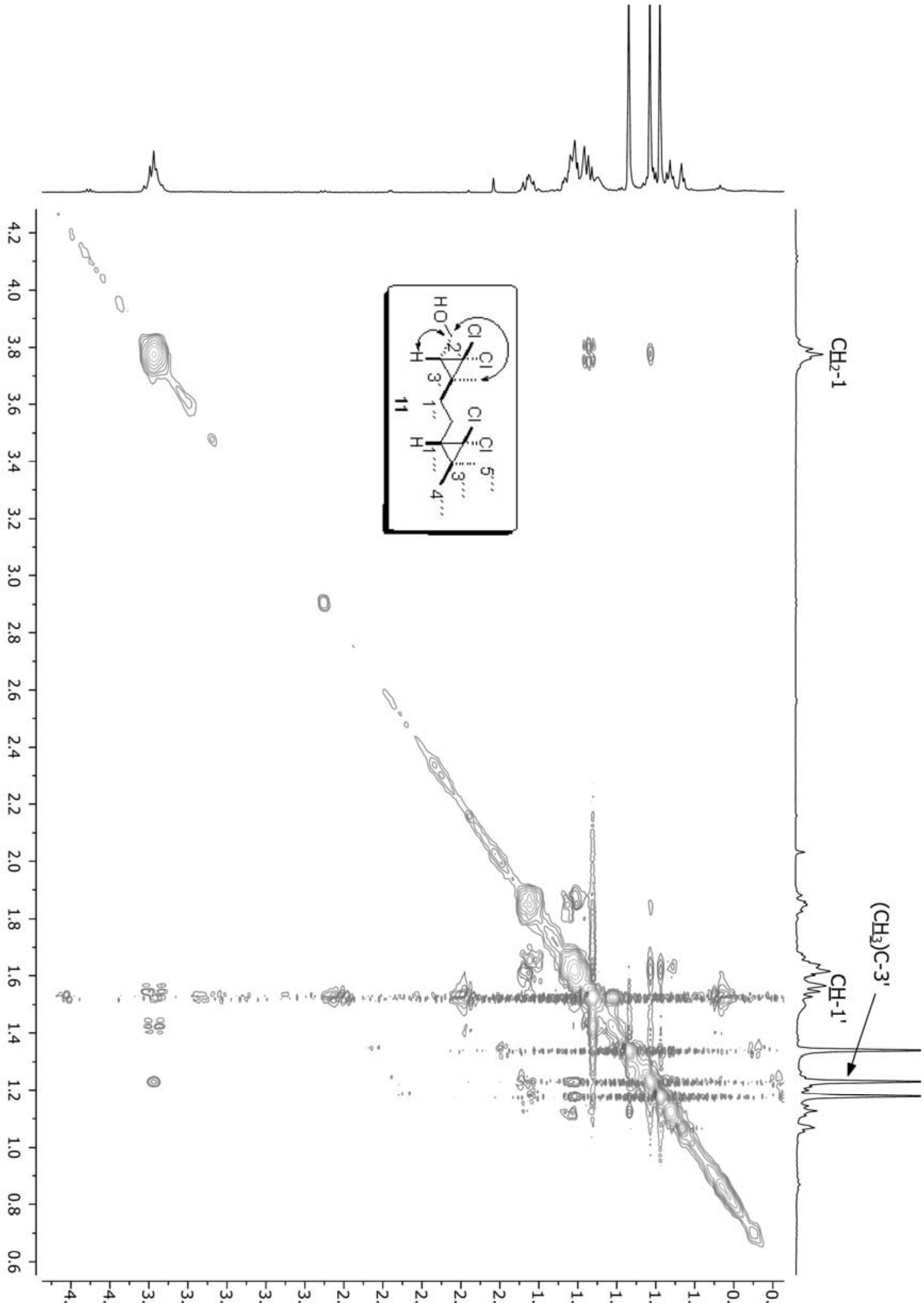
400 MHz NOESY 1D of compound 7 in C_6D_6



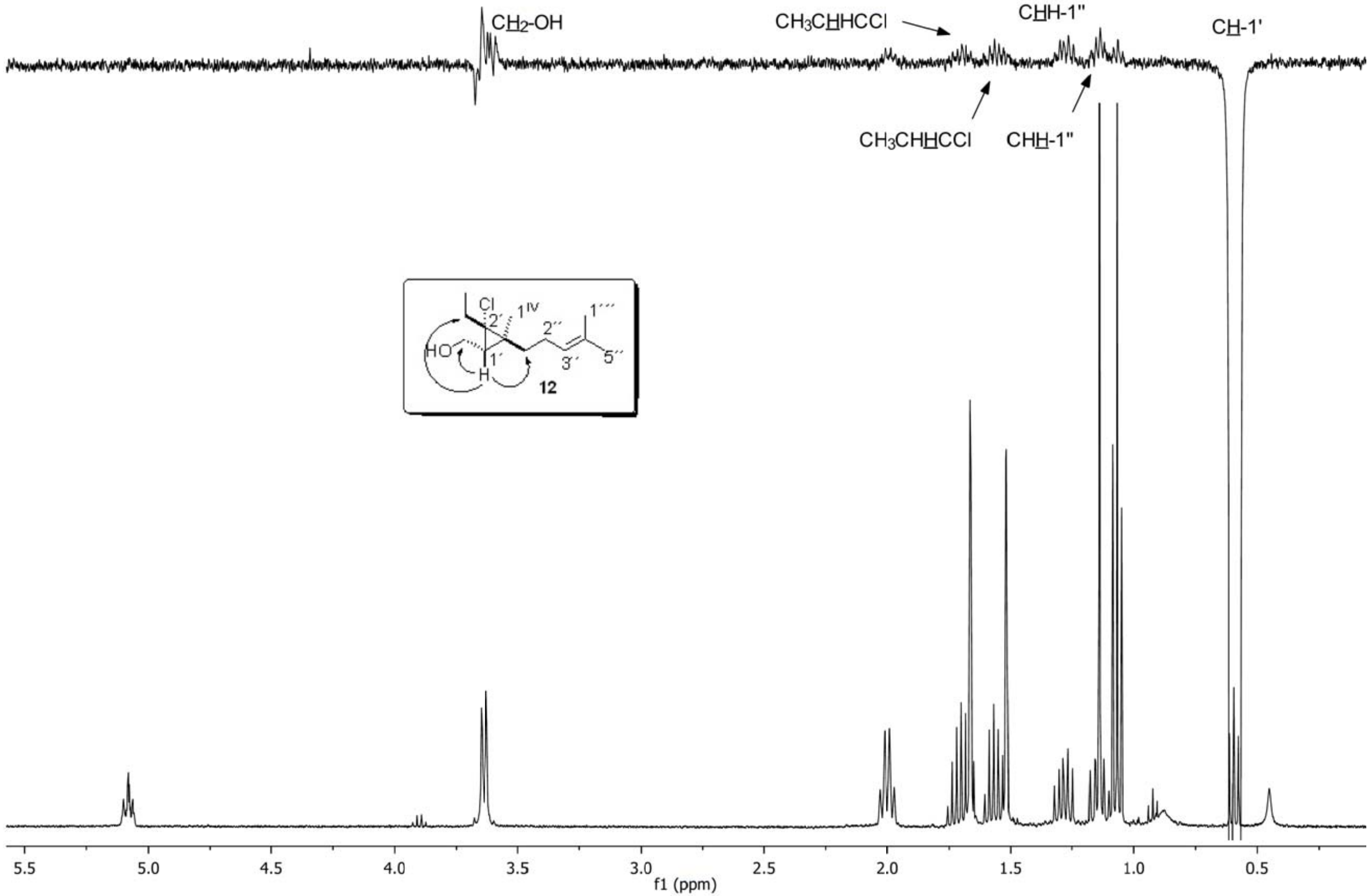
500 MHz NOESY 2D correlation spectrum for compound **8** in $CDCl_3$



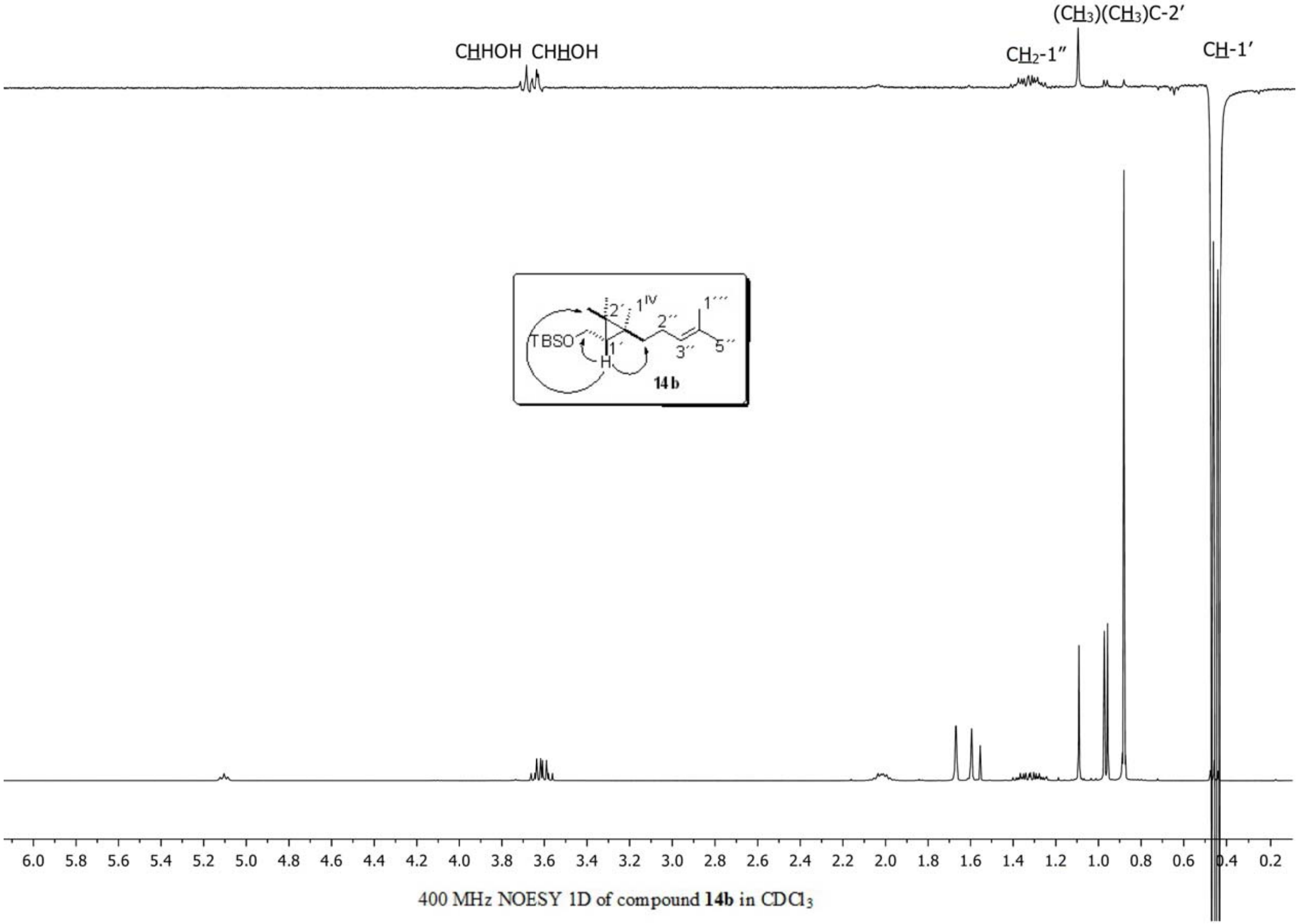
600 MHz NOESY 1D of compound **9** in $CDCl_3$



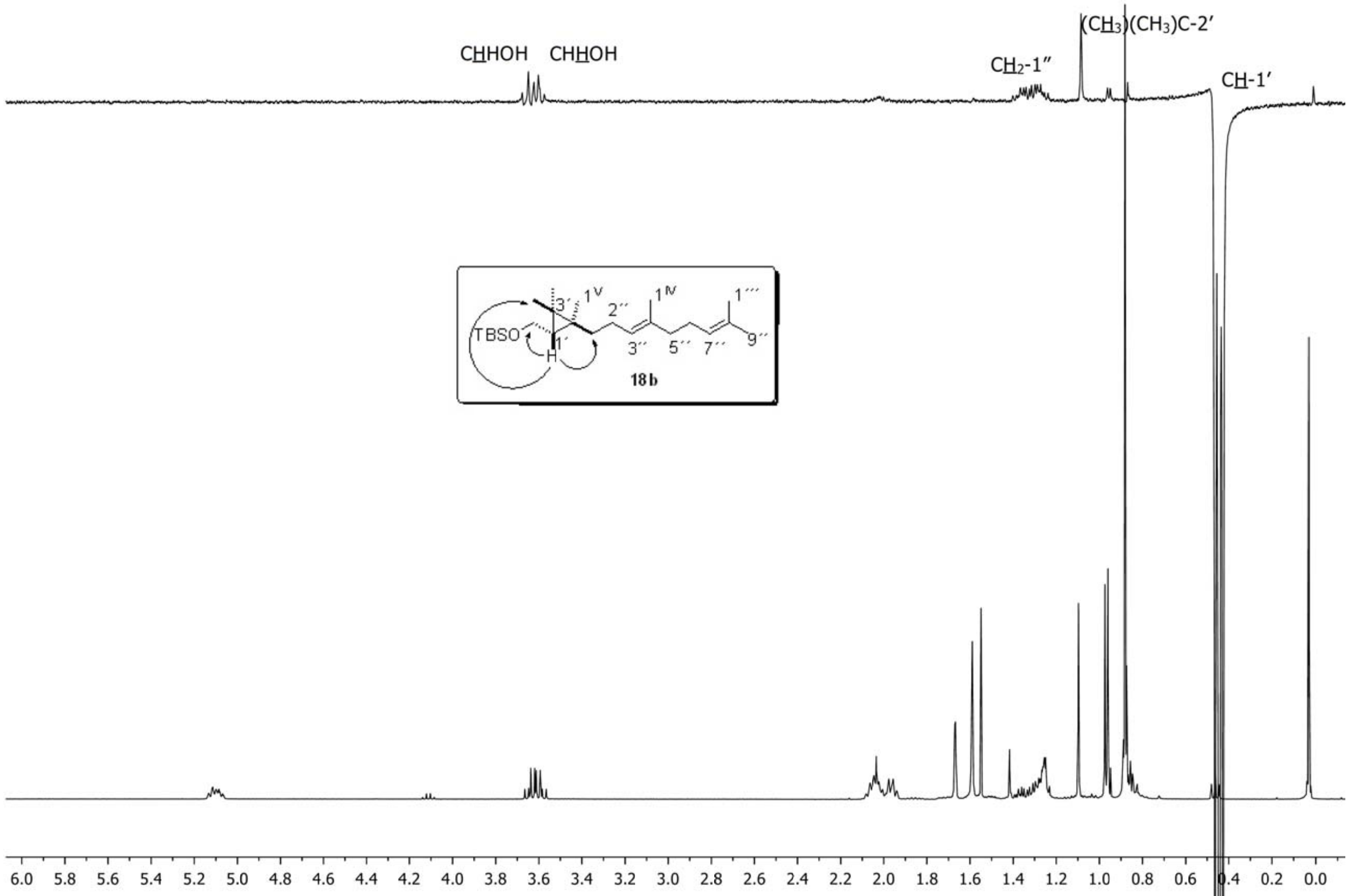
400 MHz NOESY 2D of compound **11** in CDCl$_3$



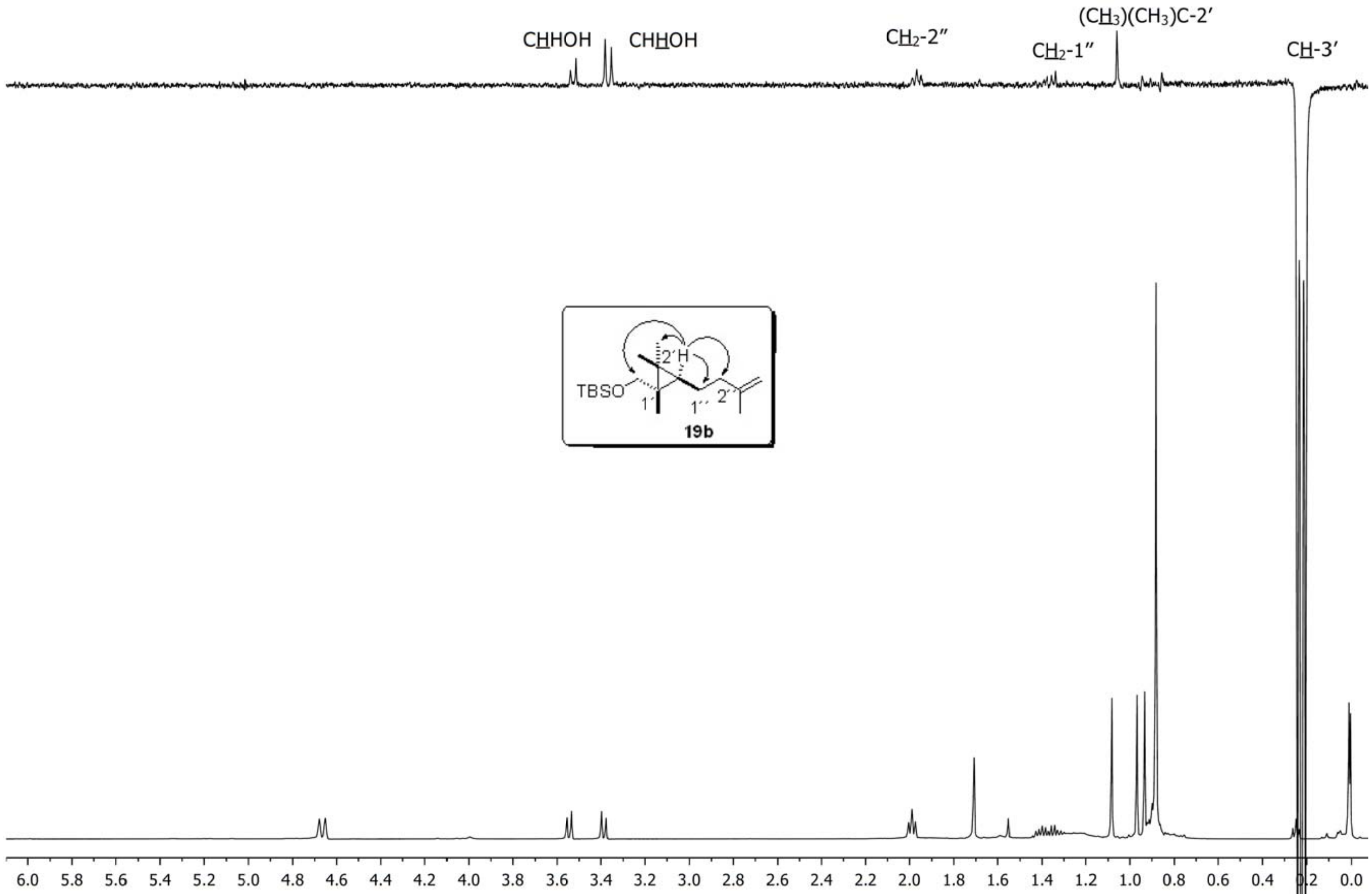
400 MHz NOESY 1D of compound **12** in C_6D_6



400 MHz NOESY 1D of compound **14b** in $CDCl_3$



400 MHz NOESY 1D of compound **18b** in $CDCl_3$



400 MHz NOESY 1D of compound **19b** in $CDCl_3$