C^C* Cyclometalated Platinum(II) N-Heterocyclic Carbene Complexes with a Sterically Demanding β-Diketonato Ligand – Synthesis, Characterization and Photophysical Properties

Supporting Information

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Details of the Structure Determination

Intensity data were collected on a NONIUS κ-CCD diffraction system, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The reflections were merged and corrected from Lorentz, polarization and decay effects. An absorption correction was applied using SADABS[1]. The structures were solved by a combination of direct methods[2] and difference Fourier synthesis. Full-matrix least square refinements against all data were carried out with anisotropic displacement parameters applied to non-hydrogen atoms. Hydrogen atoms attached to carbon were included in geometrically calculated positions using a riding model and were refined isotropically. All calculations were performed with the programs COLLECT,[3] DIRAX,[4] EVALCCD,[5] SIR97,[2] SADABS,[1] the SHELXL-97 package,[6] and ENCIFER[7]. Images of the solid state structures were generated with ORTEP-3.[8]

Table S1. Crystallographic Data for Compounds **4** and **20**.

	4	**20**
empirical formula	$C_{20}H_{19}N_3O_2Pt$	$C_{36}H_{35}N_3O_2Pt$
formula weight	528.47	736.76
temperature (K)	198(2)	198(2)
wavelength (Å)	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
unit cell dimensions (in Å and °)	a = 11.7630(5), α = 90 b = 11.8750(17), β = 110.504(6) c = 13.1410(19), γ = 90	a = 15.575(2), α = 90 b = 11.872(4), β = 127.70(2) c = 21.594(6), γ = 90
volume (in $Å^3$)	1831.6(4)	3159.2(14)
Z	4	4
density (g/cm^3, calculated)	1.916	1.549
absorption coeff. (mm^{-1})	7.680	4.477
F(000)	1016	1464
crystal size (mm)	0.35 x 0.20 x 0.12	0.60 x 0.37 x 0.25
θ range for data collection (°)	3.11 to 23.26	2.09 to 23.26
index ranges	$-13 \le h \le 13$ $-13 \le k \le 13$ $-14 \le l \le 14$	$-17 \le h \le 17$ $-12 \le k \le 13$ $-23 \le l \le 23$
reflections collected	19834	19739
independent reflections	2626 [*R*(int) = 0.0564]	4065 [*R*(*int*) = 0.0797]
absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	2626/0/237	4065/0/385
goodness of fit on F^2	1.043	1.238
final R indices [$I>2\sigma(I)$]	*R*1 = 0.0246, w*R*2 = 0.0329	*R*1 = 0.0496, w*R*2 = 0.1203
R indices (all data)	*R*1 = 0.0434, w*R*2 = 0.0361	*R*1 = 0.0893, w*R*2 = 0.1357
largest diff. peak and hole ($e \cdot A^{-3}$)	0.517 and -0.501	0.838 and -1.236

Predicted and measured emission wavelengths

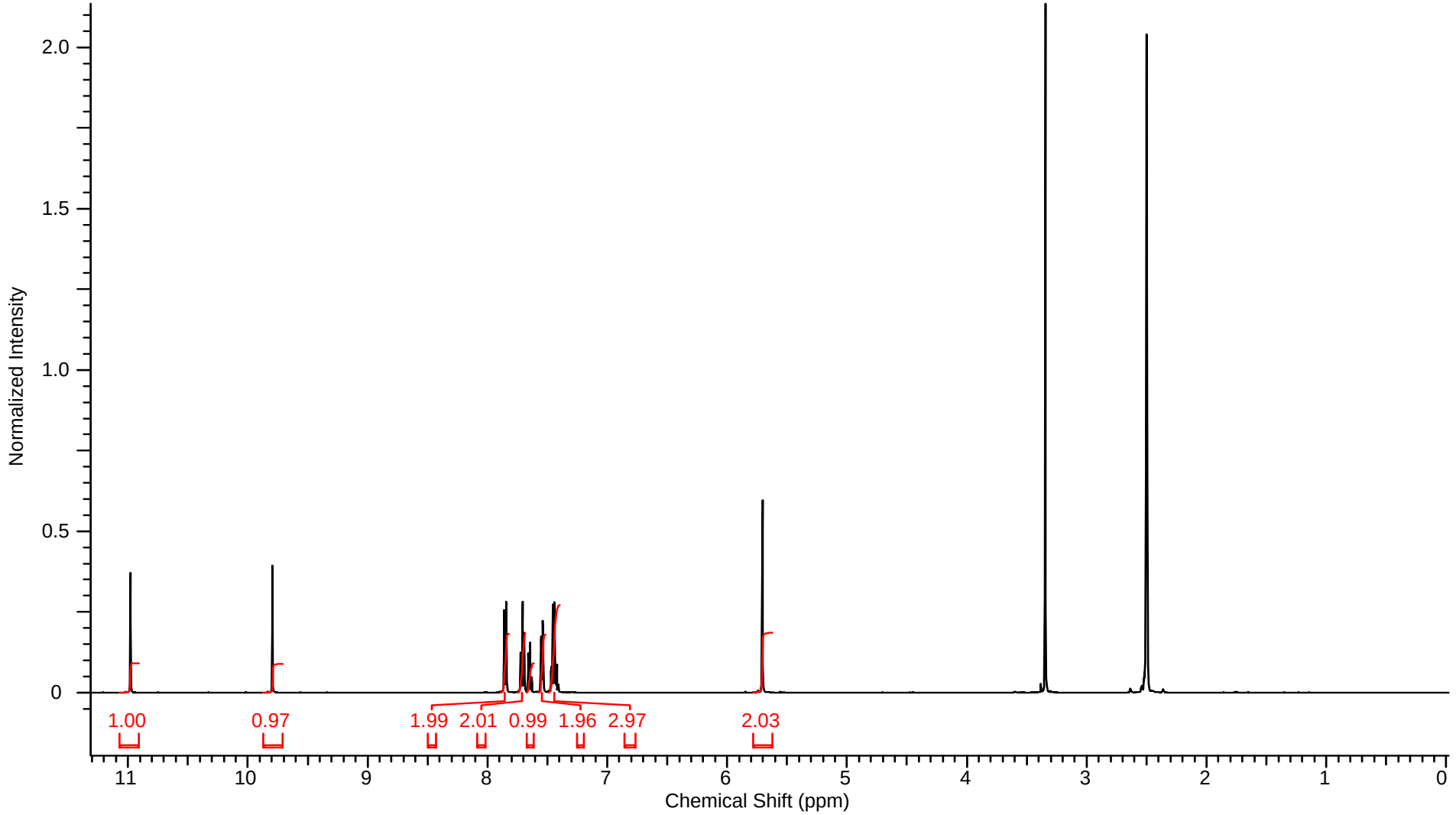
Table S2. Predicted and measured emission wavelengths of complexes **4-6** and **16-22** (BP86/6-31G*).

	λ_{calc} [nm] (BP86)	λ_{em} [nm] [a]
4	453	432
5	482	477
6	486	477
16	456	455
17	485	478
18	480	477
19	465	475
20	487	477
21	488	478
22	463	471

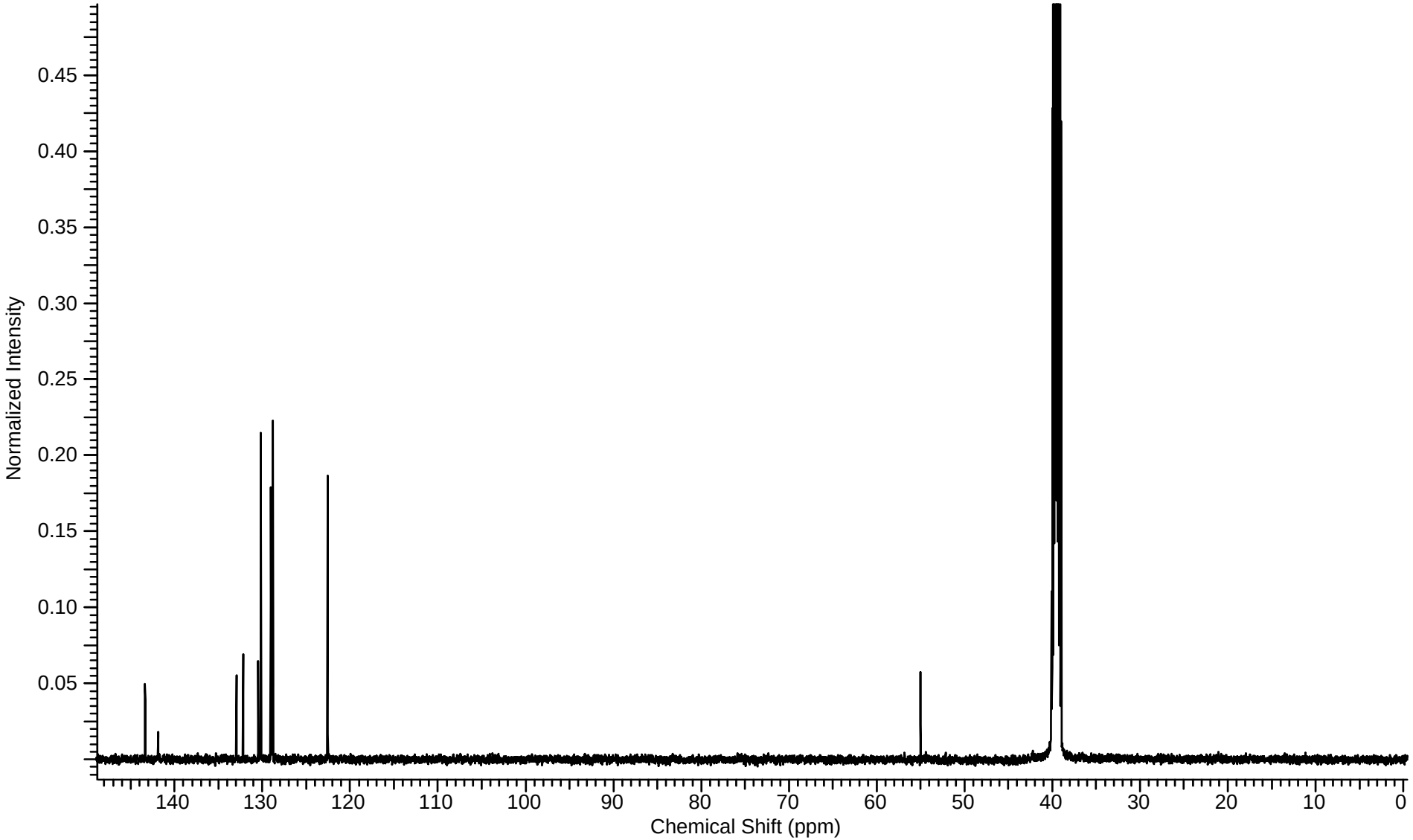
[a] Max. emission wavelength.

NMR-spectra

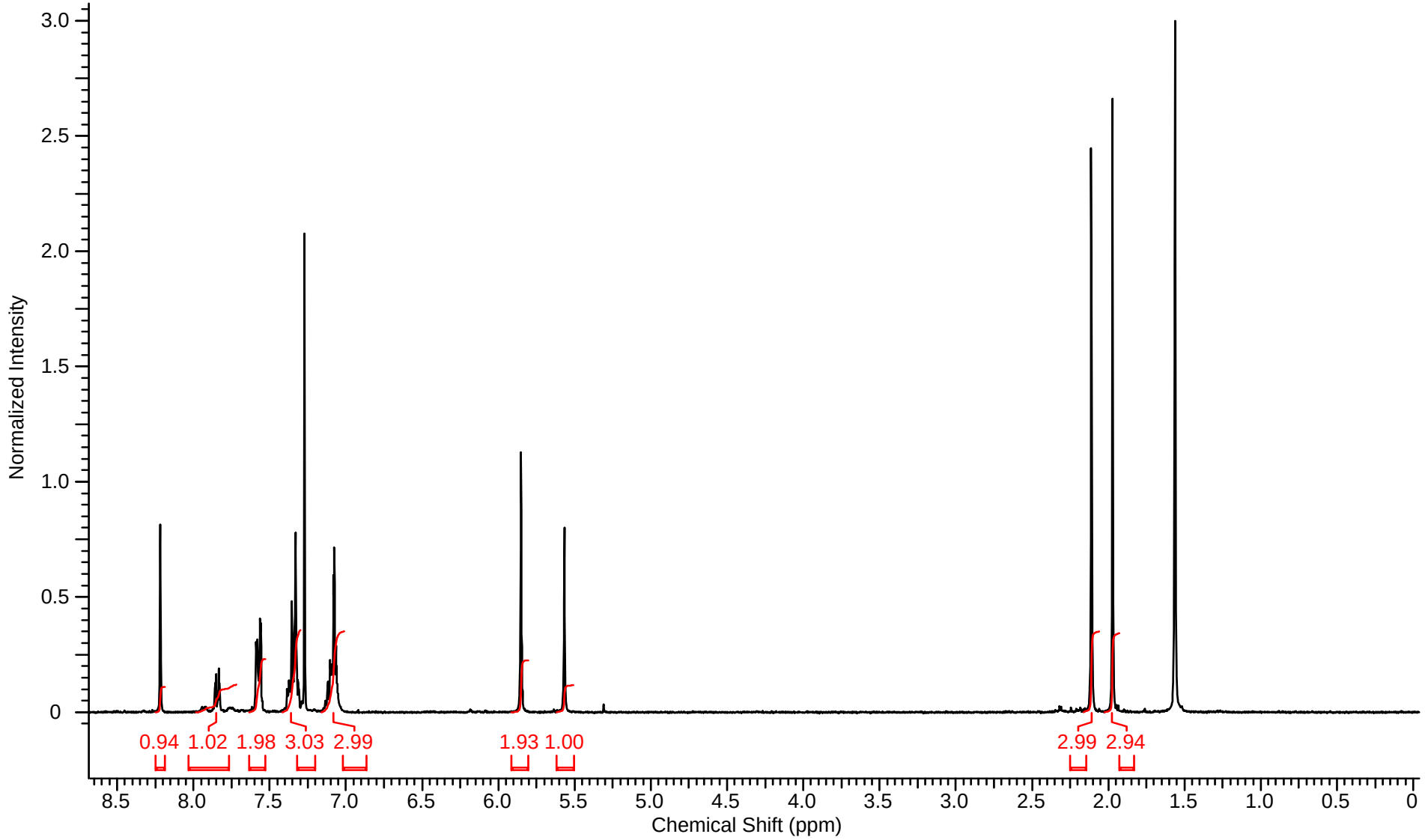
compound 3 – ^{1}H-NMR



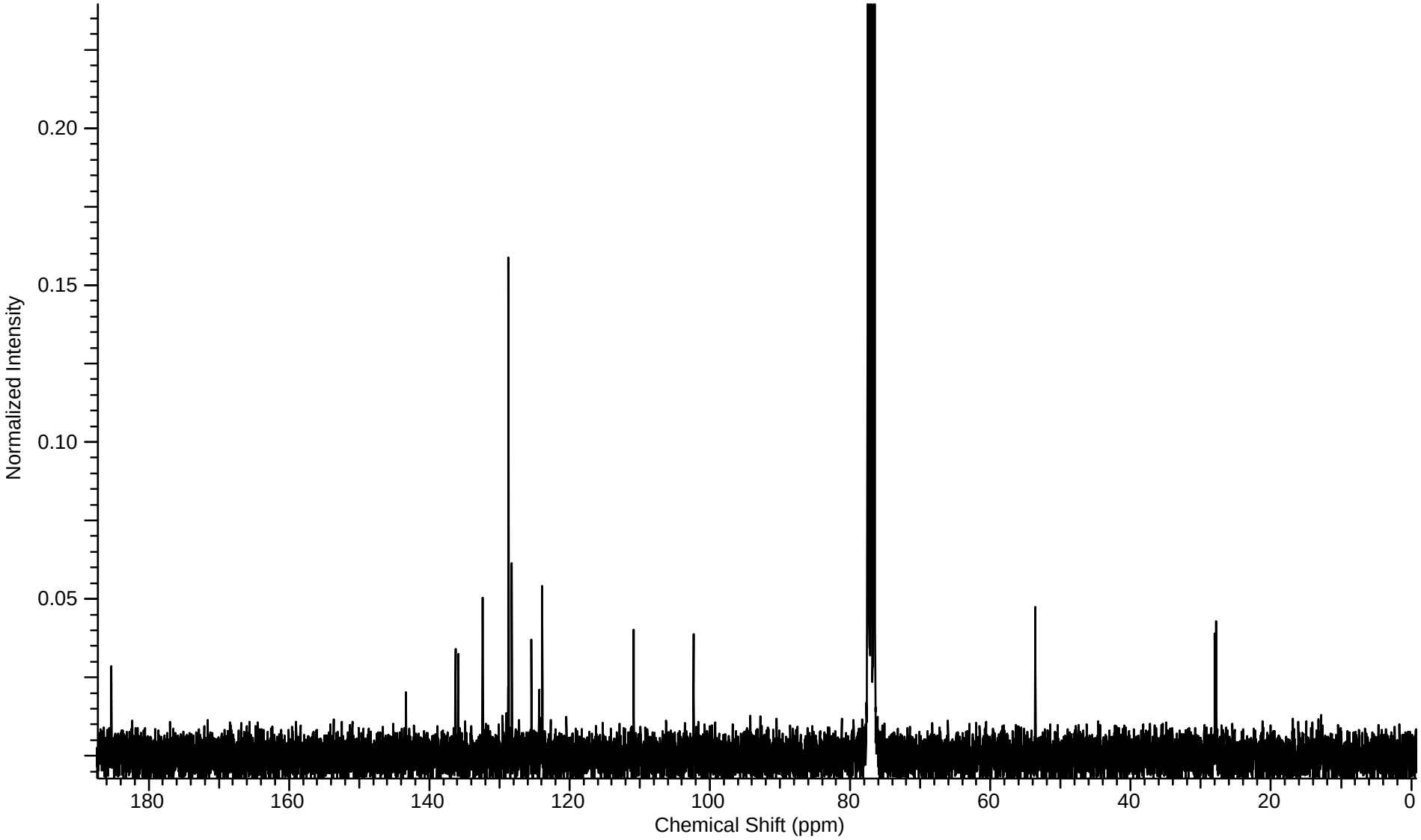
compound 3 – ^{13}C-NMR



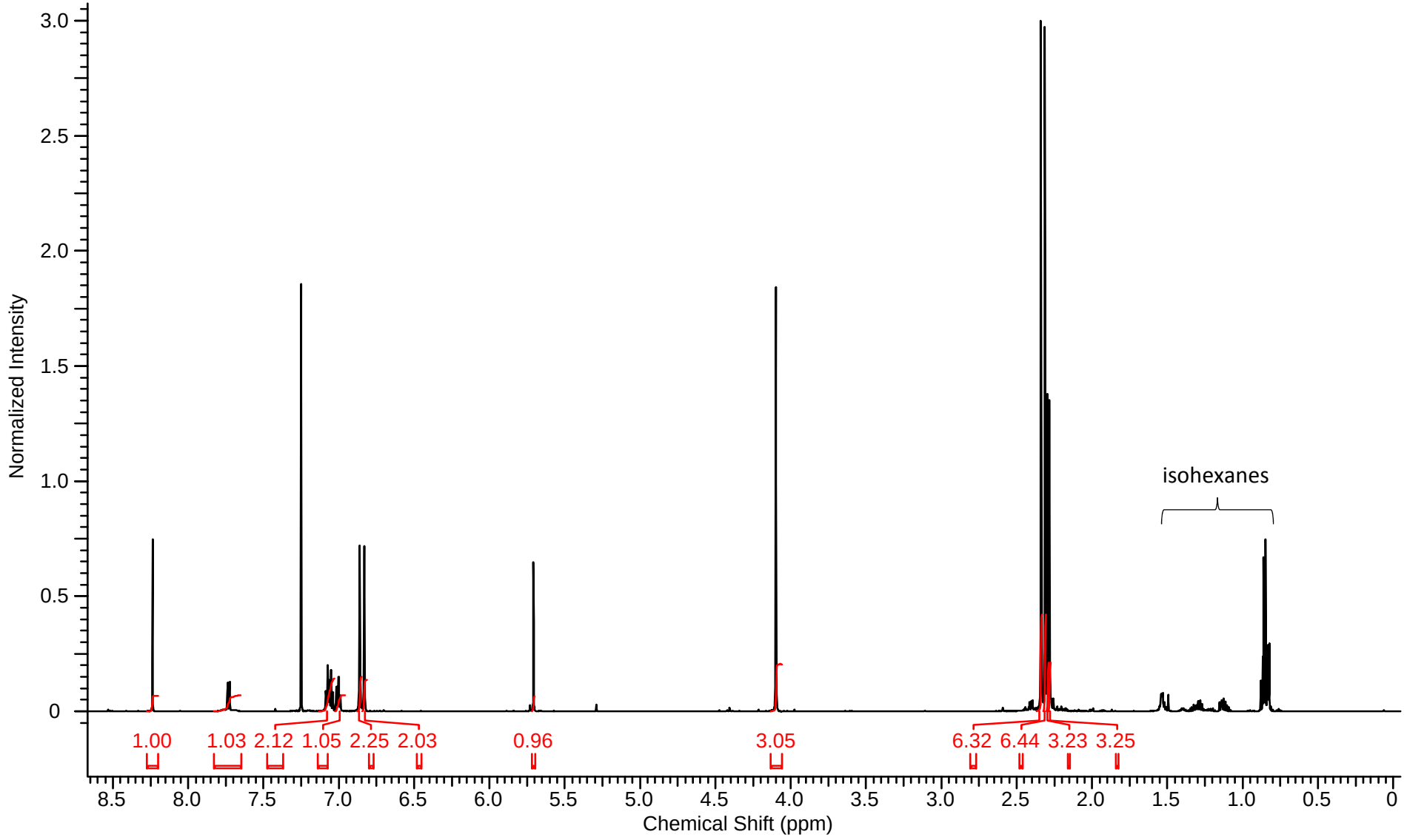
compound 4 – ^{1}H-NMR



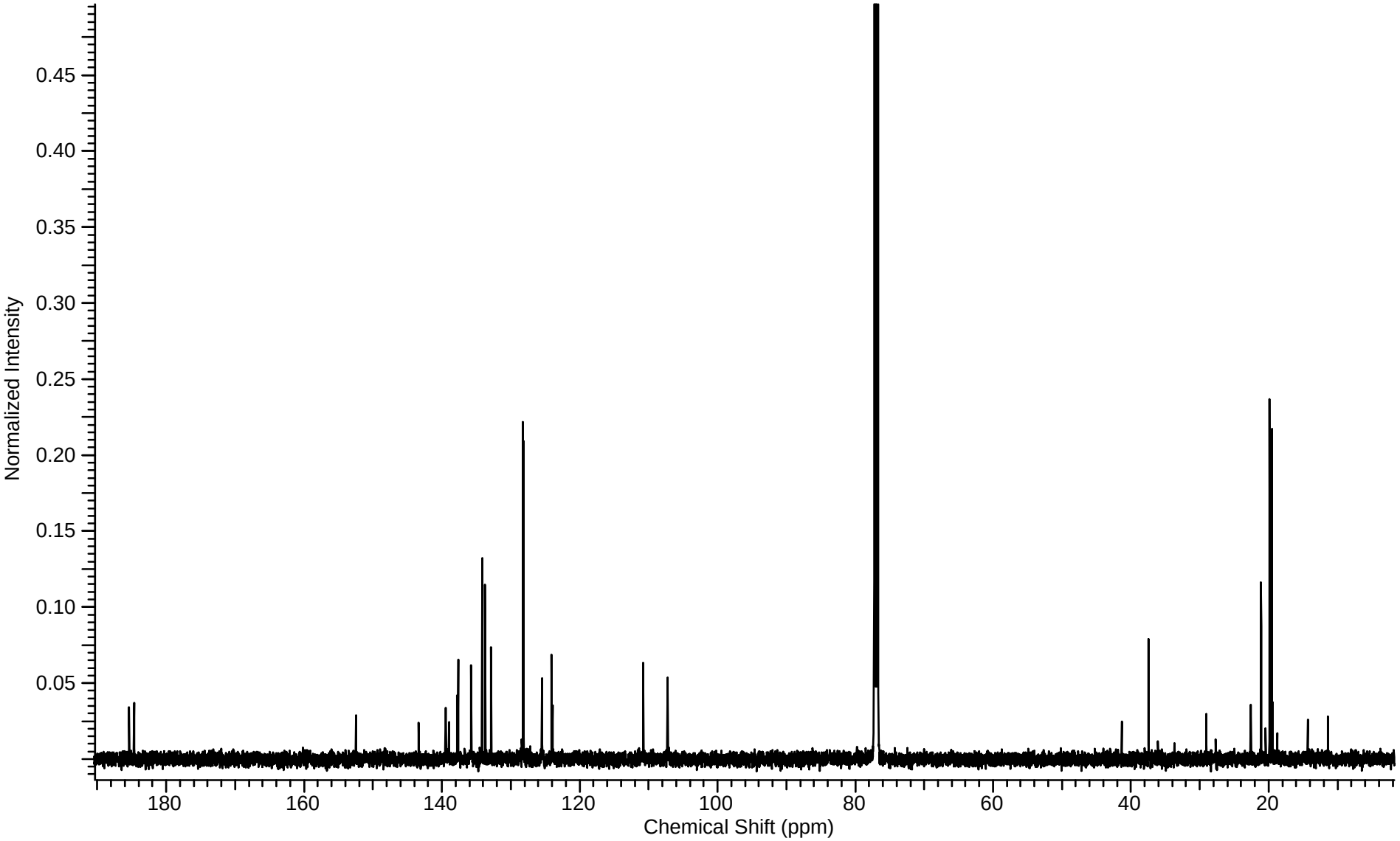
compound 4 – ^{13}C-NMR



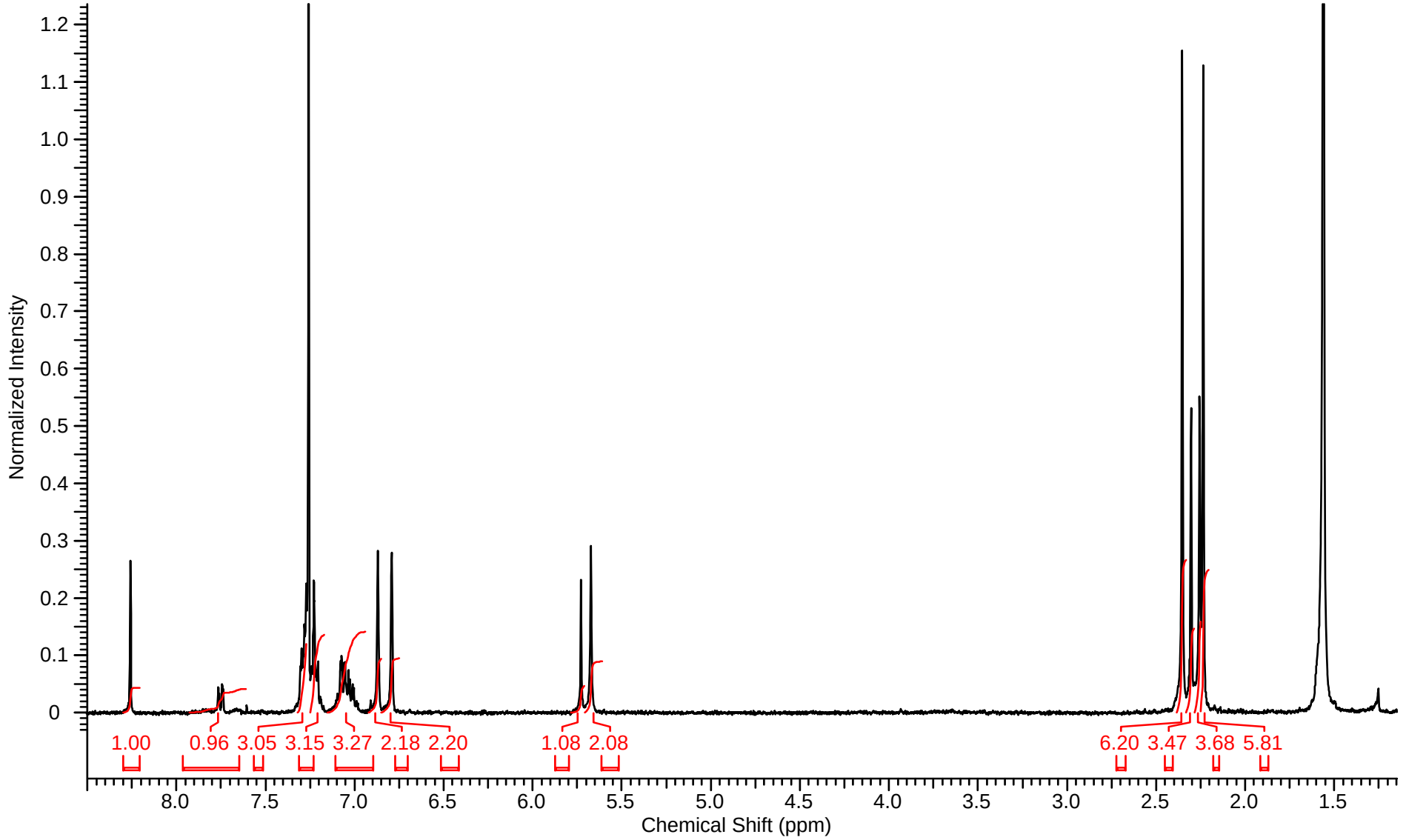
compound 5 – ^{1}H-NMR



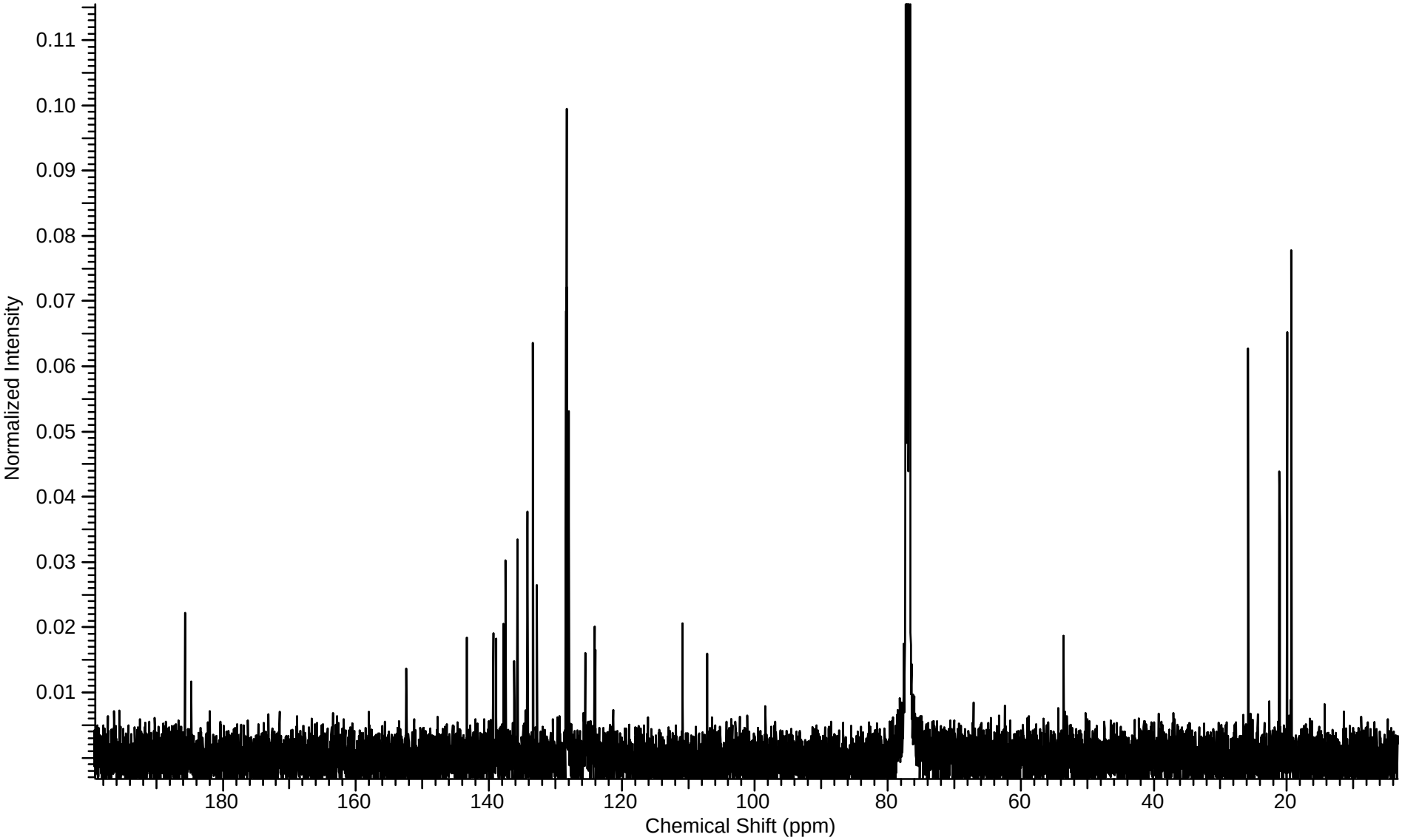
compound 5 – ^{13}C-NMR



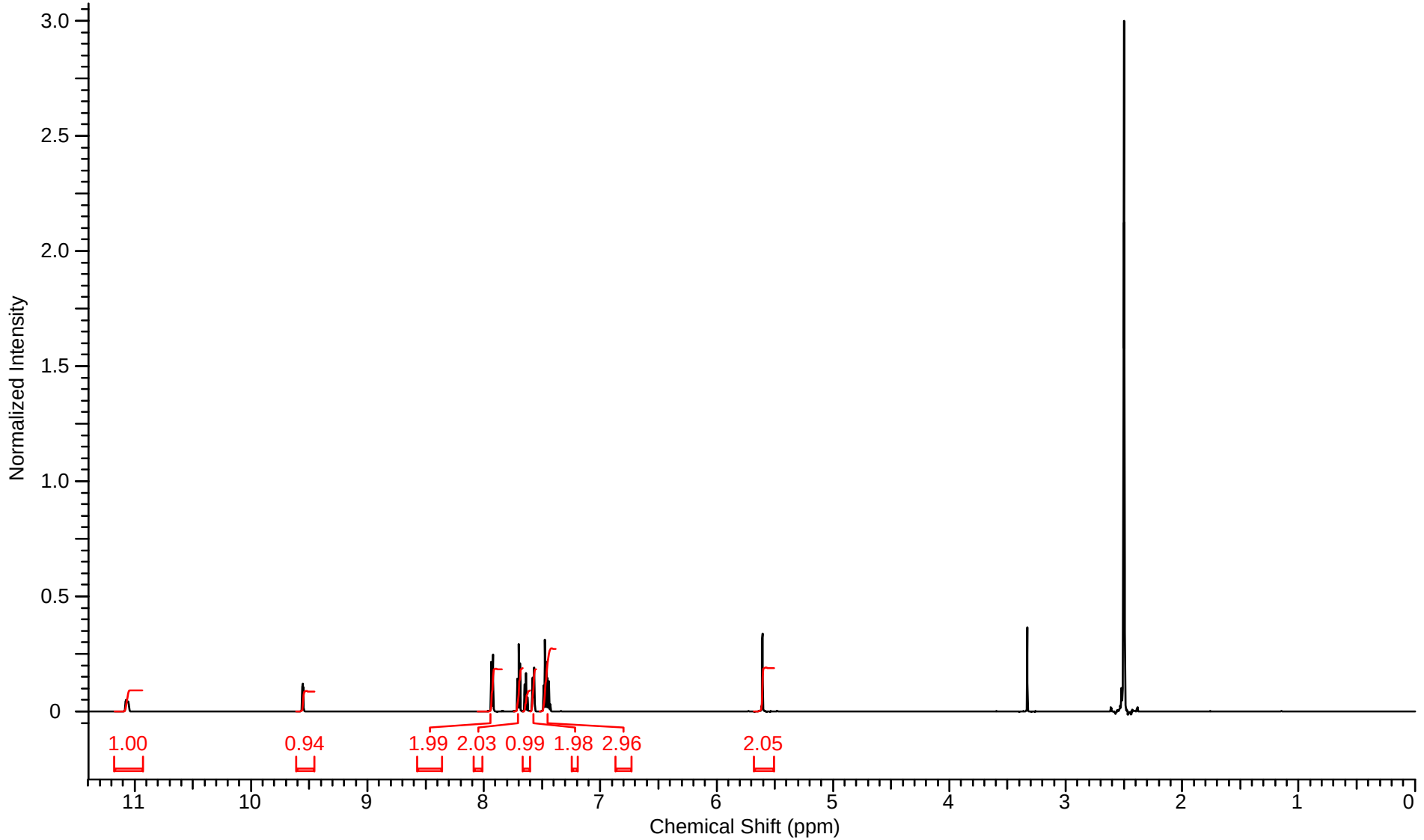
compound 6 – ^{1}H-NMR



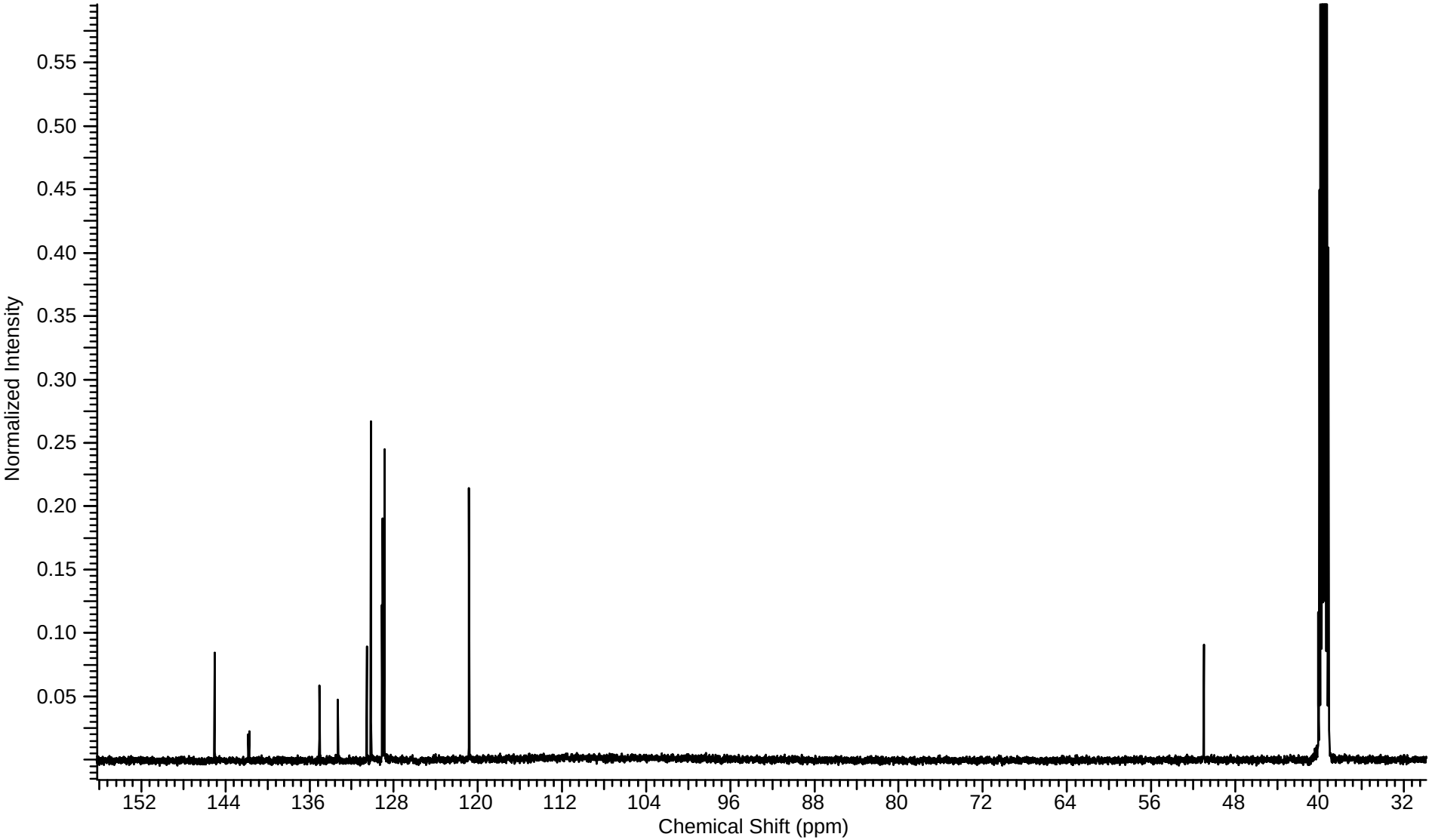
compound 6 – ^{13}C-NMR



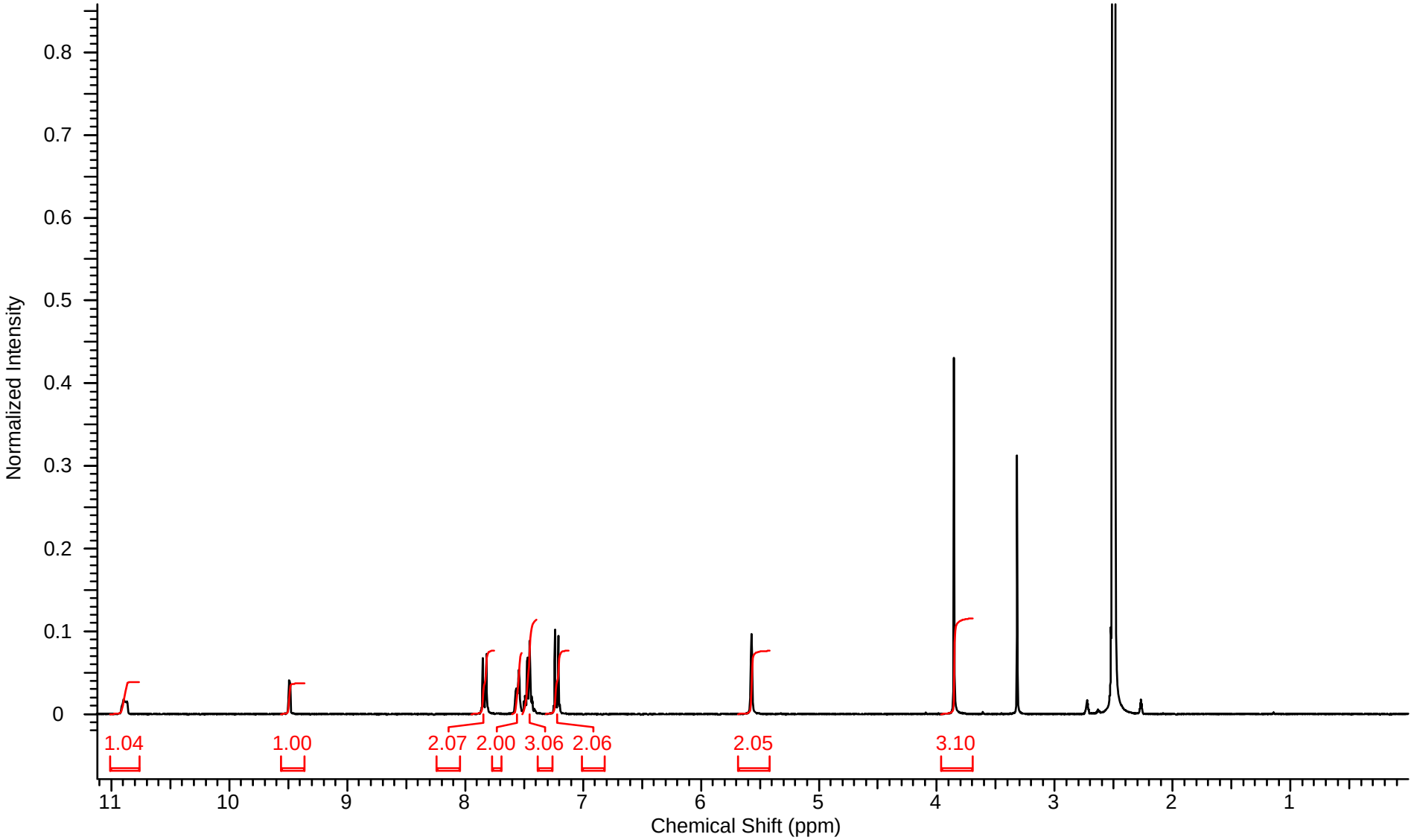
compound 13 – ^{1}H-NMR



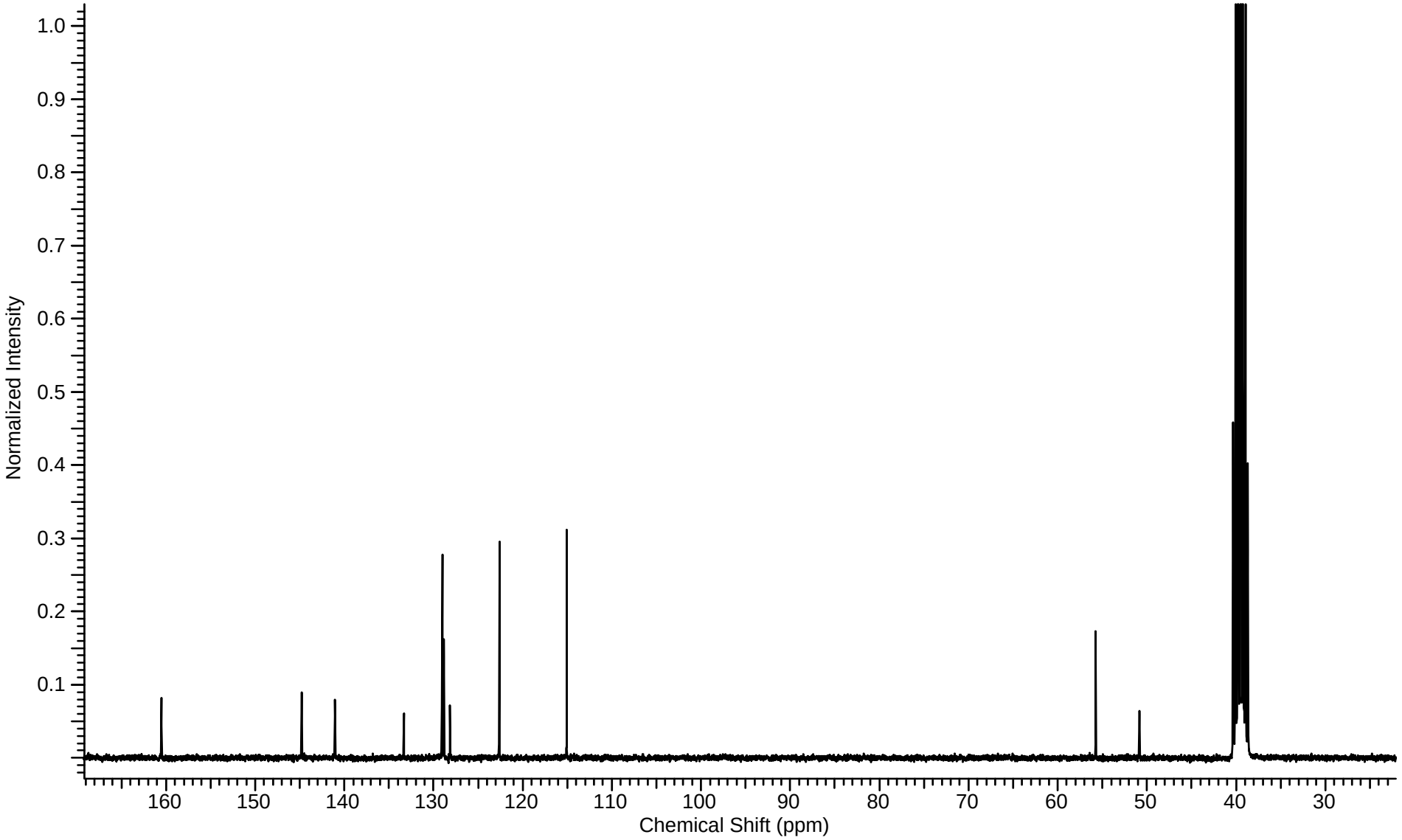
compound 13 – ^{13}C-NMR



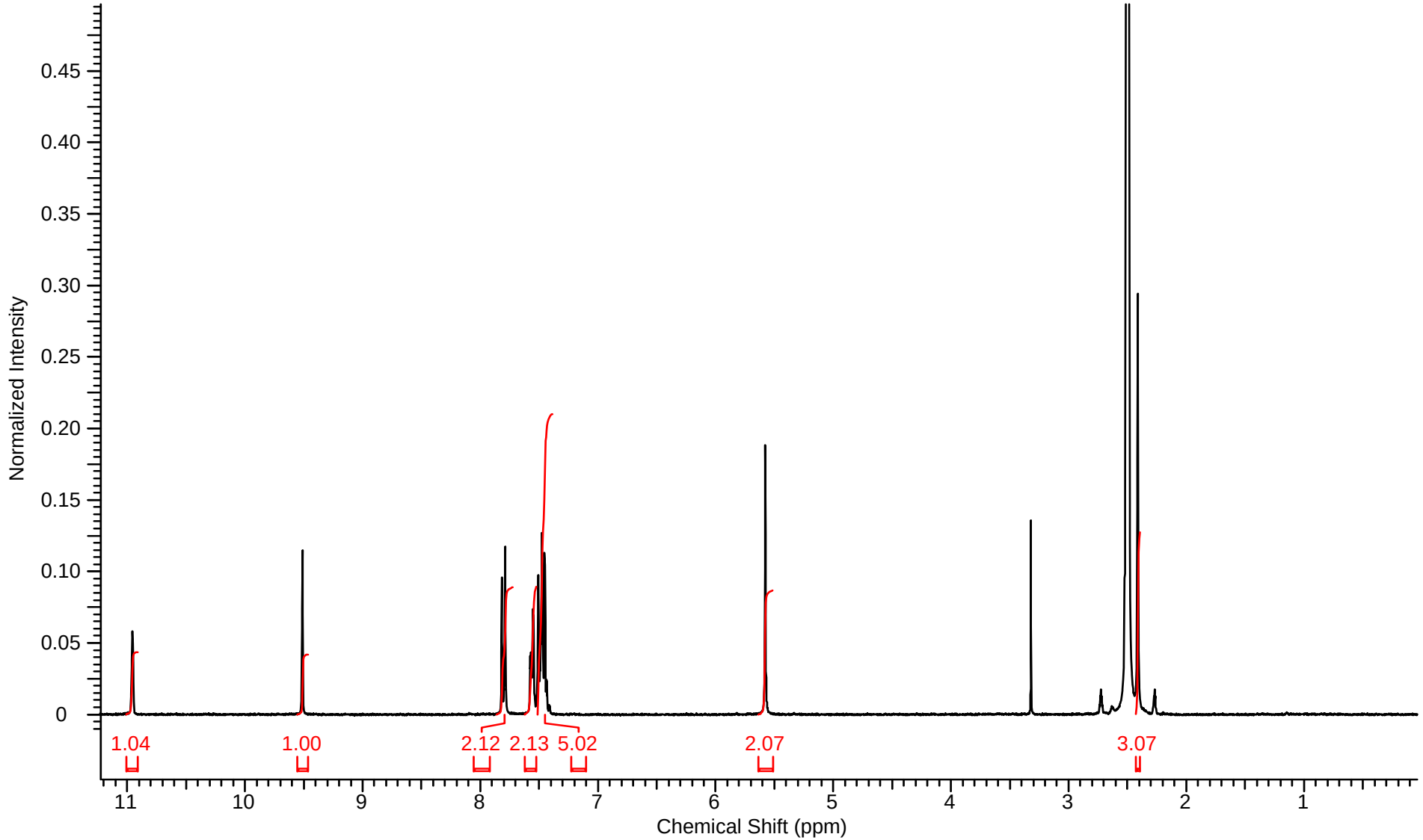
compound 14 – ^{1}H-NMR



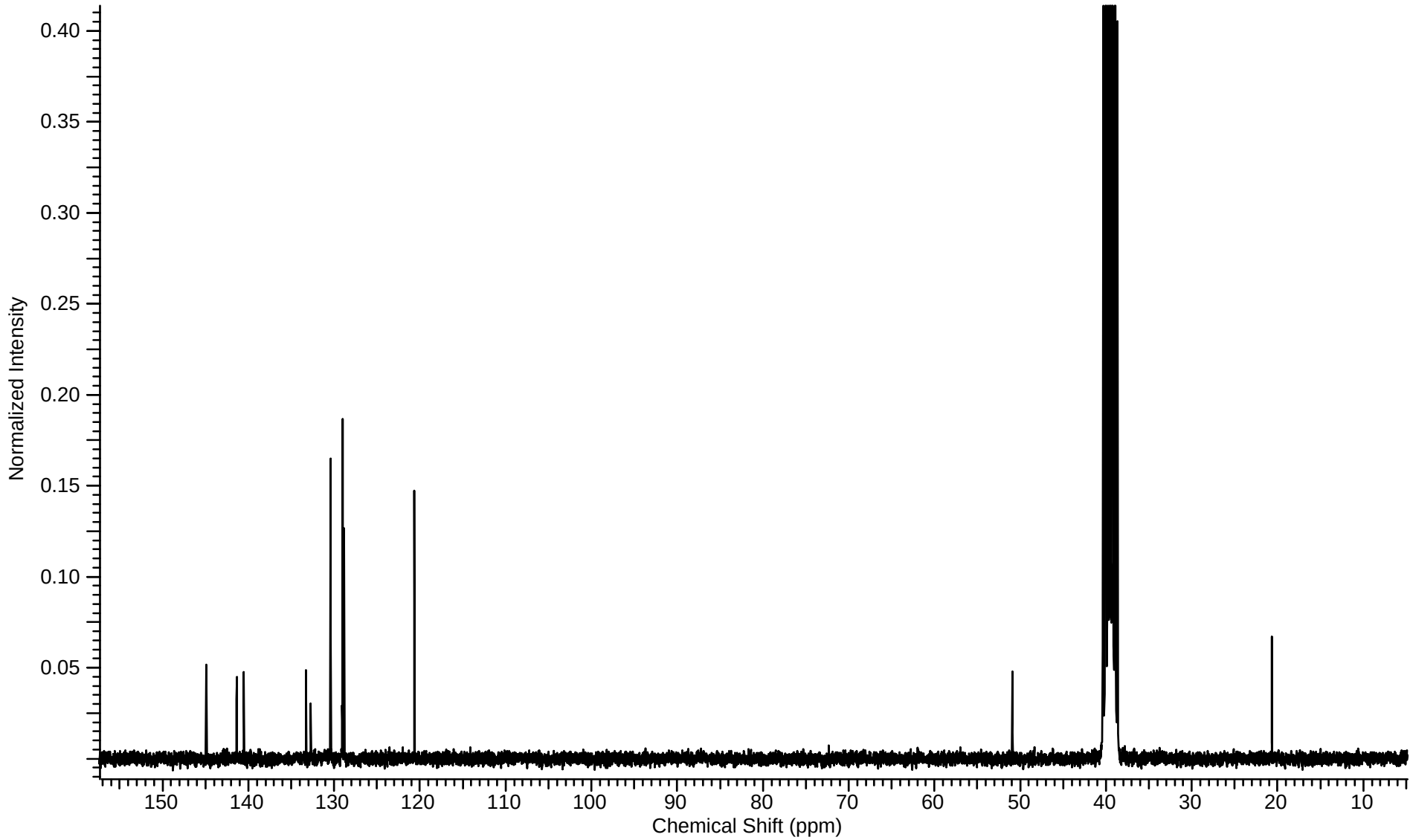
compound 14 – ^{13}C-NMR



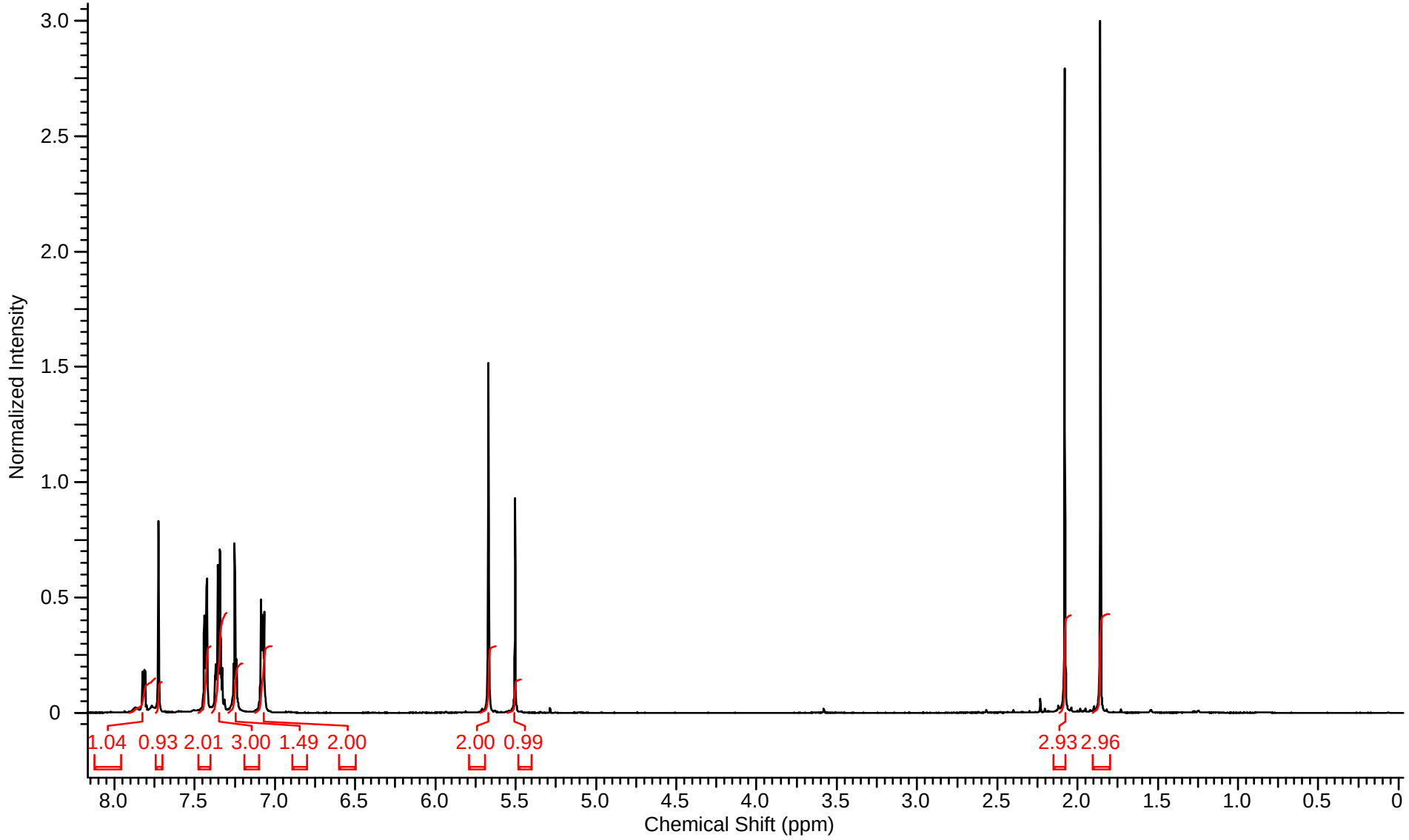
compound 15 – ^{1}H-NMR



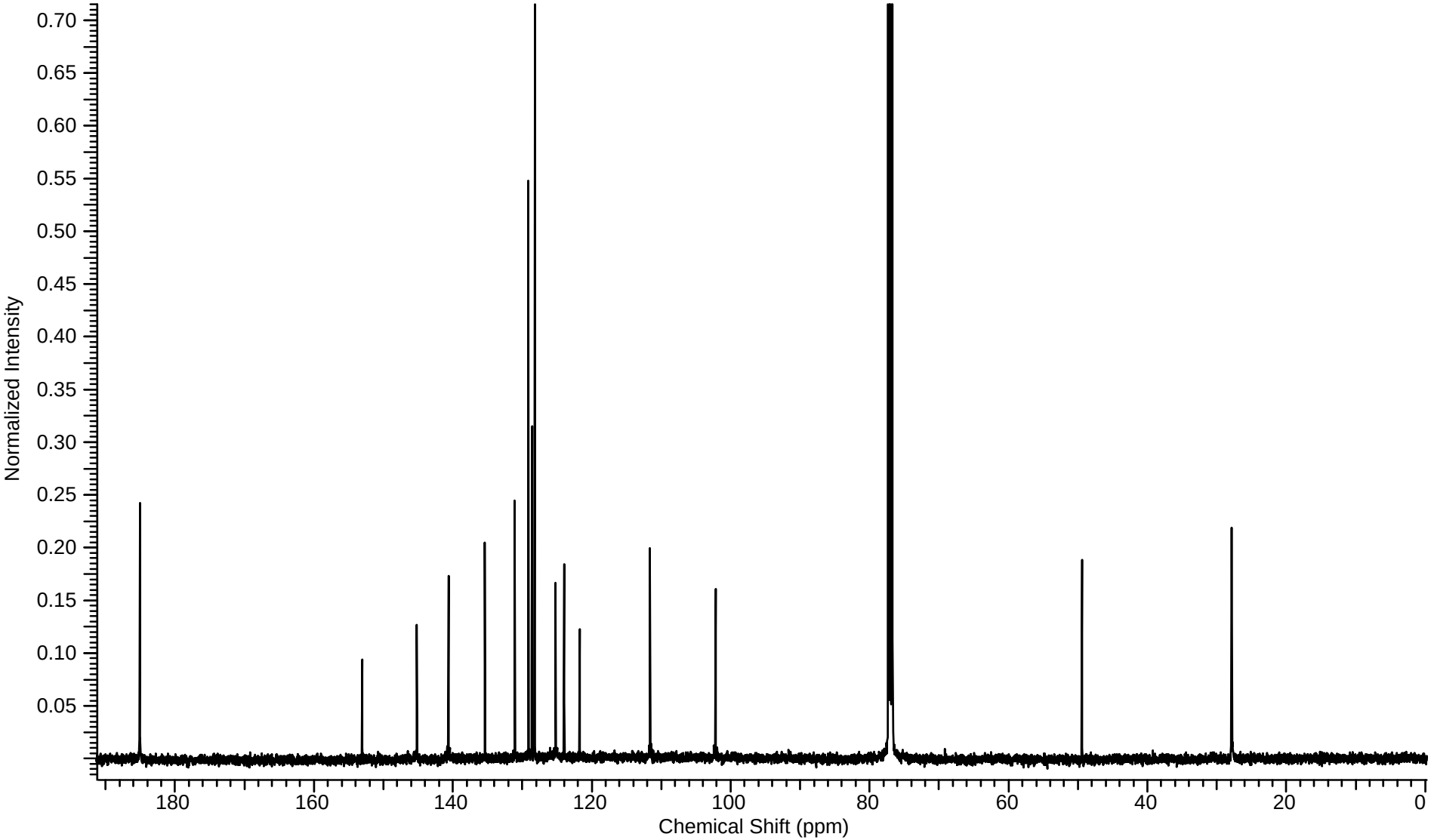
compound 15 – ^{13}C-NMR



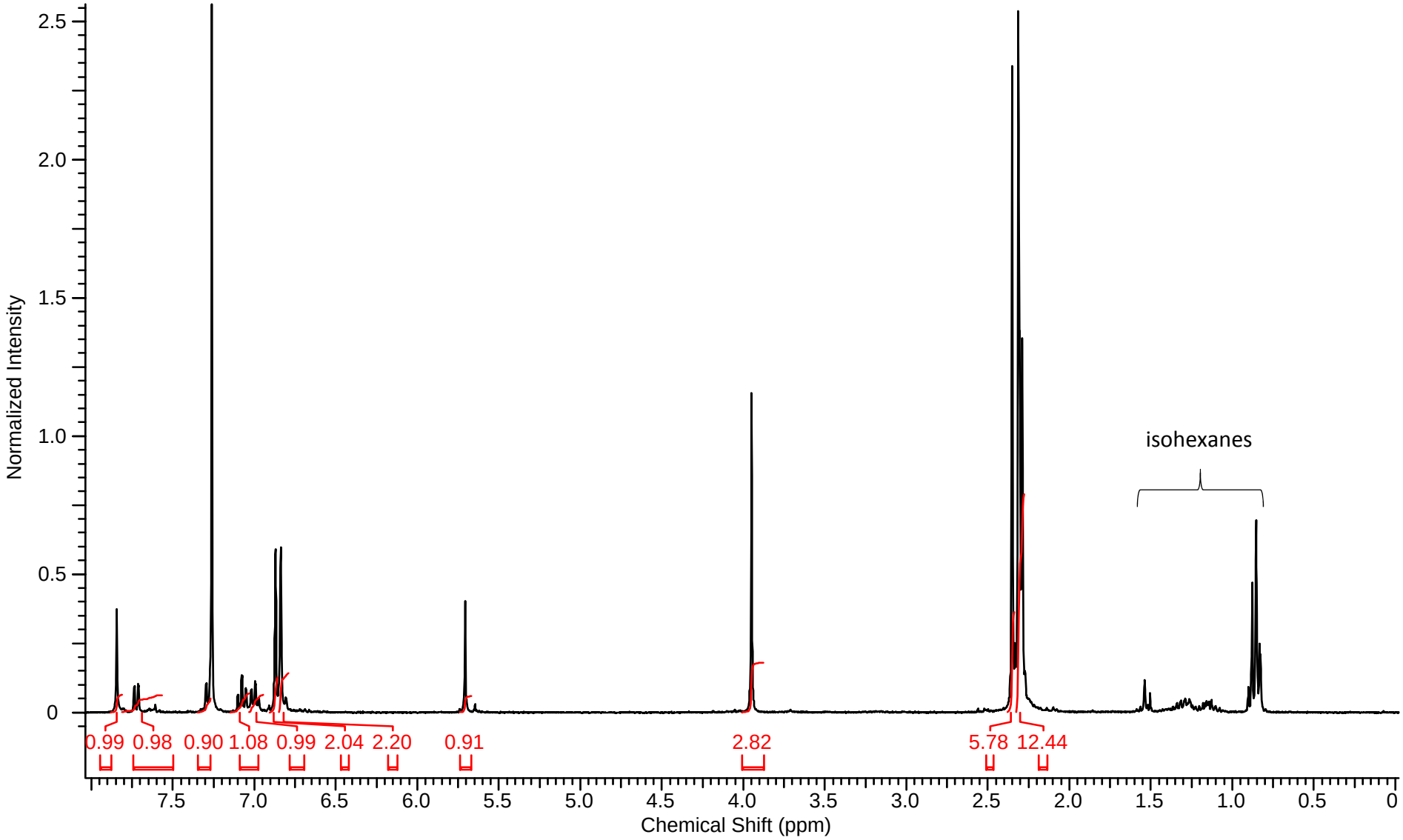
compound 16 – ^{1}H-NMR



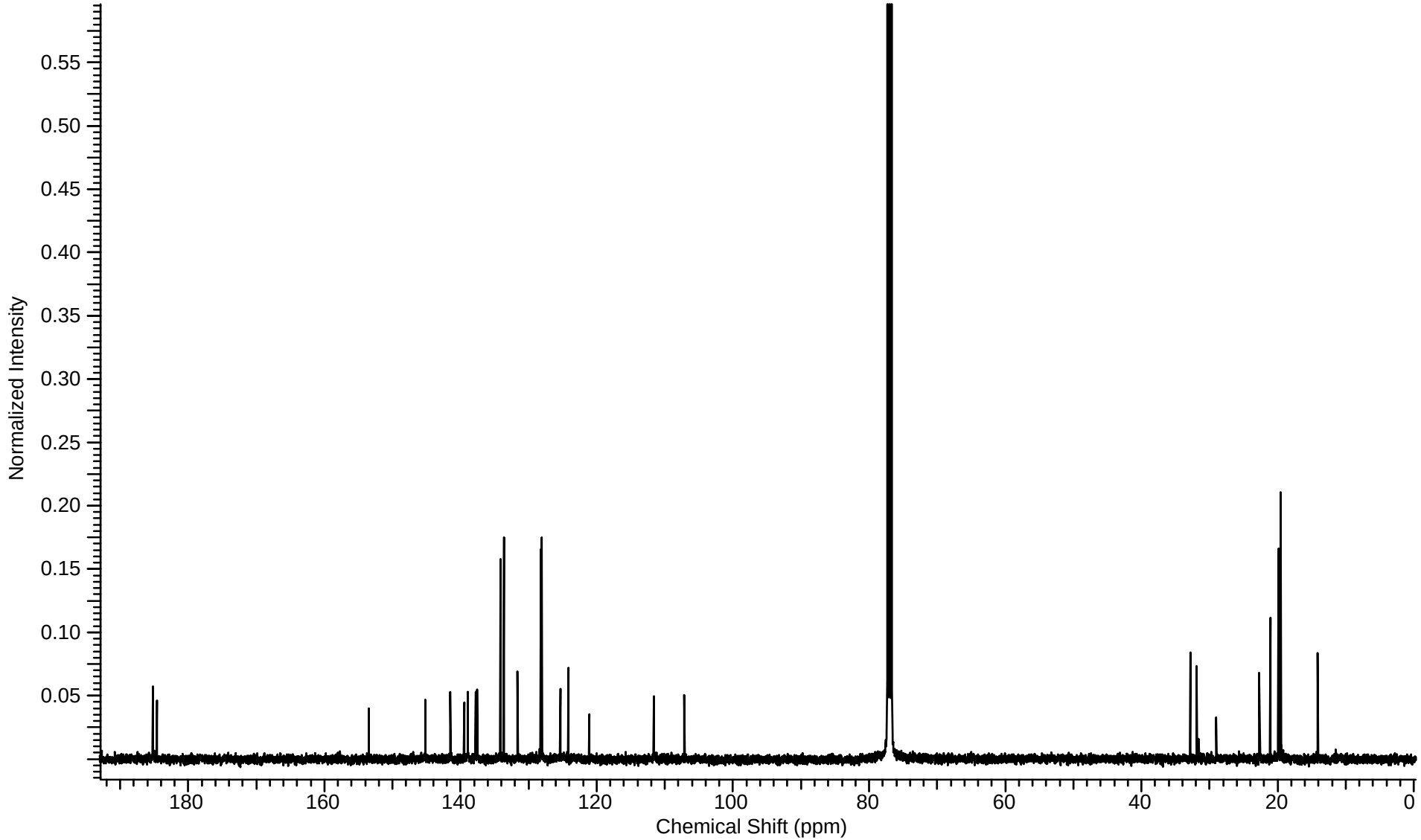
compound 16 – ^{13}C-NMR



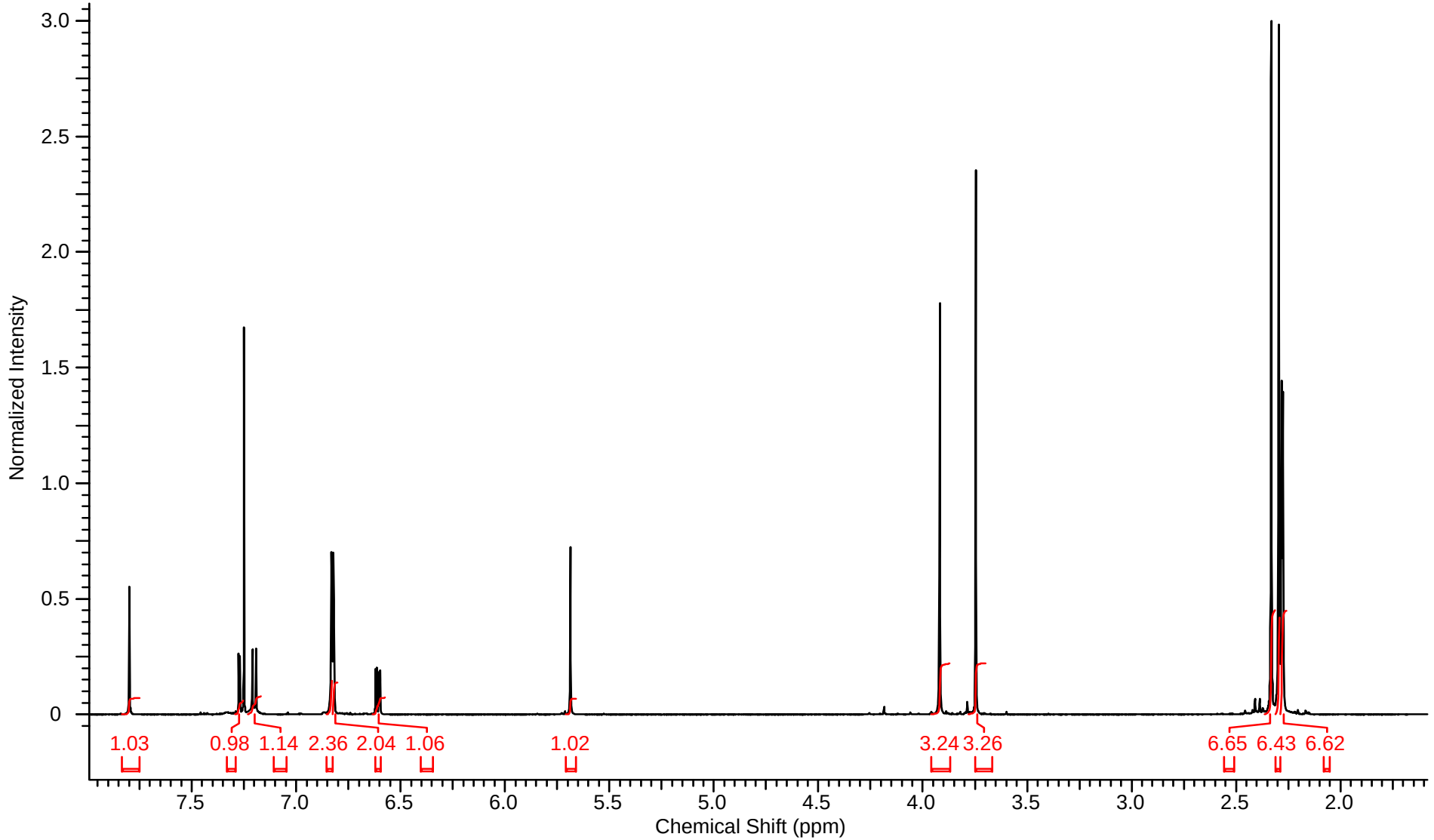
compound 17 – ^{1}H-NMR



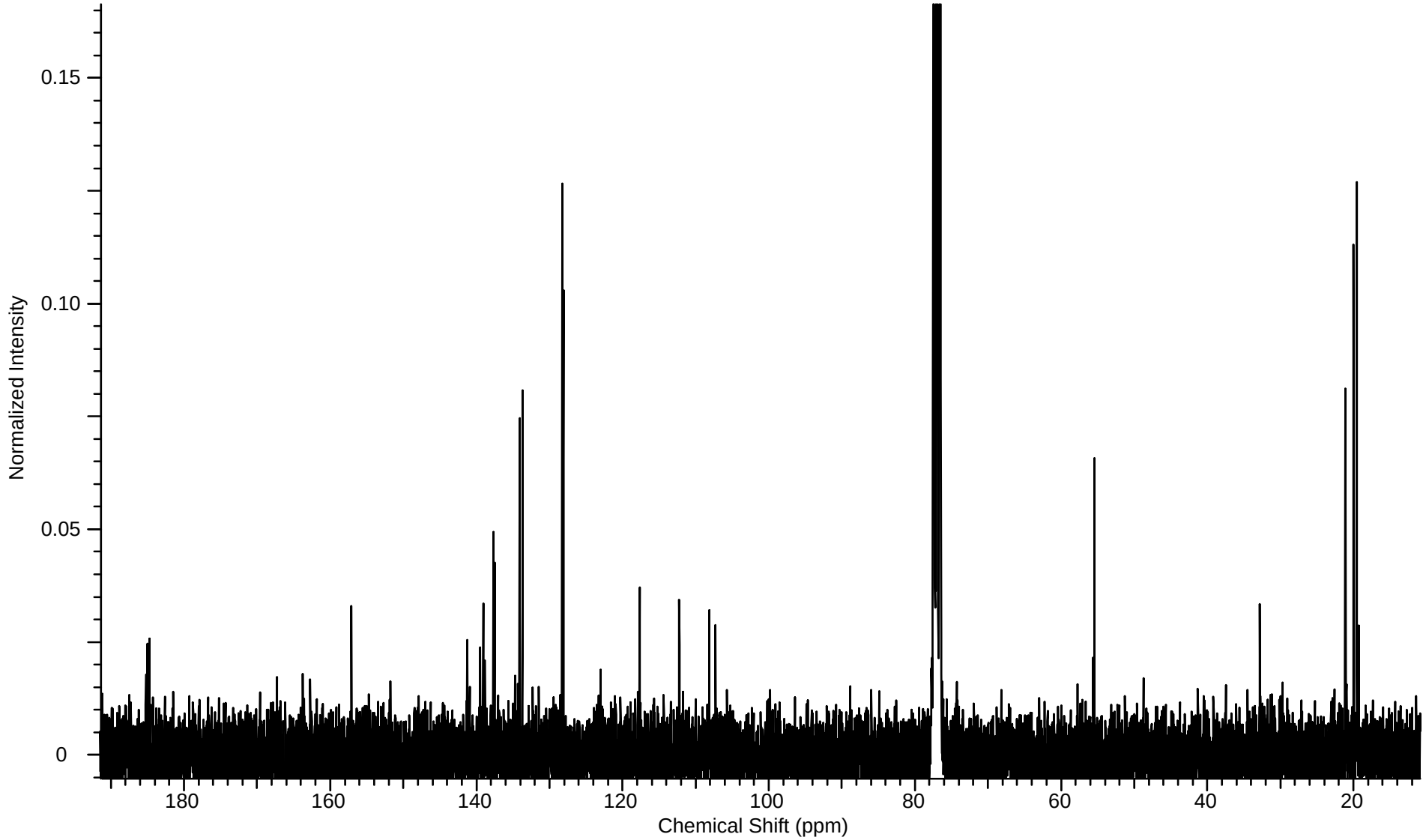
compound 17 – ^{13}C-NMR



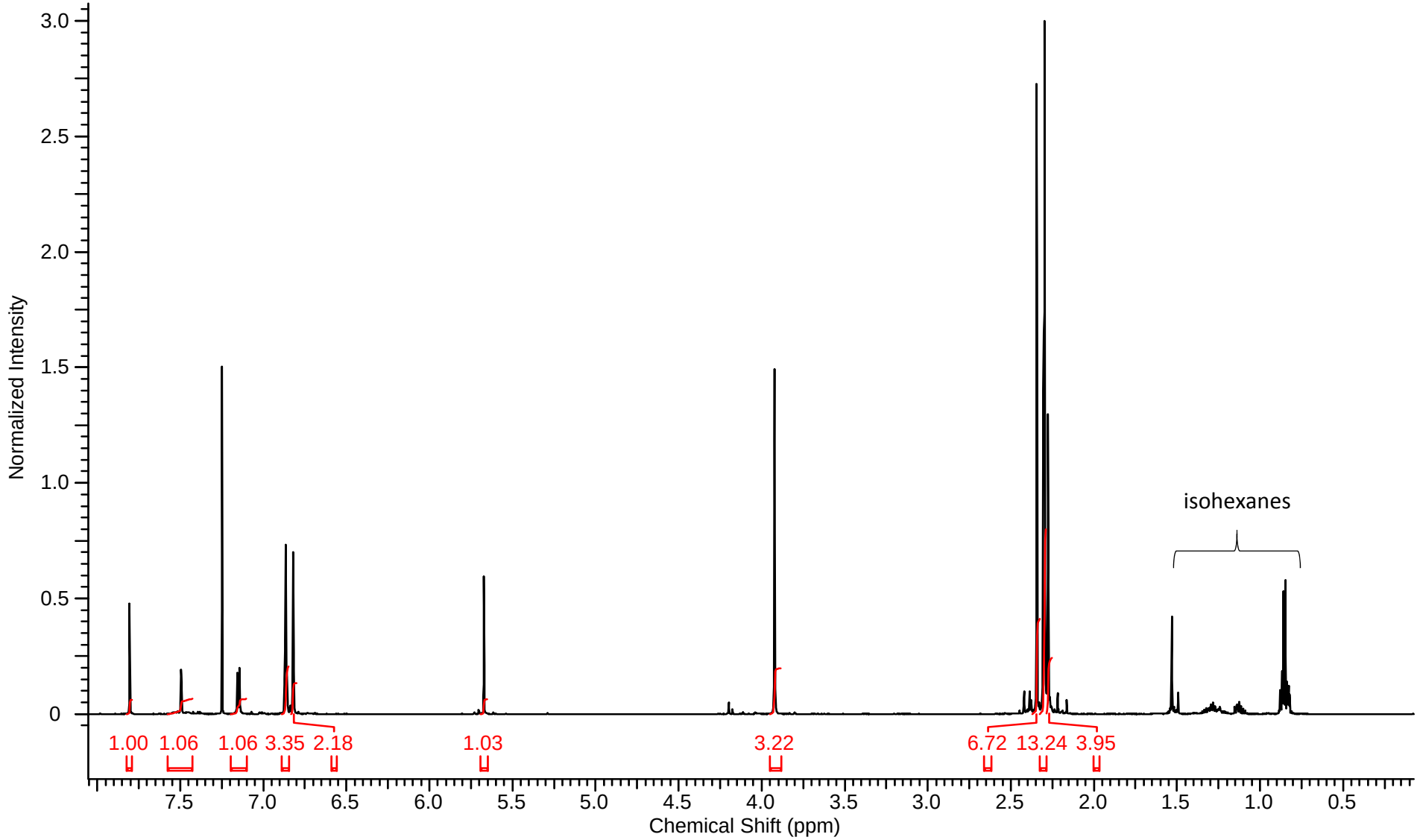
compound 18 – ^{1}H-NMR



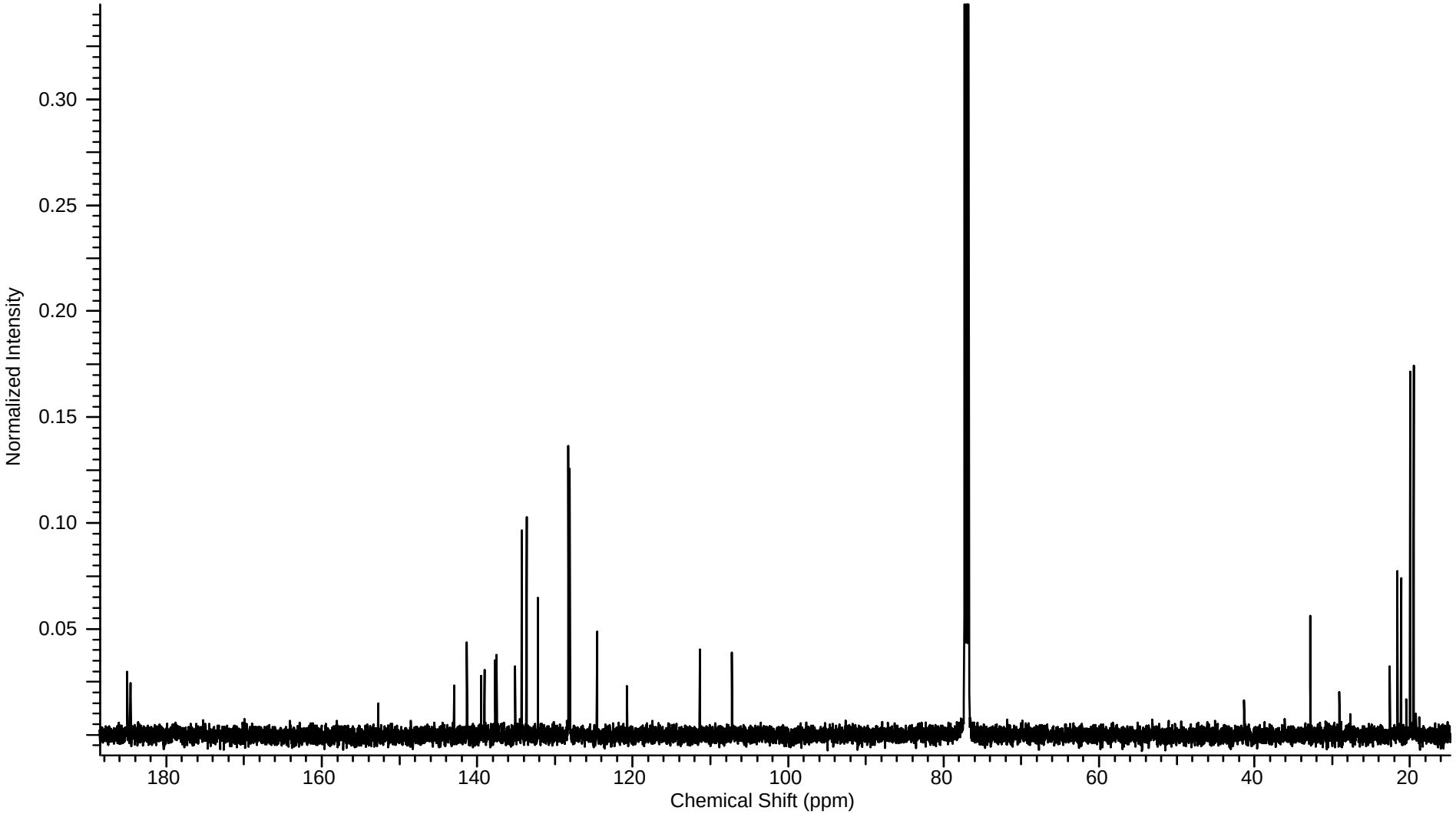
compound 18 – ^{13}C-NMR



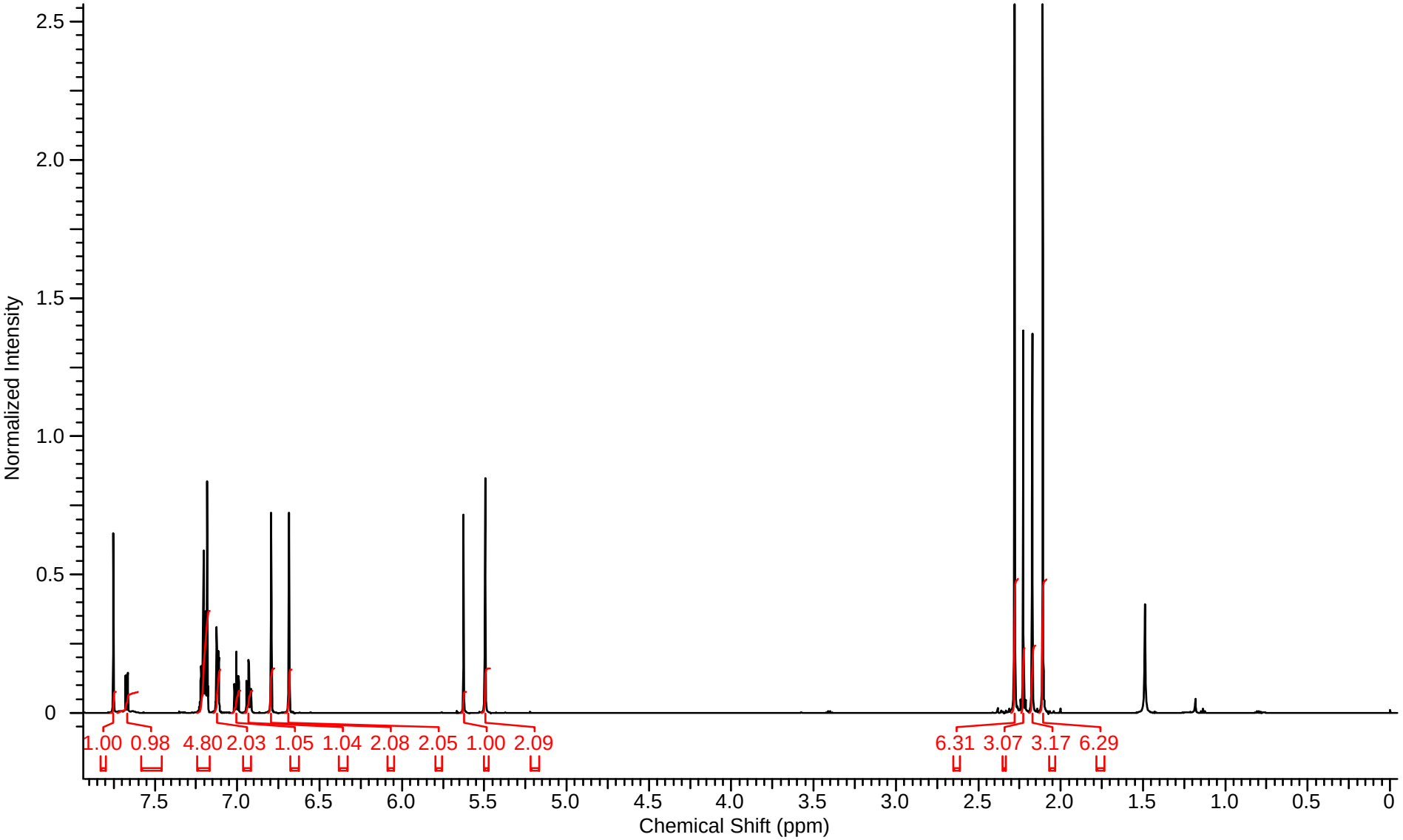
compound 19 – ^{1}H-NMR



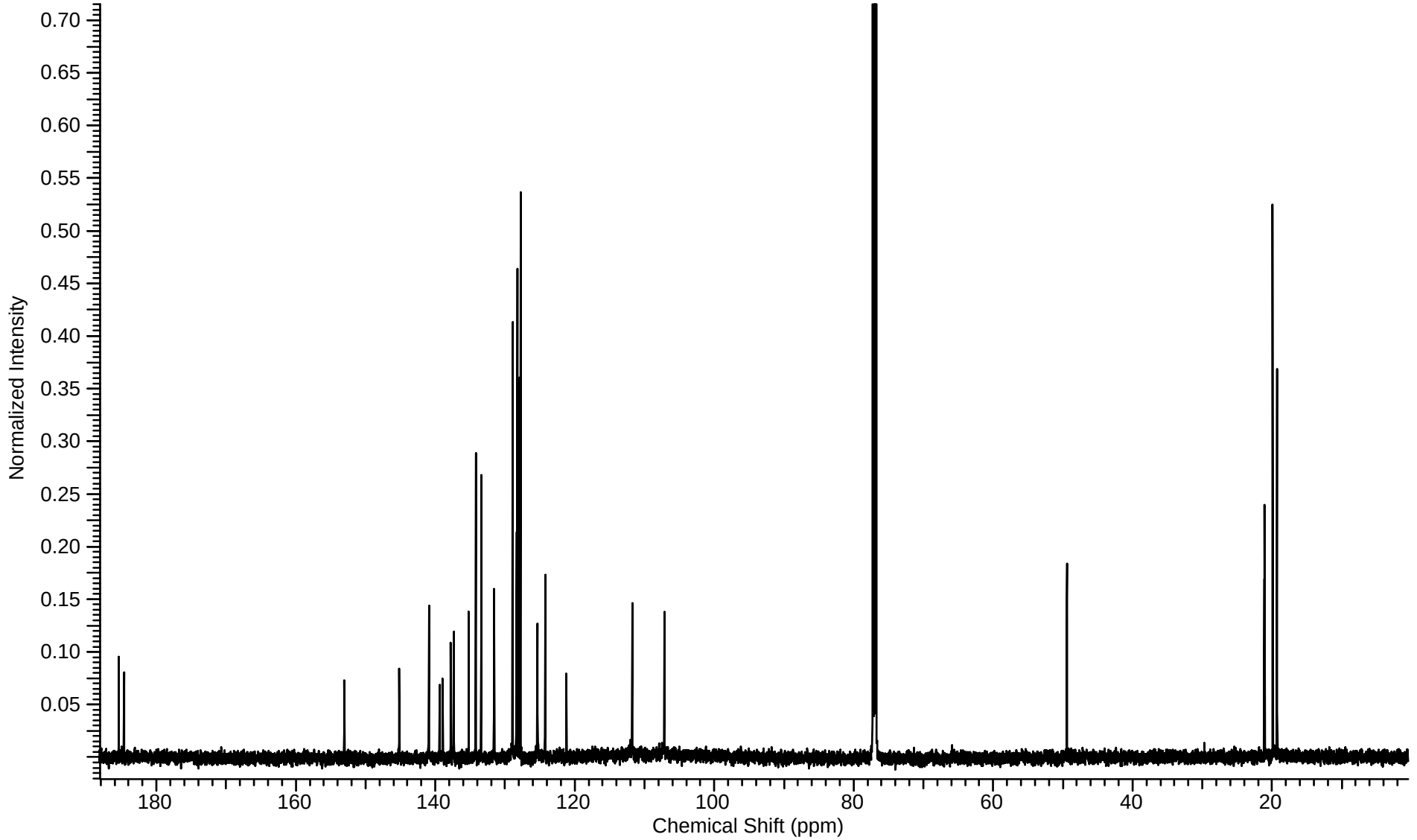
compound 19 – ^{13}C-NMR



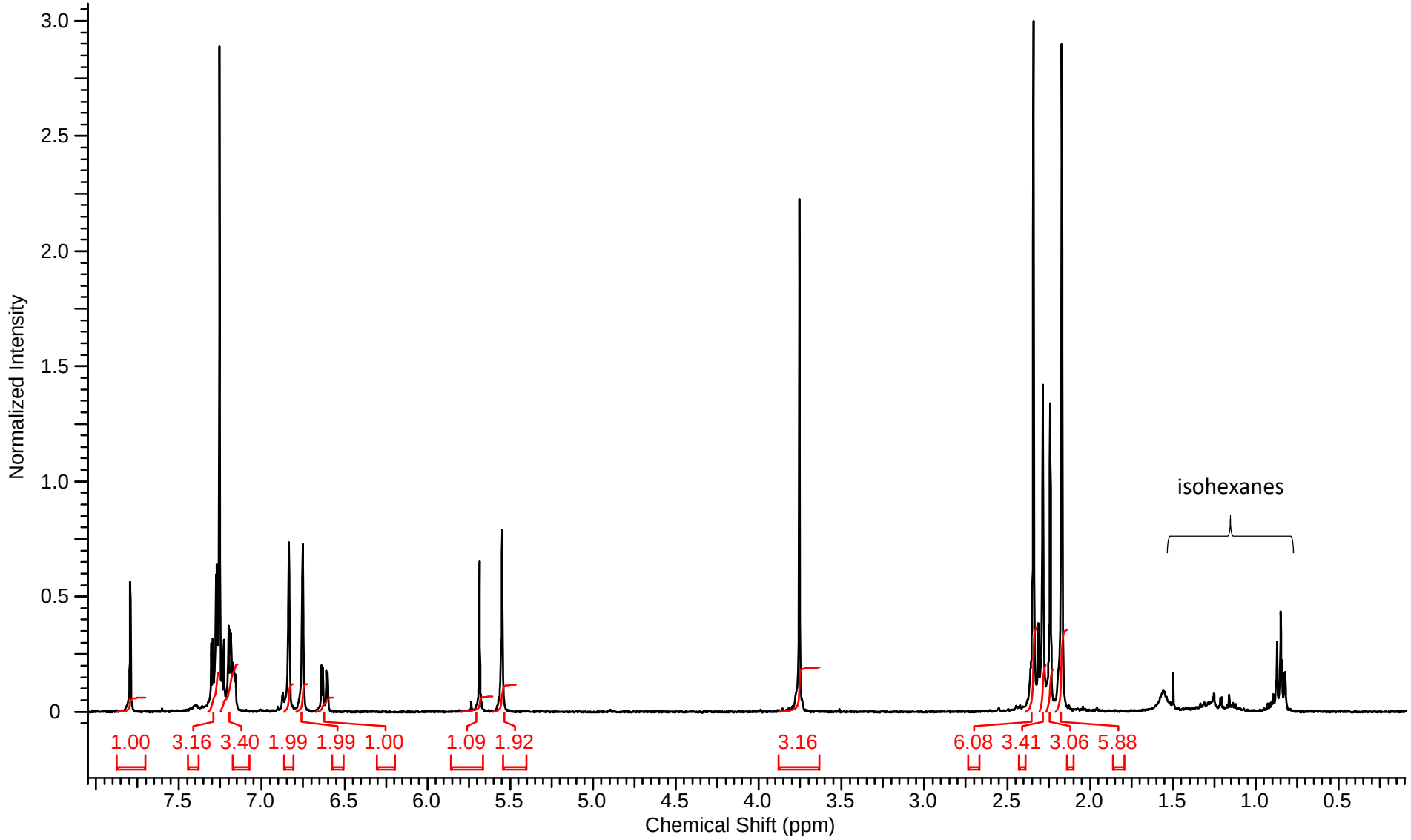
compound 20 – ^{1}H-NMR



compound 20 – ^{13}C-NMR



compound 21 – ^{1}H-NMR



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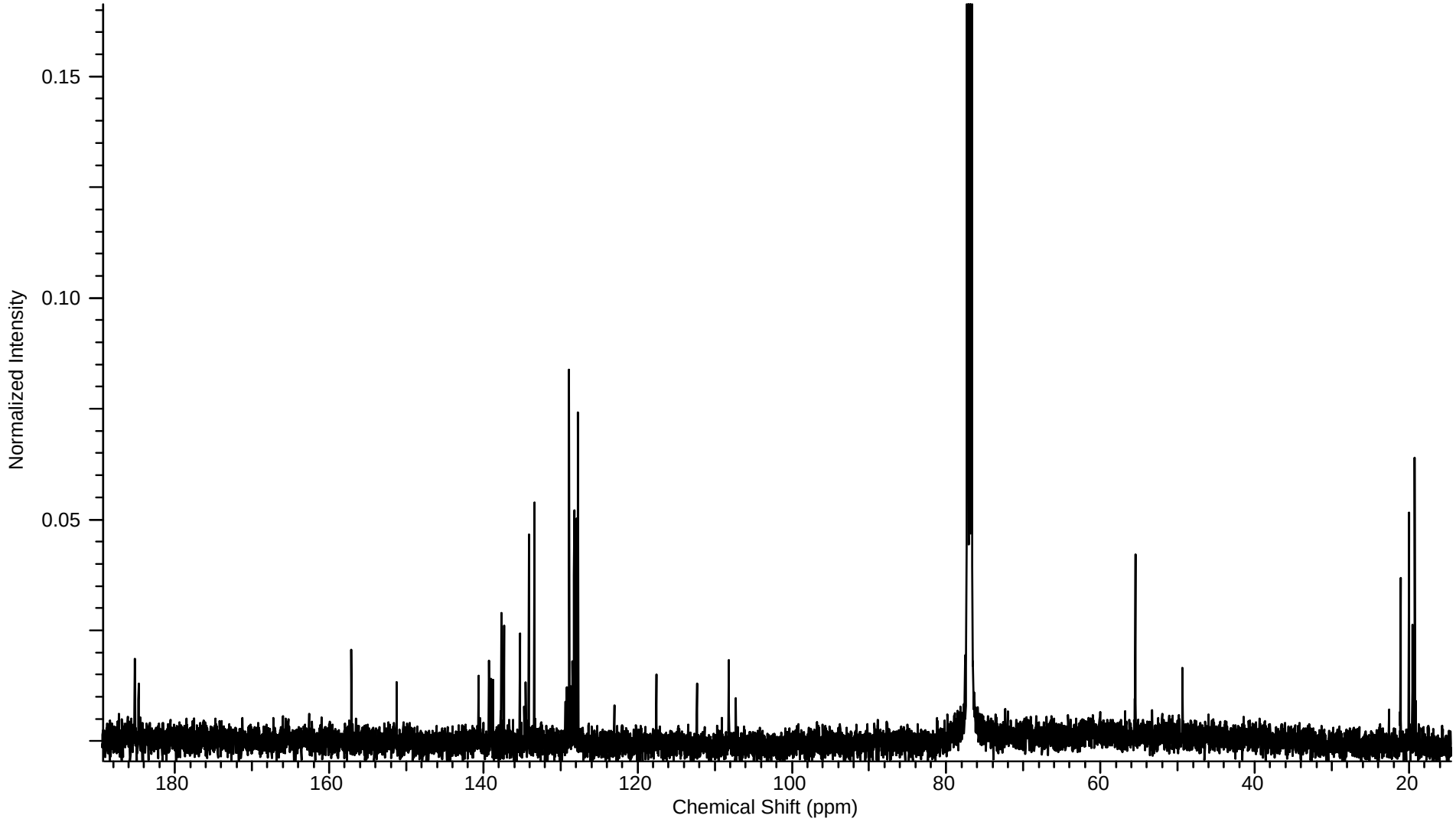
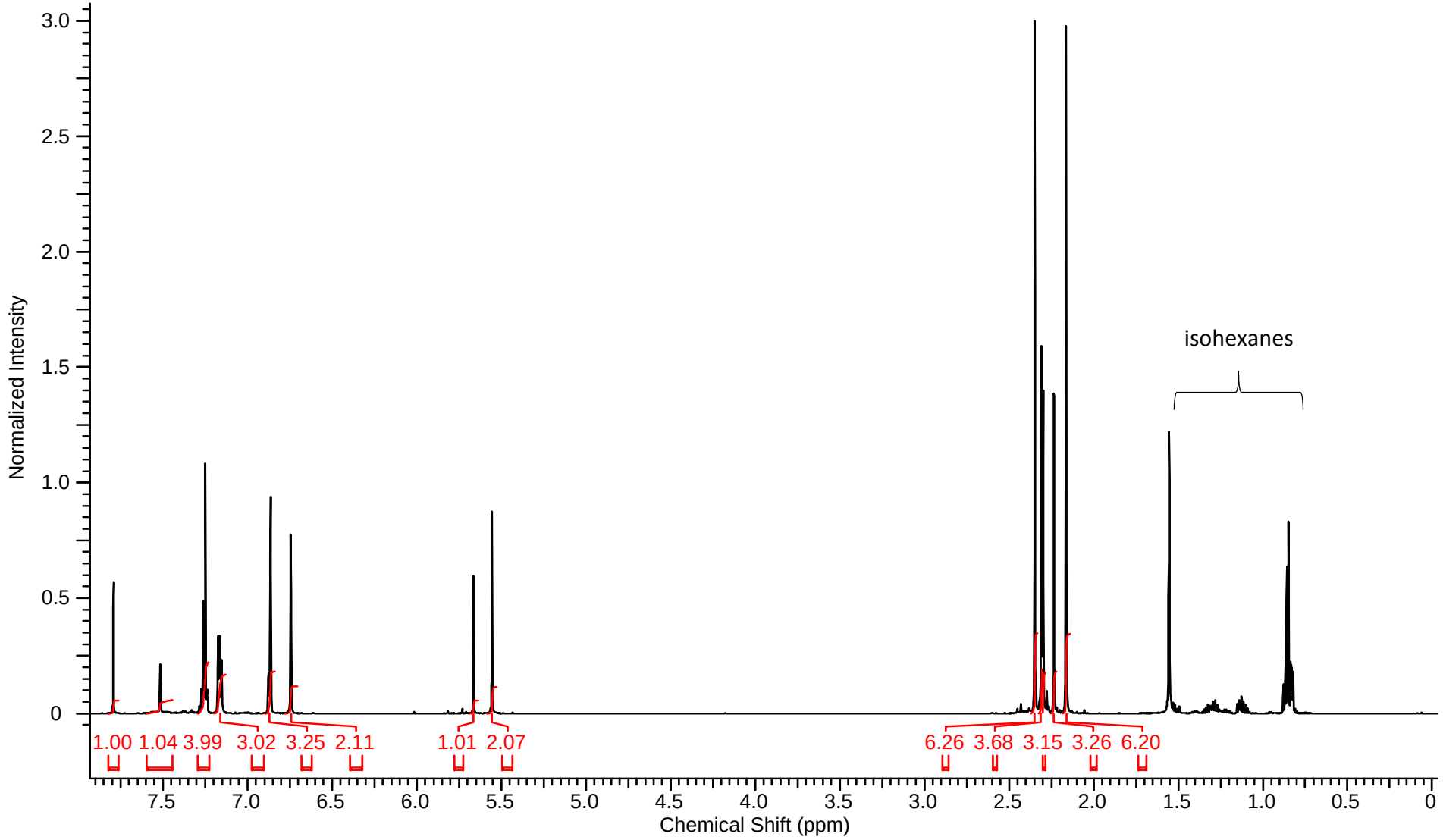
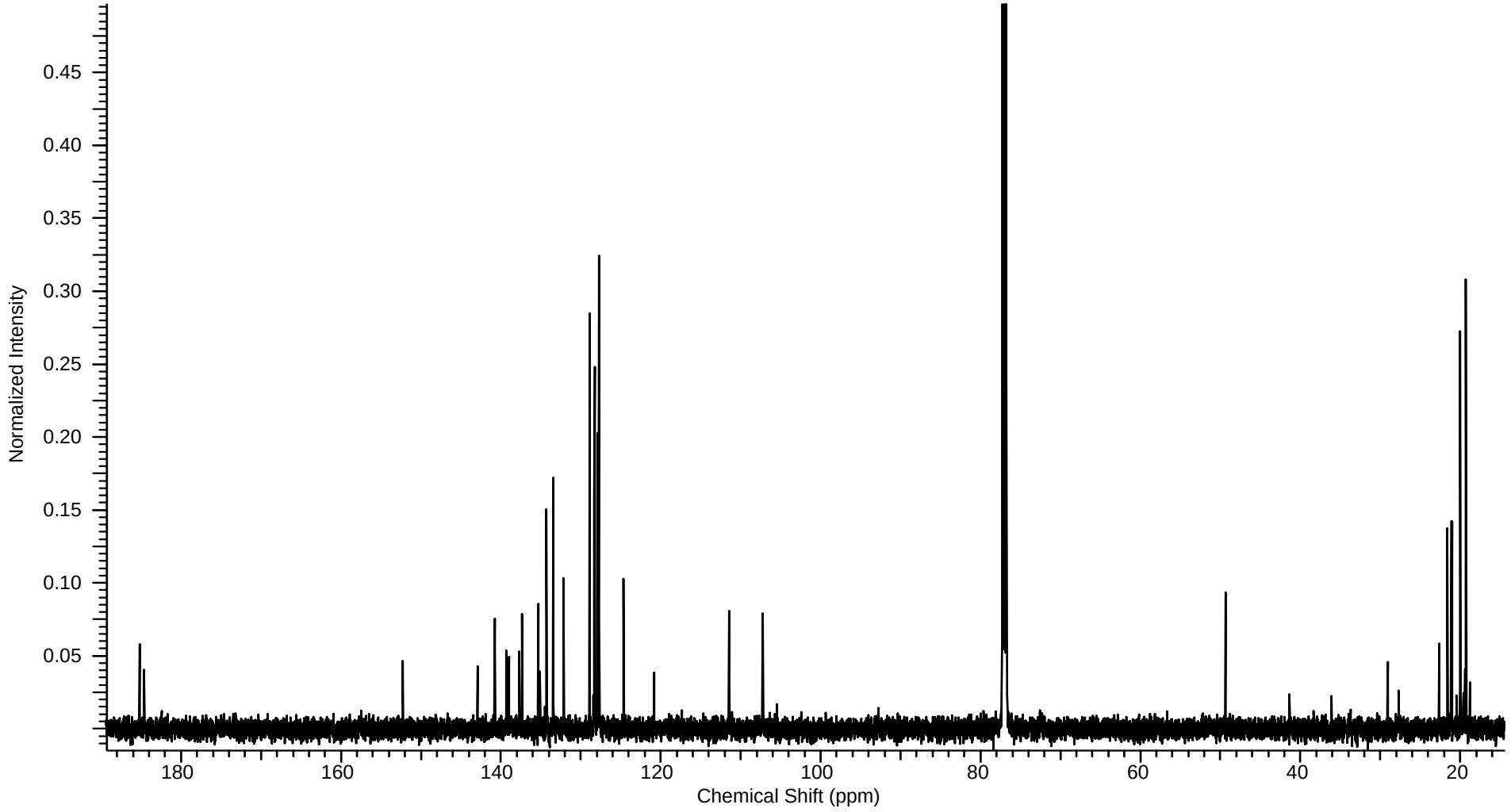


- Additional signals result from decomposition of the complex as the complex is not stable in $CDCl_3$ over the period of the measurement.

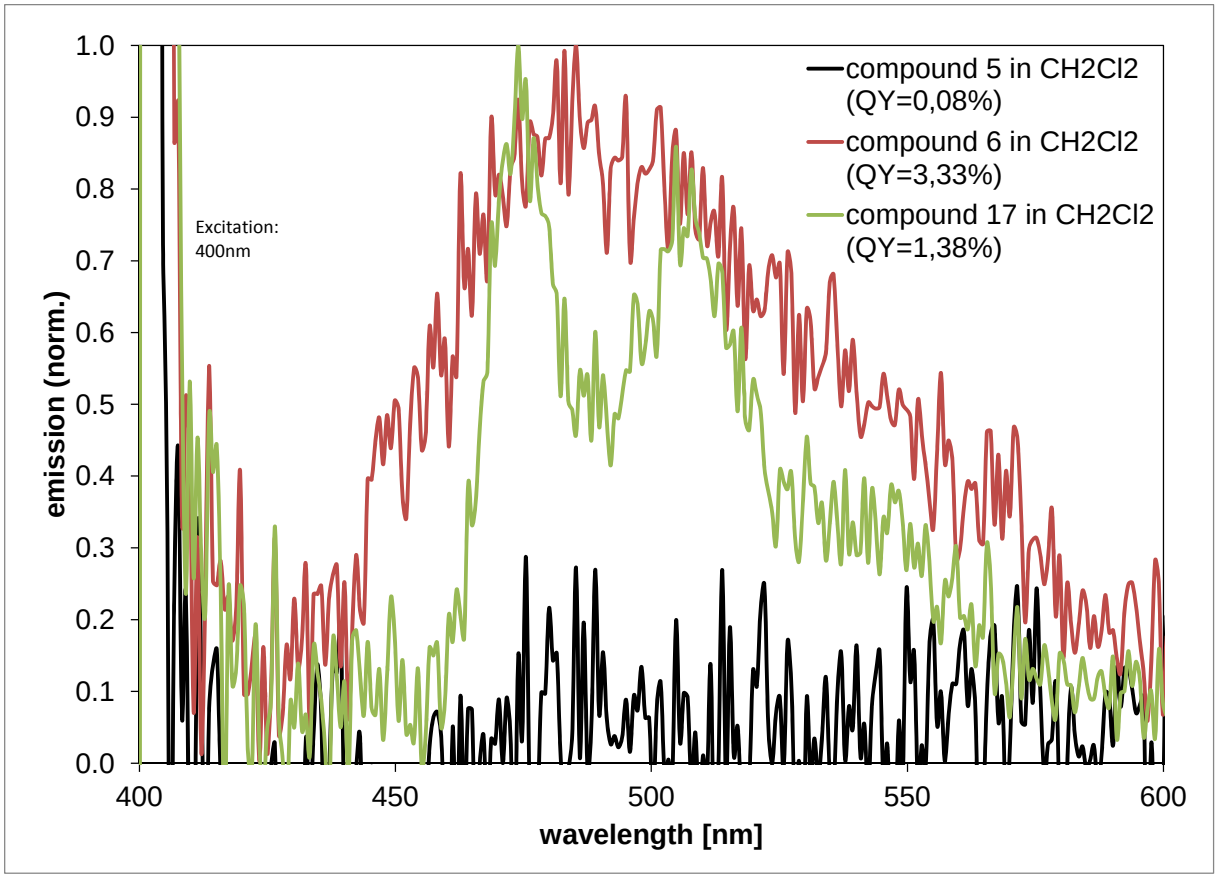
compound 22 – ^{1}H-NMR



compound 22 – ^{13}C-NMR



EMISSION SPECTRA IN DICHLOROMETHANE



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