# Chemistry 344: Spectroscopy and Spectrometry Problem Set 2

Name (print): _____

TA Name (print): _____

I. For each of the molecules below, predict the splitting pattern and chemical shift using Curphy-Morrison parameters and/or a chemical shift table for each of the signals in the ^{1}H-NMR spectrum. Make a rough sketch on the horizontal ppm axis provided. Be sure to consider the relative intensity of each signal and label its integration. Draw a TMS signal and label it on each spectrum.
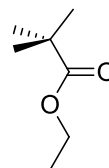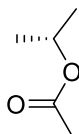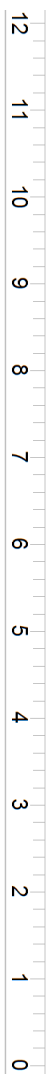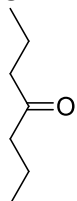
II.   For the IR, EI-Mass, ^{1}H-NMR and ^{13}C-NMR spectra shown below of propyl acetate ($C_5H_{10}O_2$), analyze the structure and each of the spectra as instructed.

A.   For the IR spectrum below of propyl acetate, label the absorptions for the $C(sp^3) - H$, a $C - O$, and the C=O bond stretches.
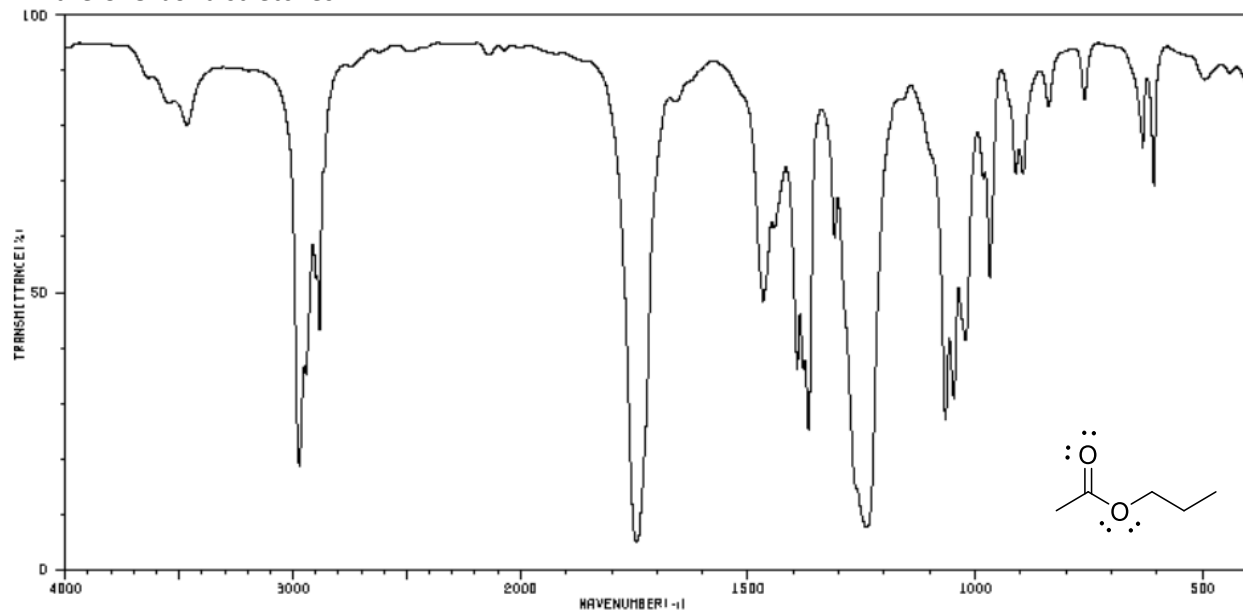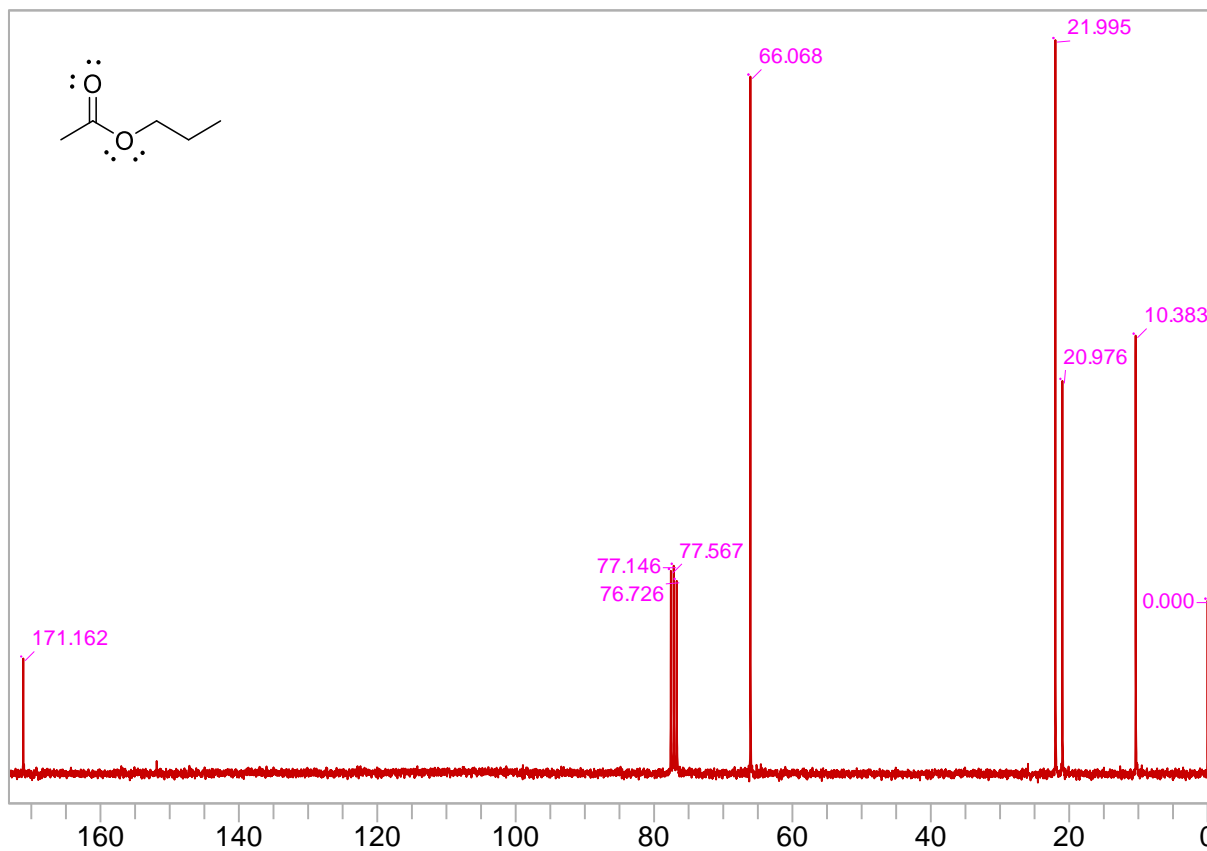

B.   For the EI-MS shown below of propyl acetate, provide an electron-pushing mechanism that accounts for the generation of the base peak ion, m/z = 43 from the molecular ion of propyl acetate.
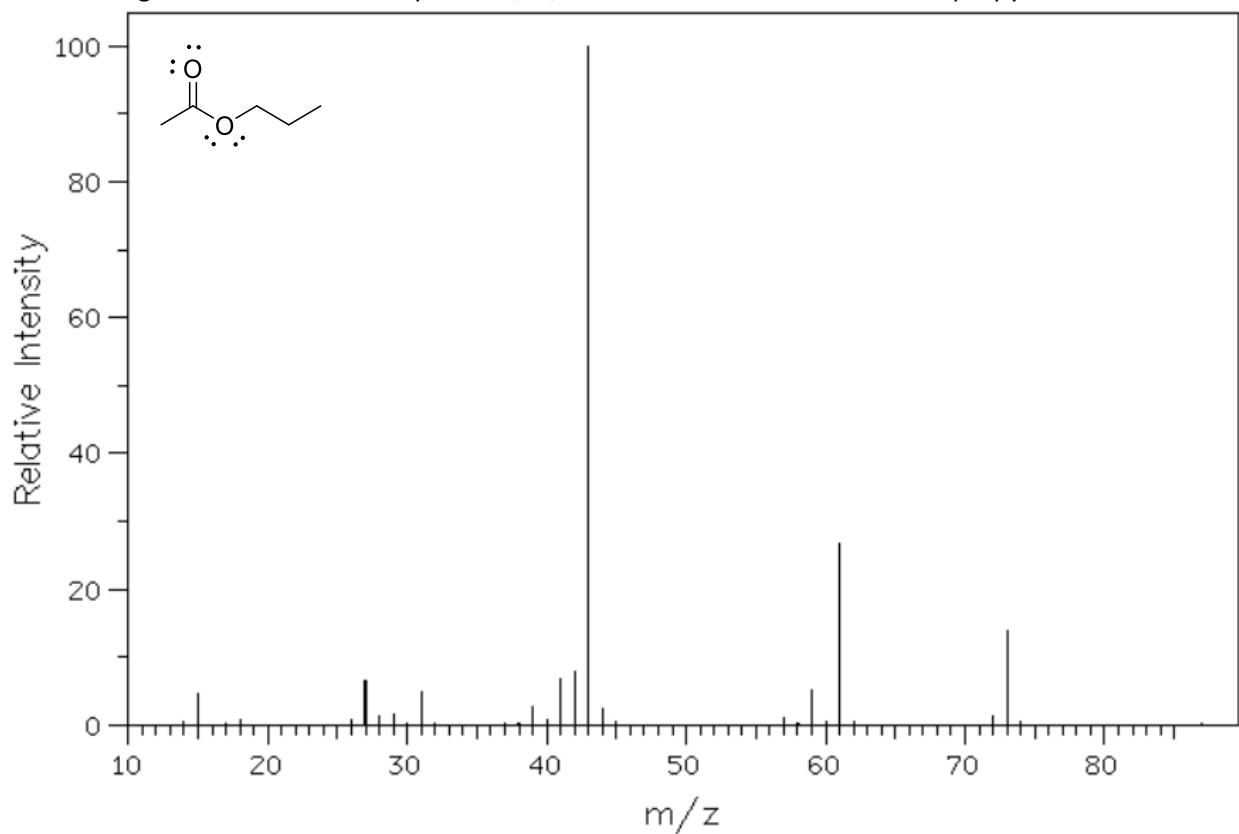
C. In the ^{13}C-NMR spectrum of propyl acetate shown below, label the hybridization of each ^{13}C-atom signal and state the number of different ^{13}C-atom environments. Additionally, label the likely functional group of each ^{13}C-atom signal and the peaks due to ^{13}CDCl$_3$ and [^{13}C]-TMS.

75 MHz ^{13}C NMR
In CDCl3

21.995
66.068
10.383
20.976
0.000
77.567
77.146
76.726
171.162

160   140   120   100   80   60   40   20   0

D. Before analyzing the ^{1}H-NMR spectrum on the subsequent page, estimate the chemical shift of each ^{1}H-atom in propyl acetate. Additionally, predict the coupling pattern and integration value that should be observed for each signal.
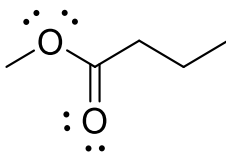

12   11   10   9   8   7   6   5   4   3   2   1   0

3
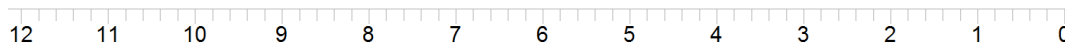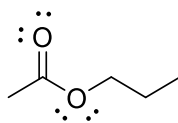
E. Assign each of the signals in the ^{1}H-NMR spectrum below to their corresponding ^{1}H-atoms in propyl acetate. Use the designations provided under each signal in your assignments.

300 MHz ^{1}H NMR
In CDCl3
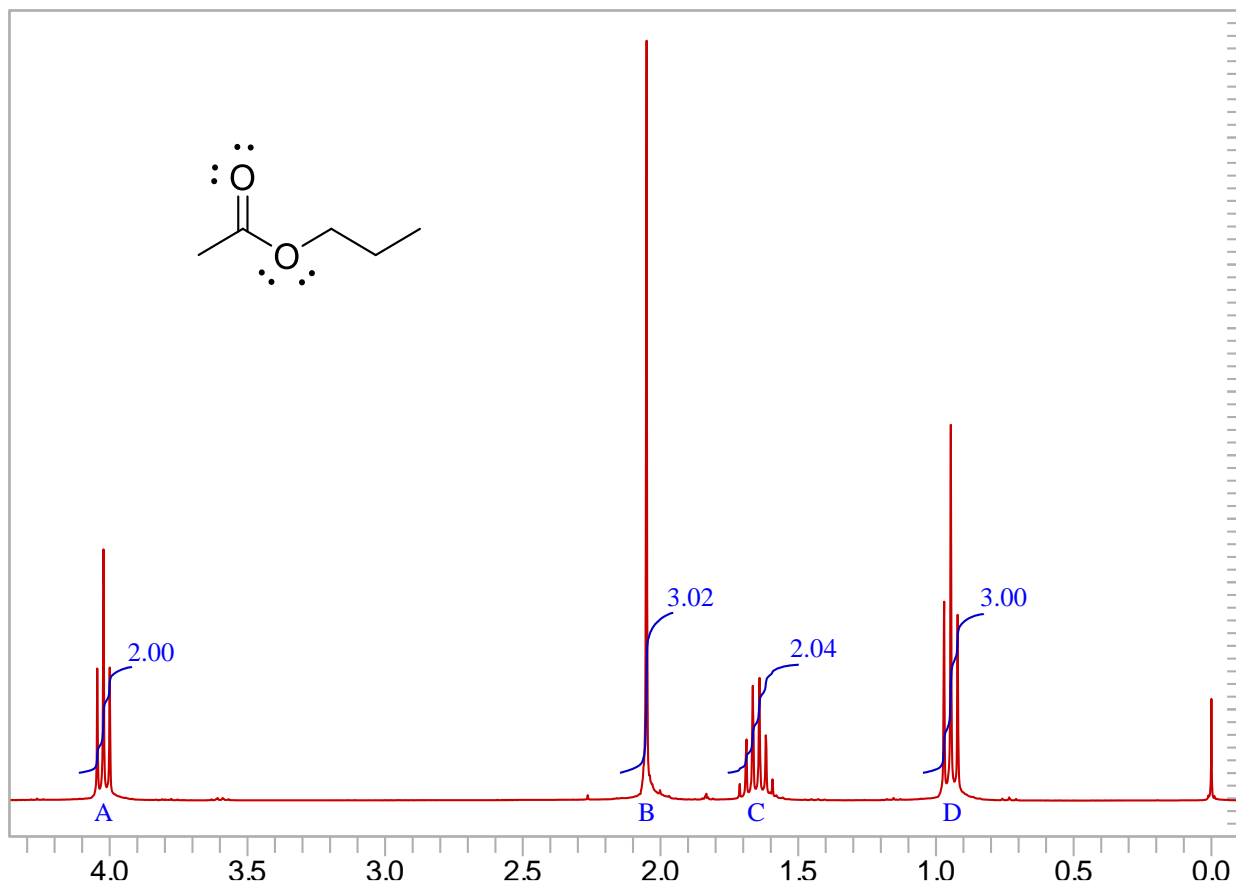
F. How would you expect the ^{1}H-NMR spectrum of methyl butyrate to differ? Be specific and include a rough sketch of the spectrum.

III.   The ^{13}C-NMR and ^1H-NMR spectra of *p*-diisopropylbenzene are shown below; analyze the structure and each of the spectra as instructed.

A.   In the ^{13}C-NMR spectrum of *p*-diisopropylbenzene shown below, label the hybridization of each ^{13}C-atom signal and state the number of different ^{13}C-atom environments. Additionally, label the likely functional group of each ^{13}C-atom signal and the peaks due to $^{13}CDCl_3$ and [^{13}C]-TMS.

75 MHz ^{13}C NMR
In CDCl3
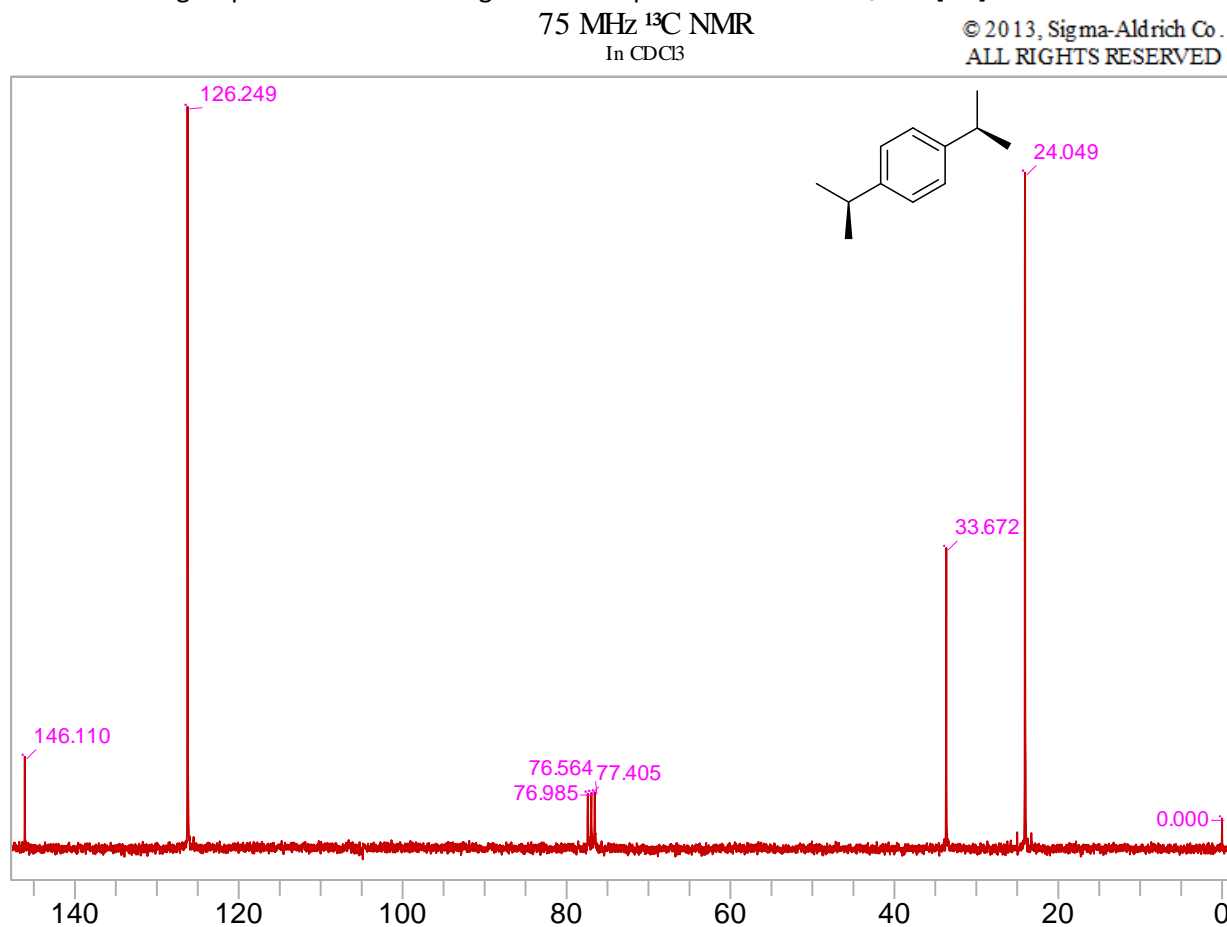
B.   Despite 12 C-atoms in *p*-diisopropylbenzene, its spectrum shows only four ^{13}C-NMR environments. Explain how the structure results in so few ^{13}C-NMR signals. How many ^1H-NMR signals would you expect to observe?

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C. Assign each of the signals in the ¹H-NMR spectrum below to their corresponding ¹H-atoms in *p*-diisopropyl benzene. Use the designations provided under each signal in your assignments.

300 MHz ¹H NMR
In CDCl3
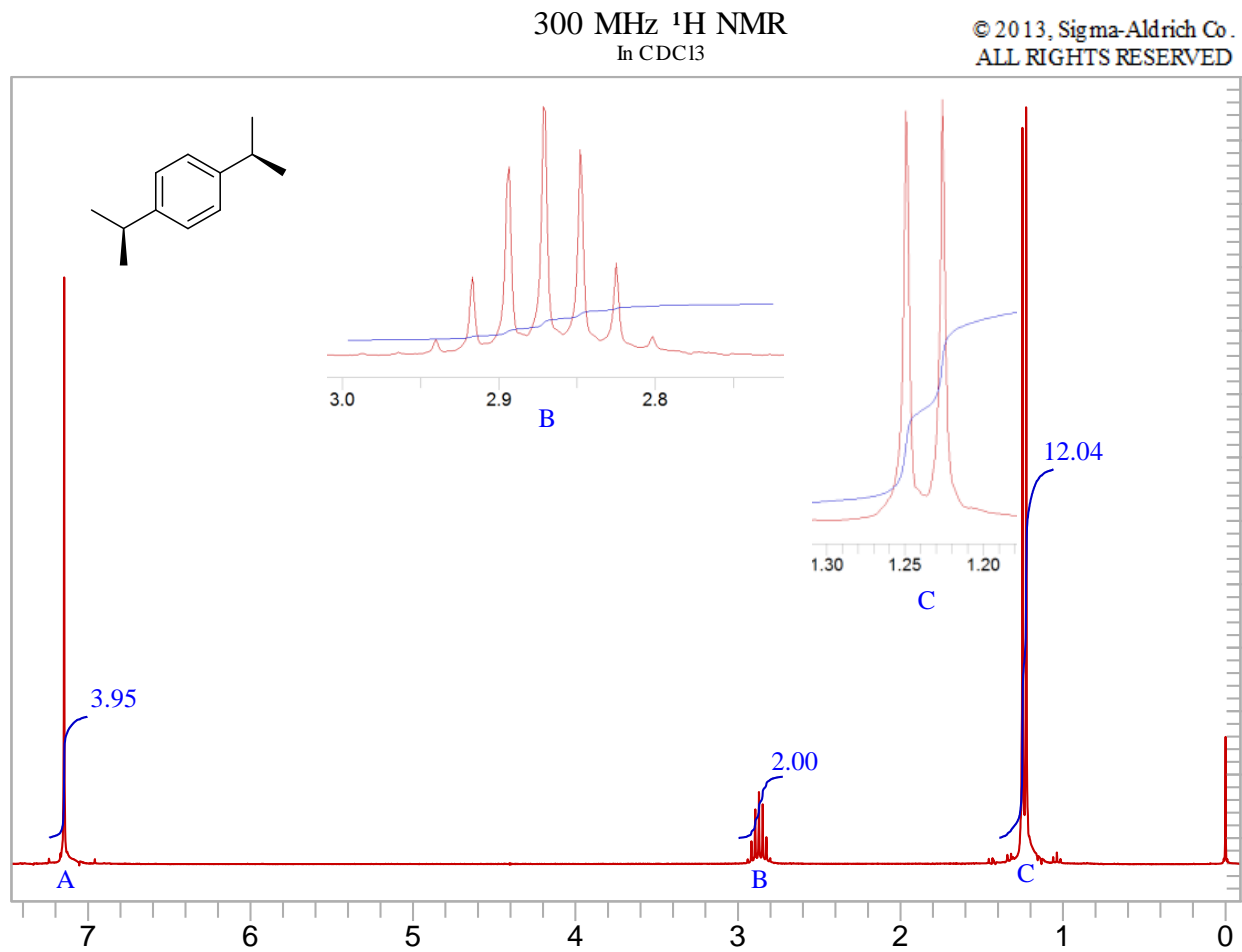
D. For the signal labeled B shown below, label the approximate signal intensities for each individual peak. Provide an explanation for the observed intensities.
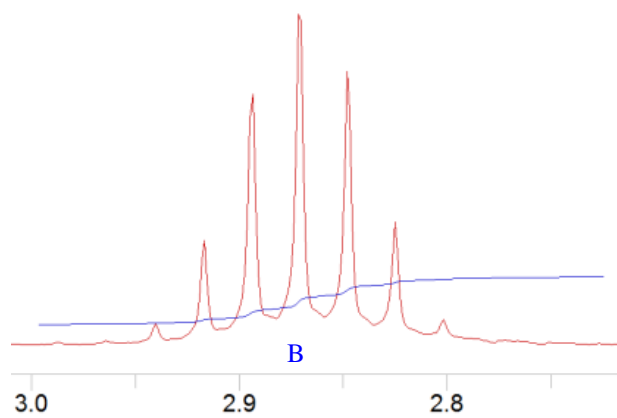
IV.   For a molecule with a chemical formula of $C_3H_4Br_2O$, answer the following questions.
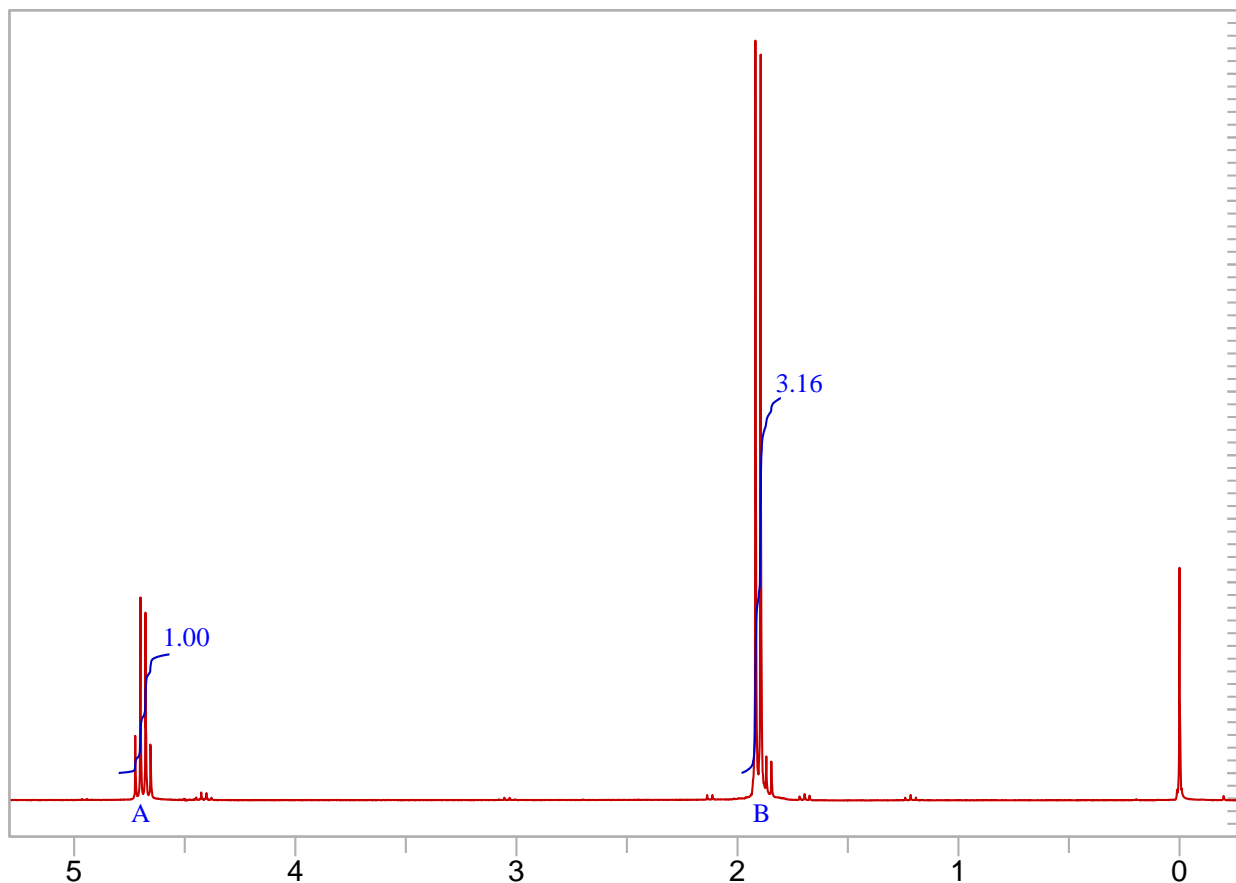
A. What is the unsaturation number (**U**) or index of hydrogen deficiency (**IHD**)? What does this indicate about which functional groups or structural units are possible for this molecule?

$$U = IHD = \frac{2C + 2 + N - H - X}{2}$$

B. The ^{1}H-NMR spectrum of $C_3H_4Br_2O$ is provided below. Draw part structures that account for the integration and coupling observed in each signal.
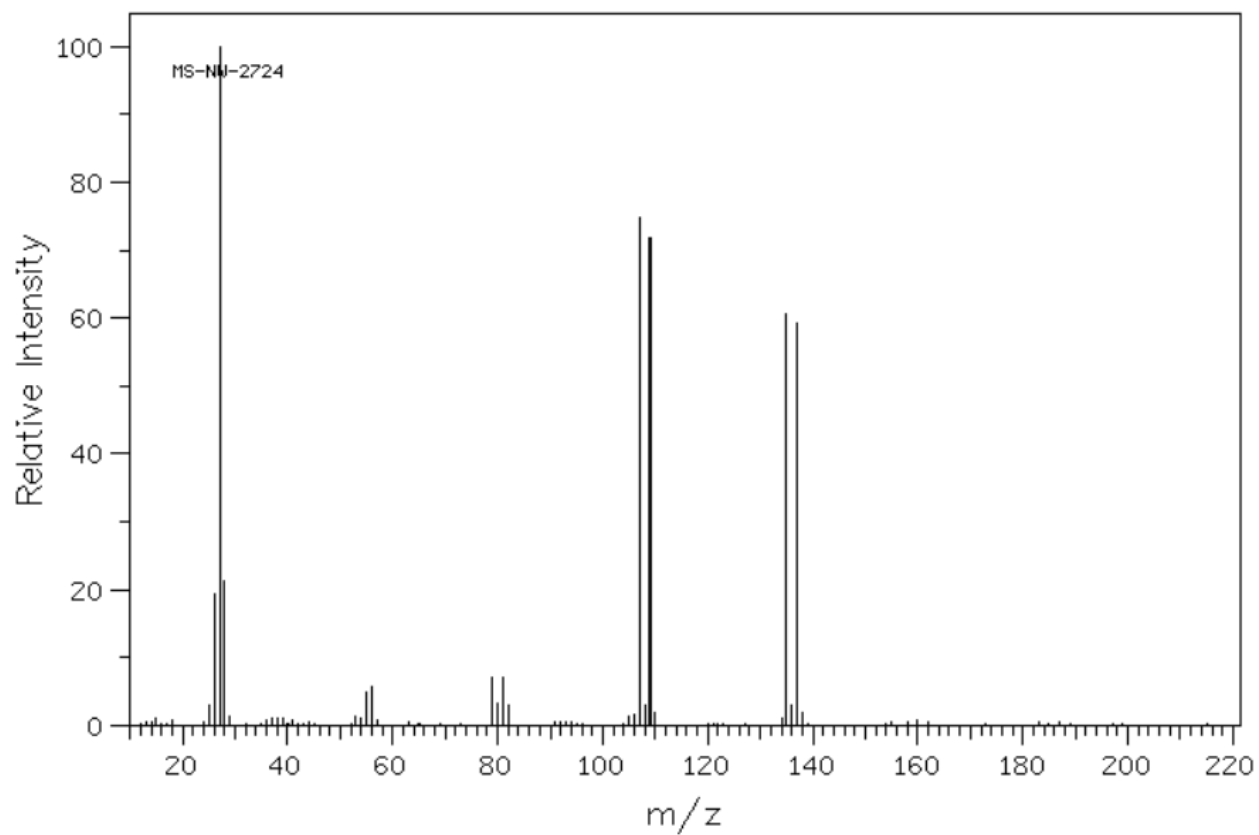
300 MHz ^{1}H NMR
In CDC13

C. Based upon the part structures drawn in part B and the relative chemical shifts of each signal, draw two potential molecules, one carbonyl containing molecule and one epoxide. Label the ^{1}H-atoms in each structure as H_a and H_b.

D. The identity of the correct $C_3H_4Br_2O$ molecule can be confirmed in several independent techniques. Explain how each piece of evidence presented below can confirm the identity of the correct molecular structure.

75 MHz ^{13}C NMR
In CDCl3
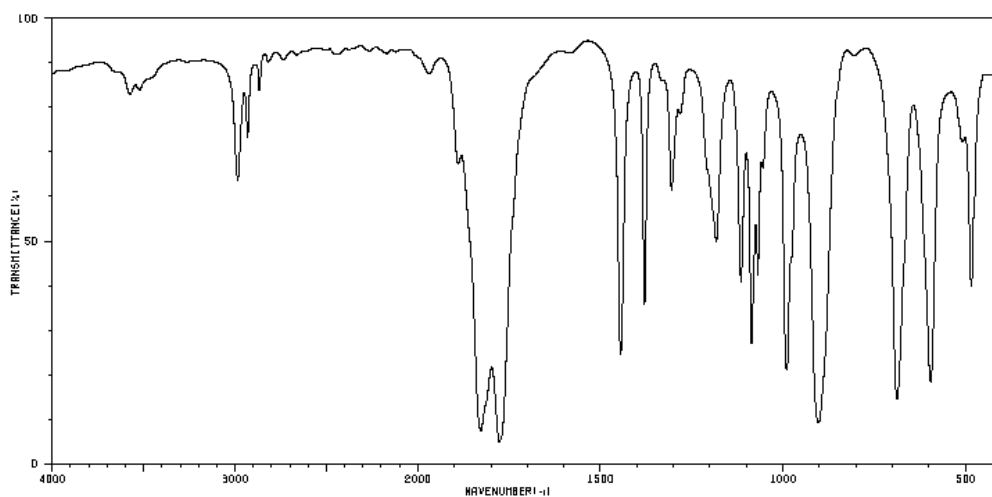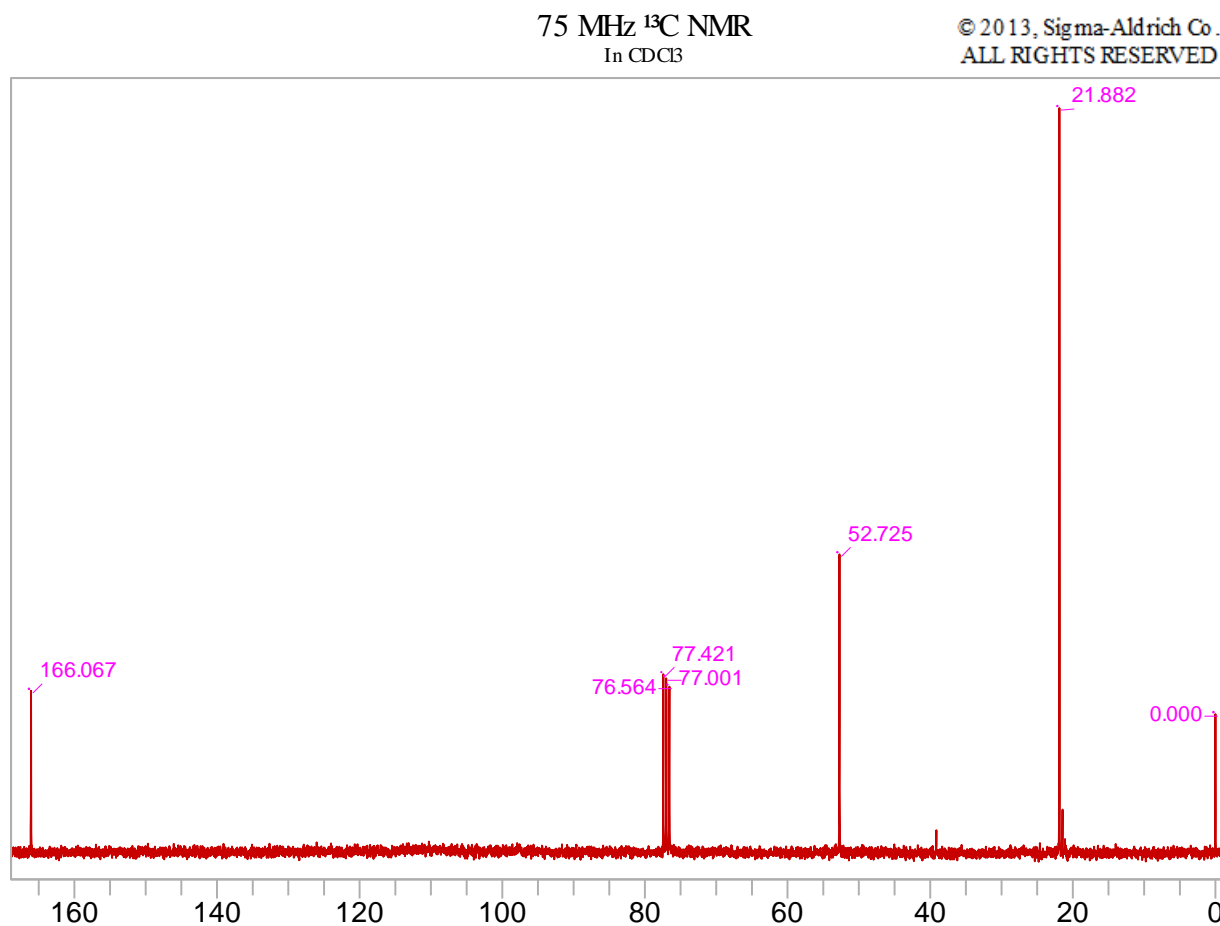
SDBSWeb : http://sdbs.riodb.aist.go.jp (National Institute of Advanced Industrial Science and Technology)

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V.   For a molecule with a chemical formula of $C_{12}H_{19}N$, answer the following questions.

A. What is the unsaturation number (**U**) or index of hydrogen deficiency (**IHD**)?   What does this indicate about which functional groups or structural units are possible for this molecule?

$$U = IHD = \frac{2C + 2 + N - H - X}{2}$$

B. Using the ^{1}H-NMR and ^{13}C-NMR spectra below, identify the molecule and fully analyze the NMR spectra.


300 MHz ^{1}H NMR
In CDCl3
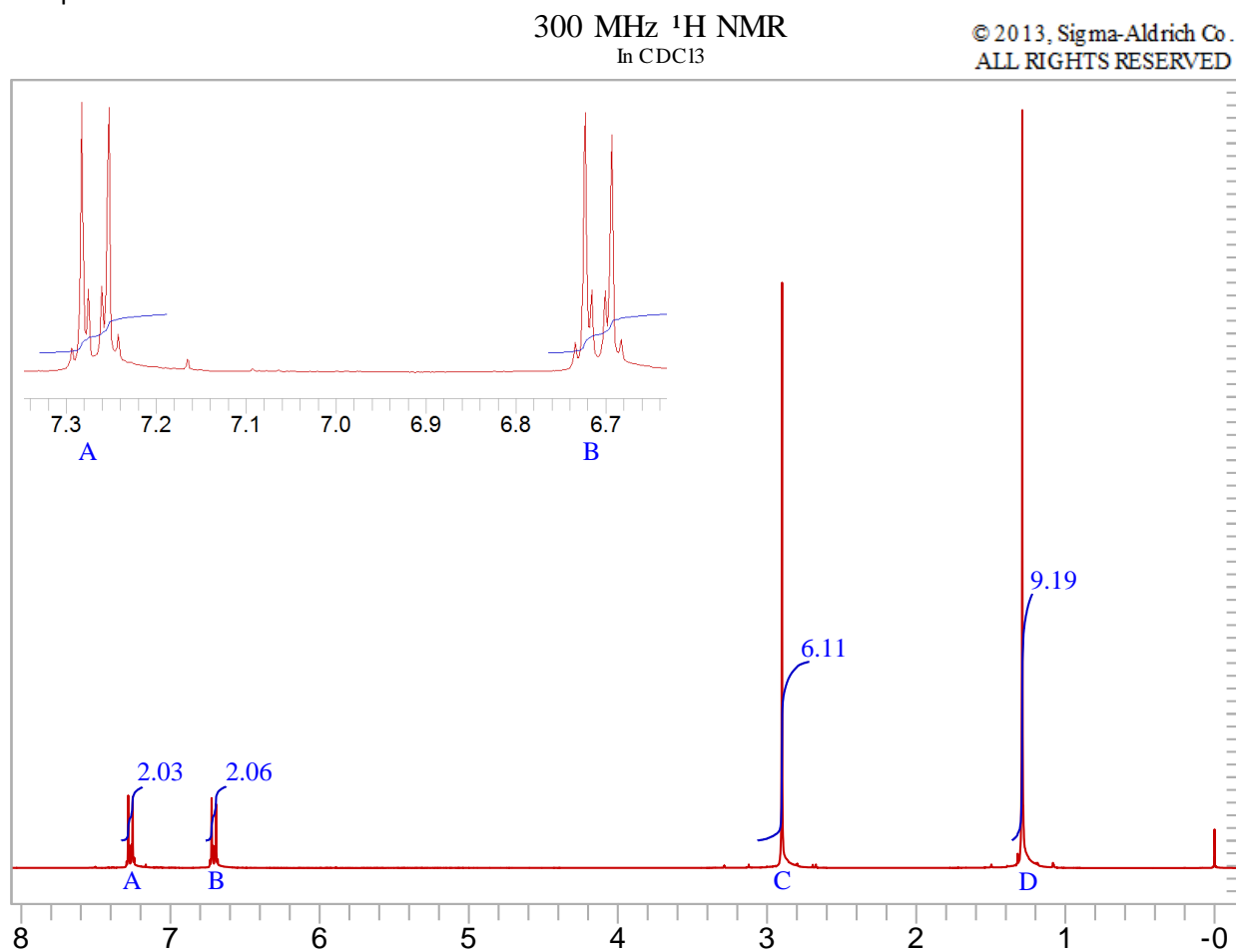
75 MHz ^{13}C NMR
In CDCl3
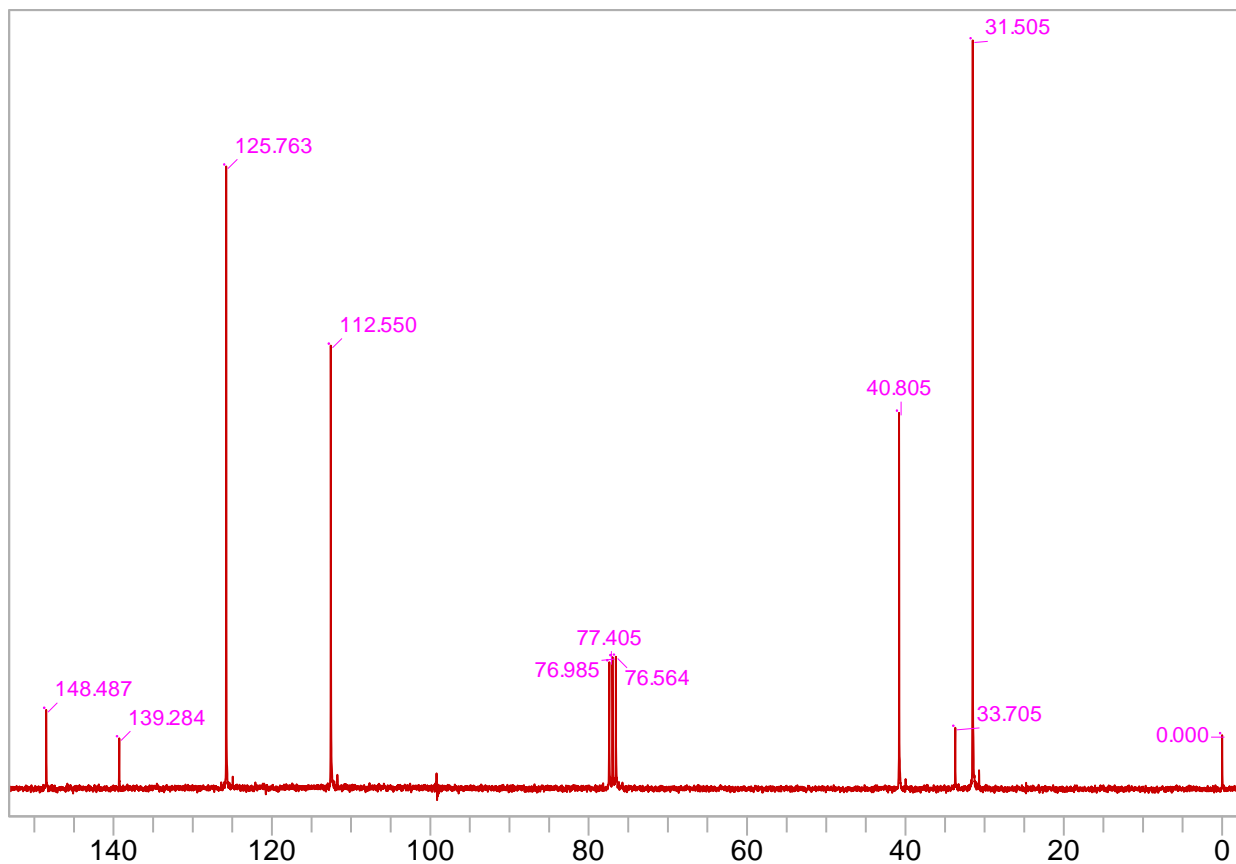
C. The ^{13}C-NMR signals at 148.487 and 139.284 ppm are much smaller than the neighboring signals at 125.763 ppm and 112.550 ppm. Provide two reasons that the signals at 148.487 and 139.284 ppm are lower in amplitude.

VI.   Determine the structure of the molecule with formula C_9H_{10} that corresponds to the spectra shown below. Fully analyze each spectrum.
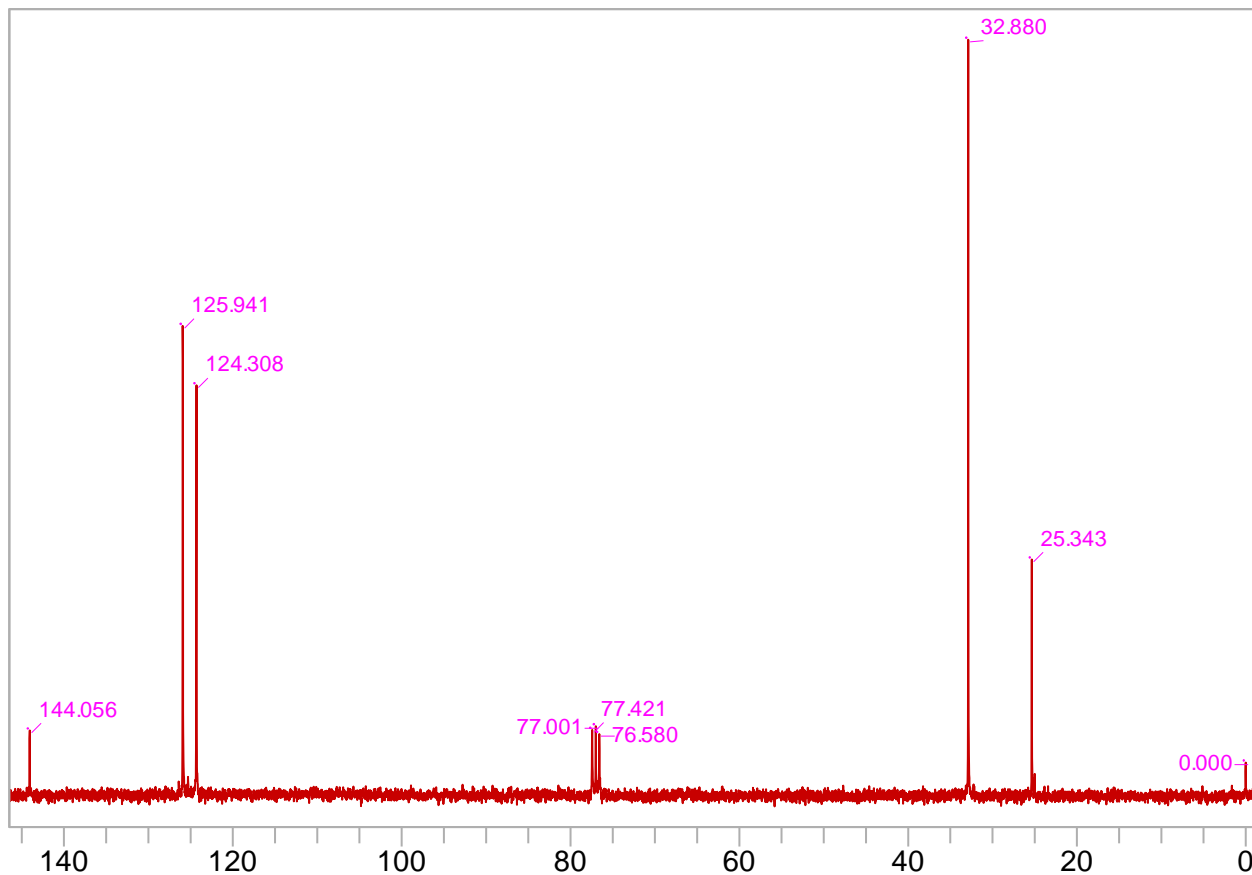
300 MHz ¹H NMR
In CDCl3
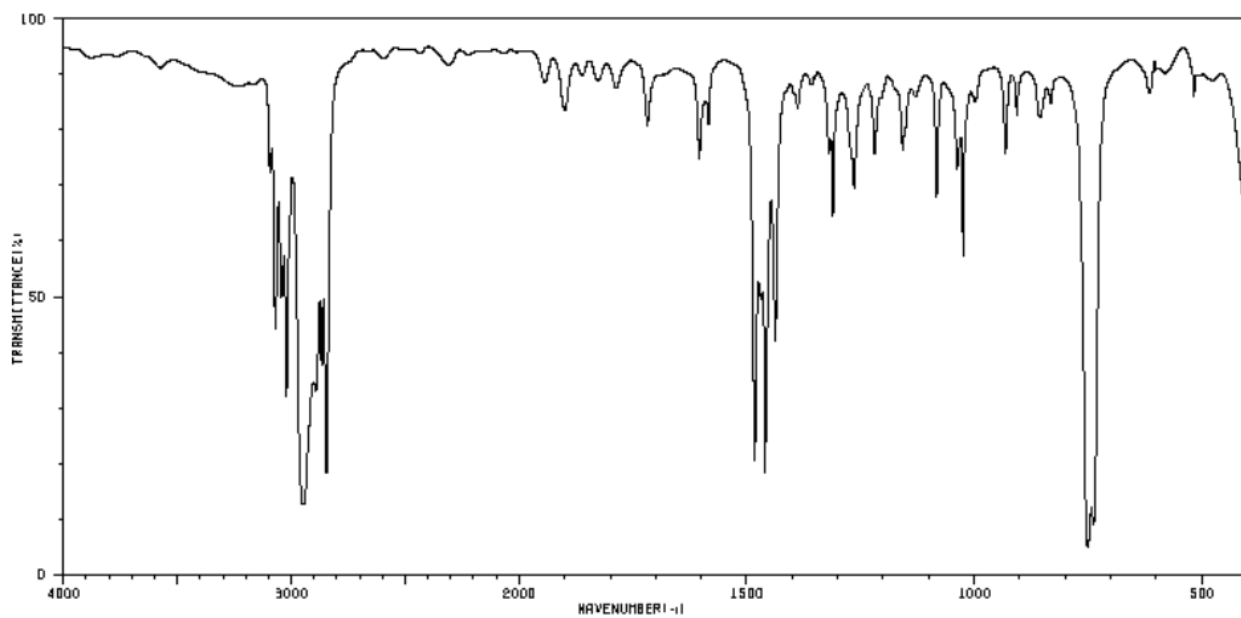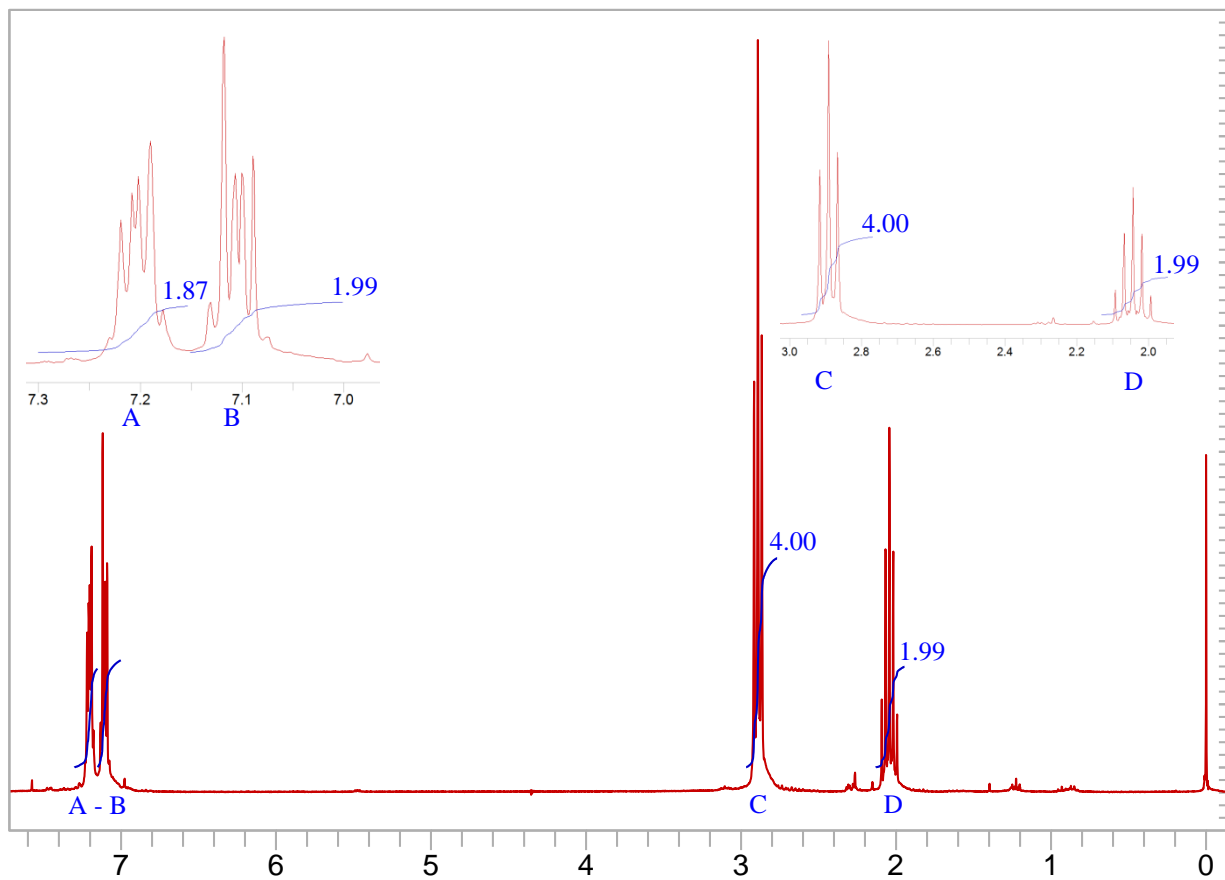
75 MHz ¹³C NMR
In CDCl3

VII. Using the ^{1}H-NMR spectrum and questions below, determine the relative amount of acetone and isopropyl alcohol in a mixture of the two molecules. For more information on determining ratios by ^{1}H-NMR. *(https://www.chem.wisc.edu/content/experiment-6-elimination-reactions-e1e2#Q1)*

A. For each of the molecules shown below, identify the likely observed coupling pattern and estimate the likely chemical shift.

acetone

isopropanol
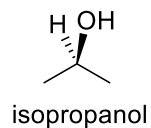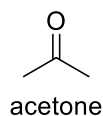
B. Assign each of the signals in the ^{1}H-NMR spectrum below to their corresponding ^{1}H-nuclei in the molecules above using the letter designations A-D.

C. Using the spectrum below, determine the relative amount of acetone and isopropyl alcohol in the spectrum of a mixture relative to the least abundant molecule. Report the ratio with the lowest abundance species set to a value of 1.00.
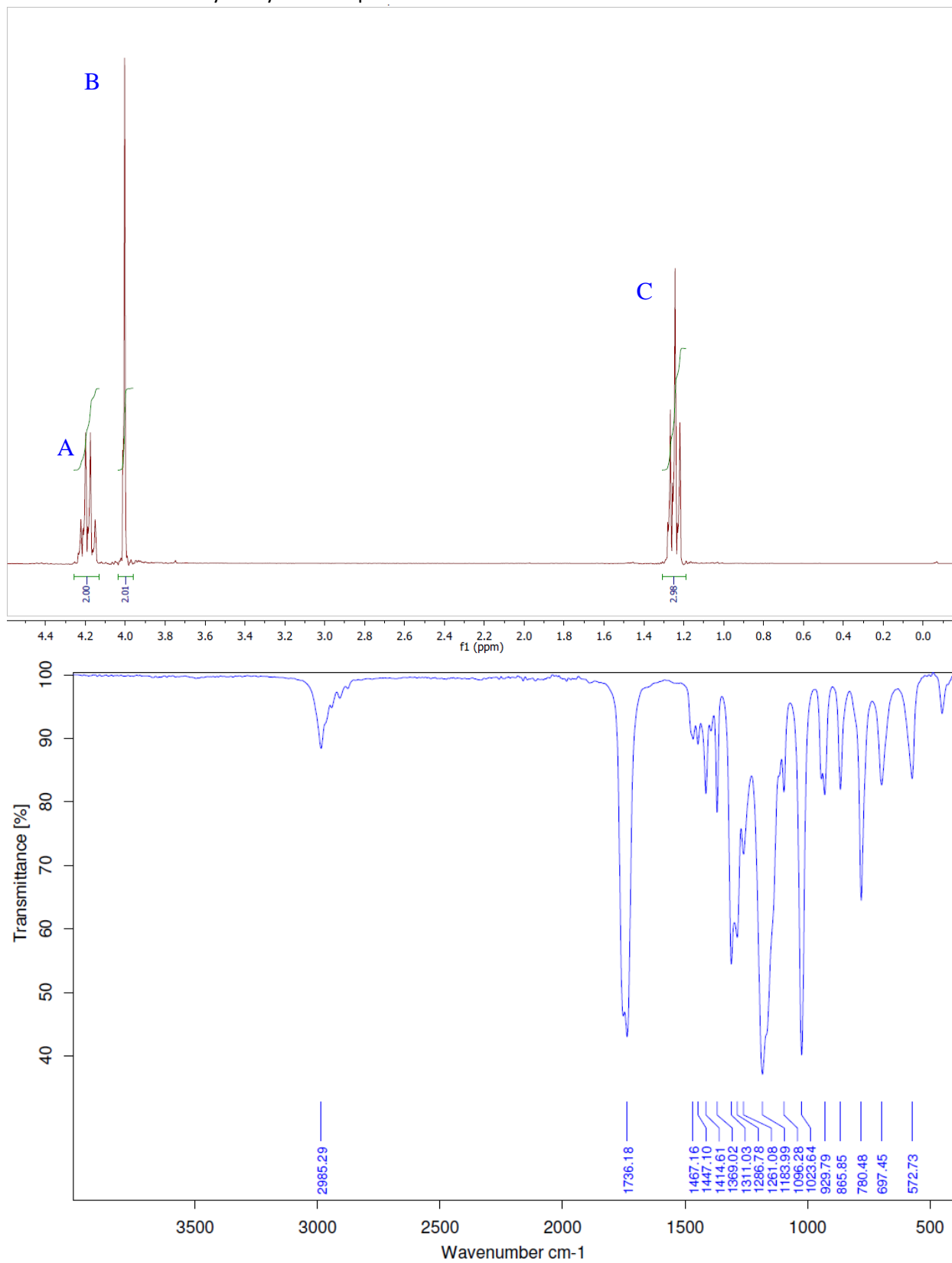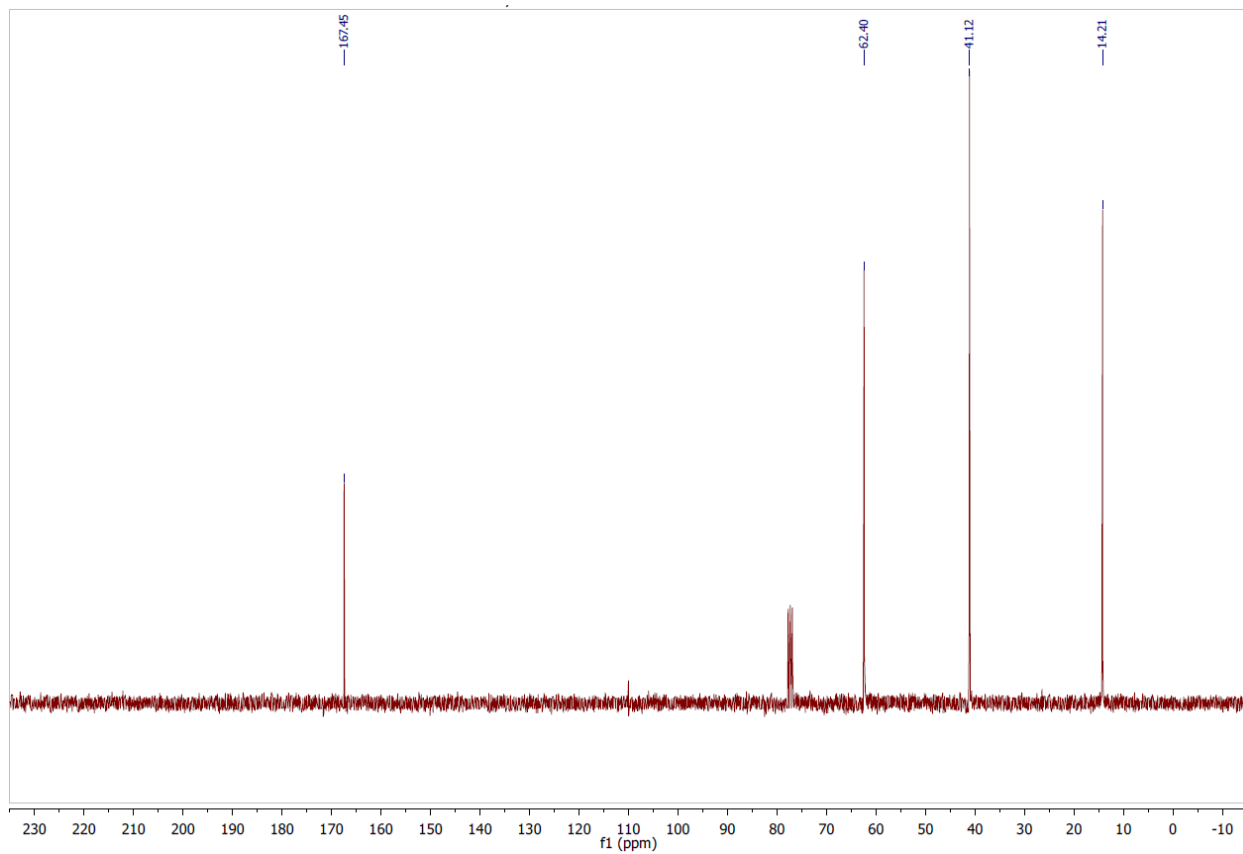

1H-NMR Mixture of Acetone and Isopropanol in CDCl3
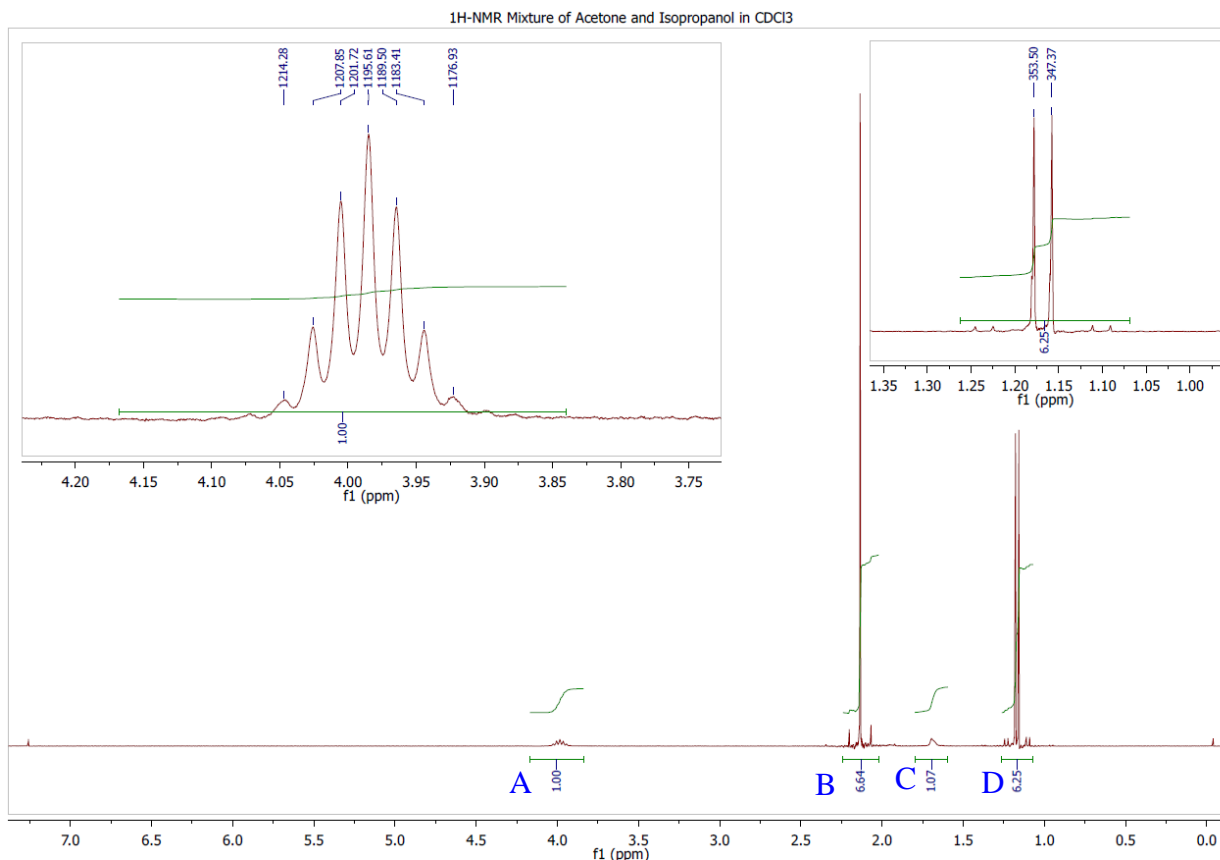
VIII.   Determine the structure of the molecule with formula C₅H₉ClO that corresponds to the spectra shown below. Fully analyze each spectrum.

MS-NW-3537
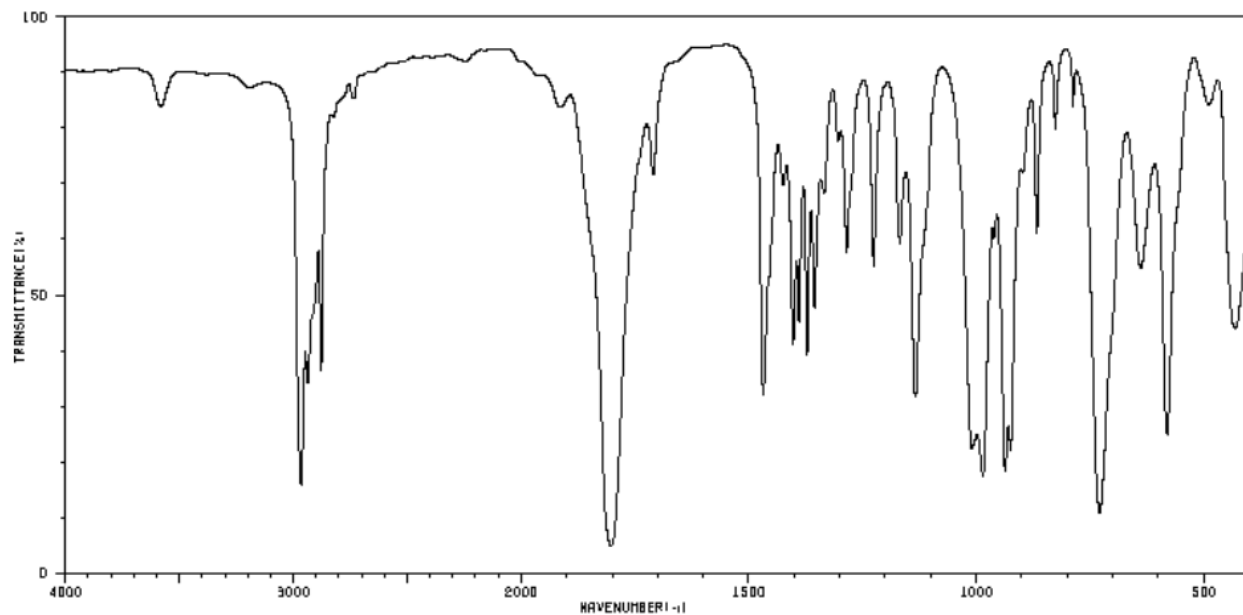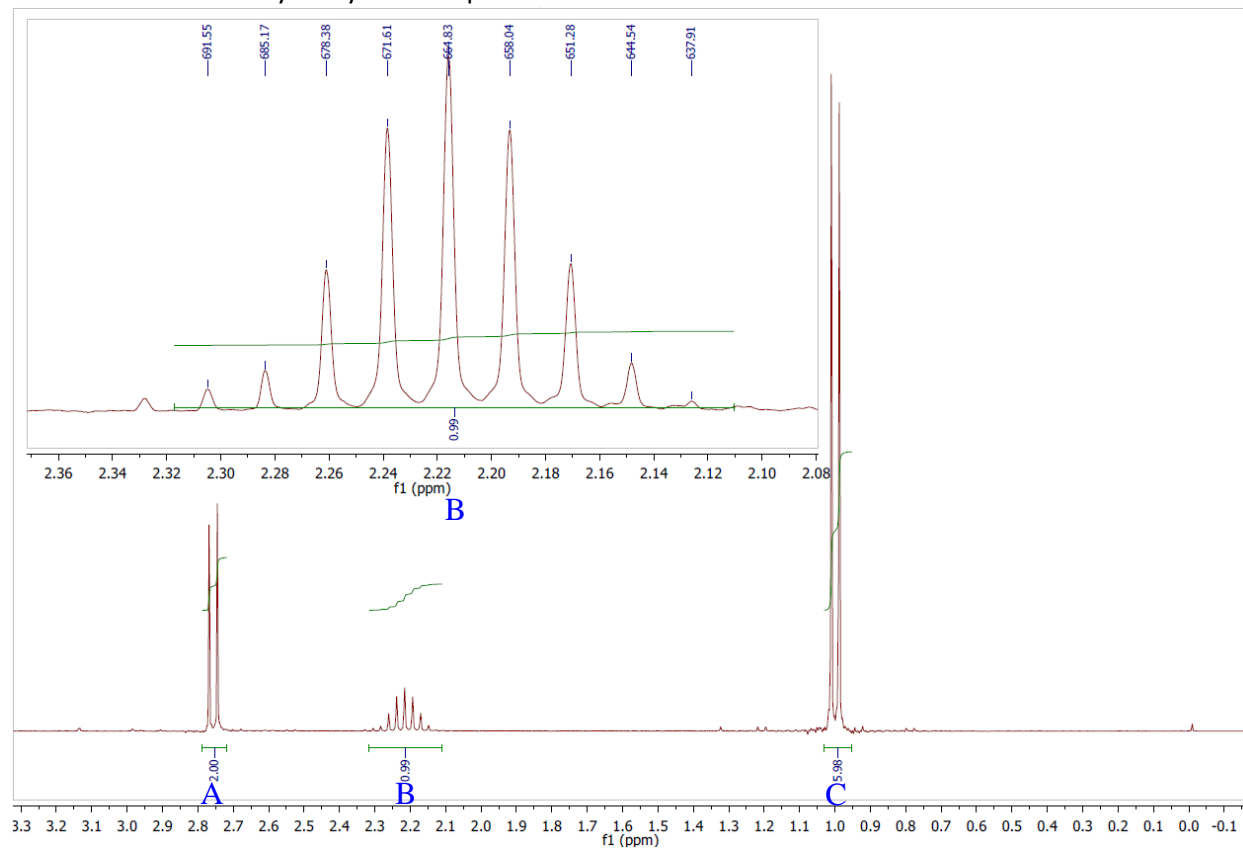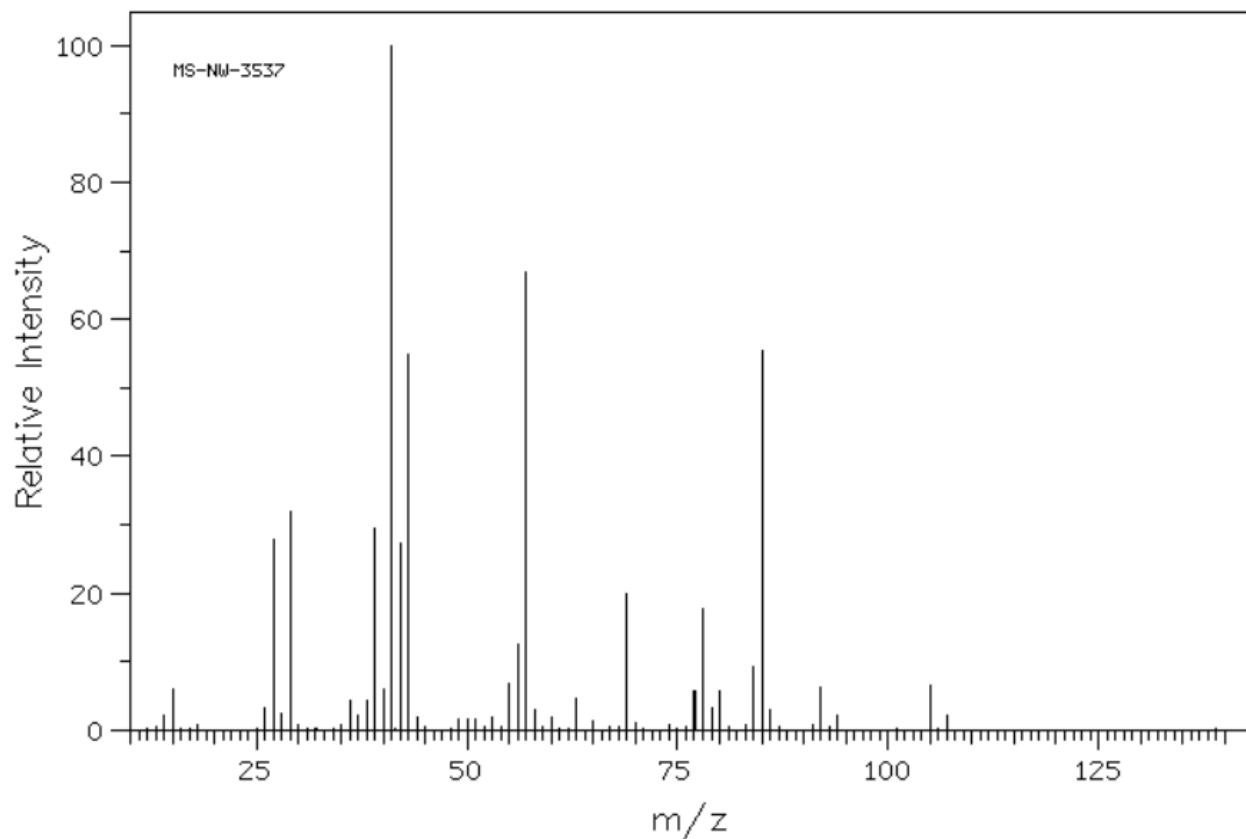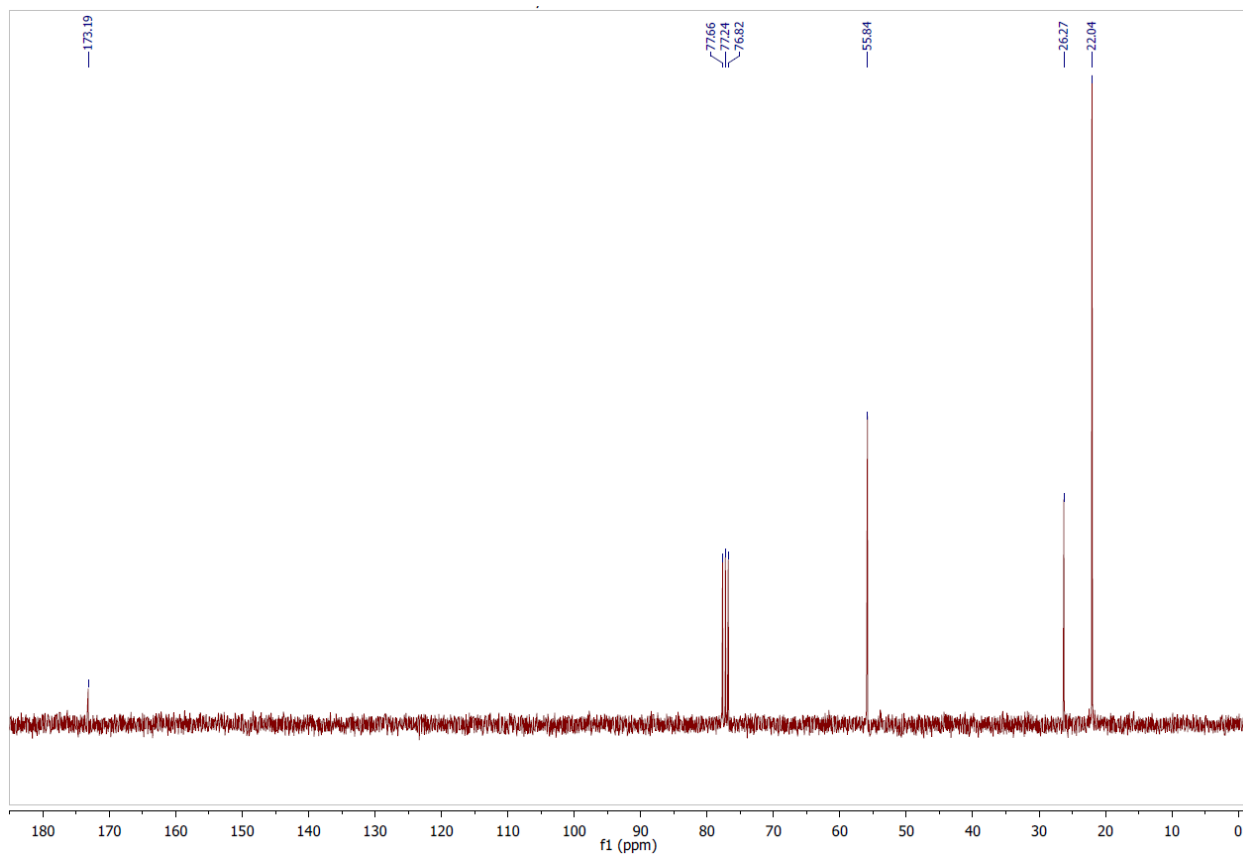
IX.   Determine the structure of the molecule with formula $C_4H_7ClO_2$ that corresponds to the spectra shown below. Fully analyze each spectrum.

Peak#:1   R.Time:2.6(Scan#:69) MassPeaks:76