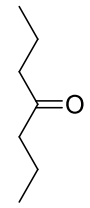
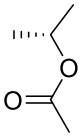
Chemistry 344: Spectroscopy and Spectrometry Problem Set 2

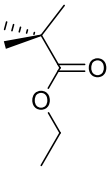
Name (print): _____

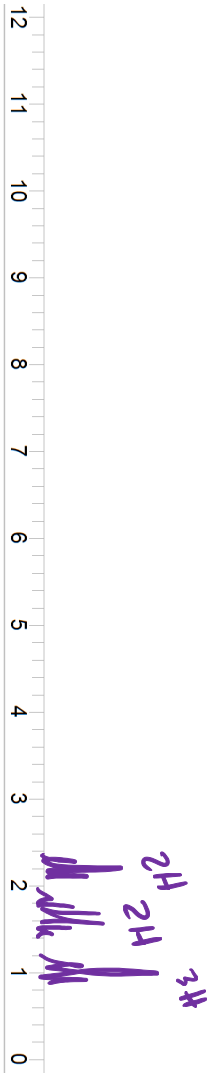
TA Name (print): _____

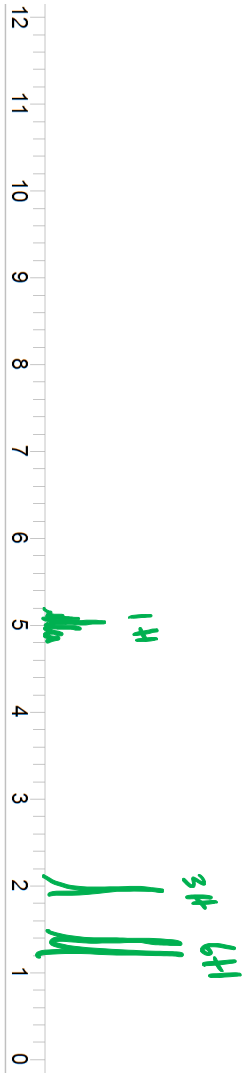
I. For each of the molecules below, predict the splitting pattern and chemical shift using Curphy-Morrison parameters and/or a chemical shift table for each of the signals in the ^{1}H-NMR spectrum. Make a rough sketch on the horizontal ppm axis provided. Be sure to consider the relative intensity of each signal and label its integration. Draw a TMS signal and label it on each spectrum.

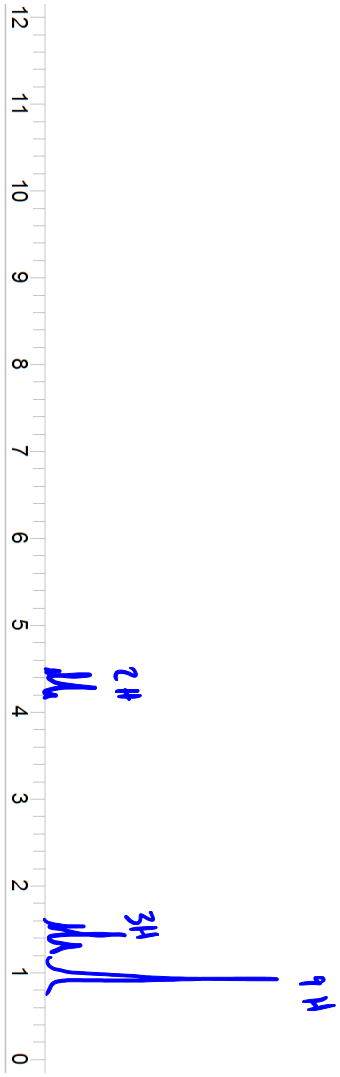






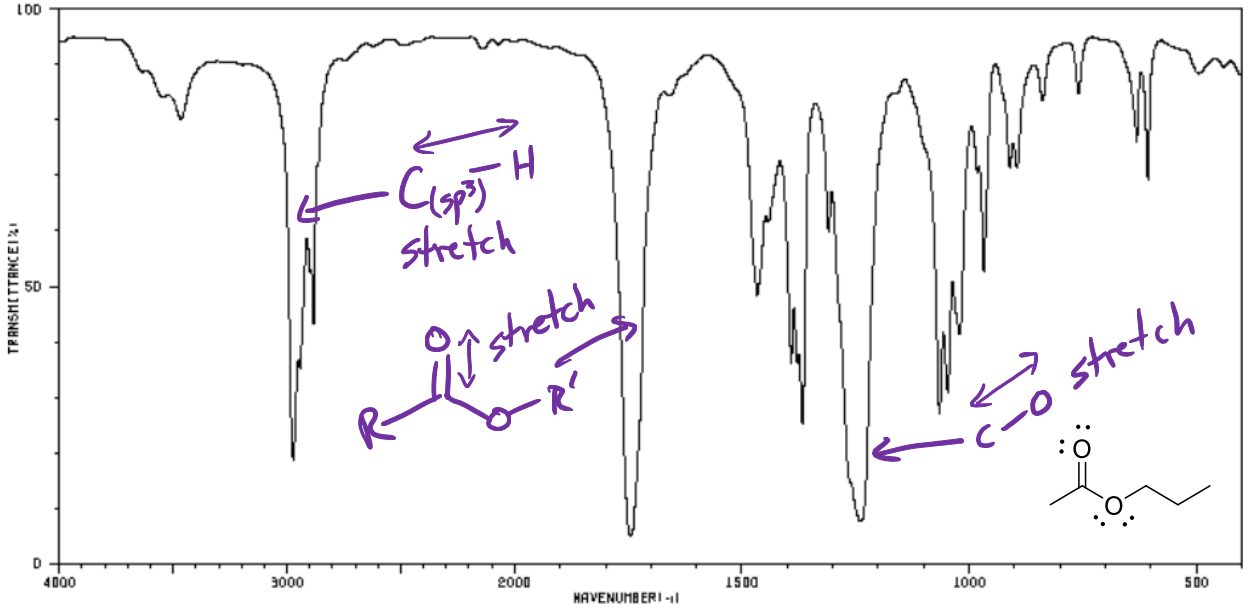




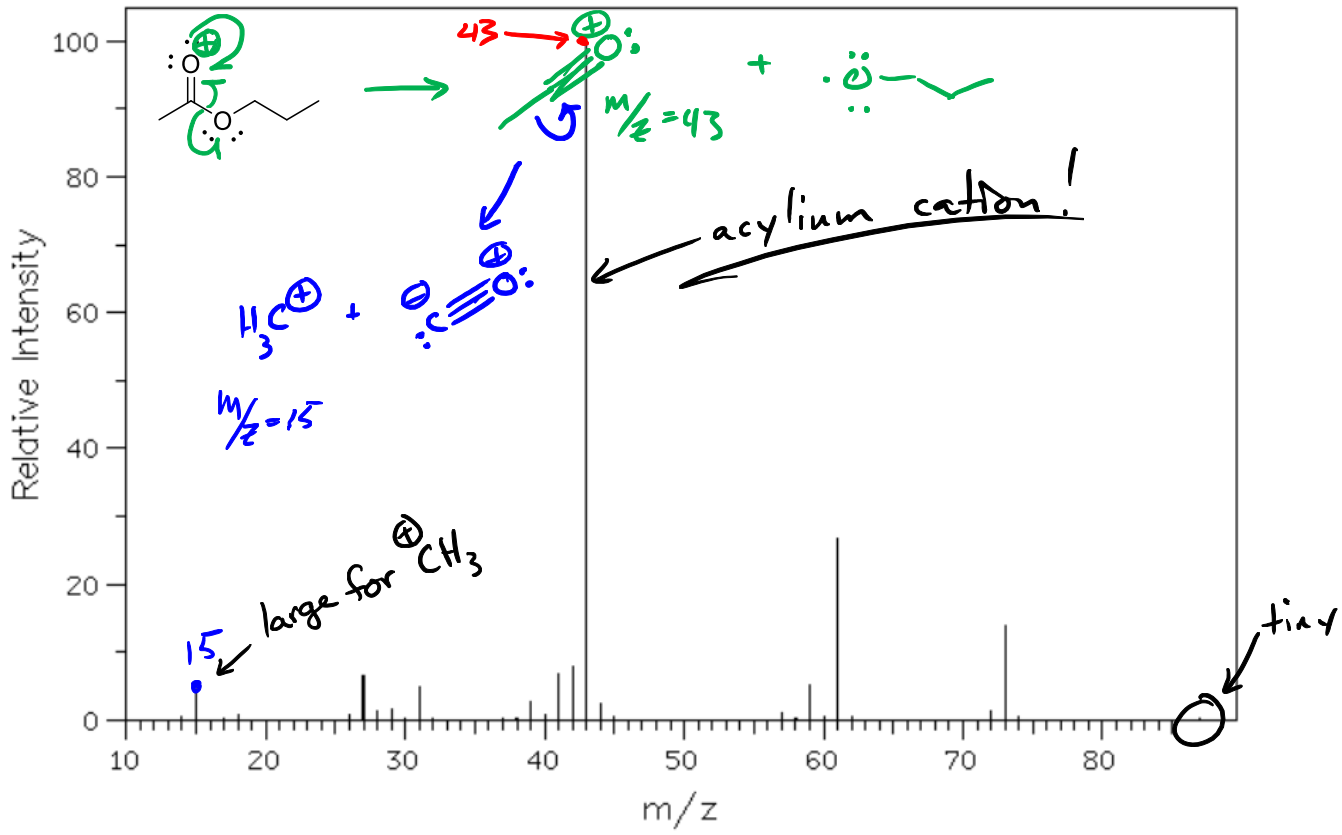


II. For the IR, EI-Mass, ^{1}H-NMR and ^{13}C-NMR spectra shown below of propyl acetate ($C_5H_{10}O_2$), analyze the structure and each of the spectra as instructed.

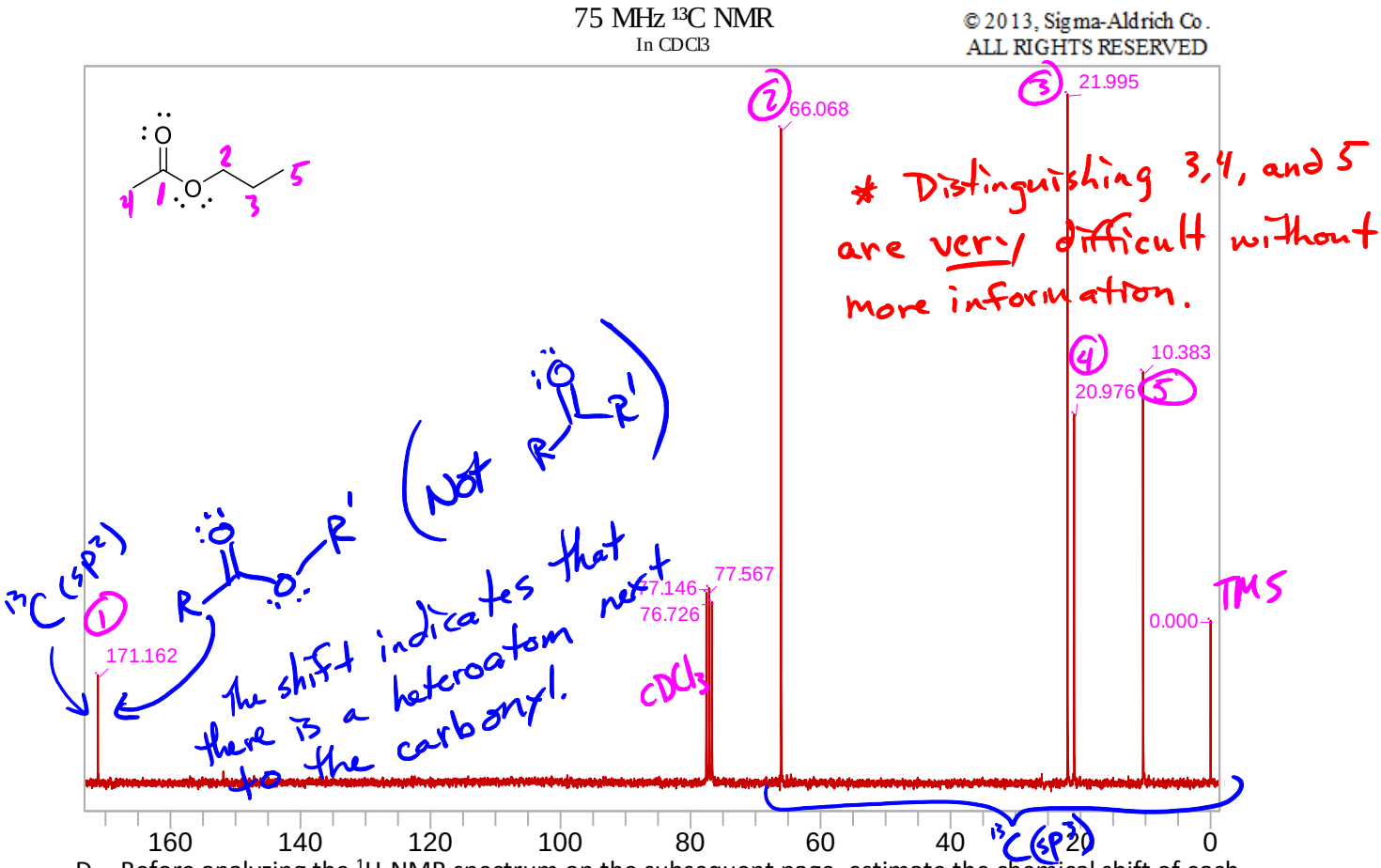
A. For the IR spectrum below of propyl acetate, label the absorptions for the C(sp^3) – H, a C – O, and the C=O bond stretches.



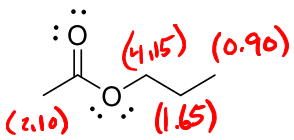
B. For the EI-MS shown below of propyl acetate, provide an electron-pushing mechanism that accounts for the generation of the base peak ion, *m/z* = 43 from the molecular ion of propyl acetate.

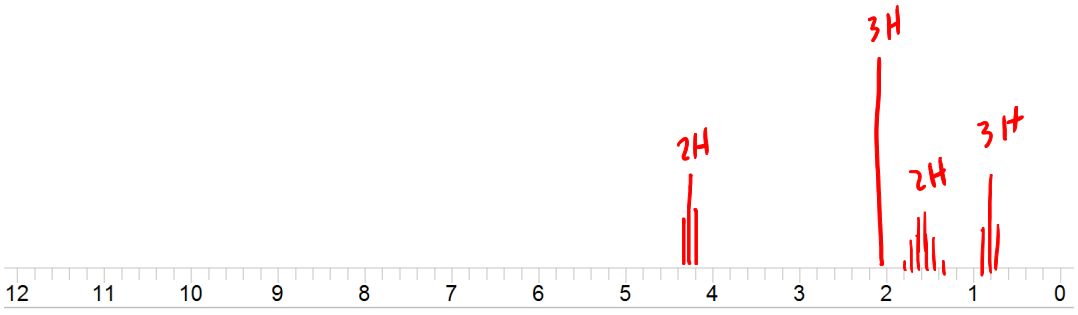


C. In the ^{13}C-NMR spectrum of propyl acetate shown below, label the hybridization of each ^{13}C-atom signal and state the number of different ^{13}C-atom environments. Additionally, label the likely functional group of each ^{13}C-atom signal and the peaks due to $^{13}CDCl_3$ and [^{13}C]-TMS.

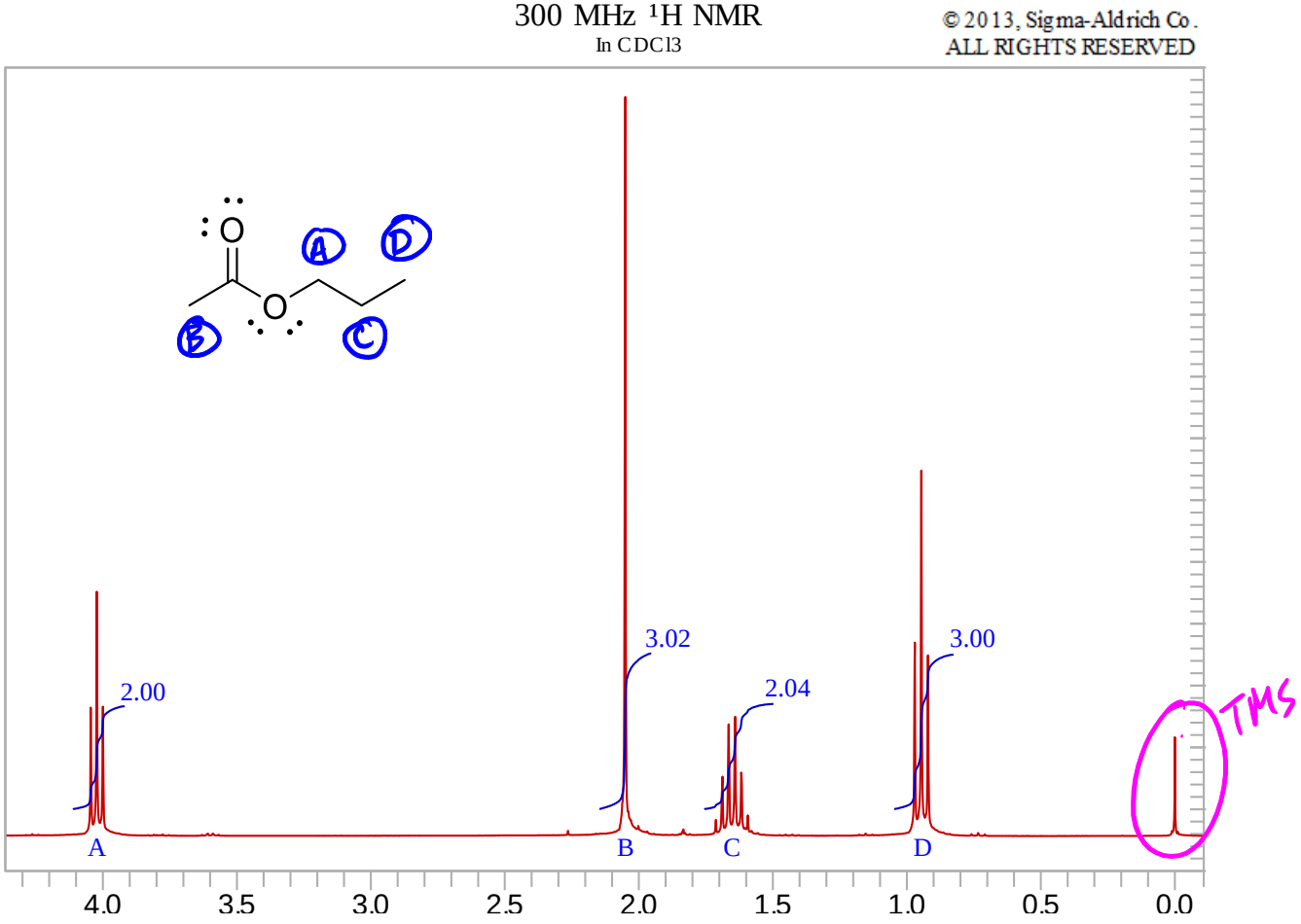


D. Before analyzing the ^{1}H-NMR spectrum on the subsequent page, estimate the chemical shift of each ^{1}H-atom in propyl acetate. Additionally, predict the coupling pattern and integration value that should be observed for each signal.

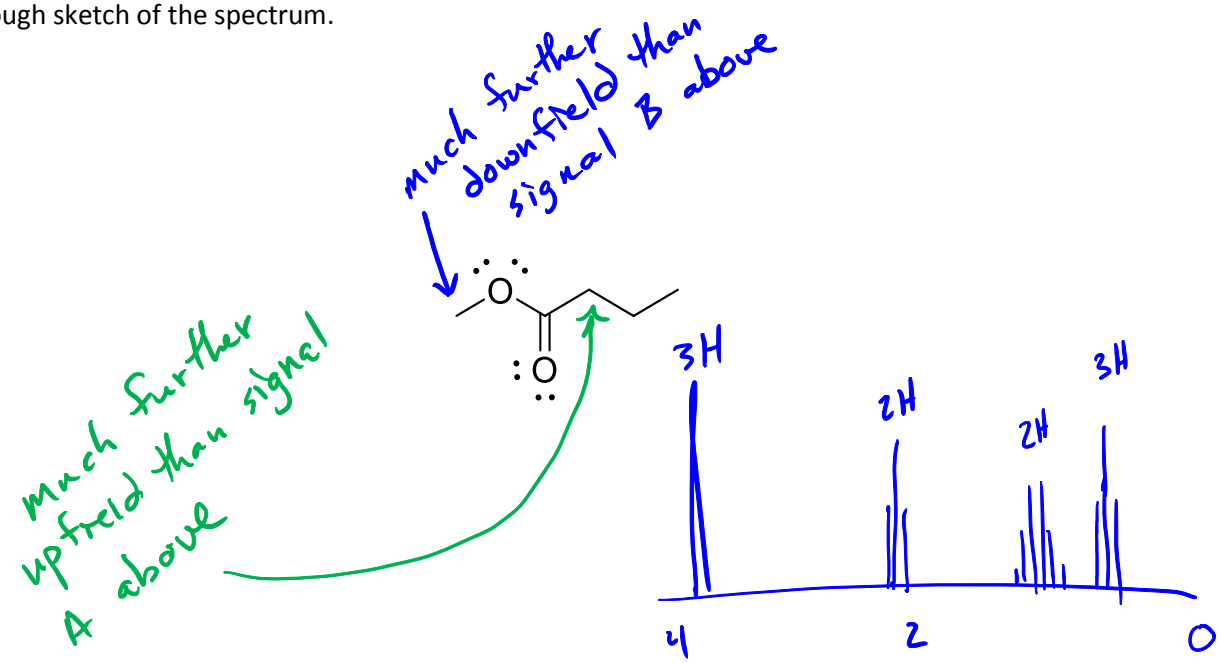




E. Assign each of the signals in the ^{1}H-NMR spectrum below to their corresponding ^{1}H-atoms in propyl acetate. Use the designations provided under each signal in your assignments.

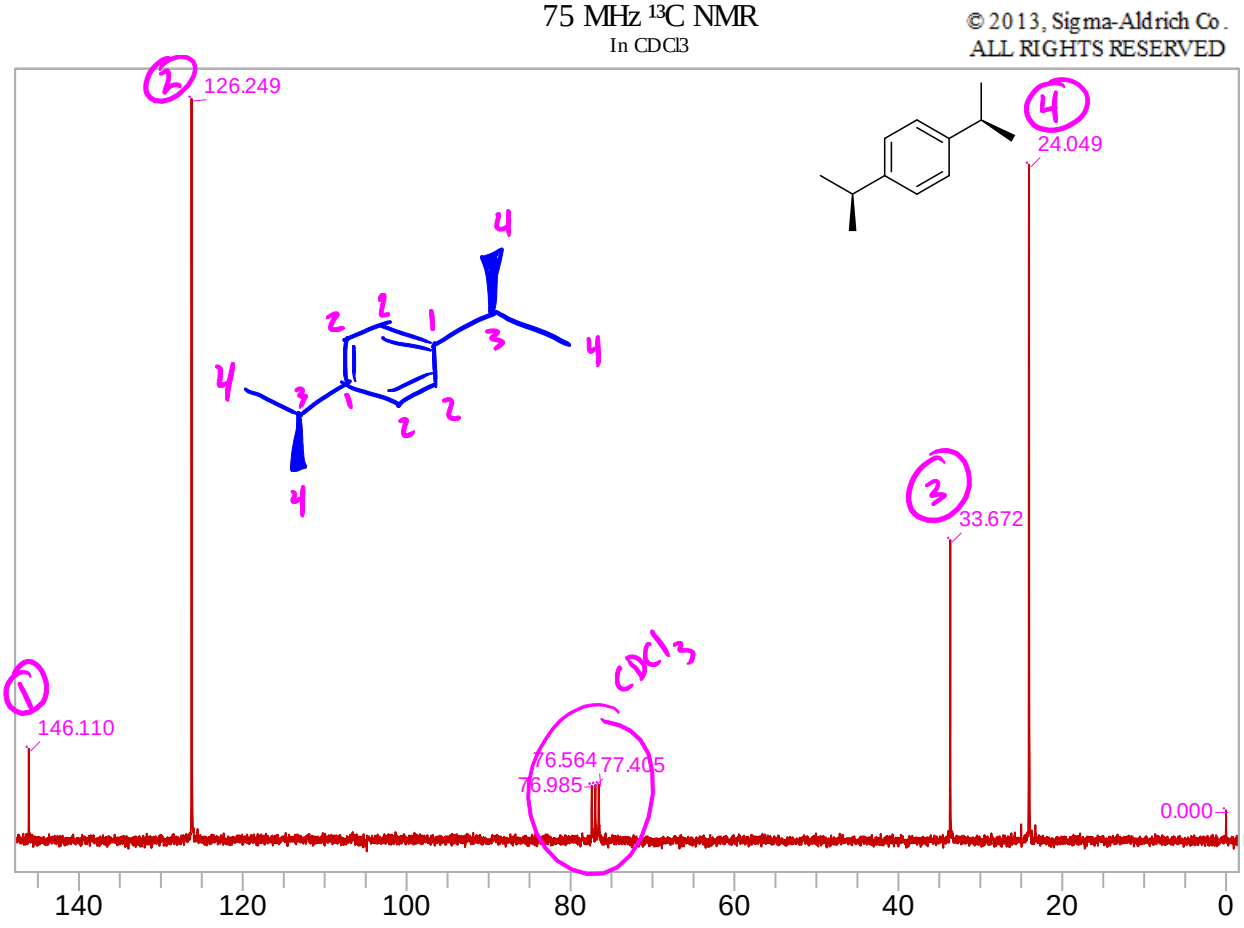


F. How would you expect the ^{1}H-NMR spectrum of methyl butyrate to differ? Be specific and include a rough sketch of the spectrum.



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

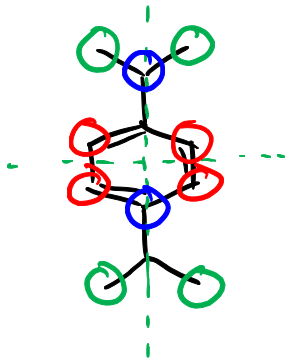
A. In the ^{13}C-NMR spectrum of *p*-diisopropylbenzene shown below, label the hybridization of each ^{13}C-atom signal and state the number of different ^{13}C-atom environments. Additionally, label the likely functional group of each ^{13}C-atom signal and the peaks due to $^{13}CDCl_3$ and [^{13}C]-TMS.



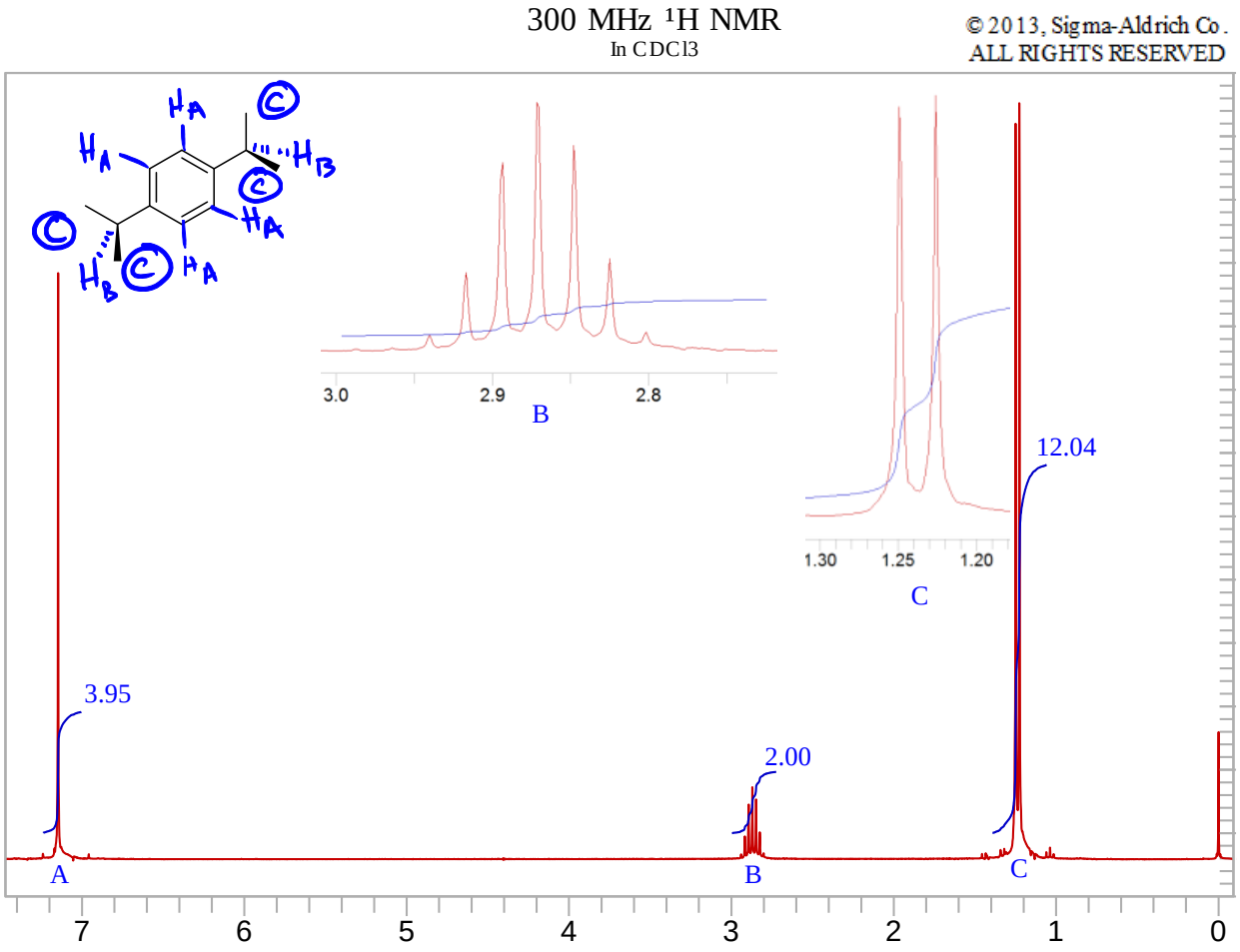
B. Despite 12 C-atoms in *p*-diisopropylbenzene, its spectrum shows only four ^{13}C-NMR environments. Explain how the structure results in so few ^{13}C-NMR signals. How many ^{1}H-NMR signals would you expect to observe?

There will be 3 ^{1}H-NMR signals

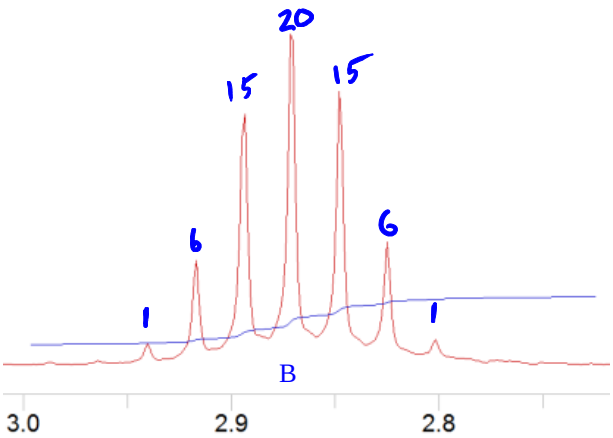
* four methyl groups as a doublet
* two methine groups as a septet
* four aryl ring ^{1}H atoms as a singlet



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



D. For the signal labeled B shown below, label the approximate signal intensities for each individual peak. Provide an explanation for the observed intensities.



1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1

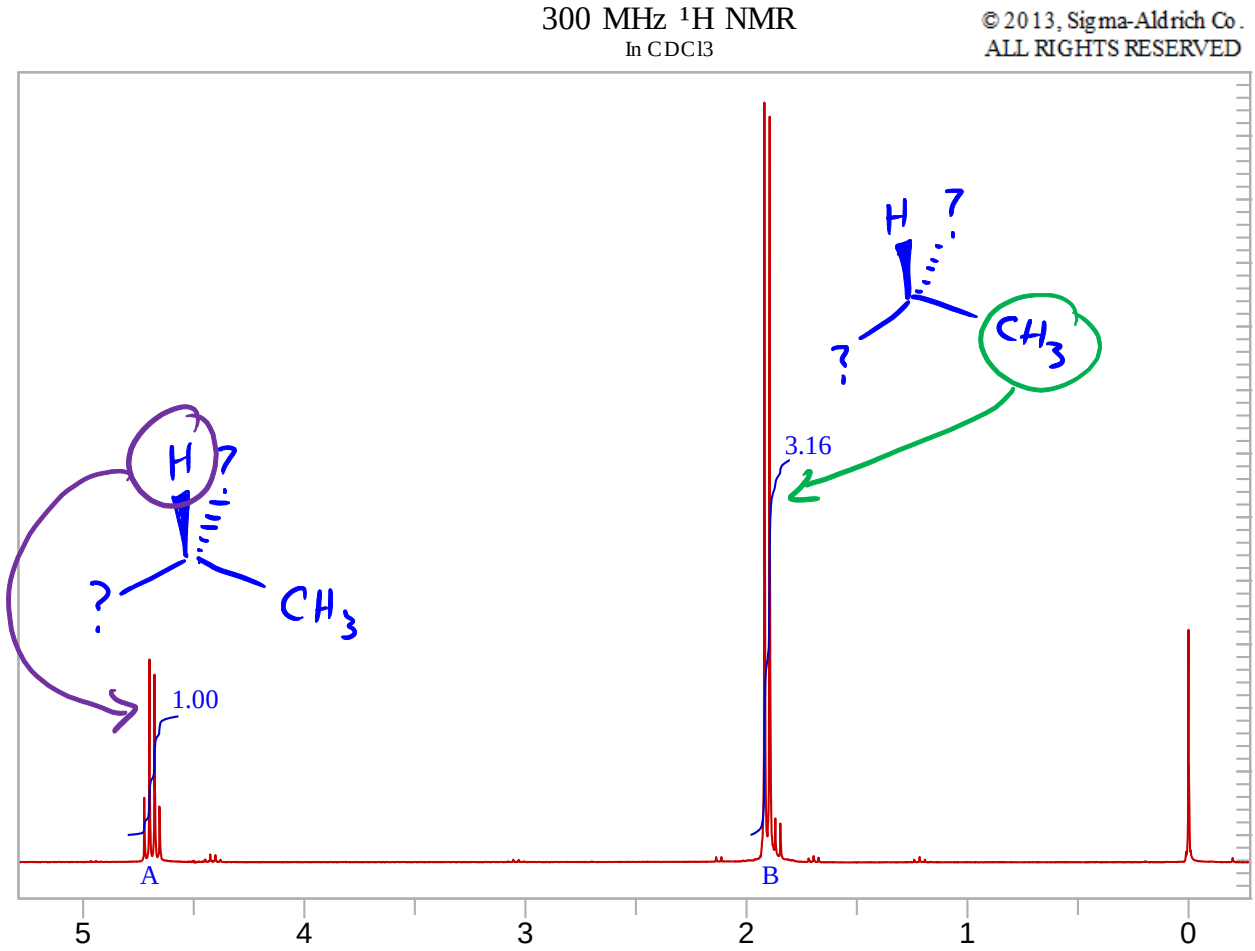
IV. For a molecule with a chemical formula of $C_3H_4Br_2O$, answer the following questions.

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?

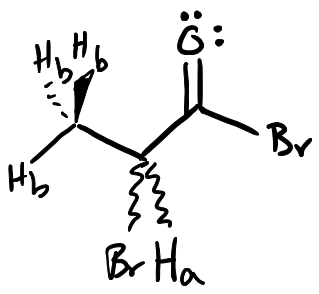
* a single double-bond or ring $U = IHD = \frac{2C + 2 + N - H - X}{2} = 1$

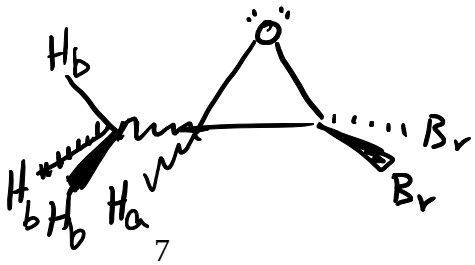
ketone, aldehyde, alkene, acid bromide, cyclic ether, ...

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.

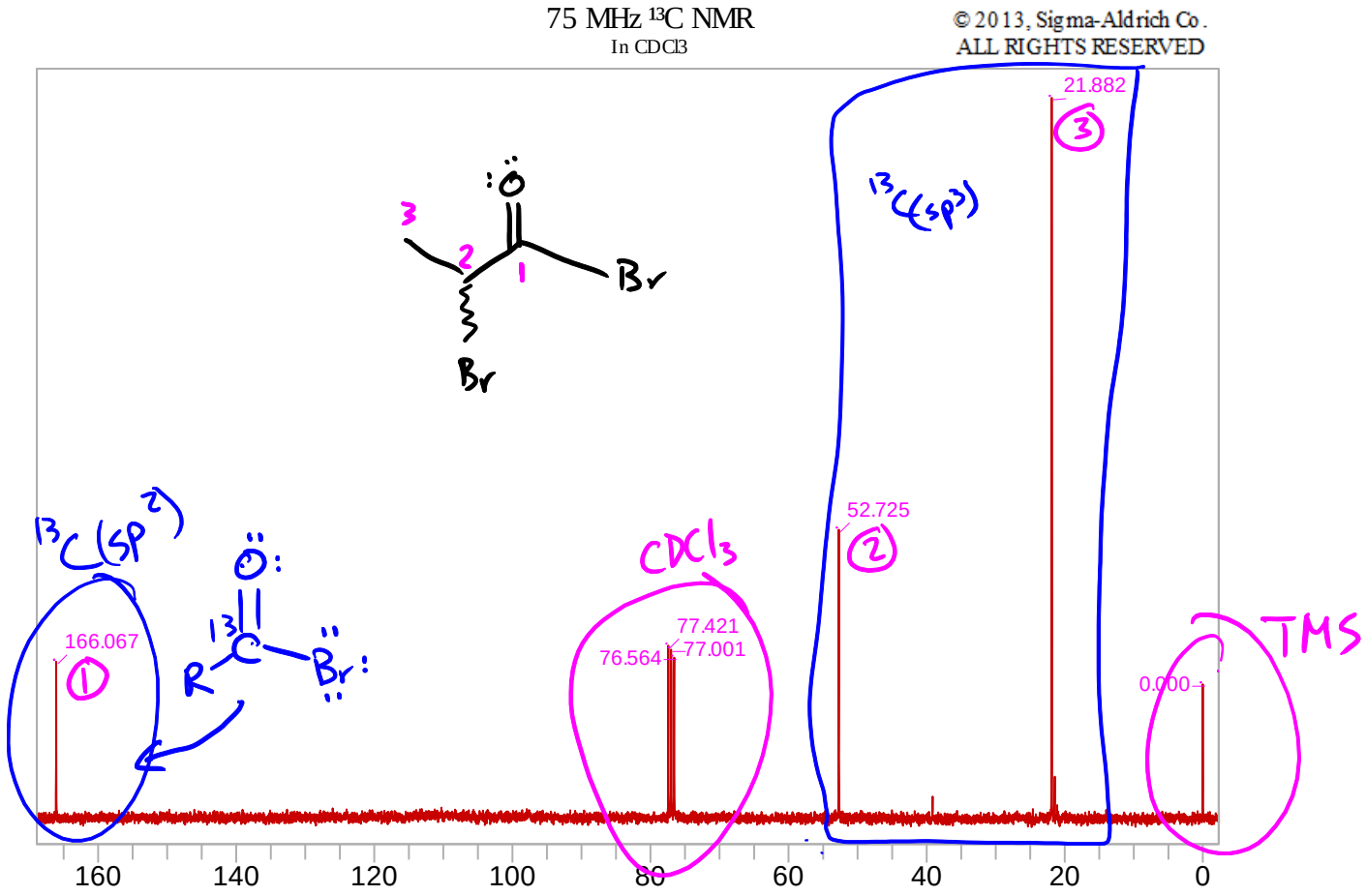


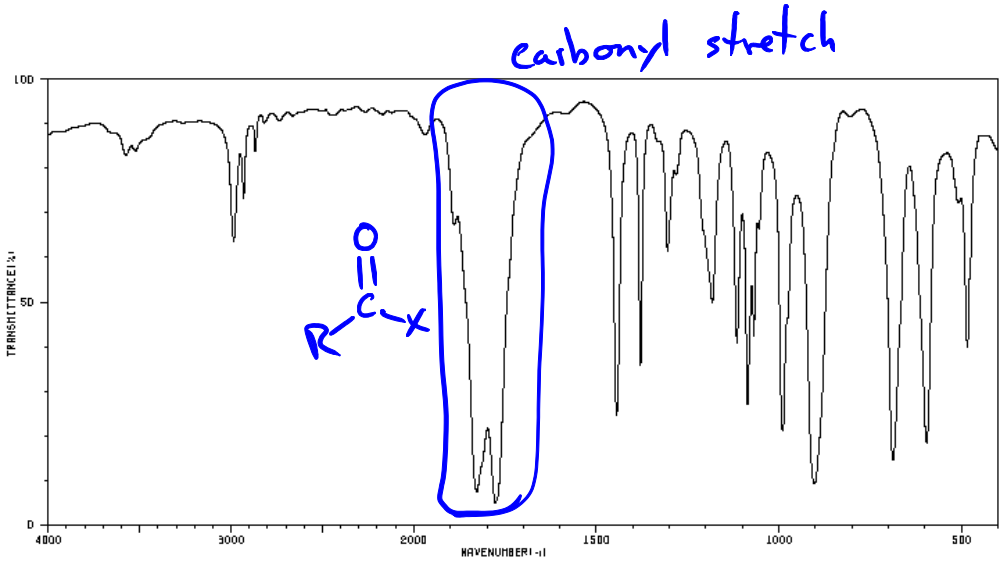
C. Based upon the part structures drawn in part B and the relative chemical shifts of each signal, draw two potential molecules, one carbonyl containing molecule and one epoxide. Label the ^{1}H-atoms in each structure as H_a and H_b.



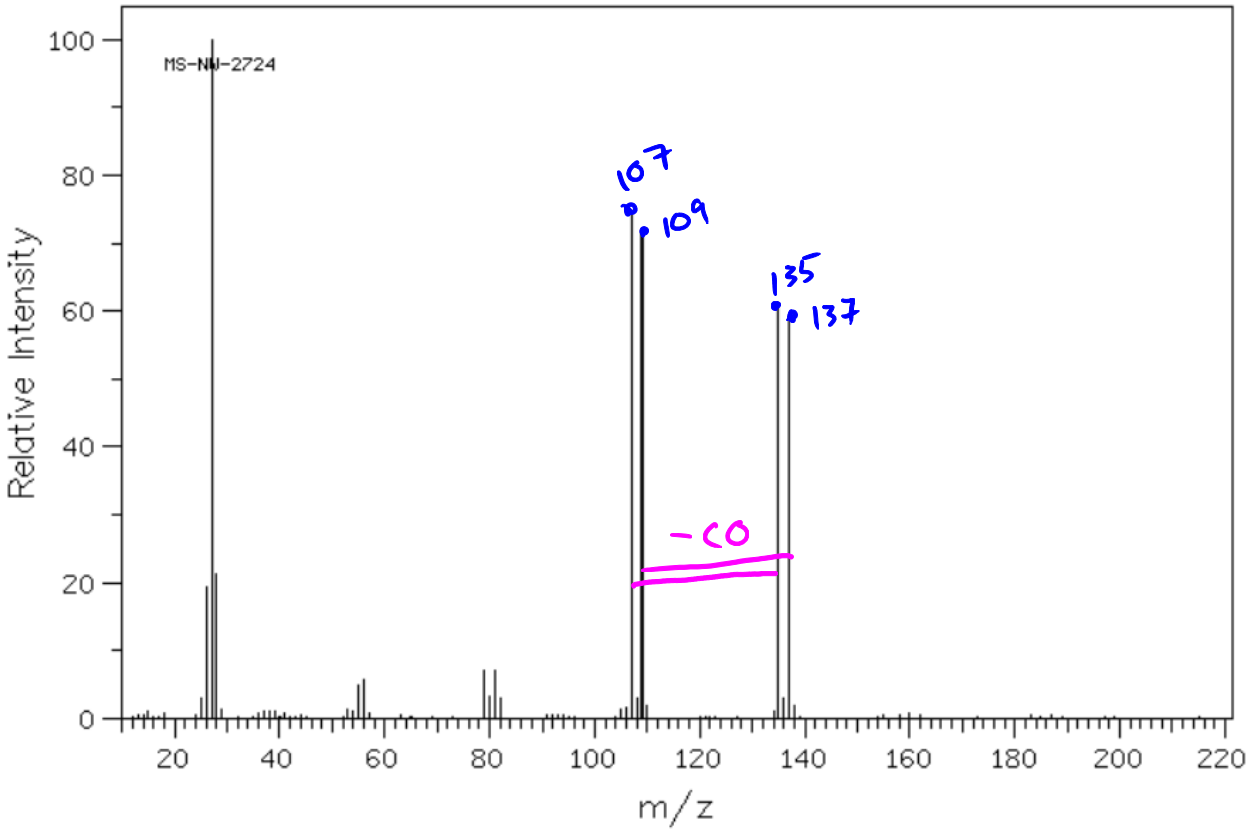


D. The identity of the correct $C_3H_4Br_2O$ molecule can be confirmed in several independent techniques. Explain how each piece of evidence presented below can confirm the identity of the correct molecular structure.





SDBSWeb : http://sdbs.riodb.aist.go.jp (National Institute of Advanced Industrial Science and Technology)



SDBSWeb : http://sdbs.riodb.aist.go.jp (National Institute of Advanced Industrial Science and Technology)

m/z = 214, 216, 218

m/z = 135, 137

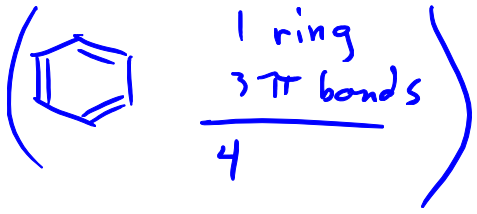
m/z = 107, 109

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

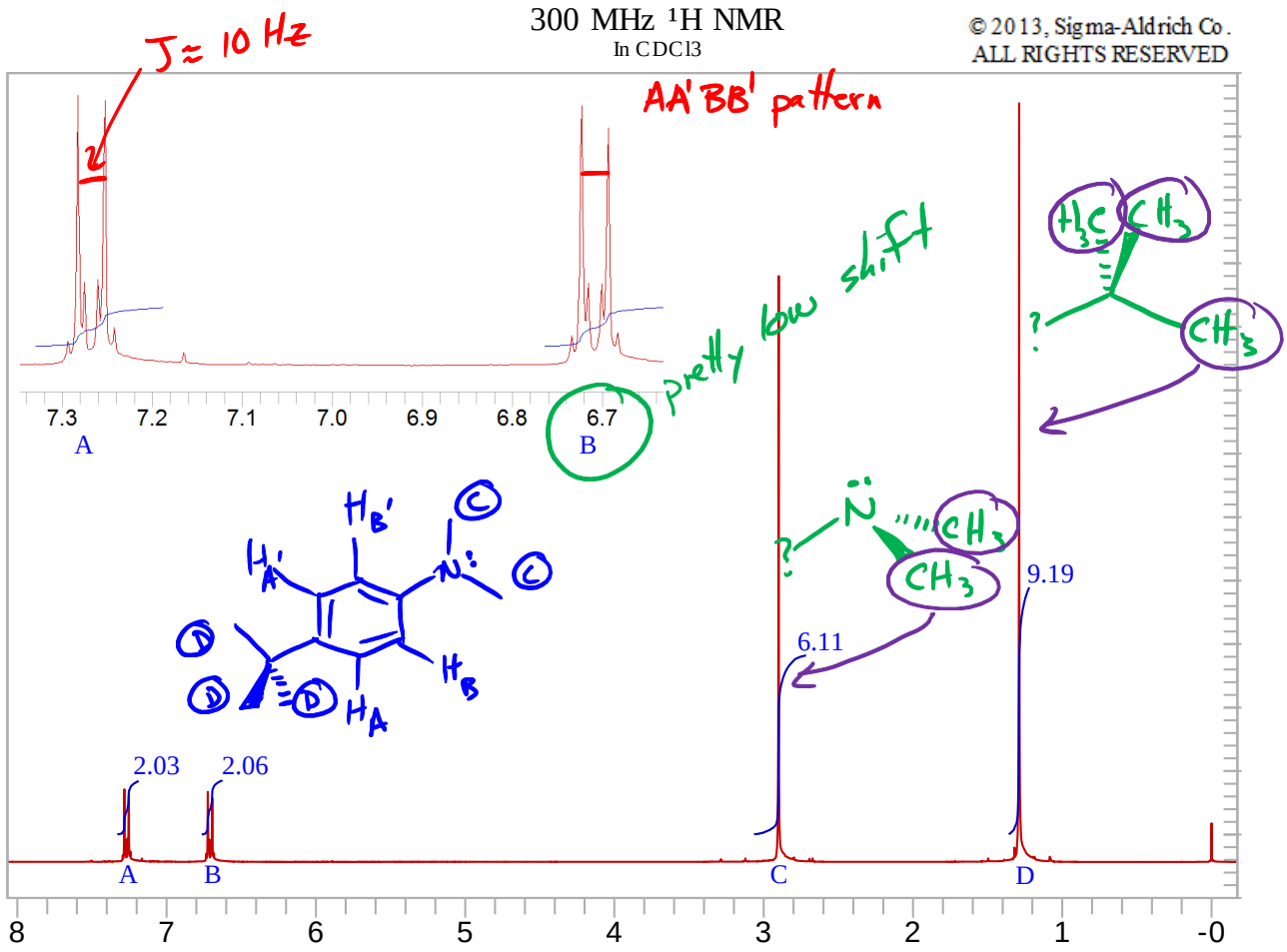
A. What is the unsaturation number (**U**) or index of hydrogen deficiency (**IHD**)? What does this indicate about which functional groups or structural units are possible for this molecule?

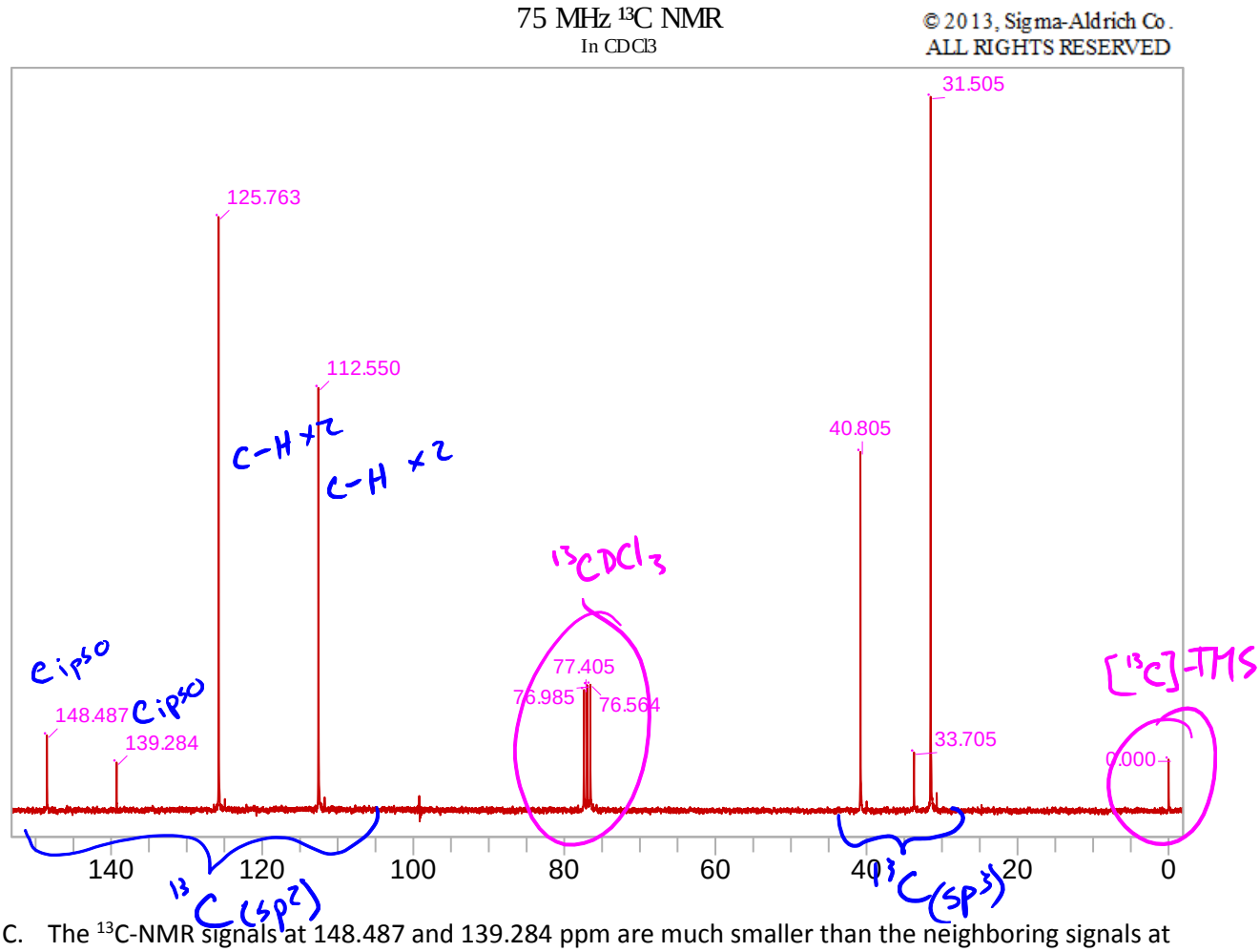
$$U = IHD = \frac{2C + 2 + N - H - X}{2} = 4$$

* lots of rings and/or double-bonds
* often a single aromatic ring



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

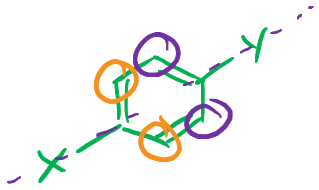




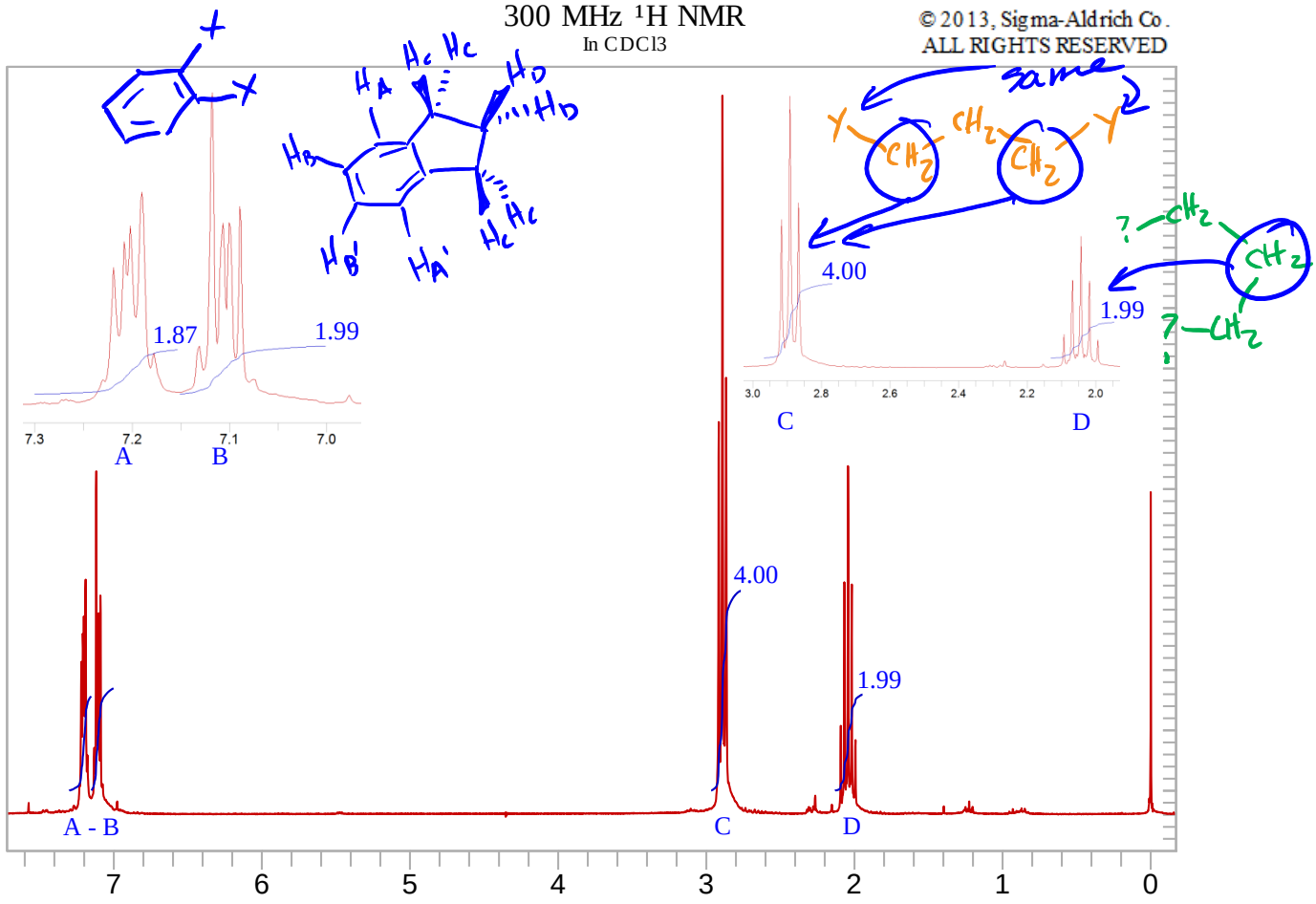
C. The ^{13}C-NMR signals at 148.487 and 139.284 ppm are much smaller than the neighboring signals at 125.763 ppm and 112.550 ppm. Provide two reasons that the signals at 148.487 and 139.284 ppm are lower in amplitude.

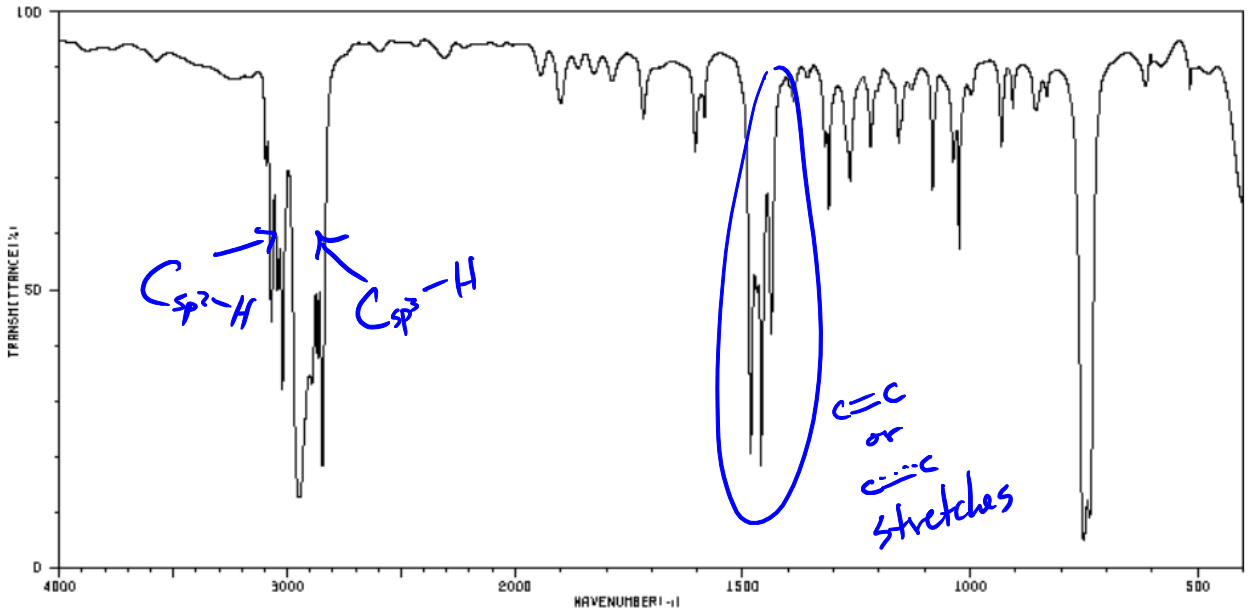
The taller ^{13}C signals usually have ^{1}H-atoms attached. Decoupling of the ^{1}H atoms transfers signal intensity to the ^{13}C-atom signals.

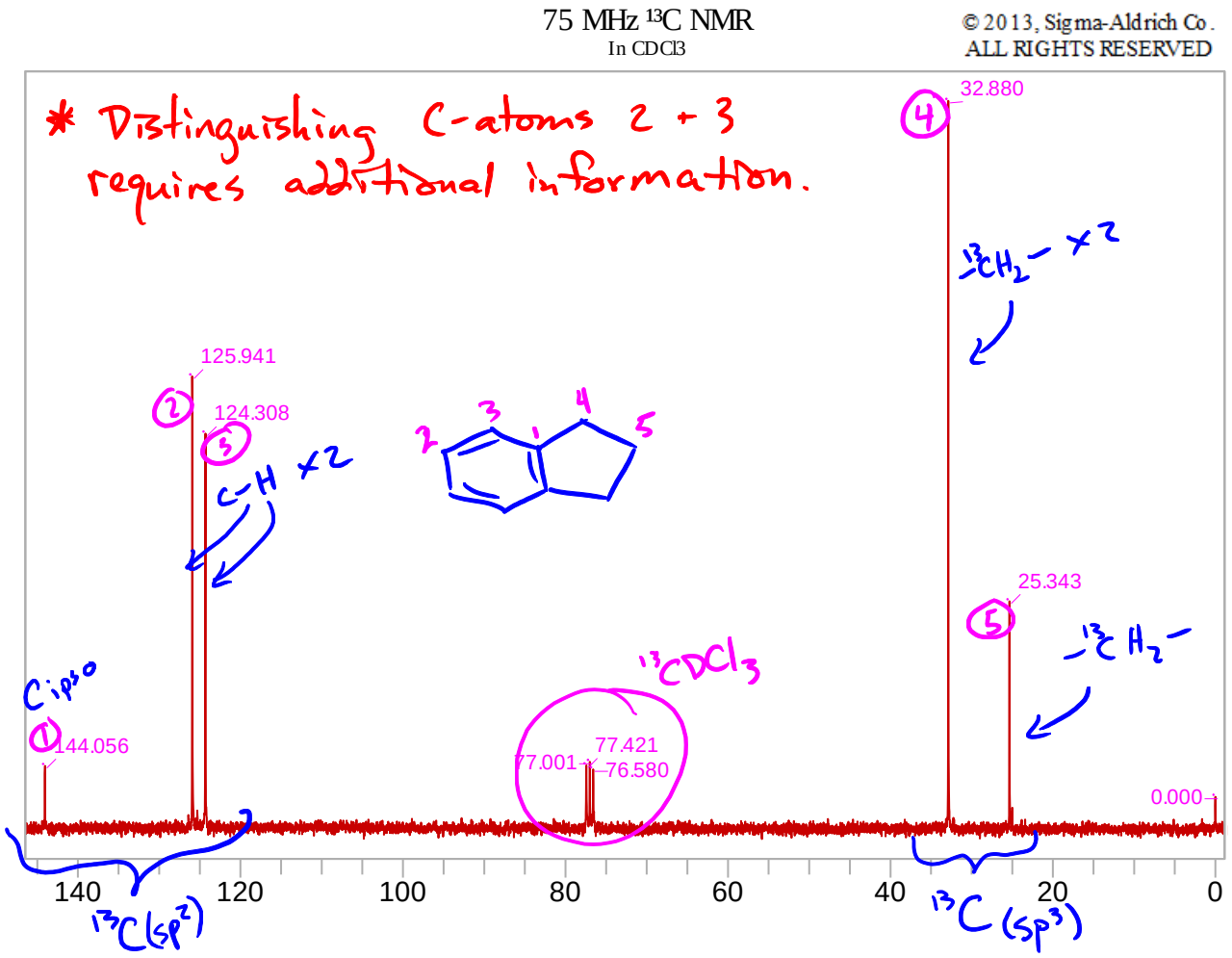
Furthermore, symmetry doubles the intensity for the ^{13}C-H signals in a para-substituted aromatic ring.



VI. Determine the structure of the molecule with formula C_9H_{10} that corresponds to the spectra shown below. Fully analyze each spectrum.






75 MHz 13C NMR
In CDCl3
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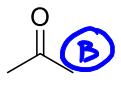
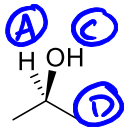
* Distinguishing C-atoms 2 + 3 requires additional information.
32.880
125.941
124.308
25.343
144.056
77.421
77.001
76.580
0.000
C-H x2
13CH2- x2
13CH2-
13CDCl3
C ipso
13C (sp2)
13C (sp3)
140
120
100
80
60
40
20
0

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

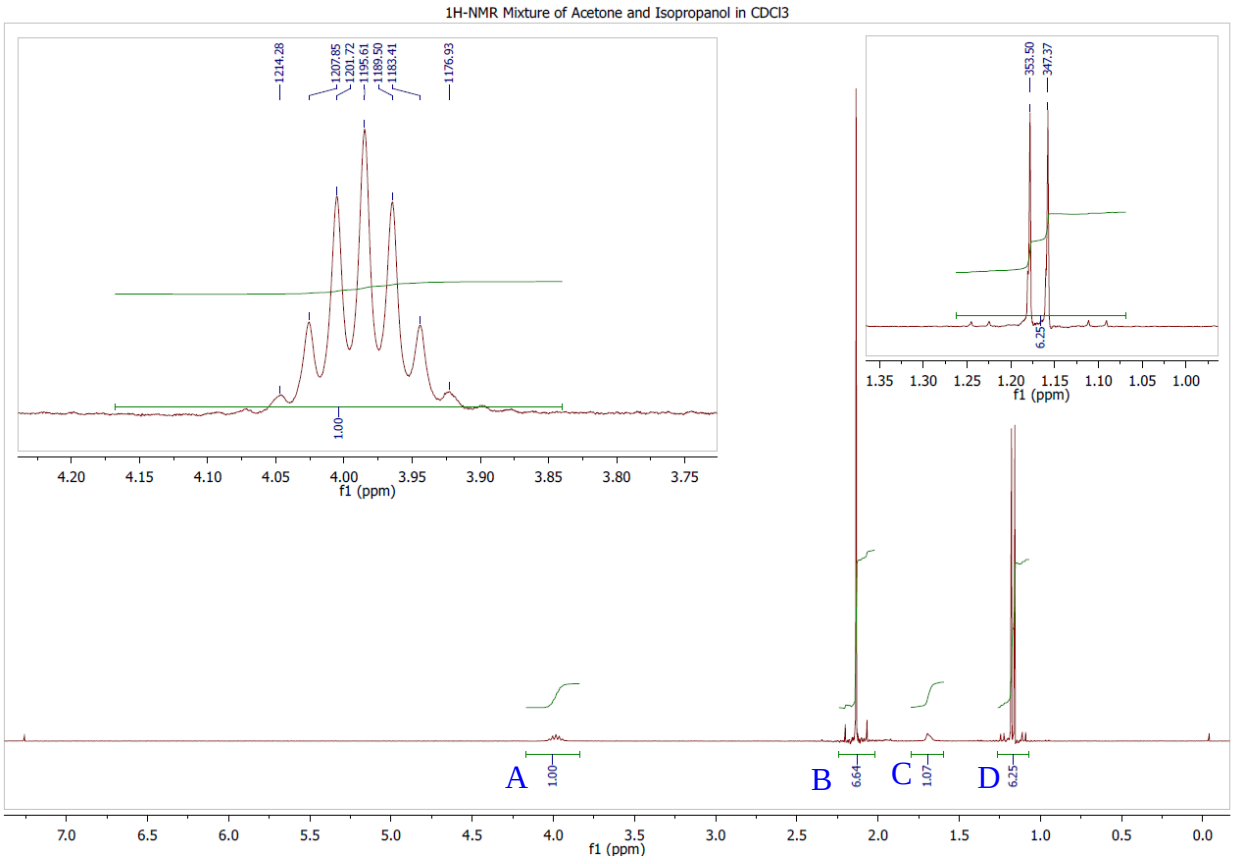


isopropanol

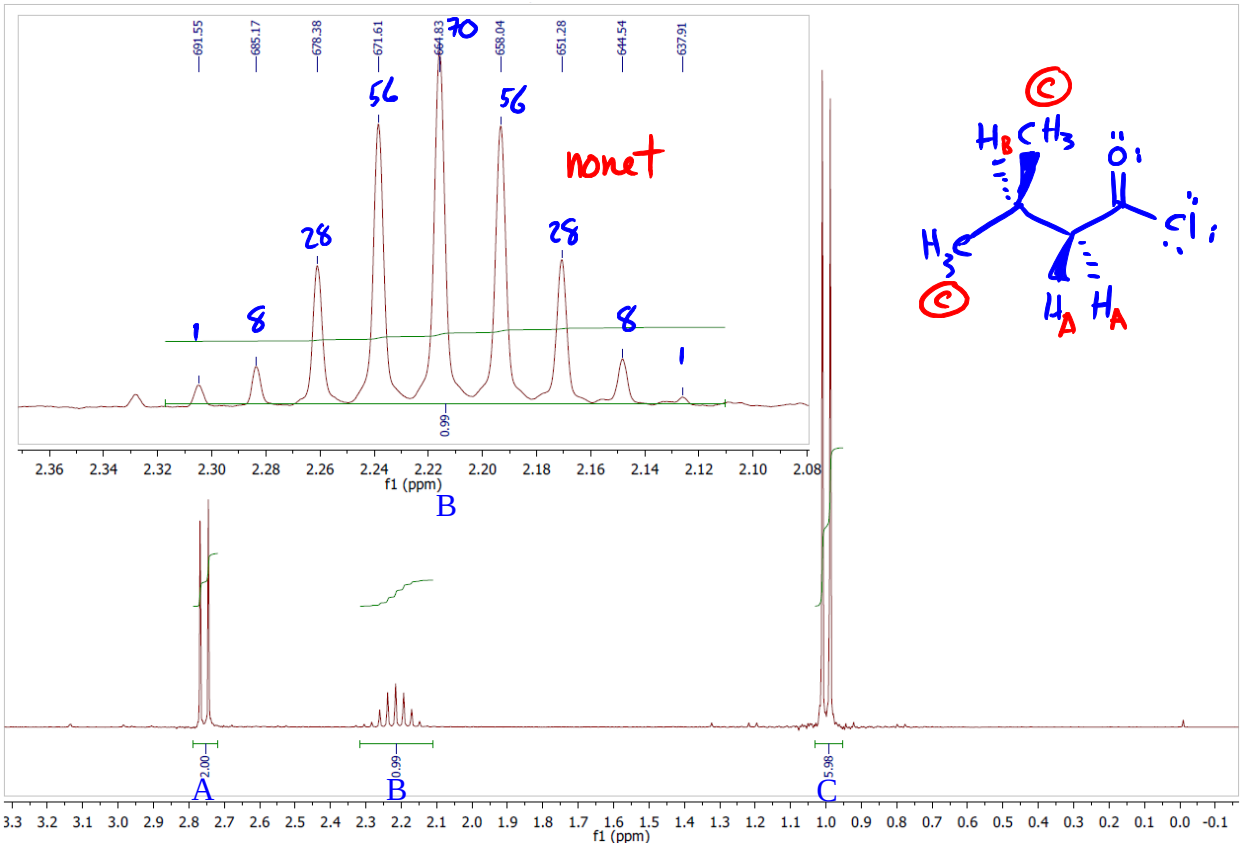
B. Assign each of the signals in the ^{1}H-NMR spectrum below to their corresponding ^{1}H-nuclei in the molecules above using the letter designations A-D.

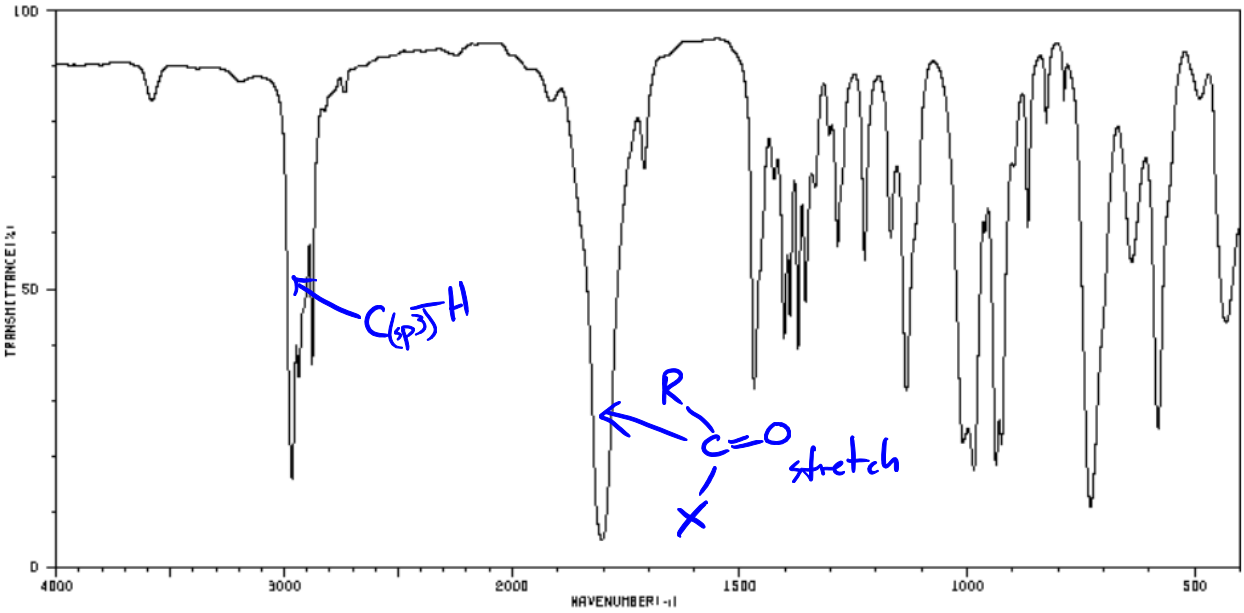
C. Using the spectrum below, determine the relative amount of acetone and isopropyl alcohol in the spectrum of a mixture relative to the least abundant molecule. Report the ratio with the lowest abundance species set to a value of 1.00.

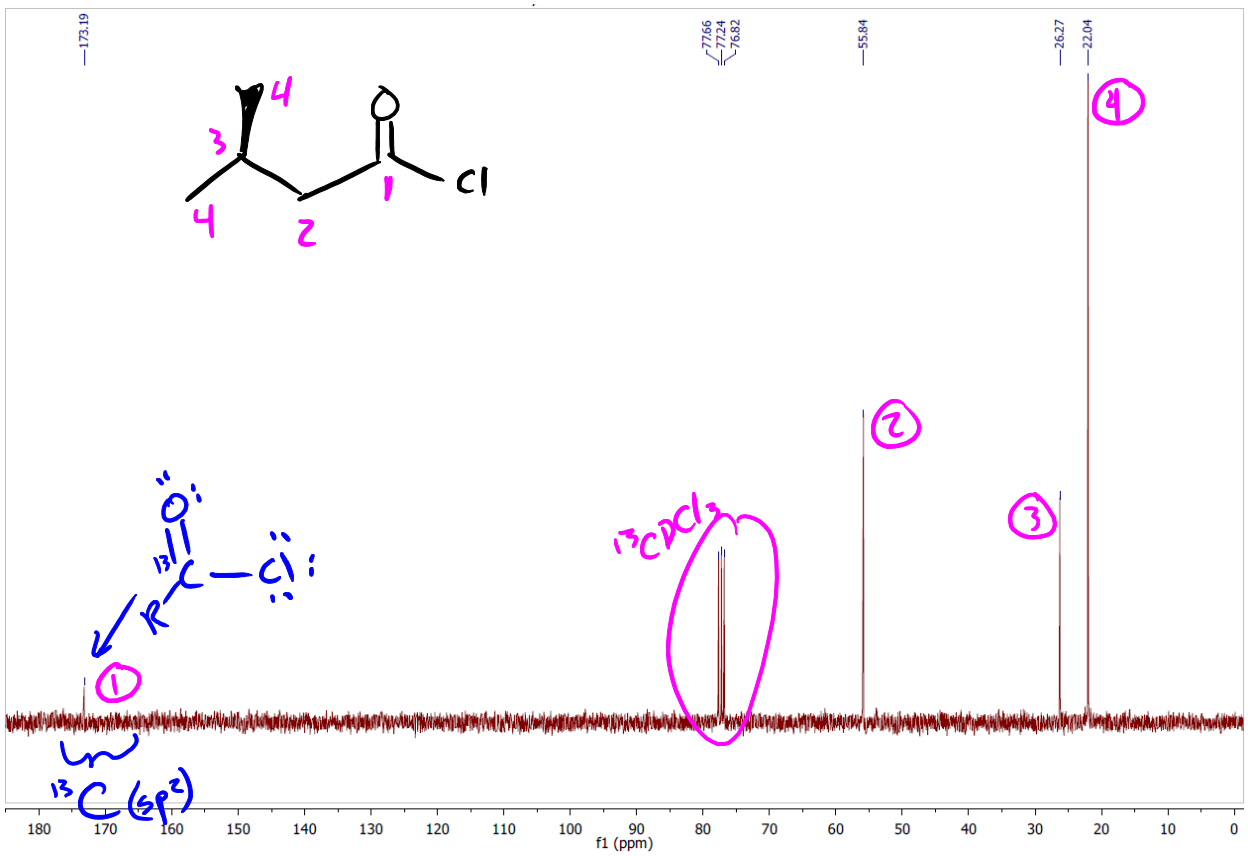
$$\frac{6.64/6 \text{ H-atoms in acetone}}{1.00/1 \text{ H-atom in isopropanol}} = 1.10 \text{ acetone : 1 isopropanol.}$$

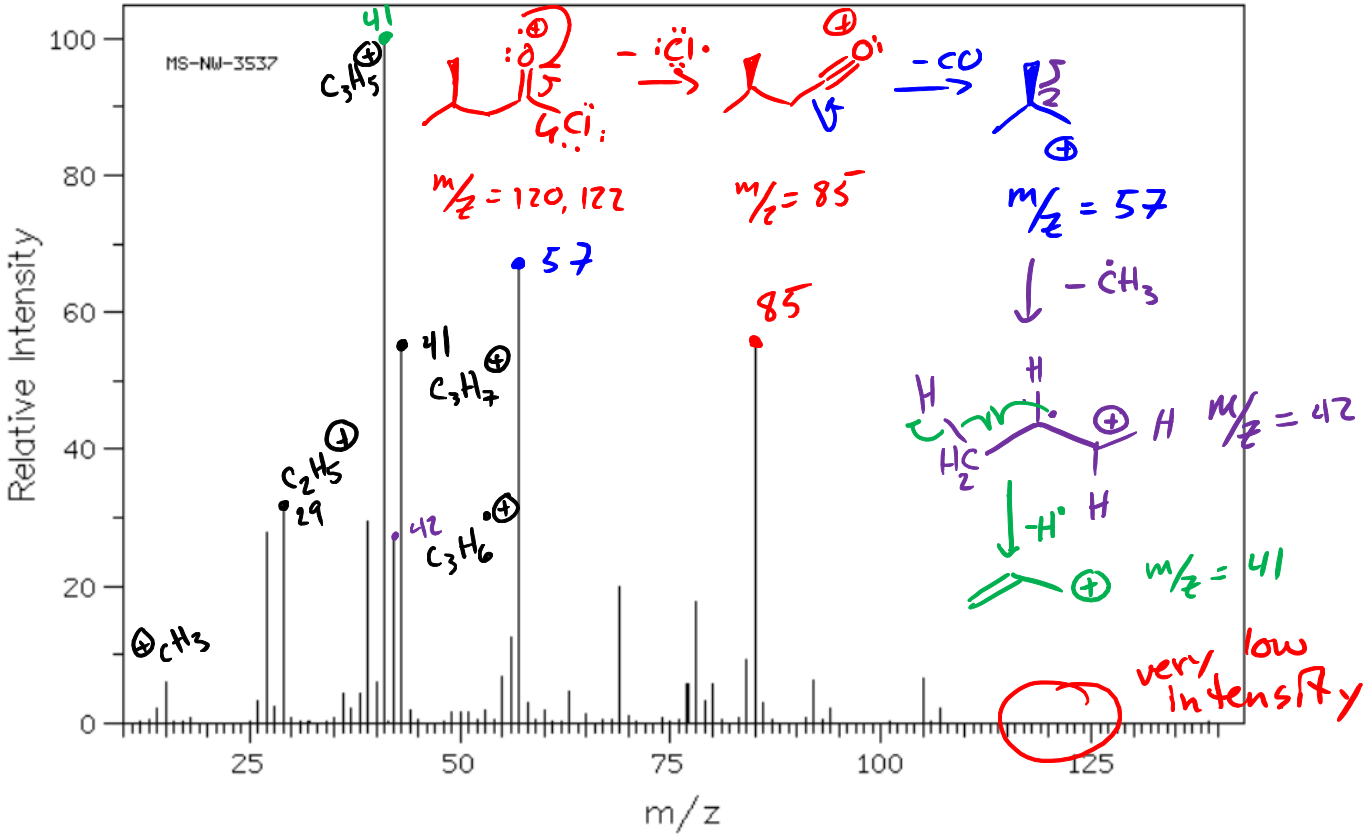


VIII. Determine the structure of the molecule with formula C_5H_9ClO that corresponds to the spectra shown below. Fully analyze each spectrum.

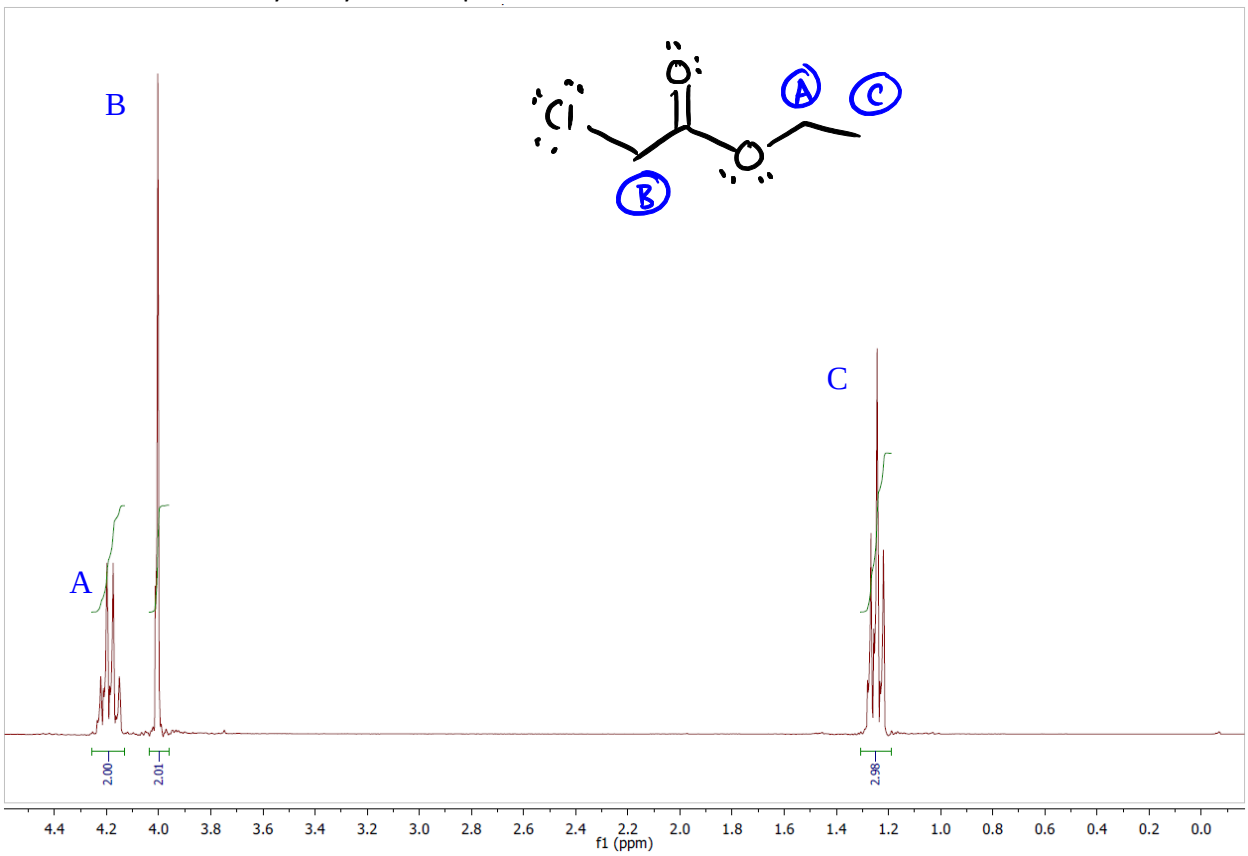


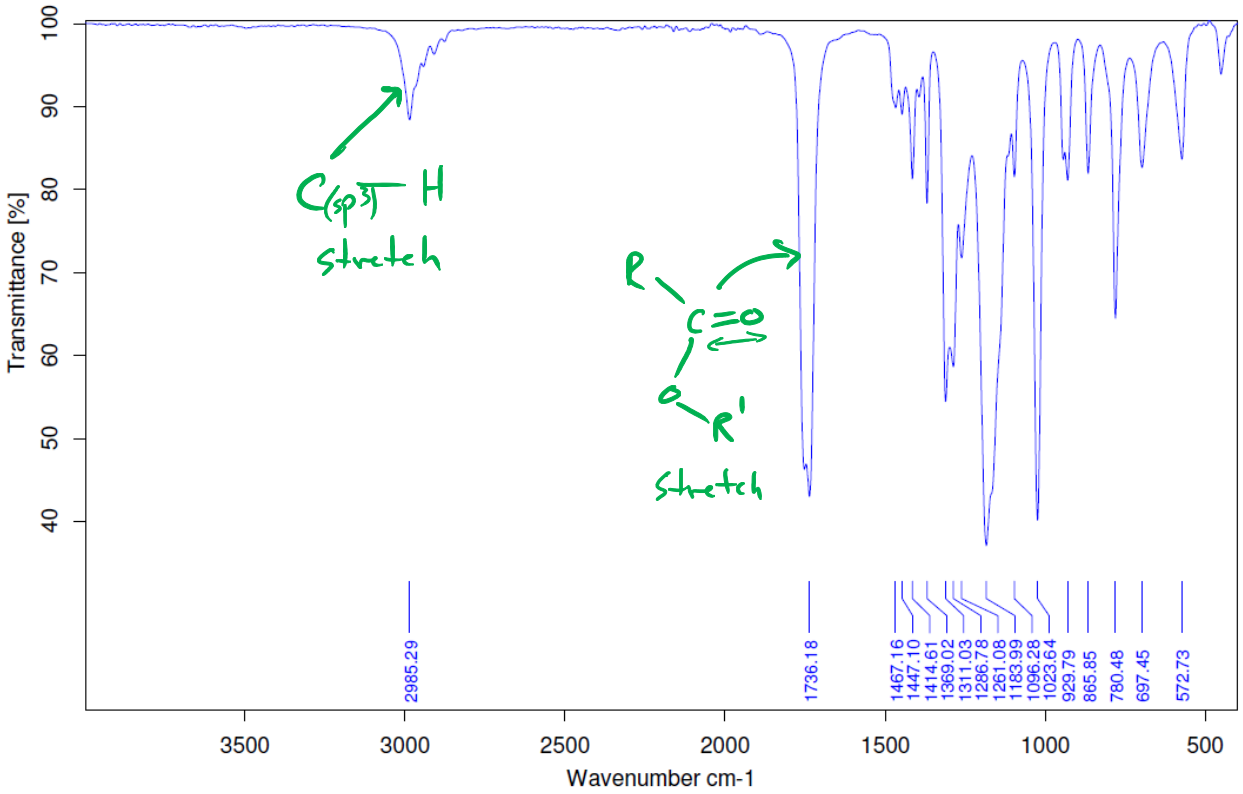


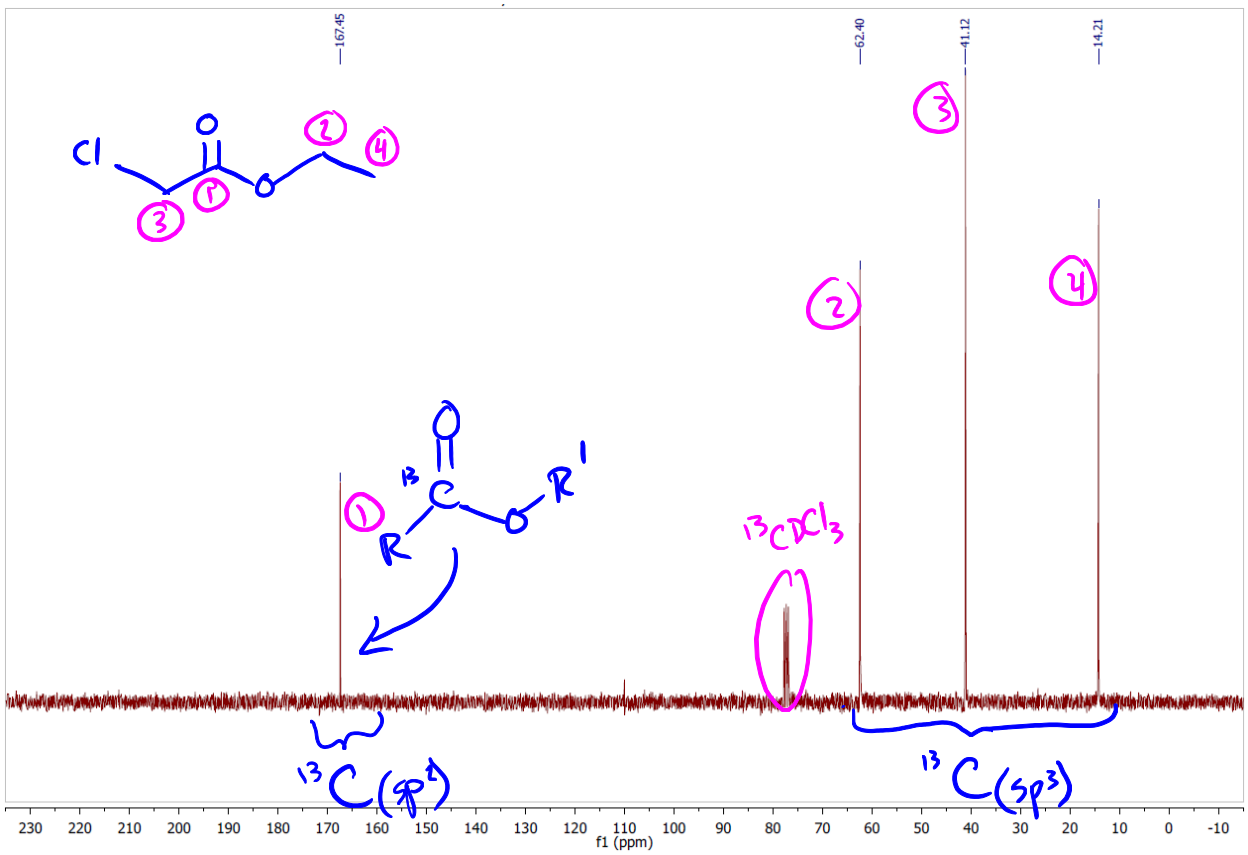

173.19
77.66
77.24
76.82
55.84
26.27
22.04
f1 (ppm)

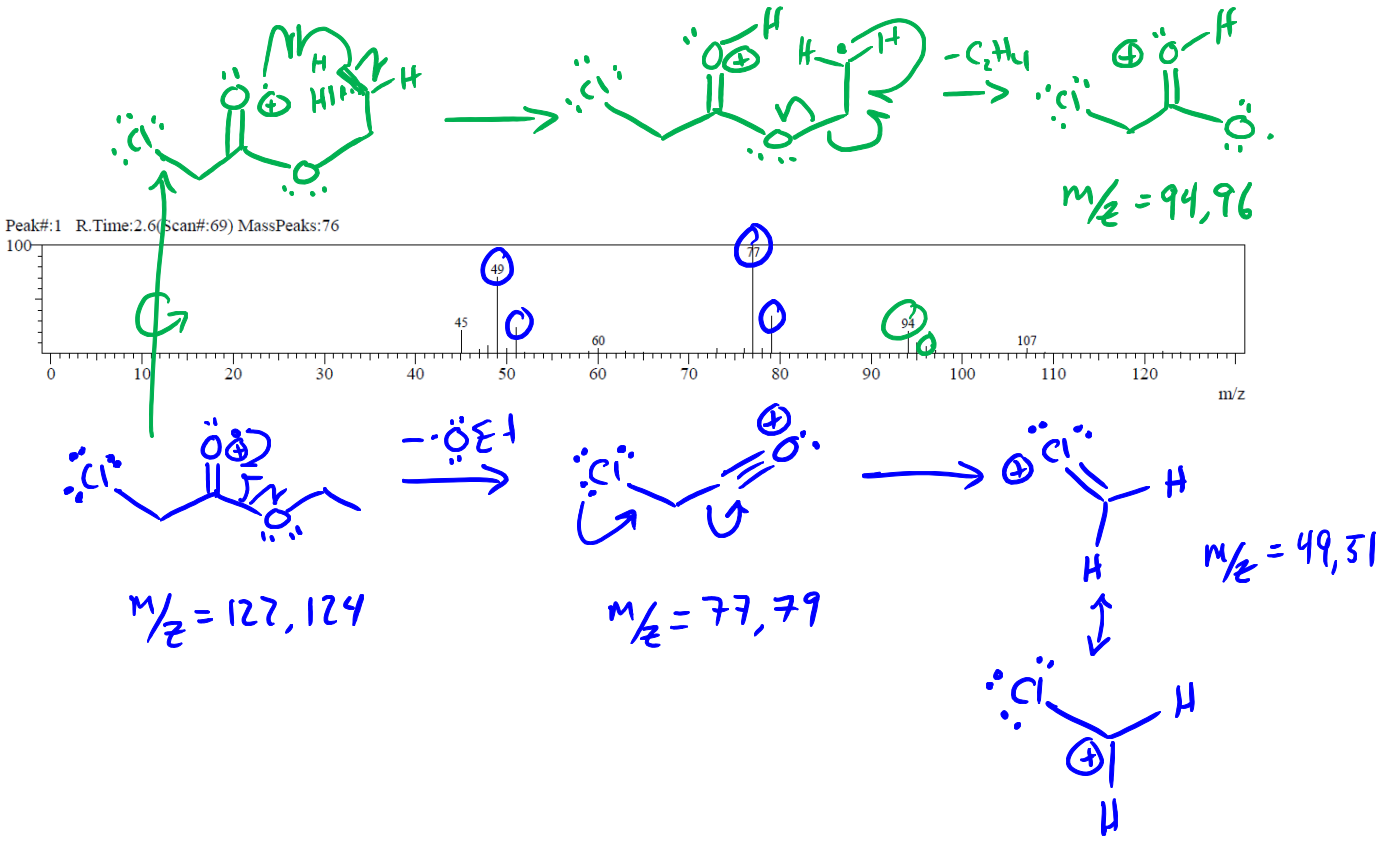

MS-NW-3537
Relative Intensity
m/z
m/z = 120, 122
m/z = 85
m/z = 57
m/z = 42
m/z = 41
very low intensity

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






167.45
62.40
41.12
14.21
f1 (ppm)
$^{13}CDCl_3$
$^{13}C(sp^2)$
$^{13}C(sp^3)$


$-C_2H_4$
m/z = 94,96
Peak#:1 R.Time:2.6(Scan#:69) MassPeaks:76
m/z
m/z = 122, 124
$-\dot{O}Et$
m/z = 77, 79
m/z = 49, 51