CHEM 344 Spring 2015 Spectroscopy Exam – A (50 pts)

Name:

TA Name:

Directions for drawing molecules and electron-pushing mechanisms:

Clearly show all bonds, arrows, formal charges, and lone pairs.

Directions for analyzing spectra:

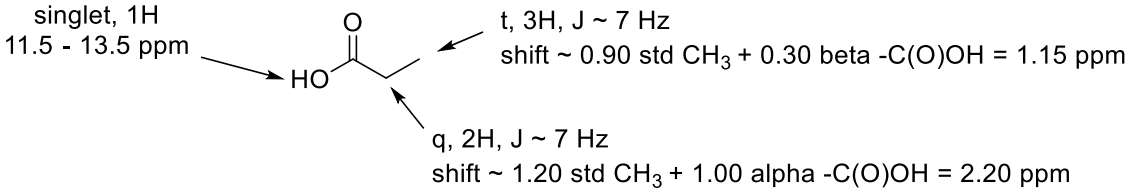
- Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. Assign each **^{1}H-NMR** signal and write your assignments directly onto the spectrum. Use the empirical chemical shift parameters (Curphy-Morrison parameters) or chemical shift tables found at the end of the exam to assist your ^{1}H-NMR analysis and signal assignments.

- Label each **^{13}C-NMR** signal as either alkyl, vinyl, alkynyl, aryl, nitrile, imine, or carbonyl (you do not need to assign individual carbon atoms to each signal).

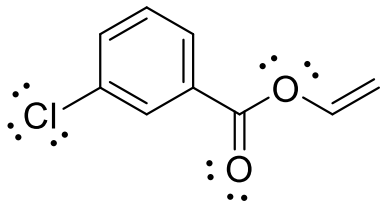
- Assign each key **IR** absorption band >1500 cm^{-1} to a specific functional group.

- Draw fragments for all labeled peaks in the **EI-MS** directly onto the spectrum (you do not need to show the fragmentation mechanism unless directed to do so).

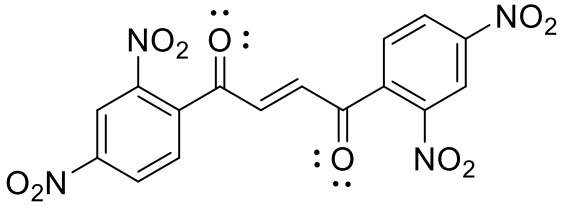
1) Predict the multiplicity, integration value, and chemical shift using empirical (Curphy-Morrison) parameters of all signals in the ^{1}H-NMR spectrum of each molecule shown below. When estimating the chemical shift, show all work including which substituent (R) and corresponding parameter is selected. No estimations are required for aldehyde, phenol, or carboxylic acid ^{1}H-atoms. Where coupling is present provide an estimate of the coupling constant (Hz). **(6 pts total)** See the example below.



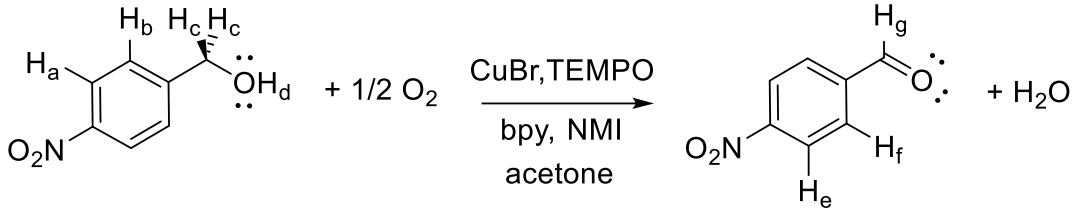
a)



b)



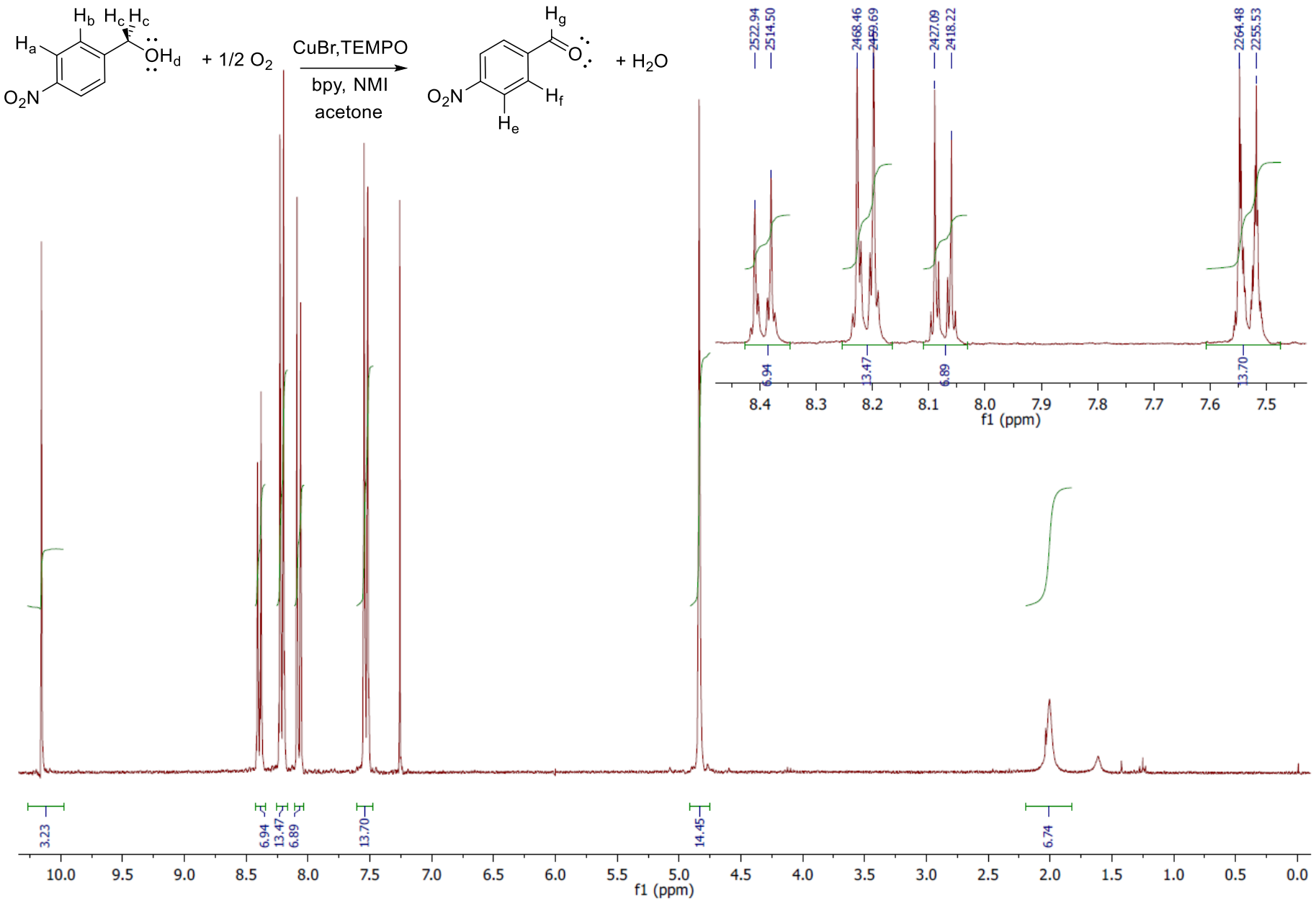
2) Later in CHEM 344 you will perform the aerobic oxidation of a benzyl alcohol to the corresponding aldehyde. The reaction is catalyzed by a mixture of CuBr, TEMPO (a stable free radical), 2,2'-bipyridine (bpy), and NMI (a nitrogen base). The oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde under these conditions is shown below. **(6 pts. total)**



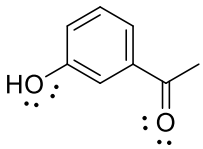
A sample of the reaction mixture was obtained after 30 min reaction time, purified, and submitted for ^{1}H-NMR analysis. The ^{1}H-NMR spectrum of the reaction mixture is provided on the next page.

i) Assign all ^{1}H-NMR signals due to the product using the H_a, H_b *etc*. labeling system given. Write all assignments on the ^{1}H-NMR spectrum. **(2 pts)**

ii) Use the ^{1}H-NMR spectrum to calculate the ratio of products to starting materials in this reaction mixture. Express the ratio in the form x:y where y = 1. Show all work in the space below. **(4 pts)**


Hb Hc Hc
Ha
OHd
O2N
+ 1/2 O2
CuBr,TEMPO
bpy, NMI
acetone
Hg
O
O2N
Hf
He
+ H2O
2522.94
2514.50
2468.46
2459.69
2427.09
2418.22
2264.48
2255.53
6.94
13.47
6.89
13.70
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
f1 (ppm)
3.23
6.94
13.47
6.89
13.70
14.45
6.74
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3) The ^{1}H-NMR spectrum of 3'-hydroxyacetophenone is on the subsequent page. An expansion of the aromatic region is included for clarity. **(13 pts total)**



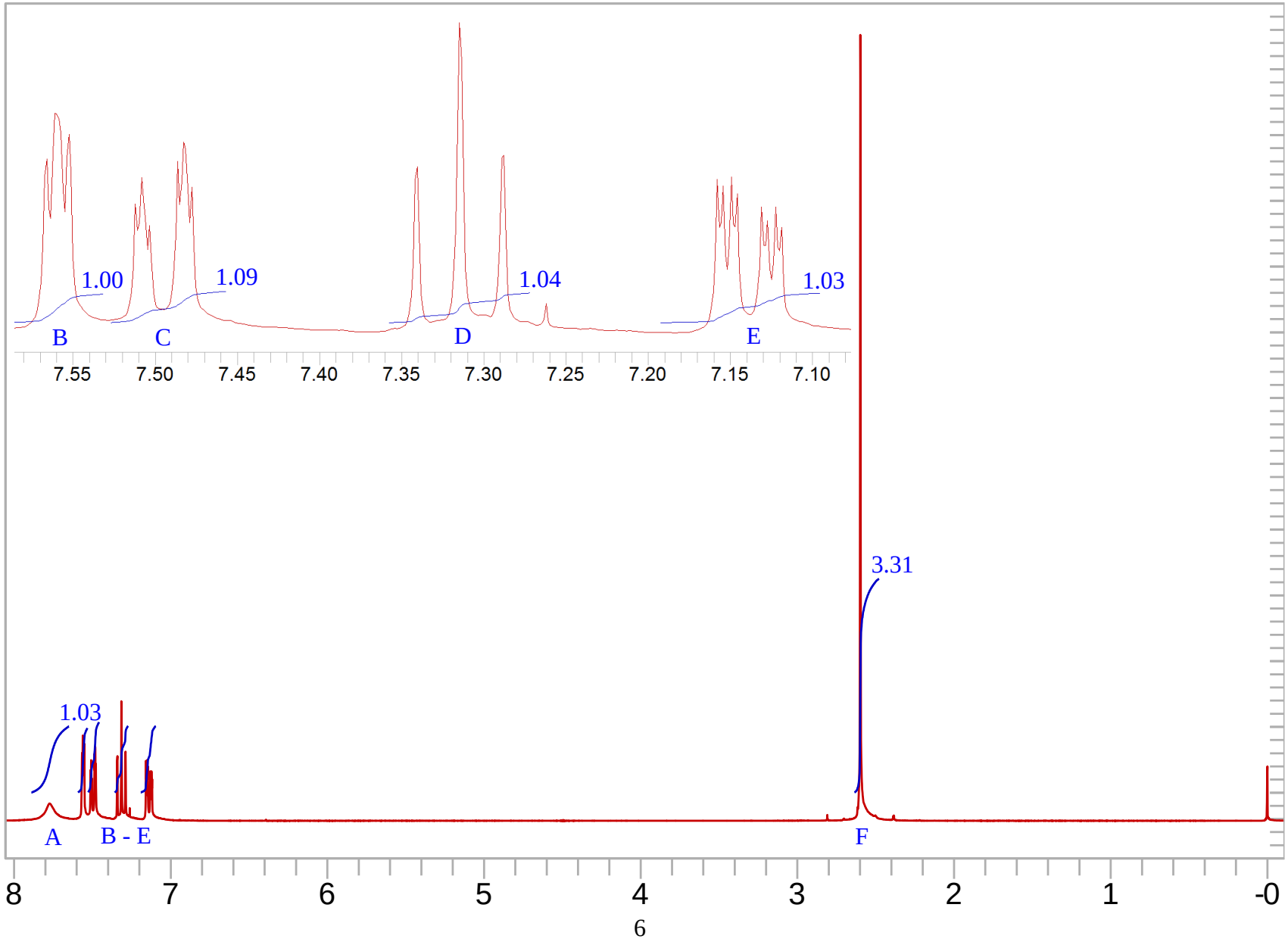
a) Assign the ^{1}H-nuclei of 3'-hydroxyacetophenone to the appropriate signals in the ^{1}H-NMR spectrum. **Draw your assignments directly onto the ^{1}H-NMR spectrum using the H_a, H_b etc. convention shown in the lectures and practice problem sets. (3 pts)**

b) ***In the space below***, draw all important resonance structures of 3'-hydroxyacetophenone which may help guide your assignments of signals B-E. **(6 pts)**

c) Explain why the resonance structures alone are insufficient in this case to predict the chemical shifts of the ^{1}H-nuclei in this molecule. Provide a description of how you might more effectively predict these chemical shifts. **(4 pts)**

300 MHz ^{1}H NMR

In CDCl3

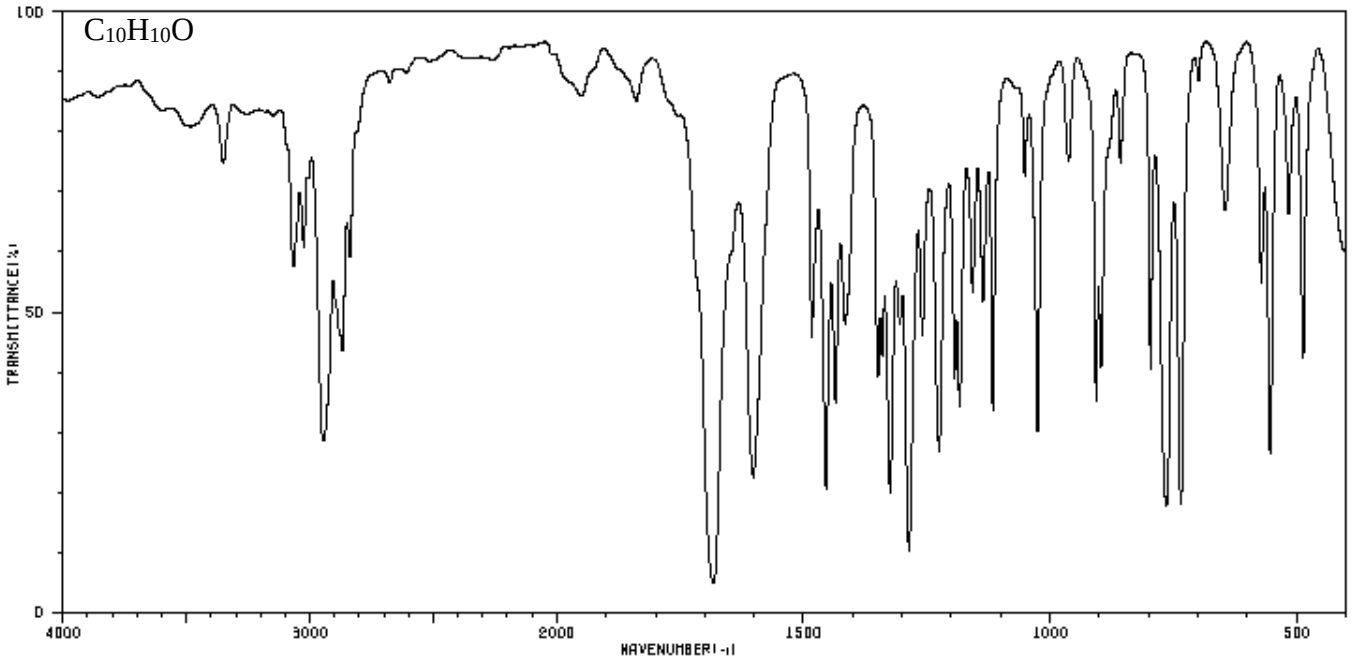


4) The spectra below were obtained from an organic molecule ($C_{10}H_{10}O$). Determine the structure of the molecule using the spectra provided and by answering the questions below. **(25 pts total)**

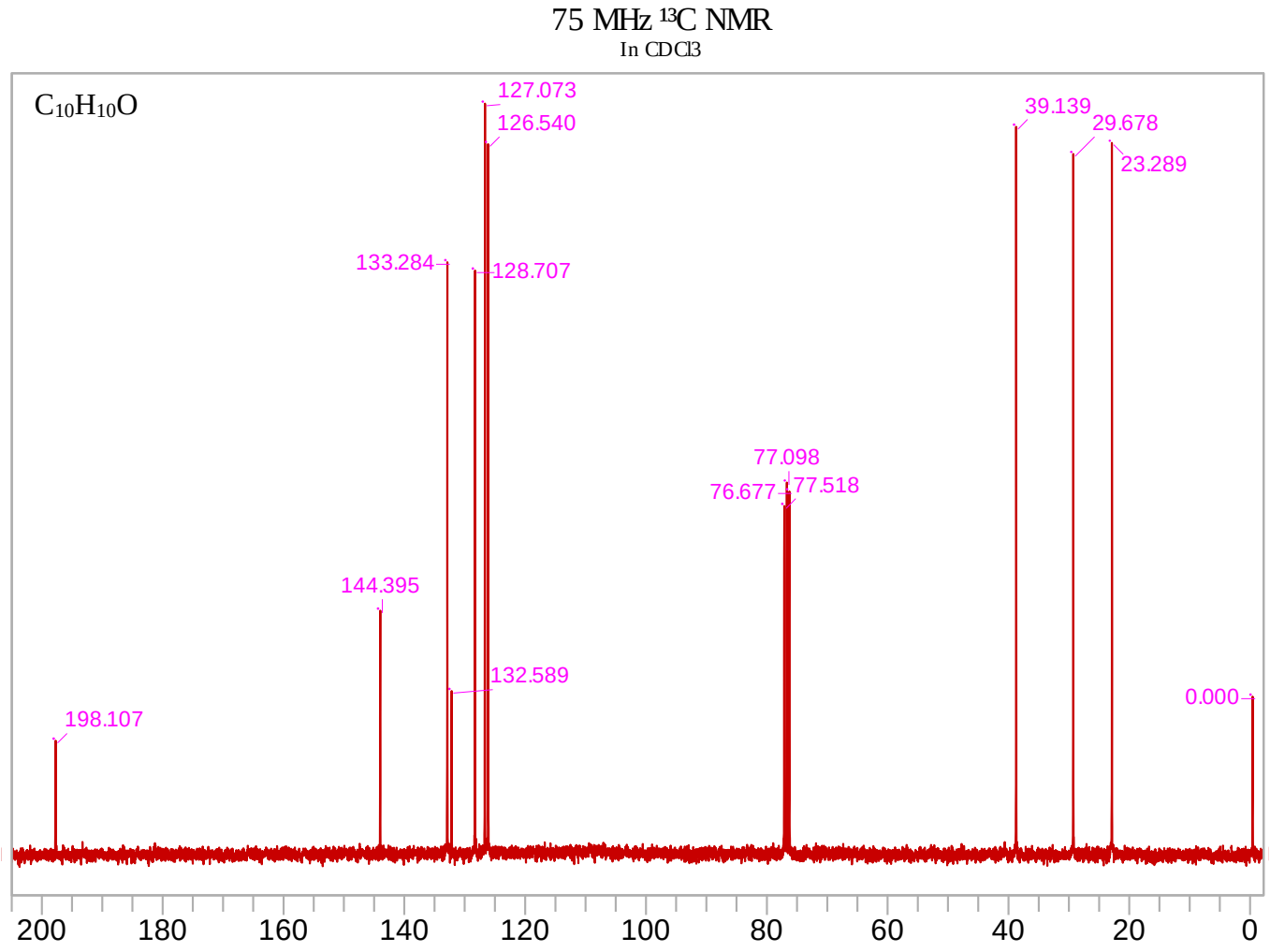
a) Calculate the number of double bond equivalencies, unsaturation number, or the index of hydrogen deficiency for this molecule using the equation provided. **(2 pt)**

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

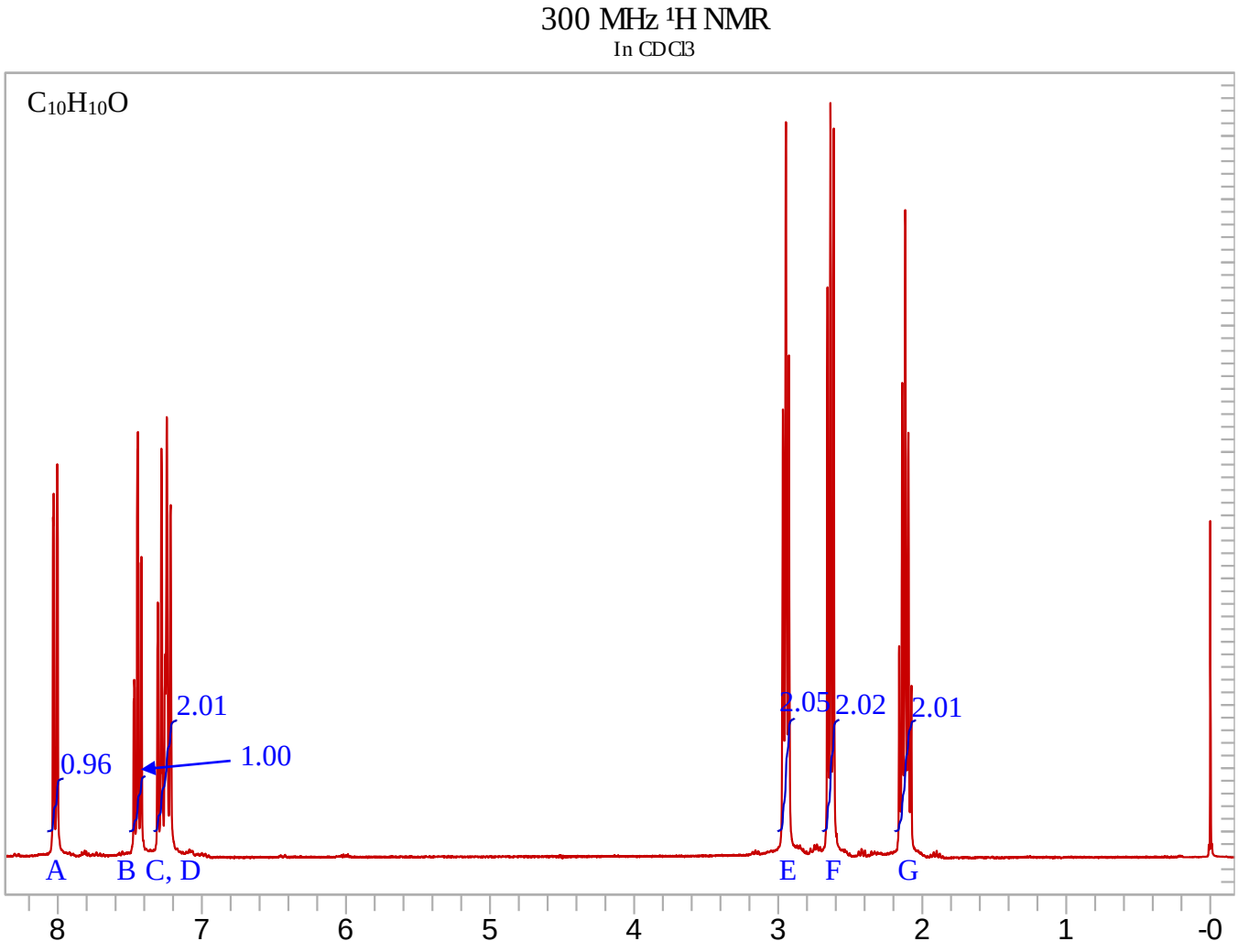
b) Based upon the chemical formula, index of dehydration, and the IR spectrum below, suggest which organic functional groups are possible/likely in this molecule. **(3 pts)**

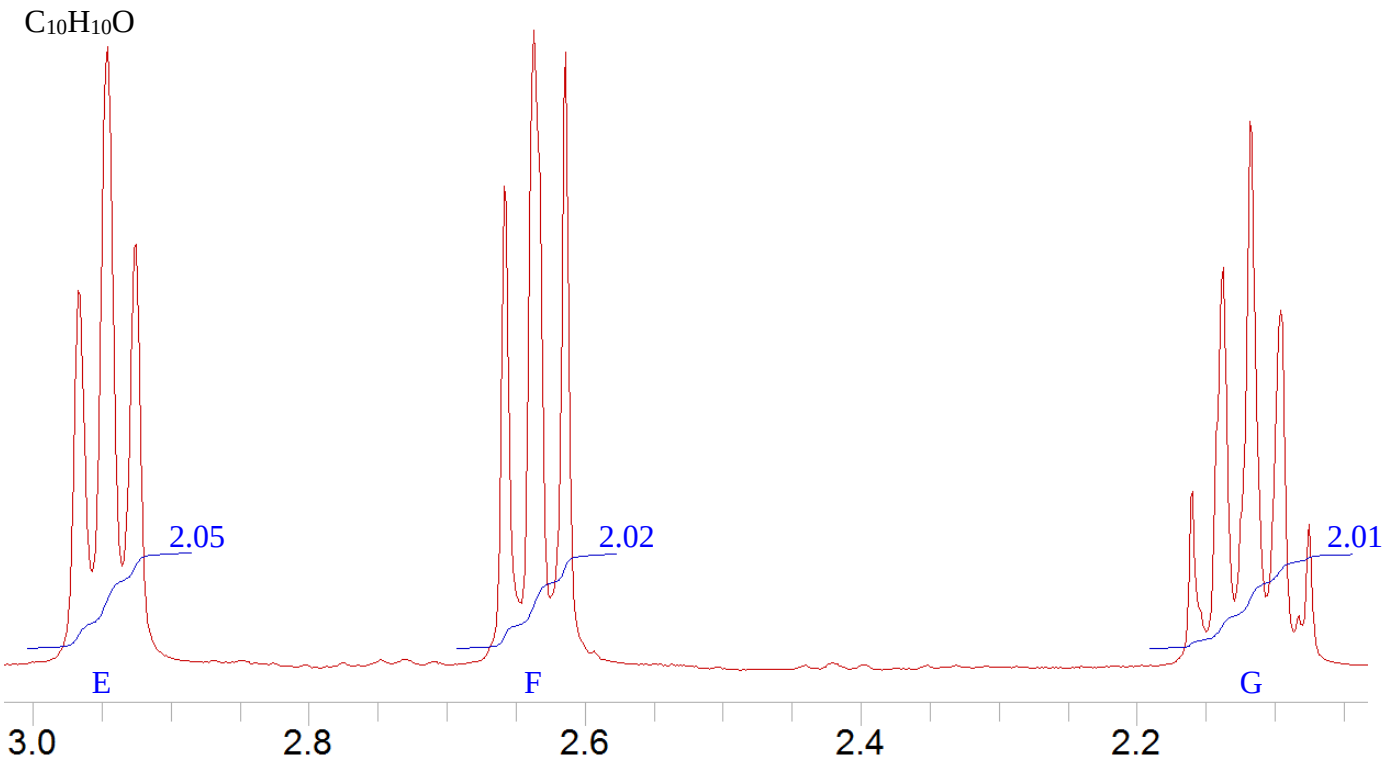


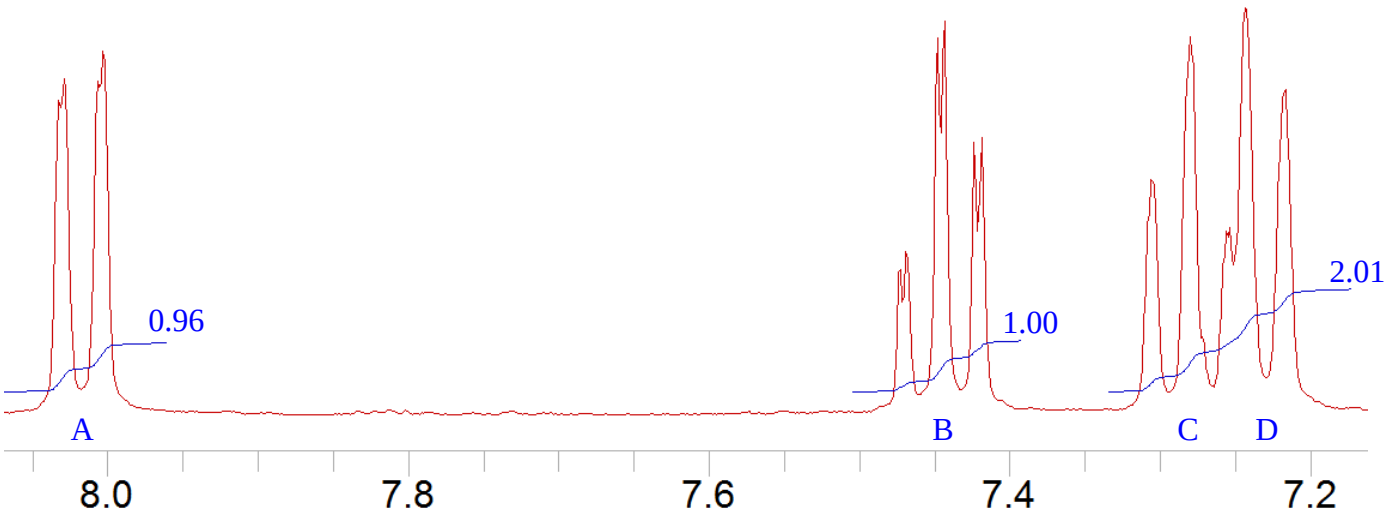
c) Use the ^{13}C-NMR spectrum below, collected in $CDCl_3$, to identify each ^{13}C-atom as either alkyl, vinyl, alkynyl, aryl, nitrile, imine, or carbonyl. **(3 pts)**



d) Use the information from parts a – c and the ^{1}H-NMR spectrum (collected in $CDCl_3$) below, to determine the structure of the molecule and assign each ^{1}H-atom. Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. Draw your answer in the box on this page. Spectra of key regions are provided on the subsequent page. **(10 pts)**

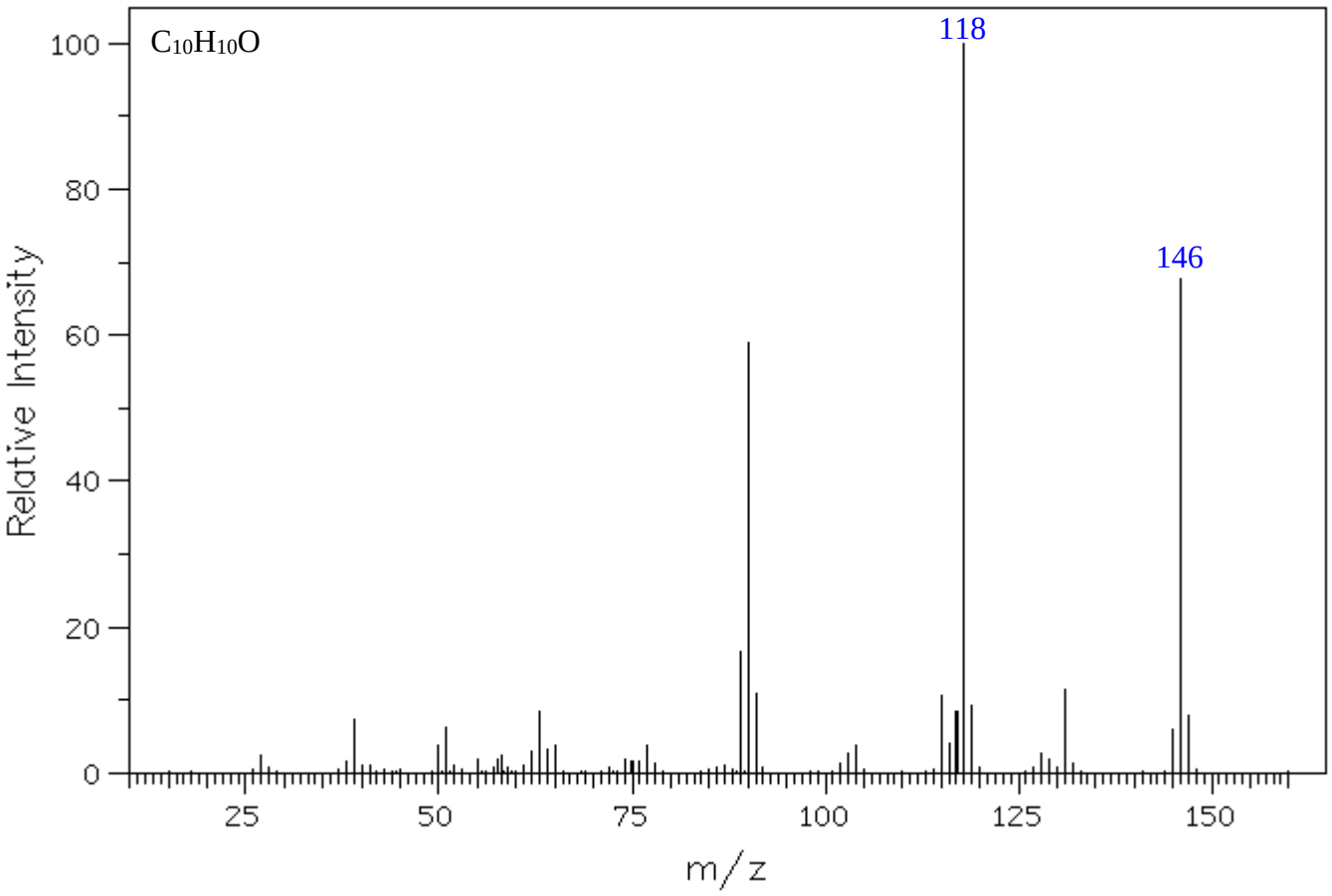



C10H10O
2.05
2.02
2.01
E
F
G
3.0
2.8
2.6
2.4
2.2


0.96
1.00
2.01
A
B
C
D
8.0
7.8
7.6
7.4
7.2

e) Confirm your structure determination by use of the EI-Mass spectrum provided below. **(7 points total)**

i. Provide three distinct ions (not resonance structures) responsible for the signal with *m/z* = 146 and two separate e^--pushing fragmentation mechanisms that could produce two different ions responsible for the signal with *m/z* = 118. Show all lone pairs and formal charges. **(7 points)**



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1) _____ **/6**

2) _____ **/6**

3) _____ **/13**

4) _____ **/25**

Total = _____ **/50**