CHEM 344 Fall 2014 Spectroscopy Quiz – A (50 pts)

Name:

Key – A

TA Name:

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. Justify your assignments by use of the empirical chemical shift parameters (Curphy-Morrison parameters) or chemical shift tables found at the end of the exam.

- Identify 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.

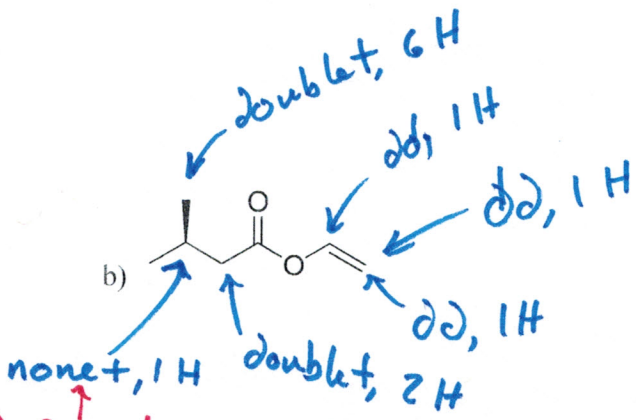
- Draw fragments for all labeled peaks in the **EI-MS** directly onto the spectrum (you do not need to show the fragmentation mechanism unless directed to do so).

1) Predict the multiplicity and integration value of all signals in the ^{1}H-NMR spectrum of each molecule shown below. **(8 pts total)** See the example below.

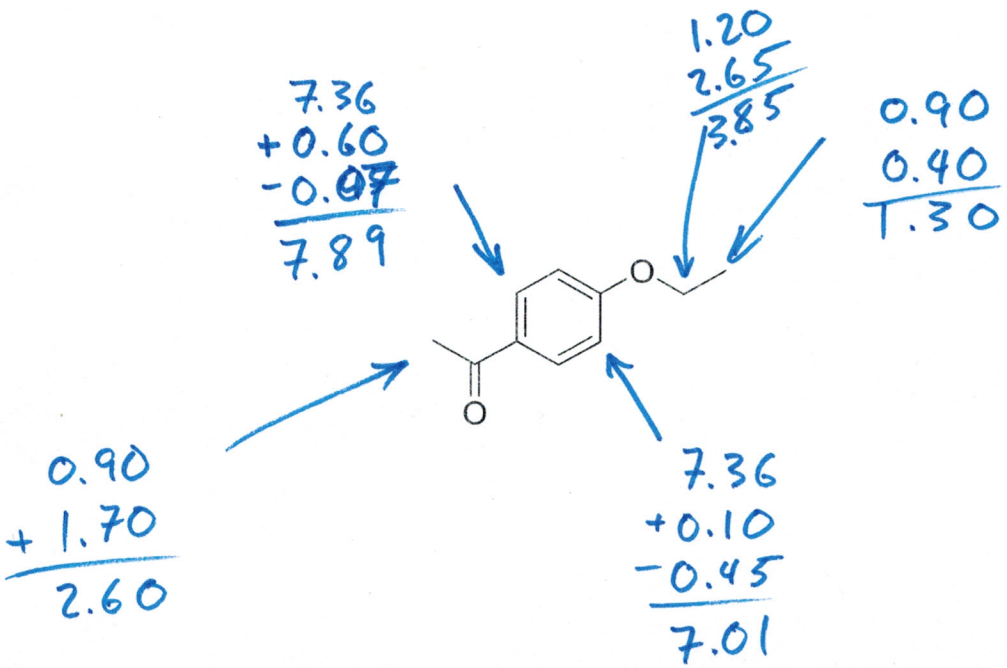
4 pts each
4= all correct
3= any single error
2= 2 + errors
1= at least 1 correct

a)

b)

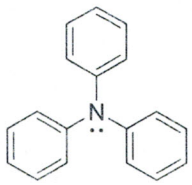


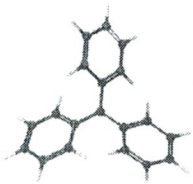
2) For the molecule below, use the empirical (Curphy-Morrison) parameters available at the end of the exam to predict the chemical shift of each unique ^{1}H-nucleus. **(4 pts total)**



4= all correct
3= any errors
2= 2+ errors
1= at least 1 correct

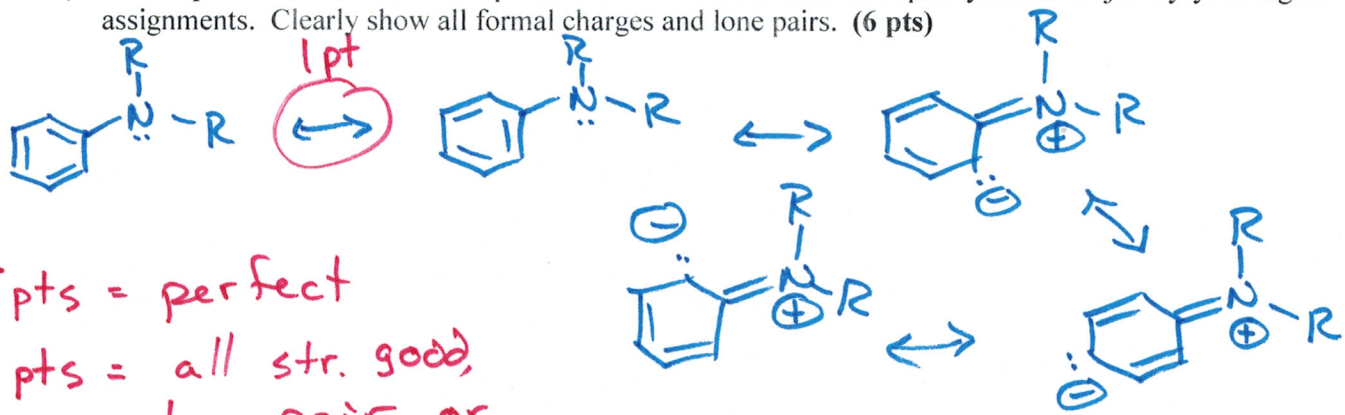
3) The ^{1}H-NMR spectrum of triphenylamine is on the subsequent page. An expansion of the aromatic region is included for clarity. **(13 pts total)**





a) Assign the ^{1}H-nuclei of triphenylamine 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 triphenylamine to justify your signal assignments. Clearly show all formal charges and lone pairs. **(6 pts)**



5 pts = perfect

4 pts = all str. good, alone pair or charge err.

4 pts = missing structure (incorrect)

3 pts = missing 2 structures (incorrect)

2 pts

1 pt

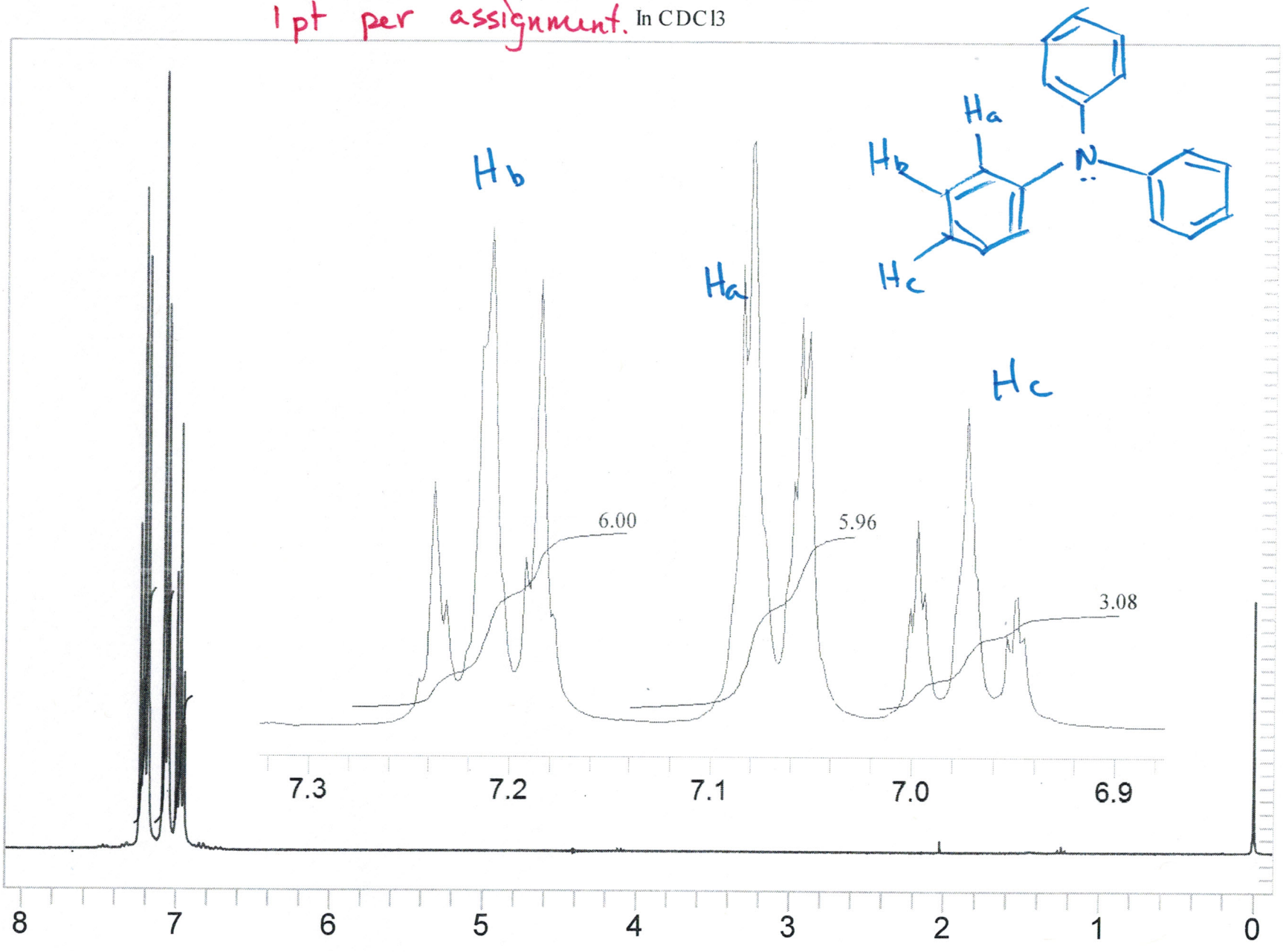
c) Assuming that resonance structures are sufficient to predict the chemical shifts of the H-nuclei in this molecule, provide a brief written explanation of your assignments. **(4 pts)**

The resonance structures indicate an increase in e⁻ density at the ortho/para C-atoms. (2 pts)

Increased electron density at those C-atoms causes extra shielding at those attached H-atoms. (2 pts)

300 MHz ^{1}H NMR

1 pt per assignment. In CDCl3



4) The spectra below were obtained from a brominated organic molecule ($C_9H_9BrO_2$). 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)**

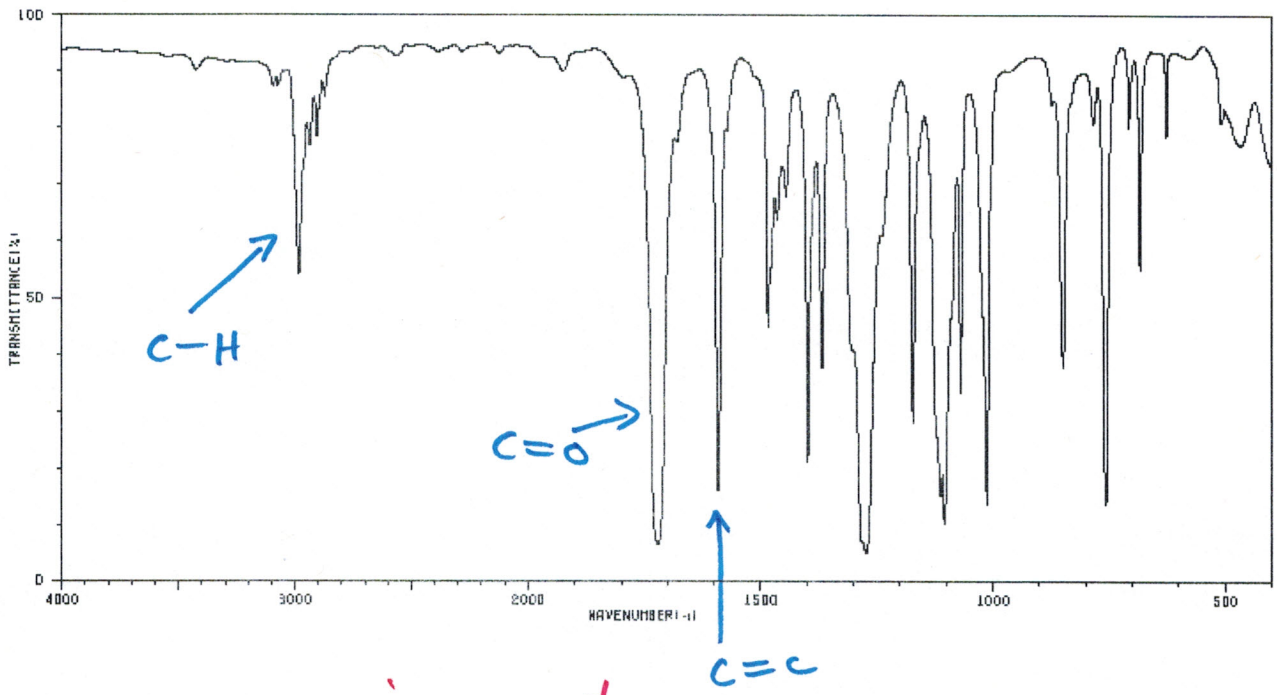
2pts. all or nothing

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

C_9H_{20}

IHD = 5

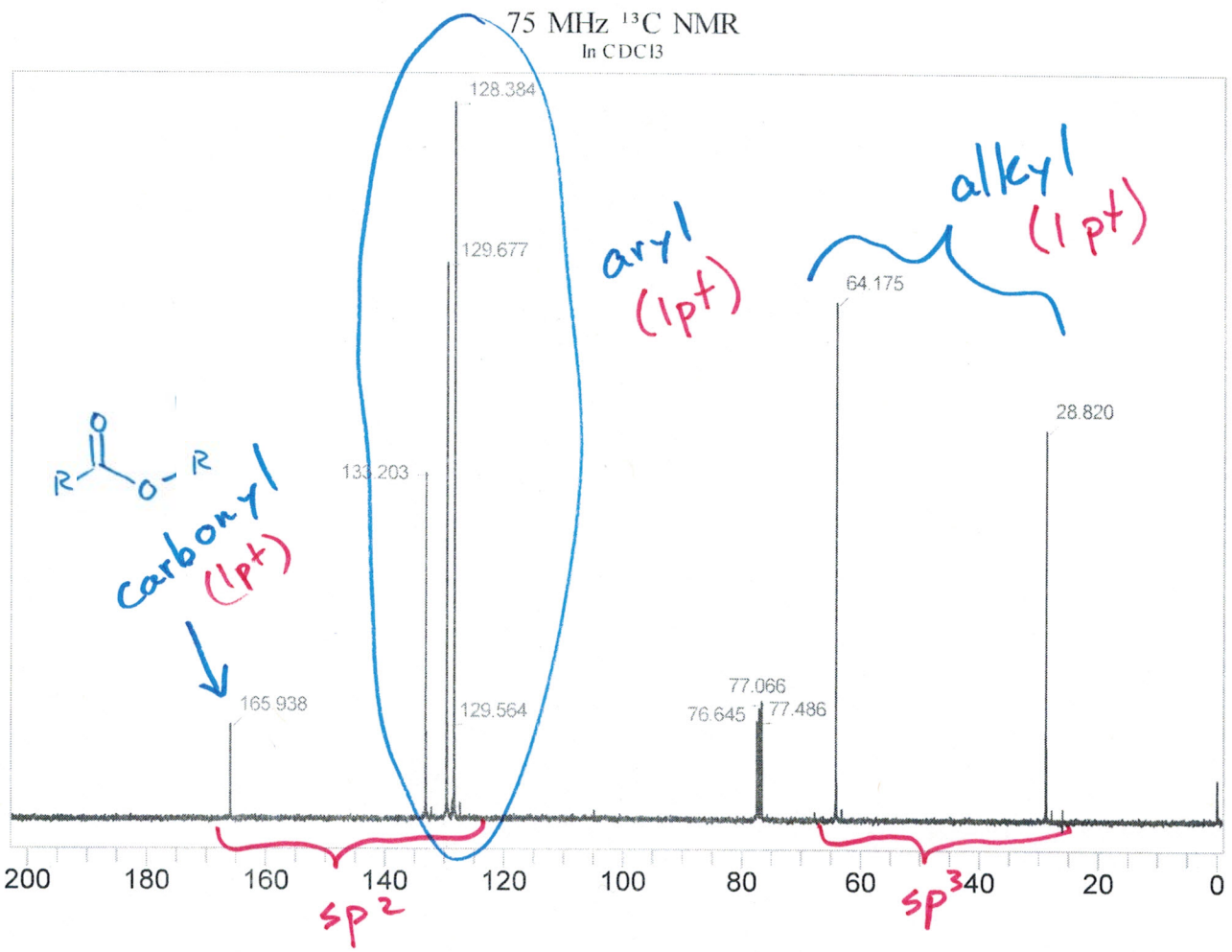
b) Based upon the chemical formula, index of dehydration, and the IR spectrum below, what organic functional groups are possible/likely in this molecule? **(3 pts)**



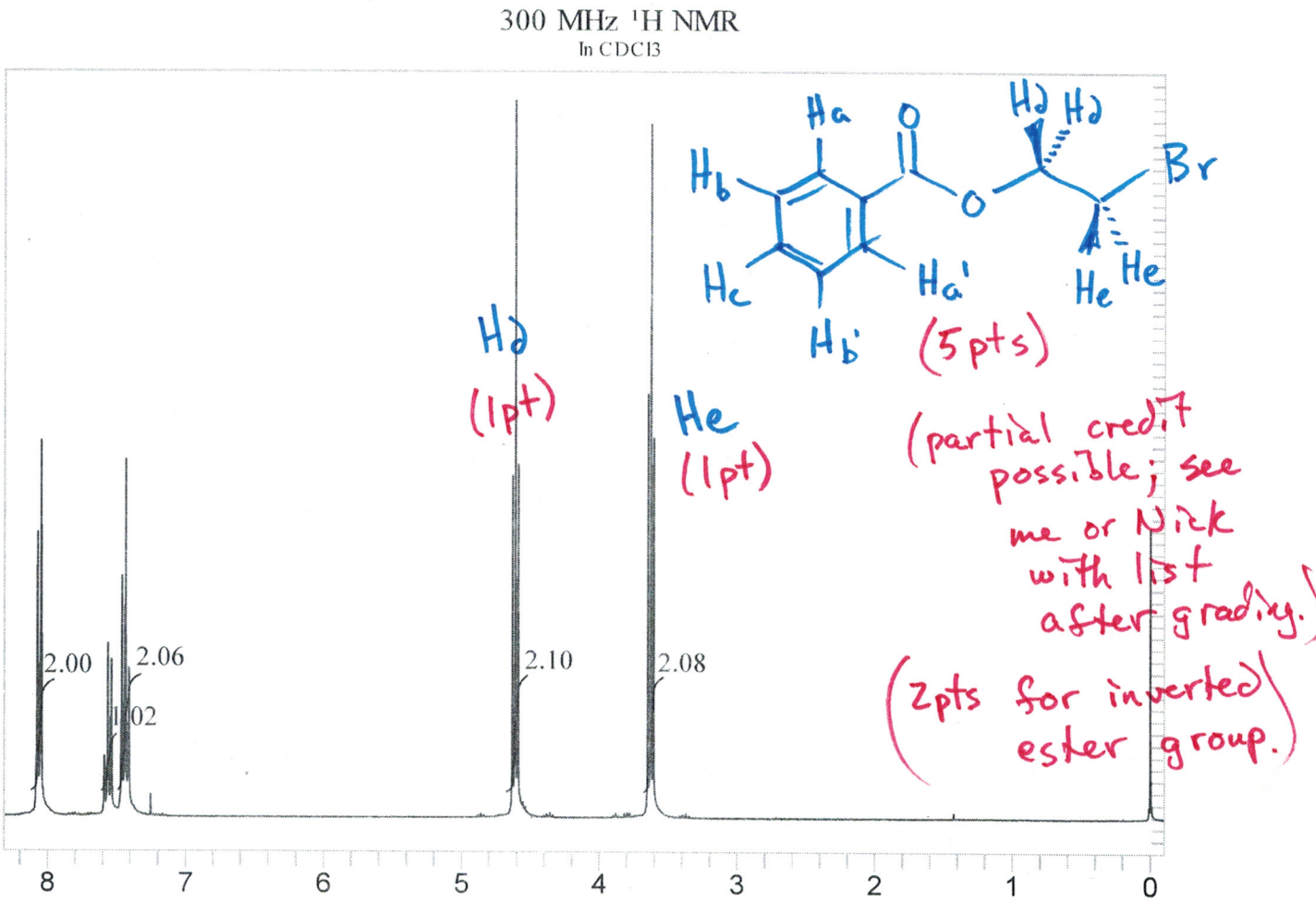
1pt per assignment

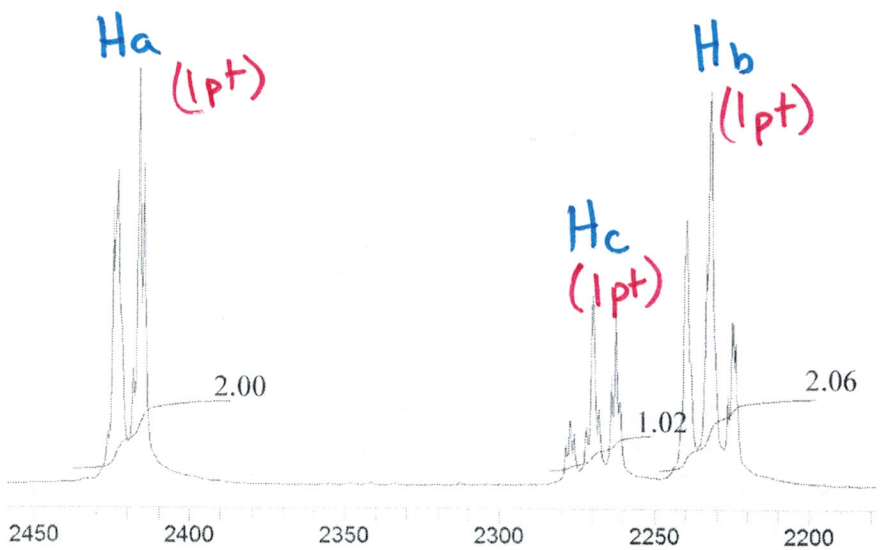
- words are okay
- more specific okay

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)**



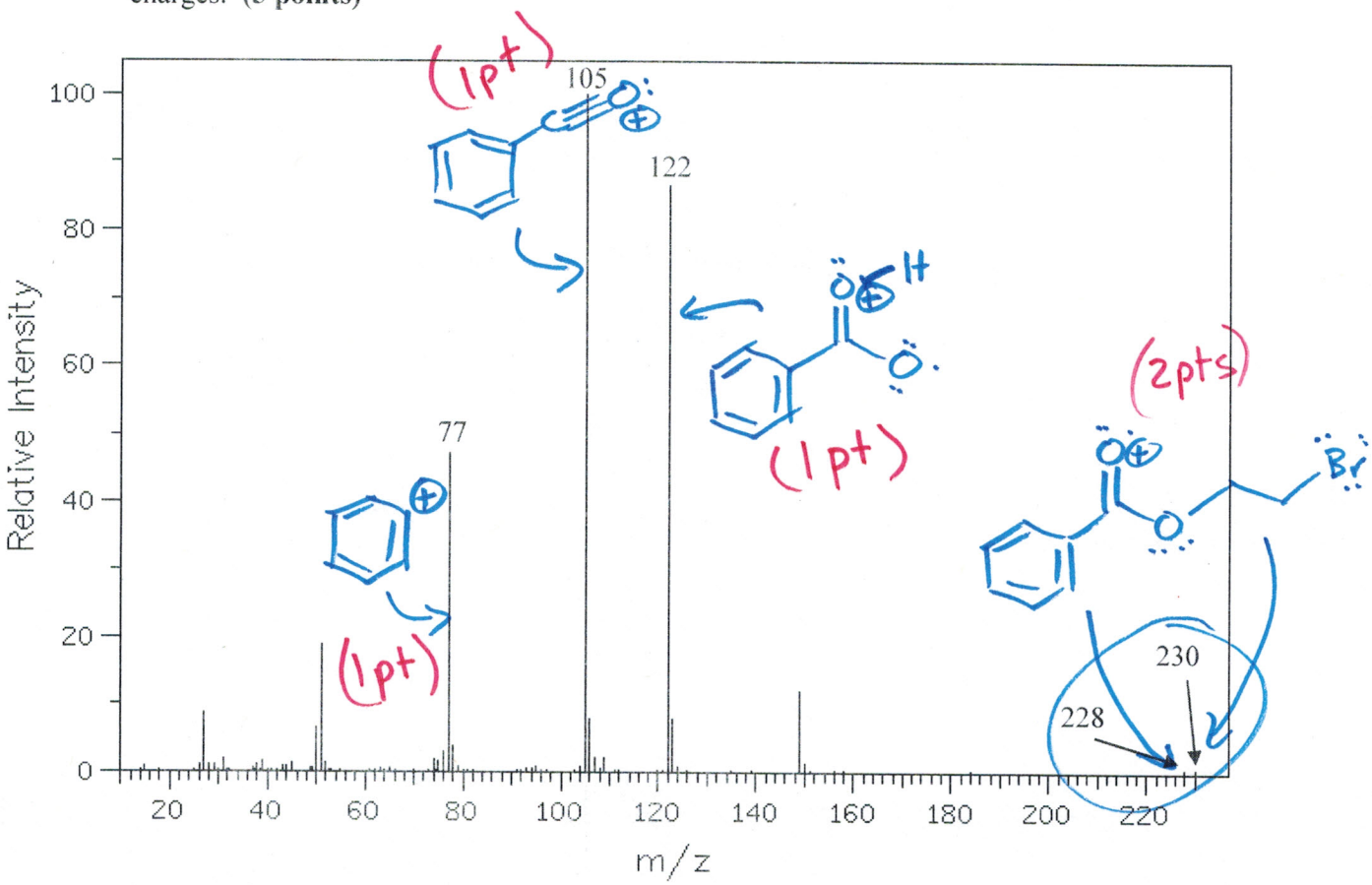
d) Use the information from parts a – c and the ^{1}H-NMR spectrum (collected in $CDCl_3$) below, to determine the structure of the molecule and assign each ^{1}H-atom. Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. **(10 pts)**





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

i. Provide the most likely ions responsible for the signals at *m/z* = 230, 228, 122, 105, and 77. Draw the fragments on the spectrum and clearly label them. Show all lone pairs and formal charges. **(5 points)**



ii. Which of the signals in the EI-Mass spectrum contain the bromine atom? Circle one or more signals on the EI-Mass spectrum that contain bromine. Explain briefly how you can identify presence of bromine atoms in the species responsible for these signals. **(2 points)**

They are a 1:1 doublet of M and M+2 (1pt) corresponding to a nearly equal abundance of ^{81}Br and ^{79}Br (1pt)