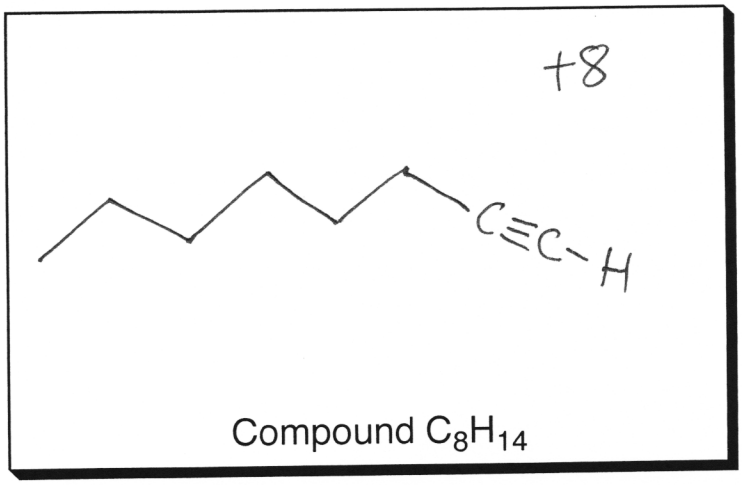
Answer Key
Name

1. (20 points) Assign all IR-absorption bands you can recognize as meaningful and informative for an unknown compound with molecular formula (C_8H_{14}) and provide its structure:

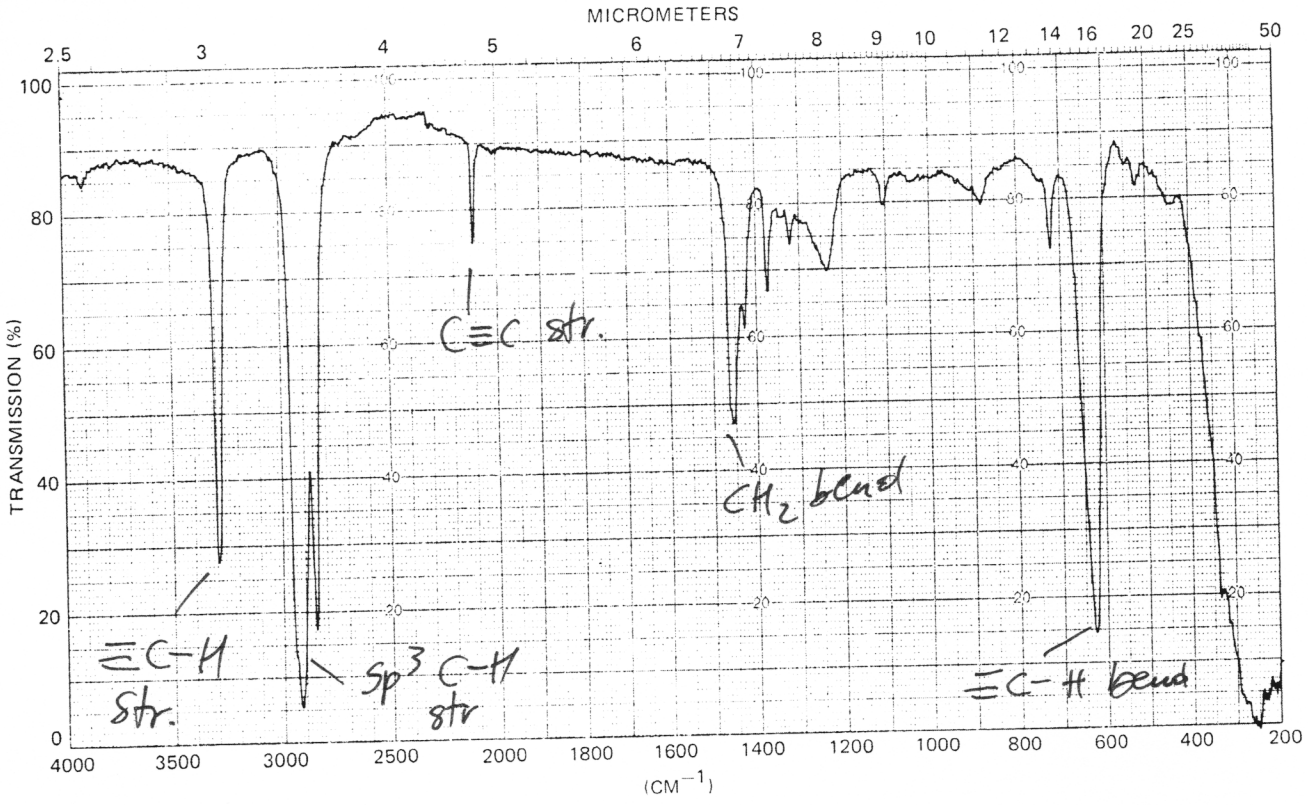
x 12

3300 ($\equiv$C–H str.)
2900 (sp^3 C–H str.)
2100 (C$\equiv$C str.)
1450 (CH_2 bend)
625 ($\equiv$C–H bend



(use as many lines as necessary)

Infrared spectrum (neat)



Answer Key
Name

2. (20 points) Estimate the **dihedral angles** (e.g. 130°) and corresponding **coupling constants** for the following compound using the Karplus relationship shown below or other sources if necessary. Be sure to consider all factors affecting these parameters:

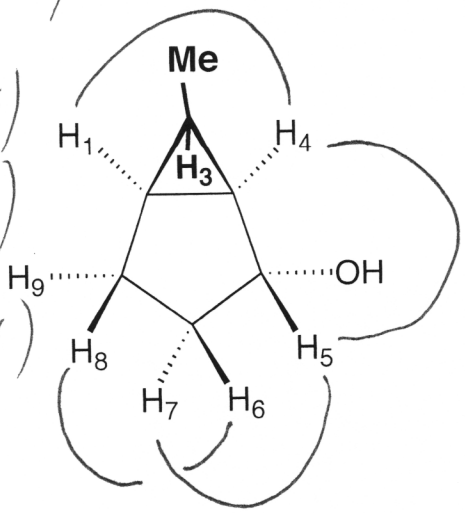
(+4)

a) Dihedral angle (H_1-C-C-H_4): 0° $J_{1,4}$: 8-10 Hz

b) Dihedral angle (H_4-C-C-H_5): 120° $J_{4,5}$: 2-4 Hz (+4)

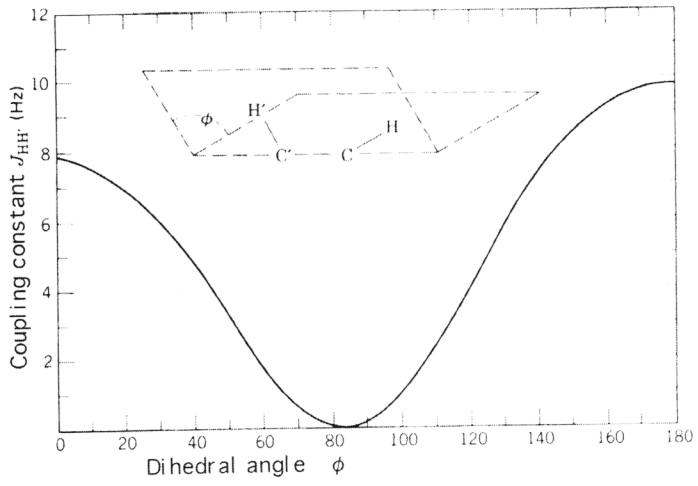
c) Dihedral angle (H_5-C-C-H_7): 120° $J_{5,7}$: 2-4 Hz (+4)

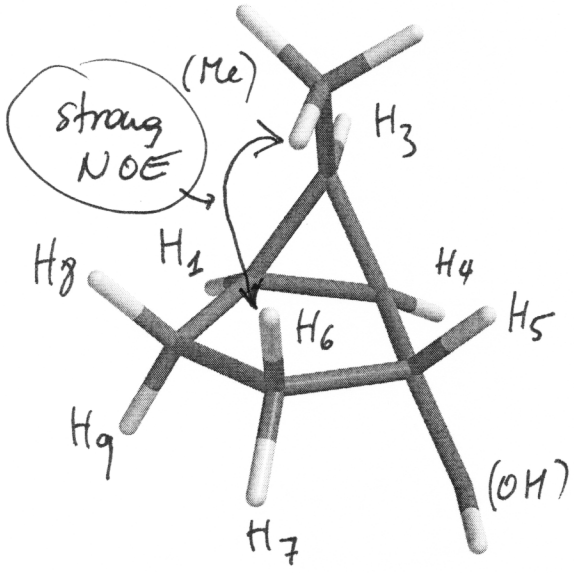
d) Dihedral angle (H_6-C-C-H_8): 10° $J_{6,8}$: 8-10 Hz (+4)



e) Other than for *geminal* and *vicinal* protons, draw a curved double-headed arrow for **the strongest** NOE enhancement you expect to observe with this molecule

(+4)

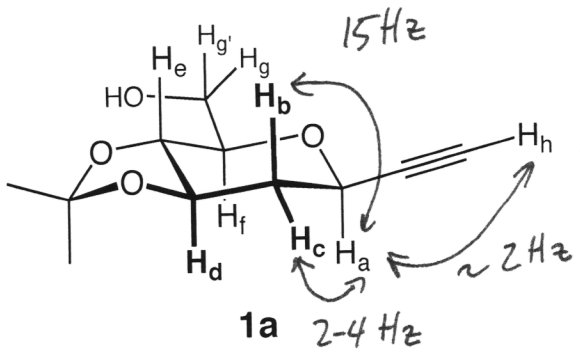




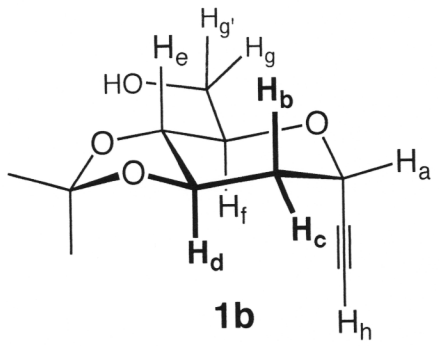
(calculated structure)

Answer Key
Name

3. (50 points). a) (20 points) Describe *two* distinct NMR techniques that will help differentiate and assign the diastereomers **1a** and **1b**:



1a



1b

Technique 1:

look at coupling constants:
- Ha of cpd 1a will have a large J (≥ 15Hz) between H_a and H_b, but not in 1b (two gauche vicinal protons)

+10

Technique 2:

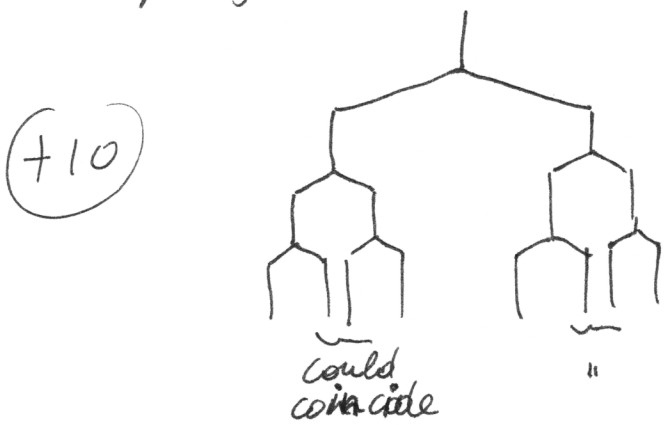
Do decoupling experiment (NOE interactions)
- For isomer 1b, H_h should have NOE enhancement with H_c, H_d, and H_f present (but no NOE at all in 1a)

+10

Answer Key
Name

b) (20 points) Draw a tree coupling diagram (split forks) and the corresponding ^{1}H NMR signal for proton H_a of diastereomer **1a** in question 3a above.

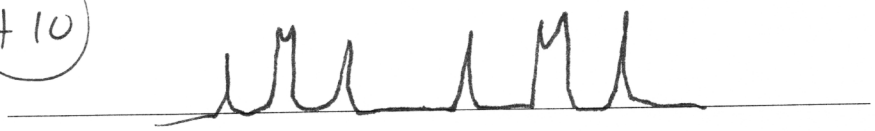
Tree diagram: Three coupling constants: ~15, ~4, ~2 Hz



(+10)

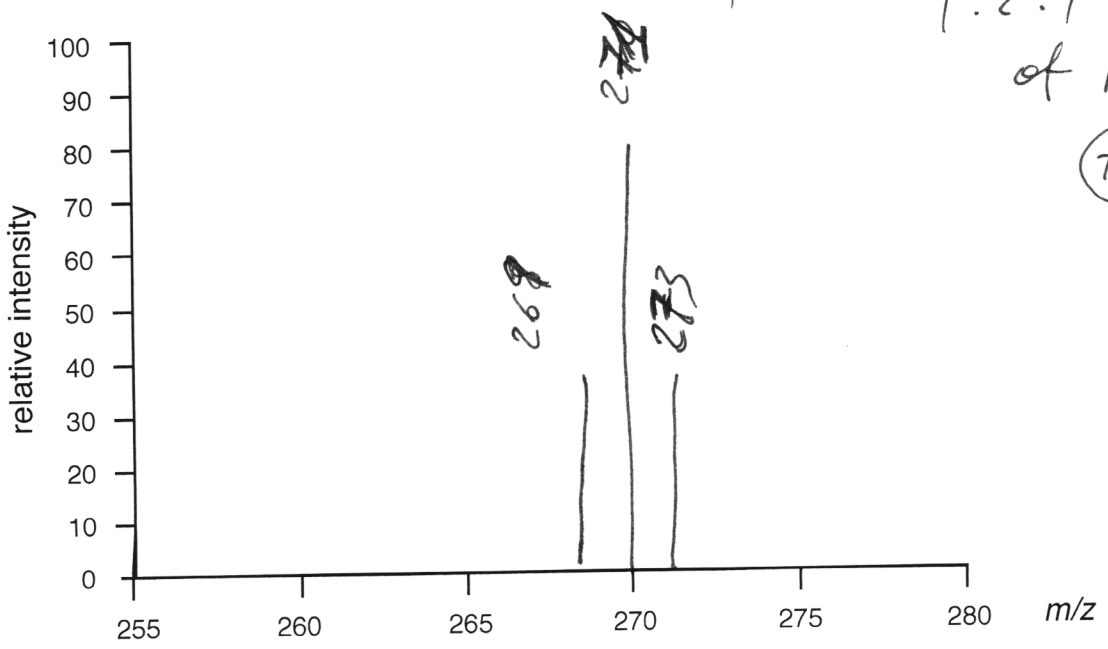
(+10)

^{1}H NMR signal:



c) (10 points) Mass spectrometry: Sketch the isotopic pattern for the parent ion (M^+) of a compound with formula $C_5H_5Br_2NO_2$:

~~isotopic~~ masses (+5)



1:2:1 ratio of peaks

(+5)

Answer Key

Name

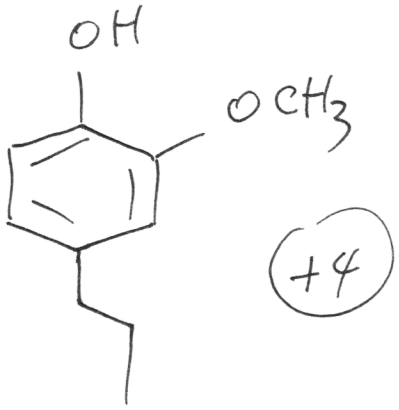
4. (40 points) A compound has the molecular formula $C_{10}H_{14}O_2$. Deduce its structure from the IR, ^1H NMR, ^{13}C NMR, 2D-COSY and 2D HMQC spectra shown below. You must provide peak assignments in all spectra to get maximum credit.

$\frac{(10\times2)+2-14}{2}=$

Draw the structure in the space below:

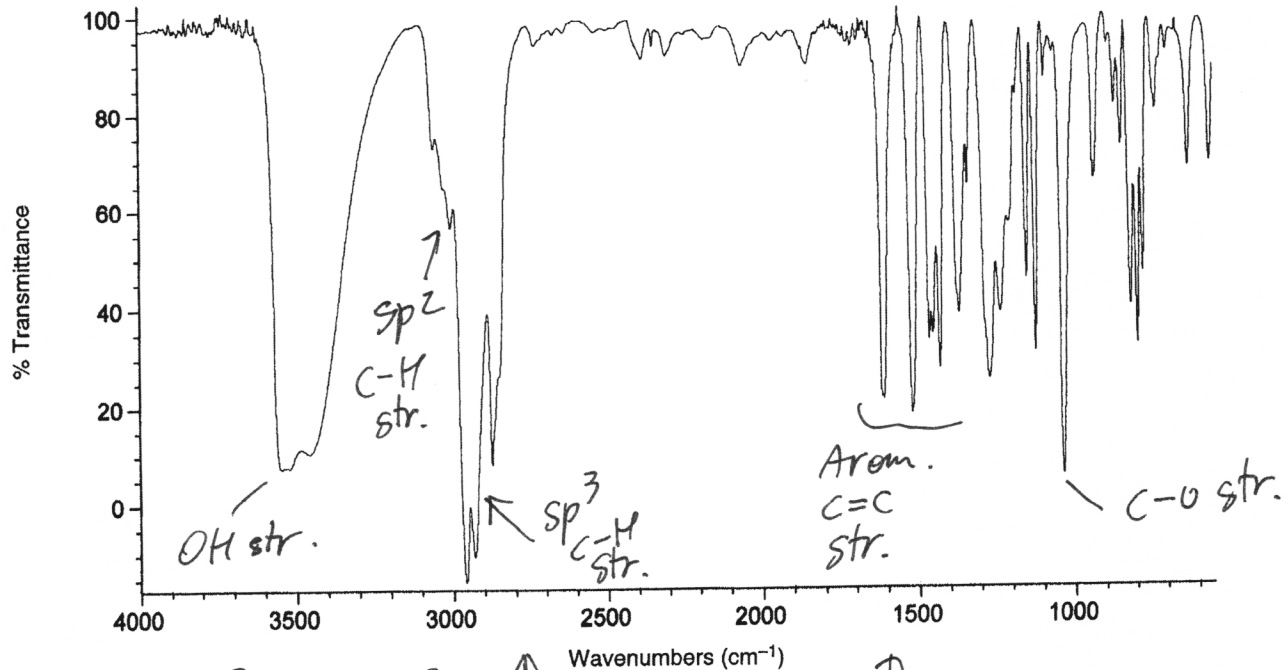
Degree of unsaturation: 4

+2



+4

INFRARED



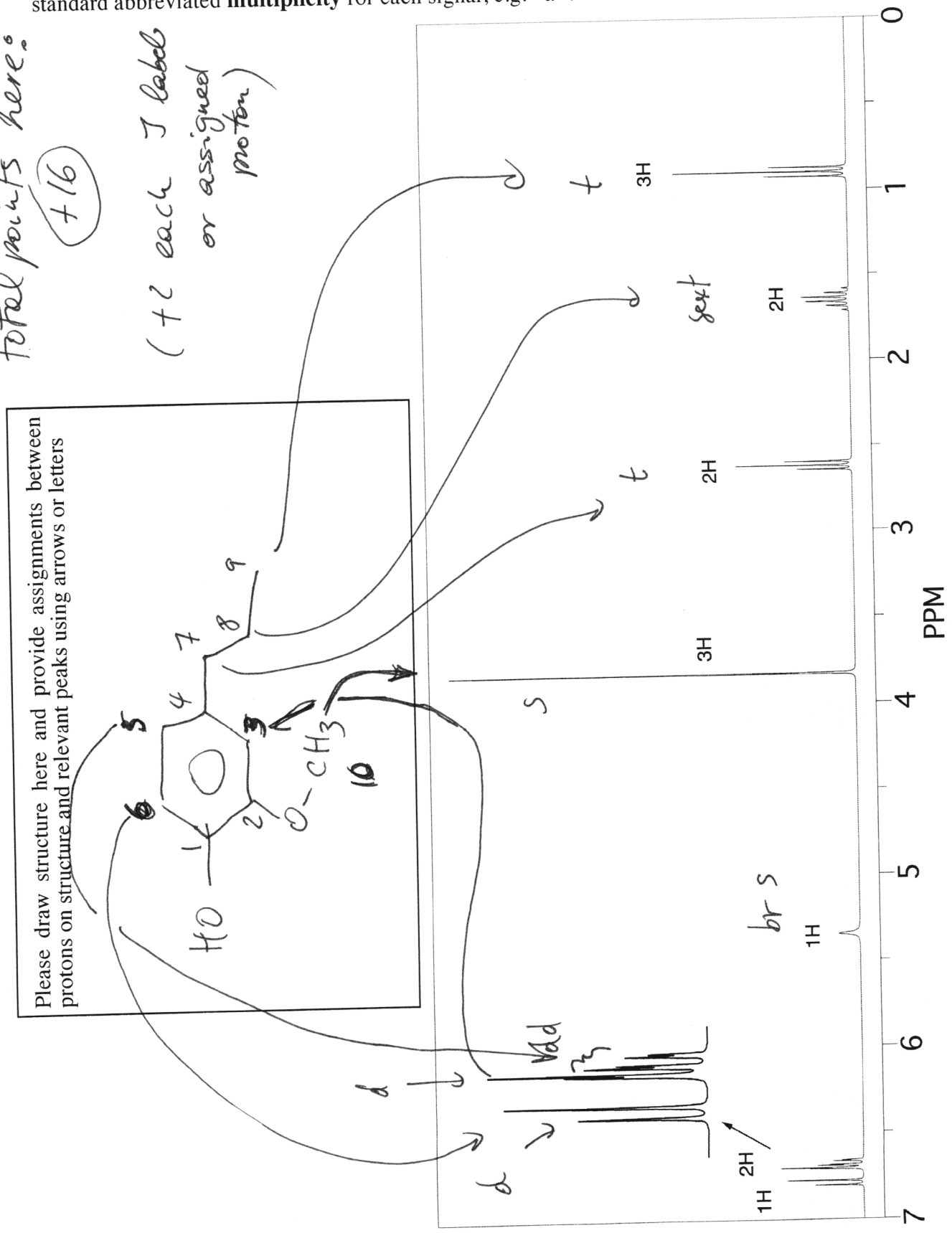
+2 +2 +2 +2

Answer key
Name

^{1}H NMR spectrum for (**show your structure also here and assign each peak**). Also provide the standard abbreviated **multiplicity** for each signal, e.g. *"d"*:

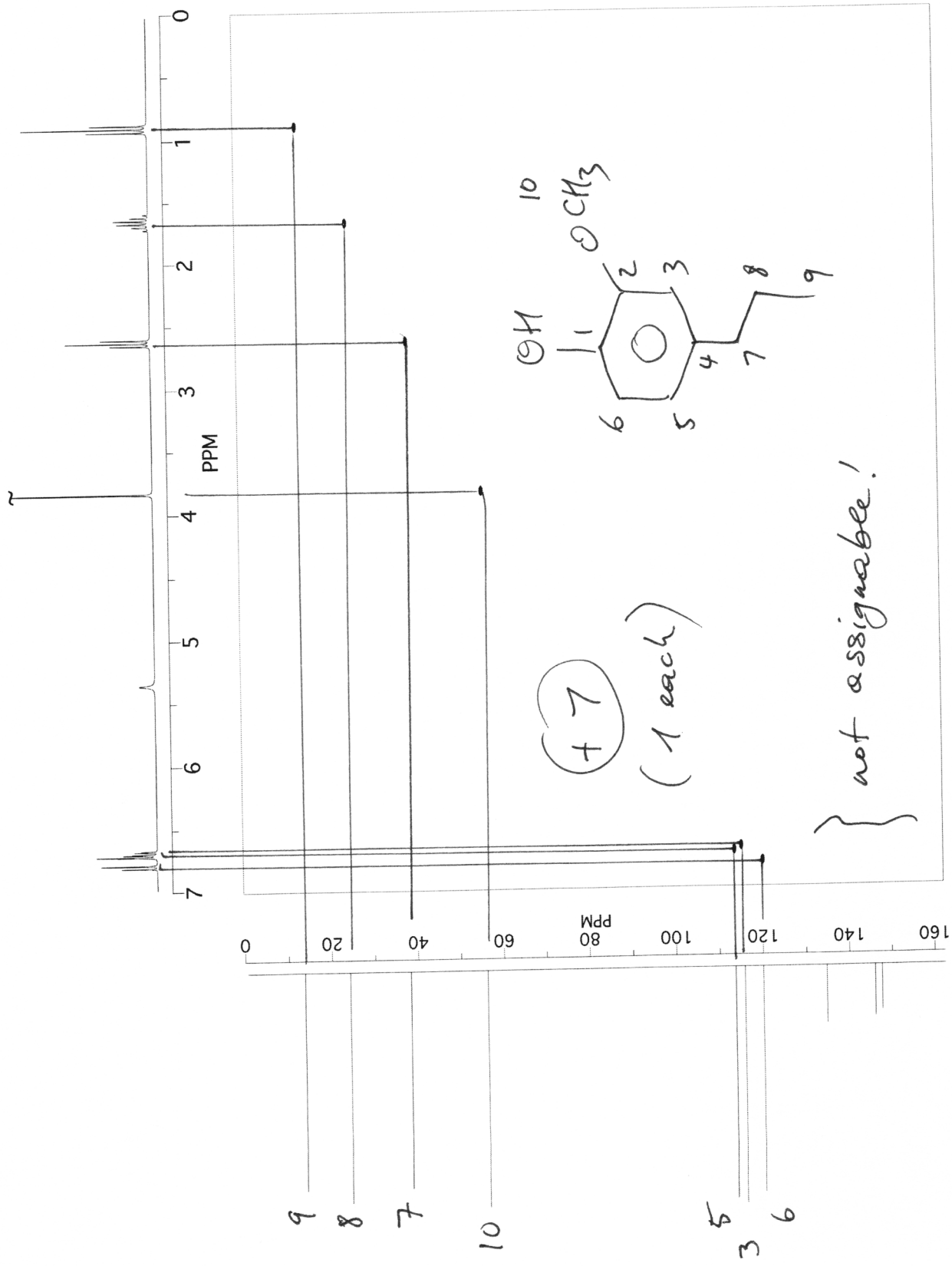
total points here: +16

(+2 each J label or assigned proton)



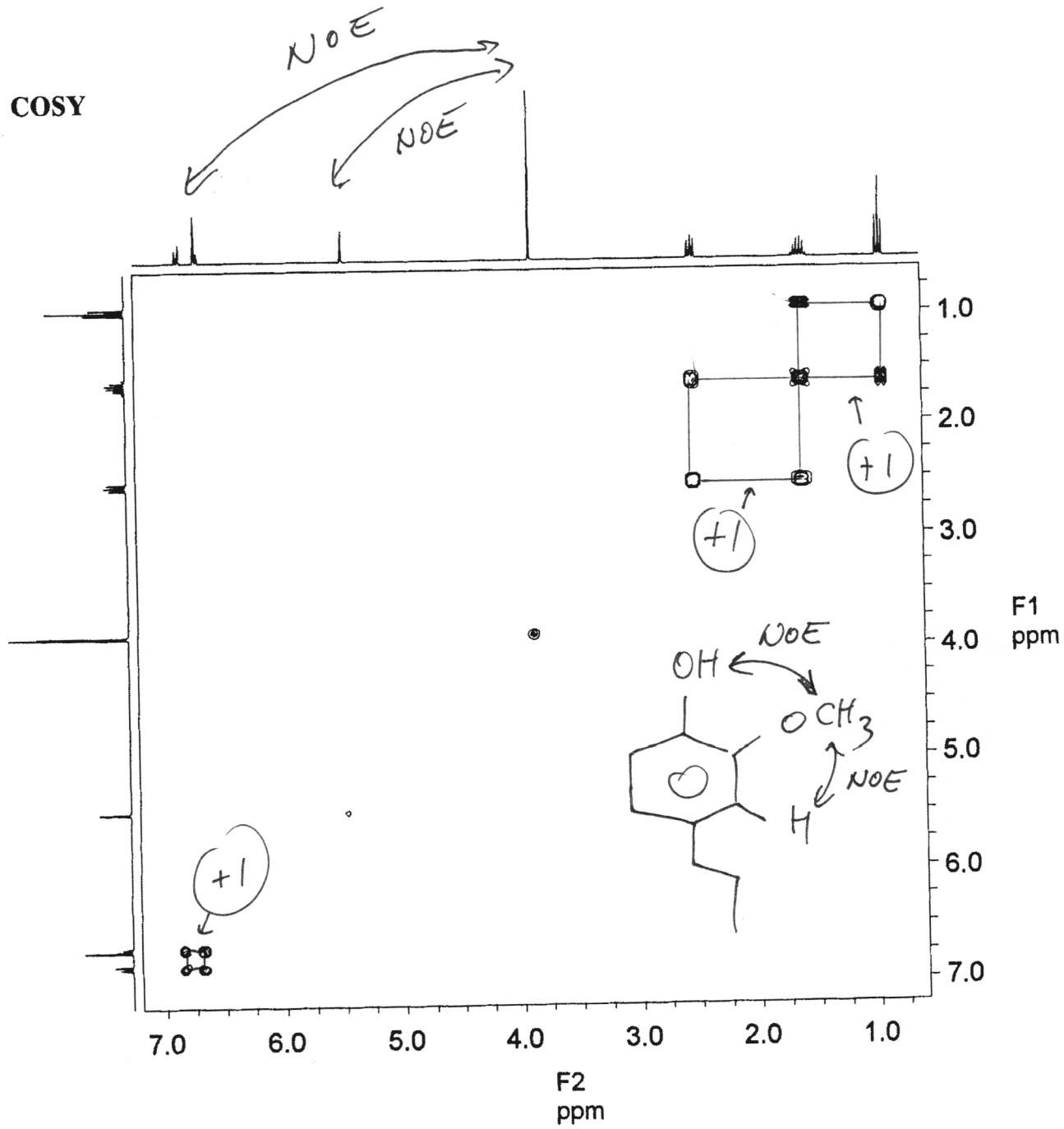
Answer Key
Name

2D HMQC spectrum for question 4 (**show your structure also here and assign each ^{13}C peak that is correlated with protons**):



Answer Key
Name

2D COSY NMR spectrum for question 4:



Note: Irradiation of the peak at 3.8 ppm gives strong NOE enhancements for the peaks at 5.5 and 6.7 ppm.

Answer Key
Name

5. (50 points) A compound has the molecular formula $C_{12}H_{16}O_5$. Deduce its structure from the IR, ^1H NMR, and ^{13}C NMR spectra given below. You must provide peak assignments in all spectra to get maximum credit.

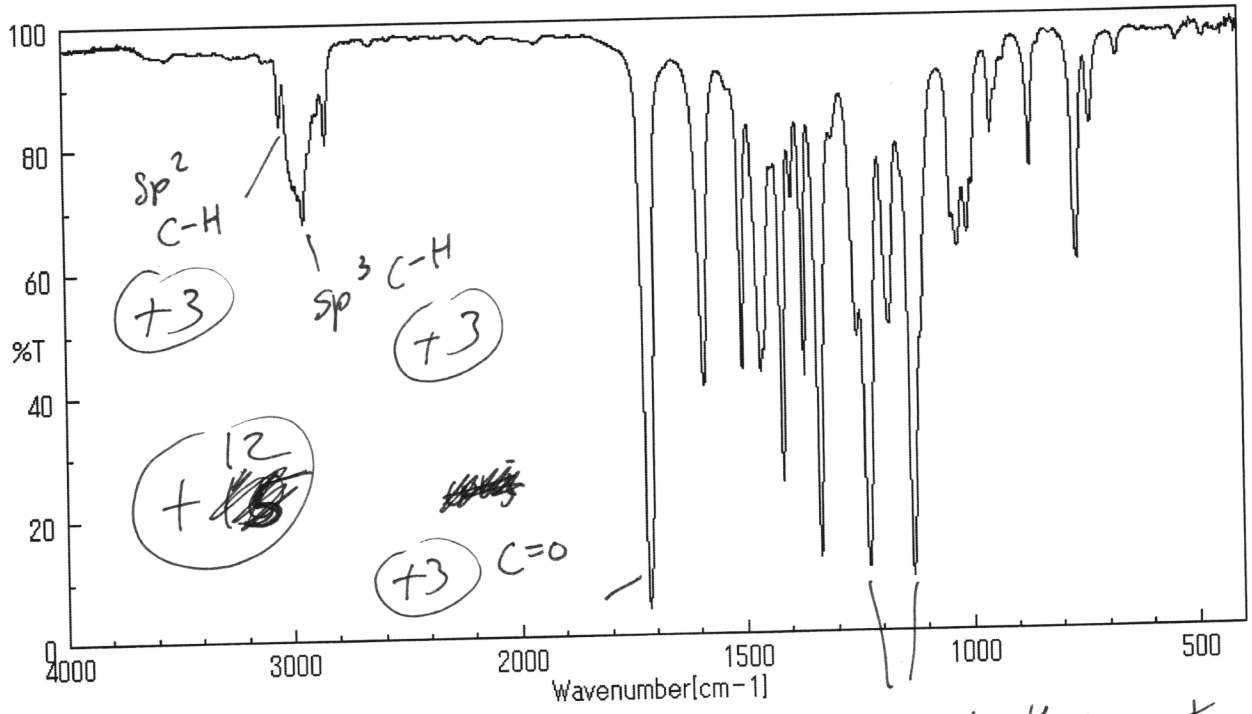
$\frac{(12\times2)+2-16}{2} = 5$

Degree of unsaturation: 5 (+5)

Draw the structure in the space below:

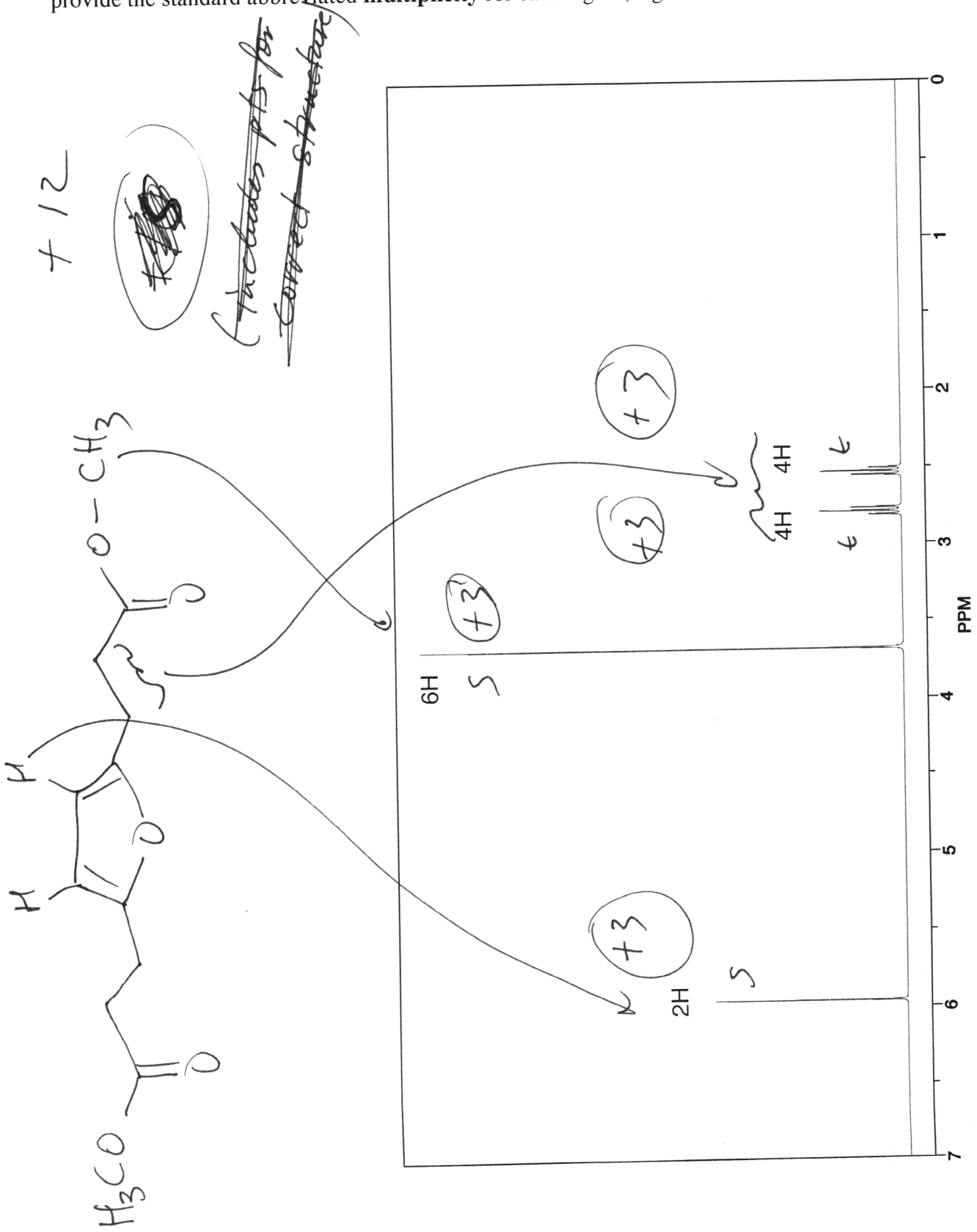
+5

IR spectrum (liquid film):



Answer Key
Name

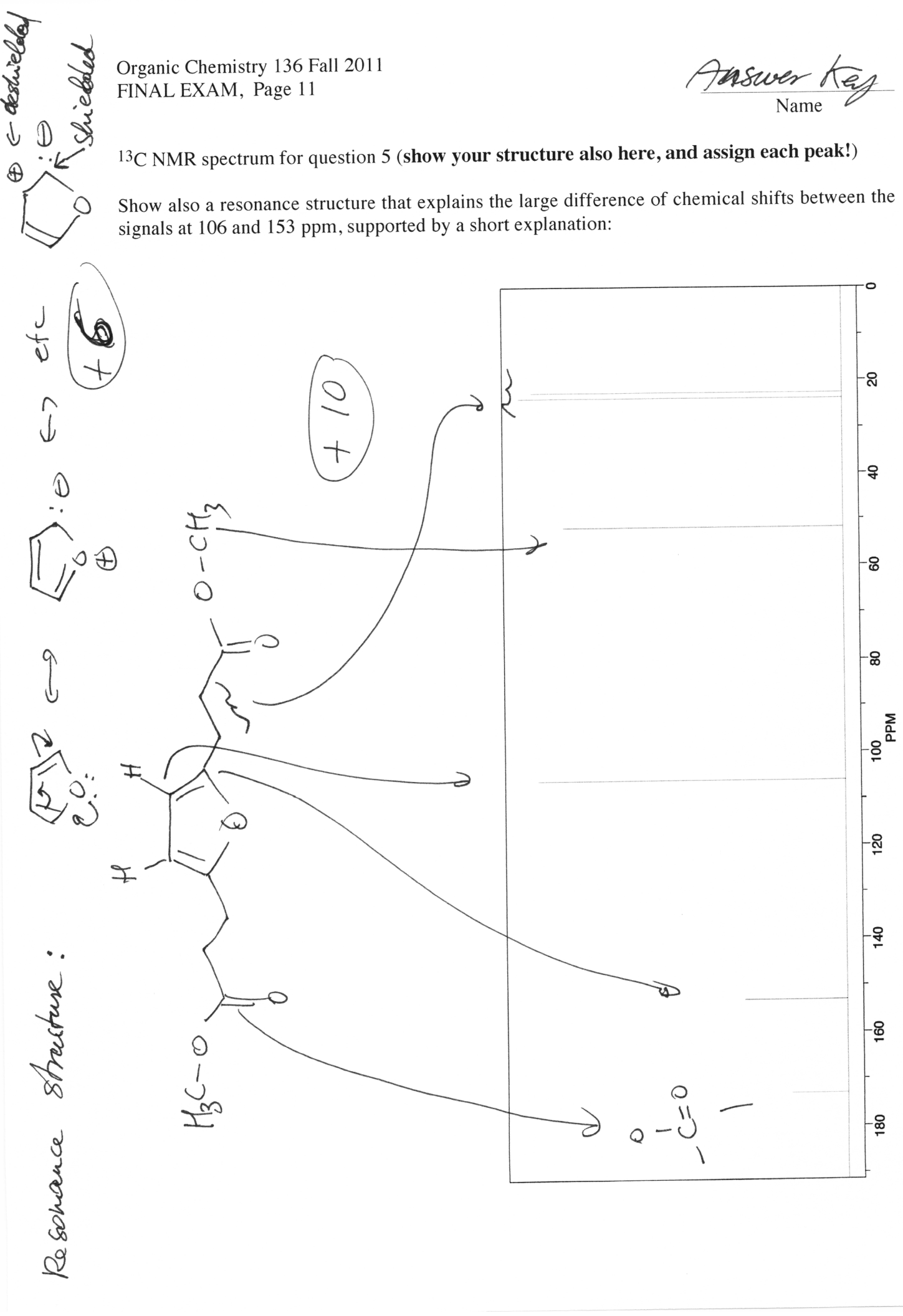
^{1}H NMR spectrum for question 5 (**show your structure also here and assign each peak**). Also provide the standard abbreviated **multiplicity** for each signal, e.g. *"d"*:



Answer Key
Name

^{13}C NMR spectrum for question 5 (**show your structure also here, and assign each peak!**)

Show also a resonance structure that explains the large difference of chemical shifts between the signals at 106 and 153 ppm, supported by a short explanation:



Answer Key
Name

6. (20 points) Assign all the carbons in the ^{13}C NMR spectrum of the compound below using its 2D INADEQUATE spectrum:

Structure: