Answer Key
Name

1. a) (10 points) Explain using only a *few sentences and/or a diagram* why the C–H stretching frequency of $CHCl_3$ appears at 3000 cm^{-1}, while the C–D stretching frequency for $CDCl_3$ appears at 2260 cm^{-1}.

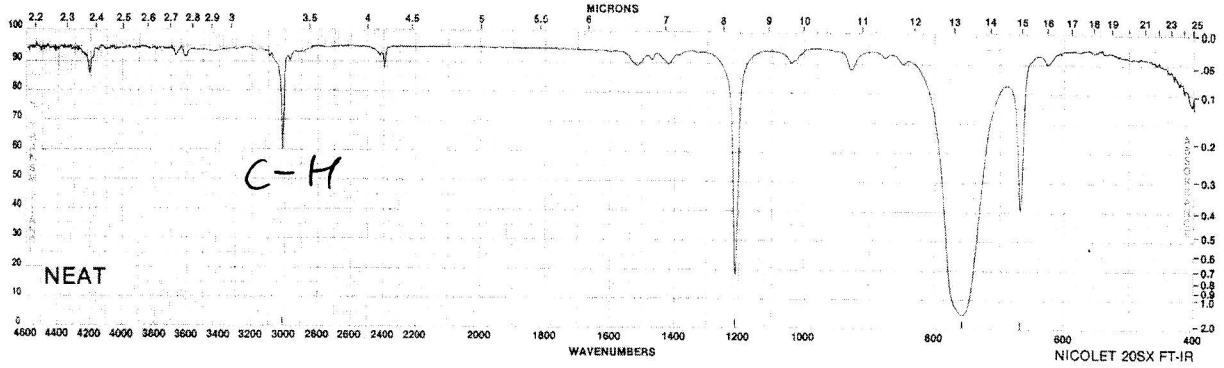


FIGURE 8.2b IR spectrum of $CHCl_3$.

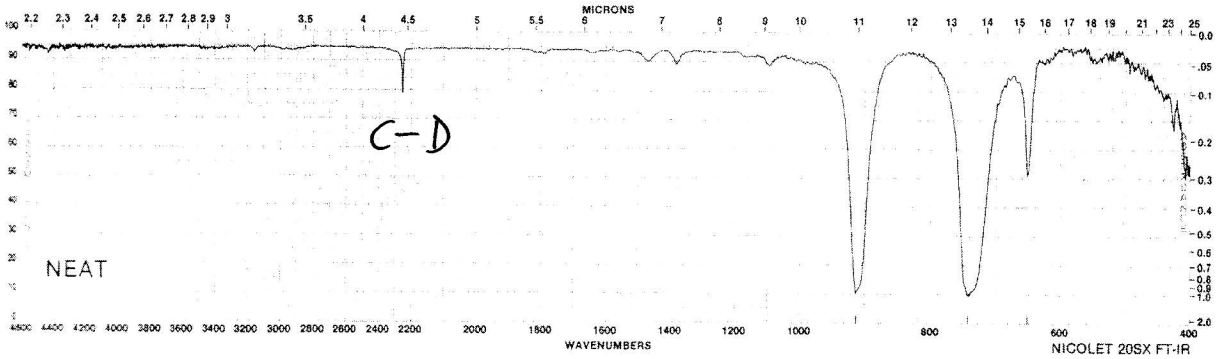


FIGURE 8.2c IR spectrum of $CDCl_3$.

Frequency equation:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \left(\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}\right)$$

larger ~~term~~ denominator (H to D)

⇓

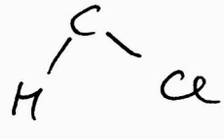
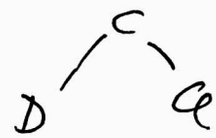
smaller $\bar{\nu}$

The reduced mass (term) (μ) gets larger with higher masses, and therefore decreases the value of $\bar{\nu}$ since it is the numerator of $\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

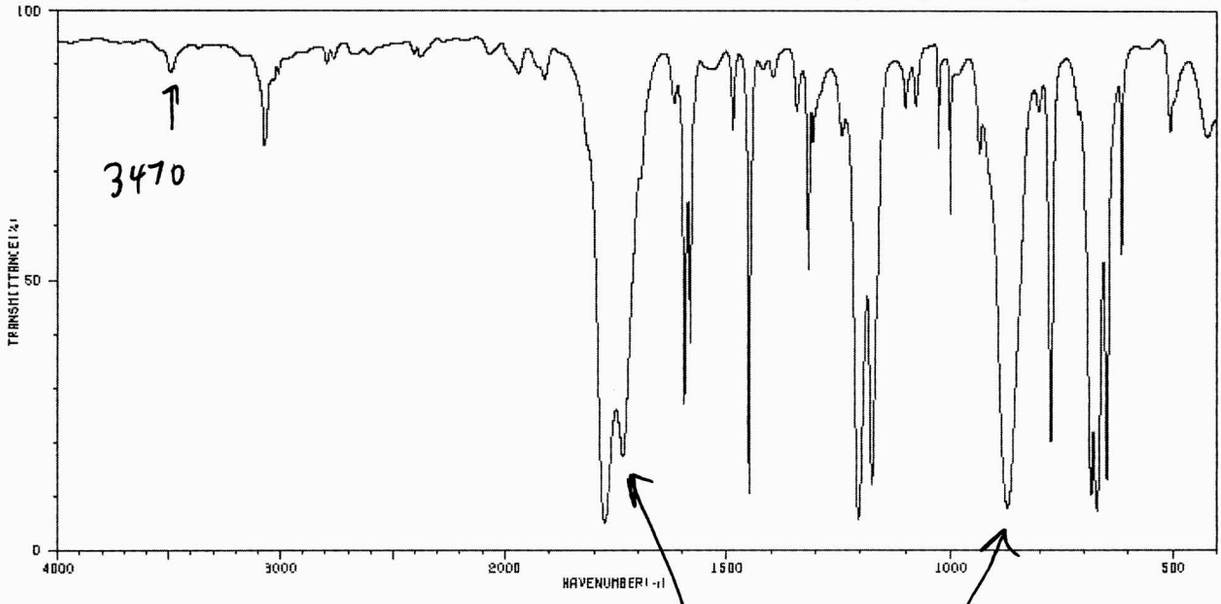
Answer Key
Name

Question 1 continued:

b) (5 points) What are the absorption bands at 1205 and 907 cm^{-1} in the IR spectra of $CHCl_3$ and $CDCl_3$, respectively?

Bending modes for  and 

c) (10 points) Explain the doubled peak at 1775 and 1733 cm^{-1} in the following IR spectrum. Also, what vibration does the *associated fundamental* frequency correspond to?



(1733 × 2 = 867 cm^{-1})

Fermi resonance with C=O stretch from band at ~867 cm^{-1} (which is a Ph-oop) but did not need to know

d) (5 points) Explain the absorption peak at 3470 cm^{-1} in the IR spectrum above:

3470 × 2 = 1735 cm^{-1}

this is the overtone of the C=O stretch.

Answer Key

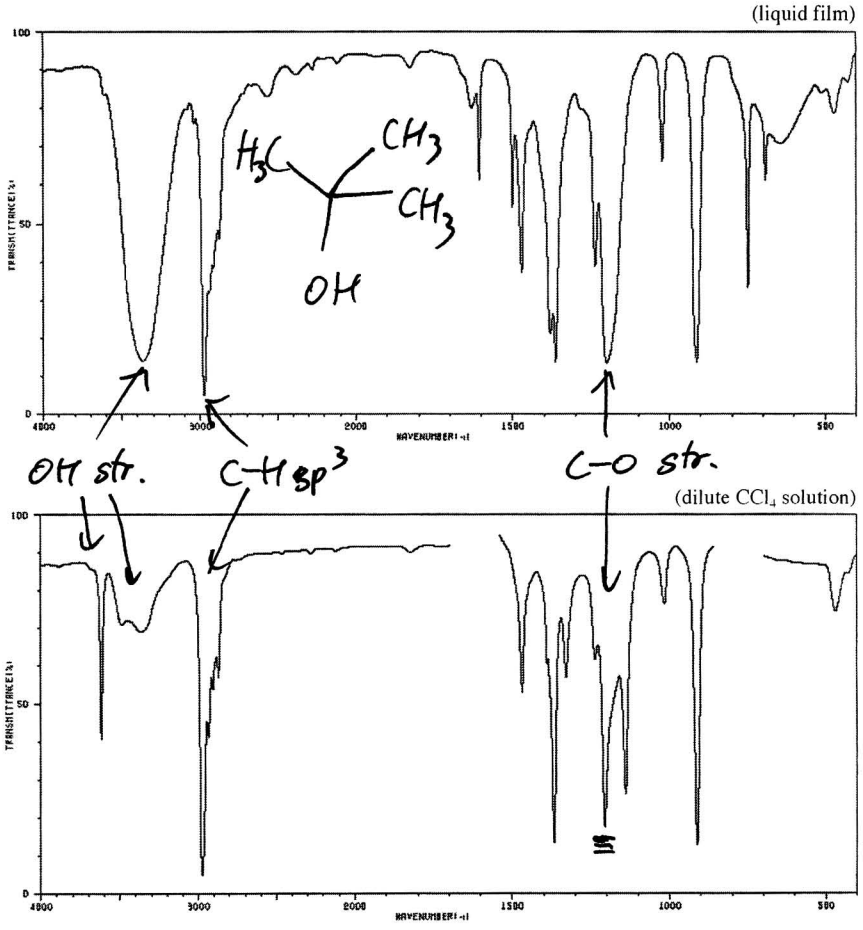
Name

2. a) (10 points) A compound contains 4 carbon atoms and displays only 1 *sharp* singlet in its ^{1}H NMR spectrum along with one broad singlet. Using its IR spectra recorded in two different media (neat film or dilute CCl_4 solution), assign recognizable absorptions in both spectra, labeling clearly what type they are, and provide the structure that fits these data:

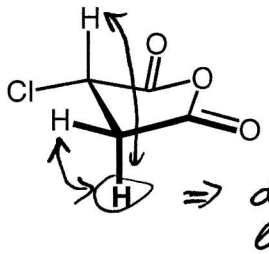
^{1}H NMR:
2 lines, 1 sharp s
1 broad s

Formula:
4 carbon atoms
⇒ high symmetry

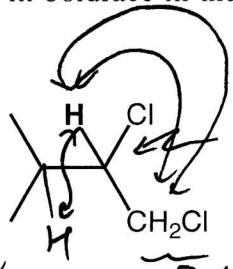
IR: strong broad absorption at 3350 cm^{-1}
⇒ sharp med. absorption at 3600 cm^{-1} dilute
⇒ OH group



b) (10 points) Draw theoretical ^{1}H NMR *coupling patterns* (i.e. the way splittings would appear in a ^{1}H NMR spectrum) for the **H**'s highlighted in boldface in the following two compounds. Also label the pattern (e.g. t, dd):



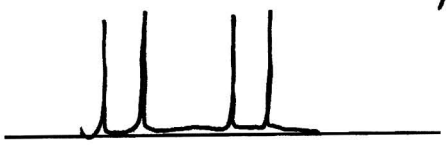
⇒ dd with large + medium couplings

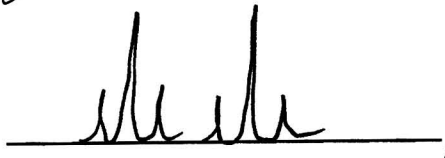


chiral center

⇒ two t's

⇒ diastereotopic protons (2 different chemical shifts)





(may look overlapped)

(the 9 not likely)

Answer Key
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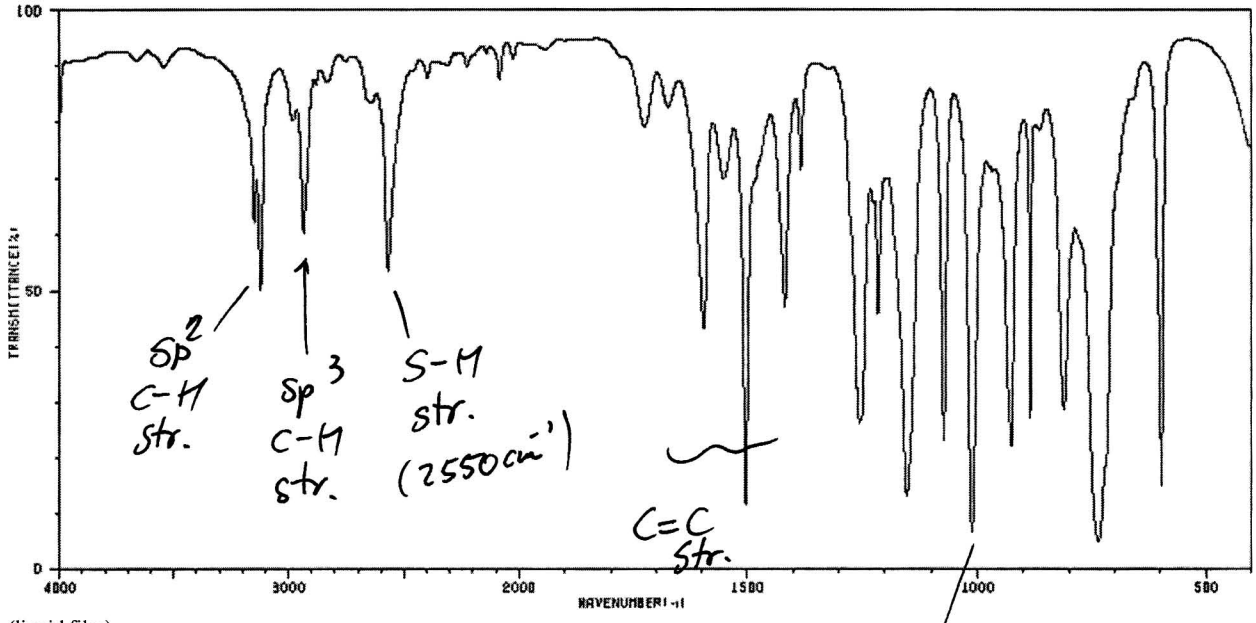
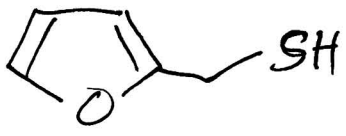
3. a) (25 points) In addition to carbon and hydrogen atoms, the exact number of which you can determine from the ^{1}H and ^{13}C NMR spectra provided below, the following compound contains only two heteroatoms, 1 oxygen and 1 sulfur. Its IR spectrum is also provided to help you with structure determination. Assign recognizable IR absorptions, as well as *all* the signals of the ^{1}H NMR spectrum (but not carbons in this problem). Then provide the structure of this compound and provide your reasoning:



(liquid film)

Structure:



Reasoning on how you deduced your structure:

IR: unusual absorption at 2550 cm^{-1} => SH str. most likely

sp^2 C-H str. prominent

sp^3 C-H str. simple => not many C-H sp^3 bonds

C=C str. lines => likely aromatic system (+ ^{1}H NMR)

^{1}H NMR: two different spin systems: - CH_2SH

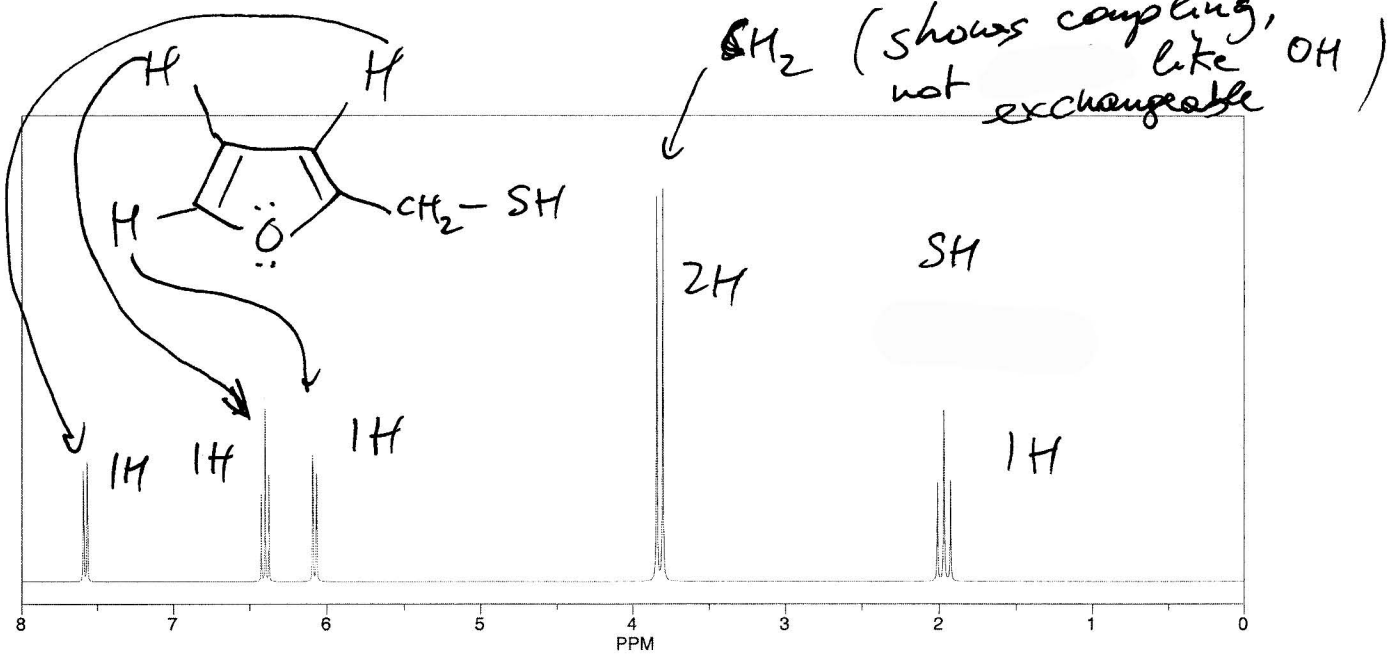
- H--- H--- H aromatic system (d, t, d)

^{13}C NMR: unusual spread of chemical shifts in aromatic region: only heterocycle with O matches

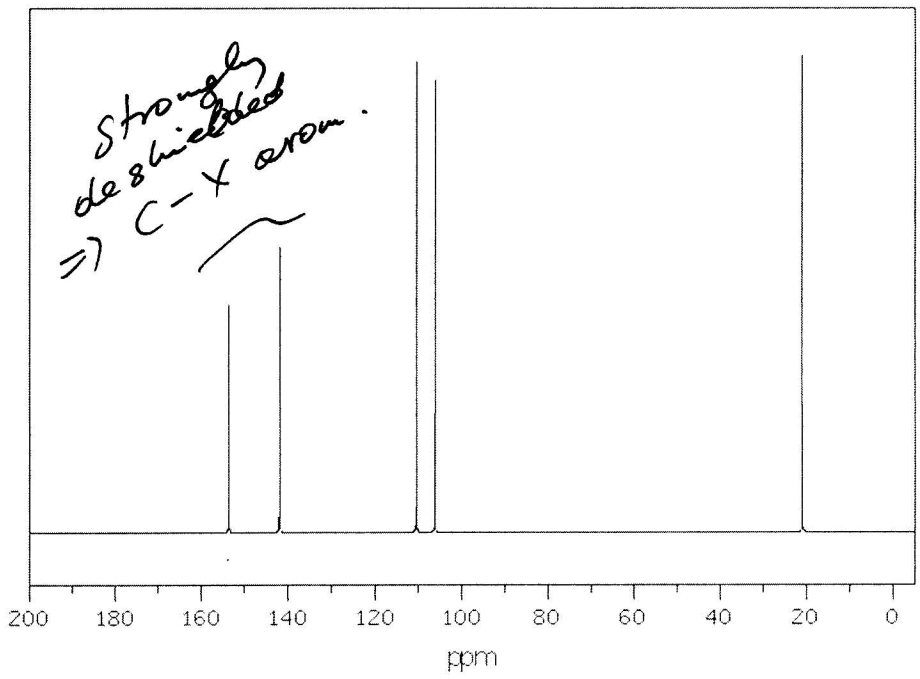
Answer Key
Name

Problem 3 continued…

^{1}H NMR spectrum, with 1:1:1:2:1 integral ratios from left-to-right. Coupling constants for peaks within the same sequence: 7.58 (J = 2.9, 0.9 Hz), 6.40 (J = 3.2, 2.9 Hz), 6.08 (J = 3.2, 0.9 Hz), 3.73 (J = 7.7 Hz), 1.90 (J = 7.7 Hz):



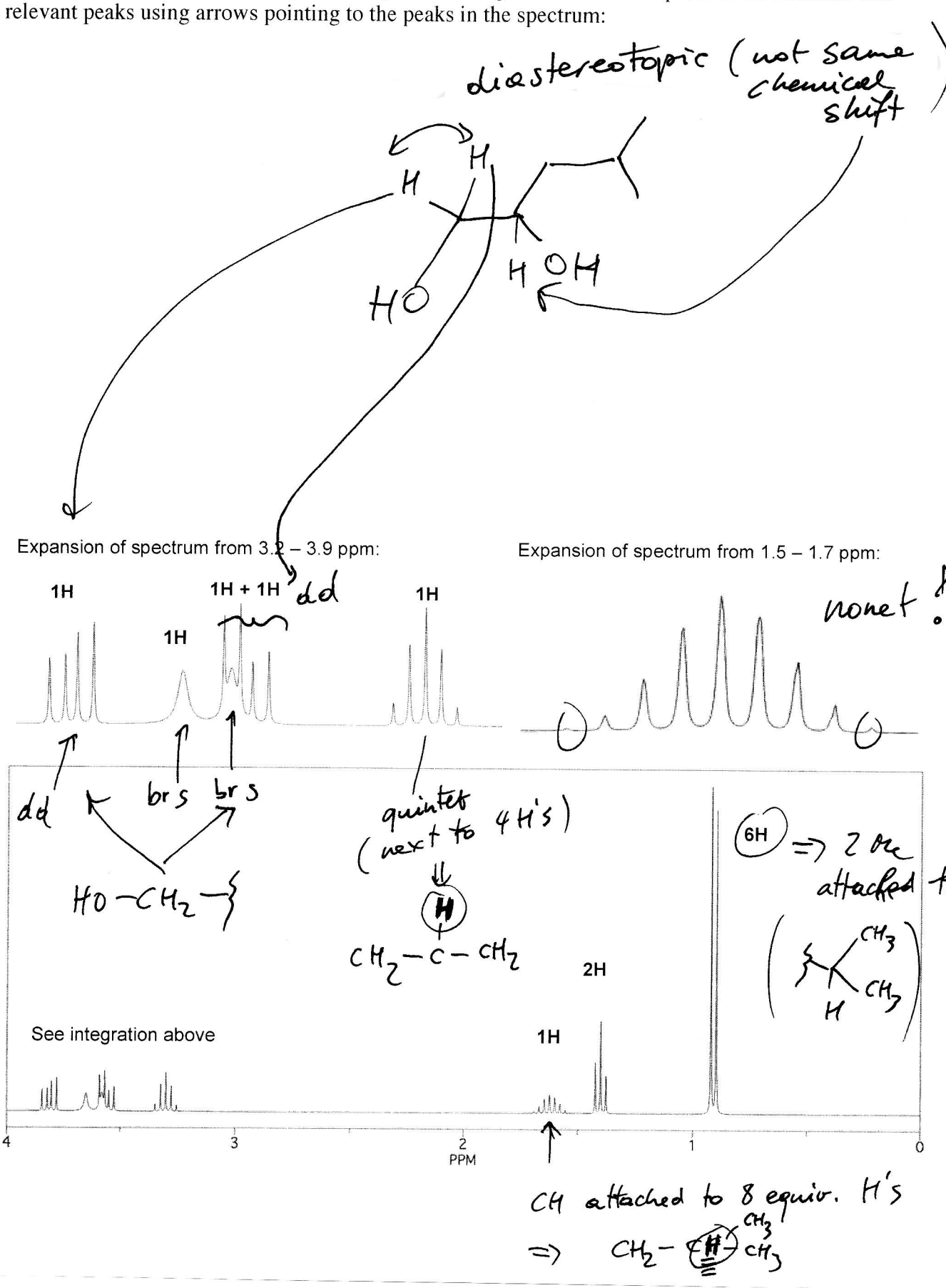
^{13}C NMR spectrum:



Answer Key
Name

^{1}H NMR spectrum for question 4:

Please draw structure here as well, and provide assignments between protons on structure and relevant peaks using arrows pointing to the peaks in the spectrum:

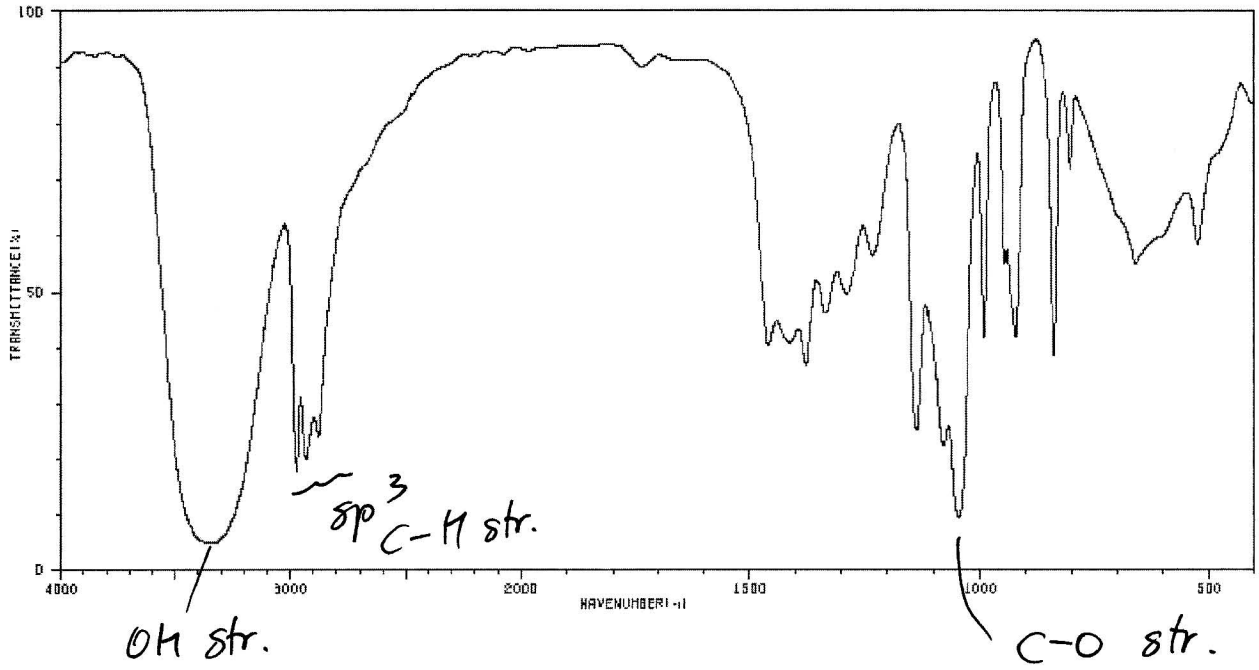


Answer Key
Name

4. (25 points) A compound has the molecular formula $C_6H_{14}O_2$. Deduce its structure from the IR, ^1H NMR and ^{13}C NMR spectra given below:

Degree of unsaturation: 0 $\qquad \frac{(2\times 6)-14+2}{2} = 0$

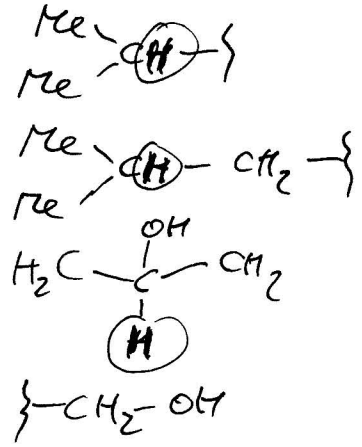
IR spectrum (neat film):



Explain your analysis of the data and deduction of the final structure here:

IR: Shows OH stretch strongly => alcohol
+ C-O "
No unsaturation (D.U. + IR)

^1H NMR: " " (peaks only up to 3.7 ppm)
Difficult pattern, but can be assembled piece-by-piece:



Answer Key
Name

^{13}C NMR spectrum for question 4:

Please draw structure here again, and provide assignments for all carbons on the structure and relevant peaks using arrows or letters (note that carbons at 67 and 74 ppm can be assigned based on their degree of substitution).