

## Chemistry 605 (Reich)

FIRST HOUR EXAM

Thur, March 3, 2011

Question/Points

R-10A \_\_\_\_\_/7

R-10B \_\_\_\_\_/15

R-10C \_\_\_\_\_/23

R-10D \_\_\_\_\_/25

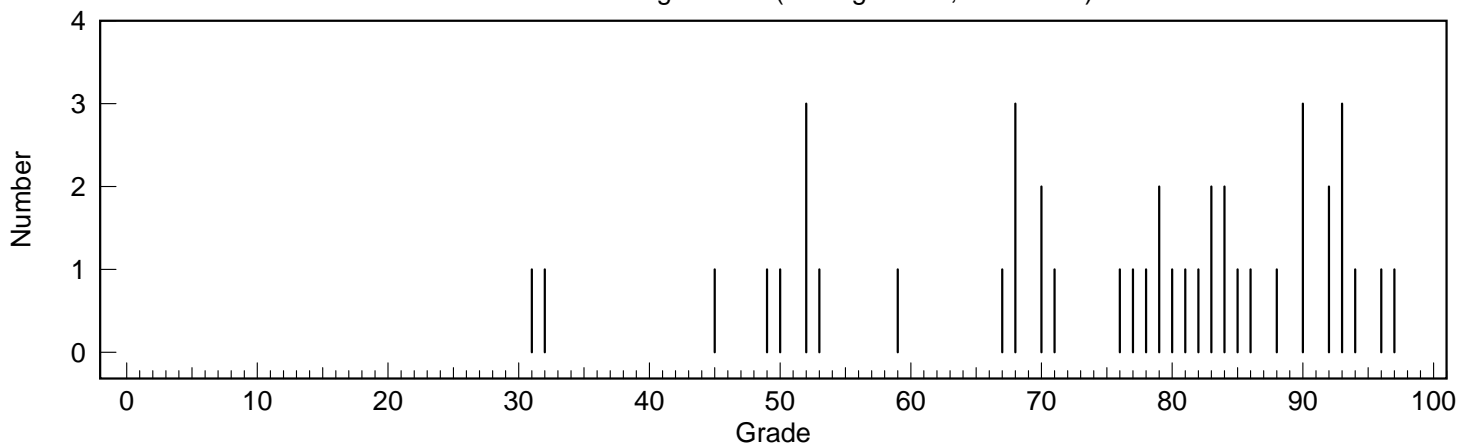
R-10E \_\_\_\_\_/30

Total \_\_\_\_\_/100

Hi 87  
Average 74  
Median 79

AB 82  
BC 55  
CD 40

Distribution from grade list (average: 74.5; count: 43)



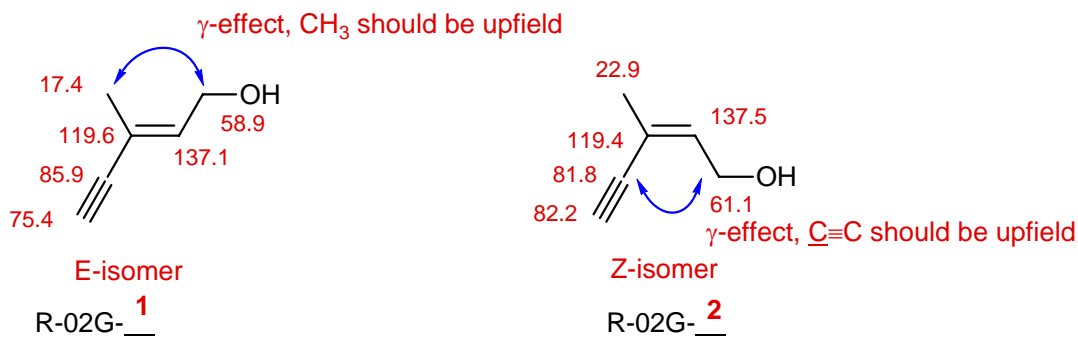
**Grading Copy**

Name \_\_\_\_\_

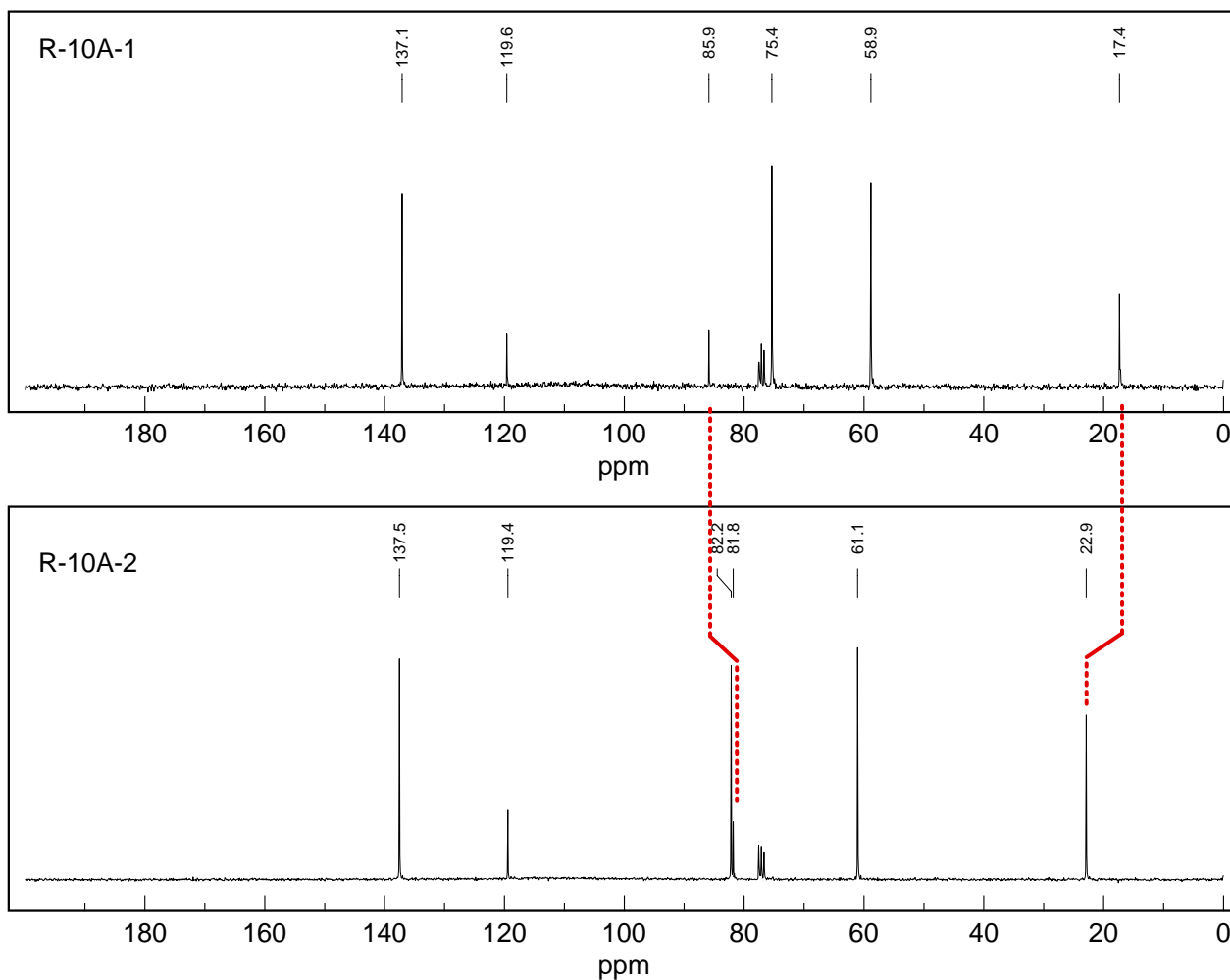
If you place answers anywhere else except in the spaces provided, (e.g. on the spectra or on extra pages) clearly indicate this on the answer sheets.

7

**Problem R-10A** ( $C_6H_8O$ ). Below are given the  $^{13}C$  NMR spectra of two stereoisomers of 3-methyl-pent-2-ene-4-yn-1-ol. Assign structures, and assign the signals by writing the  $\delta$  values next to the appropriate carbons on each structure (Source: Aldrich Spectra Viewer).



3

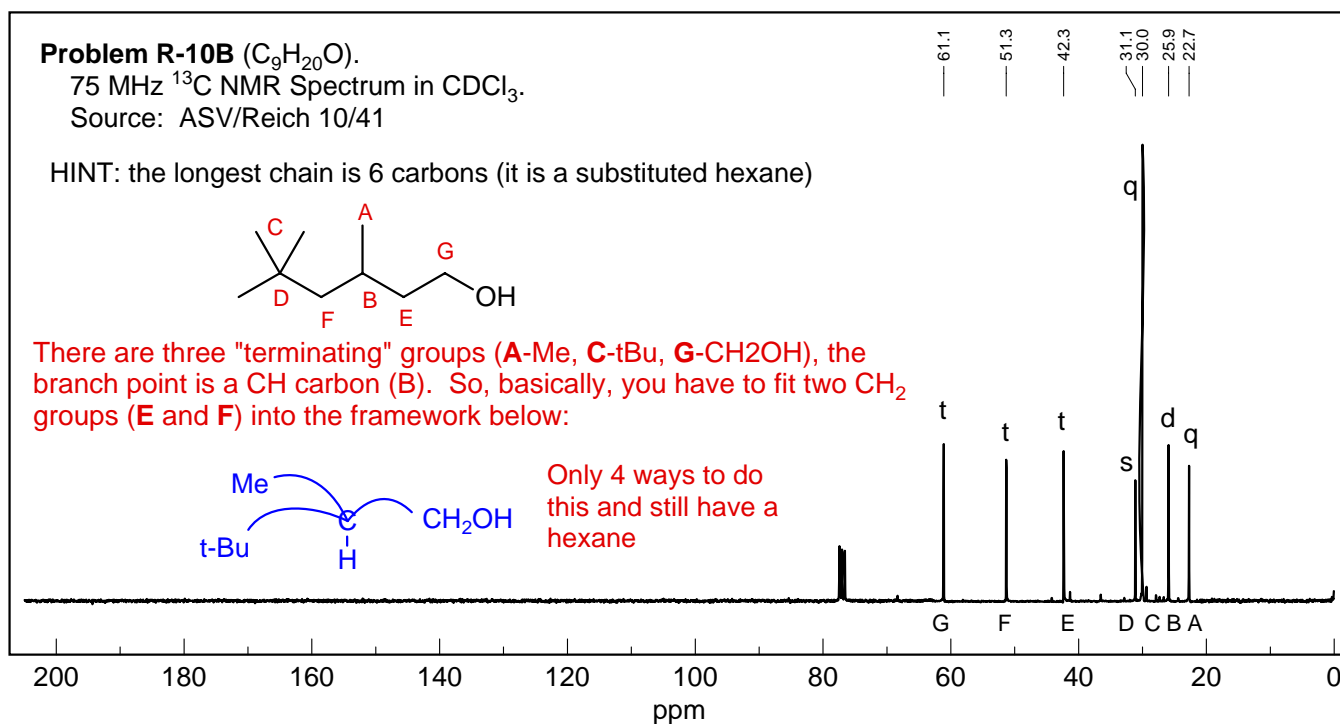


Briefly explain the basis for your assignment. Be specific.

- 4  $\gamma$ -Interaction across double bonds causes upfield shifts (vs H at one of the positions). Thus in the E-isomer the  $CH_3$  would be upfield ca 5 ppm compared to the Z-isomer. Similarly, the first  $C\equiv C$  carbon would be upfield in the Z-isomer compared to the E

For some reason the terminal acetylene carbon also moves a lot between isomers, but this is not a predictable  $\gamma$ -effect.

**Problem R-10B** (C<sub>9</sub>H<sub>20</sub>O). Identify the compound whose <sup>13</sup>C NMR spectrum is given below.



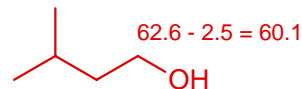
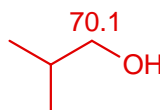
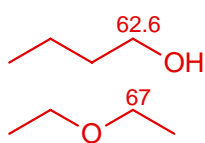
2 (a) DBE 0. What functional groups might be present? C-OH or C-O-C (alcohol, ether)

(b) What does the signal at  $\delta$  61.1 tell you about the structure?

From the H-count (only 19 H on carbon), we know we have an alcohol (also absence of two downfield carbons)

The shift really requires:

-CH<sub>2</sub>-CH<sub>2</sub>-OH



4

(c) Plausible structures? Circle your choice. Assign the signals by placing the appropriate letters (A-G) on the structure.

$$-2.1 + 2\alpha + 4\beta + 2\gamma_C + 2^\circ(4^\circ) + 2^\circ(2^\circ)$$

$$= -2.1 + 2(9.1) + 4(9.4) - 2(2.5) - 7.5 - 0 = 41.2$$

$$-2.1 + 2\alpha + 3\beta + 3\gamma_C + \Gamma_{OH} 2^\circ(3^\circ) + 2^\circ(2^\circ)$$

$$= -2.1 + 2(9.1) + 3(9.4) - 3(2.5) - 5 - 0 = 31.8$$

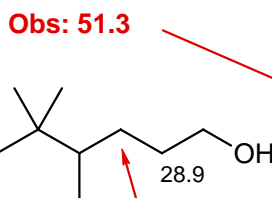
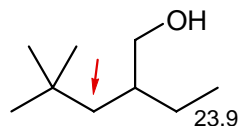
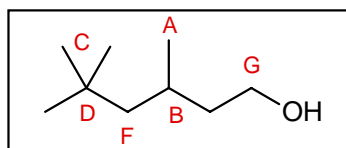
Pieces:

-CH<sub>2</sub>-CH<sub>2</sub>-OH

-C(CH<sub>3</sub>)<sub>3</sub>

-CH<sub>3</sub>

-CH



Obs: 51.3

$$-2.1 + 2\alpha + 3\beta + 3\gamma_C + \gamma_{OH} + 2^\circ(3^\circ) + 2^\circ(2^\circ)$$

$$= -2.1 + 2(9.1) + 3(9.4) - 3(2.5) - 5 - 2.5 - 0 = 29.3$$

$$70.1 + \gamma = 67.6$$

Obs: 51.3

Obs: 61.1

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$$\text{Calc F: } -2.1 + 2\alpha + 5\beta + \gamma + \gamma_{OH} + 2^\circ(3^\circ) + 2^\circ(4^\circ) + \delta_{OH}$$

$$= -2.1 + 2(9.1) + 5(9.4) - 2.5 - 5 - 2.5 - 7.5 = 45.6$$

(d) Do a chemical shift calculation for the carbon to which you have assigned the signal F ( $\delta$  51.3) using the Grant-Cheney parameters.

$$\text{Calc F: } -2.1 + 2\alpha + 5\beta + \gamma + 2^\circ(3^\circ) + 2^\circ(4^\circ) + \delta_{OH}$$

$$= -2.1 + 2(9.1) + 5(9.4) - 2.5 - 2.5 - 7.5 = 50.6$$

Obs: 51.3

$$\text{Calc B: } -2.1 + 3\alpha + 2\beta + 3\gamma + \gamma_{OH} + 3^\circ(2^\circ) + 3^\circ(2^\circ)$$

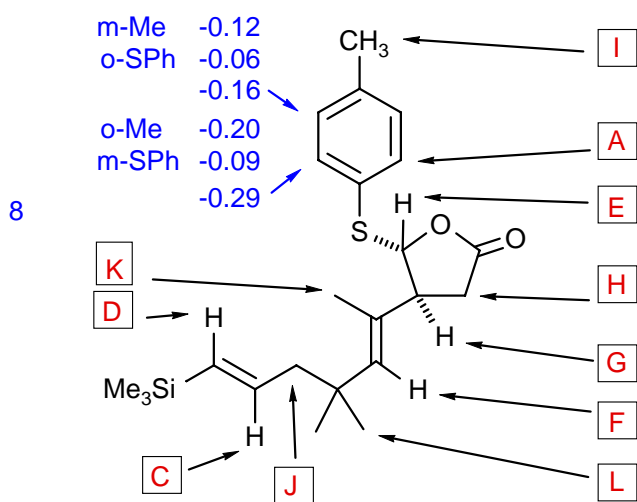
$$= -2.1 + 3(9.1) + 2(9.4) - 3(2.5) - 5 - 2(3.7) = 24.1$$

Obs: 25.9

3

**Problem R-10C** ( $C_{23}H_{34}O_2Si$ ) A 500 MHz  $^1H$  spectra is provided.

(a) The structure of R-10C is given below. All of the important signals in the  $^1H$  NMR spectrum are labeled (A, B, C etc). Assign the proton signals by placing appropriate labels on the structure. **For parts (b), (c) and (d), identify the couplings (e.g. for (b):  $J_{GX} = 22$  Hz,  $J_{GY} = 32$  Hz)**



Common errors: switch A/B, H/J, E/F. Decide between A and B with broadening of B by  $^4J$  to  $CH_3$ . Select H for a better match with coupling to G, and leaning (weak). Select E for matched coupling with G, and size of coupling.

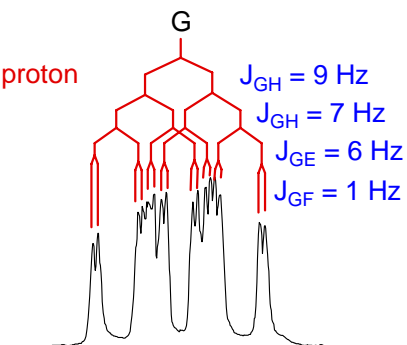
To make assignments use:

1. Chemical shifts (type of proton)
2. Integrations
3. Multiplicity
4. J-values

$$\Sigma = 23 \text{ Hz}$$

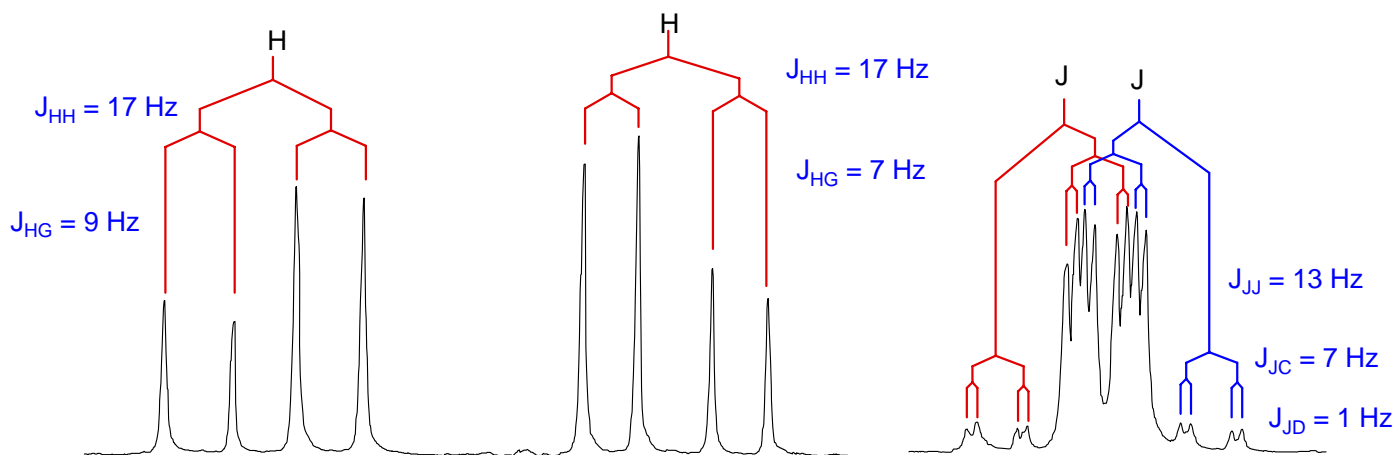
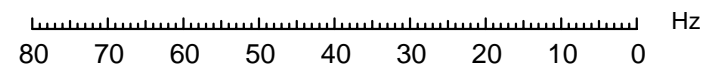
$$\text{End-to-end} = 23 \text{ Hz}$$

-3 for no J ID



8 (b) The multiplet at  $\delta$  2.9 (G) is shown above. How many other protons are coupled to this one? 4 Draw a coupling tree for G and report the coupling constants

16 lines - therefore coupled to 4 protons



This is AB of ABXY, AB coupled equally to X and Y

7 (c) What kind of pattern is the multiplet at  $\delta$  2.5 (H)? ABX (AMX) Draw a coupling tree on the multiplet, label it, and report J values.

-3 for no J ID

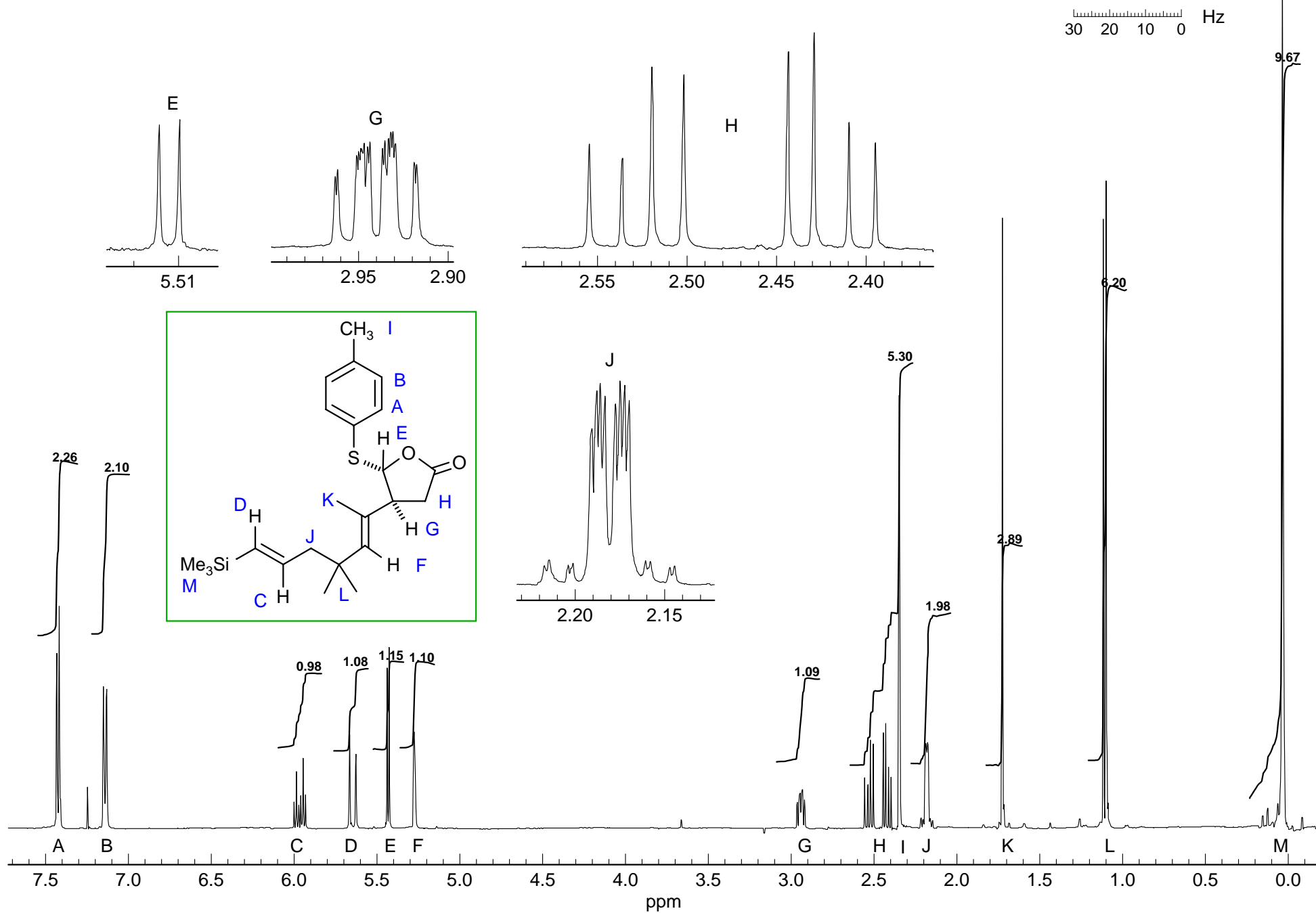
5 (d) 5 Pt. BONUS question (don't do unless you have spare time): What kind of pattern is the multiplet at  $\delta$  2.2 (J)? AB of ABXY Draw a coupling tree on the multiplet, label it, and report J values with assignments.

This is basically an AB pattern (diastereotopic  $CH_2$ ), each peak of which is split into a dd from coupling to C and D

**Problem R-10C** (C<sub>23</sub>H<sub>34</sub>O<sub>2</sub>SSi)

500 MHz <sup>1</sup>H NMR Spectrum in CDCl<sub>3</sub>

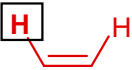
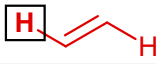
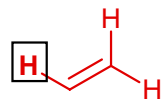
(Source: Margaret K. Jones/Burke 10/19)



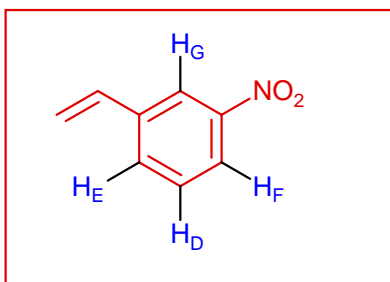
**Problem R-10D** ( $C_8H_7NO_2$ ). Determine the structure of **R-10D** from the  $^1H$  NMR spectrum provided.

2 (a) DBE 6

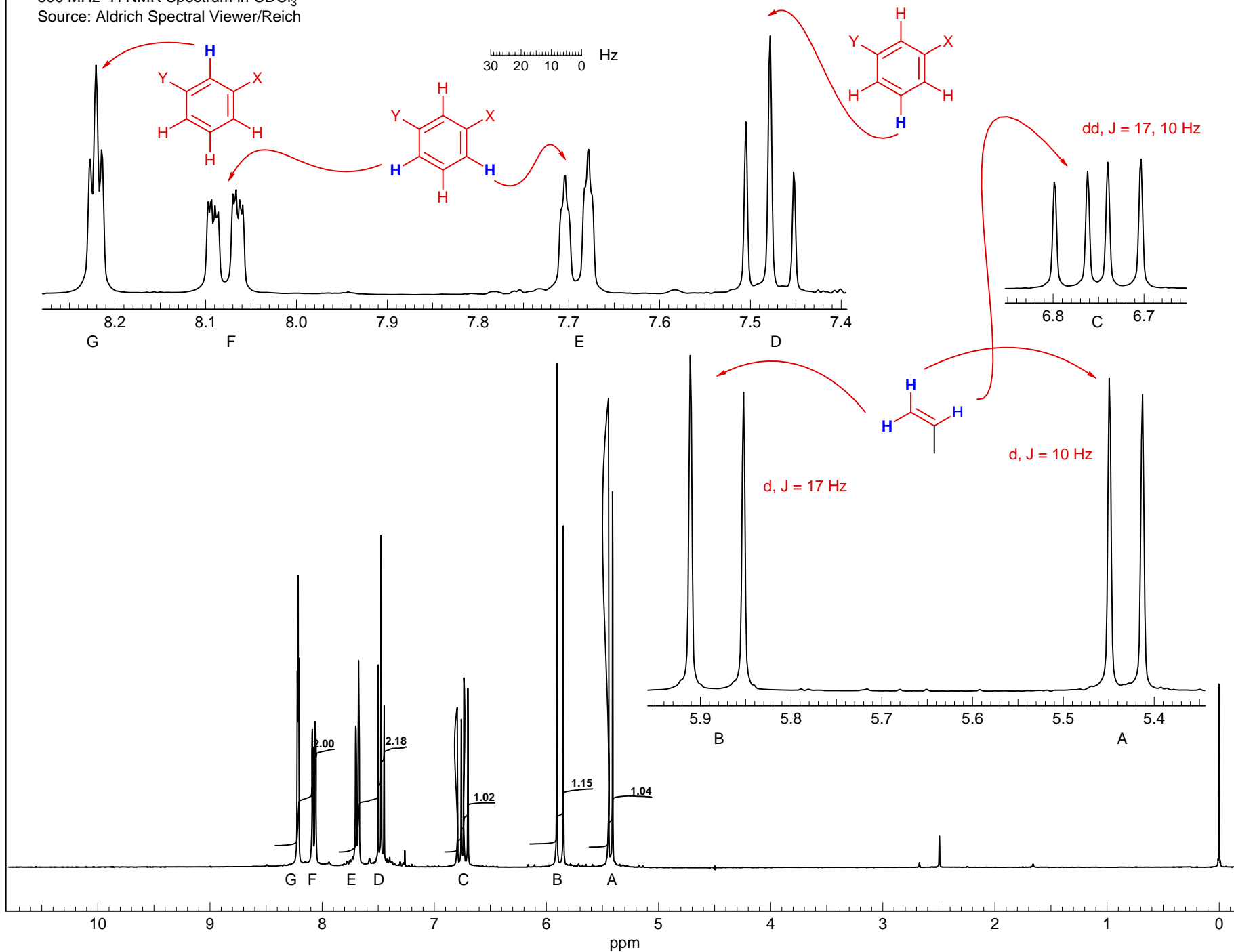
(b) Analyze the  $^1H$  NMR signals. For each of the signals listed below report multiplicity and coupling constants to the extent the signals are amenable to first order analysis, and the **part structure** each corresponds to.

A	5.43, 1H, d, $J = 10$		<p>These together require a vinyl group (<math>CH=CH_2</math>) with no other coupling</p> <p>The coupling between the gem-vinyl protons is too small to resolve</p>
B	5.88, 1H, d, $J = 17$		
C	6.75, 1H, dd, $J = 17, 10$		
10	D	7.48, 1H, t, $J = 8$	<p>These together require a meta-substituted benzene</p>
	E	7.69, 1H, dt, $J = 8, ca 1$	
	F	8.07 1H, ddd, $J = 8, 2, 1$	
	G	8.22 1H, t, $J = 1.5$ (probably dd)	

(c) Give the structure of **R-10D**. If more than one structure is possible, circle your best choice.



**Problem R-03D** ( $C_8H_7NO_2$ ) Assign proton signals  
300 MHz  $^1H$  NMR Spectrum in  $CDCl_3$   
Source: Aldrich Spectral Viewer/Reich



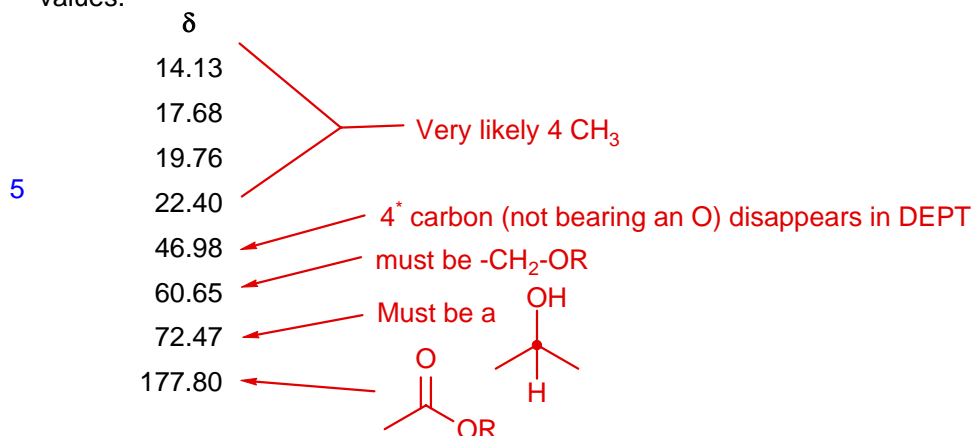
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**Problem R-10E** ( $C_8H_{16}O_3$ ). Determine the structure of **R-10E** from the  $^1H$  NMR,  $^{13}C$  NMR and IR spectra provided.

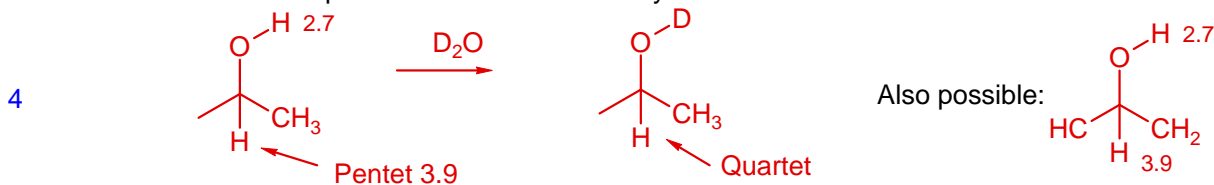
2 (a) DBE 1 (b) What information can you obtain from the IR spectrum (give frequency and peak assignment).

3 3500-3600  $cm^{-1}$  OH stretch      1730  $cm^{-1}$  Carbonyl stretch - probably an ester

(c) Interpret the  $^{13}C$  NMR spectrum, showing any part structures that can be identified, and the corresponding  $\delta$  values.



(d) The signal at  $\delta$  2.7 in the  $^1H$  NMR spectrum disappears when the sample is shaken with  $D_2O$ , and the signal  $\delta$  3.9 becomes a 1:3:3:1 quartet. What does this tell you about the structure?



(e) Analyze the  $^1H$  NMR spectrum. For each of the groups of signals marked on the spectrum, report the multiplet structure in the standard format (e.g., 0.0  $\delta$ , dtd,  $J = 0.0, 0.0, 0.0$  Hz, 2H) and any **part structure** you could obtain from the signal(s).

$\delta$  1.15, 1H, d,  $J = 7$  Hz       $\begin{matrix} H \\ | \\ CH_3-C \end{matrix}$

A  $\delta$  1.17, 1.18 - possible two methyl singlets, or isopropyl ( $J = 5$  Hz - a little small)

6 B  $\delta$  1.27, 3H, t,  $J = 7$  Hz       $CH_3-CH_2-$

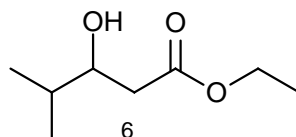
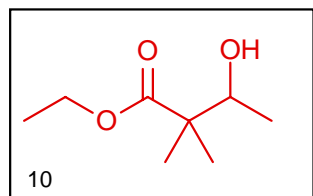
C  $\delta$  2.70, 1H, t,  $J = 7$  Hz       $-O-H$

D  $\delta$  3.86, 1H, pentet,  $J = 7$  Hz       $\begin{matrix} H \\ | \\ CH_3-C-OH \end{matrix}$

E  $\delta$  4.17, 2H, q,  $J = 7$  Hz       $-O-CH_2-CH_3$

(f) Give your answer below. If more than one structure fits the data, draw them, but indicate your best choice by circling the structure

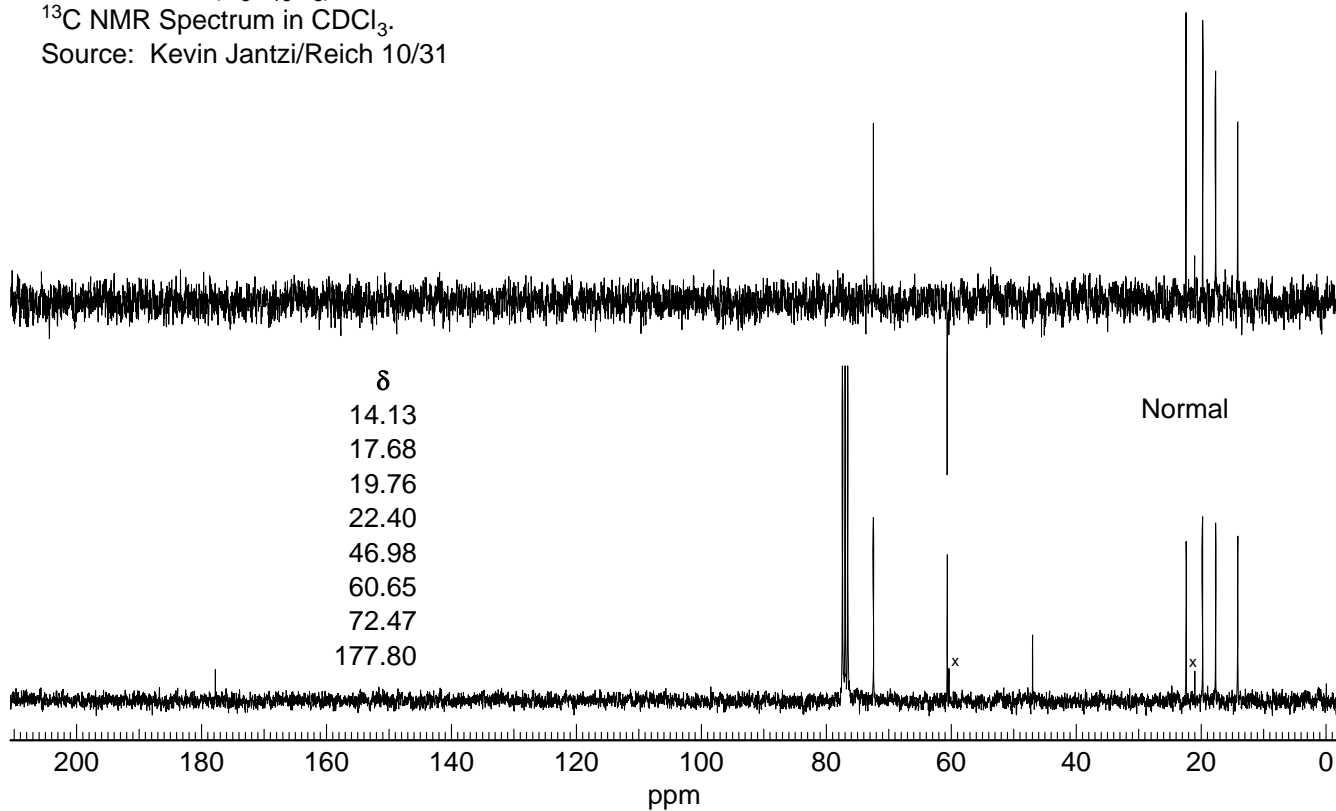
10





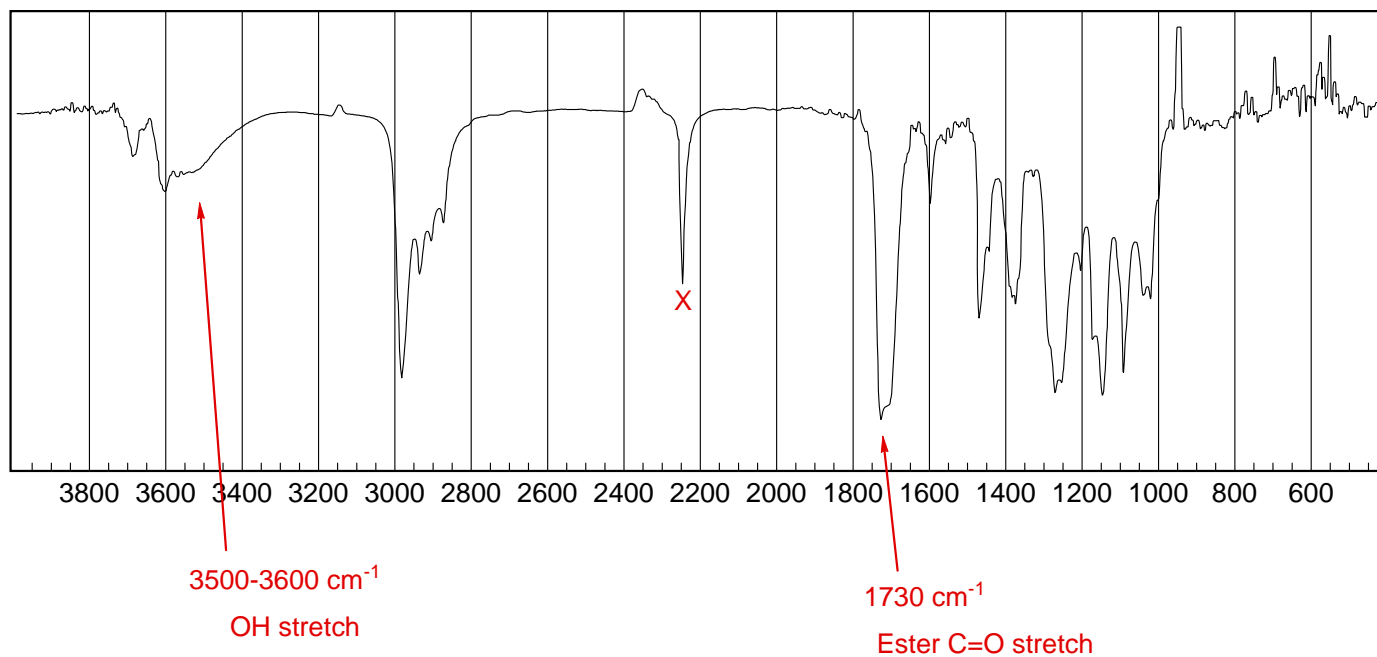
**Problem R-10E** ( $C_8H_{16}O_3$ ). $^{13}C$  NMR Spectrum in  $CDCl_3$ .

Source: Kevin Jantzi/Reich 10/31

**Problem R-10E** ( $C_8H_{16}O_3$ ).

IR Spectrum Neat

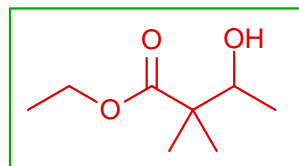
Source: Nicolet FT-IR



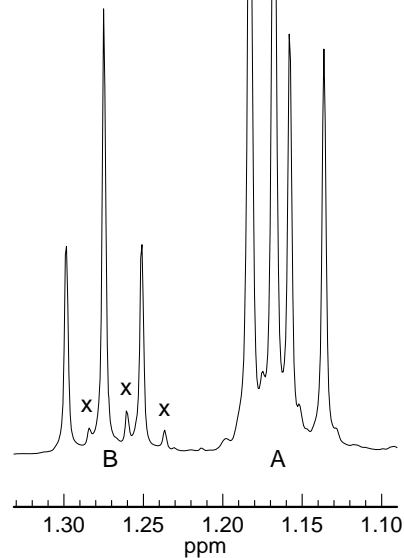
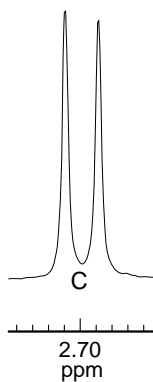
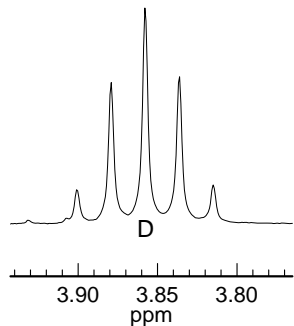
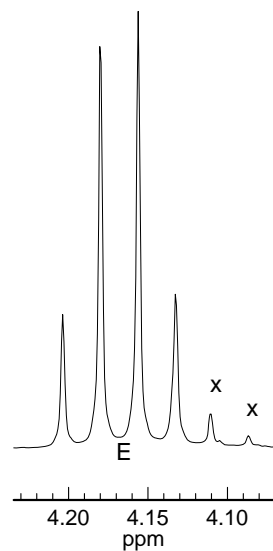
**Problem R-10E** ( $C_8H_{16}O_3$ ).

$^1H$  NMR Spectrum in  $CDCl_3$ .

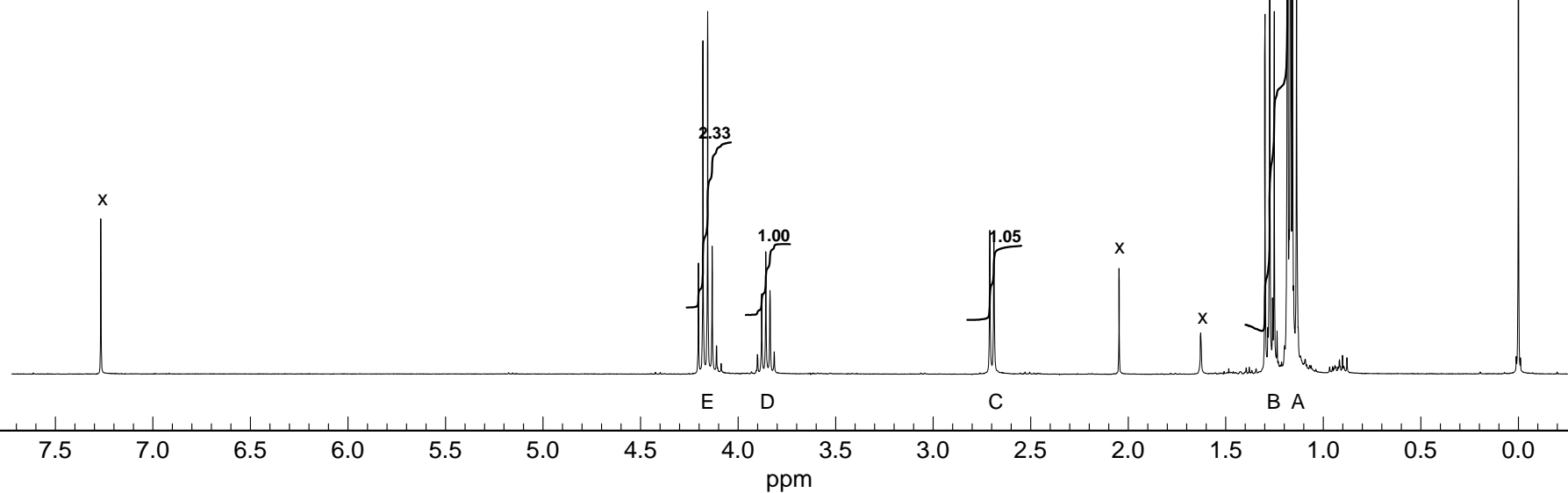
Source: Joe Langenhan/Gellman 10/31



30 20 10 0 Hz

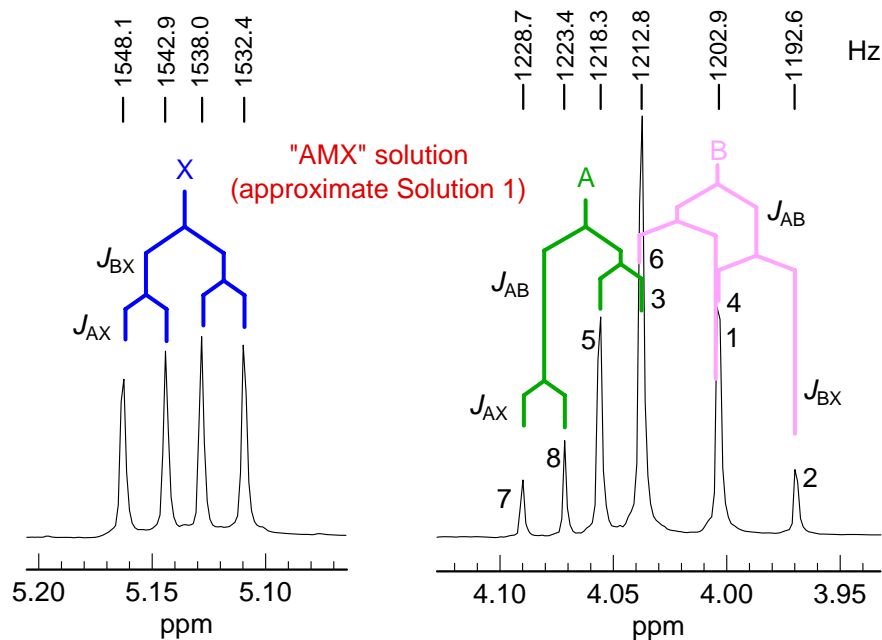
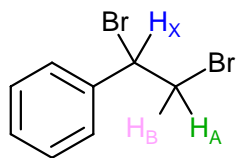


3.44



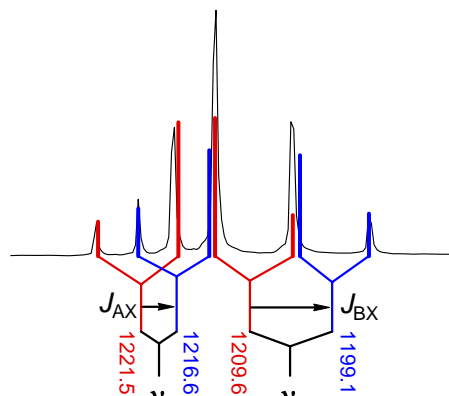
Problem **R-10G** ( $C_8H_8Br_2$ ). This problem requires you to analyze the signals at  $\delta$  4.1 and  $\delta$  5.2. You are given the structure.

(a) Do a "first order" analysis of the two multiplets shown below. Draw a coupling tree, and estimate couplings. What type of pattern is this?

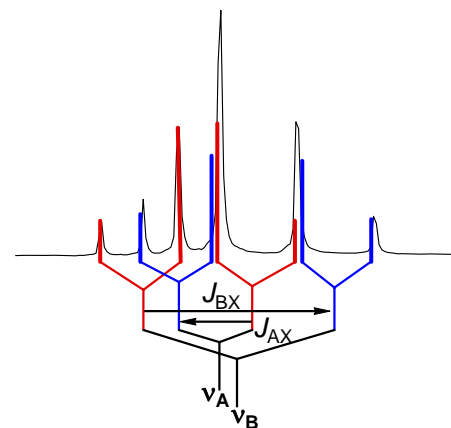


(b) Do an accurate (quantitative) analysis. Use the frequencies shown above. If more than one solution is possible, show them both, and draw the proper coupling tree on the spectra below. Use appropriate criteria to distinguish the two. Show your work, and tabulate your data in an easily readable form.

1	1202.9
2	1192.6
3	1212.8
4	1202.9
5	1218.3
6	1212.8
7	1228.7
8	1223.4



Solution 1



Solution 2

	Solution 1	Solution 2
$J_{AB}$	9.90 to 10.6	
$J_{AX}$	+4.93 (-)	-6.99 (+)
$J_{BX}$	+10.47 (-)	+22.39 (-)
$\nu_A$	1219.04	1213.09
$\nu_B$	1204.36	1210.31
$\nu_{AB}$	14.69	2.77
$i_{10} = i_{11}$	0.995	0.322
$\delta_A$	4.063	4.044
$\delta_B$	4.015	4.034

$$c^- = (5+3)/2 = 1215.55$$

$$\Delta\nu_{ab^-} = \delta^- = \sqrt{((7-1)(5-3))} = 11.9$$

$$c^- \pm \delta^-/2 = 1221.5, 1209.6$$

Solution 1 is correct:

1. Solution 2 has one negative  $^3J$ , which never happens
2. Intensity calculation fits better for Solution 1

$$c^+ = (6+4)/2 = 1207.85$$

$$\Delta\nu_{ab^+} = \delta^+ = \sqrt{((8-2)(6-4))} = 17.5$$

$$c^+ \pm \delta^+/2 = 1216.6, 1199.1$$

**Problem R-10G** ( $C_8H_8Br_2$ )

300 MHz  $^1H$  NMR Spectrum in  $CDCl_3$

(Source: Wayne Goldenberg/Reich 11/31)

