

## Problem Set 7

**Problem R-86C** ( $C_{10}H_{10}O_3$ ). From the infrared, proton NMR and carbon NMR spectra provided, determine the structure of R-86C. Whether you arrive at a satisfactory answer or not, answer each part below.

(a) DBE 6

(b) Analyze the IR spectrum.

1780  $cm^{-1}$  ester/lactone, maybe slightly strained ring (5 ring) normal ester at 1740  $cm^{-1}$

1610  $cm^{-1}$  Aromatic C=C stretch

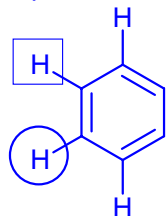
1200  $cm^{-1}$  Ester C-O stretch

No OH, so the three O must be carbonyl or ether type

(c) What does the region  $\delta$  7 to  $\delta$  8 in the  $^1H$  NMR spectrum tell you? Draw part structures.

- 4H aromatic region - unsymmetrically disubstituted aromatic ring

- The multiplets at 7.70 and 7.56 (td,  $J = 8, 1.5$  Hz) are each due to a proton with two ortho and one meta coupling



- the dt? are the other two protons, with only one ortho coupling

(d) Analyze the  $^{13}C$  NMR spectra. Draw part structures.

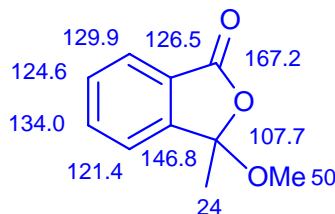
- one OMe at  $\delta$  50.3

- one C-CH<sub>3</sub> at  $\delta$  24.3 ppm

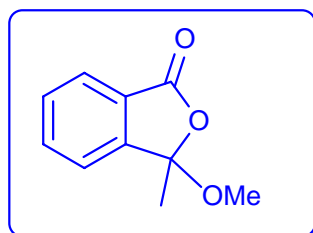
- one ester/lactone C=O  $\delta$  167.2

- one quaternary carbon at  $\delta$  107.7 C(OR)<sub>2</sub> ?

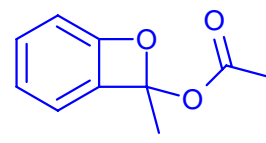
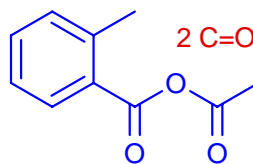
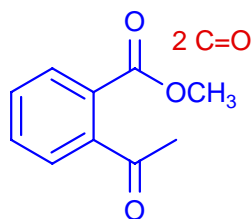
- 4 other aromatic C-H carbons



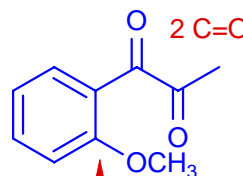
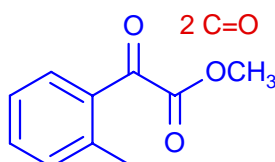
(e) Draw possible structures for R-86C below. Circle your best guess, and label it with as many of the  $^{13}C$  shifts as you can assign.



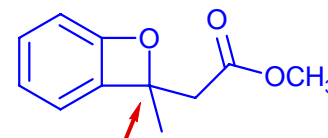
expect ca  $\delta$  160 not 147



expect  $\delta$  25, not 50



expect ca  $\delta$  160 not 147



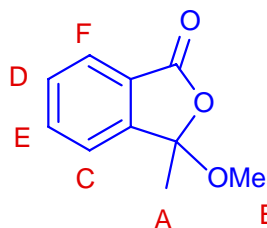
expect 70, not 108

Expect 80?

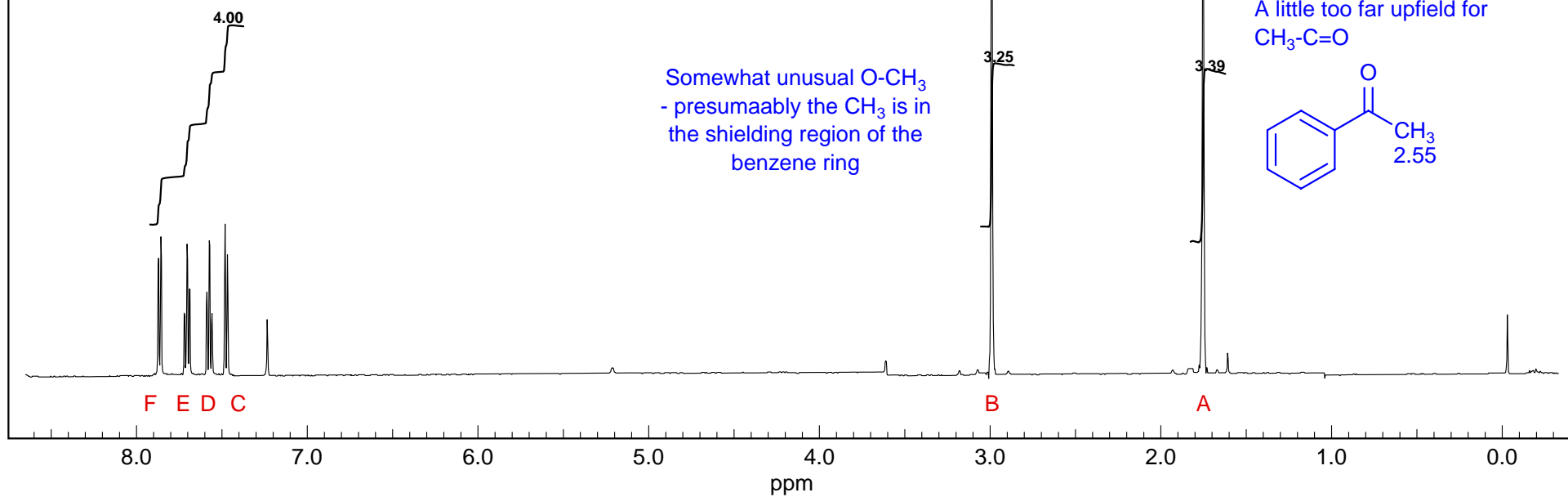
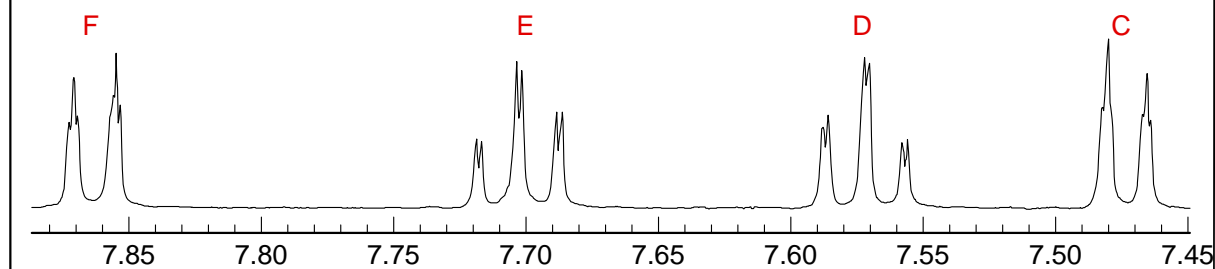
**Problem R-86C** (C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>)

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

(Source: Wesley L. Whipple/Reich 3-16)

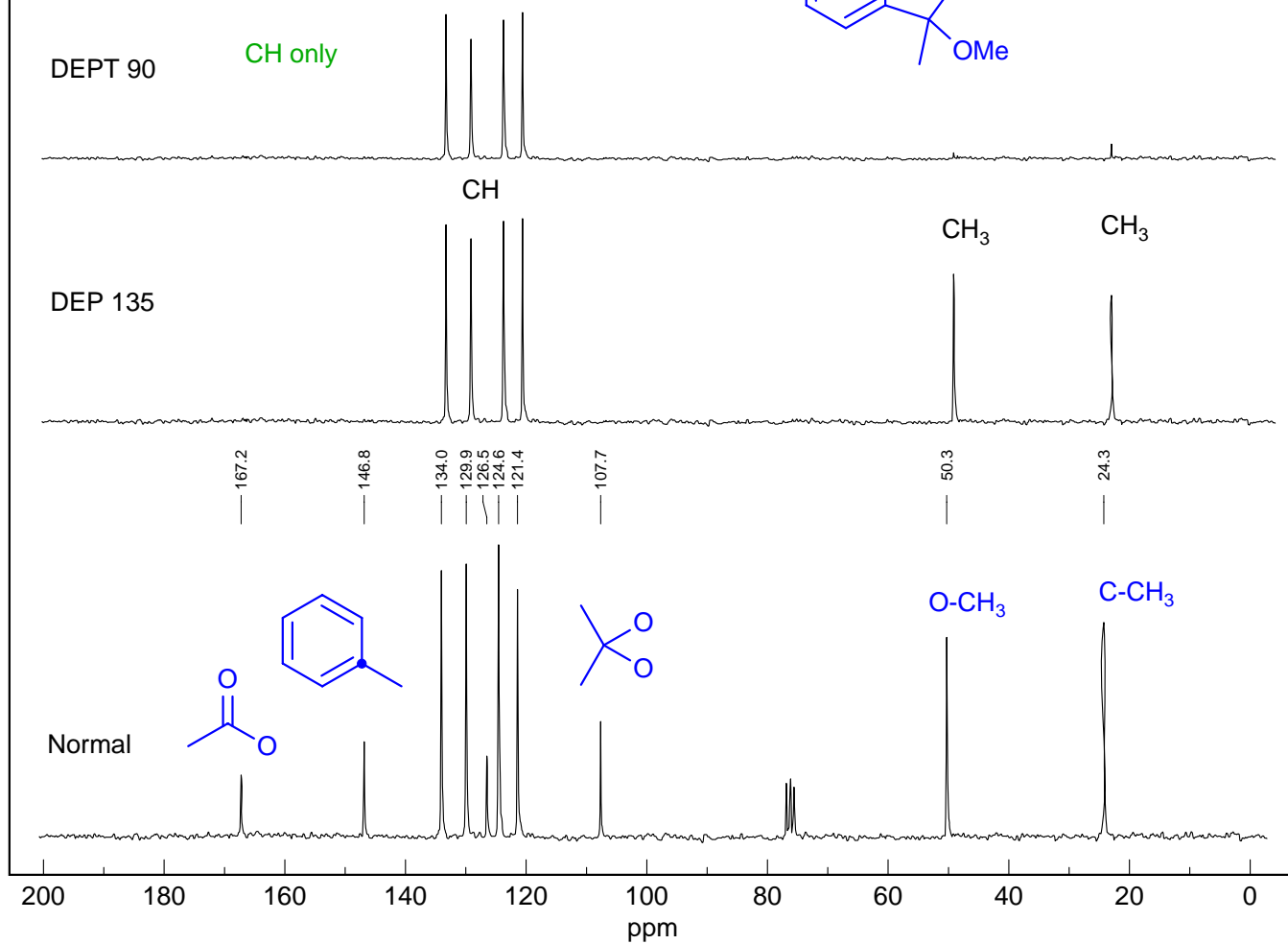
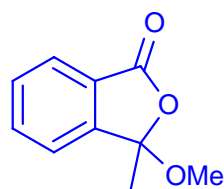


30 20 10 0 Hz



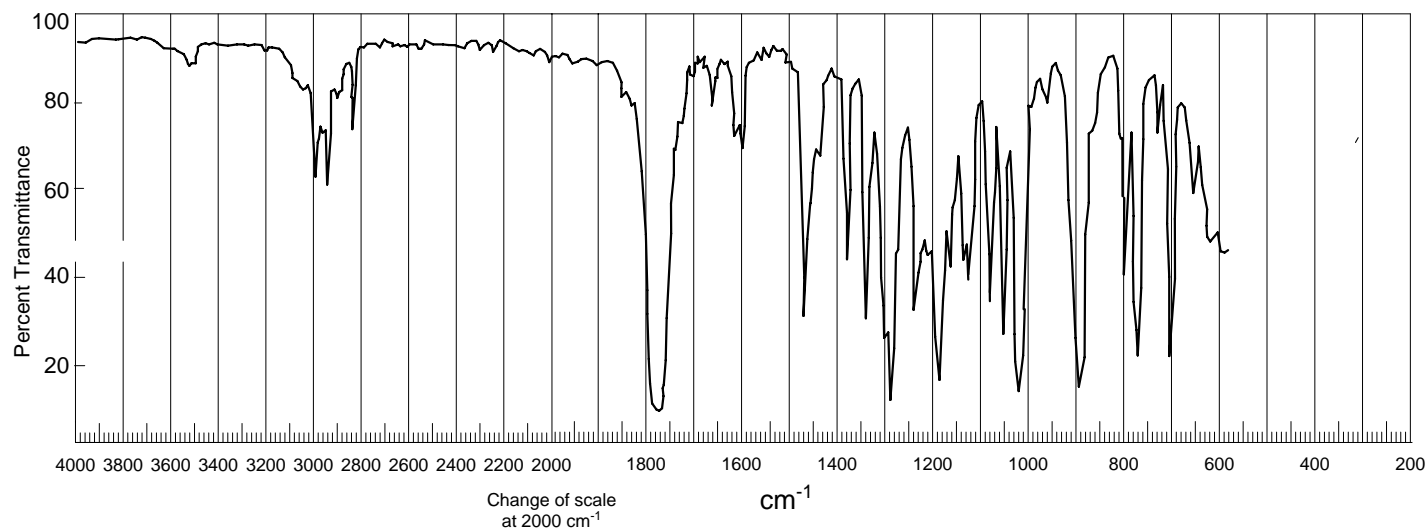
**Problem R-86C** ( $C_{10}H_{10}O_3$ )50 MHz  $^{13}C$   $\{^1H\}$  NMR Spectrum in  $CDCl_3$ 

(Source: Wesley L. Whipple/Reich 3-16)

**Problem R-86C** ( $C_{10}H_{10}O_3$ )

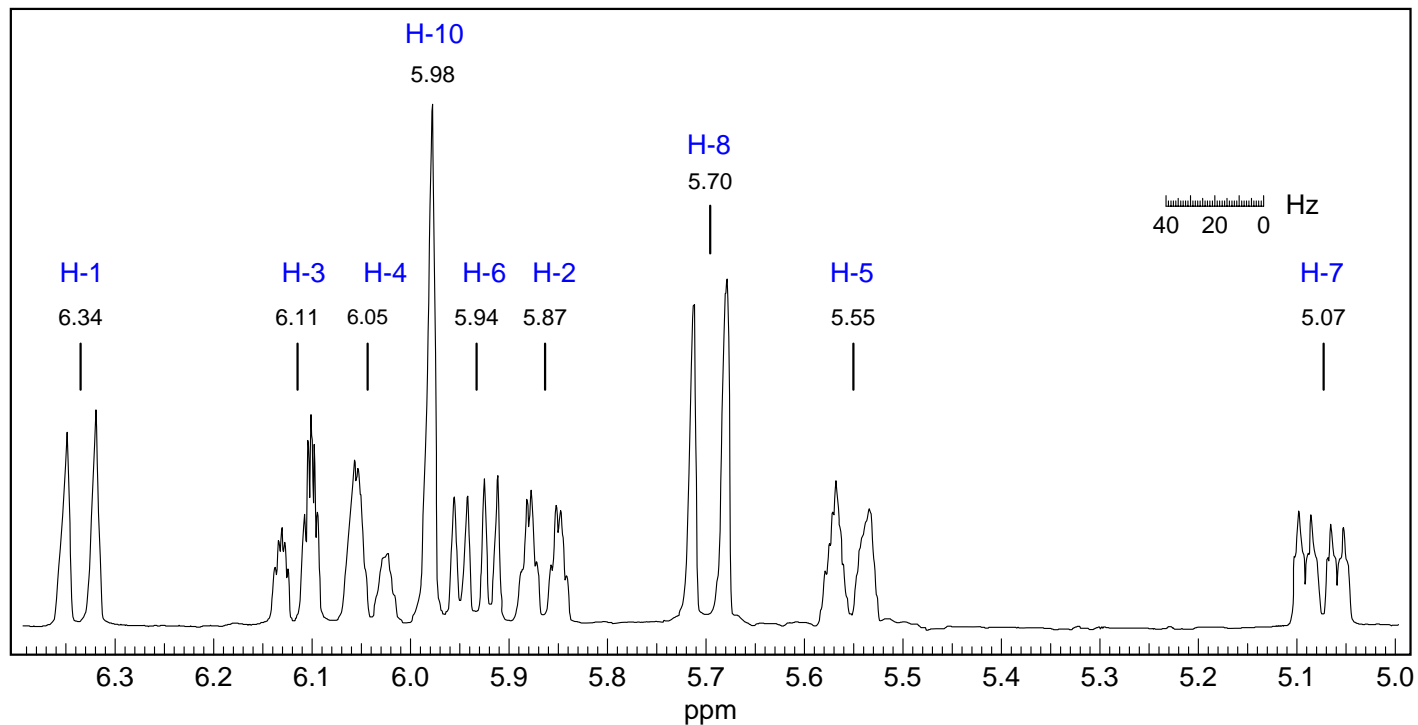
IR Spectrum neat

(Source: Wesley L. Whipple/Reich 3-16)



## R-920 (EX-3-92) - answer

**Problem R-920 (C<sub>12</sub>H<sub>15</sub>N).** Assign the individual signals of the compound whose 400 MHz <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, -10 °C ) is given below. Use couplings, chemical shifts and intensities in your analysis. From their analysis, the authors deduced the conformation shown (Otter, A.; Neuenschwander, M.; Kellerhals, H. P. *Magn. Reson. Chem.* **1986**, 24, 353).



δ

6.34	<u>1</u>
6.11	<u>3</u>
6.05	<u>4</u>
5.98	<u>10</u>
5.94	<u>6</u>
5.87	<u>2</u>
5.70	<u>8</u>
5.55	<u>5</u>
5.07	<u>7</u>

1. The two doublets without additional coupling have to be H-1 and H-8. The enamine nitrogen can only conjugate with the 7-8 double bond trans to the NMe<sub>2</sub> group, not with the 1-2 double bond (steric effects) so H7 and H5 are moved upfield (this is how you decide between H-1 and H-8). Once H-7 is assigned, then all the others fall into place by consideration of leanings and the small coupling

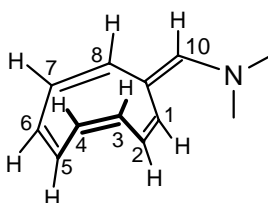
2. Start with H-8 (5.70) - leaning shows it must be coupled to 5.07 (H-7) not to 5.55, which would have to lean a lot more (observed leaning is 1.10, coupling to 5.55 would have to lean 1.6).

3. The unique small coupling to H-7 must be to H-6, 5.94

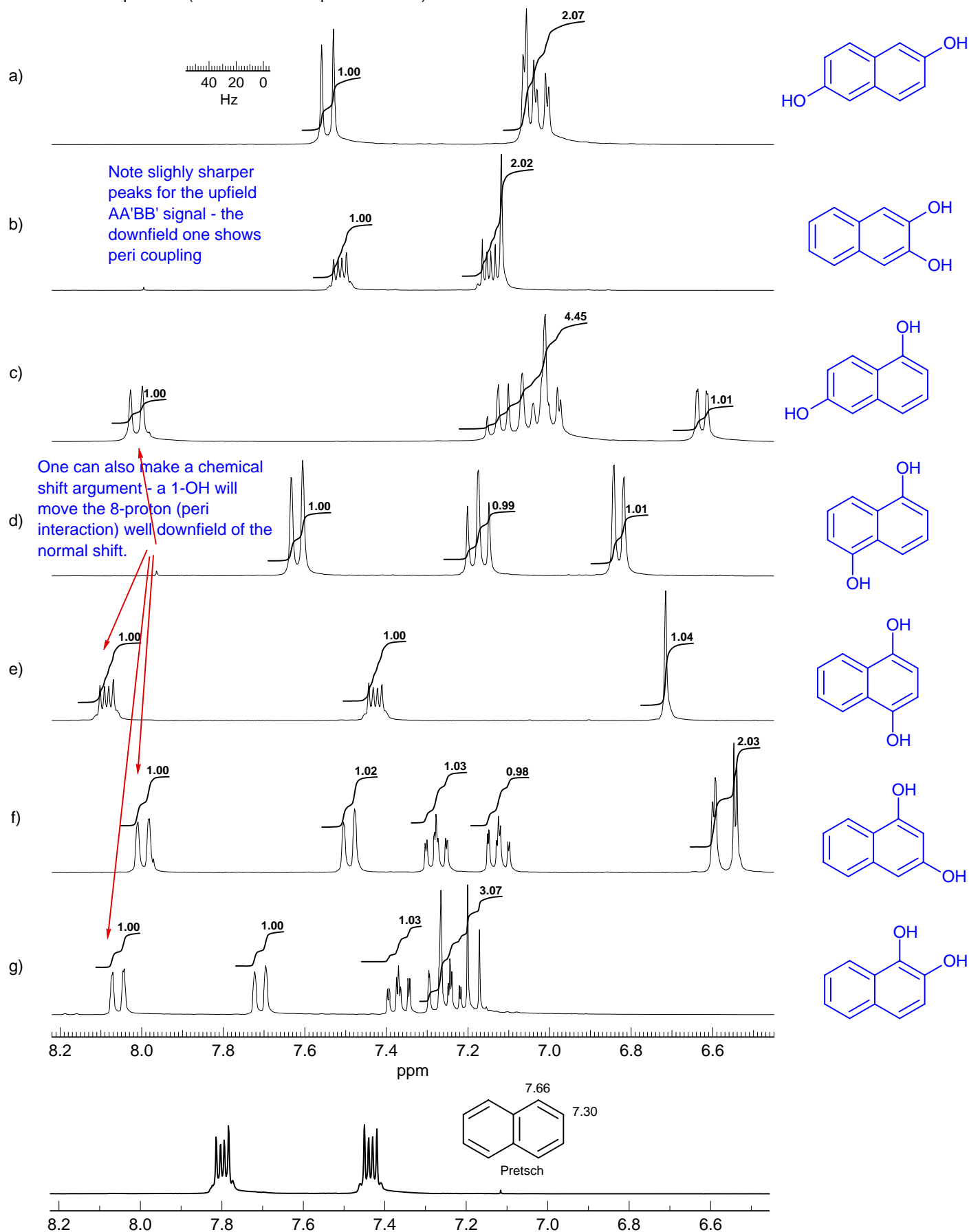
4. Leaning of H-6 means coupling to 5.55, thus H-5 (not to 5.87)

5. Now start with H-1 (6.34). Only remaining proton it can be coupled to is 5.87, thus H-2

6. This leaves H-3 and H-4, 6.11, 6.05. Hard to decide which is which.

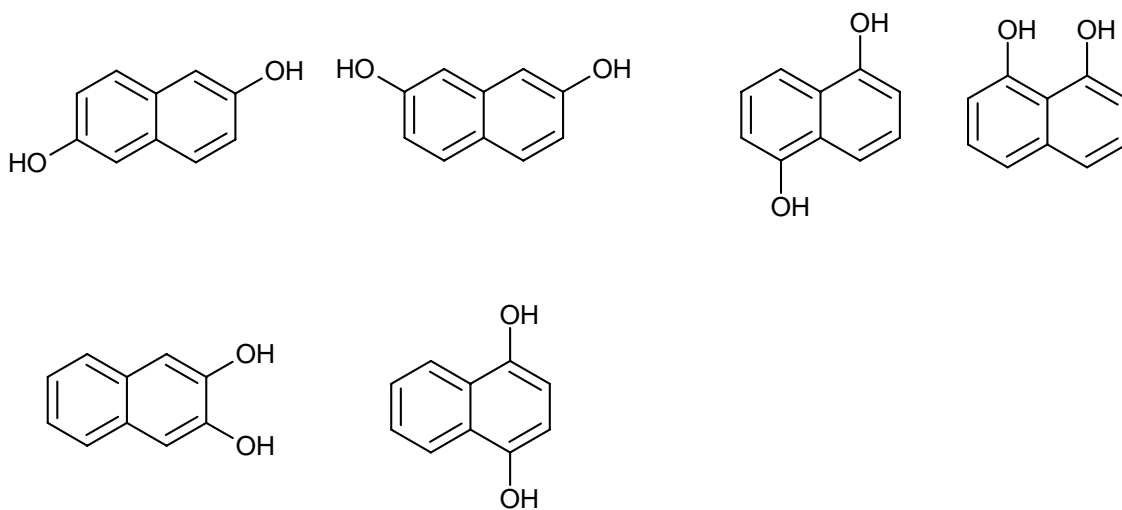


**Problem R-021H.** The partial 300 MHz  $^1\text{H}$  NMR spectra below are a series of dihydroxynaphthalenes. Determine the substitution patterns (Source: Aldrich Spectra Viewer).

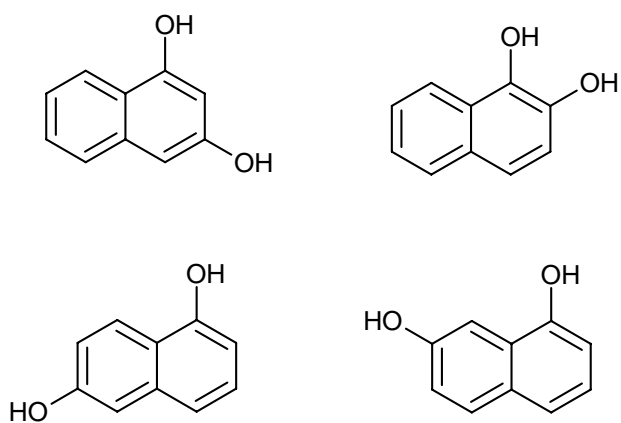


**Problem R-021H.** The partial 300 MHz  $^1\text{H}$  NMR spectra below are a series of dihydroxynaphthalenes. Determine the substitution patterns (Source: Aldrich Spectra Viewer).

**Symmetric (3 different signals)**

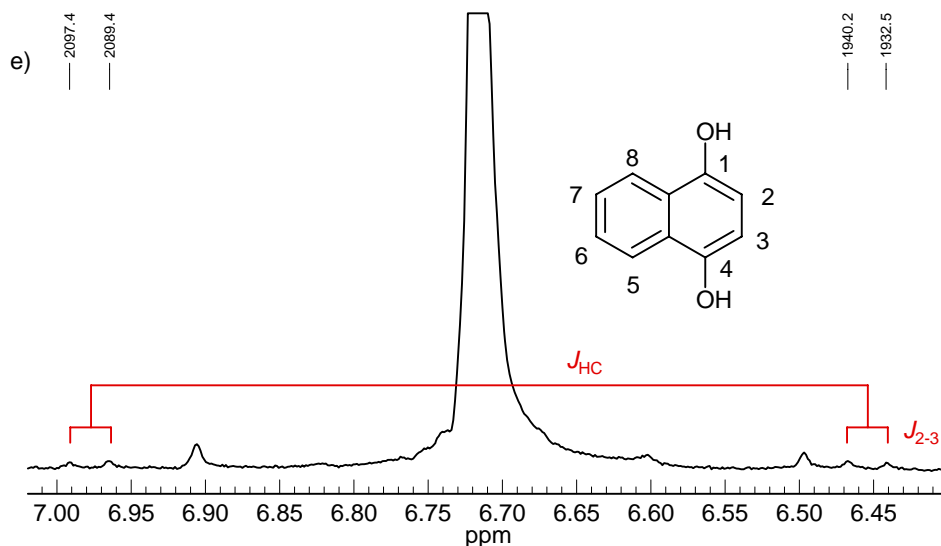
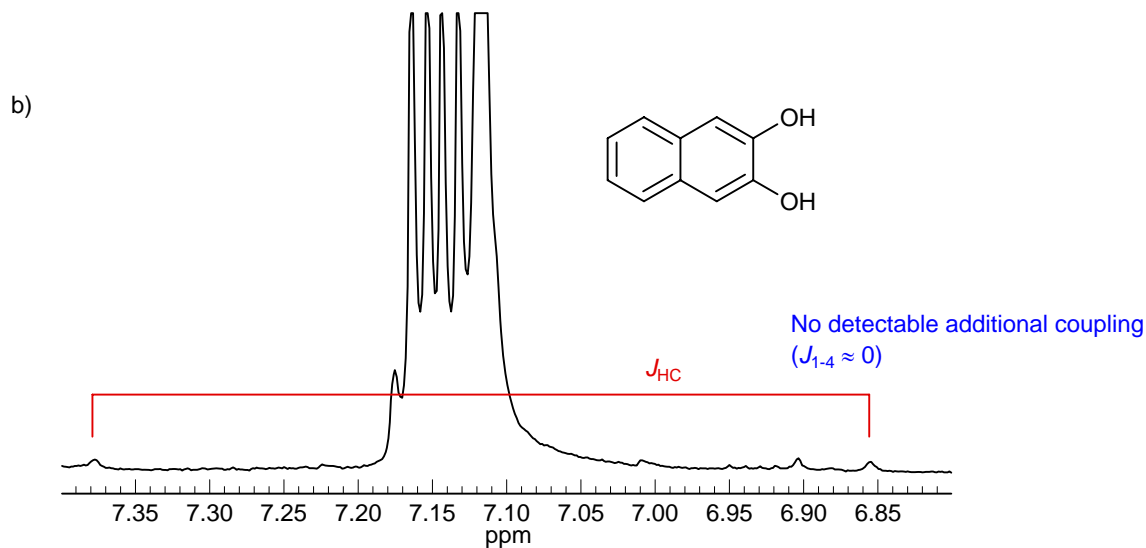


**Unsymmetric (6 different signals)**



**Problem R-021H.** The partial 300 MHz  $^1\text{H}$  NMR spectra below are a series of dihydroxynaphthalenes. Determine the substitution patterns (Source: Aldrich Spectra Viewer).

The 1,2- and 2,3-dihydroxynaphthalenes can be distinguished by observing the  $^{13}\text{C}$  satellites of the singlet corresponding to  $\text{H}^1/\text{H}^4$  or  $\text{H}^2/\text{H}^3$ . In the latter each  $^{13}\text{C}$  satellite is a doublet due to the ortho coupling, for the former the satellite peak is a singlet (para-coupling is too small to resolve)



There is another way to distinguish these isomers using the effects of long-range couplings. In the 2,3-dihydroxynaphthalene the 1 and 4 protons are going to be significantly coupled to the 5 and 8 protons, so the 1,4-singlet will be broader, as will the signals of the 5,8 protons. Note that the AA' signal at  $\delta$  7.2 is noticeably sharper and taller than the BB' signal at  $\delta$  7.5. For the 1,4-dihydroxynaphthalene the AA' and BB' signals are exactly the same height, and the 2,3-singlet is relatively taller, since there is now no significant coupling across the two rings.

These broadening effects due to cross-ring coupling can also be seen in other isomers. For example in (f) the  $\text{H}^2\text{-H}^4$  AB quartet is unsymmetrical. One doublet is broader and more poorly resolved, this must be the  $\text{H}^4$  signal

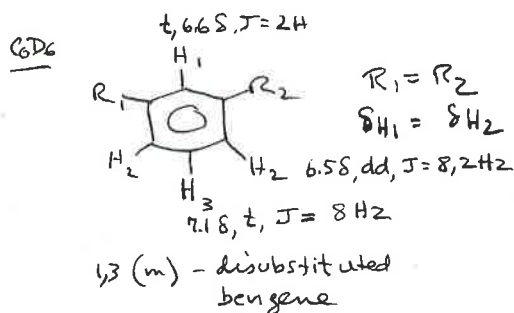
**Problem R-90F** ( $C_{12}H_{14}O_2$ ). In this problem you are required to determine a structure from the  $^{13}C$  and  $^1H$  spectra of a compound. To aid in your analysis,  $^1H$  spectra are provided in both  $CDCl_3$  and  $C_6D_6$  solution.

- 2 (a) DBE 6. (b) Summarize the information you were able to obtain from your analysis of the  $^{13}C$  NMR spectra. Identify part structures that are present in the molecule.

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- the molecule has some symmetry - only 7 signals for 12 carbons
- $CH_2$  at  $\delta$  117 must be  $CH_2=C$
- $CH_2$  at  $\delta$  68  $-CH_2-O-$
- Probably an aromatic compound with symmetrical substitution

(c) Interpret the signals at  $\delta$  6.3 to  $\delta$  7.3. What do these signals tell you about the structure? Draw a part structure, and label it with  $\delta$  and J values taken from the  $C_6D_6$  spectrum. Why is the downfield multiplet so much simpler in the  $C_6D_6$  spectrum?



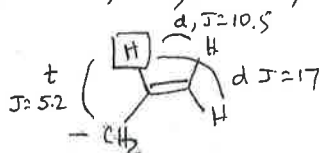
$R_1 = R_2$ . These groups must be electron donating, since  $H_1$  and  $H_2$  are upfield of normal aromatic region

The 7.18 signal is more complicated in the  $CDCl_3$  spectrum because  $H_1$  and  $H_2$  are strongly coupled, thus  $H_3$  shows virtual coupling effects

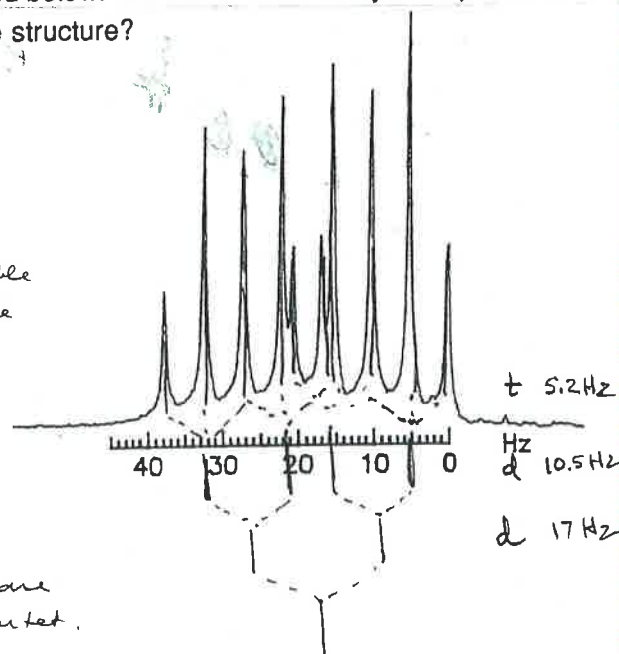
(d) The multiplet at  $\delta$  6.0 in the  $^1H$  NMR spectrum is reproduced below. Do a first-order analysis, report multiplicity and J values. What does this signal tell you about the structure?

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$ddt, J = 17, 10.5, 5.2 Hz$



Since each of the signals is double intensity, must be two of these



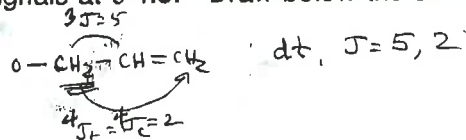
(e) Interpret the signals  $\delta$  5.2 to  $\delta$  5.5.

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These are the terminal vinyl protons:  $\delta$  5.2,  $dq, J = 10, 2$   
 $\delta$  5.3,  $dq, J = 17, 2$

The long range  $^4J$  and  $^2J_{gem}$  are essentially same, hence quartet.

(f) Interpret the signals at  $\delta$  4.5. Draw below the structure of R-90F.





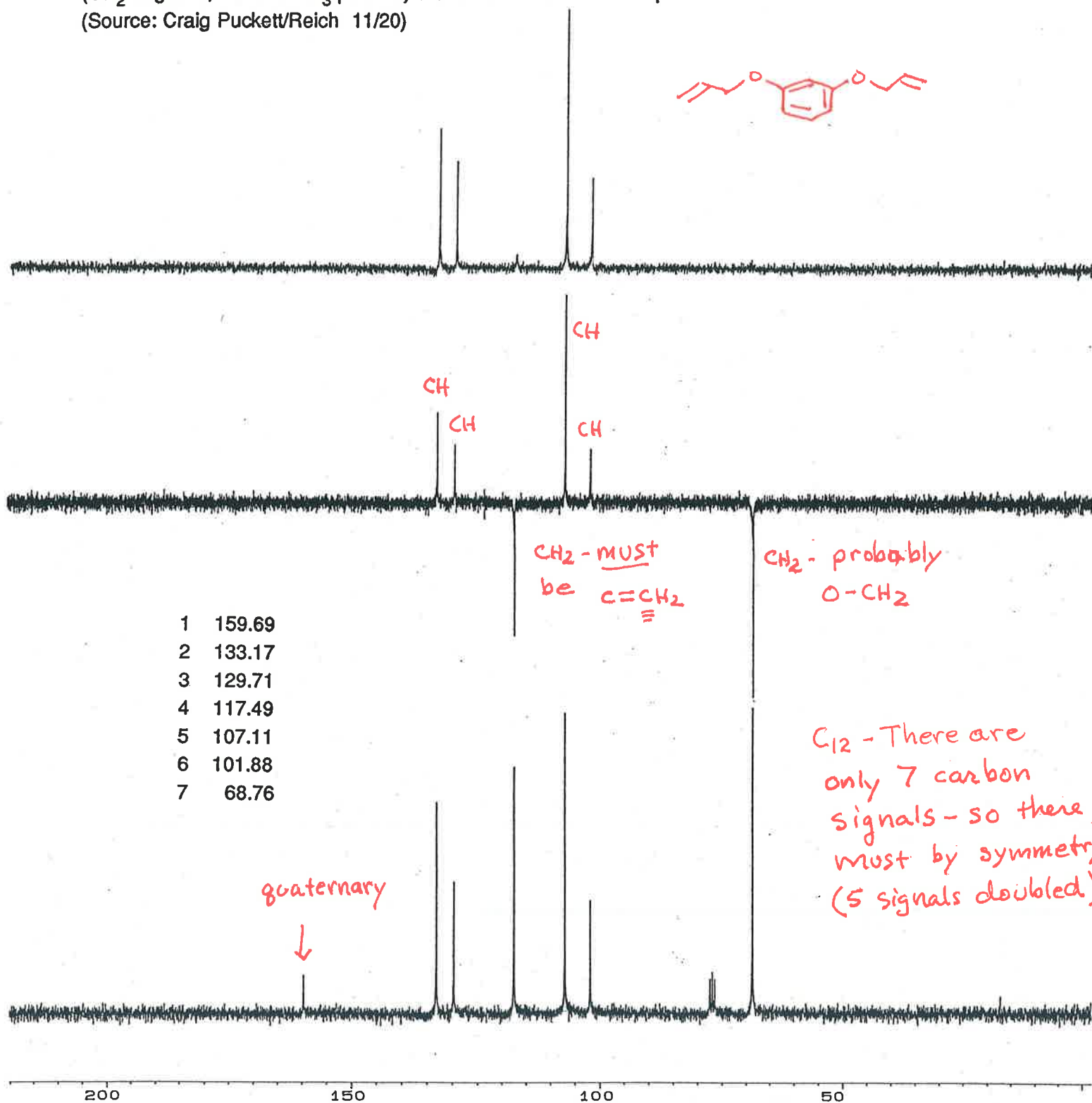
Problem R-90F (C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>)

67.5 MHz <sup>13</sup>C NMR Spectra in CDCl<sub>3</sub>

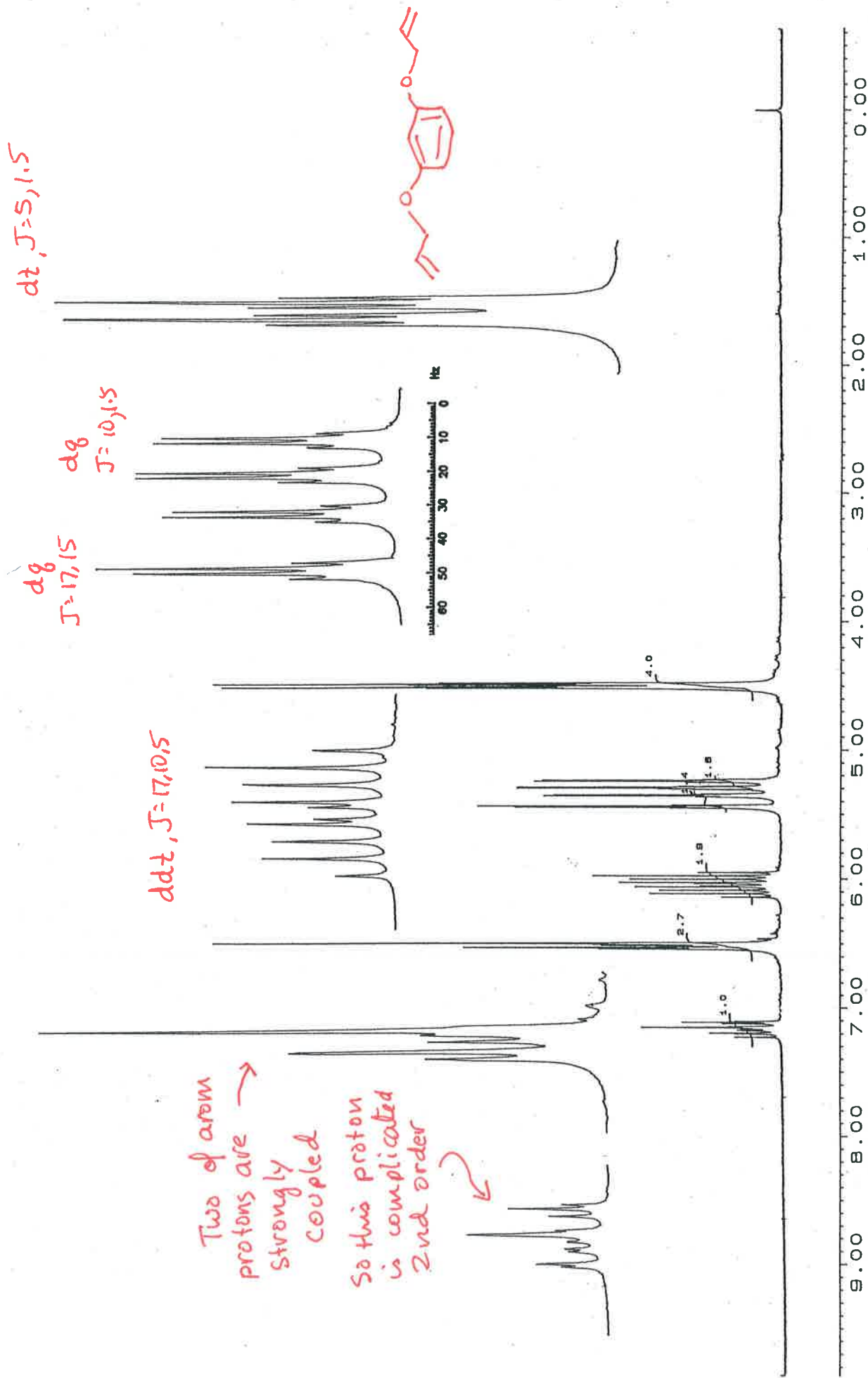
The upper spectrum is a DEPT 90, the middle one a DEPT 135 spectrum

(CH<sub>2</sub> negative, CH and CH<sub>3</sub> positive) the lower one a normal acquisition.

(Source: Craig Puckett/Reich 11/20)



Problem R-90F ( $C_{12}H_{14}O_2$ )  
 200 MHz  $^1H$  NMR Spectrum in  $CDCl_3$   
 (Source: Craig Puckett/Reich 11/20)



Problem R-90F (C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>)

200 MHz <sup>1</sup>H NMR Spectrum in C<sub>6</sub>D<sub>6</sub>

(Source: Craig Puckett/Reich 11/20)

