

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 _____

(b) Analyze the IR spectrum.

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

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

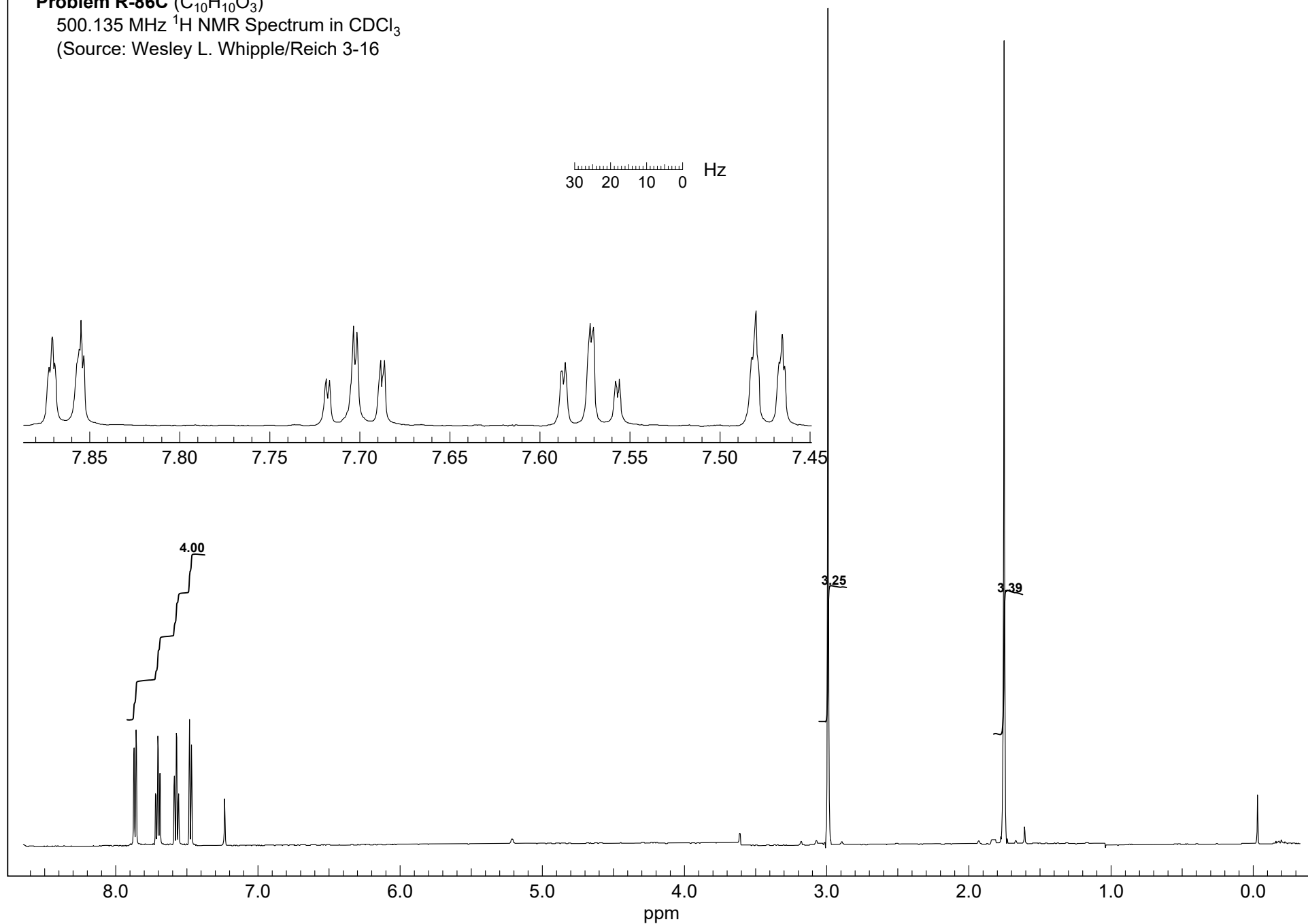
(e) Draw possible structures for R-86C below. Circle your best guess, and label it with as many of the ^{13}C shifts as you can assign.

Problem R-86C ($\text{C}_{10}\text{H}_{10}\text{O}_3$)

500.135 MHz ^1H NMR Spectrum in CDCl_3

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

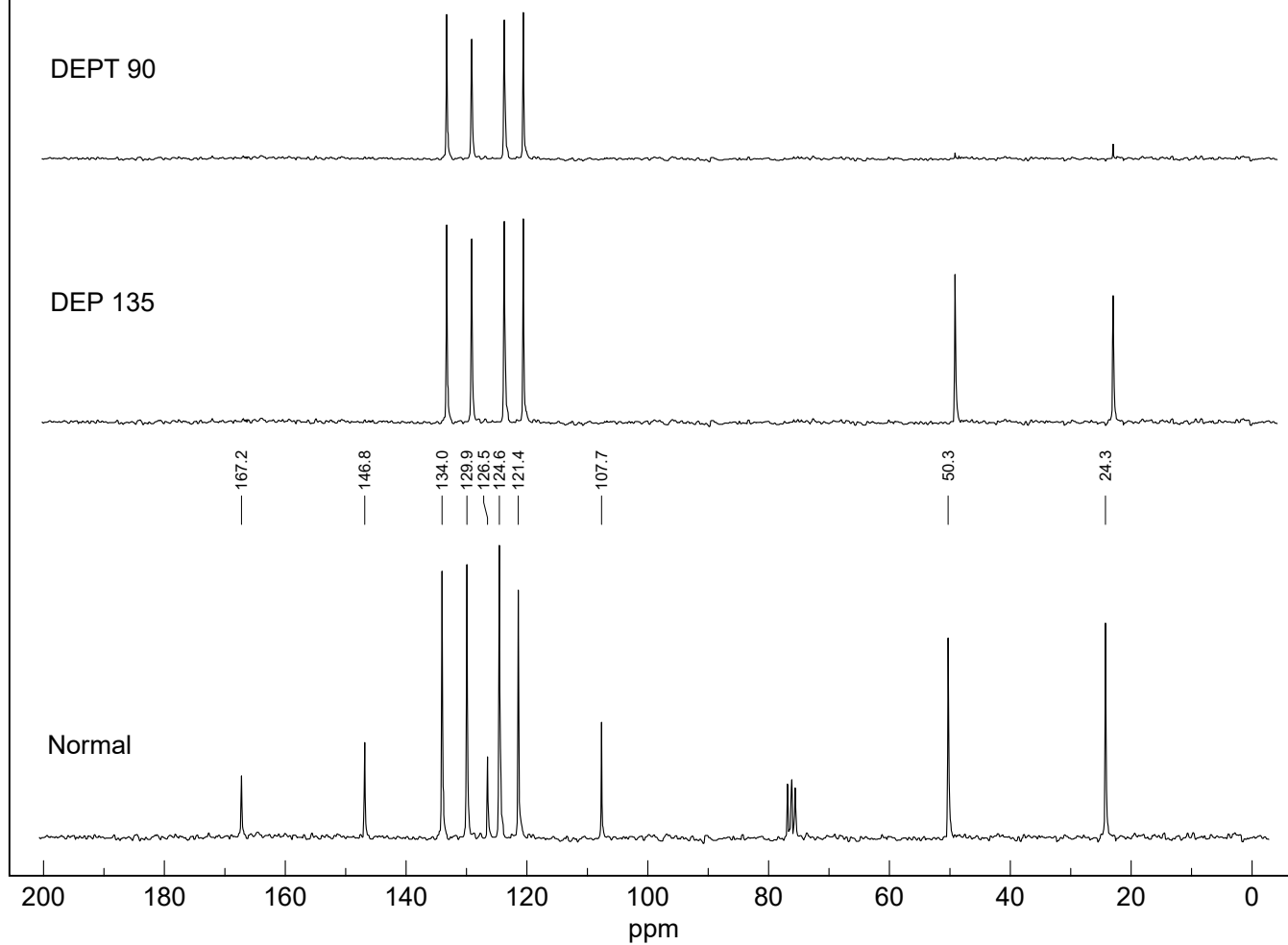
30 20 10 0 Hz



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

50 MHz ^{13}C $\{^1H\}$ NMR Spectrum in $CDCl_3$

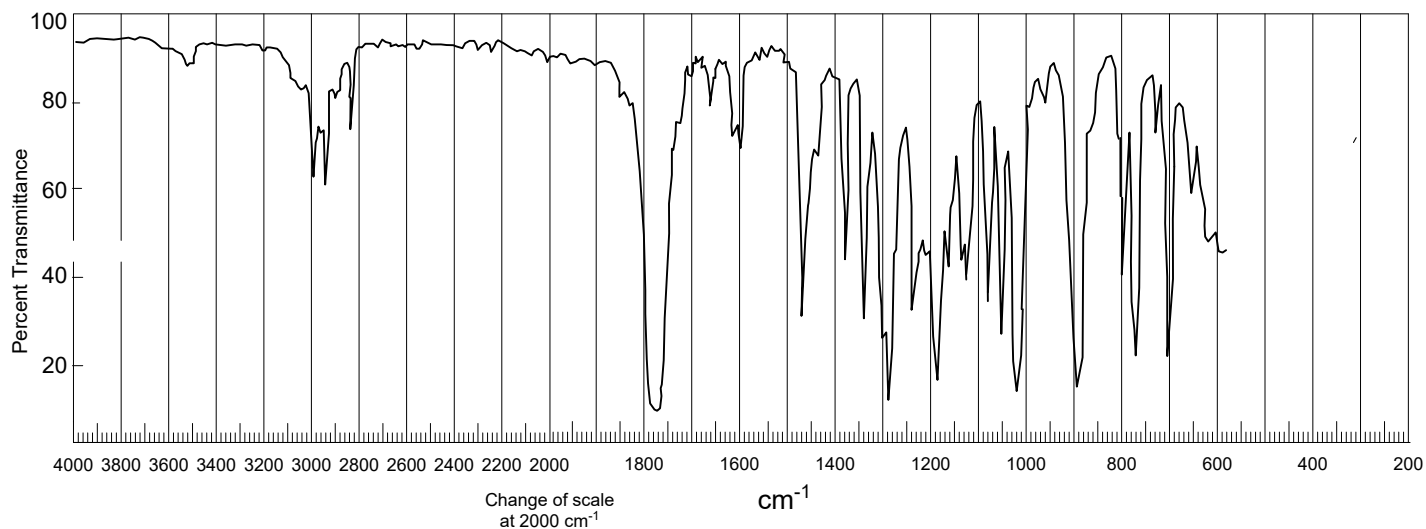
(Source: Wesley L. Whipple/Reich 3-16)



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

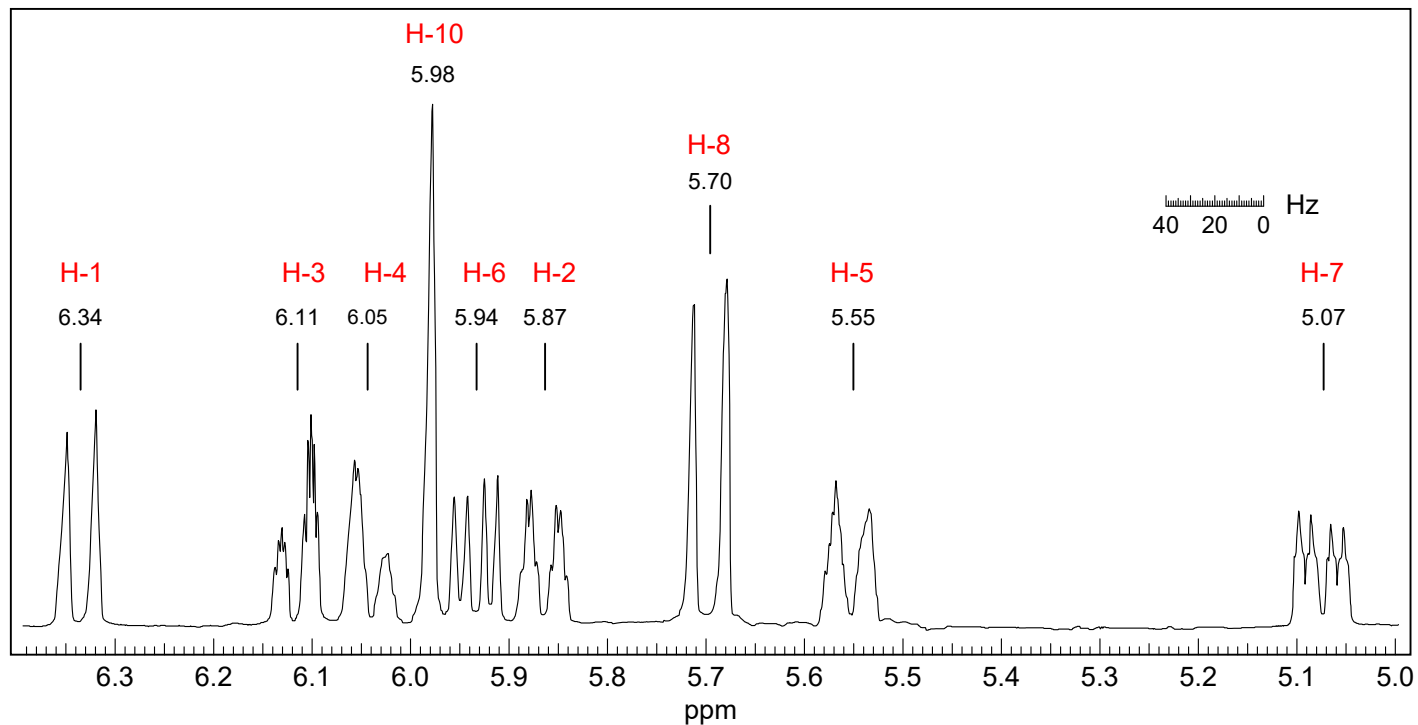
IR Spectrum neat

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



R-92O (EX-3-92) - answer

Problem R-92O (C₁₂H₁₅N). Assign the individual signals of the compound whose 400 MHz ¹H NMR spectrum (CDCl₃, -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 NMe₂ 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

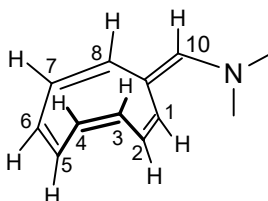
2. Start with H-8 (5.70) - leaning shows it must be coupled to 5.07 (H-7) not to 5.55, which would have to lean a lot more (observed leaning is 1.10, coupling to 5.55 would have to lean 1.6).

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

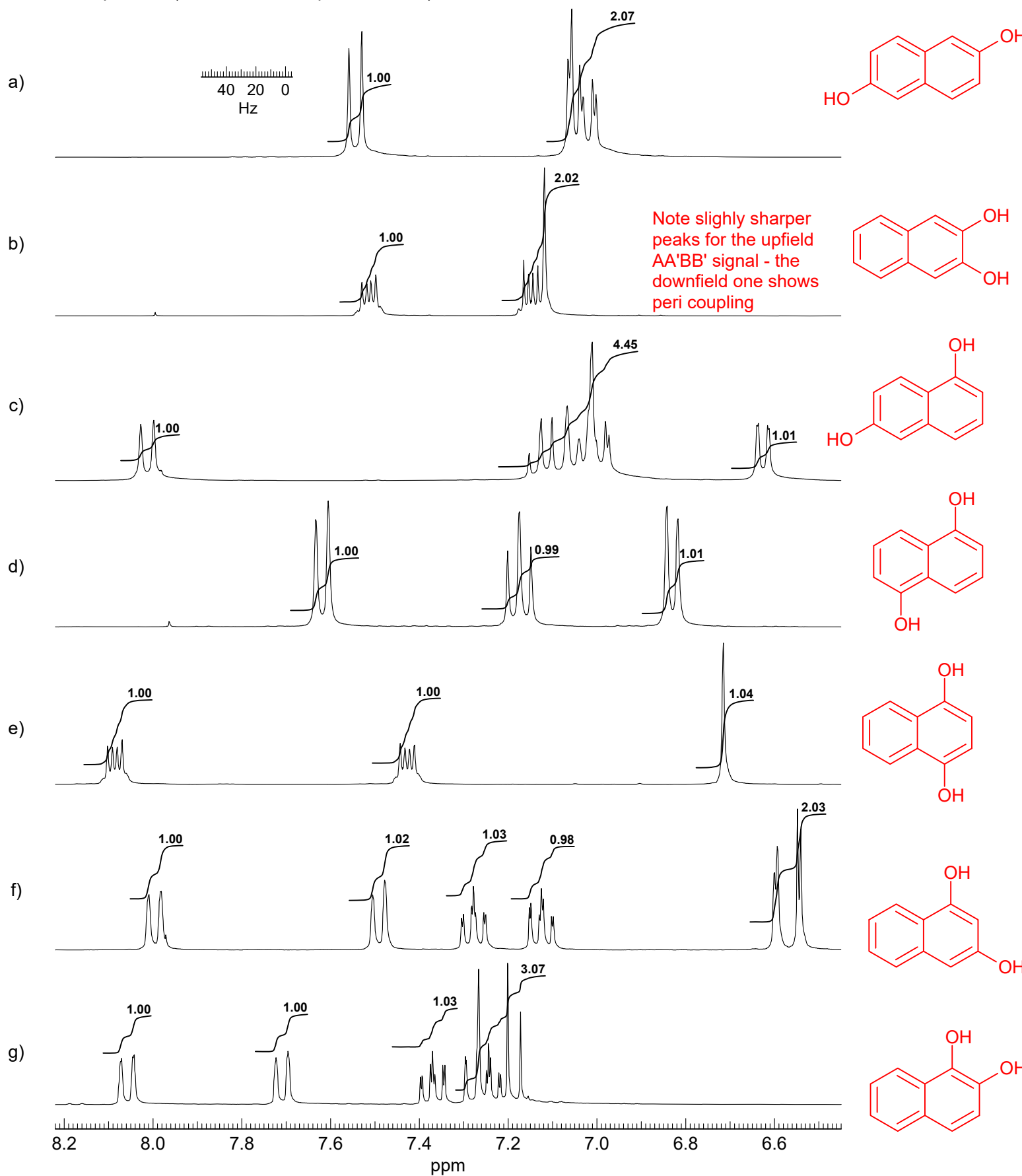
4. Leaning of H-6 means coupling to 5.55, thus H-5 (not to 5.87)

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.

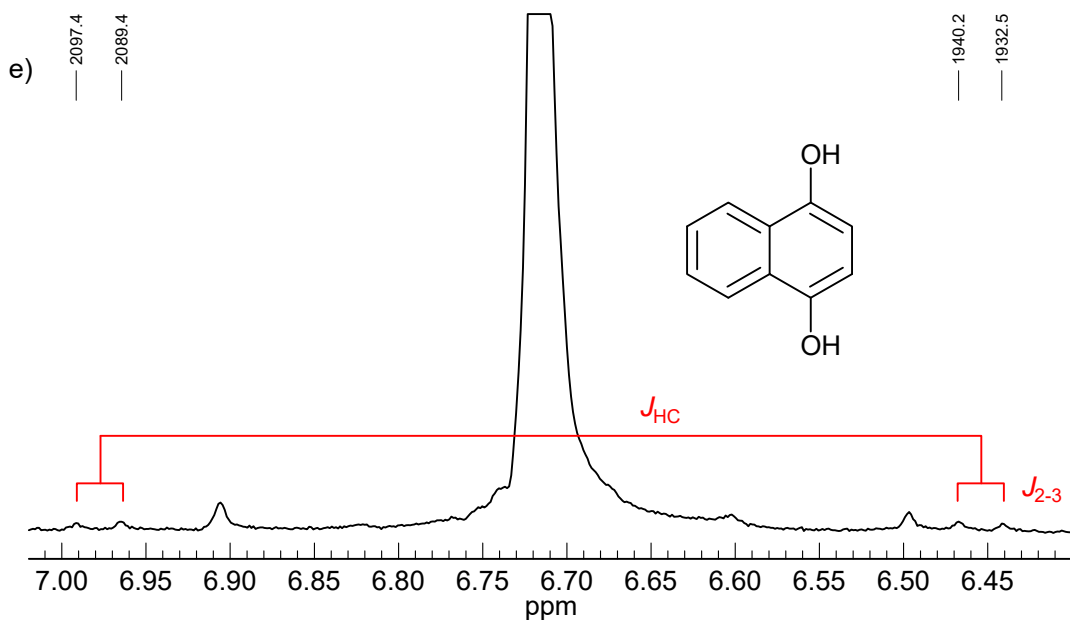
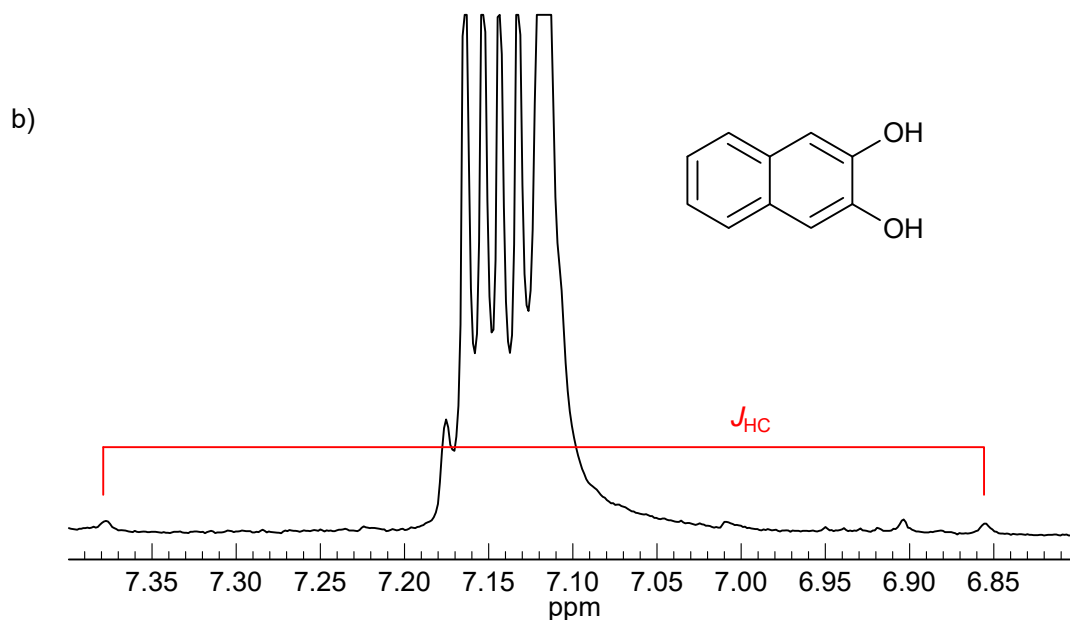


Problem R-021H. The partial 300 MHz ^1H NMR spectra below are a series of dihydroxynaphthalenes. Determine the substitution patterns (Source: Aldrich Spectra Viewer).



Problem R-021H. The partial 300 MHz ^1H 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}C satellites of the singlet corresponding to H^1/H^4 or H^2/H^3 . In the latter each ^{13}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 δ 7.2 is noticeably sharper and taller than the BB' signal at δ 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 H^4 signal