Chemistry 605 (Reich)

SECOND HOUR EXAM

Thur. April 14, 2011

Practice Exam 2 Answer

Question/Points

R-10F_____/25

R-10G_____/20

R-10H_____/10

R-10I_____/25

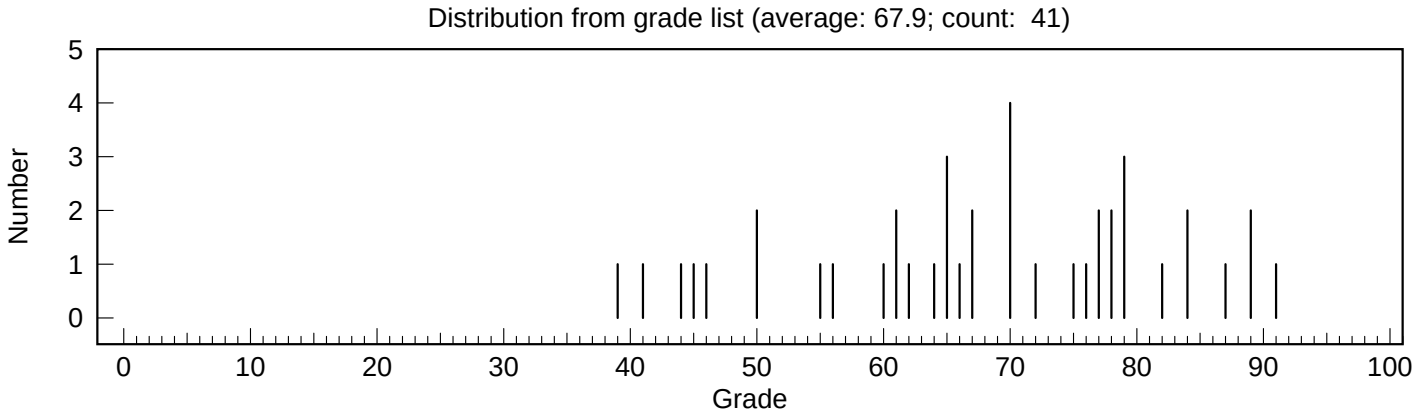
R-10J_____/20

Total _____/100

Hi	91
Average	68
Median	70
AB	78
BC	50
CD	40

Grading

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.

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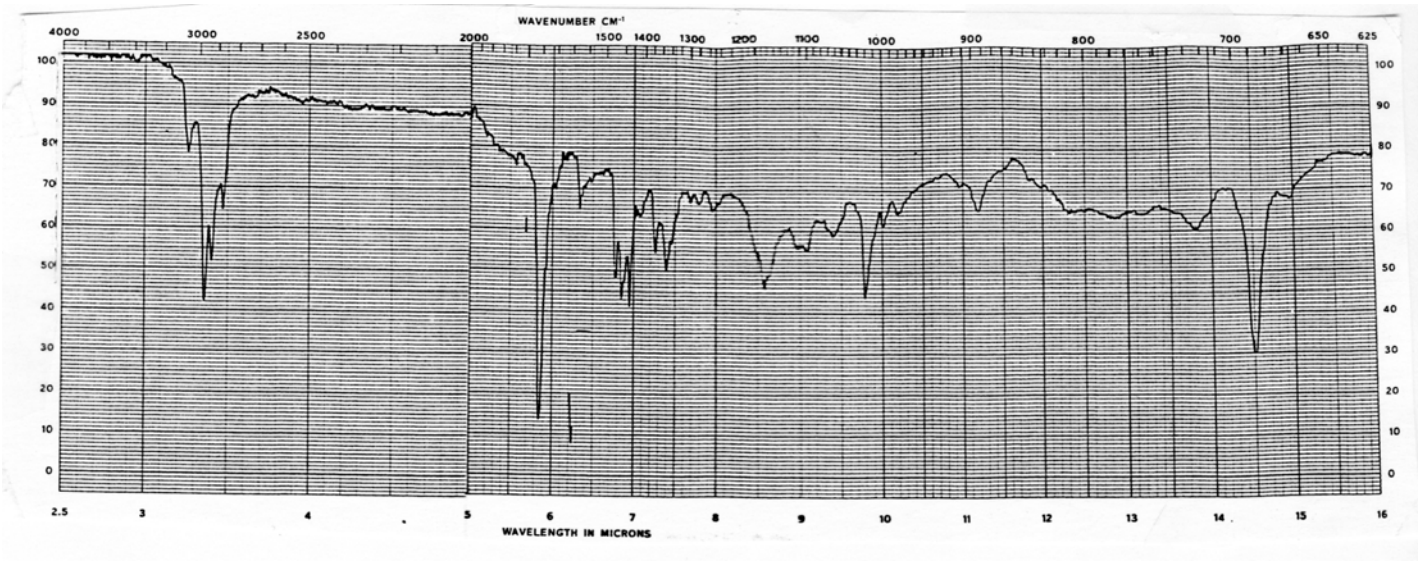
Problem R-10F ($C_{12}H_{16}OSe$). In this problem you are required to determine a structure from the IR and ^1H NMR spectra of a compound. The compound contains a Ph-Se group.

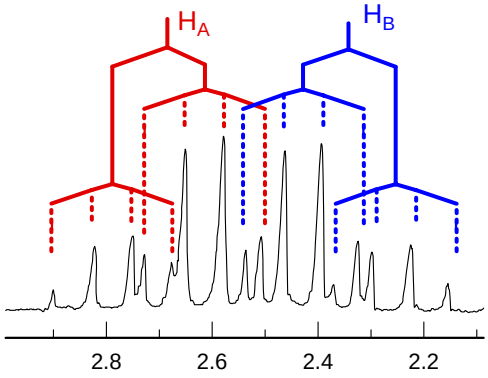
2 (a) DBE 5. (b) Report your analysis of the IR spectrum (CCl_4). List the data and any conclusions you drew from it.

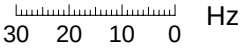
1710 cm^{-1} Ketone No triple bond

4 3050 cm^{-1} Ar-CH



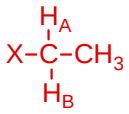
(c) Interpret the 2-proton multiplet at δ 2 to δ 3. What do these signals tell you about the structure. Draw a coupling tree above it to show you understand the multiplet.





This AB part of an ABX_3 pattern (an AB quartet of quartets)

6 cannot be a quartet of quartets - separation is wrong



X can't be O, but could be Se, Ar, or C=O

(c) Interpret the remaining multiplets in the NMR spectrum. Give multiplicity, coupling constants and part structures you were able to obtain from the signal.

δ 1.0 6H 2 triplets, J = 7 Hz, 2x $\underline{CH_3}CH_2$

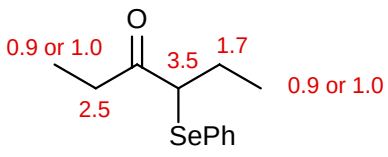
δ 1.7 2H m (actually AB of ABX_3Y)

6 δ 3.5 1H t (J=7 Hz) X-C(H)-CH_2

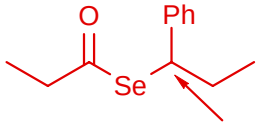
CH_3 of ABX_3 above

These define this fragment:

e} Draw the structure of R-10F below. Label it with chemical shifts.

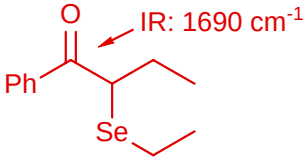


Without the PhSe hint, other structures (from 2004 exam)

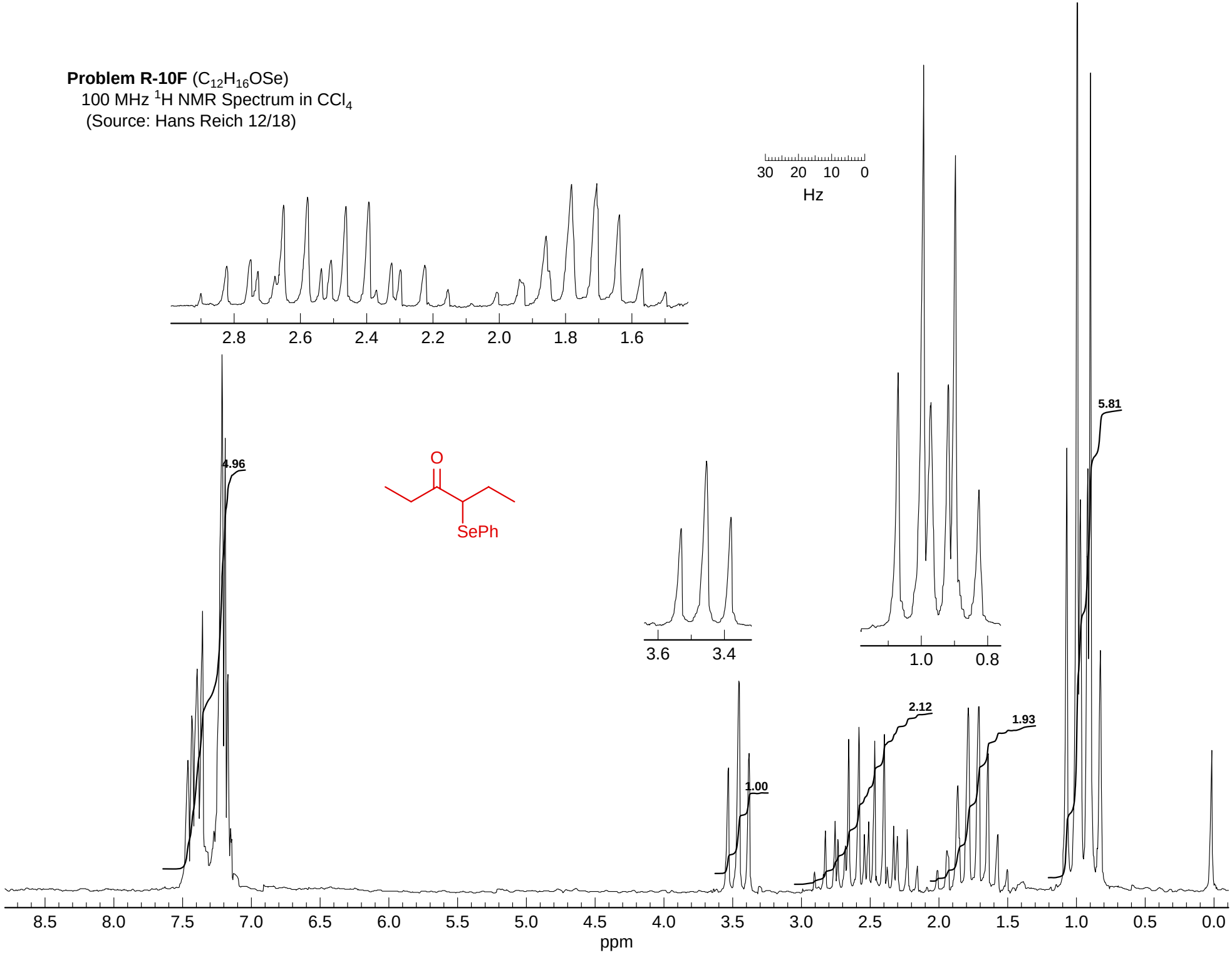


1.55
1.60
1.35

NMR OK, except δ 4.50 (obs 3.5)



Problem R-10F ($C_{12}H_{16}OSe$)
100 MHz ^{1}H NMR Spectrum in CCl_4
(Source: Hans Reich 12/18)



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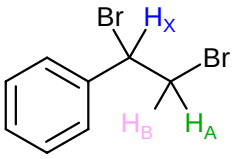
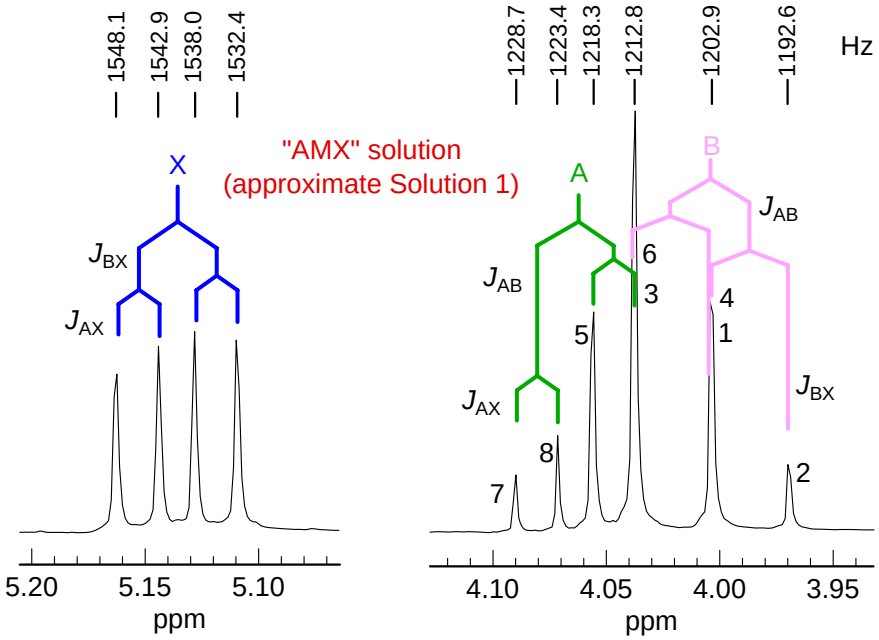
Problem **R-10G** ($C_8H_8Br_2$). This problem requires you to analyze the signals at δ 4.1 and δ 5.2. You are given the structure.

(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?





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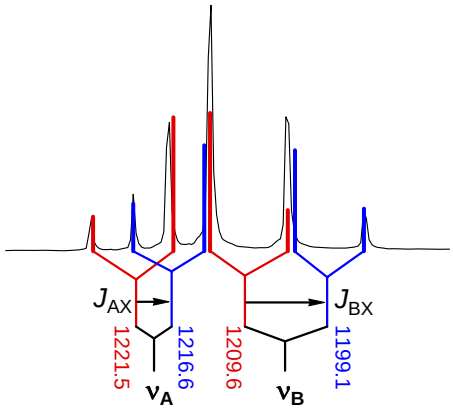
(b) Do an accurate (quantitative) analysis. Use the frequencies shown above. If more than one solution is possible, show them both, and draw the proper coupling tree on the spectra below. Use appropriate criteria to distinguish the two. Show your work, and tabulate your data in an easily readable form.

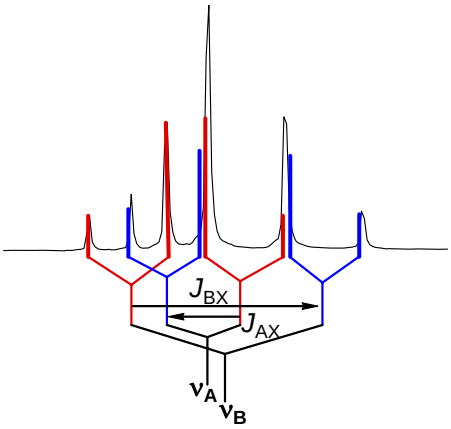
1	1202.9
2	1192.6
3	1212.8
4	1202.9
5	1218.3
6	1212.8
7	1228.7
8	1223.4

15

	Solution 1	Solution 2
J_{AB}	9.90 to 10.6	
J_{AX}	+4.93 (-)	-6.99 (+)
J_{BX}	+10.47 (-)	+22.39 (-)
ν_A	1219.04	1213.09
ν_B	1204.36	1210.31
ν_{AB}	14.69	2.77
$i_{10} = i_{11}$	0.995	0.322
δ_A	4.063	4.044
δ_B	4.015	4.034



Solution 1



Solution 2

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

Δνab- = δ- = sqrt((7-1)(5-3)) = 11.9

c- ± δ-/2 = 1221.5, 1209.6

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

Δνab+ = δ+ = sqrt((8-2)(6-4)) = 17.5

c+ ± δ+/2 = 1216.6, 1199.1

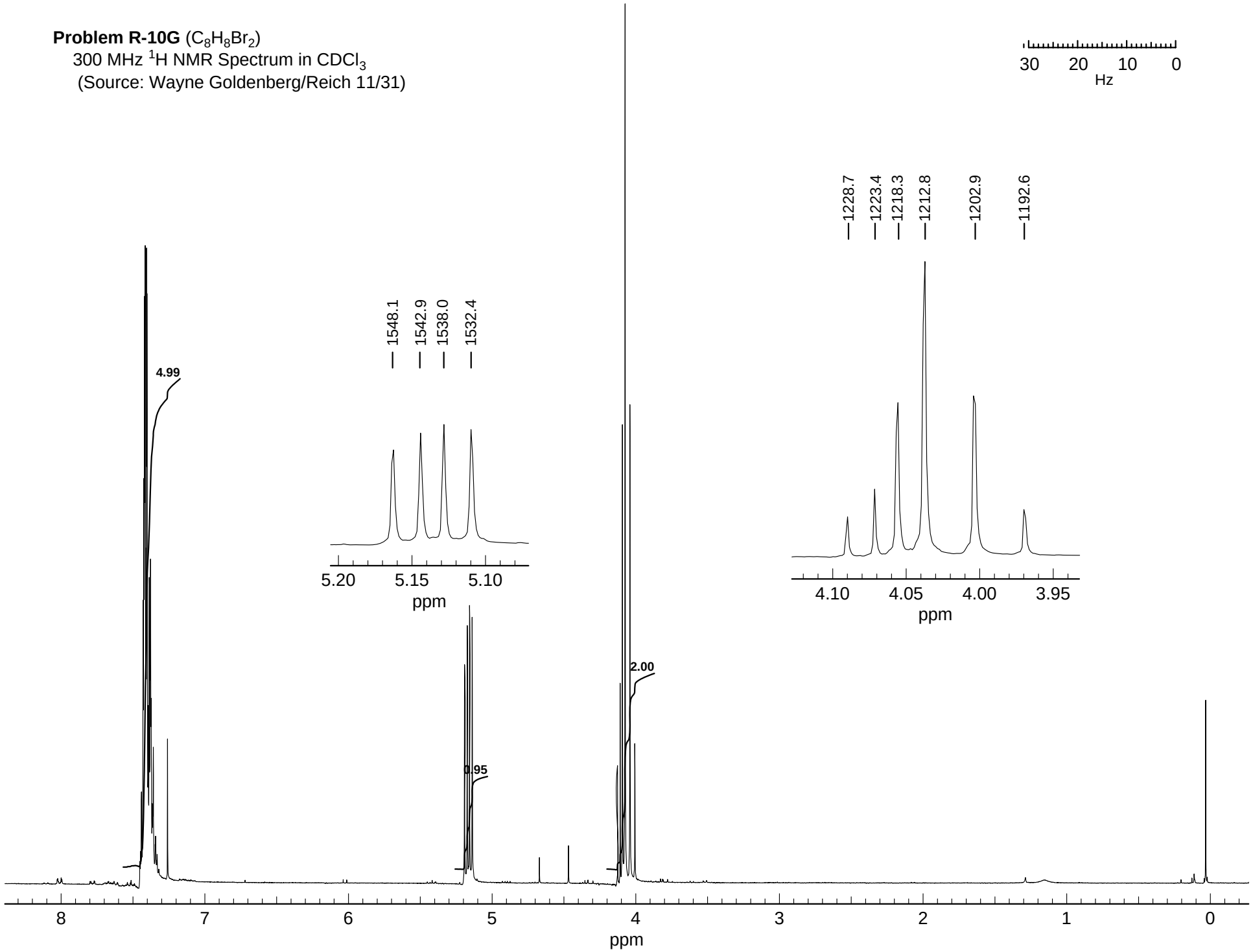
Solution 1 is correct:

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

Problem R-10G ($C_8H_8Br_2$)

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

(Source: Wayne Goldenberg/Reich 11/31)



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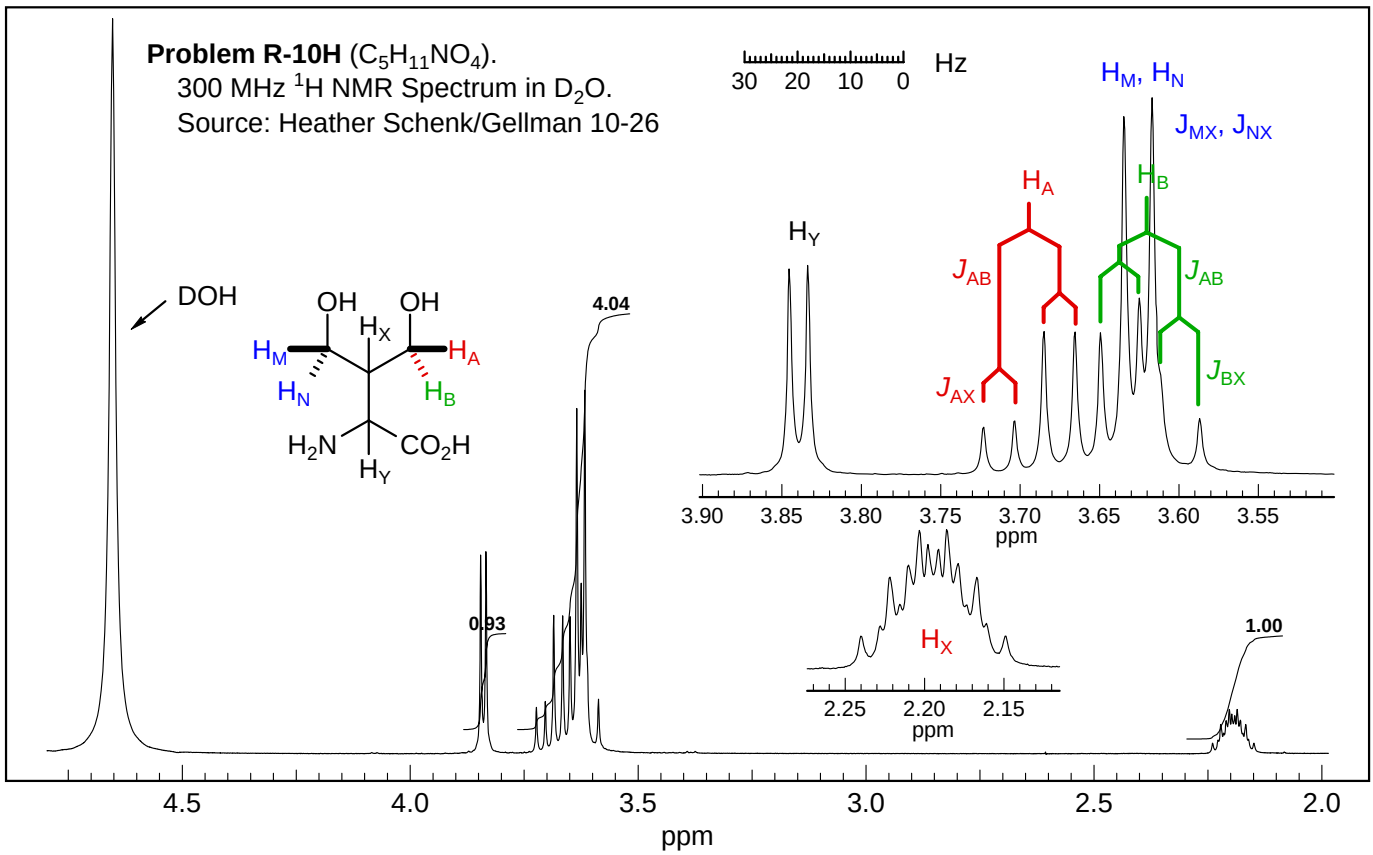
Problem R-10H ($C_5H_{11}NO_4$). A graduate student thought she had prepared the compound below, but was worried about the NMR spectrum (taken in D_2O), which seemed more than a little odd. Does the NMR spectrum fit the structure? Analyze and assign each of the multiplets. In particular, provide an explanation for the appearance of the key multiplet δ 3.5-3.8.



- The key here is that the two CH_2OH groups are diastereotopic, and each of the CH_2 groups are themselvees diastereotopic. So the protons form an AB MN XY system

- One CH_2 group (labelled AB) has a reasonably large AB shift, J_{AB} = 11, J_{AX} = 5.5, J_{BX} = 7.5

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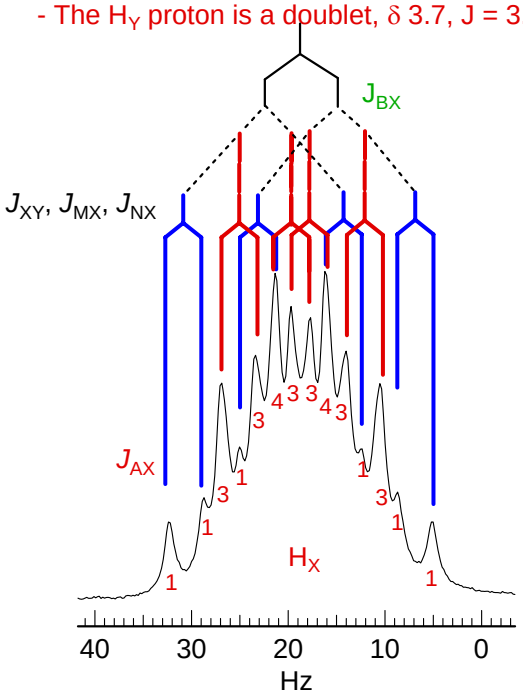
- The other CH_2 group (labelled MN) has no detectable shift between the two protons, and so appears as a doublet, with apparently equal couplings $J_{MX} = J_{NX}$ = 5.5 Hz

- The H_Y proton is a doublet, δ 3.7, J = 3.5 Hz.



To show you understand the spectrum, draw a coupling tree for the multiplet at δ 2.2 (start with an intensity assignment).

Expect this proton (X) to be coupled as follows:

J_{AX}=5.5
J_{BX}=7.5
J_{MX}=5.5
J_{NX}=5.5

Thus dqd, J = 7.5, 5.5, 3.5

5

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Problem R-10I ($C_{12}H_8Cl_4$). You are provided the ^1H NMR spectrum of a compound. Interpret the NMR spectrum, and determine the structure or structures. Use the A, B, etc labels on the spectrum. Show the chemical shift and multiplet structure in the form: 0.0 δ, dtd, J_{AB} = 0.0, 0.0, 0.0 Hz, 1H . You may use first order analysis.

2 (a) DBE 7

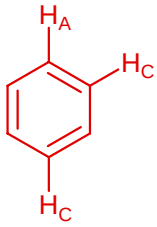
(b) Analyze the multiplets A, B, C. Provide part structure(s) defined by these protons. **Note: Do not attempt to distinguish among the several isomers which are consistent with this pattern**.

A δ 7.39, d, J = 8 Hz (J-ortho)

5 B δ 7.32, d, J = 2 Hz (J-meta)

C δ 7.08, dd, J = 8, 2 Hz (J-ortho + J-meta)

These are aromatic protons and define a 1,2,4-trisubstituted benzene



(c) Interpret the signals D-H. Provide part structure(s) defined by these protons.

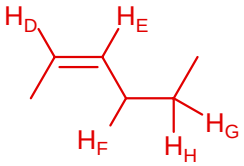
D δ 6.04, dd, J = 9, 2 Hz

E δ 5.79, dd, J = 10, 4 Hz

8 F δ 3.78, dddd, J = 11, 10, 4, 2 Hz

G δ 2.97, dd, J = 17, 9.5 Hz

H δ 2.78, dd, J = 17, 11 Hz



(d) Draw the structure of **R-00F** below. If more than one structure fits the data, draw them, but circle your first choice. Assign the protons (label them with the letters A-H). If any assignments are ambiguous, indicate the basis for your choice.

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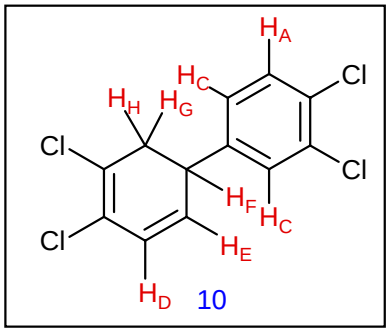

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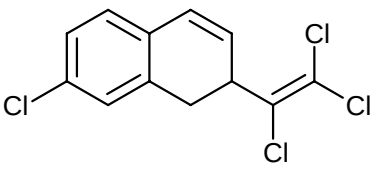

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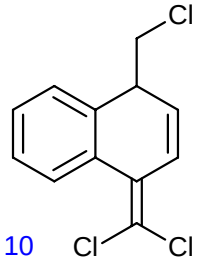

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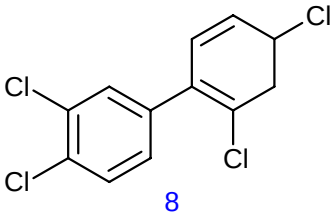

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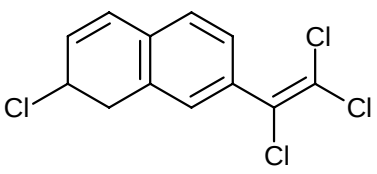

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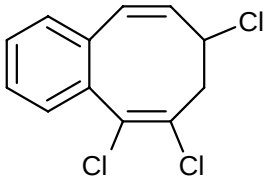

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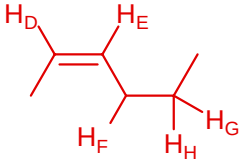
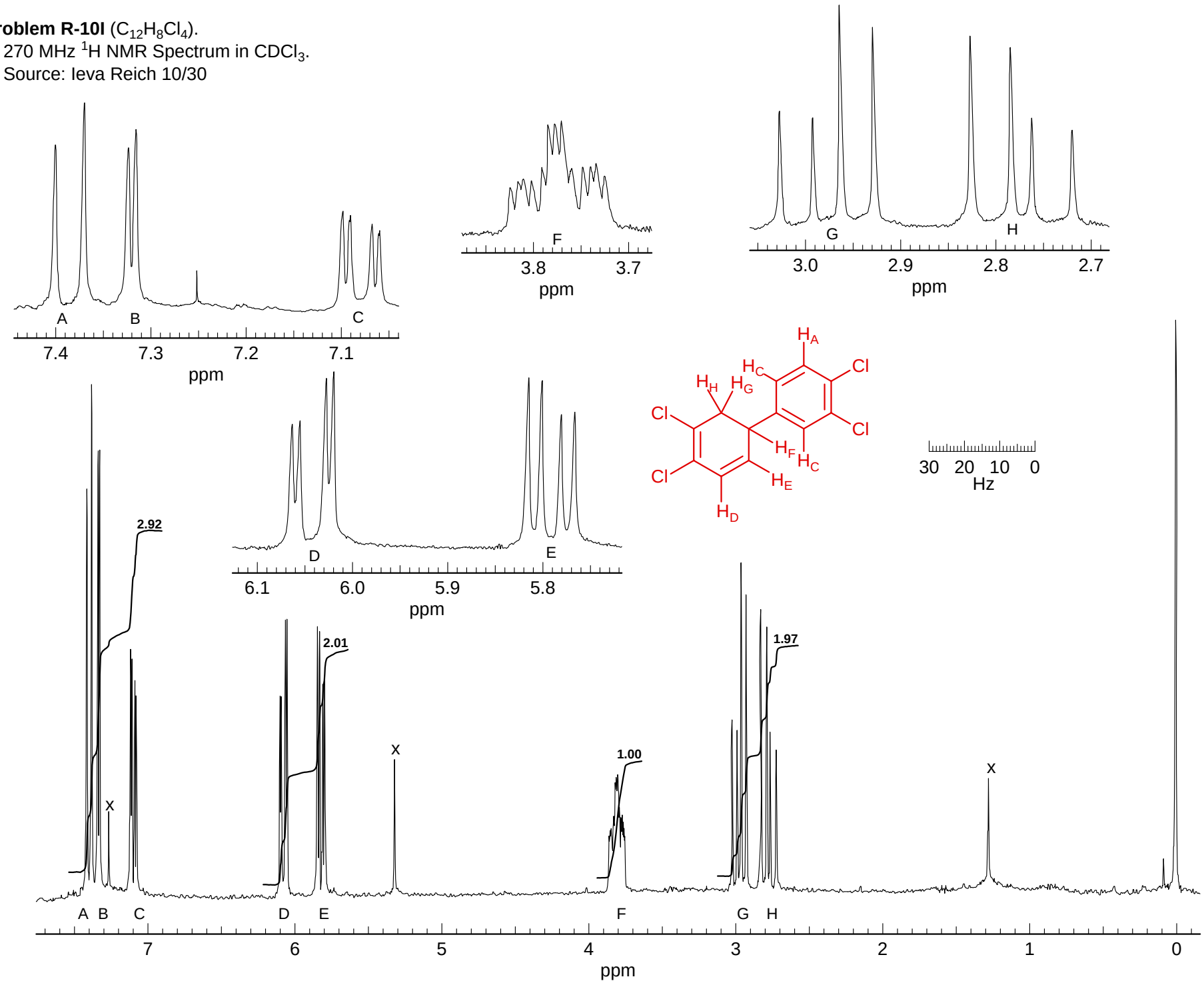


This question elicitated many answers - not a good problem since there are too many hidden carbons.

Problem R-10l ($C_{12}H_8Cl_4$).
270 MHz ^{1}H NMR Spectrum in $CDCl_3$.
Source: Ieva Reich 10/30



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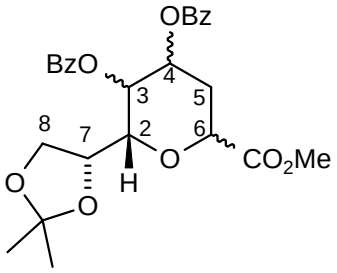
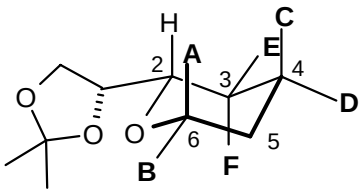
Problem R10J ($C_{24}H_{28}O_9$). This problem requires you to analyze part of the ^{1}H NMR spectrum of a tetrahydropyran, and determine the stereochemistry at three centers. A planar projection and conformational drawing is shown below.





Bz = PhC(=O)-

3 pts for correct answer
3 or 4 for reasoning

(a) Determine the stereochemistry at C-6. Explain what signal(s) you used, give their shift and multiplicity (e.g. δ 0.00, tq, J =0, 0) and briefly describe how you made the stereochemical assignment using the data:

A = H , B = CO_2Me (**H** or **CO_2Me**).

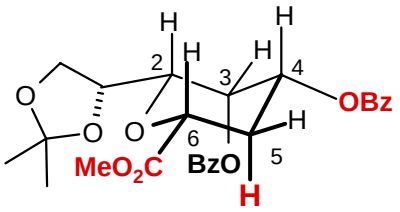
δ 4.31

δ 2.24, q, J = 12 Hz

The quartet at δ 2.24 (J = 12 Hz) is the axial proton at C-5. The three couplings must be a J_{gem} and two $J_{ax\text{-}ax}$, thus protons on both sides are axial, and the substituents at C-6 and C-4 must both be equatorial.

7

The couplings of the equatorial proton H^{5e} (dddd J = 12, 5, 2.5, 1) also help identify the H^4 (5.40, J=5) and H^6 (4.31, J=2.5) protons



(b) Determine the stereochemistry at C-4. Explain what signal(s) you used, give their shift and multiplicity and briefly describe how you made the stereochemical assignment using the data:

C = H , D = OBz (**H** or **OBz**).

δ 5.40

See part (a)

6

The signal at 5.4 shows J = 12, 5, 3, so one axial-axial coupling (to H^5), and two ax-eq couplings to H^3 and H^5 (this also proves that H^3 must be equatorial)

(c) Determine the stereochemistry at C-3. Explain what signal(s) you used, give their shift and multiplicity and briefly describe how you made the stereochemical assignment using the data:

E = H , F = OBz (**H** or **OBz**).

δ 5.86

The "d" at 5.86 has to be H^3 - it shows only one obvious small coupling. Since H^2 is axial, this means that H^3 must be equatorial, or else it would show a large $J_{ax\text{-}ax}$

7

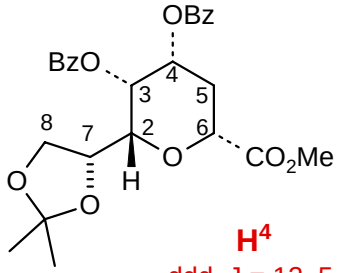
Could also use the axial proton at H^4 5.40, ddd, J = 12, 5, 3. The 12 Hz coupling is the $J_{ax\text{-}ax}$ to H^5, the two smaller coulings have to be the $J_{ax\text{-}eq}$ to H^3 and H^5, hence H^3 has to be equatorial

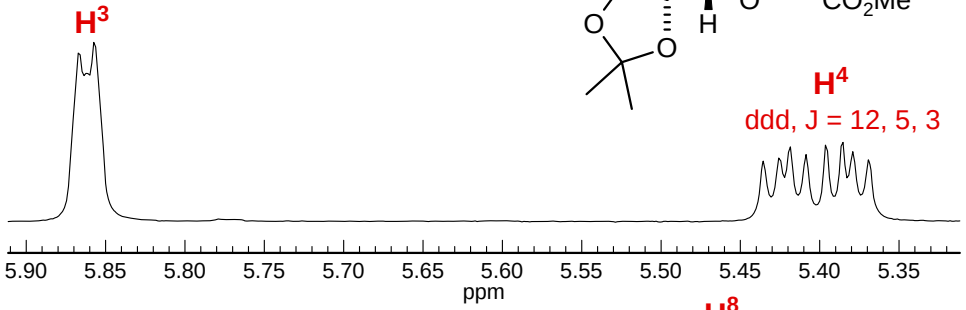
The proton at H^2 (δ 3.67, dd, J = 8, 2.) has to be axial, if it were equatorial the ring would flip. The 8 Hz coupling is to H^7, the 2 Hz couping must be to H^3. Thus H_3 must be equatorial.

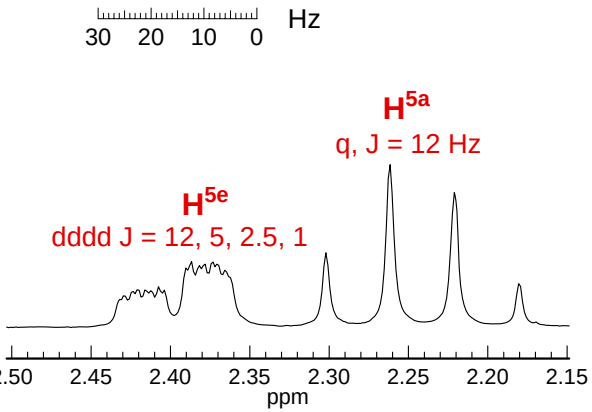
Problem R-10J ($C_{24}H_{28}O_9$)

300 MHz ^{13}C NMR Spectrum in $CDCl_3$

Source: Geoffrey Sametz/Burke 9/99







1.55