Practice Exam 2

Chemistry 605 (Reich)

SECOND HOUR EXAM

Tue. April 13, 2010

Question/Points

R-09G_____/25

R-09H_____/10

R-09I_____/15

R-09J_____/15

R-09K_____/16

R-09LM_____/18

Total _____/100

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.

Problem R-09G ($C_{12}H_{16}O_2$). Determine the structure (or part structure) of **R-09G** from the ^{1}H NMR, ^{13}C NMR provided. The IR spectrum shows no strong peaks in the region from 1650 to 1800 cm^{-1}.

(a) DBE____

(b) Interpret the ^{13}C NMR spectrum. Identify what kind of carbon each signal corresponds to, and write possible part structures (e.g. sp^3 OCH_3, Aromatic C-H, ketone C=O, N-CH_2)).

1	142.6	_____	6	126.3	_____
2	138.7	_____	7	75.6	_____
3	129.7	_____	8	71.9	_____
4	128.3	_____	9	30.4	_____
5	127.5	_____	10	29.4	_____

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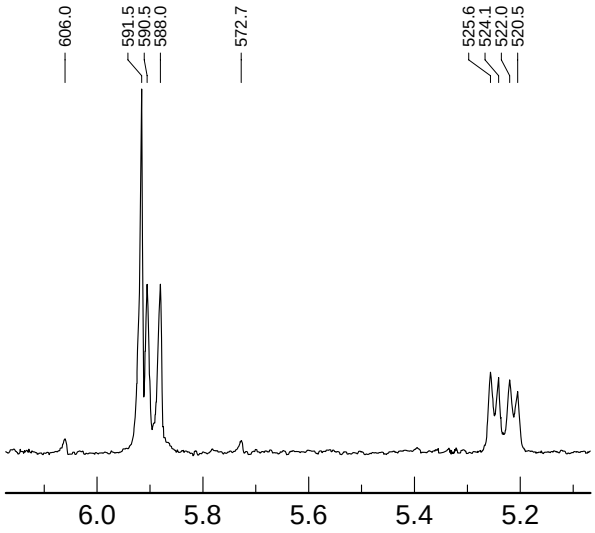
(c) Do a mathematically accurate analysis of the expansion below, and report your results. If there are two solutions, report them both. Show a coupling tree.



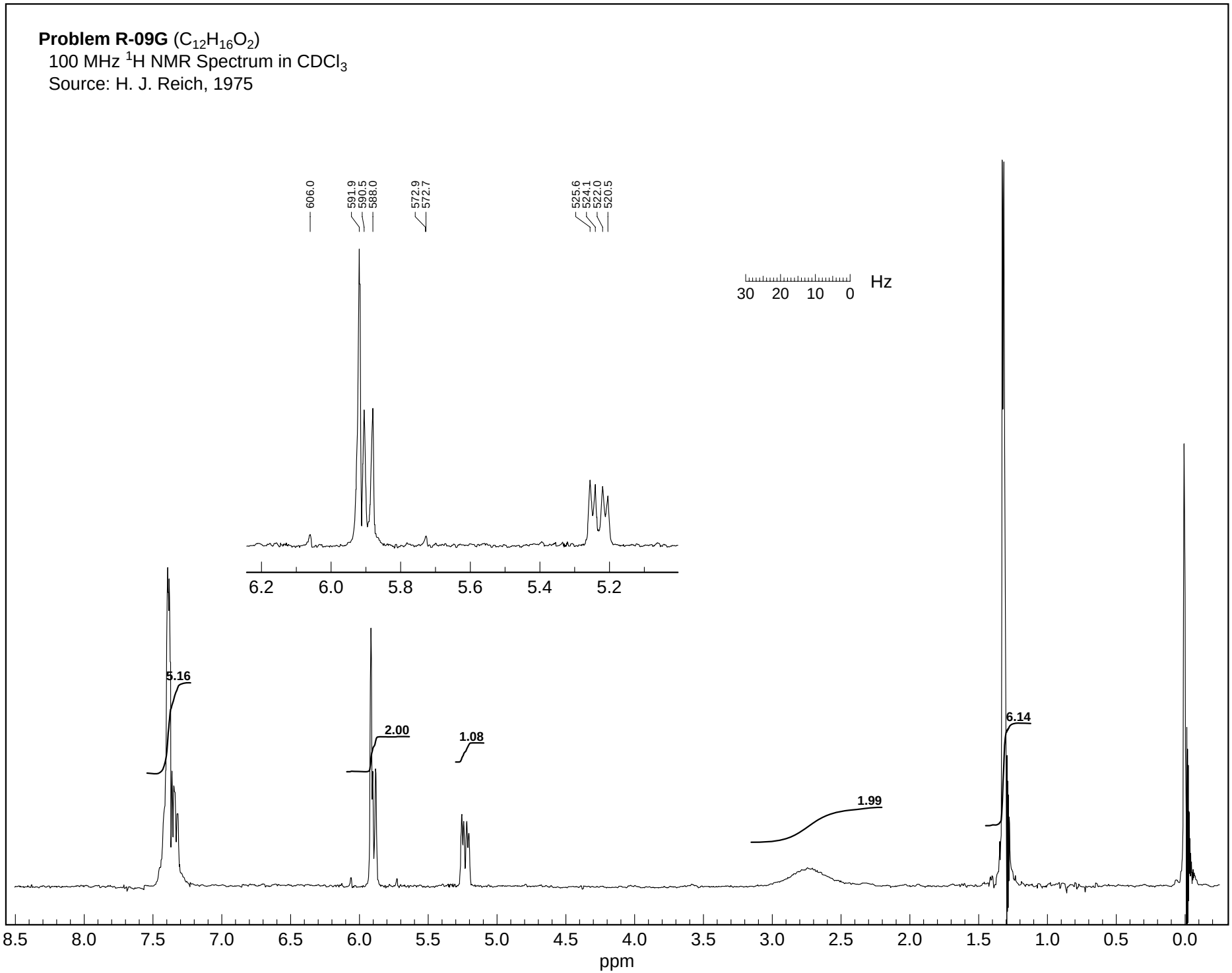
(d) What part structure is suggested by the shifts and couplings of this part of the spectrum?

(e) Determine the structure of **R-09G**. If more than one structure is possible, show them, and circle your best choice.

Problem R-09G ($C_{12}H_{16}O_2$)

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

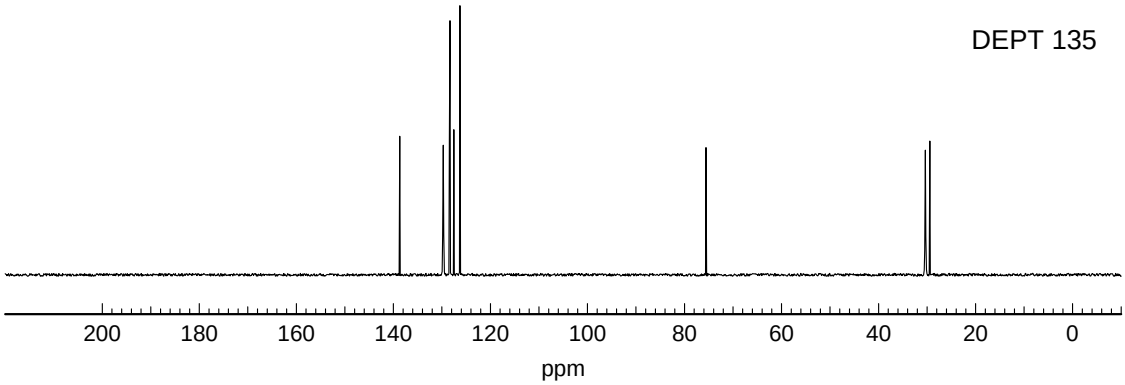
Source: H. J. Reich, 1975

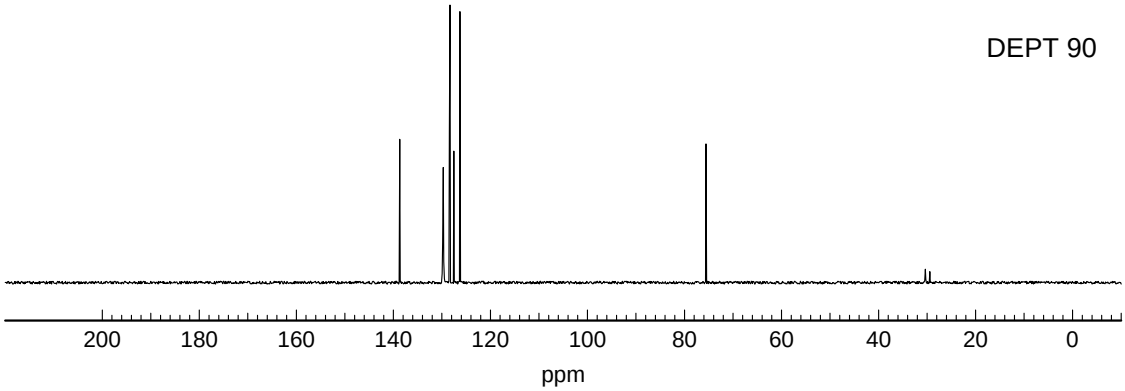


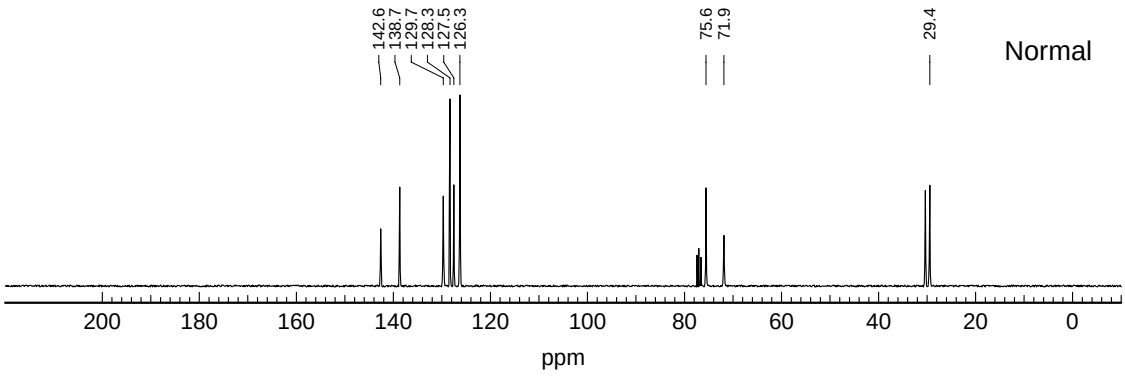
Problem R-09G ($C_{12}H_{16}O_2$)

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

Source: H. J. Reich, 05-05

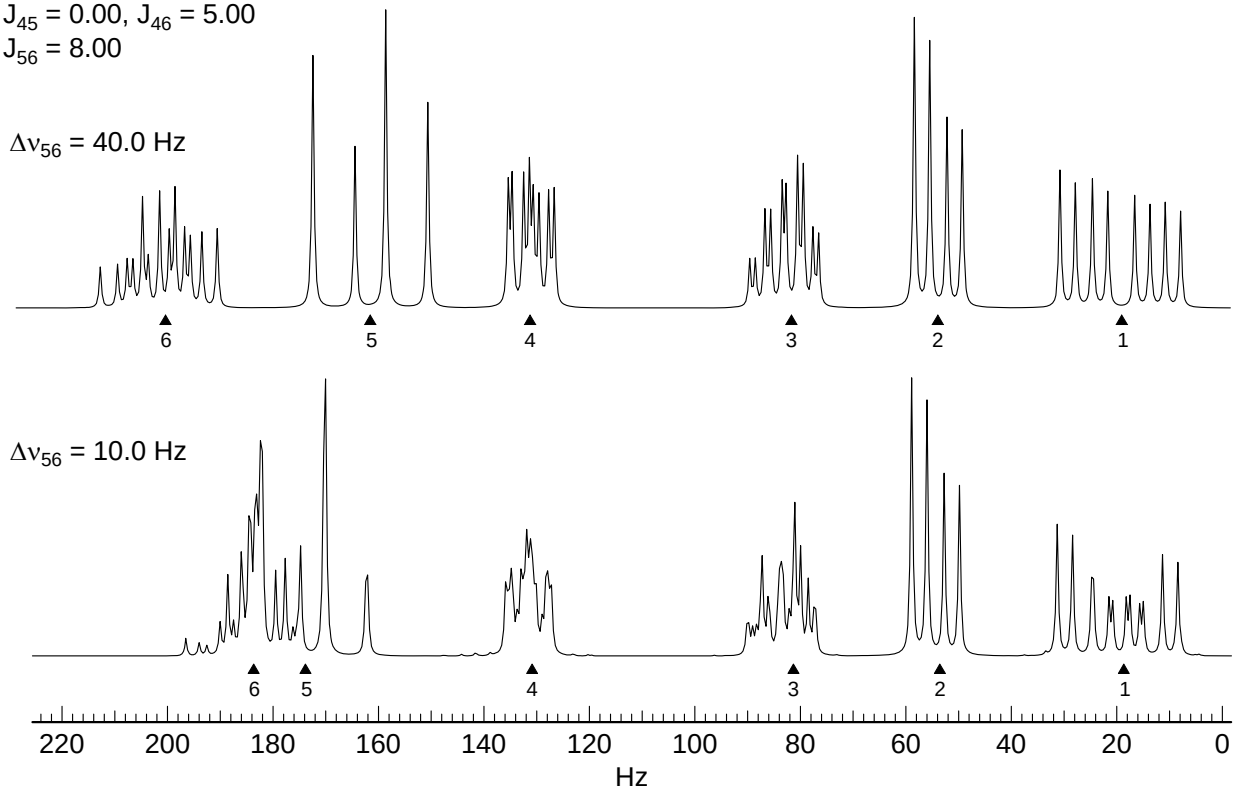






Problem R-09H. The two simulated spectra below differ *only* in the relative chemical shift of the protons ν_5 and ν_6.

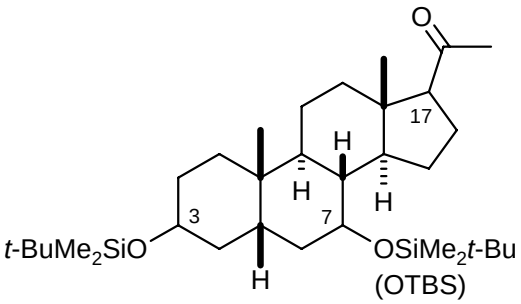
J_{12} = 0.00, J_{13} = 3.00, J_{14} = 0.00, J_{15} = 14.0, J_{16} = 6.00
J_{23} = 6.00, J_{24} = 3.00, J_{25} = 0.00, J_{26} = 0.00
J_{34} = 1.00, J_{35} = 0.00, J_{36} = 3.00
J_{45} = 0.00, J_{46} = 5.00
J_{56} = 8.00

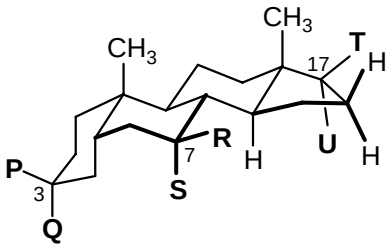


(a) Explain why most of the multiplets look so different in the two spectra. What phenomenon is this?

(b) Specifically explain why *only* H_2 is unchanged in the second spectrum.

Problem R-09l This problem requires you to analyze the ^{1}H NMR spectrum of a steroid, and determine the stereochemistry at three centers. A planar projection and conformational drawing is shown below.





(a) Assign the signal at C-3 (δ____). Explain how you identified the signal, and make a stereochemical assignment: P =_____ , Q =_____ (**H** or **OTBS**).

(b) Assign the signal at C-7 (δ____). Explain how you identified the signal, and make a stereochemical assignment: R =_____ , S =_____ (**H** or **OTBS**).

(c) Assign the signal at C-17 (δ____). Explain how you identified the signal, and make a stereochemical assignment: T =_____ , U =_____ (**H** or **$CH_3C(=O)$**).

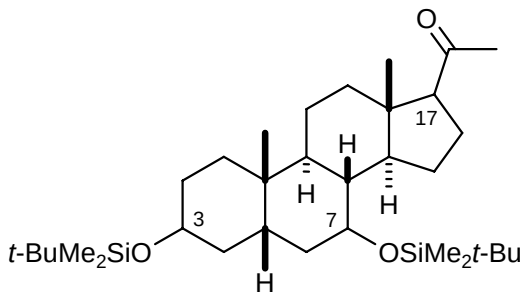
(d) Why is the methyl group at δ 2.1 so much taller (i.e. sharper) than the one at δ 0.6?

(e) Assign and explain the signals at δ 0.00 to 0.10

Problem R-09l ($C_{33}\ H_{62}\ O_2\ Si_2$)

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

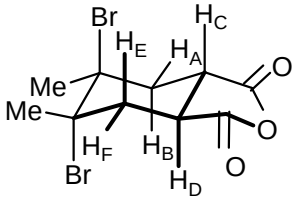
Source: I. L. Reich, K. Plessel/Reich 040-04

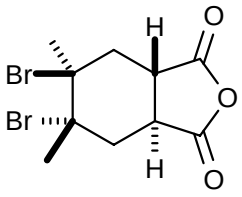


Problem R-09J. You are asked to determine which of two possible isomers of a dibromo anhydride is the correct one, and assign the protons . The complete spectrum is shown on the next page.

(a) Assign the protons, draw appropriate coupling trees on the spectrum below, and label each one with a proton assignmment (H_A, H_B, etc). It is not necessary to report couplings, although you might wish to measure them to aid in your analysis.

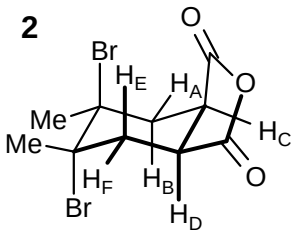
1

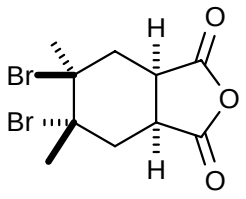


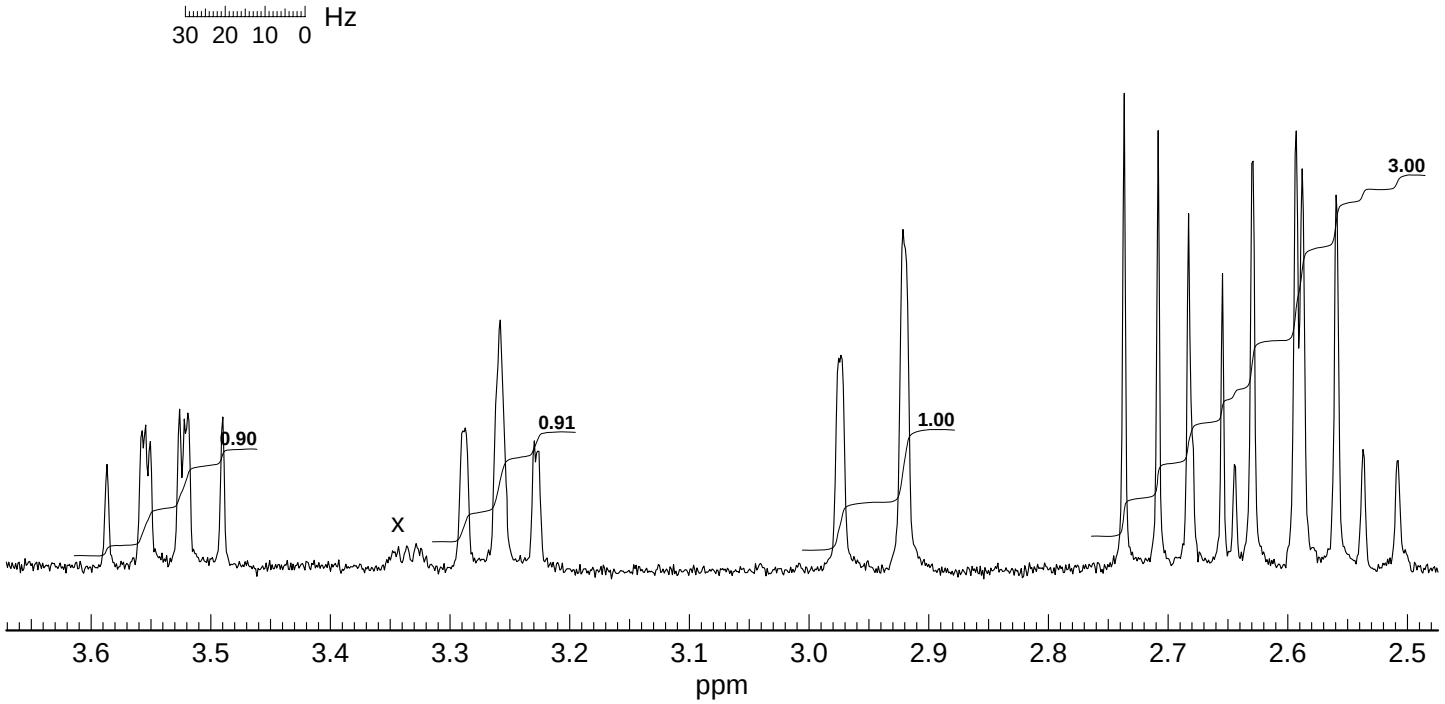


or

2







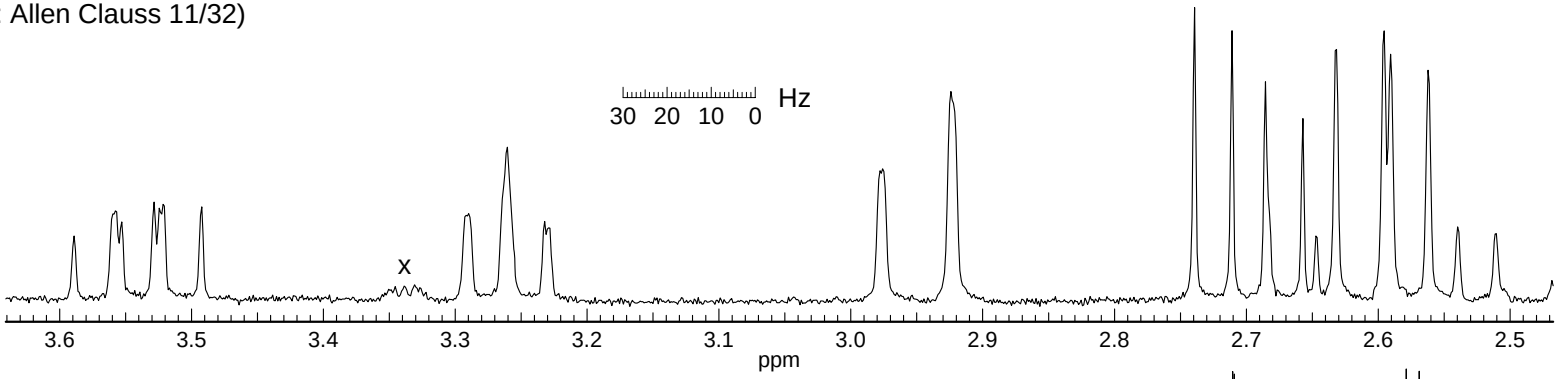
(b) Which isomer ____ (**1** or **2**) is correct? Explain briefly how you decided which was correct.

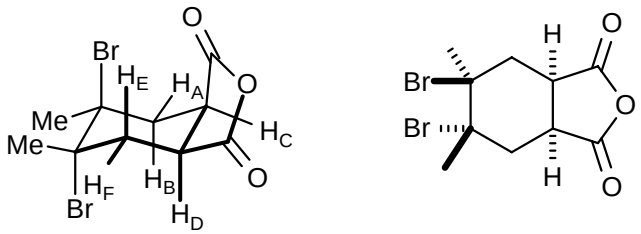
(c) Explain why the proton at δ 2.95 shows such a simple multiplet.

Problem R-09J ($C_{10}H_{12}Br_2O_3$)

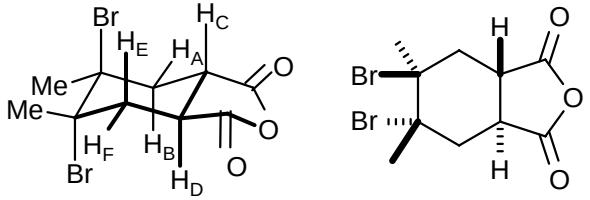
300 MHz ^{1}H NMR spectrum in $CDCl_3$

(Source: Allen Clauss 11/32)

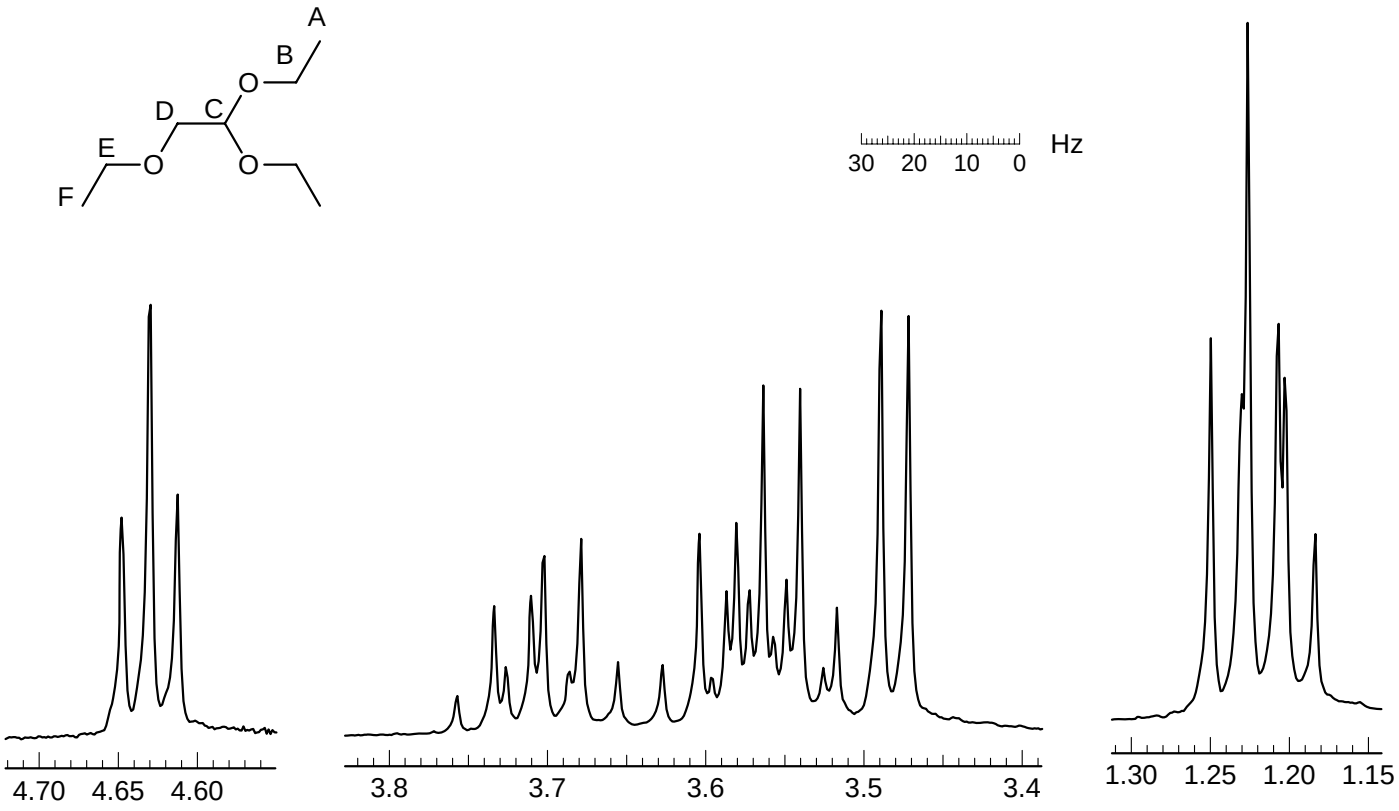




or



Problem R-09K $C_8H_{18}O_3$. This problem requires you to analyze the ^1H NMR spectrum of the diethylacetal of ethoxy acetaldehyde. The complete spectrum with integrations is on the next page.



(a) Give the chemical shift(s), multiplicity and couplings (δ 3.23, dt, J = 8, 2 Hz) of each unique proton in the spectrum. You may use first order analysis.

A _____

B _____

C _____

D _____

E _____

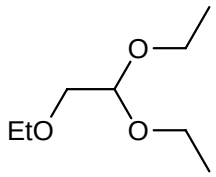
F _____

(b) To show you understand the pattern, put a marker (x) over each peak corresponding to proton **E**.

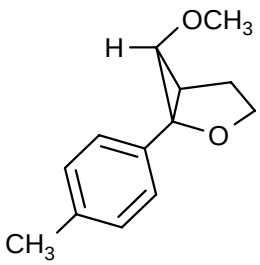
Problem R-09K: $C_8H_{18}O_3$

300 MHz ^1H NMR spectrum in $CDCl_3$

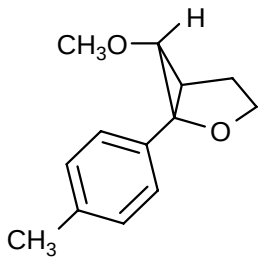
Source: Aldrich Spectra Viewer/Reich



Problem R-09L and R-09M ($C_{13}H_{16}O_2$). The 270 MHz ^1H spectra are of the isomers below:



R-09___



R-09___

(a) Identify a key feature of the spectra which allows confident assignment of the stereochemistry. Explain and label the structures above appropriately. It is not necessary to analyze the spectra completely.

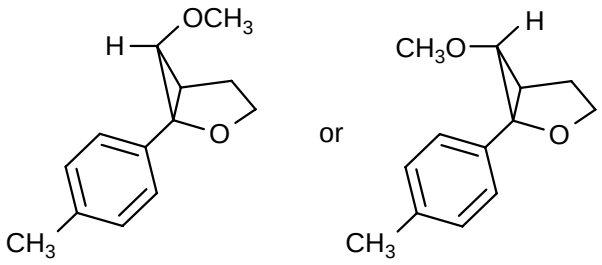
(b) Explain the differences in the chemical shift of the sharp singlet at δ 3.25 in **R-09L** and δ 2.9 in **R-09M**.

(c) Assign and interpret the signal at δ 1.65 (explain the coupling) in the spectrum of **R-09L**. Give the chemical shift of the corresponding signal in the spectrum of **R-09M**_____ .

Problem R-09L ($C_{13}H_{16}O_2$)

270 MHz ^{1}H NMR Spectrum in C_6D_6

(Source: Nora Hornung/Casey 11/16)

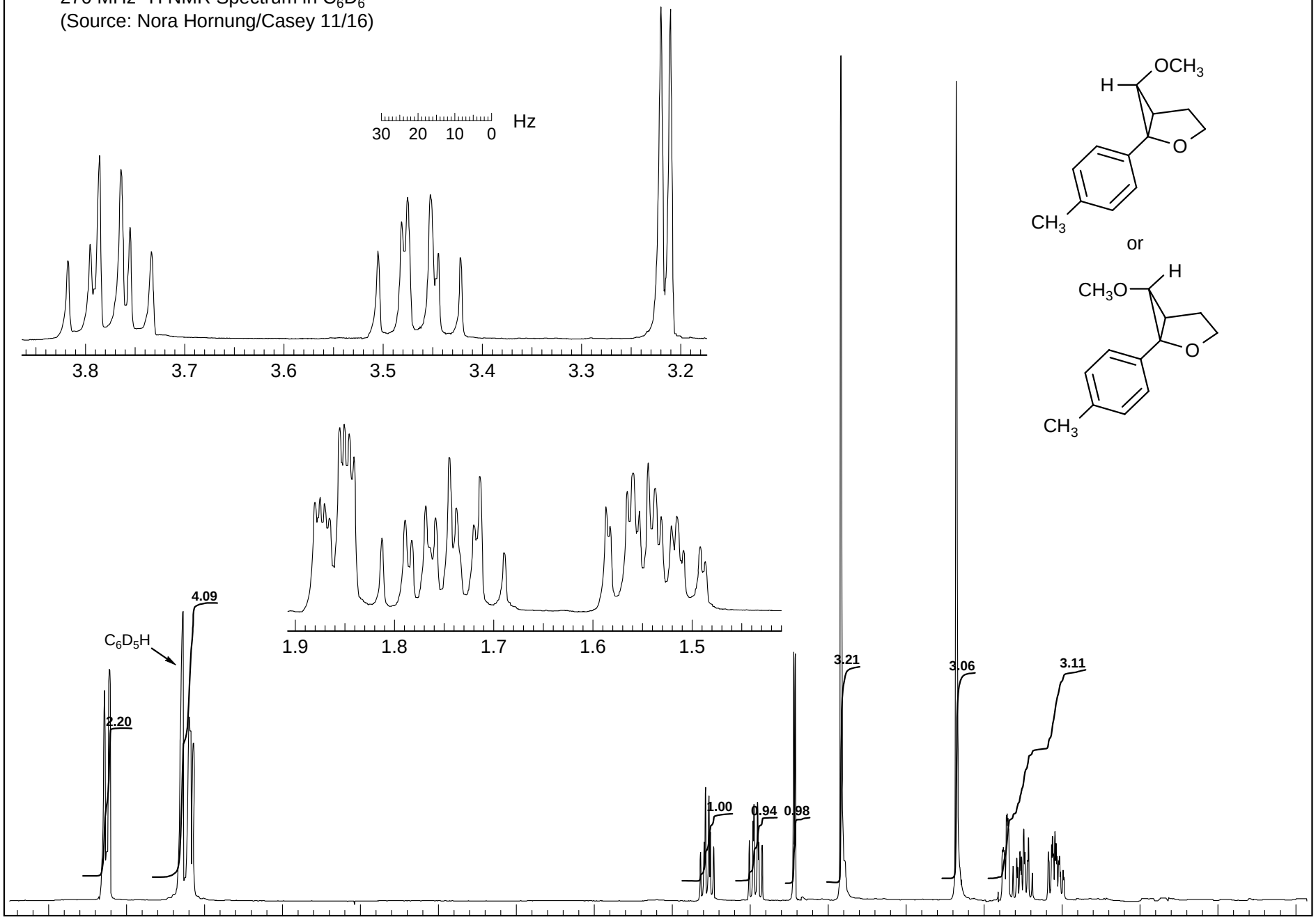


or

Problem R-09M ($C_{13}H_{16}O_2$)

270 MHz ^{1}H NMR Spectrum in C_6D_6

(Source: Nora Hornung/Casey 11/16)



or