Chemistry 605 (Reich)

SECOND HOUR EXAM

Thur. April 11, 2013

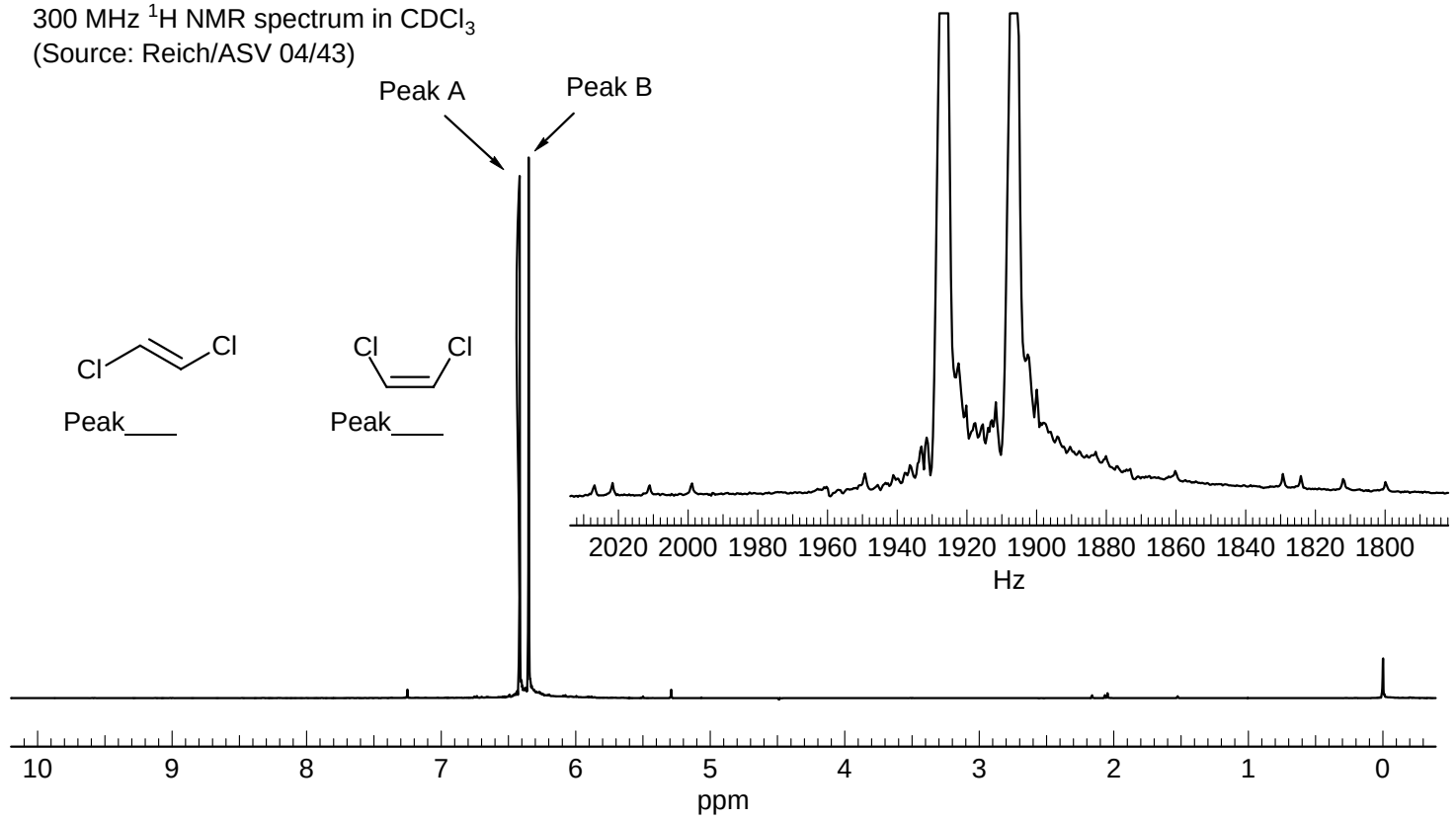
Question	Points
R-12F	/10
R-12G,H	/25
R-12I	/20
R-12J	/25
R-12K	/20
Total	/100

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-12F. Below is the 300 MHz ^{1}H NMR spectrum of a nearly 1:1 mixture of the *E* and *Z* isomers of 1,2-dichloroethylene. Also shown is a vertical and horizontal expansion.

Problem R-12F ($C_2H_2Cl_2$).
300 MHz ^{1}H NMR spectrum in $CDCl_3$
(Source: Reich/ASV 04/43)



Indicate which peak (A or B) is cis and which is trans 1,2-dichloroethylene. Summarize all chemical shift and/or coupling information you obtained from the spectrum.

Problem R-12G ($C_{11}H_{12}O_3$). **R-12G** and **R-12H** are two stereoisomers. Only the ^1H spectrum of R-12G is provided, R-12H has in addition ^{13}C and IR spectra. The compounds each contain a Ph group.

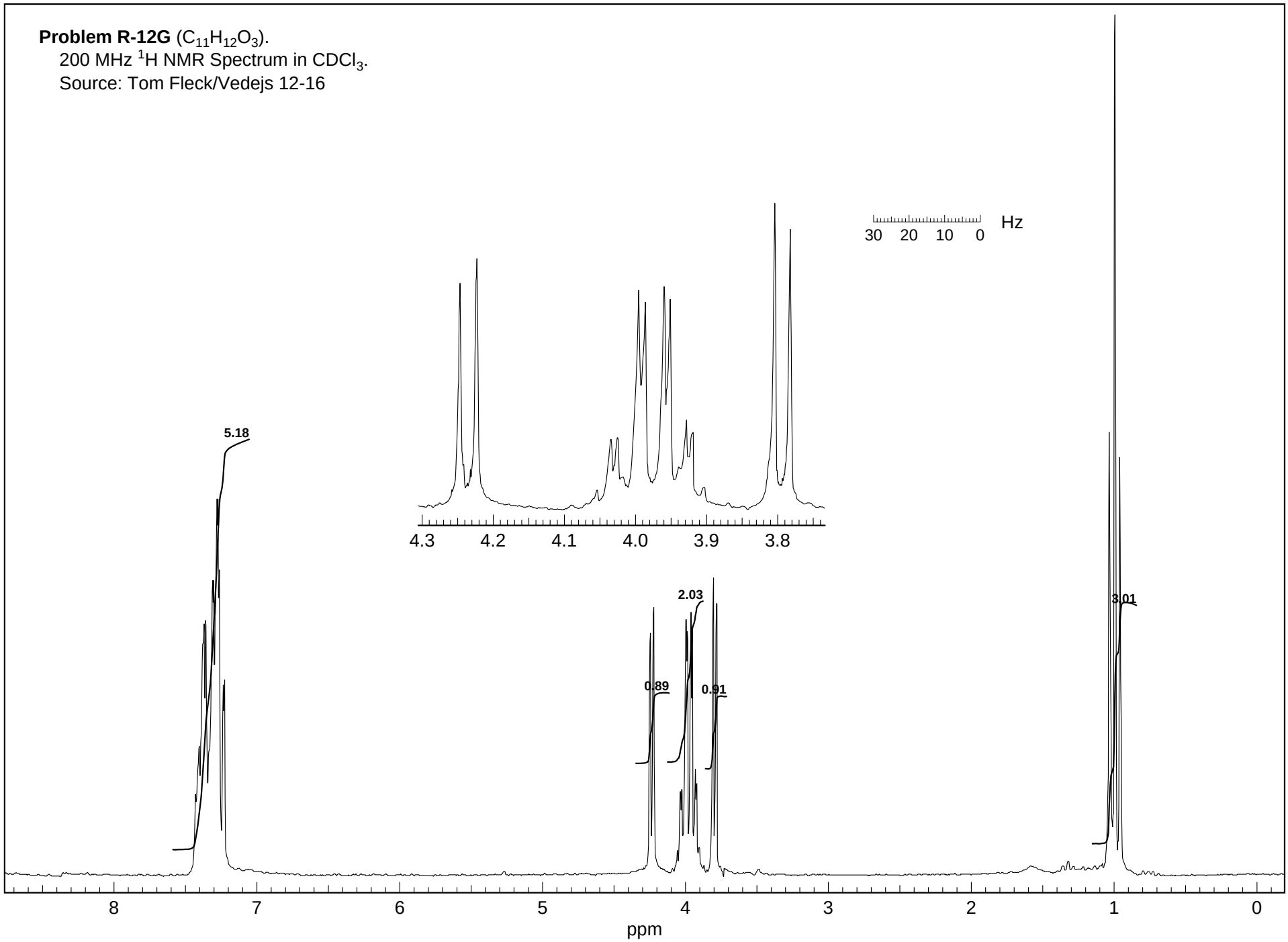
(a) DBE _____

(b) What can you learn from the IR spectrum of **R-12H**?

(b) Identify significant peaks in the ^{13}C NMR spectrum of **R-12H** and describe the structural information you obtained from them.

(c) Draw the structures of **R-12G** and **R-12H** below. Label the structures with ^1H chemical shifts and coupling constants.

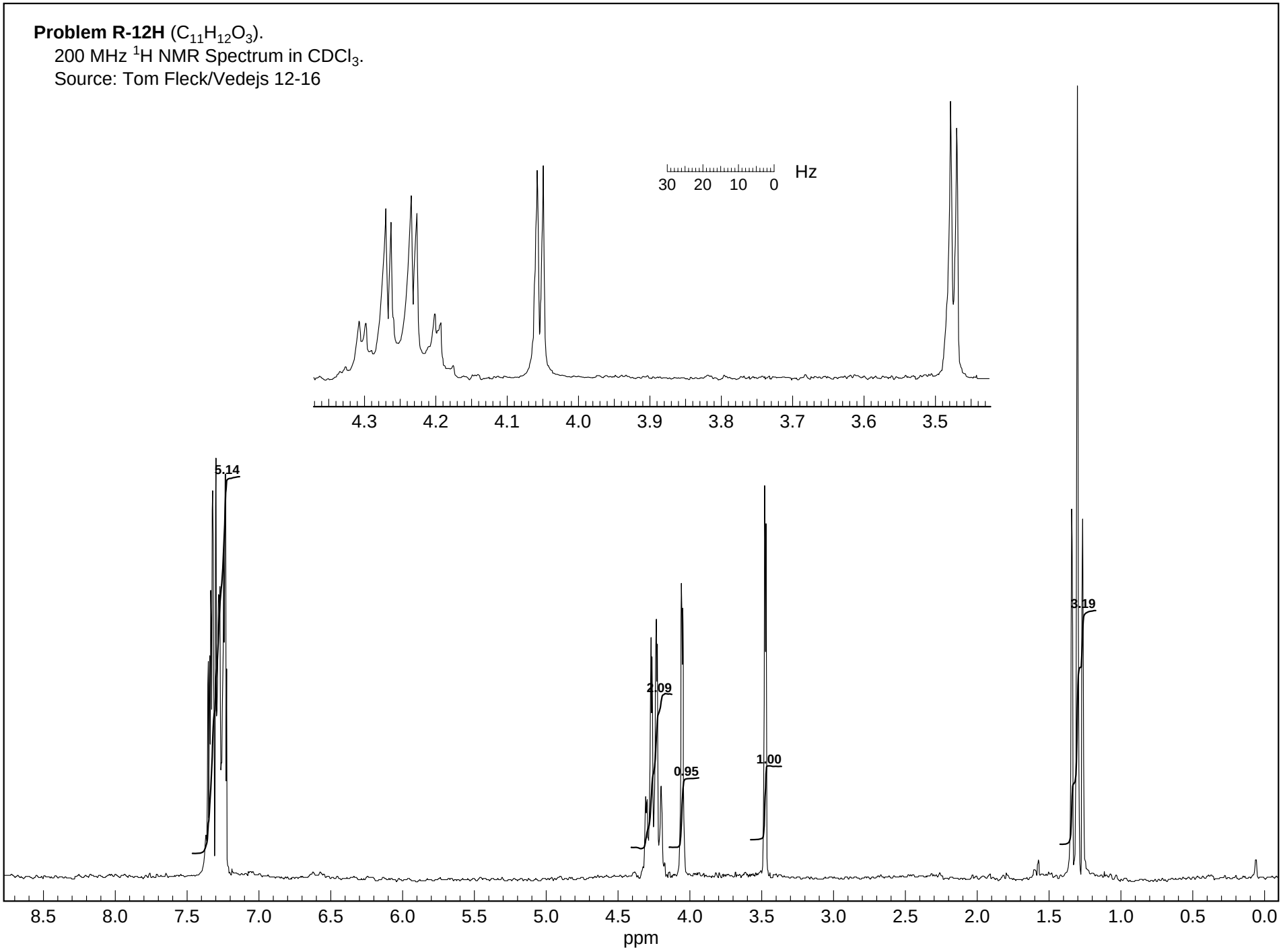
(e) What feature(s) of the spectra allowed you to make the distinction between the isomers?


Problem R-12G (C11H12O3).
200 MHz 1H NMR Spectrum in CDCl3.
Source: Tom Fleck/Vedejs 12-16
Hz
30 20 10 0
4.3 4.2 4.1 4.0 3.9 3.8
5.18
2.03
0.89
0.91
3.01
8 7 6 5 4 3 2 1 0
ppm

Problem R-12H ($C_{11}H_{12}O_3$).

200 MHz ^{1}H NMR Spectrum in $CDCl_3$.

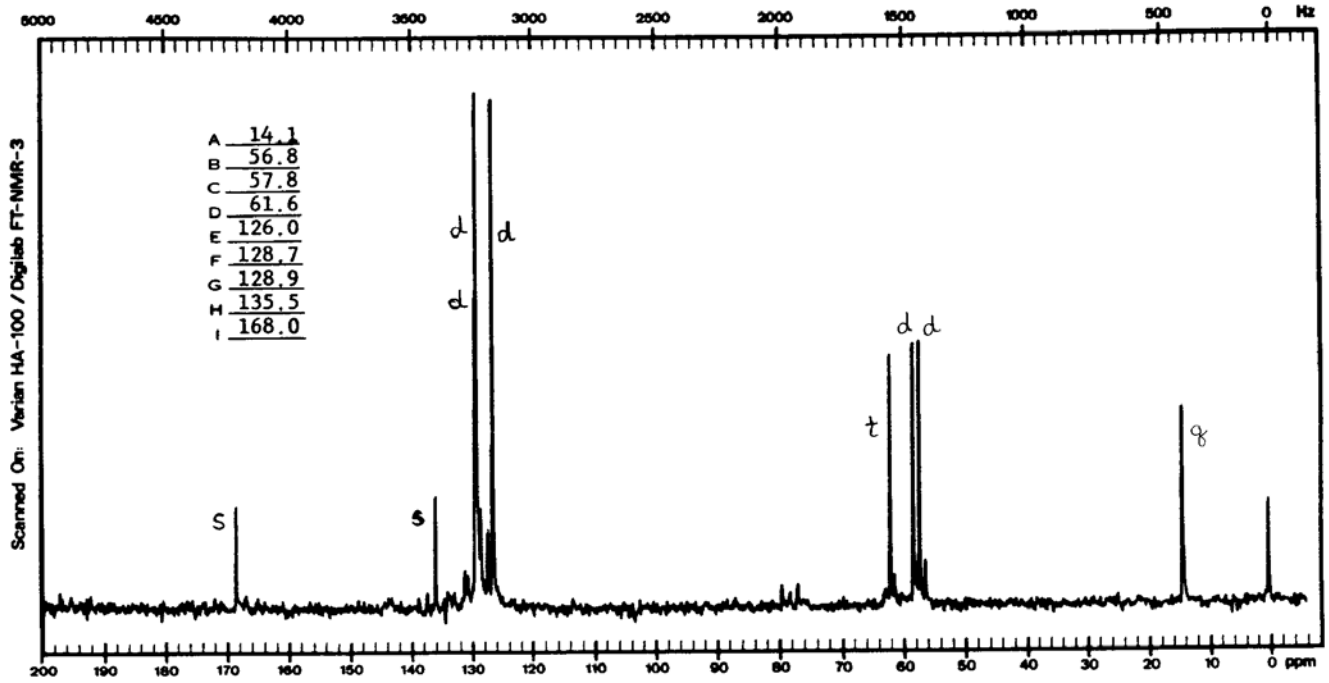
Source: Tom Fleck/Vedejs 12-16



Problem R-12H ($C_{11}H_{12}O_3$).

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

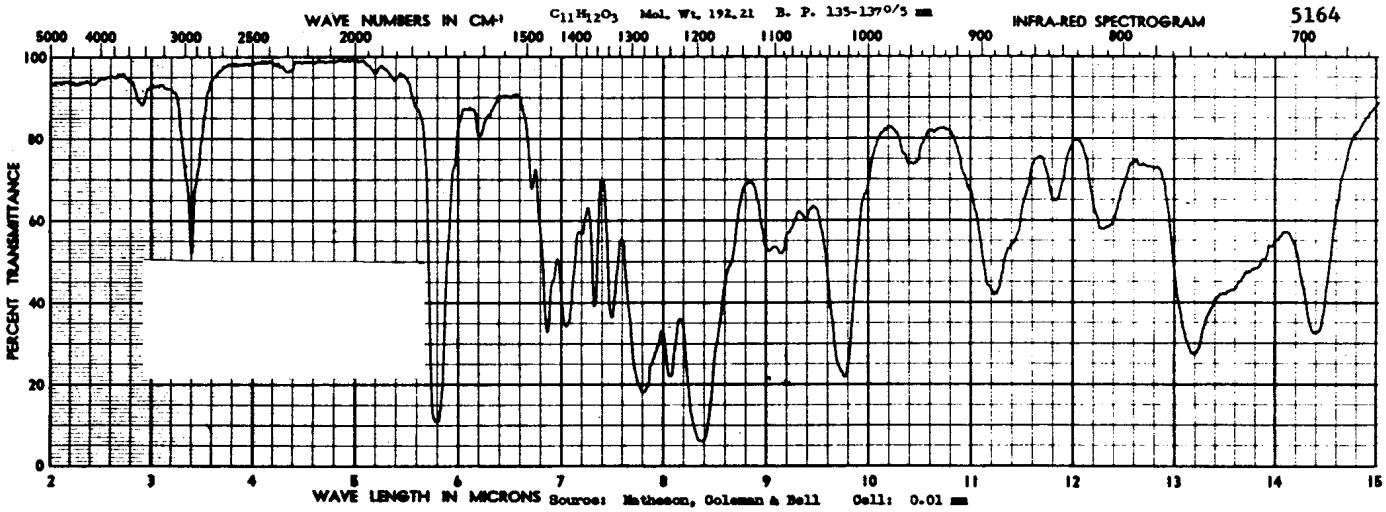
Source: Sadtler



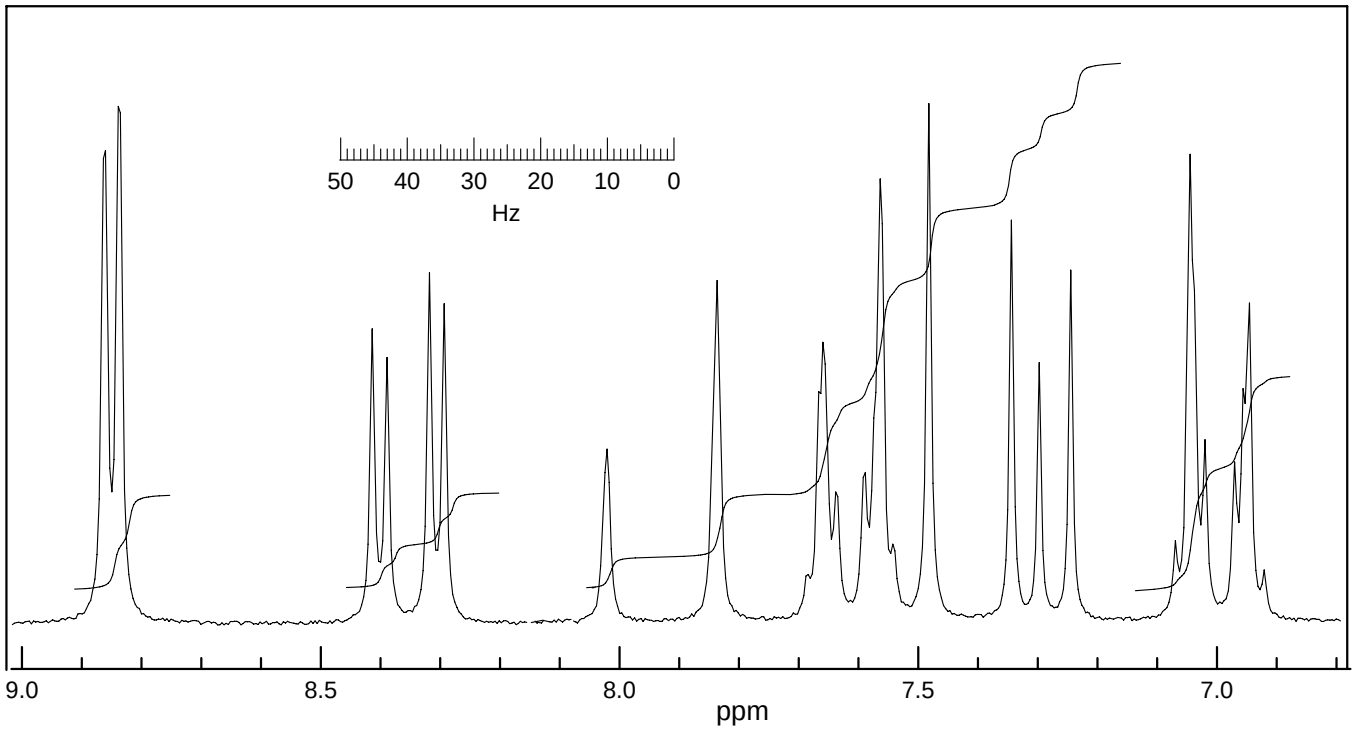
Problem R-12H ($C_{11}H_{12}O_3$).

IR Spectrum neat.

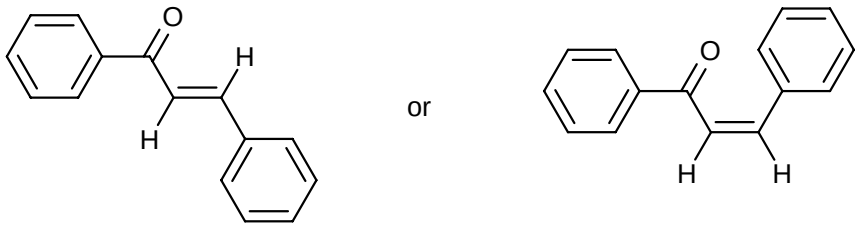
Source: Sadtler



Problem R-12l ($C_{16}H_{13}NO_4$). Shown below is the 90 MHz ^{1}H NMR spectrum of a substituted chalcone which includes all of the signals except for the methoxy group and the OH. There are a total of **three** substituents on the two aryl rings (OCH_3, OH and NO_2). You may treat the OH and OCH_3 as identical for the purposes of this problem (call them OR).



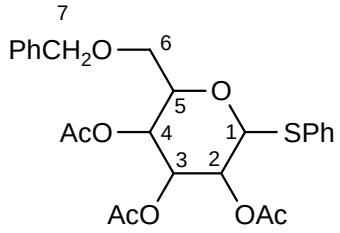
(a) Analyze the spectrum. Decide where the substituents are and whether the double bond is cis or trans. Complete the correct structure below by attaching substituents and labelling each hydrogen with δ (in ppm) and *J* (in Hz). Use the form: dt, δ 7.35, *J* = 8, 4 Hz, or, if second order, AB_2, AA'BB', etc. It is not necessary to solve second order patterns mathematically.



(b) Using chemical shift tables, calculate δ for the H you have assigned to the signal at δ 8.85.

Problem R-12J ($C_{25}H_{28}O_7S$). In this problem you are given the gross structure of a sugar. Your task is to determine the stereochemistry of the four substituents (three OAc, SPh, CH_2OCH_2Ph) around the ring by analysis of the ^1H NMR spectrum.

(a) Analyze the multiplets **C**-**H**. Report your results in the standard format: δ 9.3, dt, J = 14, 6 Hz, 3H. Indicate what structural information each signal provides, and a possible assignment (use the numbering on the structure). You may use first order analysis for this part.



C _____

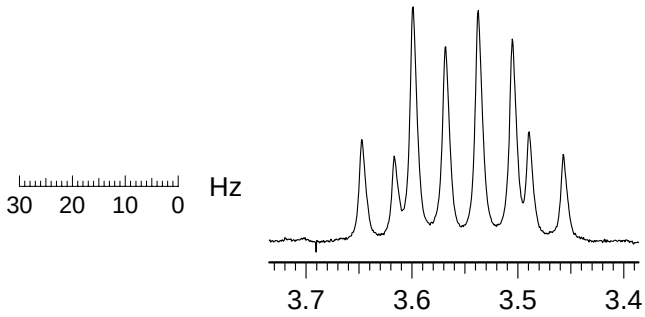
D _____

E _____

F _____

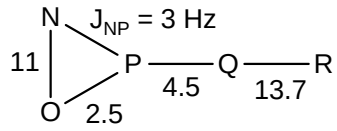
G _____

H _____

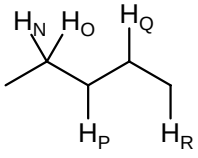


(b) Do a qualitative analysis of the signal **I** reproduced above to show you understand the pattern. Draw a coupling tree, and report the data below.

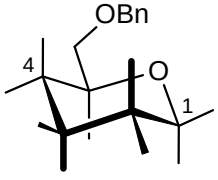
(c) Indicate the proton connectivity which your analysis provides, using a scheme such as the one below. Describe how you identified the starting point for your assignment (proton **R** in the example below).



Is equivalent to:



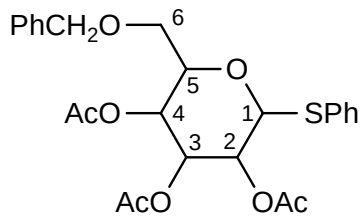
(d) Draw the complete structure of R-12J by adding appropriate substituents to the structure below. Comment on how you identified the stereochemistry at C-1 and C-4.

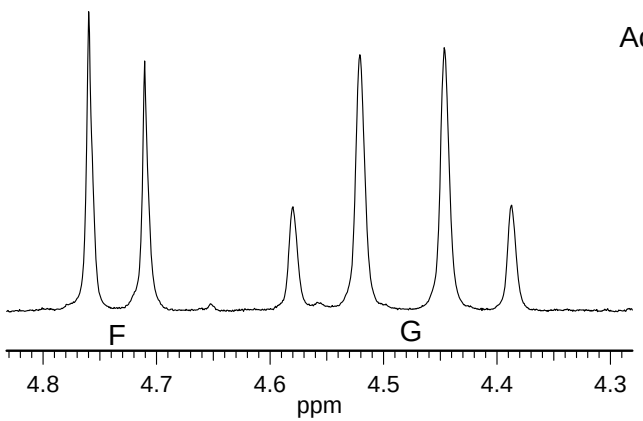


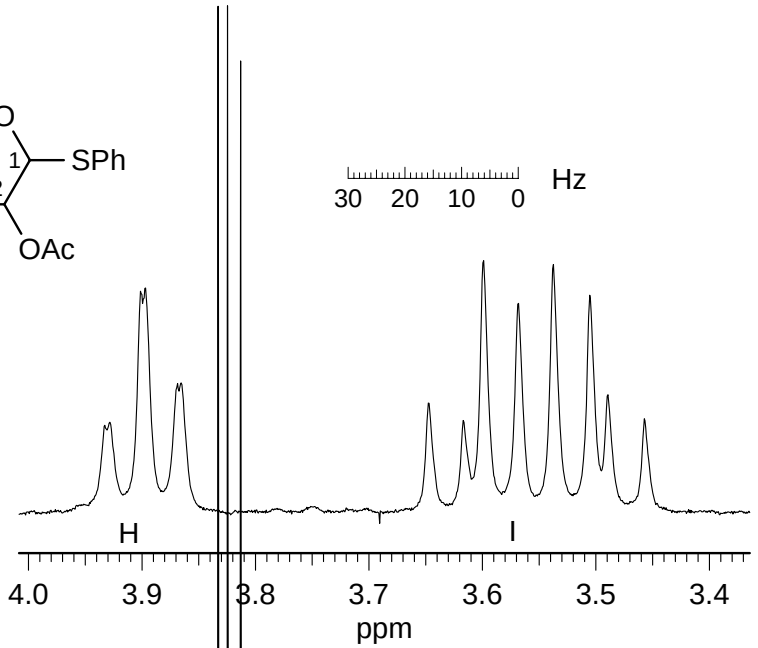
Problem R-12J ($C_{25}H_{28}O_7S$).

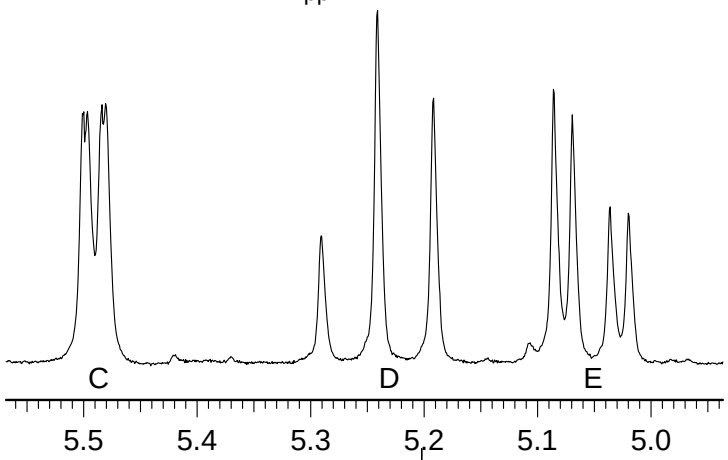
200 MHz ^{1}H NMR Spectrum in $CDCl_3$

(Source: D. Manning/K. Dantzman/Kiessling 6/12







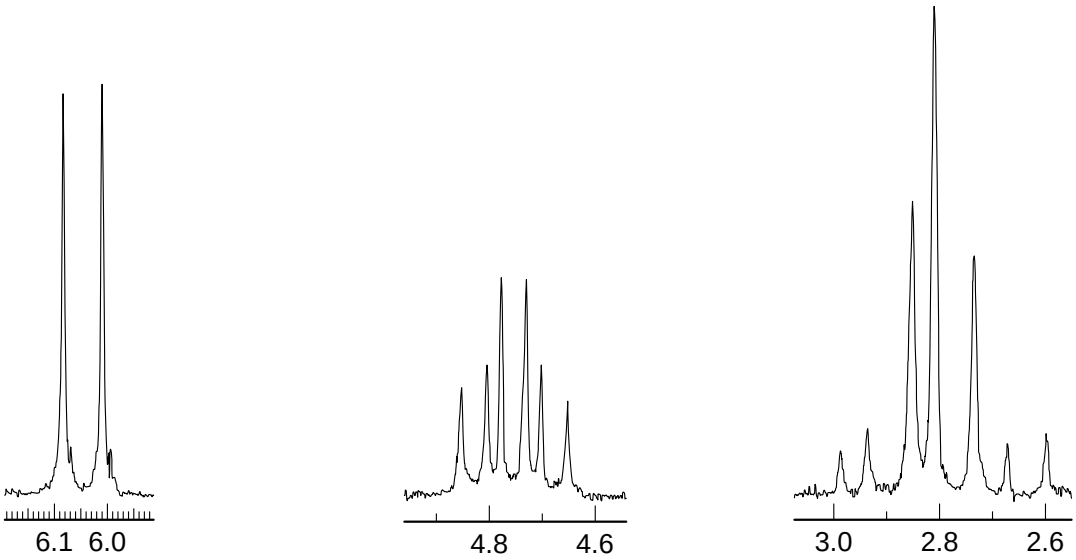


Problem R-12K ($C_{16}H_{15}ClO$). Determine the structure From the 100 MHz ^1H NMR spectrum and the information provided below. Hint: the compound contains two phenyl groups, and no other rings.

(a) DBE ____

(b) If the sample is shaken with D_2O the signal at δ 2.2 disappears. What does this tell you?

(c) Analyze the multiplets shown below. You may use first order analysis. Draw a coupling tree and report δ and *J* values in the usual format. What part structures are suggested by these multiplets?



(d) Suggest a structure for the compound. If you have more than one possibility, circle your best choice.

(e) To check your answer, do a chemical shift calculation for the signals at δ 2.8, 4.8 and 6.05.

Problem R-03L ($C_{16}H_{15}ClO$)

100 MHz ^{1}H NMR spectrum in CCl_4

Source: Ieva L. Reich 11/17