

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

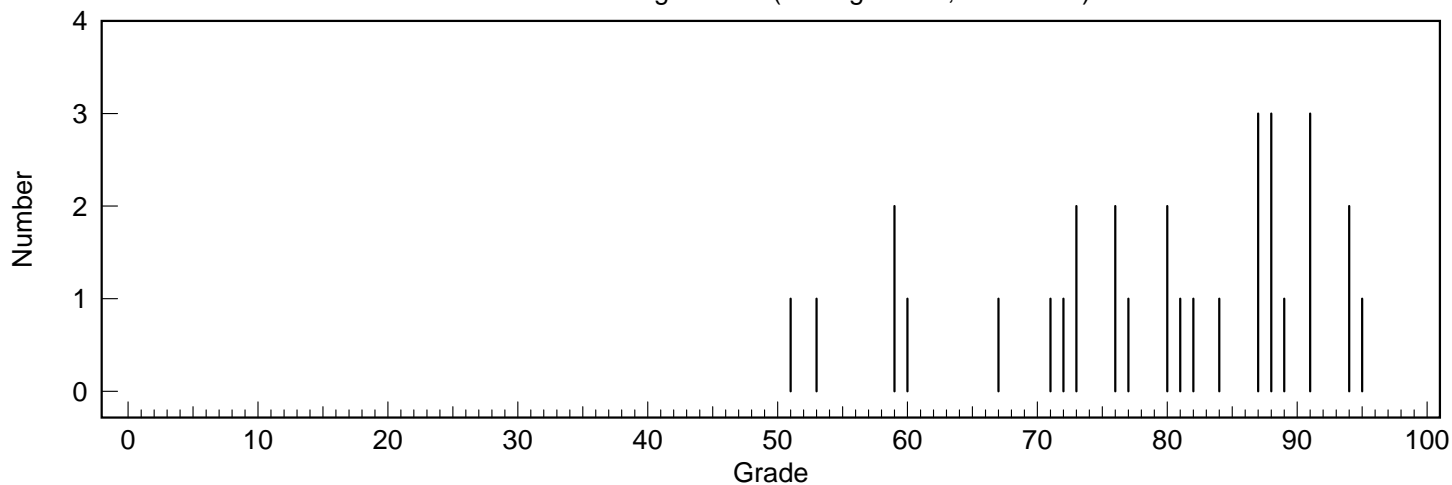
R-12K ____/20

Total ____/100

Average	79
Hi	95
Mode	87/88/91
Median	81
AB	84
BC	50

Name _____

Distribution from grade list (average: 78.8; count: 31)



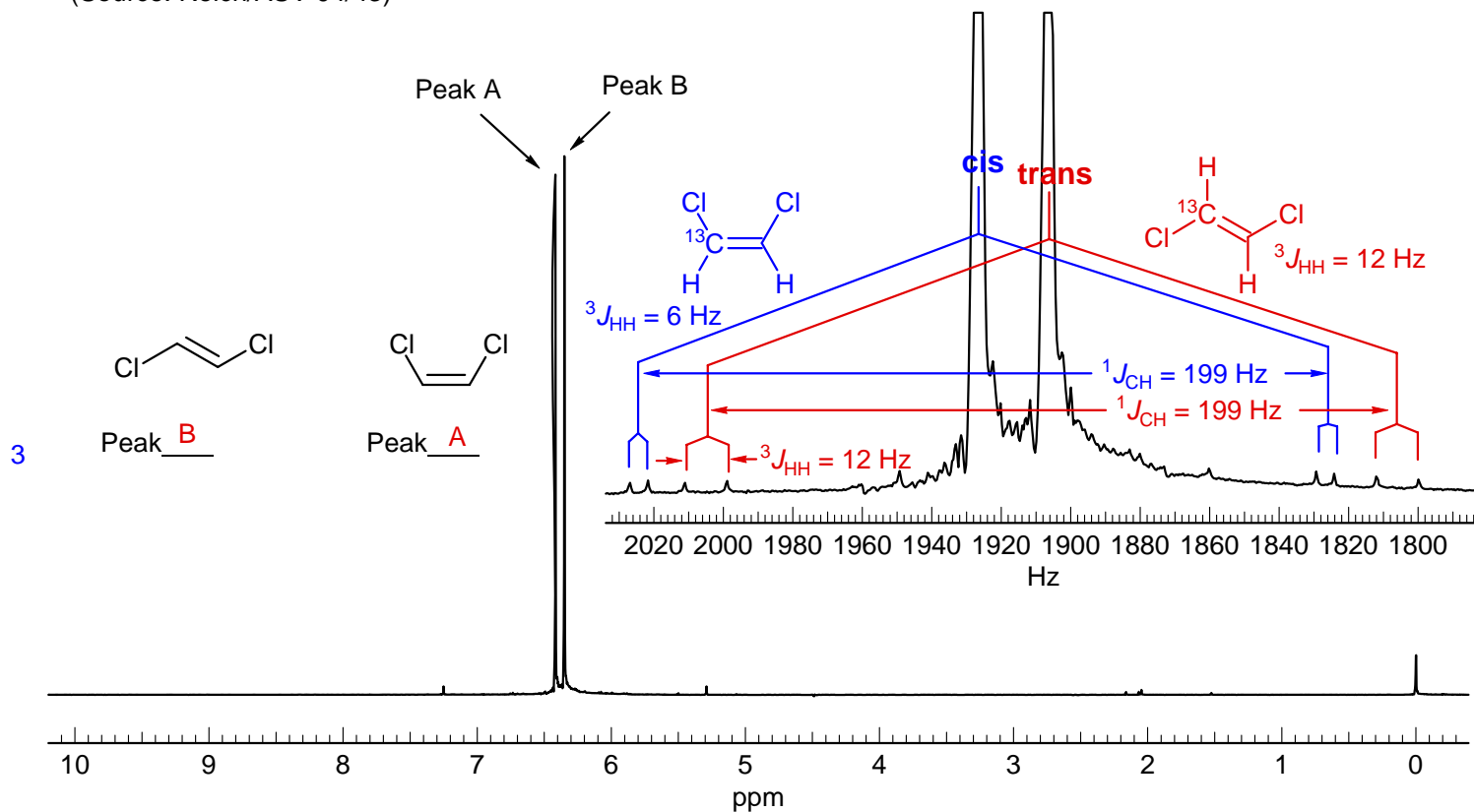
If you place answers anywhere else except in the spaces provided, (e.g. on the spectra or on extra pages) clearly indicate this on the answer sheets.

Problem R-12F. Below is the 300 MHz ^1H 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 ($\text{C}_2\text{H}_2\text{Cl}_2$).

300 MHz ^1H 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.

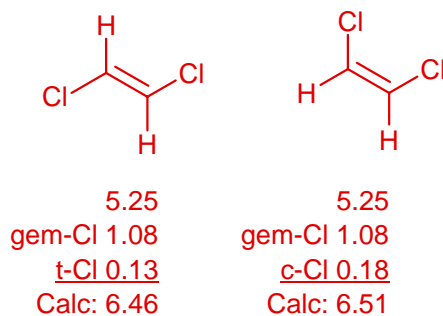
The *cis* and *trans* 3-bond J_{HH} can be measured directly from the ^{13}C satellites of each peak - the one at δ 6.42 has a coupling of 6 Hz, thus *cis* isomer, the one at δ 6.35 has $J_{\text{HH}} = 12 \text{ Hz}$, so *trans* isomer

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2 pts J_{CH}

3 pts J_{HH}

2 pts reasoning



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.

2 (a) DBE 6

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

1730 cm^{-1} possible ester $C=O$, not 4 or 5 ring

1490, 1460, 1420 aromatic

4 No OH stretch (not acid or alcohol)

1030 cm^{-1} C-O

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

168.0: Ester carbonyl

14.2: CH_3

6 61.6: CH_2-O

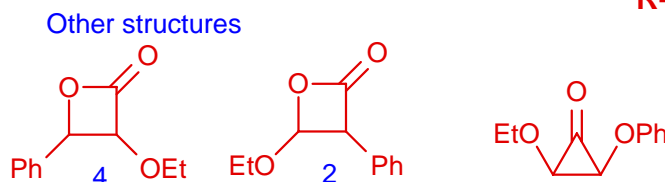
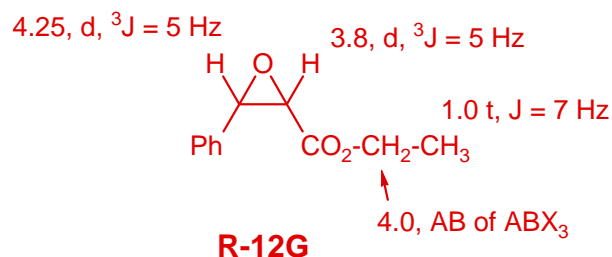
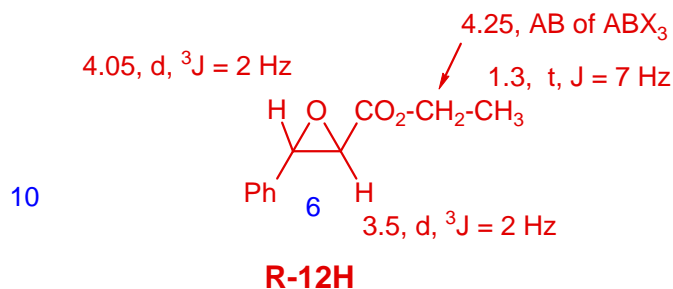
57.8, 61.6: two CH-O

135.5: quat aromatic

128.9, 128.7, 126.0: aromatic p, o, m

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

Assign the downfield epoxide proton to the PhCH because it is a little broader (not so tall) due to coupling to Ph protons Also, α -Ph (CH) is 1.35, α - CO_2R (CH) is 0.95.

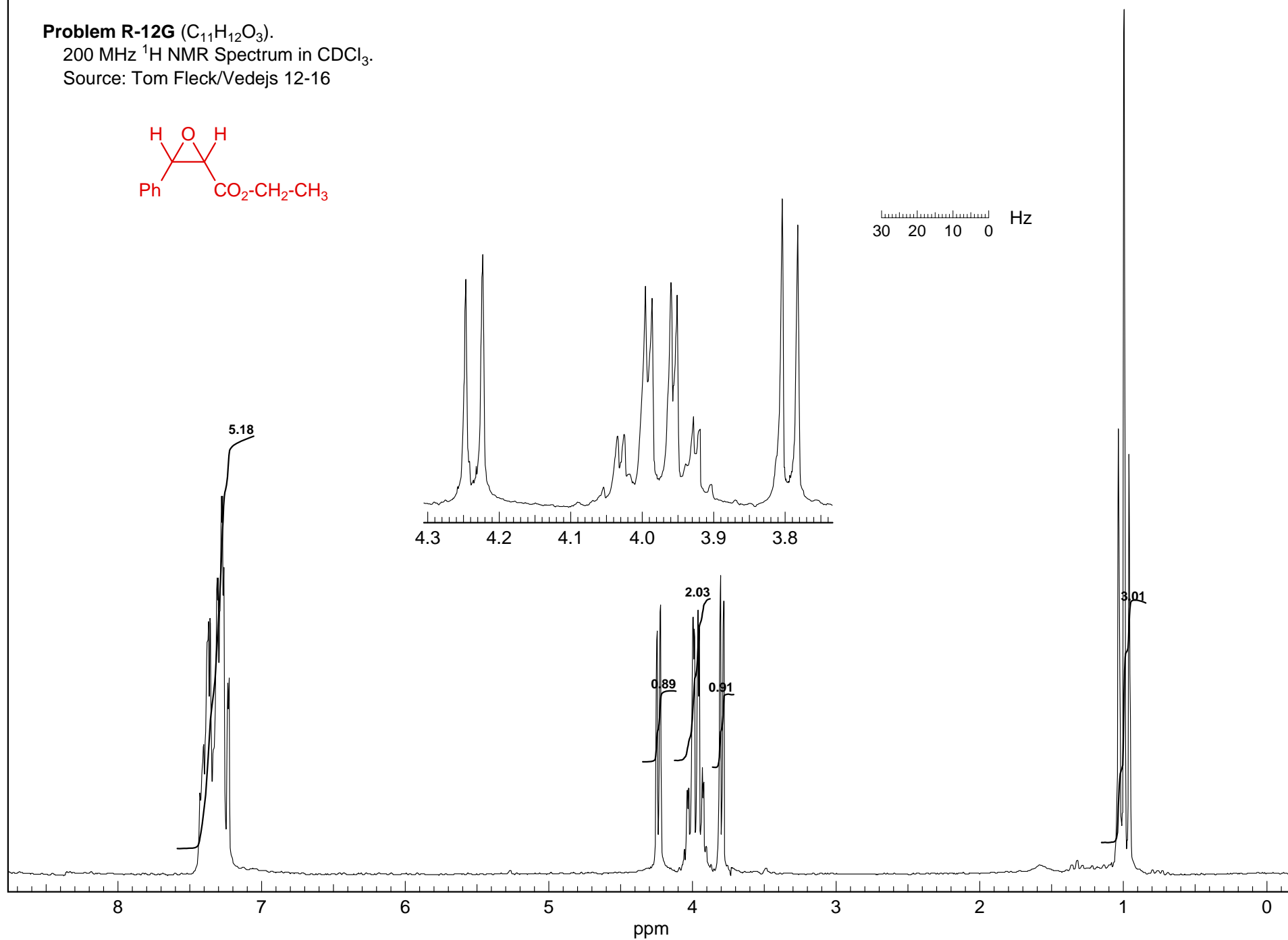
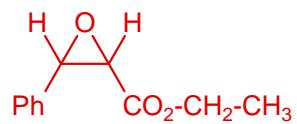


(e) What feature(s) of the spectra allowed you to make the distinction between the isomers?

In 3-membered rings J-cis is always larger than J-trans for a given system

Problem R-12G ($C_{11}H_{12}O_3$).200 MHz 1H NMR Spectrum in $CDCl_3$.

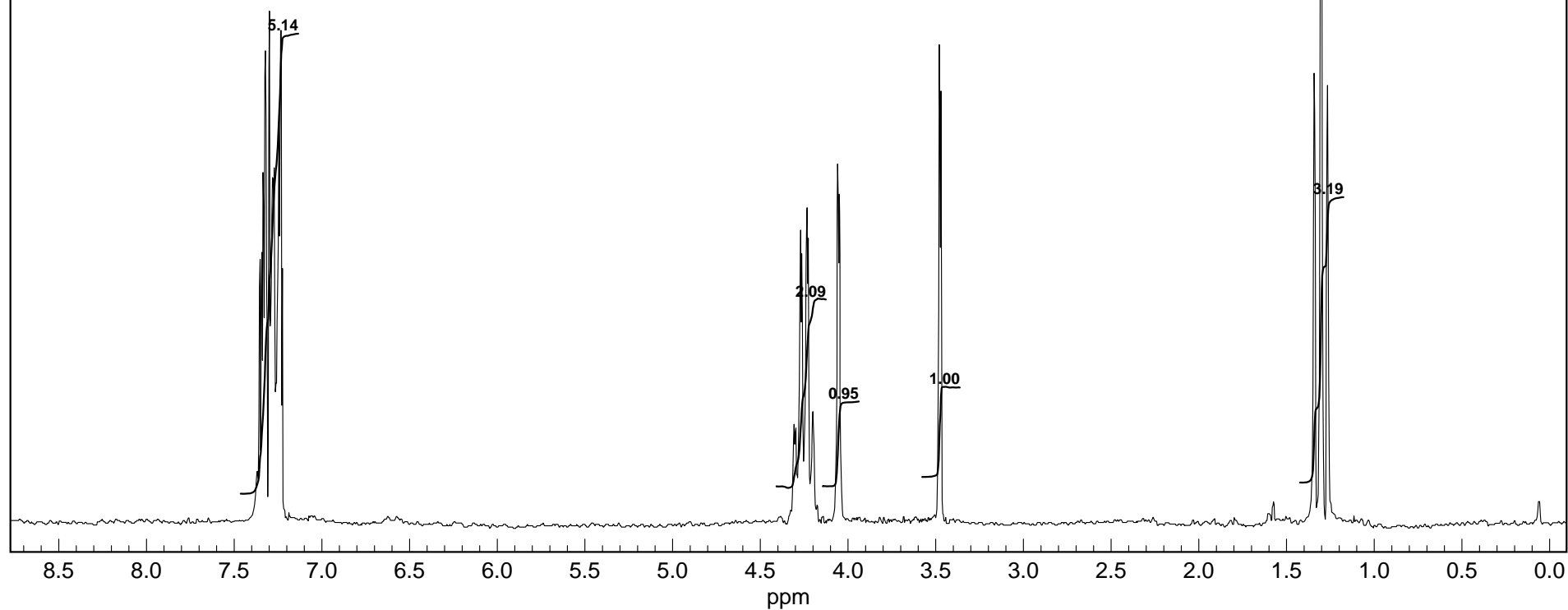
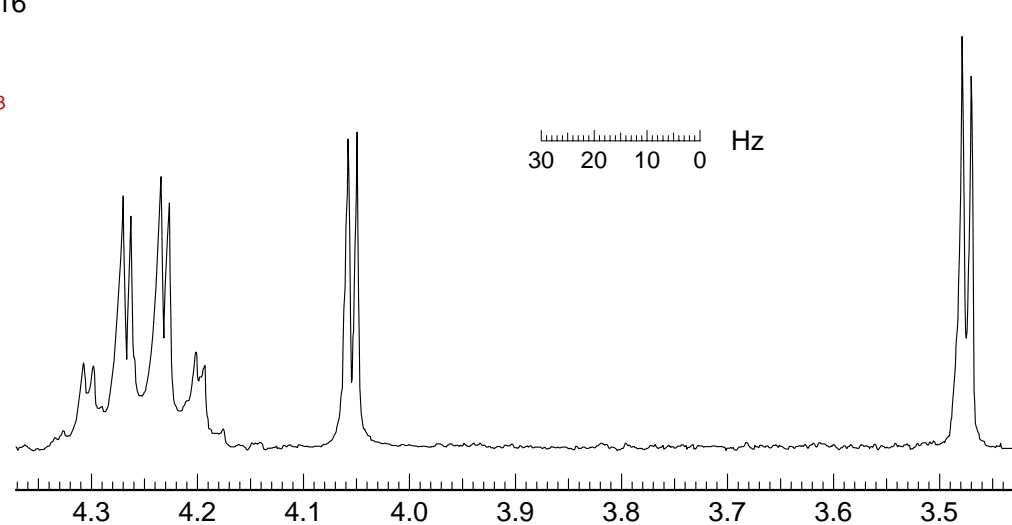
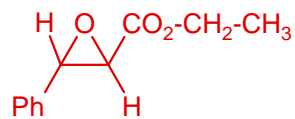
Source: Tom Fleck/Vedejs 12-16



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

200 MHz 1H NMR Spectrum in $CDCl_3$.

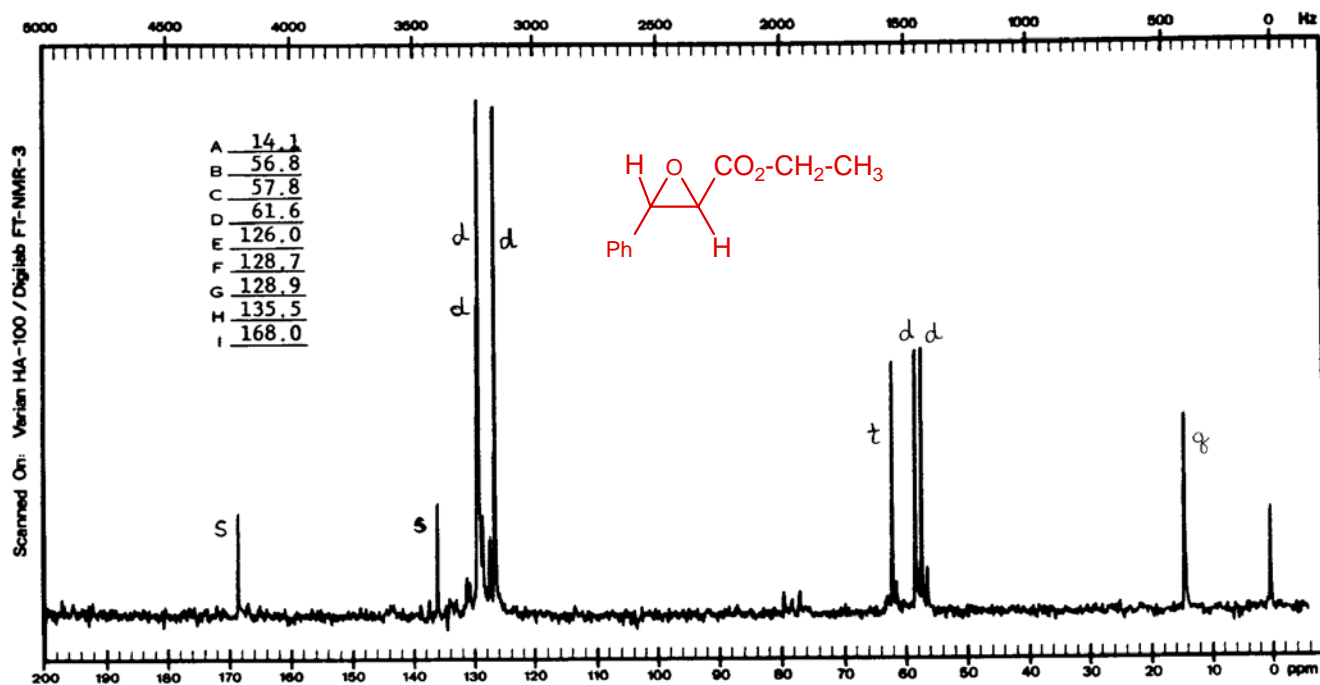
Source: Tom Fleck/Vedejs 12-16



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

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

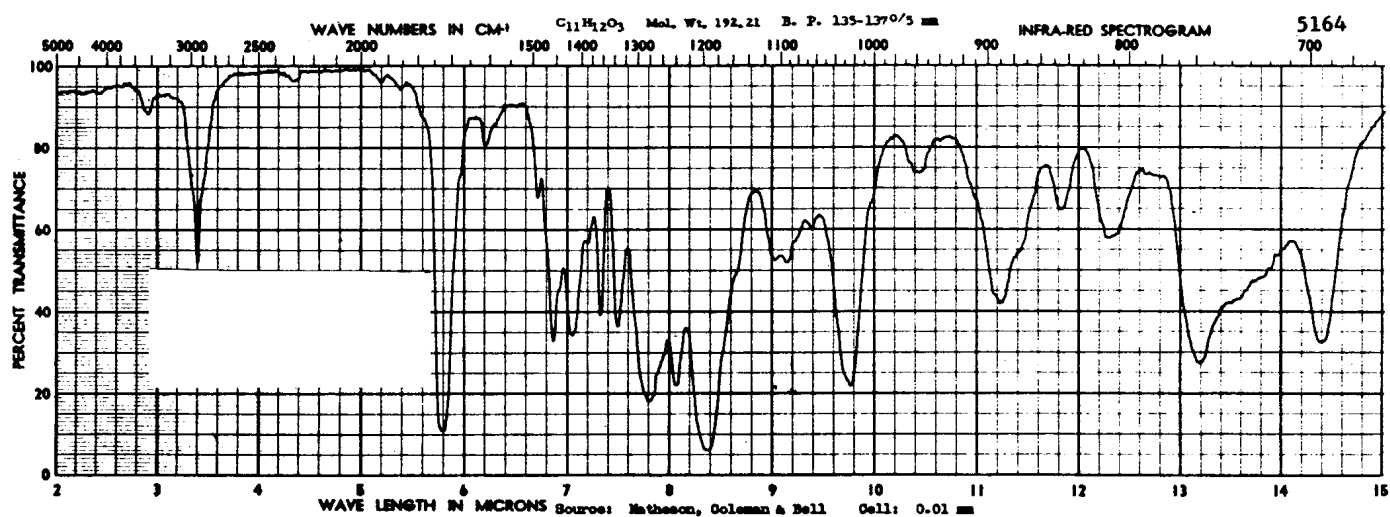
Source: Sadtler



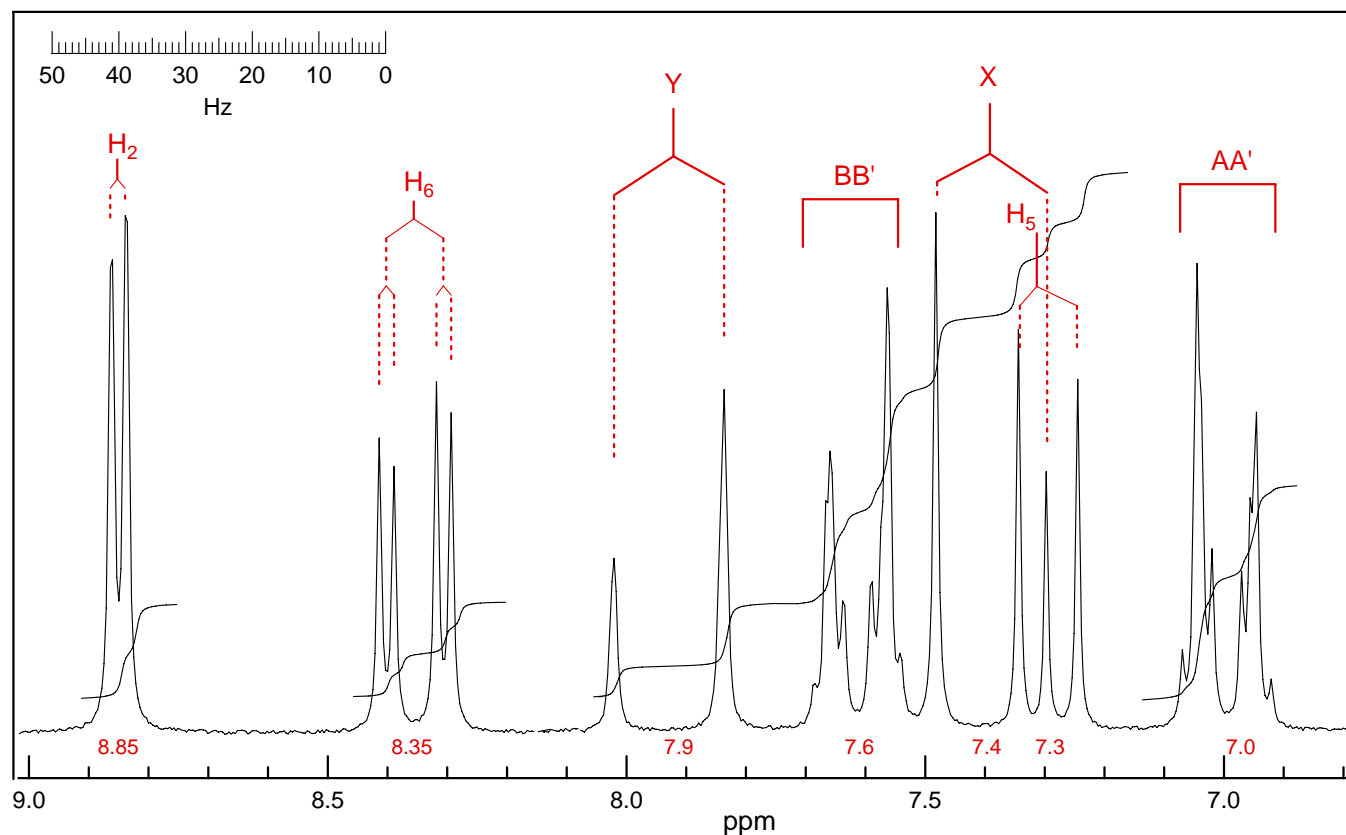
Problem R-12H ($C_{11}H_{12}O_3$).

IR Spectrum neat.

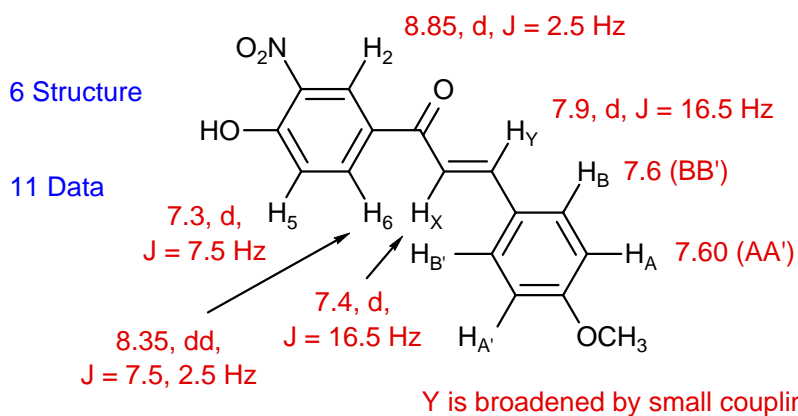
Source: Sadtler



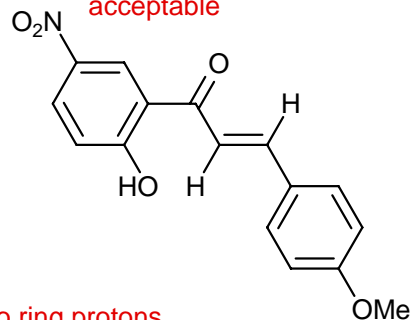
Problem R-12I ($C_{16}H_{13}NO_4$). Shown below is the 90 MHz 1H NMR spectrum of a substituted chalcone which includes all of the signals except for the methoxy group and the OH. There are a total of **three** substituents on the two aryl rings (OCH_3 , OH and NO_2). You may treat the OH and OCH_3 as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



This is also an acceptable answer - shift calculations actually come out better. Other isomers with same proton pattern also acceptable



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

Calc H_2 : Base + o- NO_2 + o-COPh + m-OH

$$7.36 + 0.87 + 0.45 - 0.14 = 8.54 \quad (OH)$$

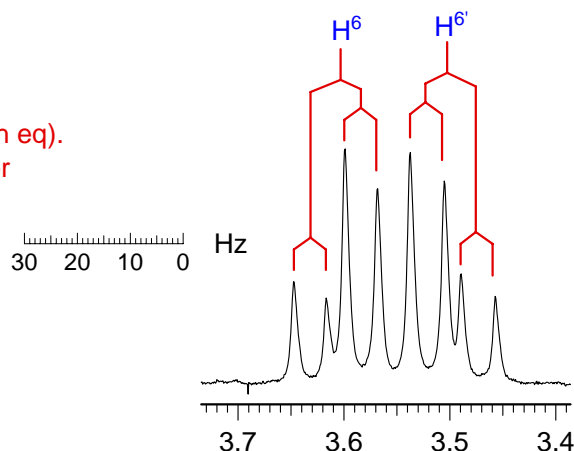
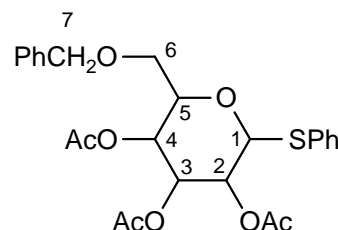
$$7.36 + 0.87 + 0.45 - 0.07 = 8.61 \quad (OMe)$$

25

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.

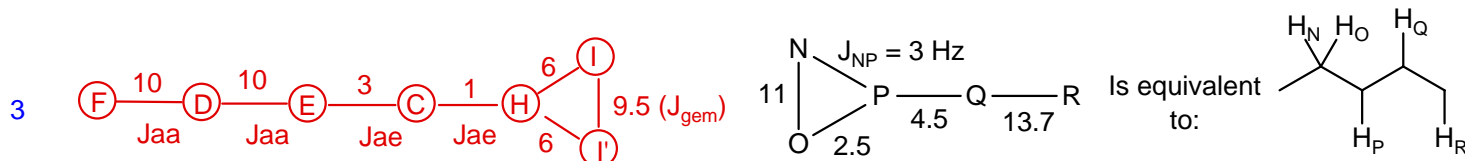
- 1 **C** H^4 δ 5.50, dd, $J = 3.2, 1$ Hz, 1H
small coupling is to E. Since E is ax, C must be eq
-
- 1 **D** H^2 δ 5.25, t, $J = 10$ Hz, 1H
Axial proton, with both axial neighbors. Must be H^2 - one coupling to F, other to E
-
- 1 **E** H^3 δ 5.05, dd, $J = 10, 3.2$ Hz, 1H
From 10 Hz coupling to D, we know E is axial, small 3 Hz coupling is to C, so C is equatorial
-
- 1 **F** H^1 δ 4.73, d, $J = 10$ Hz, 1H
This is only doublet seen, so must be H^1 , and it is axial (SPh eq).
Coupled to D, since this is the only possible coupling partner
-
- 3 **G** H^7 ABq, δ 4.54, 4.42. JAB = 11.5 Hz, 2H
This is the CH_2 of the benzyl group
-
- 1 **H** H^5 δ 3.90, td, $J = 6, 1$ Hz, 1H
This is H^5 - triplet coupling is to $H^6, H^{6'}$, doublet to H^4



(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.

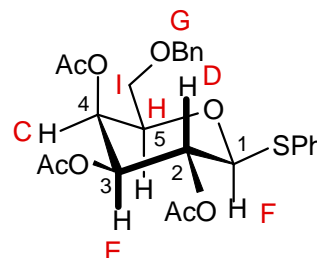
- 5 AB of an ABX system (H^6): $\delta_A = 3.6, J_{AB} = 9.5, J_{AX} = 6$ Hz
 $\delta_B = 3.5, J_{BX} = 6$ Hz
These are the diastereotopic protons at C⁶

(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).



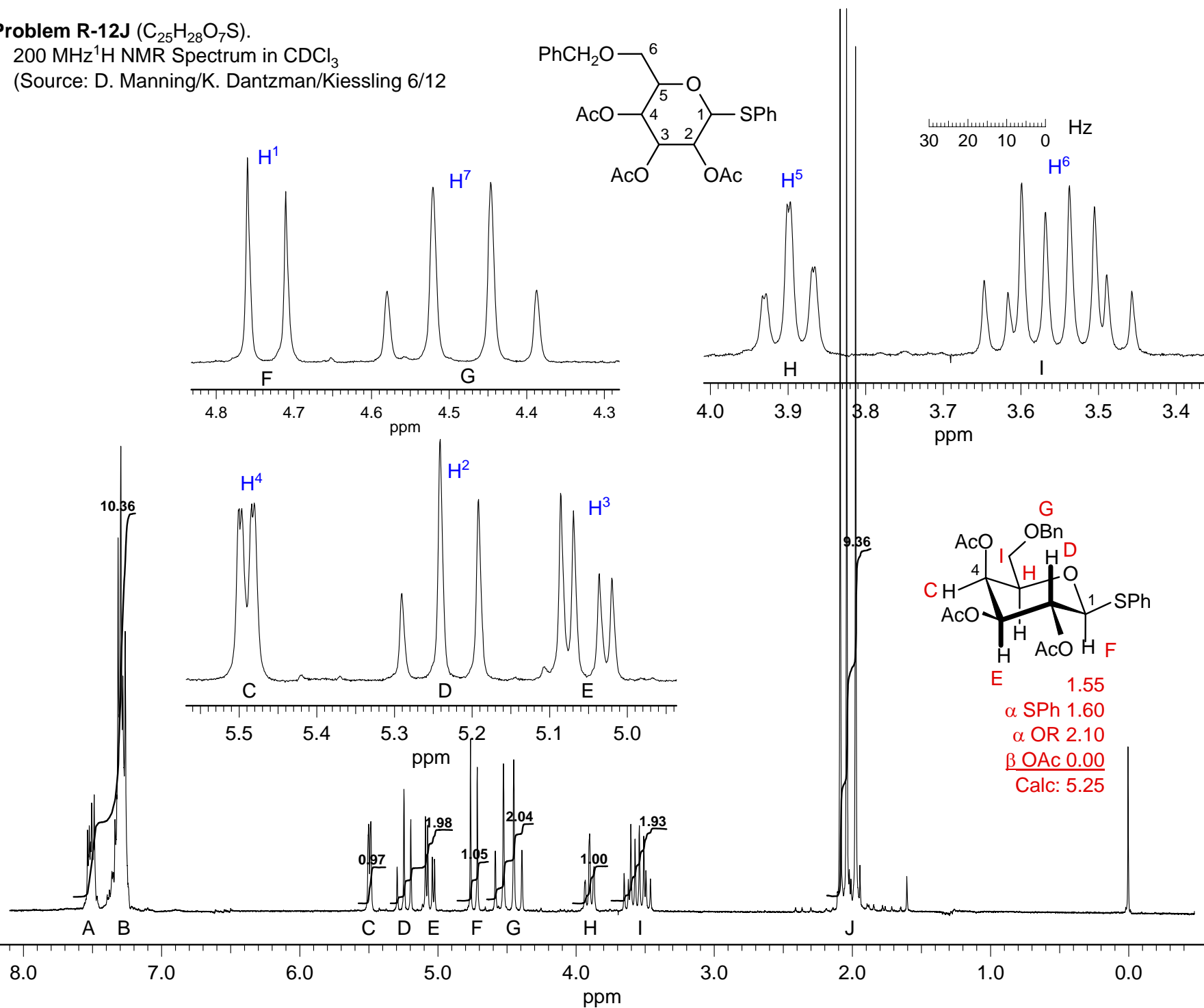
(d) Draw the complete structure of R-12J by adding appropriate substituents to the structure below. Comment on how you identified the stereochemistry at C-1 and C-4.

- 9 C¹ proton must be axial to get large 10 Hz coupling
C⁴ proton must be equatorial since C³-H and C⁵-H are axial, and there is a small coupling to each



Problem R-12J (C₂₅H₂₈O₇S).200 MHz ¹H NMR Spectrum in CDCl₃

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



20

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.

2 (a) DBE 9

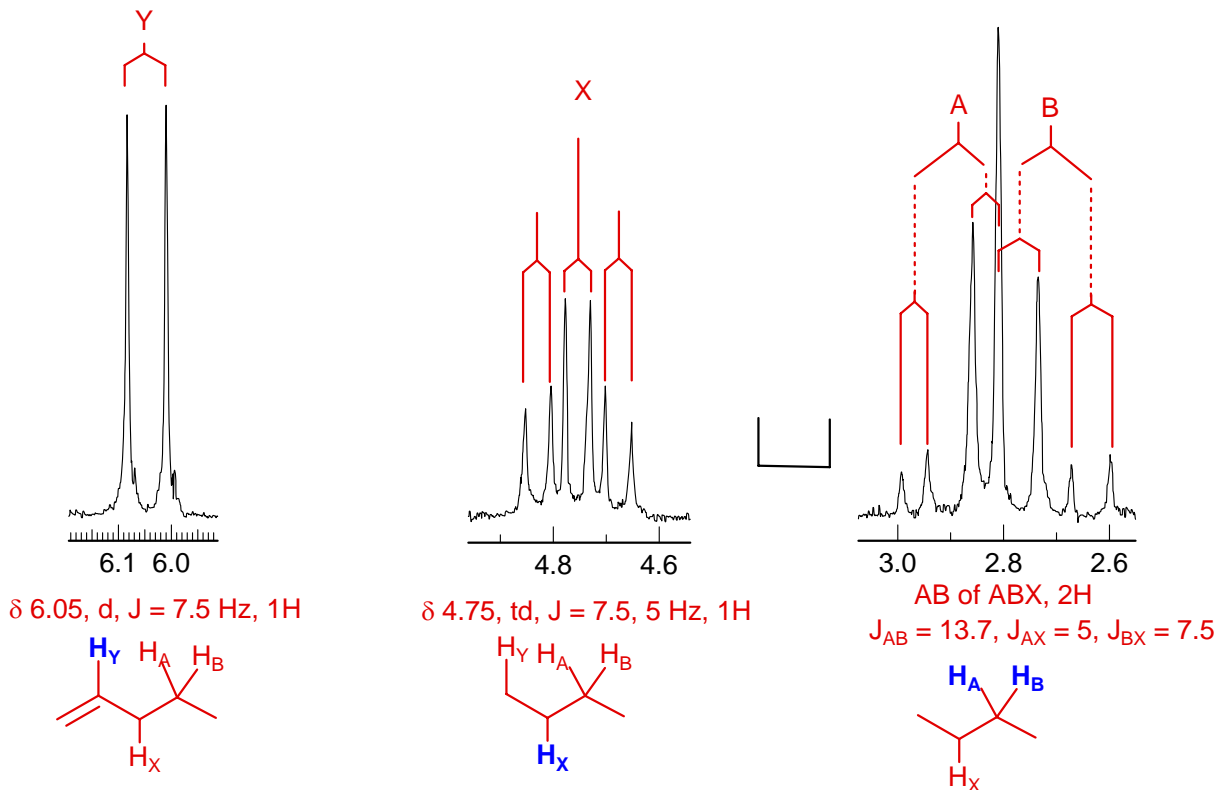
(b) If the sample is shaken with D_2O the signal at δ 2.2 disappears. What does this tell you?

2 This must be on OH peak

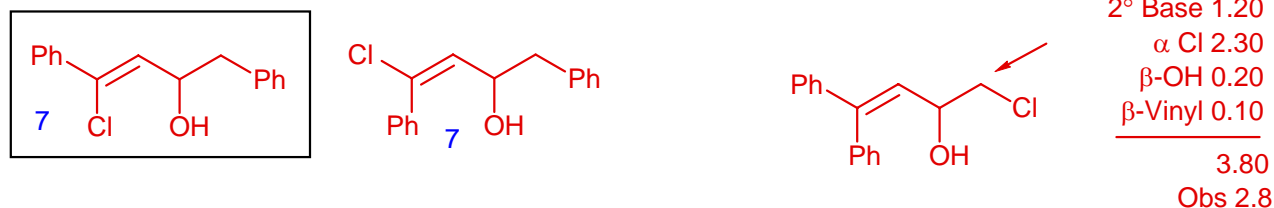


(c) Analyze the multiplets shown below. You may use first order analysis. Draw a coupling tree and report δ and J values in the usual format. What part structures are suggested by these multiplets?

6

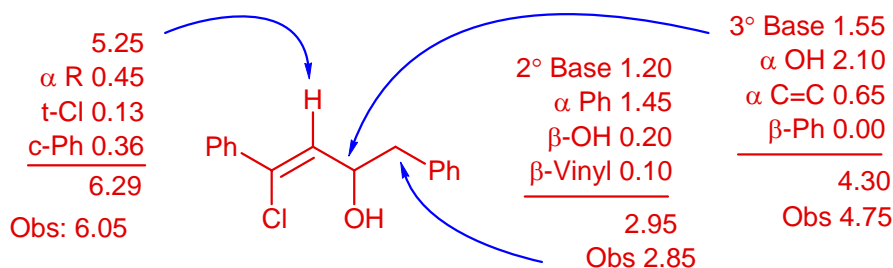


(d) Suggest a structure for the compound. If you have more than one possibility, circle your best choice.



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

3



Problem R-03L (C₁₆H₁₅ClO)100 MHz ¹H NMR spectrum in CCl₄

Source: Ieva L. Reich 11/17

