

Chemistry 605 (Reich)

SECOND HOUR EXAM

Thur. April 12, 2012

Question/Points

R-11H_____/30

R-11J,K_____/15

R-11L,M_____/30

R-11N_____/17

R-11O_____/8

Total ____/100

Practice Exam 2

Name_____

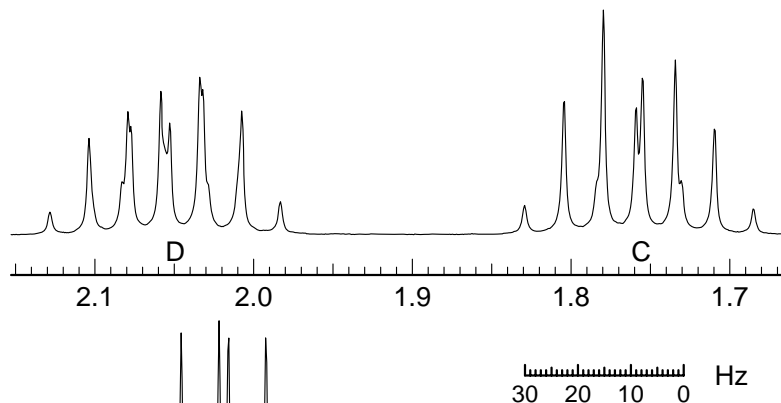
If you place answers anywhere else except in the spaces provided, (e.g. on the spectra or on extra pages) clearly indicate this on the answer sheets.

Problem R-11H ($C_{12}H_{16}O_3$). You are provided the 1H and ^{13}C NMR spectra of a compound. Interpret the spectra, and determine the structure or structures. Note that the signal at δ 6.5 disappeared when D_2O was added.

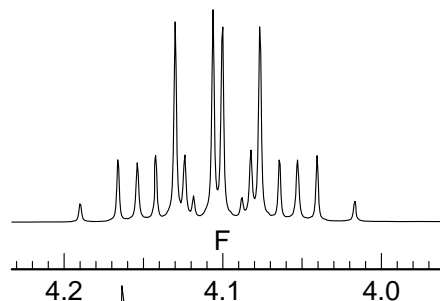
(a) DBE _____

(b) Analyze the multiplets below. Identify the patterns (e.g., ABXYZ - underline the observed nuclei). If they are first order, report them in the standard format (δ 0.00, dqt, $J = 0.0, 0.0, 0.0, 2H$). Provide part structure(s) defined by these protons.

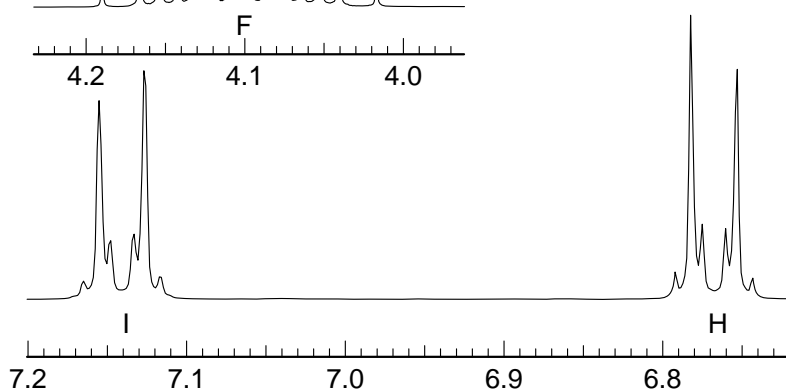
δ 1.7-2.1 _____



δ 3.9-4.1 _____



δ 6.7-7.2 _____



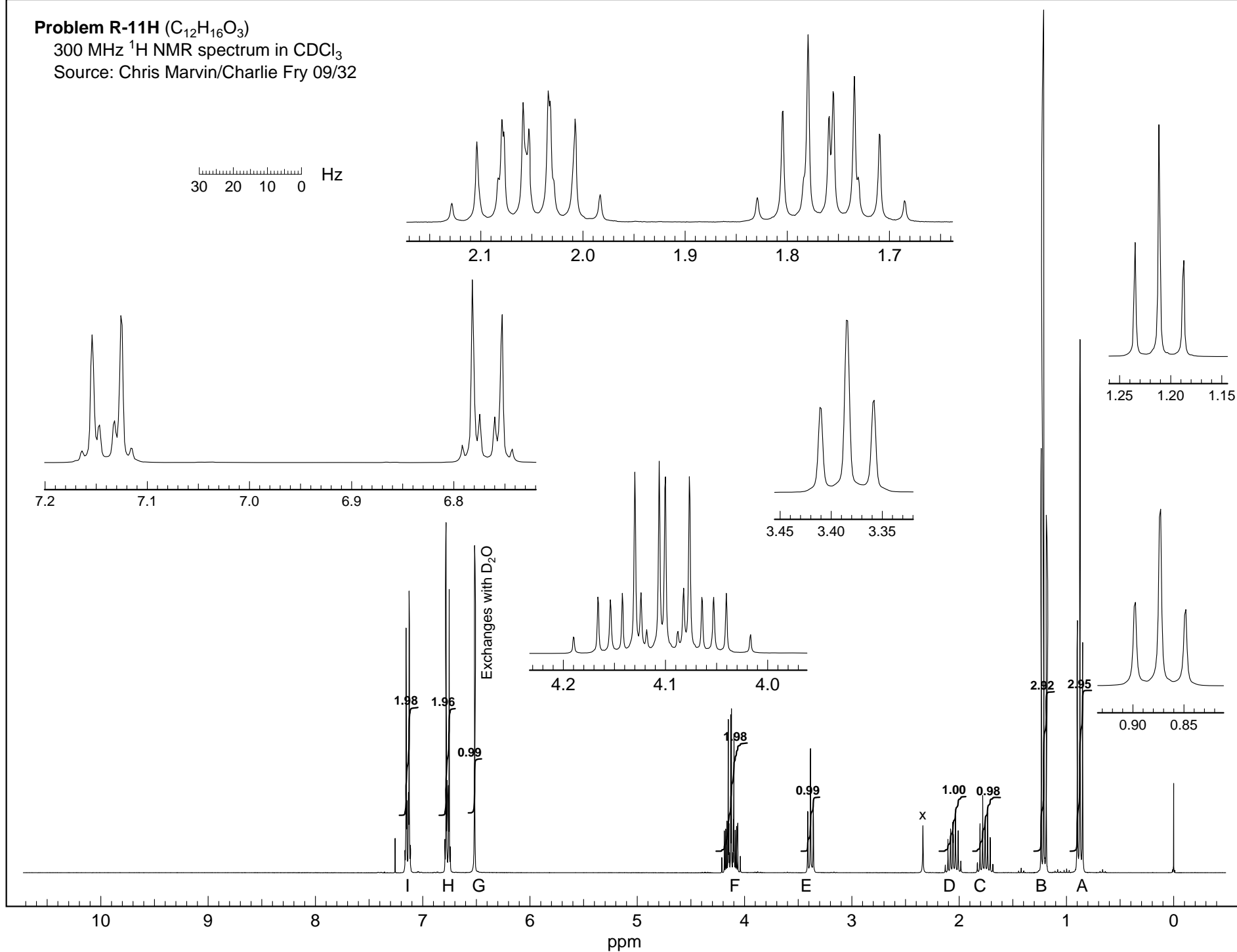
(c) Identify at least 3 signals in the ^{13}C NMR spectrum which provide significant structural information, and describe the part structures obtained from them.

(d) Draw the structure of **R-11H** below. If more than one structure fits the data, draw them, but circle your best choice.

Problem R-11H ($C_{12}H_{16}O_3$)

300 MHz 1H NMR spectrum in $CDCl_3$

Source: Chris Marvin/Charlie Fry 09/32

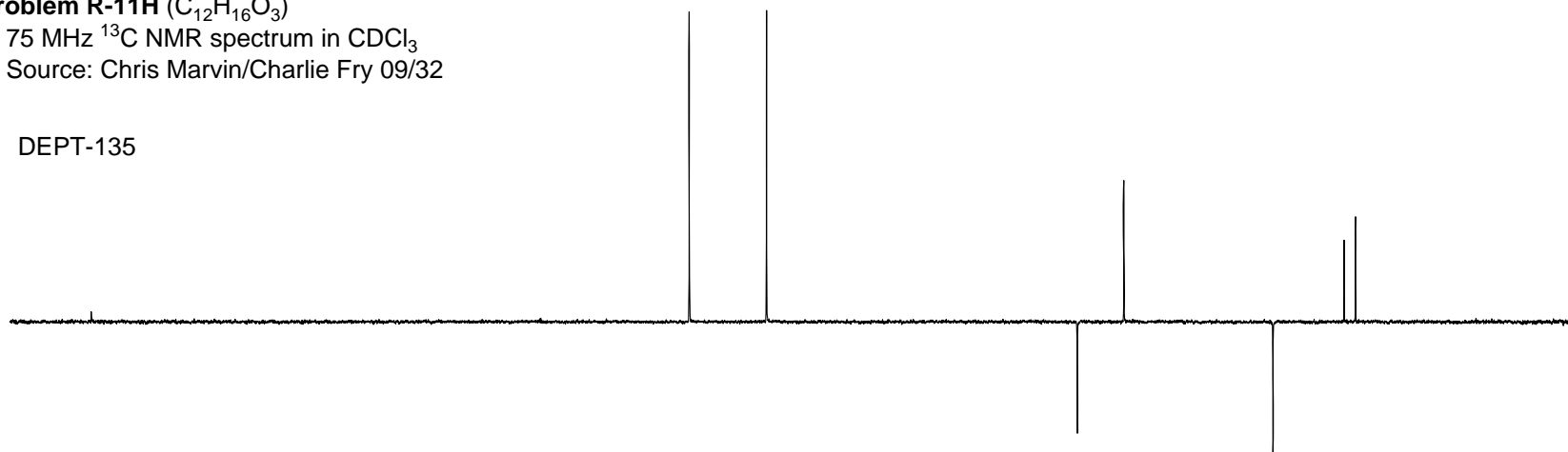


Problem R-11H ($C_{12}H_{16}O_3$)

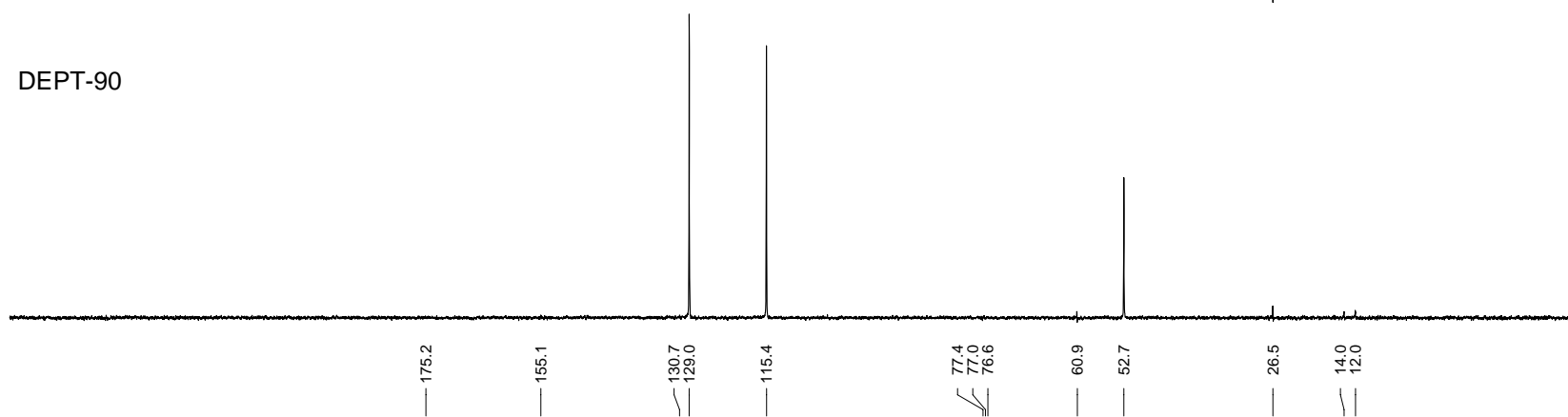
75 MHz ^{13}C NMR spectrum in $CDCl_3$

Source: Chris Marvin/Charlie Fry 09/32

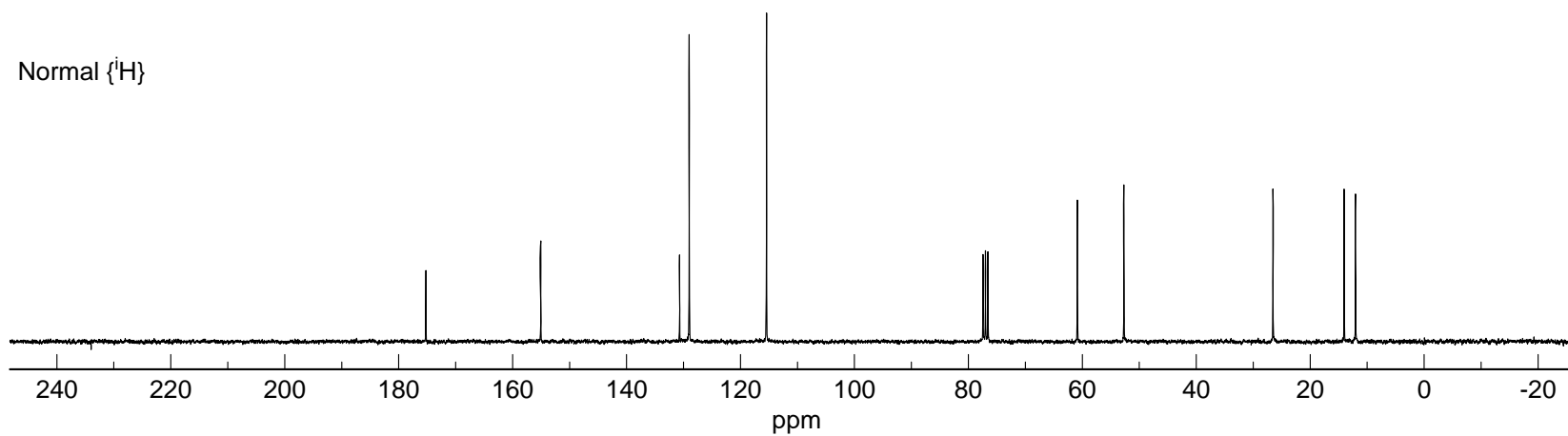
DEPT-135



DEPT-90

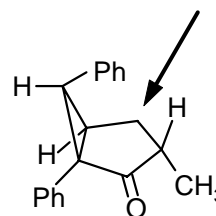


Normal $\{^1H\}$

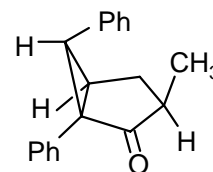


Problem R-11J and K (C₁₉H₁₈O). You are given 200 MHz ¹H NMR spectra of two **stereoisomers** of a compound which differ at one stereocenter only (i. e., **1** and **2**, or **6** and **8**), the possibilities are **1** to **8** below. Your task is to make both a structural and a stereochemical assignment. Explain the basis of your assignment below, taking care to clearly identify the signals you are using.

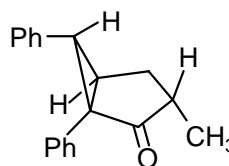
(a) What spectral features allow you to distinguish the two structural types (**1** to **4** versus **5** to **8**)?



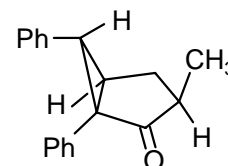
1 _____



2 _____

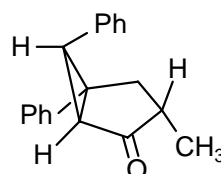


3 _____

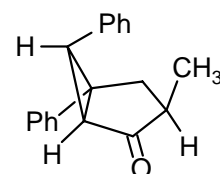


4 _____

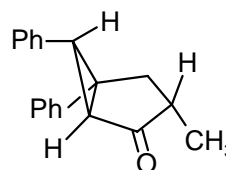
(b) What spectral features allow you to distinguish the pair of isomers? Write the spectrum number (**R-11J** or **R-11K**) in the appropriate blank.



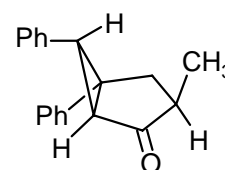
5 _____



6 _____



7 _____



8 _____

(c) Just to show you understand the spectra, give just the chemical shifts of the two protons at the CH₂ group (marked with an arrow in **1**).

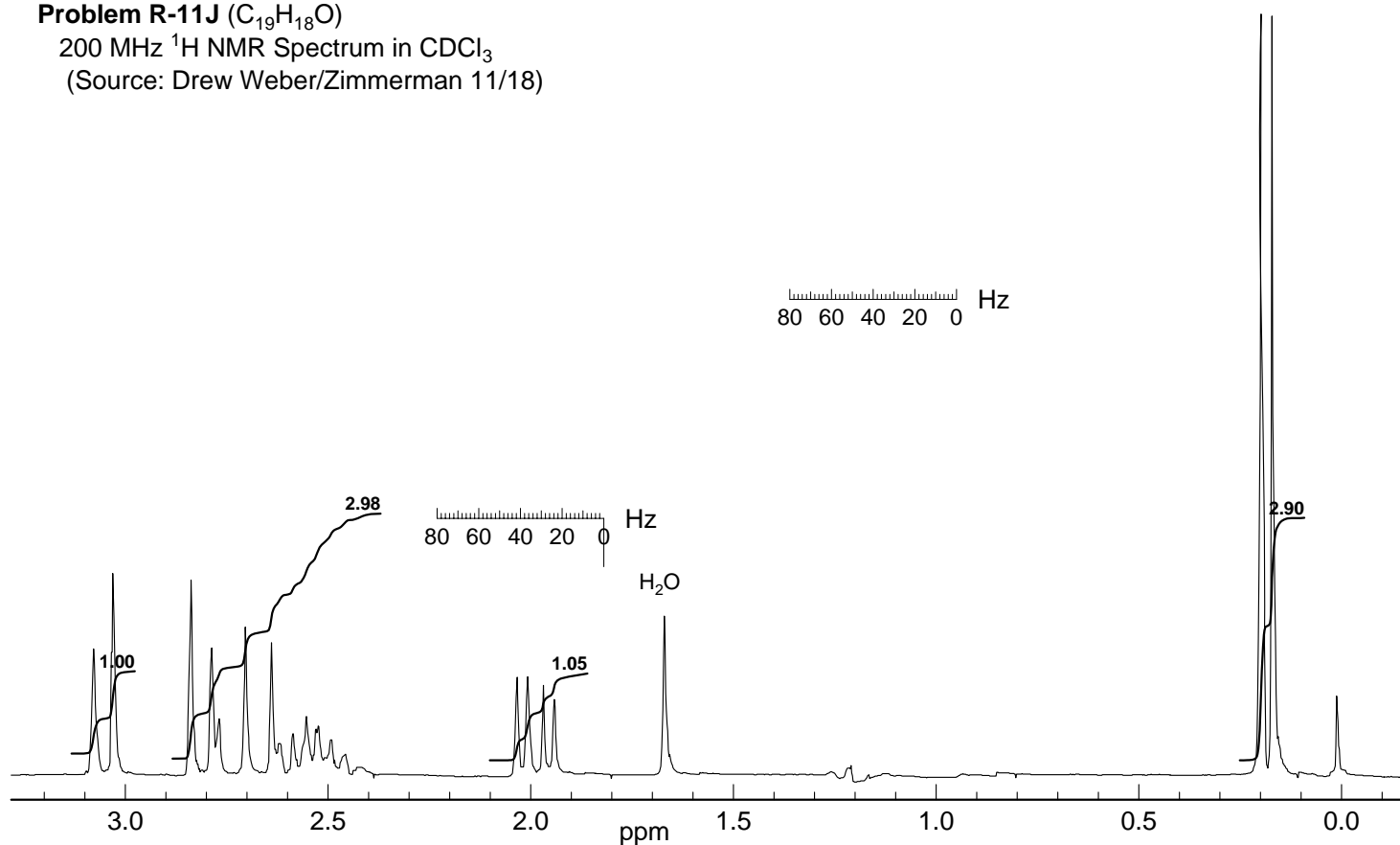
R-11J _____, _____

R-11K _____, _____

Problem R-11J ($C_{19}H_{18}O$)

200 MHz 1H NMR Spectrum in $CDCl_3$

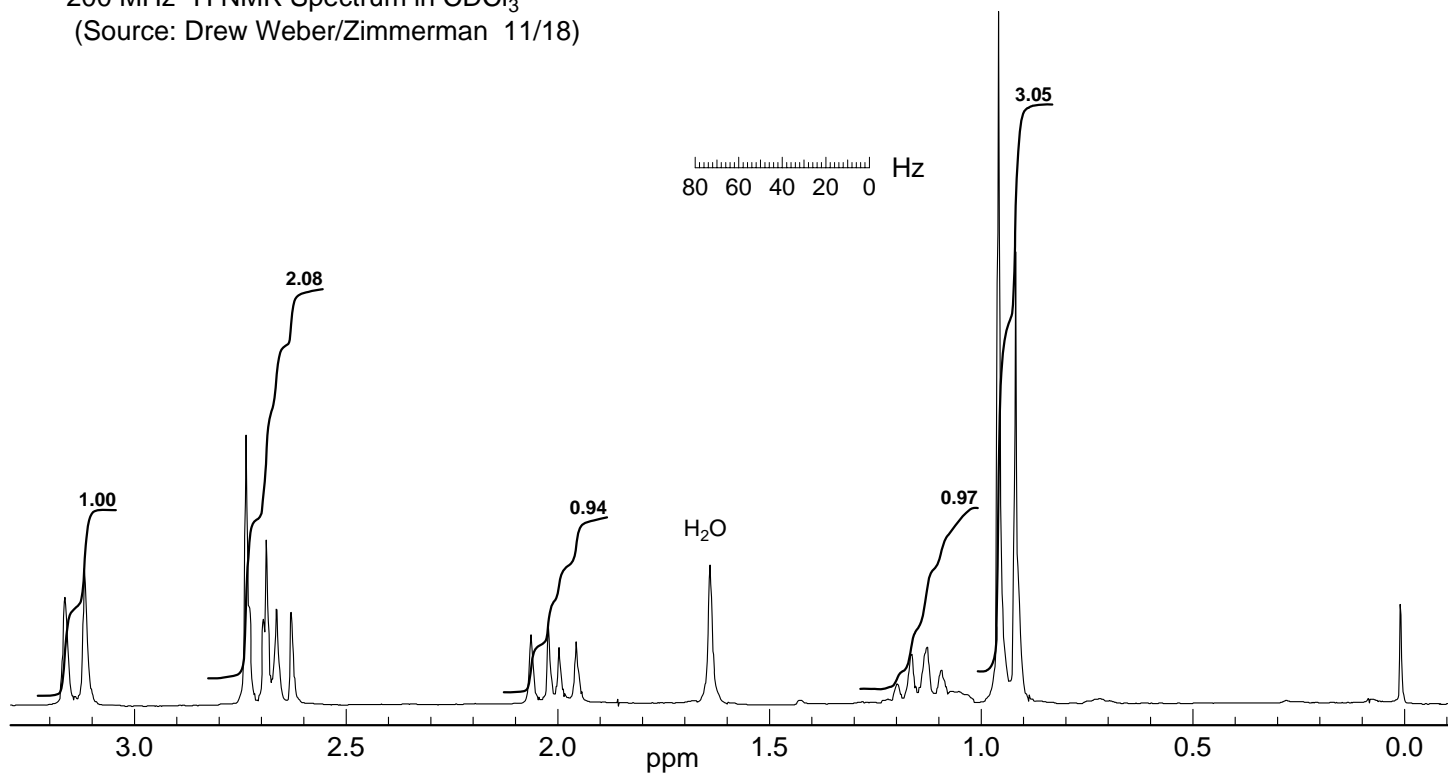
(Source: Drew Weber/Zimmerman 11/18)



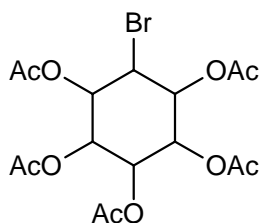
Problem R-11K ($C_{19}H_{18}O$)

200 MHz 1H NMR Spectrum in $CDCl_3$

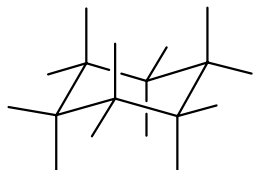
(Source: Drew Weber/Zimmerman 11/18)



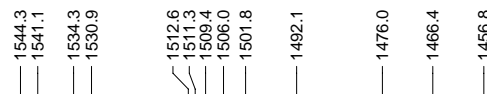
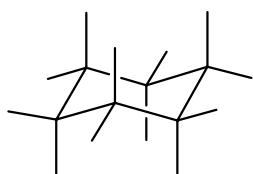
Problem R-11L and R-11M. From the 270 MHz ^1H NMR spectra of two stereoisomeric bromo pentaacetoxy cyclohexanes assign stereochemistry and conformation ("interpret" means give δ , J and multiplicity).



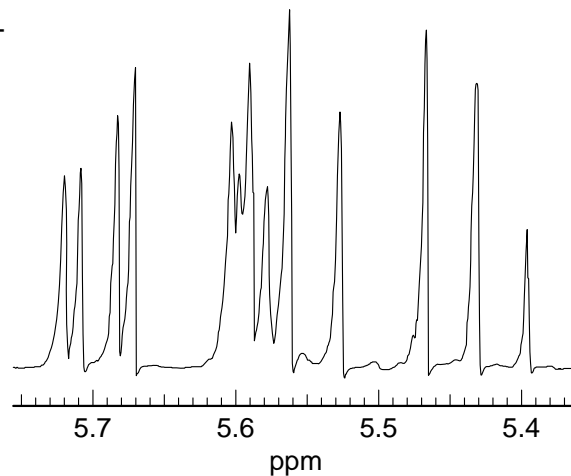
(a) Interpret the signal at δ 4.5 in **R-11L**. Suggest possible part structures. Circle the proton at δ 4.5



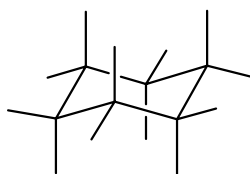
(b) Interpret the signal at δ 5.2 in **R-11L**. Suggest possible part structures. Circle the proton at δ 5.2.



(c) Identify other significant multiplets in the expansion (δ 5.3 - 5.8) on the right (**R-11L**), draw coupling trees, and identify part structures. HINT: these are all first order



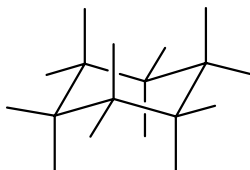
(d) Complete the structure for **R-11L** below by placing bromo and acetoxy groups with the appropriate stereochemistry on the structure.



R-11L

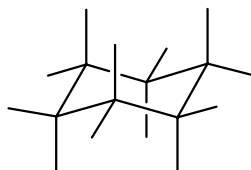
(e) What do the signals at δ 2 tell you about the structure of **R-11M** (compare them to the δ 2 signals of **R-11L**).

(f) Assign and interpret the signal at δ 4.0 in **R-11M**. Suggest possible part structures.



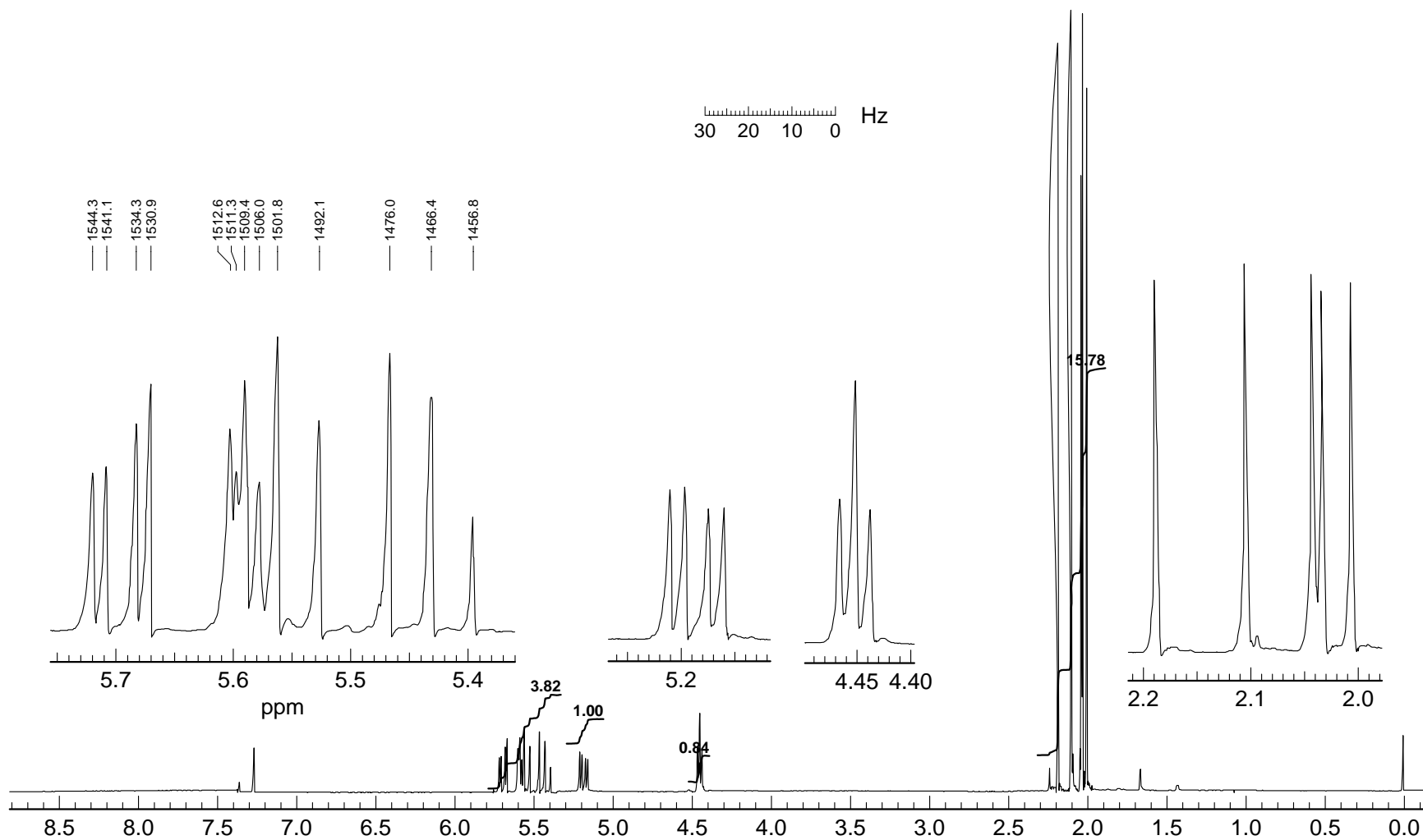
(g) Analyze the rest of the NMR spectrum of **R-11M**. Point out significant features of the spectrum which can be used to assign stereochemistry. HINT: there are some second-order effects in the multiplet δ 5.1 - 5.5.

(h) Complete the structure of **R-11M** below by placing bromo and acetoxy groups with the appropriate stereochemistry on the structure.

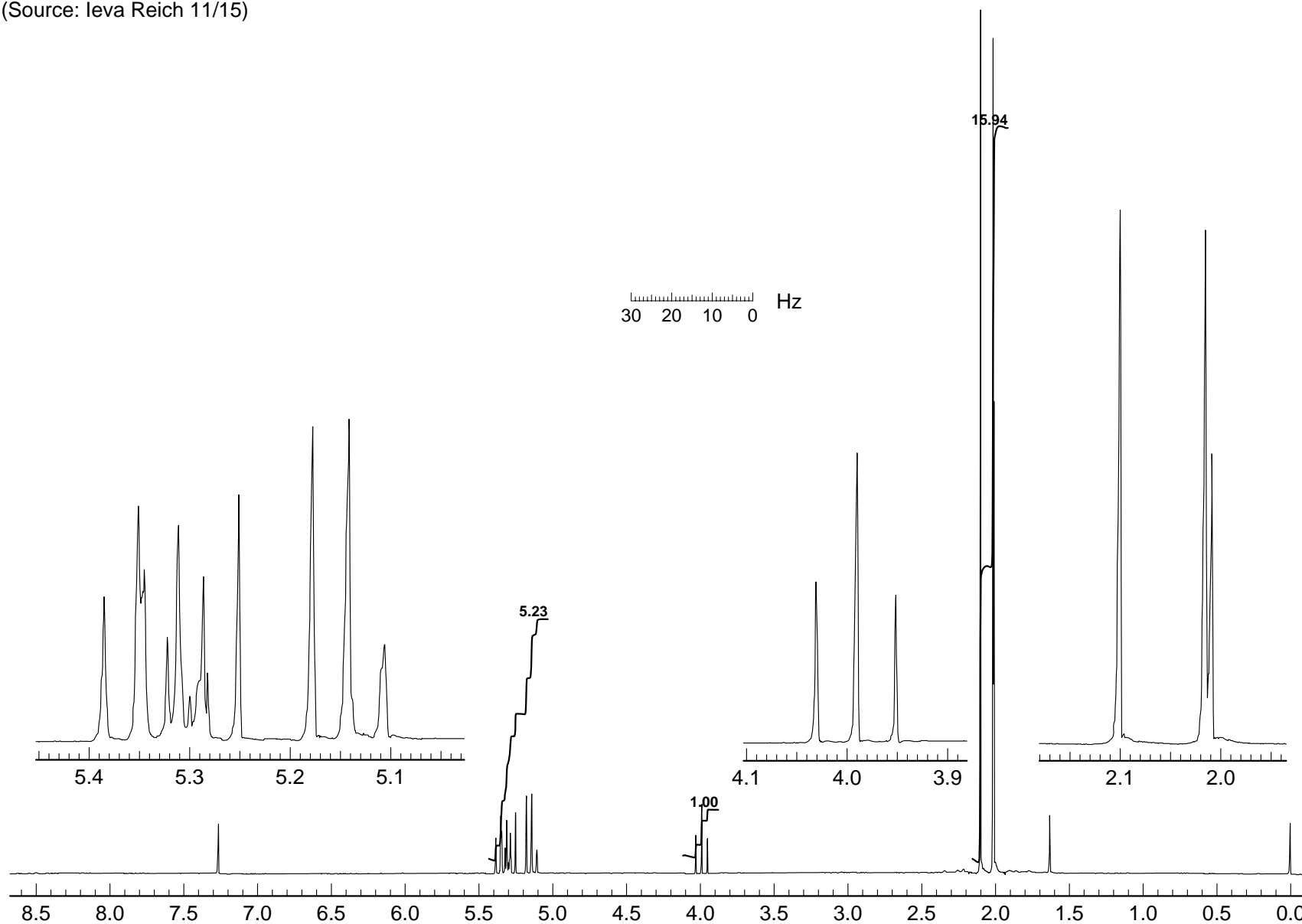


R-11M

Problem R-11L ($\text{C}_{16}\text{H}_{21}\text{BrO}_{10}$)
270 MHz ^1H NMR Spectrum in CDCl_3
(Source: Ieva Reich 11/15)



Problem R-11M ($\text{C}_{16}\text{H}_{21}\text{BrO}_{10}$)
270 MHz ^1H NMR Spectrum in CDCl_3
(Source: Ieva Reich 11/15)



Problem R-11N ($\text{C}_9\text{H}_{16}\text{ClN}$). In this problem you are required to determine the position of a Cl substituent in a 1-aza-bicyclo[2.2.2]heptane from the ^1H NMR spectra. You are given the ^1H NMR spectra of the compound and the 7,7-dideuterated analog.

(a) Analyze the coupling system of **R-11N** and report your results below. For each position either give the multiplicity, J and δ values, or enter Cl if that is where you think it is. NOTES: 1. You may use first order analysis - there are no significant second order effects. 2. There are no effects detectable due to coupling between H and D.

$$2x \underline{\hspace{10em}}$$
$$2n$$
$$3x \underline{\hspace{1.5cm}}$$

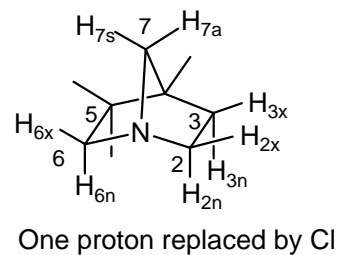
3n _____

6x _____

6n _____

7s _____

7a _____



(b) Briefly describe how you decided on the location of the chlorine

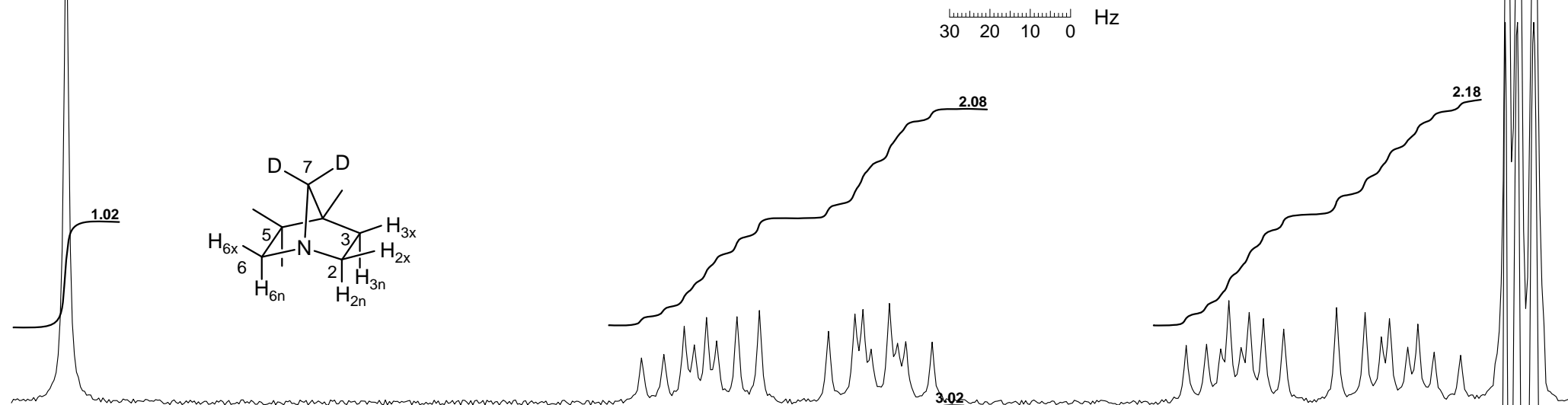
(c) Briefly describe specifically how you distinguished proton(s) at 2 from those at 3.

(d) Briefly describe how you distinguished the x and n signals at carbons 2 and 3

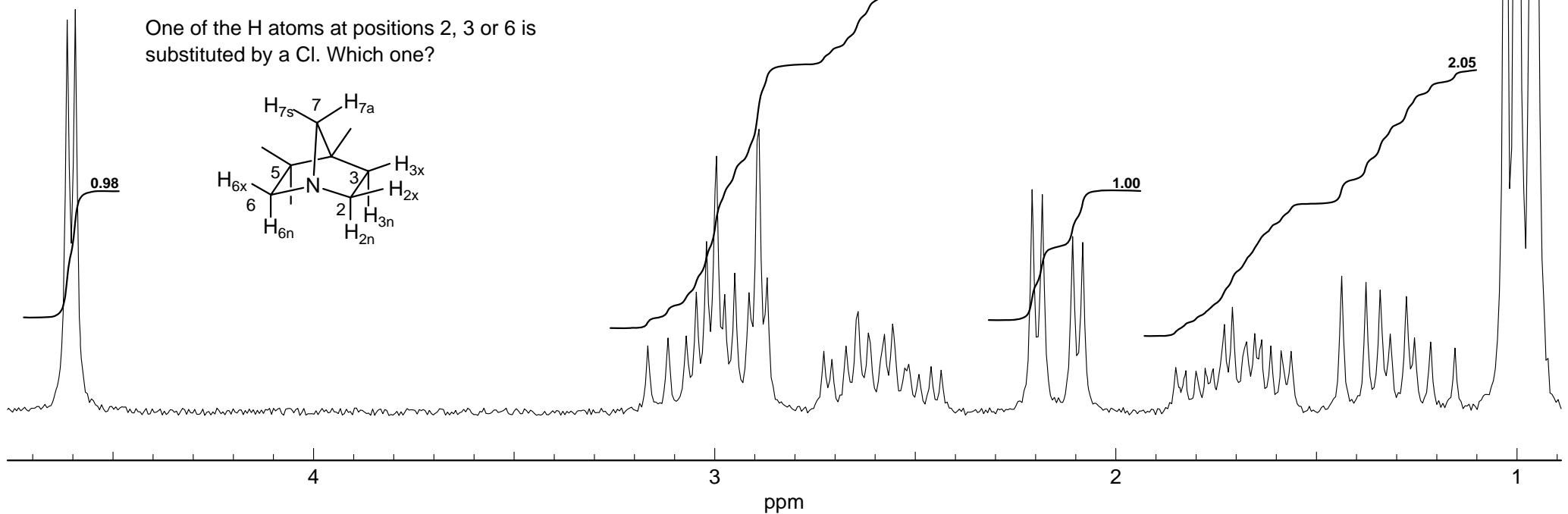
Problem R-11N ($C_9H_{16}ClN$)

100 MHz 1H NMR Spectrum in $CDCl_3$

(Source: *JACS* **1968**, 90, 13551 4/45)



One of the H atoms at positions 2, 3 or 6 is substituted by a Cl. Which one?



Problem R-110. Identify the SH protons in the two 300 MHz ^1H NMR spectra (CDCl_3) below, and explain the difference in their appearance (Source: Aldrich NMR Library).

