Practice Exam 1

Chemistry 605 (Reich)

FIRST HOUR EXAM

Mon, March 1, 2010

Question/Points

R-09A_____/12

R-09B_____/08

R-09C_____/25

R-09D_____/30

R-09E_____/17

R-09F_____/8

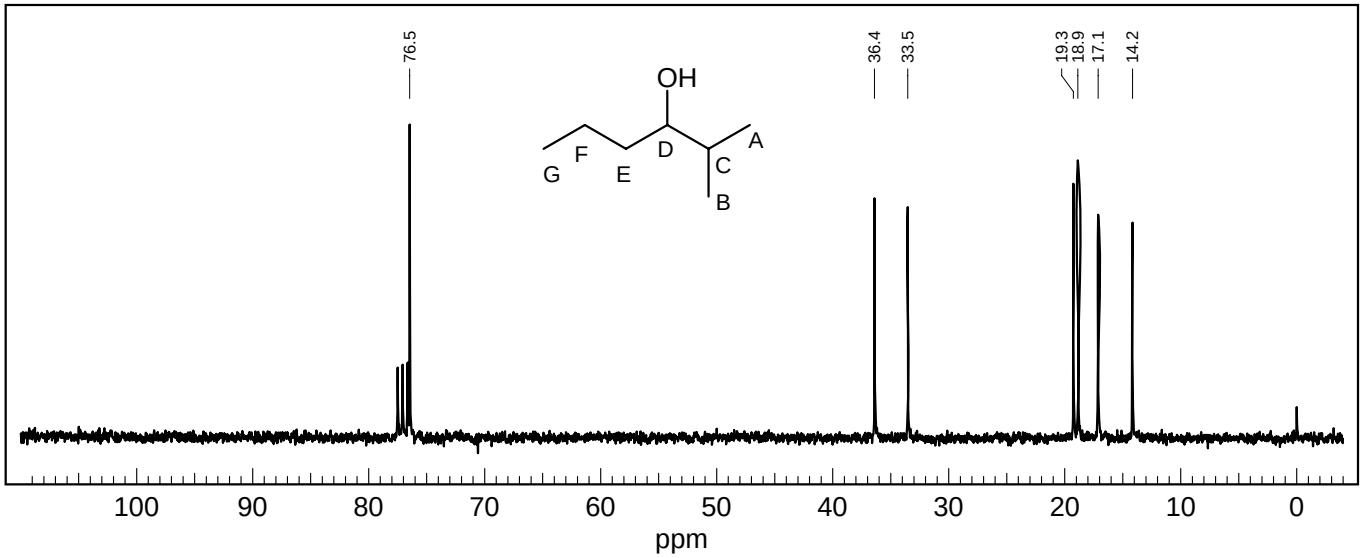
Total _____/100

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.

12

Problem R-09A ($C_7H_{16}O$). Consider the 75 MHz ^{13}C NMR spectrum below, measured in $CDCl_3$.



4 (a) Identify the two carbons which have chemical shifts at δ 36.4 and 33.5:_____

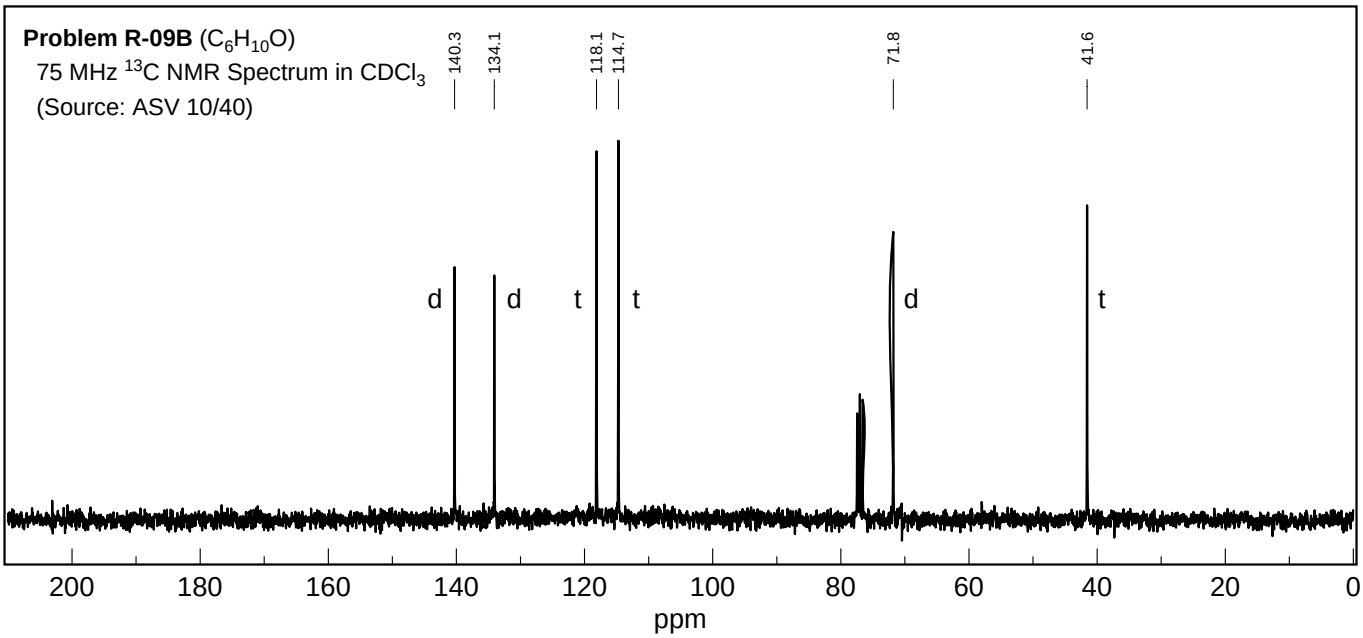
(b) Using a good model compound, calculate the ^{13}C chemical shifts of the two carbons identified in part (a) . Show your work.

4

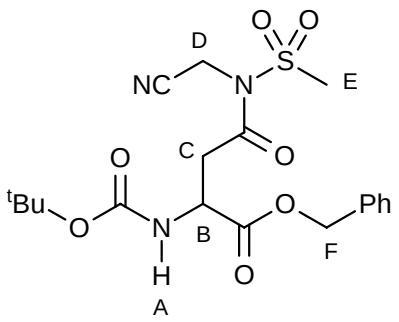
4 (c) Assign the carbons by putting the appropriate letter over each peak in the spectrum.

Problem R-09B. Determine the structure of the $C_6H_{10}O$ isomer from the ^{13}C NMR spectrum below.

8



Problem R-09C ($C_{19}H_{25}N_3O_6S$). You are given the 300 MHz ^1H NMR spectrum of a protected amino acid.



(a) Do a chemical shift calculation for protons D and F to help in the assignments below. Show your work.

D:

F:

(b) Identify the proton(s) at δ 3.1 - 3.6 (A-F):_____ What kind of pattern(s) is (are) these? Calculate accurate shifts and couplings from the peak-pick Hz values given. Report the results in the standard format (e.g. G: δ 2.88, 1H, dd, J= 12, 6 Hz)

(c) Identify the proton(s) at δ 4.5 - 4.8 (A-F):_____ What kind of pattern(s) is (are) these? Calculate accurate shifts and couplings from the peak-pick Hz values given.

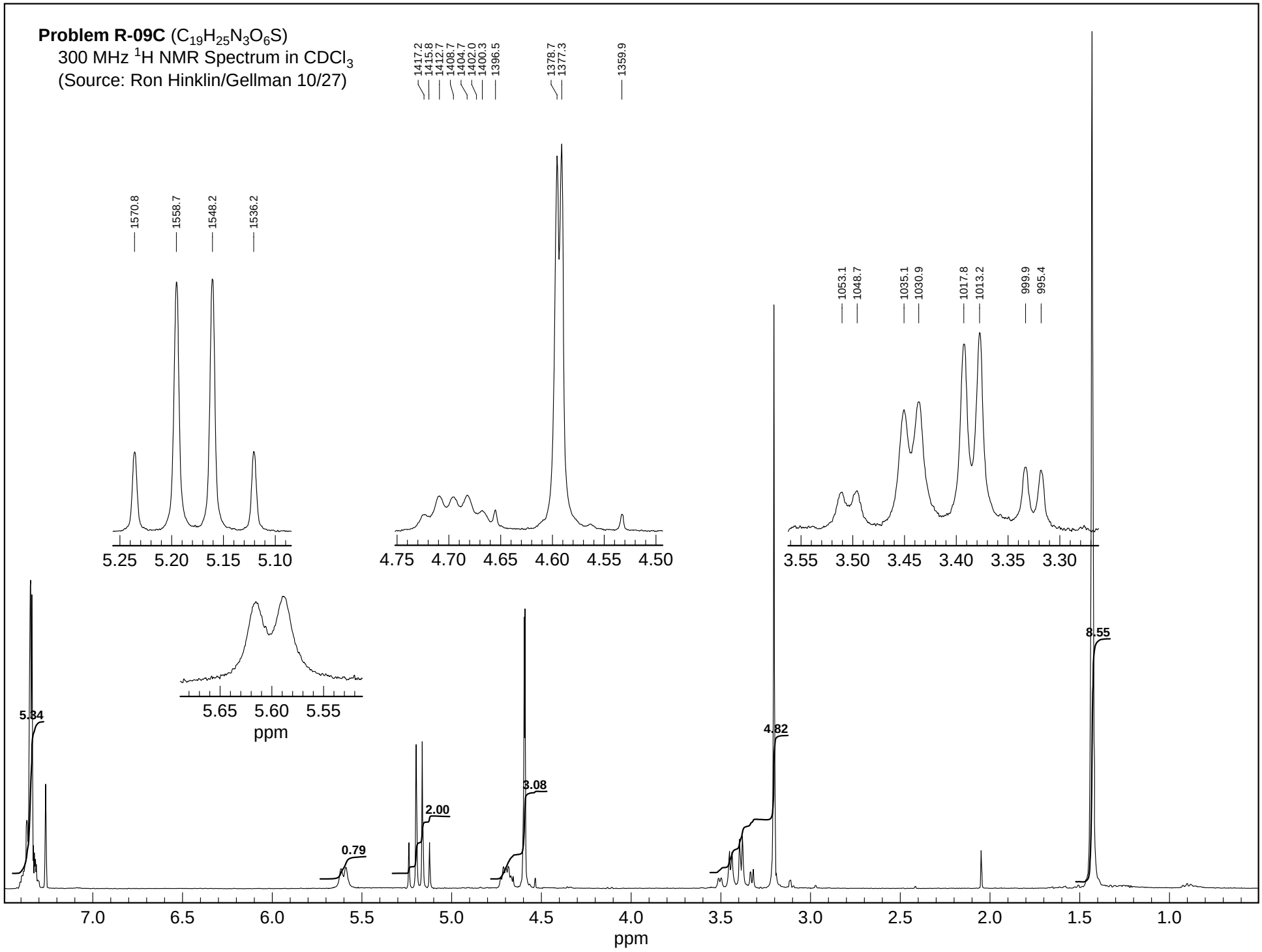
(d) Identify the proton(s) at δ 5.1 - 5.3:_____ What kind of pattern(s) is (are) these? Calculate accurate shifts and couplings from the peak-pick Hz values given.

(e) Identify the proton at δ 5.5 - 5.7:_____

Problem R-09C ($C_{19}H_{25}N_3O_6S$)

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

(Source: Ron Hinklin/Gellman 10/27)



Problem R-09D. ($C_{13}H_{16}O_2$). Determine the structure (or part structure) of **R-09D** from the ^{1}H NMR, ^{13}C NMR and IR spectra provided.

(a) DBE____ (b) What information can you obtain from the IR spectrum? List the data, and any conclusions you drew from it.

(b) Analyze the ^{1}H NMR signals. For each of the signals listed below report multiplicity and coupling constants to the extent the signals are amenable to first order analysis, and the part structure each corresponds to. (NOTE: the peaks at δ 1.9 and δ 2.8 are not strictly first order)

δ 1.9	δ 4.4
δ 2.1	δ 6.3
δ 2.2	δ 6.8
δ 2.8	δ 7.3

(c) Interpret the ^{13}C NMR spectrum. Identify what kind of carbon each signal corresponds to, and write possible part structures.

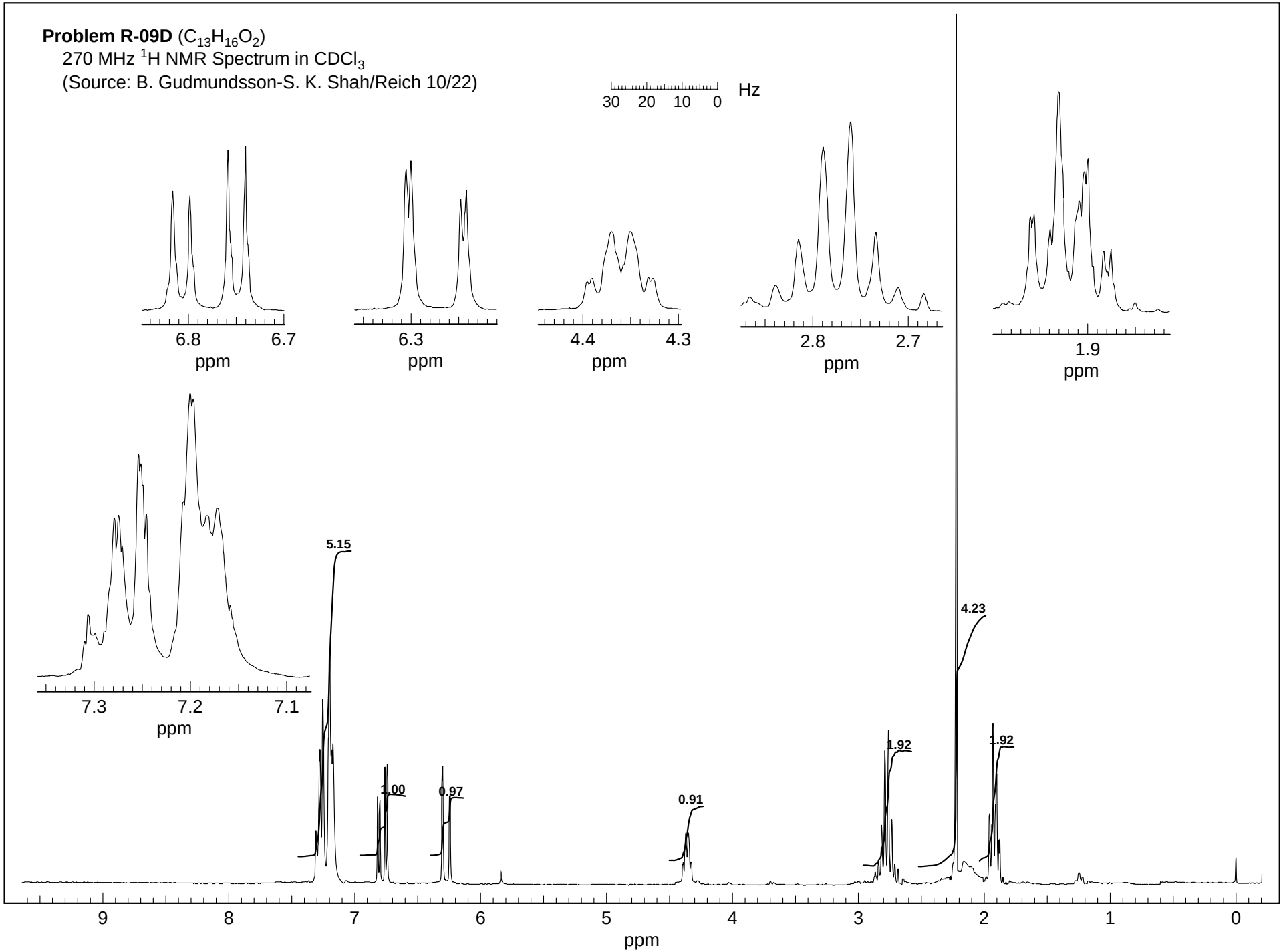
No	ppm	Type of C (e.g. sp^3 CH_2) and/or part structures (e.g. N-CH_2)
1	199.0 (s)	_____
2	149.3 (d)	_____
3	141.3 (s)	_____
4	128.9 (d)	_____
5	128.4 (d)	_____
6	128.3 (d)	_____
7	125.9 (d)	_____
8	70.3 (d)	_____
9	38.1 (t)	_____
10	31.7 (t)	_____
11	28.5 (q)	_____

(d) Determine the structure of **R-09D**. If more than one structure is possible, show them, and circle your best choice. Why are the ^{1}H NMR signals at δ 1.9 and δ 2.8 so complex?

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

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

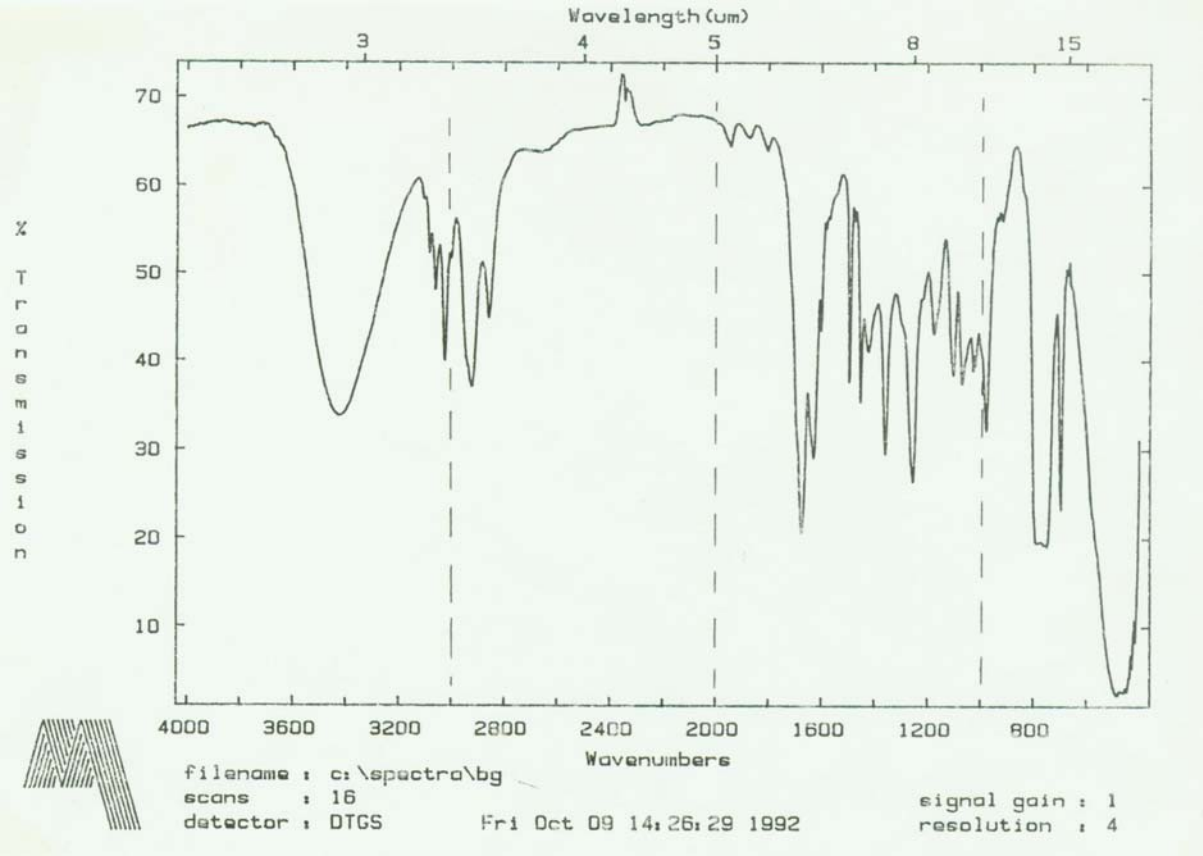
(Source: B. Gudmundsson-S. K. Shah/Reich 10/22)



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

IR spectrum (CCl_4)

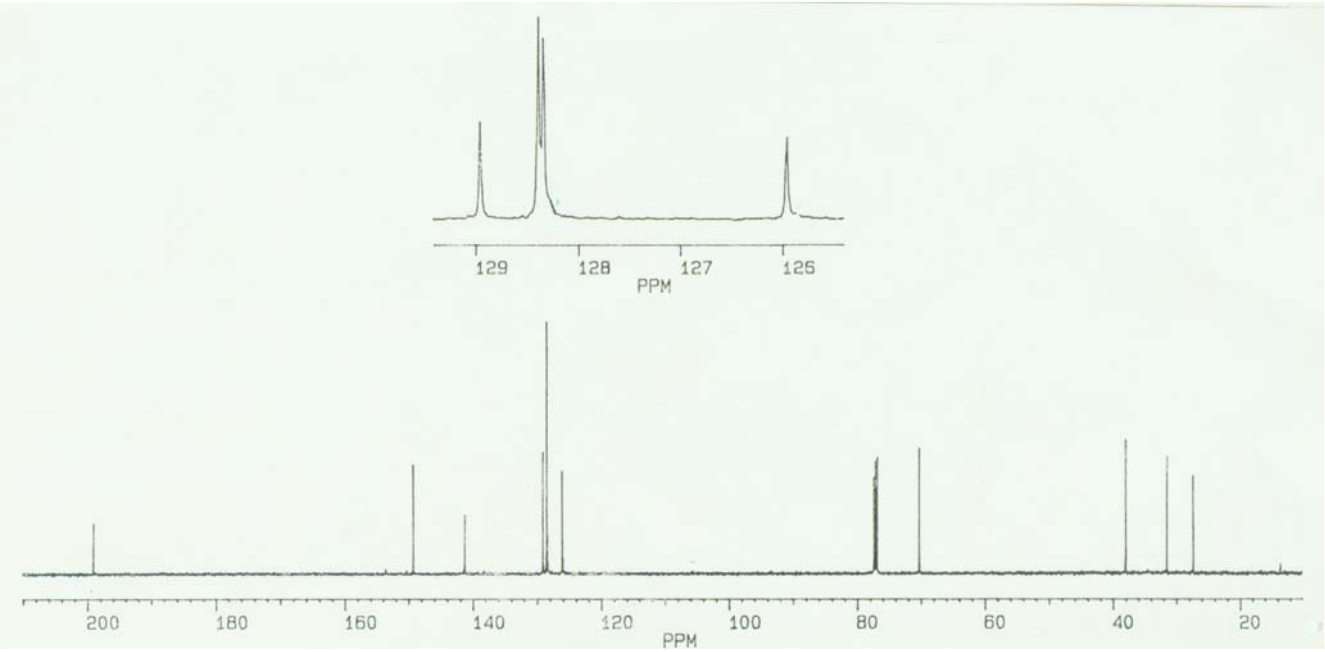
(Source: B. Gudmundsson/Reich 10/22)



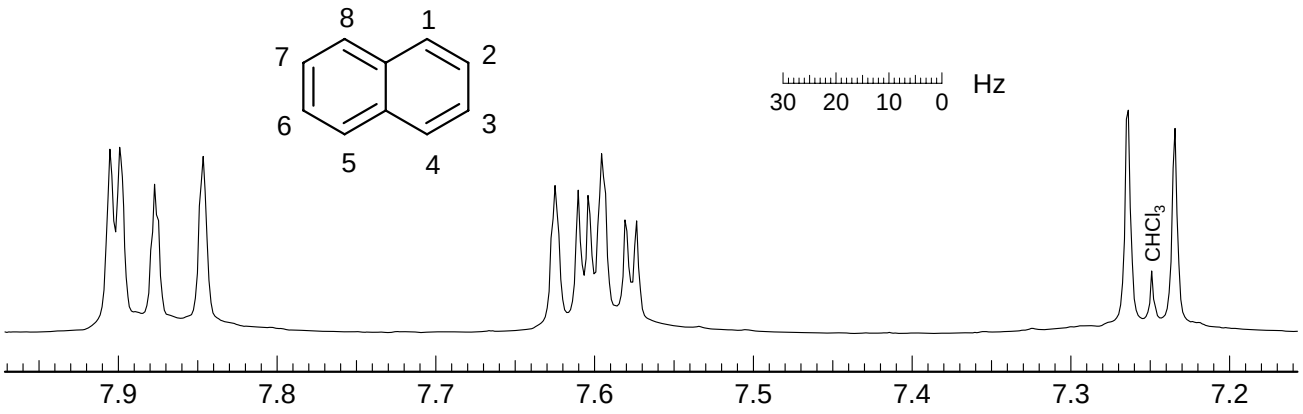
Problem R-09D ($C_{13}H_{16}O_2$)

125.76 MHz ^{13}C NMR Spectra in $CDCl_3$

(Source: B. Gudmundsson/Reich 10/22)



Problem R-09E ($C_{10}H_6Br_2O$). Shown below is the aromatic region of the 300 MHz ^1H NMR spectrum of a trisubstituted naphthalene (the substituents are **Br**, **Br** and **OH**). Your task is to analyze the NMR spectrum, and determine the substitution pattern (Source: Aldrich Spectral Viewer).



(a) For each of the 8 positions on the naphthalene as defined above, place either an X if there is a substituent, or the NMR signal (δ , multiplicity and *J* values). If there is more than one plausible structure asignment, draw the alternative structure, and indicate your preference. To simplify grading, please put the substituents on the lowest numbered positions (e.g., on carbon 1 rather than on 4).

1 _____

2 _____

3 _____

4 _____

5 _____

6 _____

7 _____

8 _____

(b) From a qualitative consideration of chemical shift effects (please don't attempt to do chemical shift calculations on all possible isomers) suggest which of the three occupied positions is most likely to be the OH, and give your reasoning.

Problem R-09F. This is the 60 MHz NMR spectrum of a commercial pain-killer APC, which a mixture of aspirin, phenacetin, and caffeine (from James M. Schoolery "A Basic Guide to NMR").

(a) Identify as many of the signals of each compound as you can, labelling the spectrum with A, P or C.