# 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
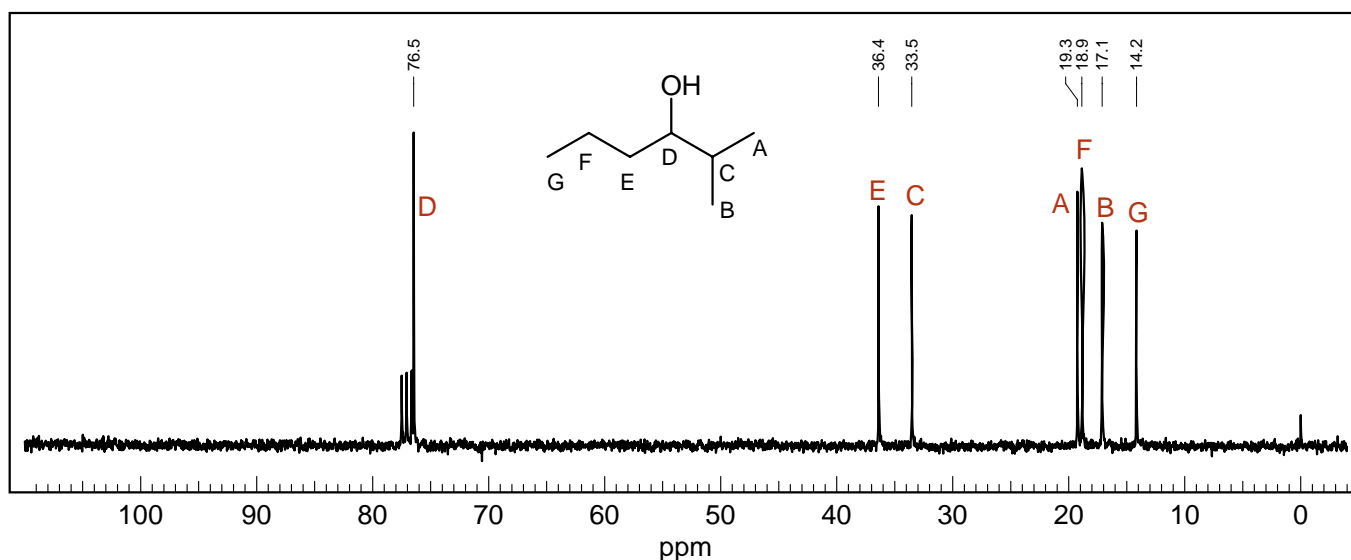
R-09F_____/8

Total _____/100

| | |
|---|---|
| Average | 73 |
| Hi | 92 |
| Mode | 74 |
| Median | 73 |
| AB | 78 |
| BC | 55 |

**Grading Copy**

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 $CDCl_3$.
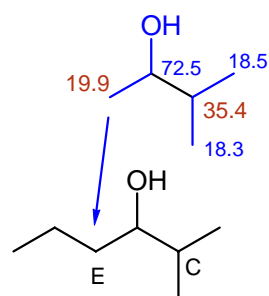


**2**

(a)  Identify the two carbons which have chemical shifts at δ 36.4 and 33.5: <u>C, E</u>

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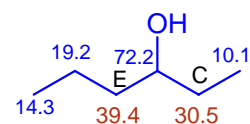Show your work.

**From model:**

$\delta_C = 35.4 + \gamma_C + \delta$

$= 35.4 - 2.5 = 32.9$   obs: 33.5

$\delta_E = 19.9 + \alpha_C + \beta_C + 2°(2°) + 2°(3°)_{OH} - 1°(3°)_{OH}$

$= 19.9 + 9.1 + 9.4 + 0 + (-2.5) - (-1.1) = 37.0$

obs: 36.4

We are assuming that branching by OH is like branching by $CH_3$

**6**

$\delta_C = 30.5 + \alpha_C + 3°(3°) + 3°(1°) -$
$2°(3°) - 2°(1°)  = 32.6$   obs: 33.5

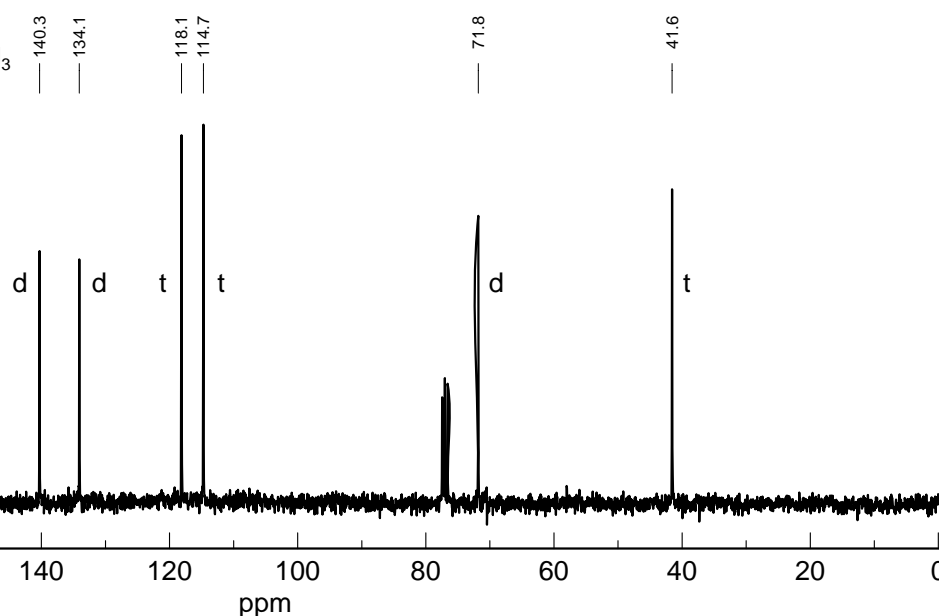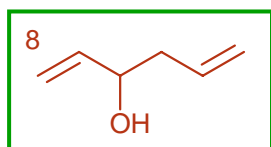$\delta_E = 39.4 + \gamma_C = 36.9$

obs: 36.4

**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.
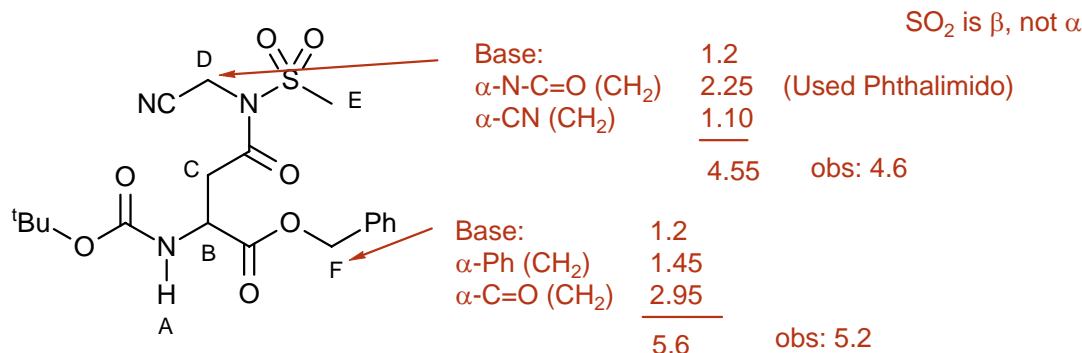
**8**

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

$SO_2$ is β, not α



| Base: | 1.2 | |
| α-N-C=O ($CH_2$) | 2.25 | (Used Phthalimido) |
| α-CN ($CH_2$) | 1.10 | |
| | 4.55 | obs: 4.6 |

| Base: | 1.2 |
| α-Ph ($CH_2$) | 1.45 |
| α-C=O ($CH_2$) | 2.95 |
| | 5.6 | obs: 5.2 |

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

4

      D:

      F:

(b)  Identify the proton(s) at δ 3.1 - 3.6 (A-F):_____ C, E   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)

5    C:  AB of  ABX.First order analysis gives dd, $J_{AB}$ = 17.9 Hz, $J_{AX}$ = 4.5 Hz; and dd, $J_{AB}$=17.9, $J_{BX}$ = 4.3 Hz
    To get accurate chemical shifts in "AMX" type of analysis have to remove $J_{AX}$ and $J_{BX}$ and calculate the
    resulting AB quartet properly (i.e., average 1&2=997.7, 3&4=1015.5, 5&6=1033.0 and 7&8=1050.9, and
    solve AB quartet: $v_{AB}$ = 30.5,  $v_{center}$ = 1024.3, $v_A$ = 1039.5 (δ 3.47), $v_B$ = 1009.0 (δ 3.36)

3    E  δ 3.2, 3H, s

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

3    B: δ 4.7, dt, 1H, J = 8, 3 Hz,

4    D:  AB quartet, $v_{AB}$ = 7.15, $J_{AB}$ = 17.8 (17.4, 18.3) , $v_{center}$ = 1378.0, $v_A$ = 1374.4, $v_B$ = 1381.6
        $\delta_A$ = 4.58, $\delta_B$ = 4.61

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

4    AB quartet

    F:  AB quartet, $v_{AB}$ = 19.0, $J_{AB}$ = 12 (12.0, 12.1) , $v_{center}$ = 1553.4, $v_A$ = 1543.9 (δ 5.15), $v_B$ = 1562.9 (δ 5.21)
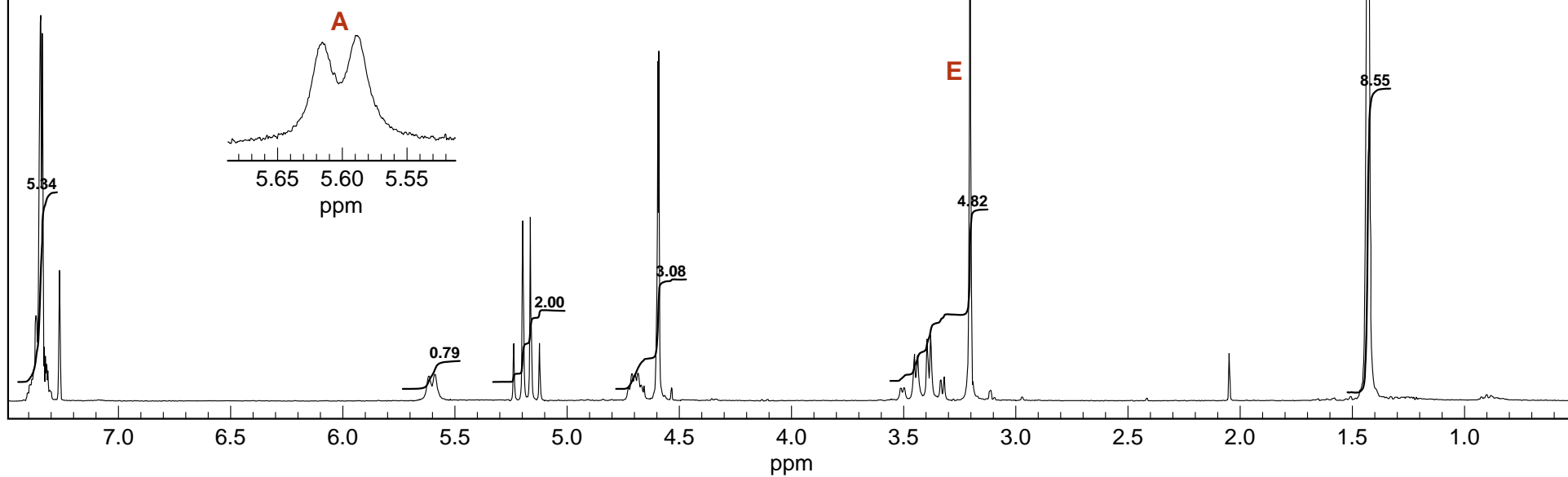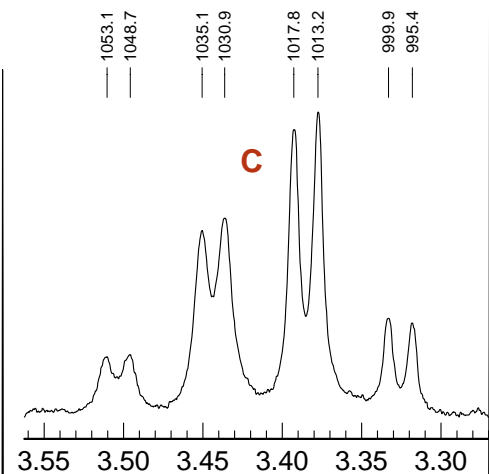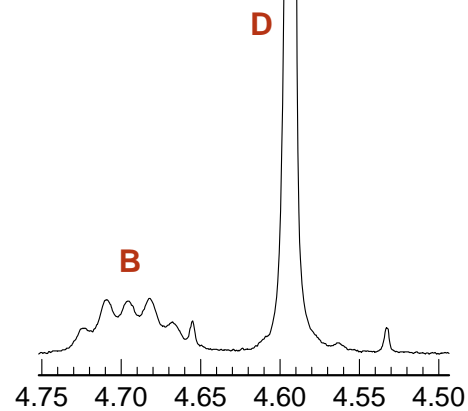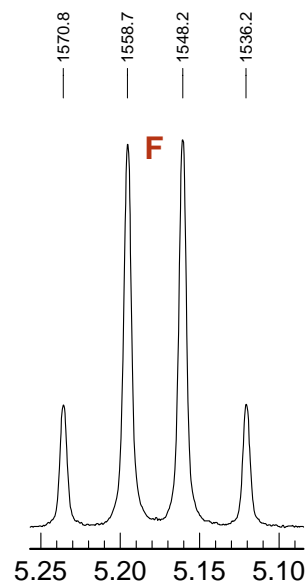
2    (e)  Identify the proton at δ 5.5 - 5.7:_____ A

N-$H_A$

**Problem R-09C** (C₁₉H₂₅N₃O₆S)

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

300 MHz ¹H NMR Spectrum in CDCl₃
(Source: Ron Hinklin/Gellman 10/27)



Peak labels (F region): 1570.8, 1558.7, 1548.2, 1536.2

Peak labels (D region): 1417.2, 1415.8, 1412.7, 1408.7, 1404.7, 1402.0, 1400.3, 1396.5, 1378.7, 1377.3, 1359.9

Peak labels (C region): 1053.1, 1048.7, 1035.1, 1030.9, 1017.8, 1013.2, 999.9, 995.4

Integrations: 5.84, 0.79, 2.00, 3.08, 4.82, 8.55
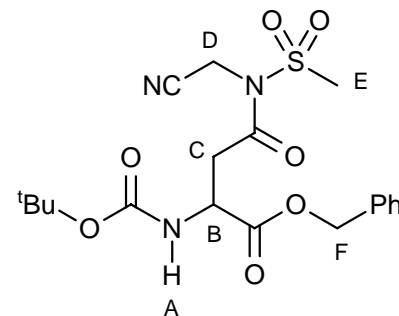
30    **Problem R-09D**. ($C_{13}H_{16}O_2$). Determine the structure (or part structure) of **R-09D** from the $^1H$ NMR, $^{13}C$ NMR and IR spectra provided.

2    (a) DBE__6__  (b) What information can you obtain from the IR spectrum?  List the data, and any conclusions you drew from it.
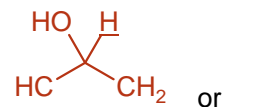
4
    3450 cm⁻1 broad OH stretch

    1680 cm⁻¹ conjugated ketone/aldehyde stretch ($CO_2H$?)

    1660 cm⁻¹ C=C stretch

    3050 cm⁻¹ sp² C-H stretch

(b) Analyze the $^1H$ 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)
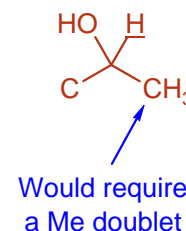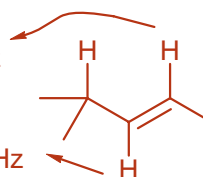
7
| | | | | | |
|---|---|---|---|---|---|
| δ 1.9 | 2H could be ≈quartet m  Ċ-CH₂-CH₂ seems to be coupled to 2.8 | δ 4.4 | 1H, qm (actually tdd, 7,5,2) | HO H | |
| δ 2.1 | 1H broad s, OH | δ 6.3 | 1H, dd, J = 15.5, 2 Hz | HC CH₂  or | |
| δ 2.2 | 3H, s, CH₃-C=O, poss CH₃-Ph | δ 6.8 | 1H, dd, J = 15.5, 5.5 Hz | HO H C CH₃ | |
| δ 2.8 | 2H, m, CH₂-CH₂-EWG ? seems to be coupled to 1.9 | δ 7.3 | 5H, m, monosubstituted Ph | Would require a Me doublet | |

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

7
| No | ppm | Type of C (e.g. sp³ CH₂) and/or part structures (e.g. N-CH₂) |
|---|---|---|
| 1 | 199.0 (s) | C=O ketone (very likely conjugated) |
| 2 | 149.3 (d) | sp² CH |
| 3 | 141.3 (s) | sp² C (ipso Ph) |
| 4 | 128.9 (d) | sp² CH |
| 5 | 128.4 (d) | sp² CH  2X, o/m phenyl |
| 6 | 128.3 (d) | sp² CH  2X, o/m phenyl |
| 7 | 125.9 (d) | sp² CH |
| 8 | 70.3 (d) | HC-O-  sp³ |
| 9 | 38.1 (t) | CH₂  sp³ |
| 10 | 31.7 (t ) | CH₂  sp³ |
| 11 | 28.5 (q) | CH₃  sp³ |

There are 2 fewer signals than carbons - 2 must be doubled

(d)  Determine the structure of **R-09D**.  If more than one structure is possible, show them, and circle your best choice.  Why are the $^1H$ NMR signals at δ 1.9 and δ 2.8 so complex?
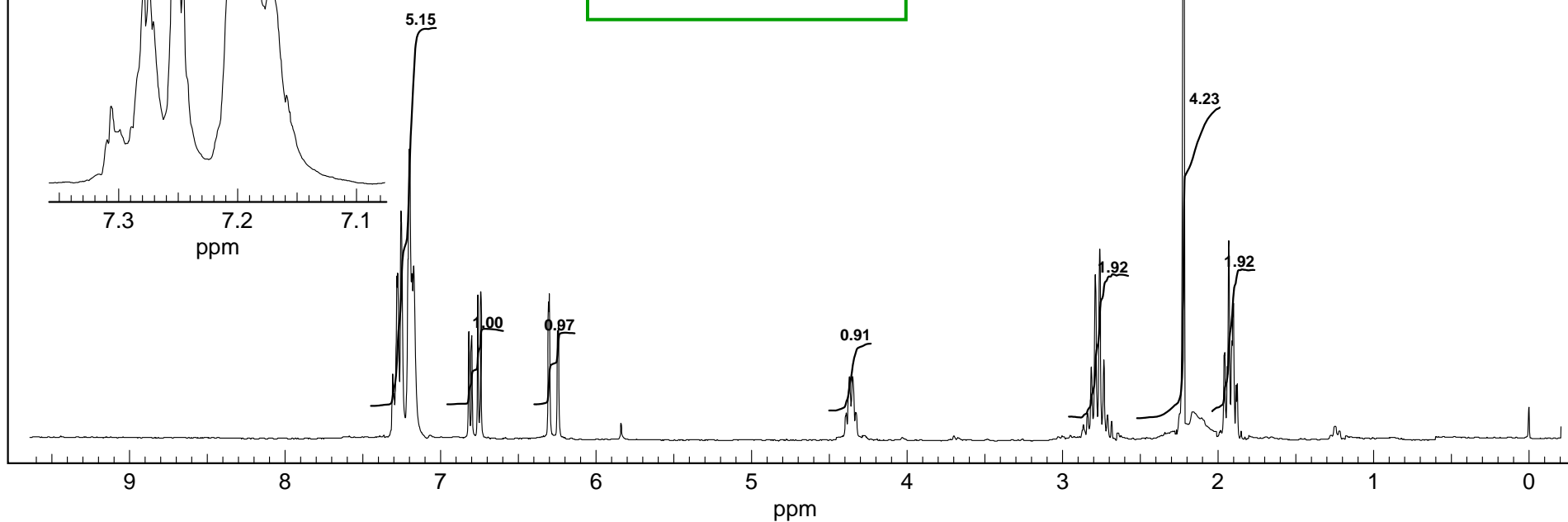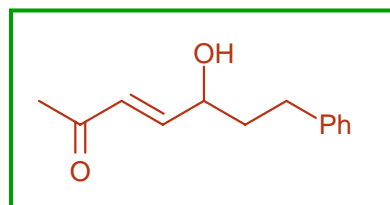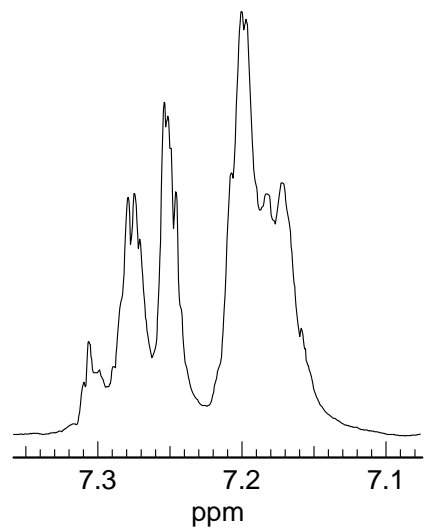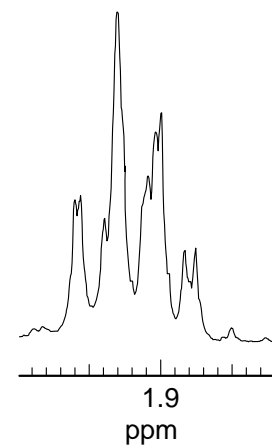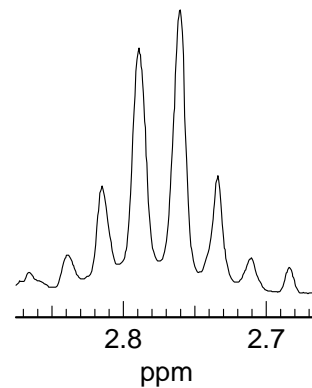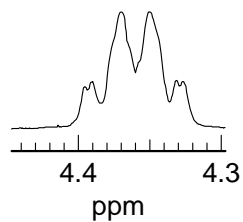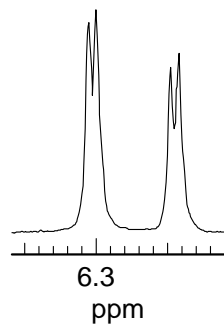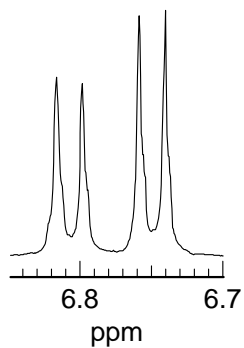
8
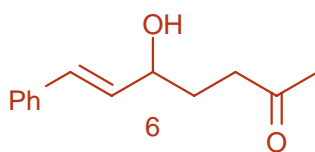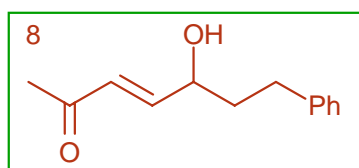

2    These are two adjacent CH₂ groups, which are each diastereotopic, hence an AB MN X system - lots of coupling

**Problem R-09D** ($C_{13}H_{16}O_2$)
  270 MHz $^1$H NMR Spectrum in CDCl$_3$
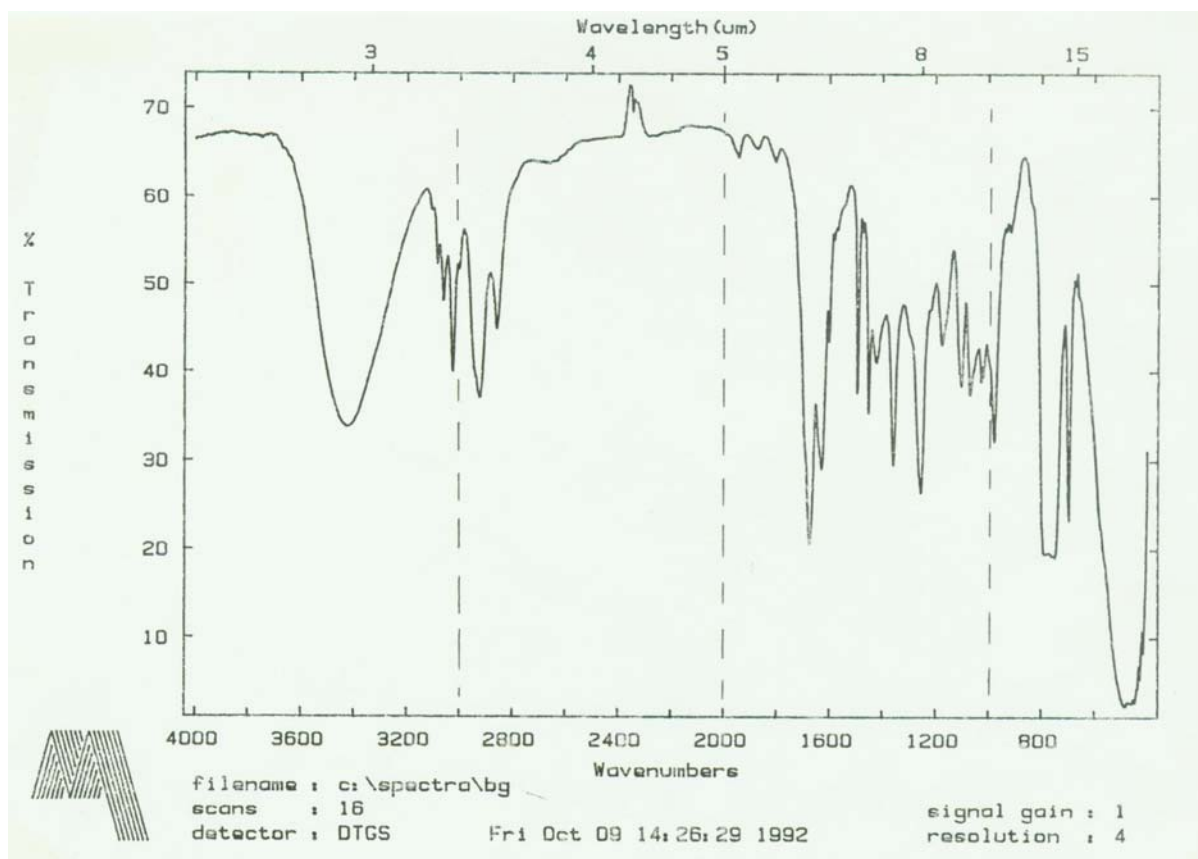  (Source: B. Gudmundsson-S. K. Shah/Reich 10/22)

30  20  10  0   Hz

6.8    6.7
ppm

6.3
ppm

4.4    4.3
ppm

2.8    2.7
ppm

1.9
ppm

7.3    7.2    7.1
ppm

5.15

4.23

1.92

1.92

1.00

0.97

0.91



9    8    7    6    5    4    3    2    1    0
ppm

**Problem R-09D** ($C_{13}H_{16}O_2$)
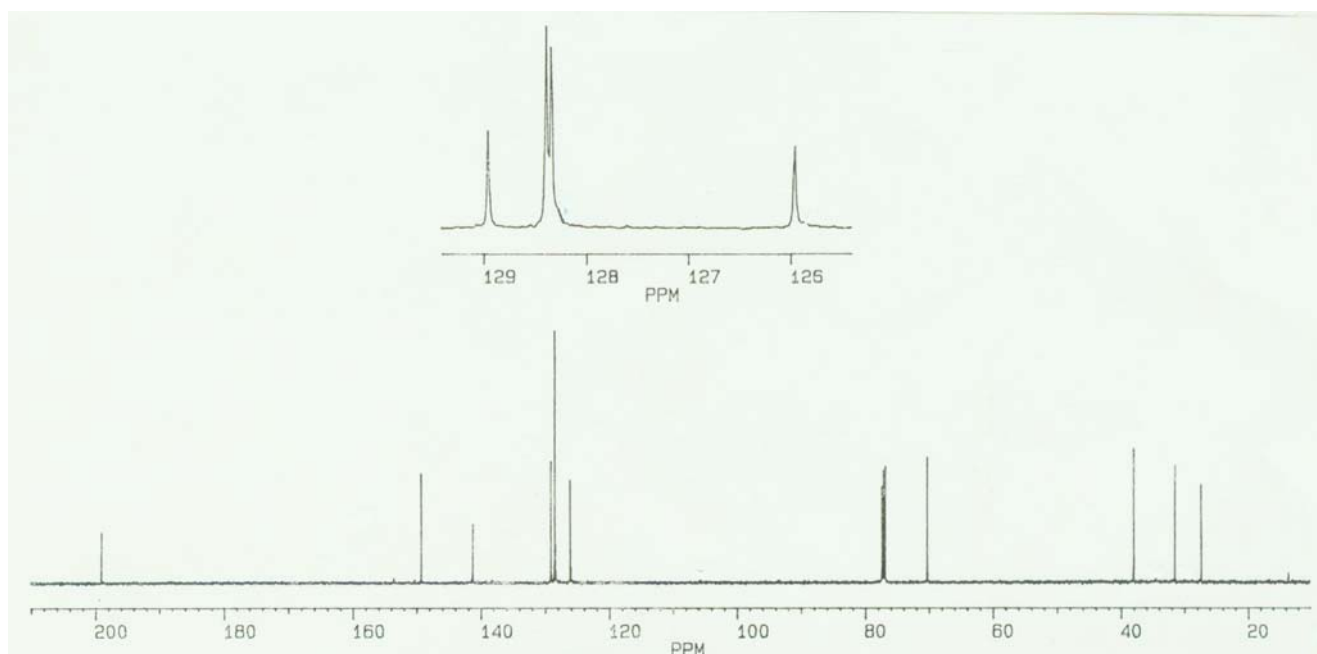    IR spectrum ($CCl_4$)
    (Source: B. Gudmundsson/Reich 10/22)



**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).
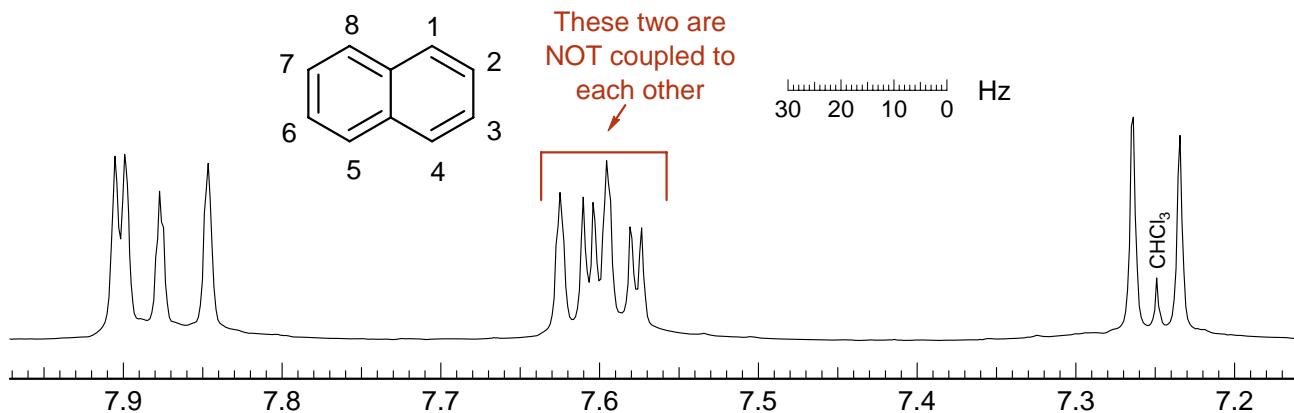


(a)  For each of the 8 positions on the naphthalene as defined above, place either an X if there is a substituent, or the NMR signal ($\delta$, multiplicity and $J$ values).  If there is more than one plausible structure asignment, draw the alternative structure, and indicate your preference.  To simplify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

13

| | | |
|---|---|---|
| 1 | X (Br) | X (Br) |
| 2 | X (OH) | X (OH) |
| 3 | $\delta$ 7.25,d, J = 9 Hz | $\delta$ 7.25,d, J = 9 Hz |
| 4 | $\delta$ 7.61, d, J = 9 Hz | $\delta$ 7.61,d (m?), J = 9 Hz |
| 5 | $\delta$ 7.90, d, J = 2 Hz | $\delta$ 7.86, d, J = 9 Hz |
| 6 | X (Br) | $\delta$ 7.59,dd, J = 9, 2 Hz |
| 7 | $\delta$ 7.59,dd, J = 9, 2 Hz | X (Br) |
| 8 | $\delta$ 7.86, d, J = 9 Hz | $\delta$ 7.90, d, J = 2 Hz |
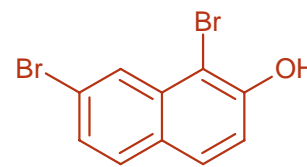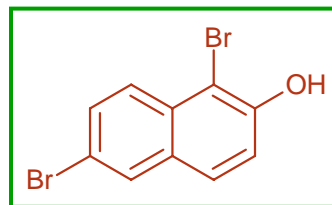


Both OK, Br-OH swapped also works
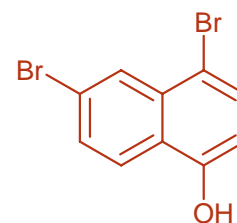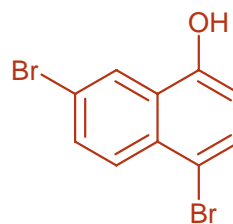
Reasonable, but $J_{HH}$ would be smaller (6 Hz instead of 9 Hz, as observed)

(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.
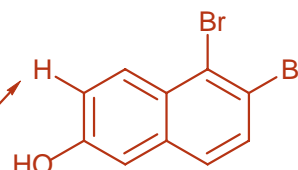


4
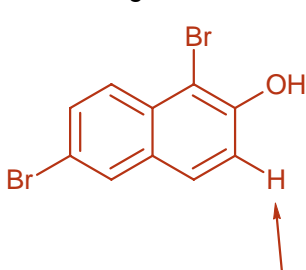
Should be most upfield proton (as observed)
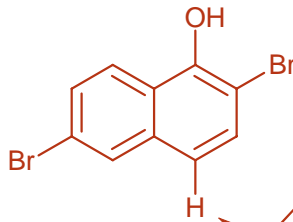
Should be most upfield proton

8   **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.

Aspirin

Phenacetin

Caffeine

not shown