# Chemistry 605 (Reich)

FIRST HOUR EXAM

Thursday, March 7, 2013

Question/Points

R-12A_____/20

R-12B_____/30

R-12C_____/20

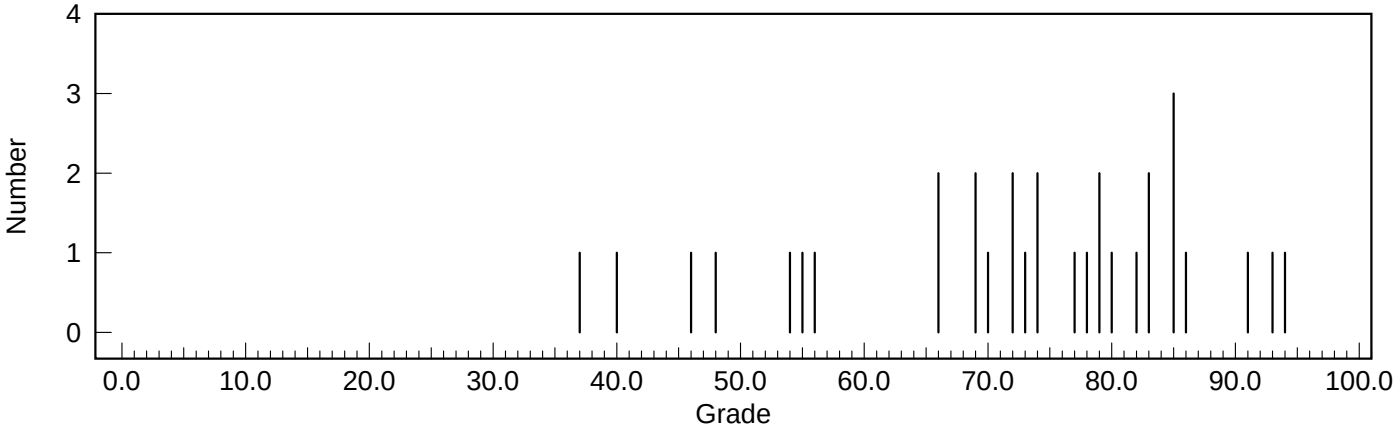
R-12D_____/14

R-12E_____/16

Total _____/100

| | |
|---|---|
| Average | 72 |
| Hi | 94 |
| Mode | 85 |
| Median | 74 |
| AB | 80 |
| BC | 55 |

Distribution from grade list (average: 71.9; count: 32)

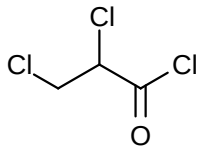



**Grading**

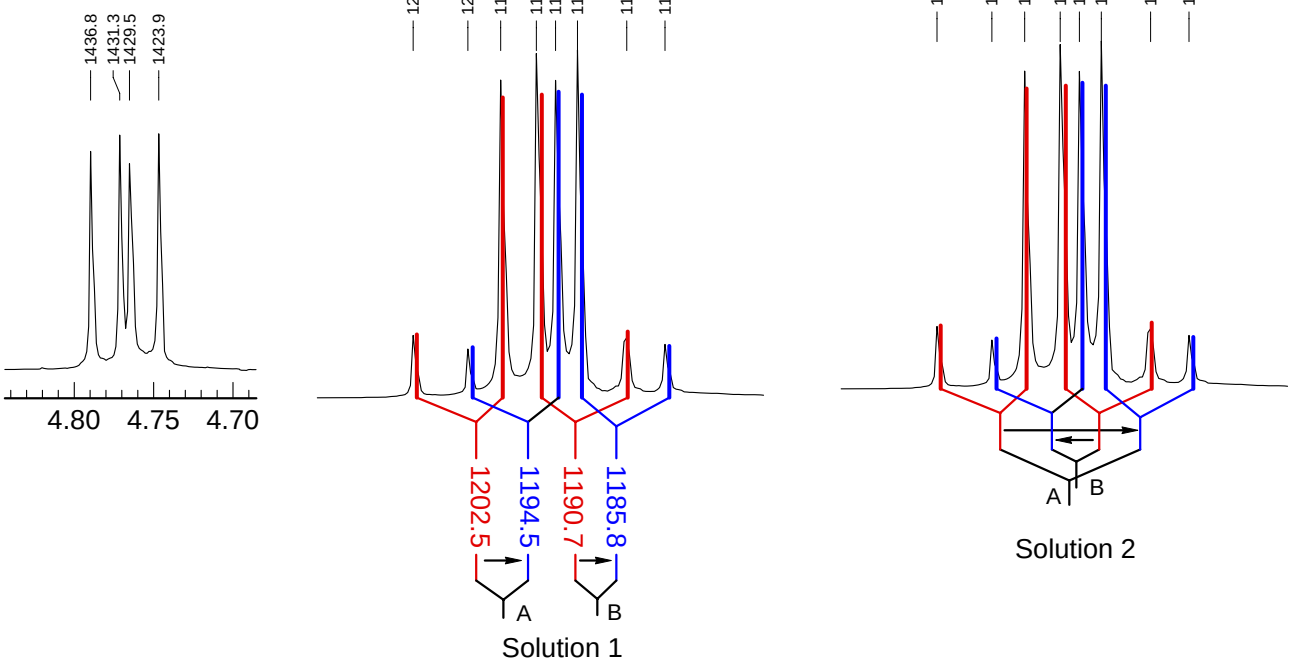
Name_____

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-12A** ($C_3H_3Cl_3O$). The complete 300 MHz $^1H$ NMR spectrum of R-12A is shown below.




Got all possible assignments of quartets, only one gives proper $J_{AB}$ 4 times

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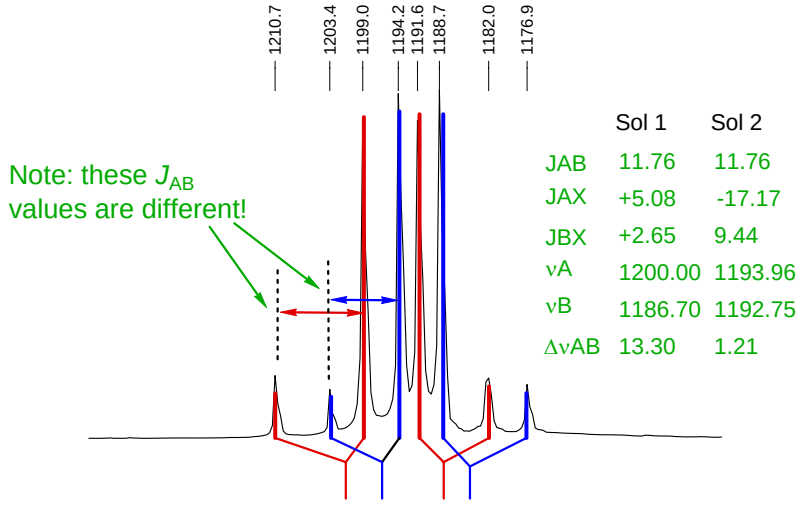
(a) Show a coupling tree, and do a mathematically accurate analysis of this spectrum. If there are two solutions, report them both. Show your work, and tabulate your data in an easily readable form.

8

| | Sol. 1 | Sol. 2 | |
|---|---|---|---|
| $J_{AB}$ | 11.8 | 11.8 | or |
| $J_{AX}$ | 7.9 | -16.7 | +16.7 |
| $J_{BX}$ | 5.0 | +3.8 | -3.8 |
| $\nu_A$ | 1198.5 | 1194.1 | |
| $\delta_A$ | 3.995 | 3.980 | |
| $\nu_B$ | 1188.2 | 1192.6 | |
| $\Delta_B$ | 3.96 | 3.98 | |
| $\Delta\nu_{AB}$ | 10.3 | 1.5 | |
| $i_{10} = i_{11}$ | 0.996 | 0.580 | |
| $i_{14}=i_{15}$ | 0.004 | 0.420 | |

**Most common wrong assignment of lines**



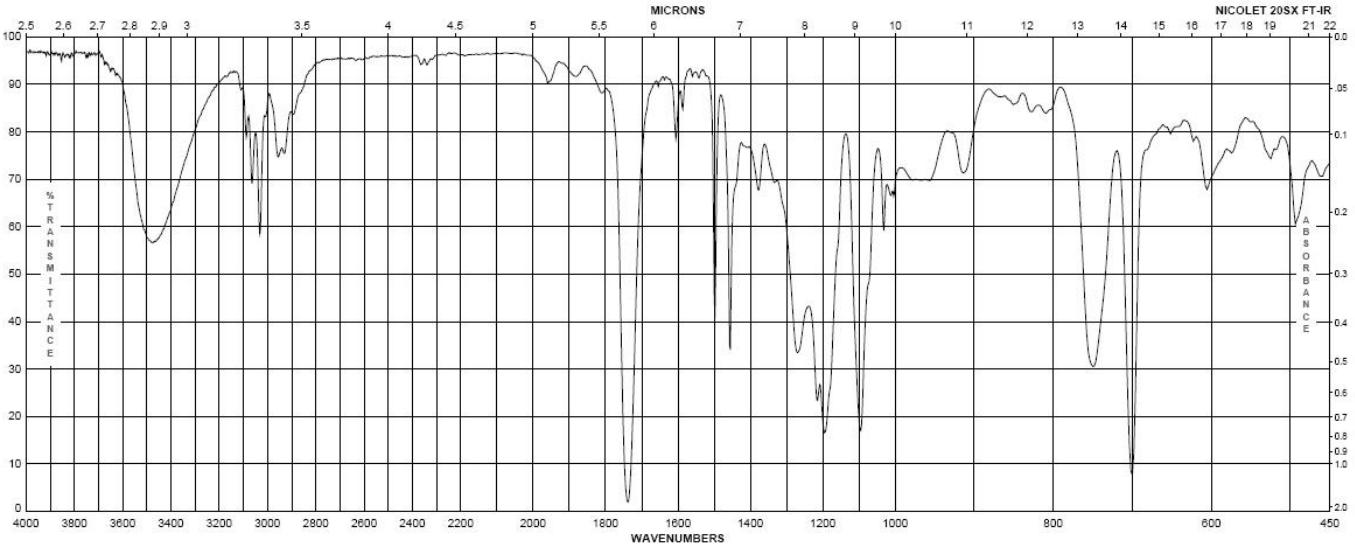

(b) If you are proposing two solutions, suggest at least one criterion which allows you to identify the correct one.

3

Given the structure, the signs of $J_{AX}$ and $J_{BX}$ must be both be positive, so Sol. 1 is correct. Can also use calculated intensities, which are very different for Sol 1 and Sol 2. Size of the couplings is not a very solid criterion in this case.

**Problem R-12B** ($C_{16}H_{16}O_3$). Determine the structure (or part structure) of **R-12B** from the IR, $^1$H NMR and $^{13}$C NMR spectra provided.

2 (a) DBE 9 (b) What information can you obtain from the IR spectrum? Give frequency and assignment.




4

3470 $cm^{-1}$ OH stretch
3040, 3060 $sp^2$ C-H stretch (aromatic C-H)
1740 $cm^{-1}$ C=O stretch, probably of an ester

(c) Interpret the $^{13}$C NMR spectrum. The multiplicity of each signal is given on the spectrum. Identify what kind of carbon each signal corresponds to (be as specific as possible) and write likely part structures.

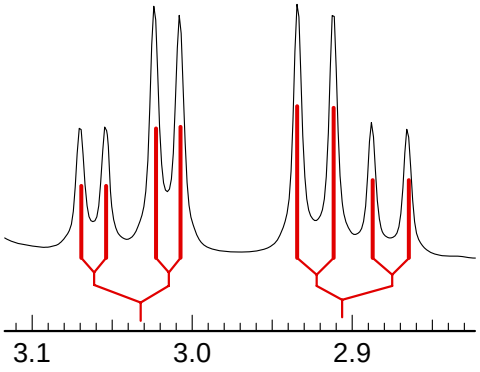
Type of C (e.g. $sp^3$ $\underline{C}H_2$) and/or part structures (e.g. N-$\underline{C}H_2$)

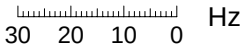
| ppm | | ppm | |
|---|---|---|---|
| 40.3 | $sp^3$ $CH_2$ | 128.5 | $sp^2$ CH 3x? |
| 67.1 | $sp^3$ OCH | 129.4 | $sp^2$ CH 2x |
| 71.2 | $sp^3$ $OCH_2$ | 135.0 | $sp^2$ C |
| 126.6 | $sp^2$ CH 2x | 136.2 | $sp^2$ C |
| 128.2 | $sp^2$ CH 2x | 173.8 | $CO_2R$ |
| 128.4 | $sp^2$ CH | | |

4

(d) Analyze the 2-proton multiplet between δ 2.8 and 3.1 (reproduced below). Draw a coupling tree and report coupling constants (in the standard form: e.g., δ 3.9, tq, J = 12, 4 Hz, 1H) and part structure you could obtain from the signal. You may use first-order analysis.

δ 3.03 dd, J = 14, 4.5 δ 2.91 dd, J = 14, 6.5

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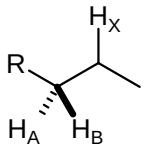



From the chemical shift
R is likely to be C=O or Ph

What kind of pattern is this? AB of ABX What other signal is coupled to these protons? 4.4 δ

(e) Analyze the two-proton multiplet between δ 5.0 and 5.2 in the $^1$H NMR spectrum. The multiplet is reproduced below. Draw a coupling tree and report exact coupling(s) and chemical shifts, and a part structure.

$J_{AB}$ = 12.2

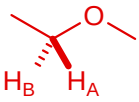
c=(5+3)/2 = 1524.08

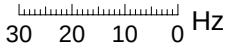
$\Delta\nu_{ab}$ = sqrt((4-1)(3-2)) = 8.9

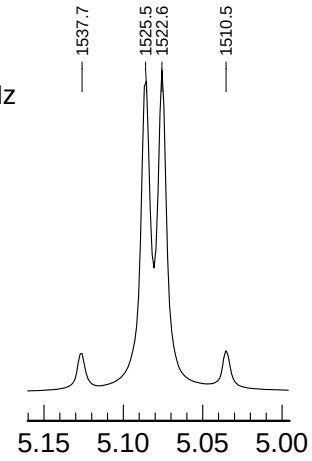
c ± $\nu_{ab}$/2 = 1528.6 1519.6

$\delta_A$, $\delta_B$ = 5.095 5.065

6




What kind of pattern is this? AB

(e) Show a structure for **R-12B**. If there is more than one possibility, circle your best choice.

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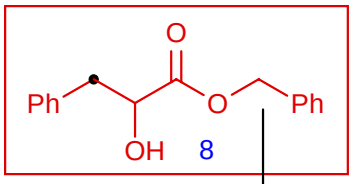
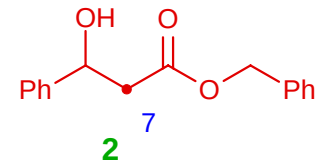



1

| | |
|---|---|
| Base | 1.20 |
| α-OC(O)Alk | 2.95 |
| α-Ph | 1.45 |
| | 5.60 |

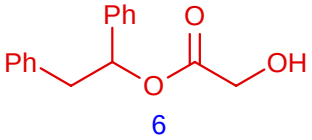
Obs: 5.07

17 other structures, including:




7

2

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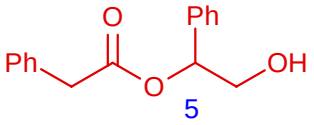


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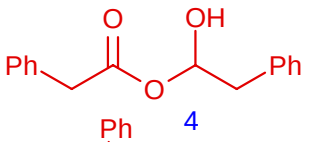
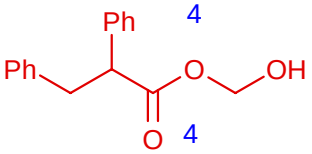



4 (nutty)




4 (nutty)

(f) Do a chemical shift calculation (from methane as model) of the carbon in your structure you have assigned the signal at δ 40.3. Show parameters you used.

4

1

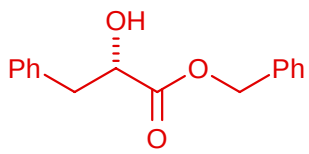
| | |
|---|---|
| Base | -2.1 |
| $\alpha_{Ph}$-n | 23 |
| $\alpha_C$ | 9,1 |
| $\beta_{CO2R}$-n | 3 |
| $\beta_{OH}$-iso | 8 |
| | 41.0 |

2

| | |
|---|---|
| Base | -2.1 |
| $\alpha_{CO2R}$-n | 20 |
| $\alpha_C$ | 9,1 |
| $\beta_{Ph}$-n | 9 |
| $\beta_{OH}$-iso | 8 |
| | 44.0 |

Observed: 40.3

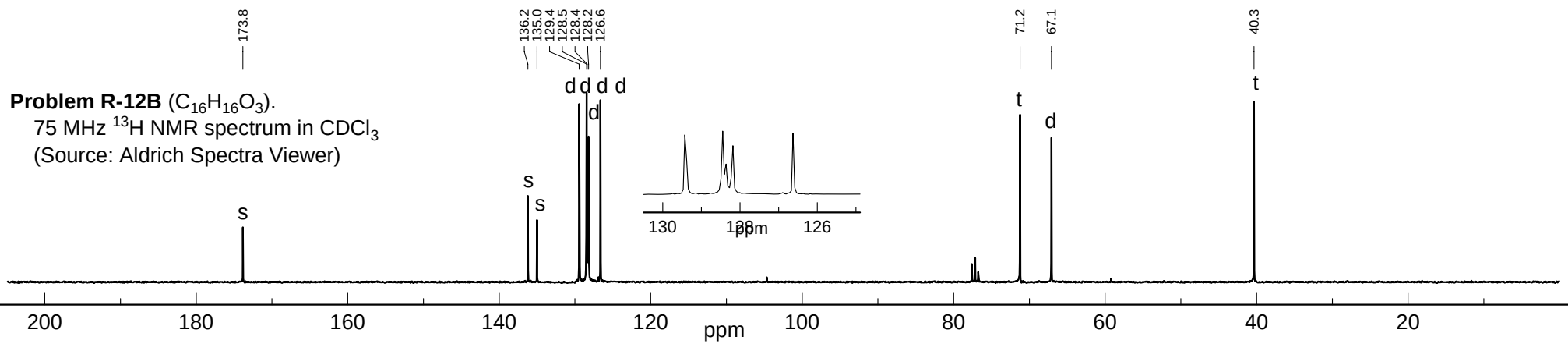
**Problem R-12B** ($C_{16}H_{16}O_3$).
300 MHz $^1$H NMR spectrum in $CDCl_3$
(Source: Aldrich Spectra Viewer)





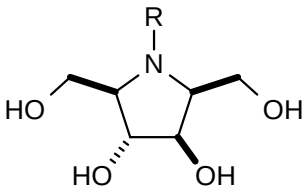


**Problem R-12B** ($C_{16}H_{16}O_3$).
75 MHz $^{13}$H NMR spectrum in $CDCl_3$
(Source: Aldrich Spectra Viewer)

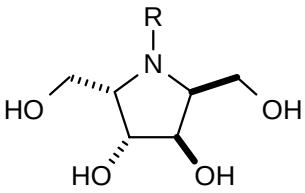


IN XLS

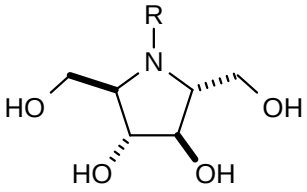
**Problem R-12C** The 100 MHz $^{13}C$ NMR spectra of three substituted pyrrolidines is shown on the next page. Their structures are shown below (ttc = trans-trans-cis). R = para-fluorophenyl.



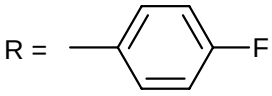

ttc




ctc




ttt

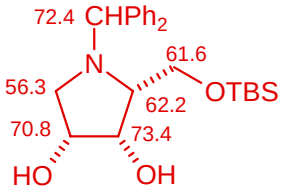



(a) Identify the compound (ttc, ctc or ttt) which corresponds to spectrum **R-12C-1**. Give your reasoning.

ttt

This must be either the ctc or ttt isomer, each of which has an axis of symmetry.

6

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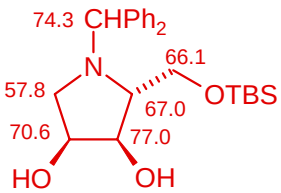



JOC-00-5693

(b) Identify the compound which corresponds to spectrum **R-12C-2**. Give your reasoning.

ctc

6

This must be either the ctc or ttt isomer, each of which has an axis of symmetry. In the ctc isomer two of the groups (an OH and a $CH_2OH$) on each side are cis to each other, and thus there is a $\gamma$-gauche interaction between them that is largely absent in the ttt isomer, so expect an upfield shift of the $CH_2OH$ carbon. So this must be the ctc isomers since all carbons are upfield of the ttt isomer

(c) Identify the compound which corresponds to spectrum **R-12C-3**. Give your reasoning.

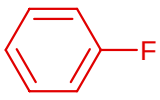
ttc

6

This is the only isomer which has all carbons different (no symmetry), so must be ttc

(d) In each of the spectra there are two peaks at $\delta$ 155 ppm. Assign and explain these peaks.

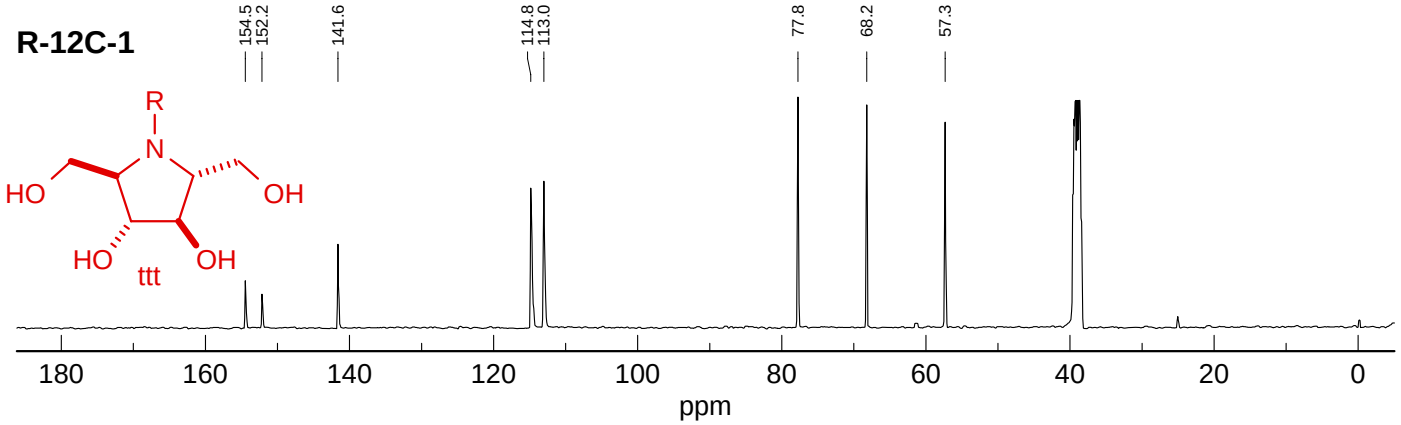
2



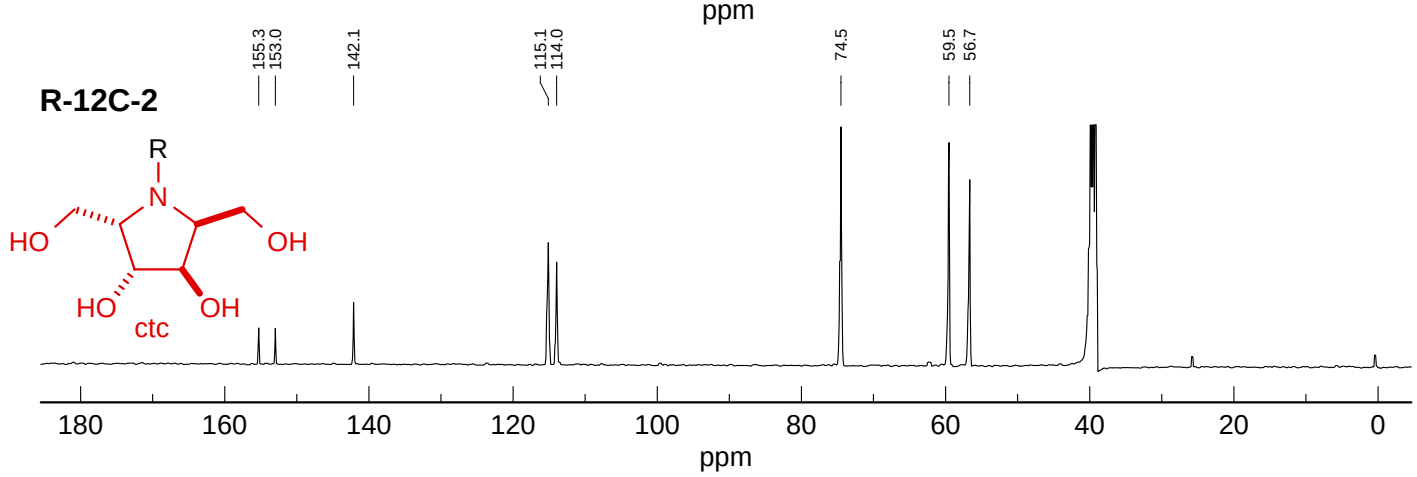

This is the C-F carbon, split into a doublet by $J_{CF}$

**Problem R-12C** ($C_{12}H_{16}FNO_4$).
100 MHz $^{13}C$ NMR spectra in DMSO-d6
(Source: Allen B. Reitz/JOC 1994, 59, 3175)

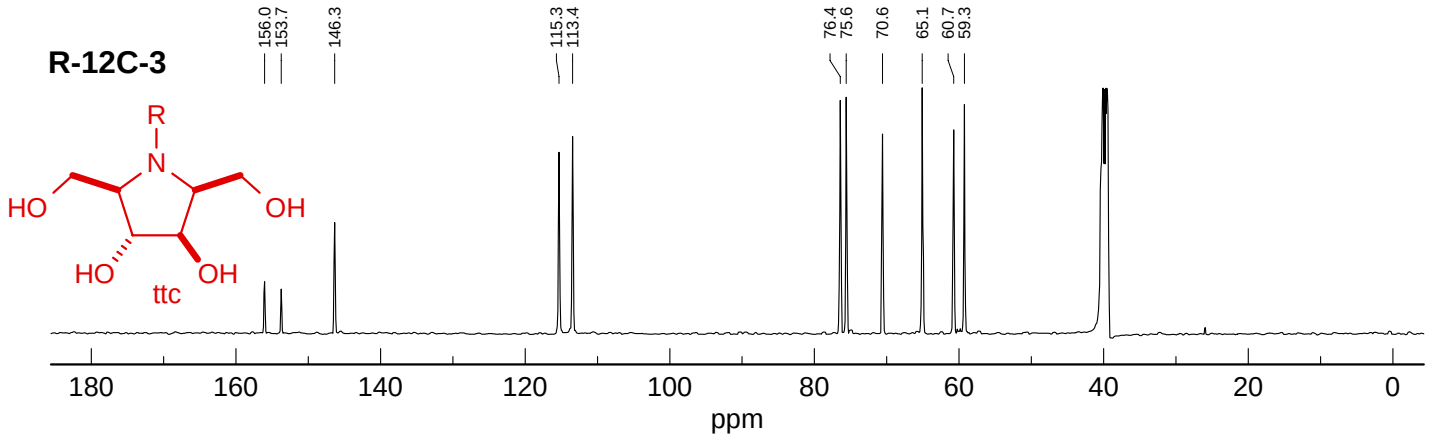
**R-12C-1**



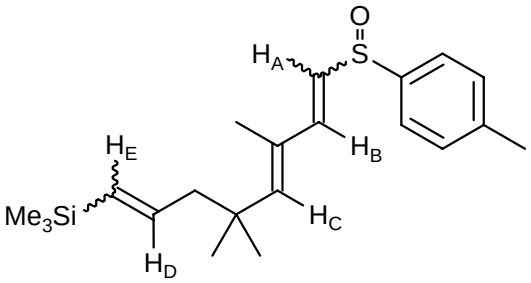

**R-12C-2**



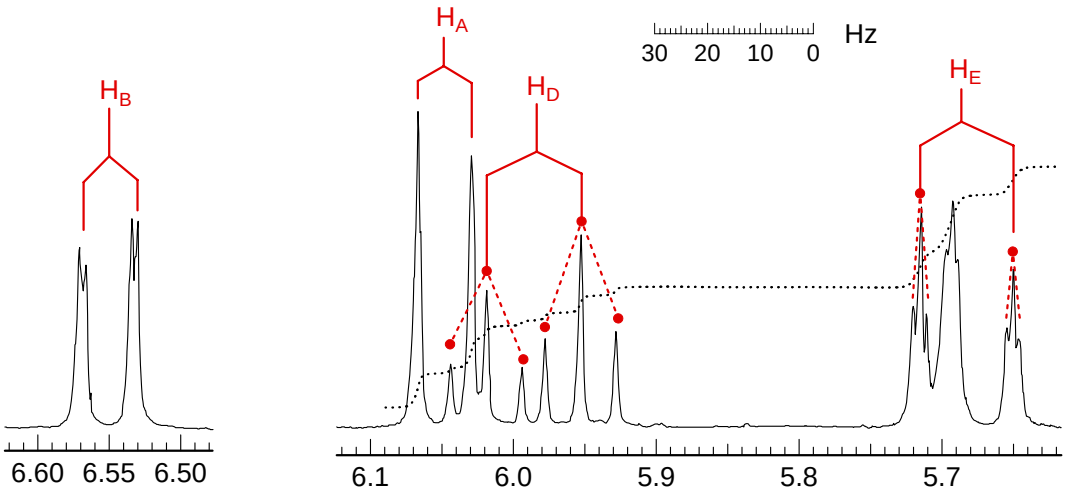

**R-12C-3**



**Problem R-12D**. Interpret the partial spectrum of the triene shown below, and assign stereochemistry to two of the double bonds. The complete spectrum is on the next page.




(a) On the expansion reproduced below, mark clearly the assignment of the protons $H_A$ to $H_E$. Draw a coupling tree for each one to show that you understand the line assignments. You may use first order analysis.

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(b) Report the data below in the standard format (e.g., δ 5.31, dq, J = 8.2, 3.3 Hz)

$H_A$ δ 6.05, d, J = 11 Hz

$H_B$ δ 6.55, dd, J = 11, 1 Hz

$H_C$ δ 5.69, t, J = 1.5 Hz

$H_D$ δ 5.98, dt, J = 18, 7 Hz

$H_E$ δ 5.68, dt, J = 18, 1 Hz

5

(c) What is the stereochemistry at the $H_A$ - $H_B$ double bond? Explain briefly.

Double bond must be cis - 11 Hz coupling too small for trans

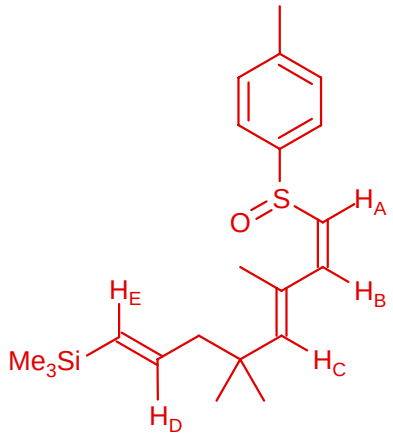
2

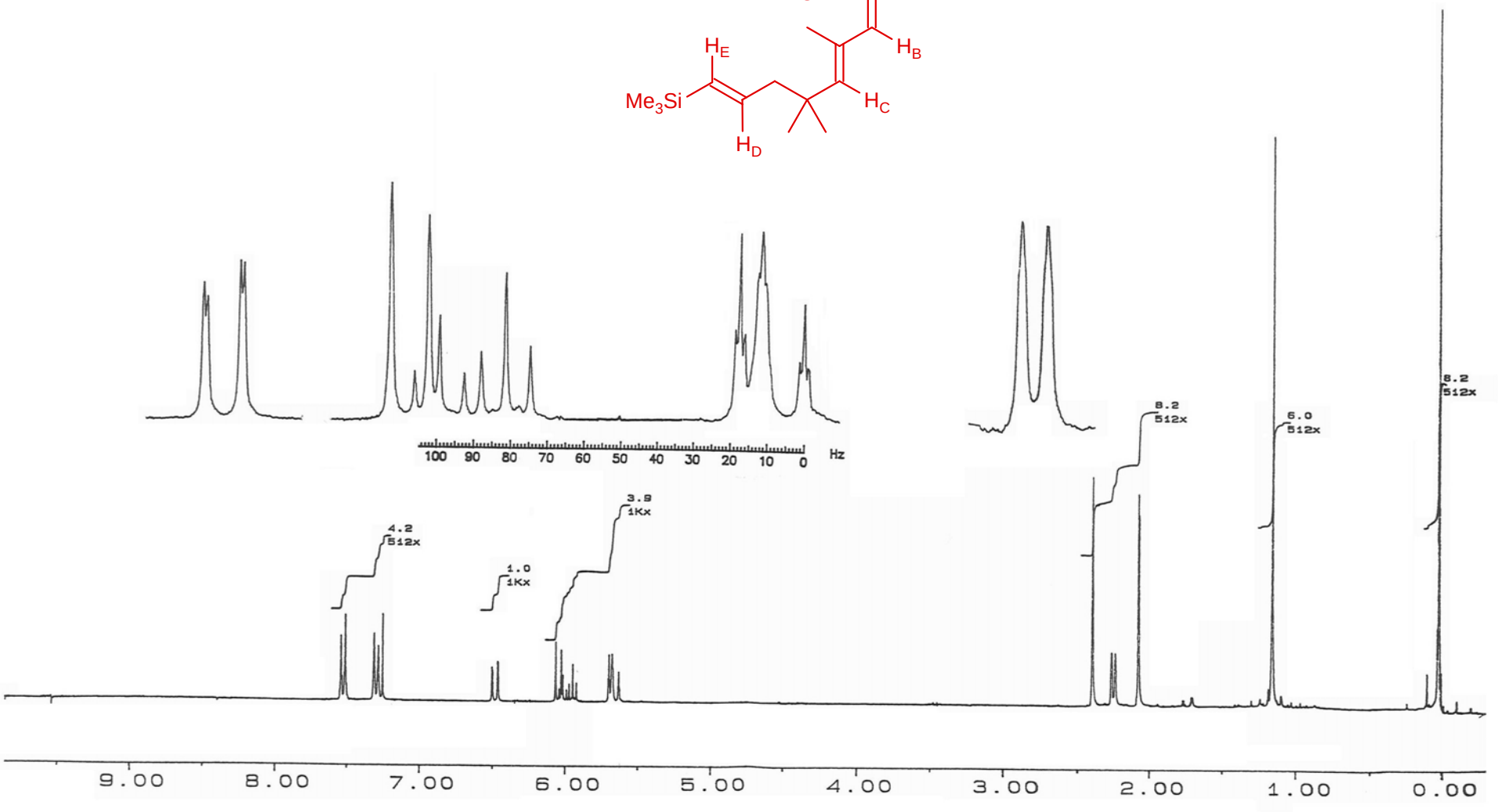
(d) What is the stereochemistry at the $H_D$ - $H_E$ double bond? Explain briefly.

Double bond must be trans - 18 Hz coupling

2

**Problem R-12D** ($C_{21}H_{32}OSSi$).
270 MHz $^1H$ NMR spectrum in $CDCl_3$
(Source: Margaret K. Jones/Burke)



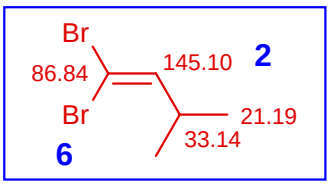
**Problem R-12E** ($C_5H_8Br_2$). Determine the structure (or part structure) of **R-12E** from the $^1$H NMR, $^{13}$C NMR and IR spectra provided.

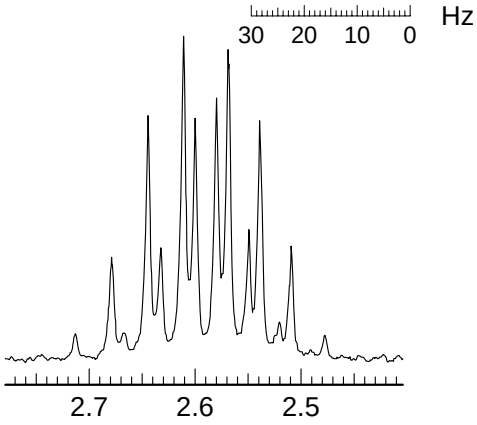
**2** (a) DBE 1. (b) Analyze the $^1$H NMR signals, in particular the multiplet at δ 2.6. Report δ, multiplicities and *J* values. Show the structure of **R-12E**.

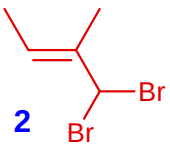
**5** δ 2.6, 1H, d septets, J = 8.5, 7 Hz

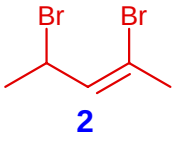
δ 6.2, 1H, d, J = 8.5 Hz

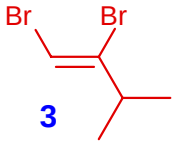
δ 1.0, 6H, d, J = 7 Hz



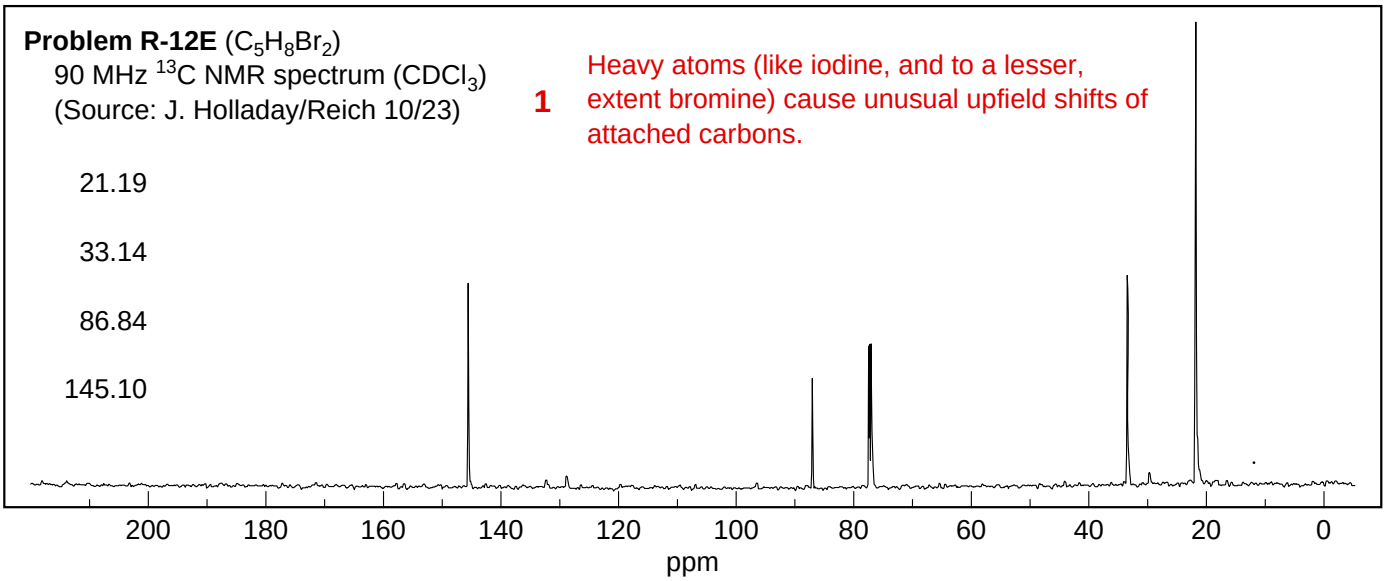




4 other structures, none fit the data

(c) Assign the $^{13}$C NMR signals (write them on a structure). Explain the signal at δ 86.8 ppm.

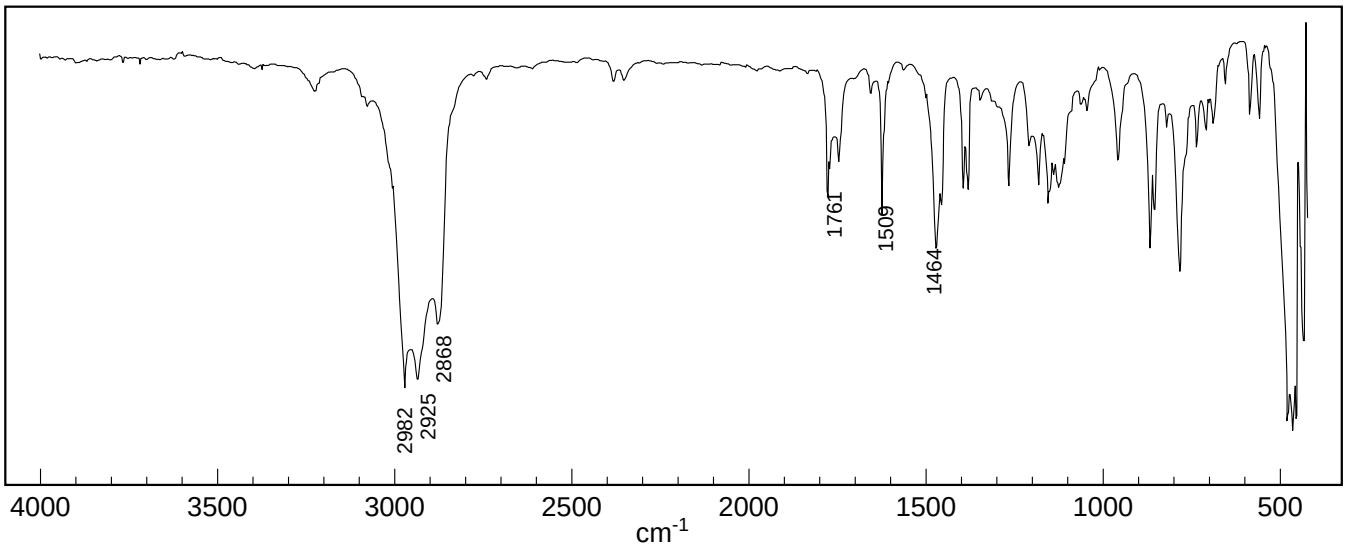



(d) IR spectrum.

**Problem R-12E** ($C_5H_8Br_2$)

IR spectrum ($CDCl_3$)

(Source: J. Holladay/Reich 10/23)



**Problem R-12E** ($C_5H_8Br_2$)

200 MHz $^1$H NMR spectrum ($CDCl_3$)

(Source: J. Holladay/Reich 10/23)