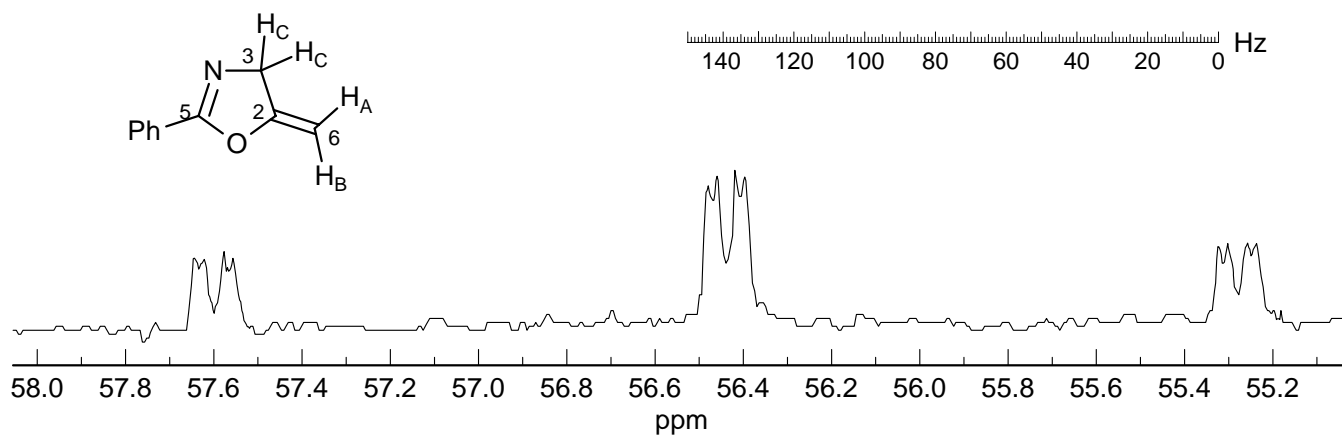15

Problem R-12M ($C_{10}H_{09}NO$). You are asked to interpret the coupled ^{13}C NMR spectrum of an oxazoline.

(a) Which carbon are we looking at? _____ C^3 _____

2

(b) Analyze the spectrum, report all coupling constants in the standard format ($^nJ_{X-Y}$ = 00.0 Hz).

     tdd, J = 146, 8, 3

 $^1J_{C-H}$ = 146 Hz

5      $^3J_{C-H}$ (trans) = 8 Hz

     $^3J_{C-H}$ (cis) = 3 Hz

(c) The spectrum below is of the same compound with one H replaced by D. Where is the deuterium? Place it on the structure, and explain briefly.

Only the small cis $^3J_{C-H}$ remains in the deuterated compound, so the trans proton must have been replaced by deuterium. The C-D coupling would be only about 1.3 Hz. so is not detectable at this resolution.
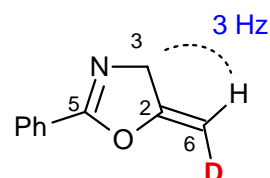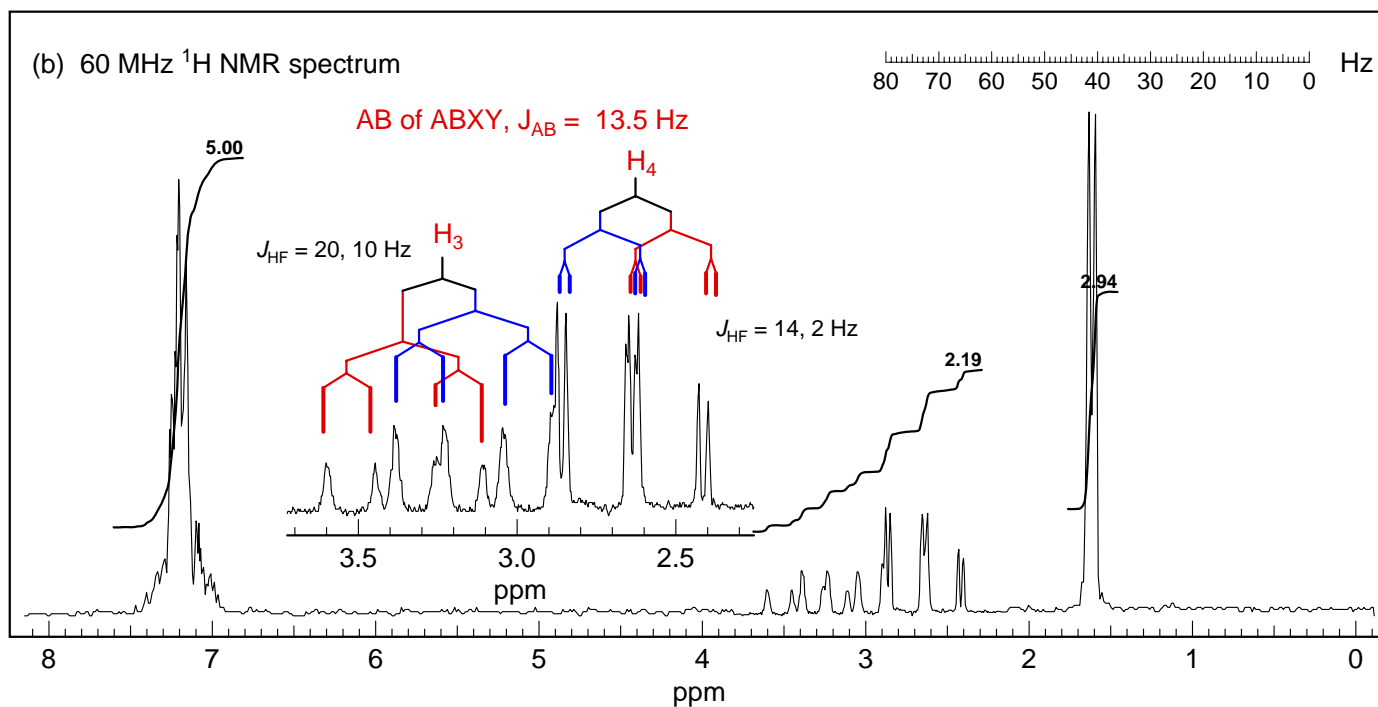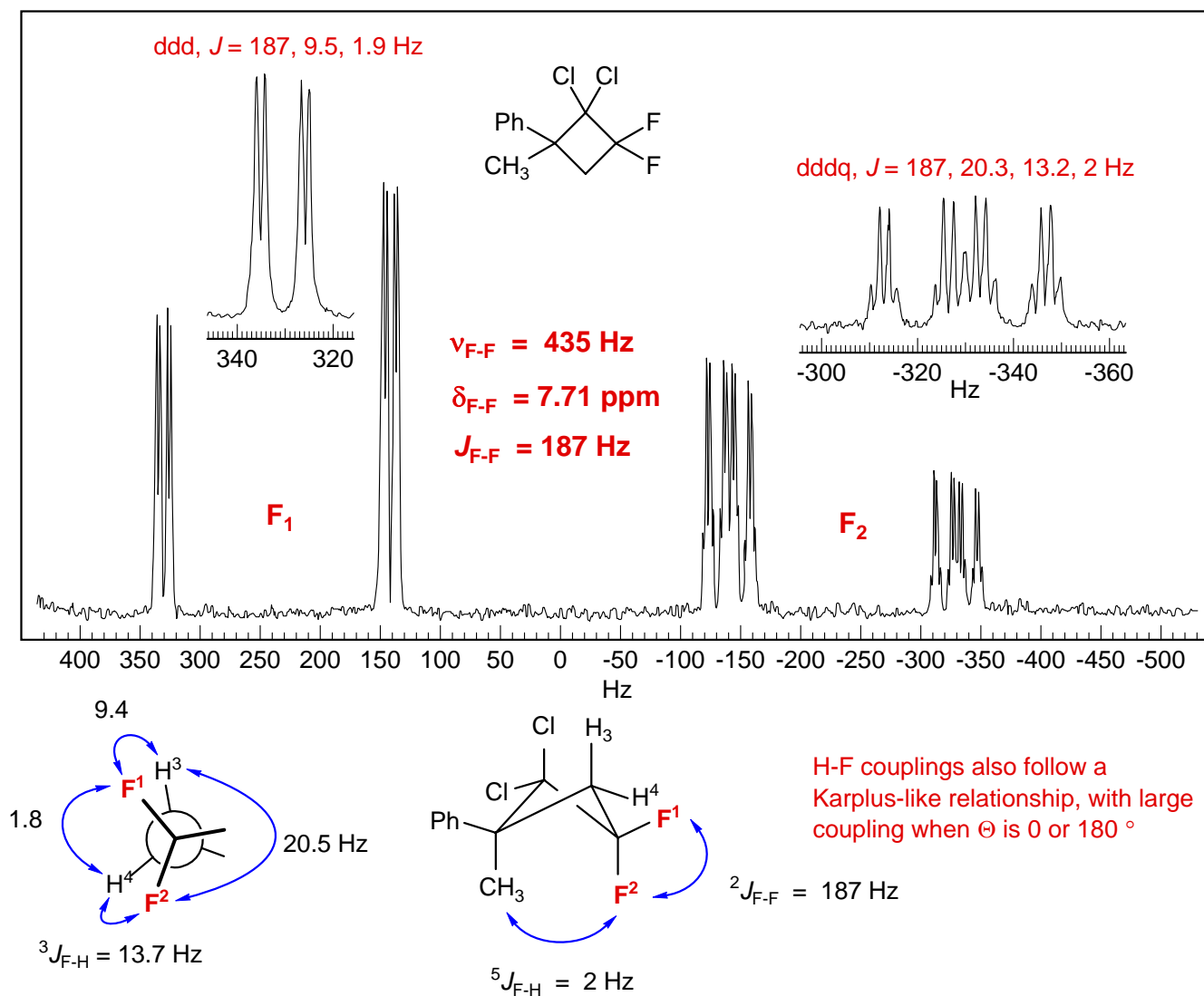

5
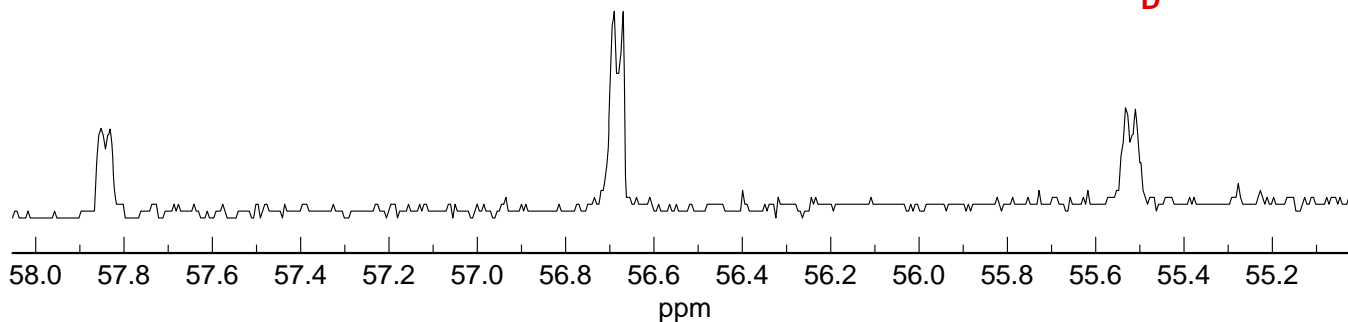
(d) What is the proton NMR frequency of the spectrometer they were using? _____ 497 MHz _____

1 ppm = 125 Hz in the ^{13}C NMR spectrum, so the ^{13}C frequency is 125 MHz. Thus the proton frequency is 125x(100/25.14) = 497.2 MHz

3

Problem R-310 ($C_{11}H_{10}Cl_2F_2$). Interpret the 56.4 MHz ^{19}F NMR spectrum below (CCl_4 solvent). Determine the chemical shifts of the fluorines, and estimate the various coupling constants. Consider conformations of the cyclobutane ring (*J. Am. Chem. Soc.* **1962**, *84*, 2935).

ddd, J = 187, 9.5, 1.9 Hz

dddq, J = 187, 20.3, 13.2, 2 Hz

340   320

-300   -320   -340   -360
Hz

ν_{F-F} = 435 Hz

δ_{F-F} = 7.71 ppm

J_{F-F} = 187 Hz

F_1

F_2

400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 -450 -500
Hz

9.4

F^1 H^3

1.8

H^4 20.5 Hz

F^2

$^3J_{F-H}$ = 13.7 Hz

Cl H_3

Cl

Ph H^4

F^1

CH_3 F^2 $^2J_{F-F}$ = 187 Hz

$^5J_{F-H}$ = 2 Hz

H-F couplings also follow a Karplus-like relationship, with large coupling when Θ is 0 or 180 °

(b) 60 MHz ^1H NMR spectrum

80 70 60 50 40 30 20 10 0   Hz

AB of ABXY, J_{AB} = 13.5 Hz

5.00

H_4

J_{HF} = 20, 10 Hz H_3

J_{HF} = 14, 2 Hz

2.94

2.19

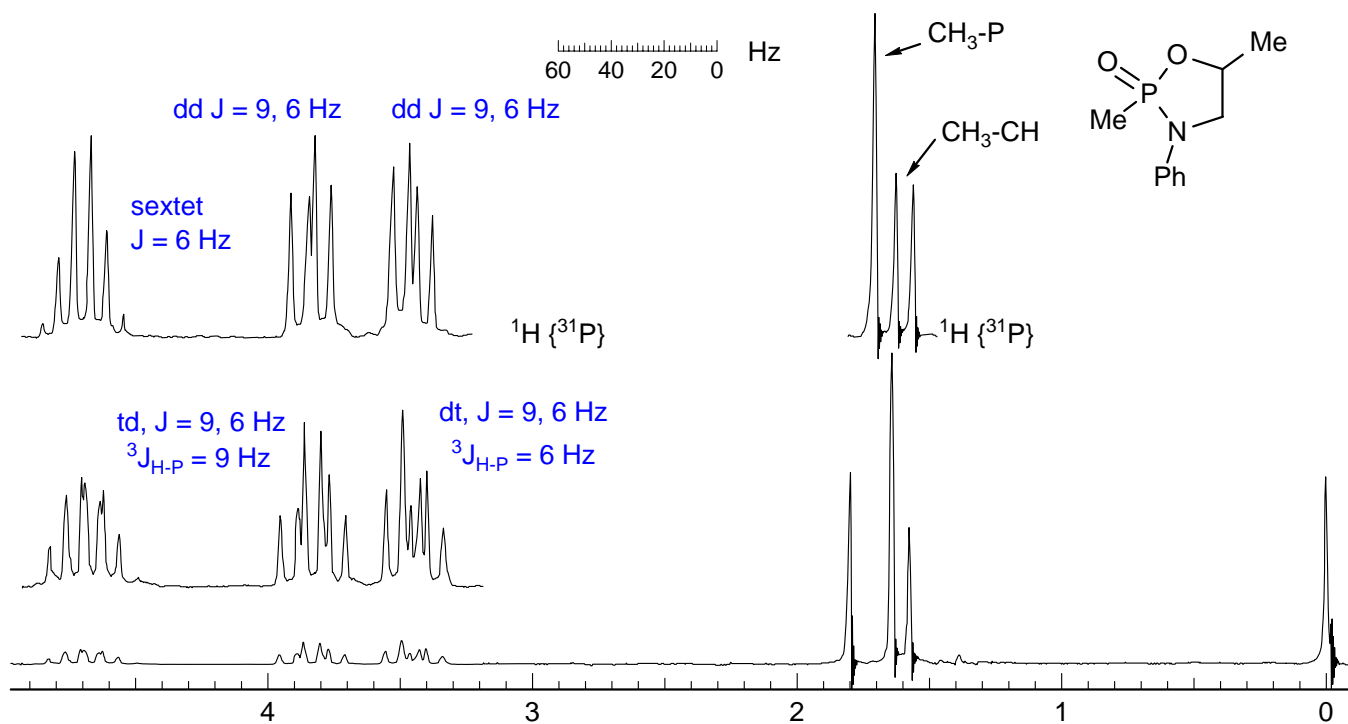3.5   3.0   2.5
ppm

8   7   6   5   4   3   2   1   0
ppm

Problem R-308 (C_8H_{10}).   Below is the ^3H NMR spectrum of the ethyl region of randomly tritium (^3H) labeled ethylbenzene. Interpret the splitting pattern. Note: <1% of the molecules are labeled (Tiers,G. V. D.; Brown, C. A.; Jackson, R. A.; Lahr, T. N. J. Am. Chem. Soc. 1964, 86, 2526-7).

^1H I = 1/2 100 MHz

^3H I = 1/2 106.66 MHz

30 20 10 0   Hz

dq J = 14, 8 Hz

tt J = 13, 8 Hz

3   2

2   1
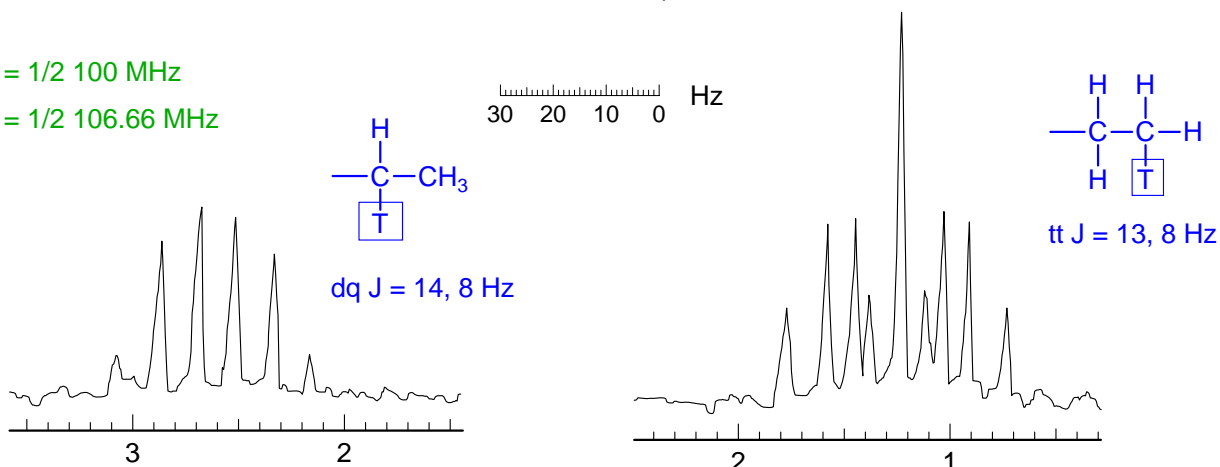
Problem R-309 ($C_9H_{14}NOP$). Interpret the 100 MHz ^1H NMR spectrum below. The phenyl region is not shown. {^{31}P} signifies decoupling of the phosphorus signal (*Org. Magn. Res..* **1980**, *13*, 165)

60 40 20 0   Hz

dd J = 9, 6 Hz   dd J = 9, 6 Hz

sextet
J = 6 Hz

^1H {^{31}P}

CH$_3$-P

CH$_3$-CH

^1H {^{31}P}

td, J = 9, 6 Hz
$^3J_{H-P}$ = 9 Hz

dt, J = 9, 6 Hz
$^3J_{H-P}$ = 6 Hz

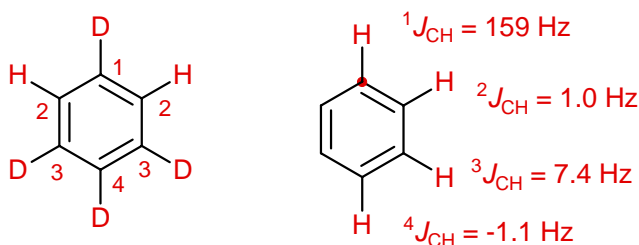4   3   2   1   0

Problem R-311 ($C_6H_2D_4$). Assign the peaks in the ^{13}C NMR spectrum below. The spectrum is not ^1H decoupled. Estimate the coupling constants (*J. Am. Chem. Soc.* **1967**, *88*, 2967).
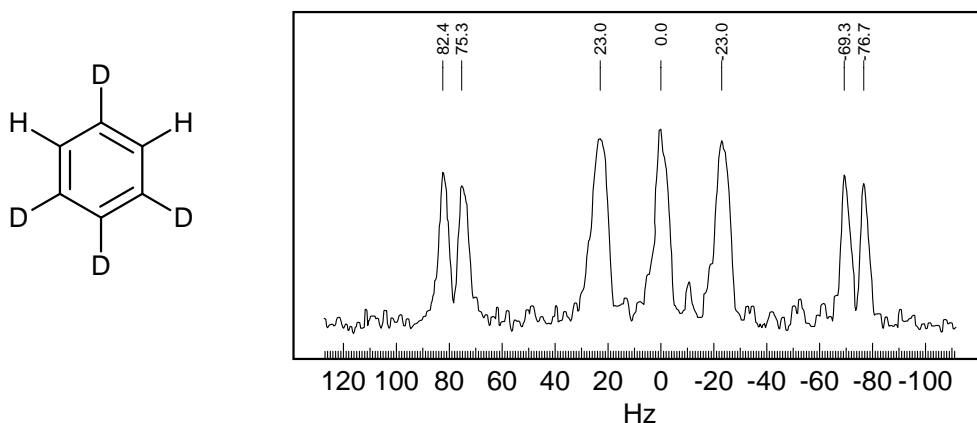

ANSWER

There are four kinds of carbons in this molecule

$^1J_{CH}$ = 159 Hz
$^2J_{CH}$ = 1.0 Hz
$^3J_{CH}$ = 7.4 Hz
$^4J_{CH}$ = -1.1 Hz

C-1: The only significant coupling is $^1J_{CD}$ = 23 Hz. The $^2J_{CH}$ will be 1 Hz, too small to resolve

C-2: These carbons will be a double intensity dd, with $^1J_{CH}$ = 159 Hz and $^3J_{CH}$ = 7 Hz. There will also be a $^3J_{CD}$ of about 1Hz, too small to resolve

C-3: These will be a double intensity 1:1:1 triplet of 1:1:1 triplets, $^1J_{CD}$ = 23 Hz and $^3J_{CD}$ = 1 Hz
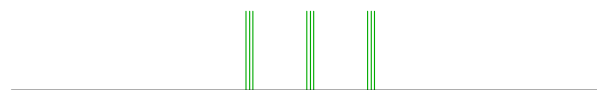

C-4: Carbon 4 will be a 1:1:1 triplet of 1:2:1 triplets, $^1J_{CD}$ = 23 Hz and $^3J_{CH}$ = 7 Hz the outer lines of the triplets are too small to be visible
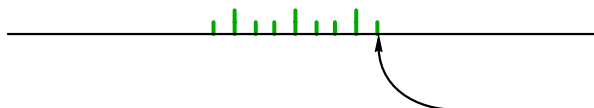
These outer triplet peaks will be approximately 1/16 of the intensity of the central peaks, hence not detectable at this signal to noise. The central lines are superimposed on C-1 and C-3.

Problem R-82E ($C_{16}H_{30}Sn$). Consider carefully the ^1H NMR spectrum of R-82E shown on the next page (the compound contains a tri-n-butyltin group, tin is tetravalent).

(a) DBE?____3____ What is the structure of R-82E?

4 Hz is too small   4 Hz is definitely too small
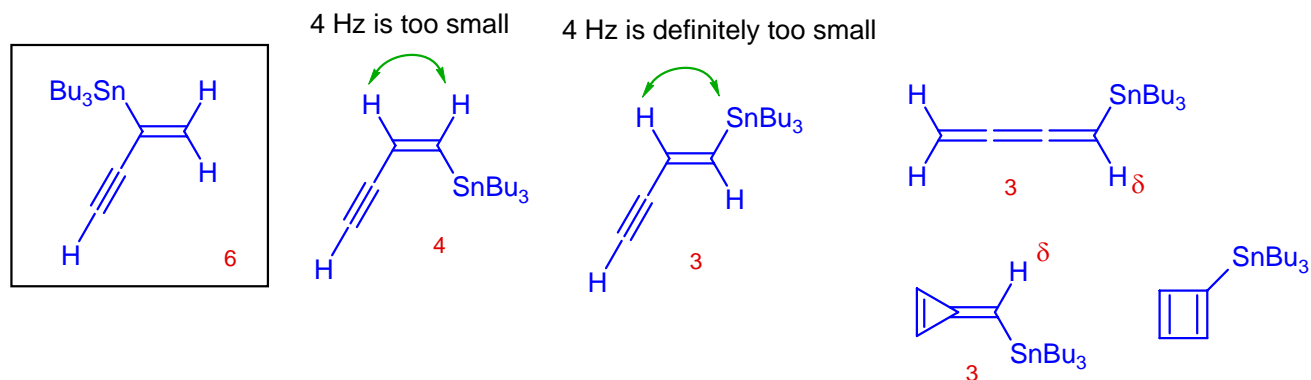
(b) Explain the origin and shape of the multiplets at δ 6.05 and 6.6.

Sn has two main spin 1/2 isotopes (the third one is not abundant enough to detect in these spectra:

^{119}Sn 8.7%   37.28

^{117}Sn 7.1%   35.63

^{115}Sn 0.34% 32.17

Thus each peak will have two pairs of satellites, one set due to ^{117}Sn and one to ^{119}Sn

(c) Determine (approximately) <u>all</u> coupling constants that can be obtained from the spectrum. Identify them in the form $^4J_{XY}$ = Z Hz. Label your structure so that it is clear which atom you are referring to.

^3J (H^A-^{117}Sn) = 107 Hz

^3J (H^B-^{117}Sn) = 52 Hz

^3J (H^A-^{119}Sn) = 113 Hz

^3J (H^B-^{119}Sn) = 54 Hz

$^5J_{AC}$ ca 0.5 Hz

$^2J_{AB}$ = 4 Hz

$^5J_{BC}$ = 1 Hz
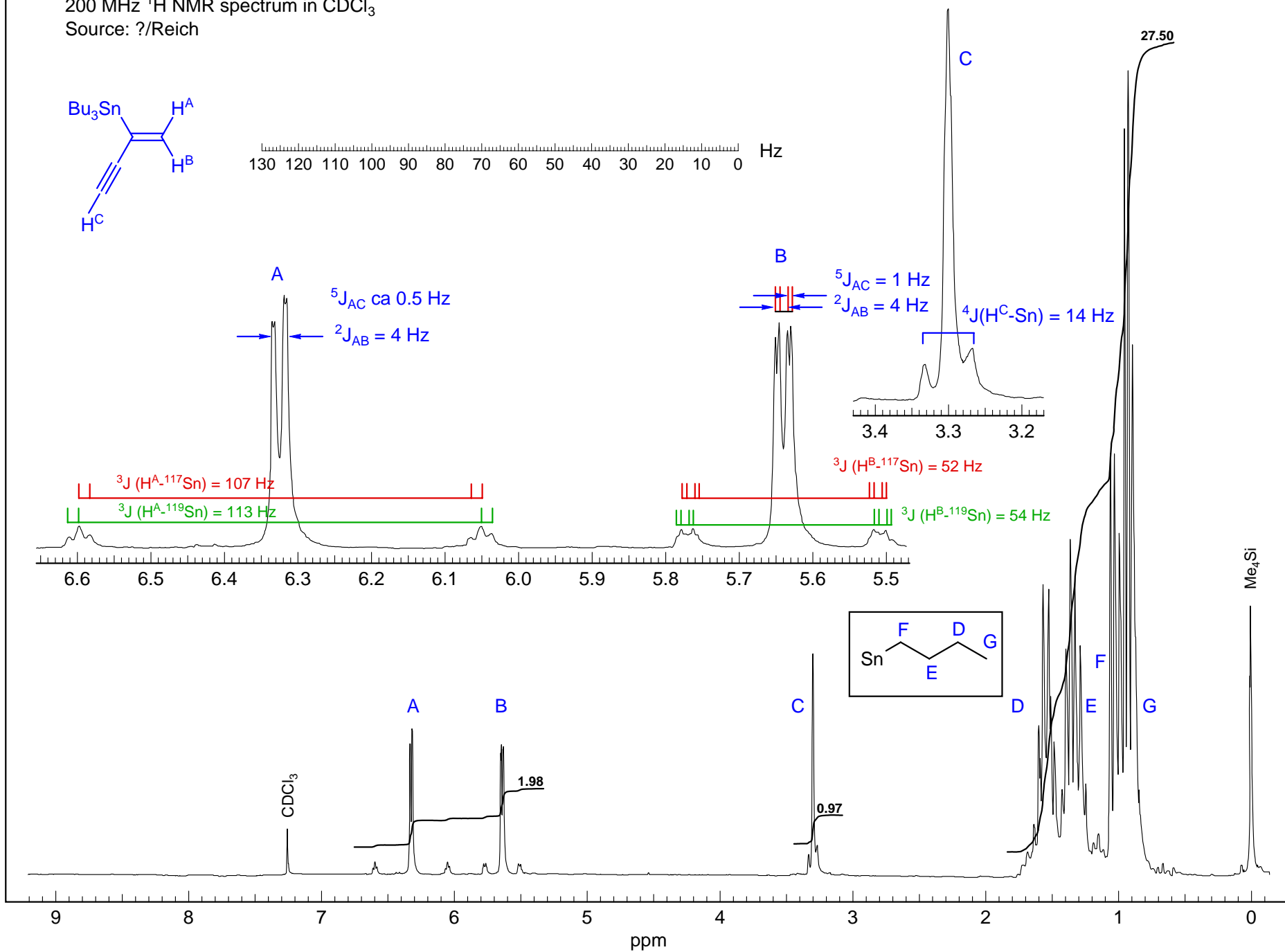
$^2J_{BA}$ = 4 Hz

$^4J(H^C$-Sn) = 14 Hz

$$\frac{\gamma\,(^{119}Sn)}{\gamma\,(^{117}Sn)} = \frac{37.28}{35.63} = 1.046$$

Thus get two sets of satellites, differing by ca 4% in J

Problem R-82E $C_{16}H_{30}Sn$
200 MHz ^1H NMR spectrum in $CDCl_3$
Source: ?/Reich

Bu_3Sn H^A

H^B

H^C

Hz
130 120 110 100 90 80 70 60 50 40 30 20 10 0

A

$^5J_{AC}$ ca 0.5 Hz

$^2J_{AB}$ = 4 Hz

B

$^5J_{AC}$ = 1 Hz
$^2J_{AB}$ = 4 Hz

C

27.50

$^4J(H^C$-Sn) = 14 Hz

3.4   3.3   3.2

^3J (H^A-^{117}Sn) = 107 Hz

^3J (H^A-^{119}Sn) = 113 Hz

^3J (H^B-^{117}Sn) = 52 Hz

^3J (H^B-^{119}Sn) = 54 Hz

6.6   6.5   6.4   6.3   6.2   6.1   6.0   5.9   5.8   5.7   5.6   5.5

F   D
G
Sn
E

A   B
1.98

C
0.97

D   E   F   G

Me_4Si

CDCl$_3$

9   8   7   6   5   4   3   2   1   0
ppm
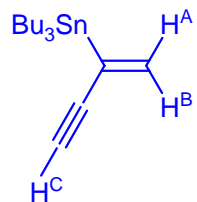
Problem R-94G ($C_{28}H_{24}BP$).
Interpret the δ2 - δ3 region of the
300 MHz ^{1}H NMR spectrum of the
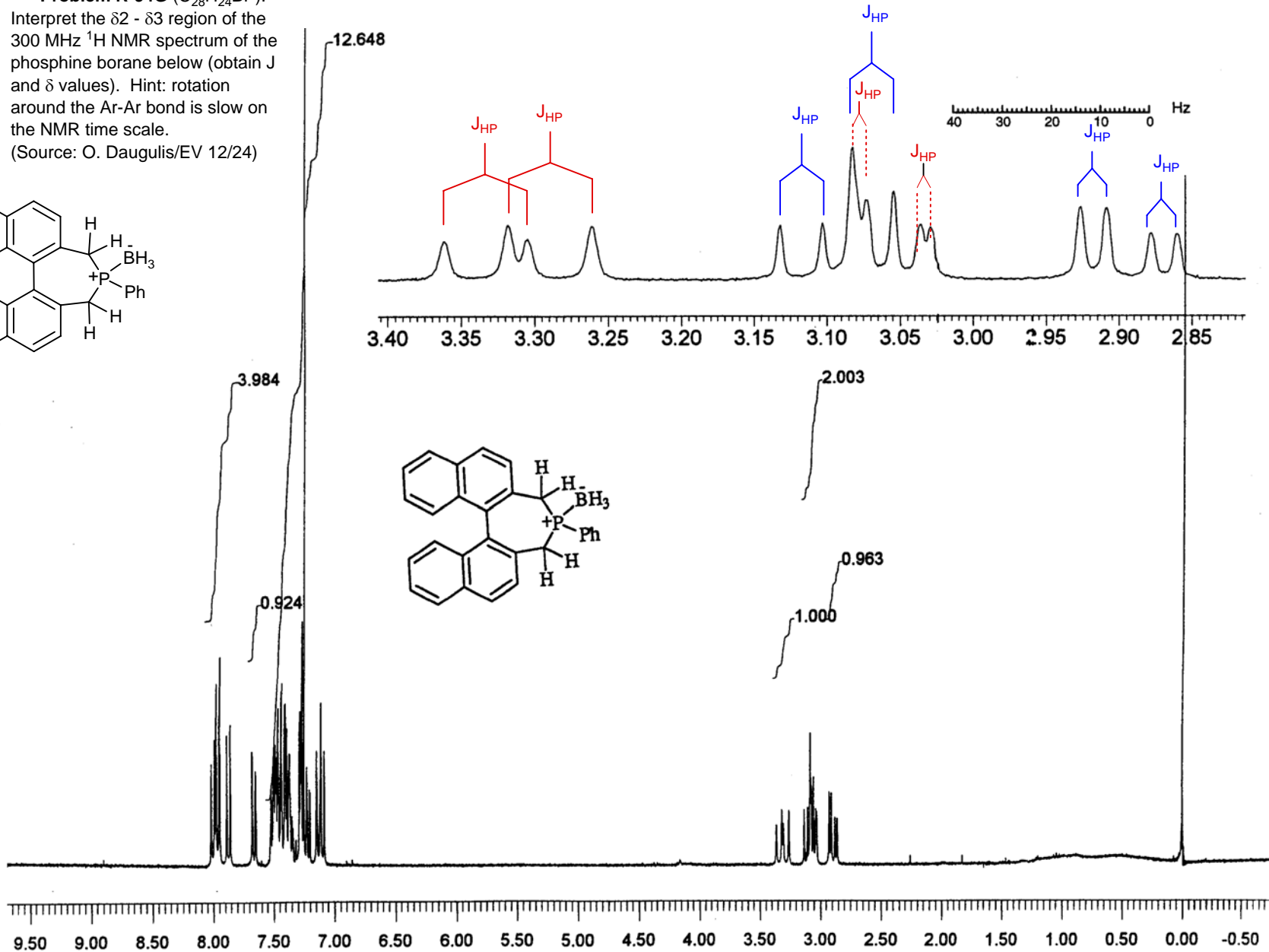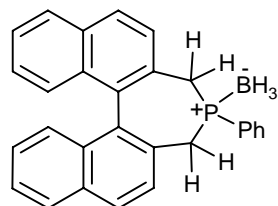phosphine borane below (obtain J
and δ values). Hint: rotation
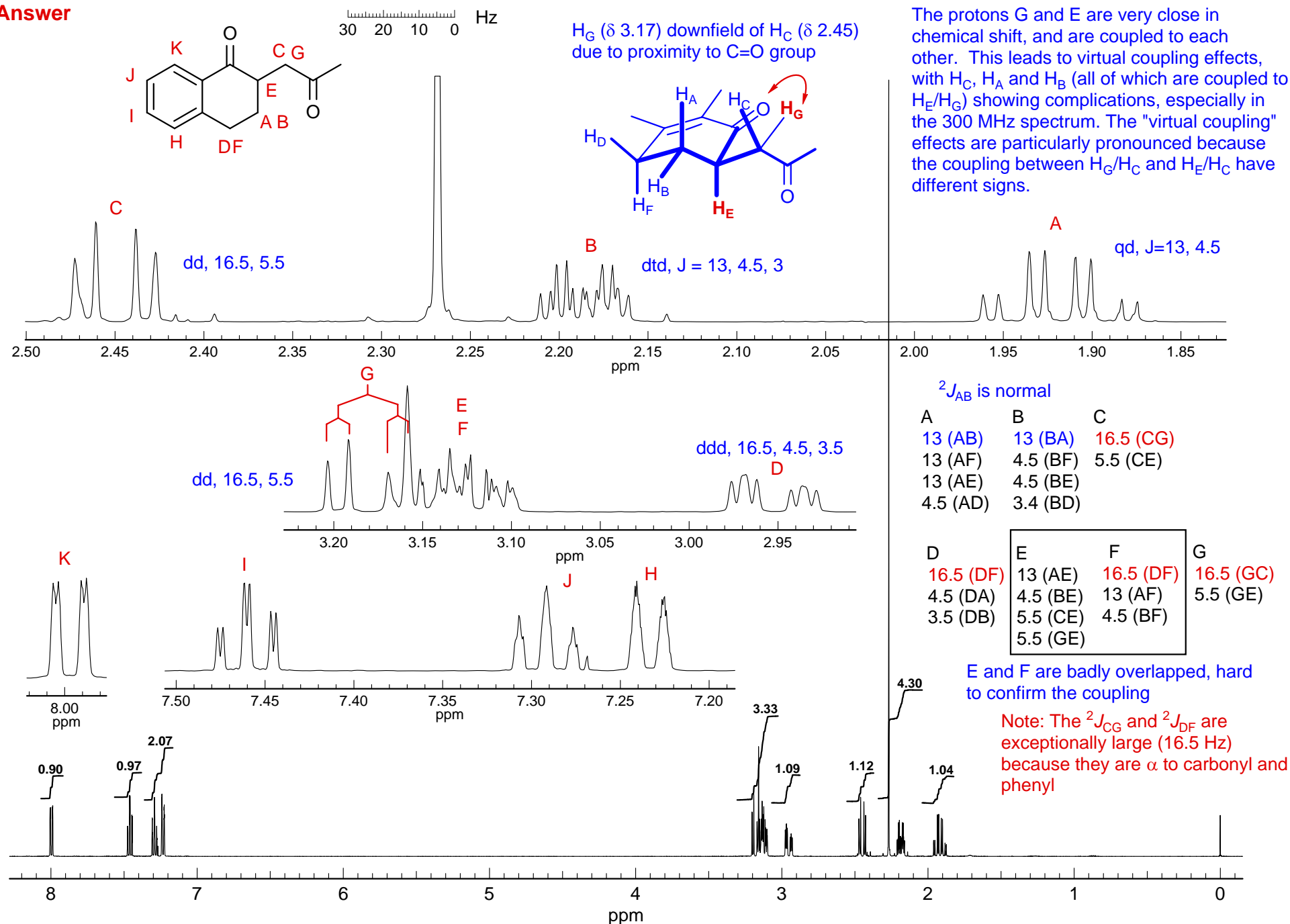around the Ar-Ar bond is slow on
the NMR time scale.
(Source: O. Daugulis/EV 12/24)

Problem R-28D ($C_{13}H_{14}O_2$)
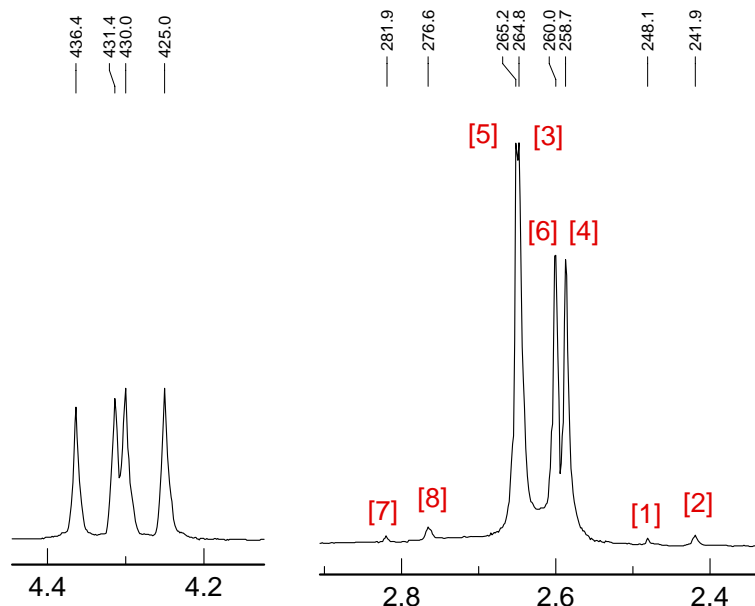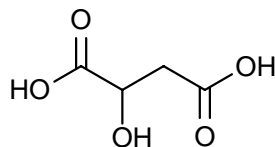500 MHz ^{1}H NMR in CDCl$_3$
Source: Wilds/C. Fry (C82)

Assign all protons in this molecule, using the 500 MHz ^{1}H NMR spectrum, and the 300 MHz COSY spectrum. The 300 MHz ^{1}H spectrum is also provided. Explain specifically why some of the peaks are more complicated in the 300 compared to the 500 MHz spectrum. Draw a conformation, and label with chemical shifts.

Answer

H_G (δ 3.17) downfield of H_C (δ 2.45) due to proximity to C=O group

The protons G and E are very close in chemical shift, and are coupled to each other. This leads to virtual coupling effects, with H_C, H_A and H_B (all of which are coupled to H_E/H_G) showing complications, especially in the 300 MHz spectrum. The "virtual coupling" effects are particularly pronounced because the coupling between H_G/H_C and H_E/H_C have different signs.

C — dd, 16.5, 5.5

B — dtd, J = 13, 4.5, 3

A — qd, J=13, 4.5

G

E
F
dd, 16.5, 5.5

ddd, 16.5, 4.5, 3.5
D

$^2J_{AB}$ is normal

A	B	C
13 (AB)	13 (BA)	16.5 (CG)
13 (AF)	4.5 (BF)	5.5 (CE)
13 (AE)	4.5 (BE)	
4.5 (AD)	3.4 (BD)	

D	E	F	G
16.5 (DF)	13 (AE)	16.5 (DF)	16.5 (GC)
4.5 (DA)	4.5 (BE)	13 (AF)	5.5 (GE)
3.5 (DB)	5.5 (CE)	4.5 (BF)	
	5.5 (GE)		

E and F are badly overlapped, hard to confirm the coupling

Note: The $^2J_{CG}$ and $^2J_{DF}$ are exceptionally large (16.5 Hz) because they are α to carbonyl and phenyl

K

I

J

H

8.00 ppm

0.90   0.97   2.07

4.30

3.33   1.09   1.12   1.04

Problem R-08I ($C_4H_6O_5$). The 100 MHz NMR spectrum of malic acid in D_2O is shown below.

F

436.4 431.4 430.0 425.0   281.9 276.6   265.2 264.8   260.0 258.7   248.1   241.9

[5] [3]

[6] [4]

[7] [8]   [1] [2]

4.4   4.2   2.8   2.6   2.4

(a) Do a mathematically accurate analysis of this spectrum. If there are two solutions, report them both. Show a coupling tree.

	Solution 1	Solution 2
J_{AB}	16.7	16.7
J_{AX}	4.2	0.4
J_{BX}	7.0	10.8
ν_A	264.8	262.9
ν_B	259.6	261.5
$\Delta\nu_{AB}$	5.2	1.4
δ_A	2.65	2.63
δ_B	2.59	2.61

15

$c_+=(6+4)/2 \quad = 259.37$

$\Delta\nu_{ab}+ = \delta_+ = sqrt((8-2)(6-4)) \quad = 6.6$

$c_+ \pm \Delta\delta_+/2 = \quad 262.7 \quad 256.1$

$c_-=(5+3)/2 \ = 264.98$

$\Delta\nu_{ab}- = \delta_- = sqrt((7-1)(5-3)) \quad = 3.8$

$c_- \pm \Delta\delta_-/2 = \quad 266.9 \quad 263.1$

Intensity Calculation

Solution 1

$\Phi1+ = 0.5\ arcsin(J_{AB}/2D+) = 34.2$

$\Phi1- = 0.5\ arcsin(J_{AB}/2D-) = 38.6$
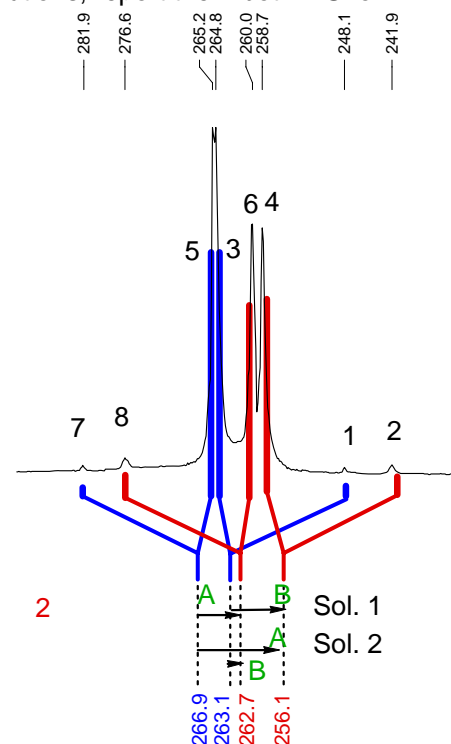
$i_{10} = i_{11} = 0.994$

$i_{14} = i_{15} = 0.006$

Solution 2

$\Phi_2+ = \Phi1 = 34.2$

$\Phi_2- = 90 - \Phi1- = 51.4$

$i_{10} = i_{11} = 0.913$

$i_{14} = i_{15} = 0.087$

281.9 276.6   265.2 264.8   260.0 258.7   248.1   241.9

6 4

5 3

7 8   1 2

2

A   B   Sol. 1
A   Sol. 2
B

266.9 263.1 262.7 256.1

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

5

In both solutions the signs are appropriate for a ^3J, although magnitude is better for solution 1 (vicinal couplings of 0.4 Hz in an acyclic CH-CH_2 system probably are never seen).

The intensity calculation predicts 9% size for the extra peaks 14 and 15, and these should have been clearly visible in the spectrum