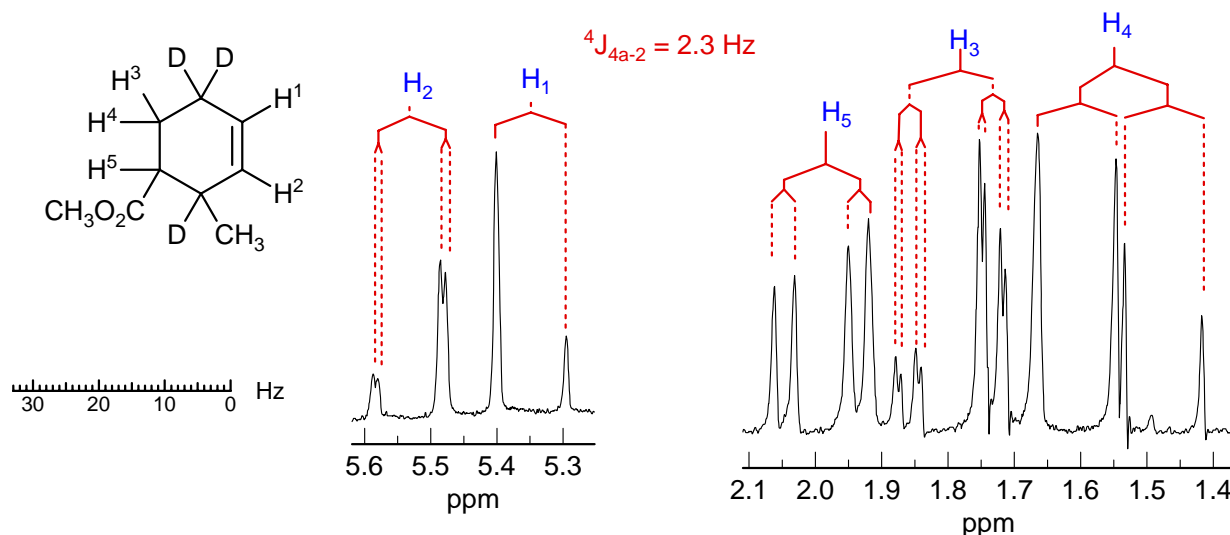# Problem Set 9 - Answers

Reich
Chem 605

Problem R-84I ($C_9H_{14}O_2$). Shown below is the partial NMR spectrum (100 MHz, CS_2 solvent, deuterium decoupled) of a deuterated cyclohexene derivative (the CH_3 resonances are not shown).


$^4J_{4a-2}$ = 2.3 Hz

(a) Provide a complete interpretation of the signals shown. Give chemical, shifts and coupling constants. Assume first order analysis.

H^1 ___5.53___ δ, J = ___10, 0.8___ Hz, coupled to: ___H_2, H_3___

H^2 ___5.36___ δ, J = ___10___ Hz, coupled to: ___H_1___

H^3 ___1.77___ δ, J = ___13, 3, 0.8___ Hz, coupled to: ___H_4, H_5, H_2___

H^4 ___1.57___ δ, J = ___13, 12___ Hz, coupled to: ___H_3, H_5___

H^5 ___1.98___ δ, J = ___12, 3___ Hz, coupled to: ___H_4, H_3___

Source *Org. Magn. Reson.* **1973**, v. 5, #10, Spect. #0635

(b) Using this information, draw a good representation of the conformation of compound **R-84I**. Label the hydrogens (1, 2, etc.) of your structure. Are the CH_3 and CO_2CH_3 groups cis or trans? (Hint: which group is larger in a cyclohexane?)

Coupling scheme:

A_{Me} = 1.70

A_{COOMe} = 1.27
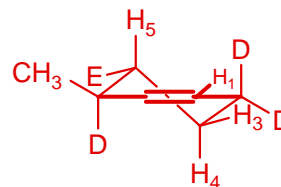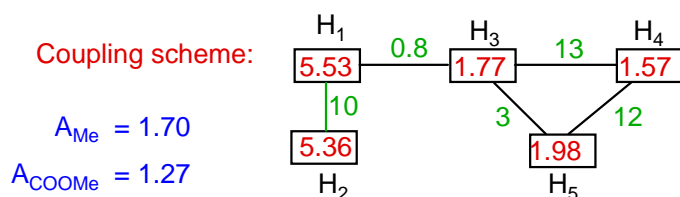
We only know that H_5 must be axial, because of the large coupling to H_4, thus the CO_2Me group is equatorial. Since Me is larger than CO_2Me in a cyclohexane, we assume that this is also the case for cyclohexene, thus placing the methyl equatorial. If the methyl were axial, the ring would flip, H_5 would be equatorial, and the NMR spectrum would not fit the structure.

"W" coupling (0.8 Hz)
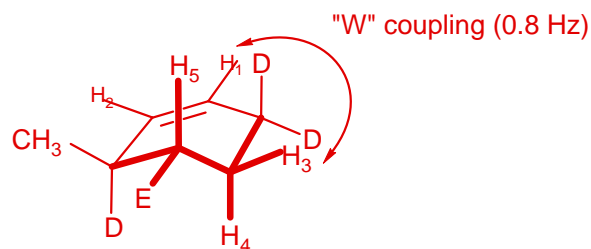
Problem N-156. The major photoaddition product of anisole and cyclooctene has been assigned to structure A and B by different groups. Assign the protons in the 270 MHz NMR spectrum below, showing whether A or B is the currect structure. The bottom spectrum shows two portions of the ^{1}H NMR spectrum (270 MHz) of the adduct. Upper plots show effects of decoupling at positions shown by arrows.
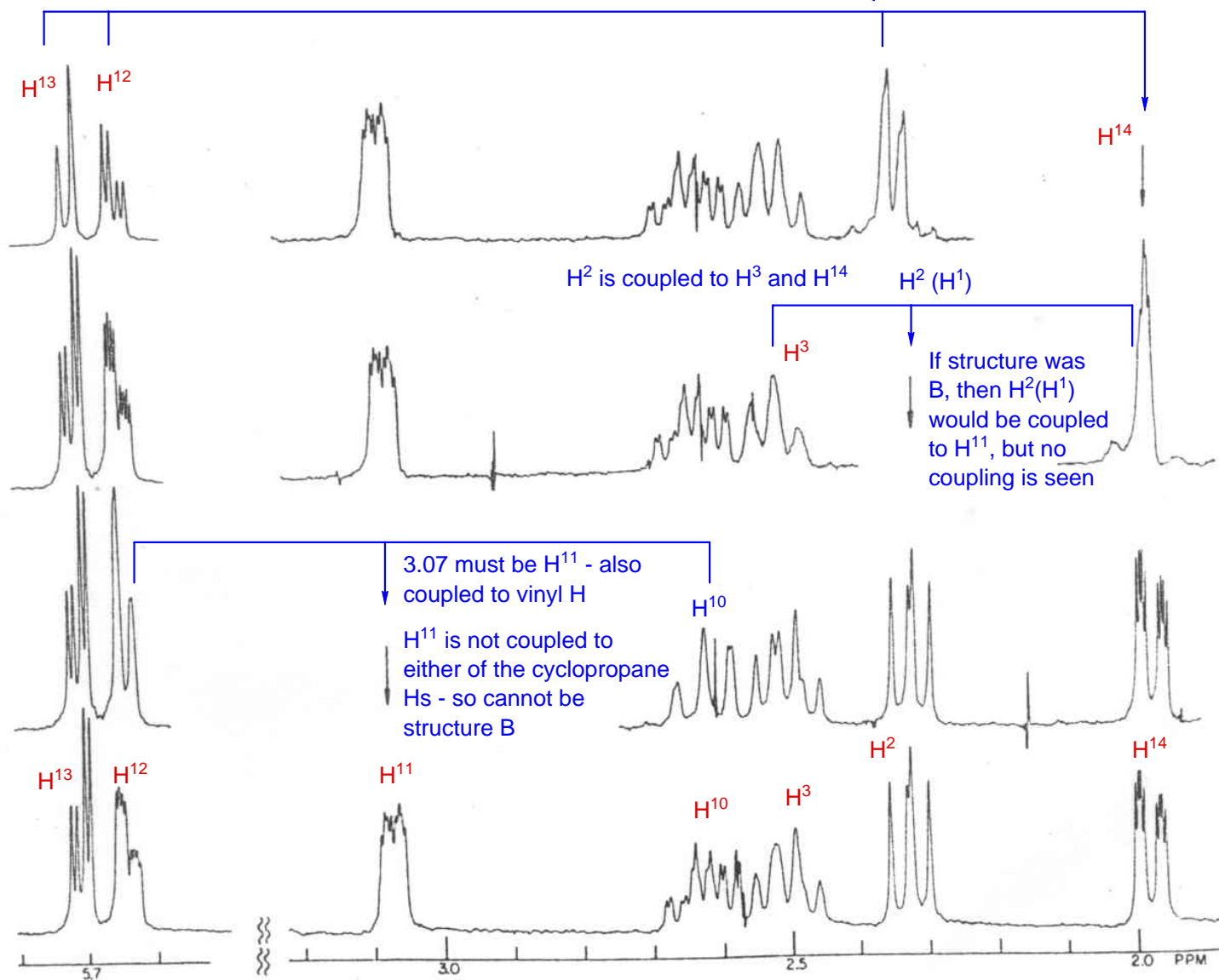
(Sheridan, Tet. Lett. **1982**, 23, 267).

A

B

B

A
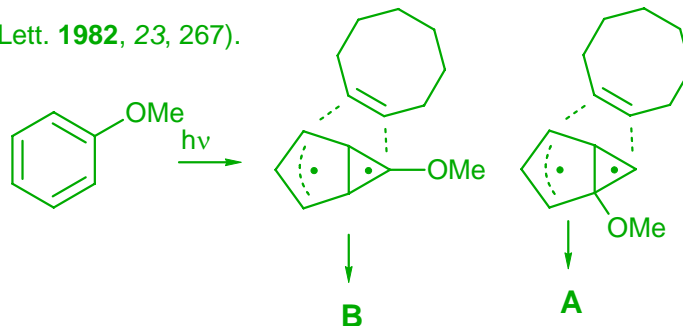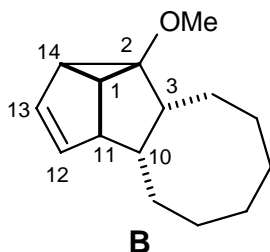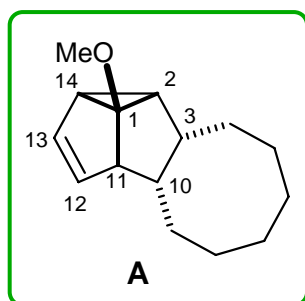
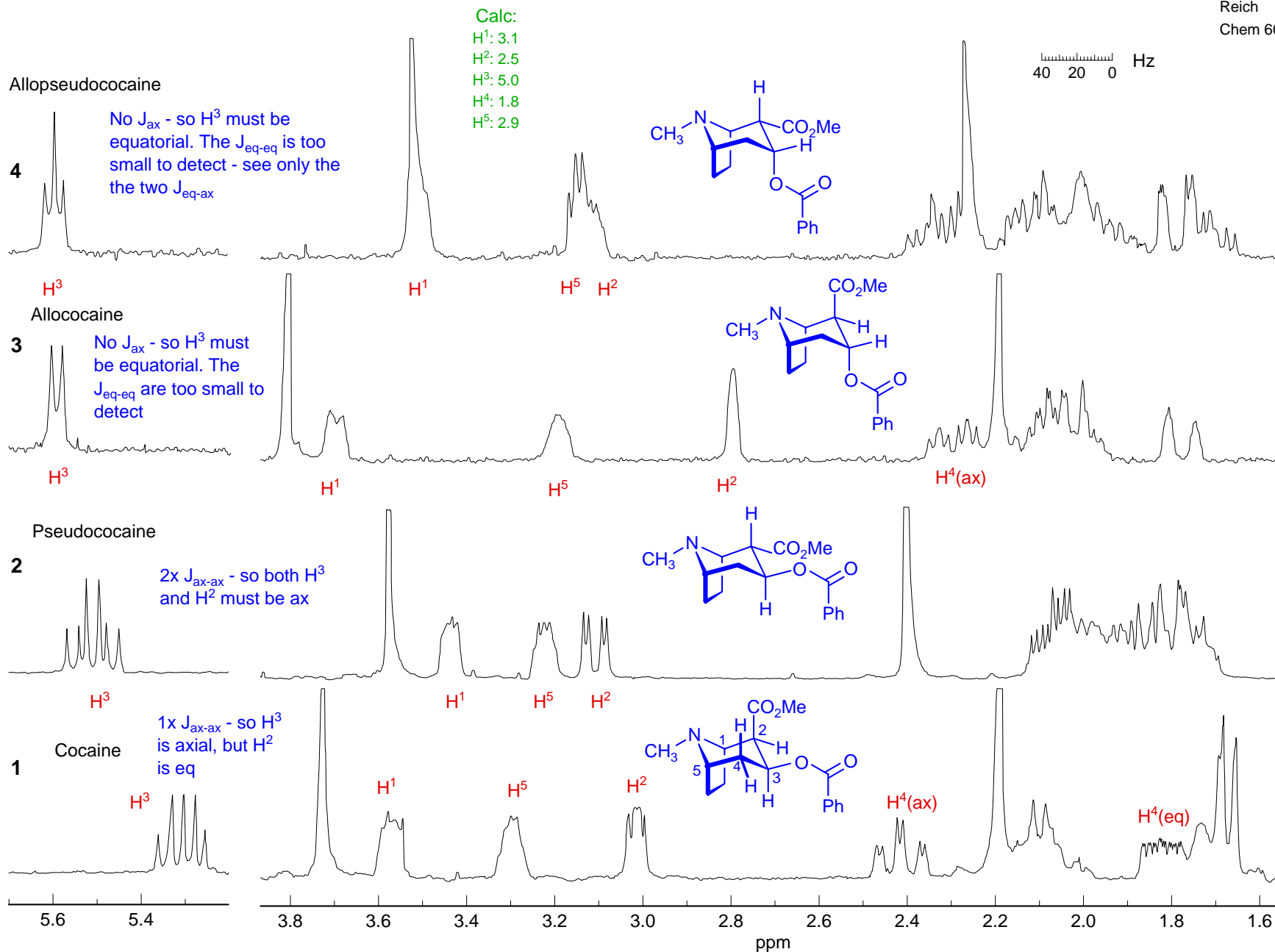Expected **B** - OMe should stabilize the radical center

2.53 is coupled to H^{14}, so must be H^2 if A is correct or H^1 if B is correct

1.98 must be H^{14}, since it is coupled to both H^{12} and H^{13}

H^{13} H^{12}

H^{14}

H^2 is coupled to H^3 and H^{14}

H^2 (H^1)

H^3

If structure was B, then H^2(H^1) would be coupled to H^{11}, but no coupling is seen

3.07 must be H^{11} - also coupled to vinyl H

H^{10}

H^{11} is not coupled to either of the cyclopropane Hs - so cannot be structure B

H^{13} H^{12}

H^{11}

H^{10} H^3

H^2
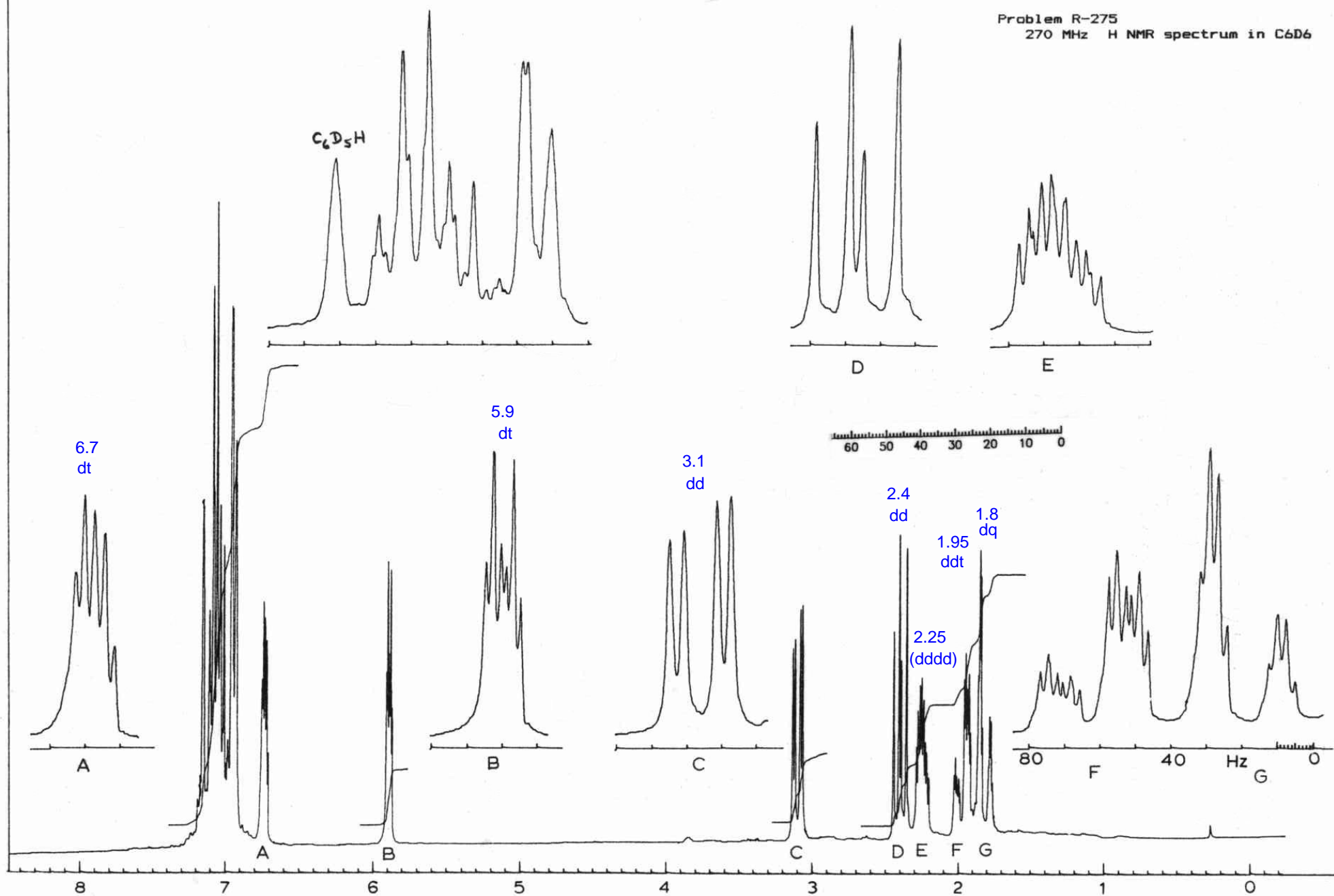
H^{14}

5.7

3.0

2.5

2.0   PPM

Problem N-302 ($C_{17}H_{19}NO_4$): 250 MHz ^1H NMR spectra of the four isomers of cocaine are shown below. Which proton appears at δ 5.3-5.6?
Assign relative stereochemistry to the four isomers. Assign the protons at δ 1.8 and 2.5 for 1 and 2.1 for **2** (*JOC* **1982**, *47*, 13).

Reich
Chem 605

Calc:
H^1: 3.1
H^2: 2.5
H^3: 5.0
H^4: 1.8
H^5: 2.9

Allopseudococaine

4

No J_{ax} - so H^3 must be equatorial. The J_{eq-eq} is too small to detect - see only the the two J_{eq-ax}

H^3 H^1 H^5 H^2 CO_2Me

Allococaine

3

No J_{ax} - so H^3 must be equatorial. The J_{eq-eq} are too small to detect

H^3 H^1 H^5 H^2 H^4(ax)

Pseudococaine

2

2x J_{ax-ax} - so both H^3 and H^2 must be ax

H^3 H^1 H^5 H^2 CO_2Me

1   Cocaine

1x J_{ax-ax} - so H^3 is axial, but H^2 is eq

H^3 H^1 H^5 H^2 H^4(ax) H^4(eq)

5.6   5.4   3.8   3.6   3.4   3.2   3.0   2.8   2.6   2.4   2.2   2.0   1.8   1.6
ppm

Problem R-275
270 MHz H NMR spectrum in C6D6

C₆D₅H

6.7 dt

5.9 dt

3.1 dd

2.4 dd

1.95 ddt

1.8 dq

2.25 (dddd)

A   B   C   D   E   F   G

8   7   6   5   4   3   2   1   0

Problem R-275 ($C_{12}H_{12}O$)
270 MHz ^1H NMR spectrum in C_6D_6
Source: E. K. Eisenhart/Reich

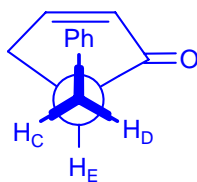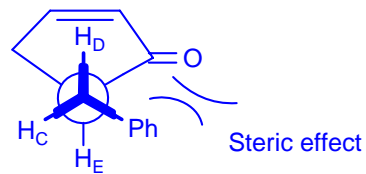|	A	B	C	D	E	F	G
δ	6.7	5.9	3.1	2.4	2.25	1.95	1.8
	dt	dt	dd	dd	(dddd)	ddt	dq
J	5.5	5.5	13.0	13.0	(9.3)	18.6	18.6
	2.5	2.2	3.9	9.3	(6.5)	6.5	2.5
	2.5	2.2			(3.9)	2.4	2.5
					(2.5)	2.4	2.5

+ C=O + Ph
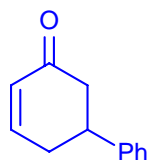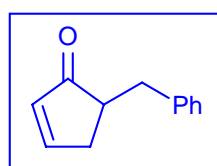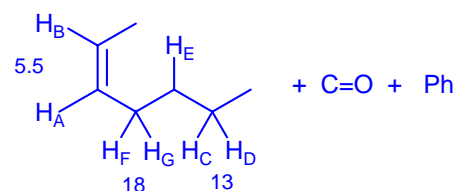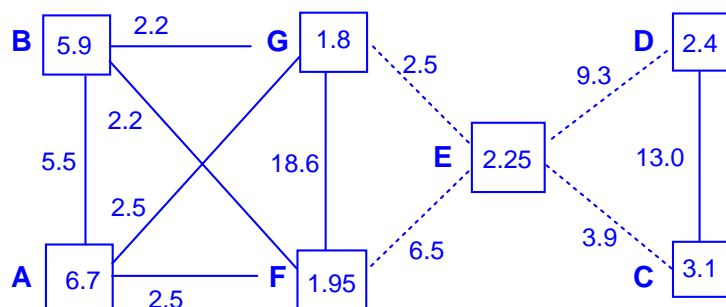
Conformation of benzyl:
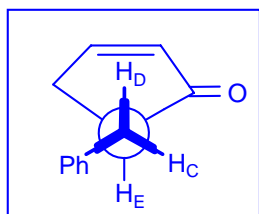
J_{DE} large
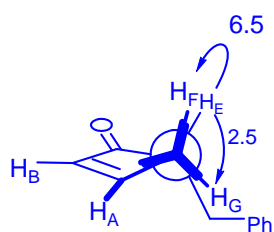J_{CE} small, H_C downfield (C=O anisotropy)

This fits best

$J_{DE} \approx J_{CE}$
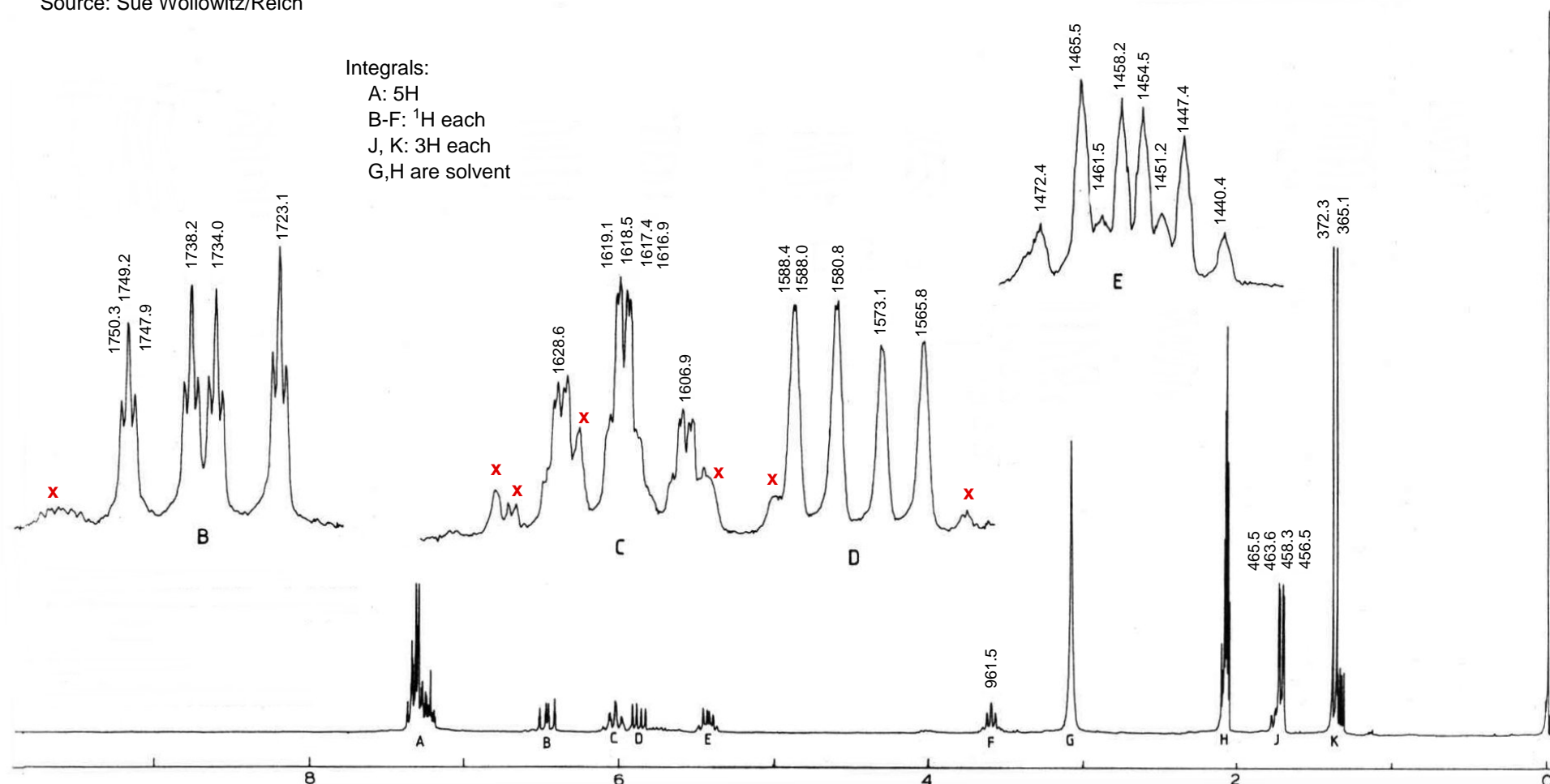
J_{DE} large
J_{CE} small
Chemical shift of H_C?
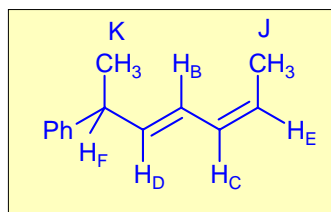
Steric effect
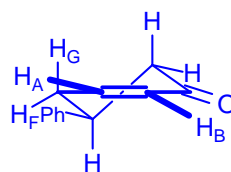
$^3J_{AB} = 10$ Hz, not 5.5 Hz

$^3J_{AF}$ and $^3J_{AG}$ usually different in cyclohexenes

Problem N-152 $C_{13}H_{16}$, a conjugated diene
270 MHz ^{1}H NMR spectrum in $(CD_3)_2C=O$
Source: Sue Wollowitz/Reich

Answer

Integrals:
A: 5H
B-F: ^{1}H each
J, K: 3H each
G,H are solvent

A	B	C	D	E	F	J (CH₃)	K (CH₃)
m	ddt	tqd	dd	dq	pentet	dd	d
	15.2	11	15.2	10.8	7(pent)		
	10.9	11	7.4	6.9(q)			
	1.1	1.7(q)	(0.5)				
	1.1	0.5					

Start the structure with **J**. The methyl dd suggests a CH_3-CH=CH unit

The only vinyl proton with a 7 Hz quartet coupling is E, so the end vinyl proton is E (CH_3-CH_E=CH)

H_C also ahows a small quartet (long range) splitting, so it can be assigned to the next proton in the chain. Since the H_C-H_E coupling is only 11 Hz, the double bond must be cis. One can rule out H_B and H_D for the one coupled to H_E because each shows a 15 Hz coupling, which is not possible for the coupling partner of H_E.
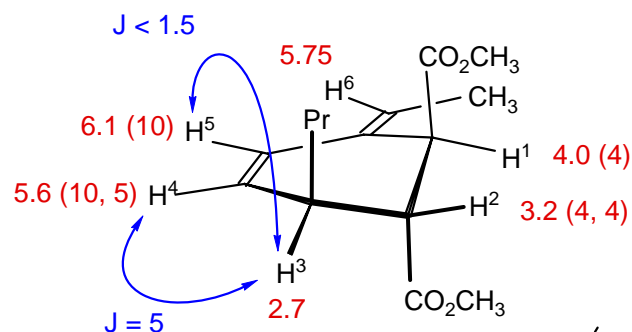
The next proton must be B, since it has couplings of 10 and 15, whereas D has 10 and 7 Hz.

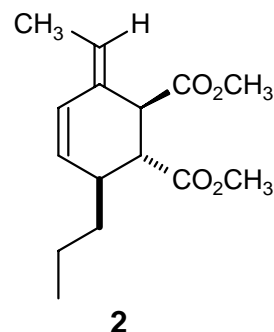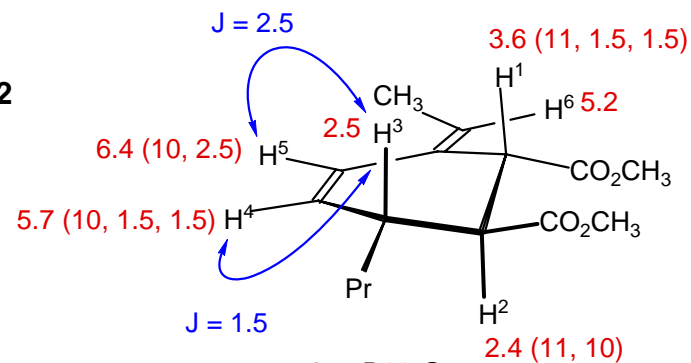H_F is a pentet from nearly equal coupling to the methyl K and H_D
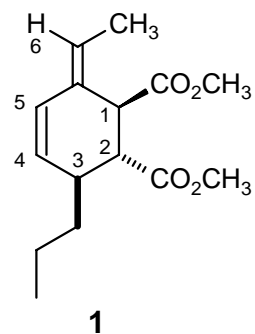
For this isomer the all-equatorial conformation would have serious buttressing interactions, hence the ring flip to all-axial substituents
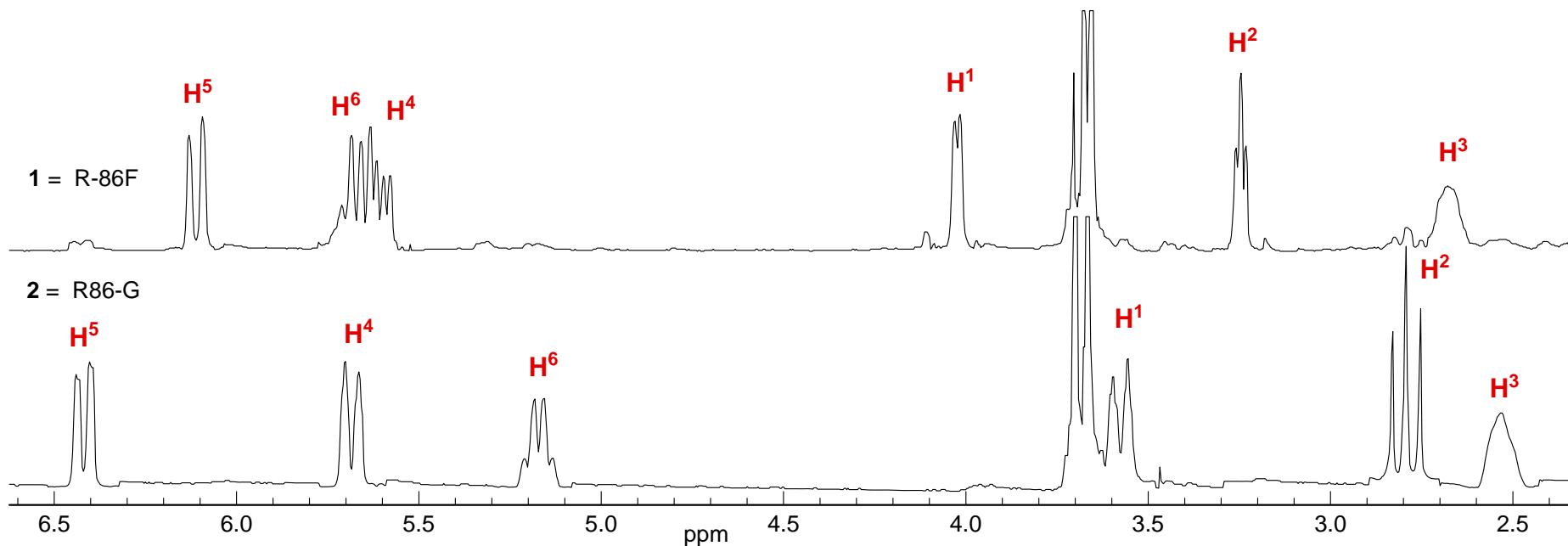
1

J < 1.5

5.75

6.1 (10) H^5

5.6 (10, 5) H^4

H^6

Pr

CO$_2$CH$_3$

CH$_3$

H^1 4.0 (4)

H^2 3.2 (4, 4)

H^3

2.7

CO$_2$CH$_3$

J = 5

1 = R-86F

2

J = 2.5

6.4 (10, 2.5) H^5

5.7 (10, 1.5, 1.5) H^4

2.5 H^3

CH$_3$

Pr

H^2

J = 1.5

3.6 (11, 1.5, 1.5)

H^1

H^6 5.2

CO$_2$CH$_3$

CO$_2$CH$_3$

2.4 (11, 10)

2 = R86-G

Note: this is the enantiomer of **R-86G**

H^5

H^6 H^4

H^1

H^2

H^3

H^2

1 = R-86F

2 = R86-G

H^5

H^4

H^6

H^1

H^2

H^3

6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5

ppm

Problem R-65. The 300 MHz ^{1}H NMR spectrum of phenylsuccinic acid in CDCl$_3$-DMSO-d$_6$ is shown below. From the line positions given, calculate the coupling constants J_{ax}, J_{bx} and J_{ab} (Source: Aldrich Spectral Viewer).
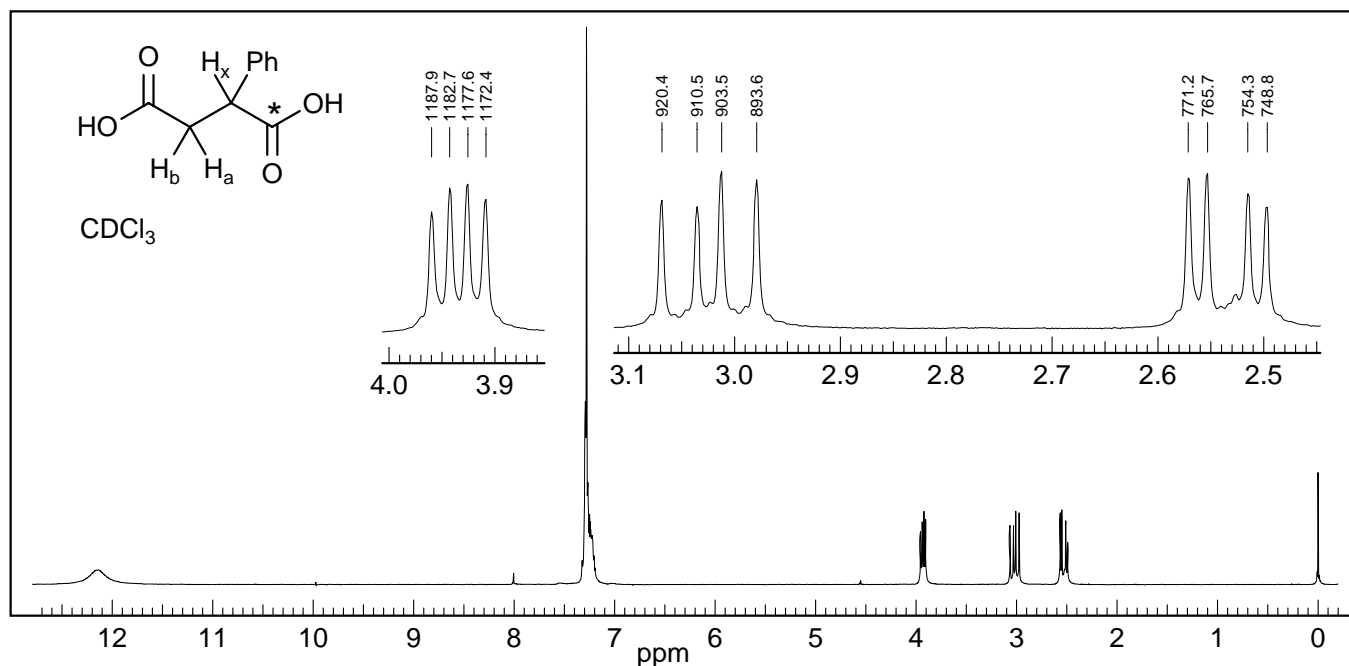

Phenylsuccinic acid partially labeled with ^{13}C at the carboxyl group marked gave the 100 MHz ^{1}H NMR spectrum below (δ 2.2-3.3, acetone-d$_6$). What is the fraction of ^{13}C incorporation?   Estimate the carbon-proton couplings $^3J_{C-Ha}$ and $^3J_{C-Hb}$ from this spectrum.

These are the peaks of the ^{13}C compound

J_{AX} = 10.2

J_{AC} = 3.1

J_{BX} = 5.5

J_{BC} = 7.3

These are the peaks of the ^{12}C compound
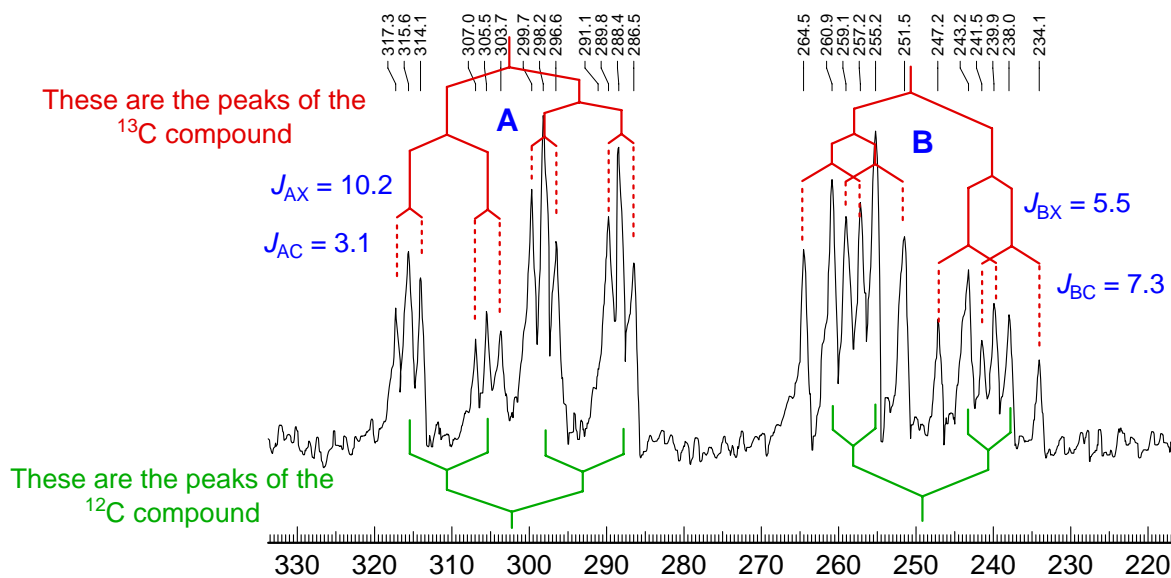
Draw Newman projections for the three possible staggered conformations of phenylsuccinic acid and determine which is the major one in acetone-d$_6$ solution.
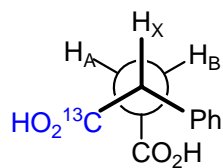
Found:

J_{AX} 10.2 large

J_{BX} 5.5 small

J_{AC} 3.1 small

J_{BC} 7.3 large

Expect:

| J_{AX} | small | not true |
| J_{BX} | small | |

J_{AC} small
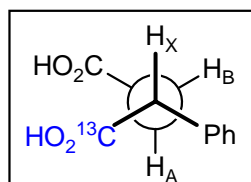
J_{BC} large

Expect:

J_{AX} large

J_{BX} small

J_{AC} small

J_{BC} large

True
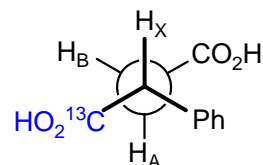
Expect:

J_{AX} large

J_{BX} small

| J_{AC} | small | |
| J_{BC} | small | not true |

Problem R-259 (C$_{11}$H$_{12}$S)
   200 MHz ^{1}H NMR Spectrum in CDCl$_3$
   (Source: Eric Eisenhart/Reich 8-14)

30 20 10 0 Hz

7.4   7.3   7.2   7.1

4.79

3.1   3.0   2.9

2.4   2.3

2.0   1.9   1.8

2.90

2.00

1.88

9   8   7   6   5   4   3   2   1   0

ppm