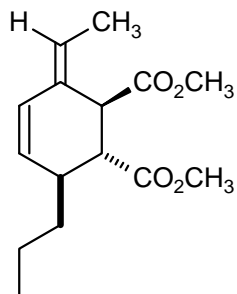


**Problem R-86F** (C<sub>15</sub>H<sub>22</sub>O<sub>4</sub>)

270 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>

Source: Eric Eisenhart/Wes Whipple/Reich 3-15 (digitized hard copy) g



30 20 10 0 Hz

3.30 3.25 3.20

1.7 1.6

0.9 0.8

6.15 6.10 6.05

5.7 5.6

4.05 4.00 3.95

6.80

6.98

3.66

1.00

2.19

0.89

1.04

0.92

2.96

8

7

6

5

ppm

4

3

2

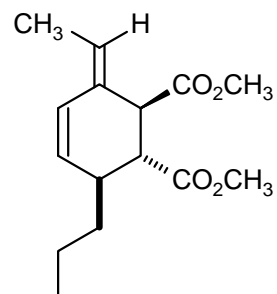
1

0

**Problem R-86G** (C<sub>15</sub>H<sub>22</sub>O<sub>4</sub>)

270 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>

Source: Eric Eisenhart/Wes Whipple/Reich 3-15 (digitized hard copy) g



**2**

30 20 10 0 Hz

3.60 3.55 3.50

2.8 2.7 2.6 2.5

6.5 6.4

5.7 5.6

5.2 5.1

7.18

1.8 1.7

5.49 0.9

3.17

2.90

1.00

1.10

0.92

1.16

1.02

8

7

6

5

ppm

4

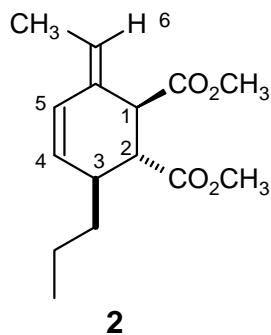
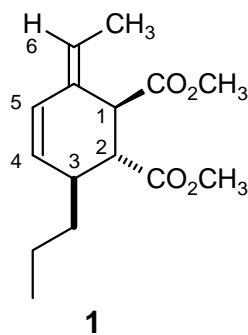
3

2

1

0

**Problem R-86F and R-86G.** The 270 MHz  $^1\text{H}$  spectra provided are of the compounds below:



(a) Analyze the multiplets and assign the signals by placing the data on the proper row (use the format  $\delta$  0.25, dt,  $J$  = 3, 9 Hz).

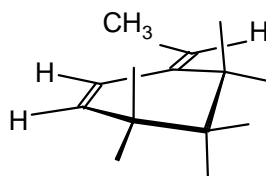
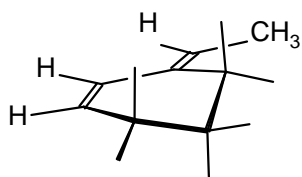
**R-86F**

$\text{H}^1$   $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\text{H}^2$   $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\text{H}^3$   $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\text{H}^4$   $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\text{H}^5$   $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\text{H}^6$   $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_

**R-86G**

$\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_  
 $\delta$  \_\_\_\_\_  $J$  = \_\_\_\_\_

(b) A typical conformation (MM2) of this type of molecule is shown below. Attach substituents and identify the spectrum (i.e., say **1** = 86F or **1** = 86G). Briefly explain the basis for your choice. Discuss at least  $\text{H}^1$ ,  $\text{H}^2$  and  $\text{H}^4$ .



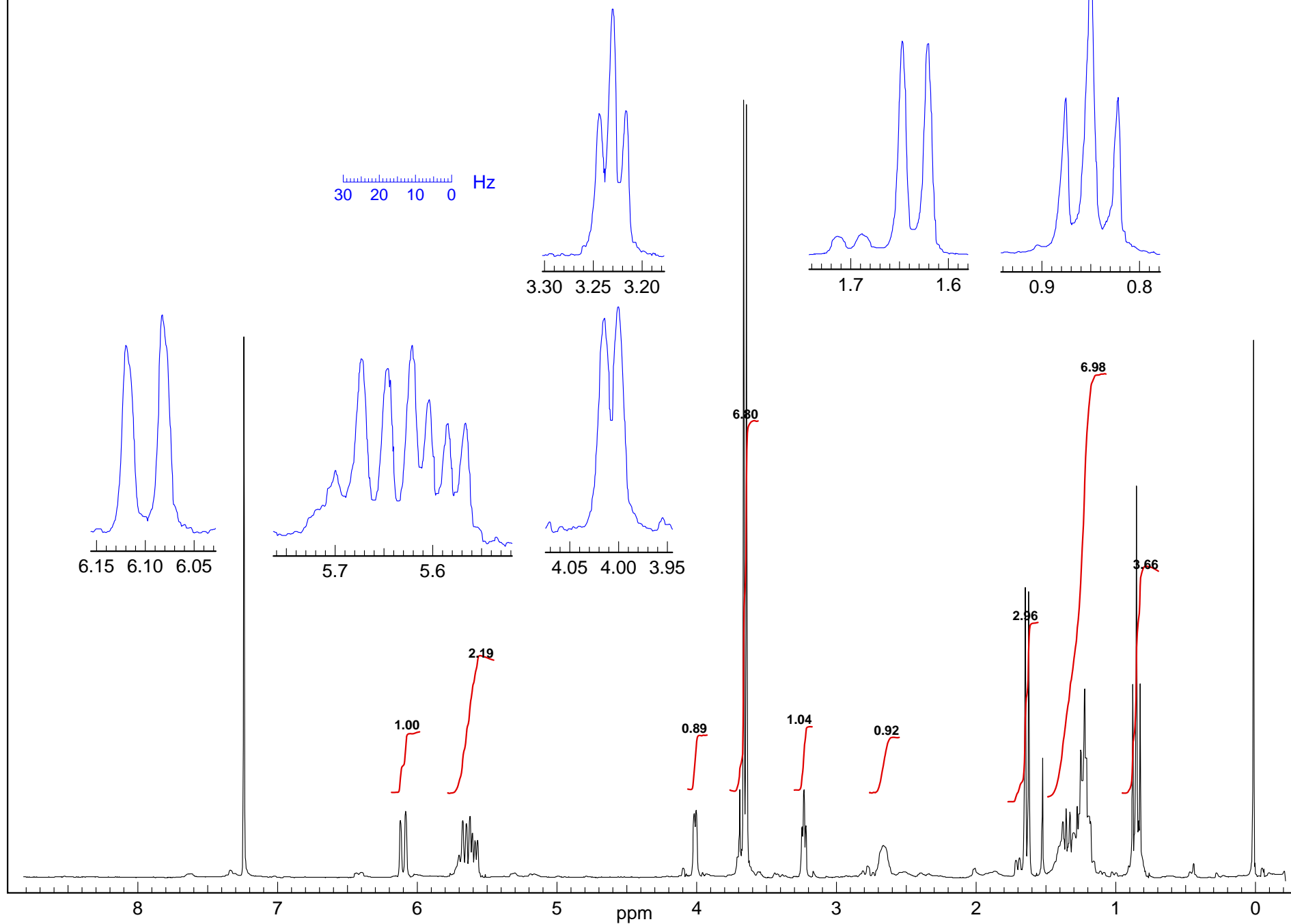
Note: either one of these conformations could be the enantiomer of the structures shown above.

(c) Explain why the lowest field signal at  $\delta$  6.1 in **86F** is only a doublet, whereas the one at  $\delta$  6.4 in **86G** is a doublet of doublets.

**Problem R-86F** ( $C_{15}H_{22}O_4$ )

270 MHz  $^1H$  NMR spectrum in  $CDCl_3$

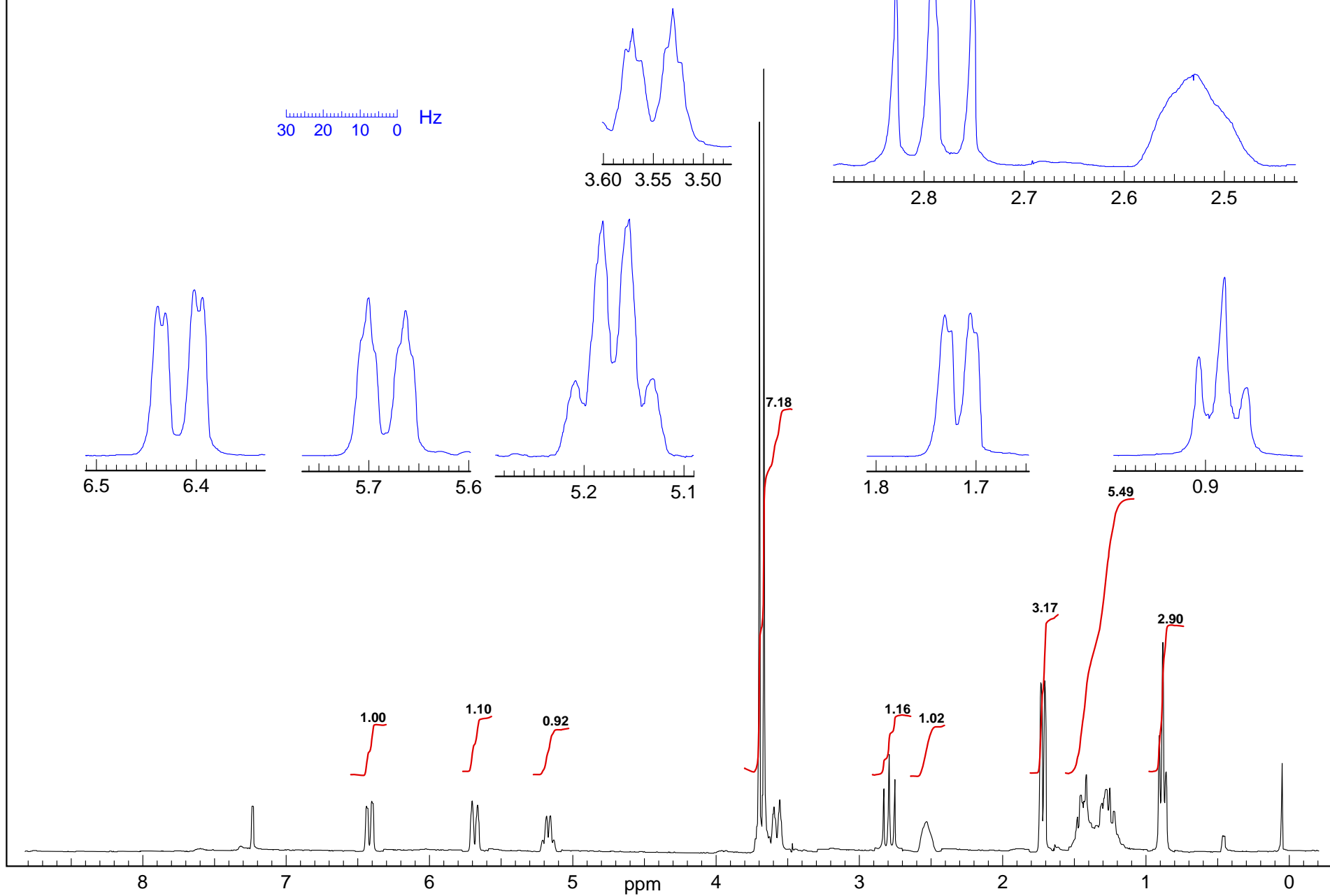
Source: Eric Eisenhart/Wes Whipple/Reich 3-15 (digitized hard copy) g



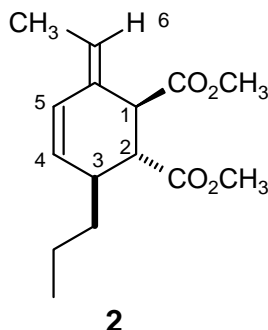
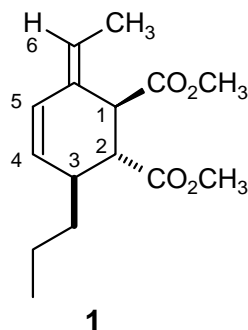
**Problem R-86G** ( $C_{15}H_{22}O_4$ )

270 MHz  $^1H$  NMR spectrum in  $CDCl_3$

Source: Eric Eisenhart/Wes Whipple/Reich 3-15 (digitized hard copy) g



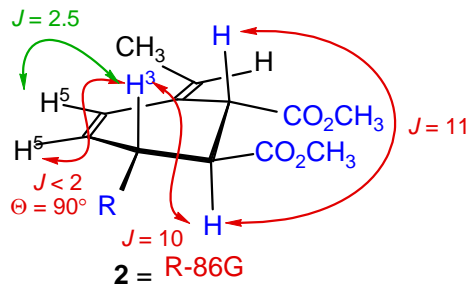
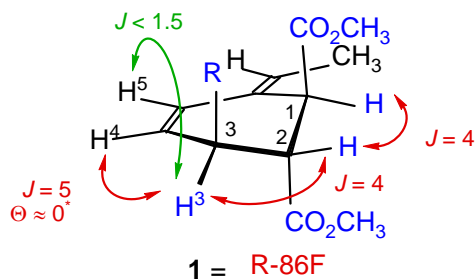
**Problem R-86F and R-86G.** The 270 MHz  $^1\text{H}$  spectra provided are of the compounds below:



(a) Analyze the multiplets and assign the signals by placing the data on the proper row (use the format  $\delta$  0.25, dt,  $J$  = 3, 9 Hz).

	<b>R-86F</b>	<b>R-86G</b>
H <sup>1</sup>	$\delta$ <u>4.01, d</u> $J$ = <u>4 Hz</u>	$\delta$ <u>3.56, dt</u> $J$ = <u>11, 1 Hz</u>
H <sup>2</sup>	$\delta$ <u>3.23, t</u> $J$ = <u>4 Hz</u>	$\delta$ <u>2.79, dd</u> $J$ = <u>11, 10 Hz</u>
H <sup>3</sup>	$\delta$ <u>2.7, m</u> $J$ = <u>        </u>	$\delta$ <u>2.5, m</u> $J$ = <u>        </u>
H <sup>4</sup>	$\delta$ <u>5.59, dd</u> $J$ = <u>10, 5 Hz</u>	$\delta$ <u>5.68, dt</u> $J$ = <u>10, 1.5 Hz</u>
H <sup>5</sup>	$\delta$ <u>6.10, d</u> $J$ = <u>10 Hz</u>	$\delta$ <u>6.42, dd</u> $J$ = <u>10, 2.5 Hz</u>
H <sup>6</sup>	$\delta$ <u>5.66, q</u> $J$ = <u>7 Hz</u>	$\delta$ <u>5.17, q</u> $J$ = <u>7 Hz</u>

(b) A typical conformation (MM2) of this type of molecule is shown below. Attach substituents and identify the spectrum (i.e., say **1** = 86F or **1** = 86G). Briefly explain the basis for your choice. Discuss at least H<sup>1</sup>, H<sup>2</sup> and H<sup>4</sup>.



Note: either one of these conformations could be the enantiomer of the structures shown above.

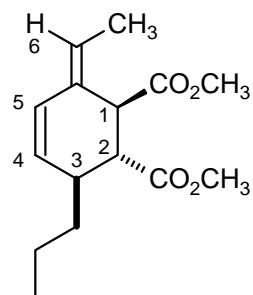
The small H<sup>1</sup>-H<sup>2</sup> as well as H<sup>2</sup>-H<sup>3</sup> coupling in R-86F (each 4 Hz) means these three protons are all equatorial, the three substituents are axial. This unusual conformation is an example of a buttressing effect - in the all-equatorial conformation the *cis* oriented methyl group interacts with the equatorial groups, which also interact with each other, making the all-axial conformer the stable one (it helps the three of the carbons in the ring are sp<sup>2</sup>, with no axial groups). In R-86G the methyl group is oriented away from the substituents, and a normal, all-equatorial conformation results.

(c) Explain why the lowest field signal at  $\delta$  6.1 in **86F** is only a doublet, whereas the one at  $\delta$  6.4 in **86G** is a doublet of doublets.

The long-range  $^4J$  H<sup>3</sup>-H<sup>5</sup> coupling is substantial in R-86G because the axial H<sup>3</sup> proton has an optimal relationship with H<sup>5</sup> - C-H<sup>3</sup> is perpendicular to the plane of the double bond. In R-86-F the equatorial proton is near the plane of the double bond, and  $^4J$  is small.

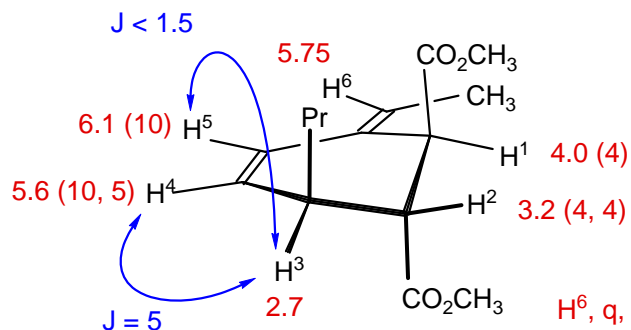
The same relationships work in opposite direction for  $^3J$  between H<sup>3</sup> and H<sup>4</sup>. The near 90° degree relationship in R-86G means small  $^3J$ , whereas the near coplanar dihedral angle in R-86F results in a significant coupling ( $J_{3-4}$  = 5 Hz).

# Problem R-86F, G

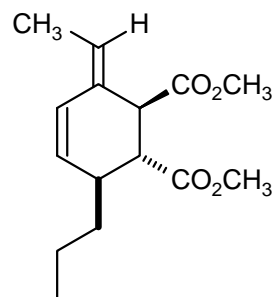


For this isomer the all-equatorial conformation would have serious buttressing interactions, hence the ring flip to all-axial substituents

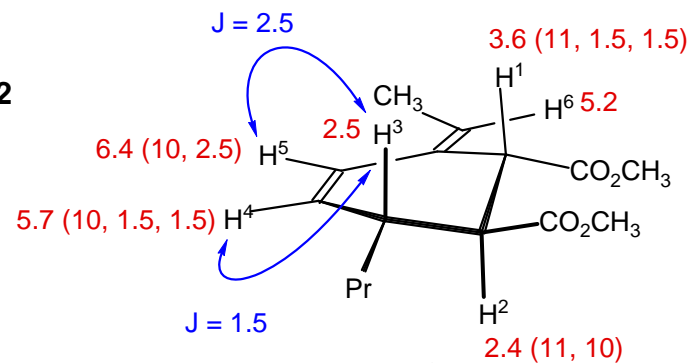
1



1 = R-86F



2



2 = R86-G

Note: this is the enantiomer of R-86G

