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

270 MHz ^{1}H NMR spectrum in CDCl$_3$

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

Hz
30 20 10 0

Insets: 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

Integrals: 1.00, 2.19, 0.89, 6.80, 1.04, 0.92, 2.96, 6.98, 3.66

ppm axis: 8, 7, 6, 5, 4, 3, 2, 1, 0

PLT pr-080-to-86.plt

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

270 MHz ^{1}H NMR spectrum in CDCl$_3$

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

2

Hz

30 20 10 0

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

1.8 1.7

0.9

7.18

5.49

3.17

2.90

1.16 1.02

1.00

1.10
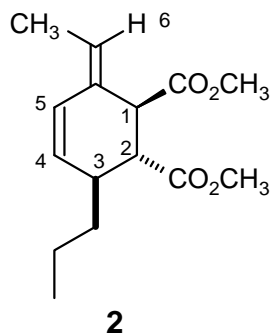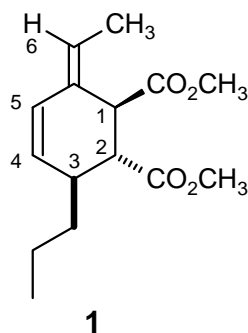
0.92

8 7 6 5 ppm 4 3 2 1 0

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

1   2

(a) Analyze the multiplets and assign the signals by placing the data on the proper row (use the format δ 0.25, dt, J = 3, 9 Hz).
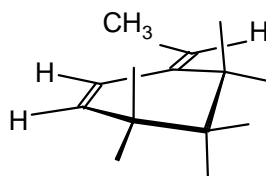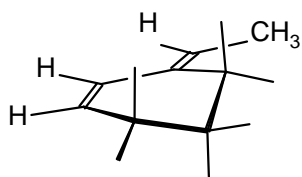
R-86F   **R-86G**

H^1 δ _____ J = _____   δ _____ J = _____

H^2 δ _____ J = _____   δ _____ J = _____

H^3 δ _____ J = _____   δ _____ J = _____

H^4 δ _____ J = _____   δ _____ J = _____

H^5 δ _____ J = _____   δ _____ J = _____

H^6 δ _____ J = _____   δ _____ 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 H^1, H^2 and H^4.

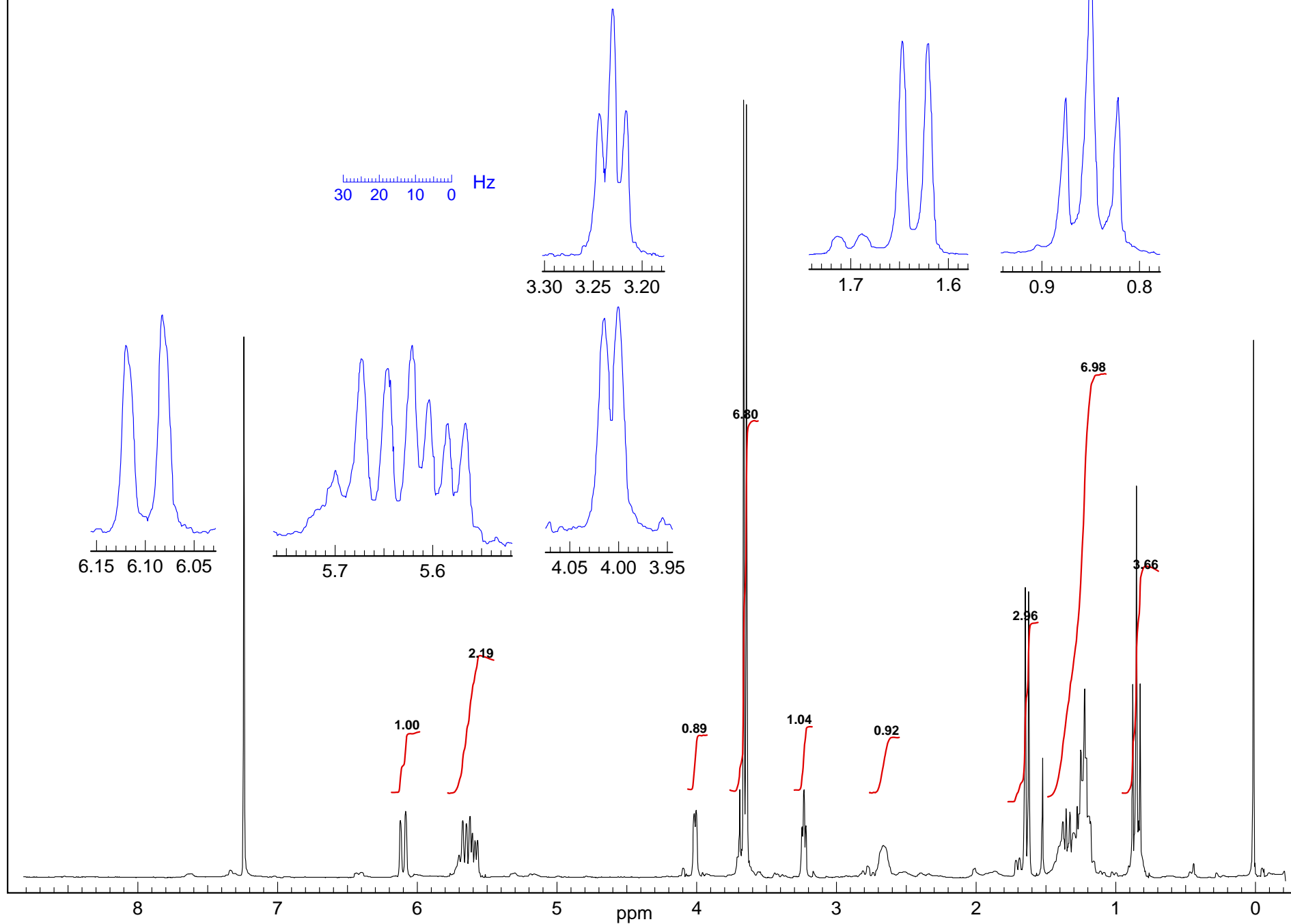**1** = __   **2** = __

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

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

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

270 MHz ^{1}H NMR spectrum in CDCl$_3$

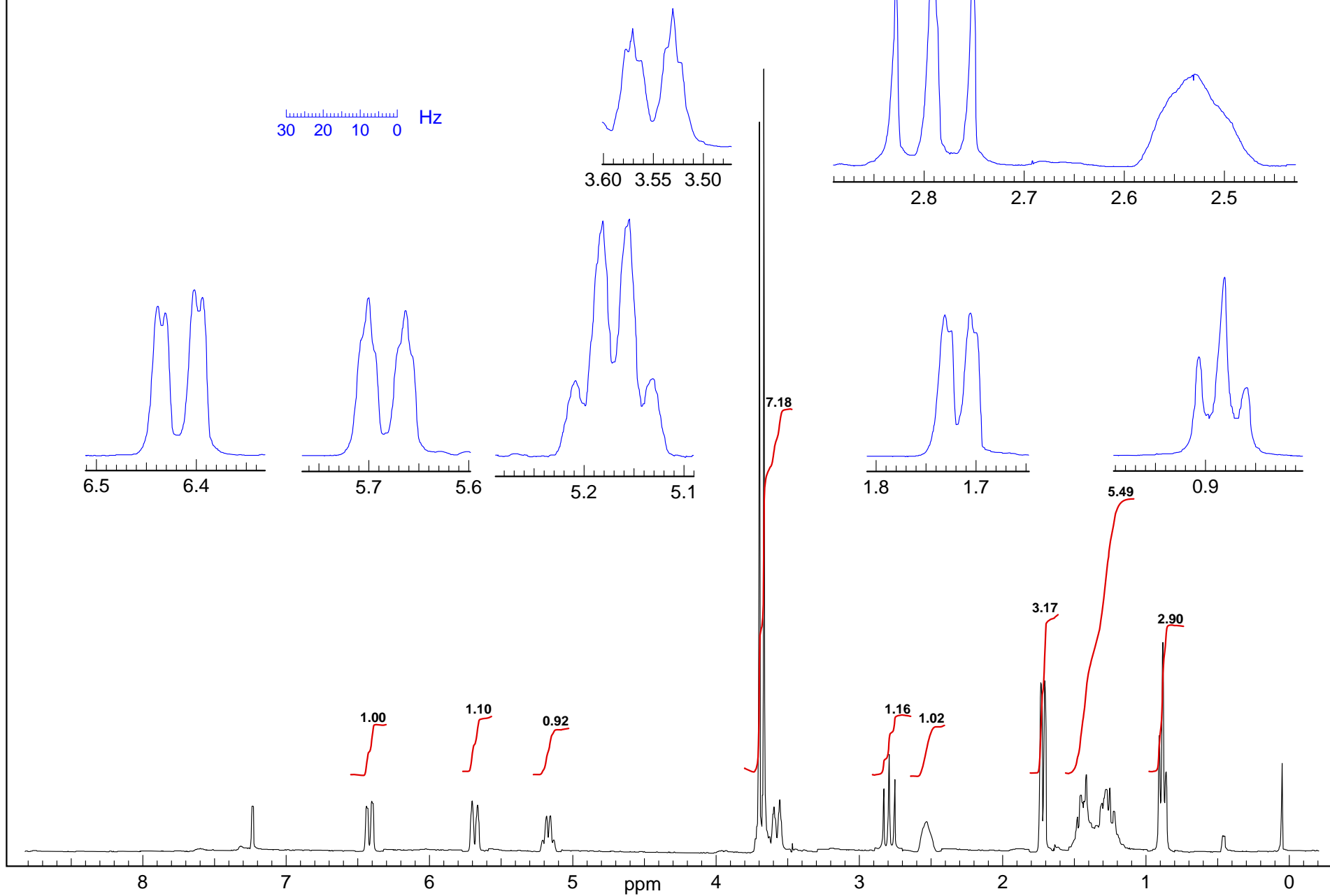Source: Eric Eisenhart/Wes Whipple/Reich 3-15 (digitized hard copy) g

Hz
30 20 10 0

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

6.98

6.80

3.66

2.96

2.19

1.00

0.89

1.04
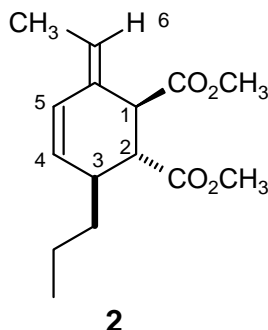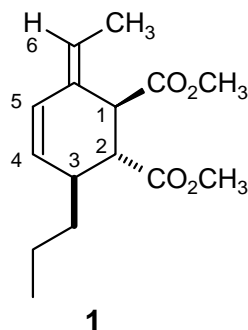
0.92

8 7 6 5 ppm 4 3 2 1 0

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

270 MHz ^{1}H NMR spectrum in CDCl$_3$

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

Hz

30 20 10 0

3.60 3.55 3.50

2.8 2.7 2.6 2.5

7.18

6.5 6.4

5.7 5.6

5.2 5.1

1.8 1.7

0.9
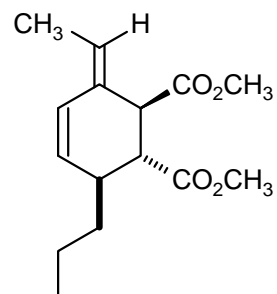
5.49

3.17

2.90

1.00

1.10

0.92

1.16 1.02

8 7 6 5 ppm 4 3 2 1 0

PLT pr-080-to-86.plt

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

1   **2**

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

	R-86F			**R-86G**	
H^1	δ 4.01, d	J = 4 Hz	δ 3.56, dt	J = 11, 1 Hz
H^2	δ 3.23, t	J = 4 Hz	δ 2.79, dd	J = 11, 10 Hz
H^3	δ 2.7, m	J =	δ 2.5, m	J =
H^4	δ 5.59, dd	J = 10, 5 Hz	δ 5.68, dt	J = 10, 1.5 Hz
H^5	δ 6.10, d	J = 10 Hz	δ 6.42, dd	J = 10, 2.5 Hz
H^6	δ 5.66, q	J = 7 Hz	δ 5.17, q	J = 7 Hz

(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^1, H^2 and H^4.

1 = R-86F   **2** = R-86G
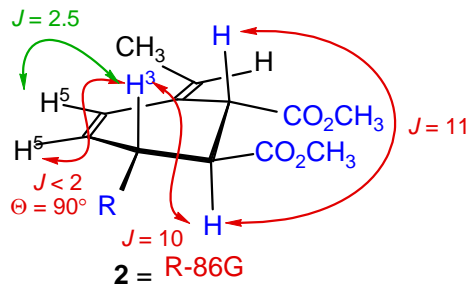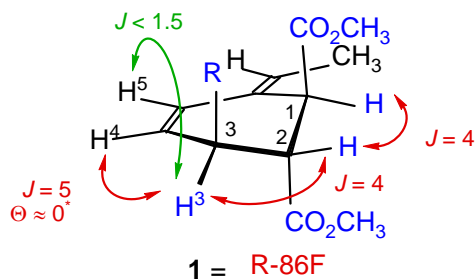
Note: either one of these conformations could be the enantiomer of the structures shown above.

The small H^1-H^2 as well as H^2-H^3 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^2, 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 δ 6.1 in **86F** is only a doublet, whereas the one at δ 6.4 in **86G** is a doublet of doublets.

The long-range ^4J H^3-H^5 coupling is substantial in R-86G because the axial H^3 proton has an optimal relationship with H^5 - C-H^3 is perpendicular to the plane of the double bond. In R-86-F the equatorial proton in near the plane of the double bond, and ^4J is small.
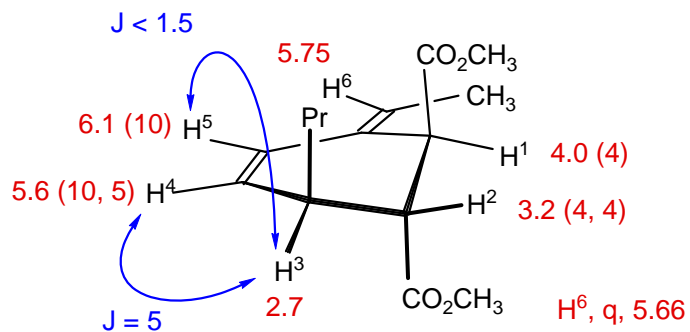
The same relationships work in opposite direction for ^3J between H^3 and H^4. The near 90* degree relationship in R-86G means small ^3J, whereas the near coplanar dihedral angle in R-86F results in a significant coupling (J_{3-4} = 5 Hz).
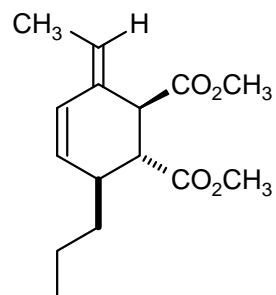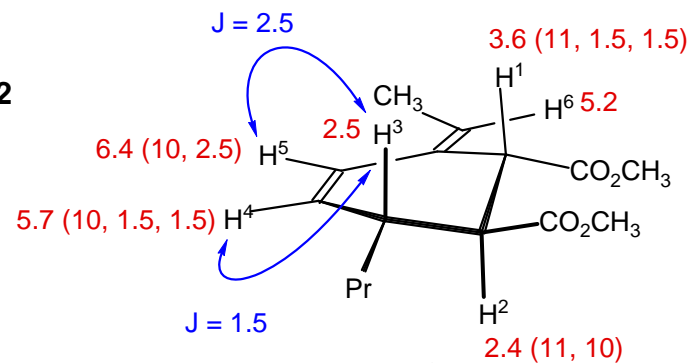
Problem R-86F, G
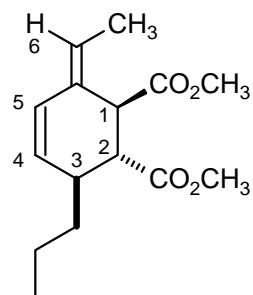
For this isomer the all-equatorial conformation would have serious buttressing interactions, hence the ring flip to all-axial substituents

1 = R-86F

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 = R86-G

J = 2.5
6.4 (10, 2.5) H^5
5.7 (10, 1.5, 1.5) H^4
J = 1.5
2.5 H^3
CH$_3$
3.6 (11, 1.5, 1.5)
H^1
H^6 5.2
CO$_2$CH$_3$
CO$_2$CH$_3$
Pr
H^2
2.4 (11, 10)

2 = R86-G

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

H^6, q, 5.66
H^4, dd, 5.59

1 = R-86F

OAc

2 = R86-G

H^5 H^6 H^4 H^1 H^2 H^3 H^2

H^5 H^4 H^6 H^1 H^2 H^3 H^2

6.5   6.0   5.7   5.6   5.5   5.0   4.5   4.0   3.5   3.0   2.5

ppm