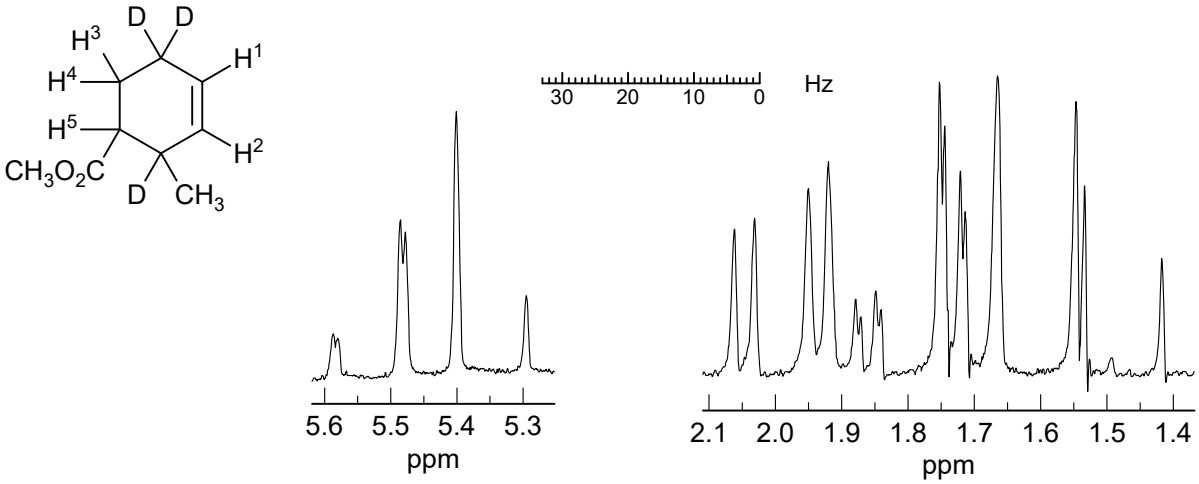
Problem Set 9

Problem R-84l ($C_9H_{14}O_2$). 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).



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

H^1 _____ δ, J = _____ Hz, coupled to: _____

H^2 _____ δ, J = _____ Hz, coupled to: _____

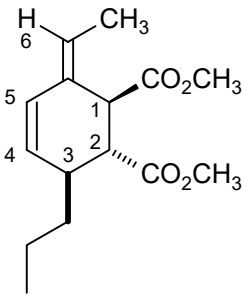
H^3 _____ δ, J = _____ Hz, coupled to: _____

H^4 _____ δ, J = _____ Hz, coupled to: _____

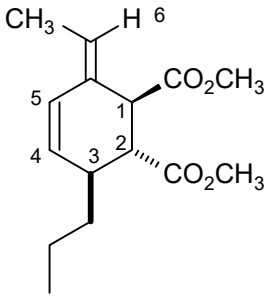
H^5 _____ δ, J = _____ Hz, coupled to: _____

(b) Using this information, draw a good representation of the conformation of compound **R-84l**. 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?)

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



1

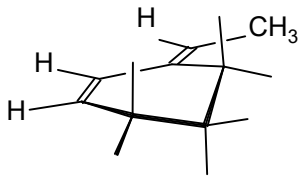


2

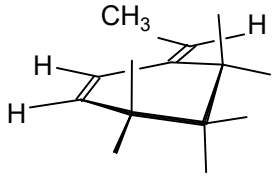
(a) Analyze the multiplets and assign the signals by placing the data on the proper row (use the format δ 0.25, dt, *J* = 3, 9 Hz).

	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 = __

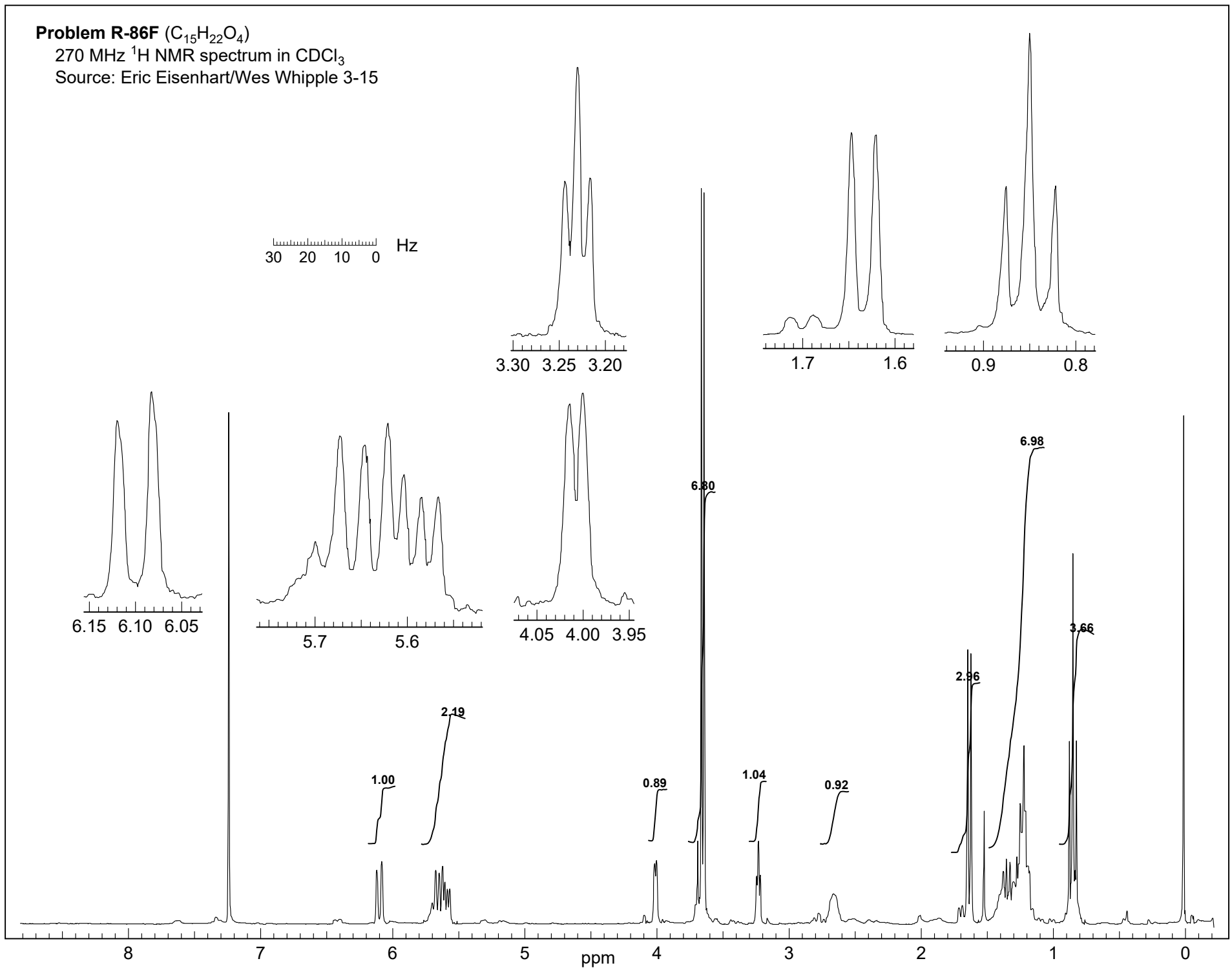
Note: either one of these conformations could be the enantiomer of the structures shown above.

(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 $CDCl_3$

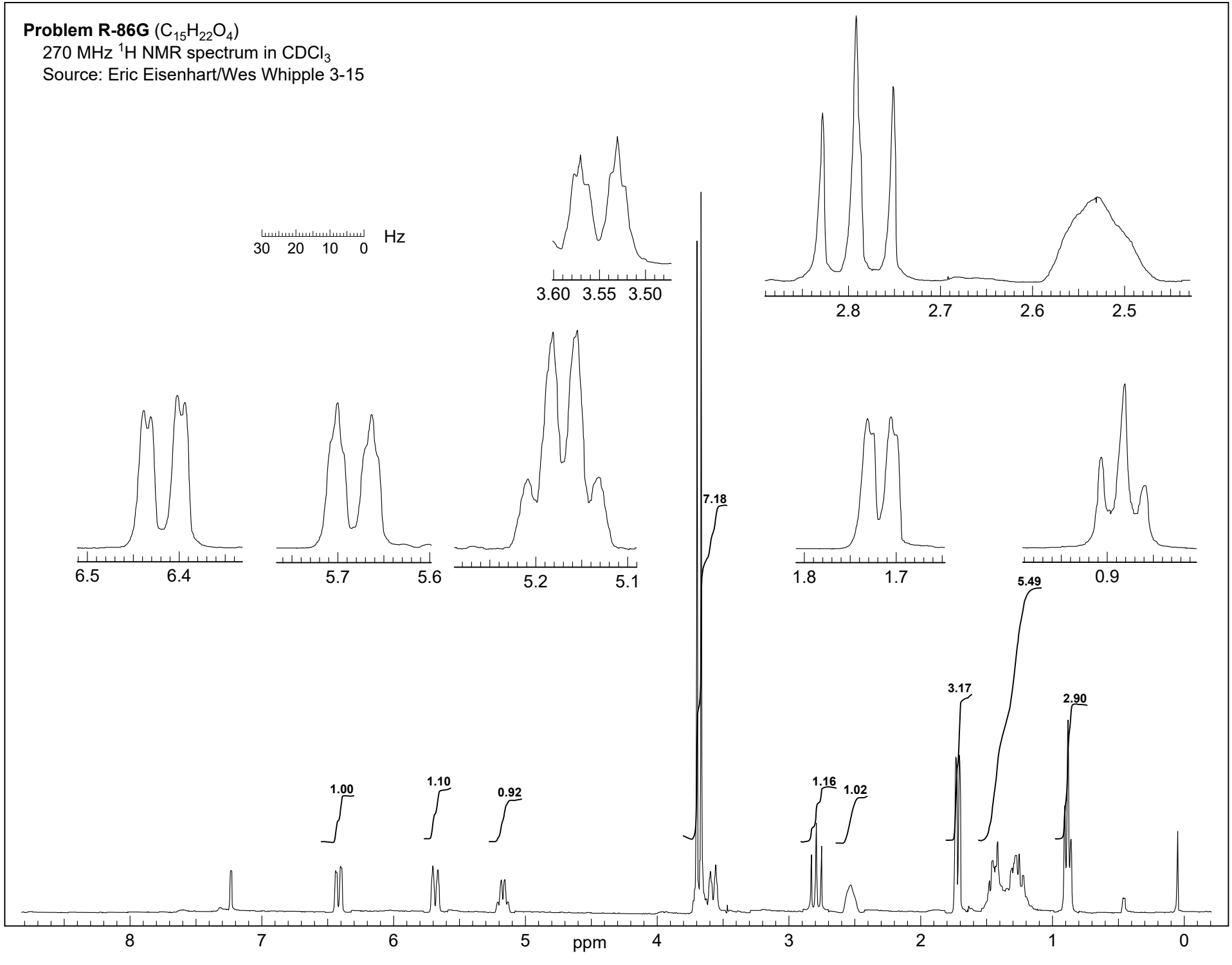
Source: Eric Eisenhart/Wes Whipple 3-15



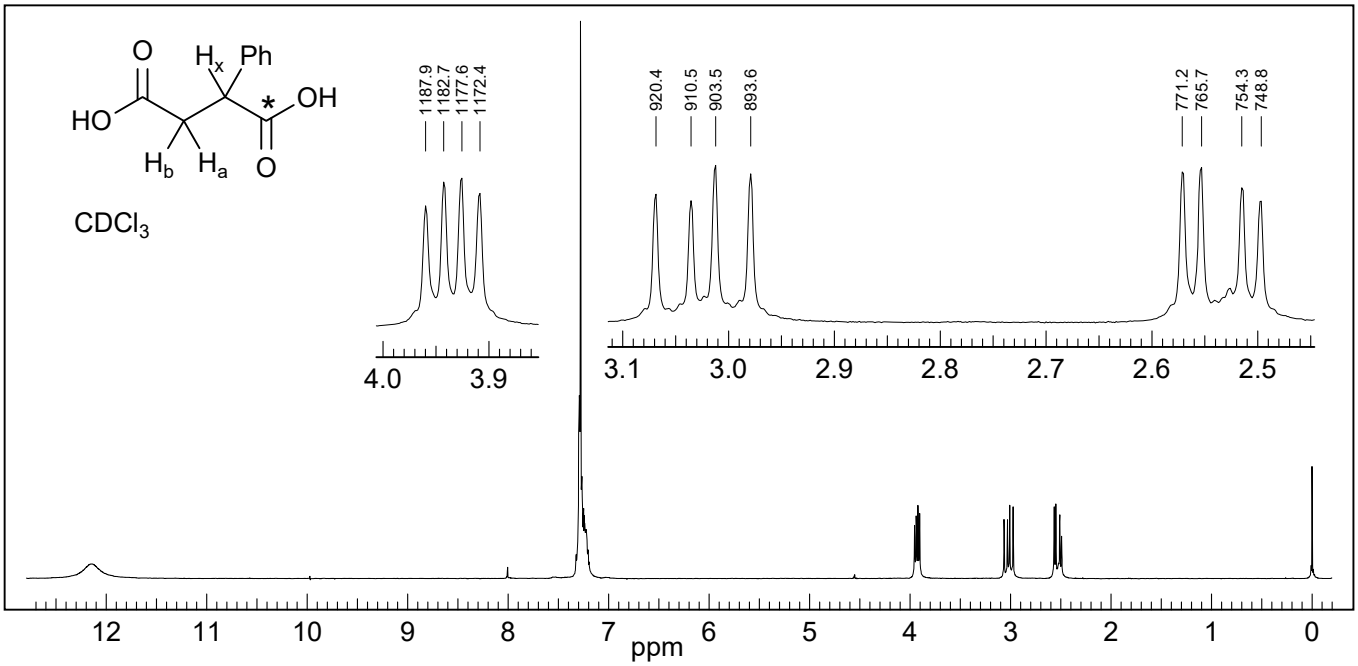
Problem R-86G ($C_{15}H_{22}O_4$)

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

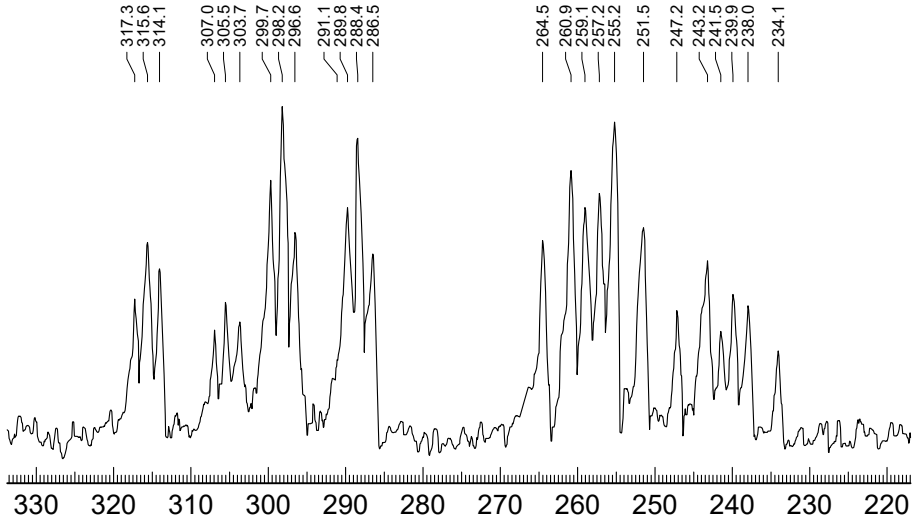
Source: Eric Eisenhart/Wes Whipple 3-15



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 $^3J_{C\text{-}Ha}$ and $^3J_{C\text{-}Hb}$ from this spectrum.



Draw Newman projections for the three possible staggered conformations of phenylsuccinic acid and determine which is the major one in acetone-d_6 solution.

Problem R-256 ($C_{22}H_{20}O$). The 200 MHz ^1H spectrum of R-256 is provided.

(a) DBE _____

(b) For each of the multiplets at δ 4.0, 3.1 and 2.8 show a "coupling tree" (work on the spectrum), indicate the type of multiplet and the coupling constants derived from each multiplet. Report them in the standard format

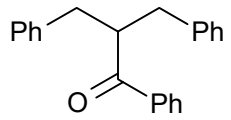
δ 4.0 _____

δ 3.1 _____

δ 2.8 _____

(c) What type of pattern is this (e.g., AA'BB')? _____

(d) Suggest a partial structure for the molecular fragment which includes these protons.



(e) There is a strong IR absorption at 1695 cm^{-1}. Suggest a structure for compound **R-256**. If you have more than one possible structure, circle the one you like best.

Problem R-259 ($C_{11}H_{12}S$)

200 MHz ^{1}H NMR Spectrum in $CDCl_3$

(Source: Eric Eisenhart/Reich 8-14)