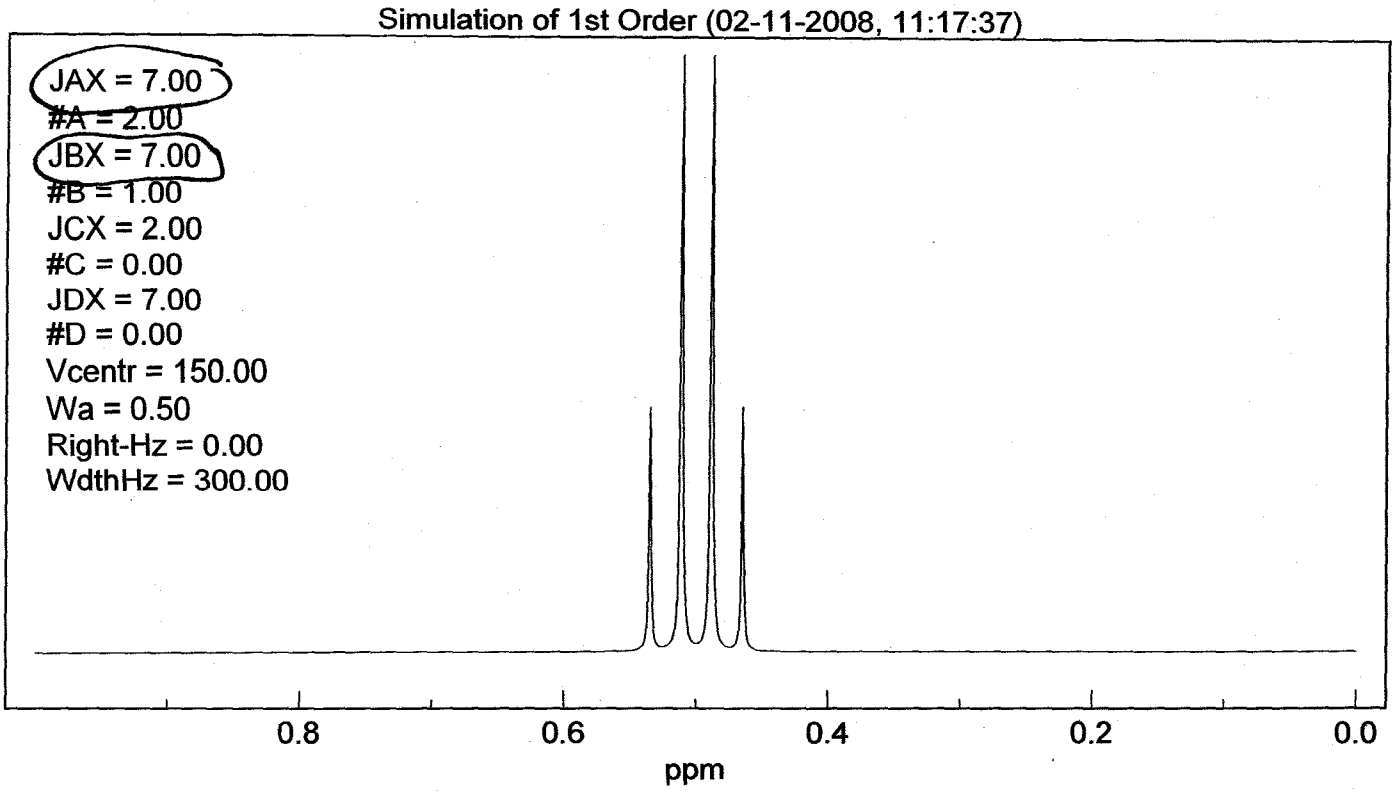
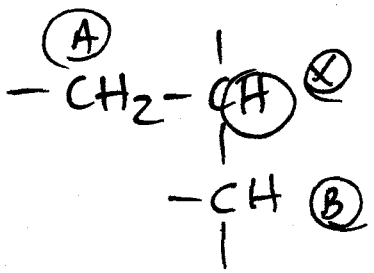
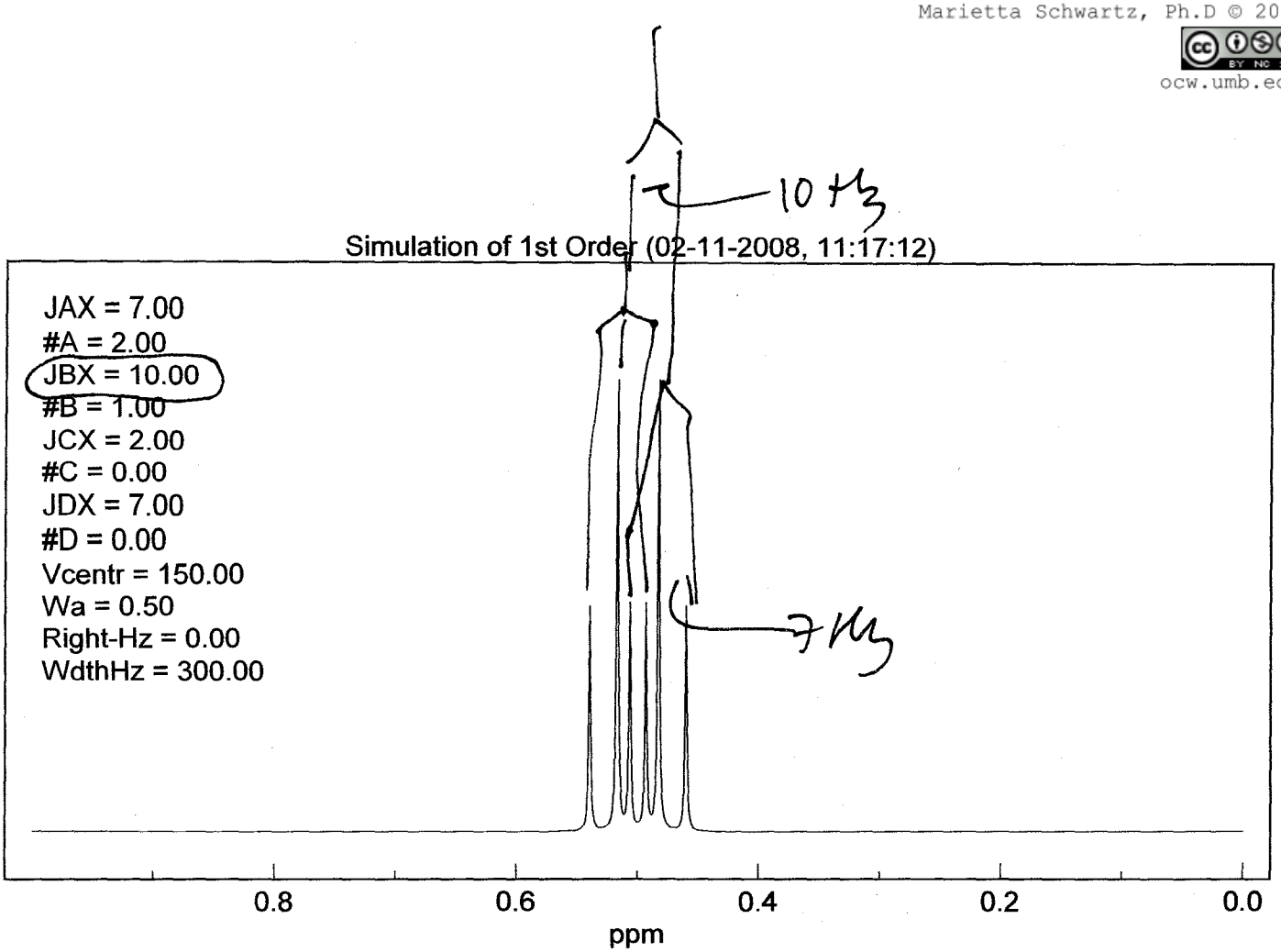
coupling constants

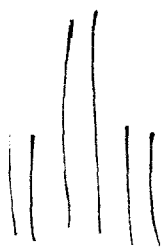




X has 3 neighbors
⇒ quartet

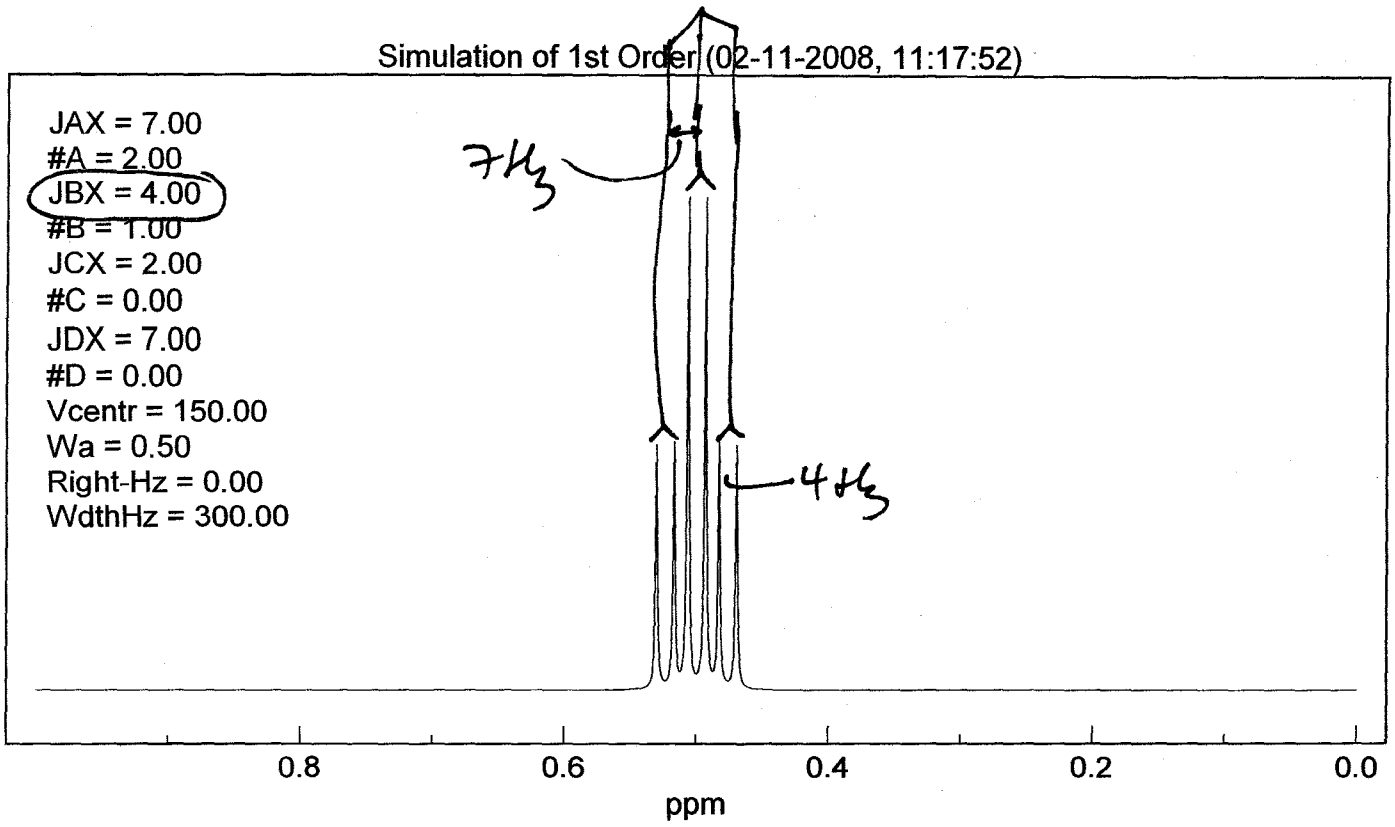
$J_{AX} = J_{BX}$





$J_{AX} < J_{BX}$

WINDNMR Scale: 0.80

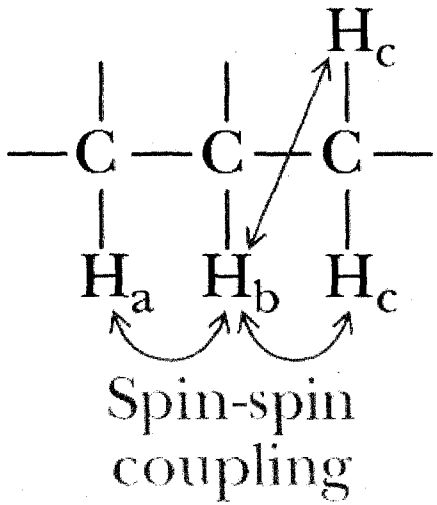


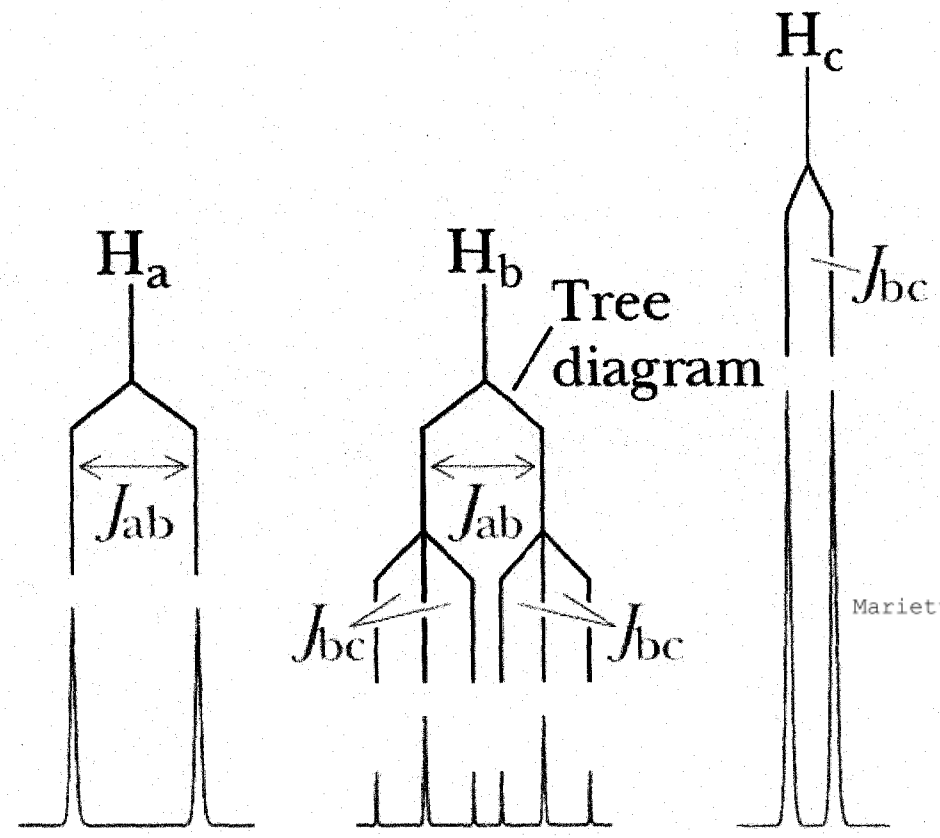
$J_{AX} > J_{BX}$

WINDNMR Scale: 0.80

More Complex Splitting Patterns

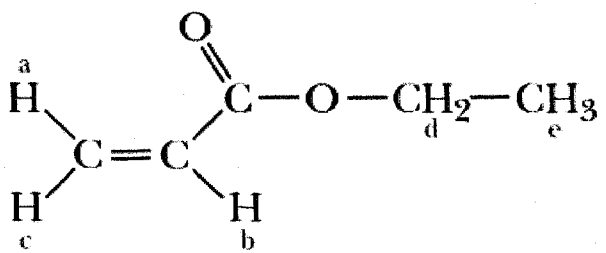
- **if H_c is a set of two equivalent H, then the observed splitting is a doublet of triplets**

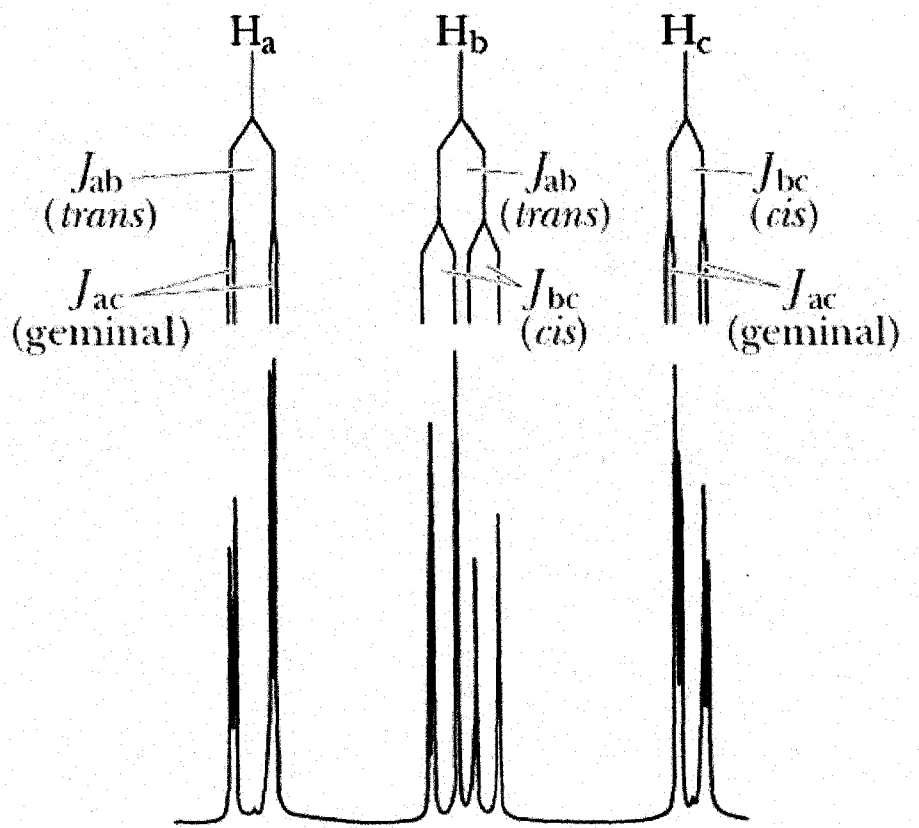




More Complex Splitting Patterns

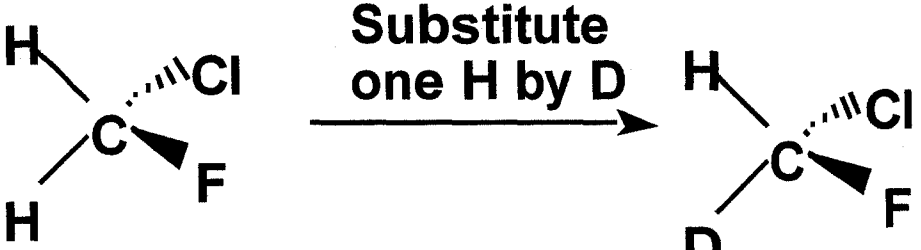
- **a tree diagram for the complex coupling of the three vinylic hydrogens in ethyl propenoate**





Stereochemistry & Topicity

◆ Enantiotopic groups

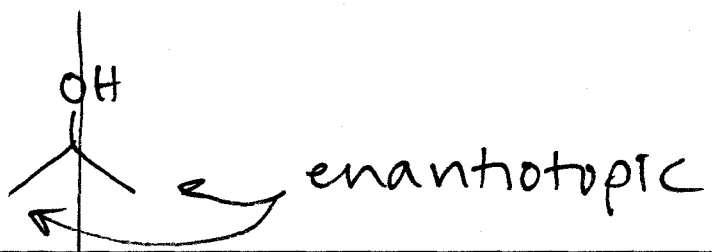


Chlorofluoro-methane (achiral)

Chiral

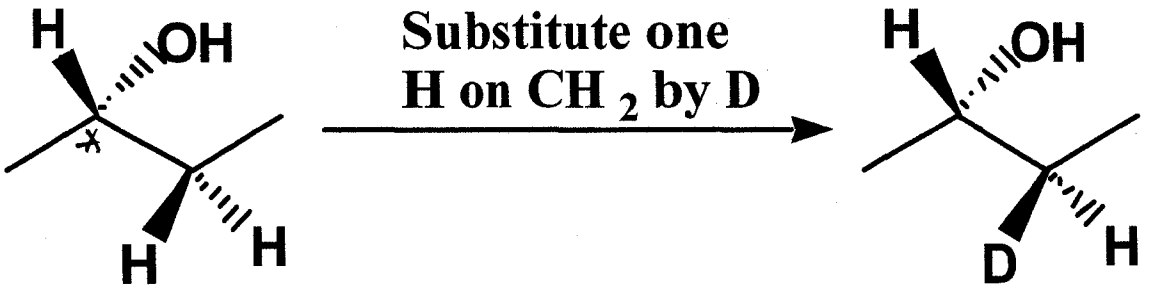
Substitution produces a stereocenter; therefore, hydrogens are enantiotopic. Both hydrogens are prochiral; one is pro-R-chiral, the other is pro-S-chiral.

- **enantiotopic atoms or groups have identical chemical shifts in achiral environments**
- **they have different chemical shifts in chiral environments**



Stereochemistry & Topicity

- **Diastereotopic groups**
  - H atoms on C-3 of 2-butanol are diastereotopic
  - substitution by deuterium creates a chiral center
  - because there is already a chiral center in the molecule, diastereomers are now possible



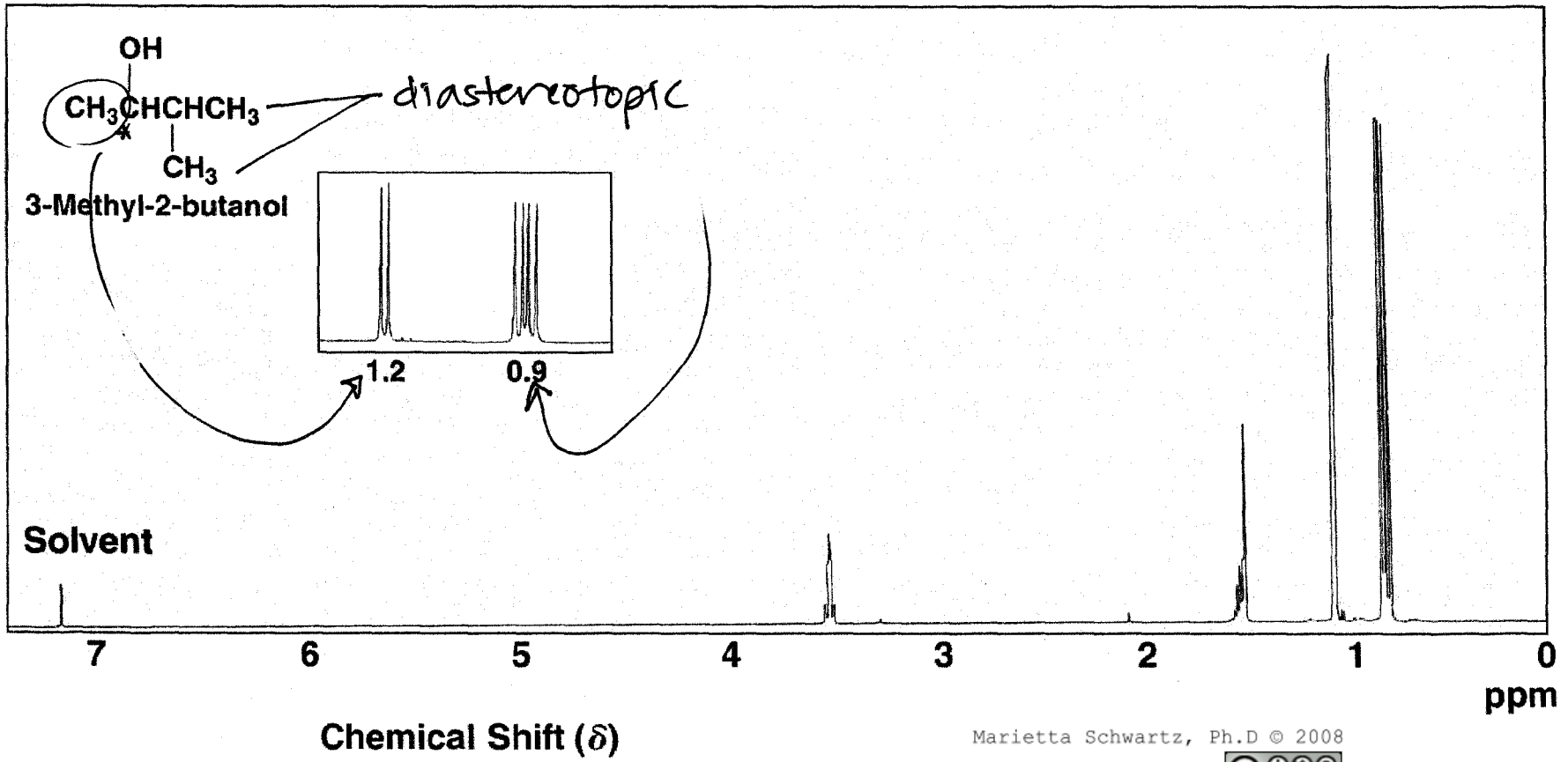
2-Butanol (chiral)

Chiral

  - diastereotopic hydrogens have different chemical shifts under all conditions

Stereochemistry and Topicity

- ^{1}H-NMR spectrum of 3-methyl-2-butanol
  - the methyl groups on carbon 3 are diastereotopic and appear as two doublets



^{13}C NMR Spectroscopy

The principles of ^{13}C NMR are the same as those of ^{1}H NMR, in that we have a nucleus with spin ½, we place the sample in an external magnetic field to create a separation of the two possible spin states, and we scan through the appropriate radiofrequencies to detect the different types of nuclei.

Differences:

1. ^{13}C has about 1.1% natural abundance. Therefore we need a much more sensitive spectrometer to be able to do ^{13}C NMR with any degree of accuracy. The development of FT-NMR made this possible.

2. Since ^{13}C has only about 1.1% natural abundance, the chances of a molecule containing two ^{13}Cs next to each other are slim to none. Therefore, we don't see spin-spin splitting in ^{13}C NMR. This simplifies the spectrum considerably.

3. However, the ^{13}Cs can be split by the ^{1}Hs attached to them - this splitting can be removed by using a technique called **broad-band decoupling**. So not a problem.

4. Integrals are meaningless in ^{13}C NMR because of a phenomenon called **relaxation.** We won't discuss relaxation, but will take advantage of the absence of integrals to simplify the interpretation of the ^{13}C spectra.

5. Where the ^{1}H NMR spectrum has a scale that runs from 0 to about 12 ppm, ^{13}C NMR spectra run from 0 to about 200 ppm. Much larger scale. TMS is still used as a reference.

Basics:

We see one peak for each unique carbon. A monosubstituted benzene, for instance, would show four different peaks.

Chemical shift is the important thing here. (~~See the table on p. 394.~~)

Alkyls (sp^3)	0-50, generally.
Alkyl halide or amine	10-65
C next to an oxygen (alcohol or ether)	50-90
Alkyne (sp)	60-90
Alkene (sp^2)	100-170
Aromatic	100-170
(note: benzene itself comes at 128.5 ppm)	
Nitriles (the C of the CN)	120-130
(note, very different from alkynes unlike IR)	
Amide carbonyl	150-180
Carboxylic acid or ester carbonyl	160-185
Aldehyde or ketone carbonyl	182-215
(note the large difference in different carbonyls)	