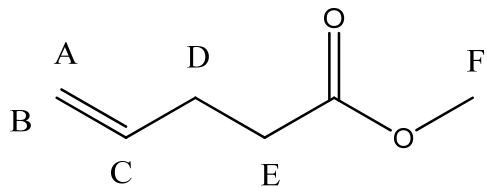
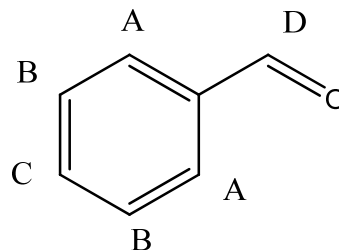


Selected answers to Handout 5: Proton NMR

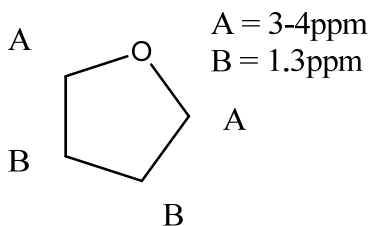
1. For the following molecules, mark each set of equivalent protons, then give an approximate chemical shift for that signal.



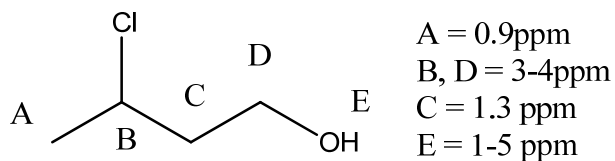
A, B, C = 5-6ppm
 D, E = 2-3ppm
 F = 3-4ppm



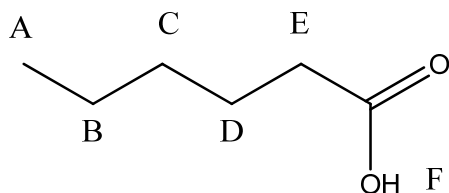
A, B, C all make one signal 7-8ppm
 D = 9-10ppm



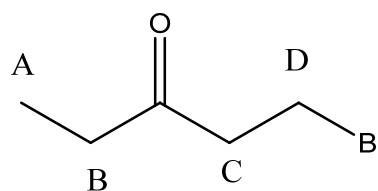
A = 3-4ppm
 B = 1.3ppm



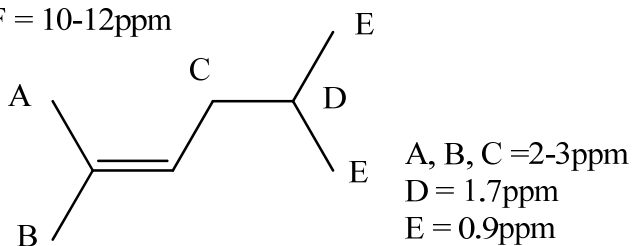
A = 0.9ppm
 B, D = 3-4ppm
 C = 1.3 ppm
 E = 1-5 ppm



A = 0.9ppm
 B, C, D = 1.3ppm
 E = 2-3ppm
 F = 10-12ppm

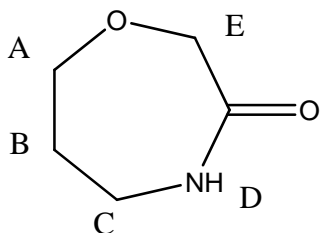


A = 0.9ppm
 B, C = 2-3ppm
 D = 3-4ppm

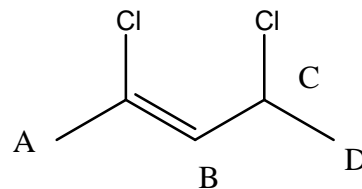


A, B, C = 2-3ppm
 D = 1.7ppm
 E = 0.9ppm

2. Do the same as problem 1, but consider any additive effects.

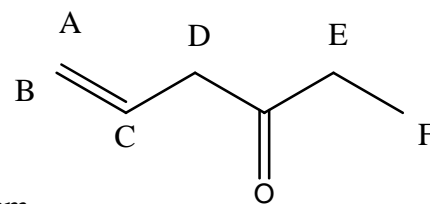
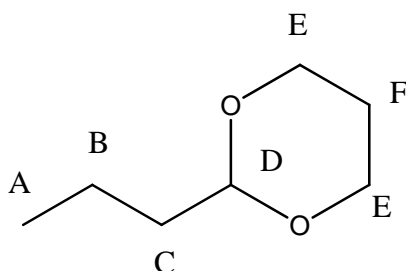


A = 3-4ppm
 B = 1.3ppm
 C = 3-4ppm
 D = 1-5ppm
 E = 3-4ppm PLUS

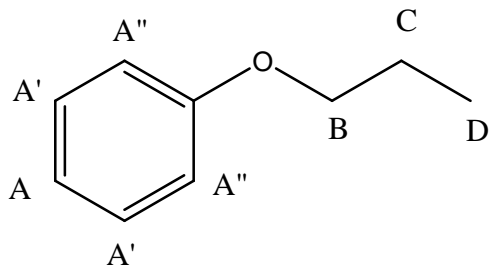


A = 2-3ppm
 B = 5-6ppm
 C = 3-4ppm PLUS
 D = 0.9ppm

A = 0.9ppm
 B, C = 1.3ppm
 D = 3-4ppm PLUS
 E = 3-4ppm
 F = 1.3ppm



A, B, C = 5-6ppm
 D = 2-3ppm PLUS
 E = 2-3ppm
 F = 0.9ppm

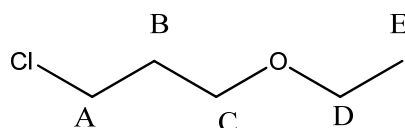
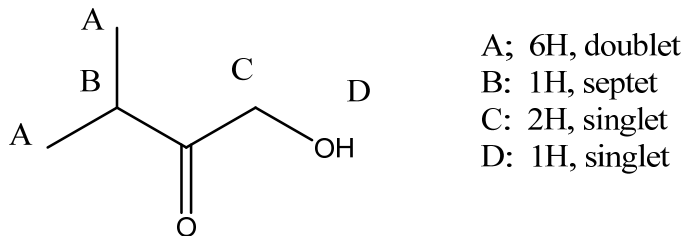


A = 1 signal 7-8ppm
 B = 3-4ppm
 C = 1.3ppm
 D = 0.9 ppm

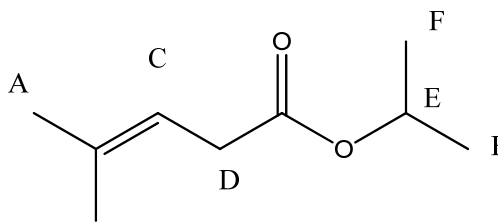
3. No matter how many sets of equivalent protons an aromatic ring has, we treat it as one signal in proton NMR. (This is a simplification which we will sometimes not apply in the future, but it works well for most problems.)

4. An exchangeable proton is one which is somewhat acidic—it is acidic enough under the conditions to have its bond to one compound broken and reform a new bond with another molecule through an acid/base reaction. Thus, these protons (especially alcohol and acid protons) will be exchanged between molecules many times over the timeframe of the NMR experiment.

5. For the compounds below, indicate sets of equivalent protons. For each set, give its integration and multiplicity. Example:

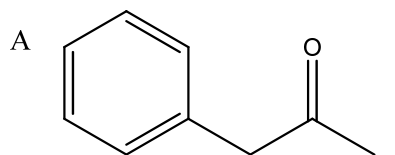


A: 2H, t
 B: 2H, qn
 C: 2H, t
 D: 2H, q
 E: 3H, t

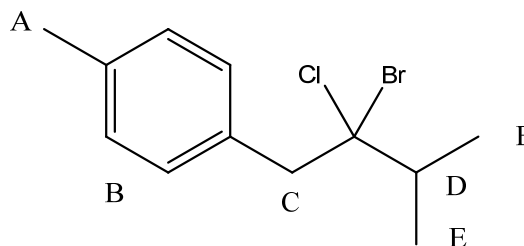


A: 3H, s
 B: 3H, s
 C: 1H, t
 D: 2H, d
 E: 1H, sp
 F: 6H, d

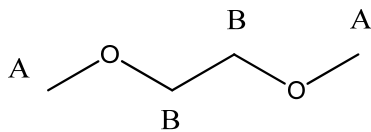
Note: It is possible that C and B will have a small coupling. In that case, B will be a doublet, and C will be a triplet of quartets



A: 5H, m
 B: 2H, s
 C: 3H, s

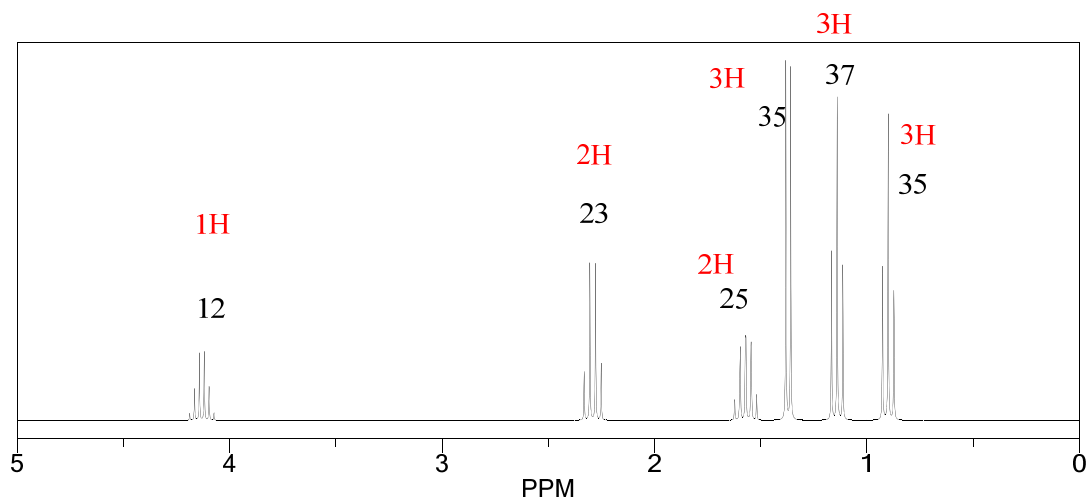


A: 3H, s
 B: 4H, m
 C: 2H, s
 D: 1H, sp
 E: 6H, d



A: 6H, s
 B: 4H, s (equiv H's don't split)

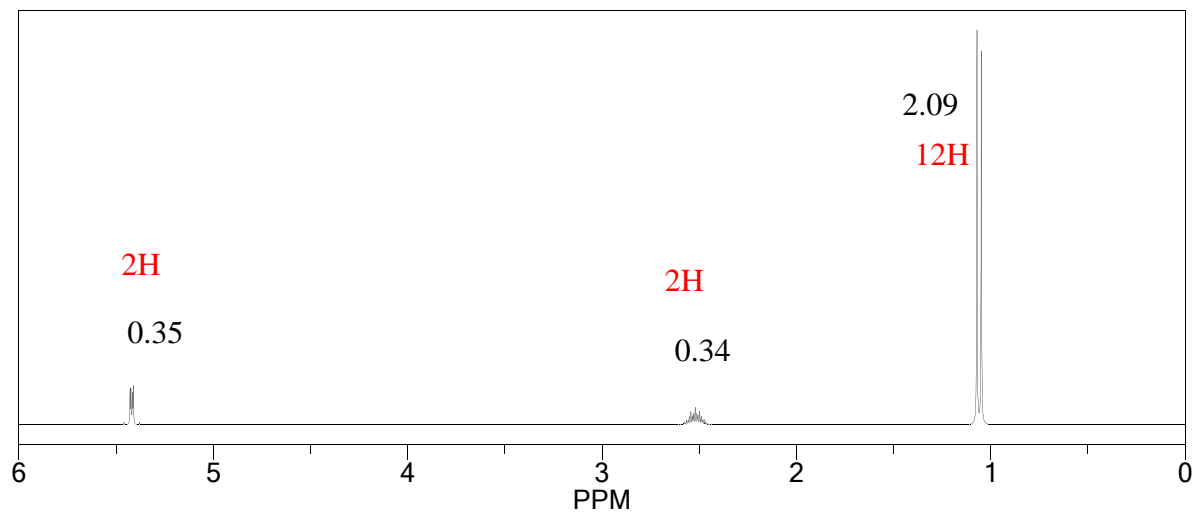
6. How many protons are represented by each signal in this spectrum of a $C_7H_{14}O_2$ compound?



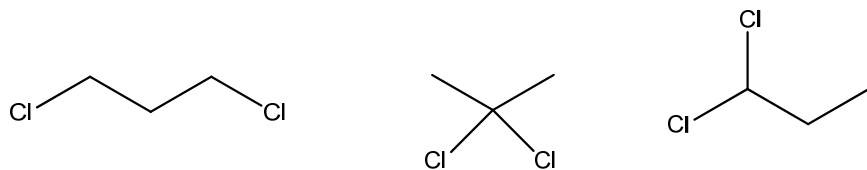
Add all integrations and divide by number of Hs $(12+23+25+35+37+35)/14 = 12$

Divide each signal by 12 to get the number of Hs represented.

7. How many protons are represented by each signal in this spectrum of a C_8H_{16} compound?

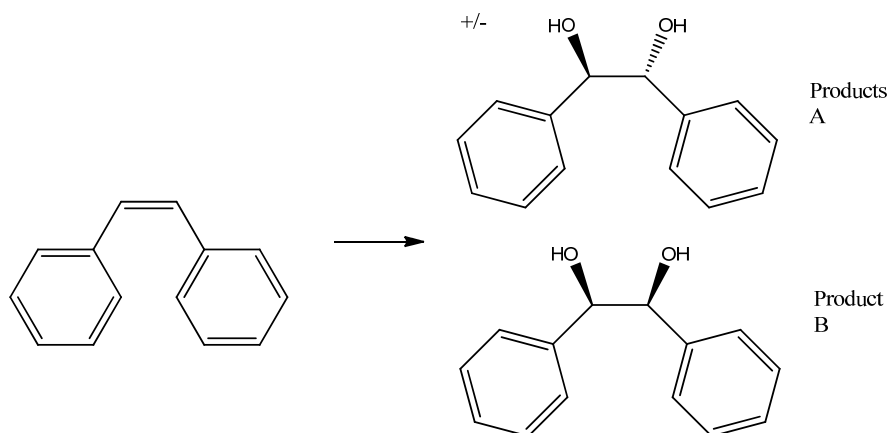


8. Draw the predicted proton and carbon spectra for these isomers. Can they be distinguished by NMR?



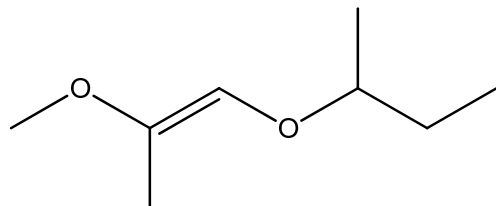
Use ChemDraw to check your answers. Yes, they can be easily distinguished by proton MNR based only on the number of signals: 2 signals for the first, one signal for the middle, and three signals for the right compound.

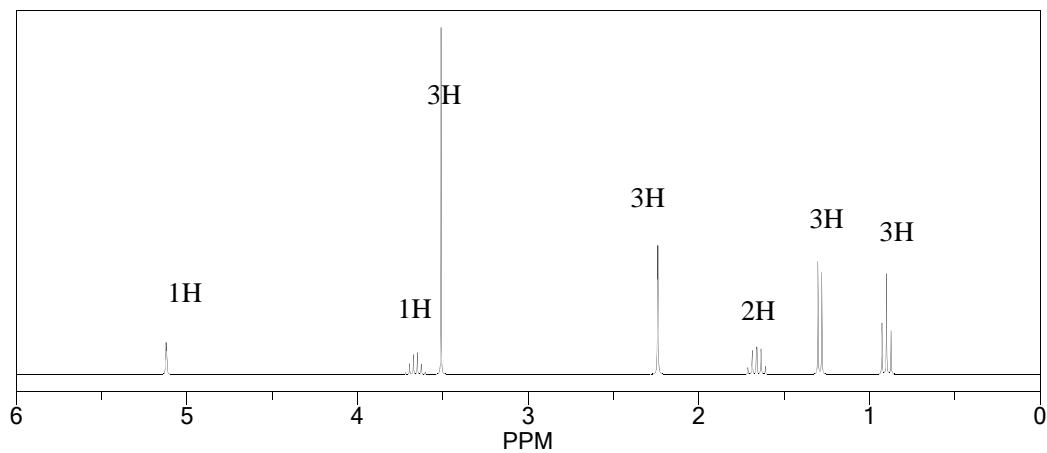
9. A dihydroxylation reaction of this alkene could potentially lead to either a racemic mix (A) or a meso product (B.) Can NMR be used to distinguish between these outcomes? Draw predicted proton and carbon NMR for both A and B as part of your answer.



Based on predicted proton and carbon NMR alone, they are indistinguishable. (Using an authentic compound spectrum could help distinguish them.) Both are symmetrical (product A has an axis and product B has an internal plane). Both would have 5 carbon signals in the same regions, and both would have three proton signals in the same regions.

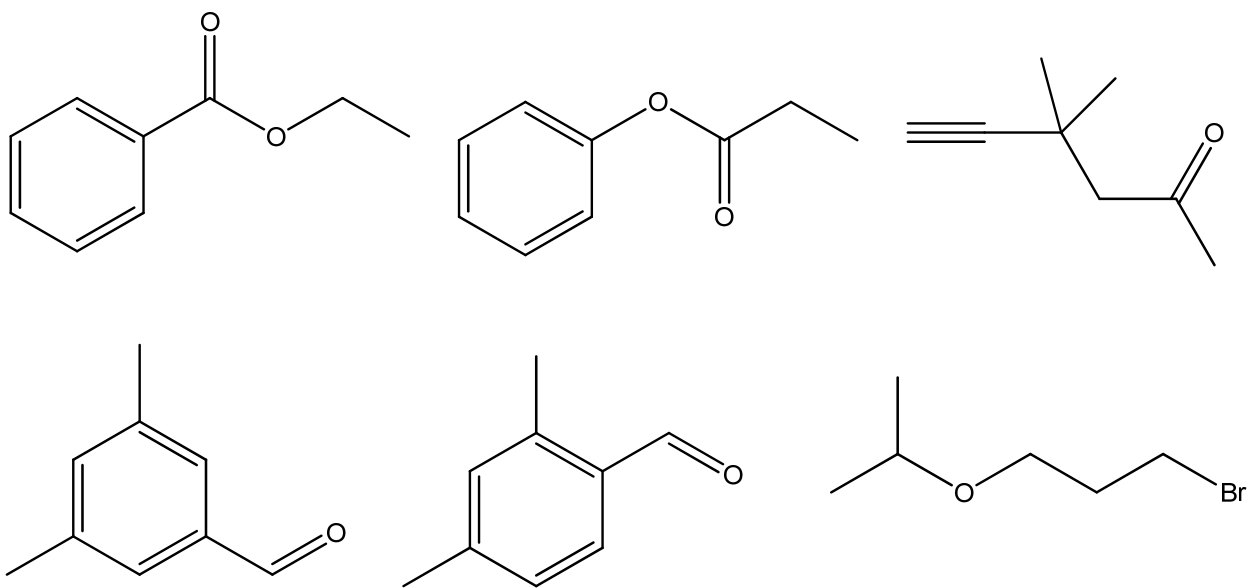
10. Is the proton NMR spectrum below consistent with this structure? Why or why not?





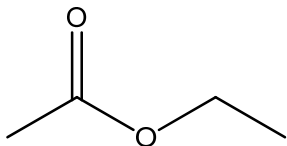
It is consistent. A good answer would have a table of predicted data based on the structure, with each peak matched to a signal on the proton NMR spectrum.

11. Draw predicted proton NMR spectra for these compounds.

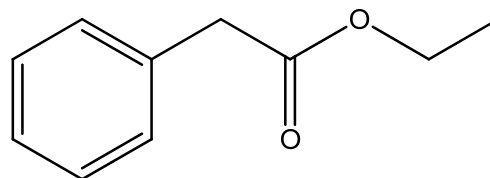


Use ChemDraw to check your answers.

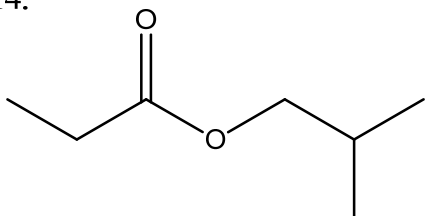
12.



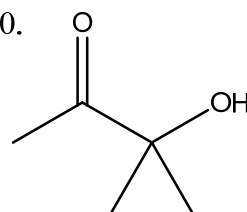
18.



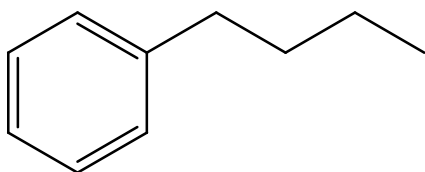
14.



20.

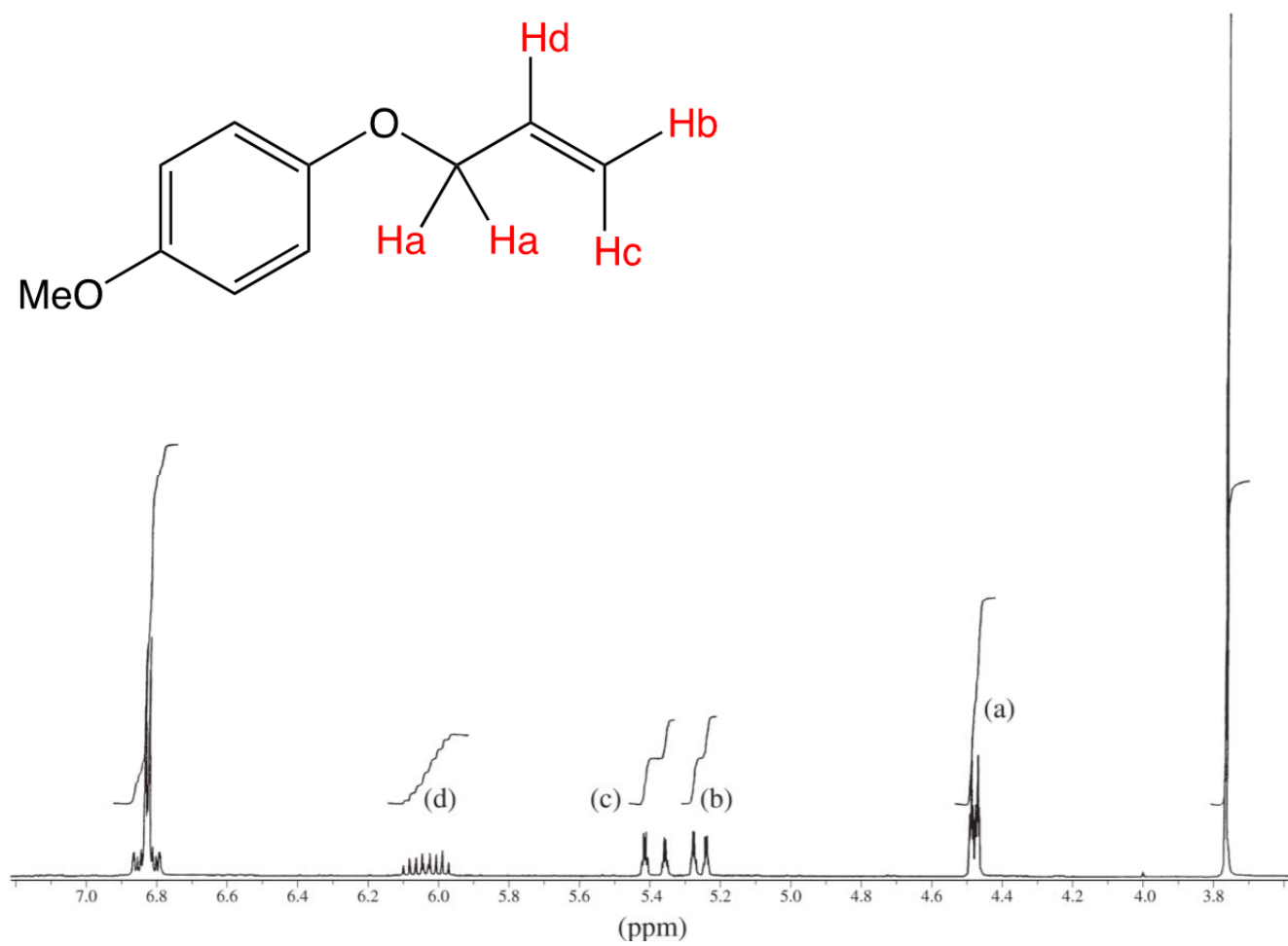
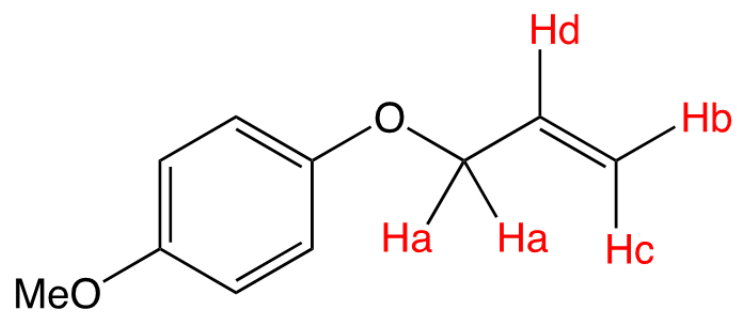


16.

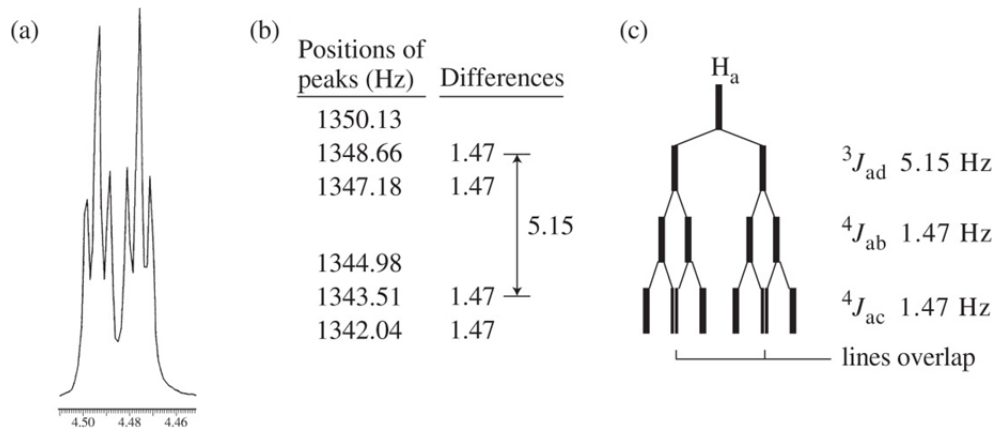


22. The proton NMR below is for allyloxylanisole (shown below). Expansions are shown for each of the five unique types of protons other than the aromatic protons (which you can ignore) and the OMe at 3.78 ppm. Hertz values are given for each peak.

- Describe each multiplet in terms of doublet, triplet, etc. in the spaces provided.
- Determine all coupling constants for each multiplet and label them appropriately (i.e. J_{ab} , J_{cd} , etc.).
 Tree diagrams are provided along with the Hoyer method for each multiplet. Note – the methylene protons Ha are enantiotopic, so they will split other protons into a triplet. Knowing this, we can use “t” where appropriate, instead of “dd”. See below for explanation.
- Assign the protons directly on the structure below using the letters a, b, c, and d.

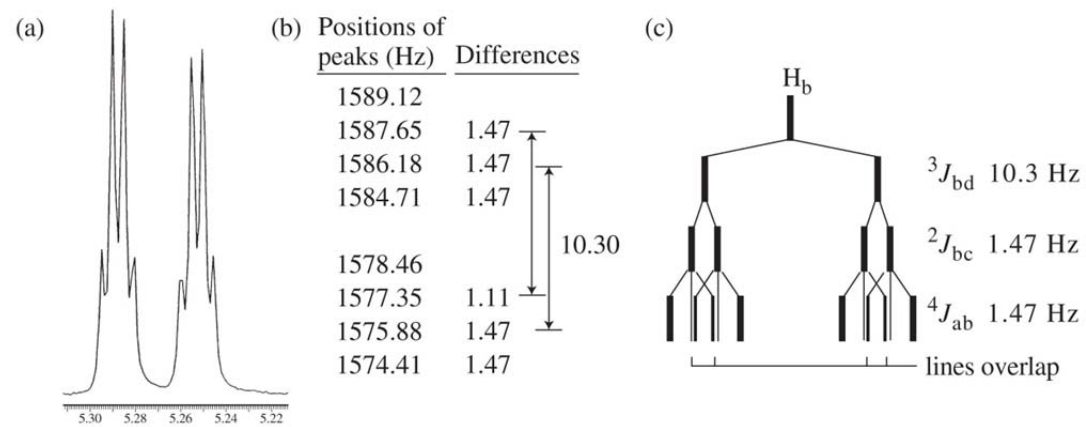


Ha



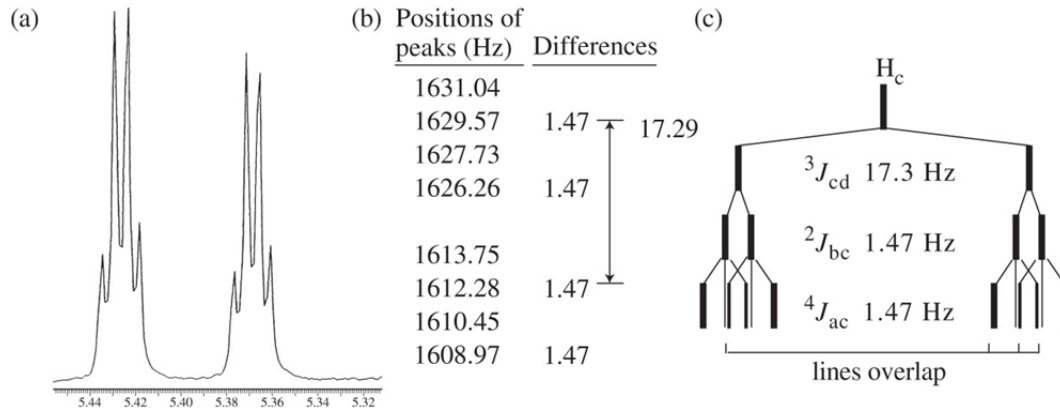
multiplet? ddd

Hb



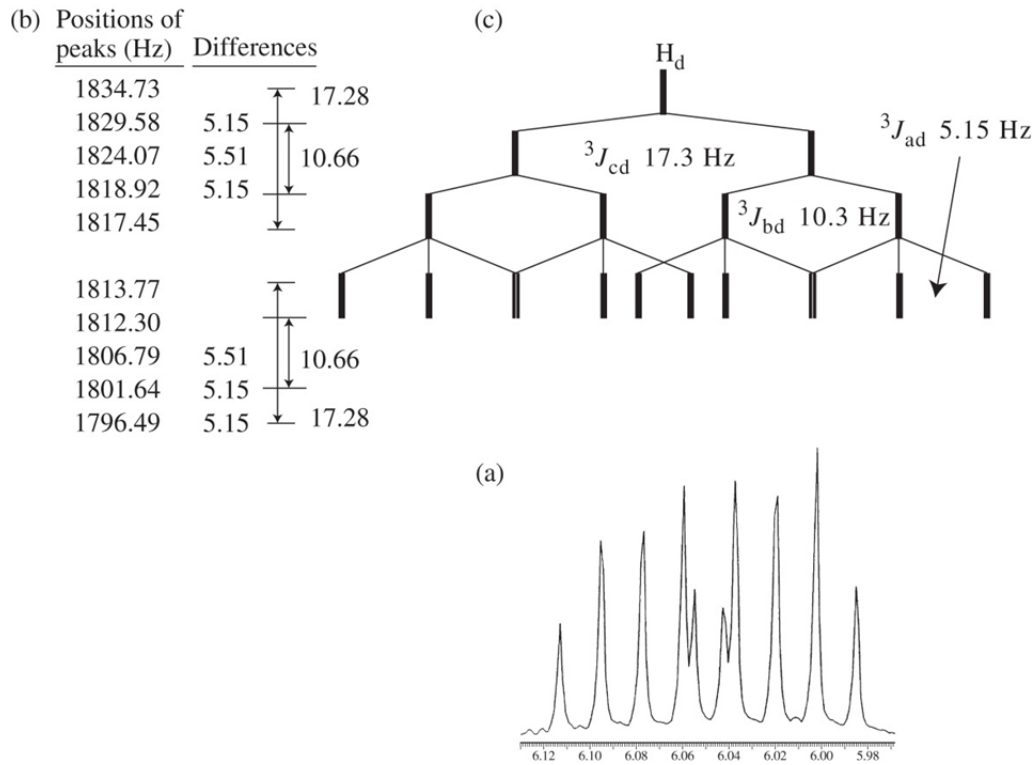
multiplet? ddt

Hc



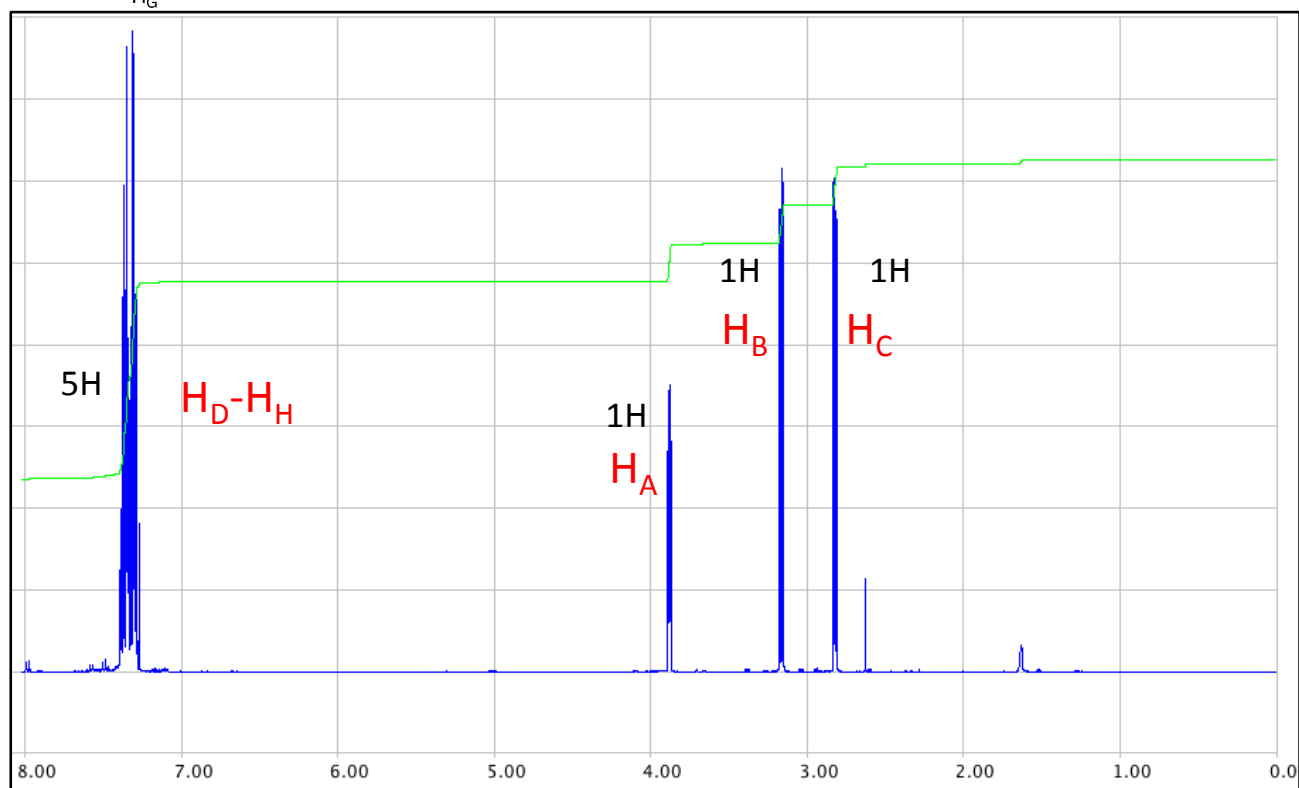
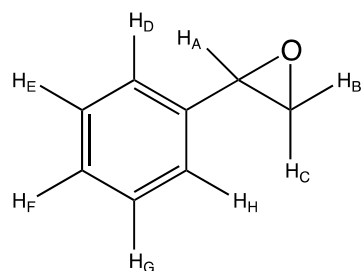
multiplet? ddt

Hd



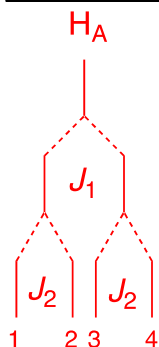
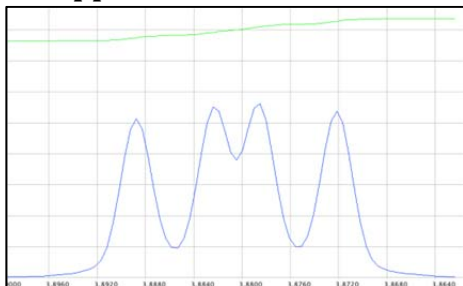
multiplet? ddt

23. Below is the ^1H NMR spectrum of epoxystyrene:



- Assign peaks for protons H_A , H_B , and H_C . (Label the peaks directly on the spectrum).
- Given the ppm values shown in the expansions on the next page, calculate all relevant coupling constants for H_A , H_B , and H_C , and analyze each multiplet that is shown on the next page. Use tree diagrams to show the splitting pattern in each case, and describe each one (doublet, triplet, quartet, doublet of doublets, doublet of triplets, etc.). You do not need to analyze the multiplet in the aromatic region.

3.88 ppm - H_A



We assigned H_A based on its chemical shift - closest to the aromatic ring = farthest downfield.

Splitting pattern: dd

$$J_1 = 1-3 = 345.31 \text{ Hz} - 341.25 \text{ Hz} = 4.06 \text{ Hz} = J_{AB}$$

$$J_2 = 1-2 = 345.31 \text{ Hz} - 342.75 \text{ Hz} = 2.56 \text{ Hz} = J_{AC}$$

Peak data in Hz:

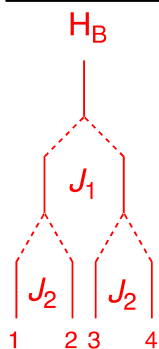
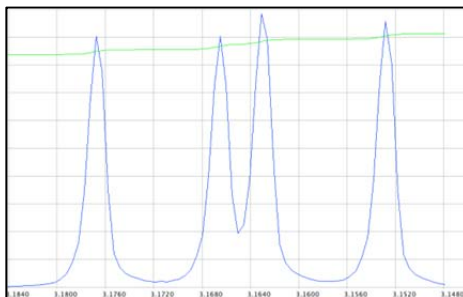
345.31

342.75

341.25

338.69

3.17 ppm - H_B



We assigned H_B based on its coupling constants - it has a cis-relationship to H_A, and it will have a geminal coupling with H_C.

Splitting pattern: dd

$$J_1 = 1-3 = 282.00 \text{ Hz} - 276.50 \text{ Hz} = 5.50 \text{ Hz} = J_{BC}$$

$$J_2 = 1-2 = 282.00 \text{ Hz} - 277.94 \text{ Hz} = 4.06 \text{ Hz} = J_{AB}$$

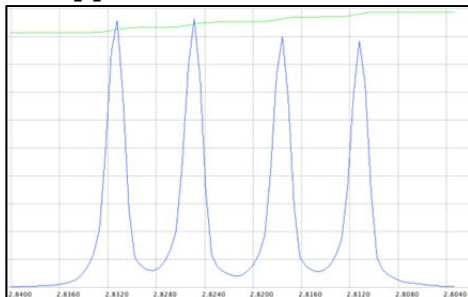
(J_{AB} was found above)

Peak data in Hz

282.00

277.94
276.50
272.44

2.82 ppm - H_C



H_C

We assigned H_C based on its coupling constants - it has a trans-relationship to H_A, and it will have a geminal coupling with H_B.

J₁

Splitting pattern: dd

J₂

J₂

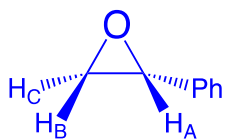
J₁ = 1-3 = 250.56 Hz - 245.06 Hz = 5.50 Hz = J_{BC}

J₂ = 1-2 = 250.56 Hz - 248.00 Hz = 2.56 Hz = J_{AC}

1 2 3 4 (both J_{BC} and J_{AC} were found above)

Peak data in Hz

250.56
248.00
245.06
242.50



The sigma bonds C-H_A and C-H_B (cis in this case) have better overlap than C-H_A and C-H_C (trans) and are better able to transmit spin information, leading to a larger coupling constant.