

Chemistry 381
Mid-Term Exam – Monday
March 16, 2009

Name: _____

Read all questions carefully. You have a large amount of space to write your answers. If appropriate, clearly indicate your answer.

1. Attached is a one-page lab report. This lab report does not include spectra or copies of the notebook page. Read the lab report, and comment on the various problems present in this lab report. For time purposes, make your comments short (a phrase). Do not fix the problems, just indicate what is wrong.

Abstract – full of subjective language (very, easily, highly), no yield or activity data, begins like an intro

Intro – incorrect citation style, no figure label, figures have different settings, no compound numbers, research plan belongs in R&D section

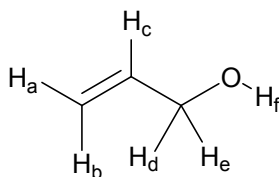
R&D – borderline too much experimental detail

Conclusion – no real information (yield or activity)

Experimental – sig figs, repetitive and verbose, NMR data needs to have multiplicity and J -values

References – abbreviate journal, give ending page number

2. Find the expansion plot for question 2. This complex peak corresponds to the vinylic proton (H_c) on the middle carbon of allyl alcohol. As best as you can, determine the various coupling constants that give rise to this peak. The spectrum was obtained on a 400 MHz instrument. [This is not a simple 202-style peak. It involving complex splitting, like a doublet-of-doublets. You cannot simply count the number of neighbors and then expect $n+1$ peaks.]



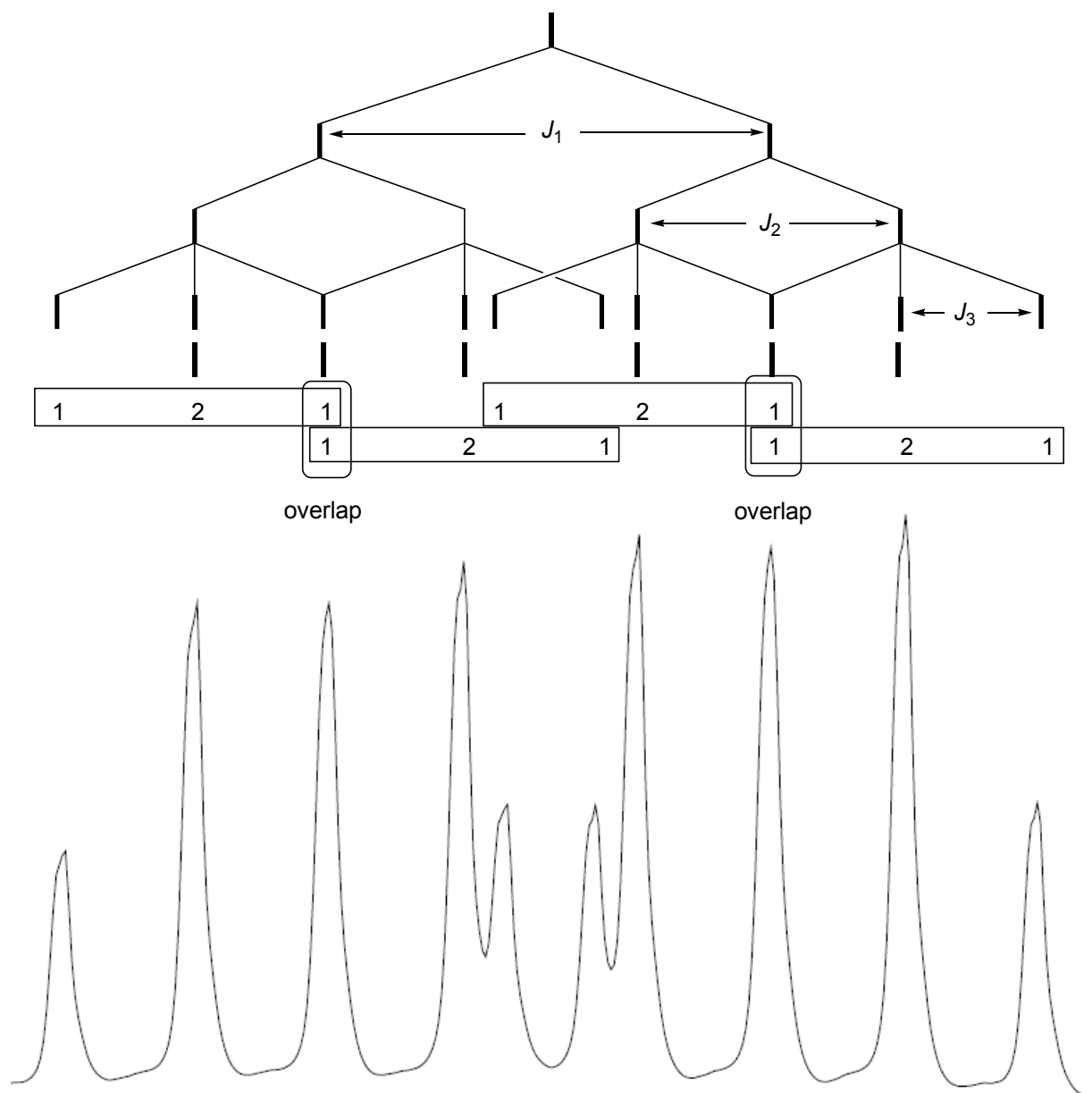
H_c has four neighbors. Two are identical (H_d and H_e). H_a and H_b are unique. H_c therefore has three different neighbors and likely three different coupling constants (J -values). The signal of H_c should be split into a doublet by H_a , a doublet by H_b , and a triplet by H_d and H_e . H_c will therefore be a doublet of doublets of triplets, or a *ddt*. That means there should be 12 total lines ($2 \times 2 \times 3$). Whoops. We only have 10 lines. Some of the lines are overlapping.

The different J -values can be calculated from a number of different peaks. The J -values are shown below.

$$J_1 (J_{bc}) = 5.9769 - 5.9339 = 0.0430 \text{ ppm} = 17.2 \text{ Hz (dihedral is } 180^\circ \text{ so massive coupling)}$$

$$J_2 (J_{ac}) = 5.9467 - 5.9207 = 0.0259 \text{ ppm} = 10.4 \text{ Hz (dihedral is } 0^\circ \text{ so a large coupling)}$$

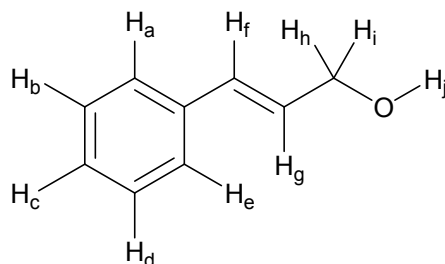
$$J_3 (J_{cd}) = 5.9207 - 5.9079 = 0.0128 \text{ ppm} = 5.1 \text{ Hz}$$



3. Find the page for question 3. This is a page from SciFinder. Write out an ACS-compliant citation of this abstract. Follow the format that you would see in *JOC* (and use for our lab reports). Indicate italics by underlining. Indicate bold by double underlining.

Reich, H. J.; Sikorski, W. H.; Sanders, A. W.; Jones, A. C.; Plessel, K. N. *J. Org. Chem.* **2009**, *74*, 719-729.

4. Find the several pages of spectra that correspond to this question. Fully assign the proton spectrum of cinnamyl alcohol through analysis of the ^1H , ^{13}C , COSY, and HETCOR spectra. As you assign each signal, fill in the table. Also, write out the ^1H NMR data for cinnamyl alcohol as if you are recording the data for an experimental section (without assignments). Note that you can do this second part of the question with only the ^1H spectrum with expansion plots.



cinnamyl alcohol

letter	multiplicity (single letter)	<i>J</i> -value (Hz)
A	m (or d)	cannot tell
B	m (or t)	cannot tell
C	m (or t)	cannot tell
D	m (or t)	cannot tell
E	m (or d)	cannot tell
F	d	15.8
G	dt	16.1 & 5.5
H	dd	5.8 & 1.5
I	dd	5.8 & 1.5
J	s	n/a

Getting through this spectrum is fairly straightforward. The five aromatic protons ($\text{H}_a - \text{H}_e$) are in a lump from 7.22 to 7.40 ppm. Individually, the *ortho*, *meta*, and *para* hydrogens can be picked out based on integration (*ortho* – 2H at 7.36-7.40 with a rough doublet look; *meta* – 1H at 7.22-7.28 with a rough triplet [or triplet of triplets] look, *para* – 2H at 7.29-7.35 with a rough triplet look). The alkene hydrogens are a bit downfield from their expected 5-6 range. Based on their splitting patterns, H_f with one neighbor must be the one at 6.61 ppm, a doublet. The signal at 6.36 ppm (H_g) is a *dt*, a doublet of triplets. H_h and H_i are identical and appear as a doublet of doublets at 4.30 ppm. With only one neighbor, the extra splitting is a surprise. There must be some long-range coupling into H_f . Indeed, H_h and H_i show a crosspeak with both alkene hydrogens in the COSY spectrum. Why doesn't H_f show the extra coupling (appear as a *dt* instead of just a *d*)? It actually does. The “doublet” at 6.61 definitely has a funny peak shape, which implies that the peak has extra splitting that just is not being resolved. Finally, the OH (H_j) is a broad singlet around 2.3 ppm. You really do not need the ^{13}C or HETCOR to solve this structure.