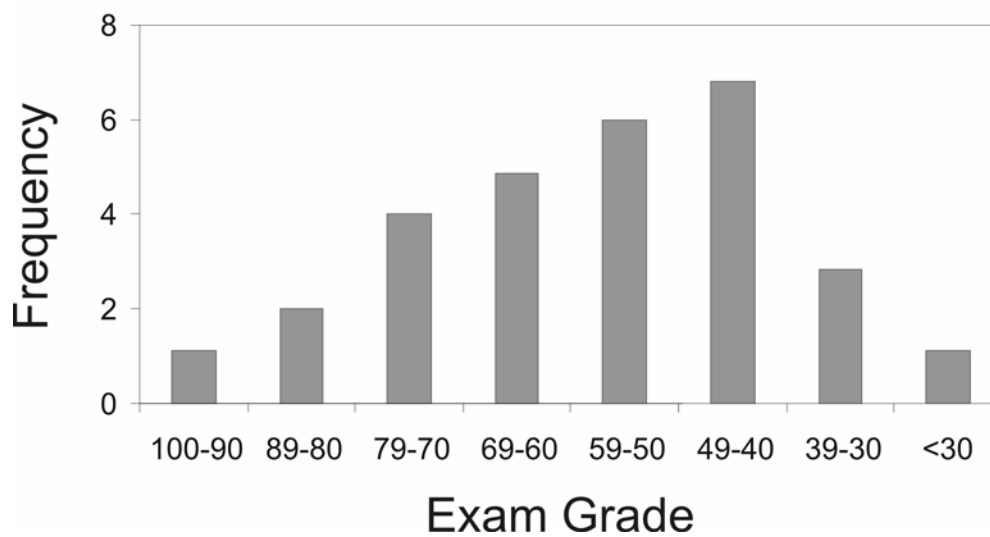


**Midterm Exam 1
Answer Key**

Exam 1 Mean: 57
Exam 1 Median: 58
Exam 1 St. Dev.: 16

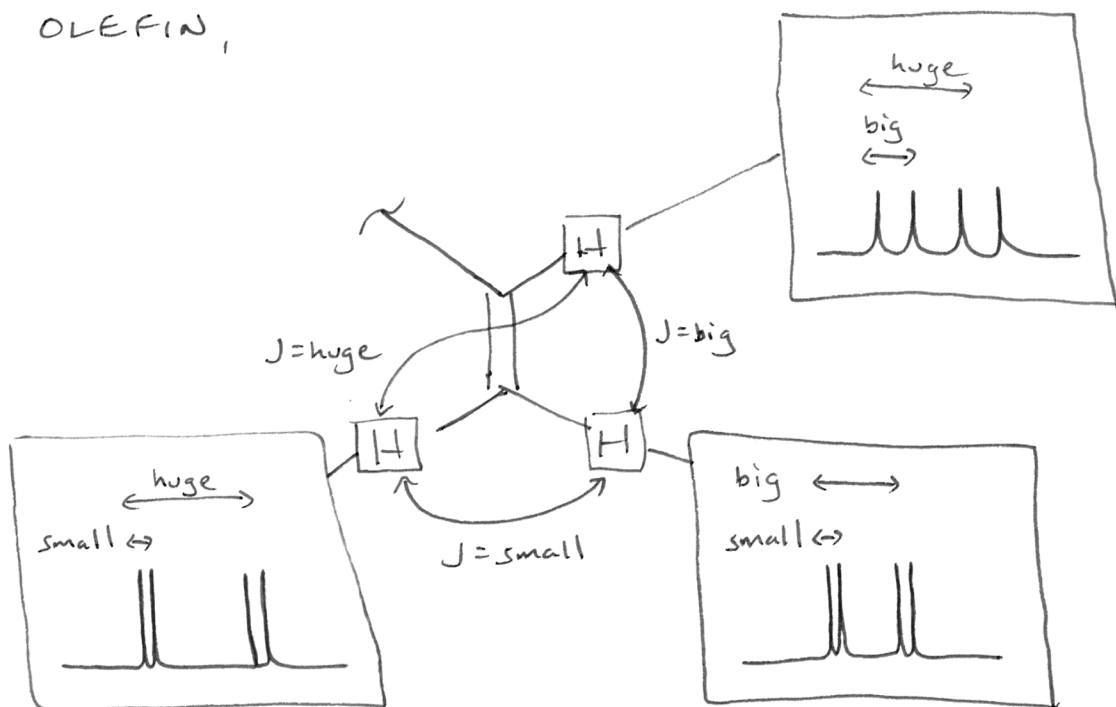


1. a) IN THE FIRST PART OF THIS QUESTION, YOU ARE NOT ASKED TO DISTINGUISH BETWEEN DIASTEREOMERIC STRUCTURES JUST YET; RATHER, YOU ARE ASKED TO ASSIGN SPECTRUM OF 1, ¹H SPECTRUM OF 1 HAS SOME VERY PROMINENT FEATURES =

- 6 OLEFIN RESONANCES;
- A SHARP 3H SINGLET THAT SCREAMS "METHYL GROUP";
- A VERY CLOSE 6H PAIR OF SINGLETS THAT ARE 2 MORE METHYL GROUPS;
- A TOTAL OF 4 PROTONS IN THE ALKYL REGION THAT ARE AN AWFUL SPLIT-UP MESS;
- ONE LONE 1H TRIPLET @ 4.1 ppm THAT MIGHT BE α TO A HETEROATOM.

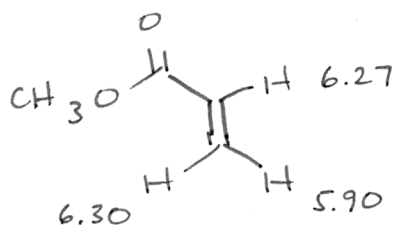
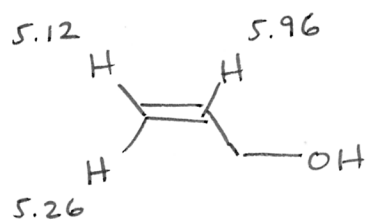
CHART ASKS ONLY TO ASSIGN α TO HETEROATOM (H₆) AND 6 OLEFIN RESONANCES. ASSIGNING H₆ TO δ = 4.10 ppm MAKES VERY GOOD SENSE - IT'S A TRIPLET, AND PROBABLY COUPLES w/ H_{5a} & H_{5b} ~~SAME~~ THE SAME. QUESTION IS, WHICH PEAK IN OLEFINS IS WHICH?

YOU MIGHT IMAGINE THAT, FOR EACH OLEFIN,



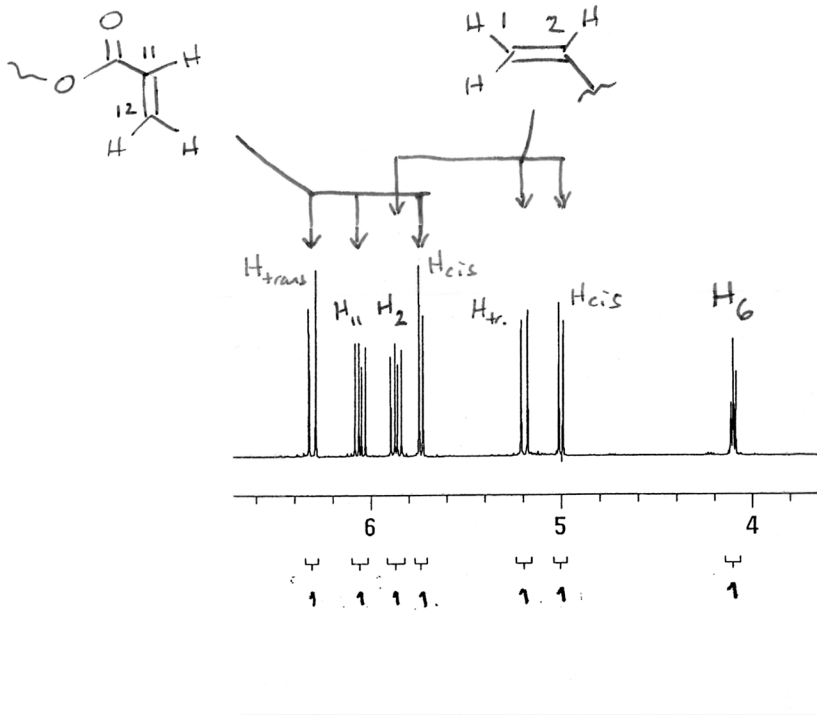
AND SURE ENOUGH, THAT'S WHAT WE HAVE. BUT WHICH IS WHICH? TWO WAYS TO APPROACH THIS:

- PRETSCH TABLES. CHEMICAL SHIFT PREDICTIONS FROM p. 170 SAY

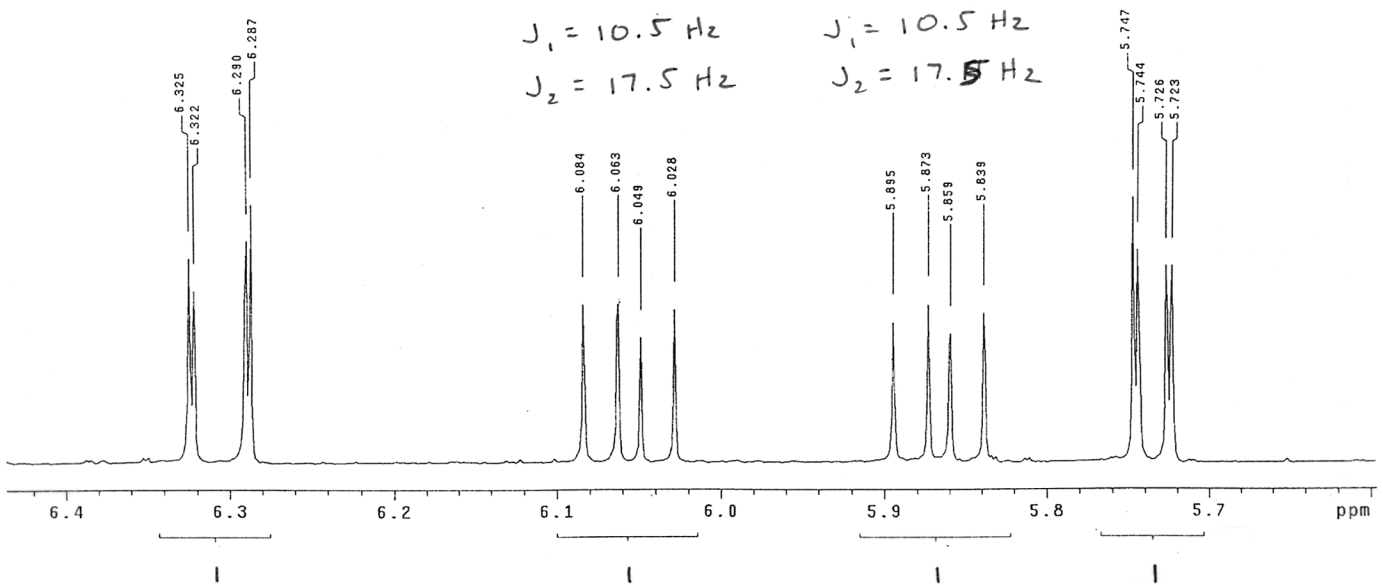


THESE AREN'T EXACT, BUT THEY ARE VERY CLOSE.

- THINK ABOUT IT. ESTER CARBONYL IS VERY ELECTRON-WITHDRAWING, & WILL SHIFT EVERYTHING DOWNFIELD. SO DOWNFIELD ONE IS



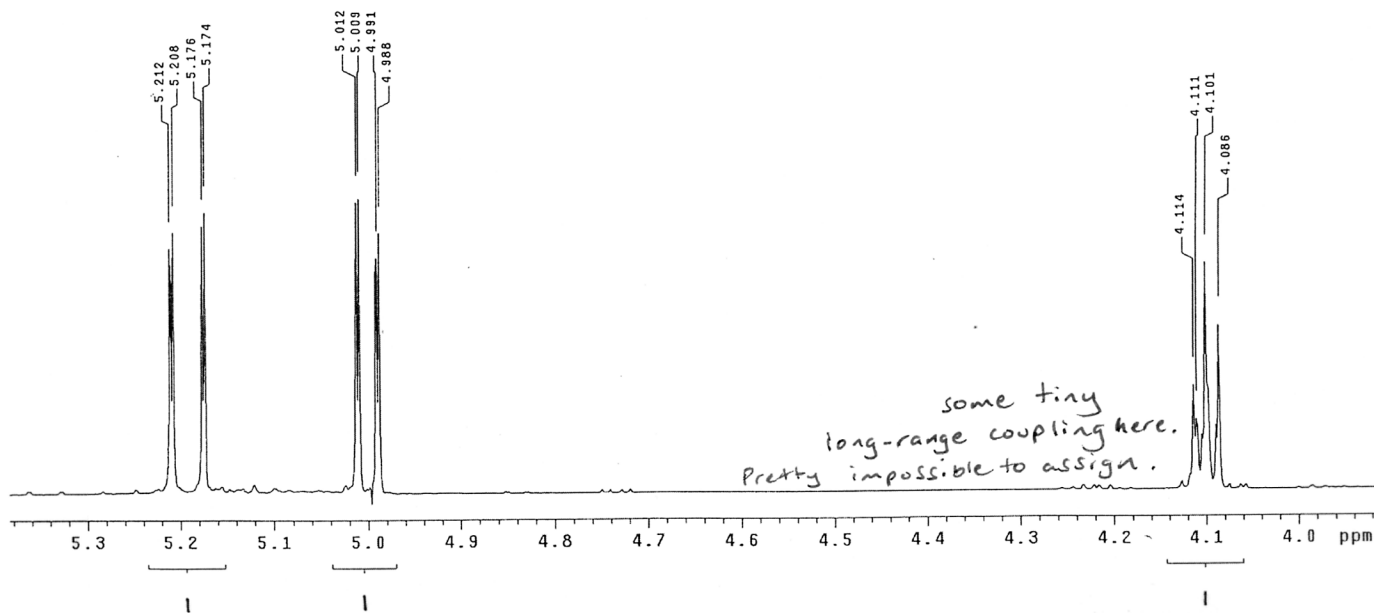
ONE METHOD THAT DIDN'T WORK FOR ASSIGNING WHICH IS WHICH: COUPLING CONSTANTS. COUPLING IS IDENTICAL FOR BOTH TRIOS OF MULTIPLETS.



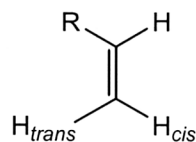
$$J_1 = 1.5 \text{ Hz} \quad J_1 = 1.5 \text{ Hz}$$

$$J_2 = 17.5 \text{ Hz} \quad J_2 = 10.5 \text{ Hz}$$

$$J_1 = J_2 = 7.0 \text{ Hz}$$

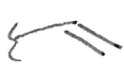


Format for labeling double bonds:



Proton	Chemical shift (δ , ppm)	Multiplicity (e.g., "dd")	Coupling partners, constants (e.g., " $J(H_4, H_5) = X$ Hz")
H _{1,cis}	5.00	dd	$J(H_{1,cis}, H_{1,trans}) = 1.5$ Hz $J(H_{1,cis}, H_2) = 10.5$ Hz
H _{1,trans}	5.19	dd	$J(H_{1,trans}, H_2) = 17.5$ Hz $J(H_{1,trans}, H_{1,cis}) = 1.5$ Hz
H ₂	5.86	dd	$J(H_2, H_{1,trans}) = 17.5$ Hz $J(H_2, H_{1,cis}) = 10.5$ Hz
H ₆	4.10	t	$J(H_6, H_{5a/b}) = 7.0$ Hz
H ₁₁	6.05	dd	$J(H_{11}, H_{12,cis}) = 10.5$ Hz $J(H_{11}, H_{12,trans}) = 17.5$ Hz
H _{12,cis}	5.73	dd	$J(H_{12,cis}, H_{12,trans}) = 1.5$ Hz $J(H_{12,cis}, H_{11}) = 10.5$ Hz
H _{12,trans}	6.31 or 6.30	dd	$J(H_{12,trans}, H_{12,cis}) = 1.5$ Hz $J(H_{12,trans}, H_{11}) = 17.5$ Hz

1 point for each box, all or nothing (no $\frac{1}{2}$ points).

b) THIS QUESTION ASKS, WHICH IS ON THE SAME FACE OF THE THF RING - THE OLEFIN  OR METHYL GROUP?

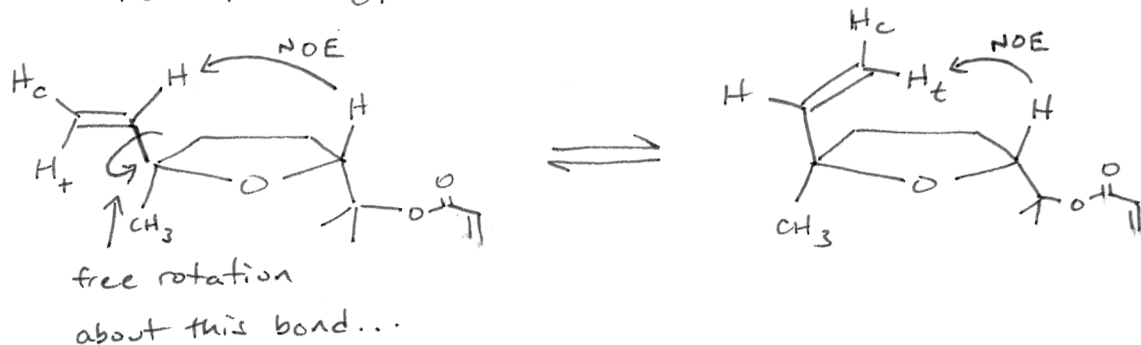
1: NOE IS TRANSFERRED TO OLEFIN

~~AND~~ AND TO PAIR OF METHYLS AT

$\delta = 1.53$. ACTUALLY, WHAT'S COOL ABOUT

THIS NOE IS THAT IT IS ONLY TRANSFERRED

TO TWO OF THREE OLEFIN H'S:

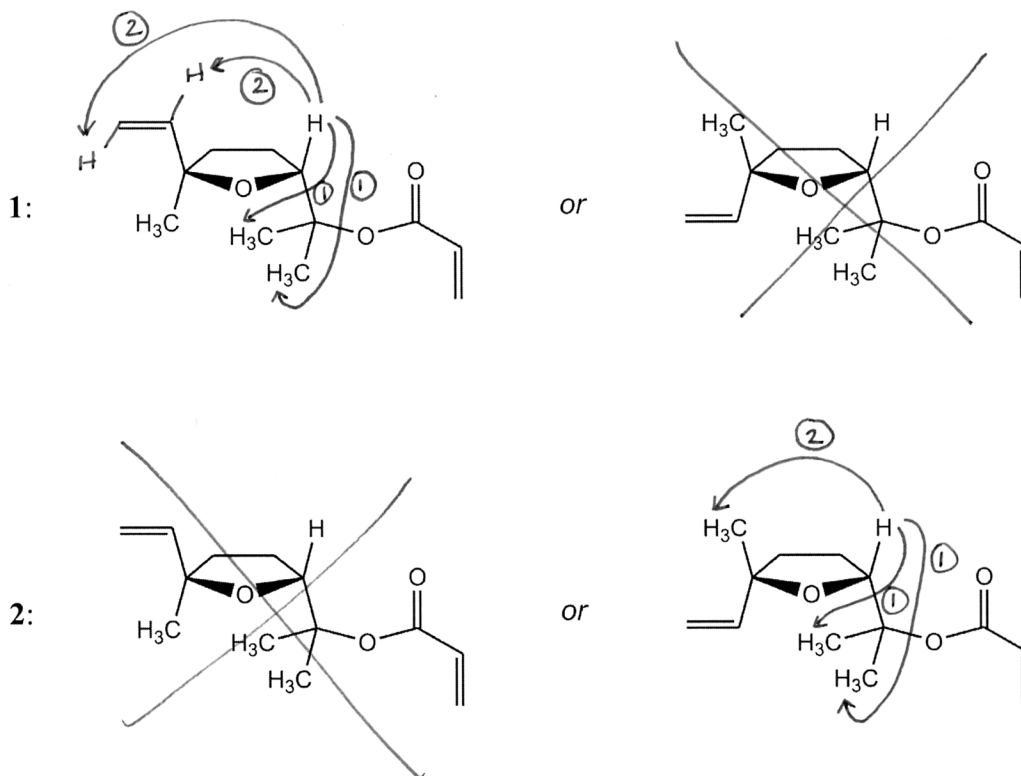


SO H_b IS ON SAME SIDE AS OLEFIN.

2: NOE IS TRANSFERRED TO METHYL (ACTUALLY ALL THREE METHYLS).

IN BOTH CASES, THERE ARE BOTH POSITIVE & NEGATIVE SIGNALS FOR $H_{4a/b}$ AND $H_{5a/b}$. VERY DIFFICULT TO DETERMINE WHETHER THIS IS ACTUALLY NOE OR JUST SUBTRACTION ERROR.

- b. (14 pts) On the structures below, indicate which diastereomer represents which molecule for **1** and **2** by drawing all of the NOE interactions observed for the correct structure with curved arrows. (If you like, draw an X through the incorrect diastereomeric structures.)



+ 2 POINTS EACH FOR CHOOSING
CORRECT DIASTEREOMER.

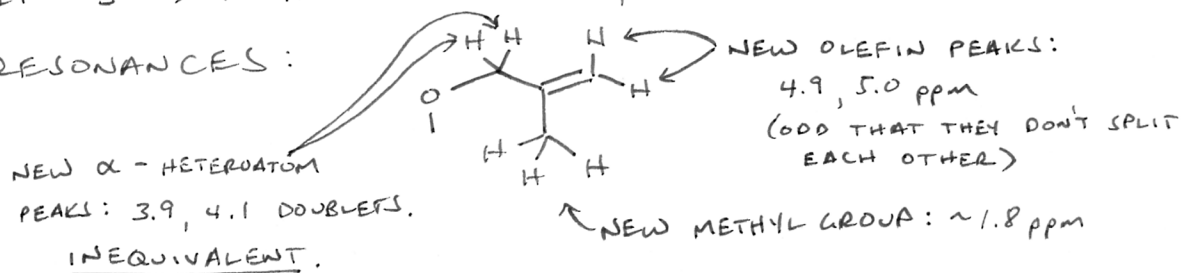
~~NOT~~ (CORRECT NOE'S LABELED ON INCORRECT
DIASTEREOMER RECEIVE FULL CREDIT.)

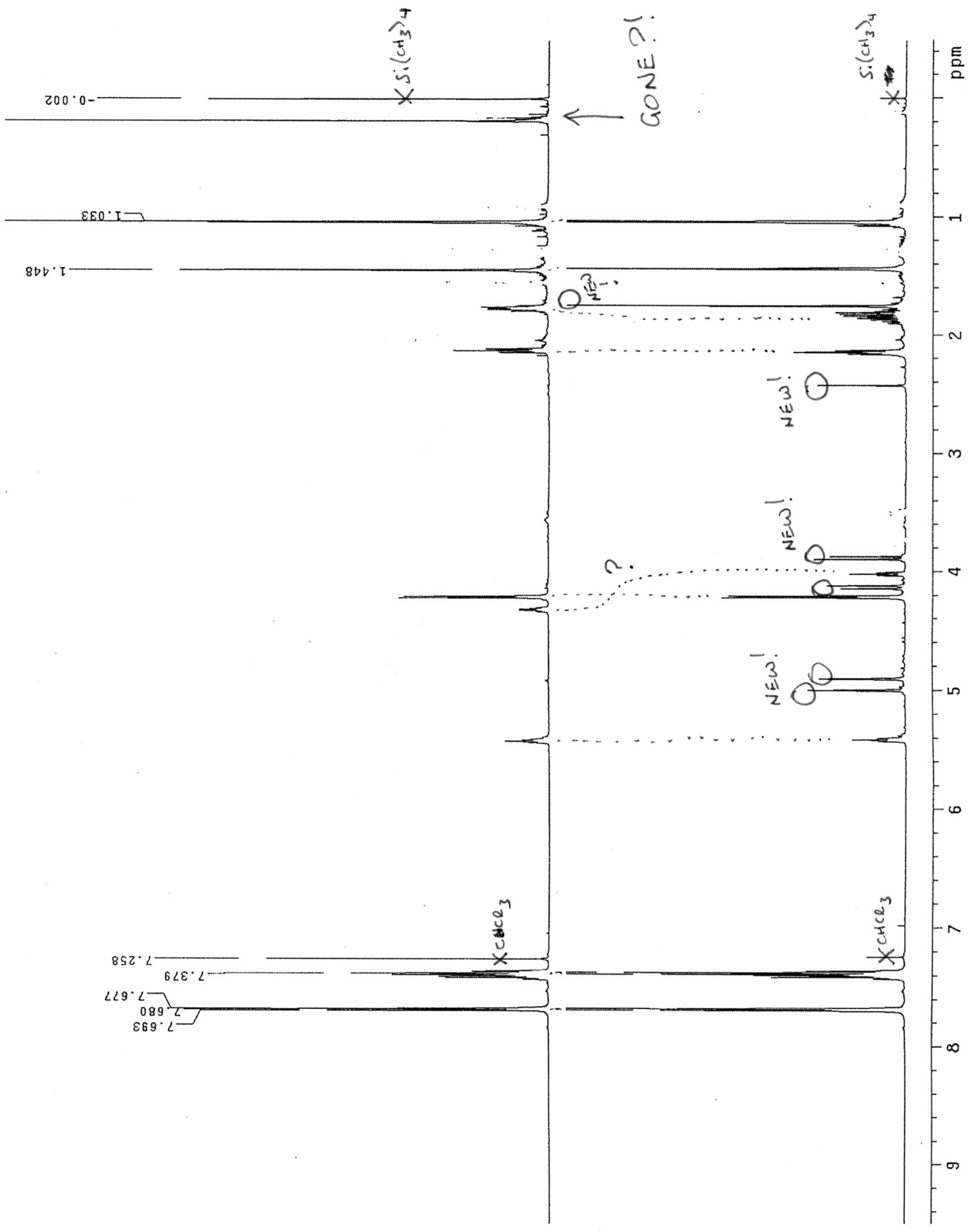
2. a) THE FIRST THING TO DO HERE WAS TO COMPARE SPECTRA OF 3 AND 5. WHAT CHANGES? BEST WAY: OVERLAP SPECTRA & HOLD UP TO THE LIGHT. (SEE NEXT PAGE FOR MY VERSION OF THIS.) SOME THINGS HAVE CLEARLY STAYED THE SAME. PHENYL GROUP PROTONS STILL THERE. (SO, -TBDPS PROBABLY STILL THERE.) 3 HAS ONE OLEFIN PROTON (H_7), AND IT'S STILL THERE. 3 HAS TWO PROTONS α TO OTBPPS ~~###~~ ($H_{8a/b}$) THAT LOOK LIKE THEY ARE STILL AT $\delta = 4.2$ ppm. WE WOULD ~~#~~ EXPECT H_3 (α TO ALCOHOL) TO SHIFT, AND IT DOES. PEAKS CORRESPONDING TO $H_{4a/b}$, $H_{5a/b}$ ARE UGLY BLOBS IN BOTH SPECTRA. $-CH_3$ (H_9) LOOKS FINE. IMPORTANT:

~~### 3 & 4 WORKED, WE WOULD #~~

I CAN'T FIND THE ALCOHOL PROTON. THIS IS NOT UNUSUAL, MAY BE BURIED UNDER OTHERS.

IF $3 \rightarrow 4$ HAD SUCCEEDED, WOULD EXPECT NEW RESONANCES:



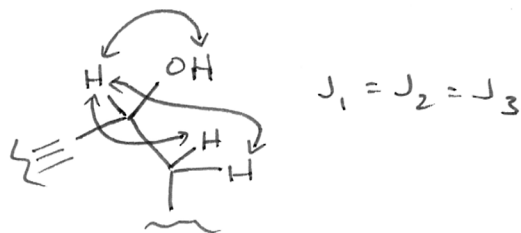


3

5

ALL THIS MAKES SENSE. BUT THERE ARE THREE
ODD THINGS, ABOUT $\underline{3} \rightarrow \underline{5}$.


- 9 H WORTH OF METHYL GROUPS ARE GONE!
SINCE WE KNOW TBDPS IS STILL THERE,
MUST BE THAT TMS HAS FALLEN OFF.
- NEW ~~NEW~~ PEAK @ 2.4 ppm, 1H, DOUBLET.
- H_3 HAS CHANGED FROM A QUARTET



TO A DOUBLET OF TRIPLETS, SO, WHILE IT
HAS LOST A PARTNER, IT HAS GAINED
A NEW ONE. (MAYBE THAT NEW DOUBLET?)

SO, TO FILL OUT THE CHART...

- a. (16 pts) Based on differences between the ^1H NMR spectra of **3** and **5**, Chris concluded that methallyl chloride had added to the alcohol group as planned, but that something about the rest of the molecule had changed. For each of the resonances listed on the chart below, either assign the resonances of **5** to a (numbered) proton that corresponds to one in the proposed structure **4**, or check the box that indicates that the proton does not correspond to any proton in structure **4**.

Chemical shift (δ , ppm), 5	Assignment ("H _N ")	OR	Does not correspond to proton in 4
5.42	H ₇	OR	
5.00	H _{12a}	OR	
4.91	H _{12b}	OR	
4.22	H _{8a/b}	OR	
4.14	H _{10a}	OR	
4.02	H ₃	OR	
3.89	H _{10b}	OR	
2.43		OR	

2 POINTS
EACH. NO
"a"/"b"
NOTATION
NECESSARY,
ONLY NUMBER.

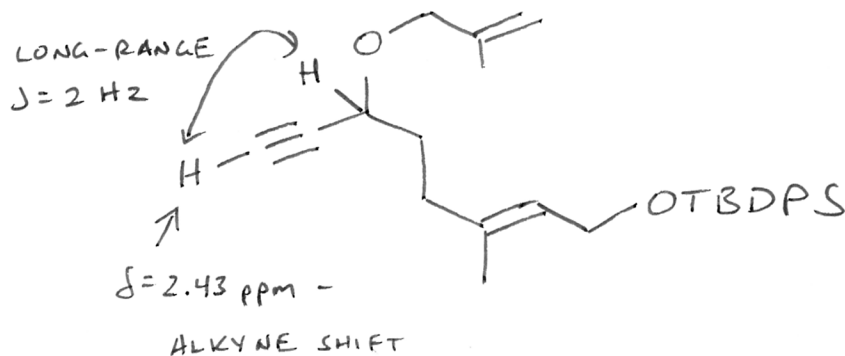
b) H_3 (dt) AND H_{NEW} (d) ARE COUPLED TO
(2.43 ppm)

EACH OTHER ($J = 2$ Hz) AND CAN'T BE
ASSIGNED TO ANY PAIR OF PROTONS IN

4

5 POINTS FOR " H_3 "
5 POINTS FOR DOUBLET @ 2.43 ppm
1 POINT FOR ANY DISCUSSION.

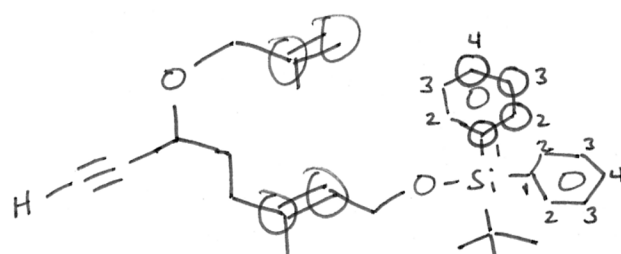
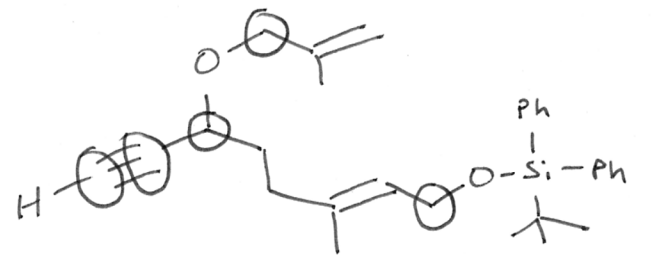
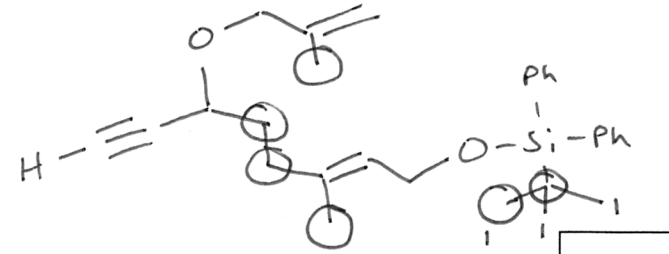
c) MOLECULE HAS LOST -TMS, ~~AND~~ AND HAS
GAINED 1 PROTON THAT CAN COUPLE w/ H_3
WITH VERY SMALL J .



5 POINTS FOR CORRECT STRUCTURE.
3 POINTS FOR EXPLANATION OF $\delta = 2.43$ ppm NEW PEAK.
(STRUCTURE CAN BE INCORRECT.)
~~3~~
3 POINTS FOR EXPLANATION OF COUPLING TO H_3 .
(STRUCTURE CAN BE INCORRECT, BUT COUPLING
MUST MAKE SENSE.)

- d. (15 pts) The ^{13}C NMR of **5** has three groups of peaks: 110-145 ppm, 60-85 ppm, and 10-40 ppm. Does the number of peaks in each group correspond to the number of equivalent carbons in your proposed structure for **5**? In the chart below, draw your proposed structure and circle the carbons that you would expect to observe in each chemical shift range. Indicate where multiple carbons are equivalent.

AROMATIC /
ALKENE
REGION

Chemical shift range (ppm)	Expected resonances from proposed structure of 5 (circle carbons)
110-145 number of peaks: <div style="border: 1px solid black; padding: 5px; display: inline-block; width: 40px; text-align: center;">8</div>	 <p style="text-align: right;">number of resonances expected: <div style="border: 1px solid black; padding: 5px; display: inline-block; width: 40px; text-align: center;">8</div></p>
60-85 number of peaks: <div style="border: 1px solid black; padding: 5px; display: inline-block; width: 40px; text-align: center;">5</div>	 <p style="text-align: right;">number of resonances expected: <div style="border: 1px solid black; padding: 5px; display: inline-block; width: 40px; text-align: center;">5</div></p>
10-40 number of peaks: <div style="border: 1px solid black; padding: 5px; display: inline-block; width: 40px; text-align: center;">6</div>	 <p style="text-align: right;">number of resonances expected: <div style="border: 1px solid black; padding: 5px; display: inline-block; width: 40px; text-align: center;">6</div></p>

AL-HETEROATOM /
ALKYNE
REGION

ALKANE
REGION


1 POINT FOR EACH CORRECT CIRCLE UP TO 15. (INCORRECT STRUCTURES STILL GET POINTS FOR CONSISTENT CIRCLES.)

- e. (12 pts) One of the resonances in the ^{13}C DEPT spectra of **5** is inconsistent with the number of protons attached to the corresponding carbon. Which resonance? Which carbon in the structure of **5** does this resonance correspond to? Why is the DEPT intensity incorrect for this carbon?

$\delta =$ 73.7

2 POINTS.
1 POINT FOR
82.9 ppm.

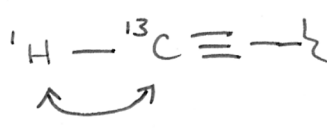
which carbon? (draw as substructure)



4 POINTS.

why?

110-140 REGION SHOWS 2 QUATERNARY / NO H CARBONS, BUT MOLECULE ONLY HAS ONE. REASON: DEPT METHOD ASSUMES THAT ALL $J(^{13}\text{C}-^1\text{H})$ VALUES ARE THE SAME, AROUND 135 HZ, BUT



$J = 250 \text{ HZ}.$

SO, DEPT INTENSITY IS SCREWED UP.

6 POINTS,
3 POINTS FOR ANY DISCUSSION OF J .
0 POINTS FOR RELAXATION TIME T_1 . THIS
~~IS~~ IS NOT WHY DEPT IS INCORRECT.