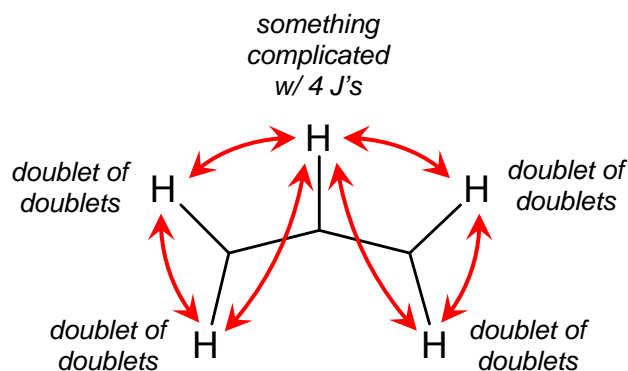


Exam 1 Solutions Answer Key

Exam 1 Mean: 71
Exam 1 Median: 71
Exam 1 St. Dev.: 18

1. Our two candidate molecules have very similar structures, so I think it was actually possible to get all of the answers to this problem correct without choosing the correct structure. Both molecules have an aromatic part and an aliphatic part, and we can deal with these separately. On the aromatic side, the *para*-disubstituted benzene ring has only two inequivalent sets of protons: one set (H2' and H6') is closer to the chlorine atom, and the other set (H3' and H5') is closer to the oxygen. Chemical shift tables—like the one on p. 178 of Pretsch—say that aromatic H's that are *ortho* to an -OR group are shifted quite a bit upfield of those that are *ortho* to a -Cl. (Presumably because -OR is a better π -donor than -Cl. If we assume that substituent contributions are additive, the table predicts $\delta = 6.77$ ppm for H3' and H5', and $\delta = 6.93$ ppm for H2' and H6'. Doesn't match our spectrum perfectly, but the trend is there.)

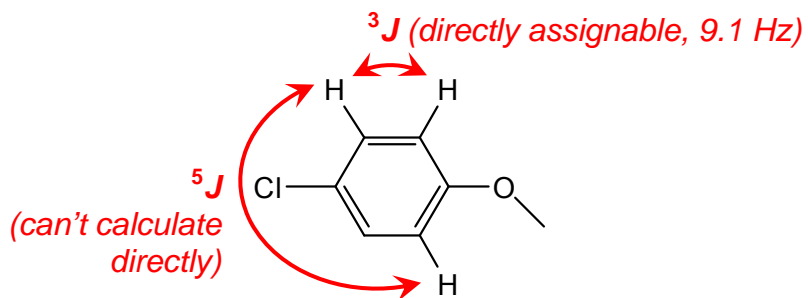
On the aliphatic side, things are a little more complicated. For both molecules, we would expect all five protons to be inequivalent, and to couple to one another. Things would look something like the diagram at right. The spectrum matches this diagram. We do indeed have four doublet of doublets—or three obvious dd's, and one triplet that doesn't have a 1:2:1 intensity ratio that



probably is a dd—and one complicated multiplet. Two of the dd's are upfield, and two are downfield. This actually makes sense for both molecules (though, to be honest, I think it makes better sense for one than the other). In the case of **1** (the epoxide), protons that are on the epoxide will be upfield of those that aren't, according to chemical shift tables, due to ring strain. And in the case of **2** (the chloride), the -O(aryl)-substituted side should be downfield of the -Cl substituted side. So, in either case, we've got:

δ (ppm)	Name(s) of proton(s) (H_n)	Coupling constants J (Hz)	Assign coupling constants $J(H_m, H_n)$
7.24	H2' & H6'		
6.85	H3' & H5'		
4.21	H1a		
3.90	H1b		
3.34	H2		
2.91	H3a		
2.75	H3b		

Now we can work on assigning J partners and values. The aryl protons are represented by doublets, with some funny business near the baseline caused by coupling to multiple magnetically inequivalent protons. Here, we can only read the large, *ortho* 3J coupling constant directly, even though we know that each proton is also coupled with a 5J to a chemically equivalent, but magnetically inequivalent, para-partner.



Looking at the aliphatic protons, we've got four doublets of doublets that will be easy to interpret, and one complex multiplet that will be harder. Most importantly, all of the coupling constants in the dd's will be present in the complicated multiplet. So I think the easiest way to answer this question was to analyze the dd's first. I'll start by just calculating coupling constants, without trying to figure out what partners with what:

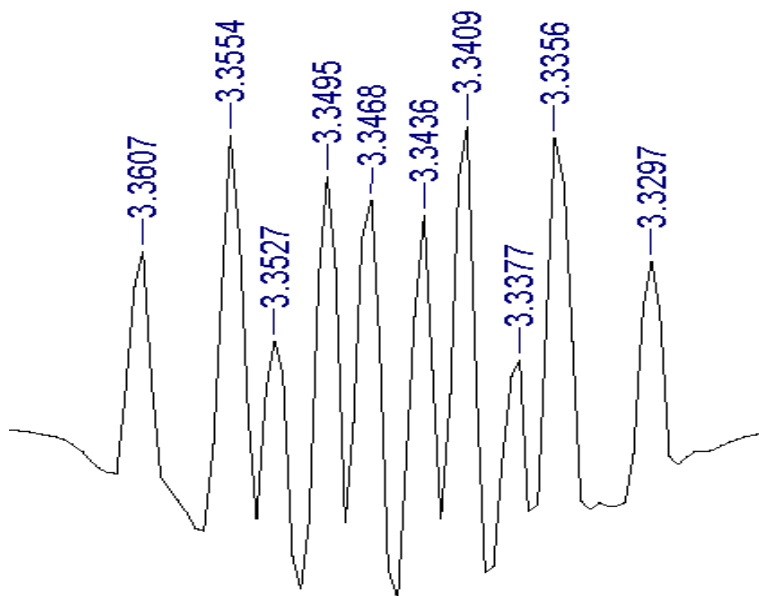
δ (ppm)	Name(s) of proton(s) (H_n)	Coupling constants J (Hz)	Assign coupling constants $J(H_m, H_n)$
7.24	H2' & H6'	9.1 Hz	$J(H2', H3')$ & $J(H5', H6')$
6.85	H3' & H5'	9.1 Hz	$J(H2', H3')$ & $J(H5', H6')$
4.21	H1a	11.0 Hz	
		3.0 Hz	
3.90	H1b	11.0 Hz	
		5.9 Hz	
3.34	H2	<i>we'll deal with this one later</i>	
2.91	H3a	4.8 Hz	
		4.8 Hz	
2.75	H3b	4.9 Hz	
		2.7 Hz	

Out of these J values, the 4.8 Hz ones for H3a are probably not so reliable because the "triplet" actually has two, slightly different J 's. But they're probably close to 4.8 Hz.

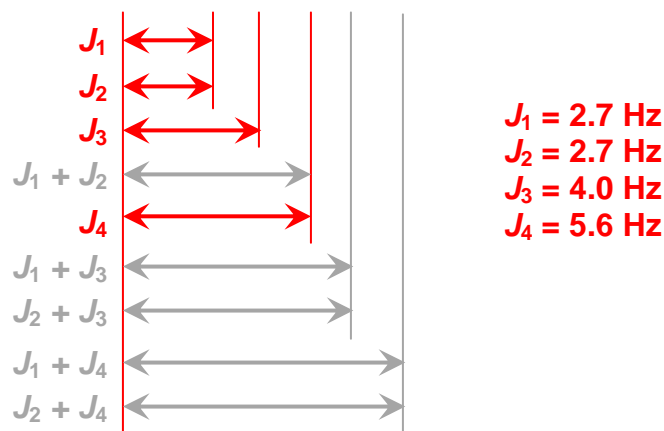
We know right off the bat that the two H1 protons and the two H3 protons exhibit geminal coupling constants, and so there should be one J value that each pair shares. All of the other coupling constants should be to the central, H2 proton. So, without even evaluating the resolution-enhanced multiplet, we can fill in the chart:

δ (ppm)	Name(s) of proton(s) (H_n)	Coupling constants J (Hz)	Assign coupling constants $J(H_m, H_n)$
7.24	H2' & H6'	9.1 Hz	$J(H2', H3')$ & $J(H5', H6')$
6.85	H3' & H5'	9.1 Hz	$J(H2', H3')$ & $J(H5', H6')$
4.21	H1a	11.0 Hz	$J(H1a, H1b)$
		3.0 Hz	$J(H1a, H2)$
3.90	H1b	11.0 Hz	$J(H1a, H1b)$
		5.9 Hz	$J(H1b, H2)$
3.34	H2	3.0 Hz	$J(H1a, H2)$
		5.9 Hz	$J(H1b, H2)$
		4.8 Hz	$J(H2, H3a)$
		2.7 Hz	$J(H2, H3b)$
2.91	H3a	4.8 Hz	$J(H3a, H3b)$
		4.8 Hz	$J(H2, H3a)$
2.75	H3b	4.9 Hz	$J(H3a, H3b)$
		2.7 Hz	$J(H2, H3b)$

Here, I've just listed coupling constants for H2 that I measured for the other multiplets. I think that this was actually enough—I bet if we determined the J 's from the complex multiplet, we'd get the same answers. So let's find out!



1 3 6 8 10 ...
 2 4 5 7 9



These numbers mostly match the grey ones on the chart, except the 4.0 Hz value that we said probably wasn't reliable. For all J values, we accepted any answers within 0.5 Hz of the outermost bounds of what you might calculate for each J , using either multiplet. So for example, for that unreliable J that we calculated to be 4.0 Hz using the complex multiplet, and 4.8 Hz using the triplet, we accepted answers anywhere from 3.5-5.3 Hz.

So, going back to our chart, here's what we used to grade your answer:

δ (ppm)	Name(s) of proton(s) (H_n)	Coupling constants J (Hz)	Assign coupling constants $J(H_m, H_n)$
7.24	H2' & H6' 4 points	8.6-9.6 Hz 1 point	$J(H2', H3')$ & $J(H5', H6')$ (can have both these names, or even just one, for full credit) 1 point
6.85	H3' & H5' 4 points	8.6-9.6 Hz 1 point	$J(H2', H3')$ & $J(H5', H6')$ (can have both these names, or even just one, for full credit) 1 point
4.21	H1a 3 points	10.5-11.5 Hz 1 point	$J(H1a, H1b)$ 1 point
		2.2-3.5 Hz 1 point	$J(H1a, H2)$ 1 point
3.90	H1b 3 points	10.5-11.5 Hz 1 point	$J(H1a, H1b)$ 1 point
		5.1-6.4 Hz 1 point	$J(H1b, H2)$ 1 point
3.34	H2 3 points	2.2-3.5 Hz 1 point	$J(H1a, H2)$ 1 point
		5.1-6.4 Hz 1 point	$J(H1b, H2)$ 1 point
		3.5-5.3 Hz 1 point	$J(H2, H3a)$ 1 point
		2.2-3.2 Hz 1 point	$J(H2, H3b)$ 1 point
2.91	H3a 3 points	4.3-5.4 Hz 1 point	$J(H3a, H3b)$ 1 point
		4.3-5.3 Hz 1 point	$J(H2, H3a)$ 1 point
2.75	H3b 3 points	4.3-5.4 Hz 1 point	$J(H3a, H3b)$ 1 point
		2.2-3.2 Hz 1 point	$J(H2, H3b)$ 1 point

Rubric: (51 points total this part.)

We did not grade your a/b assignments in this problem (because you haven't defined what they mean yet)—we only graded the number on the H.

Aromatic protons: 2 points each proton name. (4 points total each box.)

One point partial for each—so two points per box—if aromatic answers are switched.

Aliphatic protons: 3 points each proton name.

1 point partial for each box where H1a/b is switched with H3a/b.

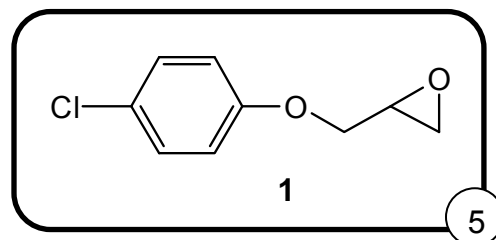
1 point each coupling constant value, to within 0.5 Hz.

We graded the values in the boxes only, independent of your answers in columns 2 and 4.

1 point each coupling assignment.

Assignment must match number in column 2; no points for just having a correct pair name in column 3. If you put incorrect entries in the “name of proton” column, the graders did their best to use this information to give you credit in the “assign coupling constants” column. In other words, you didn't have to get the second column right to receive points for the fourth, but the two columns did have to match. So, in other words, if you listed the $\delta = 4.2$ and 3.9 ppm protons at H3a and H3b, you would get one point each in column 2, but you would still get full credit for listing $J = 11$ Hz as $J(\text{H3a}, \text{H3b})$ [because that's consistent with your answer in column 2].

2. There were a couple of pieces of info here that pointed towards the epoxide. The first was the large difference in chemical shift between the H1 and H3 protons. In the NMR spectrum, these protons are separated by over 1 ppm. In Pretsch's chemical shift tables, a -Cl substituent and an -O(aryl) substituent should show a difference of only 0.5 ppm, but



other tables put epoxide protons very near where they are in the NMR spectrum of the unknown. The second bit of evidence is the small value for $J(\text{H3a}, \text{H3b}) \sim 5$ Hz. Pretsch says that geminal 2J values for chloroalkanes are > 10 Hz, but for epoxides 2J values are ~ 5 Hz. Put together, I think this points to the epoxide.

3. The two protons attached to C3 are

enantiotopic ,

diastereotopic

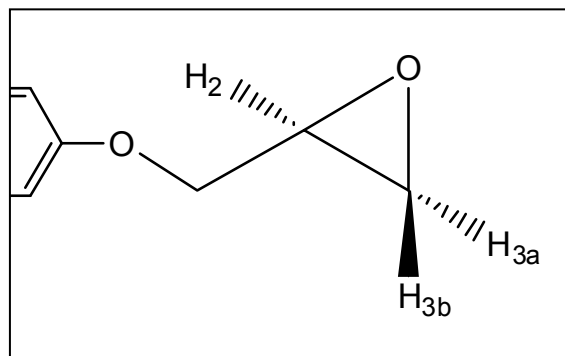
or

neither

3

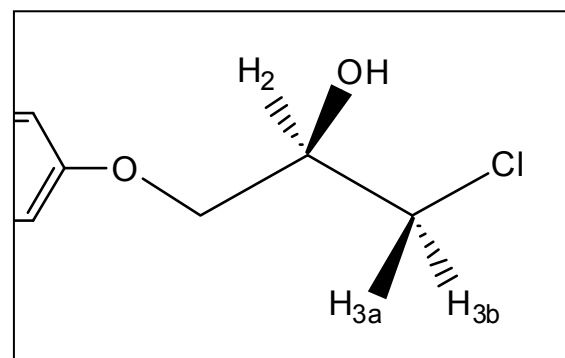
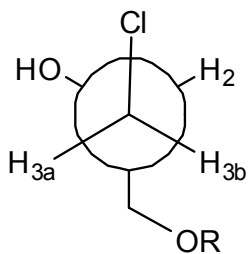
Both candidate molecules have a chiral center at C2. Replacing either H3a or H3b with another atom (X) would create a second chiral center, and two different diastereomers. So, the protons are diastereotopic.

4. I think this problem was easier to answer if you chose **1** as your unknown. In this scenario, your answer was dictated by the vicinal coupling constants $J(\text{H}_2, \text{H}_{3a})$ and $J(\text{H}_2, \text{H}_{3b})$. The way I defined H_{3a} and H_{3b} in my chart for problem 1, $J(\text{H}_2, \text{H}_{3a}) > J(\text{H}_2, \text{H}_{3b})$. For an monosubstituted epoxide, $J(\text{cis}) > J(\text{trans})$, according to the Karplus equation (where $\phi[\text{cis}] = 0^\circ$, and $\phi[\text{trans}] \approx 140^\circ$). That means that H_{3a} is on the same face of the epoxide as H_2 . It doesn't matter whether you drew H_2 in front or in back— H_{3a} needs to be on the same face. (If, in your chart, you defined H_{3a} and H_{3b} opposite from me, then H_{3b} should be on the same face as H_2 .)



If you chose the chloroalcohol **2** as your unknown, the story is a bit more complicated. The only way to explain the difference between $J(\text{H}_2, \text{H}_{3a})$ and $J(\text{H}_2, \text{H}_{3b})$ is to look at conformational preferences of the C2-C3 bond. The most stable conformation at this bond places the $-\text{Cl}$ opposite the largest, $-\text{CH}_2\text{O}(\text{aryl})$ group.

Let's assume that the molecule spends most of its time in this conformation. If so, the pair of H's with the largest coupling constant would be the *anti*-pair, with $\phi = 180^\circ$. According to the chart in problem 1, that must be H_{3a} .



(If you defined H_{3a} and H_{3b} opposite from me in that chart, then they would be opposite the drawing above.)

Rubric:

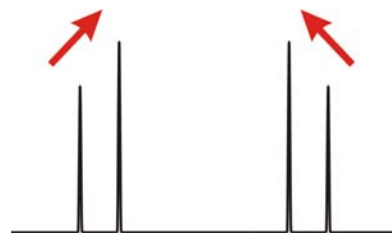
6 points, no partial credit.

Grading on this problem did not depend on your answer to problem 2. It did depend closely on your answer to problem 1:

- If you defined H's in problem the way I did, either answer above was correct.
- If you named H_{3a} and H_{3b} opposite from me, your answer should be opposite mine.

- If you assigned H3a and H3b to be the resonances at $\delta = 4.21$ and 3.90 , then whichever one you assigned to be $\delta = 3.90$ has the larger coupling constant, and should take the place of H3a in my drawings above.

5. The multiplets at $\delta = 7.24$ and 6.85 ppm are “tented”, with the peaks closer to each other taller than the peaks farther from each other. This occurs when H’s are coupled to one another, and when the difference between the chemical shifts of their multiplets ($\Delta\delta$) is on the same order as the coupling constant between them (J). Or, put in another way, when $\Delta\delta/J \approx 1$.



Rubric:

6 points for stating that the resonances represent coupled protons, and that $\Delta\delta/J \approx 1$ (or that $\Delta\delta$ is on the same order as J).

2 points partial for just pointing out that the two resonances represent coupled protons.

6. Once again, we can deal with the aromatic and aliphatic resonances separately. Of the four peaks in the aromatic, $\delta = 100$ - 150 ppm region, two are much shorter than the other two; this usually indicates that the carbon doesn’t have any protons attached, and that incomplete relaxation during the pulse delay leads to low integral intensity in the NMR. Sure enough, our molecule has two inequivalent aromatic carbons with no attached protons. Chemical shift tables say that the carbon attached to oxygen (C4’) should be downfield of the one attached to chlorine (C1’). Those same tables say that an *ortho*-oxygen shifts a carbon *upfield* (presumably due to resonance), such that C3’ and C5’ should be upfield of C2’ and C6’. So, so far we’ve got

δ (ppm)	Name of carbon
157.3	C4’
129.6	C2’, C6’
126.3	C1’

δ (ppm)	Name of carbon
116.2	C3’, C5’
69.3	

δ (ppm)	Name of carbon
50.3	
44.8	

For the aliphatic carbons, I think the answers are the same regardless of whether you chose **1** or **2** as your unknown. Pretsch predicts that R-CH₂-O-aryl should appear at $\delta = 65$ ppm, which sets C1. If you chose **1** as your unknown, the more substituted carbon of the epoxide (C2) should be downfield of the less-substituted one. If you chose **2**, the -OH group at C2 shifts its carbon downfield relative to the -Cl. Either way, we get

δ (ppm)	Name of carbon
157.3	C4'
129.6	C2', C6'
126.3	C1'

δ (ppm)	Name of carbon
116.2	C3', C5'
69.3	C1

δ (ppm)	Name of carbon
50.3	C2
44.8	C3

Rubric: (21 points total this part.)

Full credit if you only wrote one of two carbons for (C3',C5') and/or (C2',C6'). The instructions asked for you to assign each resonance to "a" carbon, so if you only wrote one, that's fine.

3 points each box.

1 point partial for each aromatic (aliphatic) carbon box that is incorrect, but still contains the name of an aromatic (aliphatic) carbon. You only get this once per name; if you wrote C5' in all four aromatic boxes, you only get one point.

7. There are two, connected reasons why the peaks for ¹³CDCl₃ in the ¹³C NMR are small relative to the amount of that material in the tube. The first reason is that the carbon atom in CDCl₃ has no attached protons. Peak intensity depends on efficient relaxation of magnetization in the observed nucleus, and in ¹³C NMR, the main mechanism for T₁ relaxation is the nuclear Overhauser effect (NOE) to attached protons. CDCl₃ has no protons (and NOE to deuterium is 7 times less efficient than NOE to protons), so it doesn't relax as efficiently as the molecule being studied.

But there are also carbon atoms in **1** and **2** that have no attached protons, and, although the peaks for these protons are small, they are still larger than what we might expect for CDCl₃ based on abundance alone. So, while "no attached protons" is most of the answer, it isn't the whole answer. The other part of the story is that the broadband, ¹H-decoupling pulse accelerates NOE, such that even nearby H atoms facilitate relaxation. This accentuates the peaks from the molecule of interest relative to CDCl₃.

Rubric: *(8 points total this part.)*

4 points for saying that there are no protons attached to CDCl_3 .

2 points for relating this to relaxation of magnetization. (Or, in fact, for just using the word "relaxation".)

2 points for mentioning the role of broadband decoupling in facilitating NOE. (Or, in fact, just for using the term "broadband decoupling".)