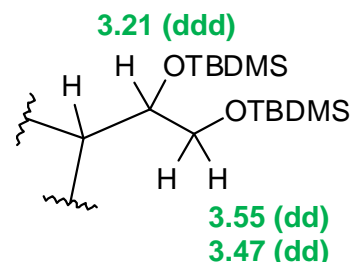


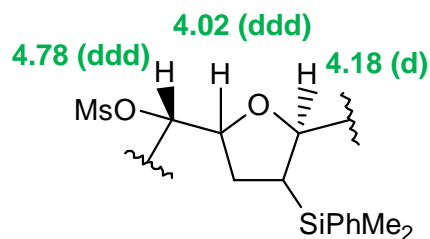
**Problem Set 3 Solutions**  
Multi-Pulse NMR

1. I started analyzing the molecule on the right, with the three resonances at  $\delta = 3.21$ , 3.47, and 3.55 ppm, under the premise that these corresponded to the three protons on the right side of the molecule. The coupling patterns of these multiplets were consistent with this assignment. One unusual thing about this set of protons was that, although it was easy to identify the secondary -CHX- proton (from the two primary -CH<sub>2</sub>X protons) based on multiplicity, the coupling constant to the ring proton was so small that it was difficult to determine, and wasn't even visible in one of the peaks.



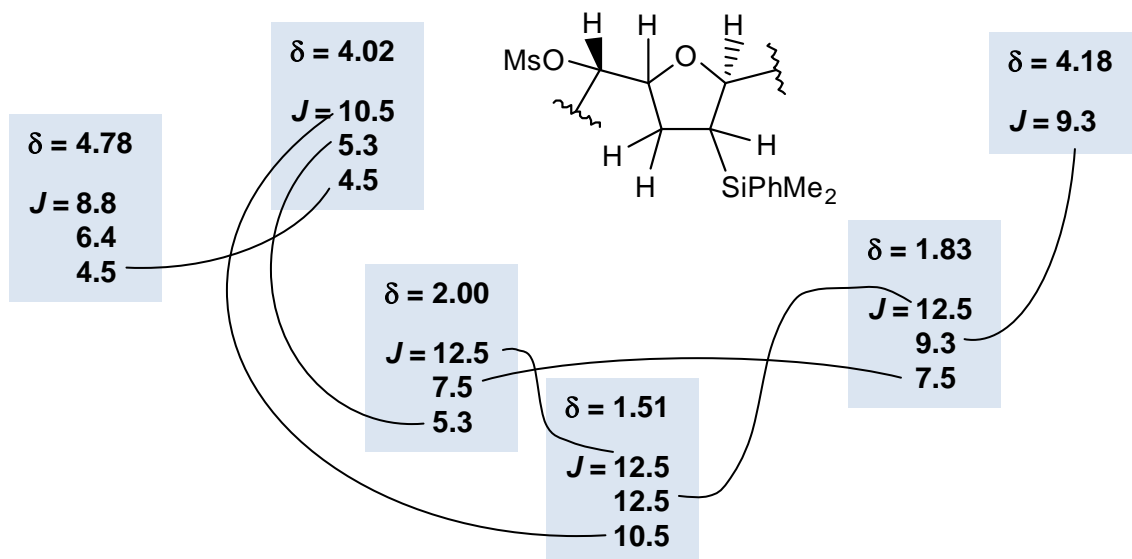
$\delta$ (ppm)	$J$ values (Hz)
3.21	8.0, 5.4, 1.0 (?)
3.47	9.8, 5.4
3.55	9.8, 8.0

Next, we can try to assign all the other protons that are adjacent to oxygen atoms, which must be represented by the multiplets at  $\delta = 4.02$ , 4.18, and 4.78 ppm. The mesylate group is extremely electron-deficient, and Pretsch tables estimate that an -OSO<sub>2</sub>R group shifts  $\alpha$  protons  $\sim 0.5$  ppm further downfield than an -OR group. So we can assign the  $\delta = 4.78$  ppm peak to the -CH(OMs)- proton. Of the other two, the  $\delta = 4.02$  multiplet is complicated and could correspond to a proton with a number of coupled neighbors; only the  $\delta = 4.18$  doublet could be the ring proton on the right side. We don't see that 1.0 Hz  $J$  value in the doublet, but it's small enough we almost didn't see it for its partner either, so this isn't surprising.



$\delta$ (ppm)	$J$ values (Hz)
4.02	10, 5.3, 4.5
4.18	9.3 (+ 1.0?)
4.78	8.8, 6.4, 4.5

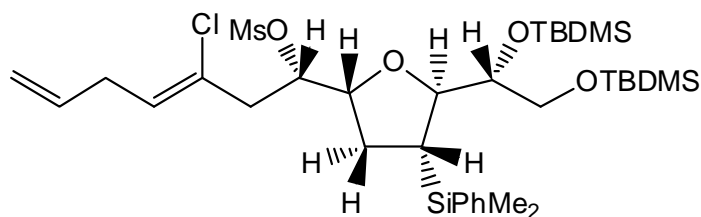
Now we can deal with the H's on the back of the tetrahydrofuran ring. We need to match all of the coupling constants above with the coupling constants that we measure for the protons at  $\delta = 1.51$ , 1.83, and 2.00. Here's that matchup (next page):



So what do the NOE experiments now tell us about the stereochemistry of these protons?

- Irradiation at 4.2 ppm doesn't lead to significant NOE transfer to any ring protons. It does show NOE to alkyl and TBDMS protons on the right side (meaning the experiment did work), but no NOE to other ring protons.
- Irradiation at 4.0 ppm shows no transfer to 4.18 ppm. There is an expected NOE to 4.78, which is adjacent. Then there are informative NOE's to 2.00 and 1.83, but not to 1.51; this suggests that maybe 4.02, 2.00, and 1.83 are all on the same face, and opposite from 4.18.
- Irradiation at 1.8 shows expected NOEs to the alkyl and OTBDMS protons on the right side. There is also positive NOE to 2.0, but negative NOE to 1.5, indicating that the transfer to 1.5 must occur via two transfer steps. Transfer to 4.02 suggests it is on the same side. Transfer to 4.18 here is a little confusing; it may be because the protons are adjacent carbons.

I think all of this is consistent with the stereochemical picture below:



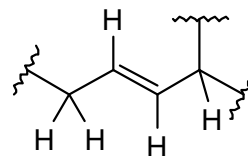
2. The  $^{13}\text{C}$  NMR shows 20 inequivalent carbon atoms. Of these, the DEPT spectra says

4 are $\text{CH}_3$ carbons;	[peak up in DEPT-135, no peak in DEPT-90]
9 are $\text{CH}_2$ carbons;	[peak down in DEPT-135]
4 are CH carbons; and	[peak up in both DEPT-135 and DEPT-90]
3 are C carbons (with no H's).	[no peak in either DEPT spectrum]

Our molecule already has, not counting  $\text{R}_1$  and  $\text{R}_2$ ,

0  $\text{CH}_3$  carbons;  
5  $\text{CH}_2$  carbons;  
2 CH carbons; and  
3 C carbons.

So  $\text{R}_1$  and  $\text{R}_2$  have to be composed of 4  $\text{CH}_3$ 's, 4  $\text{CH}_2$ 's, and 2 CH's.  $^{13}\text{C}$  chemical shifts for the 2 CH's ( $\delta = 133, 132$  ppm) indicate that these must be the two carbons of a double bond, and the  $^1\text{H}$  NMR confirms this. The  $^1\text{H}$  NMR also shows that the two alkenyl protons have two proton neighbors on one side of the alkene, and one on the other.



All of this is consistent with  $\text{R}_2$  being a 3-butenyl group, and  $\text{R}_1$  being an ethyl group:

