NMR Analysis/Interpretation. Concepts and expectations are similar to the Scheme 1 report.

1. An **abbreviated summary report** process will again be required. Draw the structure and label the different carbons. Then make a table with the chemical shifts for the actual **non-aromatic, non-alkenyl C-H's**, and by each one write the letter of the carbon to which it is attached. This will demonstrate that you have analyzed and understand your spectrum.

   - **Also include integration**.
   - But you do not need to analyze/report the splitting (although you may do so.)
   - Which signal is from the β-H, which from the α-H's, which are the benzyl H's, and which the crotonate methyl?
   - Which signals are the methyls or methoxy signals in **3b, 3c,** and **3e?**
   - Does your product look reasonably pure?

2. **Does your NMR confirm that the reaction, and the solvent-removal basically worked**?
   - Does it look like your starting reactant **6** is still present, or gone?
   - Does it look like there is significant amount of solvent left? (Dichloromethane leaves a singlet at about 5.3 ppm.)
3. **The Crotonate Methyl Doublet:** If the reaction worked and you attached the new crotonate portion, that should introduce a new methyl group into your NMR that was not present in **6**. Because the new CH_3 group is attached to an alkene, and there is one H on the neighboring alkene, **the new methyl group should be a 3H doublet. It's allylic, but it's chemical shift will typically be around 1.9 ppm (just underneath 2).**
   - The present of the methyl doublet is the clearest signature for formation of product **10**
   - Ideally there will be one pretty clean doublet around 1.9. Extra doublets in that area reflect impurities. (Other contaminants may also have been "crotonated".)
4. **Chirality, H-non-equivalency, and chemical shift**: The chirality of the β-carbon makes the two β-H's and the two hydrogens on the benzyl carbon nonequivalent.
5. **Chirality, H-non-equivalency, and splitting**:
   - Each of the two α-hydrogens will usually appear as a four-line "doublet of doublets".
   - The β-H will typically also look like a 4-line "doublet of doublets", unless further split by the methyl group in **3e**.
   - The two benzyl H's are each split by each other, so each should look like a doublet.
6. For some of the samples **10**, you will see some **surprising changes in the splitting for the α- and β-hydrogens**. In some 5-membered rings, hydrogens which are trans to each other don't actually split. So it's possible that your β-hydrogen will be a doublet rather than a doublet-of-doublets, because it's split by the cis α-hydrogen but not by the trans α-hydrogen. Likewise it may be that one of the α-hydrogens will be 4-line doublet-of-doublets (the cis α-hydrogen, which is split by the β-hydrogen and the other α-hydrogen.) But the other α-hydrogen might be a simple doublet, split only by the other α-hydrogen but not by the β-hydrogen.
7. For your reports, **account for all and only the hydrogens connected to sp^3 carbons.** You don't need to discuss/present N-H hydrogens **or alkenyl hydrogens** or aromatic hydrogens . (There are so many overlapping aromatic H's that they aren't interpretively useful in this case.)
8. **Signature signals**: As mentioned above, inclusion of a new allylic methyl doublet around 1.9 ppm is diagnostic of product formation. All of the samples **10** will also have the interesting α- and β-hydrogens, and the benzyl hydrogens (5 hydrogens combined, in addition do the 3H crotonate methyl.) But there will be other additional signature methyl peaks for **6c**; **6b**; and **6e**.
9. **Signal Movement**: Notice that the α- and β-hydrogens, and the benzylic hydrogens have moved again. The chemical environment may be similar to in previous structures **3** and **6**, but the environments are not identical, so the chemicals shifts move to varying extent.

10. **Chemical shift logic**:
    - The α-hydrogens, being next to a carbonyl, but being also β to nitrogen and perhaps also an aromatic, should fall in the high 2's or perhaps the low 3's.
    - The β-hydrogen in **3a-3d** should show up around the low 4's. For the β-hydrogen in **3e**, we'd anticipate the β-hydrogen to show up in the 3's.
    - For the benzyl hydrogens, they are on a carbon that has both a nitrogen (+2) and a benzene (+1) attached, so we'd expect them to come around the low 4's or high 3's as well.
    - The crotonate methyl doublet is allylic, so you might expect it in the 2's. In reality, it is likely to "overlap" into the 1.8-2.0ppm region.
11. **The two alkene hydrogens** should actually appear probably in the high 6's, or perhaps even overlapping with the aromatic signals in the 7's. The electronic impact of the strongly electron-withdrawing carbonyl group on the alkene has a strong deshielding impact. You can ignore these in your simplified summary report.
12. **Impurities/contamination**: Recognizing which signals come from the desired product and which do not is again significant.
    - Remember that there should be a logical integration ratio for the main H's in product **10**
    - Between carry-over contaminants, the dimethylaminopyridine, the large excess of triethylamine, and the excess of Mukayama's reagent, there were a lot of other chemicals in your Scheme 3 mixture. It won't be surprising if the cleanup procedure didn't remove all of them. So your mix could be fairly contaminated at this point.
13. **Likely contaminants**:
    a. Unconverted starting material **6**.
    b. Residual solvents that didn't all boil off.
        a. Dichloromethane gives a singlet at around 5.28 ppm.
        b. Ether gives a quartet in the 3's and a triplet in the low 1's.
        c. Triethylamine, which gives a triplet in the low 1's and a quartet in the upper 2's.
    c. Carry-over contaminants that were already in reactant **6**. (Garbage in, garbage out).
    d. Material from the Mukayama reagent **9**. The intent is that the silica will have retained all of that, but maybe not entirely?

    a. If your NMR-**10** looks highly contaminated by solvents, it's possible that another 5 minutes of vacuum at hot-plate setting of 5 while stirring vigorously might get rid of some of the contaminants.
14. **Comparison to Other NMR's**: It may be very interesting to look at how your NMR **6** looks compared to how other NMR's look.
    - How different is your **10** from the **6** that you began with in Scheme 3?
    - How different is your **10** compared to classmates who made different versions of **10**?
    - How clean is your NMR compared to that of classmates who made the same version of **10**?
15. **GC-MS: NOT REQUIRED.** None for product **10**. Some of the larger versions are getting so big so that it's hard to vaporize them, as needed for gas chromatography. And for some the injector needs to be so hot in order to vaporize them that they partially decompose under such hot temperatures, in which case the purity-measurement becomes confusing or misleading.

Scheme 3/Week 3 Lab Report + Overall Project Data Summary:

- For this week, I want both a synthesis-style lab report for Scheme 3, AND a summary report and collection of all of your NMR's/GC's.

1. Write a standard synthesis style lab report for your Scheme 3 reaction (**6 → 10**);
2. Make sure that all structures are drawn explicitly.
   - As always for a synthesis style report, you'll want to draw out the reactants and the products. In this case, be sure you draw your **actual** reactant **6** and product in your reaction.
   - None of your pictures should have an "R1": you should illustrate each structure with your actual R1 group drawn, whether that's methyl or phenyl or 4-methoxyphenyl or whatever.
3. Show all calculations. (Including any mole => mass for reactants or products)
4. When listing your chemicals/reactants and showing gram → mol calculations, make sure that you include your main reactant **6**!
5. Include procedural details.
6. For this report, you can skip the observations, just to keep the report shorter and since you've written up enough of these by now.
7. Calculate mass yields, and percent yields, etc., for product **10**.
8. Include your **NMR-10**, with clear labels, structures drawn, **and the abbreviated summary report** for non-aromatic and non-alkenyl C-H hydrogens for **NMR-10**. But assuming you hand in both your Scheme 3 report and your Data-Summary report at the same time, you could just include the NMR with the data-summary packet.
9. Include a results/data/discussion/analysis section. The analysis/discussion section needs to address what the yield information told you, and what the NMR data tells you about both the success and the efficiency of your reaction, and the purity of your product **10**.
   - The results/data/discussion/analysis section should summarize what the mass/yield/NMR data is, and what conclusions can be drawn from them. Just attaching the NMR without discussing or showing that you understand them will not be good. What is the summary for the key non-aromatic, non-alkenyl C-H hydrogens in your NMR? Does the NMR show that all of reactant **6** reacted, or is there still some reactant **6** left showing up in your NMR? Can you see how your carryover hydrogens, hydrogens that were already in reactant **6** and are still in product **10**, all have variably changed chemicals shifts? (The α- and β–hydrogens and the benzylic hydrogens). Does your product **10** look reasonably clean, or is it obviously significantly contaminated? Does it look cleaner or more contaminated than the reactant **6**? If it's less clean, is it much more contaminated, or only modestly more so? Was the yield respectable, or terrible?

Overall Project Data Summary:

1. Fill out the overall project data sheet on the following page.

2. Attach copies of all NMR's and GC-MS's.

Final Report Data Sheet.

1. Which Series Did You Make? (a,b,c,d,e..)_____ _____

2. GC Results Table:

Substrate ID (ex **3a** or **3b…**)	Retention Time	Product Purity	Did the molecular ion show in the mass spec?	Retention Times and %'s for 3 Largest Impurities (if you have 3…)
3				
6				

- the molecular ion is the "molecular weight" ion, basically the unbroken molecule

3. Mass and % Yields Results Table:

Substrate ID	Molar Mass	Yield in grams	Yield in mmol	% yield
3				
6				
10				

4. NMR Results Table.

- Unless the header indicates otherwise, enter the chemical shifts.
- Some of the boxes will be blank, depending on the structure. For example, products **3** don't have any benzyl hydrogens yet. And only the "e" family has a methyl group attached to the β-carbon.

Substrate ID	β-H	α-H's (list both)	Benzyl H's (list both)	Methyl Doublet (in "e" series)	4-Methyl Singlet (in "b" series)	4-methoxy Singlet (in "c" series)	Crotonate Methyl group (only in product **10**)
3			-None				None
6							None
10							

5. Draw Structures for your Three Substrates: (may do on back if you want more space)

3 **6** **10**

6. Attach labeled NMR's and GC-MS's for products 3, 6, and 10. Include standard summary reports on the NMR's (unexpanded page only).