NMR and GC-MS Data in the Research Module.

1. How to notate the spectra.	**3. How to understand the Data.**
2. How to report the data.	**4. How to use your Mass Spectra for your main GC peak(s).**

How to notate the spectra and refer to them in the reports.

Each NMR and each GC/MS will need to have a clear label that corresponds to the identity of the chemical. If the chemical is **3c**, then the NMR for that sample should be labeled as **NMR-3c**, and the GC/MS should be labeled as **GC/MS-3c**.

A labeling system like this is invaluable for synthesis reports. You can refer to **NMR-3c** in your procedure and in your data analysis sections, and you can label your actual NMR printouts (or GC-MS printouts) with the same labels.

These labels should be written on the upper right-hand corner of each spectra, relative to how a spectrum will be stapled into an actual report. Just as a page number is normally shown in the upper right-hand corner where it's easy to see as you page through a book, so too should spectra be labeled where it's easy to find the labels.

You MUST also draw the actual structure of your product on both your NMRs and your GC/MS's. (If you do several horizontal expansions, you don't need to redraw it on each page. But you should on the front page. And you should draw the label **3a-e** on every page.)

When discussing NMR's or GC/MS's in the reports, always do so by label. (For example, "GC-MS 3c was taken", or "as shown in NMR-3C, the product was very pure….")

NMR Analysis/Interpretation, General Considerations,

1. An **abbreviated summary report** process will be useful and required. Draw the structure and label the different carbons. Then make a table with the chemical shifts for the actual non-aromatic 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, and which signals are from the α-H's?
   - Which signals are the methyls or methoxy signals in **3b, 3c, and 3e?**
   - Does your product look pretty pure? If so, there should be a fairly limited number of non-aromatic signal sets.

2. **Does your NMR confirm that your heat-vacuum completed ring-closure, and removed water and hydrazine**? If your heat-vacuum concentration of product **3** was successful, you should NOT see a big broad lump that appears in the non-aromatic region. If you do have a big lump, that probably reflects residual water and/or hydrazine. Does it look like the hydrazine/water is gone?
3. **Chirality, H-non-equivalency, and chemical shift**: In your NMR, the β-carbon will be chiral. When you have a chiral carbon, it makes the two α-hydrogens (on the CH2 group next to the carbonyl) unequal to each other. One α-H is cis and the other is trans to your β-H, so they are not in the same chemical environment. These unequal α-hydrogens usually (not always) come at different chemical shifts. (Depending on which **3** you made.)
4. **Chirality, H-non-equivalency, and splitting**: The non-equivalence of the two α-hydrogens also complicates the splitting. They now are split by each other, as well as by the neighboring β-H. Plus the splitting magnitudes are different because of the differing distances. (The "other" α-H is closer than the β-H, so they don't usually provide equivalent magnetic splitting, and don't usually provide a nice triplet.) In practice, each of the two α-hydrogens will usually appear as a four-line "doublet of doublets", and the two α-hydrogens should normally combine to show eight lines. The β-H will typically also look like a 4-line "doublet of doublets", unless

further split by the methyl group in **3e**. (In one of the **3**'s, the two α-hydrogens have almost exactly the same chemical shift and could look like just a simple doublet that integrates for 2H, in which case the β-H may look like a simple triplet.)

5. **N-H hydrogens**, like OH hydrogens, are typically broad and unpredictable. In many cases you won't be able to see them at all. Don't look for them or try to assign them
6. For your reports, **account for all the hydrogens connected to sp^3 carbons.** You don't need to discuss/present N-H hydrogens or aromatic hydrogens. (There are so many overlapping aromatic H's that they aren't interpretively useful in this case.)
7. **Signature signals**: All of the samples will have the interesting α- and β-hydrogens. But there will be other signature peaks for other situations:
   - the para methoxy methyl in **3c**;
   - the para methyl group in **3b**;
   - the methyl doublet in the **3e**.
   - **3a** and **3d** won't have any non-aromatic C-H's other than the three on C-α and C-β.
8. **Nitrogen impact on chemical shift**: The impact of a nitrogen attachment on chemical shifts is similar to the impact of an oxygen attachment. In other words it has an addition factor of about +2. This will impact the chemical shift for hydrogen on the β-carbon (β relative to the carbonyl).
9. **Chemical shift logic**:
   - For the α-hydrogens in each of 3a-3e, they are next to a carbonyl. So we'd expect them to come in the 2's. They are also β to nitrogen and perhaps also an aromatic, which further pushes them a bit downfield. So typically they should fall in the high 2's or perhaps slip into the low 3's.
   - For the β-hydrogen in **3a-3d**, the β-carbon has both a nitrogen (+2) and an aromatic (+1) attached, so normally we'd anticipate the β-hydrogen to show up in the 4's. For the β-hydrogen in **3e**, the β-carbon has a nitrogen (+2), so we'd anticipate the β-hydrogen to show up in the 3's.
10. **Impurities/contamination**: Real products often are accompanied by many impurities. The present of impurities, can complicate NMR interpretation. Recognizing which signals come from the desired product and which do not is significant. And qualitatively recognizing whether a spectrum is relatively clean or is pretty contaminated is important.
    - Remember that there should be a logical integration ratio for the main H's in your actual product **3**
    - Often there will be a variable amount of smaller signals in the baseline resulting from contaminants, side products, and product-decomposition. The less, the better.
    - In the cases of **3b** and **3c**, if you see "extra" methyl groups, those might result from side products or from starting reactants **1b** and **1c** that never reacted at all. Again, the less the better.
11. **Comparison to Other NMR's**: It may be very interesting to look at how your NMR looks compared to how NMR's of other students look.
    - How different is yours from different versions of **3**?
    - If you compare yours to somebody else who made the same version of **3**, how clean is yours compared to theirs?

GC-MS Analysis/Interpretation

12. Clearly label each page of each GC/MS printout with the appropriate GC/MS-**3a-e** label in the upper right corner.
13. Draw the structure for your specific product on each GC-MS sheet, and write the molecular weight underneath the picture. (No "R" groups; write the specific structures.)

14. **Retention time**? What is the retention time for your **3**?
    - Bigger structures will have longer retention times. Next week, your product **6** should have a longer retention time than this week's **3**. Likewise this week heavier versions of **3** should have longer retention times than smaller versions.
15. **Purity:** How pure is your **3** by GC?
    - Many contaminants will NOT appear, since they come off fast during the solvent delay. So your purity reading will be deceptively high. NMR, which shows everything, is qualitatively more representative.
16. **Mass Spec and Molecular Ion**: For your major product **3**, check in the mass-spec whether there is a molecular ion peak that matches the molecular weight for your product.
17. **Lab report**: In your lab report, make sure that you have not only attached the labeled GC-MS information, but that you also discuss/present the retention time and purity in your data/results/discussion section.

Scheme 1/Week 1 Lab Report:

1. Write a standard synthesis style lab report for your Scheme 1 reaction (**1** → **3**).
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 the **actual** reactant 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 mass => mole for products)
4. Include procedural details and observations as usual.
5. Calculate mass yields, and percent yields, etc., for product **3**.
6. Include your NMR-**3** (**3a** or **3b** or **3c** or **3d** or **3e**, as your case may be).
    - This must be clearly labeled.
    - Be sure to draw your structure, and then provide an abbreviated summary report. This should include a listing of chemical shifts for **non-aromatic C-H hydrogens**, integrations for them, and a matchup-assignment between signals and hydrogens in the molecule.
    - **Note: you do not need to include aromatic H's, N-H's, or impurities/solvents/contaminants in the abbreviated NMR summary report**. There are so many overlapping aromatic H's that they are not really interpretively useful.
7. By putting definite labels on your NMR (for example, **NMR-3b**…), you will be able to easily refer to that that NMR in your report. (For example, "NMR-3b was submitted at this point." Or "NMR-3b shows considerable product, but it is clearly not clean. There is extensive solvent visible…".)
8. Include your GC-MS-3, and **print and attach mass spectra**.
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 and GC-MS data tells you about both the success and the efficiency of your reaction, and the purity of your product **3**.
10. The results/data/discussion/analysis section should summarize what the mass/yield/NMR/GC-MS data is, and what conclusions can be drawn from them. Just attaching the NMR's and GC-MS's without discussing or showing that you understand them will not be good. What is the summary for the key non-aromatic C-H hydrogens in your NMR? What is your GC-retention time? Between the NMR and the GC, did it look like the product **3** was formed successfully, and does it look reasonably clean? Or is it obviously significantly contaminated?
11. Note: Keep two extra copies of your NMR and your GC-MS's. Pyrazolidinone **3** functions as the product in week one report, but it is the reactant in the week two report. So when writing up and analyzing Scheme 2, you'll need information about mass, molecular weight, structure, and mmol of your reactant **3**. You'll also need to have NMR and GC for **3** so that you'll be able to compare your product **6** to reactant **3** and tell whether the reaction really worked. You'll also want copies of **3** for your Final Report after week 3.