An Exhaustive Guide to Tackling NMR Problems
(a.k.a. the Problems that Give Spectral Info)

1. Before anything else, calculate hydrogen deficiency (amount of Hydrogens missing); this is mega important!! Write down this number and what it tells you about your molecule (ex: 2 Hydrogen’s Missing = 1 Unit of Deficiency = 1 π-bond or ring present in molecule)

2. Assuming the problem gives every type of spectral data possible, we’re going to look first at the IR spectra. If there is any $^1$H/$^{13}$C NMR given, ignore it at first. We’ll burn that bridge when we get to it.

3. Alright, now look at your Infrared (if you have any). Look only for stuff that can identify your molecule, like peaks for carbonyl groups, or alcohol groups. There are a few ‘groups of peaks’ that are classic for some functional groups; you may want to learn them just to simplify your life.

4. Make an initial guess as to which functional group you’re dealing with. You don’t have to 100% sure; make a few guesses if you like. Confirming the functional group’s identity is Step 5’s job.

5. Look at the $^{13}$C NMR list. Preferably, look at the hugest number; this is usually the give-away for the identity of your molecule’s functional group. Compare this with your educated guess from the IR data. If the information between the two matches, then great! You got your educated guess for the molecule’s functional group and can skip step 6. If not, it’s step 6 for you.

6. Okay, you’re here because the happy accident of guessing right from IR alone didn’t happen. For example, say from the IR spectra you supposed that your molecule was a ketone, but the $^{13}$C NMR shows no indication of a ketone being there. In other words, your assumption from the IR alone was incorrect. This part of the process involves a lot of back and forth, looking between the $^{13}$C NMR data and the IR spectra. Don’t worry if it takes you a while to figure out how to do this; practice makes all things easier.

7. Example time! Okay, you’ve got your functional group. Now, we’re looking at Mr. $^1$H NMR, the one that’ll give your molecule its actual structure. It may seem confusing as heck at first, but this is the simplest way I know how to deal with spectral problems.

<table>
<thead>
<tr>
<th>$^1$H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.94 (t, 3H)</td>
</tr>
<tr>
<td>1.39 (m, 2H)</td>
</tr>
<tr>
<td>1.62 (m, 2H)</td>
</tr>
<tr>
<td>2.35 (t, 2H)</td>
</tr>
<tr>
<td>12.0 (s, 1H)</td>
</tr>
</tbody>
</table>

Suppose for a moment that you are given the $^1$H NMR table for a carboxylic acid that has the molecular formula C$_4$H$_9$O$_2$. →

See the table and all its pretty numbers? Well, those numbers outside the parentheses are pretty useful to chemists trying to figure out what molecule they just made and stuff like that. The problem is we’re not chemists and even they have a hard time with this stuff. So, what are we gonna do?
Yes, I know, it sounds sacrilegious, but we do what we must, even if we must become heretics to the laws and beliefs of ORGO professors. Besides, it’s only a temporary condition.

Every time you see a \(^1\)H NMR table, please see this much happier version of it.

<table>
<thead>
<tr>
<th>(^1)H NMR</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>: D (t, 3H)</td>
<td></td>
</tr>
<tr>
<td>: D (m, 2H)</td>
<td></td>
</tr>
<tr>
<td>: D (m, 2H)</td>
<td></td>
</tr>
<tr>
<td>: D (t, 2H)</td>
<td></td>
</tr>
<tr>
<td>: D (s, 1H)</td>
<td></td>
</tr>
</tbody>
</table>

8. Alright, let’s get down to business. We’re going to write down everything we know about the different pieces of the molecule that the \(^1\)H NMR tells us.

\[
\begin{array}{cccc}
    & H & H & H \\
H & C & H & \text{m} \\
t & m & \text{m} & \text{t} \\
\end{array}
\]

Is anyone out there wondering how in the heck I got these structures? You are? That’s wonderful; you’ve been listening! ^_^

Okay, look at the methyl group in the line-up (all the way to the left, folks). Now look at our ‘happy’ \(^1\)H NMR table. You see the (t, 3H)? Well, that line corresponds to the methyl structure I drew. The meaning of 3H is ‘3 Hydrogens on this Carbon’. The meaning of t is ‘this peak shows up as a triplet on the \(^1\)H NMR graph’ also meaning ‘this group of Hydrogens is split by two Hydrogens on another group’. If you don’t understand what I just said, you need to go back and learn more about basic theory of NMR.

Do you understand where all the other C-H structures come from? A hint: all the structures correspond to our ‘happy’ \(^1\)H NMR table. You got it? Good! If you’re asking where the O-H is from, I will remind you that this is a carboxylic acid and there is only 1H structure here; that has to be the O-H. You just can’t skip that one over. You’ll end up getting the answer wrong.

9. Notice, we have a 5-carbon molecule and only 4 carbons showing up on the table. Don’t panic! This just means that one of the Carbons is invisible on the \(^1\)H NMR spectrum. The only way that can happen is if a Carbon has no Hydrogens on it; we assume that this Carbon, since we are dealing with a carboxylic acid, is the carbonyl group. So, our structures get a wee bit of revision:

\[
\begin{array}{cccc}
    & H & H & H \\
H & C & H & \text{m} \\
t & m & \text{m} & \text{t} \\
\end{array}
\]

Now, we have all the different pieces in our molecule and we can start to guess the structure. This, my friends, is where things become a pain in the buttocks and only practice helps.
10. You have a few options as to how to deal with this next part. If you have a relatively short Carbon chain, you can try by writing out all the different isomers and figuring out which isomer matches the structural and spectral information you’ve gathered like a squirrel over these past nine steps. I myself tend to wing it and just scribble until I get a structure that ‘feels’ right before moving on to the final steps. But, for those of you not yet perfectly in tune with NMR, here’s another suggestion.

You’ve got all your ‘pieces’ for this puzzle, given up by the ‘happy’ $^1$H NMR table, correct? Well, let’s figure out who sits next to whom, shall we? For example, the methyl group, which we know is a triplet, has to sit next to a group that has only two Hydrogens on it. For now, we’ll assume it’s like this:

```
H H H
\_\_\_\_
C C
```

The reason I chose one of the multiplet 2H Carbons is because the triplet 2H Carbon is an impossibility. If we put any 2H Carbon next to that methyl group, the peak of our 2H Carbon will split into a quartet at the bare minimum. That means Mr. Triplet 2H Carbon is a no-no. But, since we’re already talking about him, let’s figure out who he’s sitting next to.

11. Well, for one, the triplet 2H Carbon *has to be* next to a 2H Carbon group, right? I mean, the only way you get a triplet is if you have two Carbons splitting your peak, and the only group we have capable of that is a 2H Carbon group (again, if these NMR wise-cracks ain’t doin’ it for ya, you need to study some NMR, preferably with the teacher, in their office, alone, with awkward pauses all throughout). Anyway, we know that on one side of our triplet 2H Carbon we have a 2H Carbon. What’s on the other?

I’ll tell you what: nothing... or at least something *invisible to the $^1$H NMR spectrum*. Is that phrase ringing any bells? It should. Remember how I said our carbonyl group is *invisible to the $^1$H NMR spectrum*? I’m going to assume that you now know what the two groups next to the triplet 2H Carbon are, but just in case:

```
H H H
\_\_\_\_
C C
```

12. Let’s see our newly-revised list of structures, shall we? It’s always good to review the info you have.
13. Hey, lookit! Doesn’t it look like we can join up those two ends that have question marks?

Well, it looks alright, doesn’t it? But is it our answer? And how do we confirm whether or not it is?

14. If you guessed ‘look back at the data in the problem’, you guessed right. Look back at the ‘unhappy’ $^1$H NMR table, please.

<table>
<thead>
<tr>
<th>$^1$H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.94 (t, 3H)</td>
</tr>
<tr>
<td>1.39 (m, 2H)</td>
</tr>
<tr>
<td>1.62 (m, 2H)</td>
</tr>
<tr>
<td>2.35 (t, 2H)</td>
</tr>
<tr>
<td>12.0 (s, 1H)</td>
</tr>
</tbody>
</table>

Do you see all the numbers outside of the parentheses? Well, look at’em now. See if you can match each number to a piece of your new structure.

Remember only this; as your pieces are farther away from the functional group, they are less ‘deshielded’ and have smaller numbers. Don’t worry about matching exact numbers; just put down the numbers that are most likely to correspond to each piece.

Here’s what I would probably propose as the ‘matches’:

\[
\begin{array}{cccccc}
0.94 & 1.39 & 1.62 & 2.35 & 12.0 \\
\hline
\end{array}
\]

Did you notice that, as the Hydrogens appear farther from our carboxylic acid group, their $^1$H NMR placement number gets smaller? If you’ve got the same thing going on with your proposed molecule, you’re in!

15. Here’s where we end our problem-solving. At this point, the structure you have should pair up with your $^1$H NMR data (meaning, things should fit about as closely as they ever do in ORGO). Take your structure and look to see if it matches your other spectral data. The matches don’t have to be perfect, but they have to correspond in at least a consistent way. If something doesn’t fit, go back and rearrange your ‘puzzle pieces’.

16. Huh? Whattaya mean the ‘data matches up’…? Holy snickers! You solved it! You won! You beat that problem like a drum! You’re ready for more… 😊