THE FRAGMENT APPROACH

While it's very tempting to make notes directly on the spectra themselves, a much better approach is to collect the data on a separate sheet of paper. The problem with writing on the spectra is that it probably results in scattered and disconnected information that can be difficult to navigate as you get deeper in to the problem. If you write on a separate sheet, you can develop a logical and ordered collected of information that is easier to work back through if you need to.

Organic molecules tend to be overall neutral compounds (therefore pay attention to formal charges), it is highly unlikely that you will have molecule that isn't overall neutral.

MS identify M+, get MW, look for the isotope patterns esp. for Cl and Br. Nitrogen rule?

IR identify important and common functional groups : C=O, OH, NH, C=C etc.

C-NMR	how many types of C ?	(number of peaks)
	what types of C ?	(chemical shift)
H-NMR	how many types of H ?	(number of peak groups)
	how many of each type ?	(integration)
	what types of H ?	(chemical shift)
	how are they connected together ?	(coupling patterns)

Draw out the fragments identified as structural units showing any bonds that still need to be made.... kind of like pieces from a model kit.

Take care not to duplicate a specific fragment (*e.g.* saying that there is an ester group present but also saying there is an -OR group and hence counting the oxygen twice).

Determine the masses of each of the fragments.

Compare the sum of the masses of the fragments with the MW from the mass spectra.

Do they agree? (note they should match exactly, + or - even 1 unit means it's wrong!)

No ? Then review the spectra and refine the fragments. Look for:

(i) missed atoms *e.g.* O = 16

(ii) missed small pieces *e.g.* C=O = 28

(iii) missed pieces due to duplication *i.e.* symmetry

Remember that you can't add new types of C or H.... any pieces you add must still be consistent with all the spectra.

Repeat this process until MW and hence MF is found.

Yes...Good, then move on....

THERE IS LITTLE POINT IN MOVING ON TO ASSEMBLE THE FRAGMENTS UNTIL YOU HAVE IDENTIFIED ALL THE PIECES SINCE THERE IS NO WAY YOU CAN GET THE CORRECT ANSWER AND YOU WILL LIKELY MAKE MISLEADING CONNECTIONS.

Calculate the IHD from the MF (this helps define the types of structural units that might be present such as multiple bonds and rings).

Organise the fragments according to number of unfilled valances *i.e*. 4 unfilled = quaternary C, 3 = CH, 2 = CH_2, 1 = CH_3, OH, X *etc*.
Note: Think of non-hydrocarbon pieces as substituents... it's often better to incorporate these later (key information from H NMR chemical shifts)

Now we start to join the pieces together but REMEMBER that you MUST obey the basic rules of valence! Note that sometimes simple logic can help dictate where specific fragments must go. Pay attention to symmetry if there is any.

First look at the hydrocarbon fragments and start to join them together based on the H-NMR coupling patterns. It can also useful to note what pieces can't be joined...

Now add the substituents using (in terms of importance and usefulness) H-NMR > C-NMR > IR : Pay close attention to chemical shifts (H and maybe C-NMR) and may be coupling patterns (H-NMR).

CHECK to make sure the structure (or partial structures) fit the spectroscopic data, especially the H-NMR data.... it's the most obvious to review.

Does it work ? If not, disconnect back the fragments (or partially disconnect) and start again...

If you think it works, recheck the IHD and the MF again, then number of types of C, then review the H-NMR to make sure they are consistent with the structure.

Does it work ? If not, disconnect back the fragments (or partially disconnect) and refine....

OK ? **DONE**