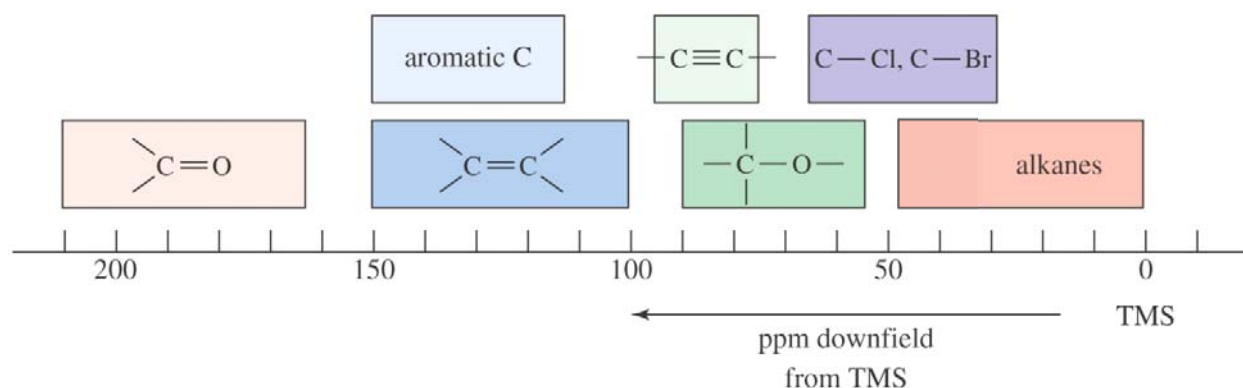


Workshop 2 Solutions
Structure Determination w/ Complex 1D NMR

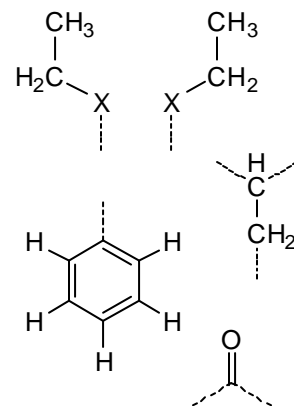
1. a. I looked at the ^{13}C NMR spectrum first on this one, but you could also start with the ^1H spectrum. Looking at the chemical shifts of the ^{13}C peaks, it looks like our molecule has a carbonyl carbon, four aryl/alkene carbons, one alcohol/ether carbon, two alkyl carbons, and one carbon either in the halide section or on the alkyl/alcohol border.



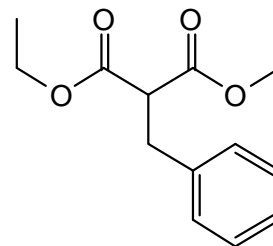
Our ^1H NMR has 5 aryl protons but no alkene protons, so I'm betting that the four aryl/alkene carbons are aryl carbons. There are only four, so that means our aryl group has some symmetry to it—probably a $-\text{C}_6\text{H}_5$ group given the 5 protons.

The ^1H NMR has four multiplets. Starting with the smallest one ($\delta = 3.8$ ppm), we have one lone proton coupled to two neighbors (because it's a triplet). I would say a strong candidate for those two neighbors is the doublet at $\delta = 3.1$ ppm, which represents two protons coupled to one neighbor. Those two multiplets match up nicely.

The quartet at $\delta = 4.1$ ppm corresponds to four protons, which can't all be attached to the same carbon, coupled to three neighbors. The chemical shift of these is downfield, suggesting that they may be on carbons that also bear electronegative atoms (like oxygens). The triplet at $\delta = 1.1$ ppm has intensity 6H, suggesting two methyl groups next to $-\text{CH}_2-$ units. In fact, this quartet-triplet pair looks very much like two equivalent ethyl groups, maybe ethoxy groups. Summing up what we know so far:

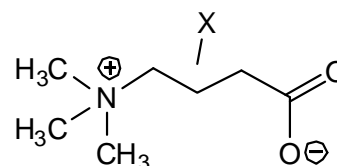


Important to keep in mind, the $-\text{CH}-\text{CH}_2-$ segment probably aren't attached directly to the electronegative atoms X (based on chemical shift). That means our structure could be:



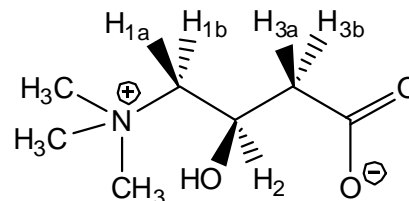
- b. In the ^1H -coupled ^{13}C NMR, the ethyl groups make great sense--one resonance is a triplet of quartets, and the other is a quartet of triplets. The $-\text{CH}-$ group also works, but the central $-\text{CH}_2-$ group looks like it is split too much (a triplet of quartets). My guess is that that carbon is coupling with the two *ortho*-phenyl ring protons. The rest is a bit messy.
2. a. Our ^1H NMR does indeed have a giant (9H) singlet that could represent a $-\text{N}(\text{CH}_3)_3^+$ group. And the ^{13}C NMR has a peak at $\delta = 181$ ppm that could be the carboxylate group. So our spectra are definitely consistent with these groups.

- b. Our mystery molecule has five carbons (or types of carbons)--a carboxylate, an $-\text{N}(\text{CH}_3)_3^+$ group, and three more in the middle. The molecule also has five unexplained H's. If we assume the three carbons are sp^3 -hybridized (otherwise they would appear in different parts of the ^{13}C spectrum), we're looking at:



I have an “-X” hanging out in space, because we don't know where it's attached yet. The two H's at $\delta = 2.4$ ppm must be α to the carboxylate—chemical shift tables say that exactly where they would be.

Those protons are inequivalent, and each is a doublet of doublets—split by each other and just one neighbor. The only way that would be true is if the “-X” is in the middle.



- c. H_{1a} and H_{1b} are chemically inequivalent and coupled to one another, but are so close in chemical shift that their multiplets are distorted severely. H_{3a} and H_{3b} have the same problem, though less severe. We might call this system an “ABMX Y ” system, or two separate “ABX” systems. We wouldn't use any prime notation (*e.g.*, AA'B) here because we reserve that for cases of chemical equivalence and magnetic non-equivalence. None of the protons here are chemically equivalent.
- d. This was a weird one. The triplets are clearly not 1:2:1 triplets—they look more like 1:1:1 triplets, like the kind you would see for ^{13}C - ^2H coupling. But our molecule doesn't have any deuterium in it. D_2O would exchange with the alcohol

-OH to turn it into -OD, but because that -OD would be fluxional and H-bonded, it wouldn't show consistent coupling.

The coupling here is actually due to ^{13}C - ^{14}N coupling. ^{14}N has spin $I = 1$, so it will split neighbors just like deuterium does. The fact that ^{14}N has an incredibly short T_1 (microseconds) means that ^{14}N - ^1H and ^{14}N - ^{13}C coupling isn't typically observed in 1D NMR. But when the nitrogen is cationic, T_1 slows down and it is possible to see splitting. (Ammonium salts in CDCl_3 show the same behavior in ^1H NMR, with very large ^{14}N - ^1H coupling constants.)