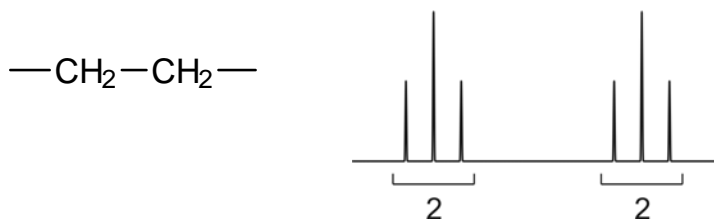
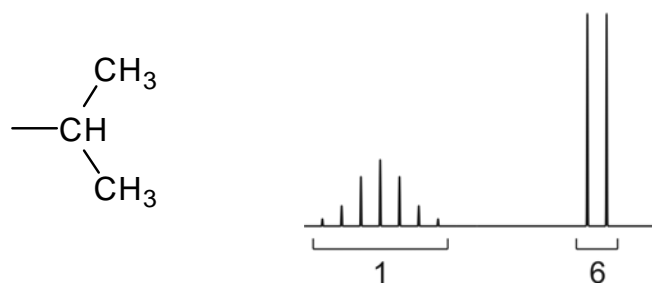
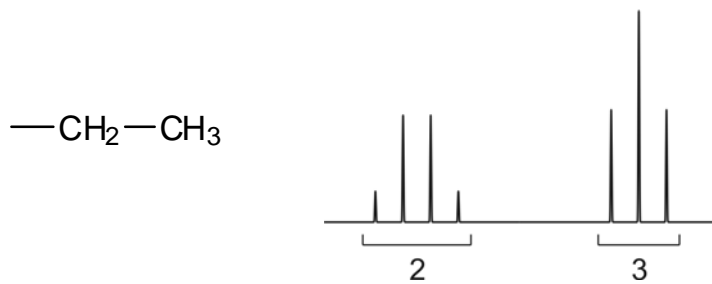


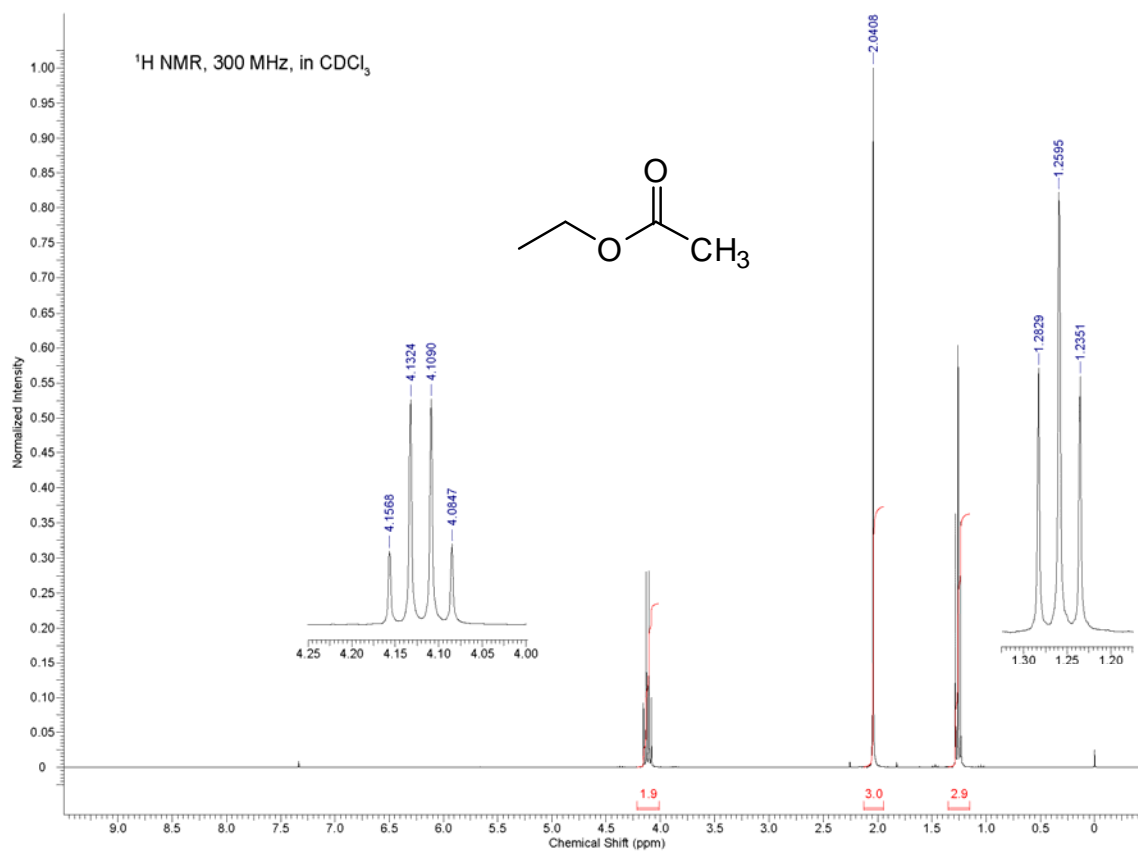
**Discussion Section Exercise Solutions**  
**Simple NMR Assignments**

Before answering these problems, it would be helpful to think about what kinds of peak patterns you might expect for different arrangements of protons in common alkyl groups. Examples:

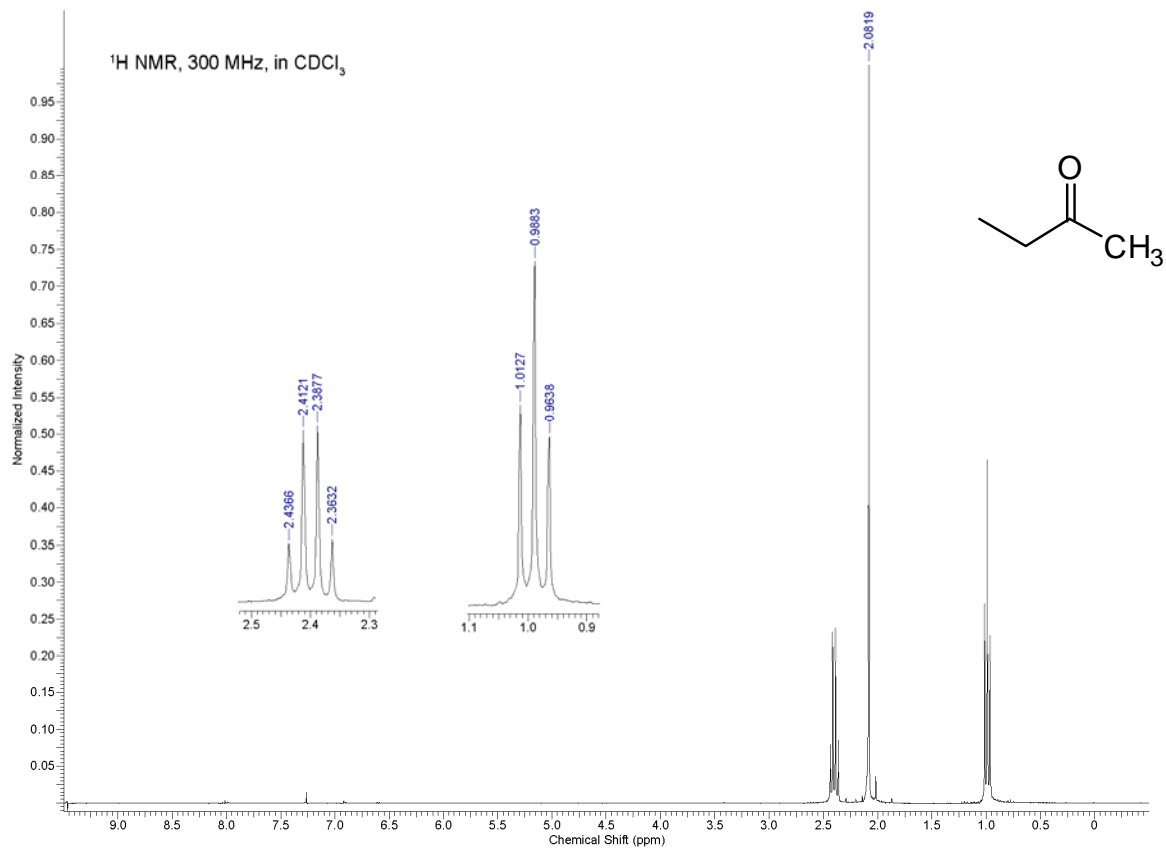


As you get used to doing problems in this class, you will gradually get better at finding these patterns in complicated spectra, and identifying what alkyl groups are present in a molecule.

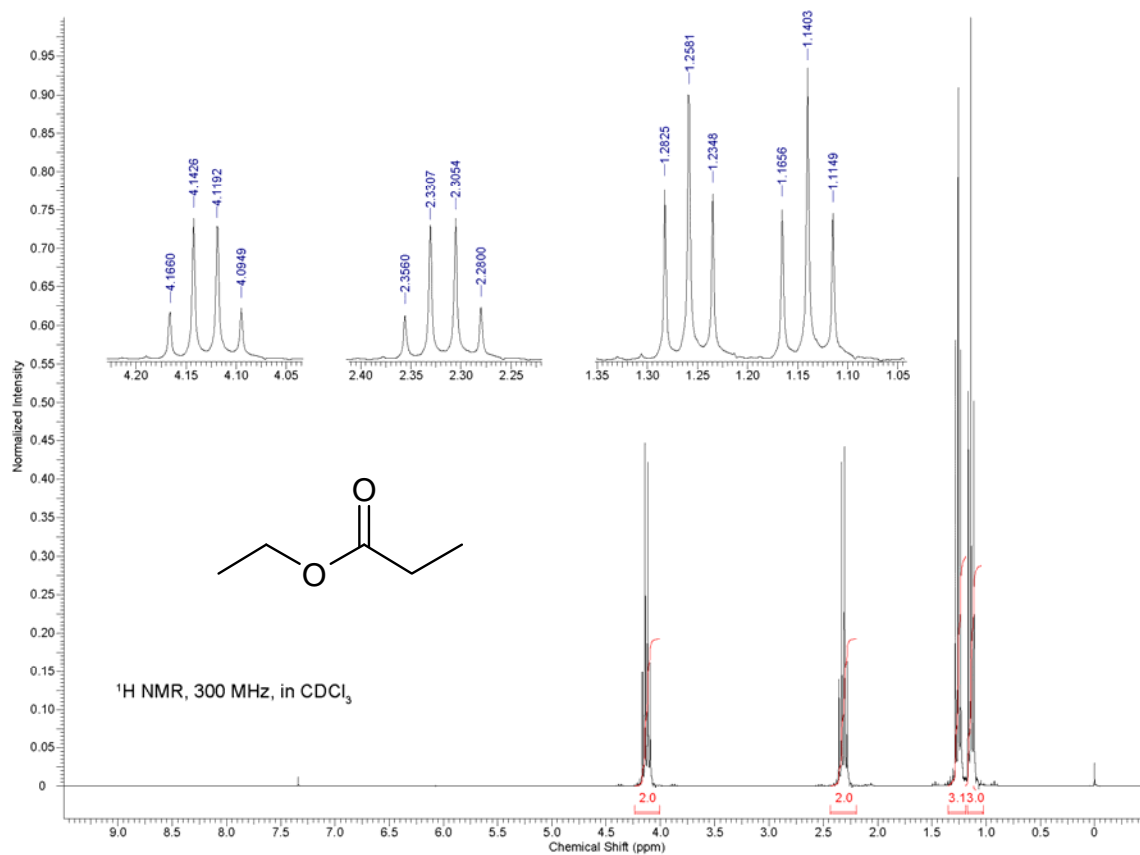
So how about those molecules?



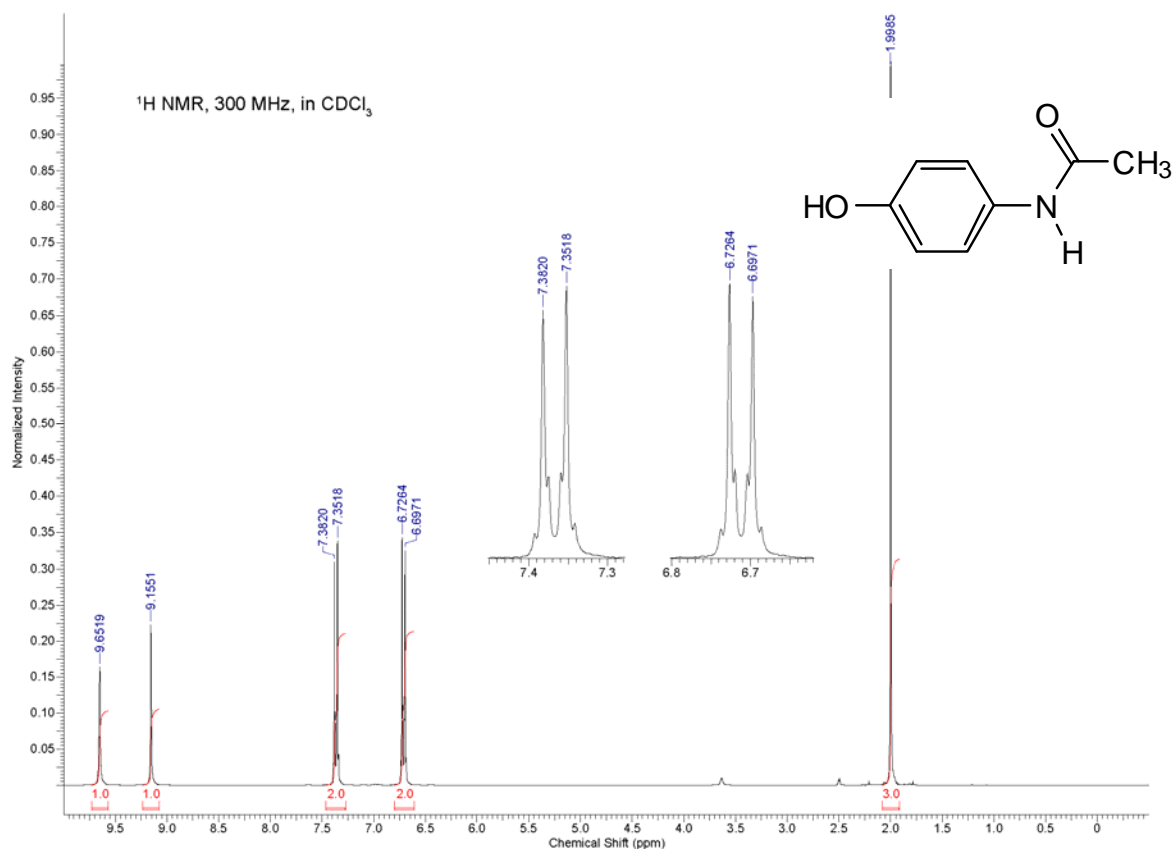
This molecule has that quartet-triplet pattern that is characteristic of an ethyl group. There is also a 3H-intensity singlet that is indicative of a methyl group. The quartet is pretty far downfield, suggesting that its protons are attached to something very electron withdrawing, like an oxygen atom. But our methyl group is not that far downfield, so it isn't attached to that same atom.



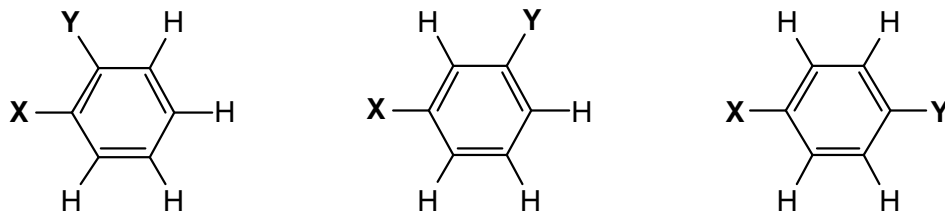
Same ethyl group pattern, but this time the quartet H's aren't attached to something quite as electron-withdrawing.



Here we've got two ethyl groups, one attached to something more electron withdrawing, the other attached to something less electron withdrawing, and no other protons in the molecule.



Here we have some peaks in unique parts of the spectrum—two multiplets in the 6.5–8.5 ppm, aromatic region, and two singlets in the > 9 ppm region. So our molecule probably has a benzene ring, and some other fun functional groups. The two multiplets look like doublets, but the zoom-ins reveal some little details; for now, let's just consider them doublets, with 2H intensity each. How might a benzene be substituted with 4 protons?



Of these, the *ortho*-disubstituted one on the left has four inequivalent protons, the *meta*-disubstituted one has three, and the *para*-disubstituted one has two. So the benzene ring is probably *para*-disubstituted. For that *para*-disubstituted benzene, each proton has only one inequivalent vicinal neighbor, which explains the doublet. (Each proton also has an inequivalent 4-bond neighbor, which is partially responsible for the fine

structure (with a different coupling constant) around each peak. We'll talk a little about multiple coupling constants in a couple of class periods. The big difference between the chemical shift of the two doublets probably indicates that X and Y are different.

The spectrum also has a 3H-intensity methyl group, and those two 1H-intensity protons that are very far downfield—they could be anything, but they aren't coupled to any partners. Looking at chemical shift tables, that makes them either isolated aldehydes, or protons attached to very electronegative groups (like carboxylic acid, amide, or phenol H's). I think there are a few different ways you could arrange the groups you have to work with here, so I'm not sure that this  $^1\text{H}$  NMR gives you all the information you need to know to solve the problem, but it's certainly consistent with the structure on the previous page.