

Additional Problems for practice.

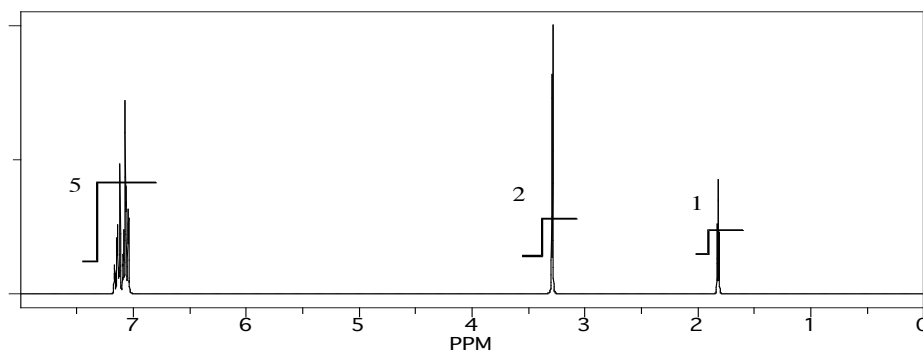
1. Predict the structure of the molecules given by the following spectral data:

a

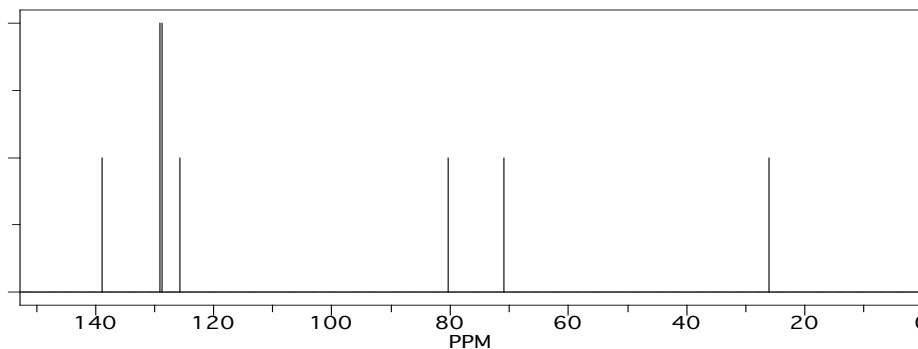
Mass spectrum:  $M^+ = 116$

IR: weak absorption at  $2190\text{ cm}^{-1}$   
medium absorption at  $1600\text{ cm}^{-1}$

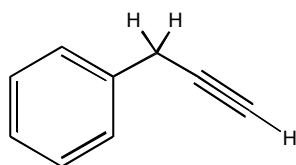
$^1\text{H NMR}$



$^{13}\text{C NMR}$

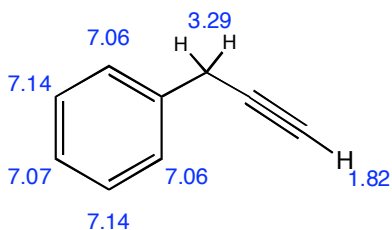


There are five aromatic protons at 7.1 ppm. This indicates a mono-substituted benzene ring, the IR absorption at  $1600\text{ cm}^{-1}$  (Ar-H stretch) confirms this. There is a singlet at 3.3 ppm accounting for 2 protons, thus this is a  $\text{CH}_2$  group with no protons on neighboring carbon atoms. There is a singlet at 1.8 ppm accounting for one proton, so this proton is attached to a carbon with no protons on neighboring carbon. The weak  $2190\text{ cm}^{-1}$  absorption in the IR is indicative of a triple bond.  $^{13}\text{C}$  shows aromatic carbons between 120 and 140 ppm; the two peaks at 71 and 81 ppm must account for alkyne carbons; the peak at 25 ppm is an aliphatic carbon atom, but because it is deshielded relative to a normal alkane, it must be next to an aromatic ring. Putting these pieces together, you may come up with the following structure:

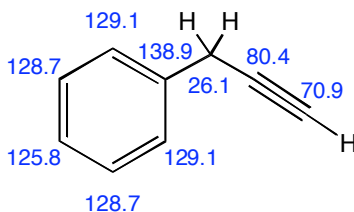


mass=116 g/mol

$^1\text{H}$  NMR chemical shifts:



$^{13}\text{C}$  NMR chemical shifts:

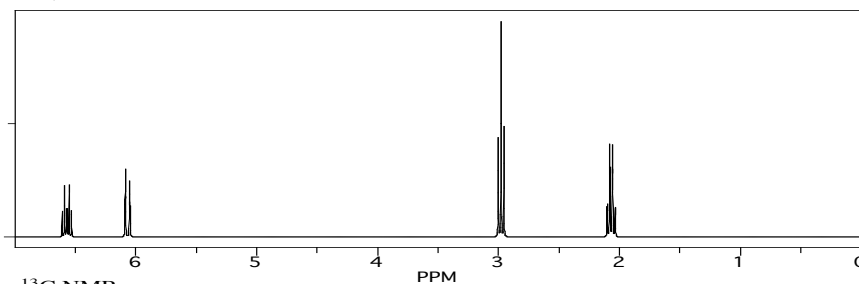


b.

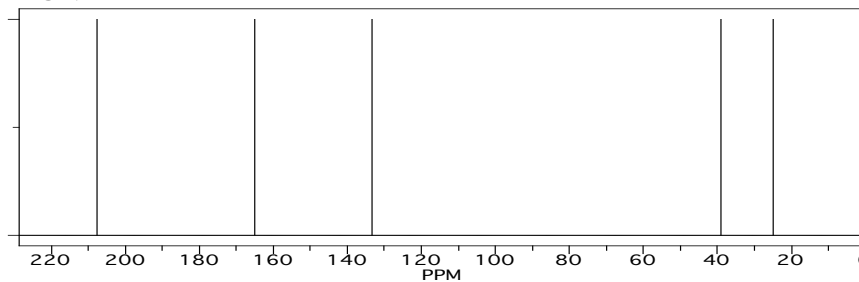
Mass spectrum:  $M^+$  = 82  
molecular formula:  $\text{C}_5\text{H}_6\text{O}$

IR:  $1690\text{ cm}^{-1}$  (strong) with a shoulder at  $1626\text{ cm}^{-1}$

$^1\text{H}$  NMR

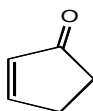


$^{13}\text{C}$  NMR



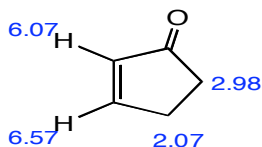
The  $^{13}\text{C}$  absorption at  $208\text{ ppm}$  can only indicate the present of a ketone carbonyl carbon; the peaks at  $135\text{ ppm}$  and  $165\text{ ppm}$  are likely to be alkene carbons; Now the IR indicates a strong  $1690\text{ cm}^{-1}$  which is definitely  $\text{C}=\text{O}$ , but it is conjugated since the ordinary  $\text{C}=\text{O}$  stretch occurs at  $1710\text{ cm}^{-1}$ . The shoulder at  $1626\text{ cm}^{-1}$  indicates the

alkene that is conjugated with the carbonyl. Indeed, the  $^1\text{H}$  NMR confirms this assignment: the absorptions at 6.1 and 6.6 ppm are indicative of two alkene protons. One of the alkene protons shows up as a doublet, indicating that there is only a single proton next door; the other alkene proton shows up as a doublet of triplets, which means that the proton is being split by two different types of protons: a single proton splits the absorption into a doublet, and a pair of other neighboring protons splits the resulting doublet into a pair of triplets. At 3.0 ppm we see a triplet, which indicates two protons neighboring this set of protons; its chemical shift indicates that these protons are next to the carbonyl unit, and the carbon atom to which they are attached absorbs at 40 ppm in the  $^{13}\text{C}$  NMR. The 3.0 ppm absorption also leans toward the quartet at 2.1 ppm, indicating the protons giving rise to these two absorptions are spin-spin coupled. The quartet at 2.1 ppm indicates protons that have three neighboring protons. The carbon atom to which these protons are bound absorbs at 25 ppm, deshielded relative to the alkane carbons, indicating that either an alkene or an aromatic ring (discounted based on molecular formula) is nearby. The molecular formula,  $\text{C}_3\text{H}_6\text{O}$ , indicates three degrees of unsaturation. We have already accounted for two: a  $\text{C}=\text{O}$  unit conjugated to a  $\text{C}=\text{C}$  unit. The remaining unsaturation can only be accounted for by a ring:

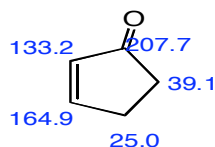


mass= 82 g/mol

$^1\text{H}$  NMR chemical shifts:



$^{13}\text{C}$  NMR chemical shifts:

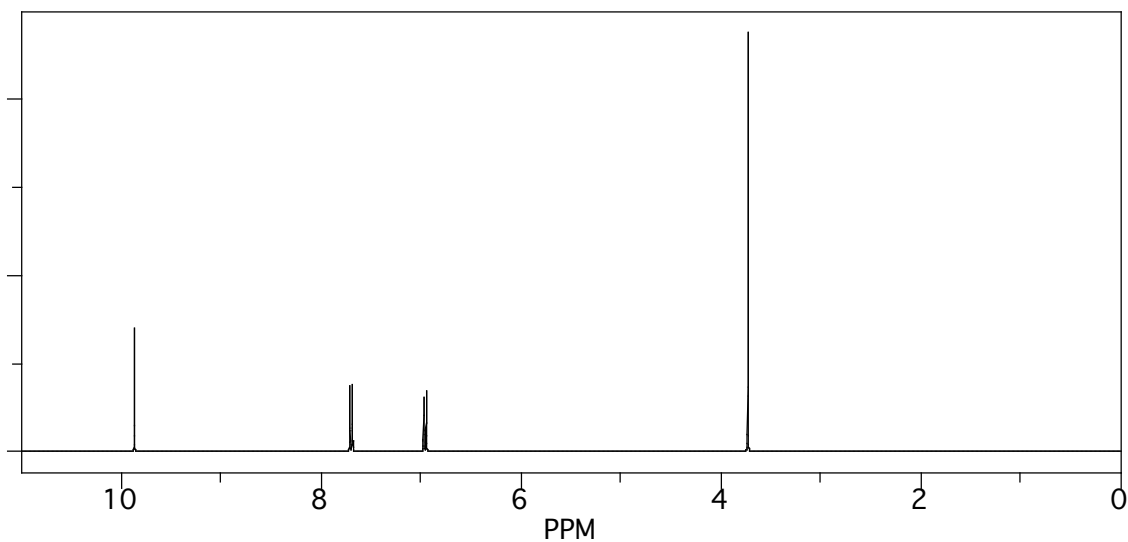


c.

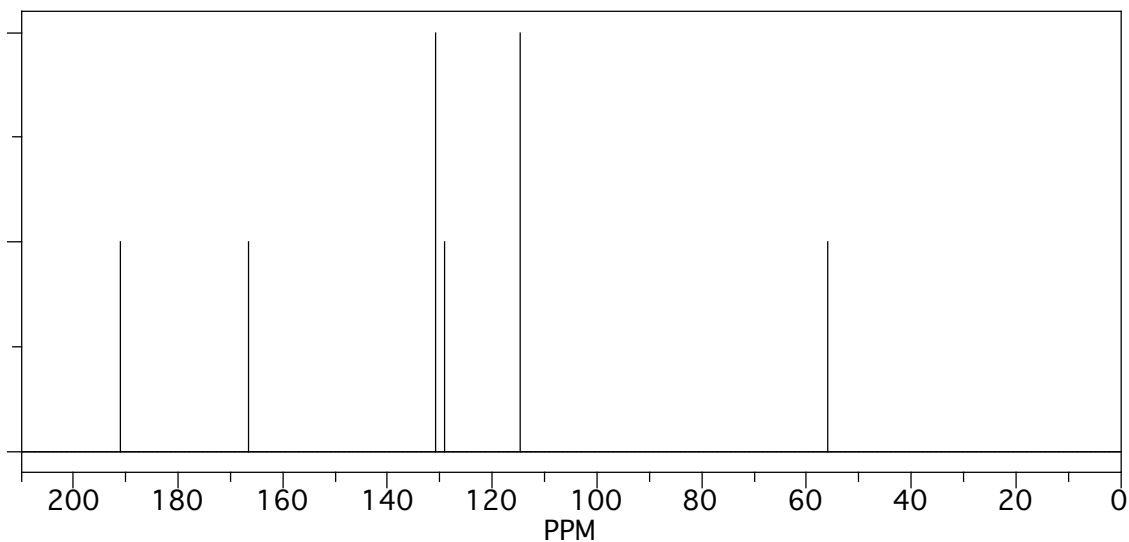
mass spectrum:  $M^+ = 136$

IR:  $1691\text{ cm}^{-1}$  (strong);  $1600\text{ cm}^{-1}$  (medium)

$^1\text{H NMR}$

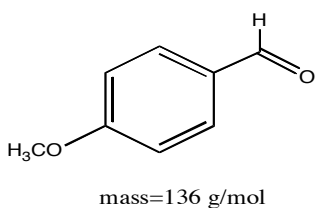


$^{13}\text{C NMR}$

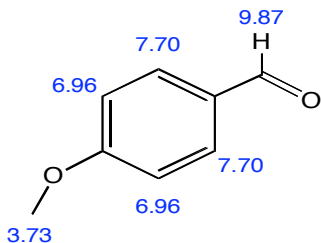


The IR again indicates the presence of a conjugated carbonyl: strong absorption at  $1691\text{ cm}^{-1}$ ; there is no alkene shoulder, but the absorption at  $1600\text{ cm}^{-1}$  is indicative of an aromatic ring, so we can assume that the carbonyl is directly bonded to (conjugated with) the aromatic ring. Looking at the  $^1\text{H NMR}$ , we can immediately tell what kind of carbonyl compound it is: the singlet at 9.8 ppm is characteristic of aldehyde protons. The carbonyl carbon of the aldehyde shows up at 191 ppm in the  $^{13}\text{C NMR}$ . We can also tell the substitution pattern of the aromatic ring: there are only two sets of absorptions in the 7-8 ppm region, and both are doublets, which means

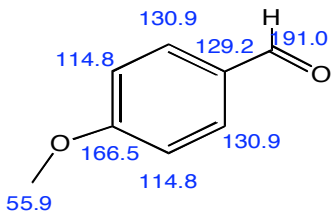
the protons giving rise to those absorptions have only a single other proton nearby. A high degree of symmetry is implied, thus we may guess that the aromatic ring is 1,4 disubstituted, with one of the substituents being an aldehyde. Now in the  $^{13}\text{C}$  spectrum, we see a strongly deshielded aromatic carbon shows at 168 ppm; this indicates that an electronegative element like oxygen, chlorine, bromine, etc is directly bound to that carbon atom. We also see the regular aromatic carbons at 128 and 131 ppm, respectively, but we can also see an unusually shielded absorption at 115 ppm, looking like roughly 2 carbons. Only an electron donating group on the aromatic ring could give rise to this type of shielding, so the other substituent on the aromatic ring is also an electron-donor. Looking back at the proton NMR, we see a large singlet at 3.8 ppm, probably indicating a methyl group attached to an oxygen (as we have seen in methanol), so a good candidate for the electron-donating group is the methoxy group. The methyl carbon directly bonded to oxygen absorbs at 57 ppm in the  $^{13}\text{C}$  spectrum. Putting all this information together gives us the following structure:



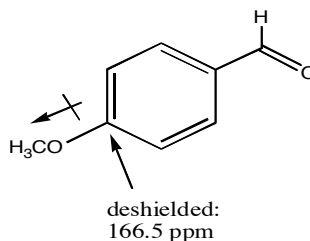
$^1\text{H}$  NMR chemical shifts:



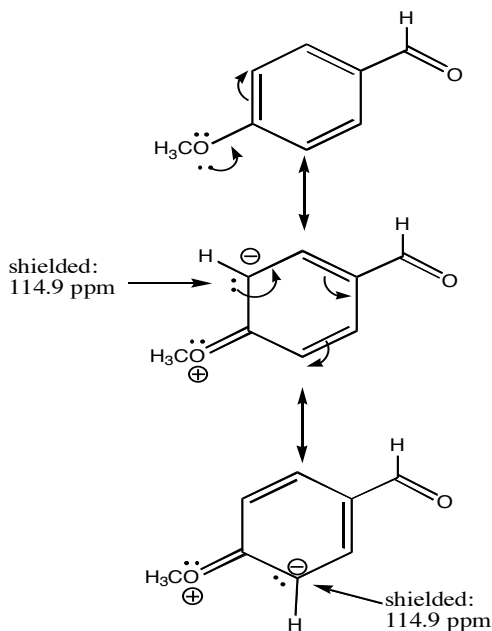
$^{13}\text{C}$  NMR chemical shifts:



Note: deshielding effect of OMe due to oxygen's electronegativity:



shielding effect of MeO (oxygen is a pi electron donor):



d.

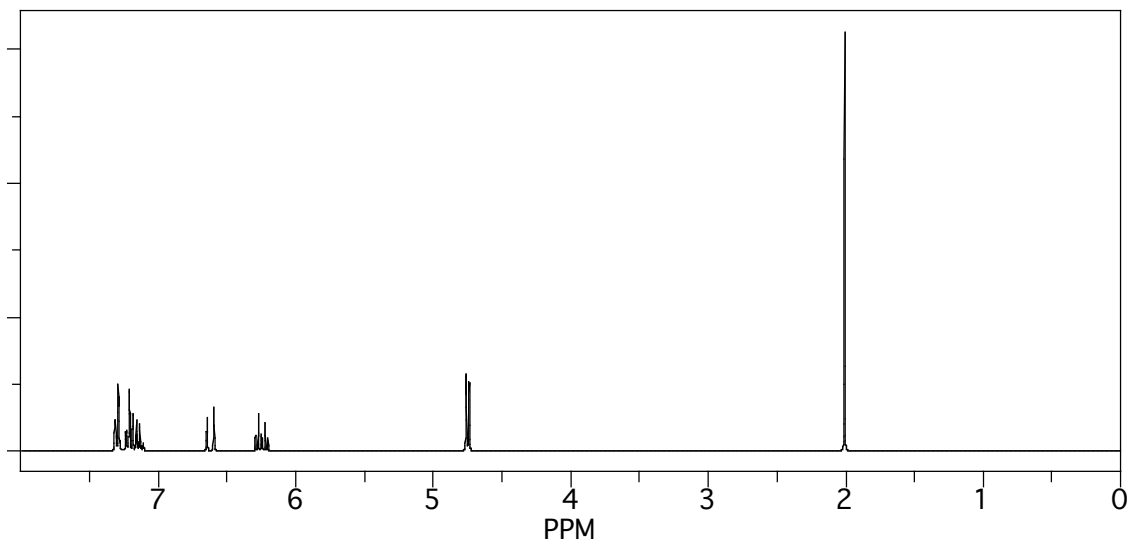
Mass spectrum:  $M^+ = 176$

molecular formula:  $C_{11}H_{12}O_2$

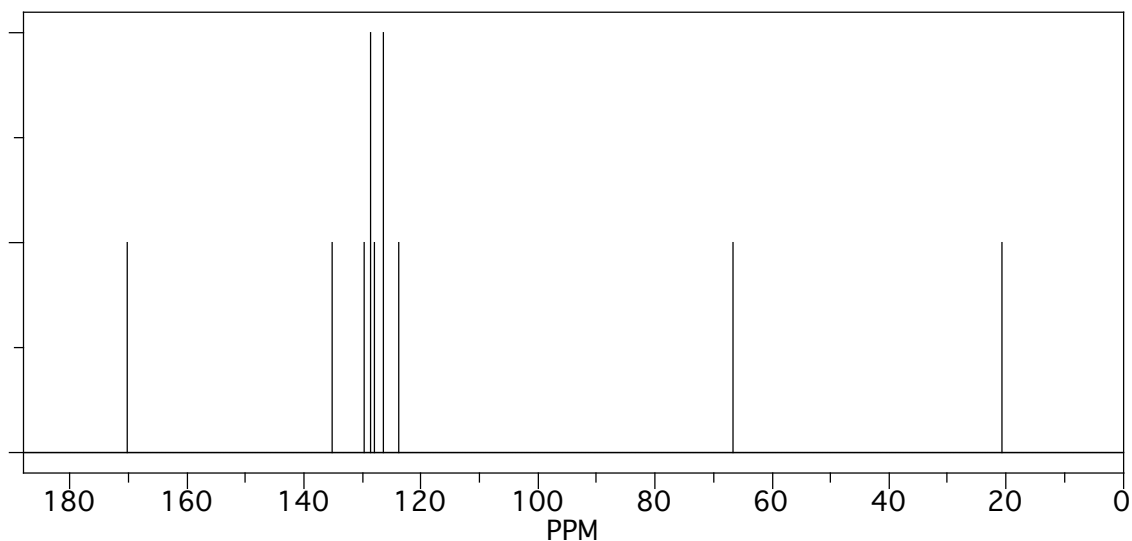
IR:  $1735\text{ cm}^{-1}$  (strong);  $1660\text{ cm}^{-1}$  (medium)

$1600\text{ cm}^{-1}$  (medium)

$^1\text{H NMR}$

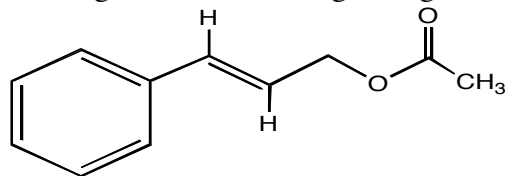


$^{13}\text{C NMR}$



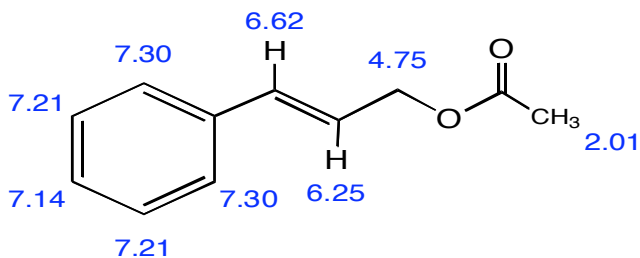
This compound shows aromatic protons (7.2-7.3 ppm) and alkene protons (6.2 and 6.6 ppm); we can confirm the presence of these functional groups in IR: the  $1600\text{cm}^{-1}$  absorption and  $1660\text{ cm}^{-1}$  absorptions indicate the aromatic C-H stretch and the C=C stretch, respectively. Now we also see the presence of an ester in the IR: a C=O

absorbing at  $1735\text{ cm}^{-1}$  is characteristic of esters. The  $^{13}\text{C}$  NMR confirms the ester carbonyl carbon at 190 ppm; all the aromatic protons show up between 125 and 135 ppm. The absorption at 65 ppm indicates a group bound to an electronegative atom; since the molecular formula only has oxygen in it, this atom must be oxygen. Atom. Now the splitting pattern for the alkene protons tells us a lot of information: the deshielded alkene proton at 6.6 ppm is a doublet, indicating only one other proton next door; this other proton could be another alkene proton. Since there seems to be a large splitting (coupling constant  $\sim 15$  ppm), we may be looking at a trans alkene. The other alkene proton at 6.2 ppm is a doublet of triplets, indicating two distinct types of protons next to this proton; one of the neighboring protons must be an alkene proton (trans) which the absorption to a doublet; two other protons are present which splits each of the doublet peaks into a triplet. Thus the alkene has a  $\text{CH}_2$  next to it. We can verify this if we look at the next absorption in the  $^1\text{H}$ NMR: at 4.7 ppm we see a doublet, which is the  $\text{CH}_2$  being split by a single neighboring proton (an alkene proton), and this chemical shift value indicates the presence of a nearby electronegative oxygen atom. The only other absorption in the proton NMR is a singlet at 2.0 ppm (probably a methyl group); its chemical shift (and also that of its corresponding carbon at 20 ppm in the  $^{13}\text{C}$  NMR) indicate that it is next to a carbonyl. Putting all of this info together gives the following structure:

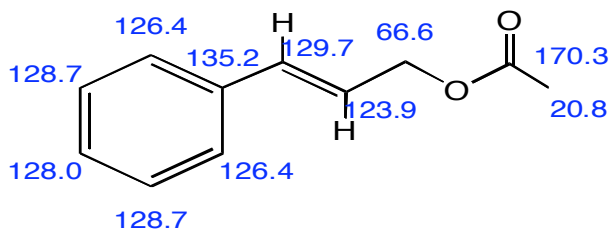


mass=176 g/mol,  $\text{C}_{11}\text{H}_{12}\text{O}_2$

$^1\text{H}$  NMR chemical shifts:



$^{13}\text{C}$  NMR chemical shifts:



2. Show a splitting tree for the Ha, Hb, and Hc protons in the following compound, and match your predicted multiplet patterns with the spectrum shown below. Indicate rough values for coupling constants on your diagram.

