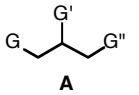
question 2: 35 points

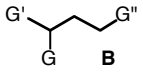
Fragments:

- IHD = 4, 1 point
- 10 H's on C's, 1 point
- $NH_2$, 1 point
- OH, 1 point
- Phenyl group, 3 points

By looking at the $C^{13}$ spectrum, a phenyl group can be recognized. This assignment is supported by 5 protons in the aromatic region of the $^1H$ NMR spectrum (7.40-7.22 ppm). Also from the $^{13}C$ spectrum, one can deduce that there must be an amino and hydroxyl group (since 3 H's are not on C).
This assignment is further supported by the IR spectrum.
At this point, there are 3 resonances that are unassigned in the $^{13}$ C spectrum: 66.2, t; 54.1, d; 40.8, t
Since all units of unsaturation have been accounted for, we know that the three groups must be positioned on a propane backbone with no methyl groups. The possibilities are:



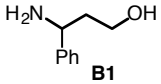

**A**



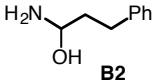

**B**

G = Ph, $NH_2$, OH

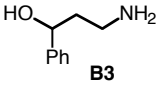
We can rule out **B** in several ways. One way would be to consider the $^1H$ chemical shifts of the methine protons of structures **B**. None of the possible structures (B1-3)gives an acceptable value for the methine chemical shift.




**B1**

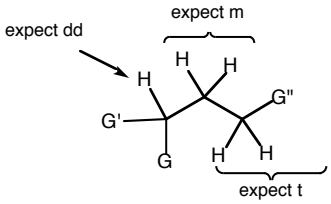



**B2**

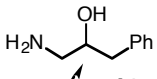



**B3**

In each case, we would expect the methine proton to resonate at > 4 ppm, since the effect of having more than one electron withdrawing group on the same carbon atom is additive (see table 13.1). Furthermore, the coupling constants cannot be explained by structures B:

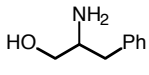



Thus, we are left with structures **A1-3**. **A1** is ruled out because of the $^1H$ and $^{13}C$ chemical shift of the methine. Structures **A2** and **A3** can only be discerned by their mass spectra (see below).

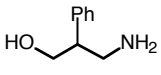



**A1**

This is ruled out because
54 ppm and 3.17 ppm are
too far upfield for this methine

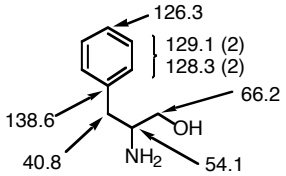



**A2**

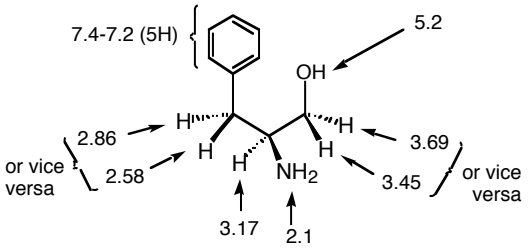



**A3**

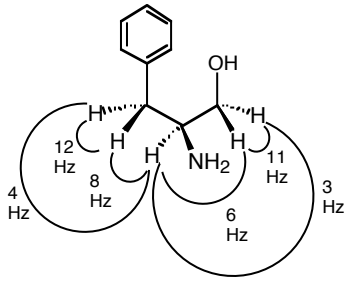
**$^{13}$C assignments**




**$^{1}$H assignments**



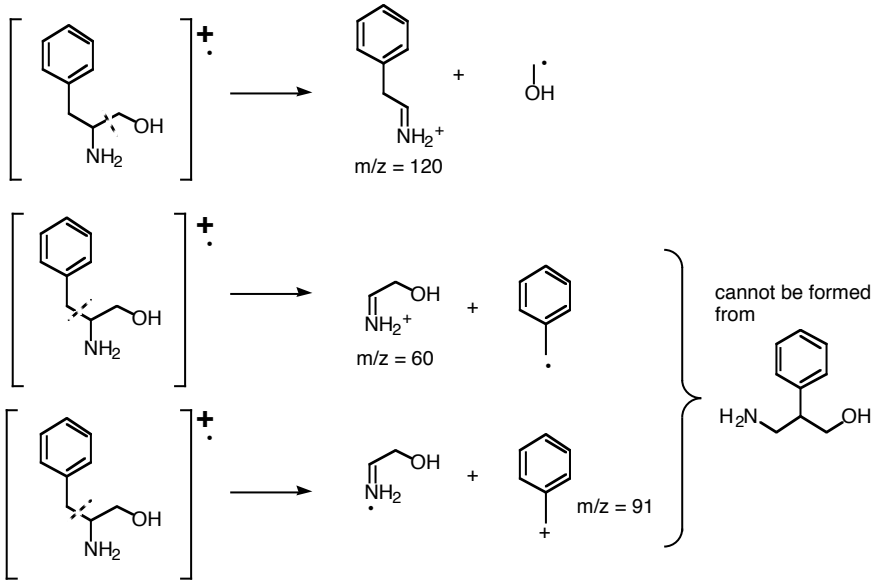

**$J_{H\text{-}H}$ assignments**




**IR assignments**

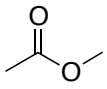
various acceptable answers

Mass Spec assignments



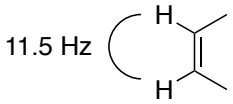
question 3: 35 points

Fragments
IHD = 2 (1 point); H's on C = all 18 (1 point)

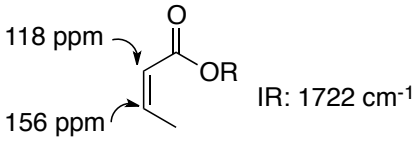


ester, 2 points

alkene, 2 points

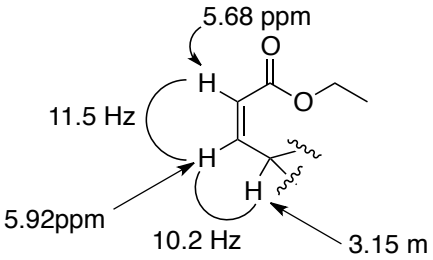



cis-alkene (2 points)



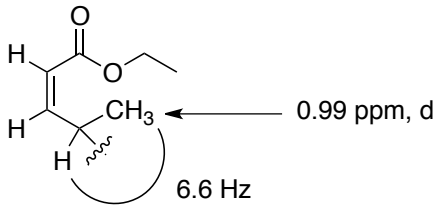

α,β-unsaturated ester
(2 points)

The structure can be elucidated by noting first that the group on oxygen must be a methylene ($^1$H: 4.15, q; $^{13}$C: 59.7, t). The proton resonance tells us that this is an ethyl ester, and the coupling constant (7.2 Hz) tells us that the methylene is coupled to either the methyl group at 1.27 ppm (J=7.1 Hz) or the methyl at 0.88 Hz (J = 7.2 Hz). Either assignment was accepted, although the correct one is the 1.27 ppm resonance (an error bar of +/- 0.1 Hz is not uncommon)

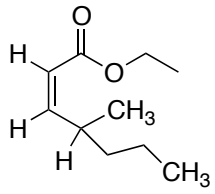



We proceed by noting that the alkene resonance at 5.68 ppm is coupled to only 1 proton (J=11.5 Hz), but that the other olefinic resonance is a doublet of doublets, with J= 11.5 and 10.2 Hz. This means that there is a single proton on the 'other side'. The only possibility is that it is coupled to the methine proton: 3.50 ppm, m.

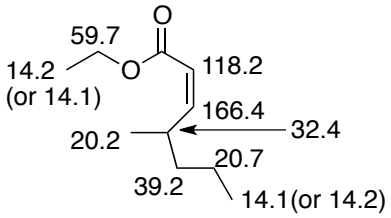
We can further note that the methyl group at 0.99 ppm is a doublet, and must also be coupled to the methine.



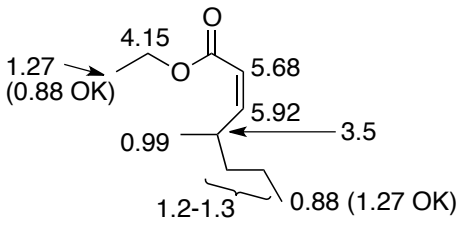

Only 2 methylenes and a methyl group remain. They are filled in as follows:



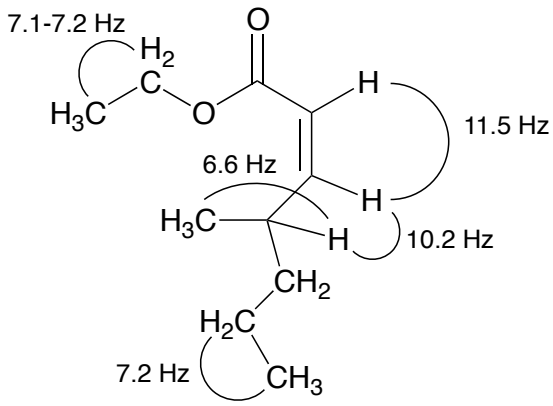
**$^{13}$C assignments**




**$^{1}$H assignments**




***J*$_{H-H}$ assignments**




**IR assignments**

must note:

1722 cm$^{-1}$ $\alpha,\beta$ unsaturated ester