question 2: 35 points

Fragments:
• IHD = 4, 1 point
• 10 H's on C's, 1 point
• NH₂, 1 point
• OH, 1 point
• Phenyl group, 3 points

By looking at the C¹³ 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 ¹³C 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 ¹³C 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:

![Chemical Structures](image)

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.

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 ¹³C chemical shift of the
methine. Structures A2 and A3 can only be discerned by their mass spectra (see below).

This is ruled out because
54 ppm and 3.17 ppm are
too far upfield for this methine
**$^{13}$C assignments**

- 138.6
- 138.1 (2)
- 126.3
- 129.1 (2)
- 128.3 (2)
- 66.2
- 54.1

**$^1$H assignments**

- 7.4-7.2 (5H)
- 2.86
- 2.58
- 2.1
- 3.17
- 3.69

**J_{HH} assignments**

- 12 Hz
- 11 Hz
- 8 Hz
- 6 Hz
- 3 Hz

**IR assignments**

- various acceptable answers

**Mass Spec assignments**

- \[
\begin{array}{c}
\text{[\text{mass spec structure}]^+} \\
\text{m/z = 120}
\end{array}
\]

- \[
\begin{array}{c}
\text{[\text{mass spec structure}]^+} \\
\text{m/z = 60}
\end{array}
\]

- \[
\begin{array}{c}
\text{[\text{mass spec structure}]^+} \\
\text{m/z = 91}
\end{array}
\]

\[
\begin{align*}
\text{cannot be formed from} & \\
\text{H}_2\text{N} & \xrightarrow{\cdot} \text{OH}
\end{align*}
\]
question 3: 35 points

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

\[
\begin{align*}
\text{ester, 2 points} & \quad \text{alkene, 2 points} & \quad \text{cis-alkene (2 points)} & \quad \text{\(\alpha,\beta\)-unsaturated ester (2 points)}
\end{align*}
\]

The structure can be elucidated by noting first that the group on oxygen must be a methylene (\(^1\H: 4.15, \text{q}; ^{13}\text{C}: 59.7, \text{t}\)). 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:
\[ ^{13}C \text{ assignments} \]

\[
\begin{align*}
14.2 & \quad \text{(or 14.1)} \\
20.2 & \quad 118.2 \\
39.2 & \quad 166.4 \\
& \quad 20.7 \\
& \quad 32.4 \\
& \quad 14.1 \text{(or 14.2)}
\end{align*}
\]

\[ ^{1}H \text{ assignments} \]

\[
\begin{align*}
1.27 & \quad \text{(0.88 OK)} \\
4.15 & \quad 5.68 \\
0.99 & \quad 5.92 \\
1.2-1.3 & \quad 0.88 \text{ (1.27 OK)}
\end{align*}
\]

\[ J_{H-H} \text{ assignments} \]

\[
\begin{align*}
7.1-7.2 \text{ Hz} \\
6.6 \text{ Hz} \\
10.2 \text{ Hz} \\
11.5 \text{ Hz} \\
7.2 \text{ Hz}
\end{align*}
\]

\[ \text{IR assignments} \]

must note:

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