1. Rank the following compounds in the trend requested. (15 points each)
   a. Rank by downfield shift in a $^1H$ NMR spectrum. Consider the hydrogen that has the
downfield shift in each compound. The compound that has the farthest downfield shift
is 1, while the compound with the least downfield shift is 5.

   ![Chemical structures](image1)

   1  2  3  4  5

   b. Rank by number of signals in a spin decoupled $^{13}C$ NMR spectrum. The compound with
the least number of signals is 1, while the compound with the most number of signals is 5.

   ![Chemical structures](image2)

   1  2  3  4  5

   c. Rank by energy of multiple bond stretch in an infrared spectrum. Consider only the
multiple bonded part of each compound that shows the highest energy stretch for each compound
in the IR spectrum. The compound with the highest energy stretch is 1, while the compound
with the lowest energy stretch is 5.

   ![Chemical structures](image3)

   1  2  3  4  5
2.(32) Each IR spectrum shown below corresponds to one of the ten compounds listed. Write the letter corresponding to the appropriate structure next to each IR.

---

B
(ester carbonyl with no sp² C-H)

D
(amide N-H stretch)

F
(aldehyde C-H stretch with sp³ C-H)

I
(nitrile stretch, no terminal alkyne)
3. The MS for three alcohols with molecular formula \( \text{C}_4\text{H}_{10}\text{O}_1 \) are shown. They are either 1-butanol, 2-butanol or 2-methyl-2-propanol (all with parent m/z = 74). Draw the structure corresponding to each MS next to the appropriate MS. (4 points each)

all three methyls are equivalent – loss of one methyl is strong peak at m/z = 59

strong peak at m/z = 56 represents loss of water

two different \( \alpha \)-cleavages possible, peaks at 59 and 45

b.(12) Draw the structure representing the most intense peak in each MS. For the first MS this corresponds to m/z = 59, the second m/z = 56 and m/z = 45 in the third.

\[
\begin{align*}
\text{OH} & \quad \text{m/z} = 59 \\
[\text{\text{CH}_2\text{CH}_2\text{OH}}]^+ & \quad \text{m/z} = 56 \\
\text{OH} & \quad \text{m/z} = 45
\end{align*}
\]
4. The IR and spin-decoupled $^{13}$C NMR are shown for four different compounds. The molecular formula is also given for each compound. Indicate what structure corresponds to each compound. (8 points each)

a. $\text{C}_4\text{H}_8\text{O}_2$

\[
\begin{array}{c}
\text{HO} \\
\text{C} \\
\text{OH}
\end{array}
\]

have alcohol in IR and see alkene carbon in $^{13}$C with 2 different types of carbons

b. $\text{C}_4\text{H}_8\text{O}_1$

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{O}
\end{array}
\]

have aldehyde in IR and only observe three types of carbons in $^{13}$C

c. $\text{C}_3\text{H}_6\text{O}_2$

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

have one degree of unsaturation, but have no carbonyl in IR and no alcohol functionality, $^{13}$C shows no alkene carbons and two types of carbon, so therefore must have ring as shown

d. $\text{C}_4\text{H}_6\text{O}_4$

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{HO}
\end{array}
\]

have carboxylic acid in IR and only two carbons in $^{13}$C, must have symmetry as shown for two degrees of unsaturation with given molecular formula
5. Indicate the preferred product for the following reactions. Assume proper work-up for each step. (7 points each)

a. 

\[ \text{OH} \quad \xrightarrow{\text{HBr}} \quad \text{CH}_3\text{CH}(\text{Br})_2 \]

b. 

\[ \text{OH} \quad \xrightarrow{1) \text{TsCl, pyridine}} \quad \text{CH}_3\text{CH} \quad \xrightarrow{2) \text{CH}_3\text{CH} \text{Br}} \quad \text{Br} \]

c. 

\[ \text{OH} - \text{OH} \quad \xrightarrow{\text{H}_2\text{Cr}_2\text{O}_7, \text{pyridine}} \quad \text{CH}_3\text{CH}_2\text{CO} \]

d. 

\[ \text{OH} \quad \xrightarrow{\text{PhCOCl}} \quad \text{PhCH}_2\text{CO} \]

e. 

\[ \text{PhOH} \quad \xrightarrow{1) \text{CrO}_3} \quad \text{PhCO} \quad \xrightarrow{2) \text{CH}_3\text{OH (excess)}, \text{H}^+} \quad \text{PhCO} \]

f. 

\[ \text{OH} \quad \xrightarrow{\text{PBr}_3} \quad \text{Br} \]

g. 

\[ \text{OH} - \text{OH} \quad \xrightarrow{\text{NaIO}_4} \quad \text{CH}_3\text{CH}_2\text{CO} \]
6. The $^1$H NMR of five isomers with molecular formula C$_6$H$_{12}$O$_2$ are shown. Indicate the structure that corresponds to each $^1$H NMR. The integration for each spectrum is indicated. (8 points each)

all compounds have 1 degree of unsaturation

a.  

\[
\begin{array}{c}
\text{splitting pattern indicates an ethyl ester}
\end{array}
\]

c.  

\[
\begin{array}{c}
\text{have an acid (due to peak at ~12ppm) with this symmetry to have only 2 singlets}
\end{array}
\]

e.  

\[
\begin{array}{c}
\text{must have alcohol (due to peak disappearing with D$_2$O at 3.8 ppm and symmetry of other three singlets proves structure}
\end{array}
\]

b.  

\[
\begin{array}{c}
\text{splitting pattern indicates an isopropyl ester}
\end{array}
\]

d.  

\[
\begin{array}{c}
\text{have acetate and splitting indicates this isobutyl substituent}
\end{array}
\]

7.(28) A combustion analysis was performed on an unknown compound A and it was determined that it contained nine carbons and eleven hydrogens in its molecular formula. Any other elements, however, were not tested so it is unknown what else it might contain. The mass spectrum for compound A determined the parent molecular ion peak to have a m/z of 154. The MS and $^1$H NMR for A are shown on the following page. (In the $^1$H NMR for A the peak at 7.11 ppm is a triplet and the peak at 7.04 ppm is a doublet. The peak at 1.5 ppm is due to a water impurity in the sample – not part of the compound). Compound A was then reacted with sodium hydroxide to generate compound B. Compound B was then reacted to generate compound C. The parent molecular ion peak for compound C was determined to be m/z = 145. The IR for compound C is shown. Indicate the structures for compounds A, B and C and list the reagents required to synthesize compound C from compound B.

<table>
<thead>
<tr>
<th>Compound A</th>
<th>Compound B</th>
<th>Compound C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS shows Cl</td>
<td>IR shows nitrile</td>
<td>reagents to convert B to C</td>
</tr>
</tbody>
</table>

1) TsCl  
2) NaCN