1. Give the name or structure for each of the following. (15 points)

   a) \[ \text{Benzaldehyde} \]
   
   b) \[ \text{3-ethyl-3-butenal} \]
   
   c) \[ \text{cis-1,2-cyclopentanediol} \]
   
   d) \[ S-2\text{-methoxy cyclopentanone} \]

2. Match the following compounds with the correct boiling points at 1 atm pressure. Place the appropriate letter in the blank provided. (4 points)

   a) 3-methylpentane \[ \underline{D} \]
   
   b) 3-pentanol \[ \underline{C} \]
   
   c) 3-pentanone \[ \underline{B} \]
   
   d) butyl methyl ether \[ \underline{A} \]

3. Which of the following is/are acetals/ketals? (4 points)

   a)
   
   b)
   
   c)
   
   d)

4. Show, by drawing a detailed stepwise mechanism, how the following dimethyl ketal is hydrolyzed under acidic conditions. Be sure to use the proton correctly as a catalyst. Show the movement of electrons with the curved arrows is each step. (6 points)
5. Draw the structures of the major organic products expected in the following reactions. If mixtures of products are expected, indicate the relative amounts of each. If no reaction is expected, so state. (4 points each).

   a) \( \text{H}_2\text{C} = \text{CH}_2 - \text{Br} \)
      1. \( \text{PPh}_3 \), \( \text{PhLi} \)
      2. \( \text{Ph} = \text{C} = \text{O} \)
      3. \( \text{H}^+ / \text{H}_2\text{O} \)

   b) \( \text{BrCH}_2\text{CH}_3 \)
      1. \( \text{Mg} / \text{ether} \)
      2. \( \text{Ph} = \text{C} = \text{O} \)
      3. \( \text{H}^+ / \text{H}_2\text{O} \)

   c) \( \text{C}_{\text{yclohexene}} \)
      \( \text{NH}_2\text{NH} - \text{C} - \text{NH}_2 \)

   d) \( \text{H}_3\text{C} \)
      \( \text{H}_3\text{C} \)
      1. \( \text{LiAlH}_4 / \text{ether} \)
      2. \( \text{H}_2\text{O} \)

   e) \( \text{C}_{\text{yclohexene}} \)
      1. \( \text{C}_6\text{H}_5\text{CO}_2\text{H} / \text{CH}_2\text{Cl}_2 \)
      2. \( \text{H}^+ / \text{H}_2\text{O} \)

   f) \( \text{C}_{\text{yclohexene}} \)
      1. \( \text{DIBAL-H} / \text{toluene} / -78^\circ \)
      2. \( \text{CH}_3\text{OH} \)

   g) \( \text{CH}_2\text{C} = \text{Cl} \)
      \( \text{Ph} \text{C}_3 \text{CH}_3 \)
      1. \( \text{AlCl}_3 \)
      2. \( \text{H}_2\text{O} \)

   h) \( \text{C}_{\text{yclohexene}} \)
      1. \( \text{BH}_3 / \text{THF} \)
      2. \( \text{H}_2\text{O}_2 / \text{NaOH} \)

   i) \( \text{C} = \text{C} \)
      1. \( \text{NaNH}_2 \)
      2. \( \text{O} = \text{CH}_3 \)
      3. \( \text{H}_2\text{O} \)

   j) \( \text{H}_3\text{C} \)
      \( \text{H}_3\text{C} \)
      \( \text{NaOCH}_3 \)
      \( \text{HOCH}_3 \)

6. Write the complete stepwise mechanism for the following reactions. (5 points)

   \( \text{Cyclohexene} \)
   1. \( \text{NaH} \)
   2. \( \text{CH}_3 \), \( \text{ether} \)

   \( \text{Cyclohexene} \)
   \( \text{CH}_3\text{I} \)
   \( \text{Na}^+ \)
   \( \text{CH}_3\text{I} \)
   \( \text{Na}^+ \)
7. Mechanistically, the Williamson ether synthesis shown in the previous problem is: (3 points)
   a) an SN1 process 
   b) an SN2 process 
   c) an E2 process 
   d) an E1 process

8. The following para and meta-nitrophenols have the pKa values listed. (6 points)
   a) Which is the stronger acid? para
   b) How do you account for the difference in acidity between meta and para-nitrophenol? Be sure to take into account both inductive and resonance effects in your answer.

   \[
   \begin{align*}
   \text{para} & : pK_a = 7.17 \\
   \text{meta} & : pK_a = 8.28
   \end{align*}
   \]

   The nitro group is strongly electron withdrawing at both positions; the para form has an additional resonance form that places a (−) charge on the electronegative oxygen - making the conjugate base more stable than the meta-

9. Provide reagents and conditions to carry out the following transformations. The route chosen should produce the desired product in good yield with minimum number of steps. (4 points each)

   a) 

   \[
   \text{OH} \quad \text{CH}_2
   \]

   \[
   \xrightarrow{\text{POCl}_3/\text{CH}_2\text{Cl}_2}
   \]

   \[
   \text{OH}
   \]

   b) 

   \[
   \text{OH}
   \]

   \[
   \xrightarrow{1. \text{NaOH, Ce}}
   \]

   \[
   \xrightarrow{2. 200^\circ \text{C}}
   \]

   c) 

   \[
   \text{HO} \quad \text{CH}_2
   \]

   \[
   \xrightarrow{\text{Jones oxidation}}
   \]

   \[
   \text{HO} \quad \text{CO}
   \]

   10. Starting with an alkyl halide (R-Br), and magnesium, prepare the following using a Grignard reaction in the key step. (5 points)

   \[
   \text{Br
   } \xrightarrow{\text{Mg}} \text{MgBr} \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_2\text{CH}_2\text{OH}
   \]

   \[
   \text{Br
   } \xrightarrow{\text{Mg}} \text{MgBr} \xrightarrow{\text{CH}_2} \text{H}_2\text{O}^+
   \]
Bonus (5 points)

Propose a structure that is consistent with the following $^{13}$C-NMR spectrum in CDCl$_3$. Assign the signals to carbons in your structure. (Note the small singlet at 210 ppm.)

- 1 - un saturated
- 4 different C's
- 1 C = O

```
\text{C}_3\text{H}_4\text{O}
```

Chemical shift (δ, ppm)
1. Give the name or structure for each of the following. (15 points)

   a) 4-methylbenzoic acid
   b) Methyl butanoate (structure)
   c) Succinic anhydride (structure)
   d) (proper name)
   e) (name)

2. Rank the following according to their relative acid strength, strongest acid first. (5 points)

   A  >  C  >  B  >  D  >  E

   Bonus (4 points): Provide the approximate pKₐ for the most acidic hydrogen in A-E.

3. Provide a detailed reasonable stepwise mechanism to explain the following transformation. (5 points)
4. Which one of the following compounds is capable of forming a δ-lactone? (4 points)

5. Draw the structures of the major organic products expected in the following reactions. If mixtures of products are expected, indicate the relative amounts of each. If no reaction is expected, so state. Be concerned about stereochemistry, where important. (5 points each)
6. Starting with diethyl malonate or ethyl acetoacetate, prepare each of these using an acetoacetic ester or malonic ester synthesis. (5 points each)

\[
\begin{align*}
\text{EtO}^+ & \quad \text{OEt} \\
\text{or} & \\
\text{EtO}^+ & \quad \text{OEt}
\end{align*}
\]

\[
\begin{align*}
a) \quad & \text{OEt} \\
& \quad \text{EtO}^+ \\
& \quad \text{OEt}
\end{align*}
\]

\[
\begin{align*}
b) \quad & \text{OEt} \\
& \quad \text{EtO}^+ \\
& \quad \text{OEt}
\end{align*}
\]

1. NaOEt/HOEt
2. CH₃CH₂CH₂Br
3. NaO/H₂O
4. H⁺/Heat
5. NaOEt/HOEt
6. CH₂Br
7. Ce
8. H⁺/Heat

\[
\begin{align*}
& \quad \text{OEt} \\
& \quad \text{EtO}^+ \\
& \quad \text{OEt}
\end{align*}
\]

7. Provide reagents and conditions to carry out the following transformations. The route chosen should produce the desired product in good yield with minimum number of steps. (5 points each)

\[
\begin{align*}
a) \quad & \text{H₃C} \\
& \quad \text{H₃C} \\
1. & \text{Br}_2/\text{HAc} \\
2. & \text{Peridin} \\
& \quad \text{Heat}
\end{align*}
\]

\[
\begin{align*}
b) \quad & \text{CH₃} \\
& \quad \text{CH₃} \\
1. & \text{Mg}_2/\text{ether} \\
2. & \text{CO}_2 \\
3. & \text{H}⁺/\text{H₂O} \\
& \quad \text{Heat}
\end{align*}
\]

\[
\begin{align*}
c) \quad & \text{HO} \\
& \quad \text{HCl} \\
1. & \text{NaO} \text{DMSO} \\
2. & \text{H}⁺/\text{H₂O} \\
& \quad \text{Heat}
\end{align*}
\]

\[
\begin{align*}
d) \quad & \text{CH₃CO} \\
1. & \text{Br}_2/\text{PH₃} \\
2. & \text{H₂O}
\end{align*}
\]

(3 points each)

8. The mass spectrum of a compound showed a molecular ion peak at M and another at M+1 in the ratio of approximately 94.7:5.4. The compound most likely has \_\_\_碳？

\[
a) \quad 2 \quad b) \quad 3 \quad c) \quad 5 \quad d) \quad 8 \quad e) \quad 10
\]

9. In the McLafferty rearrangement of an acetate ester in a mass spectrometer, which of the following is NOT a probable product?

\[
\begin{align*}
a) \text{alcohol} & \quad \text{b) alkene} \\
& \quad \text{c) acetic acid} \\
& \quad \text{d) cation radical} \\
& \quad \text{e) neutral molecule}
\end{align*}
\]
1. Provide the name or structure for each of the following. (3 points each)
   a) \( \text{H}_2\text{C} \text{C} \text{C} \text{N} \text{C} \text{C} \text{H}_3 \) (IUPAC Name)
   b) N-ethylpiperidine (Structure)
   c) \( \text{H}_2\text{C} \text{N} \text{C} \text{CH}_3 \) (name)
   N-ethyl-N-methylbutanamine
   m-toluidine
   3-methylaniline

2. Classify each amine in problem 1 as primary, secondary, tertiary, or quaternary. (3 points)
   a) \( \text{3}^0 \)
   b) \( \text{3}^0 \)
   c) \( \text{1}^0 \)

3. Which amine in problem 1 would be the weakest base? \( \text{C} \) (3 points)

4. Predict the structures of the organic products expected the following reactions. When mixtures of products are expected, indicate the relative amounts of each. If no reaction is expected, please state. Be concerned about stereochemistry, where important. (4 points each)

   a) \[ \text{HO-} \text{HO-} \text{HO-} \text{CH}_2\text{OH} \]
   \[ \text{NH}_2\text{NHPH (excess)} \]
   \[ \text{HO-} \text{HO-} \text{HO-} \text{CH}_2\text{OH} \]
   (draw in Haworth form)

   b) \[ \text{CH}_3\text{OH} \]
   \[ \text{H}^+ \]
   \[ \text{(draw in Haworth form)} \]

   c) \[ \text{HO-} \text{HO-} \text{HO-} \text{CH}_2\text{OH} \]
   \[ \text{NaBH}_4 \]
   \[ \text{CH}_2\text{OH} \]
5. Use the following structures in answering the next questions.

If there is none that match the statement, write none. (18 points)

a) Which are L-sugars? \( \text{C} \)  

b) Which are aldotetroses? \( \text{none} \)  

c) Which are \( \beta \)-anomers? \( \text{B, D, G} \)  

d) Which are ketoses? \( \text{D, H} \)  

e) Which are non-reducing sugars? \( \text{B, D, E} \)  

f) Which are deoxy sugars? \( \text{G} \)  

g) Draw the open chain form of A using a Fischer projection, and give its name.  

d-\text{galactose}  

h) Draw the most stable chair form of E.  

6. What is the pI of proline? The structure and pK\(_a\) values are shown below. (4 points)

a) 6.30  
b) 6.00  
c) 5.30  
d) 8.60  
e) 2.00  

\( \text{pK}_a = 10.60 \)

\( \frac{10.60}{2} = 5.30 \)

\( \frac{2.00}{2} = 1.00 \)

\( 10.60 / 2 = 6.30 \)
7. Provide the correct information for the missing items regarding natural amino-acids. (12 points)

<table>
<thead>
<tr>
<th>Classification</th>
<th>Structure</th>
<th>name</th>
<th>Symbols</th>
</tr>
</thead>
</table>
| Acidic         | \[
\begin{align*}
\text{Asp: } & \quad \text{HOOC-CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{NH}_\text{2} \\
\text{Glu: } & \quad \text{HOOC-CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{NH}_\text{2} \\
\end{align*}
\] | aspartic acid | asp |
|                | \[
\begin{align*}
\text{Lys: } & \quad \text{H}_\text{2}N-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{COOH} \\
\end{align*}
\] | glutamic acid | glu |
| Basic          | H\(_2\)N-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{COOH} | lysine | lys K |
| Neutral        | \[
\begin{align*}
\text{Ala: } & \quad \text{CH}_\text{3}-\text{CH}(-\text{COOH}) \quad \text{NH}_\text{2} \\
\text{Val: } & \quad \text{CH}_\text{3}-\text{CH}(-\text{COOH}) \quad \text{CH}_\text{3} \quad \text{NH}_\text{2} \\
\end{align*}
\] | Alanine | Ala A |
| Neutral        | H\(_2\)N-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{CH}_\text{2}-\text{COOH} | Valine | Val V |

8. Consider the reaction below to answer the following question:

\[
\begin{align*}
\text{H} & \quad \text{K} \\
\text{NaOEt} & \quad \text{H} \\
\text{HOEt} & \quad \text{H}_2\text{O} \\
\end{align*}
\]

Write the complete stepwise mechanism for the reaction above. Show all intermediate structures and all electron flow with arrows. (5 points)

9. This previous reaction is an example of:

a. an intramolecular Claisen condensation
b. an intramolecular aldol condensation
c. a Robinson annulation
d. a Michael reaction
10. In the reaction to the right, which carbonyl compound functions as the electrophile? (3 points)

\[
\text{A} + \text{B} \rightarrow \text{C} \quad \text{5\% NaOCH}_3, \text{CH}_3\text{OH}
\]

11. Predict the structures of the organic products expected the following reactions. When mixtures of products are expected, indicate the relative amounts of each. If no reaction is expected, please state. Be concerned about stereochemistry, where important. (4 points each)

a) \[
\text{Ph-CH=CH}_2 + \text{EtO-CO-Ph} \quad 1. \text{NaOEt/HOEt} \quad 2. \text{H}^+ \rightarrow \text{Ph-CH}_2\text{CCH}_2\text{CPh} + \text{HOEt}
\]

b) \[
\text{CH}_2=\text{CH-COEt} + \text{H}_2\text{C-COEt} \quad \text{NaOEt/HOEt} \rightarrow \text{CH}_2=\text{CH-COEt}
\]

c) \[
\text{C}=\text{O} + \text{HN} \quad \text{H}^+ \rightarrow 1. \text{PhCH}_2\text{Cl} \quad 2. \text{H}_3\text{O}^+
\]

d) \[
\text{Ph-CH}_2\text{N(CH}_3)_2 \quad 1. \text{LiAlH}_4/\text{Et}_2\text{O} \quad 2. \text{H}_2\text{O}
\]

e) \[
\text{Ph-CH=CH} + \text{HN} \quad \text{H}_2 \quad \text{Ni}
\]

f) \[
\text{Ph-CH=CH-OTs} \quad 1. \text{NaN}_3 \quad 2. \text{LiAlH}_4/\text{ether} \quad 3. \text{H}_2\text{O}
\]

g) \[
\text{Ph-Cl} \quad 1. \text{HNO}_3/\text{H}_2\text{SO}_4 \quad 2. \text{Fe/HCl} \quad 3. \text{AcCl/py} \quad 4. \text{Br}_2/\text{FeBr}_3 \quad 5. \text{NaOH/H}_2\text{O} \quad 6. \text{NaNO}_2/\text{H}^+\text{/H}_2\text{O} \quad 7. \text{CuCN}
\]