1. (24 points) Rank the items in each set below.

(a) (3 points) Rank the items below in order of increasing nucleophilicity in water (1 = weakest Nu, 4 = strongest Nu).

- $F^-$
- $Cl^-$
- $Br^-$
- $I^-$

(b) (3 points) Rank the items below in order of increasing oxidation state (1 = lowest oxidation state, 5 = highest oxidation state).

- $O=C=O$
- $Ph\text{-}OH$
- $Ph\text{-}OH$
- $Ph\text{-}Me$
- $Ph\text{-}H$

(c) (3 points) Rank the items below in order of increasing rate of $S_N2$ reaction with sodium cyanide (1 = slowest rate, 5 = fastest rate).

- $Me$-I
- $Me\text{-}Me\text{-}Me\text{-}Br$
- $Me\text{-}Br$
- $Br$-cyclopentane
- $Me\text{-}Me\text{-}Me\text{-}Br$

(d) (3 points) Rank the items below in order of increasing rate of $S_N1$ reaction (1 = slowest rate, 5 = fastest rate).

- $Me\text{-}Br$-cyclohexane
- $Me\text{-}Br$
- $Me\text{-}Me\text{-}Br$
- $Me\text{-}Me\text{-}Me$
- $Me\text{-}Br$
(e) (3 points) Rank the items below in order of increasing number of hydrogen bond donors and acceptors (1 = fewest H-bond donors and acceptors, 5 = most H-bond donors and acceptors).

(f) (3 points) Rank the items below in order of increasing solubility in water (1 = least soluble, 5 = most soluble).

(g) (3 points) Rank the items below in order of increasing acidity of the hydrogen in bold (1 = least acidic, 5 = most acidic).

(h) (3 points) Rank the following free radicals in order of increasing stability. (1 = least stable, 5 = most stable)
2. (16 points) Follow the directions to answer each question below.

a) (8 points) Label each molecule as **chiral** or **achiral**. **Indicate the chiral centers** and **assign each one as R or S**.

- [Structure 1]
- [Structure 2]
(d) (8 points) Consider the following aldol reaction.

(i) Fill in the substituents in the lowest energy chair transition state that explain the stereoselectivity in the deprotonation (step 1).
(ii) Fill in the substituents in the lowest energy chair transition state that explain the stereoselectivity in the enolate addition to the aldehyde (step 2).
3. (30 points) Predict the products of the following reactions. Clearly indicate stereochemical outcomes.

(a) (5 points)

1. dehydratase
2. NADPH, H⁺ NADP⁺

(b) (5 points)

1. pyridine
2. NaCN, DMF

(c) (5 points)

1. mCPBA, CH₂Cl₂
2. H₃O⁺, heat
(d) (5 points)

\[
\text{Et} \quad \text{Me} \\
\text{Ph} \quad \text{Br}
\]

\[\text{KOT-Bu, DMF}\]

(e) (5 points)

\[\text{1. } \text{H}_2\text{N-NH}_2, \text{EtOH} \]

\[\text{2. } \text{Me}^+ \text{COCO} \text{Me} \]

\[\text{pyridine}\]

(f) (5 points)

\[
\text{Me} \quad \text{O}
\]

\[\text{1. } \text{EtO} \text{COCOEt} \]

\[\text{NaOEt, EtOH}\]

\[\text{2. } \text{NH}_4\text{Cl} \]

\[\text{3. } \text{NaBH}_4, \text{MeOH}\]
4. (34 points) Provide the necessary reagents to accomplish the following transformations. Number the steps and note that some reactions will require more than one step.

(a) (4 points)

(b) (5 points)
(c) (5 points)

\[
\text{苯} \quad \xrightarrow{} \quad \text{苯}^{\text{NO}_2} \quad \text{Me}^{\text{Me}}
\]

(d) (5 points)

\[
\text{对甲苯二甲酸} \quad \xrightarrow{} \quad \text{对甲基苯二甲酸}^{\text{双键}}
\]
5. (46 points) Provide a detailed arrow-pushing mechanism for the following transformations.

(a) (5 points)
(b) (6 points)

\[
\begin{align*}
\text{cyclohexanone} & \xrightarrow{H^+, \text{EtOH}} \text{cyclohexyl acetate} \\
\end{align*}
\]
(c) (6 points)

\[
\begin{align*}
\text{H}_3\text{O}^+, \text{H}_2\text{O} & \xrightarrow{\text{heat}} \\
& \quad \longrightarrow \\
& \quad \text{acetophenone}
\end{align*}
\]
(d) (8 points)

1. NaOMe, MeOH
2. NaOMe, heat
(e) (6 points)

\[
\text{Me-SACP} \xrightarrow{\text{ketosynthase}} \text{Me-CO-SACP}
\]
(f) (7 points)

\[ \text{Me-} \overset{\text{O}}{\text{C}} \text{SCoA} \xrightarrow{\text{dehydrogenase}} \text{Me-} \overset{\text{O}}{\text{C}} \text{SCoA} \]

\[ \text{FAD} = \begin{array}{c} \text{Me} \\ \text{N} \\ \text{N} \\ \text{N} \\ \text{O} \\ \text{R} \end{array} \]

\[ \text{FADH}_2 = \begin{array}{c} \text{Me} \\ \text{N} \\ \text{N} \\ \text{N} \\ \text{O} \\ \text{R} \end{array} \]
(g) (8 points)

\[
\begin{align*}
\text{Ph} & \quad \text{O} \quad \text{O} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{Me} \\
\text{2-O}_{3} \text{PO} & \\
\end{align*}
\]

\[
\begin{align*}
\text{O}_{2} \text{C} & \quad \text{CH} \quad \text{CO}_{2} \quad \text{O} \\
\text{aminotransferase} & \quad \rightarrow \\
\text{Ph} & \quad \text{O} \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{O}_{2} \text{C} & \quad \text{CH} \quad \text{CO}_{2} \quad \text{O} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{Me} \\
\text{2-O}_{3} \text{PO} & \\
\end{align*}
\]