1. (5 pts. each, 50 pts. total) Draw the major product of each of the following reactions. Assume aqueous workup in all cases (that is, draw neutral products). Do not draw mechanisms!

(a) 

\[
\begin{align*}
\text{CN} & \quad \text{LDA; PhCH}_2\text{Br} \\
& \quad \text{PhCN} \\
& \quad \text{PhCN}
\end{align*}
\]

(b) 

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

(c) 

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \text{EtOH} \\
& \quad \text{EtOH} \\
& \quad \text{cat. H}_2\text{SO}_4 \\
& \quad \text{CO}_2\text{Et}
\end{align*}
\]

(d) 

\[
\begin{align*}
\text{CN} & \quad \text{excess NaOH} \\
& \quad \text{CO}_2\text{H}
\end{align*}
\]

(e) 

\[
\begin{align*}
\text{OMe} & \quad \text{O}_2 \\
& \quad \text{OMe}
\end{align*}
\]
(f) \[
\begin{align*}
\text{NH}_2\text{CO} & \xrightarrow{\text{SOCl}_2} \text{CN} \\
\end{align*}
\]

(g) \[
\begin{align*}
\text{MeNH}_2 & \xrightarrow{\text{H}_2, \text{Pd/C}} \text{NHMe} \\
\end{align*}
\]

(h) \[
\begin{align*}
\text{O}_2\text{N} & \xrightarrow{\text{Br}_2, \text{FeBr}_3} \text{O}_2\text{N} & \text{Br} \\
\end{align*}
\]

(i) \[
\begin{align*}
\text{O} & \xrightarrow{\text{LDA}} \text{Ph} & \xrightarrow{\text{O}} \text{Ph} \\
\end{align*}
\]

(j) \[
\begin{align*}
\text{CO}_2\text{Et} & \xrightarrow{\text{LiAlH}_4} \text{OH} \\
\end{align*}
\]
2. (20 pts. each, 60 pts. total) Design syntheses of the two compounds below from the indicated starting materials. Both syntheses will require two or more steps. Show each intermediate compound and all reagents you will need for each step. (Don’t panic if you can’t remember the reagents for a particular step; partial credit will be given.) **Do not show mechanisms.**

(a)

\[
\begin{align*}
\text{Retrosynthesis:} \\
\text{Forward:}
\end{align*}
\]

\[
\begin{align*}
\text{one or more alcohols} \\
\text{2} \\
\text{EtOH, H}_2\text{SO}_4 \\
\text{NaOEt}
\end{align*}
\]

\[
\begin{align*}
\text{Retrosynthesis:} \\
\text{Forward:}
\end{align*}
\]
(b) $\text{H}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \Rightarrow \quad \text{benzene}$

Retrosynthesis:

$\text{H}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \Rightarrow \quad \text{H}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \Rightarrow$

$\text{O}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \Rightarrow \quad \text{H}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \Rightarrow \quad \text{H}_2\text{N-}\text{O-}\text{C-}\text{O}$

Forward:

$\text{H}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \xrightarrow{\text{Ac}_2\text{O}} \quad \text{H}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \xrightarrow{\text{HNO}_3} \quad \text{H}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \xrightarrow{\text{SnCl}_2} $

$\text{H}_2\text{N-}\text{O-}\text{C-}\text{O} \quad \xrightarrow{\text{mCPBA}} \quad \text{H}_2\text{N-}\text{O-}\text{C-}\text{O}$
(c)

Retrosynthesis:

Forward:
3. (45 pts. total) Draw reasonable mechanisms for each of the following reactions.

(a) (10 pts.)

See exam 3.
(b) (15 pts.)

![Chemical reaction diagram]

**Explanation:**

1. **Starting Material:** The reaction starts with a brominated compound with an ester group (BrOEt).
2. **Addition of CH₃MgBr:** The compound is treated with CH₃MgBr, which adds to the double bond of the ester group, forming a new carbon-carbon bond.
3. **Formation of Ring Structure:** The addition leads to the formation of a six-membered ring, with the resulting structure showing the new bonds and the placement of the CH₃ groups.

The reaction sequence demonstrates the nucleophilic addition of the Grignard reagent to the double bond, followed by cyclization to form a six-membered ring.
(c) (20 pts.)

\[ \text{OH} \rightarrow \text{CH}_{3}\text{CN} \rightarrow \text{N} \rightarrow \text{O} \rightarrow \text{CH}_{3} \]

\[ \text{OH} \rightarrow \text{H}^{+} \rightarrow \text{OH}_{2} \rightarrow \text{N} \rightarrow \text{C} \rightarrow \text{CH}_{3} \]

\[ \text{N} \rightarrow \text{H} \rightarrow \text{O} \rightarrow \text{C} \rightarrow \text{CH}_{3} \]

\[ \text{N} \rightarrow \text{H} \rightarrow \text{O} \rightarrow \text{C} \rightarrow \text{CH}_{3} \]
4. (5 pts. each, 20 pts. total) When the Friedel–Crafts reaction shown below is carried out, *four* ketones are obtained. Two of the products contain the phenol (aromatic alcohol) functional group and the two others contain the ester functional group.

![Chemical Reaction Diagram]

(a) What spectroscopic technique would allow you to distinguish the two ester products from the two phenol products? Be specific about how the technique would allow you to distinguish them.

IR: presence or absence of carbonyl stretch  
NMR: presence or absence of C=O or CH₃

(b) Draw the two products that contain the phenol functional group.

![Phenol Products]

(c) On the next page is a ¹H NMR spectrum of one of the phenol products. Circle the compound you drew in (a) which would give rise to this ¹H NMR spectrum.

The para product

(d) What ¹H NMR feature would distinguish the other phenol product from the one you circled?

The other phenol product would have four different resonances for the aromatic H’s.
5. (5 pts. each, 25 pts. total) Answer each of the following questions.

(a) Why do Claisen condensations such as the one below require a full equivalent of base such as NaOEt to proceed to completion?

![Claisen condensation reaction]

Because the product is very acidic and consumes the basic catalyst.

(b) Why doesn’t the following reaction work as written?

![Ketone reduction reaction]

Because ketones are reduced with LiAlH$_4$, too. The product is a diol.

(c) Why is F an ortho–para director in Friedel–Crafts reactions, even though it is the most electronegative element?

It has lone pairs that can stabilize a neighboring + charge by resonance.
(d) Why doesn’t the following reaction work as written?

\[
\text{MeNH}_2 + \text{PhCH}_2\text{Br} \rightarrow \text{MeNHCH}_2\text{Ph}
\]

Multiple alkylations of the N occur.

(e) How many resonances will you see in the $^1\text{H}$ NMR spectrum of the following compound?

Five. The two H’s of the CH$_2$ group are diastereotopic.