Question I. (22 points)
A) $\text{pK}_a$ of the most acidic proton in each molecule (1 point each, 6 points total)

1) $\text{pK}_a = 4.0$

2) $\text{pK}_a = 10$

3) $\text{pK}_a = 20$

4) $\text{pK}_a = 10$

5) $\text{pK}_a = 5$

6) $\text{pK}_a = 45$

B) Draw the reaction between 2 and NaH. Give the $K_{eq}$ and $\Delta G$. (3 points)

\[
\begin{align*}
\text{pK}_a &= 10 \\
\text{pK}_a &= 35 \\
\text{NaH} &\quad \rightarrow \\
K_{eq} &= 10^{\text{pK}_a - \text{pK}_a} = 10^{35-10} = 10^{25} \\
\Delta G &= -RT \ln K_{eq} \\
&= -1.36 \times 25
\end{align*}
\]

C) Draw the chemical structures (1.5 point each, 9 points total)

MCPBA

\[
\begin{align*}
\text{Cl} &\quad \text{Cl} \\
\text{OH} &\quad \text{OH}
\end{align*}
\]

m-xylene

\[
\begin{align*}
\text{anisole}
\end{align*}
\]

pyrrole

\[
\begin{align*}
\text{thiophene}
\end{align*}
\]

D) Nomenclature (1 point each, 4 points total)

Nitroanilines

\[
\begin{align*}
\text{p-chlorobenzenesulfonic acid}
\end{align*}
\]

\[
\begin{align*}
(o,p,m)
\end{align*}
\]

\[
\begin{align*}
\text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{Br}
\end{align*}
\]

\[
\begin{align*}
\text{OMe}
\end{align*}
\]
Question II. Reactions: provide major product or the starting materials for the following reactions (3 points each, 30 points total)

- \( \text{P618} \)
  - \( \text{P621 12.43 e} \)
  - \( \text{P621 13.43 g} \)

\[
\text{Reactions:}
\]

- \( \text{P714 15.30 b} \)
- \( \text{P75 1540} \)

\[
\text{Chemistry 2211} \quad \text{Spring 2016}
\]
Question III. Solve the structure based on the given information (20 points total)
A) 13C NMR (3 points)

B) 1H NMR (3 points)
C) MW 148 (4 points)

D) MW 180. Make sure label each H with the signals (5 points)

$C_{10}H_{12}O_3$

$D\nu = 5$
E) MW 148. Make sure label each H with the signals (5 points)

C_1 H_16
DQV = 4

CHCH

CH3

Question IV. Mechanism (20 points total)
A) Give an example of Swern oxidation with detailed mechanism (4 points)

\[
\begin{align*}
R - R' & \xrightarrow{\text{DMSO}} \xrightarrow{\text{Et_3N, -78°C}} R' - R'' \\
R' &= H, \text{ aldehyde} \\
R'' &= \text{alkyl, ketone}
\end{align*}
\]

Mechanism:

\[
\begin{align*}
\text{Et}_3\text{S}_+ & \xrightarrow{\text{Et}_3\text{N}^-} \text{Et}_3\text{S}^+ \\
\xrightarrow{\text{Et}_3\text{N}^-} & \text{Et}_3\text{S}^- \\
\end{align*}
\]
B) Draw the product and detailed electron pushing mechanism (4 points)

\[
\text{苯} + \text{环氧化合物} \xrightarrow{\text{H}_2\text{SO}_4} \text{产物}
\]

C) Draw the detailed electron pushing mechanism (4 points)

\[
\text{化合物} \xrightarrow{\text{HBr, AcOH, heat}} \text{产物}
\]

D) Draw detailed electron pushing mechanism for the following reactions. (4 points)

\[
\text{双键} \xrightarrow{\text{NBS, hv}} \text{溴化双键} \quad \text{溴化双键}
\]
E) Draw detailed electron pushing mechanism for the formation of $\text{NO}_2^+$ and $\text{SO}_3\text{H}^+$. (4 points)

Question V. Synthesis (24 points)
A) Provide the products in each block (1.5 point each, 15 points total)

B) (4 points)

---

Quiz #5
4)
C) (5 points)

\[
\begin{array}{c}
\text{P715} \\
15.39
\end{array}
\]

\[\text{苯} + \text{酯} \rightarrow \text{芳烃} \]

Question VI. Assays and synthesis (28 pts).

A) Rank the acidity of the following molecules and explain why. (4 points)

1. \[
\text{碳} \text{酸} \text{酯} 
\]
2. \[
\text{碳} \text{酸} 
\]
3. \[
\text{环己酮} 
\]
4. \[
\text{甲基环己酮} 
\]
5. \[
\text{甲基环己酮} 
\]

1. \[
\text{碳} \text{酸} \text{酯} 
\]
   - Most acidic because the hydrogen is between two \( \equiv \) group which best help to stabilize the negative charge in the conjugate base.
2. "O" can have resonance with the "\( \equiv \)" in ester group, which makes it weaker to stabilize the negative charge in "\( \equiv \)" compared with ketone. Thus \[
\text{甲基环己酮} 
\]
   - Is more acidic than \[
\text{甲基环己酮} 
\]. Same reason for \[
\text{环己酮} 
\] and \[
\text{甲基环己酮} 
\].

B) Rank the acidity of the following C-H bonds and clearly explain why (2 points)

4) \[
\text{a} \quad \text{b} \quad \text{c} 
\]

3. "N" is a better electron donor compared with "O", making \[
\text{甲基环己酮} 
\] less stable, thus \[
\text{甲基环己酮} 
\] has a higher pKa than \[
\text{甲基环己酮} 
\].
C) Identify whether the following molecules are chiral or achiral (1 pt each, 5 points total)

achiral  achiral  achiral  chiral

D) Which one of the following molecule is more polar? Why (2 pt each and 4 points total)
Acetone vs DMSO

aromatic, contributes more to the real structure, separate charge, more polar

E) Identify the aromatic, non-aromatic and non-aromatic. (1 pt each, 5 points total)

aromatic  aromatic  aromatic  aromatic  anti-aromatic

F) Which one of the following molecule is more acidic and why? (3 points)
Aniline and pyridine

aniline is more acidic
Aniline: \( pK_a \approx 35 \)
Pyridine: \( pK_a \approx 40 \)

G) Identify all the chemical shift non-equivalent Hs. Clear label the relationship of the chemical shift equivalent Hs (5 points)

8 non-equivalent Hs in total
All chemical shift equivalent Hs are enantiomers.

The end!