1. Nomenclature

(a) (15 points) Rates and substitution patterns in electrophilic aromatic substitution (EArS) reactions change depending on the groups attached to the ring. In the box below each benzene derivative, indicate whether the next EArS reaction would be directed to the ortho & para (o/p) positions or meta (m) position. Also circle whether the next EArS reaction would occur faster or slower than benzene.

(b) (25 points) Draw structures corresponding to any five of the following names (skip one, by drawing a large X over the name).

- 2,4-hexanediol
- (E)-2-ethyl-2-buten-1-ol
- para-hydroxyacetophenone
- (5S)-5-hydroxy-3-oxohexanal
- Isopropyl methyl ether
- 3-methoxypentane
2. Acid-Base Chemistry

(a) (10 points) The following compounds are arranged from most (left) to least (right) acidic. Fill in the pKa values of each in the boxes provided.

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<tbody>
<tr>
<td>HCl</td>
<td>H3O+</td>
<td>CH3COOH</td>
<td>H2S</td>
<td>NH4+</td>
<td>H2O</td>
<td>CH4</td>
</tr>
<tr>
<td>-7</td>
<td>0</td>
<td>5</td>
<td>7</td>
<td>10</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>50</td>
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(b) (10 points) Rank the following sets of compounds in terms of acidity where 1 is the most acidic and 4 is the least acidic.

Set 1

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<tbody>
<tr>
<td>NO2</td>
<td>H3O+</td>
<td>CH3COOH</td>
<td></td>
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<tr>
<td>&lt;10</td>
<td>&gt;10</td>
<td>5</td>
<td>&gt;5</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>1</td>
<td>2</td>
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</tbody>
</table>

Set 2

<p>| | | | | |</p>
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<tbody>
<tr>
<td>Br</td>
<td>H3O+</td>
<td>CH3COOH</td>
<td>Cl</td>
<td>CF3OH</td>
</tr>
<tr>
<td>&lt;16</td>
<td>&gt;10</td>
<td>5</td>
<td>&lt;10</td>
<td>&lt;=16</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>3</td>
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(c) (20 points) Draw two non-equivalent resonance structures of aniline to explain why it directs the next EAS substituent to the ortho and para positions. Use curved arrow notation to tell the story of this electron dance. No verbal explanation.

* must have Θ at ortho & para

-2 per missing charge

5 pts/ arrow set
3. (50 points) Single Step Reactions. Choose five, skip one reaction ("X" it out, otherwise a-e are graded). Fill in the missing product, reagent, or reactants in each reaction.

(a) 
\[
\text{excess} \\
1. \text{LiAlH}_4 \\
2. \text{H}_3\text{O}^+ \\
\]

(b) 
\[
\text{Cyclohexanol} \\
\text{CrO}_3, \text{H}_2\text{SO}_4 \\
\]

(c) 
\[
\text{H}_3\text{CO}_2\text{CH}_2\text{COH} \\
1. \text{NaBH}_4 \\
2. \text{H}_3\text{O}^+ \\
\text{LiAlH}_4/\text{LAH} \\
\]

(d) 
\[
1. \text{Excess CH}_3\text{MgBr} \\
2. \text{H}_3\text{O}^+ \\
\]

(e) 
\[
\text{DMP} \quad \text{or PCC} \\
\text{CrO}_3, \text{H}_3\text{O}^+ \quad \text{or Na}_2\text{Cr}_2\text{O}_7 \\
\]

(f) 
\[
\text{Cl}_2, \text{FeCl}_3 \\
\text{Cl}_2 \\
\]
4. (70 points) Reaction Puzzle – Fill in the missing reagents and products.

- **CH3Cl**
- **AlCl3**
- **NBS**
- **(PhCO2)2**
- **KOH**
- **NaOH**
- **Kmno4**
- **HNO3**
- **H2SO4**
- **H2**
- **Pd/C**
- **FeCl3**
5. Mechanisms – complete any two mechanisms. Skip one by placing a large X over the entire reaction, otherwise the first two will be graded.

(50 points) Show the product and full arrow-pushing mechanisms for any two reactions (including all acid-base steps). Be sure to clearly indicate all charged atoms and intermediates after each step.

Redraw starting materials if necessary to highlight bond.

Draw a large X over the problem to skip – we will not choose the best one for you!
6. (50 points) Multi-Step Synthesis – Choose any two

Carry out the synthesis of the indicated target molecules using the starting material provided and any other reagents or sources of carbon needed. Show the product after each reaction. No mechanisms. Partial credit is given where possible so if you’re stuck, take a deep breath then work your way backwards and/or forwards. Don’t forget to count your carbons!

**CHOSE ANY TWO, SKIP TWO, LARGE X OVER PROBLEMS TO SKIP**

(a)

(b)

(c)

(d)

Alternate sol’ns attached. Point breakdowns not given. Graded as consistently as possible for partial credit. Details $^*$ when to use reagents make a difference!

Draw a large X over the problem to skip – we will not choose the best one for you!
Alternate Solns to pg 6

(a) \[ \text{H}_2\text{O} / \text{H}_2\text{SO}_4 \quad \overset{\text{HBr}}{\longrightarrow} \quad \overset{\text{HBr}}{\text{hydroboration}} \quad \overset{\text{oxidation}}{\longrightarrow} \quad \overset{\text{DMF}}{\longrightarrow} \quad \overset{1. \text{MeMgBr}}{\longrightarrow} \quad \overset{2. \text{H}_2\text{O}^+}{\uparrow} \quad \overset{\Delta}{\longrightarrow} \quad \text{H}_2\text{SO}_4 \]

\[ \overset{1. \text{Mg}}{\downarrow} \quad \underset{2. \text{CH}_3\text{Br}}{\longrightarrow} \quad \overset{\text{Cl}_2 / h\text{v}}{\longrightarrow} \quad \overset{\text{KOH}}{\longrightarrow} \quad \overset{\text{HCl}}{\uparrow} \quad \overset{\text{POCl}_3 / \text{py}}{\longrightarrow} \quad \overset{1. \text{BH}_3}{\longrightarrow} \quad \underset{2. \text{H}_2\text{O}_2 / \text{OH}}{\longrightarrow} \]
(b) \[ \text{Li, NH}_3 \xrightarrow{\text{Hz, Lindlar}} \]

\[
\begin{align*}
\text{Hg}_2\text{SO}_4 & \xrightarrow{\text{H}_2\text{SO}_4} \text{H} & \text{LATT} & \xrightarrow{1. \text{NaBH}_4} \xrightarrow{2. \text{H}_3\text{O}^+} \text{OH} \\
\text{POCl}_3 & \xrightarrow{\text{Py}} & 1. \text{H}_2\text{(OAc)}_2 & \xrightarrow{1. \text{NaH}} \xrightarrow{2. \text{CH}_3\text{Br}} \text{OCH}_3 \\
\text{H}_2\text{(OAc)}_2 & \xrightarrow{\text{H}_2\text{O}} & 1. \text{NaBH}_4 & \xrightarrow{2. \text{CH}_3\text{Br}} \text{OH} \\
\end{align*}
\]

(c) \[ \text{Ph}^+ \xrightarrow{\text{HBr}} \Delta \xrightarrow{\text{Mg}} \text{Ph}^+ \xrightarrow{1. \text{H}_2\text{H}_2\text{O}} \sqrt{2. \text{H}_3\text{O}^+} \text{Ph}^+ \xrightarrow{\text{OH}} \]