1. SHORT ANSWERS:

(a) Put an O in the box beside each transformation that is an oxidation. Put an X in the box beside each transformation that is a reduction. (3 pt)

\[
\begin{align*}
\text{H}_2 & \quad \text{Pd/C} \\
\text{OH} & \quad \text{H}_3\text{O}^+ \\
\text{OH} & \quad \text{NaOCl, NaCl, HOAc, H}_2\text{O}
\end{align*}
\]

(b) Draw the structure of TMS, the common internal standard used in NMR. (3 pt)

\[
\begin{align*}
\text{CH}_3 \\
\text{H}_3\text{C-Si} \cdots \text{CH}_3
\end{align*}
\]

(c) Briefly, why does one see two bands in the N-H stretching region of a 1° amide? Draw a generic 1° amide as part of your answer. (3 pt)

\[
\begin{align*}
\text{O} & \quad \text{R} \\
\text{N} & \quad \text{R} \\
\text{H} & \quad \text{H}
\end{align*}
\]

symmetric stretch

asymmetric stretch

(d) What are the chemical constituents of household bleach? (3 pt) Why should it never be mixed with strong acid in household use? (2 pt)

Chemical constituents: \text{NaOCl (sodium hypochlorite)}, \text{NaCl, H}_2\text{O}

Why mixing it with acid is a problem: it generates \text{Cl}_2 gas, which is quite toxic.
(e) Draw the structure of a solvent that should not be used for a Grignard reaction. (2 pt)

H₂O, MeOH, EtOH
(other possibilities)

(f) Certain precautions must be taken when using Et₂O as a solvent. Briefly, why? (2 pt)

Et₂O is not only highly flammable, but highly volatile as well. The vapors can creep along the floor or benchtop and be ignited by a source of spark or flame at some distance.

(g) A recrystallization is properly carried out by which procedure(s)? (circle the number for each answer that is correct): (3 pt)

1. dissolve the solid in lots of hot solvent and then cool the solution rapidly in ice water;
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(h) The clear disks used in sampling liquids as thin films for IR spectroscopy are made of what material? Write a chemical formula. (2 pt)

NaCl

(i) Describe the Diels-Alder using another well-accepted term that describes some aspect of the reaction (there are several possible correct answers). (2 pt)

cycloaddition; pericyclic reaction; concerted reaction

(j) 2,4-Dinitrophenylhydrazine is a reagent commonly used to derivatize aldehydes and ketones. Draw the structure of the reagent. (2 pt)

(k) 9,10-Diphenylanthracene was used for what purpose in your Cyalume experiment? (2 pt)

9,10-Diphenylanthracene is the fluoroscer that actually emits the light. It is thought that it forms a charge-transfer complex with an unstable H₂O₂ oxidation product of Cyalume. Decomposition to CO₂ results in formation of the excited singlet state of 9,10-diphenylanthracene, which then fluoresces.
(l) For each of the following compounds, record the number of peaks in the $^{13}$C($^1$H) NMR spectrum. (3 pt)

![Compound 1](attachment:compound1.png) 4  
![Compound 2](attachment:compound2.png) 5  
![Compound 3](attachment:compound3.png) 7

(m). What is the common name of the following compound? What is it's utility? (2 pt)

![Aspirin](attachment:aspirin.png)
Aspirin - acetylsalicylic acid, a common analgesic (pain reliever)

(n) The Fischer esterification, shown below, is an acid-catalyzed, thermodynamically-controlled (equilibrium) reaction. What can be done to force the reaction shown to the desired product? (Be specific. One method will suffice.) (3 pt)

$$
\begin{align*}
\text{R.CO}_2\text{H} + \text{R'.OH} & \xrightleftharpoons{H^+} \text{R.CO}_2\text{R'} + \text{H}_2\text{O} \\
\text{OH} & \xrightleftharpoons{H^+} \text{OH} \\
\text{O} & \xrightleftharpoons{H^+} \text{O}
\end{align*}
$$

- Remove H$_2$O by azeotropic distillation or by use of a dehydrating agent (molecular sieves, CaCl$_2$, etc.)
- Use a large excess of alcohol if it happens to be an inexpensive solvent that is easily removed.

(o) The three IR spectra (A, B, and C) on the following page correspond to three of the following four structures. Fill in the boxes below with the appropriate letters (A, B, or C). One box must be left empty. (3 pt)

![Structure 1](attachment:structure1.png)  
![Structure 2](attachment:structure2.png)  
![Structure 3](attachment:structure3.png)  
![Structure 4](attachment:structure4.png)  

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<td><img src="" alt="Structure 3" /></td>
</tr>
<tr>
<td>B</td>
<td><img src="" alt="Structure 4" /></td>
</tr>
</tbody>
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2. Predict the major product of each of the following reactions. Show stereochemistry where appropriate. (3 pt each; 24 pt total)

\[
\begin{align*}
\text{CH}_2=\text{CH} + \text{MeO}_2\text{C}-\text{CH} & \quad \rightarrow \quad \text{CH}_2=\text{CH}\text{CO}_2\text{Me} \\
& \quad \text{(toluene)}
\end{align*}
\]

\[
\begin{align*}
\text{PhCl} & \quad \rightarrow \quad \text{OH} \\
& \quad \text{(rac)}
\end{align*}
\]

\[
\begin{align*}
\text{C}_5\text{H}_4 + \text{O}_2 & \quad \rightarrow \quad \text{C}_5\text{H}_4\text{O}_2 \\
& \quad \text{(hexanes)}
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5\text{Br} & \quad \rightarrow \quad \text{CO}_2\text{H} \\
& \quad \text{(hfs)}
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5\text{OH} + \text{COCl}_2 & \quad \rightarrow \quad \text{C}_6\text{H}_5\text{Cl}_2\text{Cl}_2\text{Cl} \\
& \quad \text{(Et}_3\text{N)}
\end{align*}
\]
Write a detailed mechanism with "electron pushing". (Use the back of the previous page if you run out of room.) (10 pt)

```
\[
\begin{align*}
\text{CH}_3\text{CO}_2\text{H} & \xrightarrow{\text{cat. H}^+} \text{CH}_3\text{CO}_2\text{H}^+ \\
\text{CH}_3\text{CO}_2\text{H}^+ + \text{MeOH} & \rightarrow \text{CH}_3\text{CO}_2\text{Me} + \text{H}_2\text{O}
\end{align*}
\]
4. Unknown compound X has molecular formula C₉H₁₂O. This entire problem concerns Unknown X.

(a) Calculate the number of double bond equivalents (put answer in box). (2 pt)

(b) The IR of X is shown on an attached page. Interpret the spectrum. Cite important absorptions and the types of vibrations they correspond to. What functional group(s) is(are) indicated? (5 pt)

- broad intense band ~3400-3500 cm⁻¹ - OH stretching
- >3000 cm⁻¹ C-H stretching for Csp²-H₁₅ bonds - olefinic or aromatic
- <3000 cm⁻¹ C-H stretching for Csp³-H₁₅ bonds - aliphatic
- NO carbonyl

An alcohol or phenol is indicated

(c) Unknown X is insoluble in H₂O, insoluble in 5% aqueous NaHCO₃, but soluble in 5% aqueous NaOH. Taken together with your interpretation of the IR (above), what functional group is indicated? (3 pt) Write a general equation showing the reaction associated with the reaction of unknown X with 5% aqueous NaOH. (3 pt)

A phenol (pKᵣ = ~10) is indicated - no reaction with the NaHCO₃, but reaction with the stronger base NaOH

\[
\text{C₉H₁₂O} + \text{Na}⁺ \text{OH}^- \rightarrow \text{C₉H₁₂O}⁻ \text{Na}^⁺ + \text{H₂O}
\]
(d) The 90 MHz $^1$H NMR spectrum of X is shown on an attached page. Complete the table to analyze the spectrum. Under the "Interpretation" heading, draw part-structures, making sure in each case to specify the protons that are responsible for the resonance and those that give rise to coupling. In each case, underline the protons that are responsible for the resonance signal. (7 pt)

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<td>1</td>
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<td>$\text{Ar}$ $\text{CH}_3\text{-CH-CH}_3$</td>
</tr>
<tr>
<td>4.7</td>
<td>1</td>
<td>br s</td>
<td>$\text{Ar-OH}$</td>
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(e) The $^1$H($^{13}$C) spectrum of X is also shown on the attached page. Use that information in combination with your interpretations from parts (a)-(d) to deduce the structure of X. (6 pt)

(Could also have been meta, but not para on the basis of the $^{13}$C NMR. Have a look at your notes...we went through this particular example.)
Unknown $X$

$^{1}H$ NMR

$CDCl_{3}$

$90$ MHz

$2$ peaks

$6H$

$1H$

$4H$

$IR$ (thin film)

$^{13}C$($^{1}H$) NMR

$2$ peaks

$13C$($^{1}H$) NMR

Unknown $X$
1. SHORT ANSWERS:

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\[
\begin{align*}
\text{benzyl alcohol} & \xrightarrow{\text{NaOCl, NaCl, HOAc, H}_2\text{O}} \text{benzaldehyde} & \text{O} \\
\text{cyclohexene} & \xrightarrow{\text{H}_3\text{O}^+} \text{cyclohexanol} & \text{X} \\
\text{cyclohexadiene} & \xrightarrow{\text{H}_2, \text{Pd/C}} \text{cyclohexane} & \text{X}
\end{align*}
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(b) Draw the structure of TMS, the common internal standard used in NMR. (3 pt)

\[
\begin{align*}
\text{CH}_3 & \\
\text{H}_3\text{C-Si(CH}_3)_2
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\begin{array}{c}
\text{R'OH} \\
\text{H}^+ \\
\text{R'OH} \\
\end{array} \xrightarrow{\text{H}^+} \begin{array}{c}
\text{R'COO} \\
\text{R'COO} \\
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\[
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\]

\[
\begin{align*}
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& \xrightarrow{2) \text{ CO}_2 (s)} \text{C}_{12}H_{10} \\
& \xrightarrow{3) \text{ H}_3\text{O}^+} \text{C}_{12}H_{10}
\end{align*}
\]

\[
\begin{align*}
\text{C}_{12}H_{10} & \xrightarrow{\text{xs Et}_3\text{N}} \text{C}_{12}H_{10}OCl
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \xrightarrow{\text{C}_{12}H_{10}COCl} \text{Ph}
\end{align*}
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\[
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Unknown X

90 MHz $^1$H NMR

CDCl$_3$

$^1$H NMR

$^1$C($^1$H) NMR

2 peaks