1) (30 points) Consider the following reaction schemes:

1) PCC, CHCl₂
   ii) Δ, toluene
   iii) O₃, CH₂Cl₂
   iv) Zn, AcOH

\[ \text{C}_{15}\text{H}_{22}\text{O}_3 \]

2) CH₃COCl, AlCl₃
   ii) mCPBA, CH₂Cl₂
   i) NaBH₄, EtOH
   iv) KOH, THF / H₂O

\[ \text{C}_{15}\text{H}_{22}\text{O}_2 \]

a) Provide the structures of all the intermediates and products.

b) Write detailed reaction mechanisms for the steps highlighted with bold/oversized letters.
2) (20 points) Cyclopentadiene (A) cannot be bought as such because it spontaneously dimerizes to form biscyclopentadiene (B). In order to get pure cyclopentadiene you have to displace the equilibrium shown below to the right by heating B and distilling off A, a process known as cracking:

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A ⇌ B
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What famous reaction is involved in the equilibrium between A and B? Present detailed mechanisms for the forwards and backwards reactions controlling it.
3) (20 points) The $^1$H spectrum of nitrobenzene is shown below. Notice that all the $^1$H resonances are downfield with respect to those of plain benzene (7.28 ppm):

![NMR spectrum of nitrobenzene]

- **a)** Assign all the $^1$H resonances of nitrobenzene (i.e., to what signals in the spectrum do protons H(a), H(b), and H(c) belong to…).

- **b)** Why are all the $^1$H signals of nitrobenzene downfield with respect to those of plain benzene? In particular, how can you explain the large deshielding of the protons corresponding to the signal at 8.23 ppm in nitrobenzene?

**Hint:** Think of the electron withdrawing/donating character of the nitro group, which resonant in the ring forms will be stabilized by the presence of this group, and what will happen to the electron density of the protons in the ring…
4) (20 points) Consider the following alcohols:

Alcohol A oxidizes spontaneously in the presence of air to the corresponding ketone. However, you find that alcohol B does not oxidize to a ketone even under the action of strong oxidizing agents.

Explain these observations based on the structures of the expected products of the oxidation reactions.
5) (30 points) A certain aromatic ether, compound A, is subjected to the following reactions:

\[
\begin{align*}
A (C_7H_6O) & \xrightarrow{CH_3COCl, AlCl_3} B & C (C_9H_{10}O_2) \\
B (C_9H_{10}O_2) & \xrightarrow{i) NaBH_4, EtOH, ii) SOCl_2, CH_2Cl_2} D (C_9H_{11}OCl) \\
D (C_9H_{11}OCl) & \xrightarrow{NaOH, \Delta} E (C_9H_{10}O)
\end{align*}
\]

In addition to the information provided above, you recorded NMR spectra for compounds A, B, C, and E, which are provided in the following pages.

With all these data, elucidate the structures of compounds A through E. You do not need to write detailed mechanisms for the reactions or present extensive spectral assignments. However, it would help if you draw the molecules in the spectra and draw arrows from the different protons to their corresponding signals…
Name: ______________________
Problem 5 - Compound A
Problem 5 - Compound B

Additional peak at ~200 ppm
Problem 5 - Compound C

Additional peak at ~200 ppm