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

1) [Diagram of compound with reaction steps]
   - i) PCC, CH₂Cl₂
   - ii) Δ, toluene
   - iii) O₃, CH₂Cl₂
   - iv) Zn, AcOH

   → C₁₅H₂₂O₃

2) [Diagram of compound with reaction steps]
   - i) CH₃COCl, AlCl₃
   - ii) mCPBA, CH₂Cl₂
   - i) NaBH₄, EtOH
   - iv) KOH, THF / H₂O

   → C₁₅H₂₂O₂

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

b) Write detailed reaction mechanisms for the steps highlighted with bold/oversized letters.
2) (30 points) For each of the following compounds:

1) Fe^{2+}

2) 

3) 

a) Calculate their degree of unsaturation, and, if appropriate, show in the structure what gives rise to this number (i.e., double bonds, rings, etc...).

b) Determine how many $^1$H and $^{13}$C NMR signals you will find in their spectra (i.e., identify magnetically equivalent and non-equivalent nuclei).

c) For each set of magnetically equivalent protons, specify their multiplicity, assuming that all coupling constants are equal. Please, try to show them on the molecules to make grading easier...

d) To which of the three compounds shown above do the $^1$H and $^{13}$C NMR spectra given in the following pages belong to?

Note: 

\[ \text{Note: } \text{ benzene ring } = \text{ five-membered ring} \]
3) (40 points) The reaction presented below takes place through an important variation of the aldol condensation known as the **Knoevenagel Condensation**:

![Reaction Diagram]

a) Write the detailed mechanism of the Knoevenagel condensation presented above. If you don’t want to draw piperidine each time you need to, you can use a generic base (say, “B”). It’s very easy if you work by analogy to the aldol condensation mechanism…

b) If you take the product above and cook it up in aqueous acid, you can get to cinnamic acid:

![Reaction Diagram]

The last step of this transformation is a decarboxylation (i.e., loss of CO$_2$). Propose a reasonable mechanism for this last reaction step.

*Hint:* CO$_2$ will behave as a leaving group, and once it leaves two electrons will resonate making an allene (≥C=C=C≤) intermediate…
4) (30 points) A certain aromatic compound (A) is subjected to the following reactions:

\[
\begin{align*}
A \ (C_8H_8) & \xrightarrow{\text{Conditions I}} B \\
& \xrightarrow{\text{Conditions II}} C \ (C_9H_8O_2) \\
& \xrightarrow{\text{Conditions III}} E \ (C_9H_8O) \\
& \xrightarrow{\text{Conditions IV}} D \\
\end{align*}
\]

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

With all these data, and taking into account that I’m giving you the structures of compounds B and D, elucidate the structures of compounds A, C, and E, as well as reaction conditions I through IV needed to accomplish the conversion of A to B and B to C. 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 protons to the signals.

*Hint:* Conditions I and III are protection/deprotection steps. Conditions IV are done in two steps, and the reagent in one of them is also formed during lightning storms…
5) (20 points) After several months of arduous work, you finished with one of the target compounds for your thesis (A). Unfortunately, as soon as you rise the temperature of the reaction mixture above -40 °C, it decomposes to give you two moles of a liquid of molecular formula C₆H₆ which has a single ¹H NMR signal at 7.28 ppm and a single ¹³C NMR signal at 128.0 ppm (compound B):

![Chemical structure of A and B](image)

a) Propose a detailed mechanism for the transformation of A into B. We've looked at this reaction 1 x 10⁶ times, and yes, Otto and Kurt came up with it while they where still *uber alles*…

b) Why is this decomposition reaction spontaneous? Two reasons, one of which is a lot more important than the other…
Name: ______________________
Name: ______________________
Problem 4 - Compound C

1. 10.3 ppm
2. 7.90 - 7.65 ppm
3. 2.7 - 2.6 ppm
All these integrate to 1 each...
Problem 4 - Compound E (expansions)