Statistics:
- **Average:** 77 pts (77%);
- **Highest:** 99 pts (99%); **Lowest:** 40 pts (40%)
- Number of students performing at or above average: 25 (54%)

1. (8 pts) Mark as true (T) or false (F) the following statements. Do not explain!
   - (F) All π-donor substituents are activating;
   - (F) The Wolf-Kishner reduction transforms a ketone to an alcohol;
   - (T) The chemical shift is independent of the operating frequency of the NMR;
   - (T) The gyromagnetic ratio is independent of the operating frequency of the NMR;
   - (T) Only charged species are observed by MS;
   - (T) Organometallic compounds are strong bases;
   - (T) Organometallic compounds are strong nucleophiles;
   - (T) Carbenes are electron-deficient;

2. Circle ALL that apply:
   A. (3 pts) The following reactions are not possible:
      a. Benzene + bromine in the presence of FeBr₃;
      b. Nitrobenzene + butyl chloride, in the presence of AlCl₃;
      c. Benzaldehyde + acetyl chloride, in the presence of AlCl₃;
      d. Toluene + nitric/sulfuric acid mixture, upon heating;
   B. (3 pts) In NMR, one observes nuclei that have:
      a. Odd atomic number but even mass number;
      b. Even atomic number but odd mass number;
      c. Odd atomic number and odd mass number;
      d. Even atomic number and even mass number;
   C. (3 pts) The following reactions are used to prepare tertiary alcohols:
      a. Reaction of aldehyde with an organolithium compound, followed by acid;
      b. Reaction of ketone with an organolithium compound, followed by acid;
      c. Reaction of a Grignard reagent with an ester, followed by acid;
      d. Acid-catalyzed hydration of alkynes;

3. Write and complete a chemical equation for each of the following reactions:
   A. (3 pts) Anisole + isopropyl chloride, in the presence of AlCl₃;
      \[
      \text{OCH}_3 + \text{Cl} - \xrightarrow{\text{AlCl}_3} \text{OCH}_3 + \text{PhCH}_3
      \]
   B. (3 pts) Acetophenone + nitric acid/sulfuric acid, upon heating;
      \[
      \text{O} \xrightarrow{\text{HNO}_3} \text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{NO}_2
      \]
   C. (3 pts) Acetone + phenyllithium, followed by acid;
      \[
      \text{O} \xrightarrow{1) \text{PhLi/ether}} \text{OH} \xrightarrow{2) \text{H}_3\text{O}^+} \text{OCH}_3
      \]
D. (3 pts) Ethyl formate + 2 equivalents of ethylmagnesium bromide, followed by acid;

\[
\text{HCOO} \quad 1) \ C_2H_5MgBr \quad 2) \ H_3O^+ \quad \text{OH}
\]

4. (25 pts) Indicate the principal organic product of each of the following reactions. If \( o-p \)-mixture is expected, write both products.

5. (6 pts) Predict the major product of monobromination of the following compounds with \( \text{Br}_2/\text{FeBr}_3 \):

6. (8 pts) Suggest an appropriate combination of a carbonyl compound (aldehyde or ketone) or ester AND an organolithium or organomagnesium compound that can be used for the preparation of each of the compounds listed below. Write the complete chemical equation in each case.

A. 3-Pentanol;
B. 3-Phenyl-3-hexanol;

7. (6 pts) Give the structure of the organometallic reagent necessary to carry out each of the following reactions.

8. (5 pts) While chlorination and bromination of benzene are easily accomplished with Br₂ or Cl₂ as reagents, iodination cannot be conducted with I₂, because it is not reactive enough. Instead, the compound iodine monochloride (ICl) is used. Write a detailed mechanism for the reaction below.

9. (5 pts) Predict TWO likely MS fragmentations for 3,3-dimethyl-1-butanol.
10. (5 pts) You are given three bottles containing \textit{o}-dichlorobenzene, \textit{m}-dichlorobenzene and \textit{p}-difluorobenzene, along with three on-resonance decoupled $^{13}$C NMR spectra. Assign each spectrum to a particular compound and briefly explain your reasoning.

\begin{itemize}
  \item A: $\delta$ 127.0, 128.9, 130.6, 135.1
  \item B: $\delta$ 127.7, 130.5, 132.6
  \item C: $\delta$ 116.5, 159.1
\end{itemize}

The dashed lines represent internal planes of symmetry:

\begin{itemize}
  \item three types of unequivalent C-atoms, 3 signals in $^{13}$C NMR, spectrum B
  \item four types of unequivalent C-atoms, 4 signals in $^{13}$C NMR, spectrum A
  \item two types of unequivalent C-atoms, 2 signals in $^{13}$C NMR, spectrum C
\end{itemize}

11. (5 pts) Shown below are four eight-membered ring compounds and four $^1$H NMR spectra. Assign the appropriate spectrum to each compound and briefly explain your reasoning.

\begin{itemize}
  \item All H-atoms are equivalent, hence 1 signal in $^1$H NMR. H-atoms are attached to C=C bonds: Spectrum B
  \item Four types of H-atoms, hence 4 signals in $^1$H NMR: Spectrum D
  \item Two types of H-atoms, hence 2 signals in $^1$H NMR: Spectrum C
  \item All H-atoms are equivalent, hence 1 signal in $^1$H NMR. H-atoms are attached to C-C bonds: Spectrum A
\end{itemize}

\begin{itemize}
  \item A: $\delta$ 1.54 (singlet)
  \item B: $\delta$ 5.74 (singlet)
  \item C: $\delta$ 2.39 (multiplet, 8H), 5.60 (multiplet, 4H)
  \item D: $\delta$ 1.45 (multiplet, 4H), 2.20 (multiplet, 4H), 5.43 (multiplet, 2H), 5.78 (multiplet, 2H)
\end{itemize}

12. (6 pts) Compound C$_9$H$_{12}$ is an alkylbenzene. It is subjected to a Friedel-Crafts acylation, followed by a Clemmensen reduction, giving a product, C$_{12}$H$_{18}$, whose $^1$H NMR spectrum is shown below. Write the structural formula of C$_{12}$H$_{18}$. Write a structural formula for C$_9$H$_{12}$.

\begin{itemize}
  \item There are two types of propyl groups (a propyl and an isopropyl) with their characteristic NMR patterns. The downfield region shows the characteristic pattern for a p-disubstituted benzene ring.
\end{itemize}
13. (3 pts) BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!). When aromatic compounds are treated with formaldehyde, CH₂O, and HCl, the CH₂Cl group is introduced onto the aromatic ring. The reaction is known as chloromethylation. Propose a detailed mechanism for the following chloromethylation reaction:

```
H₂H₂O HCl  [1H]
formaldehyde

H₂H₂O + HCl  →  H₂H₂O⁺  +  Cl⁻

H₂H₂O⁺ + H⁺  →  H₂H₂O

S₂Ar

H₂O

H₂O + HCl  →  H₂O⁺  +  Cl⁻
```

*Diagram showing the reaction mechanism*