1. (8 pts) **Indicate which** of the following molecules will react with Br₂/FeBr₃ to give *ortho/para* isomers as the major products and which will react to give the *meta* product as the major isomer.
2. (10 pts) A newly isolated compound was found to have the formula C\textsubscript{7}H\textsubscript{14}O\textsubscript{2} from mass spectrometry data and the following signals in the \textsuperscript{1}H and \textsuperscript{13}C spectra. \textbf{Give a structure} for the compound that agrees with the NMR spectral data then \textbf{match the \textsuperscript{1}H NMR data} to the protons in your answer.

\textsuperscript{1}H NMR (ppm): 1.24 (s, 6H), 1.71 (t, 2H, \textit{J} = 7.1 Hz), 2.40 (q, 2H, \textit{J} = 7.1 Hz), 3.30 (s, 3H), 9.72 (t, 1H, \textit{J} = 7.1 Hz)

\textsuperscript{13}C NMR (ppm): 28.1 (double intensity), 34.0, 34.8, 49.0, 81.8, 202.2

3. (10 pts) \textbf{Provide an efficient synthesis} of the following molecule beginning from benzene and using any of the reactions and reagents seen thus far in 3719 and 3720. \textbf{Show the organic product(s)} from each step and assume isomer mixtures may be separated.
4. (20 pts) **Give the major products** from each step of the following reaction sequences.

a. 

\[ \text{CH}_3 \]

1. HNO_3, H_2SO_4
2. Sn, HCl

\[ \text{CH}_3 \]

1. \text{CH}_3\text{NO}_2 + \text{CH}_3 \]

2. \text{CH}_3\text{NH}_2 + \text{CH}_3 \]

b. 

\[ \text{CH}_3 \]

1. \text{Cl}_2, \text{AlCl}_3
2. Cl, AlCl_3
3. Zn, HCl

\[ \text{CH}_3 \]

1. \text{CH}_3\text{O} + \text{CH}_3 \]

2. \text{CH}_3\text{O} + \text{CH}_3 \]

3. \text{CH}_3\text{Cl} + \text{CH}_3 \]

4. \text{CH}_3\text{Cl} + \text{CH}_3 \]

c. 

\[ \text{CH}_3 \]

1. HNO_3, H_2SO_4
2. Br_2, FeBr_3
3. Mg, ether
4. D_2O

\[ \text{NO}_2 \]

1. \text{NO}_2 \]

2. \text{NO}_2 \]

3. \text{NO}_2 \]

4. \text{NO}_2 \]

d. 

\[ \text{CH}_3 \]

1. CH_3Cl, AlCl_3
2. KMnO_4
3. NaOH

\[ \text{CH}_3 \]

1. \text{CH}_3 \]

2. \text{CO}_2\text{H} \]

3. \text{CO}_2\text{Na} \]

e. 

\[ \text{C(CH}_3)_3 \text{CH}_3 \]

1. HNO_3, H_2SO_4
2. Br_2, heat

\[ \text{C(CH}_3)_3 \text{CH}_3 \]

1. \text{C(CH}_3)_3\text{NO}_2 \]

2. \text{C(CH}_3)_3\text{CH}_2\text{Br} \]

5. (12 pts) From the $^1$H and $^{13}$C NMR data below, **provide the structure** of the unknown organic compound having the molecular formula C$_{12}$H$_{16}$O$_3$. **Match the $^{13}$C NMR** signals to the carbons in the unknown.

$^1$H NMR (ppm): 1.09 (d, 6H, $J = 6.9$ Hz), 1.32 (t, 3H, $J = 7.0$ Hz), 2.67 (septet, 1H, $J = 6.9$ Hz), 4.09 (q, 2H, $J = 7.0$ Hz), 6.83 (m, 3H), 7.31 (m, 1H)

$^{13}$C NMR (ppm): 14.8, 19.1 (double intensity), 33.6, 64.6, 107.8, 111.2, 113.2, 129.7, 153.7, 159.8, 175.4

Mass spectrum: $\text{M}^+ = 208.25$
Infra-Red: 1740, 770, 690 cm$^{-1}$
6. (20 pts) **Provide the major regioisomer(s)** from the following reactions and **give mechanistic explanations** for your answers (i.e. draw the mechanisms and use resonance structures to explain the products).

**a)**

![Reaction a diagram](image)

Even though the electron-withdrawing CF₂CF₃ group will destabilize all cations formed in this reaction, the *meta* substitution avoids the buildup of charge at the ring C immediately next to the CF₂CF₃ group and is therefore, by default, the preferred pathway.

**b)**

![Reaction b diagram](image)

The electron-donating CH₃ group will stabilize the cations formed when the electrophile adds at the *ortho* and *para* positions since there will be a contributor to the overall hybrid that has tertiary character (in the box); this does not occur for the *meta* situation.
7. (10 pts) For a pending criminal trial a Forensic Chemist has to prove, absolutely conclusively, the structure of a flammable material used in the crime. The unknown is one of the five compounds shown below; choose the correct structure and match the \( ^1 \text{H} \) and \( ^{13} \text{C} \) NMR data to that molecule.

\[
\begin{align*}
\text{\(^1\text{H} \text{ NMR (ppm):}\)} & \quad 1.11 (t, 3\text{H}, J = 7.0 \text{ Hz}), 2.98 (q, 2\text{H}, J = 7.0 \text{ Hz}), 6.90 (d, 1\text{H}, J = 12.0 \text{ Hz}), \\
& \quad 7.19 (d, 1\text{H}, J = 12.0 \text{ Hz}) \\
\text{\(^{13}\text{C} \text{ NMR (ppm):}\)} & \quad 7.9, 33.0, 121.2, 136.7, 200.4 \\
\text{IR (cm}^{-1}) & \quad 1730, 1650
\end{align*}
\]

\( J = 12.0 \) relates to \textit{cis}-aligned protons on a double bond

8. (10 pts) On the axis given below, draw the approximate \( ^1 \text{H} \text{ NMR spectrum} \) for the following molecule.