Note: There is a heavy picture in Question 5. After scrolling down, please wait a moment if your computer has not displayed the image.
1 Question 1

a) Assume the force constant $k$ is the same between 2 compounds.

Reduced mass of each nitrile group is:

$$\mu_1 = \frac{12 \times 14}{12 + 14} = 6.46 \text{ a.u. and } \mu_{1^*} = \frac{13 \times 15}{13 + 15} = 6.96 \text{ a.u.}$$

Due to the relation:

$$\nu = 2\pi \sqrt{\frac{k}{\mu}} \Rightarrow \frac{\nu_{1^*}}{\nu_1} = \sqrt{\frac{\mu_1}{\mu_{1^*}}} \Rightarrow \nu_{1^*} = \nu_1 \sqrt{\frac{\mu_1}{\mu_{1^*}}} = 2225 \times \sqrt{\frac{6.46}{6.96}} = 2144 \text{ cm}^{-1}$$

b) For compound 2-4, the maximum absorption wavelength $\lambda_{\text{max}}$ depends on the conjugation range of $\pi$ electrons.

In biphenyl (compound 2), 2 benzene rings are slightly twisted and the dihedral angle between them is 44.4°. Meanwhile, in the compound 4, 2 benzene rings are even more distorted due to high steric effect caused from bulky iPr substituent. Hence, the conjugation of $\pi$ electrons in compound 4 is less efficient than in compound 2. Moreover, in fluorene (compound 3), 2 benzene rings are fixed mostly co-planar. Therefore, the conjugation here is maximized. Finally: $\lambda_{\text{max},3} > \lambda_{\text{max},2} > \lambda_{\text{max},4}$. 
c) From MS data: \( M_r = 133 \). Rule of 13: 
\[
\frac{133}{13} = 10 + \frac{3}{13}
\]
\( \Rightarrow \) The molecular formula: \( \text{C}_{10}\text{H}_{13} \) or \( \text{C}_9\text{H}_{11}\text{N} \) or \( \text{C}_8\text{H}_7\text{NO} \).
The molecule has 4 equivalent aliphatic H. Hence, the unsaturation index \( U \) cannot be too high. Choose the \( \text{C}_9\text{H}_{11}\text{N} \) formula with \( U = 5 \).
From the IR spectra, the highest absorption bands are only around 2950 cm\(^{-1} \) which is in C-H vibration range. Hence, there is no N-H bond in the molecule.
The resonance at \( \delta = 29.6 \) ppm in \(^{13}\text{C} \) NMR belongs to the aliphatic C attached to electronegative group.
From the above analysis, we can propose the structure of compound 5 as follow:

\[ \text{\begin{figure}
\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}
\end{figure}} \]

\[ \text{5} \]

\[ \text{\begin{figure}
\begin{center}
\includegraphics[width=0.8\textwidth]{diagram.png}
\end{center}
\end{figure}} \]

d) From the magnetic anisotropy of C≡C triple bond, the H situated next to a triple bond will be downfield shifted.
Question 2

From ¹H NMR spectrum, the resonance at δ 12.5 ppm corresponds to 2 carboxylic acidic protons. Hence, compound 8 is a dicarboxylic acid.
The broad singlet at δ 5.5 ppm should be 1 alcohol proton.
The doublet of doublet at δ 4.2 ppm represents for 1 H attached to electronegative group.
In ¹³C NMR, there are 4 signals showing 4 types of Carbon. 2 of them are carboxylic acid Carbons.
From the above analysis, we can conclude the structure of compound 8 is Malic acid:

Due to the chiral center, 2 H in -CH₂ group show the different chemical shifts and 2 coupling patterns have vicinal coupling. Of course, only from the spectrum we cannot say it is D or L isomer. The structure is showing L isomer just because it is the natural form.

Characteristic IR bands:
\( \tilde{\nu} = 1700 \text{ cm}^{-1} \): C=O stretching.
\( \tilde{\nu} = 1300 \text{ cm}^{-1} \): C-O (carboxylic acid) stretching.
\( \tilde{\nu} = 2700-3200 \text{ cm}^{-1} \): broad band of O-H stretching.

EI-MS fragmentation can form some fragments with m/z = 134 (M⁺), 117, 89 and 45. The mechanism is shown below:
b) Compound 9. Molecular formula: C₉H₈O₂. Unsaturation index: U = 6. From ¹H NMR spectrum, 2 triplets at δ 2.8 and 3.0 ppm should come from 2 -CH₂ groups attached to each other. The chemical shifts imply that this -CH₂-CH₂- chain is attached both sides by electronegative groups or aryl groups, but not directly attached to O atoms. In IR spectrum, the sharp absorption peak at $\tilde{\nu} = 740$ cm⁻¹ indicates that this molecule contains an ortho-disubstituted benzene ring. In addition, the absorption peak at $\tilde{\nu} = 1780$ cm⁻¹ from carbonyl stretching and 2 peaks at $\tilde{\nu} = 1150$ and 1220 cm⁻¹ show that this compound is an ester. From the above analysis, we can conclude the structure of compound 9 is 2-Chromanone:

![2-Chromanone](image)

DEPT 135 spectrum of 9 will have similar structure with ¹³C NMR spectrum except that 2 signals at δ 24 and 30 ppm will flip down.

c) Compound 10. Molecular formula: C₉H₉NO₃. Unsaturation index: U = 6. EI-MS spectrum contains m/z = (M-15) and (M-43) peaks. Hence, the compound probably has acetyl group CH₃CO-. The broad singlet at δ 6.48 ppm in ¹H NMR spectrum corresponds to 2 H ⇒ The molecule may contain -NH₂ group. The molecule only has 9 Carbons. 6 of them are in the benzene ring. 2 of them are in the acetyl group. The last one should be a -CH₂- group of a cyclic ketal. Because the singlet of this -CH₂- is very downfield shifted (δ 5.90 ppm). Two sharp absorption peaks at $\tilde{\nu} = 3350$ and 3420 cm⁻¹ support for the prediction about -NH₂ group. Hence, the molecular structure should be:

![Compound 10](image)

d) The resonance with -NH₂ group and benzene ring decreases the order of C=O bond. Therefore, the absorption of C=O stretching in IR spectrum is at $\tilde{\nu} = 1650$ cm⁻¹ (lower than normal value of 1715 cm⁻¹). The mechanism is shown above.
3 Question 3

The complex structure:

\[
\begin{array}{c}
\text{H} \\
\text{R}_3\text{P} \longrightarrow \text{Rh} \longrightarrow \text{H} \\
\text{PR}_3
\end{array}
\]

a) The Rh-H signal in $^1$H NMR spectrum: It should be a doublet of doublet of doublet (ddd) due to the coupling with 1 Rh, 1 cis-PR$_3$ and 1 trans-PR$_3$. This ddd should appear in negative region of chemical shift $\delta$.

b) Similarly to $^1$H NMR, the $^{31}$P{$^1$H} NMR signal is also a ddd formed by the coupling with 1 Rh, 1 cis-H and 1 trans-H.

c) The signal in $^{109}$Rh NMR is a triplet of triplet (tt). The splitting pattern caused from coupling with 2 equivalent H and 2 equivalent PR$_3$ ligands.
4 Question 4

The complexes’ structures:

\[
\begin{align*}
\text{cis-isomer} & \quad \text{trans-isomer} \\
\text{cis-isomer} & \quad \text{trans-isomer}
\end{align*}
\]

a) In \(^{31}\text{P}\{^1\text{H}\}\) NMR, both isomers give a singlet with Pt satellites. The separation between 2 Pt satellites is determined by coupling constant \(^1J_{\text{Pt-P}}\). The cis-isomer has larger \(^1J_{\text{Pt-P}}\) as compared to the trans-isomer because in trans-isomer, 2 phosphine ligands are bonded to the same \(d\) orbital of Pt and hence, there is a competition of electron density in \(\pi\) backbonding from Pt to 2 phosphine ligands.

b) In \(^{195}\text{Pt}\) NMR, both isomers give a triplet. The separation between each peak within a triplet is determined by coupling constant \(^1J_{\text{Pt-P}}\). Due to the reason mentioned above, the peaks within the triplet of cis-isomer should be more separated than the one of trans-isomer.
5 Question 5

Simulated spectra of all phosphine ligands.

After summing up all the component spectra, we got the final total NMR spectrum as follow (all the components are still plotted out for reference):