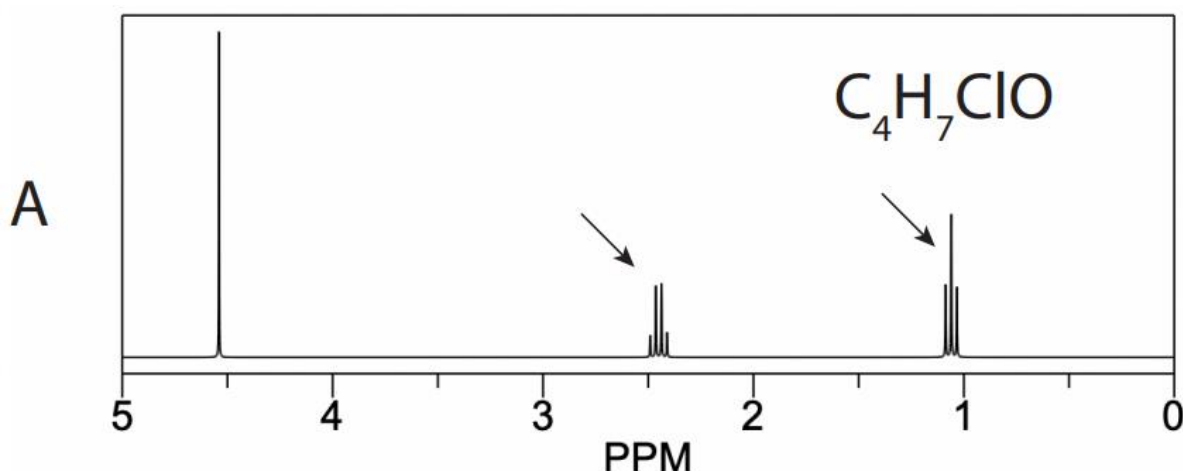


Jigsaw 1: Synthesis

Keeler Chapter 2. Setting the scene



Consider the given 1H spectrum and chemical formula given above.

1. [Section 2.1] Estimate the separation in ppm for the two peaks indicated with arrows. Calculate this separation in Hz for a 400.130000 MHz and for a 900.130000 MHz spectrometer.

Estimation in ppm: $\Delta\delta = 1,3$

Calculation in Hz: $\Delta\nu = 10^{-6} \times \Delta\delta \times \nu_{ref}$

For a 400.130000 MHz spectrometer:

$$\Delta\nu = 10^{-6} \times 1,3 \times 400.13 \text{ MHz} = 520.039 \text{ Hz}$$

For a 900.130000 MHz spectrometer:

$$\Delta\nu = 10^{-6} \times 1,3 \times 900.13 \text{ MHz} = 1170.039 \text{ Hz}$$

2. [Section 2.2] Determine the integral of each multiplet

All peaks seem to have the same width (very thin), so it should be enough to compare their heights. The first multiplet is a singlet at about 4.5 ppm. The second multiplet is a quartet at about 2.4 ppm. The two middle peaks are about a fourth of the height of the singlet at 4.5 ppm and the smallest outer peaks each about a twelfth. The total length of these four peaks thus seems about two thirds of the singlet peak. The third multiplet is a triplet at about 1.1 ppm. The middle peak is about half of the singlet peak and the outer peaks are each about a fourth. The total length of the third multiplet is thus about the same as the singlet peak. These estimations give a ratio of 3:2:3. It is impossible to distribute the 7 protons over this ratio. It could be that the first

singlet was overestimated, but this is just a guess. That could give a ratio of 2:2:3, so the integrals are 2 protons, 2 protons and 3 protons respectively.

3. [Section 2.3] Based on the multiplicity, your answer from (b), and the chemical formula, determine the molecule corresponding to this spectrum and indicate which protons correspond to which peaks.

The triplet with 3 protons at 1.1 ppm comes from having two neighboring protons giving 3 possible spin combinations: both up, both down or one down and one up. These 2 neighboring protons are in the quartet at 2.4 ppm. The quartet comes from having 3 neighboring protons. The triplet and quartet are thus linked to CH₃ and CH₂ respectively. Together they form an ethyl group: -CH₂-CH₃.

The remaining atoms are C₂H₂ClO. These last two protons form the singlet at 4.5 ppm, indicating that they are probably not coupled to neighboring protons. This can be explained by a CH₂ group attached to an electronegative atom: O or Cl.

This information leads us to the following possible molecule: CH₃-CH₂-CO-CH₂-Cl.

4. [Section 2.4] How many peaks would the ¹³C spectrum have with and without proton decoupling?

There are 4 carbons in the molecule: C1 (CH₃), C2 (CH₂), C3 (CO-) and C4 (CH₂Cl). With proton decoupling, the couplings between C and directly attached H's are removed. Since there are no carbons equivalent in energy, this gives a spectrum with 4 singlet peaks. Without decoupling, each multiplet will depend on the amount of protons attached to the carbon: C1 has 3 attached protons and will thus be a quartet, C2 has 2 attached protons and will be a triplet, C3 has 0 attached protons and will be a singlet and C4 has 2 attached protons and will be a triplet.

5. [Section 2.5] Convert the peak separation from (a) to rad s⁻¹.

The angular frequency differences are found using the following formula: $\omega = 2\pi/T = 2\pi\nu$. For a 400.130000 MHz spectrometer this gives: $\omega = 3267.501 \text{ rad/s}$. For a 900.130000 MHz spectrometer this gives: $\omega = 7351.572 \text{ rad/s}$.

Jigsaw 1: Synthesis

Keeler Chapter 2. Setting the scene

Consider the given ^1H spectrum and chemical formula on the following page.

- [Section 2.1] Estimate the separation in ppm for the two peaks indicated with arrows. Calculate this separation in Hz for a 400.130000 MHz and for a 900.130000 MHz spectrometer.

$$\Delta\delta \text{ (ppm)} \approx 2.45 - 1.15 = 1.30 \text{ ppm}$$

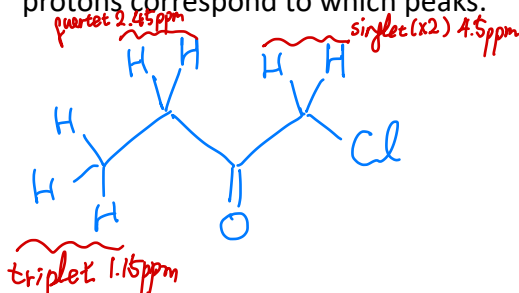
$$10^{-6} \times \delta \times \nu_{\text{ref}} = \Delta\nu, \quad \text{for } 400.130000 \text{ MHz} : 520.17 \text{ kHz}$$

$$900.130000 \text{ MHz} : 1170.17 \text{ kHz}$$

- [Section 2.2] Determine the integral of each multiplet

$$7 \text{ H in total} \rightarrow (\text{maybe}) 2:2:3$$

- [Section 2.3] Based on the multiplicity, your answer from (b), and the chemical formula, determine the molecule corresponding to this spectrum and indicate which protons correspond to which peaks.



- [Section 2.4] How many peaks would the ^{13}C spectrum have with and without proton decoupling?

with decoupling: 4 single peaks

without decoupling: CH_3 quartet

CH_2 triplet

CO singlet

CH_2Cl triplet

- [Section 2.5] Convert the peak separation from (a) to rad s^{-1} .

$$400.130000 \text{ MHz} : 2\pi \times 520.17 \approx 3268.4 \text{ rad/s}$$

$$900.130000 \text{ MHz} : 2\pi \times 1170.17 \approx 7352.4 \text{ rad/s}$$

Jigsaw 1: Synthesis

Keeler Chapter 2. Setting the scene

Consider the given ^1H spectrum and chemical formula on the following page.

- [Section 2.1] Estimate the separation in ppm for the two peaks indicated with arrows. Calculate this separation in Hz for a 400.130000 MHz and for a 900.130000 MHz spectrometer.

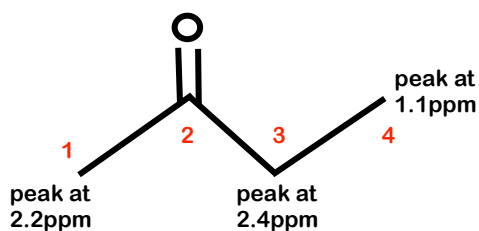
Separation in ppm for the two peaks is $2.4\text{ppm} - 1.1\text{ppm} = 1.3\text{ppm}$

frequency separation in Hz = $(\delta_1 - \delta_2) \times \nu_{\text{ref}}(\text{in MHz}) =$
 $= (2.4 - 1.1) \times 400.13 = 520.169\text{Hz}$ for 400.130000 MHz spectrometer
 $= (2.4 - 1.1) \times 900.13 = 1170.169\text{Hz}$ for 900.130000 MHz spectrometer

- [Section 2.2] Determine the integral of each multiplet

Singlet at 2.2 ppm \rightarrow 3 H
Quartet at 2.4 ppm \rightarrow 2 H
Triplet at 1.1 ppm \rightarrow 3 H

- [Section 2.3] Based on the multiplicity, your answer from (b), and the chemical formula, determine the molecule corresponding to this spectrum and indicate which protons correspond to which peaks.



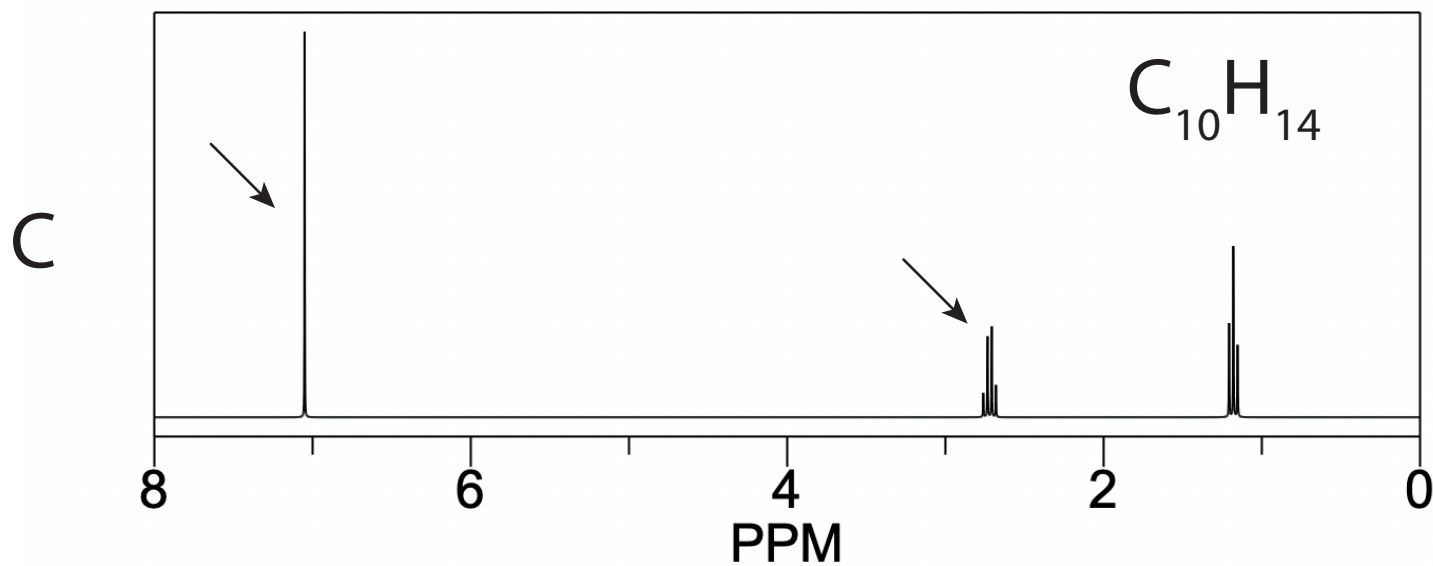
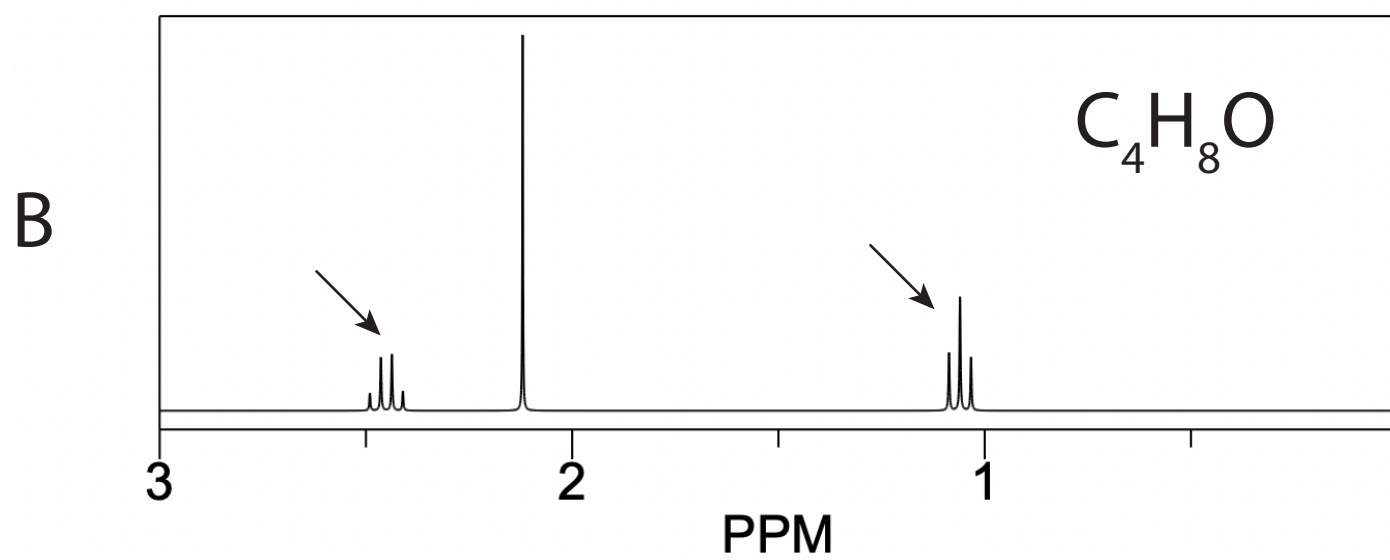
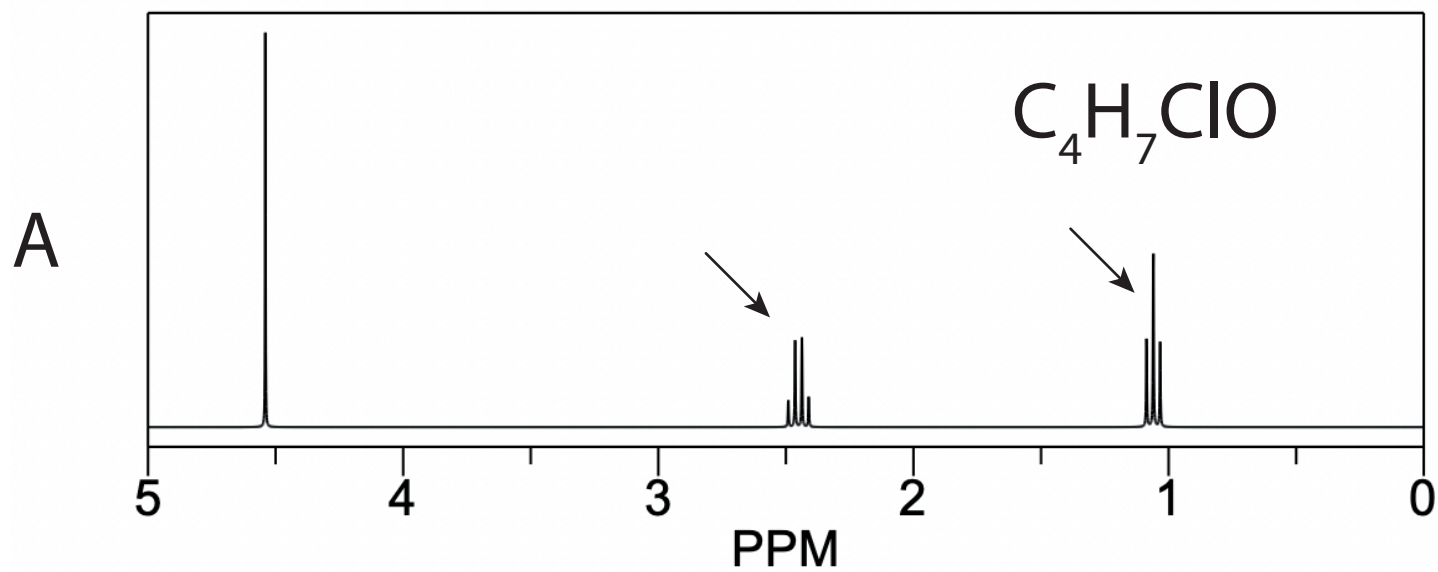
- [Section 2.4] How many peaks would the ^{13}C spectrum have with and without proton decoupling?

With proton decoupling : 4 singlets
Without proton decoupling :
C1 \rightarrow singlet
C2 \rightarrow quartet
C3 \rightarrow triplet
C4 \rightarrow quartet

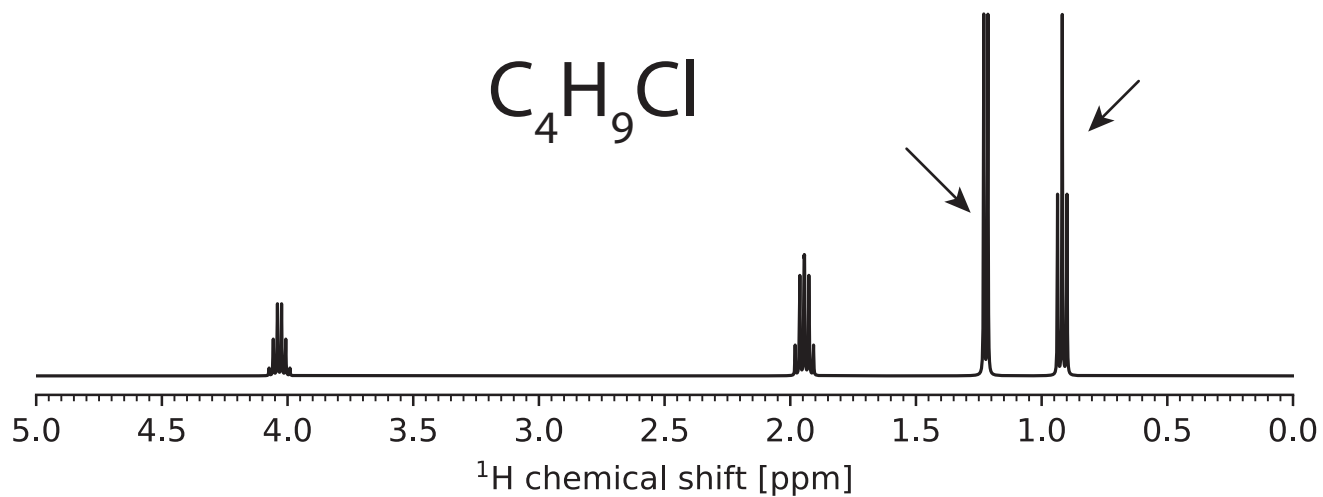
- [Section 2.5] Convert the peak separation from (a) to rad s^{-1} .

$\omega = 2\pi \Delta\nu =$
 $= 2\pi \times 520.169 = 3268.3 \text{ rad/s}$ for 400.130000 MHz spectrometer
 $= 2\pi \times 1170.169 = 7352.4 \text{ rad/s}$ for 900.130000 MHz spectrometer

Jigsaw 1. Synthesis



D



E

