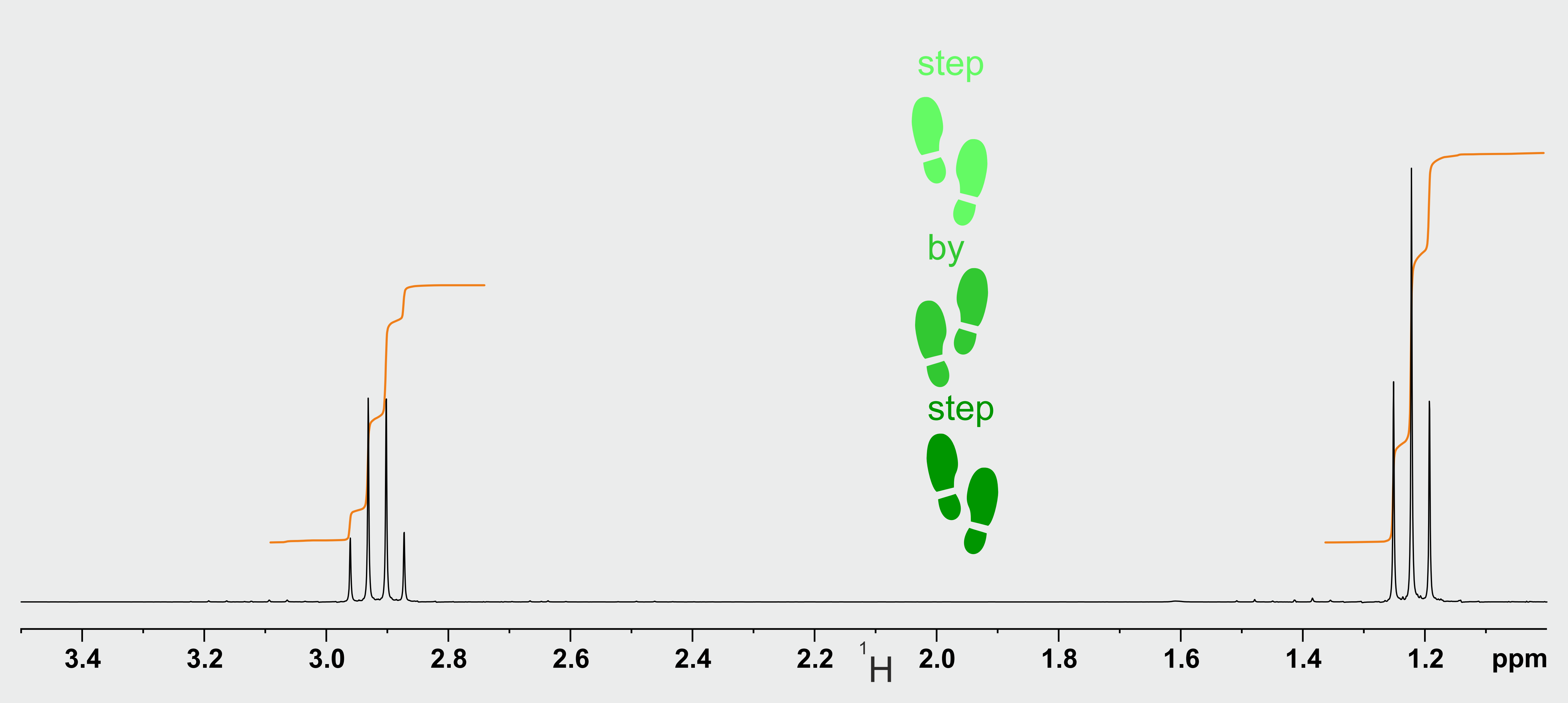
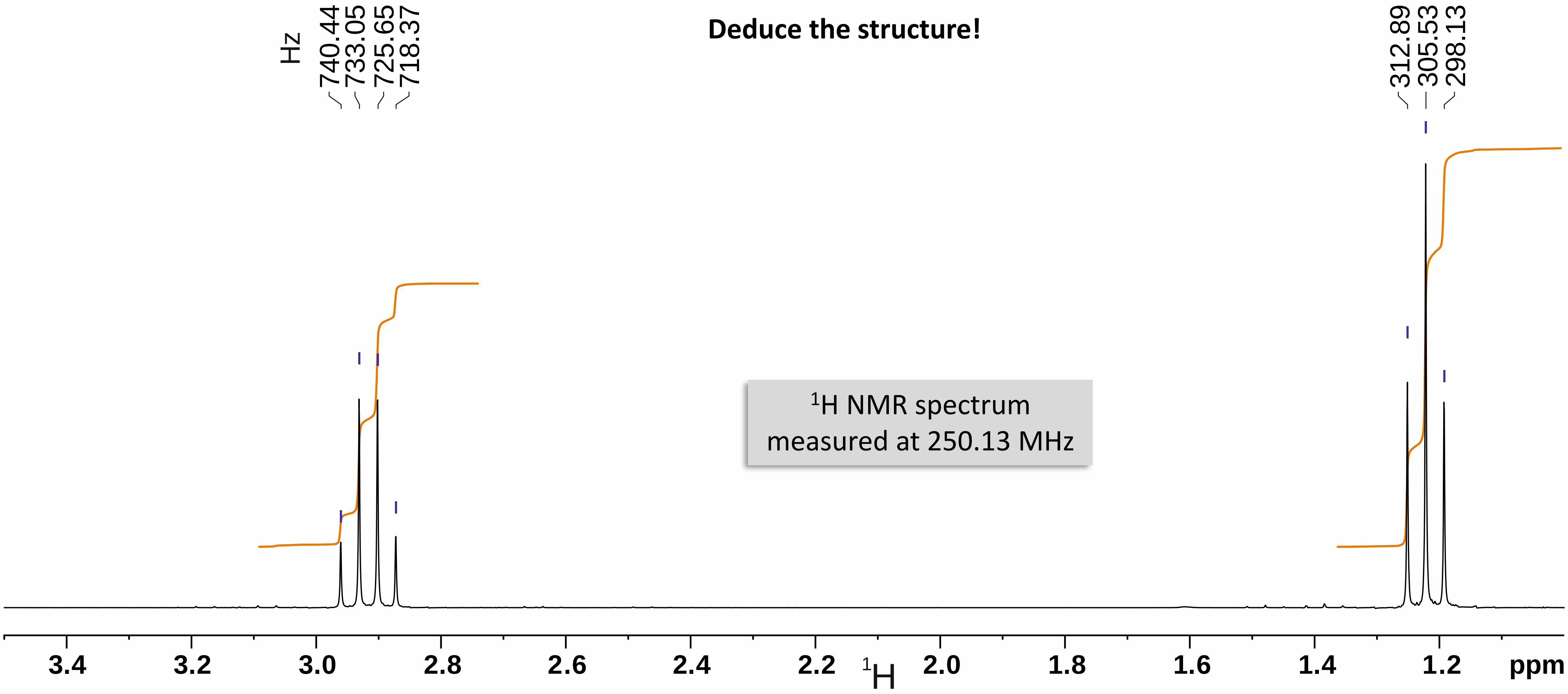
Exercise plus Solution – Quick overview

It is recommended to use this version only for a quick overview of the NMR challenge. All animations of the PowerPoint version are missing, under certain circumstances quality deficiencies may also occur.
The higher quality PowerPoint files are freely available for download at any time.



C_3H_5ClO measured in $CDCl_3$

Deduce the structure!



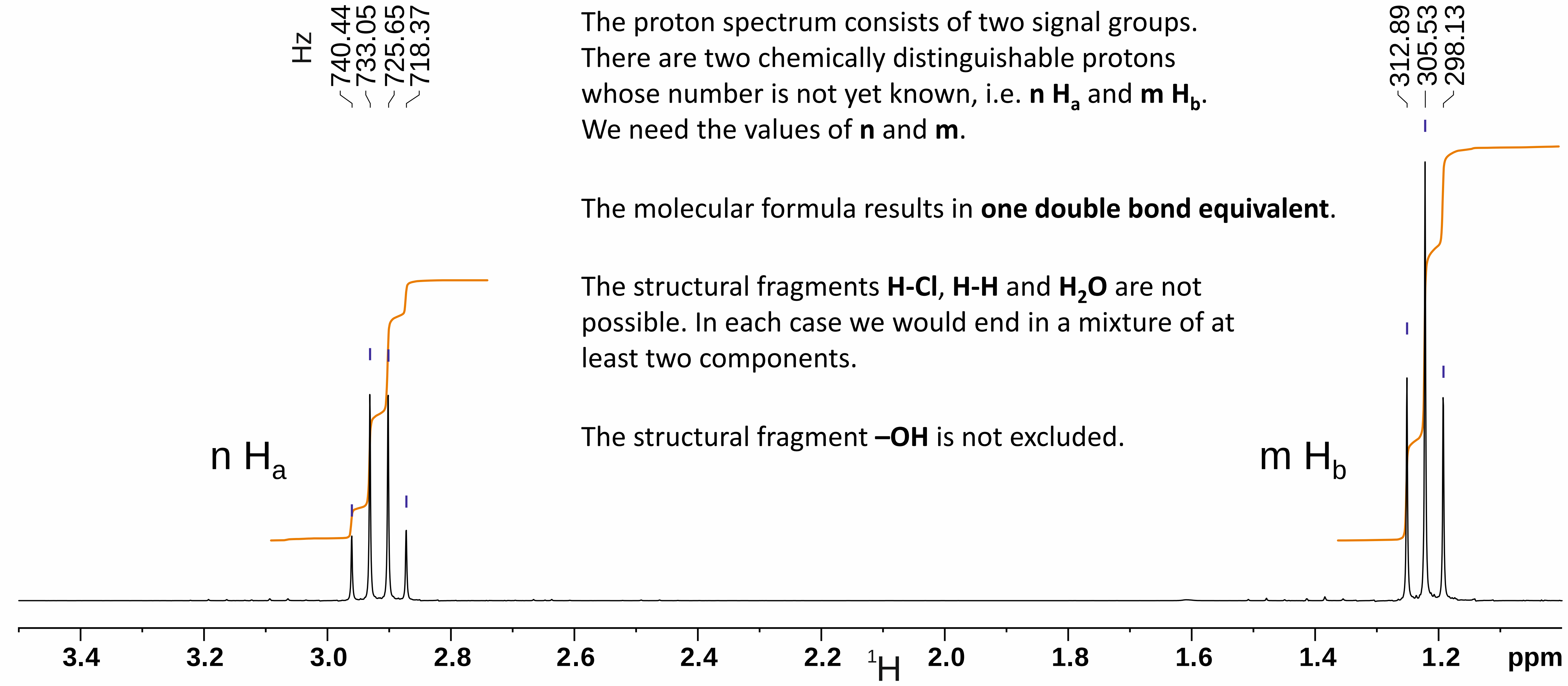
First Considerations

The proton spectrum consists of two signal groups.
There are two chemically distinguishable protons whose number is not yet known, i.e. **n H_a** and **m H_b**.
We need the values of **n** and **m**.

The molecular formula results in **one double bond equivalent**.

The structural fragments **H-Cl**, **H-H** and **H_2O** are not possible. In each case we would end in a mixture of at least two components.

The structural fragment **–OH** is not excluded.

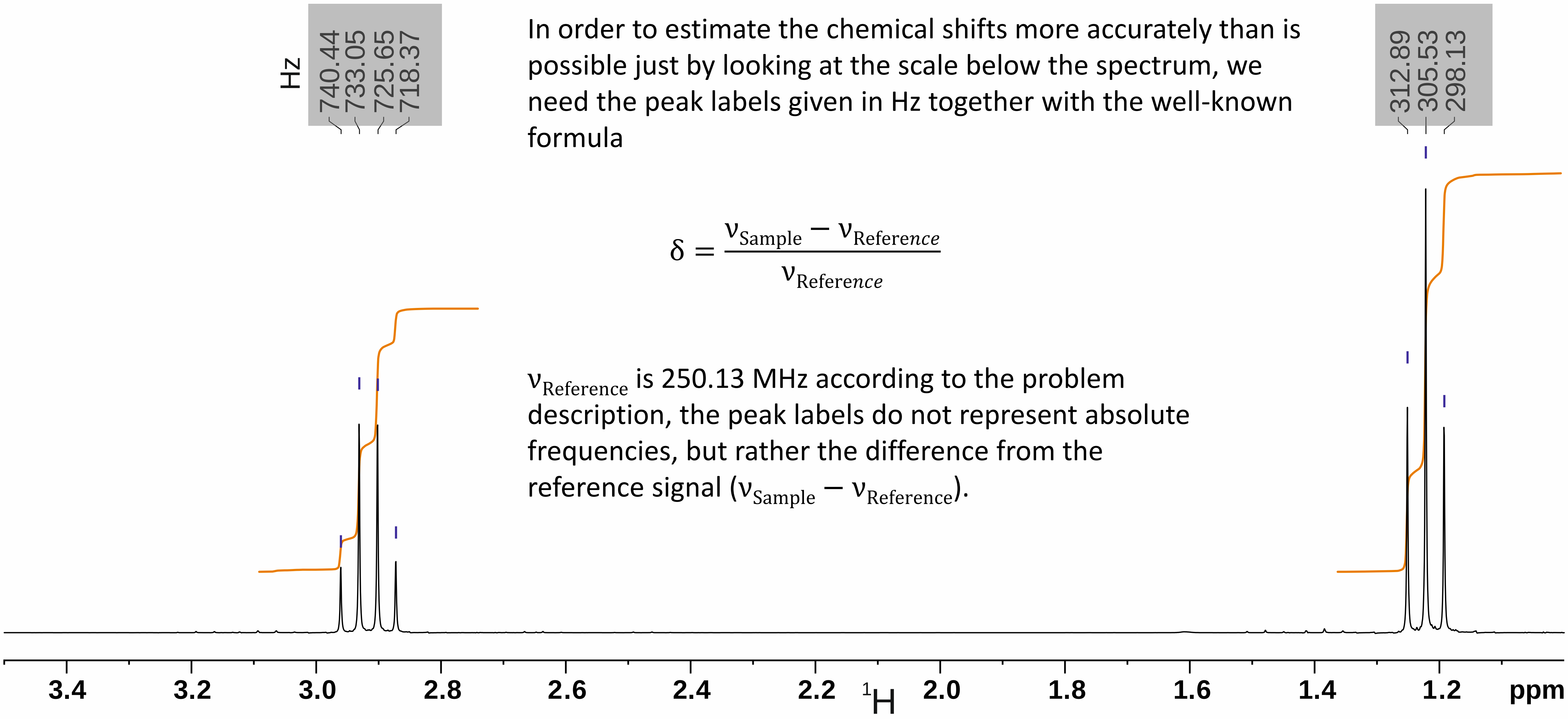


Chemical shifts

In order to estimate the chemical shifts more accurately than is possible just by looking at the scale below the spectrum, we need the peak labels given in Hz together with the well-known formula

$$\delta = \frac{\nu_{\text{Sample}} - \nu_{\text{Reference}}}{\nu_{\text{Reference}}}$$

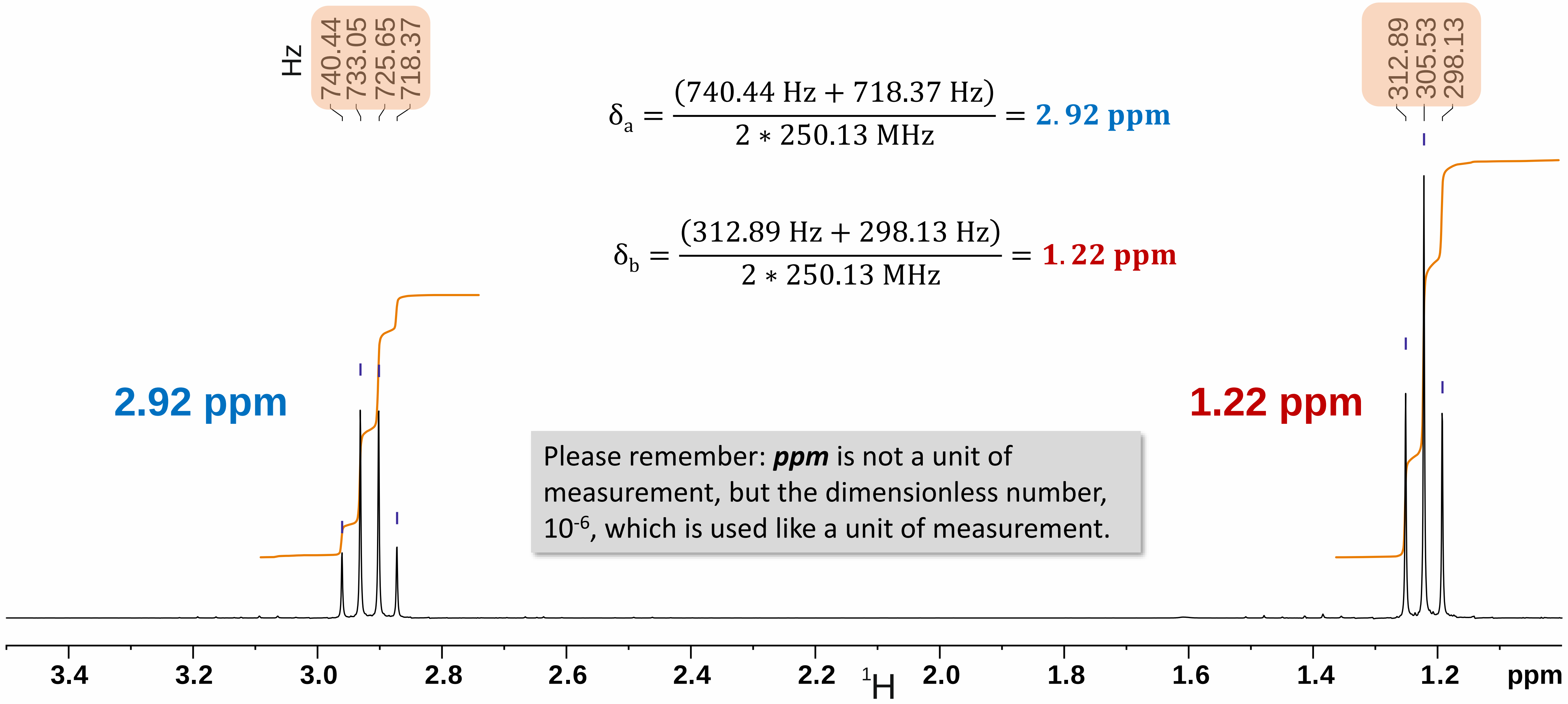
$\nu_{\text{Reference}}$ is 250.13 MHz according to the problem description, the peak labels do not represent absolute frequencies, but rather the difference from the reference signal ($\nu_{\text{Sample}} - \nu_{\text{Reference}}$).



Chemical shifts

$$\delta_a = \frac{(740.44\ \text{Hz} + 718.37\ \text{Hz})}{2 * 250.13\ \text{MHz}} = \mathbf{2.92\ ppm}$$

$$\delta_b = \frac{(312.89\ \text{Hz} + 298.13\ \text{Hz})}{2 * 250.13\ \text{MHz}} = \mathbf{1.22\ ppm}$$



Please remember: ***ppm*** is not a unit of measurement, but the dimensionless number, 10^{-6}, which is used like a unit of measurement.

Integration

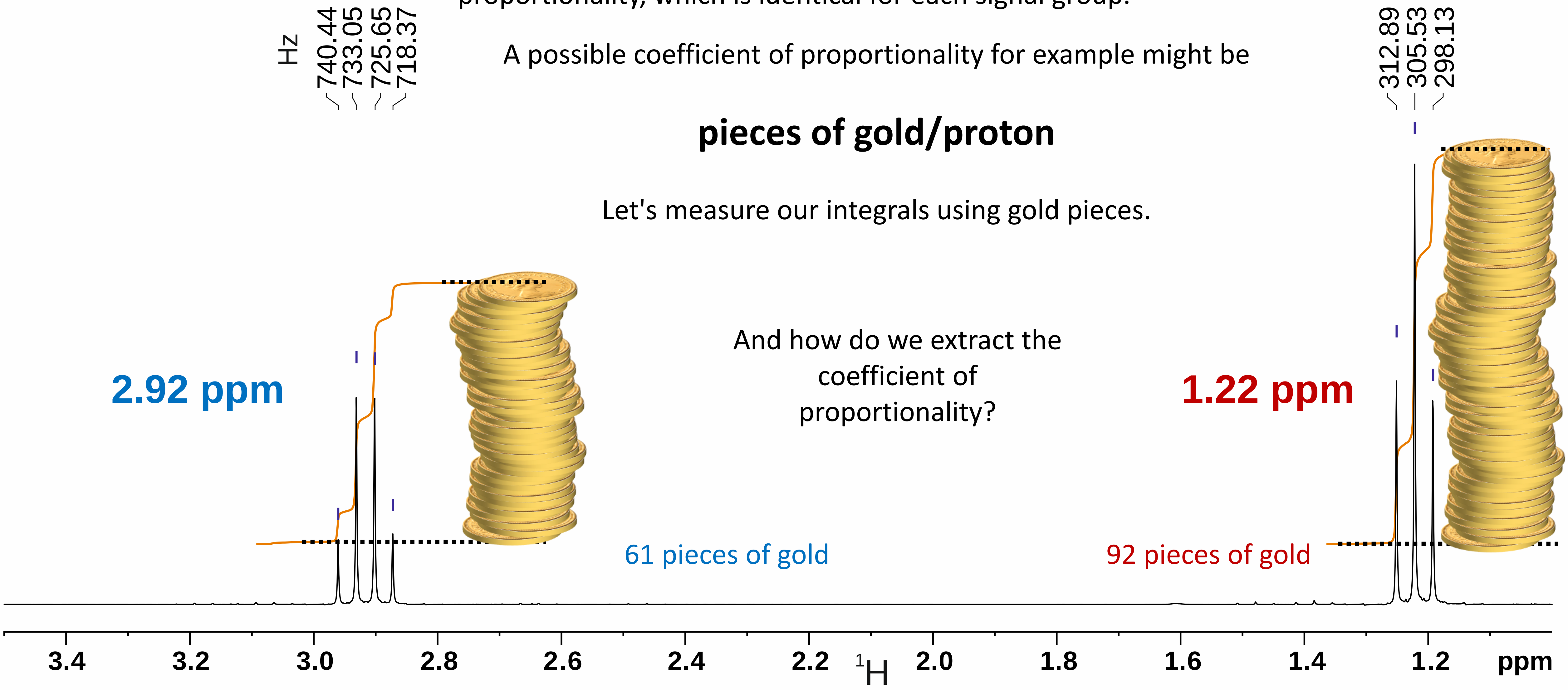
The area of both signal groups contains an unknown coefficient of proportionality, which is identical for each signal group.

A possible coefficient of proportionality for example might be

pieces of gold/proton

Let's measure our integrals using gold pieces.

And how do we extract the coefficient of proportionality?



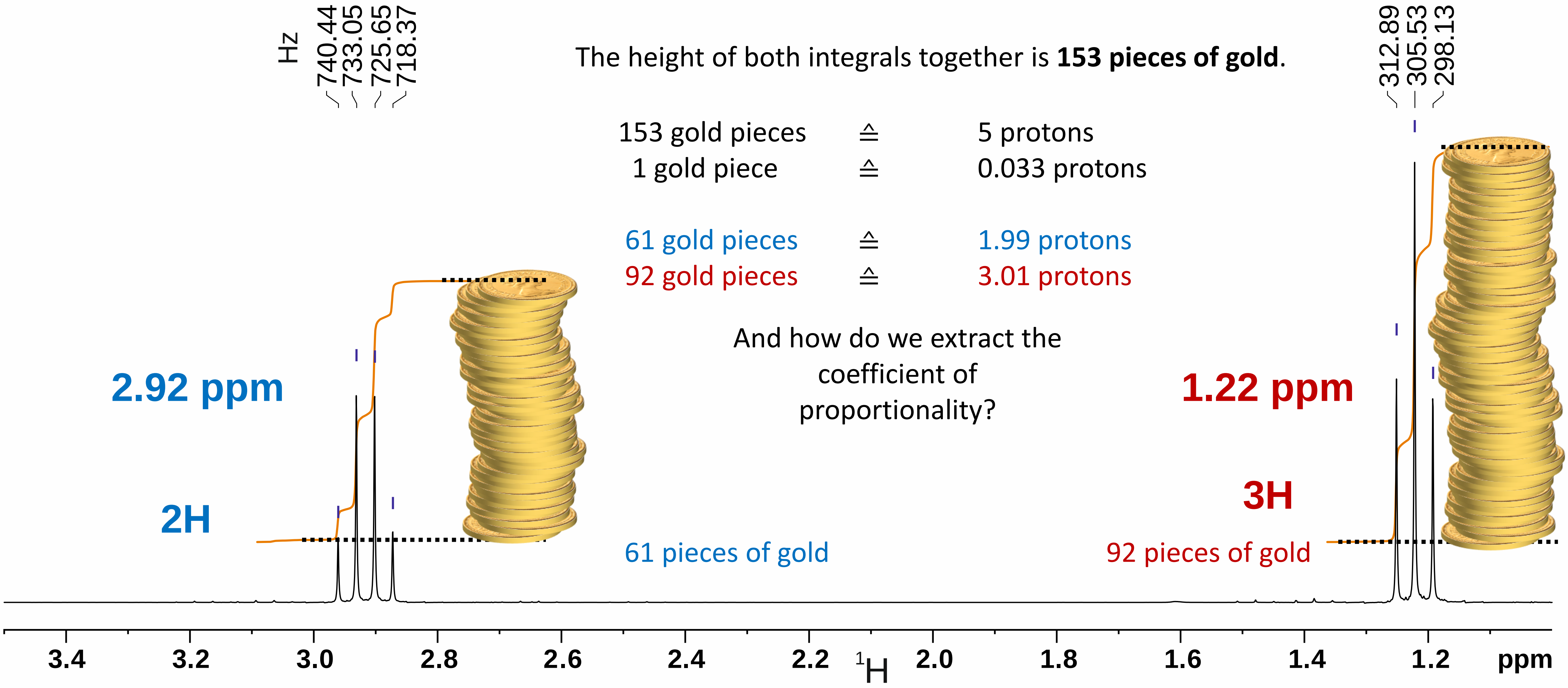
Integration

The molecular formula (C_3H_5ClO) includes 5 protons.

The height of both integrals together is **153 pieces of gold**.

153 gold pieces	≙	5 protons
1 gold piece	≙	0.033 protons
61 gold pieces	≙	1.99 protons
92 gold pieces	≙	3.01 protons

And how do we extract the coefficient of proportionality?



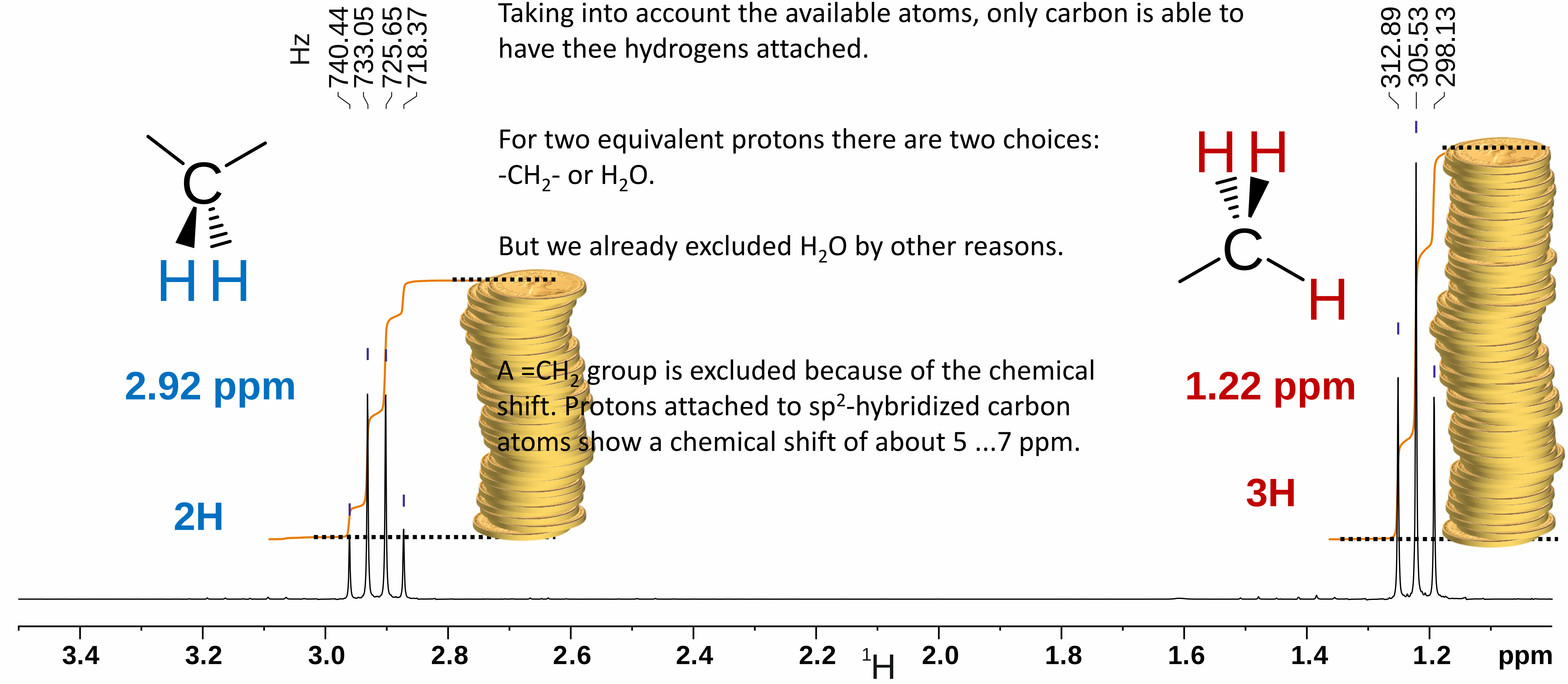
Struktural fragments

Taking into account the available atoms, only carbon is able to have thee hydrogens attached.

For two equivalent protons there are two choices: -CH_2- or H_2O.

But we already excluded H_2O by other reasons.

A =CH_2 group is excluded because of the chemical shift. Protons attached to sp^2-hybridized carbon atoms show a chemical shift of about 5 ...7 ppm.

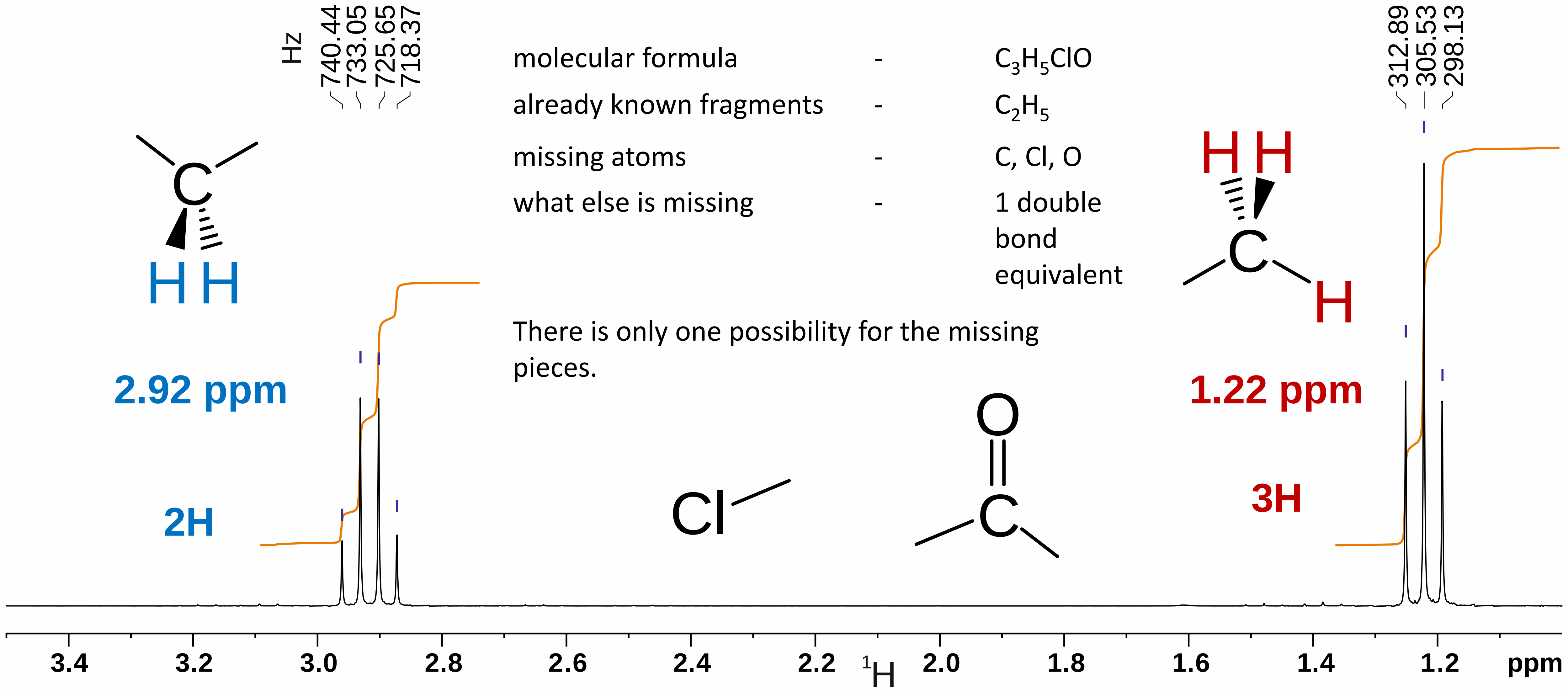


Struktural fragments

A short inventory

molecular formula	-	C_3H_5ClO
already known fragments	-	C_2H_5
missing atoms	-	C, Cl, O
what else is missing	-	1 double bond equivalent

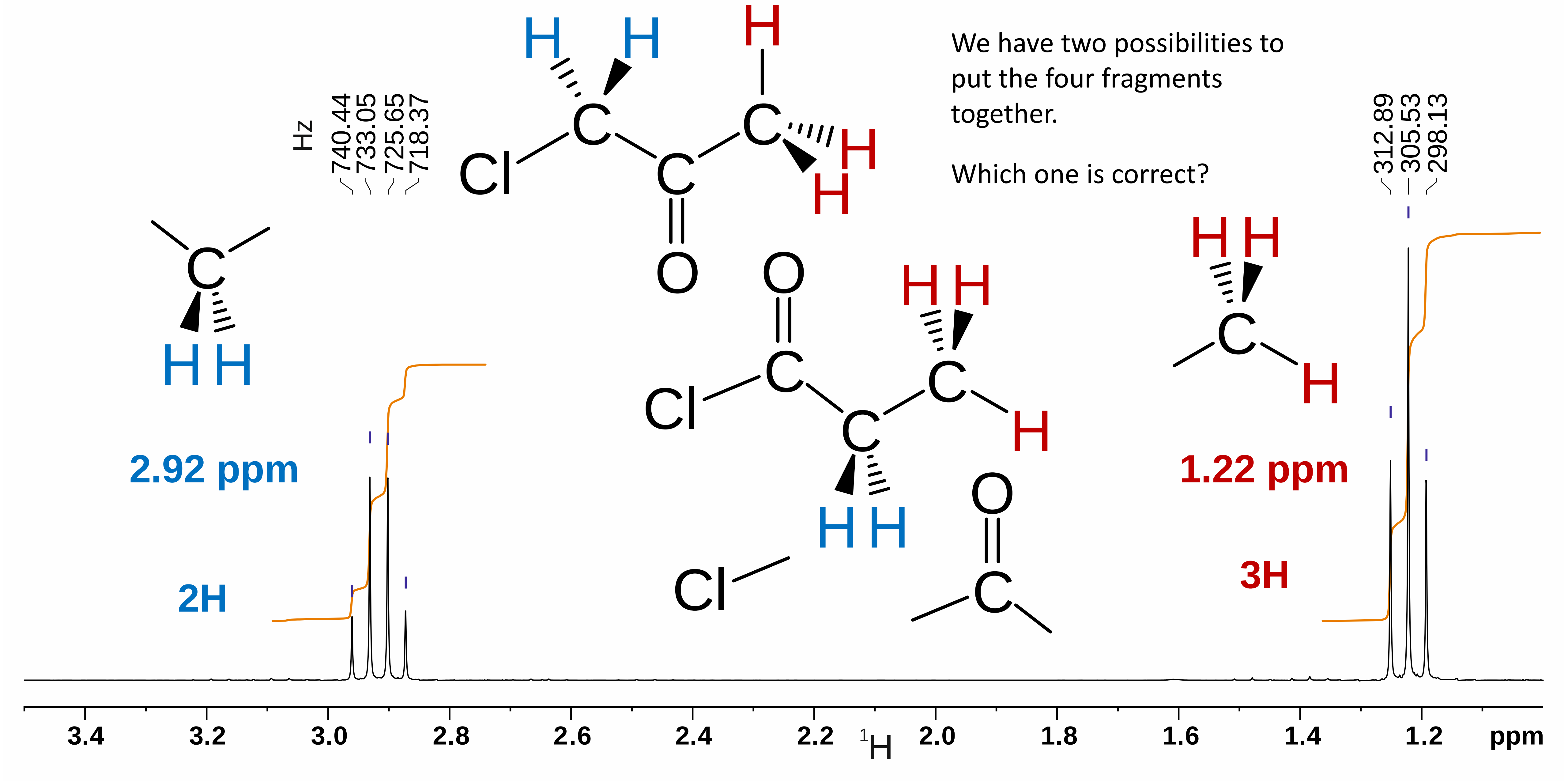
There is only one possibility for the missing pieces.



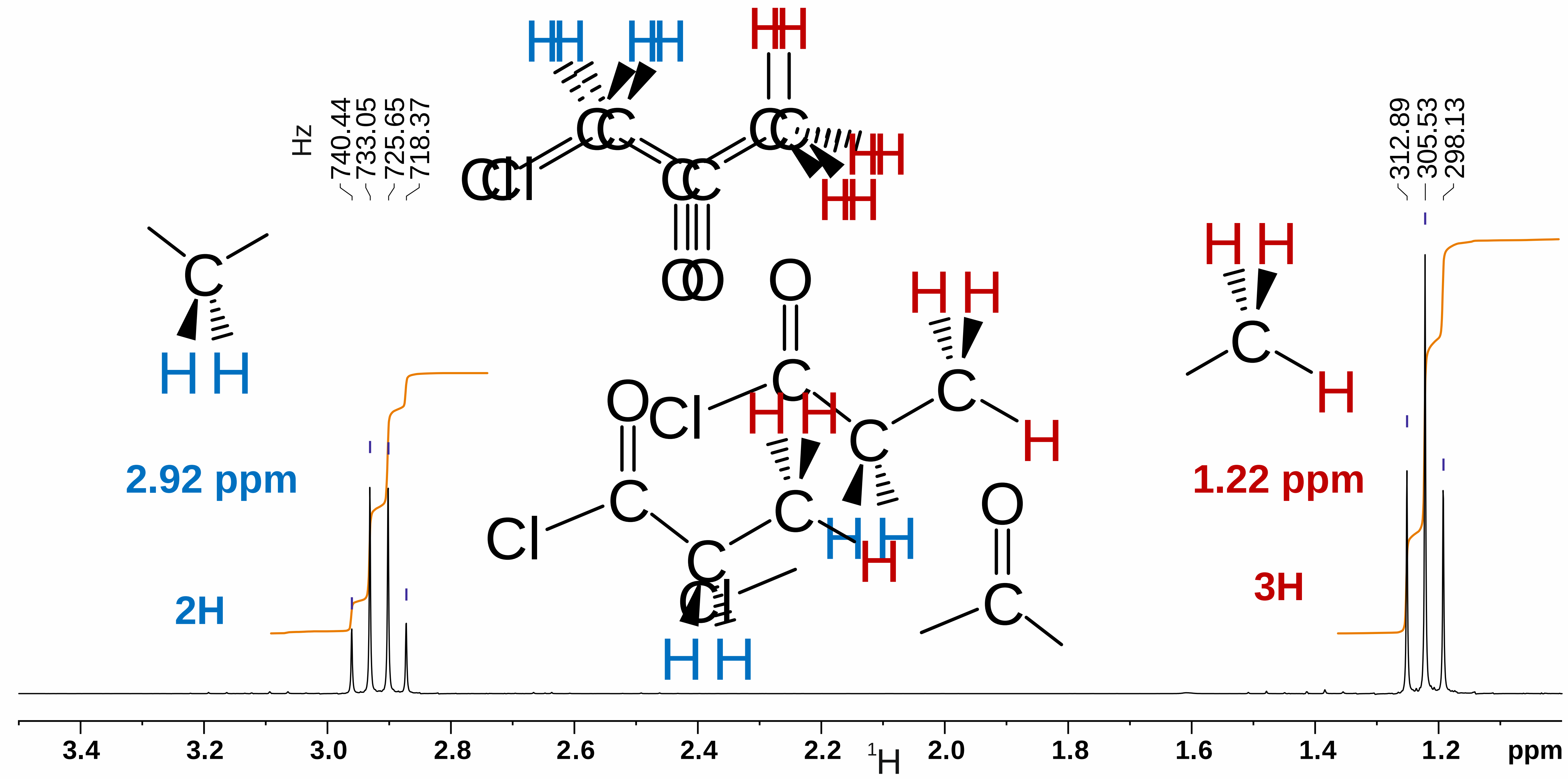
Struktural fragments

We have two possibilities to put the four fragments together.

Which one is correct?

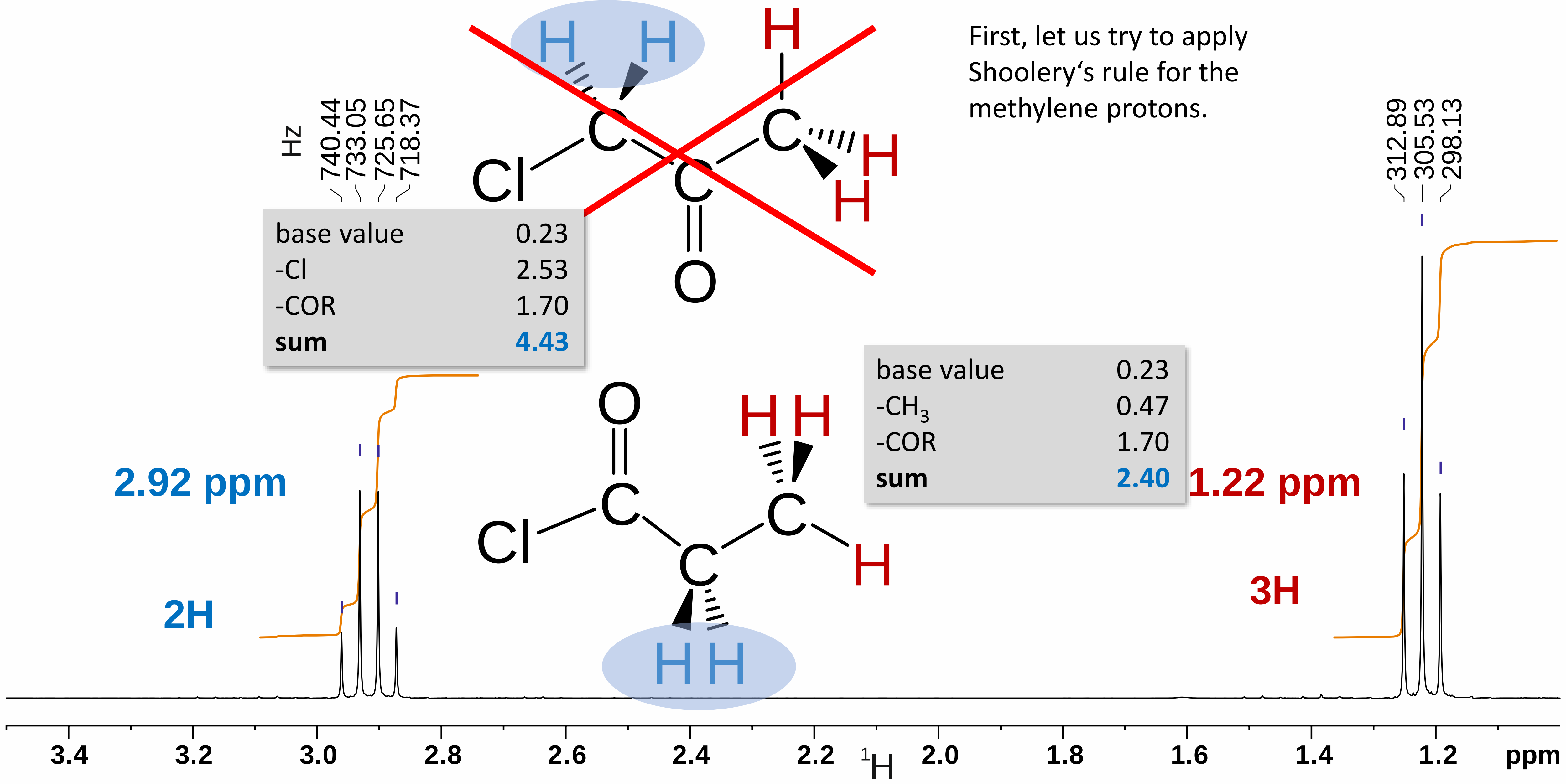


Struktural fragments



Final structures

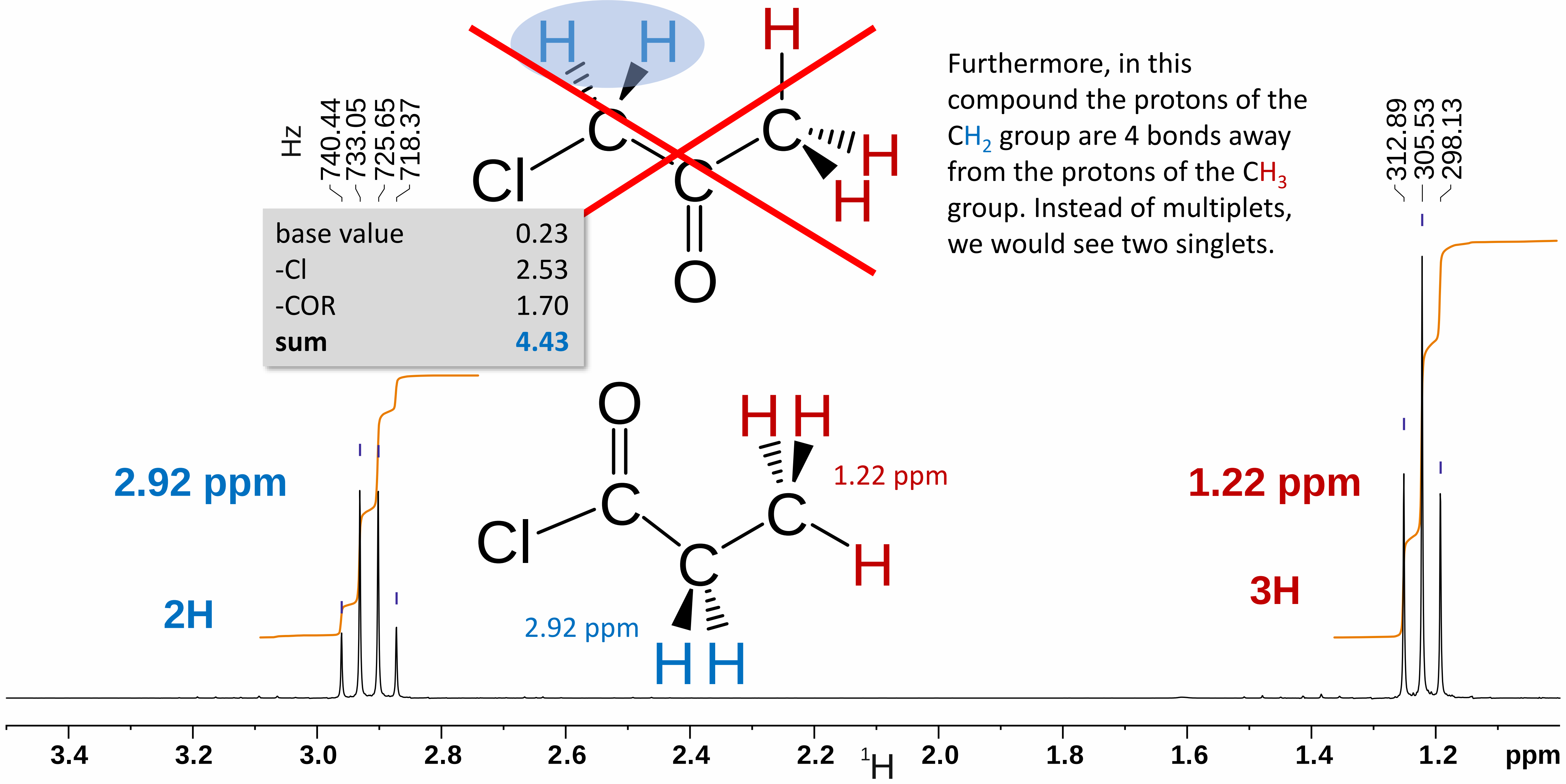
First, let us try to apply Shoolery's rule for the methylene protons.



base value	0.23
-Cl	2.53
-COR	1.70
sum	**4.43**

base value	0.23
$-CH_3$	0.47
-COR	1.70
sum	**2.40**

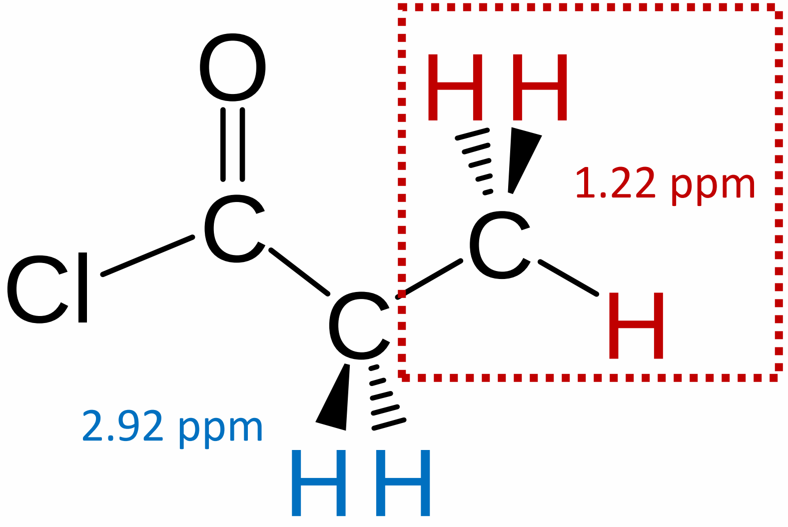
Final structures



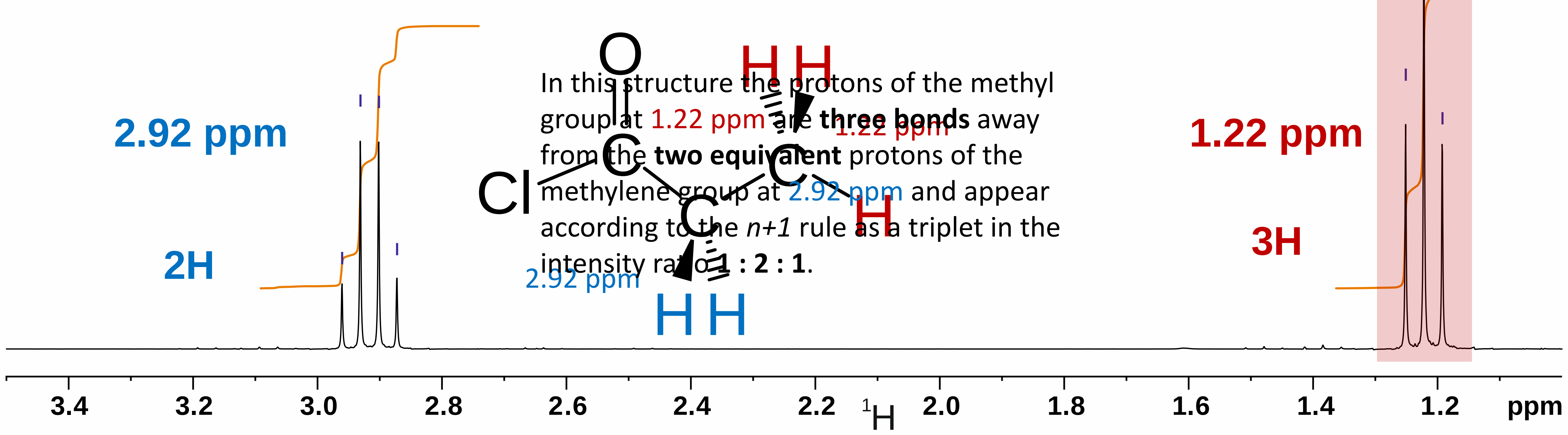
base value	0.23
-Cl	2.53
-COR	1.70
sum	**4.43**

Furthermore, in this compound the protons of the CH_2 group are 4 bonds away from the protons of the CH_3 group. Instead of multiplets, we would see two singlets.

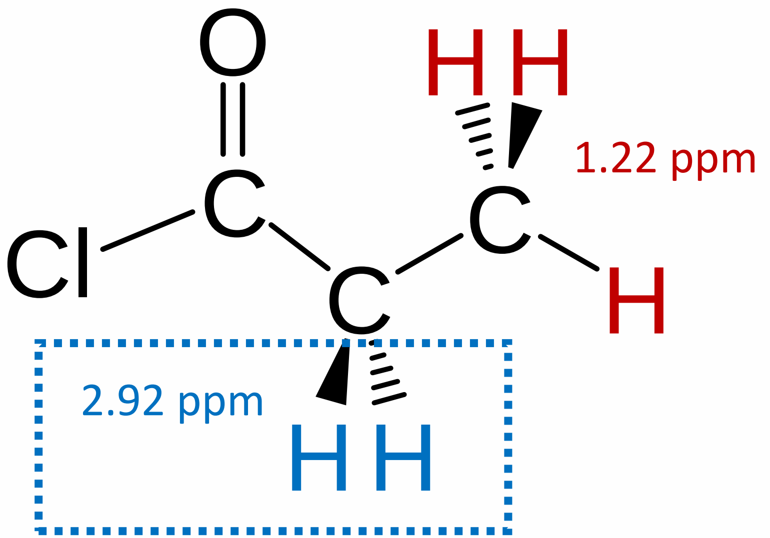
Finale structure

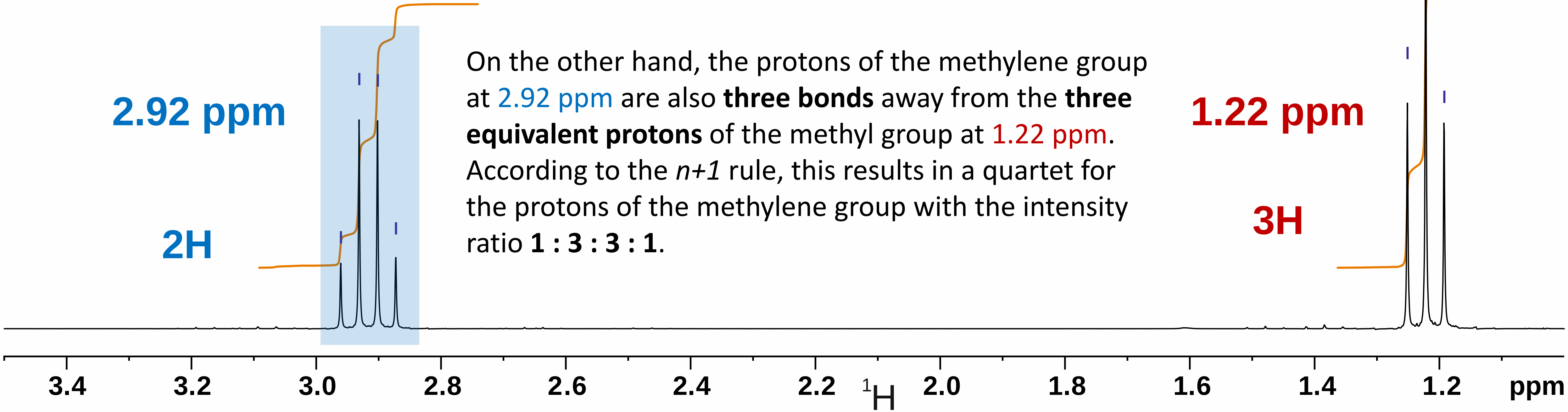


In this structure the protons of the methyl group at 1.22 ppm are **three bonds** away from the **two equivalent** protons of the methylene group at 2.92 ppm and appear according to the *n+1* rule as a triplet in the intensity ratio **1 : 2 : 1**.



Finale structure



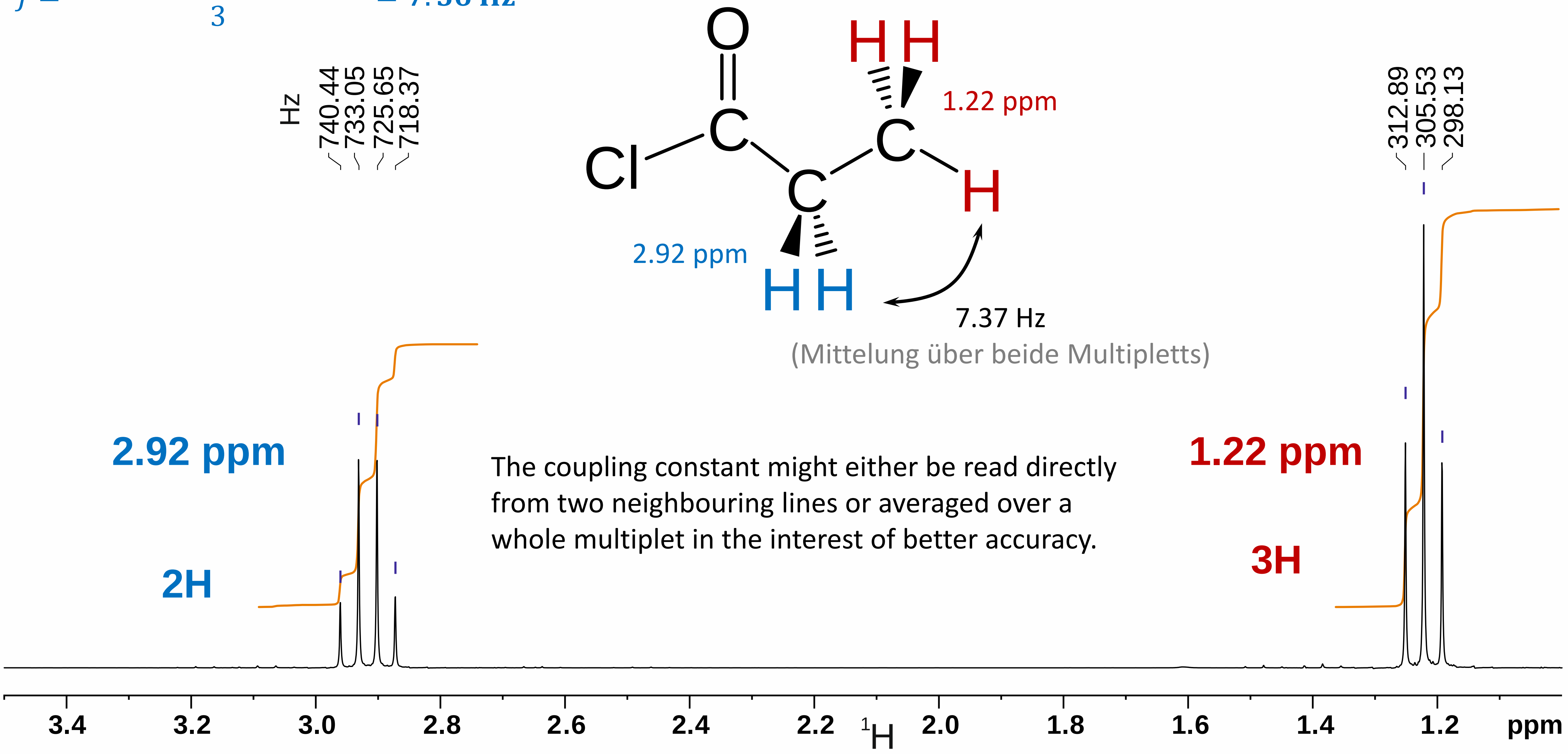


On the other hand, the protons of the methylene group at 2.92 ppm are also **three bonds** away from the **three equivalent protons** of the methyl group at 1.22 ppm. According to the *n+1* rule, this results in a quartet for the protons of the methylene group with the intensity ratio **1 : 3 : 3 : 1**.

Finale structure

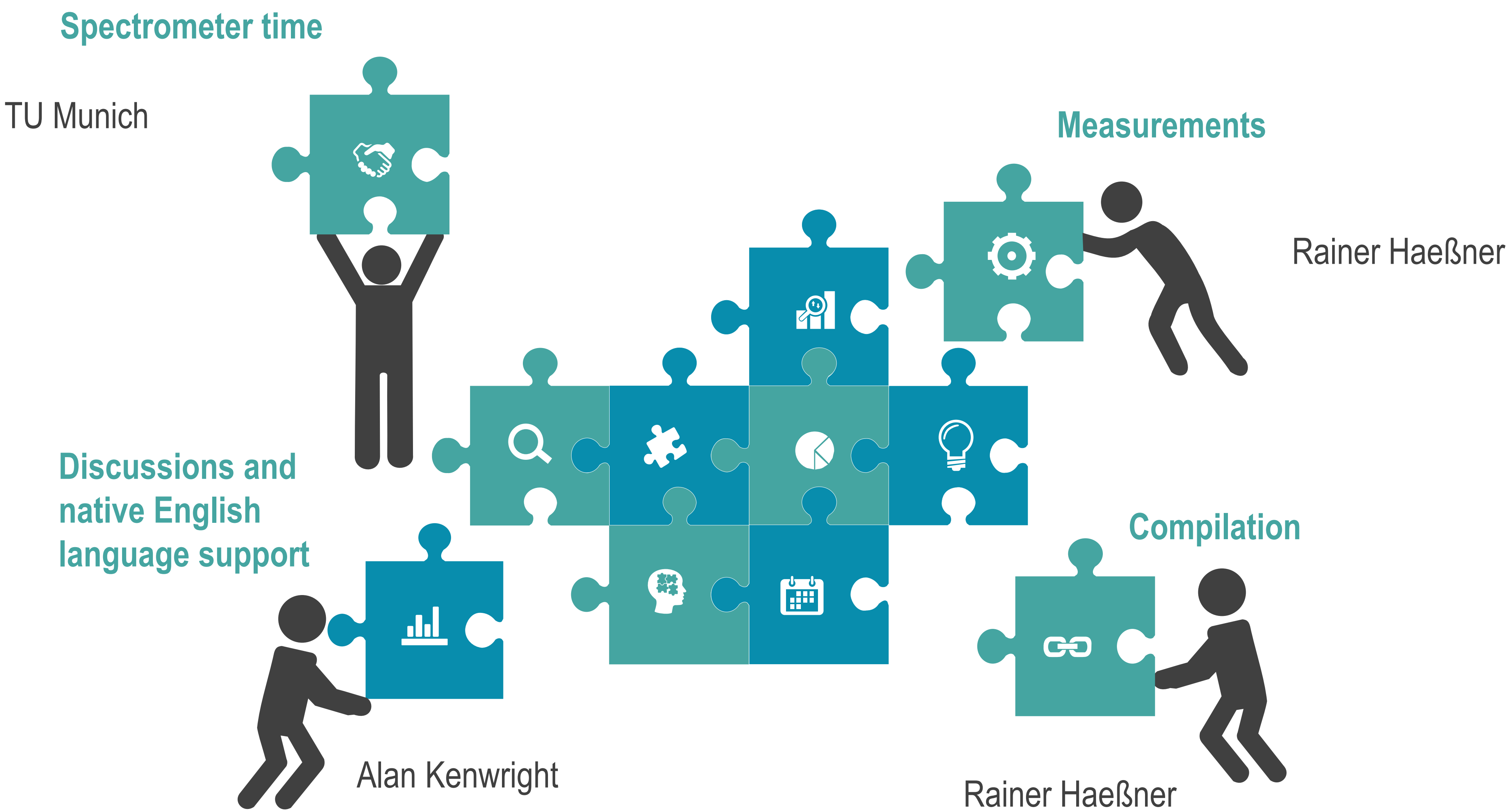
$$J = \frac{740.44\ \text{Hz} - 718.37\ \text{Hz}}{3} = \mathbf{7.36\ Hz}$$

$$J = 305.53\ \text{Hz} - 298.13\ \text{Hz} = \mathbf{7.40\ Hz}$$



The coupling constant might either be read directly from two neighbouring lines or averaged over a whole multiplet in the interest of better accuracy.

Contributions



More exercises …