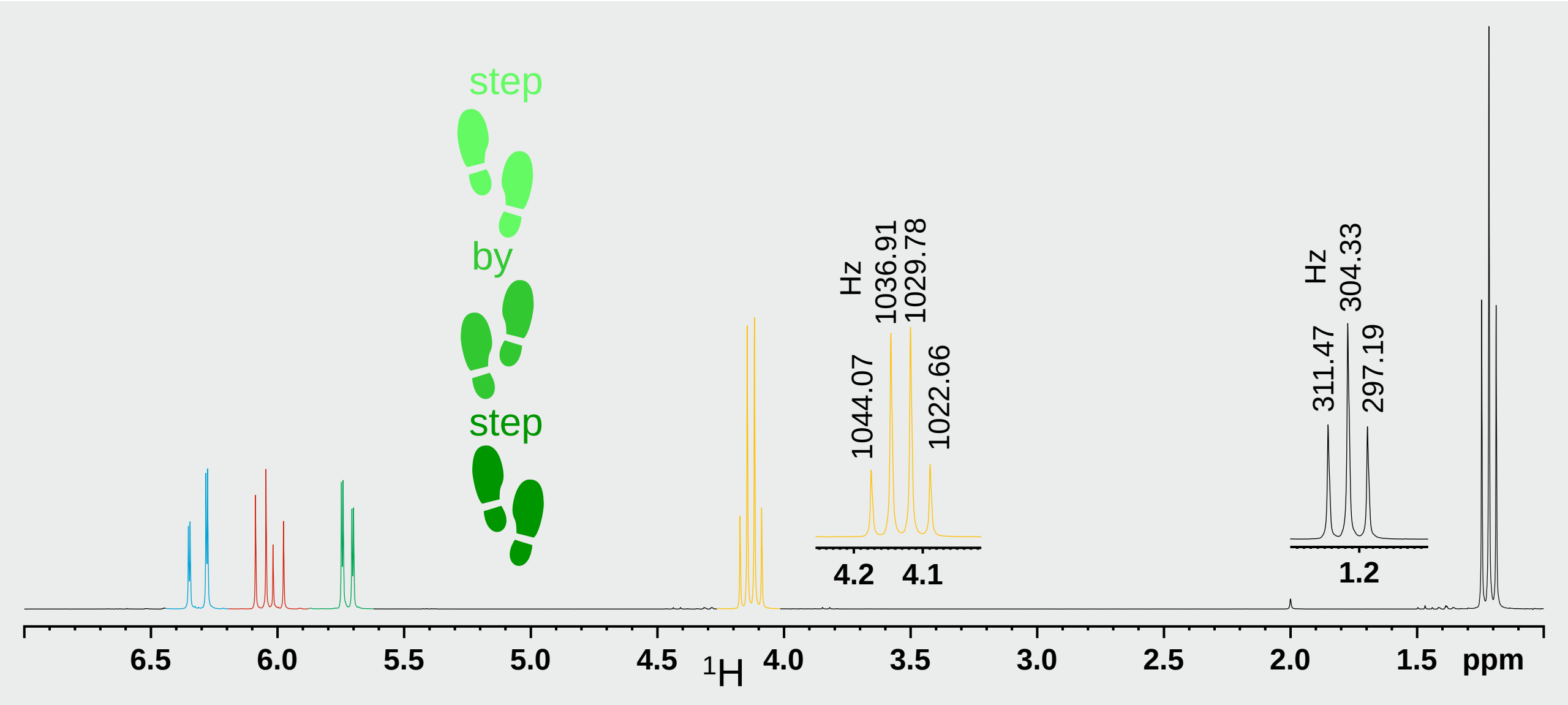
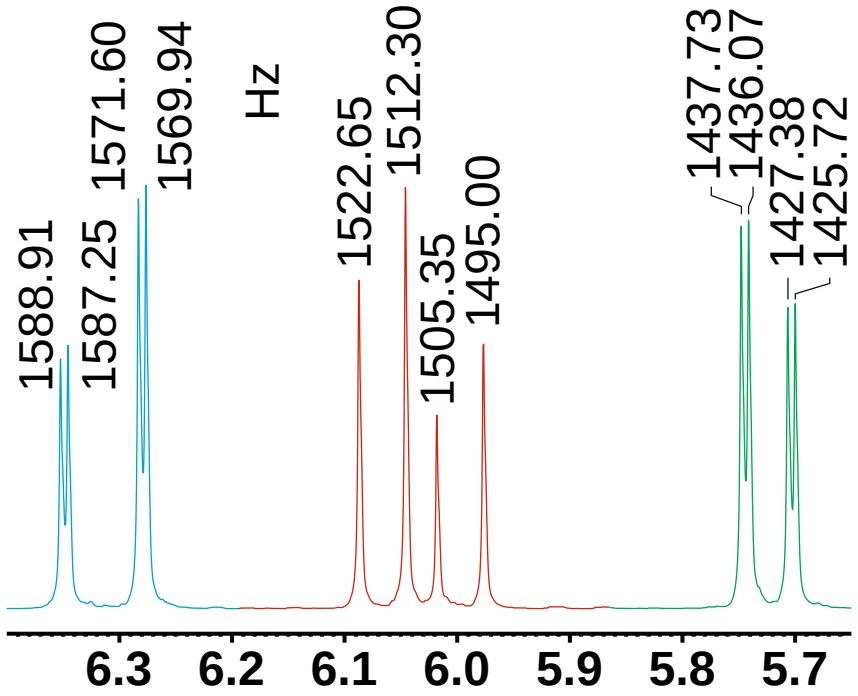
Exercise plus Solution – Quick overview

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.

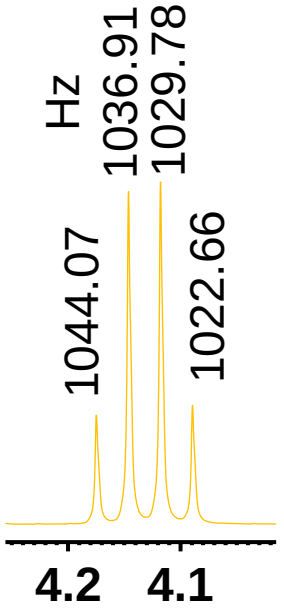


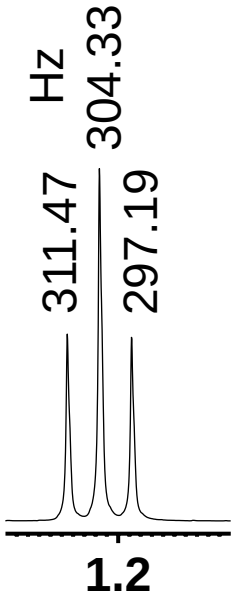
$C_5H_8O_2$ measured in $CDCl_3$

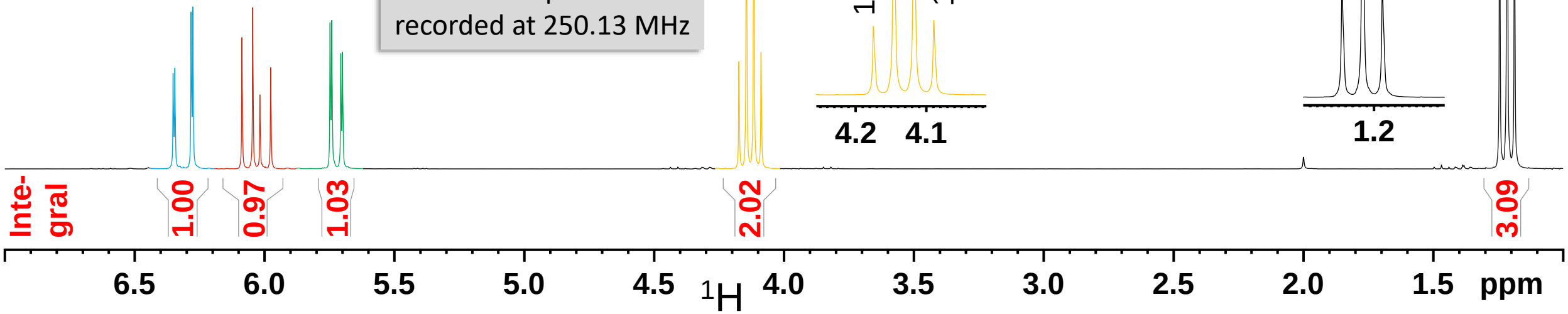
Deduce the structure. Analyze the multiplets between 5.5 and 6.5 ppm and extract all coupling constants.
Make a stereochemically correct assignments of the protons belonging to these signals.



^{1}H NMR spectrum recorded at 250.13 MHz



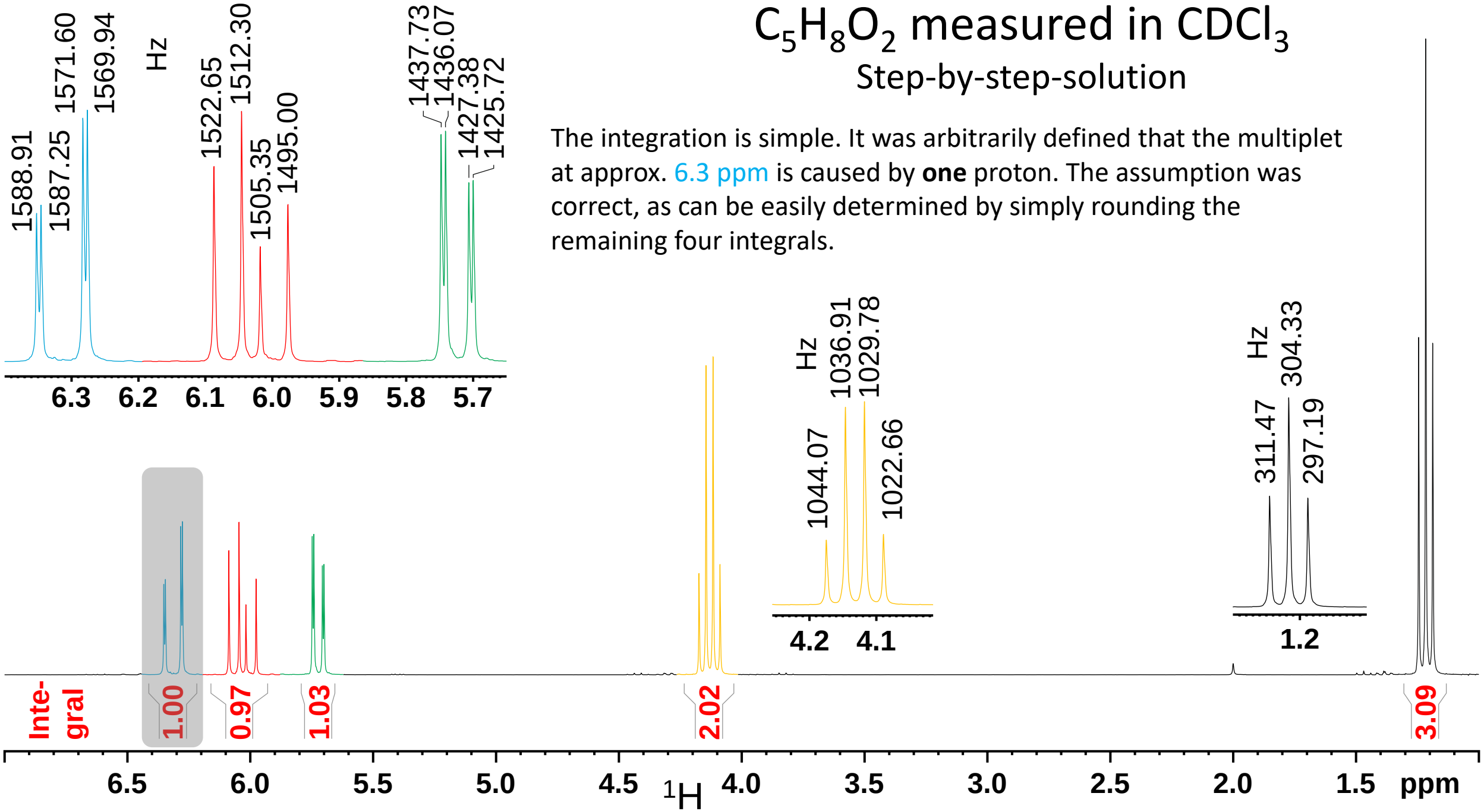




$C_5H_8O_2$ measured in $CDCl_3$

Step-by-step-solution

The integration is simple. It was arbitrarily defined that the multiplet at approx. 6.3 ppm is caused by **one** proton. The assumption was correct, as can be easily determined by simply rounding the remaining four integrals.



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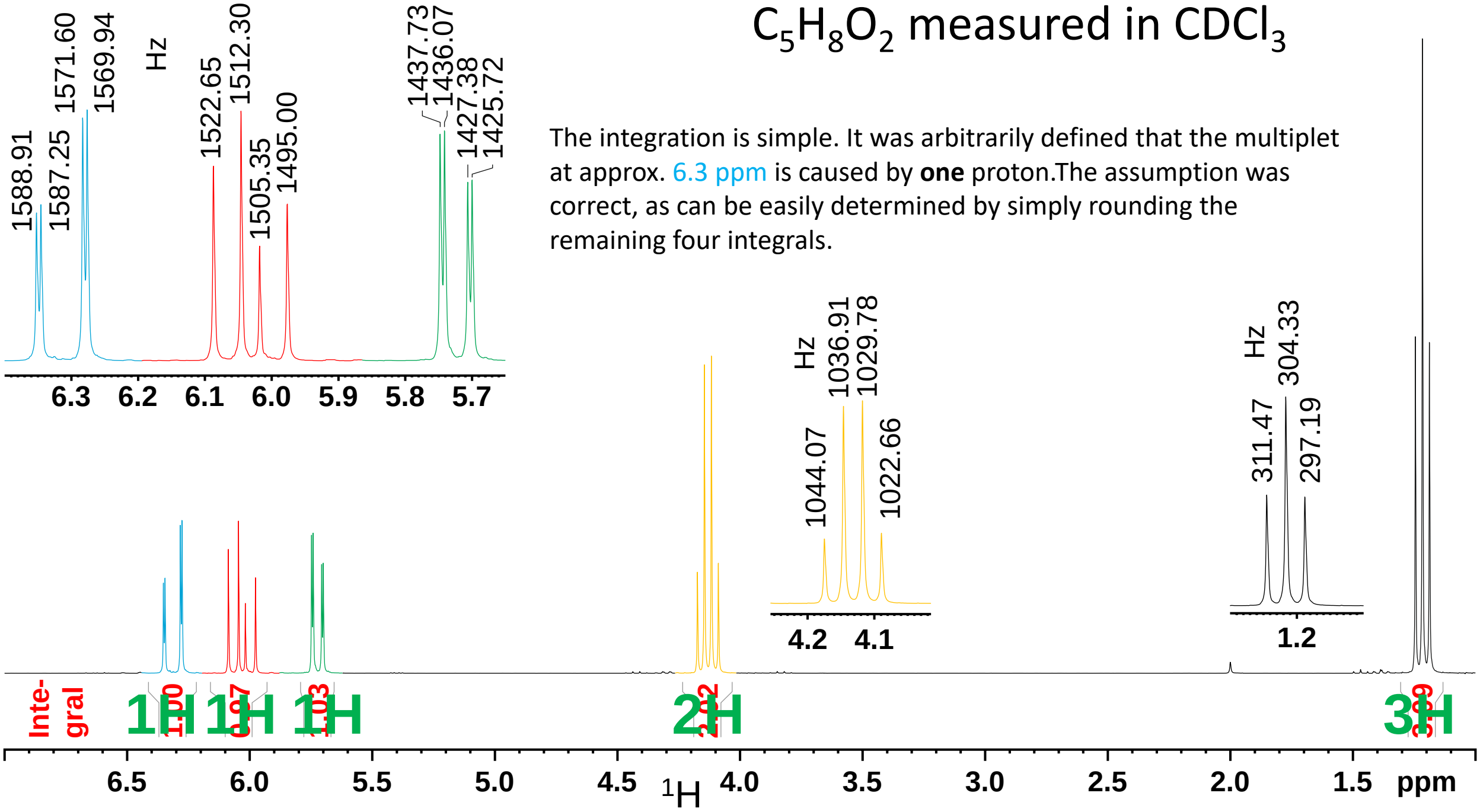
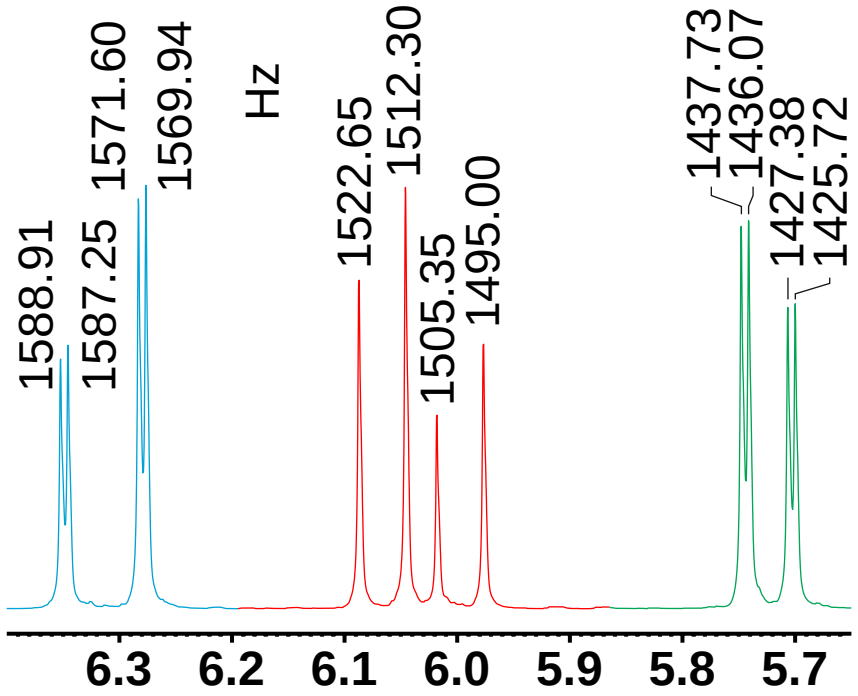


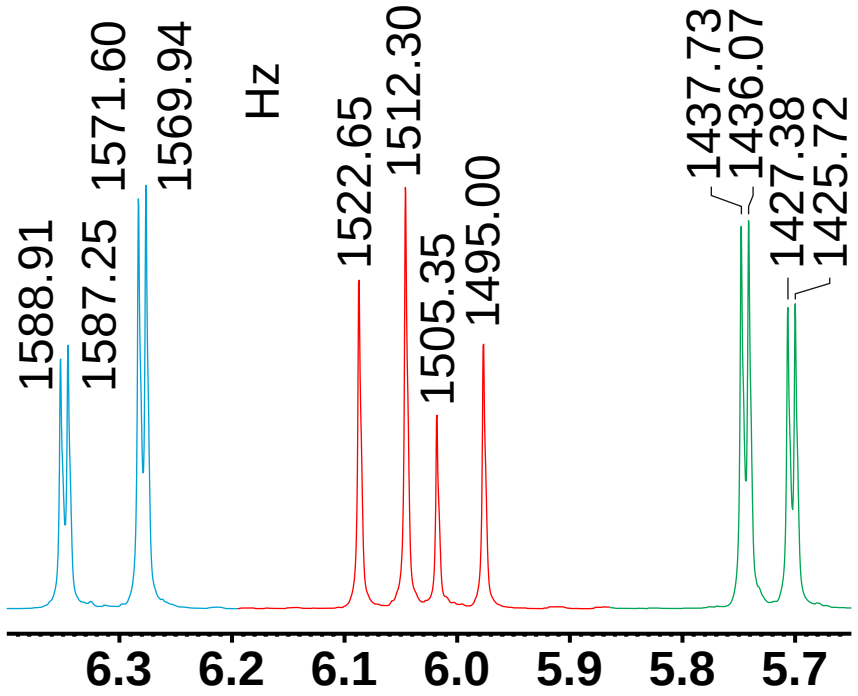
$C_5H_8O_2$ measured in $CDCl_3$

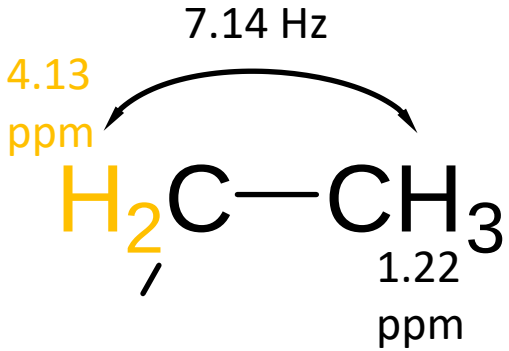
The quartet and the triplet are due to an ethyl group. The step-by-step derivation will not be discussed. The focus here is on the signals at about 6 ppm.

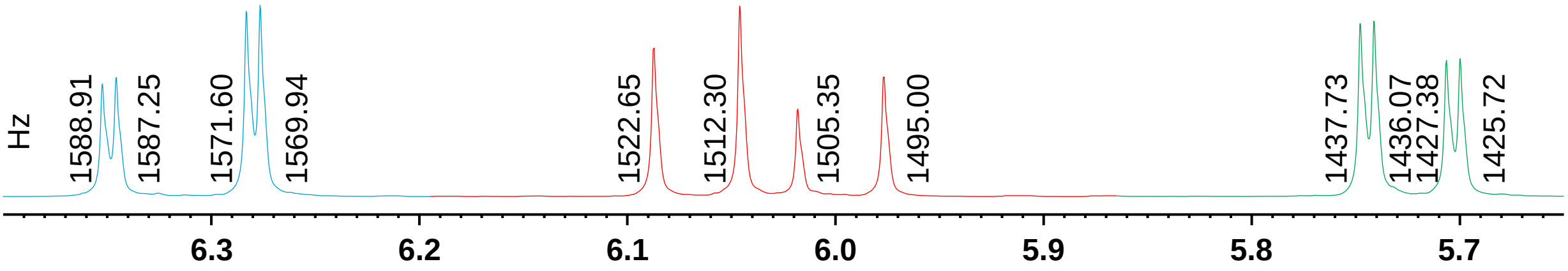


$C_5H_8O_2$ measured in $CDCl_3$

How to understand the multipletts at about 6 ppm - especially the middle one?





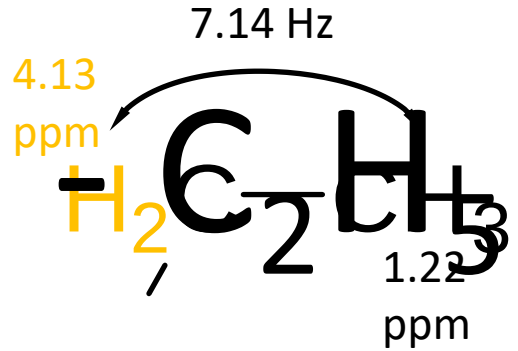


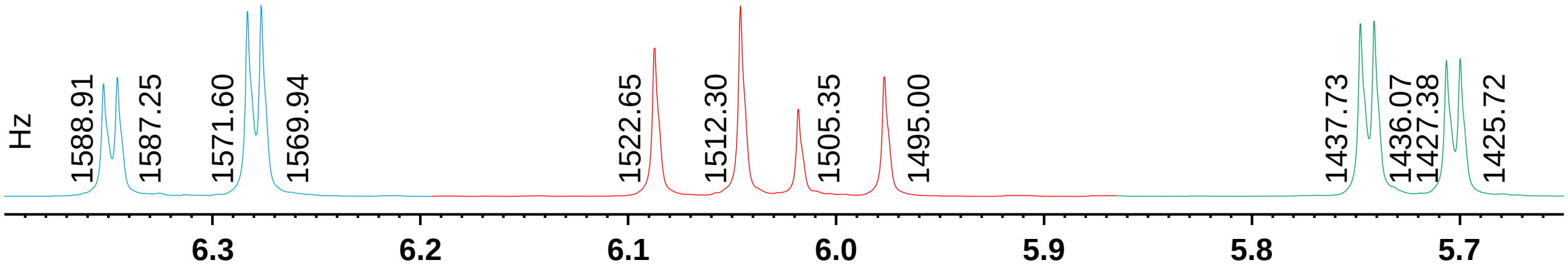
molecular formula: $C_5H_8O_2$ found so far: - C_2H_5 missing: 2DBE + $C_3H_3O_2$

$C_5H_8O_2$ measured in $CDCl_3$

What is still missing?

On the one hand, we got **2 double bond equivalents** (DBE) from the molecular formula, none of which has been assigned so far, and on the other hand, a residue **$C_3H_3O_2$** remains after the ethyl group has been subtracted.





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Even if the intensity distribution of the four lines does not perfectly correspond to the ratio 1 : 1 : 1 : 1, the multipletts at approx. 6.3 ppm and approx. 5.7 ppm should each be doublets of doublets (the two calculations are examples for extracting the values).

6.314 ppm

$$\delta = \frac{1588.91\ \text{Hz} + 1569.94\ \text{Hz}}{2\ * 250.13\ \text{MHz}} = 6.314\ \text{ppm}$$

17.31 Hz

$$J = \frac{(1437.73\ \text{Hz}\ + 1436.07\ \text{Hz})}{2} - \frac{(1427.38\ \text{Hz}\ + 1425.72\ \text{Hz})}{2}$$

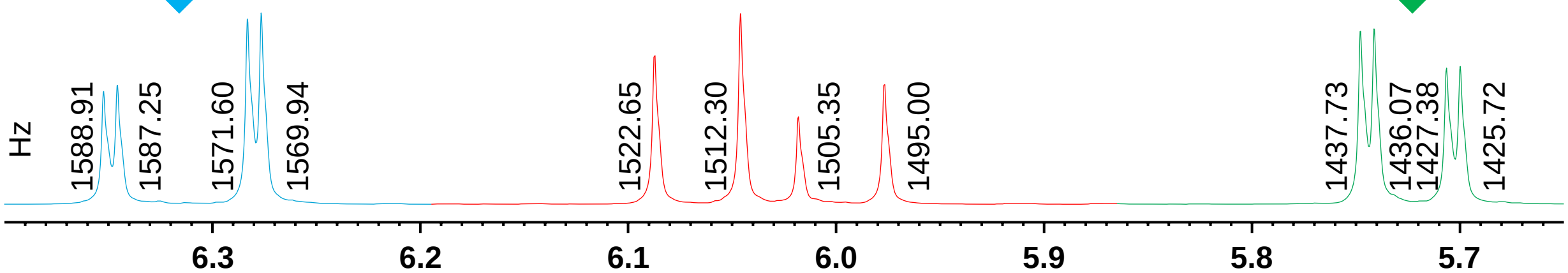
$J = 10.35\ \text{Hz}$

1.66 Hz

5.724 ppm

10.35 Hz

1.66 Hz



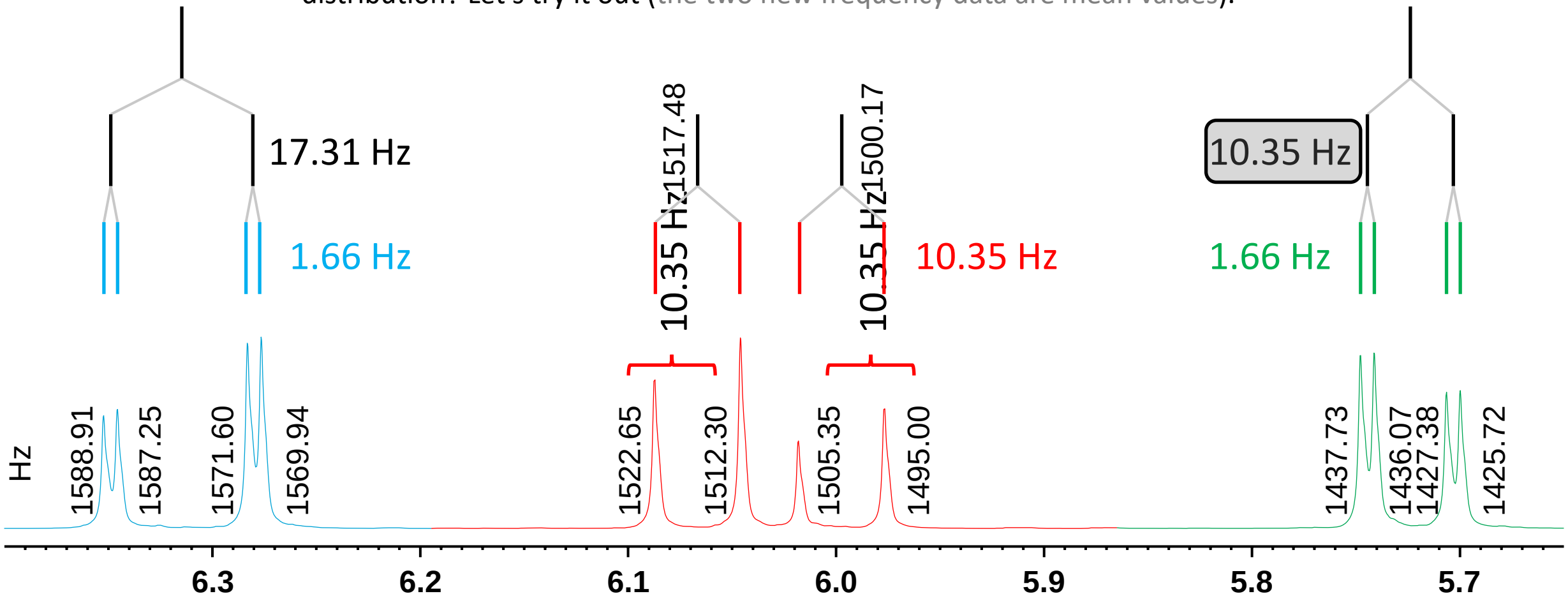
molecular formula: $C_5H_8O_2$ found so far: - C_2H_5 missing: 2DBE + $C_3H_3O_2$

If we measure the distance between the first two and the last two lines of the middle multiplet, we find there the **10.35 Hz** from the doublet of doublets at 5.724 ppm.

6.314 ppm

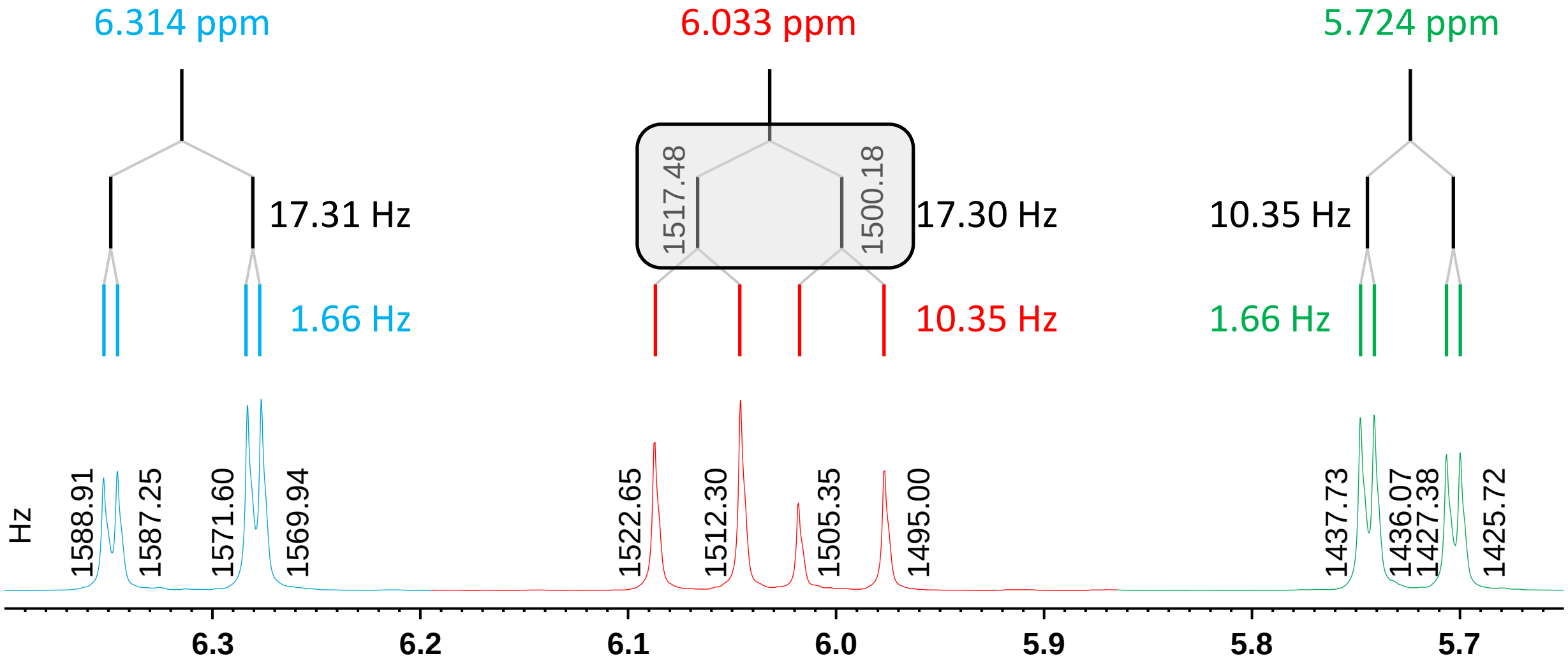
Are that two doublets despite the somewhat unexpected intensity distribution? Let's try it out (the two new frequency data are mean values).

5.724 ppm



molecular formula: $C_5H_8O_2$ found so far: - C_2H_5 missing: 2DBE + $C_3H_3O_2$

Now we have two lines exactly **17.30 Hz** apart. Despite the unusual intensity distribution, there is also a doublet of doublets at about 6 ppm.



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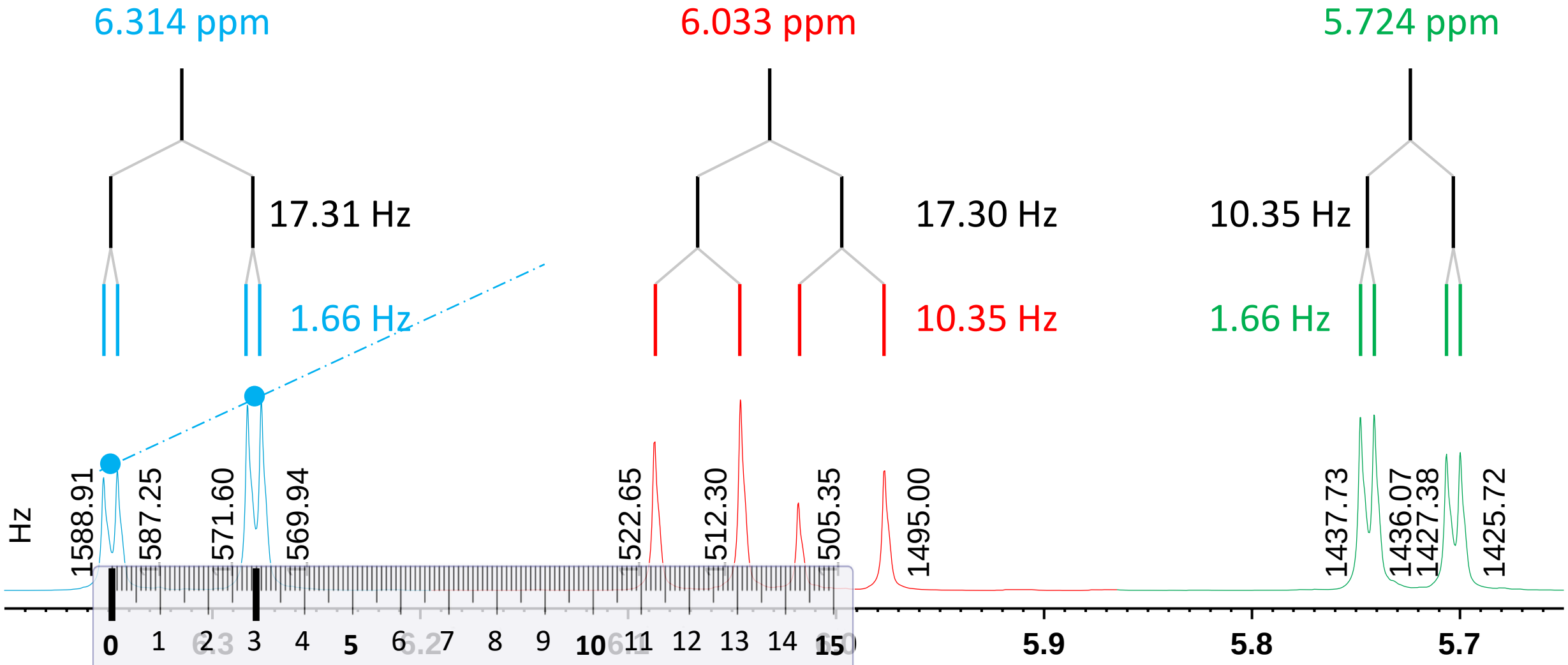
And the strange intensity distribution?

The roof effect, because due to the small chemical difference compared to the coupling constants, a consideration according to the 1st order rules is no longer valid without restrictions.



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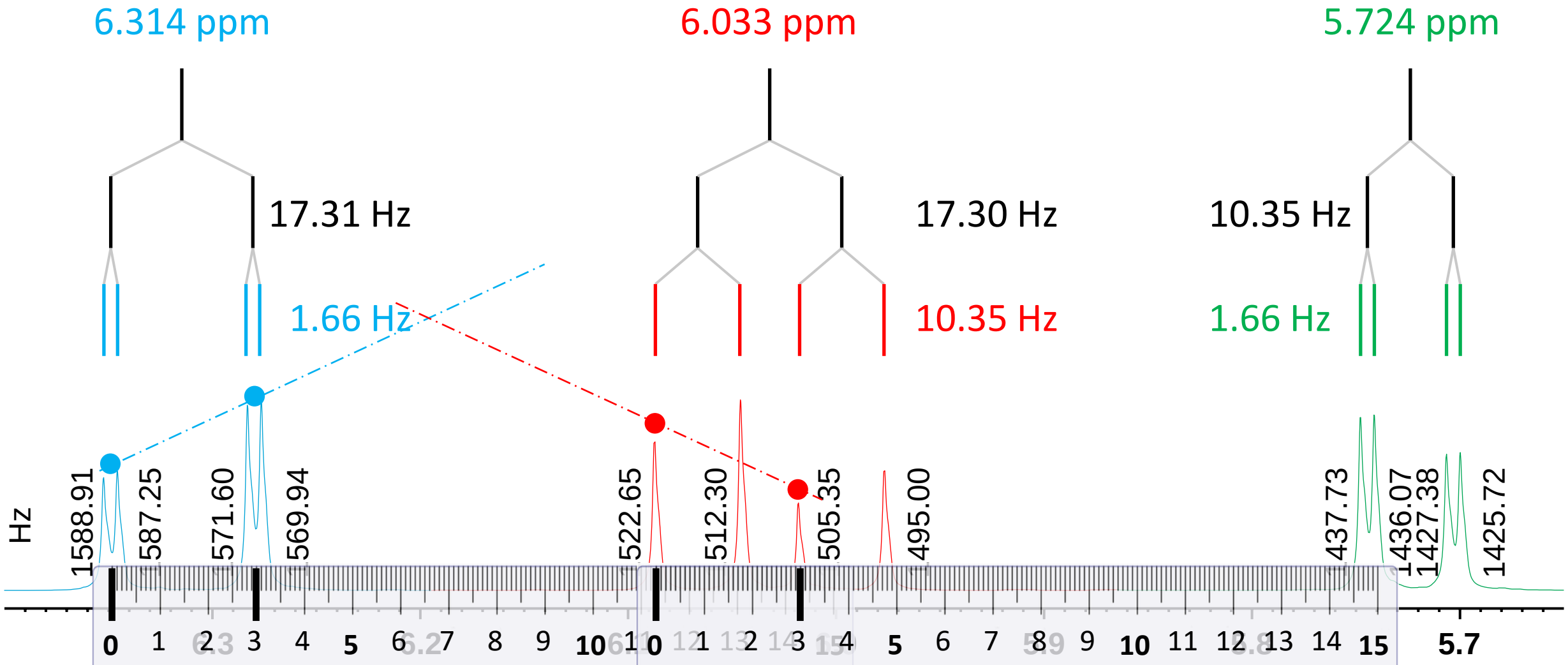

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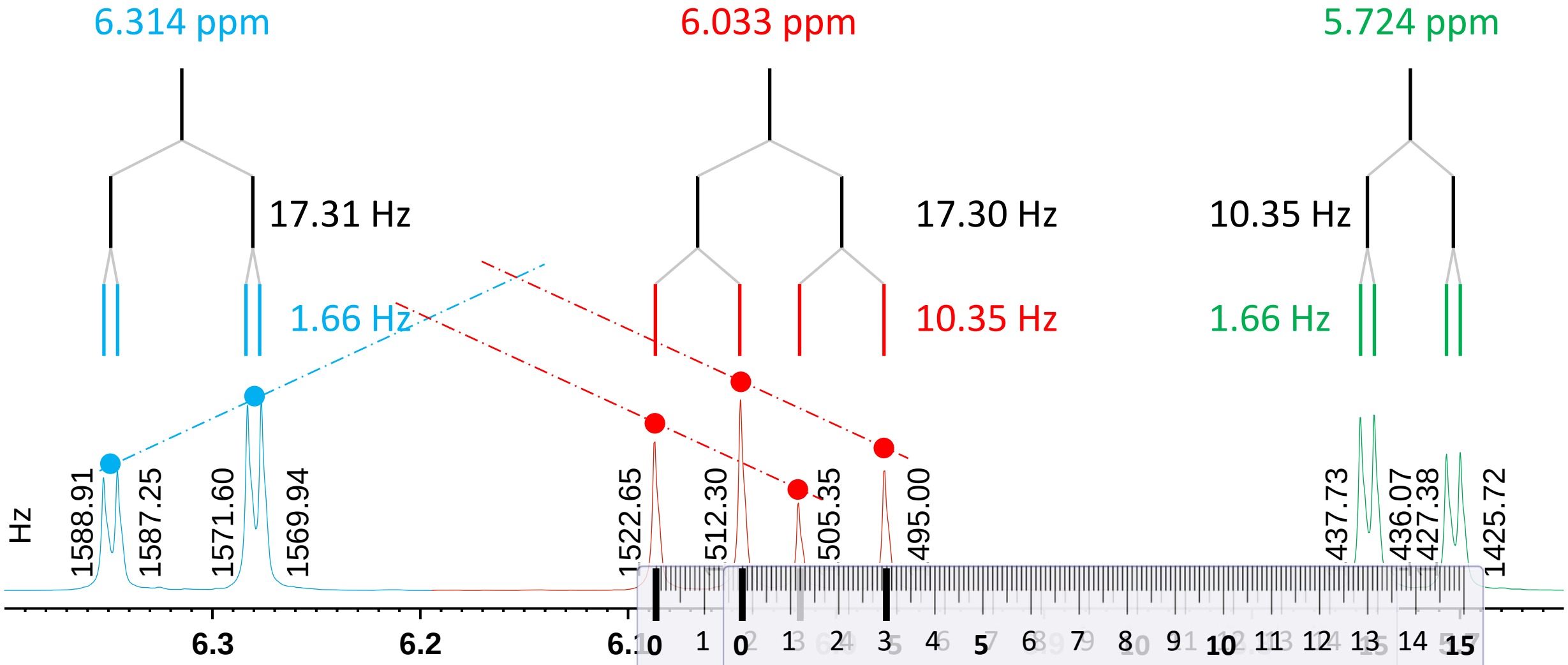

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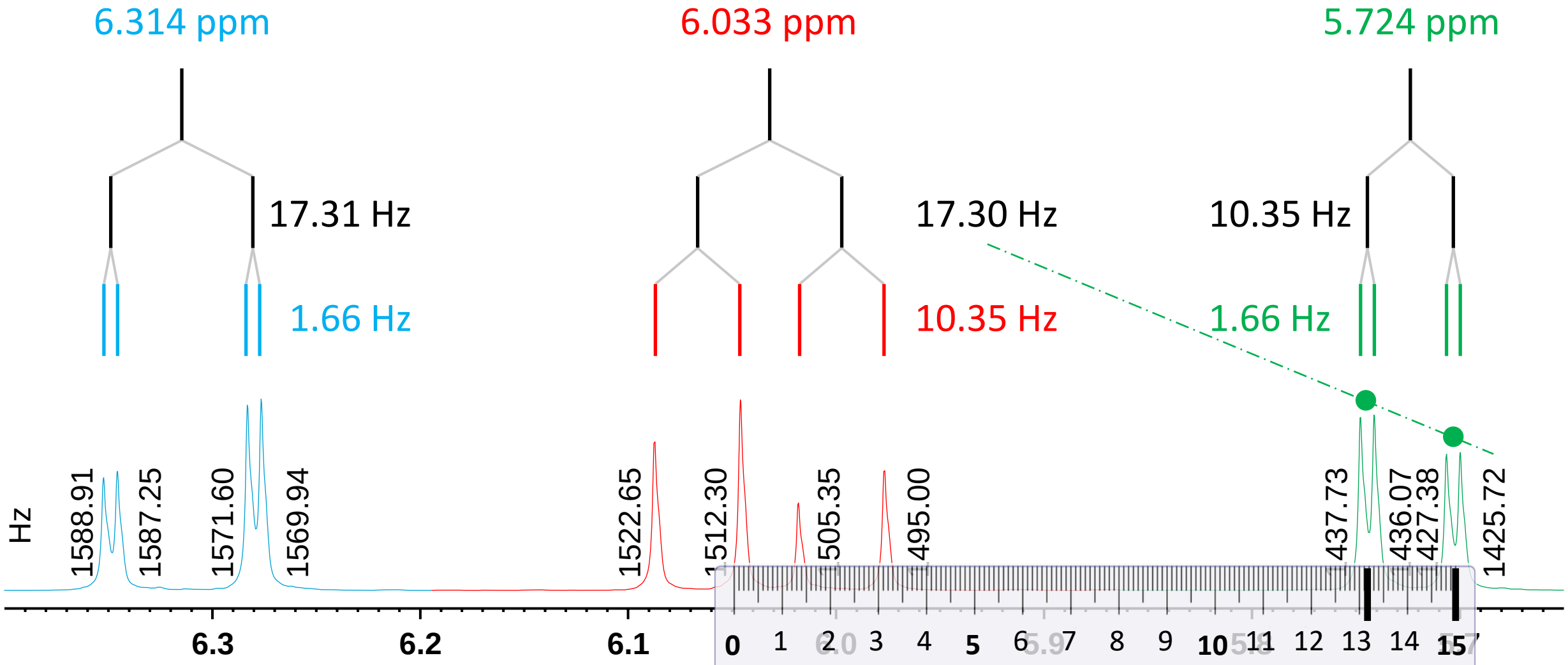
To demonstrate the roof effect between the signals at 6.314 ppm and 6.033 ppm, we had used the lines with a distance of **17.31 Hz** each.

For the second roof effect, the lines with a distance of **10.35 Hz** each are now of interest.



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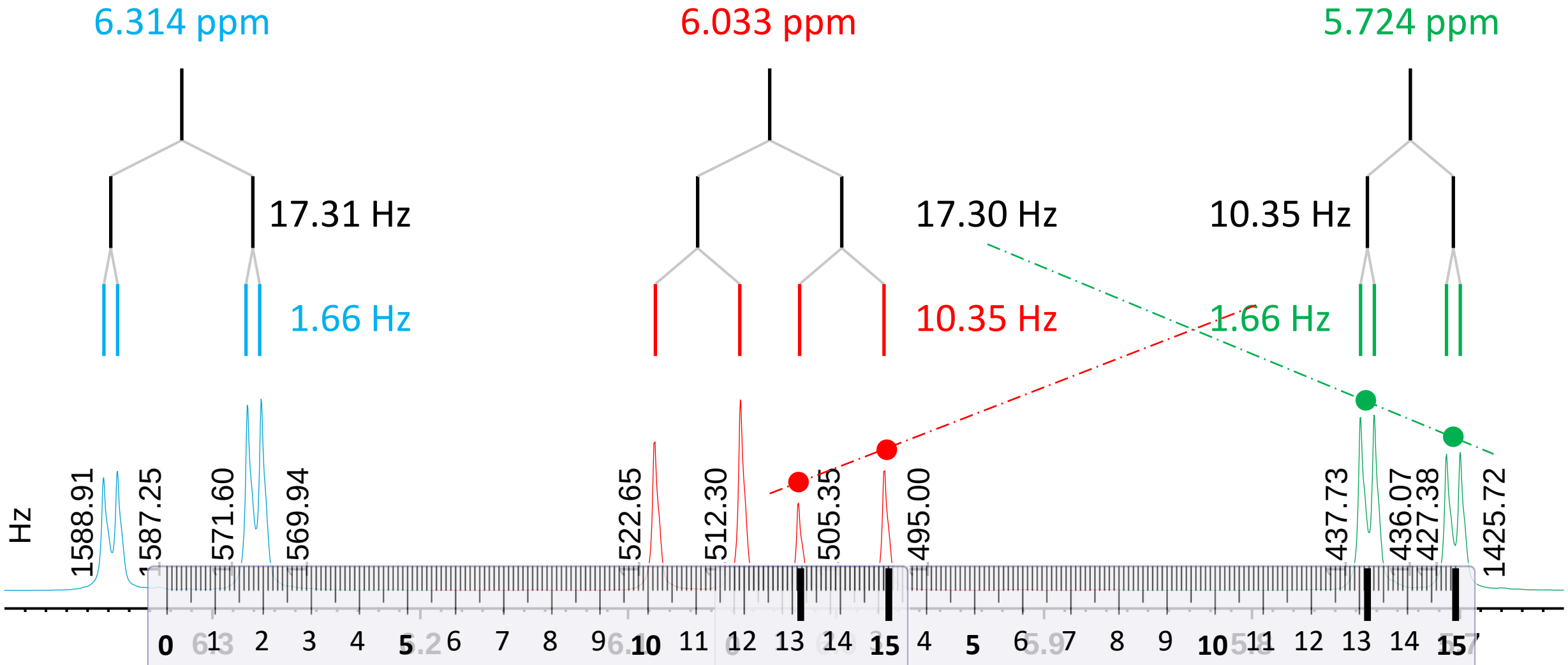

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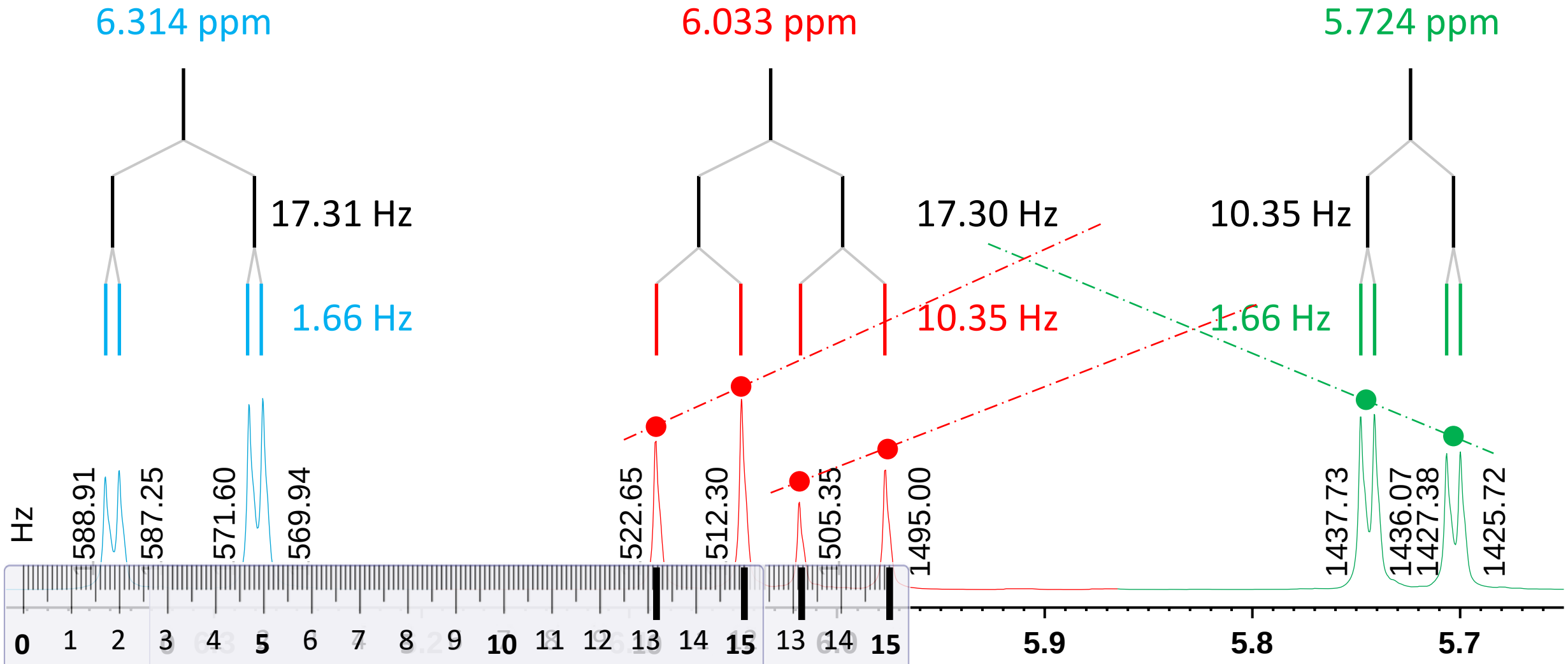

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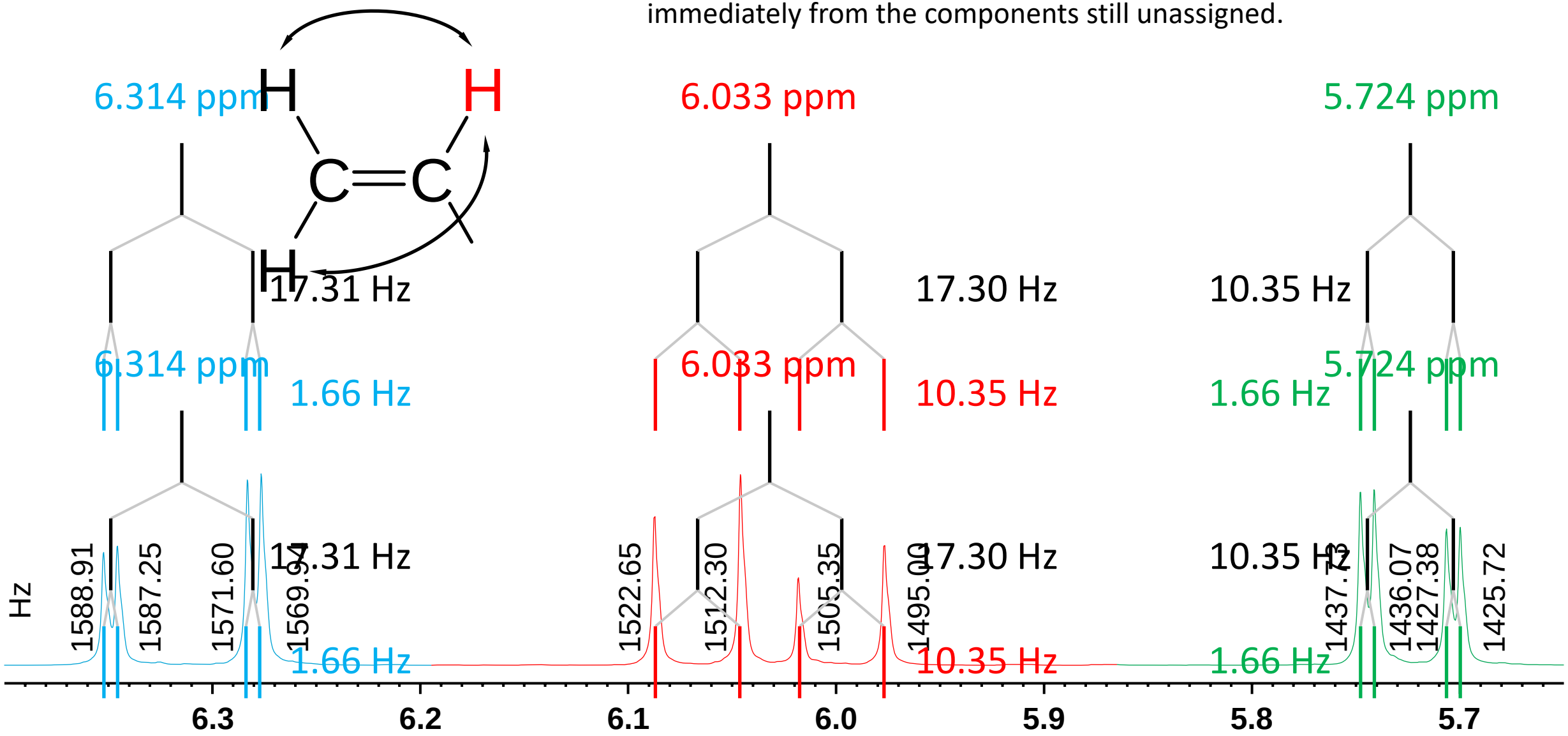
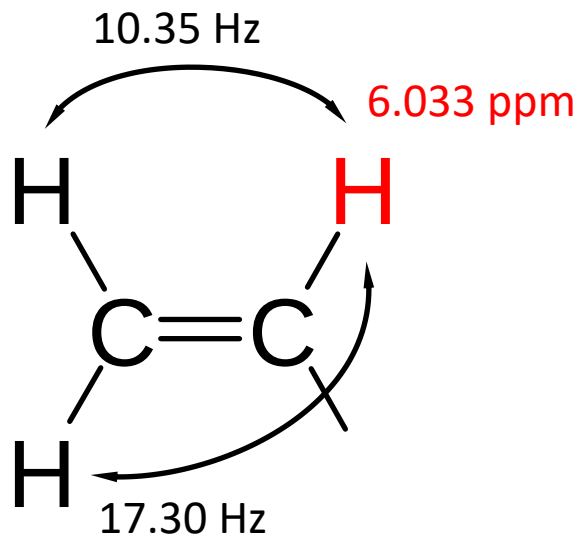
From the chemical shift of 6.033 ppm and the two coupling constants of **10.35 Hz** and **17.30 Hz**, a structural fragment can be derived immediately from the components still unassigned.



molecular formula: $C_5H_8O_2$ found so far: - C_2H_5 + CH_2=CH- missing: 2DBE + O_2C



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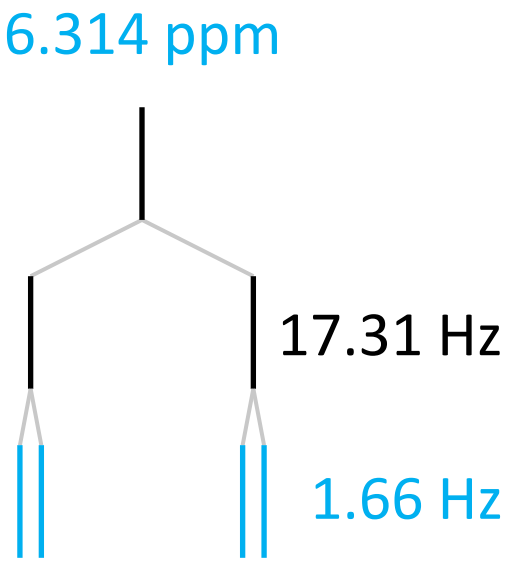
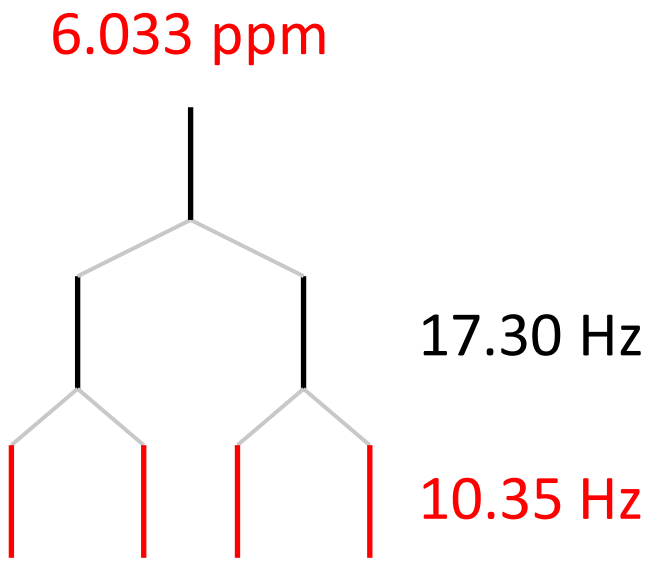
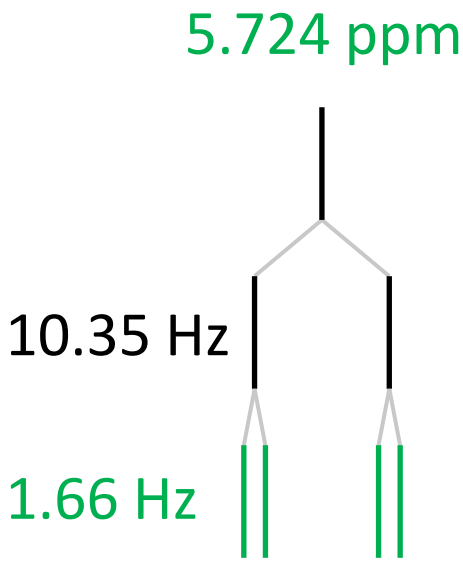
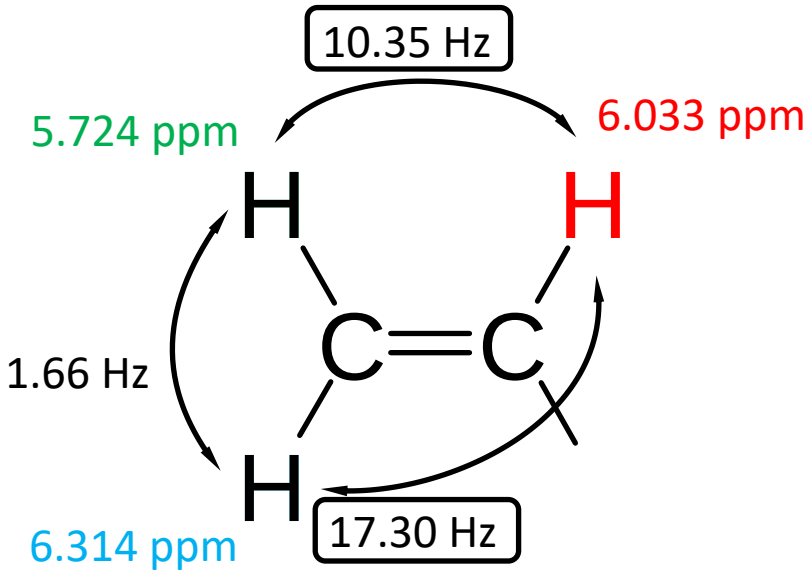
The two coupling constants are perfect textbook values for protons in E- (**17.30 Hz**) and Z-position (**10.35 Hz**) to each other, bound to sp^2-hybridised carbon atoms.







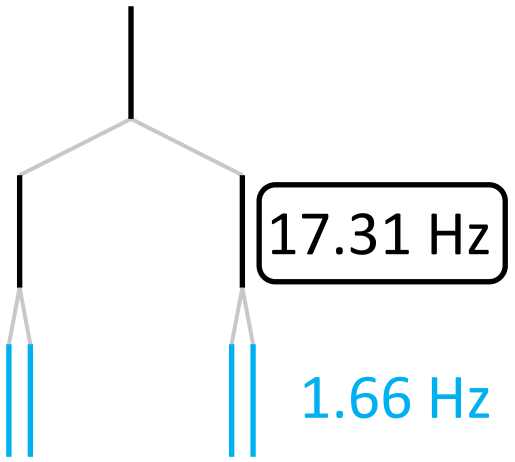
molecular formula: $C_5H_8O_2$ found so far: - C_2H_5 + CH_2=CH- missing: 1DBÄ + CO_2



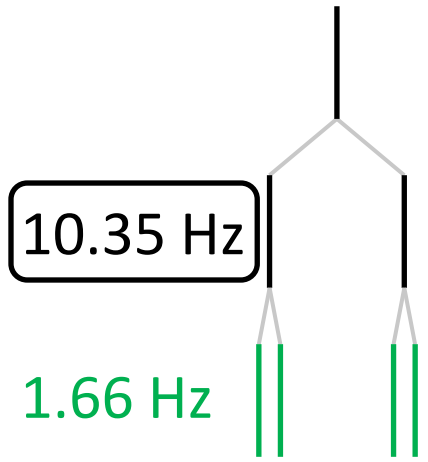
The chemical shifts of the protons in geminal position to each other can now be easily assigned via the coupling constants.

The value of **1.66 Hz** is the geminal coupling constant between those protons.

6.314 ppm



5.724 ppm



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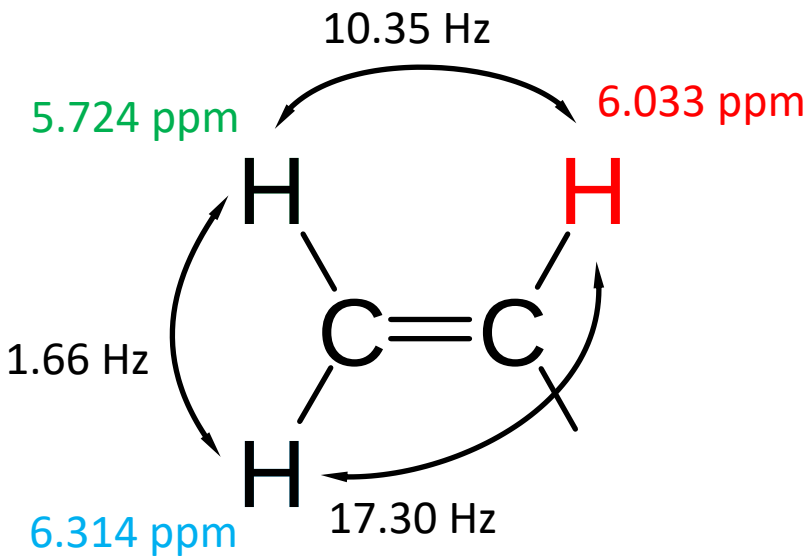

The new structural fragment contains one double bond equivalent, two carbon atoms and 3 protons.

For the complete structure, a partial structure with the molecular formular CO_2 including two open bonds and one double bond equivalent is then missing.

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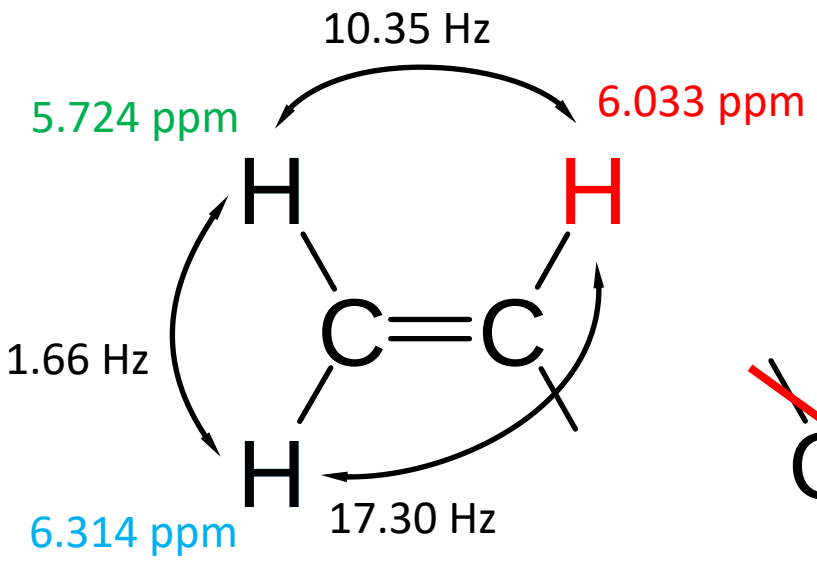
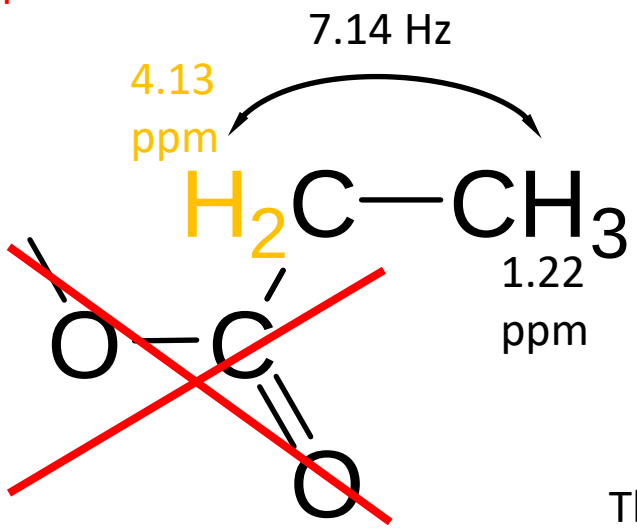
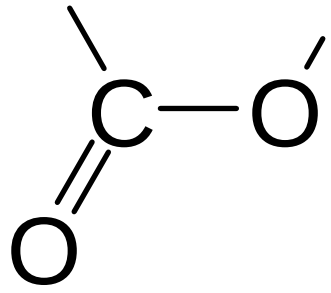
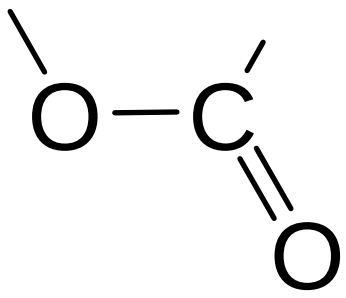




δ = 0.47 ppm + 1.55 ppm
= **2.12 ppm**

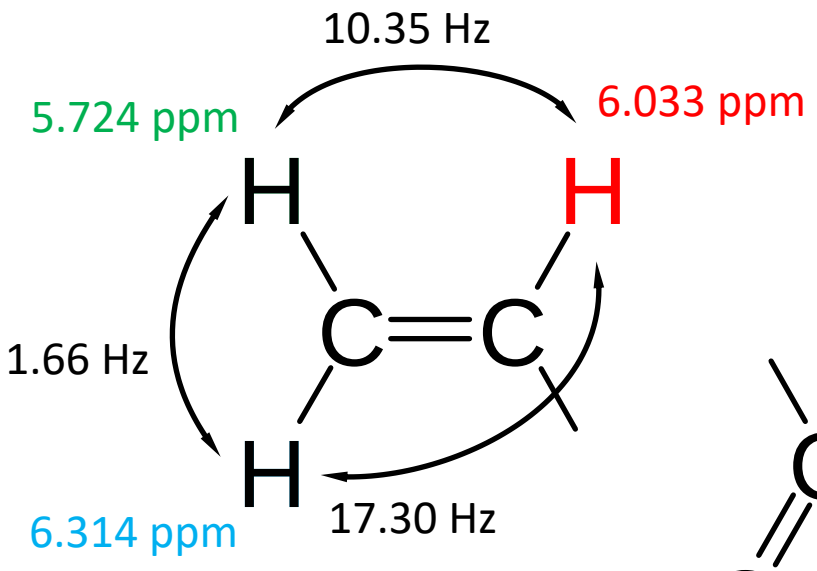
The estimated value differs significantly from the measured value 4.13 ppm.

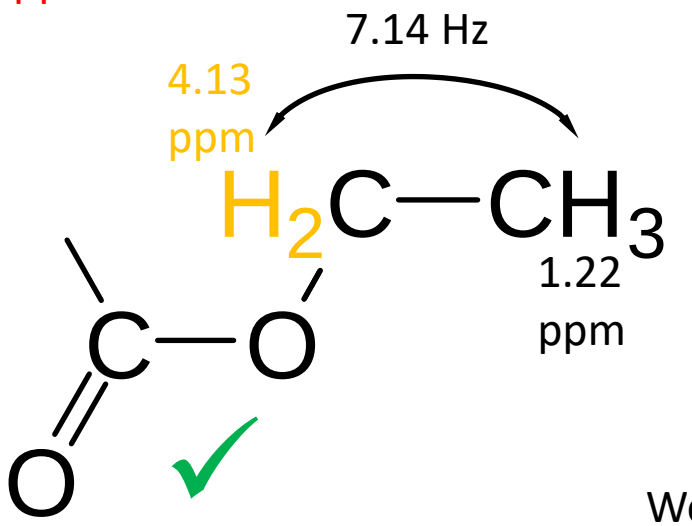




There are only two structures which fulfil all three conditions at the same time.

Let's just try one of them and estimate the chemical shift of the **methylene protons** using the Schoolery rules.

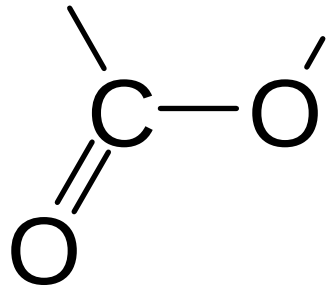


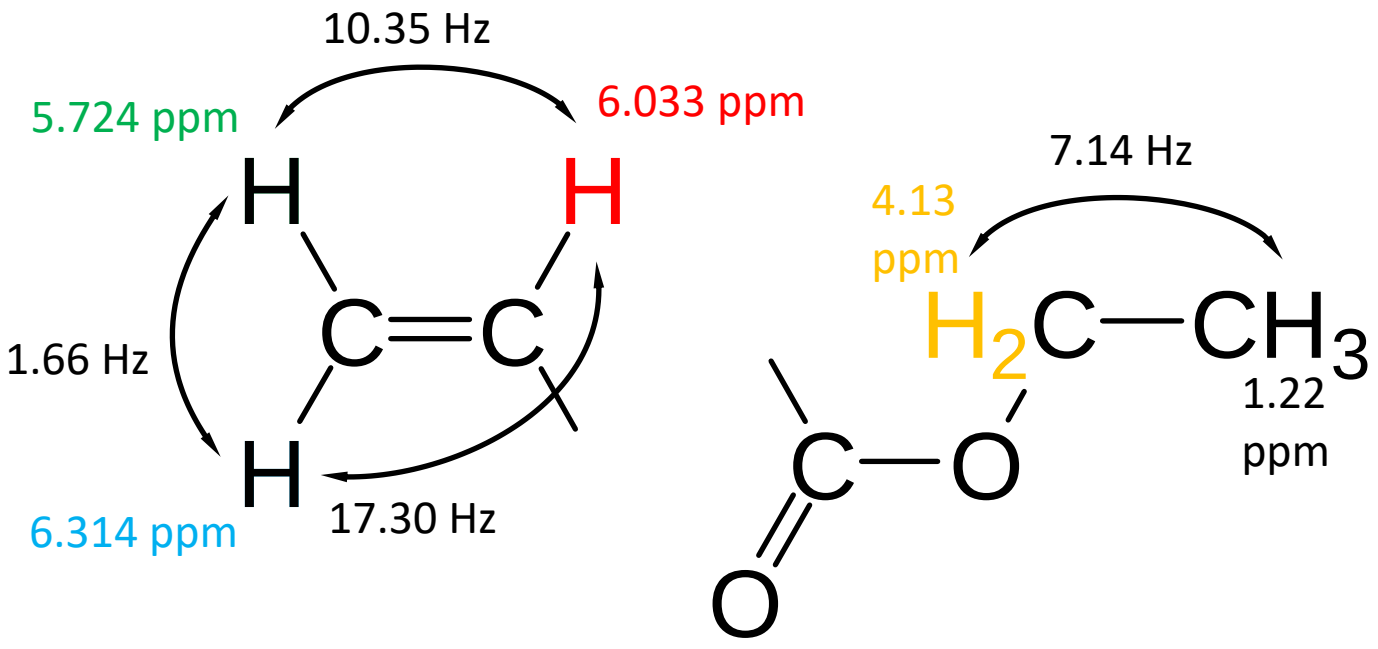


δ = 0.47 ppm + 3.13 ppm
= **3.60 ppm**

Now the estimated value differs significantly less from the measured value 4.13 ppm.

We still have one shot left.





It's not too hard now to get to the final solution …

Contributions

Spectrometer time

TU Munich

Measurements

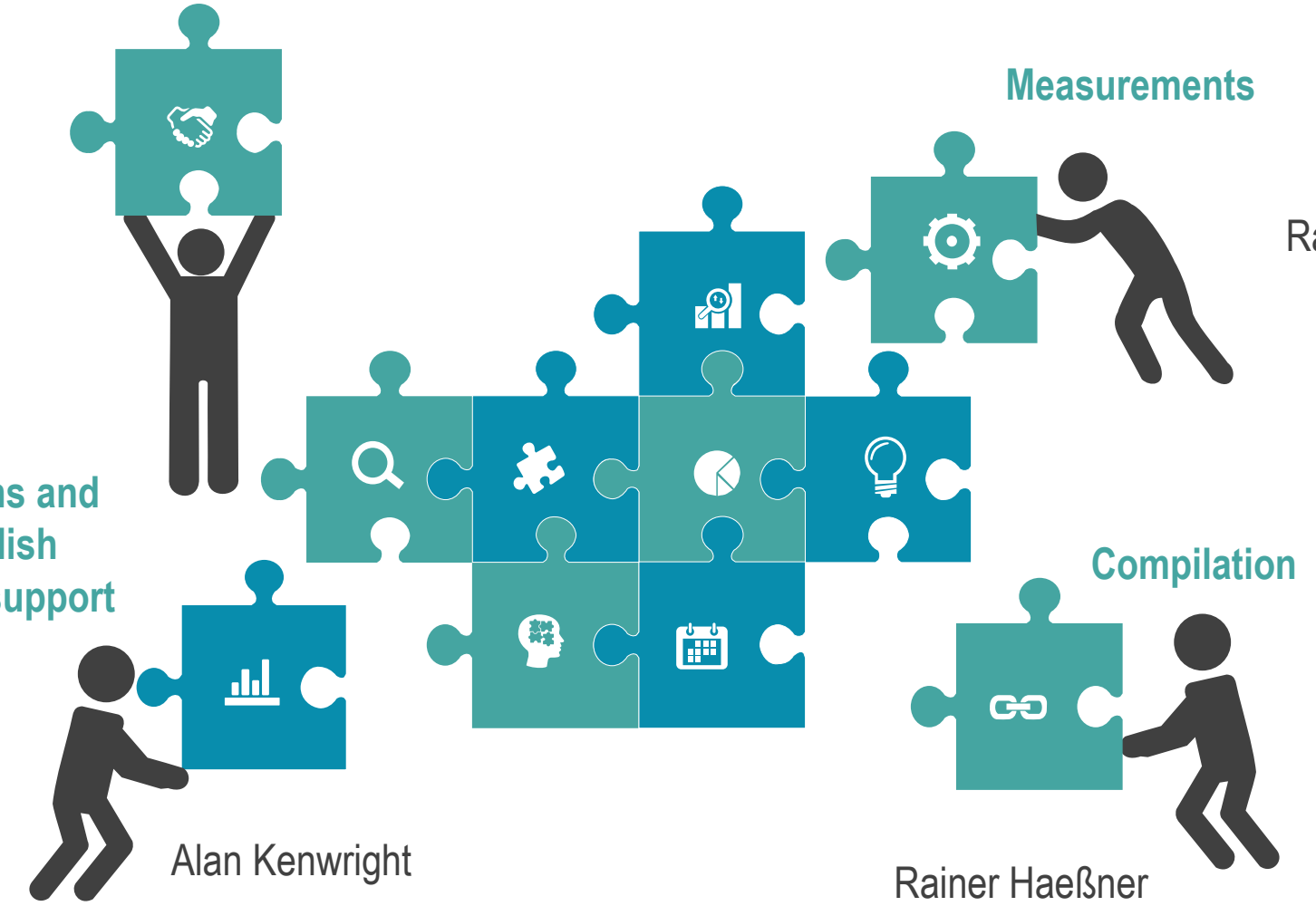
Rainer Haeßner

Discussions and native English language support

Alan Kenwright

Compilation

Rainer Haeßner



More exercises …