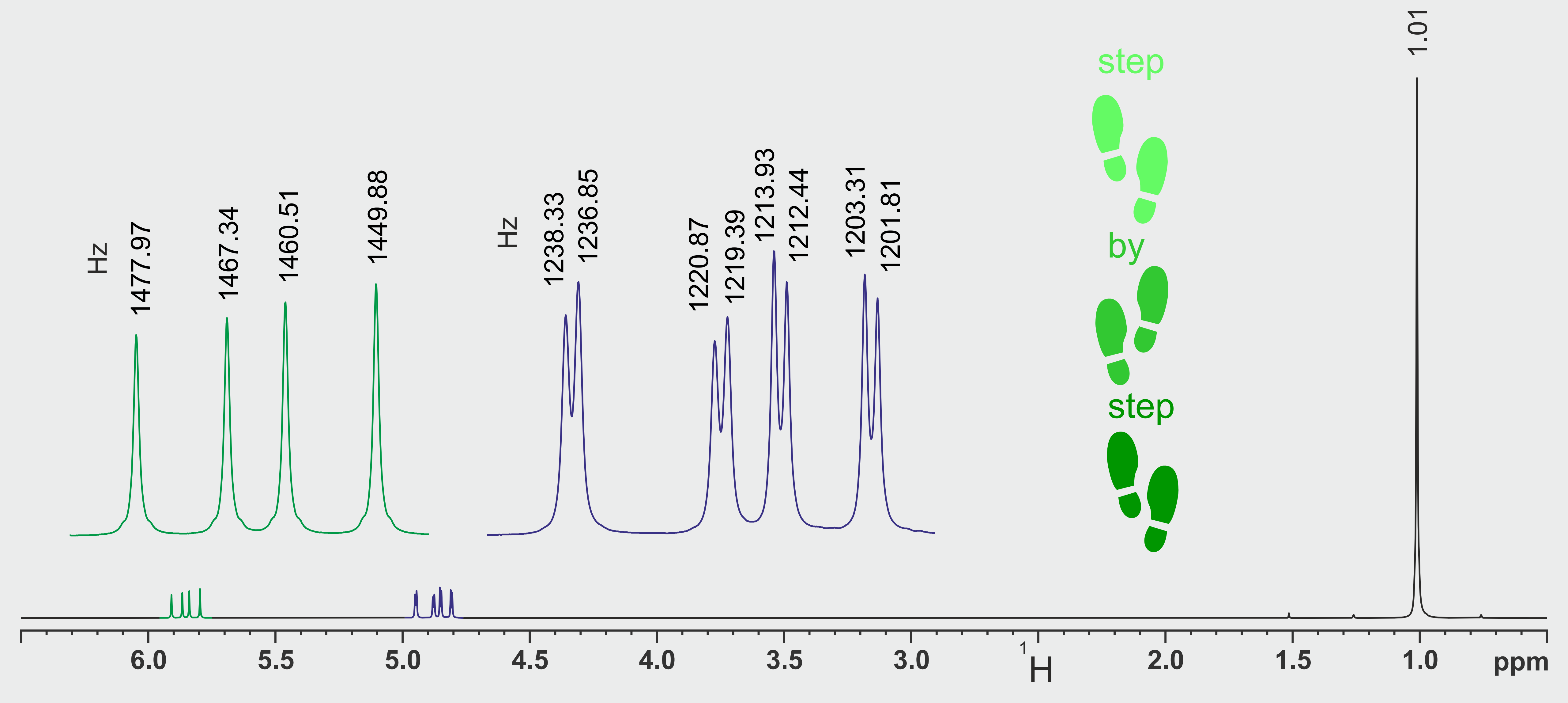
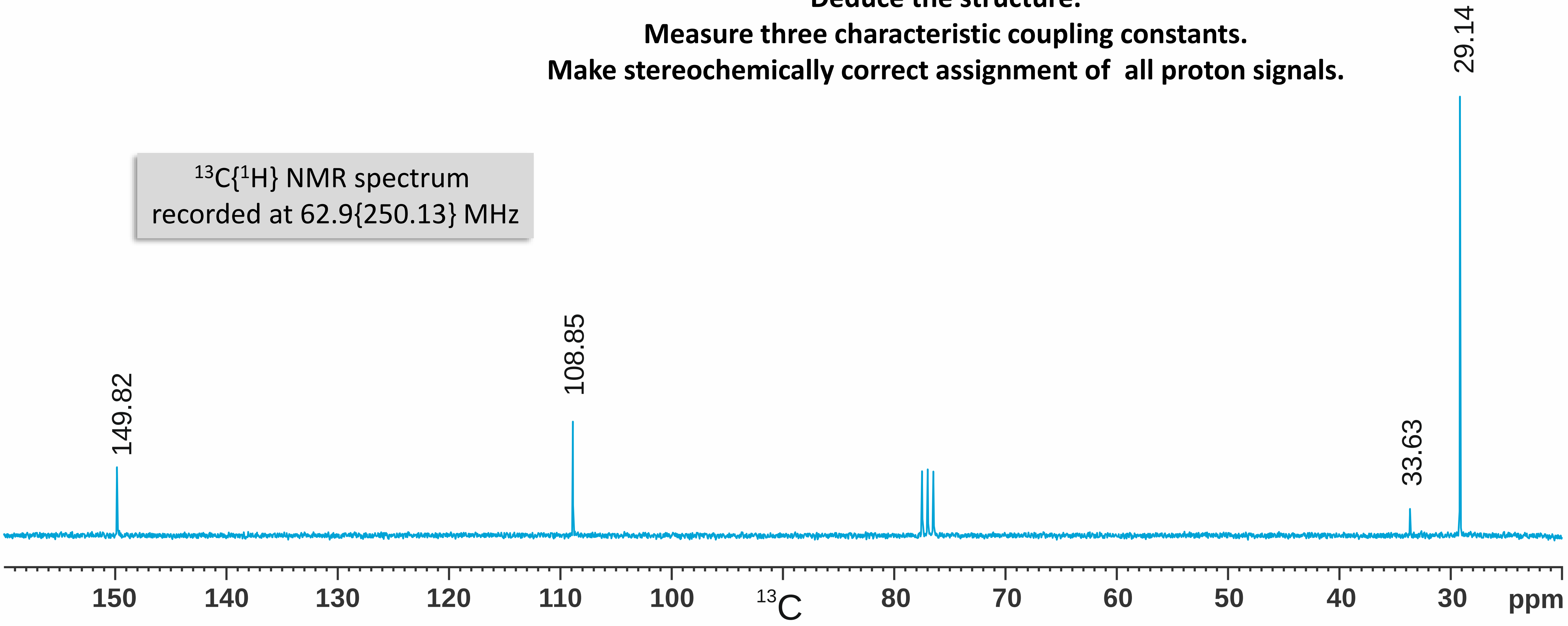
Exercise plus Solution – Quick PDF overview

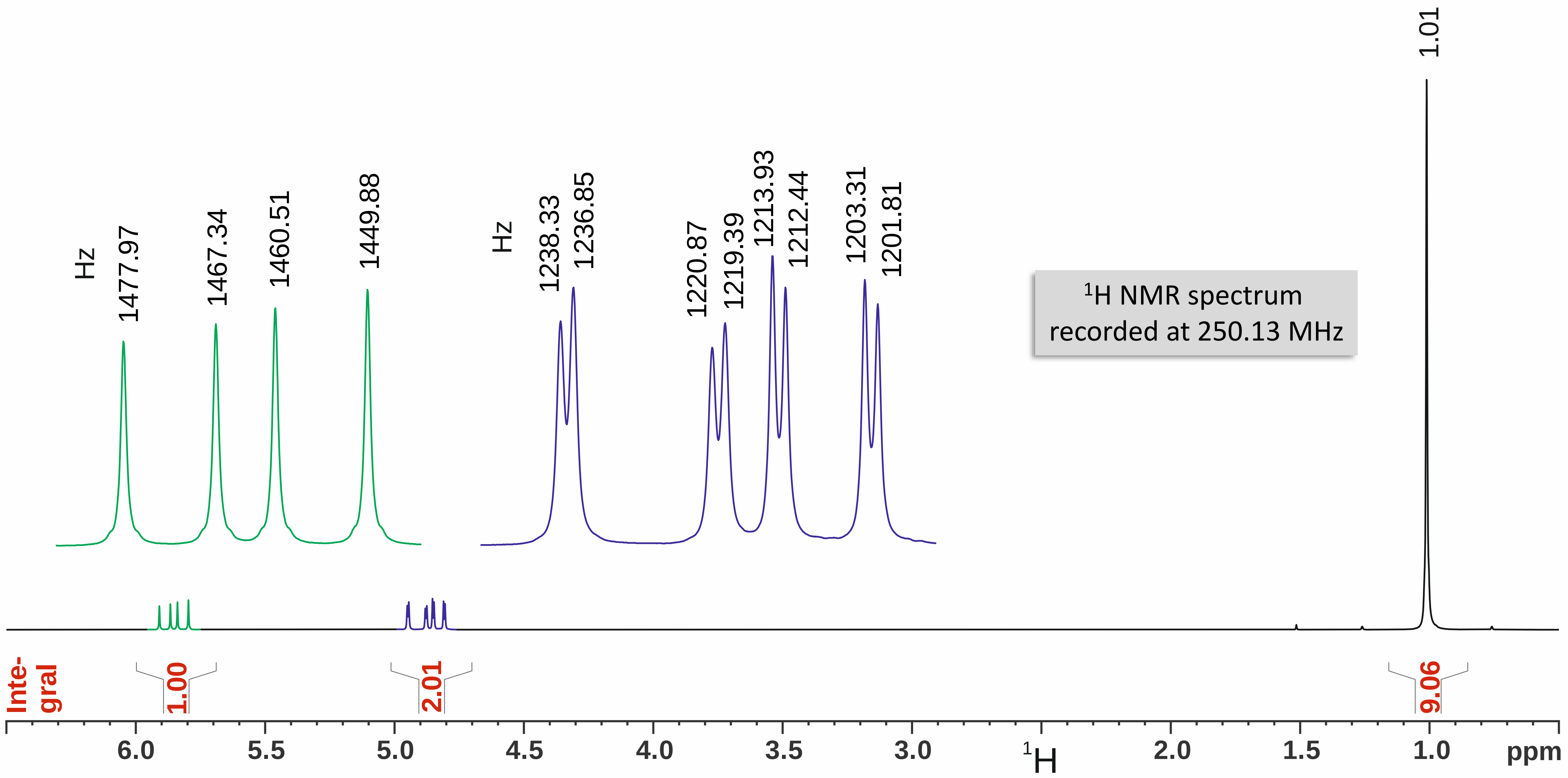
It is recommended to use this PDF version only for a quick overview of the NMR challenge. All animations of the PowerPoint version are missing, under certain circumstances quality deficiencies may also occur.
The higher quality PowerPoint files are freely available for download at any time.



C_6H_{12} measured in $CDCl_3$

Deduce the structure.
Measure three characteristic coupling constants.
Make stereochemically correct assignment of all proton signals.





Hz
1477.97
1467.34
1460.51
1449.88
Hz
1238.33
1236.85
1220.87
1219.39
1213.93
1212.44
1203.31
1201.81
1.01
^{1}H NMR spectrum
recorded at 250.13 MHz
Inte-
gral
1.00
2.01
9.06
6.0
5.5
5.0
4.5
4.0
3.5
3.0
^{1}H
2.0
1.5
1.0
ppm

First pieces of information

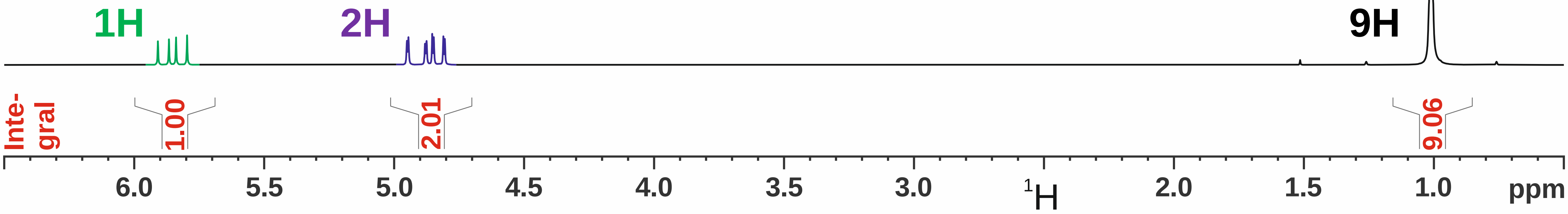
According to the molecular formula, the protons can **only** be bound to carbon atoms.

The integration is quite simple. The proportionality factor happens to be close to 1. This coincidence results from the fact that the integral of the lowest field multiplet was set to 1.

With 12 protons and 6 carbon atoms, according to the equation

$$n_{\mathrm{dbe}} = \frac{2n_{\mathrm{C}} - n_{\mathrm{H}} + 2}{2}$$

we get **one double bond equivalent** (dbe).



5.85 ppm

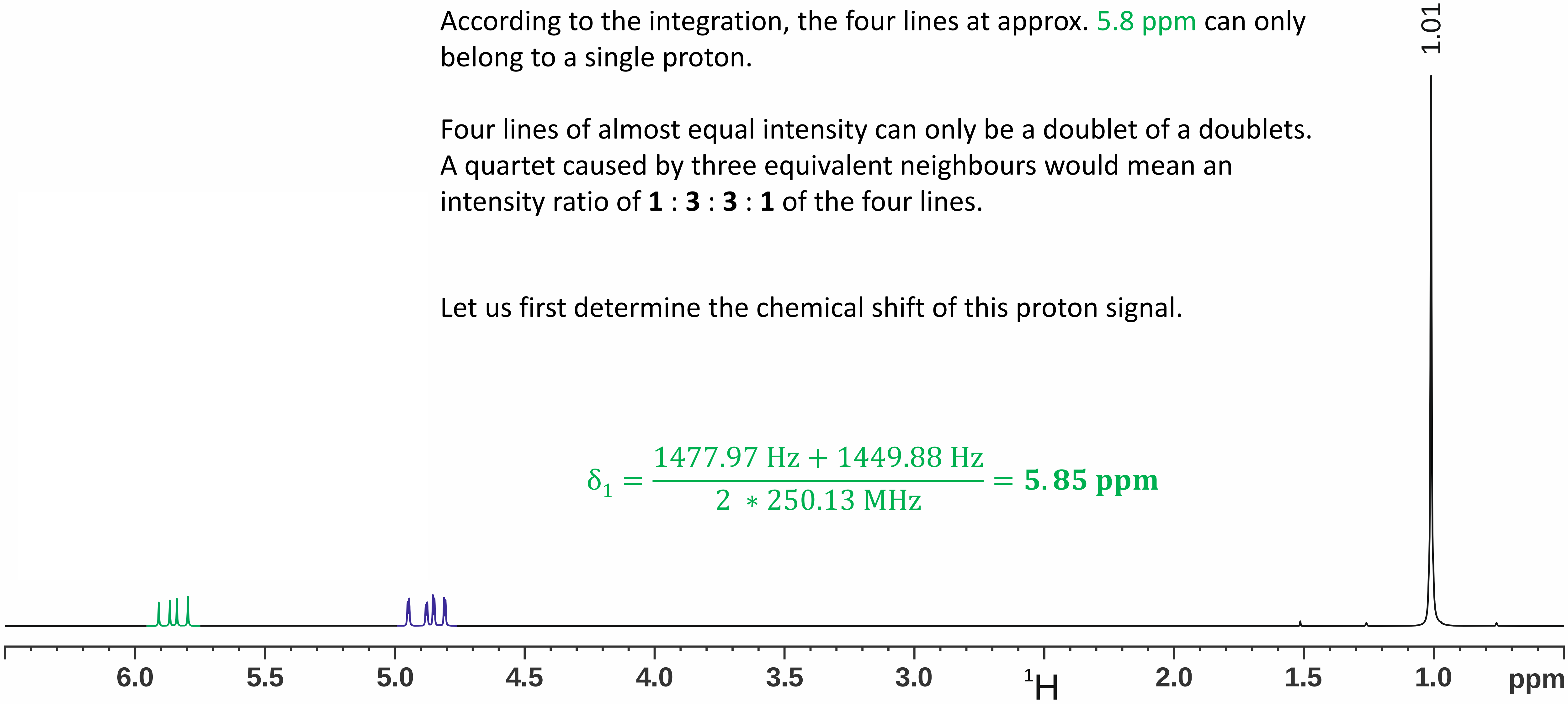
Analysis of the first multiplet

According to the integration, the four lines at approx. 5.8 ppm can only belong to a single proton.

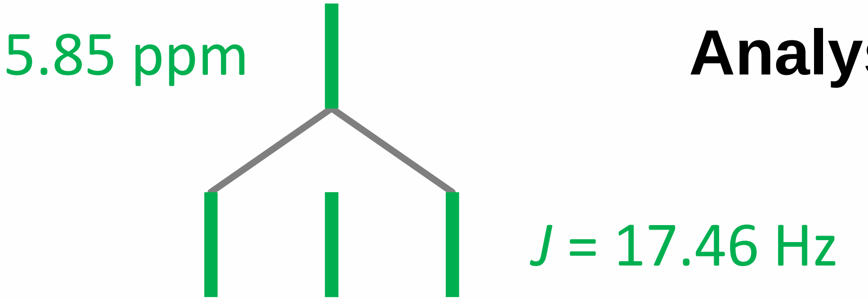
Four lines of almost equal intensity can only be a doublet of a doublets. A quartet caused by three equivalent neighbours would mean an intensity ratio of **1** : **3** : **3** : **1** of the four lines.

Let us first determine the chemical shift of this proton signal.

$$\delta_1 = \frac{1477.97\ \text{Hz} + 1449.88\ \text{Hz}}{2\ * 250.13\ \text{MHz}} = \mathbf{5.85\ ppm}$$

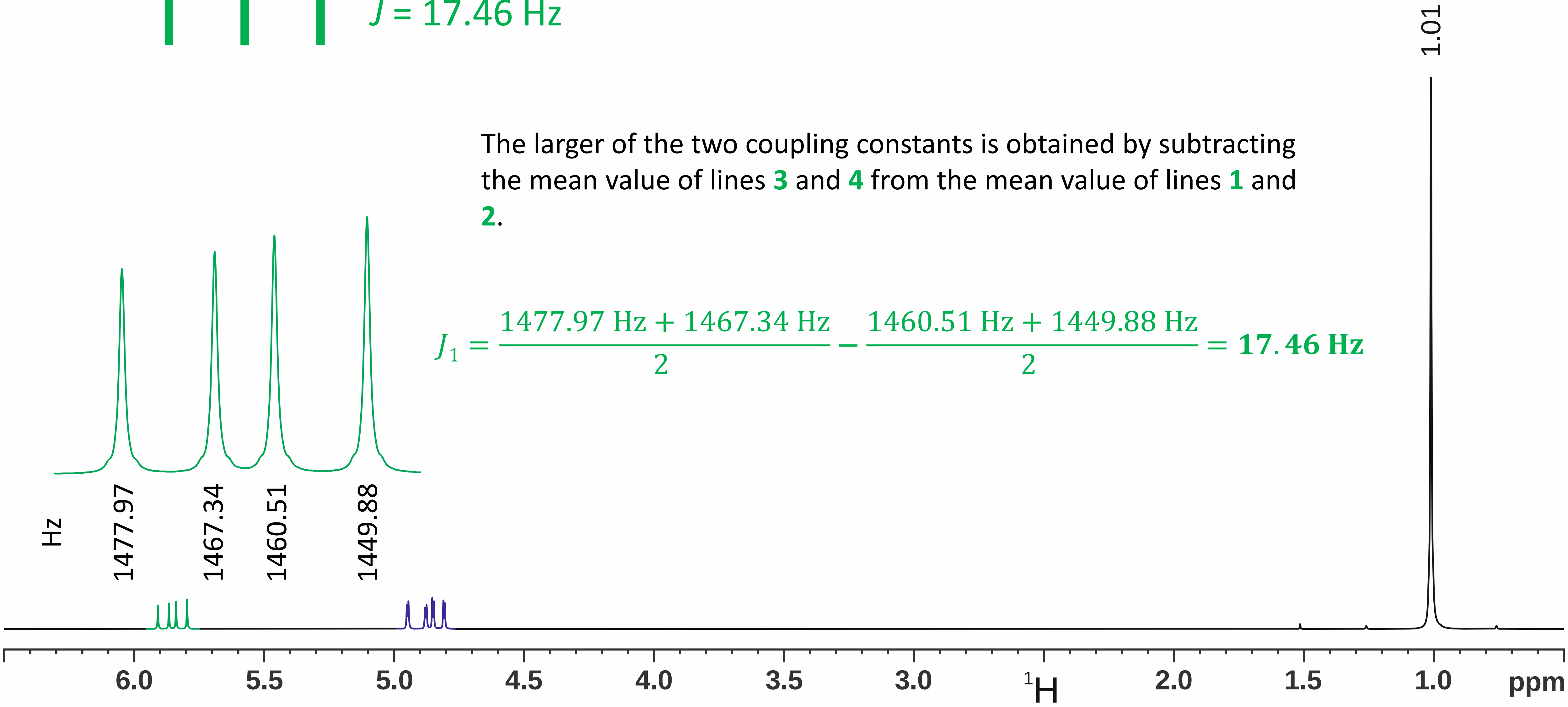


Analysis of the first multiplet

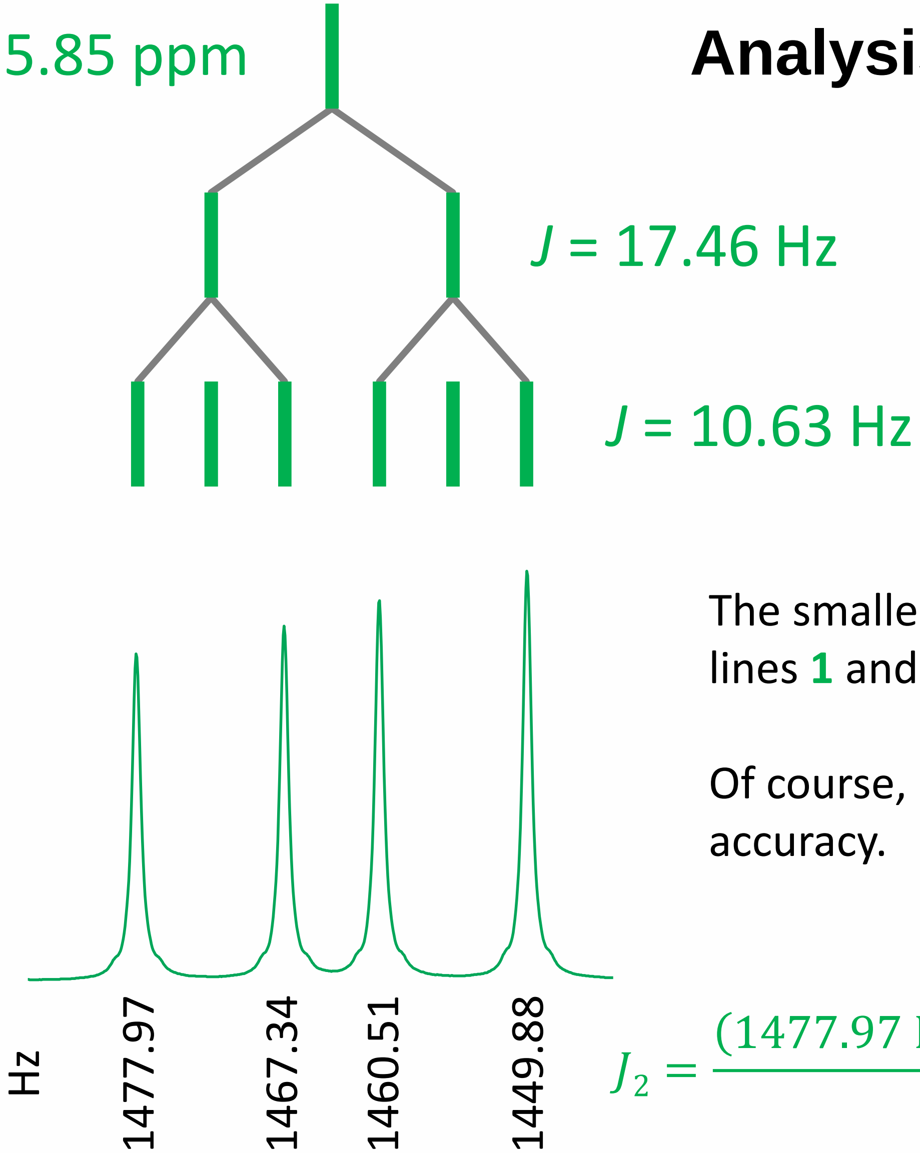


The larger of the two coupling constants is obtained by subtracting the mean value of lines **3** and **4** from the mean value of lines **1** and **2**.

$$J_1 = \frac{1477.97\ \text{Hz} + 1467.34\ \text{Hz}}{2} - \frac{1460.51\ \text{Hz} + 1449.88\ \text{Hz}}{2} = \mathbf{17.46\ Hz}$$



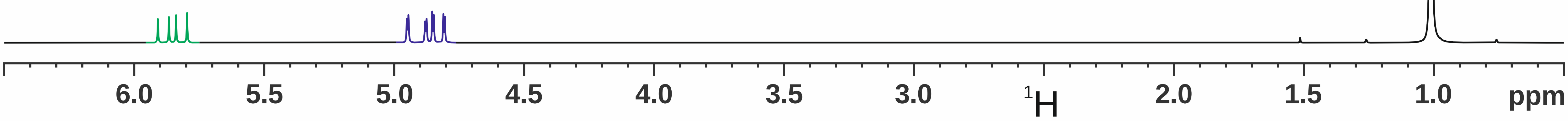
Analysis of the first multiplet

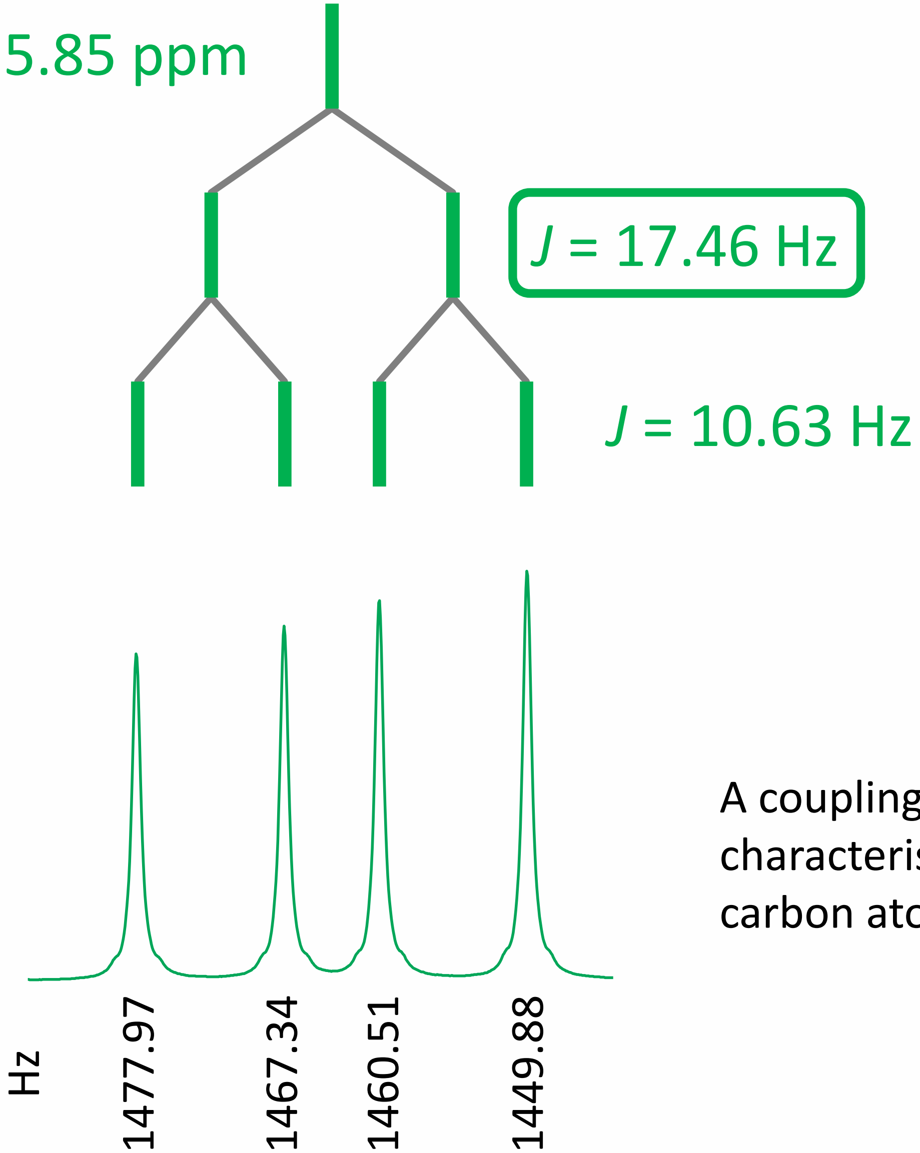


The smaller of the two coupling constants is the difference between lines **1** and **2** or **3** and **4**.

Of course, one can also use the mean value in the interest of better accuracy.

$$J_2 = \frac{(1477.97\ \text{Hz} - 1467.34\ \text{Hz}) + (1460.51\ \text{Hz} - 1449.88\ \text{Hz})}{2} = \mathbf{10.63\ Hz}$$

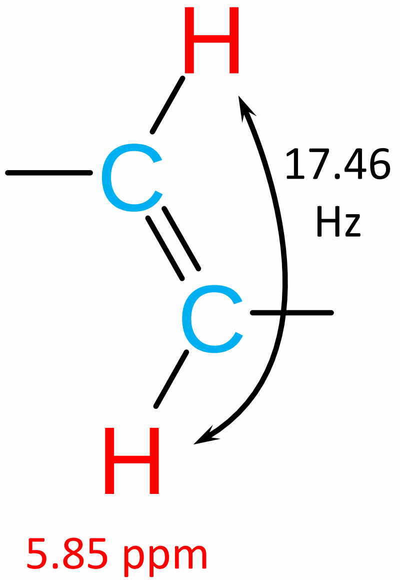


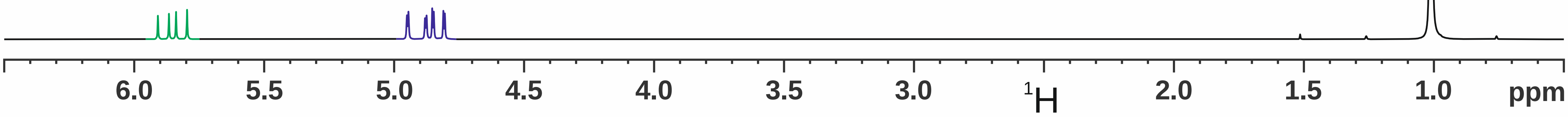


First steps to get the structure

According to the chemical shift, the signal at 5.85 ppm belongs to a C**H** group with sp^2 hybridised carbon. Thus, the double bond equivalent is also assigned.

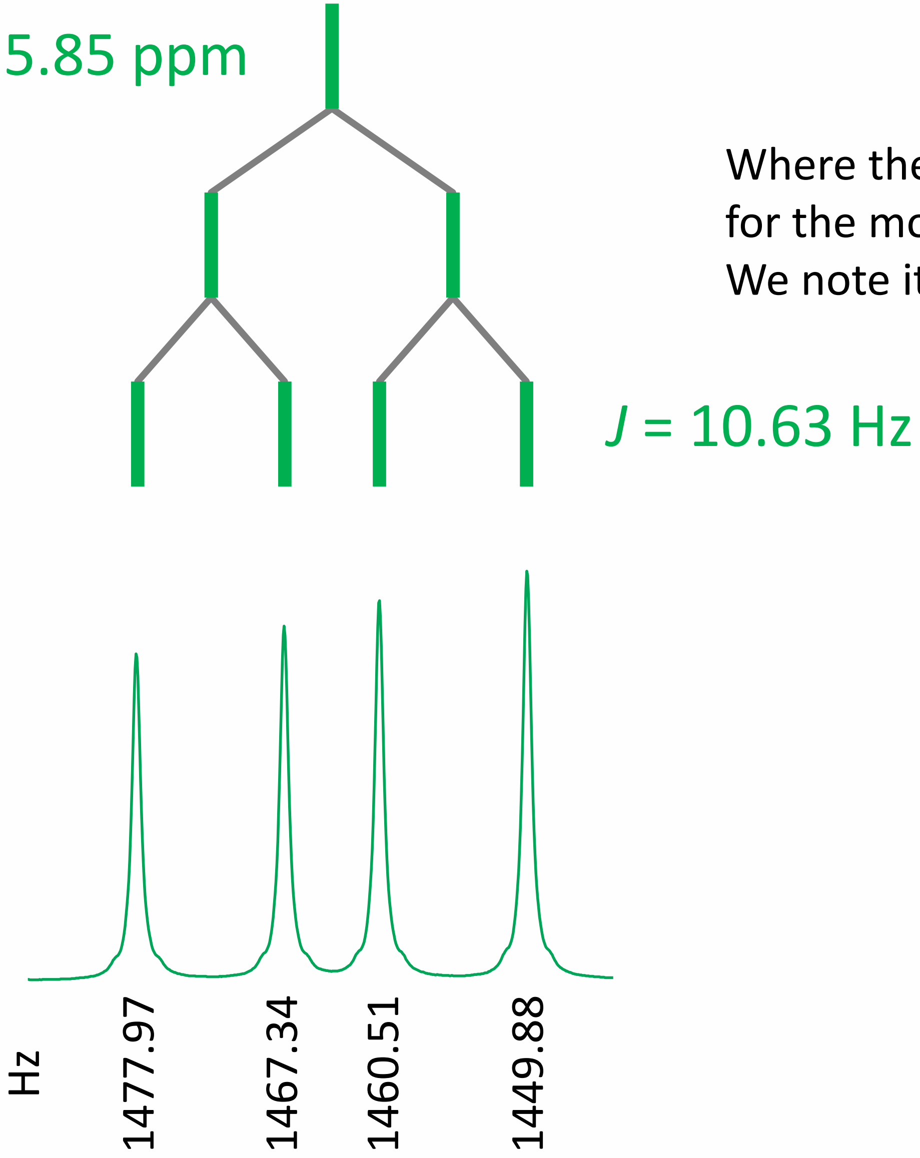
A coupling constant of **17.46 Hz** is highly characteristic of two protons on sp^2-hybridised carbon atoms in the **E**-position to each other.

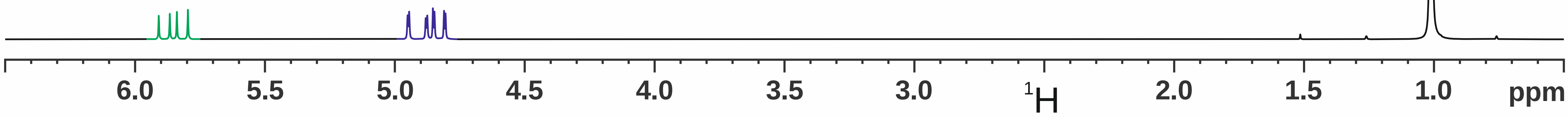


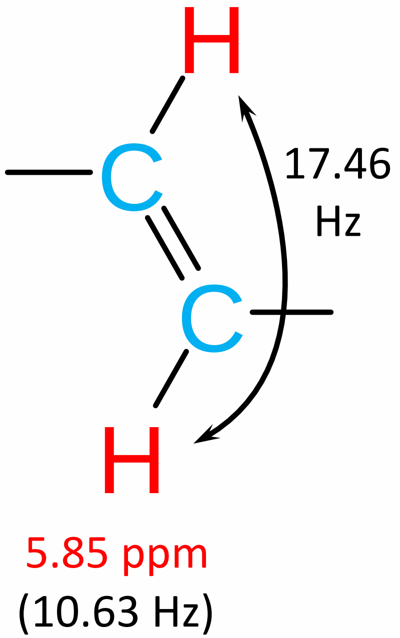


First steps to get the structure

Where the coupling constant of 10.63 Hz comes from is not clear for the moment.
We note it next to the chemical shift for later use.



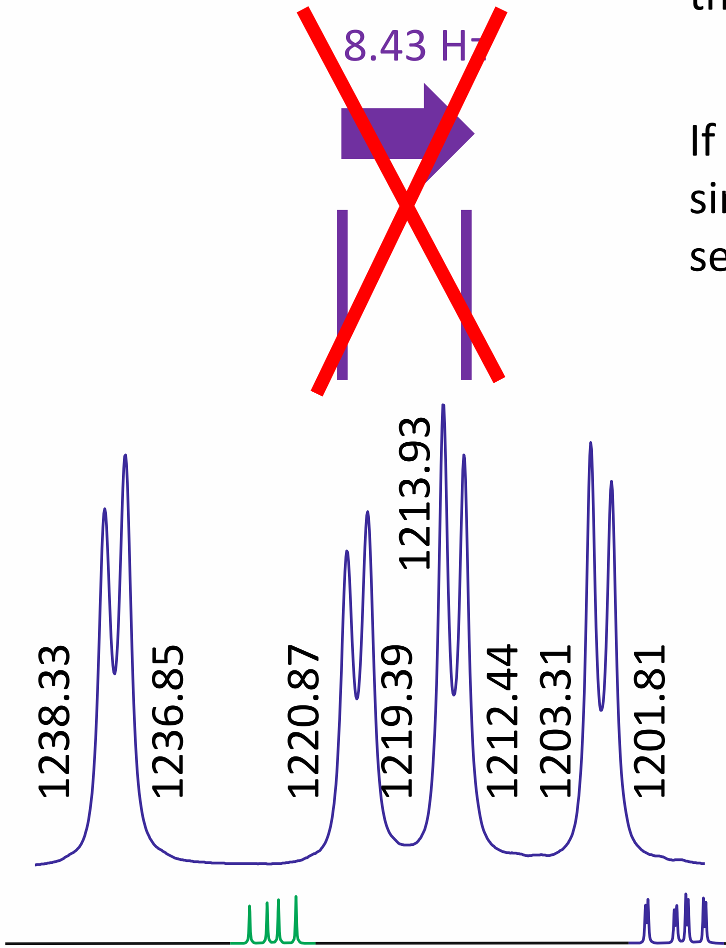




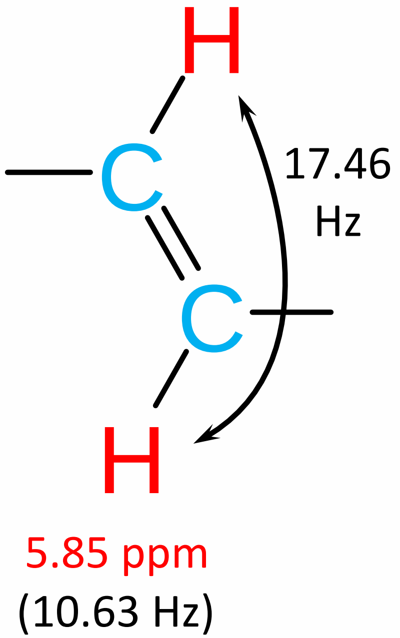
Multiplet of the second proton

The coupling constant of **17.46 Hz** must appear again somewhere in the confusing multiplet around 4.9 ppm.

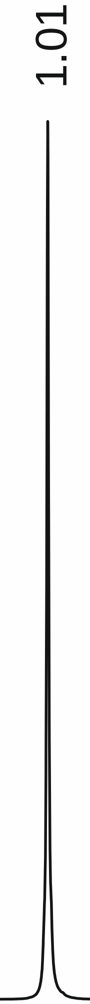
If the multiplet structure is not immediately obvious, you can simply try to measure the difference between two randomly selected lines.

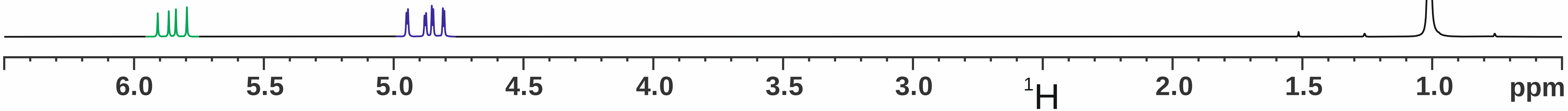


First attempt



Give it another try.





Multiplet of the second proton

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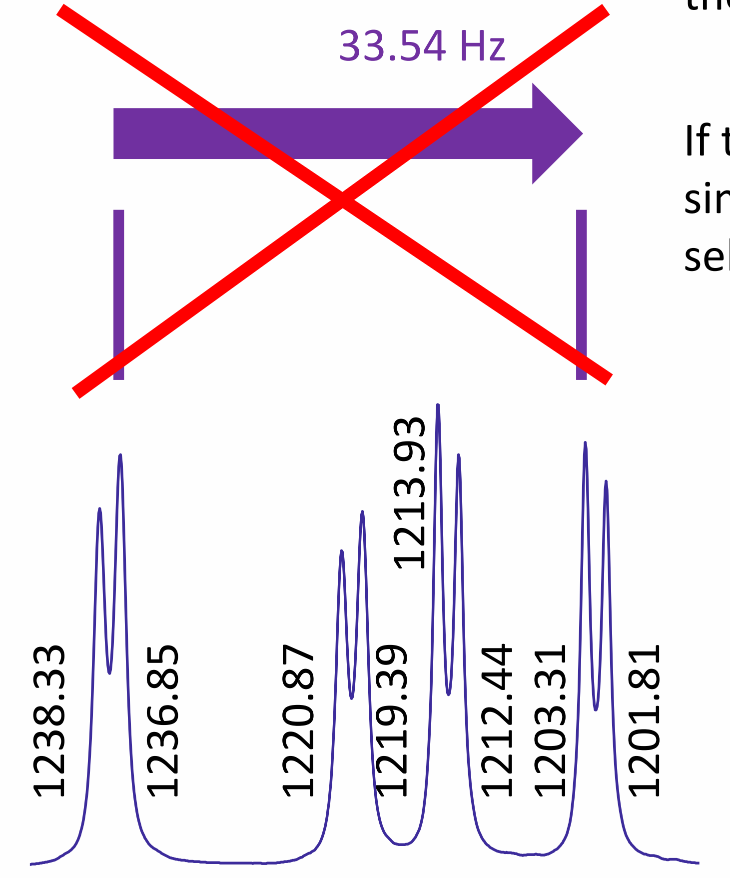
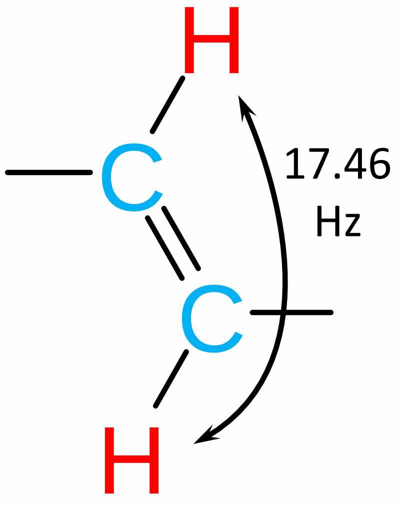
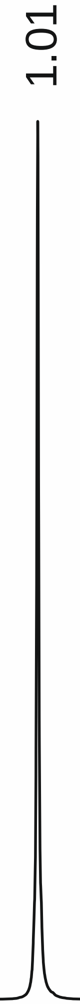


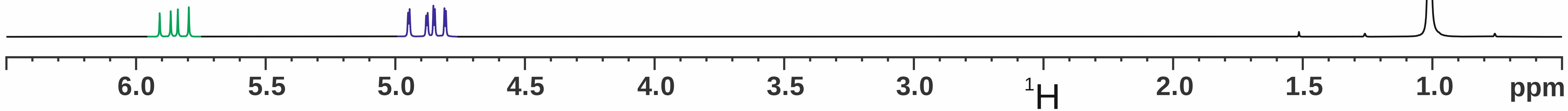
If the multiplet structure is not immediately obvious, you can simply try to measure the difference between two randomly selected lines.



Second attempt

Don‘t give up.

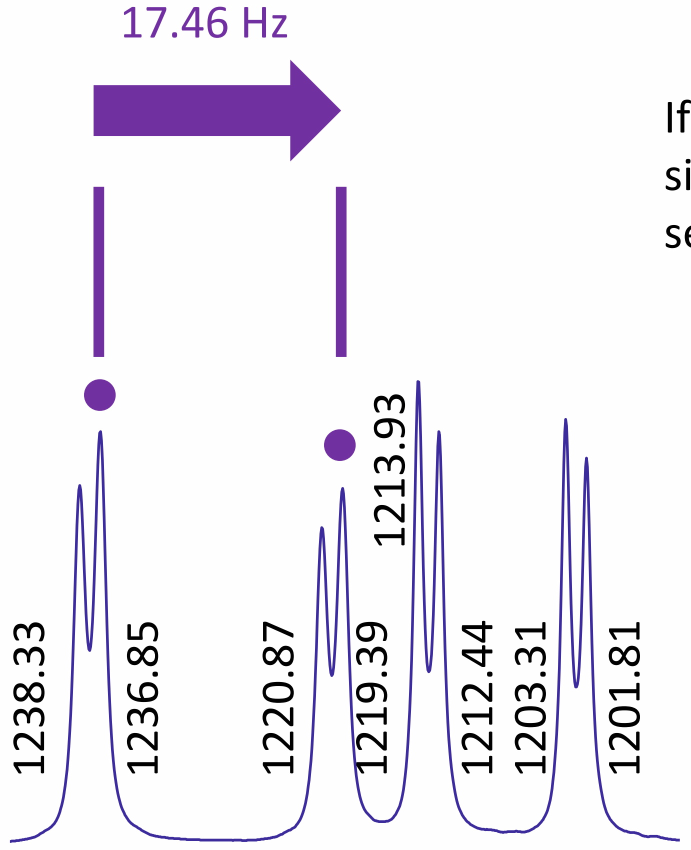




Multiplet of the second proton

The coupling constant of **17.46 Hz** must appear again somewhere in the confusing multiplet around 4.9 ppm.

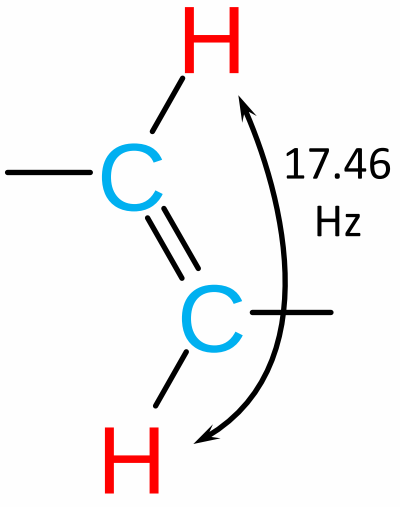
If the multiplet structure is not immediately obvious, you can simply try to measure the difference between two randomly selected lines.

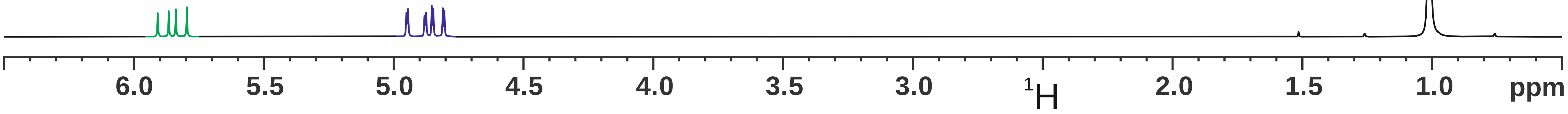


Third attempt

Hooray!

Let's mark these two lines, maybe it will work again.

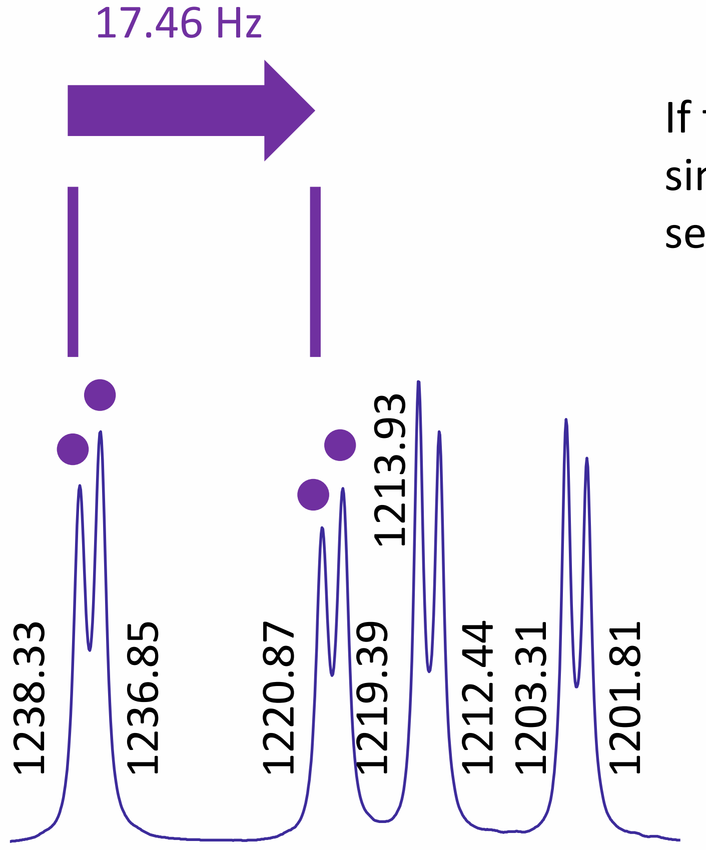




Multiplet of the second proton

The coupling constant of **17.46 Hz** must appear again somewhere in the confusing multiplet around 4.9 ppm.

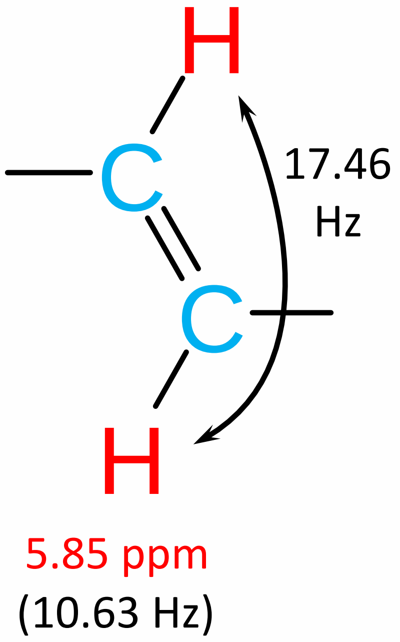
If the multiplet structure is not immediately obvious, you can simply try to measure the difference between two randomly selected lines.

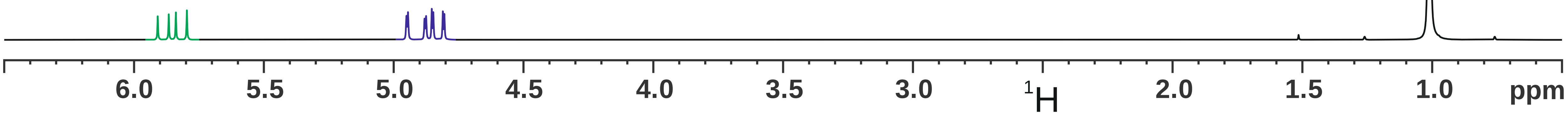


Fourth attempt

Yes!

Let's label both lines too.





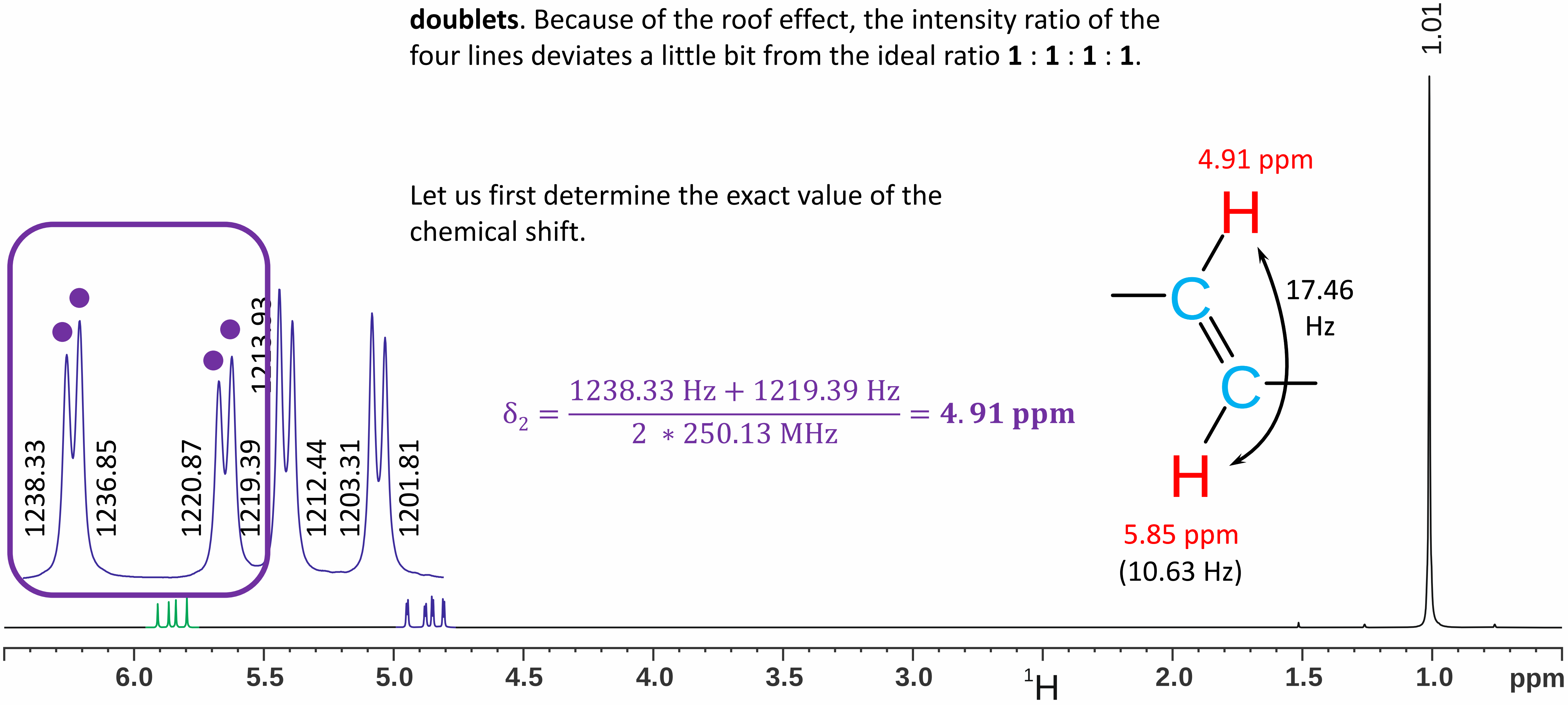
4.91 ppm

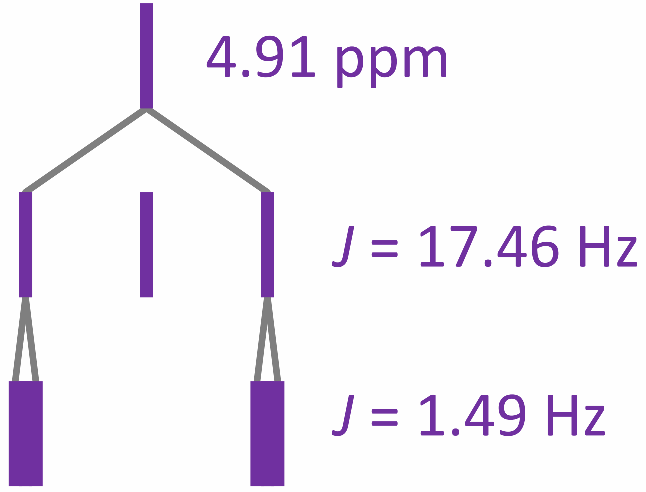
Multiplet of the second proton

The four labelled signals can now be recognised as **doublet of doublets**. Because of the roof effect, the intensity ratio of the four lines deviates a little bit from the ideal ratio **1** : **1** : **1** : **1**.

Let us first determine the exact value of the chemical shift.

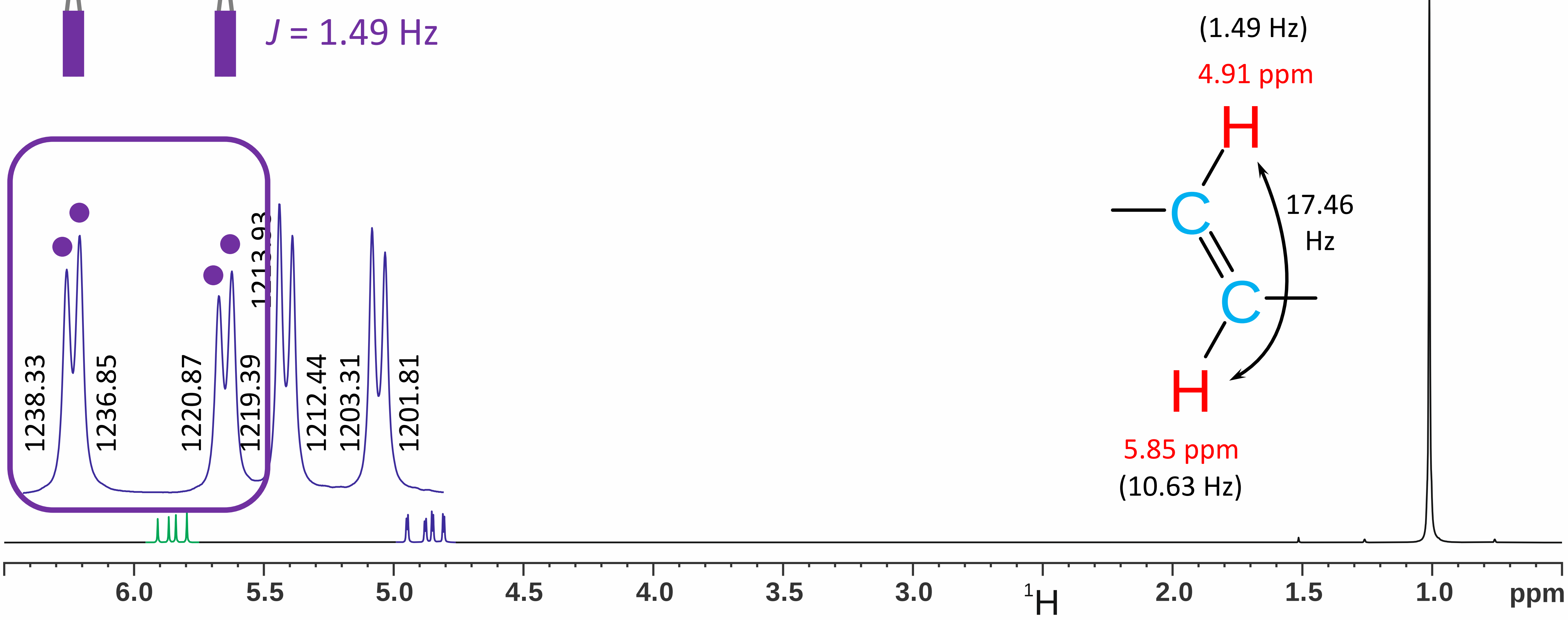
$$\delta_2 = \frac{1238.33\ \text{Hz} + 1219.39\ \text{Hz}}{2\ *\ 250.13\ \text{MHz}} = \mathbf{4.91\ ppm}$$

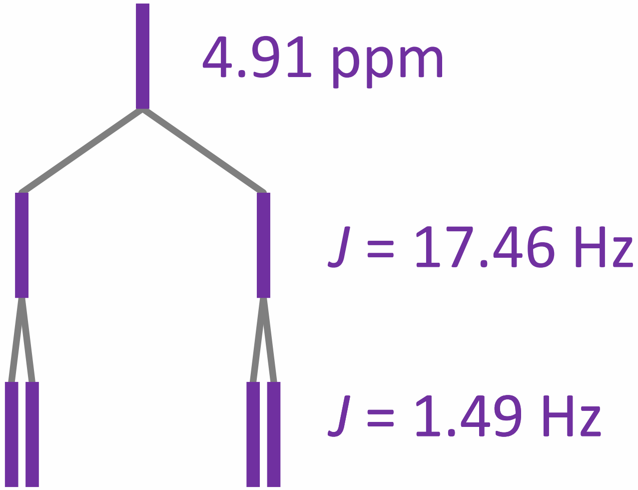




Multiplet of the second proton

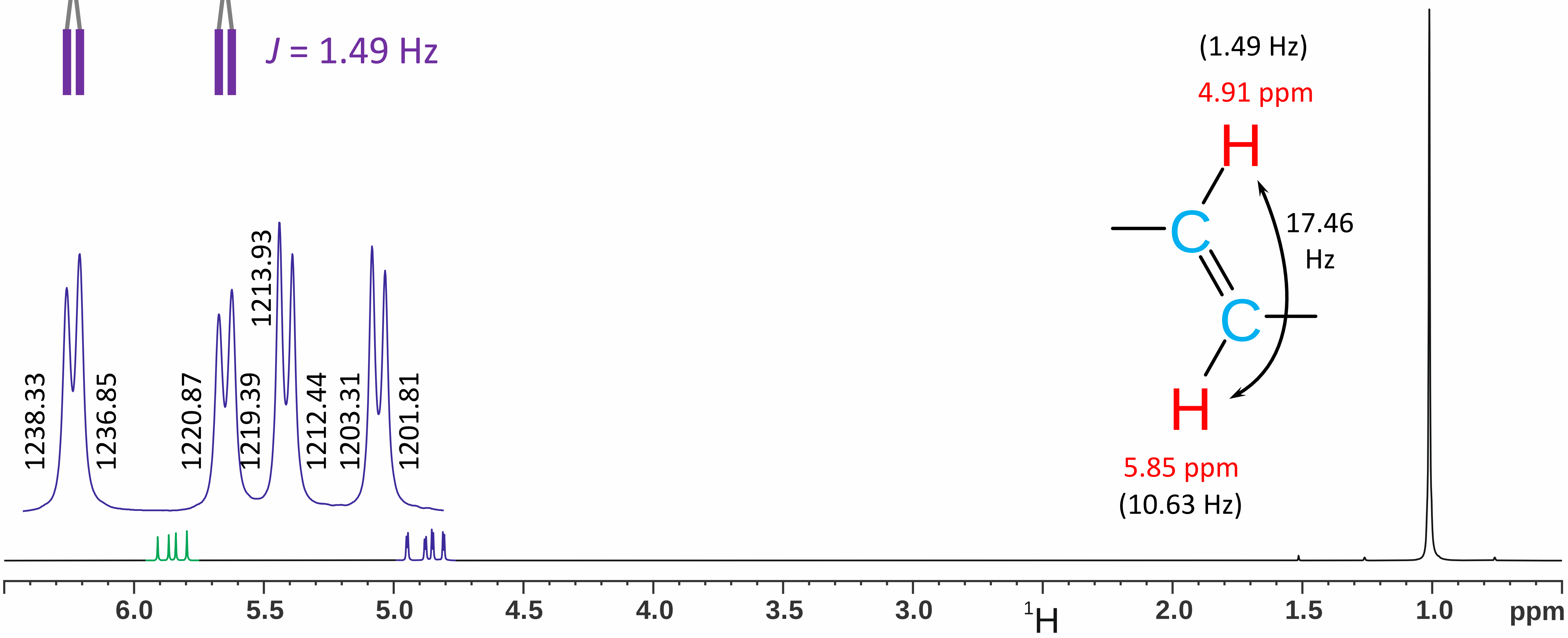
The evaluation of the **doublet of doublets** is done in the same way as for the proton with the chemical shift of 5.85 ppm.



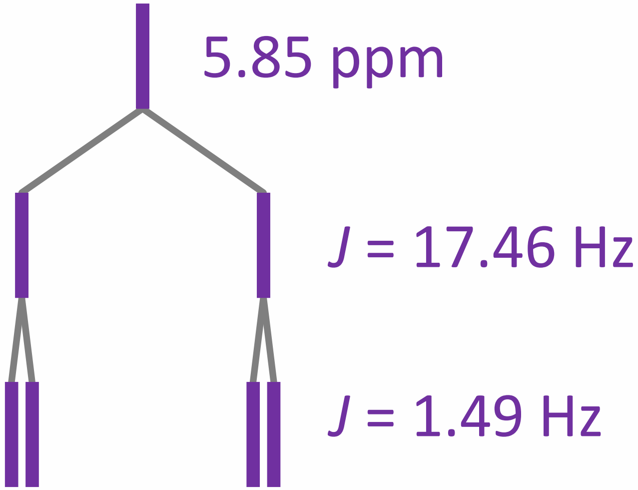


Multiplet of the second proton

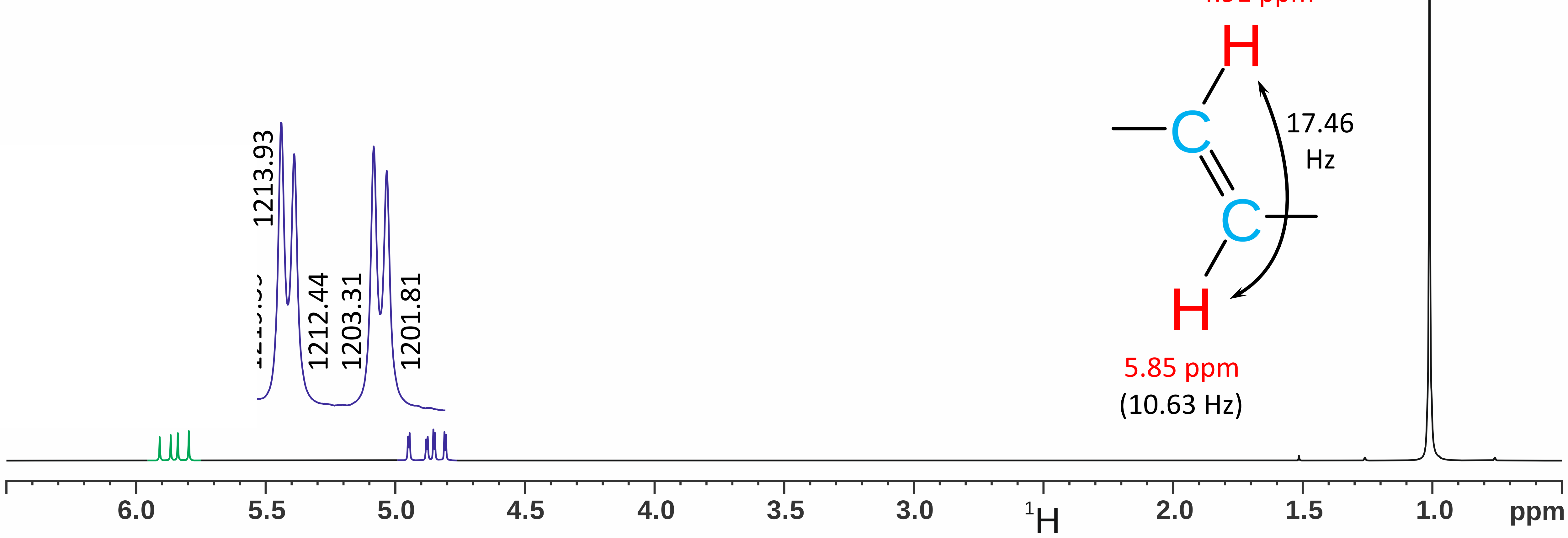
The coupling constant of **1.49 Hz** is not immediately understandable. We note it next to the chemical shift of the associated proton.



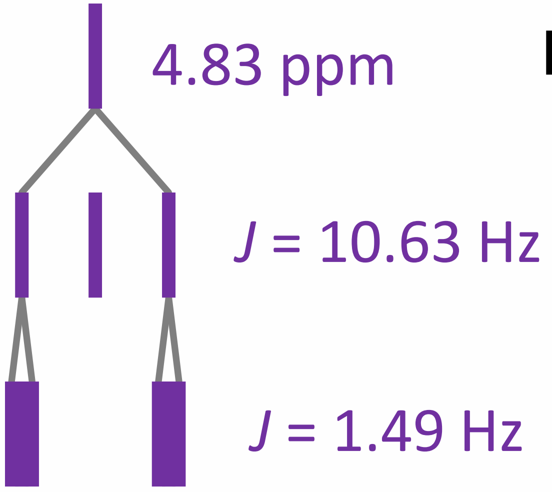
Multiplet of the third proton



If we now delete the multiplet we have just evaluated, we are left with a clearly recognisable further doublet of doublets.

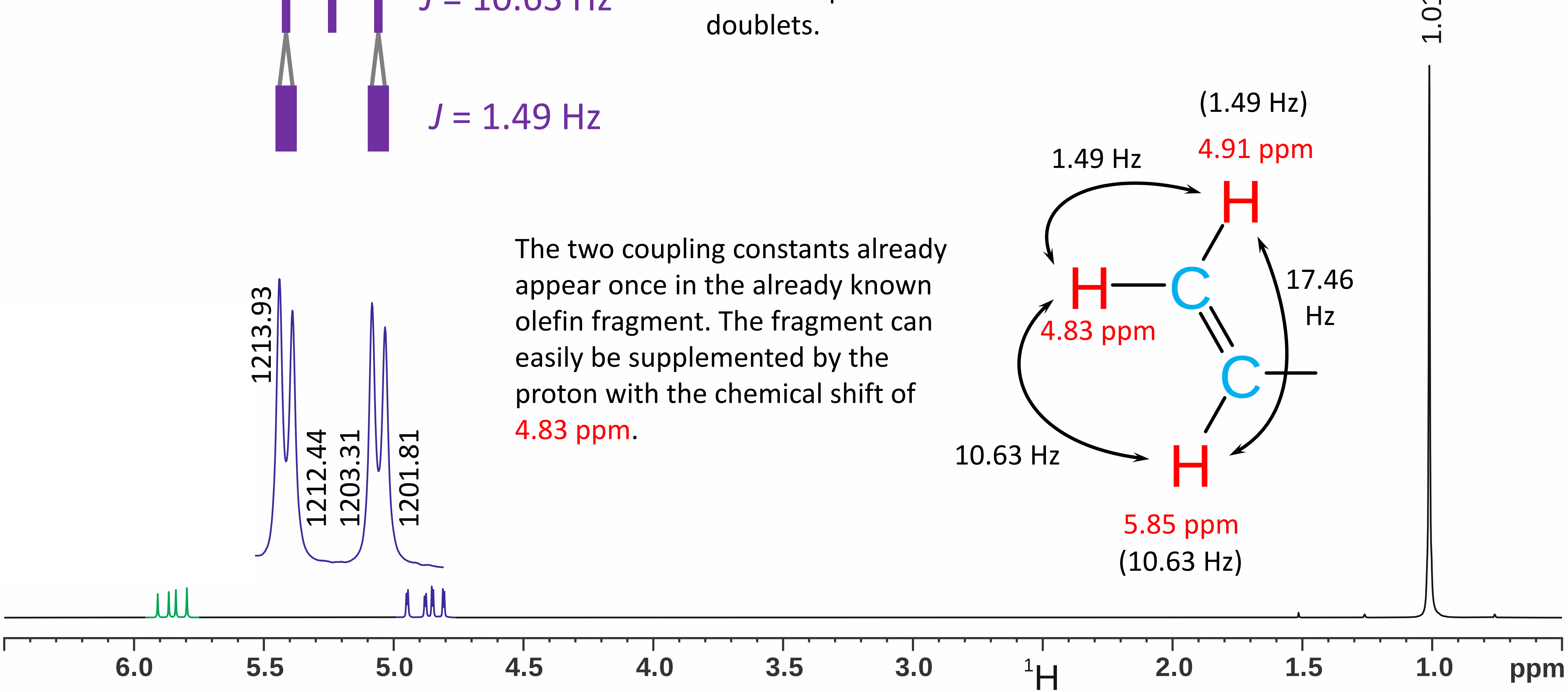


Multiplet of the third proton

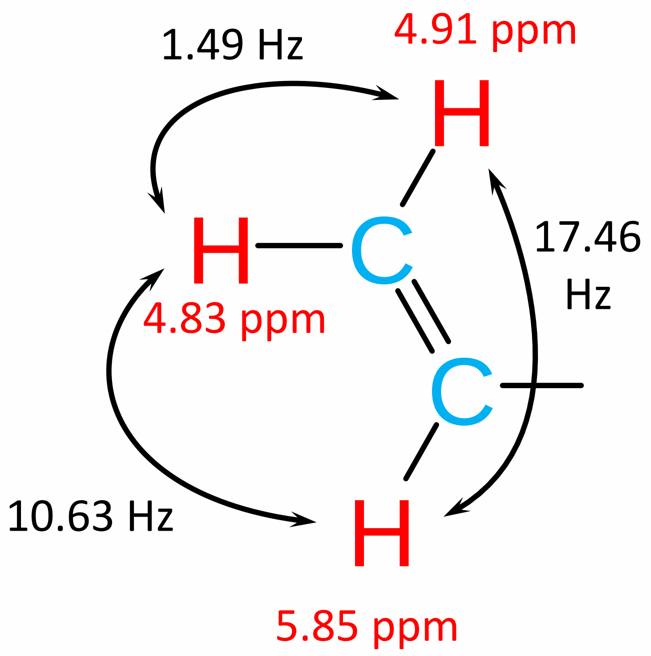


Its evaluation is carried out in the same way as for the previous two doublets of doublets.

The two coupling constants already appear once in the already known olefin fragment. The fragment can easily be supplemented by the proton with the chemical shift of 4.83 ppm.



Intermediate resume

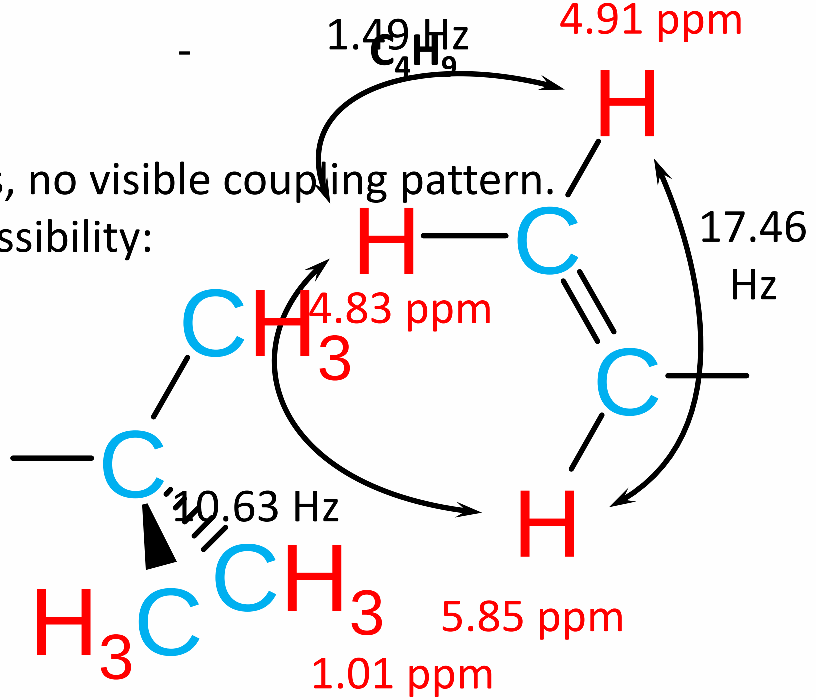


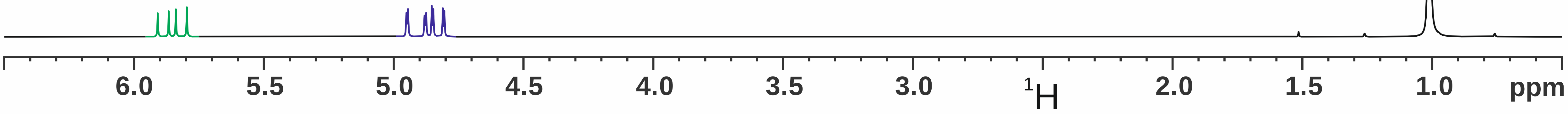
molecular formula - C_6H_{12}

assigned so far - C_2H_3
one double bond equivalent

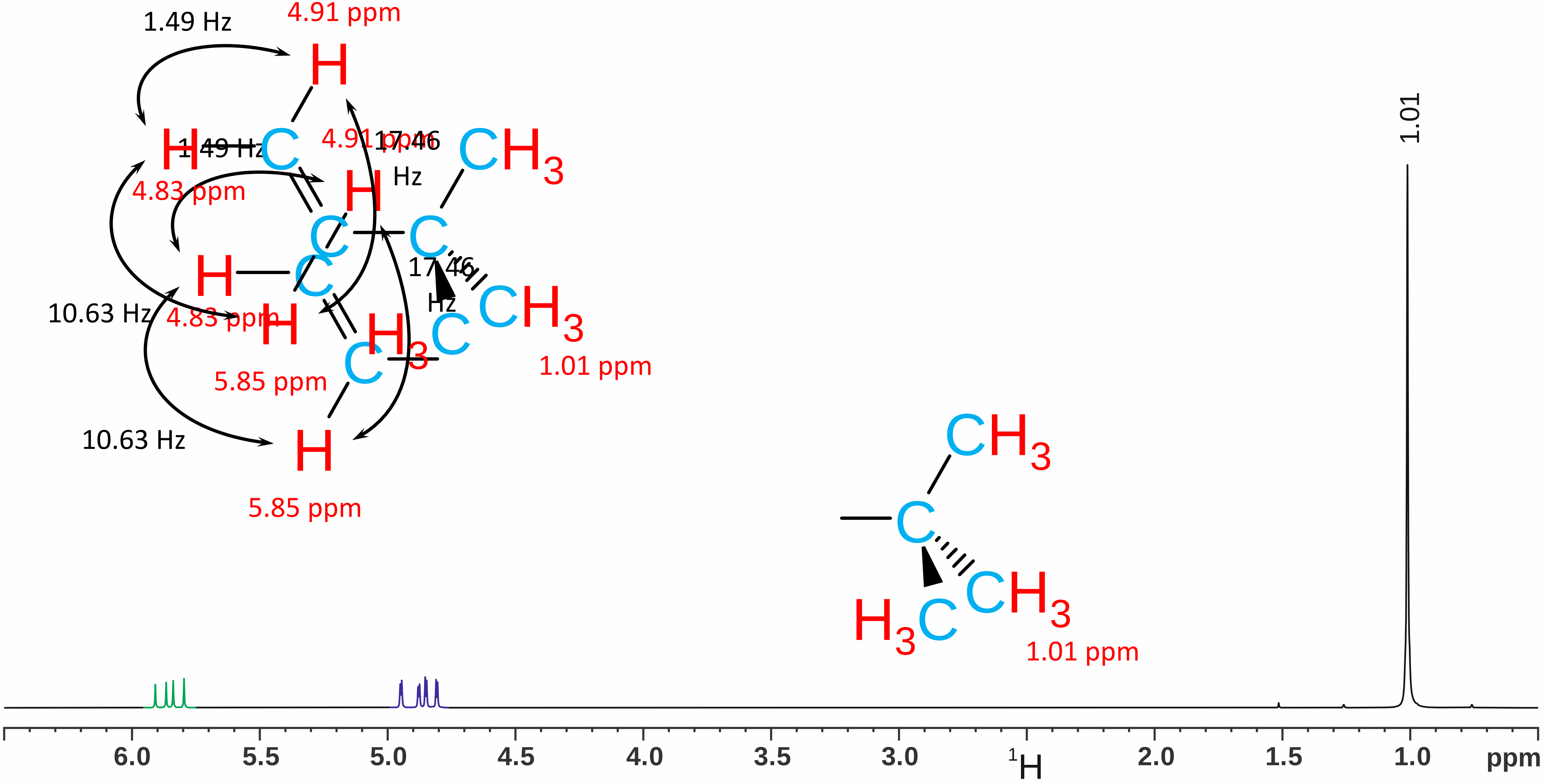
still missing - C_4H_9

9 equivalent protons, no visible coupling pattern.
There is only one possibility:

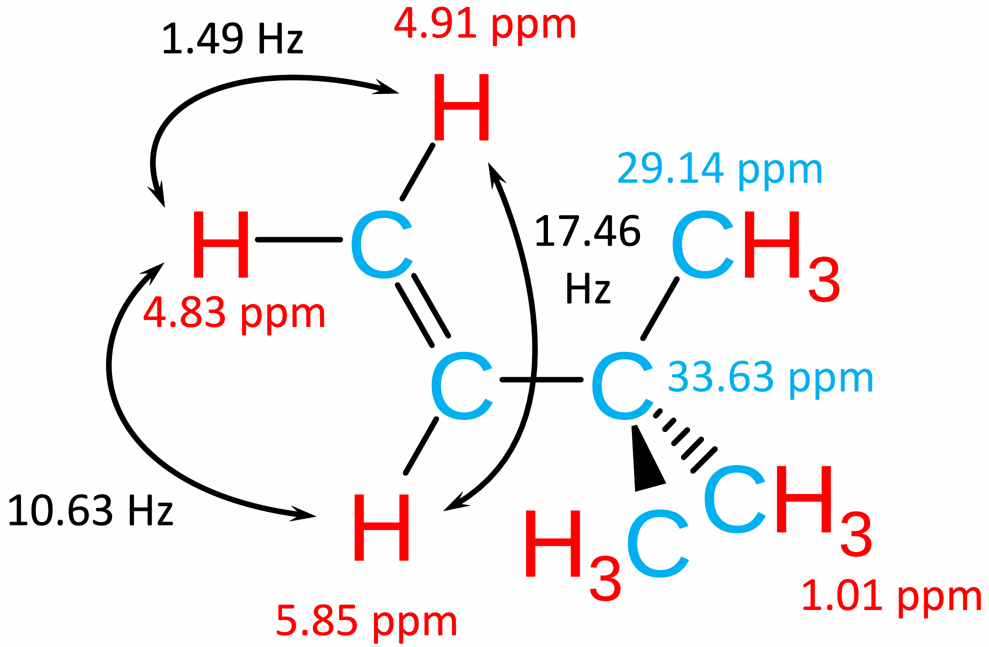




Final structure



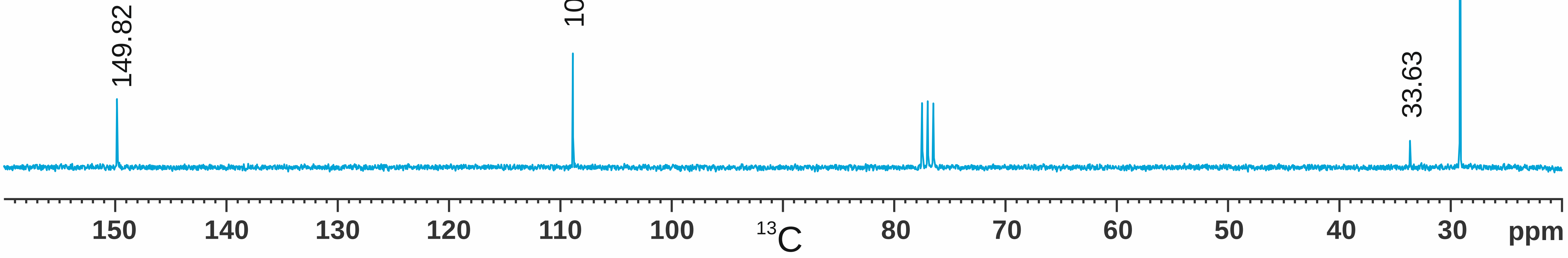
Assignment of the carbon signals



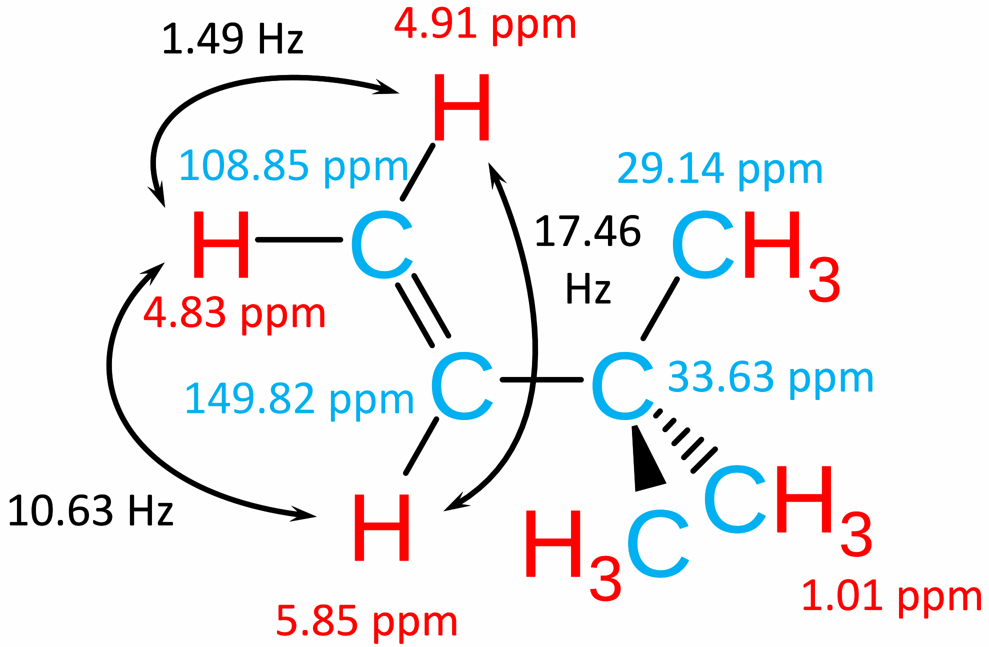
The signals at 29.14 and 33.63 ppm belong to sp^3 hybridised carbon atoms and the signals at 108.85 and 149.82 ppm belong to sp^2 hybridised carbon atoms..

Even if you have to be careful, when integrating carbon signals, the line at 29.14 ppm can be clearly assigned to the methyl carbon atoms.

This signal is clearly more intense compared to the signal at 33.63 ppm. This is due to a combination of the three identical carbon atoms, the NOE effect of the attached protons, and the shorter relaxation time.



Assignment of the carbon signals



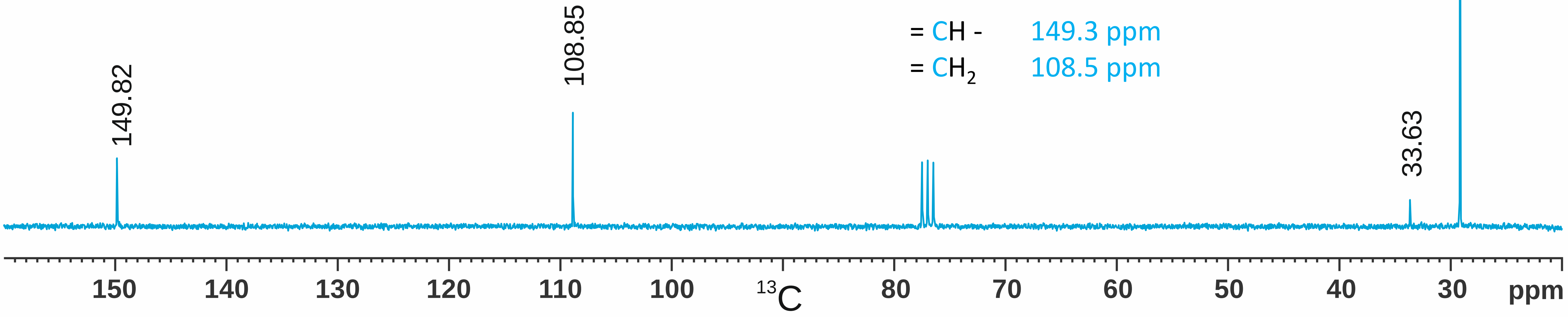
Using a common incremental schema to estimate the chemical shifts of the sp² hybridised carbon atom results in two very different values.

Given this large difference, the estimate can be trusted 100%.

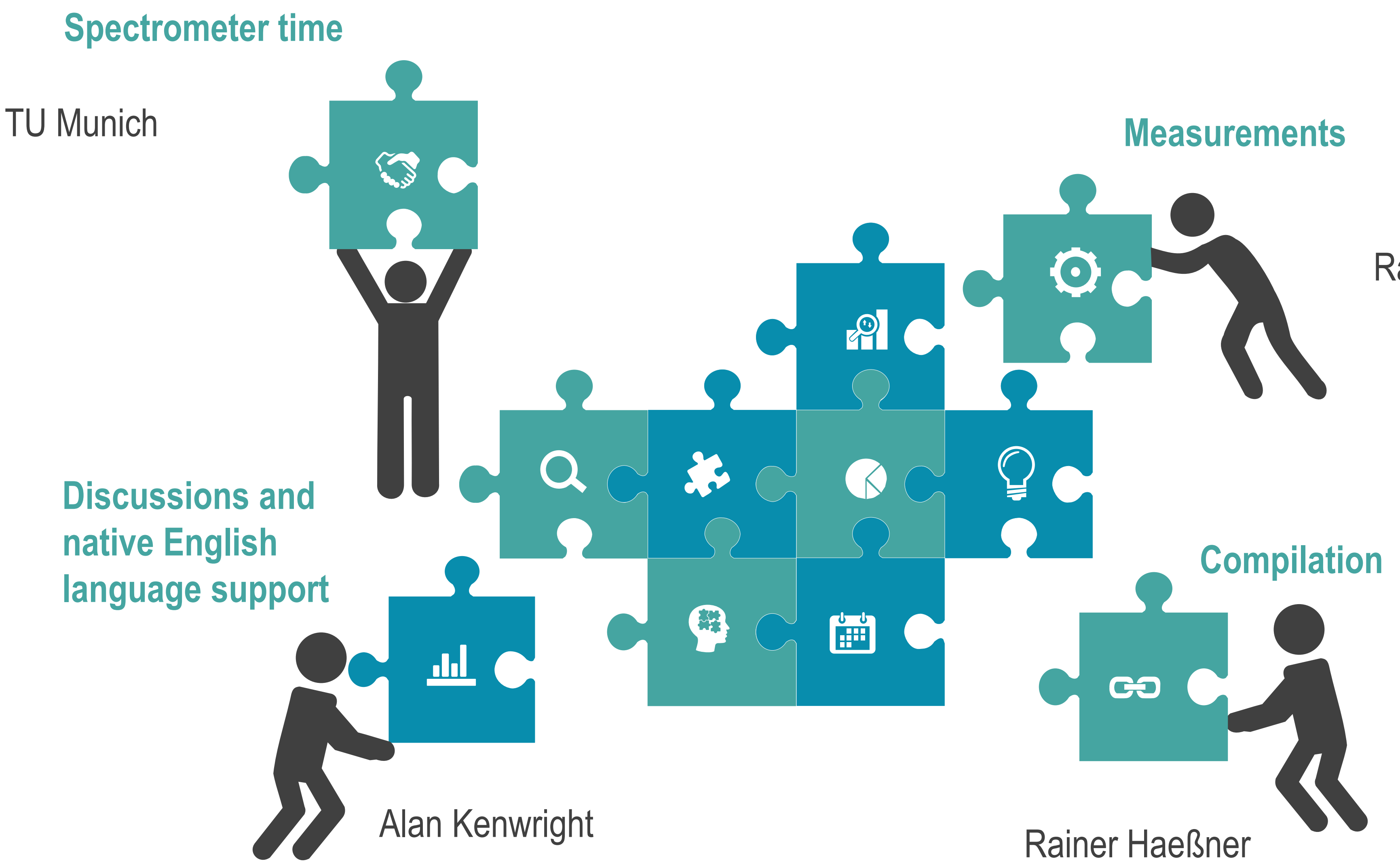
If the difference were not large, we could use an (additional) DEPT experiment to distinguish the CH from the CH_2.

The result from the incremental scheme:

= CH -	149.3 ppm
= CH_2	108.5 ppm



Contributions



More exercises …