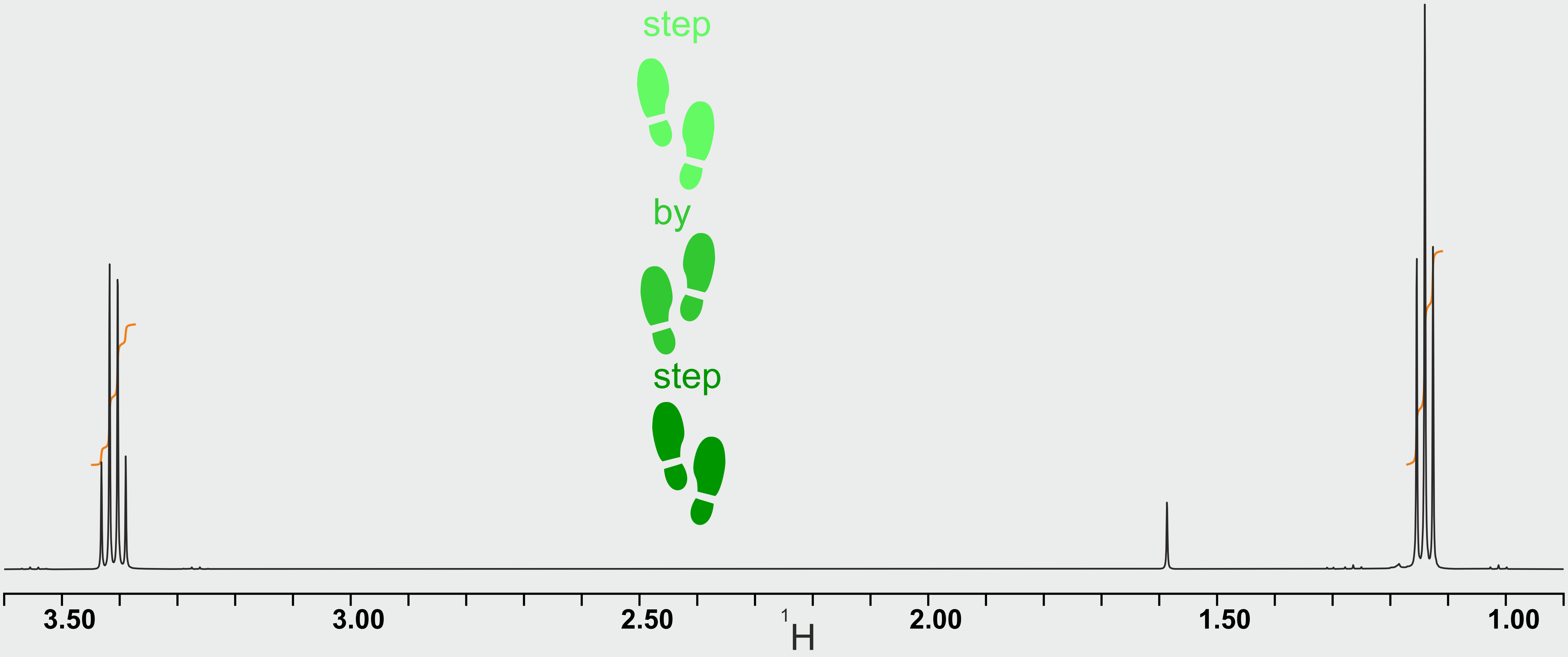
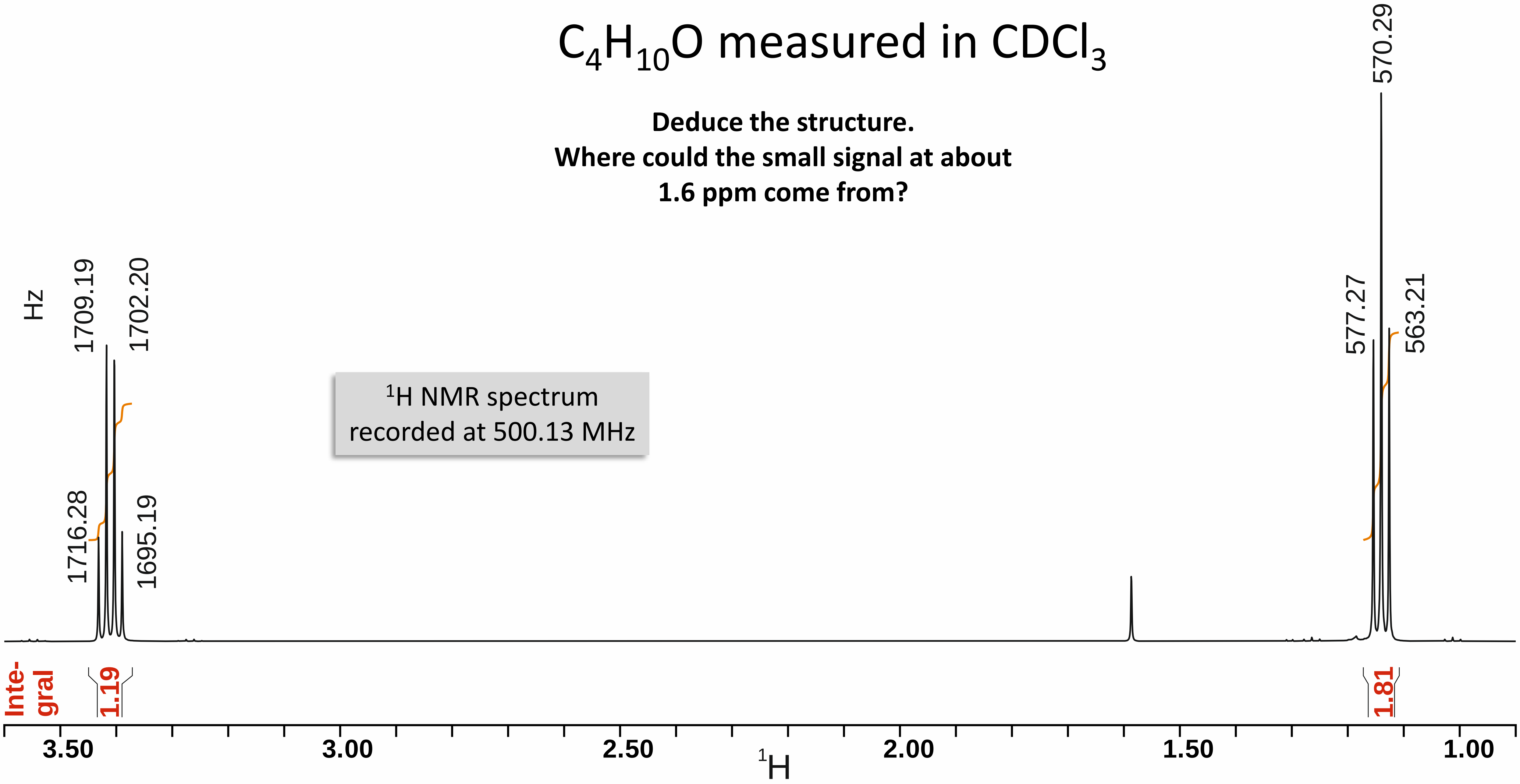
Exercise plus Solution – Quick PDF overview

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.



$C_4H_{10}O$ measured in $CDCl_3$

Deduce the structure.
Where could the small signal at about 1.6 ppm come from?



^1H NMR spectrum recorded at 500.13 MHz

Solution

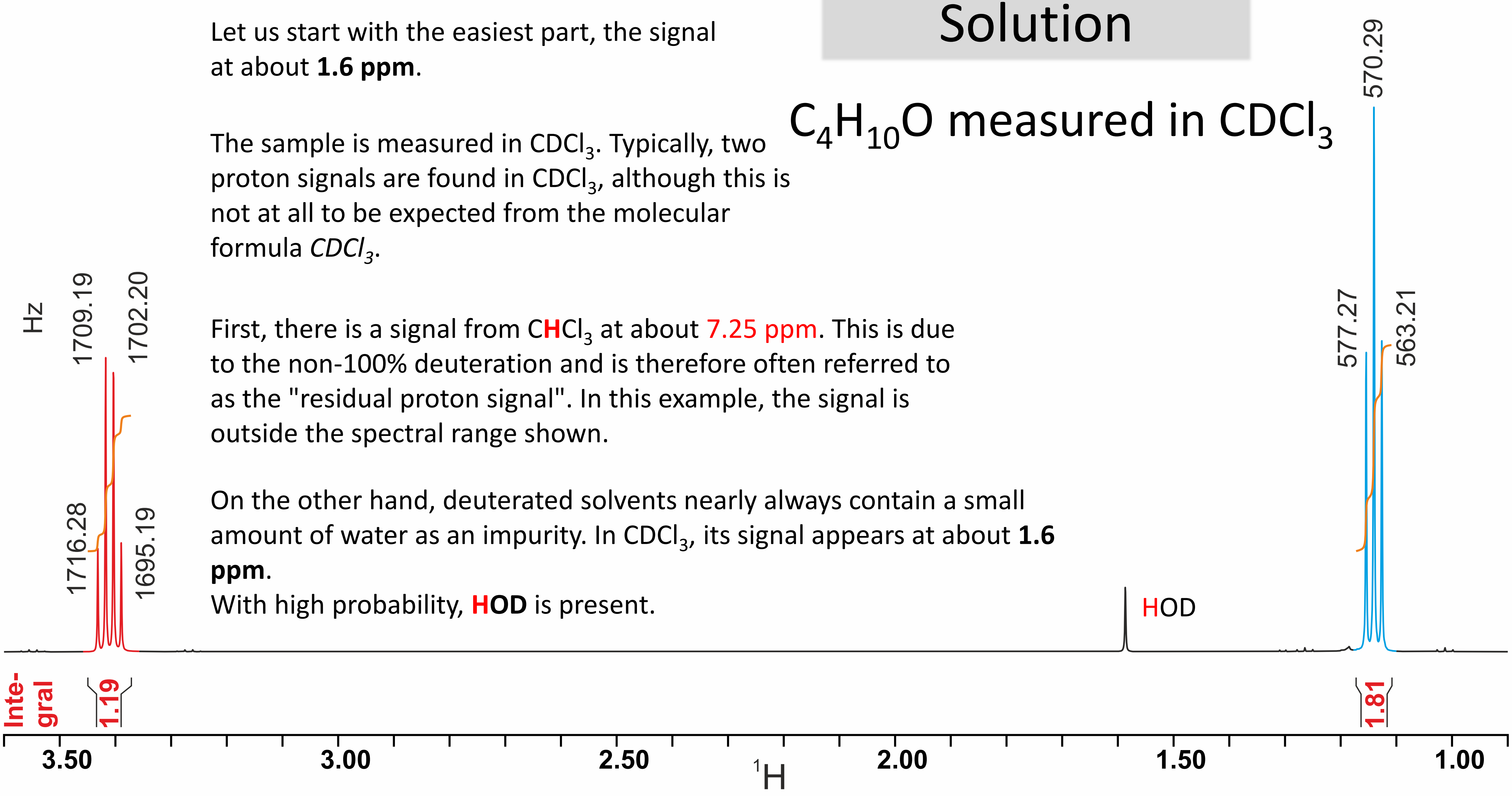
$C_4H_{10}O$ measured in $CDCl_3$

Let us start with the easiest part, the signal at about **1.6 ppm**.

The sample is measured in $CDCl_3$. Typically, two proton signals are found in $CDCl_3$, although this is not at all to be expected from the molecular formula *$CDCl_3$*.

First, there is a signal from C**H**Cl_3 at about 7.25 ppm. This is due to the non-100% deuteration and is therefore often referred to as the "residual proton signal". In this example, the signal is outside the spectral range shown.

On the other hand, deuterated solvents nearly always contain a small amount of water as an impurity. In $CDCl_3$, its signal appears at about **1.6 ppm**.
With high probability, **HOD** is present.



Solution

$C_4H_{10}O$ measured in $CDCl_3$

There are no double bond equivalents.

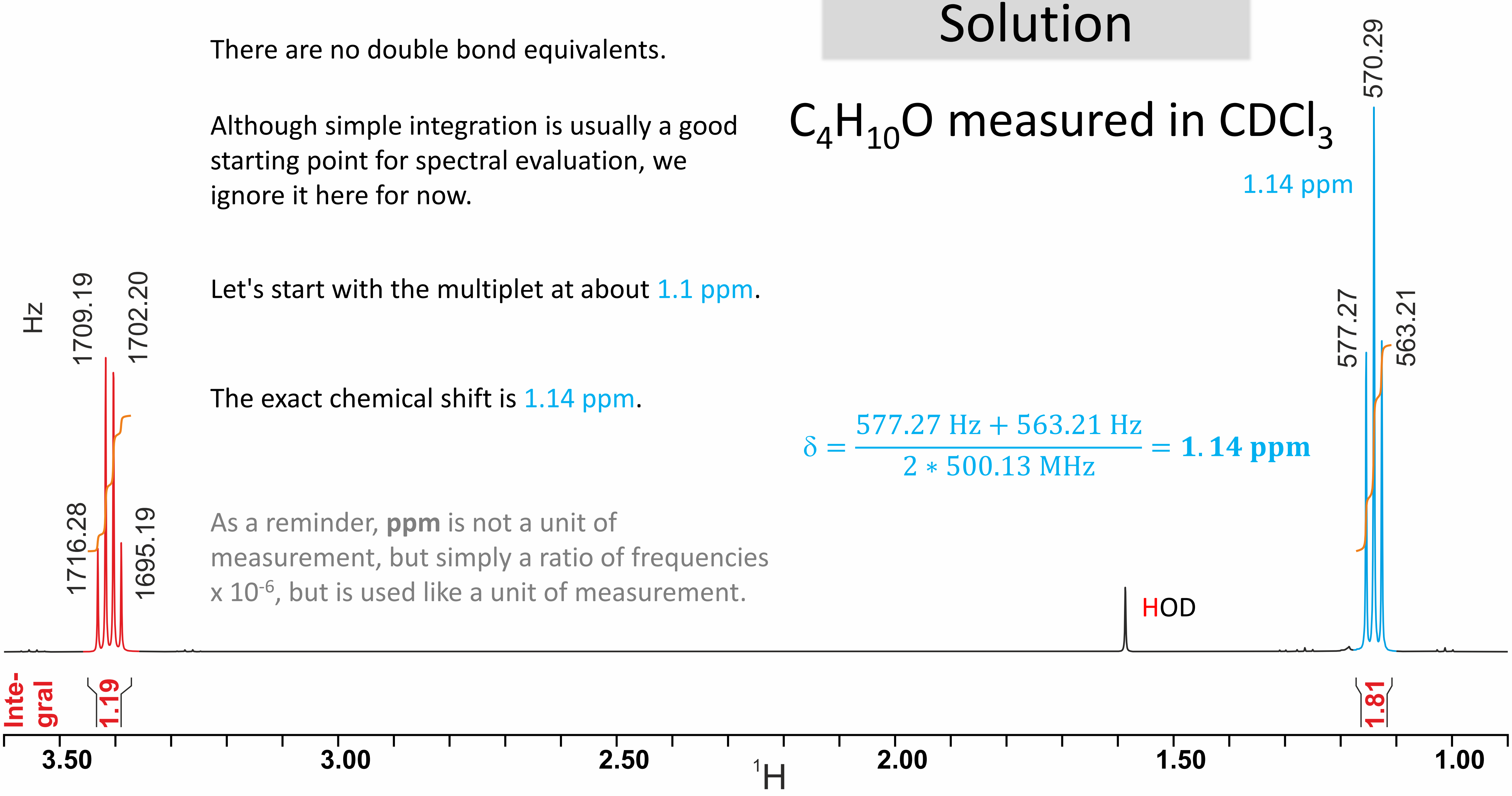
Although simple integration is usually a good starting point for spectral evaluation, we ignore it here for now.

Let's start with the multiplet at about 1.1 ppm.

The exact chemical shift is 1.14 ppm.

$$\delta = \frac{577.27\ \text{Hz} + 563.21\ \text{Hz}}{2 * 500.13\ \text{MHz}} = \mathbf{1.14\ ppm}$$

As a reminder, **ppm** is not a unit of measurement, but simply a ratio of frequencies x 10^{-6}, but is used like a unit of measurement.



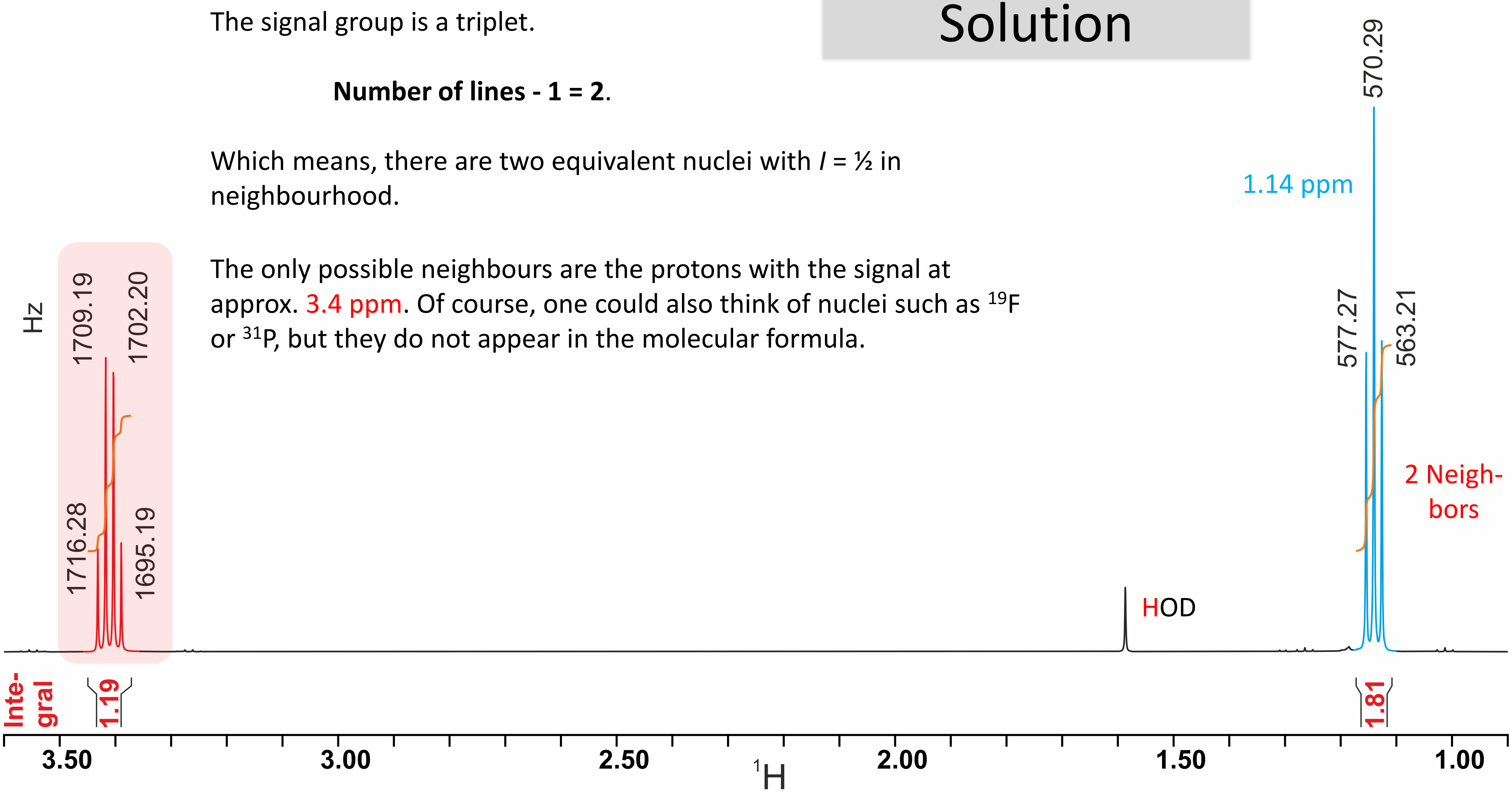
Solution

The signal group is a triplet.

Number of lines - 1 = 2.

Which means, there are two equivalent nuclei with *I* = ½ in neighbourhood.

The only possible neighbours are the protons with the signal at approx. 3.4 ppm. Of course, one could also think of nuclei such as ^{19}F or ^{31}P, but they do not appear in the molecular formula.

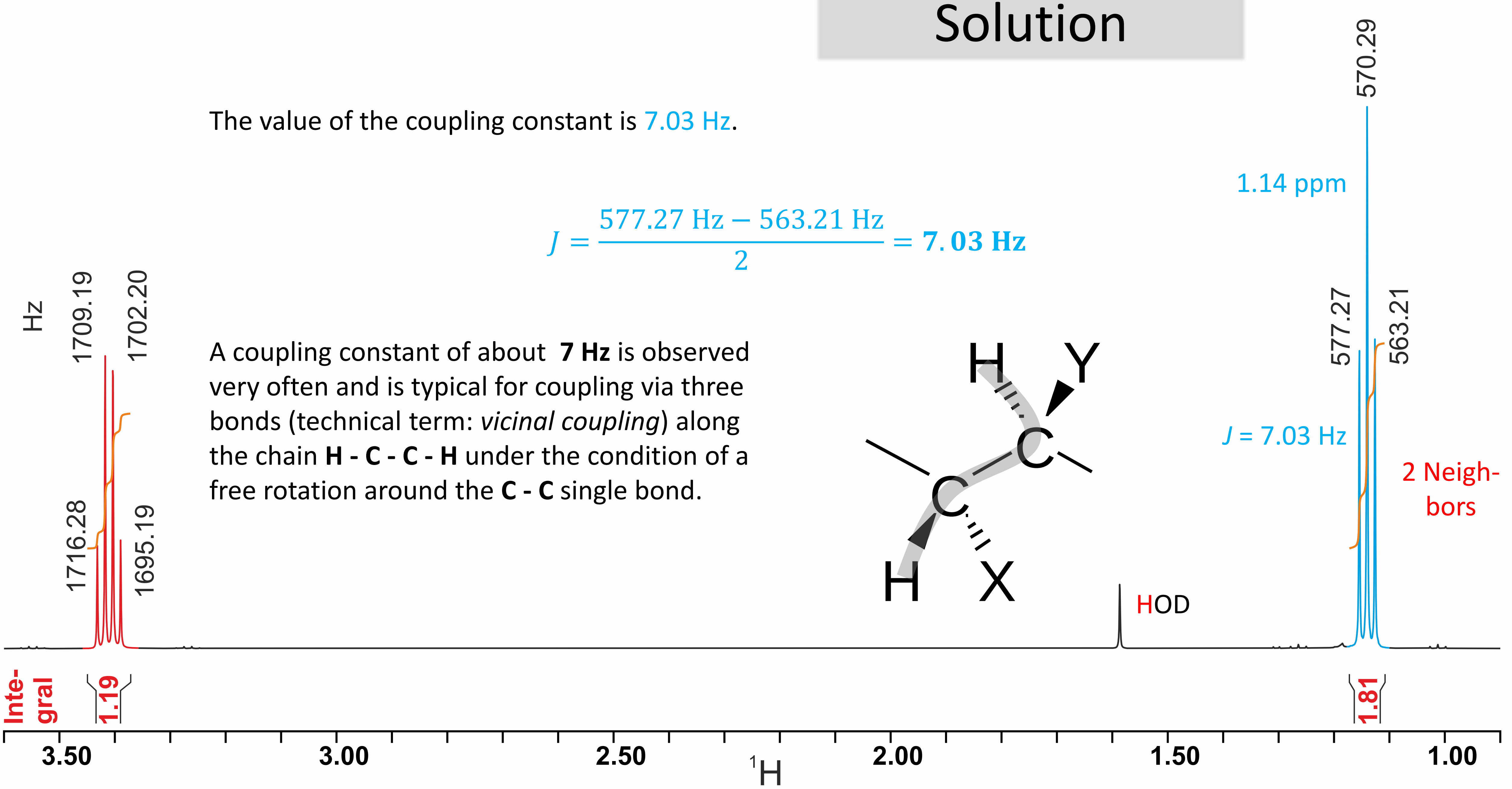


Solution

The value of the coupling constant is 7.03 Hz.

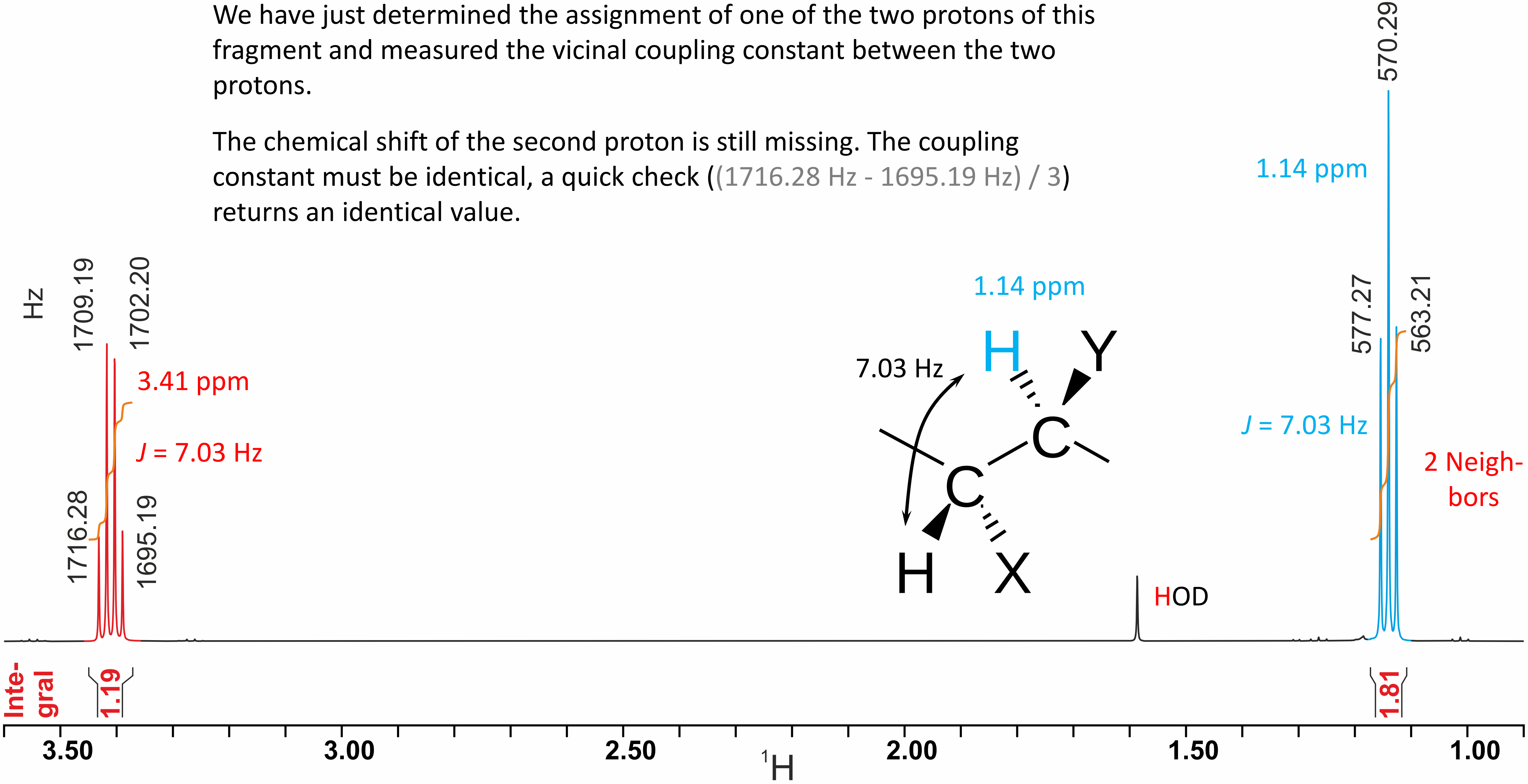
$$J = \frac{577.27\ \text{Hz} - 563.21\ \text{Hz}}{2} = \mathbf{7.03\ Hz}$$

A coupling constant of about **7 Hz** is observed very often and is typical for coupling via three bonds (technical term: *vicinal coupling*) along the chain **H - C - C - H** under the condition of a free rotation around the **C - C** single bond.



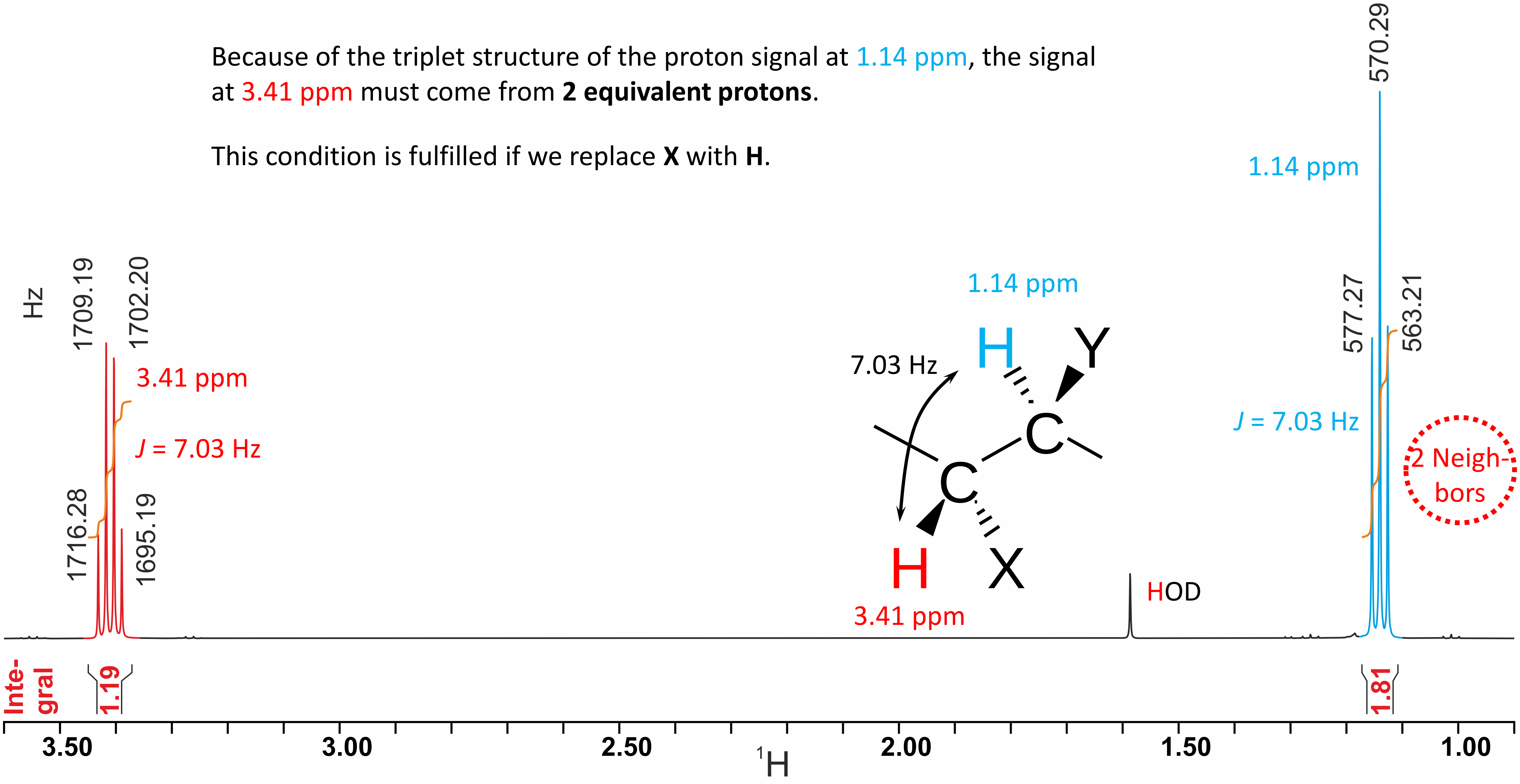
We have just determined the assignment of one of the two protons of this fragment and measured the vicinal coupling constant between the two protons.

The chemical shift of the second proton is still missing. The coupling constant must be identical, a quick check ((1716.28 Hz - 1695.19 Hz) / 3) returns an identical value.



Because of the triplet structure of the proton signal at 1.14 ppm, the signal at 3.41 ppm must come from **2 equivalent protons**.

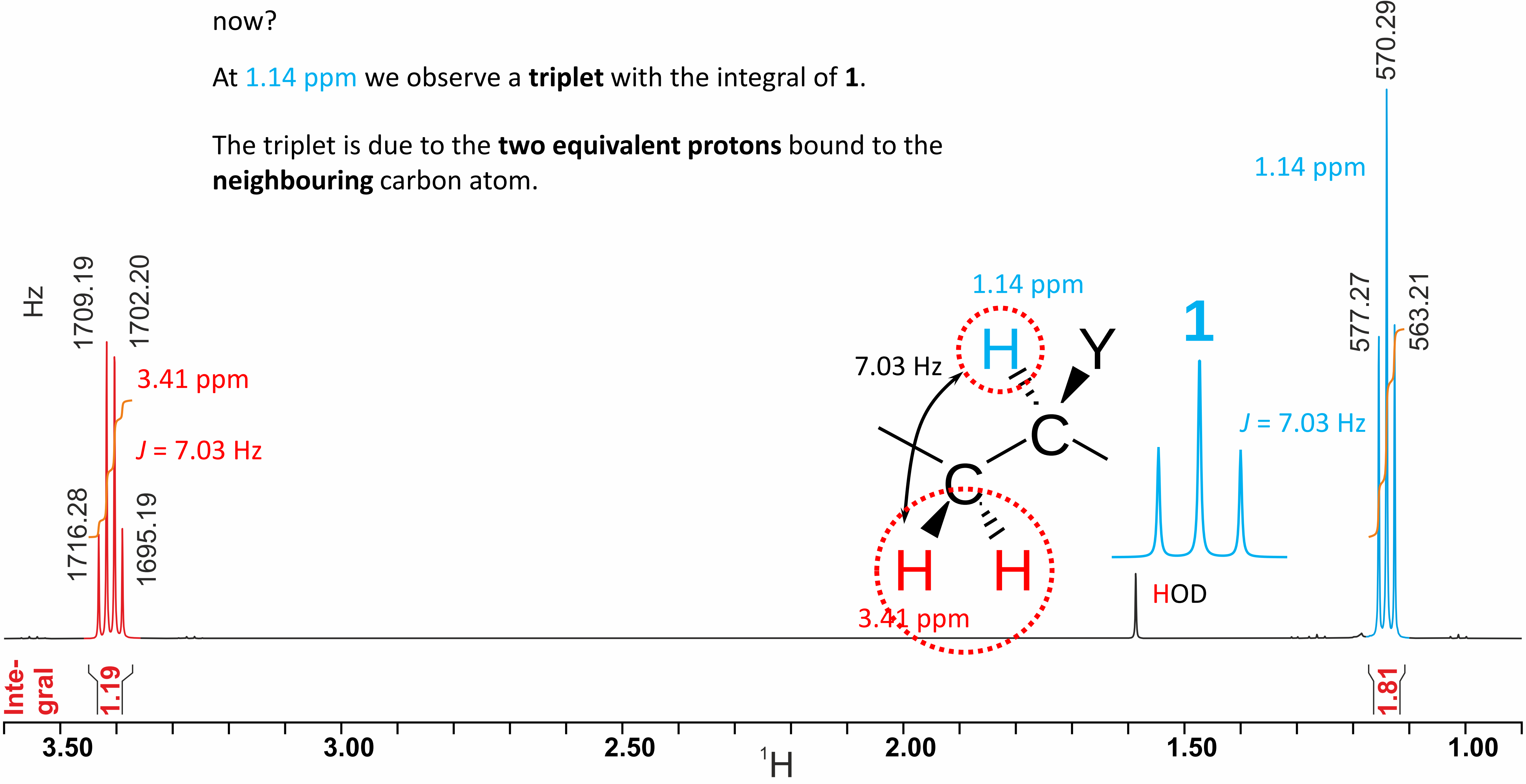
This condition is fulfilled if we replace **X** with **H**.



What does the proton spectrum of this hypothetical molecule look like now?

At 1.14 ppm we observe a **triplet** with the integral of **1**.

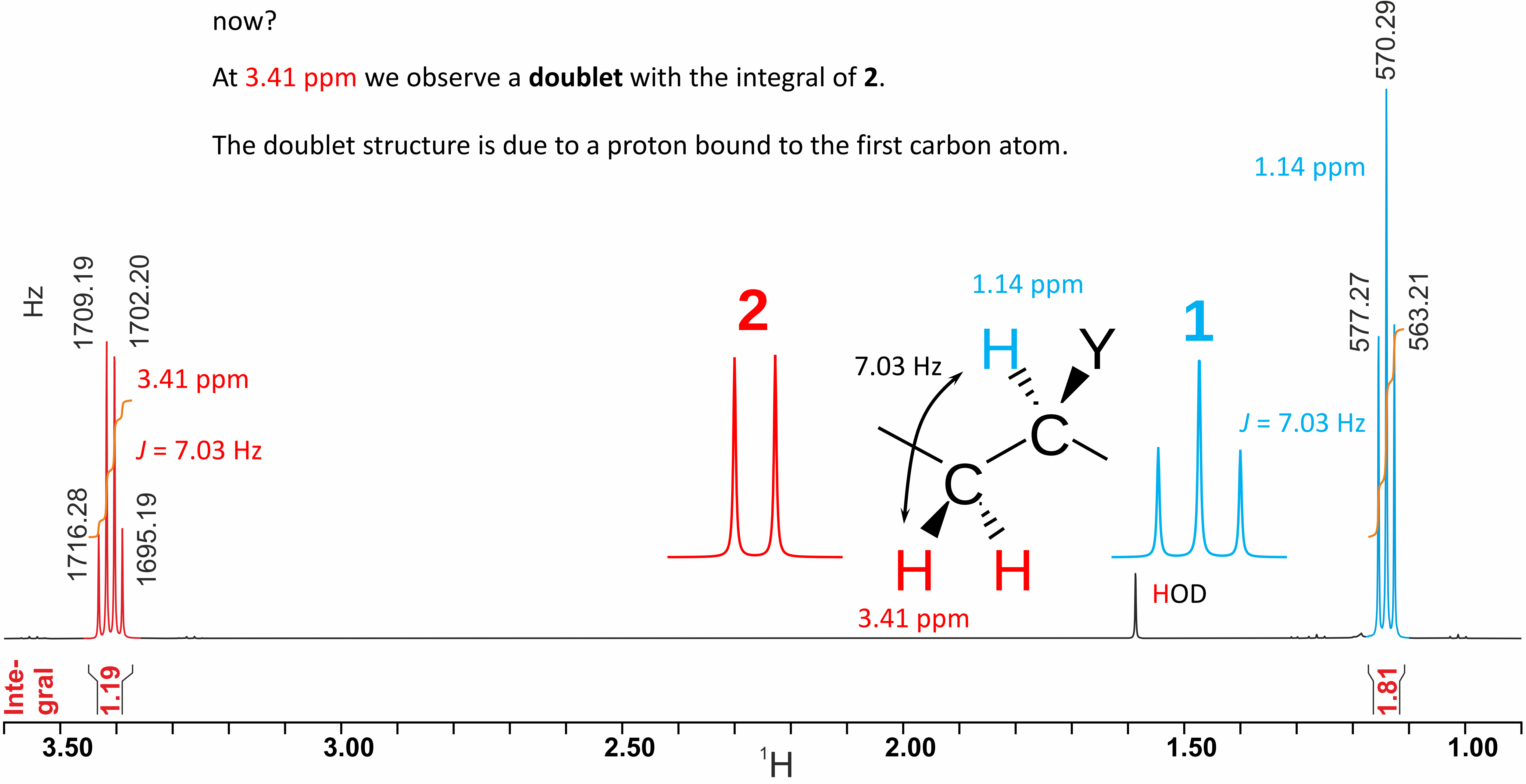
The triplet is due to the **two equivalent protons** bound to the **neighbouring** carbon atom.



What does the proton spectrum of this hypothetical molecule look like now?

At 3.41 ppm we observe a **doublet** with the integral of **2**.

The doublet structure is due to a proton bound to the first carbon atom.

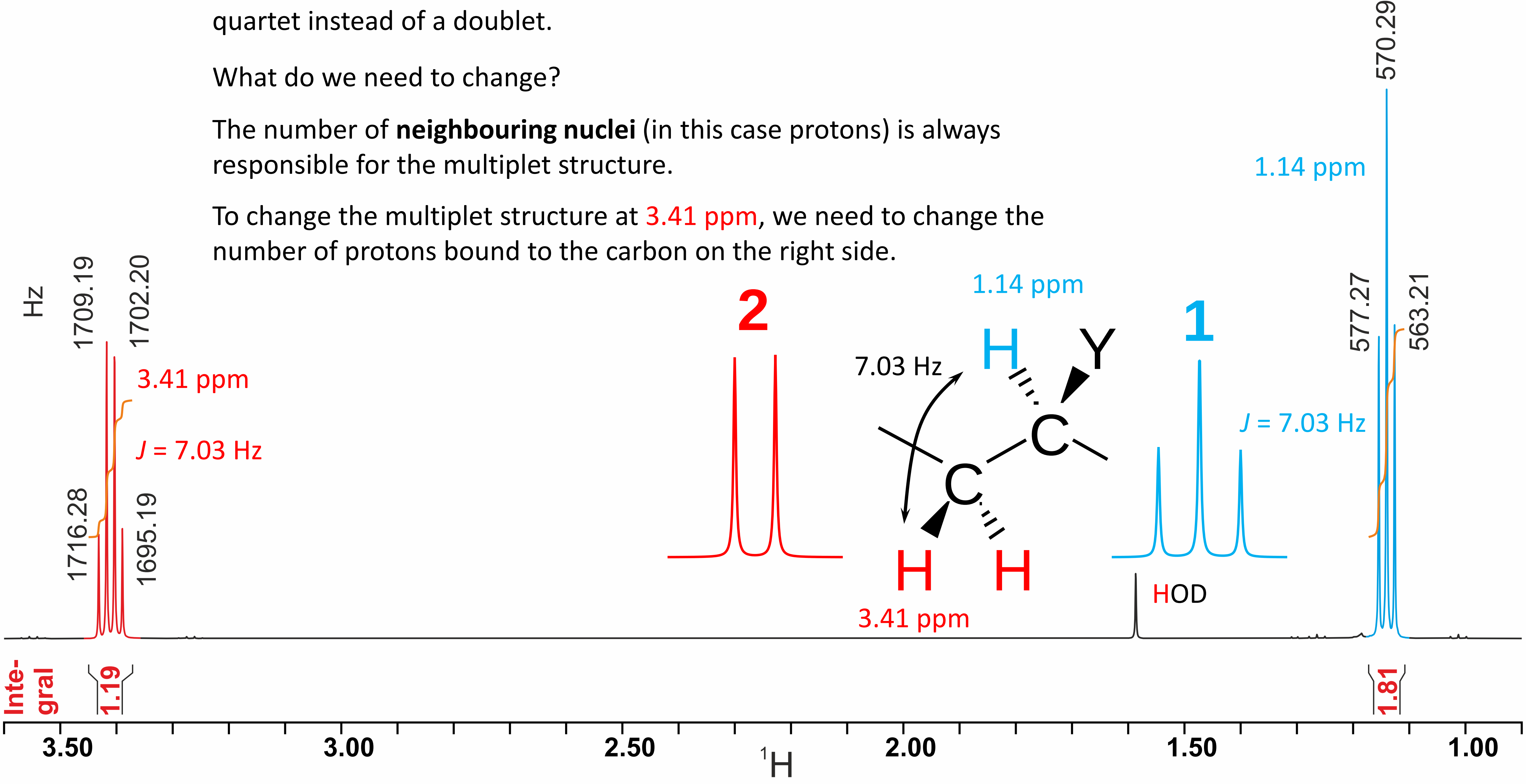


The triplet is fine. But for the multiplet at 3.41 ppm we should have a quartet instead of a doublet.

What do we need to change?

The number of **neighbouring nuclei** (in this case protons) is always responsible for the multiplet structure.

To change the multiplet structure at 3.41 ppm, we need to change the number of protons bound to the carbon on the right side.

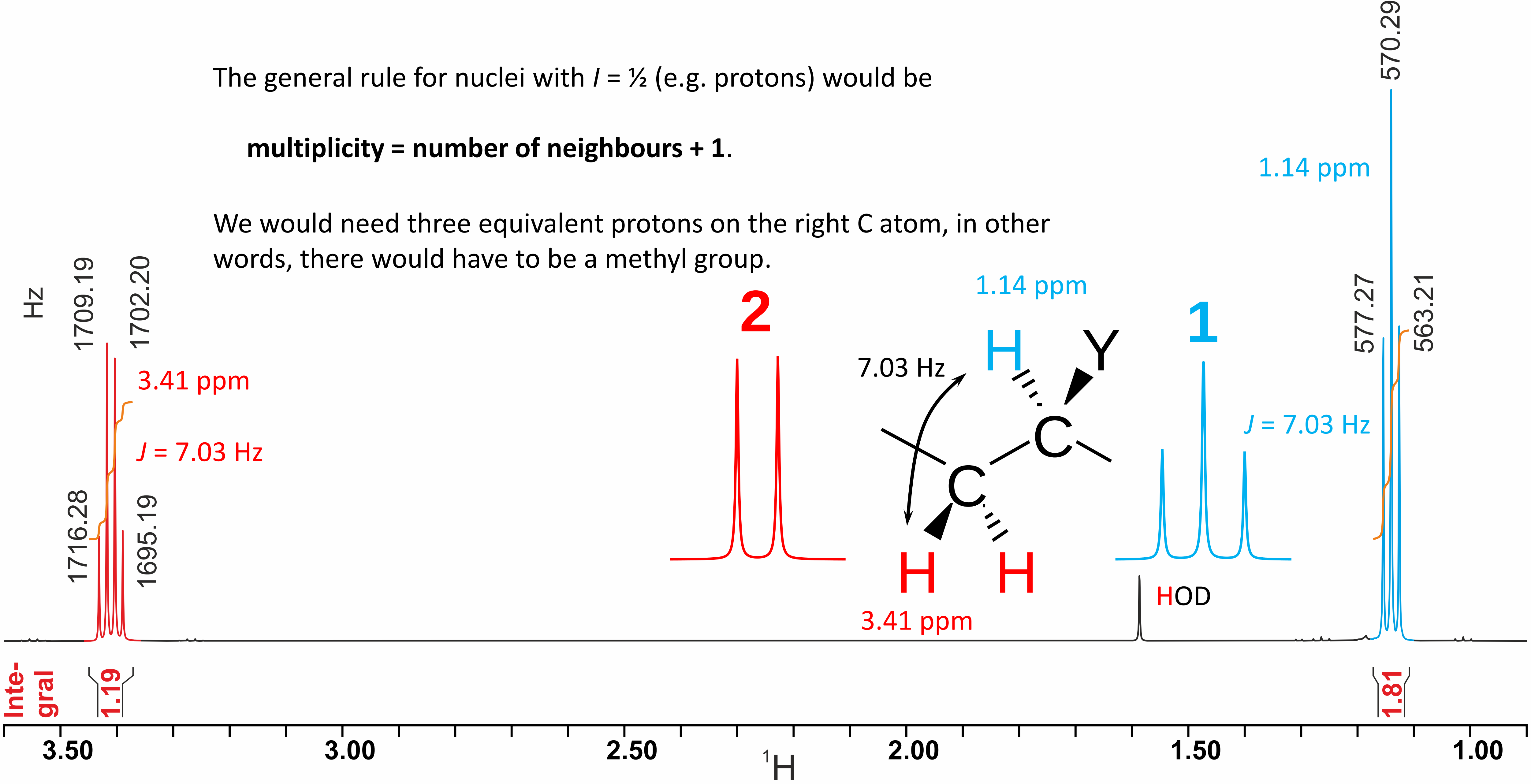


How much protons do we need to get a quartet at 3.41 ppm?

The general rule for nuclei with $I = ½$ (e.g. protons) would be

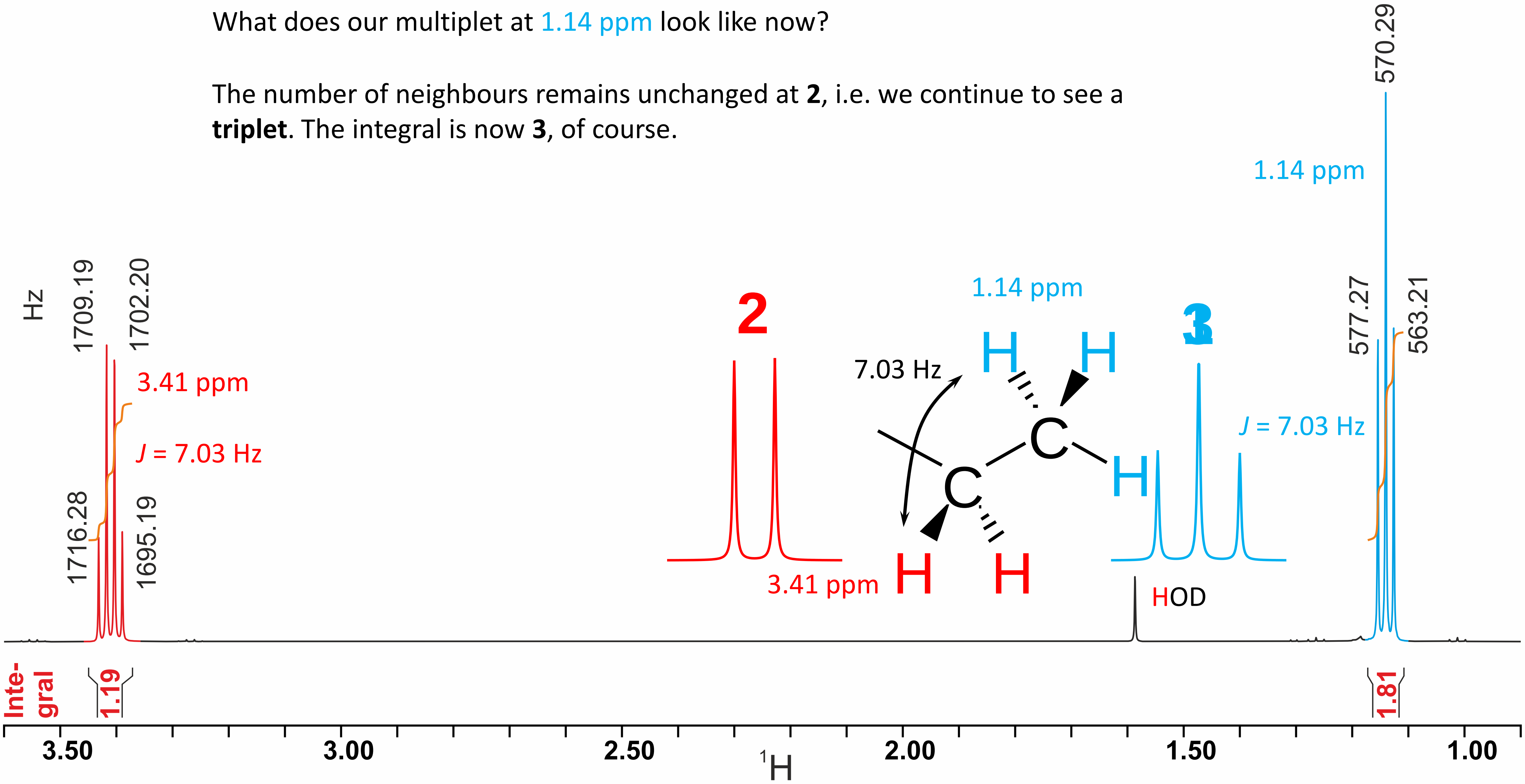
multiplicity = number of neighbours + 1.

We would need three equivalent protons on the right C atom, in other words, there would have to be a methyl group.



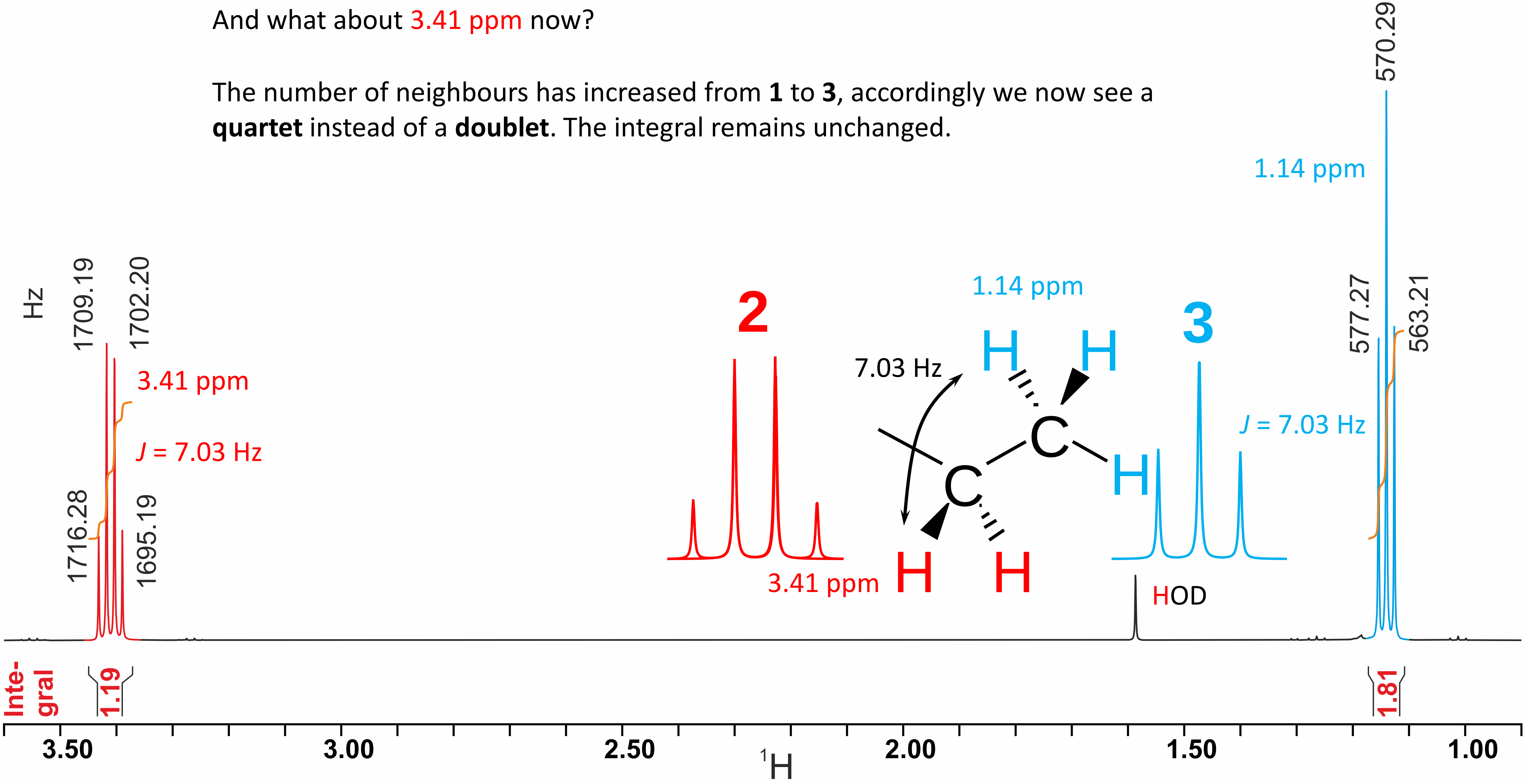
What does our multiplet at 1.14 ppm look like now?

The number of neighbours remains unchanged at **2**, i.e. we continue to see a **triplet**. The integral is now **3**, of course.



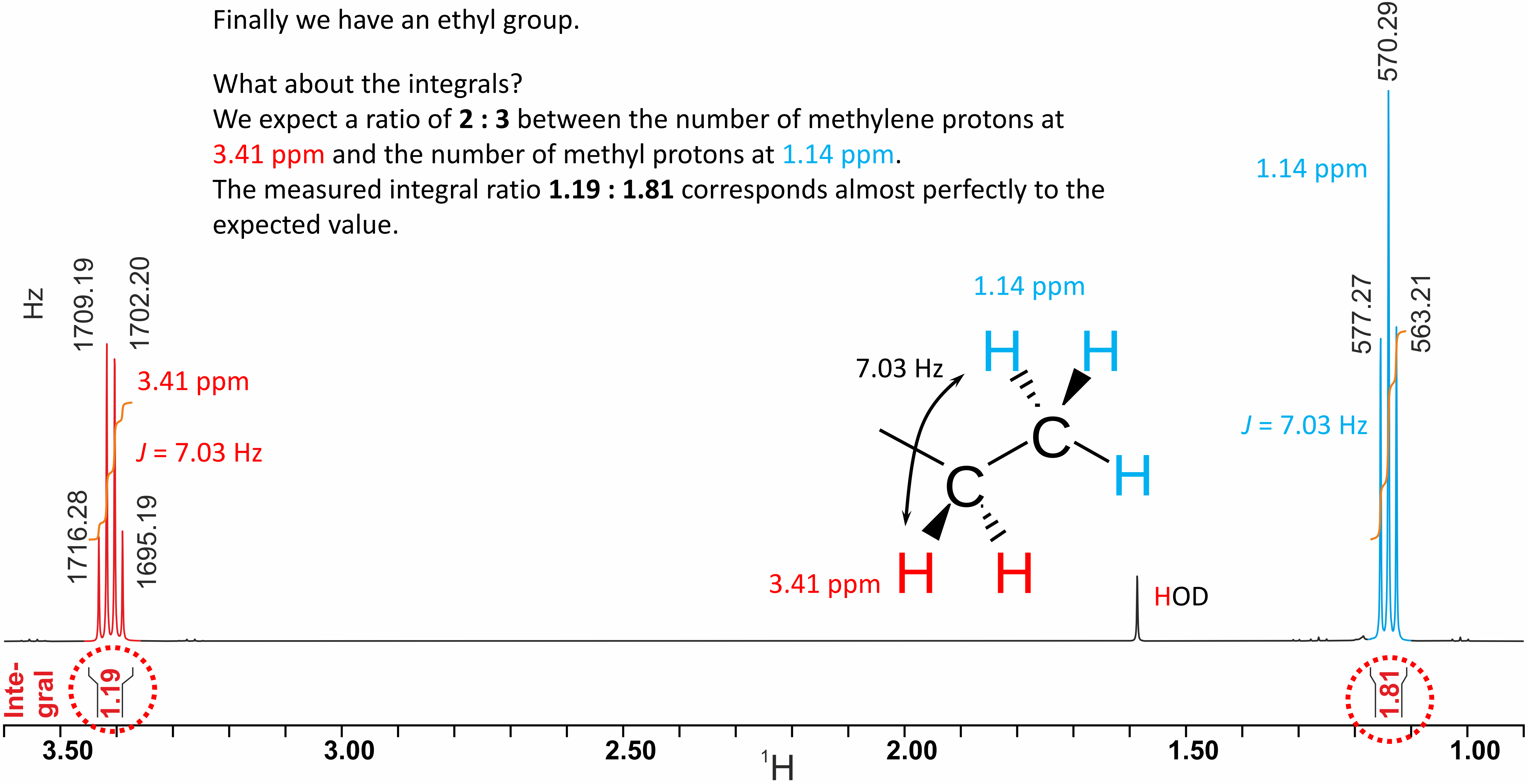
And what about 3.41 ppm now?

The number of neighbours has increased from **1** to **3**, accordingly we now see a **quartet** instead of a **doublet**. The integral remains unchanged.



Finally we have an ethyl group.

What about the integrals?
We expect a ratio of **2 : 3** between the number of methylene protons at 3.41 ppm and the number of methyl protons at 1.14 ppm.
The measured integral ratio **1.19 : 1.81** corresponds almost perfectly to the expected value.



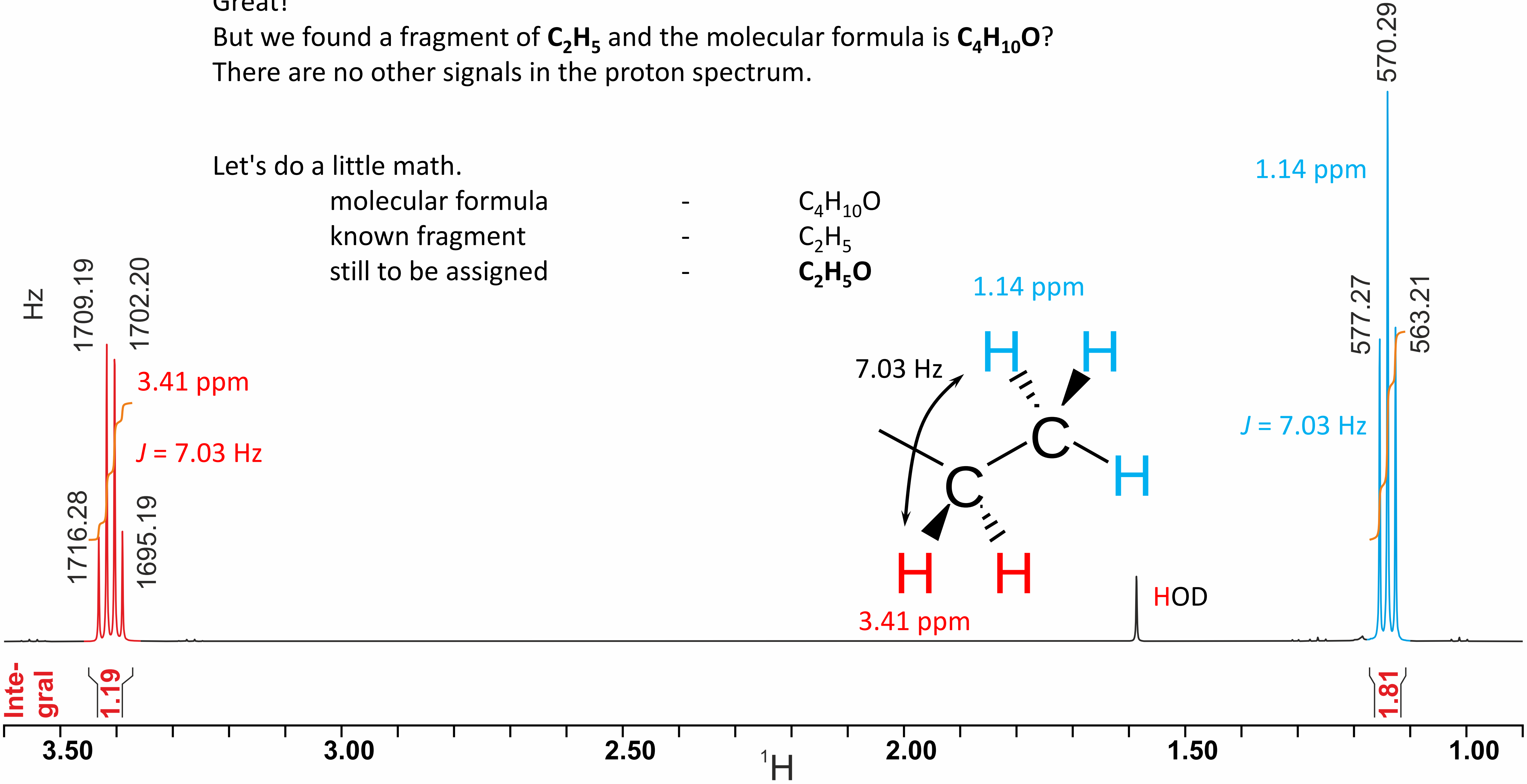
Great!

But we found a fragment of **C_2H_5** and the molecular formula is **$C_4H_{10}O$**?

There are no other signals in the proton spectrum.

Let's do a little math.

molecular formula - $C_4H_{10}O$
known fragment - C_2H_5
still to be assigned - **C_2H_5O**



Let's do a little math.

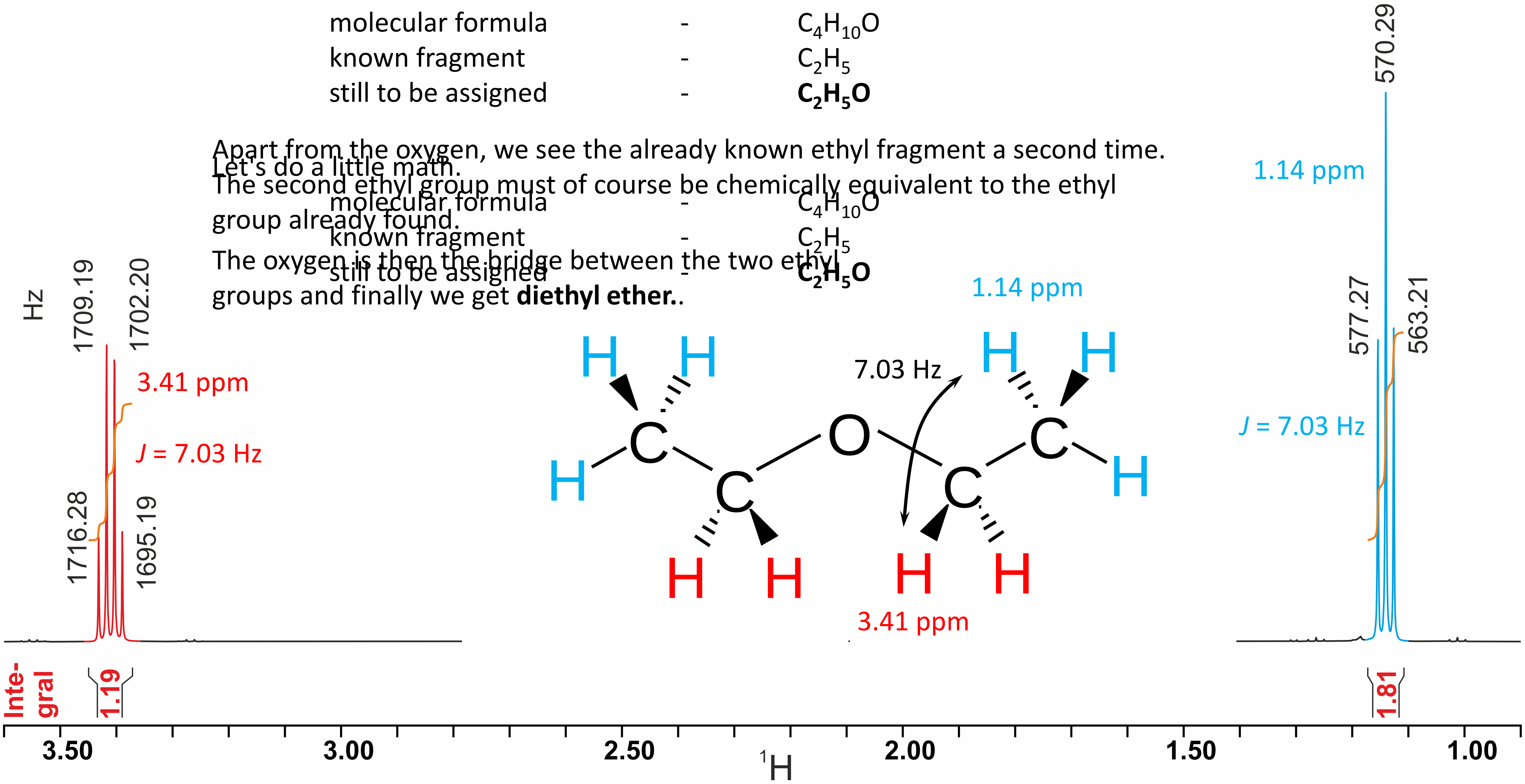
molecular formula - $C_4H_{10}O$
known fragment - C_2H_5
still to be assigned - $\mathbf{C_2H_5O}$

Apart from the oxygen, we see the already known ethyl fragment a second time. The second ethyl group must of course be chemically equivalent to the ethyl group already found.

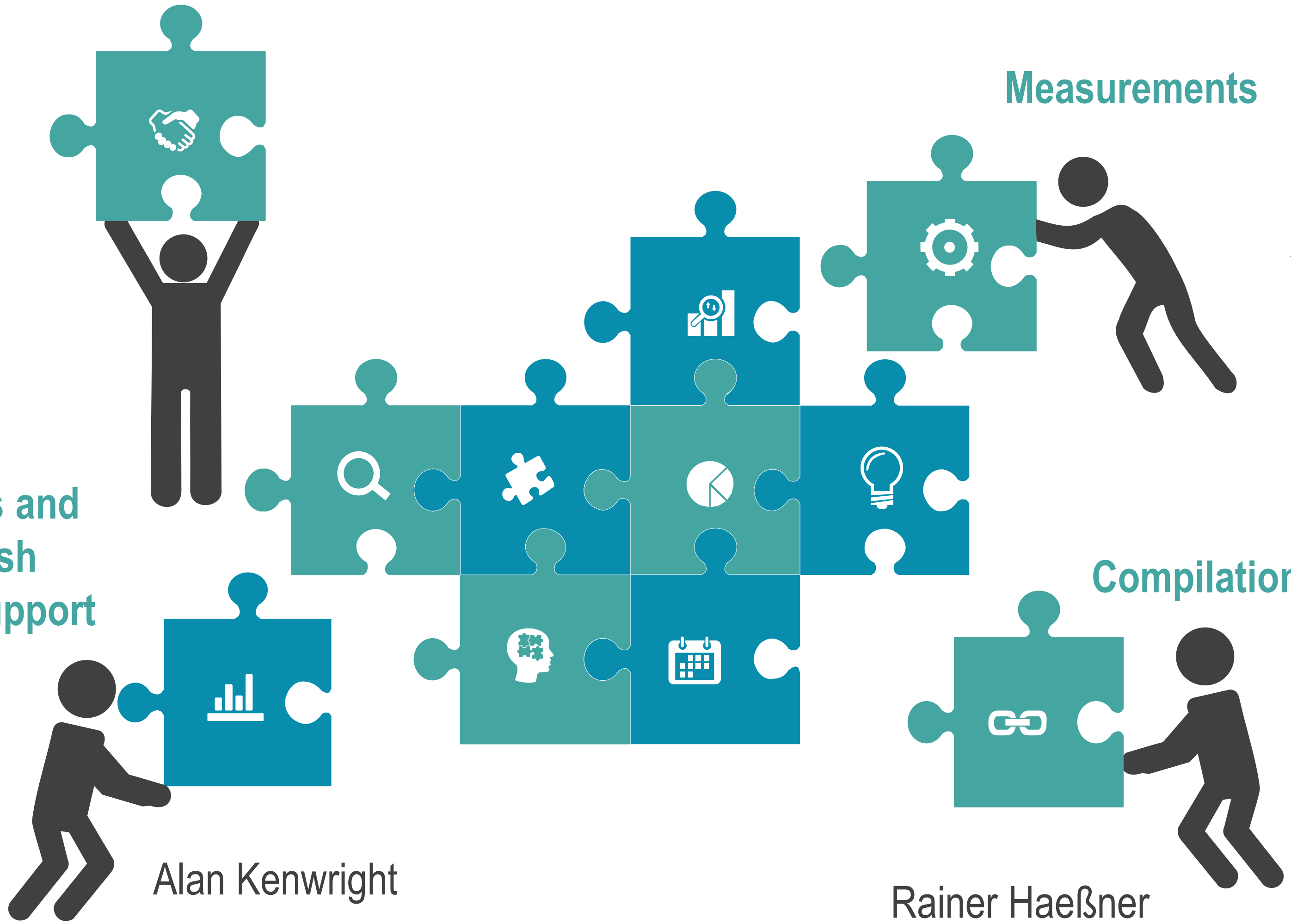
The oxygen is then the bridge between the two ethyl groups and finally we get **diethyl ether.**.

Let's do a little math.

molecular formula - $C_4H_{10}O$
known fragment - C_2H_5
still to be assigned - $\mathbf{C_2H_5O}$



Contributions



Spectrometer time

Humboldt-Universität
zu Berlin

Measurements

André Dallmann

Discussions and native English language support

Alan Kenwright

Compilation

Rainer Haeßner

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