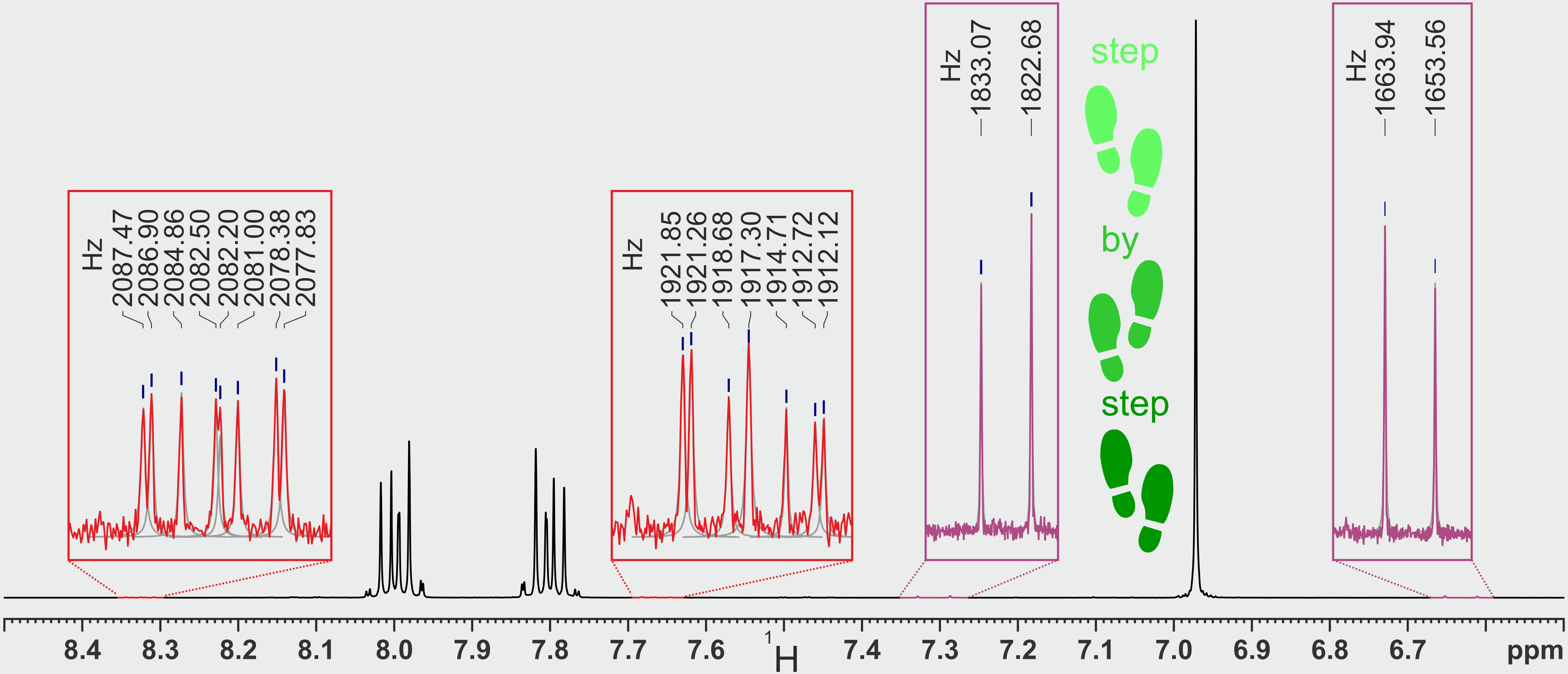
Übung plus Lösung – PDF-Schnellüberblick

Diese PDF-Version soll nur dem schnellen Überblick über die Fragestellung dienen. Sämtliche PowerPoint-Animationen fehlen, in einigen Fällen könnte die Umsetzung von PowerPoint auf PDF merkwürdig aussehen.
Die qualitativ hochwertigen PowerPoint-Originale stehen jederzeit zum freien Download zur Verfügung.



Herausforderung des Monats

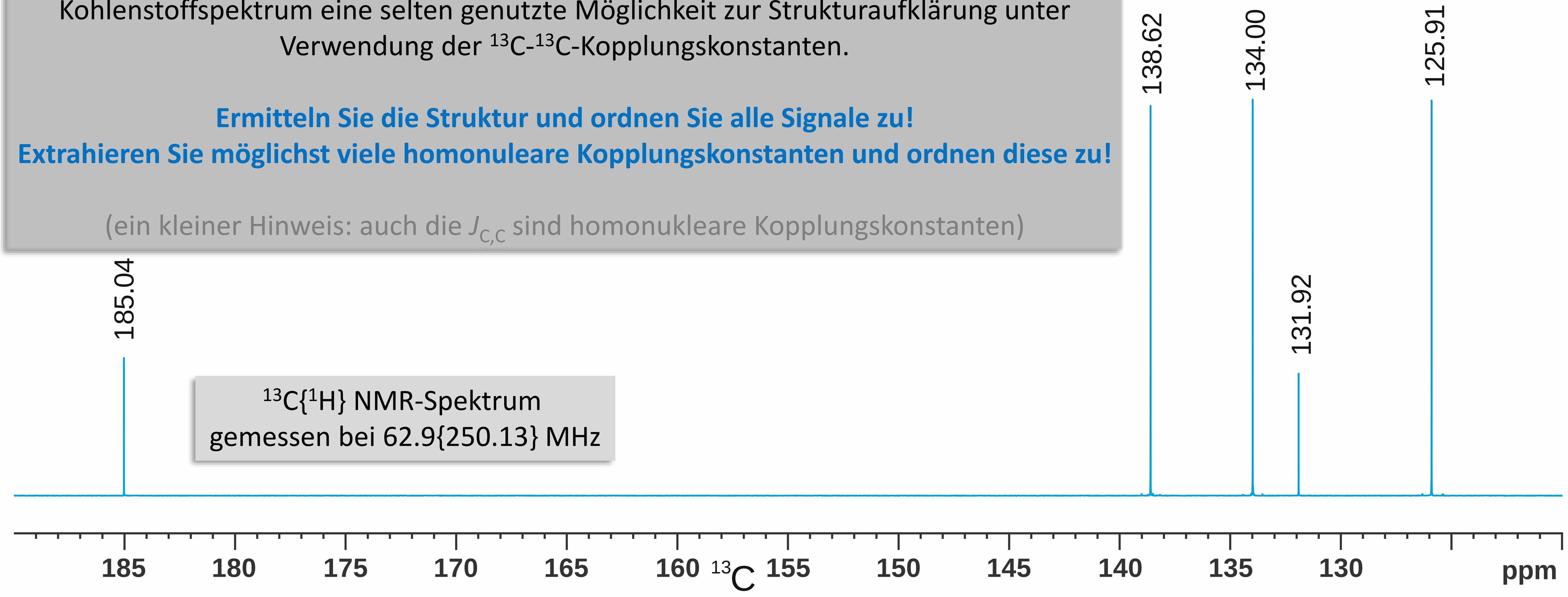
August 2021

$C_{10}H_6O_2$ in CD_3CN

Zur Ermittlung der Struktur dieser Verbindung ist nicht einmal eine Datenbank nötig. Die Eingabe der Summenformel in jede gängige Suchmaschine würde ausreichen.
In diesem speziellen Fall bietet jedoch das ausgezeichnete Signal-Rausch-Verhältnis im Kohlenstoffspektrum eine selten genutzte Möglichkeit zur Strukturaufklärung unter Verwendung der ^{13}C-^{13}C-Kopplungskonstanten.

Ermitteln Sie die Struktur und ordnen Sie alle Signale zu!
Extrahieren Sie möglichst viele homonuleare Kopplungskonstanten und ordnen diese zu!

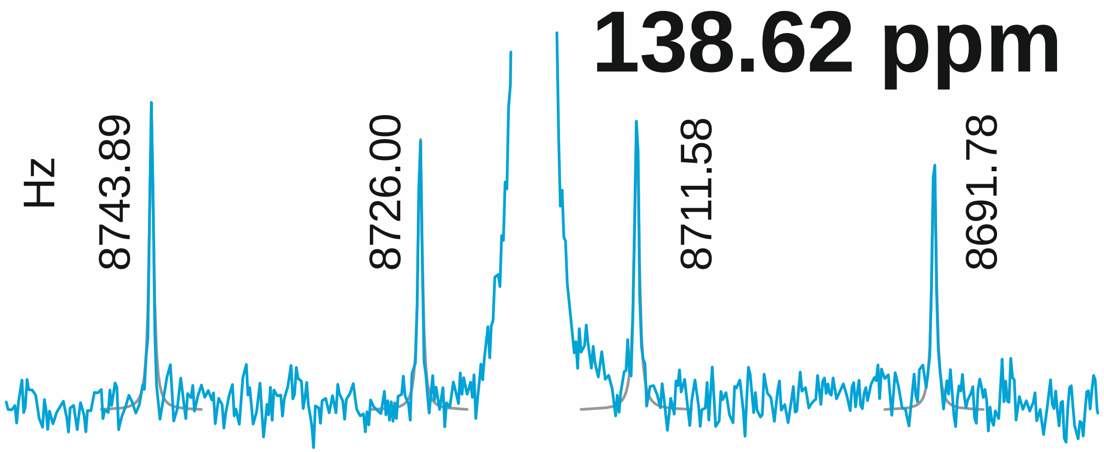
(ein kleiner Hinweis: auch die $J_{C,C}$ sind homonukleare Kopplungskonstanten)

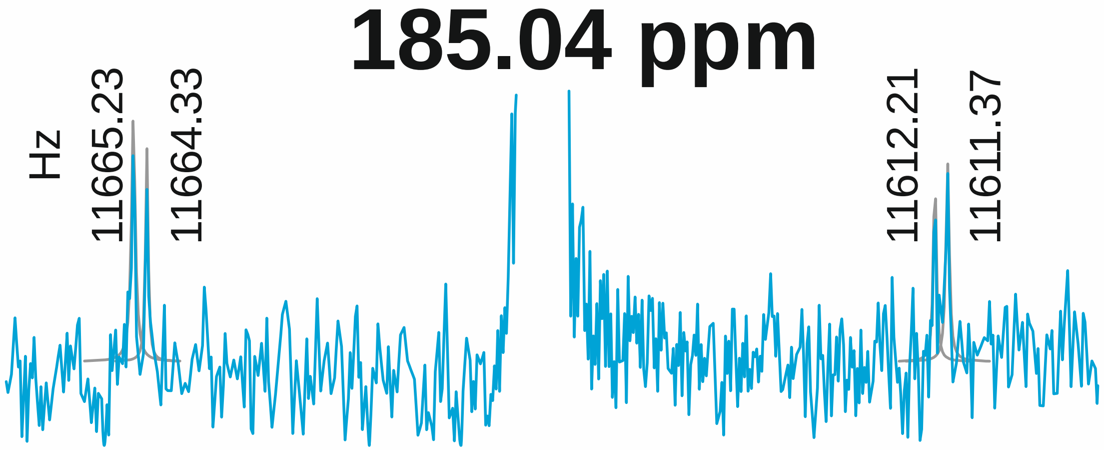


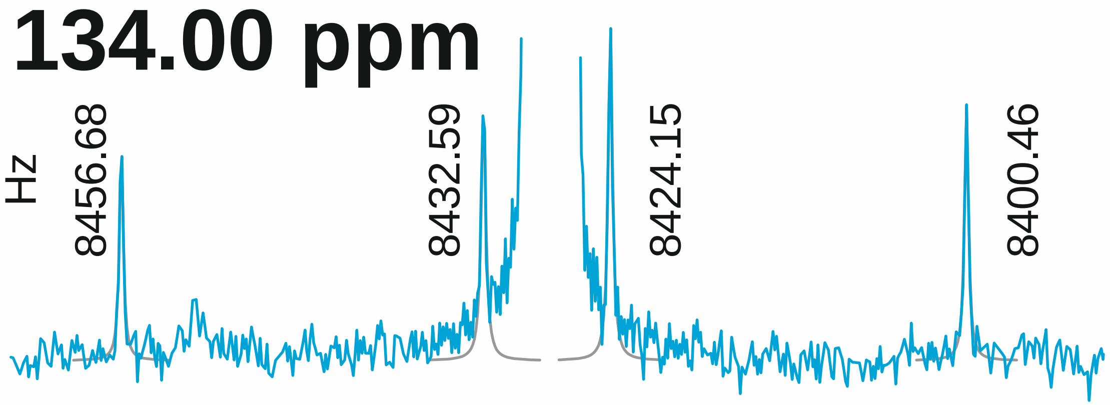
$^{13}C\{^1H\}$ NMR-Spektrum
gemessen bei 62.9{250.13} MHz

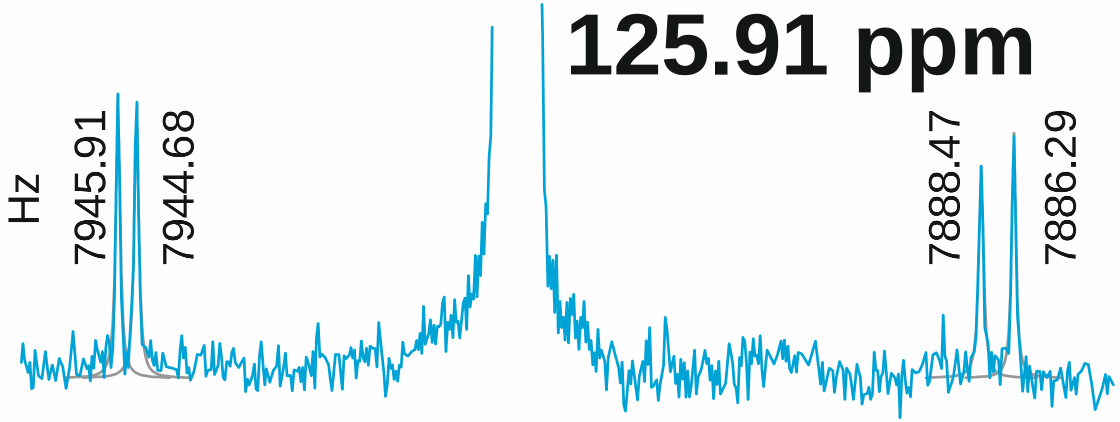
Starke Vergrößerung der 5 Kohlenstoffsignale

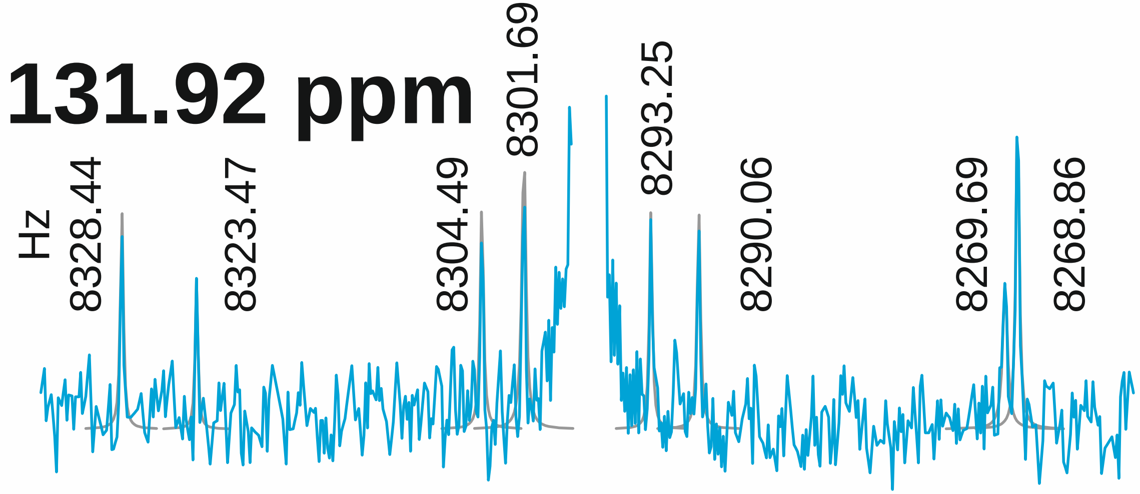
$^{13}C\{^1H\}$ NMR-Spektrum
gemessen bei 62.9{250.13} MHz





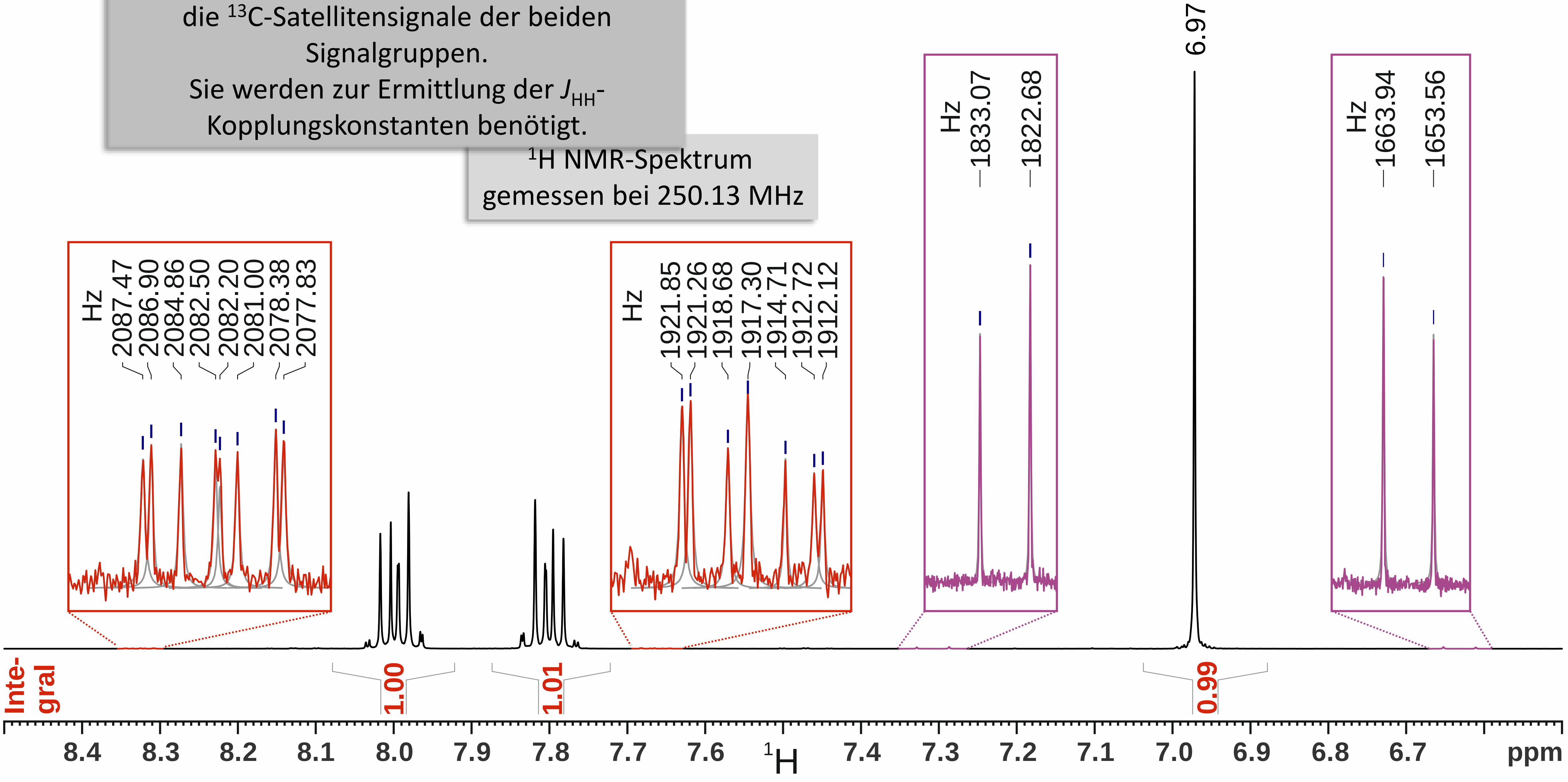


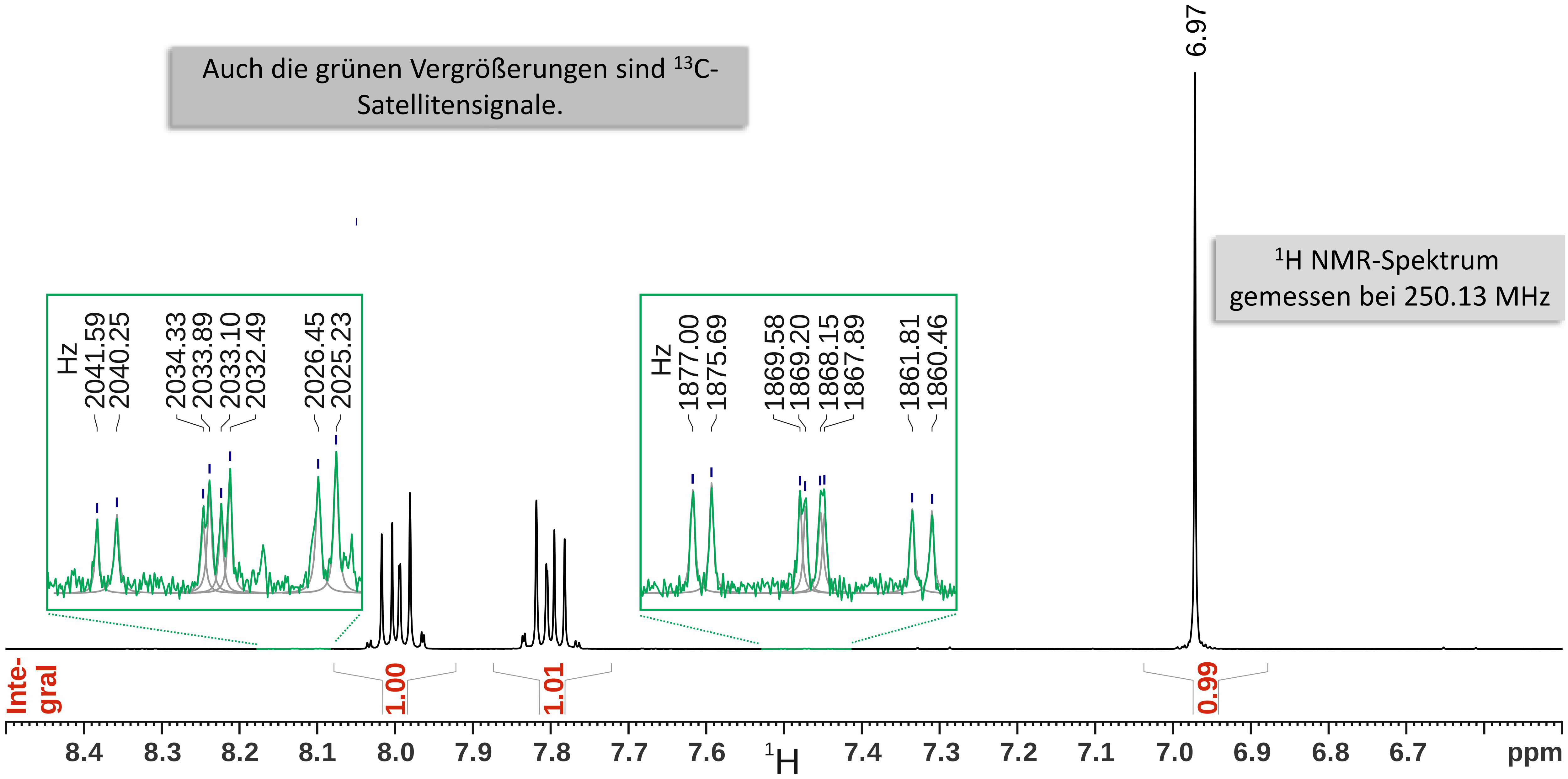




Die roten und violetten Vergrößerungen sind die ^{13}C-Satellitensignale der beiden Signalgruppen.
Sie werden zur Ermittlung der J_{HH}-Kopplungskonstanten benötigt.

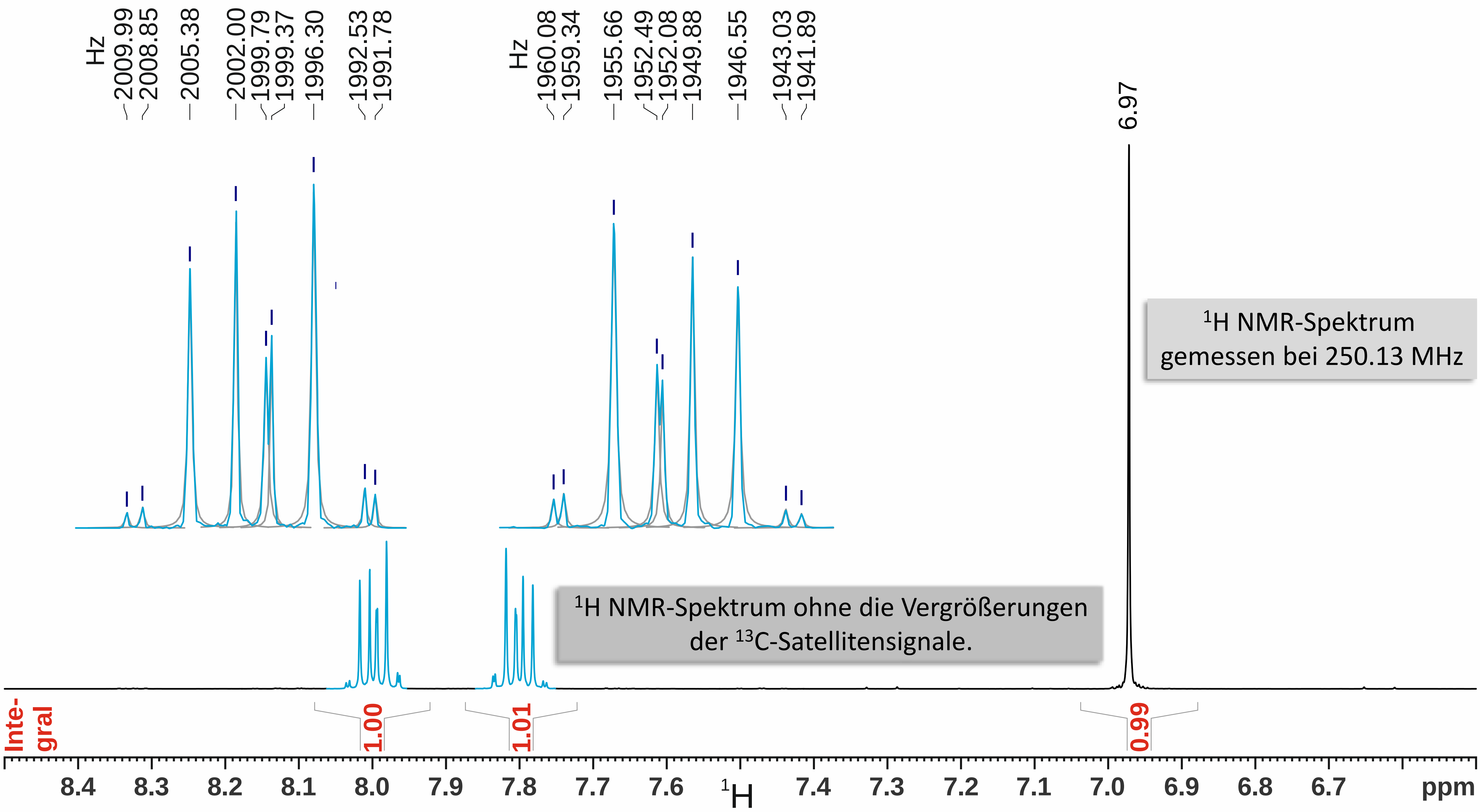
^{1}H NMR-Spektrum
gemessen bei 250.13 MHz





Auch die grünen Vergrößerungen sind ^{13}C-Satellitensignale.

^{1}H NMR-Spektrum gemessen bei 250.13 MHz

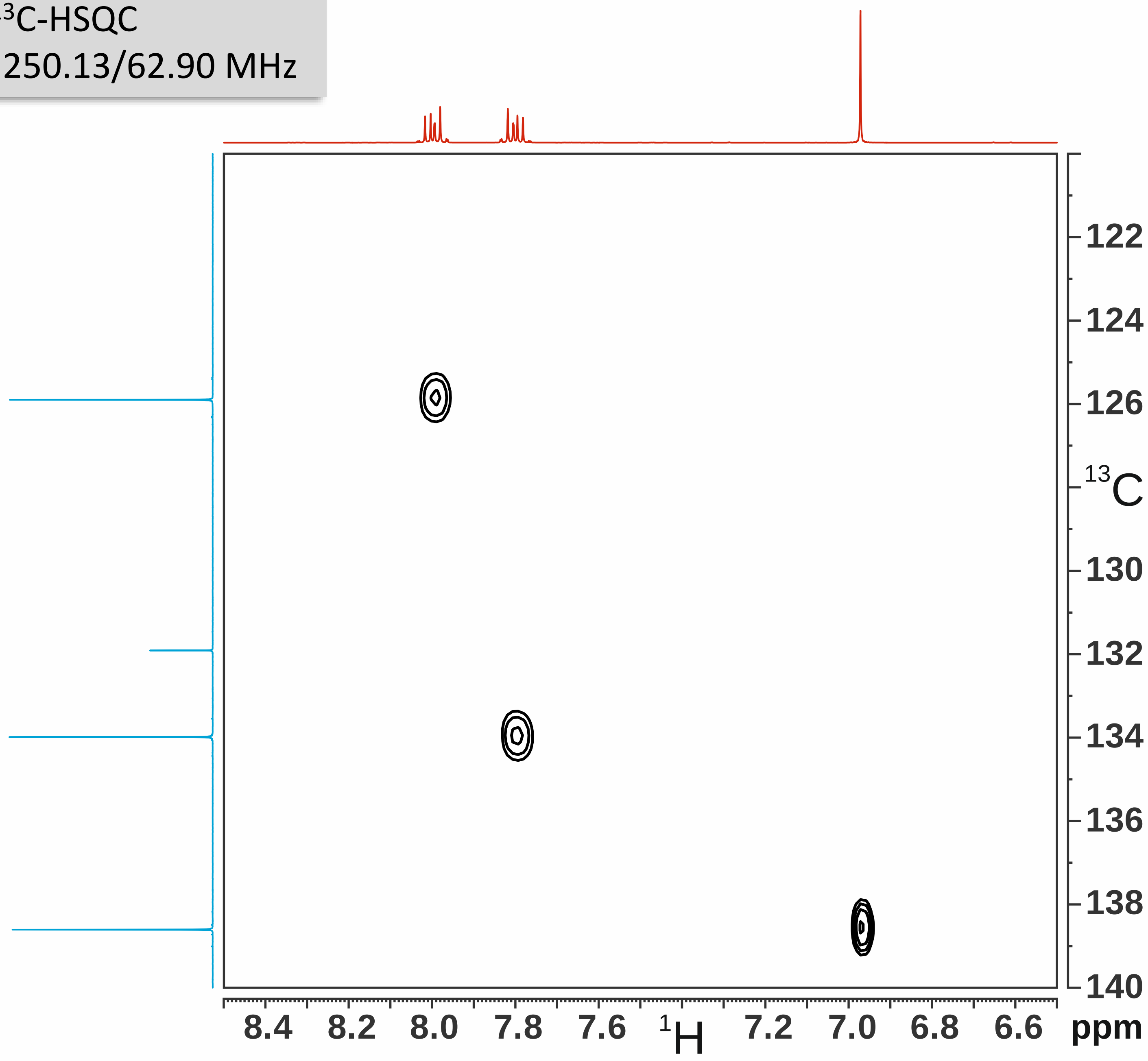


^{1}H NMR-Spektrum
gemessen bei 250.13 MHz

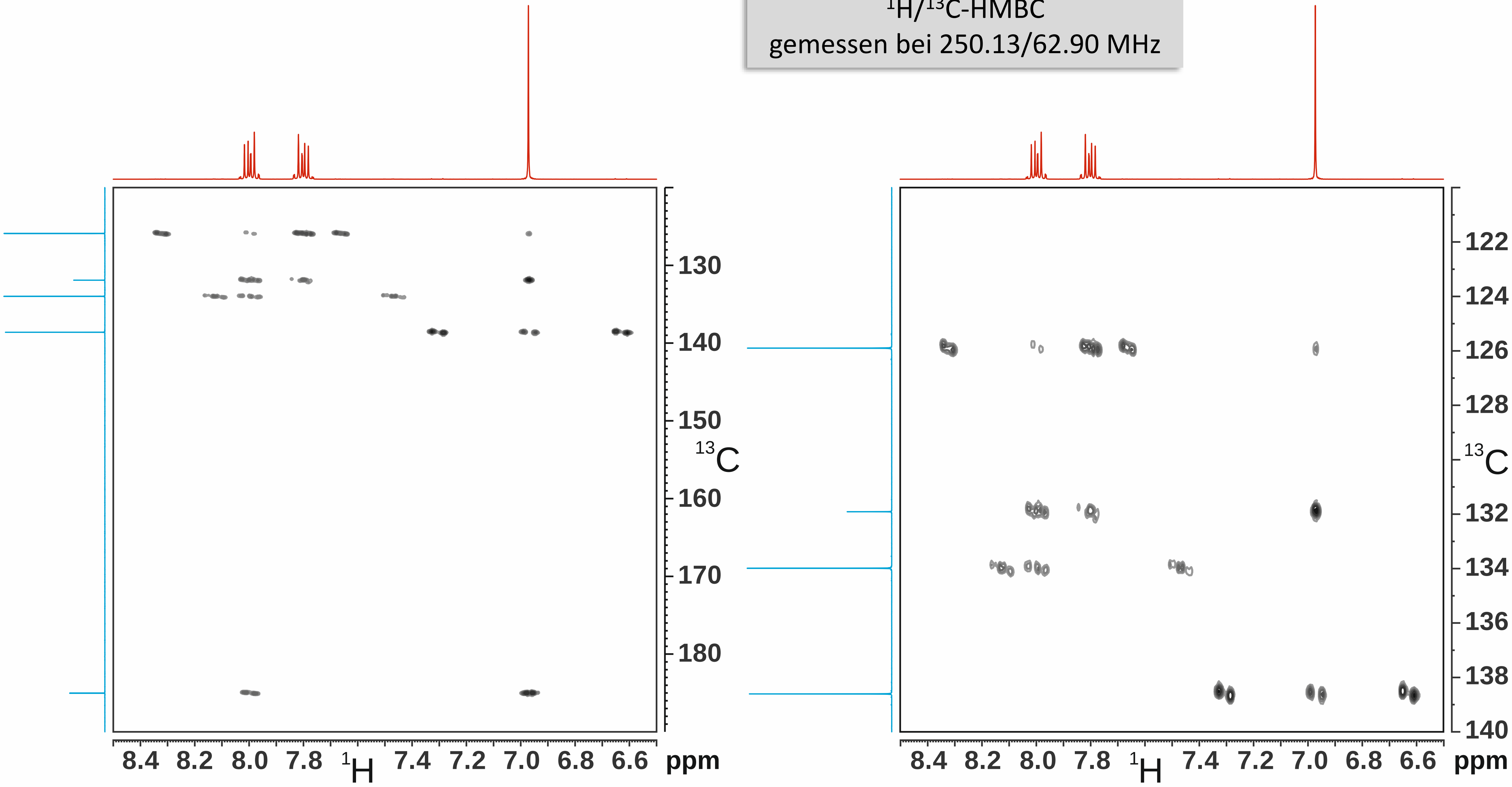
^{1}H NMR-Spektrum ohne die Vergrößerungen
der ^{13}C-Satellitensignale.

$^1H/^{13}C$-HSQC
gemessen bei 250.13/62.90 MHz

Zur Lösung dieser Aufgabe ist das HMBC auf der nächsten Seite nicht unbedingt erforderlich. Das HMBC bietet einen unabhängigen Weg, die gefundene Lösung zu überprüfen.



$^{1}H/^{13}C$-HMBC
gemessen bei 250.13/62.90 MHz



Basic considerations

Double bond equivalents,
symmetry

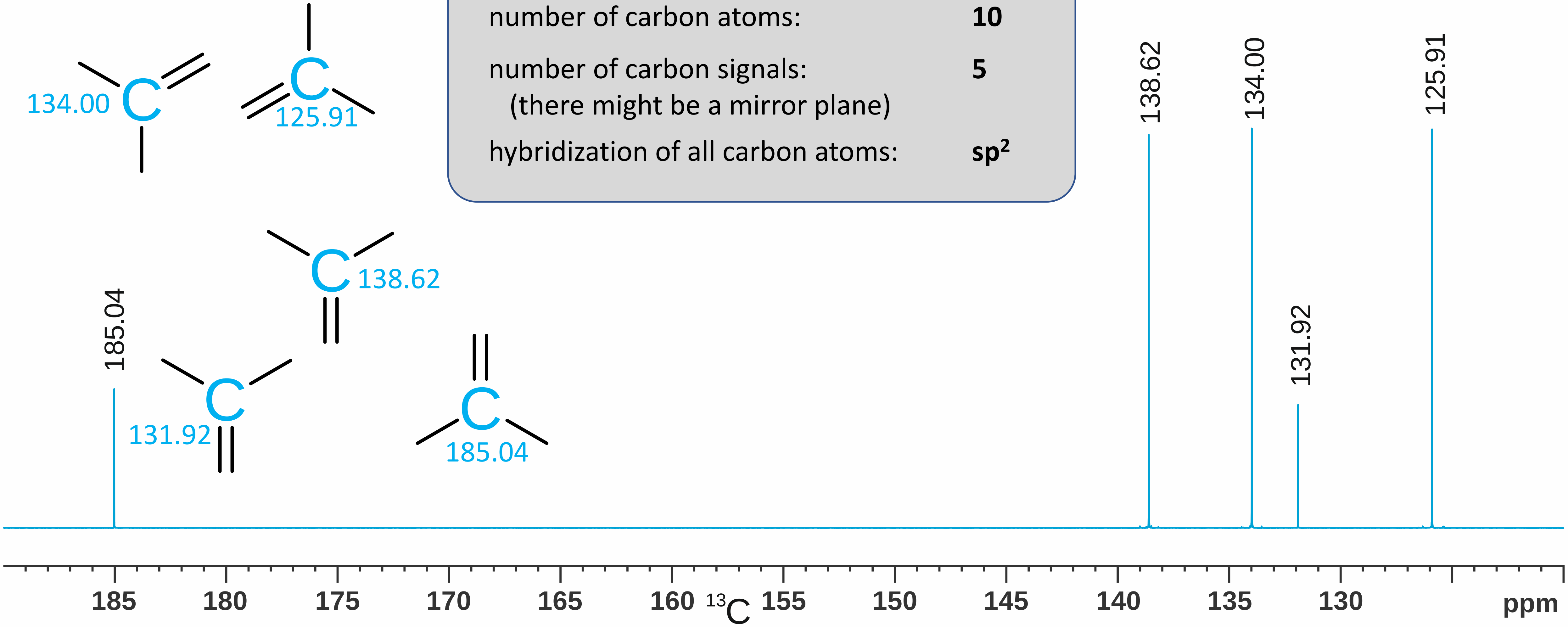
$C_{10}H_6O_2$

double bond equivalents: **8 (!)**

number of carbon atoms: **10**

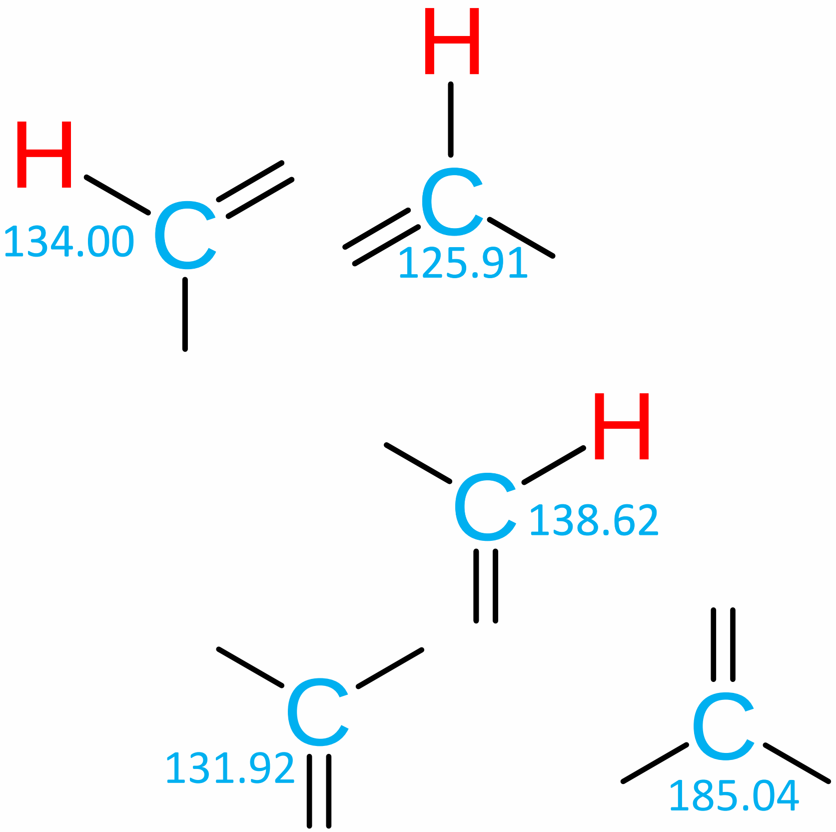
number of carbon signals: **5**
(there might be a mirror plane)

hybridization of all carbon atoms: **sp^2**

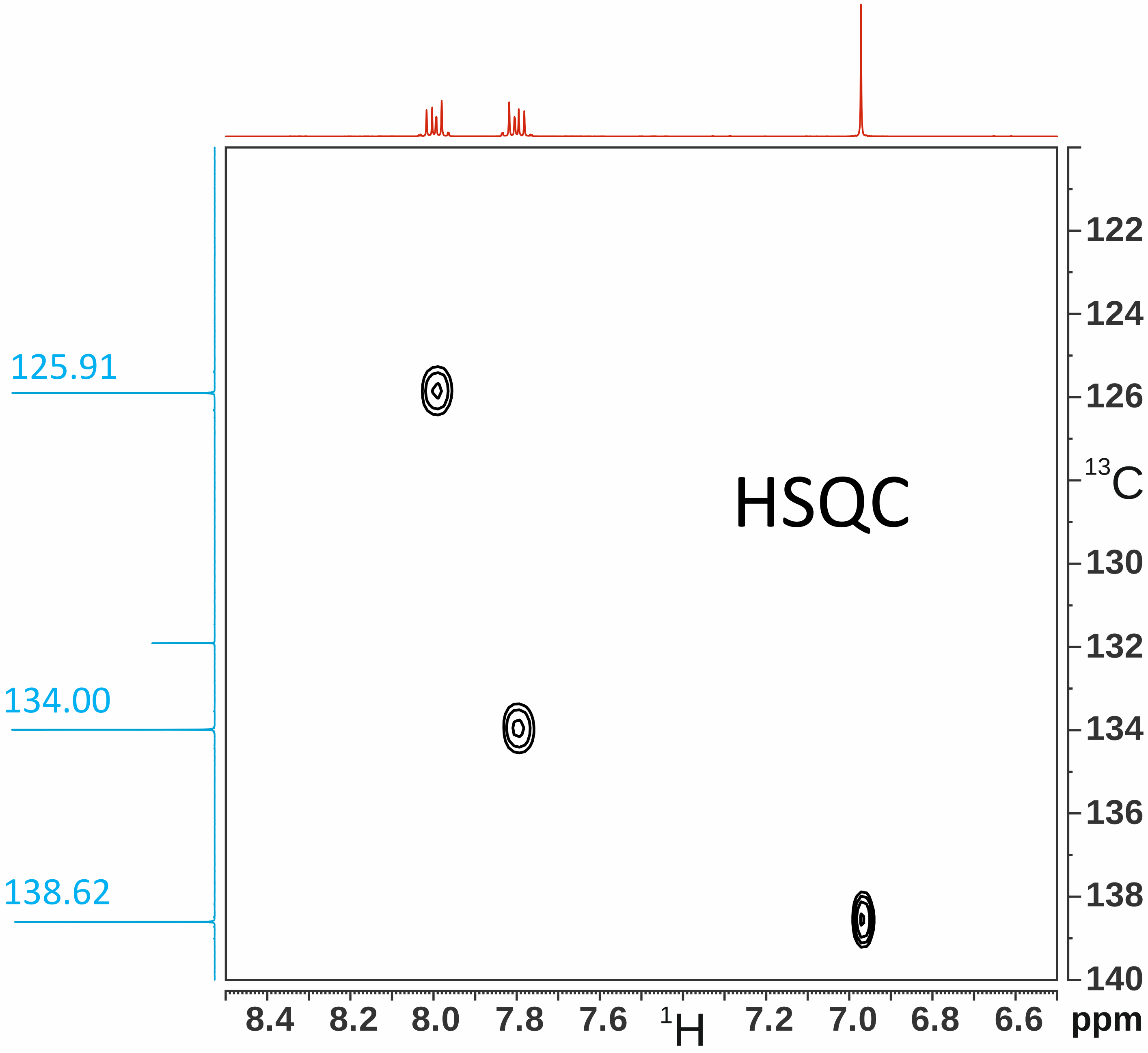


Some more details

Double bond equivalents,
symmetry

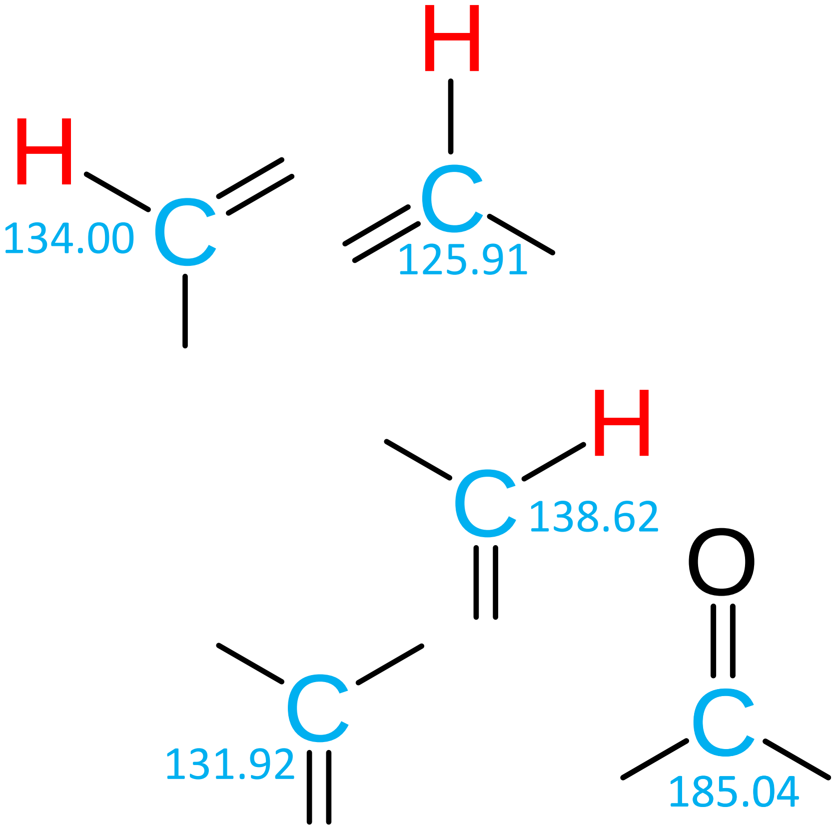


According to the HSQC three of the carbon atoms have to be =CH$_n$ groups. For the moment we don‘t deal with the number of attached protons.



Some more details

Double bond equivalents, symmetry



With a very high amount of probability, we have **n = 1**, which means **=CH-** and no **=CH_2**.

Why?

If we summarize all atoms found so far, we have exactly half the number of carbon atoms and protons (assuming **n = 1**) in the molecular formula. A mirror plane would double both the number of carbon atoms and protons.

But what about the carbon with the chemical shift of 185.04 ppm?

We have

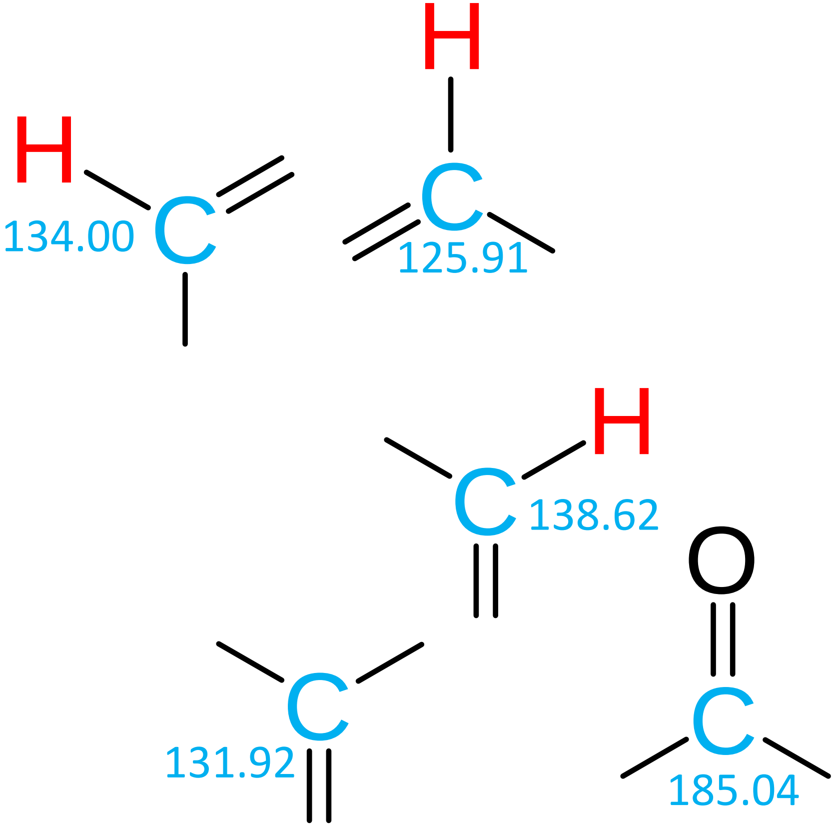
- the very low field chemical shift
- the hight number of double bond equivalents and
- the oxygen from the molecular formula

and we can deduce a **carbonyl group**.

If we now count all of the atoms at the left side of this slide, we have exactly half of the molecular formula.

Carbon-carbon couplings

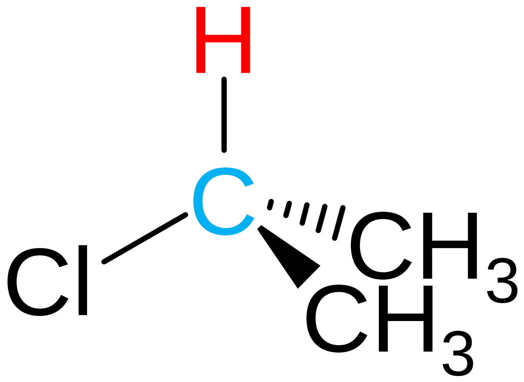
Probability and spectra



Because of the excellent signal-to-noise-ratio in the one dimensional carbon spectrum, we might think about using one bond carbon-carbon coupling constants to get the backbone of this molecule.

But first let us try to understand some basics.

As you know, in 2-chloro-propane you see a septet for the proton attached to C-2. But what about the carbon-carbon coupling pattern for C-2? Is it a triplet due to the chemical equivalence of carbon atoms C-1 and C-3? (No! Why?)



Let us simulate some carbon spectra using a backbone similar to 2-chloro-propane.

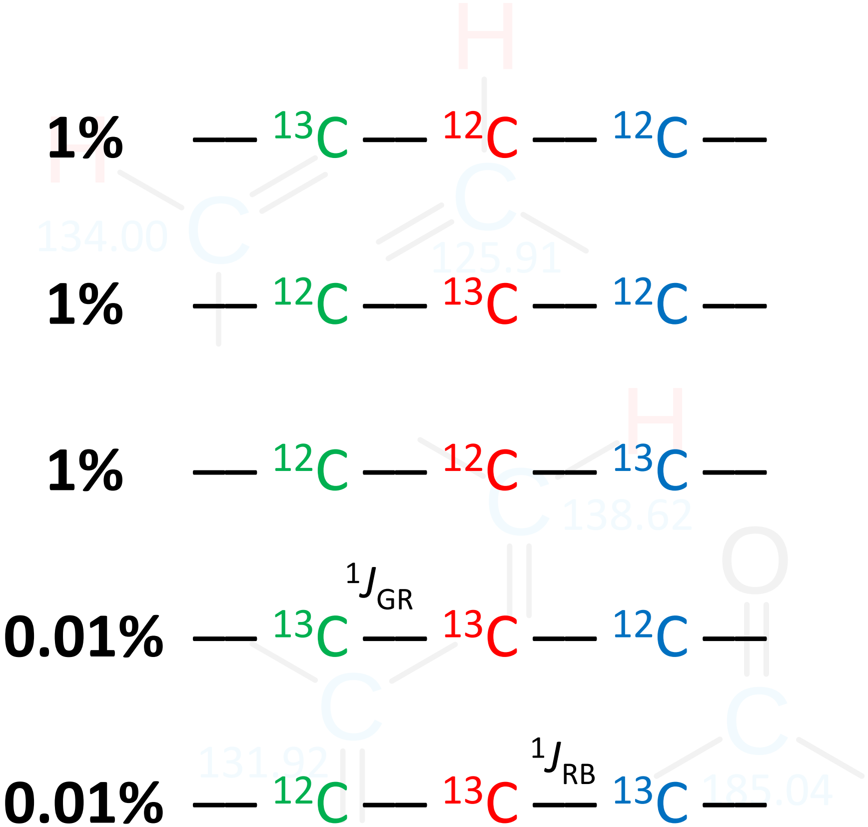
Carbon-carbon couplings

Probability and spectra

We should remember, that **every** NMR spectrum is **not** the result of **one molecule**, but of a huge ensemble of molecules.

Let‘s simulate the carbon spectrum of the single (asymmetric) model compound

— C — C — C —



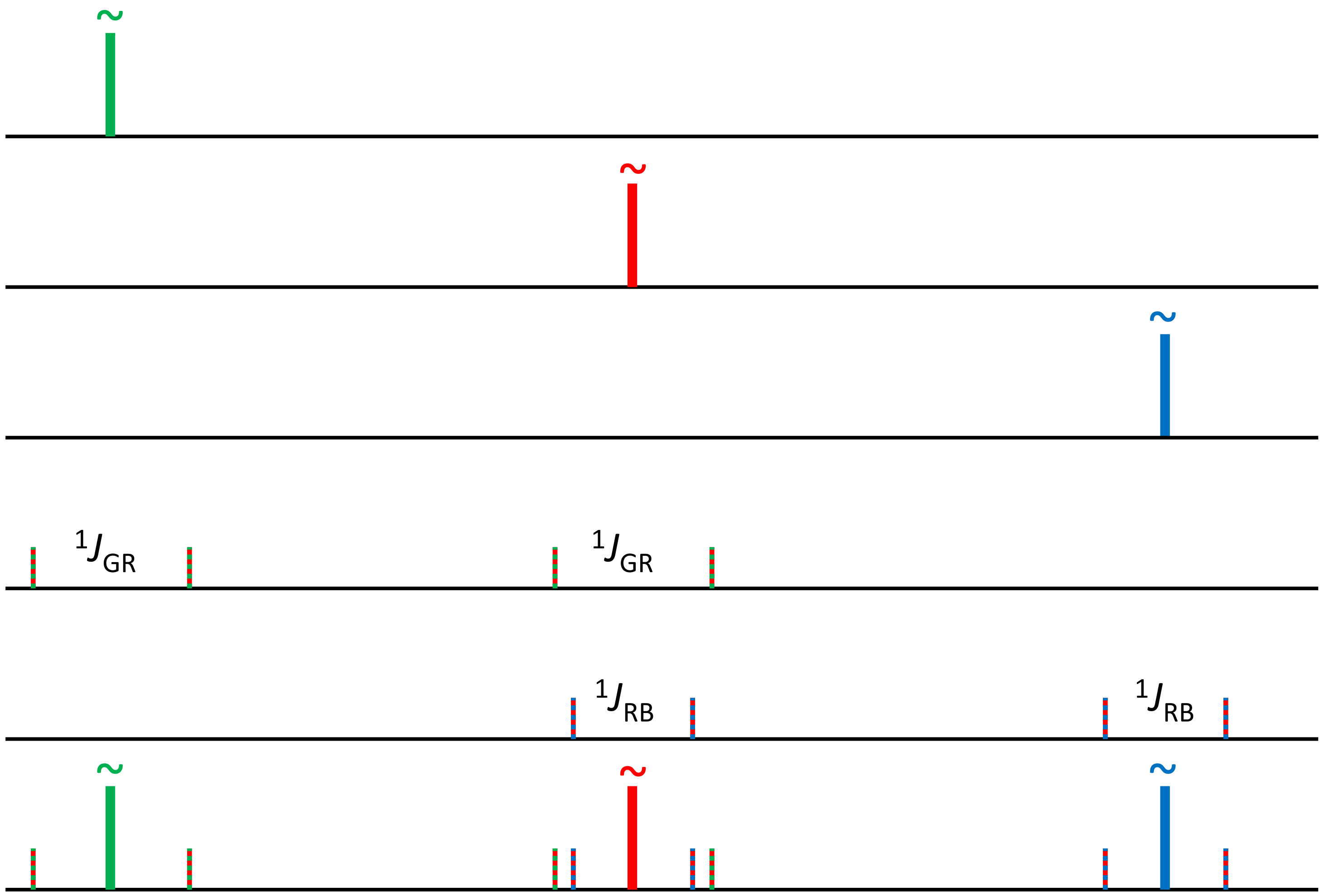
1% — ^{13}C — ^{12}C — ^{12}C —

1% — ^{12}C — ^{13}C — ^{12}C —

1% — ^{12}C — ^{12}C — ^{13}C —

0.01% — ^{13}C $\overset{^1J_{GR}}{—}$ ^{13}C — ^{12}C —

0.01% — ^{12}C — ^{13}C $\overset{^1J_{RB}}{—}$ ^{13}C —



Sum of all components

(there is no signal at all from about 97% of all sample molecules)

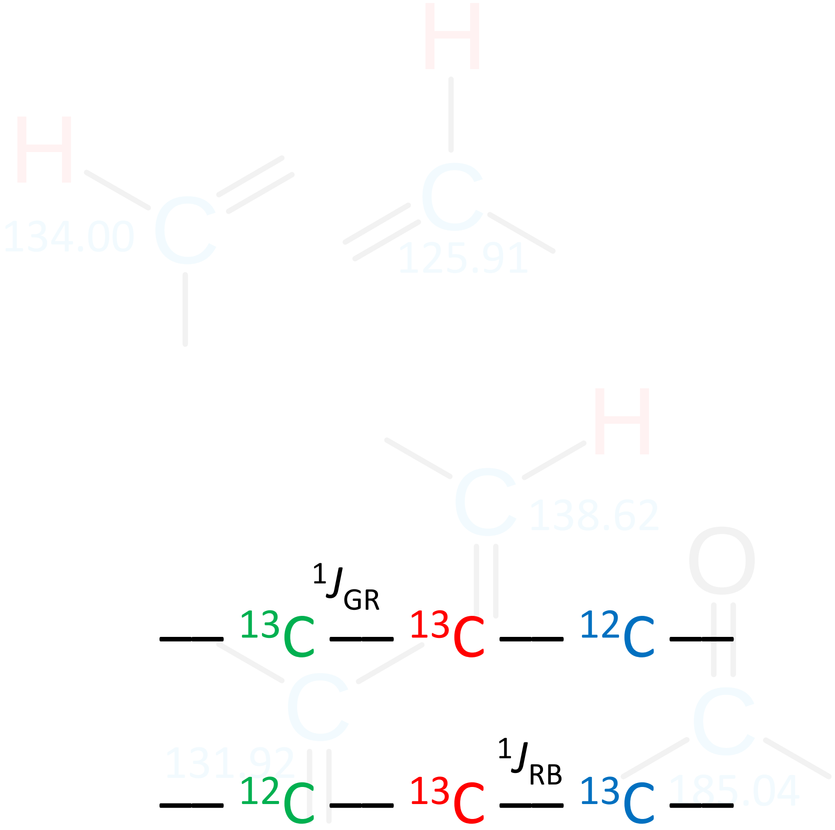
Carbon-carbon couplings

Probability and spectra

Let us inspect the final sum in some more detail with our focus to the carbon-carbon coupling pattern.

It seems to be trivial to measure both $^1J_{GR}$ and $^1J_{RB}$.(Green, Red, Blue)

But …

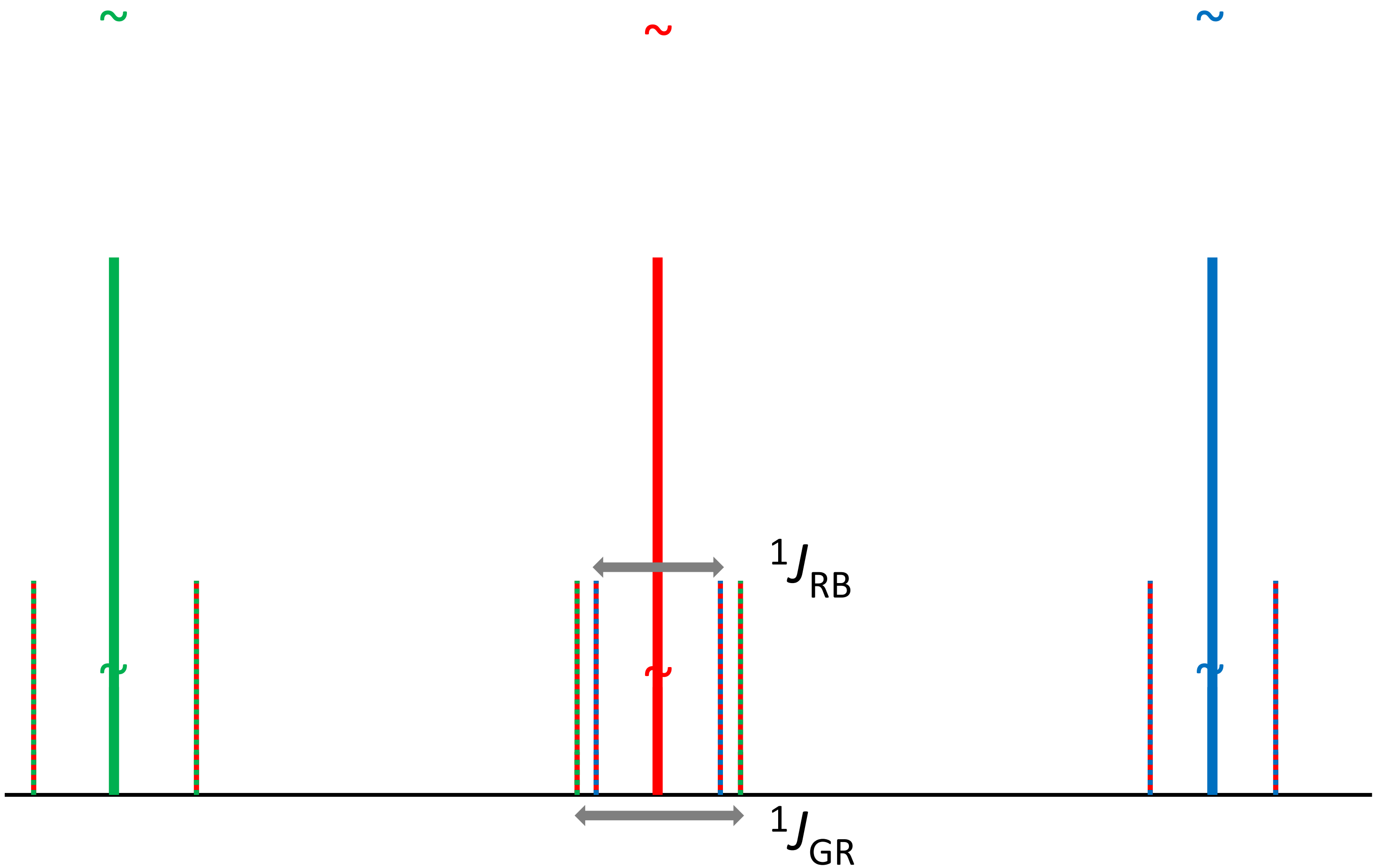


$^1J_{GR}$

— ^{13}C — ^{13}C — ^{12}C —

$^1J_{RB}$

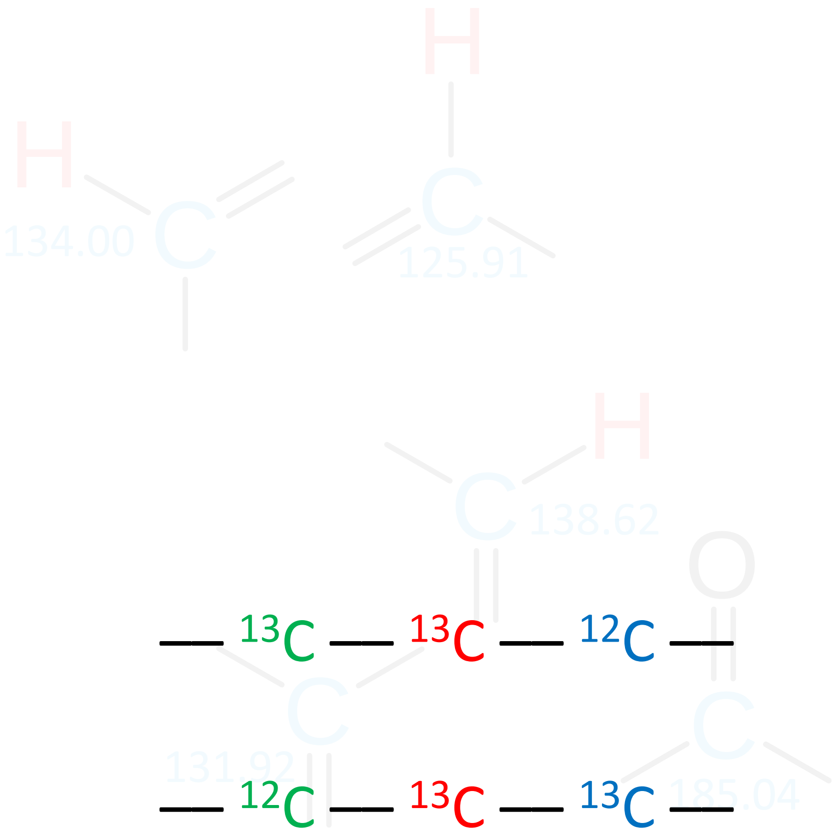
— ^{12}C — ^{13}C — ^{13}C —



Carbon-carbon couplings

Possible higher order spectra

The chemical shift difference between two directly connected carbon atoms might be as low as 1 ppm, which is about 63 Hz at 5.9 Tesla magnetic field strength. A typical value for $^{1}J_{CC}$ is 50 Hz, which means we would have an **AB** system.



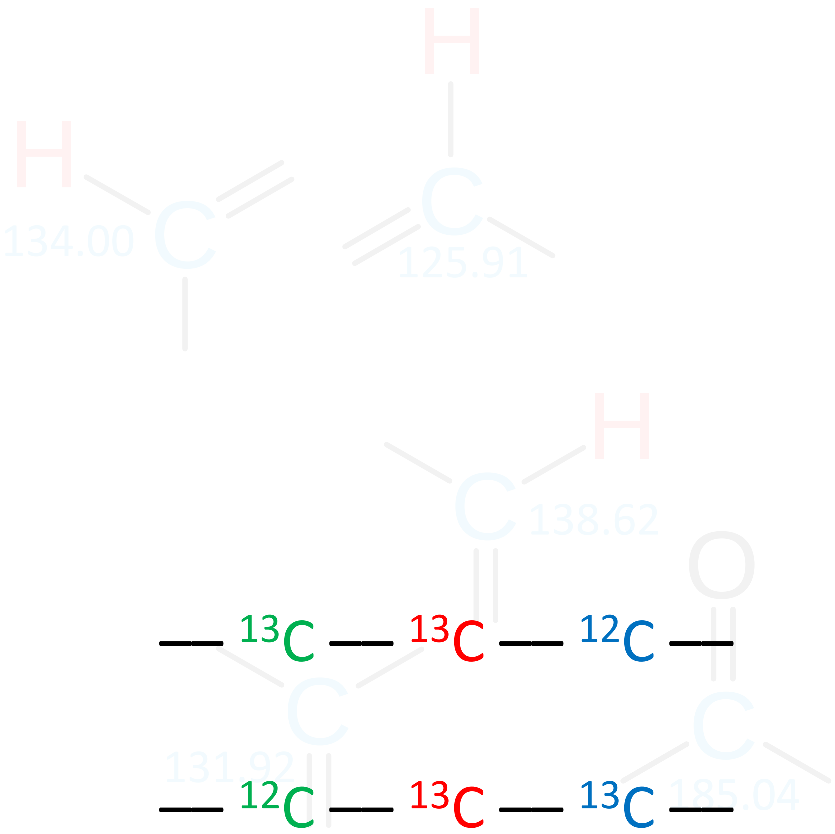
— ^{13}C — ^{13}C — ^{12}C —

— ^{12}C — ^{13}C — ^{13}C —

Carbon-carbon couplings

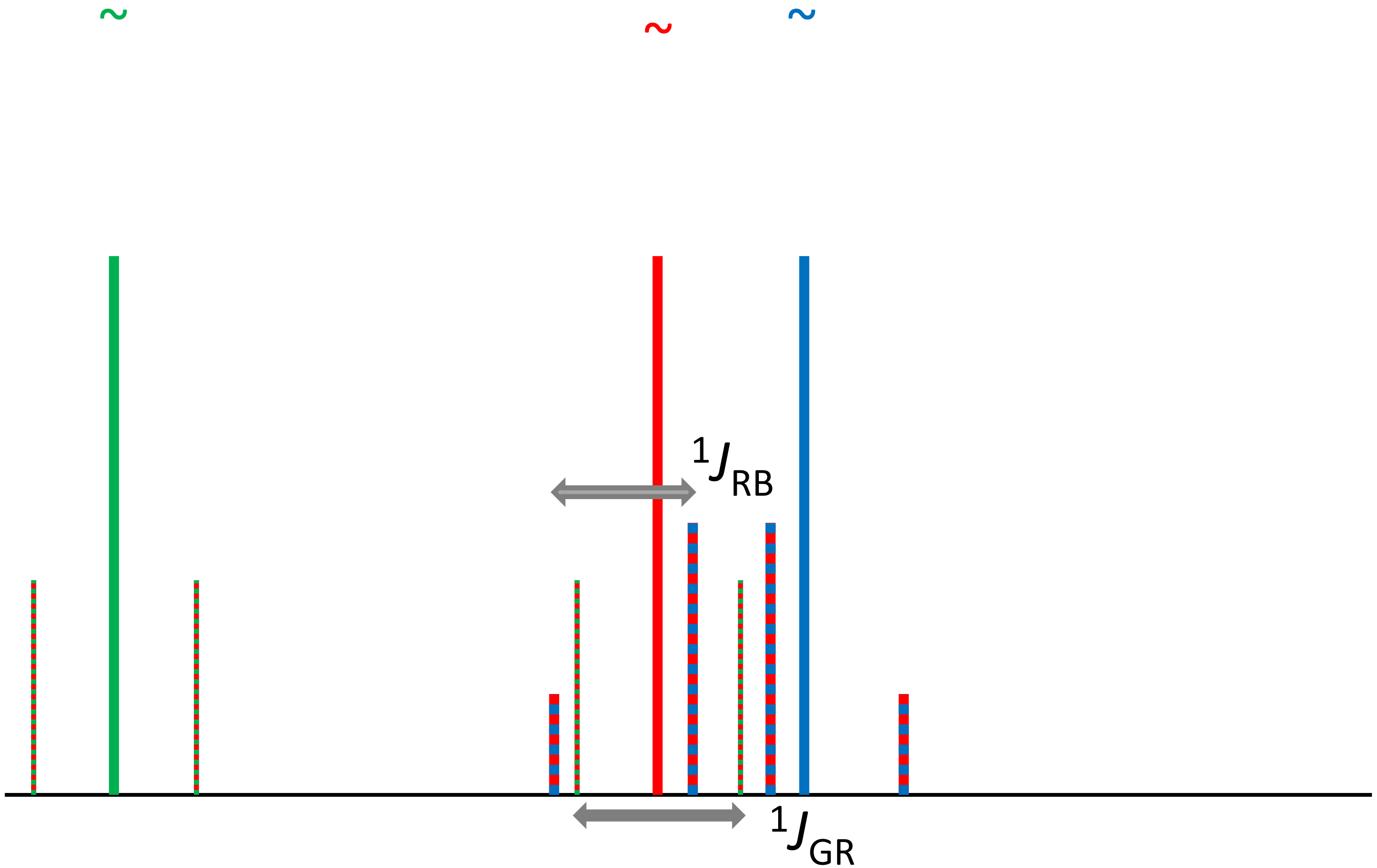
Possible higher order spectra

And now we have to be careful how me measure the coupling constants. If we are not sure about the chemical shift difference between coupling carbon atoms, we have to extract four possible coupling constants from the satellites around the red line



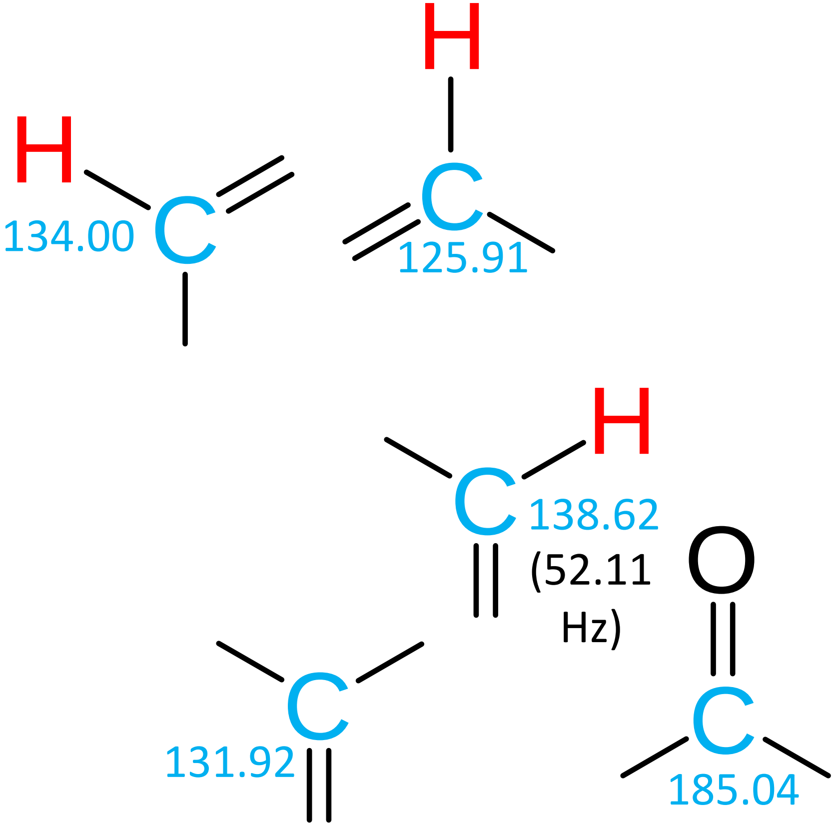
— ^{13}C — ^{13}C — ^{12}C —

— ^{12}C — ^{13}C — ^{13}C —



Carbon-carbon couplings

Detailed analysis

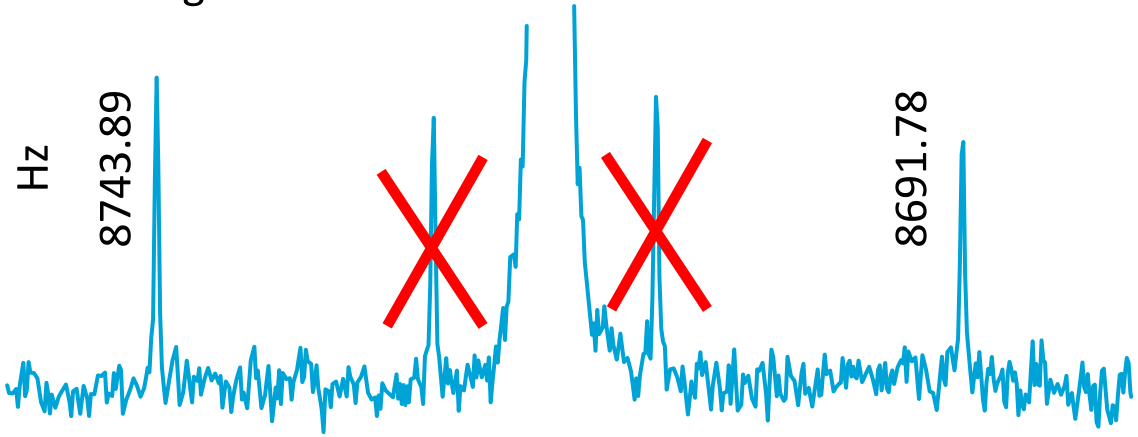


To start the detailed analysis let us select a carbon signal with a low number of satellites coming from carbon-carbon couplings.

The signal at 138.62 ppm appears to be well suited.

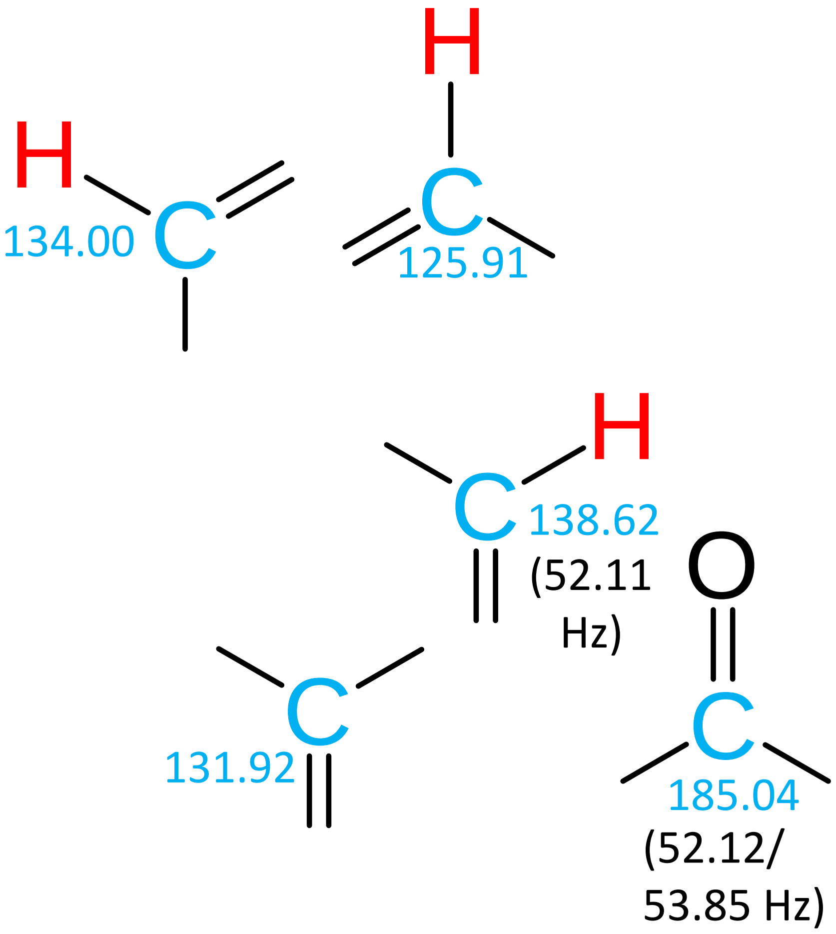
A typical value for $^1J_{CC}$ is between 40 and 60 Hz, which means that the two satellite signals marked with red crosses are due to carbon-carbon coupling over more than one bond.

If we use the two remaining satellite peaks we get a coupling constant of $^1J_{CC}$ = 52.11 Hz. We note this value next to the carbon chemical shift of this signal.



Carbon-carbon couplings

Detailed analysis

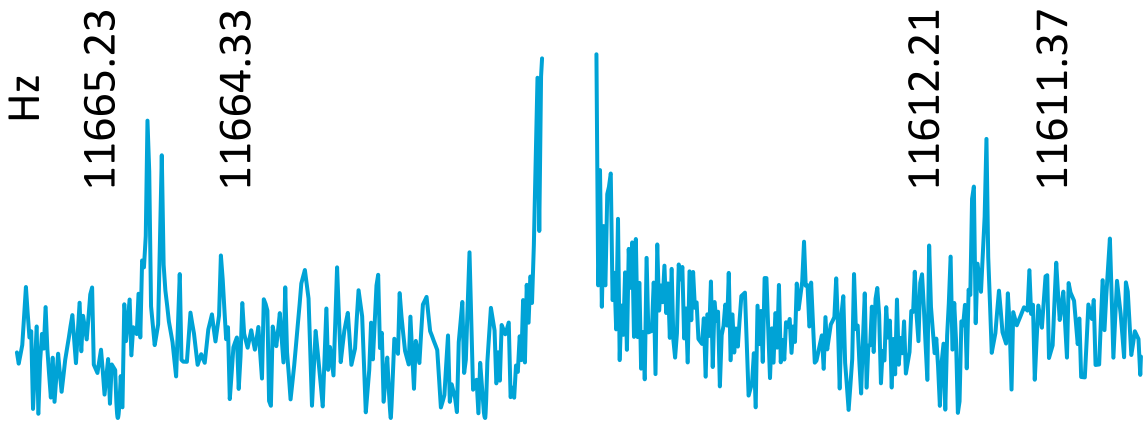


The coupling constant of 52.12 Hz must appear a second time in one of the four remaining carbon signals.

To shorten the search, here the result. We will see the coupling constant a second time in the coupling pattern of the satellite signals at 185.04 ppm.

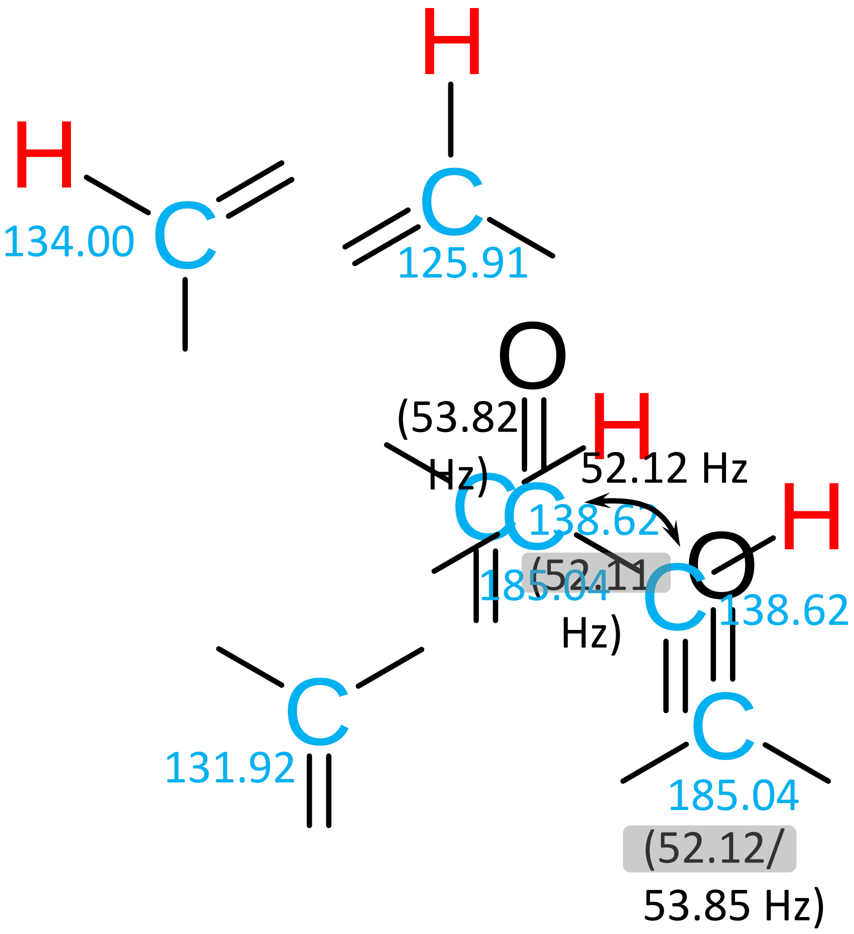
185.04 ppm is far away from all other carbon signals, we don‘t have to worry about **AB** effects, described earlier.

Our evaluation yields two carbon-carbon coupling constants of **52.12 Hz** (11664.33 – 11612.21) and **53.85 Hz**, respectively, which we will note next to the corresponding chemical shift.

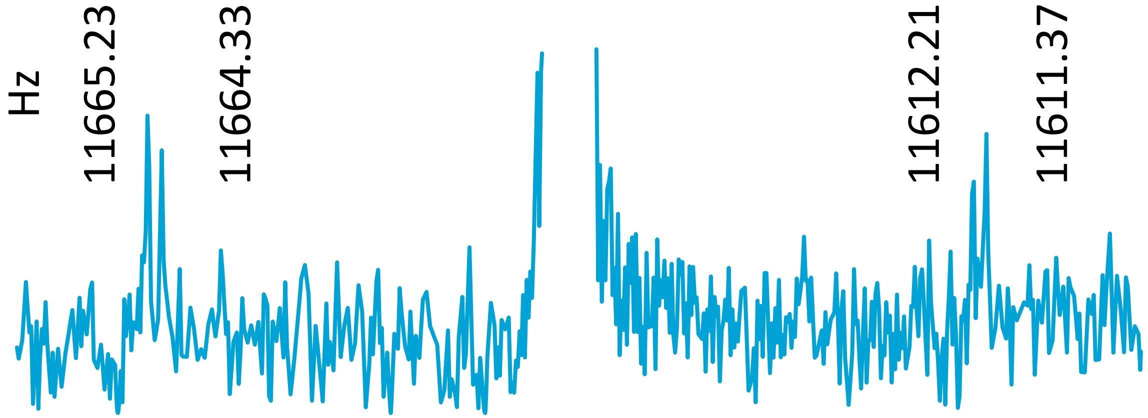


Carbon-carbon couplings

Detailed analysis

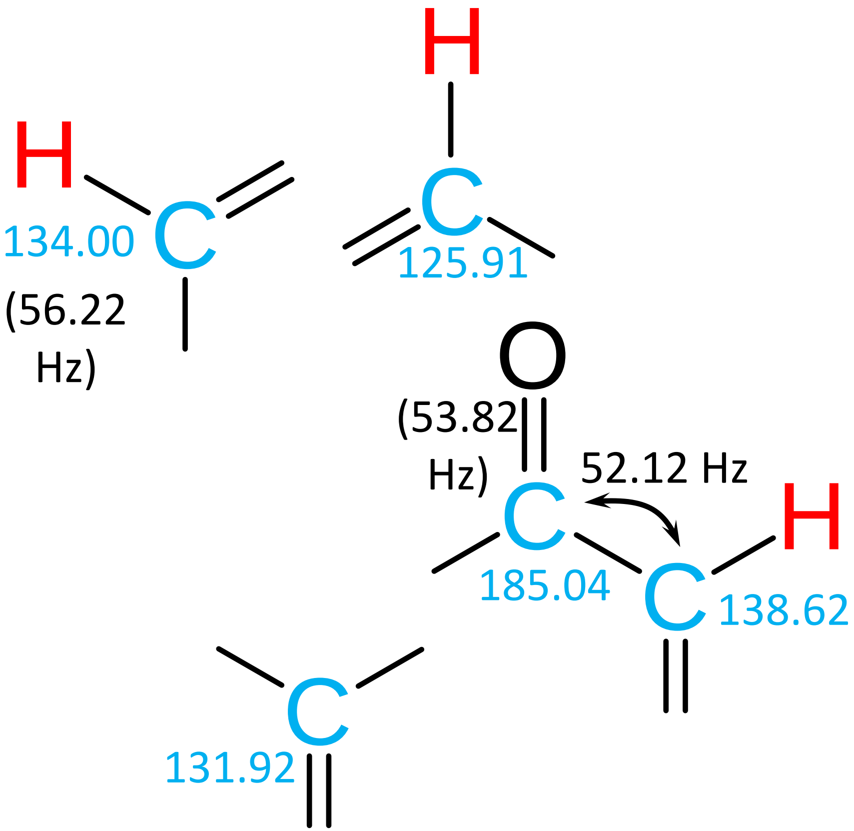


One $^{1}J_{CC}$ (52.11/52.12 Hz) exists twice. The corresponding carbon atoms have to be connected.



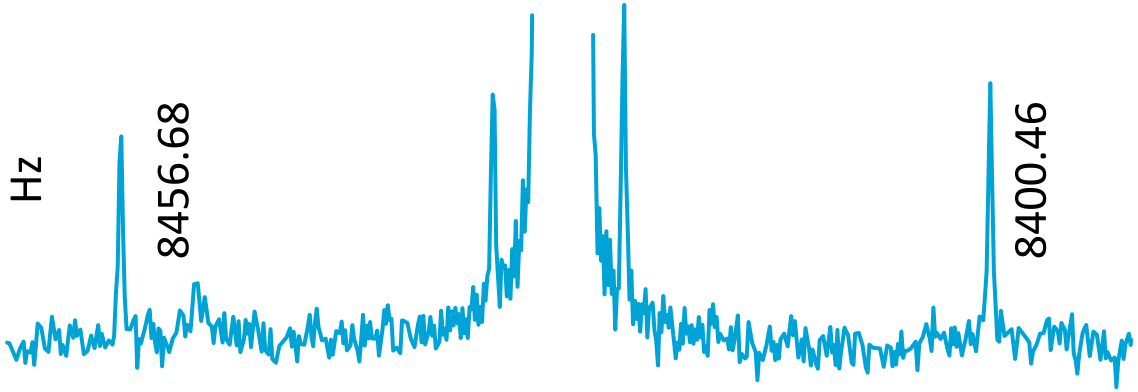
Carbon-carbon couplings

Detailed analysis



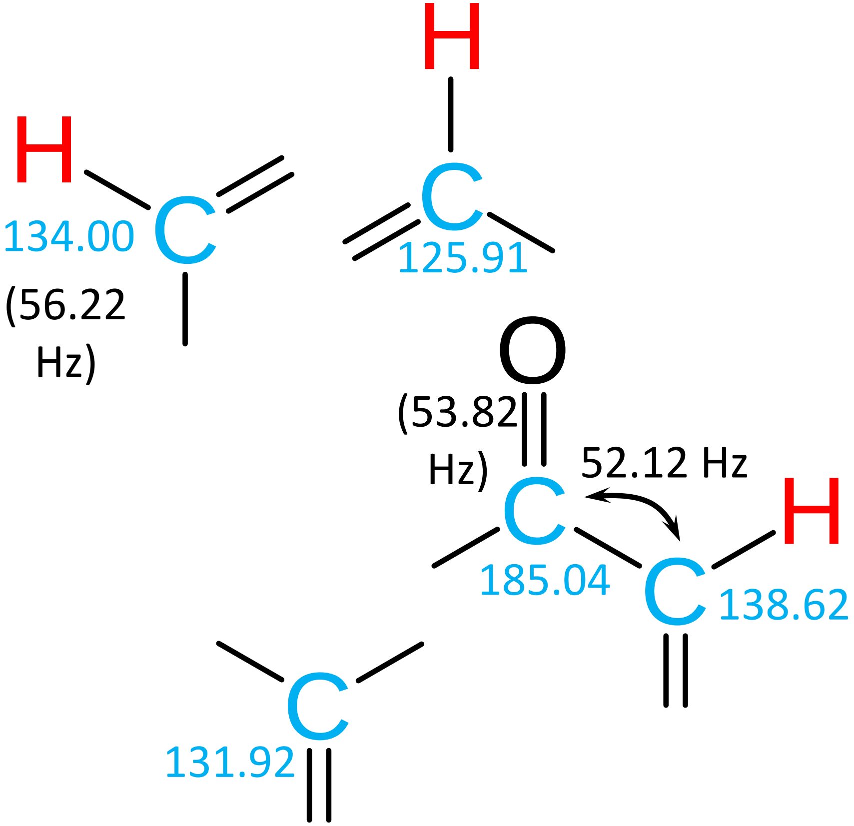
There is another carbon signal at 134.00 ppm from which only one $^1J_{CC}$ can be extracted.

As done before, we note the result of **56.22 Hz** next to the carbon chemical shift.



Carbon-carbon couplings

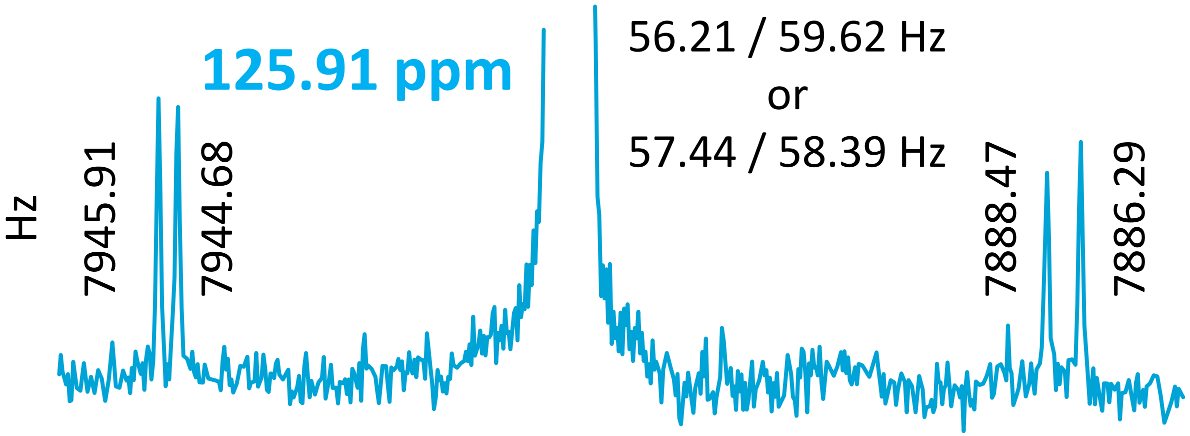
Detailed analysis



The coupling constant of **56.22 Hz** must appear a second time in the satellite signals of either the carbon atom at 125.91 ppm or at 131.92 ppm.

In both cases, however, the satellite signals are sometimes so close together that the **AB** case discussed above cannot be ruled out. We therefore have to determine four possible $^1J_{CC}$ on a trial basis.

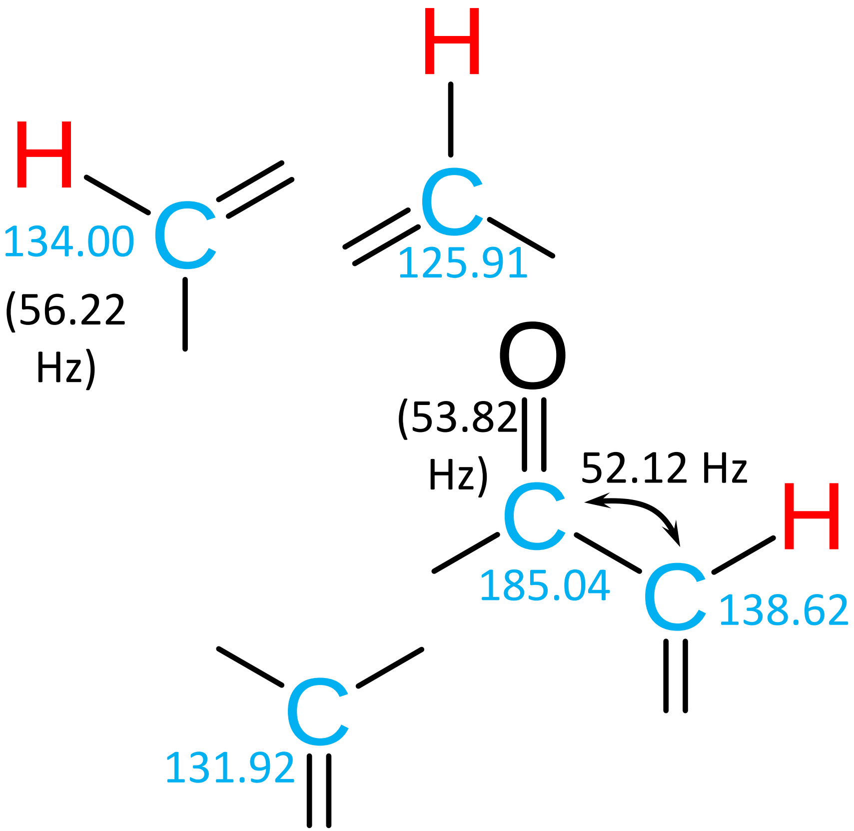
Let us start with the analysis of the carbon signal at 125.91 ppm. We get two possible combinations of two values for $^1J_{CC}$.

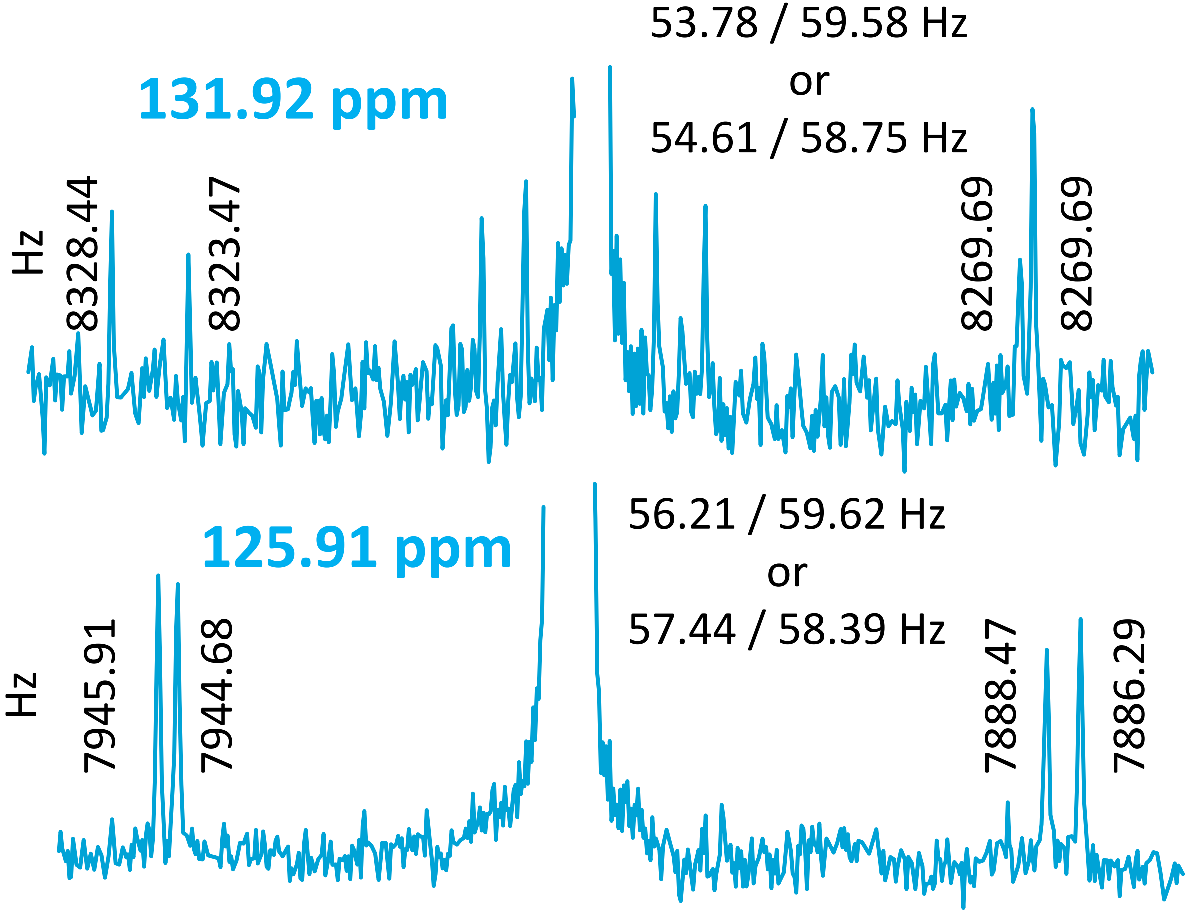


Carbon-carbon couplings

Detailed analysis

Doing the same calculation for the satellites of the carbon signal at 131.92 ppm we get two further pairs of possible values for $^1J_{CC}$. Only one pair is the correct one, but for the moment we cannot decide which one.



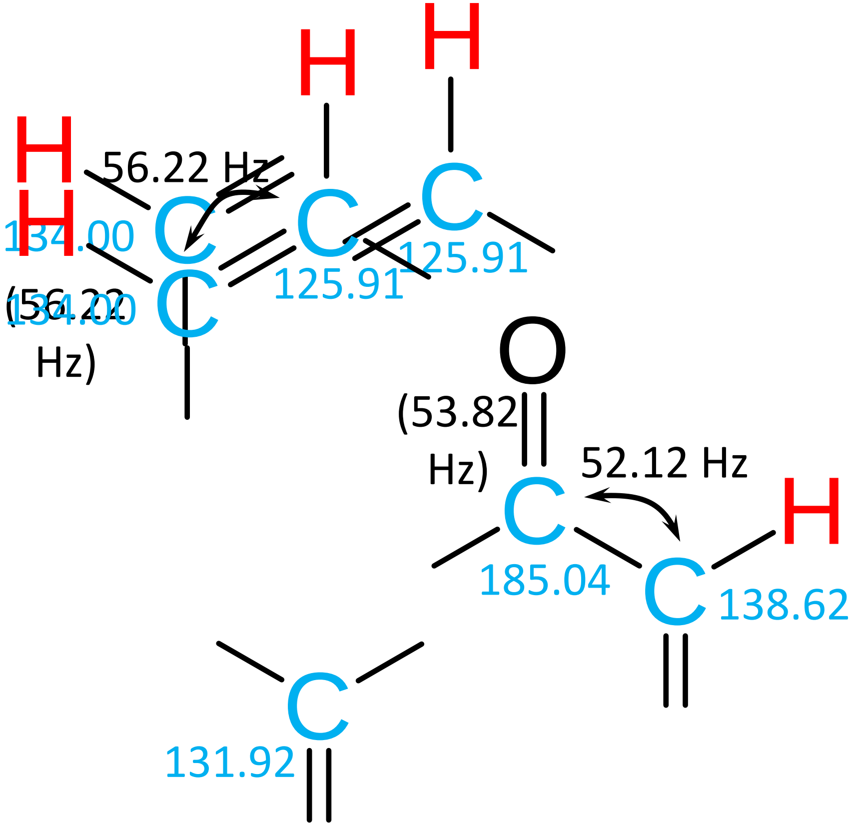


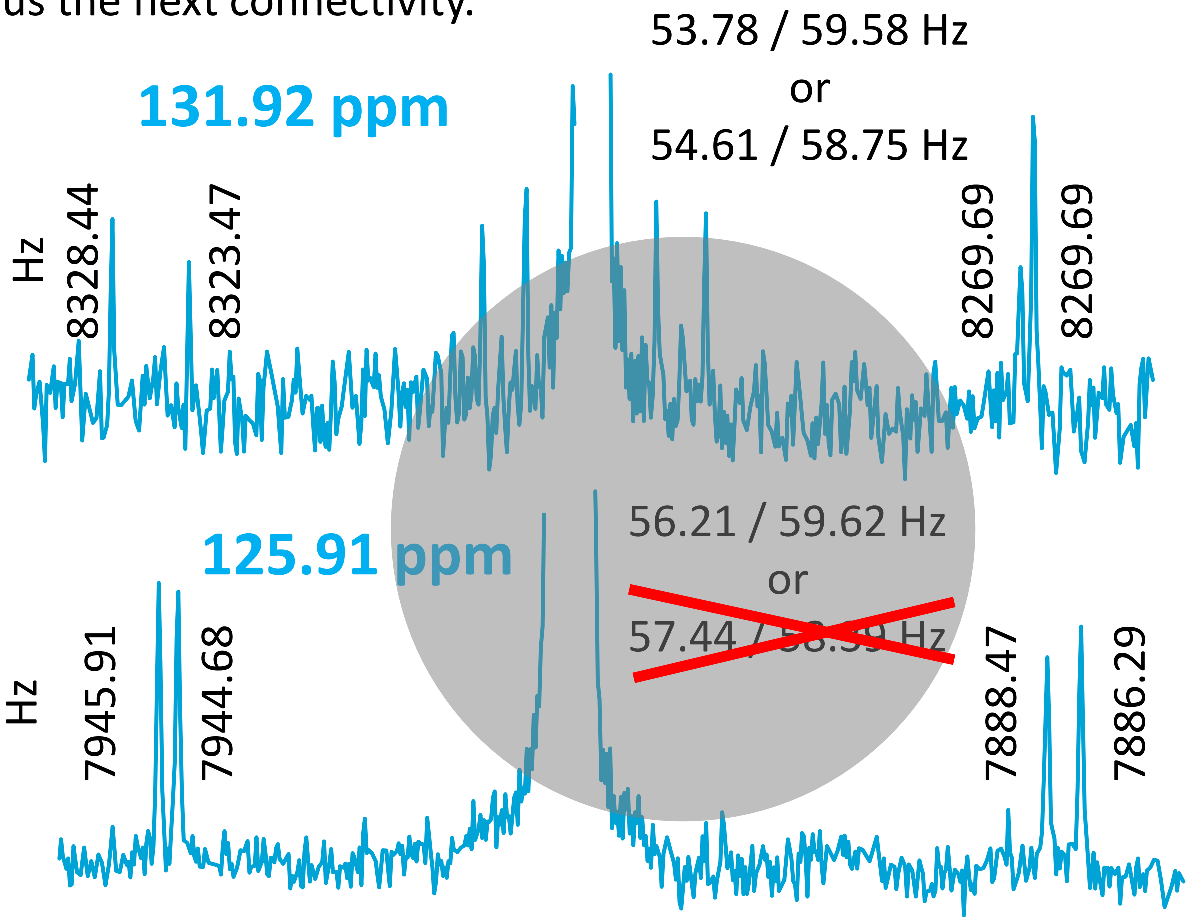
Carbon-carbon couplings

Detailed analysis

The carbon-carbon coupling constant of **56.22 Hz** appears the second time as part of the satellite pattern of the signal at 125.91 ppm.

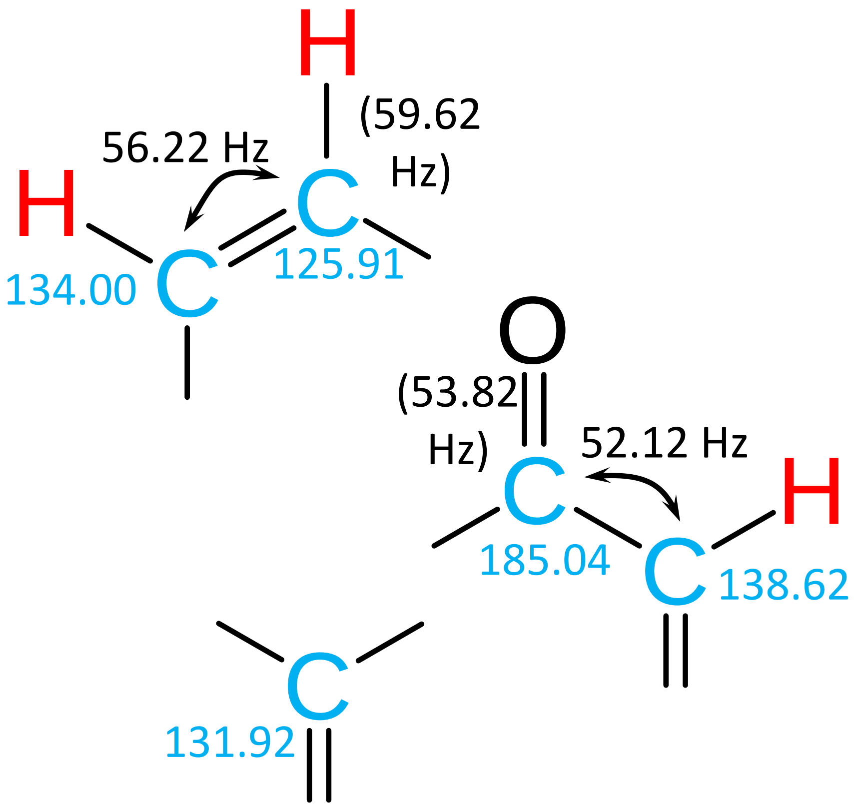
This rules out one pair of possible carbon carbon coupling constants and shows us the next connectivity.



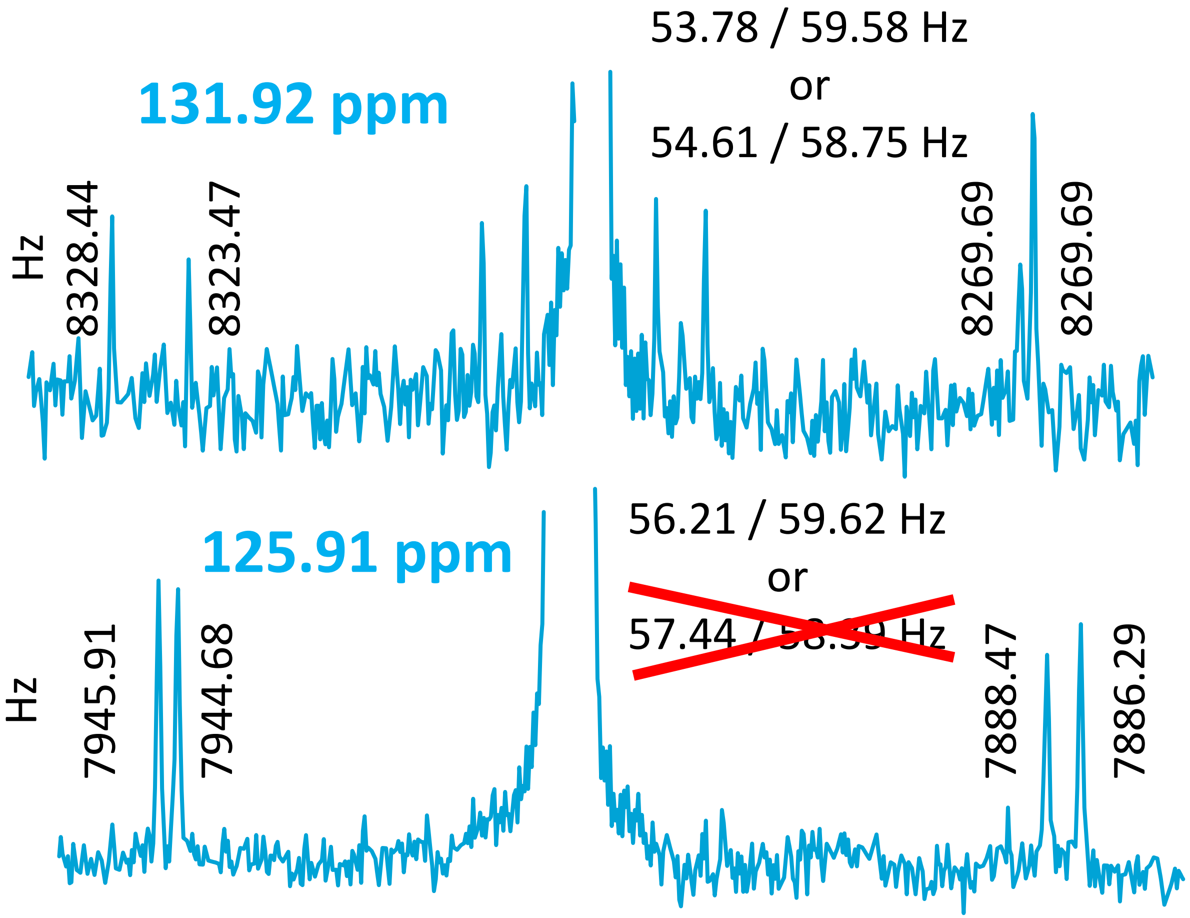


Carbon-carbon couplings

Detailed analysis



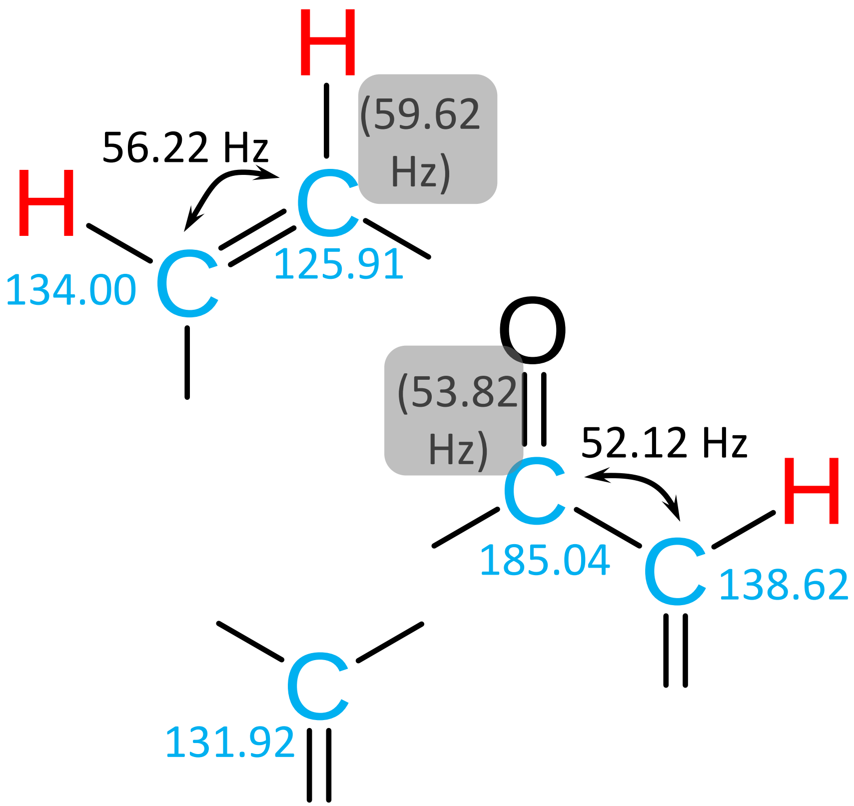
As second carbon-carbon coupling constant from the satellite pattern of the carbon signal at 125.91 ppm we note the value of **59.62 Hz** next to the carbon signal for further use.



We no longer need the lower part of the carbon spectrum.

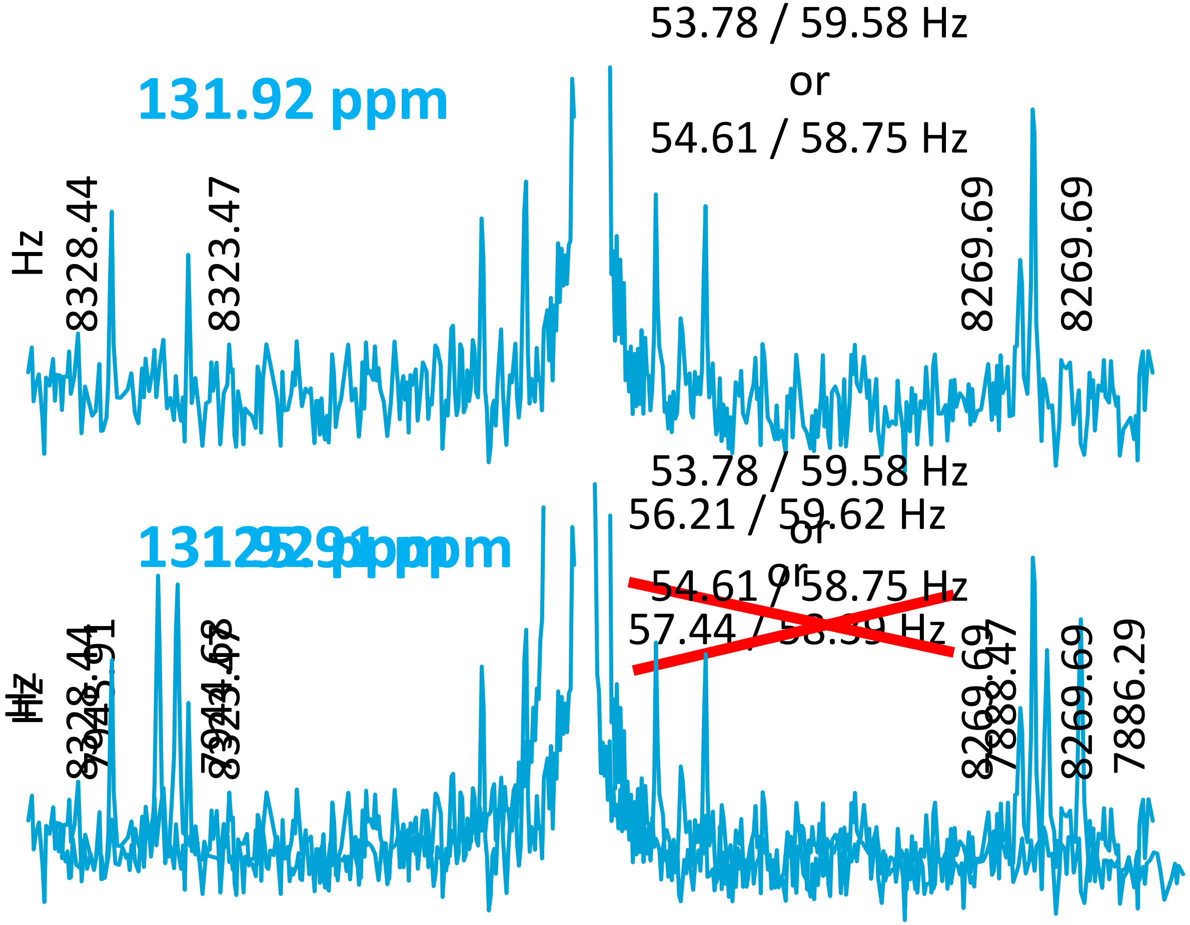
Carbon-carbon couplings

Detailed analysis



As second carbon-carbon coupling constant from the satellite pattern of the carbon signal at 125.91 ppm we note the value of **59.62 Hz** next to the carbon signal for further use.

The two carbon-carbon coupling constants of **59.62 Hz** and **53.82 Hz** have to be hidden in the satellite pattern of the carbon signal at 131.92 ppm. There is no other remaining carbon atom.



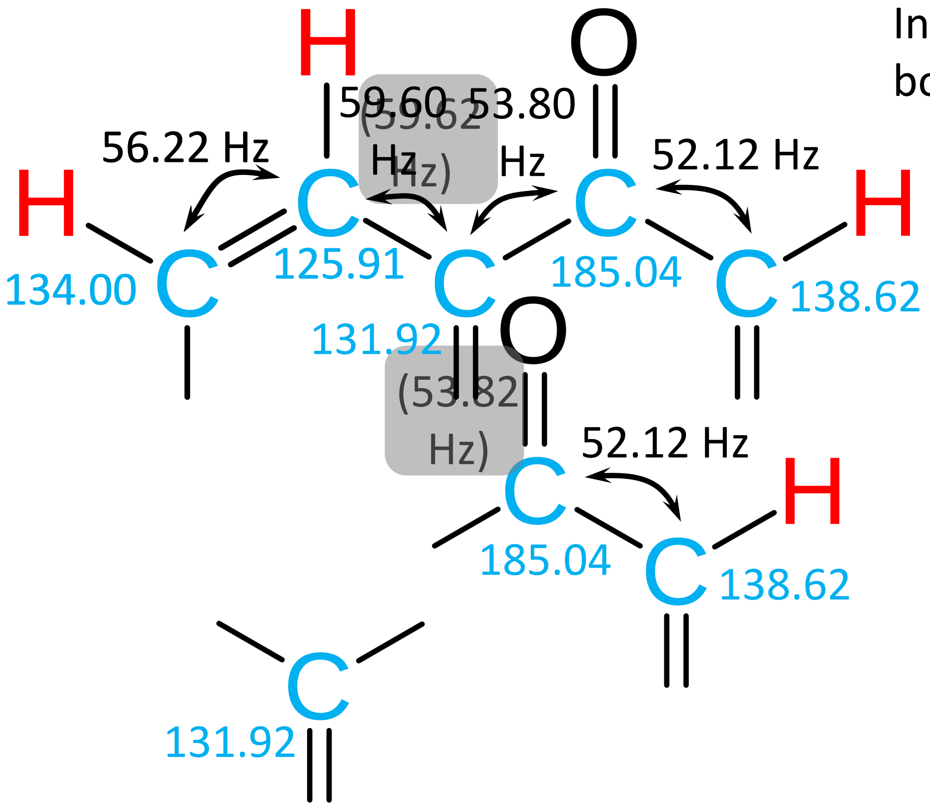
We no longer need the lower part of the carbon spectrum.

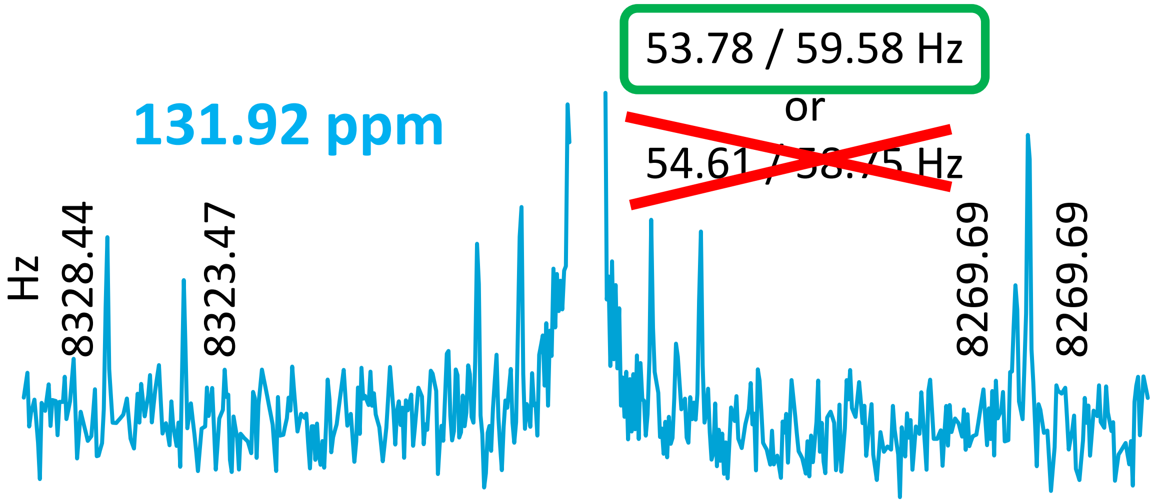
Carbon-carbon couplings

Detailed analysis

The two carbon-carbon coupling constants of **59.62 Hz** and **53.82 Hz** have to be hidden in the satellite pattern of the carbon signal at 131.92 ppm. There is no other remaining carbon atom.

Indeed, one of the pair of coupling constants measured before contains both values with deviations in the range of some 0.01 Hz.

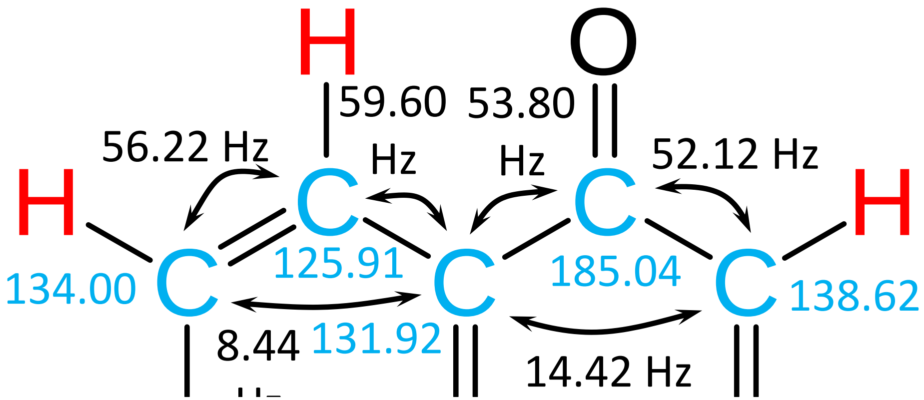




Now we are able to link all fragments.

Symmetry

Final structure



Mirroring the whole fragments gives our final structure. There will be no carbon-carbon coupling visible between equivalent carbon atoms.

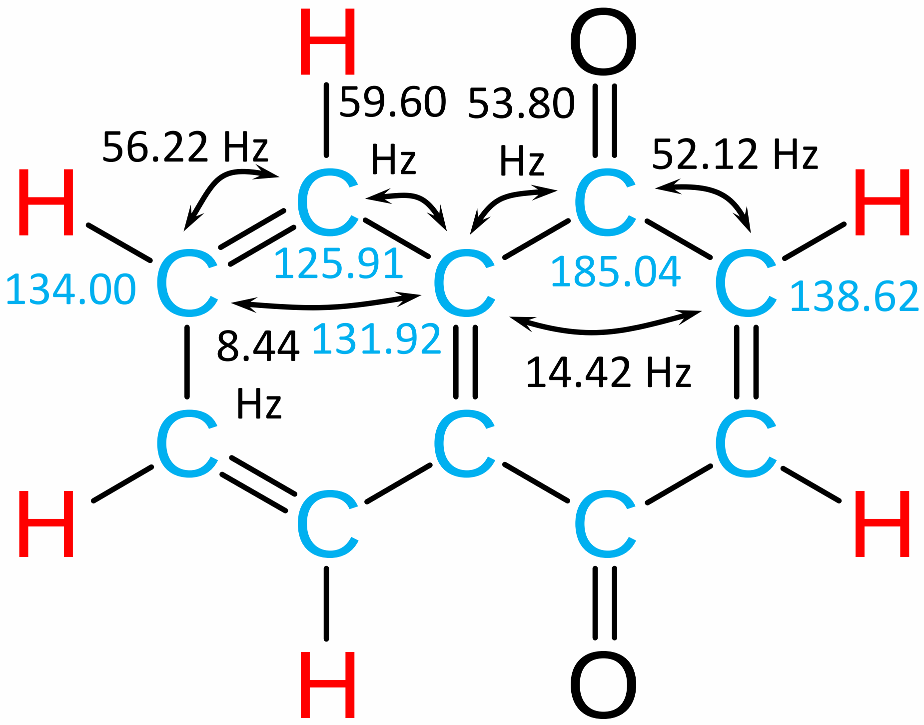
Inspecting the satellites of the carbon signals at 134.00, 131.92 and 138.62 ppm reveals two further carbon carbon coupling constants of **8.44** and **14.42 Hz**.

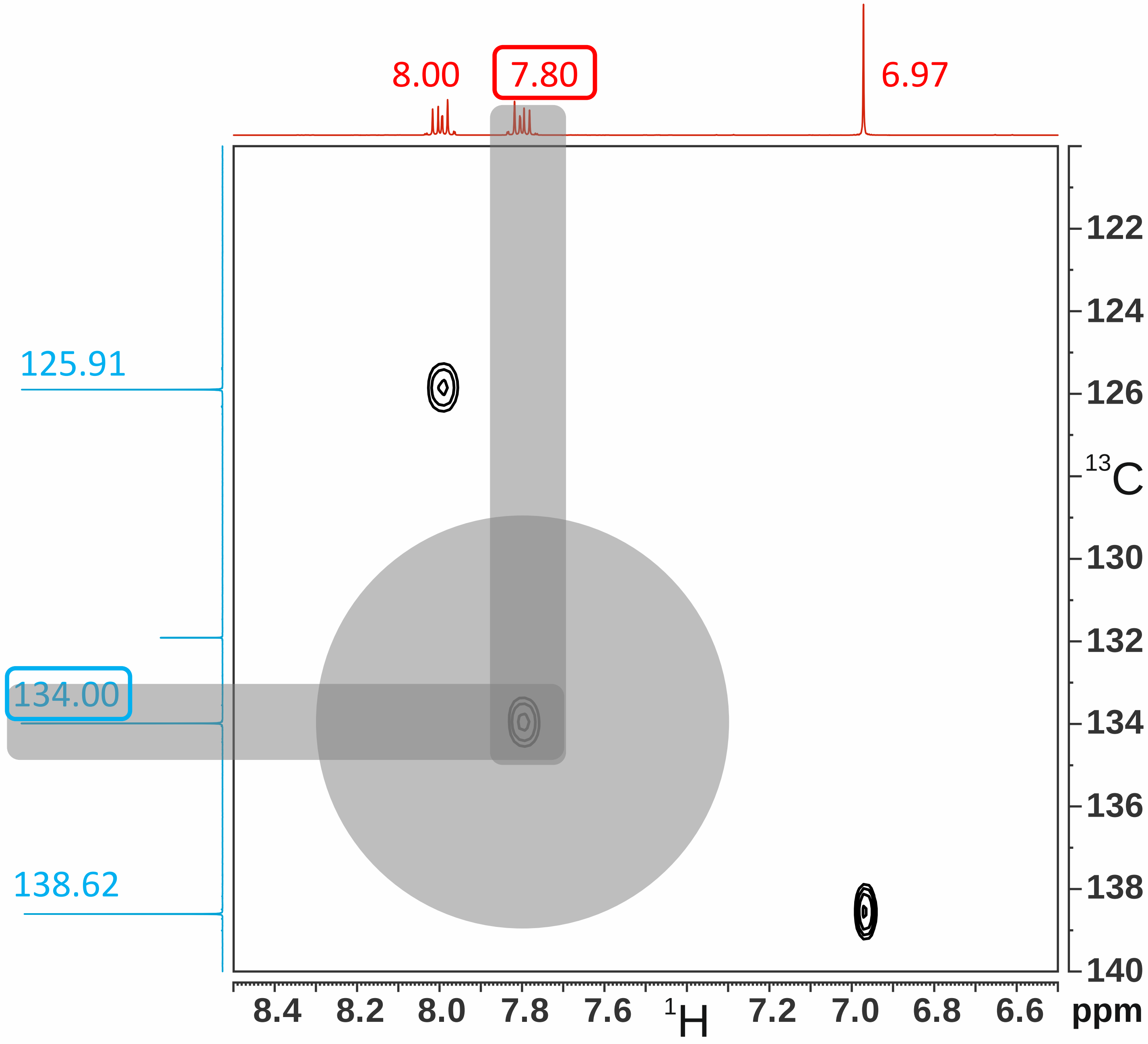
Because structure and carbon assignment are already known, those have to be geminal coupling constants.

Of course there are more carbon carbon coupling constants, but they cannot be resolved using the spectra presented here.

Proton assignment

The last step



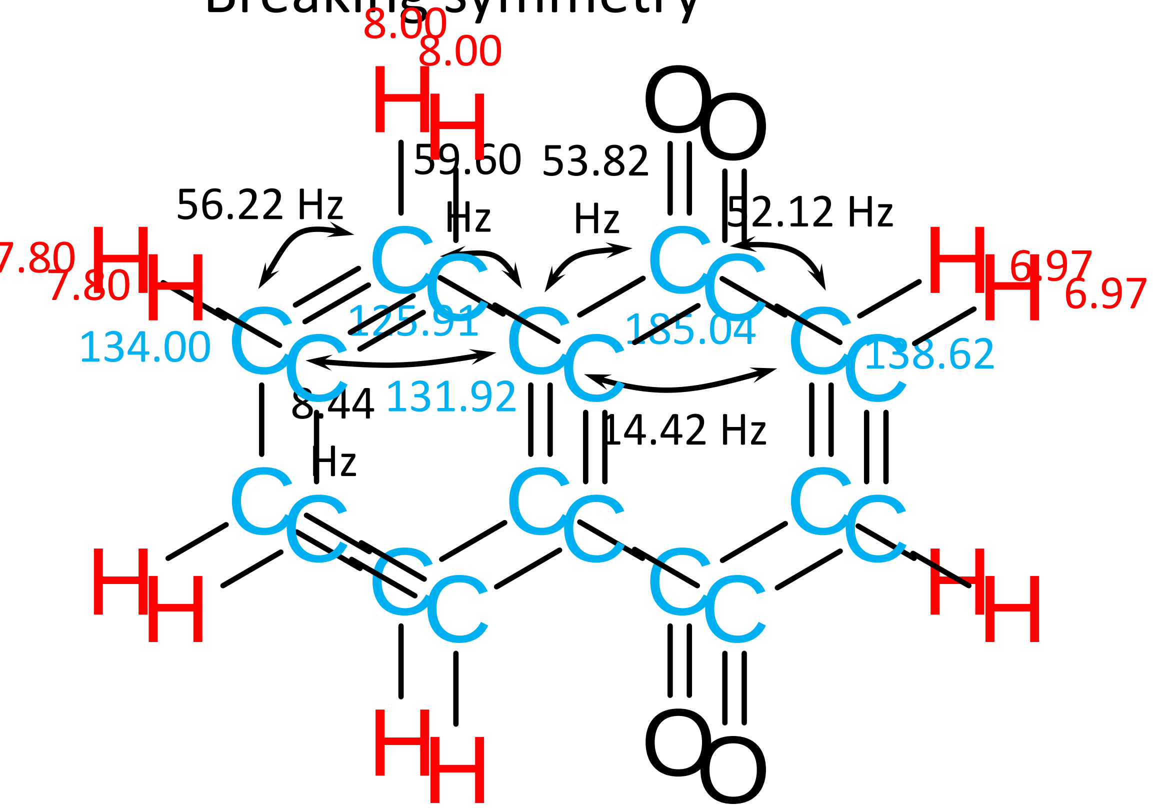


The proton assignment is possible using the HSQC.

Only one example is presented here.

Proton proton coupling constants

Breaking symmetry

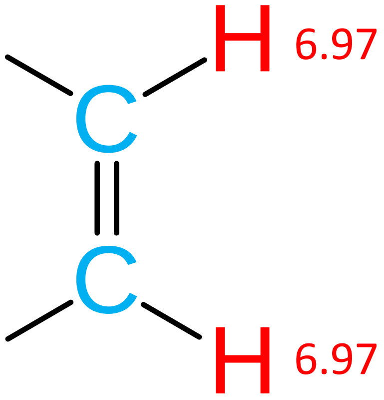


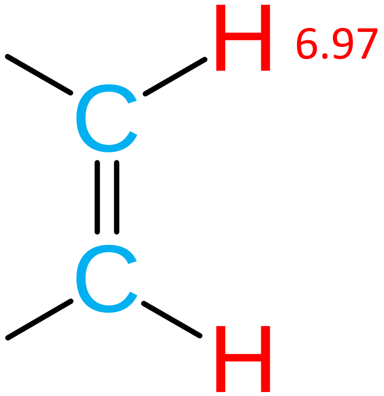
But how can we measure coupling constants between protons with the same chemical shift?

Let us start with the protons with the chemical shift of 6.97 ppm. They are clearly separated from the other protons. In the ^{1}H-NMR spectrum the signal at 6.97 ppm is a singlet. Let us neglet the rest of the molecule for the sake of clarity.

Proton proton coupling constants

Breaking symmetry

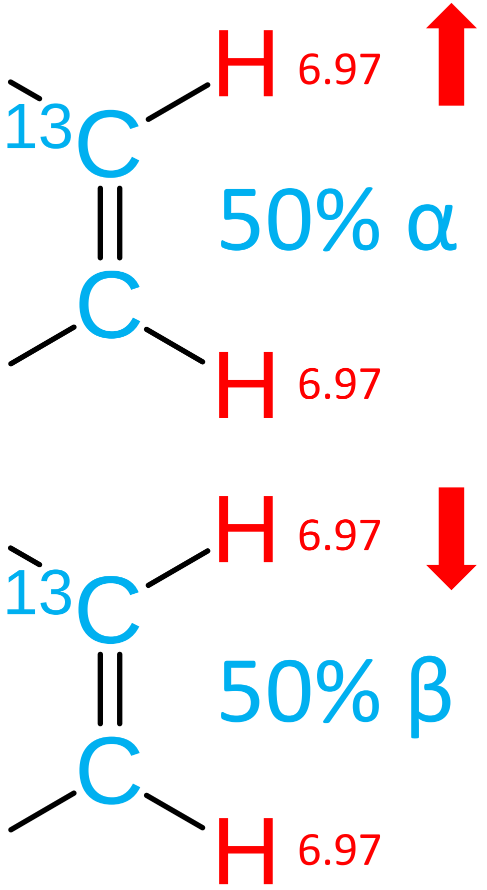




With a probability of about 1% the carbon next to one of the protons is a ^{13}C isotope.

Proton proton coupling constants

Breaking symmetry



With a probability of about 1% the carbon next to one of the protons is a ^{13}C isotope.

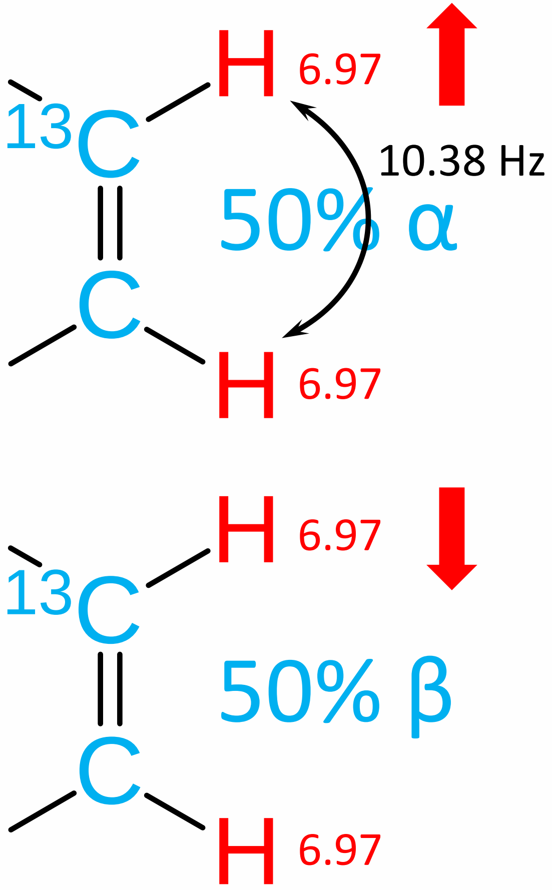
According to the Boltzmann statistics the orientation of the the ^{13}C nucleus is with a nearly perfect 50% probability either **α** or **β**.

Due to the additional magnetic field coming from the ^{13}C nucleus, the signal of the proton attached to this carbon becomes shifted up- or downfield depending on the orientation of the ^{13}C nucleus.

The second proton becomes less influenced from the orientation of the ^{13}C nucleus. Finally we get two different chemical shifts for both protons and are able to measure the homonuclear coupling constant between them.

Proton proton coupling constants

Breaking symmetry



Because of the low natural abundance of ^{13}C, the signals we are interested in appear as low-intensity satellites.

Now it is easy to get the coupling constant from one of the doublets.

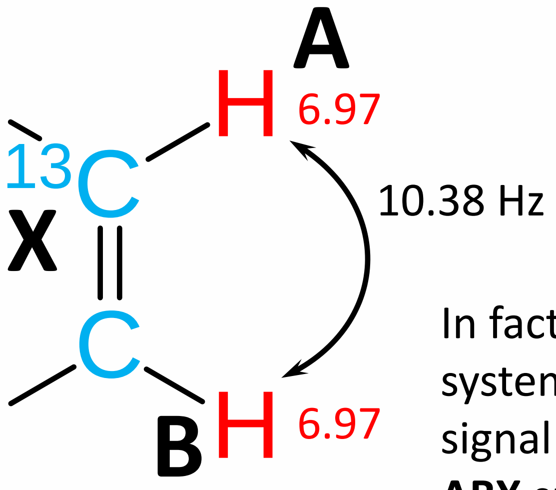
We have the **correct result** now and might be happy.

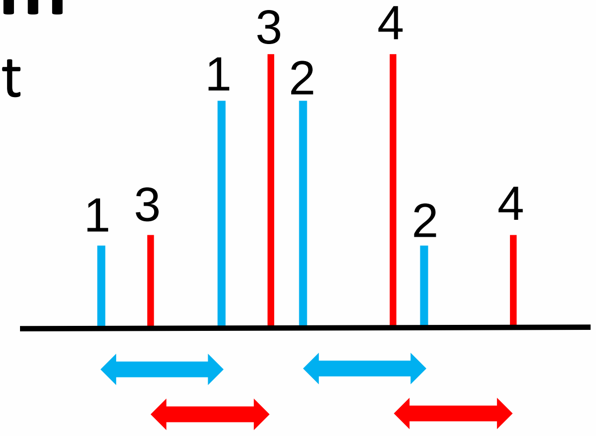
But...

In spite of the correct result the explanation is wrong.

Some theory about the ABX spin system

Location of A and B part

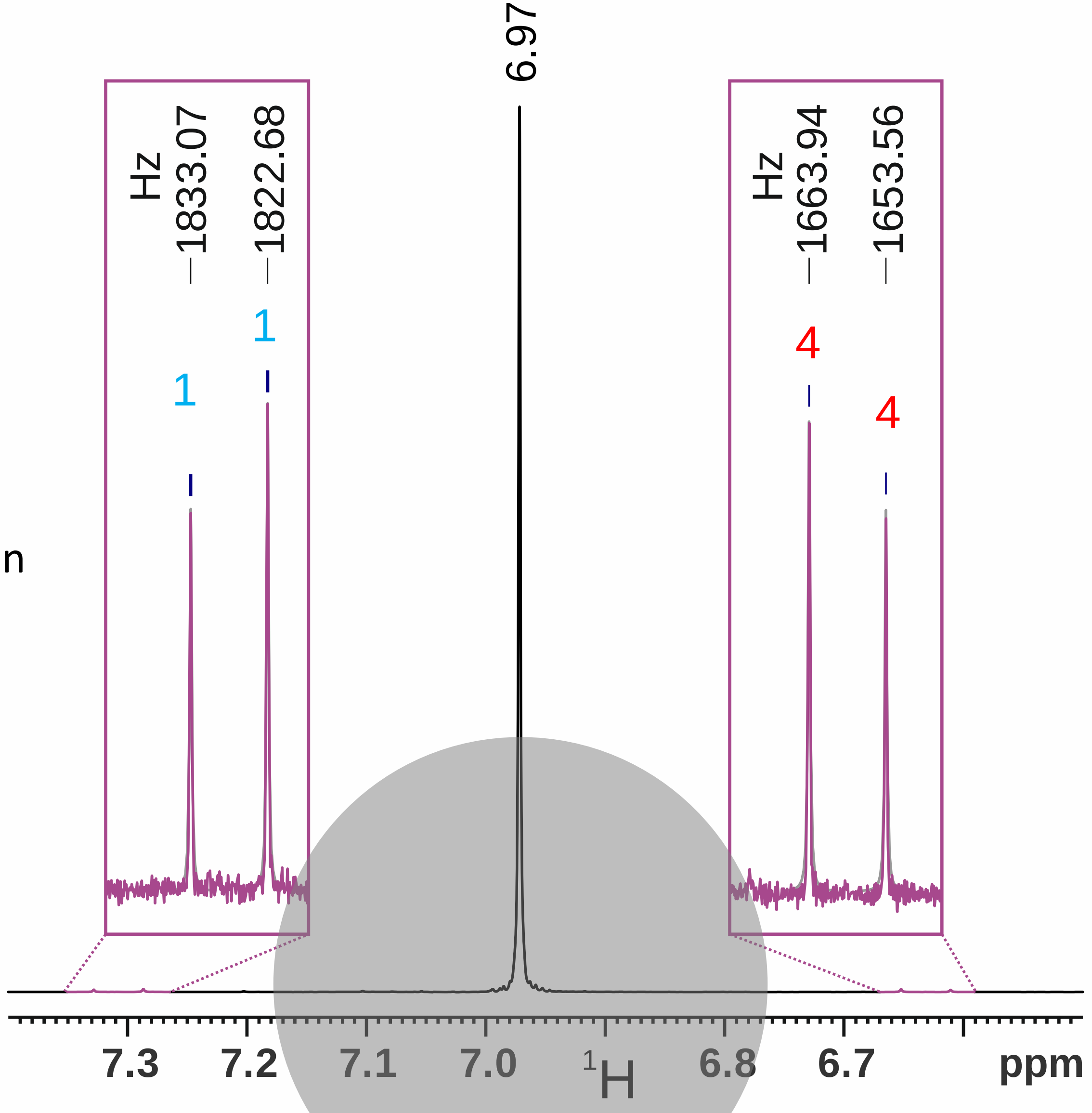




In fact we have to deal with a three spin system. In the carbon satellites of the proton signal we are looking at the **AB** part of an **ABX** spin system.

The **AB** part of an **ABX** spin system consists always of 8 lines. The coupling constant between the nuclei **A** and **B** appears four times. You get the value of J_{AB} as difference between the line pairs with the same number.

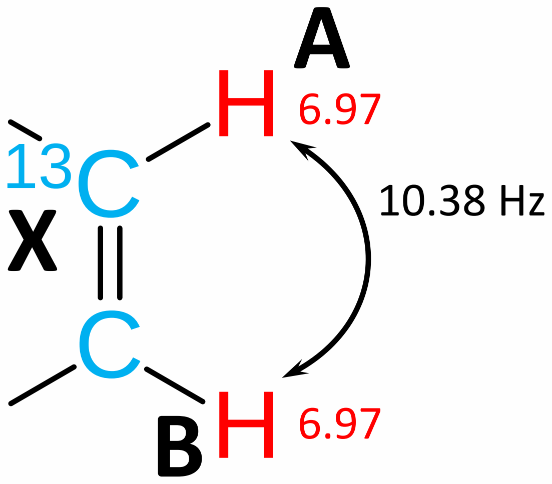
In our spectrum we see only four of the eight lines. Which ones? Compare the numbering in the line spectrum and in the real spectrum. The coupling constant you are looking for can be determined from the four visible signals as shown before. But where are the lines labelled with **2** and **3**?

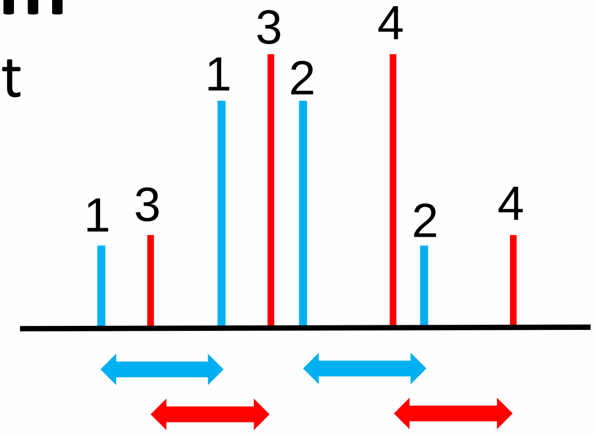


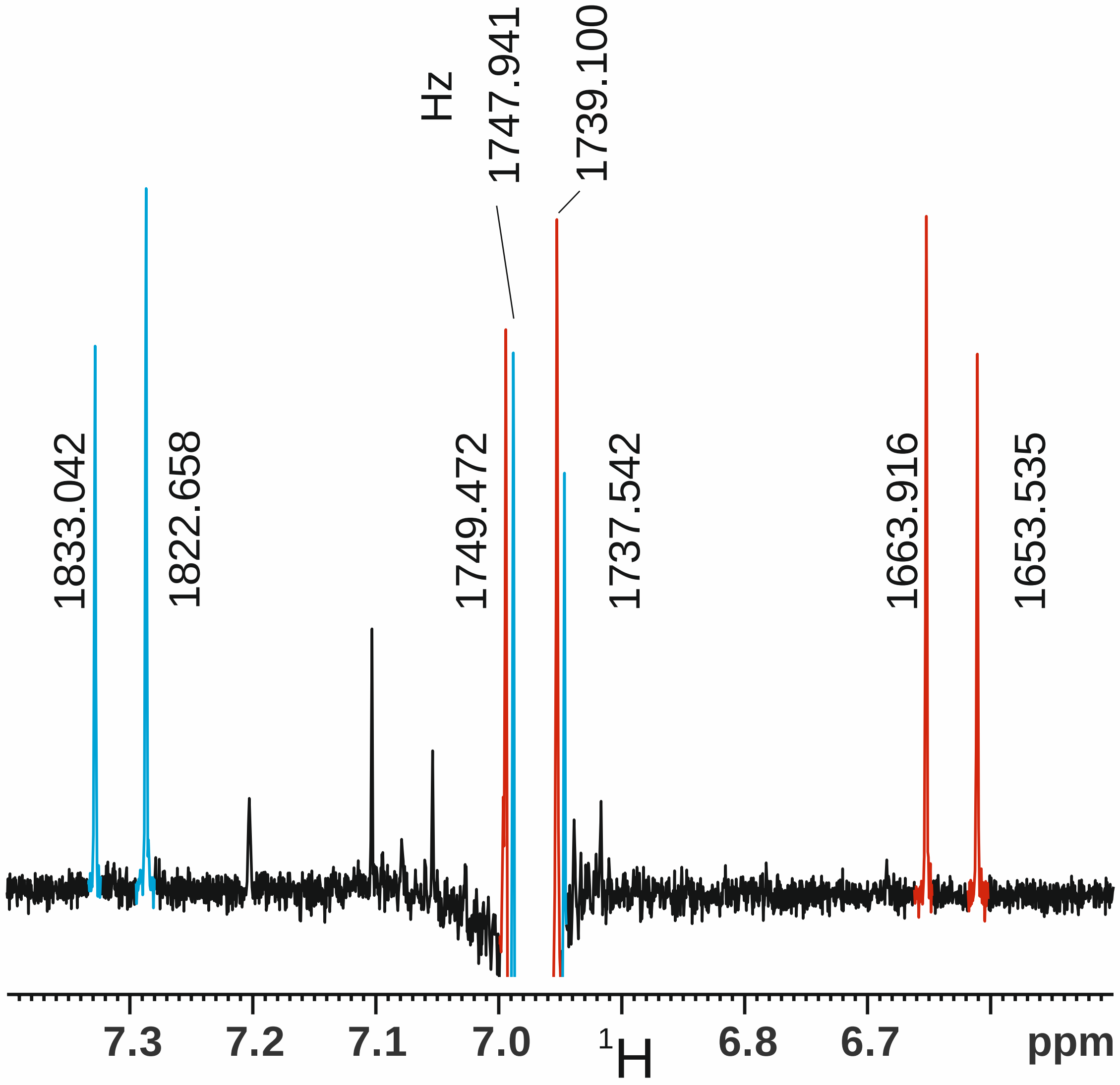
Let us investigate this part of the spectrum in some more detail.

Some theory about the ABX spin system

Location of A and B part







After some signal enhancement processing, removing the strong center line, removing four further satellite lines very close to the center line coming from coupling with ^{13}C=O, we get our eight lines of the **AB** system.

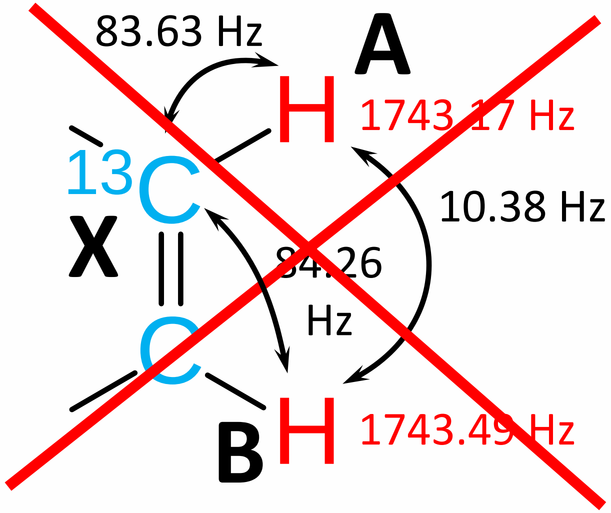
We get our coupling constant of **10.38 Hz** four times with a deviation of +/- 0.01 Hz.

Recognizing the **A** and the **B** part is far from being trivial, the coupling constant will help a little bit.

These lines were intentionally not part of the problem set to avoid confusion by a huge number of lines. They are not necessary to get the homonuclear coupling constant, but now we need them to describe the theory.

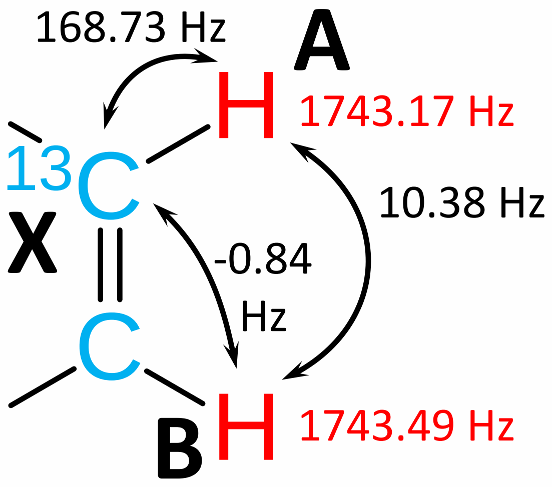
Some theory about the ABX spin system

Some mathematics

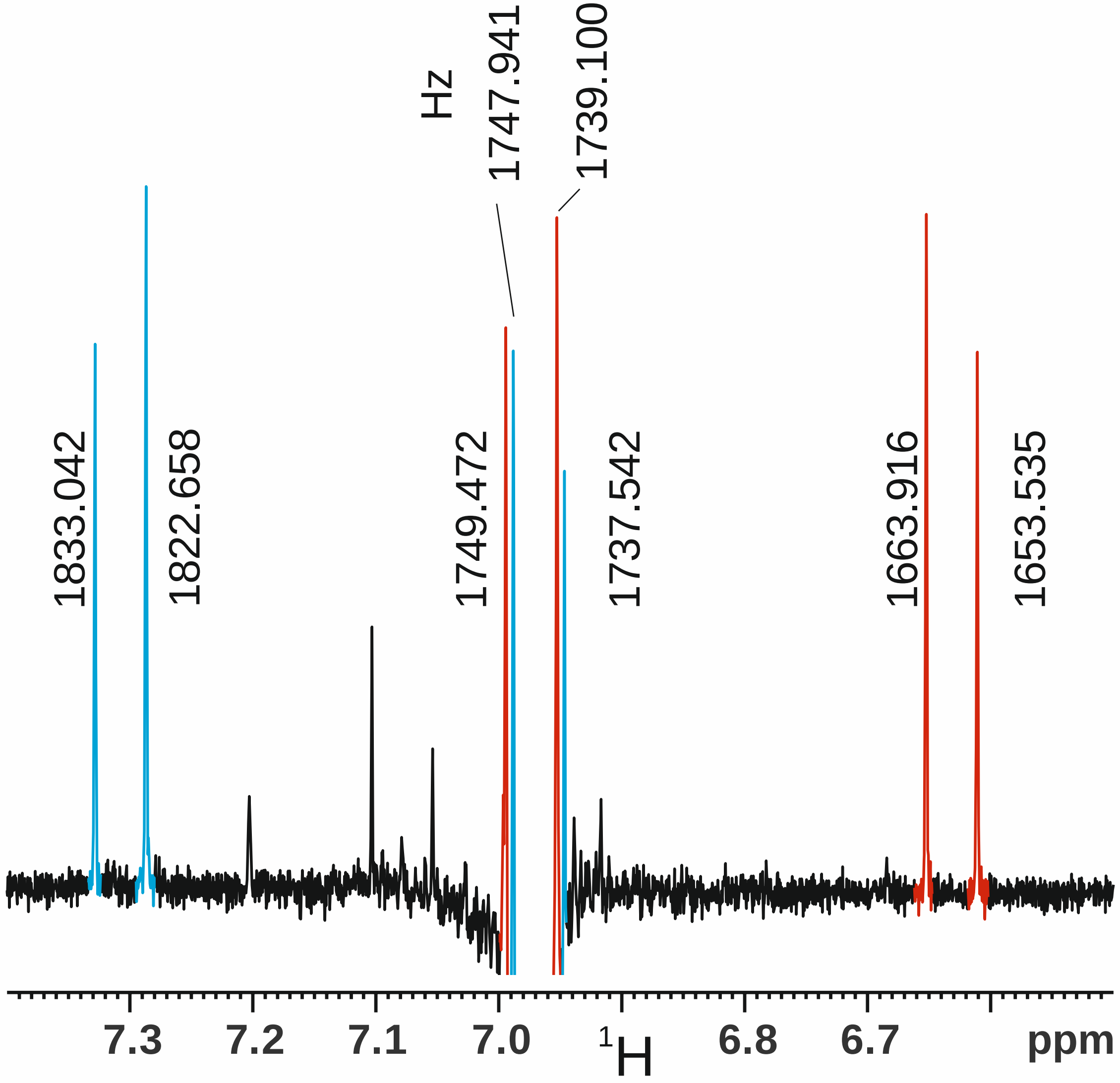


Solving the **AB** part of the **ABX** spin system (the full mathematics is available as an appendix) results in two possible solutions.

Even not being able to see the **X** part, we easily can exclude the first solution.



The reason for presenting chemical shifts on the Hz scale is the small difference between the two values, which is not visible in the ppm scale.



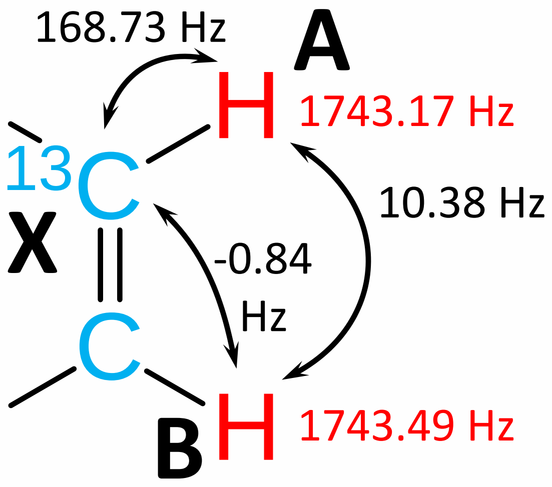
Some theory about the ABX spin system

A last question?

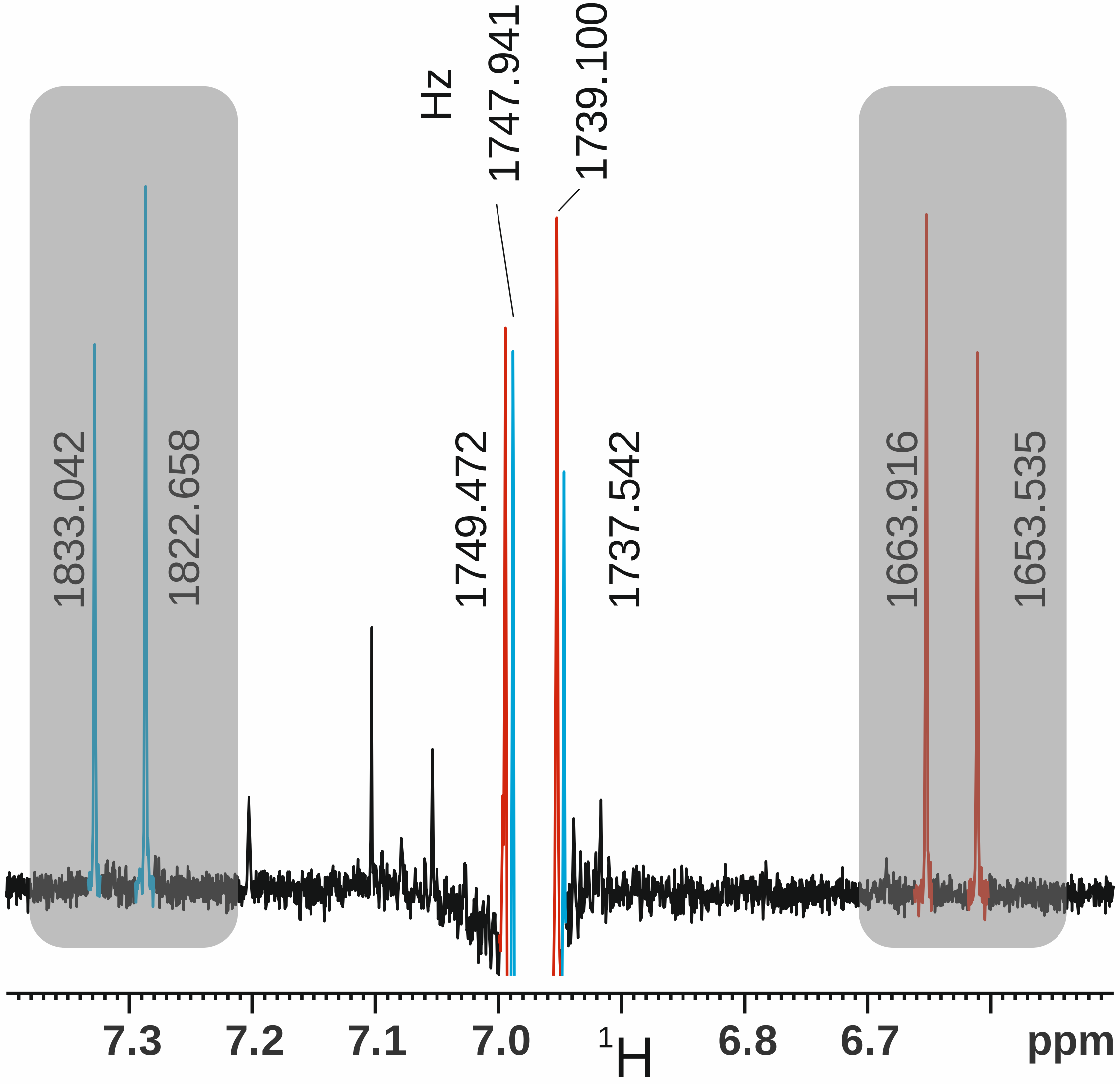
Are we able to simply extract $^1J_{AX}$ from these lines?

No!

Because it looks as though both J_{BX} and the chemical shift difference between **A** and **B** are very low in our case (we would end with J = 168.81 Hz), but each pair of lines corresponds to a different orientation of the **B** spin. The difference doesn‘t reveal the desired information directly.



(If it is still confusing, the last paragraph on page 1 of the first appendix may also be helpful for understanding.)

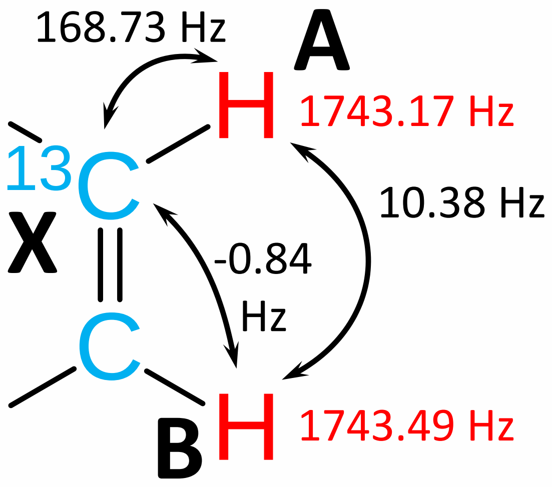


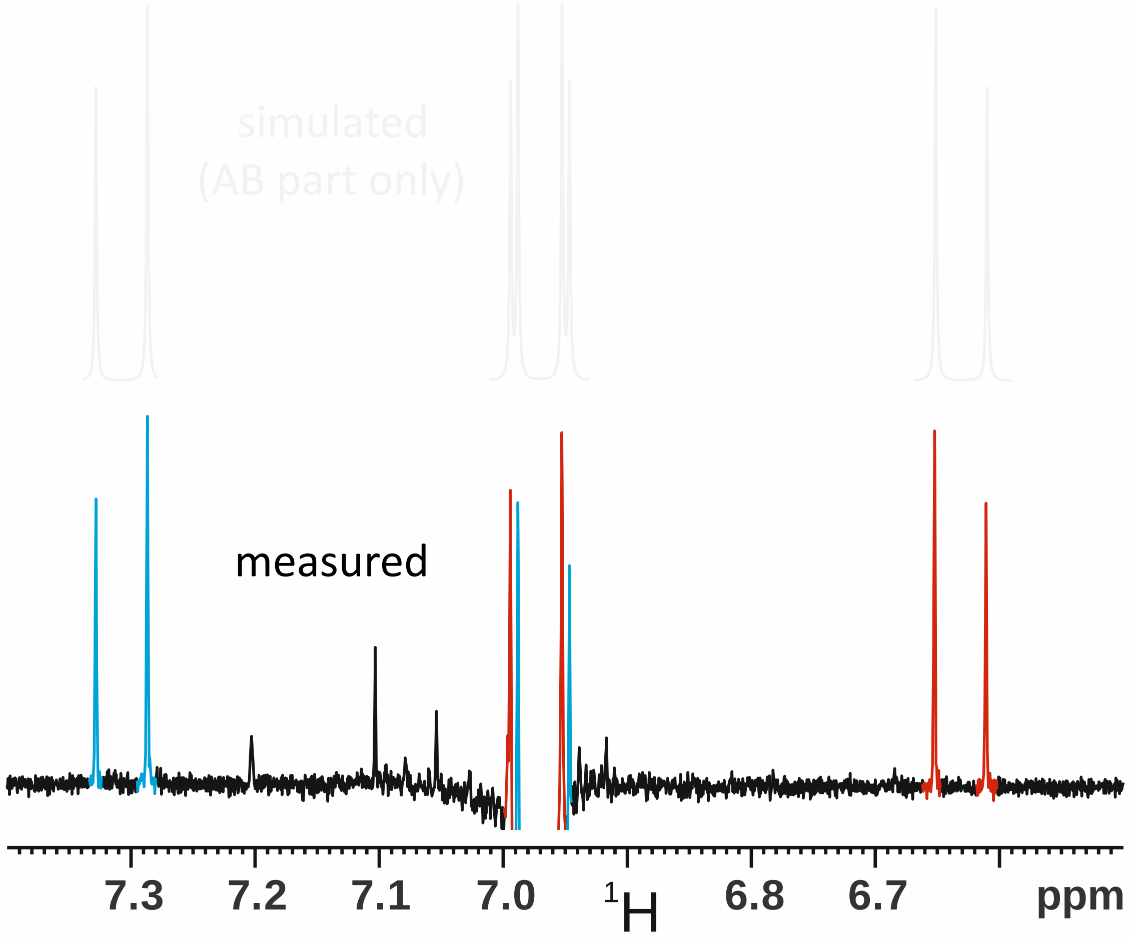
Some theory about the ABX spin system

Correct analysis?

We cannot see the **X** part of the spin system. But to check our calculated coupling constants it is sufficient to assume the absolute frequency of the **X** nucleus at about 25% of the chemical shifts for the protons.

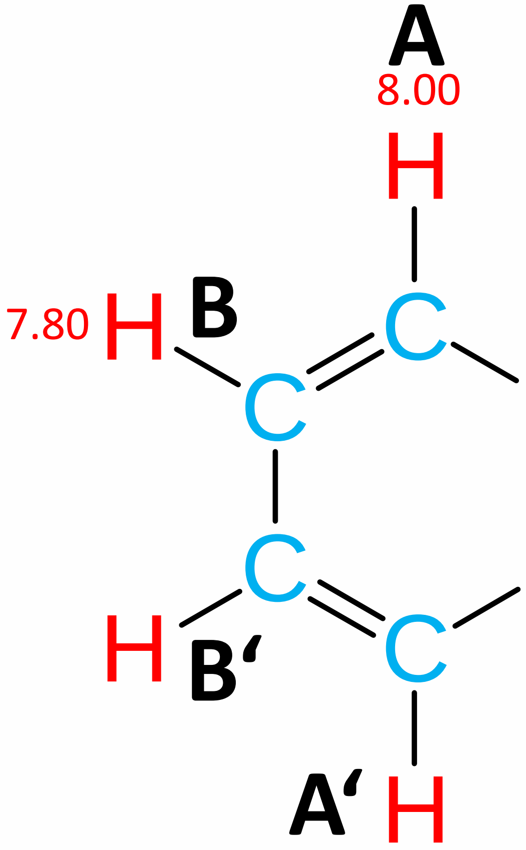
(Please don‘t calculate 25% from 1743 Hz …
You still have to add the frequency of the reference signal, resulting in about 250.132 MHz)





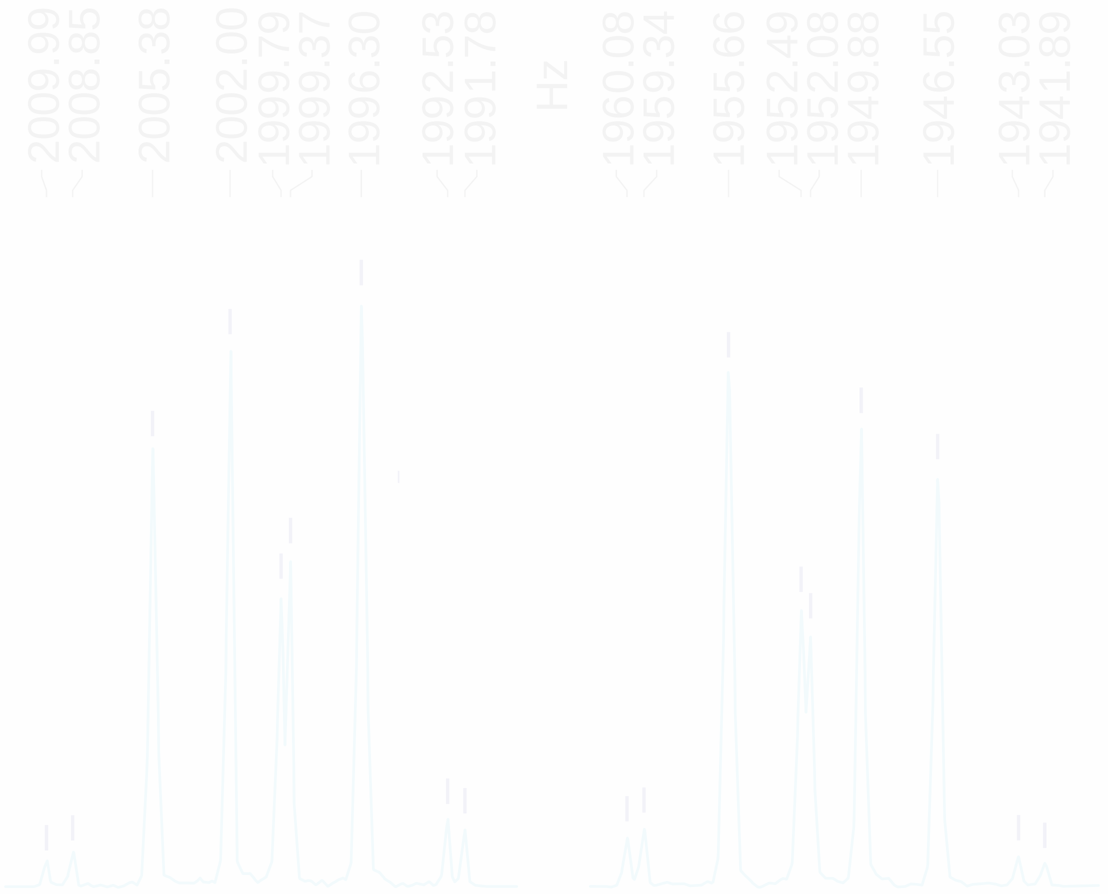
Proton proton coupling constants

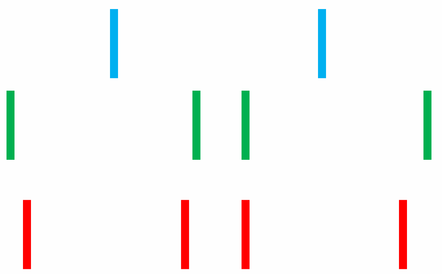
The second ring



The spin system of the remaining four protons is of the type AA‘BB‘.

There is an analytical solution available for the AA‘XX‘ type (see appendix).
Let us try to use this solution for our spectrum. After extracting the values we may simulate our spectrum and maybe some fine tuning is sufficient to get the final parameters.

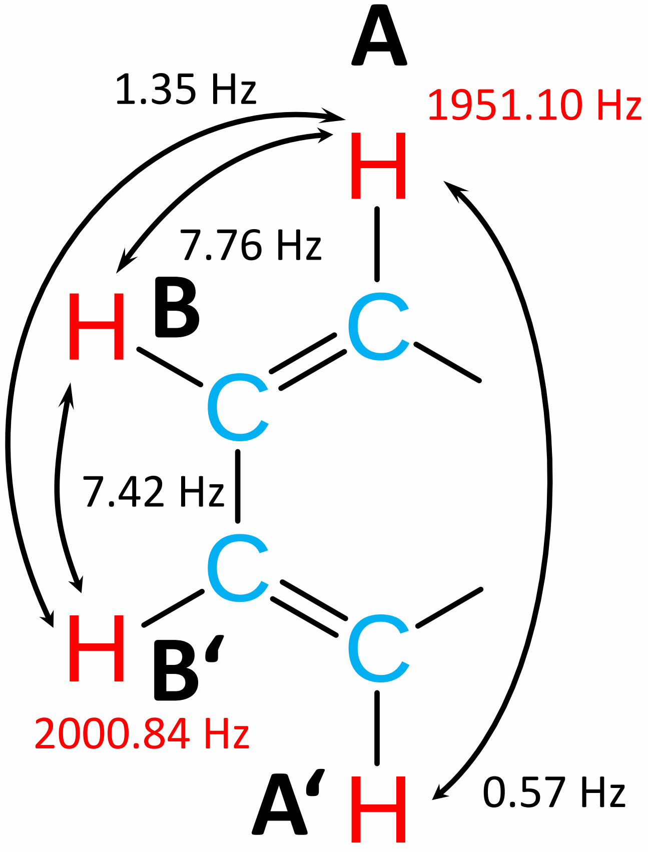




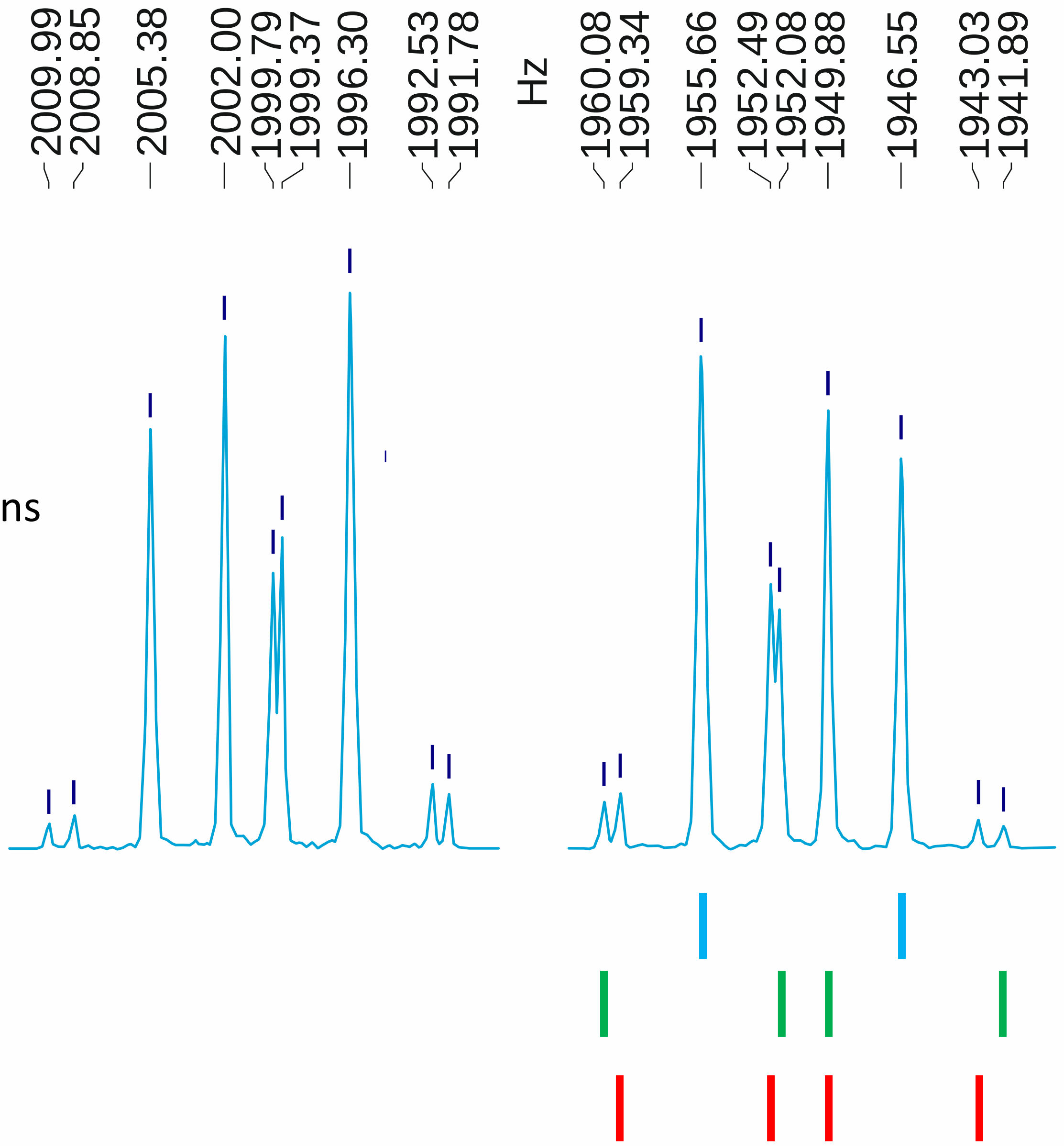
To do the calculations described in the appendix you have to recognize three groups of signals. Without some training in pattern recognition this is a little bit difficult. That‘s why the necessary signals groups are labelled here using three different colours.

Proton proton coupling constants

The second ring

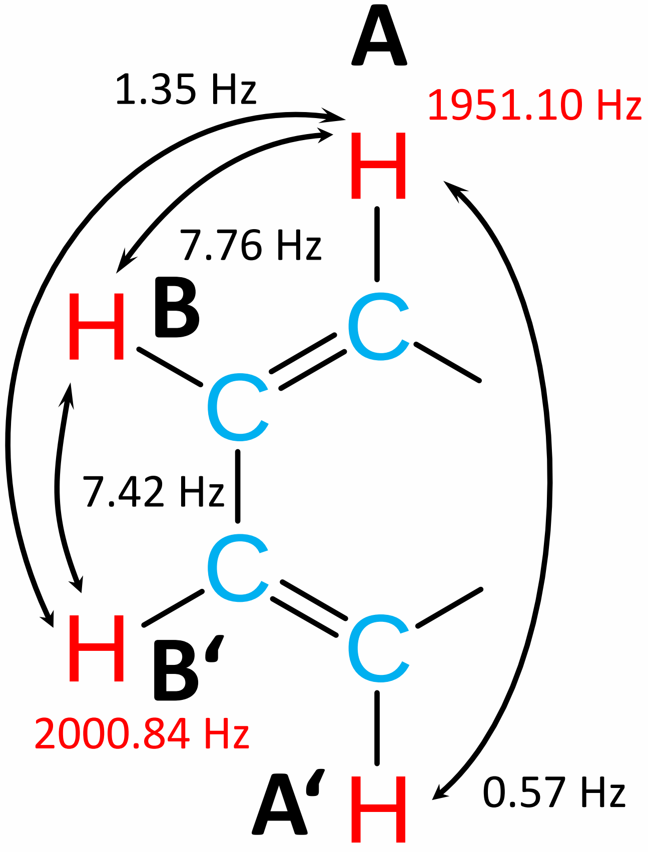


Using the formalism presented as appendix to analyze AA‘XX‘ patterns we end in four coupling constants and two chemical shifts.

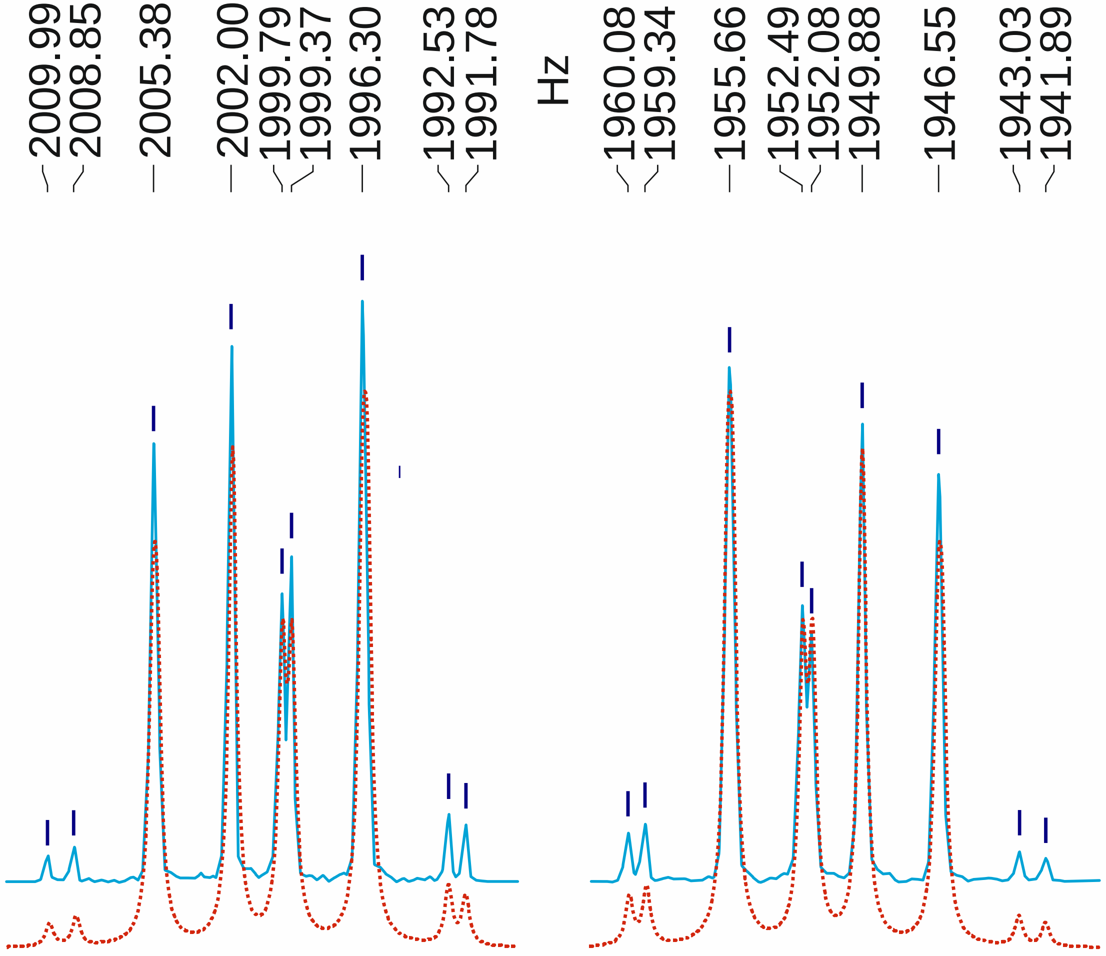


Proton proton coupling constants

The second ring



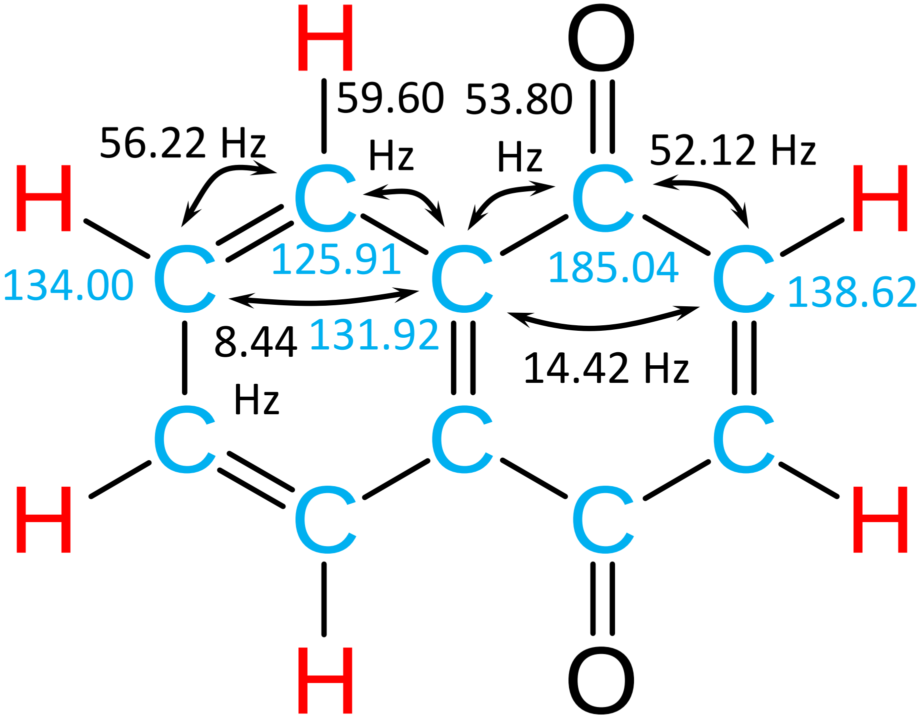
And with only minor modification of both chemical shifts, the simulation of the spin system using those parameters is perfect.



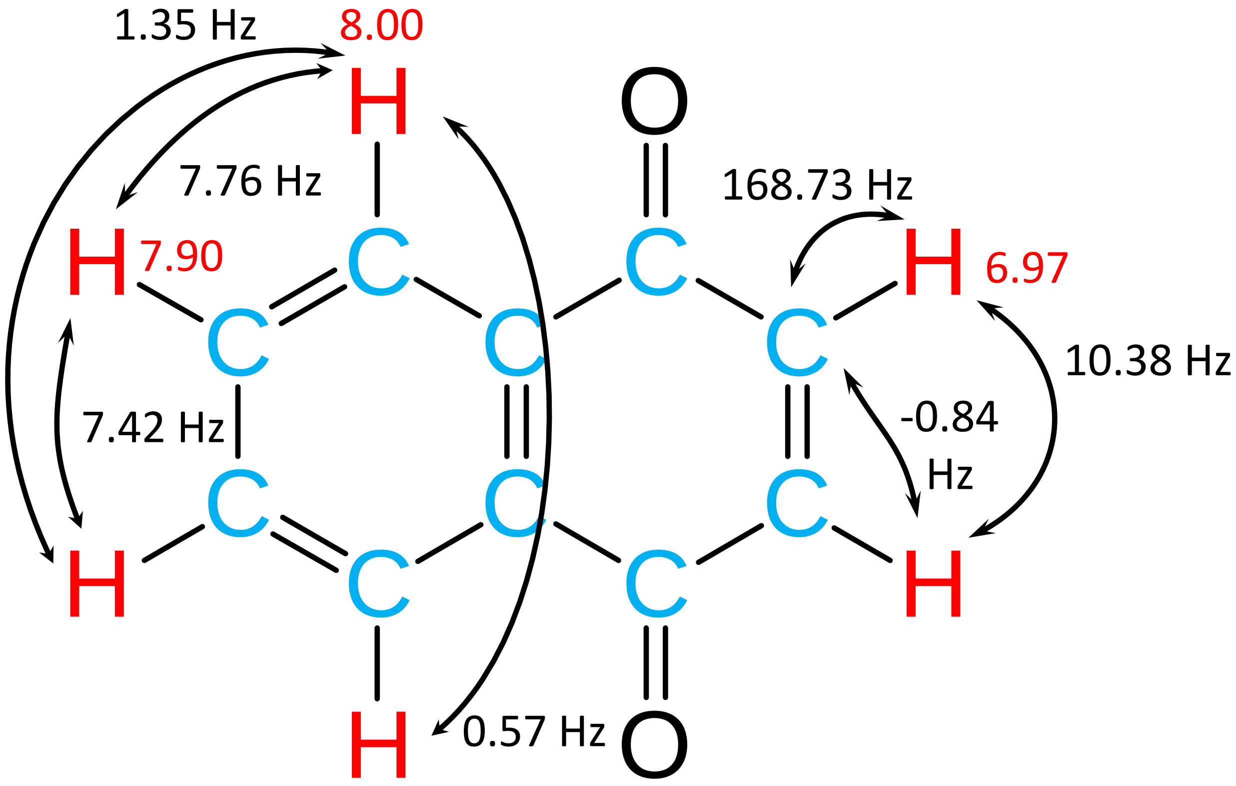
2000.84 Hz
->
2000.54 Hz

1591.10 Hz
->
1591.40 Hz

Summary

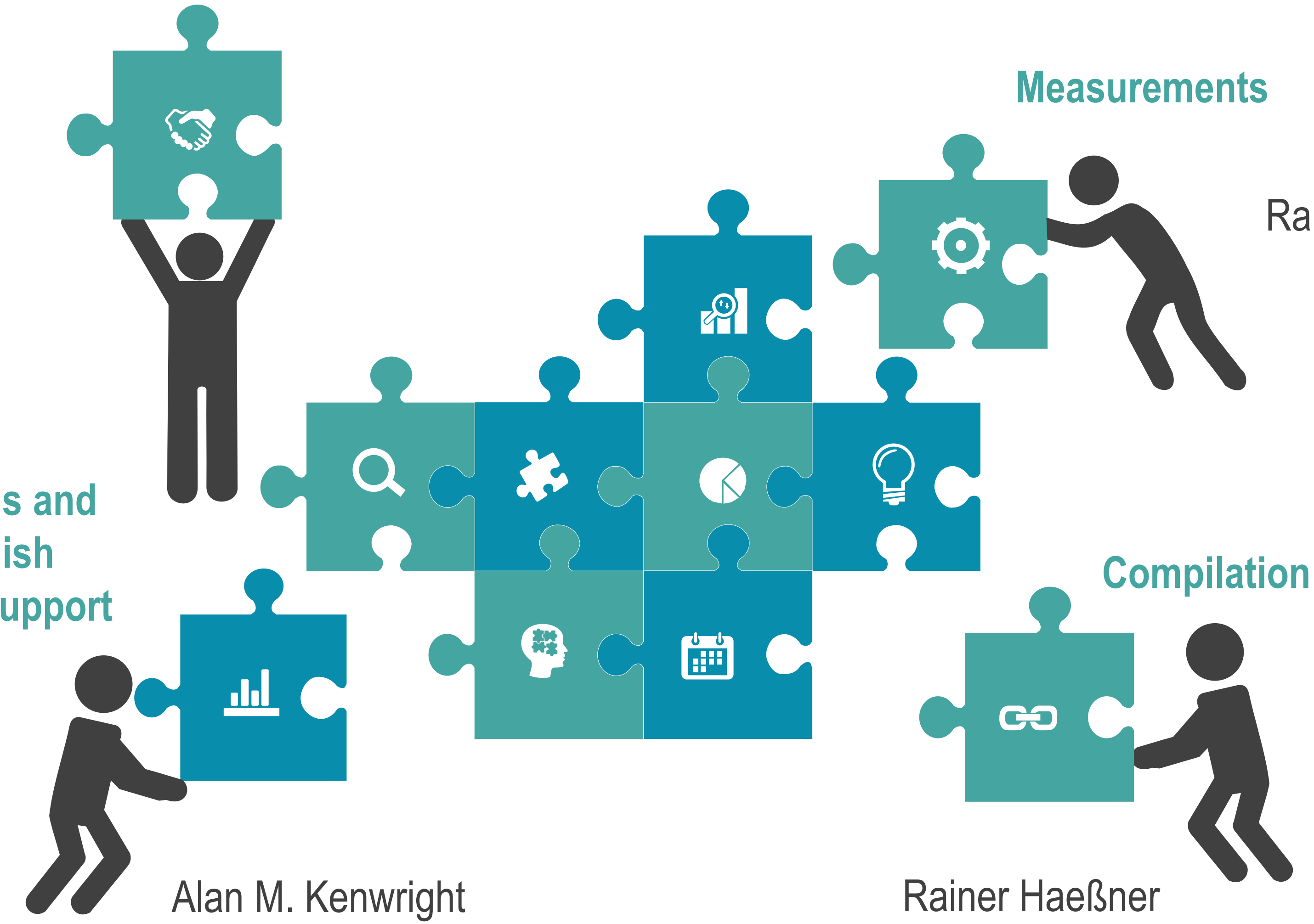


H
O
59.60 Hz
53.80 Hz
56.22 Hz
52.12 Hz
H
C
C
H
134.00
125.91
185.04
138.62
C
C
C
8.44 Hz
131.92
14.42 Hz
C
C
C
H
C
C
H
H
O



1.35 Hz
8.00
H
O
7.76 Hz
168.73 Hz
H
7.90
C
C
H
6.97
C
C
C
10.38 Hz
7.42 Hz
-0.84 Hz
C
C
C
H
C
C
H
H
0.57 Hz
O

Contributions



Spectrometer time

TU Munich

Measurements

Rainer Haeßner

Discussions and native English language support

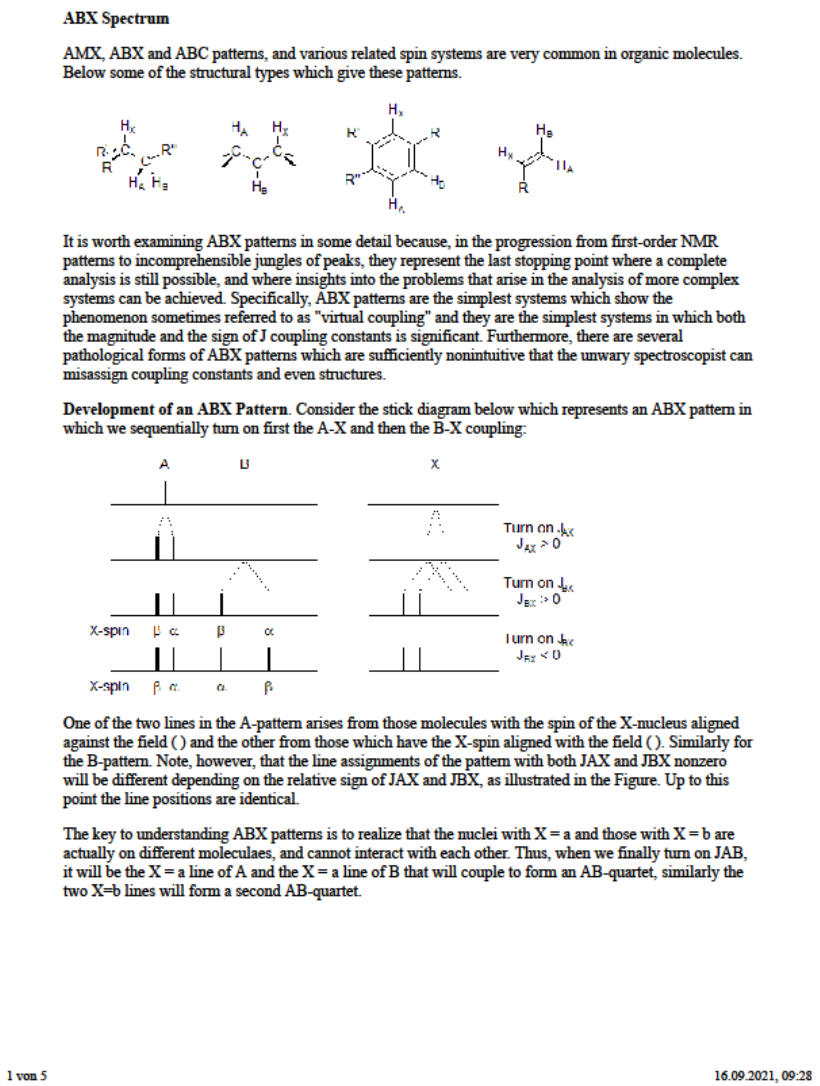
Alan M. Kenwright

Compilation

Rainer Haeßner

Appendix

ABX spin system



ABX Spectrum

AMX, ABX and ABC patterns, and various related spin systems are very common in organic molecules. Below some of the structural types which give these patterns.

It is worth examining ABX patterns in some detail because, in the progression from first-order NMR patterns to incomprehensible jungles of peaks, they represent the last stopping point where a complete analysis is still possible, and where insights into the problems that arise in the analysis of more complex systems can be achieved. Specifically, ABX patterns are the simplest systems which show the phenomenon sometimes referred to as "virtual coupling" and they are the simplest systems in which both the magnitude and the sign of J coupling constants is significant. Furthermore, there are several pathological forms of ABX patterns which are sufficiently nonintuitive that the unwary spectroscopist can misassign coupling constants and even structures.

Development of an ABX Pattern. Consider the stick diagram below which represents an ABX pattern in which we sequentially turn on first the A-X and then the B-X coupling:

One of the two lines in the A-pattern arises from those molecules with the spin of the X-nucleus aligned against the field ( ) and the other from those which have the X-spin aligned with the field ( ). Similarly for the B-pattern. Note, however, that the line assignments of the pattern with both JAX and JBX nonzero will be different depending on the relative sign of JAX and JBX, as illustrated in the Figure. Up to this point the line positions are identical.

The key to understanding ABX patterns is to realize that the nuclei with X = a and those with X = b are actually on different moleculaes, and cannot interact with each other. Thus, when we finally turn on JAB, it will be the X = a line of A and the X = a line of B that will couple to form an AB-quartet, similarly the two X=b lines will form a second AB-quartet.

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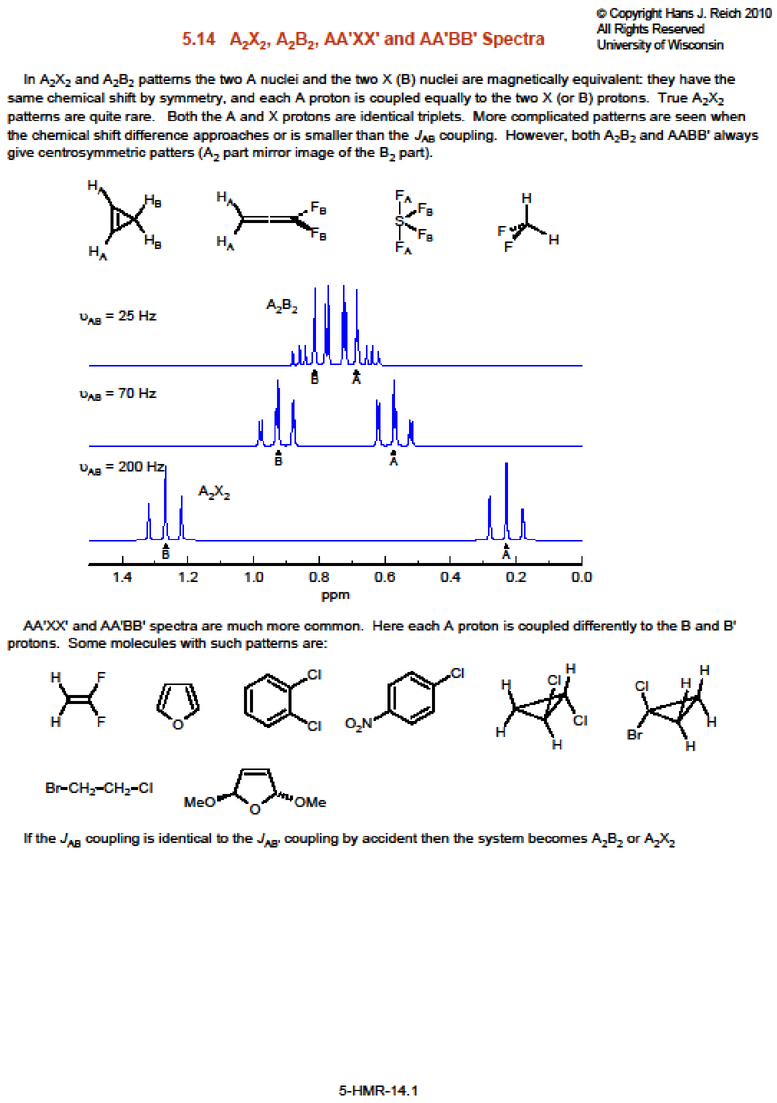
AA‘XX‘ spin system



5.14 A_2X_2, A_2B_2, AA'XX' and AA'BB' Spectra

In A_2X_2 and A_2B_2 patterns the two A nuclei and the two X (B) nuclei are magnetically equivalent: they have the same chemical shift by symmetry, and each A proton is coupled equally to the two X (or B) protons. True A_2X_2 patterns are quite rare. Both the A and X protons are identical triplets. More complicated patterns are seen when the chemical shift difference approaches or is smaller than the J_{AB} coupling. However, both A_2B_2 and AABB' always give centrosymmetric patters (A_2 part mirror image of the B_2 part).

AA'XX' and AA'BB' spectra are much more common. Here each A proton is coupled differently to the B and B' protons. Some molecules with such patterns are:

If the J_{AB} coupling is identical to the $J_{AB'}$ coupling by accident then the system becomes A_2B_2 or A_2X_2