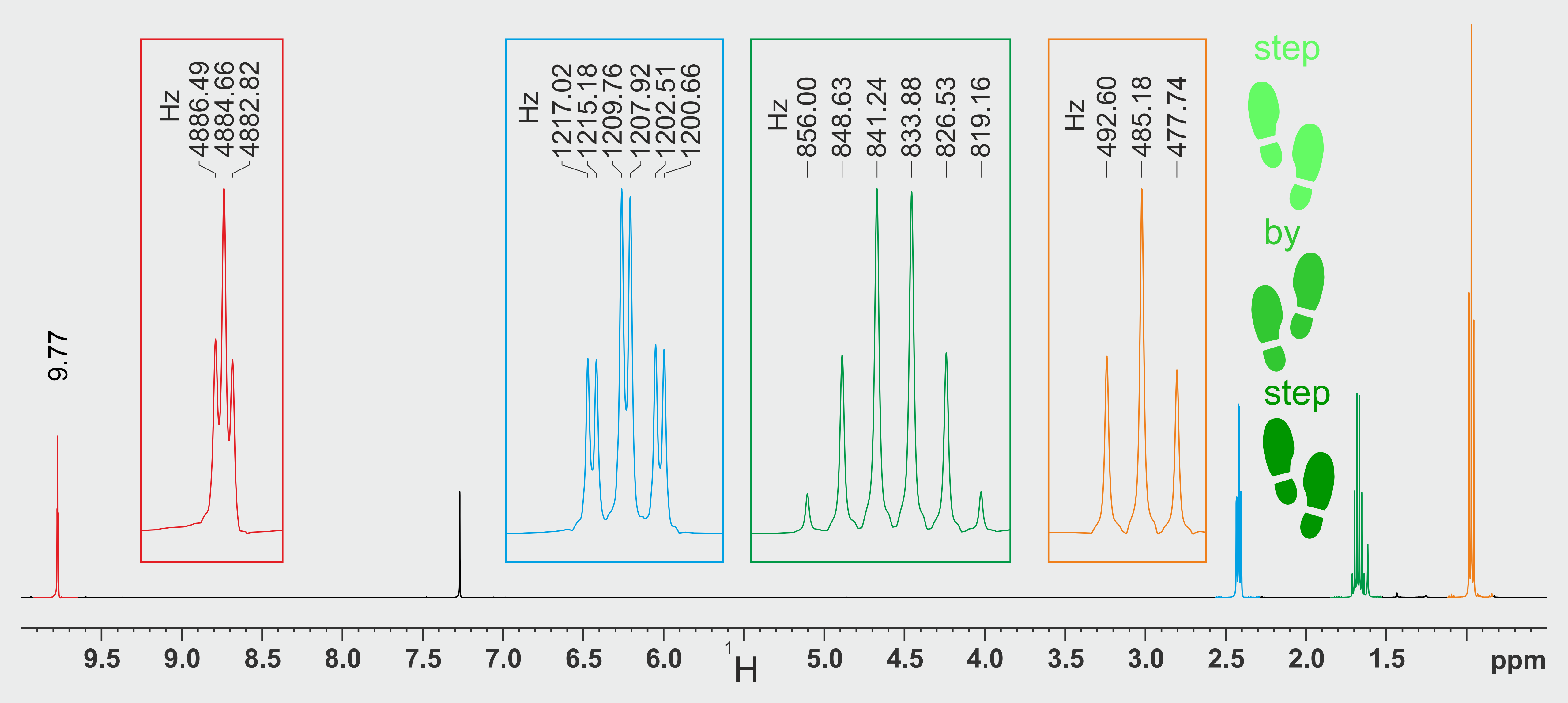
Exercise plus Solution – Quick PDF overview

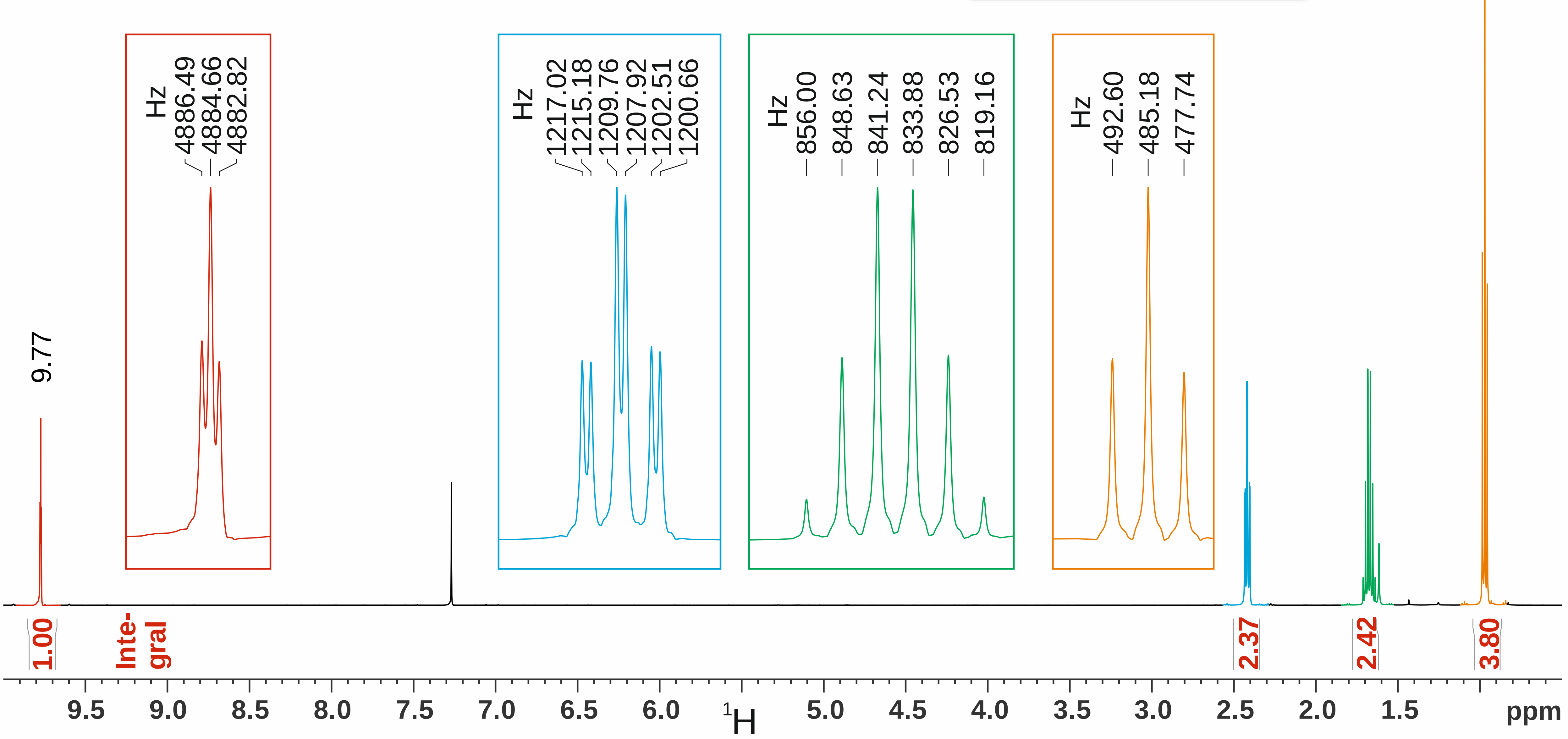
It is recommended to use this PDF version only for a quick overview of the NMR challenge. All animations of the PowerPoint version are missing, under certain circumstances quality deficiencies may also occur.
The higher quality PowerPoint files are freely available for download at any time.

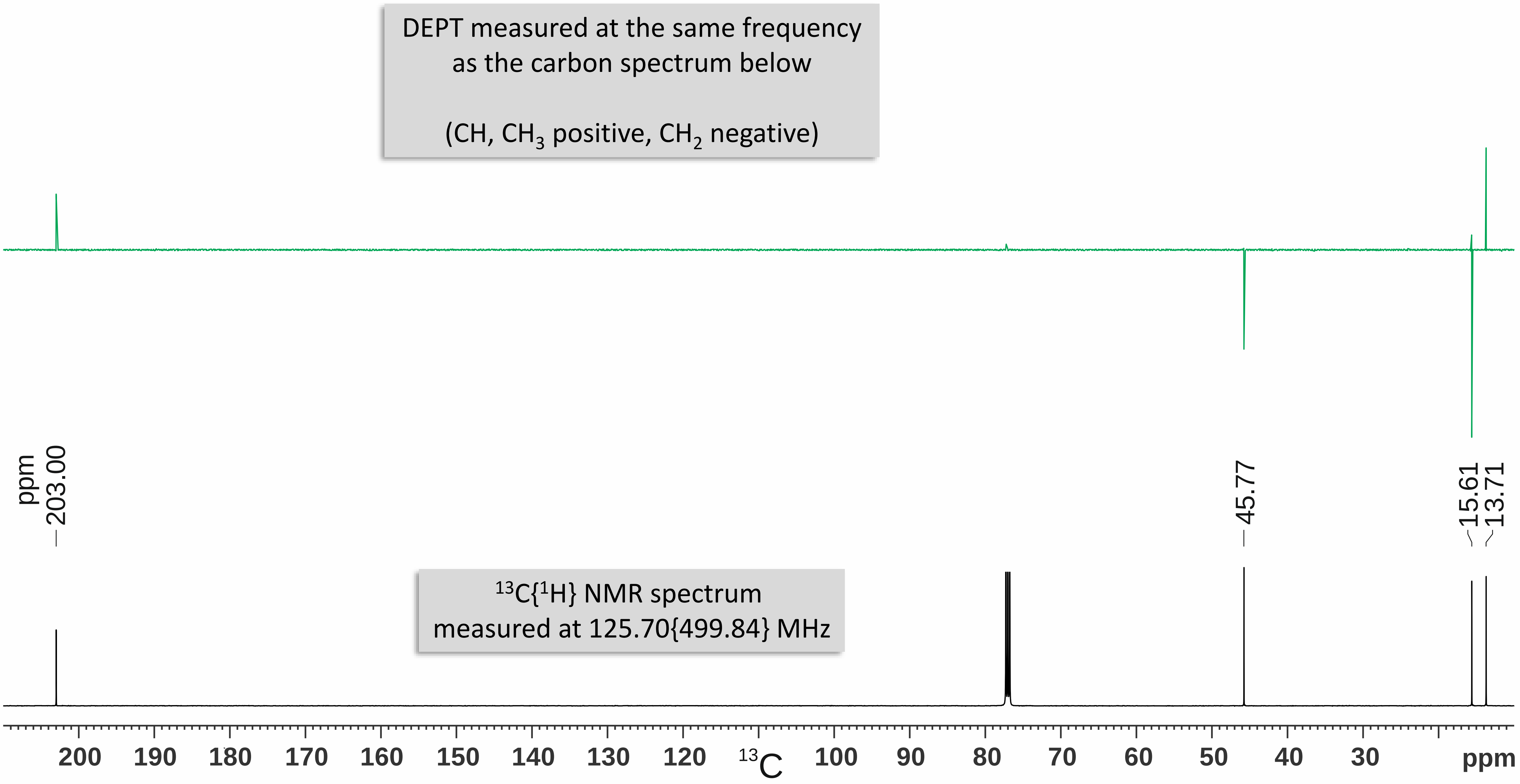


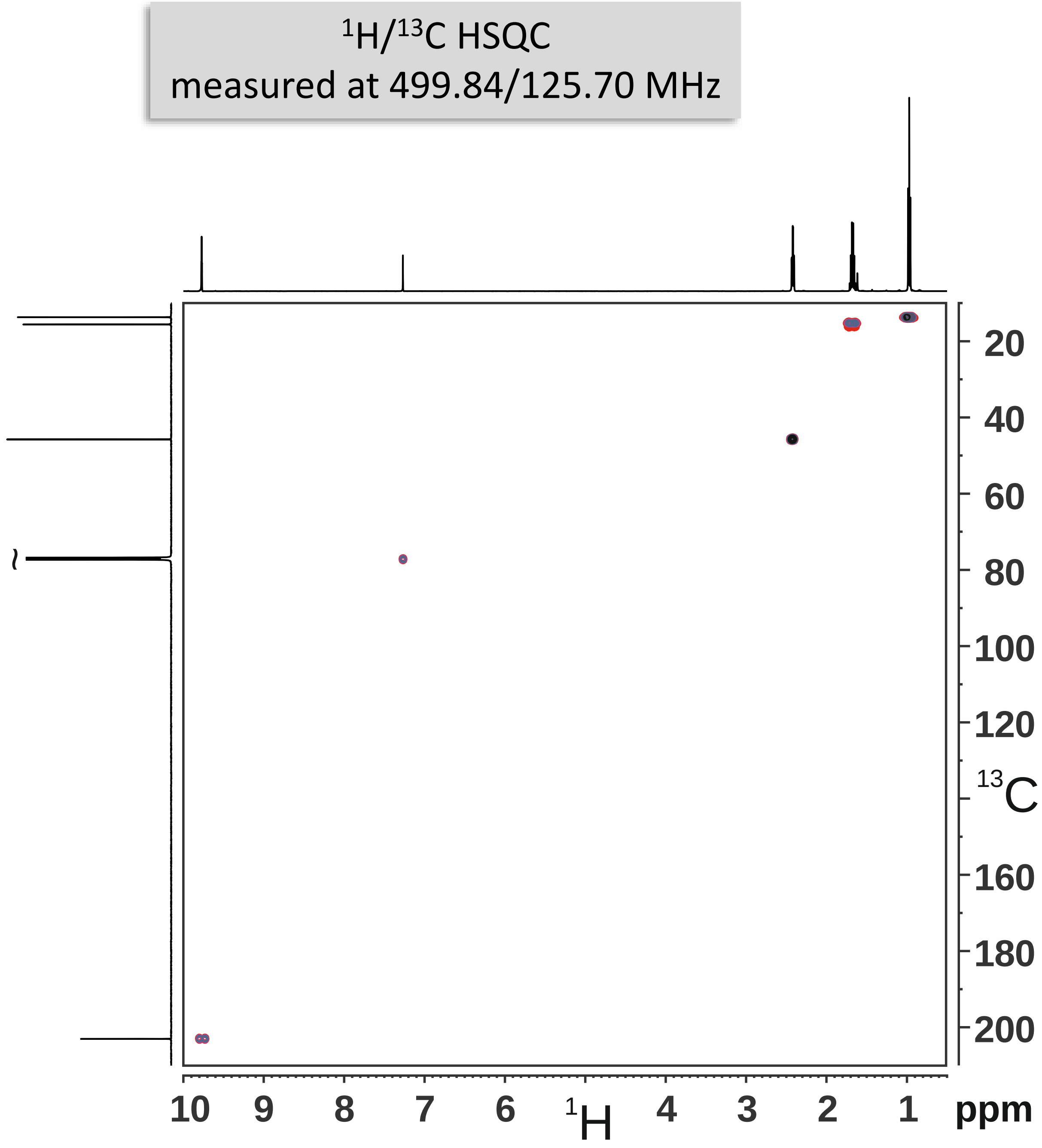
C_4H_8O measured in $CDCl_3$

Deduce the structure!

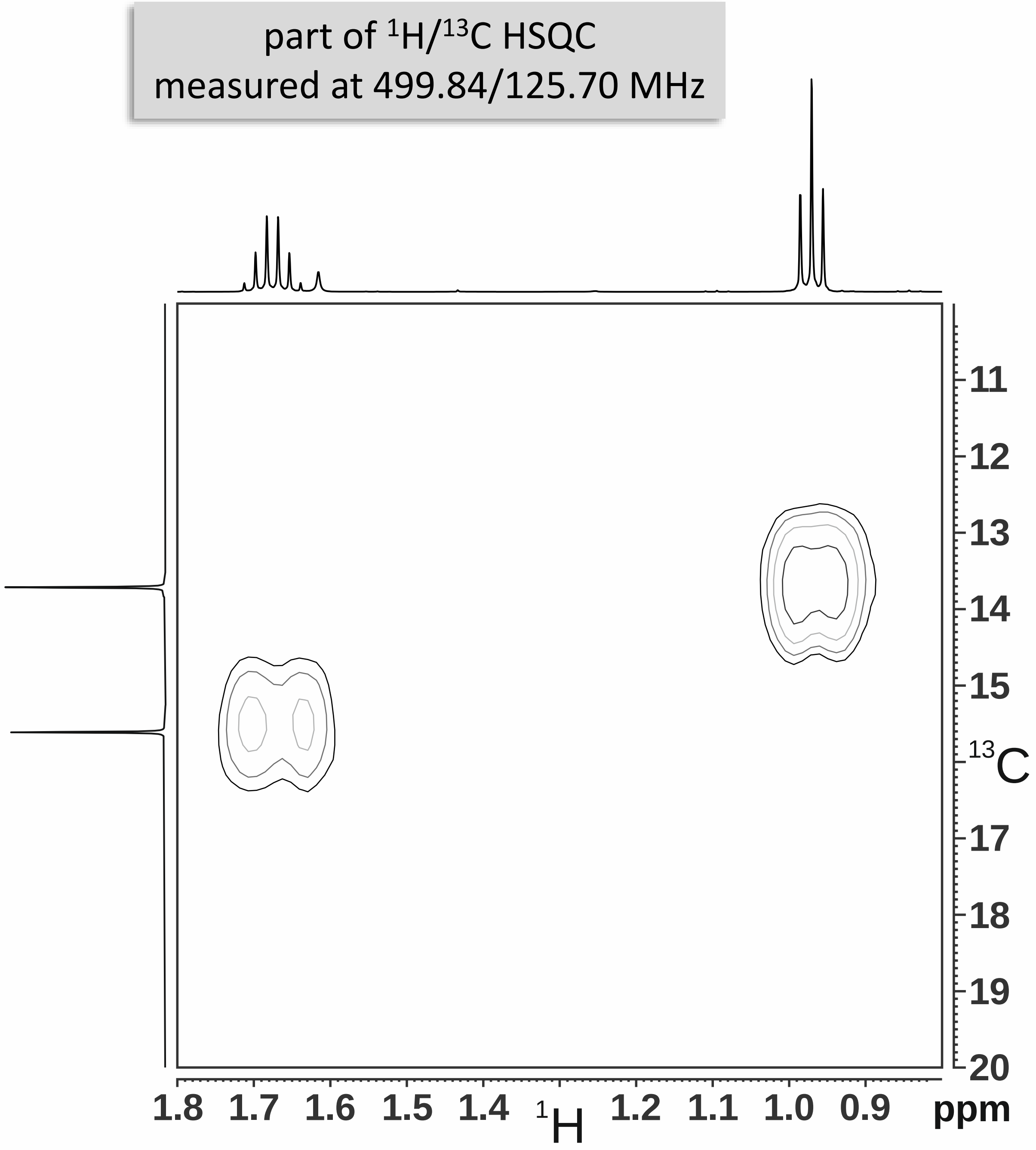
^{1}H NMR spectrum
measured at 499.84 MHz



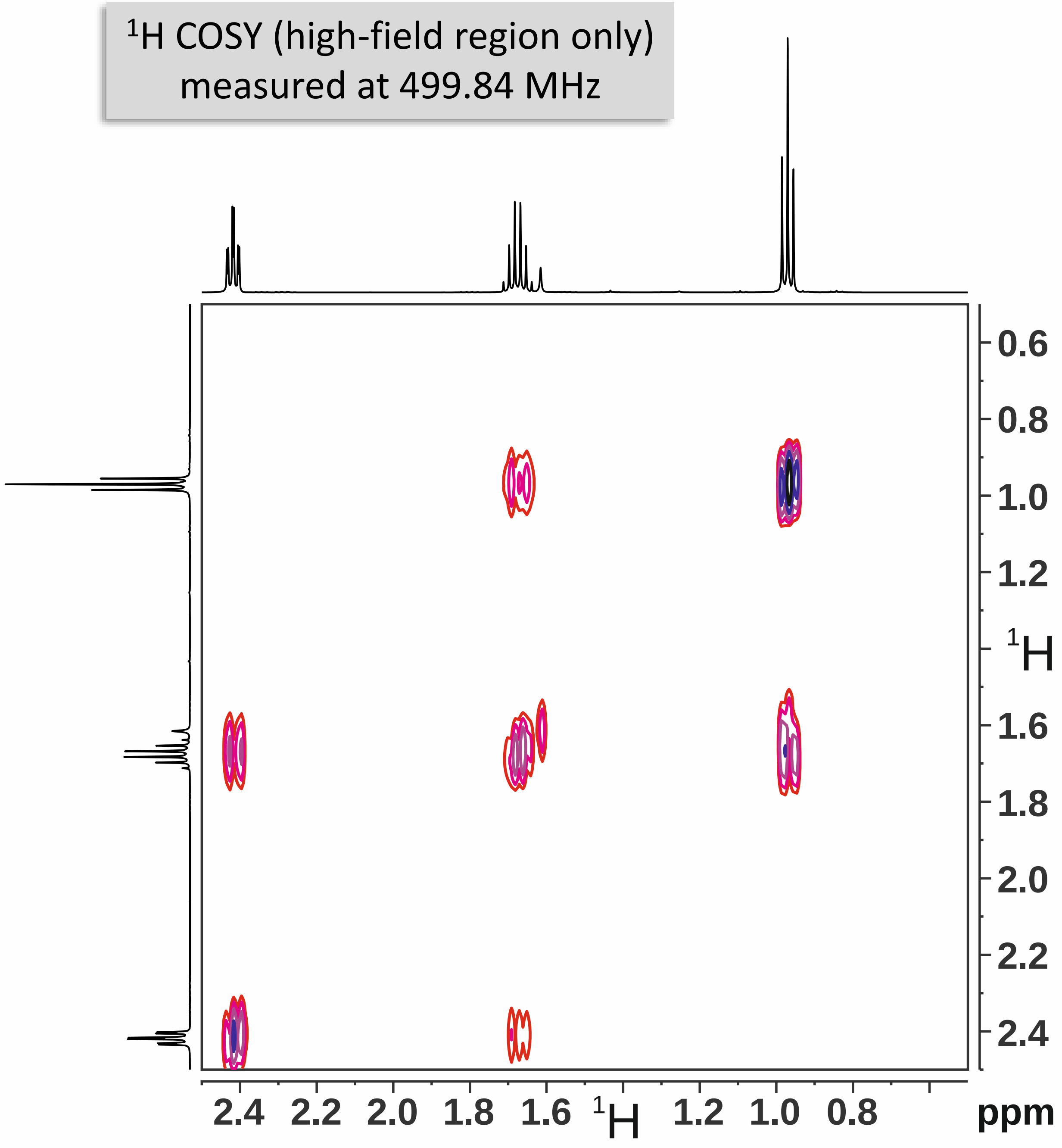

DEPT measured at the same frequency as the carbon spectrum below
(CH, CH3 positive, CH2 negative)
ppm
203.00
45.77
15.61
13.71
13C{1H} NMR spectrum
measured at 125.70{499.84} MHz
200
190
180
170
160
150
140
130
120
13C
100
90
80
70
60
50
40
30
ppm



^{1}H/^{13}C HSQC
measured at 499.84/125.70 MHz
20
40
60
80
100
120
^{13}C
160
180
200
10
9
8
7
6
^{1}H
4
3
2
1
ppm



part of ^{1}H/^{13}C HSQC
measured at 499.84/125.70 MHz
11
12
13
14
15
^{13}C
17
18
19
20
1.8
1.7
1.6
1.5
1.4
^{1}H
1.2
1.1
1.0
0.9
ppm



^{1}H COSY (high-field region only)
measured at 499.84 MHz
0.6
0.8
1.0
1.2
^{1}H
1.6
1.8
2.0
2.2
2.4
2.4
2.2
2.0
1.8
1.6
^{1}H
1.2
1.0
0.8
ppm

Solution

Part 1 - Integration

Measured: 1.00 a.u. + 2.37 a.u. + 2.42 a.u. + 3.80 a.u. = **9.59 a.u.**

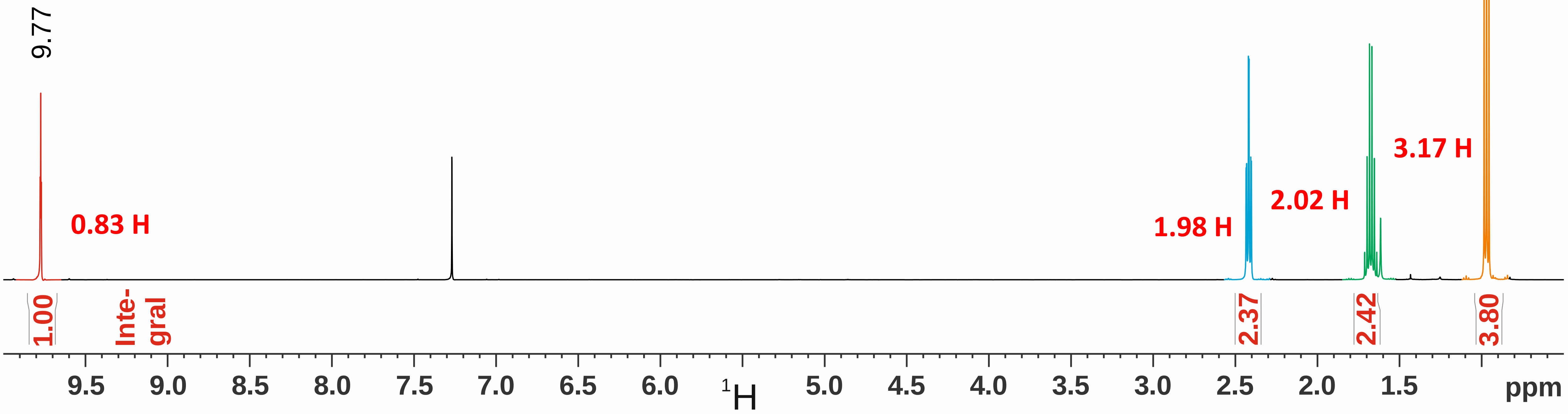
According Formula: **8H**

Ratio: **1.2 a.u. / H**

a.u. ???

arbitrary units

This depends on the output device and your home country. For example, using a tablet in Europe, you could think about "**centimeters**".



Solution

Part 1 - Integration

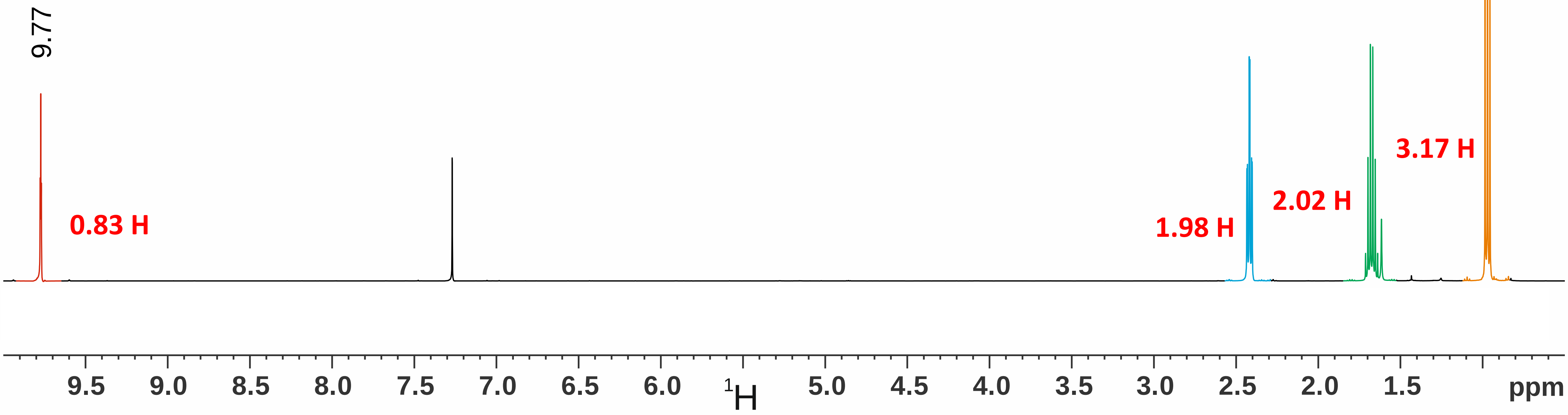
After rounding to whole numbers, the integral ratio becomes

1 : 2 : 2 : 3

a.u. ???

arbitrary units

This depends on the output device and your home country. For example, using a tablet in Europe, you could think about "**centimeters**".



Solution

Part 2 – Building blocks

If available, the HSQC/HMQC is nearly always the best starting point to collect all or at least a large number of partial structures as an unordered pile of building blocks.

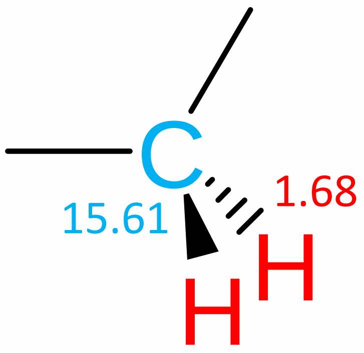
The integrals from the proton spectrum have just been determined, the chemical shifts of the carbon signals may be taken from the one-dimensional carbon spectrum.

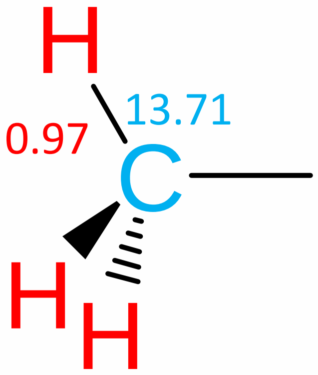
To get the average chemical shifts of the proton multiplets some basic calculations are necessary.
Example for the triplet:
(492.60 Hz + 477.74 Hz/ (2 * 499.86 MHz)

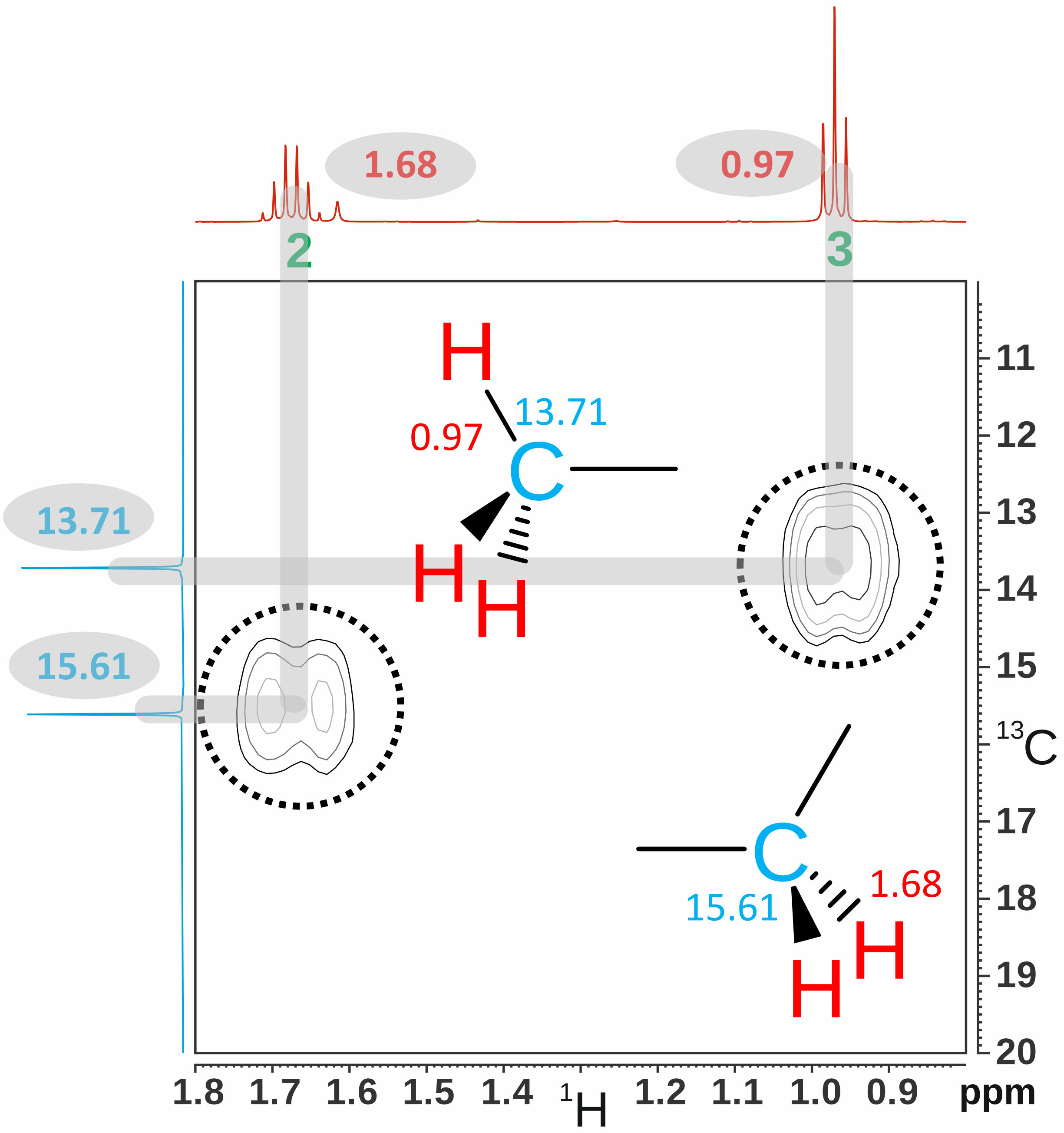
Solution

Part 2 – Building blocks

To distinguish between two cross peaks with very similar carbon chemical shifts, a selected small piece of the HSQC is helpful.



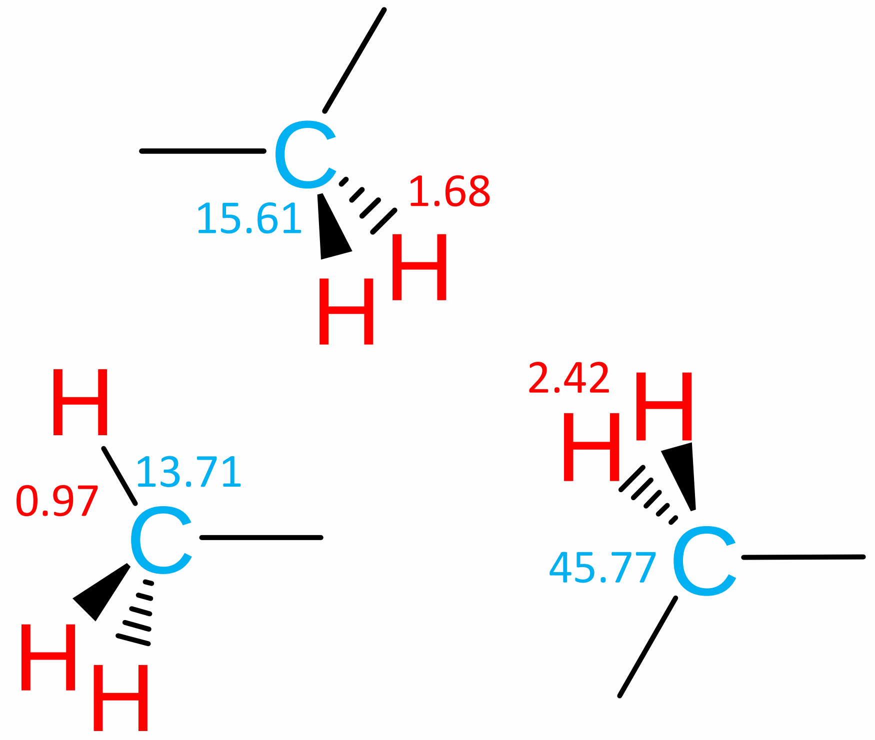


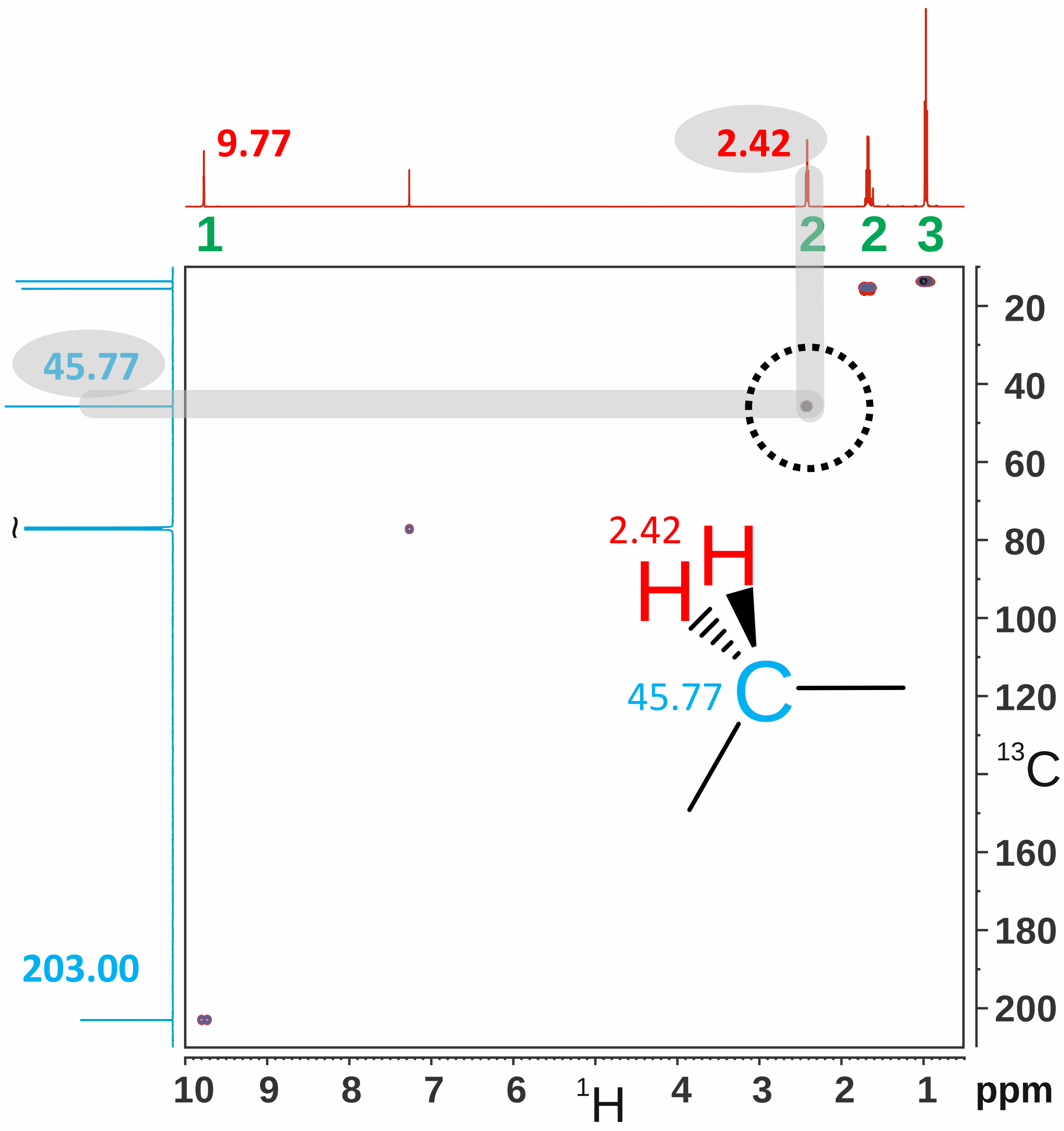


Solution

Part 2 – Building blocks

Two further cross peaks can be easily identified in the full spectrum.



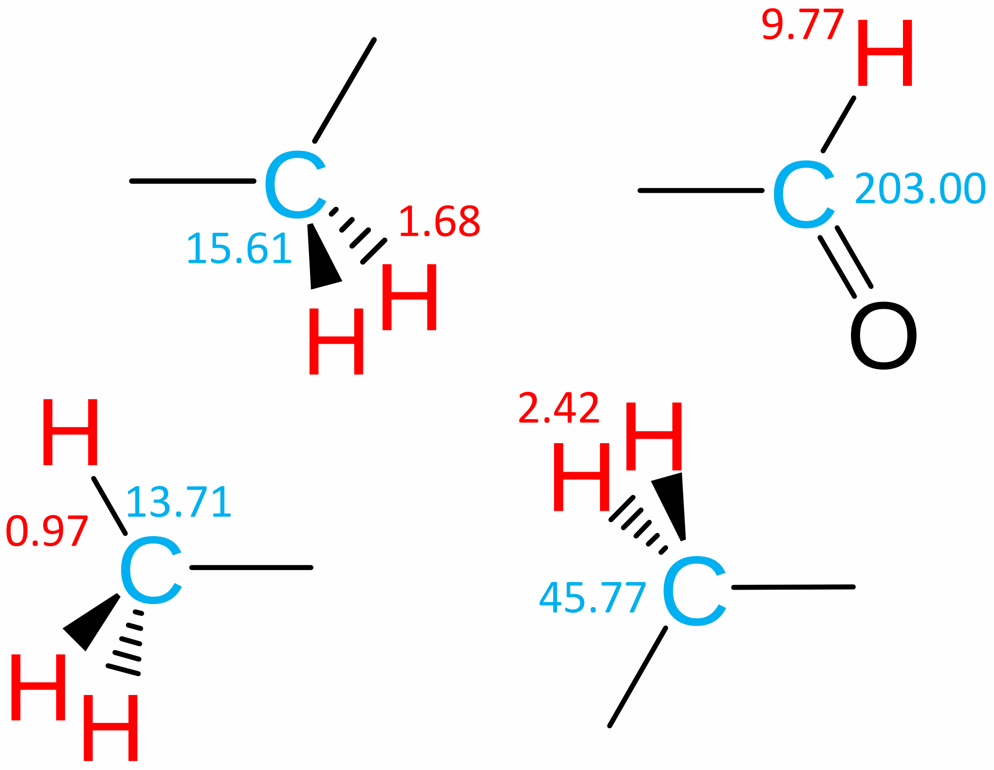


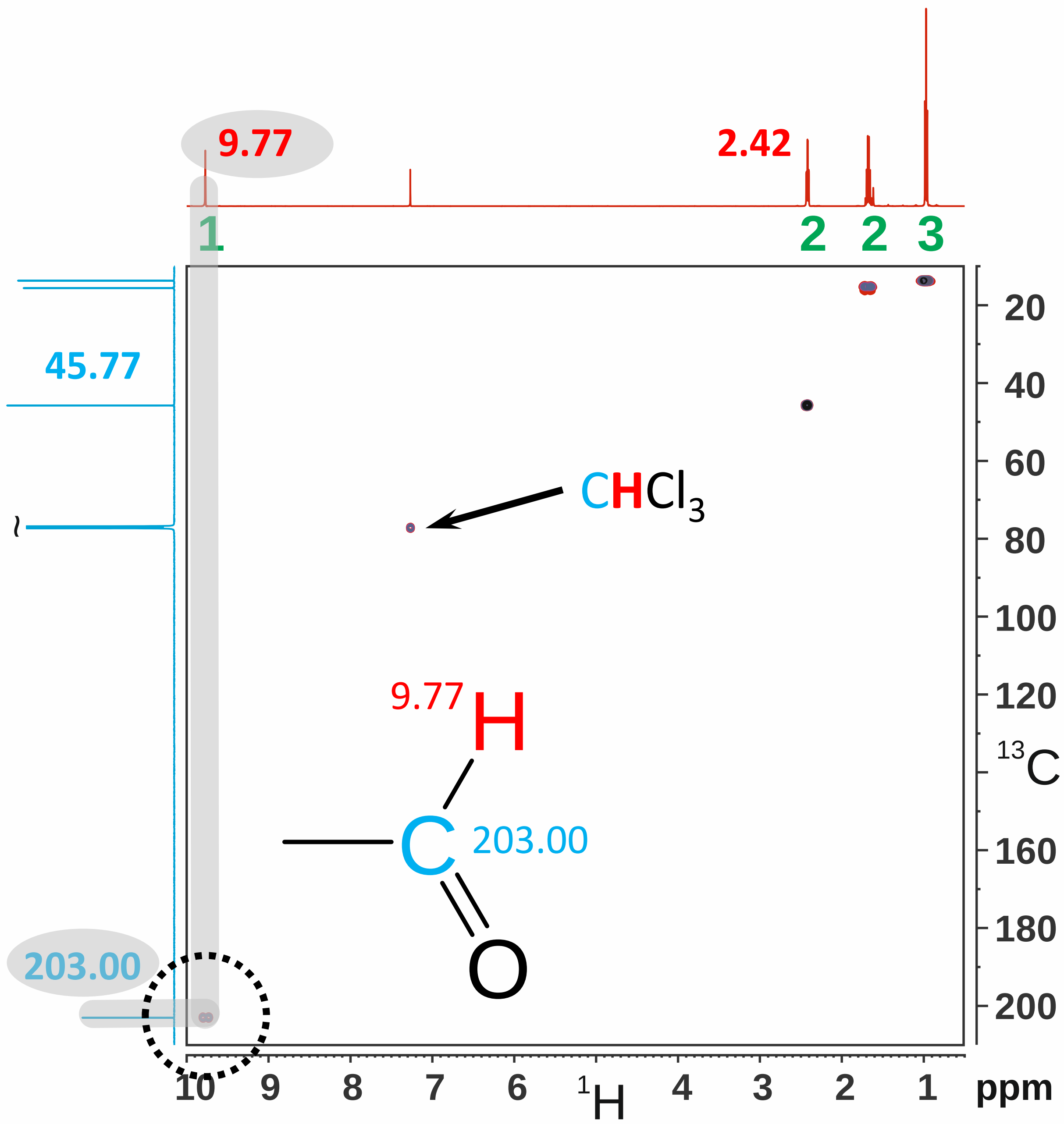
Solution

Part 2 – Building blocks

Two further cross peaks can be easily identified in the full spectrum.

The aldehyde structure results from both the still missing double bond equivalent and the very characteristic chemical shifts.

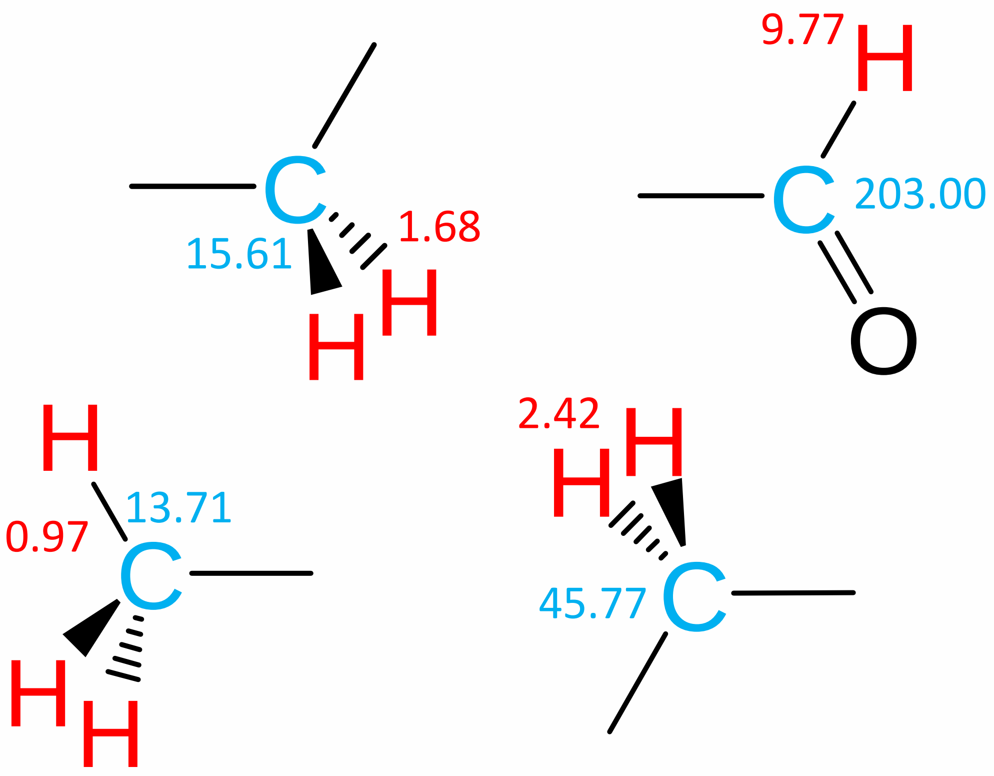




Solution

Part 3 – Bringing all together

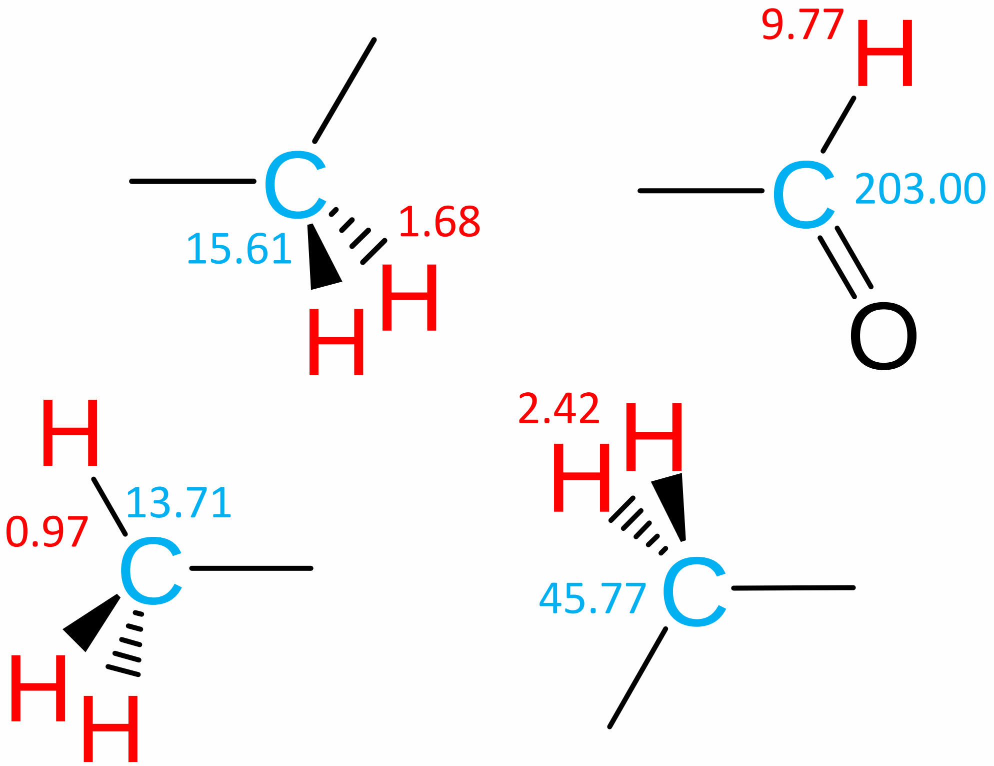
The COSY is a good way to combine the unordered collection of building blocks.

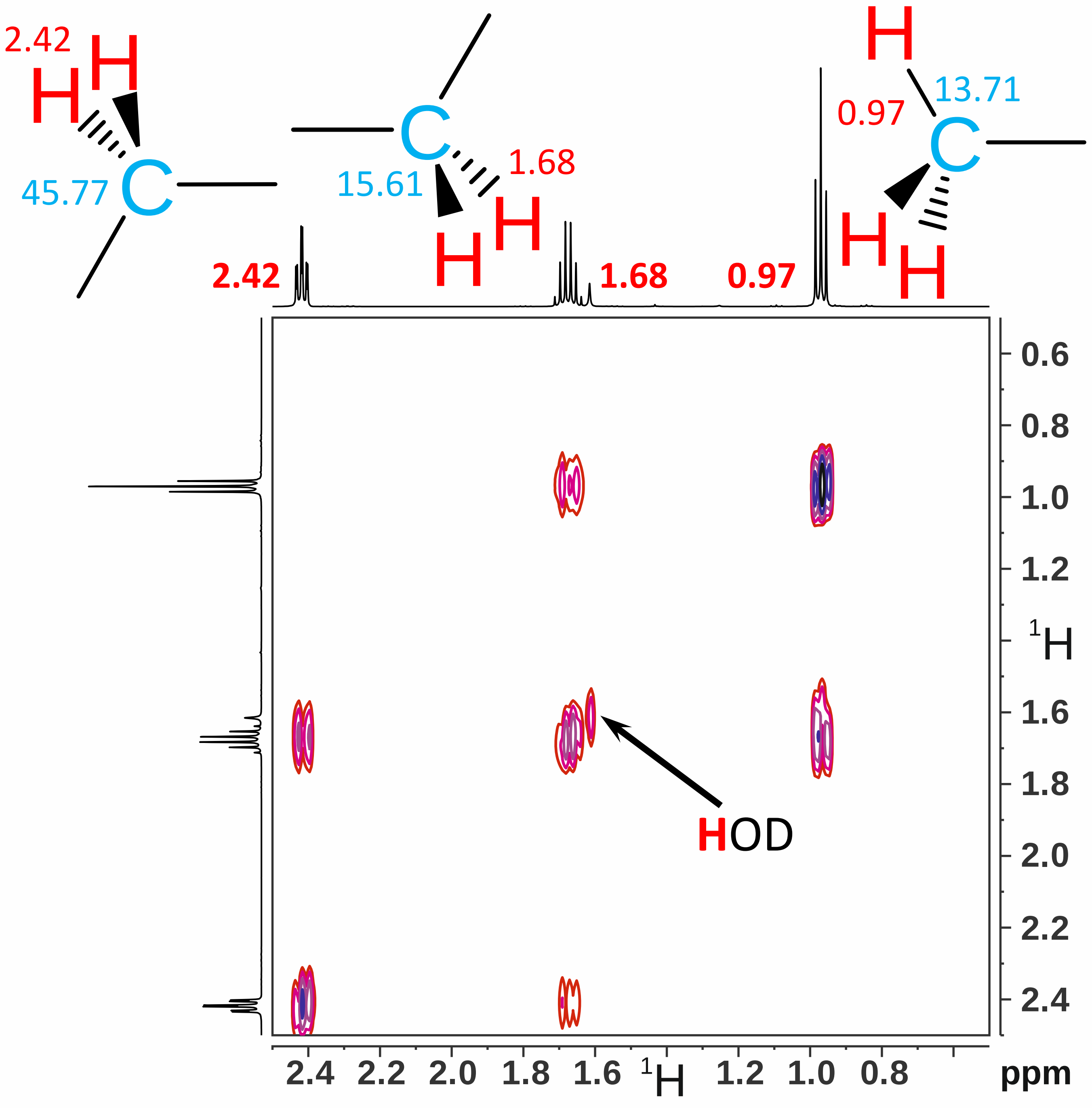


Solution

Part 3 – Bringing all together

Initially one has to order the structural fragments according to the chemical shifts of their proton signals along the projection of the COSY.

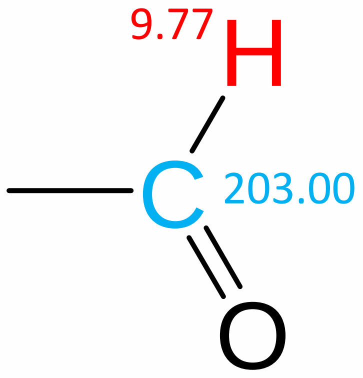


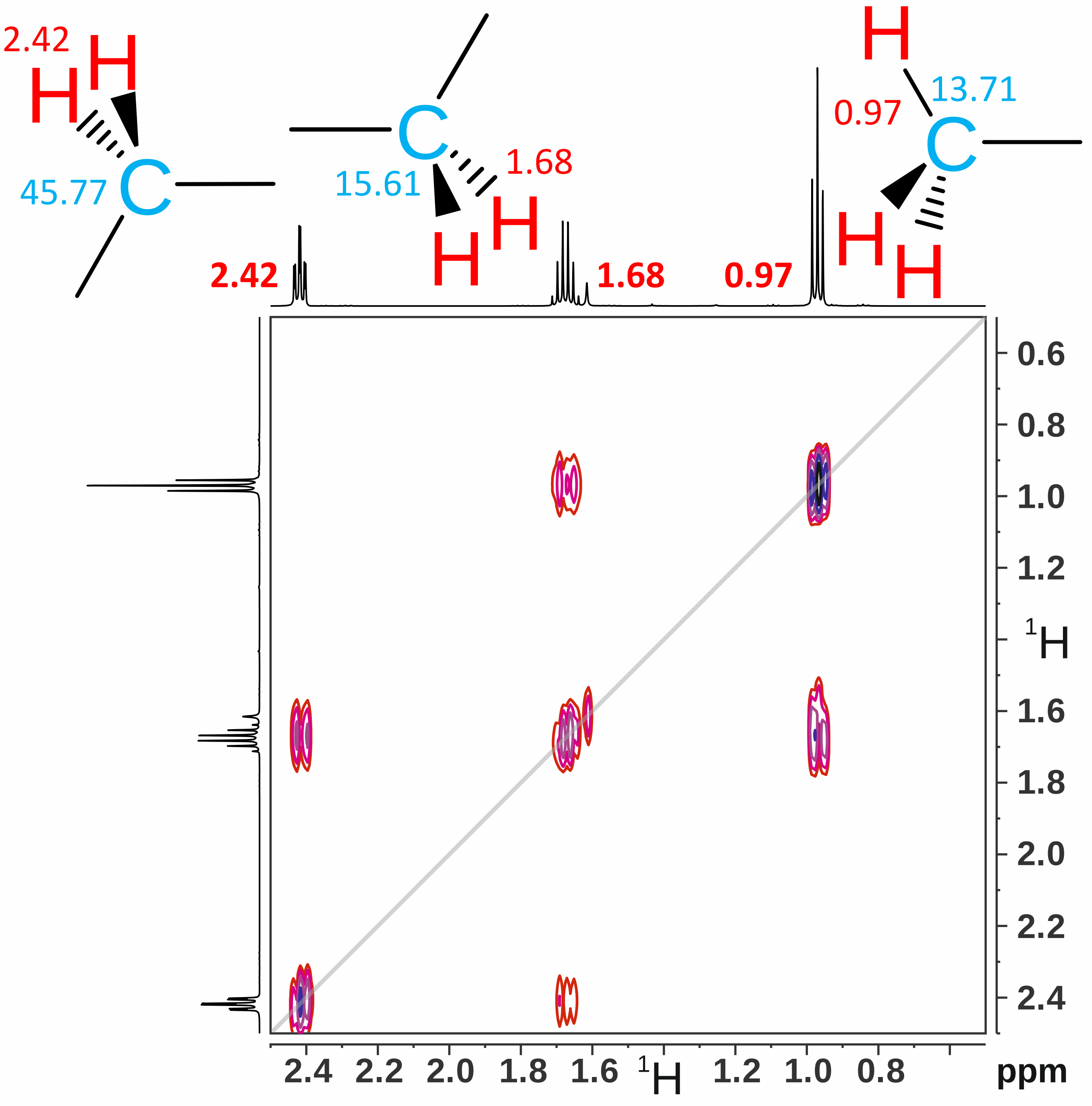


Solution

Part 3 – Bringing all together

Initially one has to order the structural fragments according to the chemical shifts of their proton signals along the projection of the COSY.



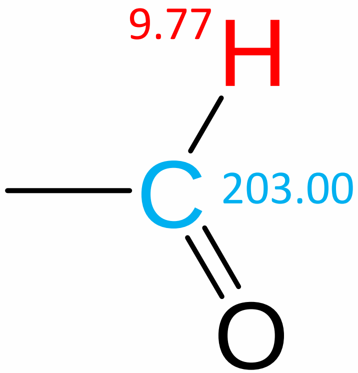


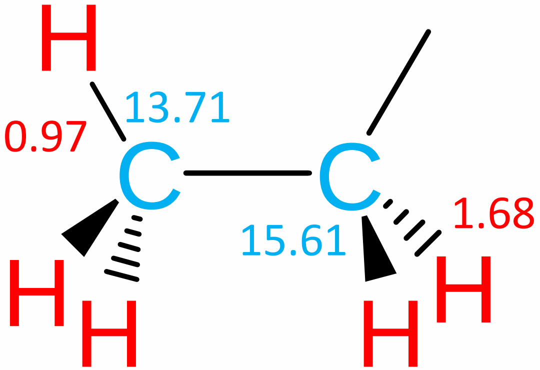
The COSY shown here did not cover the spectral range up to 10 ppm. Therefore there is no correlation visible involving the aldehyde group. Because of the unusual chemical shift of the aldehyde proton, this may occur in real life if the COSY was measured using standard parameters.

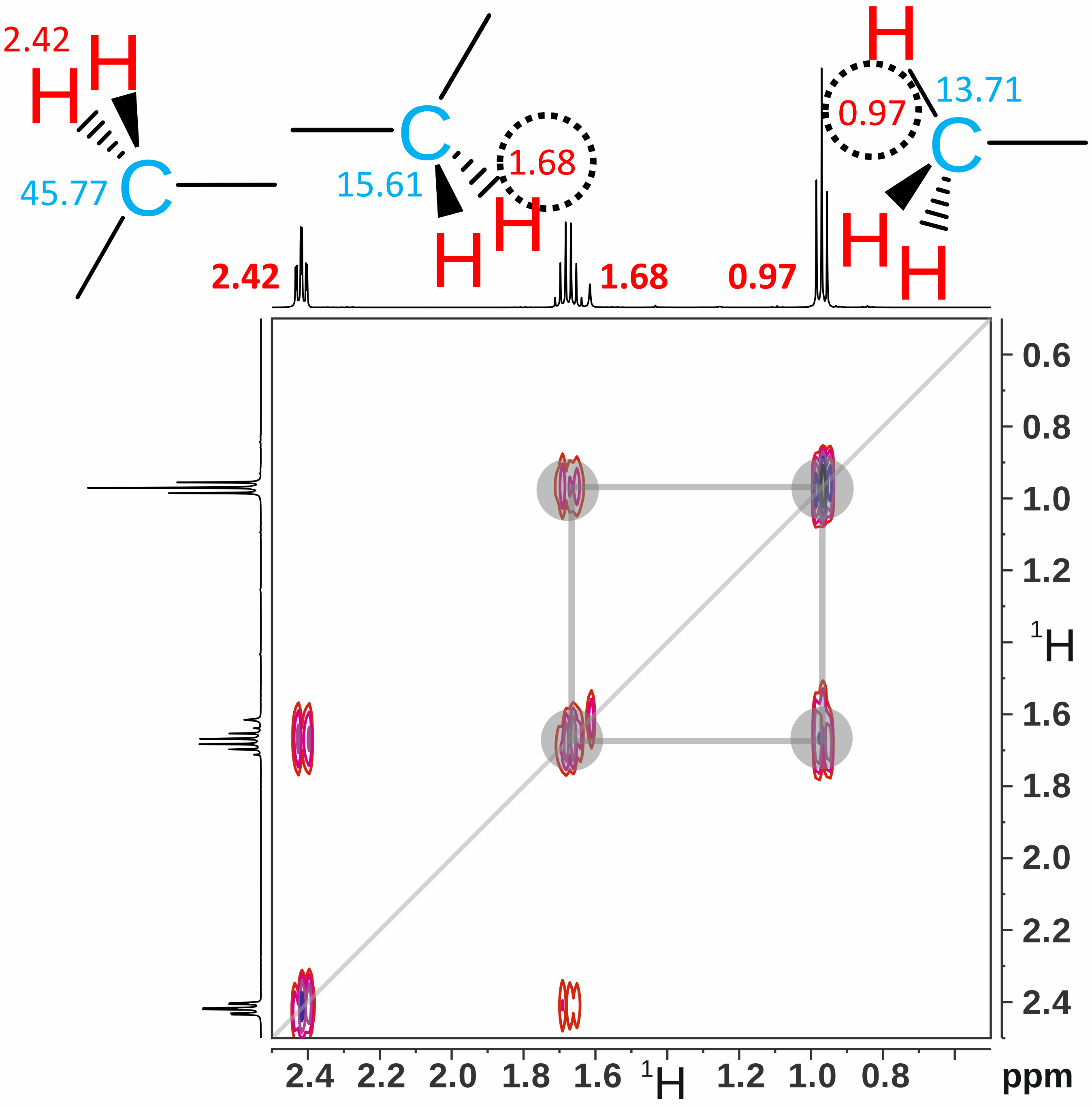
Solution

Part 3 – Bringing all together

The well-dispersed COSY shows only two correlations.



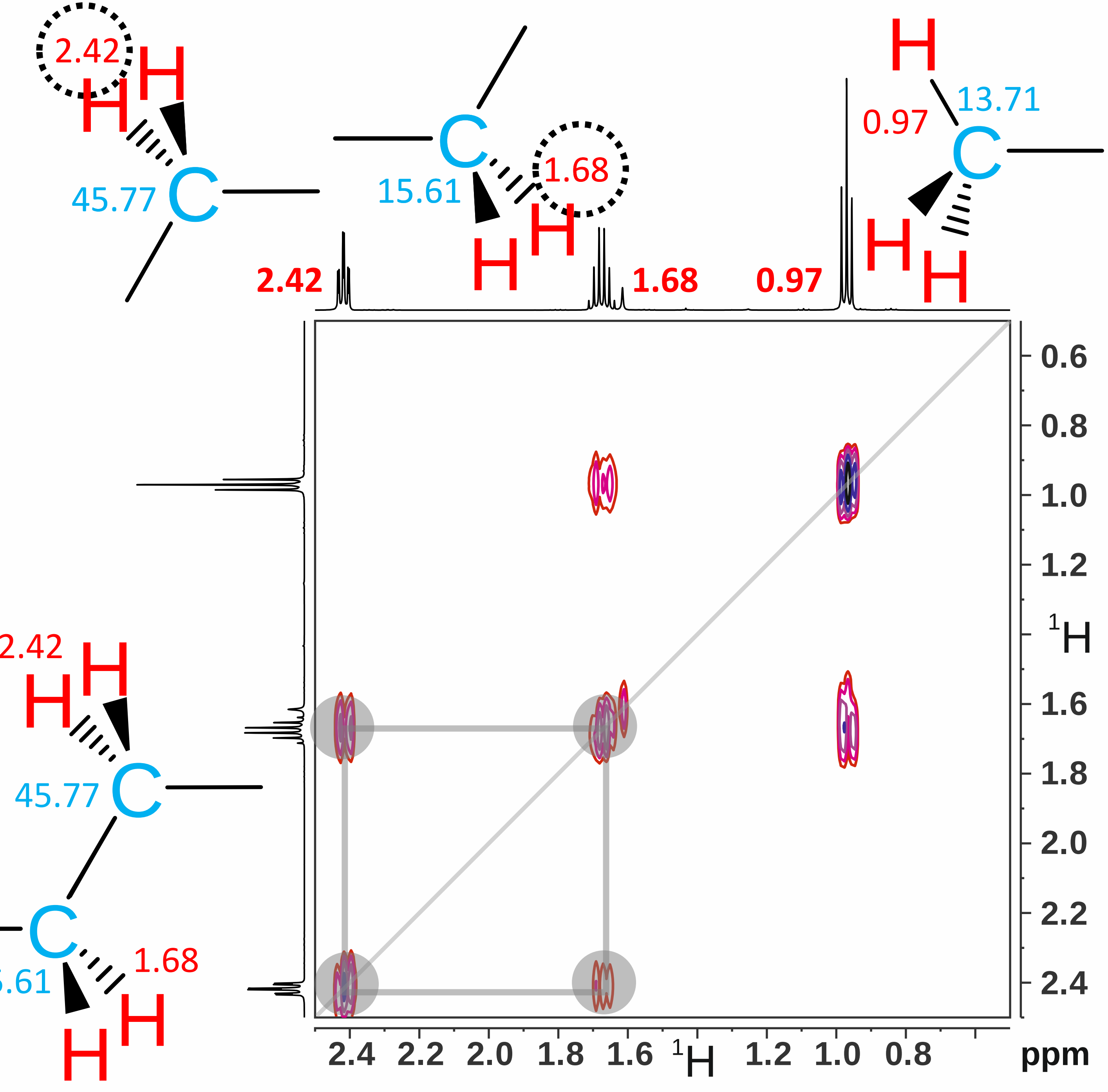


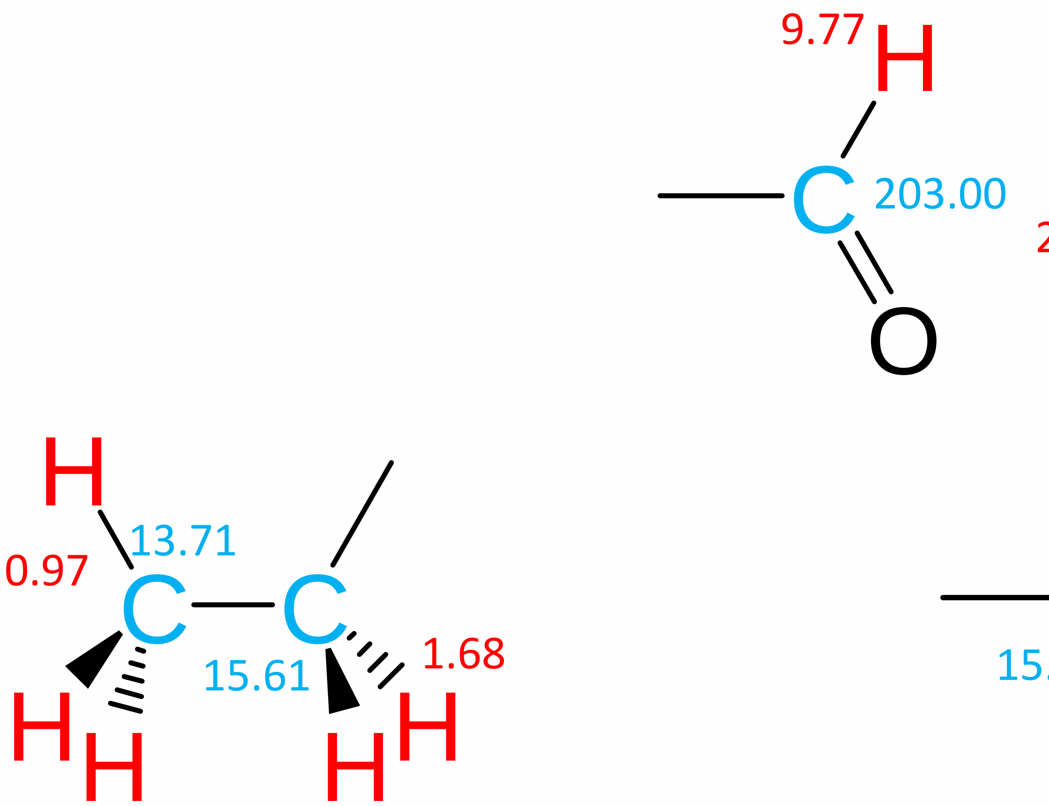


Solution

Part 3 – Bringing all together

The well-dispersed COSY shows only two correlations.

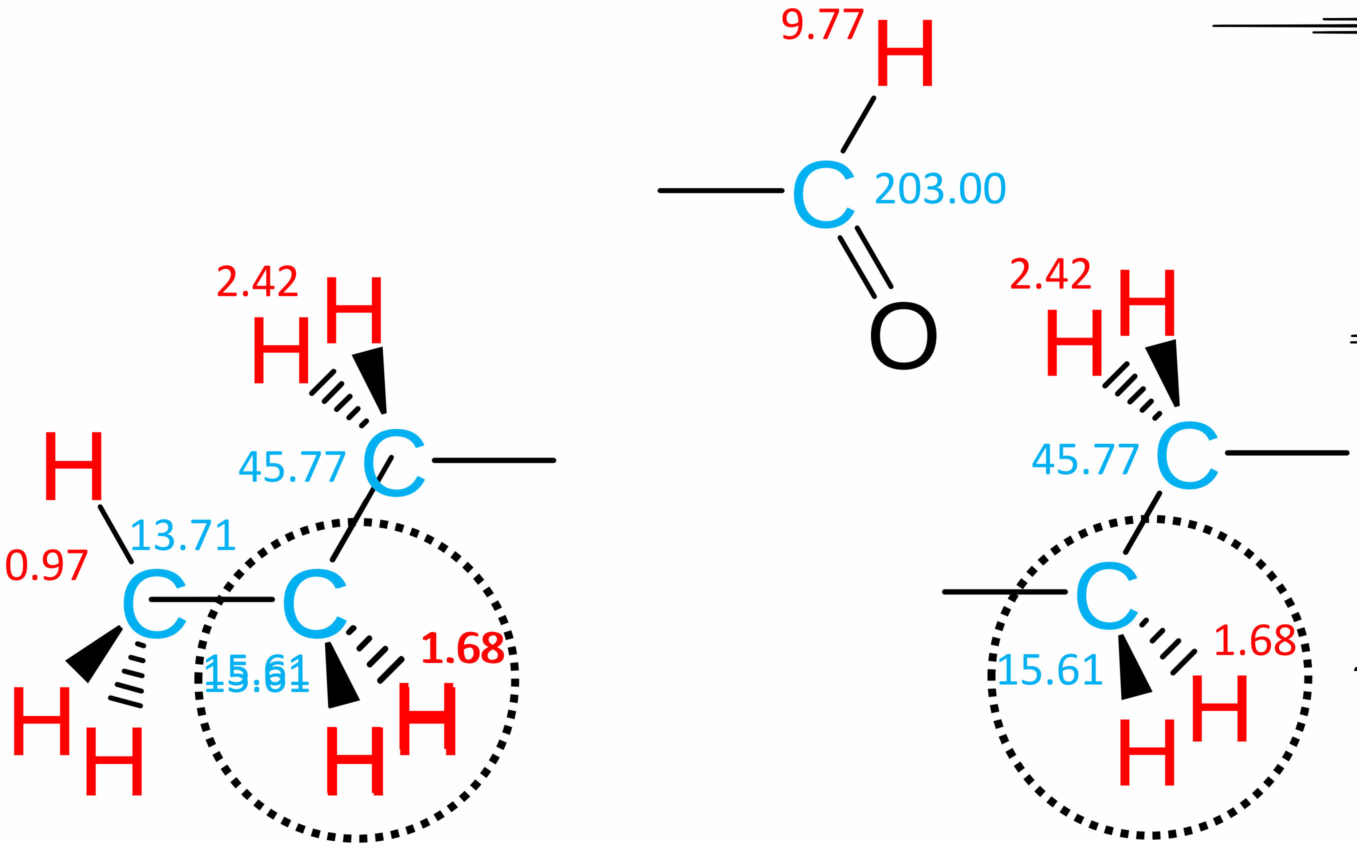


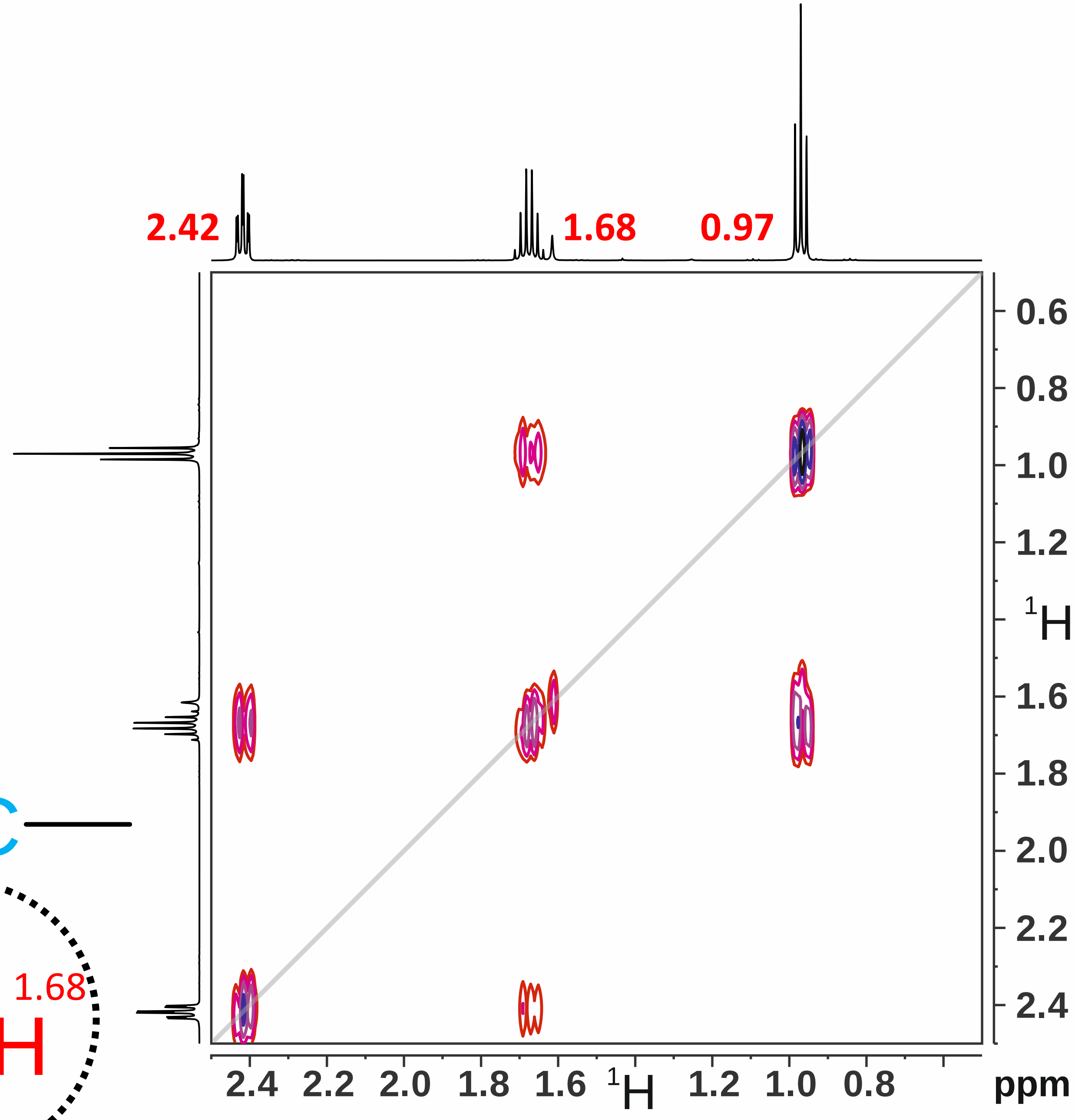


Solution

Part 3 – Bringing all together

The same CH_2 group is part of two fragments.

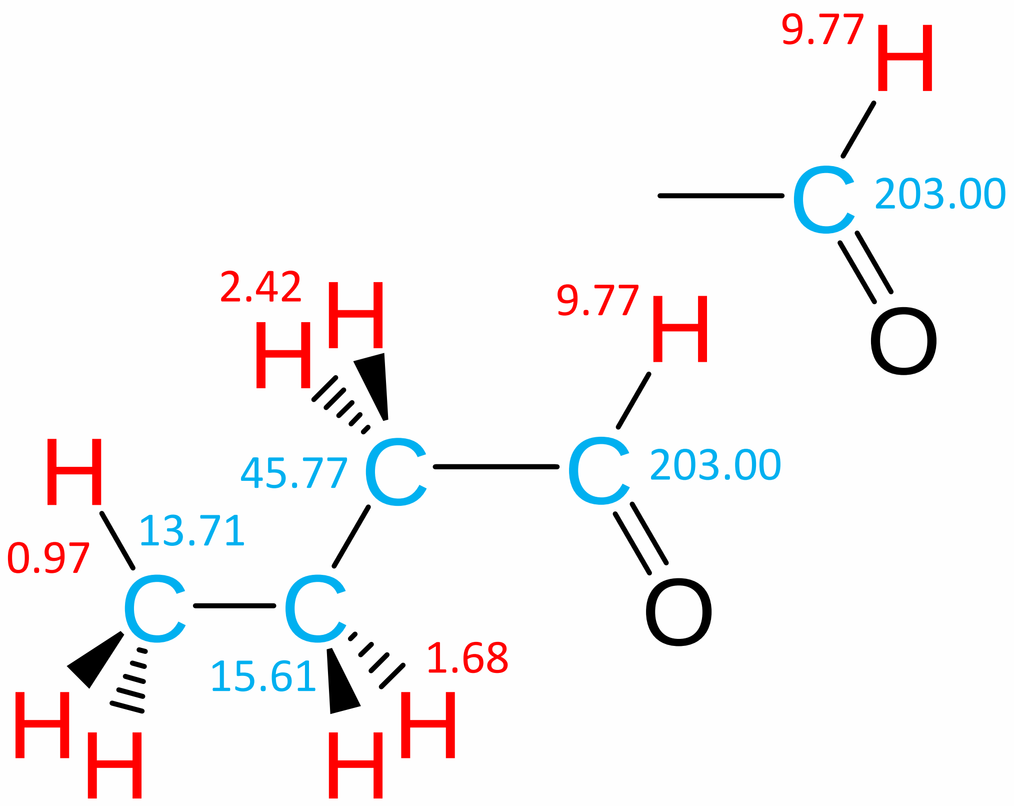


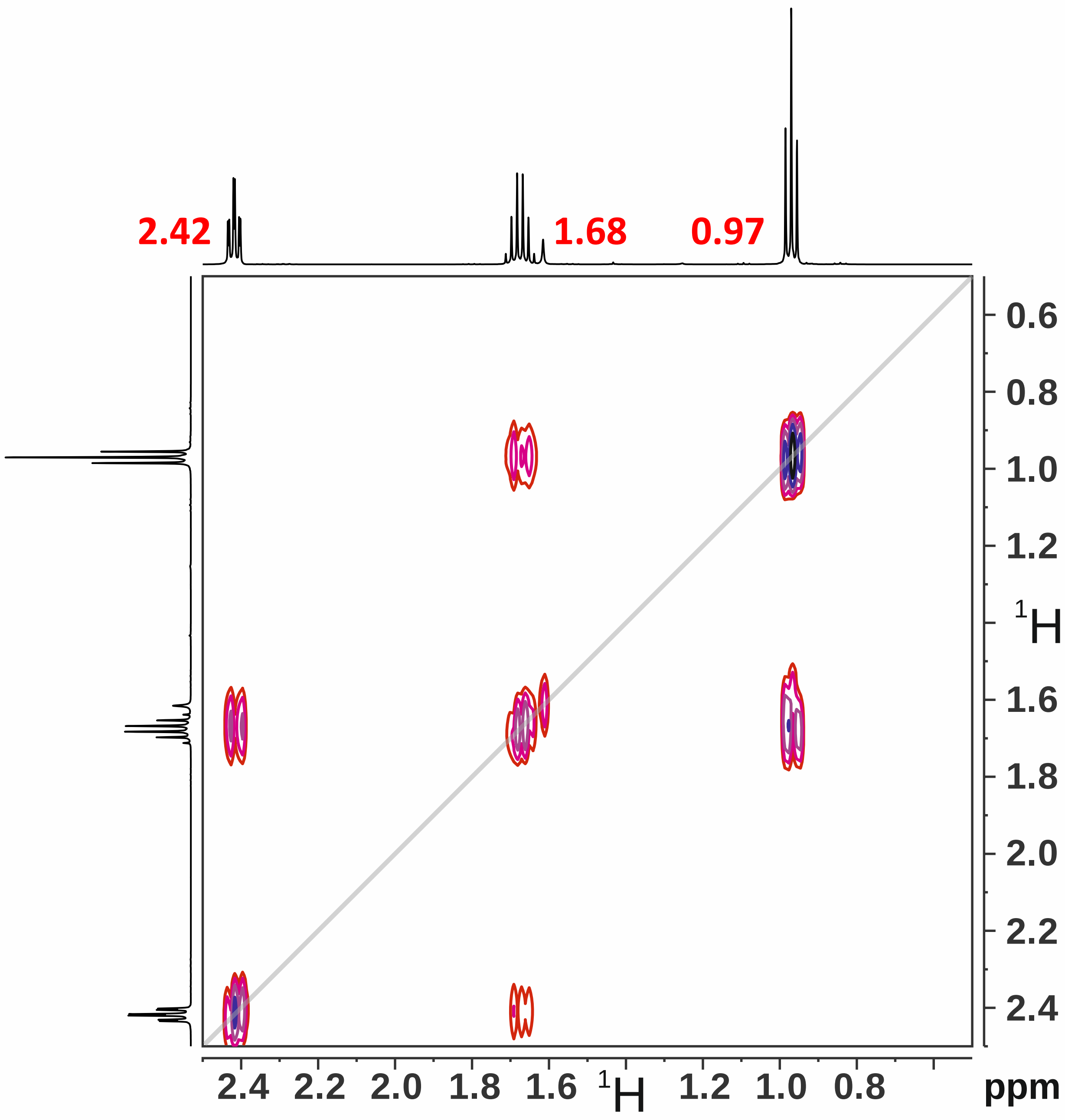


Solution

Part 3 – Bringing all together

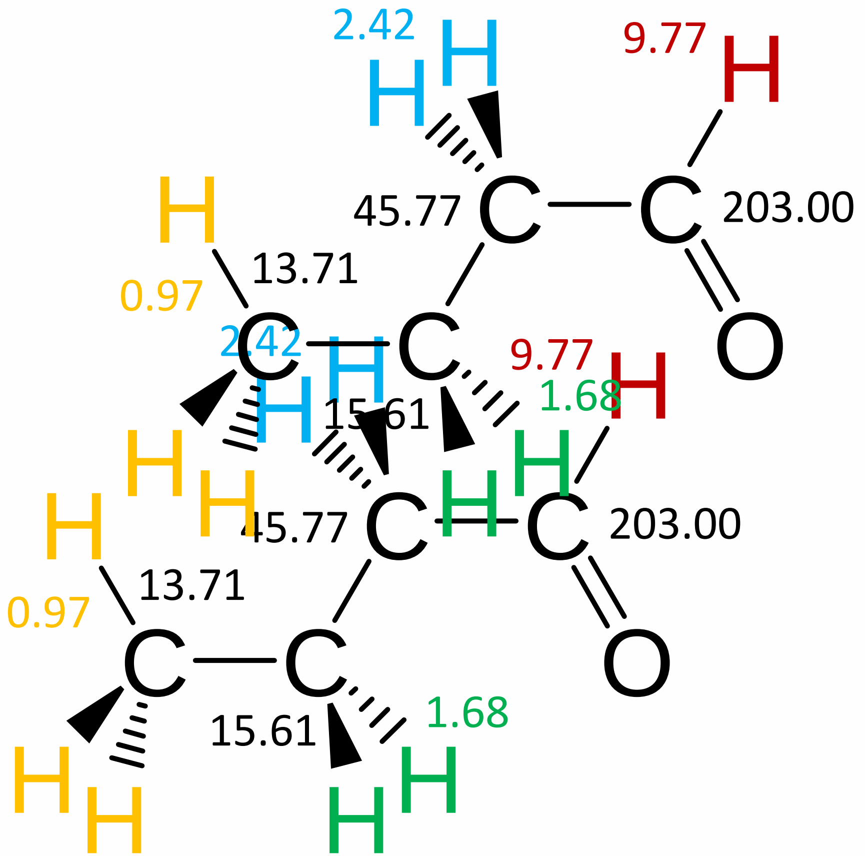
Now, in spite of the missing cross peaks, there is only one possible solution.

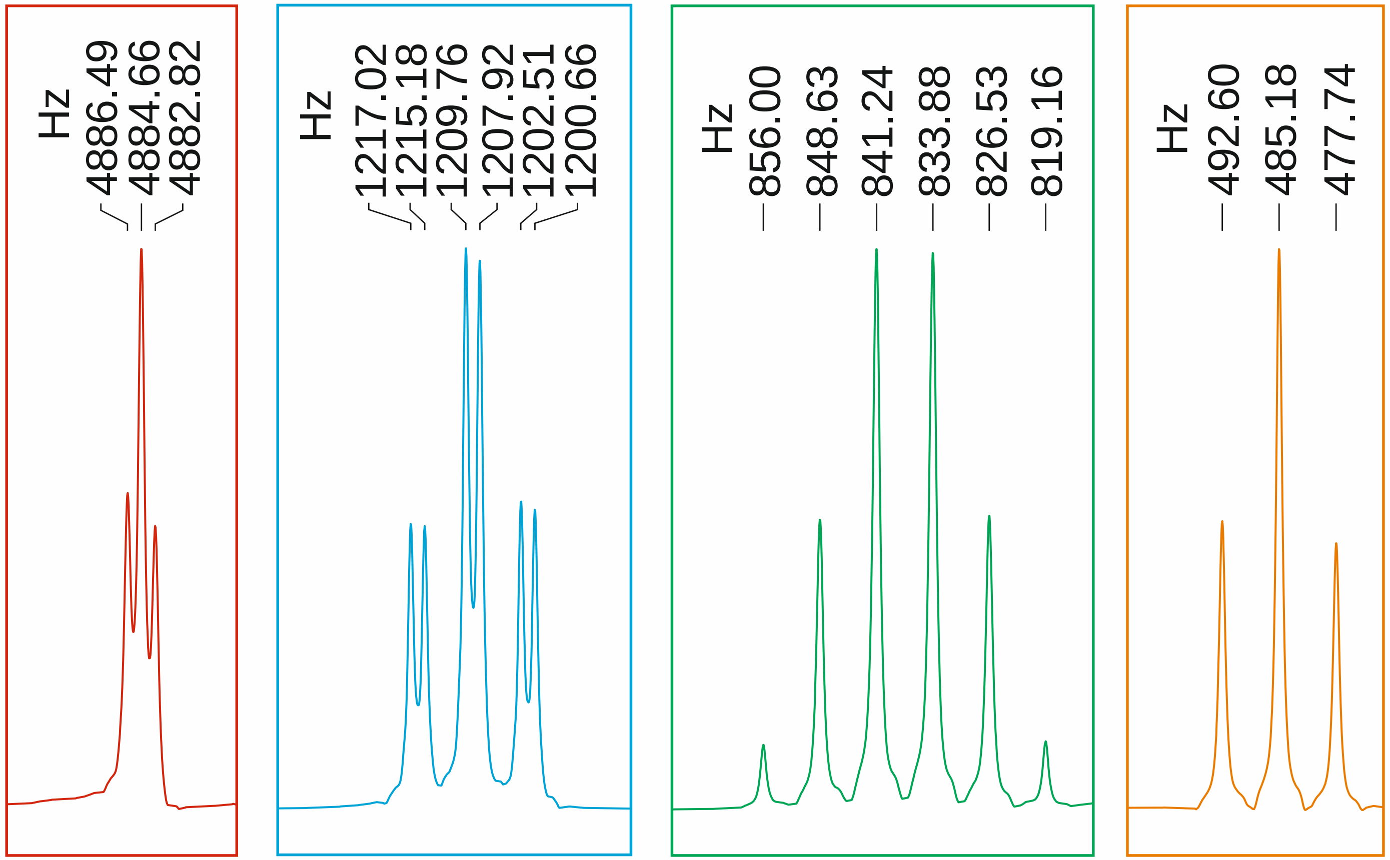




Solution

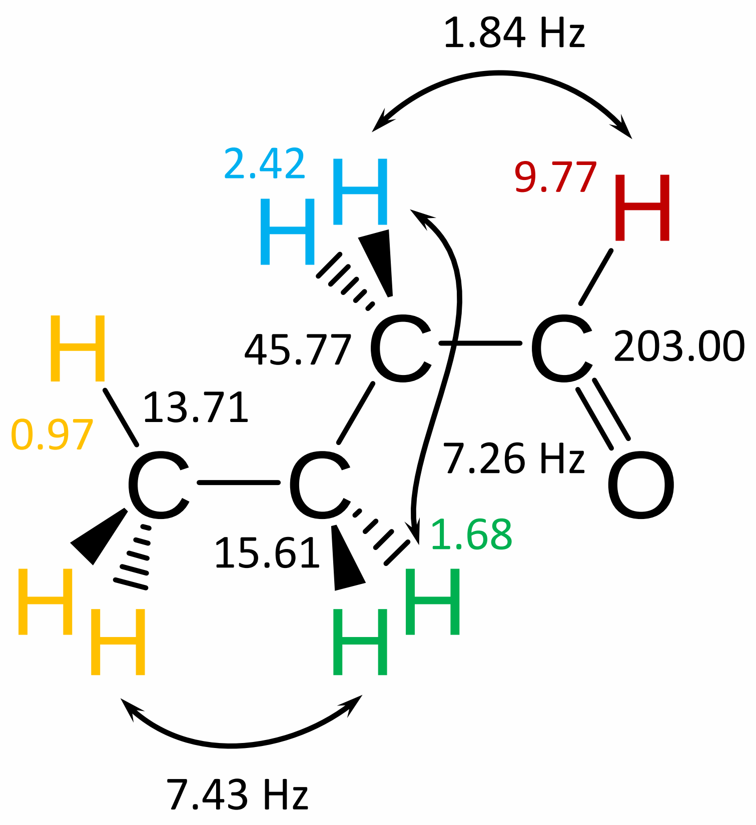
Part 4 – Bonus: Coupling constants





Solution

Part 4 – Bonus: Coupling constants



Triplet (1.84 Hz)

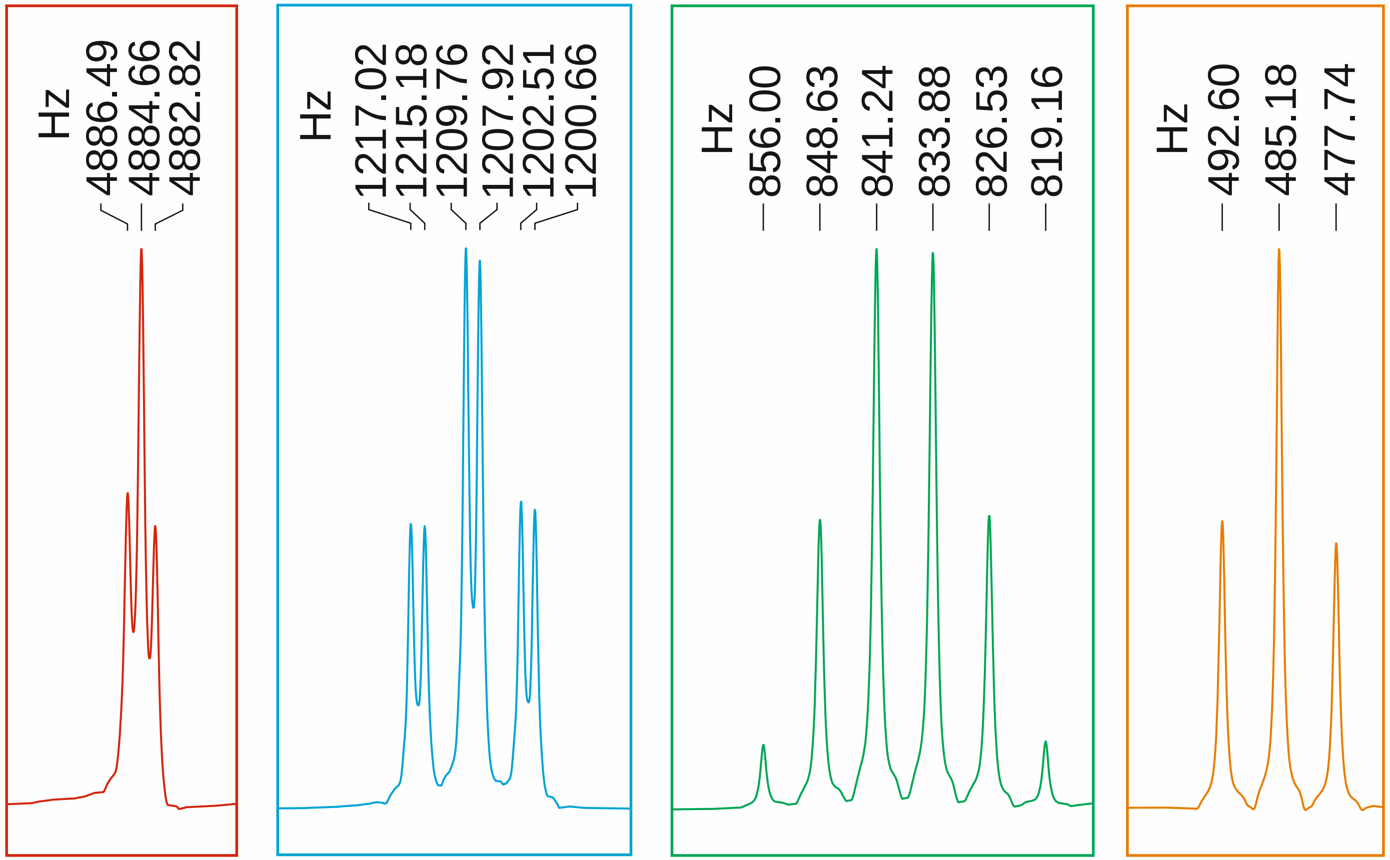
Doublet of Triplets (1.84 Hz, 7.26 Hz)

((1217.02 – 1200.66) – 1.84) / 2

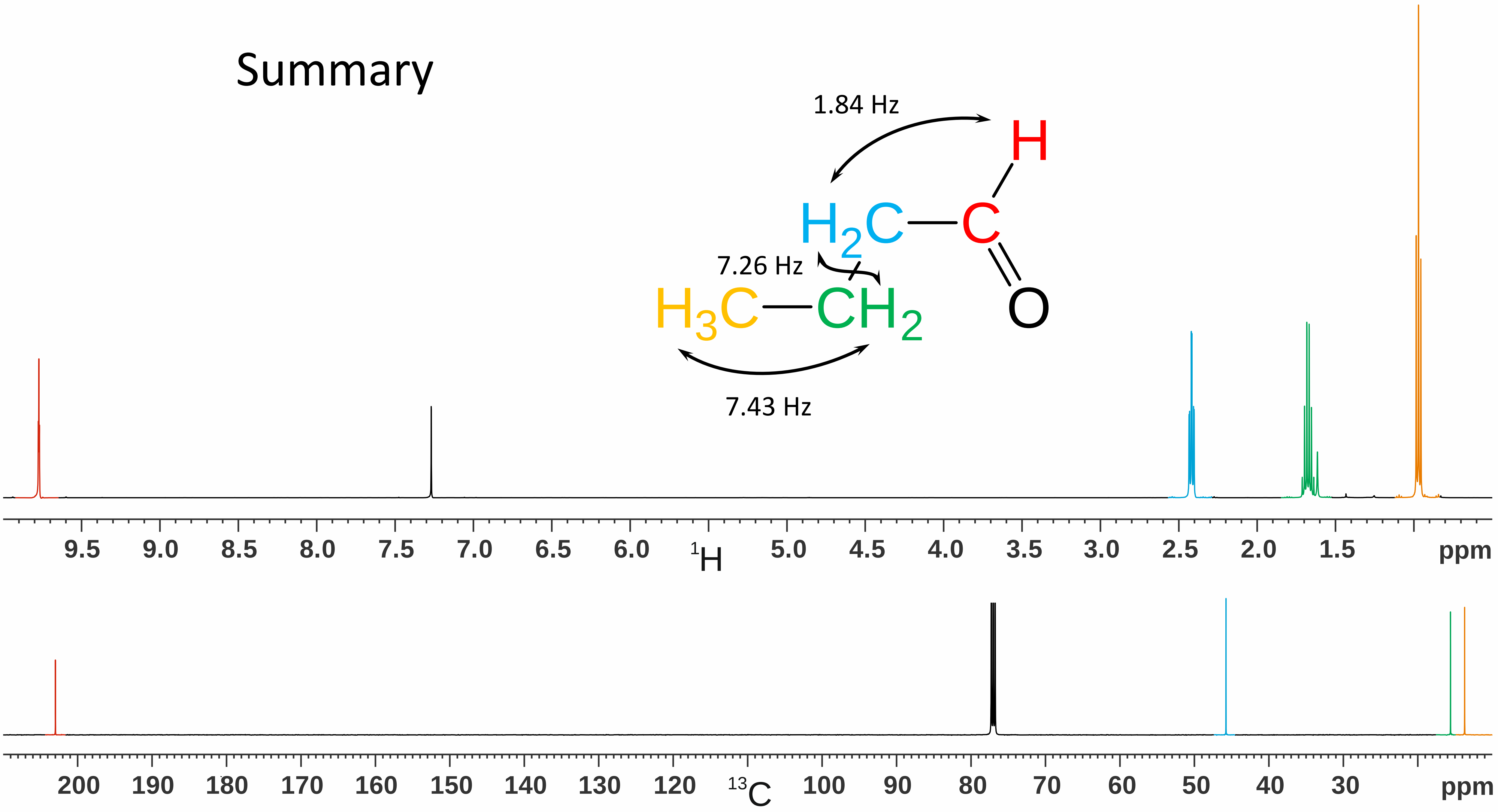
Triplet of Quartets (7.26 Hz, 7.43 Hz)

Pseudosextett because 7.26 Hz ≈ 7.43 Hz

Triplet (7.43 Hz)



Summary



1.84 Hz
H
H_2C
C
7.26 Hz
H_3C
CH_2
O
7.43 Hz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
^{1}H
200 190 180 170 160 150 140 130 120 100 90 80 70 60 50 40 30 ppm
^{13}C

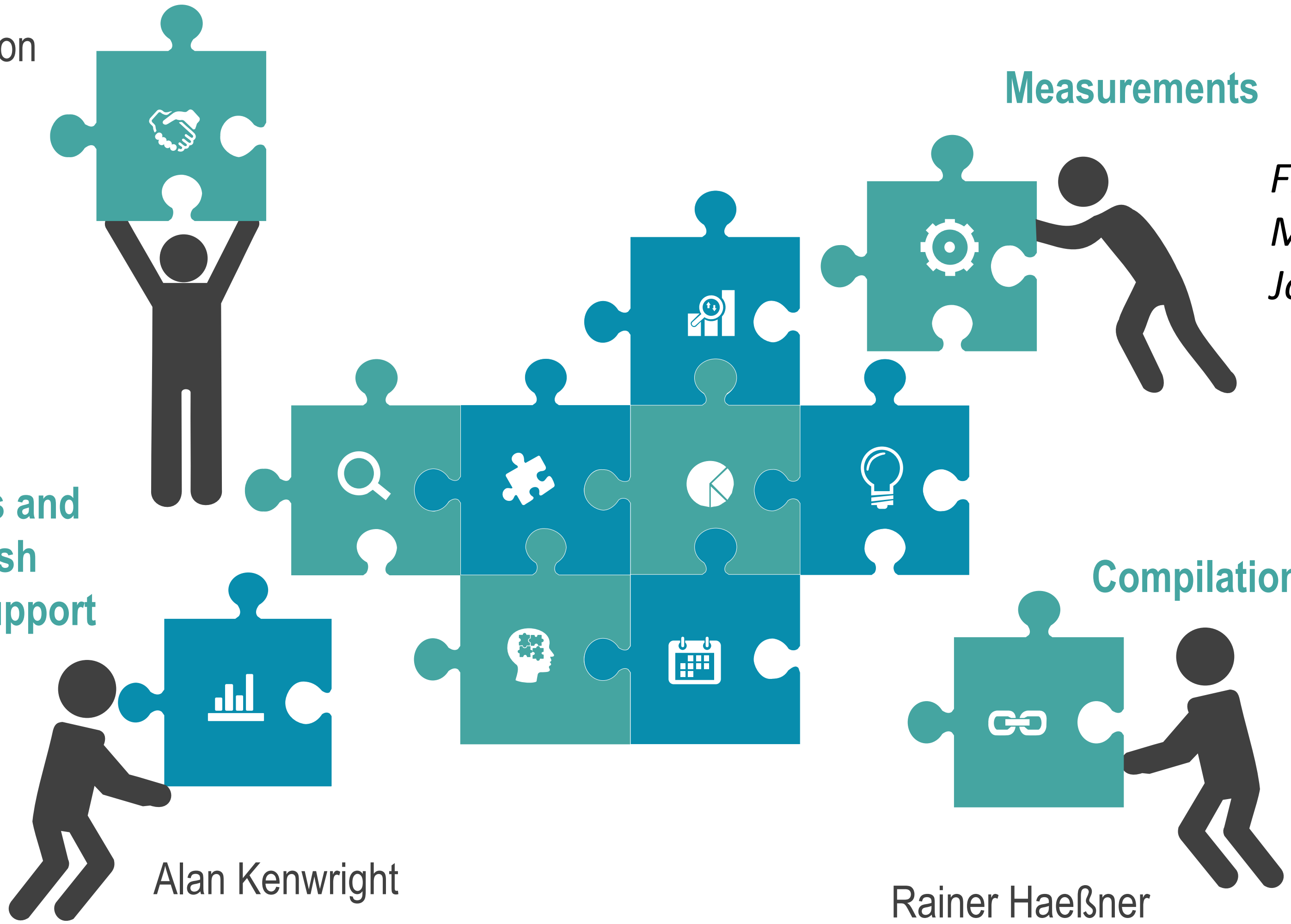
Contributions

Spectrometer time

University of Wisconsin-Madison
(BioMagResBank)

Measurements

Francisca Jofre,
Mark E. Anderson,
John L. Markley



Discussions and native English language support

Alan Kenwright

Compilation

Rainer Haeßner

More exercises …