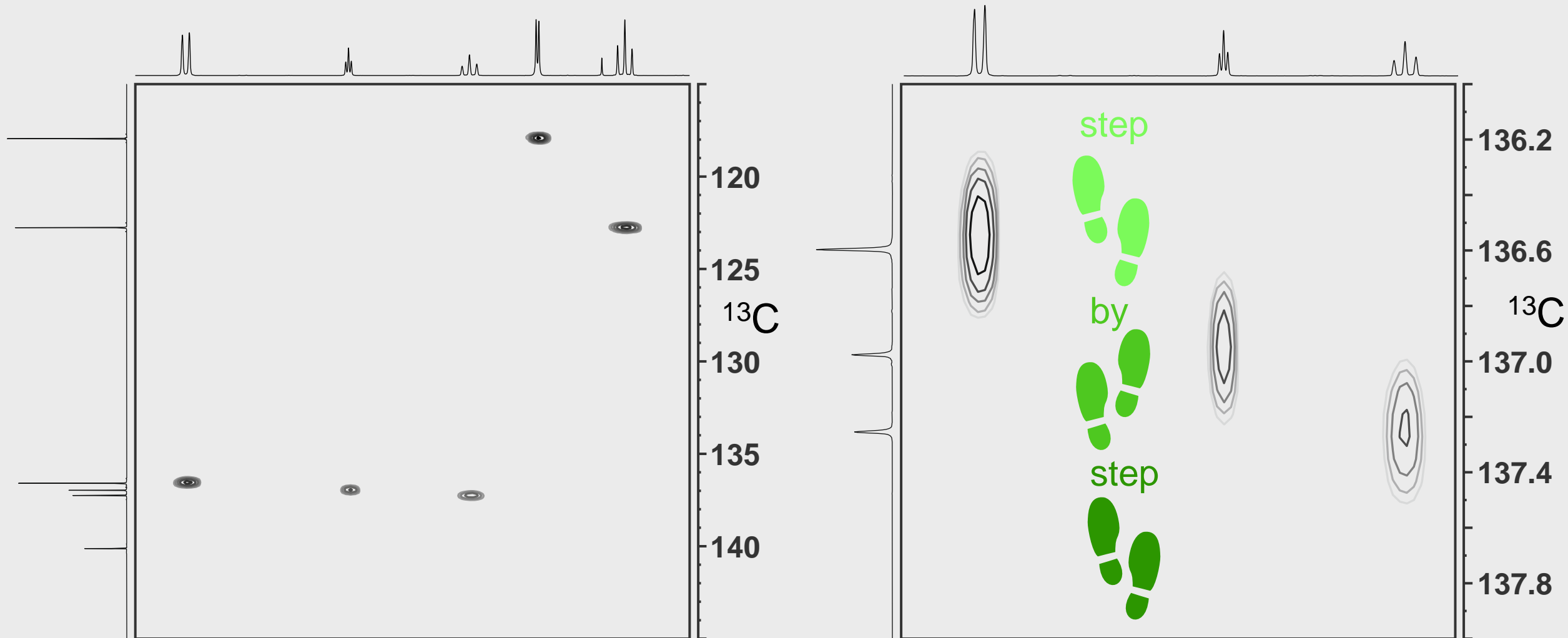# Exercise plus Solution – Quick overview

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.

C₁₀H₈ measured in CDCl₃

$C_{10}H_8$ measured in CDCl$_3$

Deduce the structure!

ppm

—140.12

—137.25
—136.97
—136.59

—122.76

—117.95

¹³C{¹H} NMR spectrum
measured at 125.70{499.84} MHz
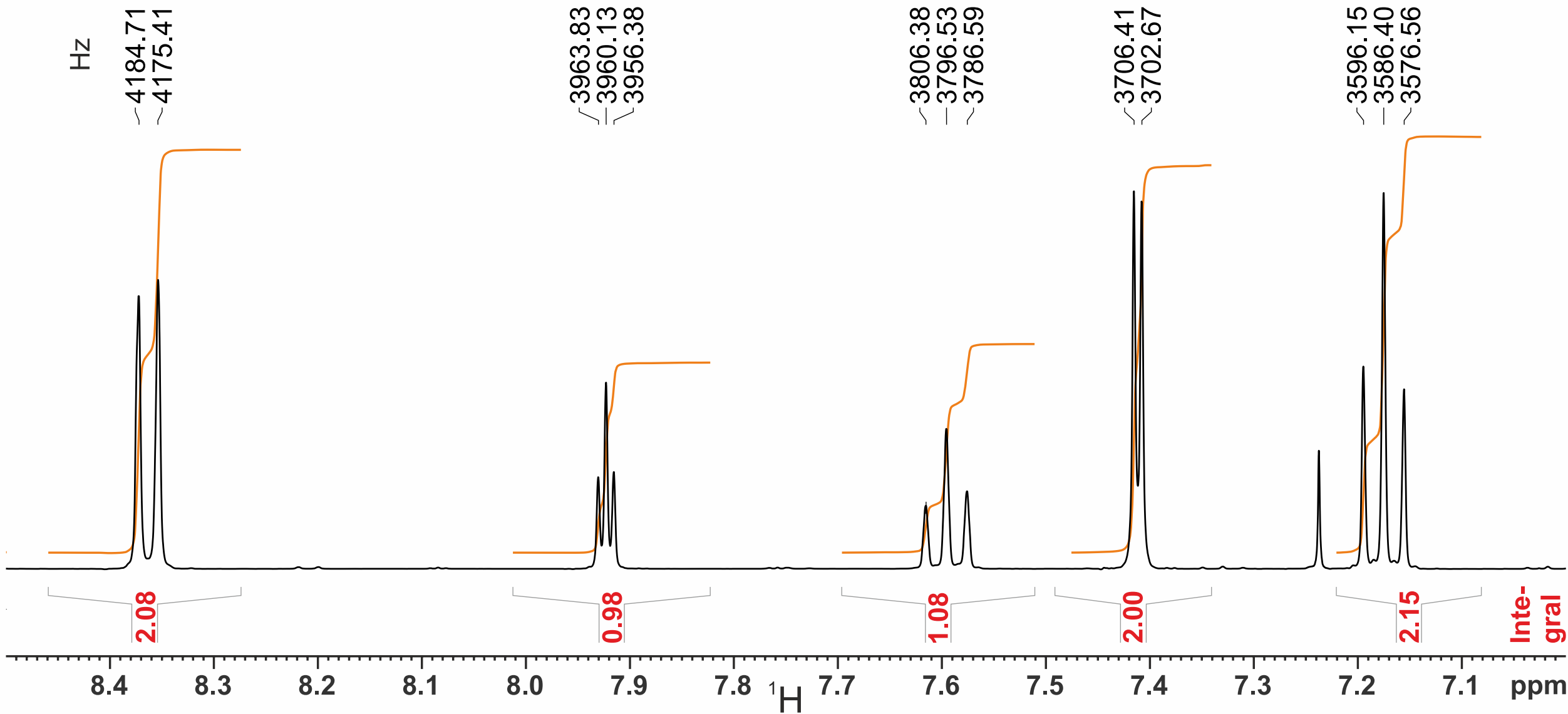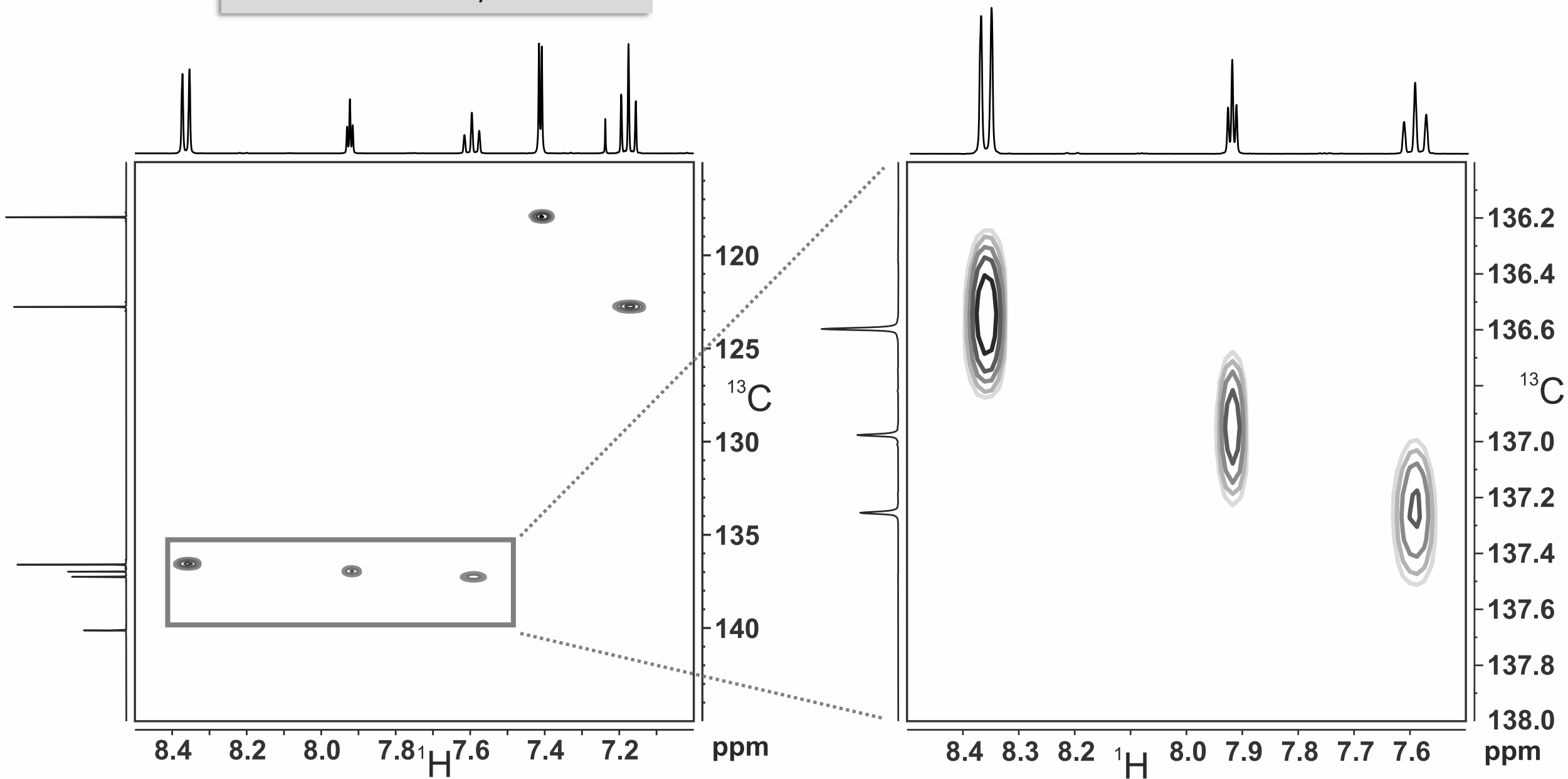
$^{13}C\{^1H\}$ NMR spectrum measured at 125.70{499.84} MHz

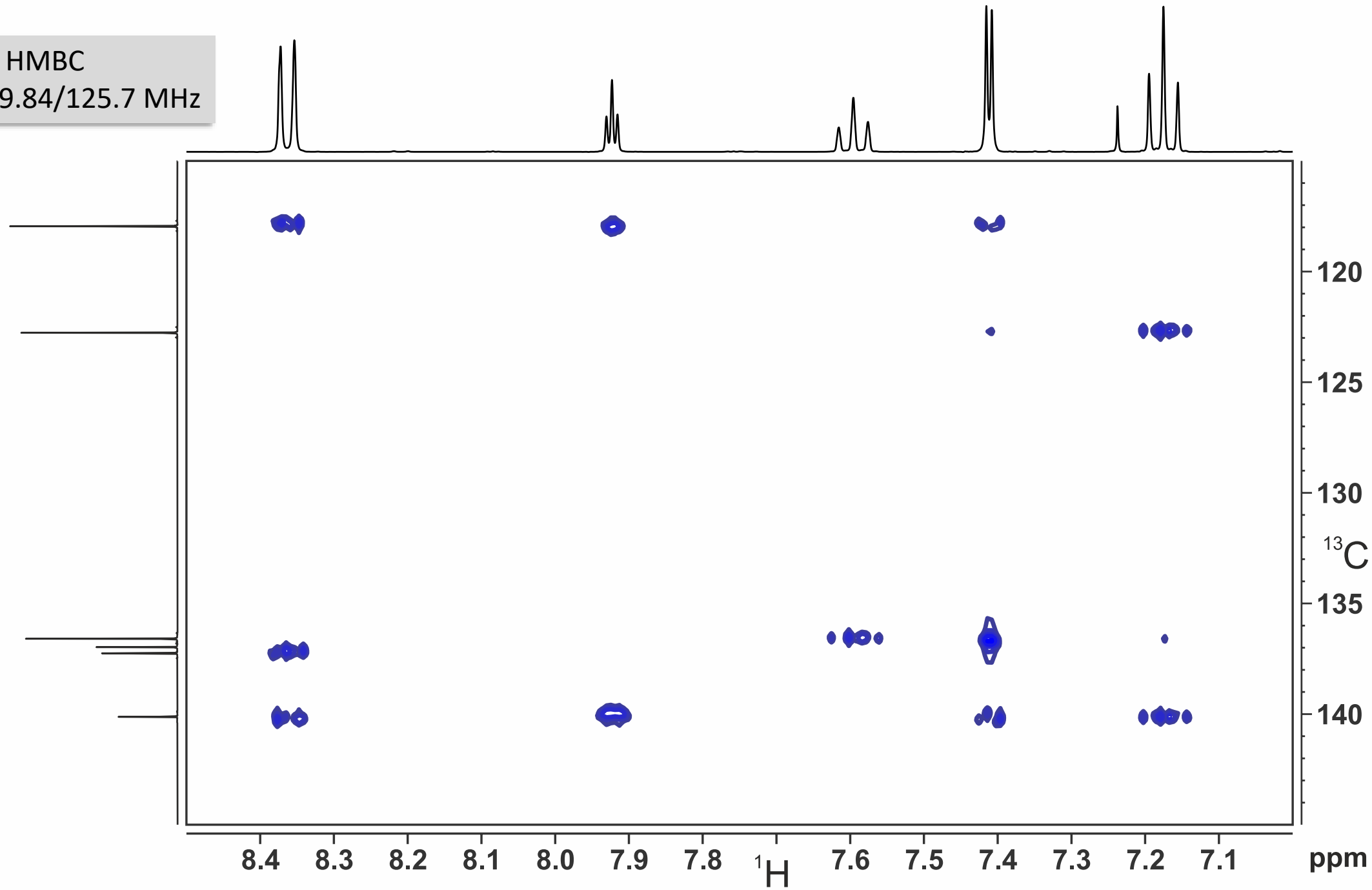144   142   140   138   136   134   132   130 ¹³C 128   126   124   122   120   118   ppm

^{1}H NMR spectrum measured at 499.84 MHz

Hz

4184.71
4175.41

3963.83
3960.13
3956.38

3806.38
3796.53
3786.59

3706.41
3702.67

3596.15
3586.40
3576.56

2.08

0.98

1.08

2.00

2.15

Integral

8.4 8.3 8.2 8.1 8.0 7.9 7.8 ^{1}H 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm

$^1H/^{13}C$ HSQC
measured at 499.84/125.70 MHz

It is tempting to think of the solution "naphthalene" immediately after seeing the molecular formula $C_{10}H_8$ and signals in the aromatic region. And to then get stuck!

The real challenge here is to break out of this mental cage.

First steps

Double bond equivalents,
Integration

$$C_{10}H_8 \text{ in CDCl}_3$$
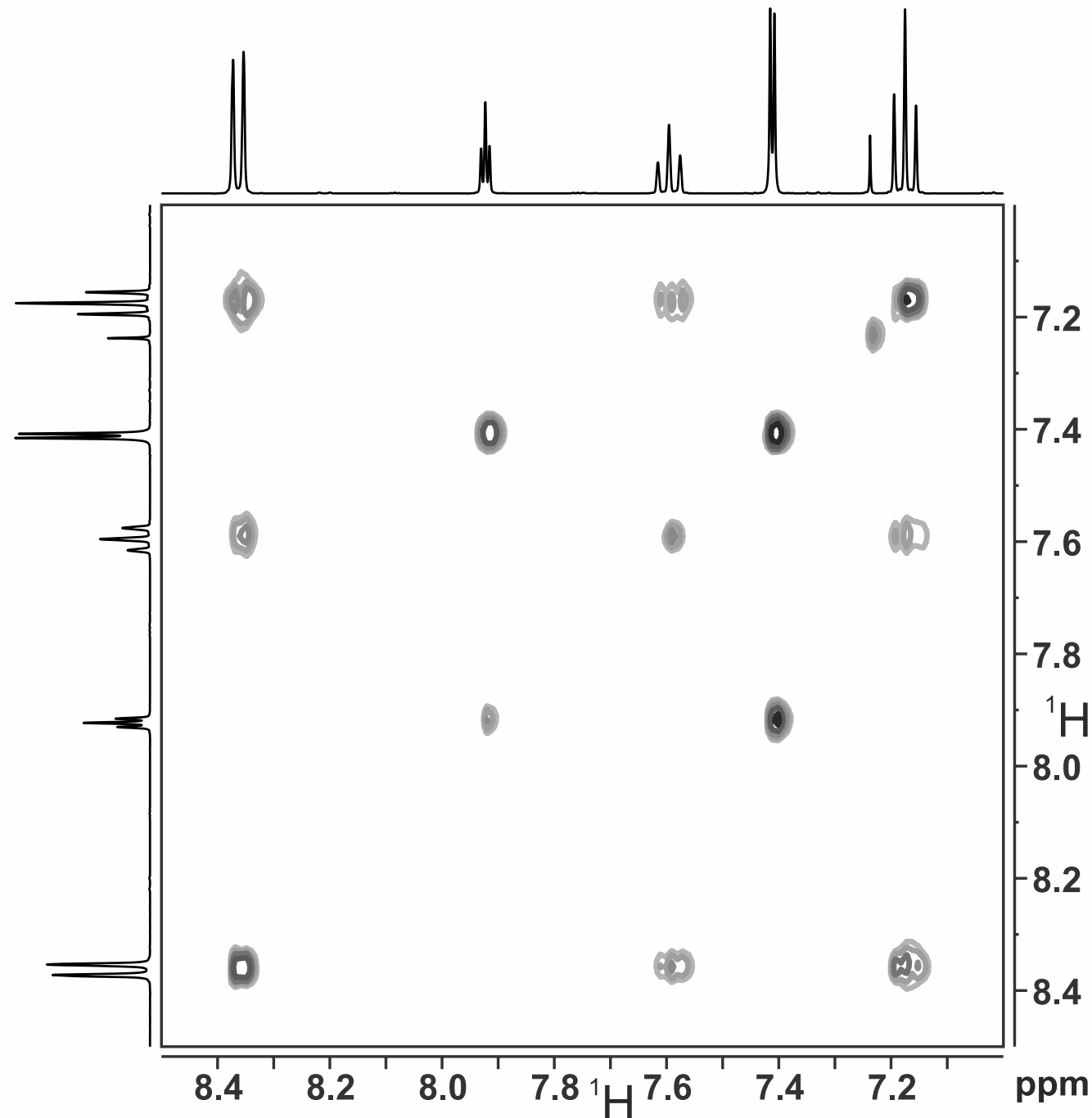
From the molecular formula, **7 double bond equivalents** can be derived immediately.

The high number of double bond equivalents, only proton signals between 7 ppm and 8.5 ppm, further only carbon signals in the range of 120 ppm to 140 ppm, and finally no oxygen at all quickly suggests the solution **naphthalene**.

However, in napththalene we would expect only **3 carbon signals** and **2 proton multiplets** because of the inherent high symmetry. The compound presented here shows **5 proton multiplets** and **6 carbon signals**.

One approach to avoid falling into the naphthalene trap again and again is to first collect the data that can be easily extracted. It is possible that ideas for the further procedure will develop from there. The proton spectrum is a good place to start. For the moment we write down the number of double bond equivalents on a small sticky note.
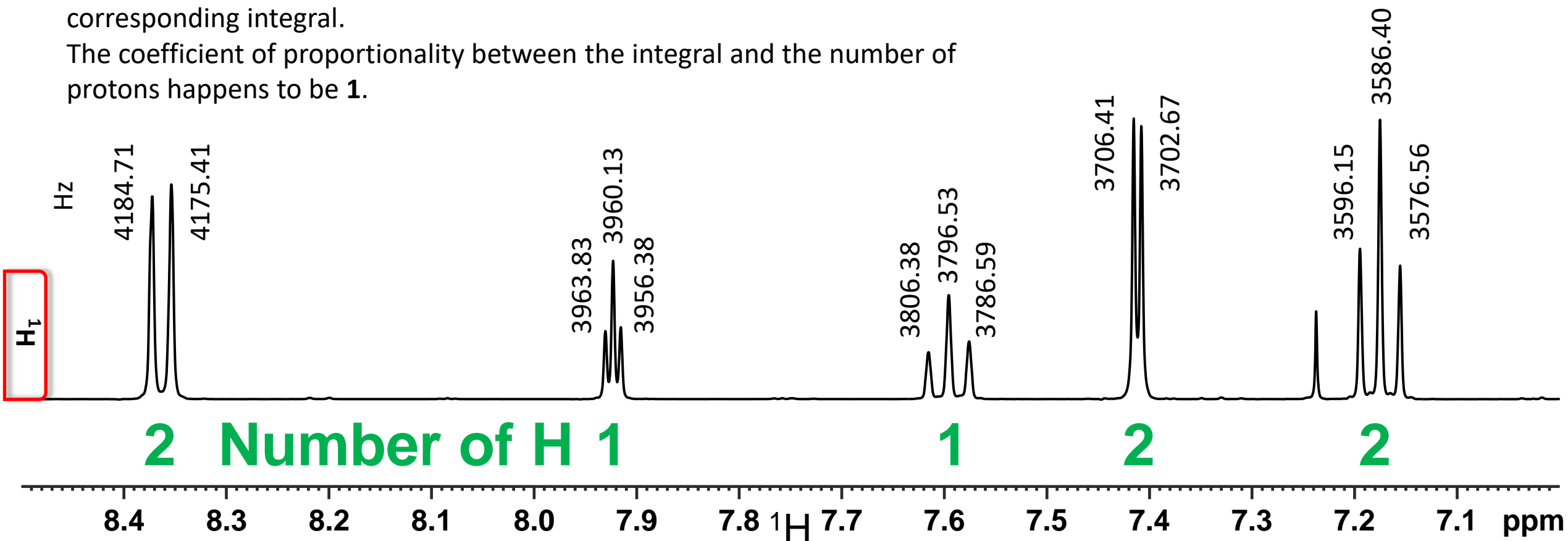
First steps

Double bond equivalents,
   Integration

$C_{10}H_8$ in $CDCl_3$

The integration is simple here. The sum of the integrals rounded to the nearest integer value is even **8**.

The proton number of a single multiplet is obtained by simply rounding the corresponding integral.

The coefficient of proportionality between the integral and the number of protons happens to be **1**.
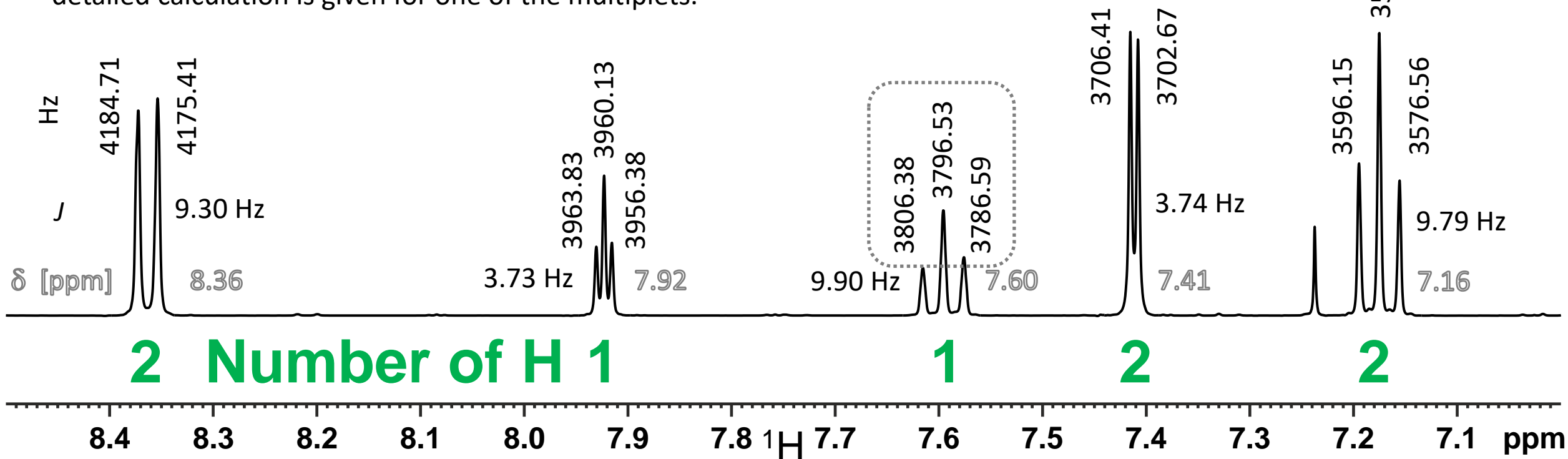
First steps

Double bond equivalents,
Integration

$C_{10}H_8$ in $CDCl_3$

The peak maxima are given in Hz to enable the determination of the coupling constants. A conversion to the ppm scale provides more common values.
The calculation of the coupling constants is based on the assumption of pure multiplets (no pseudo triplets). The detailed calculation is given for one of the multiplets.

$$\delta = \frac{3806.38\ Hz + 3786.59\ Hz}{2 * 499.84\ MHz} = 7.60\ ppm$$

$$J = \frac{(3806.38 Hz - 3786.59 Hz)}{2} = 9.90\ Hz$$

Hz

4184.71
4175.41
J   9.30 Hz

3963.83
3960.13
3956.38
3.73 Hz

3806.38
3796.53
3786.59
9.90 Hz

3706.41
3702.67
3.74 Hz

3596.15
3586.40
3576.56
9.79 Hz

δ [ppm]   8.36   7.92   7.60   7.41   7.16

2   Number of H 1   1   2   2

8.4   8.3   8.2   8.1   8.0   7.9   7.8 ¹H 7.7   7.6   7.5   7.4   7.3   7.2   7.1   ppm

First steps

Double bond equivalents,
        Integration

$C_{10}H_8$ in $CDCl_3$

For further evaluation, it is helpful to keep track of
information not yet contained in substructures.

These are the nuclei not yet assigned, and the number
of double bond equivalents.

J

9.30 Hz

3.74 Hz

9.79 Hz

δ [ppm]   8.36   3.73 Hz   7.92   9.90 Hz   7.60   7.41   7.16

2   Number of H 1   1   2   2

8.4   8.3   8.2   8.1   8.0   7.9   7.8 ¹H 7.7   7.6   7.5   7.4   7.3   7.2   7.1   ppm
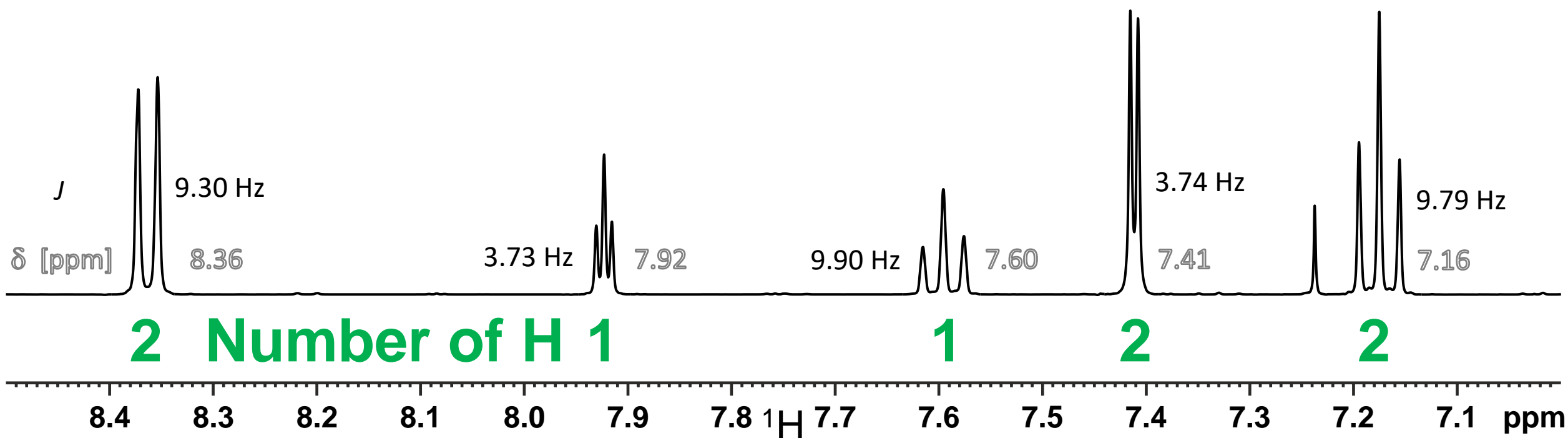
First steps

Double bond equivalents,
Integration

Two of the proton multiplets can be immediately assigned to structural fragments. Because of the molecular formula, only carbon can be adjacent to the protons. A chemical shift of about 7 ppm for the protons means an sp^2 hybridisation of these carbon atoms.

(The additionally noted coupling constants of the proton multiplets can be helpful later when determining the coupling partner.)

3.73 Hz (t)

C—H 7.92

9.90 Hz (t)

7.60 H—C

J 9.30 Hz

3.74 Hz

9.79 Hz

δ [ppm]   8.36   3.73 Hz   7.92   9.90 Hz   7.60   7.41   7.16

2   Number of H 1   1   2   2

8.4   8.3   8.2   8.1   8.0   7.9   7.8 ^{1}H 7.7   7.6   7.5   7.4   7.3   7.2   7.1   ppm
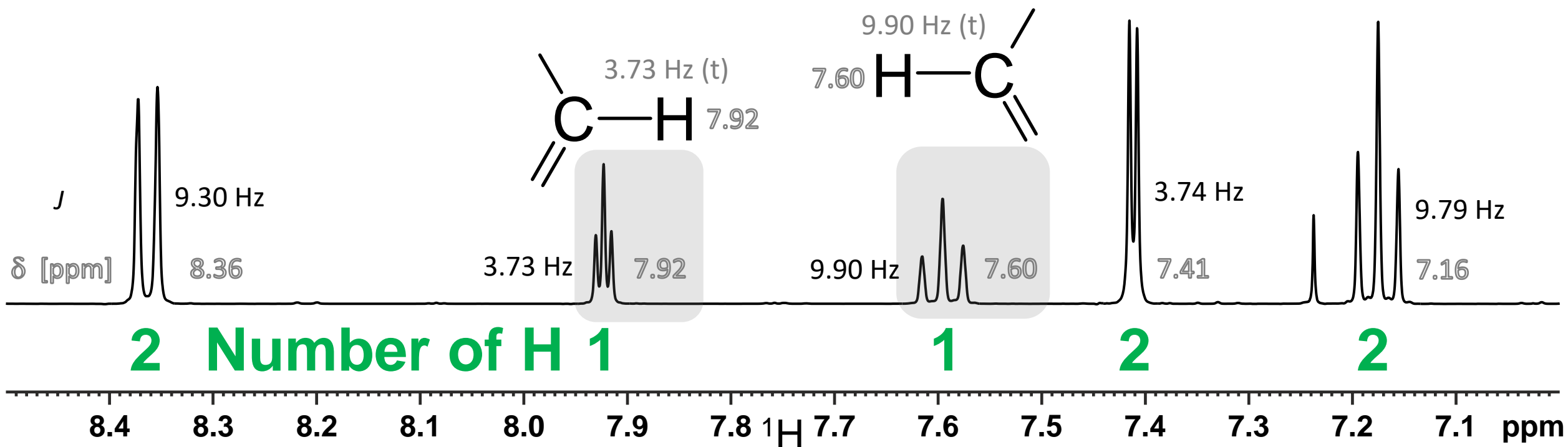
First steps

Double bond equivalents,
    Integration

Let us use identical colours for the protons and the
corresponding multiplets.

After assigning a total of C_2H_2, we still have to assign a
partial molecular formula of C_8H_6. Nothing changes
concerning the number of double bond equivalents.

C_8H_6

3.73 Hz (t)

9.90 Hz (t)

7.60 H—C

3.73 Hz (t)

C—H 7.92

J 9.30 Hz

3.74 Hz

9.79 Hz

δ [ppm]   8.36

3.73 Hz   7.92

9.90 Hz   7.60

7.41

7.16

2 **Number of H 1**   **1**   **2**   **2**

8.4   8.3   8.2   8.1   8.0   7.9   7.8 1H 7.7   7.6   7.5   7.4   7.3   7.2   7.1   ppm
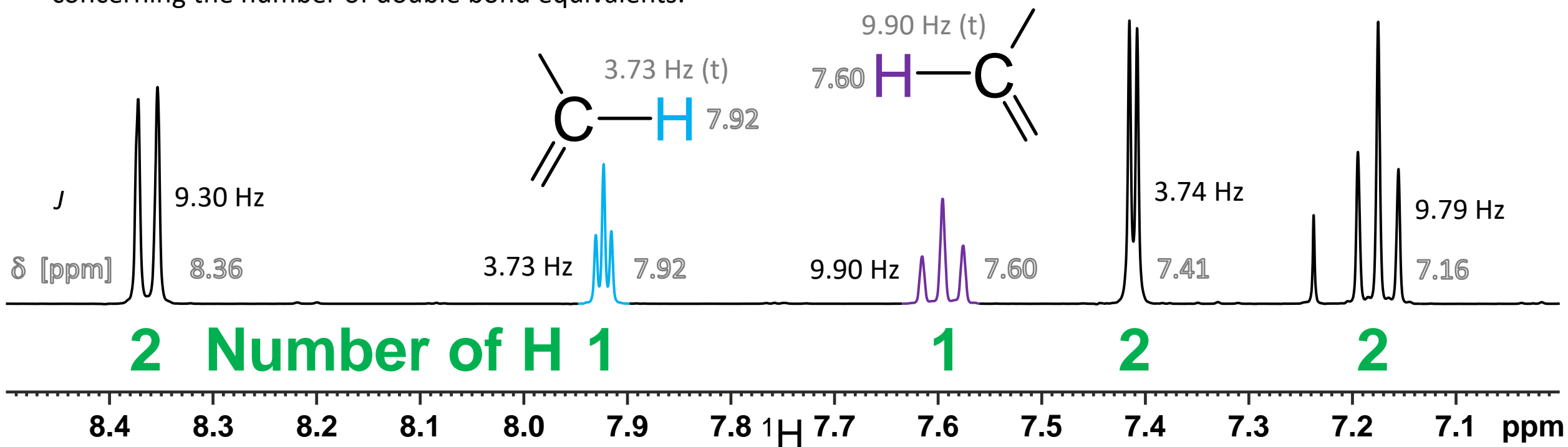
First steps

Three signal groups with 2 protons each remain.
There would be two possibilities.

a) Each of the signal groups corresponds to a =CH_2 group.
Then 5 quaternary carbon atoms would remain.

b) Each of the signal groups corresponds to 2 equivalent
=CH- groups (analogous to the structural elements
already found). In this case 2 quaternary carbon
atoms would remain.

Further considerations are possible, but **b)** is sufficiently
likely for us to continue with this version.
If it really does not work, one would have to start again
with version **a)**.

^1H

δ [ppm]   8.36   7.92   7.60   7.41   7.16

3.73 Hz (t)   7.92

9.90 Hz (t)   7.60

9.30 Hz

3.73 Hz

9.90 Hz

3.74 Hz

9.79 Hz

2   Number of H 1   1   2   2
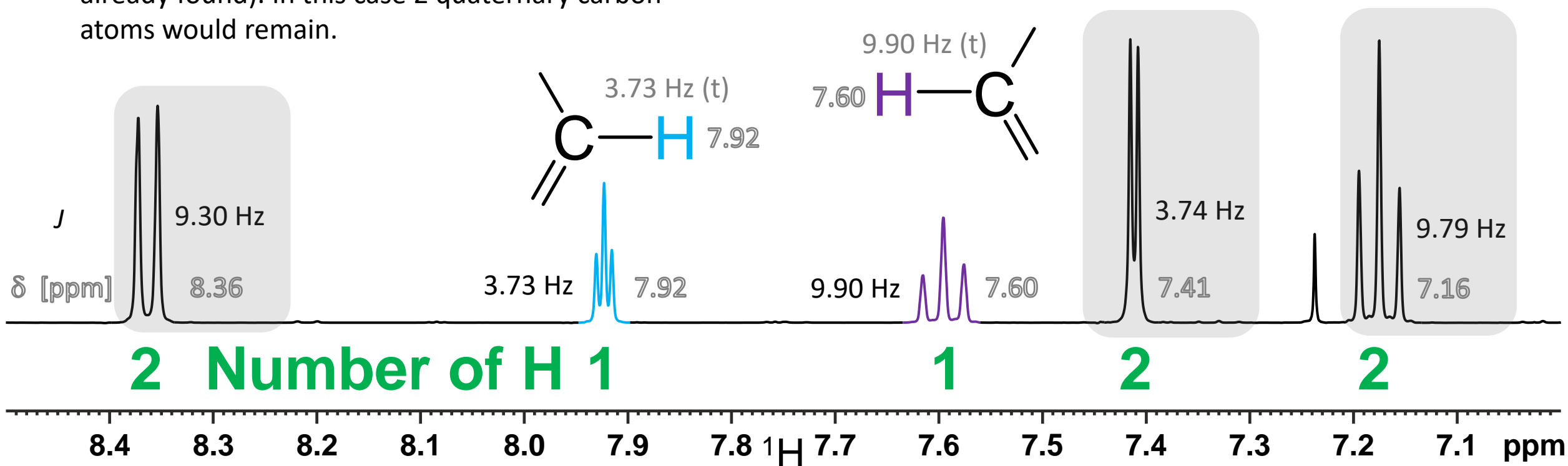
First steps

From the original molecular formula $C_{10}H_8$, partial structures are now known that add up to C_8H_8. Only two carbon atoms remain unknown.
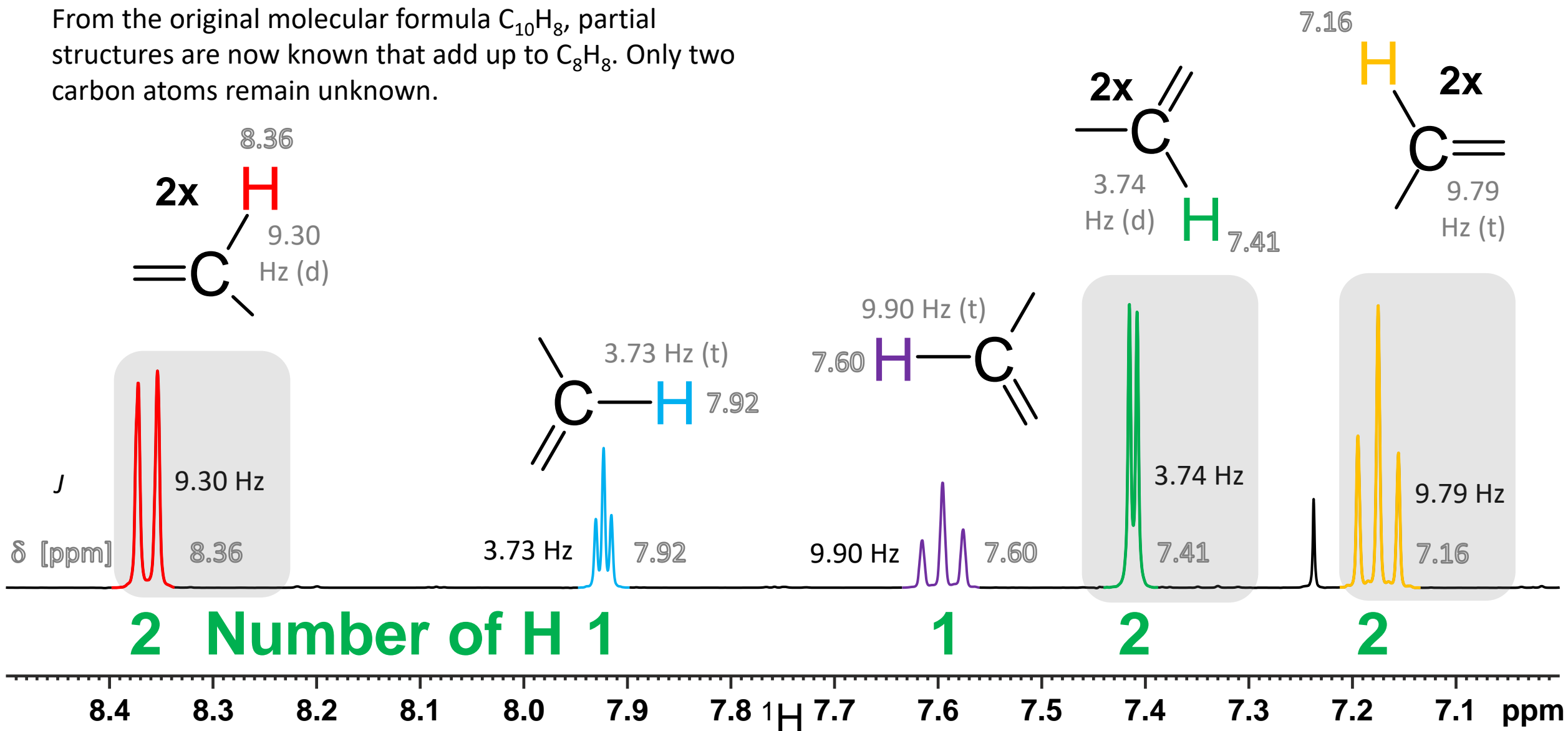
First steps

From the one-dimensional carbon spectrum, we only need the chemical shifts.
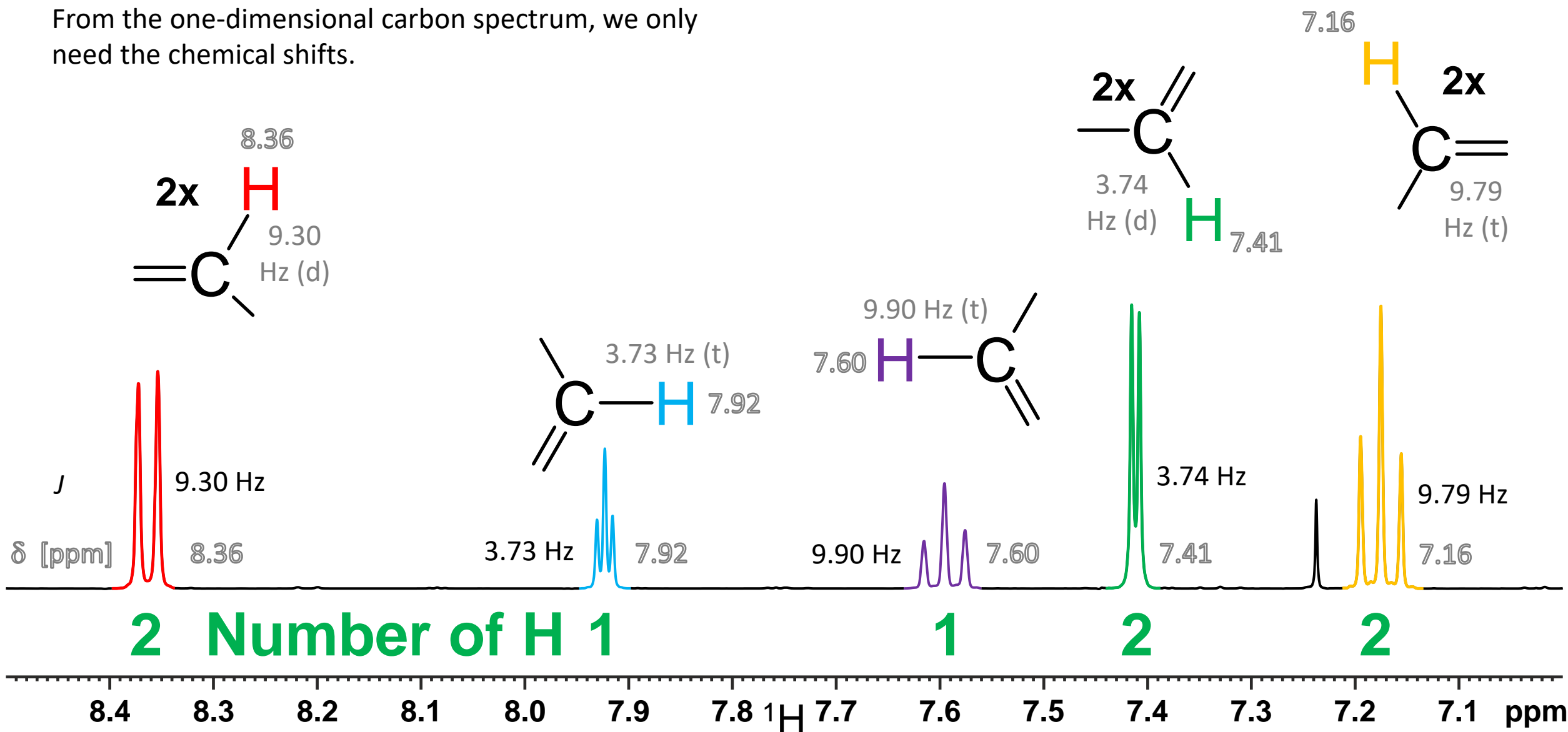
First steps
Carbon signals

not yet assigned : $\mathbb{C}_2$ 7 DBE

^{13}C

2x H 8.36 / 9.30 Hz (d) =C

2x C 3.74 Hz (d) / H 7.41

H 7.16 / 2x C= 9.79 Hz (t)

C—H 3.73 Hz (t) 7.92

7.60 H—C 9.90 Hz (t)

140.12 136.97 137.25 136.59 122.76 117.95

J 9.30 Hz 3.73 Hz 9.90 Hz 3.74 Hz 9.79 Hz

δ [ppm] 8.36 7.92 7.60 7.41 7.16

2 Number of H 1 1 2 2

144 142 140 138 136 134 132 130 128 126 124 122 120 118 ppm
^{13}C
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
^1H

First steps

Carbon signals
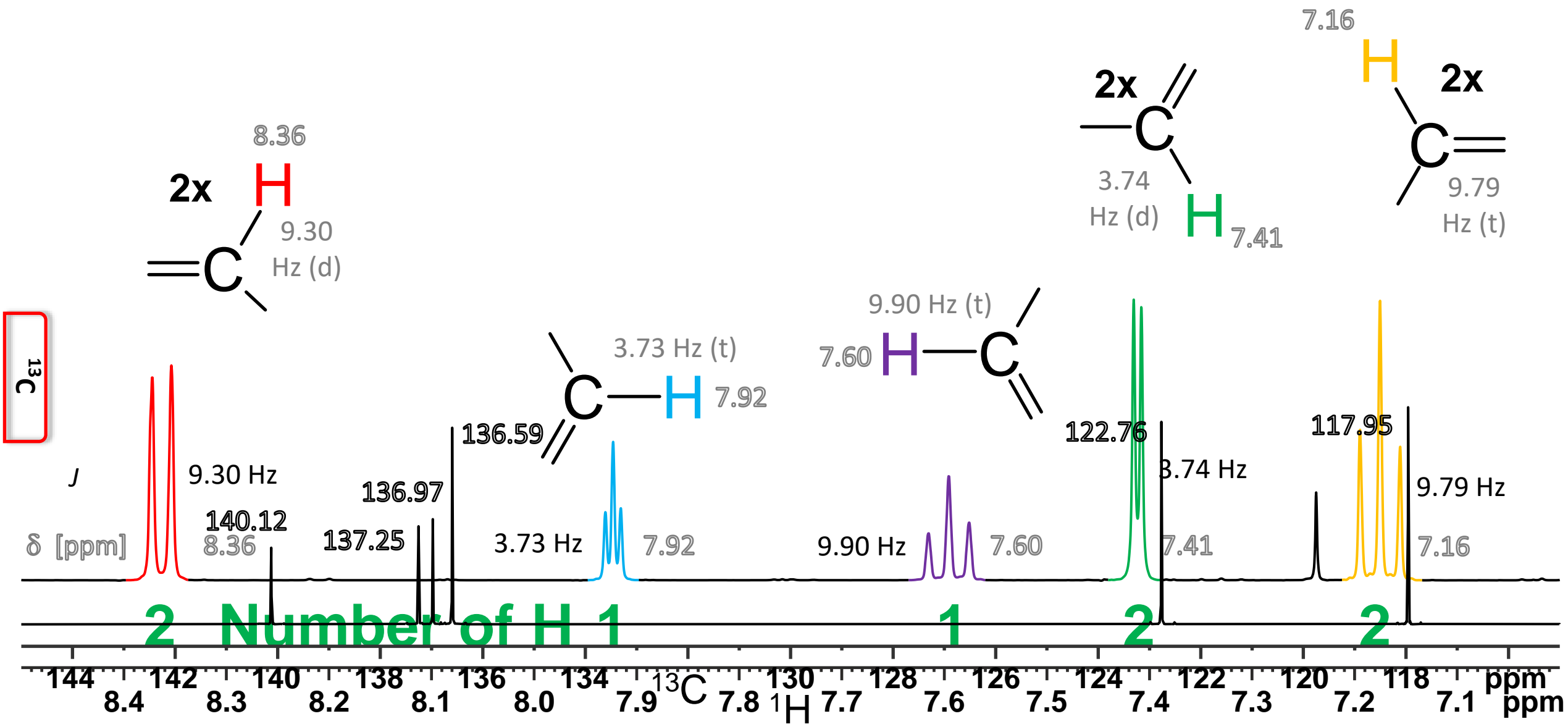
$\delta(^{13}C)$[ppm]:   140.12 / 137.25 / 136.97 / 136.59 / 122.76 / 117.95

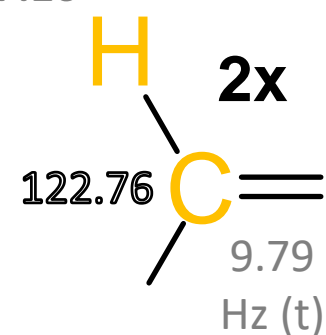The assignment of the carbon signals to the fragments is done with the HSQC.
First, let's reorder the fragments a little bit.

Carbon signal assignment

$\mathbb{C}_2$

not yet assigned :

$\delta(^{13}C)$ [ppm]:   140.12 / 137.25 / 136.97 / 136.59 / 122.76 / 117.95

For three very closely adjacent carbon signals, an enlarged section of the HSQC is necessary.
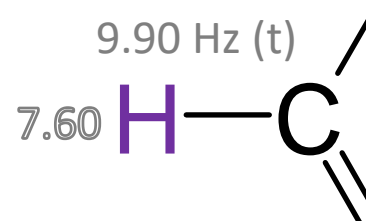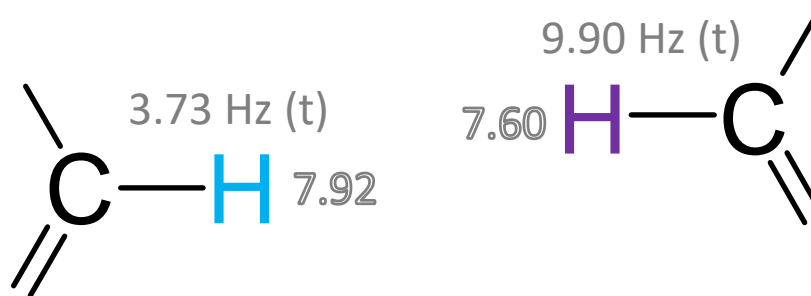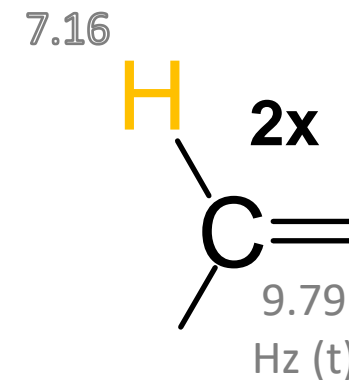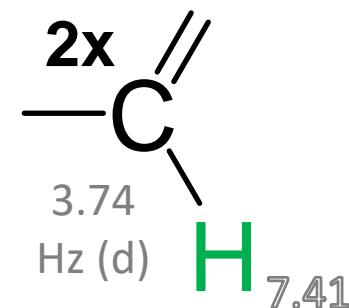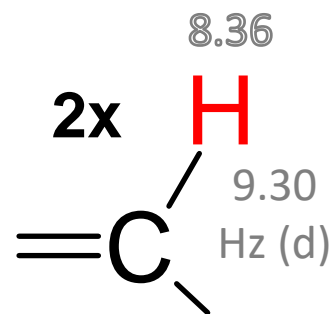
2x

8.36

H

9.30 Hz (d)

=C

2x

7.16

H

C=

9.79 Hz (t)

3.74 Hz (d)

H 7.41

—C

3.73 Hz (t)

C—H 7.92

9.90 Hz (t)

7.60 H—C

^{13}C

^{1}H

144   142   140   138   136   134 ^{13}C   130   128   126   124   122   120   118   ppm
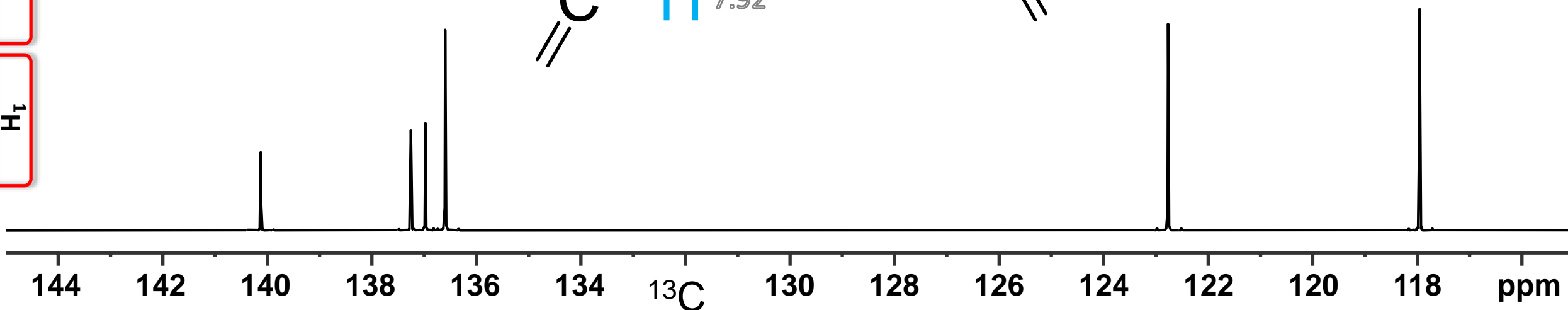
Carbon signal assignment

$\delta(^{13}C)[ppm]$:   **140.12 / 137.25 / 136.97 / 136.59 / 122.76 / 117.95**

HSQC

We can take the chemical shifts for both pseudo-projections from the list of carbon signals and the already known fragments.

8.36

2x H

9.30 Hz (d)

2x

3.74 Hz (d)

H 7.41

^{13}C

9.90 Hz (t)

7.60 H—C

7.16

H

2x

^{1}H

3.73 Hz (t)

C—H 7.92

9.79 Hz (t)

Carbon signal assignment

$\delta(^{13}C)$[ppm]: **140.12**   **122.76 / 117.95**

Having well-separated cross peaks, a proton-carbon assignment is easily possible without auxiliary lines.
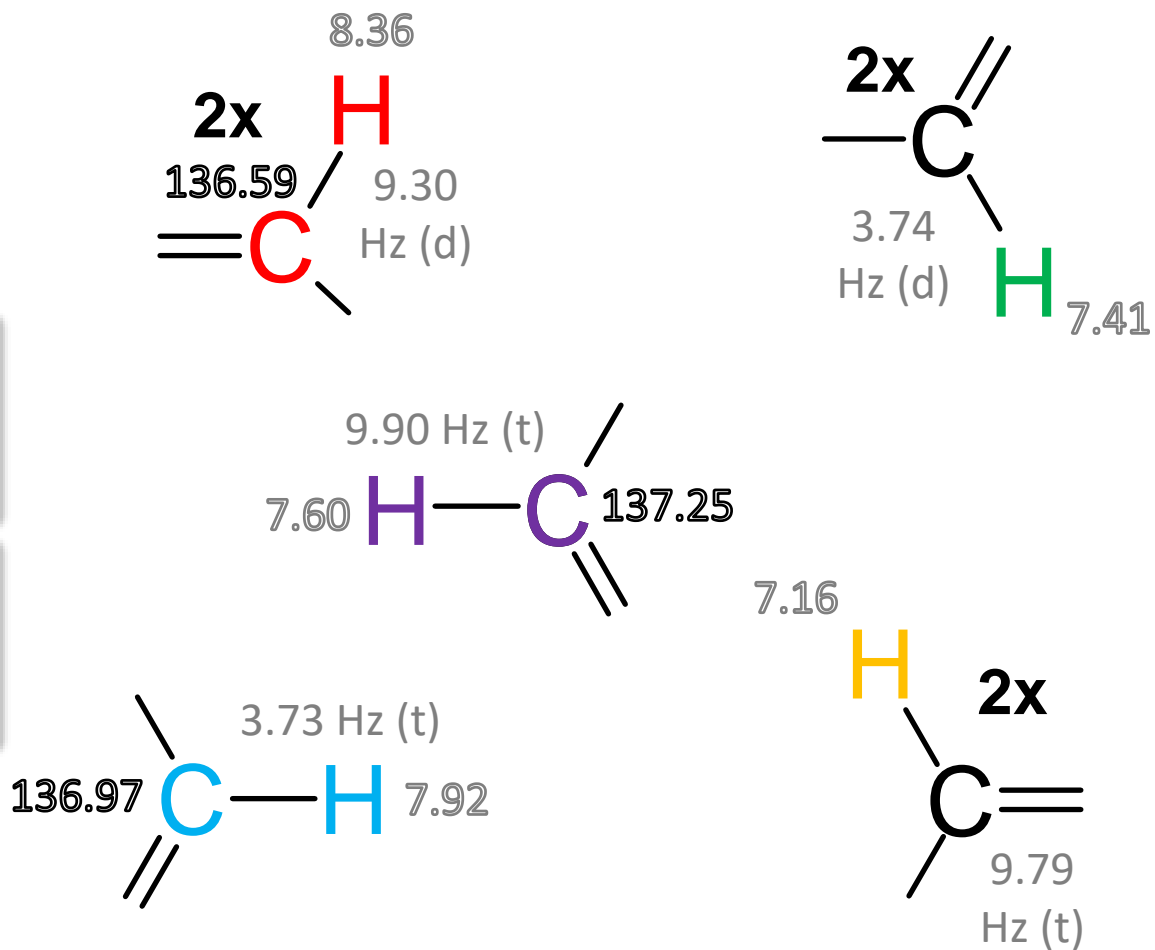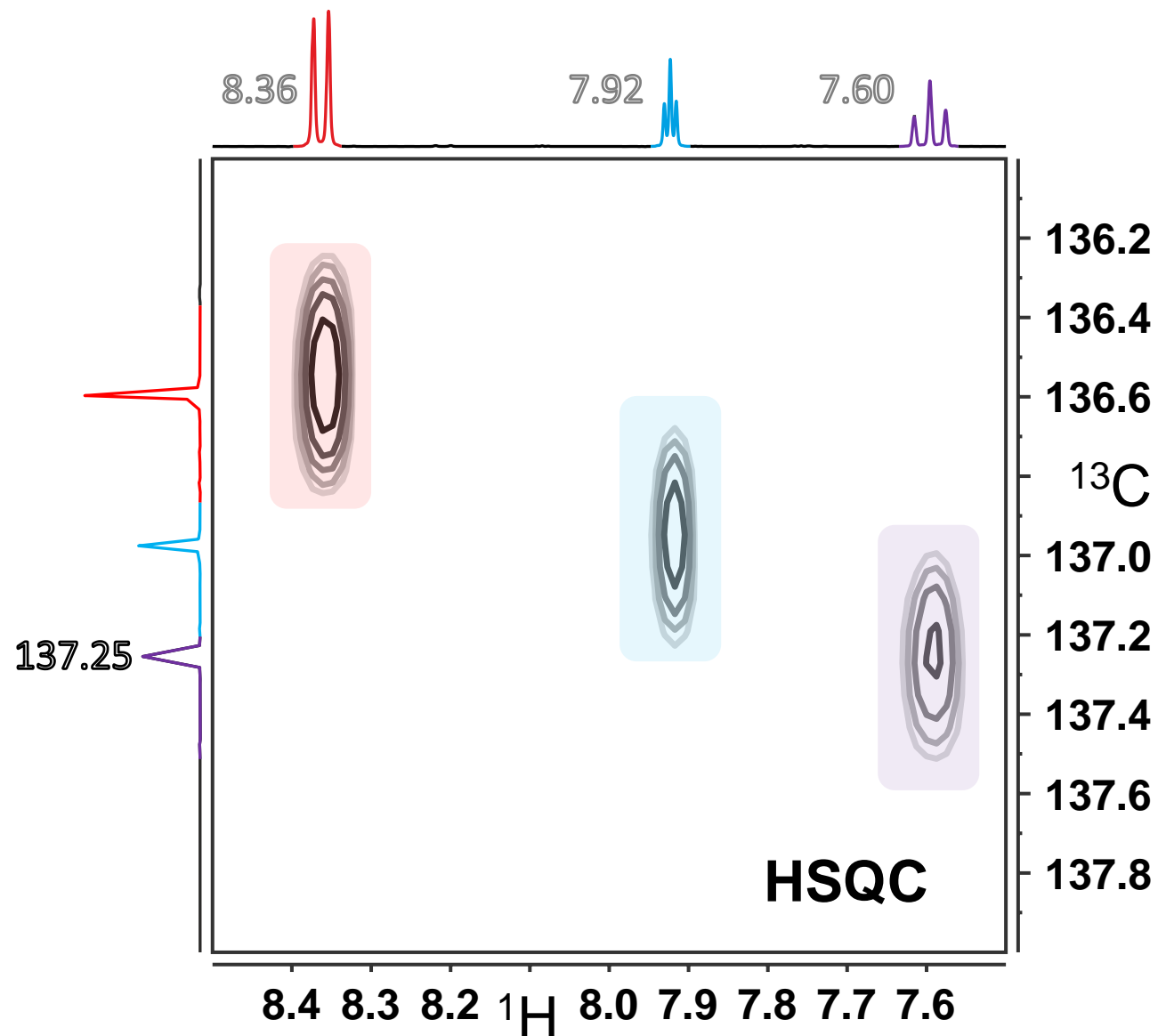
HSQC

Carbon signal assignment

$\delta(^{13}C)$[ppm]: **140.12**   **122.76 / 117.95**

For the two assignments that are still missing, we need the complete HSQC.

Carbon signal assignment

not yet assigned :

$\mathbb{C}_2$
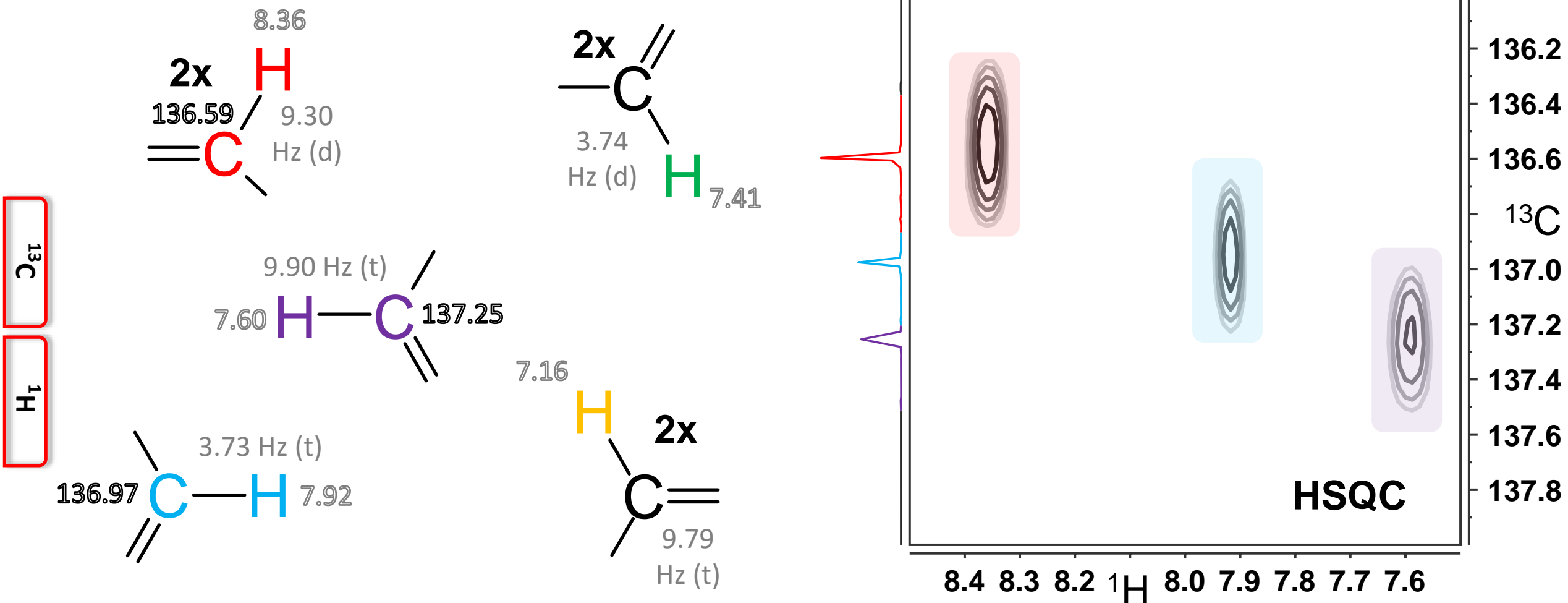
7 DBE

$\delta(^{13}C)[ppm]:$ 140.12

122.76 / 117.95

The two cross peaks in the upper right corner provide the desired information.
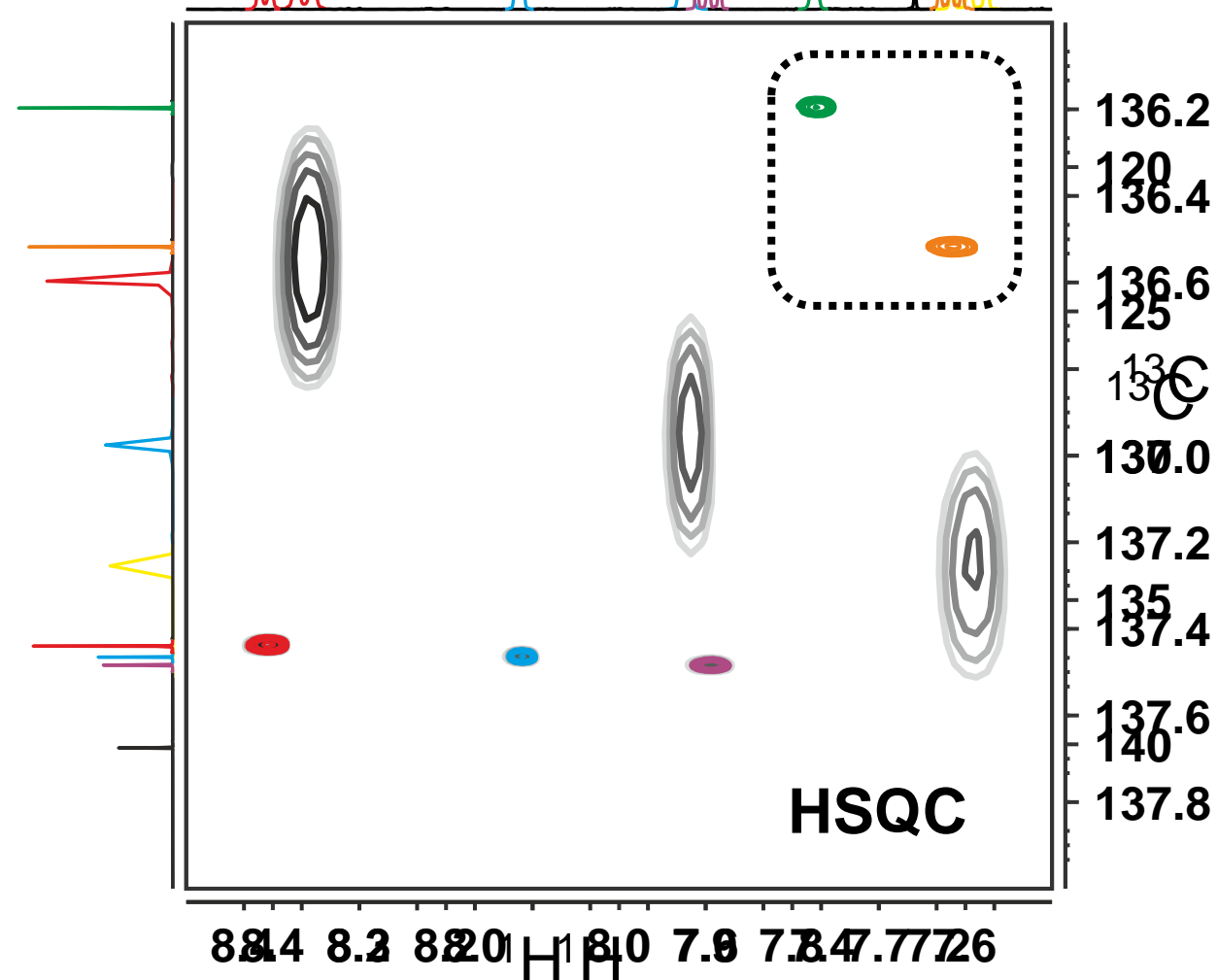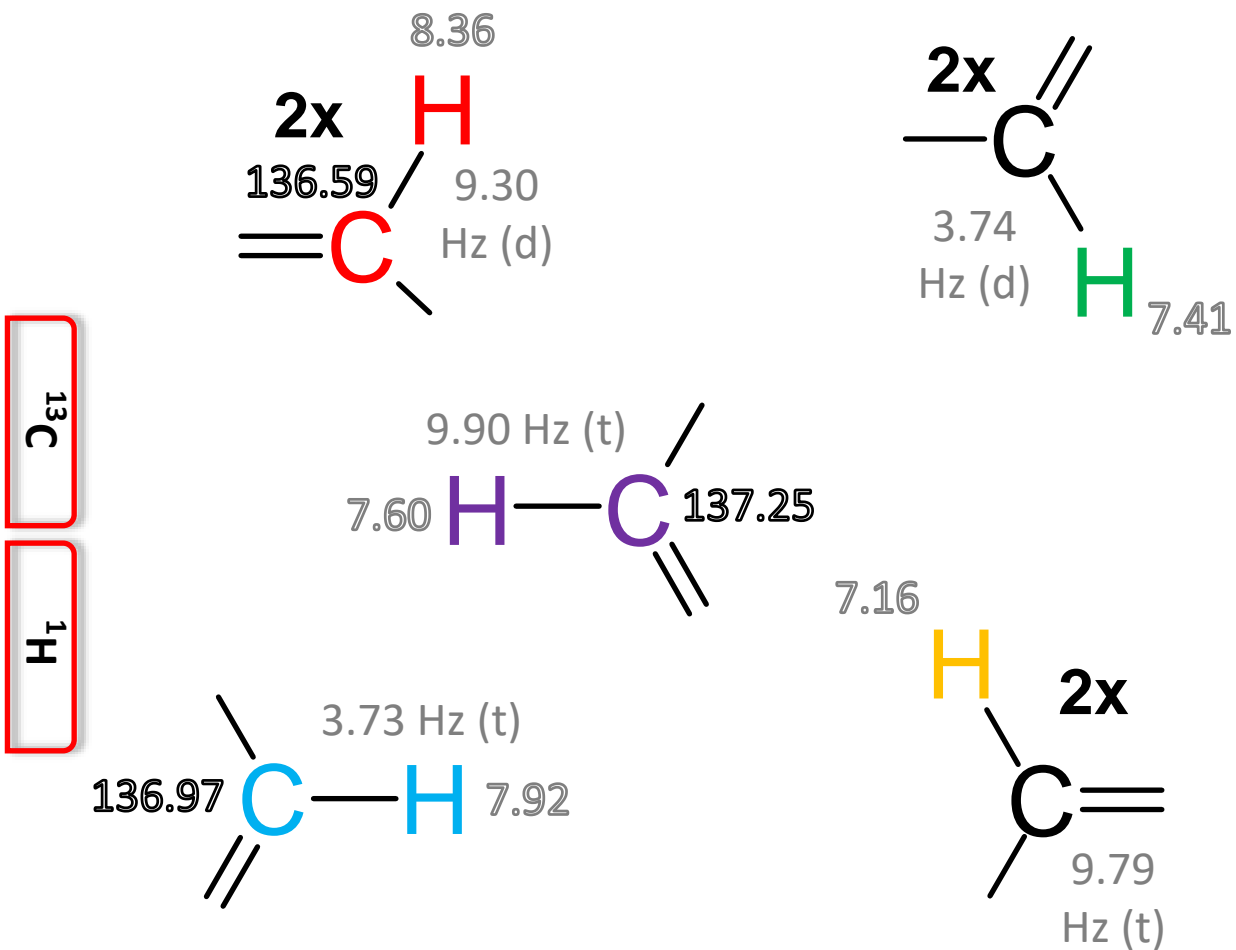
HSQC

^{13}C

^1H

Carbon signal assignment

not yet assigned :

$\mathbb{C}_2$

7 DBE

$\delta(^{13}C)$[ppm]:   140.12

122.76 / 117.95

7.41   7.16

The two C/H pairs 117.95 ppm/7.41 ppm and 122.76 ppm/7.16 ppm are easy to recognise even without auxiliary lines. We can complete the missing two assignments.

8.36

2x

H

136.59   9.30 Hz (d)

=C

2x

—C

3.74 Hz (d)

H 7.41

117.95

122.76

120

125

^{13}C

130

9.90 Hz (t)

7.60 H—C 137.25

7.16

H

2x

C=

9.79 Hz (t)

135

3.73 Hz (t)

136.97 C—H 7.92

140

HSQC

^{13}C

^{1}H

8.4   8.2   8.0 ^{1}H 7.6   7.4   7.2
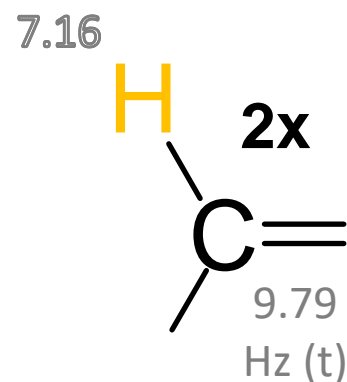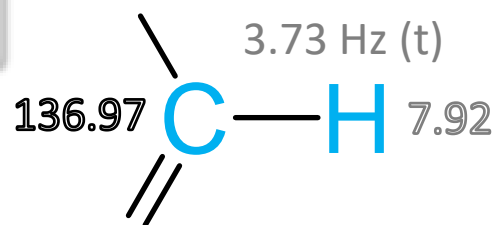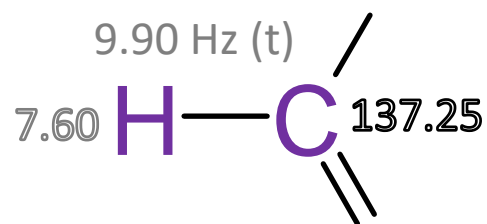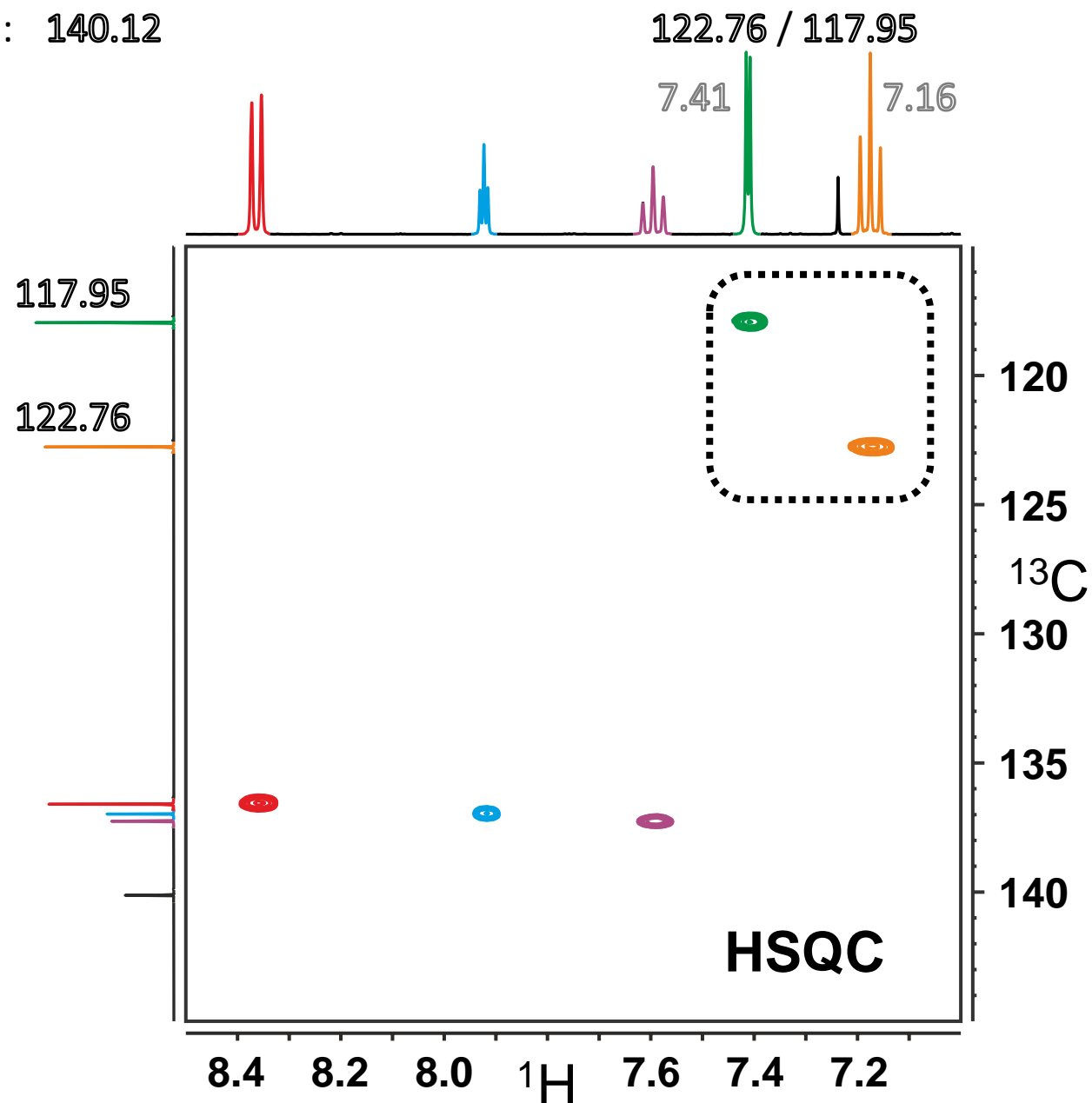
Carbon signal assignment

$\delta(^{13}C)$[ppm]:   140.12

The two C/H pairs **117.95** ppm/7.41 ppm and **122.76** ppm/7.16 ppm are easy to recognise even without auxiliary lines. We can complete the missing two assignments.

8.36

2x

136.59

H

9.30 Hz (d)

C

2x

—C **117.95**

3.74 Hz (d)

H 7.41

9.90 Hz (t)

7.60 H—C **137.25**

140.12 C— **2x**

7.16

H

122.76 C= **2x**

9.79 Hz (t)

3.73 Hz (t)

136.97 C—H 7.92

117.95

122.76

A carbon signal remains at **140.12** ppm without a directly bonded proton. The molecular formula tells us about two unassigned carbon atoms, i.e. there are two equivalent sp^2-hybridised quaternary C atoms.

All atoms are now assigned to structural fragments. The puzzle of linking these building blocks can begin.

HSQC

7.41   7.16

120

125

^{13}C

130

135

140

8.4   8.2   8.0 ^{1}H   7.6   7.4   7.2
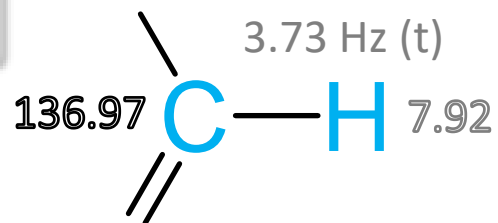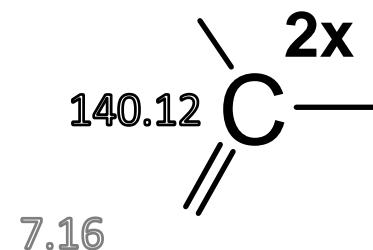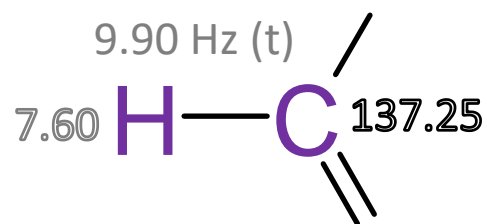
Double bond equivalents
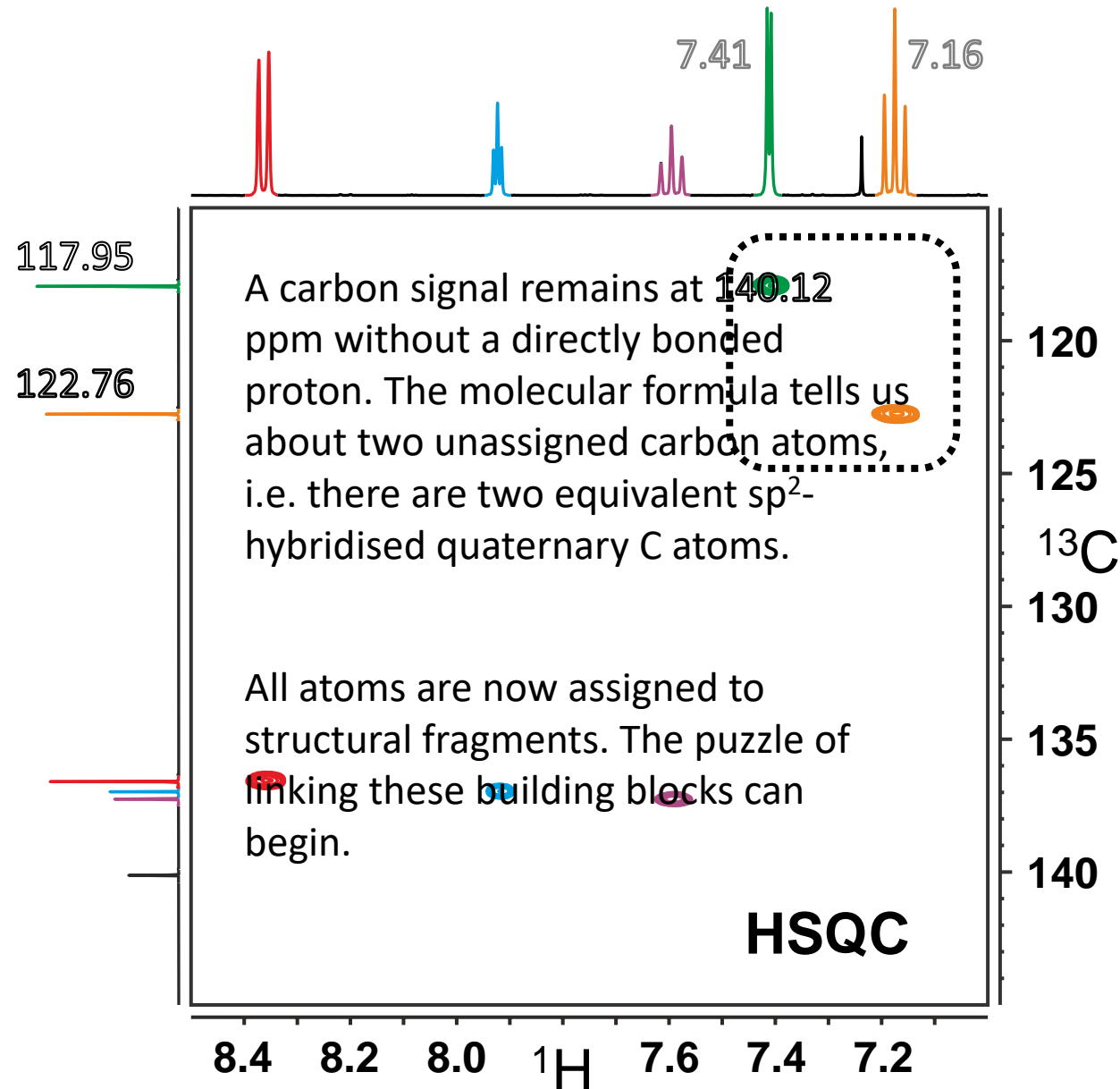
not yet assigned : 2 Rings

7 DBE

2x H 8.36
136.59 9.30 Hz (d)
C

2x C 117.95
3.74 Hz (d)
H 7.41

9.90 Hz (t)
7.60 H—C 137.25

140.12 C **2x**

7.16
H
136.97 C—H 7.92
3.73 Hz (t)

122.76 C **2x**
9.79 Hz (t)
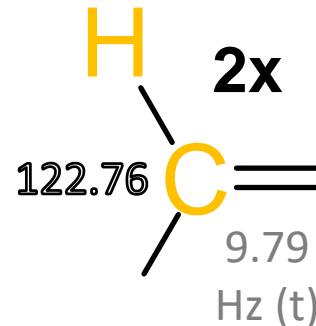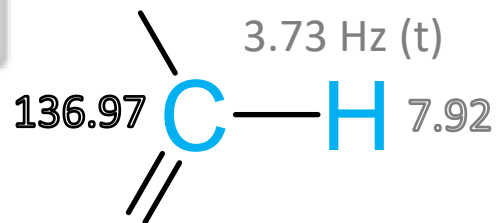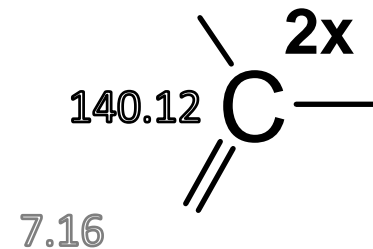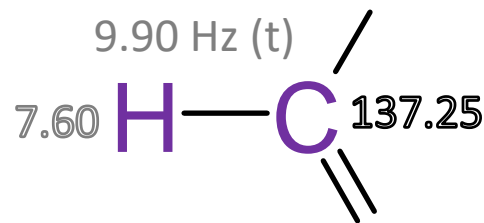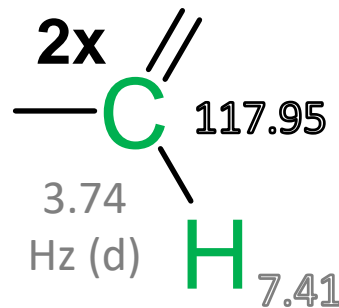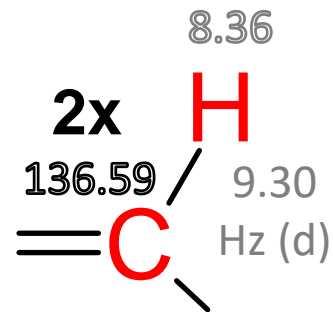
Our collection of fragments contains a total of **10** carbon atoms, each with an open double bond. No matter how the fragments are linked, a total of **5** building blocks with the structure >C=C< are created, which means that **5** of the **7** double bond equivalents would be assigned.

There are no more structural fragments, the two double bond equivalents still missing can only be two ring closures.

The TOCSY is a nice tool to get some pieces of information to link at least a few fragments.

Linking the fragments
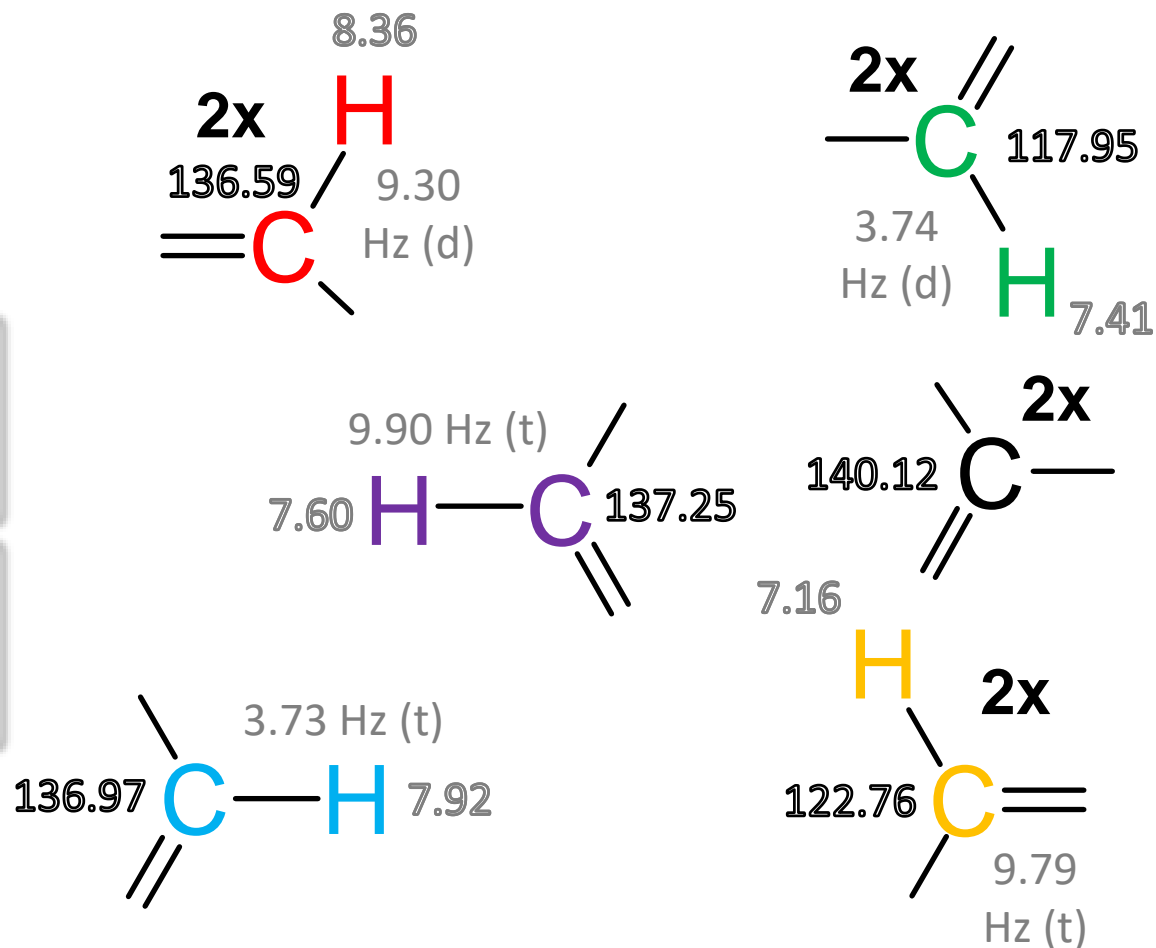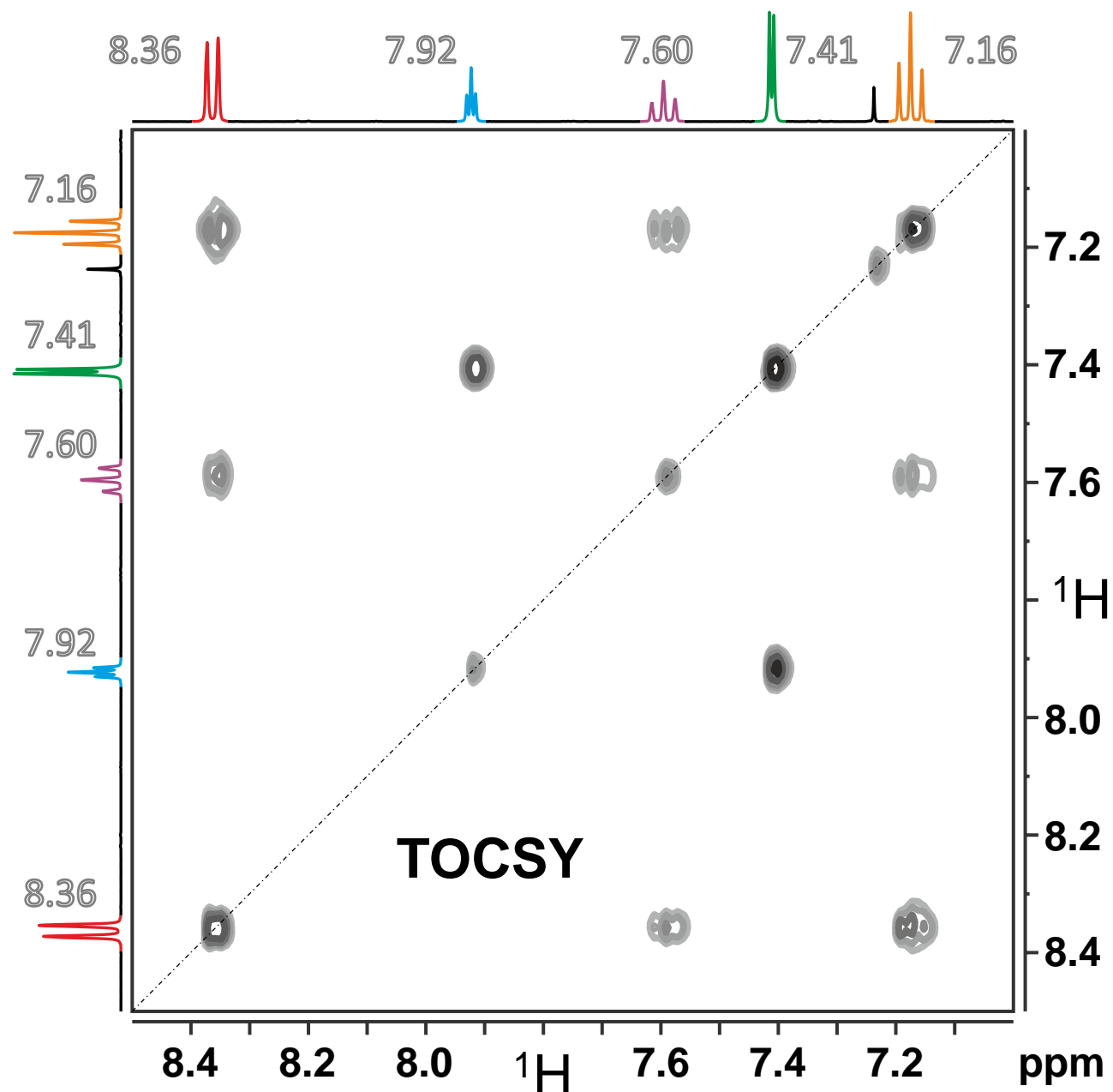
HSQC

Let's mark the associated structural fragments with solid frames.

The remaining three proton multiplets form a second spin system.

13C

1H

8.36
2x H
136.59 / 9.30 Hz (d)
C ═

2x //
— C 117.95
3.74 Hz (d)
H 7.41

9.90 Hz (t)
7.60 H — C 137.25

140.12 C **2x**
—
═

7.16
H **2x**
122.76 C ═
9.79 Hz (t)

136.97 C — H 7.92
3.73 Hz (t)

TOCSY

8.36   7.92   7.60   7.41   7.16

7.16
7.41
7.60
7.92
8.36

^{1}H

^{1}H   ppm
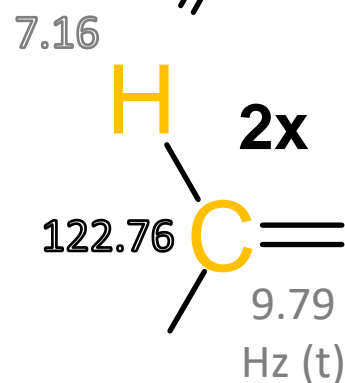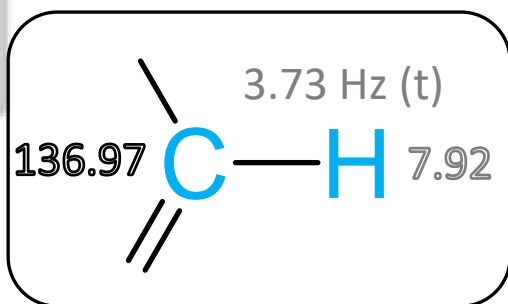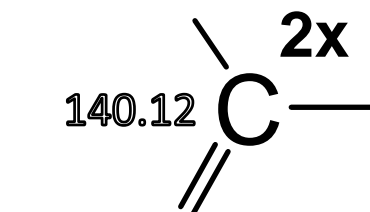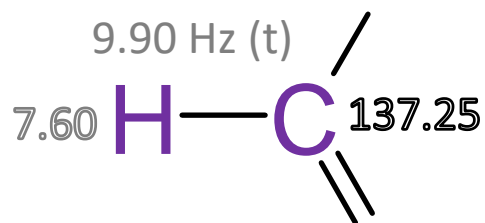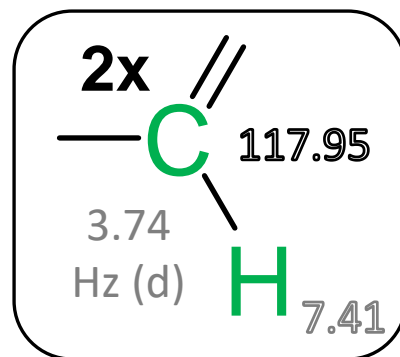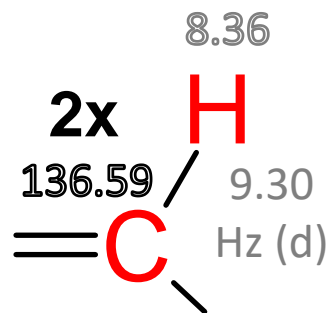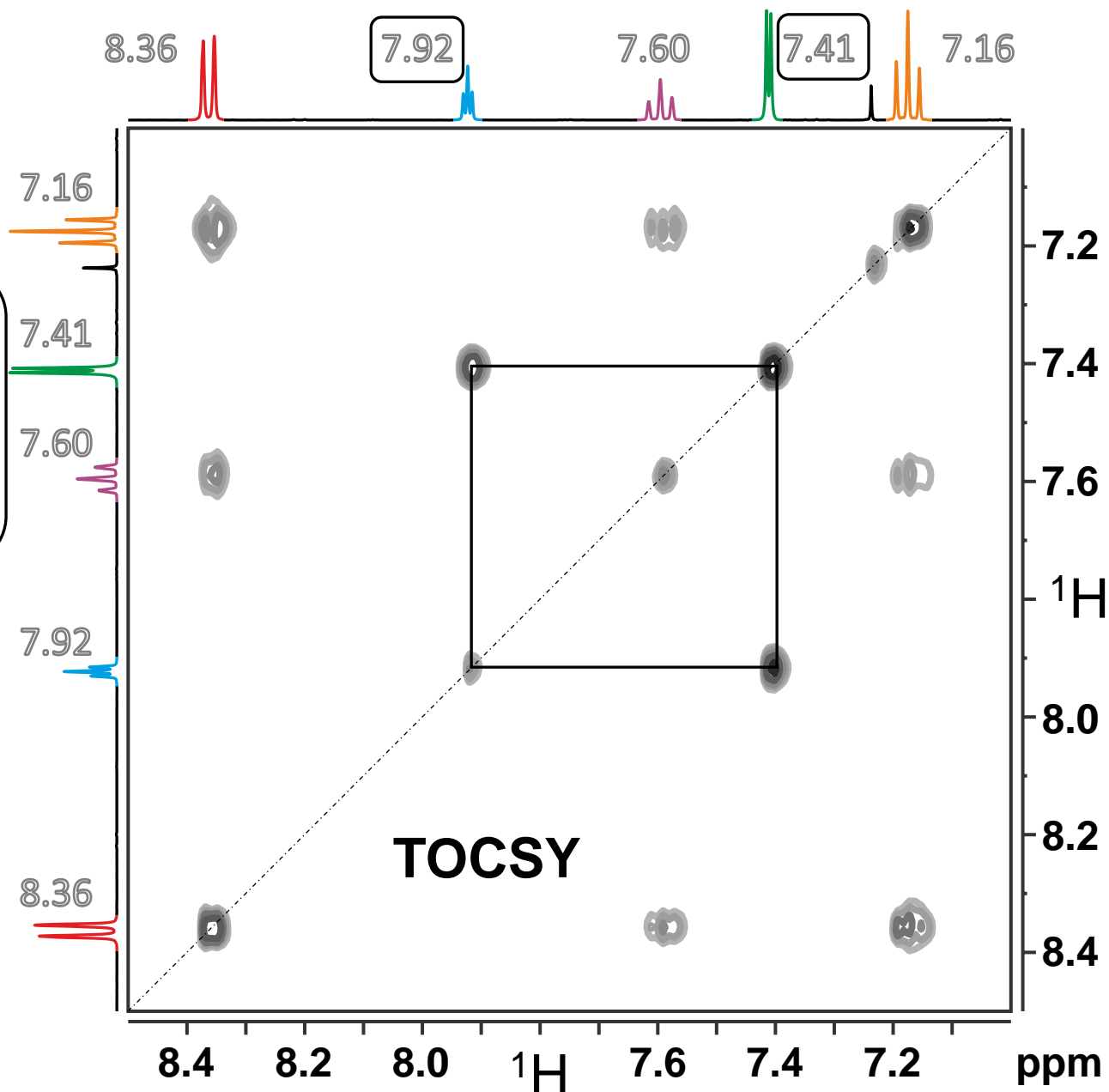
Linking the fragments

In this case we mark the associated structural fragments with dashed frames.

HSQC

13C

1H

TOCSY

Linking the fragments

Connecting the fragments belonging to the two
independent spin systems is only possible via the two
quaternary carbon atoms.

Linking the fragments

Let's start with the fragments belonging to the smaller spin system and the quaternary carbon atoms that serve as spacer.
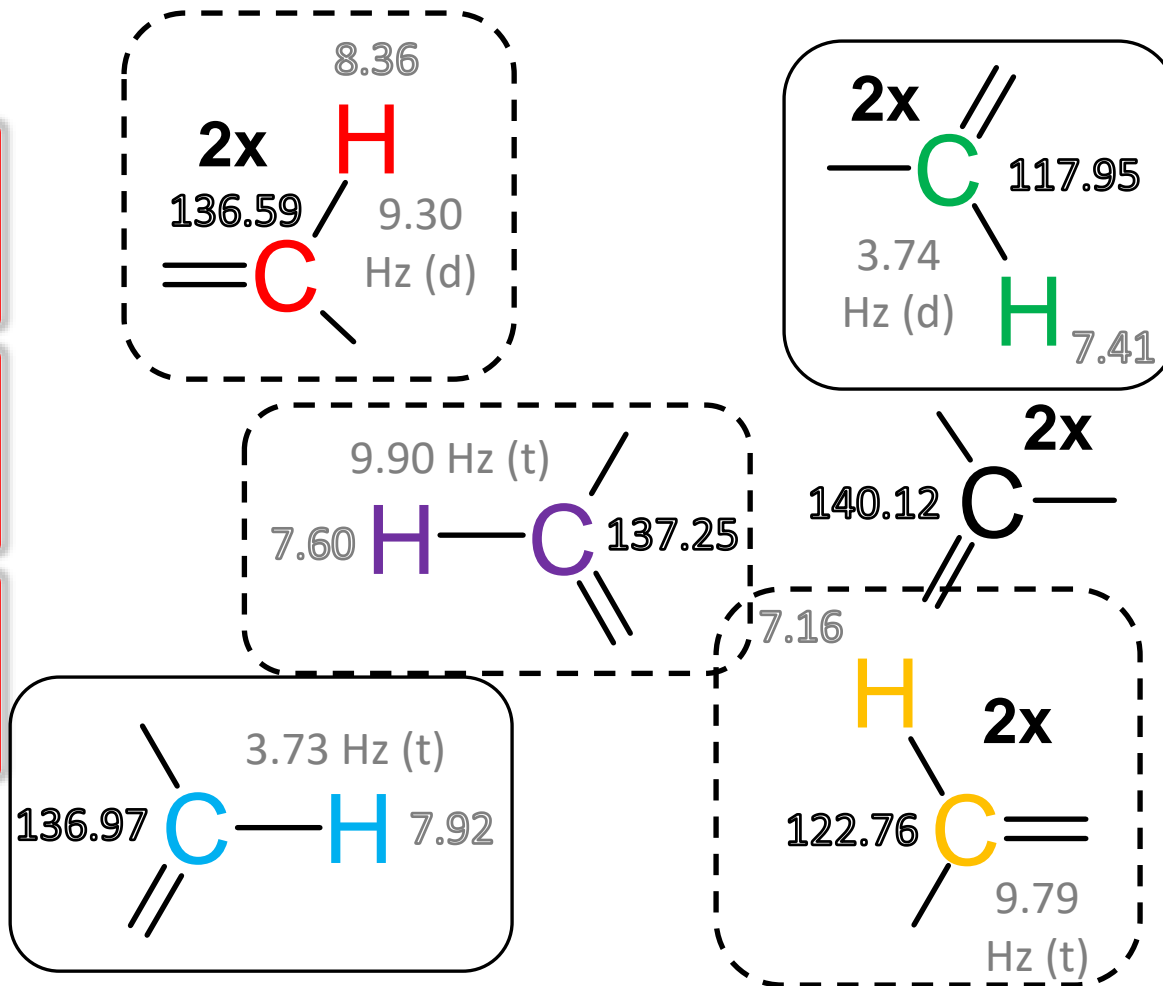
Linking the fragments

After a little cosmetic work, …
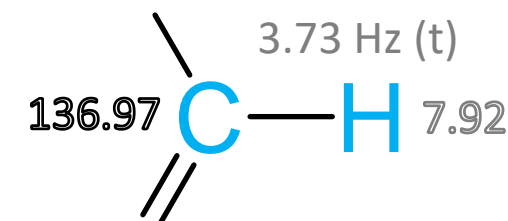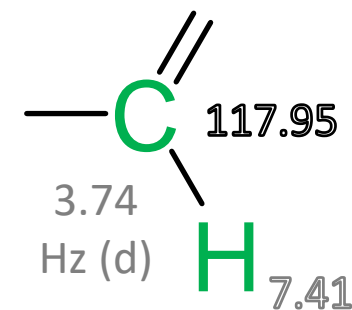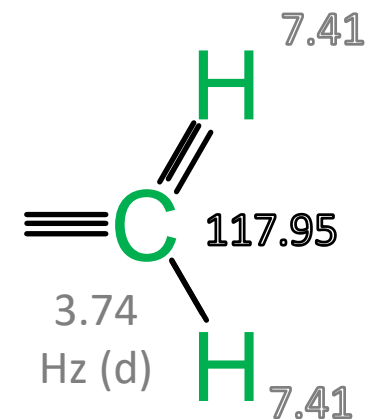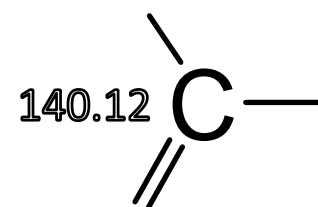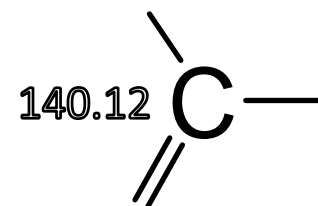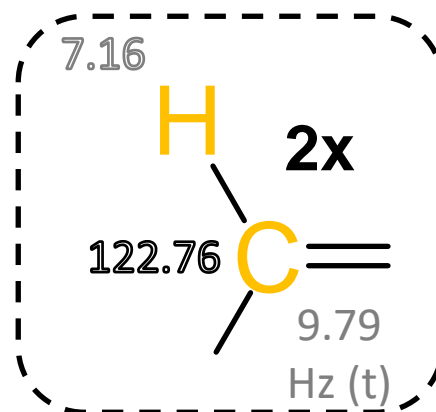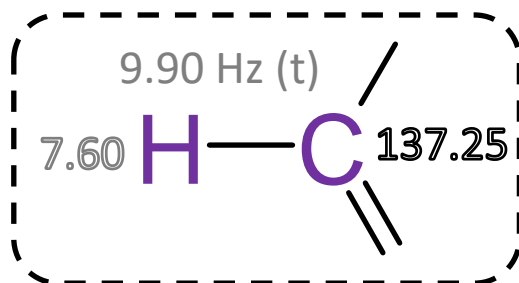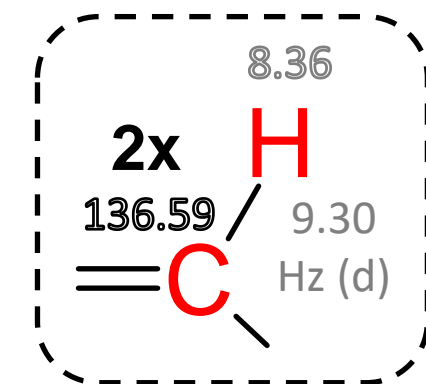
Linking the fragments

... the first fragments can be linked together.
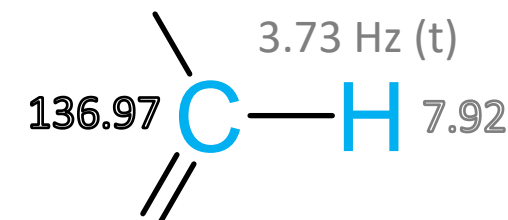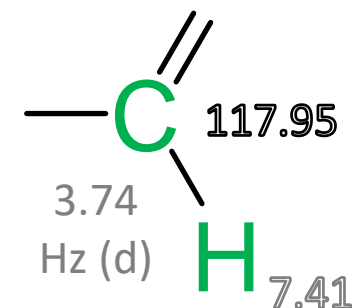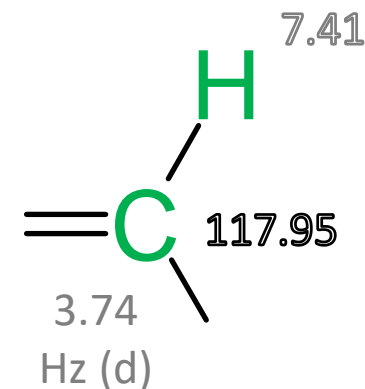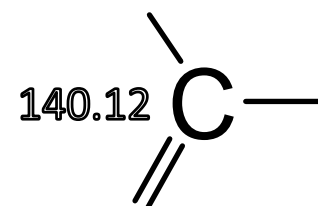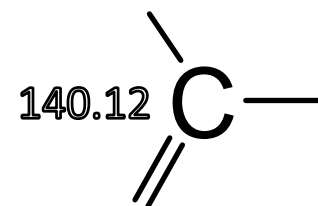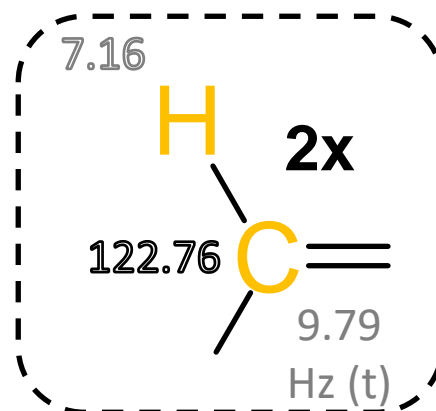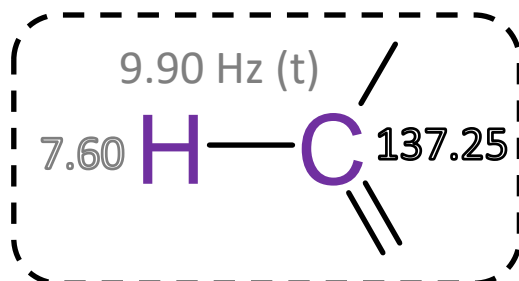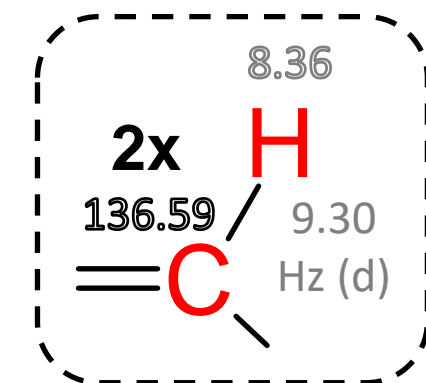
Linking the fragments

Due to the symmetry of the two CH groups, some redundant information could be removed for the sake of clarity.
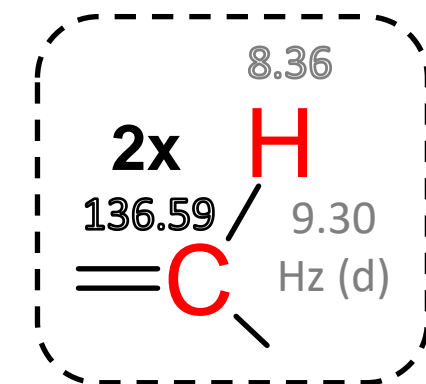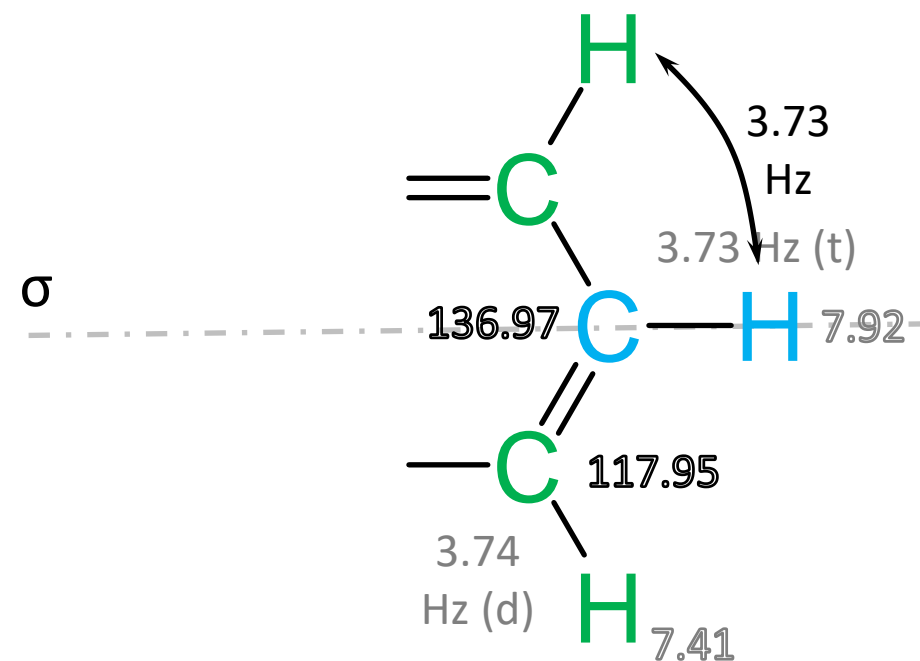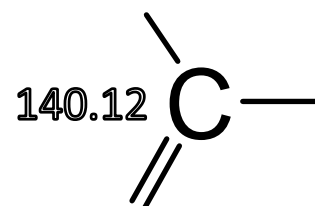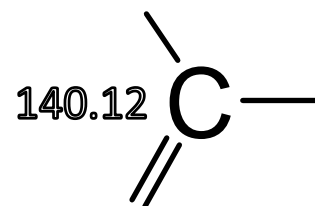
(A point symmetry with the carbon marked in blue as the centre of symmetry would also be conceivable, but somehow we have to end with two ring systems.)
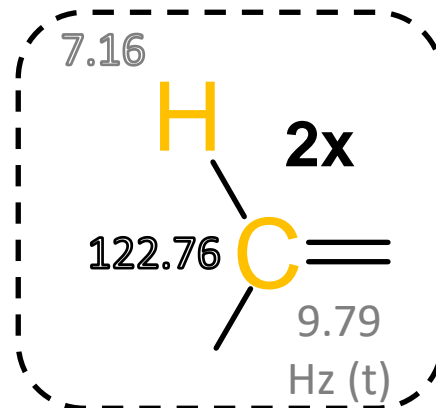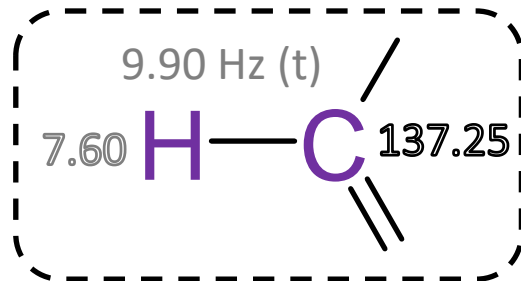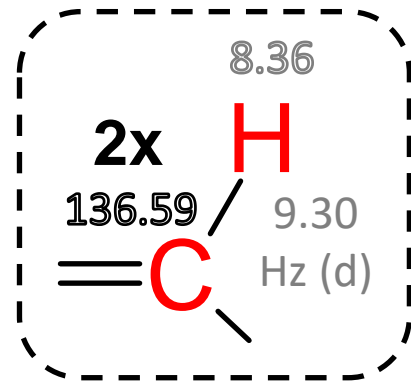
Linking the fragments

The measured coupling constants and the known multiplets are easily explained by this partial structure, although a coupling constant of 3.73 Hz is not seen every day.

140.12 C —

8.36
2x
H
136.59 / 9.30
=C Hz (d)

7.16
H
2x
122.76 C=
9.79
Hz (t)

9.90 Hz (t)
7.60 **H**—**C** 137.25

140.12 C —

H
3.73
Hz
=C
3.73 Hz (t)
σ ————— 136.97 C—H 7.92 —
C 117.95
3.74
Hz (d) H 7.41
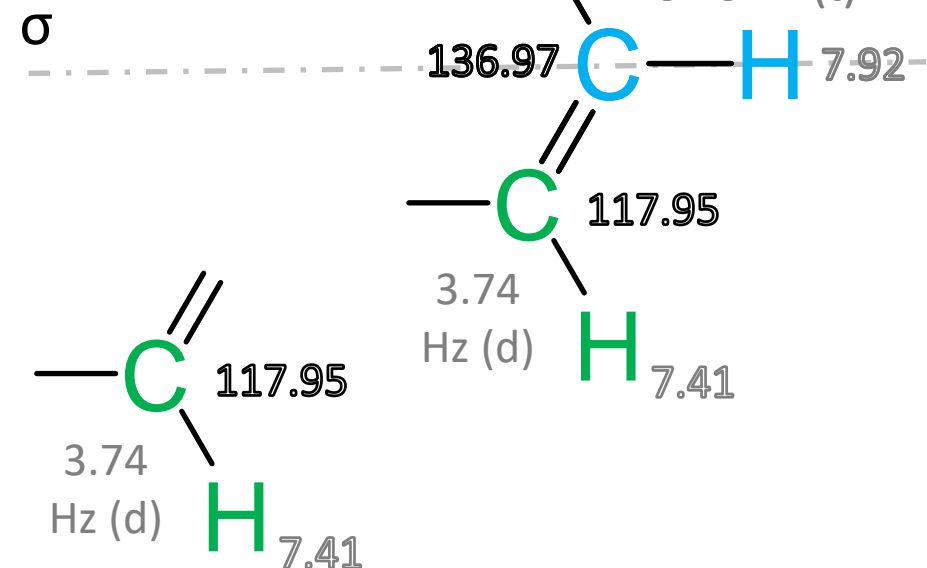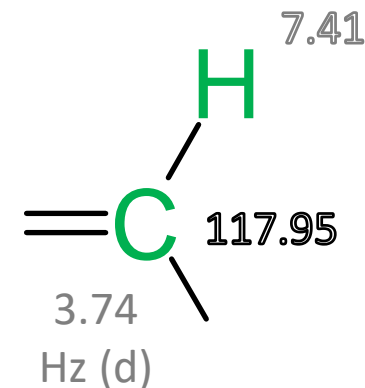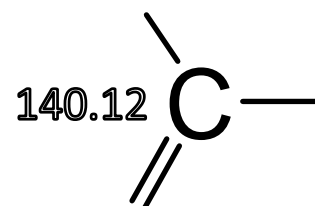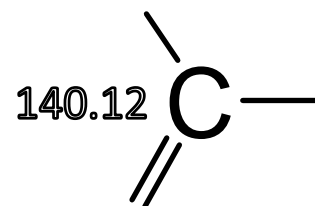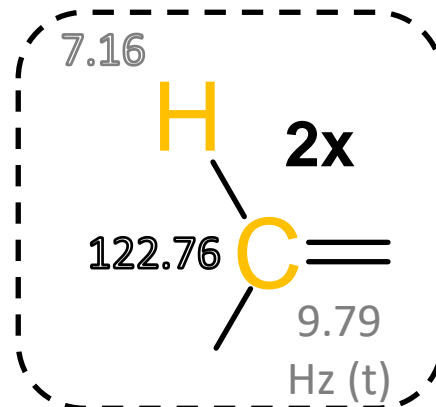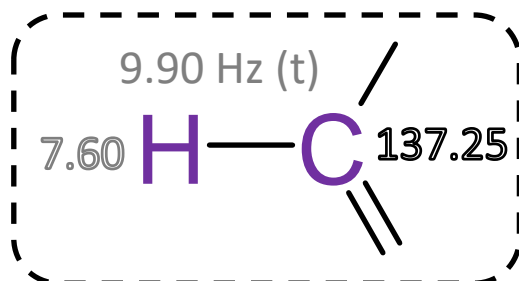
HSQC
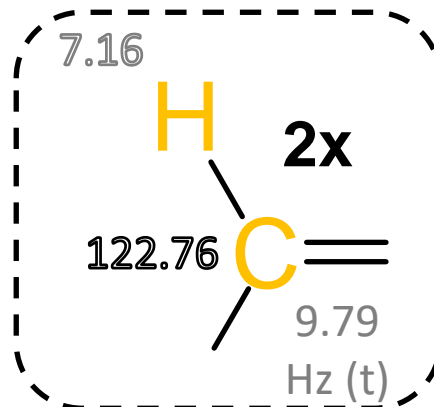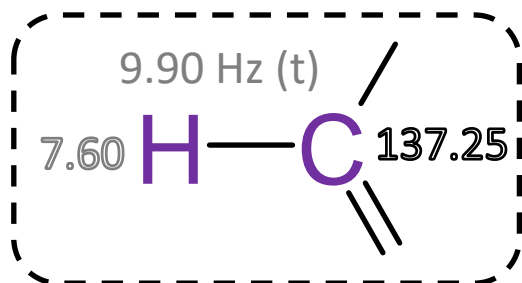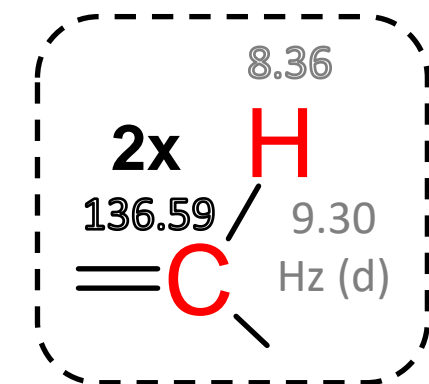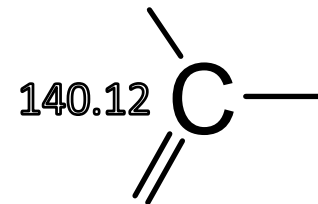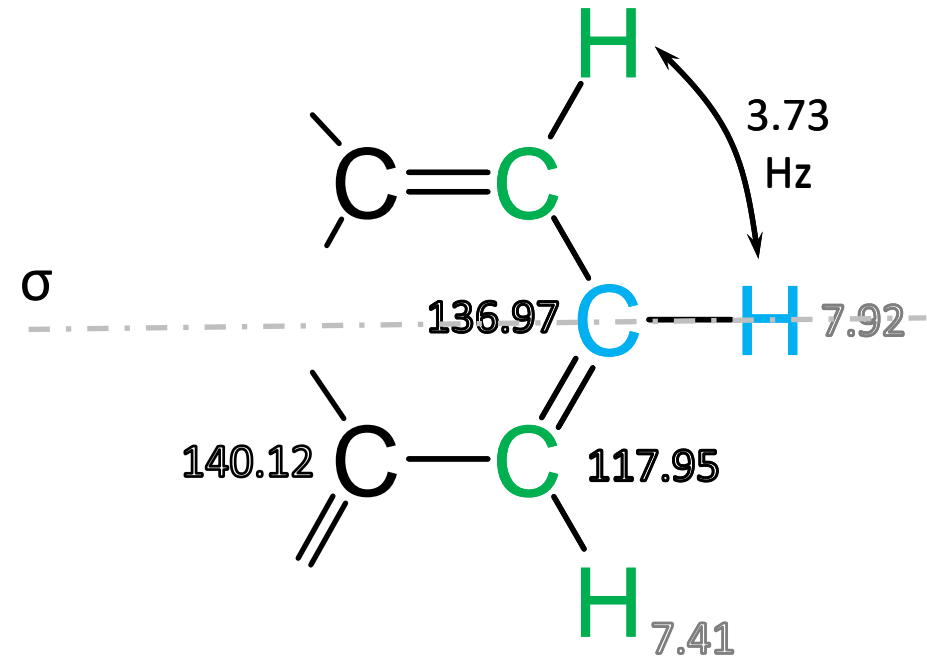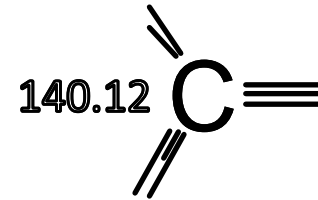
Linking the fragments

This first substructure is terminated by the quaternary carbon atoms, since according to TOCSY there is no coupling to any of the remaining CH fragments.
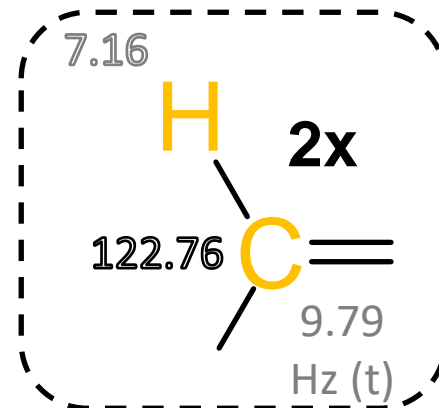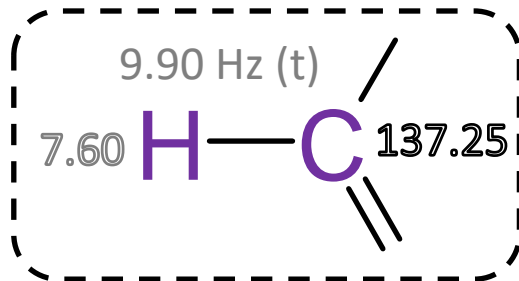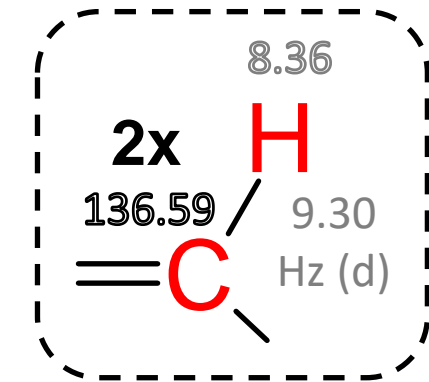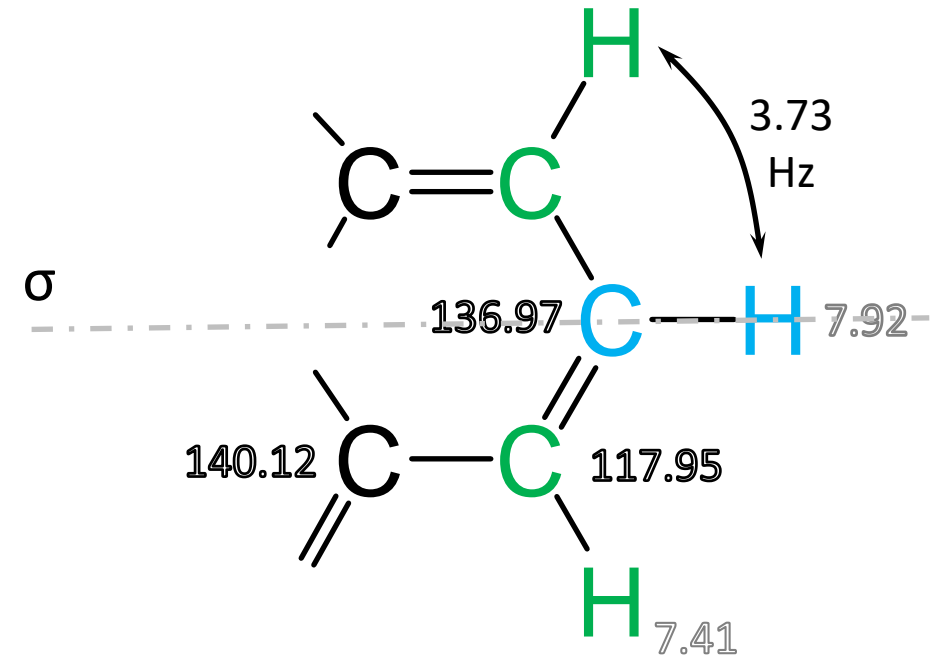
TOCSY

13C

1H

140.12 C≡

2x H 8.36
136.59 C 9.30
Hz (d)

7.16
H **2x**
122.76 C=
9.79
Hz (t)

140.12 C—

9.90 Hz (t)
7.60 H—C 137.25

σ

H
C=C 3.73 Hz
136.97 C—H 7.92
140.12 C—C 117.95
H 7.41

Linking the fragments

To continue the structure beyond the quaternary carbon atoms, but keeping the symmetry we have only two choices. We need one of the fragments existing twice each.
Which of the two?

HSQC
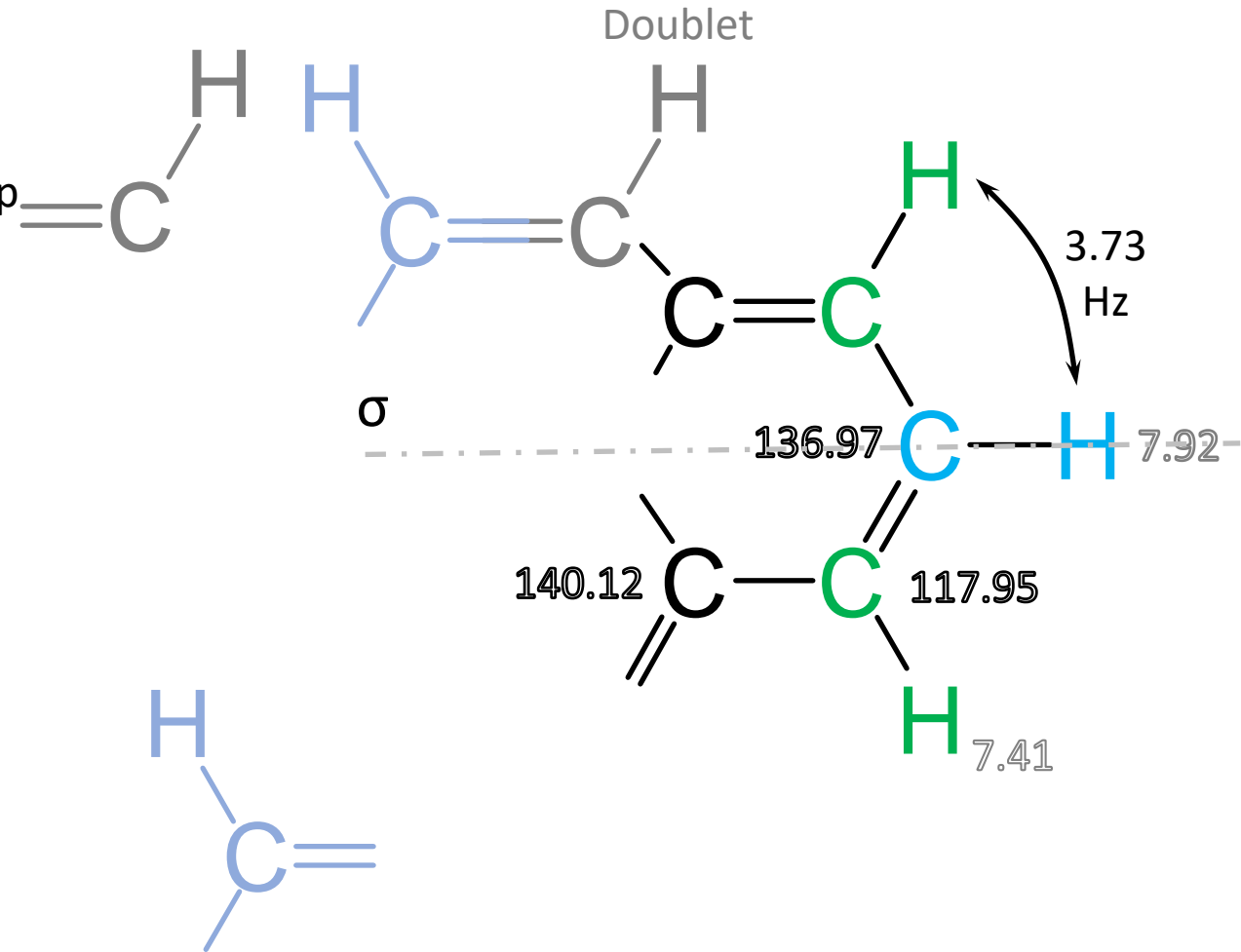
Linking the fragments

Let's take a hypothetical CH fragment and attach this to one of the the quaternary carbon atoms.

Only one more neighbour is possible, i.e. we have to observe a doublet.

The proton at 8.36 ppm appears as a doublet. The CH group containing this proton follows the quaternary C atoms.
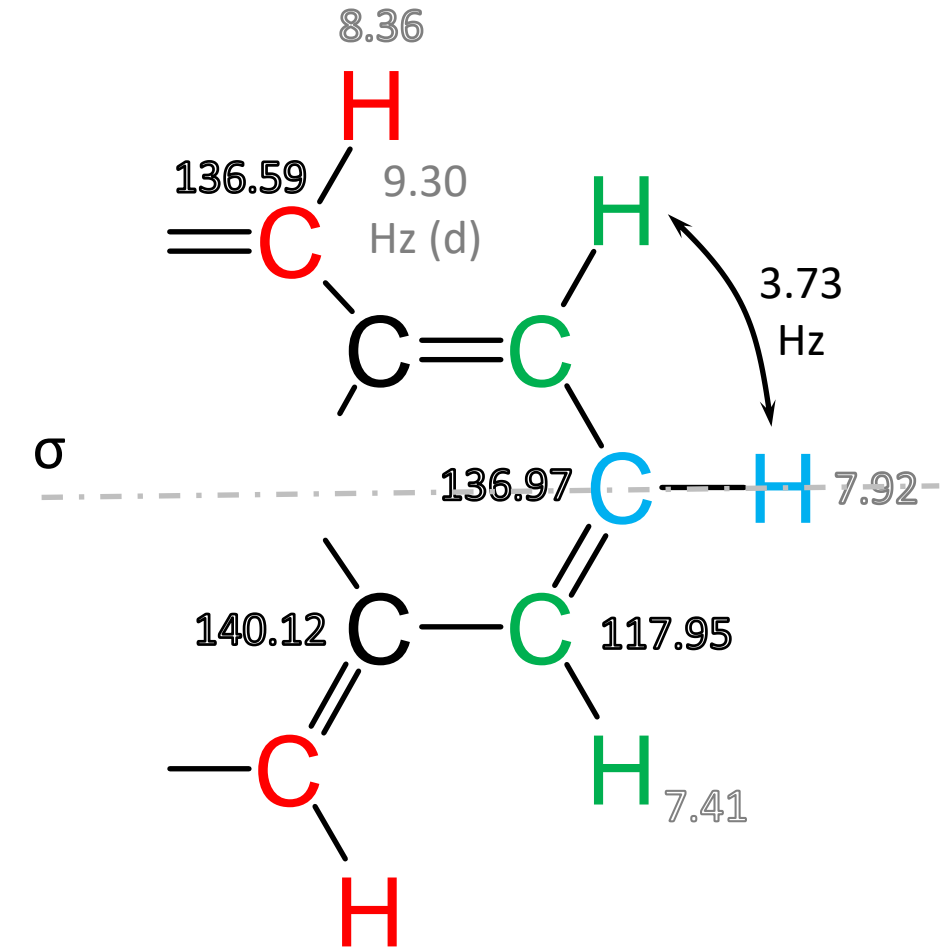
TOCSY

¹³C

¹H

Linking the fragments
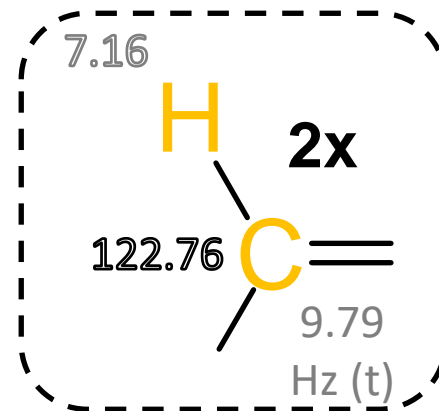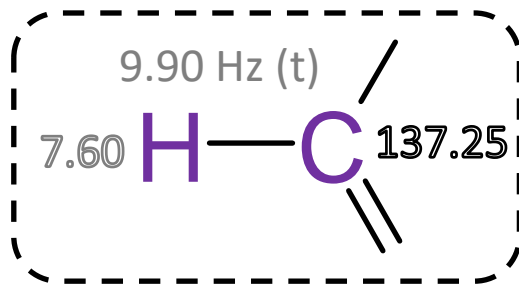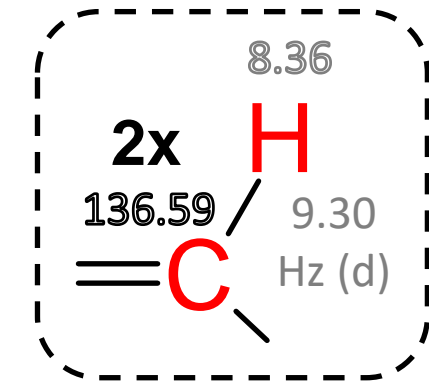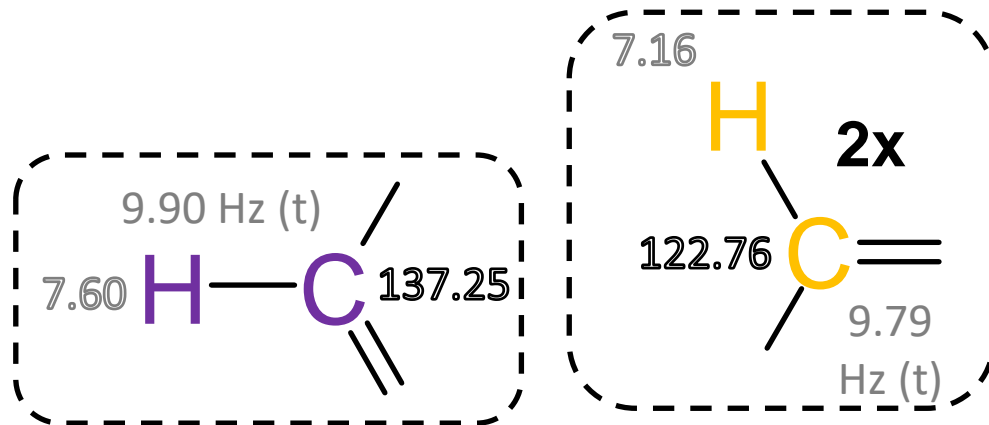
HSQC

To continue, we need two more identical fragments.
There is only one possibility.
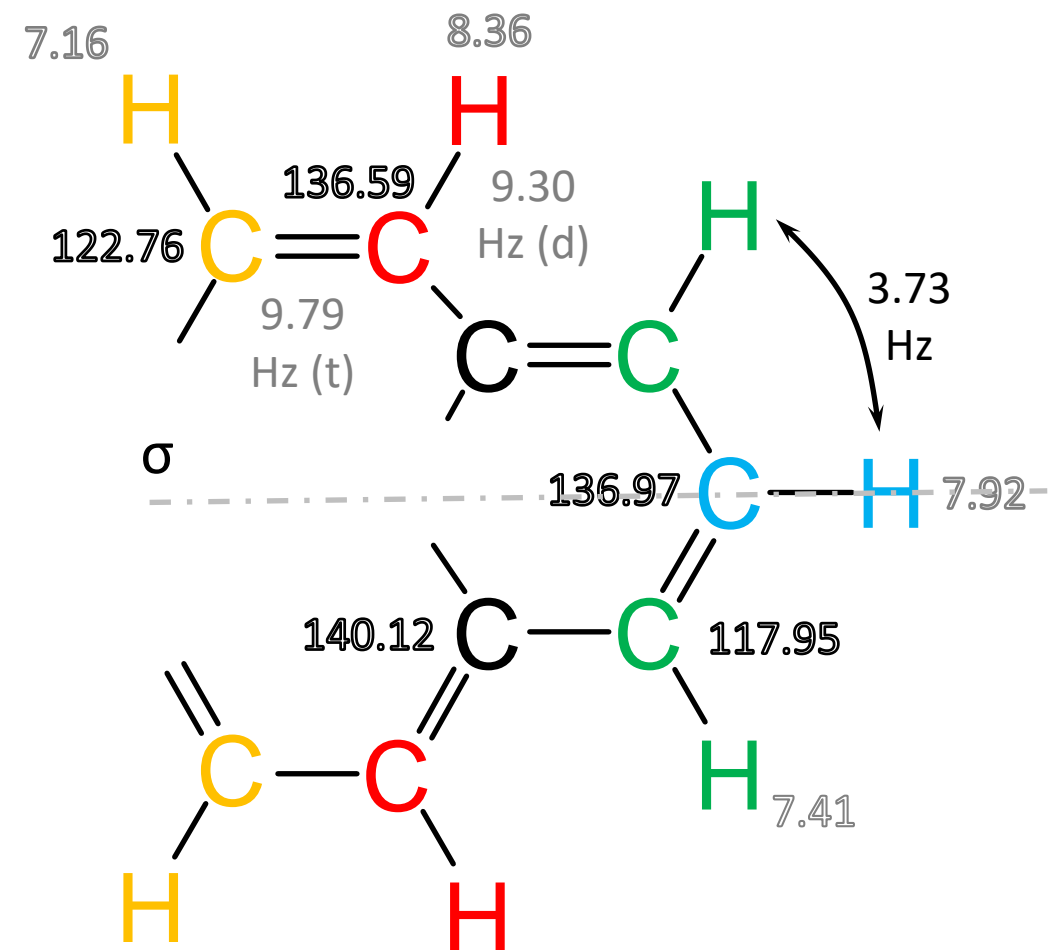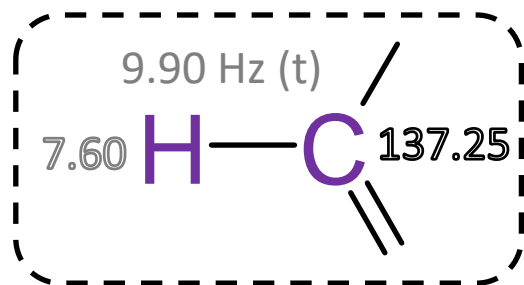
TOCSY

^{13}C

^{1}H

Linking the fragments

HSQC

There is only one possible position for the last CH group.

Of course, we create a bond using the two free valences.
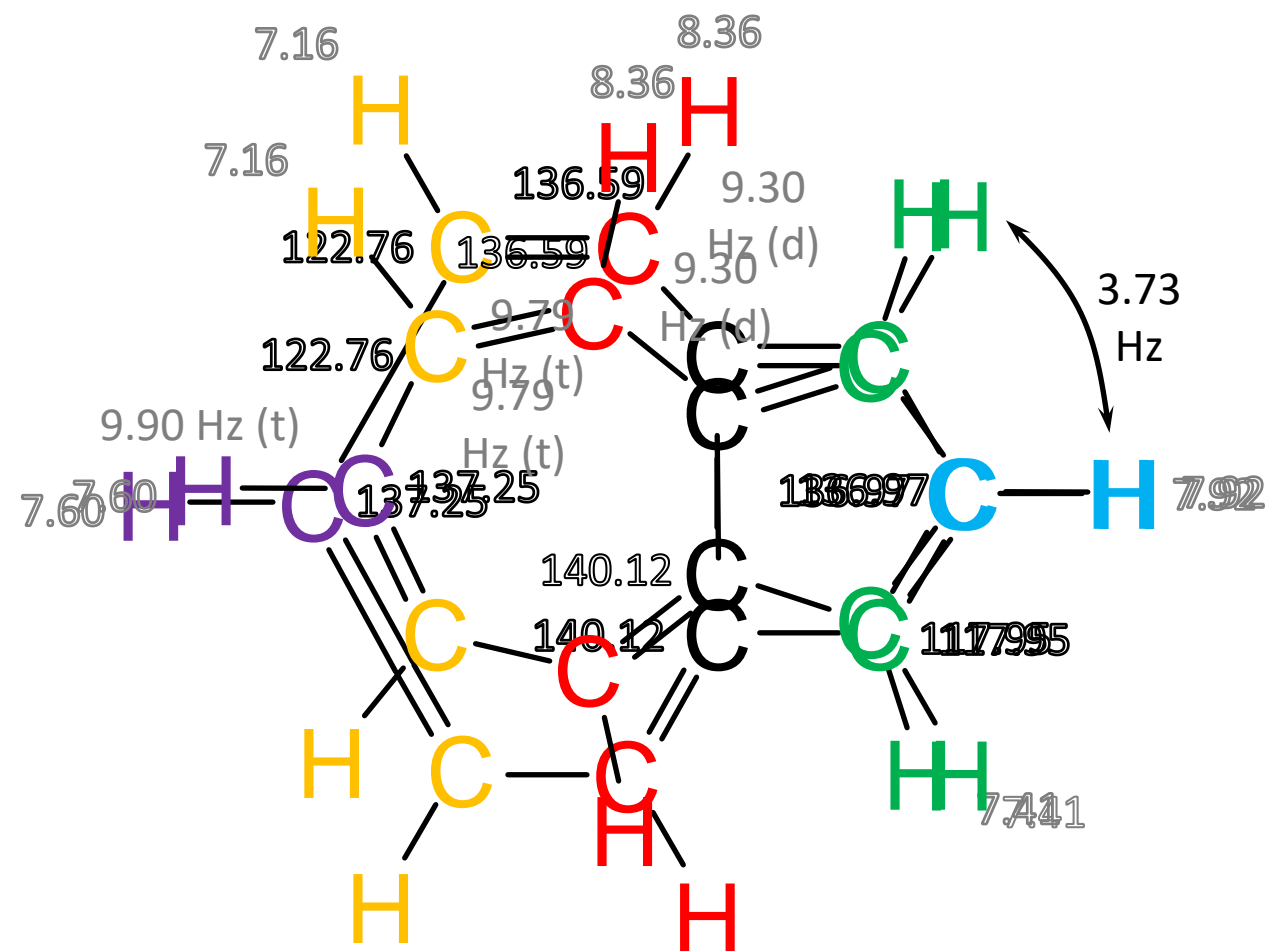Now the molecule is complete.

TOCSY

^{13}C

^{1}H
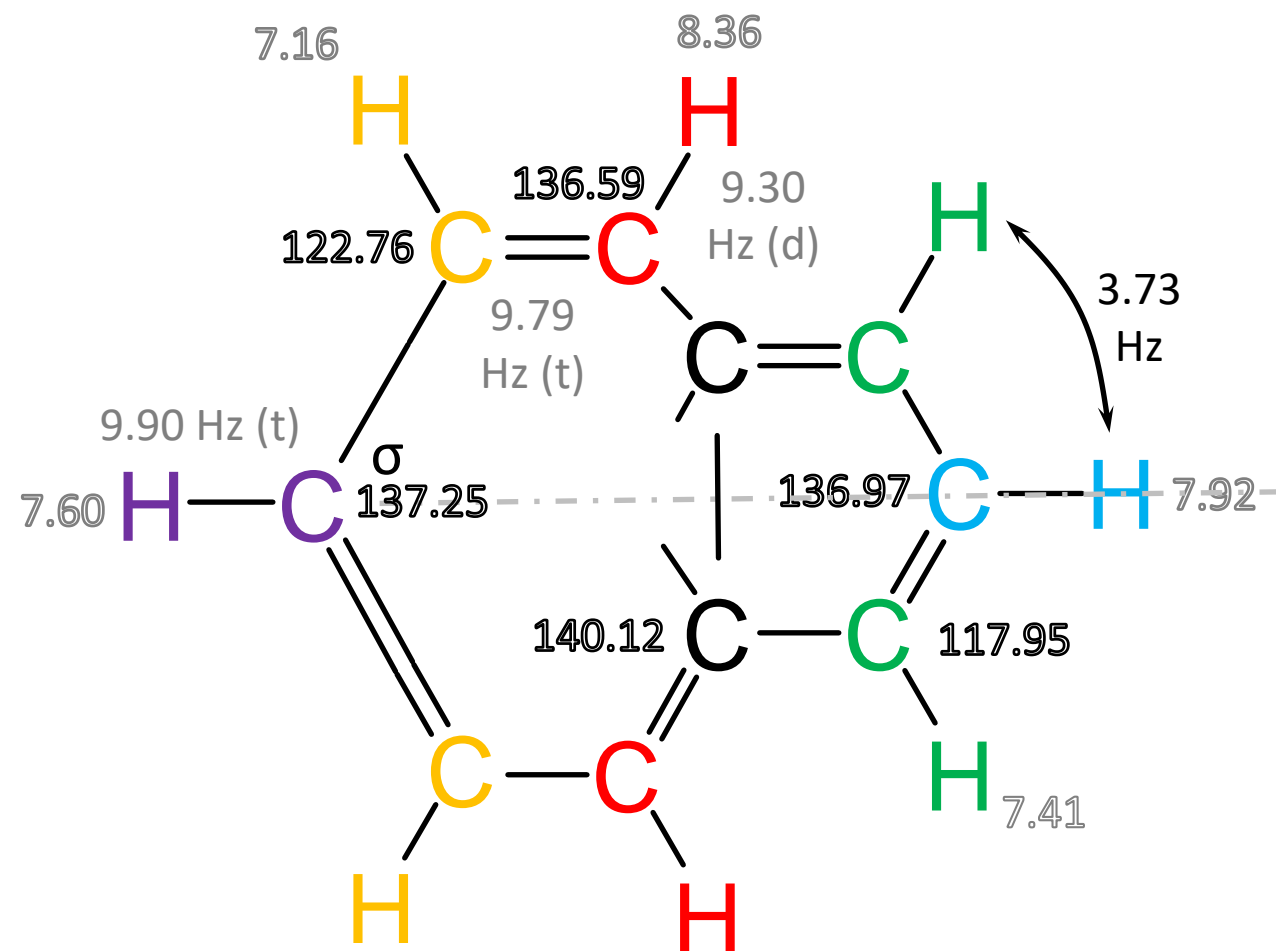
Linking the fragments

The molecule looks a little bit strange, but that's just a matter of cosmetics.

HSQC

TOCSY

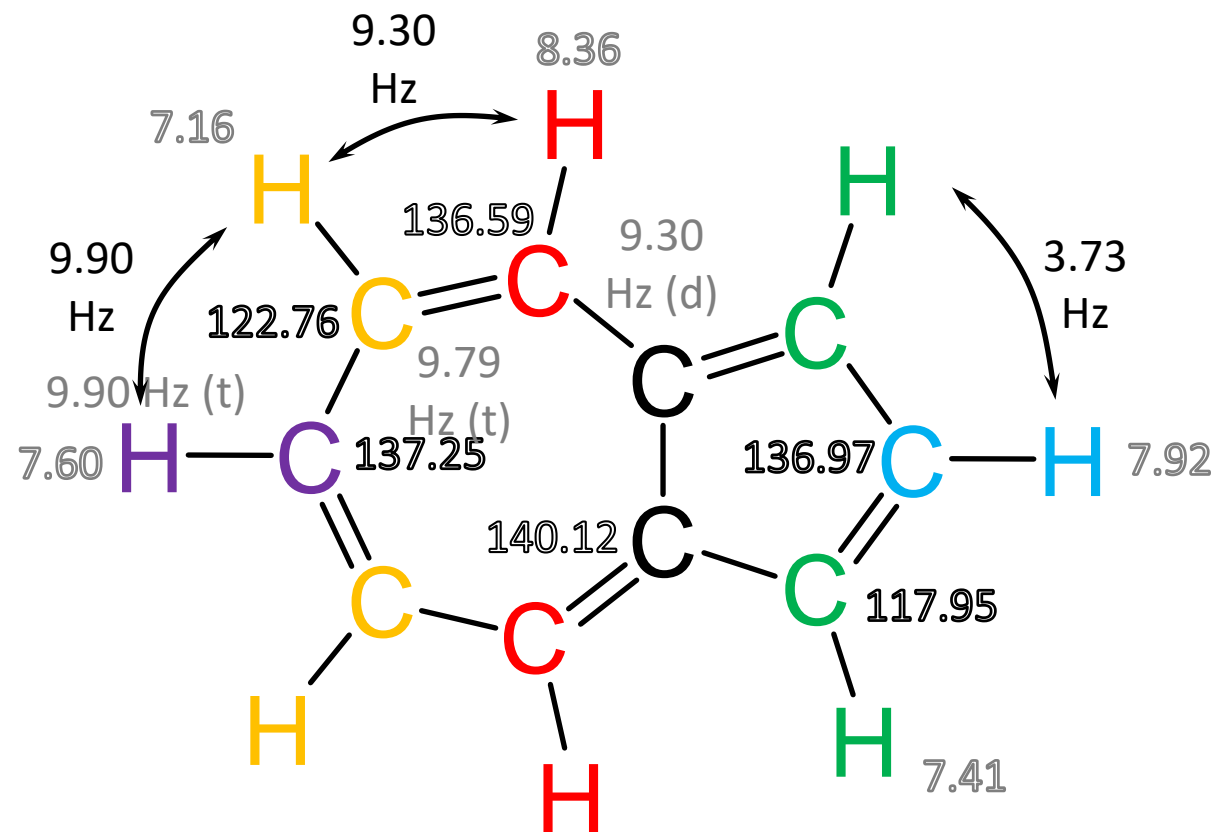¹³C

¹H

Linking the fragments

The postulated structure (azulene) also contains the two missing ring systems.

For the sake of completeness, one can add the two missing homonuclear coupling constants in the 7-ring system.

The multiplet of the proton at 7.16 ppm then, of course, is not a true triplet but, rather, a pseudo triplet.

Final check

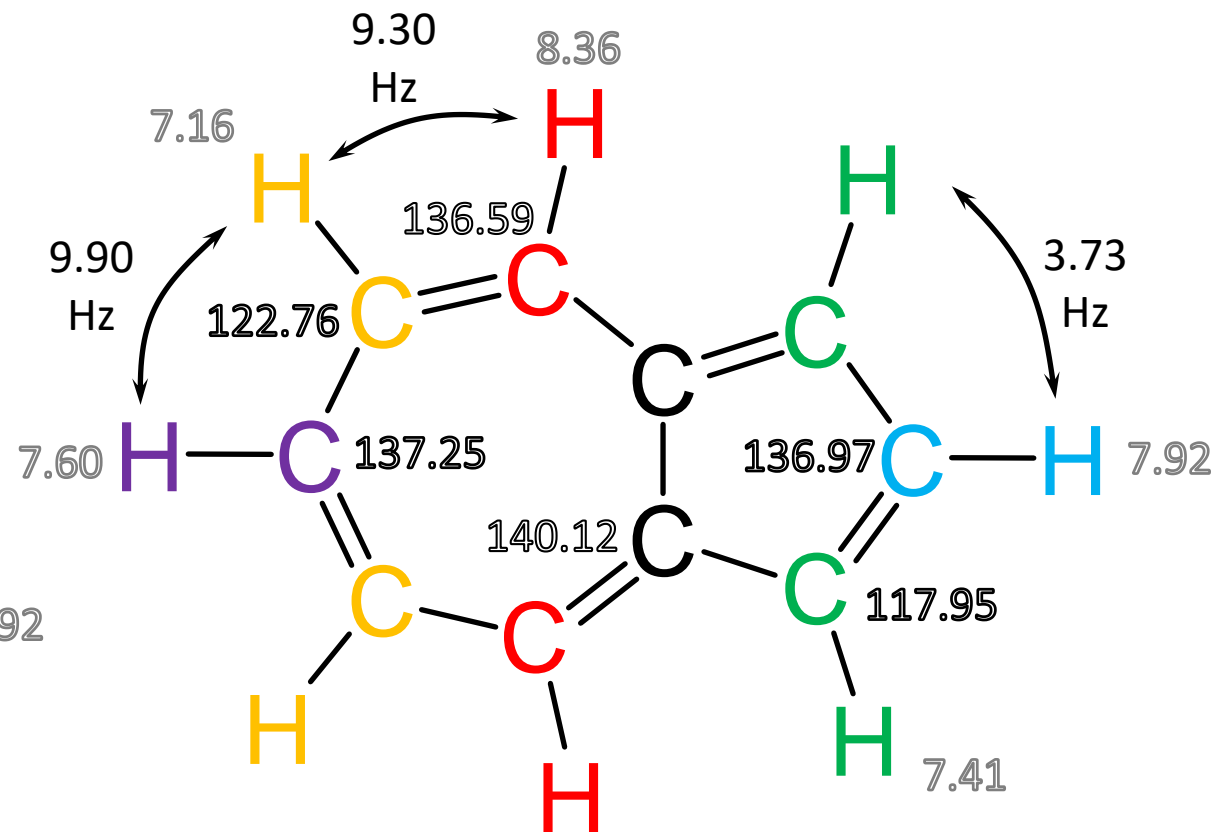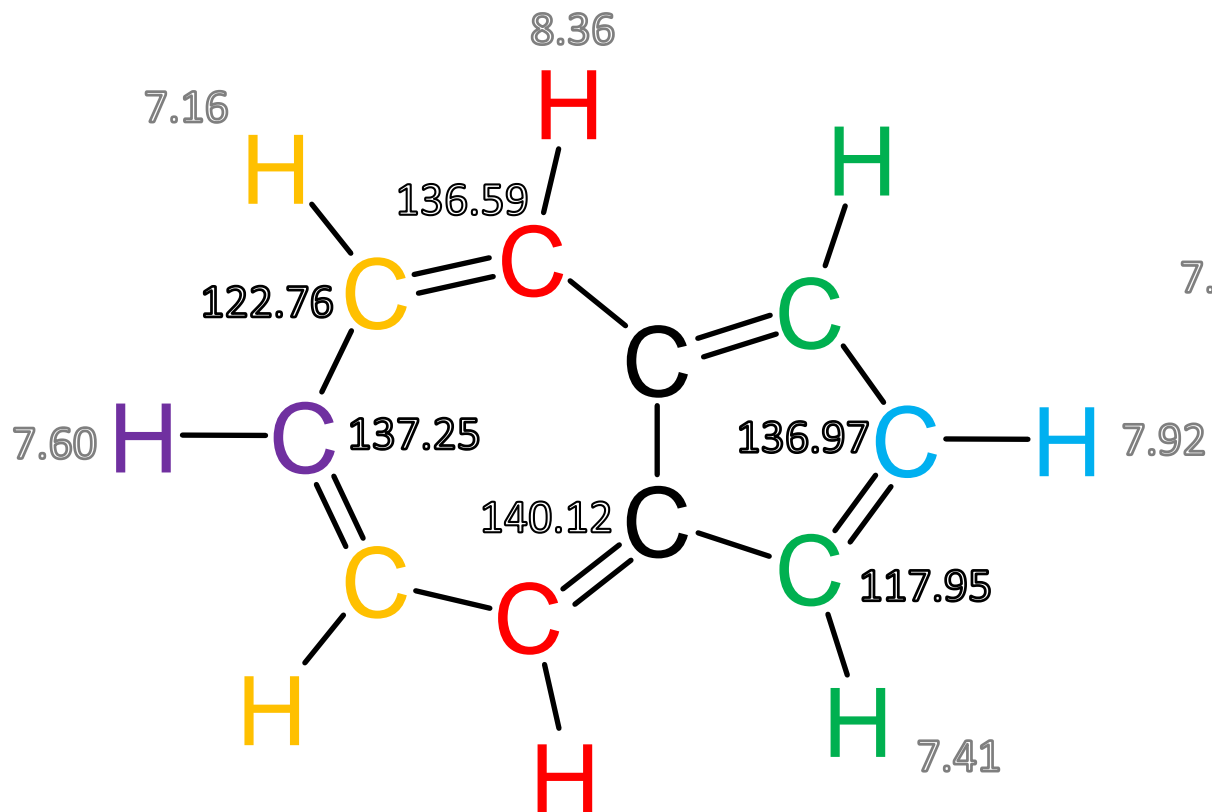Even without using the HMBC, it was possible to solve this challenge.
But, of course, we can use the HMBC to independently verify the result.

Final check

As an example let's follow the coupling path that belongs to one of the cross peaks.

HSQC

HMBC

TOCSY

^{13}C

^{1}H

8.36

7.16

136.59

122.76

137.25

7.60

140.12

136.97

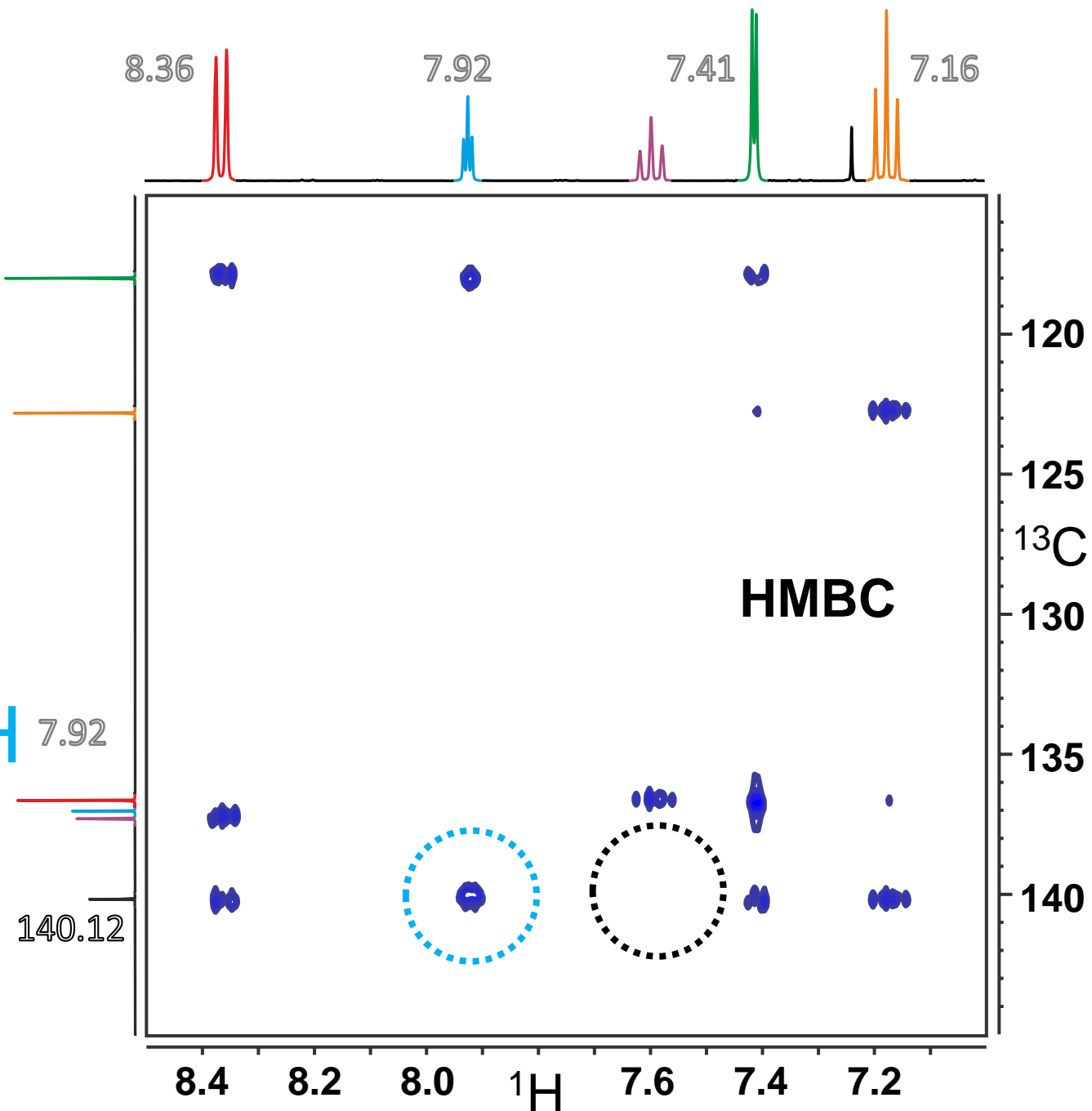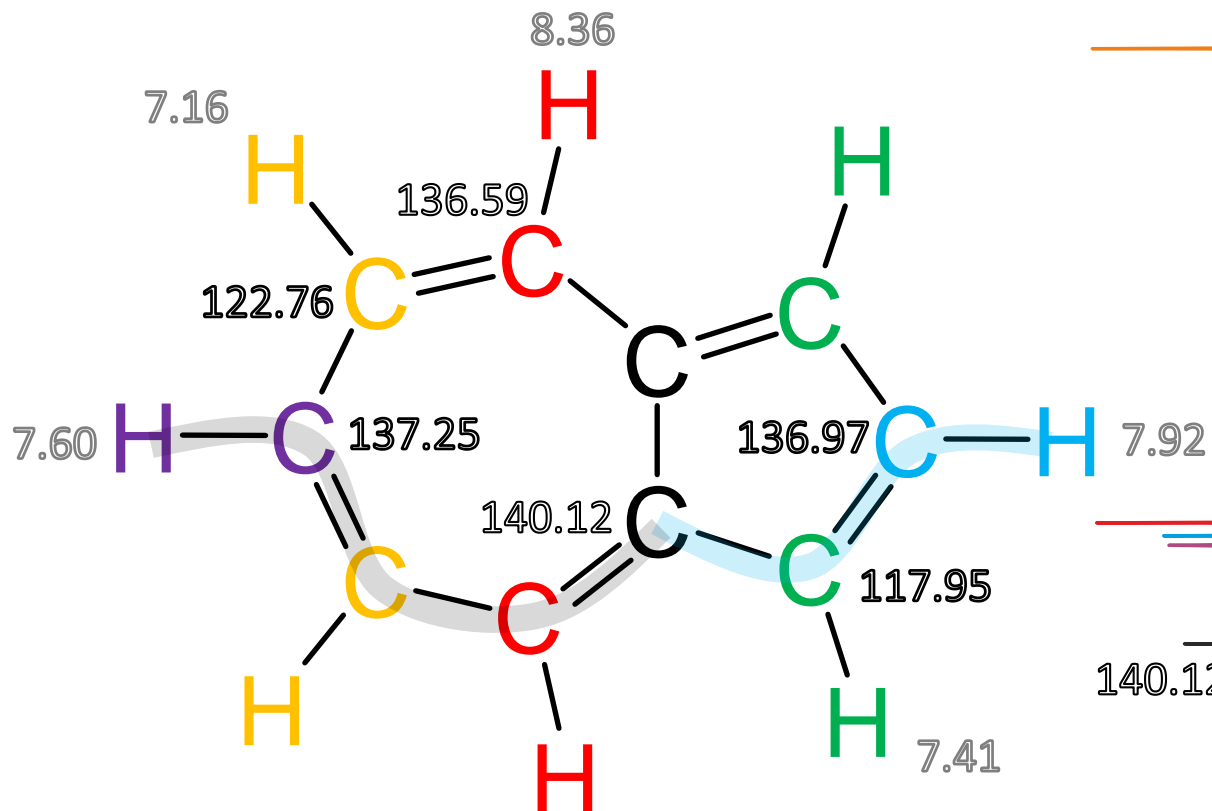7.92

117.95

140.12

7.41
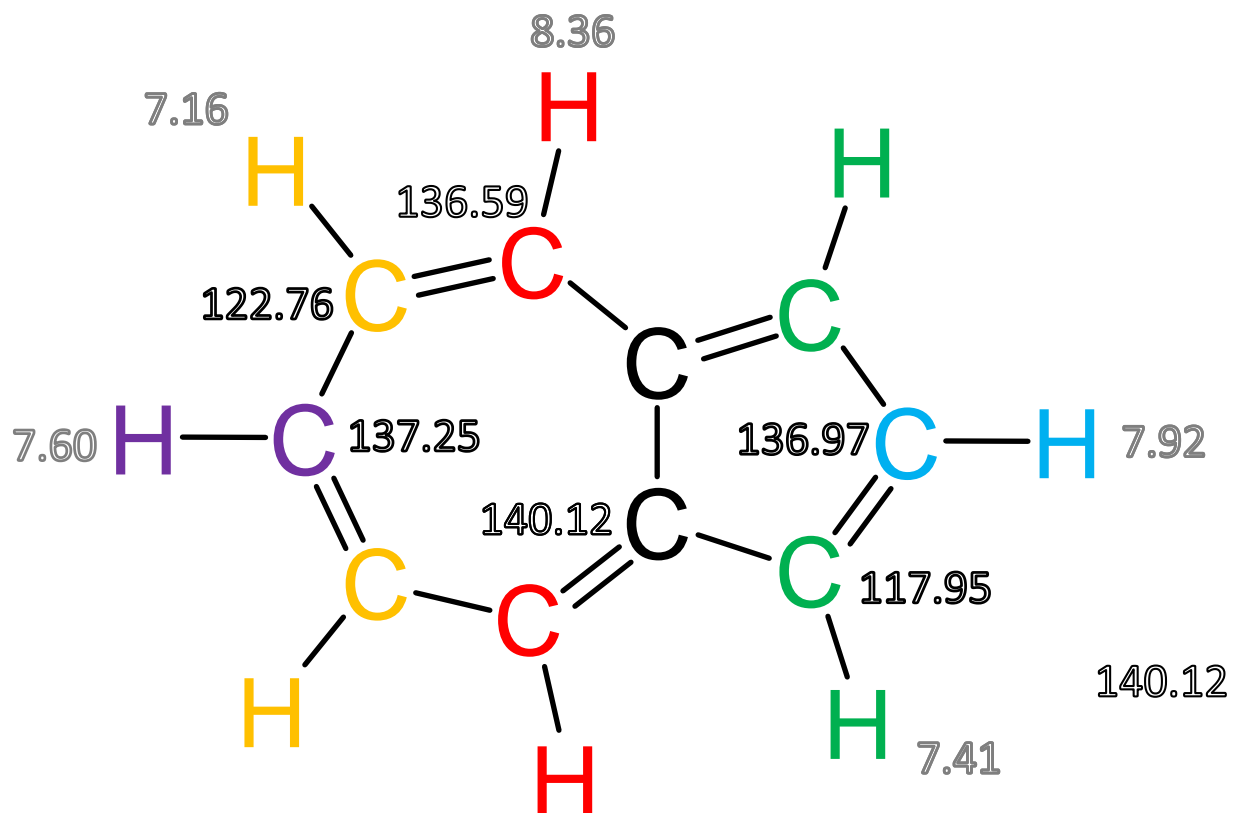
Final check

As an example let's follow the coupling path that belongs to one of the cross peaks.

On the other hand, we do not see a cross-peak for a four-bond coupling pathway.
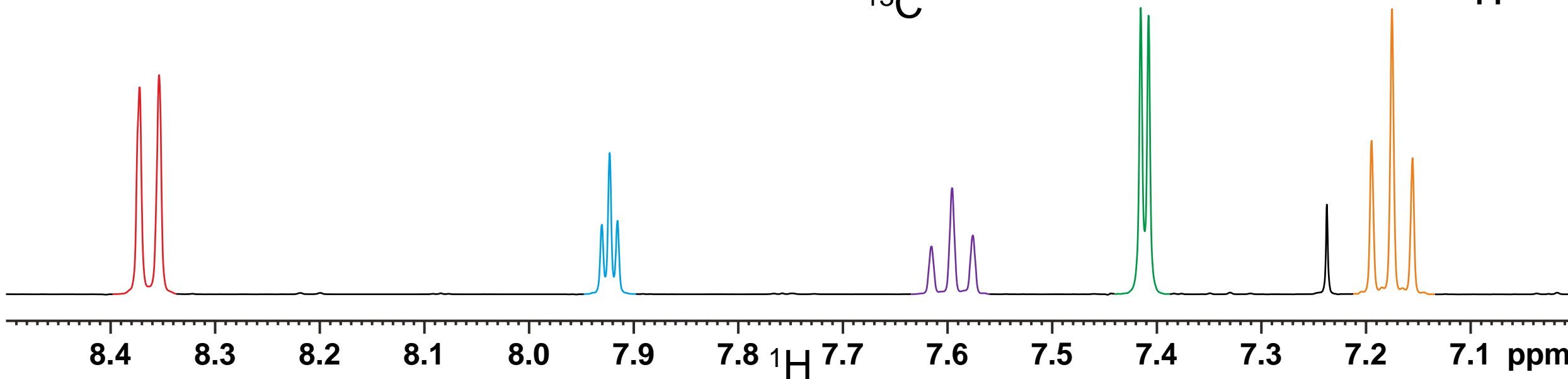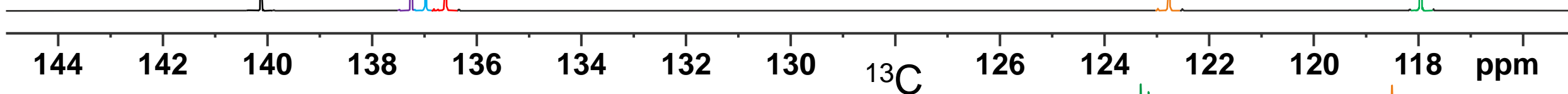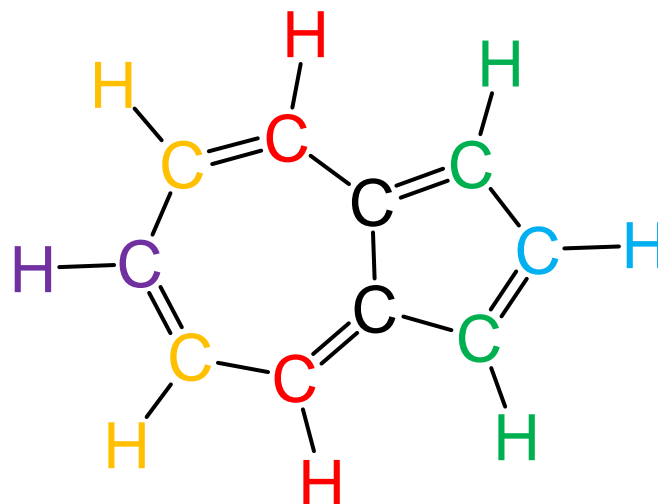
TOCSY

13C

1H

HMBC

13C

1H

Solution at a glance
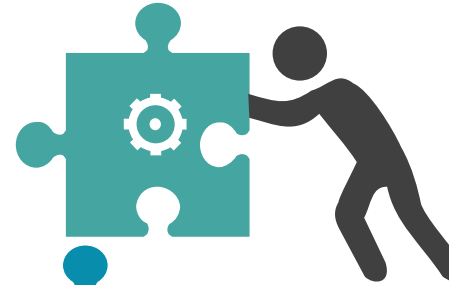
Contributions

Spectrometer time

University of Wisconsin-Madison
(BioMagResBank)

Measurements

*Maria Nesterova,
Lawrence J. Clos,
Christopher Stancic,
Mark E. Anderson,
John L. Markley*

**Discussions and
native English
language support**

Compilation

Alan Kenwright

Rainer Haeßner

More exercises ...