Problem of the Month:

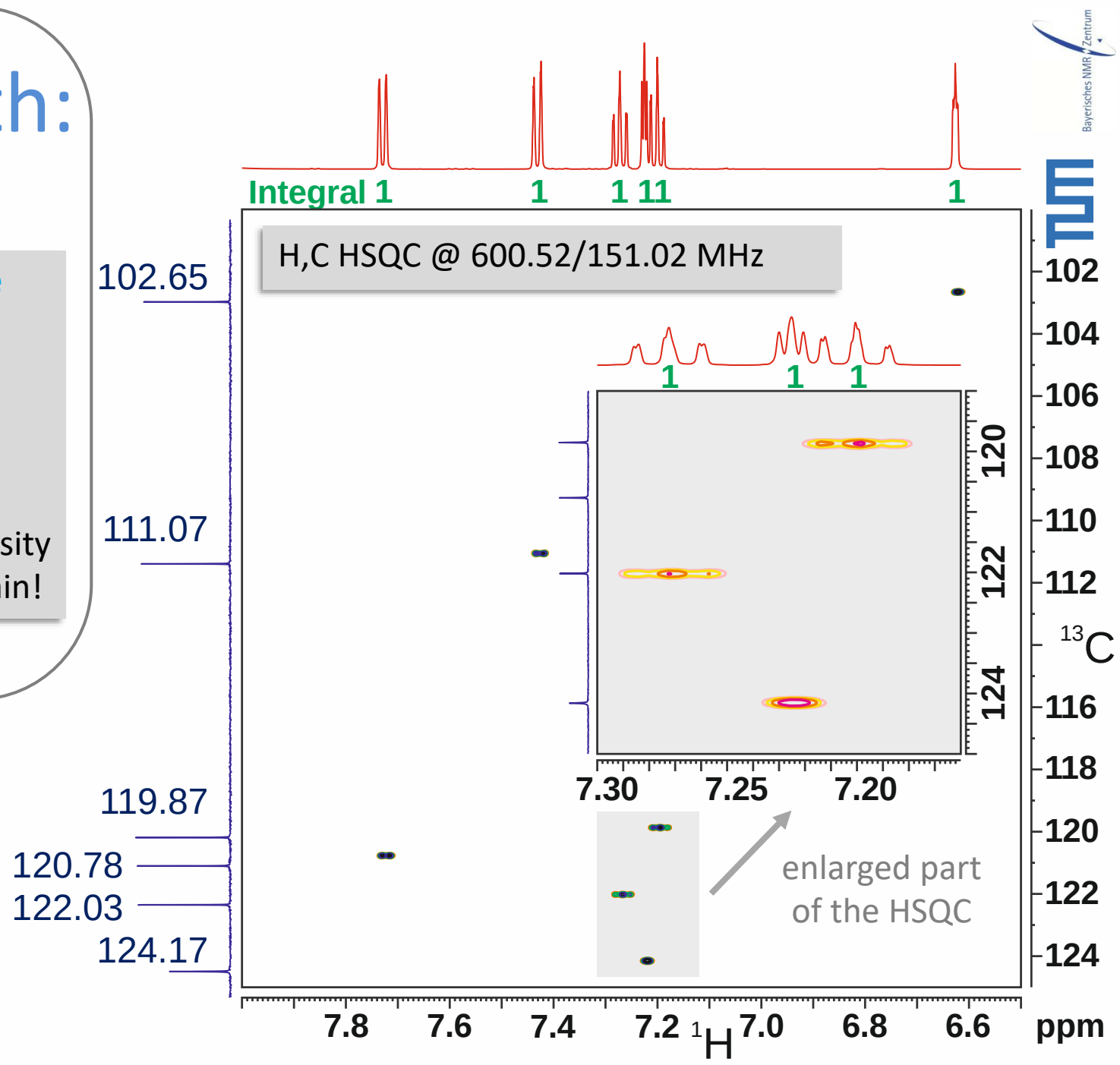
October 2020

Deduce the structure of a compound with the molecular formula C_8H_7N and try to assign *all* chemical shifts and coupling constants

Special challenge!

If you inspect the broad proton signal at about 8.08/8.13 ppm very closely, you see two low-intensity „bumps“ at about 8.04 and 8.23 ppm. Try to explain!

The HSQC looks a bit crowded due to the inset enlarged area. This was necessary due to the close proximity of two proton multiplets. Carefully identify the six cross peaks (all are positive).



^{1}H NMR spectrum recorded at 600.52 MHz

Please note:
Some of the proton multiplets have been enlarged here. For the assignment of the enlarged multiplets, please refer to their colours.

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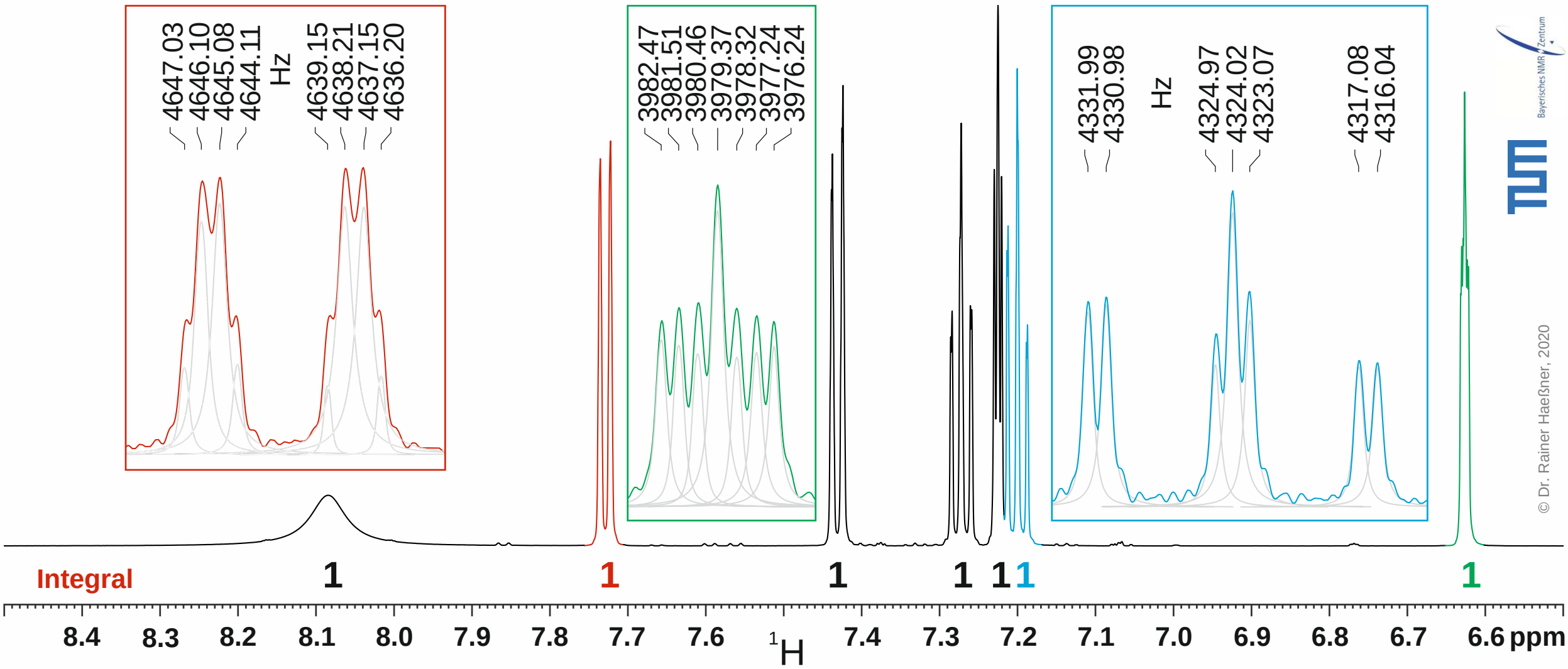

^{1}H NMR spectrum recorded at 600.52 MHz

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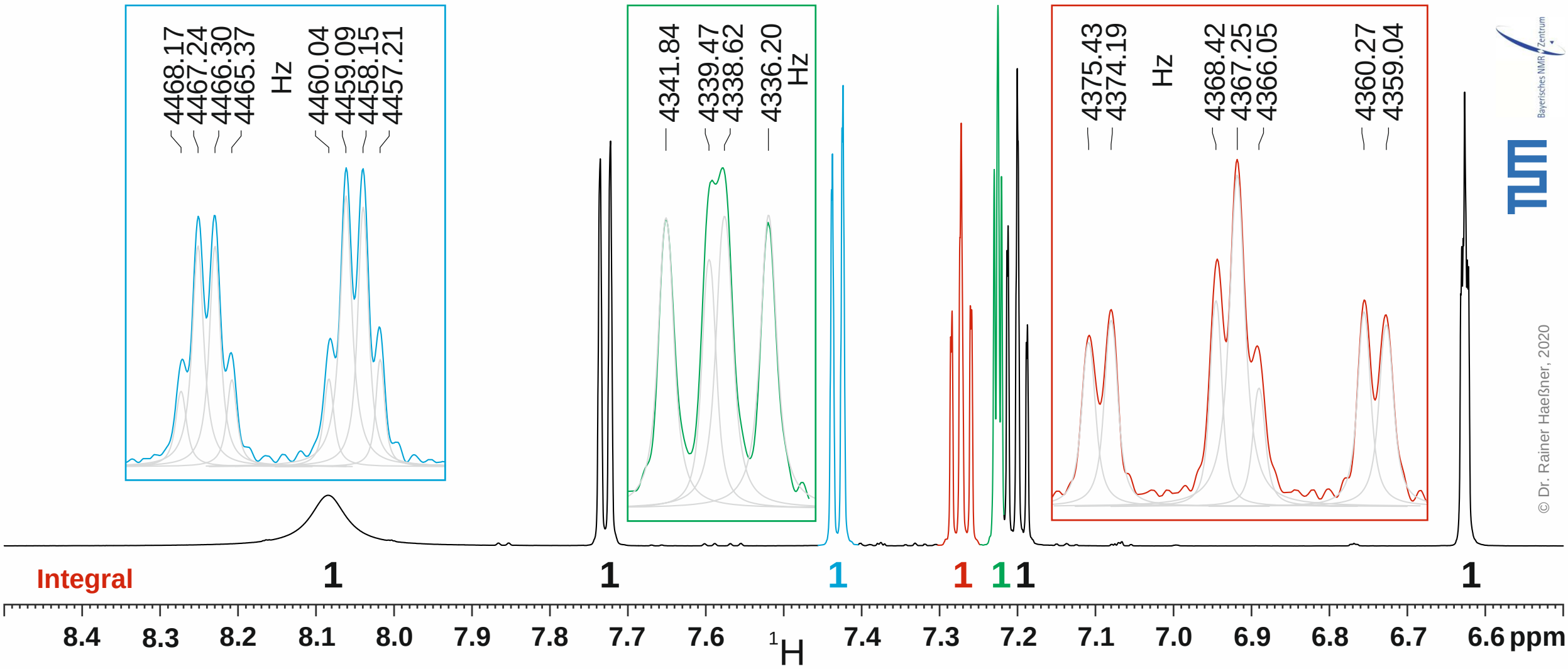

^{1}H NMR spectrum recorded at 500.14 MHz

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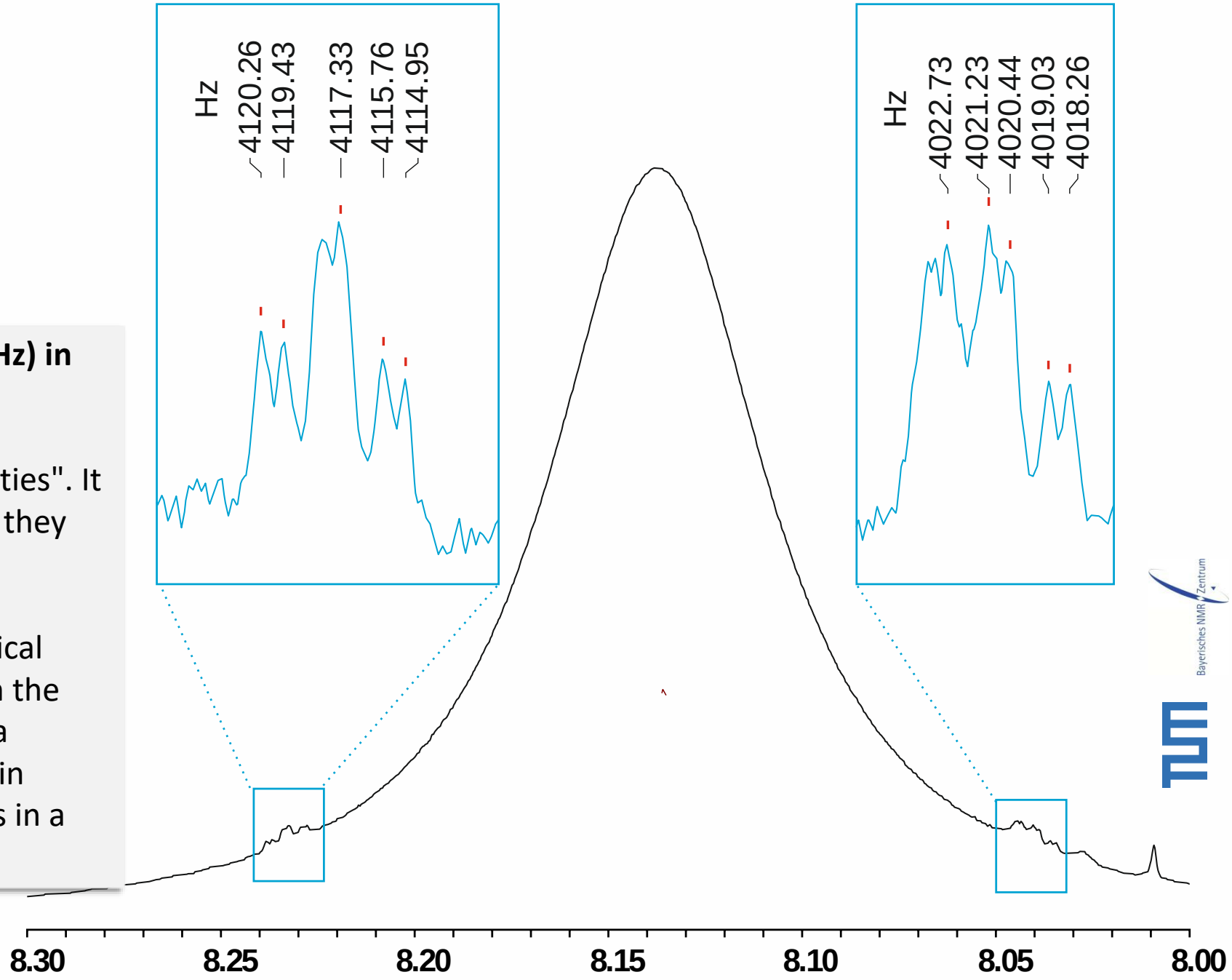
Broad signal at 8.08 ppm (600.52 MHz) in detail

Usually one ignores the marked "impurities". It is not trivial to record these signals, but they offer helpful pieces of information.

(There is a slight difference in the chemical shift compared to the spectrum given in the previous slides. This is the spectrum of a separate sample with slight differences in concentration and temperature. And it's in a different magnetic field)



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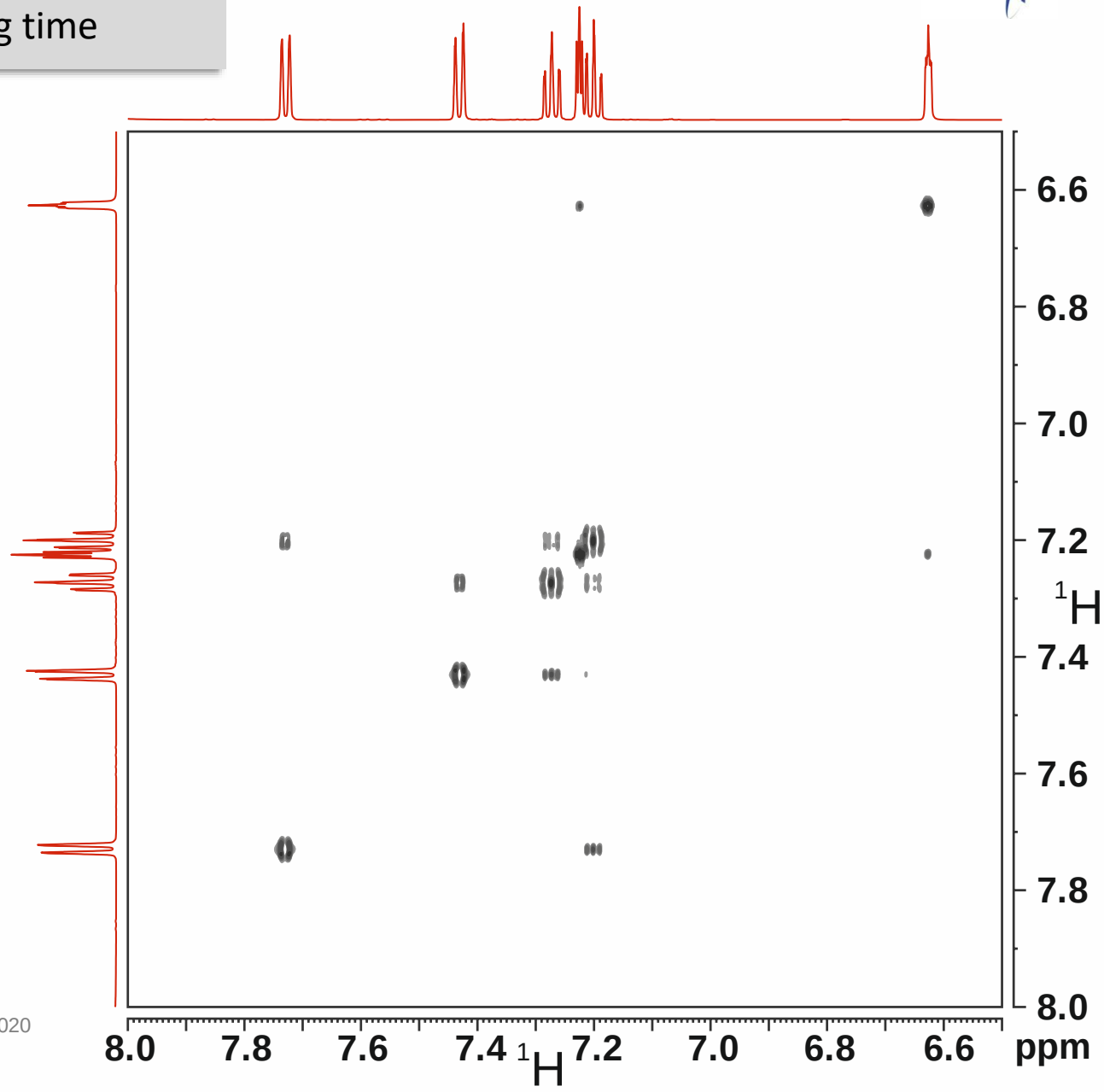
H,H TOCSY @ 600.52 MHz
using 10ms mixing time

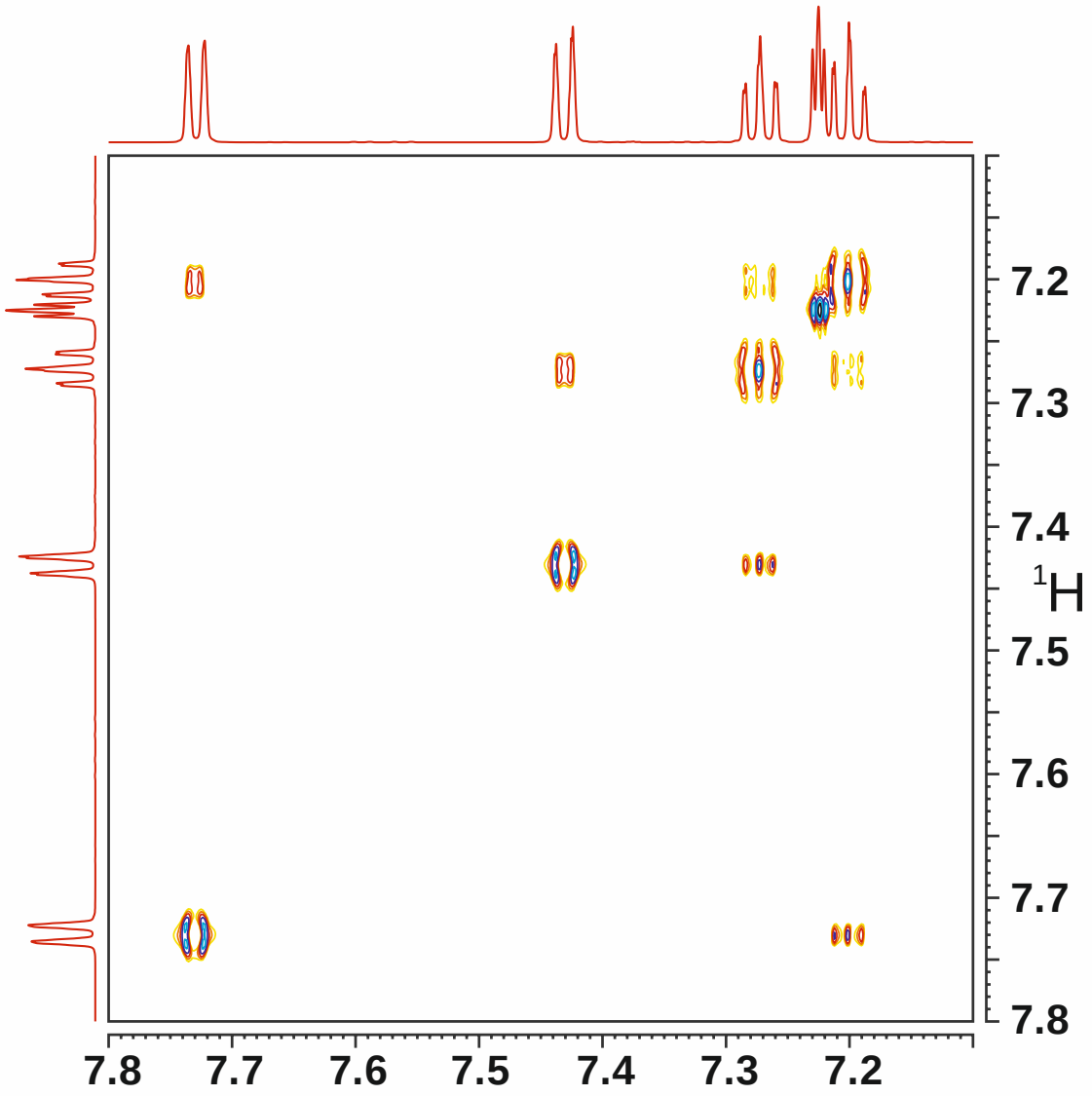
Sometimes a TOCSY with an unusually short mixing time is a good substitute for a COSY.

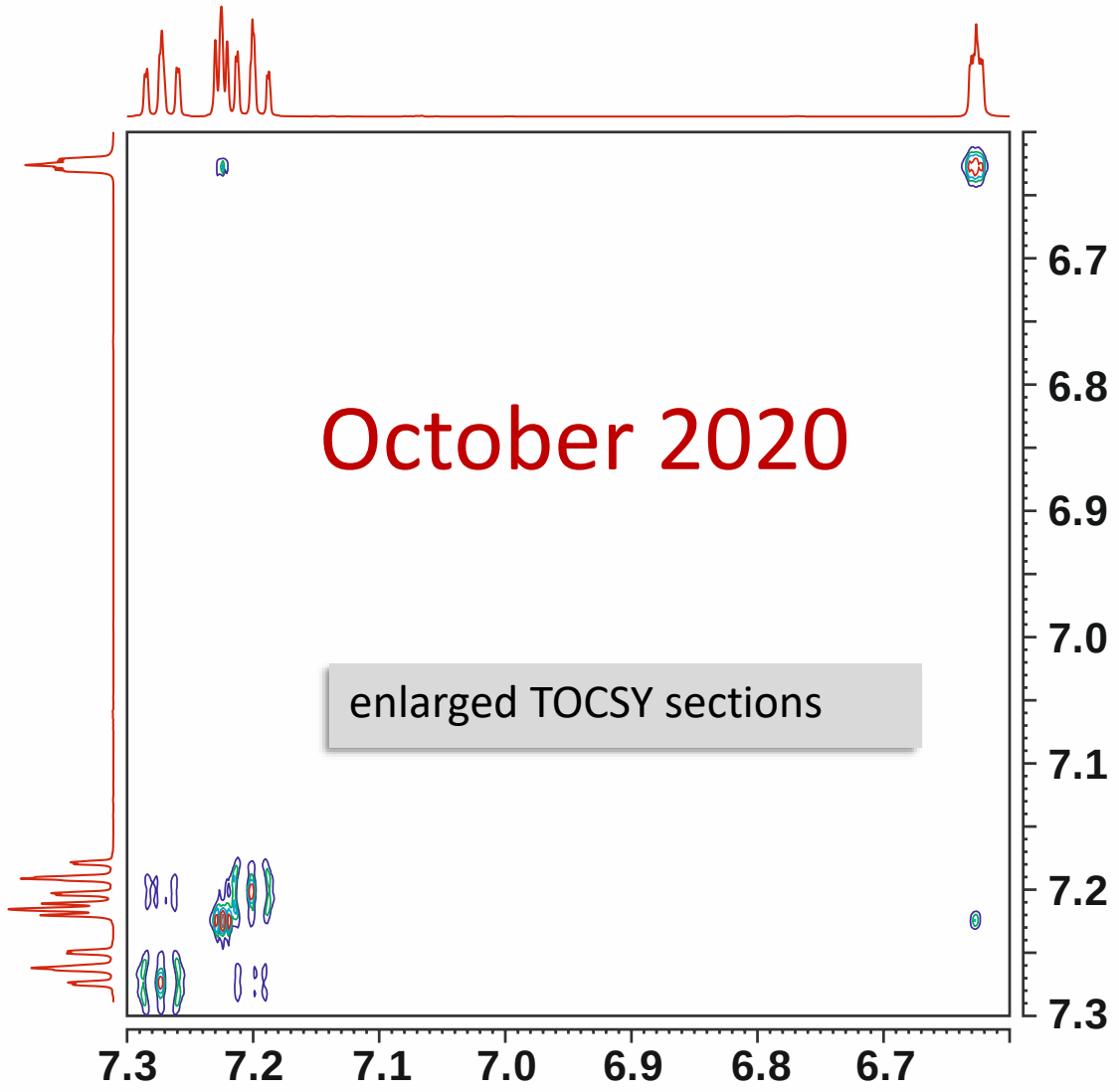
This is especially true, if you want to exclude cross peaks due to small (four and five bond) coupling constants in unsaturated spin systems, i.e. aromatics.

In such cases a TOCSY with a short mixing time only shows correlations between protons separated by two or three bonds (assuming other homonuclear coupling constants are not abnormally large).



Due to the previously mentioned proximity of two proton multiplets the TOCSY is also a bit crowded.
Fortunately it's possible to separate two spin systems almost perfectly. Almost …





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enlarged TOCSY sections

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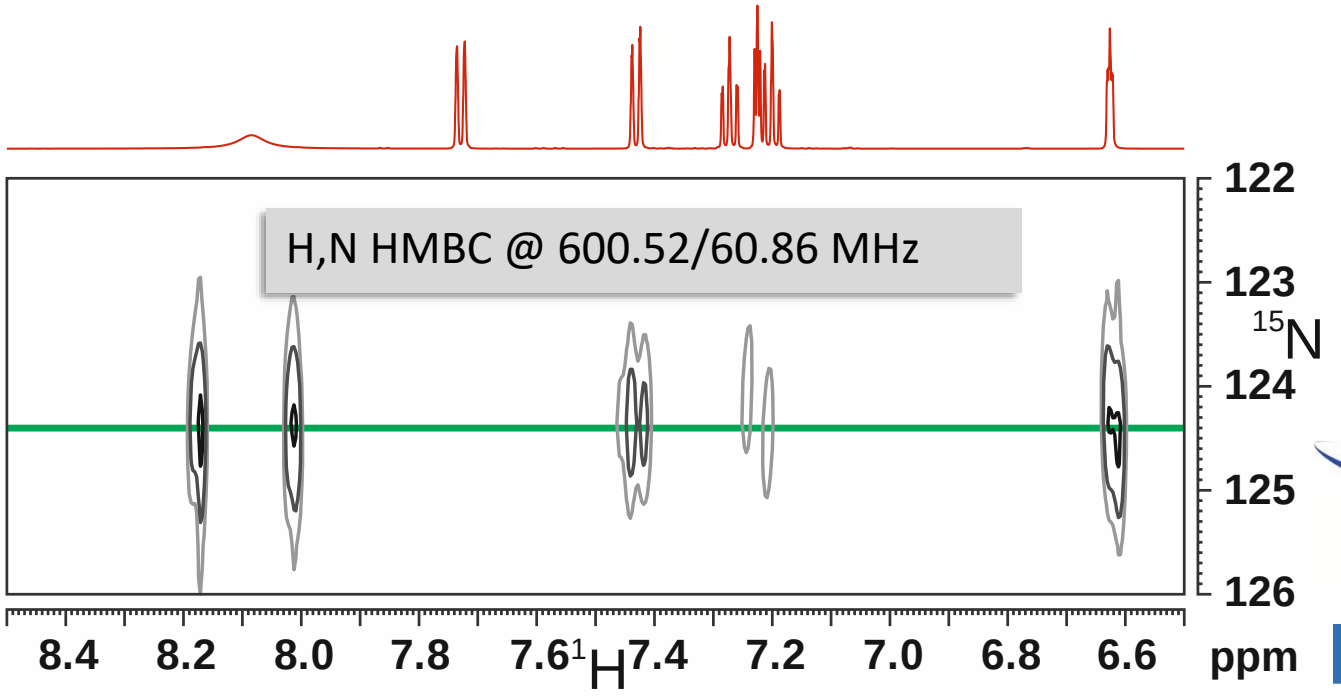
Due to the limited number of nitrogen atoms within the molecular formula, the number of peaks inside the HMBC is rather limited.

Nevertheless this HMBC is one very helpful key to get an unambiguous constitution.

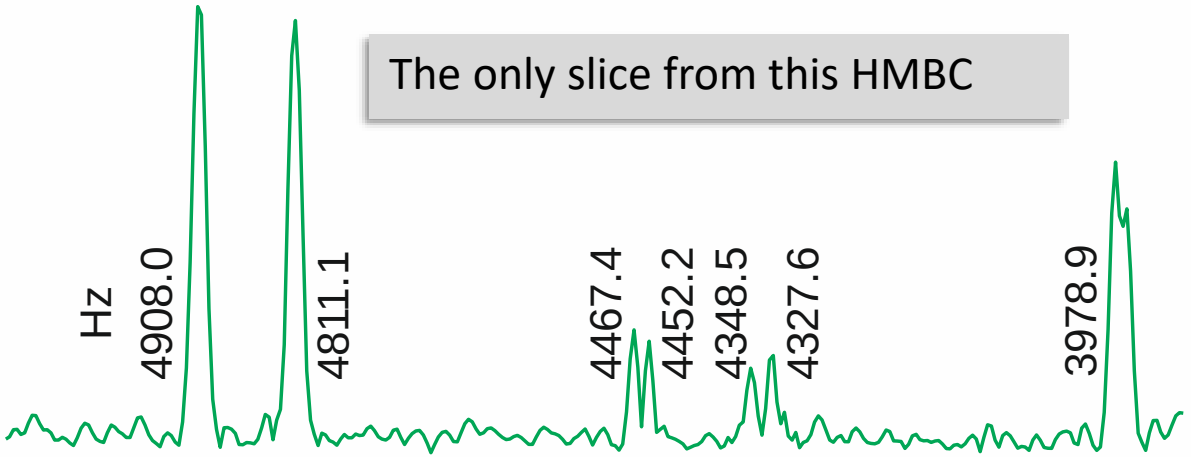
Especially have a look at the area around 8.1 ppm (^{1}H).

The cross peak with a proton chemical shift of about 7.2 ppm is a little bit ambiguous. It's very helpful to get reliable values for this shifts using the peak labels in the slice.

A not very often recorded spectrum…



The only slice from this HMBC



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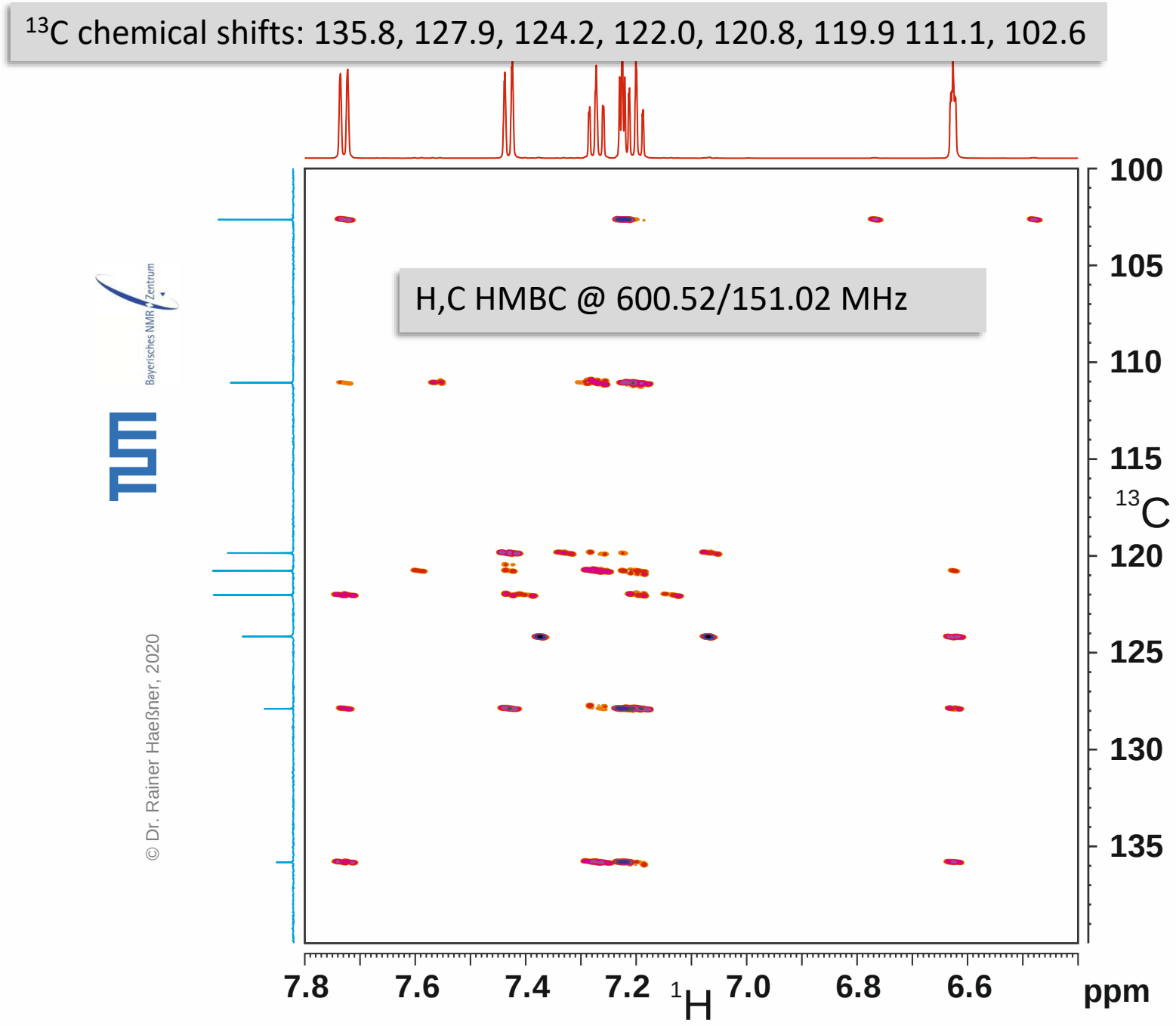
Often the HMBC contains a crazy amount of pieces for the structural puzzle.

Even in the case of simple compounds it looks like a part of the milky way.

Fortunately at this stage you should already have a lot of information about the structure coming form other measurements.

Only a few pieces of information from this HMBC should be necessary to finish the solution of this problem.

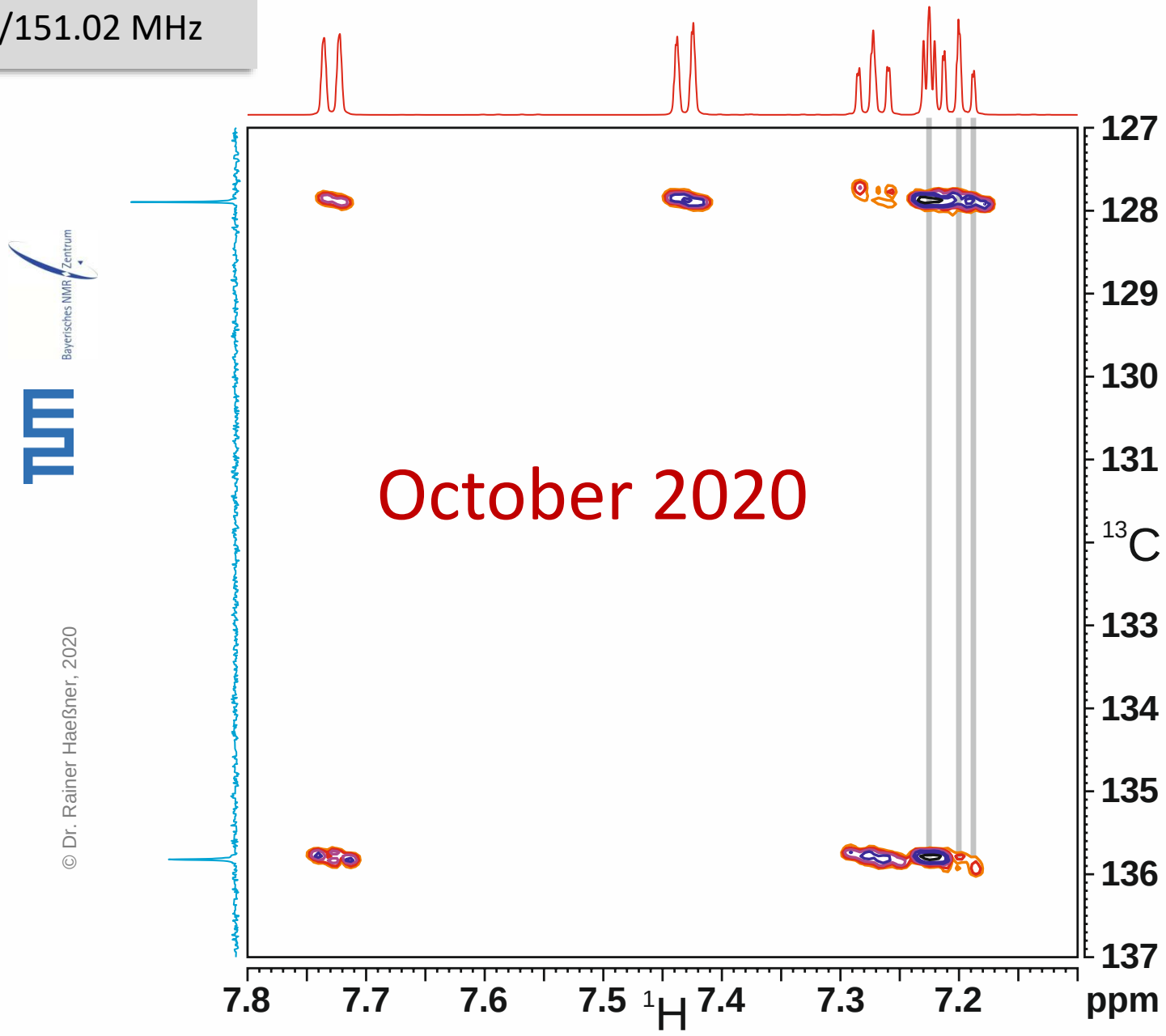


part of
H,C HMBC @ 600.52/151.02 MHz

Because it is not possible for you to zoom through the whole HMBC looking for the key pieces of information, the essential part is presented here in expanded form.

This selection of the key part of the HMBC spectrum simplifies the solution by limiting the number of correlations that you have to consider. In the real world, you would have to make this selection yourself!

The vertical grey lines should help you to assign the correct cross peaks to the adjacent proton multiplets around 7.2 ppm.



$^{1}H,^{1}H$ NOESY spectrum recorded at 500.14 MHz

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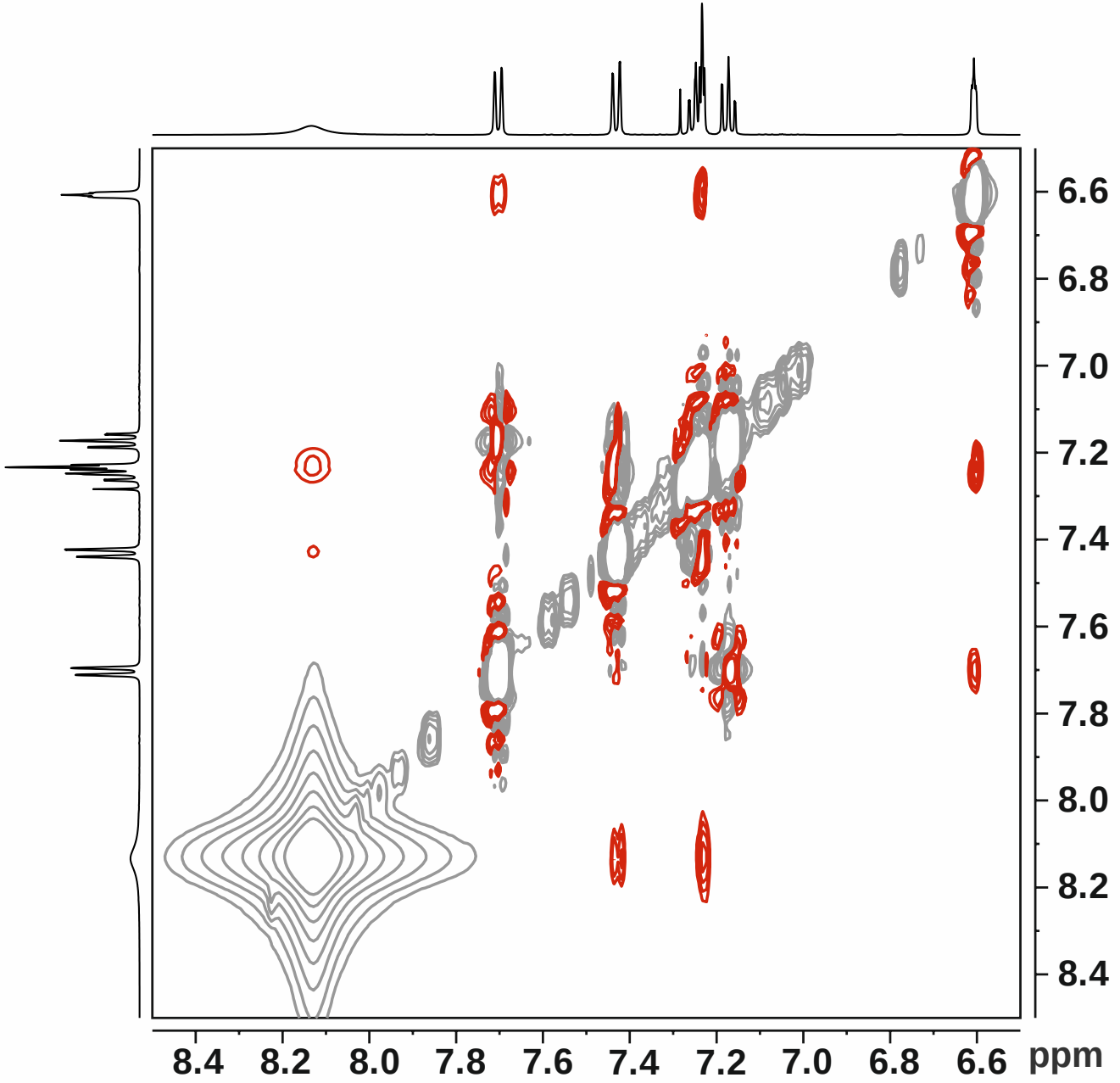
The NOESY looks almost as crowded as the HMBC.

But don't worry. You only need to be concerned with the correlations that are complementary to those you have already seen in the TOCSY, and they are well separated.



Contributions

Spectrometer time

TU Munich

Measurements

Christine Schwarz,
Wolfgang Eisenreich,
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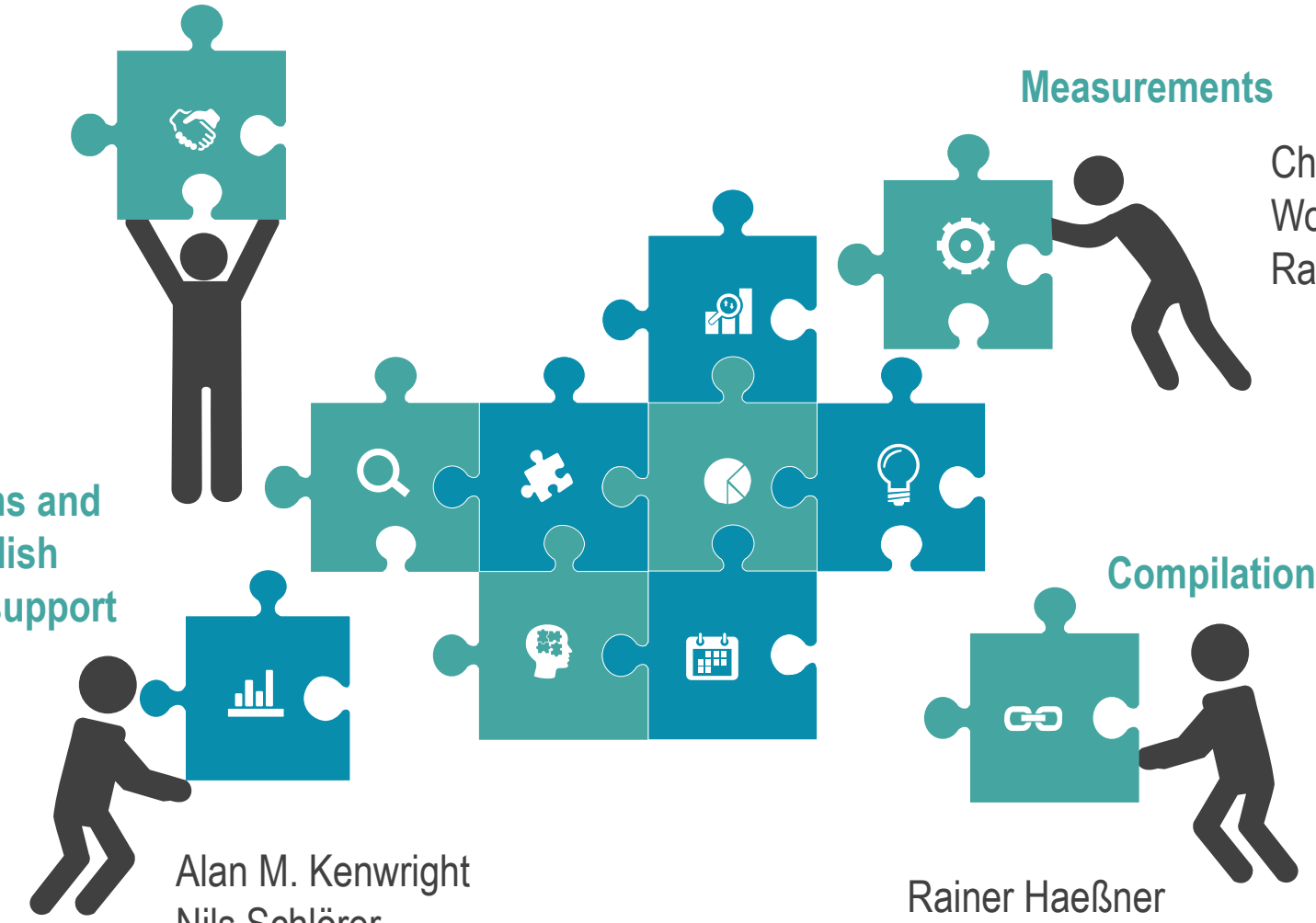

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