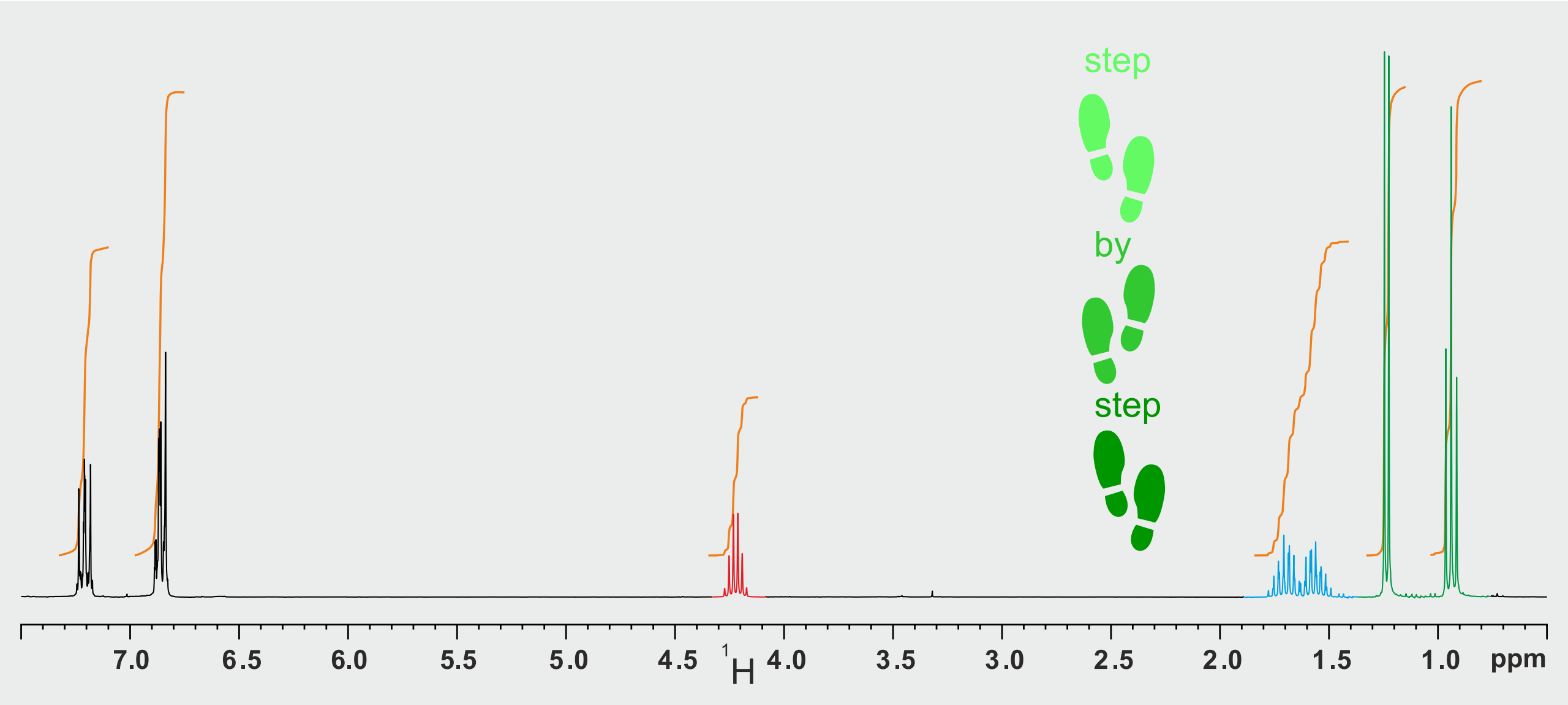
Exercise plus Solution – Quick overview

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.

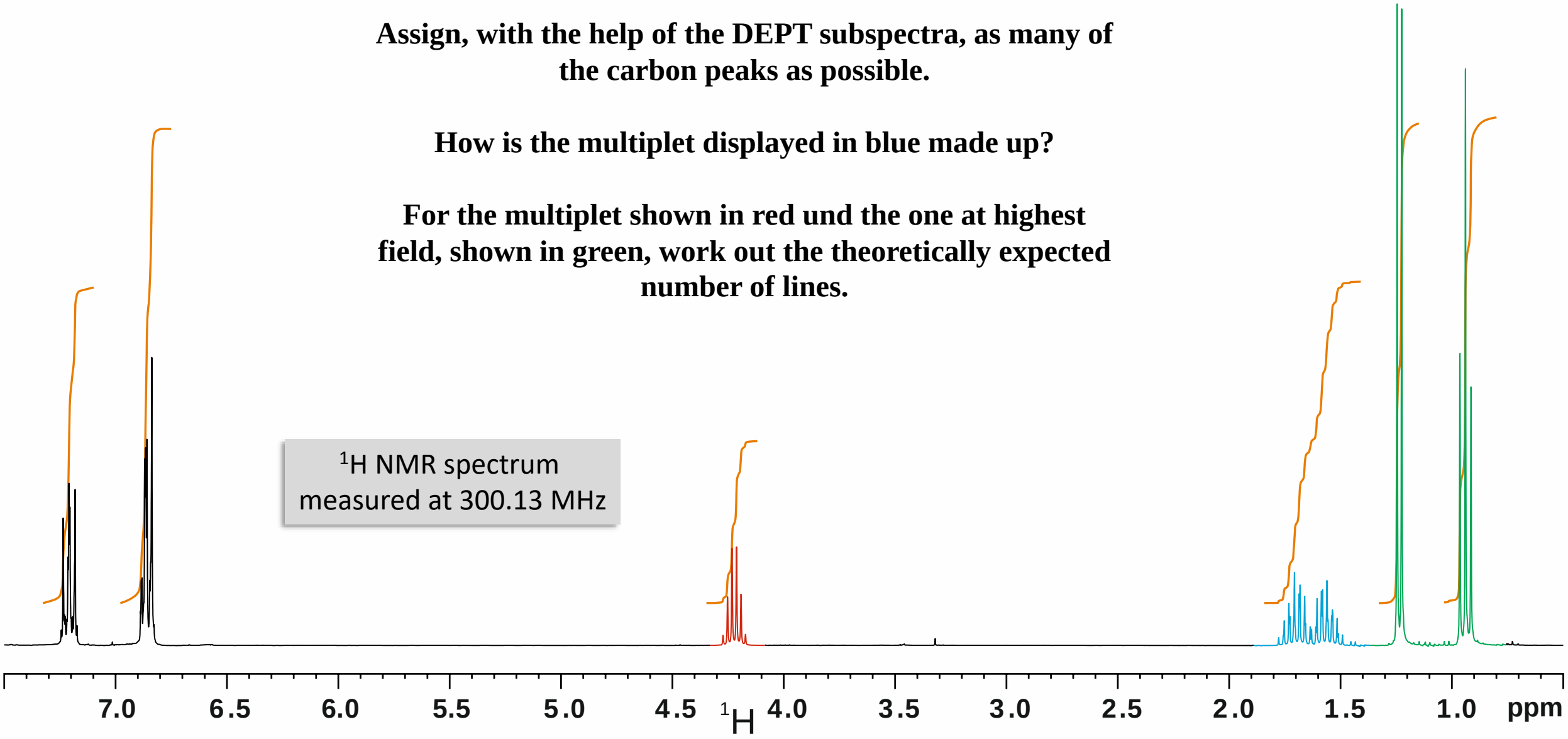


Which alkylbromide was used in the etherisation of Phenol?

Assign, with the help of the DEPT subspectra, as many of the carbon peaks as possible.

How is the multiplet displayed in blue made up?

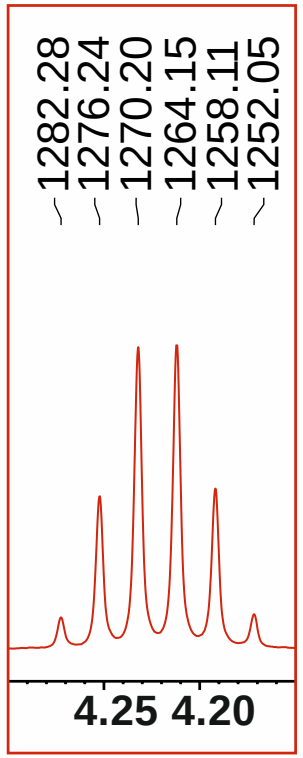
For the multiplet shown in red und the one at highest field, shown in green, work out the theoretically expected number of lines.

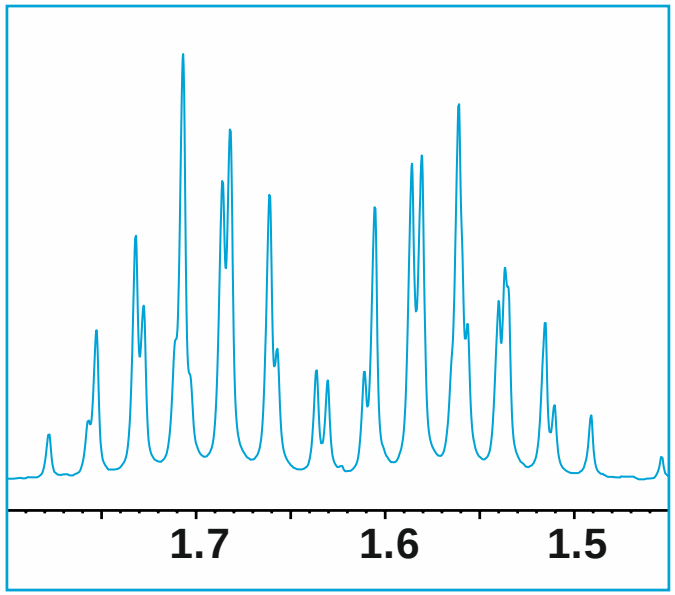


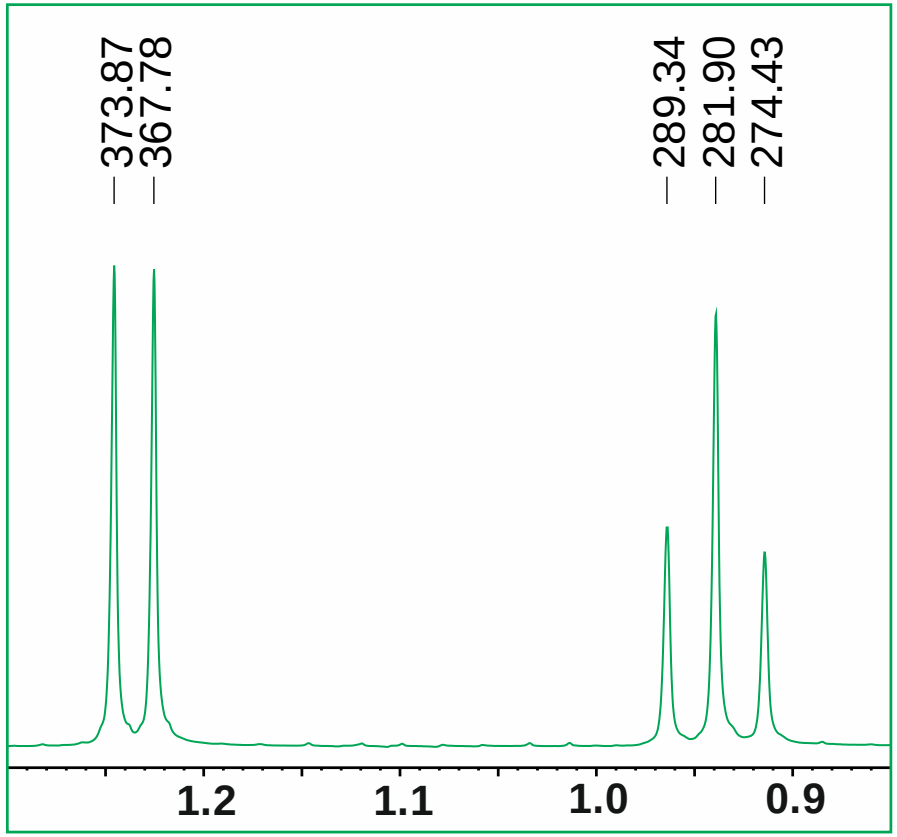
Enlarged sections of the overview spectrum on the previous page.

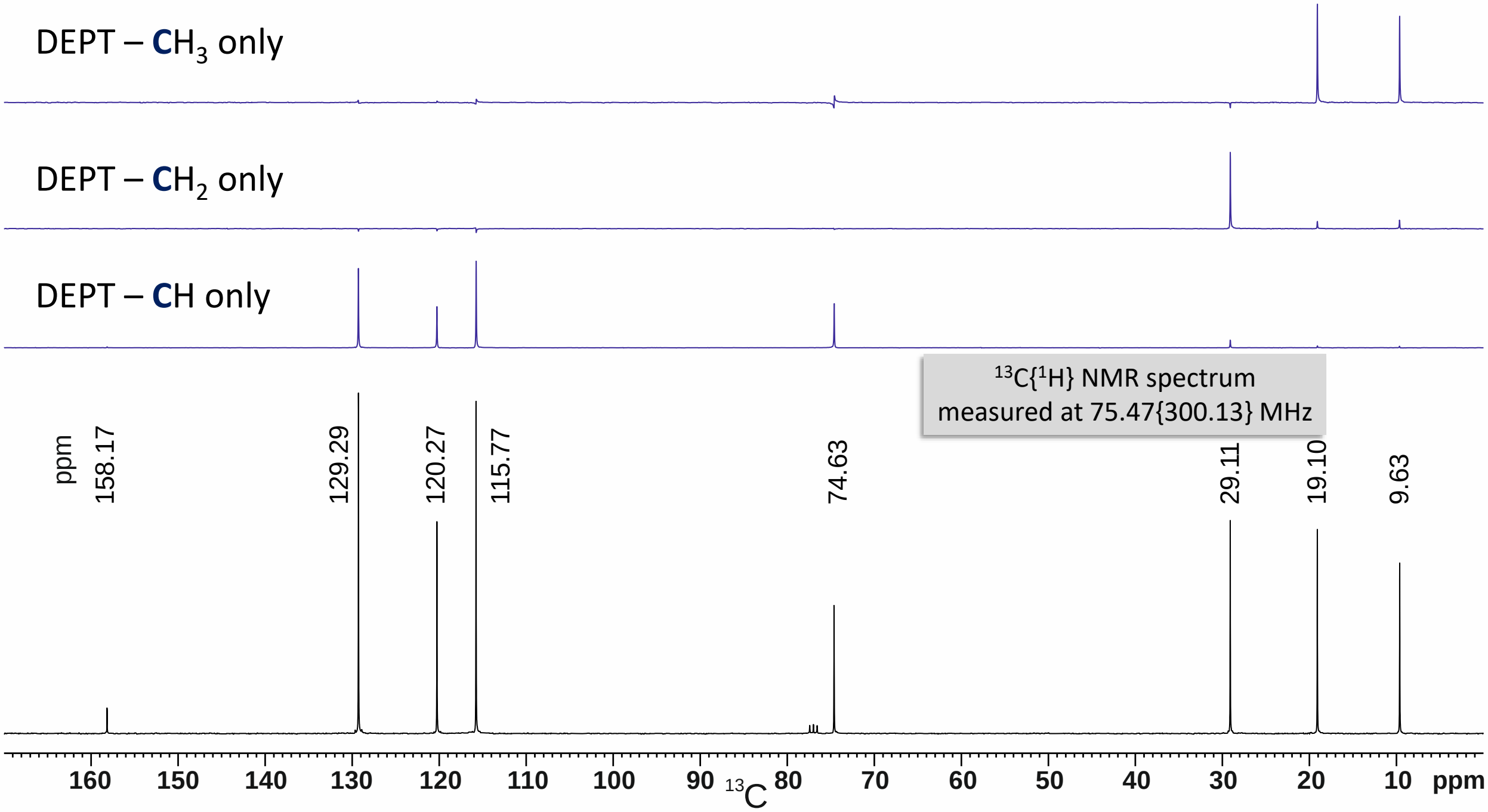
Scale division: [ppm]
Peak label: [Hz]

^{1}H NMR spectrum measured at 300.13 MHz

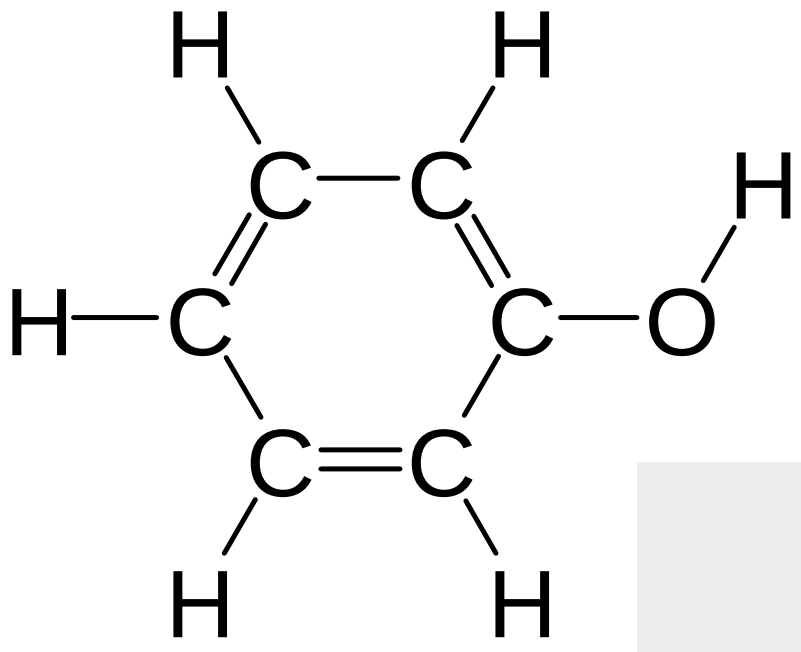






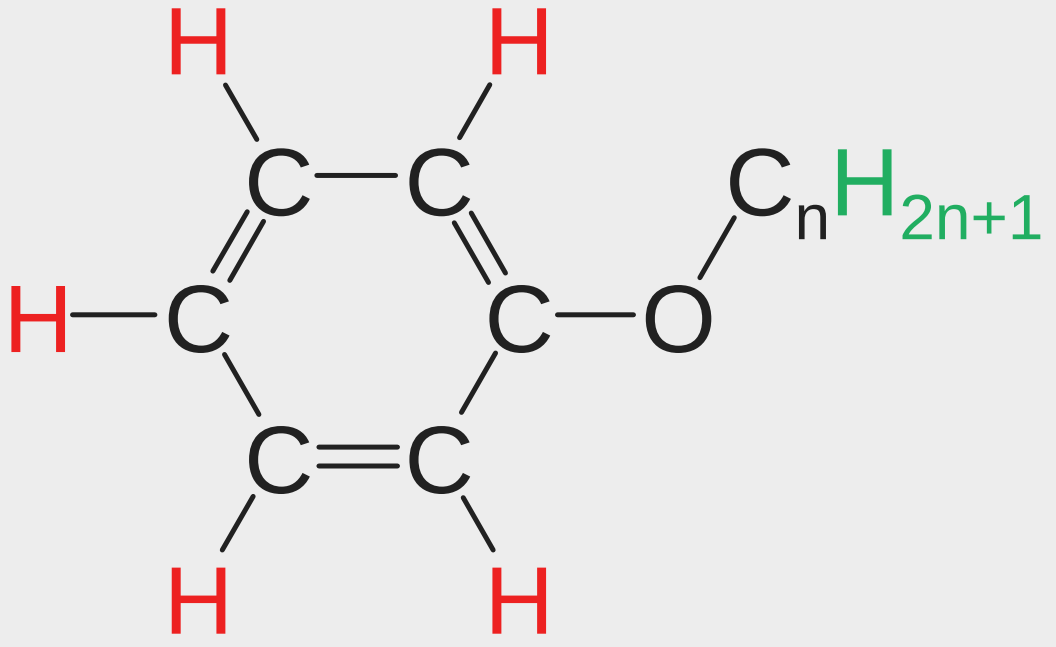

DEPT – CH3 only
DEPT – CH2 only
DEPT – CH only
13C{1H} NMR spectrum
measured at 75.47{300.13} MHz
ppm
158.17
129.29
120.27
115.77
74.63
29.11
19.10
9.63
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
13C

Step-by-step-solution



+ $Br—C_nH_{2n+1}$

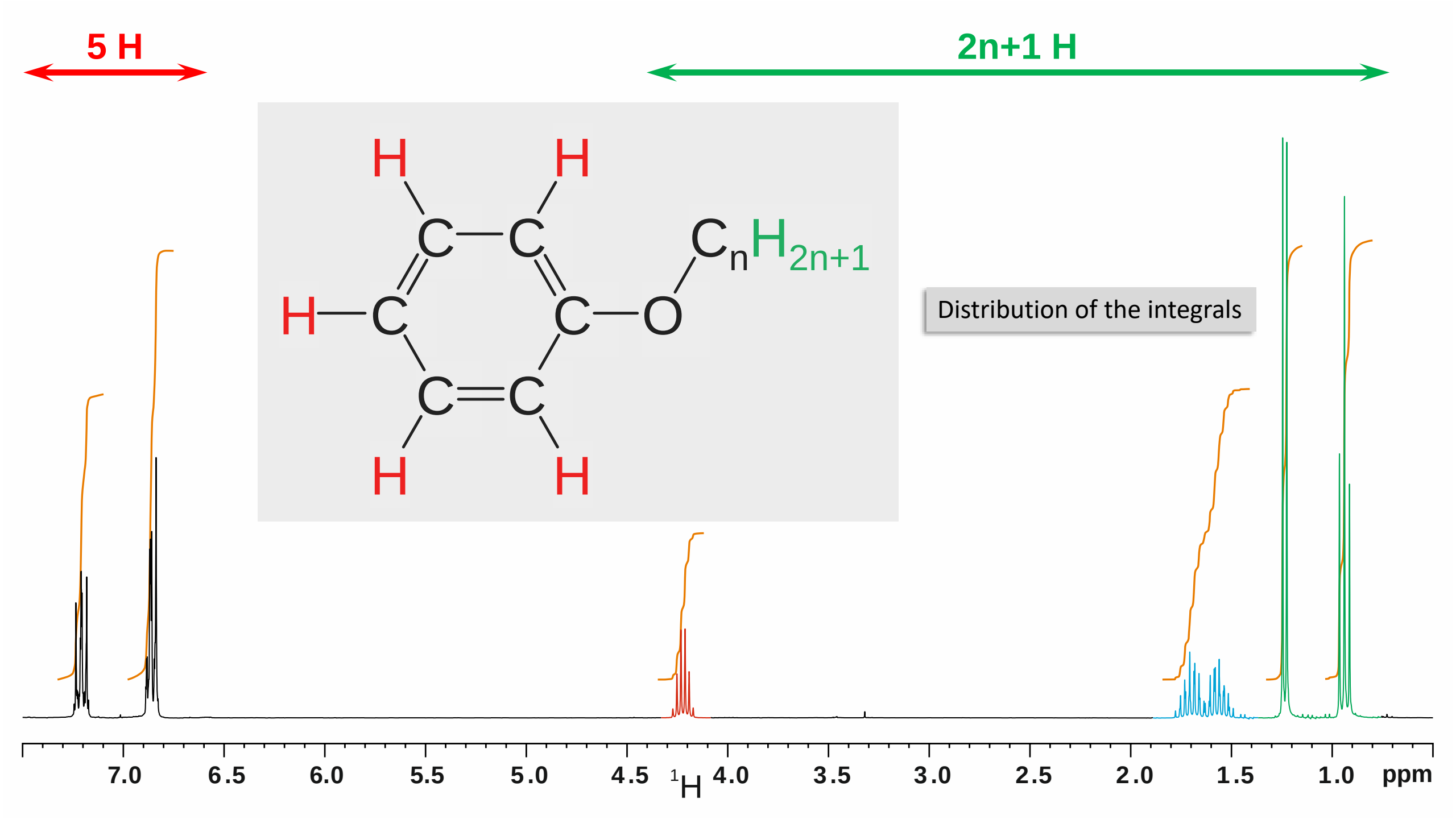
You might express one part of the task directly into chemical reaction equation.

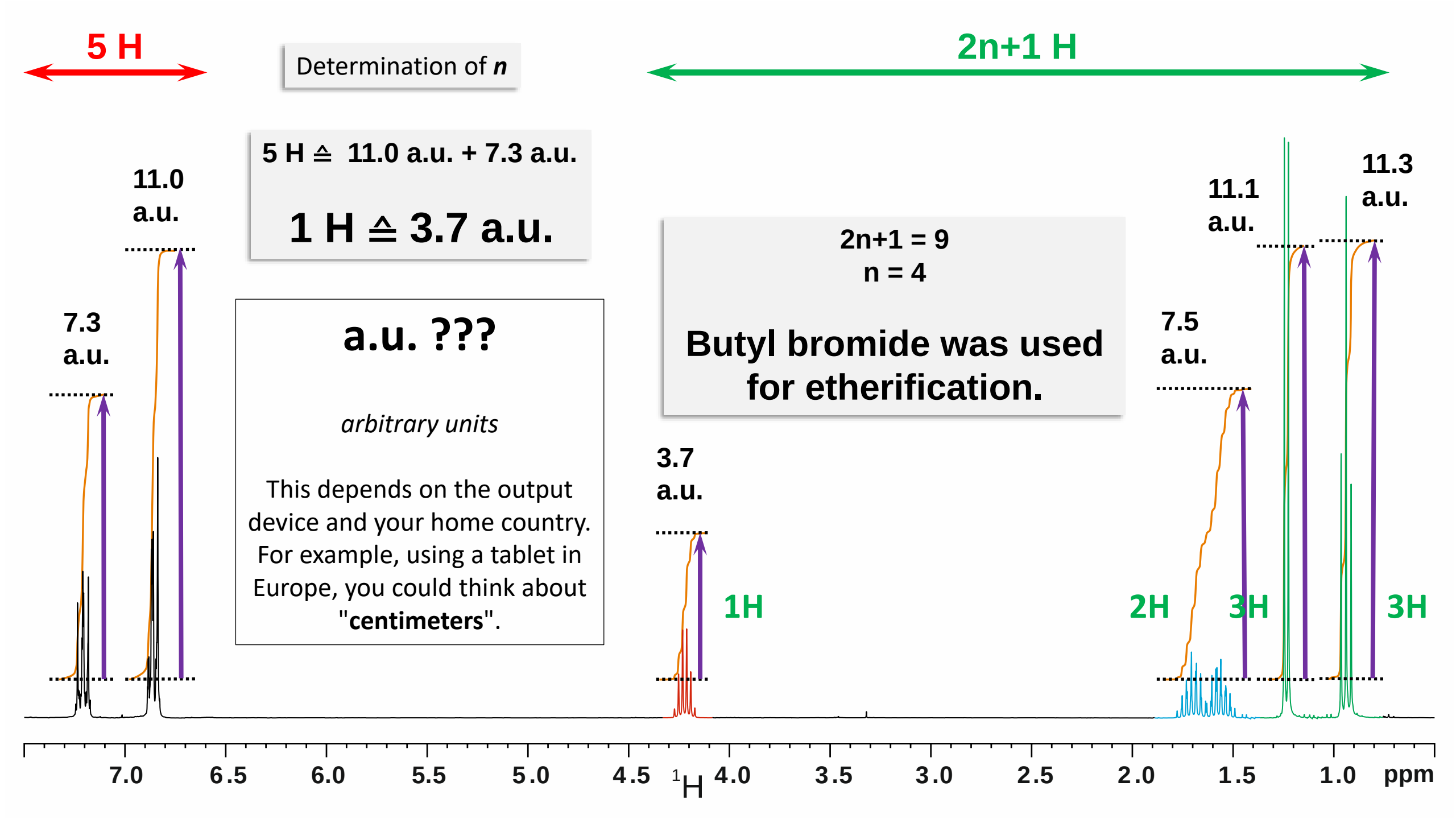


We expect signals in two well-separated spectral regions.

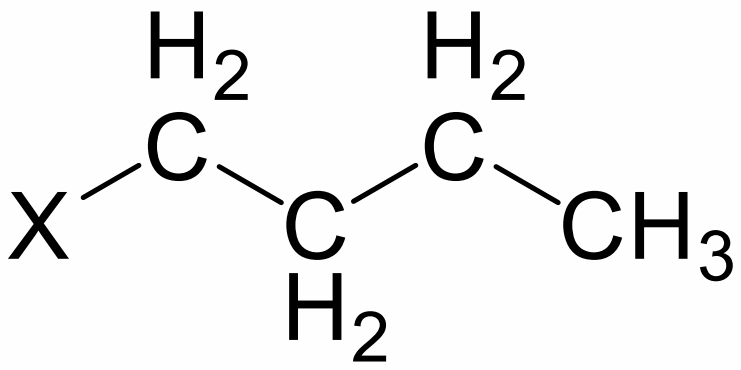
2n+1 H
δ ≈ 1 … 4 ppm

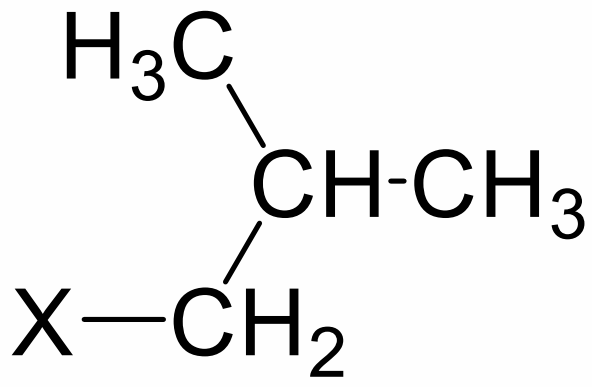
5 H
δ ≈ 6 … 8 ppm

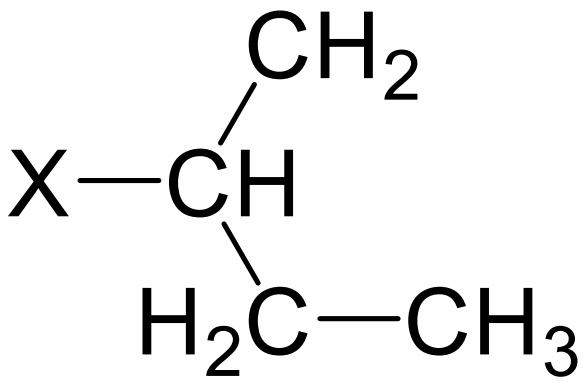

5 H
2n+1 H
H
H
C
C
H
C
C
O
C_nH_{2n+1}
H
C
C
H
H
Distribution of the integrals
7.0
6.5
6.0
5.5
5.0
4.5
^1H
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

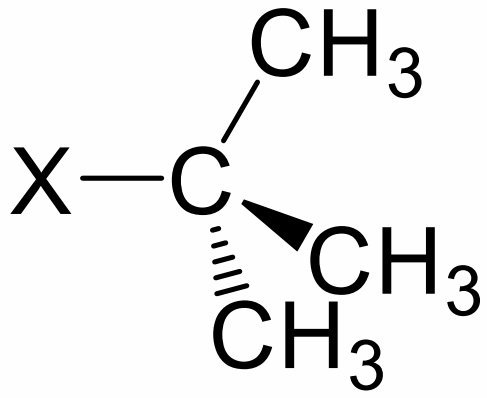

5 H
Determination of n
2n+1 H
5 H ≙ 11.0 a.u. + 7.3 a.u.
1 H ≙ 3.7 a.u.
11.0 a.u.
7.3 a.u.
a.u. ???
arbitrary units
This depends on the output device and your home country. For example, using a tablet in Europe, you could think about "centimeters".
2n+1 = 9
n = 4
Butyl bromide was used for etherification.
3.7 a.u.
1H
11.1 a.u.
11.3 a.u.
7.5 a.u.
2H
3H
3H
7.0
6.5
6.0
5.5
5.0
4.5
^{1}H
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

Four different isomers of the butyl moiety are possible.



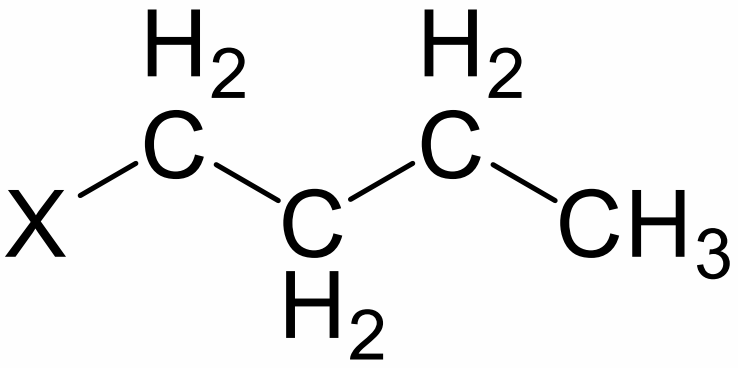




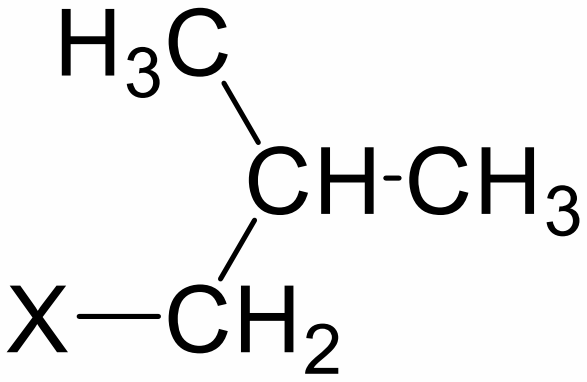


The easiest way to determine which of these is present is the use of DEPT subspectra.

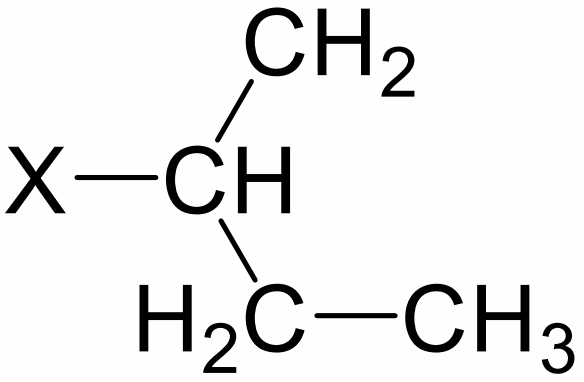
In the individual isomers we expect the following CH_n groups.



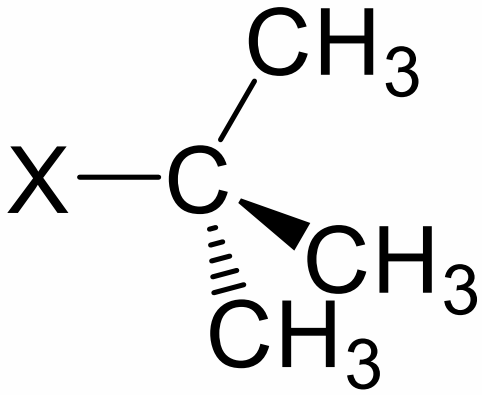
0 * **C**H
3 * **C**H_2
1 * **C**H_3



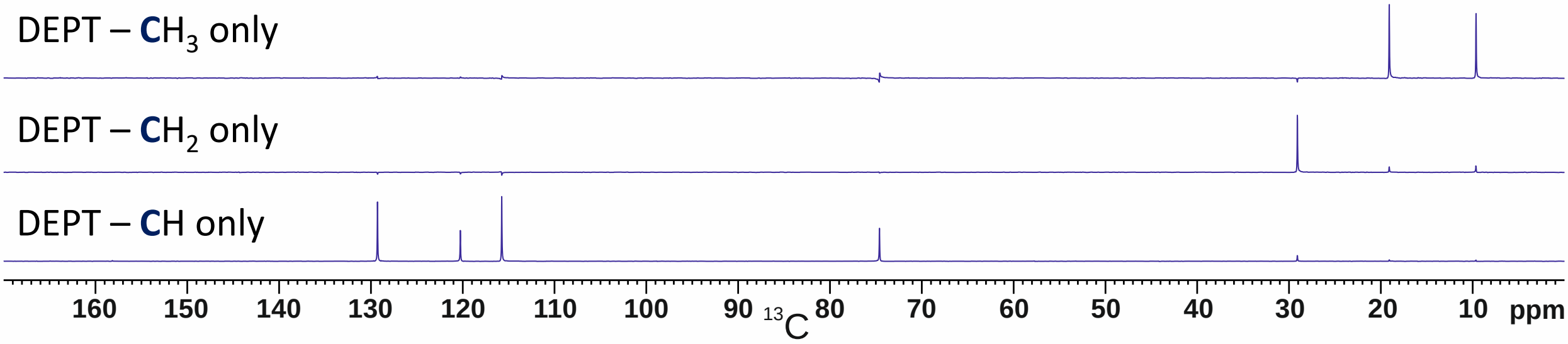
1 * **C**H
1 * **C**H_2
1 * **C**H_3 (symmetry!)



1 * **C**H
1 * **C**H_2
2 * **C**H_3

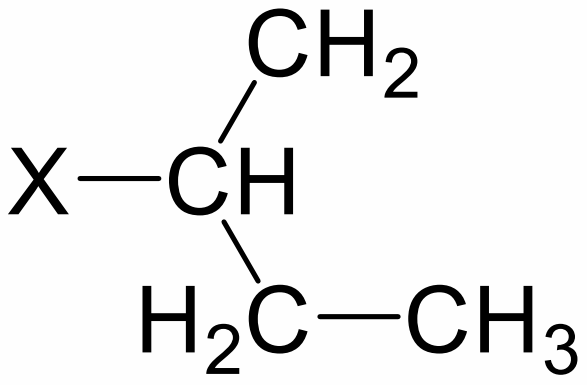


0 * CH
0 * **C**H_2
1 * **C**H_3 (sym-metry)

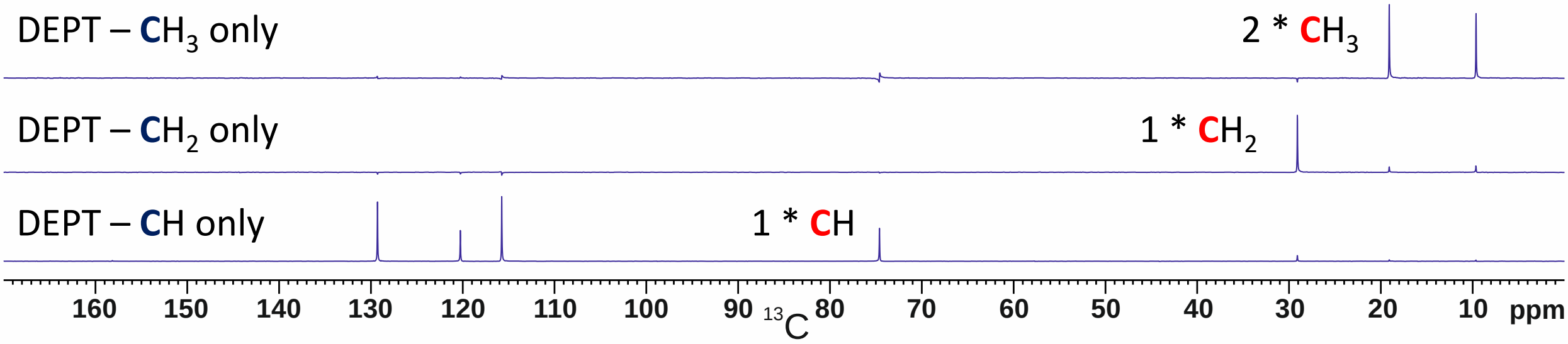


Only the 2-butyl residue is compatible with the DEPT subspectra.

(The =**C**H- signals between 110 and 130 ppm belong to the phenyl group.)

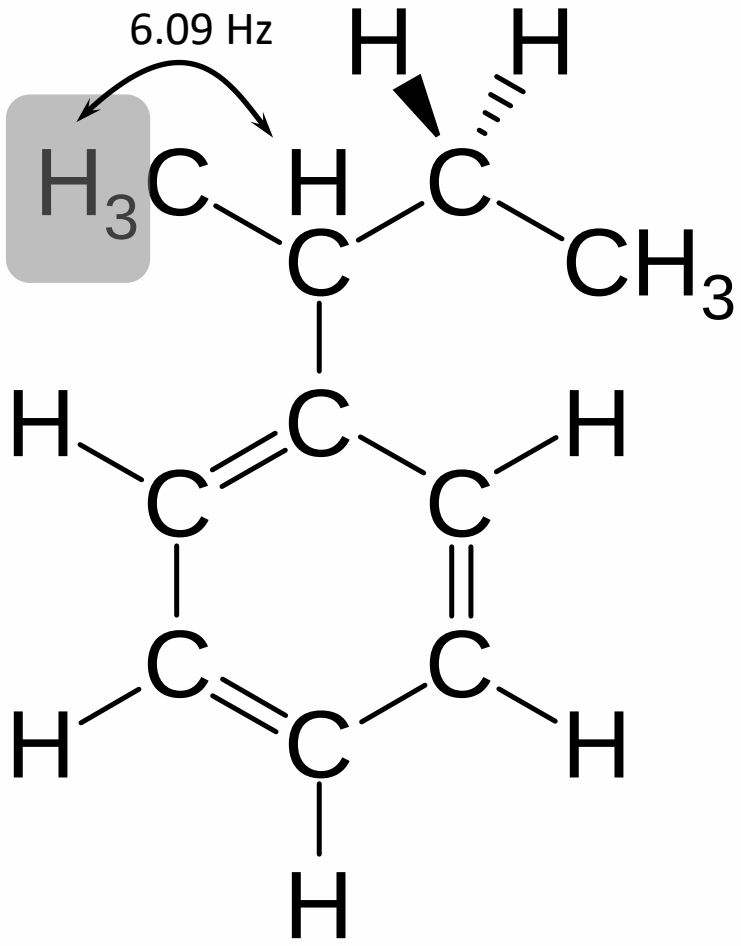


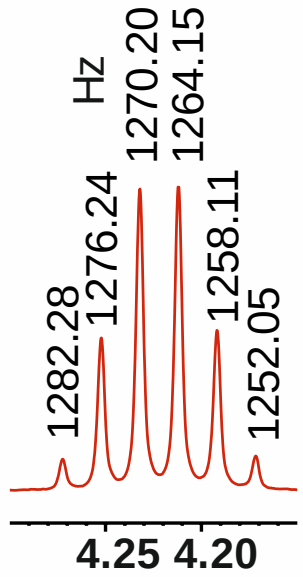
1 * **C**H
1 * **C**H$_2$
2 * **C**H$_3$



Analysis of the proton multiplets

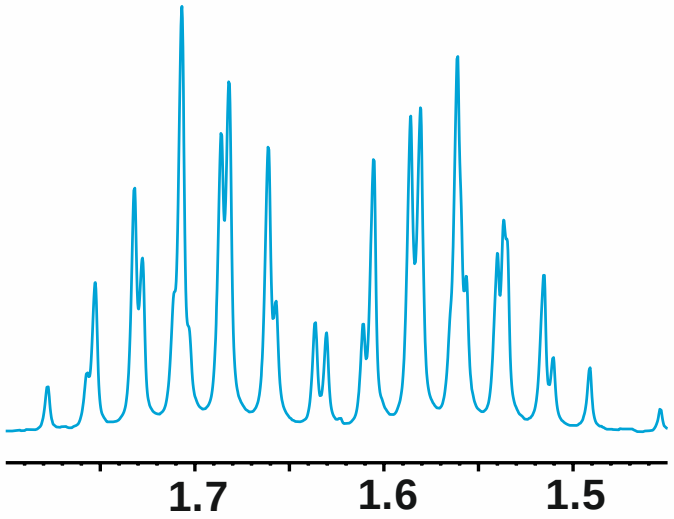
methyl protons attached to carbon 1

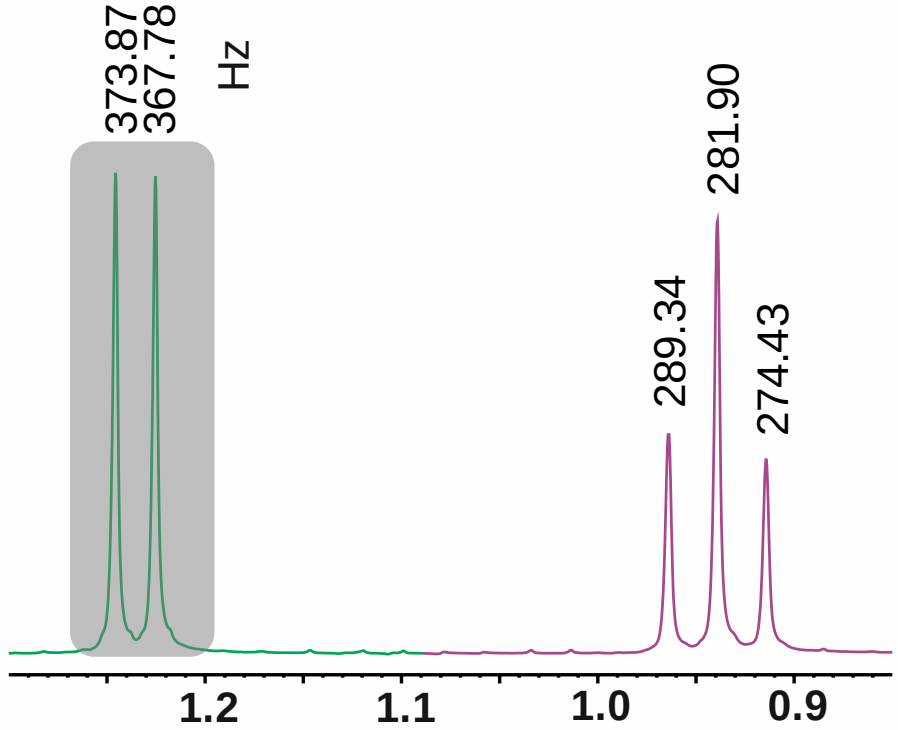




Only the proton in the 2-position is adjacent.
We expect a doublet.

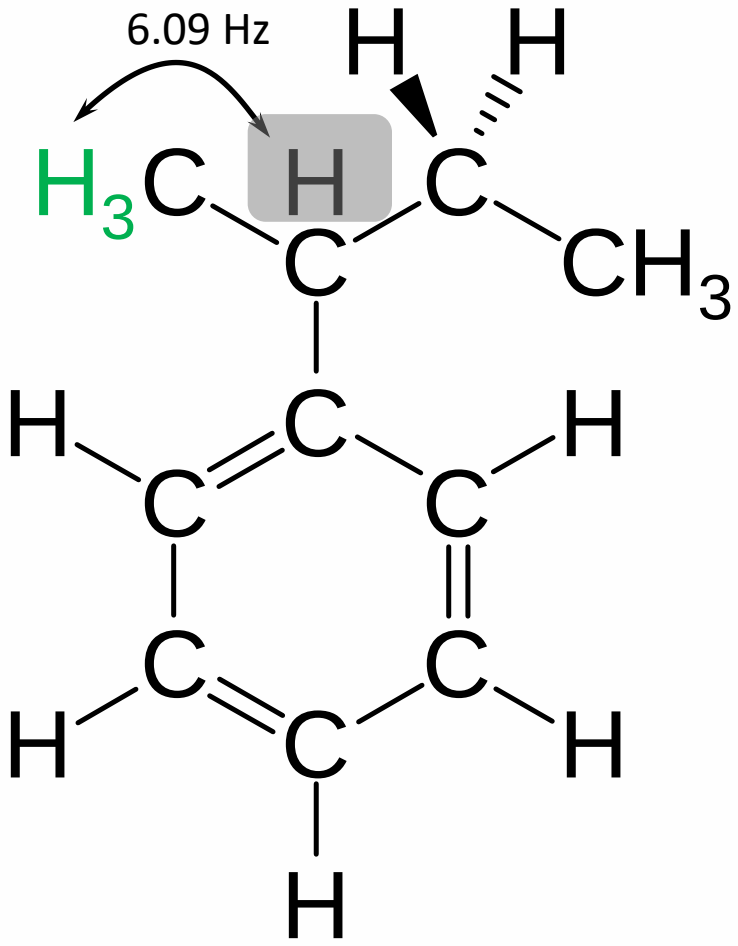
The coupling constant is **6.09 Hz**.

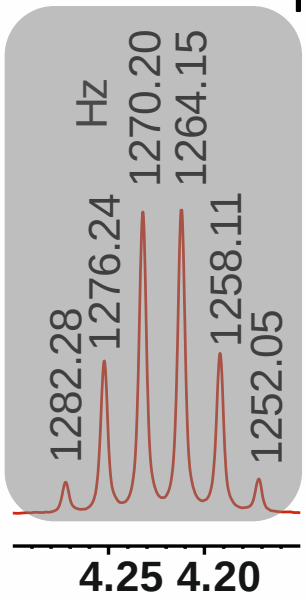




Analysis of the proton multiplets

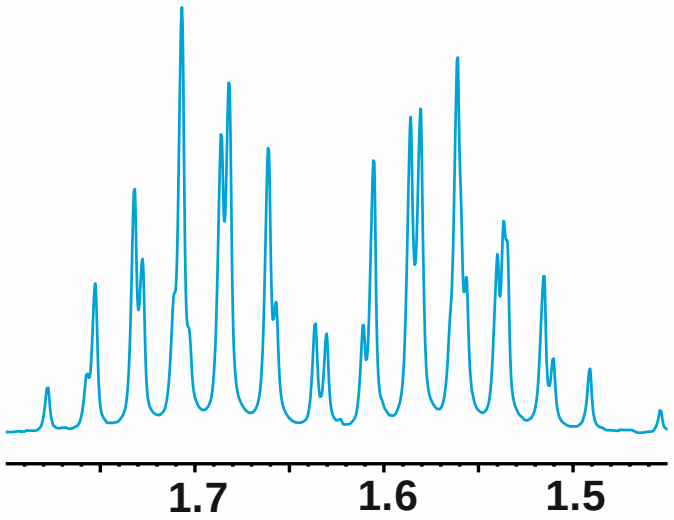
methin proton attached to carbon 2

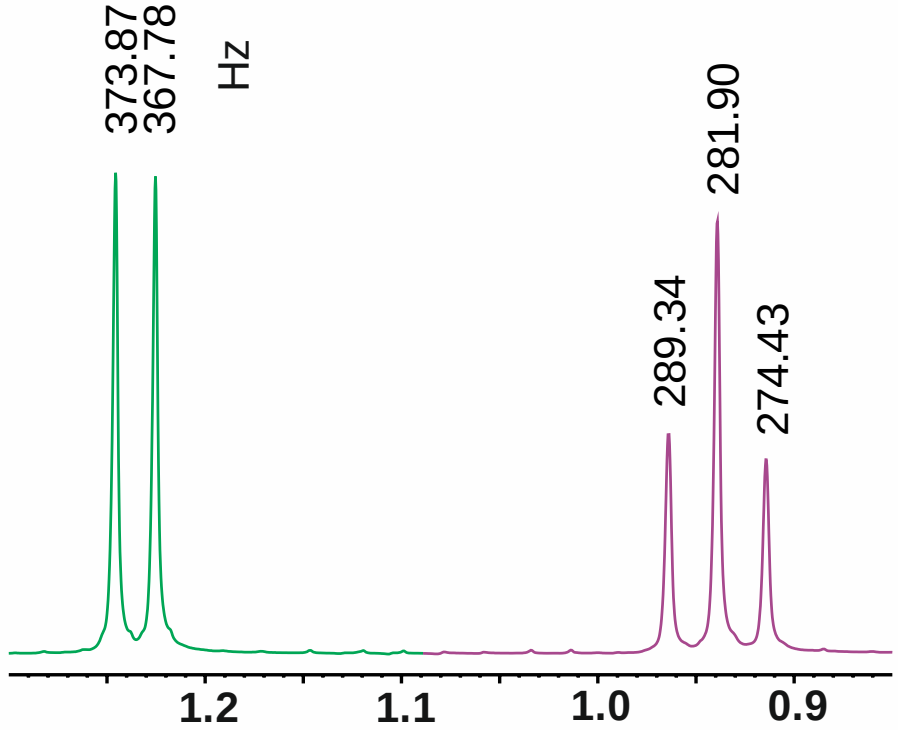




The five protons separated via three bonds are not chemically equivalent, but the size of the coupling constants should be comparable. The result is a pseudo sextet.

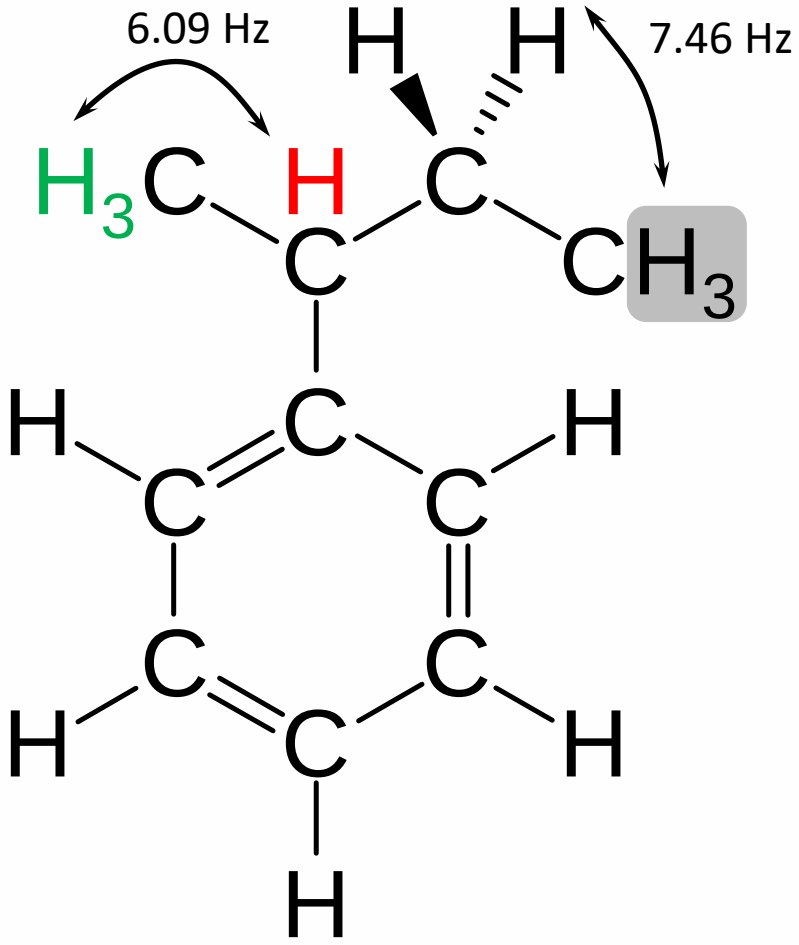
The average coupling constant is **6.05 Hz**.





Analysis of the proton multiplets

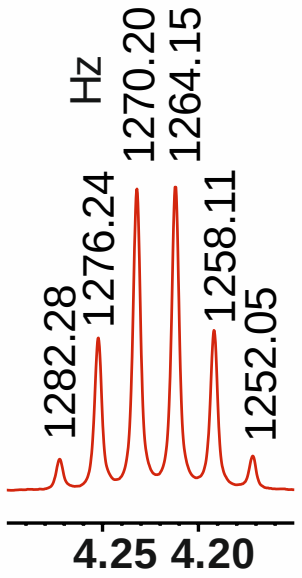
methyl protons attached to carbon 4

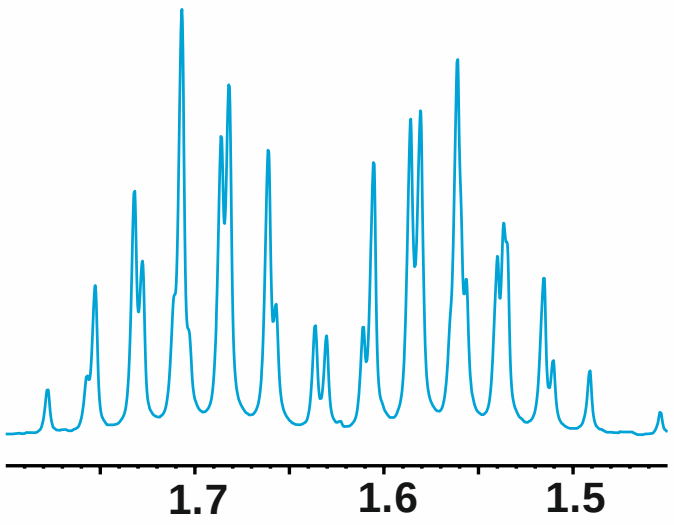


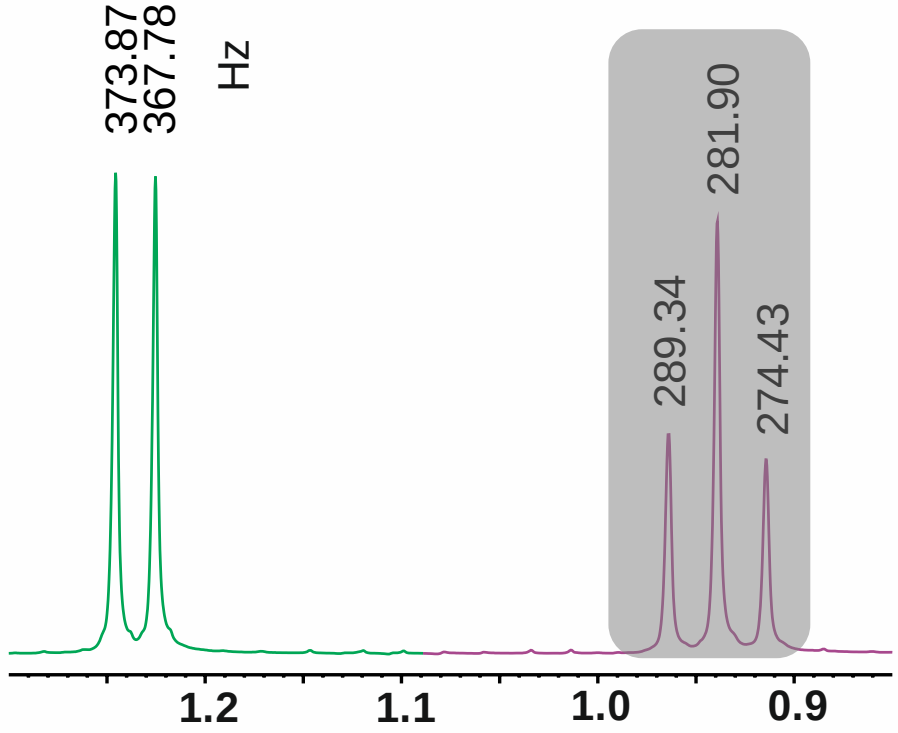
Adjacent are the two protons of the methylene group. We expect a triplet.

The coupling constant is **7.46 Hz**.

Note: Both the coupling constant and the triplet structure will need to be reviewed a little later.

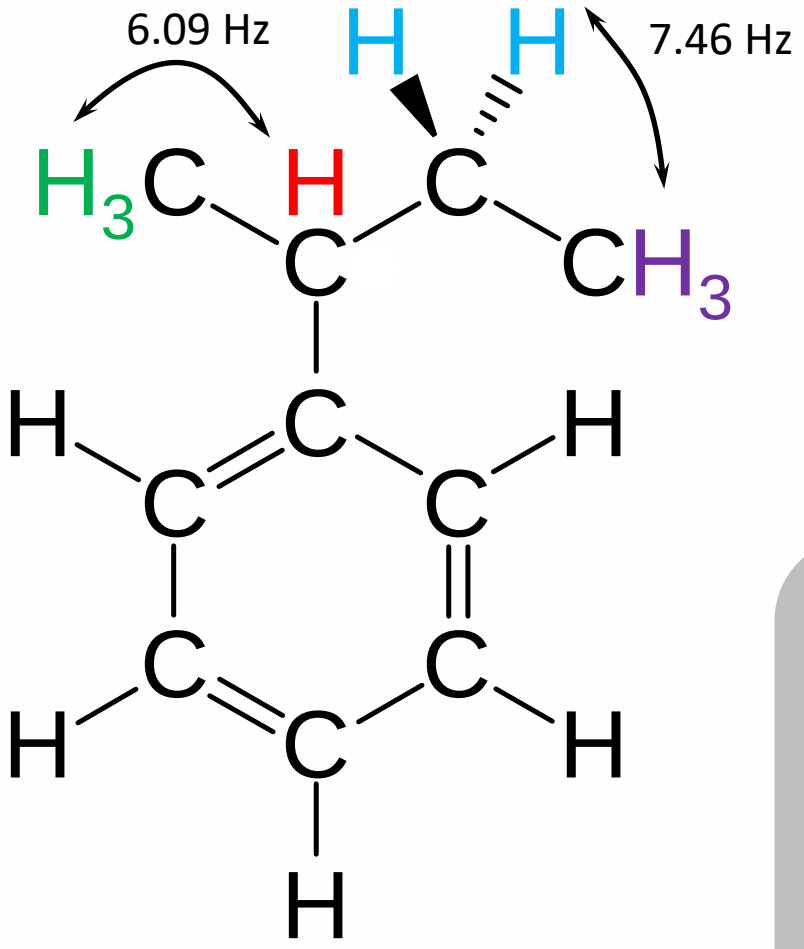


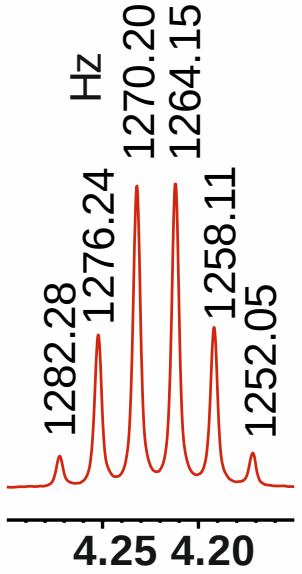




Analysis of the proton multiplets

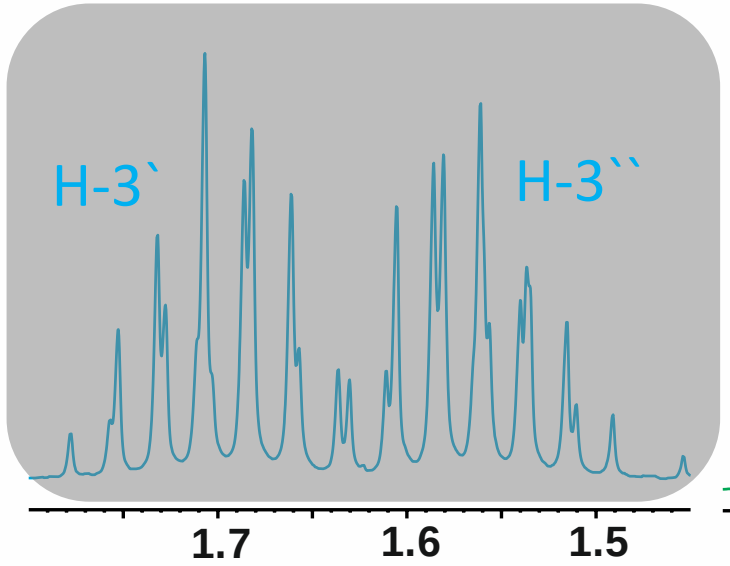
methylene protons attached to carbon 3

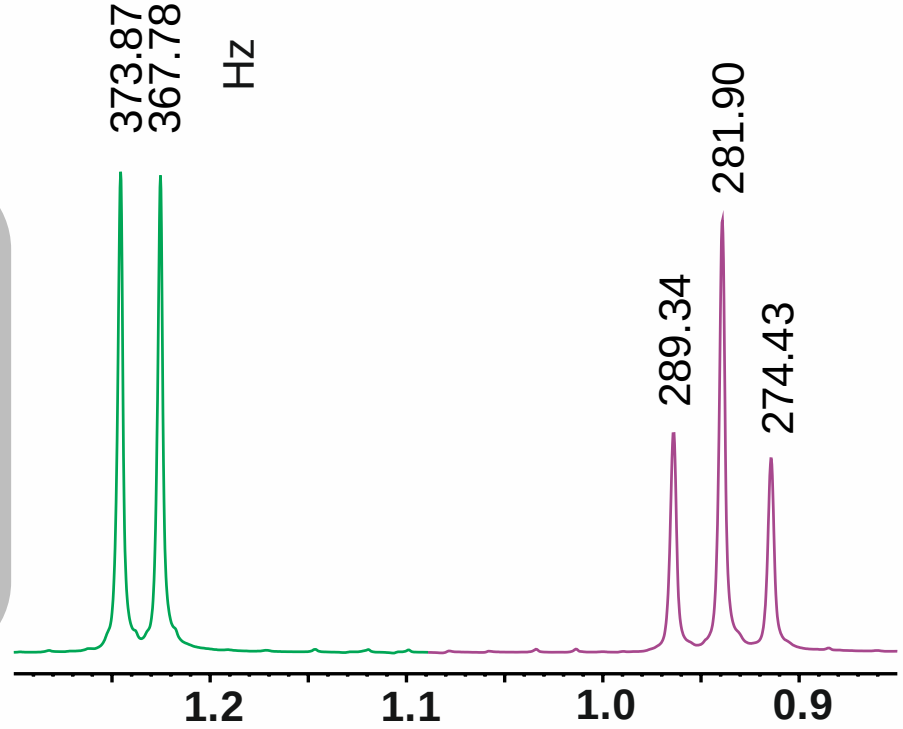




Why is the signal of the two remaining methylene protons that crowded?

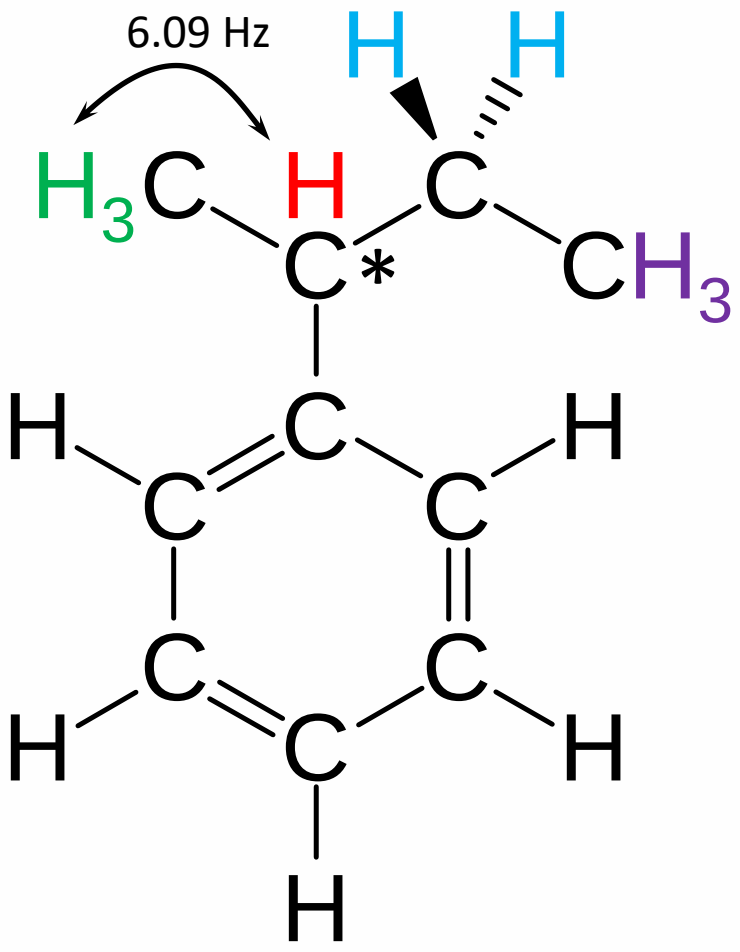
The compound has a center of chirality at C-2, so we have not one but two signals from two diastereotopic protons.

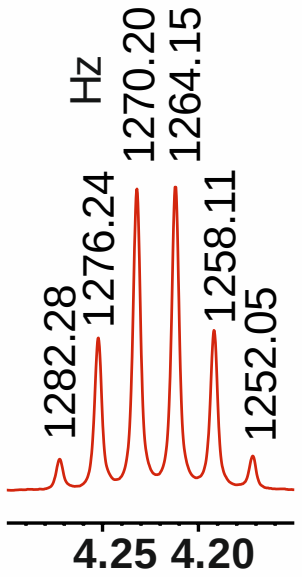




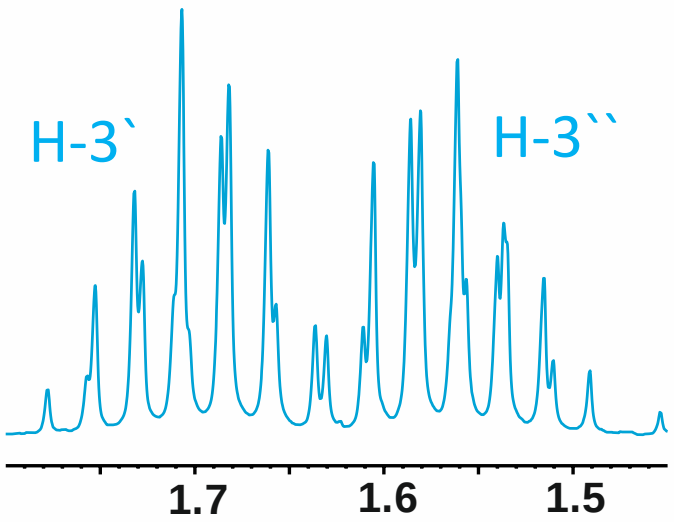
Analysis of the proton multiplets

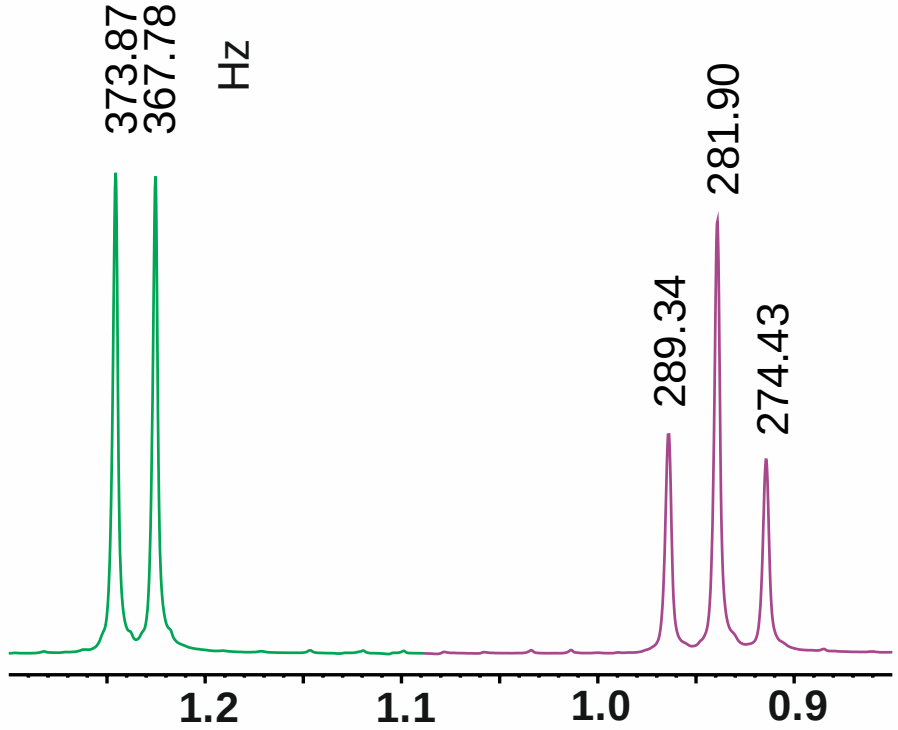
methyl protons attached to carbon 4



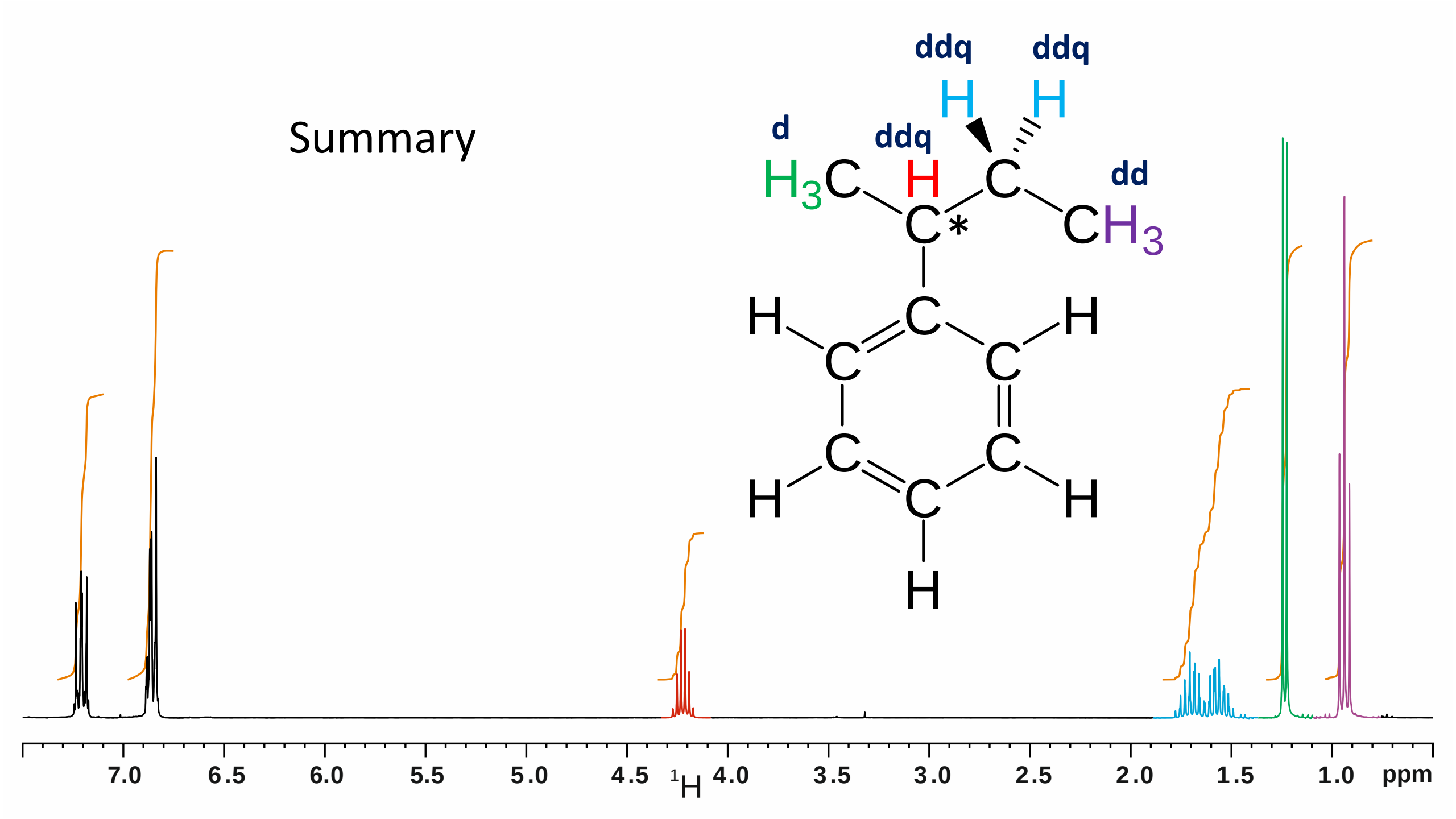


Because of the similarity of the chemical shifts of H-3' and H-3'', the whole spectrum cannot be properly evaluated according to 1st order rules. The signal of the methyl group in the 4-position is in any case not a triplet, but more likely a doublet of doublets.

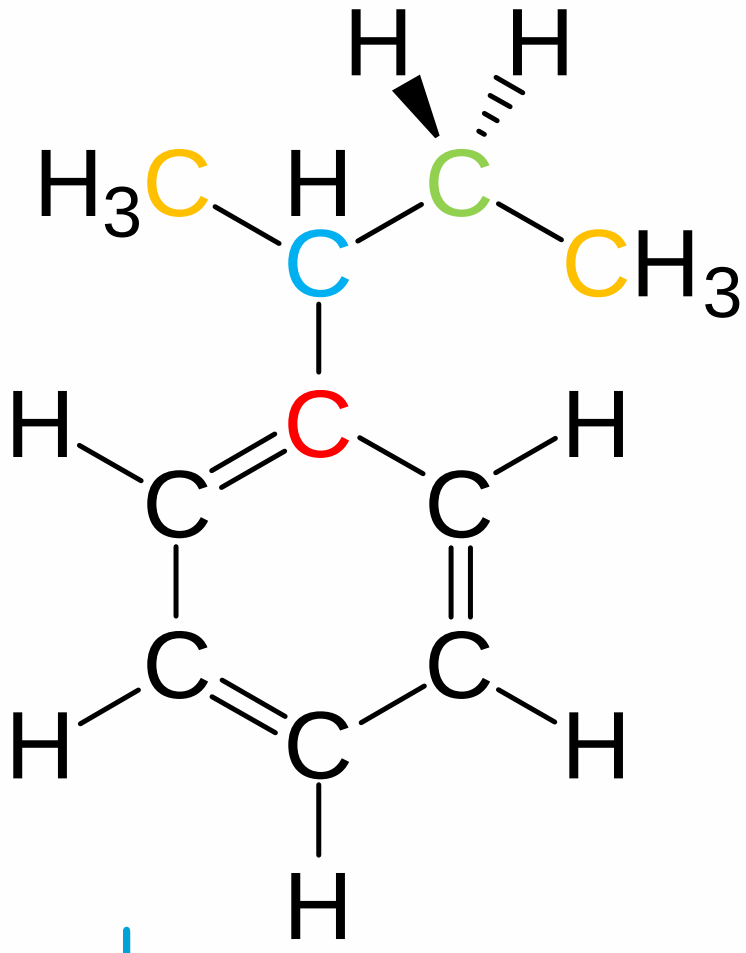


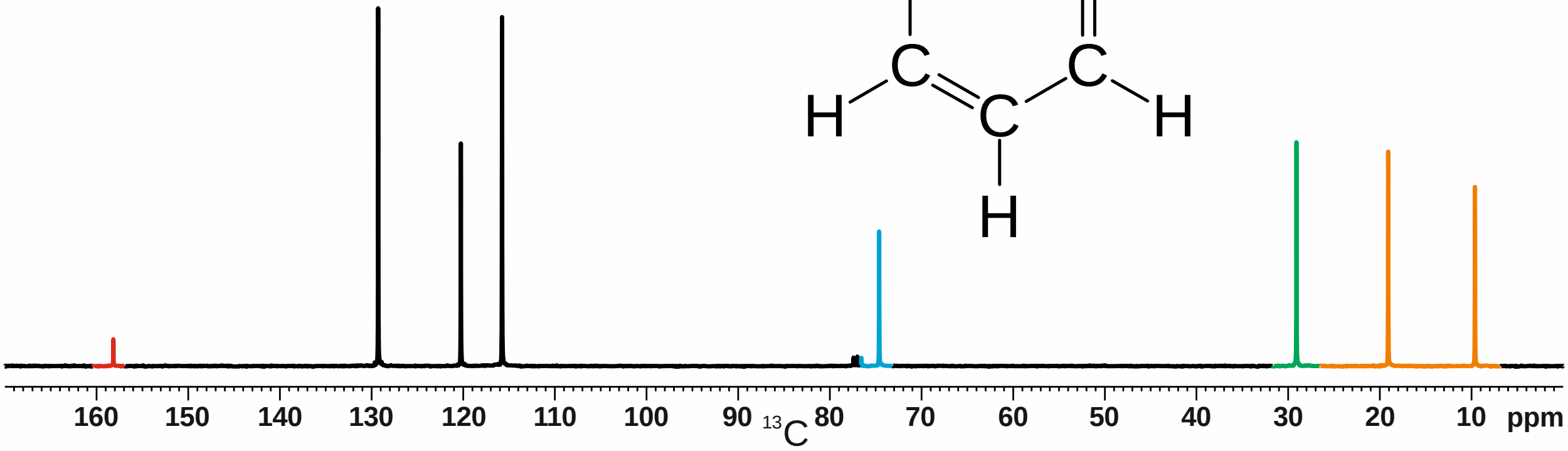


Summary


ddq
ddq
H
H
d
ddq
dd
H3C
H
C
C*
CH3
H
C
H
C
C
H
C
C
H
C
H
H
7.0
6.5
6.0
5.5
5.0
4.5
1H
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

Summary


H
H
H3C
H
C
CH3
C
H
C
H
C
C
C
C
H
H
H
H


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
13C

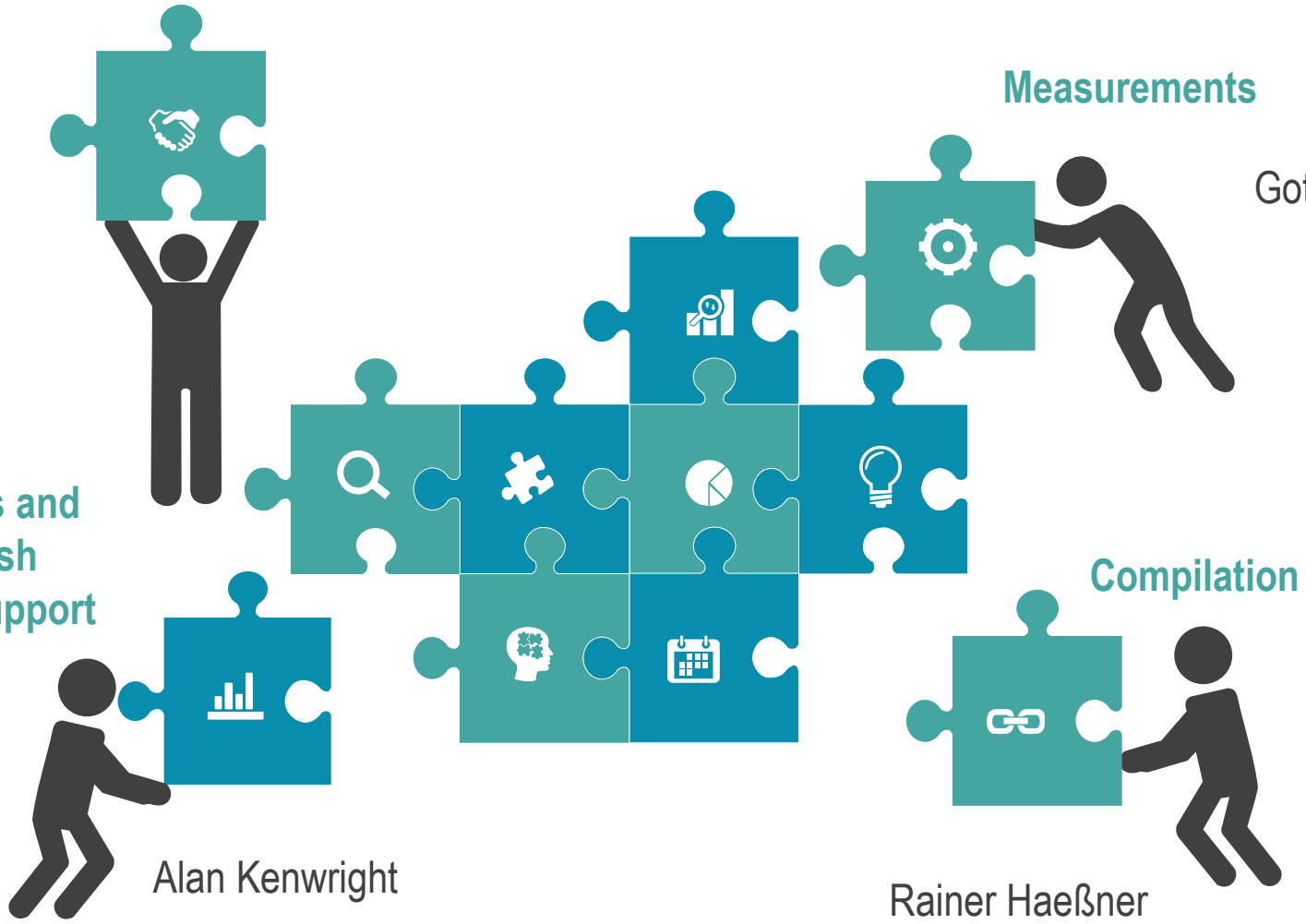
Contributions

Spectrometer time

Goethe University Frankfurt

Measurements

Gottfried Zimmermann



Discussions and native English language support

Alan Kenwright

Compilation

Rainer Haeßner

More exercises ...