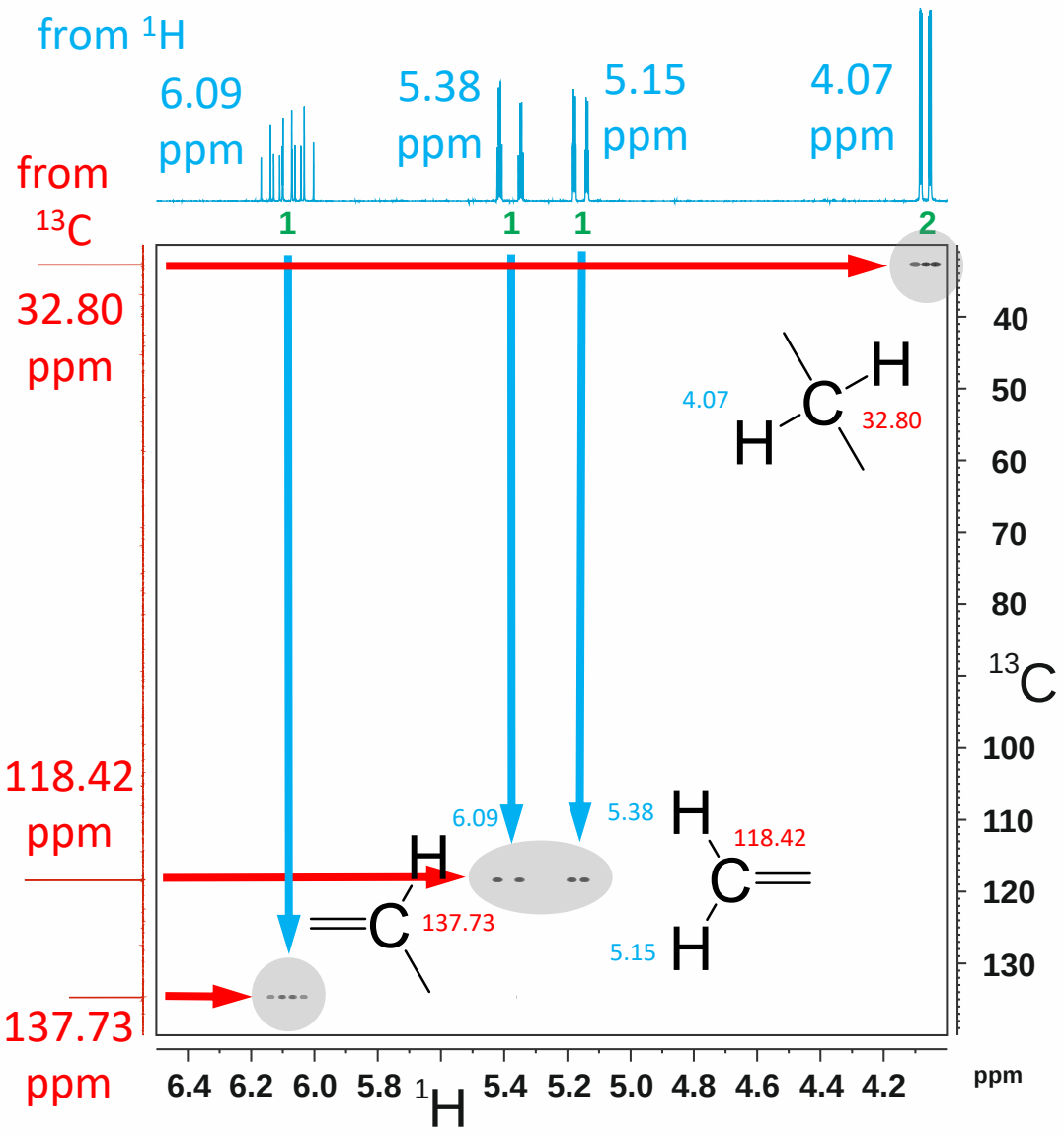
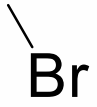
Problem of the Month:

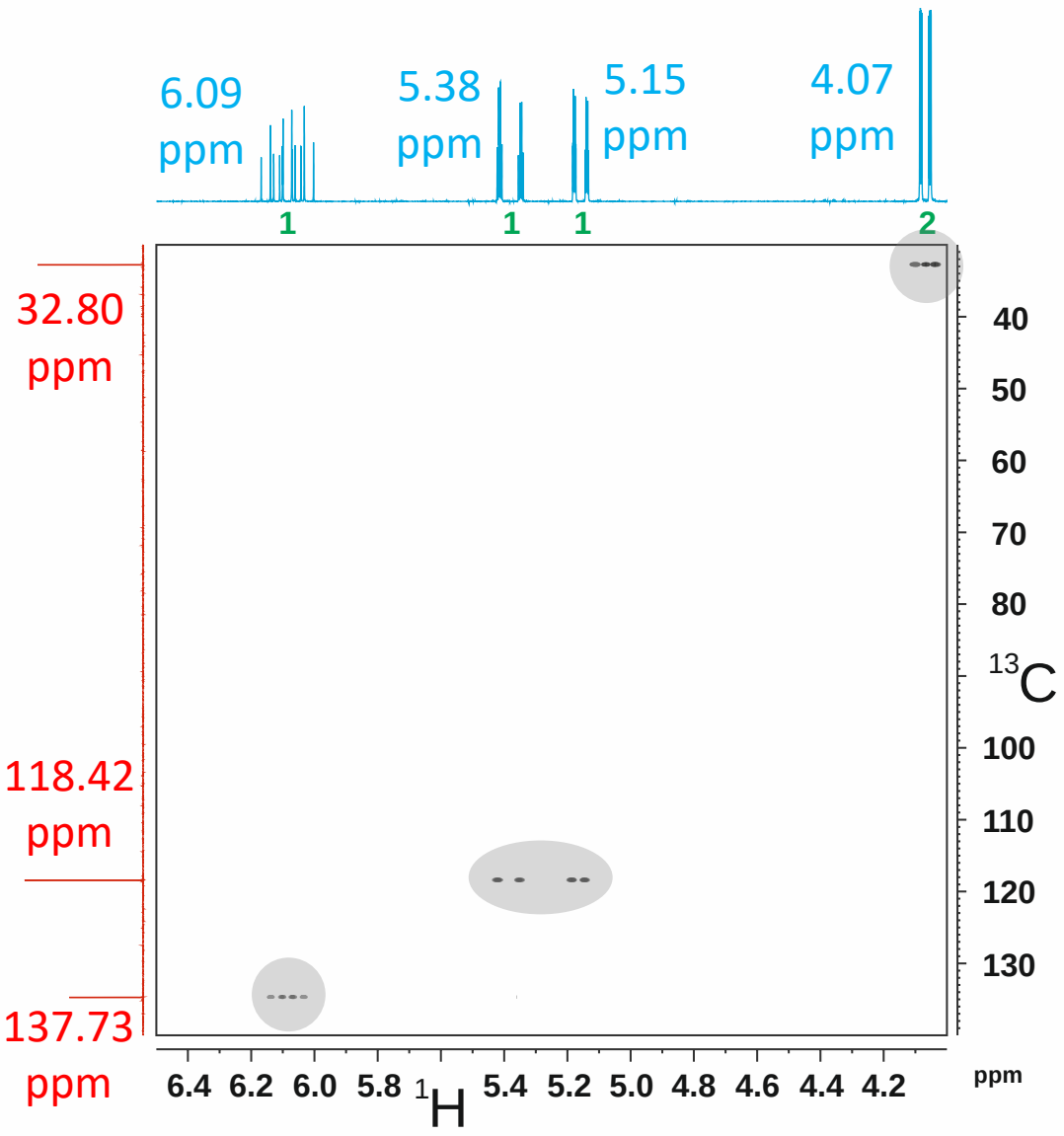
August 2020

Solution

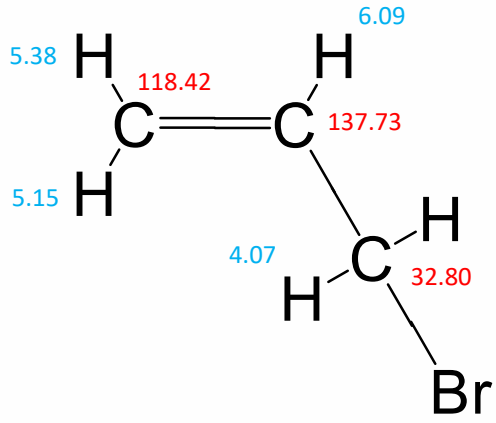


C_3H_5Br
$- C_3H_5$
Br

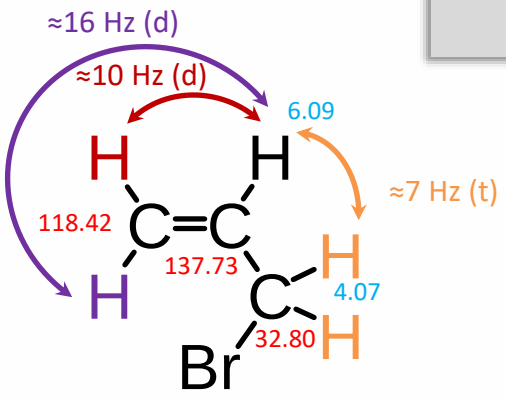




and finally …



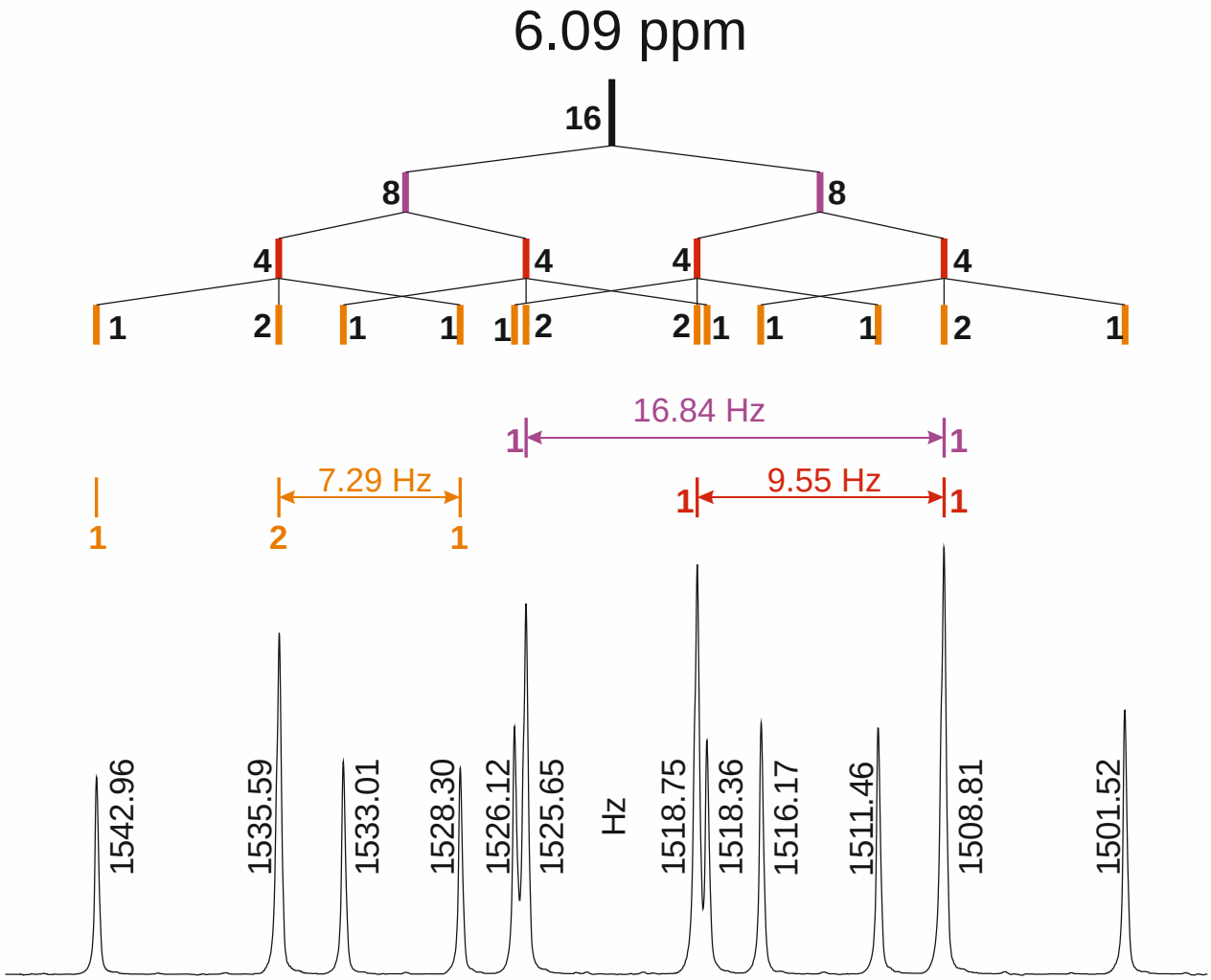
Coupling constants and stereochemical assignment
First step



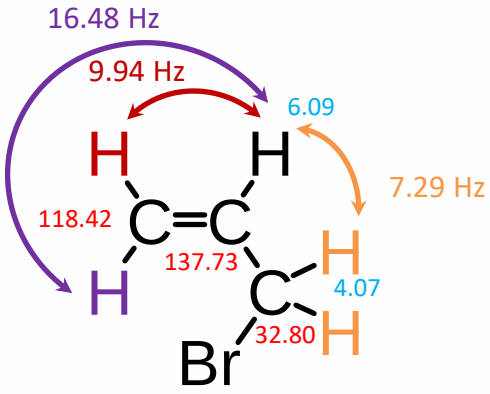
We expect a coupling constant of 7 Hz between H-2 (6.09 ppm) and H-3 (4.07 ppm)

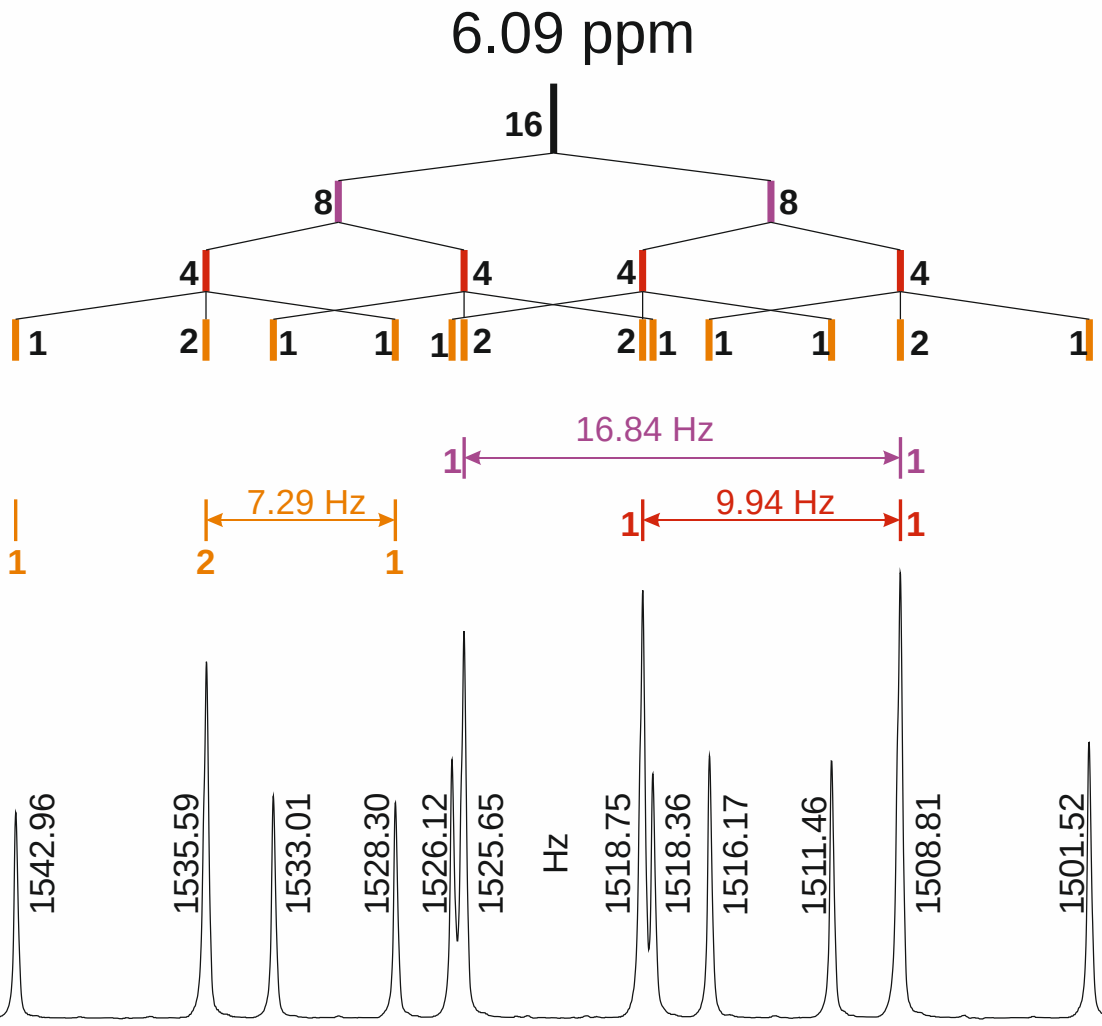
We expect a coupling constant of 10 Hz between H-2 and H-1 in Z position

We expect a coupling constant of 16 Hz between H-2 and H-1 in E position



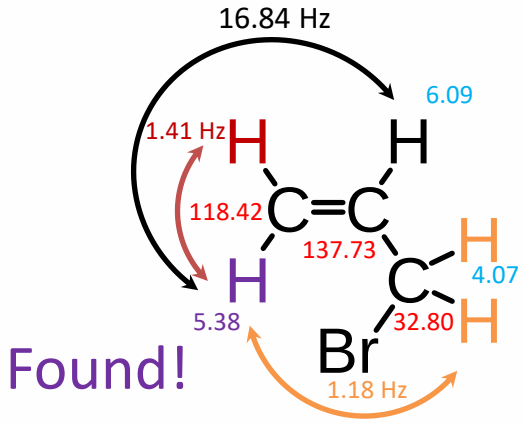
Stereochemical assigment
Step 2: the $=CH_2$ group



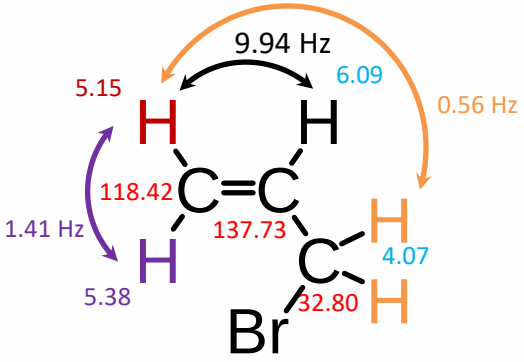


The coupling constants of 16.48 Hz and 9.94 Hz have to appear in the multiplets of the protons with δ= 5.15 and δ= 5.38 ppm.

Tentatively let's assume the violet labelled proton shows the chemical shift of δ= 5.38 ppm and contains the coupling constant of 16.48 Hz.

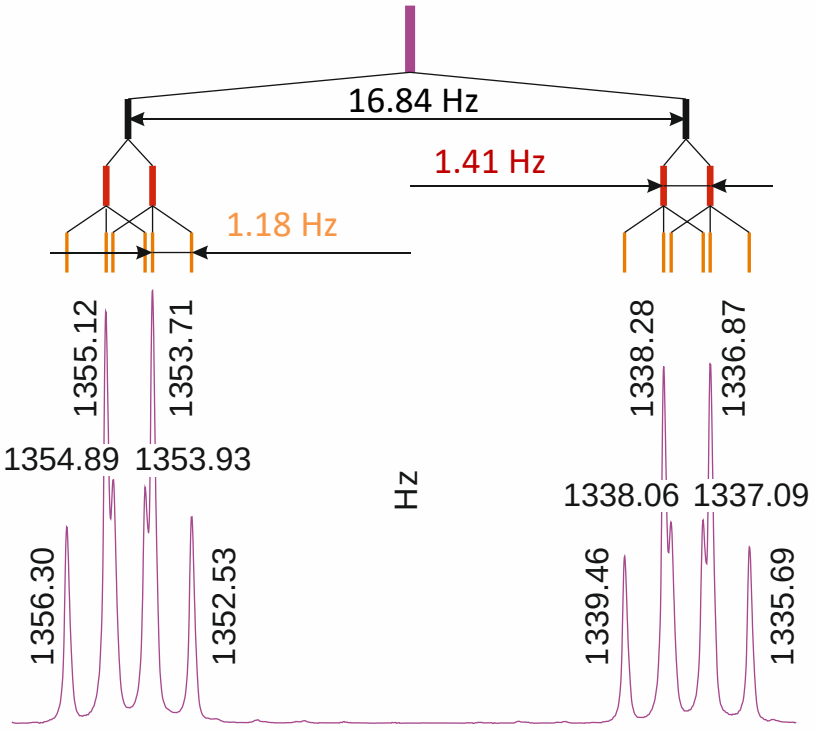


Found!

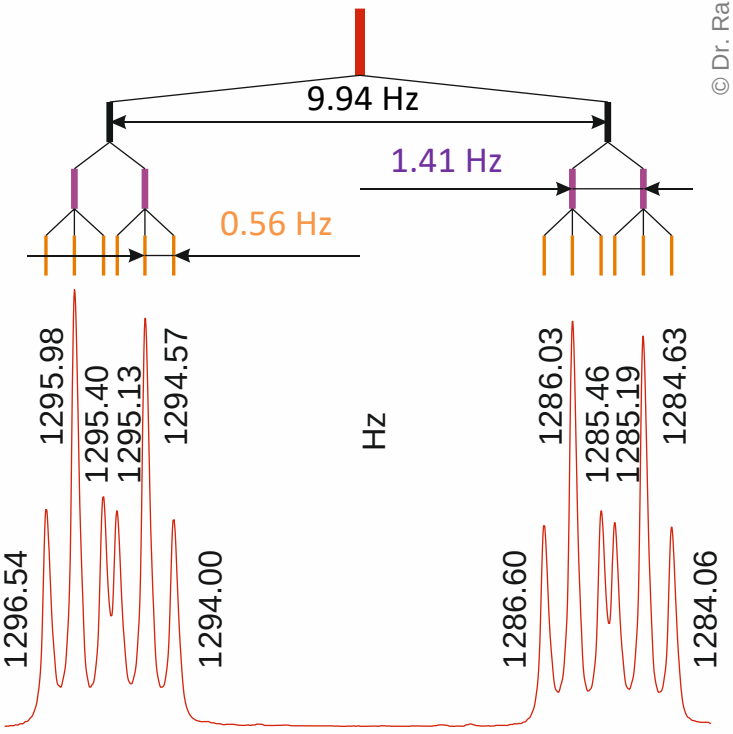


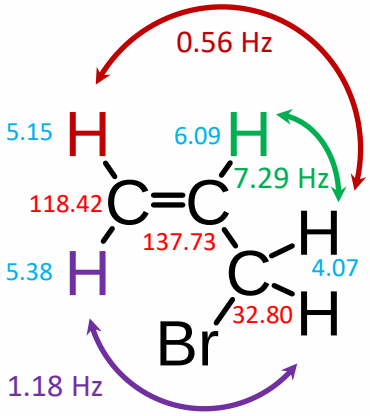
And let‘s summarize.

5.38 ppm



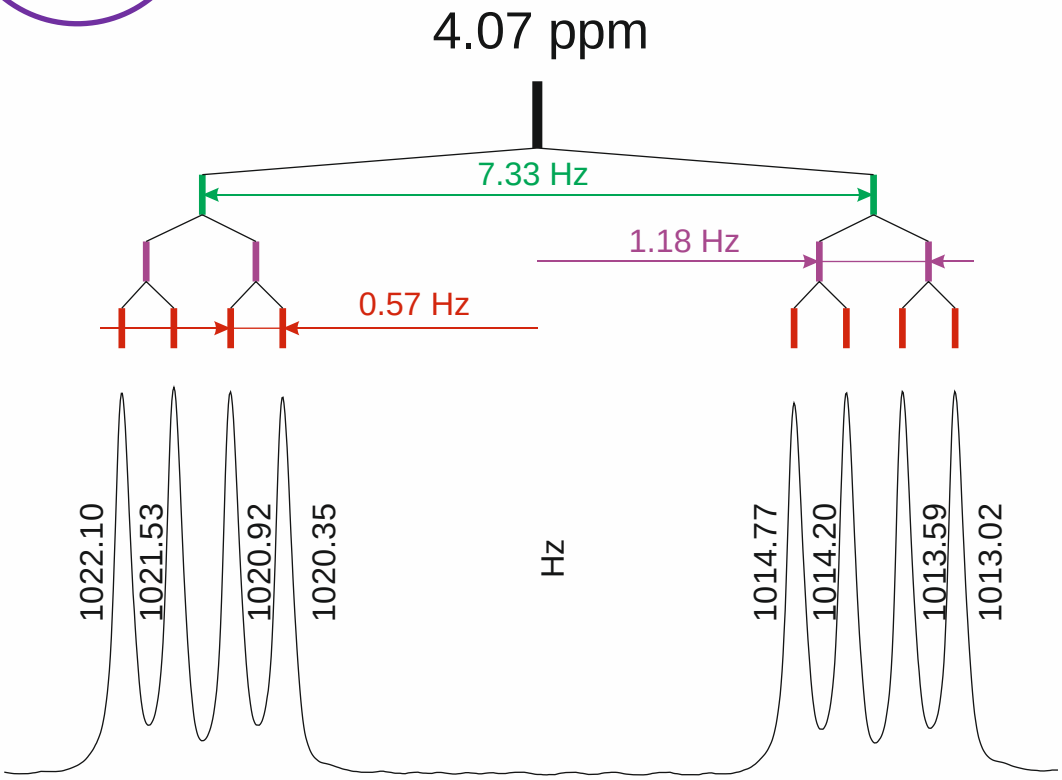
5.15 ppm

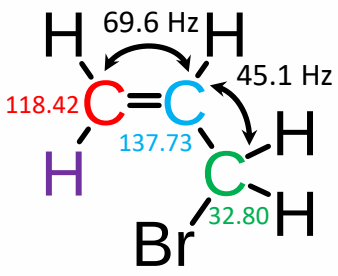




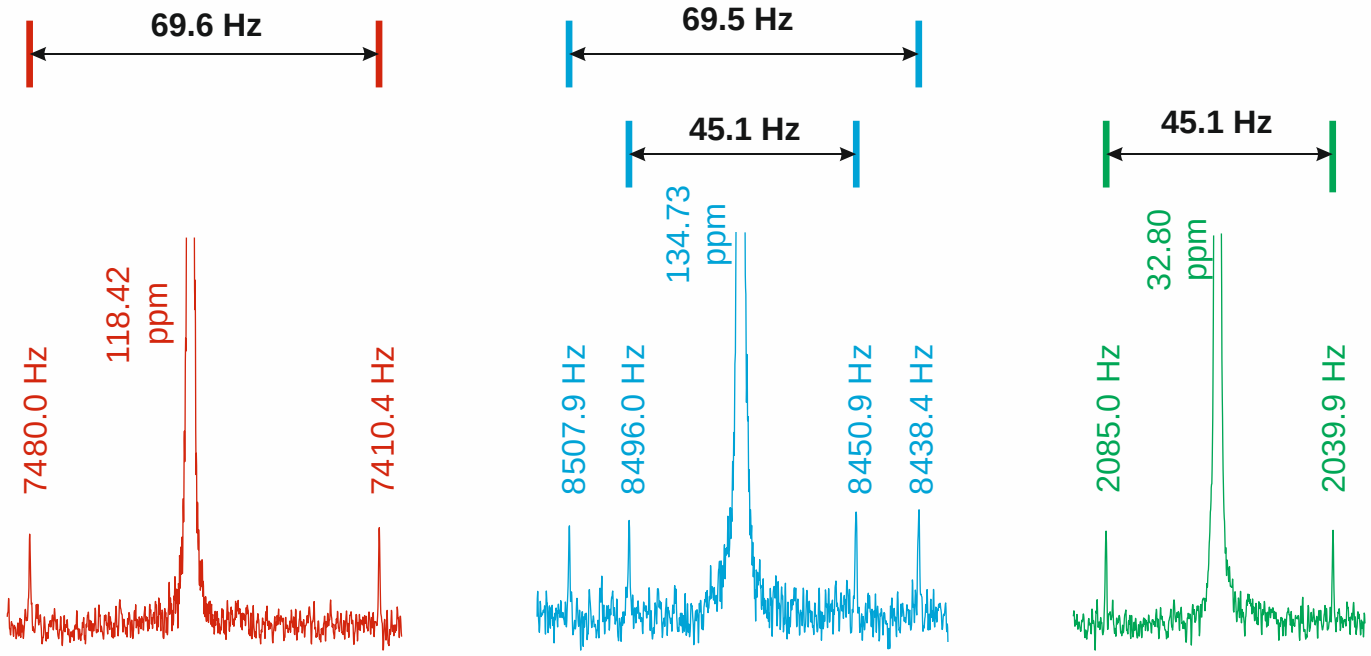
All coupling constants are now accounted for.

Three of them should be visible in the multiplet of the protons in 3-position (δ= 4.07 ppm)





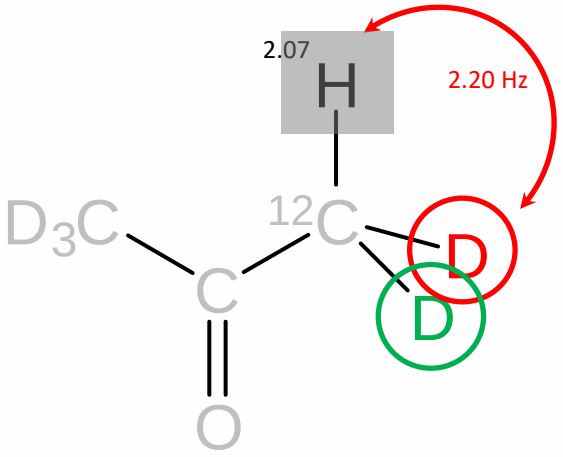
The good signal-to-noise ratio allows an additional (optional) proof of the carbon backbone using ^{13}C-^{13}C one bond couplings.

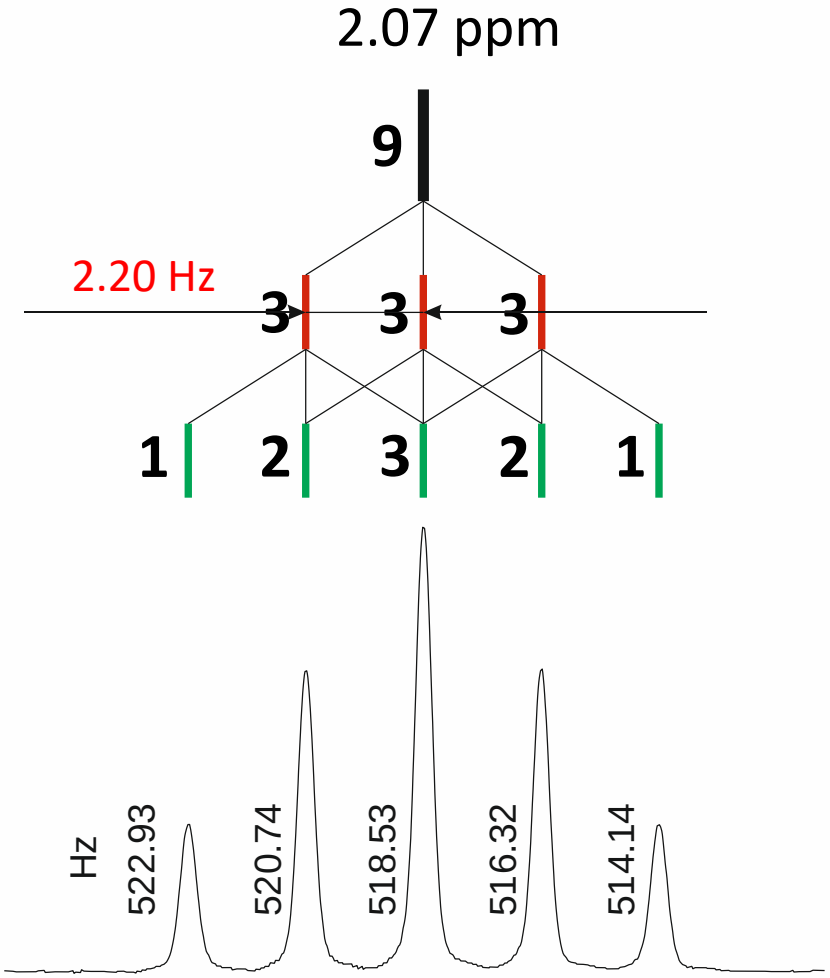


Beyond the structural challenge

The solvent signals

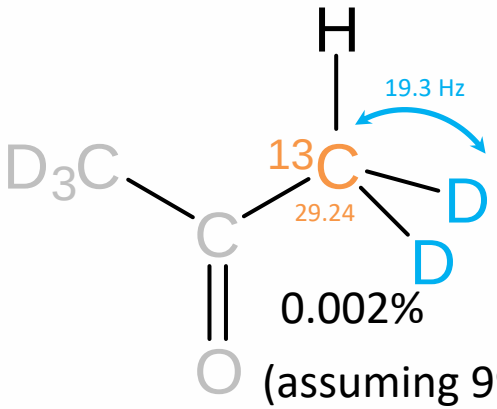
Deuterium enrichment of the solvent is not perfect.
Let‘s assume 99,8% enrichment.
In this case the solvent contains 0.2% of this compound.



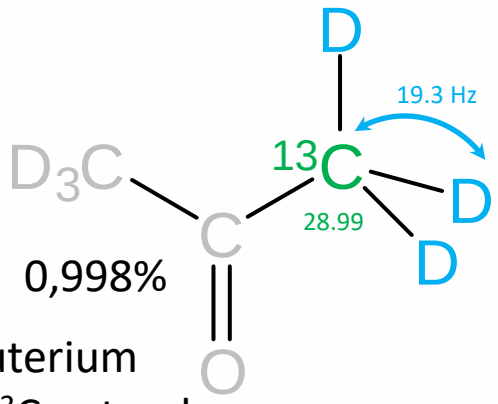


To understand the splitting of the observed proton signal keep in mind deuterium is an *I* = 1 nucleus, causing a 1:1:1 splitting.

(remember: ^{13}C spectrum is measured with proton decoupling)



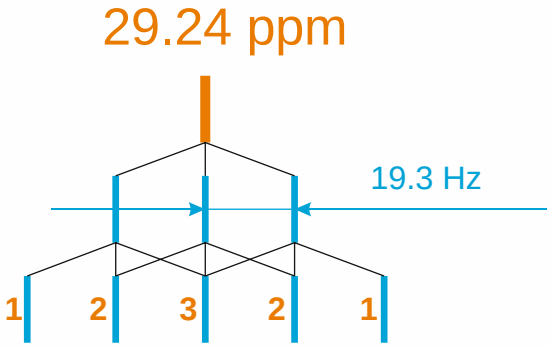
0.002%

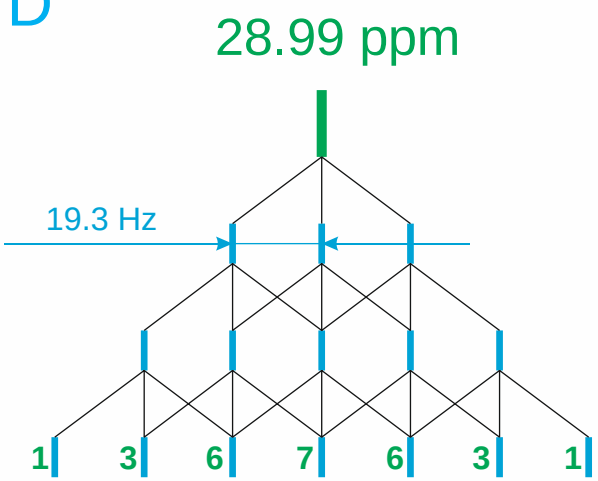


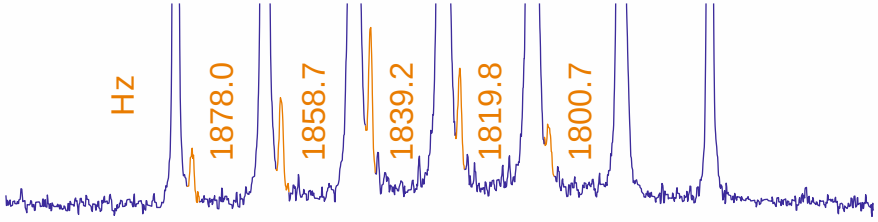
0,998%

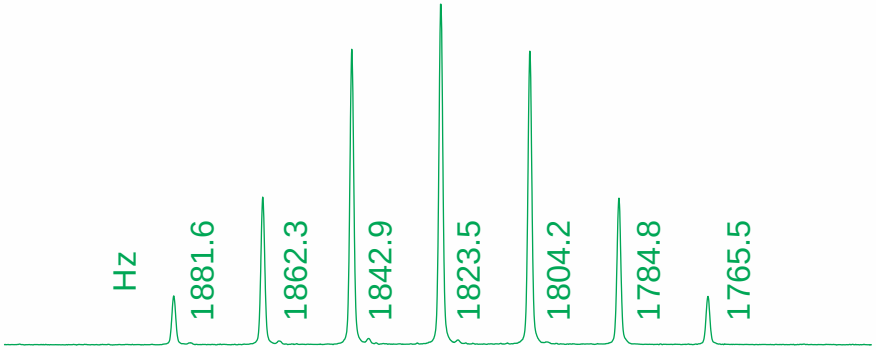
note the deuterium isotope effect of $\Delta\delta$ = 0.25 ppm

(assuming 99.8% deuterium enrichment and 1% of ^{13}C natural abundance)

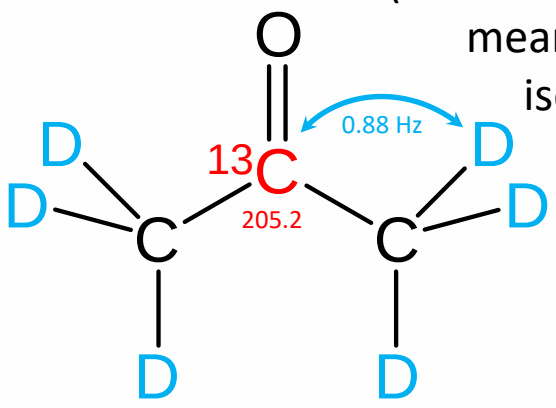




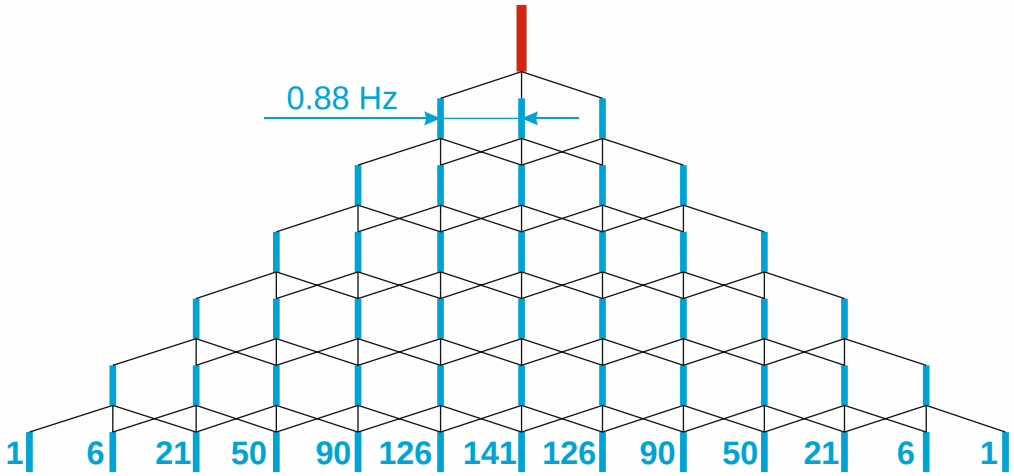




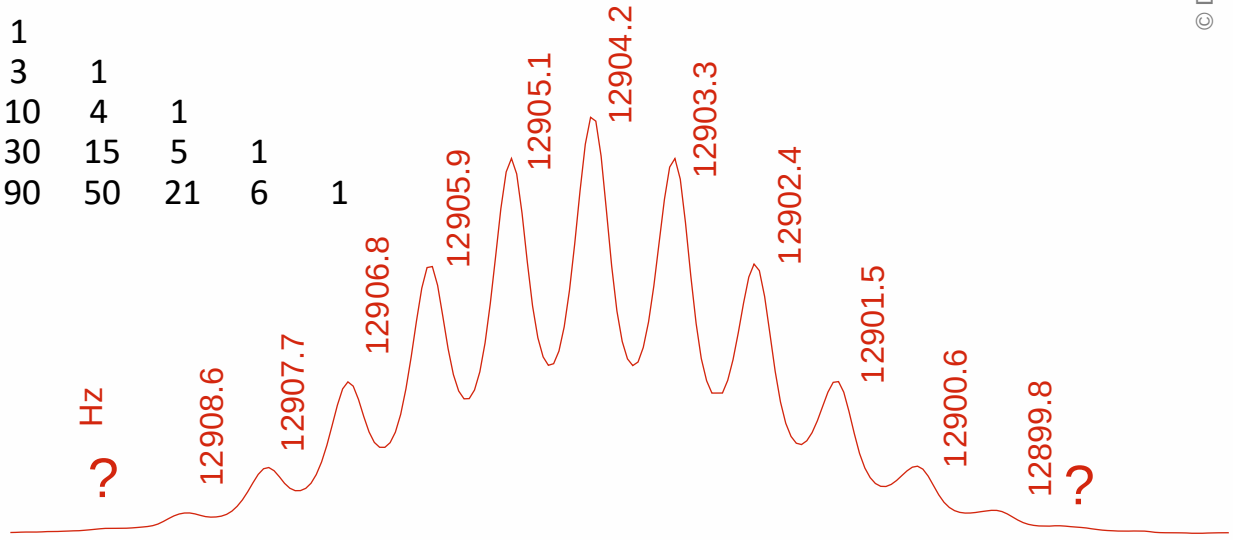
(C without superscript means the ^{12}C isotope)



205.2 ppm

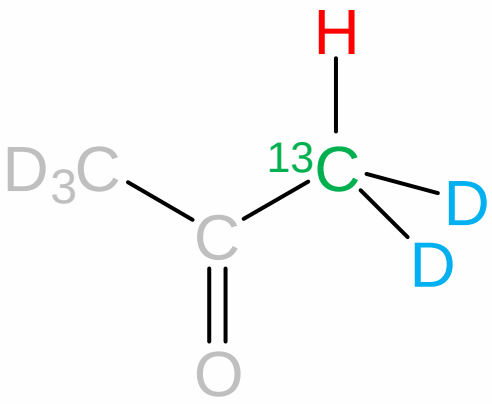


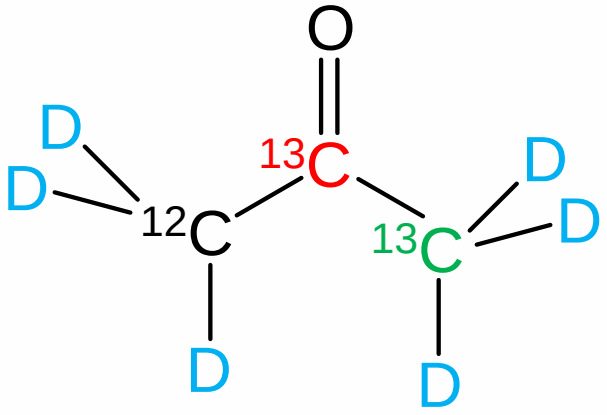
						1						
					1	1	1					
				1	2	3	2	1				
			1	3	6	7	6	3	1			
		1	4	10	16	19	16	10	4	1		
	1	5	15	30	45	51	45	30	15	5	1	
1	6	21	50	90	126	141	126	90	50	21	6	1



One additional week of measuring time would show the peaks labelled with ? …

And how about the signals of the red labelled atoms in these isotopologues?





It‘s only a question of measuring time and the amount of impurities.

Due to the impurities the exact evaluation of the satellites requires some imagination.