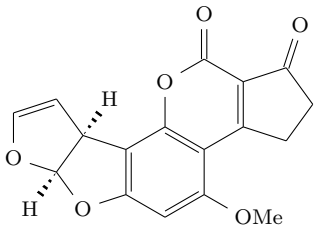
4 Determining Stereochemistry

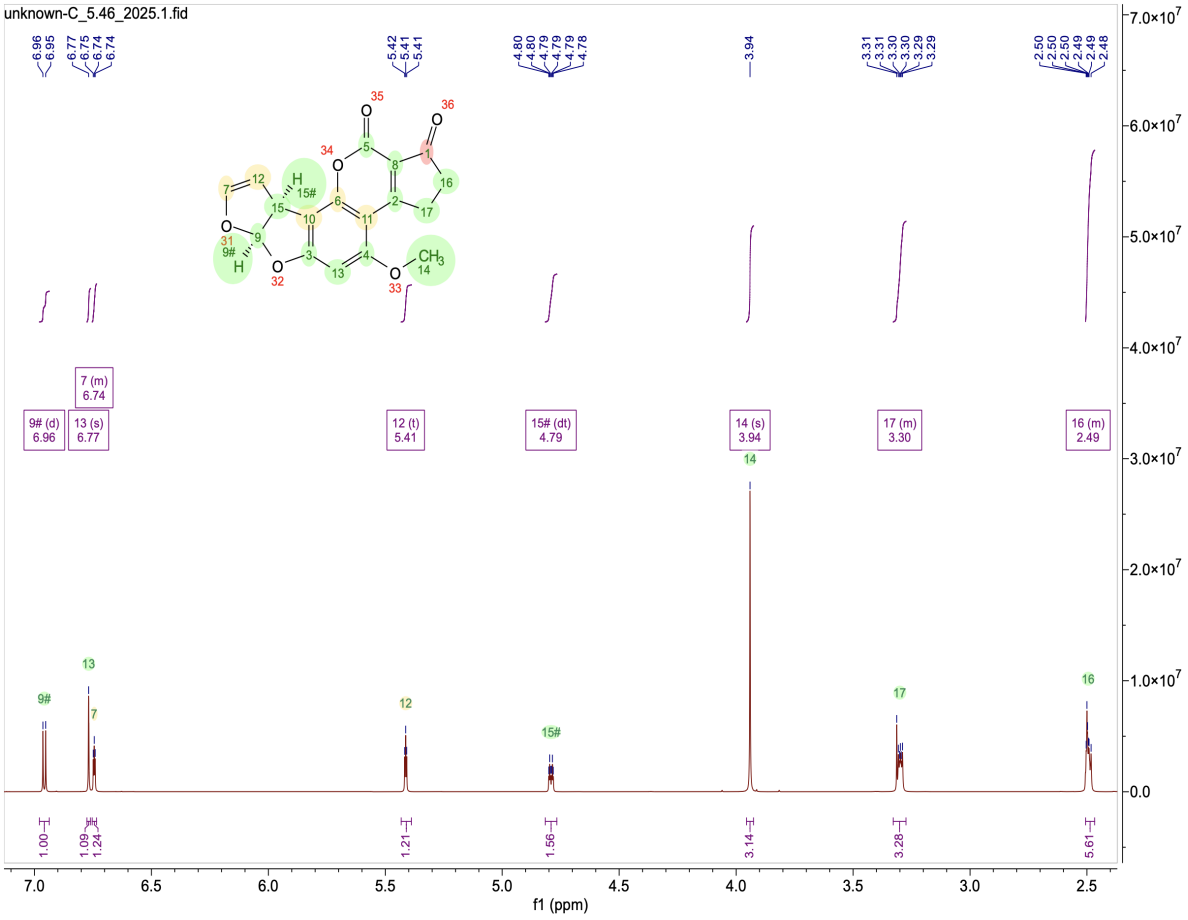
3/18: Aflatoxin B1 is a toxin produced by a fungus which grows on a number of plant species, but is best known for causing liver carcinogenicity from contaminated peanuts.

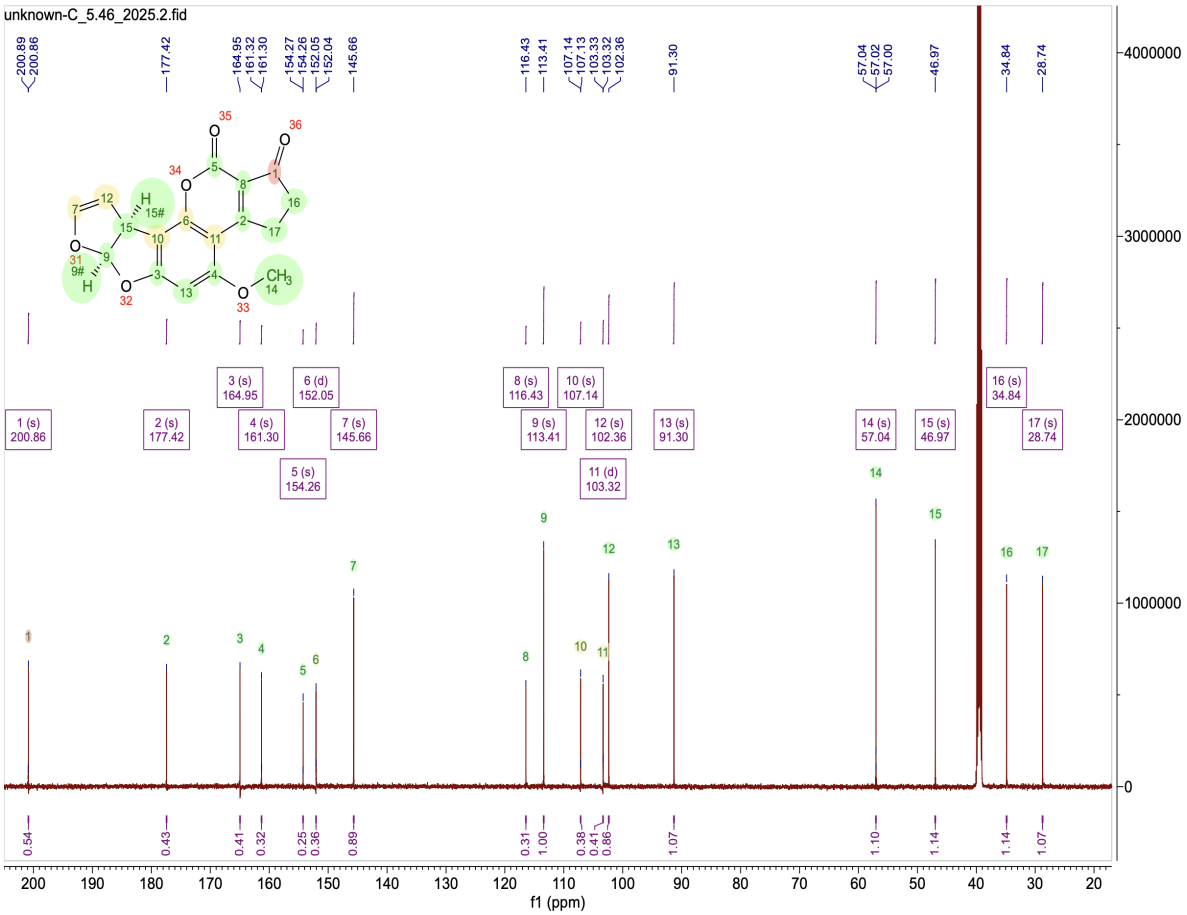


The `unknown-C_5.46_2025` dataset contains a series of spectra which you should be able to identify (if this is untrue, let me know and I'll send out a list). For this exercise, I'd like you to identify the ROESY crosspeaks in experiment #9 and the NOESY crosspeaks in #37 as follows.

1. Assign all the protons in the molecule using the standard ^{13}C-directed approach.

Answer.

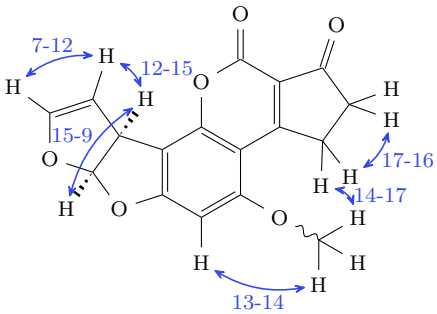




□

2. Show the ROE/NOE crosspeaks on the structure of Aflatoxin B1 and explain whether any are missing that you would expect.

Answer.



Some cross peaks are small, but all the ones I expect to see are distinguishable from noise at some level of zoom on both spectra. The 14-17 crosspeak is the hardest to distinguish on both spectra. □

3. Confirm the stereochemistry of the bridged ring.

Answer. Since we can observe a significant 15-9 NOESY, the saturated bridgehead carbons on the western fragment of Aflatoxin B1 must bear two *cis* protons. Without a chiral resolving reagent, it is impossible to determine the absolute stereochemistry of the molecule. □

4. Experiment #13 shows a ^{1}H-^{13}C HSQC in which the decoupling is turned off during acquisition; indicate on the structure which proton-carbon couplings are larger than usual and explain why you think this is.

Answer. To begin, here is an accounting of all $^{1}J_{\mathrm{CH}}$ coupling constants in the visible in the coupled HSQC spectrum.

Proton #	**Shift (ppm)**	$^{\mathbf{1}}\boldsymbol{J}_{\mathbf{CH}}$ **(Hz)**
9	6.96	188.41
13	6.77	167.62
7	6.74	202.33
12	5.41	181.30
15	4.79	146.88
14	3.94	146.80
17	3.30	139.69
16	2.49	132.41

The largest proton-carbon coupling constant corresponds to an sp^2-hybridized carbon-proton bond, as we might expect since increasing s-character means shorter bonds and more coupling. However, with all of the strain in this molecule, it is very difficult to qualitatively predict the magnitude of the $^{1}J_{\mathrm{CH}}$ couplings. □