



Department of Chemistry
NMR Facilities
Director: Dr. Carlos A. Steren

NMR NEWS

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* To find tutorials, links and more, visit our website
www.chem.utk.edu/facilities/nmr

*** Computers and software updates**

Computer and software were updated on 3 of our spectrometers.

Varian 400 MHz: A new HP Computer with VNMRJ 3.2 was installed.

Varian 600 MHz: A new HP Computer with VNMRJ 4.0 was installed.

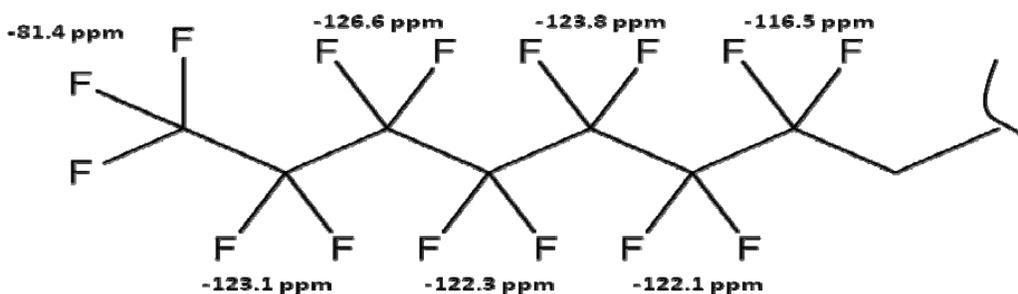
Varian 500 MHz: The VNMRJ software in this instrument was updated to version 3.2.

*** ^{19}F NMR Spectroscopy**

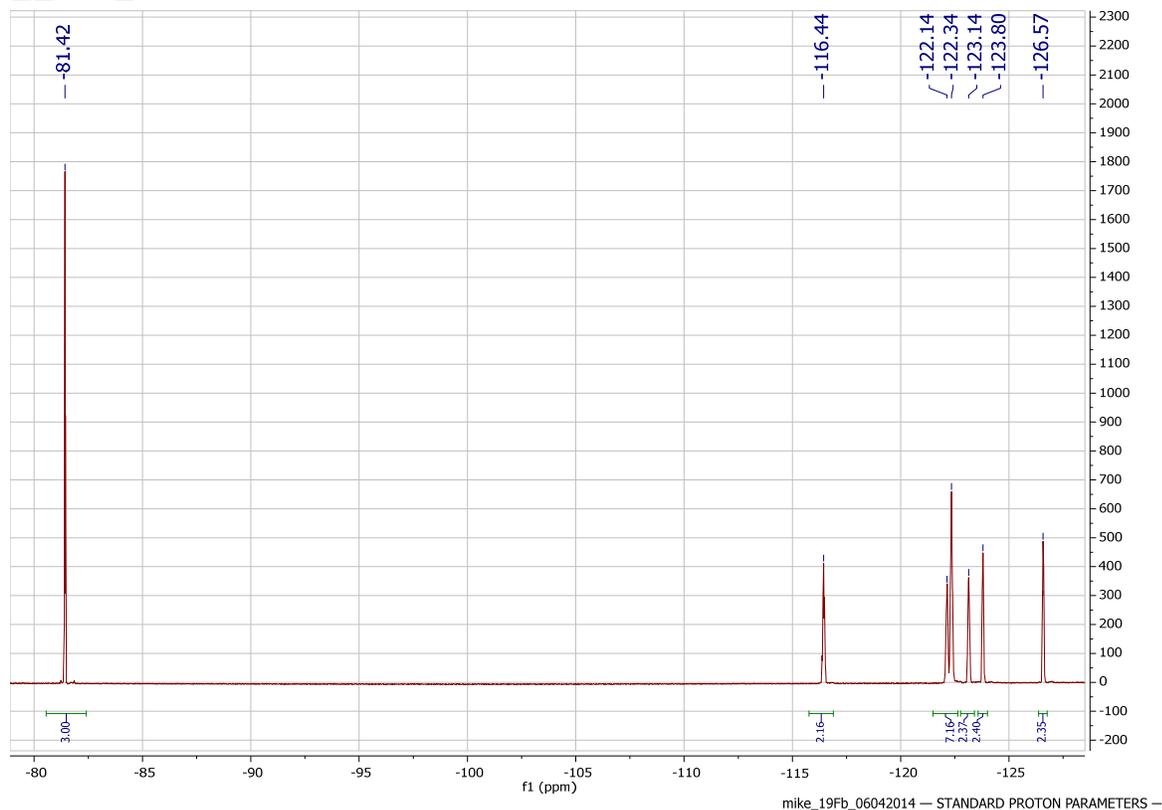
Fluorine (^{19}F) NMR is somewhat similar to proton (^1H) NMR. Both nuclei have similar resonance frequencies and natural abundance close to 100%. What is quite different though, is the chemical shift range, ~1000 ppm for ^{19}F and ~20 ppm for ^1H . However, a smaller SW can be used, if the ^{19}F NMR lines are grouped in a narrower region, like in the example shown below.

1D- ^{19}F NMR experiments are available on our Varian 300 and Varian 500 NMRs. Two dimensional (2D) homonuclear (^{19}F - ^{19}F) and heteronuclear (^{19}F - ^{13}C or ^{15}N) experiments are available on the Varian 500 MHz spectrometer. This includes ^{19}F -gCOSY, ^{19}F - ^{13}C -HMQC, ^{19}F - ^{13}C -HMBC and ^{19}F - ^{15}N -HMBC.

In the following example, ^{19}F -gCOSY and ^{19}F - ^{13}C -HMQC spectra were used to assign a CF_3 -(CF_2) $_6$ -... chain.

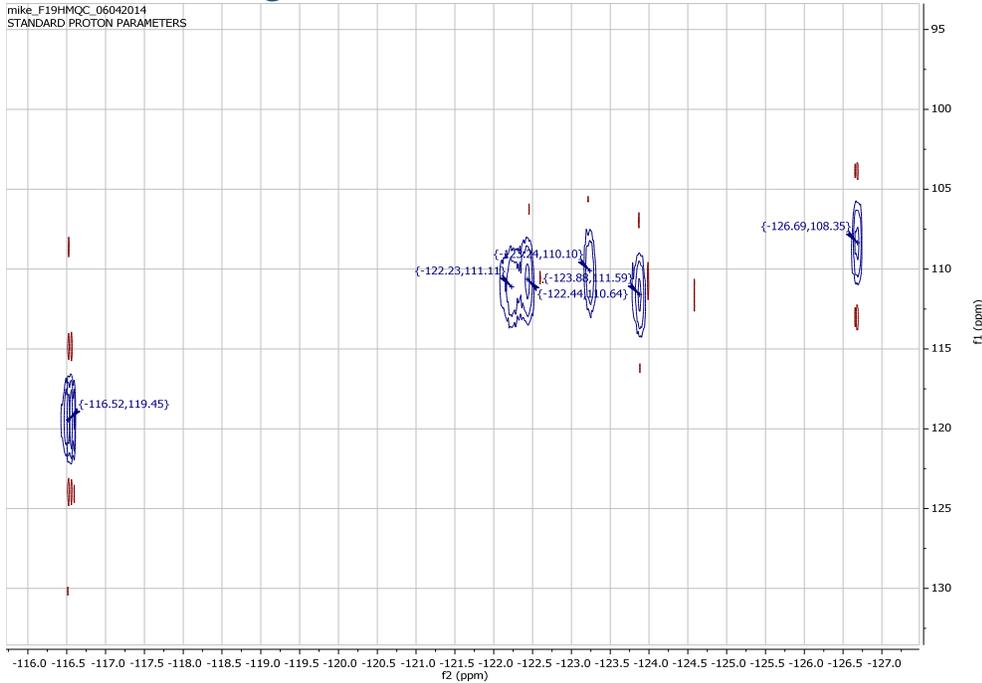


1D- ^{19}F

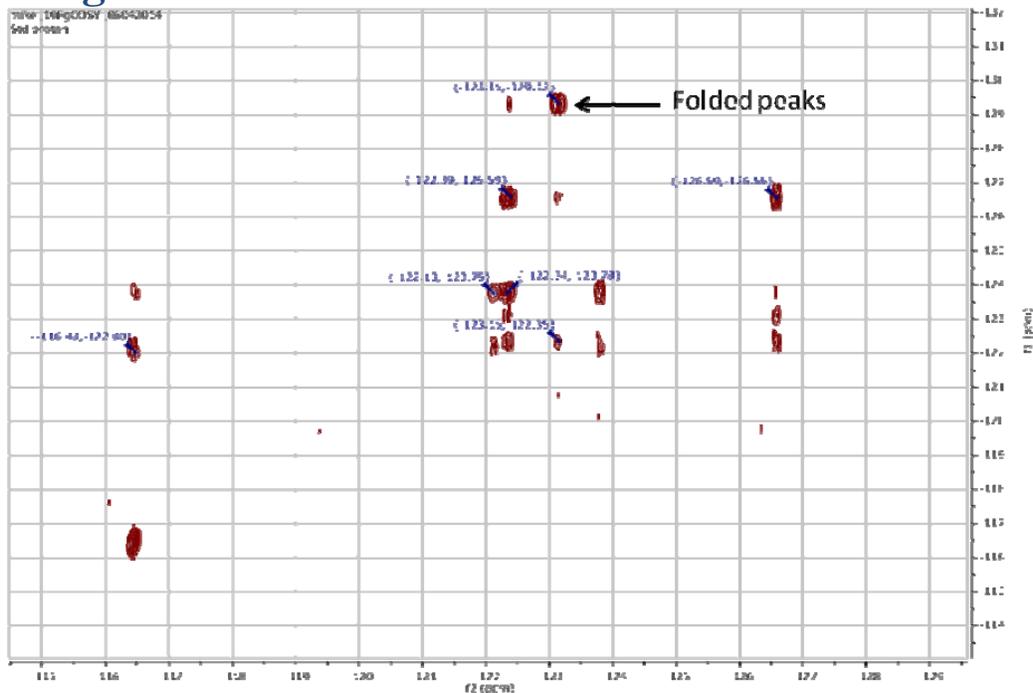


The HMQC and COSY spectra were acquired with a SW=20ppm for ^{19}F and centered at -123ppm.

^{19}F - ^{13}C -HMQC



^{19}F -gCOSY



The folded cross peaks are due to the ^{19}F line at -81.4ppm that falls outside the spectral window.

* Quantitative NMR

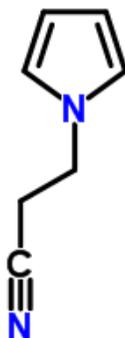
It is important to understand that the 1D-¹H (proton) and 1D-¹³C (carbon) experiments with the standard parameters, available in the spectrometers, **are not quantitative** experiments.

For the case of 1D-¹H, a quantitative spectrum requires that in the experiment, all the proton spins of the sample relax to thermal (Boltzmann) equilibrium before the next scan. This, in turn, depends on the spin-lattice relaxation times (T_1) of the protons that is different for different protons in the molecule. To fulfill this requirement, for a 90° pulse experiment, the time between successive scans (d_1) must be at least $5 * \max(T_1)$.

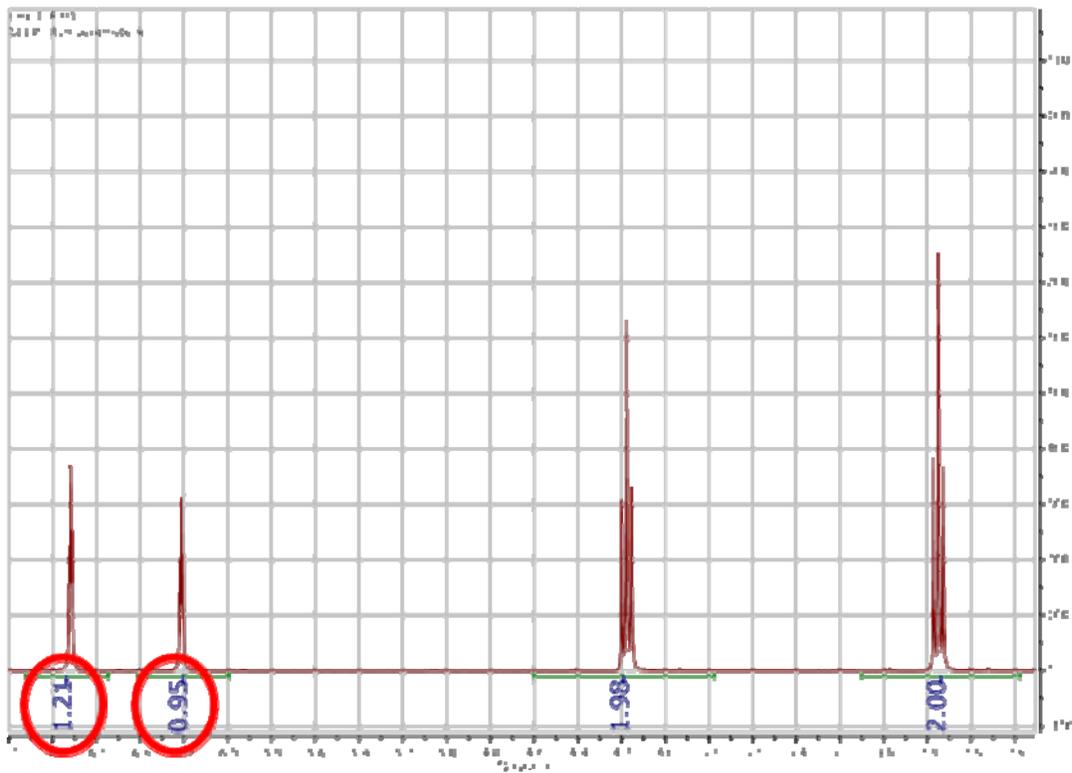
The 1D-¹H experiments in our spectrometers, with a pulse of 30° or 45° and a $d_1=1s$, are not quantitative but allow to count protons in most cases. However, one must be aware that this is not always true.

In the following example, it is shown a 1D-¹H spectrum acquired with $d_1 = 1s$ where the integrals do not match the number of protons in the ring of the molecule.

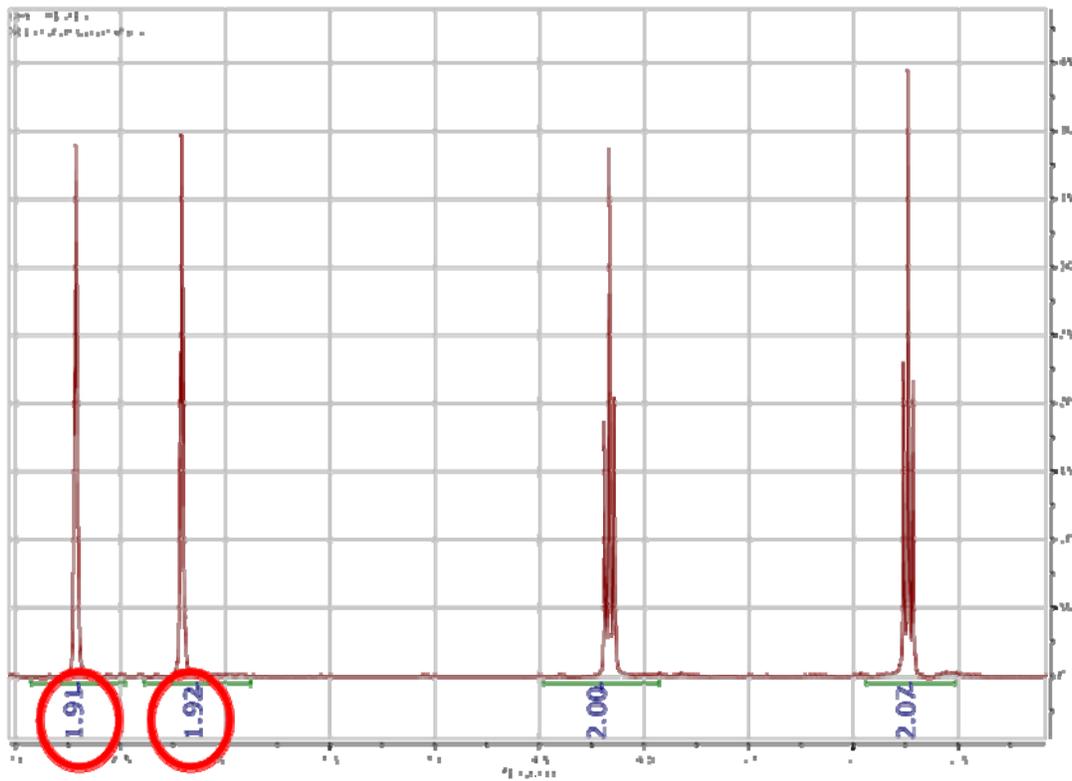
pyrrole-1-propionitrile



D1=1s

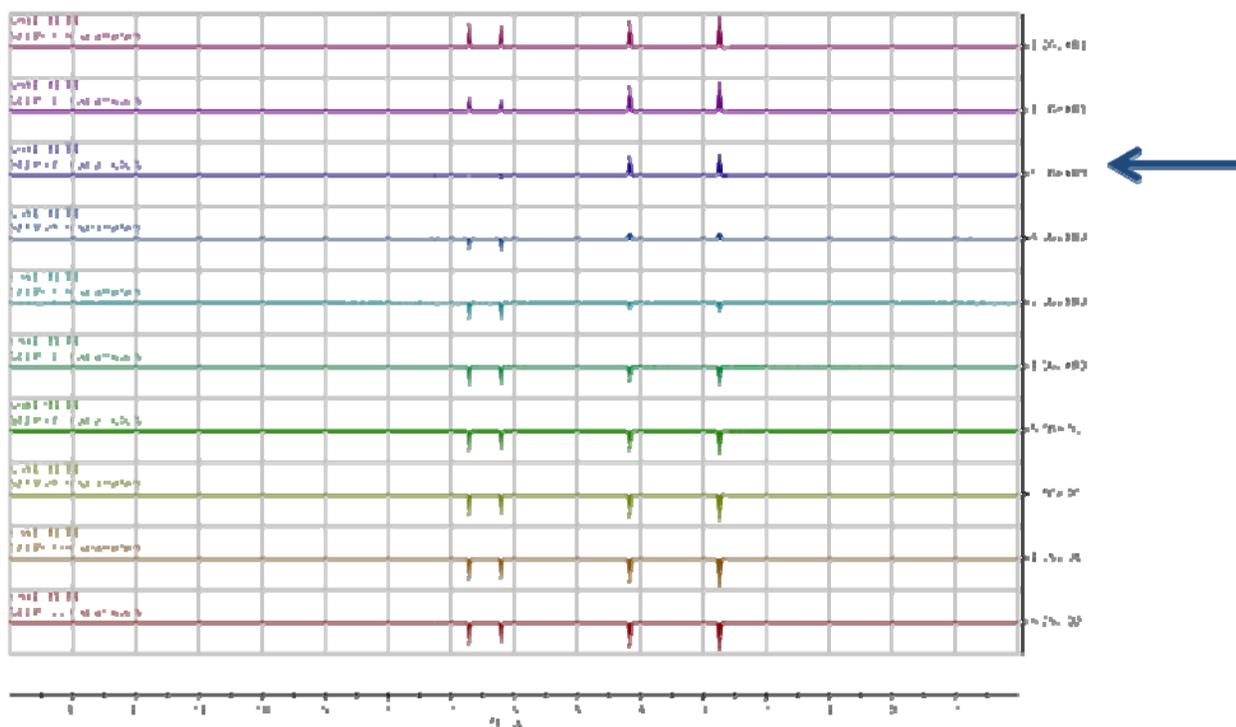


D1=30s



The Inversion-recovery experiment allows to measure the T_1 constants for the proton spins of the molecule.

$T_1 \cong d_2_null / 0.69 = 8\text{sec} / 0.69 = 11.6\text{sec}$. Thus, d_1 can be set to the right value, $d_1 > 58\text{ sec}$, in order to acquire a quantitative spectrum.



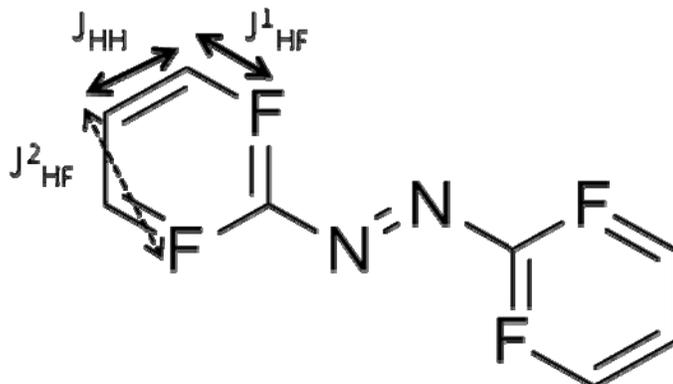
1D-CARBON experiment is not a one pulse experiment like the 1D- ^1H . The carbon experiment is a double resonance experiment where ^{13}C and ^1H spins are both irradiated. Hence, the 1D- ^{13}C spectrum **is not quantitative**.

The carbon experiment that yields a quantitative spectrum is the **Inverse Gated ^{13}C experiment**. Still, in this case, d_1 must be adjusted depending on the T_1 values of the ^{13}C spins in the sample.

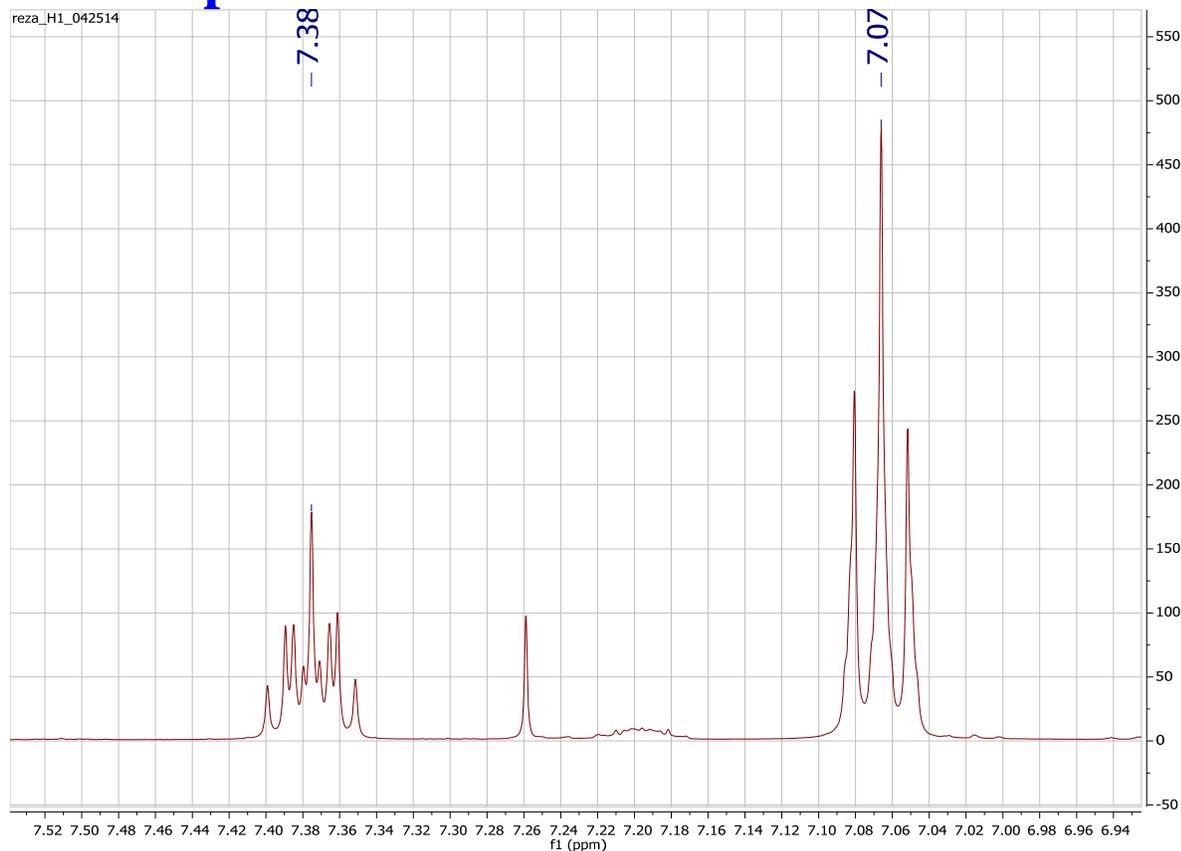
Contact us if you need further assistance with quantitative experiments.

* 2D-J Resolved ^1H NMR Spectroscopy

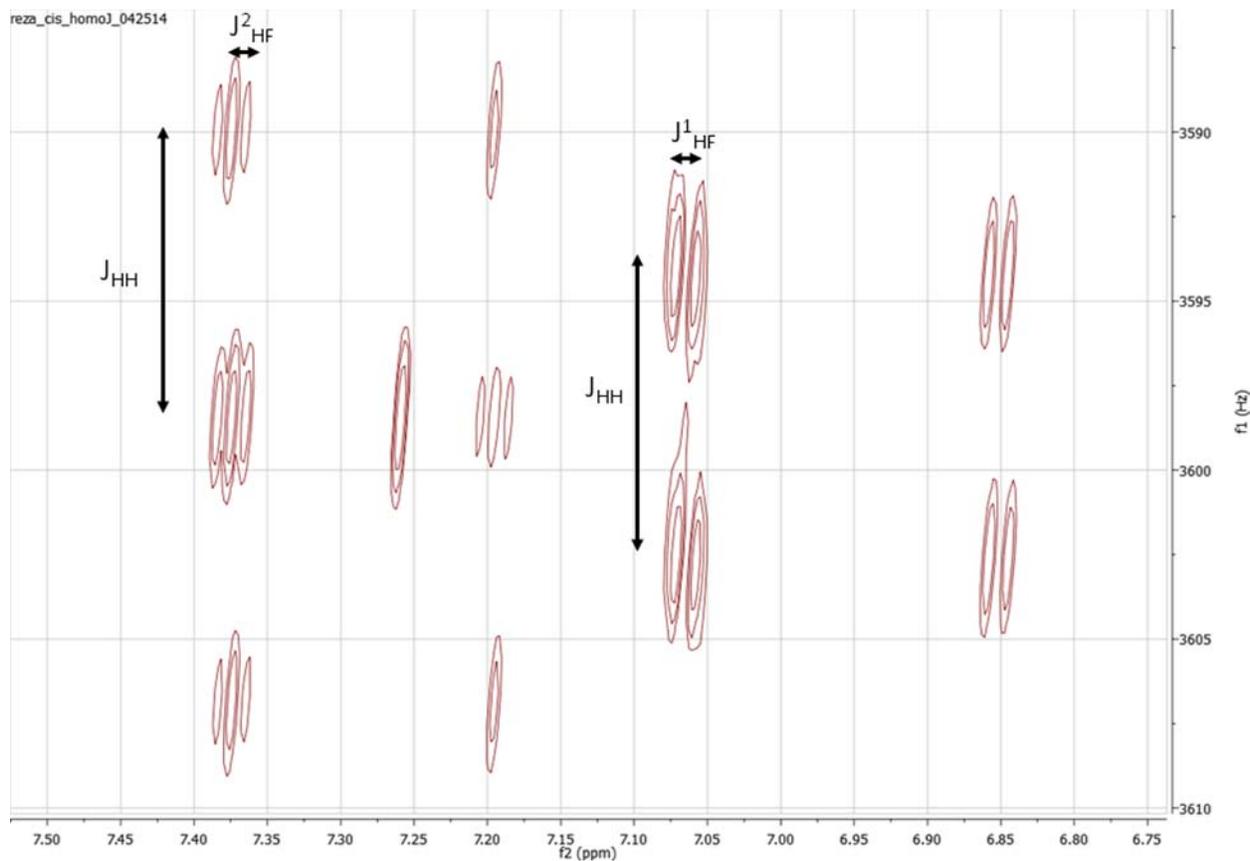
Splitting patterns of ^1H lines involving couplings to ^{19}F nuclei were solved by 2D-J Resolved Spectroscopy. The complex 2,2',6,6'-tetrafluoroazobenzene is under study in Dr. Compton's group.



1D- ^1H spectrum



2D-J Resolved ^1H spectrum



The experiment decouples the homonuclear $J_{\text{HH}}=8.5$ Hz and heteronuclear $J_{\text{HF}}^1=8.5$ Hz and $J_{\text{HF}}^2=5.9$ Hz couplings. The meta protons (7.07ppm) are doublet of doublets. The para proton (7.38ppm) is a triplet of triplets. These results are the expected ones considering the symmetry of the molecule.