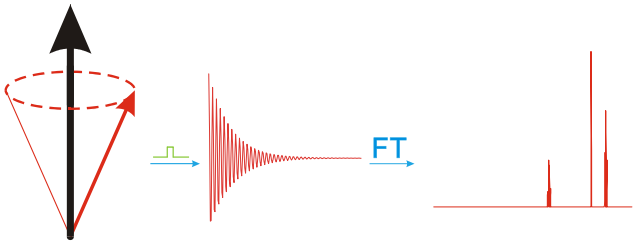
October 15, 2004



ATLANTIC REGION MAGNETIC RESONANCE CENTRE

Get Excited – But Be Selective

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NMR Operator, The ARMRC

Over the past year, I have observed the ARMRC users record more and more 2D spectra to characterize their organic, organometallic, and inorganic coordination compounds. Modern NMR spectrometers like our **AVANCE 500** make such 2D experiments fast and routine. In most cases these 2D techniques in conjunction with the higher resolution 1D experiments allow the users to fully characterize their molecules. However, I have observed a growing number of circumstances where the assignments remain ambiguous for a variety of reasons. Selective excitation experiments have proven to be indispensable tools to assist the users to fully characterize their molecules.

One example where 1D selective excitation type experiments have proved valuable is shown in Figure 1. The sample came from the Jakeman lab, and consists of a valine derivative produced by bacteria. The natural product is a minor component in the solution and many of its signals are obscured by other components, as shown in the middle trace, a routine ^{1}H-NMR spectrum. When **9** is excited (see bottom trace) in a 1D-selective TOCSY experiment, we see signals from **10** and the otherwise completely obscured **11**. Similarly, when we excite the **α** proton (in the upper trace), we see the **β** and **γ** protons as well as the **3a** proton. The comparable 2D-TOCSY spectrum was dominated by the major components in the solution; the correlations due to the valine derivative were completely obscured.

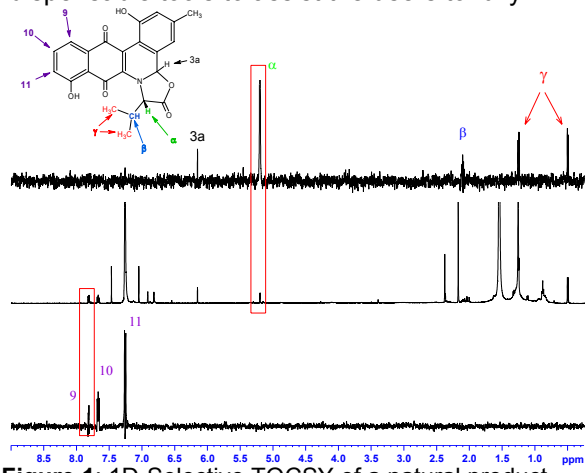

Figure 1: 1D-Selective TOCSY of a natural product mixture. Red boxes highlight the selective excitations.

Other common 1D-selective excitation experiments available to you include 1D-NOE and 1D-COSY.

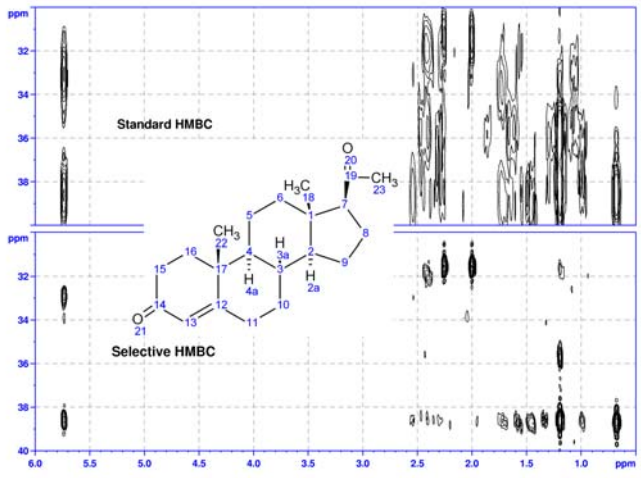

Figure 2: HMBC Spectra of progesterone.

The 2D-selective HMBC experiment can be a very powerful tool when dealing with large molecules having fairly congested ^{13}C-NMR spectra. Figure 2 shows two HMBC spectra of progesterone. The top spectrum is a standard HMBC experiment, zoomed on the region from 30-40ppm in the ^{13}C-dimension. This experiment is designed to cover the entire ^{13}C spectrum (>200ppm); to achieve high digital resolution requires a very long total experiment time.

In a selective-HMBC, only a narrow band in the F1-dimension is selected. Much higher digital resolution can be obtained in a relatively short period of time because we are focussing only on a narrow region of interest. The lower spectrum in Figure 2 shows the selective-HMBC experiment. Clearly the signals are much better resolved.

In general, the selective experiments are not well suited for automation, and so are not set up to run in ICON-NMR. The Bruker interface called “butselnmr” greatly simplifies the selective 1D-NMR experiments, so if you are interested in learning how to do these experiments, please contact the ARMRC.