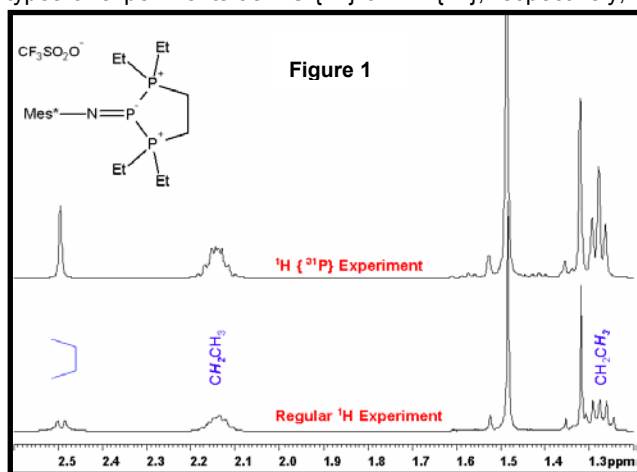


## ATLANTIC REGION MAGNETIC RESONANCE CENTRE

## Heteronuclear Decoupling – “Using It and Losing It”

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When we think about decoupling in NMR spectroscopy and how it is used, most of us immediately think about observing some heteronucleus such as  $^{13}\text{C}$  or  $^{31}\text{P}$  and using proton decoupling to simplify the observed spectrum. NMR spectroscopists refer to these types of experiments as  $^{13}\text{C}\{^1\text{H}\}$  or  $^{31}\text{P}\{^1\text{H}\}$ , respectively, where the nucleus within the curly braces is the one being decoupled. What is



not so well known is that today's modern spectrometers are capable of routinely performing the *inverse* experiment where we observe protons and decouple the heteronucleus, referred to as  $^1\text{H}\{^{13}\text{C}\}$  or  $^1\text{H}\{^{31}\text{P}\}$ . Broadband heteronuclear decoupling is generally more demanding than  $^1\text{H}$  decoupling since the chemical shift ranges (and therefore the decoupling bandwidths) are larger, requiring either more power or more efficient decoupling schemes for complete decoupling. To elaborate, a typical  $^1\text{H}$  chemical shift range of 10 ppm on a 500 MHz instrument corresponds to a decoupling bandwidth of 5 kHz for  $^{13}\text{C}\{^1\text{H}\}$  experiments whereas a 200 ppm  $^{13}\text{C}$  chemical shift range on this same 500 MHz instrument would require a decoupling bandwidth of over 25 kHz for  $^1\text{H}\{^{13}\text{C}\}$  experiments. Furthermore, as NMR moves to higher and higher external magnetic field strengths, the required decoupling bandwidths get bigger and bigger, necessitating the use of advanced decoupling schemes such as adiabatic decoupling. To illustrate, I recently performed a simple  $^1\text{H}\{^{31}\text{P}\}$  experiment for a sample from the Burford lab. The bottom spectrum in Figure 1 is the regular  $^1\text{H}$  spectrum and the top trace is the  $^1\text{H}$  spectrum with  $^{31}\text{P}$  GARP decoupling. The figure clearly shows simplification of the  $^1\text{H}$  resonances for the ethyl groups as well as the ring

methylene protons. The spectra were obtained on our Bruker AVANCE 500 MHz instrument using a 5mm BBO probe. The experiment needs “tweaking” by first observing the spectrum of the heteronucleus, allowing proper placement of the decoupler frequency as well as a suitable choice for the decoupler  $\pi/2$  pulse width, depending upon the decoupler bandwidth requirements. One must also be cognisant of minimizing sample heating when performing these and similar experiments by minimizing the decoupler duty cycle (*i.e.* use a long relaxation delay and keep the acquisition time as short as possible).

In another example, I recently solved a problem by turning off the heteronuclear decoupling. The HSQC experiment run by default at ARMRC uses gradients to select only those protons that are adjacent to  $^{13}\text{C}$  nuclei. Consequently, the HSQC correlations appear as multiplets with the primary doublet splitting due to one-bond coupling with  $^{13}\text{C}$ ,  $^1J(^{13}\text{C}, ^1\text{H})$ . During the acquisition time, broadband  $^{13}\text{C}$  decoupling is applied collapsing the multiplets into singlets. However, there are times when one wants to know the magnitude of the one-bond coupling and measuring this via the HSQC experiment, without  $^{13}\text{C}$  decoupling, is often more practical than direct carbon observe. Figure 2 shows two HSQC experiments, one with (blue contours) and one without (red contours)  $^{13}\text{C}$  decoupling. The spectra represent expansions of the anomeric region of a polysaccharide sample out of Bruce Grindley's lab. The value of  $^1J(^{13}\text{C}, ^1\text{H})$  for the anomeric protons is a critical parameter in polysaccharide structure determination as it is diagnostic of the configuration of the glycosidic linkages (*i.e.* " or \$). Measuring  $^1J(^{13}\text{C}, ^1\text{H})$  via  $^{13}\text{C}$  observe would have been impossible in this case as the quantity of sample was extremely low. When running these experiments, you may wish to increase the number of scans to compensate for the loss of intensity due to the observation of multiplets rather than singlets. Also, make sure the digital resolution in F2 is sufficient to characterize the  $J$ -values or the differences in  $J$ -values you're measuring.

