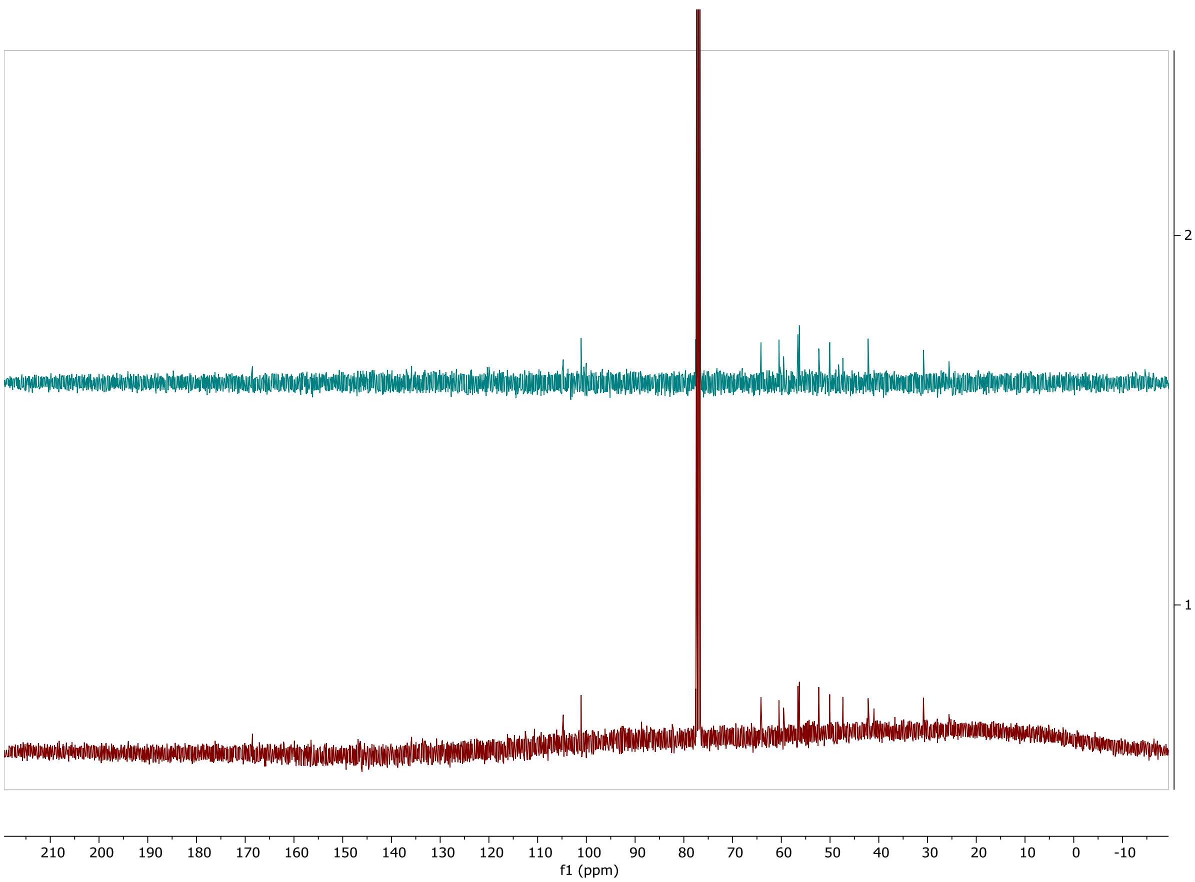
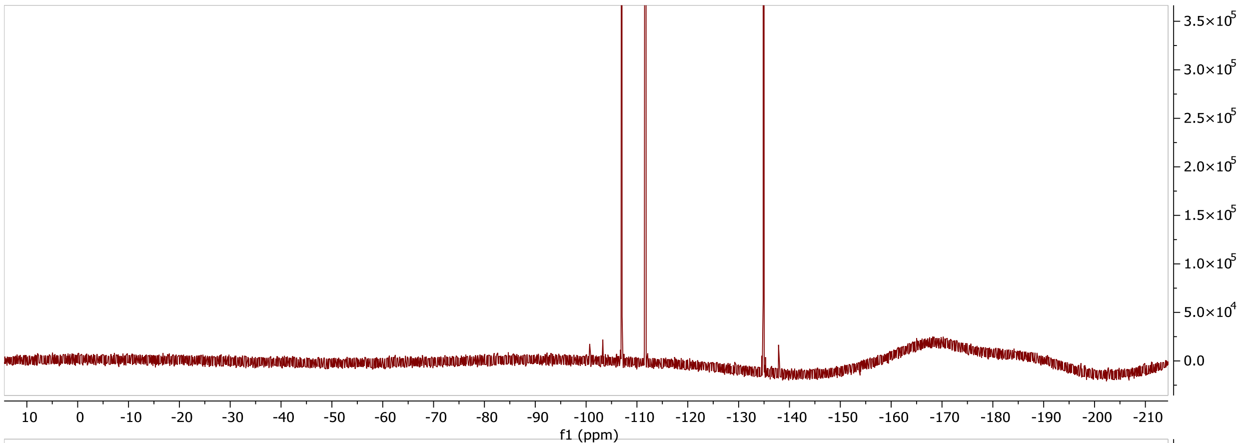
Double-echo filtering

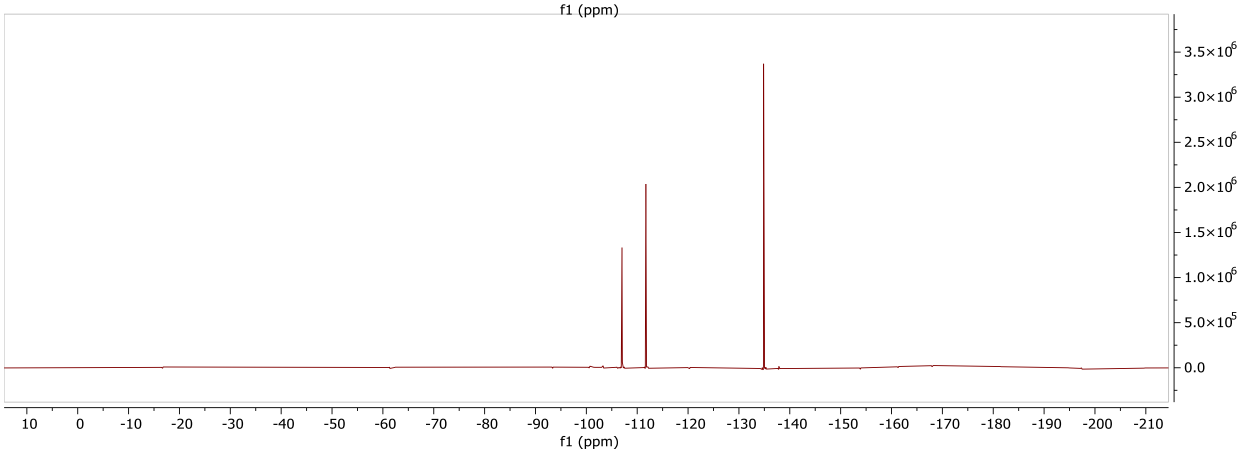
There is an inverse relationship between the duration of the time domain signal and the width of the peak in the frequency domain: FIDs that decay quickly give rise to broad peaks. Conversely, sharp(er) peaks come from long(er)-lasting FIDs. This relationship is the basis of the classic T_2 filter, which attempts to remove quickly decaying components of an FID by using a spin echo sequence. That involves a 180º pulse, and simple (rectangular, or "hard") 180º pulses were commonly used. However these are not particularly broadband, so in cases in which a wide range of frequencies needs to be observed the effectiveness of the 180º pulse can be a limiting factor. Newer "shaped" 180º pulses are much better in this regard, but many suffer from a technicality, which is that while they are very good at inverting magnetization over a wide range of frequencies they are not as good at refocusing (which is what is required for the spin echo). This problem is avoided by using two 180º pulses in a double echo sequence, extending the excellent inversion performance (bandwidth) to refocusing.

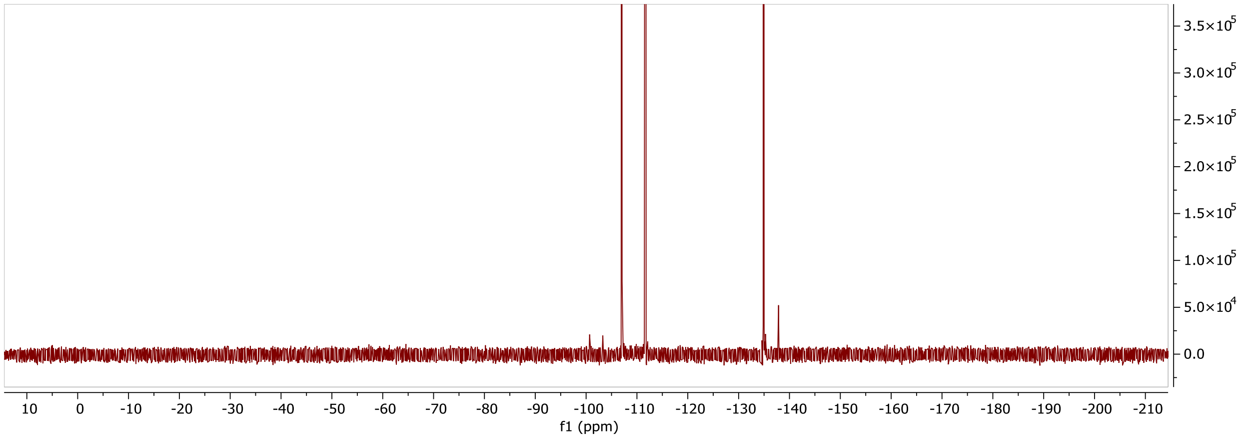
There are two common situations in which this sort of filtering may be required. The more common is probe background: materials used in the construction of the NMR probe may themselves give rise to NMR signals (typically in C13 and/or F19 spectra, arising from fluorocarbon polymers used in the probe). Because the materials are solids their NMR signals are very broad, appearing either as broad humps or just as a "rolling" baseline. An example is seen in the following figure; the bottom spectrum was acquired with the normal 1-pulse method, while the top spectrum is a double-echo spectrum.

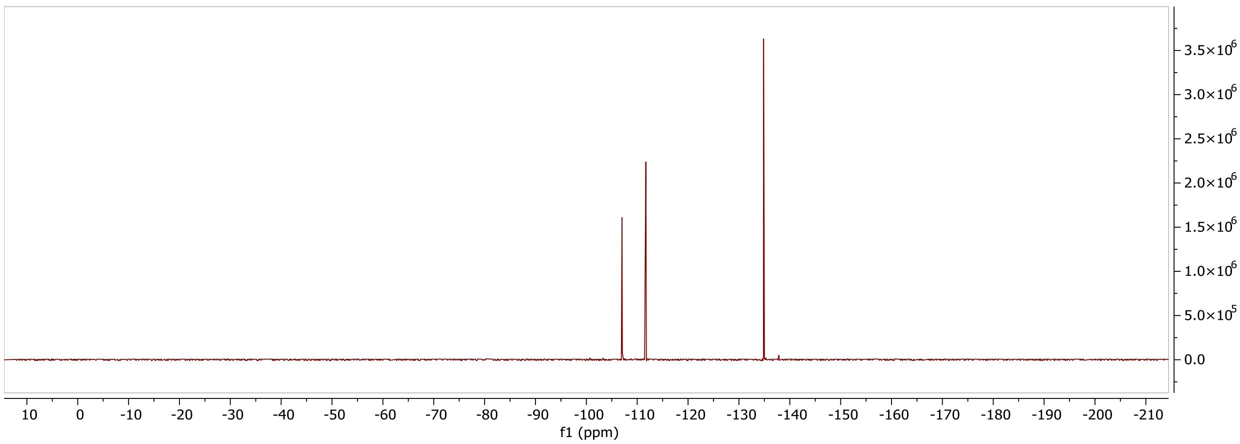


The examples above were for a relatively dilute sample, and are of C13 spectra. The following figures show a similar situation in F19 spectra of a relatively concentrated sample; in both figures the top trace is a 10-fold vertical expansion of the bottom trace.

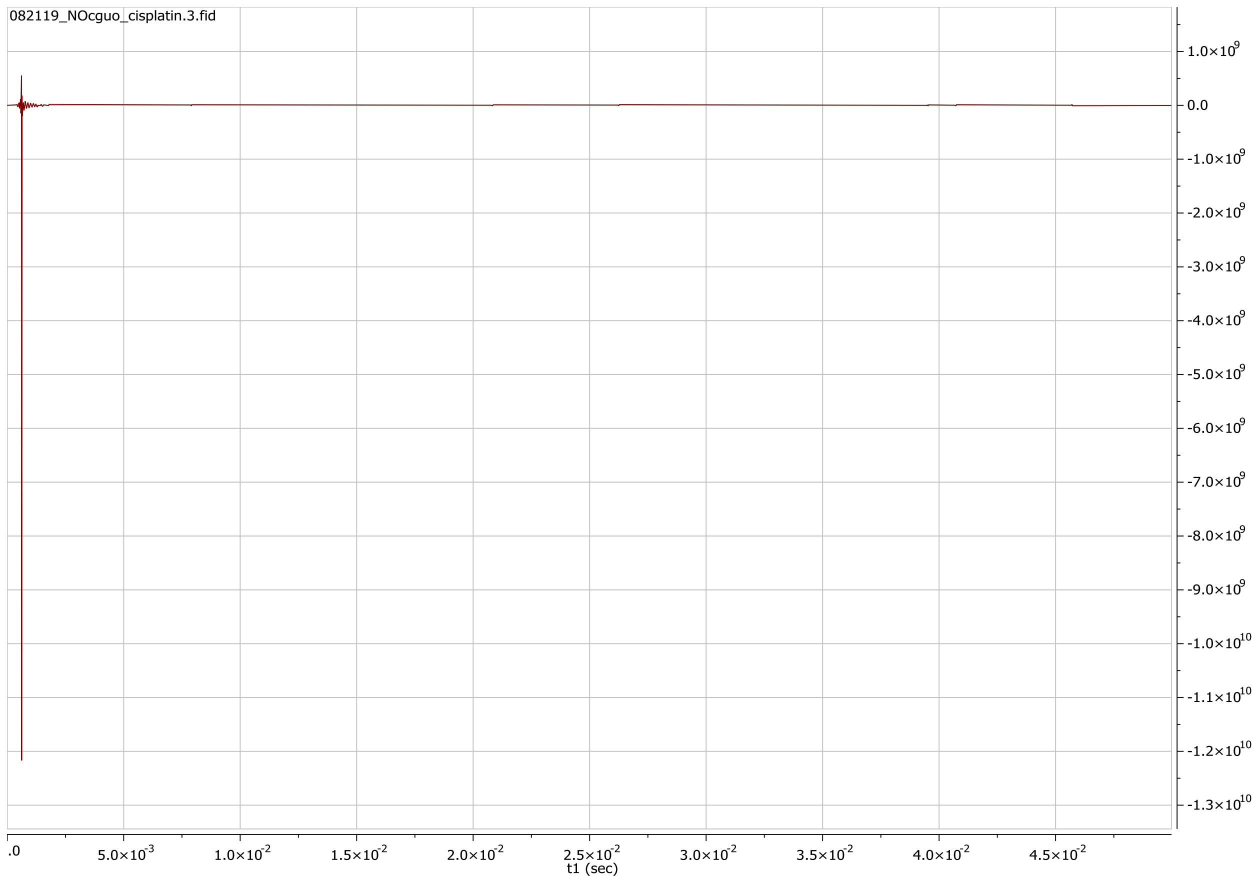


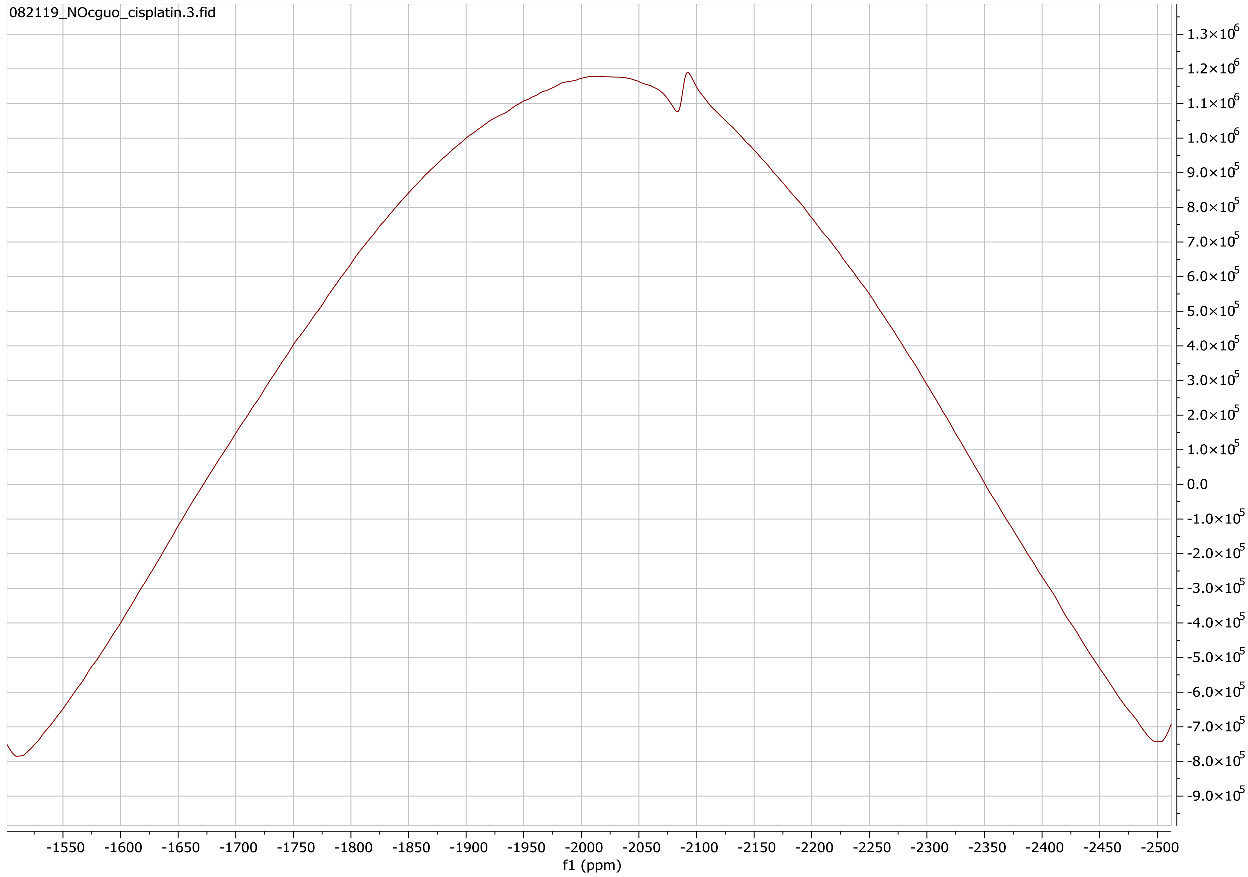






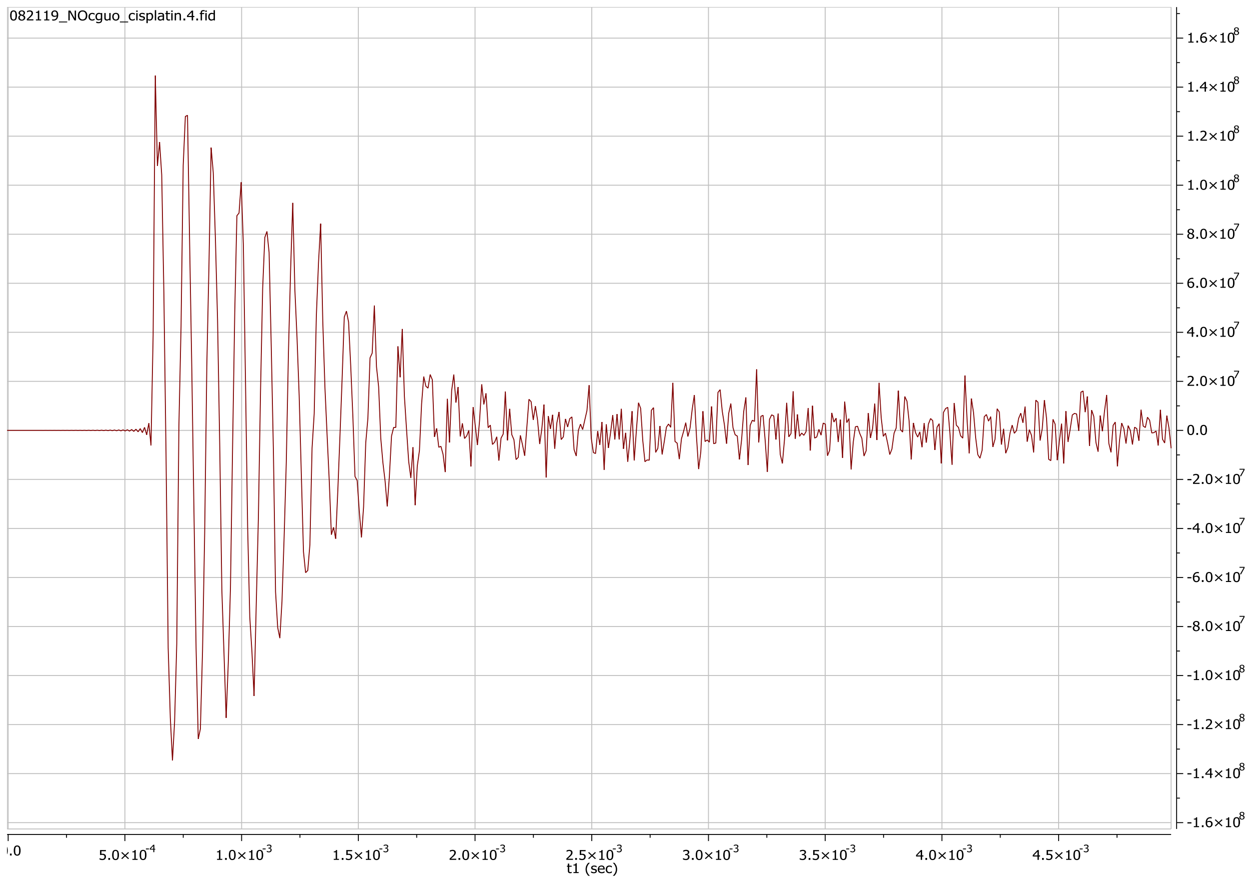
The second situation in which the double echo filter may be useful is the result of so-called "probe ringing" or "pulse breakthrough", in which the "signal" from the excitation pulse- which is typically 100s of volts while the pulse is on- has not completely decayed to zero before the start of acquisition, during which we are typically detecting signals measured in μvolts. An example of an FID that includes residual "signal" from the pulse, and the spectrum resulting from that FID, are shown in the following figures. (Pt195 is being observed.)


082119_NOcguo_cisplatin.3.fid
1.0×10^9
0.0
-1.0×10^9
-2.0×10^9
-3.0×10^9
-4.0×10^9
-5.0×10^9
-6.0×10^9
-7.0×10^9
-8.0×10^9
-9.0×10^9
-1.0×10^10
-1.1×10^10
-1.2×10^10
-1.3×10^10
.0
5.0×10^-3
1.0×10^-2
1.5×10^-2
2.0×10^-2
2.5×10^-2
3.0×10^-2
3.5×10^-2
4.0×10^-2
4.5×10^-2
t1 (sec)

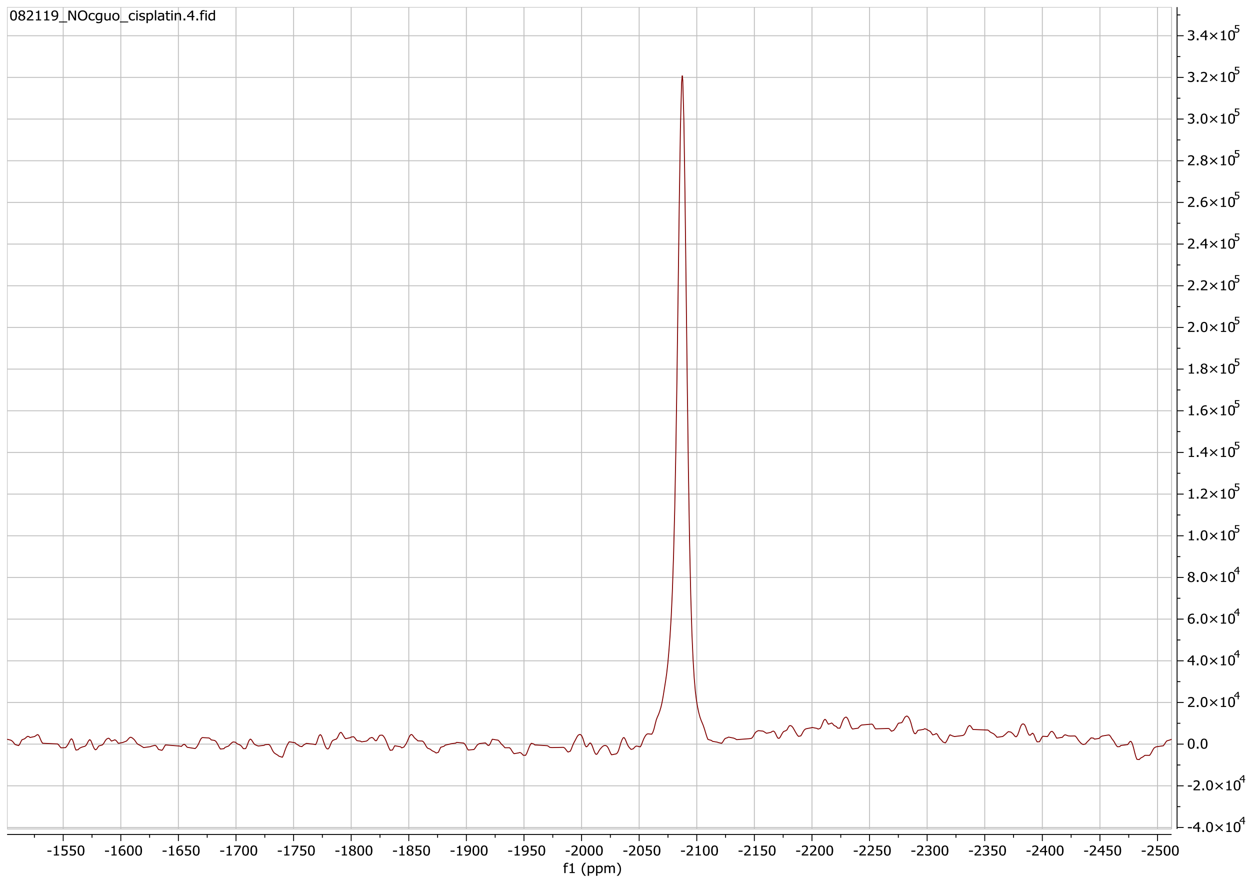


Clearly the spectrum is dominated by the spurious signal (and is very difficult to work with).

Using a double echo filter gives the FID and resultant spectrum shown in the next two figures.



082119_NOcguo_cisplatin.4.fid
1.6×10^8
1.4×10^8
1.2×10^8
1.0×10^8
8.0×10^7
6.0×10^7
4.0×10^7
2.0×10^7
0.0
-2.0×10^7
-4.0×10^7
-6.0×10^7
-8.0×10^7
-1.0×10^8
-1.2×10^8
-1.4×10^8
-1.6×10^8
0.0
5.0×10^-4
1.0×10^-3
1.5×10^-3
2.0×10^-3
2.5×10^-3
3.0×10^-3
3.5×10^-3
4.0×10^-3
4.5×10^-3
t1 (sec)



It is worth emphasizing that these spectra were acquired one after the other on the same sample.

Apart from the obvious improvement in the baseline there is a more subtle advantage that results from eliminating a strong interfering signal: when that signal is present it limits the available receiver gain, which means that the smaller signals of interest are not as effectively digitized. Removing the strong unwanted signal allows use of a higher receiver gain (signal amplification), resulting in better digitization of the signals of interest.

There is one point that needs to be kept in mind when considering the use of the double echo filter: it discriminates on the basis of signal decay (in the time domain), or of peak width (in the frequency domain). Thus if the signal(s) of interest are comparable in width to the spurious signal you wish to eliminate there will be little discrimination between desired and unwanted signals; they will both be reduced in intensity. However it is most often the case that unwanted signals are much broader, as in the examples shown here, in which case the desired removal of the unwanted signal should be possible, possibly requiring just a careful setting of the echo time. In the last case, for example, the "typical" echo time of "a few" milliseconds would result in complete loss of the desired signal, but using just 200 µseconds gave the spectrum shown.