1d TOCSY

In a TOCSY spectrum. magnetization is allowed to pass from one proton to another that is 3 bonds or less away, and to take such steps repeatedly. Thus, magnetization moves from any one proton to all others throughout the spin system of which it is a part. This is a great tool for learning which protons are connected closely.

The selectivity of the TOCSY1D sequence is based on a pair of gradient echoes employing selective inversion pulses that will invert the resonance of interest, so that it is rephrased by the second of each pair of gradients. All other resonances will experience accumulating dephasing by the sum of all four gradients.

Beginning with an experiment containing your beautiful calibrated 1d . . .
Copy the parameters into a second experiment. You will modify the second experiment to make it a 1DTOCSY but you will work in the first one to make your shaped pulse. Considering that you have your beautiful 1d in experiment A (A is a number) move the parameters to experiment b (B is a number) by typing **mp(A, B)**. If you are currently in A at the time you issue this command, you need only type **mp(B)**.

Set up the parameters for a 1D TOCSY
In experiment B,
Convert current parameters to do ....> Selective Excitation Experiments> 1D TOCSY (dpfgse). (**Figure 2**)
You see two spin echoes in which the 180° pulse is selective, and flanked by a pair of equal gradient pulses [1].
You will need to make the selective 180° pulse shape, to invert the resonance which you want to interrogate with respect to connectivity. Currently that pulse has the name q3 [2]. We will need to make our own shape to take the place of q3. For maximum flexibility, this sequence allows us to make two different shapes, but we'll just make one.

Make a shaped inversion pulse (a 180 ° pulse)
Go to experiment A (exp 9 for me) by typing jexpA (jexp9) (**Figure 3**)
Put cursors around a line or spectral region you will use as the source of magnetization [1]. In plain words, you will be asking what other protons are connected to this one by through-bond connections (any number of individual connections of 3 bonds or less). I chose a cluster of lines near 7 ppm because they are isolated in the spectrum.
Go to Edit>New Pulse Shapes (Pbox)
Again chose the 'Make Waveform' tab [2] and click on [New Waveform] [3].
For 'Shape type' choose 'inversion' [4].
For 'Shape name' I like 'iburp' but the current example shows 'g3' [5].

Check that the 'Reference pw90' and 'Reference power' are correct (and change them if need be) [6].
Click on [Select from spectrum] [7] to use your cursors to calculate the Bandwidth [8], pulse length and offset. Click [Add Waveform] [9]. .

Give your pulse a useful name such as 'inv7ppm_21Sep10' [10].
Click [Make It!] [11]
Then click [√] 'Show Z' and simulate [12].
Figure 4 shows the result. Note that the Z-magnetization changes sign from +1 to -1 and then back, but retains full amplitude: clean inversion, with very sharp spectral boundaries.
Close Pbox.

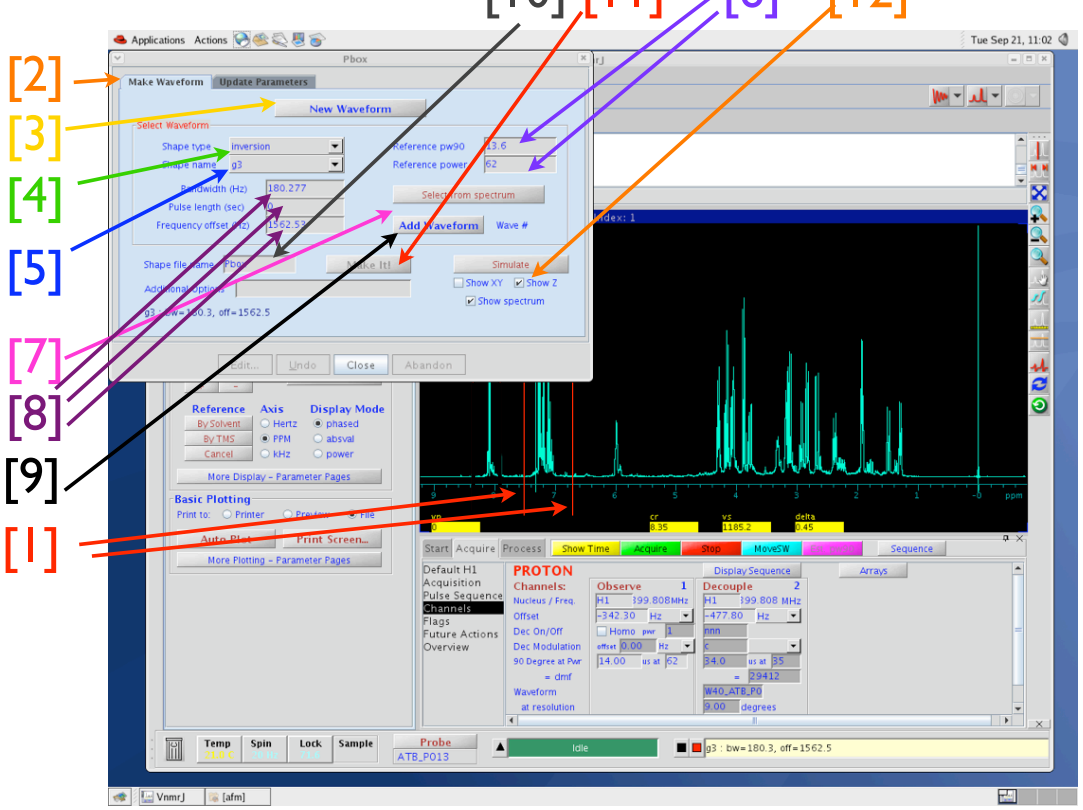
Integrating your new pulse into the 1DTOCSY experiment
Now join the experiment (B) in which you will use the shaped pulse.
BE SURE that this experiment uses identical tof and sw as the one in which you created the pulse. (Check these in Acquire>Channels and Acquire>Acquisition.)
Go to the Acquire>PulseSequence page (**Figure 5**).
Draw down Edit>New Pulse Shapes (Pbox) again and choose the 'Update Parameters' tab in the Pbox window [1]. DO NOT use the 'Set parameter values into experiment' button. If your pulse' name does not appear in the file name box, type it in (retain 'RF' among the options on the right [2]). After entering your pulse's name <return> and the rest of the window should display the duration of your pulse [3], the power required [4] and other characteristics in blue as 'values'. Just use the window as a display panel so you can copy the relevant values into your experiment's. The locations for the first pulse's name, duration (width) and power are [5], [6], [7]. (Check that your numbers are consistent with the units given for the pulse widths.) Here, I am using the same shape for both pulses. Note that the names of the shaped pulses are case-sensitive.
For now, don't touch the gradients or the spin lock. The former are generally very good as provided.
The spin lock may be varied with care. The pi/2 pulse [8] used was calculated from our pw90 and power. I recommend that you try to have $1/(4*(pi/2)) \approx sw$. our sw is ≈ 4000 so we'd like 250 us = 4*pi/2 or a 60 us pi/2 pulse. Varian's default is very close, so we'll leave it.
In Acquire>Acquistion, use the 'Arrays' button and turn off the array in nt (select nt and click 'Unarray') (**Figure 6).**
Leave two values (at least) of mix [1] but do not exceed a mix of .1 s [2]. mix is the time allowed for magnetization to move among protons in the spin system.
Be sure that your lock level is 60 or above [3], because the use of gradients in this experiment will cause repeated loss of lock, from which the spectrometer will have trouble recovering if the lock is not strong.

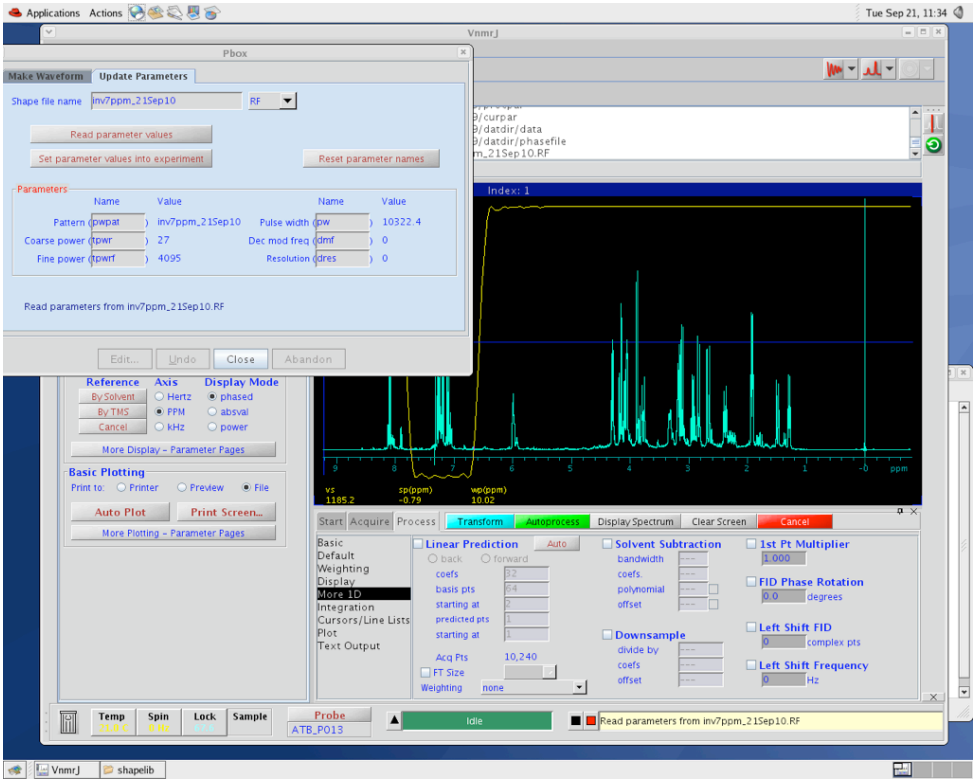
For more fun, array the mixing time, from 0-80 ms (**Figure 7**)
After selective excitation of magnetization near 7 ppm, increasingly long mix times are allowed for the magnetization to migrate to other sites. The time-dependence of

the magnitude of magnetization at another site, such as at 8 ppm, is called the build-up.
We see that aromatic protons can pass magnetization to other aromatic protons via steps of 3 bonds or less (**Figure 8**). To see what the aliphatic protons near 1.4 ppm are connected to, make a new shaped pulse that inverts only them. Using that
For this one I used a shape centered at 1.4 ppm (**Figure 9**).

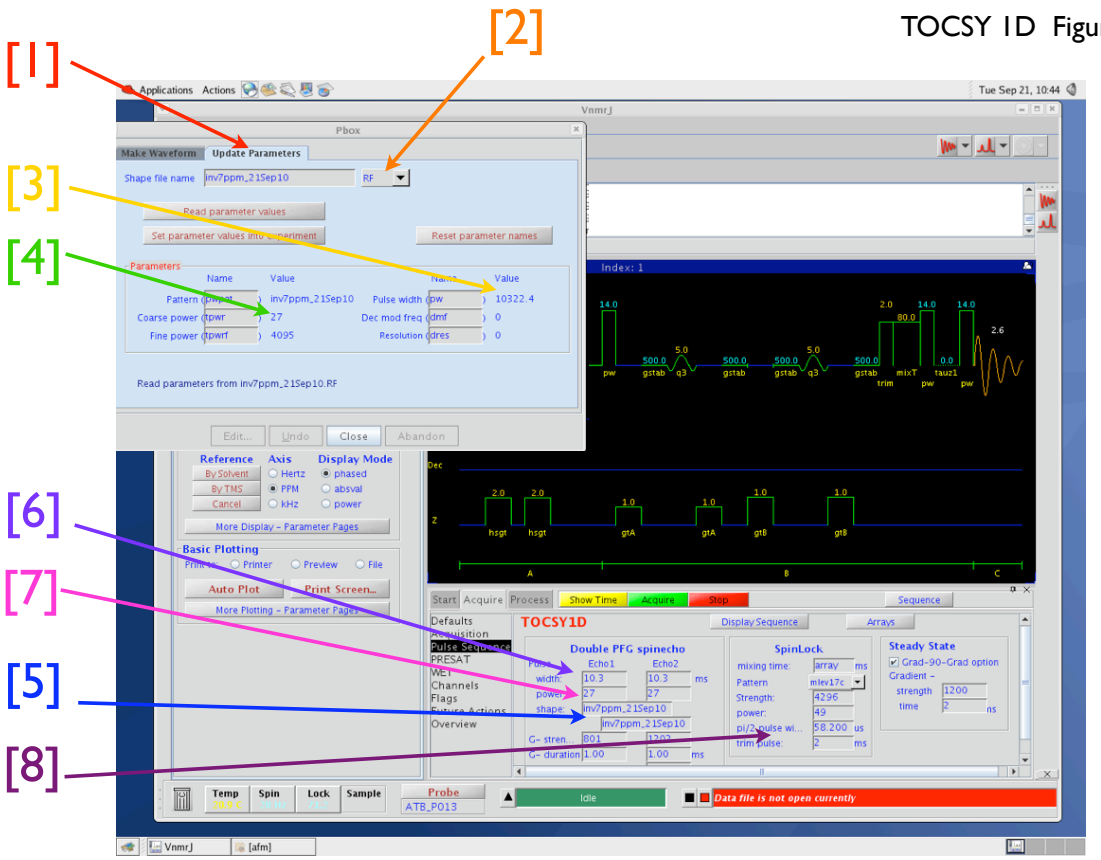
Take your T2 into account in choosing the maximum duration of spin lock (which is often called 'mix'), Take your T_1 into account in choosing d1. For clean results with this sequence, I suggest nt = 8 or multiples thereof.

Selective TOCSY: TOCSY1D

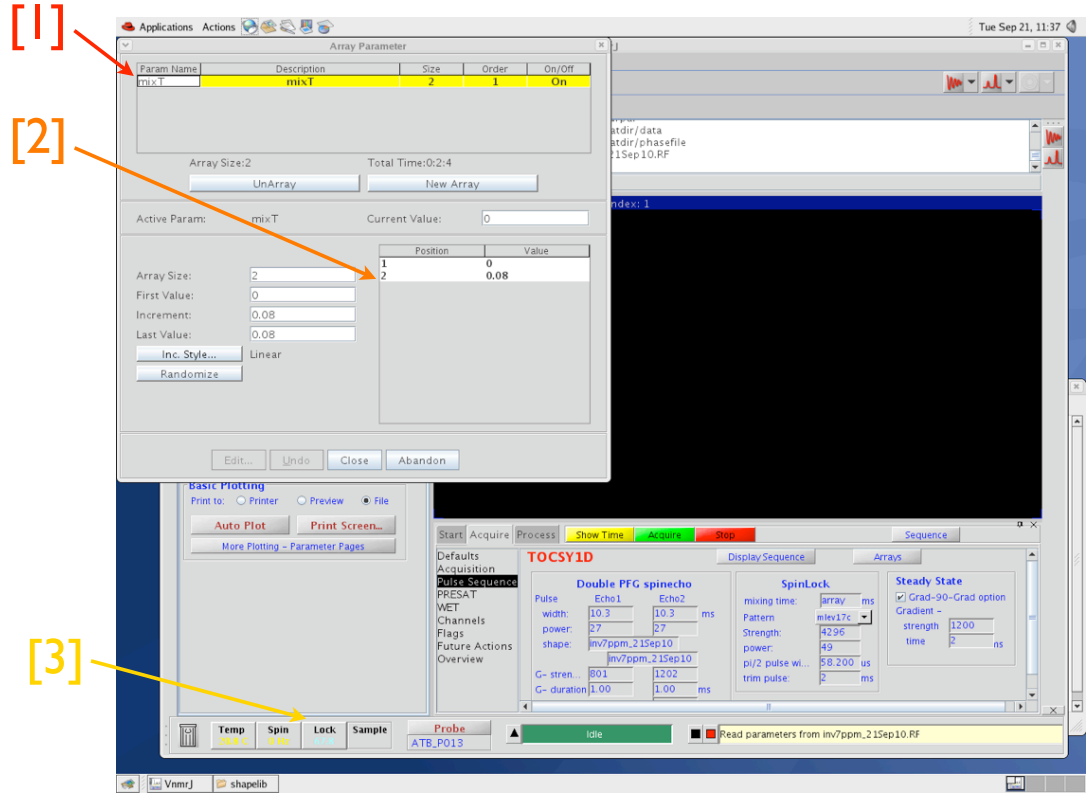


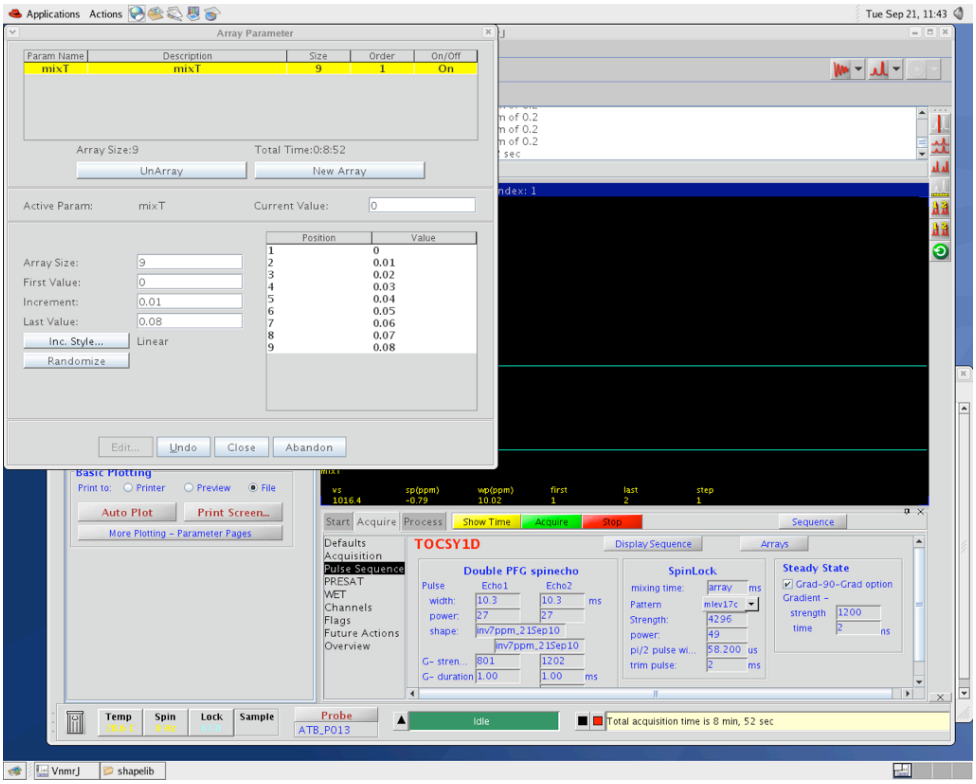


TOCSY 1D Figure 5

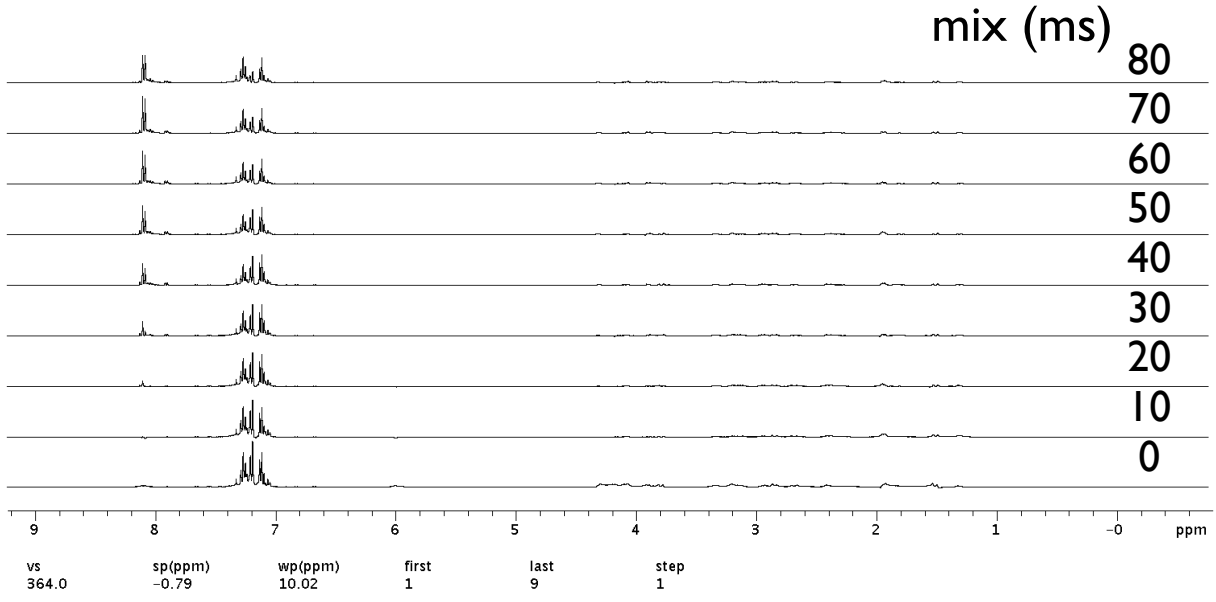


TOCSY 1D Figure 6





Bottom-to-top, longer mix times allow magnetization from near 7 ppm to migrate to other sites in the molecule.



1D TOCSY selective for cluster of resonances near 1.4 ppm.