Solvent Suppression using TopSpin 3.x

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Brief Summary

There are number of solvent suppression schemes used in NMR, and the technical details can become extensive. Here is a brief list of suggestions:

presaturation – can give cleanest, or at least, narrowest suppression, but significantly reduces exchangeable protons; sequence variations, such as using a composite pulse, assist in reducing residual water

noesy1d presat – can provide cleaner baselines; used in many metabolomics studies

purge presat – a relatively new method of presaturation, touted as superior to standard presat for quantitative studies (we have yet to test this assertion here)

wet – a prominent method used with mixed solvents (multiple-peak suppression); can reduce intensity of exchangeable protons

watergate – a number of forms exist: the basic type requires optimization, but high-quality
- **3-9-19** – the most commonly used wg variant; no effect on exchangeable protons
- **w5** – a wg variant similar to 3-9-19, but narrower notch about solvent

excitation sculpting – any solvent suppression technique that uses spin/gradient echoes — e.g., watergate flavors — can be run twice in a row; this double pulse-field gradient spin echo (DPFGSE) method produces excellent suppression (square of the single method), but also a broader notch bandwidth about the solvent peak

A significant issue with solvent suppression on Bruker spectrometers is which variants are available in the experiment you really need. **purge** may run great in a ^{1}H 1d, but does not exist (currently) in any 2D flavor. See Table 1 for an up-to-date listing of sequences available at UWChemNMR.

<u>Suggestions for how to choose:</u>

i. If exchangeable protons are important, use a watergate flavor.
   - If important solute peaks are close to the solvent, but you must also observe exchangeables, use the narrowest bandwidth (largest d19) possible. Do not use excitation sculpting.
   - If suppression is critical with exchangeables, use excitation sculpting.

ii. To observe solute peaks close to the solvent peak, and there are no (important) exchangeables, use a low-power presat flavor.

iii. If it is crucial to completely eliminate the solvent peak, use an excitation sculpting flavor.

iv. ***If multiple solvent peaks must be reduced***, use wet or presat using the selection 1D options. Start with information provided below in section **G**.

v. It is easy to try various solvent suppression flavors in the ^{1}H 1D versions. ***<u>Do this!</u>*** You will need to spend time collecting 1D spectra to judge the quality of your shims and suppression. So experiment with different types within the main categories stated above. Base the final choice (or two) on these 1D experiments.

A. ***Initial Setup:***

1. Always start by acquiring a one-scan ^{1}H spectrum.

   It is not required, but best to run solvent suppression experiments on-resonance to the solvent peak. If you believe this is not optimal, find cgfry for further discussion.

2. Put the solvent peak on-resonance by:

   a) expand about the solvent peak enough that you can easily see the center

   b) click  and then left-click with the cursor in the middle of the solvent peak

   c) choose **o1**

   d) retake the one-scan ^{1}H spectrum to verify that the peak is in the center of the spectrum.

   c) To obtain the most accurate **o1** value:

   → **rpar** the parameter set: **solvsup_setup.UW** (a standard presat exp optimized for **gs**)

   → enter the approximate **o1** value from above, then type:

   gs↵

   Adjust **o1** until the FID is minimized.

3. Write down the value for **o1** in Hz.

B. ***Presaturation:***

1. In the new expno, run **ased** and change the first parameter PULPROG to **zgpr** . Or read in the parameter set: **H1_presat.UW** and set **o1** as found in step A.3.

2. The critical new parameter with all presaturation techniques is **plw9** (or **plw32** in sequences asking for lower power presat), which will perform a low-power cw pulse on-resonance. You can raise the power of this parameter to decrease the intensity of the residual signal, but setting it too high may damage the probe!

   plw9 ≤ 0.3 mWatts (≤ 0.0003 in the 1st box on the ased screen)
   pldb9 ≥ 35 –dBW (value in 2nd box on the ased screen should ≥ 35)

3. Run **rga** prior to doing **zg** .

4. Better data can usually be obtained by using a composite pulse: **H1_presat-cp.UW** (PULPROG=zgcppr.UW).

C. **noesygppr1d *Presaturation:***

1. Do the same steps as in B, but read in the parameter set **H1_presat-noesy1d.UW** (PULPROG=noesygppr1d.UW).

2. Change **o1** to match the value found in A.3.

3. Run **rga** prior to doing **zg** .

4. **plw9** again might be smaller than optimal. Same conditions apply as in B.2.

D. purge *Presaturation:*

1. Do the same steps as in B, but read in the parameter set **H1_presat-purge.UW** (PULPROG=zgpurge.UW).
2. Change **o1** to match the value found in A.3.
3. Run **rga** prior to doing **zg** .

E. watergate 3-9-19 *suppression:*

1. Do the same steps as in B, but read in the parameter set **H1_3919.UW** or **H1_3919es.UW** (PULPROG=p3919gp.UW or p3919gpes.UW).
2. Change **o1** to match the value found in A.3.
3. Check **d19 = 1/(2Δ)** where Δ =distance to null in Hz from the solvent peak. Narrowest bandwidth may attenuate solute peaks most downfield and upfield, but will also give the narrowest (sharpest) solvent notch.
4. Run **rga** prior to doing **zg** .

F. watergate w5 *suppression:*

1. Do the same steps as in B, but read in the parameter set **H1_W5.UW** or **H1_W5es.UW** (PULPROG=zggpw5.UW or zggpw5es.UW)
2. Change **o1** to match the value found in A.3.
3. Check **d19 = 1/(2Δ)** where Δ =distance to null in Hz from the solvent peak. Narrowest bandwidth may attenuate solute peaks most downfield and upfield, but will also give the narrowest (sharpest) solvent notch.
4. Run **rga** prior to doing **zg** .

F. wet *suppression:*

1. Do the same steps as in B, but read in the parameter set **H1_wet.UW** or **H1_wetdc.UW** (PULPROG=wetdc_nodec.UW or wetdc.UW).

   Use **H1_wet.UW** to suppress water, or for an organic solvent when peaks close to the solvent are not present. Use **H1_wetdc.UW** for organic solvents when ^{13}C satellites are problematic.
2. Change **o1** to match the value found in A.3.
3. The power of the 1st wet pulse is strongly affected by cryoprobes, and even normal-coil probes. For cryoprobes, it is mandatory to optimized the power level of this pulse; we recommend optimization for all uses of wet on Bruker equipment. It is relatively simple to perform:

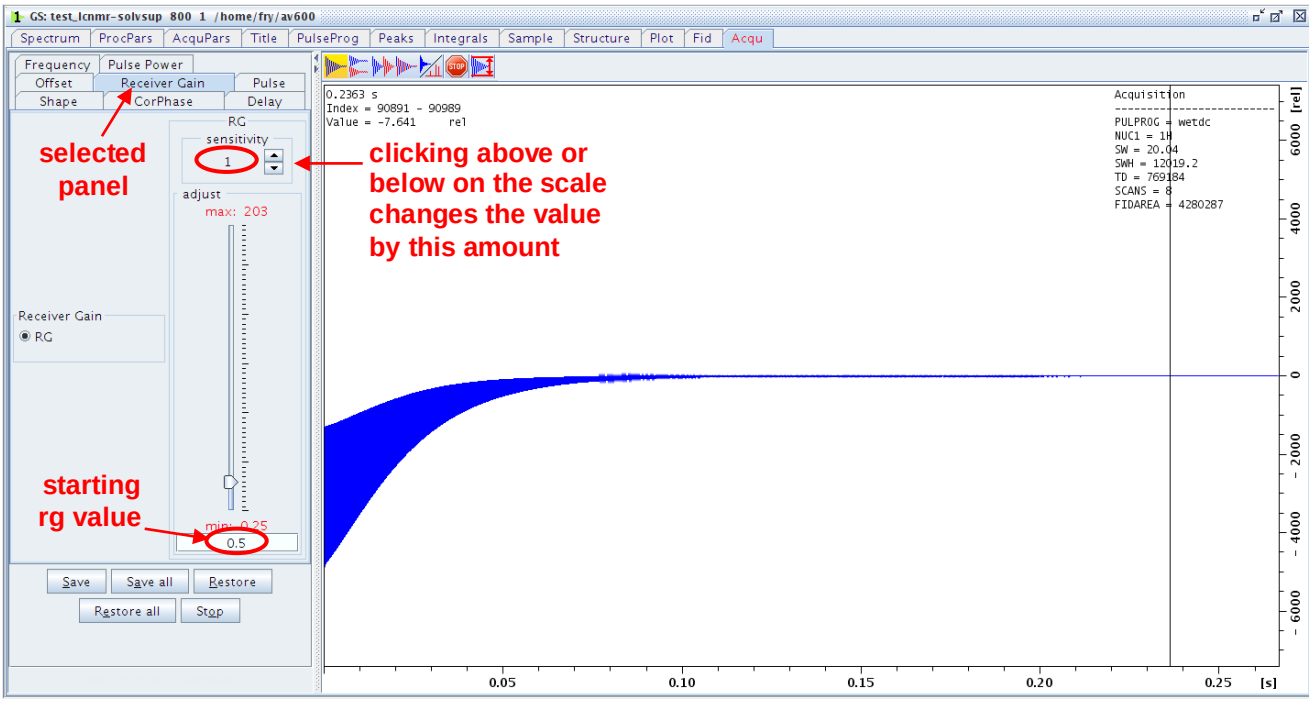
   Optimization of wet power level spdb7:

   a) Run **rga** . Good suppression should always lead to **rg** ≥ 20; the goal is to do better than that.

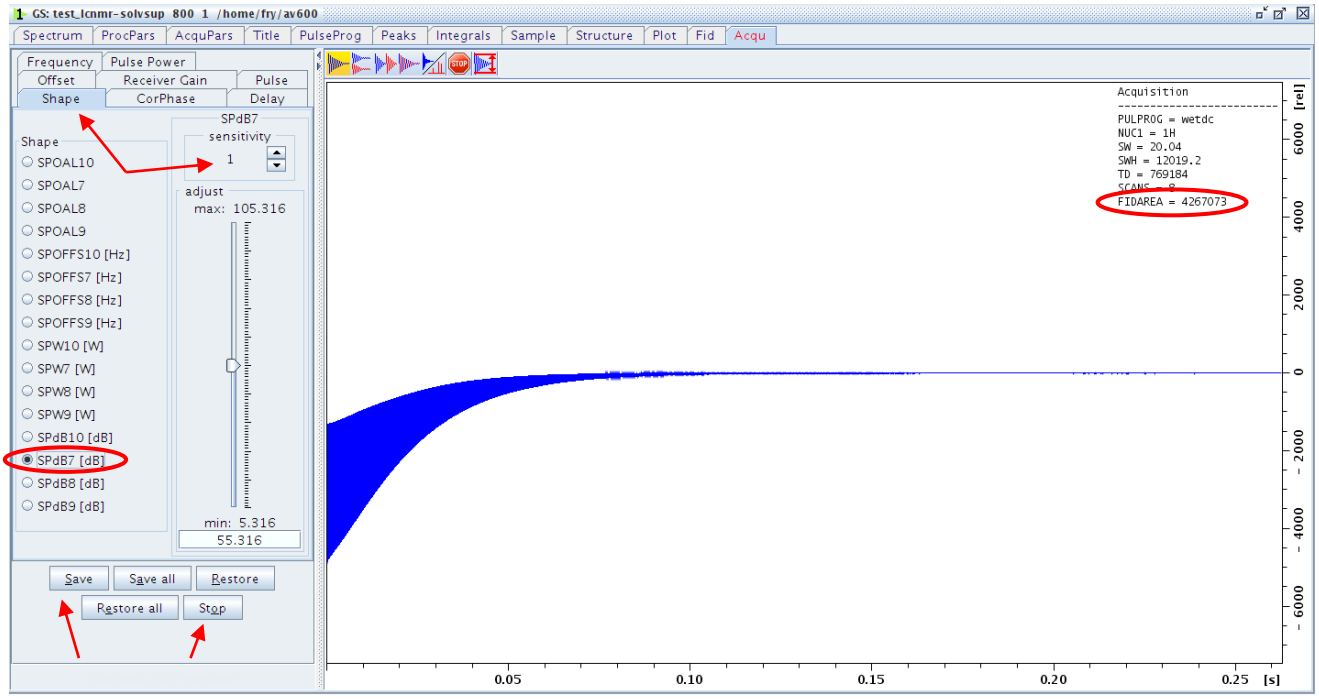
   b) Check that **aq** = 1-2 s, and **d1** =1-2 s.

c) Enter Bruker's real-time optimization routine: **gs**↵

When you first enter, the rg may be quite poor. An example setup is shown below:

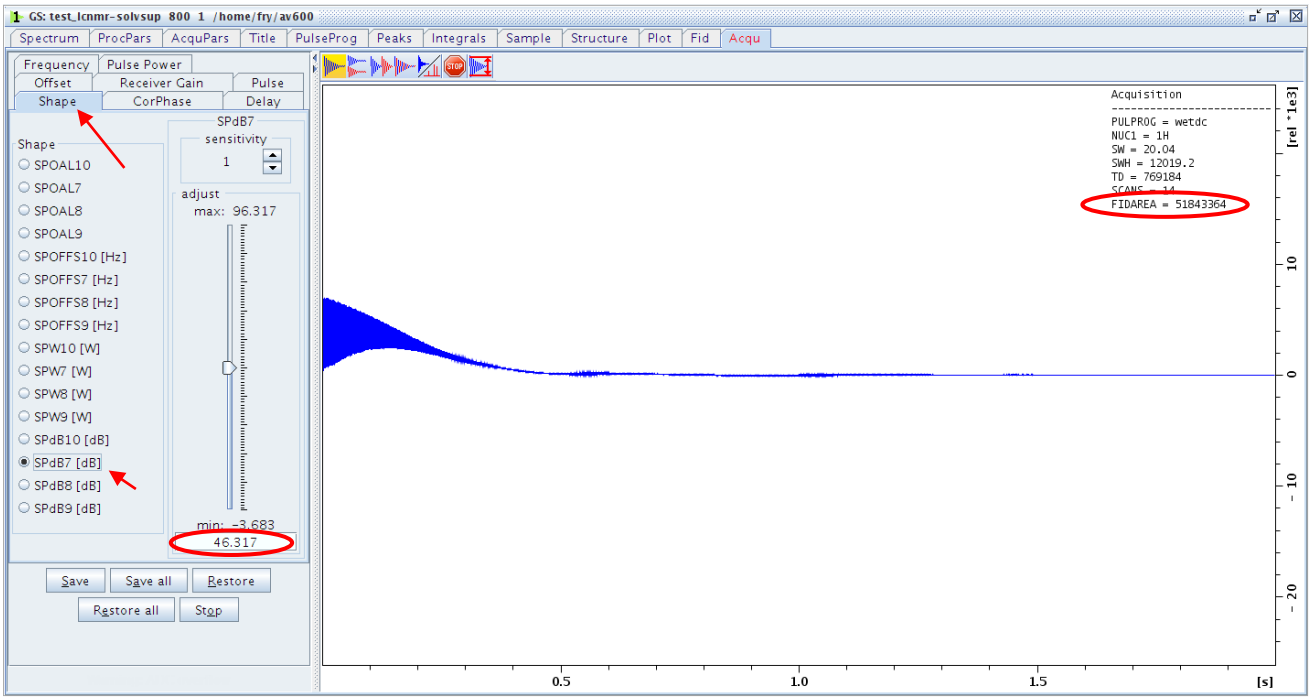


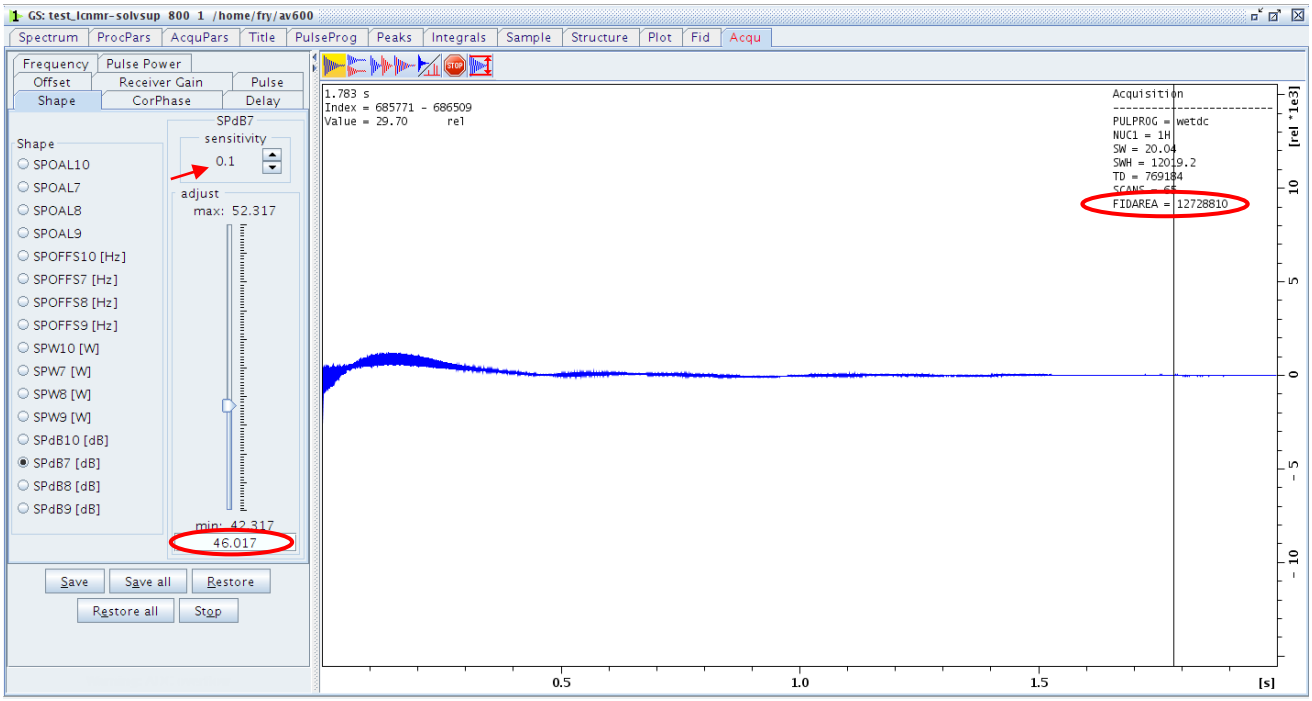
d) Adjust the Shape parameter **spdb7** , which is the power of the 1st wet pulse. On our 600 with the TCI cryoprobe, the power must be raised 5 to 10 dB (oddly, to smaller values) to obtain reasonable suppression. The start a coarse adjustment, ±1 dB, is shown below:



e) It shouldn't take long to achieve a much decreased fid size, viewed visually or by using the FIDAREA number in the upper right. At the best 1 dB position, **Save** and then **Stop** the **gs** run. Redo an **rga**↵ ; you should now achieve a much better **rg** (in this case, **rg**=90.5).

f) Re-enter **gs**↵ . Go back to **Shape** and click on **SPdB7**. Change the sensitivity to 0.1, and adjust to minimum fidarea. See the start and end example screencaps below.





f) **Save** and **Stop**. High quality wet suppression should now be achieved. Keep ds large, e.g, ds=24, if you are decoupling carbon satellites (H1_wetdc.UW).

H. ***Multiple-peak solvent suppression:***

This section uses selective 1D setup in TopSpin to create shapes for multiple-peak suppression. For more detail about selective 1D experiments, see section B of the notes at:

http://www.chem.wisc.edu/~cic/nmr/Guides/Ba3vug/HW637/HW5_Av400-sel1DbyTopSpin.pdf

Two types of suppression are provided: **wet** and **presat**. **Wet** selection is preferred if exchangeable protons are important, and especially if quantitative information is needed from exchangeables. Otherwise, as is true in general for all solvent suppression types, use **presat**.

1. Acquire a 1-scan proton spectrum as described in section A.
2. Integrate the solvent peaks to be suppressed in the proton spectrum. For **wet** suppression, keep the integral regions not too small (>20Hz; ~60 Hz is a good width), and not too dissimilar in width. For **presat** suppression, choose relatively narrow width/integrals (~15 Hz) in all cases.
3. click on: **CREATE DATASETS**

   and choose **wet** or **presat** toward the bottom of the list. Save the integrals using **Save As… reg** .
4. For **wet**, optimize **spdb7** using the method described above in section F.

Table 1. Solvent Suppression parameter sets and pulse sequences available at the UWChemNMR Facility; updated 29 July 2015.

Parameter Set[1]	Suppression Type	Pulse Sequence[2]	Critical Parameters	Bruker: par; pp	comments
1D setup					
solvsup_setup.UW	presaturation (d1)	zgpr.UW	obtain **o1**	none; zgpr	optimized for **gs**
1D experiments					
H1_presat.UW	presaturation (d1)	zgpr30.UW	plw9 ≤ 0.3mW[3]	none; zgpr	saturates exchangeable ^{1}H; presat types have narrowest suppression of base types
H1_presat-cp.UW	presaturation (d1) with composite pulse	zgcppr.UW	plw9 ≤ 0.3mW[3]	none; zgcppr (zgcpgppr; zgcpfppr)	–better baselines than zgpr
H1_presat-noesy1d.UW	presaturation (d1+d8) during noesy1d sequence	noesygppr1d.UW	plw9 ≤ 0.3mW[3] d8 typically ≤ 10ms	WATERSUP; noesygppr1d	–popular in metabolomics
H1_presat-purge.UW	presaturation (d1) with gradient echoes	zgpurge.UW	plw9 ≤ 0.3mW[3]	none; zgpurge	–better for quantitation(?)
H1_wet.UW	wet for water	wetdc_nodec.UW	manually optimize spdb7 to 0.1 dB	none	good suppression, small effect on exchangeables
H1_wetdc.UW	wet with suppression of organic solvent's ^{13}C satellite	wetdc.UW	manually optimize spdb7 to 0.1 dB	CMC_WET	good suppression, small effect on exchangeables
H1_3919.UW	watergate 3919 (W3)	p3919gp.UW	d19 = 1/(2Δ)[4]	P3919GP; p3919gp (soft v.: ZGGPWG)	most common watergate (soft variant: zggpwg)
H1_3919es.UW	watergate 3919 (W3) with excitation sculpting	p3919esgp.UW	d19 = 1/(2Δ)[4]	none; none	–excellent suppression (W5es better small MW)
H1_W5.UW	watergate W5	zggpw5.UW	d19 = 1/(2Δ)[4]	none; none	–narrower notch than 3919 (W3), but longer sequence
H1_W5es.UW	watergate W5 with excitation sculpting	zggpw5es.UW	d19 = 1/(2Δ)[4]	none; zggpw5	–best suppression of base sequences
2D coherence exps					
HC_hsqc-edited.UW HC_hsqc-nonedited.UW	coherence gradients	hsqcedetgpsisp2p3.UW hsqcetgpsisp2p2.UW	aq ≤ 0.3s aq ≤ 0.3s	HSQCEDETGPSISP2.3[5] HSQCETGPSISP.2[5]	^{1}H-^{13}C hsqc coherence gradients usually provide sufficient suppression
2D presat exps					
HH_cosy2d_presat.UW	cosy with presat (d1)	cosygpprqf.UW	plw9 ≤ 0.3mW[3]	none; cosygpprqf	magnitude-mode cosy
HH_dqfcosy2d-presat.UW	DQFcosy with presat (d1)	cosydfphpr.UW	plw9 ≤ 0.3mW[3]	none; cosydfphpr	non-gradient dqf
HH_tocsy2d-presat.UW	tocsy with presat (d1) and zero-quantum filter	mlevgpphprzf.UW	plw9 ≤ 0.3mW[3]; d9 ≤ 0.2s	none; mlevgpphprzf	good 2d tocsy sequence
HH_noesy2d-presat.UW	noesy with presat (d1+d8/mix)	noesygpphpr.UW	plw9 ≤ 0.3mW[3]; d8 ≤ T_1(shortest of interest)	none; noesygpphpr	good 2d noesy sequence
HH_roesy2d-presat.UW	roesy with presat (d1)	roesyphprp2.UW	plw9 ≤ 0.3mW[3]; P15 ≤	ROESYPHPR;	tic-toc spinlock; cw presat

			500000 (μs)	roesyphpr.2	
HC_hsqc's	see 2D Coherence exps above				
HC_hmbc-presat.UW	hmbc with presat (d1)	hmbcgplpndprqf.UW	plw9 ≤ 0.3mW[3]; cnst13 (J_{CH} ~3 to 12; default 8)	none; hmbcgplpndprqf	1-bond filtered; coherence gradients; cw presat
HN_hsqc-presat.UW	coherence gradients + presat (d1)	hsqcetgpprsisp2p2.UW	plw9 ≤ 0.3mW[3]; aq ≤ 0.3s	none; hsqcetgpprsisp2.2	coherence grads not enough suppression in HN hsqc
HN_hmbc-presat.UW	coherence gradients + presat (d1)	hmbcgplpndprqf.UW		HMBCGP_15N; hmbcgplpndprqf	coherence grads not enough suppression in HN hmbc
2D watergate exps					
HH_dqfcosy-3919.UW	3919 watergate ending sequence + low-power presat (d1)	cosydfgpph19.UW	d19 = 1/(2Δ)[4]; plw32 ≤ 0.3mW[3]	COSYDFGPPH19; cosydfgpph19	set plw32=0 (pldb32=1000) if exchangeable protons are reduced too much
HH_tocsy2d-3919.UW	3919 watergate ending sequence	mlevgpph19.UW	d19 = 1/(2Δ)[4]; d9 ≤ 0.2s	DIPSI2GPPH19; mlevgpph19[6]	dipsi spinlock in our hands has been inferior to mlev
HH_tocsy2d-W5es.UW	W5 + excitation sculpting ending sequence	mlevgpphw5es.UW	d19 = 1/(2Δ)[4]; d9 ≤ 0.2s	none; mlevgpphw5	superior suppression and baseline than 3919; but longer (not for large MW)
HH_noesy2d-3919.UW	3919 watergate ending sequence	noesygpph19.UW	d19 = 1/(2Δ)[4]; d8 ≤ T_1(shortest of interest)	NOESYGPPH19SW; noesygpph19	
HH_noesy2d-W5es.UW	W5 + excitation sculpting ending sequence + low-power presat (d1)	noesygpphw5es.UW	d19 = 1/(2Δ)[4]; d8 ≤ T_1(shortest of interest); plw32 ≤ 0.3mW[3]	none; noesygpphw5	set plw32=0 (pldb32=1000) if exchangeable protons are reduced too much
HH_roesy2d_3919.UW	3919 watergate ending sequence	roesygpph19p2.UW	d19 = 1/(2Δ)[4]; P15 ≤ 500000 (μs)	none; roesygpph19.2	

[1] .UW parameter sets often have parameters better optimized than the base Bruker setup. E.g., **d1**=2 or 3s (rather than ~1s), as is appropriate for small molecules; another example is **d19**=1/(2*5ppm) set according to field strength).

[2] .UW pulse sequences often have protections coded in: **aq** ≤ 0.3s is in all hsqc sequences; **d9** ≤ 0.2s is in all tocsy sequences (we're looking as to how to do plw9 ≤ 0.3mW). .UW sequences also have updated comments that will show in **ased** listings.

[3] Or equivalently, pldb9 (or pldb32) ≥ 35.

[4] Δ = distance in Hz to next null from **o1** (or **o1p**); nulls will occur at ±*n*Δ, where *n*=0,1,2,3,...

[5] Same sequence appended by _ADIA is best for 600 MHz and higher. The same _ADIA parameter sets can be used at low field without negative effects (and are used in the .UW sequences).

[6] DIPSI2GPPH19 uses a difference pulse sequence, dipsi2gpph19, than stated here. In our hands so far, dipsi spinlocks have been inferior to mlev spinlocks. Our observations have been limited (as of July 2015), and results may be probe and field dependent. So researchers might investigate further; please let NMR staff know of new findings. Note that Bruker has another parameter set, DIPSI2ETGPSI19, that provides sensitivity enhancement with 3919 suppression (and presat during d1).