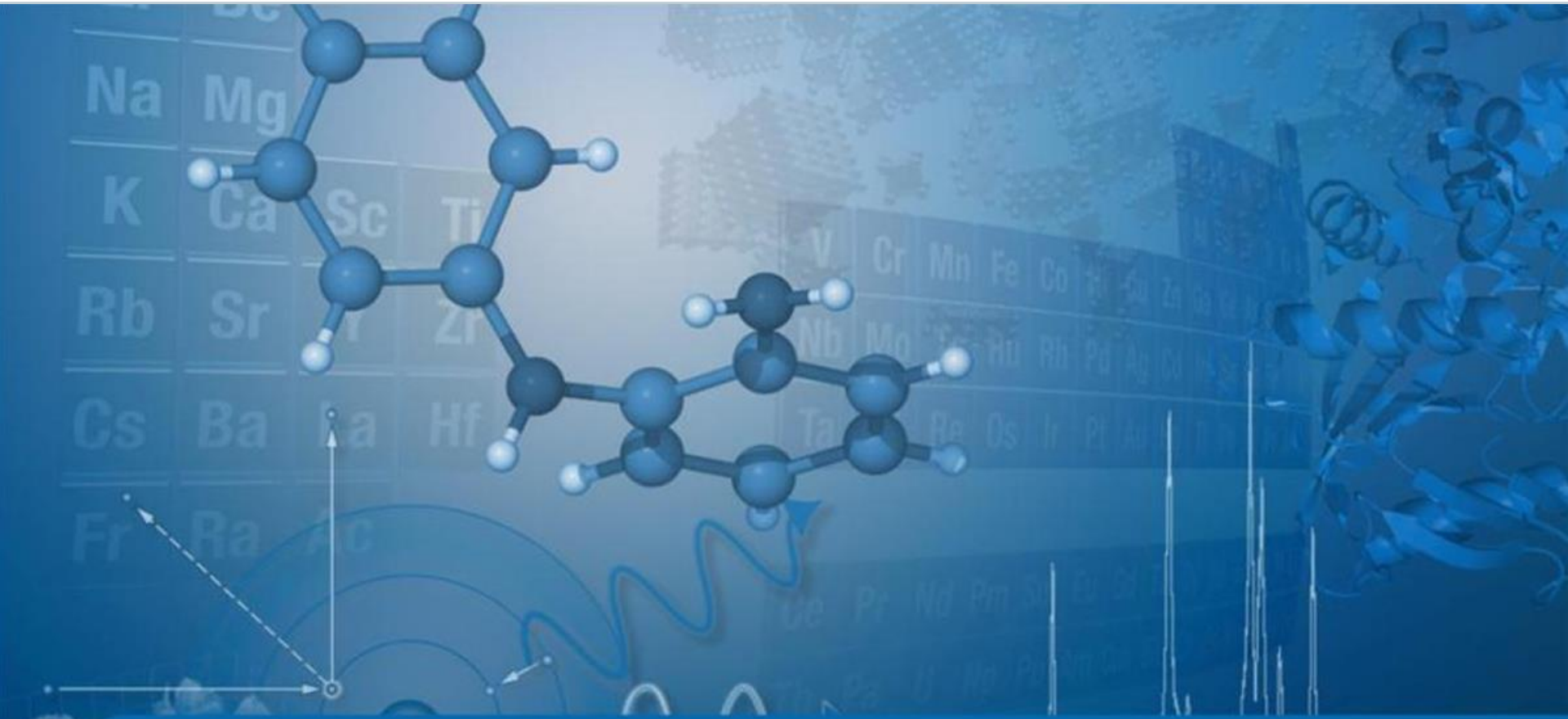
1D Acquisition

Dr. Benjamin Görling

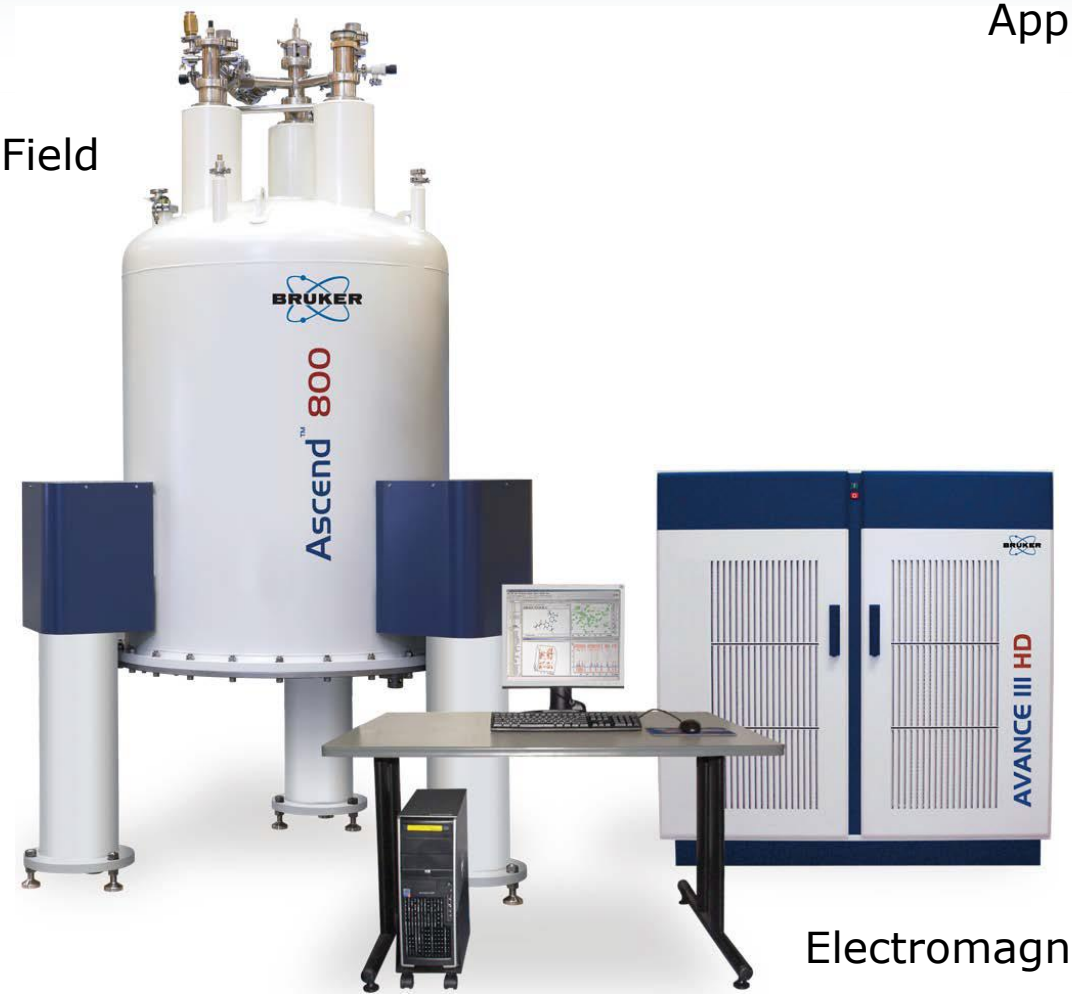


- **What is NMR?**

What do we need for NMR?

Appropriate Nucleus

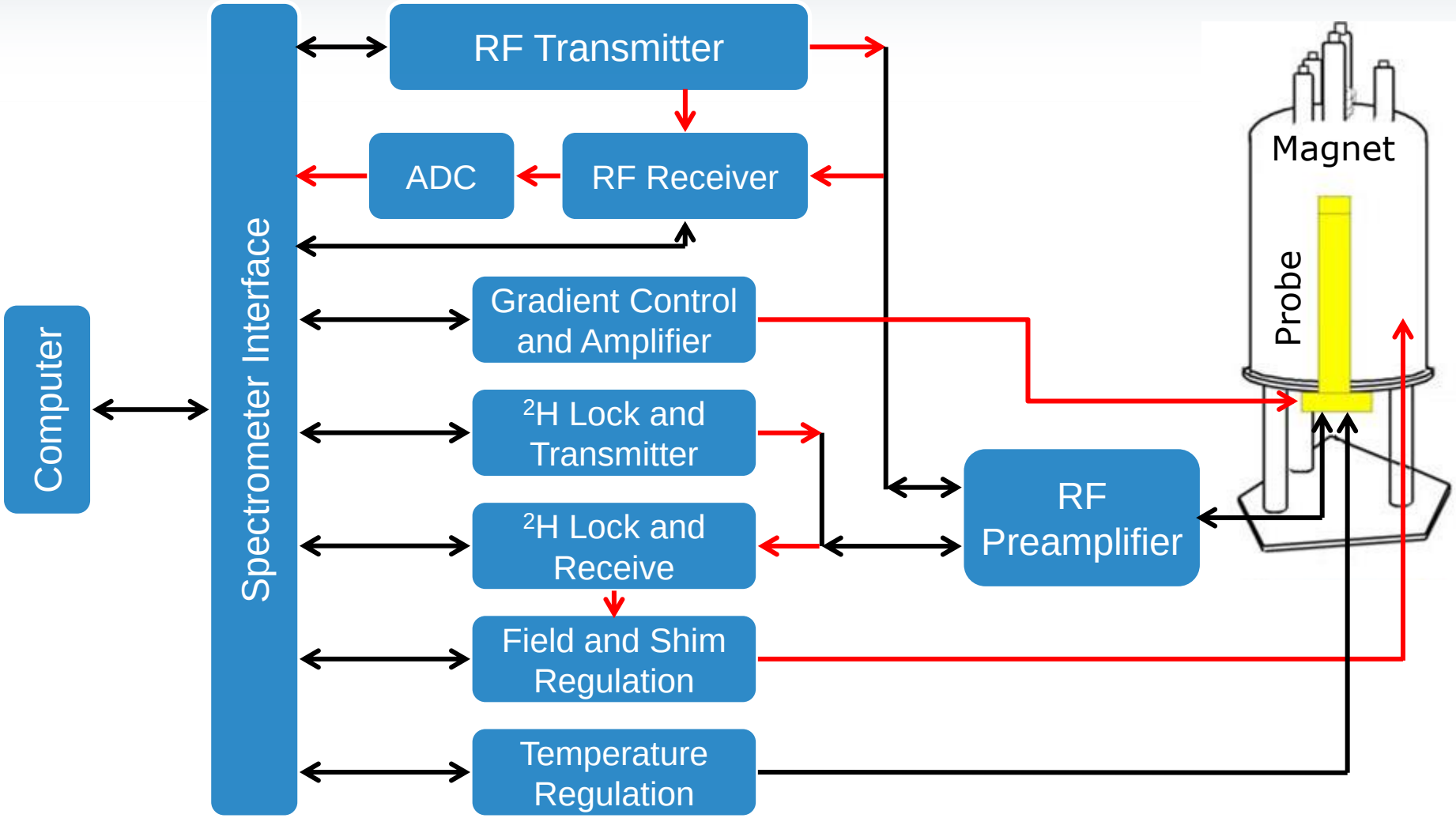
Magnetic Field



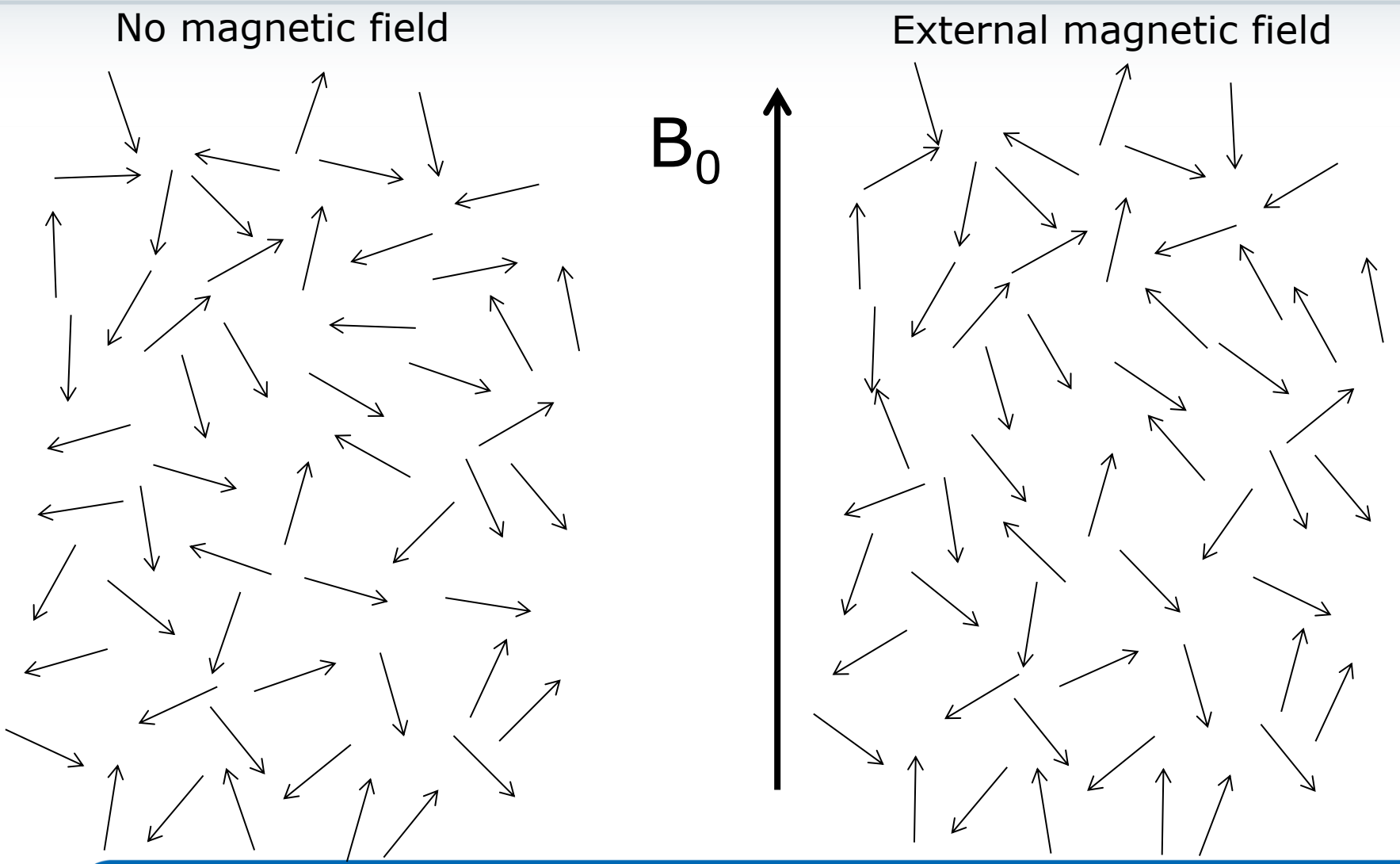
Probe

Electromagnetic Frequencies

The NMR spectrometer



What happens in the magnet?



What happens in the magnet?

No magnetic field

External magnetic field

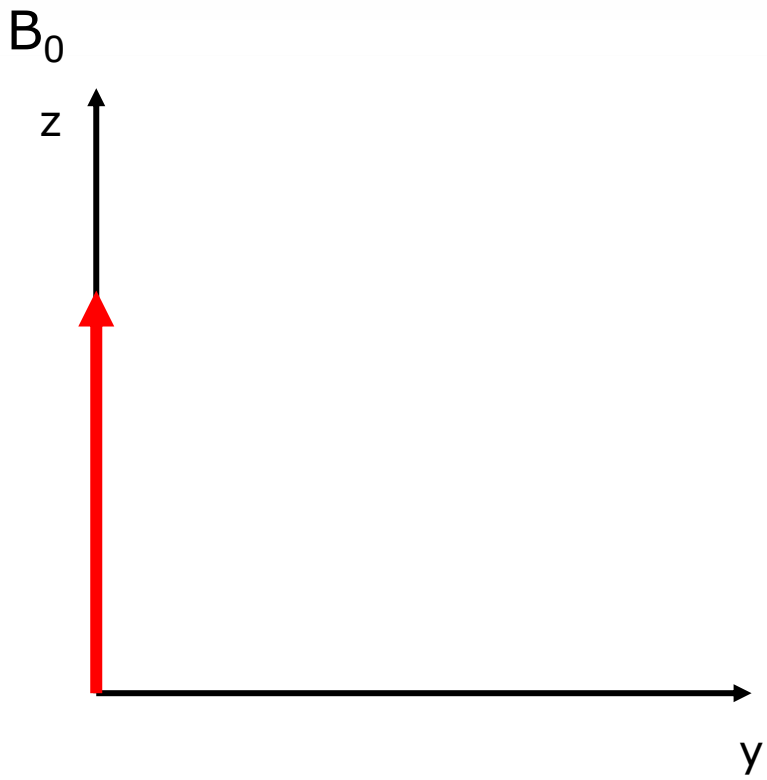
0

Sum

Sum

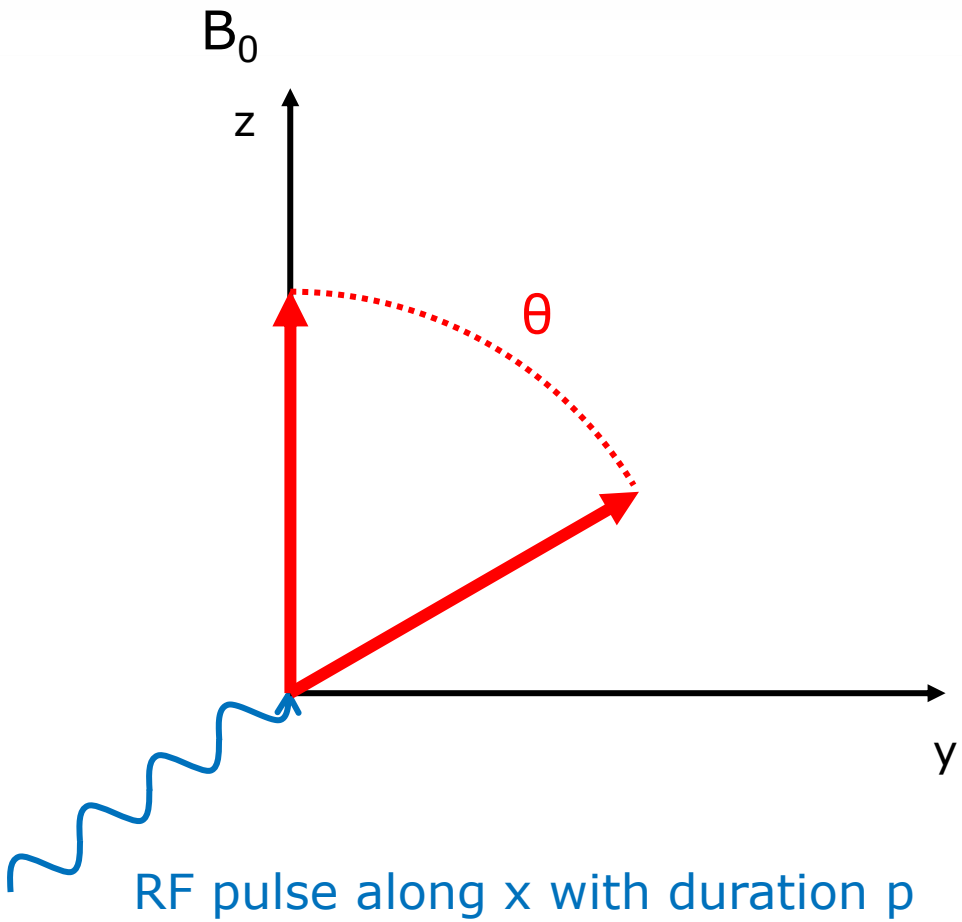
RF-Pulses

- Bulk magnetization is aligned along +z
- Can be rotated with radio frequency pulses



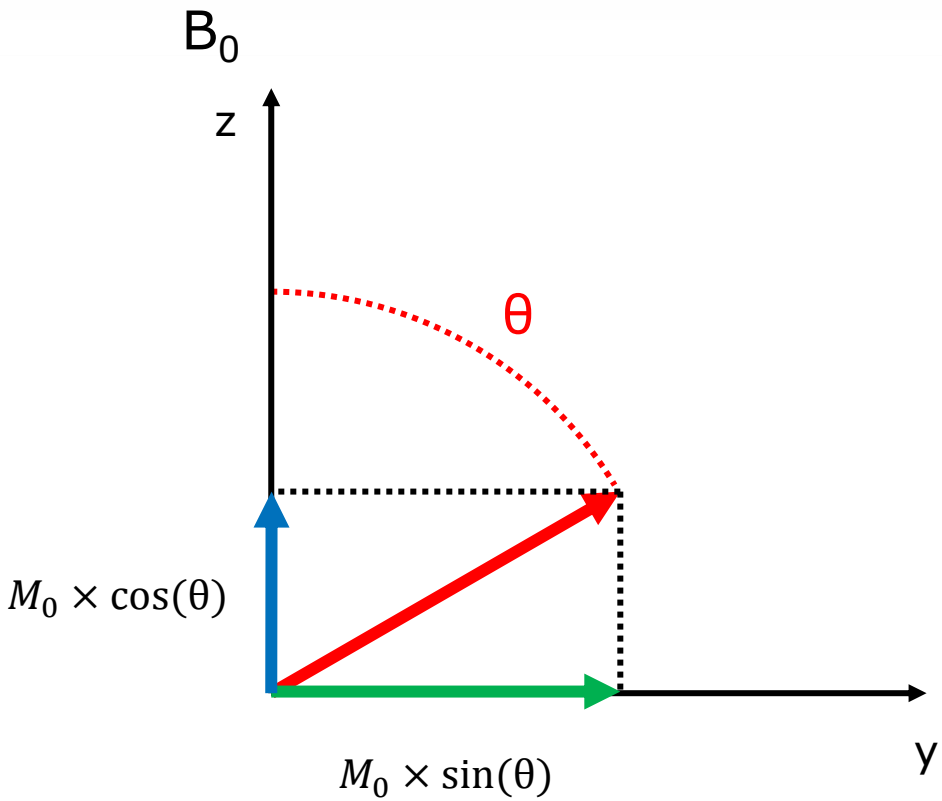
RF-Pulses

- Bulk magnetization is rotated around the axis of the pulse
- Angle θ depends on the duration (p) and the power of the pulse



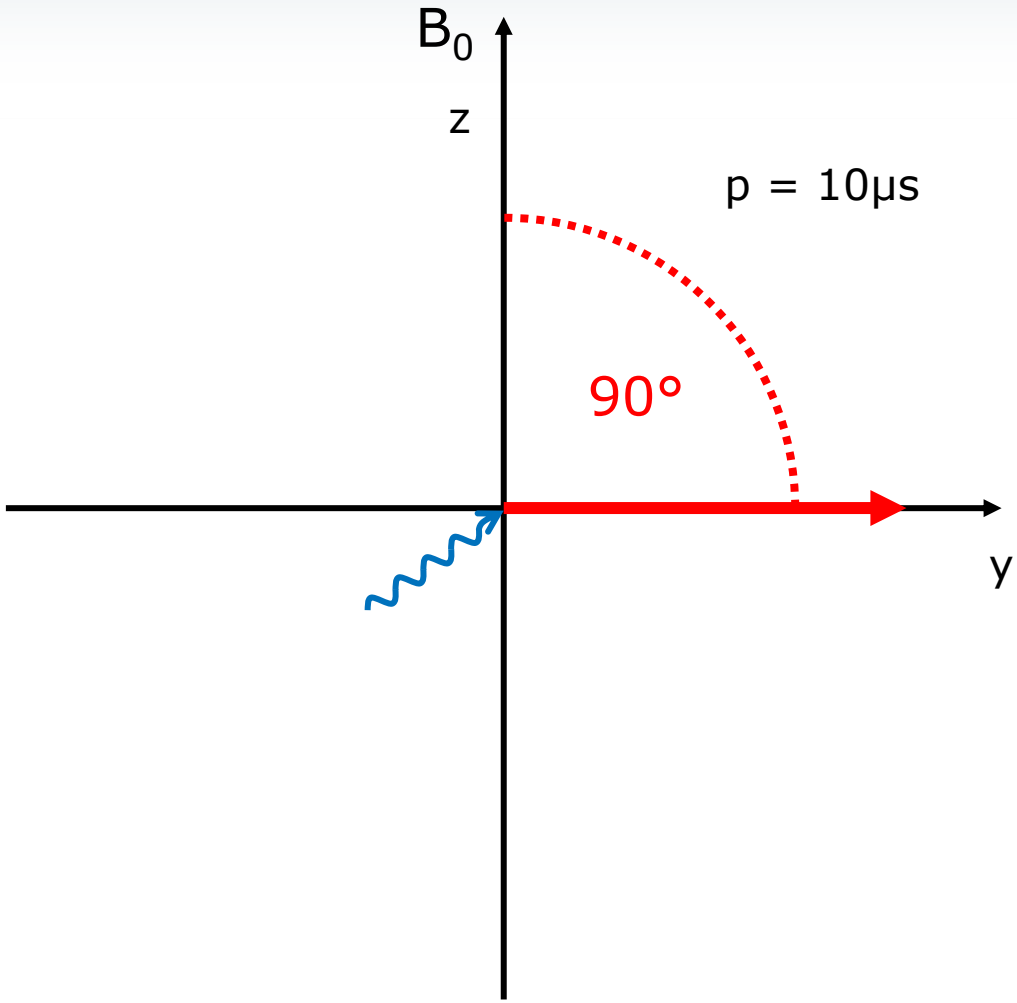
RF-Pulses

- x/y-component of the magnetization can be measured



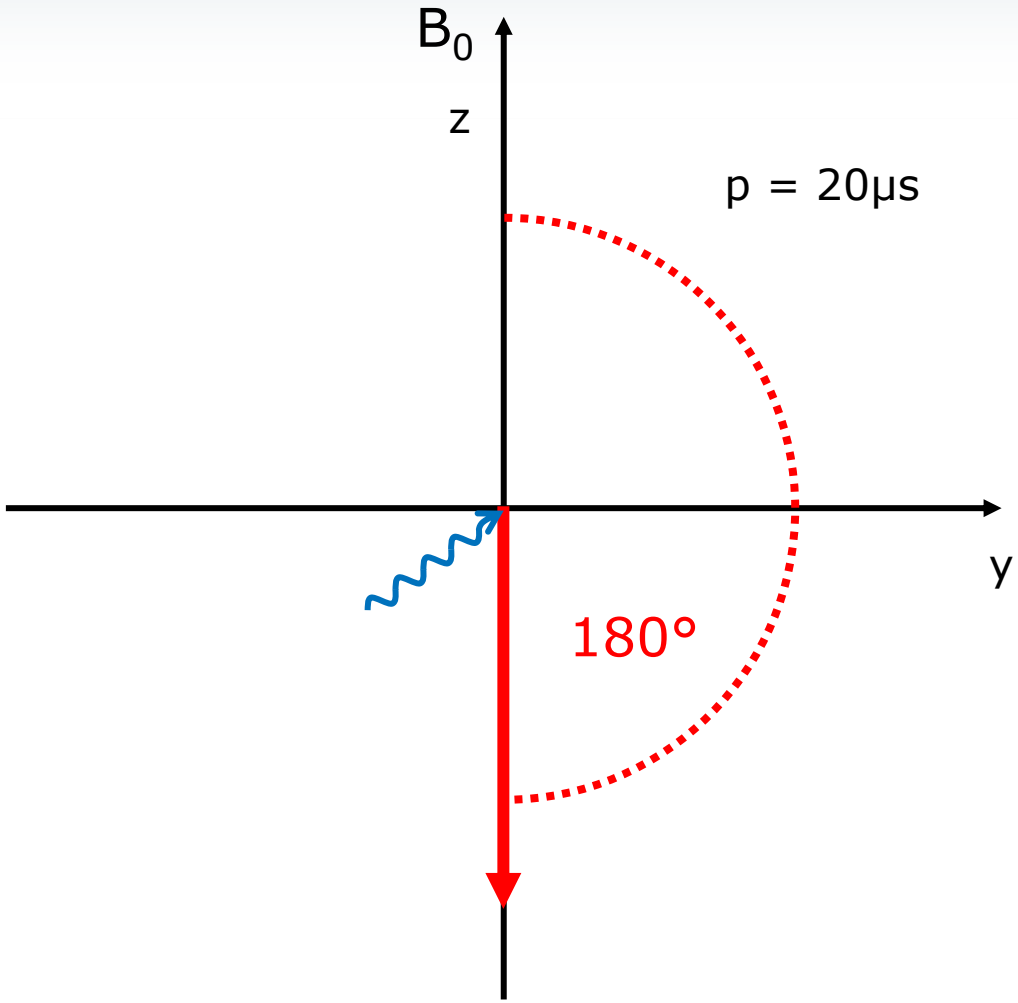
RF-Pulses

- Pulse angle is proportional to the duration p of the pulse (at constant power level)



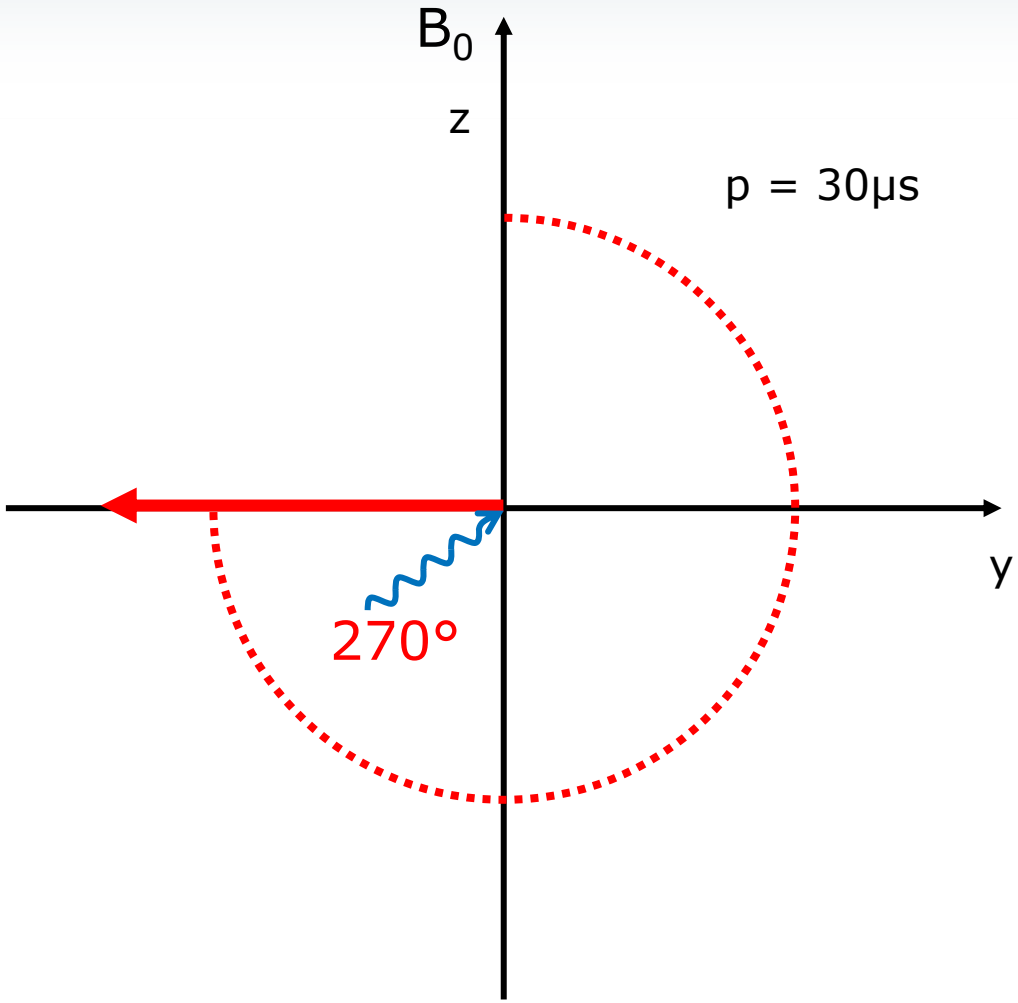
RF-Pulses

- Pulse angle is doubled if pulse length is doubled



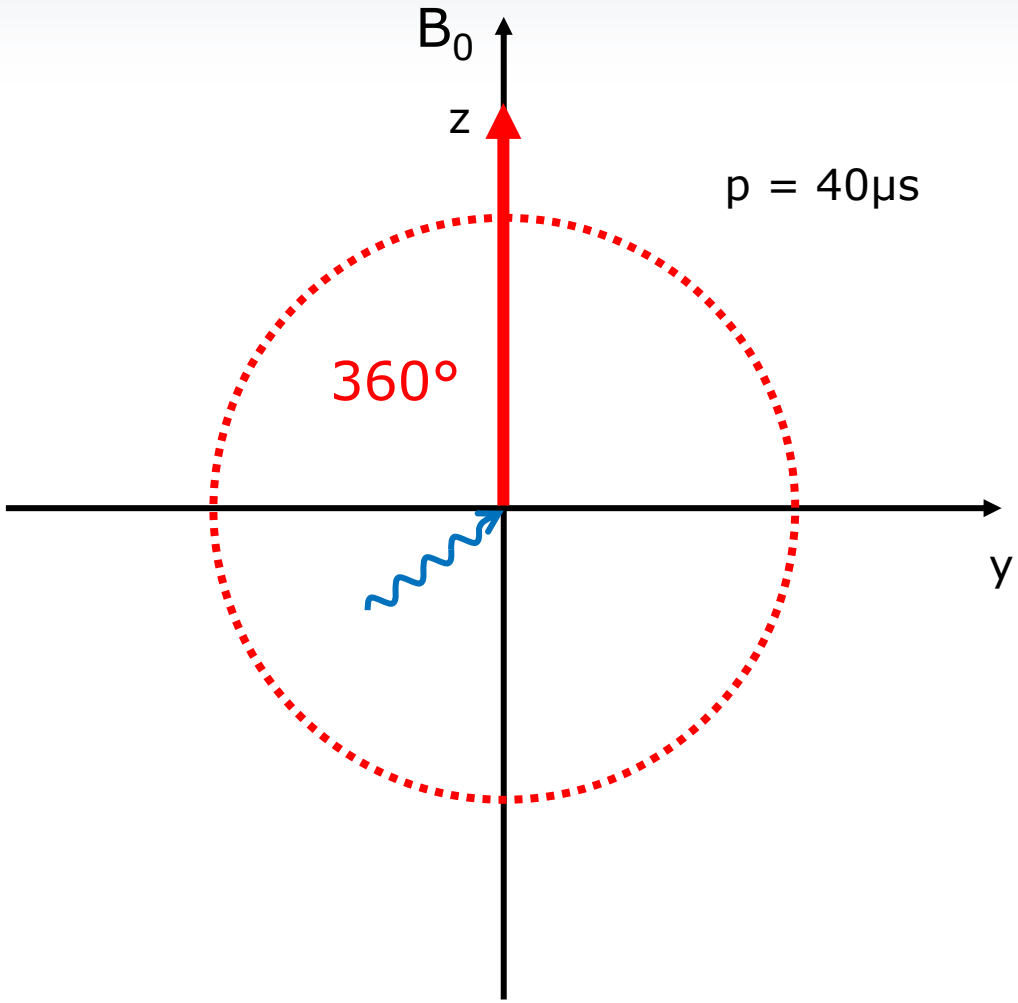
RF-Pulses

- Three times the duration results in a 270° pulse



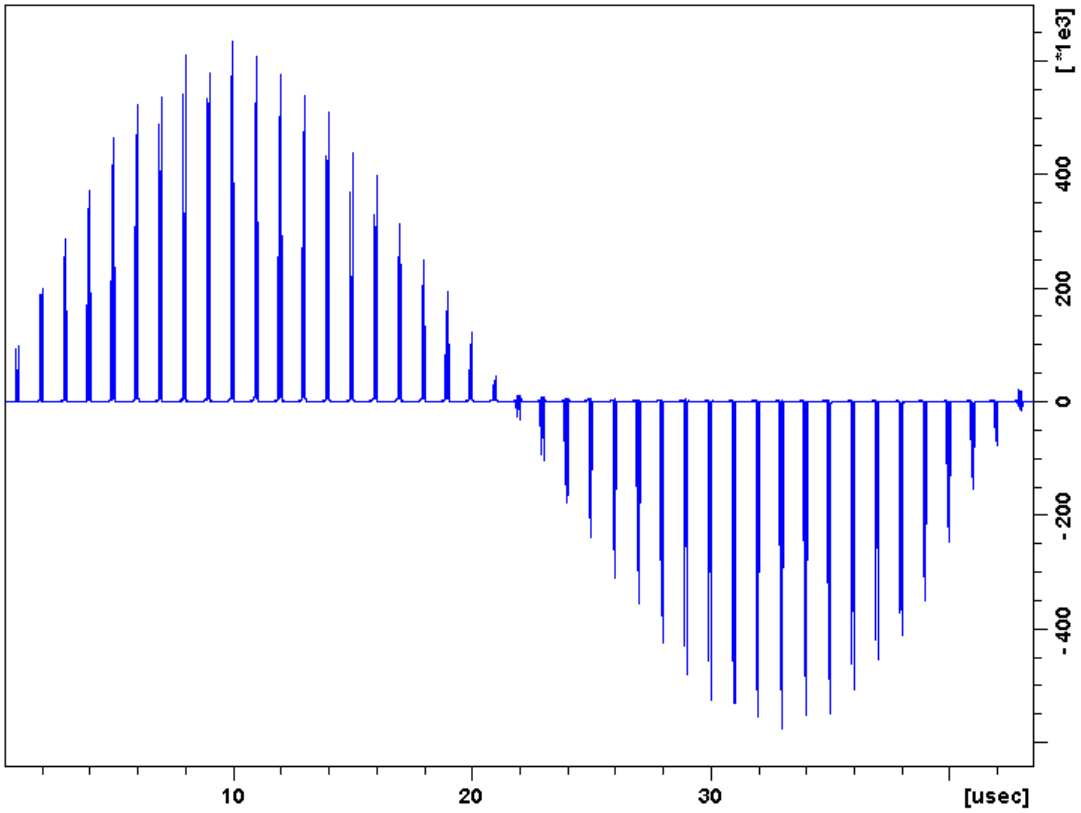
RF-Pulses

- Four times the duration results in a 360° pulse



RF-Pulses

- Maximum signal intensity can be achieved with a 90° pulse
- Length is changed to find maximum
- In practice zero crossing for 180° or 360° is used



RF-Pulses

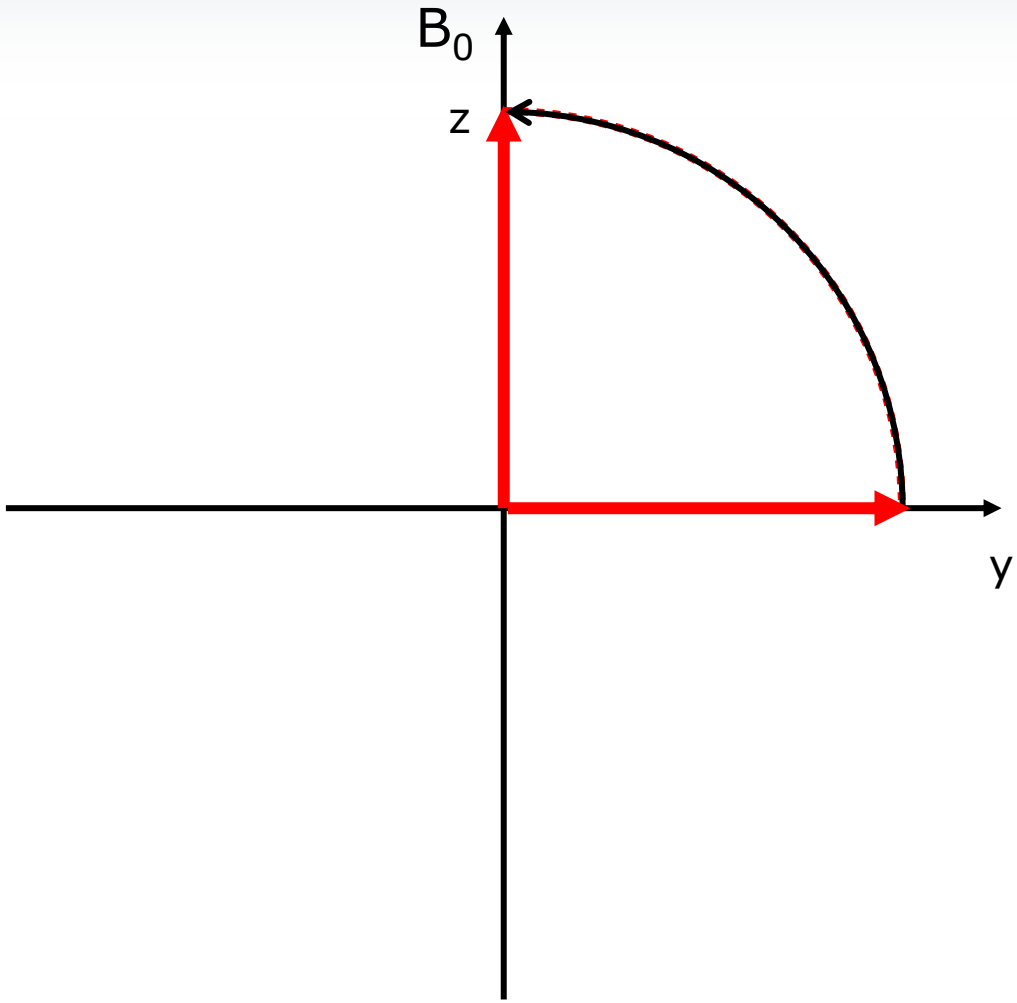
- Two parameters define a pulse: the duration of the pulse P1 and its power level PLDB1/PLW1.

- P1 is the duration of a 90º pulse (typical values are 8-10µs for a ^{1}H 90º pulse)
- PLDB1/PLW1 is the power level (given by its attenuation (dB) or in W)

Relaxation

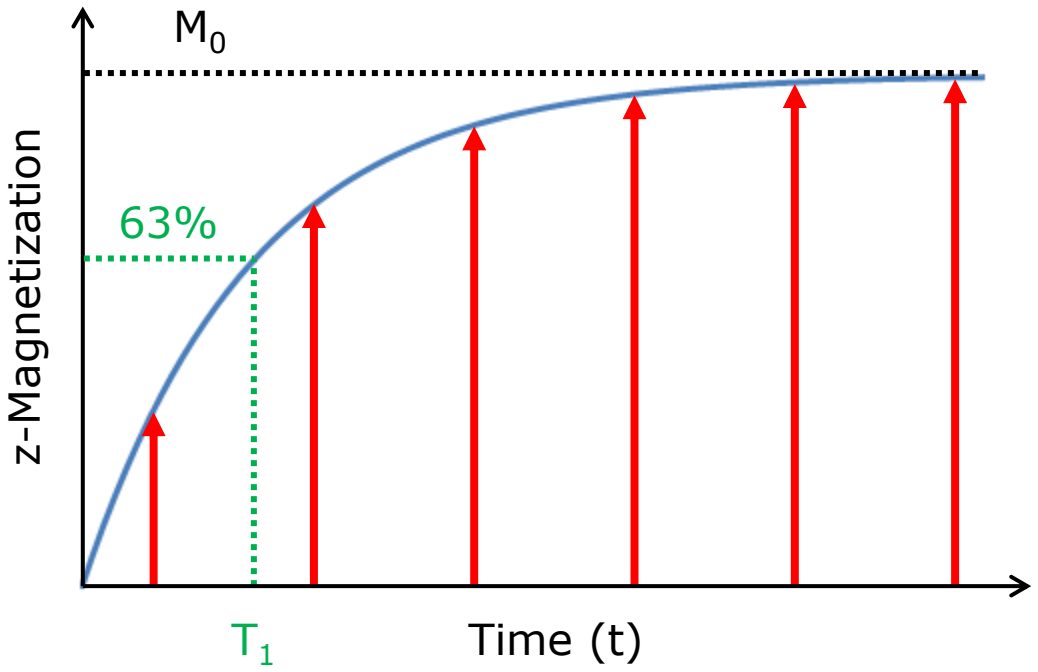
- After the excitation with the pulse, the magnetization returns back to starting position

- This is called relaxation



Relaxation

- Magnetization needs to be at starting position for next experiment to get maximum intensity
- Characterized by so called T_1 time
- Fully relaxed at $>5 \times T_1$

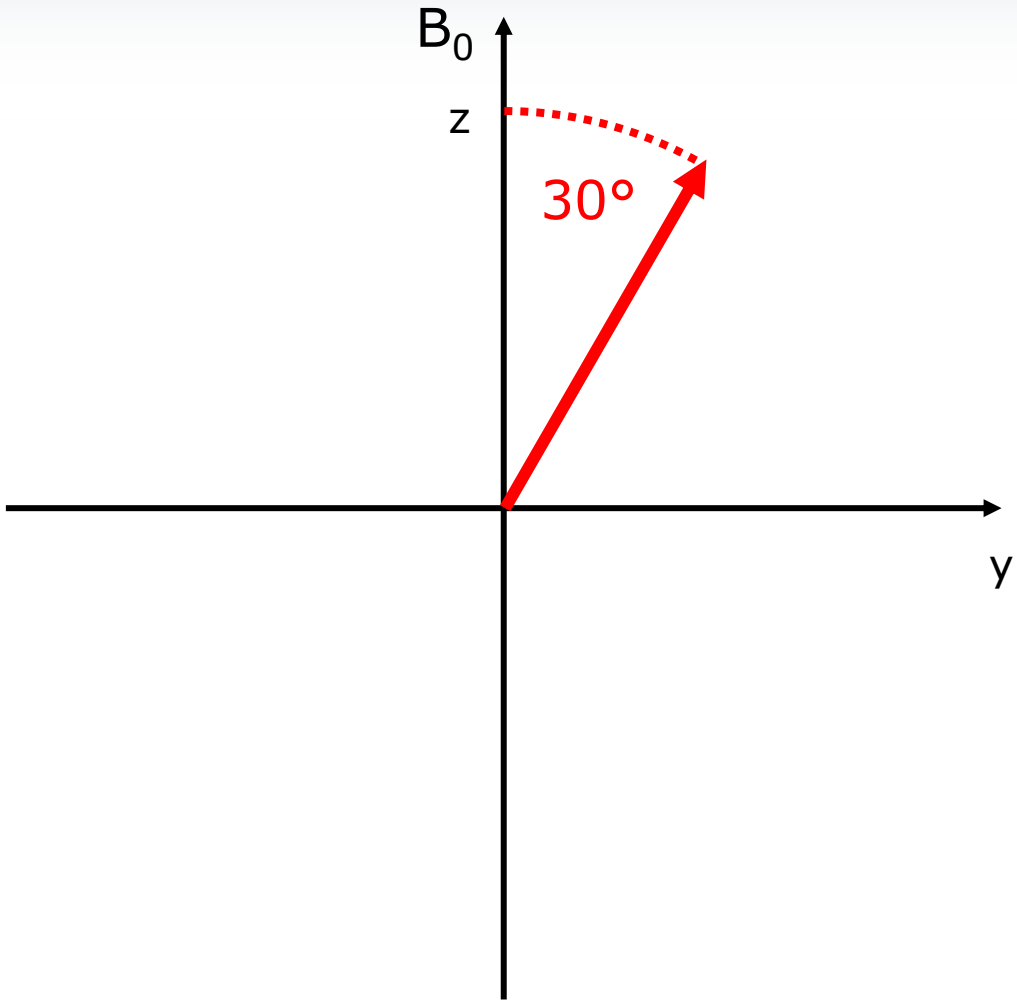


$$M = M_0 \times \left(1 - e^{-\frac{t}{T_1}}\right)$$

30° pulse

- For normal 1D experiments pulse angles of 30° are typically used

- 2D- and special 1D-experiments need well defined pulse angles



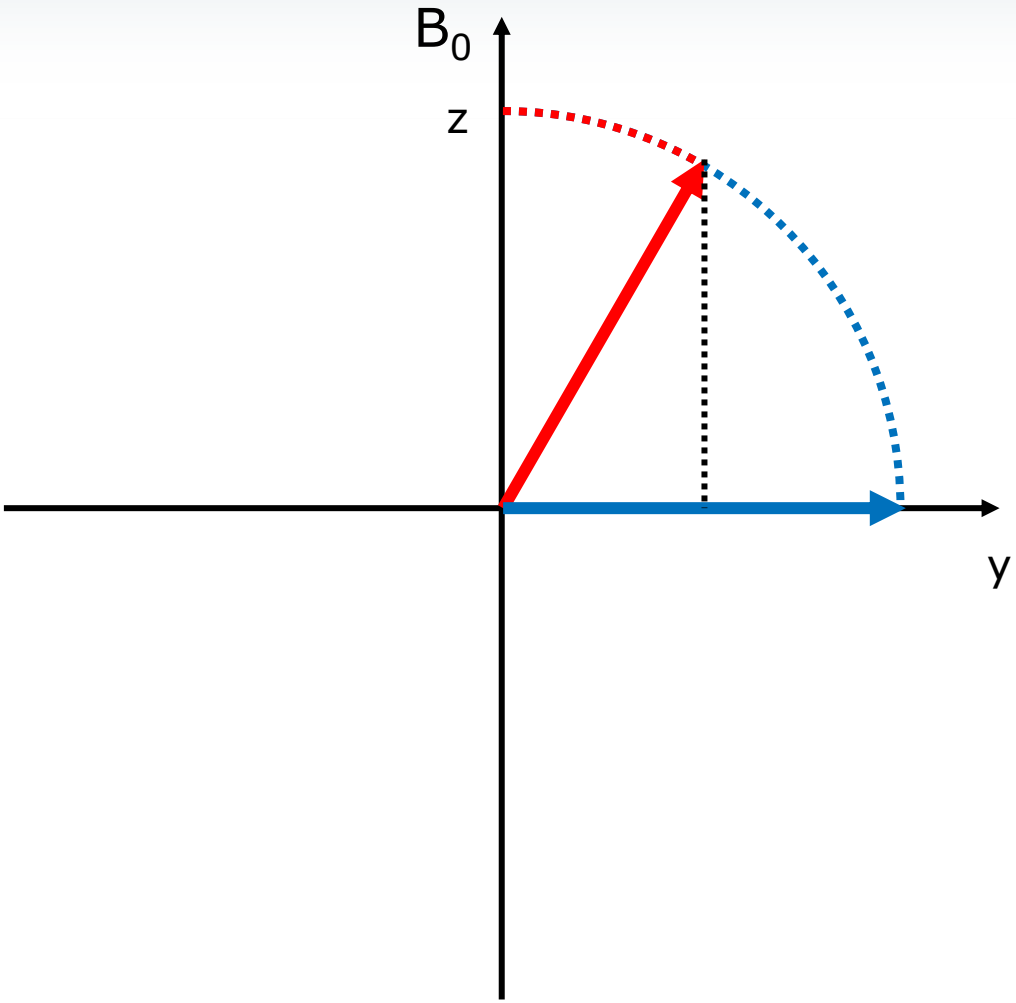
30° pulse

- Half the intensity of a 90° pulse

$$M_y = M_0 \times \sin\theta$$

$$M_y = M_0 \times \sin 30° = 0.5 \times M_0$$

- Shorter relaxation delay necessary

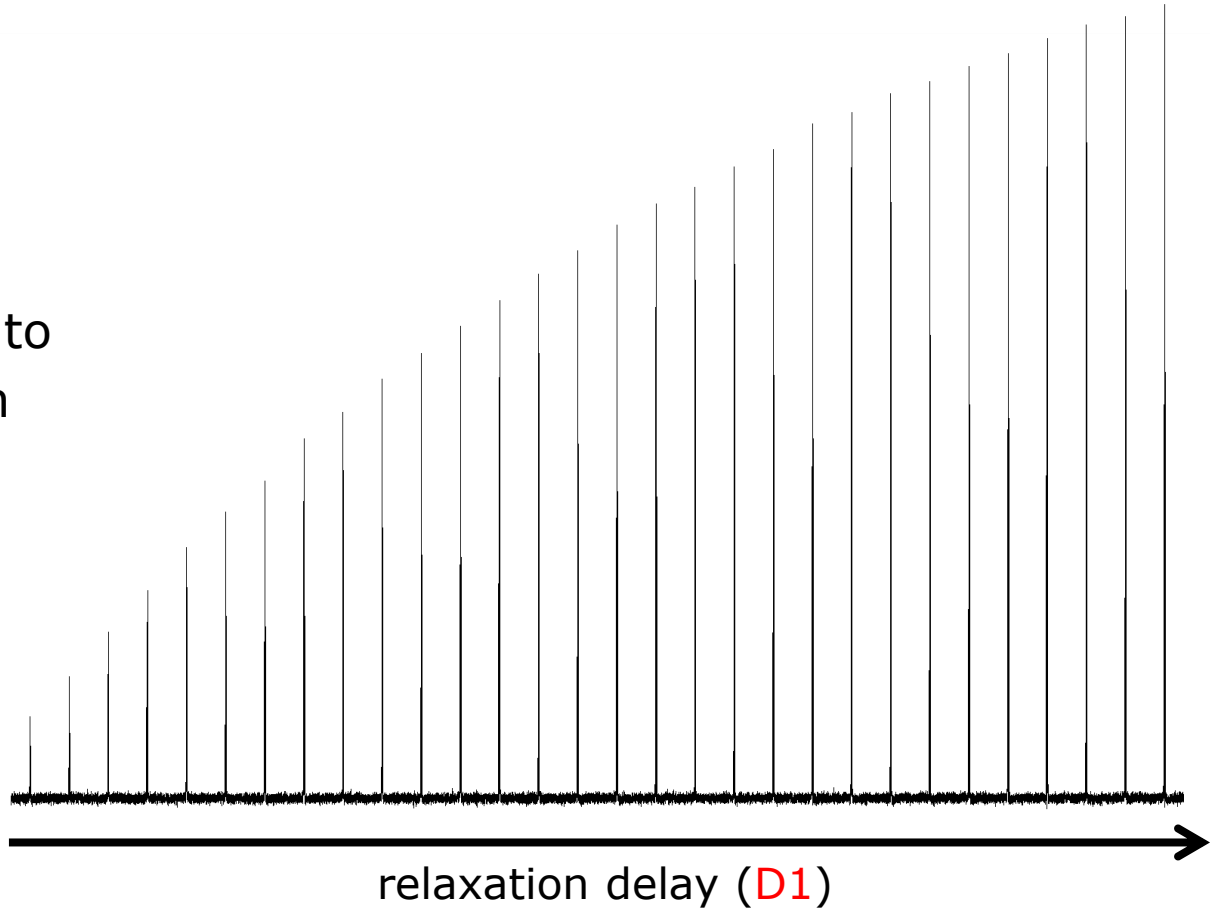


Parameters

- Other parameters are : the delay D1
  number of scans NS
  number of dummy scans DS
- D1 is executed before pulsing and is the time the sample needs to relax; typically in the range of 1 to 5s (special experiments need a longer delay like T_1 measurement).
- NS means that the pulse sequence is executed several times; typical for a 1H 1D-experiment are 16 scans.
- DS means the number of scans which are not saved. They are needed to get steady state (equilibrium).

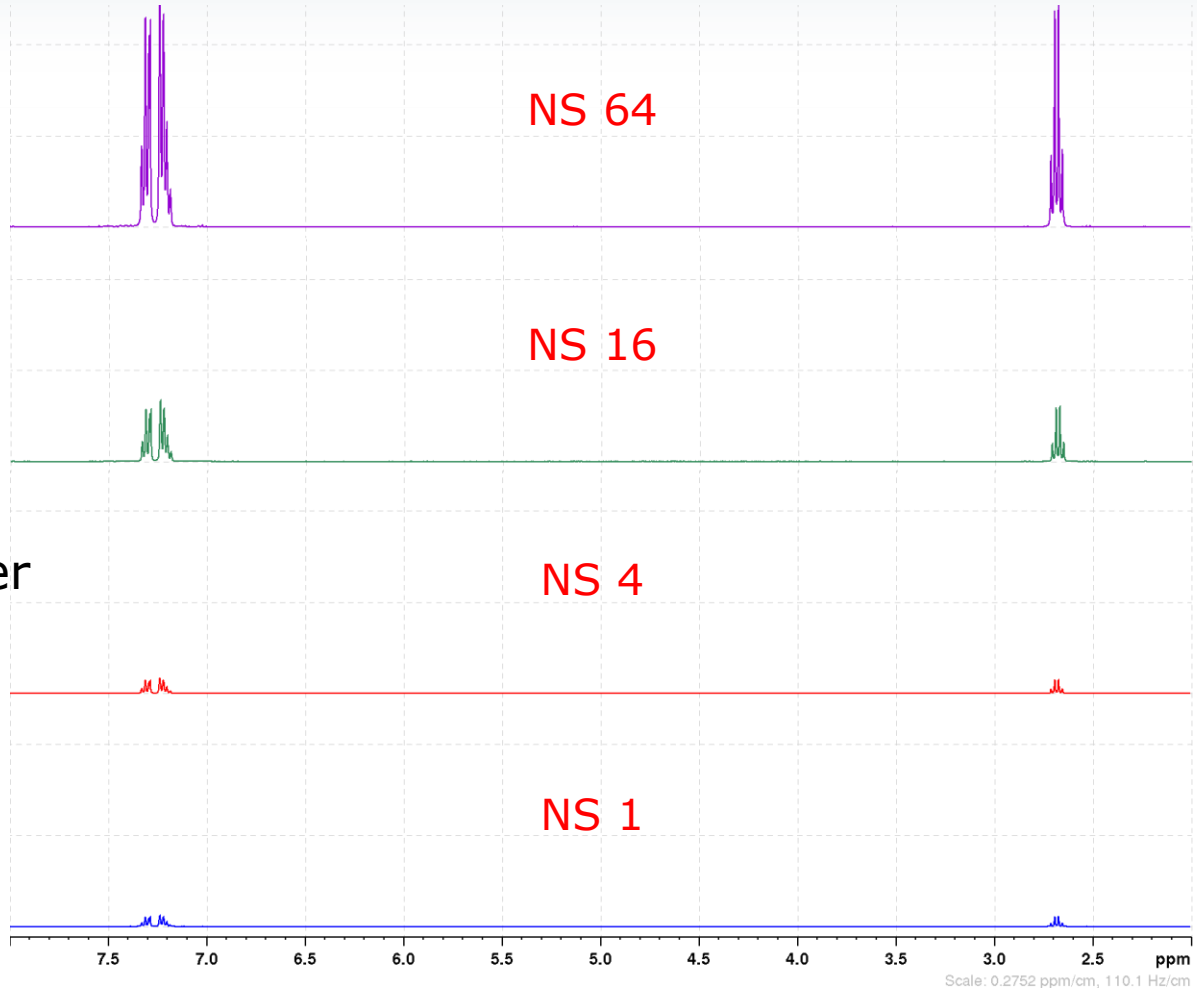
Relaxation delay

- Loss in intensity due to insufficient relaxation delay



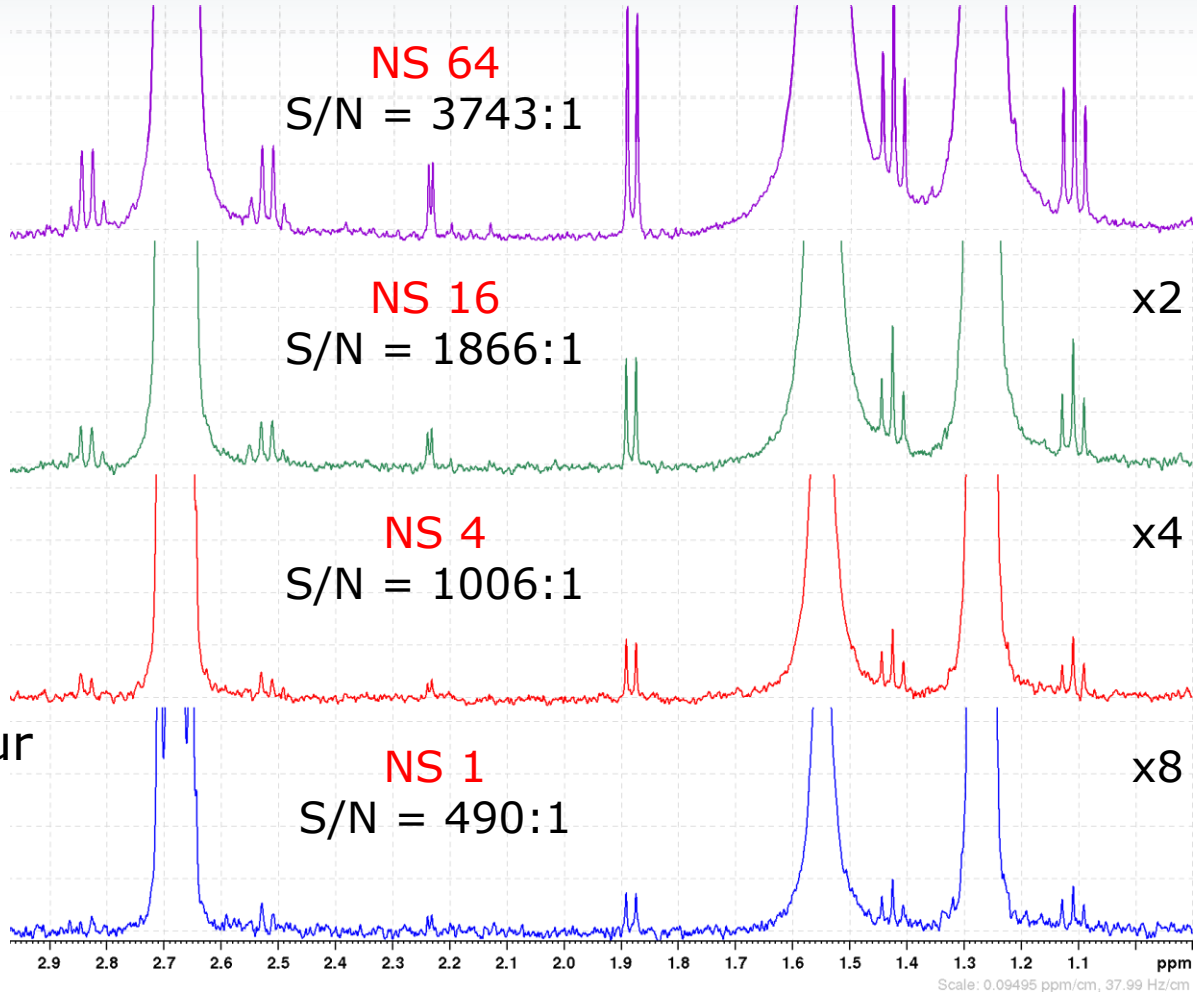
Number of scans

- Signal intensity increases with number of scans



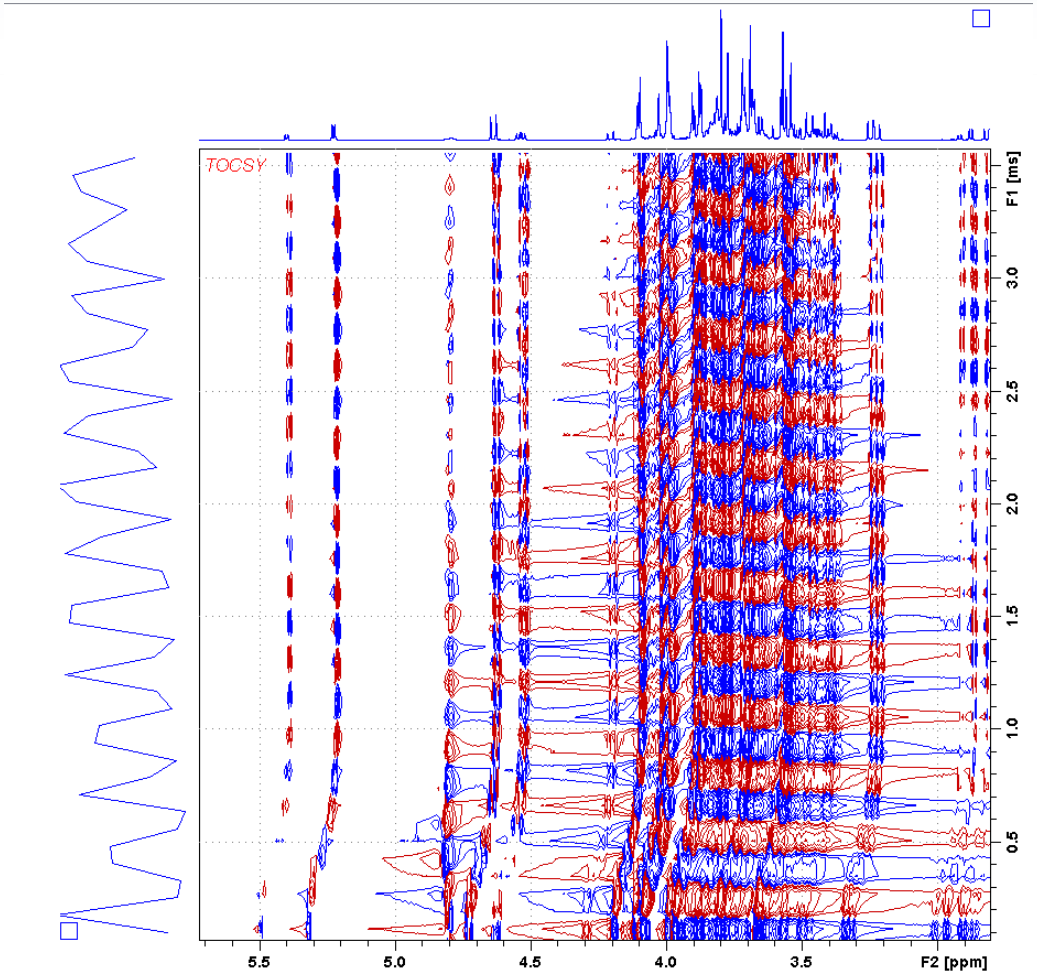
Number of scans

- Noise increases with square root of NS
- S/N increases with square root of NS as well
- Double S/N needs four times as many scans



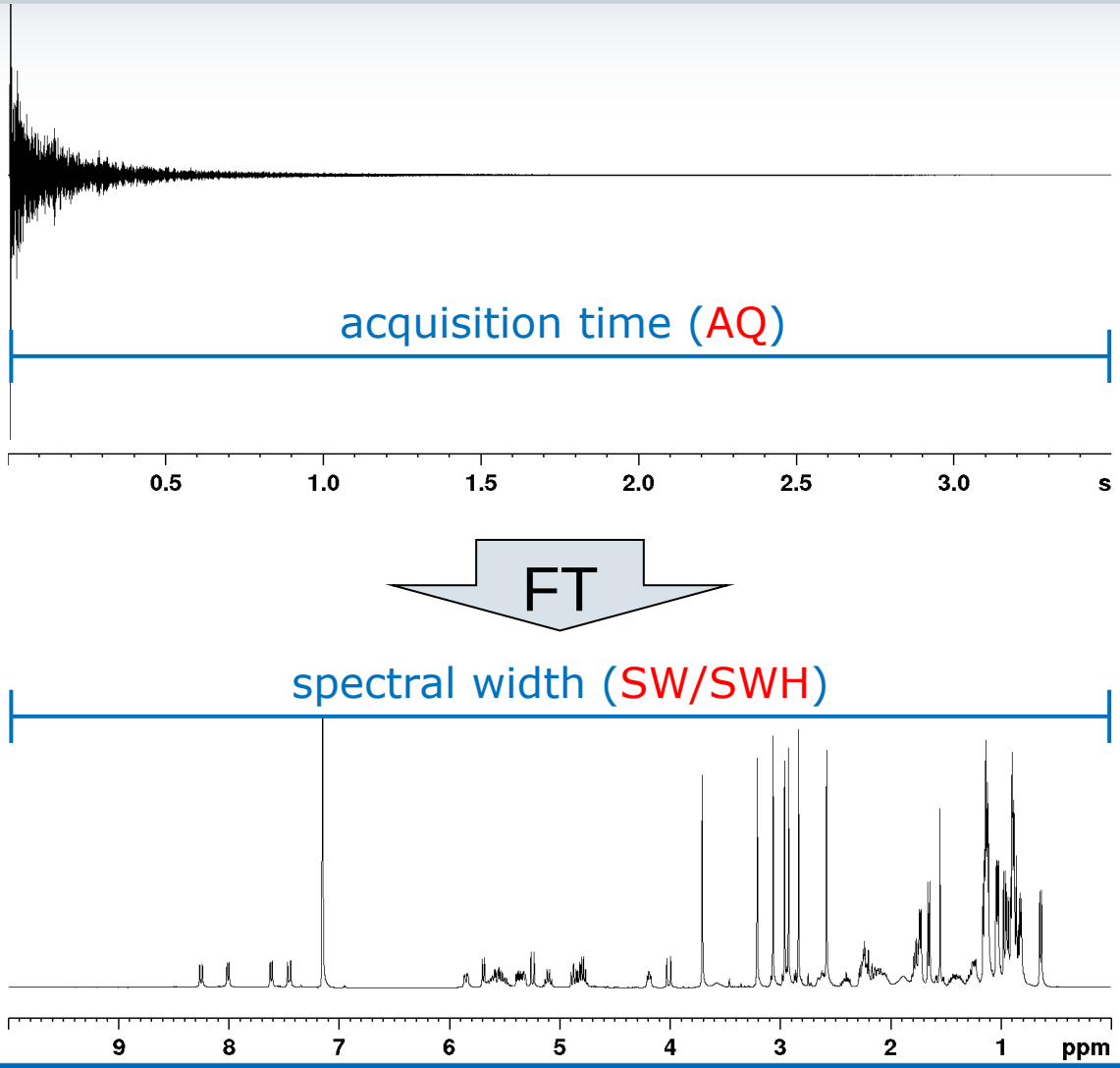
Number of dummy scans

- Not enough dummy scans
- Sample not at equilibrium



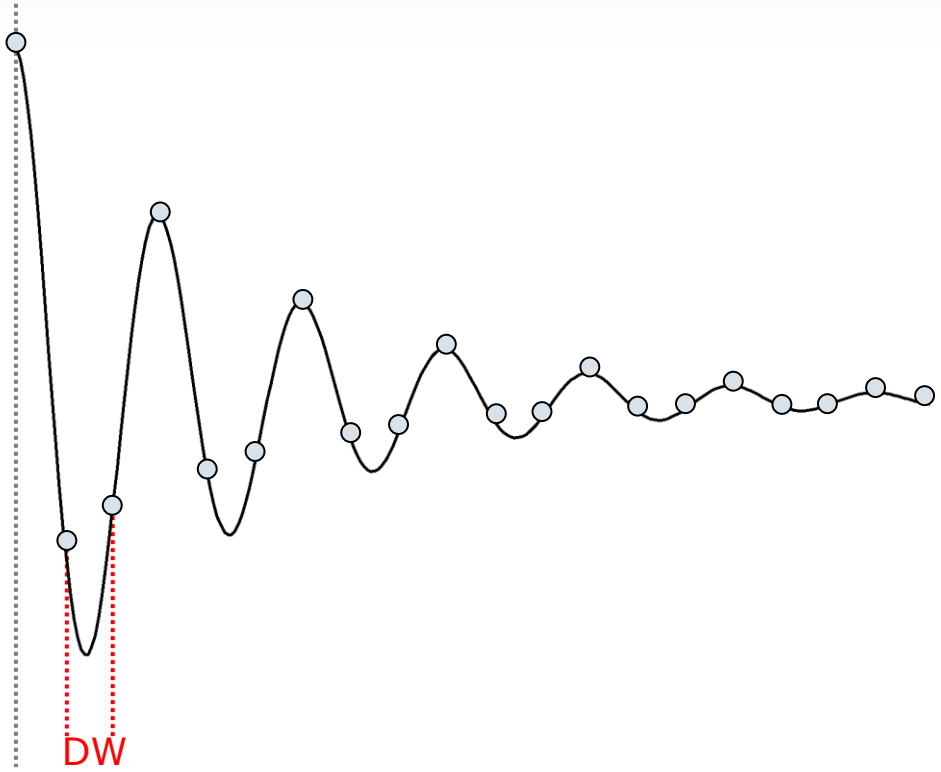
Resolution

- After the acquisition you will get the so called FID, a function of time $f(t)$.
- With the Fourier Transformation you will get a function of frequency $f(\nu)$, the spectrum.



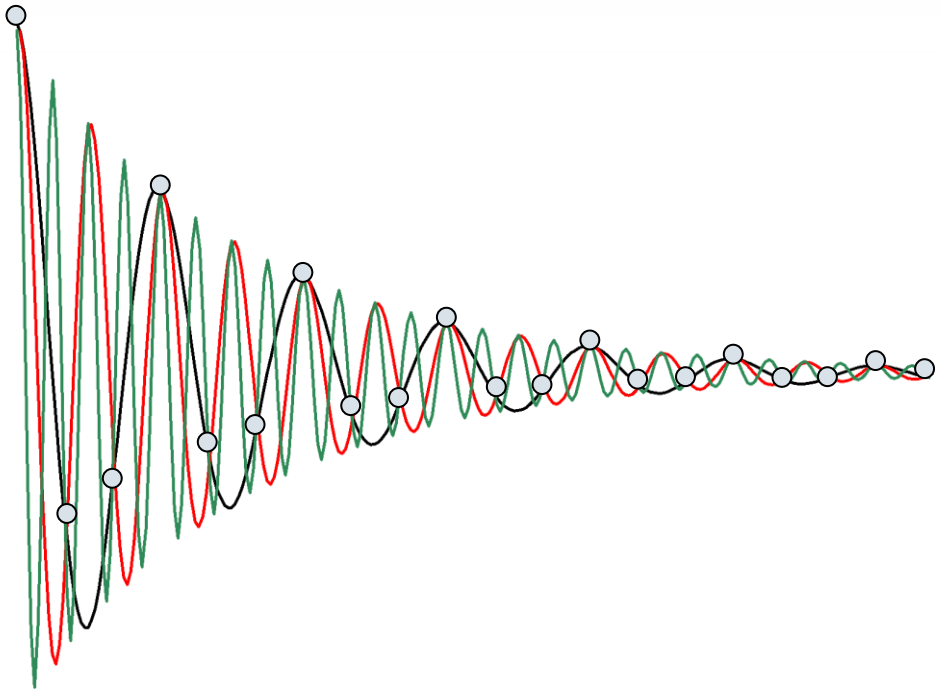
Digitization

- Data points must be equidistant
- the distance between two data points is called dwell time (DW)
- TD is the amount of data points that are acquired



Digitization

- To find a frequency f, at least two points per sine wave need to be measured



- Nyquist theorem:

$$SWH = \frac{1}{2 \cdot DW}$$

- spectral width SWH determines DW

Parameters

- Parameters are :
  time domain TD
  spectral width SW/SWH
  irradiation frequency offset O1/O1P
  dwell time DW
  acquisition time AQ
- TD number of raw data points that are acquired in one scan. For a 1D-experiment is typically set to 64k (for a 2D-experiment 1k, 2k or 4k are typical values).
- SW/SWH is the spectral width in ppm/Hz. Depends on nucleus (15ppm for 1H, 240ppm for 13C). Defines dwell time DW.
- O1/O1P represents the irradiation frequency offset in Hz/ppm
- DW (dwell time) is the time between two data points.
- AQ represents the time to acquire one FID. Defined by TD × DW.

- **Pulse programs**

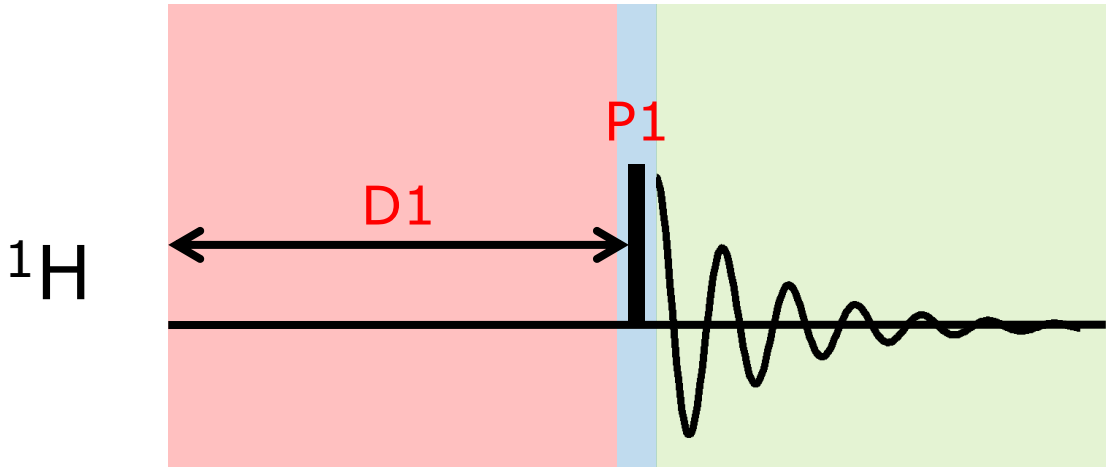
Pulse programs

- Pulse programs tell the spectrometer what to do when.

- Building blocks are:

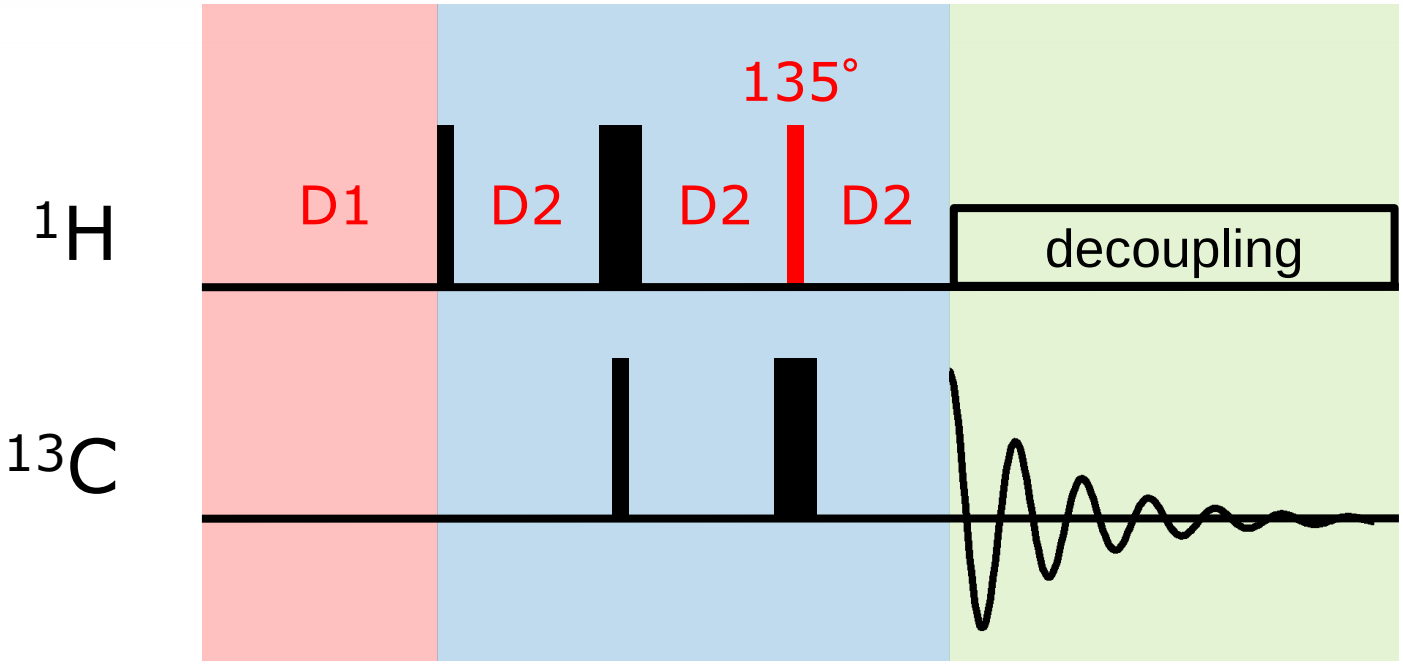
- **Relaxation delay**: time needed for relaxation
- **Preparation**: spins are excited by one or more pulses
- **Acquisition**: Signal is detected as a function of time

Pulse programs
ZG



Relaxation delay	Preparation	Acquisition

Pulse programs
DEPT135



Relaxation delay	Preparation	Acquisition

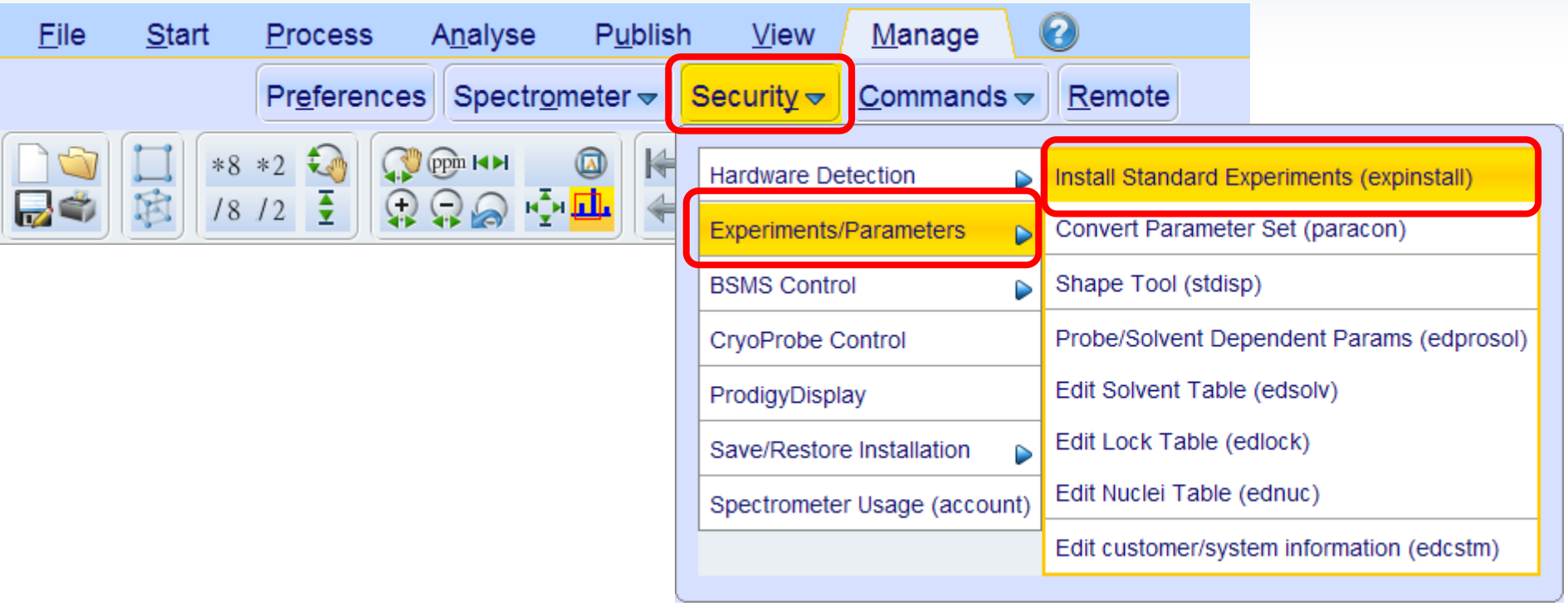
- **How to set up the spectrometer?**

Basic Settings

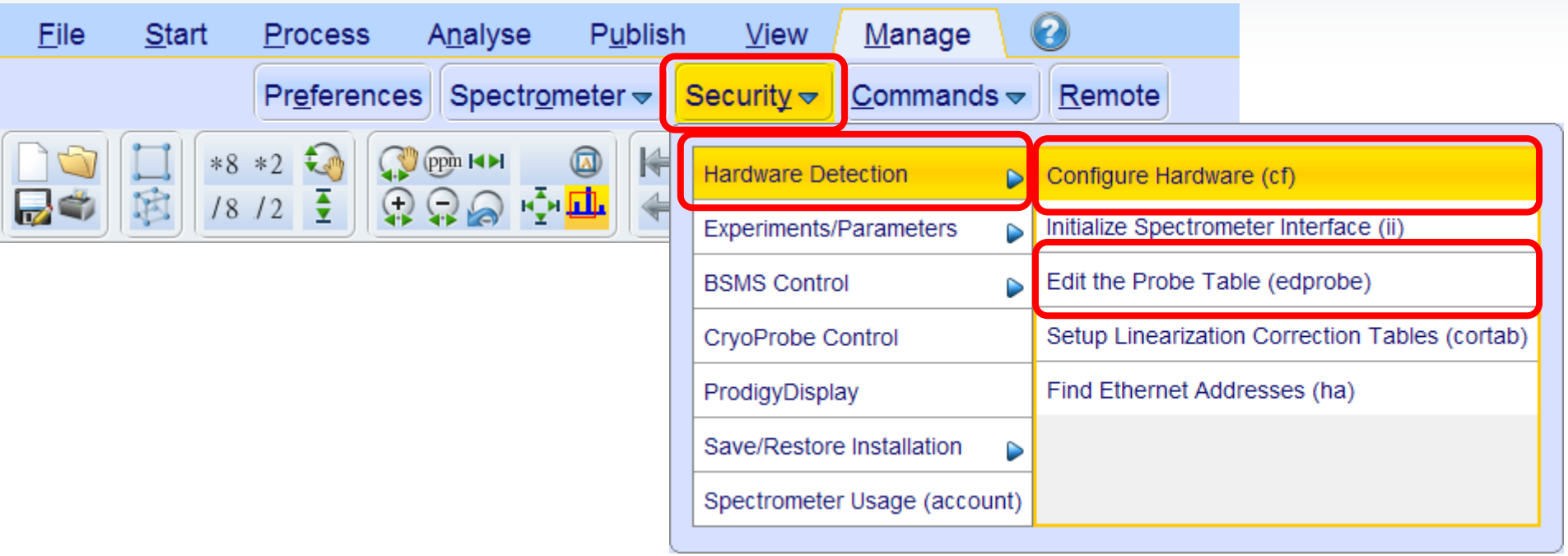
- Configuration of the spectrometer [**cf**]
- Installation of pulse programs, parameter sets etc. [**expinstall**]
- Choosing probe [**edprobe**]

- The commands [**cf**] and [**expinstall**] have to be executed when new software is installed!
- [**expinstall**] has to be executed after changing the routing of the spectrometer.
- The command [**ii restart**] can be used when there is a problem with the instrument.

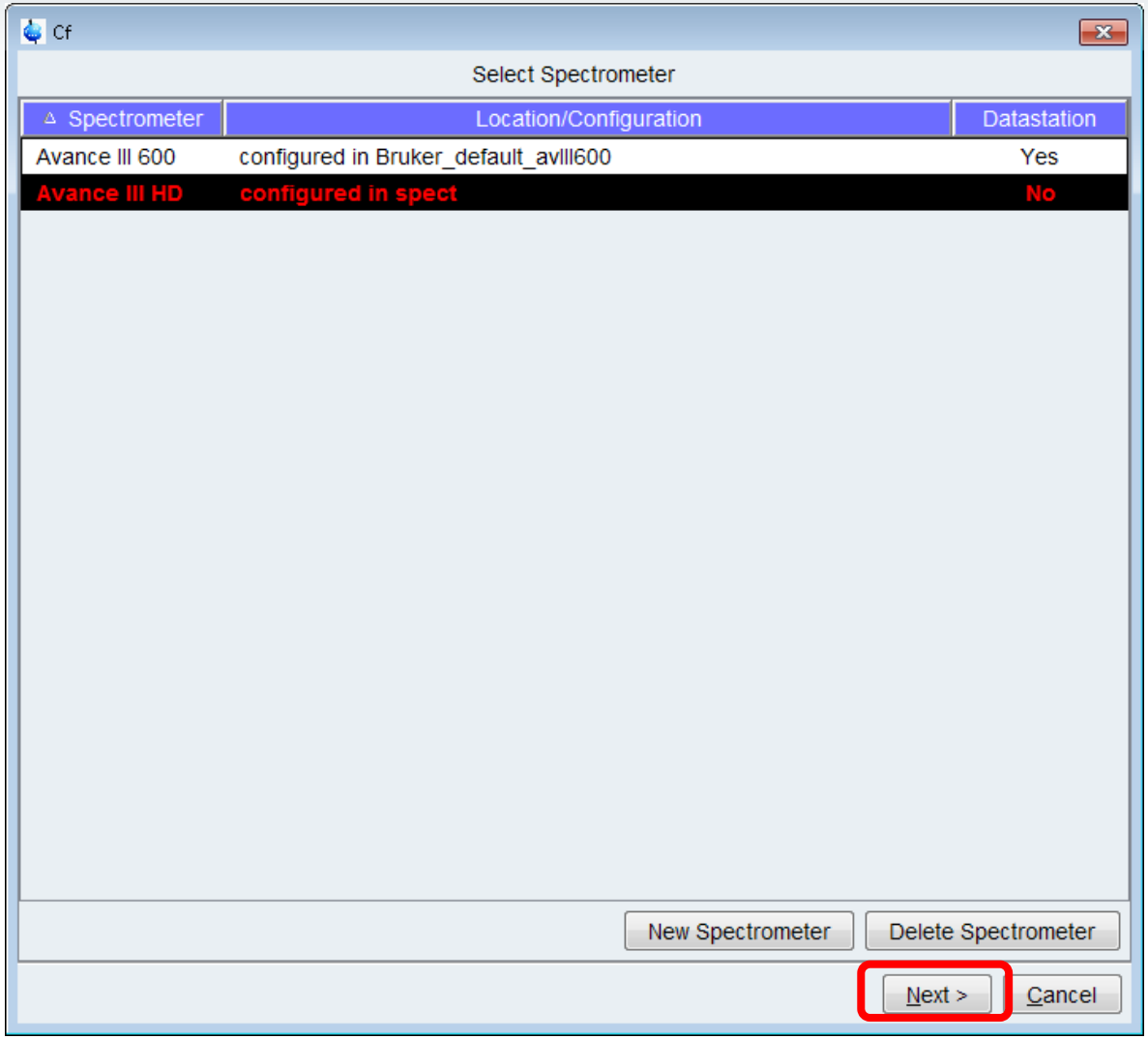
Install Standard Experiments [**expinstall**]



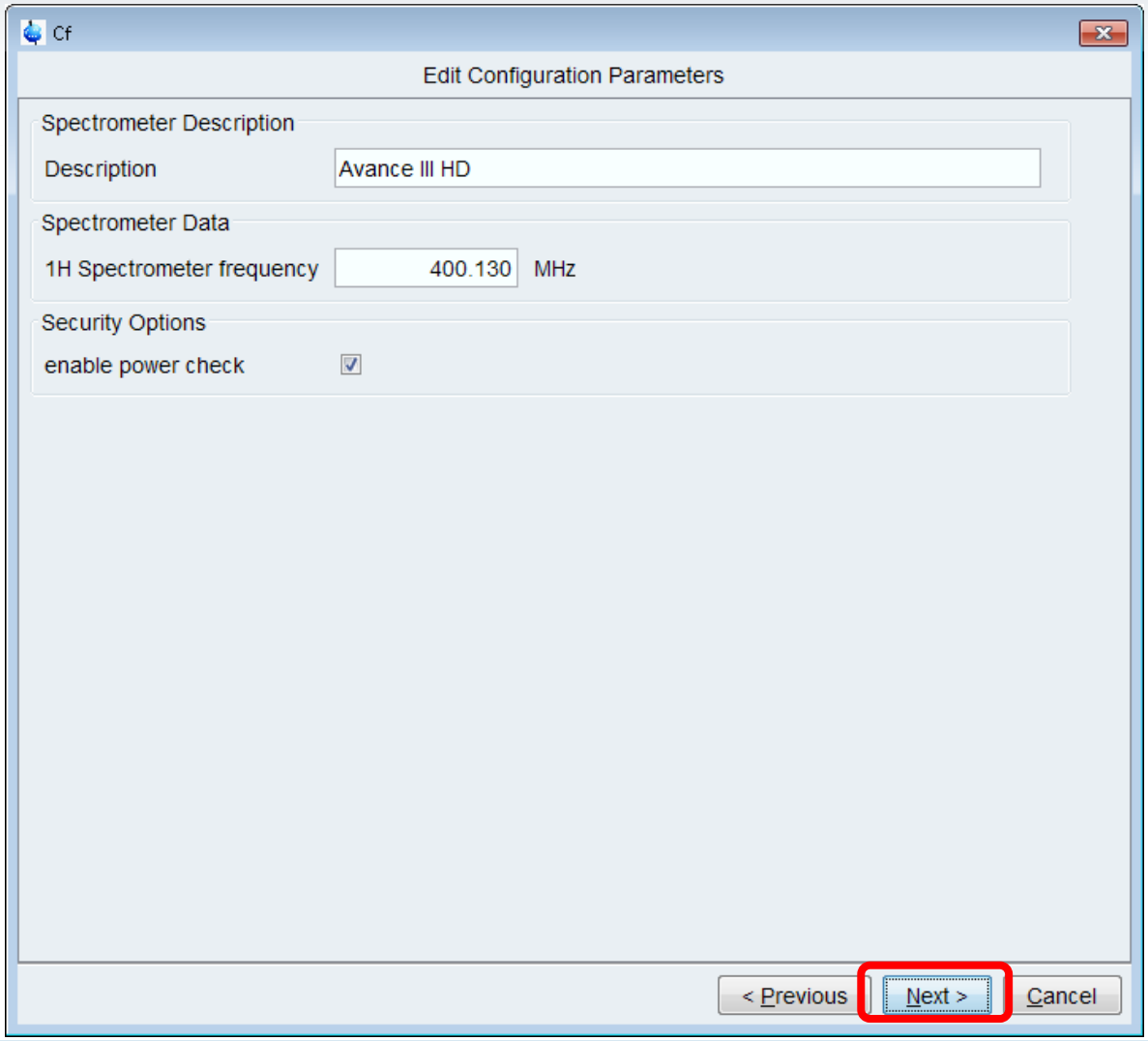
Configure hardware [cf]



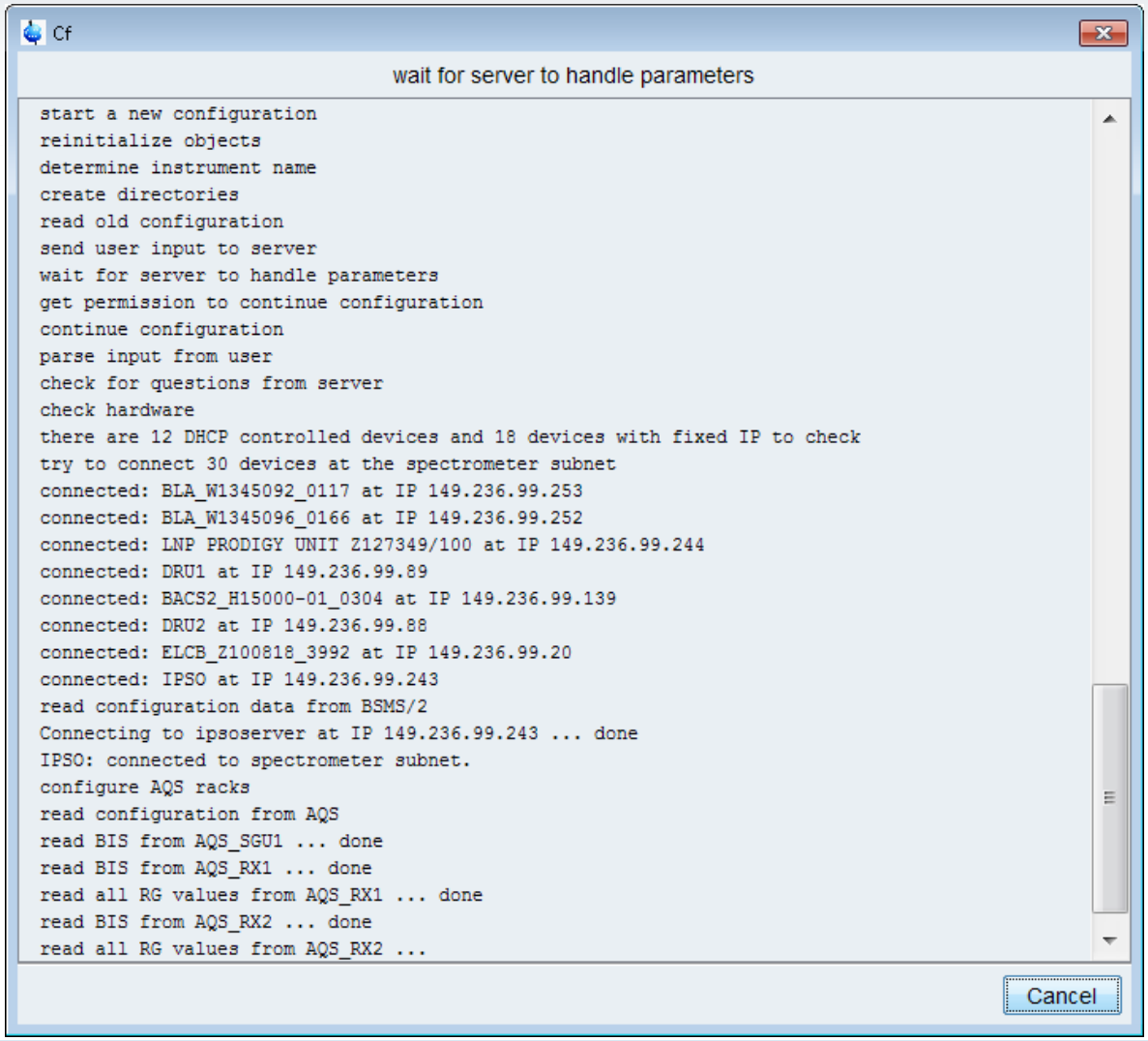
Configure hardware
[cf]



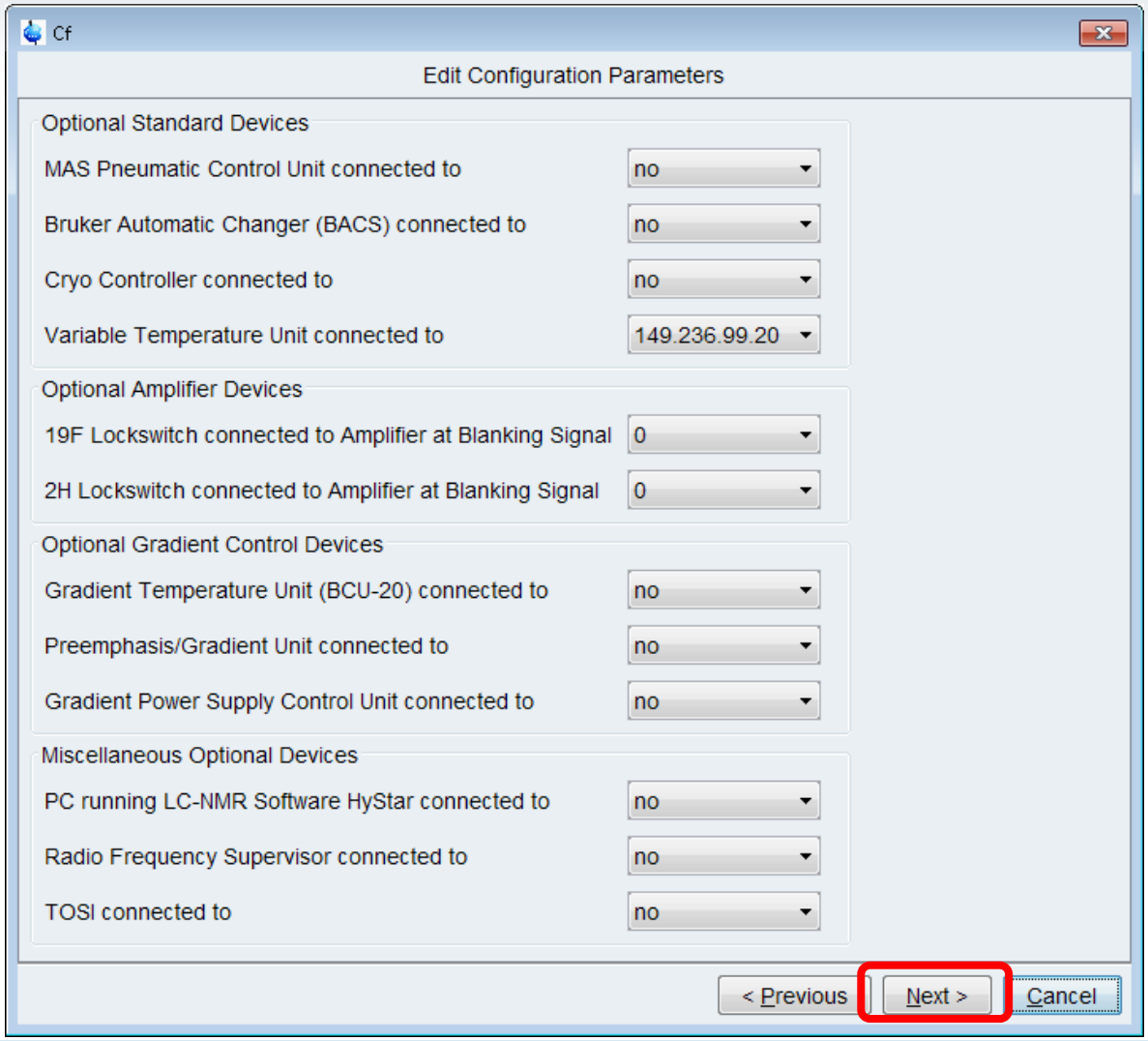
Configure hardware
[cf]



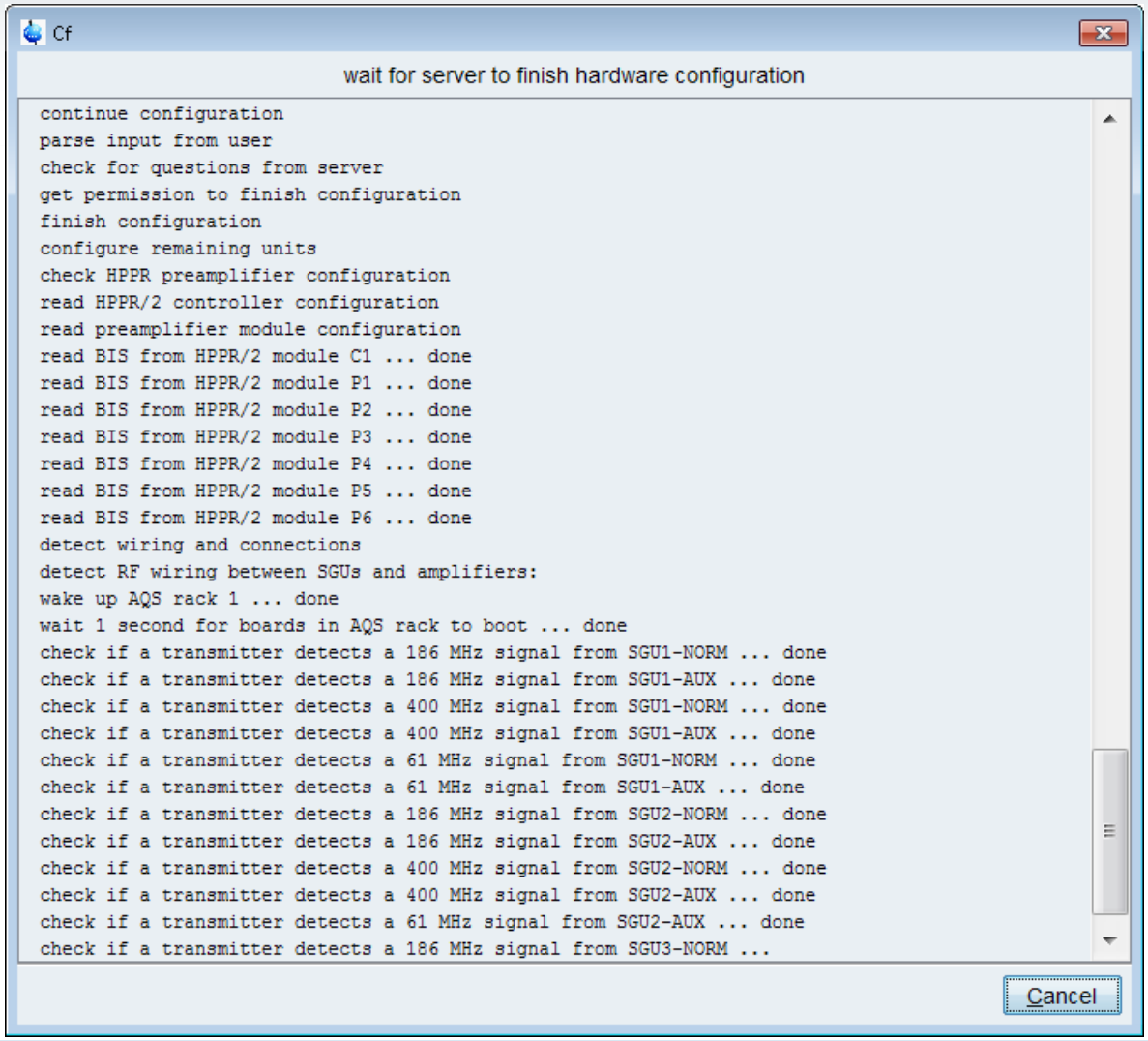
Configure hardware [cf]



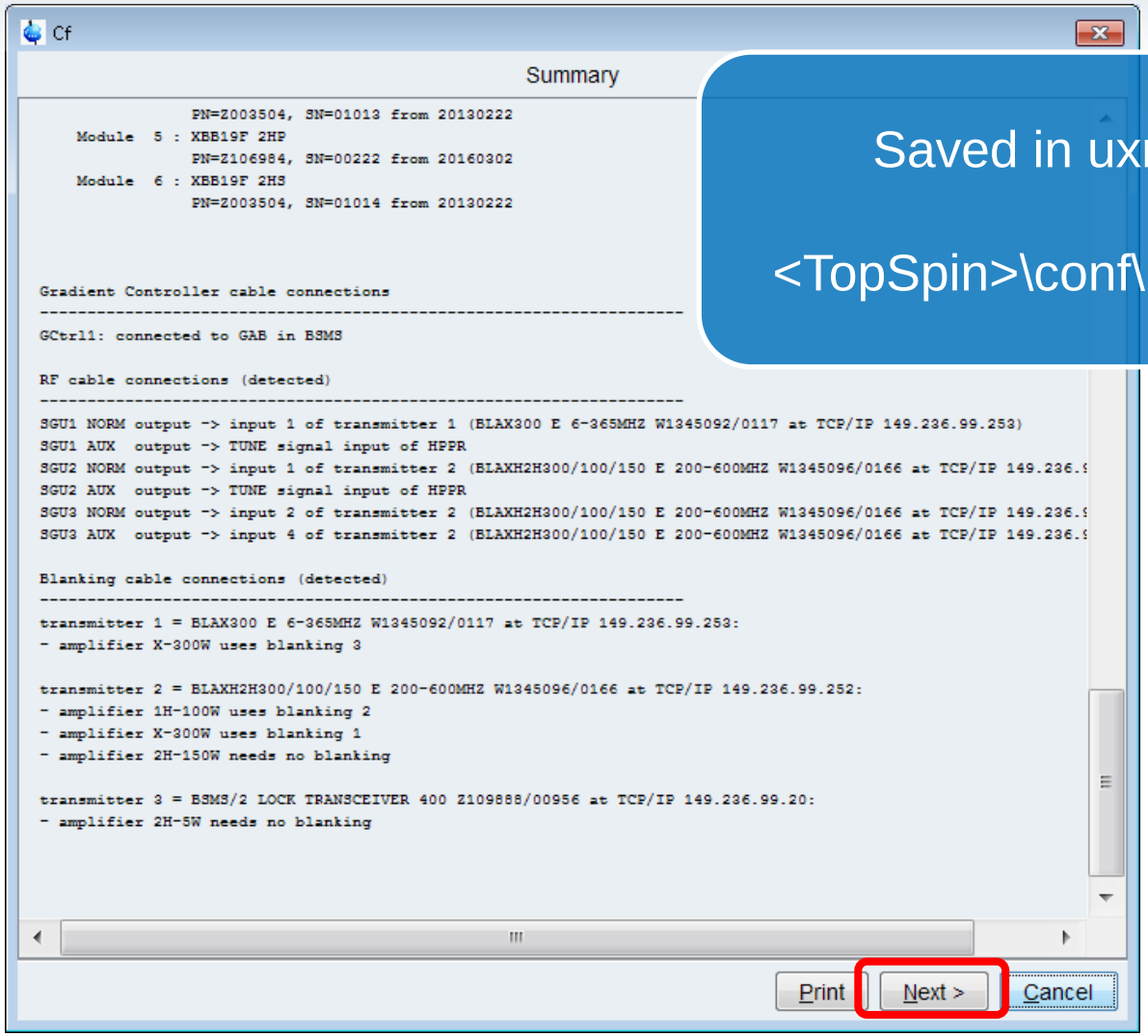
Configure hardware
[cf]



Configure hardware [cf]



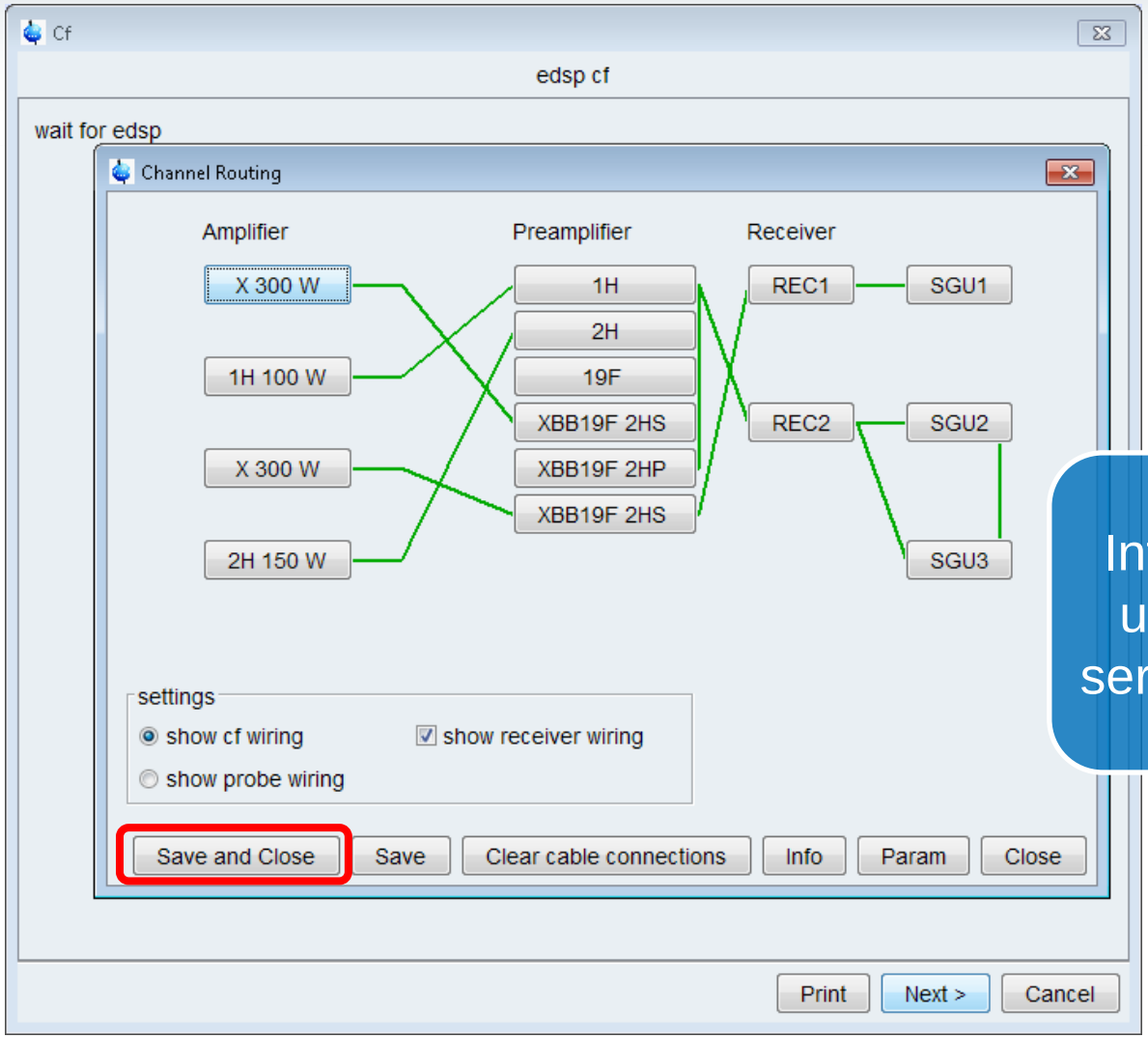
Configure hardware
[cf]



Saved in uxnmr.info

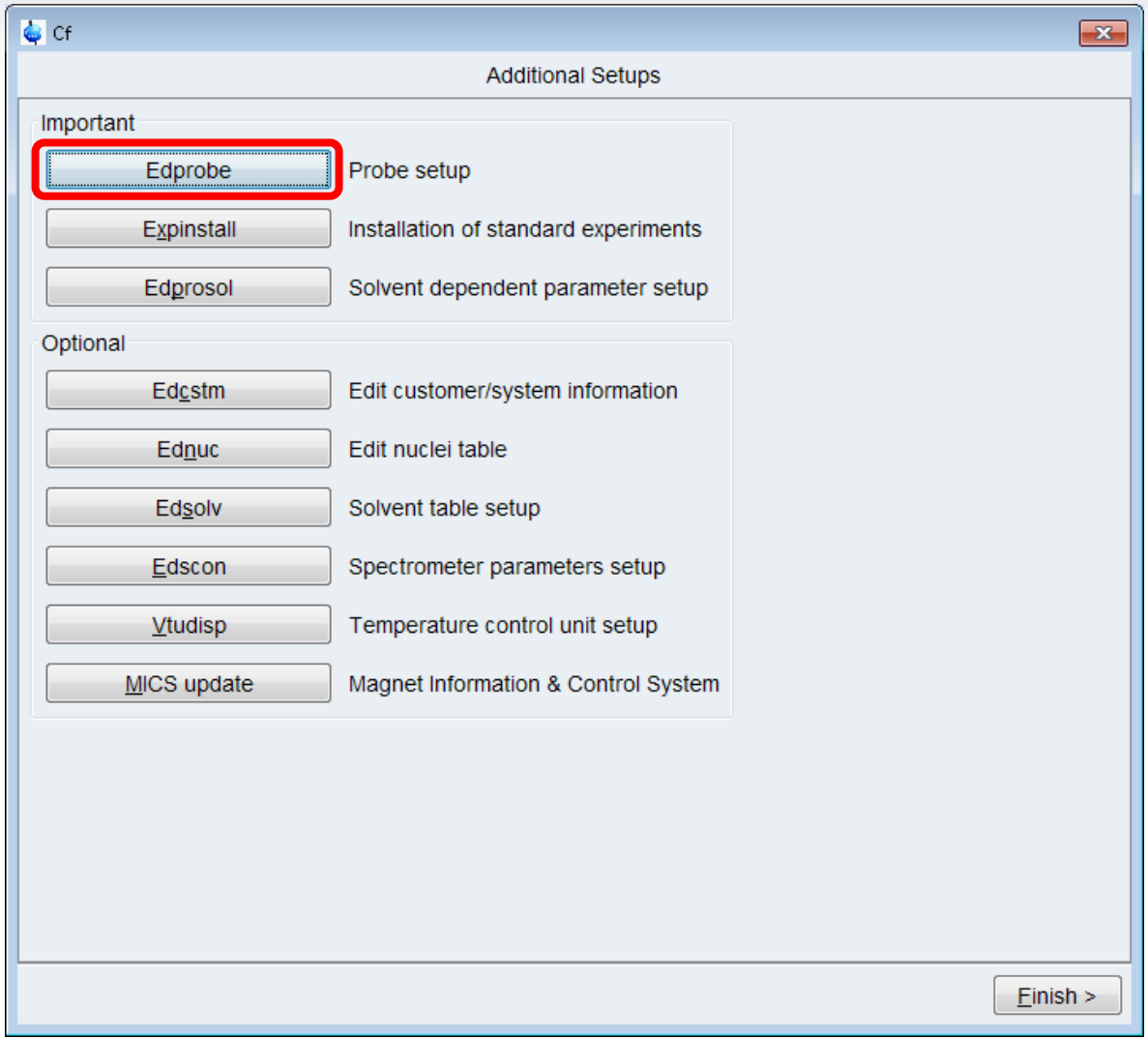
<TopSpin>\conf\instr\<spec>

Configure hardware [cf]

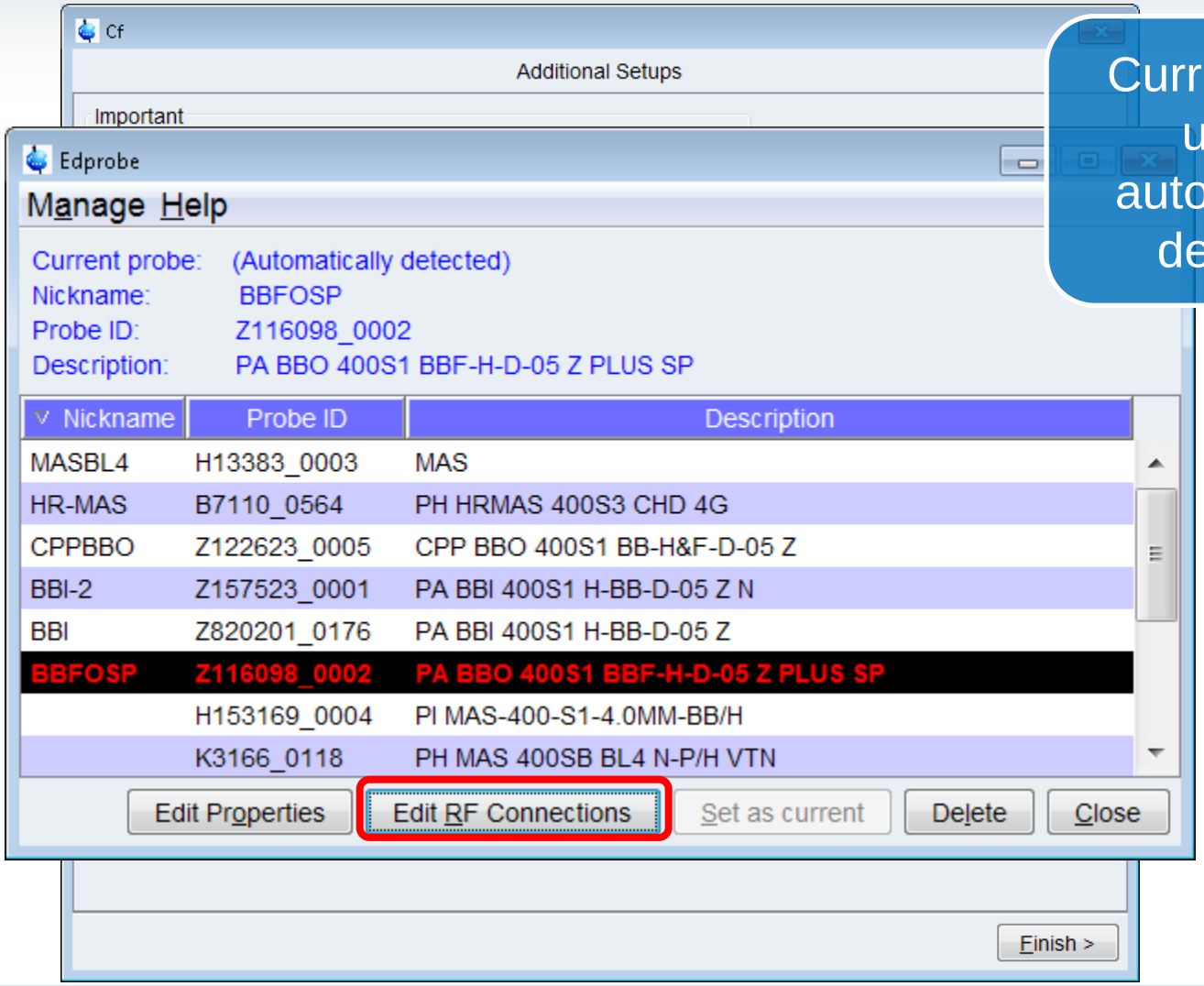


Internal routing usually set by service engineer.

Configure hardware
[cf]

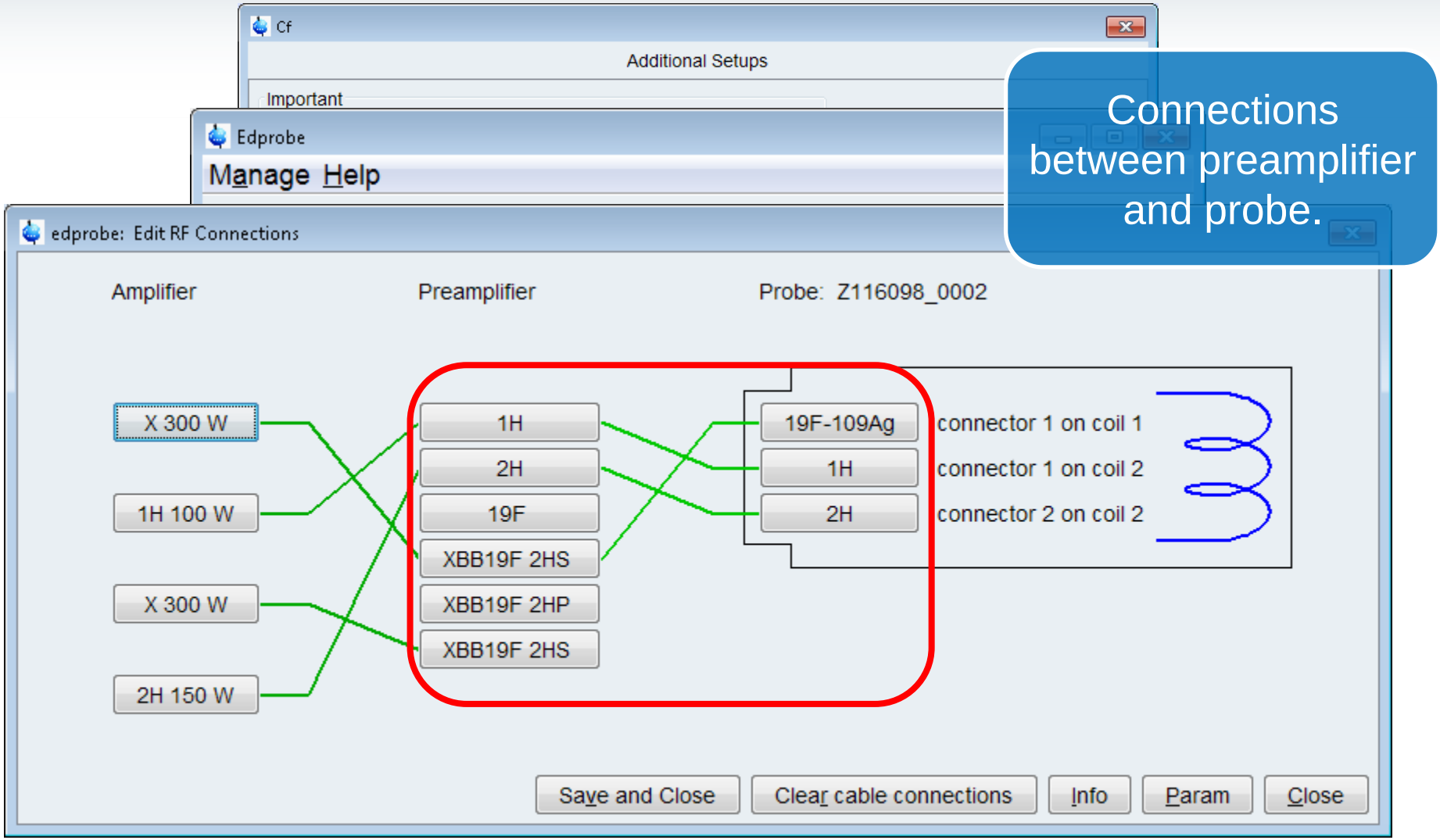


Edit Probe [**edprobe**]



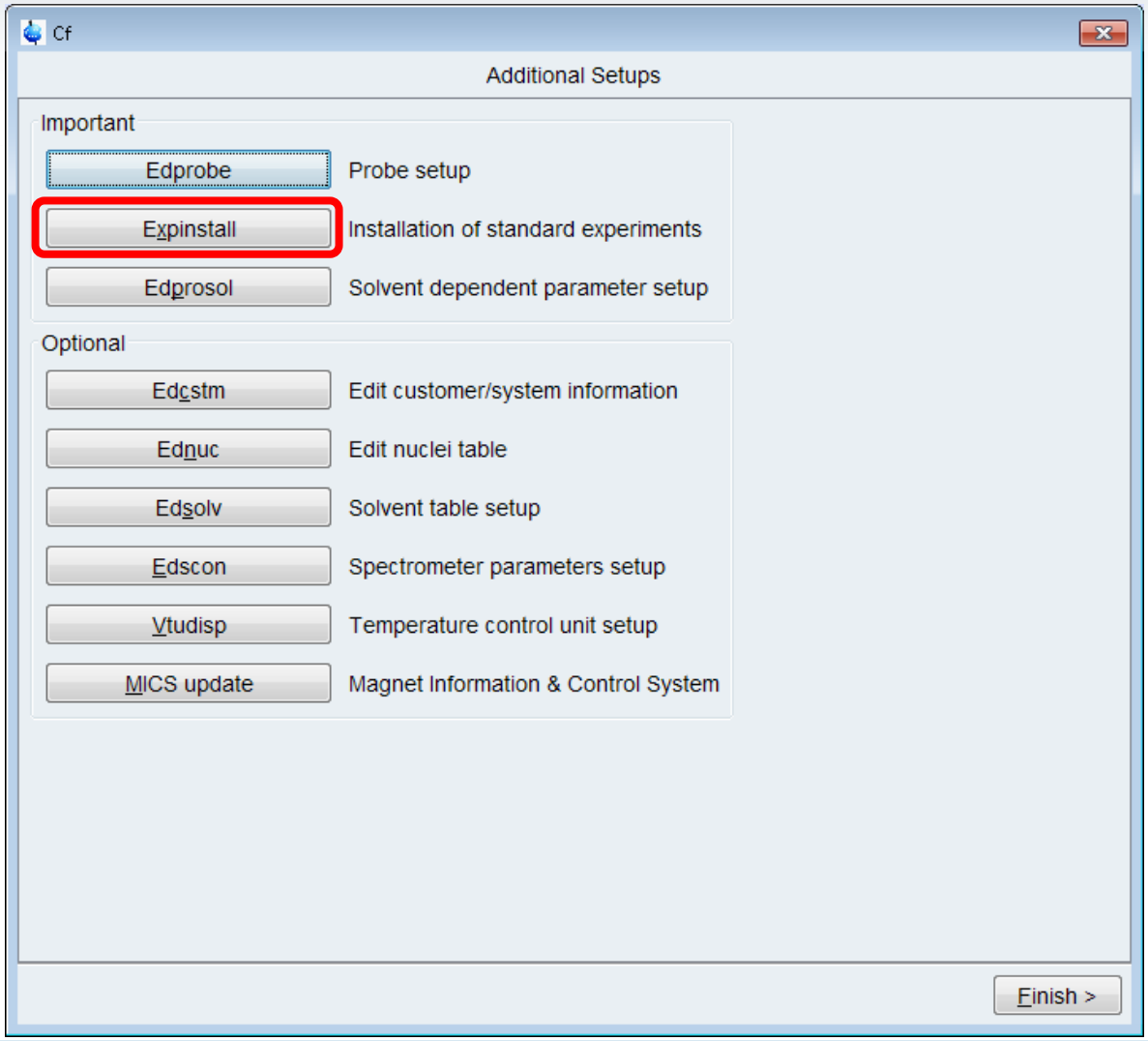
Current probe usually automatically detected.

Edit Probe [edprobe]

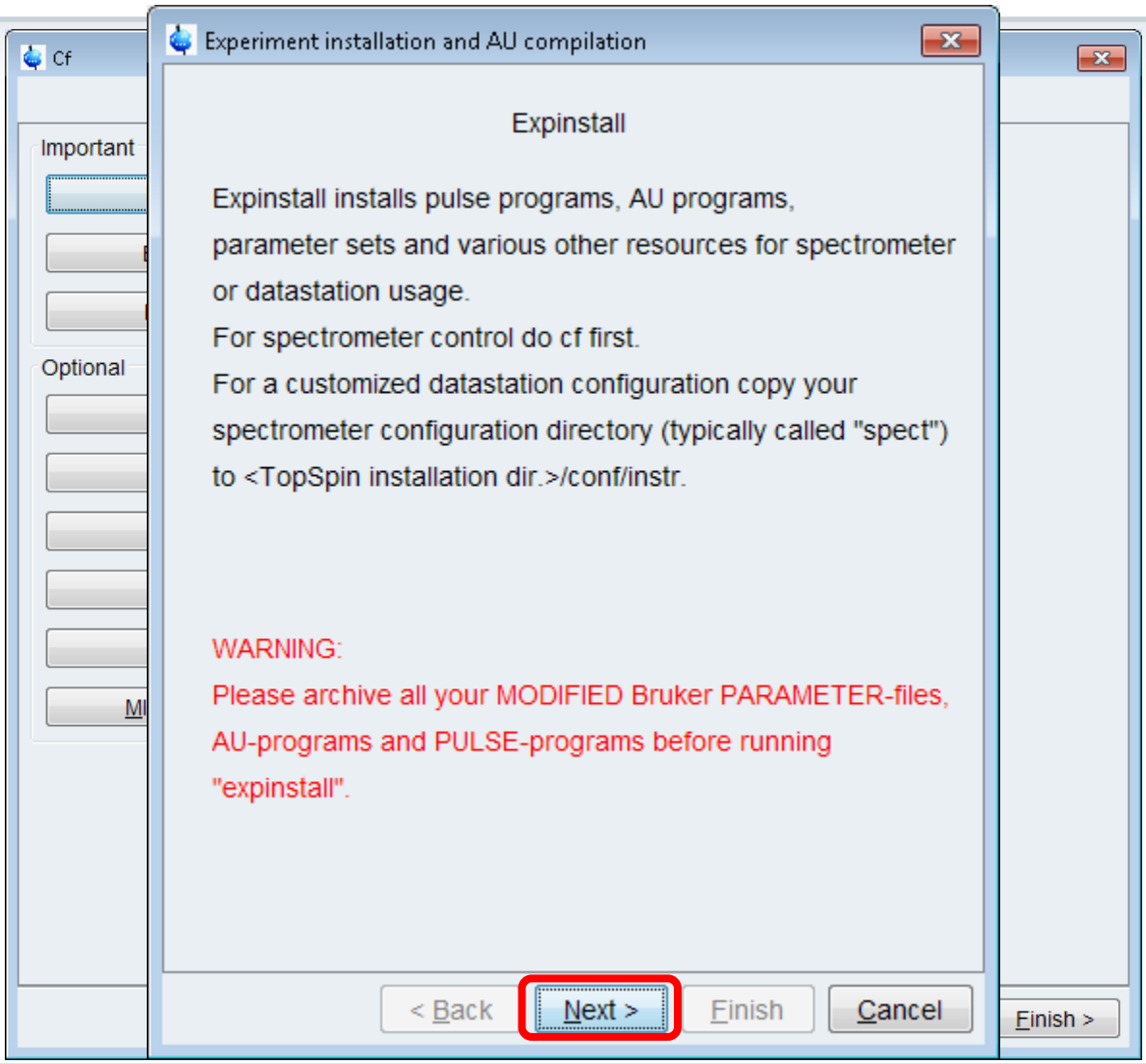


Connections between preamplifier and probe.

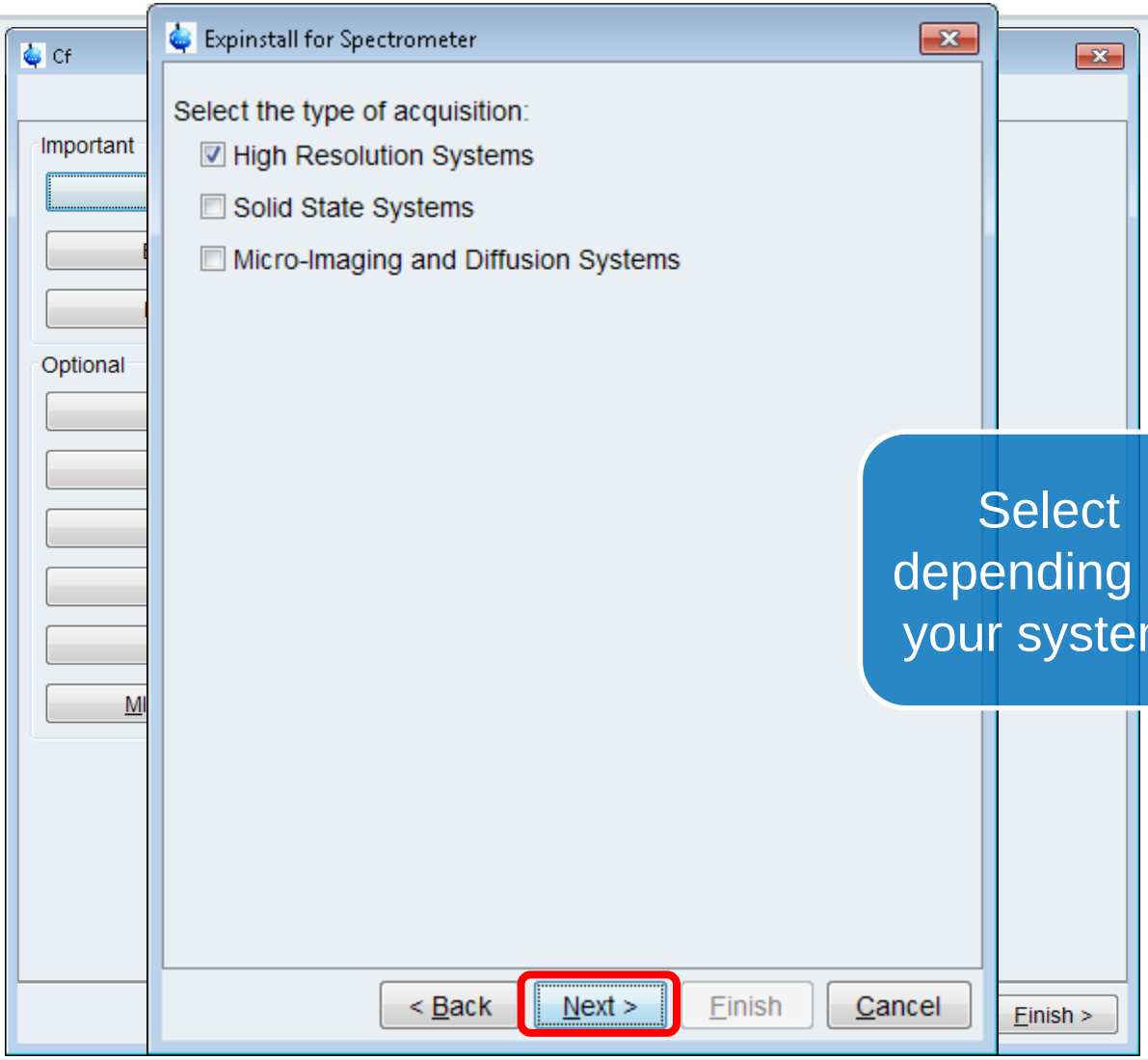
Configure hardware [cf]



Install Standard Experiments [**expinstall**]

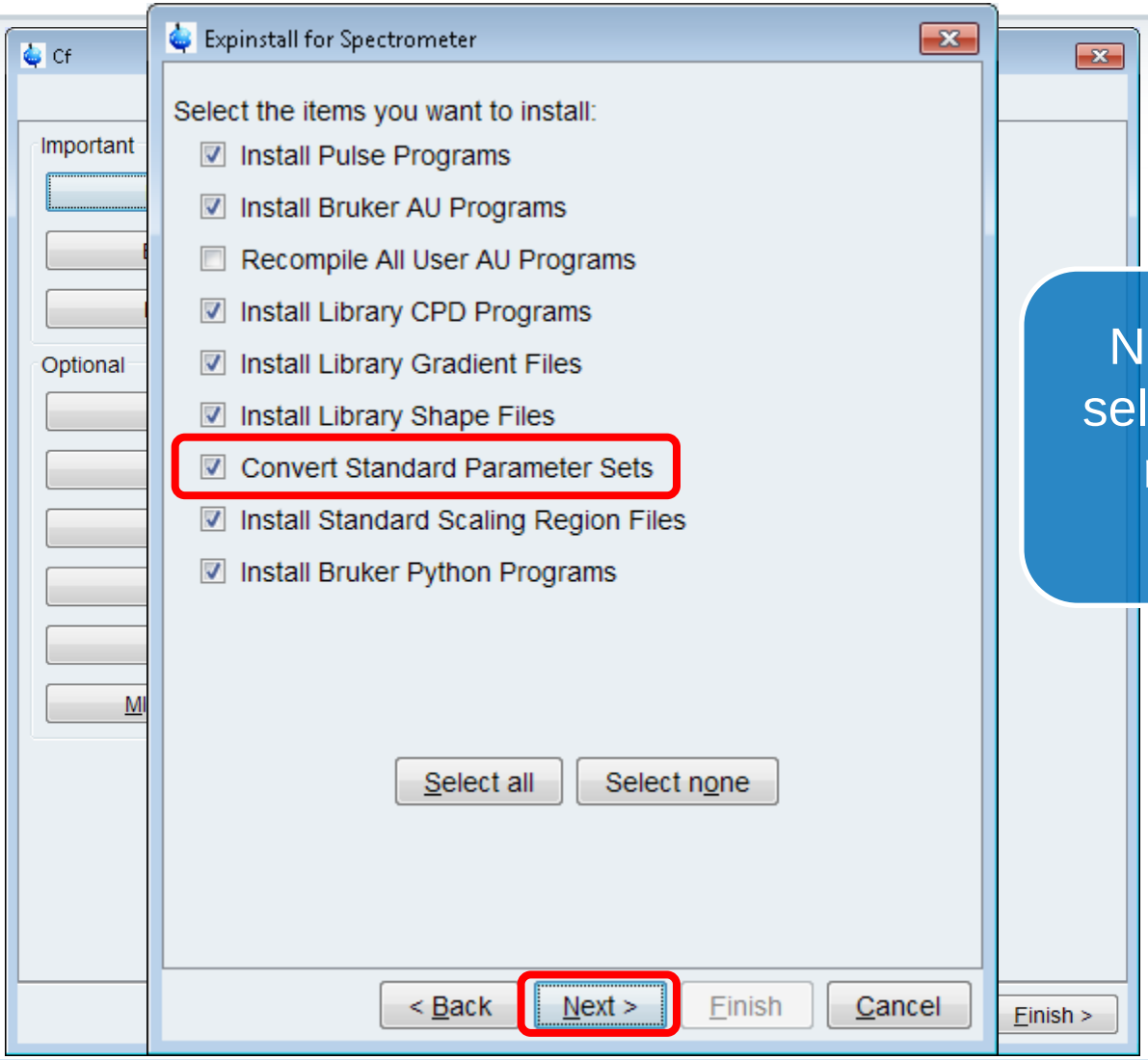


Install Standard Experiments [**expinstall**]



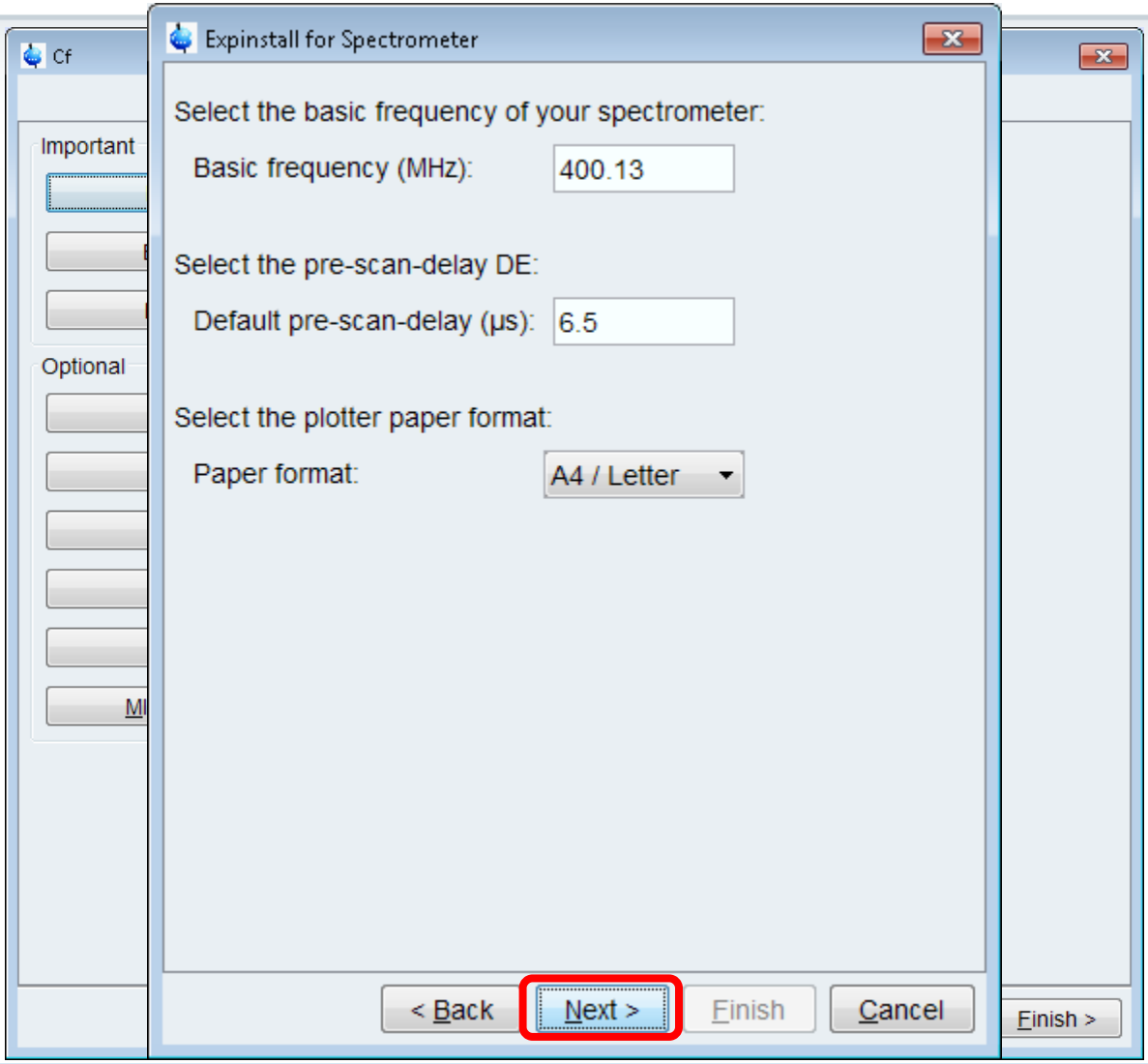
Select depending on your system.

Install Standard Experiments [**expinstall**]

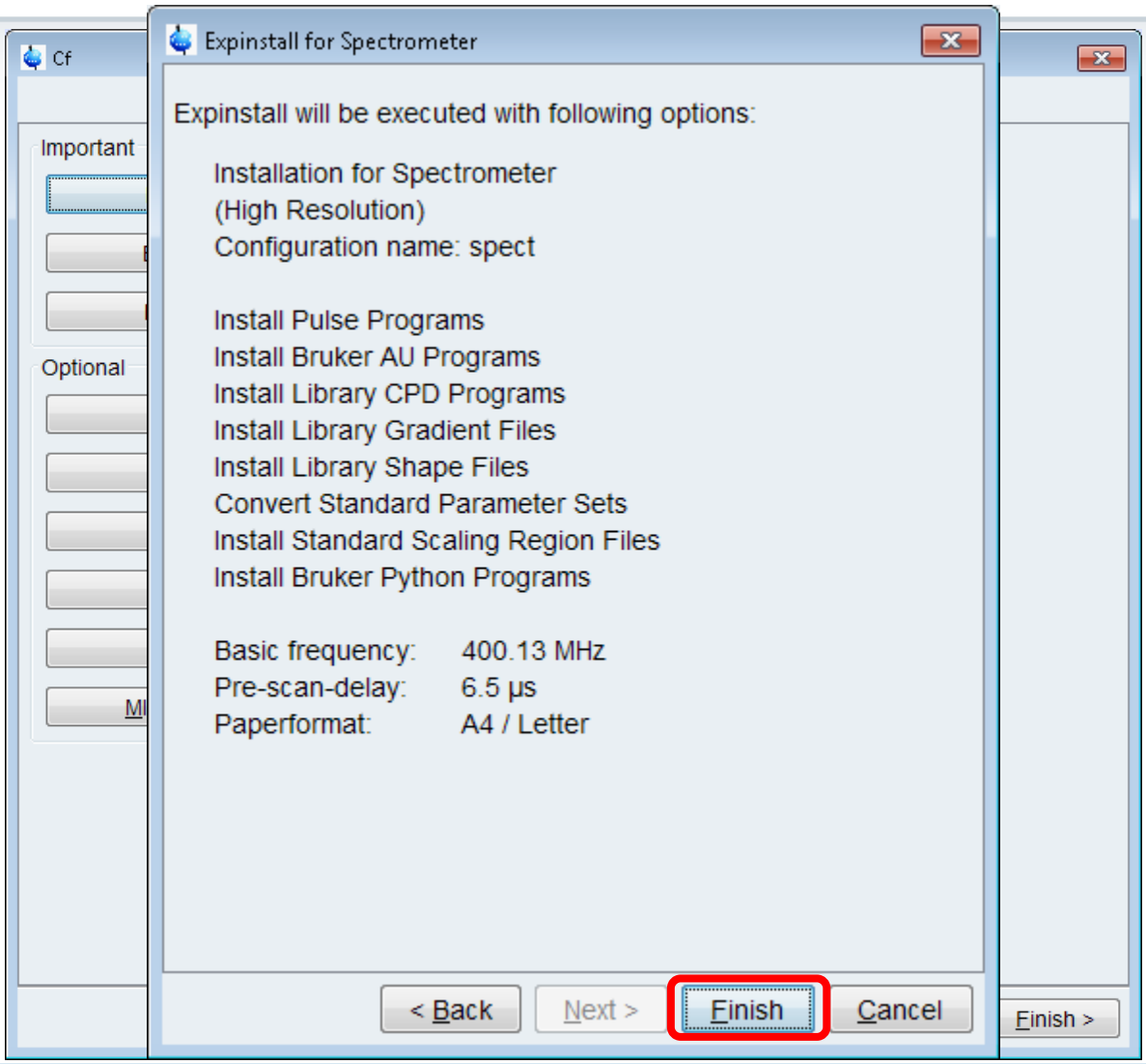


Needs to be selected when routing is changed

Install Standard Experiments [**expinstall**]

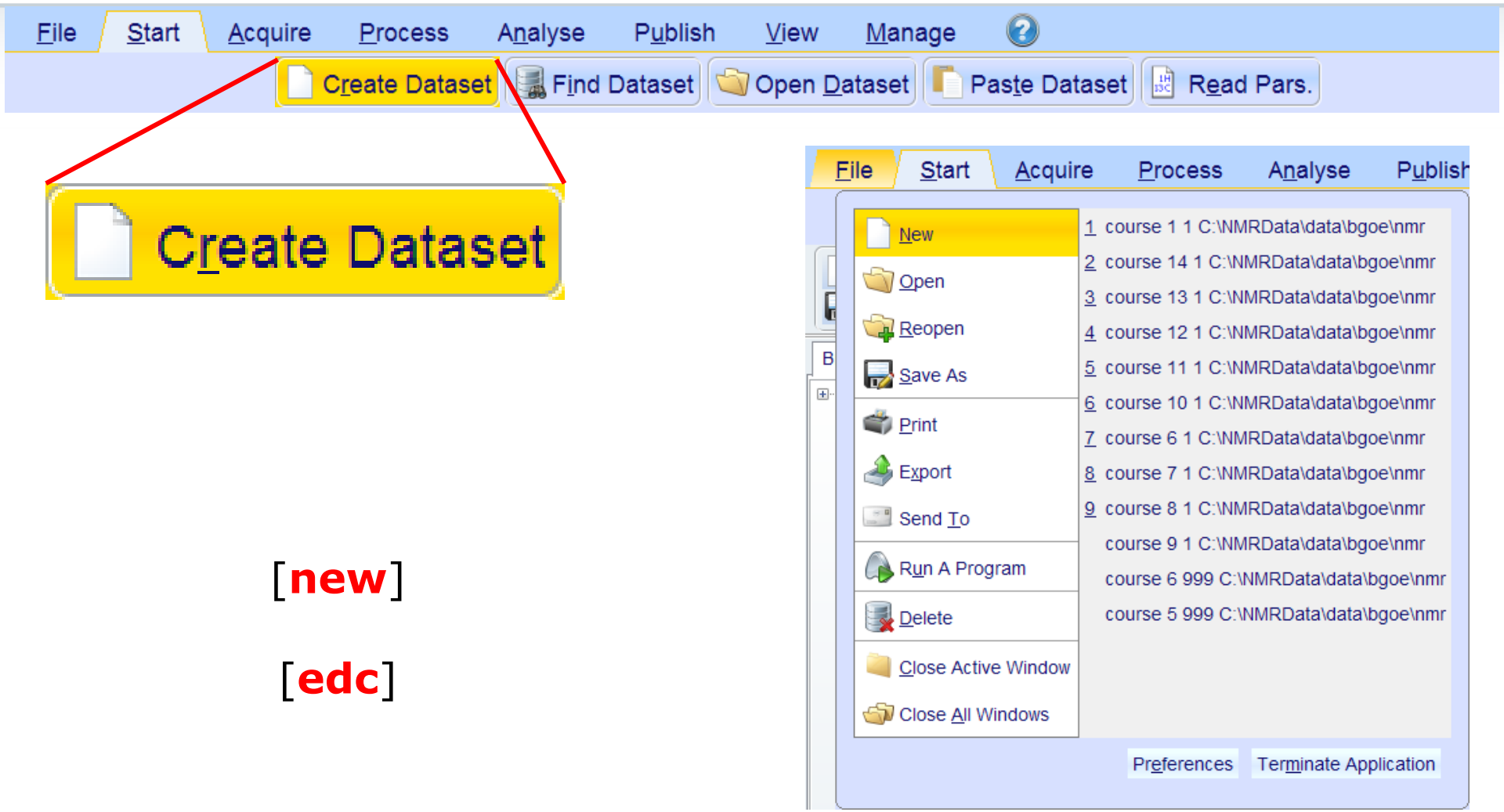


Install Standard Experiments [**expinstall**]



- **How to create a new data set?**

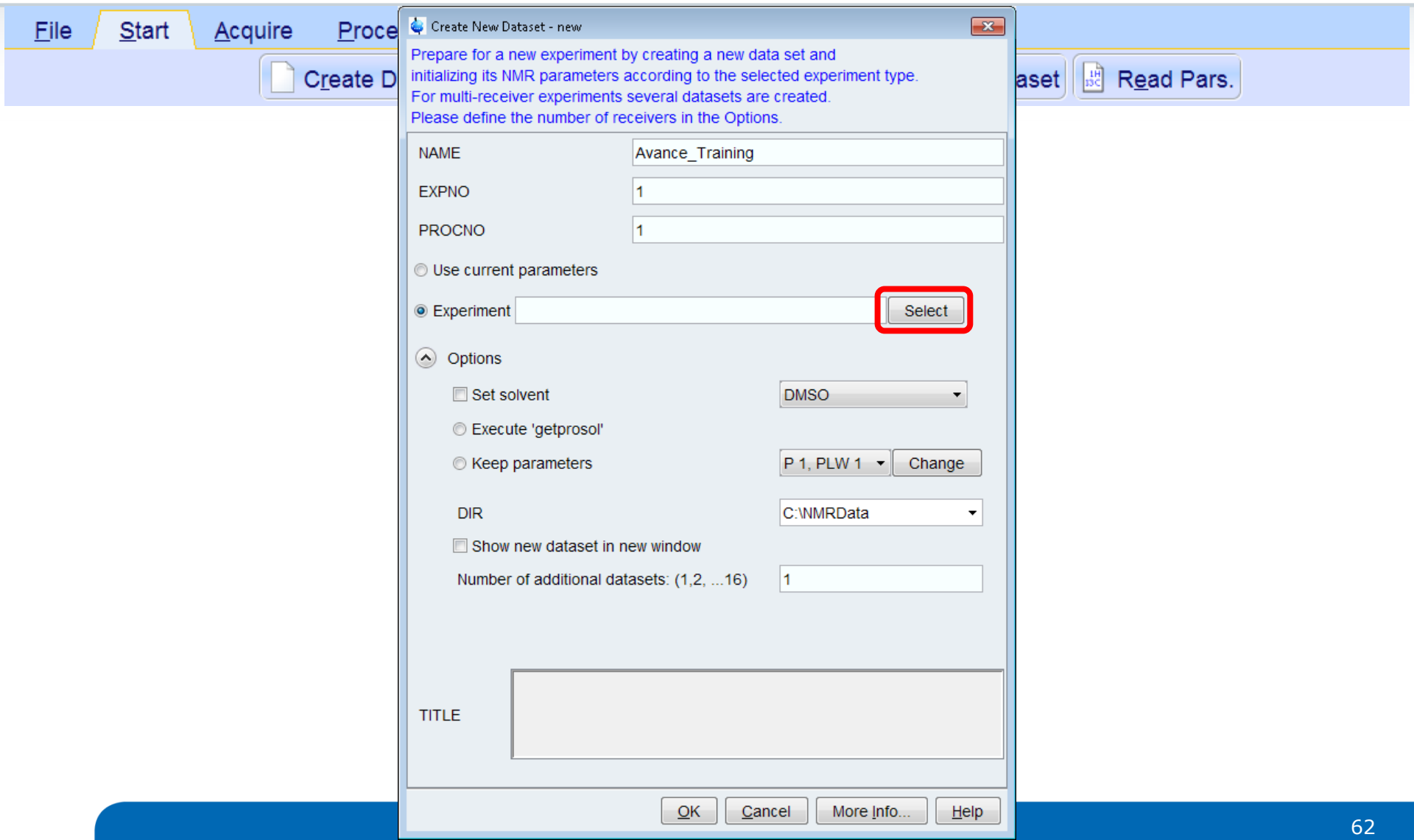
Create new data set [**new**/**edc**]



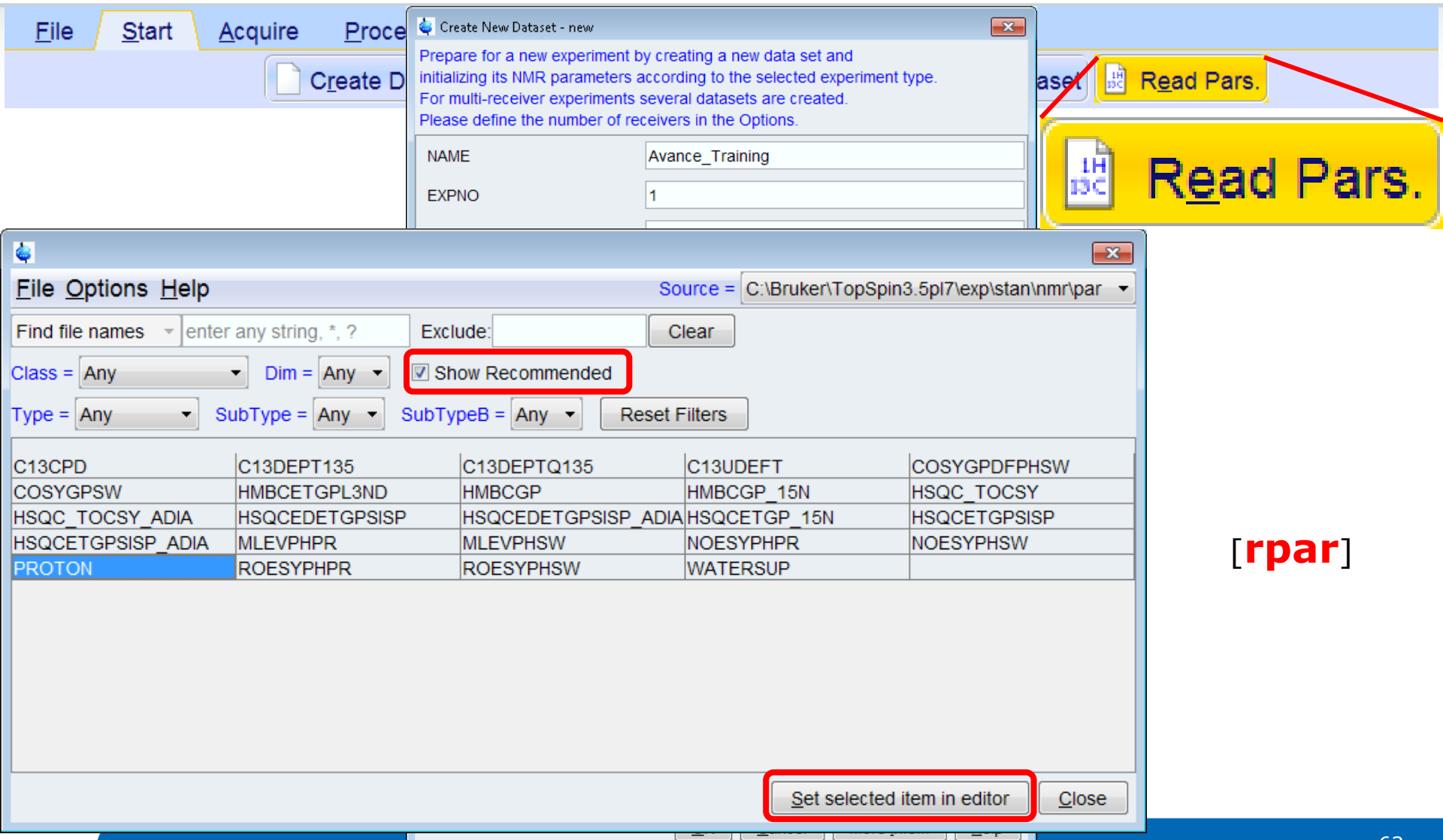
[**new**]

[**edc**]

Create new data set [**new**/**edc**]

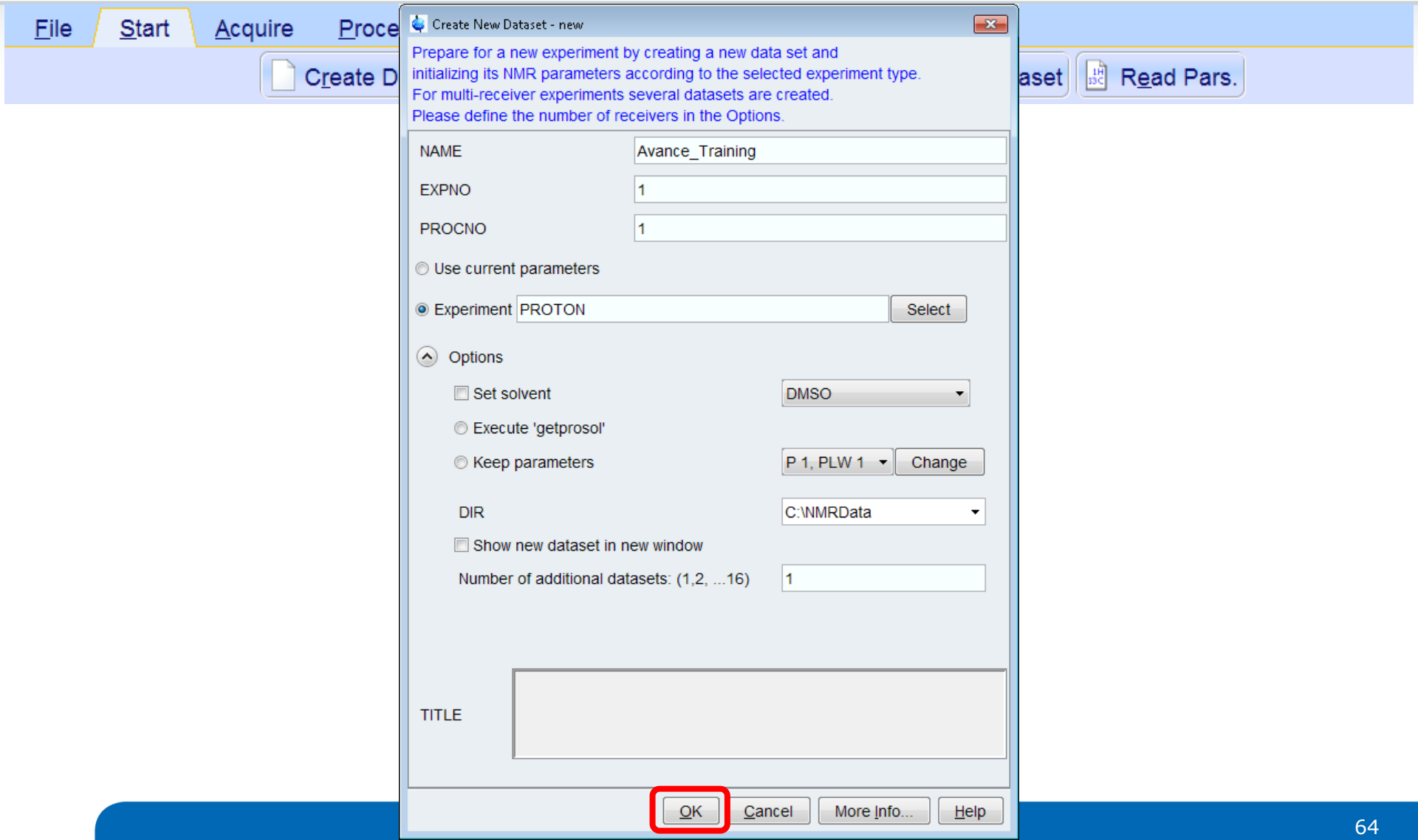


Experimental parameters are saved in parameter sets

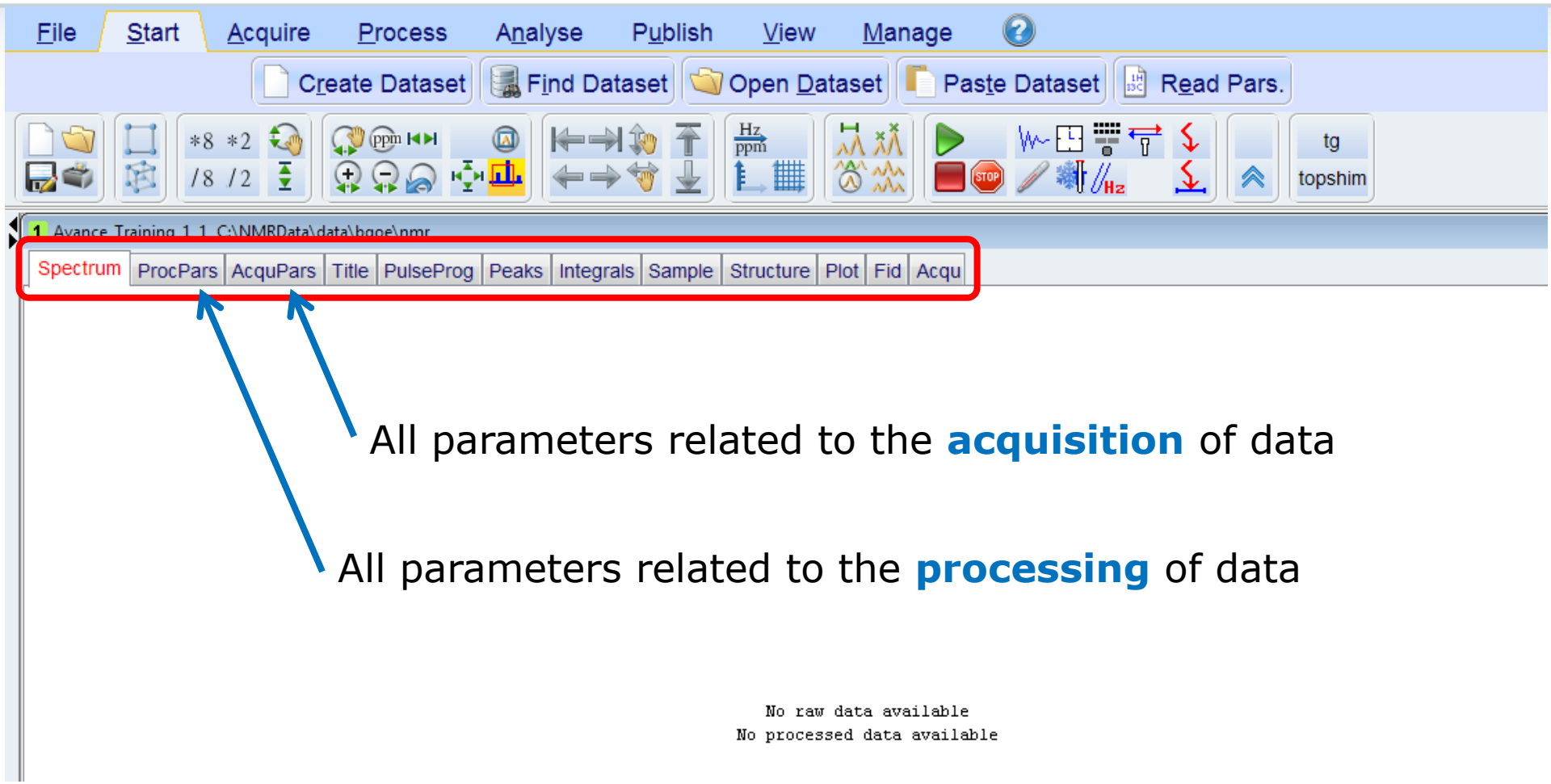


[**rpar**]

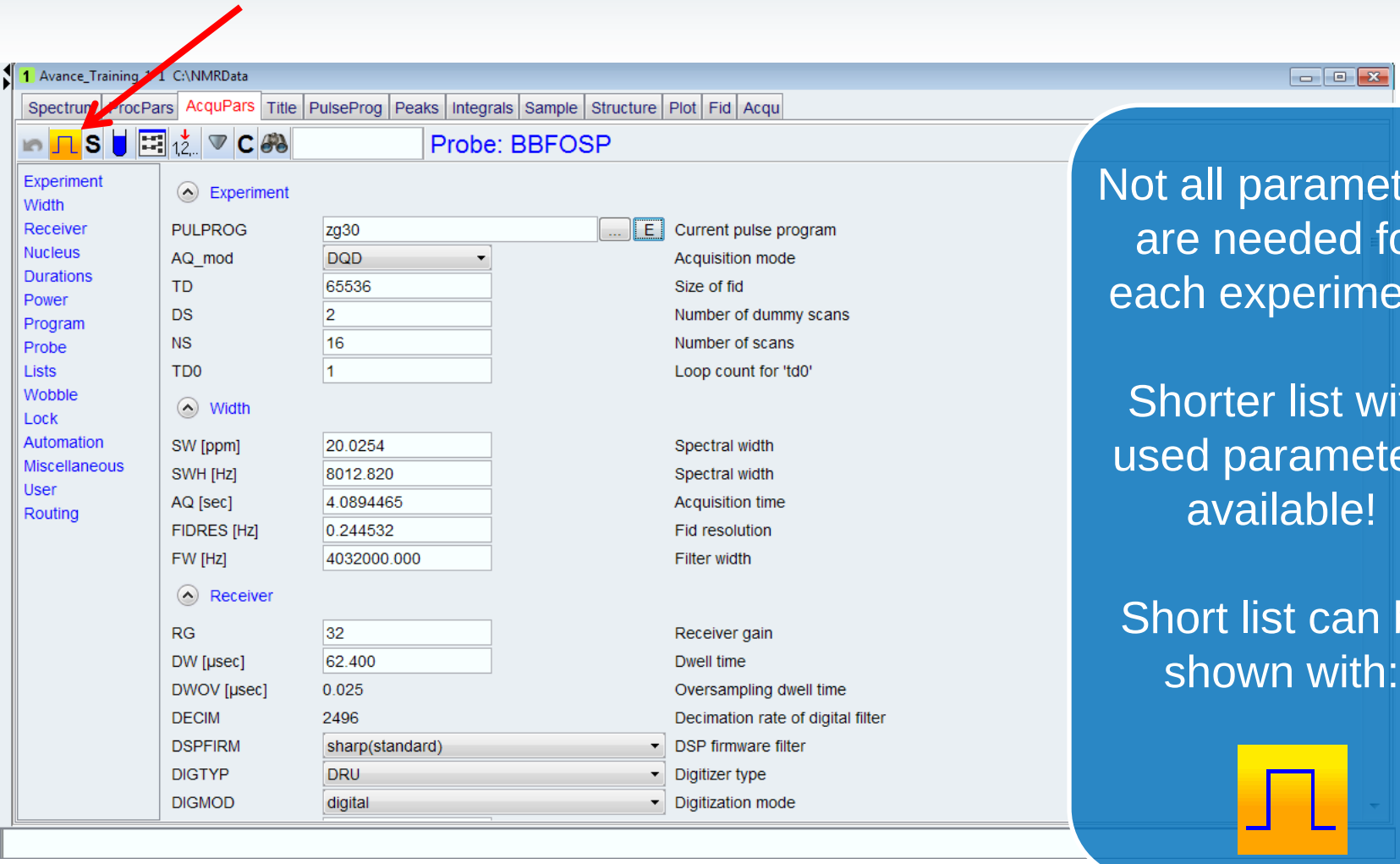
Experimental parameters are saved in parameter sets



Data set tabs



Acquisition parameters [eda]

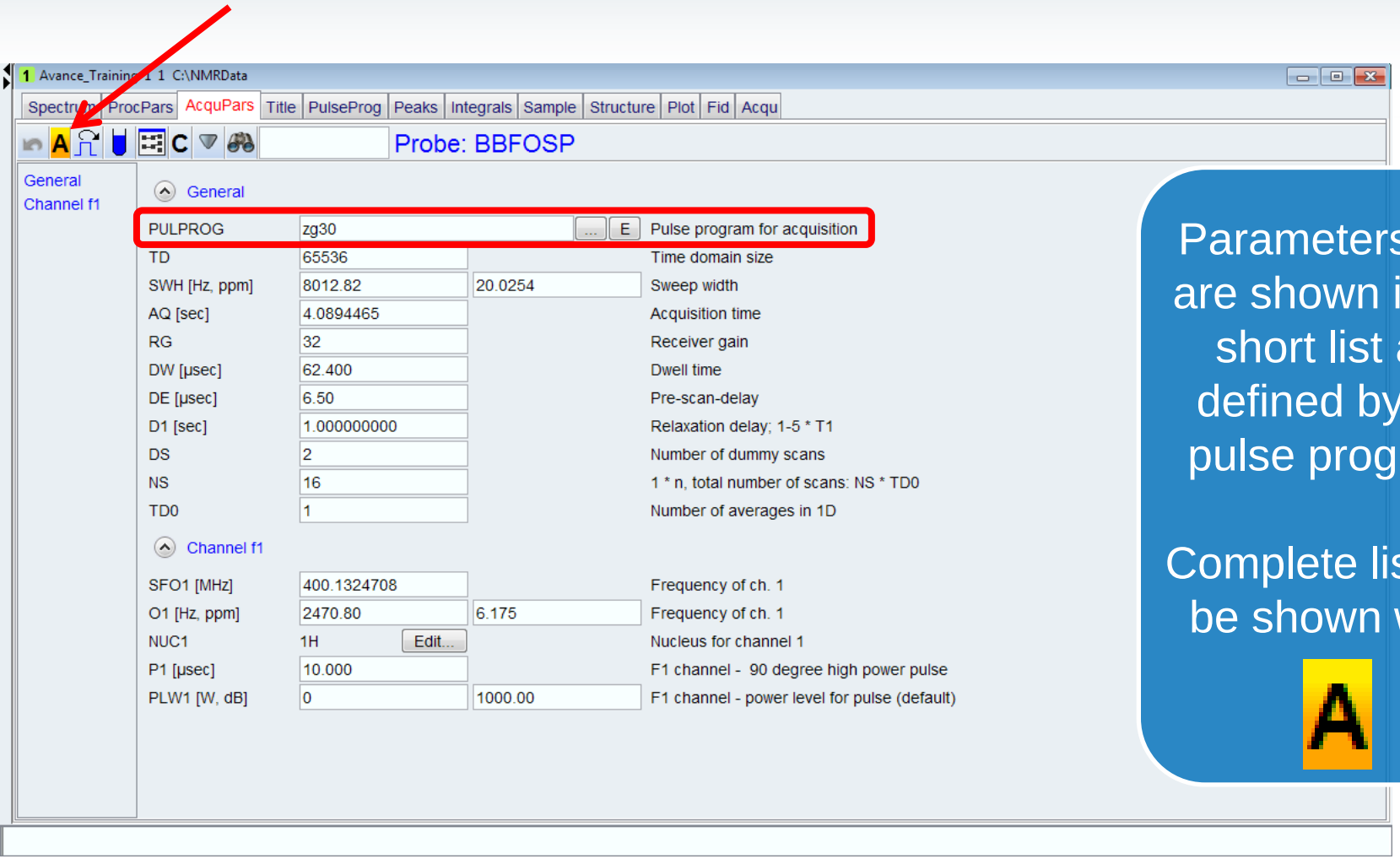


Not all parameters are needed for each experiment.

Shorter list with used parameters available!

Short list can be shown with:

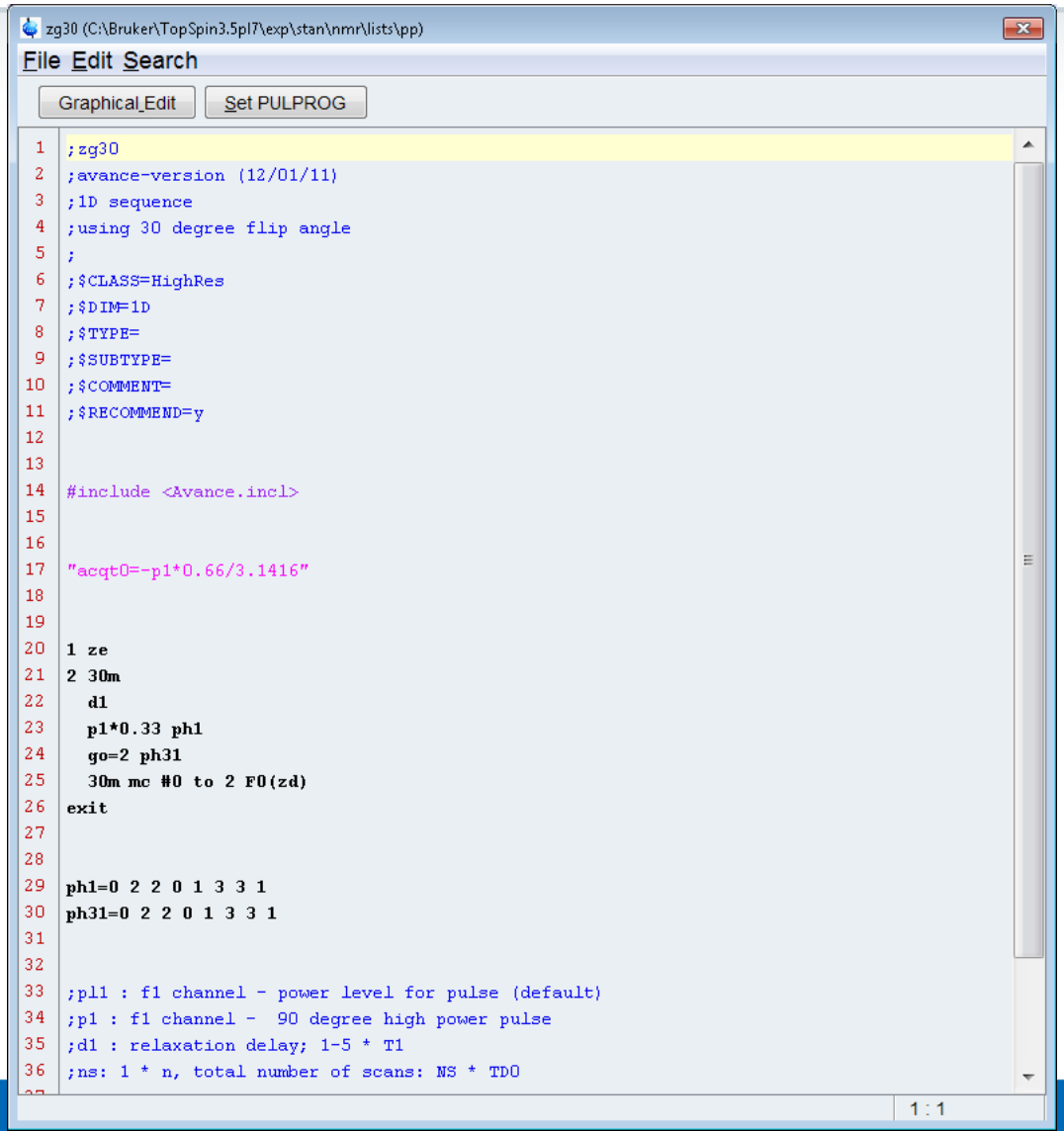
Acquisition parameters – short list [**ased**]



Parameters that are shown in the short list are defined by the pulse program.

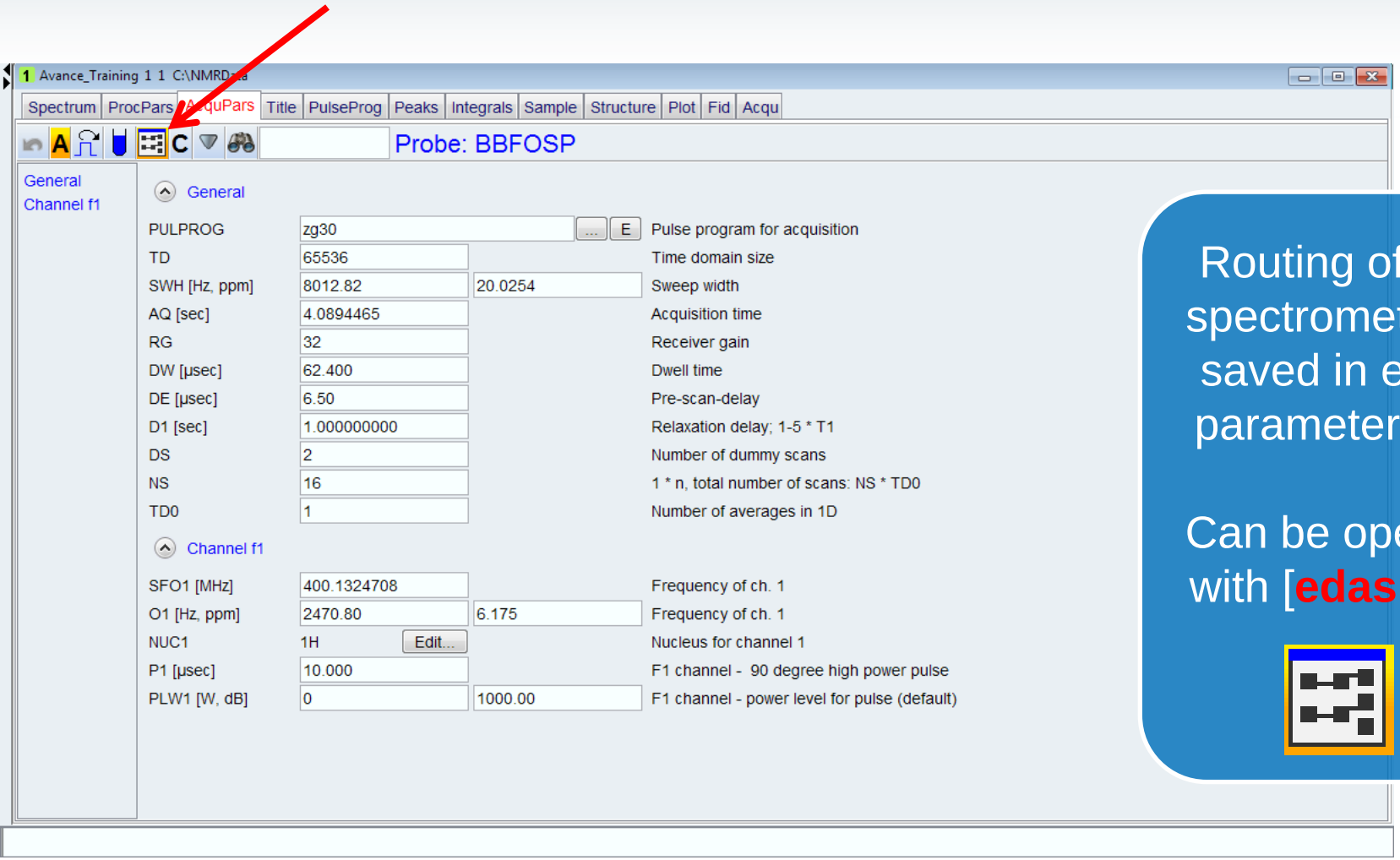
Complete list can be shown with:

Acquisition parameters



Only parameters that are mentioned here will be used.

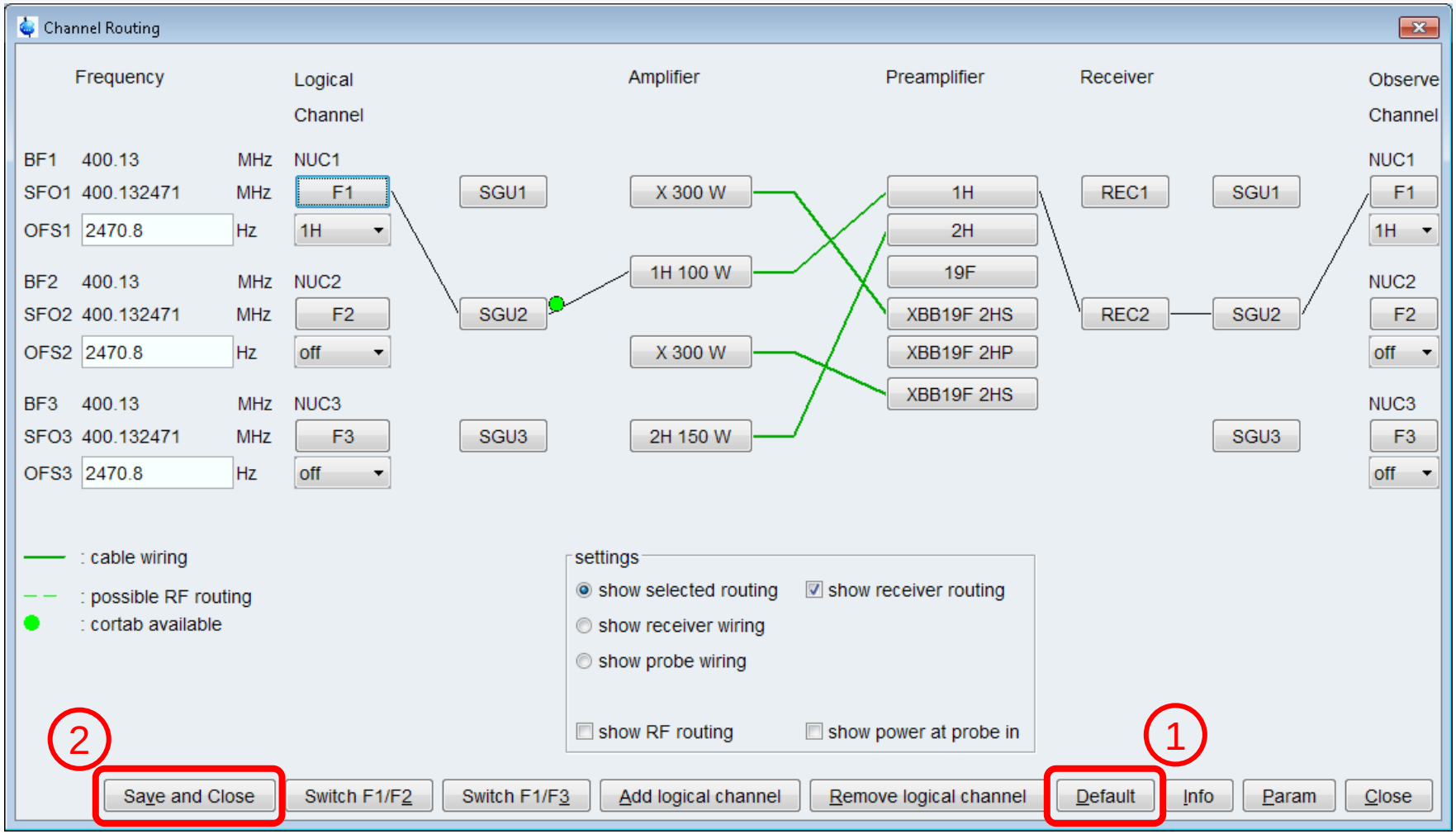
Channel Routing [edasp]



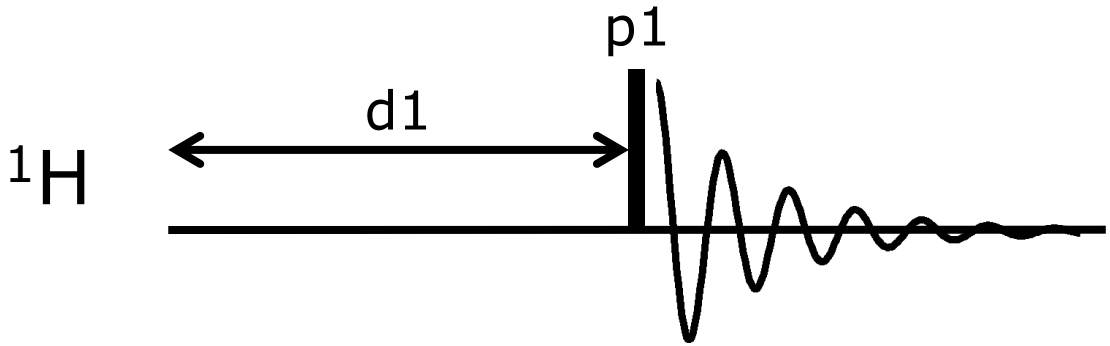
Routing of the spectrometer is saved in each parameter set.

Can be opened with [edasp] or

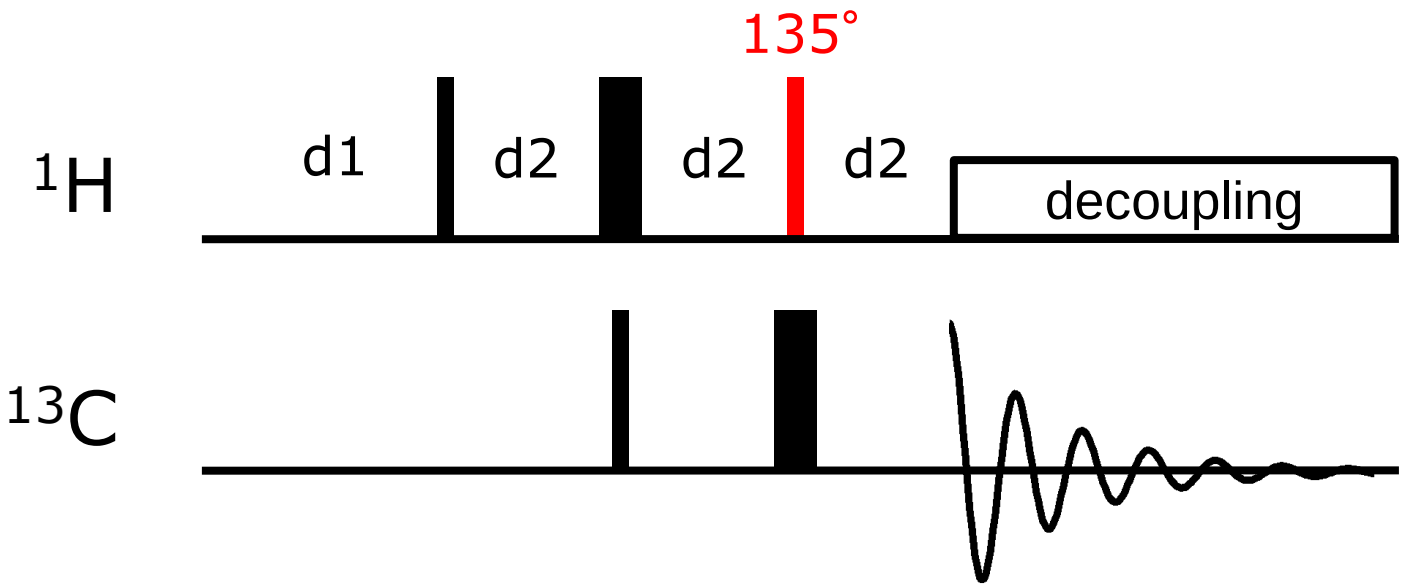
Channel Routing for 1D ^{1}H experiment [**edasp**]



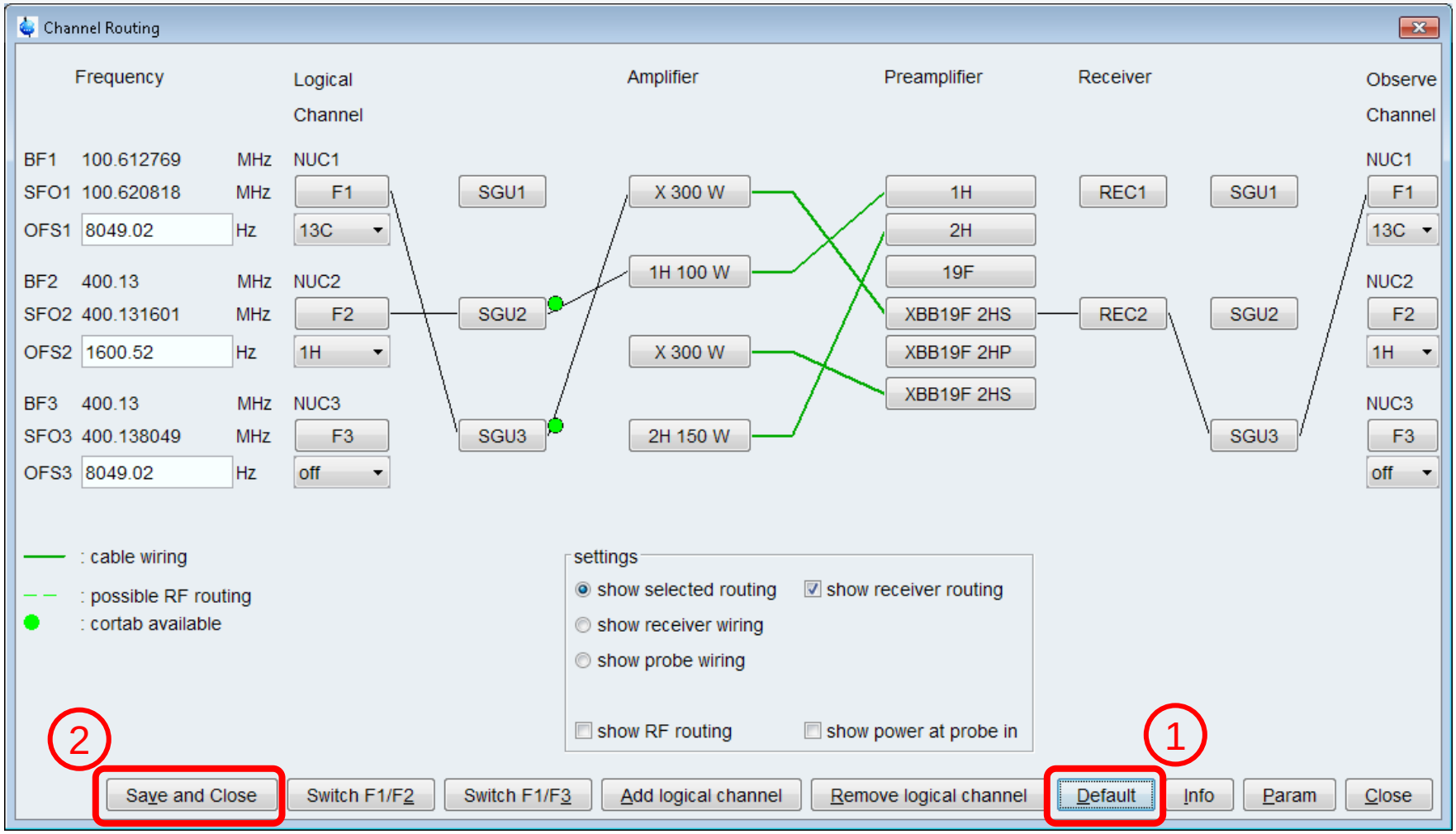
Channel Routing for 1D ^{1}H experiment



Channel Routing for 1D ^{13}C experiment with proton decoupling

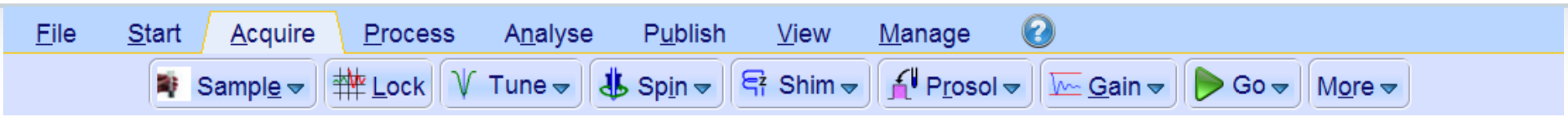


Channel Routing for 1D ^{13}C experiment with proton decoupling



- **How to acquire a spectrum?**

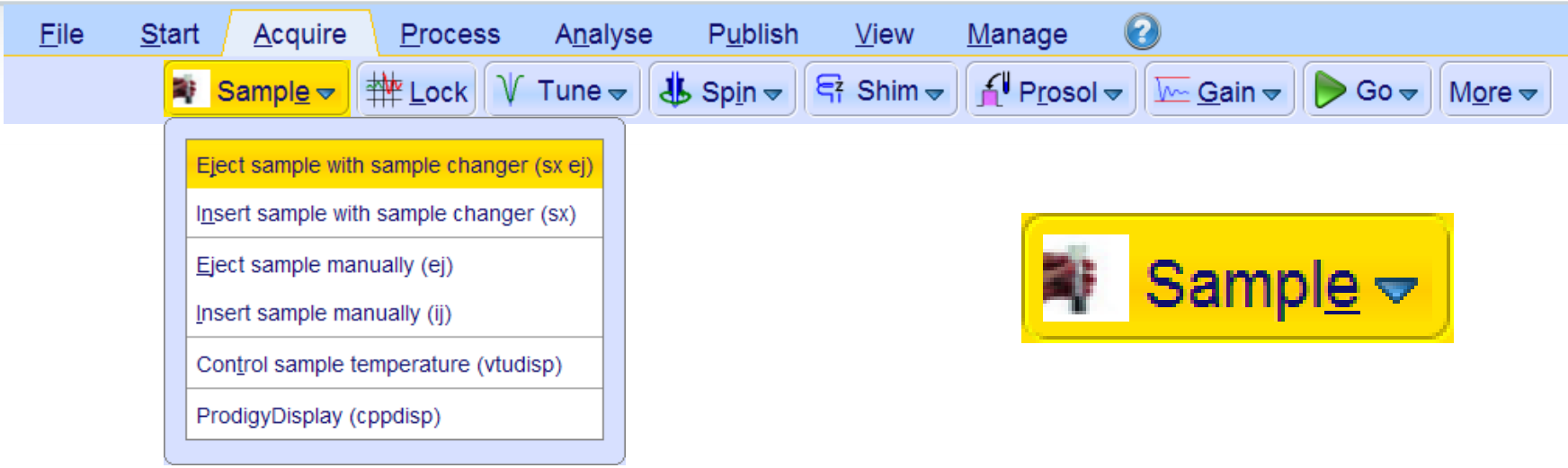
Acquire Toolbar



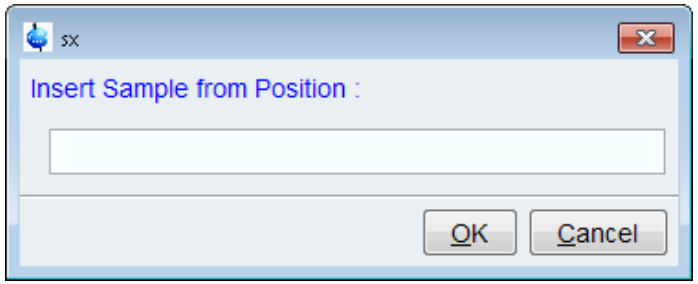
Workflow

All steps that are needed to acquire a spectrum can be done one after another from left to right.

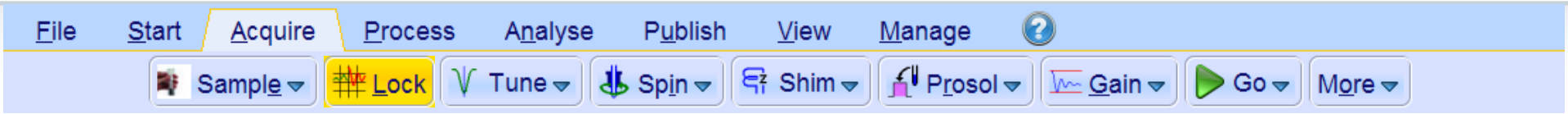
Acquire Toolbar – Sample



- Eject [**ej**] or insert [**ij**] sample manually
- If you have a sample changer you have to use [**sx ej**] to eject the sample and [**sx**] or [**sx <number>**] to insert the sample .



Acquire Toolbar – Lock



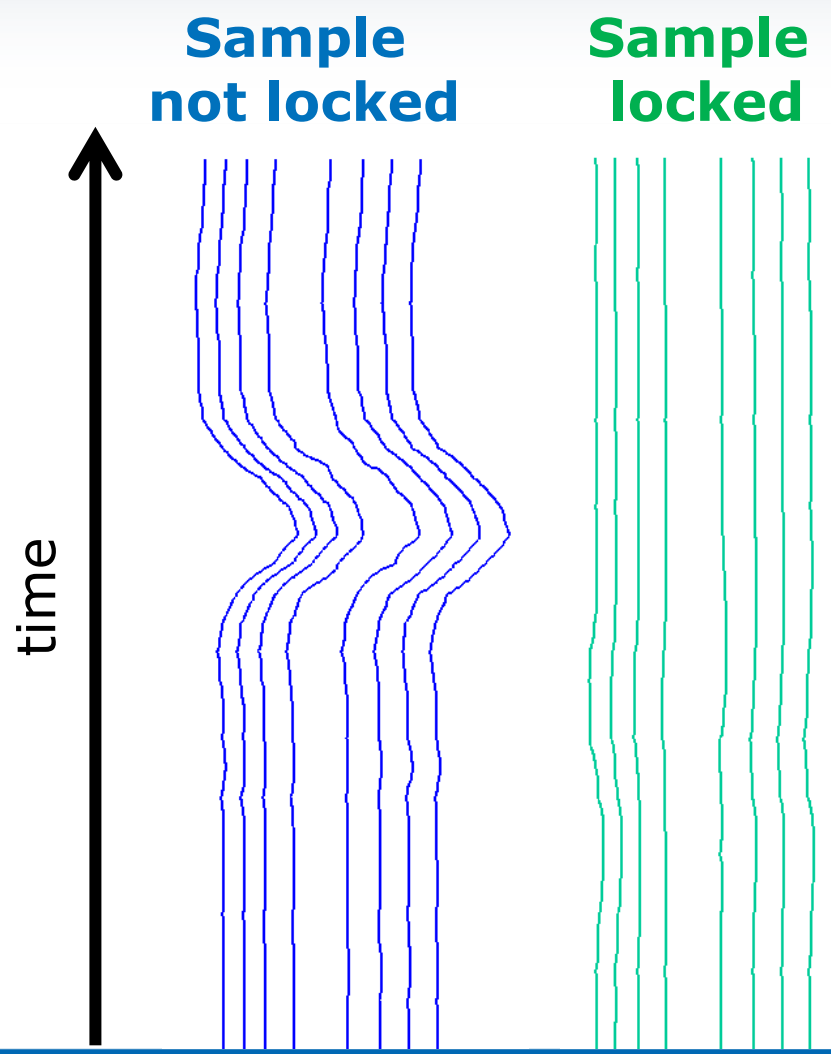
Solvents table

Solvent	Description
Acetic	acetic acid-d4
Acetone	acetone-d6
C6D6	benzene-d6
CD2Cl2	dichlormethane-d2
CD3CN	acetonitrile-d3
CD3CN_SPE	LC-SPE Solvent (Acetonitrile)
CD3OD_SPE	LC-SPE Solvent (Methanol-d4)
CDCl3	chloroform-d
CH3CN+D2O	HPLC Solvent (Acetonitril/D2O)
CH3OH+D2O	HPLC Solvent (Methanol/D2O)
D2O	deuteriumoxide
D2O_salt	deuteriumoxide with salt
Dioxane	dioxane-d8
DMF	N,N-dimethylformamide-d7
DMSO	dimethylsulfoxide-d6
EtOD	ethanol-d6
H2O+D2O	90%H2O and 10%D2O
H2O+D2O_salt	90%H2O and 10%D2O with salt
HDMSO	90%DMSO and 10%DMSO-d6
Juice	fruit juice

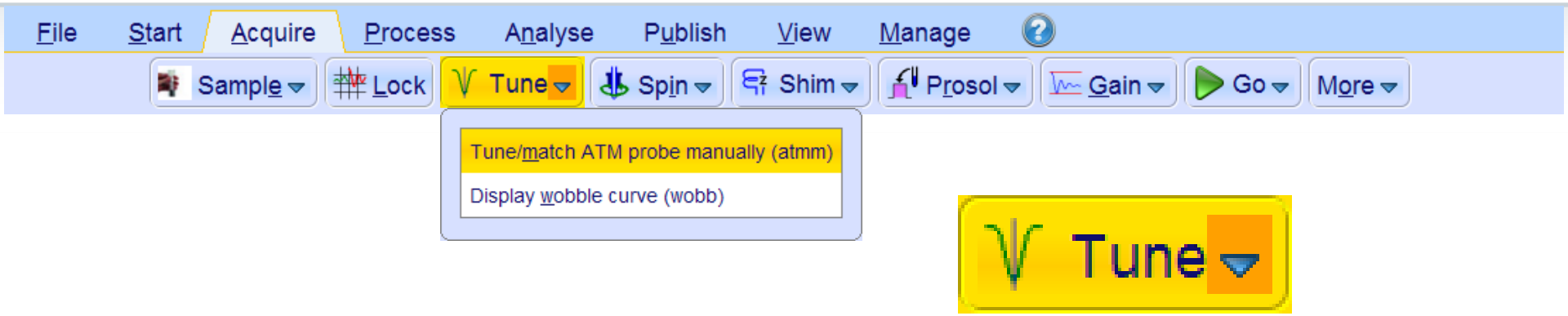
- [**lock**] or directly [**lock <solvent>**]
- Locks the spectrometer frequency to the deuterium signal of the solvent
- Eliminates influence of field drift and reduces influence of disturbances

Why lock?

- The lock is in principle an extra spectrometer
- Monitors deuterium frequency continuously
- Adjusts field to compensate disturbances

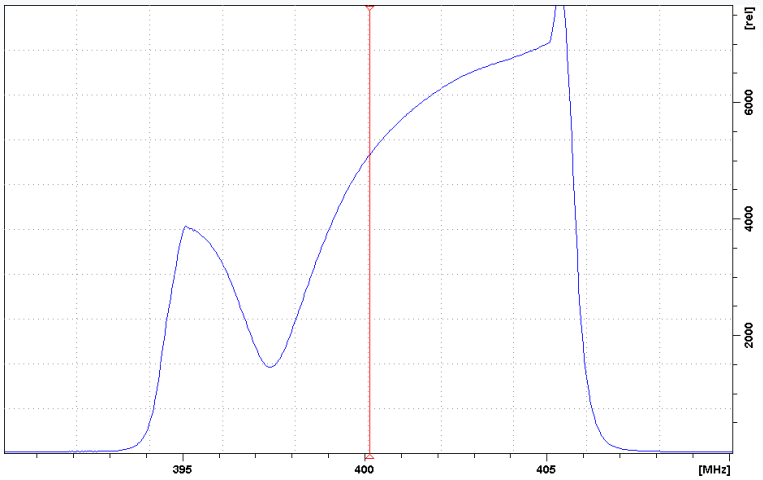


Acquire Toolbar – Tune



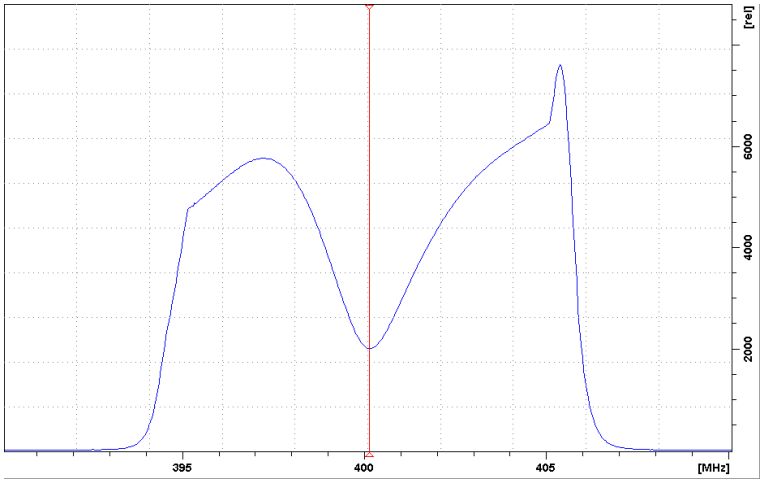
- Probe need to be tuned at matched to be most sensitive
- Automatic tuning and matching [**atma**]
- Can be tuned and matched manually as well [**atmm**]
- Needs to be done for each nucleus and when sample matrix is changed (different solvent, salty sample).

Tuning and Matching



Tuning: ✗

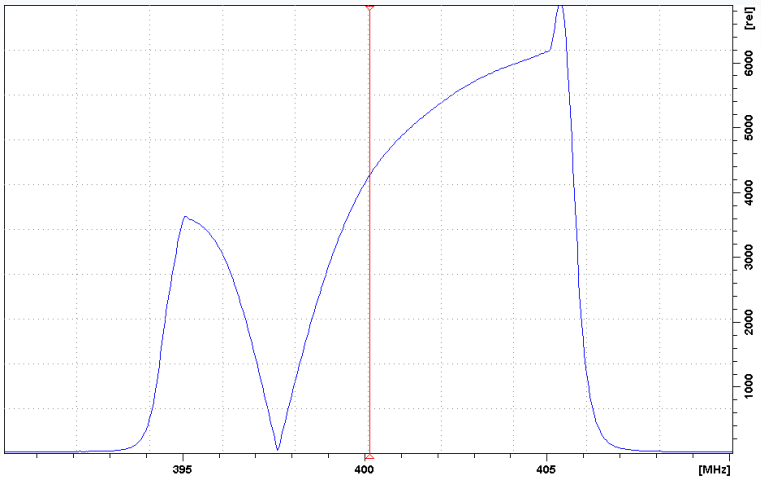
Matching: ✗



Tuning: ✓

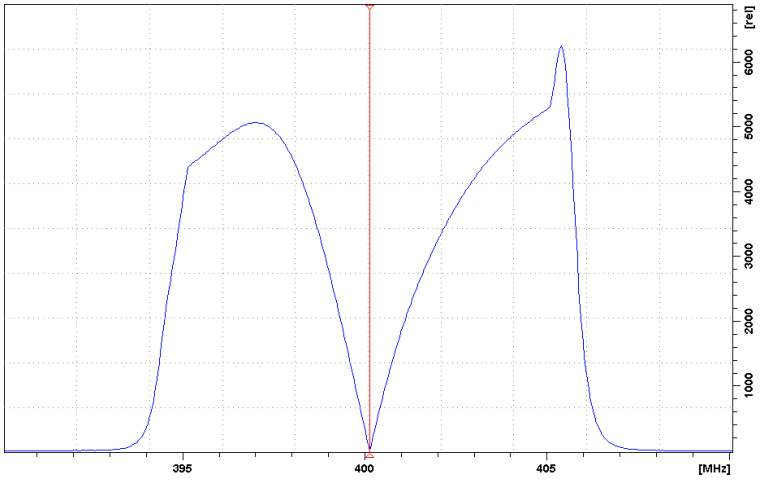
Matching: ✗

Tuning and Matching



Tuning: ✗

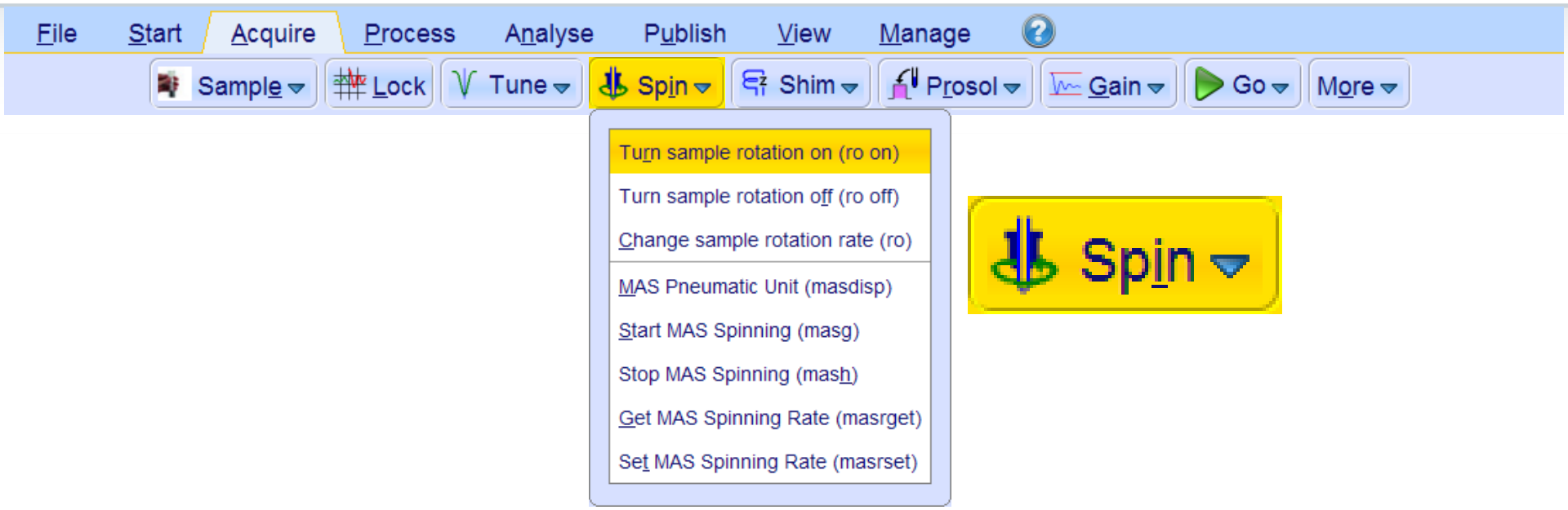
Matching: ✓



Tuning: ✓

Matching: ✓

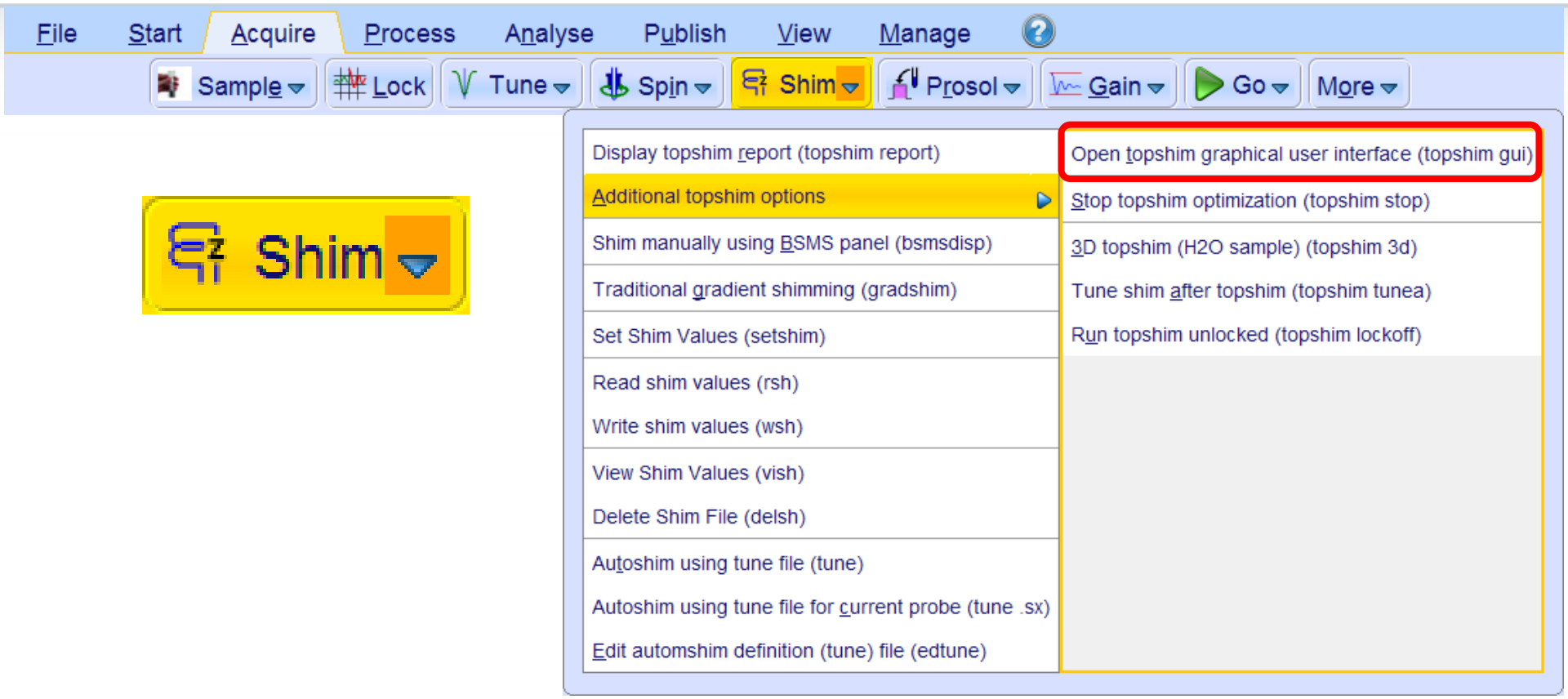
Acquire Toolbar – Spin



- Usually, sample rotation is not needed anymore
- Forbidden for some experiments (e.g. water suppression)

- MAS rotation for solids/semi-solids can be controlled as well

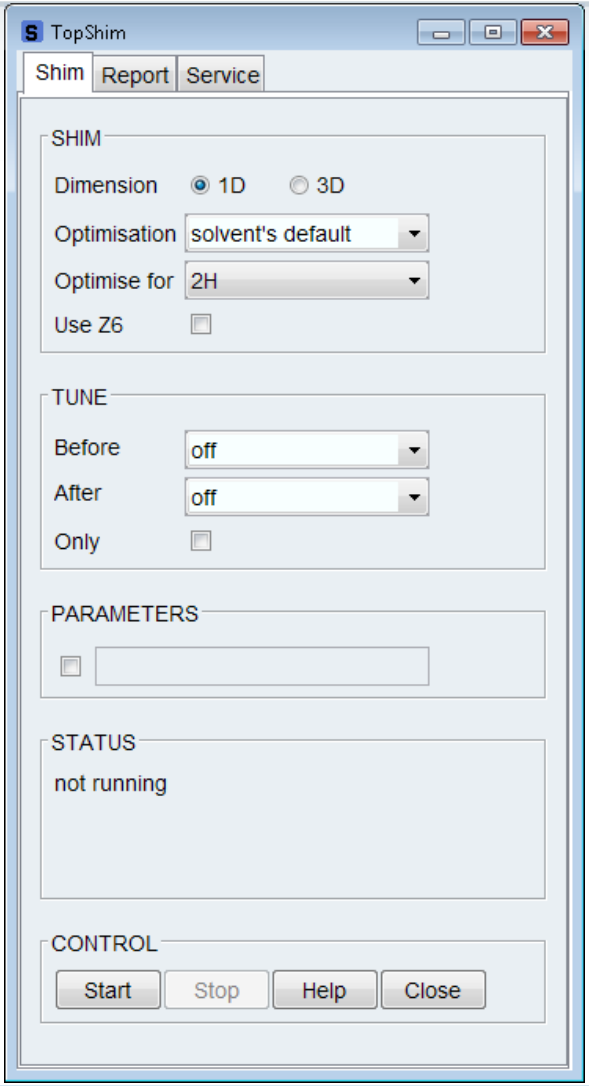
Acquire Toolbar – Shim



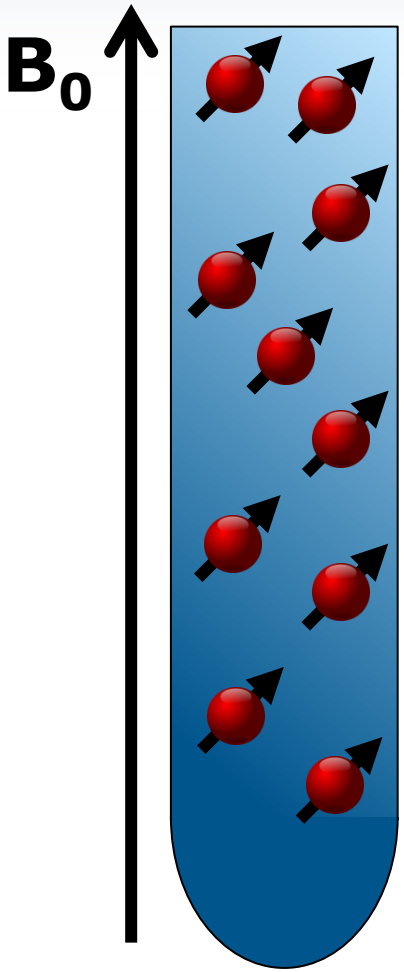
- Each sample needs to be shimmed for best homogeneity
- Automatic shimming with [**topshim**]

Topshim GUI

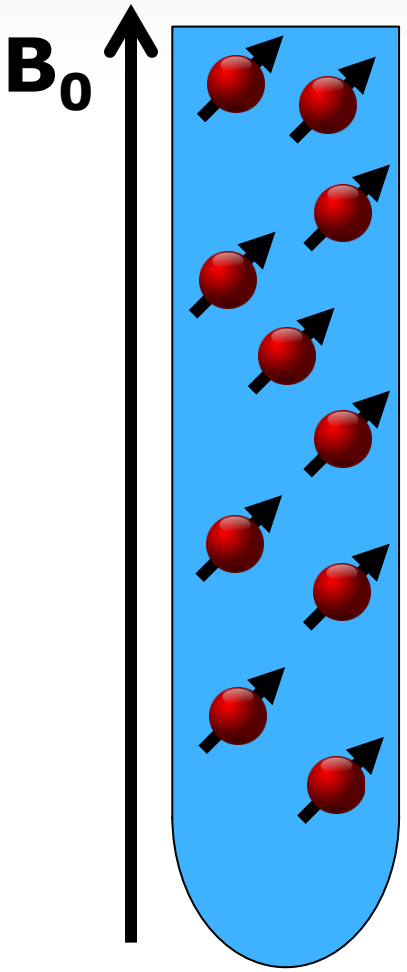
- Different options for shimming can be selected
- Standard 1D shimming is along z
- 3D shimming is only available for non-deuterated water as solvent
(90% H_2O + 10% D_2O)



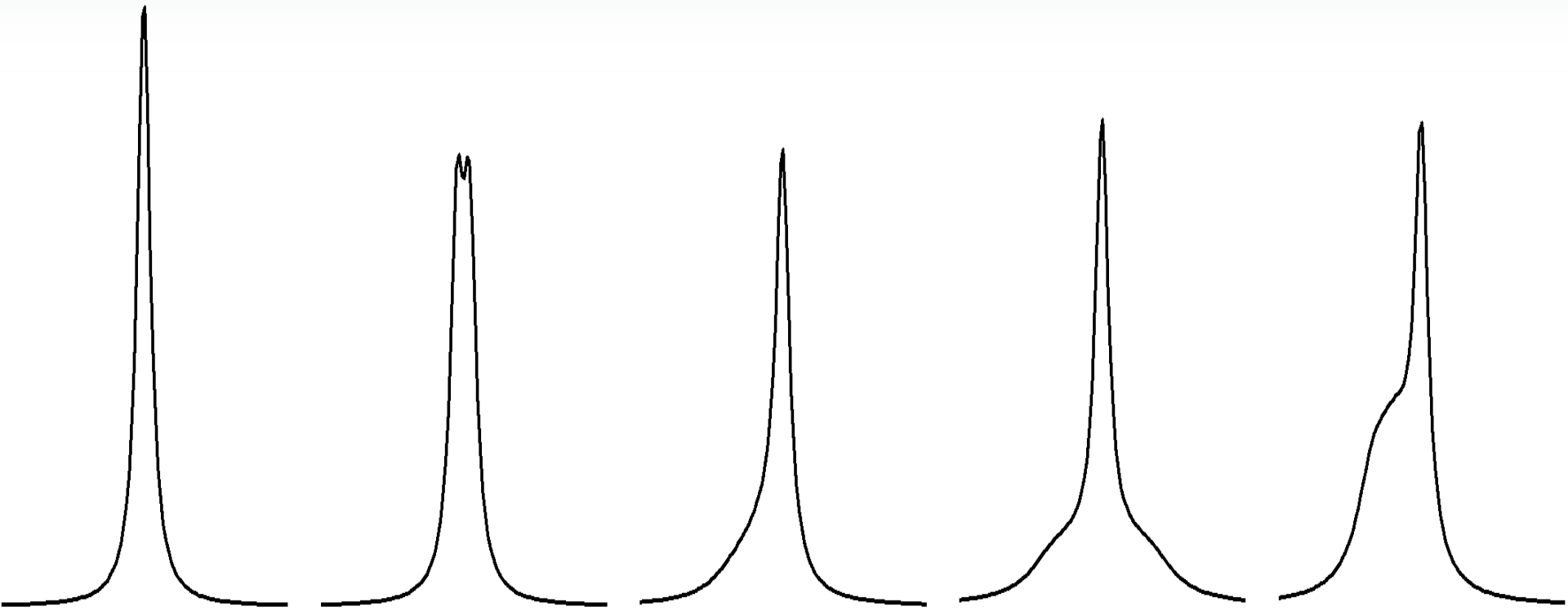
Why shimming?



- Magnetic field strength determines resonance frequency
- External magnetic field not 100% homogeneous
- External field: ~500MHz
- Resolution: < 1Hz
- Additional magnetic fields applied by shim coils



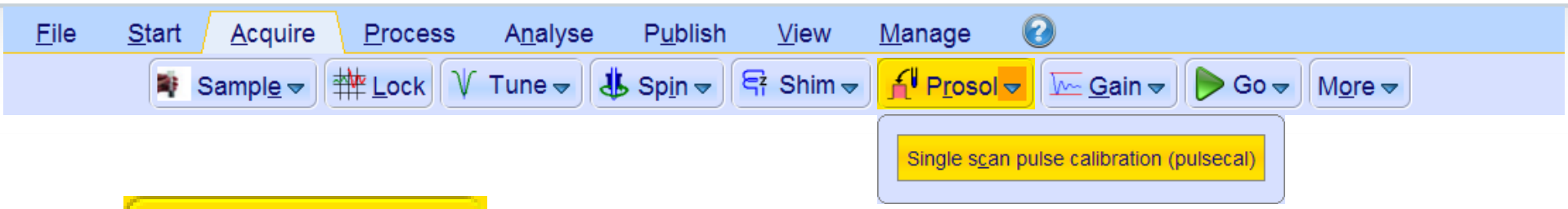
What is a good shim?



good shim | splitting or broad peak | tailing | symmetric tail | shoulder

More information about shimming:
G. Chmurny, D. Hoult, "The ancient and honorable art of shimming." *Concep. Magnetic Res.*, **1990**, *2*, 131-149.

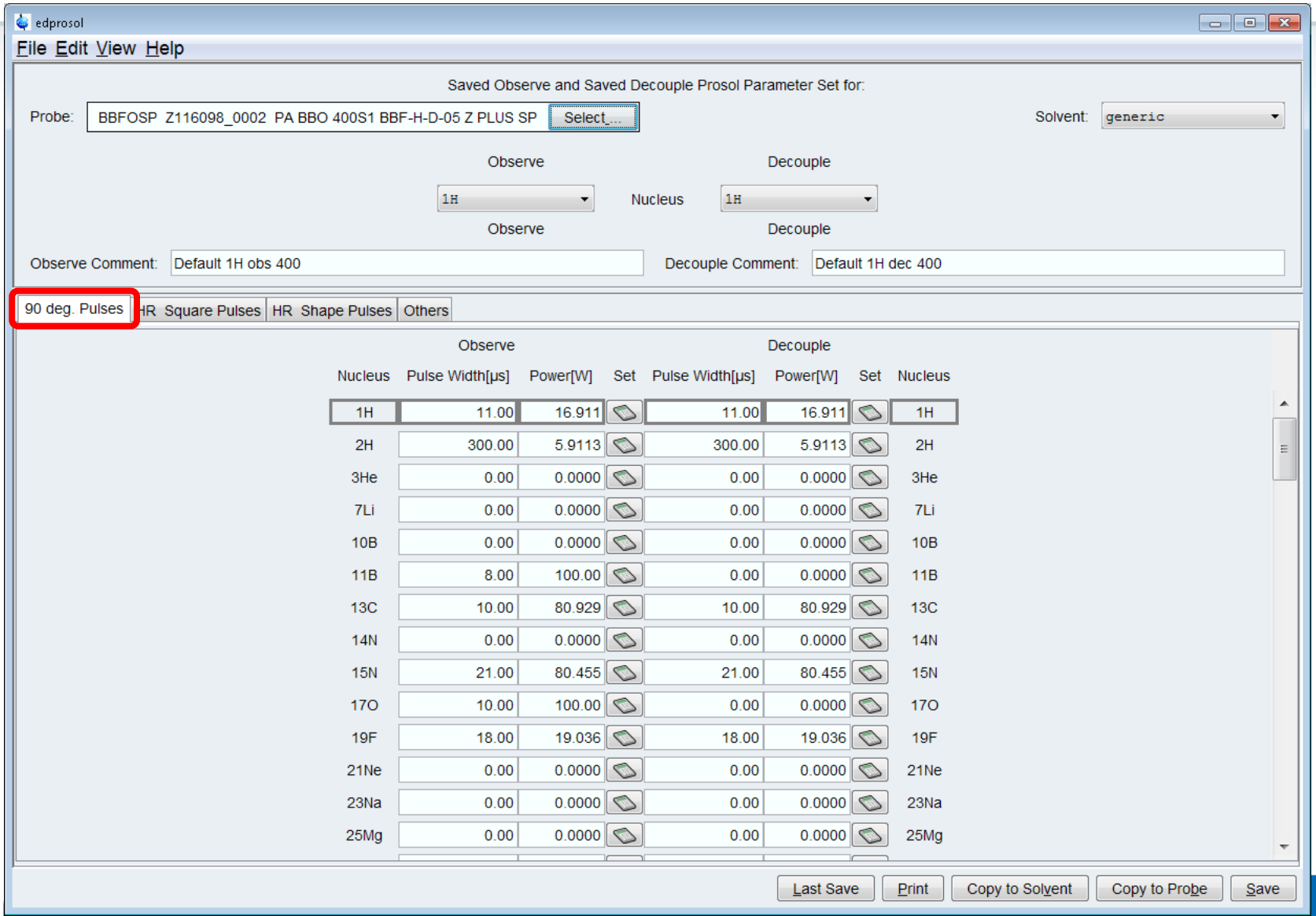
Acquire Toolbar – Prosol



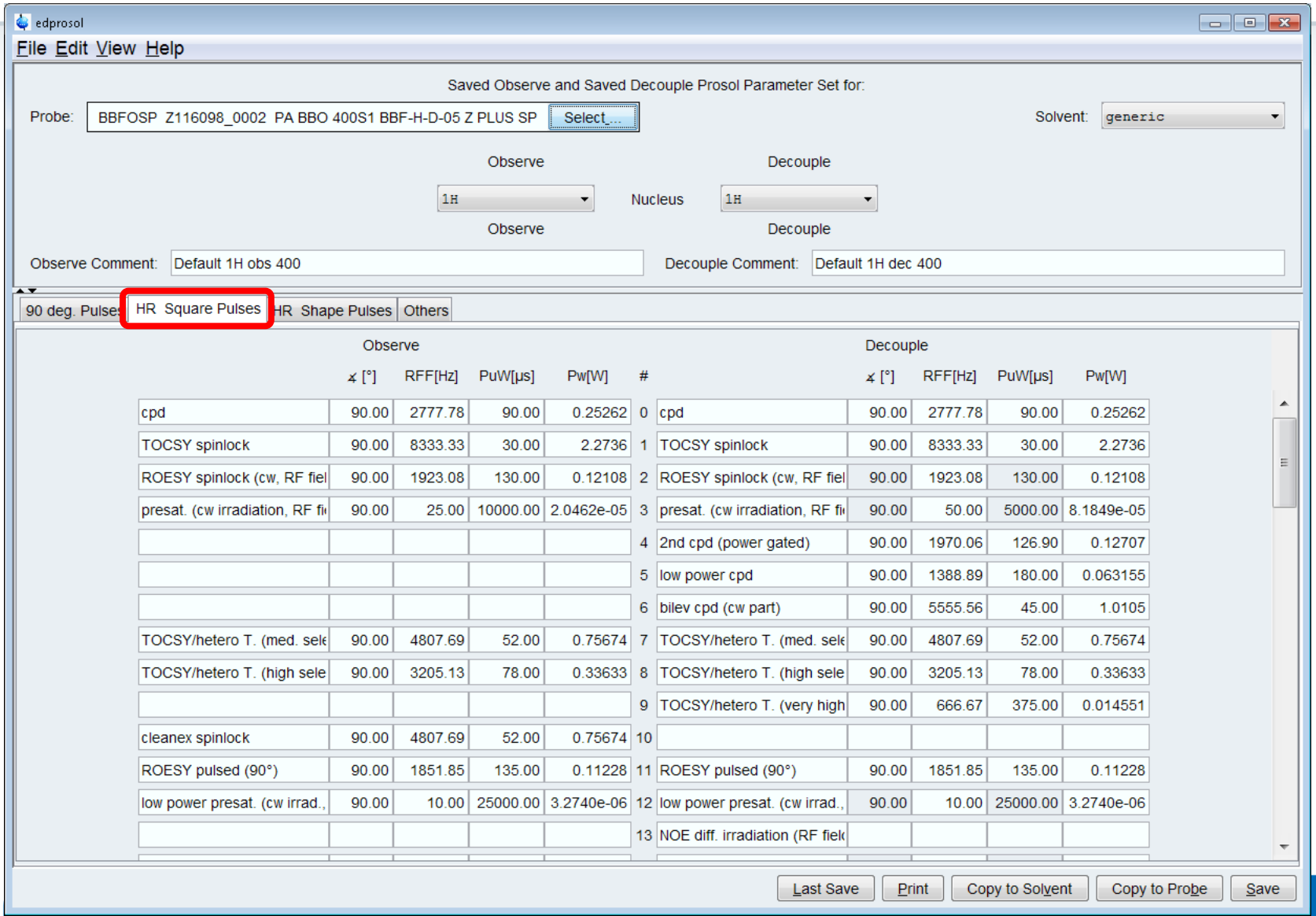
- Copies probe & solvent specific parameters to data set

- It is possible to execute getprosol with a specific pulse [**getprosol <nuc> <pulse length> <pulse power in dB>**]

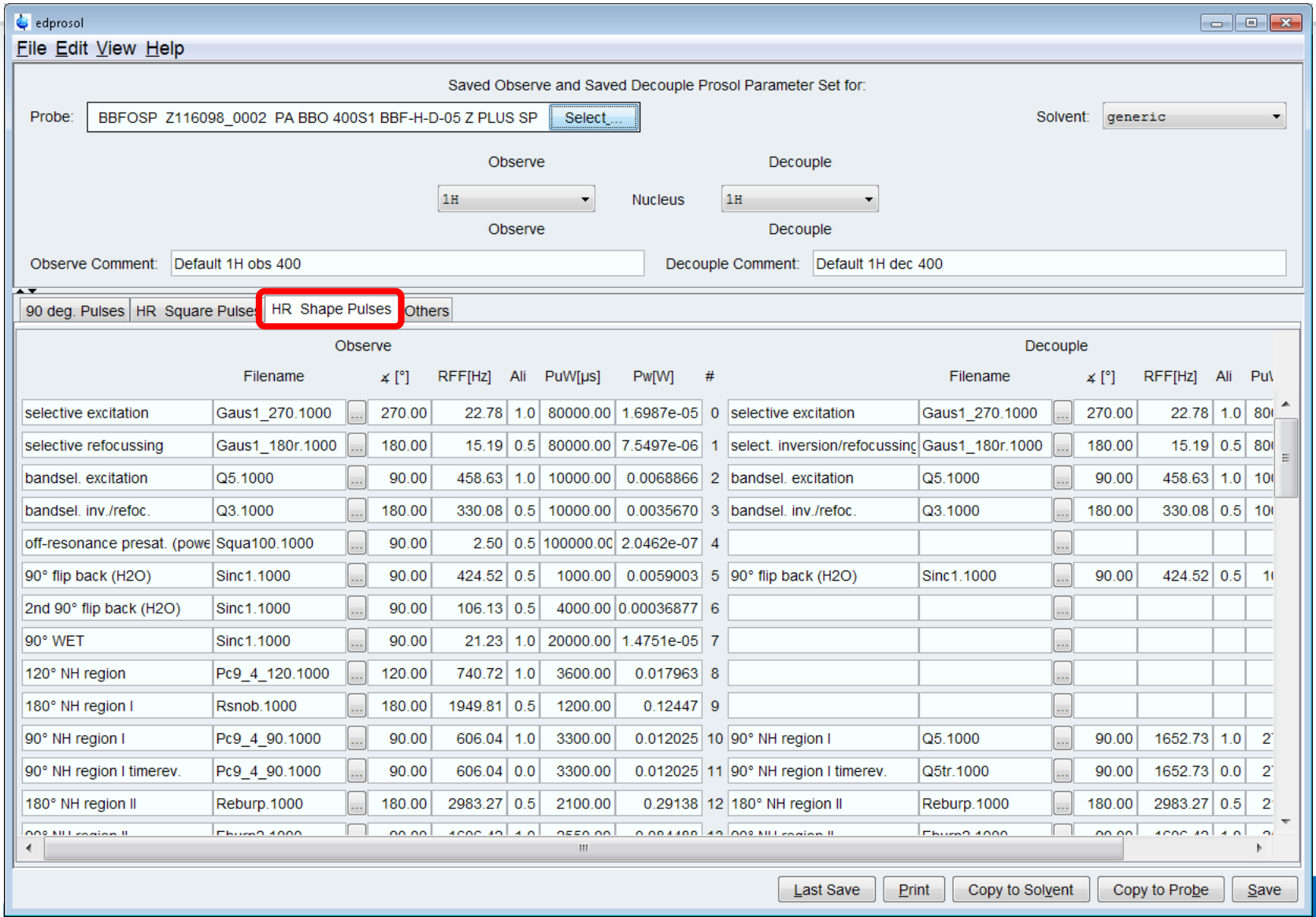
Prosol table [**edprosol**]



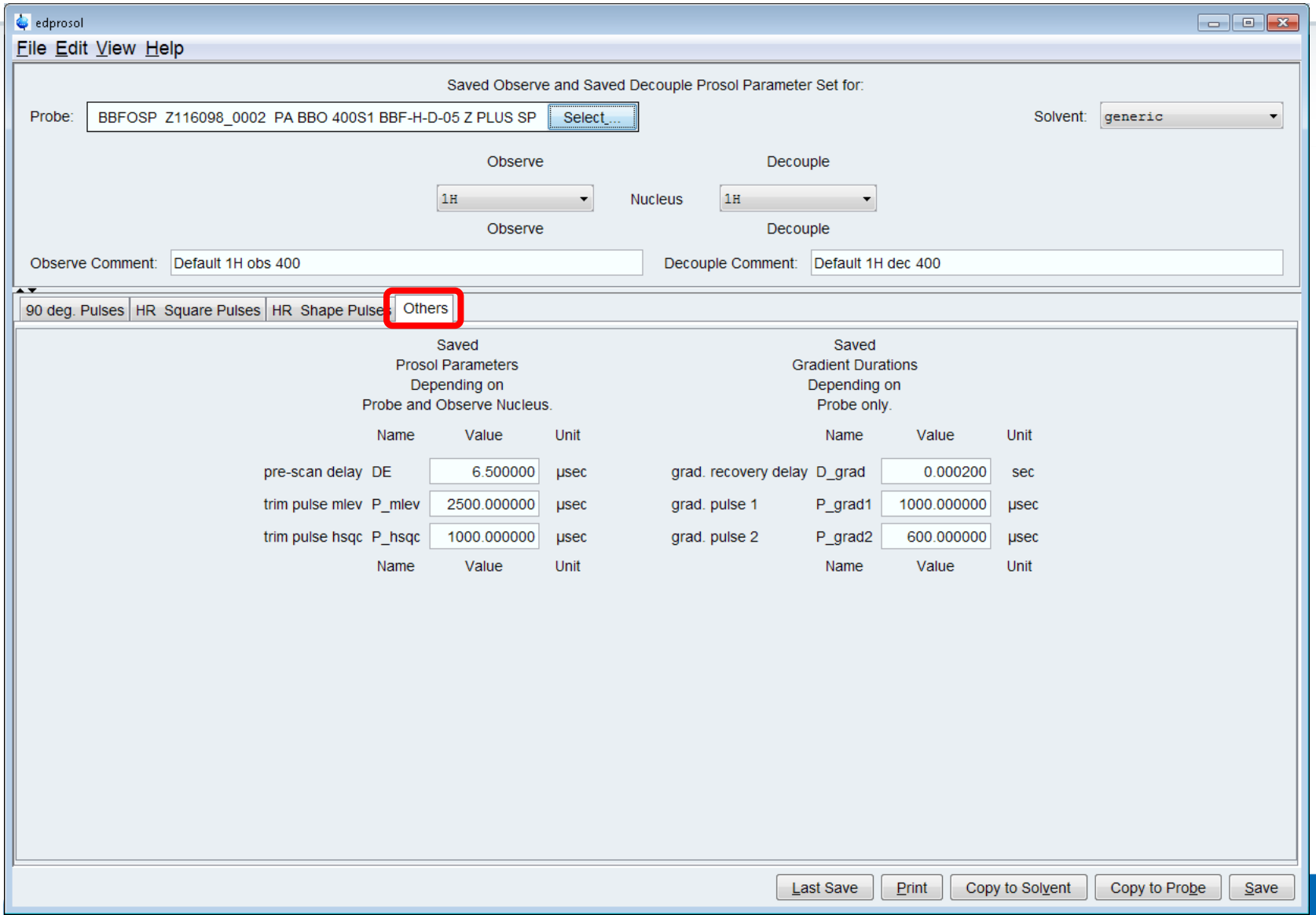
Prosol table [**edprosol**]



Prosol table [**edprosol**]



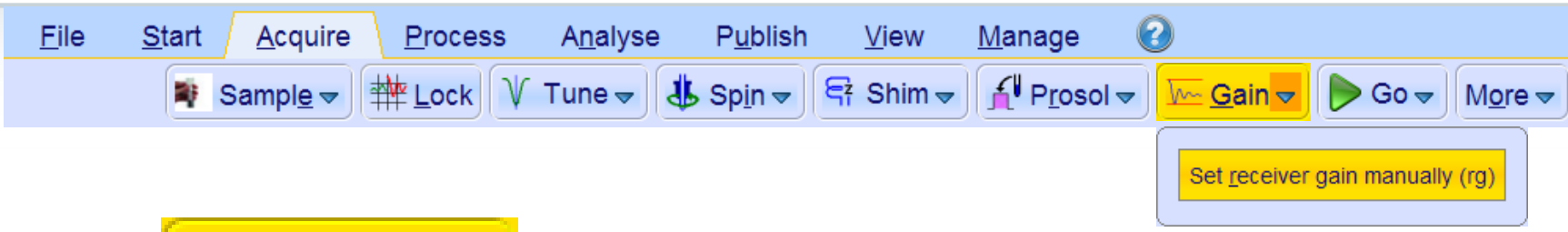
Prosol table [**edprosol**]



Pulse calibartion

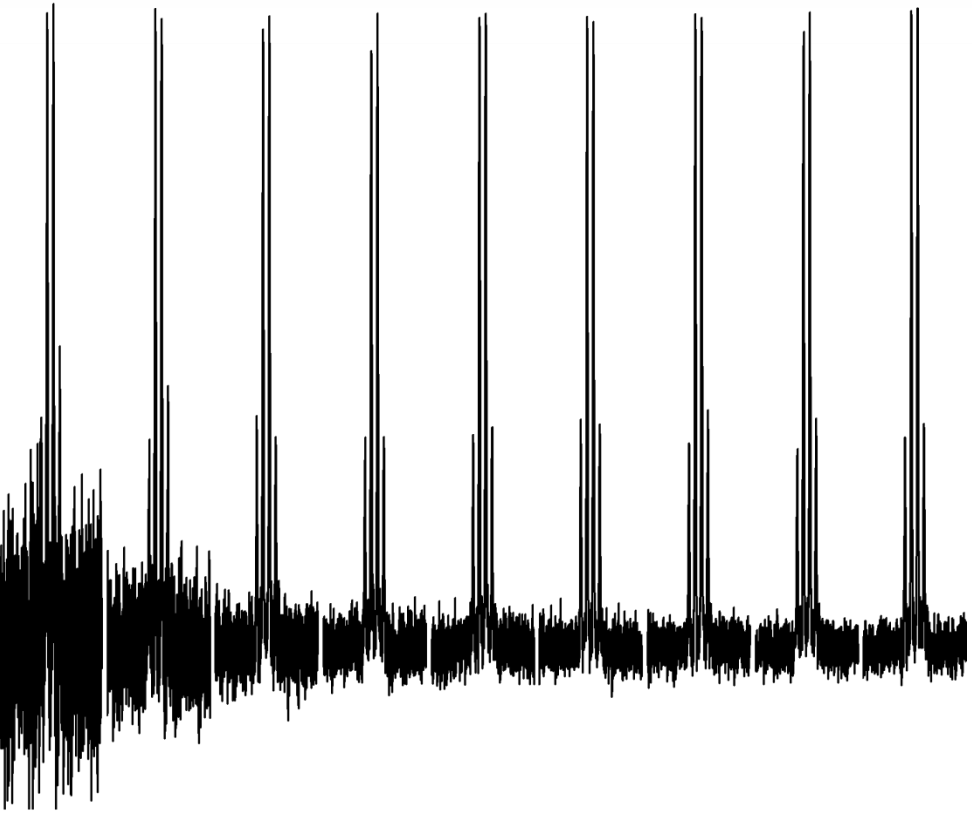
• [**pulsecal**]	AU-program to determine the 90° 1H-pulse in F1
• [**pulsecal fast**]	pulse determination without receiver gain adjustment and without search for the biggest signal
• [**pulsecal quiet**]	the result is not shown
• [**pulsecal sn**]	uses em instead of gm for processing
• [**pulsecal c13, p31, f19**]	checks the C13, P31, F19-pulse in F1

Acquire Toolbar – Gain



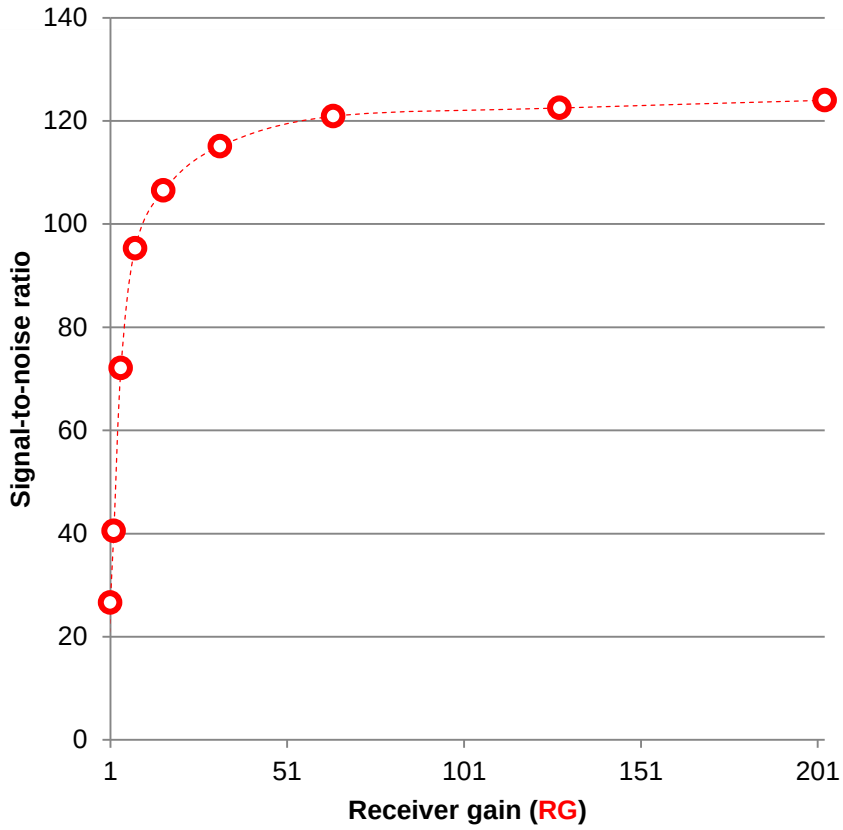
- [**rga**] runs automatic determination of optimum receiver gain (RG)
- RG controls the amplitude of the FID signal before it enters the digitizer
- Higher RG values will improve S/N (up to a certain RG value)
- Too high RG will result in distorted spectra

Effect of RG

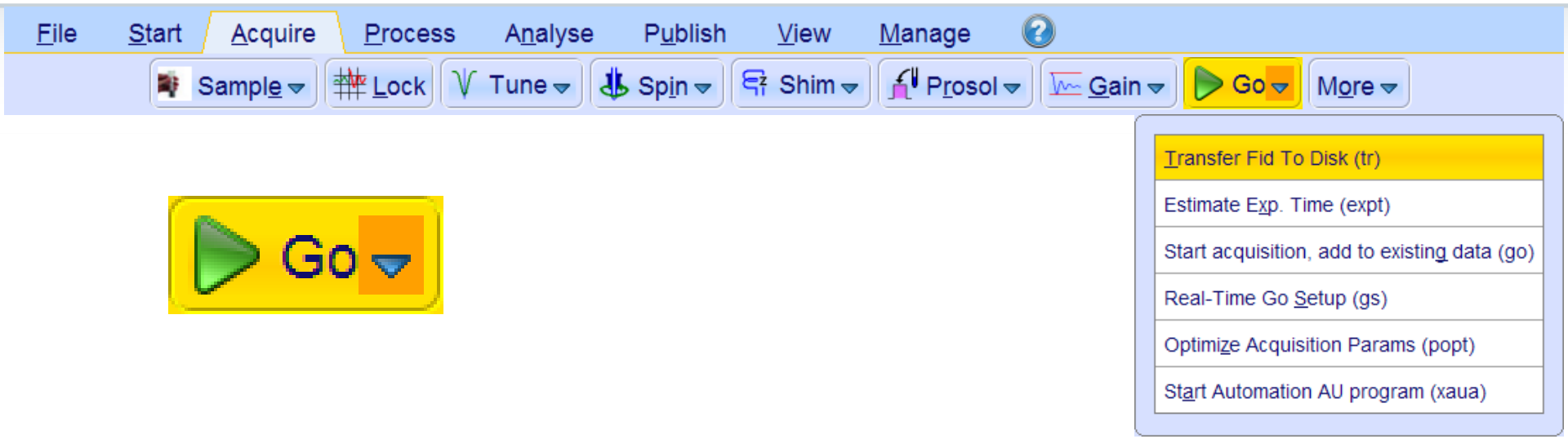


1 2 4 8 16 32 64 128 203

Receiver gain (RG)



Acquire Toolbar – Go

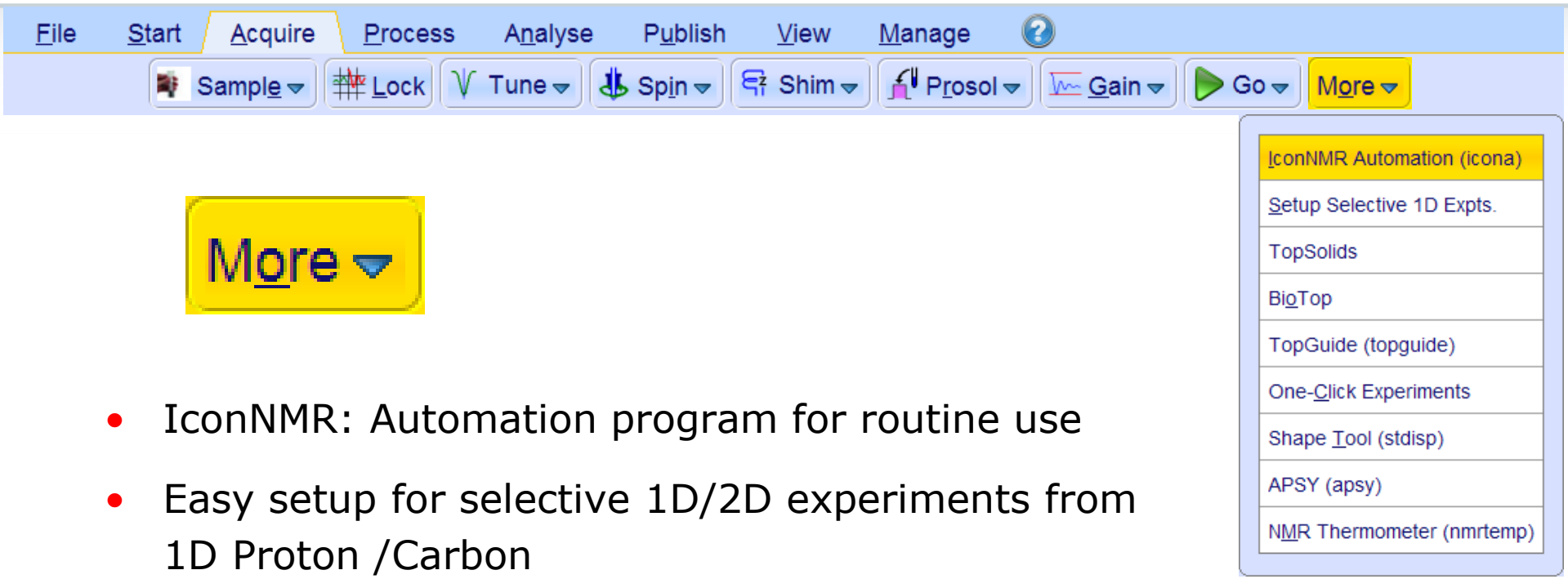


- [**zg**] zeroes data (**!**) and starts acquisition
- [**go**] starts acquisition and adds to existing data
- [**xaua**] executes AU program for acquisition

Acquire Toolbar – Go

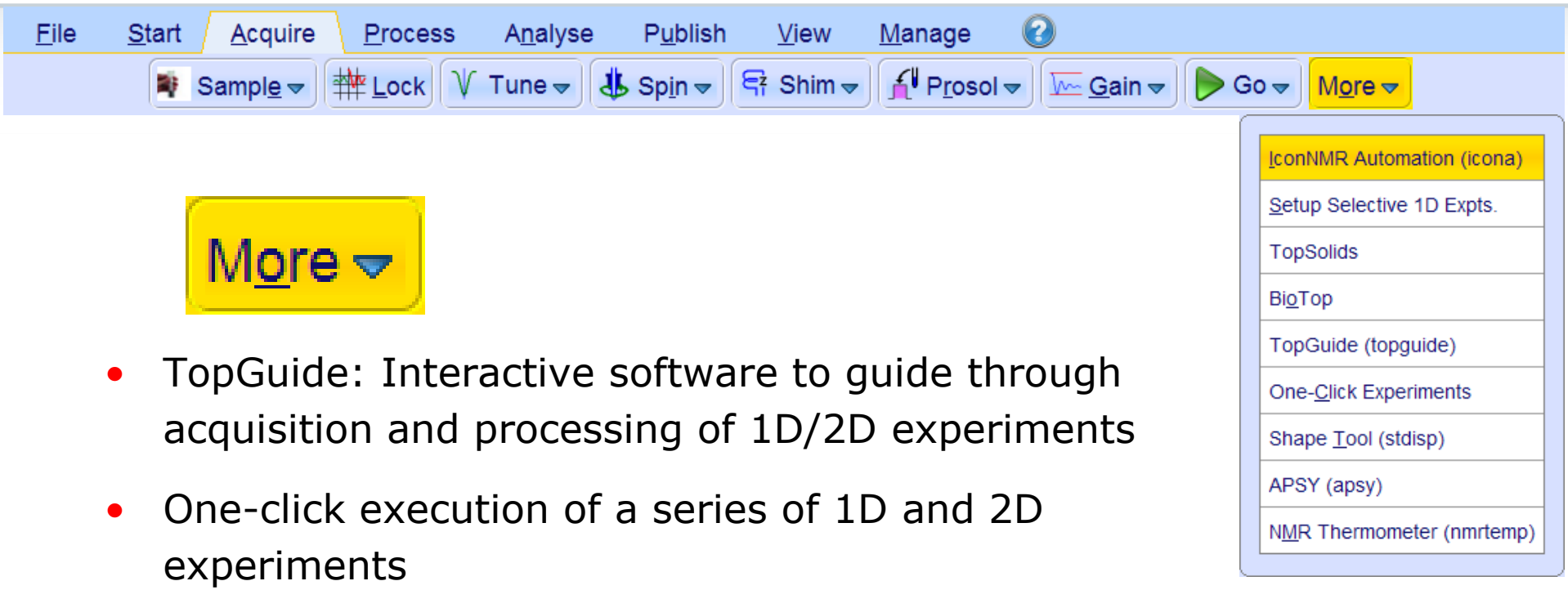
- [**stop**] stops the measurement without storing the FID ()
- [**halt**] stops the measurement and stores the FID ()
  - [**halt 4**] stops at a multiple of 4
- [**tr**] stores the FID without stopping the measurement
  - [**tr 2**] stores FID at a multiple of 2 without stopping
- [**expt**] estimates experiment time ()

Acquire Toolbar – More



- IconNMR: Automation program for routine use
- Easy setup for selective 1D/2D experiments from 1D Proton /Carbon
- TopSolids: Assisted user interface for solid-state experiments
- BioTop: Assisted user interface for high resolution experiments for biological samples

Acquire Toolbar – More



- TopGuide: Interactive software to guide through acquisition and processing of 1D/2D experiments
- One-click execution of a series of 1D and 2D experiments
- Shape Tool: Design and manipulation of pulse shapes; calculation of excitation profiles
- APSY: Automated Projection Spectroscopy; provides access to N-dimensional correlations by lower-dimensional projections

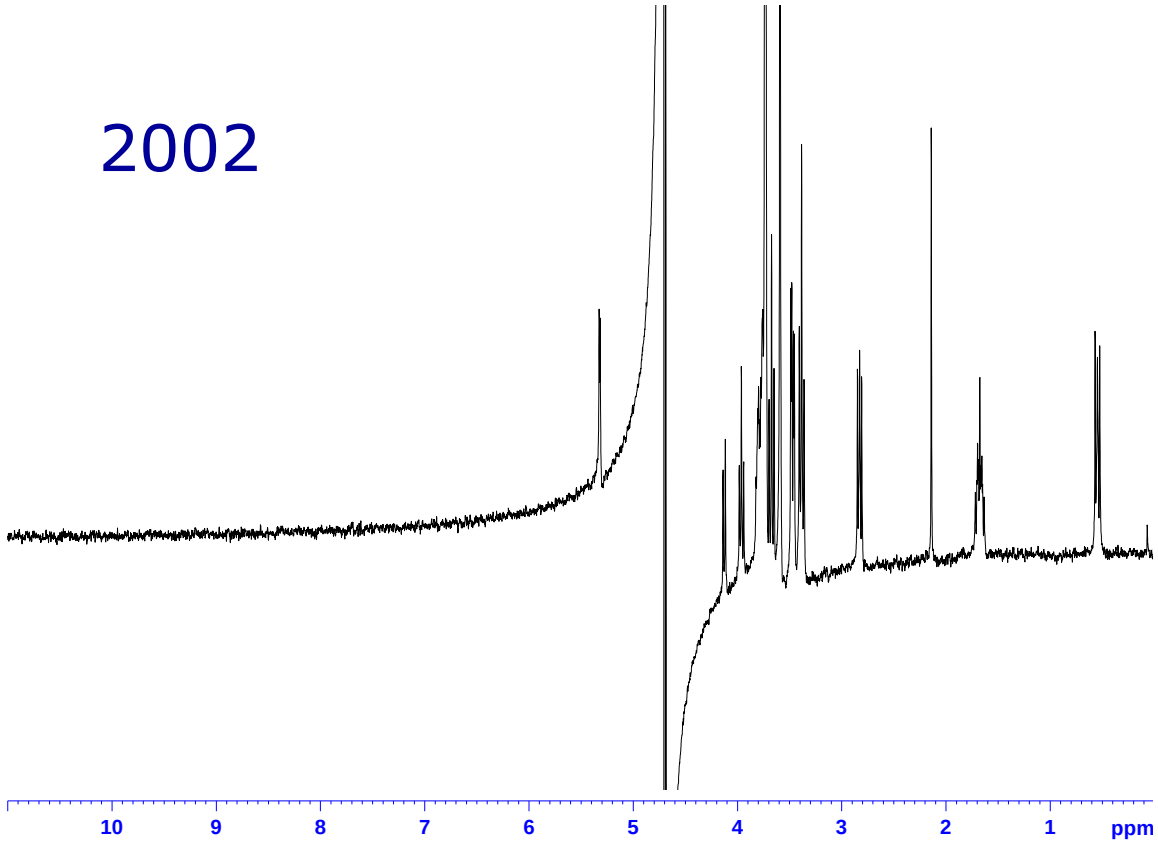
One more thing…

- Digitizer mode: DIGMOD
- Can be set in [**eda**]
- Typically set to digital (oversampling and digital filtering)

- New since TopSpin 2.0: baseopt
  - Flat baseline at 0
  - No 1st order phase correction
  - No distortions at the edge of the spectrum

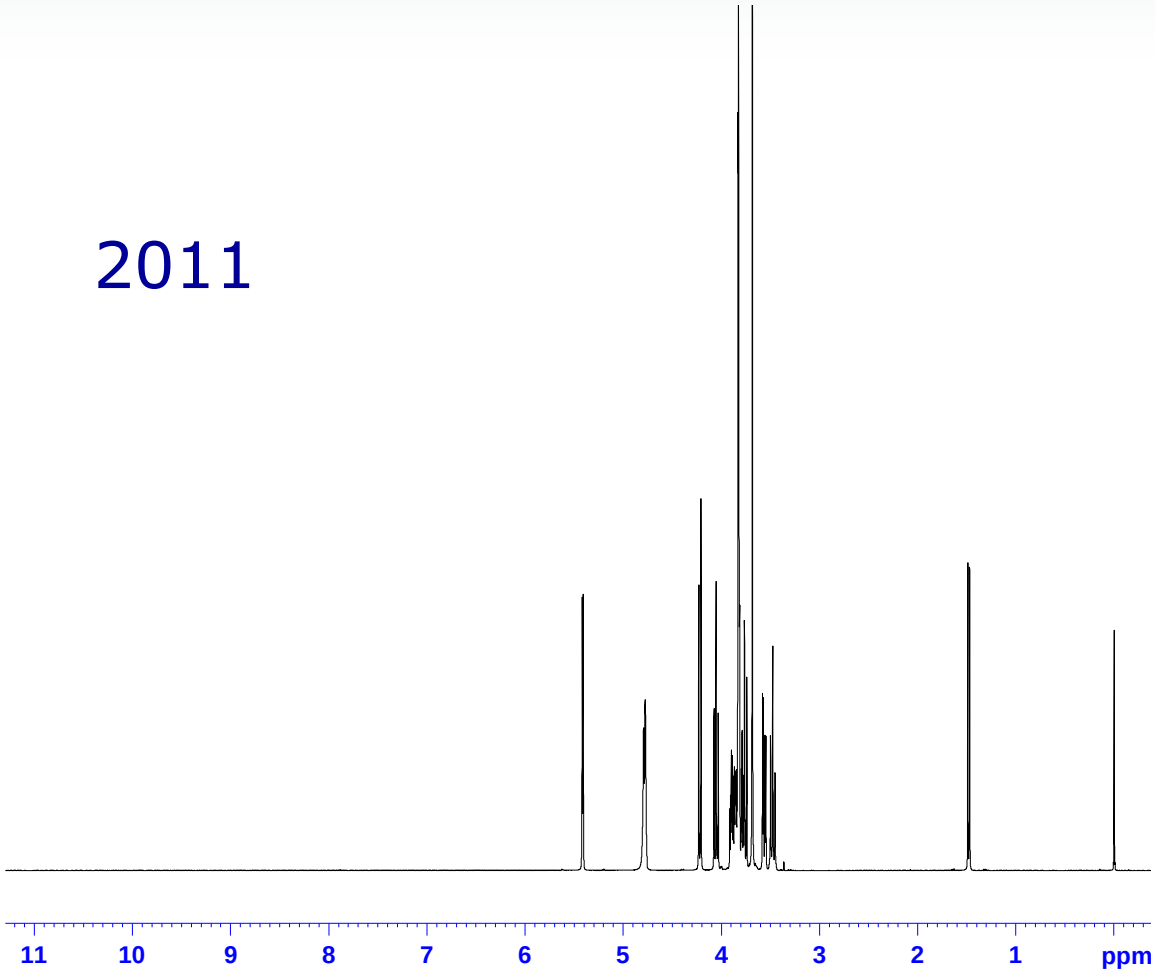
  - FILCOR parameter needs to be determined

One more thing…



One more thing…

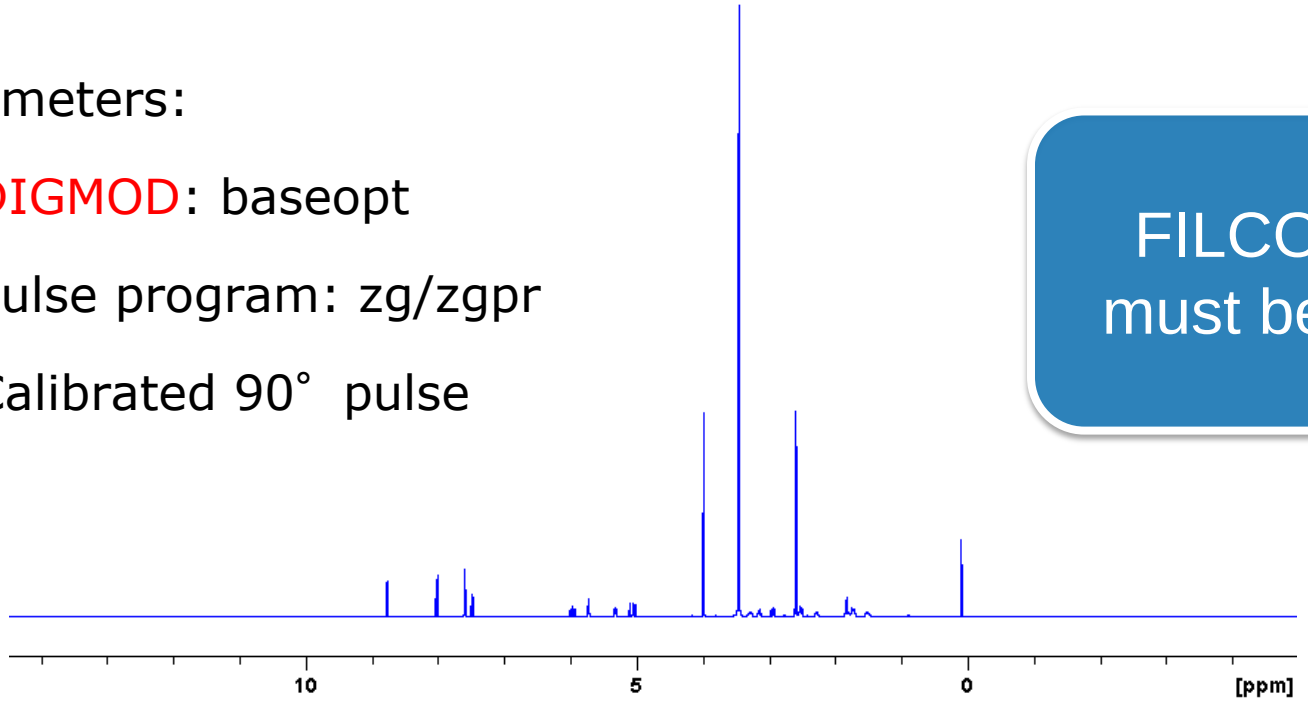
2011



Determine FILCOR parameter

- FILCOR is a hardware specific parameter
- Needs to be determined for each probe separately
- Use a sample with a wide chemical shift range

- Parameters:
  - DIGMOD: baseopt
  - Pulse program: zg/zgpr
  - Calibrated 90° pulse

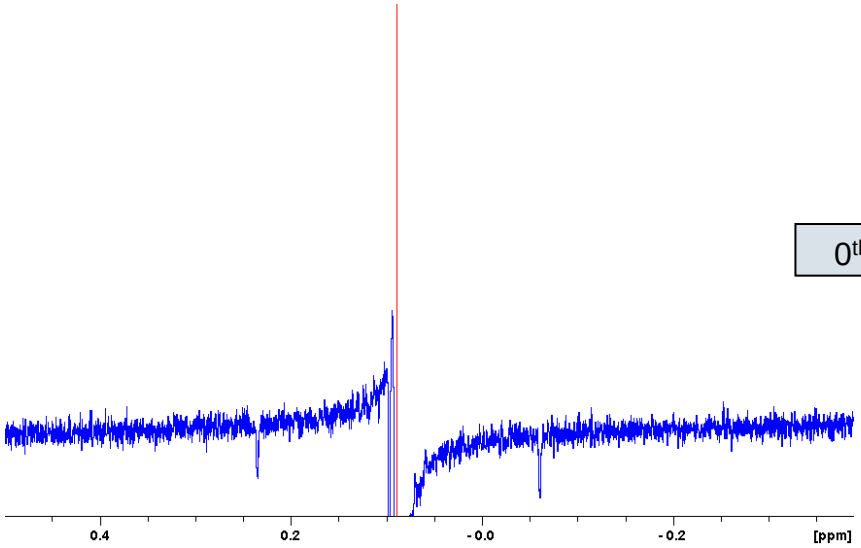


FILCOR must be 0!

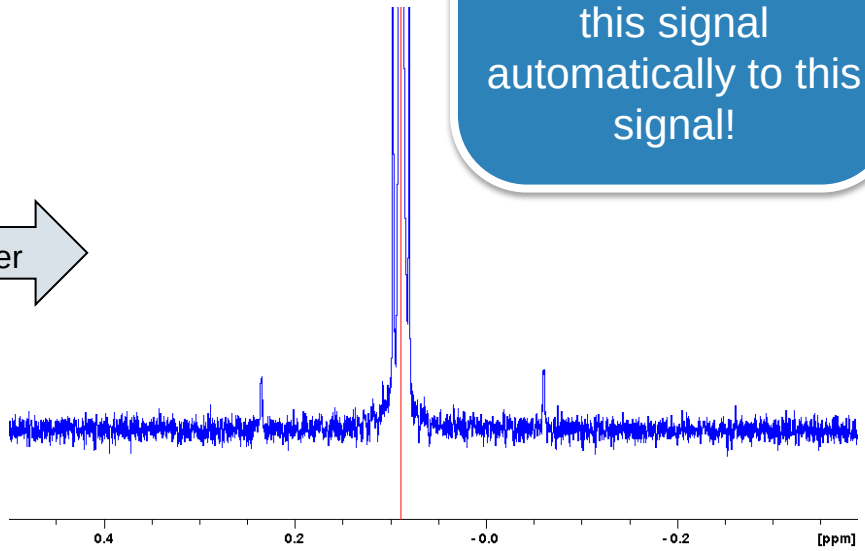
Determine FILCOR parameter

- Zoom into the rightmost signal and phase it with 0th order only
- Pivot point should be set to this signal

If you enter phasing mode after zooming into the signal, the pivot point is set to this signal automatically to this signal!

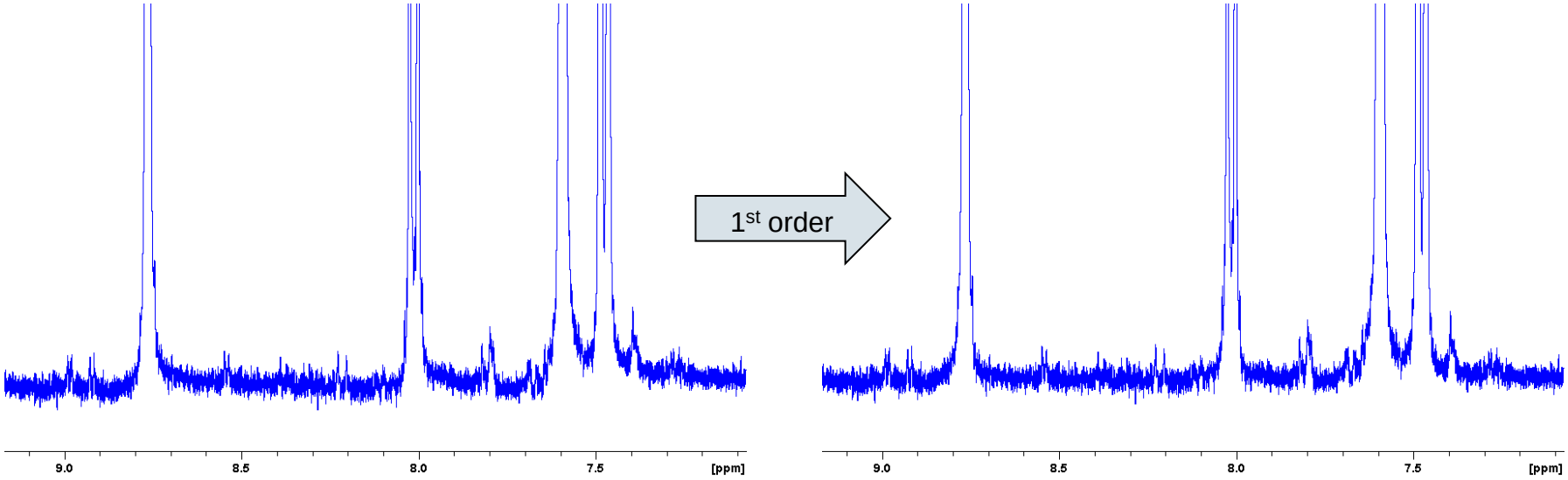


0th order



Determine FILCOR parameter

- Do not exit phasing mode!
- Zoom into the leftmost signal and phase it with 1st order only
- 1st order phase correction should be small

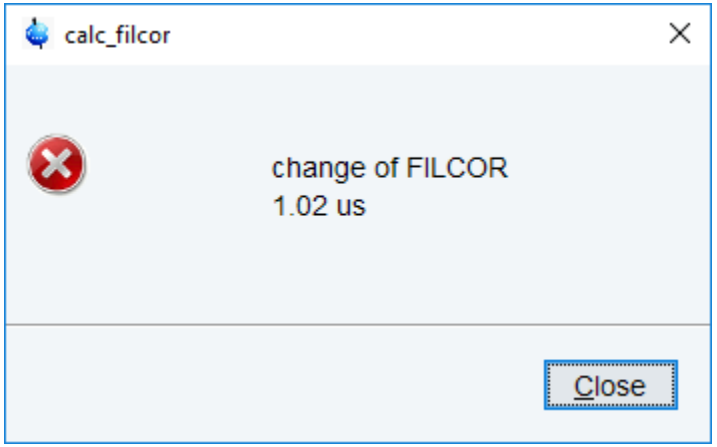


Determine FILCOR parameter

- FILCOR parameter is calculated by:

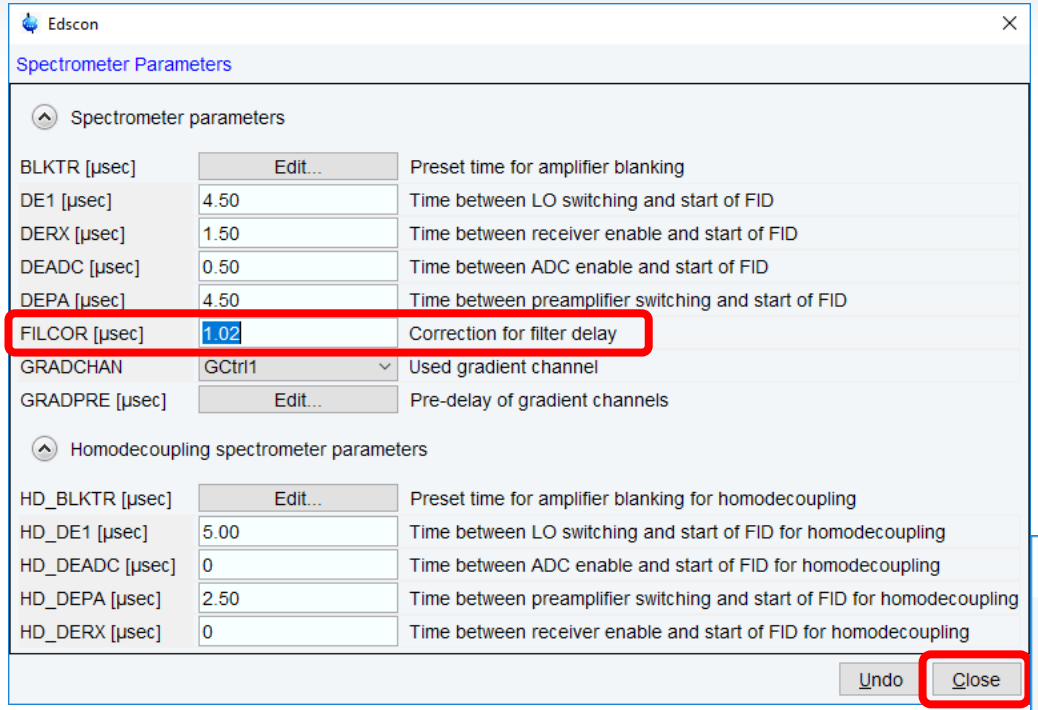
$$FILCOR = \frac{PHC1 \times DW}{180}$$

- AU program available on your USB stick for automatic calculation: calc_filcor

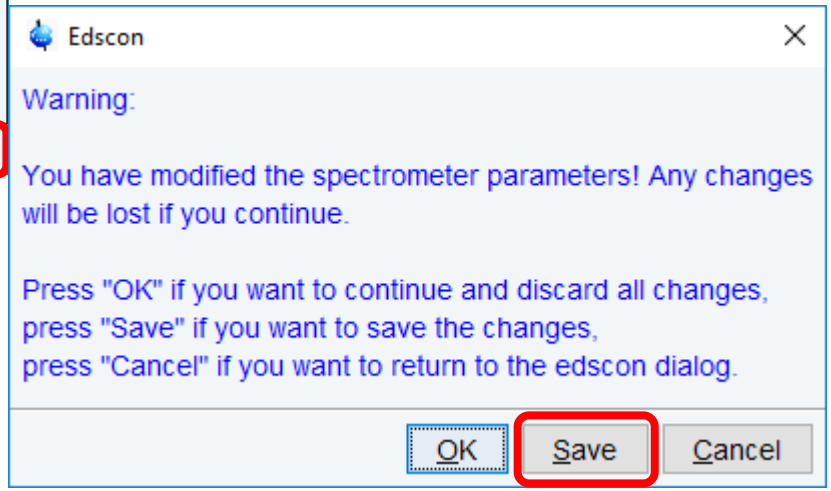


- FILCOR parameter is set as a spectrometer constant with [**edscon**]

Set FILCOR parameter

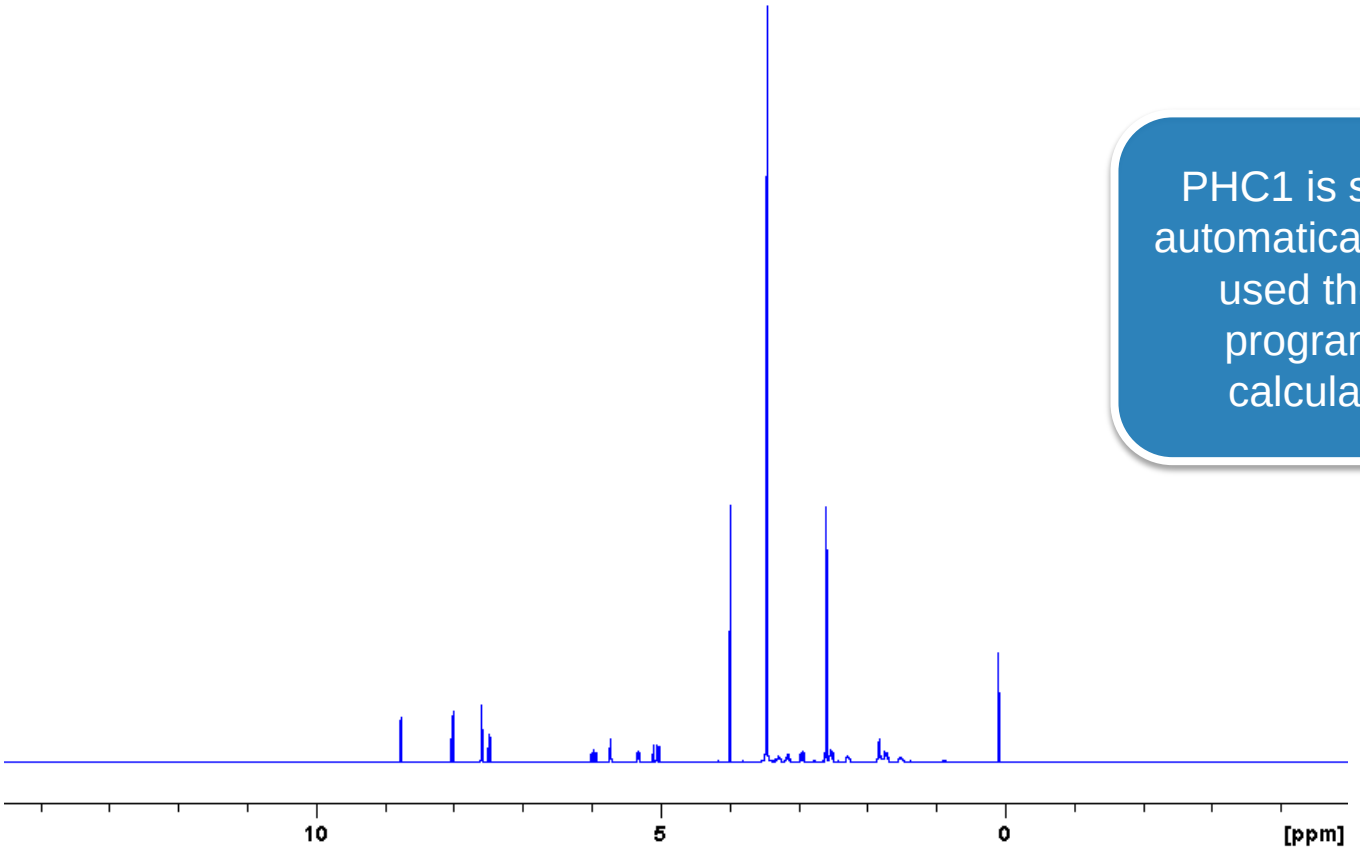


Protected by super user password.

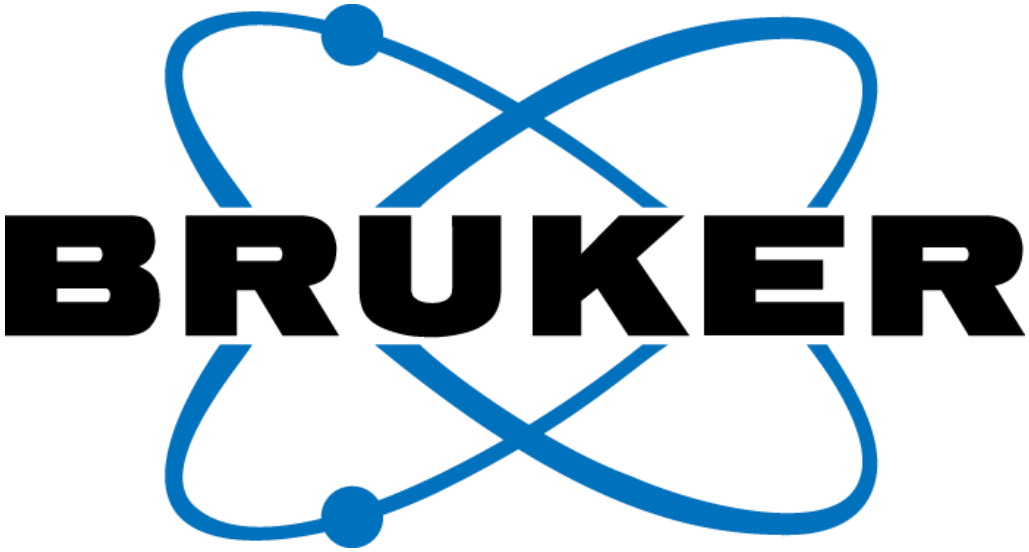


Check FILCOR parameter

- Set PHC1 to 0 and repeat experiment
- Phasing should be possible with 0th order phase correction only



PHC1 is set to 0 automatically if you used the AU program for calculation.



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