KJM 9250

1D-SELECTIVE NMR Experiments on the AVI-600
and AVII-600

Version 1.0

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Topspin 1.3 Windows XP

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1.1 Introduction

aw coded 1D-Selective experiments use soft 180° refocusing pulses with a default prosol Table linked pulse time of 80000 usec. Pulse powers are read in using the **getprosol** command.

The effective excitation window of an 80000 usec 180° soft pulse experiment is ca 25 Hz For a wider or narrower excitation window use one of the power and time combinations below. The greater the pulse power attenuation (larger the db value) the narrower the excitation window. Adding 6 db halves the pulse power.

Selective pulse power + time combinations
  Default: 80000 usec at the PLW level read in by the **getprosol** command
    Other: 40000 usec, subtract 6 db to the PLW level read in by the **getprosol** command
            120000 usec, add 3 db to the PLW level read in by the **getprosol** command
            160000 usec, add 6 db to the PLW level read in by the **getprosol** command
            240000 usec, add 9 db to the PLW level read in by the **getprosol** command

1.2 NS x TDO option

1D-SELECTIVE experiments can be run using the **NS** x **TD0** option where **NS** is a multiple of 8, 16, 32, 64 (etc) and **TD0** is any number >1.

Do NOT use the **TR** command as a **NS x TD0** experiment proceeds. Multiples of **NS** scans will be automatically saved and can be processed using the FT or EFP commands the experiment proceeds. A run can be terminated at any time using the **STOP** (*NB not the* **HALT**) command. This will ensure a multiple of 4 or 8 scans is saved as is required by some of the selective excitation experiments.

1.3 1D-SELECTIVE Experiments

The following 1D-Selective experiments have been set up on the AVI and AVII 600 MHz spectrometers

      2.1 SELCOSY spectra

      2.2 SELTOCSY spectra

      2.3 SELDIPSI2 spectra

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      2.5 SELNOESY spectra

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      2.7 SELROESY.2 spectra

      2.8 SELHSQC and SELHSQCND spectra

      2.9 SELHSQC-DIPS2 and SELHSQCND-DIPSI2 spectra

2.1 SELCOSY spectra

Parameter set: **awselcosy (+ getprosol)**
Pulse programme: **selco**

TD = 32 K, **SI** = 32 K
O1 = Frequency in Hz of signal to be selectively correlated. **O1** Excitation is applied
    on resonance at the middle of SW. Check SW is wide enough.

NS = multiple of 8 or 16, **DS** = 4 or 8.
  or **NS x TD0** scans where **TDO** = any positive number.

D1 = 1 sec or other time of your choice
D14 = $1/4J_{H-H}$. A value in the range 30-40 msec (default 35 msec) generally works well
        irrespective of J_{H-H}.

P12 = 80000 usec, **SPW2** = shaped pulse power read in using the getprosol command.

Process with **EFP** (applies **LB** = 0.1 Hz).
Phase the spectrum to afford *antiphase positive and negative signal intensities.*

Alternatively process the spectrum in **PS** (**Power**) mode to afford *positive correlation peaks* (see the next page).
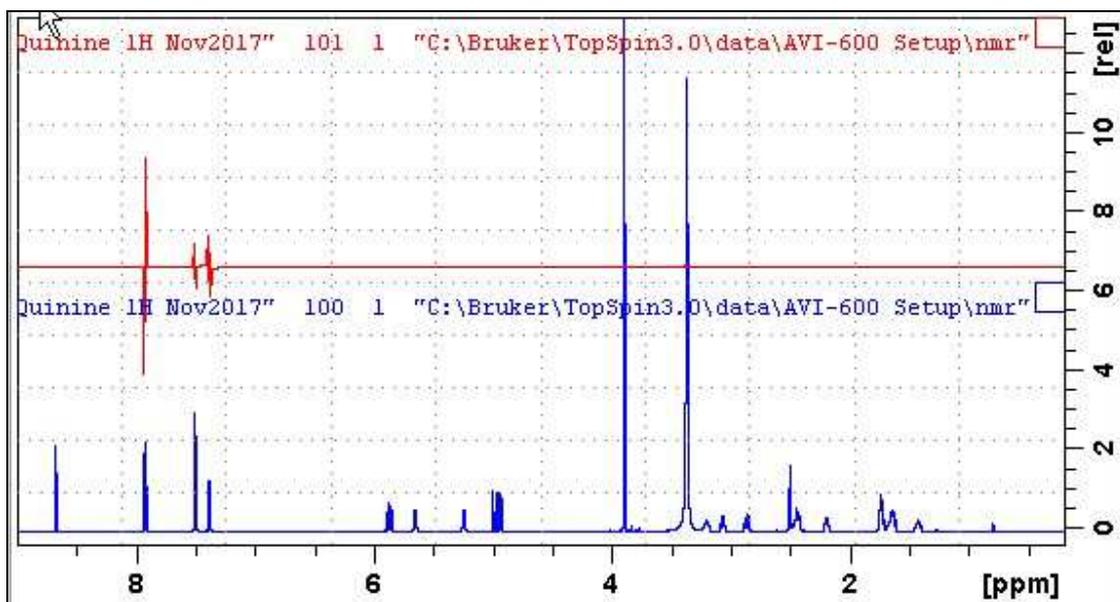
Lower: 0-9 ppm region of the 600 MHz ^{1}H NMR spectra of quinine in D_6-DMSO.
Upper: SELCOSY spectrum ex the signal at 7.39 ppm.

Power mode (PS) processing of a SELCOSY spectrum

To convert an antiphase SELCOSY spectrum generated by normal **FT** or **EF** processing to a **Power Spectrum** (intensity squared spectrum), type:

    PS (return),
    abs (return) to center the spectrum of on its baseline and
    click the **/8** button several times until the spectrum is appropriately scaled.
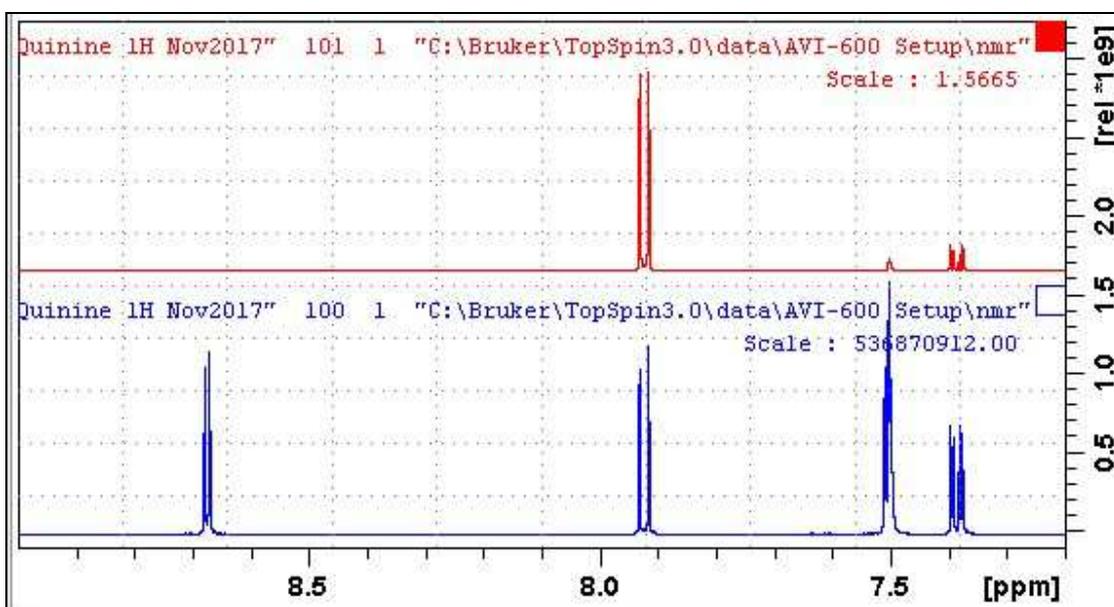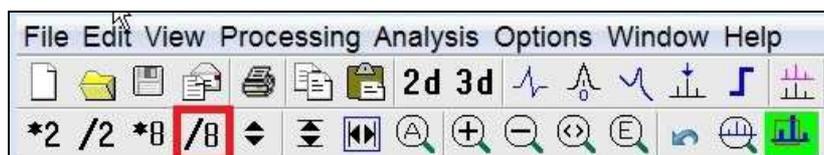
Lower: 7-9 ppm region of the 600 MHz ^{1}H NMR spectra of quinine in D_6-DMSO.
Upper: Power mode processed SELCOSY spectrum ex the signal at 7.39 ppm.

2.2 SELTOCSY spectra

Parameter set: **awseltocsy (+ getprosol)**
Pulse programme: **selmlgp**

TD = SI = 32 K or 64K
O1 = Frequency in Hz of signal to be selectively correlated. **O1** Excitation is applied
    on resonance at the middle of SW. Check SW is wide enough.

NS = multiple of 8 or 16, **DS** = 4 or 8.
  or **NS x TD0** scans where **TDO** = any positive number.

D1 = 1 sec or other time of your choice
D9 = 80 msec for medium range correlations or other time of your choice.
    160 msec for long range correlations, 6-15 msec for short range correlations.

P12 = 80000 usec, **SPW2** = shaped pulse power read in using the getprosol command.
PL10 = TOCSY spin lock power level is read in using the getprosol command.

Process with **EFP** (applies **LB,** typically use 0.1 - 0.3 Hz); all peaks should be positive.
Strongly coupled peaks may exhibit some negative artifact lines which tend to decrease
as **D9** is increased.
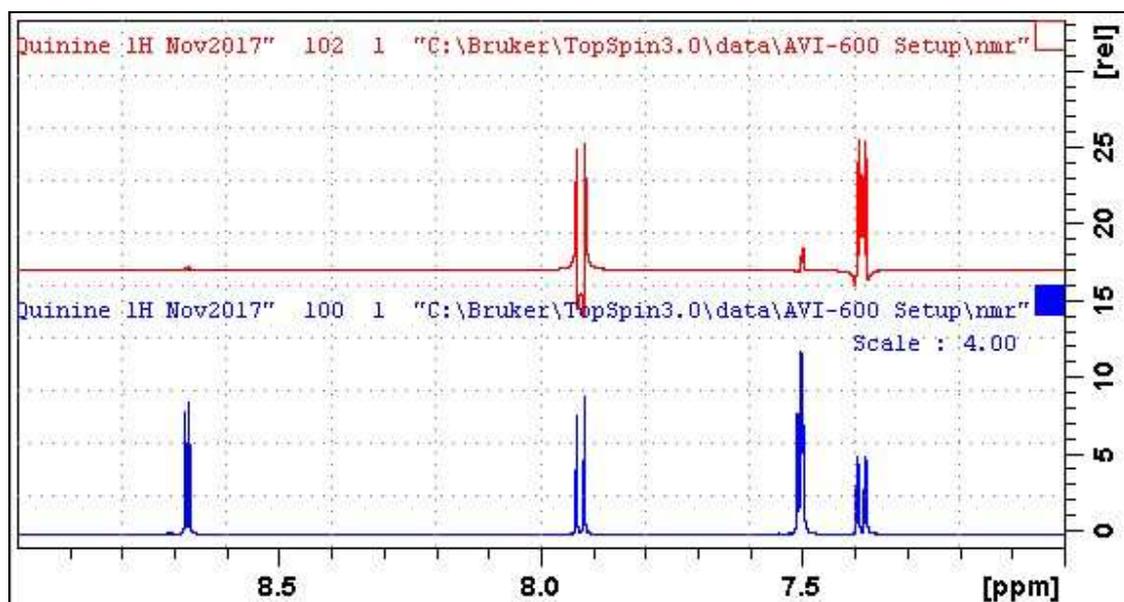
Lower: 7-9 ppm region of the 600 MHz ^{1}H NMR spectra of quinine in D_6-DMSO.
Upper: D9 = 80 msec SELTOCSY spectrum ex the signal at 7.39 ppm.

2.3 SELDIPSI2 spectra

Parameter set: **awseldipsi2 (+ getprosol)**
Pulse programme: **seldigp**

TD = 64 K, **SI** = 64 K, **SW** = 16 ppm.
O1 = Frequency in Hz of signal to be selectively correlated. **O1** Excitation is applied
 on resonance at the middle of SW. Check SW is wide enough.

NS = multiple of 8 or 16, **DS** = 4 or 8.
  or **NS x TD0** scans where **TDO** = any positive number.

D1 = 1 sec or other time of your choice.
D9 = 80 msec for medium range correlations or other time of your choice.
  160 msec for long range correlations, 6-15 msec for short range correlations.

P12 = 80000 usec, **SPW2** = shaped pulse power read in using the getprosol command.
PL10 = spin lock power level read in using the getprosol command.

Process with **EFP** (applies **LB,** typically use 0.1 - 0.3 Hz); all peaks should be positive.
Strongly coupled peaks may exhibit some negative artifact lines which tend to decrease
as **D9** is increased.
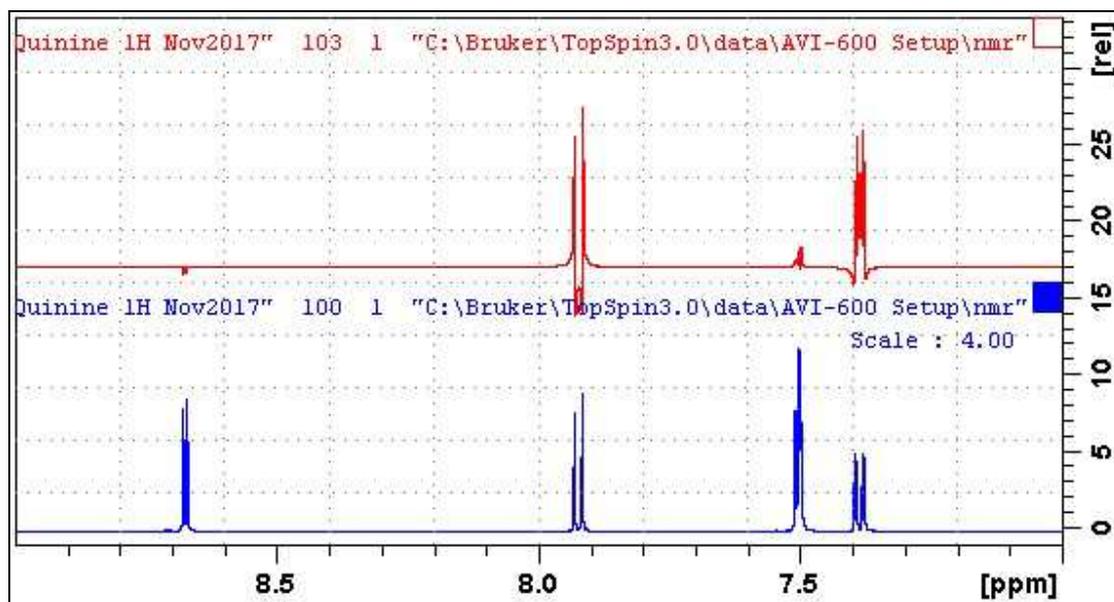
Lower: 7-9 ppm region of the 600 MHz ^{1}H NMR spectra of quinine in D_6-DMSO.
Upper: D9 = 80 msec SELDIPSI2 spectrum ex the signal at 7.39 ppm.

2.4 Phasing of 1D-SELNOESY and SELROESY spectra

NOESY and SELNOESY peaks may be positive, zero or negative depending on correlation times whereas *ROESY and SELROESY peaks are always positive.*

In a **classic NOE-difference experiment** a positive NOE is one which affords a positive enhanced signal relative to the residual negative irradiated signal observed when a reference spectrum is subtracted from the irradiated spectrum.
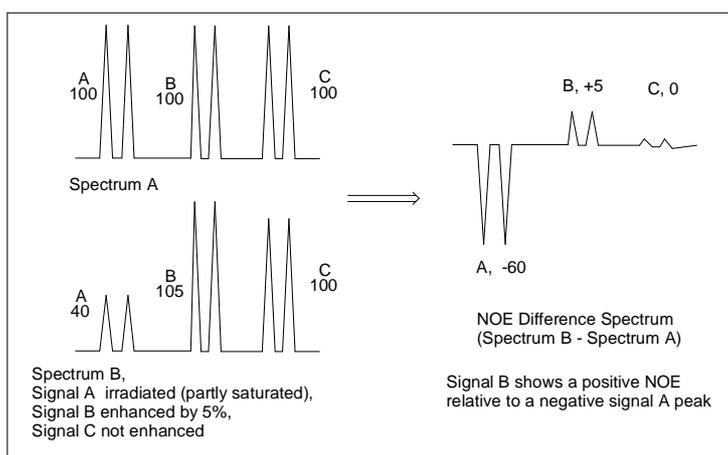
*A positive NOE is one in which a positive enhanced peak is observed relative to a **negative irradiated peak** in a 1D-SELNOESY experiment , or a **negative diagonal peak** in a 2D-NOESY experiment.*

An example of a signal showing a positive ROESY response and a negative NOESY response is shown below.
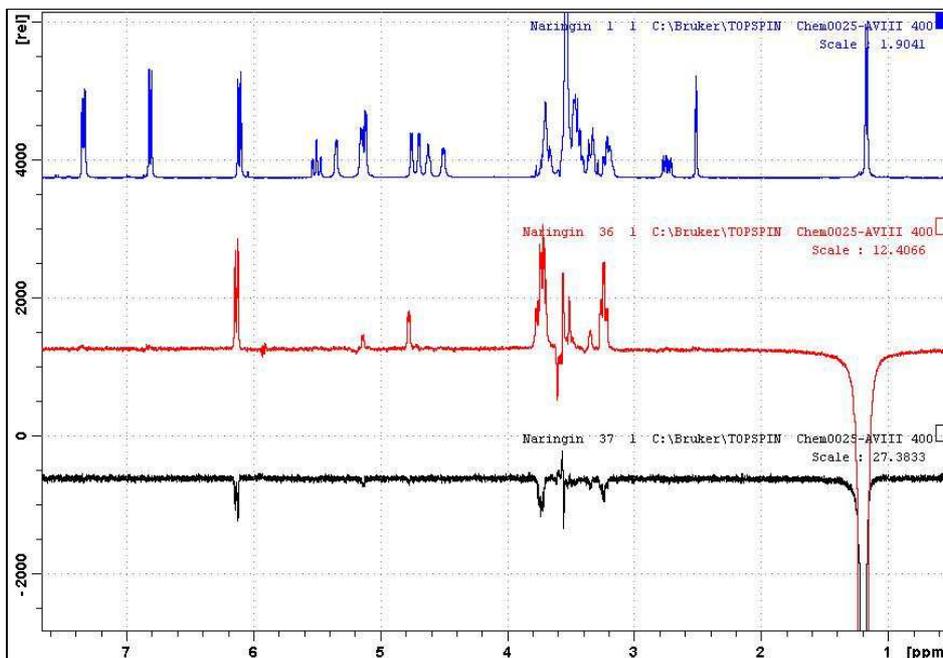
Upper: ^{1}H NMR spectrum of naringin (0.5-8 ppm region plotted).
Center: SELROESY spectrum ex the methyl signal at 1.2 ppm.
Lower: SELNOESY spectrum ex the methyl signal at 1.2 ppm.

2.5 SELNOESY spectra

Parameter set: **awselnoesy (+ getprosol)**
Pulse programme: **selnogp4**

TD = 32 K, **SI** =32 K, **SW** = 16 ppm.
O1 = Frequency in Hz of signal to be selectively correlated. **O1** Excitation is applied
   on resonance at the middle of SW. Check SW is wide enough.

NS = multiple of 4, 8 or 16, **DS** = 4 or 8.
   or **NS x TD0** scans where **TDO** = any positive number.

D1 = 1 sec or other time of your choice.
D6 = 0.5 to 0.8 sec (NOESY correlation time).

P12 = 80000 usec, **SPW2** = shaped pulse power read in using the getprosol command.
PLW10 = TOCSY spin lock power level read in using the getprosol command.

Process with **EFP** (applies **LB,** typically use 0.1 - 0.3 Hz).
Phase the spectrum to afford a **negative** excited signal. NOESY peaks may be *positive, zero or negative* depending on correlation times. COSY artifact peaks ex strongly coupled signals may occasionally be present in NOESY spectra.
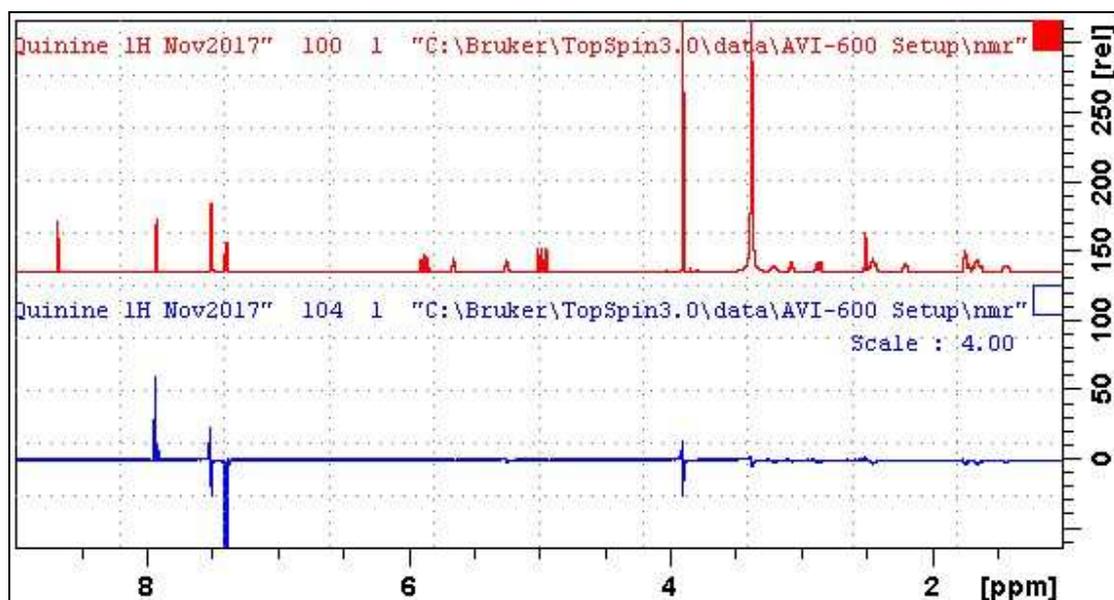
Upper: 1-9 ppm region of the 600 MHz ^{1}H NMR spectra of quinine in D$_6$-DMSO.
Lower: SELNOSY spectrum ex the signal at 7.39 ppm. The signal at 7.51 ppm is an antiphase COSY artifact peak.

2.6 SELROESY (CW spin locked) spectra

Parameter set: **awselroesy (+ getprosol)**
Pulse programme: **selrogp**

TD = 32 K, **SI** = 32 K, **SW** = 20 ppm.
O1 = Frequency in Hz of signal to be selectively correlated. **O1** Excitation is applied
    on resonance at the middle of SW. Check SW is wide enough.

NS = multiple of 4, 8 or 16, **DS** = 4 or 8.
  or **NS x TD0** scans where **TDO** = any positive number.

D1 = 2 sec or other time of your choice.
P15 = 250000 usec (ROESY spinlock time).

SPW2 = Shaped pulse power level (read in by the getprosol command).
PLW11 = ROESY CW spin lock power (read in by the getprosol command).

Process with **EFP** (applies **LB,** typically use 0.1 - 0.3 Hz). *Phase the spectrum to afford a*
negative *excited signal and positive ROESY peaks. Negative or antiphase TOCSY artifact*
peaks may be present in ROESY spectra.
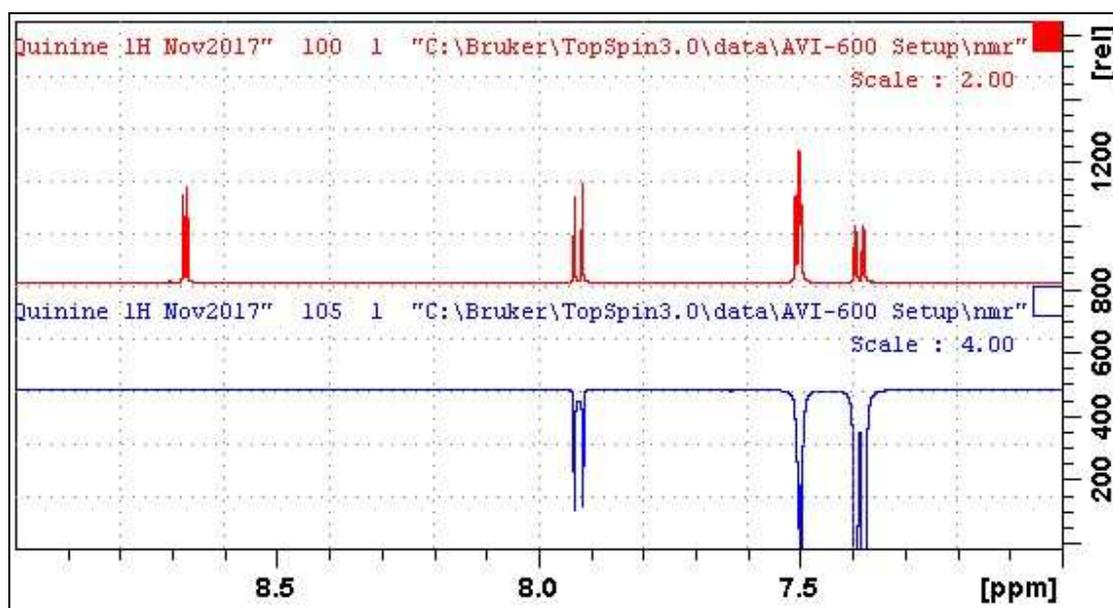
Upper: 7-9 ppm region of the 600 MHz ^{1}H NMR spectra of quinine in D$_6$-DMSO.
Lower: SELROESY spectrum ex the signal at 7.39 ppm. Only negative TOCSY artifact
peaks were observed when the SELROESY spectrum was determined d with the **prosol**
Table linked PL11 CW spin lock power level.

*TOCSY artifact peaks are generally less significant in pulsed spin locked SELROESY.2 spectra \
(see Section 2.7*

2.7 SELROESY2 (pulsed spin locked) spectra

Parameter set: **awselroesy2 (+ getprosol)**
Pulse programme: **selrogp.2**

TD = 32 K, **SI** = 324 K, **SW** = 16 ppm.
O1 = Frequency in Hz of signal to be selectively correlated. **O1** Excitation is applied
   on resonance at the middle of SW. Check SW is wide enough.

NS = multiple of 4, 8 or 16, **DS** = 4 or 8.
   or **NS x TD0** scans where **TDO** = any positive number.

D1 = 2 sec or other time of your choice.
P15 = 250000 usec (ROESY spinlock time).

SP2 = Shaped pulse power level (read in by the getprosol command).
PLW27 = ROESY pulsed ROESY spinlock power (read in by the getprosol command).

Process with **EFP** (applies **LB,** typically use 0.1 - 0.3 Hz). *Phase the spectrum to afford a **negative** excited signal and positive ROESY peaks.*
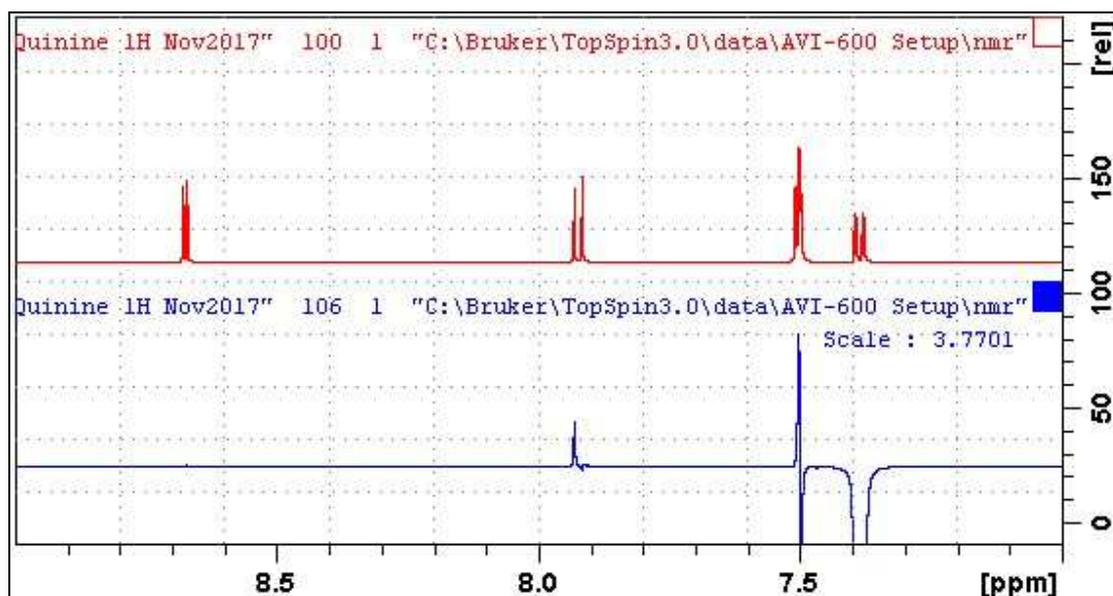
Upper: 7-9 ppm region of the 600 MHz ^{1}H NMR spectra of quinine in D_6-DMSO.
Lower: SELROESY2 spectrum ex the signal at 7.39 ppm. An antiphsase TOCSYartifact peak appears at 7.52 ppm. A weak ROESY correlation, attenuated by a significant antiphaseTOCSY artifact contribution is observed at 7.93 ppm.

Antiphase (mixed positive/negative) TOCSY artifact peaks may occasionally be present in SELROESY.2 spectra TOCSY artifact peaks are generally much less significant in pulsed spin locked SELROESY.2 spectra than is the case for CW spin locked SELROESY spectra..

2.8 SELHSQC and SELHSQCND spectra

Parameter set: **awselhsqc** o**r awselhsqcnd (+ getprosol)**
Pulse programme: **awselhsqcgpsisp** or **awselhsqcndgpsisp**

 Prior to running a **SELHSQC** experiment run a standard **^{13}C** or **DEPT** experiment and determine the **O1** frequency of the **^{13}C** signal in **Hz** to be selectively excited. Enter this value as **O2 (Hz)**.

TD = 32 K, **SI** =32 K.
SW = 12 ppm, **O1P** = 5 ppm. Adjust **SW** and **O1P** as required.
O2: frequency of the **^{13}C** signal in **Hz** to be selectively excited.

NS = multiple of 8 or 16, **DS** = 4 or 8.
   or **NS x TD0** scans where **TDO** = any positive number.

D1 = 1 sec or other value of your choice.
D24 is automatically calculated from **CNST2** ($^1J_{C-H}$).
CNST2 = $^1J_{C-H}$; typically 125 to 160 Hz for sp^3-sp^2 carbons. Furan or pyrrole ring
   carbons adjacent to hetero atoms will have ^1J = 200-220 Hz.

Shaped pulse types and powers read in by the **getprosol** command.

Process with **EFP** (applies **LB** = 0.1 Hz).
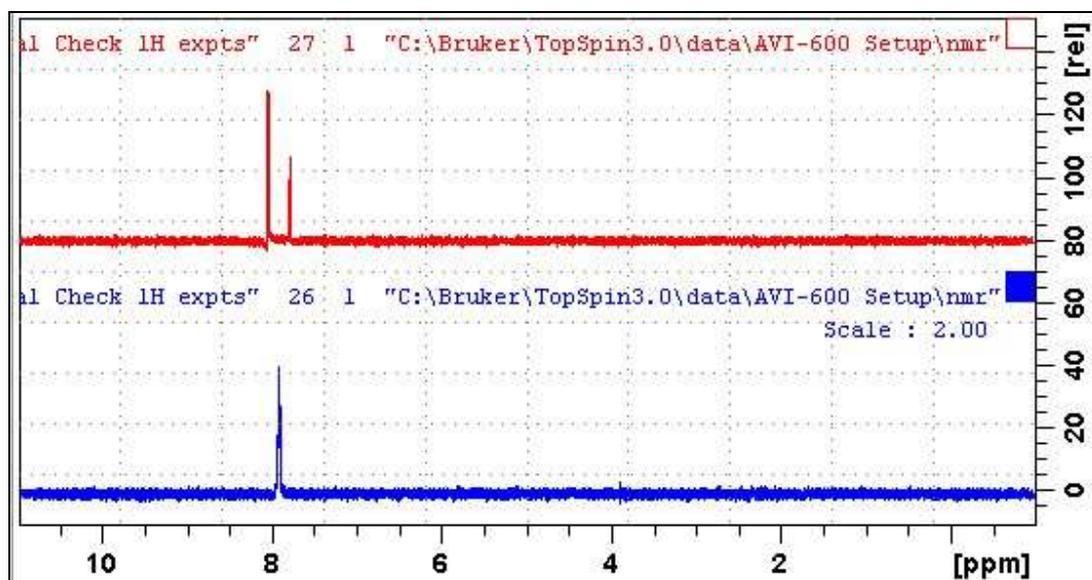
600 MHz **SELHSQC** *(lower)* and **SELHSQCND** *(upper)* spectra determined for quinine in D$_6$-DMSO with selective excitation of the ^{13}C signal at 131.6 ppm (O2 = 19857 Hz).

2.9 SELHSQC-DIPSI2 and SELHSQCND-DIPSI2 spectra

Parameter set: **awselhsqc-dipsi2** or **awselhsqcnd-dipsi2 (+ getprosol)**
Pulse programme: **awselhsqcgpdigpsisp** or **awselhsqcgpdigpndsisp**

 Prior to running a **SELHSQC-DIPSI2** experiment run a standard ^{13}C or **DEPT** experiment and determine the **O1** frequency of the ^{13}C signal in **Hz** to be selectively excited. Enter this value as **O2 (Hz)**.

TD = 32 K, **SI** =32 K.
SW = 12 ppm, **O1P** = 5 ppm. Adjust **SW** and **O1P** as required.
O2: frequency of the ^{13}C signal in **Hz** to be selectively excited.

NS = multiple of 8 or 16, **DS** = 4 or 8.
   or **NS x TD0** scans where **TDO** = any positive number.

D1 = 1 sec or other value of your choice.
D9 = 80 msec or other time of your choice (6-160 msec).
D24 is automatically calculated from **CNST2** ($^{1}J_{C-H}$).
CNST2 = $^{1}J_{C-H}$; typically 125 to 160 Hz for sp^3-sp^2 carbons. Furan or pyrrole ring
   carbons adjacent to hetero atoms will have ^{1}J = 200-220 Hz.

Shaped pulse types and powers are read in by the **getprosol** command.

Process with **EFP** (applies **LB** = 0.1 Hz).
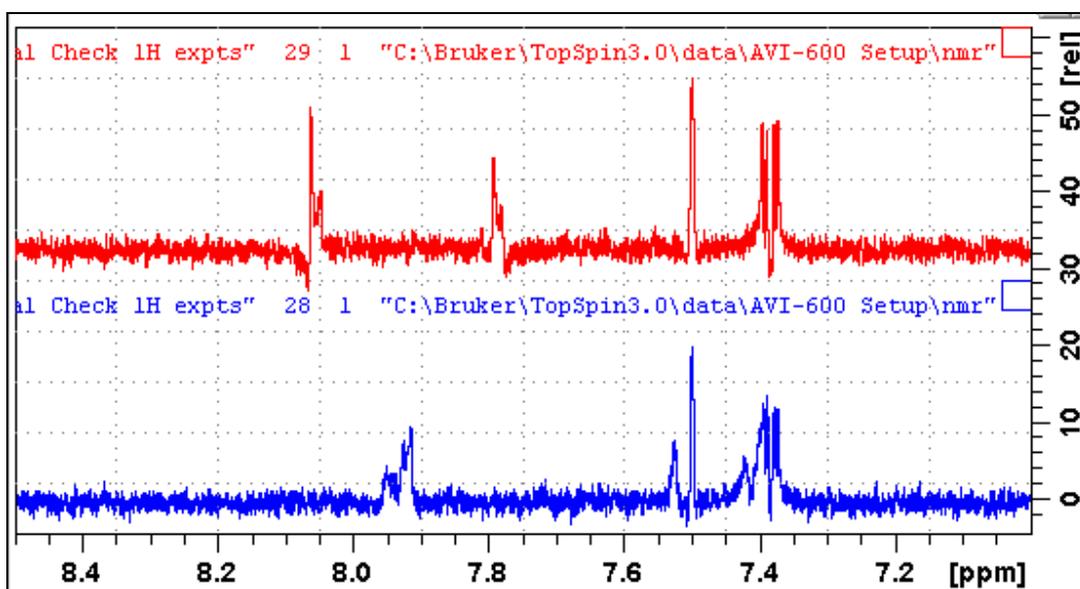
Expansions of the 7-8.5 ppm regions of the 600 MHz **SELHSQC-DIPSI2** *(lower)* and **SELHSQCND-DIPSI2** *(upper)* spectra determined for quinine in D$_6$-DMSO with selective excitation of the ^{13}C signal at 131.6 ppm (O2 = 19857 Hz). The ^{1}J correlated proton signal occurs at 7.95 ppm.

Correlated ^{1}H NMR signals observed in coupled SELHSQCND-DIPSI2 spectra show ^{1}J, ^{2}J, or ^{n}J ^{13}C-^{1}H couplings depending on the number of bonds between the selectively excited ^{13}C signal and correlated proton signals.