Supplementary Information for the manuscript:

Side-Chain to Backbone Correlations from Solid-State NMR of Perdeuterated Proteins through Combined Excitation and Long-Range Magnetization Transfers

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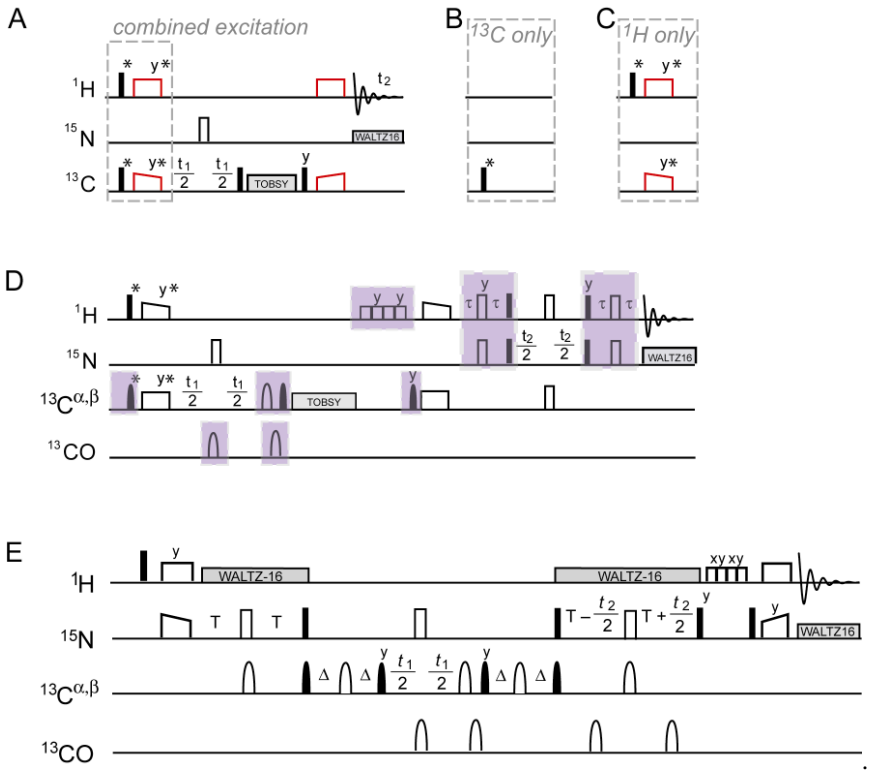
Additional Pulse Sequences:

Supplementary Figures 1 A-C show pulse sequences used for $^{13}C/^{1}H$ 2D correlations as shown in Figure 2 of the main text with different ways of excitation. For these spectra, a direct transfer to ^{1}H as the detection nucleus was pursued using long-range $^{1}H/^{13}C$ CP transfers.

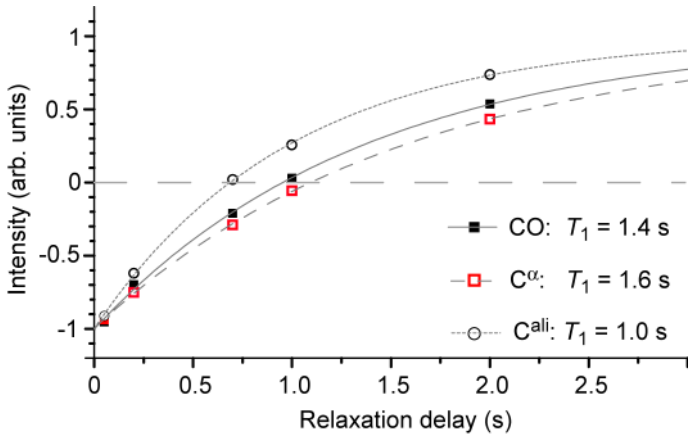


Suppplentary Figure 1: A) Pulse program for 2D $^{1}H/^{13}C$ correlations using Combined Excitation (COPORADE) and long-range transfers, as shown in main-text Figure 2. B) and C) depict excitation blocks used for main text Figures 2B and C, respectively. D) Pulse scheme for the 3D *S2B* with additional features for circumvention of potential artefacts. E) HNCACB experiment (Linser et al. 2011) used for the comparison in Figure 1C in the main manuscript. Filled and open rounded bars refer to selective ^{13}C pulses, using soft rectangular and Gaussian G3 pulses (Emsley and Bodenhausen 1990) for on- and off-resonance pulses, respectively.

As an alternative to the 3D experiment shown in the main manuscript, potential sources for artefacts can be addressed using selective aliphatic ^{13}C pulses and Bloch-Siegert phase shift compensation, or INEPT transfers (Morris and Freeman 1979) among amide-group nuclei. Selective ^{13}C pulses may be applied instead of hard pulses in order to eliminate potential ^{13}CO to ^{1}H magnetization transfer. In this work, the spectral width was chosen such that an eventual carbonyl to backbone pathway, which may be more significant with other ^{13}C mixing sequences, cannot compromise the obtained correlation for the aliphatic ^{13}C region through folded CO resonances. Selective ^{13}CO pulses for refocusing of $^{13}C^{\alpha}/^{13}CO$ couplings can be applied to decrease the achievable linewidth on $^{13}C^{\alpha}$. INEPTs can be used for the H/N transfer alternatively, which has been shown to be beneficial for certain residues dependent on their dynamics. (Linser et al. 2010) Here all these add-ons, however, are not necessary in the described case and were omitted due to actual reduction of the achievable signal to noise.

^{13}C T_1 Relaxation:

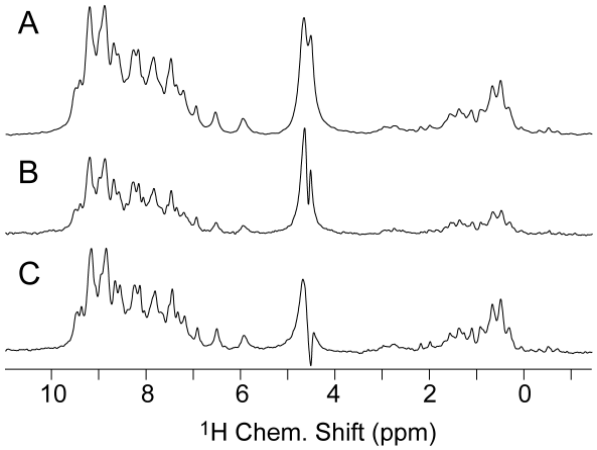
Employing paramagnetic relaxation enhancement (PRE) (Linser et al. 2007; Wickramasinghe et al. 2007), recycle delays can be shortened to below 2 s even for ^{13}C direct excitation, which is usually compromised by relatively long relaxation times. (Calucci et al. 2003) The longitudinal relaxation times of CO, C^{α} and residual aliphatic carbons (C^{ali}) were estimated by evaluation of bulk integrals of the respective species in inversion recovery experiments. The carrier frequency was set to the respective species of interest in each case.



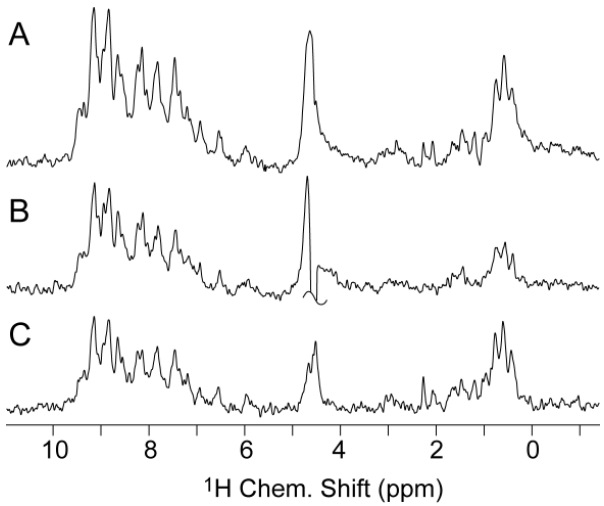
Supplementary Figure 2: T_1 relaxation for ^{13}C using 25% proton back-substitution and 75 mM Cu-edta as a paramagnetic relaxation reagent, recorded at 600 MHz and 24 kHz MAS with a 3.2 mm rotor. As has been shown previously for ^{1}H T_1 (Linser et al. 2007; Wickramasinghe et al. 2007), paramagnetic relaxation enhancement (PRE) can be used to cut down longitudinal relaxation rates.

Excitation Profiles:

Assessment of ^{13}C accessible regions of the amino acid side chain was pursued by 2D $^{13}C/^{1}H$-correlations (see Figure 2 of the main manuscript). This information is crucial in order to answer the question if all backbone chemical shifts will be present in the *S2B* experiments. The obtainable ^{13}C pattern can only be assessed by 2D spectra, since the first 1D slice (which is shown in Supplementary Figure 3 und 4) does not reflect the distribution of involved ^{13}C resonances. Particularly for the comparison between *COPORADE* and ^{13}C-only excitation, however, the bulk signal gives an estimation about the higher overall sensitivity achieved by combined excitation. The pulse sequence used for the assessment is shown in Supplementary Figure 1A-C. For the spectra A in Supplementary Figure 3 und 4, the combined excitation was used, whereas spectra B and C were obtained for direct ^{13}C excitation or proton excitation and subsequent long-range transfer only, respectively.



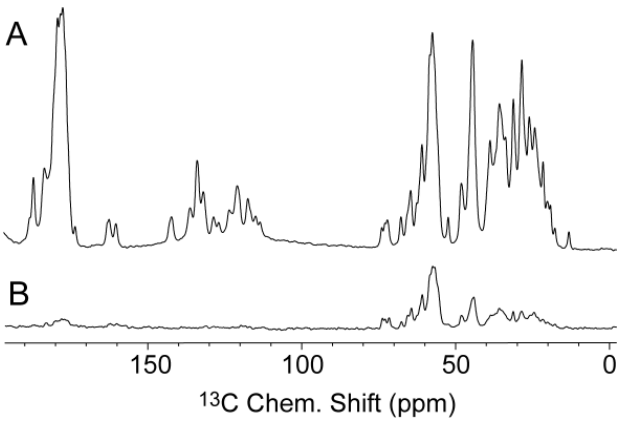
Supplementary Figure 3: Comparison of bulk intensities for different ways of excitation. For these spectra, no homonuclear mixing was employed (see Supplementray Figure 4 for a comparison with use of homonuclear mixing). Using the respective pulse sequences shown in Supplementary Figure 1A-C, **A**), **B**), and **C**) were obtained for COPORADE, ^{13}C direct excitation, and CP from ^{1}H only, respectively. Bulk amide signal intensities of the doubly excited spectrum amount to 1.85 and 1.38 fold the intensity of the ^{13}C only excitation and ^{1}H CP only, respectively. (For the bulk methyl signal, these factors amount to 2.55 and 1.26, respectively.) Spectra were recorded using 256 scans within 8 min each.



Supplementary Figure 4: Comparison of bulk intensities with homonuclear mixing, taking into account 16 ms mixing with TOBSY, but otherwise exactly like Supplementary Figure 3. **A**, **B**, and **C** were obtained for COPORADE, ^{13}C direct excitation, and CP from ^{1}H only, respectively. Bulk amide signal intensities of the doubly excited spectrum amount to 1.54- and 1.89-fold the intensity of the ^{13}C only excitation and ^{1}H CP only, respectively. (For the bulk methyl signal, these factors amount to 2.10 and 1.30, respectively.) The experiments were recorded with the pulse sequence shown in Supplementary Figures 1 A, B, and C, respectively, using 256 scans with a recycle delay of 1.8 s and 20 Hz exponential apodization. Spectra were recorded using 256 scans within 8 min each.

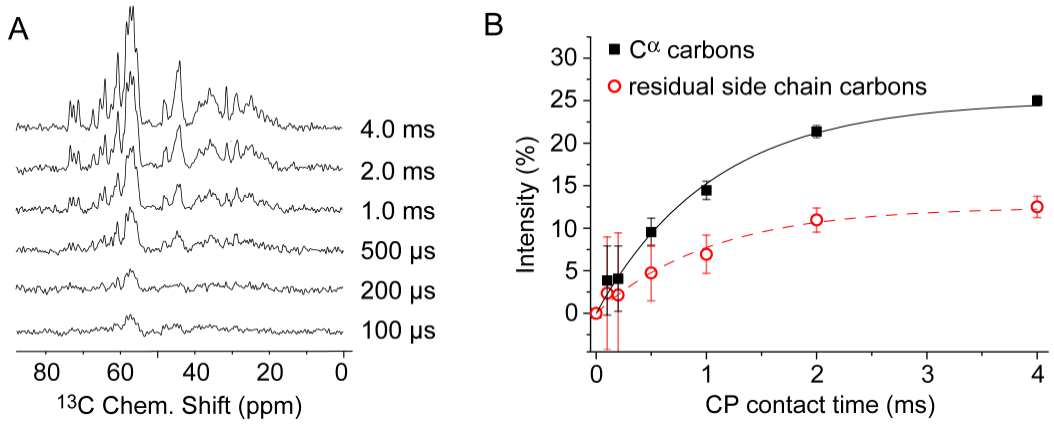
Transfer profile of $^{1}H/^{13}C$ long-range CPs:

In contrast to $^{15}N^{H}/^{13}C^{ali.}$ magnetization transfer, which effectively transports magnetization between $^{15}N^{H}$ and $^{13}C^{\alpha}$, transfers between ^{1}H and ^{13}C over large distances can be built up quickly due to the large gyromagnetic ratios of the nuclei involved. (Agarwal et al. 2010) Supplementary Figure 4 shows the ^{13}C excitation profile of a long-range CP from protons in the case of a perdeuterated sample with a 25% protonation of exchangeable sites in comparison to ^{13}C direct polarization (DP). The bulk of $^{13}C^{\alpha}$ signals amounts to 25%, the residual aliphatic carbons are excited to 13% of their DP value. Considering the H^{N} dilution to ¼ on one hand and the difference in gyromagnetic ratio on the other, the transfer efficiency between side chain carbons and backbone H^{N}s (accordingly 25 and 13% for $^{13}C^{\alpha}$ and residual aliphatic carbons, respectively) is quite reasonable even for distant side chain nuclei.



Supplementary Figure 5: Comparison of direct detection (**A**) versus CP (**B**) for aliphatic carbons in a perdeuterated and partly proton back-exchanged sample. Despite the low proton abundance (25 % in exchangeable sites and roughly 10 % in methyl groups due to incomplete deuteration (Agarwal and Reif 2008)) the cross polarization performs reasonably well even for distant side chain carbons. The difference in intensity amounts to approximately 4.0 and 8.0 fold for C^{α} and the bulk of aliphatic side chain carbons, respectively. The spectra for direct and cross polarization were recorded with 128 scans each, using 3 and 1 s for recycling, respectively, and applying 100 Hz exponential apodization. CP conditions (4ms, 50 and 85 kHz (ramped 70-100%) for ^{13}C and ^{1}H, respectively) were optimized for aliphatic carbons, using a carrier frequency of 45 ppm. Note that only a quarter of the directly excited carbons do actually contribute to the intensity of amide proton detected experiments due to their deuteron dilution.

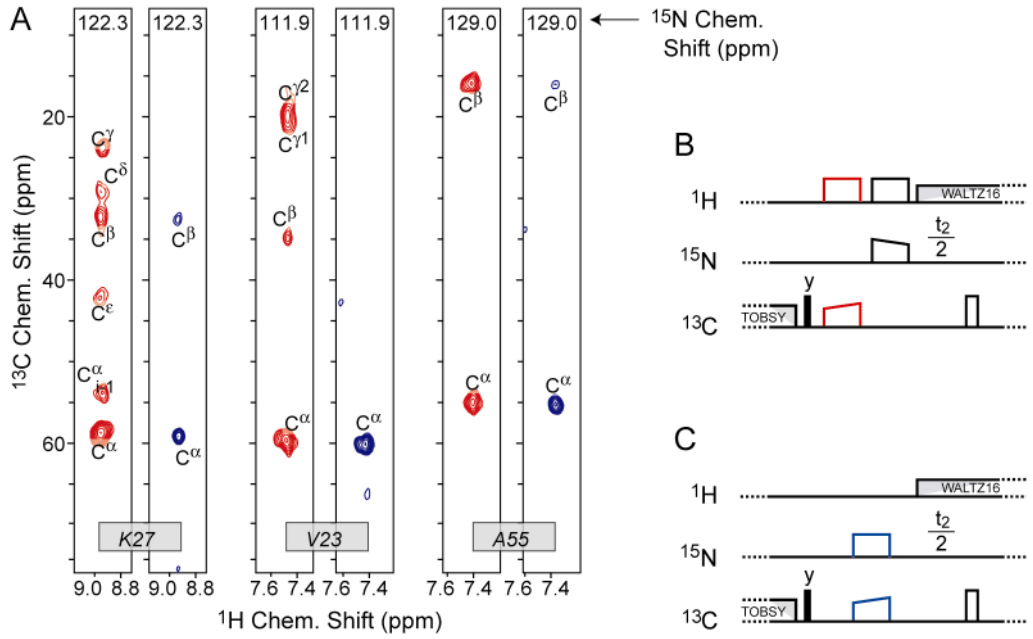
The build-up of transferred magnetization between backbone amide protons (and residual methyl protons) and side-chain carbons was quantitatively assessed using $^{1}H/^{13}C$ CP experiments with increasing contact time. For a better robustness against rf-inhomogeneity and spectrometer instability, a 70-100% ramp was used on ^{13}C. Supplementary Figure 5 shows the build-up of magnetization for the aliphatic carbons, up to a maximum duration of 4 ms, employing maximum field of 50 and 85 kHz for ^{13}C and ^{1}H, respectively. From the mono-exponential fit curves (fitted to build-up rates of 940 ± 70 and 960 ± 290 s^{-1} for the C^{α} and the non-C^{α} aliphatic side-chain carbons, respectively), a CP duration of around 3-4 ms seems advisable.



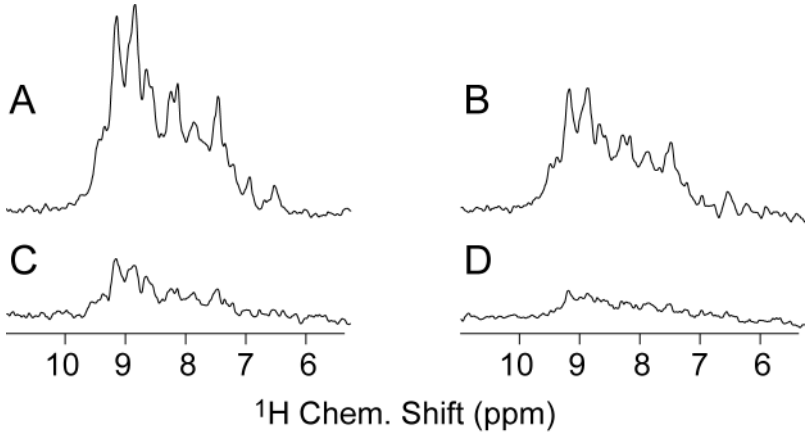
Supplementary Figure 6: Long-range CP intensity build-up on side-chain carbons. **A**) 1D spectra using 128 scans, using a ramped CP with a 75 to 100 % ramp on ^{1}H with a duration as indicated right from the strips. A ramp was used in order to provide transfer stability in the presence of potential sample heating. The quantification (B) shows the intensity of C^{α} and the residual side-chain carbons, respectively, in respect to the intensity of a direct single pulse excitation experiment. For these experiments, no ^{1}H decoupling and a recycle delay of 1 s was used. Effective maximum rf fields amounted to 50 kHz and 85 kHz on ^{13}C and ^{1}H, respectively.

Magnetization transfer to the backbone:

The viability of direct transfer of magnetization from side chain carbons to ^{15}N, rather than using long-range transfers to the amide protons, was assessed employing the pulse scheme depicted in main-text Figure 2 with a modified back-transfer, based on a ^{13}C/^{15}N CP. The comparison to the experiment using a two-step pathway is represented in Supplementary Figure 3A. The alternative pulse sequence element used for that experiment is shown in C. Although this pathway is more intuitive, involving a lower number of transfer steps, the experiment cannot provide enough magnetization for ^{13}C side-chain resonances apart from C^{α}.



Supplementary Figure 7: Comparison of an experiment recorded with long-range $^{1}H/^{13}C$ transfers and subsequent $^{1}H/^{15}N$ CP, as described in the main manuscript (red contours), with one recorded with a direct transfer from ^{13}C to ^{15}N (shown with blue contours). Both experiments were recorded and displayed under otherwise identical conditions within 3.5 d, using 40 scans and 48 and 84 increments in f2 and f1, respectively. **B**) and **C**) represent the respective pulse sequence element employed for red and blue strips, respectively, using the two-step pathway with a long-range $^{13}C/^{1}H$ transfer (shown in red) as described in the main manuscript and the direct pathway via $^{13}C/^{15}N$ cross polarisation (blue), respectively.

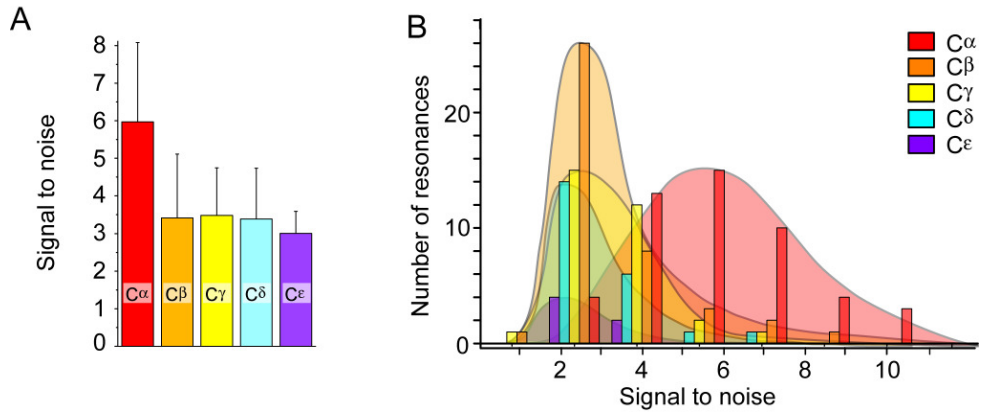


Supplementary Figure 8: A and **B**: amide bulk signal for the first slice of a 3D experiment using the indirect magnetization pathway via ^{1}H and the direct pathway from ^{13}C to ^{15}N, respectively. These strips were recorded without homonuclear mixing. **C** and **D**: According spectra with application of 16 ms of homonuclear mixing using TOBSY. Whereas the direct pathway (in comparison to the experiment using long-range CH transfers) gives rise to a bulk signal to noise that is weaker by a factor of 1.6 without homonuclear mixing (A vs. B), the obtainable bulk signal is weaker by a factor of 1.9 when 16 ms of TOBSY mixing are applied (C vs. D). TOBSY mixing reduces the bulk signal, however, it is needed for correlations between distant carbons and the backbone. In other words, in the case of a direct transfer, in which only magnetization from $^{13}C^{\alpha}$ is transferred, TOBSY

reduces the bulk signal by a factor of approximately 5, whereas only a reduction by a factor of 4 is obtained for the indirect transfer, since additional magnetization is detected originating from more distant carbons. All spectra were recorded within 8min using 256 scans each and 35 Hz exponential apodization.

Quantitative analysis:

Chemical shift assignment and assessment of peak intensities were pursued with the help of CcpNmr Analysis. Supplementary Figure 9 shows the obtained signal to noise (s/n) ratio in respect to the type of ^{13}C, depicting average intensities and their distribution. With an amount of 6 mg protein, average peak intensities amount to between 6:1 for C^{α} and 3.5:1 for other carbons, respectively, after 3.5d at 700 MHz proton Larmor frequency. Due to the moderate spinning speed necessary, s/n can principally be increased by using a 3.2 mm rotor. In addition, the achieved sensitivity is expected to be augmented considerably with ILV methyl proton labelled precursors like keto-isovalerate. (Velyvis et al. 2009) A significant increase in sensitivity and resolution would be obtained by use of a 4-channel probe providing ^{2}D-decoupling during t_1 through prevention from evolution of $^{2}H/^{13}C$ ^{1}J-couplings.



Supplementary Figure 9: Signal to noise ratio obtained for the SH3 domain of α-spectrin after 3.5 d, using ca. 6 mg protein in a 2.5 mm rotor at 700 MHz proton Larmor frequency. Whereas C^{α} shifts are obtained with an average signal to noise of approximately 6:1, residual aliphatic correlations are obtained with a quite uniform s/n of around 3.5:1 in all cases.

Chemical shift tables:

Supplementary Table 1: Chemical shifts obtained for aliphatic side-chain correlations at 25 kHz MAS and approximately 25 °C. Values were referenced to TMS. Correlations involving amide chemical shifts for residues T37 and N38 are observable only for lower temperature. The obtained peak widths are comparably high due to unrefocused ^{13}C homonuclear and $^{2}H/^{13}C$ heteronuclear scalar couplings. For a higher definition of C^{α} and C^{β} resonances, HNCA type experiments can be employed that refocus $^{1}J(^{13}C^{\alpha}/^{13}CO)$.

Residue	H^N	N^H	C^{α}	C^{β}	$C^{\gamma 1}$	$C^{\gamma 2}$	$C^{\delta 1}$	$C^{\delta 2}$	C^{ε}
Glu7	8.19	121.0	55.6						
Leu8	7.81	120.9	53.4				21.9	22.4	
Val9	8.87	111.7	58.1	35.0	19.8	23.3			
Leu10	8.92	124.0	53.1	46.2	25.9				
Ala11	9.18	127.9	52.8	19.0					
Leu12	9.10	127.9	56.1	42.3	25.4		21.8	24.7	
Tyr13	6.91	110.3	55.5						
Asp14	8.24	117.5	54.8	42.5					
Tyr15	8.52	119.3	60.3						
Gln16	7.51	126.9	54.2	28.8	33.2				
Glu17	7.65	122.6	55.9	29.6	33.5				
Lys18	8.63	119.8	55.0	34.1	24.1		27.6		
Ser19	7.17	111.6	56.8	63.1					
Pro20									
Arg21									
Glu22	7.63	122.6	56.1						
Val23	7.45	112.0	59.6	34.5	19.1	20.5			
Thr24	6.49	116.6	62.3	71.4	20.3				
Met25	9.32	121.6	54.1	35.7	31.4				20.5
Lys26	9.03	125.0	53.8	34.0	23.6		27.6		41.7
Lys27	8.94	122.2	58.6	31.9	23.4		28.8		41.9
Gly28	8.80	116.4	45.4						
Asp29	8.35	122.5	55.6						
Ile30	8.55	120.2	58.6	35.4			17.8		
Leu31	9.45	128.7	53.3	41.4	26.7		25.3	26.0	
Thr32	8.12	119.1	62.9	69.3	22.4				
Leu33	8.82	130.5	55.1	43.0	25.1		22.9	24.2	
Leu34	8.85	125.7	55.3	42.5	26.2		20.0	25.2	
Asn35	7.43	114.2	54.6	40.9					
Ser36	9.15	125.1	56.7	60.7					
Thr37									
Asn38									
Lys39	8.46	121.5	58.5	31.8	22.6		28.7		42.2
Asp40	7.91	115.5	55.8						
Trp41	8.33	123.0	56.2						
Trp42	9.16	124.1	54.1	31.5					
Lys43	8.83	123.7	54.8						
Val44	9.41	122.5	59.3	36.2	18.0	20.3			
Glu45	8.78	120.3	55.0	34.1					
Val46	8.77	125.8	60.6	32.6	18.6	19.2			
Arg47									
Arg48									

Arg49	8.02	119.7	55.6	33.4	26.7		43.4		
Gln50	8.22	117.2	54.3	30.8	33.2				
Gly51	8.61	107.1	45.9						
Phe52	9.11	119.0	59.1	42.1					
Val53	8.81	110.8	58.7	33.1	16.7				
Pro54									
Ala55	7.41	129.1	54.5	15.1					
Ala56	7.85	113.5	53.4	17.6					
Tyr57	7.30	113.8	54.9						
Val58	7.33	111.0	58.5	35.2	18.7	21.6			
Lys59	8.64	119.8	54.6	36.2	23.3		28.4		42.1
Lys60	9.12	126.8	58.5	32.3	25.0		28.7		41.5
Leu61	8.11	125.9	54.3	40.9	25.5		22.2	25.1	
Asp62	7.77	128.3	55.9	40.8					

Acquisition parameters

Supplementary Table 2: Acquisition parameters. The following parameters were employed for the different Side-chain to backbone (*S2B*) experiments described in the main text and Supplementary Information.

Experiment	*SW (in ppm, f3xf2xf1)*	*ns (f3xf2xf1)*	*Acquisition times (ms)*	*Recycle delay*	*Duration of the experiment*
3D *S2B* (HCXHNH)	40x28x110	40x48x84	40x12x2.2	1.8s	3.5d
2D *S2Bs* (HCXH)	40x110	256x116	40x3.0	1.8s	15h
3D reference *S2B* (HCXNH)	40x28x110	40x48x84	40x12x2.2	1.8s	3.5d

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Experimental Setup Supplement (Pulse Programs and Parameters)

for the manuscript
Side-Chain to Backbone Correlations from Solid-State NMR on Perdeuterated Proteins Through Combined Excitation and Long-Range Magnetization Transfers

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Spectrometer and other hardware:

Experiments were recorded with a Bruker Avance 700 spectrometer, using a triple-resonance 2.5mm probehead tuned to 1H, 13C, and 15N (for channels 1, 2, and 3, respectively) and a center-packed rotor with 6mg protein.
The experiments employed sample cooling via BCU-X at Magic Angle Spinning with 25kHz and Topspin 3.0 software.

A) Pulse program for the 13C/15N/1H correlation (3D hC^{ali}hNH pulse scheme):

(h-C-mix-h-N-H)

```
;pl4 13C soft p90 power
;p3 13C soft 90 pulse
;pl8 13C hard pulse
;p10: water purge pulses (50ms each)
;pl10: f1 channel - power level water suppression (10kHz)
;pl21: f2 channel - power long range CP
;pl20: f1 channel - power long range CP
;sp10: tanhtan shape
;spf1: ramp CP
;cnst3 13C middle of CO and Ca
;p8: f2 channel 13C broadband 180 pulse
;p7: f2 channel 13C broadband 90 pulse
;pl1 1H hard pulse
;p1 1H hard pulse
;pl3 15N hard pulse
;pl22 HC back CP power 1H
;pl23 HC back CP power 13C
;pl17 15N CP power
;pl5 13C tobsy power
;p15: HN CP duration
;pl11: HN CP on protons
;pl19:  1H decoupling
;p17: long range HC CP
;p21: f3 channel - hard 15N 90
;p22: f3 channel - hard 15N 180
;pl11 1H power during HNCP
;pl17 15N power during HN CP
;l1 number of cycles TOBSY
;p6 pulse length used in TOBSY
;d1 recycle delay
```

```
prosol relations=<triple>

#include <Avancesolids.incl>
#include <Delay.incl>

"in0=inf1/2"
"in10=inf2/2"

"d0=0.3u"
"d10=0.3u"
"d26=1.95m"
"d11=30u"
"DELTA=d0*2+larger(p14,p22)-p14"
"d2=1s/l31-(p8/2)"


aqseq 321

1 ze                    ;accumulate into an empty memory
2 1m do:f3
    1m do:f2
  d1            ;recycle delay, decoupler off in go-loop
  10u reset:f2 reset:f1
  10u fq=cnst1:f2
  10u pl8:f2
  10u pl1:f1
 1u  pl3:f3
  2u



  p1:f1 ph4         ;13C 90 pulse
  0.2u pl22:f1

  p7:f2 ph4         ;13C 90 pulse

  0.2u pl23:f2
 (p17 ph22):f2 (p17:spf1 ph22):f1

  d0
(p22 ph8):f3  ; (center (p14:sp5 ph1):f2 (p22 ph8):f3 )
  d0
;4u pl2:f2
;  (p4 ph1):f2
;  DELTA
;  (p14:sp5 ph1):f2
;4u
0.2u pl8:f2
 p7:f2 ph1
0.2u     pl5:f2

3

    (p6:spf10 ph10):f2
    (p6:spf10 ph11):f2
    (p6:spf10 ph12):f2
    (p6:spf10 ph13):f2
    (p6:spf10 ph14):f2
    (p6:spf10 ph10):f2
    (p6:spf10 ph11):f2
    (p6:spf10 ph12):f2
    (p6:spf10 ph13):f2
    (p6:spf10 ph14):f2
    (p6:spf10 ph16):f2
    (p6:spf10 ph17):f2
    (p6:spf10 ph18):f2
    (p6:spf10 ph19):f2
```

```
    (p6:spf10 ph20):f2
    (p6:spf10 ph16):f2
    (p6:spf10 ph17):f2
    (p6:spf10 ph18):f2
    (p6:spf10 ph19):f2
    (p6:spf10 ph20):f2
lo to 3 times l1



 0.2u      pl4:f2
 0.2u      pl20 :f1
p3:f2 ph3

 ;10u fq=cnst2:f2
 0.2u      pl21:f2
;0.2u pl25:f2
;2u


;  alternative direct transfer from 13C to 15N
;   0.5u      pl22:f2
; 0.5u      pl23 :f3
;2u

;  (p18 ph5):f3 (p18:spf5 ph1):f2
; 0.5u pl19:f1
; 0.5u cpds1:f1
; 0.5u       pl8:f2
; 0.5u         fq=cnst3:f2
; d10
;  (p8 ph1):f2
; d10    ;pl3:f3
;(p21 ph2):f3

; 0.5u do:f1
; 0.5u pl10:f1       ;water suppression
;(p10 ph2):f1
;(p10 ph1):f1
;(p10 ph2):f1
;(p10 ph1):f1
;4u
;(p21 ph3):f3
;
 ;0.5u pl11:f1
; 0.5u pl17:f3
;  (p15:spf4 ph1):f3 (p15 ph1):f1
;
;

;alternative INEPT based HNH transfers

 ;(p17:spf1 ph1):f1 (p17 ph1):f2
 ;0.4u         pl1:f1
 ;d26       pl8:f2
 ;(center (p2 ph1):f1 (p22 ph8):f3)
 ;d26         fq=cnst3:f2
 ;(center (p1 ph1):f1 (p21 ph5):f3)
 ;d10
 ; (center (p2 ph1):f1 (p8 ph1):f2)
 ;d10
 ;(center (p1 ph2):f1 (p21 ph1):f3)
 ; d26
 ;(center (p2 ph1):f1 (p22 ph8):f3)
 ; d26


 (p17:spf1 ph1):f1 (p17 ph1):f2
```

```
0.2u pl11:f1
 0.2u pl17:f3
  (p15:spf3 ph5):f3 (p15 ph1):f1
  0.5u pl19:f1
  0.5u  cpds1:f1
  d10   pl8:f2
  0.2u   fq=cnst3:f2
  (p8 ph8):f2
  d10
  1u do:f1
   0.5u pl11:f1
 (p15:spf4 ph1):f3 (p15 ph1):f1



 2u      pl16:f3


  0.5u cpd3:f3

  5u
  go=2 ph31              ;select appropriate decoupling sequence, cw or  10m do:f2              ;decoupler off
   1m do:f3


900u do:f3 mc #0 to 2
    F1PH(rd10 & ip4 & ip22 , id0)
    F2PH( ip5, id10 )

HaltAcqu, 1m             ;jump address for protection files
exit                    ;quit

ph1=0
ph2=1
ph3=1 1 3 3
ph4=0 2
ph5=0 0 0 0  2 2 2 2
ph8=0 0 0 0  0 0 0 0  2 2 2 2  2 2 2 2
ph22= 1 3

ph10= (360) 0
ph11= (360) 240
ph12= (360) 240
ph13= (360) 60
ph14= (360) 0
ph16= (360) 180
ph17= (360) 60
ph18= (360) 60
ph19= (360) 240
ph20= (360) 180


ph31= 2 0 0 2 0 2 2 0 2 0 0 2 0 2 2 0
```

B) Pulse program for the 13C/1H correlation (2D hC^{ali}H pulse scheme):

Spectrometer and other hardware as described above.

```
(h-C-mix-H)
;pl4 13C soft p90 power
;p3 13C soft 90 pulse
;pl8 13C hard pulse
;p10: water purge pulses (50ms each)
;pl10: f1 channel - power level water suppression (10kHz)
;pl21: f2 channel - power long range CP
;pl20: f1 channel - power long range CP
;sp10: tanhtan shape
;spf1: ramp CP
;cnst3 13C middle of CO and Ca
;p8: f2 channel 13C broadband 180 pulse
;p7 13C hard pulse
;pl1 1H hard pulse
;p1 1H hard pulse
;pl3 15N hard pulse
;pl22 NC CP power 13C
;pl23 NC CP power 15N
;pl17 15N CP power
;pl5 13C tobsy power
;p15: HN CP duration
;pl11: HN CP on protons
;pl19:  1H decoupling
;p17: long range HC CP
;p21: f3 channel - hard 15N 90
;p22: f3 channel - hard 15N 180
;l1 number of cycles TOBSY
;p6 pulse length used in TOBSY
;d1 recycle delay


#include <Avancesolids.incl>
#include <Delay.incl>

"in0=inf1/2"
"in10=inf2/2"

"d0=0.3u"
"d10=3u"
"d26=2.3m"
"d11=30u"
"DELTA=d0*2+larger(p14,p22)-p14"
"d2=1s/l31-(p8/2)"
"d7=1s/l31"

1 ze                    ;accumulate into an empty memory
2 1m do:f3
    1m do:f2
  d1            ;recycle delay, decoupler off in go-loop
  10u reset:f2 reset:f1
  10u fq=cnst1:f2
  10u pl8:f2            ; pl5 for 1H p90 pulse: pl1 CP power for X
  10u pl1:f1
 1u  pl3:f3
  2u



  p1:f1 ph4         ;13C 90 pulse
  0.2u pl22:f1

  p7:f2 ph4         ;13C 90 pulse
```

```
  0.2u pl23:f2
 (p17 ph22):f2 (p17:spf2 ph22):f1
 ; 0.5u pl19:f1
 ; 0.5u cpds1:f1
  d0
(p22 ph8):f3  ; (center (p14:sp5 ph1):f2 (p22 ph8):f3 )
  d0
;4u pl2:f2
;  (p4 ph1):f2
;  DELTA
;  (p14:sp5 ph1):f2
;4u
0.2u pl8:f2

   p7:f2 ph1
0.2u     pl5:f2

3

    (p6:spf10 ph10):f2
    (p6:spf10 ph11):f2
    (p6:spf10 ph12):f2
    (p6:spf10 ph13):f2
    (p6:spf10 ph14):f2
    (p6:spf10 ph10):f2
    (p6:spf10 ph11):f2
    (p6:spf10 ph12):f2
    (p6:spf10 ph13):f2
    (p6:spf10 ph14):f2
    (p6:spf10 ph16):f2
    (p6:spf10 ph17):f2
    (p6:spf10 ph18):f2
    (p6:spf10 ph19):f2
    (p6:spf10 ph20):f2
    (p6:spf10 ph16):f2
    (p6:spf10 ph17):f2
    (p6:spf10 ph18):f2
    (p6:spf10 ph19):f2
    (p6:spf10 ph20):f2
lo to 3 times l1


; alternative: additional water suppression
;1u do:f1
;4u pl10:f1
;(p10 ph2):f1
;(p10 ph1):f1
;(p10 ph2):f1
;(p10 ph1):f1
;4u




 0.4u      pl4:f2
p3:f2 ph2

; 10u fq=cnst2:f2
 0.4u      pl21:f2
 0.4u      pl20 :f1


 (p17:spf1 ph3):f1 (p17 ph1):f2
 2u      pl16:f3


  0.5u cpd3:f3

  5u
```

```
 go=2 ph31              ;select appropriate decoupling sequence, cw or  10m do:f2              ;decoupler off
  1m do:f3  do:f1


900u do:f3 mc #0 to 2
   F1PH(rd10 & ip4 & ip22 , id0)
   F2PH( ip5, id10 );& id29 & dd30 & dd31)

HaltAcqu, 1m            ;jump address for protection files
exit                    ;quit

ph1=0
ph2=1
ph3=0 0 2 2
ph4=0 2
ph5=0 0 2 2
ph8=0 0 0 0  0 0 0 0  2 2 2 2  2 2 2 2
ph22= 1 3

ph10= (360) 0
ph11= (360) 240
ph12= (360) 240
ph13= (360) 60
ph14= (360) 0
ph16= (360) 180
ph17= (360) 60
ph18= (360) 60
ph19= (360) 240
ph20= (360) 180


ph31= 0 2 2 0
```

Acquisition parameters (Bruker "acqus" file) for Experiment A) (3D hC^{ali}hNH):

```
##TITLE= Parameter file, TOPSPIN       Version 3.0
##JCAMPDX= 5.0
##DATATYPE= Parameter Values
##NPOINTS= 42$$ modification sequence number
##ORIGIN= Bruker BioSpin GmbH
##OWNER= nmrsu
$$ 2010-11-29 10:11:31.616 +1100  nmrsu@FELIX
$$ F:/data/ras/nmr/sh3_2.5mm/276/acqus
$$ process C:\Bruker\TopSpin3.0\prog\mod\go.exe
##$ACQT0= 1000000
##$AMP= (0..31)
100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100
100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100
##$ANAVPT= -1
##$AQSEQ= 0
##$AQ_mod= 3
##$AUNM= <au_zg>
##$AUTOPOS= <>
##$BF1= 700.36
##$BF2= 176.105662
##$BF3= 70.966862
##$BF4= 700.36
##$BF5= 700.36
##$BF6= 700.36
##$BF7= 700.36
##$BF8= 700.36
##$BYTORDA= 0
##$CAGPARS= (0..11)
0 0 0 0 0 0 0 0 0 0 0 0
##$CFDGTYP= 0
##$CFRGTYP= 9
##$CHEMSTR= <none>
##$CNST= (0..63)
1 0 0 19000 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
##$CPDPRG= <waltz16>
##$CPDPRG1= <waltz16>
##$CPDPRG2= <xix12>
##$CPDPRG3= <waltz64>
##$CPDPRG4= <mlev>
##$CPDPRG5= <mlev>
##$CPDPRG6= <mlev>
##$CPDPRG7= <mlev>
##$CPDPRG8= <mlev>
##$D= (0..63)
3e-007 1.8 0.9999968 0 0 0 0 0 0.01 0.06 3e-007 3e-005 2e-005 3e-006 0
0 4e-006 0 0 0 4e-006 0 0 0 0 0 0.00195 0 0 0 0.22 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$DATE= 1290679197
##$DBL= (0..7)
120 120 120 120 120 120 120 120
##$DBP= (0..7)
150 150 150 150 150 150 150 150
##$DBPNAM0= <>
##$DBPNAM1= <>
##$DBPNAM2= <>
##$DBPNAM3= <>
##$DBPNAM4= <>
##$DBPNAM5= <>
##$DBPNAM6= <>
##$DBPNAM7= <>
##$DBPOAL= (0..7)
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
##$DBPOFFS= (0..7)
0 0 0 0 0 0 0 0
##$DE= 12
```

```
##$DECBNUC= <off>
##$DECIM= 720
##$DECNUC= <off>
##$DECSTAT= 4
##$DIGMOD= 1
##$DIGTYP= 12
##$DL= (0..7)
0 120 120 120 120 120 120 120
##$DP= (0..7)
150 150 150 150 150 150 150 150
##$DP07= 0
##$DPNAME0= <>
##$DPNAME1= <>
##$DPNAME2= <>
##$DPNAME3= <>
##$DPNAME4= <>
##$DPNAME5= <>
##$DPNAME6= <>
##$DPNAME7= <>
##$DPOAL= (0..7)
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
##$DPOFFS= (0..7)
0 0 0 0 0 0 0 0
##$DQDMODE= 0
##$DR= 21
##$DS= 1
##$DSPFIRM= 0
##$DSPFVS= 20
##$DTYPA= 0
##$EXP= <>
##$F1LIST= <111111111111111>
##$F2LIST= <222222222222222>
##$F3LIST= <333333333333333>
##$FCUCHAN= (0..9)
0 2 3 1 0 0 0 0 0 0
##$FL1= 83
##$FL2= 83
##$FL3= 83
##$FL4= 83
##$FOV= 20
##$FQ1LIST= <freqlist>
##$FQ2LIST= <freqlist>
##$FQ3LIST= <freqlist>
##$FQ4LIST= <freqlist>
##$FQ5LIST= <freqlist>
##$FQ6LIST= <freqlist>
##$FQ7LIST= <freqlist>
##$FQ8LIST= <freqlist>
##$FRQLO3= 1236838.79999995
##$FRQLO3N= 0
##$FS= (0..7)
83 83 83 83 83 83 83 83
##$FTLPGN= 0
##$FW= 250000
##$FnMODE= 0
##$FnTYPE= 0
##$GPNAM0= <SINE.100>
##$GPNAM1= <SINE.100>
##$GPNAM10= <SINE.100>
##$GPNAM11= <SINE.100>
##$GPNAM12= <SINE.100>
##$GPNAM13= <SINE.100>
##$GPNAM14= <SINE.100>
##$GPNAM15= <SINE.100>
##$GPNAM16= <SINE.100>
##$GPNAM17= <SINE.100>
##$GPNAM18= <SINE.100>
##$GPNAM19= <SINE.100>
##$GPNAM2= <SINE.100>
##$GPNAM20= <SINE.100>
```

##$GPNAM21= <SINE.100>
##$GPNAM22= <SINE.100>
##$GPNAM23= <SINE.100>
##$GPNAM24= <SINE.100>
##$GPNAM25= <SINE.100>
##$GPNAM26= <SINE.100>
##$GPNAM27= <SINE.100>
##$GPNAM28= <SINE.100>
##$GPNAM29= <SINE.100>
##$GPNAM3= <SINE.100>
##$GPNAM30= <SINE.100>
##$GPNAM31= <SINE.100>
##$GPNAM4= <SINE.100>
##$GPNAM5= <SINE.100>
##$GPNAM6= <SINE.100>
##$GPNAM7= <SINE.100>
##$GPNAM8= <SINE.100>
##$GPNAM9= <SINE.100>
##$GPX= (0..31)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$GPY= (0..31)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$GPZ= (0..31)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$GRDPROG= <>
##$GRPDLY= 67.9895935058594
##$HDDUTY= 20
##$HDRATE= 20
##$HGAIN= (0..3)
0 0 0 0
##$HL1= 3
##$HL2= 83
##$HL3= 83
##$HL4= 83
##$HOLDER= 0
##$HPMOD= (0..7)
0 1 1 0 0 0 0 0
##$HPPRGN= 0
##$IN= (0..63)
2.58e-005 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.0002516
0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001
0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001
0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001
0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001
0.001 0.001 0.001 0.001 0.001
##$INF= (0..7)
0 51.6197875603852 503.235017119925 0 0 0 0 0
##$INP= (0..63)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$INSTRUM= <spect>
##$L= (0..31)
1 30 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
##$LFILTER= 100
##$LGAIN= -5
##$LINPSTP= 0
##$LOCKED= no
##$LOCKFLD= 2260
##$LOCKGN= 97.4095230102539
##$LOCKPOW= -9.5367431640625e-007
##$LOCKPPM= 4.69999980926514
##$LOCNUC= <2H>
##$LOCPHAS= 127.5945
##$LOCSHFT= no
##$LOCSW= 0
##$LTIME= 0.349999994039536
##$MASR= 3999
##$MASRLST= <masrlst>
##$MULEXPNO= (0..15)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

##$NBL= 1
##$NC= -5
##$NLOGCH= 4
##$NOVFLW= 0
##$NS= 40
##$NUC1= <1H>
##$NUC2= <13C>
##$NUC3= <15N>
##$NUC4= <off>
##$NUC5= <off>
##$NUC6= <off>
##$NUC7= <off>
##$NUC8= <off>
##$NUCLEUS= <off>
##$NUSLIST= <automatic>
##$O1= 4723.7
##$O2= 7211
##$O3= 8600
##$O4= 0
##$O5= 17610.64
##$O6= 17610.64
##$O7= 17610.64
##$O8= 17610.64
##$OVERFLW= 0
##$P= (0..63)
14.8 2.4 4.4 3 37.5 5.8 31.75 3 6.4 0 10000 0 0 2.5 508 280 0 4000 0 600
5 2.45 4.9 0 0 0 0 14.8 1000 0 0 0 0 0 0 0 0 0 0 0 0 2250 1500 1510 150
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 360 0
##$PACOIL= (0..15)
3 0 0 0 0 1 2 0 0 0 0 0 0 0 0 0
##$PAPS= 2
##$PARMODE= 2
##$PCPD= (0..9)
100 40 44 56 100 100 100 100 100 100
##$PEXSEL= (0..9)
1 1 1 1 1 1 1 1 1 1
##$PHCOR= (0..31)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$PHLIST= <>
##$PHP= 2
##$PH_ref= 0
##$PL= (0..63)
120 120 120 9.7 10 31.5 120 120 120 120 31.9 120 9.7 19 120 120 120 120
-1 12.5 120 120 120 120 120 120 120 120 120 50 19 120 120 120 120 120 120
120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120
120 120 120 120 120 120 120 120 120
##$PLSTEP= 0.1
##$PLSTRT= -6
##$PLW= (0..63)
0 200 8.3 450 300 60 -1 -1 300 -1 1.4 57 13 -1 300 -1 0.4 80.7 0 0.4 76
100 85 100 -1 -1 -1 -1 -1 13 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
##$PLWMAX= (0..7)
956 458 597 0 0 0 0 0
##$POWMOD= 1
##$PQPHASE= 0
##$PQSCALE= 0
##$PR= 4
##$PRECHAN= (0..15)
-1 6 0 5 3 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
##$PRGAIN= 0
##$PROBHD= <2.5 mm MAS BB/BB/1H H13621/0004
>
##$PULPROG= <rl_HcatobsyHNH_CP2>
##$PW= 0
##$PYNM= <acqu.py>
##$QNP= 1
##$RD= 0
##$RECCHAN= (0..15)
0 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0

```
##$RECPH= 0
##$RECPRE= (0..15)
0 0 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
##$RECPRFX= (0..15)
1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$RECSEL= (0..15)
0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0
##$RG= 203
##$RO= 0
##$ROUTWD1= (0..23)
1 85 48 0 0 1 0 0 0 0 0 1 0 0 0 1 0 0 0 0 0 0 0 0
##$ROUTWD2= (0..23)
1 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$RSEL= (0..9)
0 1 2 3 0 0 0 0 0 0
##$S= (0..7)
83 25 26 83 26 83 83 83
##$SELREC= (0..9)
0 0 0 0 0 0 0 0 0 0
##$SFO1= 700.3647237
##$SFO2= 176.112873
##$SFO3= 70.975462
##$SFO4= 700.36
##$SFO5= 700.37761064
##$SFO6= 700.37761064
##$SFO7= 700.37761064
##$SFO8= 700.37761064
##$SOLVENT= <H2O+D2O>
##$SOLVOLD= <off>
##$SP= (0..63)
1 9.7 9.7 120 120 0 120 120 120 0 120 120 0 0 120 0 150 150 120 120.87
118.96 122.27 114.95 150 150 150 150 150 150 120 150 120 120 120 120 120
120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120
120 120 120 120 120 120 120 120 120 120
##$SPECTR= 0
##$SPINCNT= 0
##$SPNAM0= <gauss>
##$SPNAM1= <ramp70100.100>
##$SPNAM10= <rl_tanhtan32u>
##$SPNAM11= <Gaus1.1000>
##$SPNAM12= <gauss>
##$SPNAM13= <gauss>
##$SPNAM14= <Gaus1.1000>
##$SPNAM15= <Gaus1.1000>
##$SPNAM16= <gauss>
##$SPNAM17= <gauss>
##$SPNAM18= <Gaus1.1000>
##$SPNAM19= <Gaus1.1000>
##$SPNAM2= <ramp10070.100>
##$SPNAM20= <Gaus1.1000>
##$SPNAM21= <Gaus1.1000>
##$SPNAM22= <Gaus1.1000>
##$SPNAM23= <gauss>
##$SPNAM24= <gauss>
##$SPNAM25= <gauss>
##$SPNAM26= <gauss>
##$SPNAM27= <gauss>
##$SPNAM28= <gauss>
##$SPNAM29= <Gaus1.1000>
##$SPNAM3= <ramp70100.100>
##$SPNAM30= <gauss>
##$SPNAM31= <Gaus1.1000>
##$SPNAM32= <>
##$SPNAM33= <>
##$SPNAM34= <>
##$SPNAM35= <>
##$SPNAM36= <>
##$SPNAM37= <>
##$SPNAM38= <>
##$SPNAM39= <>
```

##$SPNAM4= <ramp10070.100>
##$SPNAM40= <>
##$SPNAM41= <>
##$SPNAM42= <>
##$SPNAM43= <>
##$SPNAM44= <>
##$SPNAM45= <>
##$SPNAM46= <>
##$SPNAM47= <>
##$SPNAM48= <>
##$SPNAM49= <>
##$SPNAM5= <G3.256>
##$SPNAM50= <>
##$SPNAM51= <>
##$SPNAM52= <>
##$SPNAM53= <>
##$SPNAM54= <>
##$SPNAM55= <>
##$SPNAM56= <>
##$SPNAM57= <>
##$SPNAM58= <>
##$SPNAM59= <>
##$SPNAM6= <Gaus1.1000>
##$SPNAM60= <>
##$SPNAM61= <>
##$SPNAM62= <>
##$SPNAM63= <>
##$SPNAM7= <Gaus1.1000>
##$SPNAM8= <Gaus1.1000>
##$SPNAM9= <gauss>
##$SPOAL= (0..63)
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
##$SPOFFS= (0..63)
0 0 0 0 0 22830 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$SPPEX= (0..63)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$SPW= (0..63)
-1 -1 -1 -1 -1 2.3 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
##$SUBNAM0= <"">
##$SUBNAM1= <"">
##$SUBNAM2= <"">
##$SUBNAM3= <"">
##$SUBNAM4= <"">
##$SUBNAM5= <"">
##$SUBNAM6= <"">
##$SUBNAM7= <"">
##$SUBNAM8= <"">
##$SUBNAM9= <"">
##$SW= 39.6618745030859
##$SWIBOX= (0..19)
0 1 2 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$SW_h= 27777.7777777778
##$SWfinal= 0
##$TD= 2218
##$TD0= 1
##$TE= 279
##$TE1= 300
##$TE2= 300
##$TE3= 300
##$TE4= 300
##$TEG= 300
##$TE_PIDX= 0
##$TE_STAB= (0..8)

```
0 0 0 0 0 0 0 0
##$TL= (0..7)
0 120 120 120 120 120 120 120
##$TP= (0..7)
150 150 150 150 150 150 150 150
##$TPNAME0= <>
##$TPNAME1= <>
##$TPNAME2= <>
##$TPNAME3= <>
##$TPNAME4= <>
##$TPNAME5= <>
##$TPNAME6= <>
##$TPNAME7= <>
##$TPOAL= (0..7)
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
##$TPOFFS= (0..7)
0 0 0 0 0 0 0 0
##$TUNHIN= 0
##$TUNHOUT= 0
##$TUNXOUT= 0
##$USERA1= <user>
##$USERA2= <user>
##$USERA3= <user>
##$USERA4= <user>
##$USERA5= <user>
##$V9= 5
##$VALIST= <valist>
##$VCLIST= <CCCCCCCCCCCCCCC>
##$VD= 0
##$VDLIST= <DDDDDDDDDDDDDDD>
##$VPLIST= <PPPPPPPPPPPPPPP>
##$VTLIST= <TTTTTTTTTTTTTTT>
##$WBST= 1024
##$WBSW= 10
##$XGAIN= (0..3)
0 0 0 0
##$XL= 0
##$YL= 0
##$YMAX_a= 15169
##$YMIN_a= -16720
##$ZGOPTNS= <>
##$ZL1= 120
##$ZL2= 120
##$ZL3= 120
##$ZL4= 120
##END=
```

Acquisition parameters (Bruker "acqus" file) for Experiment B) (2D hC^{ali}H):

```
##TITLE= Parameter file, TOPSPIN       Version 3.0
##JCAMPDX= 5.0
##DATATYPE= Parameter Values
##NPOINTS= 23$$ modification sequence number
##ORIGIN= Bruker BioSpin GmbH
##OWNER= nmrsu
$$ 2010-11-30 03:30:24.407 +1100  nmrsu@FELIX
$$ F:\data\ras\nmr/sh3_2.5mm/280/acqus
$$ process C:\Bruker\TopSpin3.0\prog\mod\go.exe
##$ACQT0= 1000000
##$AMP= (0..31)
100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100
100 100 100 100 100 100 100 100 100 100 100 100 100 100
##$ANAVPT= -1
##$AQSEQ= 1
##$AQ_mod= 3
##$AUNM= <au_zg>
##$AUTOPOS= <>
##$BF1= 700.36
##$BF2= 176.105662
##$BF3= 70.966862
##$BF4= 700.36
##$BF5= 700.36
##$BF6= 700.36
##$BF7= 700.36
##$BF8= 700.36
##$BYTORDA= 0
##$CAGPARS= (0..11)
0 0 0 0 0 0 0 0 0 0 0 0
##$CFDGTYP= 0
##$CFRGTYP= 9
##$CHEMSTR= <none>
##$CNST= (0..63)
1 0 0 19000 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
##$CPDPRG= <waltz16>
##$CPDPRG1= <waltz16>
##$CPDPRG2= <xix12>
##$CPDPRG3= <waltz64>
##$CPDPRG4= <mlev>
##$CPDPRG5= <mlev>
##$CPDPRG6= <mlev>
##$CPDPRG7= <mlev>
##$CPDPRG8= <mlev>
##$D= (0..63)
3e-007 1.8 0.9999968 0 0 0 0 1 0.01 0.06 3e-006 3e-005 2e-005 3e-006 0
0 4e-006 0 0 0 4e-006 0 0 0 0 0 0 0.0023 0 0 0 0.22 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$DATE= 1290993064
##$DBL= (0..7)
120 120 120 120 120 120 120 120
##$DBP= (0..7)
150 150 150 150 150 150 150 150
##$DBPNAM0= <>
##$DBPNAM1= <>
##$DBPNAM2= <>
##$DBPNAM3= <>
##$DBPNAM4= <>
##$DBPNAM5= <>
##$DBPNAM6= <>
##$DBPNAM7= <>
##$DBPOAL= (0..7)
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
##$DBPOFFS= (0..7)
0 0 0 0 0 0 0 0
##$DE= 12
##$DECBNUC= <off>
```

##$DECIM= 720
##$DECNUC= <off>
##$DECSTAT= 4
##$DIGMOD= 1
##$DIGTYP= 12
##$DL= (0..7)
0 120 120 120 120 120 120 120
##$DP= (0..7)
150 150 150 150 150 150 150 150
##$DP07= 0
##$DPNAME0= <>
##$DPNAME1= <>
##$DPNAME2= <>
##$DPNAME3= <>
##$DPNAME4= <>
##$DPNAME5= <>
##$DPNAME6= <>
##$DPNAME7= <>
##$DPOAL= (0..7)
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
##$DPOFFS= (0..7)
0 0 0 0 0 0 0 0
##$DQDMODE= 0
##$DR= 21
##$DS= 1
##$DSPFIRM= 0
##$DSPFVS= 20
##$DTYPA= 0
##$EXP= <>
##$F1LIST= <111111111111111>
##$F2LIST= <222222222222222>
##$F3LIST= <333333333333333>
##$FCUCHAN= (0..9)
0 2 3 1 0 0 0 0 0 0
##$FL1= 83
##$FL2= 83
##$FL3= 83
##$FL4= 83
##$FOV= 20
##$FQ1LIST= <freqlist>
##$FQ2LIST= <freqlist>
##$FQ3LIST= <freqlist>
##$FQ4LIST= <freqlist>
##$FQ5LIST= <freqlist>
##$FQ6LIST= <freqlist>
##$FQ7LIST= <freqlist>
##$FQ8LIST= <freqlist>
##$FRQLO3= 1236838.79999995
##$FRQLO3N= 0
##$FS= (0..7)
83 83 83 83 83 83 83 83
##$FTLPGN= 0
##$FW= 250000
##$FnMODE= 0
##$FnTYPE= 0
##$GPNAM0= <SINE.100>
##$GPNAM1= <SINE.100>
##$GPNAM10= <SINE.100>
##$GPNAM11= <SINE.100>
##$GPNAM12= <SINE.100>
##$GPNAM13= <SINE.100>
##$GPNAM14= <SINE.100>
##$GPNAM15= <SINE.100>
##$GPNAM16= <SINE.100>
##$GPNAM17= <SINE.100>
##$GPNAM18= <SINE.100>
##$GPNAM19= <SINE.100>
##$GPNAM2= <SINE.100>
##$GPNAM20= <SINE.100>
##$GPNAM21= <SINE.100>

##$GPNAM22= <SINE.100>
##$GPNAM23= <SINE.100>
##$GPNAM24= <SINE.100>
##$GPNAM25= <SINE.100>
##$GPNAM26= <SINE.100>
##$GPNAM27= <SINE.100>
##$GPNAM28= <SINE.100>
##$GPNAM29= <SINE.100>
##$GPNAM3= <SINE.100>
##$GPNAM30= <SINE.100>
##$GPNAM31= <SINE.100>
##$GPNAM4= <SINE.100>
##$GPNAM5= <SINE.100>
##$GPNAM6= <SINE.100>
##$GPNAM7= <SINE.100>
##$GPNAM8= <SINE.100>
##$GPNAM9= <SINE.100>
##$GPX= (0..31)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$GPY= (0..31)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$GPZ= (0..31)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$GRDPROG= <>
##$GRPDLY= 67.9895935058594
##$HDDUTY= 20
##$HDRATE= 20
##$HGAIN= (0..3)
0 0 0 0
##$HL1= 3
##$HL2= 83
##$HL3= 83
##$HL4= 83
##$HOLDER= 0
##$HPMOD= (0..7)
0 1 1 0 0 0 0 0
##$HPPRGN= 0
##$IN= (0..63)
2.58e-005 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.0002516
0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001
0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001
0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001
0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001
0.001 0.001 0.001 0.001 0.001
##$INF= (0..7)
0 51.6197875603852 503.235017119925 0 0 0 0 0
##$INP= (0..63)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$INSTRUM= <spect>
##$L= (0..31)
1 30 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
##$LFILTER= 100
##$LGAIN= -5
##$LINPSTP= 0
##$LOCKED= no
##$LOCKFLD= 2246
##$LOCKGN= 97.4095230102539
##$LOCKPOW= -9.5367431640625e-007
##$LOCKPPM= 4.69999980926514
##$LOCNUC= <2H>
##$LOCPHAS= 127.5945
##$LOCSHFT= no
##$LOCSW= 0
##$LTIME= 0.349999994039536
##$MASR= 3999
##$MASRLST= <masrlst>
##$MULEXPNO= (0..15)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$NBL= 1

```
##$NC= -5
##$NLOGCH= 4
##$NOVFLW= 0
##$NS= 256
##$NUC1= <1H>
##$NUC2= <13C>
##$NUC3= <15N>
##$NUC4= <off>
##$NUC5= <off>
##$NUC6= <off>
##$NUC7= <off>
##$NUC8= <off>
##$NUCLEUS= <off>
##$NUSLIST= <automatic>
##$O1= 4723.7
##$O2= 7211
##$O3= 8600
##$O4= 0
##$O5= 17610.64
##$O6= 17610.64
##$O7= 17610.64
##$O8= 17610.64
##$OVERFLW= 0
##$P= (0..63)
14.8 2.4 4.4 3 37.5 5.8 31.75 3 6.4 0 10000 0 0 2.5 508 280 0 4000 0 600
5 2.45 4.9 0 0 0 0 14.8 1000 0 0 0 0 0 0 0 0 0 0 0 0 2250 1500 1510 150
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 360 0
##$PACOIL= (0..15)
3 0 0 0 0 1 2 0 0 0 0 0 0 0 0 0
##$PAPS= 2
##$PARMODE= 2
##$PCPD= (0..9)
100 40 44 56 100 100 100 100 100 100
##$PEXSEL= (0..9)
1 1 1 1 1 1 1 1 1 1
##$PHCOR= (0..31)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$PHLIST= <>
##$PHP= 2
##$PH_ref= 0
##$PL= (0..63)
120 120 120 9.7 10 31.5 120 120 120 120 31.9 120 9.7 19 120 120 120 120
-1 12.5 120 120 120 120 120 120 120 120 120 50 19 120 120 120 120 120 120
120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120
120 120 120 120 120 120 120 120 120
##$PLSTEP= 0.1
##$PLSTRT= -6
##$PLW= (0..63)
0 200 8.3 450 300 60 -1 -1 300 -1 1.4 57 13 -1 300 -1 0.4 80.7 0 0.4 76
100 85 100 -1 -1 -1 -1 -1 13 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
##$PLWMAX= (0..7)
956 458 597 0 0 0 0 0
##$POWMOD= 1
##$PQPHASE= 0
##$PQSCALE= 0
##$PR= 4
##$PRECHAN= (0..15)
-1 6 0 5 3 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
##$PRGAIN= 0
##$PROBHD= <2.5 mm MAS BB/BB/1H H13621/0004
>
##$PULPROG= <rl_CaliHdec>
##$PW= 0
##$PYNM= <acqu.py>
##$QNP= 1
##$RD= 0
##$RECCHAN= (0..15)
0 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$RECPH= 0
```

```
##$RECPRE= (0..15)
0 0 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
##$RECPRFX= (0..15)
1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$RECSEL= (0..15)
0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0
##$RG= 203
##$RO= 0
##$ROUTWD1= (0..23)
1 116 1 0 0 1 0 0 0 0 0 1 0 0 0 1 0 0 0 0 0 0 0 0
##$ROUTWD2= (0..23)
1 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$RSEL= (0..9)
0 1 2 3 0 0 0 0 0 0
##$S= (0..7)
83 25 26 83 26 83 83 83
##$SELREC= (0..9)
0 0 0 0 0 0 0 0 0 0
##$SFO1= 700.3647237
##$SFO2= 176.112873
##$SFO3= 70.975462
##$SFO4= 700.36
##$SFO5= 700.37761064
##$SFO6= 700.37761064
##$SFO7= 700.37761064
##$SFO8= 700.37761064
##$SOLVENT= <H2O+D2O>
##$SOLVOLD= <off>
##$SP= (0..63)
1 9.7 9.7 120 120 0 120 120 120 0 120 120 0 0 120 0 150 150 120 120.87
118.96 122.27 114.95 150 150 150 150 150 150 120 150 120 120 120 120 120
120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120 120
120 120 120 120 120 120 120 120 120 120
##$SPECTR= 0
##$SPINCNT= 0
##$SPNAM0= <gauss>
##$SPNAM1= <ramp70100.100>
##$SPNAM10= <rl_tanhtan32u>
##$SPNAM11= <Gaus1.1000>
##$SPNAM12= <gauss>
##$SPNAM13= <gauss>
##$SPNAM14= <Gaus1.1000>
##$SPNAM15= <Gaus1.1000>
##$SPNAM16= <gauss>
##$SPNAM17= <gauss>
##$SPNAM18= <Gaus1.1000>
##$SPNAM19= <Gaus1.1000>
##$SPNAM2= <ramp10070.100>
##$SPNAM20= <Gaus1.1000>
##$SPNAM21= <Gaus1.1000>
##$SPNAM22= <Gaus1.1000>
##$SPNAM23= <gauss>
##$SPNAM24= <gauss>
##$SPNAM25= <gauss>
##$SPNAM26= <gauss>
##$SPNAM27= <gauss>
##$SPNAM28= <gauss>
##$SPNAM29= <Gaus1.1000>
##$SPNAM3= <ramp70100.100>
##$SPNAM30= <gauss>
##$SPNAM31= <Gaus1.1000>
##$SPNAM32= <>
##$SPNAM33= <>
##$SPNAM34= <>
##$SPNAM35= <>
##$SPNAM36= <>
##$SPNAM37= <>
##$SPNAM38= <>
##$SPNAM39= <>
##$SPNAM4= <ramp10070.100>
```

##$SPNAM40= <>
##$SPNAM41= <>
##$SPNAM42= <>
##$SPNAM43= <>
##$SPNAM44= <>
##$SPNAM45= <>
##$SPNAM46= <>
##$SPNAM47= <>
##$SPNAM48= <>
##$SPNAM49= <>
##$SPNAM5= <G3.256>
##$SPNAM50= <>
##$SPNAM51= <>
##$SPNAM52= <>
##$SPNAM53= <>
##$SPNAM54= <>
##$SPNAM55= <>
##$SPNAM56= <>
##$SPNAM57= <>
##$SPNAM58= <>
##$SPNAM59= <>
##$SPNAM6= <Gaus1.1000>
##$SPNAM60= <>
##$SPNAM61= <>
##$SPNAM62= <>
##$SPNAM63= <>
##$SPNAM7= <Gaus1.1000>
##$SPNAM8= <Gaus1.1000>
##$SPNAM9= <gauss>
##$SPOAL= (0..63)
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
##$SPOFFS= (0..63)
0 0 0 0 0 22830 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$SPPEX= (0..63)
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$SPW= (0..63)
-1 -1 -1 -1 -1 2.3 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1
##$SUBNAM0= <"">
##$SUBNAM1= <"">
##$SUBNAM2= <"">
##$SUBNAM3= <"">
##$SUBNAM4= <"">
##$SUBNAM5= <"">
##$SUBNAM6= <"">
##$SUBNAM7= <"">
##$SUBNAM8= <"">
##$SUBNAM9= <"">
##$SW= 39.6618745030859
##$SWIBOX= (0..19)
0 1 2 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
##$SW_h= 27777.7777777778
##$SWfinal= 0
##$TD= 2218
##$TD0= 1
##$TE= 279.1
##$TE1= 300
##$TE2= 300
##$TE3= 300
##$TE4= 300
##$TEG= 300
##$TE_PIDX= 0
##$TE_STAB= (0..8)
0 0 0 0 0 0 0 0 0

```
##$TL= (0..7)
0 120 120 120 120 120 120 120
##$TP= (0..7)
150 150 150 150 150 150 150 150
##$TPNAME0= <>
##$TPNAME1= <>
##$TPNAME2= <>
##$TPNAME3= <>
##$TPNAME4= <>
##$TPNAME5= <>
##$TPNAME6= <>
##$TPNAME7= <>
##$TPOAL= (0..7)
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
##$TPOFFS= (0..7)
0 0 0 0 0 0 0 0
##$TUNHIN= 0
##$TUNHOUT= 0
##$TUNXOUT= 0
##$USERA1= <user>
##$USERA2= <user>
##$USERA3= <user>
##$USERA4= <user>
##$USERA5= <user>
##$V9= 5
##$VALIST= <valist>
##$VCLIST= <CCCCCCCCCCCCCCC>
##$VD= 0
##$VDLIST= <DDDDDDDDDDDDDDD>
##$VPLIST= <PPPPPPPPPPPPPPP>
##$VTLIST= <TTTTTTTTTTTTTTT>
##$WBST= 1024
##$WBSW= 10
##$XGAIN= (0..3)
0 0 0 0
##$XL= 0
##$YL= 0
##$YMAX_a= 220237
##$YMIN_a= -132855
##$ZGOPTNS= <>
##$ZL1= 120
##$ZL2= 120
##$ZL3= 120
##$ZL4= 120
##END=
```