Electronic Supplementary Information

Construction of a polyproline structure with hydrophobic exterior using octahydroindole-2-carboxylic acid

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Peptide synthesis

Chlorotrytil resin was pre-loaded with Fmoc-Oic using the original procedure.[S1] 2-Chlorotrytil chloride resin (1 g) was swollen in dichloromethane (10 ml). Fmoc-Oic (525 mg) in dichloromethane (2 ml) was added following addition of diisopropylethylamine (DIPEA, 440 µl). The mixture was gently stirred at the room temperature for 75 min, then DIPEA (0.5 ml) and methanol (3 ml) were added and the stirring was continued for the next 25 min. The resin was filtered, washed with dichloromethane, DMF, methanol and diethyl ether, then dried in vacuum. 1.287 g of the resin was obtained as the result. This corresponds to the loading of 0.8-0.9 mmol g^{-1}.

The synthesis of oligopeptides $Ac(Oic)_N$ was performed manually on the Fmoc-Oic pre-loaded 2-chlorotrityl resin, DMF was used as a solvent. The coupling step was performed with 2 equiv. of Fmoc-Oic, 1.95 equiv. of TBTU, 2 equiv. of HOBt and 4 equiv. of DIPEA all pre-mixed in DMF before addition to the resin. The N-terminal amino acid was installed using Ac-Oic and the coupling reagents. The coupling time was 1.-1.5 hours. Fmoc-removal was performed by treatment with piperazine:DBU:DMF 5:2:93 (w/w/w) mixture for 20-25 min.[S2] After the coupling of Ac-Oic the resin was washed with multiple solvents, and dried in vacuum. Peptide cleavage was done by treatment with hexafluoroisopropanol – dichloromethane (1:3, v/v) mixture for about 20 min.[S3] The solvents were removed by nitrogen stream, the residue was taken up in water – acetonitrile mixture and freeze-dried. The primary NMR studies were performed using crude peptide samples. Further purification was accomplished by silica gel column chromatography using ethyl acetate – methanol to dichloromethane – methanol gradient elution. $Ac(Oic)_6OMe$ was prepared by treatment of the crude peptide with acidic methanol (see procedure for Ac-Oic-OMe). Subsequent purification was done using ethyl acetate – methanol (19:1) elution (R_f = 0.5).

***para*-Bromobenzylated hexapeptide** was synthesized in analogous procedure starting from Fmoc-Rink Amide AM resin. The last acetylation step was done with 5 equiv. para-bromobenzoic acid, 4.8 equiv. TBTU, 4 equiv HOBt and 10 equiv. DIPEA, pre-mixed in DMF, and shacked for 1 hour with the hexapeptide-resin. The cleavage was done by treatment with 95 vol. % TFA for 2 hours. The crude peptide was lyophilized from acetonitrile – water mixture. Purification was done on silica gel column using ethyl acetate – methanol (20:1) mixture as an eluent (R_f = 0.3). Resulting peptide was glaceous material, which could be crystallized from its methanol solution.

GGXGG peptides were synthesised on Rink Amide resin using similar procedure. For amino acid coupling 2 equiv. of Fmoc-Oic, and 4 equiv. for other amino acids were used. The coupling conditions were same: TBTU:HOBt:DIPEA (0.98:1:2 molar ratio to the Fmoc-amino acid), pre-mixed with Fmoc-amino acid in DMF, coupling time 1-1.5 hours. The cleavage was done by treatment with 95 vol % TFA for 2 hours. Crude peptides were

purified by reverse phase HPLC on standard preparative C18 column using methanol-water gradient with 0.05 % TFA. The peptides were obtained as glaceous material.

NMR experiments

The NMR spectra were acquired at Bruker Avance III 700 and 500 MHz proton frequency machines equipped with z-gradient TXI and BBFO probes, respectively. Temperature unit calibration was made by measurements of methanol standards.[S4] The one-dimensional ^{1}H NMR spectra were acquired in 90-degree pulse experiments in one scans in order to avoid signal distortion due to relaxation differences. The proton 90-degree pulse was always calibrated prior the NMR measurements. The $^{1}H\{^{15}N\}$ sofast-HMQC spectra were recorded as described.[S5]

pK_a measurements. 5-10 mg of an analyte and 5 mg of potassium dihydrogenhosphate were dissolved in 10 ml of water. This solution was titrated by potassium hydroxide or hydrogen chloride solutions to different pH values read by a pre-calibrated pH-meter. 500 µl aliquots were taken to NMR tubes and 55 µl of deuterium oxide containing minimal amount of sodium 3-(trimethylsilyl)propane-1-sulfonate (TPS) were added to each sample. For samples with pH < 2 a rag wet with some drops of methanol was placed close to the titration vessel. This created enough background methanol vapours to be absorbed by the samples during titration procedure. The ^{1}H NMR spectra were acquired in Watergate W5 pulse sequence at 298 K. TPS (δ = 0.000 ppm) or methanol (δ = 3.349 ppm) resonances were used for referencing. The chemical shifts were plotted against pH, fitted to Boltzman fits, and 1st order derivatives of the fit curves gave the pK_as as the extremum points. The measurement errors were obtained by comparing the pK_a values delivered by different resonances and added to the Instrumental error 0.05. The final error was 0.05 – 0.10 pK_a units.

NMR samples in deuterated solvents were at 20 ± 5 g l^{-1} concentration of the analytes. The Ac-AA-OMe samples were measured in pure deuterium oxide. The Ac-AA-OH acid samples in deuterium oxide were prepared from mixtures of Ac-AA-OH and potassium hydrogensulphate pre-lyophilised from deuterium oxide. The $KHSO_4$ concentration in the samples was 20 g l^{-1}. The salt samples were prepared as following. Analyte was dissolved in water with potassium dihydrogenphosphate and potassium hydroxide was added to reach pH about 7 (by pH electrode or pH paper). Resulting solution was freeze-dried and subsequently freeze-dried from deuterium oxide, then dissolved in deuterium oxide for measurements. The phosphate concentration in the samples was about 10 g l^{-1}. The samples of oligomeric peptides $Ac(Oic)_NO^-$ were prepared analogously at about 20 g l^{-1} mass concentrations, except of the highest oligomer with N = 6, for which ~ 10 g l^{-1} concentration was reached in a saturated solution. Deuteromethanol samples were prepared by dissolving the analyte in deuteromethanol. The samples of oligomeric peptides $Ac(Oic)_NOH$ were prepared at 20 g l^{-1} concentration. The $Ac(Oic)_6O^-$ sample in deuteromethanol was of the same concentration, and was prepared by titrating the peptide with equivalent amount of potassium hydroxide solution, lyophilizing from acetonitrile – water mixture and solving in deuteromethanol.

The cross-relaxation measurements were performed by NOESY with gradients of ROESY pulse sequences. The time domain was inset to give 2-5 Hz resolution in direct, and 10-20 Hz in indirect dimensions, respectively. The indirect dimension was later linearly predicted and zero filled to reach the direct dimension resolution. Standard processing was done in Topspin 3.2 (Bruker). The cross-relaxation spectra were assisted with 1D inversion recovery spectra for estimation of the T_1 relaxation times.

For ^{1}H EXSY spectra the total relaxation times (acquisition+recycling) were inset to be $\geq 3 \cdot T_1$ for the analysed resonances. 5 ms mixing time spectra were used for referencing, and at least two exchange spectra with mixing time 250 ms – 3 s were acquired for detection of exchange. Exchange rate matrices were obtained with EXSYCalc (Mestrec) tool. Exchange errors were obtained by analysing different exchanged resonances in the EXSY spectra and do not account for the formal temperature calibration error. Activation energies were calculated using Eyring equation (eqn. S1).

$$E^{\neq} = RT(-\ln\frac{k_{\exp}}{T} + 23.76) \qquad \text{(eqn. S1)}$$

The ^{1}H NOESY spectra were recorded with mixing time 300 – 750 ms, and ^{1}H ROESY was acquired with continuous wave spin-lock 500 ms. The NOE values were obtained by integration of the NOESY spectra and calibrated to the diagonal elements. The errors were obtained by taking RMSD of the cross-peak integrals and these were combined with the errors of the diagonal element integrals to give the final error.

The diffusion measurements were conducted by stimulated echo with bipolar gradient pulses on proton spectrum at 298 K. A standard spoil gradient of 600-750 μs was also applied. The diffusion time (Δ) was 50 ms, and the gradient pulse (δ/2) was 1 ms for deuteromethanol and 1.5 ms for deuterium oxide samples. The array spectra were acquired in 128 steps of a linear gradient (2 to 98 %). The processing was done using the standard program provided with the spectrometer. Conversion to molecular sizes for deuterium oxide samples was done using eqn. 3 by taking literature value of the dynamic viscosity $\eta = 1.1 \cdot 10^{-3}$ Pa s^{-1}.[S6] For deuteromethanol however we used η for pure methanol $5.43 \cdot 10^{-4}$ Pa s^{-1} that produced a more rational interpretation of the data. The depression of the viscosity value in deuteromethanol samples could have occurred due to the presence of some residual water[S7] in commercial deuteromethanol and in the peptide solutes. The measurement error is the error of the logD read-out from the screen.

Miscellaneous experimental descriptions

Molecular modelling

Molecular modelling was done using MOPAC package from Scigress Modeling (Fujitsu). PM6-water algorithm, which accounts for water dielectric constant, was normally applied. This was used in particular for calculating COSMO volumes of the oligomeric peptides.

Crystall structures

Ac-Oic-OMe was crystallized from dichloromethane. *p*-BrBz-$(Oic)_6$-NH_2 peptide was crystallised from methanol. The X-ray diffraction was performed at 150 K at analytical facility of the Institute of Chemistry (TU Berlin). Both compounds produced crystals with $P2_12_12_1$ space groups. Likewise in analogous proline structure the Oic[3] residue was close to the solvent molecule, therefore the cyclohexane ring could not be completely resolved in the structure. The coordinate files are deposited in Cambridge Crystallographic Data Centre under the deposition numbers:

Ac-Oic-OMe CCDC 1510246

p-BrBz-$(Oic)_6$-NH_2 CCDC 1510247

Rotational rates in Ac-Oic-OMe in deuterium oxide

Table S1. Rotational rates of Ac-Oic-OMe in deuterium oxide solution as recorded by ^{1}H EXSY NMR.

calibrated temperature, K	rotation constant, s^{-1}	
	cis-to-*trans*	*trans*-to-*cis*
303.3	0.046 ± 0.014	0.003 ± 0.001
309.7	0.074 ± 0.013	0.008 ± 0.001
313.9	0.121 ± 0.018	0.013 ± 0.001
324.6	0.341 ± 0.016	0.048 ± 0.003
329.9	0.627 ± 0.005	0.080 ± 0.002
335.3	1.042 ± 0.064	0.146 ± 0.003

Properties of the peptides

Table S2. Mass spectra recorded by ESI-MS.

peptide	Theoretical mass, Da	Experimental mass, Th	assignment	RP-HPLC retention time, min
$AcGlyGlyProGlyGlyNH_2$	384.18	385.18	$[M+H]^+$	0.79
		407.16	$[M+Na]^+$	
$AcGlyGlyOicGlyGlyNH_2$	438.22	439.23	$[M+H]^+$	1.04
$Ac(Oic)_1OH$	211.12	212.13	$[M+H]^+$	2.08
		234.11	$[M+Na]^+$	
$Ac(Oic)_2OH$	362.22	363.23	$[M+H]^+$	6.52
$Ac(Oic)_3OH$	513.32	514.33	$[M+H]^+$	7.41
$Ac(Oic)_4OH$	664.42	665.43	$[M+H]^+$	8.69
$Ac(Oic)_5OH$	815.52	816.53	$[M+H]^+$	9.47
$Ac(Oic)_6OH$	966.62	967.62	$[M+H]^+$	9.96
$Ac(Oic)_6OMe$	980.64	981.64	$[M+H]^+$	11.18
p$BrBz\text{-}(Oic)_6\text{-}NH_2$	1105.56	1106.57	$[M+H]^+$ for ^{79}Br	11.10
		and 1108.57	and $[M+H]^+$ for ^{81}Br	
		1128.55	$[M+Na]^+$ for ^{79}Br	
		and 1130.55	and $[M+Na]^+$ for ^{81}Br	

RP-HPLC:

Column: Grom-Sil-120-ODS-4-HE (Grace), length 50 mm, ID 2 mm, 3 µm. Gradient using eluent 1 water + 0.1 % HCO_2H and eluent 2 acetonitrile + 0.1 % HCO_2H. The gradient:

0 - 10 min: Eluent 2: from 20 % to 100 %

10 - 13 min: Eluent 2: hold 100 %

13 - 17 min: Eluent 2: hold 20 %

flow rate: 0.3 ml min^{-1}

Table S3. Properties of $Ac(Oic)_NOH/O^-$ at 298 K and 700 MHz ^1H frequency.

N	MW, Da	theor. volume, Å^3	deuteromethanol ($Ac(Oic)_NOH$)		deuterium oxide ($Ac(Oic)_NO^-$)			
			-logD	volume, Å^3	-logD	volume, Å^3	τ_c, ns	pK_a
1	211.3	266	8.95	192	9.239 ± 0.005	171 ± 6	0.0586 ± 0.0021	3.84 ± 0.05
2	362.4	450	9.06	410	9.350 ± 0.005	368 ± 13	0.126 ± 0.010	4.06 ± 0.08
3	513.7	637	9.12	623	9.412 ± 0.009	565 ± 36	0.194 ± 0.012	4.04 ± 0.09
4	664.9	839	9.17	877	9.460 ± 0.009	787 ± 50	0.270 ± 0.017	4.13 ± 0.07
5	816.1	1015	9.21	1160	9.502 ± 0.019	1052 ± 147	0.361 ± 0.050	4.08 ± 0.07
6	967.3	1181	9.23	1328	9.532 ± 0.032	1294 ± 320	0.444 ± 0.110	4.11 ± 0.07

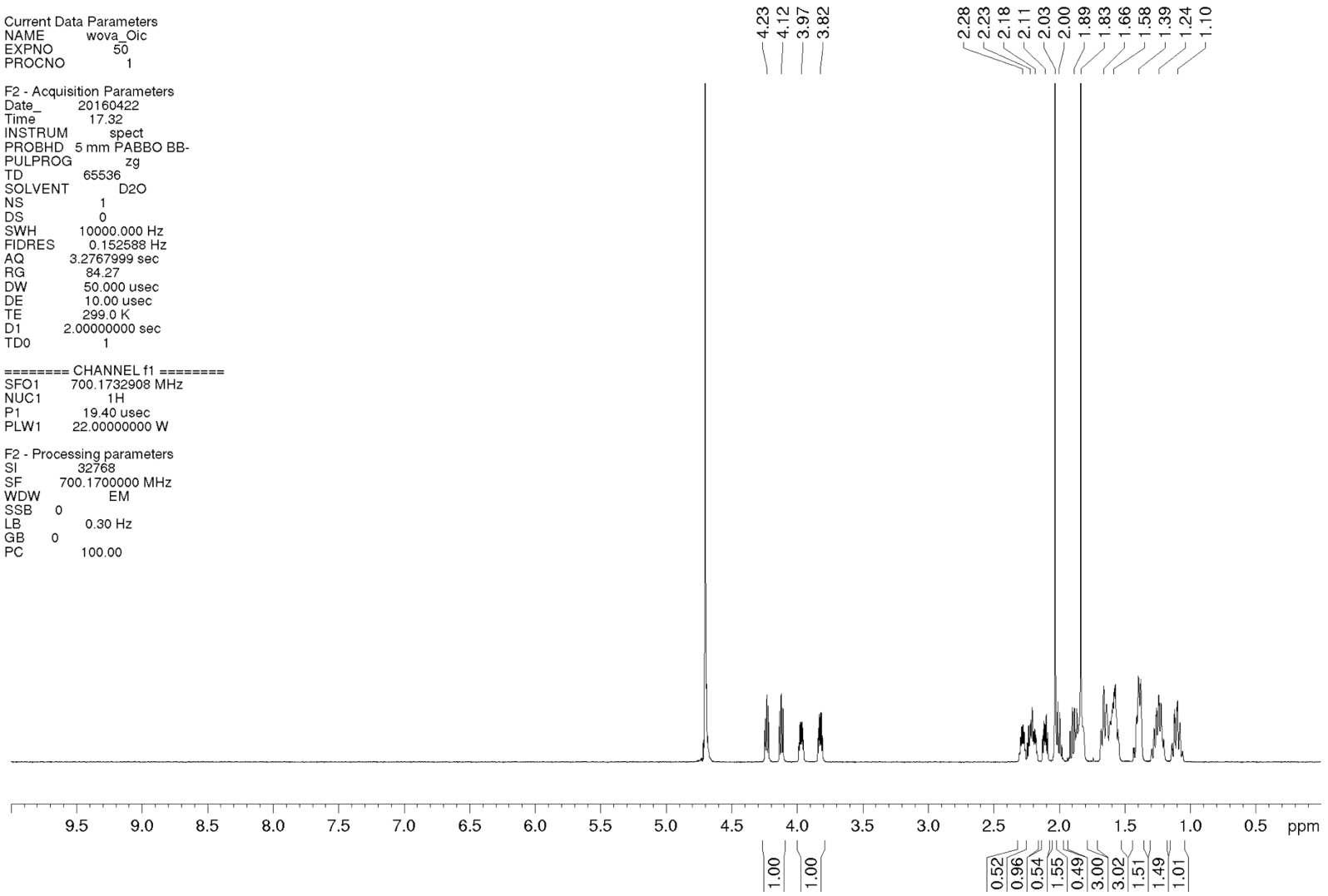
Table S4. α-CH resonances of all-*trans*-$Ac(Oic)_NOH$ in deuteromethanol (298 K, 700 MHz ^1H frequency).

N	Oic^1	Oic^2	Oic^3	Oic^4	Oic^5	Oic^6
1	4.35 dd, *J* = 10.3, 8.2 Hz	-	-	-	-	-
2	4.62 dd, *J* = 10.0, 7.5 Hz	4.42 dd, *J* = 10.5, 8.0 Hz				
3	4.68 dd, *J* = 10.0, 7.4 Hz	4.57 dd, *J* = 10.1, 7.5 Hz	4.46 dd, *J* = 10.4, 8.0 Hz			
4	4.75 dd, *J* = 10.1, 7.5 Hz; 4.61 dd, *J* = 10.5, 7.1 Hz; 4.58 dd, *J* = 10.0, 7.2 Hz			4.47 dd, *J* = 10.3, 7.9 Hz		
5	4.75 dd, *J* = 10.1, 7.4 Hz; 4.70 dd, *J* = 10.5, 7.3 Hz; 4.62 dd, *J* = 10.4, 7.2 Hz; 4.59 dd, *J* = 10.1, 7.4 Hz				4.47 dd, *J* = 10.5, 8.0 Hz	
6	4.75 dd, *J* = 10.1, 7.5 Hz; 4.71 dd*, *J* = 10.5, 7.2 Hz; 4.70 dd*, *J* = 10.4, 7.1 Hz; 4.62 dd, *J* = 10.4, 7.3 Hz; 4.59 dd, *J* = 10.0, 7.2 Hz					4.48 dd, *J* = 10.4, 8.0 Hz

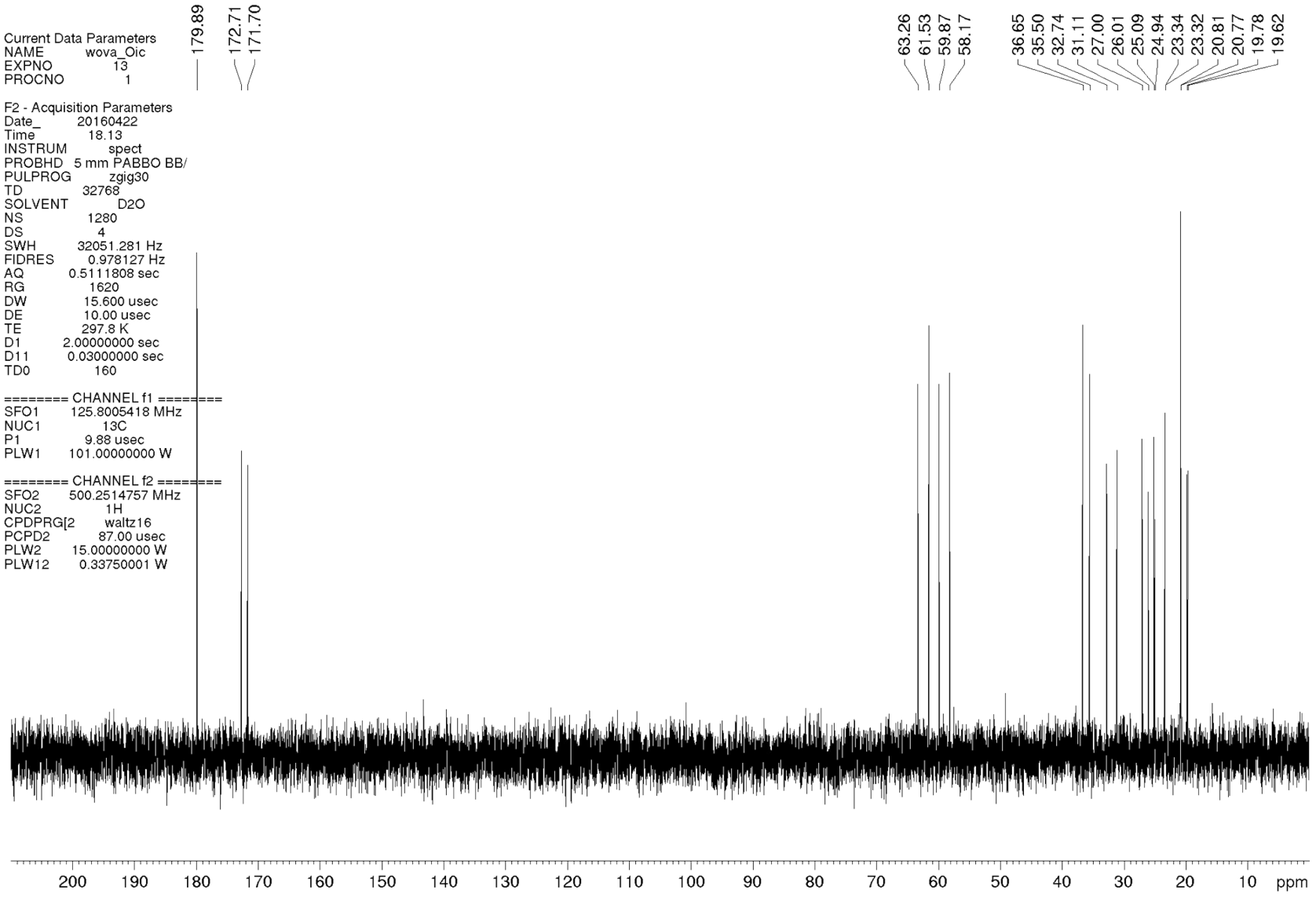
* - multiplicity was read out using ^1H *J*-resolved experiment.

Copies of the NMR spectra

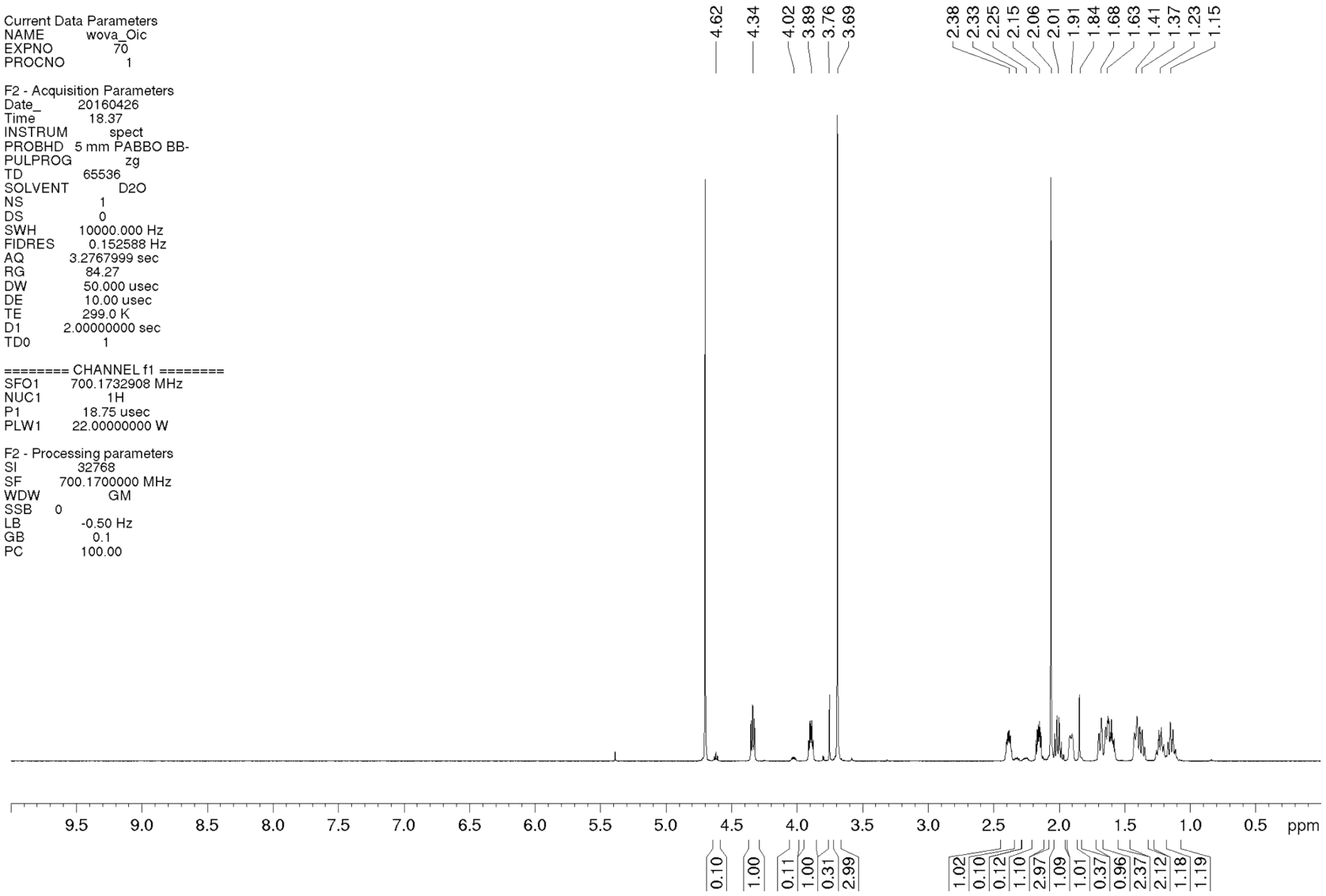
Ac-Oic-O$^-$: ^{1}H NMR spectrum in buffered deuterium oxide (pH 7) at 700 MHz



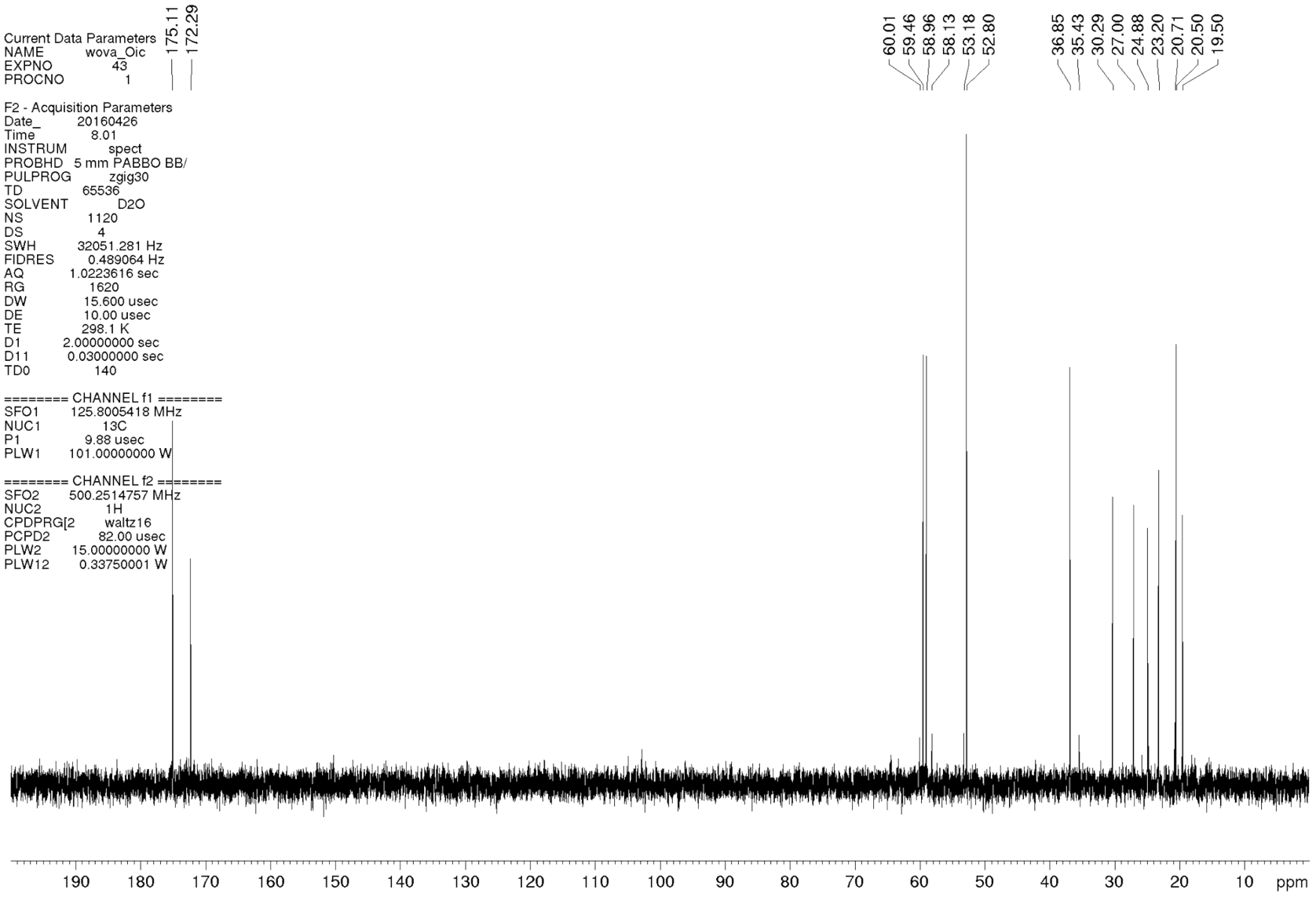
Ac-Oic-O$^-$: $^{13}C\{^1H\}$ NMR spectrum in buffered deuterium oxide (pH 7) at 126 MHz



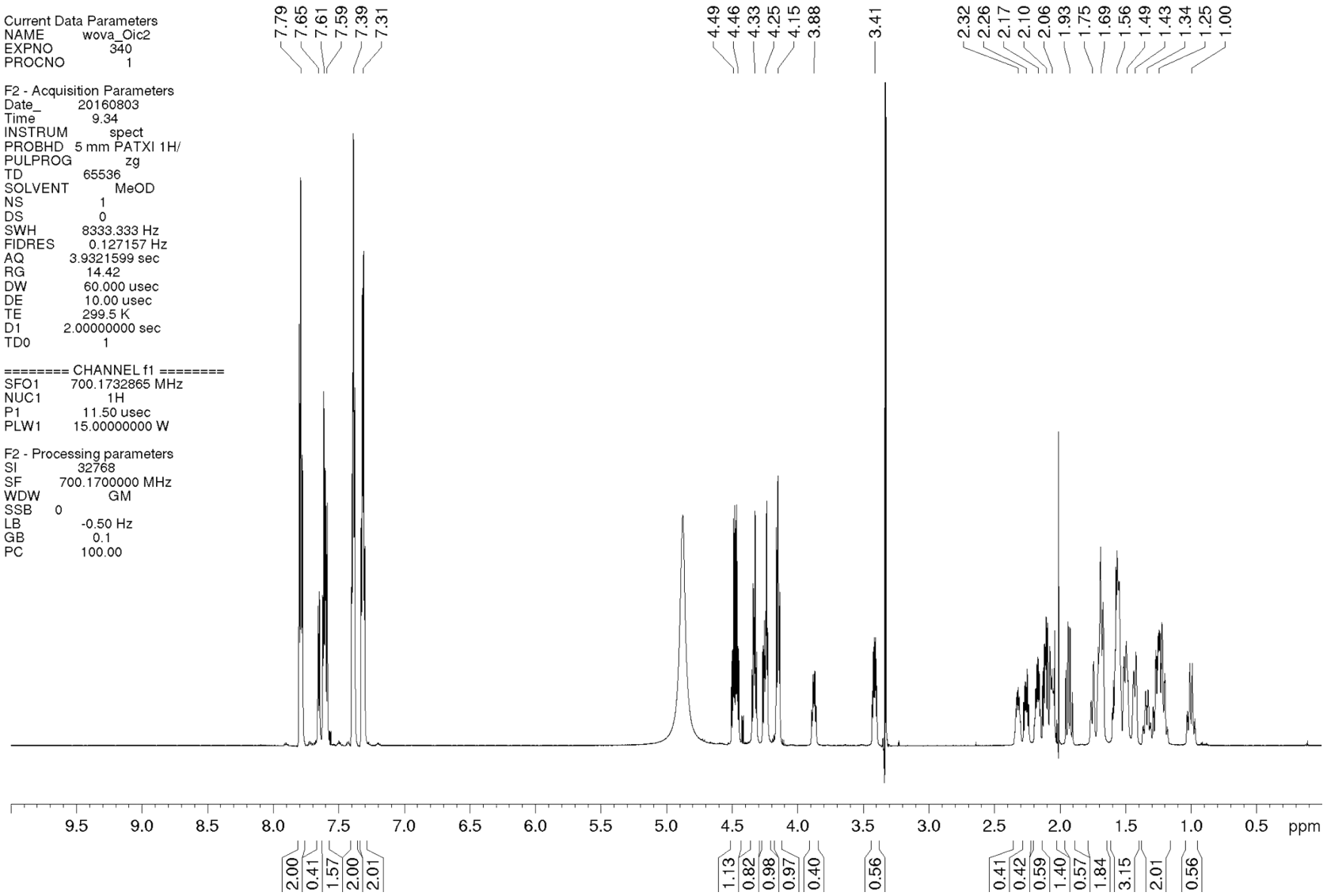
Ac-Oic-OMe: ^{1}H NMR spectrum in buffered deuterium oxide (pH 7) at 700 MHz



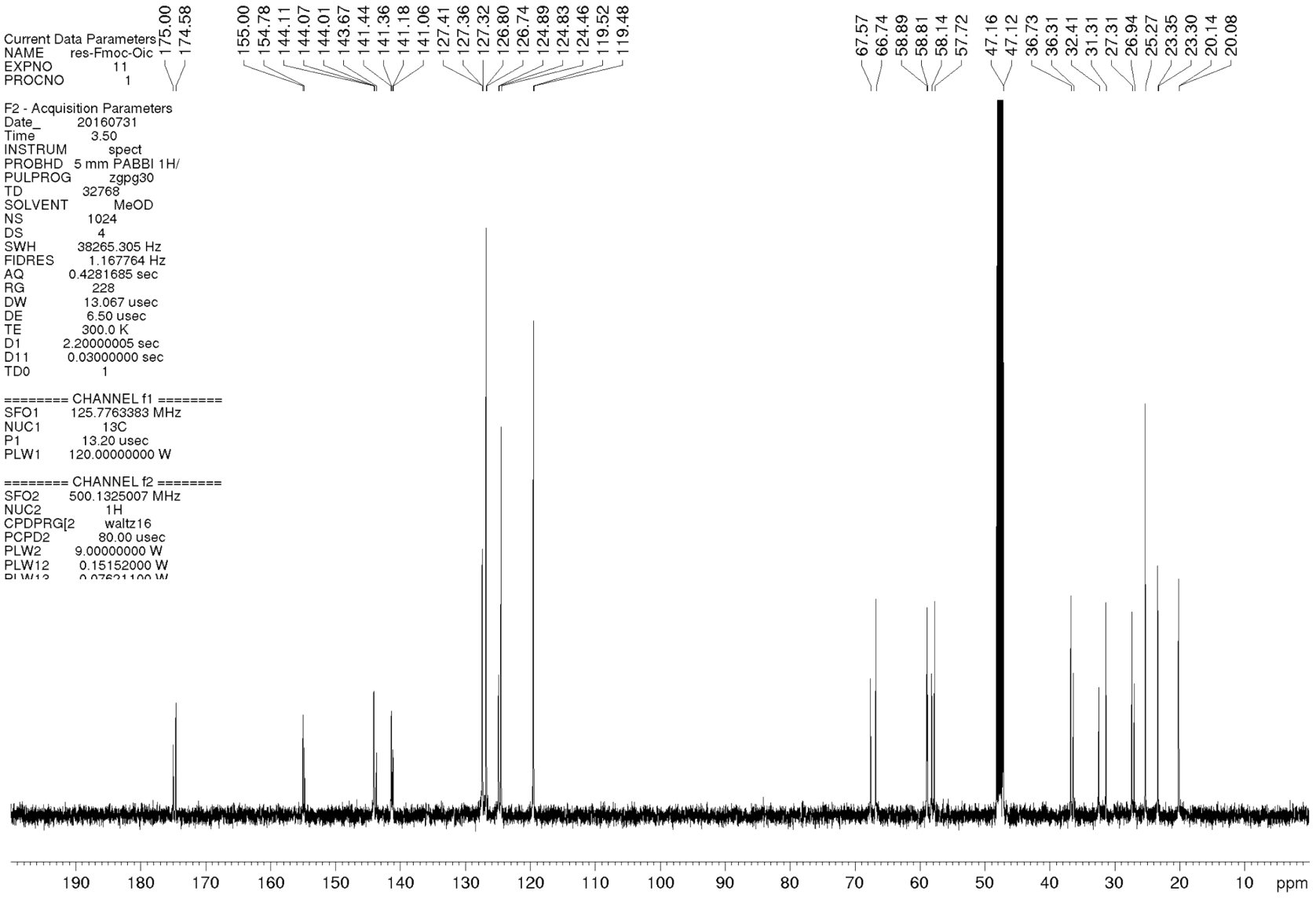
Ac-Oic-OMe: $^{13}C\{^{1}H\}$ NMR spectrum in buffered deuterium oxide (pH 7) at 126 MHz



Fmoc-Oic: ^{1}H NMR spectrum in deuteromethanol at 700 MHz

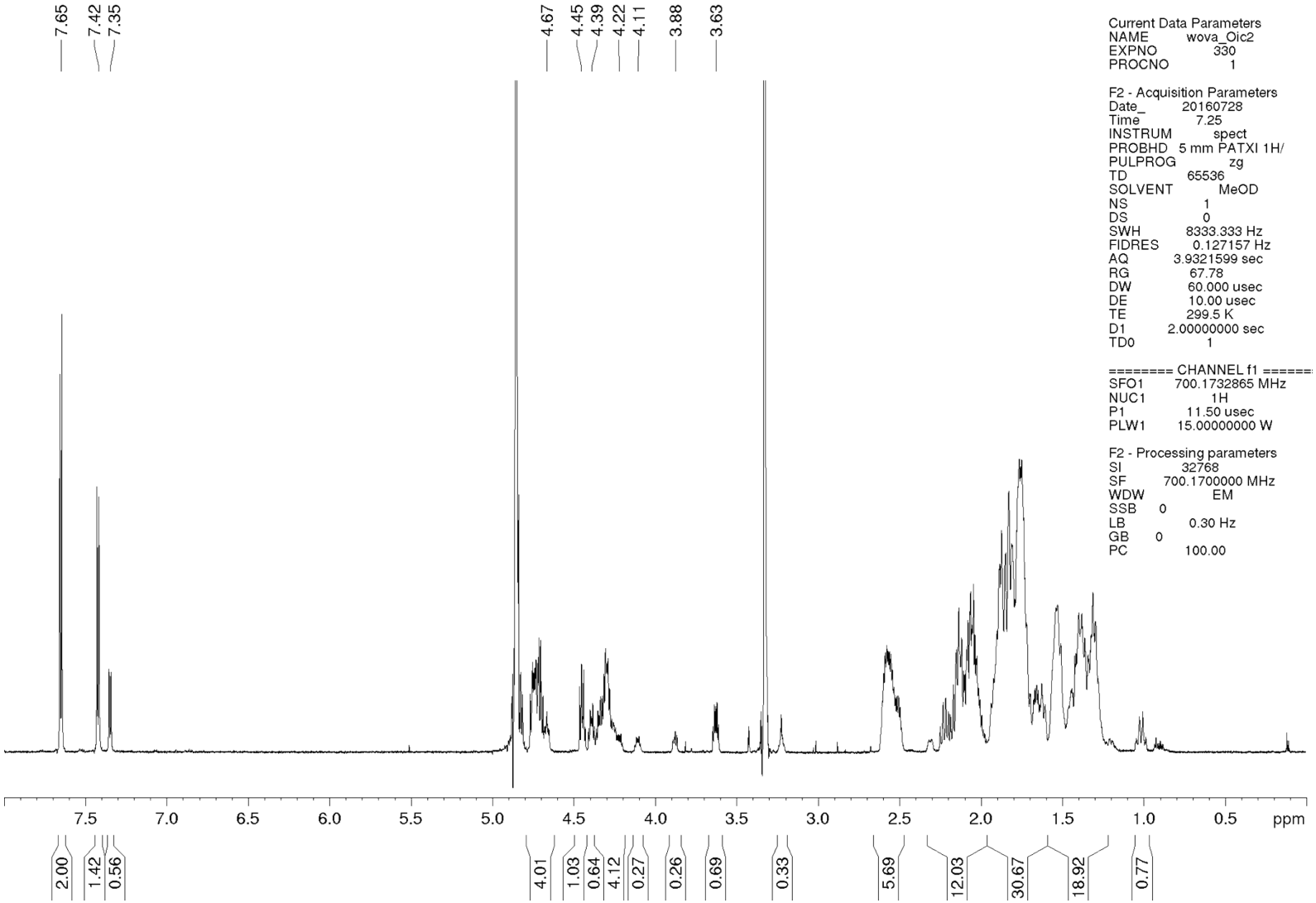


Fmoc-Oic: $^{13}C\{^{1}H\}$ NMR spectrum in deuteromethanol at 126 MHz



NMR spectra of the peptides

*p*BrBz-$(Oic)_6$-NH_2: ^1H NMR spectrum in deuteromethanol at 700 MHz



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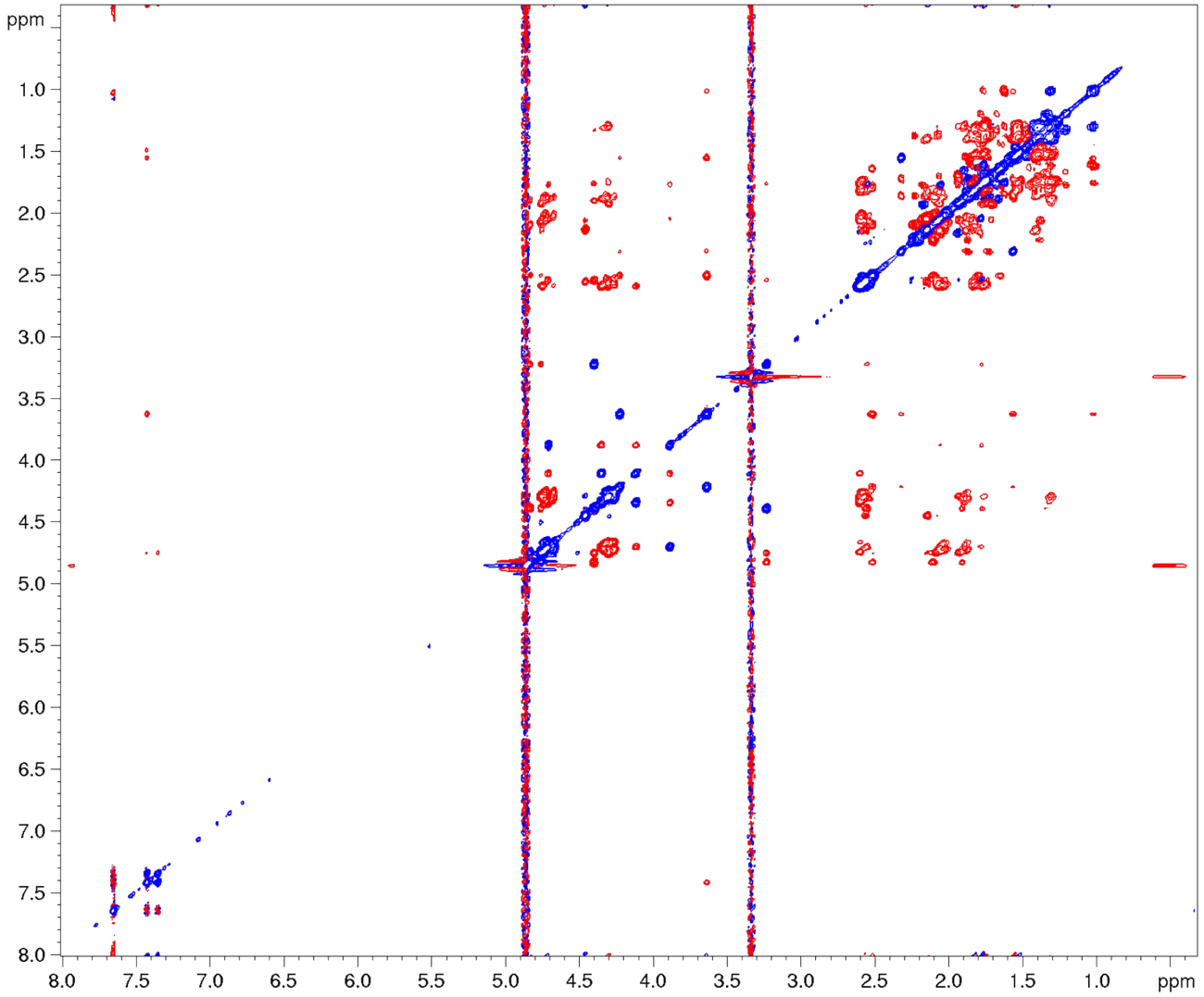

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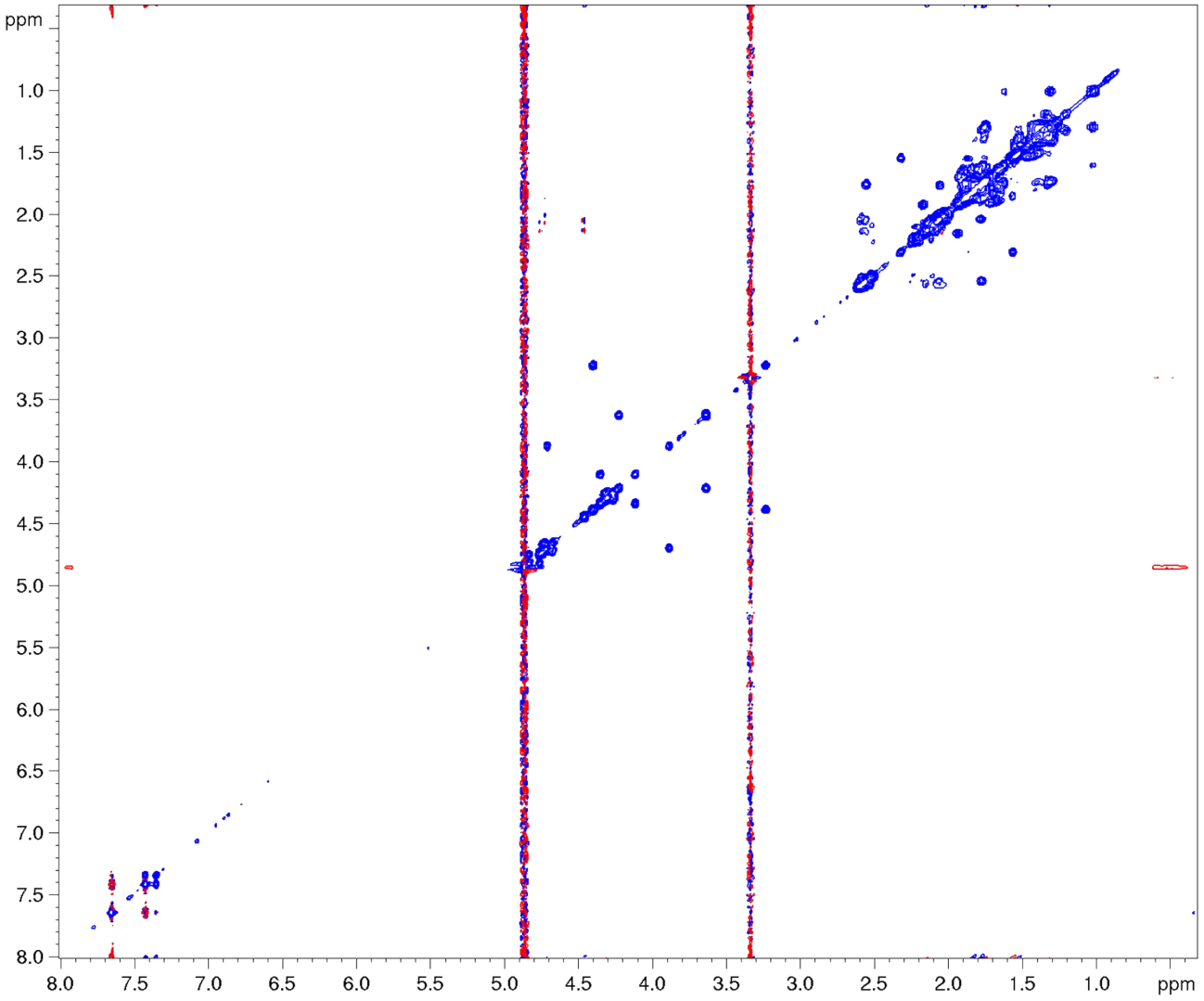
^{1}H NOESY spectrum (mixing time 500 ms):



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DW 92.800 usec
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FnMODE States-TPPI

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SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
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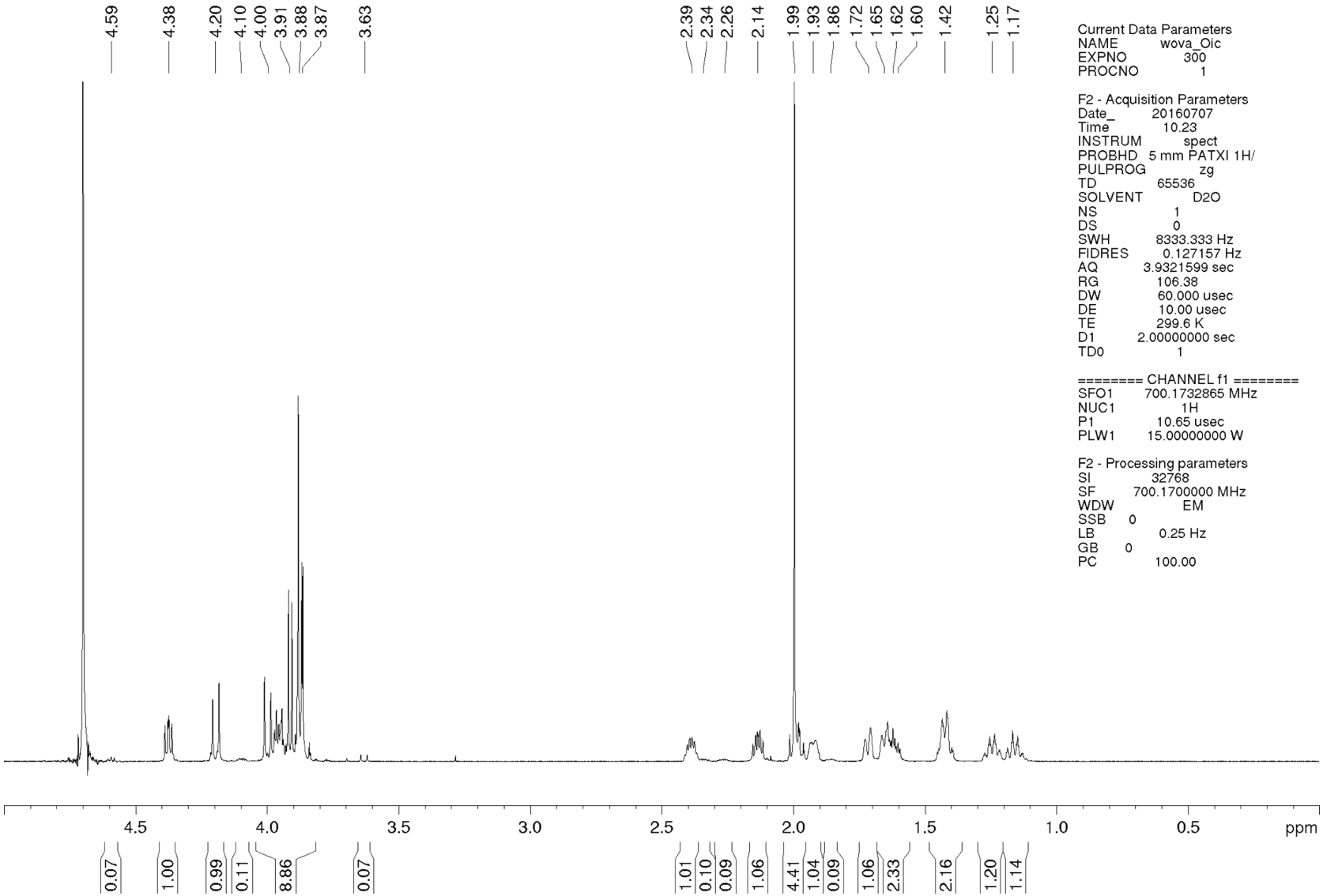
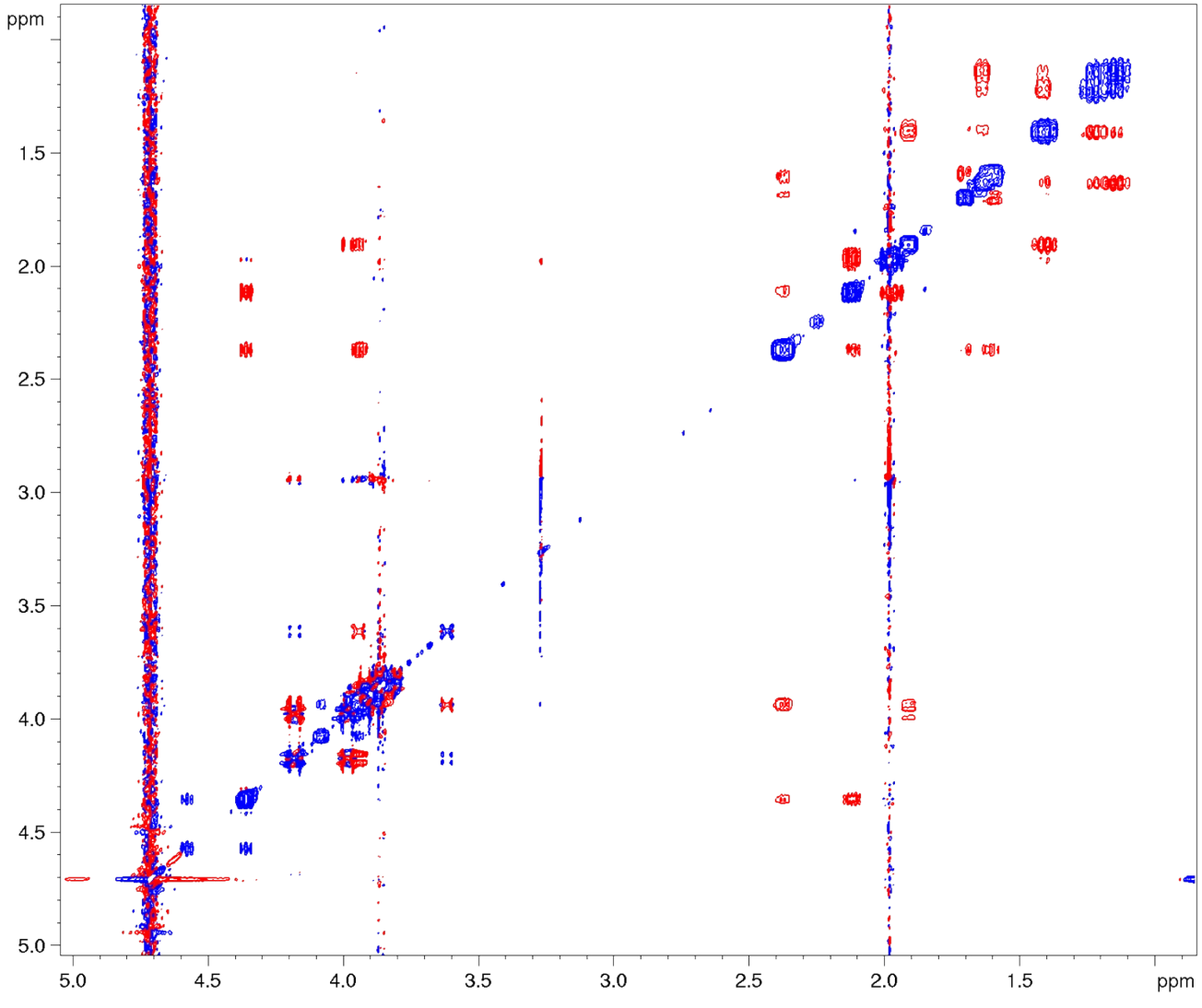
Ac-GlyGlyOicGlyGly-NH_2: ^{1}H NMR spectrum in deuteromethanol at 700 MHz



^{1}H NOESY spectrum (mixing time 1 s):



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GB 0
PC 1.00

F1 - Processing parameters
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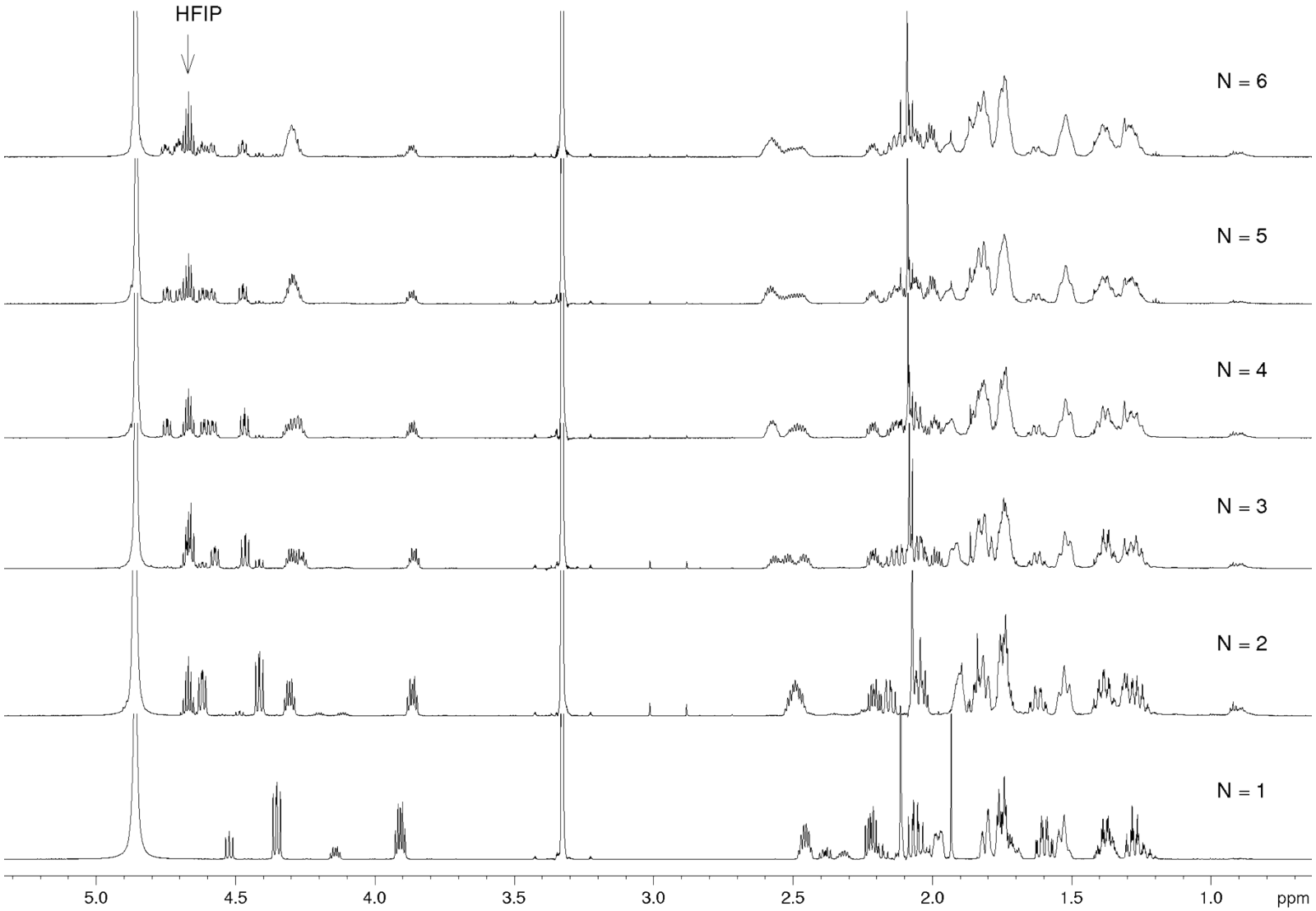
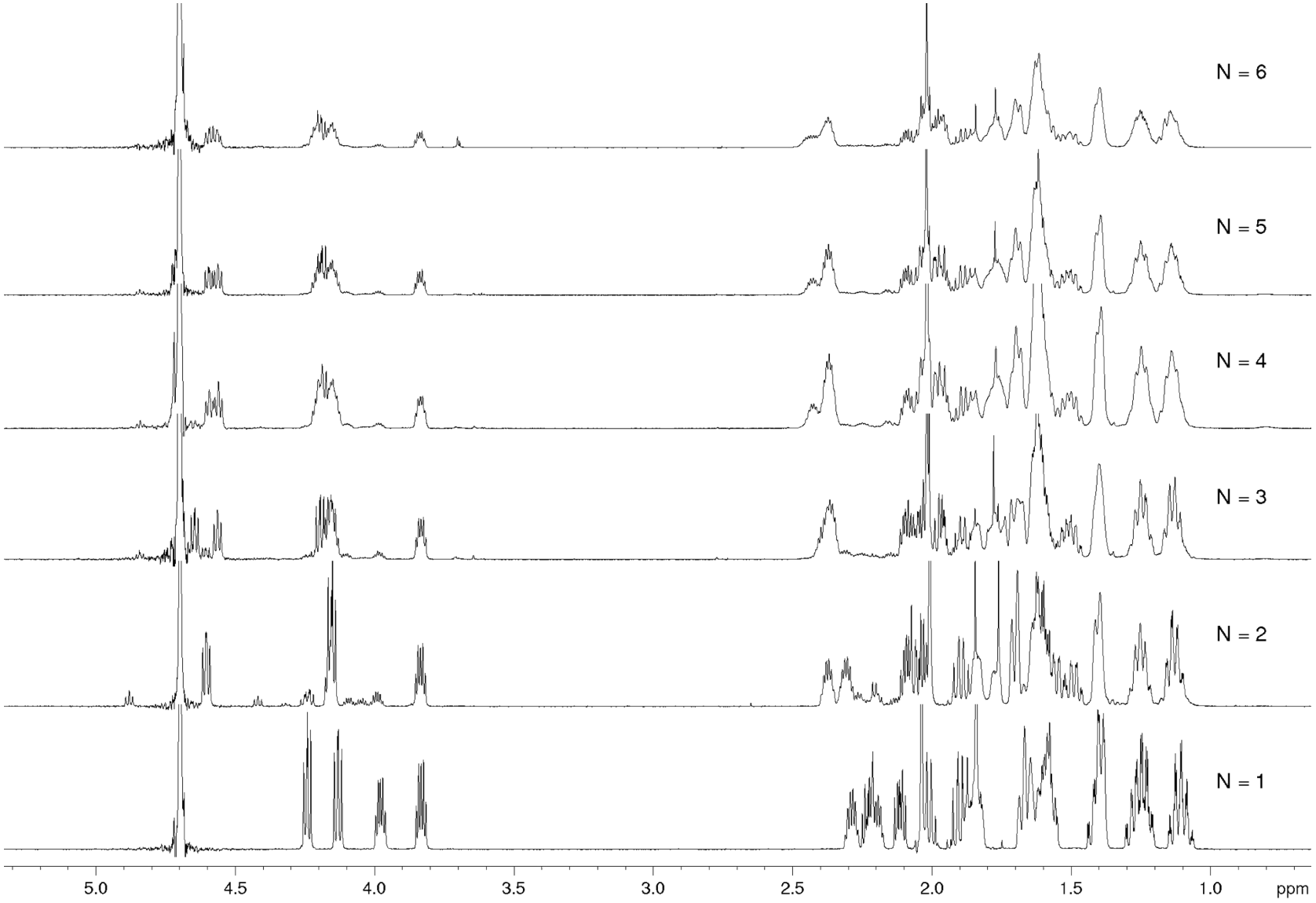
^{1}H NMR spectra of crude Ac(Oic)$_{N}$OH peptides in deuteromethanol at 700 MHz:

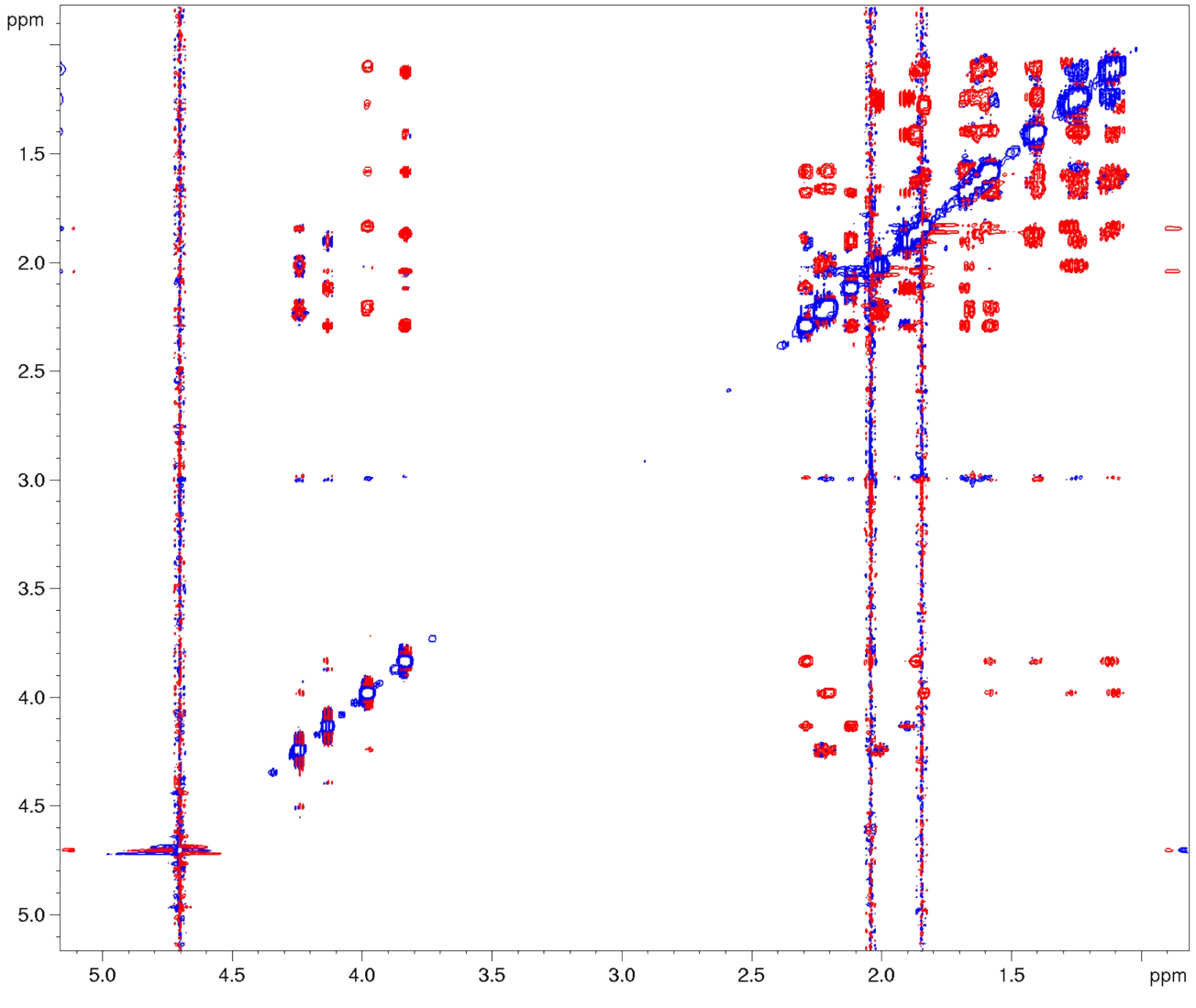


(HFIP – residual hexafluoroisopropanol)

^{1}H NMR spectra of crude Ac(Oic)$_{N}$O^{-} peptides in buffered deuterium oxide at 700 MHz:



^{1}H NOESY spectrum of Ac(Oic)$_{1}$O^{-} in buffered deuterium oxide at 700 MHz, mixing time 500 ms:



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RG 67.78
DW 164.267 usec
DE 10.00 usec
TE 299.5 K
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D1 2.00000000 sec
D8 0.50000000 sec
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IN0 0.00032840 sec

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FnMODE States

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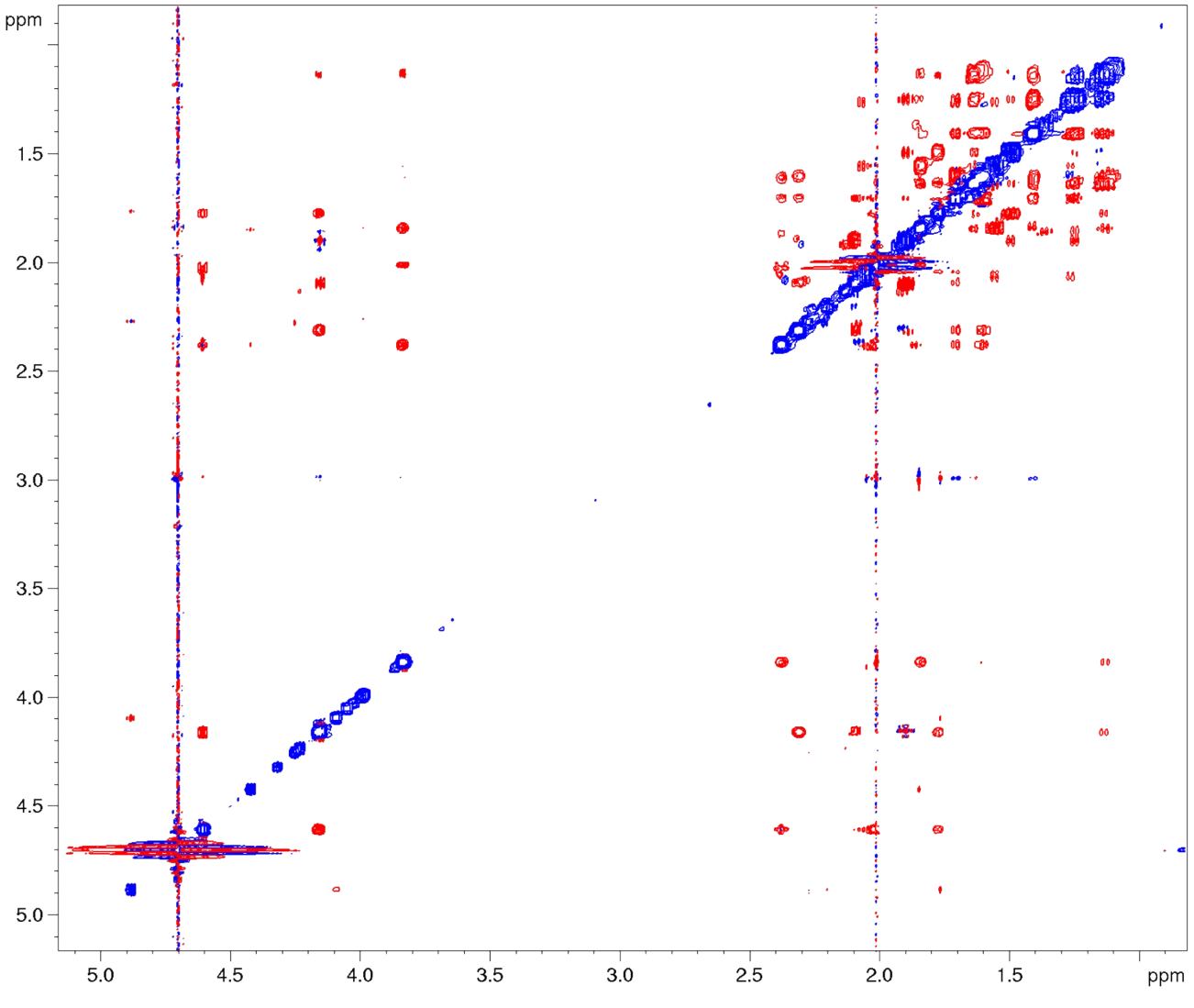
SI 1024
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 States
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY spectrum of $Ac(Oic)_2O^-$ in buffered deuterium oxide at 700 MHz, mixing time 500 ms:



Current Data Parameters
NAME wova_Oic2
EXPNO 104
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160719
Time 12.34
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG noesygpph
TD 2048
SOLVENT D2O
NS 8
DS 16
SWH 3043.831 Hz
FIDRES 1.486246 Hz
AQ 0.3364181 sec
RG 67.78
DW 164.267 usec
DE 10.00 usec
TE 299.5 K
D0 0.00014930 sec
D1 2.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
IN0 0.00032840 sec

======== CHANNEL f1 ========
SFO1 700.1720935 MHz
NUC1 1H
P1 11.70 usec
P2 23.40 usec
PLW1 15.00000000 W

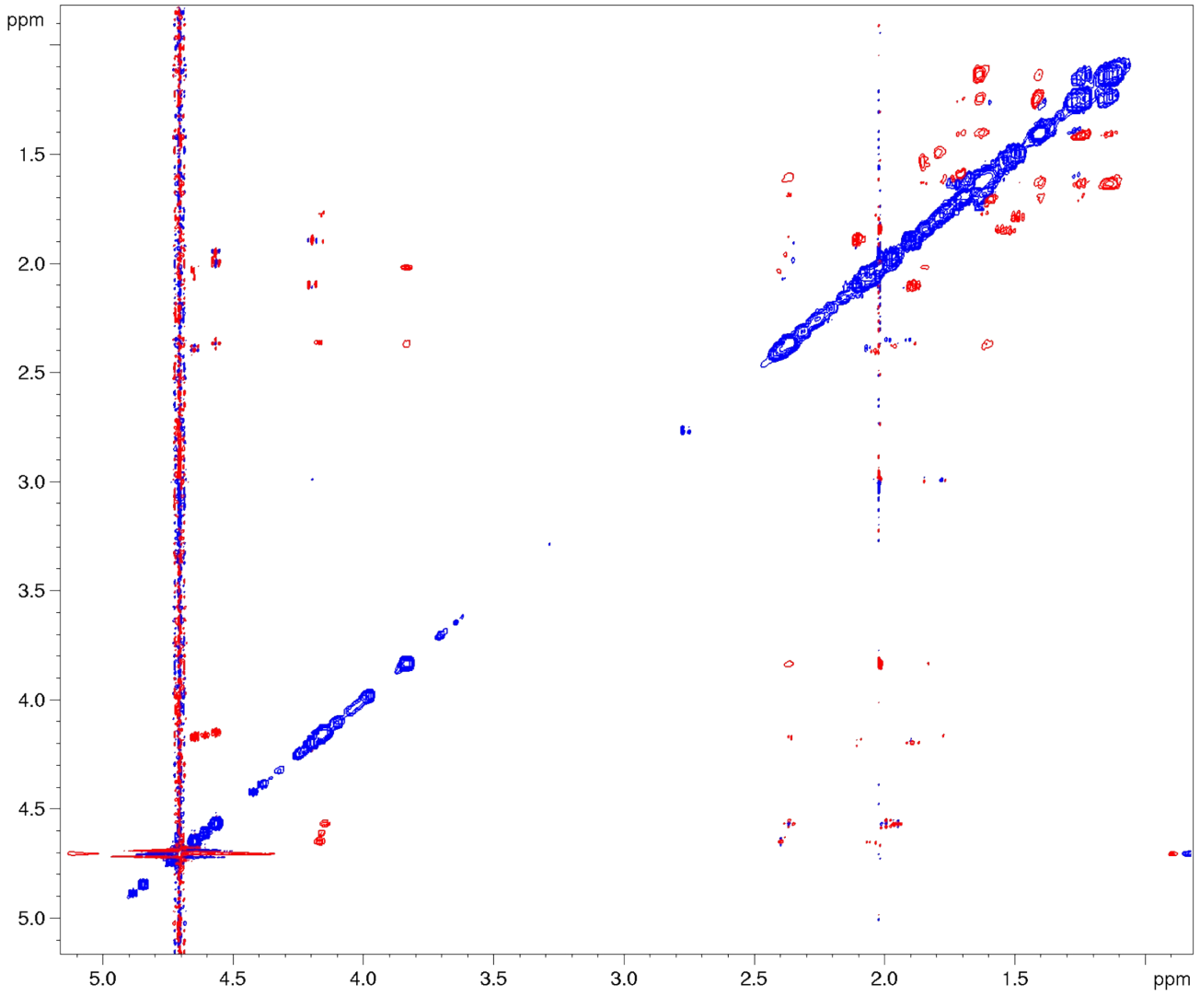
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 320
SFO1 700.1721 MHz
FIDRES 9.515835 Hz
SW 4.349 ppm
FnMODE States

F2 - Processing parameters
SI 1024
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 States
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY spectrum of $Ac(Oic)_3O^-$ in buffered deuterium oxide at 700 MHz, mixing time 500 ms:



Current Data Parameters
NAME wova_Oic2
EXPNO 115
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160726
Time 15.24
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG noesygpph
TD 2048
SOLVENT D2O
NS 8
DS 16
SWH 3043.831 Hz
FIDRES 1.486246 Hz
AQ 0.3364181 sec
RG 67.78
DW 164.267 usec
DE 10.00 usec
TE 299.5 K
D0 0.00014930 sec
D1 2.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
IN0 0.00032840 sec

======== CHANNEL f1 ========
SFO1 700.1720935 MHz
NUC1 1H
P1 11.70 usec
P2 23.40 usec
PLW1 15.00000000 W

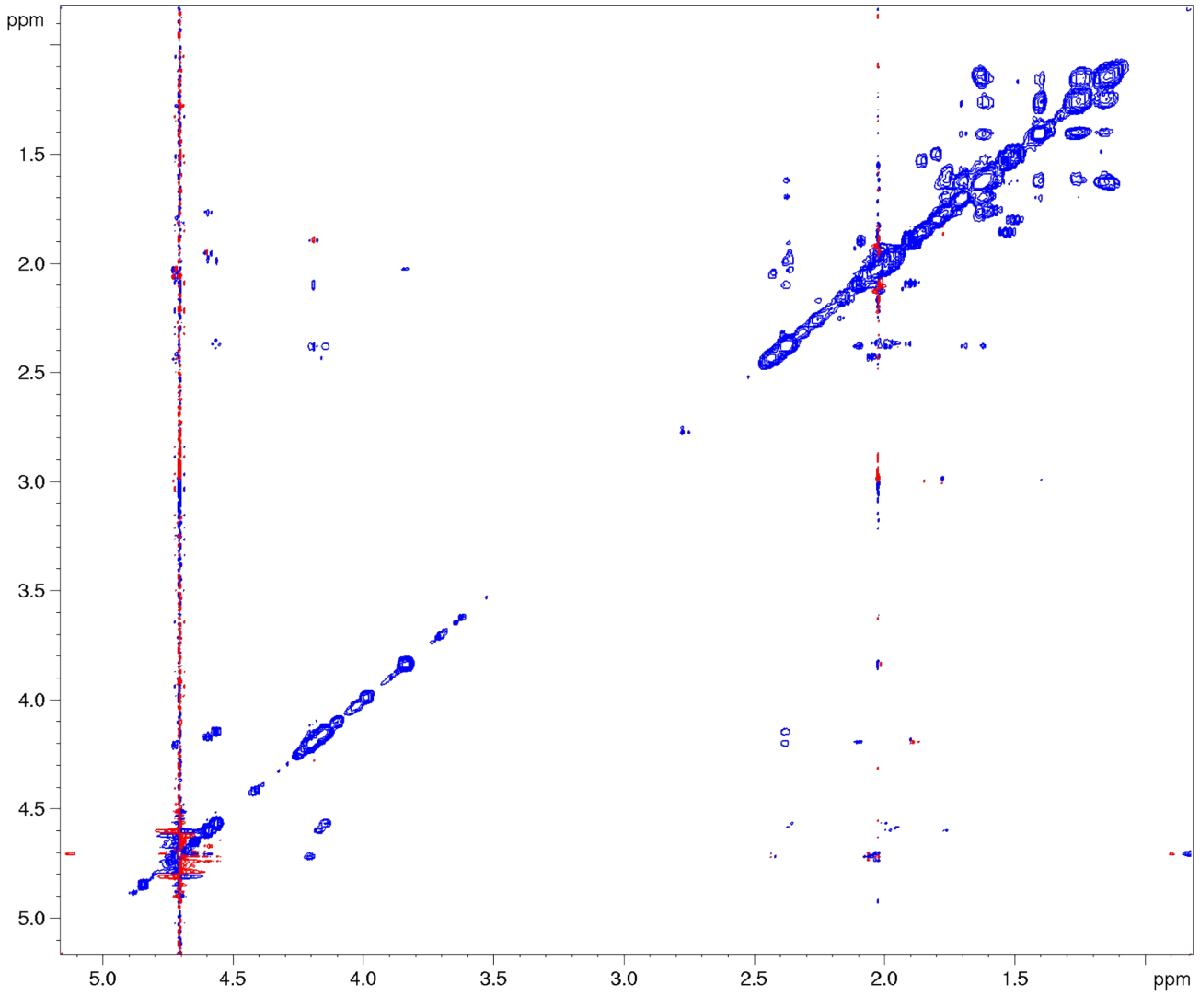
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 320
SFO1 700.1721 MHz
FIDRES 9.515835 Hz
SW 4.349 ppm
FnMODE States

F2 - Processing parameters
SI 1024
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 States
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY spectrum of $Ac(Oic)_4O^-$ in buffered deuterium oxide at 700 MHz, mixing time 500 ms:



Current Data Parameters
NAME wova_Oic2
EXPNO 142
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160720
Time 20.05
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG noesygpph
TD 2048
SOLVENT D2O
NS 8
DS 16
SWH 3043.831 Hz
FIDRES 1.486246 Hz
AQ 0.3364181 sec
RG 67.78
DW 164.267 usec
DE 10.00 usec
TE 299.5 K
D0 0.00014930 sec
D1 2.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
IN0 0.00032840 sec

======== CHANNEL f1 ========
SFO1 700.1720935 MHz
NUC1 1H
P1 11.70 usec
P2 23.40 usec
PLW1 15.00000000 W

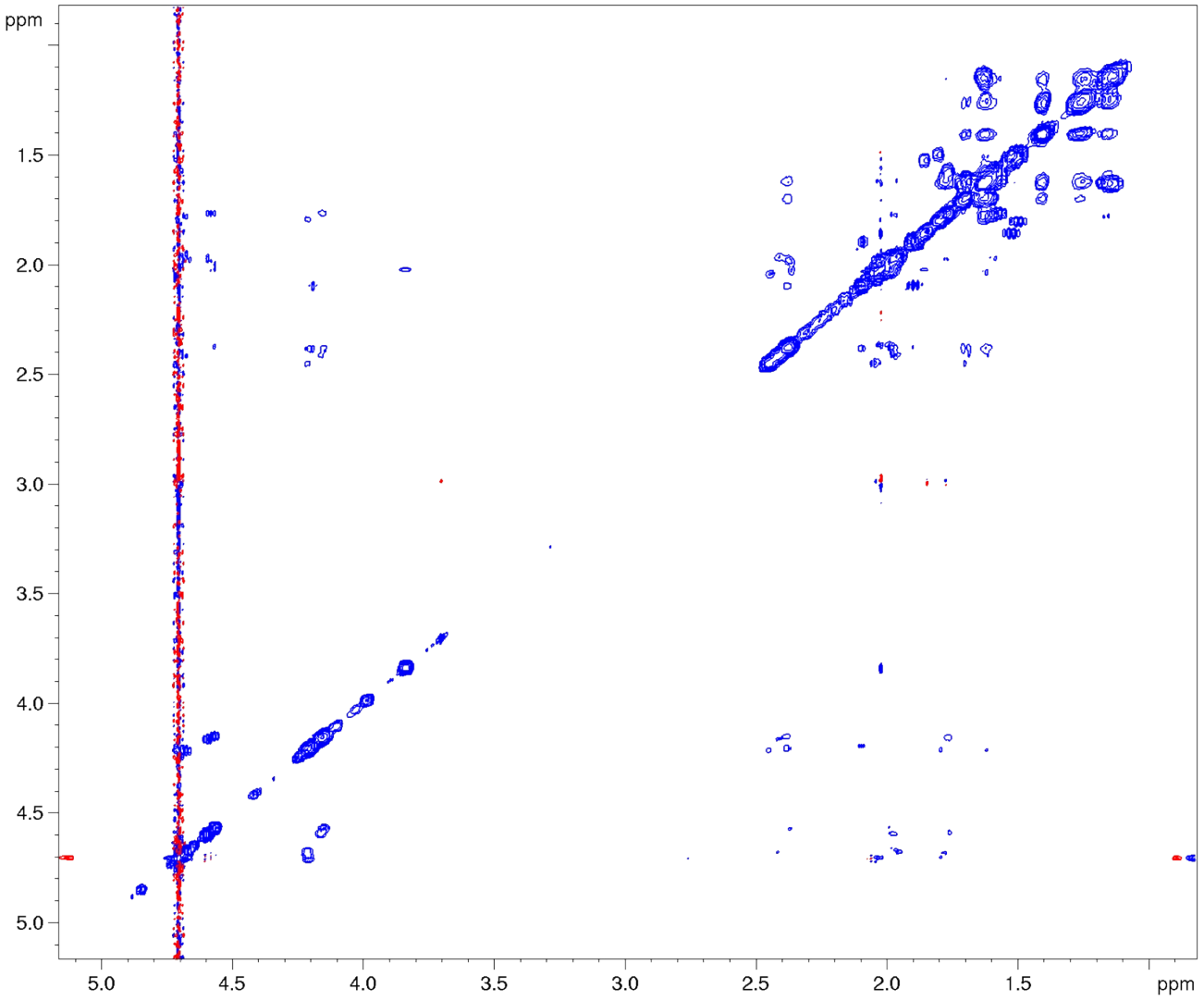
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 320
SFO1 700.1721 MHz
FIDRES 9.515835 Hz
SW 4.349 ppm
FnMODE States

F2 - Processing parameters
SI 1024
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 States
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY spectrum of $Ac(Oic)_5O^-$ in buffered deuterium oxide at 700 MHz, mixing time 500 ms:



Current Data Parameters
NAME wova_Oic2
EXPNO 164
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160726
Time 19.21
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG noesygpph
TD 2048
SOLVENT D2O
NS 8
DS 16
SWH 3043.831 Hz
FIDRES 1.486246 Hz
AQ 0.3364181 sec
RG 67.78
DW 164.267 usec
DE 10.00 usec
TE 299.5 K
D0 0.00014918 sec
D1 2.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
IN0 0.00032840 sec

======== CHANNEL f1 ========
SFO1 700.1720935 MHz
NUC1 1H
P1 11.80 usec
P2 23.60 usec
PLW1 15.00000000 W

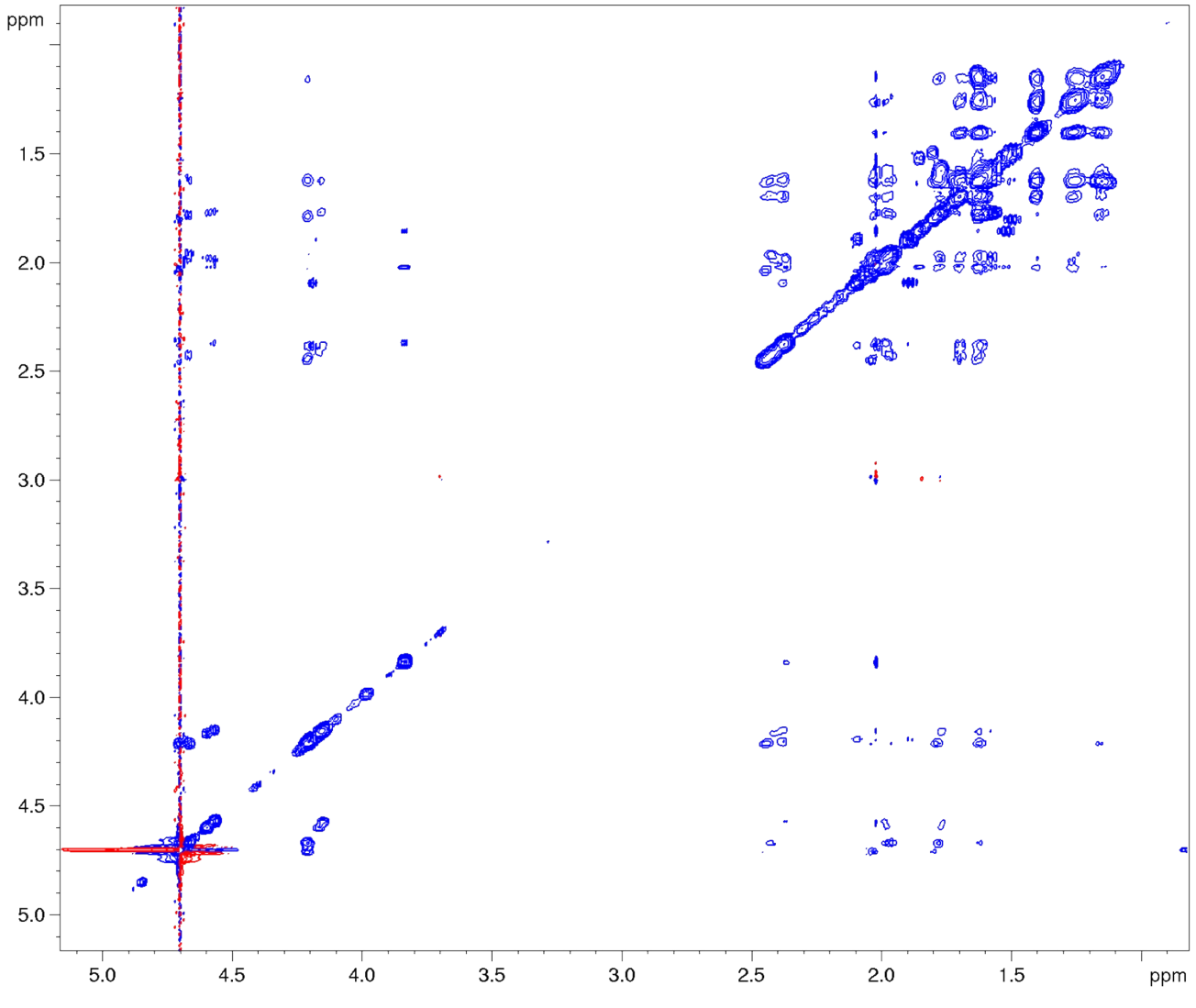
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 320
SFO1 700.1721 MHz
FIDRES 9.515835 Hz
SW 4.349 ppm
FnMODE States

F2 - Processing parameters
SI 1024
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 States
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY spectrum of $Ac(Oic)_6O^-$ in buffered deuterium oxide at 700 MHz, mixing time 500 ms:



Current Data Parameters
NAME wova_Oic2
EXPNO 174
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160727
Time 9.25
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG noesygpph
TD 2048
SOLVENT D2O
NS 8
DS 16
SWH 3043.831 Hz
FIDRES 1.486246 Hz
AQ 0.3364181 sec
RG 67.78
DW 164.267 usec
DE 10.00 usec
TE 299.5 K
D0 0.00014988 sec
D1 2.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
IN0 0.00032840 sec

======== CHANNEL f1 ========
SFO1 700.1720935 MHz
NUC1 1H
P1 11.25 usec
P2 22.50 usec
PLW1 15.00000000 W

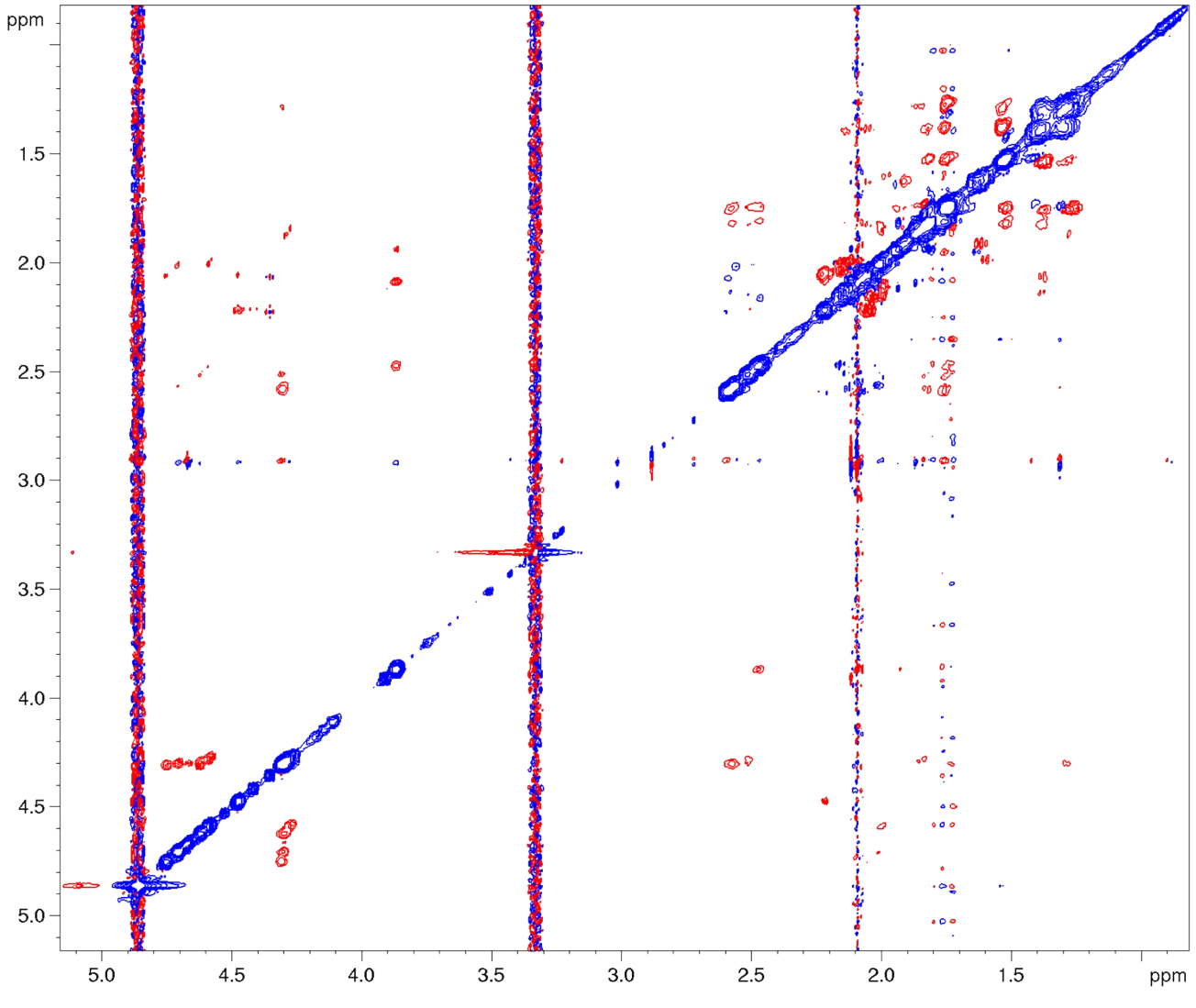
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 320
SFO1 700.1721 MHz
FIDRES 9.515835 Hz
SW 4.349 ppm
FnMODE States

F2 - Processing parameters
SI 1024
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 States
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY spectrum of Ac(Oic)$_{6}$OH in deuteromethanol at 700 MHz, mixing time 750 ms:



Current Data Parameters
NAME wova_Oic2
EXPNO 314
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160721
Time 10.29
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG noesygpph
TD 2048
SOLVENT MeOD
NS 2
DS 16
SWH 3151.260 Hz
FIDRES 1.538701 Hz
AQ 0.3249493 sec
RG 67.78
DW 158.667 usec
DE 10.00 usec
TE 299.5 K
D0 0.00014419 sec
D1 2.00000000 sec
D8 0.75000000 sec
D16 0.00020000 sec
IN0 0.00031740 sec

======== CHANNEL f1 ========
SFO1 700.1720379 MHz
NUC1 1H
P1 11.40 usec
P2 22.80 usec
PLW1 15.00000000 W

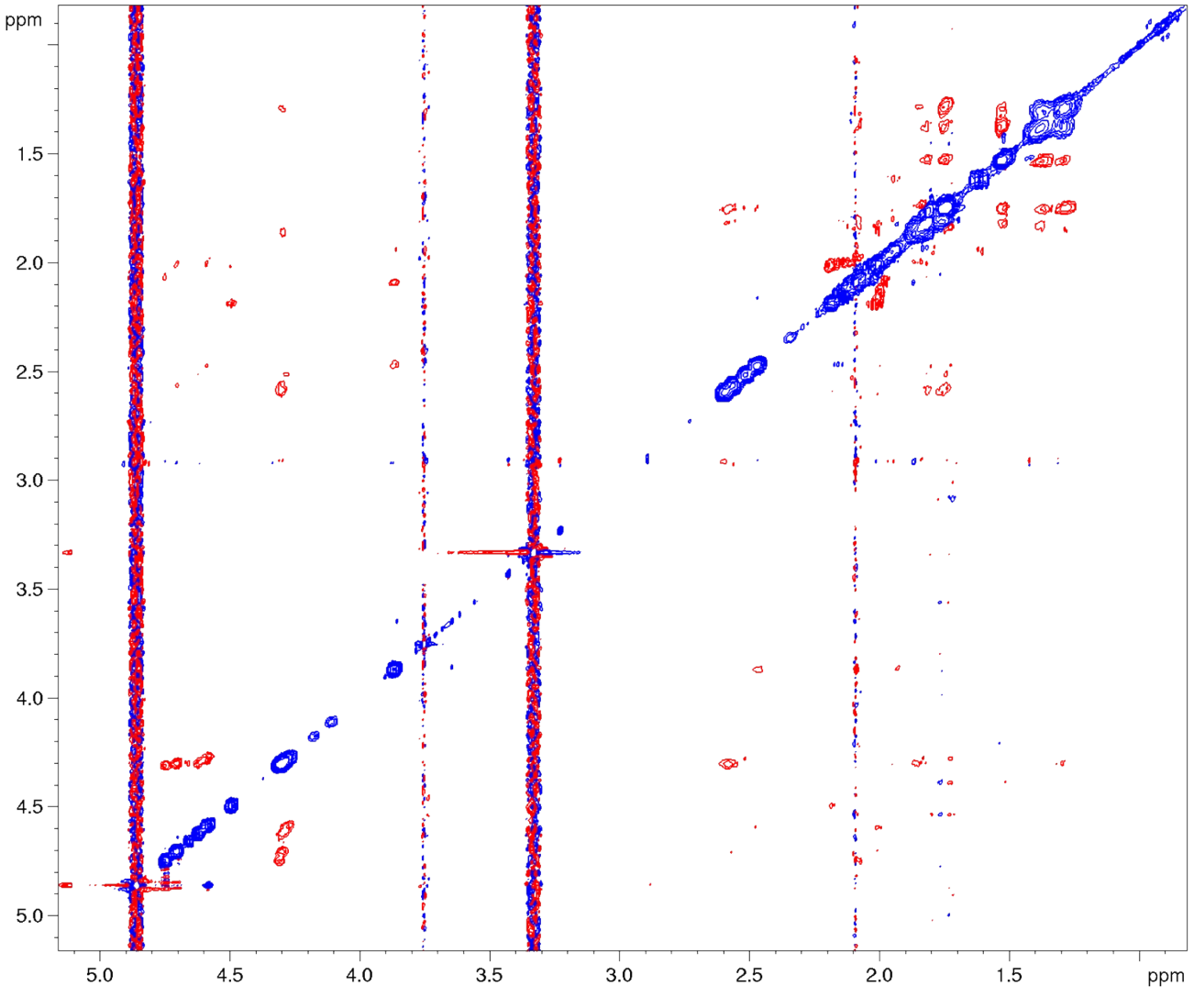
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 700.172 MHz
FIDRES 12.307026 Hz
SW 4.500 ppm
FnMODE States

F2 - Processing parameters
SI 1024
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 States
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY spectrum of Ac(Oic)$_{6}$OMe in deuteromethanol at 700 MHz, mixing time 750 ms:



Current Data Parameters
NAME wova_Oic2
EXPNO 394
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160804
Time 10.29
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG noesygpph
TD 2048
SOLVENT MeOD
NS 2
DS 16
SWH 3151.260 Hz
FIDRES 1.538701 Hz
AQ 0.3249493 sec
RG 67.78
DW 158.667 usec
DE 10.00 usec
TE 299.5 K
D0 0.00014419 sec
D1 2.00000000 sec
D8 0.75000000 sec
D16 0.00020000 sec
IN0 0.00031740 sec

======== CHANNEL f1 ========
SFO1 700.1720379 MHz
NUC1 1H
P1 11.40 usec
P2 22.80 usec
PLW1 15.00000000 W

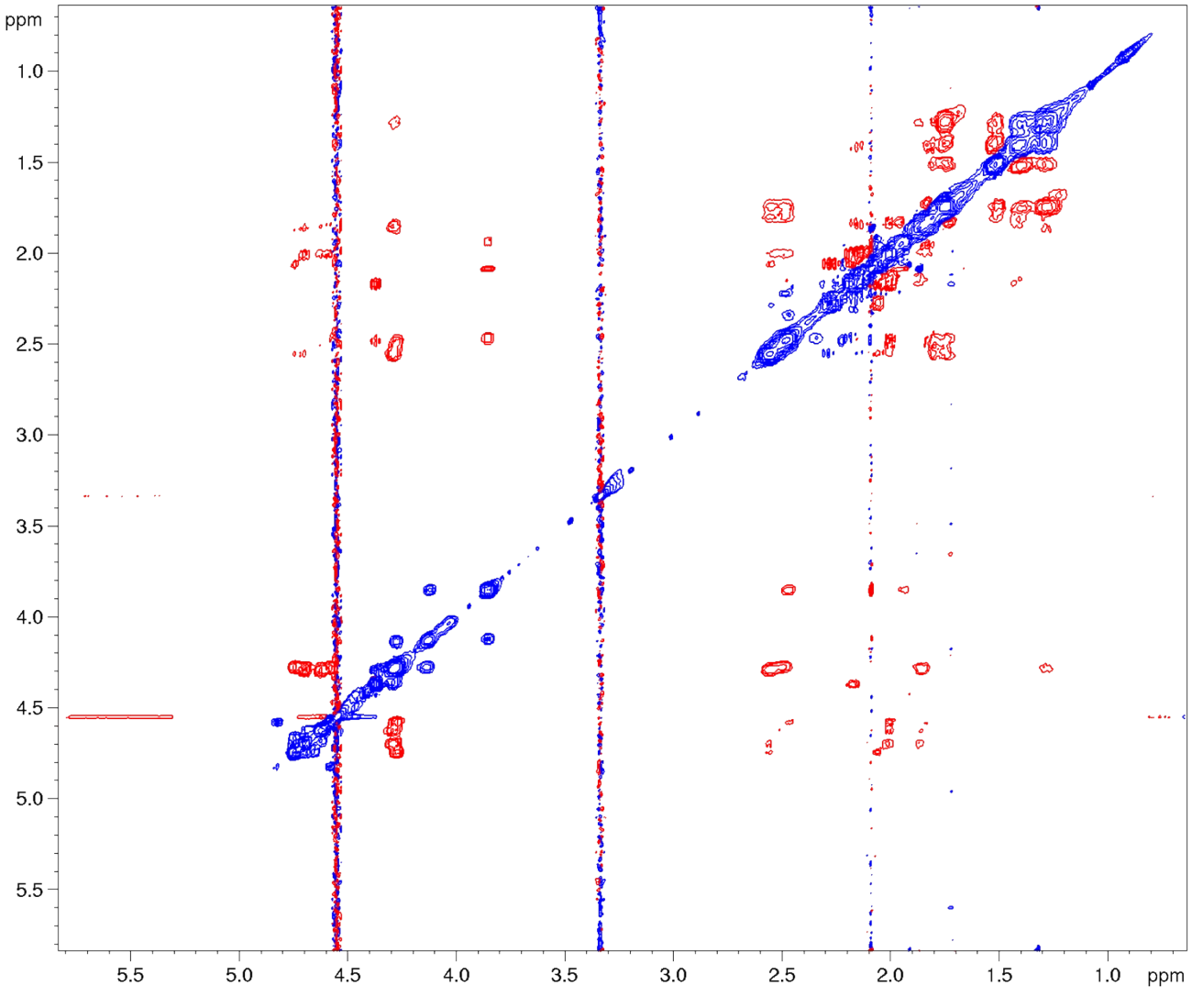
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 700.172 MHz
FIDRES 12.307026 Hz
SW 4.500 ppm
FnMODE States

F2 - Processing parameters
SI 1024
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 States
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY (EXSY) spectrum of $Ac(Oic)_6O^-$ in deuteromethanol at 330 K and 500 MHz, mixing time 1 s:



Current Data Parameters
NAME wova_Oic2
EXPNO 255
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160810
Time 21.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG noesygpph
TD 2048
SOLVENT MeOD
NS 8
DS 16
SWH 2600.555 Hz
FIDRES 1.269802 Hz
AQ 0.3937621 sec
RG 128
DW 192.267 usec
DE 10.00 usec
TE 328.0 K
D0 0.00017590 sec
D1 2.00000000 sec
D8 1.00000000 sec
D16 0.00020000 sec
IN0 0.00038440 sec

======== CHANNEL f1 ========
SFO1 500.2516183 MHz
NUC1 1H
P1 12.80 usec
P2 25.60 usec
PLW1 15.00000000 W

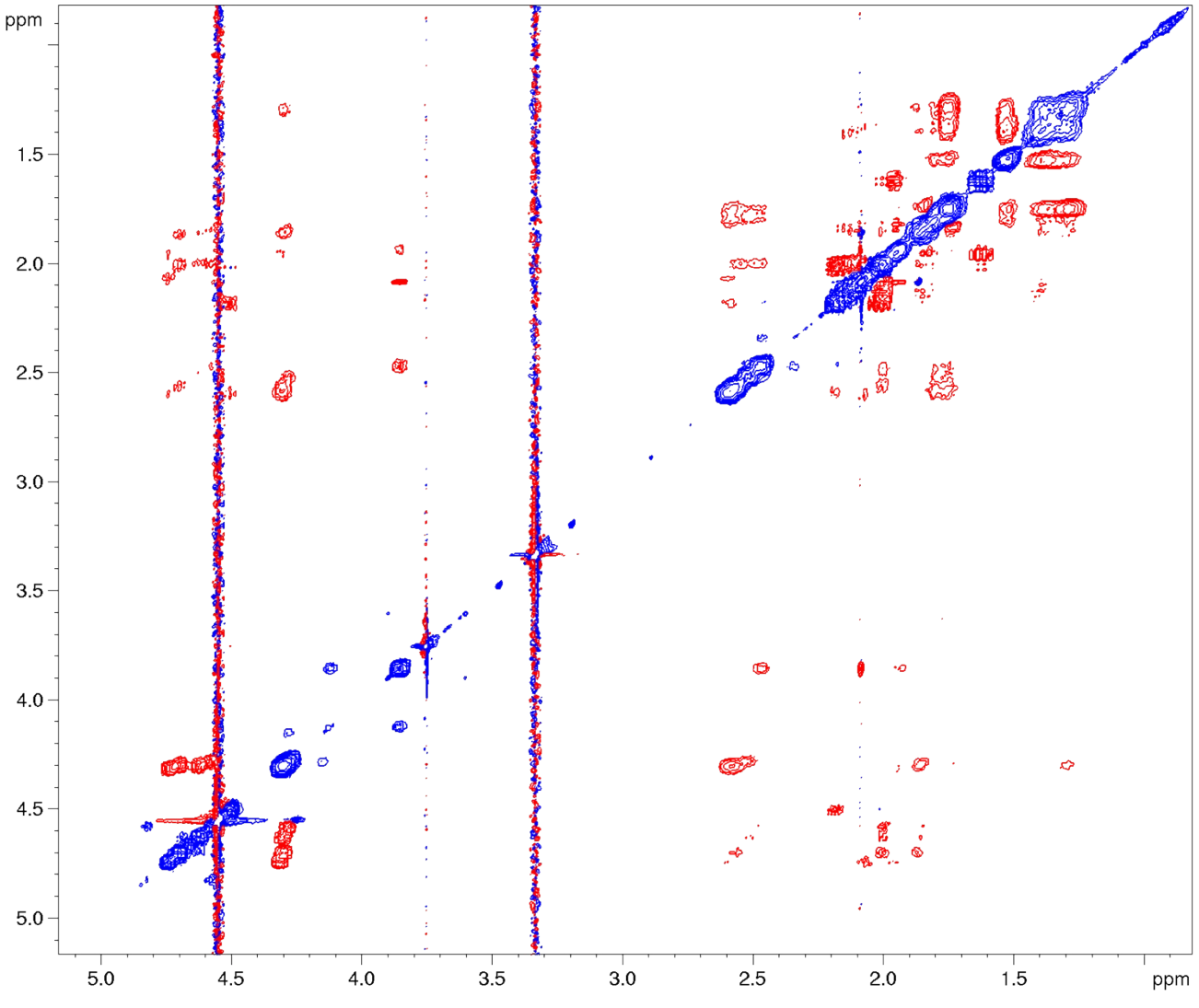
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 320
SFO1 500.2516 MHz
FIDRES 8.129553 Hz
SW 5.200 ppm
FnMODE States-TPPI

F2 - Processing parameters
SI 1024
SF 500.2500000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 States-TPPI
SF 500.2500000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NOESY (EXSY) spectrum of Ac(Oic)$_{6}$OMe in deuteromethanol at 330 K and 500 MHz, mixing time 1 s:



Current Data Parameters
NAME wova_Oic2
EXPNO 202
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160806
Time 21.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG noesygpph
TD 2048
SOLVENT MeOD
NS 8
DS 16
SWH 2600.555 Hz
FIDRES 1.269802 Hz
AQ 0.3937621 sec
RG 128
DW 192.267 usec
DE 10.00 usec
TE 328.0 K
D0 0.00017565 sec
D1 2.00000000 sec
D8 1.00000000 sec
D16 0.00020000 sec
IN0 0.00038440 sec

======== CHANNEL f1 ========
SFO1 500.2516183 MHz
NUC1 1H
P1 13.00 usec
P2 26.00 usec
PLW1 15.00000000 W

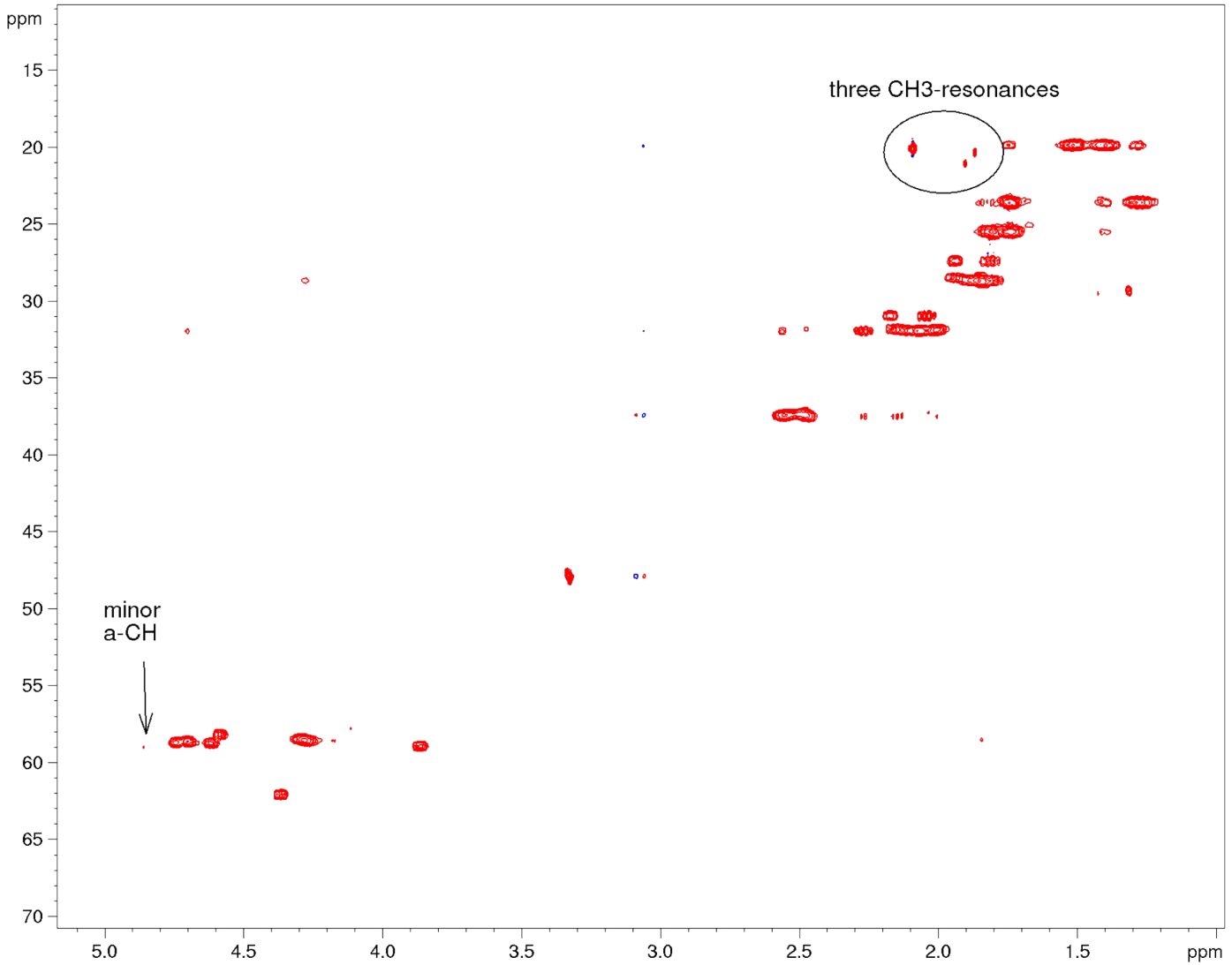
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 512
SFO1 500.2516 MHz
FIDRES 5.080970 Hz
SW 5.200 ppm
FnMODE States-TPPI

F2 - Processing parameters
SI 1024
SF 500.2500000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 States-TPPI
SF 500.2500000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

$^{1}H\{^{13}C\}$ HSQC spectrum of $Ac(Oic)_6O^-$ in deuteromethanol at 298 K and 700&176 MHz frequency:



Current Data Parameters
NAME wova_Oic8
EXPNO 82
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160811
Time 10.23
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG hsqcetgpsisp2.2
TD 2048
SOLVENT MeOD
NS 24
DS 64
SWH 2941.177 Hz
FIDRES 1.436121 Hz
AQ 0.3481600 sec
RG 2050
DW 170.000 usec
DE 10.00 usec
TE 299.5 K
CNST2 140.0000000
CNST17 -0.5000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00178571 sec
D11 0.03000000 sec
D16 0.00020000 sec
D24 0.00089286 sec
IN0 0.00004730 sec

======== CHANNEL f1 ========
SFO1 700.1721495 MHz
NUC1 1H
P1 11.75 usec
P2 23.50 usec
P28 1000.00 usec
PLW1 15.00000000 W

======== CHANNEL f2 ========
SFO2 176.0856814 MHz
NUC2 13C
CPDPRG[2 garp
P3 11.50 usec
P14 500.00 usec
P24 2000.00 usec
PCPD2 70.00 usec
PLW0 0 W
PLW2 250.00000000 W
PLW12 6.74739981 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 50.51599884 W
SPNAM[7] Crp60comp.4
SPOAL7 0.500
SPOFFS7 0 Hz
SPW7 50.51599884 W

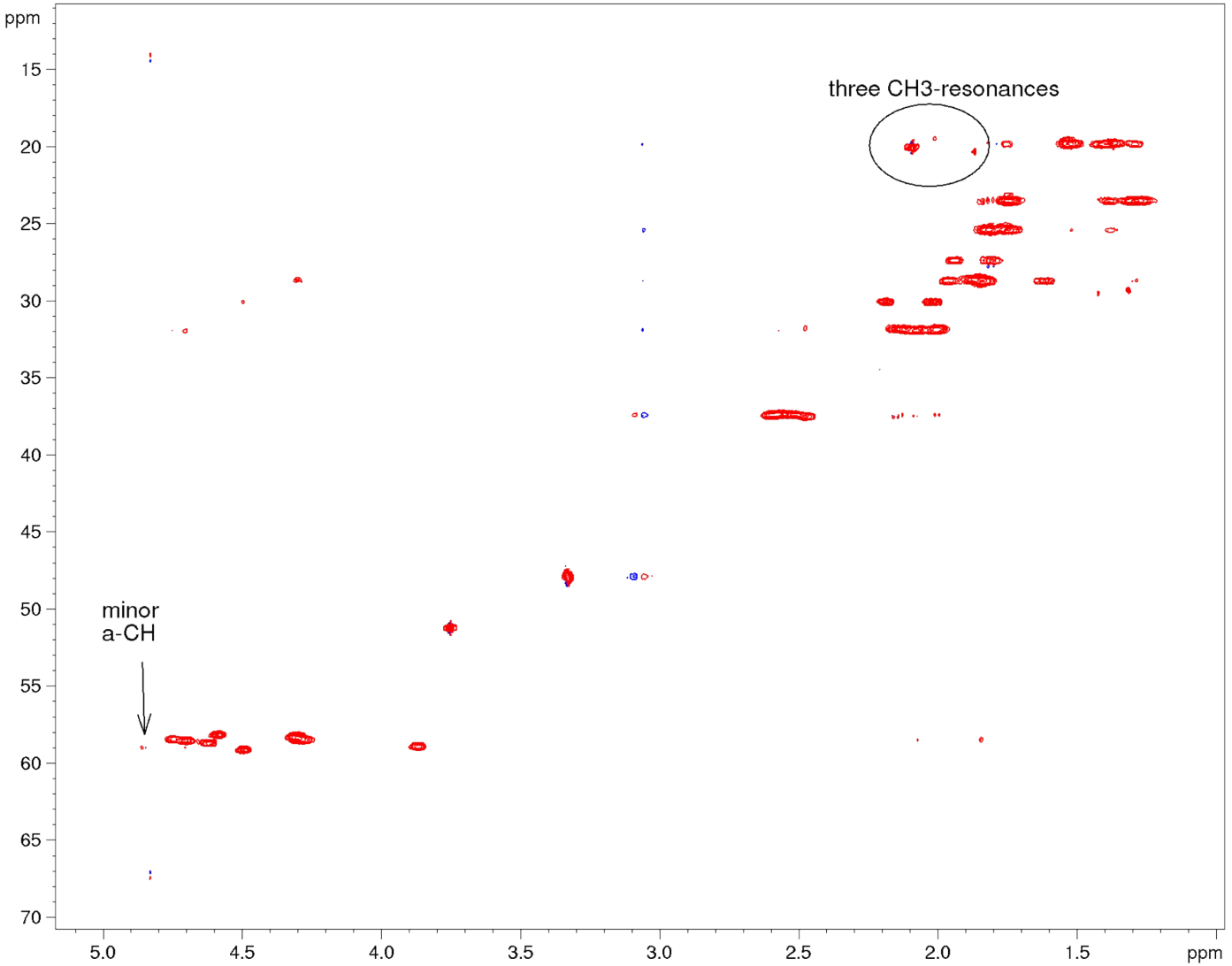
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPNAM[2] SMSQ10.100
GPNAM[3] SMSQ10.100
GPNAM[4] SMSQ10.100
GPZ1 80.00 %
GPZ2 20.10 %
GPZ3 11.00 %
GPZ4 -5.00 %
P18 1000.00 usec
P19 500.00 usec

F1 - Acquisition parameters
TD 180
SFO1 176.0851 MHz
FIDRES 66.067650 Hz
SW 60.039 ppm
FnMODE Echo-Antiecho

F2 - Processing parameters
SI 2048
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 echo-antiecho
SF 176.0578970 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

$^{1}H\{^{13}C\}$ HSQC spectrum of $Ac(Oic)_6OMe$ in deuteromethanol at 298 K and 700&176 MHz frequency:



Current Data Parameters
NAME wova_Oic8
EXPNO 36
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160810
Time 14.45
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG hsqcetgpsisp2.2
TD 2048
SOLVENT MeOD
NS 16
DS 84
SWH 2941.177 Hz
FIDRES 1.436121 Hz
AQ 0.3481600 sec
RG 2050
DW 170.000 usec
DE 10.00 usec
TE 299.5 K
CNST2 140.0000000
CNST17 -0.5000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00178571 sec
D11 0.03000000 sec
D16 0.00020000 sec
D24 0.00089286 sec
IN0 0.00004730 sec

======== CHANNEL f1 ========
SFO1 700.1721495 MHz
NUC1 1H
P1 11.40 usec
P2 22.80 usec
P28 1000.00 usec
PLW1 15.00000000 W

======== CHANNEL f2 ========
SFO2 176.0856814 MHz
NUC2 13C
CPDPRG[2 garp
P3 11.50 usec
P14 500.00 usec
P24 2000.00 usec
PCPD2 70.00 usec
PLW0 0 W
PLW2 250.00000000 W
PLW12 6.74739981 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 50.51599884 W
SPNAM[7] Crp60comp.4
SPOAL7 0.500
SPOFFS7 0 Hz
SPW7 50.51599884 W

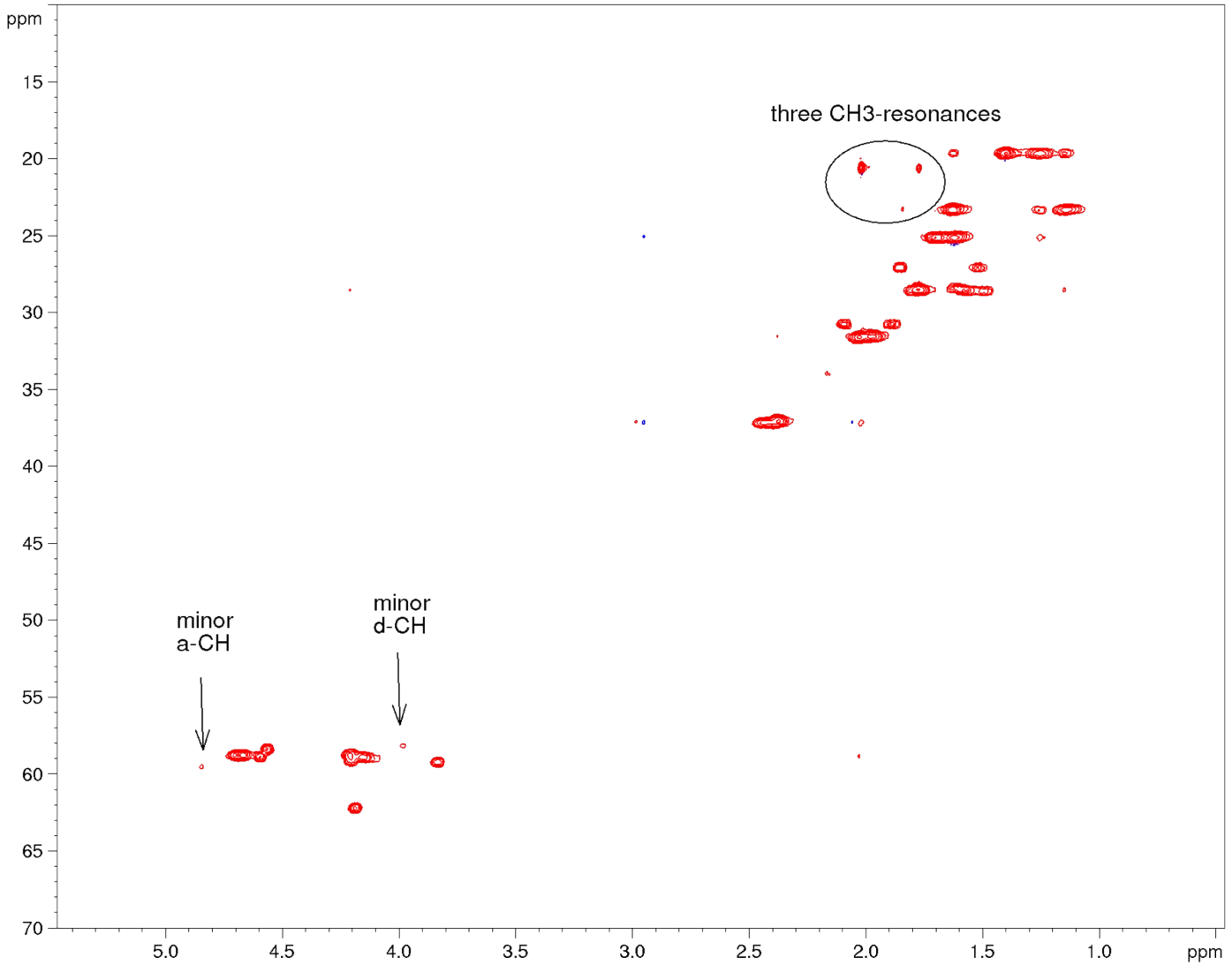
====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPNAM[2] SMSQ10.100
GPNAM[3] SMSQ10.100
GPNAM[4] SMSQ10.100
GPZ1 80.00 %
GPZ2 20.10 %
GPZ3 11.00 %
GPZ4 -5.00 %
P18 1000.00 usec
P19 500.00 usec

F1 - Acquisition parameters
TD 232
SFO1 176.0851 MHz
FIDRES 45.568900 Hz
SW 60.039 ppm
FnMODE Echo-Antiecho

F2 - Processing parameters
SI 2048
SF 700.1700000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

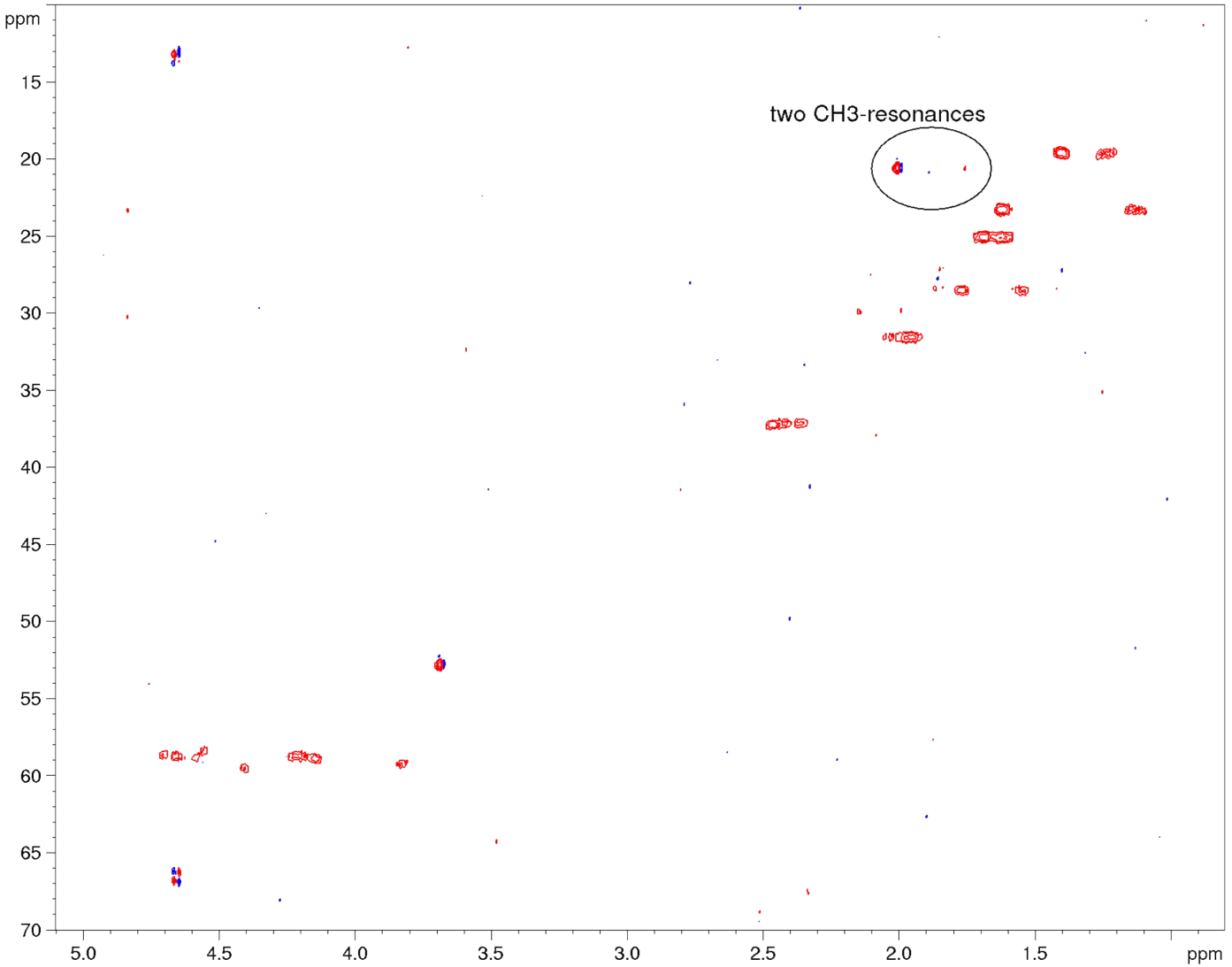
F1 - Processing parameters
SI 1024
MC2 echo-antiecho
SF 176.0578970 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

$^{1}H\{^{13}C\}$ HSQC spectrum of $Ac(Oic)_6O^-$ in buffered deuterium oxide at 298 K and 700&176 MHz frequency:




```
Current Data Parameters
NAME          wova_Oic8
EXPNO              55
PROCNO              1

F2 - Acquisition Parameters
Date_         20160810
Time              20.56
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG  hsqcetgpsisp2.2
TD                2048
SOLVENT            D2O
NS                  48
DS                 128
SWH          3501.401 Hz
FIDRES       1.709868 Hz
AQ           0.2924544 sec
RG                2050
DW           142.800 usec
DE            10.00 usec
TE            299.5 K
CNST2        145.0000000
CNST17        -0.5000000
D0           0.00000300 sec
D1           2.00000000 sec
D4           0.00172414 sec
D11          0.03000000 sec
D16          0.00020000 sec
D24          0.00086210 sec
IN0          0.00004730 sec

======== CHANNEL f1 ========
SFO1         700.1720865 MHz
NUC1               1H
P1              12.65 usec
P2              25.30 usec
P28           1000.00 usec
PLW1        15.00000000 W

======== CHANNEL f2 ========
SFO2         176.0849293 MHz
NUC2               13C
CPDPRG[2           garp
P3              11.50 usec
P14           500.00 usec
P24          2000.00 usec
PCPD2           70.00 usec
PLW0     0 W
PLW2        250.00000000 W
PLW12         6.74739981 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3          0.500
SPOFFS3  0 Hz
SPW3         50.51599884 W
SPNAM[7]   Crp60comp.4
SPOAL7          0.500
SPOFFS7  0 Hz
SPW7         50.51599884 W

====== GRADIENT CHANNEL ===
GPNAM[1]     SMSQ10.100
GPNAM[2]     SMSQ10.100
GPNAM[3]     SMSQ10.100
GPNAM[4]     SMSQ10.100
GPZ1            80.00 %
GPZ2            20.10 %
GPZ3            11.00 %
GPZ4            -5.00 %
P18           1000.00 usec
P19           500.00 usec

F1 - Acquisition parameters
TD                 180
SFO1         176.0849 MHz
FIDRES       66.067650 Hz
SW           60.089 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                2048
SF           700.1700122 MHz
WDW               QSINE
SSB                  2
LB       0 Hz
GB       0
PC             100.00

F1 - Processing parameters
SI                1024
MC2        echo-antiecho
SF           176.0578970 MHz
WDW               QSINE
SSB                  2
LB       0 Hz
GB       0
```

$^{1}H\{^{13}C\}$ HSQC spectrum of $Ac(Oic)_6OMe$ in buffered deuterium oxide at 298 K and 700&176 MHz frequency:



Current Data Parameters
NAME wova_Oic2
EXPNO 543
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160807
Time 14.14
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG hsqcetgpsisp2.2
TD 2048
SOLVENT D2O
NS 32
DS 64
SWH 3009.631 Hz
FIDRES 1.469546 Hz
AQ 0.3402411 sec
RG 2050
DW 166.133 usec
DE 10.00 usec
TE 299.5 K
CNST2 145.0000000
CNST17 -0.5000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00020000 sec
D24 0.00086210 sec
IN0 0.00004730 sec

======== CHANNEL f1 ========
SFO1 700.1720865 MHz
NUC1 1H
P1 10.25 usec
P2 20.50 usec
P28 1000.00 usec
PLW1 15.00000000 W

======== CHANNEL f2 ========
SFO2 176.0849293 MHz
NUC2 13C
CPDPRG[2 garp
P3 11.50 usec
P14 500.00 usec
P24 2000.00 usec
PCPD2 70.00 usec
PLW0 0 W
PLW2 250.00000000 W
PLW12 6.74739981 W
SPNAM[8] Cnp60,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 50.51599884 W
SPNAM[7] Cnp60comp.4
SPOAL7 0.500
SPOFFS7 0 Hz
SPW7 50.51599884 W

====== GRADIENT CHANNEL ===
GPNAM[1] SMSQ10.100
GPNAM[2] SMSQ10.100
GPNAM[3] SMSQ10.100
GPNAM[4] SMSQ10.100
GPZ1 80.00 %
GPZ2 20.10 %
GPZ3 11.00 %
GPZ4 -5.00 %
P16 1000.00 usec
P19 500.00 usec

F1 - Acquisition parameters
TD 128
SFO1 176.0849 MHz
FIDRES 82.584564 Hz
SW 60.039 ppm
FnMODE Echo-Antiecho

F2 - Processing parameters
SI 2048
SF 700.1700197 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 100.00

F1 - Processing parameters
SI 1024
MC2 echo-antiecho
SF 176.0578970 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

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