Supplementary Materials

Steroids from the Deep-Sea-Derived Fungus *Penicillium granulatum* MCCC 3A00475 Induced Apoptosis via Retinoid X Receptor (RXR)-α Pathway

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Table S1. Crystal data and structure refinement for penicisteroid D (**1**).

Identification code	penicisteroid D	
Empirical formula	C30 H48 O3	
Formula weight	456.68	
Temperature	99.98(11) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.94350(10) Å	α = 90°.
	b = 11.98440(10) Å	β = 90°
	c = 38.3459(4) Å	γ = 90°.
Volume	2731.35(6) $Å^3$	
Z	4	
Density (calculated)	1.111 Mg/m3	
Absorption coefficient	0.533 mm−1	
F(000)	1008	
Crystal size	0.15 × 0.12 × 0.05 mm3	
Theta range for data collection	2.304 to 67.080°	
Index ranges	−6<=h<=7, −14<=k<=14, −45<=l<=45	
Reflections collected	18704	
Independent reflections	4726 [R(int) = 0.0845]	
Completeness to theta = 67.080°	98.10%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.56522	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	4726/0/306	
Goodness-of-fit on F2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0797, wR2 = 0.2359	
R indices (all data)	R1 = 0.0842, wR2 = 0.2490	
Absolute structure parameter	−0.06(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.484 and -0.353 $e.Å^{-3}$	

Table S2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for penicisteroid D. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(001)	−1724(6)	−3598(2)	−6072(1)	33(1)
O(002)	−3214(7)	−5300(3)	−8968(1)	39(1)
O(003)	−4416(8)	−2368(3)	−5934(1)	46(1)
C(004)	−2069(7)	−4346(3)	−7288(1)	28(1)
C(005)	−2605(8)	−4365(3)	−8043(1)	31(1)
C(006)	−3790(8)	−3575(3)	−7462(1)	32(1)
C(007)	−2782(7)	−4605(3)	−6913(1)	30(1)
C(008)	−3289(8)	−3629(3)	−6666(1)	31(1)
C(009)	−1311(9)	−5884(4)	−6023(1)	33(1)
C(00A)	−3268(8)	−4184(3)	−6304(1)	32(1)
C(00B)	−1165(8)	−5362(3)	−6707(1)	30(1)
C(00C)	−3292(8)	−5425(4)	−8600(1)	34(1)
C(00D)	−3693(8)	−3605(3)	−7852(1)	32(1)
C(00E)	−2658(9)	−4313(4)	−8435(1)	35(1)
C(00F)	−1913(7)	−5463(3)	−7488(1)	30(1)
C(00G)	−3305(9)	−5345(4)	−5461(1)	34(1)
C(00H)	−2523(10)	−2716(4)	−5900(1)	39(1)
C(00I)	−1038(9)	−6470(4)	−6907(1)	32(1)
C(00J)	−1277(8)	−5319(4)	−7876(1)	32(1)
C(00K)	1191(8)	−4849(4)	−6664(1)	33(1)
C(00L)	−260(10)	−7029(4)	−6080(1)	42(1)
C(00M)	−1730(9)	−6334(4)	−8470(1)	36(1)
C(00N)	−781(11)	−2226(4)	−5661(1)	44(1)
C(00O)	−5211(9)	−5404(4)	−5204(1)	36(1)
C(00P)	−1849(9)	−6414(4)	−8073(1)	32(1)
C(00Q)	−4386(9)	−5467(4)	−4825(1)	35(1)
C(00R)	−2432(8)	−5396(4)	−6354(1)	31(1)
C(00S)	−2619(10)	−6381(4)	−4777(1)	43(1)
C(00T)	−3120(10)	−5966(4)	−5745(1)	36(1)
C(00U)	−371(8)	−6287(4)	−7291(1)	34(1)
C(00V)	1247(9)	−5056(4)	−7923(1)	36(1)
C(00W)	−6318(10)	−5667(4)	−4569(1)	40(1)
C(00X)	−6773(10)	−4399(5)	−5265(1)	45(1)

Table S3. Bond lengths [Å] and angles [°] for penicisteroid D.

O(001)-C(00A)	1.459(6)	C(00H)-O(001)-C(00A)	117.4(4)	C(00V)-C(00J)-C(00F)	111.9(4)
O(001)-C(00H)	1.332(6)	C(00C)-O(002)-H(002)	109.5	C(00V)-C(00J)-C(00P)	109.2(4)
O(002)-H(002)	0.84	C(006)-C(004)-H(004)	109.5	C(00B)-C(00K)-H(00N)	109.5
O(002)-C(00C)	1.421(5)	C(006)-C(004)-C(007)	110.3(4)	C(00B)-C(00K)-H(00O)	109.5
O(003)-C(00H)	1.207(7)	C(006)-C(004)-C(00F)	110.3(4)	C(00B)-C(00K)-H(00P)	109.5
C(004)-H(004)	1	C(007)-C(004)-H(004)	109.5	H(00N)-C(00K)-H(00O)	109.5
C(004)-C(006)	1.530(6)	C(007)-C(004)-C(00F)	107.8(3)	H(00N)-C(00K)-H(00P)	109.5
C(004)-C(007)	1.532(6)	C(00F)-C(004)-H(004)	109.5	H(00O)-C(00K)-H(00P)	109.5
C(004)-C(00F)	1.545(6)	C(00D)-C(005)-C(00E)	120.6(4)	C(009)-C(00L)-H(00Q)	109.5
C(005)-C(00D)	1.335(7)	C(00D)-C(005)-C(00J)	122.0(4)	C(009)-C(00L)-H(00R)	109.5
C(005)-C(00E)	1.503(7)	C(00E)-C(005)-C(00J)	117.4(4)	C(009)-C(00L)-H(00S)	109.5
C(005)-C(00J)	1.529(6)	C(004)-C(006)-H(00A)	108.9	H(00Q)-C(00L)-H(00R)	109.5
C(006)-H(00A)	0.99	C(004)-C(006)-H(00B)	108.9	H(00Q)-C(00L)-H(00S)	109.5
C(006)-H(00B)	0.99	H(00A)-C(006)-H(00B)	107.7	H(00R)-C(00L)-H(00S)	109.5
C(006)-C(00D)	1.499(6)	C(00D)-C(006)-C(004)	113.2(4)	C(00C)-C(00M)-H(00T)	109.6
C(007)-H(007)	1	C(00D)-C(006)-H(00A)	108.9	C(00C)-C(00M)-H(00U)	109.6
C(007)-C(008)	1.535(6)	C(00D)-C(006)-H(00B)	108.9	C(00C)-C(00M)-C(00P)	110.1(4)
C(007)-C(00B)	1.539(6)	C(004)-C(007)-H(007)	105.6	H(00T)-C(00M)-H(00U)	108.1
C(008)-H(00C)	0.99	C(004)-C(007)-C(008)	118.7(3)	C(00P)-C(00M)-H(00T)	109.6
C(008)-H(00D)	0.99	C(004)-C(007)-C(00B)	115.4(4)	C(00P)-C(00M)-H(00U)	109.6
C(008)-C(00A)	1.540(6)	C(008)-C(007)-H(007)	105.6	C(00H)-C(00N)-H(00V)	109.5
C(009)-H(009)	1	C(008)-C(007)-C(00B)	104.8(3)	C(00H)-C(00N)-H(00W)	109.5
C(009)-C(00L)	1.525(7)	C(00B)-C(007)-H(007)	105.6	C(00H)-C(00N)-H(00X)	109.5
C(009)-C(00R)	1.548(6)	C(007)-C(008)-H(00C)	111.2	H(00V)-C(00N)-H(00W)	109.5
C(009)-C(00T)	1.515(7)	C(007)-C(008)-H(00D)	111.2	H(00V)-C(00N)-H(00X)	109.5
C(00A)-H(00E)	1	C(007)-C(008)-C(00A)	103.1(3)	H(00W)-C(00N)-H(00X)	109.5
C(00A)-C(00R)	1.547(6)	H(00C)-C(008)-H(00D)	109.1	C(00G)-C(00O)-H(00Y)	107.9
C(00B)-C(00I)	1.534(6)	C(00A)-C(008)-H(00C)	111.2	C(00G)-C(00O)-C(00Q)	112.5(4)
C(00B)-C(00K)	1.538(6)	C(00A)-C(008)-H(00D)	111.2	C(00G)-C(00O)-C(00X)	108.5(4)
C(00B)-C(00R)	1.552(6)	C(00L)-C(009)-H(009)	108.9	C(00Q)-C(00O)-H(00Y)	107.9
C(00C)-H(00F)	1	C(00L)-C(009)-C(00R)	113.4(4)	C(00Q)-C(00O)-C(00X)	112.1(4)
C(00C)-C(00E)	1.522(6)	C(00R)-C(009)-H(009)	108.9	C(00X)-C(00O)-H(00Y)	107.9
C(00C)-C(00M)	1.515(7)	C(00T)-C(009)-H(009)	108.9	C(00J)-C(00P)-H(00Z)	108.6
C(00D)-H(00G)	0.95	C(00T)-C(009)-C(00L)	109.5(4)	C(00J)-C(00P)-H	108.6
C(00E)-H(00H)	0.99	C(00T)-C(009)-C(00R)	107.1(4)	C(00M)-C(00P)-C(00J)	114.8(4)
C(00E)-H(00I)	0.99	O(001)-C(00A)-C(008)	110.4(4)	C(00M)-C(00P)-H(00Z)	108.6
C(00F)-H(00J)	1	O(001)-C(00A)-H(00E)	110.1	C(00M)-C(00P)-H	108.6

C(00F)-C(00J)	1.547(6)	O(001)-C(00A)-C(00R)	109.0(4)	H(00Z)-C(00P)-H	107.5
C(00F)-C(00U)	1.545(6)	C(008)-C(00A)-H(00E)	110.1	C(00O)-C(00Q)-H(00)	108
C(00G)-H(00K)	0.95	C(008)-C(00A)-C(00R)	107.3(3)	C(00S)-C(00Q)-C(00O)	111.6(4)
C(00G)-C(00O)	1.504(7)	C(00R)-C(00A)-H(00E)	110.1	C(00S)-C(00Q)-H(00)	108
C(00G)-C(00T)	1.324(7)	C(007)-C(00B)-C(00R)	99.2(3)	C(00S)-C(00Q)-C(00W)	109.1(4)
C(00H)-C(00N)	1.501(8)	C(00I)-C(00B)-C(007)	106.6(3)	C(00W)-C(00Q)-C(00O)	112.0(4)
C(00I)-H(00L)	0.99	C(00I)-C(00B)-C(00K)	110.8(4)	C(00W)-C(00Q)-H(00)	108
C(00I)-H(00M)	0.99	C(00I)-C(00B)-C(00R)	115.9(3)	C(009)-C(00R)-C(00B)	121.2(4)
C(00I)-C(00U)	1.541(6)	C(00K)-C(00B)-C(007)	112.8(3)	C(009)-C(00R)-H(0AA)	105.9
C(00J)-C(00P)	1.551(6)	C(00K)-C(00B)-C(00R)	111.0(4)	C(00A)-C(00R)-C(009)	113.1(4)
C(00J)-C(00V)	1.543(7)	O(002)-C(00C)-H(00F)	108.7	C(00A)-C(00R)-C(00B)	103.8(3)
C(00K)-H(00N)	0.98	O(002)-C(00C)-C(00E)	108.2(3)	C(00A)-C(00R)-H(0AA)	105.9
C(00K)-H(00O)	0.98	O(002)-C(00C)-C(00M)	112.4(4)	C(00B)-C(00R)-H(0AA)	105.9
C(00K)-H(00P)	0.98	C(00E)-C(00C)-H(00F)	108.7	C(00Q)-C(00S)-H(1AA)	109.5
C(00L)-H(00Q)	0.98	C(00M)-C(00C)-H(00F)	108.7	C(00Q)-C(00S)-HA	109.5
C(00L)-H(00R)	0.98	C(00M)-C(00C)-C(00E)	110.0(4)	C(00Q)-C(00S)-HB	109.5
C(00L)-H(00S)	0.98	C(005)-C(00D)-C(006)	125.7(4)	H(1AA)-C(00S)-HA	109.5
C(00M)-H(00T)	0.99	C(005)-C(00D)-H(00G)	117.2	H(1AA)-C(00S)-HB	109.5
C(00M)-H(00U)	0.99	C(006)-C(00D)-H(00G)	117.2	HA-C(00S)-HB	109.5
C(00M)-C(00P)	1.528(6)	C(005)-C(00E)-C(00C)	112.5(3)	C(009)-C(00T)-H(2AA)	116.6
C(00N)-H(00V)	0.98	C(005)-C(00E)-H(00H)	109.1	C(00G)-C(00T)-C(009)	126.8(5)
C(00N)-H(00W)	0.98	C(005)-C(00E)-H(00I)	109.1	C(00G)-C(00T)-H(2AA)	116.6
C(00N)-H(00X)	0.98	C(00C)-C(00E)-H(00H)	109.1	C(00F)-C(00U)-H(3AA)	108.8
C(00O)-H(00Y)	1	C(00C)-C(00E)-H(00I)	109.1	C(00F)-C(00U)-HC	108.8
C(00O)-C(00Q)	1.537(7)	H(00H)-C(00E)-H(00I)	107.8	C(00I)-C(00U)-C(00F)	114.0(4)
C(00O)-C(00X)	1.539(7)	C(004)-C(00F)-H(00J)	106.4	C(00I)-C(00U)-H(3AA)	108.8
C(00P)-H(00Z)	0.99	C(004)-C(00F)-C(00J)	113.3(3)	C(00I)-C(00U)-HC	108.8
C(00P)-H	0.99	C(00J)-C(00F)-H(00J)	106.4	H(3AA)-C(00U)-HC	107.7
C(00Q)-H(00)	1	C(00U)-C(00F)-C(004)	110.3(4)	C(00J)-C(00V)-H(4AA)	109.5
C(00Q)-C(00S)	1.528(7)	C(00U)-C(00F)-H(00J)	106.4	C(00J)-C(00V)-HD	109.5
C(00Q)-C(00W)	1.530(7)	C(00U)-C(00F)-C(00J)	113.4(4)	C(00J)-C(00V)-HE	109.5
C(00R)-H(0AA)	1	C(00O)-C(00G)-H(00K)	117.4	H(4AA)-C(00V)-HD	109.5
C(00S)-H(1AA)	0.98	C(00T)-C(00G)-H(00K)	117.4	H(4AA)-C(00V)-HE	109.5
C(00S)-HA	0.98	C(00T)-C(00G)-C(00O)	125.2(5)	HD-C(00V)-HE	109.5
C(00S)-HB	0.98	O(001)-C(00H)-C(00N)	111.4(5)	C(00Q)-C(00W)-H(5AA)	109.5
C(00T)-H(2AA)	0.95	O(003)-C(00H)-O(001)	123.6(5)	C(00Q)-C(00W)-HF	109.5
C(00U)-H(3AA)	0.99	O(003)-C(00H)-C(00N)	125.0(5)	C(00Q)-C(00W)-HG	109.5
C(00U)-HC	0.99	C(00B)-C(00I)-H(00L)	109.3	H(5AA)-C(00W)-HF	109.5

C(00V)-H(4AA)	0.98	C(00B)-C(00I)-H(00M)	109.3	H(5AA)-C(00W)-HG	109.5
C(00V)-HD	0.98	C(00B)-C(00I)-C(00U)	111.4(3)	HF-C(00W)-HG	109.5
C(00V)-HE	0.98	H(00L)-C(00I)-H(00M)	108	C(00O)-C(00X)-H(6AA)	109.5
C(00W)-H(5AA)	0.98	C(00U)-C(00I)-H(00L)	109.3	C(00O)-C(00X)-HH	109.5
C(00W)-HF	0.98	C(00U)-C(00I)-H(00M)	109.3	C(00O)-C(00X)-HI	109.5
C(00W)-HG	0.98	C(005)-C(00J)-C(00F)	111.1(4)	H(6AA)-C(00X)-HH	109.5
C(00X)-H(6AA)	0.98	C(005)-C(00J)-C(00P)	108.4(4)	H(6AA)-C(00X)-HI	109.5
C(00X)-HH	0.98	C(005)-C(00J)-C(00V)	107.5(4)	HH-C(00X)-HI	109.5
C(00X)-HI	0.98	C(00F)-C(00J)-C(00P)	108.6(3)		

Symmetry transformations used to generate equivalent atoms.

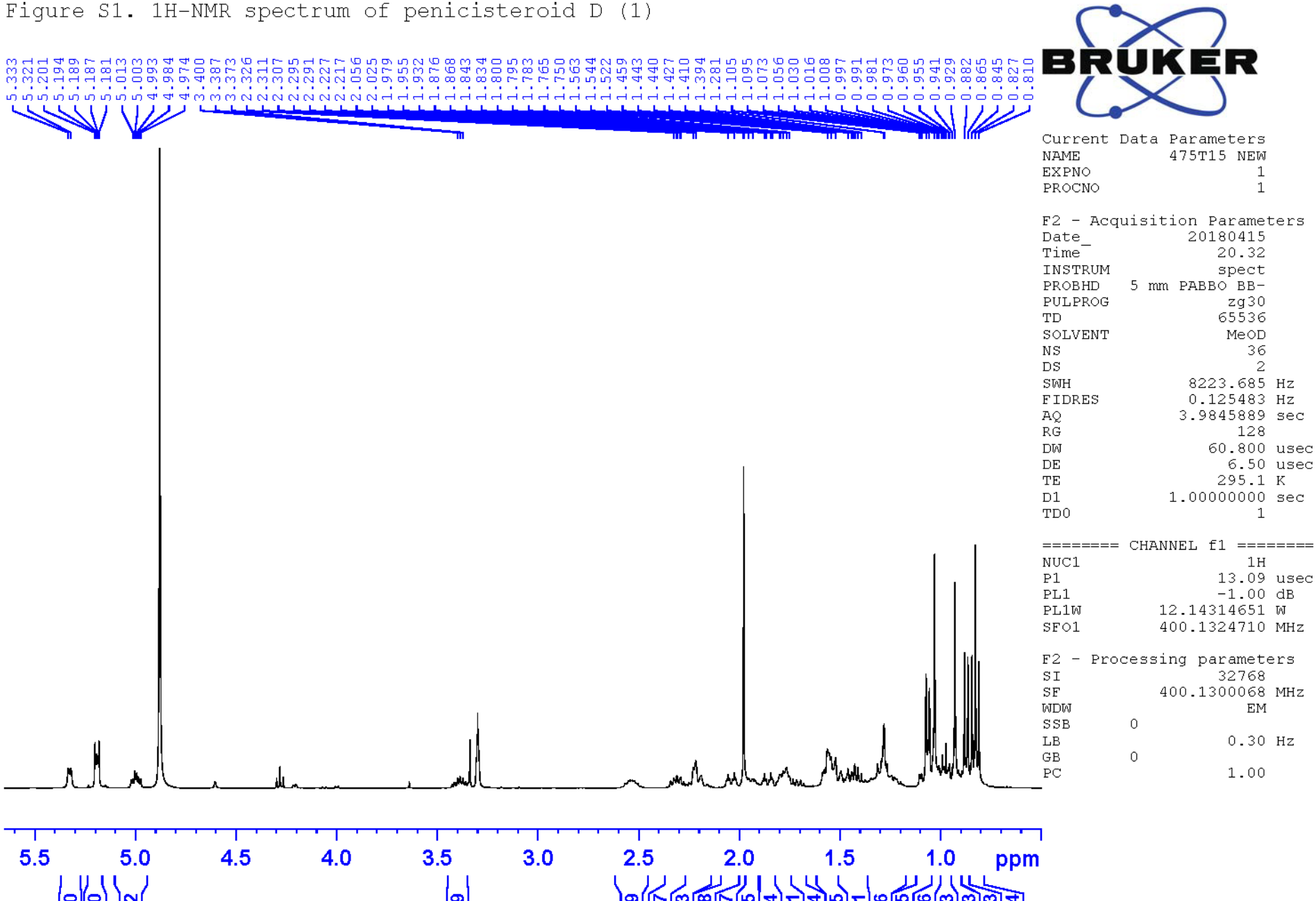
Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for penicisteroid D. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U11	U22	U33	U23	U13	U12
O(001)	35(2)	31(1)	33(2)	−3(1)	−2(1)	0(1)
O(002)	46(2)	38(2)	33(2)	1(1)	3(1)	−6(2)
O(003)	54(2)	40(2)	45(2)	−8(1)	−4(2)	14(2)
C(004)	24(2)	28(2)	32(2)	1(2)	−1(2)	0(2)
C(005)	26(2)	28(2)	39(2)	1(2)	2(2)	−5(2)
C(006)	28(2)	27(2)	40(2)	−3(2)	−2(2)	3(2)
C(007)	23(2)	27(2)	40(2)	−3(2)	2(2)	−2(2)
C(008)	30(2)	27(2)	36(2)	−1(2)	−2(2)	2(2)
C(009)	38(3)	34(2)	28(2)	0(2)	0(2)	0(2)
C(00A)	31(2)	32(2)	32(2)	−3(2)	1(2)	−1(2)
C(00B)	32(2)	29(2)	28(2)	0(2)	4(2)	0(2)
C(00C)	32(2)	35(2)	35(2)	1(2)	1(2)	−5(2)
C(00D)	33(2)	28(2)	34(2)	3(2)	−2(2)	−2(2)
C(00E)	36(2)	30(2)	39(2)	4(2)	1(2)	−1(2)
C(00F)	22(2)	29(2)	40(2)	1(2)	0(2)	−1(2)
C(00G)	38(2)	32(2)	32(2)	2(2)	1(2)	1(2)
C(00H)	55(3)	27(2)	34(2)	0(2)	−5(2)	3(2)
C(00I)	34(2)	29(2)	35(2)	0(2)	−1(2)	3(2)
C(00J)	31(2)	30(2)	36(2)	−1(2)	1(2)	2(2)
C(00K)	28(2)	35(2)	36(2)	1(2)	−1(2)	3(2)
C(00L)	50(3)	38(2)	38(2)	2(2)	0(2)	8(2)
C(00M)	40(3)	31(2)	36(2)	−3(2)	5(2)	−2(2)
C(00N)	57(3)	34(2)	41(3)	−5(2)	−6(2)	−1(2)
C(00O)	38(2)	34(2)	37(2)	−2(2)	2(2)	−1(2)
C(00P)	38(2)	30(2)	29(2)	0(2)	2(2)	2(2)
C(00Q)	41(3)	31(2)	32(2)	−1(2)	−3(2)	−1(2)
C(00R)	27(2)	30(2)	35(2)	−2(2)	1(2)	−3(2)
C(00S)	46(3)	43(2)	40(2)	4(2)	0(2)	6(2)
C(00T)	45(3)	33(2)	30(2)	2(2)	0(2)	−1(2)
C(00U)	37(3)	30(2)	35(2)	−2(2)	4(2)	7(2)
C(00V)	33(3)	46(2)	29(2)	−1(2)	−2(2)	0(2)
C(00W)	48(3)	38(2)	35(2)	0(2)	5(2)	−3(2)
C(00X)	41(3)	52(3)	41(3)	4(2)	2(2)	9(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for penicisteroid D.

	x	y	z	U(eq)		x	y	z	U(eq)
H(002)	−3899	−5833	−9062	58	H(00U)	−2168	−7057	−8574	43
H(004)	−562	−3975	−7287	34	H(00V)	542	−2714	−5656	66
H(00A)	−5319	−3794	−7386	38	H(00W)	−1405	−2158	−5426	66
H(00B)	−3523	−2801	−7382	38	H(00X)	−344	−1487	−5747	66
H(007)	−4220	−5033	−6933	36	H(00Y)	−6089	−6097	−5254	44
H(00C)	−4776	−3296	−6717	38	H(00Z)	−797	−7003	−7994	39
H(00D)	−2120	−3044	−6683	38	H	−3387	−6649	−8006	39
H(009)	−118	−5356	−5941	40	H(00)	−3672	−4736	−4765	42
H(00E)	−4819	−4185	−6203	38	H(0AA)	−3810	−5856	−6395	37
H(00F)	−4867	−5616	−8530	41	H(1AA)	−3277	−7106	−4837	64
H(00G)	−4472	−3034	−7975	38	HA	−2115	−6392	−4534	64
H(00H)	−1158	−4084	−8521	42	HB	−1333	−6231	−4930	64
H(00I)	−3757	−3739	−8509	42	H(2AA)	−4238	−6522	−5779	43
H(00J)	−3456	−5795	−7484	36	H(3AA)	−400	−7014	−7413	41
H(00K)	−2142	−4821	−5417	41	HC	1193	−6003	−7299	41
H(00L)	−2519	−6847	−6897	39	H(4AA)	1533	−4838	−8166	54
H(00M)	82	−6963	−6794	39	HD	2137	−5720	−7867	54
H(00N)	1812	−4671	−6894	49	HE	1674	−4444	−7767	54
H(00O)	2178	−5384	−6546	49	H(5AA)	−7480	−5097	−4603	60
H(00P)	1083	−4166	−6525	49	HF	−5748	−5625	−4329	60
H(00Q)	−1405	−7544	−6170	63	HG	−6965	−6408	−4610	60
H(00R)	334	−7313	−5859	63	H(6AA)	−5985	−3709	−5202	67
H(00S)	967	−6967	−6250	63	HH	−8126	−4477	−5121	67
H(00T)	−168	−6165	−8542	43	HI	−7204	−4369	−5512	67

Figure S1. 1H-NMR spectrum of penicisteroid D (1)



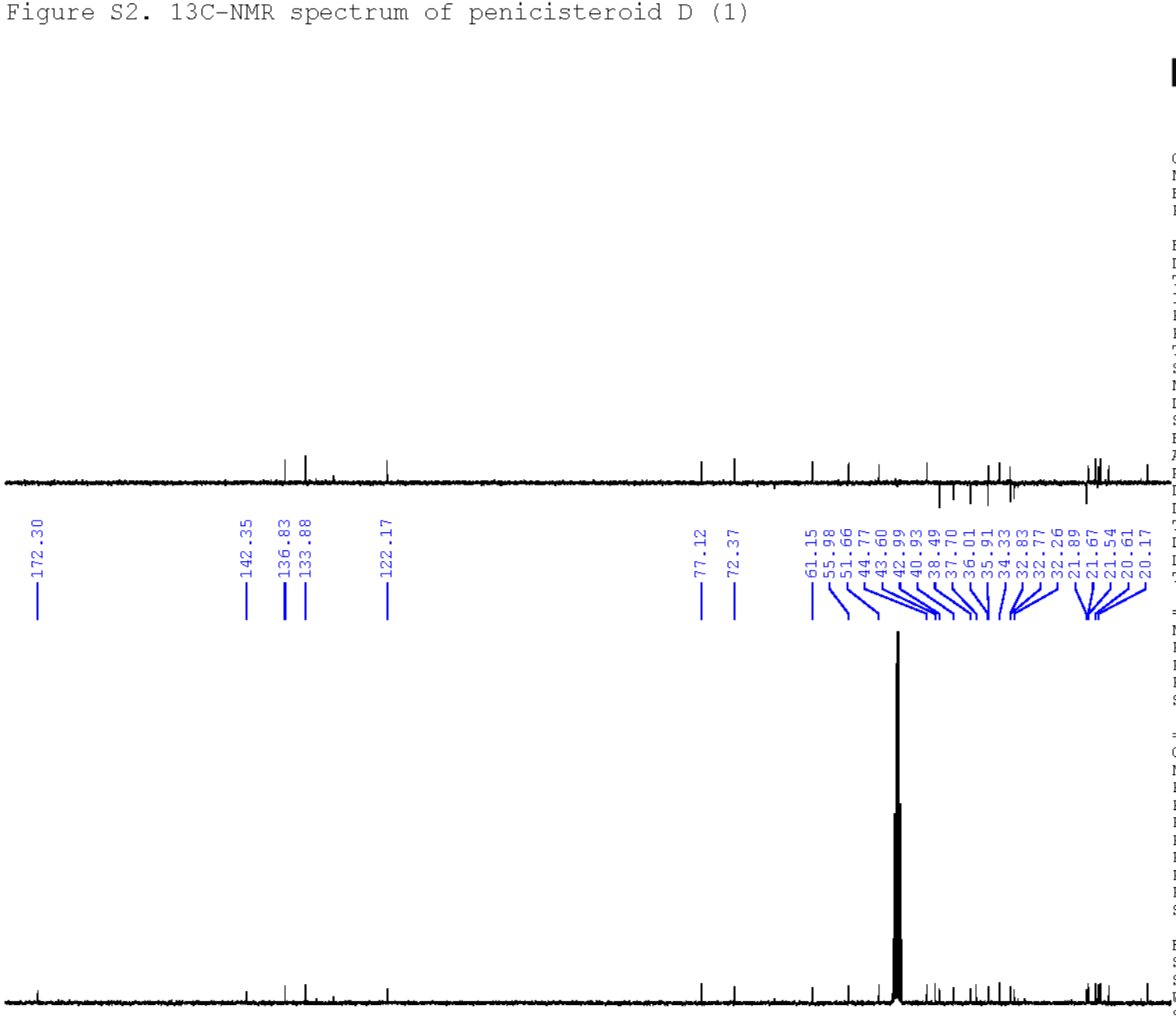

```
Current Data Parameters
NAME          475T15 NEW
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180415
Time              20.32
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT            MeOD
NS                   36
DS                    2
SWH            8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9845889 sec
RG                  128
DW                60.800 usec
DE                 6.50 usec
TE                295.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.09 usec
PL1               -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300068 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

Figure S2. 13C-NMR spectrum of penicisteroid D (1)



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```
Current Data Parameters
NAME          475T15 NEW
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180415
Time              20.35
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT             MeOD
NS                  193
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE                295.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.37 usec
PL1                1.00 dB
PL1W        28.13319778 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              14.72 dB
PL13              14.50 dB
PL2W        12.14314651 W
PL12W        0.32533529 W
PL13W        0.34224036 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6126263 MHz
WDW                   EM
SSB                   0
```

Figure S3. HSQC spectrum of the penicisteroid D (1)

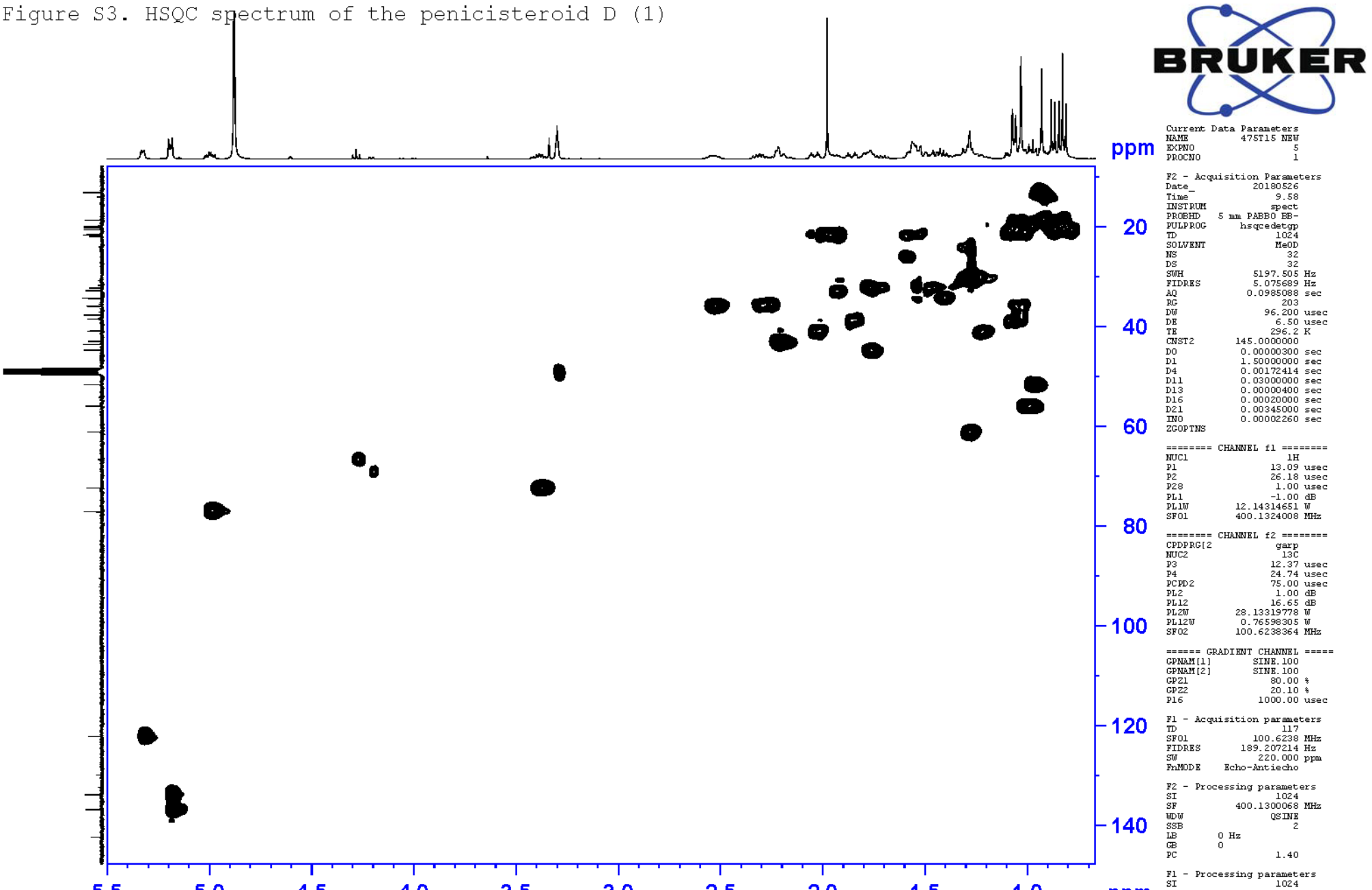
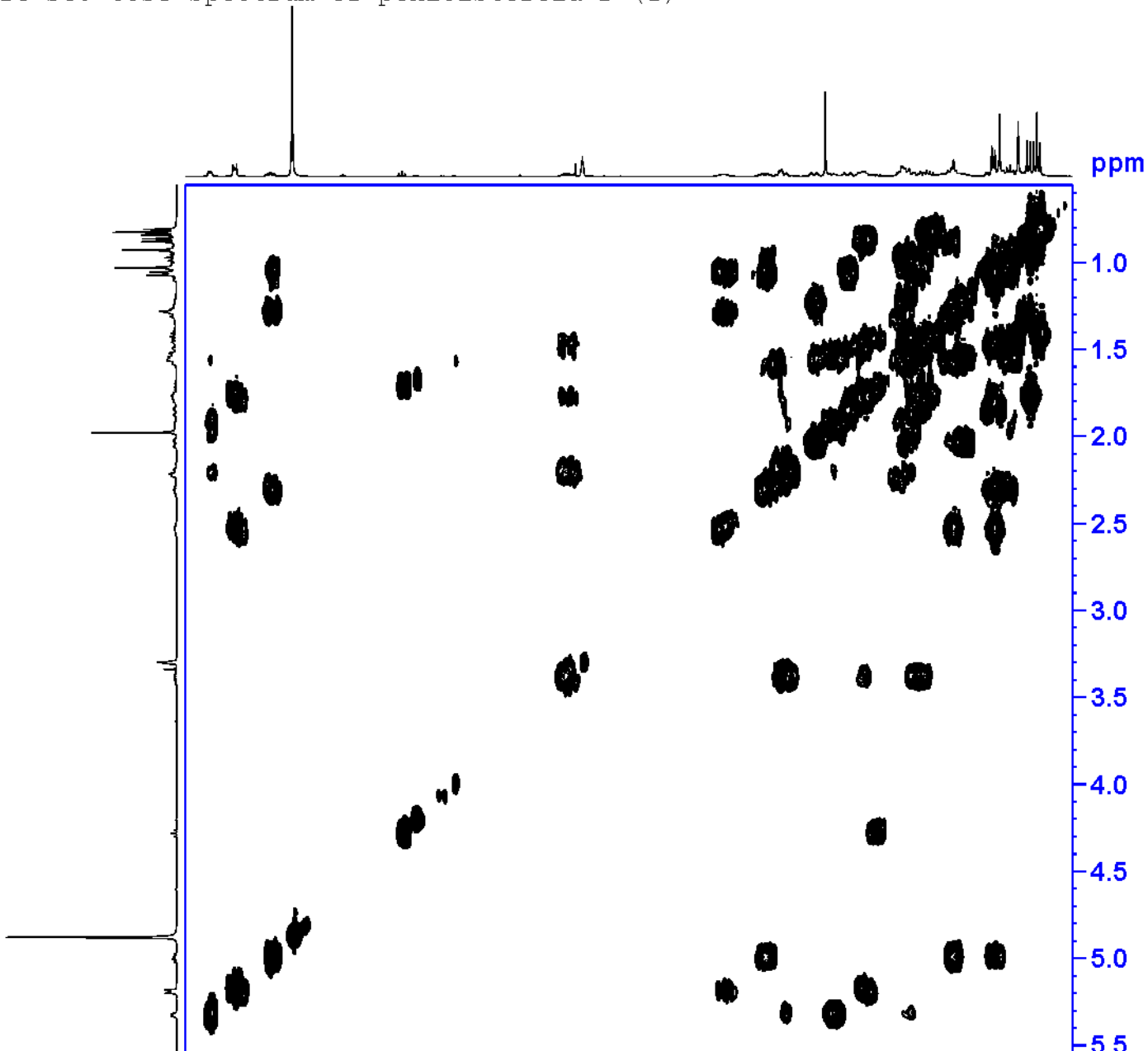
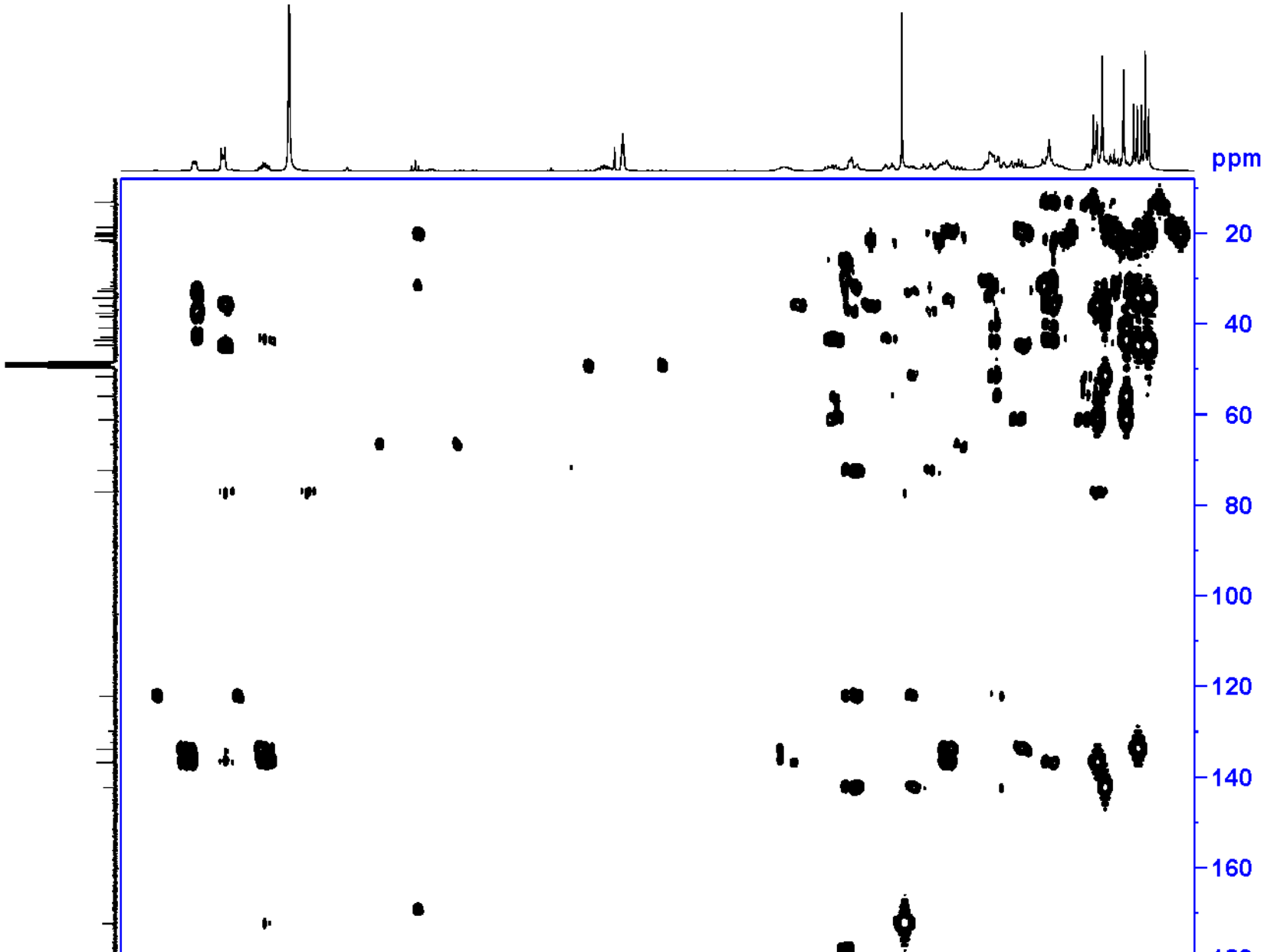


Figure S4. COSY spectrum of penicisteroid D (1)



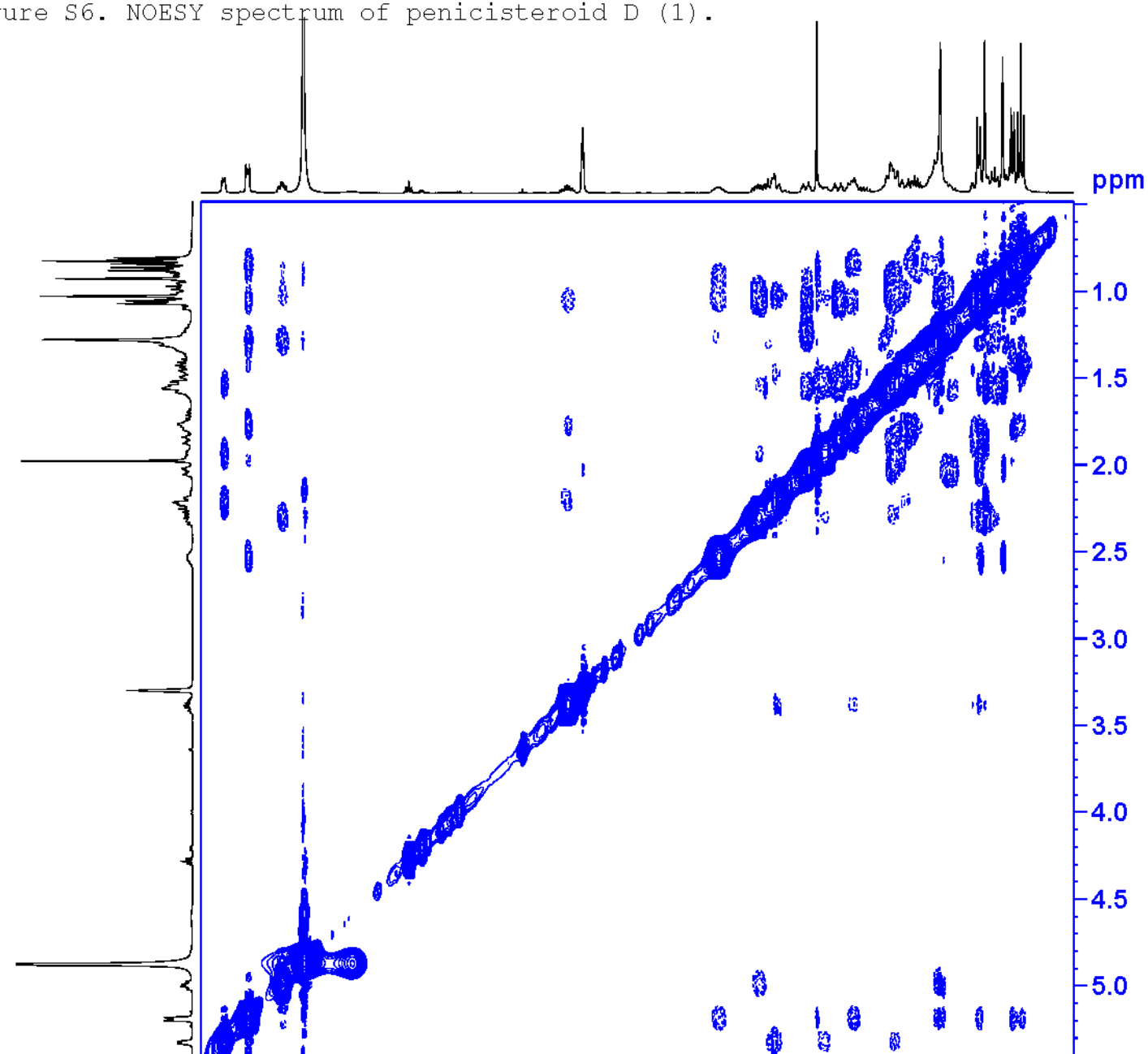

```
Current Data Parameters
NAME          475T15 NEW
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180526
Time               11.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG      cosygpmfqf
TD                 2048
SOLVENT            MeOD
NS                    8
DS                    8
SWH            4795.396 Hz
FIDRES         2.341502 Hz
AQ             0.2135381 sec
RG                  203
DW               104.267 usec
DE                 6.50 usec
TE                296.3 K
D0             0.00000300 sec
D1             1.93569195 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00020825 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.09 usec
PL1                -1.00 dB
PL1W         12.14314651 W
SFO1        400.1324008 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPZ1               16.00 %
GPZ2               12.00 %
GPZ3               40.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1           400.1324 MHz
FIDRES        37.512413 Hz
SW               12.000 ppm
FnMODE                QF

F2 - Processing parameters
SI                  1024
SF          400.1300068 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
```

Figure S5. HMBC spectrum of penicisteroid D (1)




```
Current Data Parameters
NAME          475T15 NEW
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180523
Time              19.16
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG      hmbcgpndqf
TD                 4096
SOLVENT            MeOD
NS                   40
DS                   16
SWH           4795.396 Hz
FIDRES        1.170751 Hz
AQ            0.4270763 sec
RG                 203
DW              104.267 usec
DE                6.50 usec
TE                300.0 K
CNST13         8.0000000
D0            0.00000300 sec
D1            1.37220395 sec
D6            0.06250000 sec
D16           0.00020000 sec
IN0           0.00002070 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                13.09 usec
P2                26.18 usec
PL1               -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324008 MHz

======== CHANNEL f2 ========
NUC2                13C
P3                12.37 usec
PL2                1.00 dB
PL2W        28.13319778 W
SFO2        100.6248425 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPZ1               50.00 %
GPZ2               30.00 %
GPZ3               40.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   99
SFO1          100.6248 MHz
FIDRES        243.939011 Hz
SW              240.000 ppm
FnMODE               QF

F2 - Processing parameters
SI                 1024
SF          400.1300068 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
PC                 1.40

F1 - Processing parameters
SI                 1024
```

Figure S6. NOESY spectrum of penicisteroid D (1).



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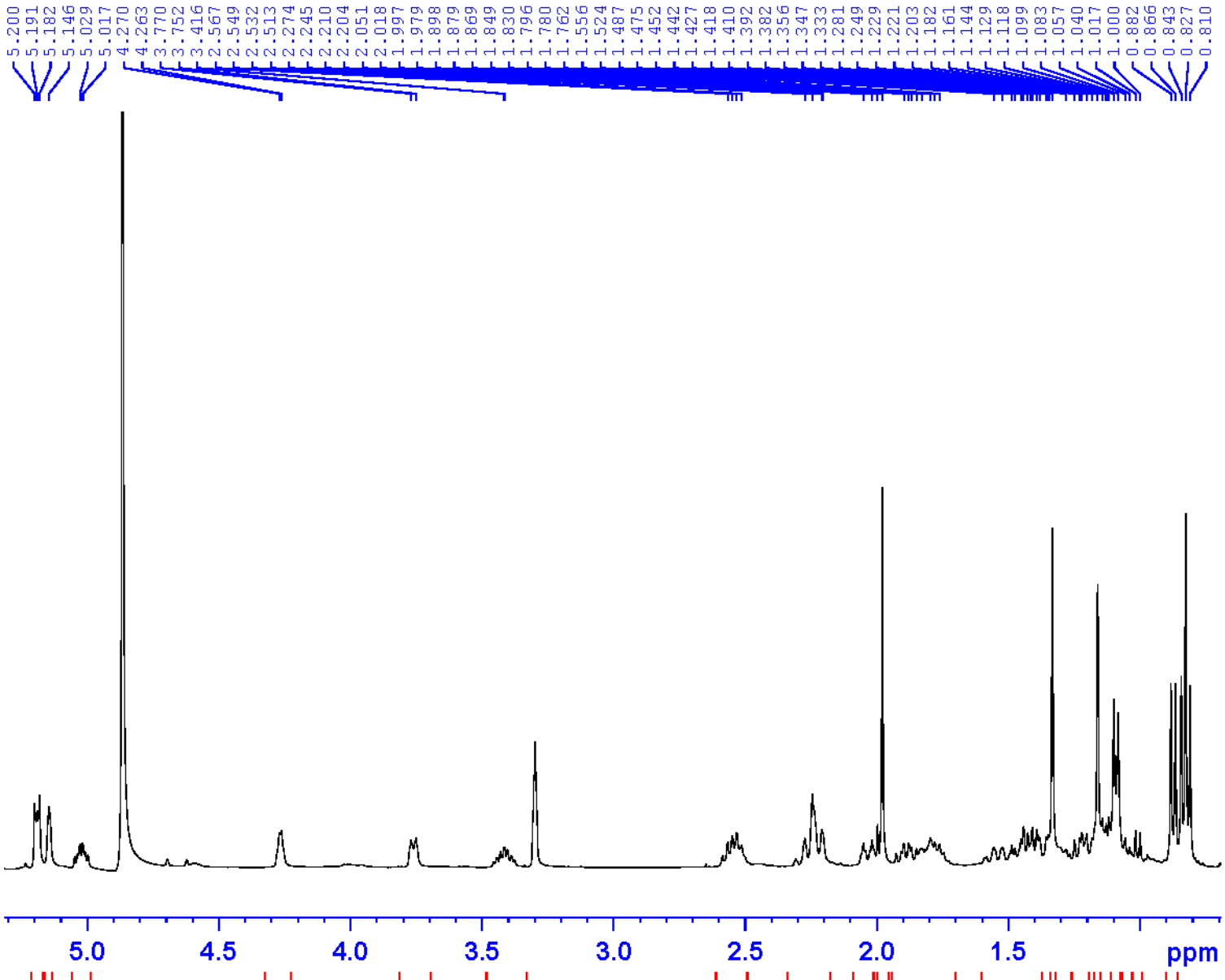
```
Current Data Parameters
NAME          475T15 NEW
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180526
Time              12.17
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         noesyph
TD                2048
SOLVENT           MeOD
NS                  36
DS                   4
SWH            4795.396 Hz
FIDRES         2.341502 Hz
AQ            0.2135381 sec
RG                 203
DW              104.267 usec
DE                6.50 usec
TE               296.0 K
D0            0.00008747 sec
D1            2.00000000 sec
D8            0.30000001 sec
IN0           0.00020825 sec

======== CHANNEL f1 ========
NUC1                1H
P1                13.09 usec
PL1               -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324008 MHz

F1 - Acquisition parameters
TD                  221
SFO1          400.1324 MHz
FIDRES       21.726646 Hz
SW              12.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                 1024
SF          400.1300068 MHz
WDW               QSINE
SSB                   2
LB        0 Hz
GB        0
PC                1.00

F1 - Processing parameters
SI                 1024
MC2         States-TPPI
SF          400.1300068 MHz
```

Figure S7. 1H-NMR spectrum of penicisteroid E (2)




```
Current Data Parameters
NAME          475T51 NEW
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180509
Time               17.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    35
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9845889 sec
RG                   128
DW                60.800 usec
DE                 6.50 usec
TE                296.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.09 usec
PL1                -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300068 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Figure S8. 13C-NMR spectrum of penicisteroid E (2)

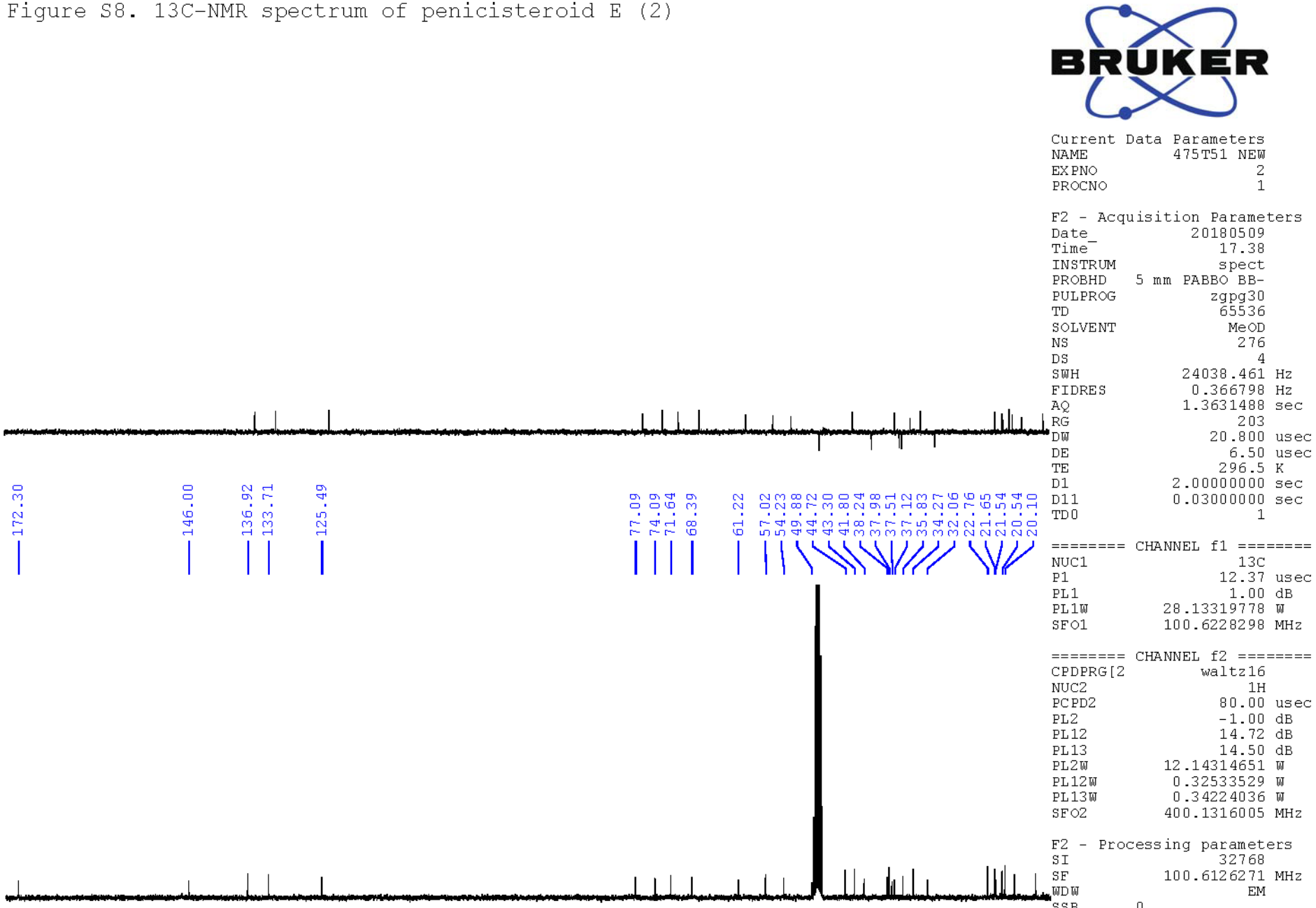
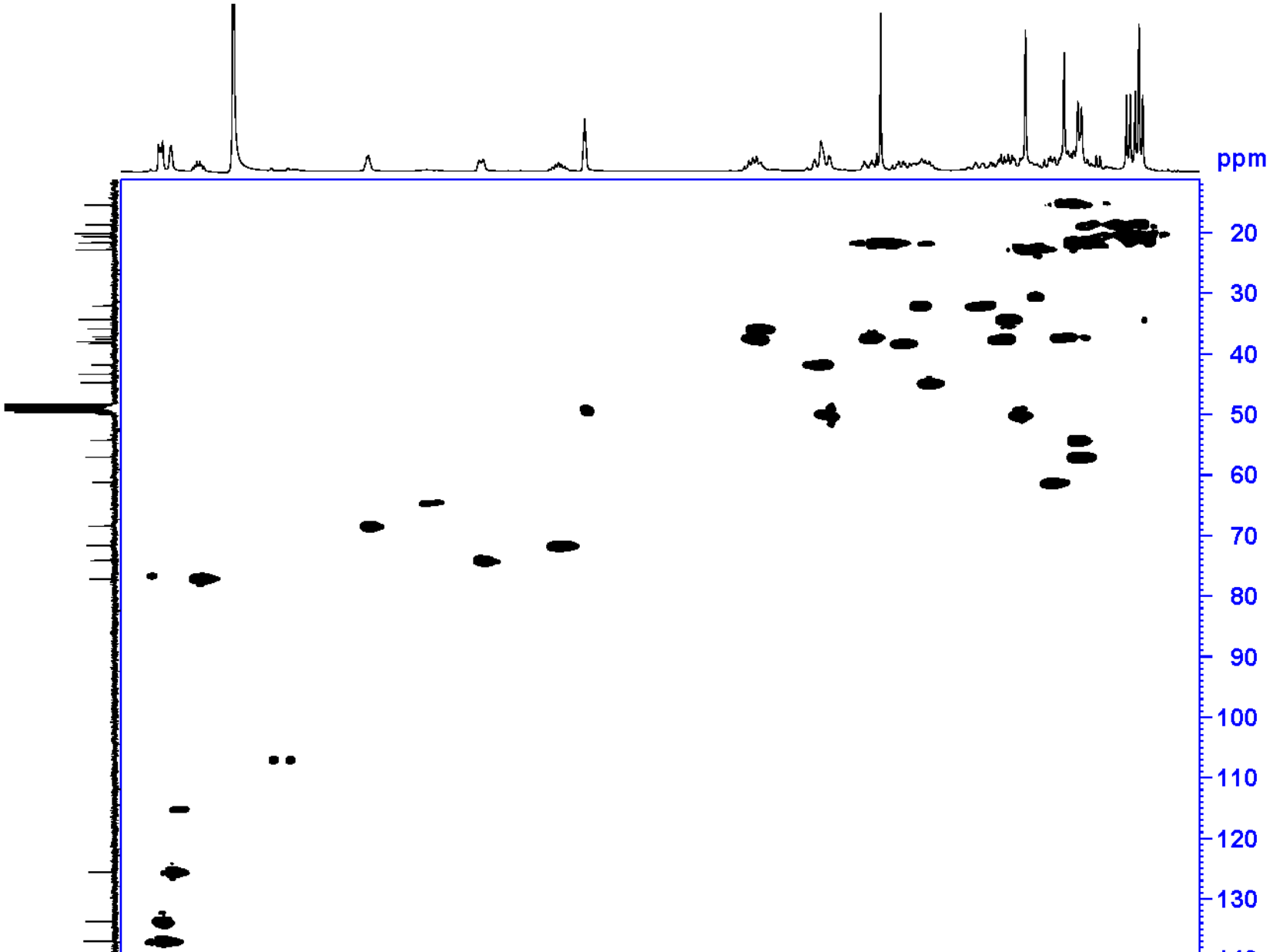
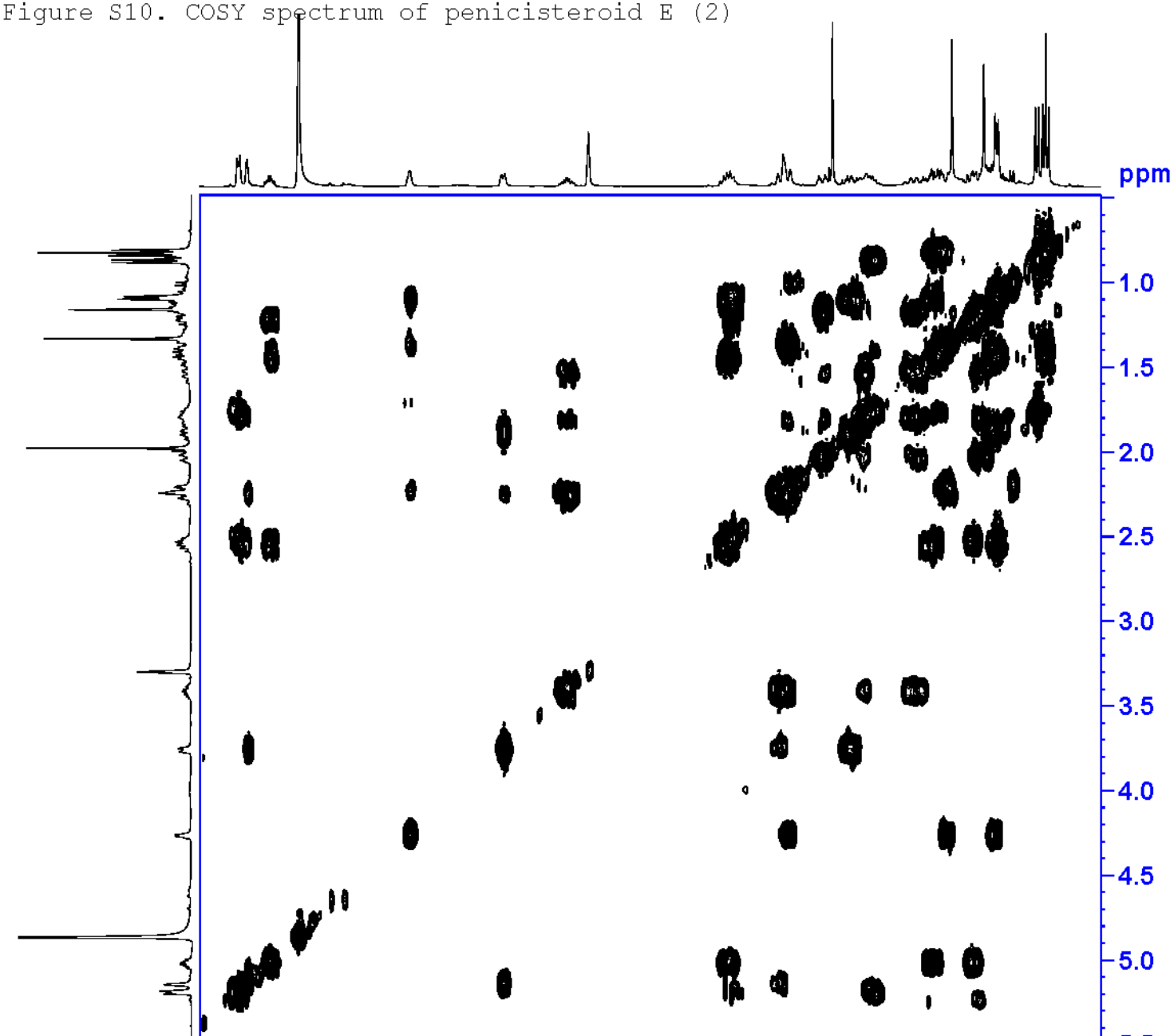


Figure S9. HSQC spectrum of penicisteroid E (2)



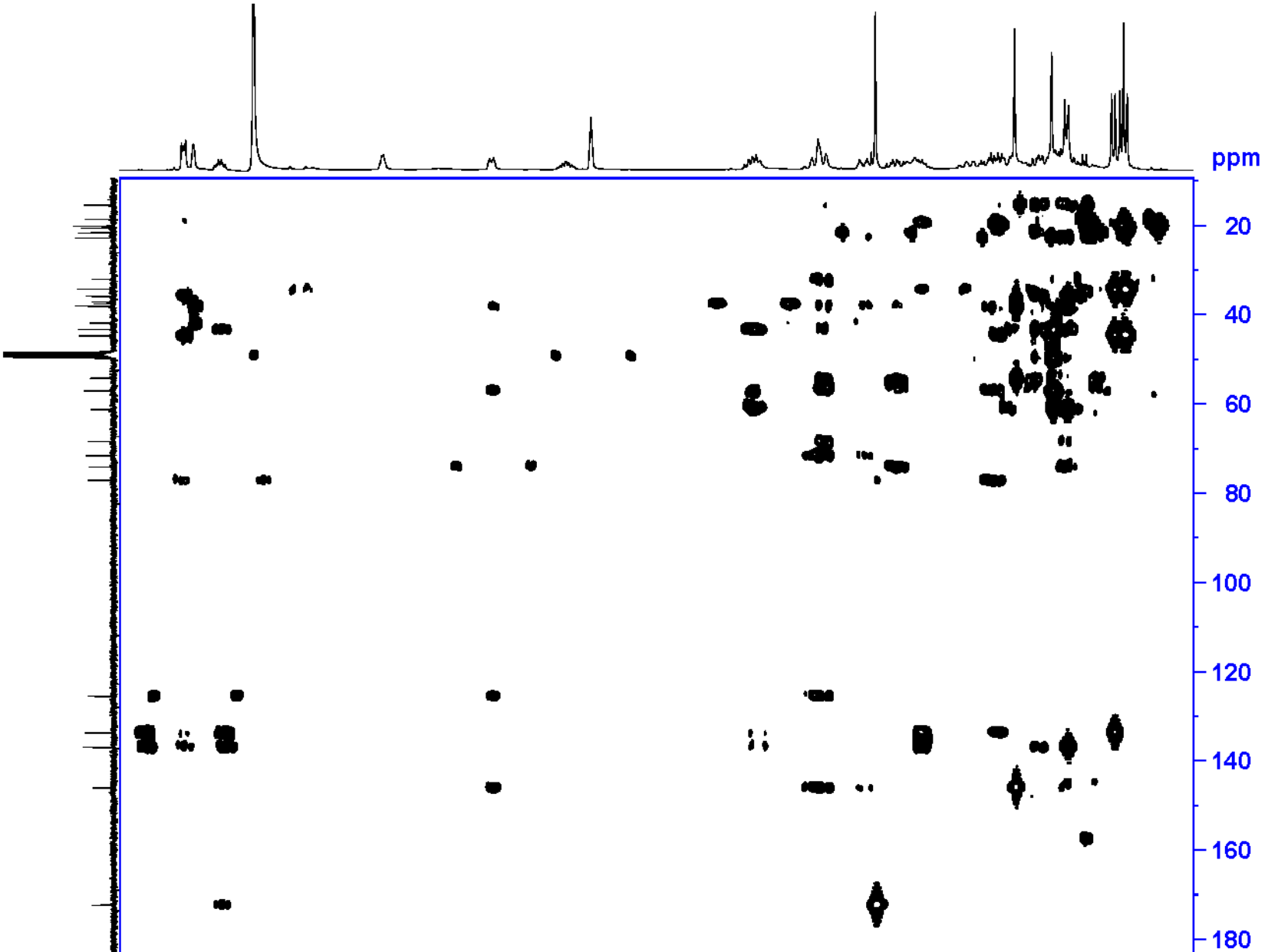

```
Current Data Parameters
NAME          475T51 NEW
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180523
Time              21.31
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG     hsqcedetgp
TD                1024
SOLVENT           MeOD
NS                  32
DS                  32
SWH            5197.505 Hz
FIDRES         5.075689 Hz
AQ           0.0985088 sec
RG                 203
DW              96.200 usec
DE               6.50 usec
TE              300.0 K
CNST2       145.0000000
D0           0.00000300 sec
D1           1.50000000 sec
D4           0.00172414 sec
D11          0.03000000 sec
D13          0.00000400 sec
D16          0.00020000 sec
D21          0.00345000 sec
IN0          0.00002260 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1               1H
P1              13.09 usec
P2              26.18 usec
P28              1.00 usec
PL1             -1.00 dB
PL1W       12.14314651 W
SFO1       400.1324008 MHz

======== CHANNEL f2 ========
CPDPRG[2           garp
NUC2              13C
P3              12.37 usec
P4              24.74 usec
PCPD2           75.00 usec
PL2              1.00 dB
PL12            16.65 dB
PL2W       28.13319778 W
PL12W       0.76598305 W
SFO2       100.6238364 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPZ1             80.00 %
GPZ2             20.10 %
P16            1000.00 usec

F1 - Acquisition parameters
TD                256
SFO1       100.6238 MHz
FIDRES      86.473610 Hz
SW           220.000 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                1024
SF         400.1300068 MHz
WDW               QSINE
SSB                  2
LB       0 Hz
GB       0
PC               1.40

F1 - Processing parameters
```

Figure S10. COSY spectrum of penicisteroid E (2)




```
Current Data Parameters
NAME          475T51 NEW
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180524
Time                1.12
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG      cosygpmfqf
TD                  2048
SOLVENT             MeOD
NS                     8
DS                     8
SWH             4795.396 Hz
FIDRES          2.341502 Hz
AQ             0.2135381 sec
RG                   203
DW               104.267 usec
DE                 6.50 usec
TE                300.0 K
D0             0.00000300 sec
D1             1.93569195 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00020825 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.09 usec
PL1                -1.00 dB
PL1W         12.14314651 W
SFO1         400.1324008 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPZ1               16.00 %
GPZ2               12.00 %
GPZ3               40.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1           400.1324 MHz
FIDRES         37.512413 Hz
SW                12.000 ppm
FnMODE                QF

F2 - Processing parameters
SI                  1024
SF           400.1300068 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
```

Figure S11. HMBC spectrum of penicisteroid E (2)



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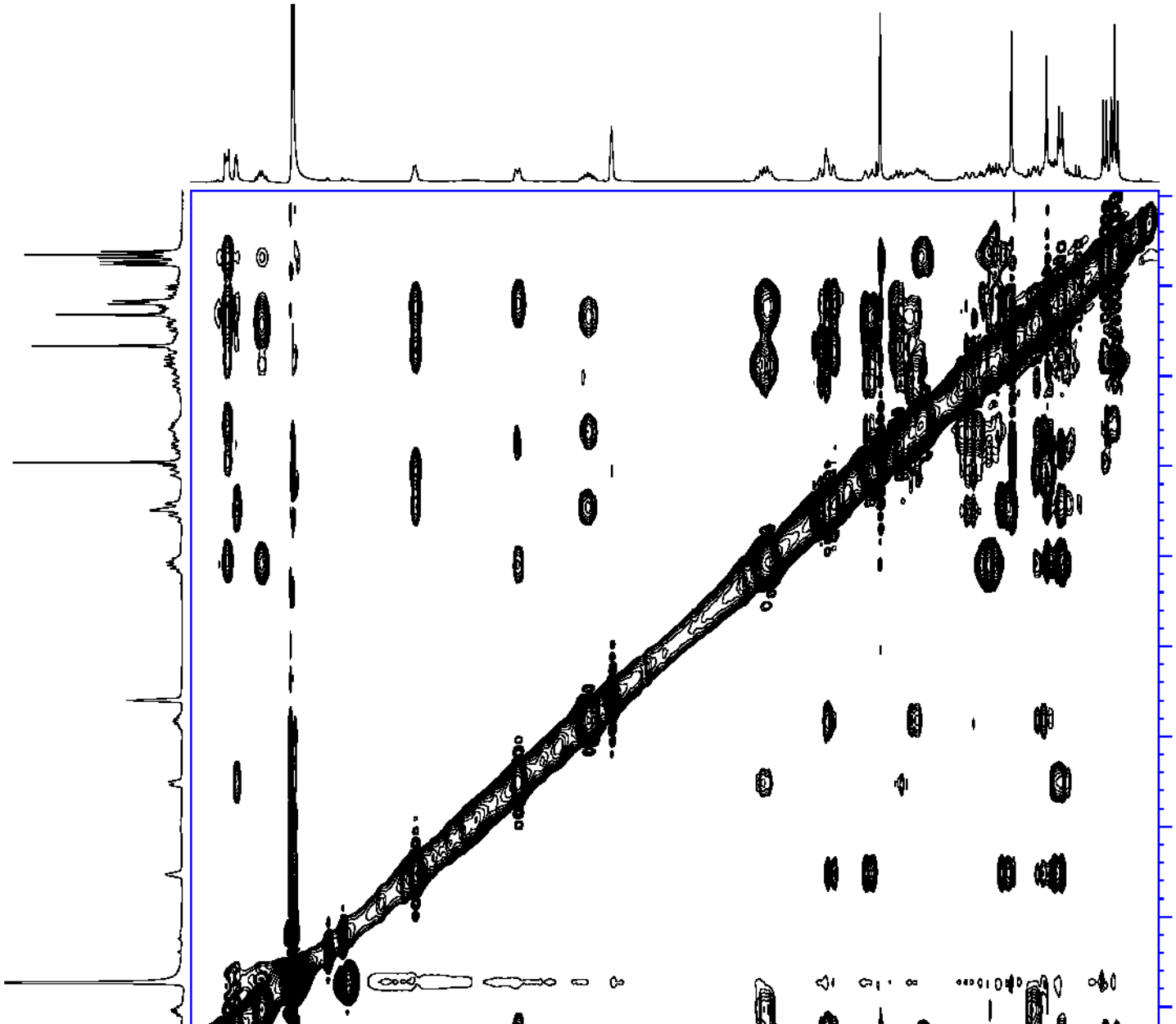
```
Current Data Parameters
NAME                 475T51 NEW
EXPNO                         7
PROCNO                        1

F2 - Acquisition Parameters
Date_               20180524
Time                    1.51
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG          hmbcgpndqf
TD                      4096
SOLVENT                 MeOD
NS                        40
DS                        16
SWH                 4795.396 Hz
FIDRES              1.170751 Hz
AQ                  0.4270763 sec
RG                        203
DW                  104.267 usec
DE                    6.50 usec
TE                    300.0 K
CNST13              8.0000000
D0                  0.00000300 sec
D1                  1.37220395 sec
D6                  0.06250000 sec
D16                 0.00020000 sec
IN0                 0.00002070 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.09 usec
P2                     26.18 usec
PL1                    -1.00 dB
PL1W               12.14314651 W
SF01               400.1324008 MHz

======== CHANNEL f2 ========
NUC2                     13C
P3                     12.37 usec
PL2                     1.00 dB
PL2W               28.13319778 W
SF02               100.6248425 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]            SINE.100
GPNAM[2]            SINE.100
GPNAM[3]            SINE.100
GPZ1                   50.00 %
GPZ2                   30.00 %
GPZ3                   40.10 %
P16                  1000.00 usec

F1 - Acquisition parameters
TD                       128
SF01                100.6248 MHz
FIDRES             188.671585 Hz
SW                    240.000 ppm
FnMODE                   QF

F2 - Processing parameters
SI                      1024
SF                 400.1300068 MHz
WDW                     SINE
SSB          0
LB           0 Hz
GB           0
PC                      1.40

F1 - Processing parameters
SI                      1024
```

Figure S12. NOESY spectrum of penicisteroid E (2).



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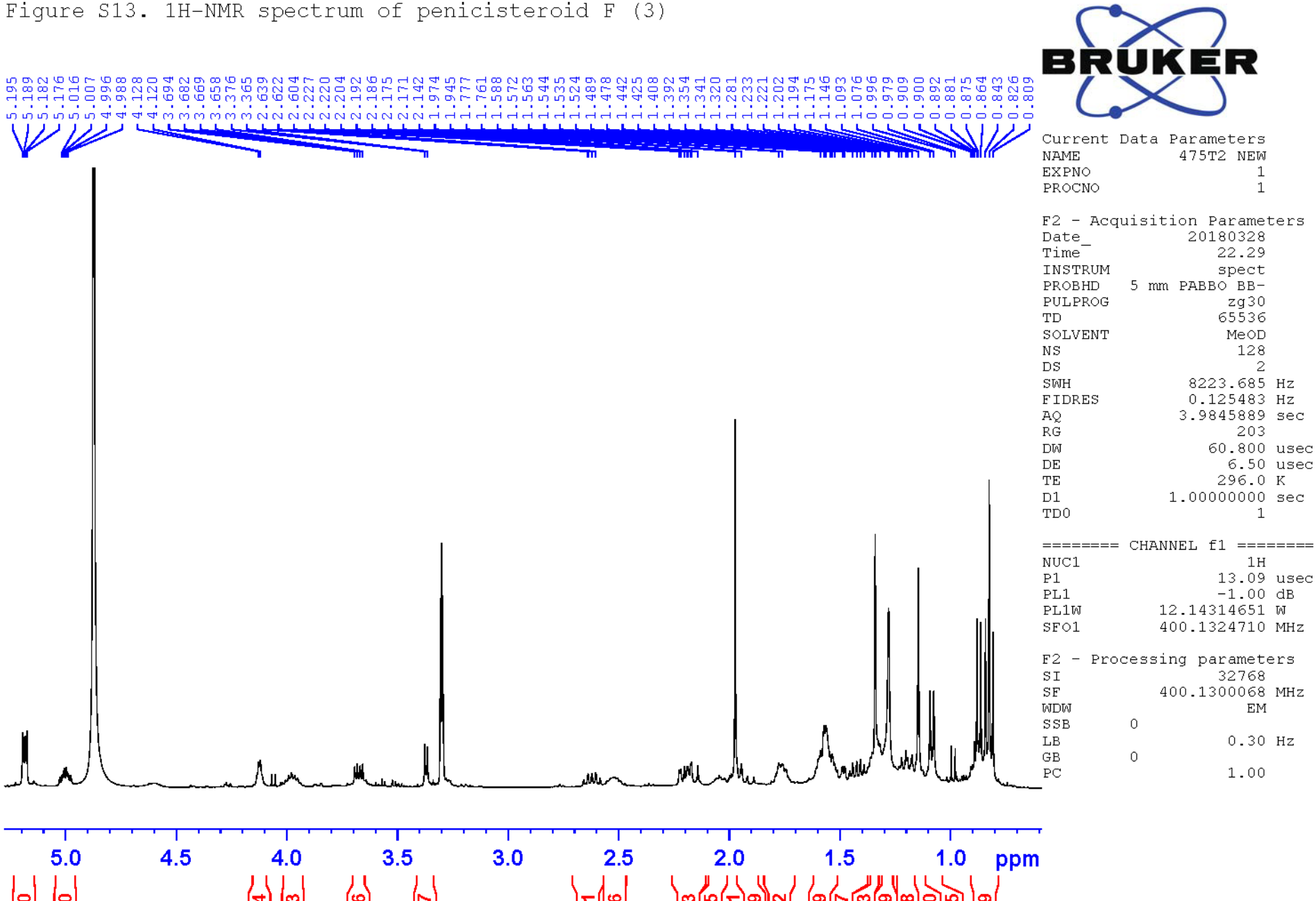
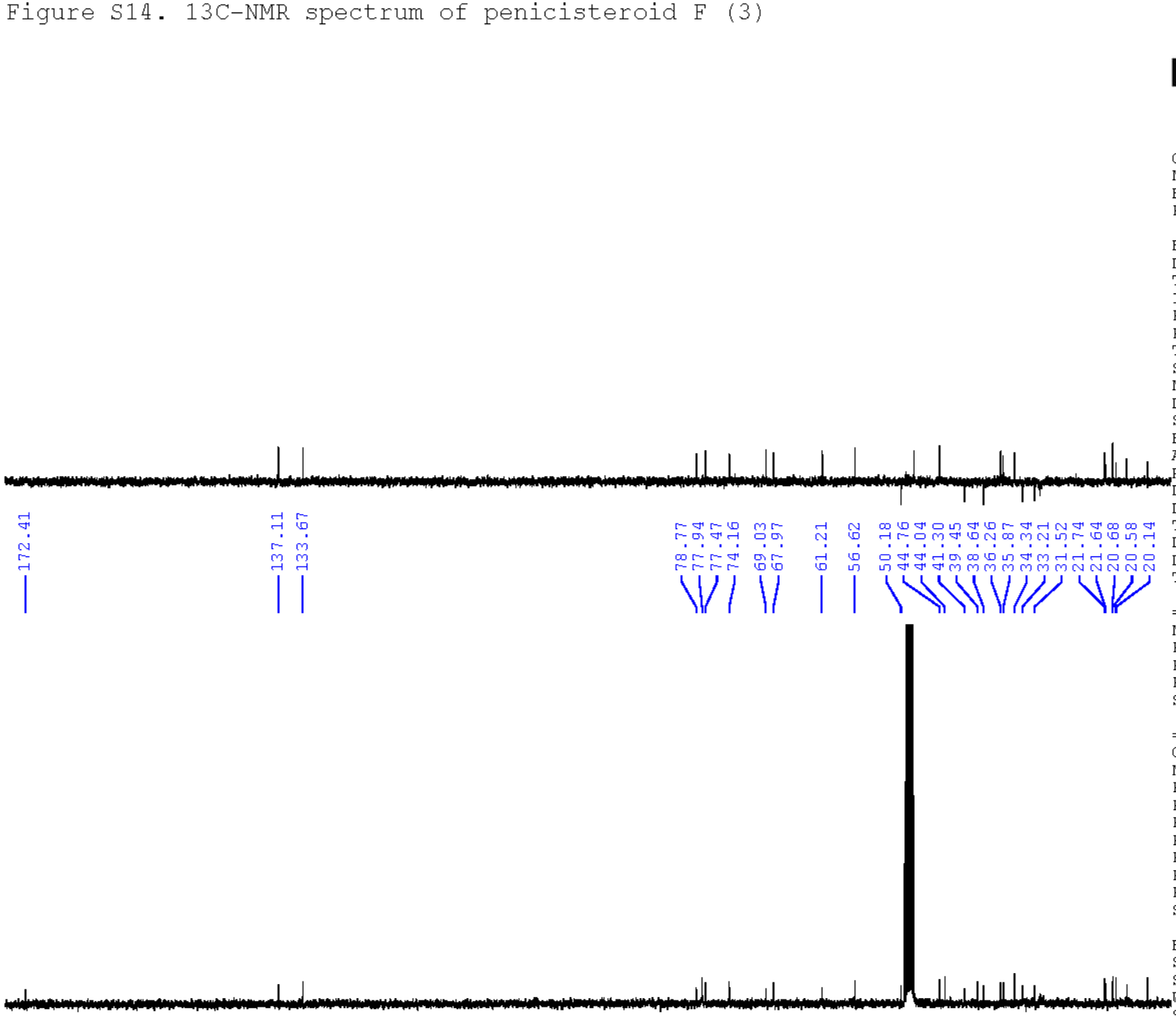
```
Current Data Parameters
NAME          475T51 NEW
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180524
Time                4.31
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         noesyph
TD                 2048
SOLVENT            MeOD
NS                   32
DS                    4
SWH           4795.396 Hz
FIDRES        2.341502 Hz
AQ            0.2135381 sec
RG                  203
DW              104.267 usec
DE                6.50 usec
TE               300.0 K
D0            0.00008747 sec
D1            2.00000000 sec
D8            0.30000001 sec
IN0           0.00020825 sec

======== CHANNEL f1 ========
NUC1                1H
P1                13.09 usec
PL1               -1.00 dB
PL1W       12.14314651 W
SFO1       400.1324008 MHz

F1 - Acquisition parameters
TD                  174
SFO1         400.1324 MHz
FIDRES      27.595339 Hz
SW             12.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                 1024
SF         400.1300068 MHz
WDW                QSINE
SSB                   2
LB       0 Hz
GB       0
PC                 1.00

F1 - Processing parameters
SI                 1024
MC2         States-TPPI
SF         400.1300068 MHz
```

Figure S13. 1H-NMR spectrum of penicisteroid F (3)




```
Current Data Parameters
NAME            475T2 NEW
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180328
Time                22.29
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              MeOD
NS                    128
DS                      2
SWH              8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9845889 sec
RG                    203
DW                60.800 usec
DE                 6.50 usec
TE                296.0 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.09 usec
PL1                -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF          400.1300068 MHz
WDW                    EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Figure S14. 13C-NMR spectrum of penicisteroid F (3)



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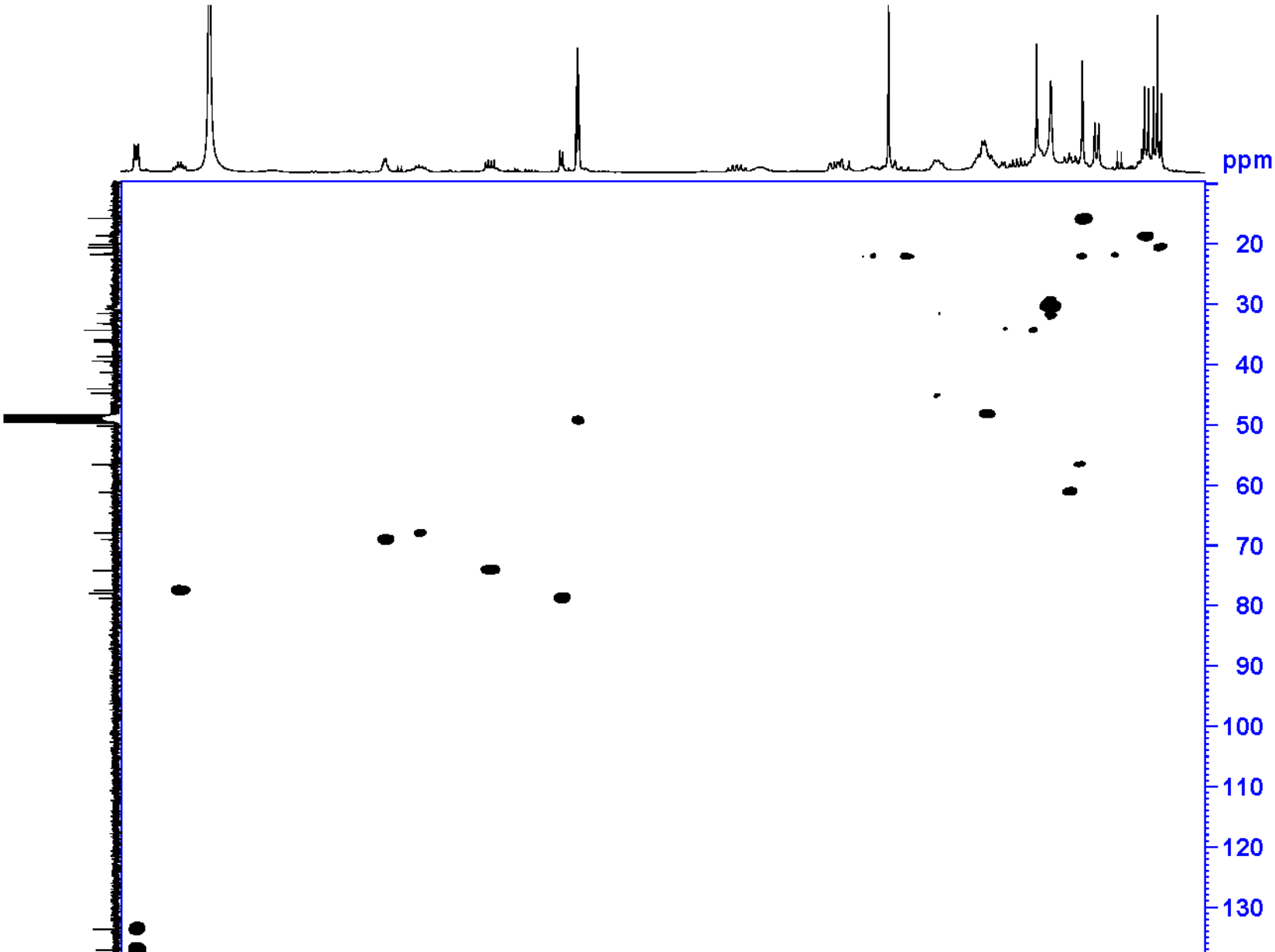
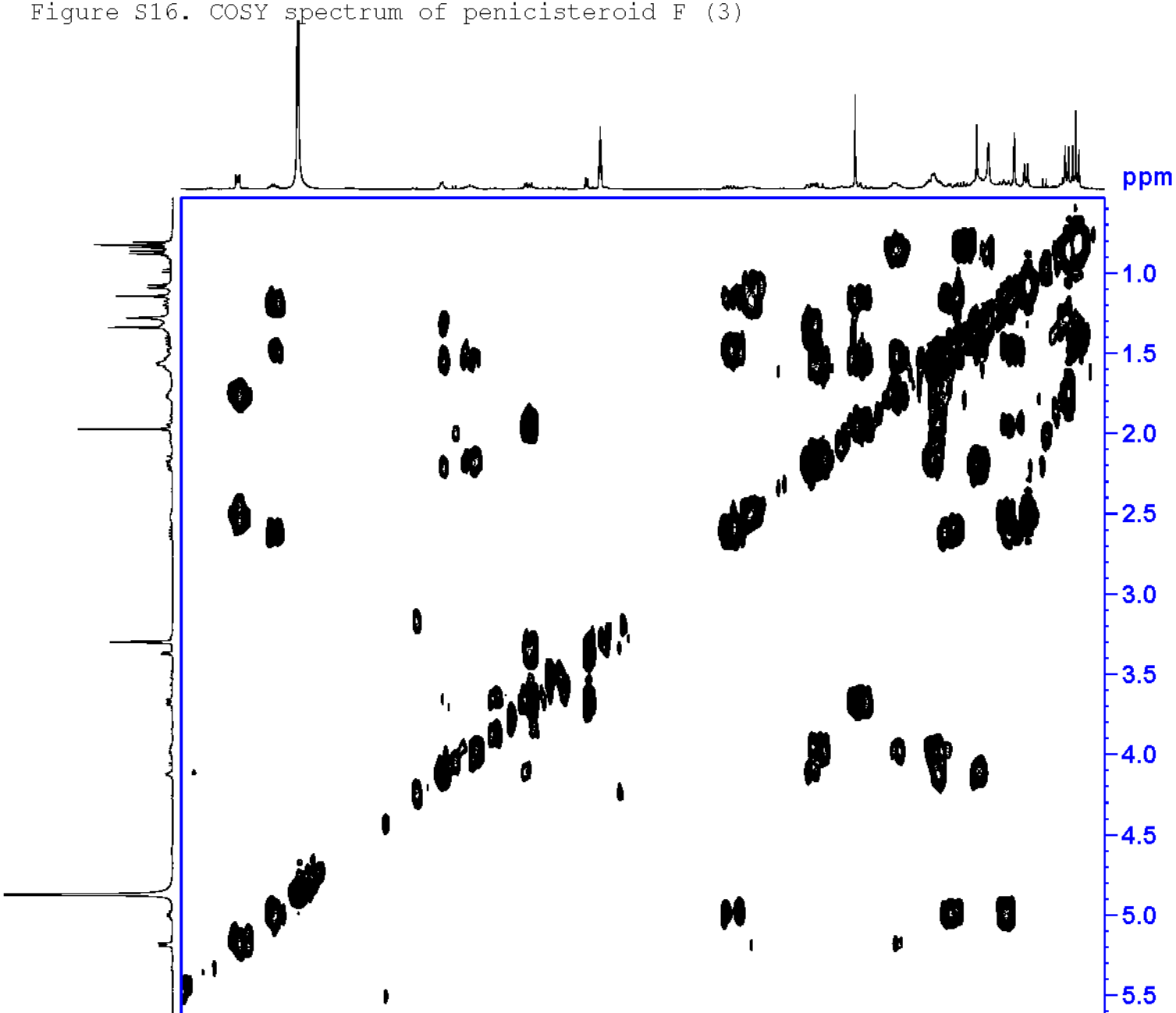
```
Current Data Parameters
NAME          475T2 NEW
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20180329
Time               3.16
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT             MeOD
NS                  5012
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                297.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.37 usec
PL1                 1.00 dB
PL1W        28.13319778 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.72 dB
PL13               14.50 dB
PL2W        12.14314651 W
PL12W        0.32533529 W
PL13W        0.34224036 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF         100.6126265 MHz
WDW                   EM
SSB                    0
```

Figure S15. HSQC spectrum of penicisteroid F (3)



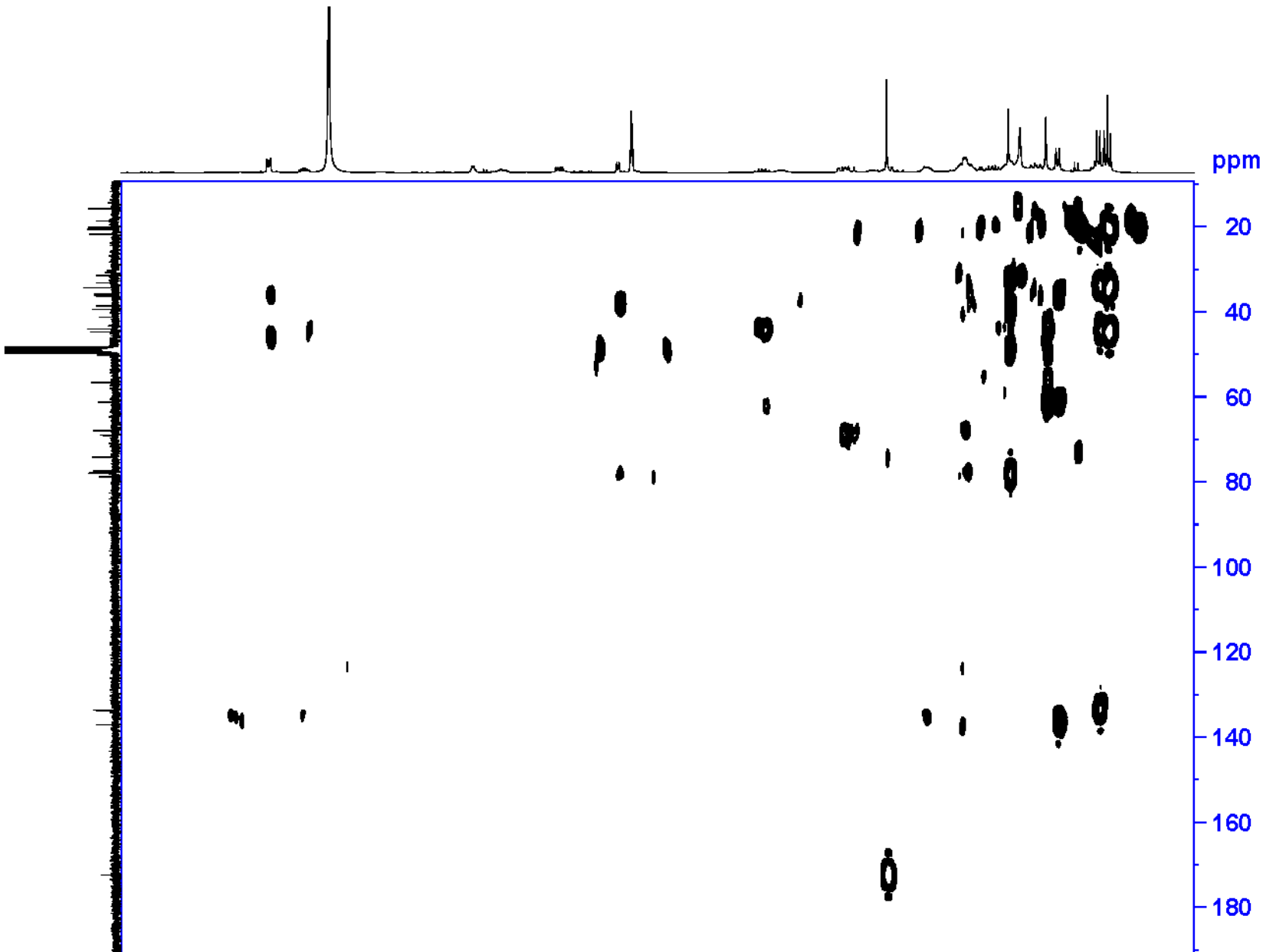

```
Current Data Parameters
NAME            475T2 NEW
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180329
Time                3.47
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG      hsqcedetgp
TD                  1024
SOLVENT             MeOD
NS                    32
DS                    32
SWH            6393.862 Hz
FIDRES         6.244006 Hz
AQ             0.0800768 sec
RG                  203
DW                78.200 usec
DE                 6.50 usec
TE                296.4 K
CNST2         145.0000000
D0             0.00000300 sec
D1             1.50000000 sec
D4             0.00172414 sec
D11            0.03000000 sec
D13            0.00000400 sec
D16            0.00020000 sec
D21            0.00345000 sec
IN0            0.00001910 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.09 usec
P2                 26.18 usec
P28                1.00 usec
PL1               -1.00 dB
PL1W          12.14314651 W
SF01          400.1332010 MHz

======== CHANNEL f2 ========
CPDPRG[2              garp
NUC2                  13C
P3                 12.37 usec
P4                 24.74 usec
PCPD2              75.00 usec
PL2                1.00 dB
PL12              16.65 dB
PL2W          28.13319778 W
PL12W          0.76598305 W
SF02          100.6258487 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                    256
SF01           100.6258 MHz
FIDRES        102.198128 Hz
SW                260.000 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF           400.1300043 MHz
WDW                  QSINE
SSB                      2
LB        0 Hz
GB        0
PC                   1.40

F1 - Processing parameters
```

Figure S16. COSY spectrum of penicisteroid F (3)



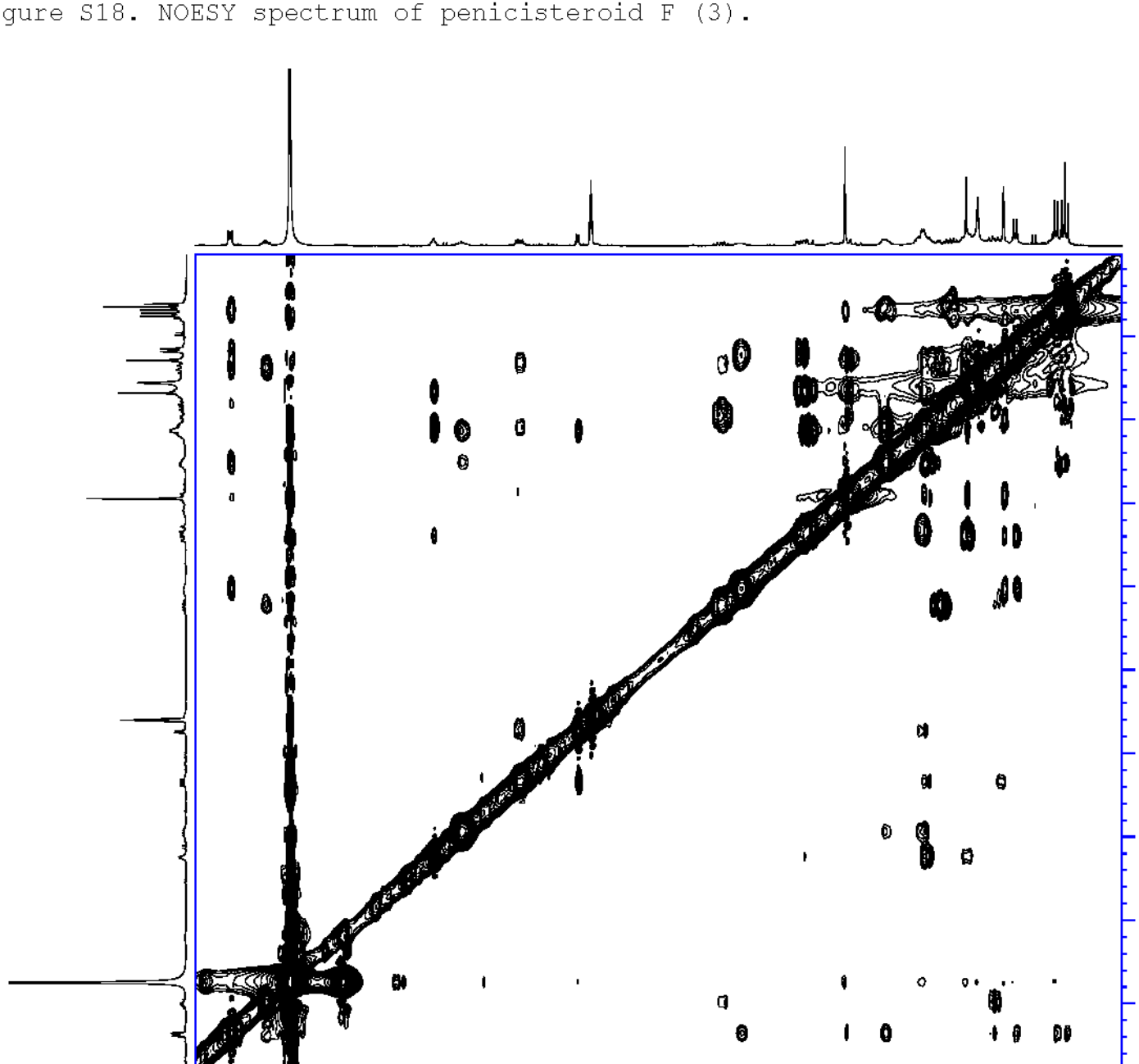

```
Current Data Parameters
NAME            475T2 NEW
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180329
Time                7.26
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG       cosygpmfqf
TD                   2048
SOLVENT              MeOD
NS                      8
DS                      8
SWH              6393.862 Hz
FIDRES           3.122003 Hz
AQ             0.1601536 sec
RG                    203
DW                 78.200 usec
DE                  6.50 usec
TE                 295.8 K
D0             0.00000300 sec
D1             1.93569195 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00015620 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.09 usec
PL1                 -1.00 dB
PL1W          12.14314651 W
SFO1         400.1332010 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPNAM[3]         SINE.100
GPZ1                16.00 %
GPZ2                12.00 %
GPZ3                40.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                     128
SFO1            400.1332 MHz
FIDRES          50.016651 Hz
SW                16.000 ppm
FnMODE                 QF

F2 - Processing parameters
SI                    1024
SF           400.1300068 MHz
WDW                  SINE
SSB       0
LB        0 Hz
GB        0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2                     QF
```

Figure S17. HMBC spectrum of penicisteroid F (3)




```
Current Data Parameters
NAME                  475T2 NEW
EXPNO                         6
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20180329
Time                       8.04
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG            hmbcgpndqf
TD                         4096
SOLVENT                    MeOD
NS                           64
DS                           16
SWH                  6393.862 Hz
FIDRES               1.561001 Hz
AQ                   0.3203072 sec
RG                         203
DW                      78.200 usec
DE                       6.50 usec
TE                      295.5 K
CNST13               8.0000000
D0                   0.00000300 sec
D1                   1.37220395 sec
D6                   0.06250000 sec
D16                  0.00020000 sec
IN0                  0.00001910 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       13.09 usec
P2                       26.18 usec
PL1                      -1.00 dB
PL1W                12.14314651 W
SFO1               400.1332010 MHz

======== CHANNEL f2 ========
NUC2                       13C
P3                       12.37 usec
PL2                       1.00 dB
PL2W                28.13319778 W
SFO2               100.6258487 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]              SINE.100
GPNAM[2]              SINE.100
GPNAM[3]              SINE.100
GPZ1                     50.00 %
GPZ2                     30.00 %
GPZ3                     40.10 %
P16                    1000.00 usec

F1 - Acquisition parameters
TD                         48
SFO1                100.6258 MHz
FIDRES              545.056702 Hz
SW                     260.000 ppm
FnMODE                     QF

F2 - Processing parameters
SI                       1024
SF                400.1300068 MHz
WDW                      SINE
SSB                 0
LB                  0 Hz
GB                  0
PC                        1.40

F1 - Processing parameters
SI                       1024
```

Figure S18. NOESY spectrum of penicisteroid F (3).



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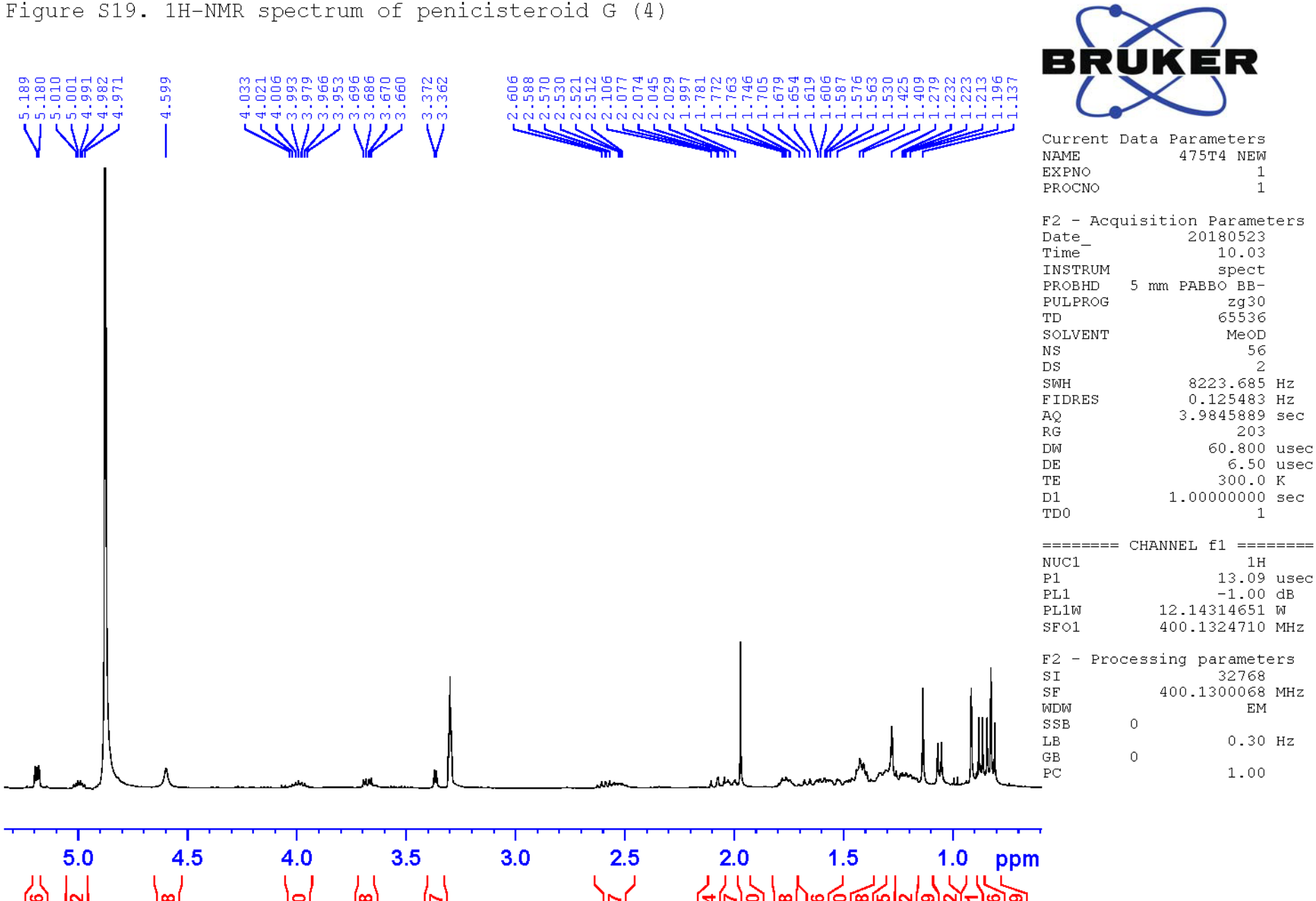
```
Current Data Parameters
NAME          475T2 NEW
EXPNO                 8
PROCNO                1

F2 - Acquisition Parameters
Date_          20180530
Time              11.55
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG        noesyph
TD                2048
SOLVENT           MeOD
NS                  48
DS                   4
SWH           4795.396 Hz
FIDRES        2.341502 Hz
AQ            0.2135381 sec
RG                 203
DW              104.267 usec
DE                6.50 usec
TE               296.3 K
D0            0.00008747 sec
D1            2.00000000 sec
D8            0.30000001 sec
IN0           0.00020825 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                13.09 usec
PL1               -1.00 dB
PL1W       12.14314651 W
SFO1       400.1324008 MHz

F1 - Acquisition parameters
TD                  250
SFO1          400.1324 MHz
FIDRES       19.206356 Hz
SW              12.000 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                 1024
SF         400.1300068 MHz
WDW                QSINE
SSB                   2
LB       0 Hz
GB       0
PC                 1.00

F1 - Processing parameters
SI                 1024
MC2         States-TPPI
SF         400.1300068 MHz
```

Figure S19. 1H-NMR spectrum of penicisteroid G (4)




```
Current Data Parameters
NAME            475T4 NEW
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180523
Time                10.03
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              MeOD
NS                     56
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9845889 sec
RG                    203
DW                 60.800 usec
DE                  6.50 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.09 usec
PL1                 -1.00 dB
PL1W         12.14314651 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300068 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

Figure S20. 13C-NMR spectrum of penicisteroid G (4)

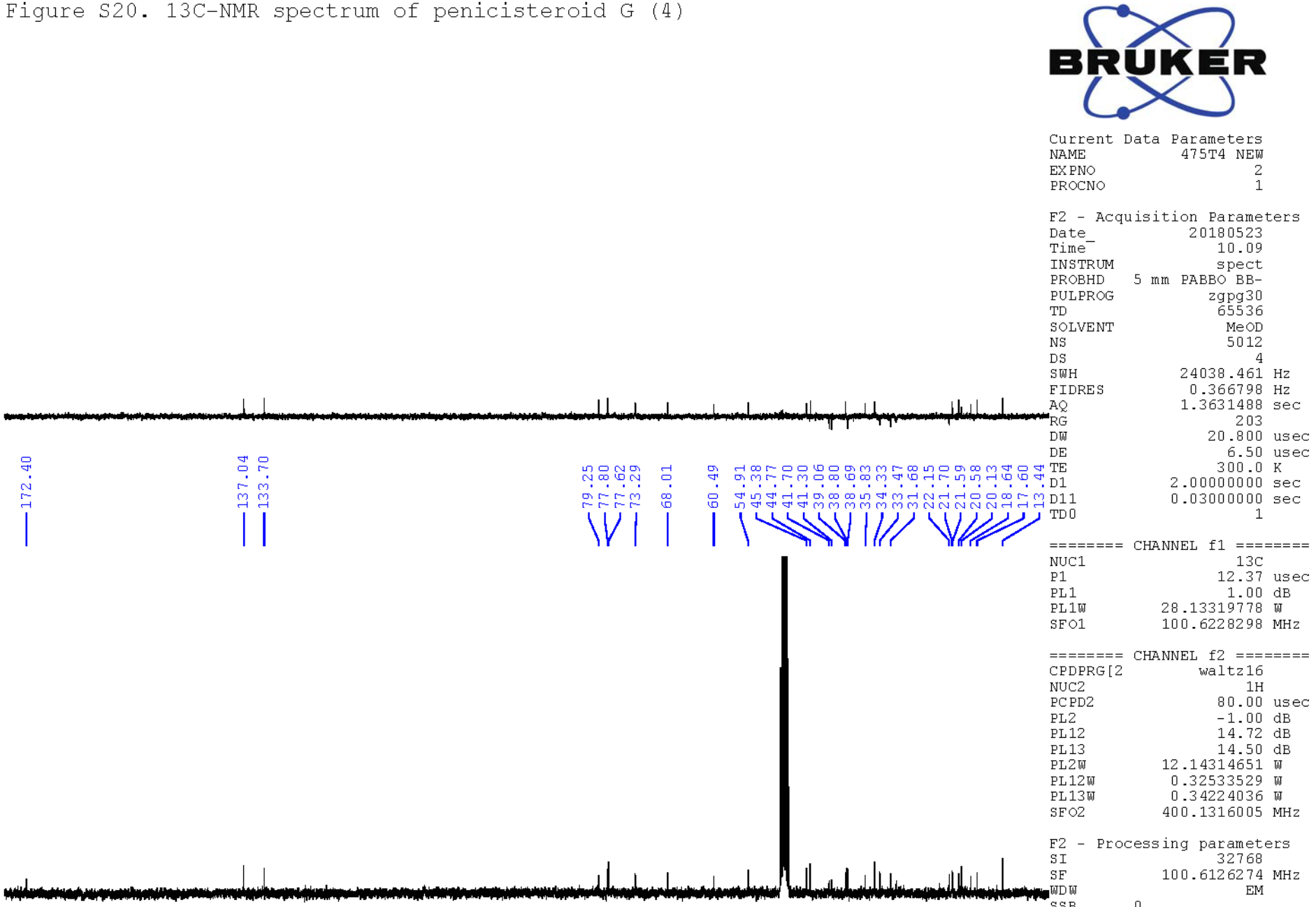
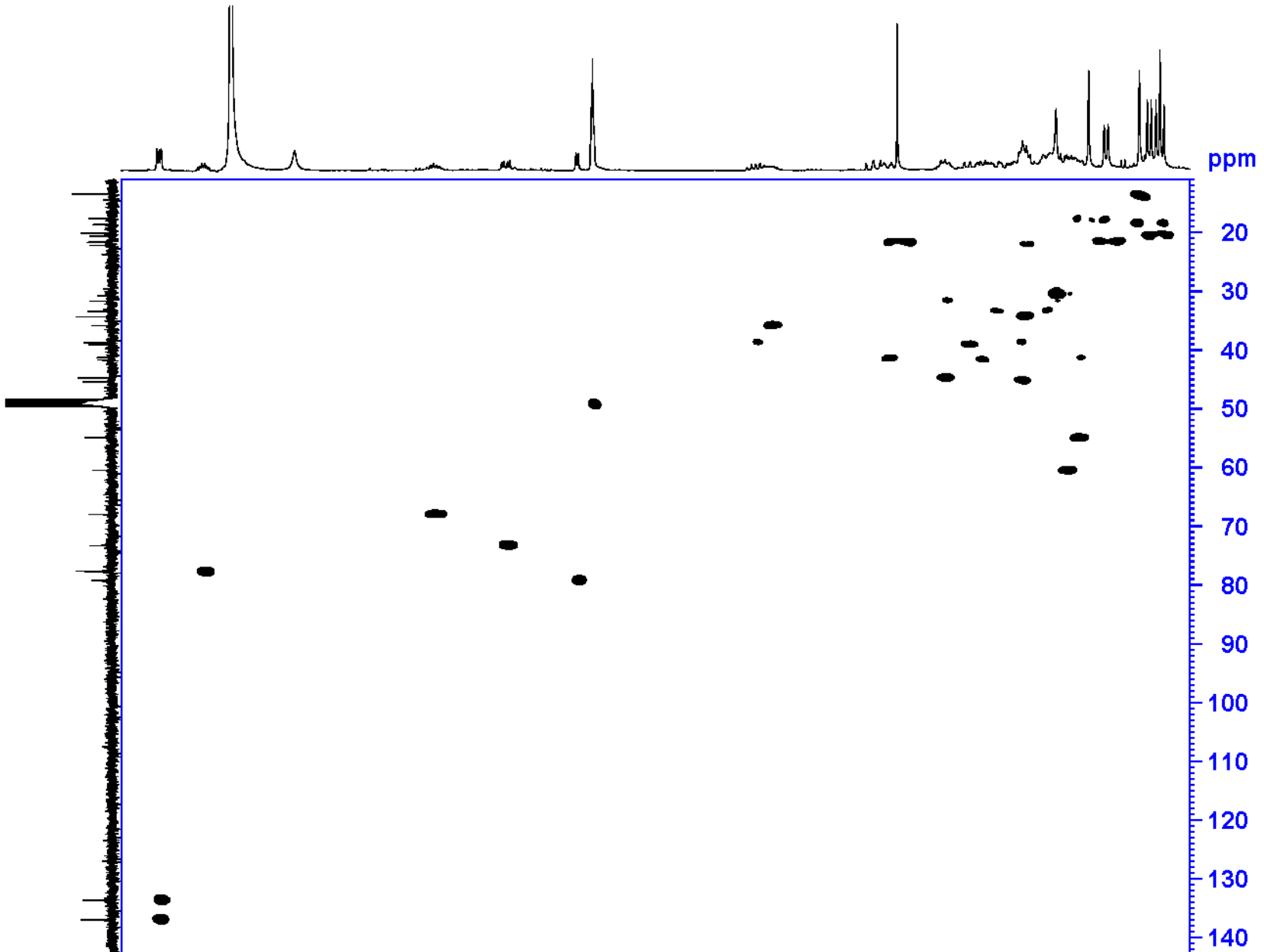
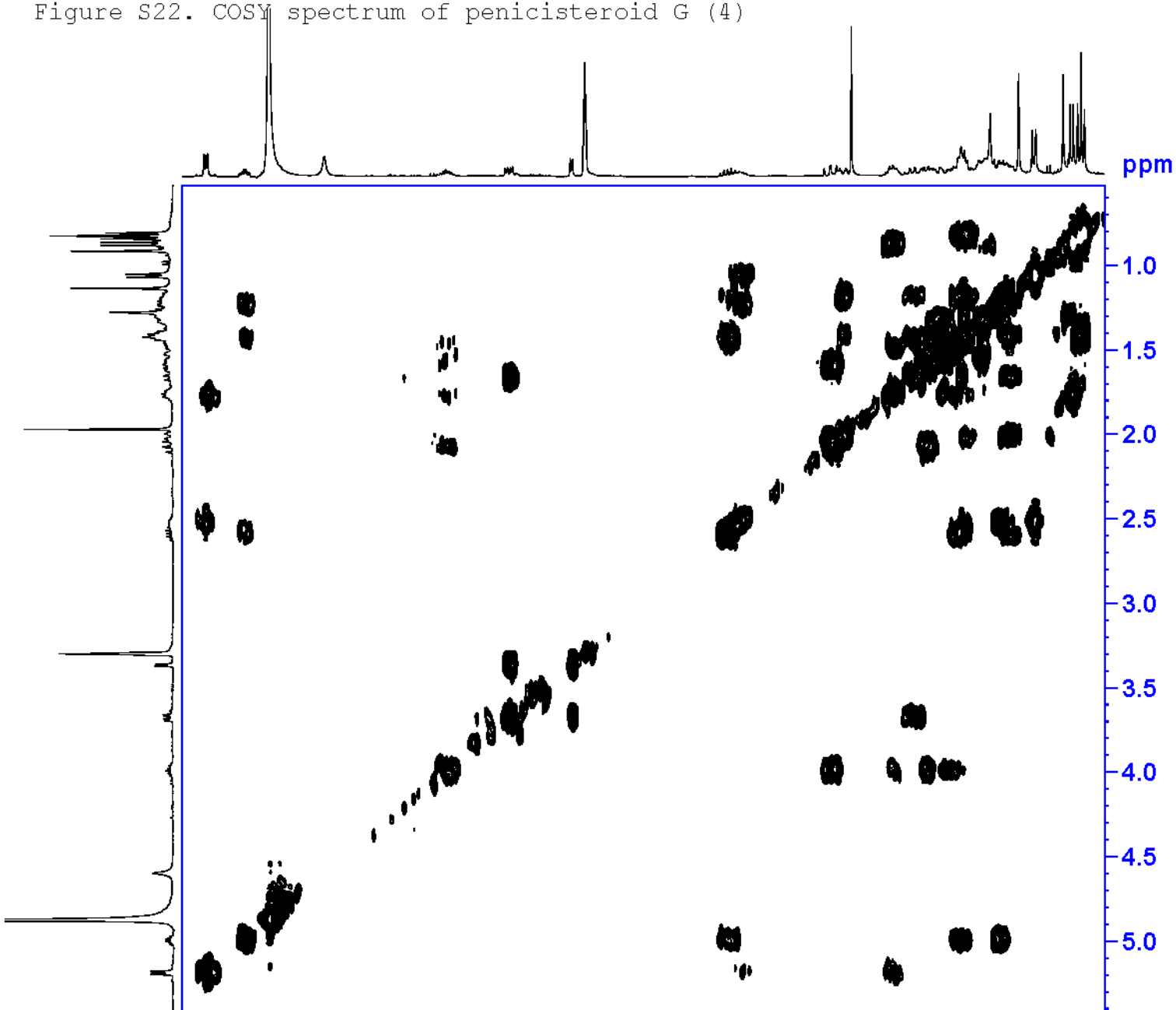


Figure S21. HSQC spectrum of penicisteroid G (4)




```
Current Data Parameters
NAME            475T4 NEW
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180526
Time                18.17
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG      hsqcedetgp
TD                   1024
SOLVENT              MeOD
NS                     40
DS                     32
SWH              5197.505 Hz
FIDRES           5.075689 Hz
AQ               0.0985088 sec
RG                     203
DW                96.200 usec
DE                 6.50 usec
TE                296.3 K
CNST2        145.0000000
D0            0.00000300 sec
D1            1.50000000 sec
D4            0.00172414 sec
D11           0.03000000 sec
D13           0.00000400 sec
D16           0.00020000 sec
D21           0.00345000 sec
IN0           0.00002260 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.09 usec
P2                 26.18 usec
P28                 1.00 usec
PL1                -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324008 MHz

======== CHANNEL f2 ========
CPDPRG[2              garp
NUC2                  13C
P3                 12.37 usec
P4                 24.74 usec
PCPD2              75.00 usec
PL2                 1.00 dB
PL12               16.65 dB
PL2W        28.13319778 W
PL12W        0.76598305 W
SFO2        100.6238364 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                    256
SFO1           100.6238 MHz
FIDRES         86.473610 Hz
SW               220.000 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF           400.1300068 MHz
WDW                 QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                   1024
```

Figure S22. COSY spectrum of penicisteroid G (4)



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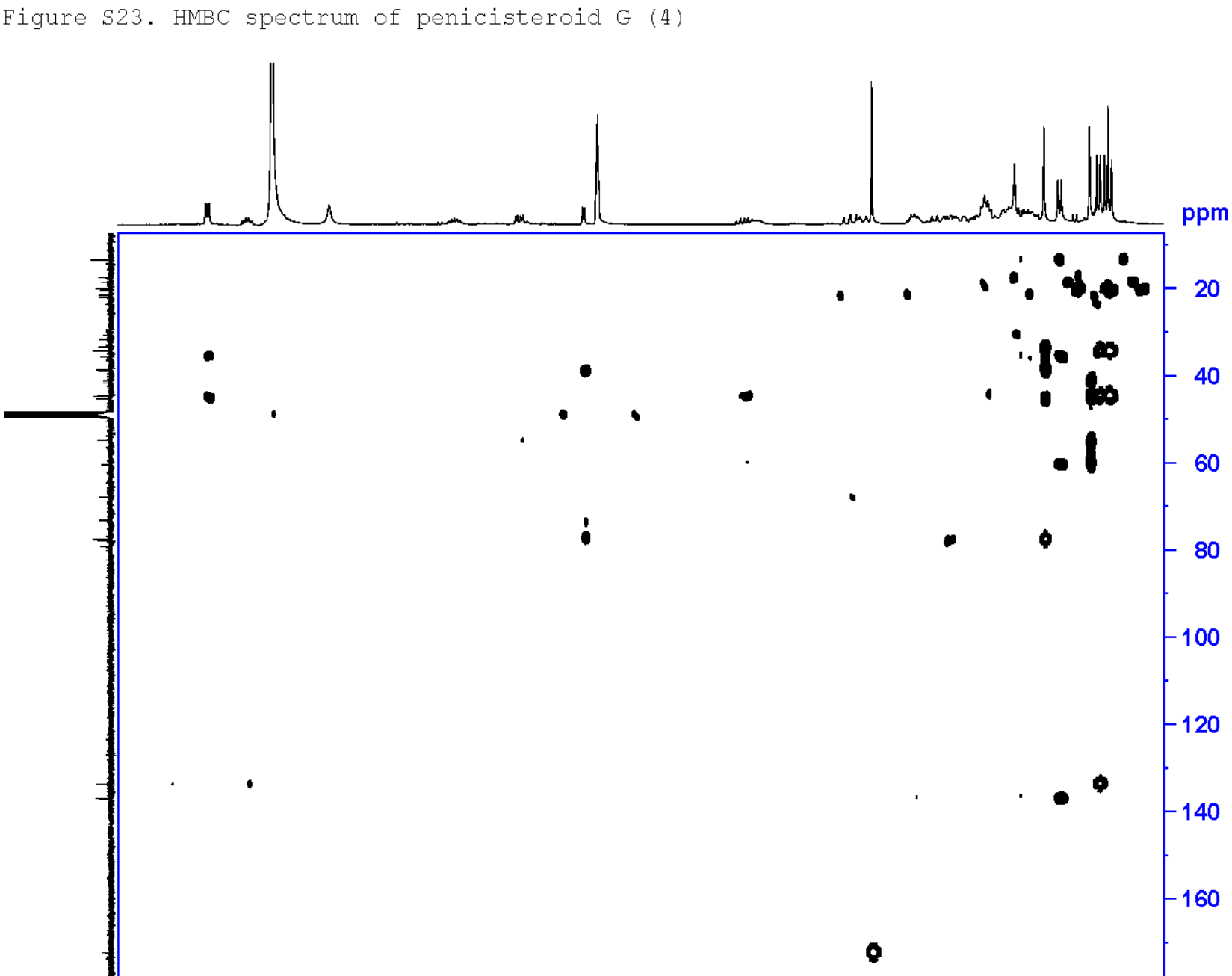
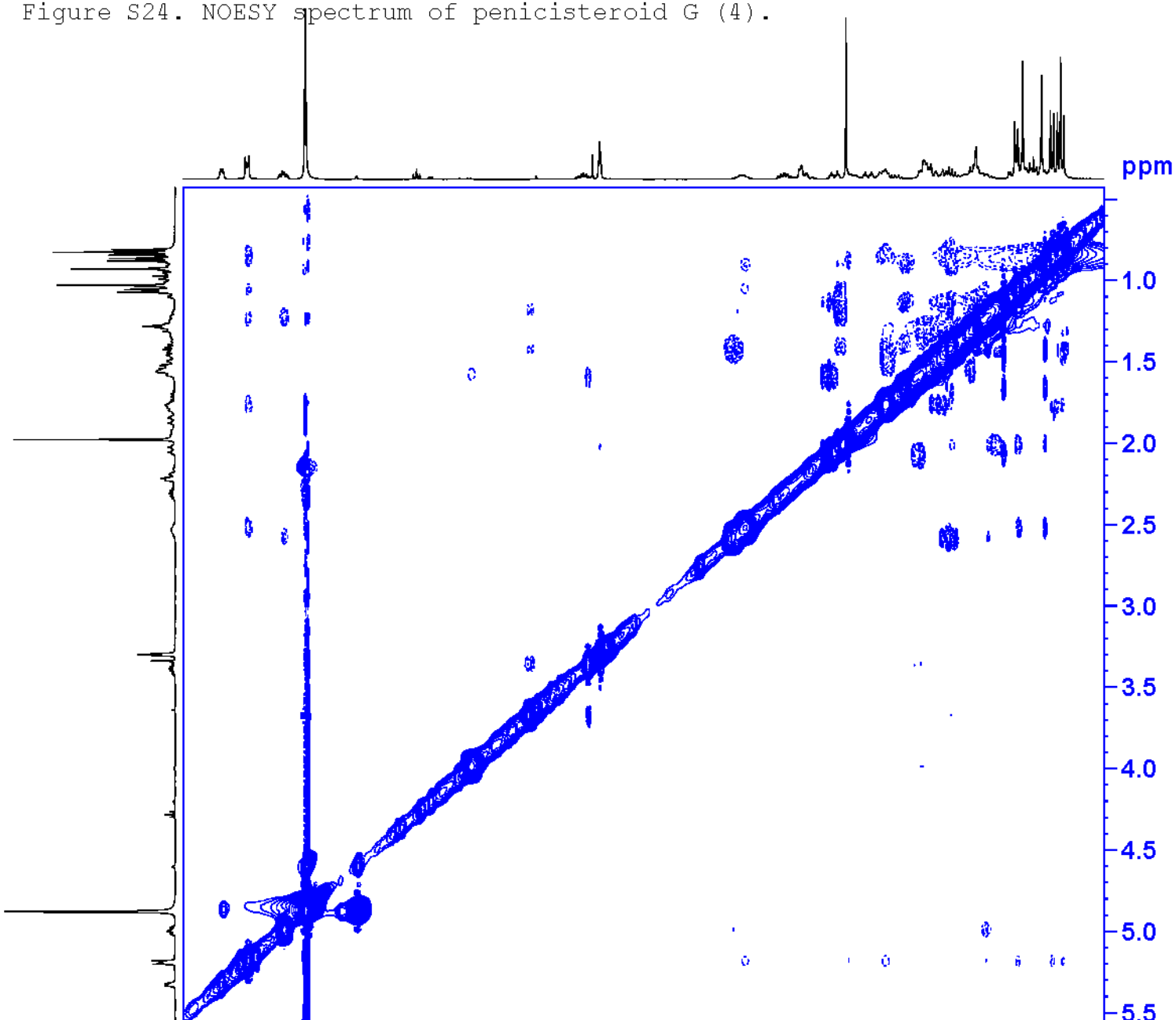
```
Current Data Parameters
NAME            475T4 NEW
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180526
Time                22.53
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG       cosygpmfqf
TD                  2048
SOLVENT             MeOD
NS                    16
DS                     8
SWH              4795.396 Hz
FIDRES           2.341502 Hz
AQ               0.2135381 sec
RG                    203
DW                104.267 usec
DE                   6.50 usec
TE                  296.5 K
D0             0.00000300 sec
D1             1.93569195 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00020825 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.09 usec
PL1                 -1.00 dB
PL1W          12.14314651 W
SFO1         400.1324008 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPNAM[3]         SINE.100
GPZ1                16.00 %
GPZ2                12.00 %
GPZ3                40.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                    128
SFO1             400.1324 MHz
FIDRES          37.512413 Hz
SW                 12.000 ppm
FnMODE                QF

F2 - Processing parameters
SI                   1024
SF            400.1300068 MHz
WDW                  SINE
SSB       0
LB        0 Hz
GB        0
PC                    1.40

F1 - Processing parameters
SI                   1024
MC2                    QF
```

Figure S23. HMBC spectrum of penicisteroid G (4)



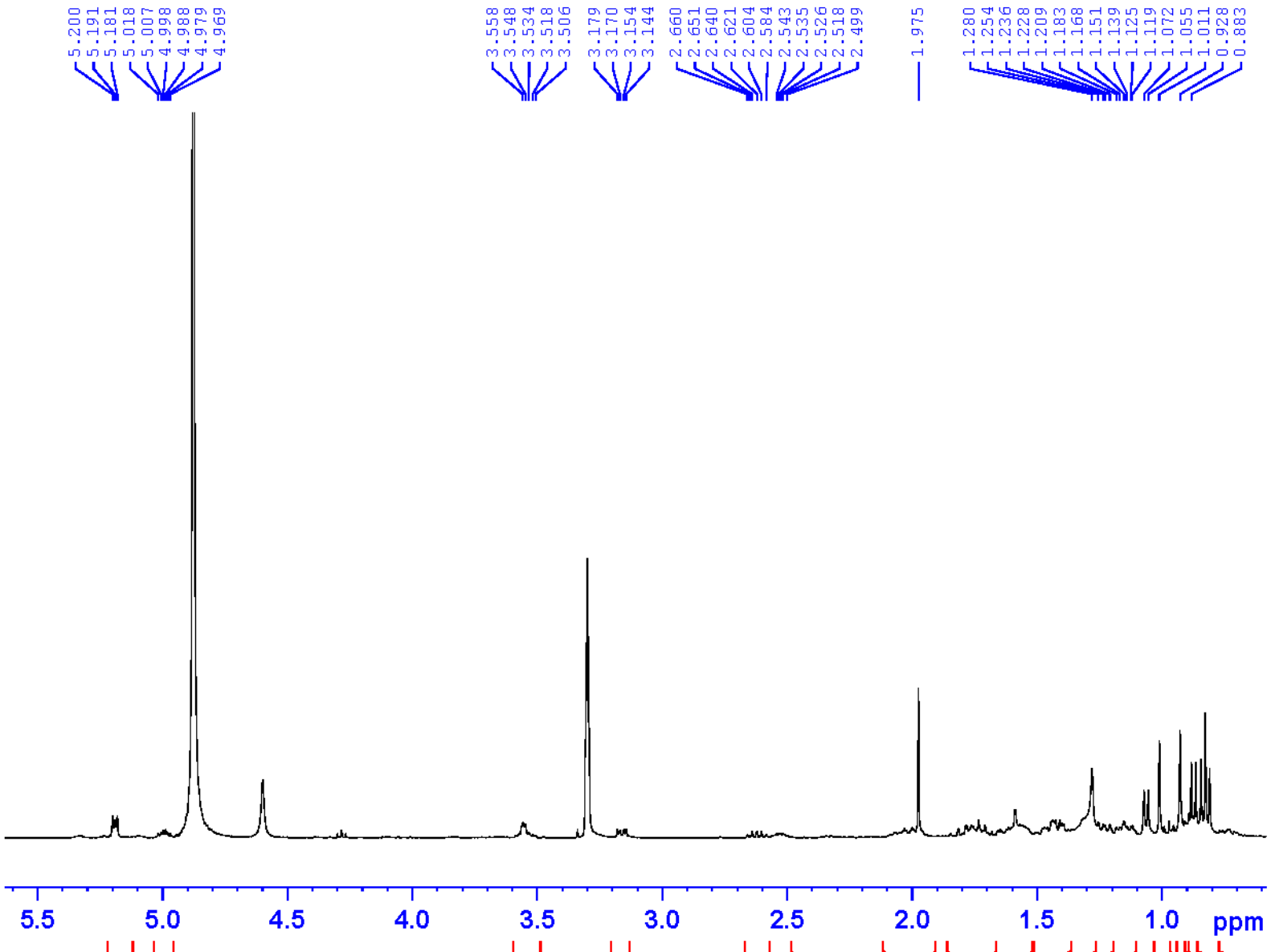

```
Current Data Parameters
NAME                 475T4 NEW
EXPNO                        7
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20180527
Time                      0.09
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG          hmbcgpndqf
TD                        4096
SOLVENT                   MeOD
NS                          48
DS                          16
SWH                 4795.396 Hz
FIDRES              1.170751 Hz
AQ                  0.4270763 sec
RG                        203
DW                    104.267 usec
DE                      6.50 usec
TE                     296.1 K
CNST13               8.0000000
D0                  0.00000300 sec
D1                  1.37220395 sec
D6                  0.06250000 sec
D16                 0.00020000 sec
IN0                 0.00002070 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.09 usec
P2                      26.18 usec
PL1                     -1.00 dB
PL1W               12.14314651 W
SF01               400.1324008 MHz

======== CHANNEL f2 ========
NUC2                      13C
P3                      12.37 usec
PL2                      1.00 dB
PL2W               28.13319778 W
SF02               100.6248425 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]              SINE.100
GPNAM[2]              SINE.100
GPNAM[3]              SINE.100
GPZ1                    50.00 %
GPZ2                    30.00 %
GPZ3                    40.10 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         128
SF01                100.6248 MHz
FIDRES              188.671585 Hz
SW                     240.000 ppm
FnMODE                      QF

F2 - Processing parameters
SI                        1024
SF                 400.1300068 MHz
WDW                       SINE
SSB          0
LB           0 Hz
GB           0
PC                        1.40

F1 - Processing parameters
SI                        1024
```

Figure S24. NOESY spectrum of penicisteroid G (4).




```
Current Data Parameters
NAME                 475T4 NEW
EXPNO                        8
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20180527
Time                      3.21
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                noesyph
TD                        2048
SOLVENT                   MeOD
NS                          40
DS                           4
SWH                  4795.396 Hz
FIDRES               2.341502 Hz
AQ                   0.2135381 sec
RG                         203
DW                   104.267 usec
DE                     6.50 usec
TE                     296.1 K
D0                   0.00008747 sec
D1                   2.00000000 sec
D8                   0.30000001 sec
IN0                  0.00020825 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.09 usec
PL1                     -1.00 dB
PL1W              12.14314651 W
SFO1              400.1324008 MHz

F1 - Acquisition parameters
TD                         256
SFO1                400.1324 MHz
FIDRES             18.756207 Hz
SW                     12.000 ppm
FnMODE           States-TPPI

F2 - Processing parameters
SI                        1024
SF                400.1300068 MHz
WDW                       QSINE
SSB                          2
LB             0 Hz
GB             0
PC                        1.00

F1 - Processing parameters
SI                        1024
MC2               States-TPPI
SF                400.1300068 MHz
```

Figure S25. 1H-NMR spectrum of penicisteroid H (5)



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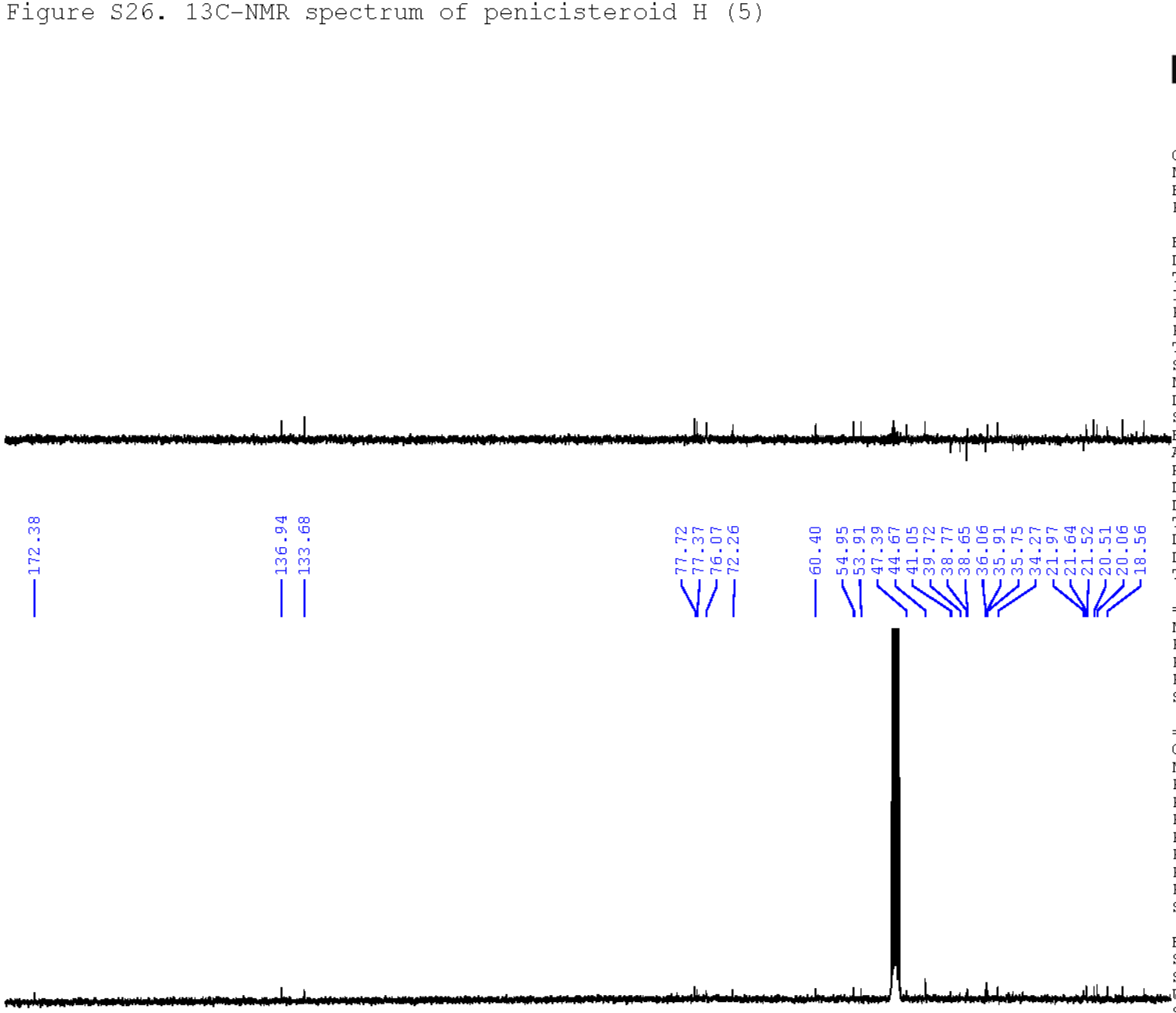
```
Current Data Parameters
NAME        475T48 D NEW
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180509
Time               21.49
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    49
DS                     0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9845889 sec
RG                   203
DW                60.800 usec
DE                 6.50 usec
TE                296.1 K
D1           2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.09 usec
PL1               -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300065 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

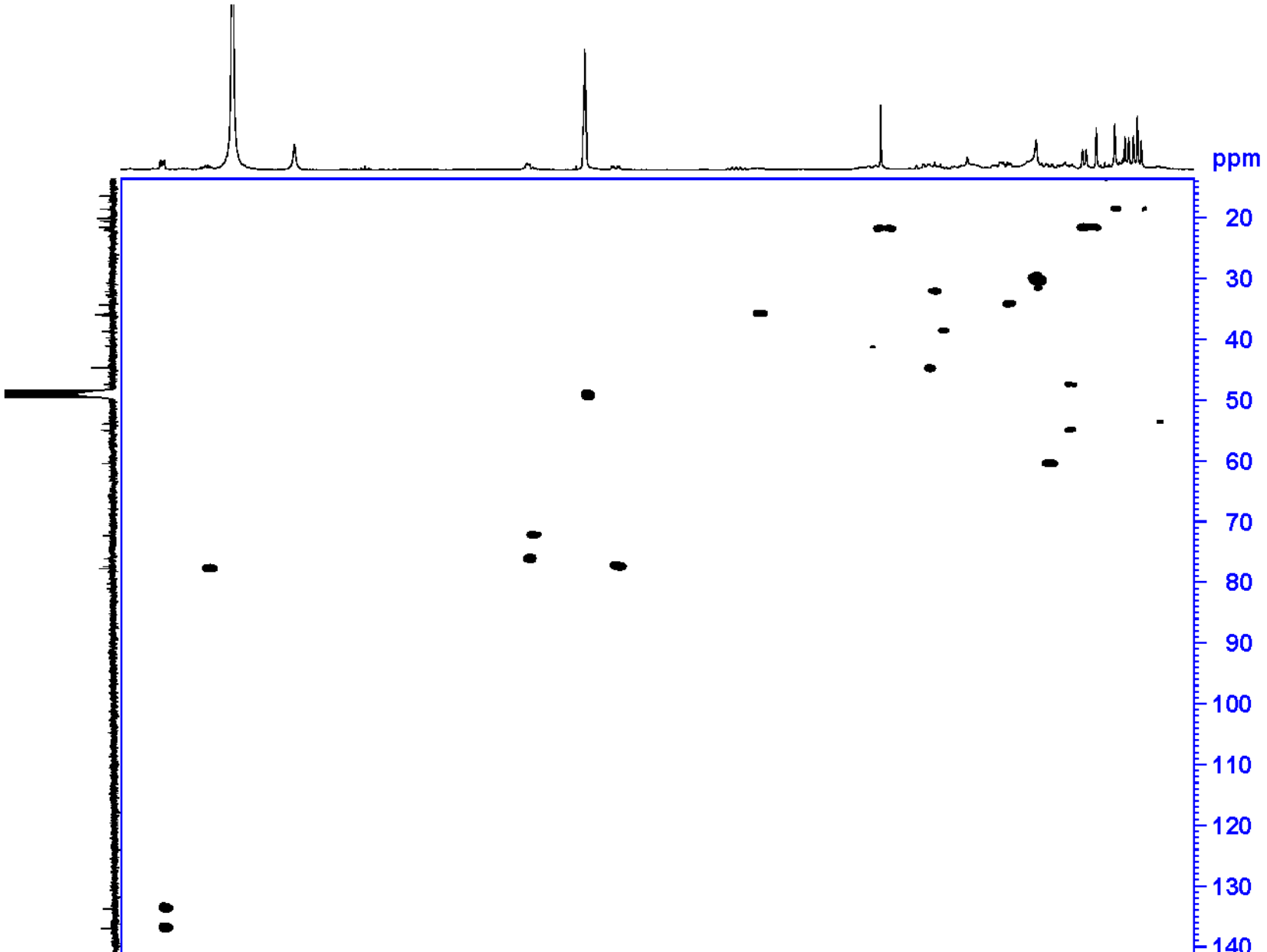
Figure S26. 13C-NMR spectrum of penicisteroid H (5)



BRUKER

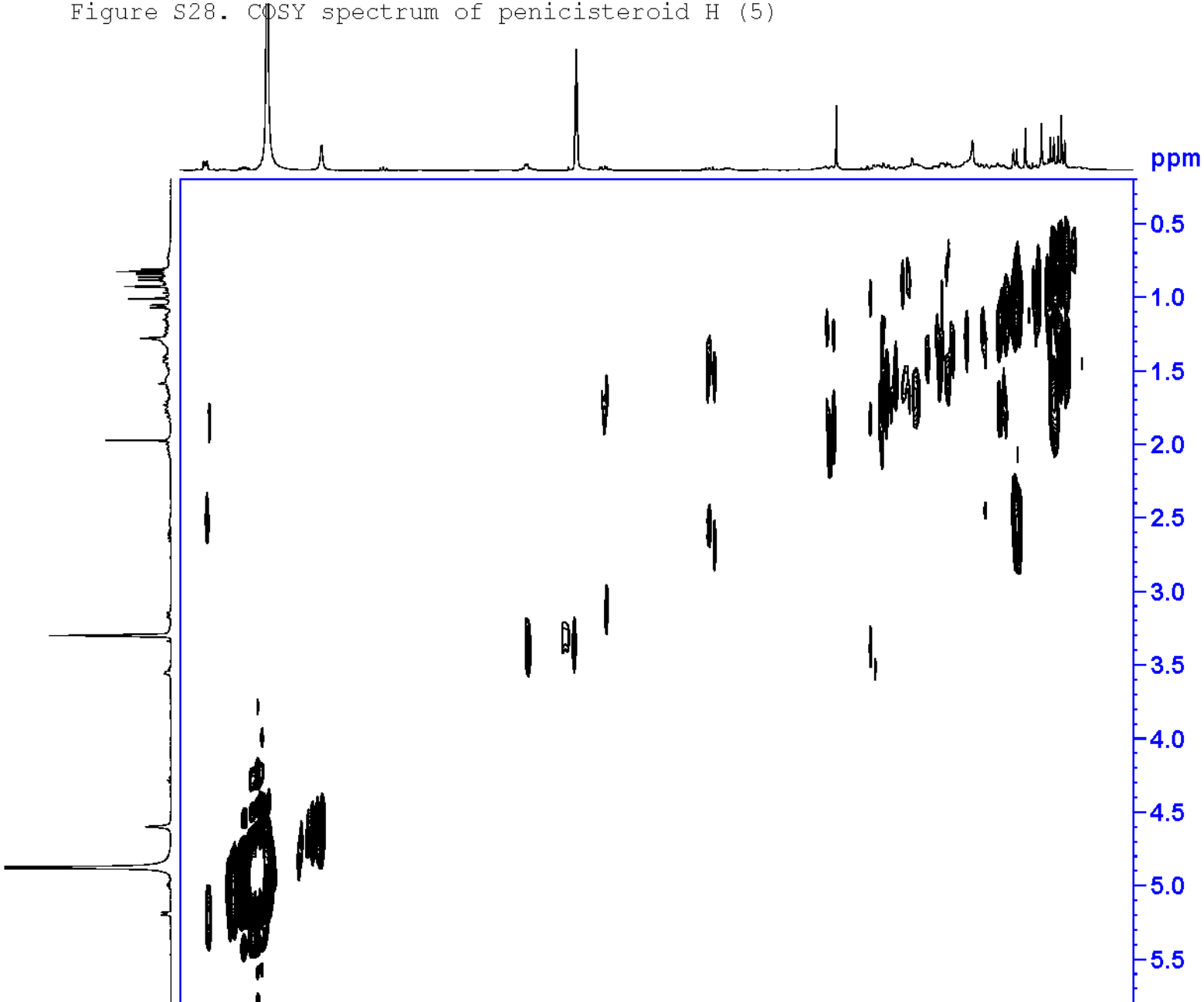
```
Current Data Parameters
NAME       475T48 D NEW
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20180531
Time               8.37
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT             MeOD
NS                12800
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.37 usec
PL1                1.00 dB
PL1W         28.13319778 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              14.72 dB
PL13              14.50 dB
PL2W         12.14314651 W
PL12W         0.32533529 W
PL13W         0.34224036 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6126271 MHz
WDW                   EM
SSB                    0
```

Figure S27. HSQC spectrum of penicisteroid H (5)



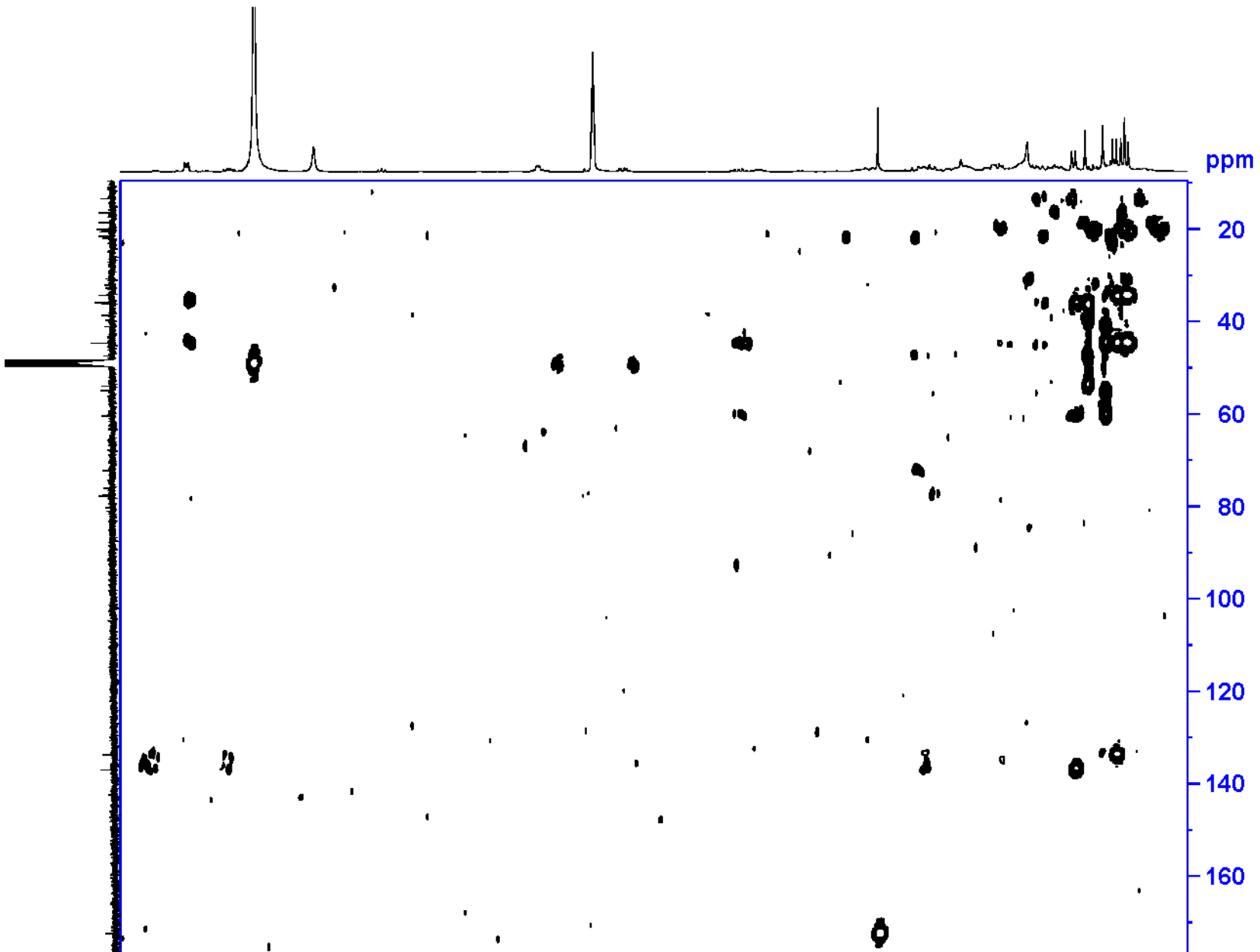

```
Current Data Parameters
NAME        475T48 D NEW
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180616
Time              10.08
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG      hsqcedetgp
TD                 1024
SOLVENT            MeOD
NS                  180
DS                   32
SWH           5197.505 Hz
FIDRES        5.075689 Hz
AQ           0.0985088 sec
RG                 203
DW              96.200 usec
DE               6.50 usec
TE              296.2 K
CNST2       145.0000000
D0           0.00000300 sec
D1           1.50000000 sec
D4           0.00172414 sec
D11          0.03000000 sec
D13          0.00000400 sec
D16          0.00020000 sec
D21          0.00345000 sec
IN0          0.00002260 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                 1H
P1                13.09 usec
P2                26.18 usec
P28                1.00 usec
PL1               -1.00 dB
PL1W        12.14314651 W
SFO1       400.1324008 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp
NUC2                13C
P3                12.37 usec
P4                24.74 usec
PCPD2             75.00 usec
PL2                1.00 dB
PL12              16.65 dB
PL2W        28.13319778 W
PL12W        0.76598305 W
SFO2       100.6238364 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1          100.6238 MHz
FIDRES        86.473610 Hz
SW              220.000 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                 1024
SF          400.1300068 MHz
WDW               QSINE
SSB                   2
LB        0 Hz
GB        0
PC                 1.40

F1 - Processing parameters
```

Figure S28. COSY spectrum of penicisteroid H (5)



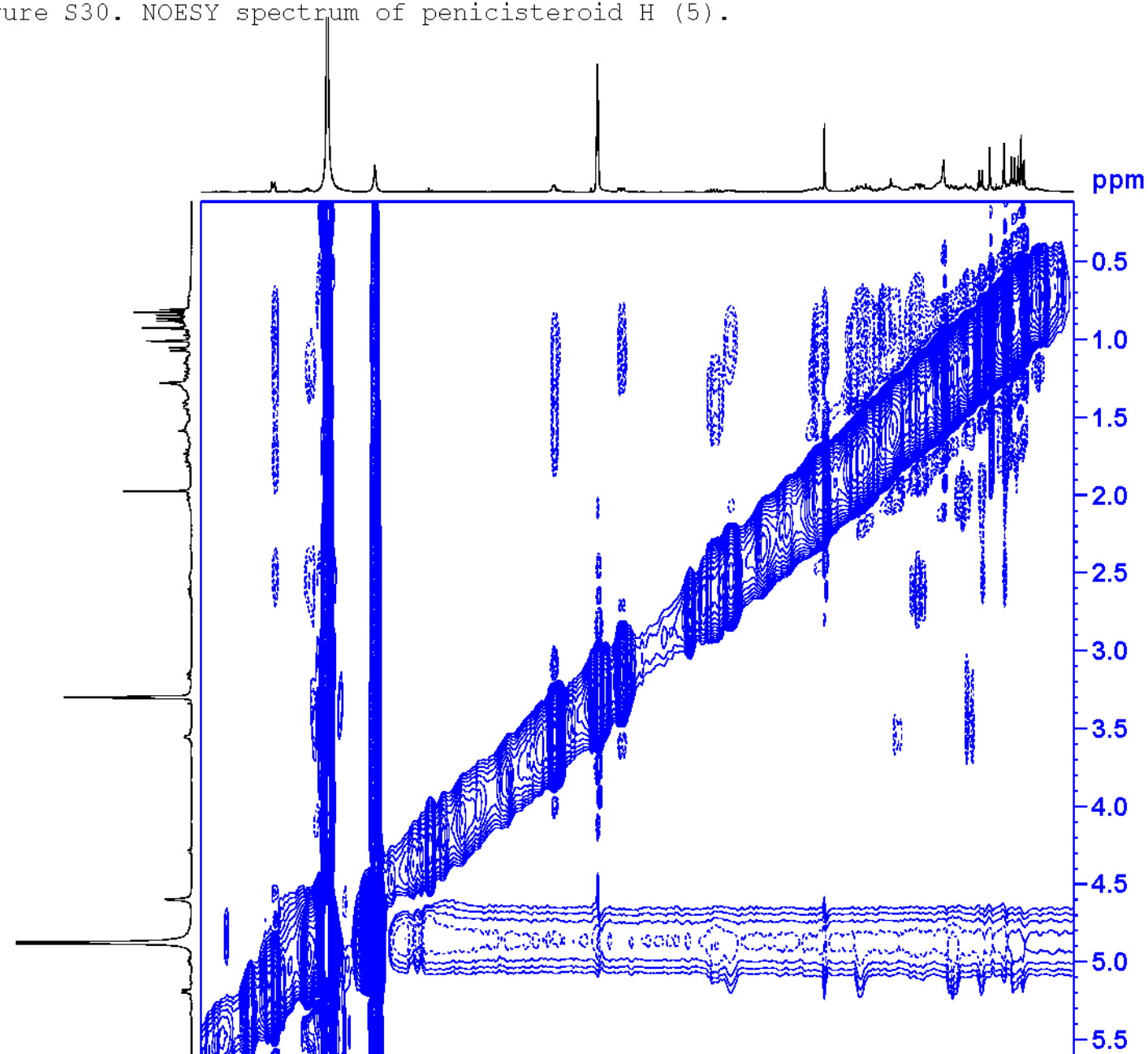

```
Current Data Parameters
NAME        475T48 D NEW
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180614
Time                6.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG      cosygpmfqf
TD                 2048
SOLVENT            MeOD
NS                   32
DS                    8
SWH            4795.396 Hz
FIDRES         2.341502 Hz
AQ            0.2135381 sec
RG                  203
DW              104.267 usec
DE                6.50 usec
TE               295.9 K
D0           0.00000300 sec
D1           1.93569195 sec
D13          0.00000400 sec
D16          0.00020000 sec
INO          0.00020825 sec

======== CHANNEL f1 ========
NUC1                1H
P1                13.09 usec
PL1               -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324008 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPZ1              16.00 %
GPZ2              12.00 %
GPZ3              40.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   26
SFO1          400.1324 MHz
FIDRES       184.676498 Hz
SW               12.000 ppm
FnMODE               QF

F2 - Processing parameters
SI                 1024
SF          400.1300068 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
PC                 1.40

F1 - Processing parameters
SI                 1024
MC2                  QF
```

Figure S29. HMBC spectrum of penicisteroid H (5)




```
Current Data Parameters
NAME        475T48 D NEW
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180613
Time              17.45
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG      hmbcgpndqf
TD                 4096
SOLVENT            MeOD
NS                  200
DS                   16
SWH           4795.396 Hz
FIDRES        1.170751 Hz
AQ            0.4270763 sec
RG                  203
DW              104.267 usec
DE                6.50 usec
TE                296.2 K
CNST13         8.0000000
D0          0.00000300 sec
D1          1.37220395 sec
D6          0.06250000 sec
D16         0.00020000 sec
IN0         0.00002070 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                13.09 usec
P2                26.18 usec
PL1               -1.00 dB
PL1W        12.14314651 W
SFO1        400.1324008 MHz

======== CHANNEL f2 ========
NUC2                13C
P3                12.37 usec
PL2                1.00 dB
PL2W        28.13319778 W
SFO2        100.6248425 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPZ1              50.00 %
GPZ2              30.00 %
GPZ3              40.10 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  128
SFO1          100.6248 MHz
FIDRES       188.671585 Hz
SW            240.000 ppm
FnMODE               QF

F2 - Processing parameters
SI                 1024
SF          400.1300068 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
PC                1.40

F1 - Processing parameters
SI                 1024
```

Figure S30. NOESY spectrum of penicisteroid H (5).



BRUKER

```
Current Data Parameters
NAME        475T48 D NEW
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180617
Time               6.49
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG        noesyph
TD                2048
SOLVENT           MeOD
NS                  80
DS                   4
SWH           4795.396 Hz
FIDRES        2.341502 Hz
AQ           0.2135381 sec
RG                 203
DW             104.267 usec
DE                6.50 usec
TE               296.1 K
D0           0.00008747 sec
D1           2.00000000 sec
D8           0.30000001 sec
IN0          0.00020825 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                13.09 usec
PL1               -1.00 dB
PL1W        12.14314651 W
SFO1       400.1324008 MHz

F1 - Acquisition parameters
TD                    62
SFO1          400.1324 MHz
FIDRES       77.444984 Hz
SW               12.000 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                  1024
SF          400.1300068 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF          400.1300068 MHz
```