Electronic Supplementary Information

for

Structure-Activity Studies of the Pelorusides: New Congeners and Semi-Synthetic Analogues

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Table 1. 600 MHz NMR data for peloruside C-11 hemiacetal (**5**) in C_6D_6.

Position	^{13}C		^{1}H		COSY	HMBC
	δ_C[a]	mult.	δ_H	mult. (J,Hz)		
1	171.9[b]	C	-	-	-	-
2	76.0	CH	4.10	dd (8.1, 5.4)	2-OH, 3	1
2-OH	-	-	2.34	d (5.6)	2	1
3	76.6	CH	3.79	ddd (8.5, 5.7, 3.1)	2, 4a, 4b	-
3-OMe	56.5	CH_3	3.13	s	-	3
4a	31.2	CH_2	1.40	ddd (16.2, 5.9, 2.8)	3, 4b, 5	-
4b			2.14	dt (15.6, 3.6)	3, 4a, 5	-
5	79.1	CH	3.98	m	4a, 4b, 6b	-
6a	28.1	CH_2	1.41	m	6b, 7a, 7b	7
6b			1.79	m	5, 6a, 7a, 7b	5
7a	34.9	CH_2	1.84	m	6a, 6b, 7b	6, 8
7b			2.17	m	6a, 6b, 7a	6,8
8	106.5[b]	C	-	-	-	-
9	215.9[b]	C	-	-	-	-
10	45.5[b]	C	-	-	-	-
11	82.1	CH	4.42	dd (11.9, 2.0)	12a, 12b	8, 9, 10, 21
12a	37.4	CH_2	1.41	m	11, 12b, 13	-
12b			2.00	ddd (13.6, 12.0, 2.6)	11, 12a, 13	-
13	74.1	CH	3.94	dt (10.5, 2.8)	12a, 12b, 14a, 14b	-
13-OMe	55.8	CH_3	3.29	s	-	13
14a	36.7	CH_2	1.49	ddd (14.0, 11.3, 3.1)	13, 14b, 15	-
14b			2.60	ddd (14.2, 11.2, 3.0)	13, 14a, 15	-
15	71.7	CH	5.71	dd (11.3, 3.1)	14a, 14b, 17	-
16	135.5[b]	C	-	-	-	-
17	132.2	CH	4.99	d (10.6)	15, 18, 23	-
18	43.2	CH	2.65	m	17, 24a, 24b	-
19a	24.3	CH_2	0.90	m	19b, 20	-
19b			1.19	m	19a, 20	-
20	12.1	CH_3	0.72	t (7.4)	19a, 19b	18, 19
21	25.0	CH_3	0.95	s	-	9, 10, 11, 22
22	18.0	CH_3	0.92	s	-	9, 10, 11, 21
23	17.7	CH_3	1.77	d (1.3)	17	15, 16, 17
24a	66.6	CH_2	3.42	ddd (14.7, 9.8, 5.2)	18, 24b	17
24b			3.65	ddd (10.5, 6.4, 4.6)	18, 24a	17

[a] Assigned from HSQC data. [b] Assigned from HMBC data.

Table 2. 600 MHz NMR data for *seco*-peloruside A δ-lactone (**6**) in C_6D_6.

Position	^{13}C		^{1}H		COSY	HMBC
	δ_C [a]	mult.	δ_H	mult. (J,Hz)		
1	173.7 [b]	C	-	-	-	-
2	72.4	CH	3.89	dd (6.0, 2.5)	2-OH, 3	1, 3
2-OH	-	-	3.32	d (2.5)	2	1
3	78.5	CH	3.12	dt (6.5, 1.6)	2, 4b	2
3-OMe	56.6	CH_3	3.14	s	-	3
4a	35.7	CH_2	1.24	ddd (15.2, 11.0, 7.2)	3, 4b, 5	-
4b			1.50	dt (15.2, 2.1)	4a, 5	-
5	72.1	CH	4.62	m	4a, 4b, 6a, 6b	-
6a	35.2	CH_2	1.66	m	5, 6b, 7	-
6b			1.71	m	5, 6a, 7	-
7	76.6	CH	4.10	ddd (9.6, 3.8, 2.8)	6a, 6b, 8	-
7-OMe	56.9	CH_3	3.22	s	-	7
8	73.4	CH	4.91	dd (6.0, 4.2)	7, 8-OH	7, 9
8-OH	-	-	3.59	d (6.0)	8	9
9	215.3 [b]	C	-	-	-	-
10	51.6 [b]	C	-	-	-	-
11	73.8	CH	4.37	d (10.8)	11-OH, 12a, 12b	-
11-OH	-	-	3.99	d (1.7)	11	-
12a	32.7	CH_2	1.67	m	11, 12b, 13	-
12b			1.78	ddd (15.5, 10.7, 4.9)	11, 12a, 13	-
13	77.2	CH	3.74	app. sextet (4.3)	12a, 12b, 14a, 14b	-
13-OMe	56.2	CH_3	3.03	s	-	13
14a	34.2	CH_2	1.86	ddd (14.3, 8.7, 3.1)	14b	-
14b			1.92	ddd (14.2, 9.1, 4.4)	13, 14a, 15	-
15	73.9	CH	3.96	br d (7.8)	14a, 17	-
16	134.8 [b]	C	-	-	-	-
17	125.0	CH	5.43	d (4.1)	15, 18, 23	-
18	36.5	CH	1.69	m	17, 19, 24a, 24b	-
19	26.5	CH_2	1.36	m	18, 20	- -
20	11.6	CH_3	0.84	t (7.5)	19	-
21	19.1	CH_3	1.27	s	22	9, 10, 11, 22
22	21.5	CH_3	1.15	s	21	9, 10, 11, 21
23	19.2	CH_3	1.49	s	17	15, 16, 17
24a	66.1	CH_2	3.49	dd (11.0, 4.1)	18, 24b	-
24b			3.56	dd (11.1, 3.4)	18, 24a	-

[a] Assigned from HSQC data. [b] Assigned from HMBC data.

Table 3. 600 MHz ^{1}H and NOESY NMR data for *seco*-peloruside A δ-lactone (**6**) in C_6D_6.

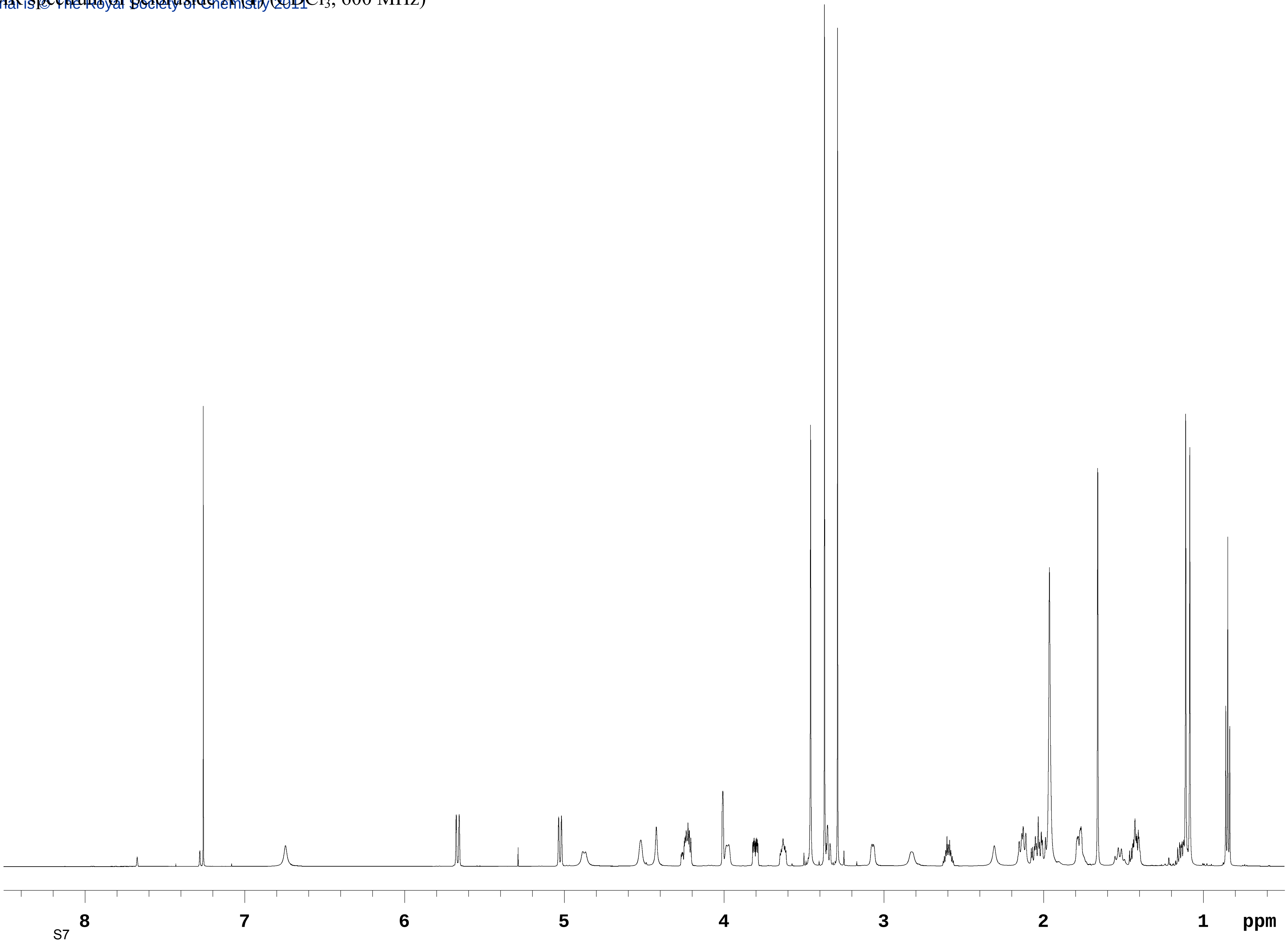
Position	^{1}H δ_H	^{1}H mult., J (Hz)	NOESY
1	-	-	-
2	3.89	dd (6.0, 2.5)	2-OH, 3, 3-OMe, 4b, 5
2-OH	3.32	d (2.5)	2, 3
3	3.12	dt (6.5, 1.6)	2, 2-OH, 4a, 4b
3-OMe	3.14	s	2, 4b
4a	1.24	ddd (15.2, 11.0, 7.2)	3, 4b, 6a
4b	1.50	dt (15.2, 2.1)	3, 4a, 5, 6b
5	4.62	m	2, 4b, 6a/6b, 7(w)
6a	1.66	m	5
6b	1.71	m	4b, 5
7	4.10	ddd (9.6, 3.8, 2.8)	5(w), 6a/6b, 7-OMe, 8, 21, 22
7-OMe	3.22	s	5, 7, 8, 21, 22
8	4.91	dd (6.0, 4.2)	7, 7-OMe, 11, 21, 22
8-OH	3.59	d (6.0)	6a/6b, 8
9	-	-	-
10	-	-	-
11	4.37	d (10.8)	8, 11-OH, 14a, 6a/12a, 21, 22
11-OH	3.99	d (1.7)	11
12a	1.67	m	13, 15
12b	1.78	ddd (15.5, 10.7, 4.9)	13, 13-OMe, 15
13	3.74	app. sextet (4.3)	12a, 12b, 13-OMe, 14a, 14b,
13-OMe	3.03	s	12b, 13, 14a, 14b
14a	1.86	ddd (14.3, 8.7, 3.1)	11, 13, 13-OMe, 14a, 23
14b	1.92	ddd (14.2, 9.1, 4.4)	11, 13, 13-OMe, 14b, 23
15	3.96	br d (7.8)	12a, 12b, 14a, 14b, 24a, 23
16	-	-	-
17	5.43	d (4.1)	12b, 18, 19, 20, 23
18	1.69	m	17, 24a, 24b, 19, 20
19	1.36	m	17, 18, 20
20	0.84	t (7.5)	12b, 17, 18, 19
21	1.27	s	7, 7-OMe, 8, 11, 12a, 12b, 22
22	1.15	s	7, 7-OMe, 8, 11, 12a, 12b, 21
23	1.49	s	14a, 14b, 17, 23
24a	3.49	dd (11.0, 4.1)	15, 18
24b	3.56	dd (11.1, 3.4)	18
24-OH	-		

Table 4. Mean IC_{50} and cell cycle arrest values (HL-60) for compounds **3**–**6**.

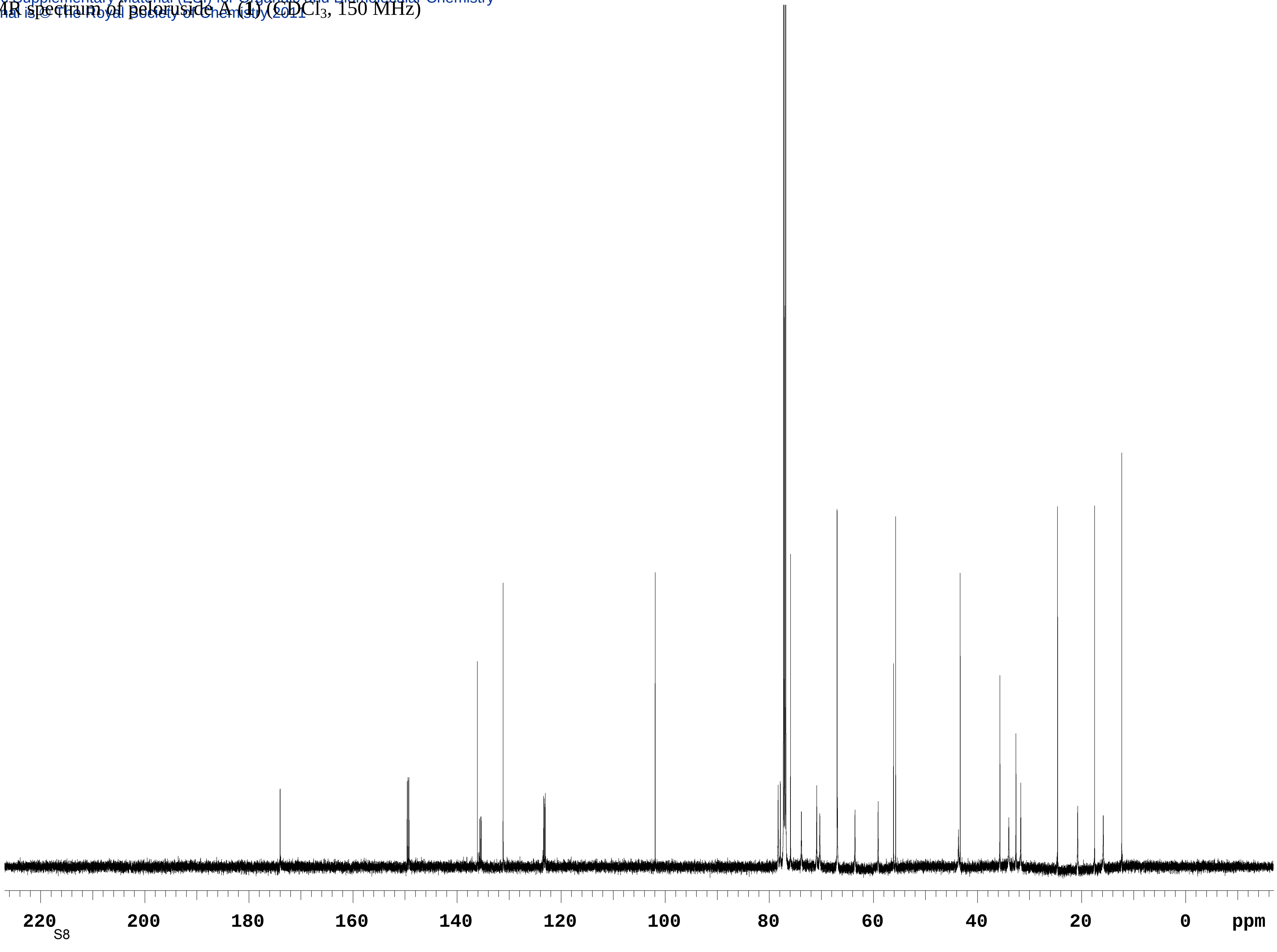
Compound	IC_{50} [IC_{50} (**1**)]	G_2/M Accumulation (**1**, Control)
3	221 ± 19 nM (15 ± 1 nM) (n = 2)[a]	13 ± 1 (68 ± 8%, 20 ± 4%)[b] (n = 3)
4	> 2 μM (10 ± 4 nM) (n = 3)	-[c]
5	> 15 μM[b]	-[c]
6	> 7 μM	-[c]

[a] Number of separate preparations. [b] HL-60 and 1A9 cell lines. [c] Not performed.

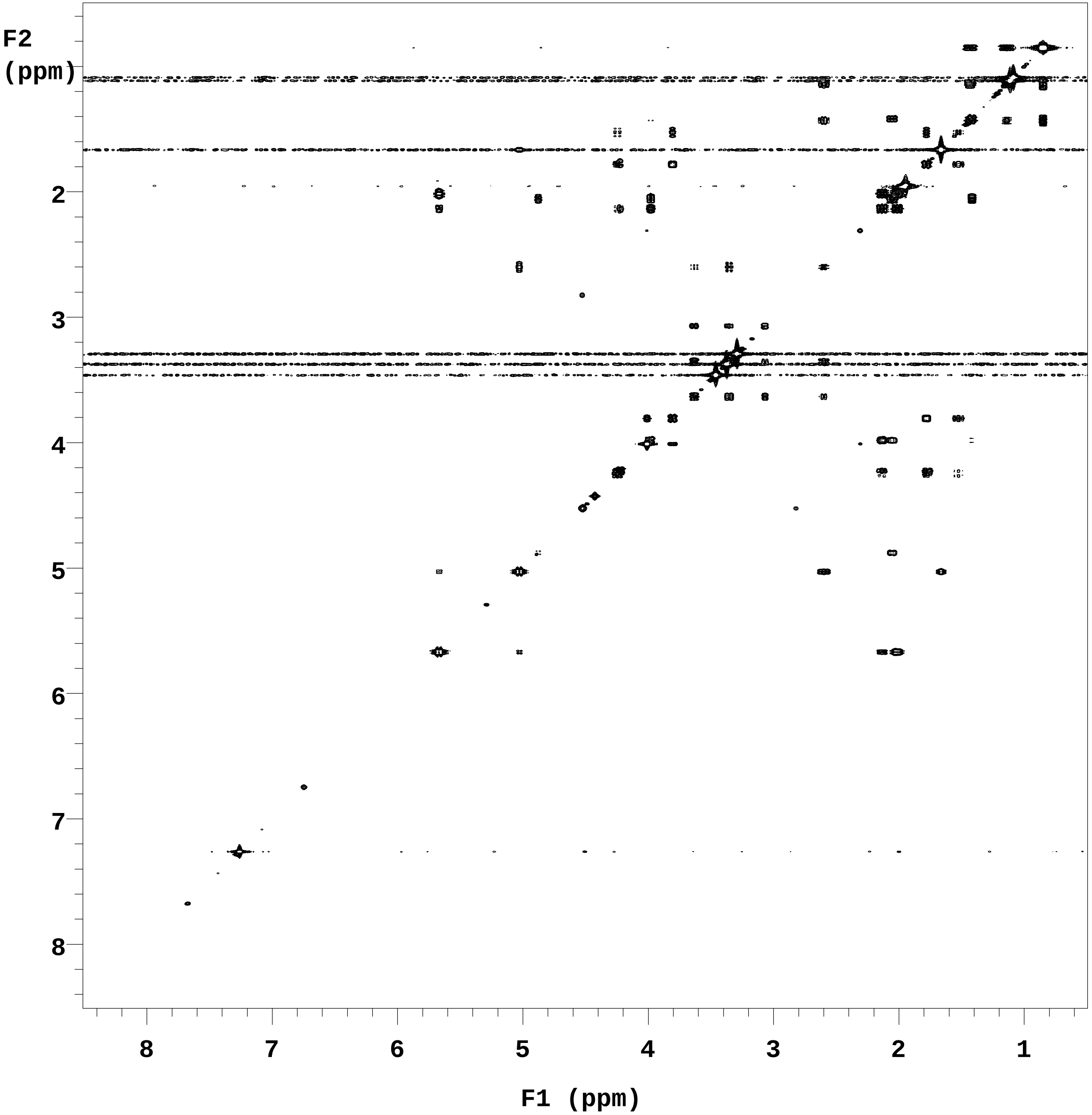
^{1}H NMR spectrum of peloruside A (**1**) ($CDCl_3$, 600 MHz)



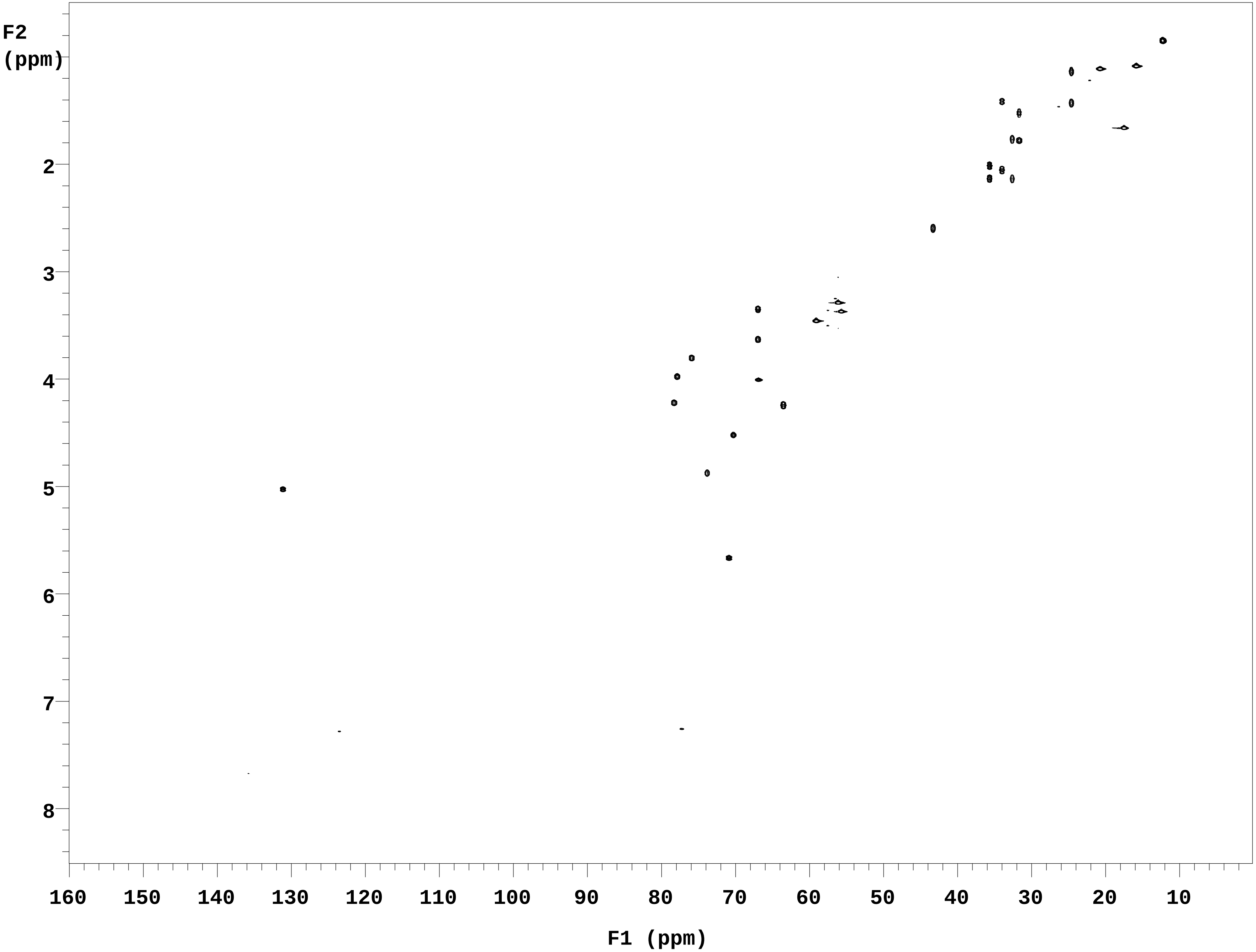
^{13}C NMR spectrum of peloruside A (1) ($CDCl_3$, 150 MHz)



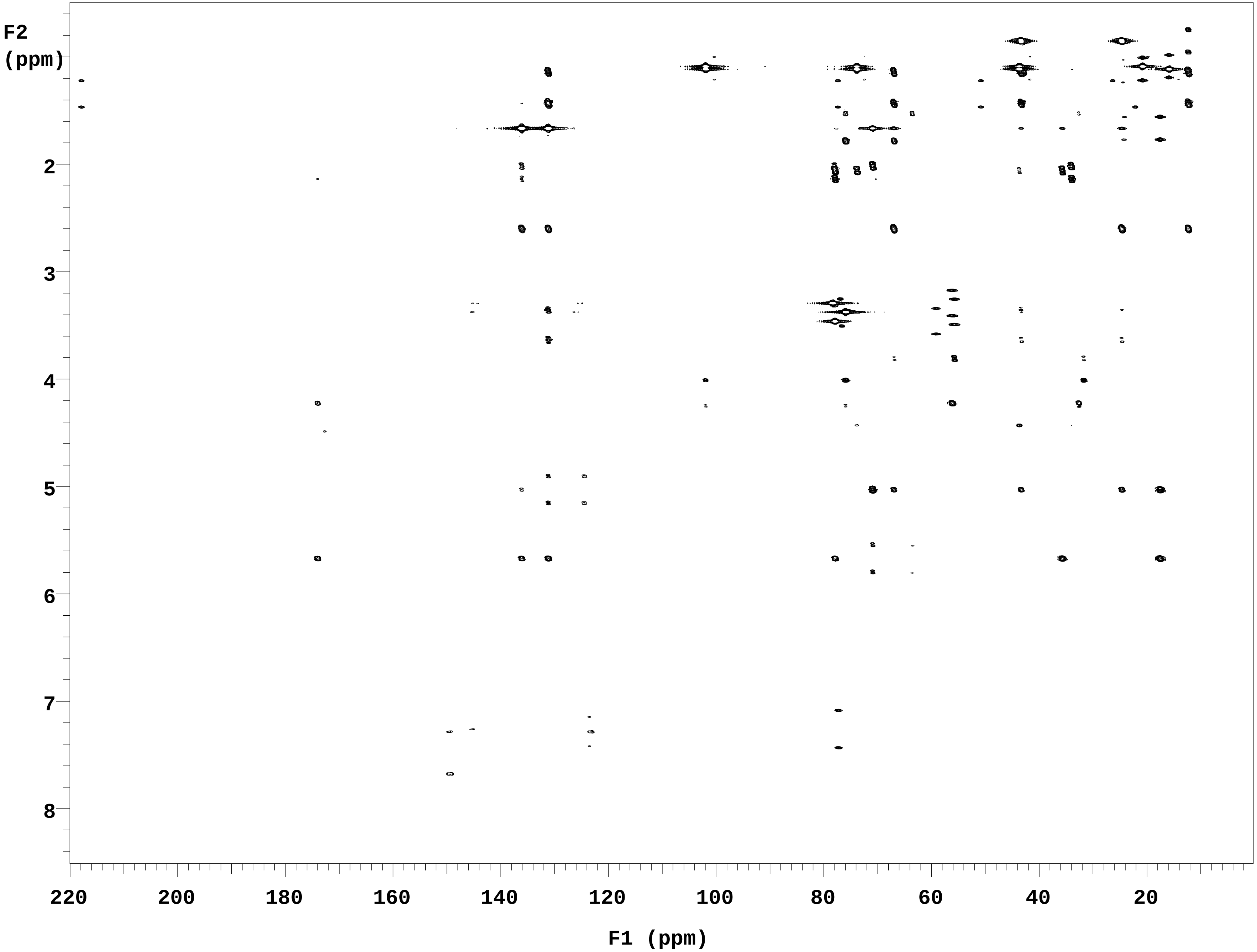
gCOSY NMR spectrum of peloruside A (1) ($CDCl_3$, 600 MHz)



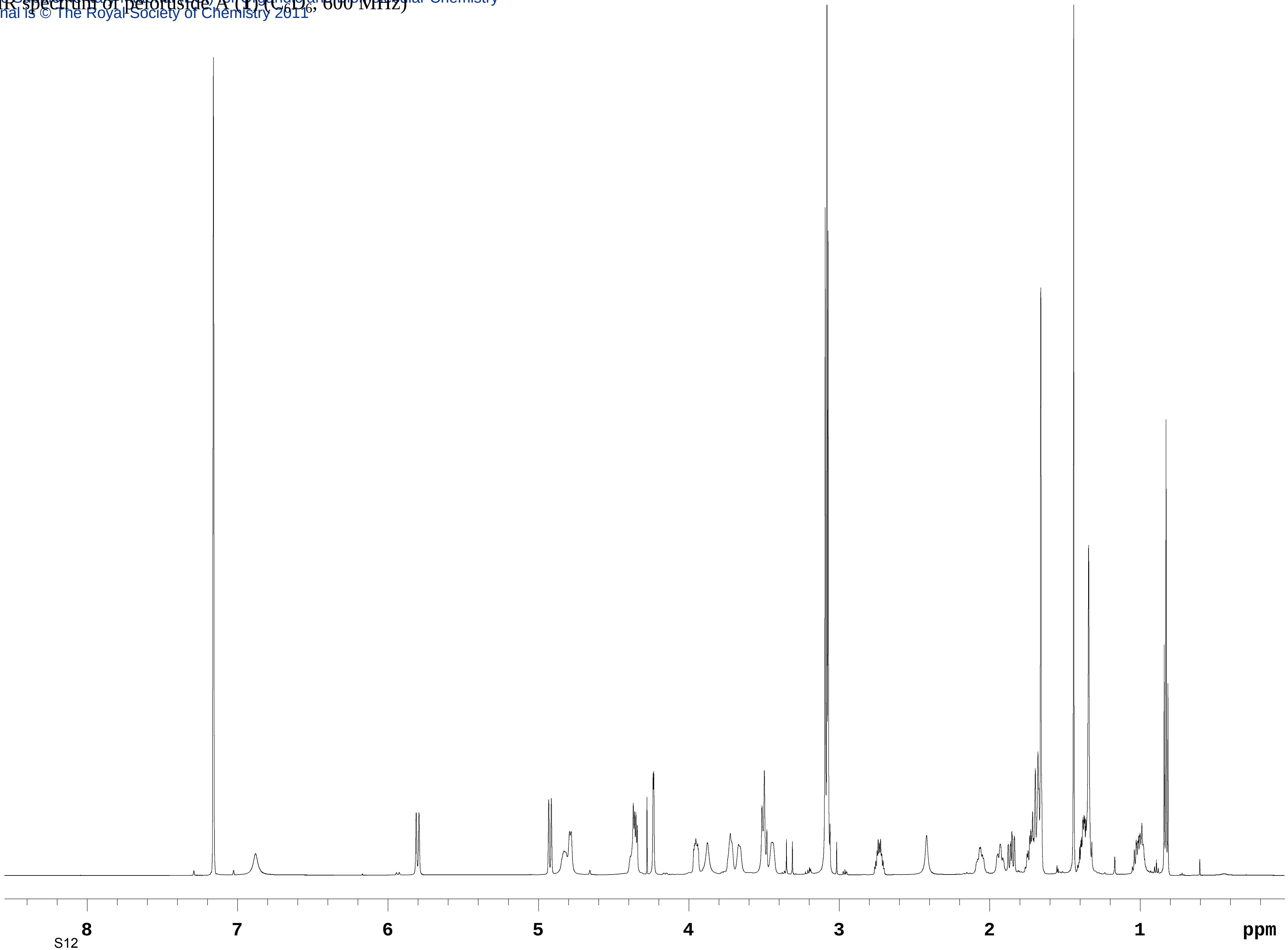
HSQCad NMR spectrum of pelorusides A (1) ($CDCl_3$, 600 MHz)



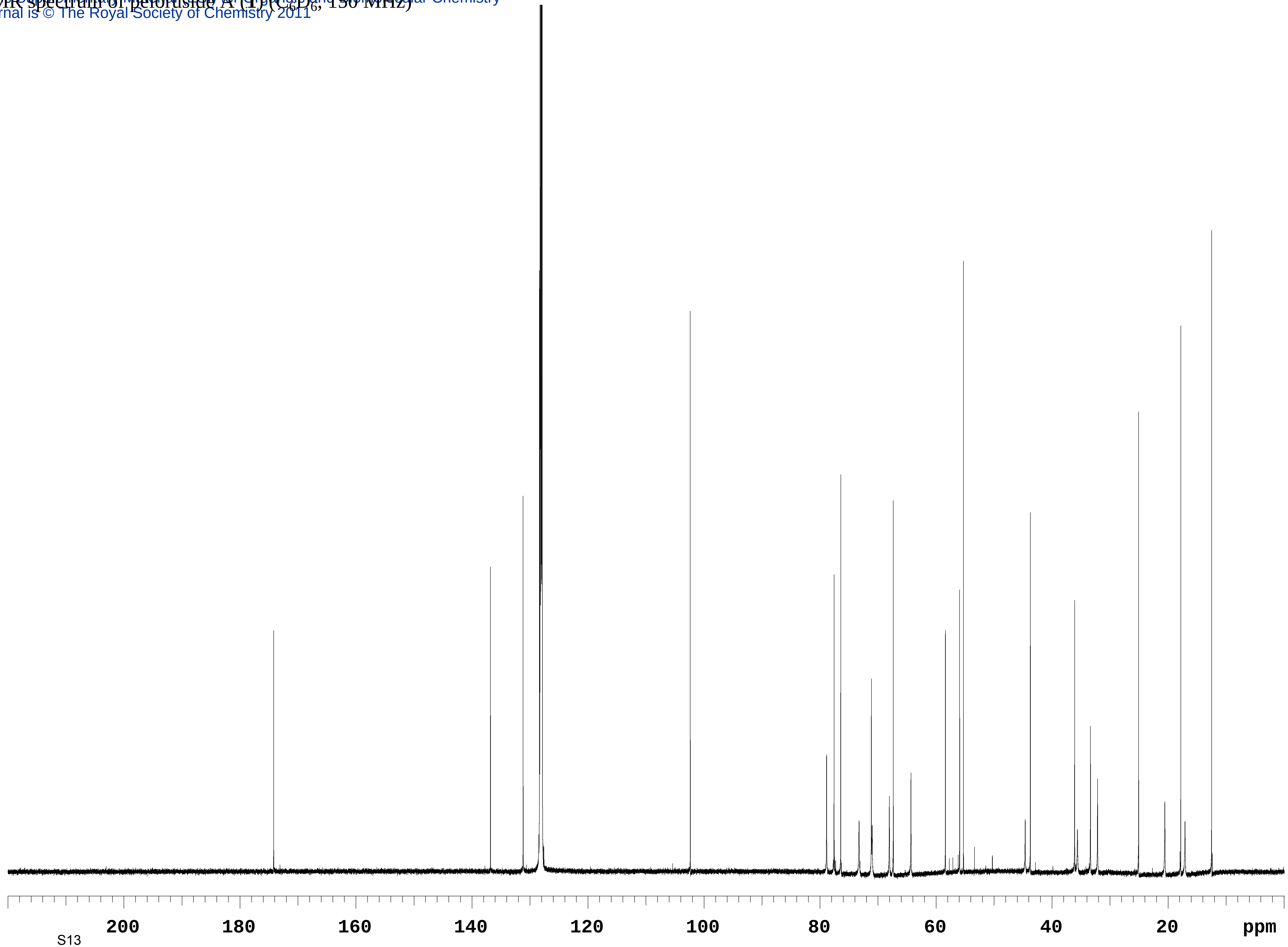
gHMBC NMR spectrum of pelorusside A (1) ($CDCl_3$, 600 MHz)



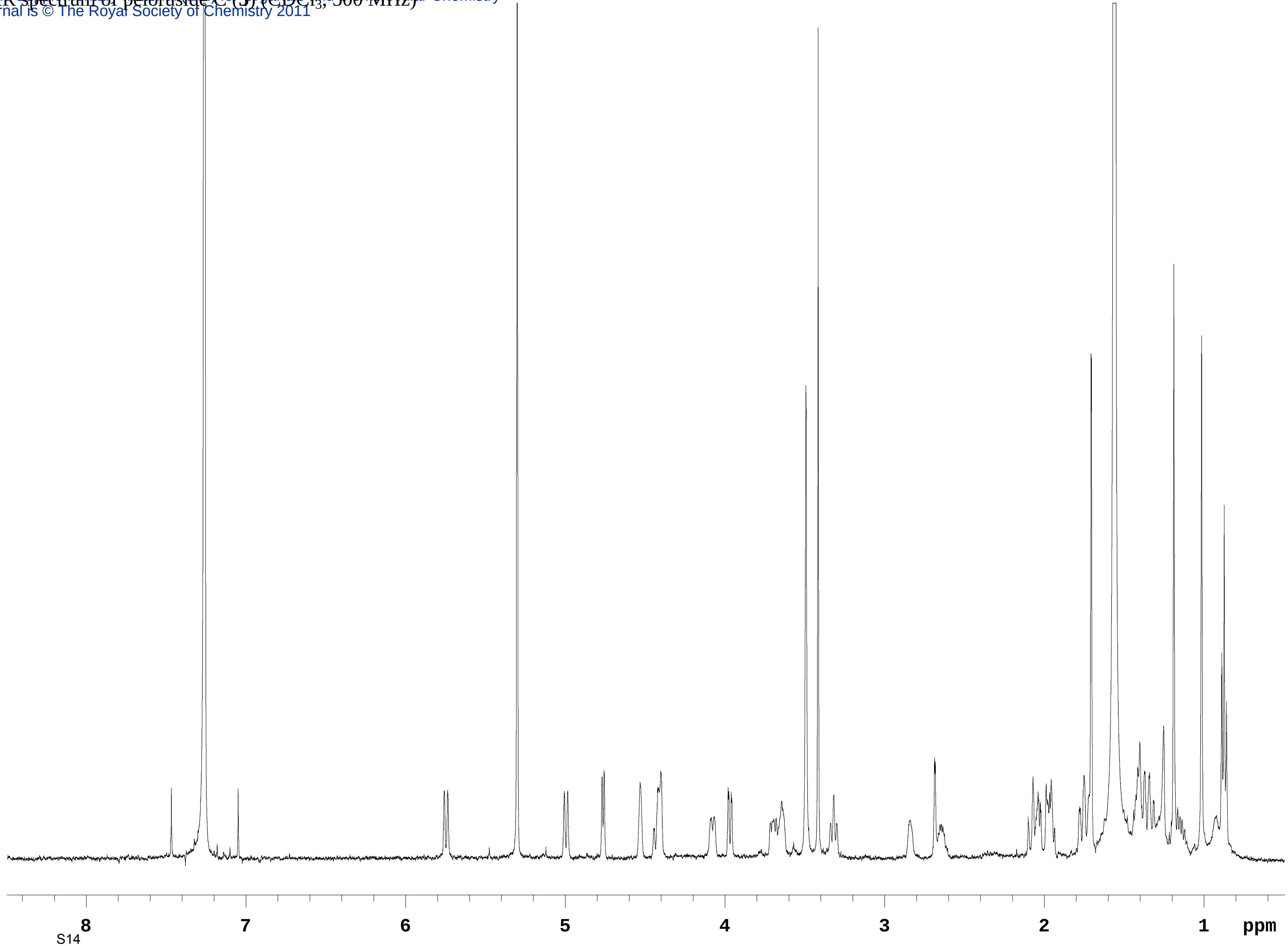
^1H NMR spectrum of peloruside A (1) (C_6D_6, 600 MHz)



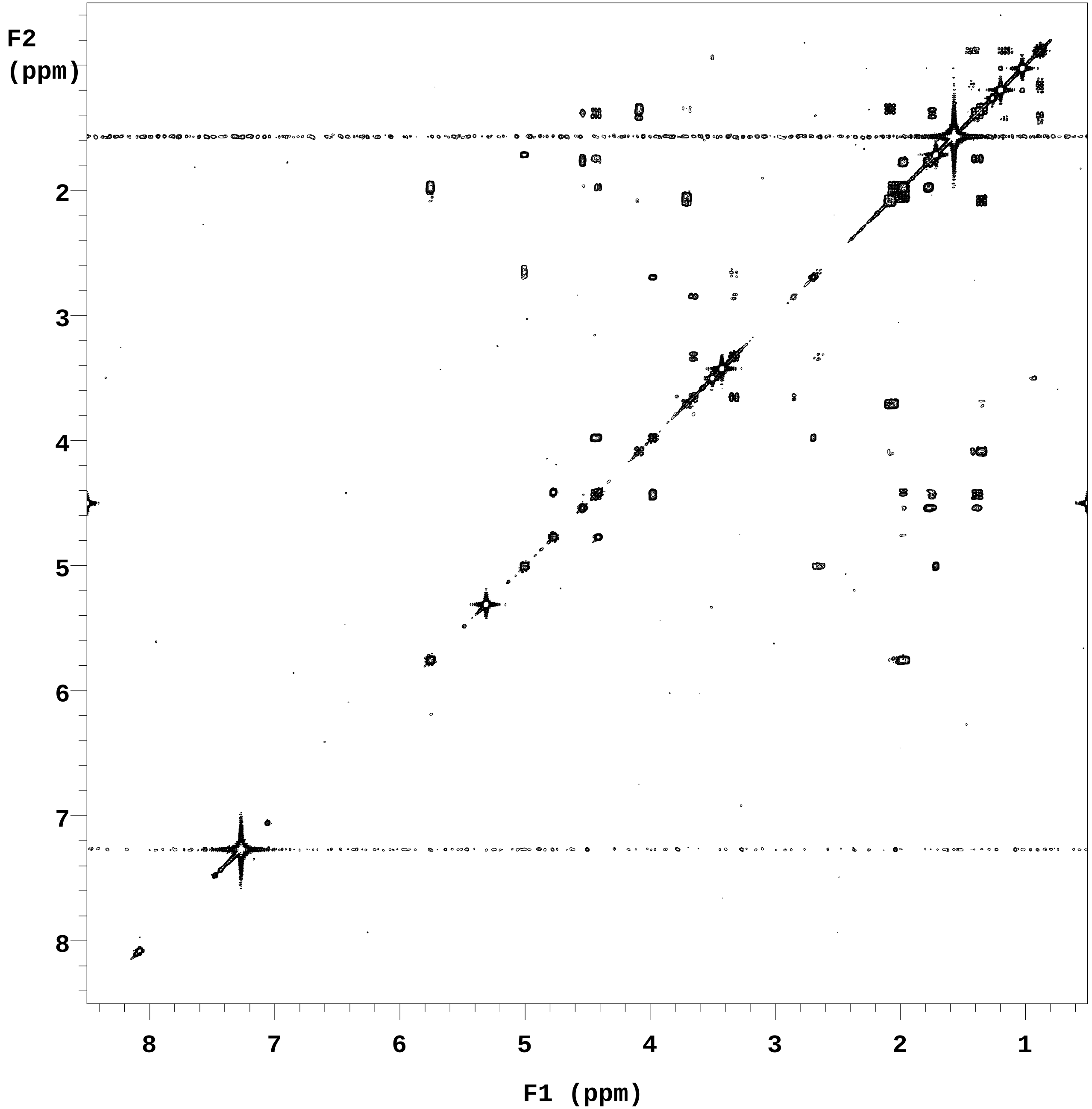
^{13}C NMR spectrum of pelorusid A (1) (C_6D_6, 150 MHz)



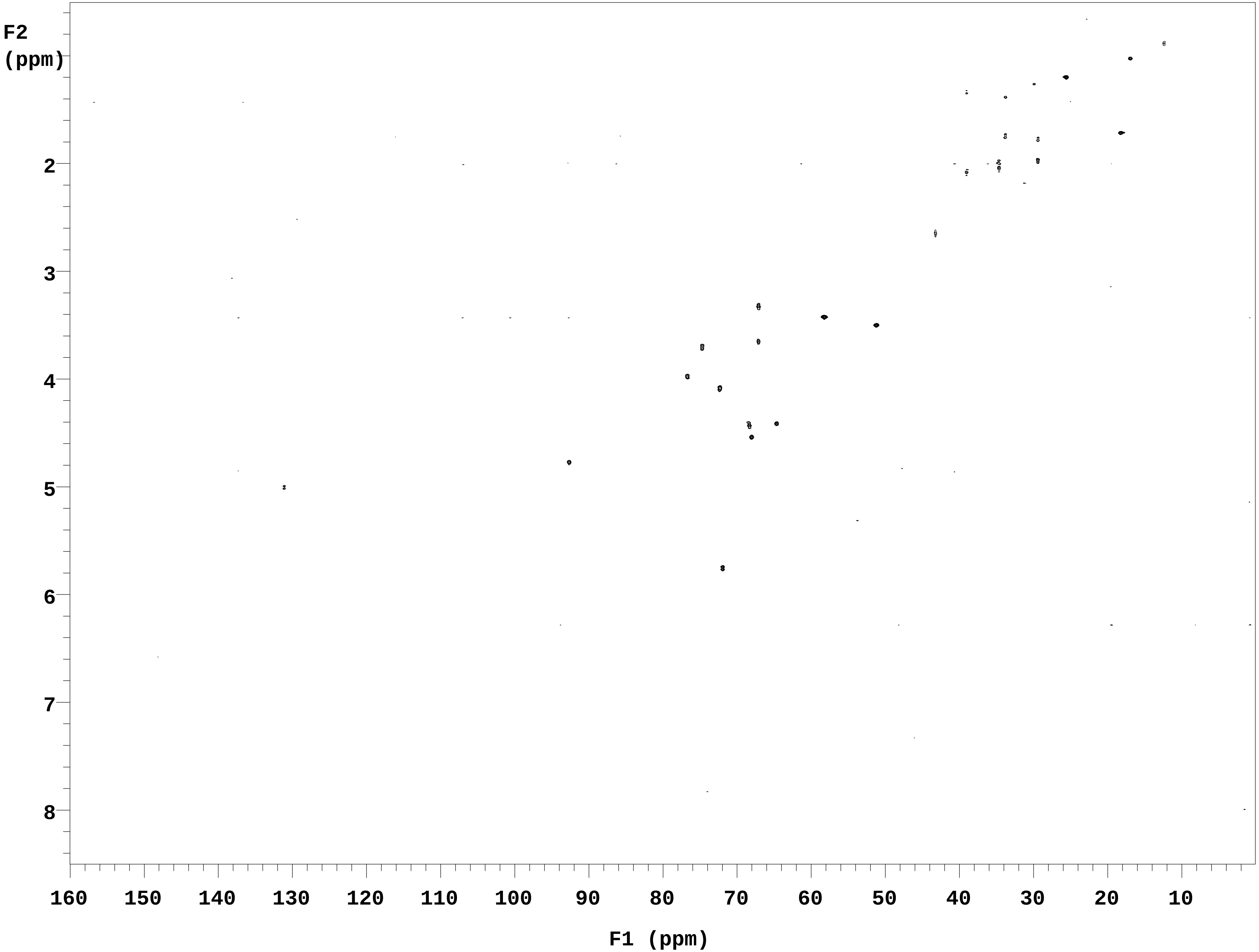
^{1}H NMR spectrum of peloruside C (**3**) ($CDCl_3$, 500 MHz)



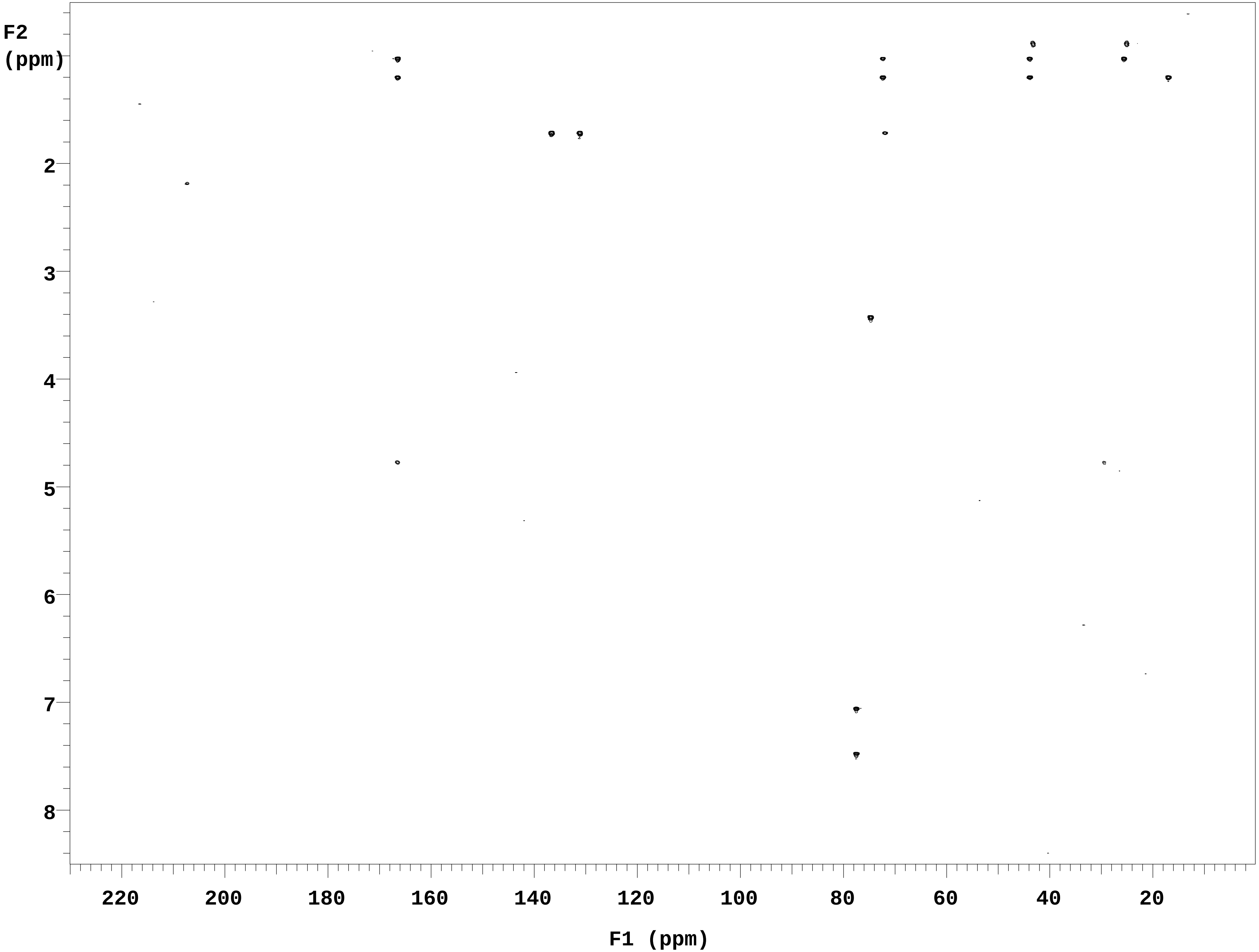
gCOSY NMR spectrum of peloruside C (3) ($CDCl_3$, 500 MHz)



HSQC NMR spectrum of pelorusside C (3) ($CDCl_3$, 500 MHz)



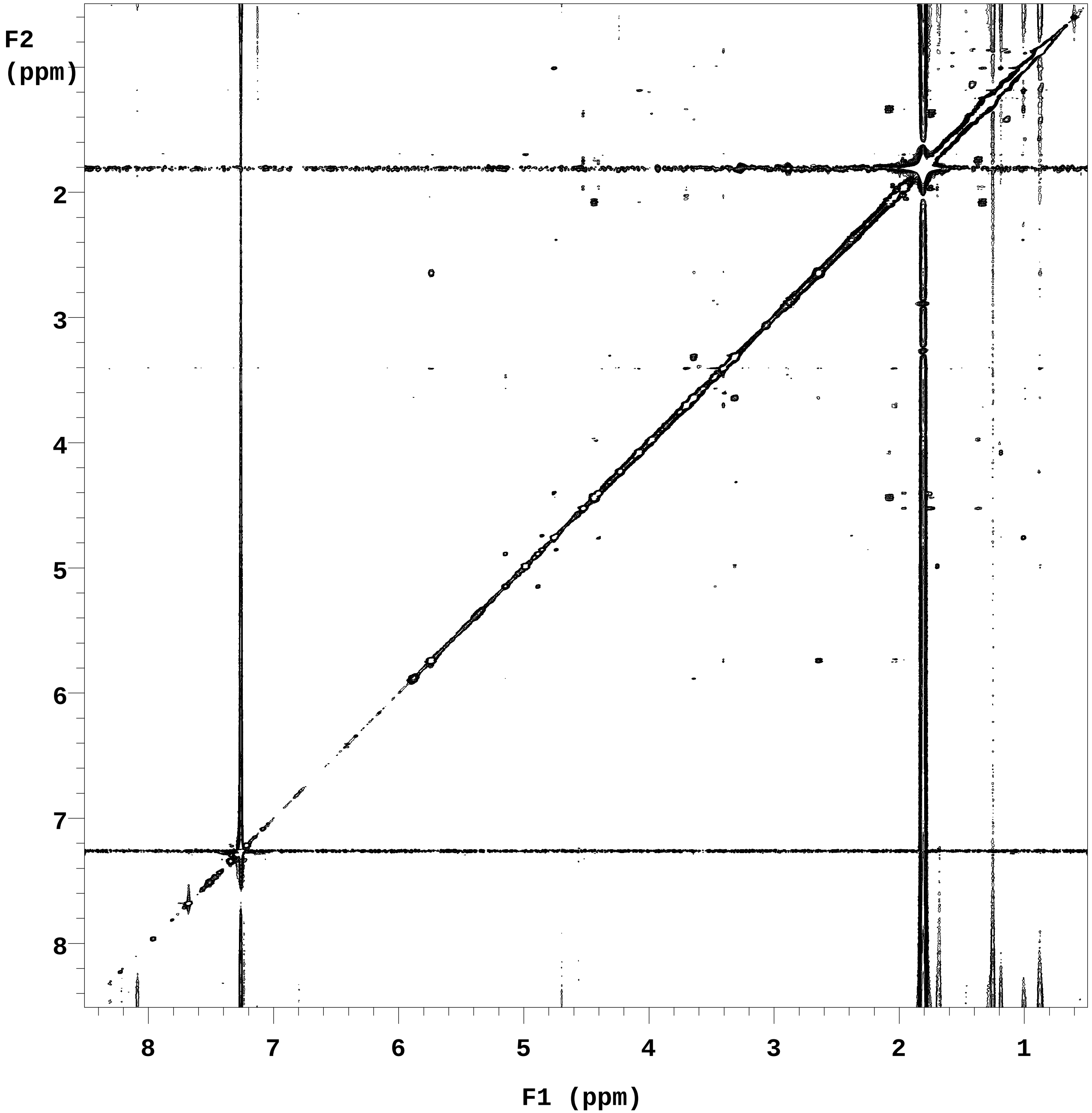
gHMBC NMR spectrum of peloruside C (3) ($CDCl_3$, 500 MHz)



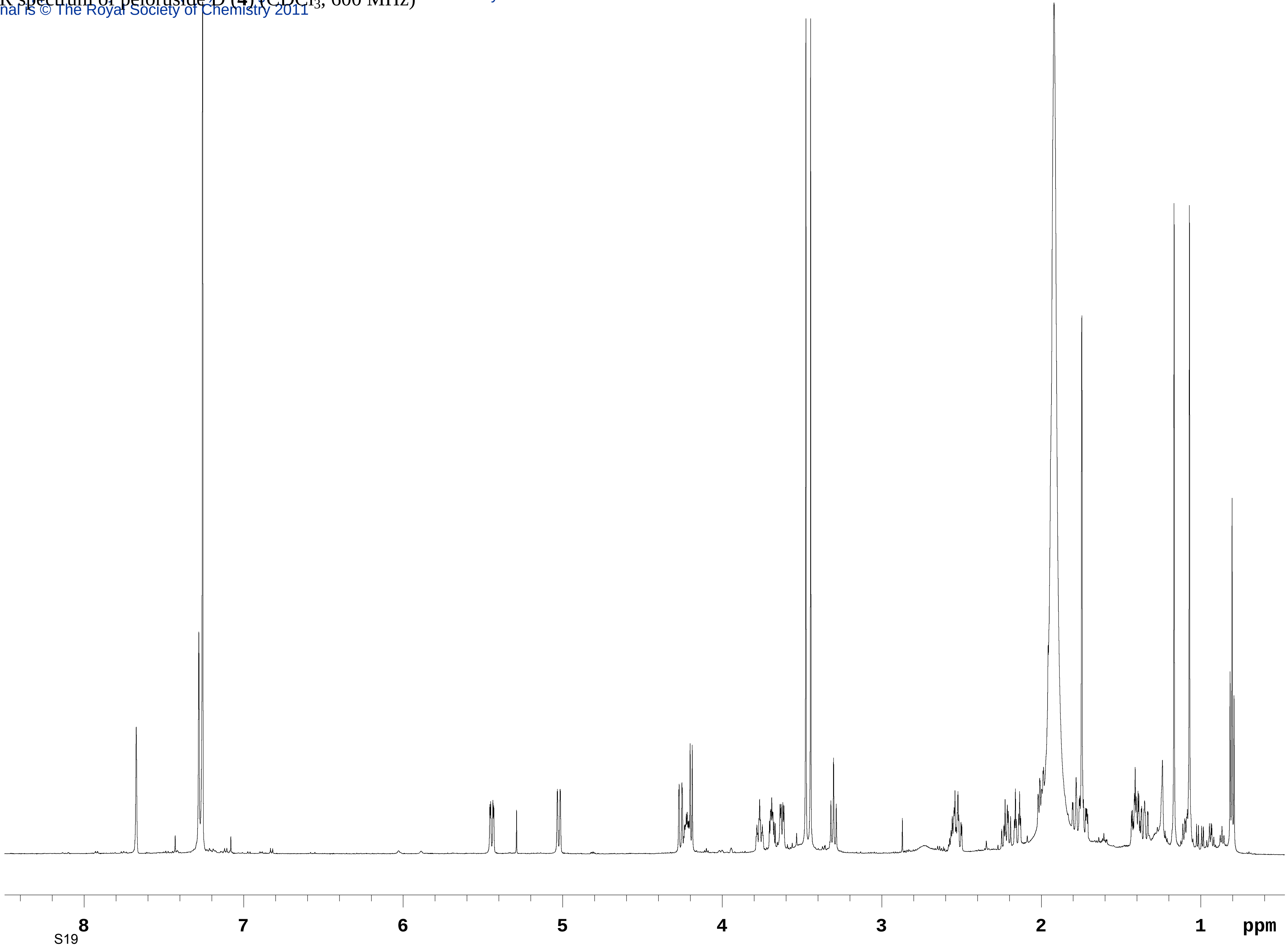
Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

NOESYzd NMR spectrum of peloruside C (**3**) ($CDCl_3$, 600 MHz)

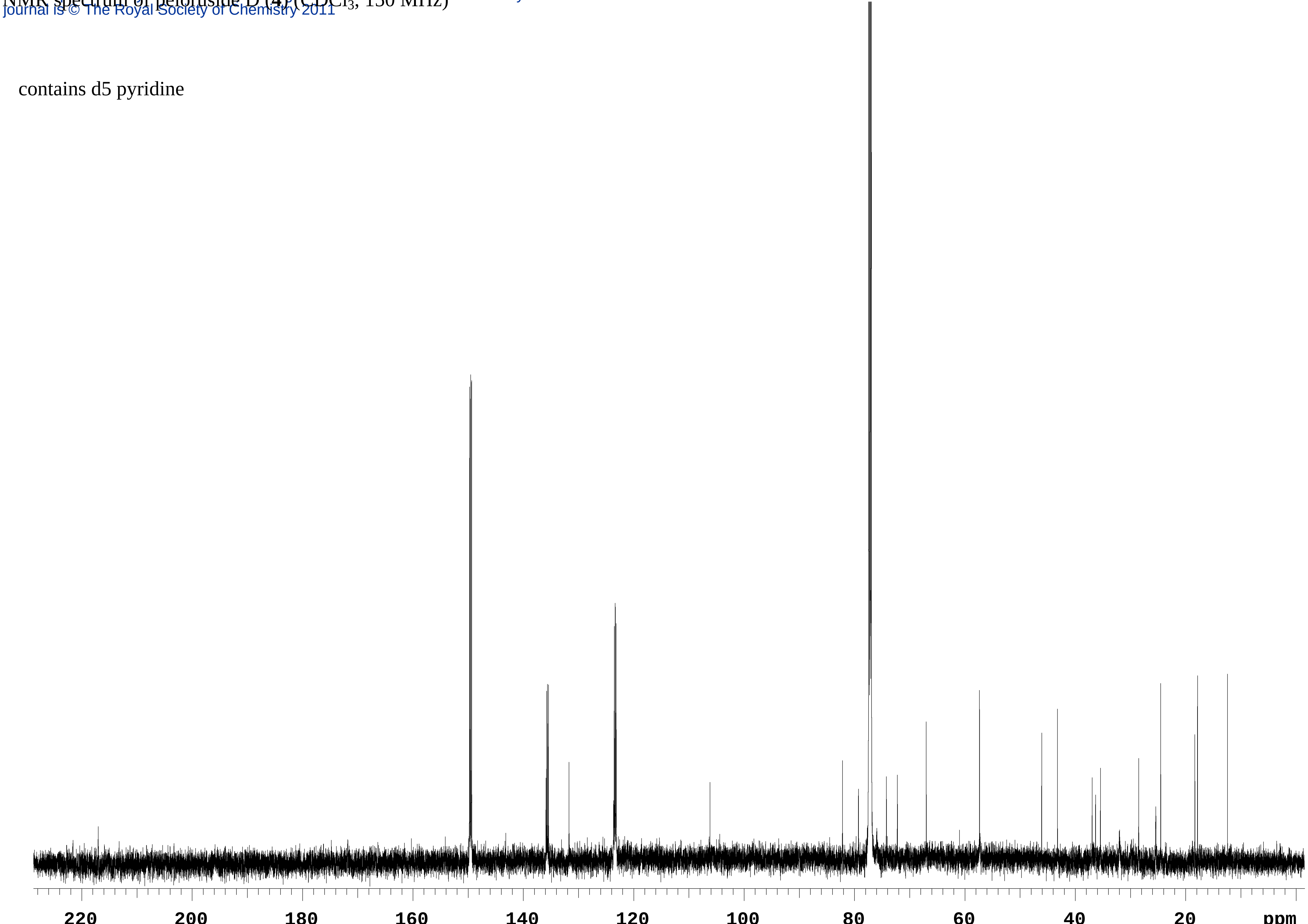
(sample is a mixture of peloruside C and mycalamide A)



^{1}H NMR spectrum of peloruside D (4) (CDCl$_3$, 600 MHz)

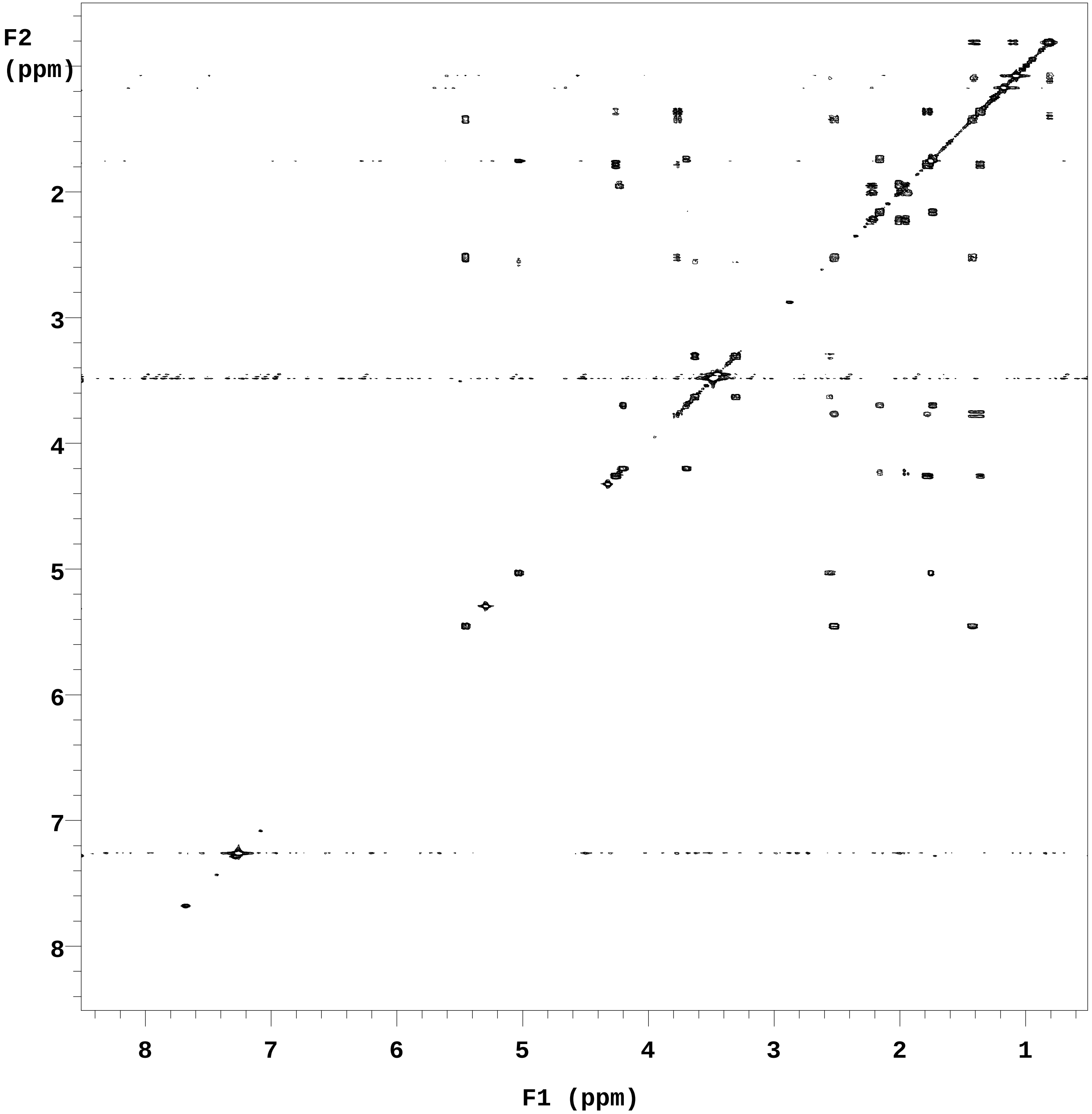


^{13}C NMR spectrum of peloruside D (4) ($CDCl_3$, 150 MHz)

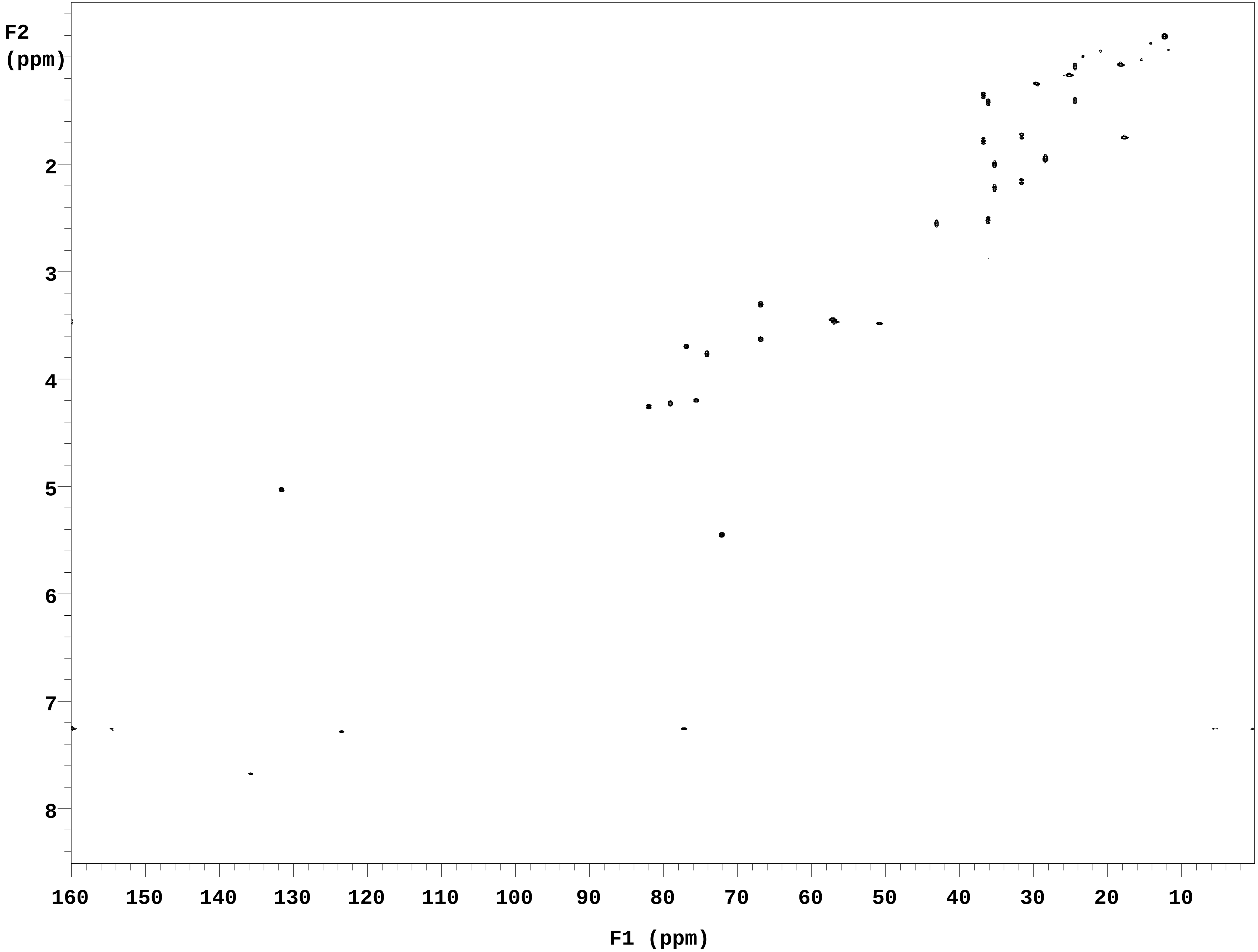


Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

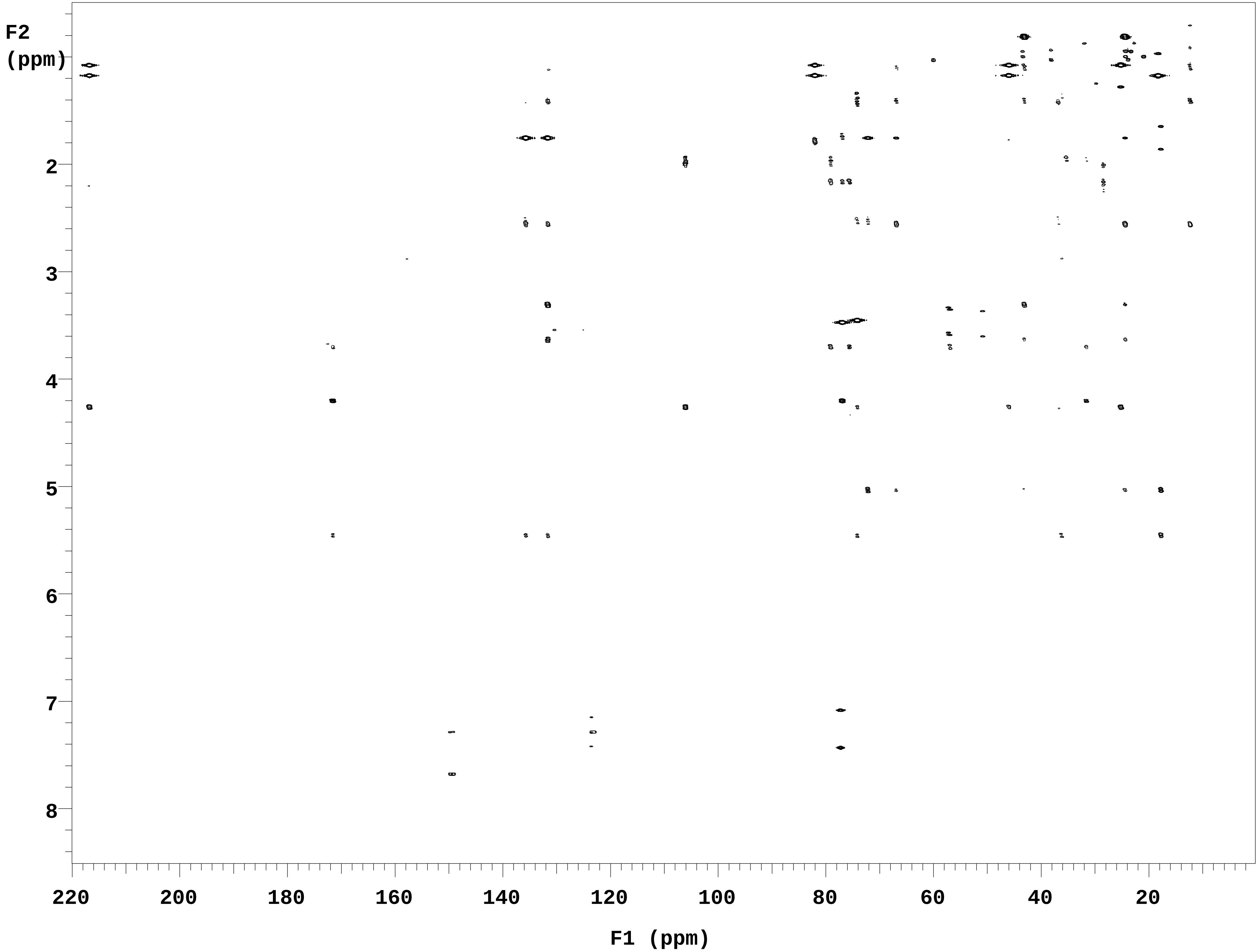
gCOSY NMR spectrum of pelorusside D (4) ($CDCl_3$, 600 MHz)



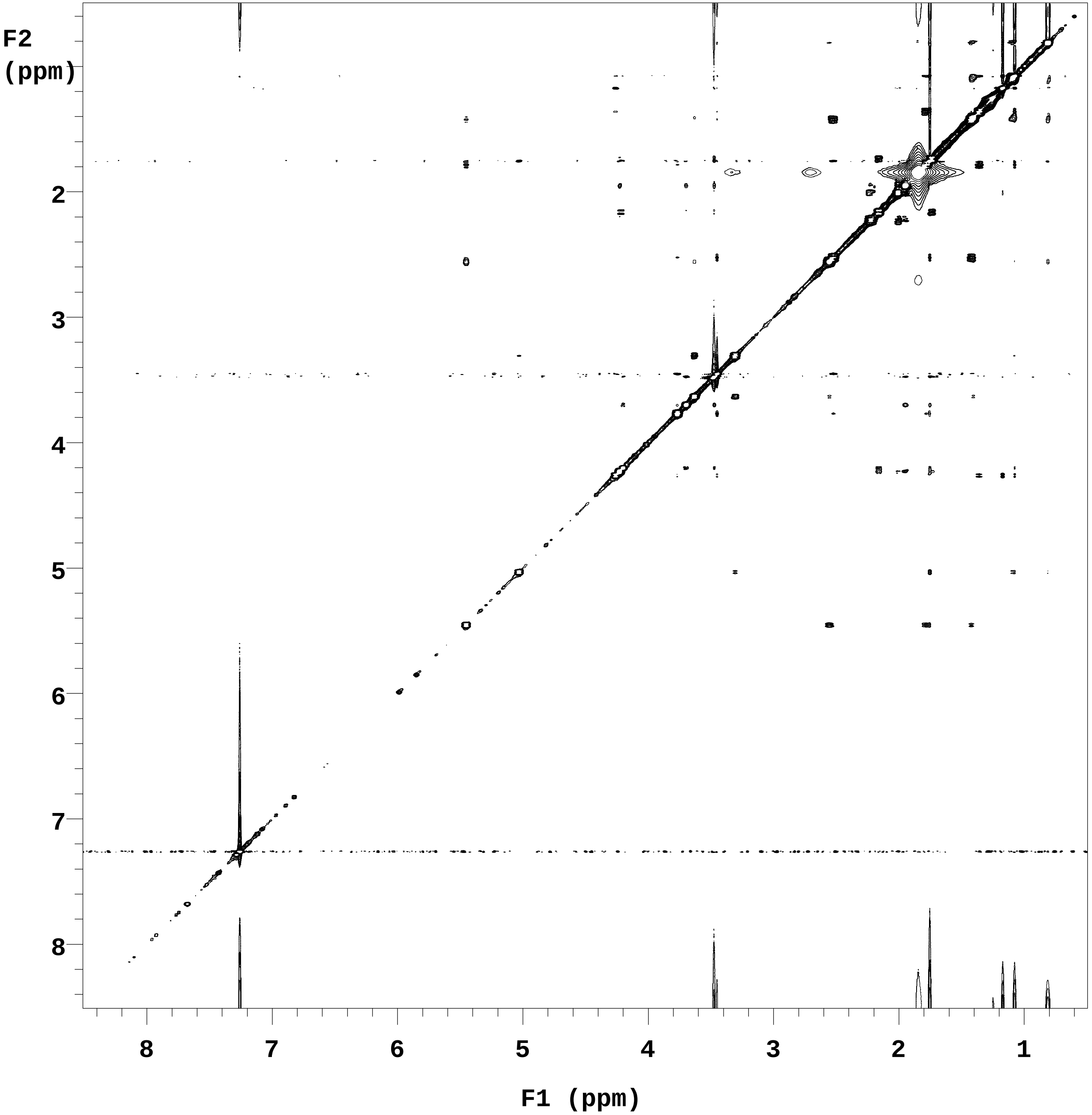
HSQCad NMR spectrum of peloruside D (4) ($CDCl_3$, 600 MHz)



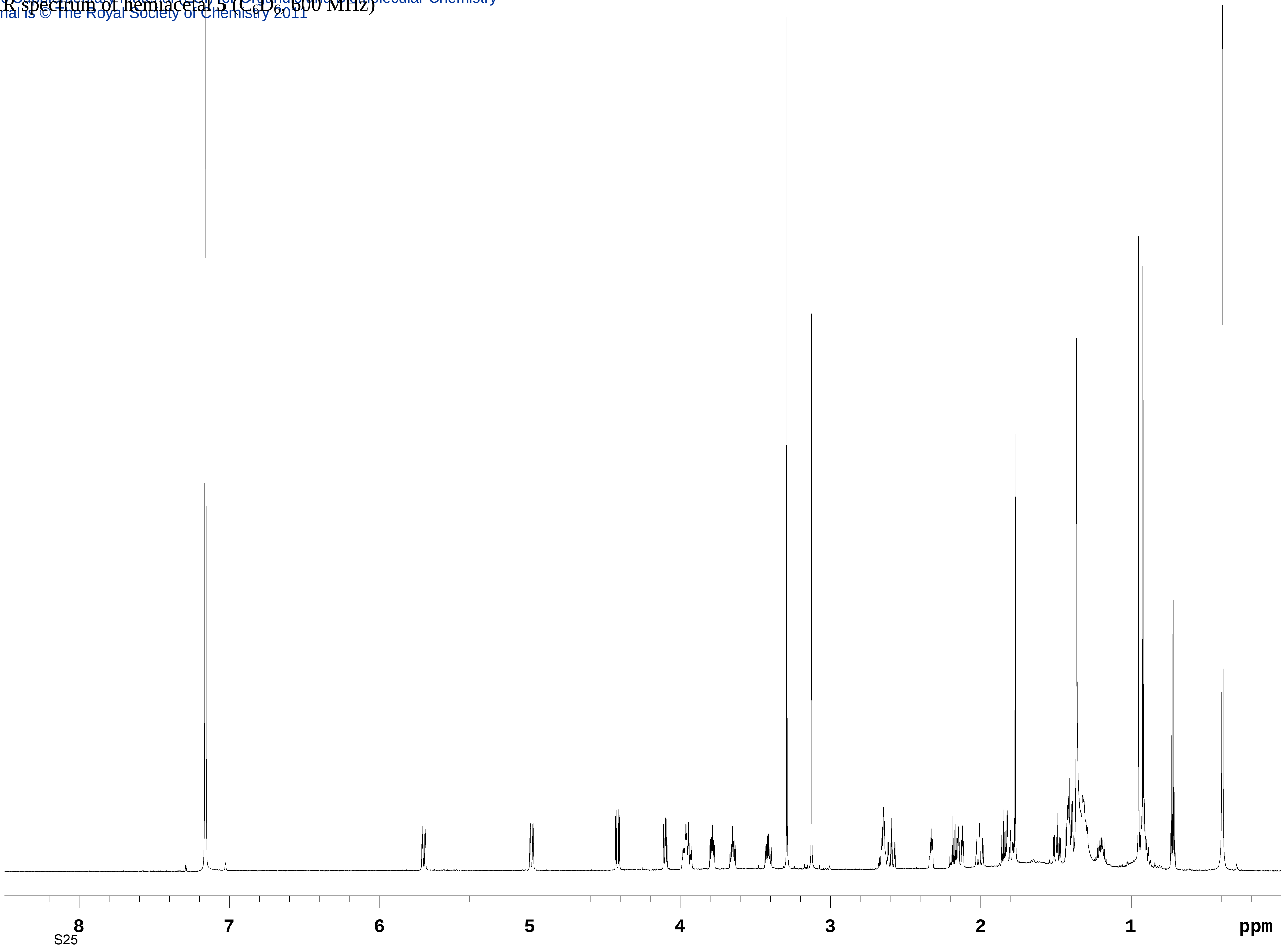
gHMBC NMR spectrum of peloruside D (4) ($CDCl_3$, 600 MHz)



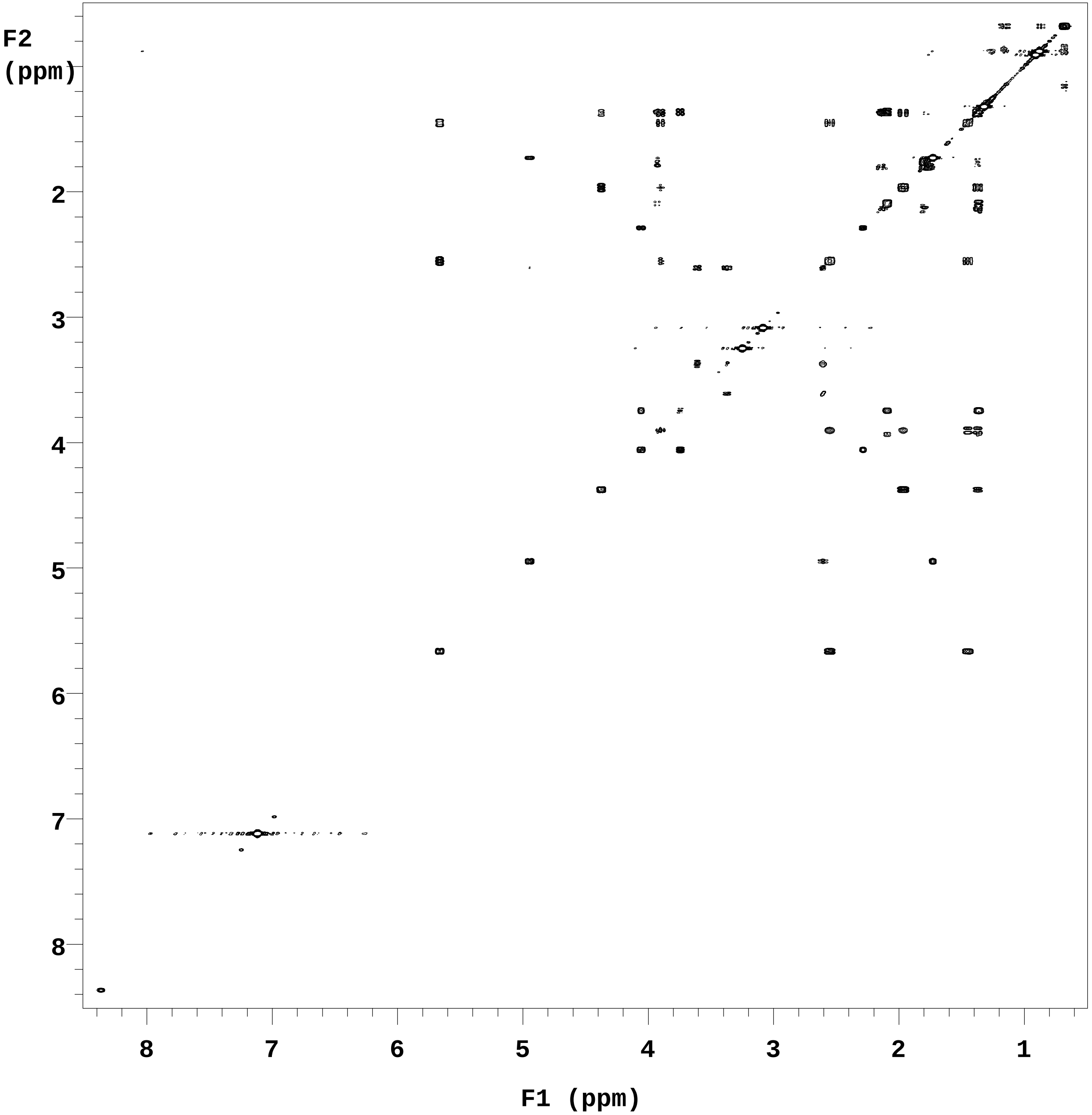
NOESYzq NMR spectrum of peloruside D (4) ($CDCl_3$, 600 MHz)



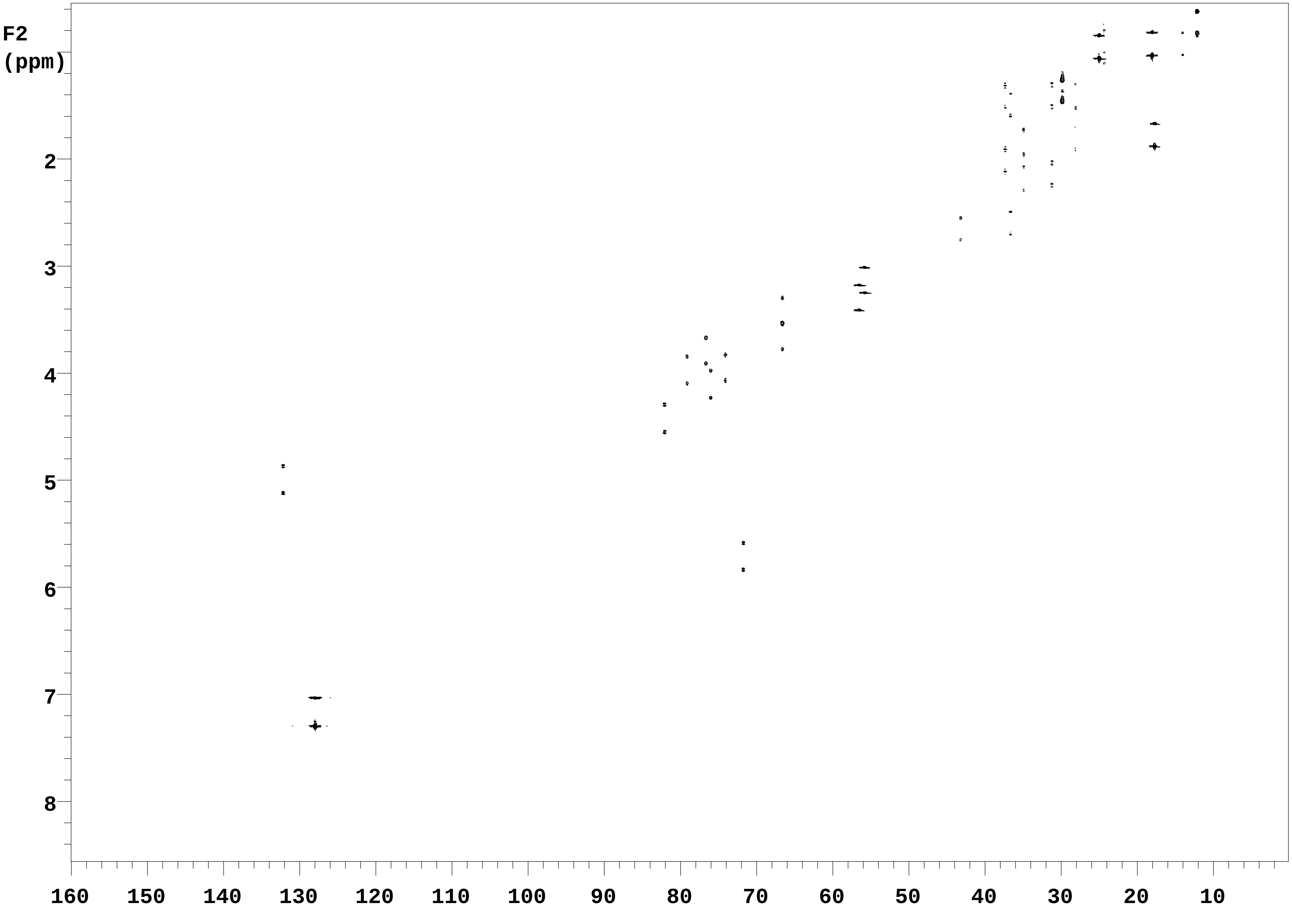
1H NMR spectrum of hemiacetal 5 (C_6D_6, 600 MHz)



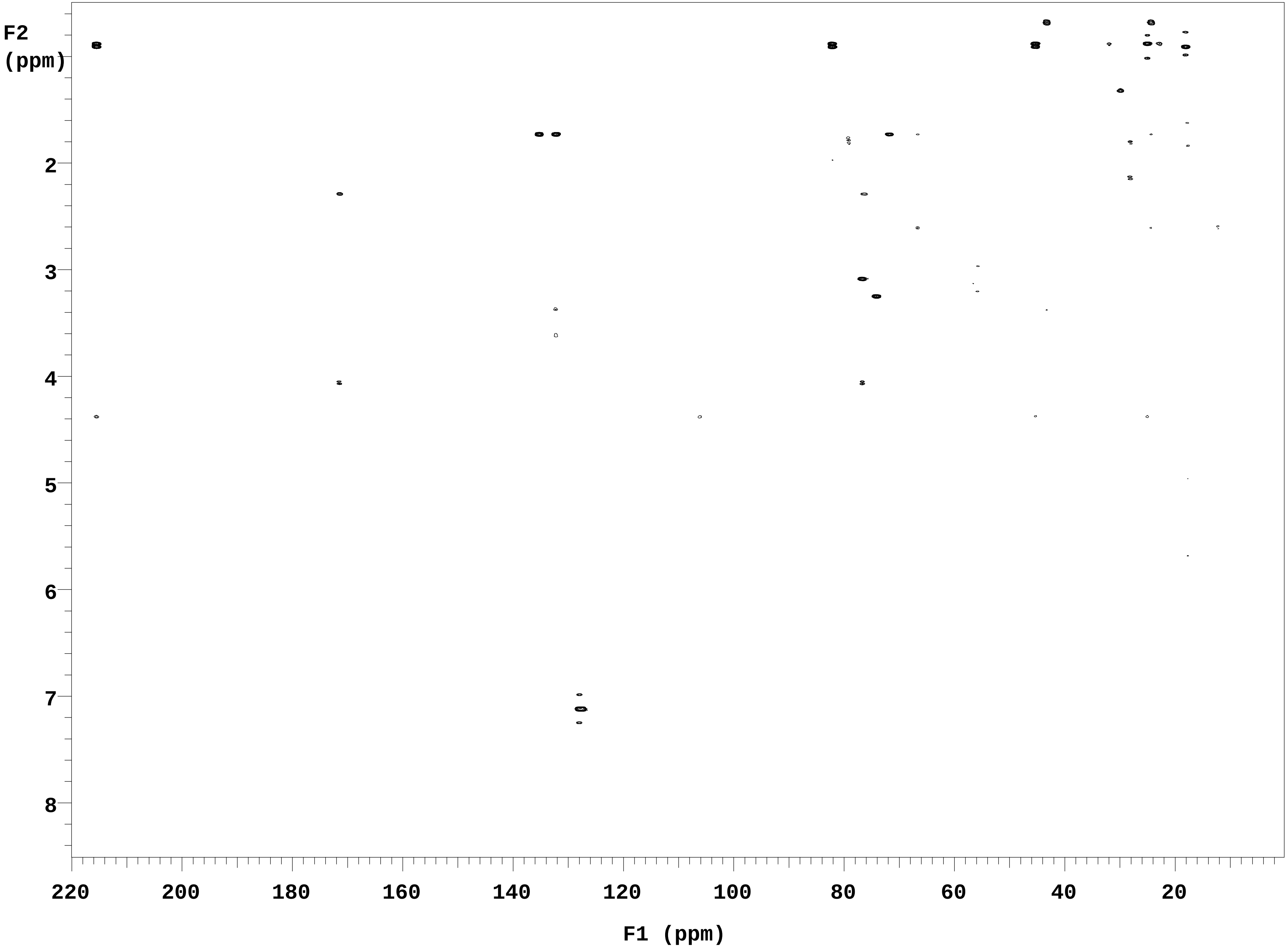
COSY NMR spectrum of hemiacetal 5 (C_6D_6, 600 MHz)



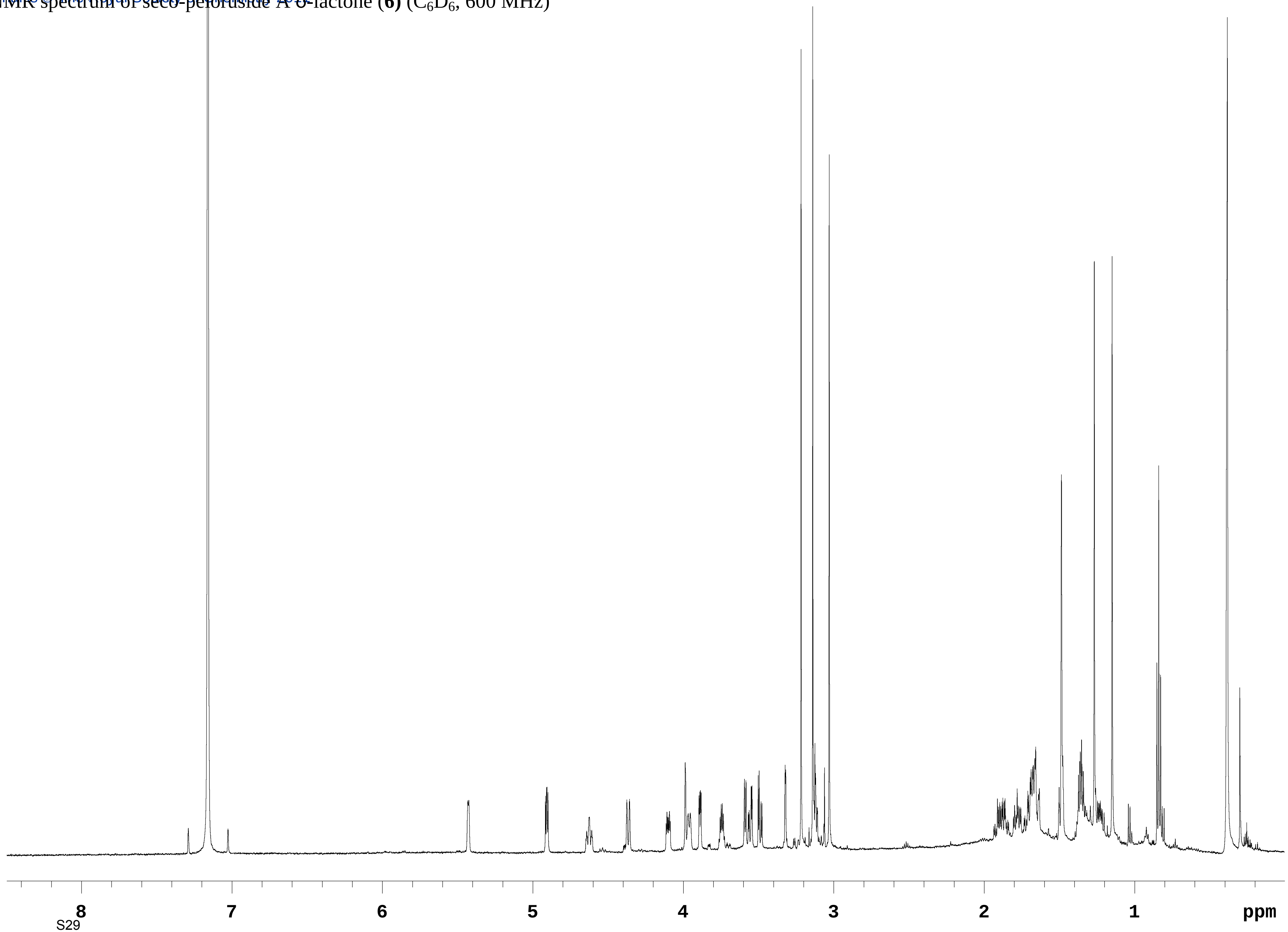
Coupled HSQCad NMR spectrum of hemiacetal **5** (C_6D_6, 600 MHz)



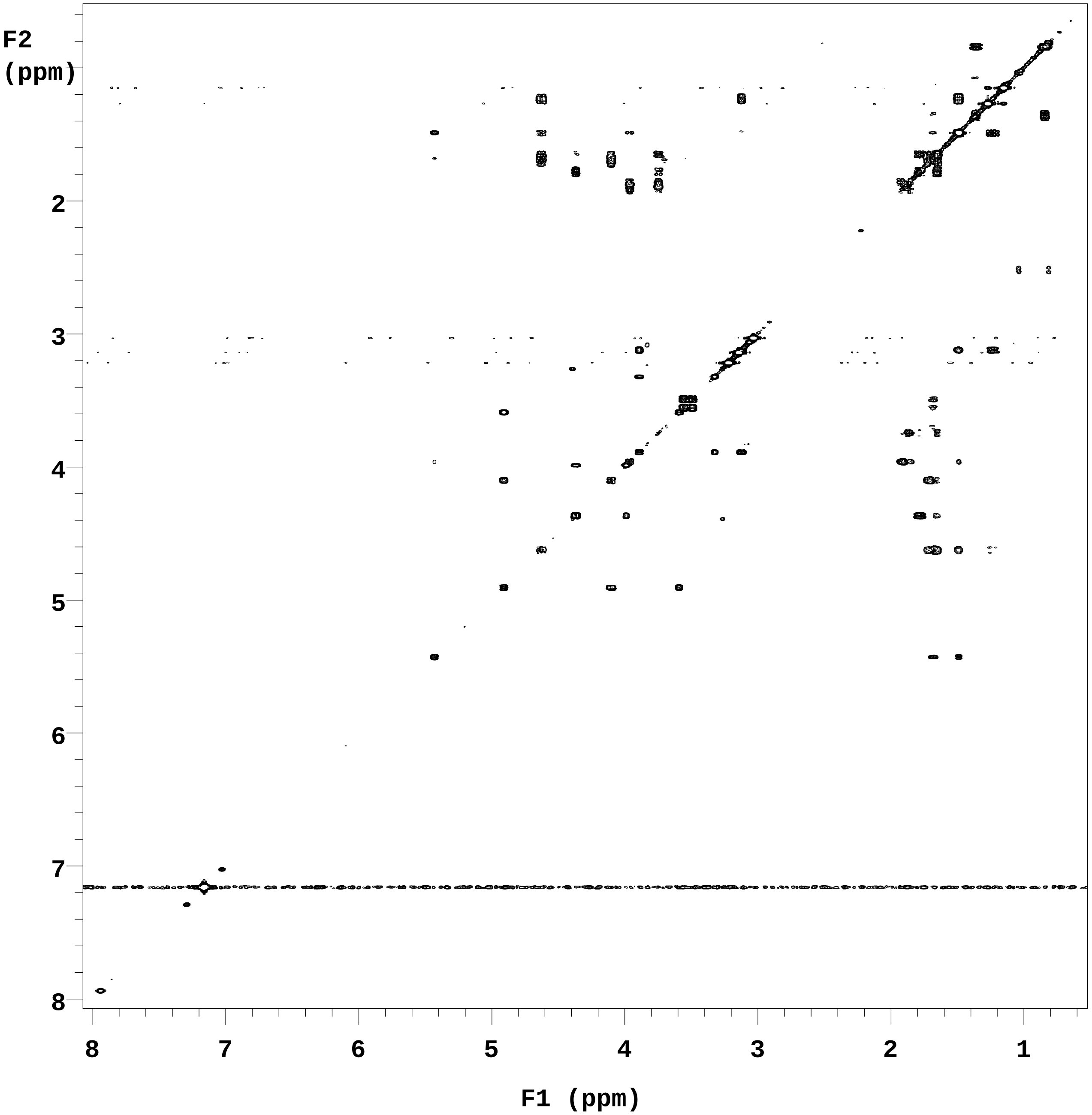
gHMBC NMR spectrum of hemiacetal 5 (C_6D_6, 600 MHz)



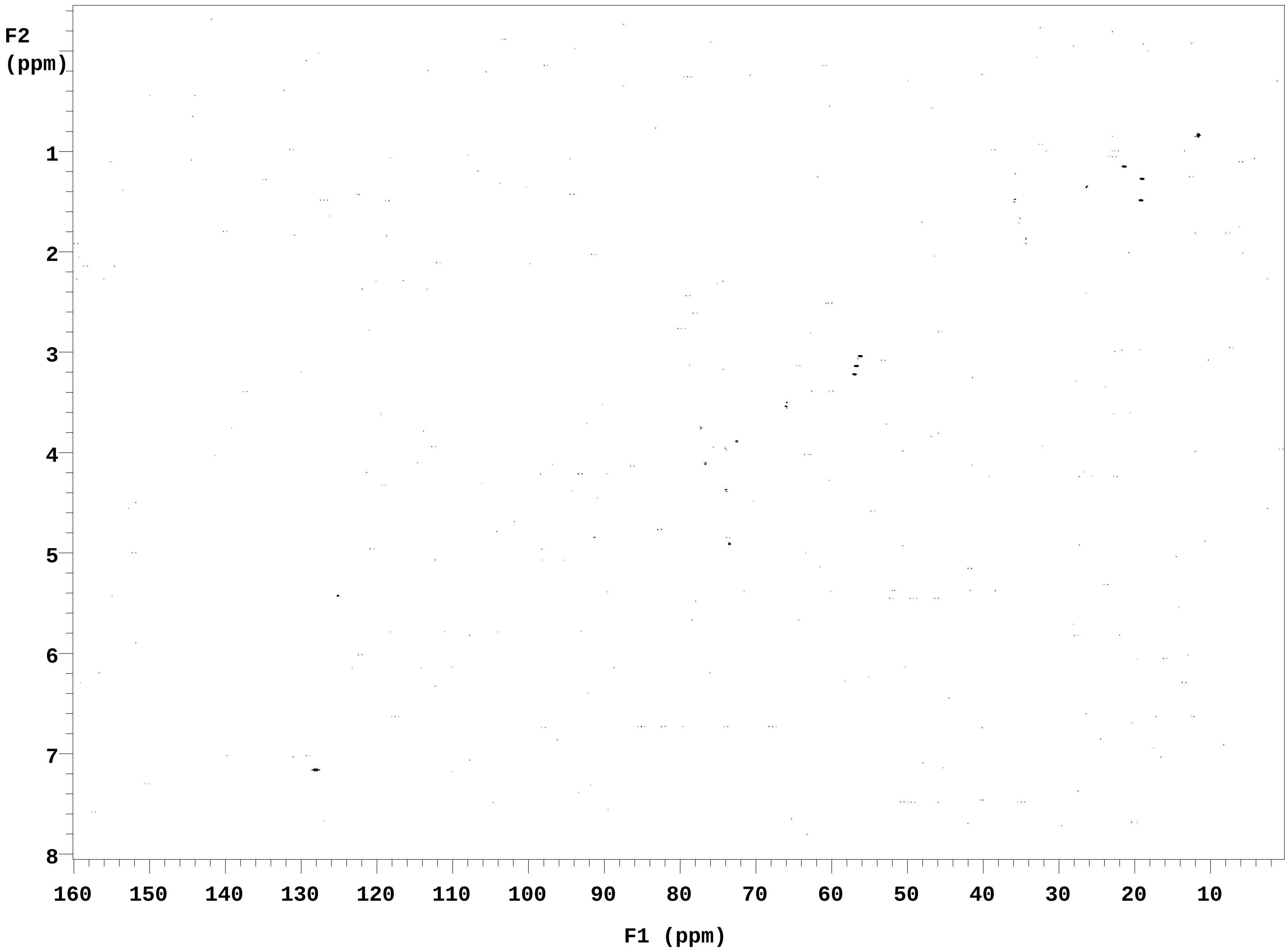
^{1}H NMR spectrum of seco-peloruside A δ-lactone (**6**) (C_6D_6, 600 MHz)



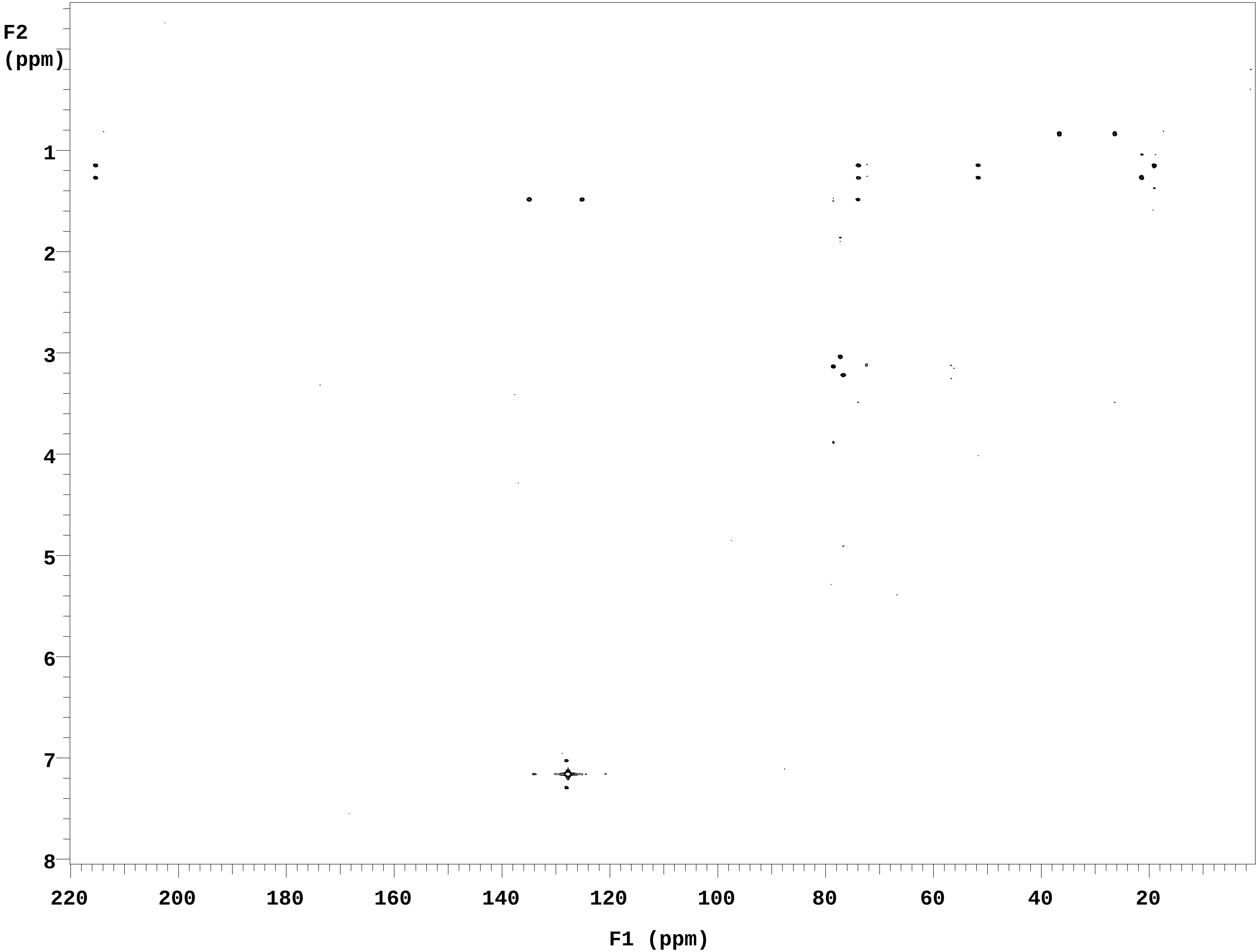
COSY NMR spectrum of seco-peloruside A δ-lactone (**6**) (C_6D_6, 600 MHz)



HSQCad NMR spectrum of seco-peloruside A δ-lactone **(6)** (C_6D_6, 600 MHz)



gHMBC NMR spectrum of seco-peloruside A δ-lactone (**6**) (C_6D_6, 600 MHz)



NOESYzs NMR spectrum of seco-peloruside A δ-lactone (**6**) (C_6D_6, 600 MHz)