

**Electronic Supplementary Information for
New Hamigerans from the New Zealand Marine Sponge
Hamigera tarangaensis: NMR-Directed Isolation, Structure
Elucidation and Antifungal Activity**

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Appendix A

Hamigera tarangaensis Images



Figure A.1. Underwater photograph of PTN2.66E, collected from Cape Karikari, New Zealand.

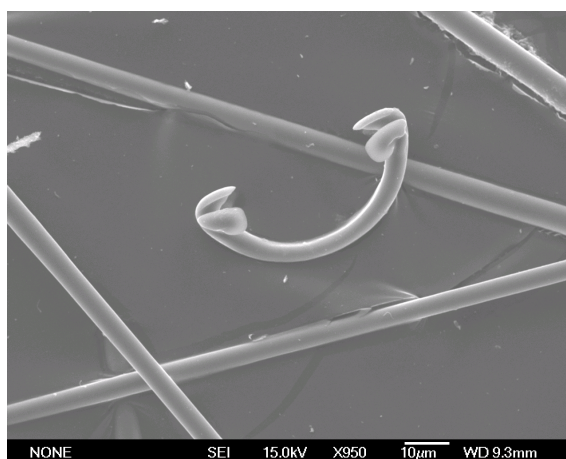
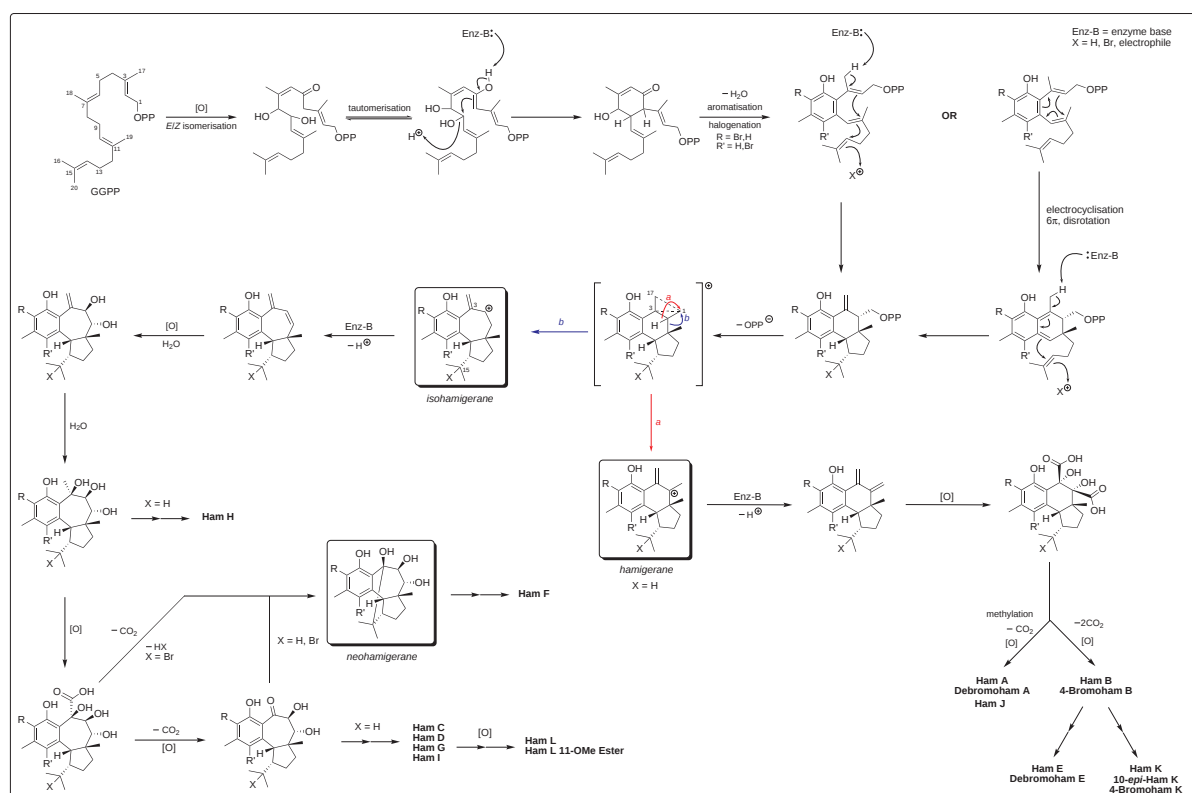


Figure A.2. *Hamigera tarangaensis* isochelae, 950 $\times$ magnification.

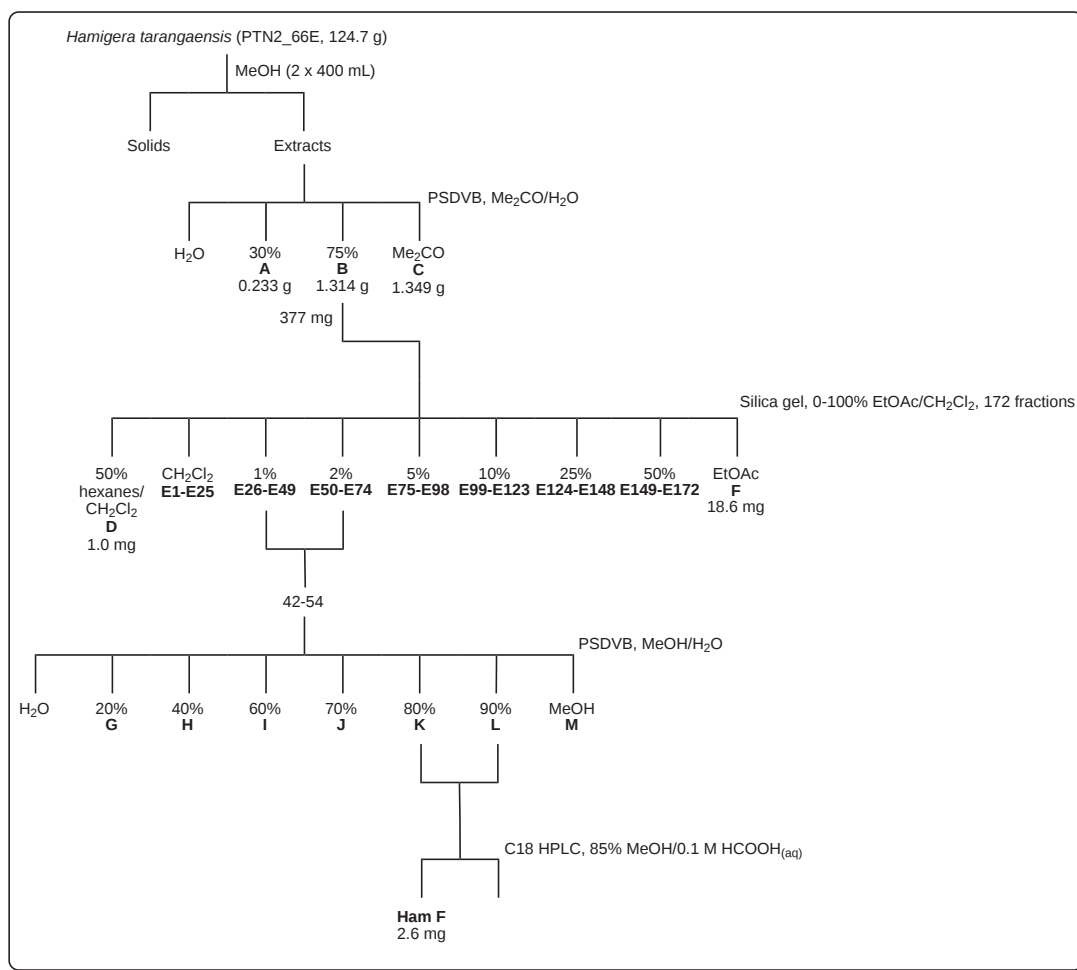
Appendix B

Proposed Biogenesis

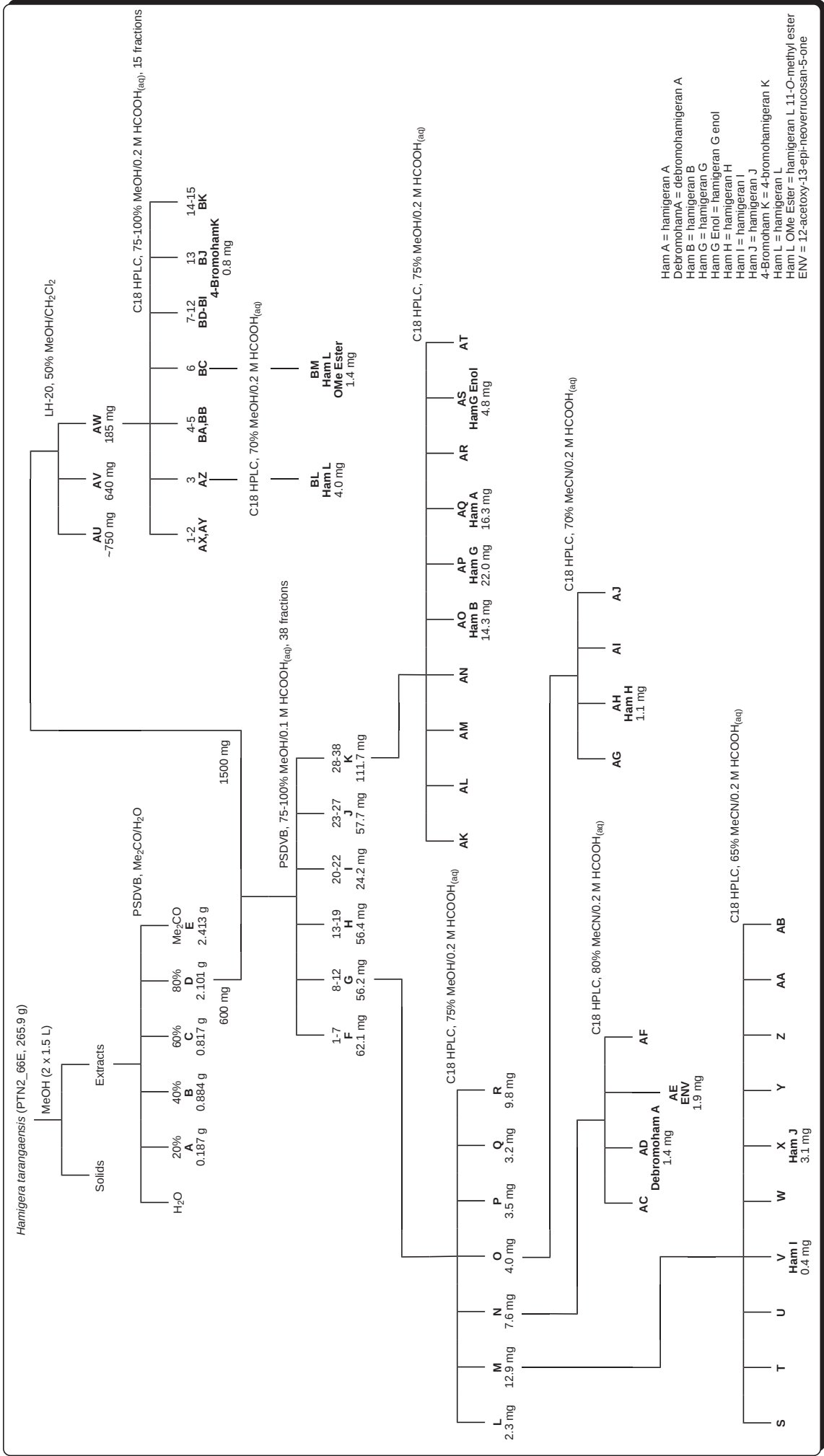


Appendix C

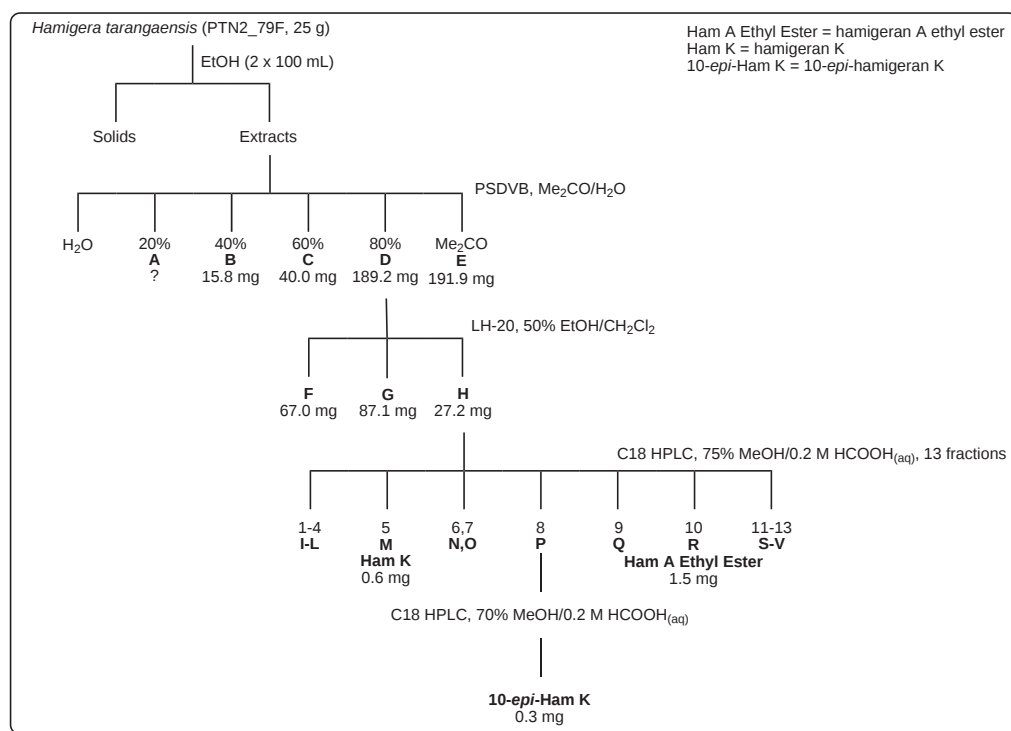
Isolation Schemes



Scheme C.1. Isolation of hamigeran F (**6**) from *Hamigera tarangaensis*, collected from Cape Karikari, New Zealand.



Scheme C.2. Isolation of compounds **8–12** and **15–17** from *Hamigera tarangaensis*, collected from Cape Karikari, New Zealand.



Scheme C.3. Isolation of hamigeran K (**13**), 10-*epi*-hamigeran K (**14**) and hamigeran A ethyl ester (**19**) from *Hamigera tarangaensis*, collected from Cavalli Island, New Zealand.

Appendix D

NMR Tables

Table D.1. ^{13}C and ^1H NMR Data for Hamigeran A (**2**), Debromohamigeran A (**3**), Hamigeran B (**4**) and Hamigeran A Ethyl Ester (**19**) in CDCl_3 .

Position	Hamigeran A (2) [†]			Debromohamigeran A (3) [†]			Hamigeran B (4) [†]			Hamigeran A Ethyl Ester (19)		
	δ_{C}	mult.	δ_{H}	δ_{C}	mult.	δ_{H}	δ_{C}	mult.	δ_{H}	δ_{C}	mult.	δ_{H}
1	157.6	C		161.2	C		160.8	C		157.7	C	
1-OH			11.75			10.97			12.64			11.81
2	110.5	C		115.1	CH	6.64	111.6	C		110.4	C	
3	148.3	C		149.1	C		150.2	C		148.3	C	
3	122.4	CH	6.79	121.5	CH	6.66	124.3	CH	6.82	122.3	CH	6.78
4a	142.8	C		144.1	C		142.8	C		143.0	C	
5	50.0	CH	3.50	50.2	CH	3.53	56.2	CH	3.39	50.3	CH	3.48
6	53.4	CH	2.03	53.4	CH	2.02	51.3	CH	2.31	53.5	CH	2.02
7	26.9	CH ₂	0.70	26.9	CH ₂	0.70	26.8	CH ₂	1.69	27.0	CH ₂	0.71
			1.62			1.62			1.81			1.64
8	34.0	CH ₂	1.55	34.1	CH ₂	1.55	33.8	CH ₂	1.56	34.2	CH ₂	1.52
			1.72			1.73			2.63			1.74
9	47.2	C		47.2	C		57.0	C		47.3	C	
10	83.9 [‡]	C		83.7	C		199.1	C		84.0	C	
10-OH			4.33			4.40						4.29
11	198.1	C		197.7	C		184.4	C		198.5	C	
11a	114.7	C		113.7	C		117.3	C		115.0	C	
12	27.3	CH	1.58	27.3	CH	1.58	28.1	CH	1.21	27.5	CH	1.58
13	23.4	CH ₃	1.22	23.4	CH ₃	1.21	19.7	CH ₃	0.53	23.5	CH ₃	1.21
14	22.0	CH ₃	0.83	22.0	CH ₃	0.82	23.3	CH ₃	0.45	22.1	CH ₃	0.83
15	24.3	CH ₃	1.36	24.4	CH ₃	1.37	24.3	CH ₃	1.29	24.4	CH ₃	1.35
16	24.6	CH ₃	2.47	22.7	CH ₃	2.35	24.4	CH ₃	2.51	24.8	CH ₃	2.46
17	169.5	C		169.2	C					169.2	C	
18	53.1	CH ₃	3.61	52.9	CH ₃	3.60				52.9	CH ₂	4.04
19										1.40	CH ₃	1.11

[†]Wellington et al., *J. Nat. Prod.*, **2000**, 63, 79–85.

[‡]The chemical shift for C-10 was originally reported as δ 89.3.

Table D.2. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for Hamigeran F (**6**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC		NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm)		J (Hz)	(¹ H → ¹³ C)	
1	152.2	C						
1-OH				8.97			1(w),2(w),12a(w)	
2	113.3	C						
3	138.8	C						
4	121.8	CH	160					
4a	135.0	C		6.52	5(w),17		1(w),2,3(w),4a(w),5,12(w),12a,17	5,16,17
5	53.9	CH	134	2.90		8.4	1(w),4,4a,6,9,10,12a,13,16	4,6,7(w),8a(w),15(w),16
6	47.4	CH	135	2.41	4(w),6	8.7,3.8	5,8(w),9,12(w),13	5,7,14,15
7	27.9	CH ₂	129	2.13			8(w),9(w),13	5(w),6,8a,8b,11,14
8	36.5	CH ₂	130 [†]	1.75	7,8b		6(w),7(w),9,10(w),16(w)	5(w),7,8b,16
9	58.3	C	133 [†]	2.00	7,8a	14.5,8.1,6.7	5,6,10	7,8a,11,14(w),16(w)
10	202.9	C						
11	79.3	CH	145	5.71			10,12,12a,13,18	7,8b,14
12	81.0	C						
12-OH				3.76			12(w),12a(w),13(w)	
12a	119.6	C						
13	42.2	C						
14	20.0	CH ₃	127	1.28	15		6,12,13,15	6,7,8b(w),11,15
15	28.8	CH ₃	127	0.81	14		6,12,13,14	5(w),6,14
16	22.3	CH ₃	126	1.13			5,8,9,10	4,5,8a,8b(w)
17	23.3	CH ₃	128	2.33	4		2,3,4,12a	4
18	171.6	C						
19	21.0	CH ₃	130	2.22			11(w),18	

[†]Estimated value due to distorted overlap.

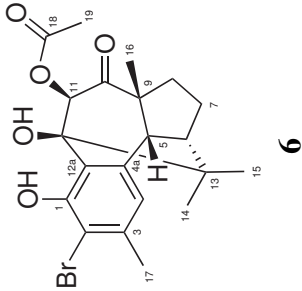


Table D.3. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for Hamigeran F Rearrangement Product (**7**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC (¹ H → ¹³ C)	NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm)	mult.	J (Hz)	
1	158.6	C					
1-OH							
2	112.2	C		12.98	s		1,2,3,12,12a
3	147.7	C					
4	121.7	CH	160				
4a	139.7	C		6.49	s		1(w),2,4a(w),5,12(w),12a,17
5	50.2	CH	135	3.54	d	7.1	4,4a,6,7,8,9,12a,16
6	47.0	CH	131	2.60	td	9,4,7.1	4a,5,12,13,15
7	27.6	CH ₂	131	1.53	m		5,6,8,9,13
			131	2.07	m		5,6,8,9
8	33.0	CH ₂	130	1.52	m		6,7,9,16
			126	1.86	m		6(w),7,9(w),10(w),16
9	60.5	C					
10	206.9	C					
11	67.0	CH ₂	147	4.11	d	16.8	9(w),10,18
			146	4.73	d	16.9	9(w),10,18
12	209.1	C					
12a	114.3	C					
13	45.3	C					
14	22.3	CH ₃	127	1.26	s		6,12,13,15
15	28.4	CH ₃	128	1.14	s		6,12,13,14
16	25.1	CH ₃	128	1.44	s		5,8,9,10
17	24.0	CH ₃	129	2.39	s		1(w),2,3,4,12a(w)
18	170.2	C					
19	20.7	CH ₃	129	2.14	s		11,18

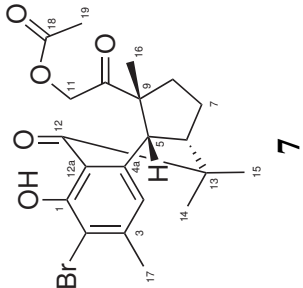


Table D.4. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for the Major Conformer of Hamigeran G (**8**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC		NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm)		J (Hz)	(¹ H → ¹³ C)	
1	160.4	C						
1-OH								
2	113.2	C		12.18			1,2,3(w)12(w),12a	
3	148.3	C						
4	128.1	CH	162	6.78	5,17		1(w),2,3(w),4a(w),5,12(w),12a,17	5,15(w),17
4a	141.9	C						
5	60.8	CH	129	3.39		11.3		
6	53.6	CH	126	2.01				4,6,16
7	31.4	CH ₂	126	1.16	5,7a,7b,13		1(w),3(w),4,4a,7,8(w),9,10,12a,13,16	5,7b,14,15
			131	1.74	6,7b,8a		4a,5,7,13,14	7b,8a,13(w),14
8	40.7	CH ₂	126	1.62	6,7a		6,8,13	6,7a,14
			132	1.98	7a,8b		5,6,8,9	7a,8b,16
9	45.4	C			8a		7,9,10	8a,10a(w),16(w)
10	53.5	CH ₂	135	2.58		12.0	4a(w),5,8,9,11,12,12a(w),16	8b(w),10b,16
			126	2.71	10a	12.0	5,8,9,11,16	10a,16
11	195.8	C						
12	190.8	C						
12a	118.6	C						
13	29.9	CH	124	0.84	6,14,15		5,6,7(w),9(w),14,15	7a(w),14,15
14	22.2	CH ₃	125	0.69	13,15	6.5	6,13,15	6,7a,7b,13,15
15	22.4	CH ₃	124	0.25	13,14	6.5	6,13,14	4(w),6,13,14
16	31.9	CH ₃	126	1.29			5,8,9,10	5,8a,8b(w),10a,10b
17	24.2	CH ₃	128	2.48	4		1(w),2,3,4,4a,12a(w)	4

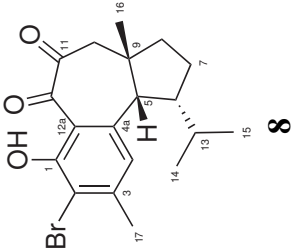


Table D.5. ¹³C (150 MHz), ¹H (600 MHz) and NOESY (600 MHz) NMR Data for the Minor Forms of Hamigeran G (8) in CDCl₃.

Position	Minor Conformer (8)						Enol (9)					
	¹³ C			¹ H			¹³ C			¹ H		
	δ (ppm)	mult.	¹ J _{CH} (Hz)	Δδ (ppm) [†]	δ (ppm)	mult.	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm)	mult.	J (Hz)
1	158.6	C		+1.9			160.6	C		13.39	s	
1-OH					11.28	s						
2	112.1	C		+1.2			113.5	C				
3	147.6	C		+0.8			147.2	C				
4	121.8	CH	161	+6.4	6.90	s	126.7	CH	161	6.71	s	
4a	141.2	C		0.0			140.9	C				
5	53.0	CH	130	+7.8	2.87	d	59.7	CH	125	3.08	d	10.8
6	50.4	CH	120	+0.6	2.21	m	51.8	CH	129	1.96	m	
7	27.8	CH ₂	129	-5.7	1.76	m	31.5	CH ₂	n/a [‡]	1.50	m	
			125		2.19	m			130	1.94	m	
8	37.1	CH ₂	128	+12.9	1.76	m	43.8	CH ₂	125	1.54	m	11.5,6.0
			130		1.79	m			132	1.81	dd	
9	43.0	C		+2.4			46.4	C		5.84	d	1.2
10	51.9	CH ₂	136	+1.6	2.52	d	127.2	CH	152			
			130		2.68	d						
11	194.3	C		+1.5			146.3	C				
12	192.3	C		-1.5			189.9	C				
12a	119.1	C		-0.5			118.0	C				
13	29.3	CH	126	+0.6	2.04	m	32.1	CH	128	1.22	m	
14	22.2	CH ₃	125	0.0	0.98	d	22.1	CH ₃	125	0.74	d	6.6
15	22.8	CH ₃	125	-0.4	0.57	d	23.1	CH ₃	124	0.09	d	6.0
16	25.3	CH ₃	126	+6.6	1.22	s	25.1	CH ₃	126	1.13	s	
17	24.8	CH ₃	128	-0.7	2.50	s	23.9	CH ₃	129	2.44	s	

[†] Δδ = δ(major) - δ(minor).

[‡]Not observed due to severe spectral overlap.

Table D.6. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for Hamigeran H (**10**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC (¹ H → ¹³ C)	NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm)			
1	158.4	C					
1-OH				8.84			18
2	119.3	CH	160	6.76	4,17	1,2,3(w),12a 1,4,12a,17	17
3	138.8	C					
4	129.4	CH	157	6.55	2,5,17	1(w),2,4a(w),5,12(w),12a,17	5,15,17
4a	135.0	C					
5	61.5	CH	128	3.51	4,6	4,4a,6,7,8(w),9,10,12a,13(w),16	4,6,10(w),15,16
6	53.1	CH	121	1.90	5,7a,7b,13	4a,5,7,8(w),13,15	5,7b,13(w),14,15,16
7	31.3	CH ₂	123	1.11	6,7b,8a,8b	5,6,8,13	7b,8b,13(w),14,18
			130	1.59	6,7a,8a,8b	5,6,8,9	6,7a,8a,14
8	34.2	CH ₂	133	1.28	7a,7b,8b	7,9,10,16	7b,8b
			132	2.27	7a,7b,8a	5,6,7,9,10	7a,8a
9	47.9	C					
10	80.0	CH	149	5.15		5,8,9,11,16,19	5(w),12-OH,16
11	202.9	C					
12	80.3	C					
12-OH				4.70	18	11(w),12(w),18	10,18
12a	123.1	C					
13	27.7	CH	125	0.96	6,14,15	5,6,14,15	6(w),7a(w),14,15,18
14	21.5	CH ₃	124	0.70	13	6,13,15	6,7a,7b,13,15,18
15	23.6	CH ₃	122	0.61	13	6,13,14	4,5,6,13,14,18
16	30.0	CH ₃	127	1.30	s	5,8,9,10	5,10
17	20.9	CH ₃	123	2.26	2,4	1(w),2,3,4,12a(w)	2,4
18	22.0	CH ₃	127	1.81	12-OH	11,12,12a	1-OH,7a,12-OH,13,14,15
19	172.7	C					
20	20.8	CH ₃	128	2.16	s	10,19	

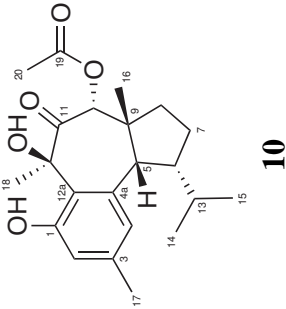


Table D.7. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for Hamigeran I (**11**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC (¹ H → ¹³ C)	NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm) mult.			
1	160.9	C					
1-OH				13.30	s	1,2,12a	
2	113.6	C					
3	148.2	C					
4	128.4	CH	161				
4a	141.9	C					
5	61.2	CH	128	6.77	s	1(w),2,3(w),4a(w),5,12,12a(w),17	5,15,17
6	53.9	CH	127	3.44	d	4,4a,6,7(w),9,10,12a,16	4,6,8a(w),16
7	32.5	CH ₂	135	2.22	m	5(w),7(w),13(w),15(w)	5,7b,14,15
				1.58	m	6(w),8(w),13(w)	7b,11,14
8	34.6	CH ₂	130	1.92	dddd	5,6(w),8(w),9	6,7a,8a,8b(w),14
				1.42	m	6(w),7,9,10,16	5(w),7b,8b,16
				2.57	ddd	5,6,7(w),9(w),10(w)	7b(w),8a,11
9	47.9	C					
10	74.45 [†]	CH	144	3.32	d	8,9,11,12,16	11,16
10-OH				4.15	br s	10,11(w)	
11	74.43 [†]	CH	148	4.59	d	9,10,12	7a,8b,10,13
11-OH				3.17	br s	10,10-OH(w)	
12	204.9	C					
12a	116.3	C					
13	29.6	CH	123	1.10	m	6,14,15	11,14,15
14	22.1	CH ₃	125	0.77	d	6,13,15	6,7a,7b,13,15
15	23.5	CH ₃	125	0.20	d	6,13,14	4,6,13,14
16	30.1	CH ₃	124	1.25	s	5,8,9,10	5,8a,10
17	24.0	CH ₃	129	2.45	s	4	4

[†] Interchangeable.

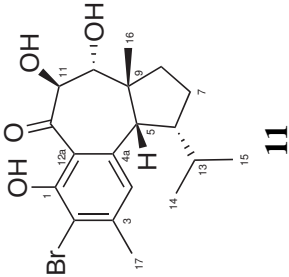


Table D.8. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for Hamigeran J (**12**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC		NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm)		mult.	¹ H → ¹³ C	
1	151.8	C						
2	112.0	C						
3	139.7	C						
4	125.0	CH	159	6.78	5,16	s	1,2,3,4a,5,11,11a,16	5,6,12,14,16
4a	136.6	C						
5	57.0	CH	129	3.34		d	2(w),3(w),4,4a,6,9,10,11(w),11a,12,15	4,6,7b(w),8a(w),14(w),15
6	51.2	CH	130	2.16	4,6	tt	4a(w),5,7,8,9,12,13	4,5,7a,7b,8a(w),12,13,14
7	27.4 [†]	CH ₂	122	1.62	5,7a,13	m	5,6,8,9,12	6,7b,8a,8b,13,14
8	35.6	CH ₂	130	1.72	6,7b,8a,8b	m	5,6,8,9,12	5,6,7a,8a,8b,13,14
9	55.2	C			7a,7b,8b	dt	5,6,7,9,10,11(w),15	5,6(w),7a,7b,8b,15
10	210.1	C			7a,7b,8a	ddd	5,6,7,9,10,15(w)	7a,7b,8a,13,15
11	76.8	C						
11a	120.0	C						
12	27.5 [†]	CH	117	1.37	6,13,14	m	5,6,7,13,14	4,6,13,14
13	20.1	CH ₃	125	0.54	12	d	6,12,14	6,7a,7b,8b,12,14
14	23.4	CH ₃	125	0.45	12	d	6,12,13	4,5(w),6,7a,7b,12,13
15	25.9	CH ₃	130	1.31		s	5,8,9,10	5,8a,8b,18
16	23.6	CH ₃	128	2.42	4	s	1(w),2,3,4,4a(w),11(w),11a(w)	4
17	170.6	C						
18	53.8	CH ₃	149	3.74		s	11(w),17	15

[†]Interchangeable.

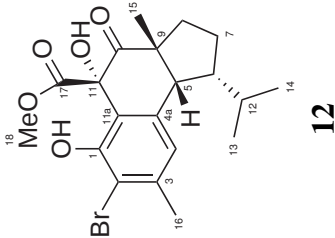


Table D.9. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for Hamigeran K (**13**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC (¹ H → ¹³ C)	NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm)			
1	158.1	C					
1-OH				12.22		1,2,11a	
2	110.8	C					
3	148.1	C					
4	124.5	CH	161	6.66	5,16	2,5,11,11a,16	5,6(w),12,16
4a	142.4	C					
5	52.2	CH	126	3.13		4,4a,6,9,10,11a,12,15	4,6,8a,15
6	48.0	CH	126	2.64		5,7,9,12,13,14	4(w),5,7b,12,13
7	24.8	CH ₂	121	1.75		6,8,12	7b,8b,10,13(w),14
			130	1.86		5,6,8,9	6,7a,8a
8	36.0	CH ₂	122	1.45		7,9,10,15	5,7b,8b,15
			126	2.23		5,6,7,9,10	7a,8a,10,15
9	50.4	C					
10	73.7	CH	140	4.43	10-OH,15	8,9,11,15	7a,8b,12,14
10-OH				3.47	10		
11	204.2	C					
11a	113.8	C					
12	28.4	CH	120	1.81	13,14	6,7,13,14	4,6,10,13,14
13	23.6	CH ₃	124	0.81	12	6,12,14	6,7a(w),12,14
14	17.7	CH ₃	122	0.43	12	6,12,13	7a,10,12,13
15	19.7	CH ₃	124	1.00	10	5,8,9,10	5,8a,8b
16	24.4	CH ₃	128	2.46	4	2,3,4	4

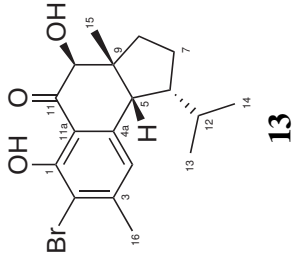


Table D.10. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for 10-*epi*-Hamigeran K (**14**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC (¹ H → ¹³ C)	NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm)	mult.	J (Hz)	
1	156.6	C					
1-OH				11.63	s		1,2,11a
2	110.8	C					
3	147.3	C					
4	123.1	CH	162	6.73	s	5.16	5,12,13,16
4a	140.2	C					
5	50.5	CH	131	3.20	d	6.1	4,4a,6,9,10,11a,12,15
6	53.6	CH	119	2.01	m		4a,5,7,8,12,13,14
7	28.0	CH ₂	113	0.71	m		5(w),6,8,12
			123	1.66	m		5,8,9
8	31.9	CH ₂	133	1.36	m		5,7,9,10,15
9	44.5	C	127	1.64	m		6,7a,8a,14
10	78.1	CH	141	4.25	s		5,10-OH,15
10-OH				3.67	br s	10	10
11	202.7	C					
11a	115.5	C					
12	26.9	CH	120	1.49	m		5(w),6,13,14
13	23.6	CH ₃	122	1.18	d	6.3	4,5,6,12,14
14	21.9	CH ₃	122	0.79	d	6.6	6,8a,12,13
15	28.6	CH ₃	124	1.43	s		5,6,8a,10
16	24.6	CH ₃	126	2.46	s	4	4

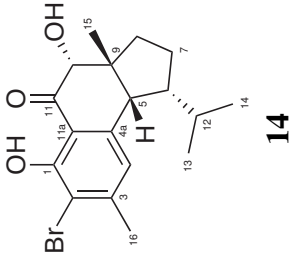


Table D.11. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for 4-Bromohamigeran K (**15**) in CDCl₃.

Position	¹³ C		¹ H		COSY	HMBC (¹ H → ¹³ C)	NOESY
	δ (ppm)	mult.	¹ J _{CH} (Hz)	δ (ppm) mult.			
1	157.8	C					
1-OH				12.62 s		1,2,11a	
2	112.7	C					
3	148.2	C					
4	119.3	C					
4a	142.7	C					
5	54.9	CH	128	3.33 d	6	4,4a,6,9,10,11a,12,15	6,15
6	46.4	CH	128	2.93 m	5	4a,5,7,9,12,13,14	5,7b,13
7	24.2	CH ₂	123	1.73 m	7b,8a,8b	6,8,12	7b,8b,10,14
			123	1.92 m	6(w),7a,8a,8b	5,6,8,9	6,7a,8a(w),14(w)
8	36.0	CH ₂	124	1.46 m	7a,7b,8b	7,9,10,15	7b(w),8b,15
			132	2.25 m	7a,8a	4a,5,6,7,9,10	7a,8a,15
9	50.6	C					
10	73.0	CH	139	4.49 s	15	5(w),8,9,11,11(w),15	7a,14
11	204.9	C					
11a	114.7	C					
12	28.7	CH	120	1.66 m	6,13,14	6,7,13,14	10,13,14
13	23.5	CH ₃	119	0.80 d	12,14	6,12,14	6,7b,12,14
14	18.1	CH ₃	123	0.47 d	12,13	6,12,13	6(w),7a,7b(w),10,12,13
15	19.4	CH ₃	124	0.98 s	10	5,8,9,10	5,8a,8b
16	26.4	CH ₃	128	2.73 s		1(w),2,3,4,4a(w),11a(w)	

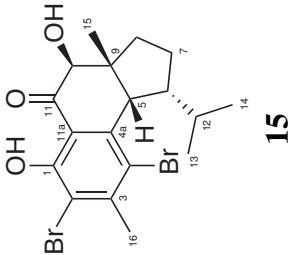


Table D.12. ^{13}C (150 MHz) and ^1H (600 MHz) NMR Data for Hamigeran L (**16**) in CDCl_3 .

Position	^{13}C		^1H		J (Hz)	COSY	HMBC ($^1\text{H} \rightarrow ^{13}\text{C}$)	NOESY
	δ (ppm)	mult.	$^1J_{\text{CH}}$ (Hz)	δ (ppm)				
1	159.0	C						
2	112.3	C						
3	144.6	C						
4	123.6	CH	160	6.56		17	1(w),2,4a(w),5,12,12a,17	7a,8b,13,17
4a	144.2	C						
5	50.1	CH	136	4.55	6.9	6	4,4a,6,7,8,9,12a,16	6,13,15,16
6	51.6	CH	124	2.34		5,7a,7b(w),13(w)	4a,5,7,13,14,15	5,7a,7b,13,14,15,16
7	28.8	CH_2	122	1.64		6,7b,8a,8b	6,8,9,13	4,6,7b,13,14,16
8	38.7	CH_2	125	2.16		6,7a,8a,8b	5,6,8,9(w),10(w)	6,7a,8a,14
9	47.2	C	122	1.57	12.4,9,9,2,1	7a,7b,8b	5,6,7,9,16	7b,8b,10b,16
10	42.4	CH_2	117	1.77	12.5,7,5	7a,7b,8a,16	9,10,16	4,8a,10a,10b
11	180.0	C						
12	177.3	C						
12a	113.1	C						
13	30.7	CH	120	1.40		10b,16	5,8,9,11,16	8b,10b
14	22.5	CH_3	125	0.91	6.5	10a	5,8,9,11,16	10a,16
15	22.0	CH_3	124	0.69	6.4			
16	27.7	CH_3	126	1.31				
17	24.6	CH_3	128	2.45				
						6,14,15	6,14,15	4,5,6,7a,14,15
						13,15	6,13,15	6,7a,7b,13,15
						13,14	6,13,14	5,6,13,14
						8b,10a	5,8,9,10	5,6,7a,8a,10b
						4	1(w),2,3,4	4

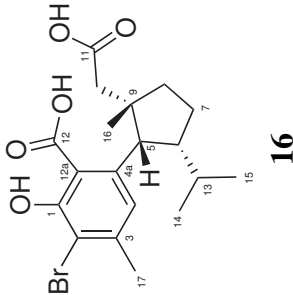


Table D.13. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for Hamigeran L 11-*O*-Methyl Ester (**17**) in CDCl₃.

Position	¹³ C		¹ H		¹ J _{CH} (Hz)	HMBC (¹ H → ¹³ C)		COSY	NOESY
	δ (ppm)	mult.	δ (ppm)	mult.					
1	156.7	C							
2	111.8	C							
3	143.4	C							
4	123.2	CH	6.53	s	160	1(w), 2, 4a(w), 5, 12(w), 12a, 17	17	7a, 8b, 10b, 13, 17	
4a	141.7	C							
5	52.9	CH	3.87	d	135	3(w), 4, 4a, 6, 7, 8, 9, 12a, 16	6	6, 15, 16	
6	51.7	CH	2.23	m	121	4a, 5, 7, 13, 14	5, 7a, 7b, 13	5, 7a(w), 7b, 13(w), 14, 15, 16	
7	29.1	CH ₂	1.64	m	124	6, 8, 9, 13	6, 7b, 8a, 8b	4, 6(w), 7b, 8a, 8b, 13, 14	
			2.08	m	131	5, 6(w), 8, 9	6, 7a, 8a, 8b	6, 7a, 8a, 8b, 14	
8	37.9	CH ₂	1.78	m	130	5, 6, 7, 9, 16	7a, 7b, 8b	7a, 7b, 8b, 16	
			1.92	m	121	6(w), 7, 9, 10, 16	7a, 7b, 8a	4, 7a, 7b, 8a, 10a, 10b	
9	46.2	C							
10	43.4	CH ₂	2.02	d	126	5, 8, 9, 11, 16	10b	8b, 10b, 16	
			2.38	d	125	5(w), 8, 9, 11, 16	10a	4, 8b, 10a, 16	
11	174.8	C							
12	172.1	C							
12a	115.4	C							
13	30.1	CH	1.12	m	123	5(w), 6, 7(w), 15	6, 14, 15	4, 6(w), 7a, 14, 15	
14	22.3	CH ₃	0.82	d	122	6, 13, 15	13	6, 7a, 7b, 13, 15	
15	22.2	CH ₃	0.63	d	121	6, 13, 14	13	5, 6, 13, 14	
16	28.2	CH ₃	1.25	s	124	5, 8, 9, 10	8b, 10a	5, 6, 8a, 10, 10b	
17	24.6	CH ₃	2.43	s	125	2, 3, 4	4		
18	51.9	CH ₃	3.59	s	145	11			

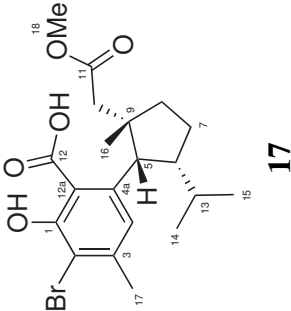
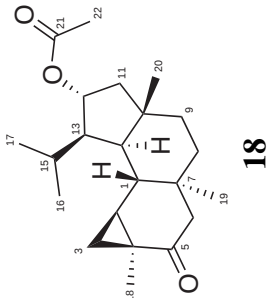


Table D.14. ¹³C (150 MHz) and ¹H (600 MHz) NMR Data for 12-Acetoxy-13-*epi*-neoverrucosan-5-one (**18**) in CDCl₃.

Position	¹³ C		¹ H		¹ J _{CH} (Hz)	δ (ppm)	COSY		HMBC (¹ H → ¹³ C)	NOESY
	mult.	δ (ppm)	mult.	J (Hz)						
1	CH	46.9	128	1.75	1.75	1.75	1,2,13,14 [†]	1,3,6(w),7,8,9,10,11,12,13(w),14,19,20 [†]	2,3a,3b,6a,6b,8b,9a,11a,13,15,19,20 [†]	
2	CH	32.1	161	1.27	1.27	1.27	1,3a,3b	3,4,5,14,18	1,3a,14,15,16,19(w)	
3	CH ₂	29.3	153	0.97	0.97	0.97	2,3b	1,2,4,5,18	2,3b	
4	C	30.6	157	1.22	1.22	1.22	2,3a	1,5,18	3a,15	
5	C	211.4								
6	CH ₂	53.8	121	1.90	1.90	1.90	6b,19	1,5,7,8,19	1,6b,8b	
7	C	40.9	131	1.97	1.97	1.97	6a	1,4,5,7,8,19	6a,8a,8b,19	
8	CH ₂	35.1	126	1.16	1.16	1.16	8b,9a,9b	1,6,7,9,19	6b,8b,9a,9b,19	
9	CH ₂	31.9	121	1.29	1.29	1.29	8a,9a,9b	1,6,7,9,19	6a,8a,9b,11a,14	
10	C	41.0	124	1.34	1.34	1.34	8a,8b,9b	8,10,11,14	8a,9b,11a,11b,20	
11	CH ₂	43.9	122	1.54	1.54	1.54	8a,8b,9a	8,10,11,12,20	8a,9a,19,20	
12	CH	76.2	126	1.64	1.64	1.64	11b,12,20	10,12,20	8b,9a,11b,14	
13	CH	55.4	131	1.96	1.96	1.96	11a,12	13,14,20	9a,11a,12,20	
14	CH	48.5	117	5.14	5.14	5.14	11a,11b,13	10,14,21	11a,11b,13,17,20	
15	CH	25.1	132	2.07	2.07	2.07	12,14,15	1,14,15,16	2,12,14,15,16,17	
16	CH ₃	24.0	128	1.75	1.75	1.75	dsept	1,2,13,14 [†]	1,3,6(w),7,8,9,10,11,12,13(w),14,19,20 [†]	2,3a,3b,6a,6b,8b,9a,11a,13,15,19,20 [†]
17	CH ₃	22.2	126	2.36	2.36	2.36	d	13,16,17	12,13,14,16,17	1,2,3b,13,16,17
18	CH ₃	20.8	127	1.04	1.04	1.04	d	15,17	12(w),13,15,17	2,15,17,20
19	CH ₃	16.4	125	0.89	0.89	0.89	s	15,16	13,15,16	12,15,16
20	CH ₃	32.3	124	1.23	1.23	1.23	s	6a	2,3,4,5	19
21	C	170.7		0.81	0.81	0.81	s	11a	1,6,7,8	2(w),6b,9b,11a,18
22	CH ₃	21.6	128	1.05	1.05	1.05	s		8(w),9,10,11,14	9a,9b,11b,12,13,16



[†]2D-NMR correlations for H-1 and H-14 were indistinguishable due to high second-order effects arising from overlapping signals.

[‡]Estimated value from HSQC experiment due to overlap with H₃-20.

Table D.15. ^{13}C (150 MHz), ^1H (600 MHz) and NOESY (600 MHz) NMR Data for 12-Acetoxy-13-*epi*-neoverrucosan-5-one (**18**) in C_6D_6 .

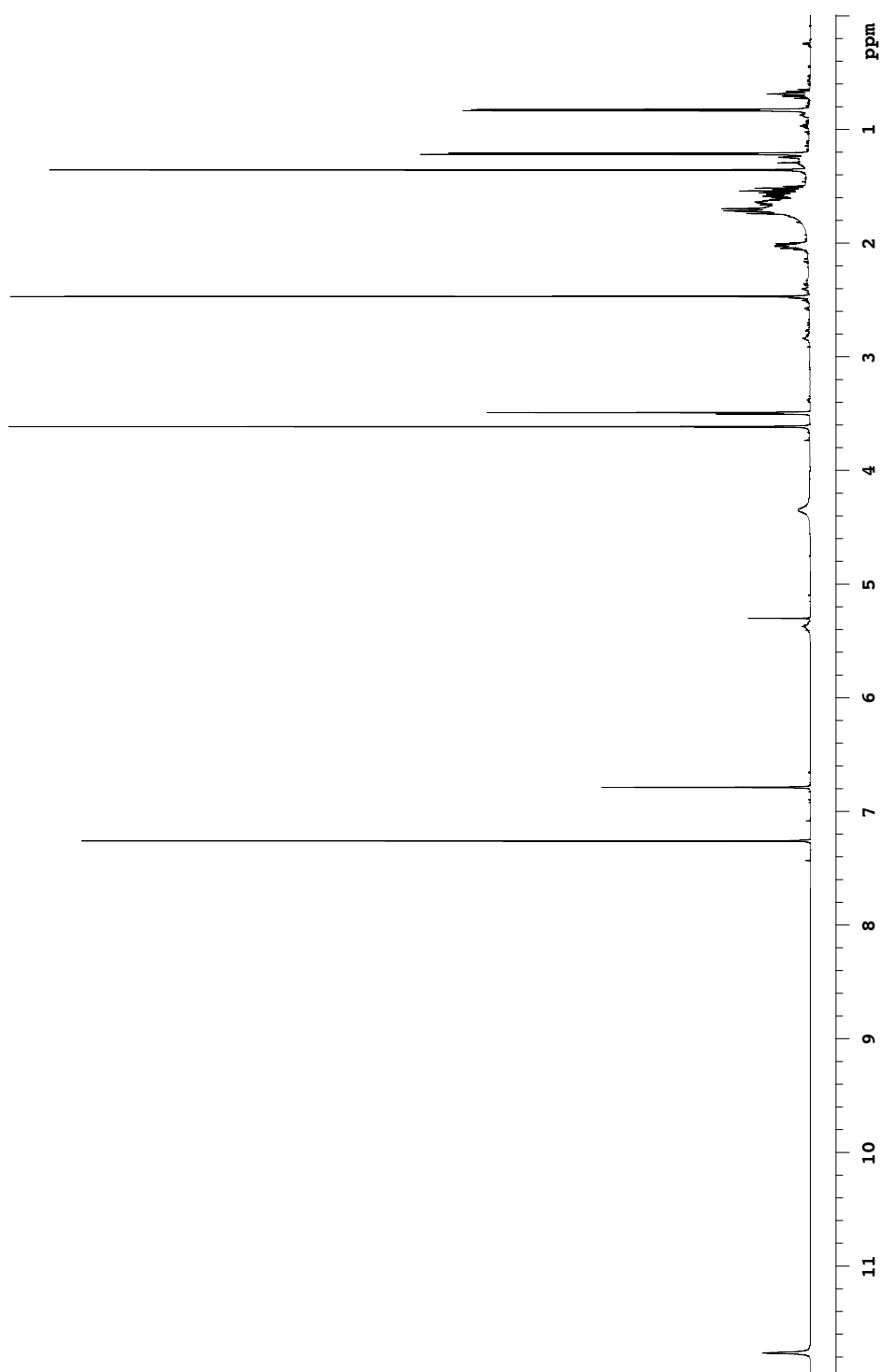
Position	^{13}C			^1H			NOESY
	δ (ppm)	mult.	$^1J_{\text{CH}}$ (Hz)	δ (ppm)	mult.	J (Hz)	
1	46.9	CH	125	1.61	dd	11.8,4.2	2(w),3a,6a,8b,14,15(w)
2	31.4	CH	158	1.02	m		1(w),3a,3b,14,15,18
3	28.4	CH_2	160	0.69	dd [†]	4.8,4.8 [†]	1,2,3b,6a
			162	0.86	dd [†]	8.0,4.4 [†]	2,3a,18
4	30.3	C					
5	208.3	C					
6	53.9	CH_2	122	1.65	d	15.0	1,3a,6b,8b
			132	2.01	d	15.3	6a,8a,8b(w),19
7	40.4	C					
8	35.1	CH_2	127	0.79	ddd	13.5,4.6,2.5	6b,8b,9b(w),14,19
			123	0.94	td	13.6,4.2	1,6a,8a,9a,9b(w),11a
9	32.1	CH_2	125	1.01	m		9b,11b(w),20
			124	1.26	td	14.2,4.6	8a(w),8b(w),9a,19
10	40.8	C					
11	44.2	CH_2	127	1.53	m		8b,9a,11b,12(w)
			130	1.80	m		9a(w),11a,12,20
12	75.7	CH	155	5.20	ddd	8.0,8.0,2.4	11a(w),11b,13,16,17,20(w)
13	55.5	CH	120	1.82	m		12,14,15,16,17
14	48.8	CH	135	1.50	dd	12.0,5.0 [†]	1,2,8a,13,16,17,19
15	25.1	CH	130	2.30	dsept	11.2,6.4	1,2(w),3a,12(w),13,16,17
16	22.2 [‡]	CH_3	125	0.87 [‡]	d	6.6 [‡]	12,13,14,15
17	23.8 [‡]	CH_3	124	0.87 [‡]	d	6.1 [‡]	12,13,14,15
18	21.1	CH_3	127	1.30	s		2,3b,19
19	16.4	CH_3	124	0.68	s		6b,8a,9b,14,18
20	32.2	CH_3	124	0.78	s		9a,9b,11b,12(w),13,14
21	169.4	C					
22	21.0	CH_3	128	1.66	s		

[†]Multiplicities and J -values observed from a 1D-TOCSY experiment.

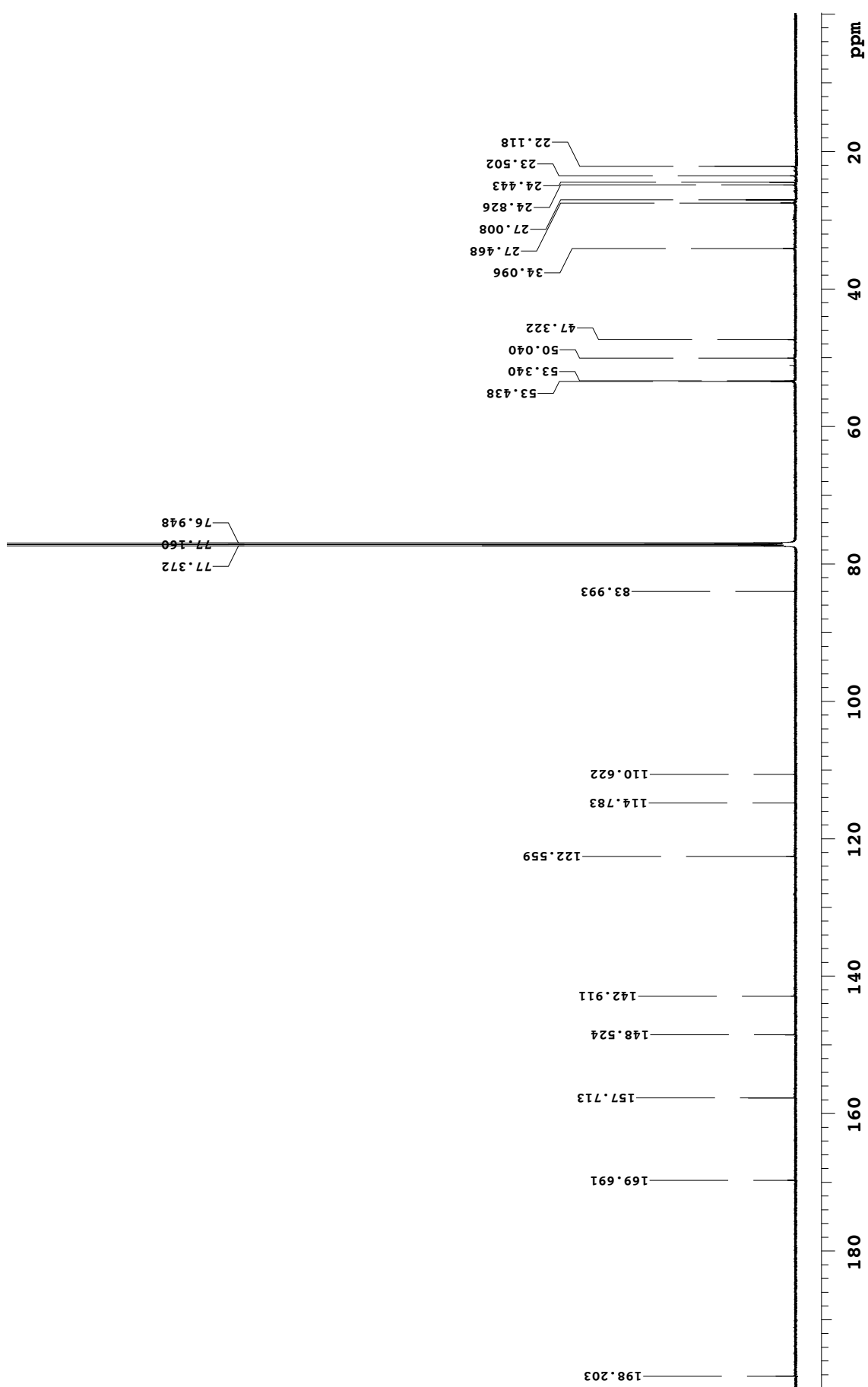
[‡]Interchangeable.

Appendix E

Hamigeran A Spectra



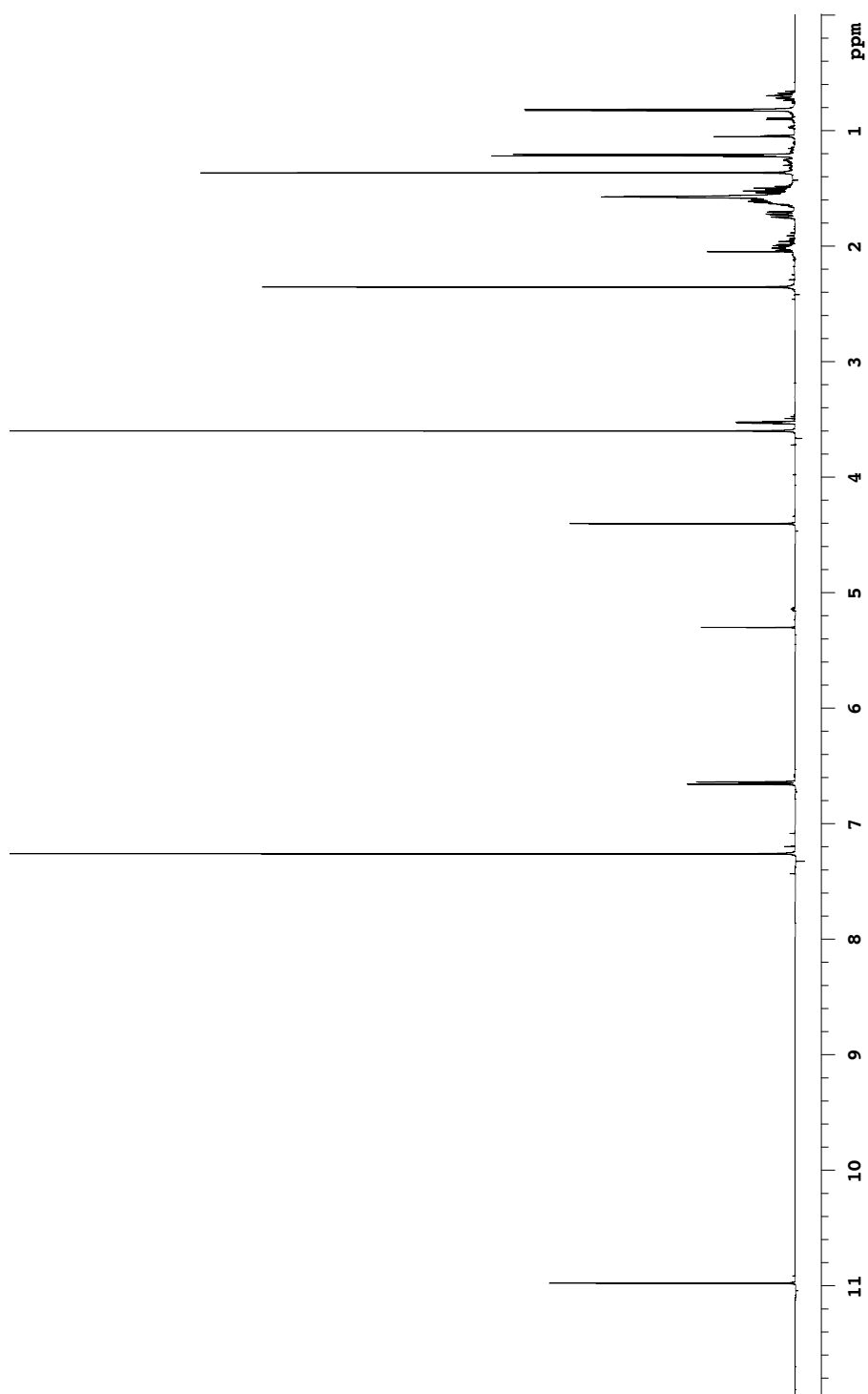
¹H NMR spectrum of hamigeran A (**2**) in CDCl₃ (600 MHz).



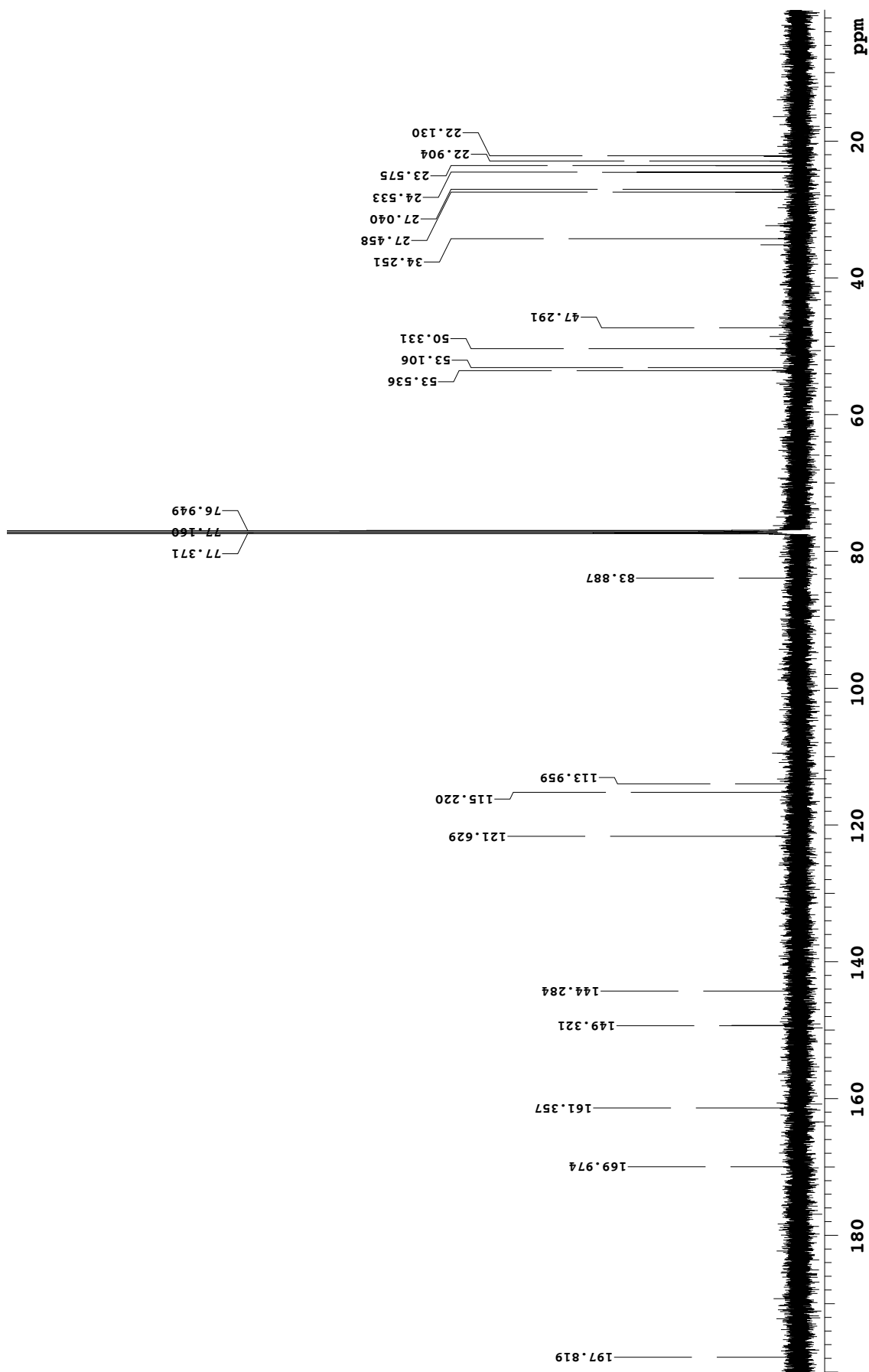
¹³C NMR spectrum of hamigeran A (**2**) in CDCl₃ (150 MHz).

Appendix F

Debromohamigeran A Spectra



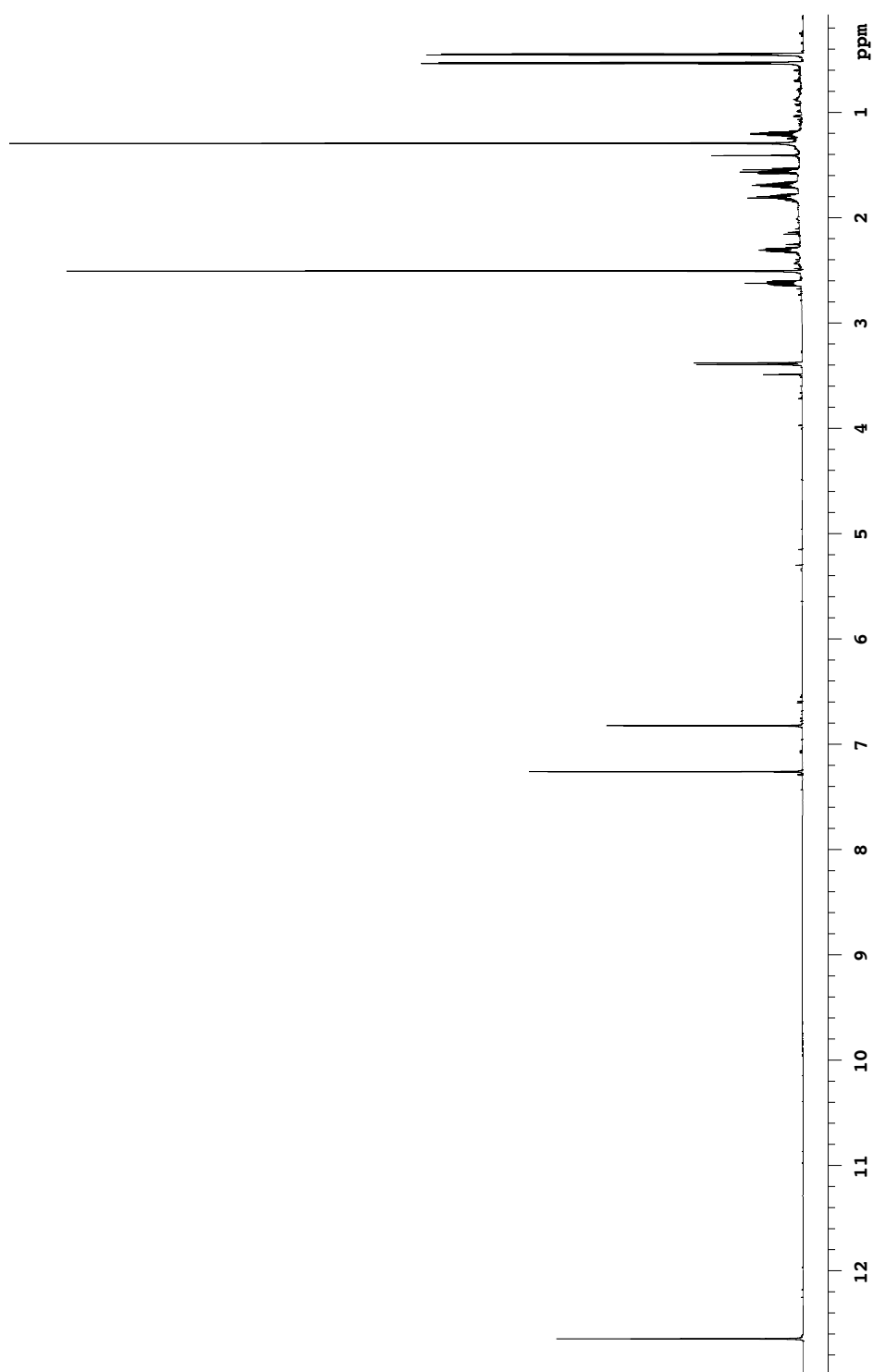
^1H NMR spectrum of debromohamigeran A (**3**) in CDCl_3 (600 MHz).



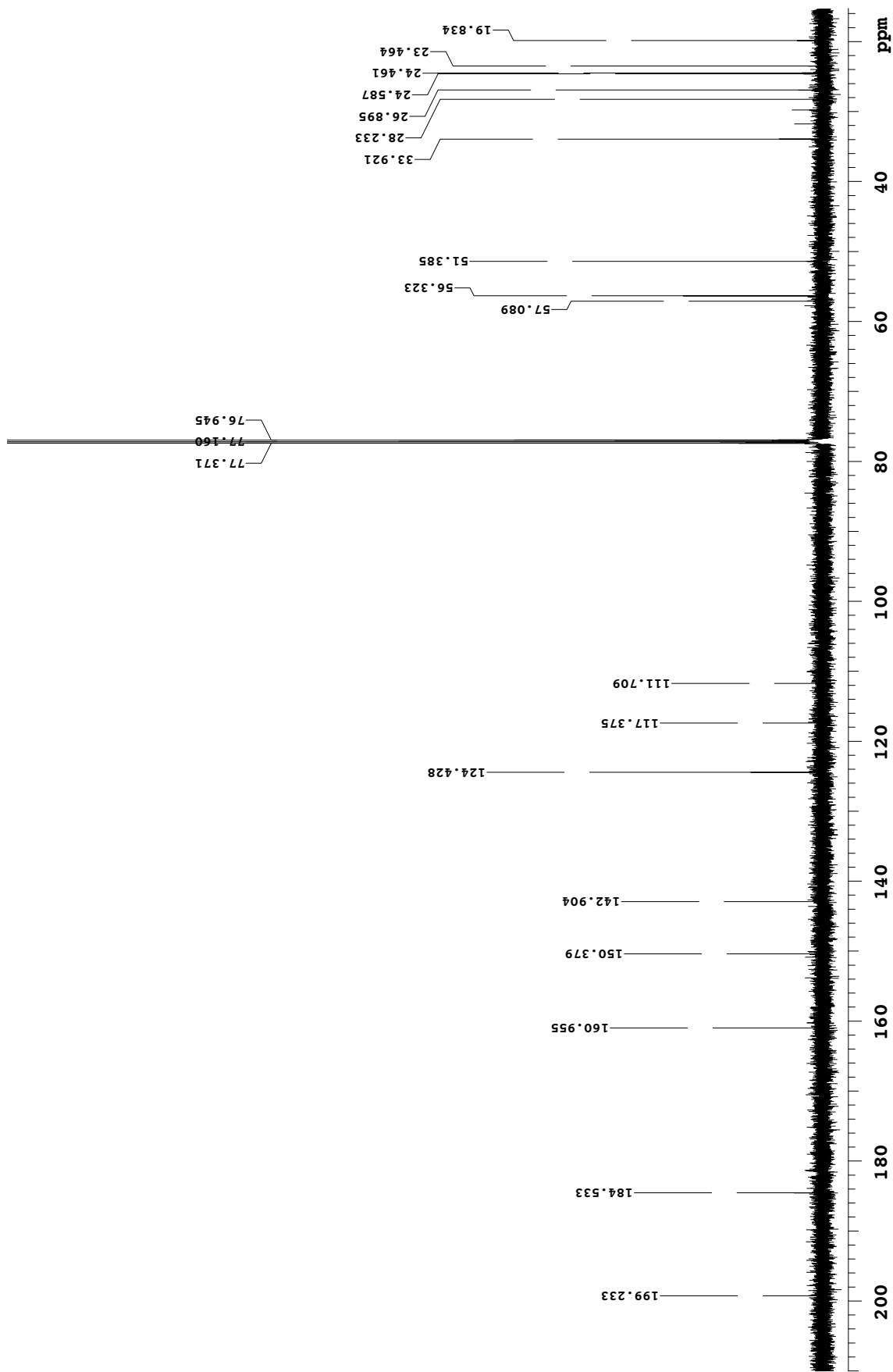
¹³C NMR spectrum of debromohamigeran A (**3**) in CDCl₃ (150 MHz).

Appendix G

Hamigeran B Spectra



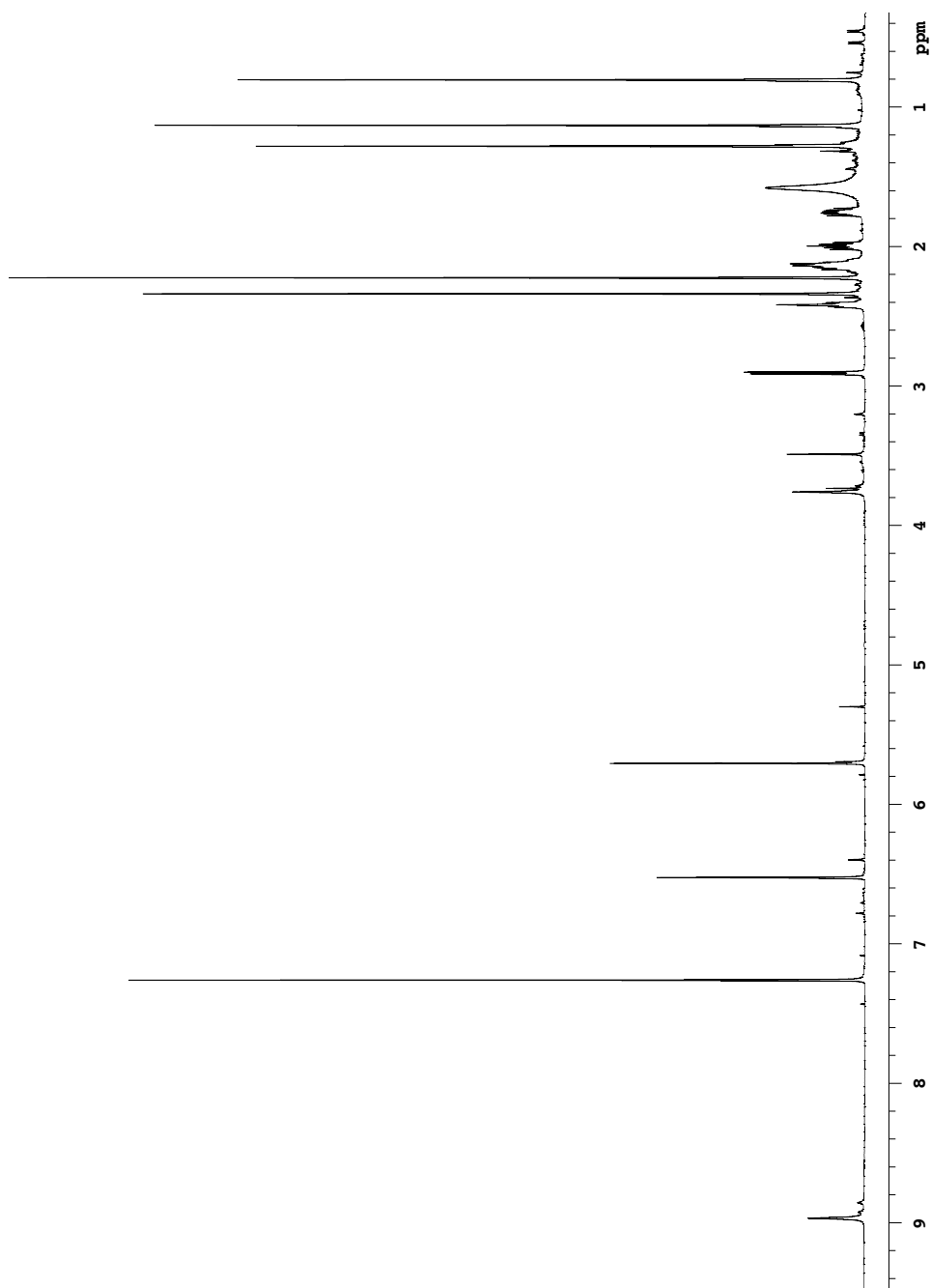
^1H NMR spectrum of hamigeran B (**4**) in CDCl_3 (600 MHz).



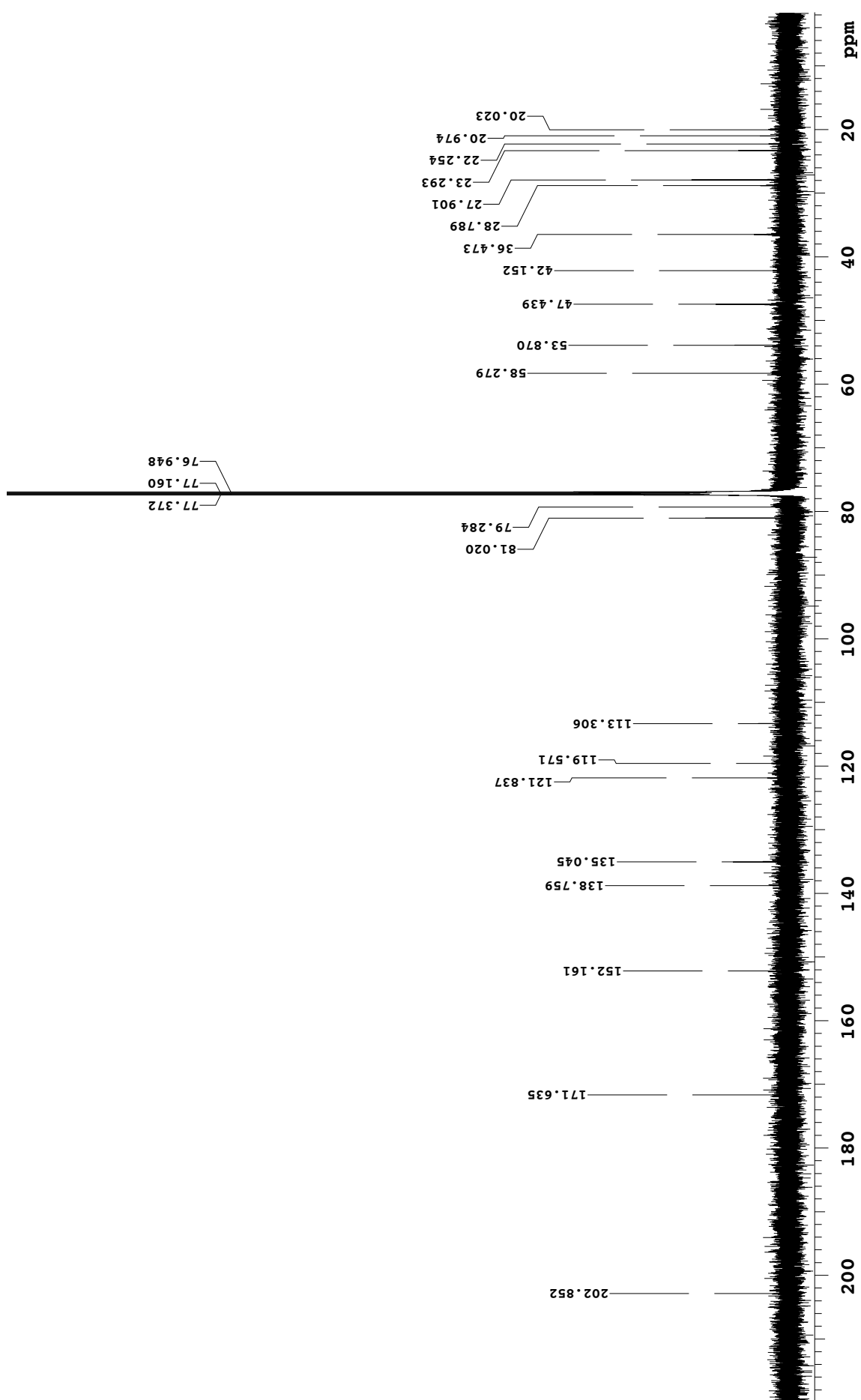
¹³C NMR spectrum of hamigeran B (**4**) in CDCl₃ (150 MHz).

Appendix H

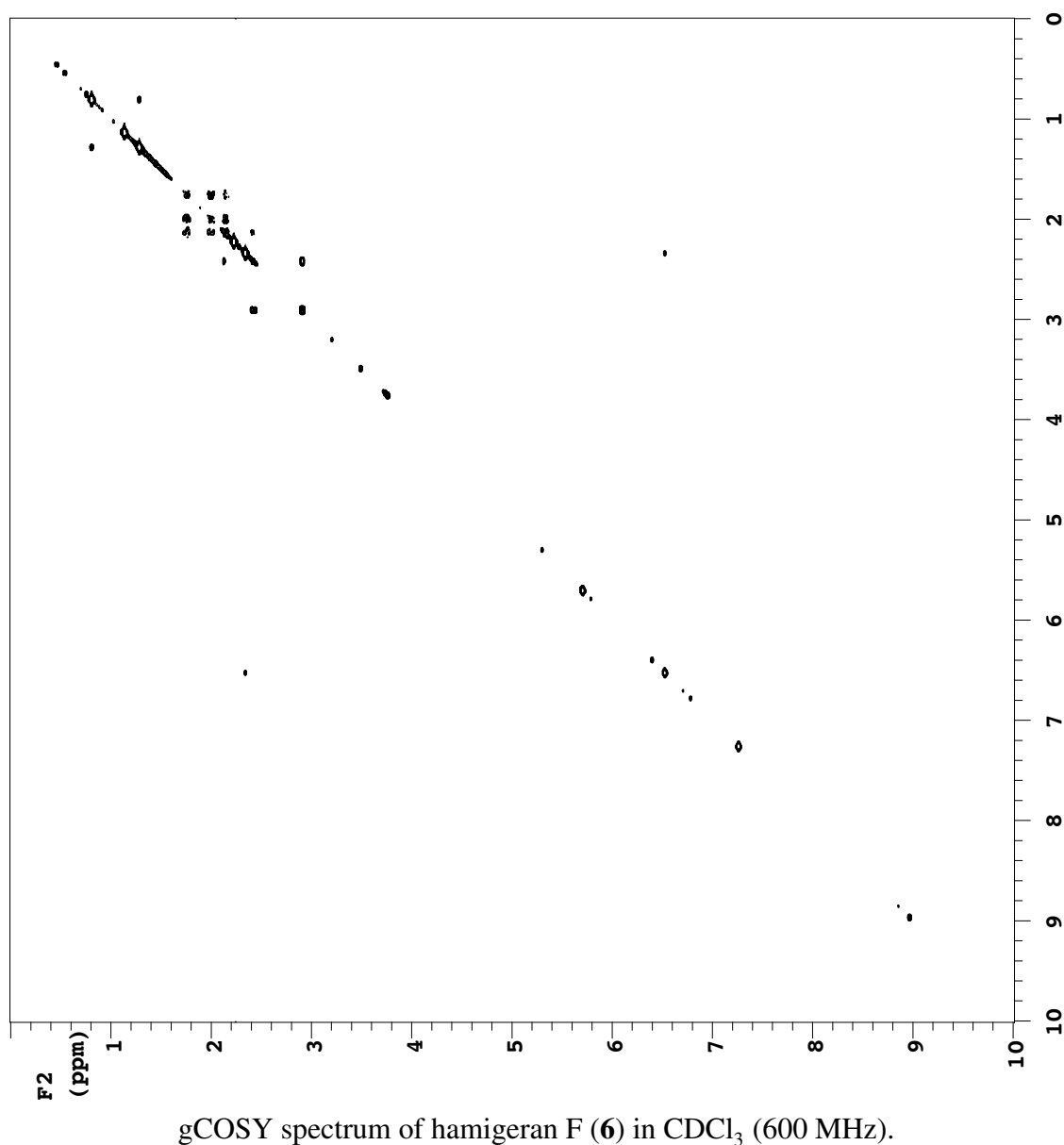
Hamigeran F NMR Spectra

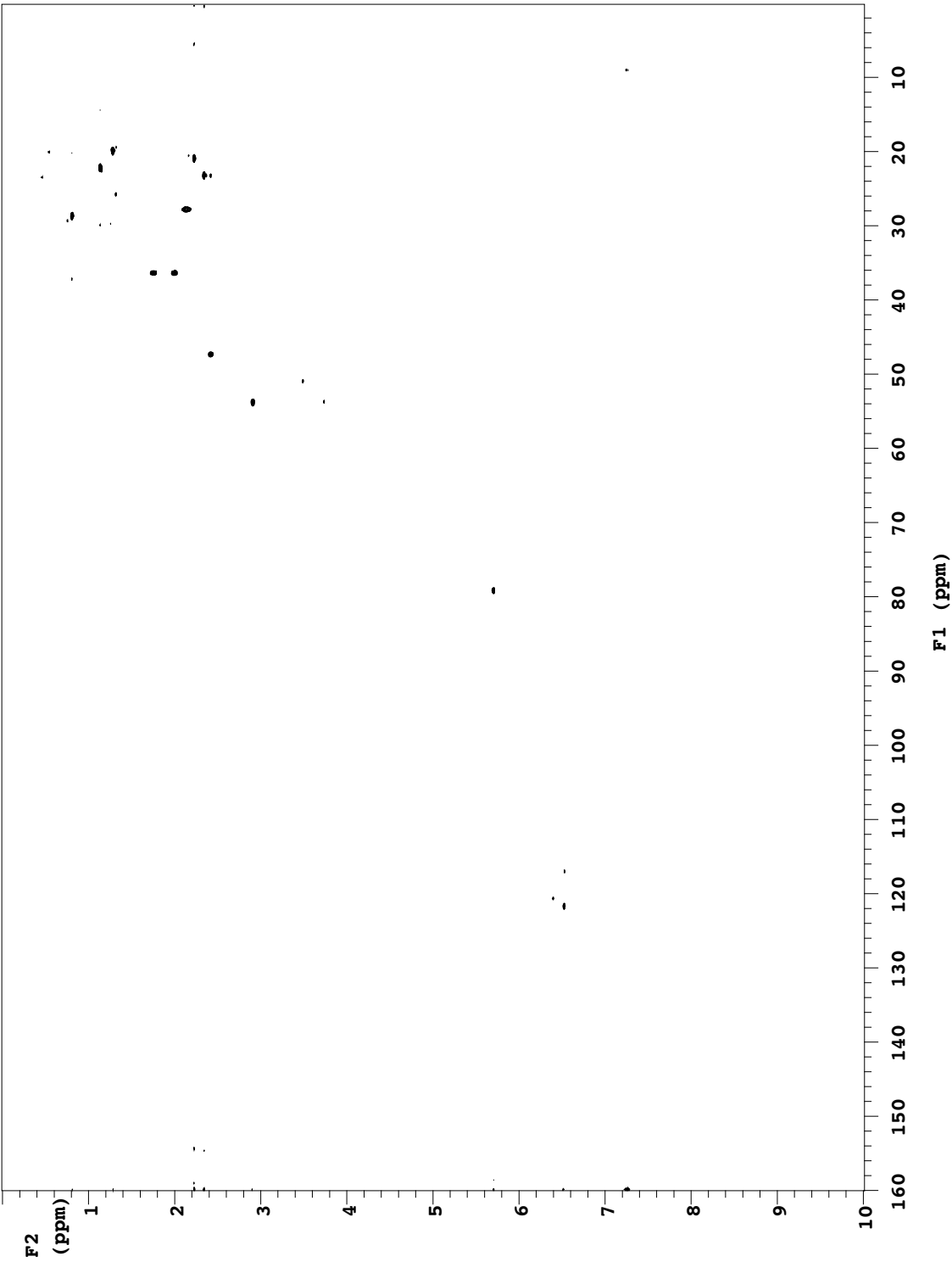


^1H NMR spectrum of hamigeran F (**6**) in CDCl_3 (600 MHz).

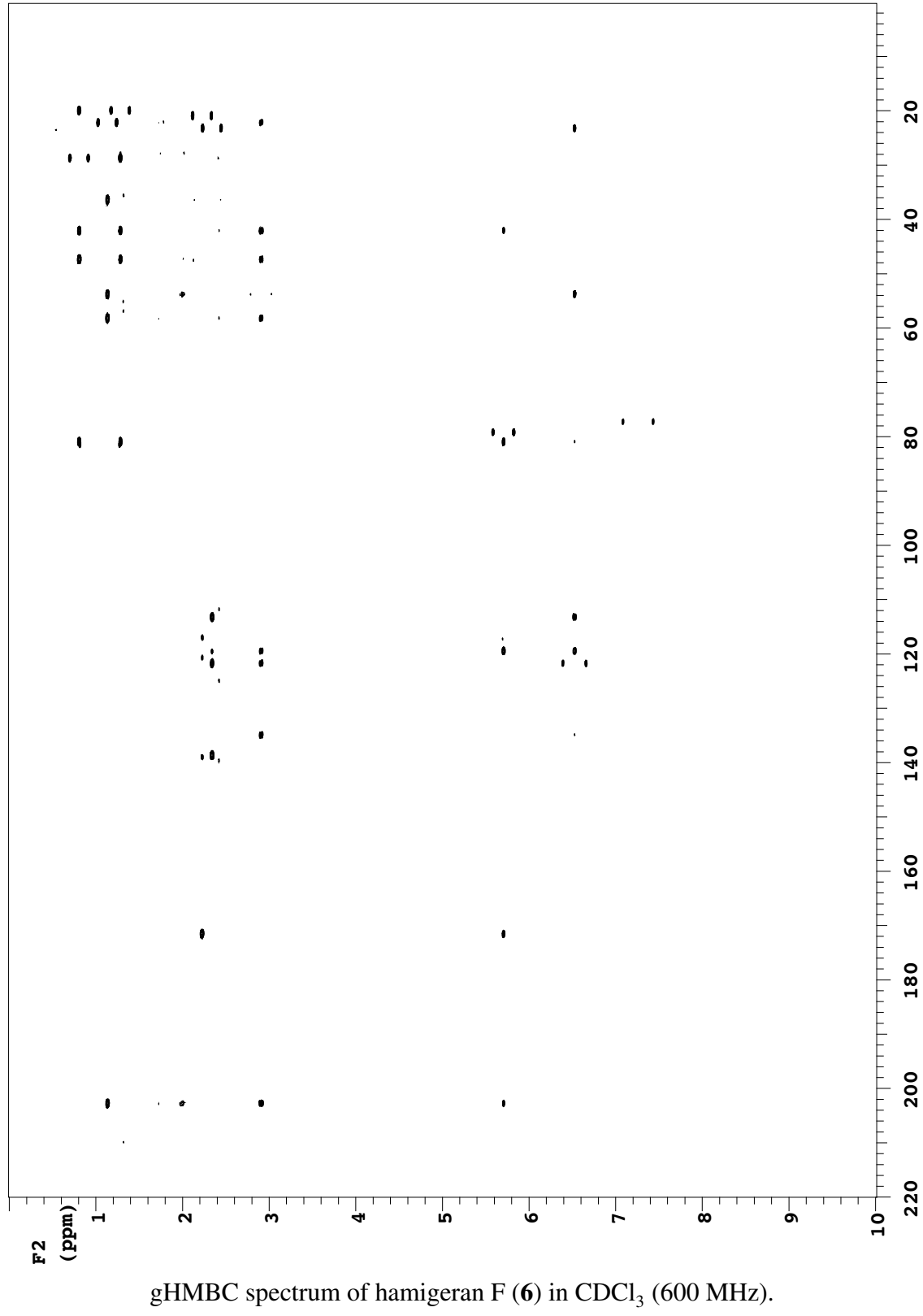


¹³C NMR spectrum of hamigeran F (6) in CDCl₃ (150 MHz).

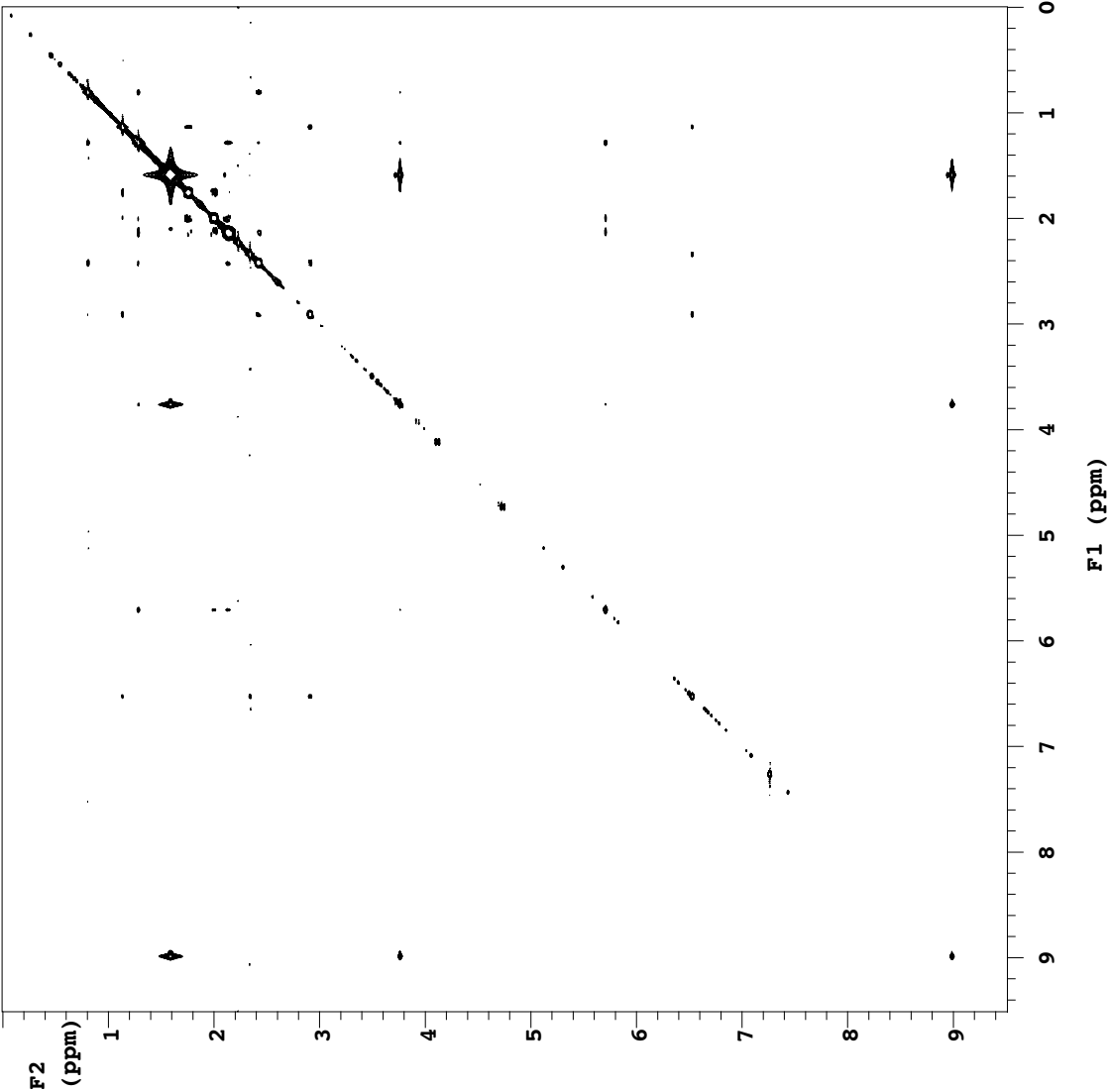




HSQCAD spectrum of hamigeran F (**6**) in CDCl₃ (600 MHz).



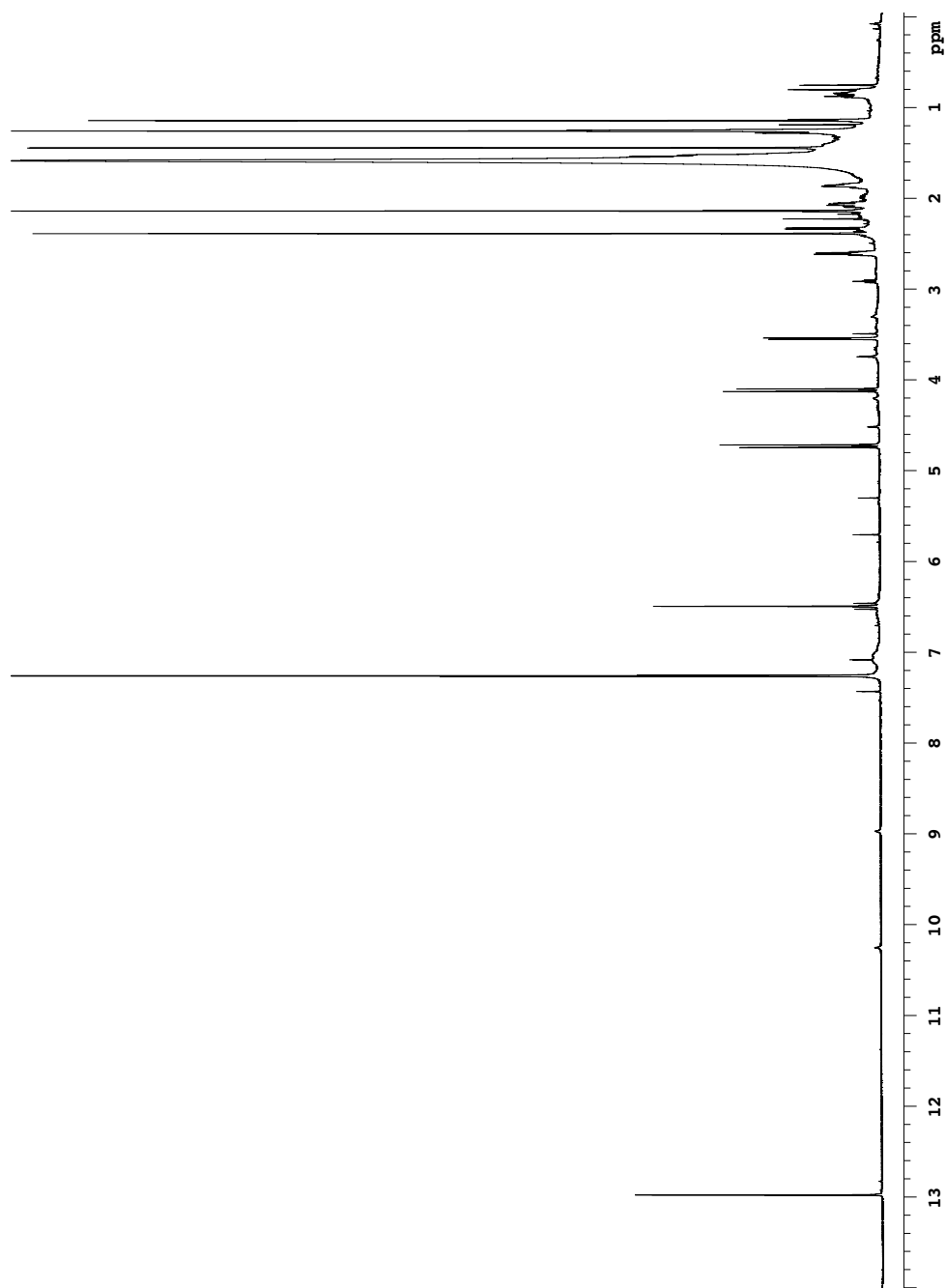
gHMBC spectrum of hamigeran F (**6**) in CDCl₃ (600 MHz).



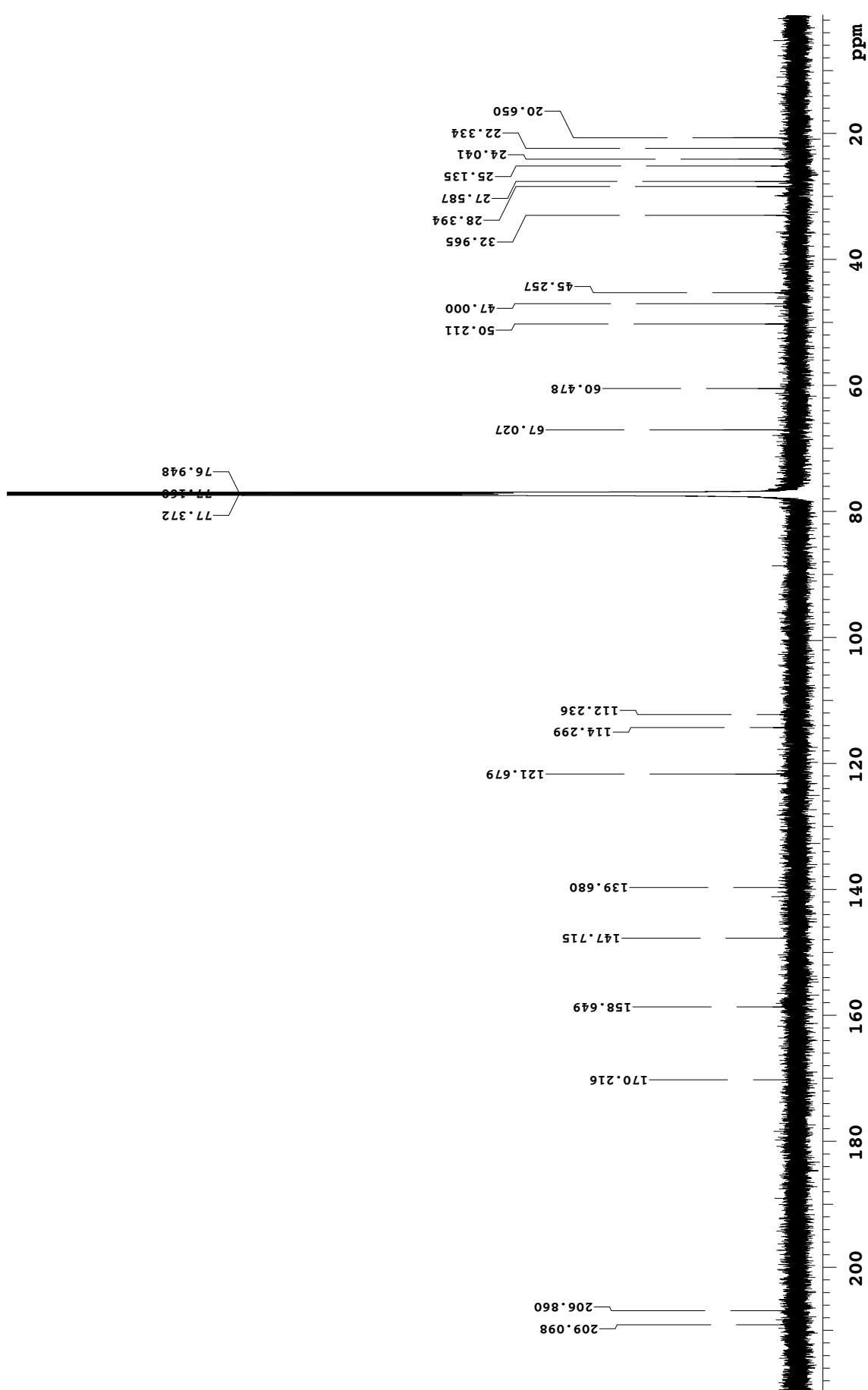
NOESY spectrum of hamigeran F (**6**) in CDCl₃ (600 MHz).

Appendix I

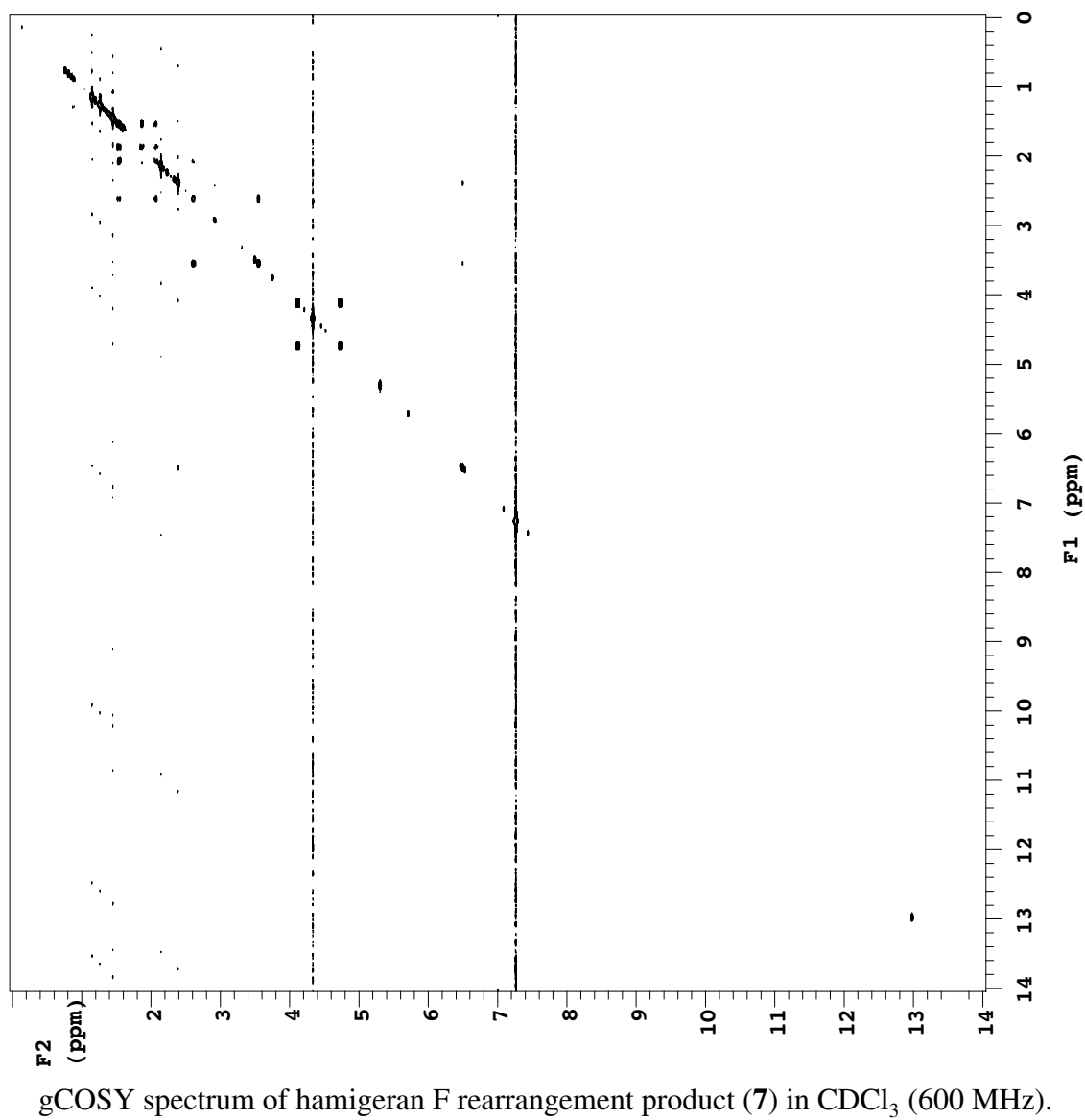
Hamigeran F Rearrangement Product NMR Spectra



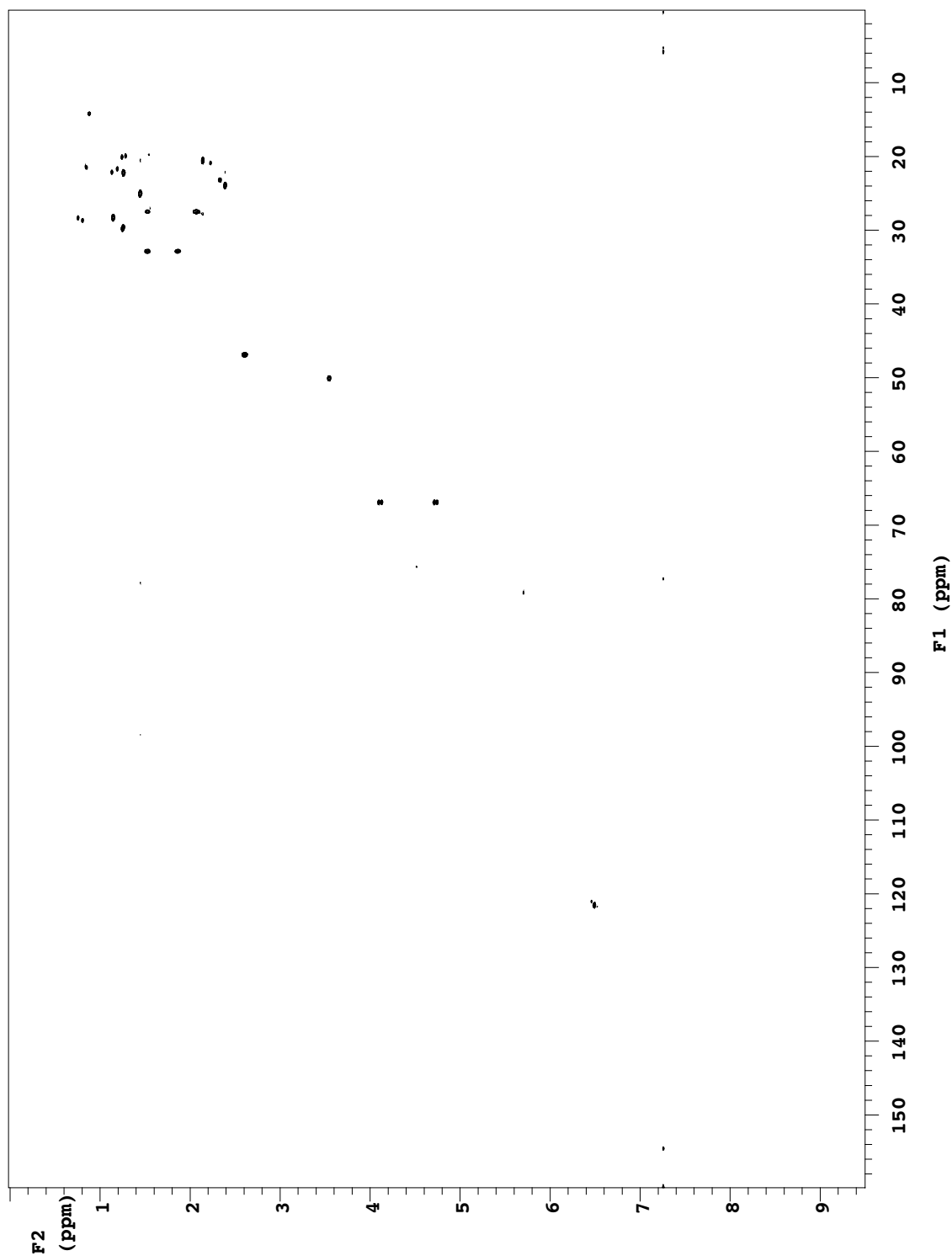
^1H NMR spectrum of hamigeran F rearrangement product (**7**) in CDCl_3 (600 MHz).



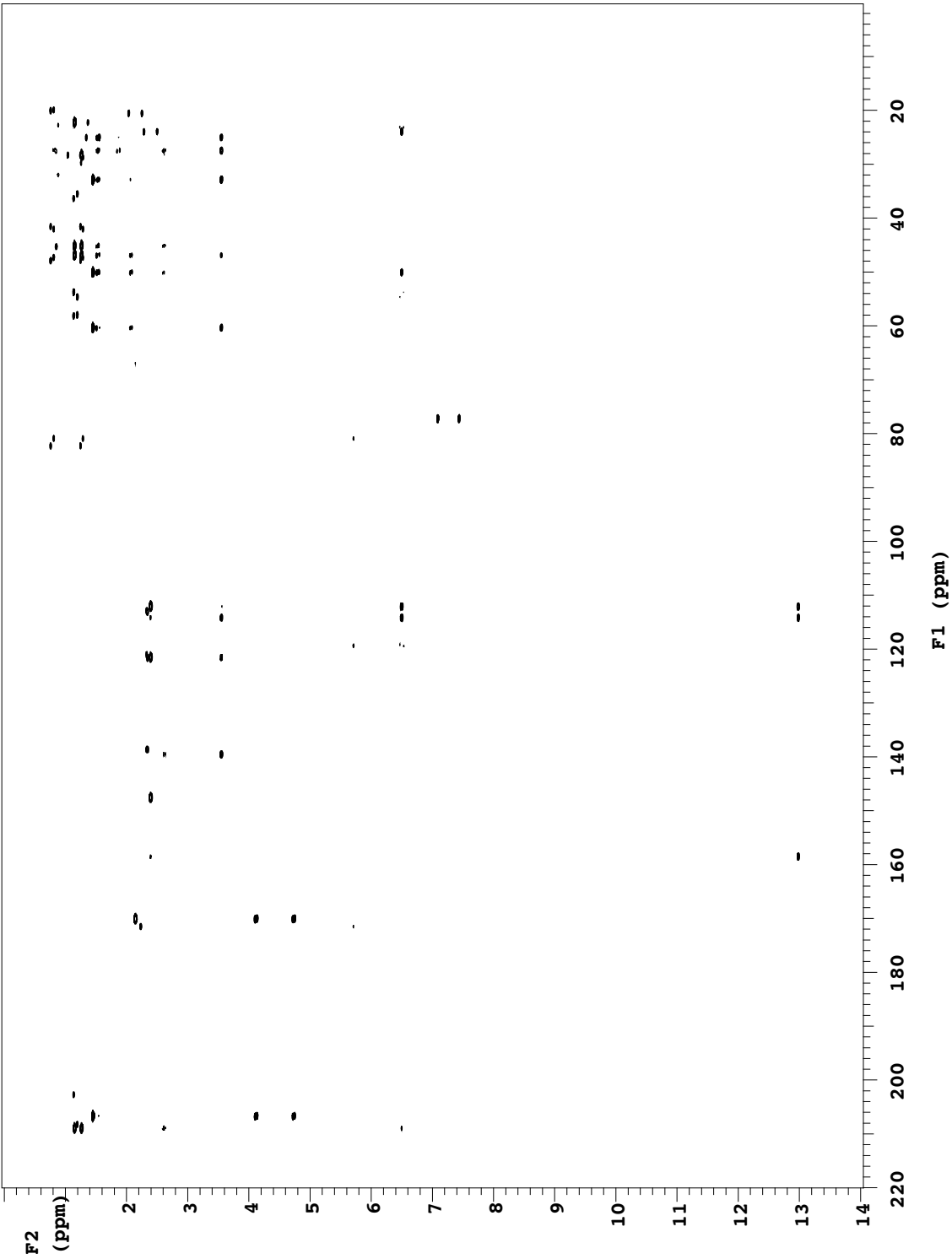
¹³C NMR spectrum of hamigeran F rearrangement product (**7**) in CDCl₃ (150 MHz).



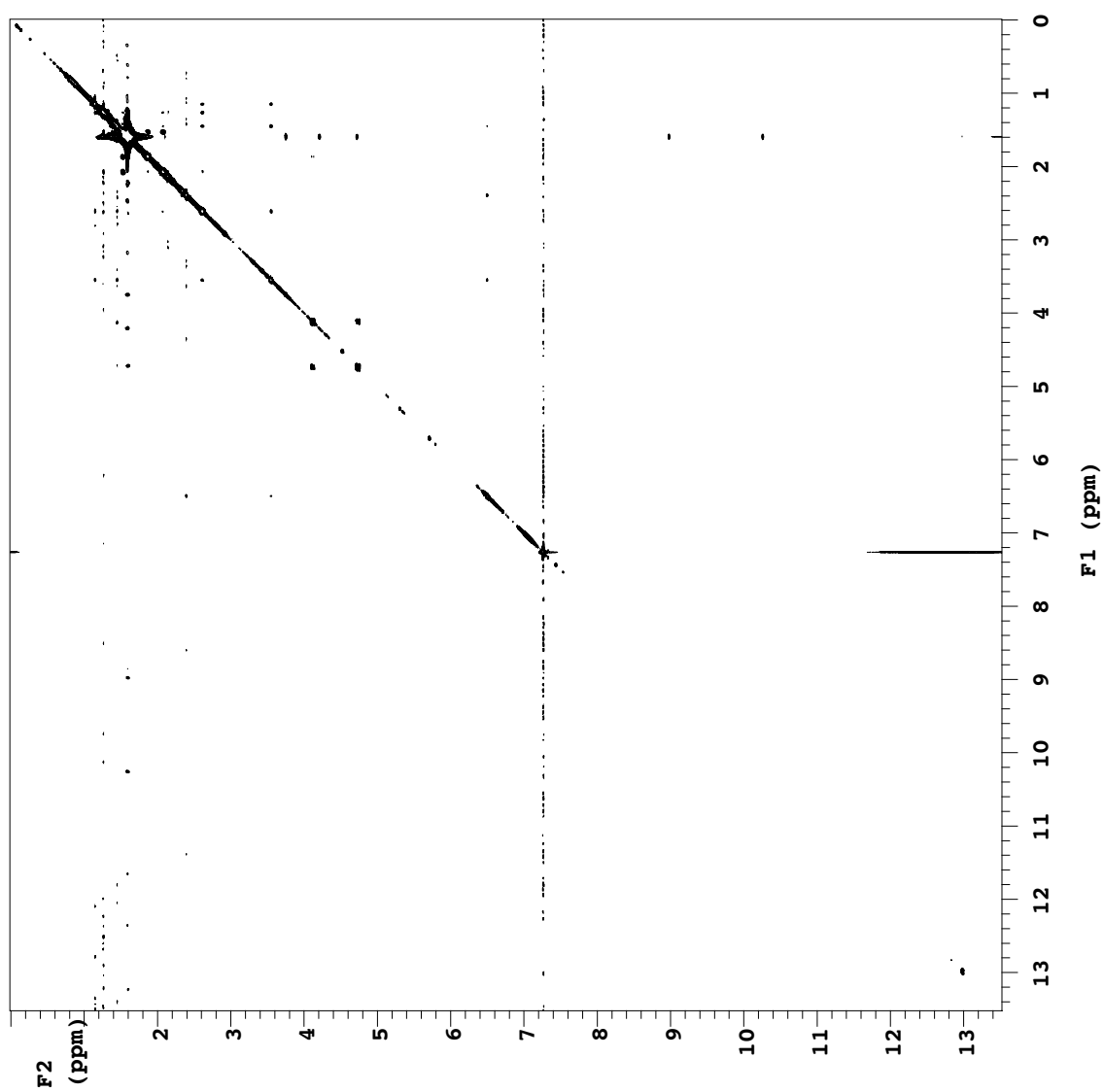
¹H COSY spectrum of hamigeran F rearrangement product (**7**) in CDCl₃ (600 MHz).



HSQCAD spectrum of hamigeran F rearrangement product (**7**) in CDCl₃ (600 MHz).



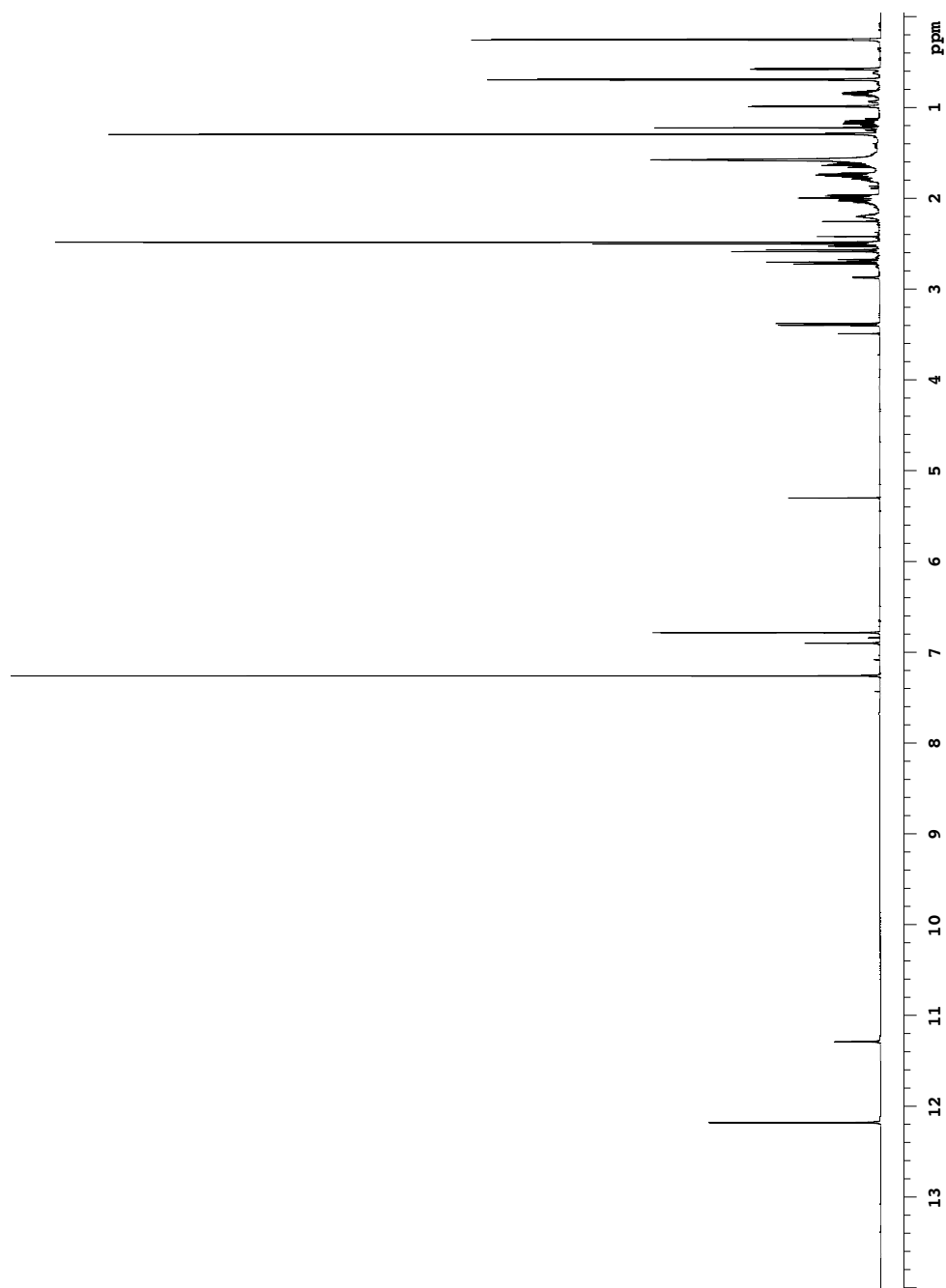
gHMBC spectrum of hamigeran F rearrangement product (**7**) in CDCl₃ (600 MHz).



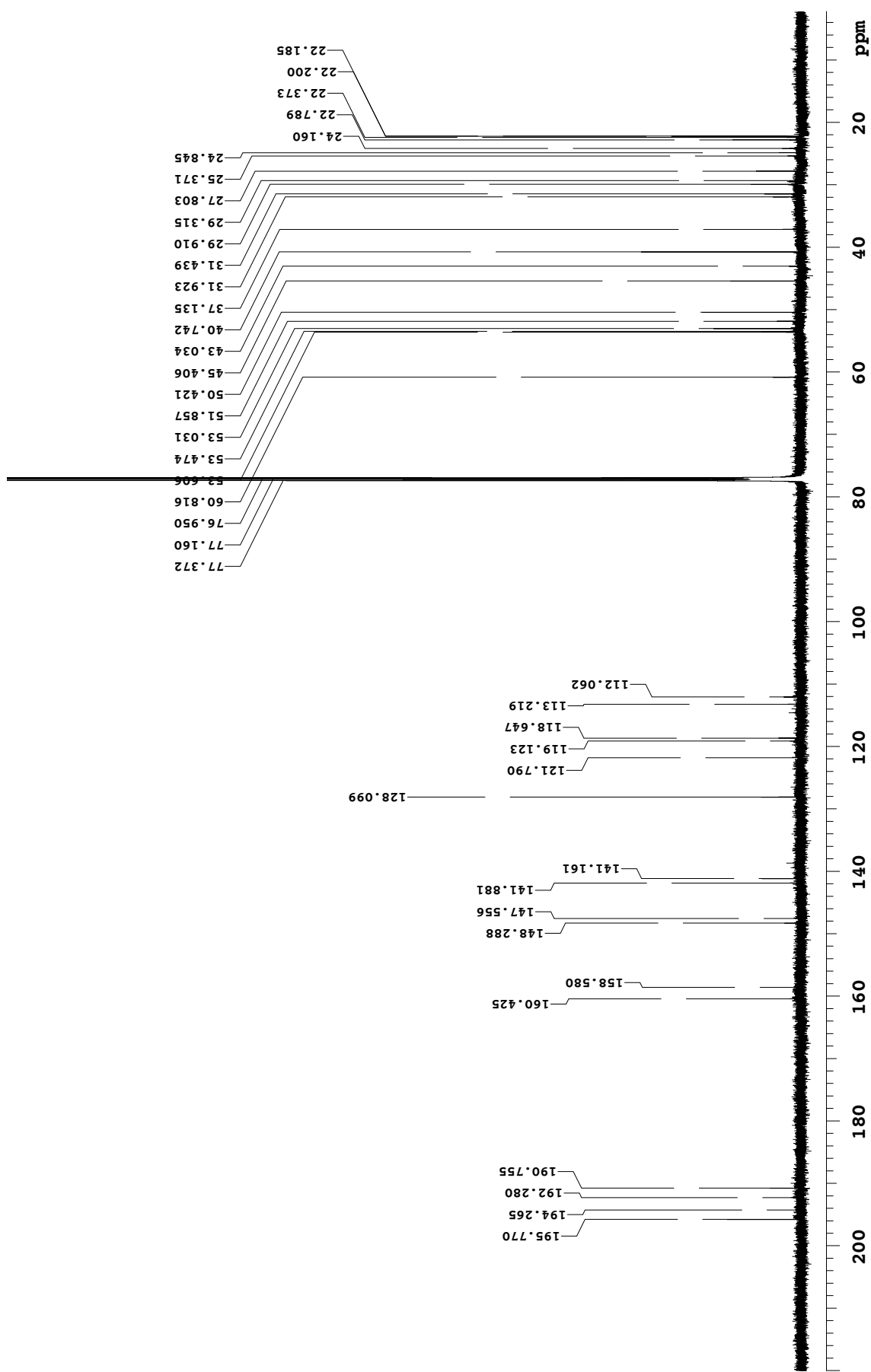
NOESY spectrum of hamigeran F rearrangement product (**7**) in CDCl₃ (600 MHz).

Appendix J

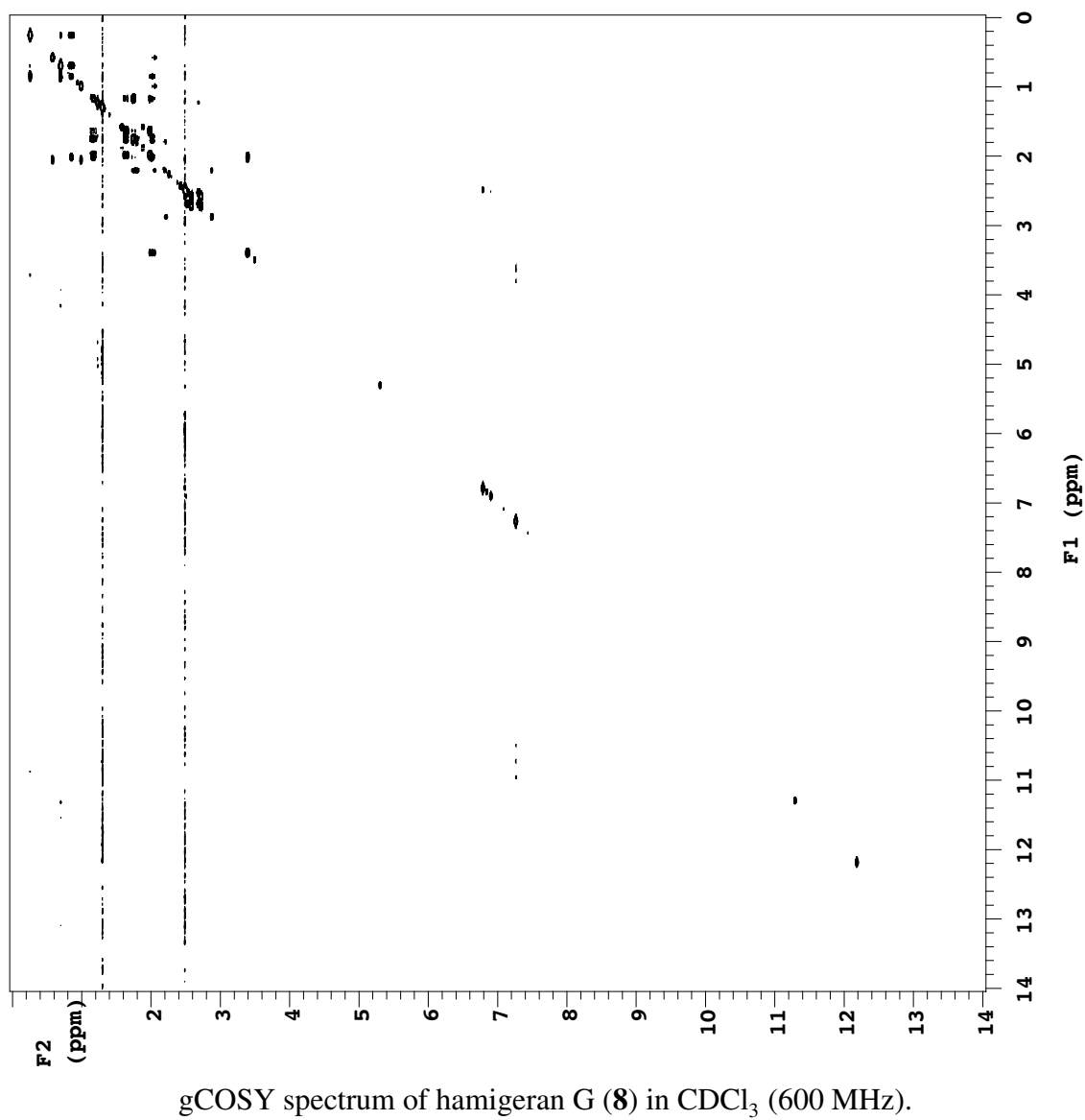
Hamigeran G NMR Spectra

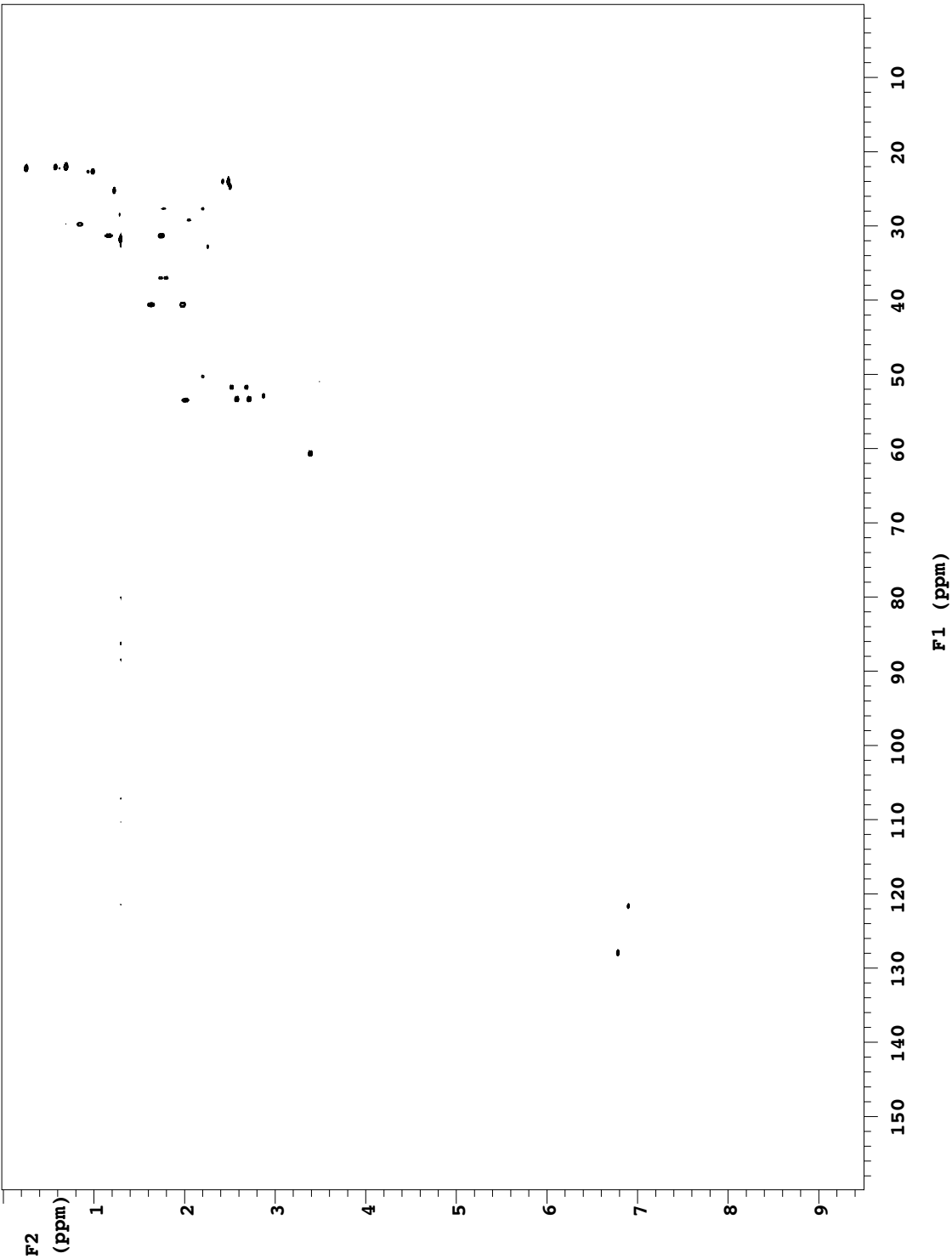


^1H NMR spectrum of hamigeran G (**8**) in CDCl_3 (600 MHz).

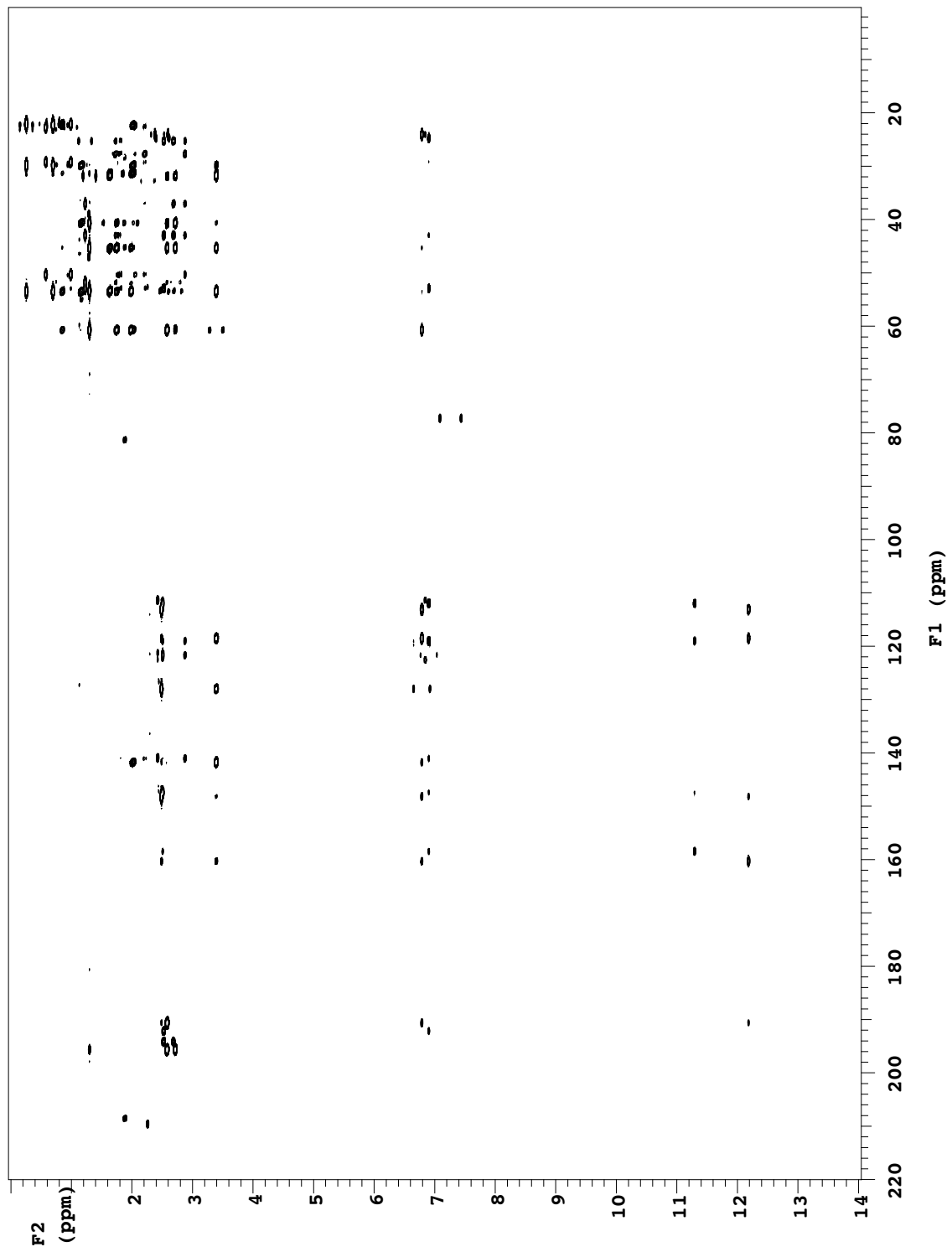


¹³C NMR spectrum of hamigeran G (**8**) in CDCl₃ (150 MHz).

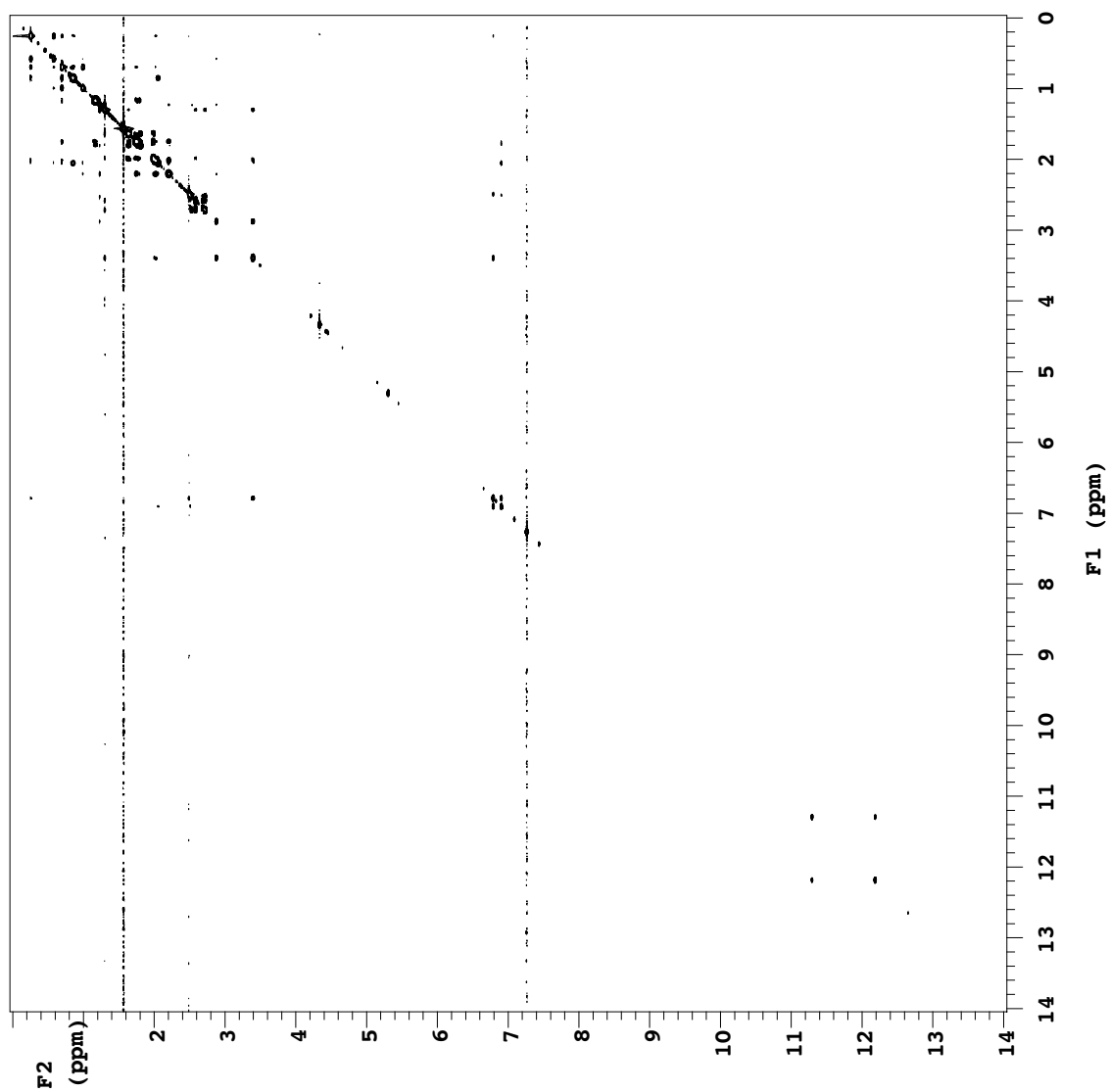




HSQCAD spectrum of hamigeran G (**8**) in CDCl₃ (600 MHz).



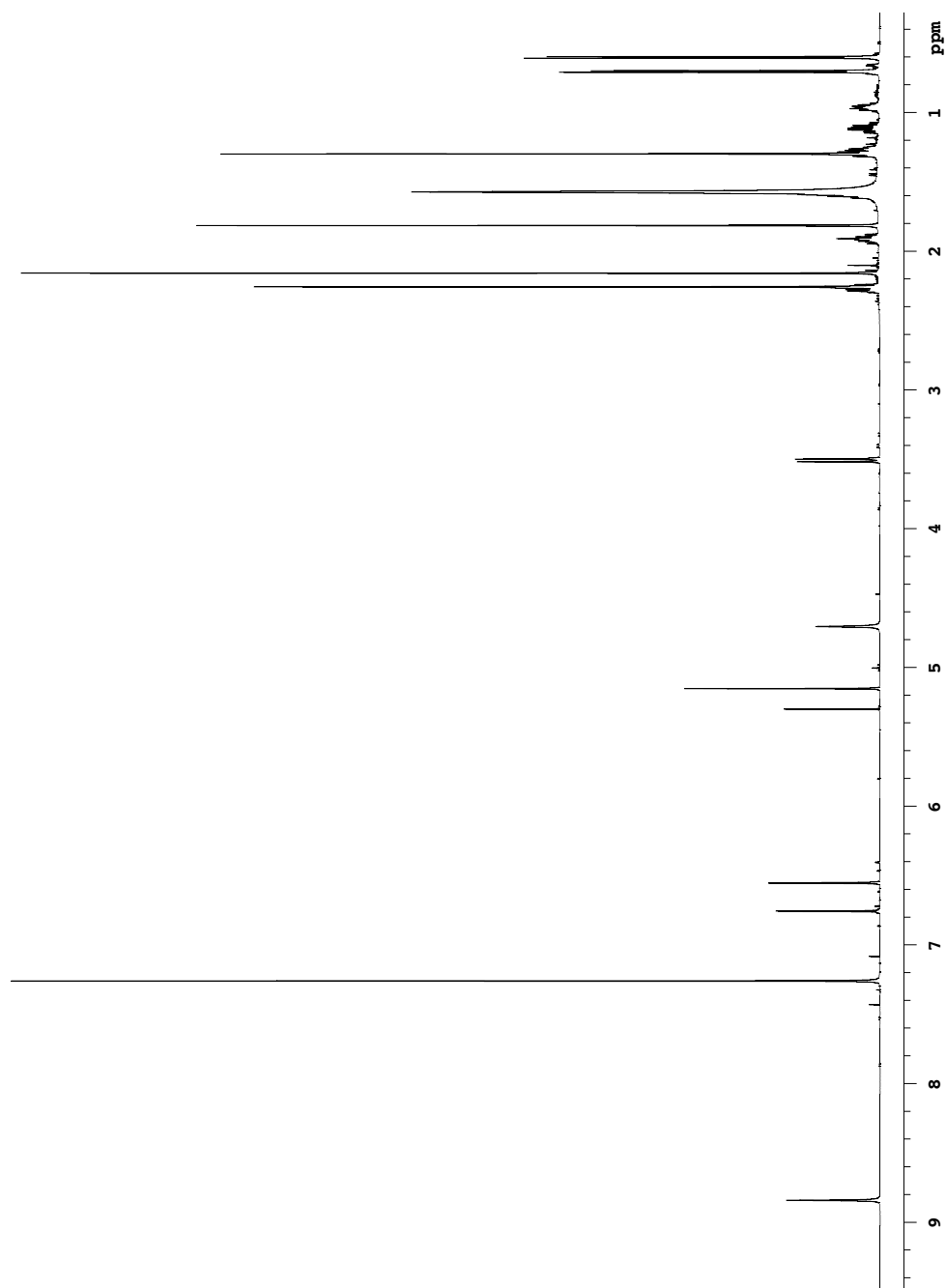
gHMBC spectrum of hamigeran G (**8**) in CDCl₃ (600 MHz).



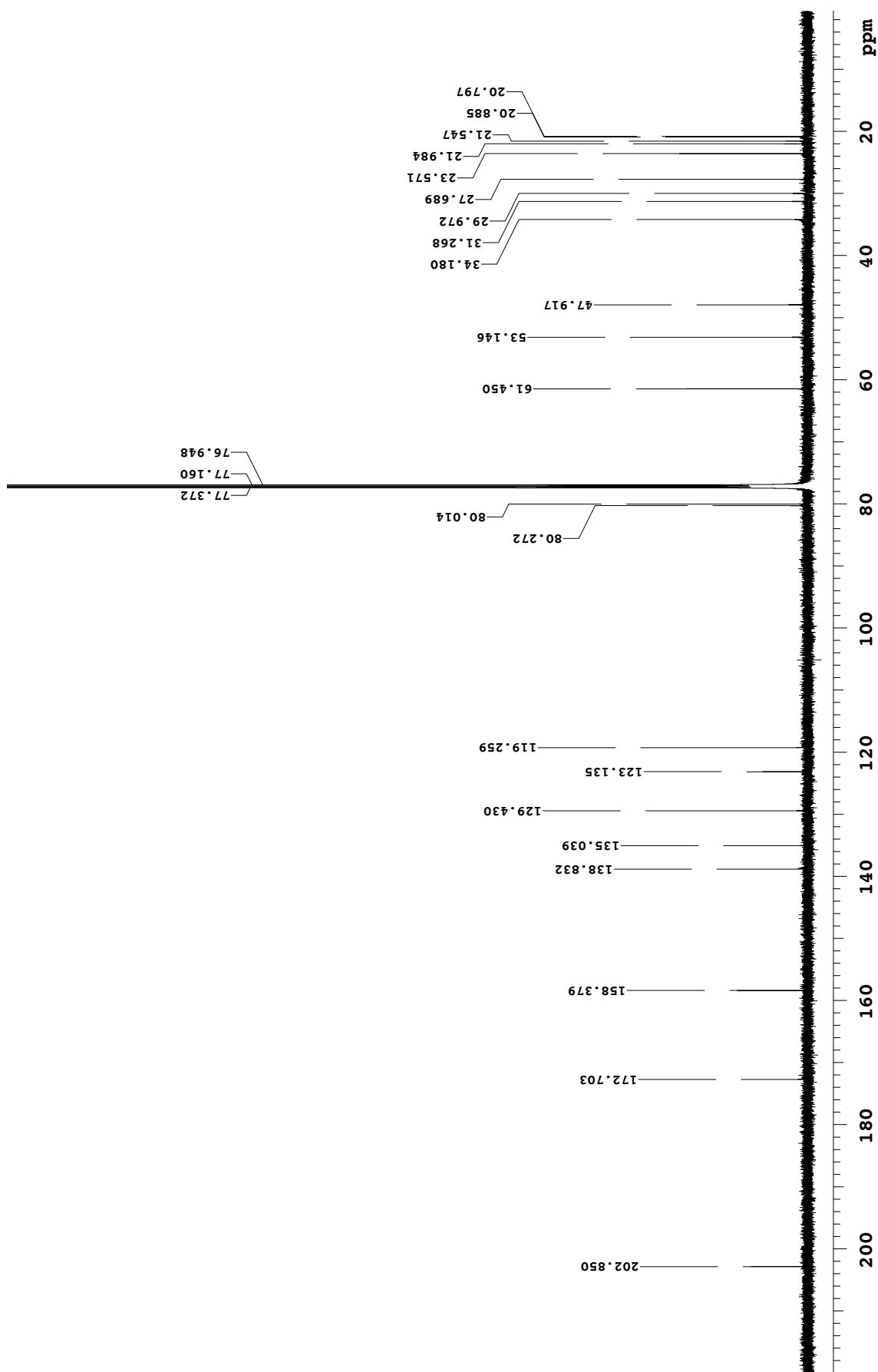
NOESY spectrum of hamigeran G (**8**) in CDCl₃ (600 MHz).

Appendix K

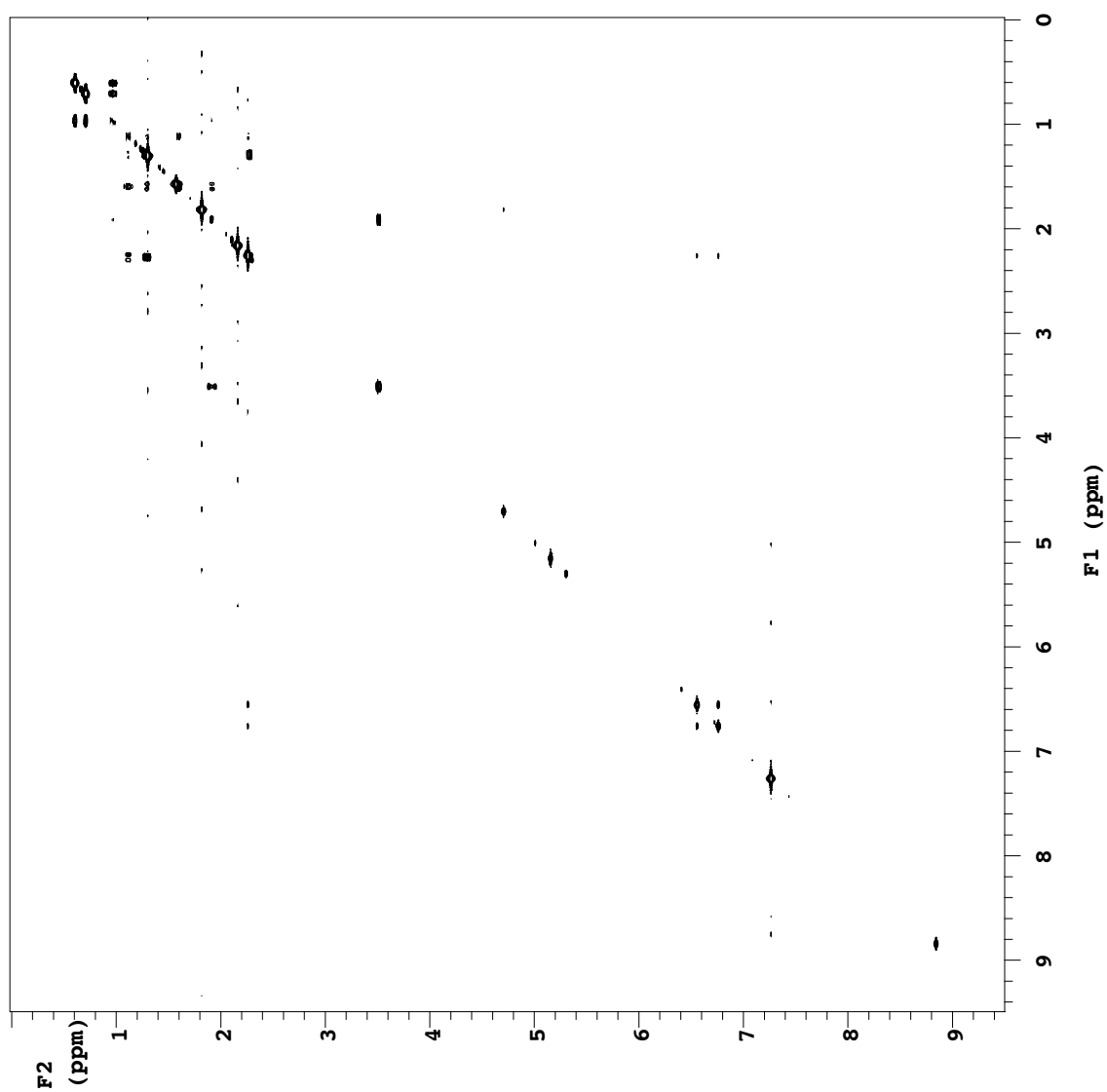
Hamigeran H NMR Spectra



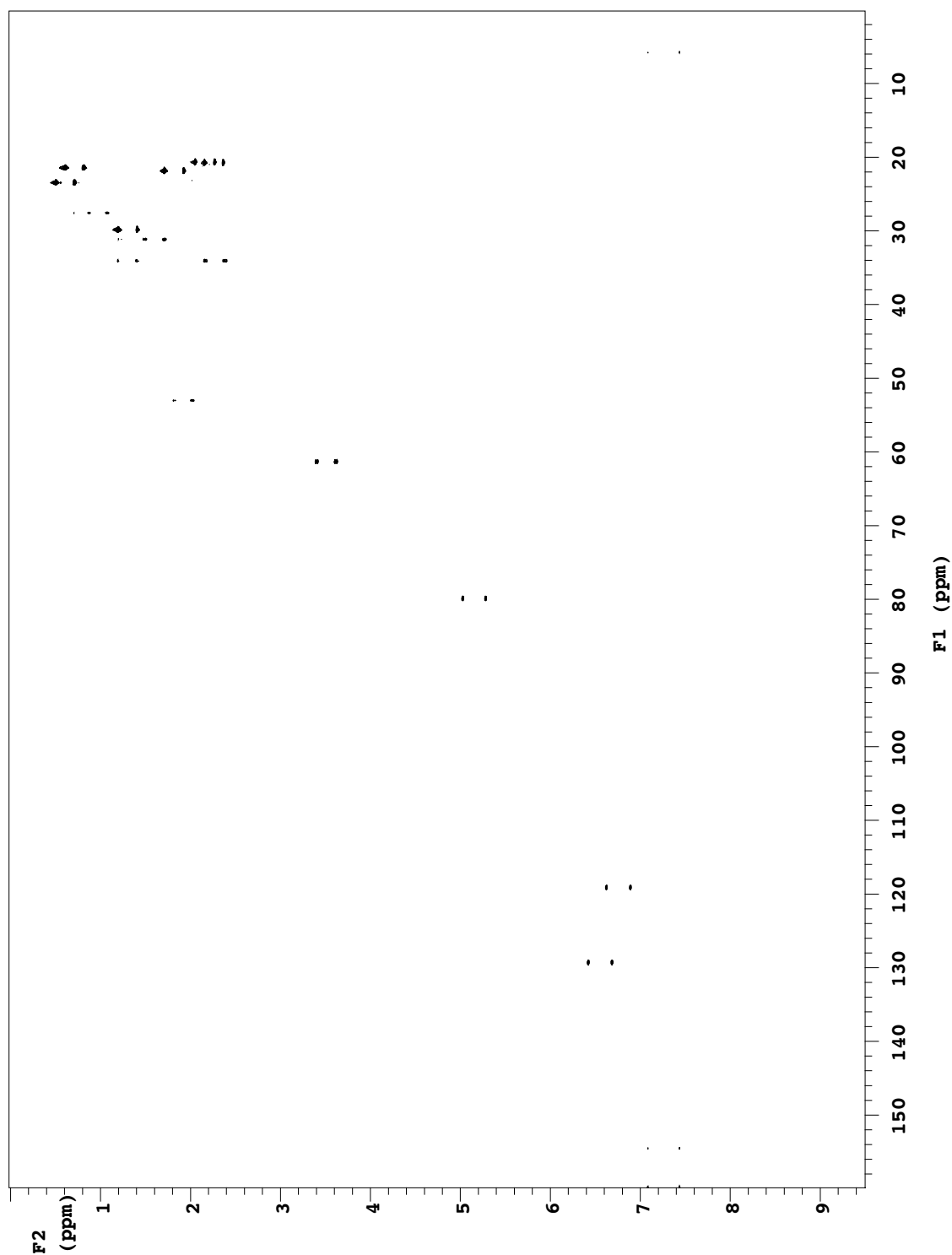
^1H NMR spectrum of hamigeran H (**10**) in CDCl_3 (600 MHz).



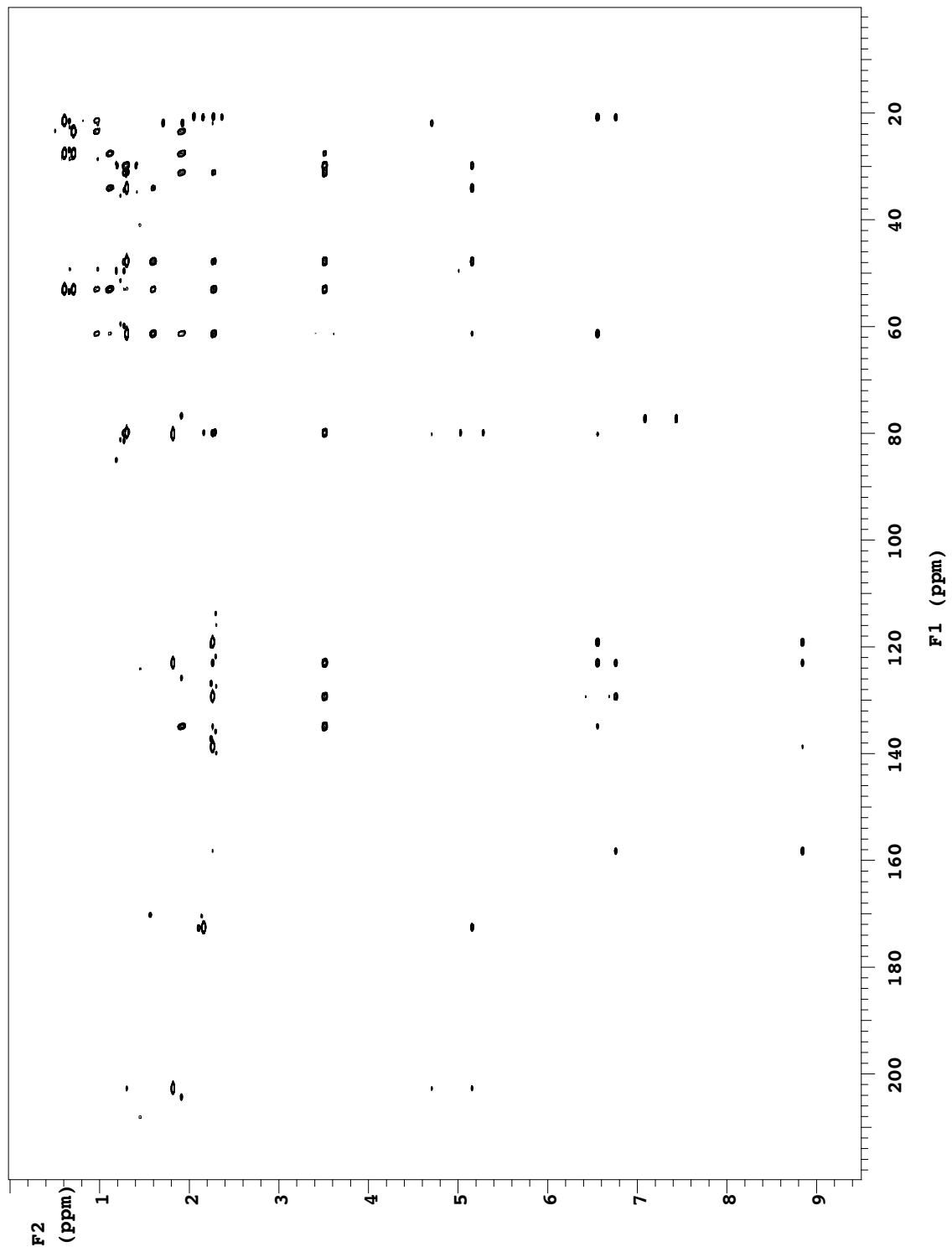
¹³C NMR spectrum of hamigeran H (**10**) in CDCl₃ (150 MHz).



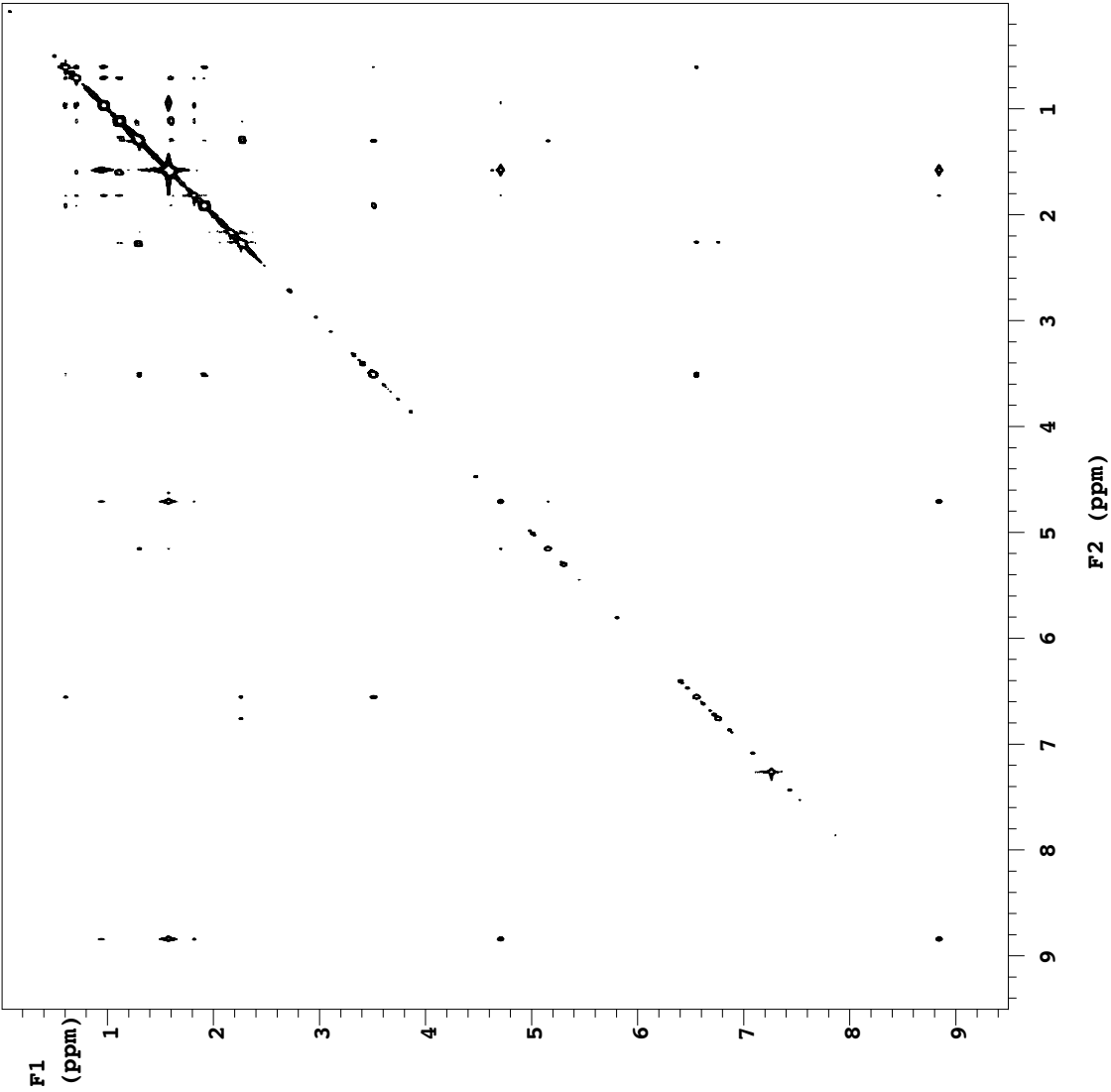
gCOSY spectrum of hamigeran H (**10**) in CDCl₃ (600 MHz).



Fully-coupled HSQCAD spectrum of hamigeran H (**10**) in CDCl₃ (600 MHz).



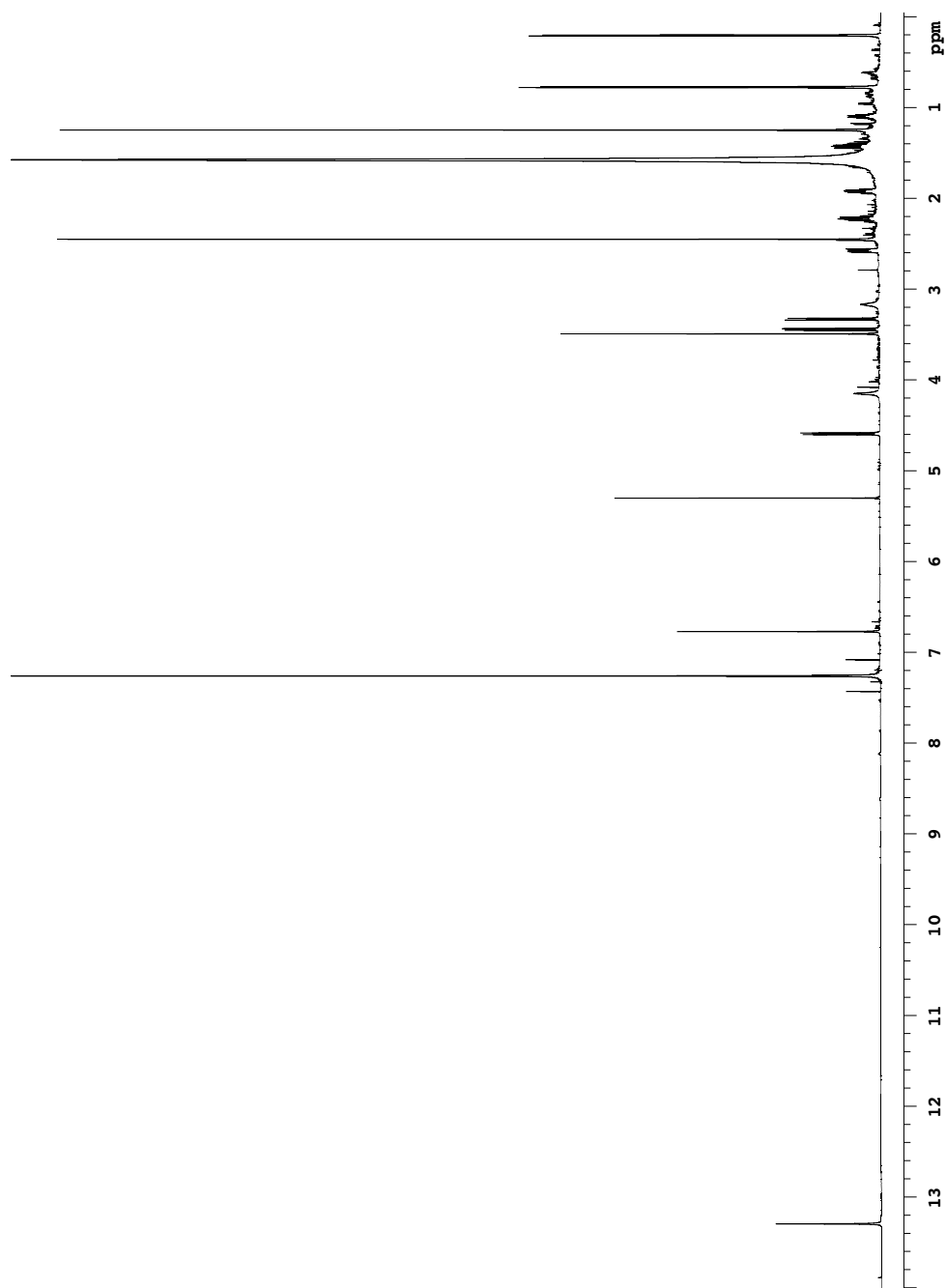
gHMBC spectrum of hamigeran H (**10**) in CDCl₃ (600 MHz).



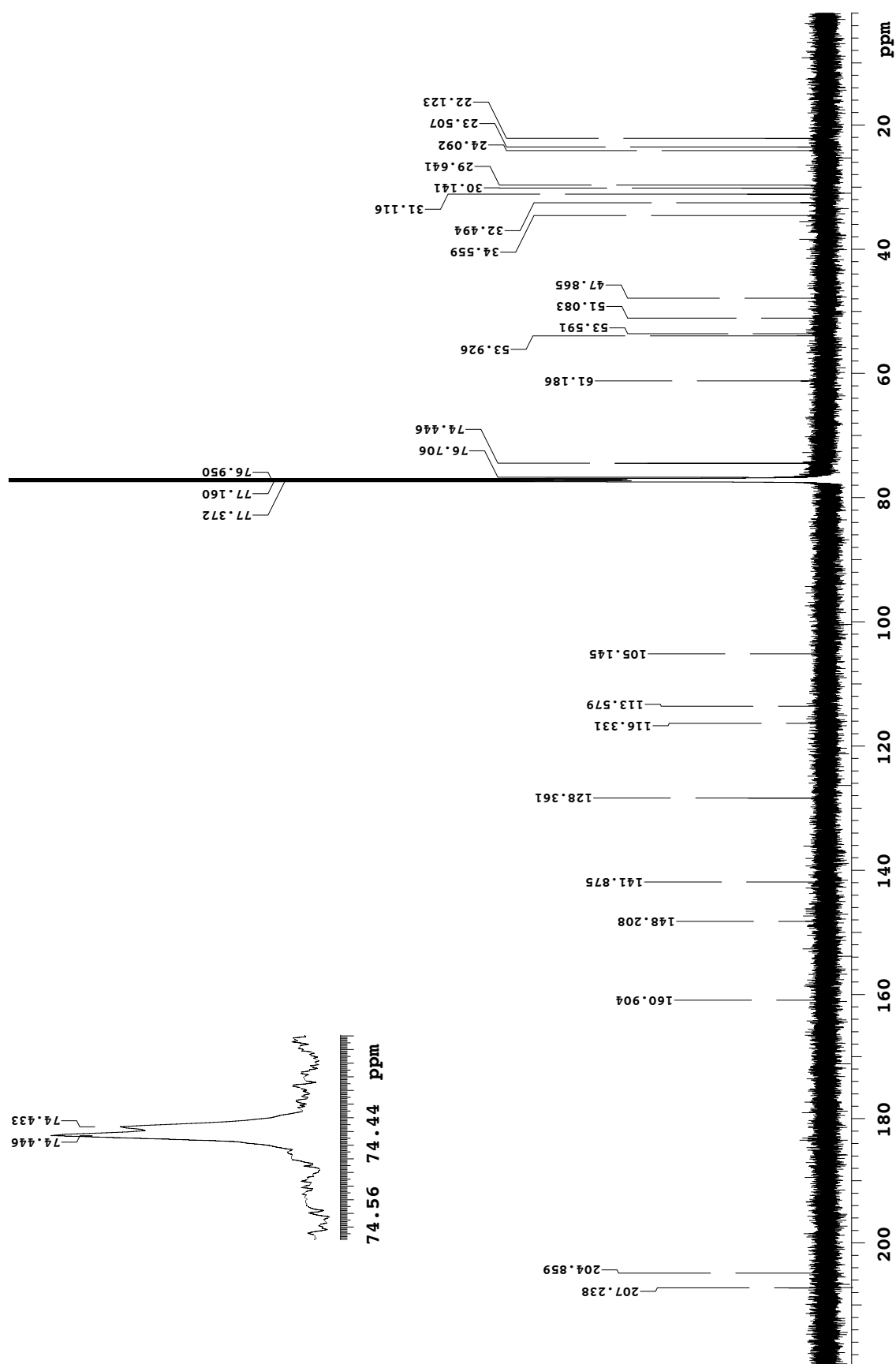
NOESY spectrum of hamigeran H (**10**) in CDCl₃ (600 MHz).

Appendix L

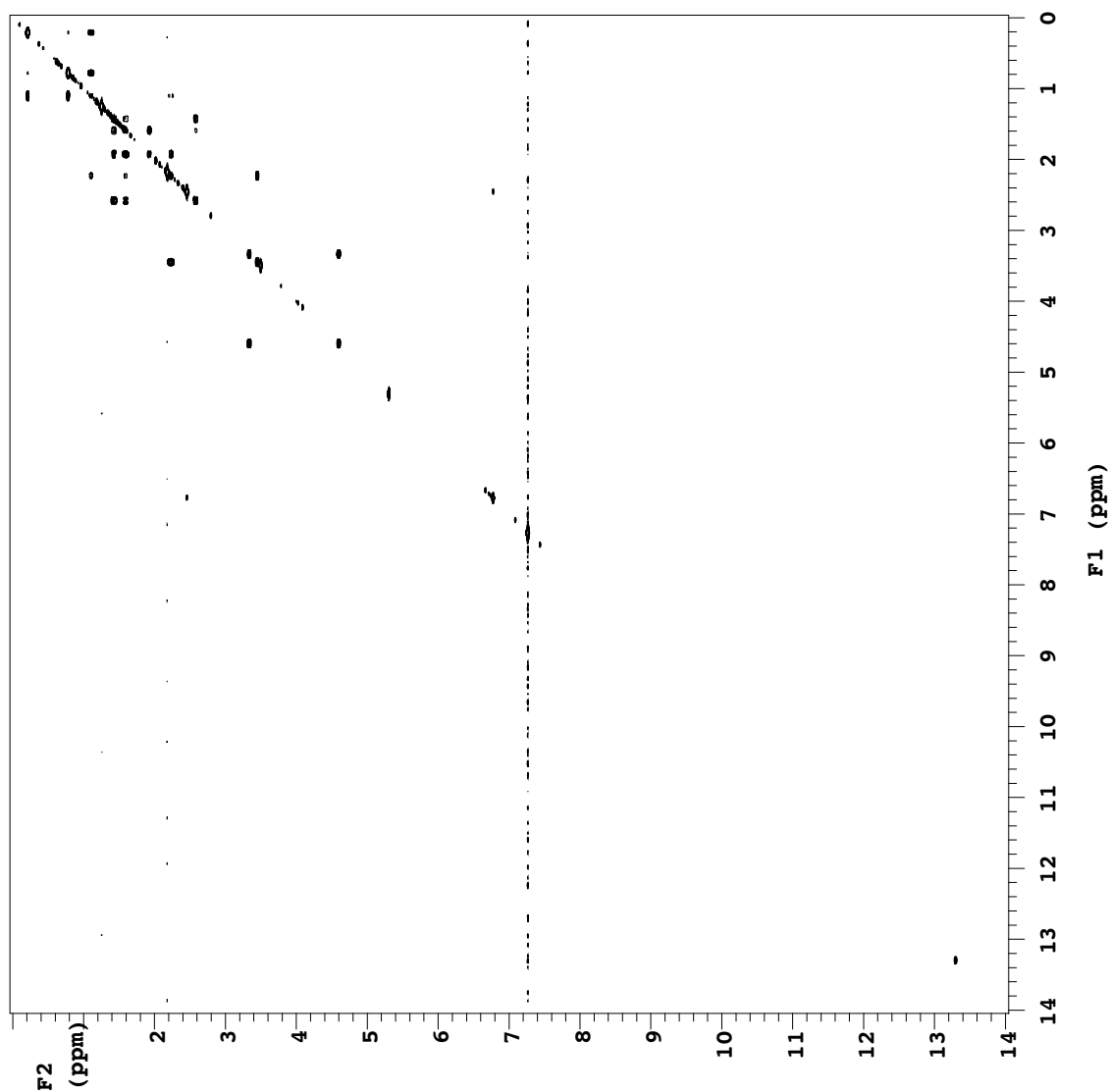
Hamigeran I NMR Spectra



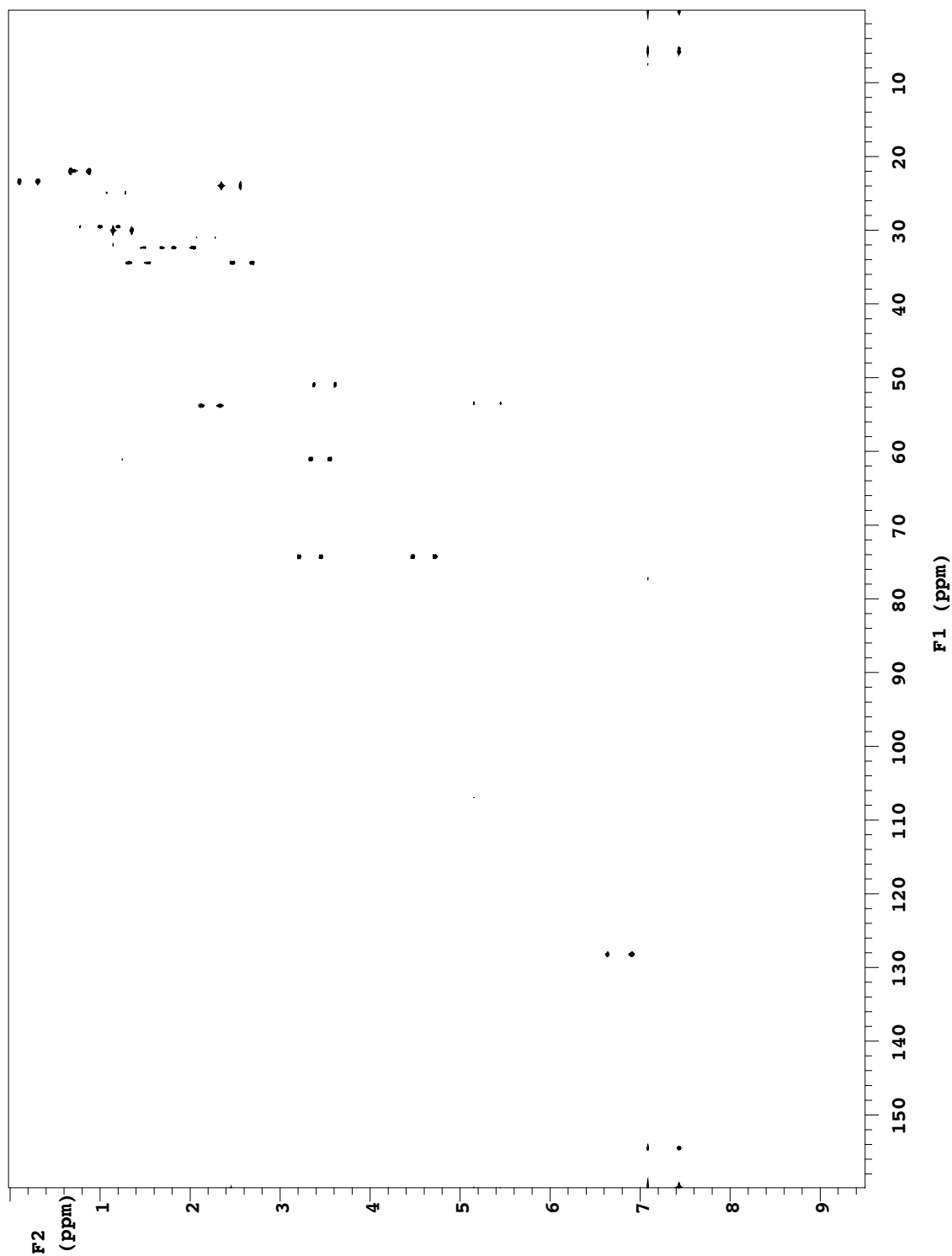
^1H NMR spectrum of hamigeran I (**11**) in CDCl_3 (600 MHz).



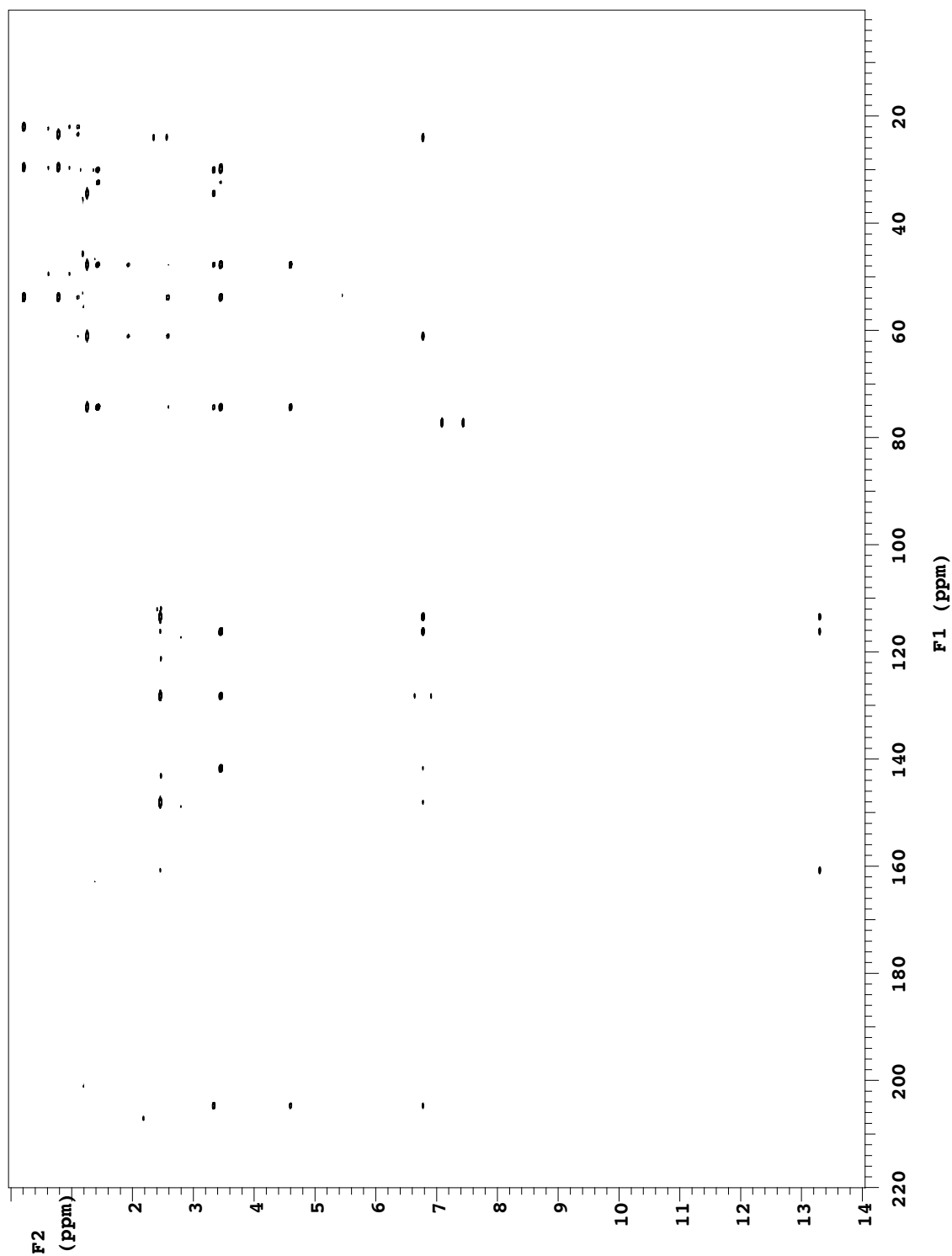
¹³C NMR spectrum of hamigeran I (**11**) in CDCl₃ (150 MHz).
(δ_{C} 207.2; 31.1 = Me₂CO, δ_{C} 105.1 = transmitter spike, δ_{C} 53.6 = CH₂Cl₂)



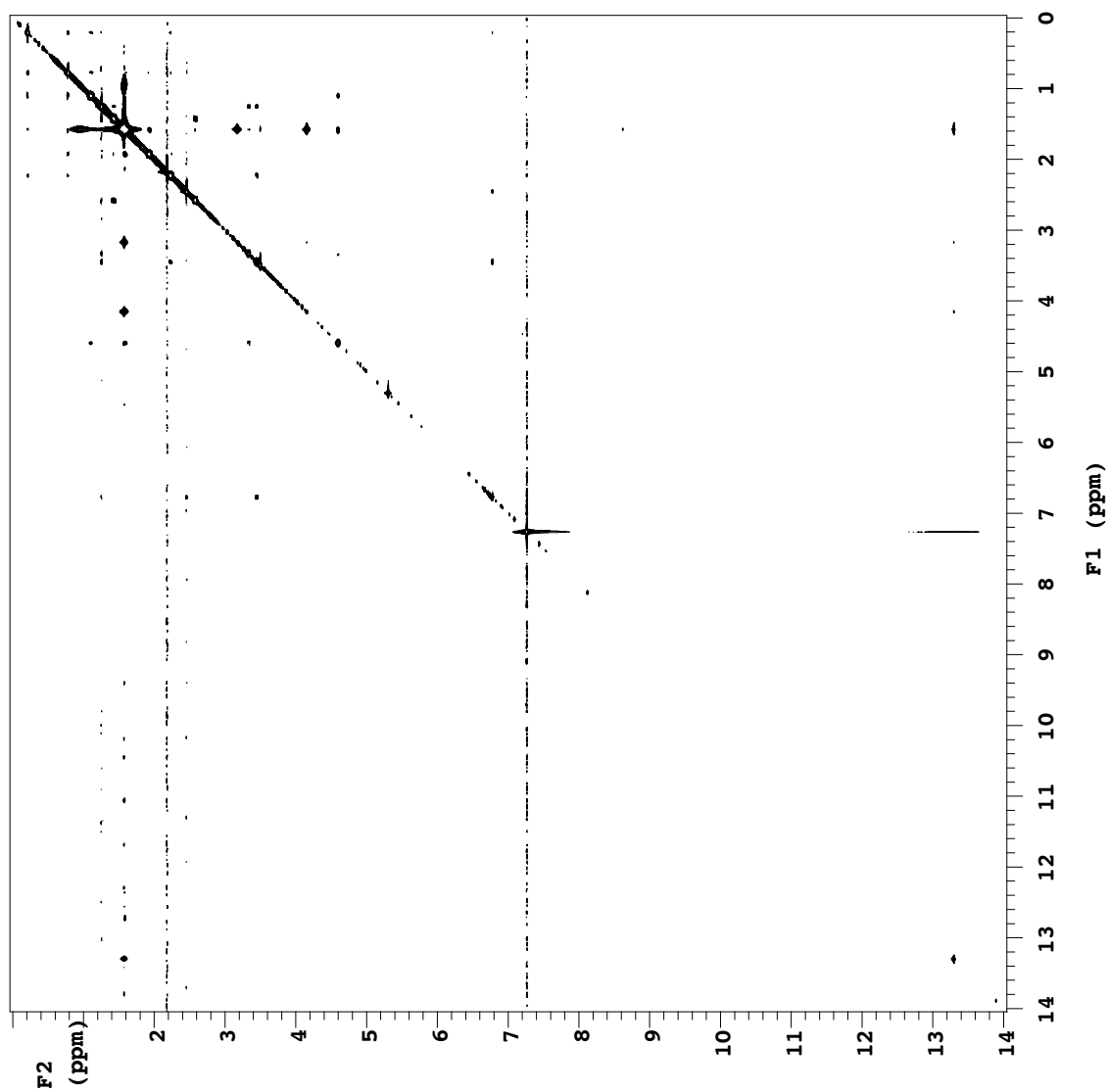
gCOSY spectrum of hamigeran I (**11**) in CDCl₃ (600 MHz).



Fully-coupled HSQCAD spectrum of hamigeran I (**11**) in CDCl₃ (600 MHz).



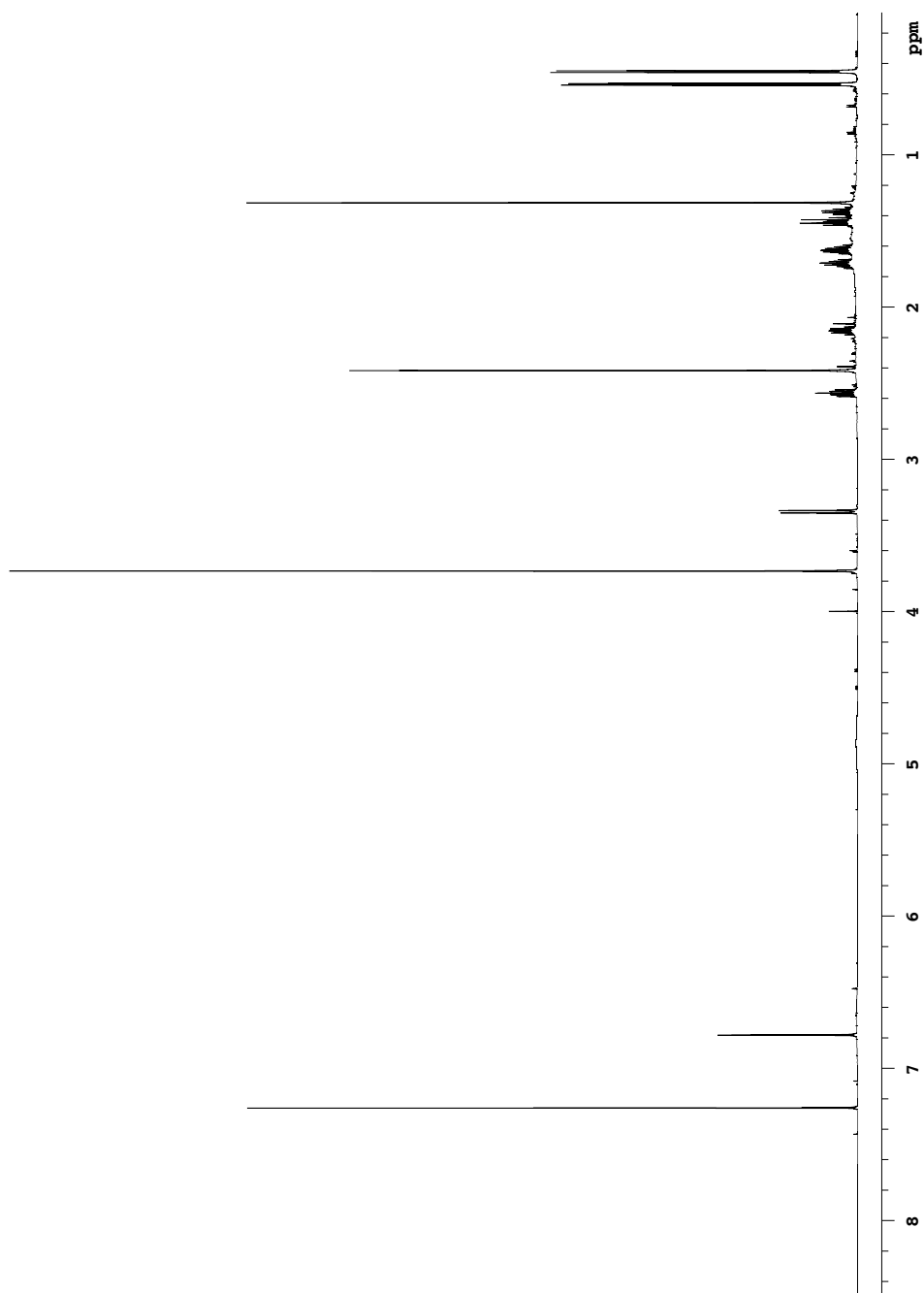
gHMBC spectrum of hamigeran I (**11**) in CDCl₃ (600 MHz).



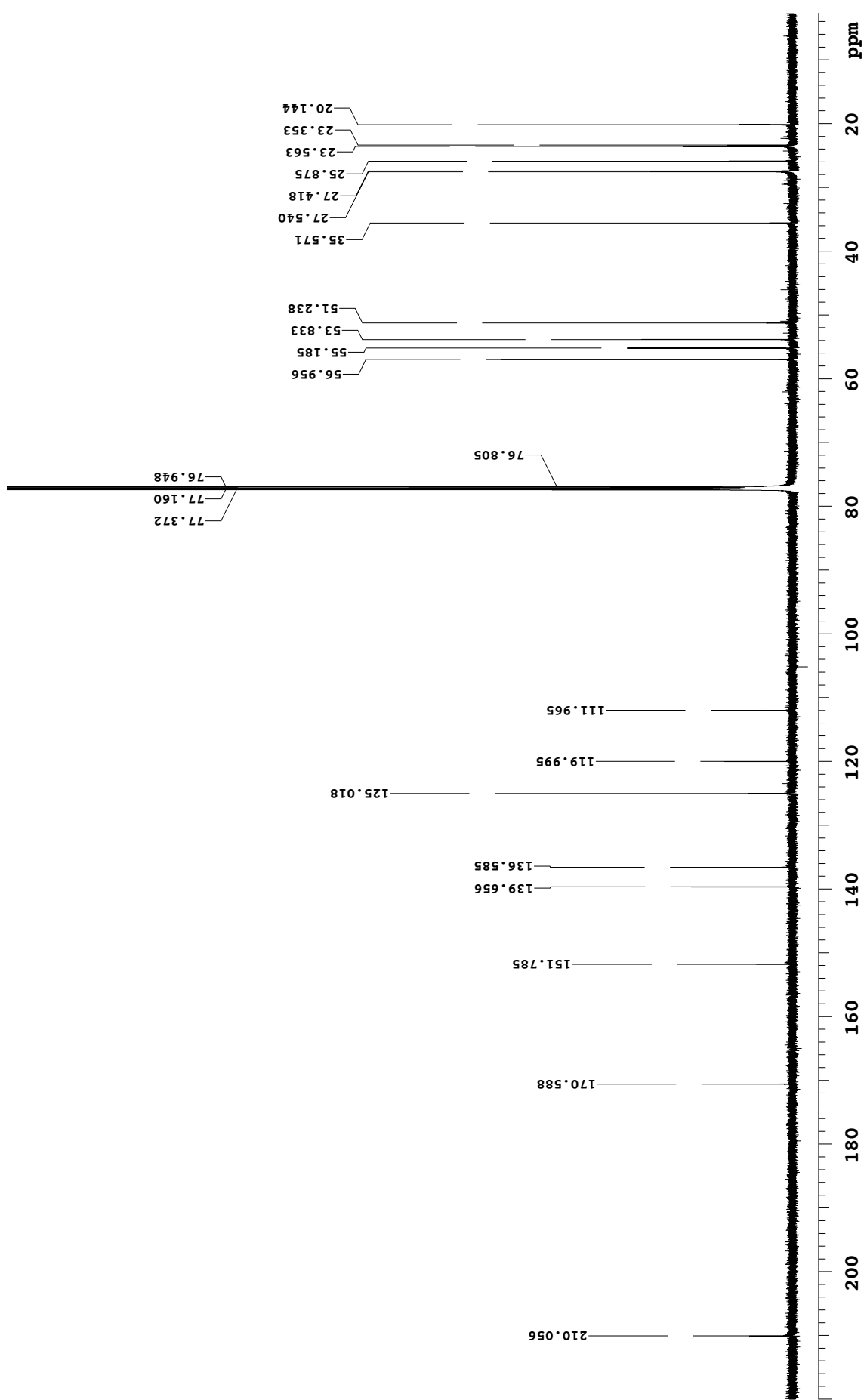
NOESY spectrum of hamigeran I (**11**) in CDCl₃ (600 MHz).

Appendix M

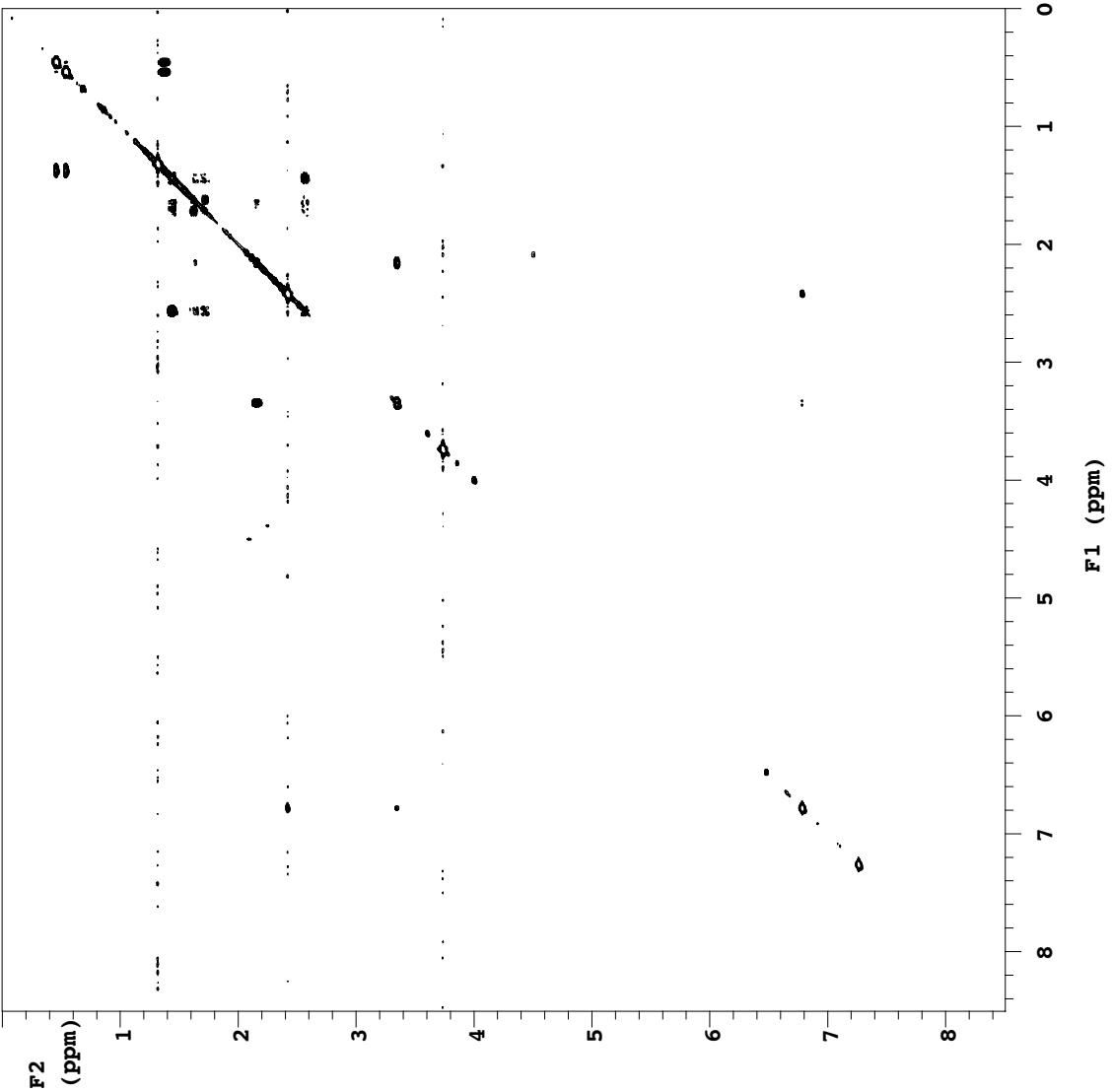
Hamigeran J NMR Spectra



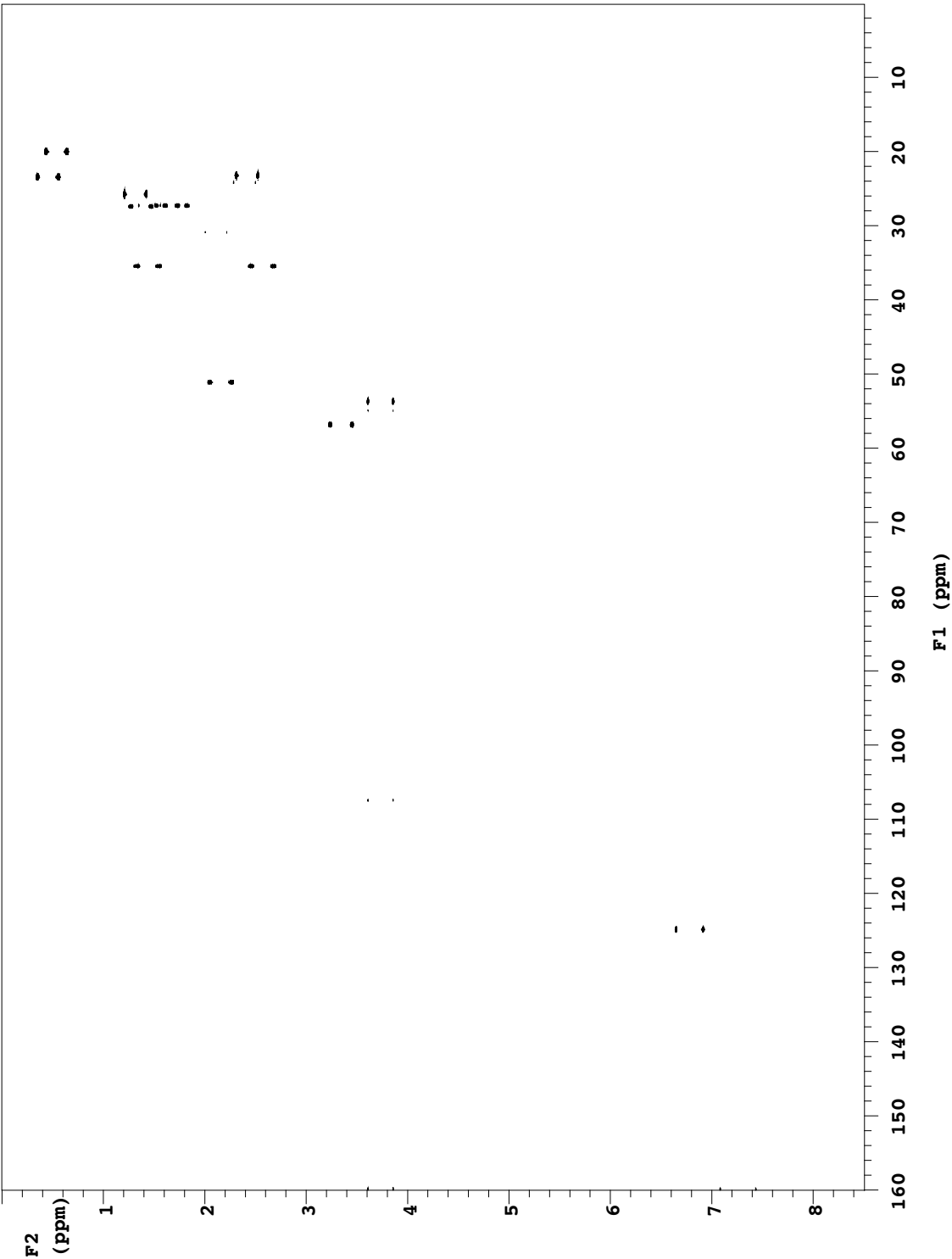
^1H NMR spectrum of hamigeran J (**12**) in CDCl_3 (600 MHz).



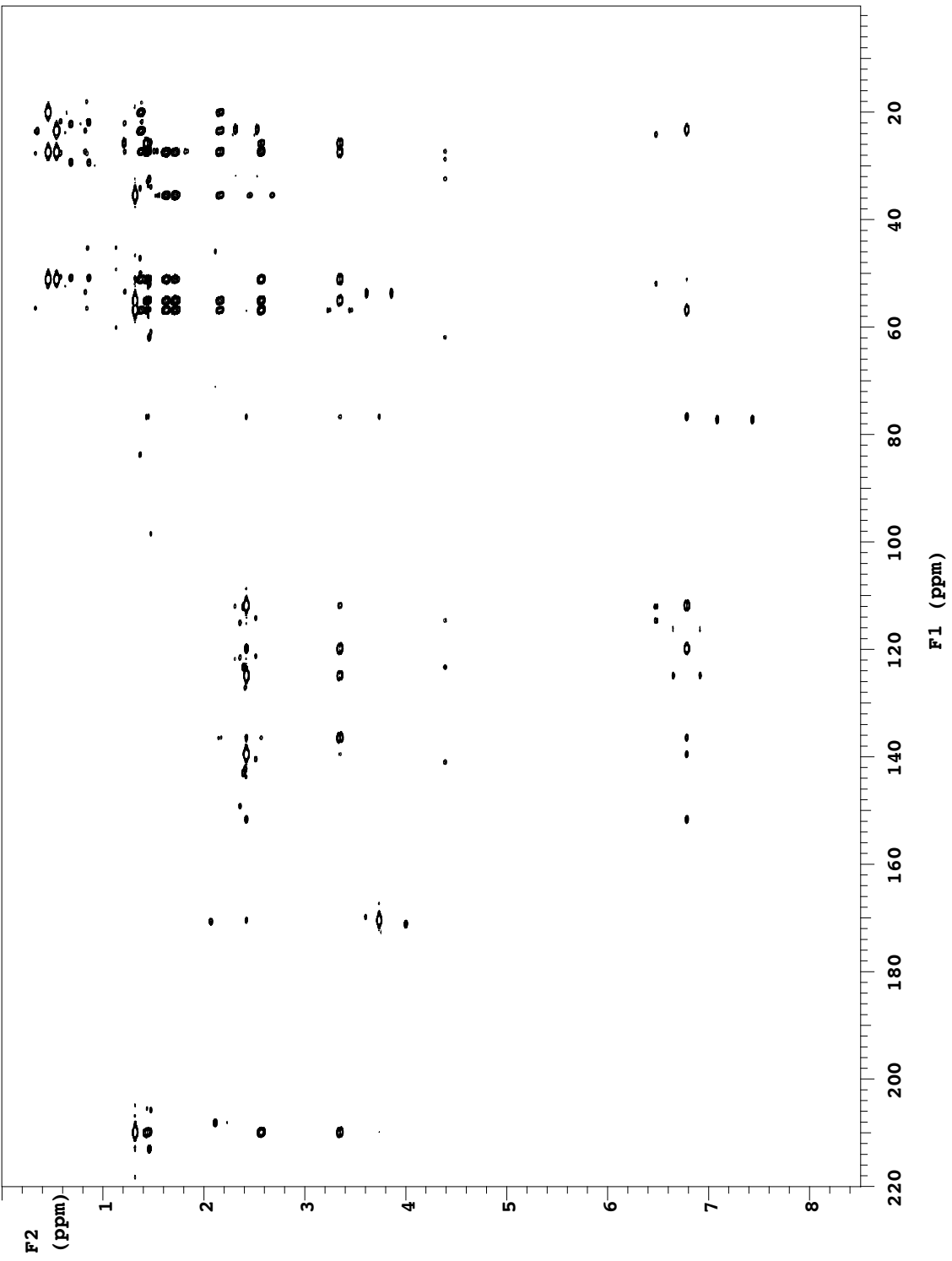
¹³C NMR spectrum of hamigeran J (**12**) in CDCl₃ (150 MHz).



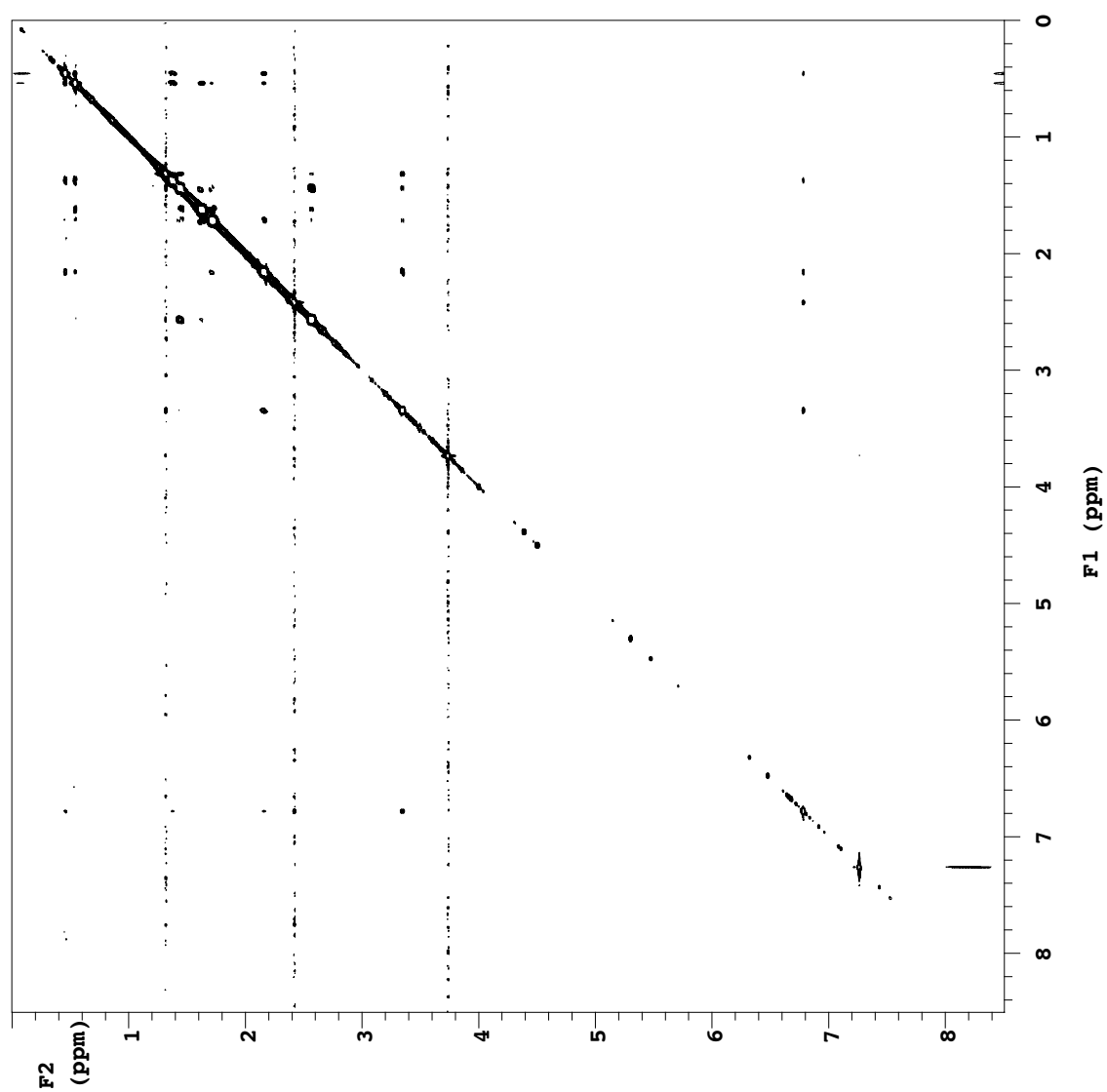
gCOSY spectrum of hamigeran J (**12**) in CDCl₃ (600 MHz).



Fully-coupled HSQCAD spectrum of hamigeran J (**12**) in CDCl₃ (600 MHz).



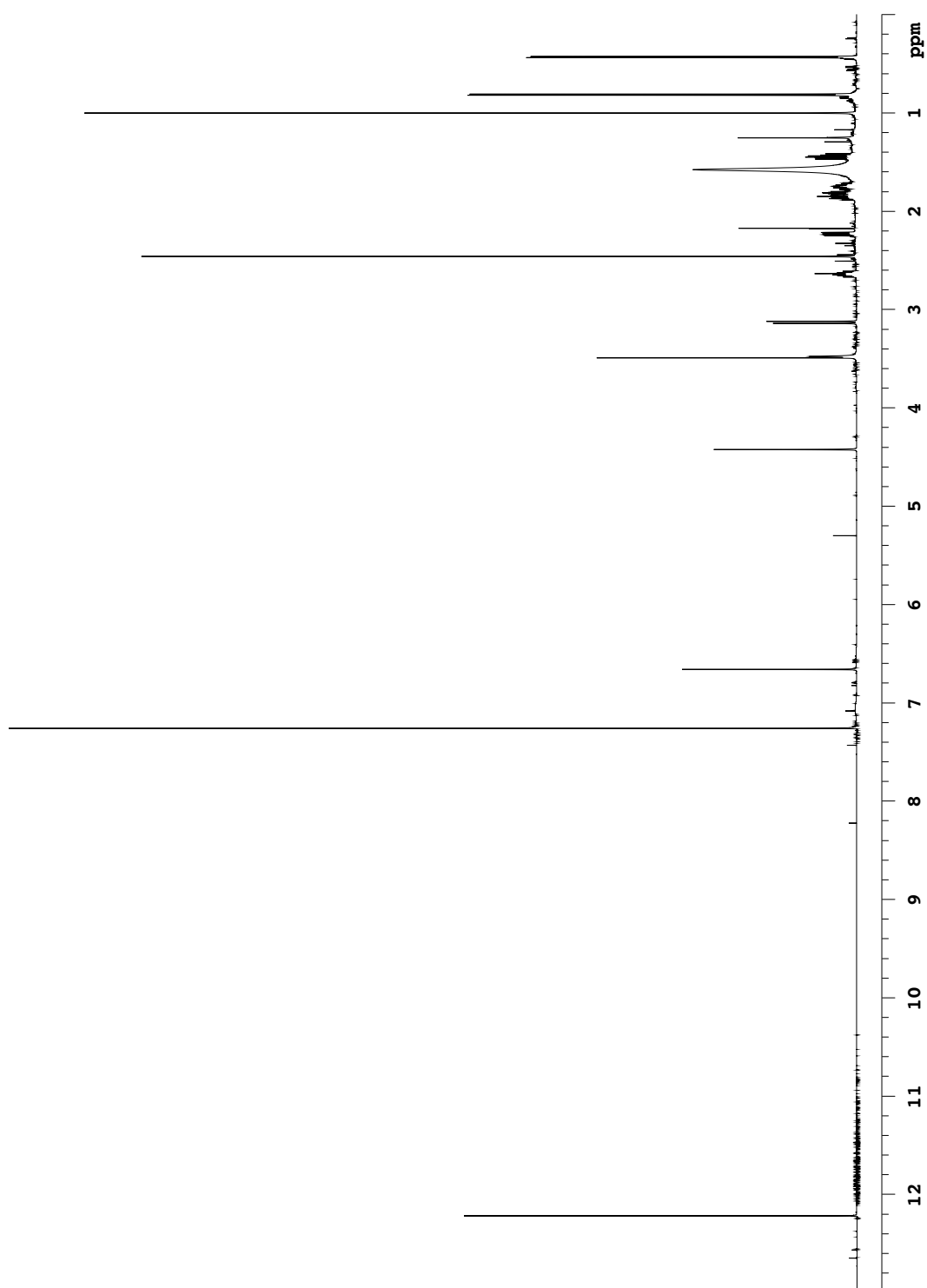
gHMBC spectrum of hamigeran J (**12**) in CDCl₃ (600 MHz).



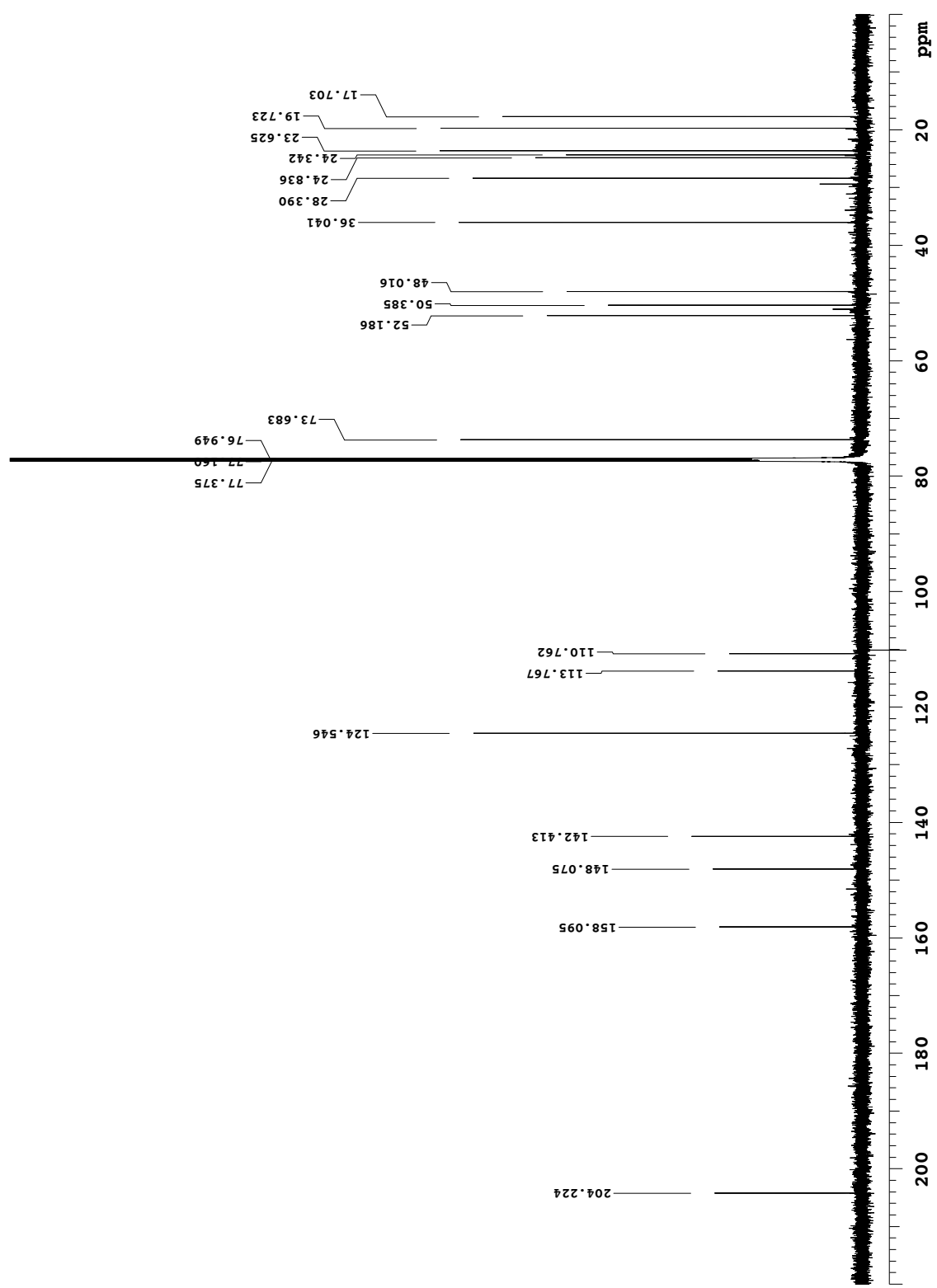
NOESY spectrum of hamigeran J (**12**) in CDCl₃ (600 MHz).

Appendix N

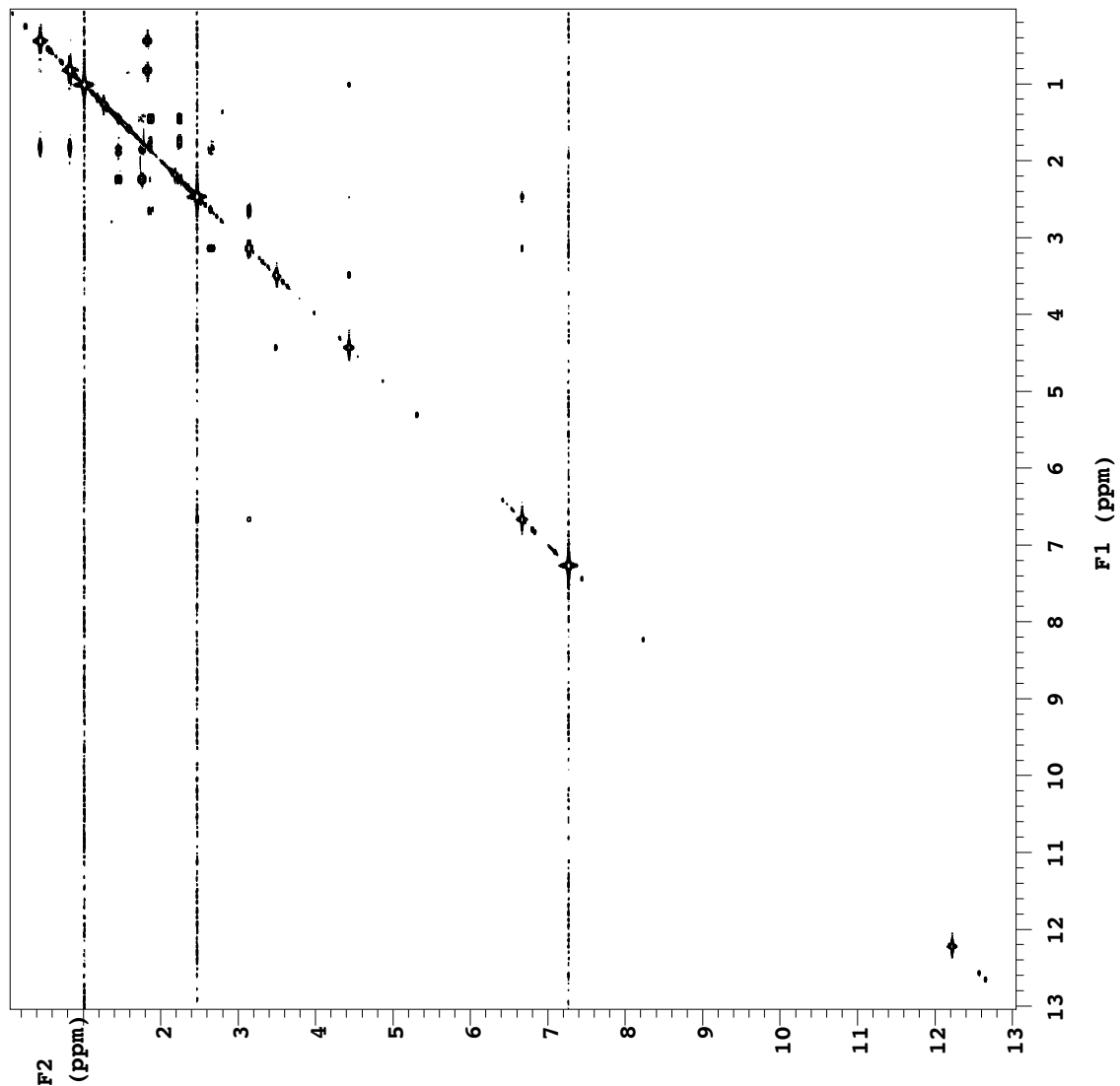
Hamigeran K Spectra



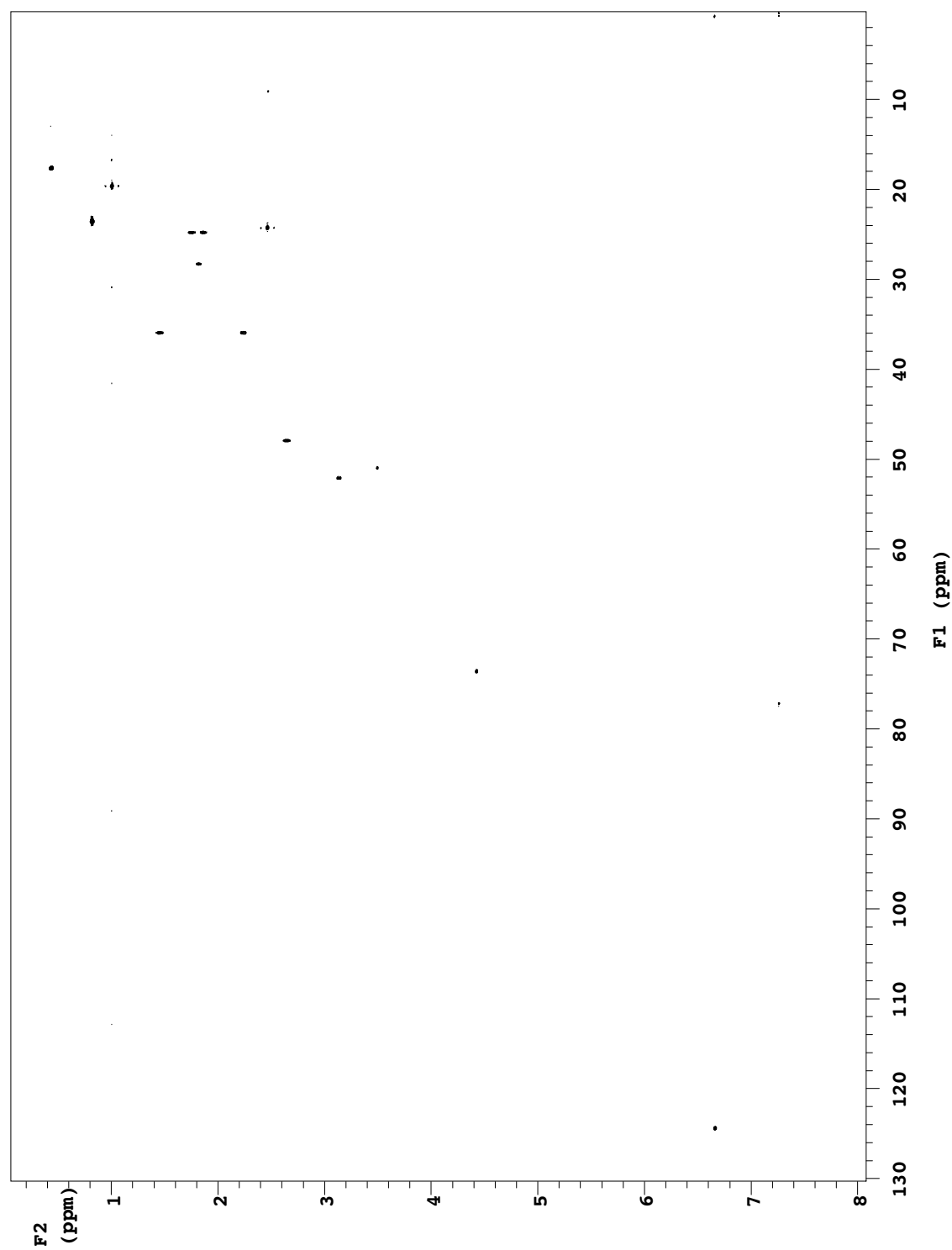
^1H NMR spectrum of hamigeran K (**13**) in CDCl_3 (600 MHz).



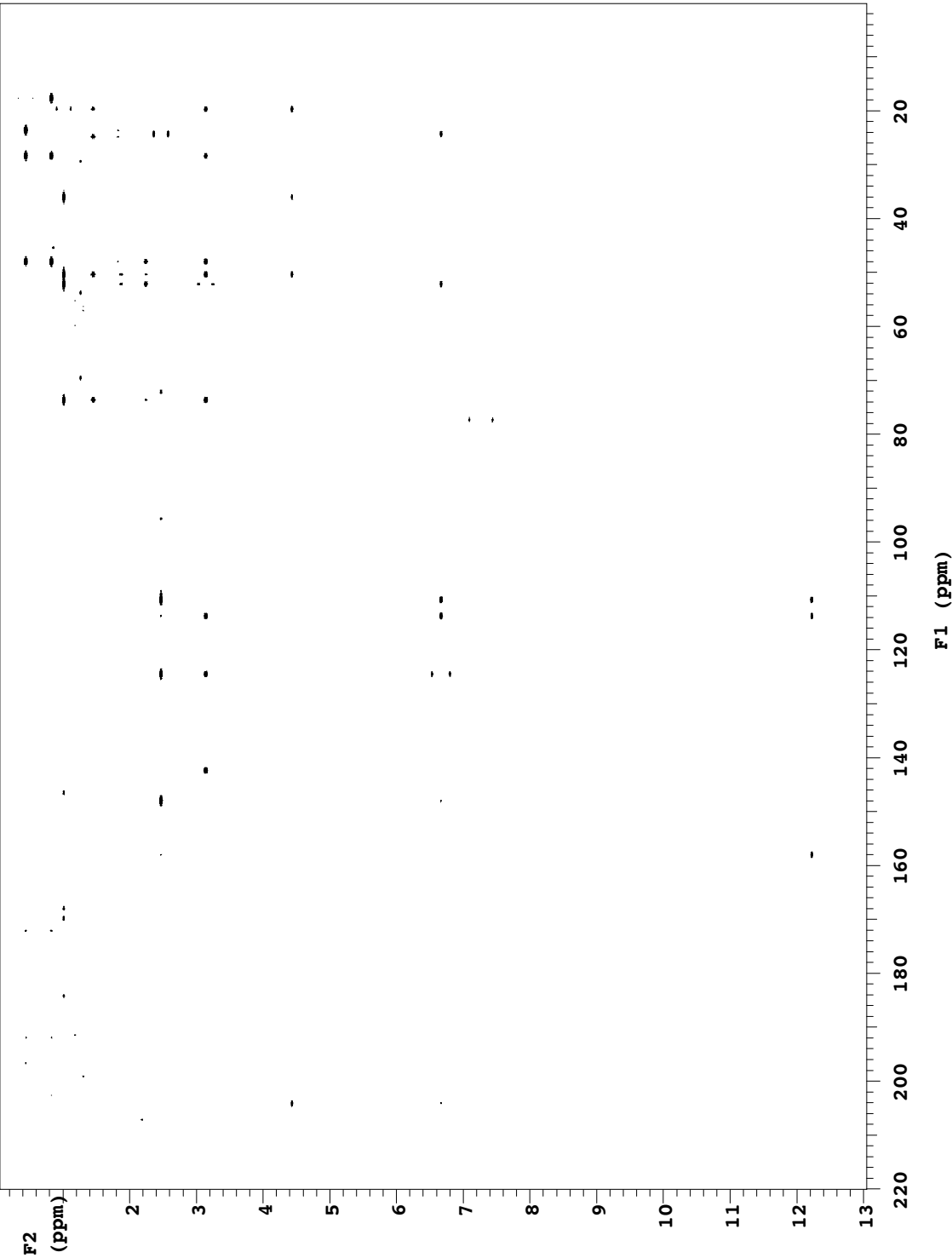
¹³C NMR spectrum of hamigeran K (**13**) in CDCl₃ (150 MHz).



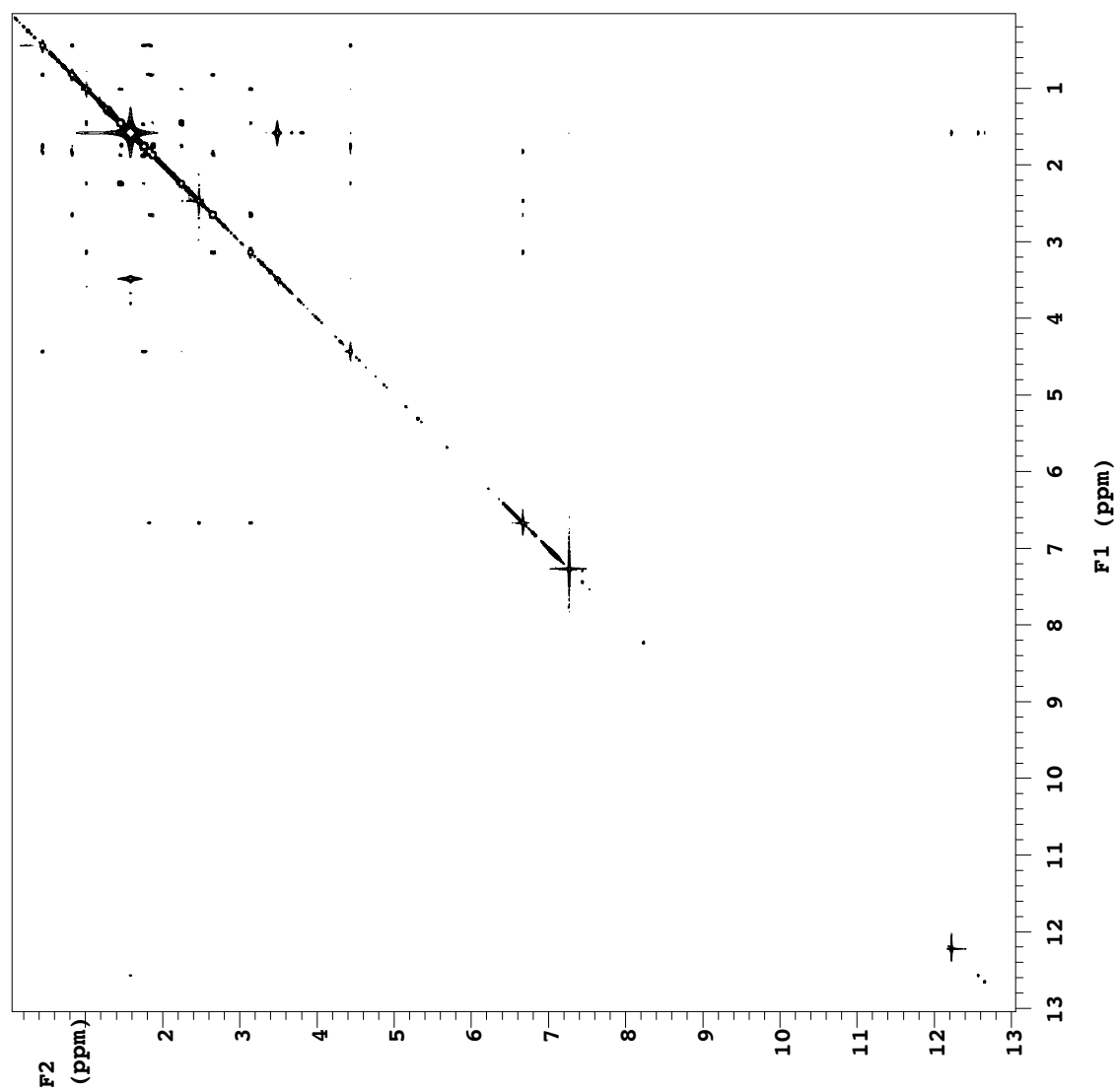
gCOSY spectrum of hamigeran K (**13**) in CDCl₃ (600 MHz).



HSQCAD spectrum of hamigeran K (**13**) in CDCl₃ (600 MHz).



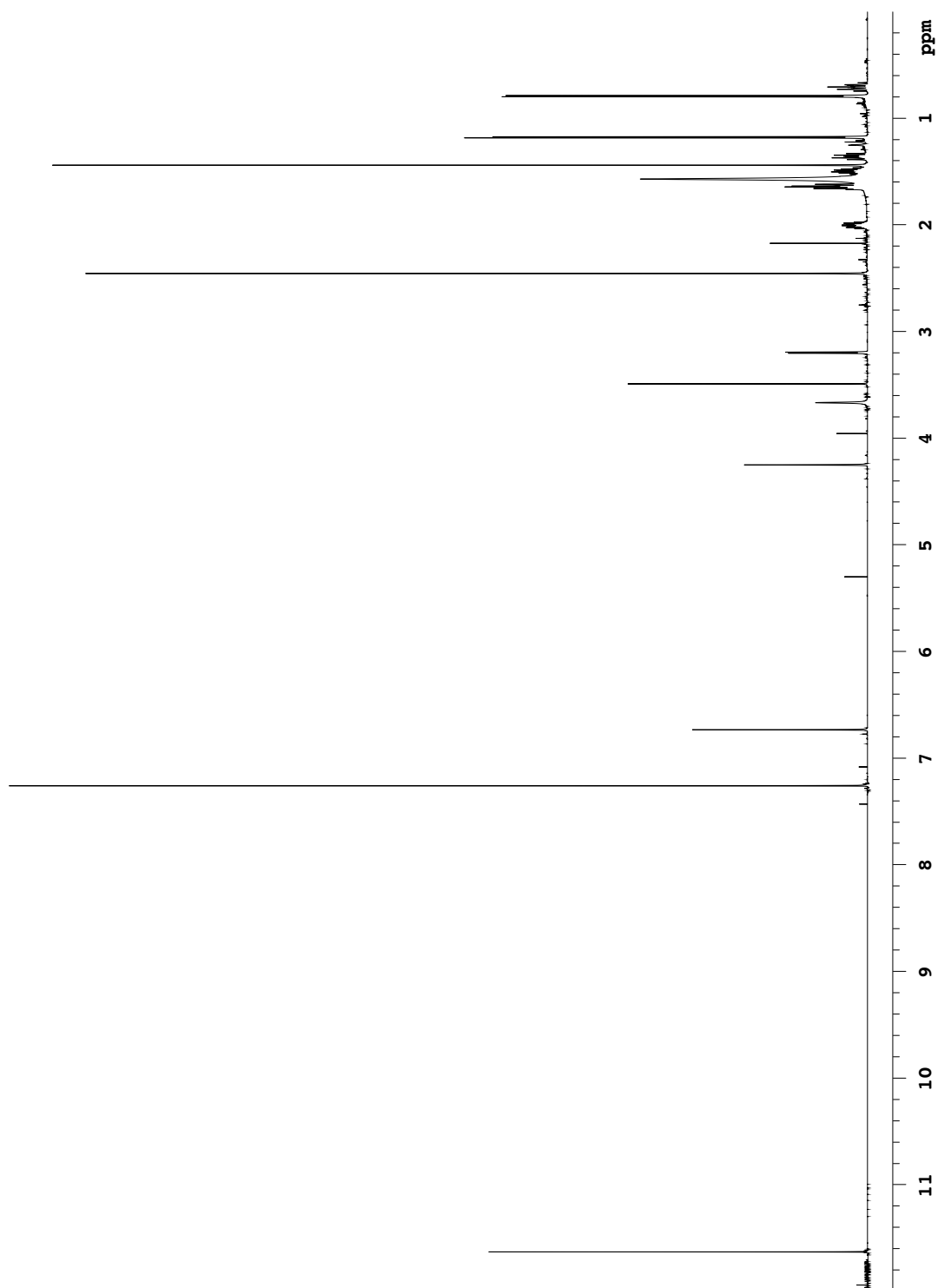
gHMBC spectrum of hamigeran K (**13**) in CDCl₃ (600 MHz).



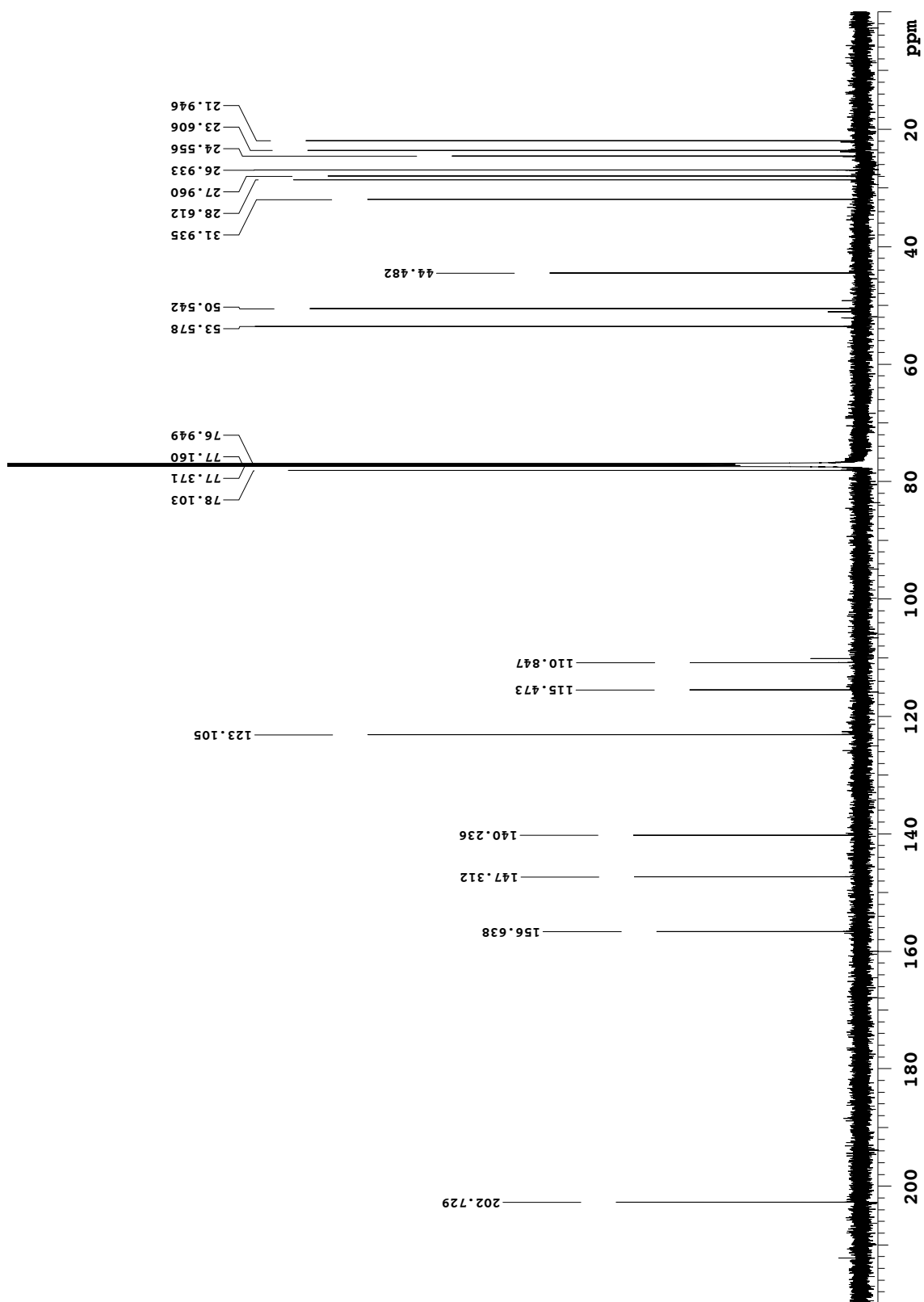
NOESY spectrum of hamigeran K (**13**) in CDCl₃ (600 MHz).

Appendix O

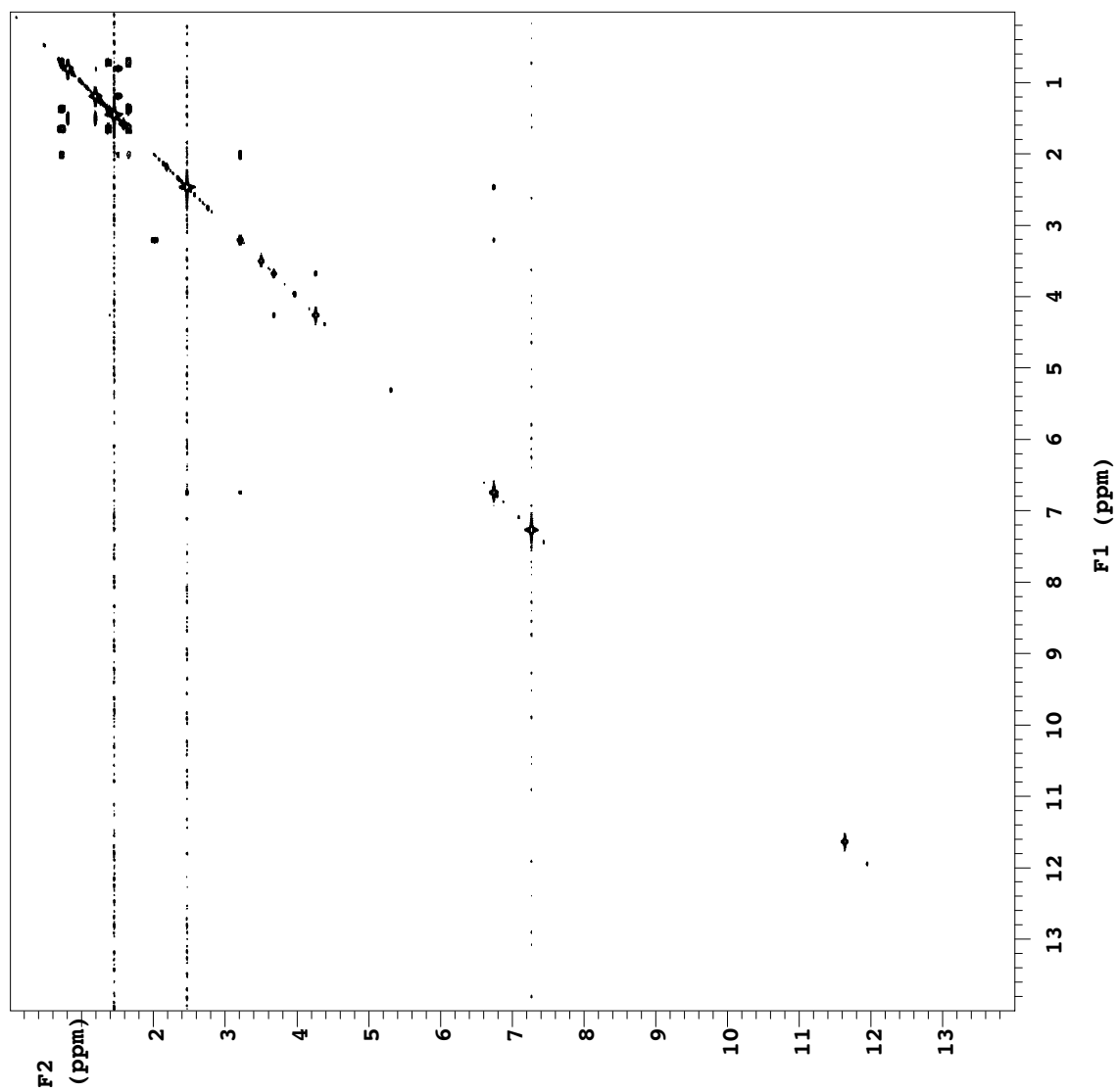
10-*epi*-Hamigeran K Spectra



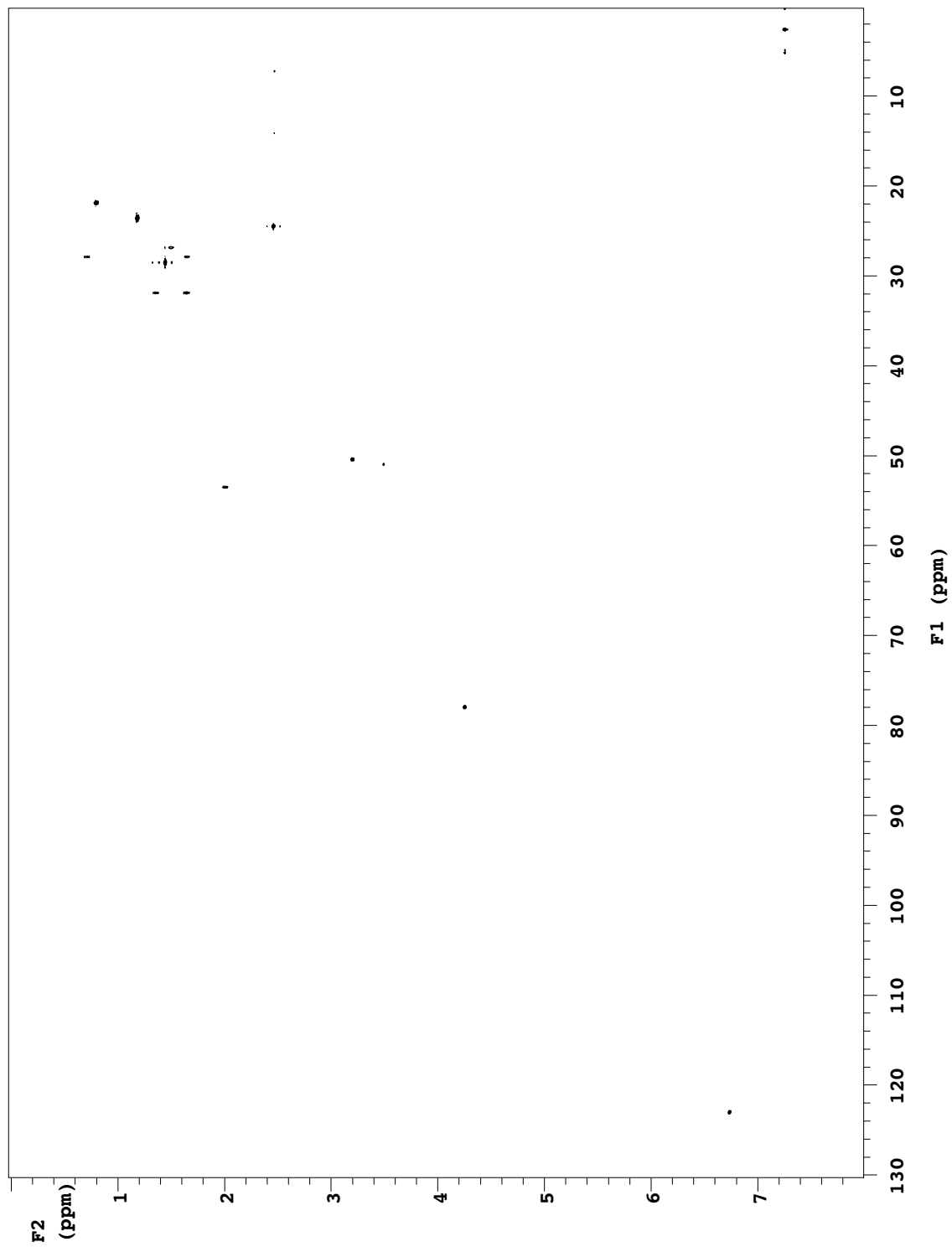
¹H NMR spectrum of 10-*epi*-hamigeran K (**14**) in CDCl₃ (600 MHz).



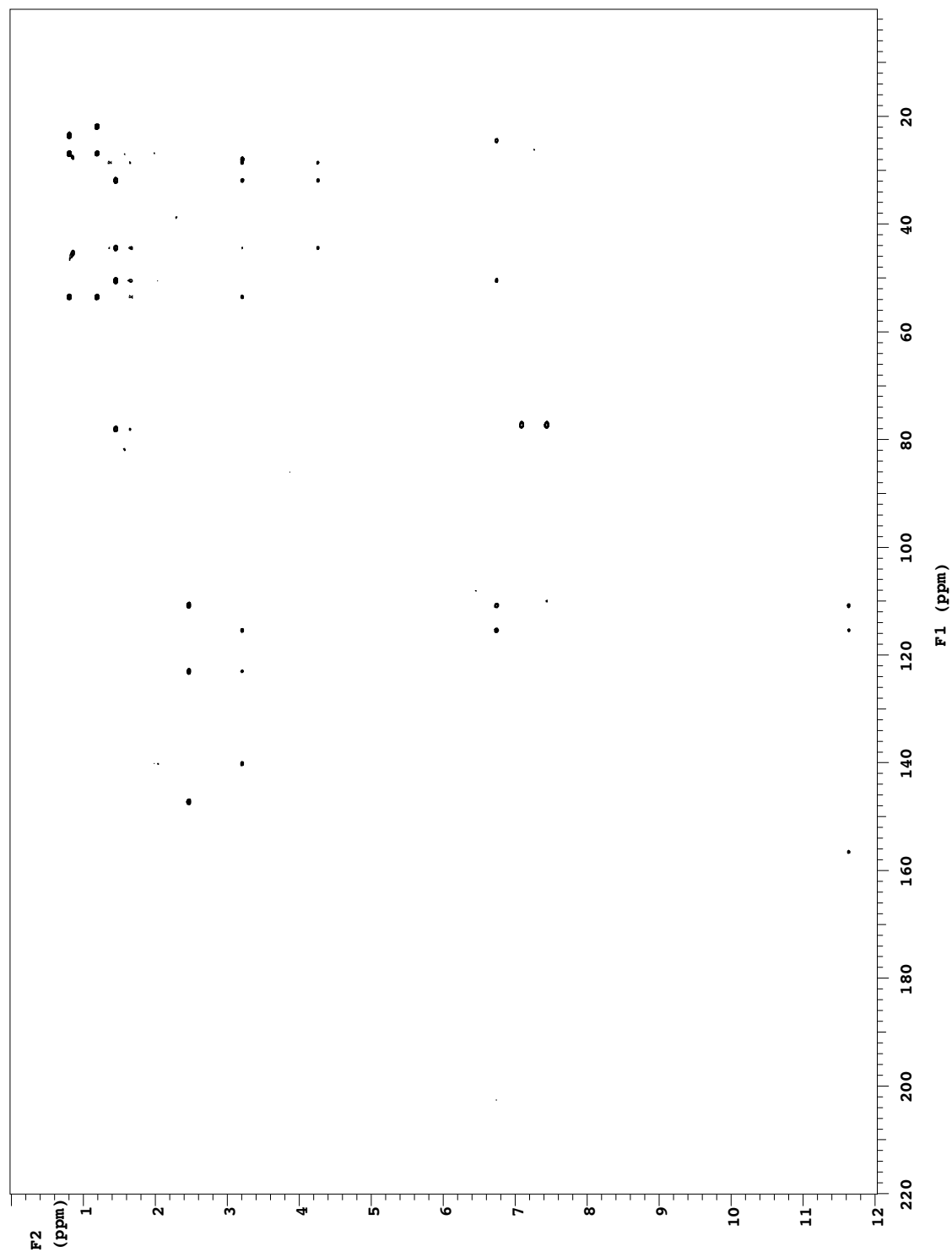
¹³C NMR spectrum of 10-*epi*-hamigeran K (**14**) in CDCl₃ (150 MHz).



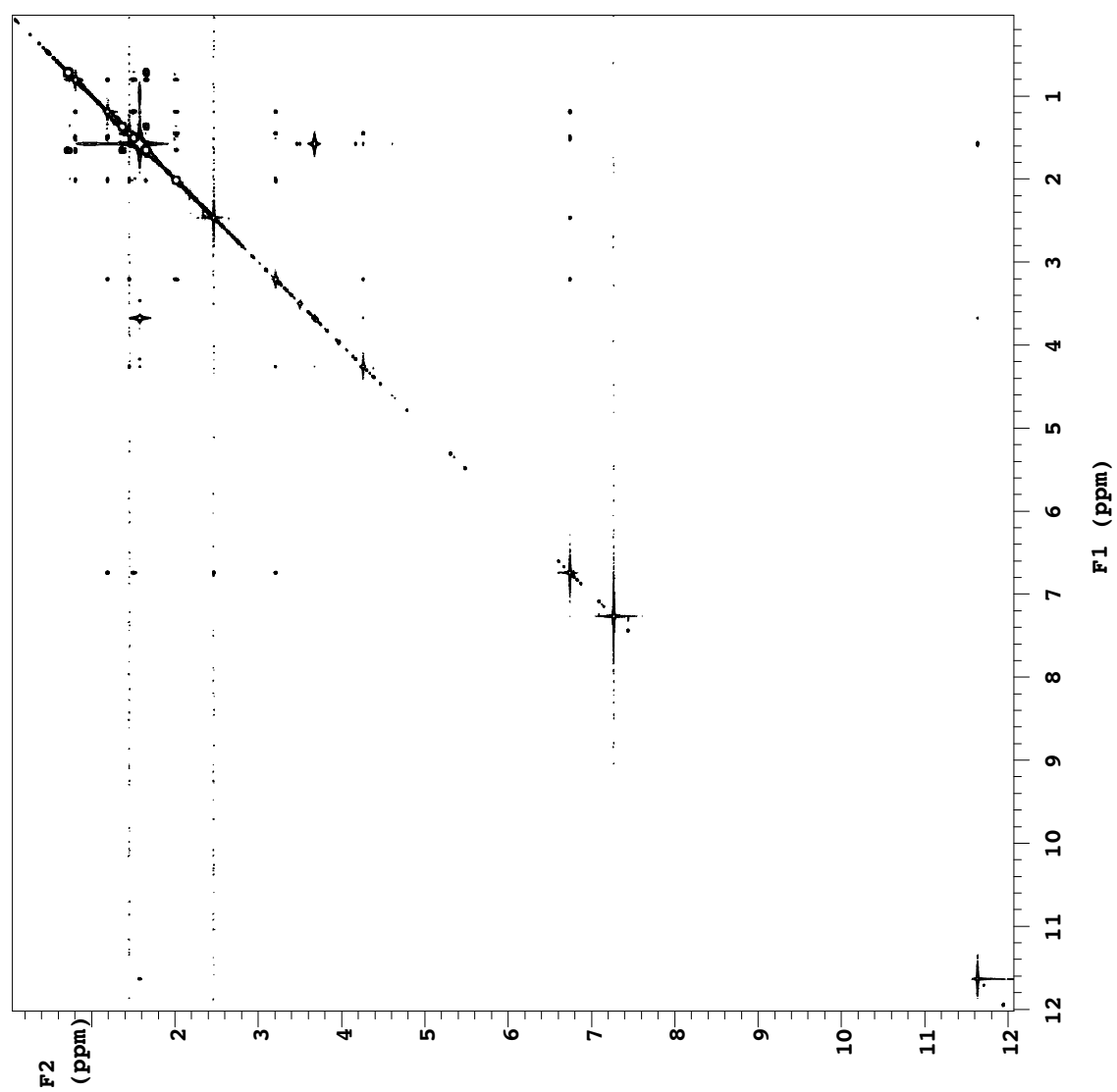
gCOSY spectrum of 10-*epi*-hamigeran K (**14**) in CDCl₃ (600 MHz).



HSQCAD spectrum of 10-*epi*-hamigeran K (**14**) in CDCl₃ (600 MHz).



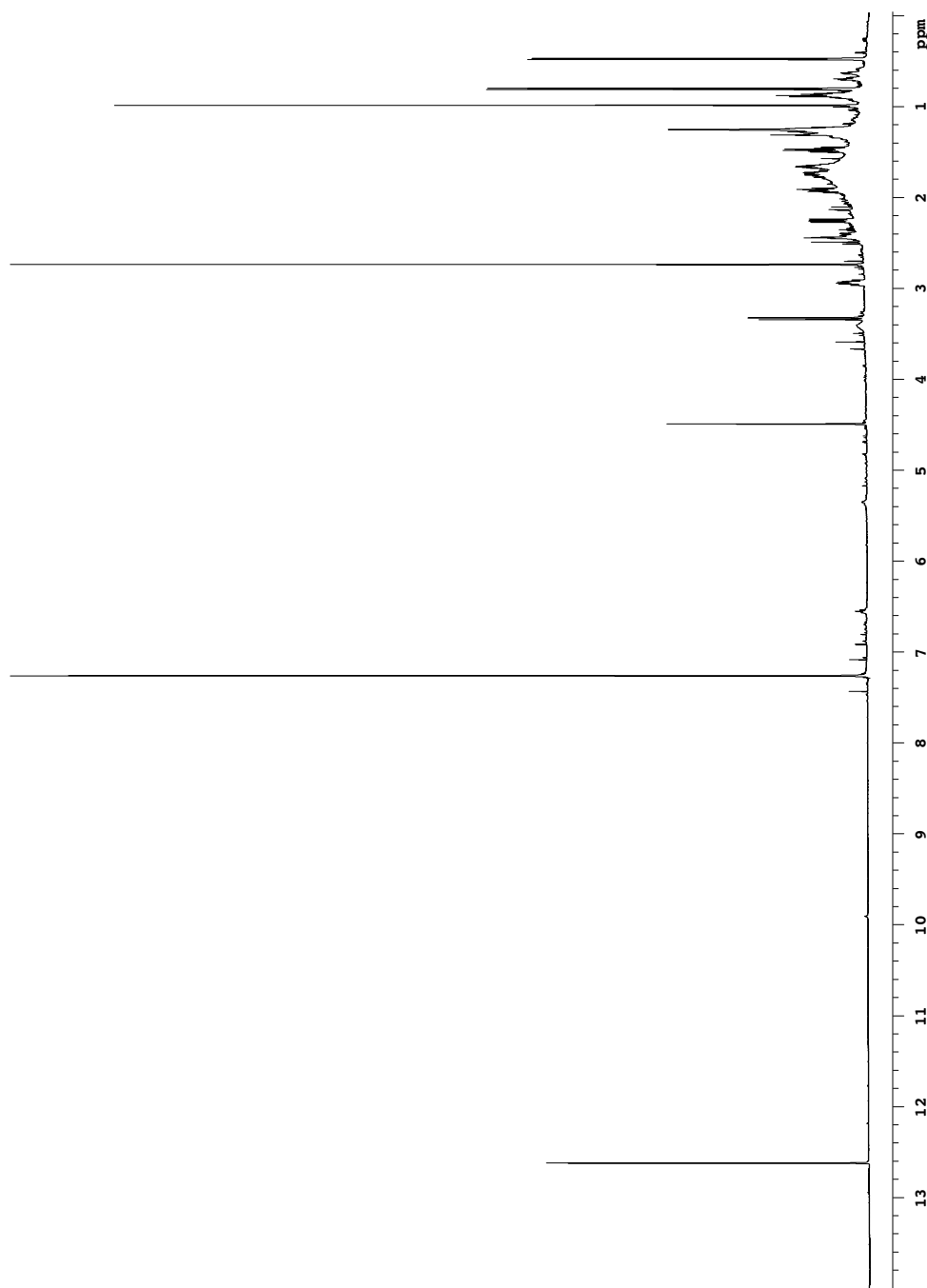
gHMBC spectrum of 10-*epi*-hamigeran K (**14**) in CDCl₃ (600 MHz).



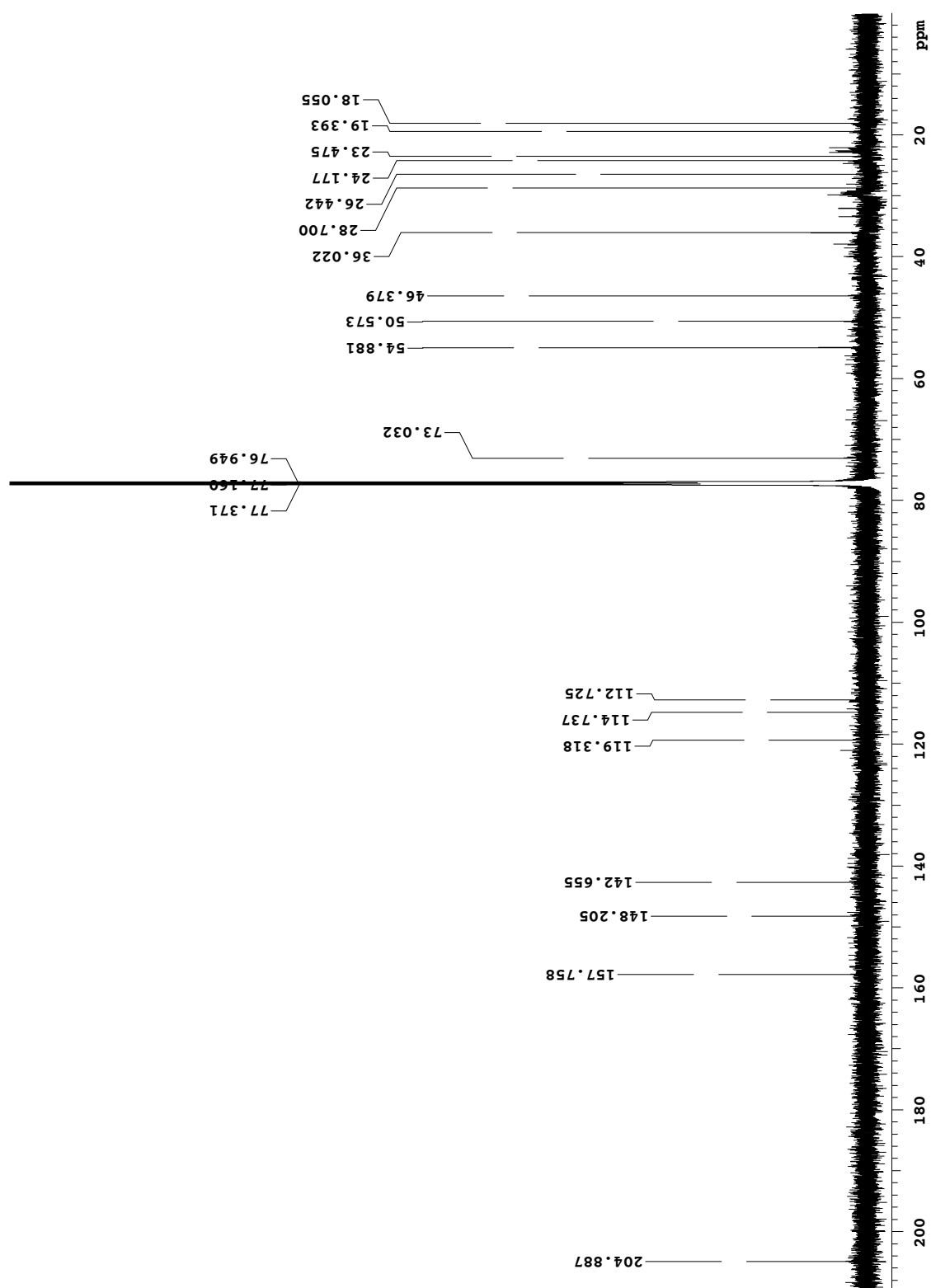
NOESY spectrum of 10-*epi*-hamigeran K (**14**) in CDCl₃ (600 MHz).

Appendix P

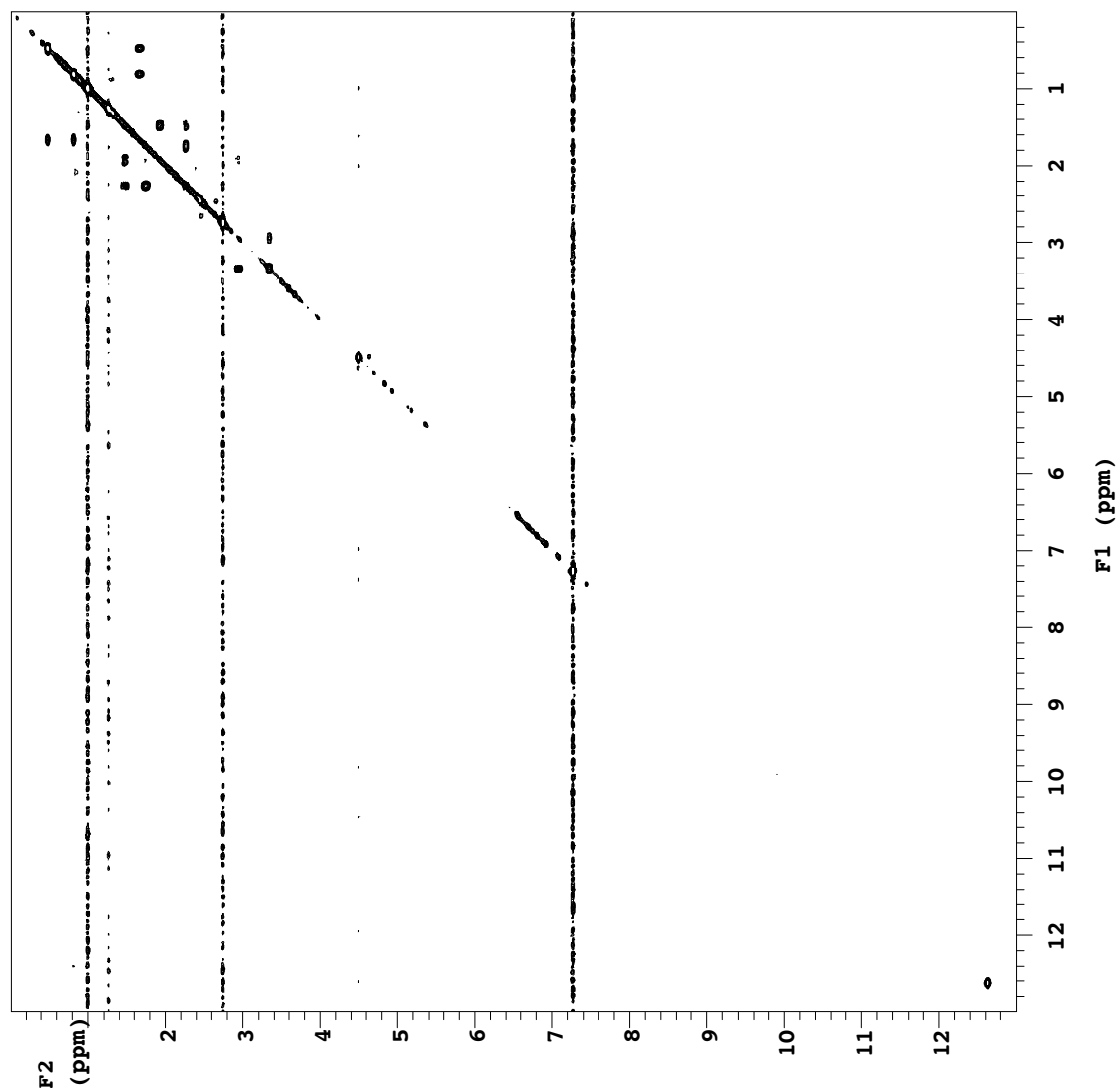
4-Bromohamigeran K Spectra



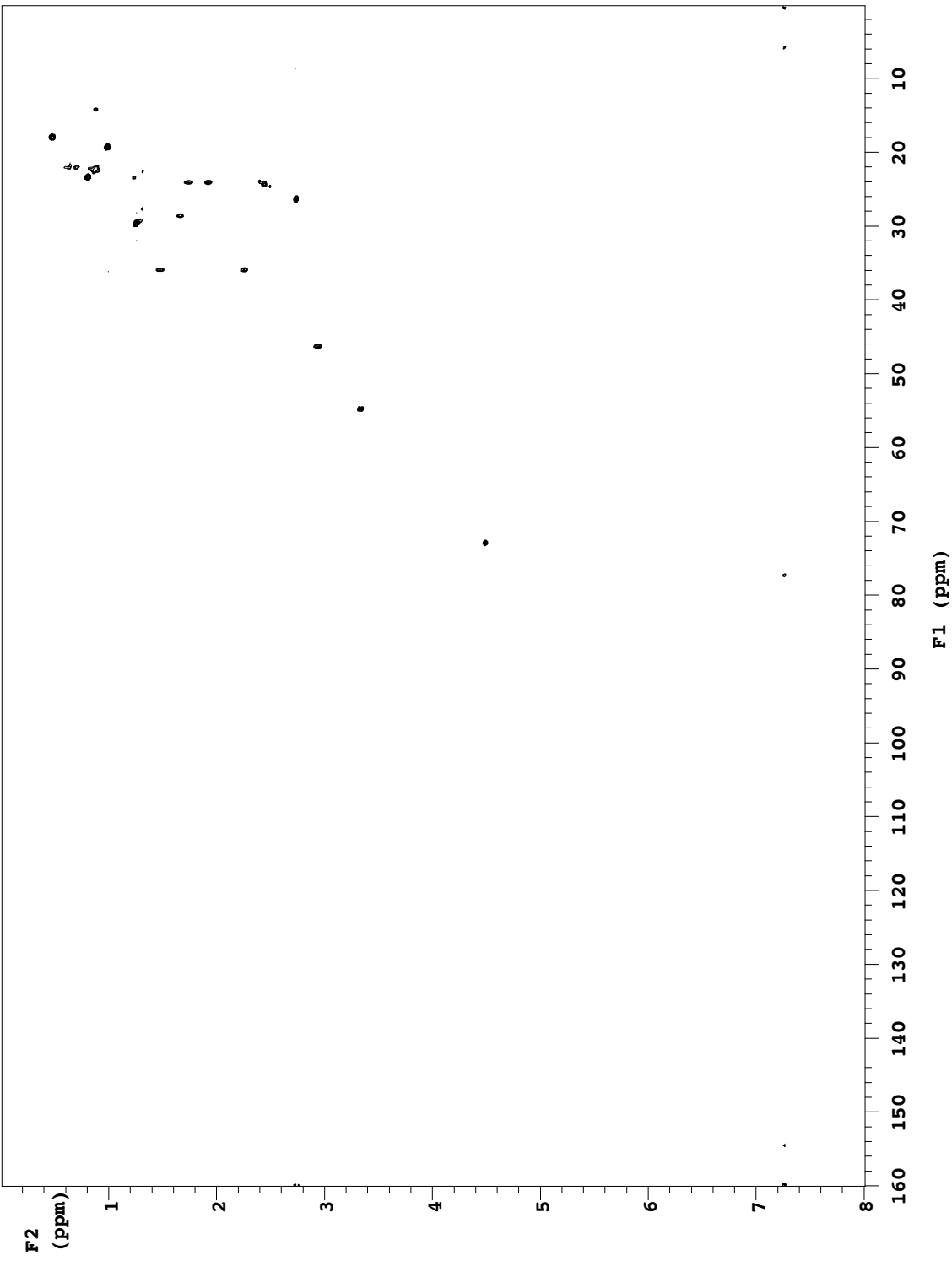
^1H NMR spectrum of 4-bromohamigeran K (**15**) in CDCl_3 (600 MHz).



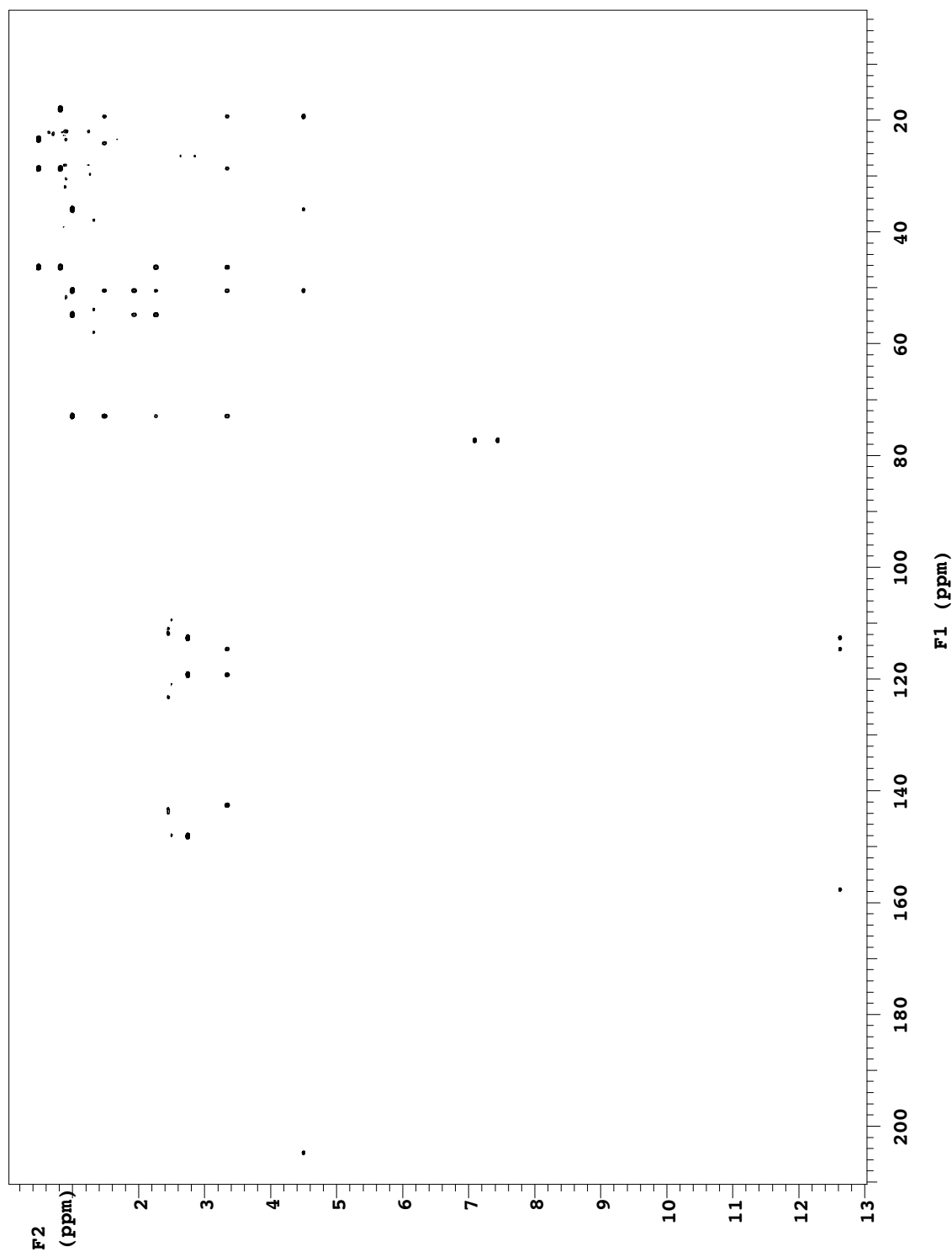
¹³C NMR spectrum of 4-bromohamigeran K (**15**) in CDCl₃ (150 MHz).



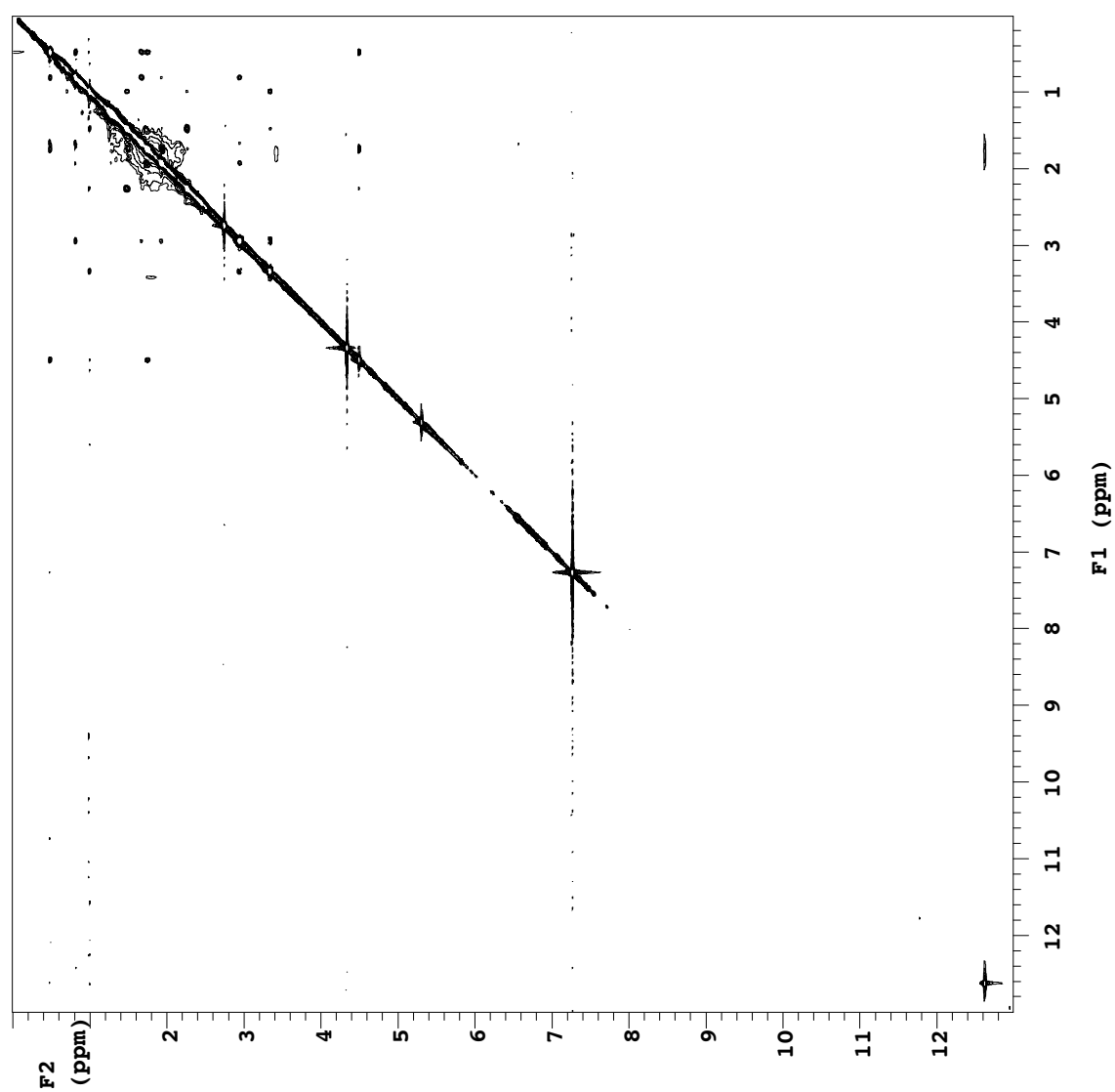
gCOSY spectrum of 4-bromohamigeran K (**15**) in CDCl₃ (600 MHz).



HSQCAD spectrum of 4-bromohamigeran K (**15**) in CDCl₃ (600 MHz).



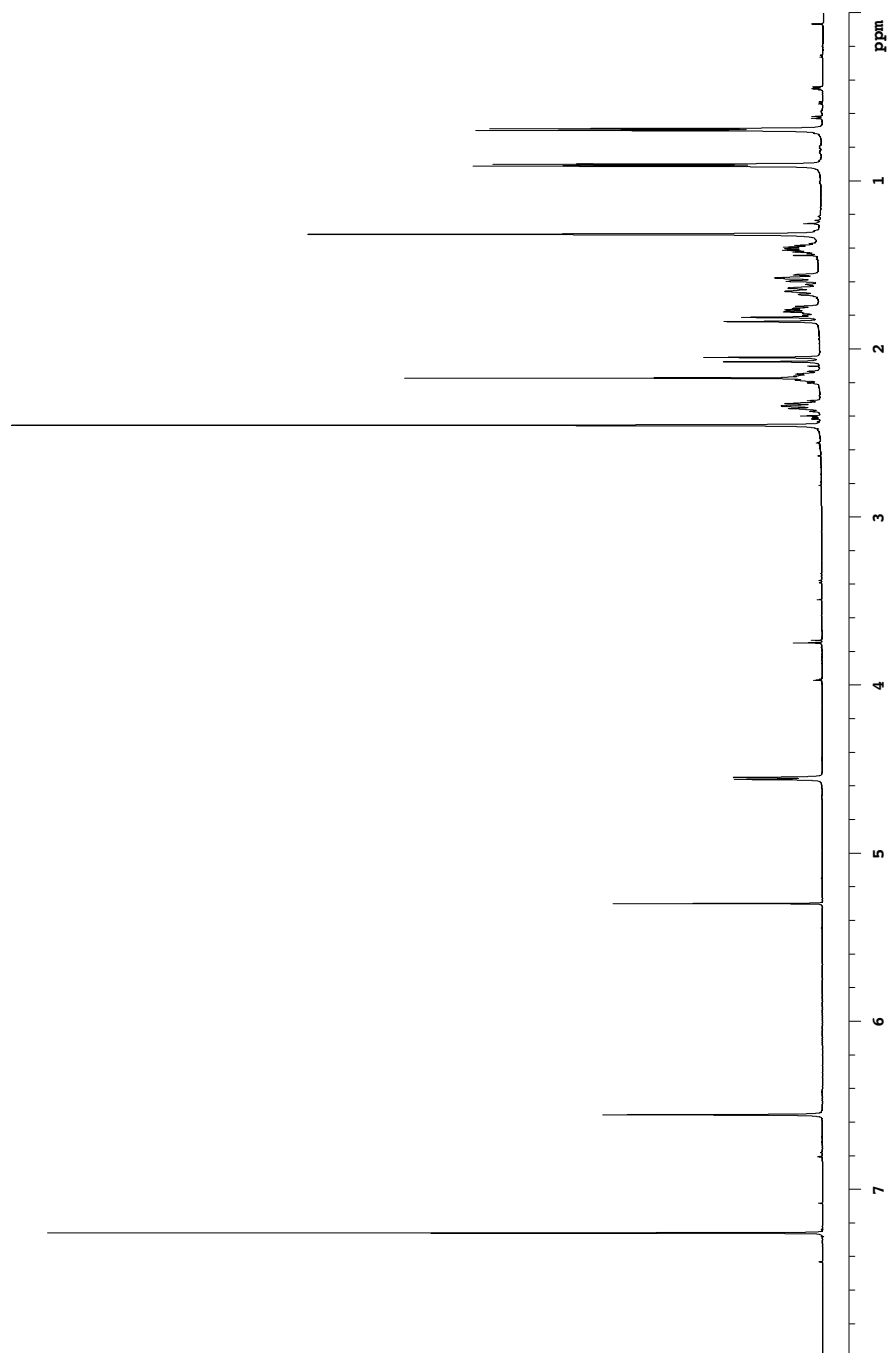
gHMBC spectrum of 4-bromohamigeran K (**15**) in CDCl₃ (600 MHz).



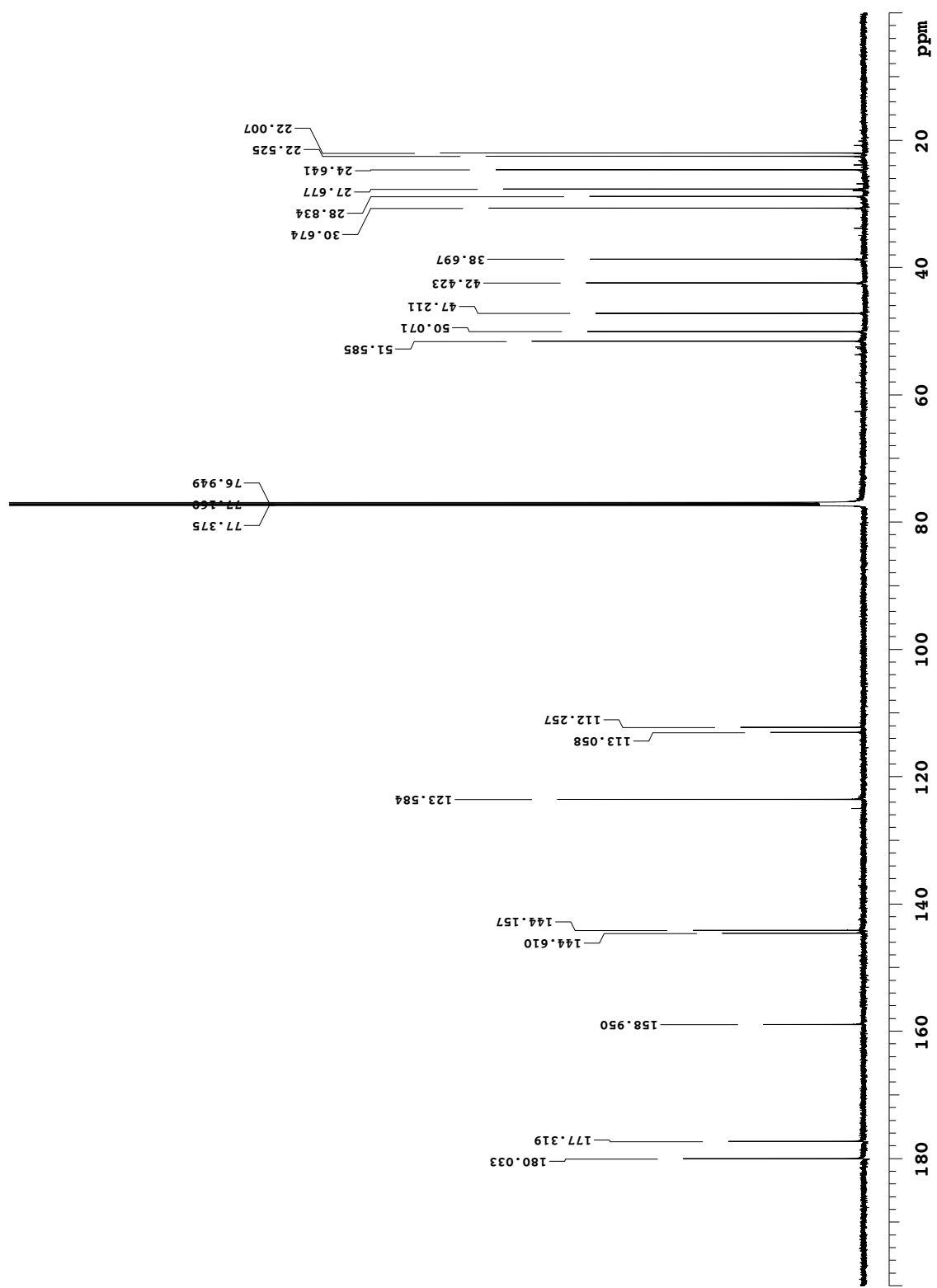
NOESY spectrum of 4-bromohamigeran K (**15**) in CDCl₃ (600 MHz).

Appendix Q

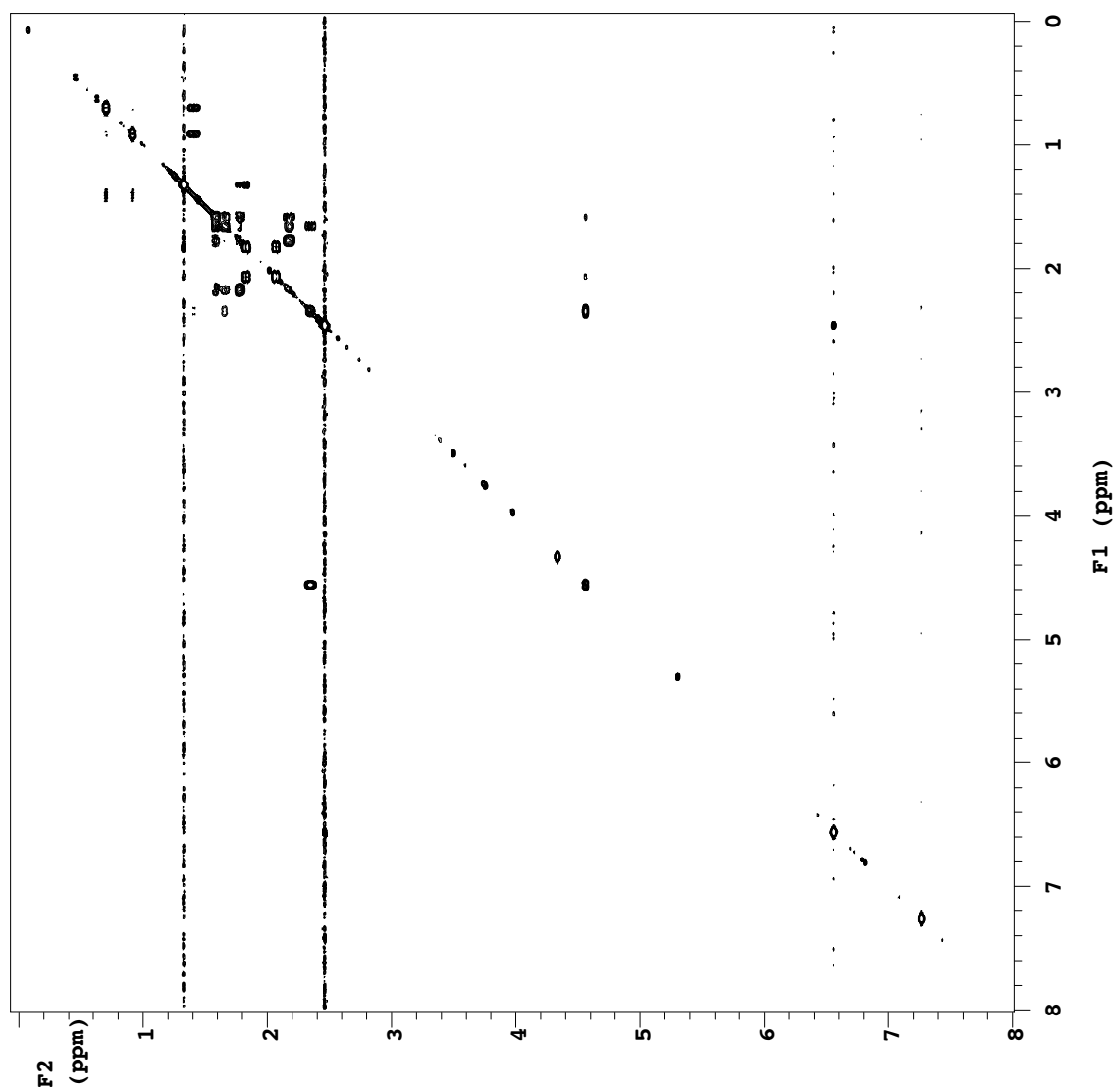
Hamigeran L Spectra



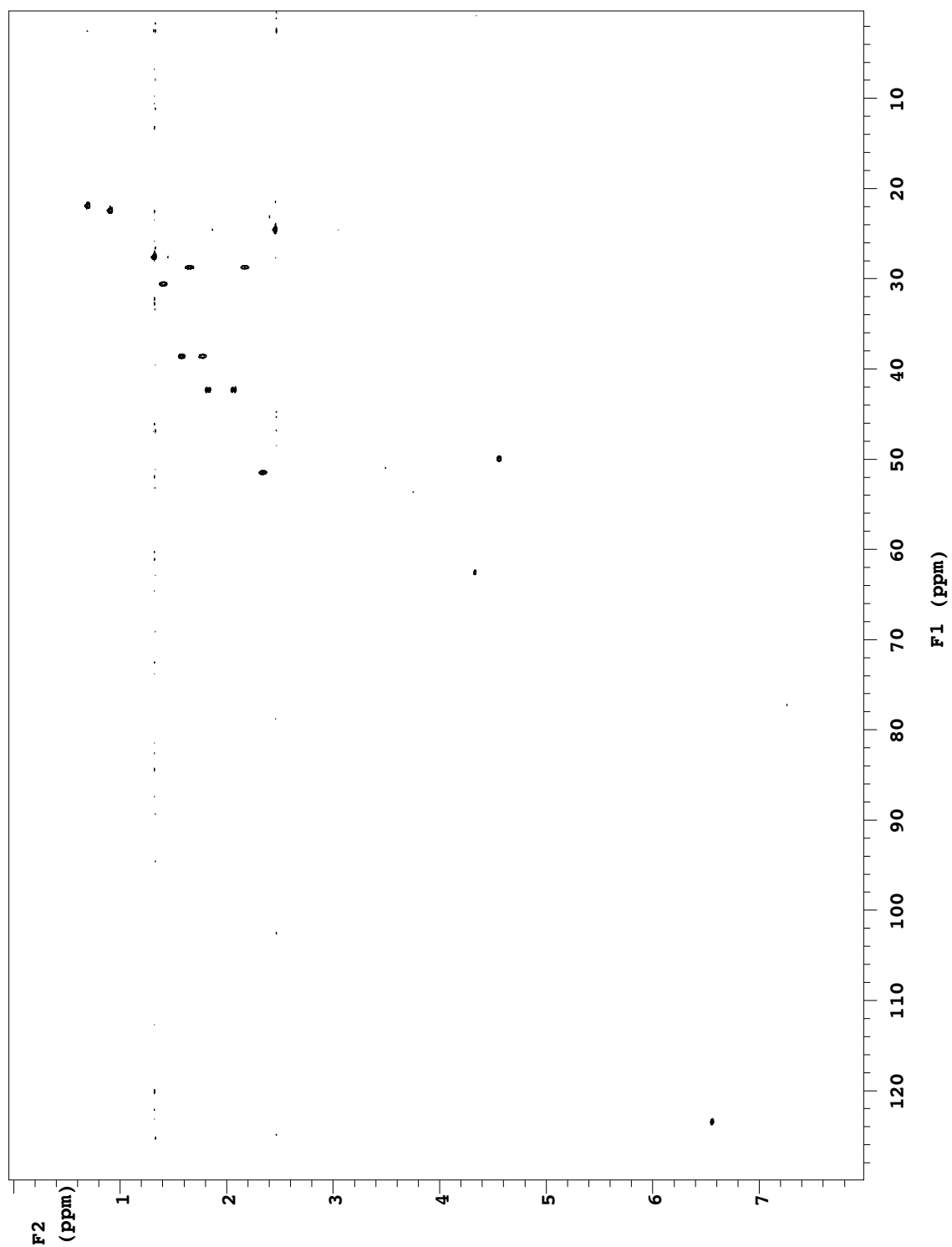
^1H NMR spectrum of hamigeran L (**16**) in CDCl_3 (600 MHz).



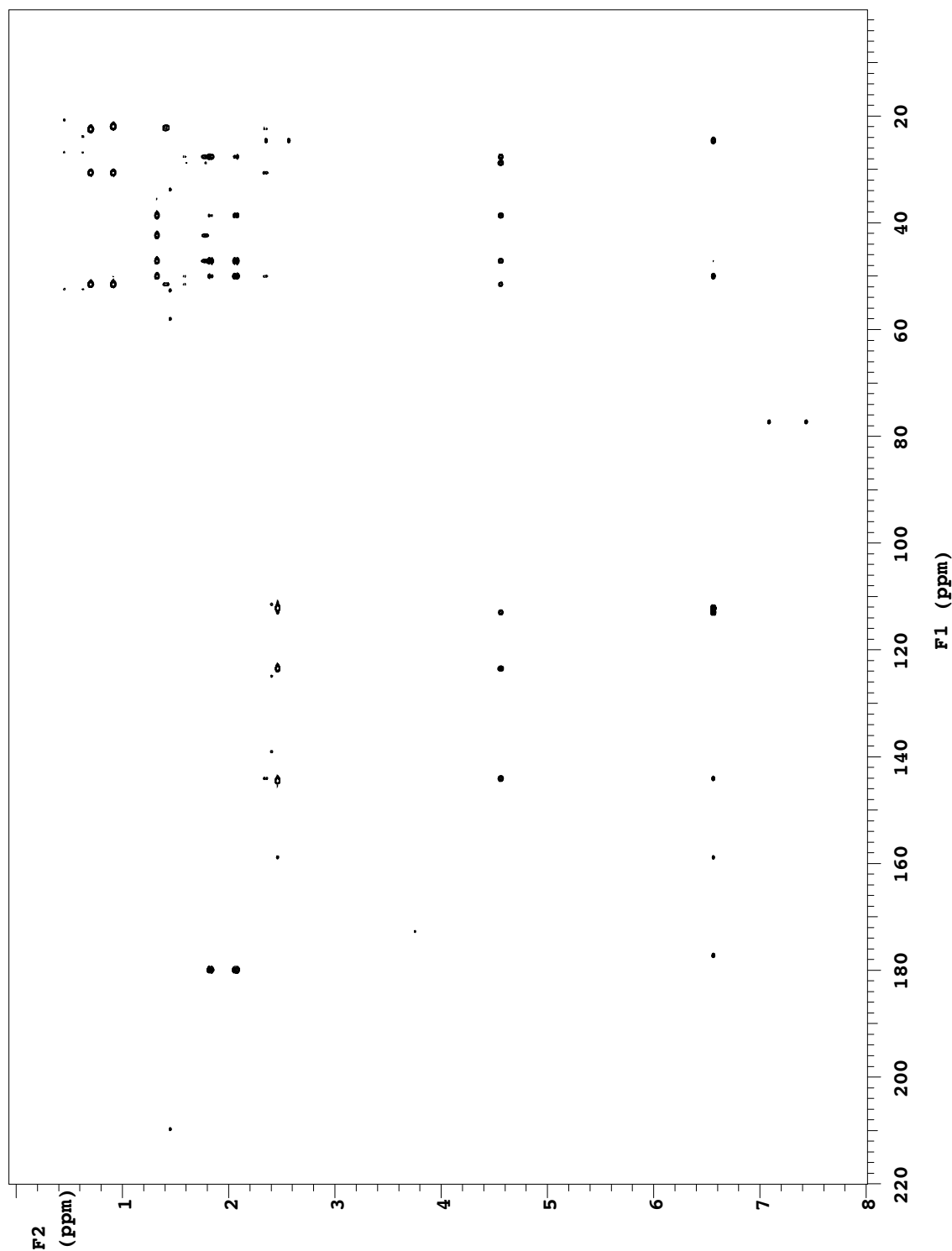
¹³C NMR spectrum of hamigeran L (**16**) in CDCl₃ (150 MHz).



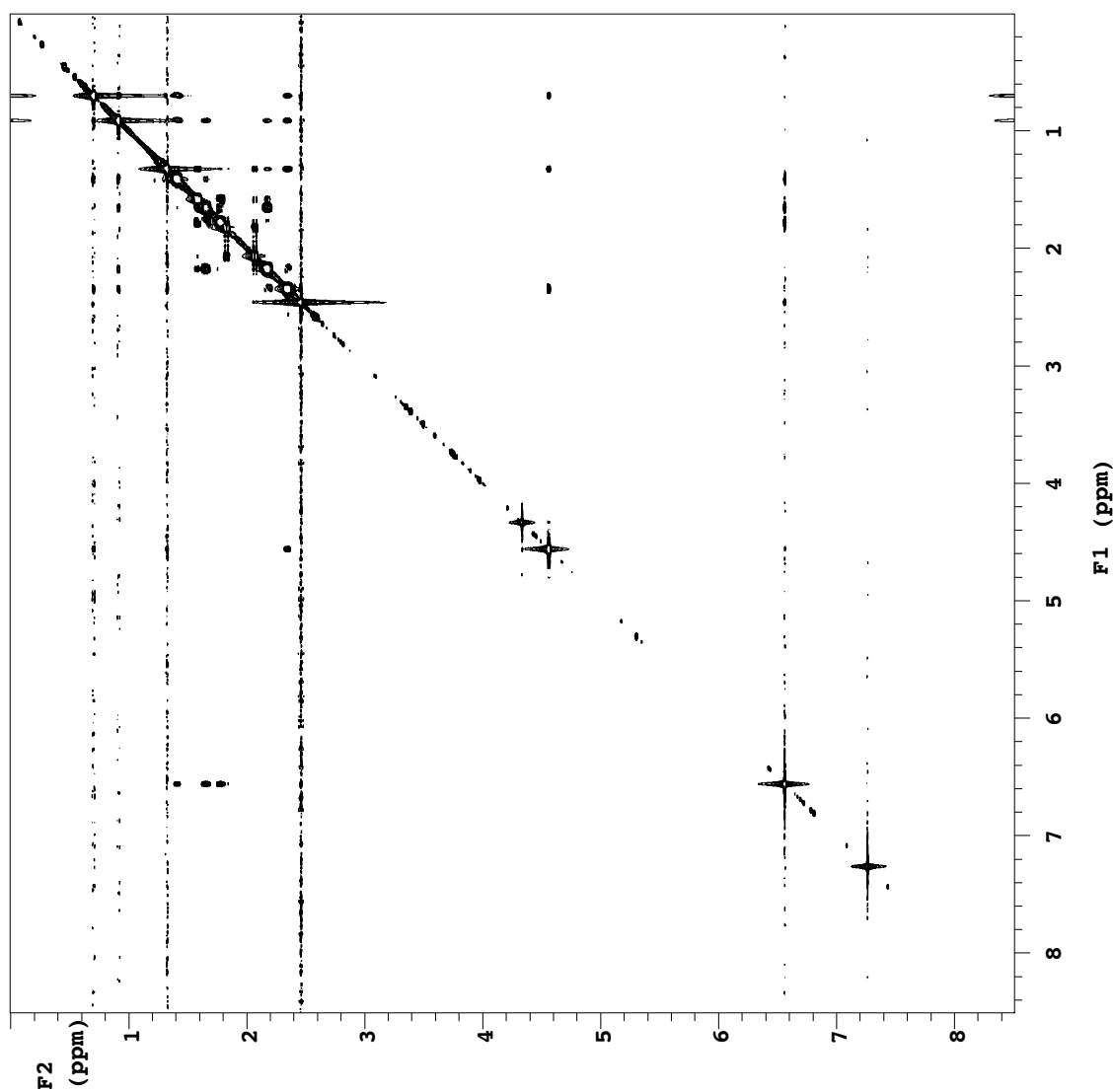
gCOSY spectrum of hamigeran L (**16**) in CDCl₃ (600 MHz).



HSQCAD spectrum of hamigeran L (**16**) in CDCl₃ (600 MHz).



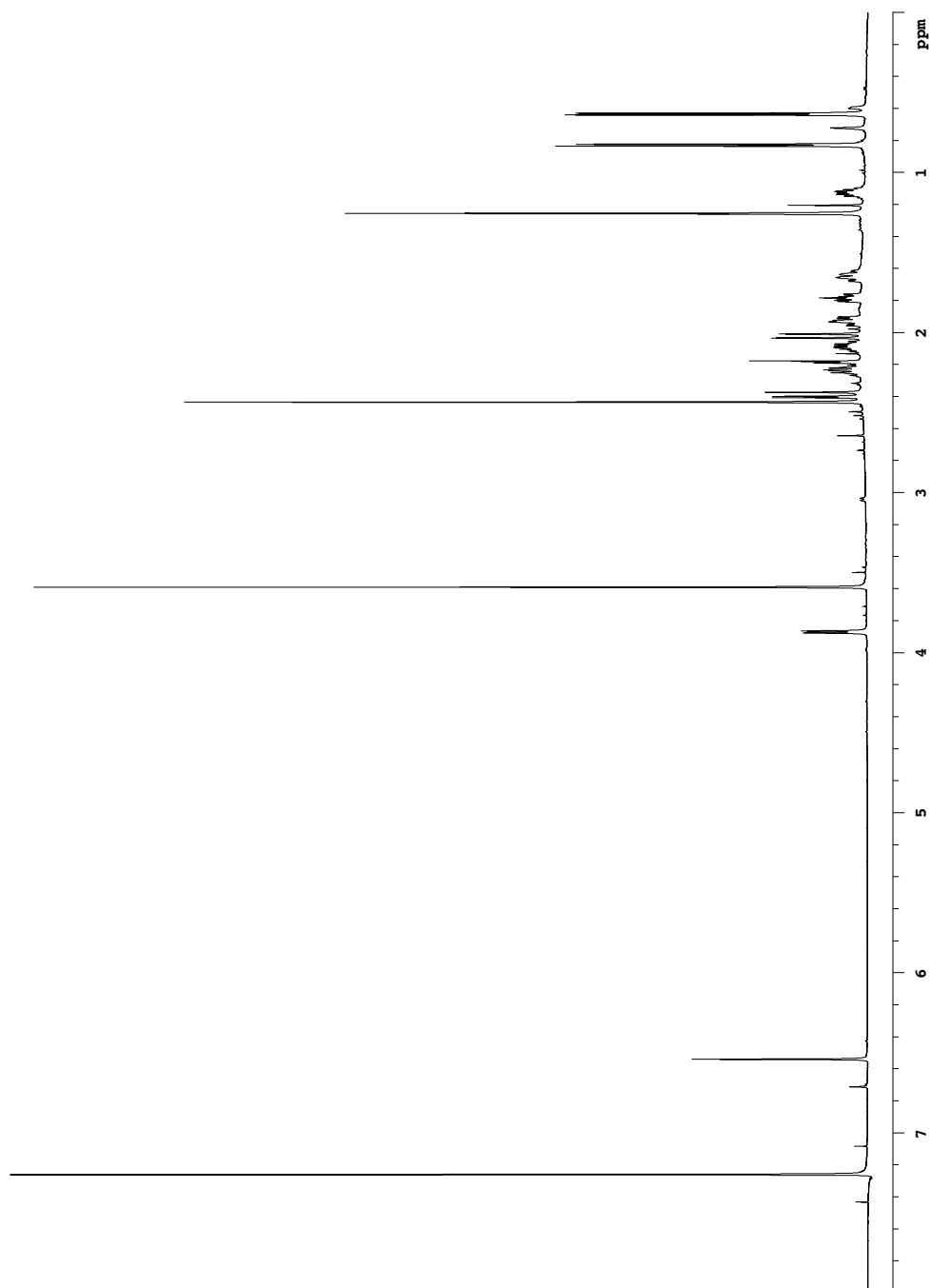
gHMBC spectrum of hamigeran L (**16**) in CDCl₃ (600 MHz).



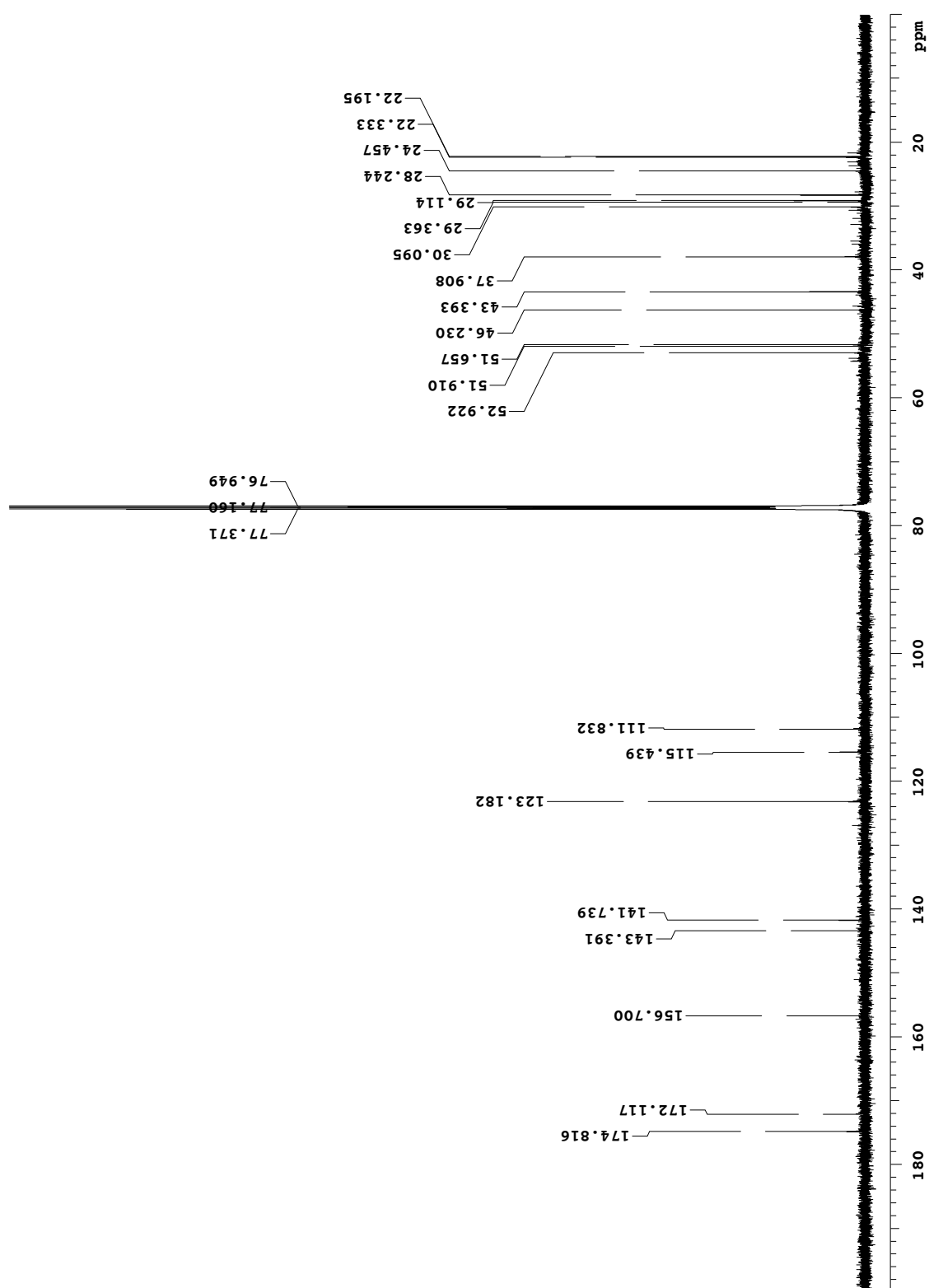
NOESY spectrum of hamigeran L (**16**) in CDCl₃ (600 MHz).

Appendix R

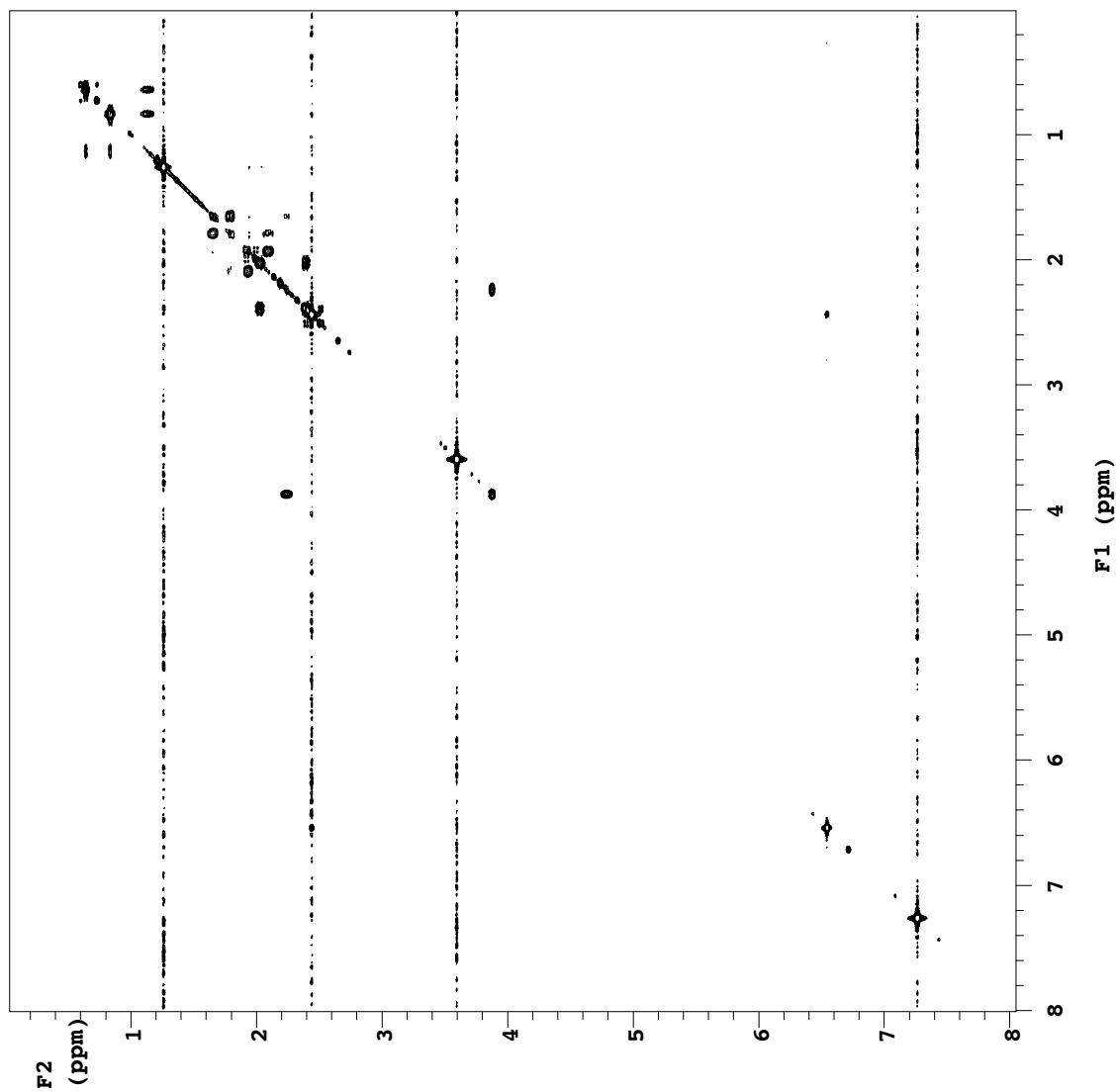
Hamigeran L 11-*O*-Methyl Ester Spectra



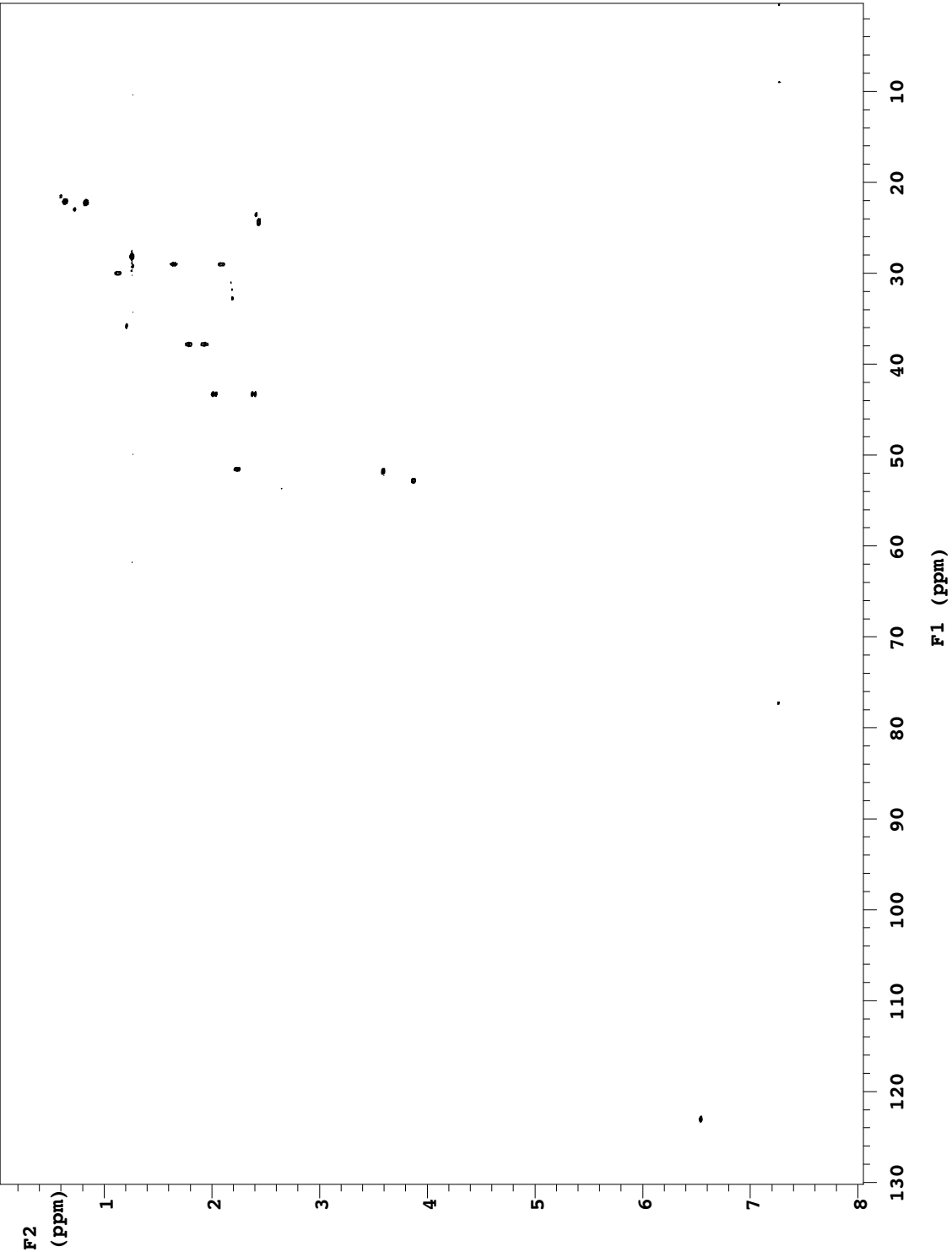
¹H NMR spectrum of hamigeran L 11-*O*-methyl ester (**17**) in CDCl₃ (600 MHz).



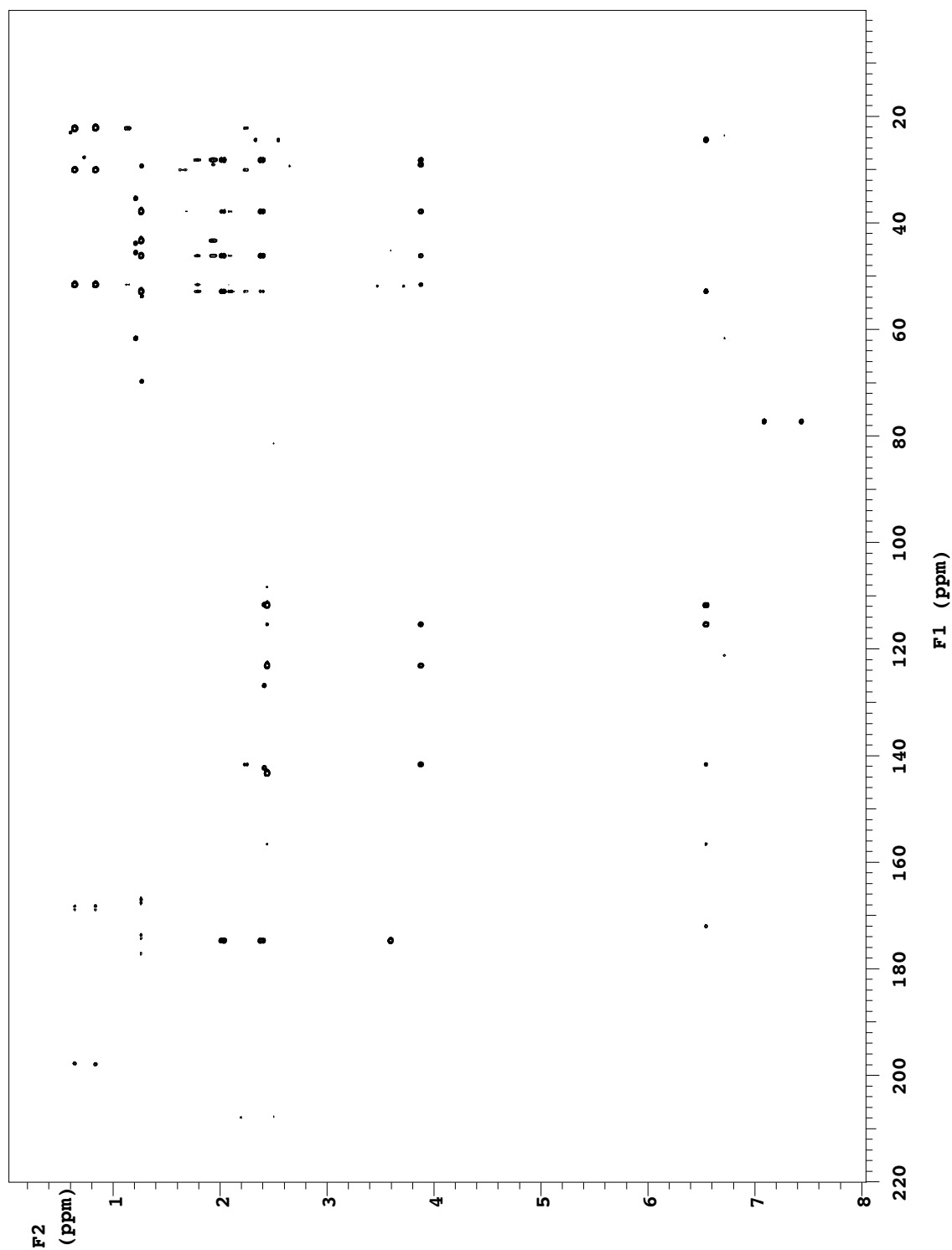
¹³C NMR spectrum of hamigeran L 11-*O*-methyl ester (**17**) in CDCl₃ (150 MHz).



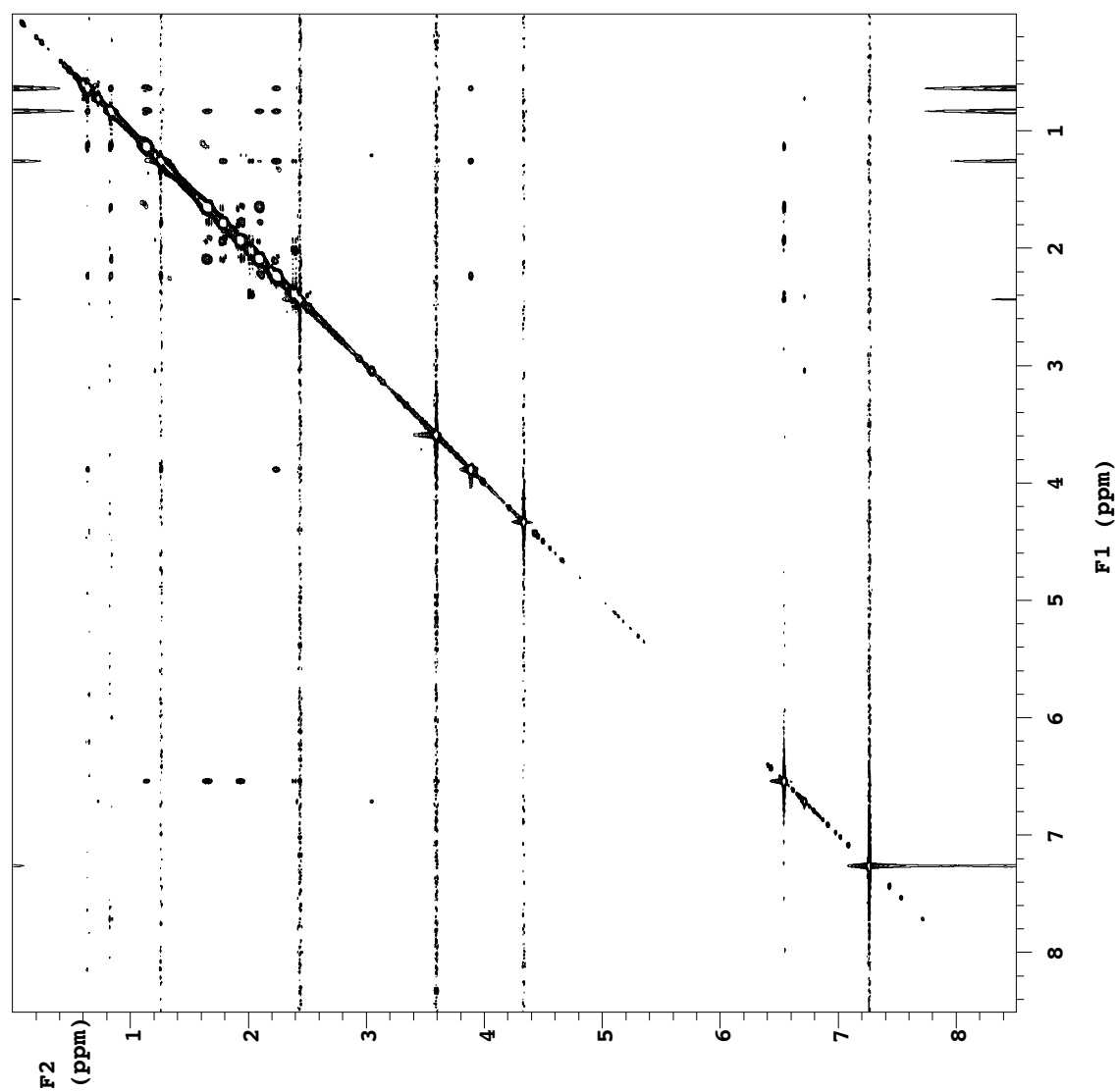
gCOSY spectrum of hamigeran L 11-*O*-methyl ester (**17**) in CDCl₃ (600 MHz).



HSQCAD spectrum of hamigeran L 11-*O*-methyl ester (**17**) in CDCl₃ (600 MHz).



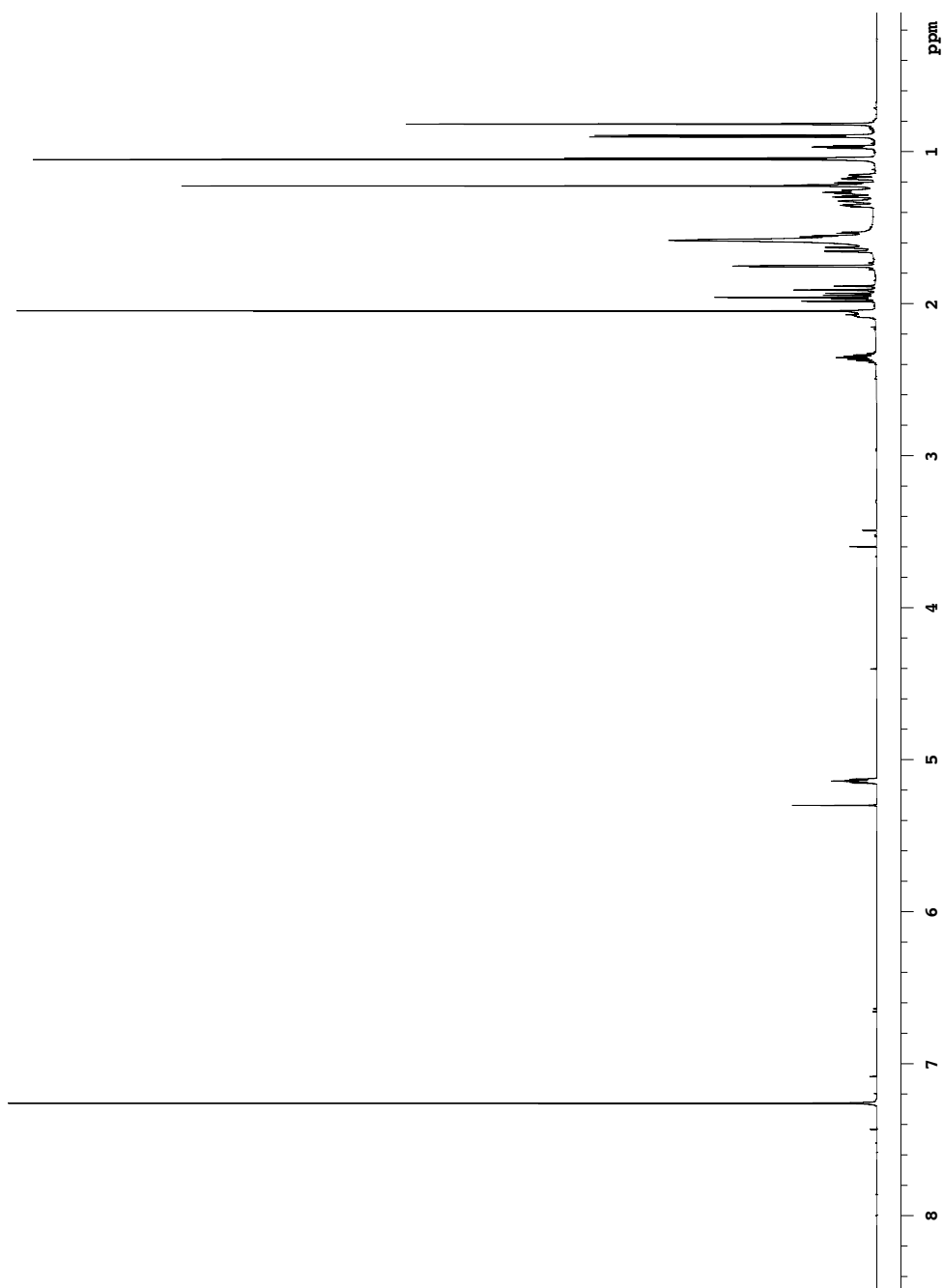
gHMBC spectrum of hamigeran L 11-*O*-methyl ester (**17**) in CDCl₃ (600 MHz).



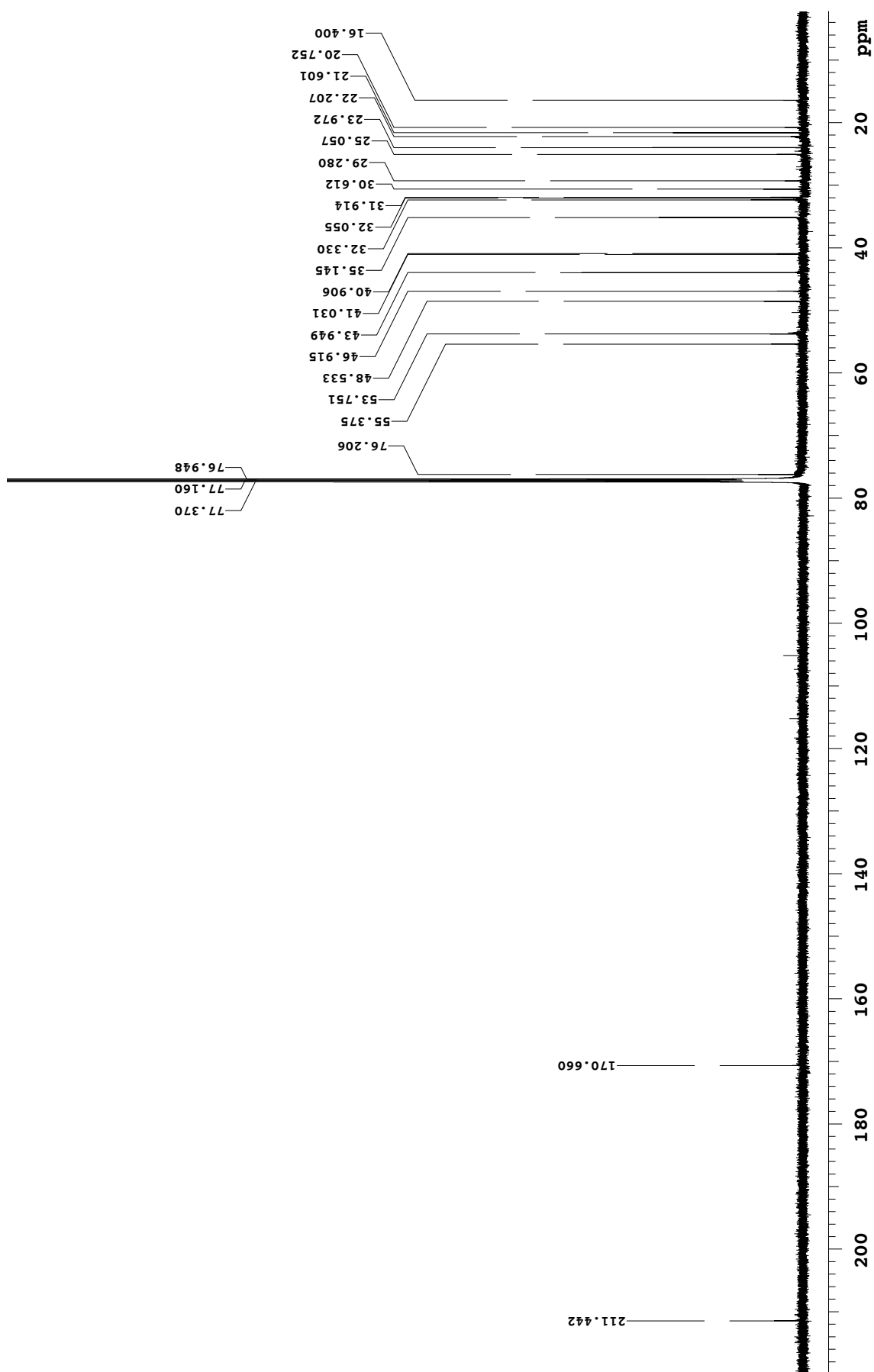
NOESY spectrum of hamigeran L 11-*O*-methyl ester (**17**) in CDCl_3 (600 MHz).

Appendix S

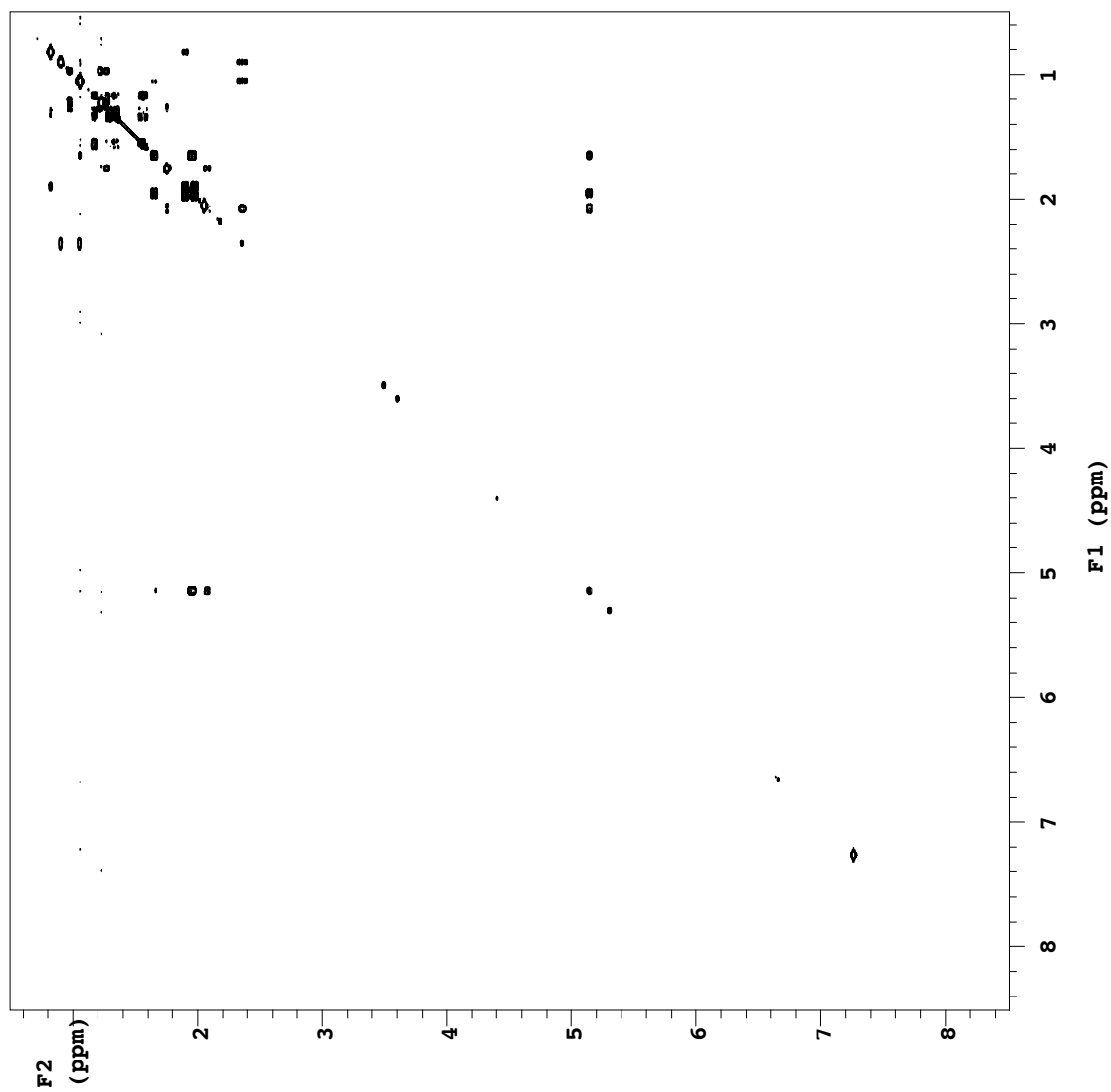
12-Acetoxy-13-*epi*-neoverrucosan-5-one NMR Spectra



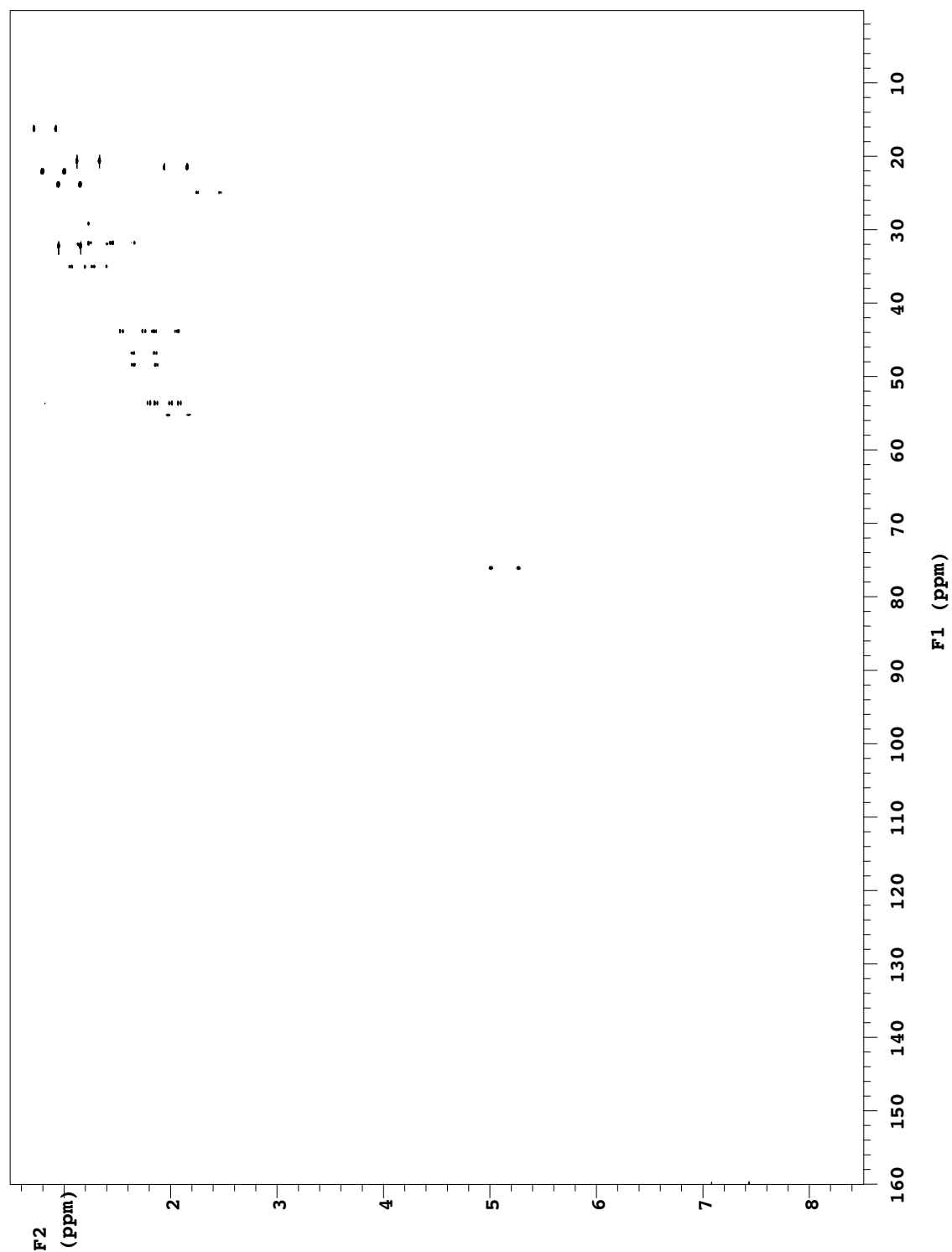
^1H NMR spectrum of 12-acetoxy-13-*epi*-neoverrucosan-5-one (**18**) in CDCl_3 (600 MHz).



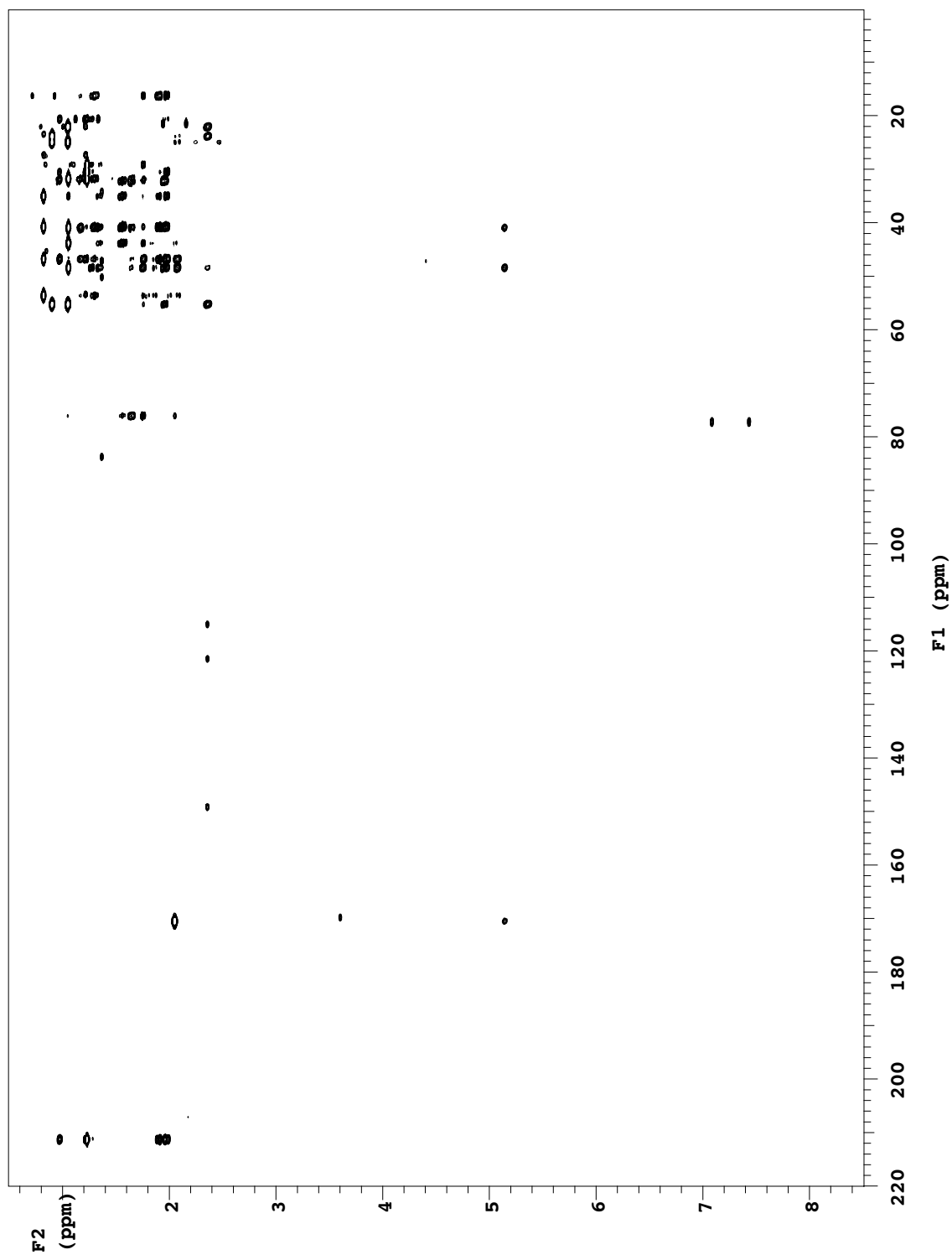
¹³C NMR spectrum of 12-acetoxy-13-*epi*-neoverrucosan-5-one (**18**) in CDCl₃ (150 MHz).



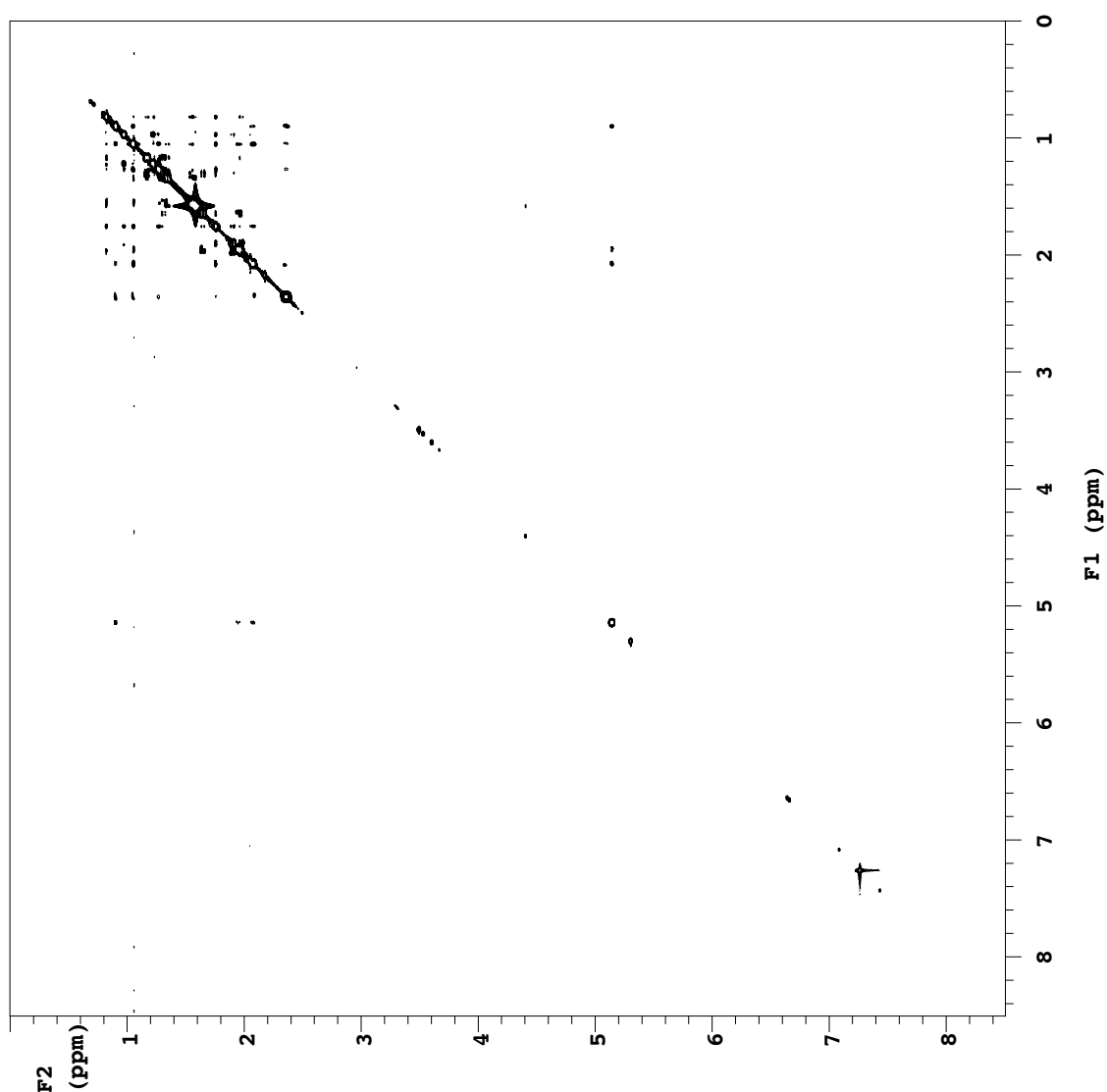
gCOSY spectrum of 12-acetoxy-13-*epi*-neoverrucosan-5-one (**18**) in CDCl₃ (600 MHz).



Fully-coupled HSQCAD spectrum of 12-acetoxy-13-*epi*-neoverrucosan-5-one (**18**) in CDCl₃ (600 MHz). $^1J_{\text{CH}} = 140$ Hz.



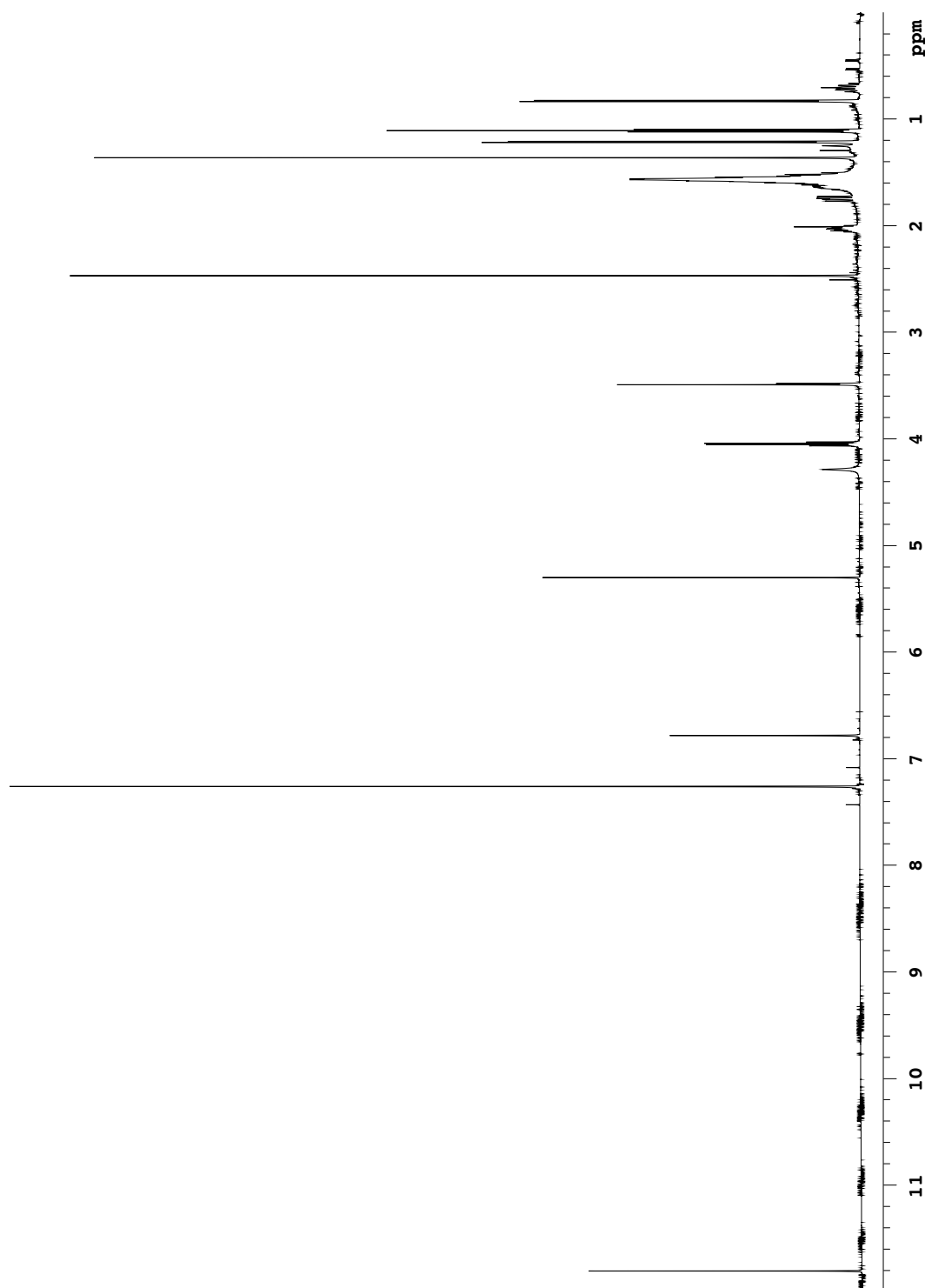
gHMBC spectrum of 12-acetoxy-13-*epi*-neoverrucosan-5-one (**18**) in CDCl₃ (600 MHz).



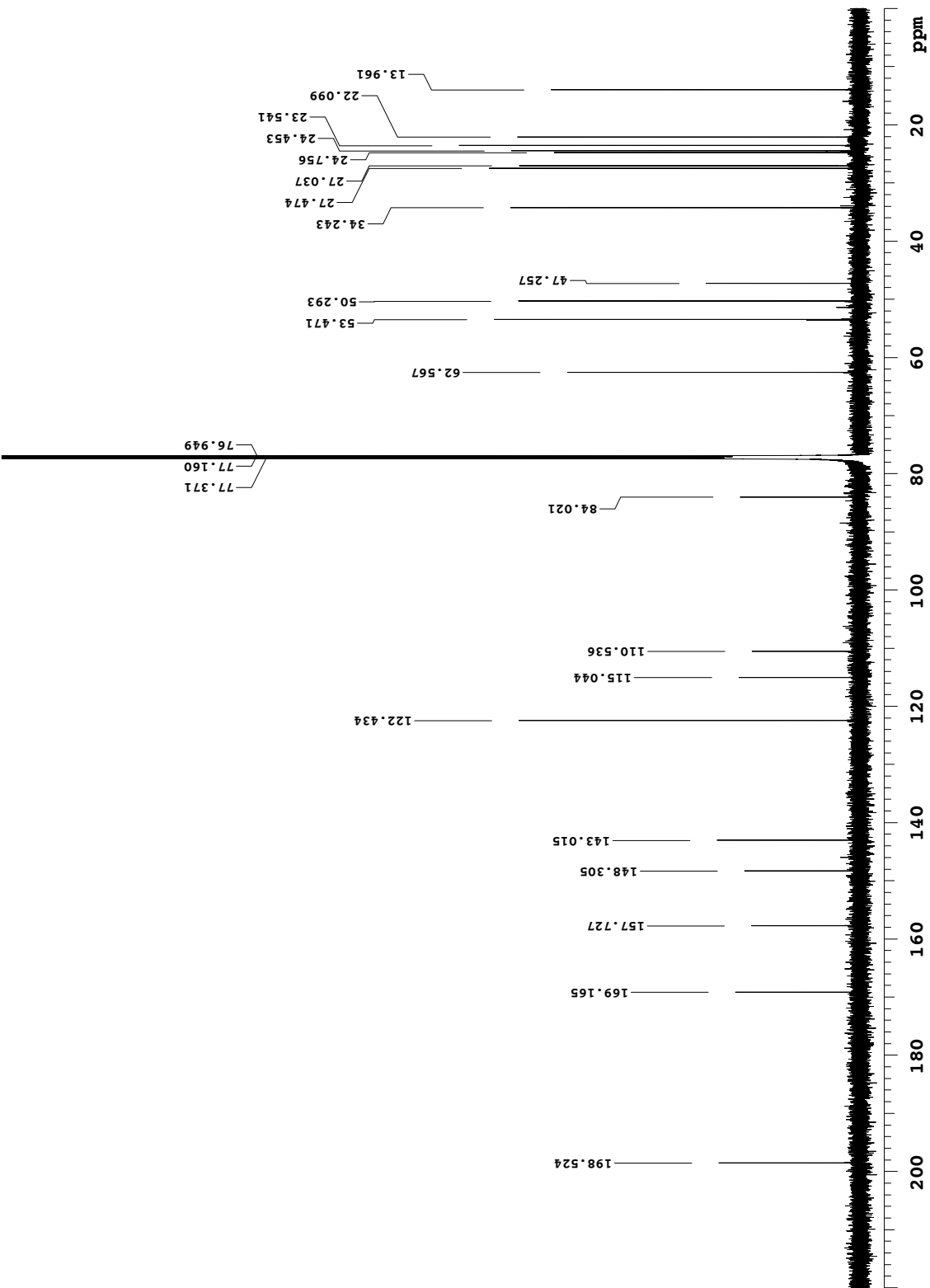
NOESY spectrum of 12-acetoxy-13-*epi*-neoverrucosan-5-one (**18**) in CDCl₃ (600 MHz).

Appendix T

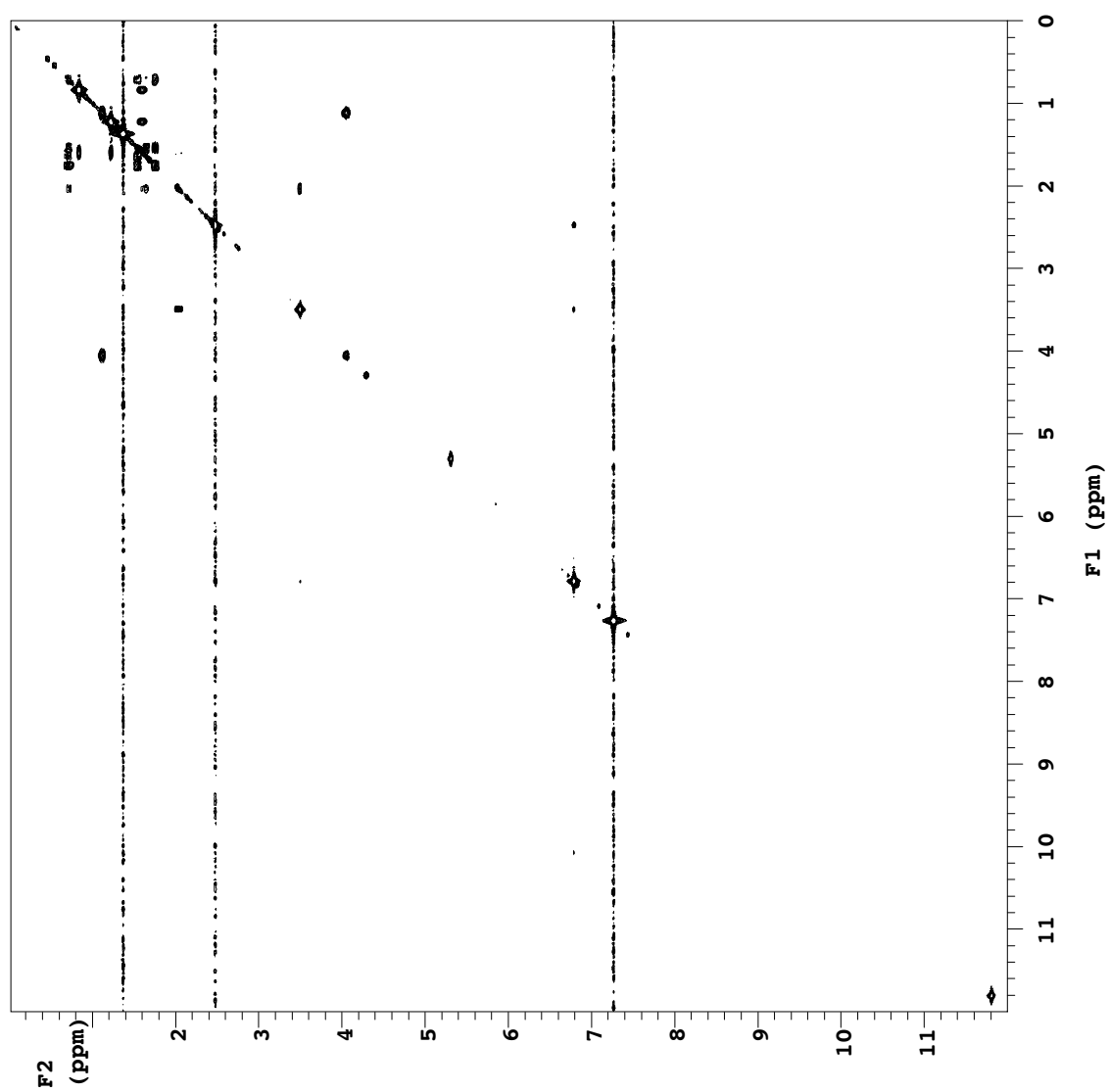
Hamigeran A Ethyl Ester NMR Spectra



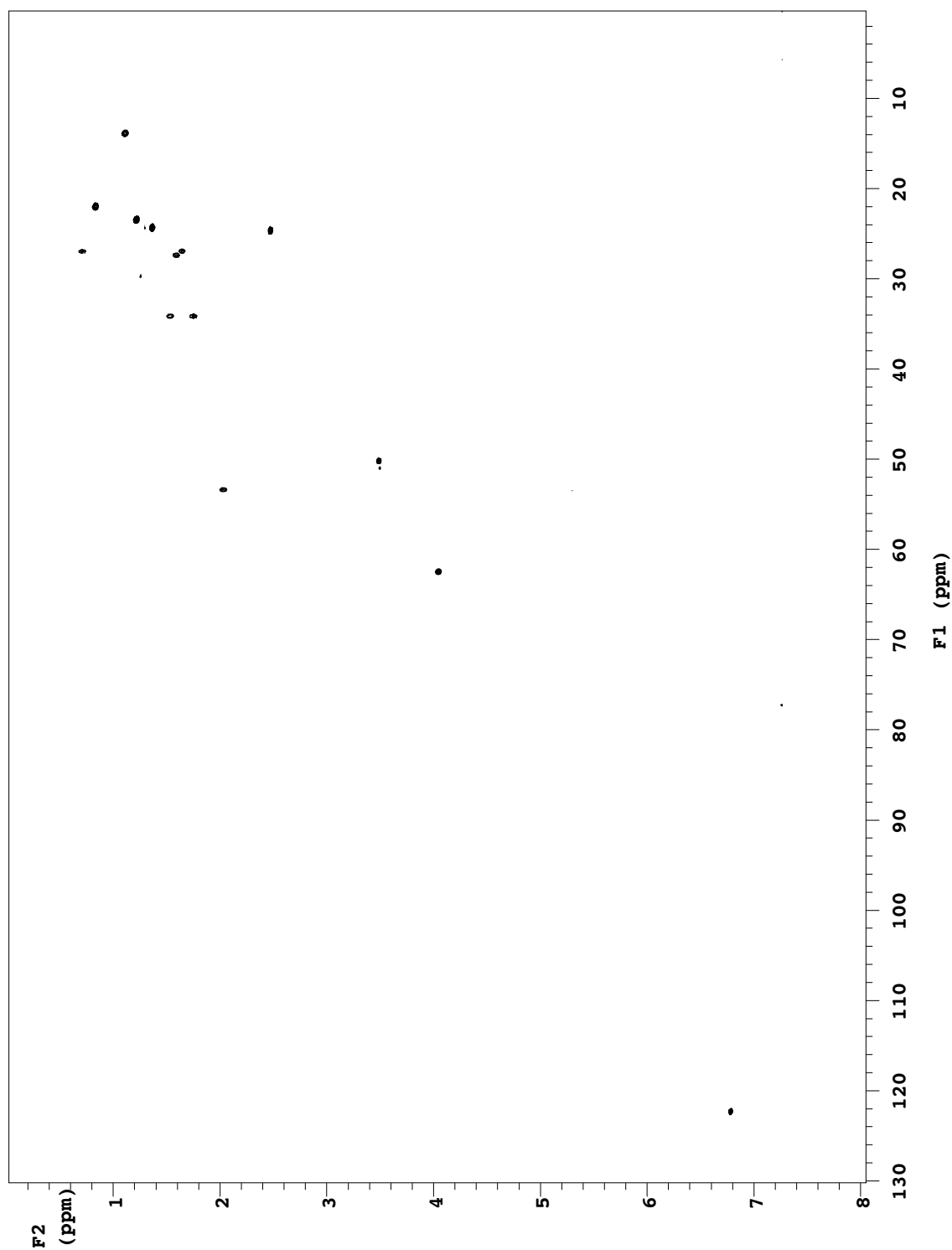
^1H NMR spectrum of hamigeran A ethyl ester (**19**) in CDCl_3 (600 MHz).



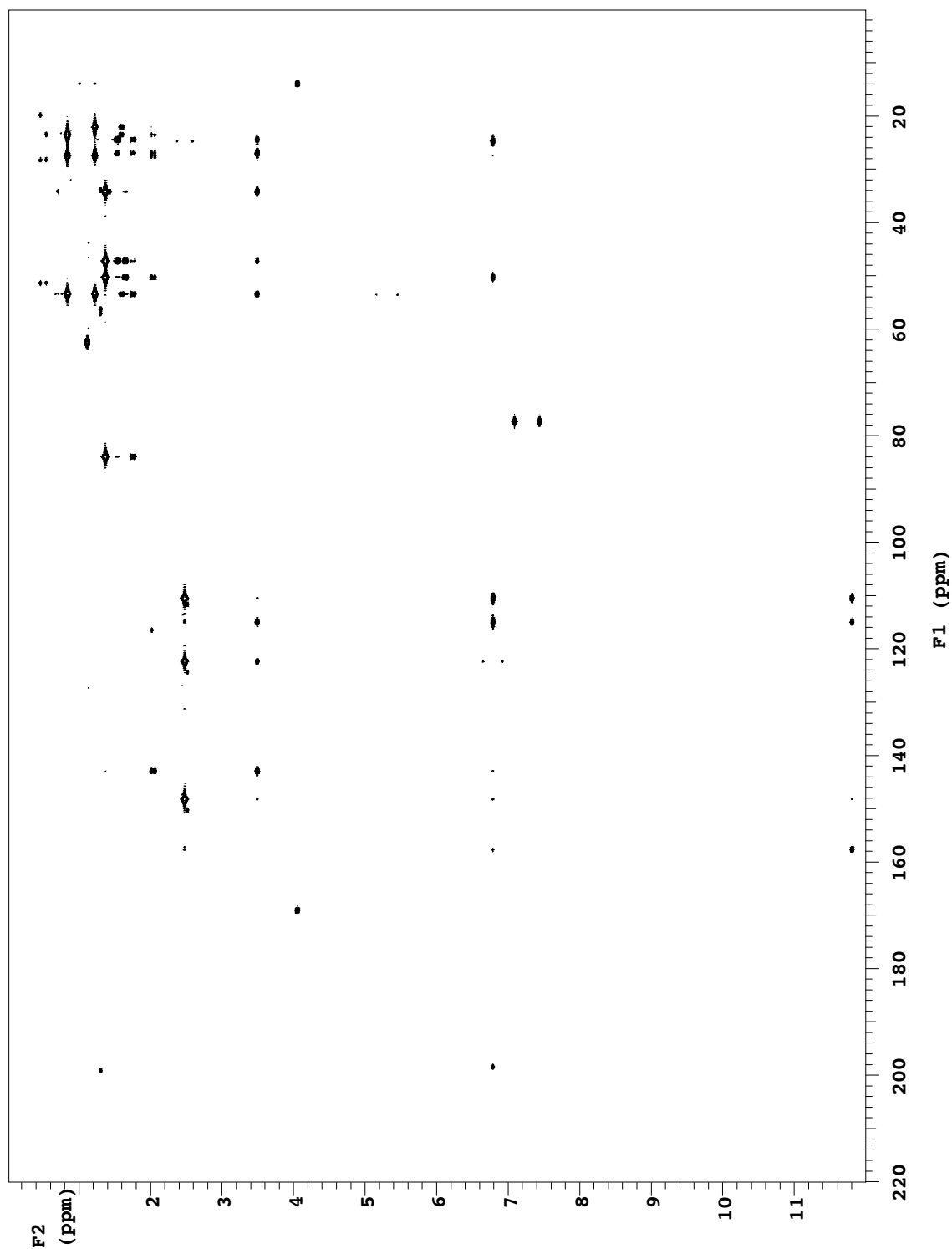
¹³C NMR spectrum of hamigeran A ethyl ester (**19**) in CDCl₃ (150 MHz).



gCOSY spectrum of hamigeran A ethyl ester (**19**) in CDCl_3 (600 MHz).



HSQCAD spectrum of hamigeran A ethyl ester (**19**) in CDCl₃ (600 MHz).



gHMBC spectrum of hamigeran A ethyl ester (**19**) in CDCl₃ (600 MHz).