

Supplementary Material

Three New Spongian Diterpenes from the Marine Sponge *Dendrilla rosea*

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Experimental

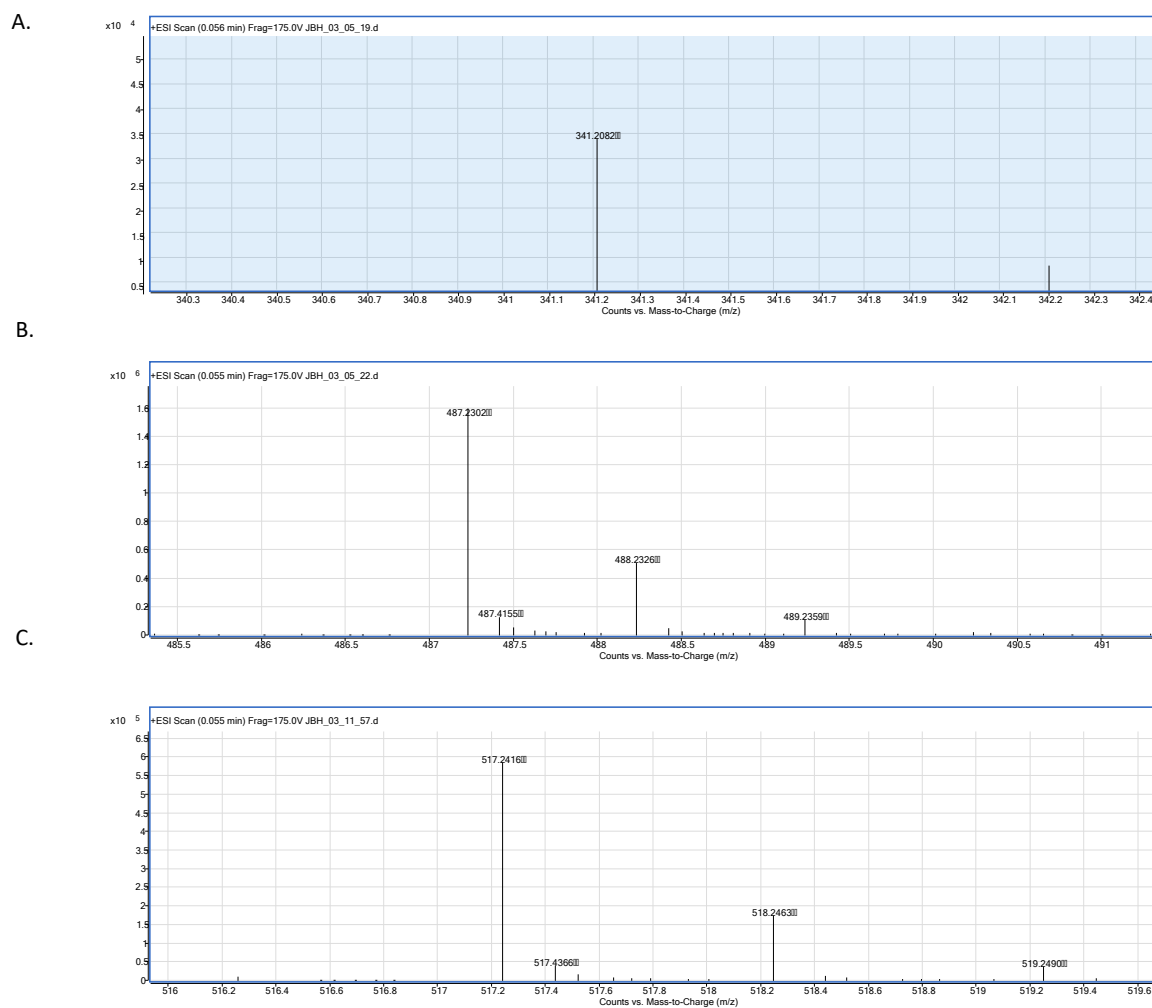


Figure S1. HRESIMS spectra of (A) aplyroseol 20 (**2**), (B) aplyroseol 21 (**3**) and (C) aplyroseol (**4**).

Table S1. Complete NMR data for aplyroseol-20 (**2**) acquired in CDCl₃ at 25°C.

Position	¹³ C (δ , ¹ J _{CH} in Hz) ^a	¹ H (δ , mult., <i>J</i> in Hz) ^a	COSY ^a	HMBC ^a	NOESY ^a
1 α	38.0	0.92 (td, 14.2, 4.1)	1 β , 2 β	20	1 β , 2 α , 3 α , 11 α
1 β		1.61 (m)	1 α	3, 5	1 α
2 α	19.0	1.47 (dddt, 14.1, 4.6, 4.1, 3.1)		1, 4, 3, 10	1 α , 3 α
2 β		1.61 (m)	1 α , 3 α , 3 β	1, 3	
3 α	42.0	1.16 (td, 13.2, 4.6)	2 β	4, 18, 19	1 α , 2 α , 3 β
3 β		1.41 (m)	2 β	1, 2, 4, 5, 18, 19	3 α
4	33.1				
5	56.7	1.00 (dd, 12.5, 2.6)	6 β	1, 3, 4, 6, 9, 10, 18, 19, 20	
6 α	19.5	1.67 (dddd, 14.0, 4.1, 3.4, 2.6)	6 β	5, 7, 8, 10	718
6 β		1.37 (m)	5, 6 α , 7 α	5, 7, 10	7 β , 17
7 α	34.8 (126) ^b	1.17 (td, 13.4, 4.1)	6 α , 7 β	17	7 β , 4
7 β		1.93 (dt, 13.4, 3.4)	7 α	5, 6, 8, 9, 14	6 β , 7 α , 15b, 17
8	45.9				
9	54.9	1.59 (m)	11 β	8, 10, 11, 17, 20	
10	37.8				
11 α	19.4	1.72 (dddd, 12.9, 4.7, 4.5, 1.9)	9, 11 α	7, 8, 9, 10	1 α , 11 β , 12 β
11 β		1.37 (m)	11 β , 12 α	8, 9, 12	11 α , 12 β , 20
12 α	30.0	1.63 (m)	12 α	14, 16, 17	12 β , 13, 14
12 β		2.09 (dtd, 13.0, 4.5, 2.2)	11 α , 12 β , 13	9, 11, 14	11 α , 11 β , 12 α , 13
13	46.9	2.81 (m)	12 α	11, 12, 14, 16, 17	12 α , 12 β , 14, 15a
14	46.0	1.89 (ddd, 4.7, 2.9, 1.1)	15b	15, 16, 17	7 α , 12 α , 13, 15a, 15b
15a	70.0 (151) ^b	3.78 (d, 8.8)	15b	8, 17	13, 14, 15b
15b		4.08 (dd, 8.8, 4.7)	14, 15a	13, 14, 17	7 β , 14, 15a
16	173.1				
17	103.9 (182) ^b	5.65 (d, 1.1)		7, 14, 15, 16	6 β , 7 β , 20
18	33.3 (121) ^b	0.87 (s)		3, 4, 5, 18	6 α
19	21.4 (124) ^b	0.84 (s)		3, 4, 5, 19	
20	15.3 (129) ^b	0.96 (s)		1, 5, 9, 10	11 β , 17

^a Spectra recorded in CDCl₃ (¹H, 800 MHz; ¹³C, 200 MHz), ^b ¹H (δ , mult., *J* in Hz)^b ¹J_{CH} values measured in HMBC spectrum

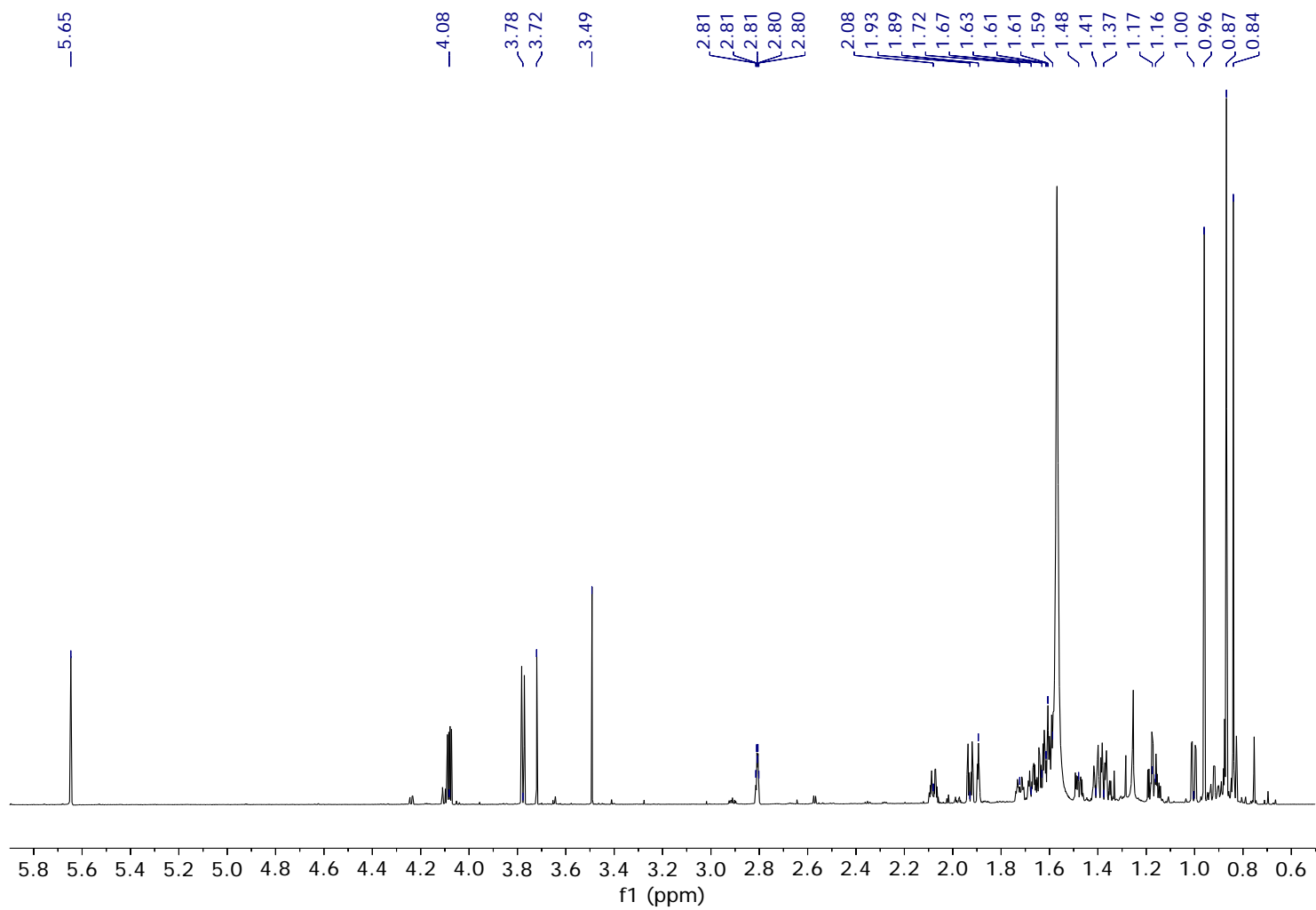


Figure S2. ^1H NMR (800 MHz) spectrum of aplyroseol-20 (**2**) in CDCl_3 .

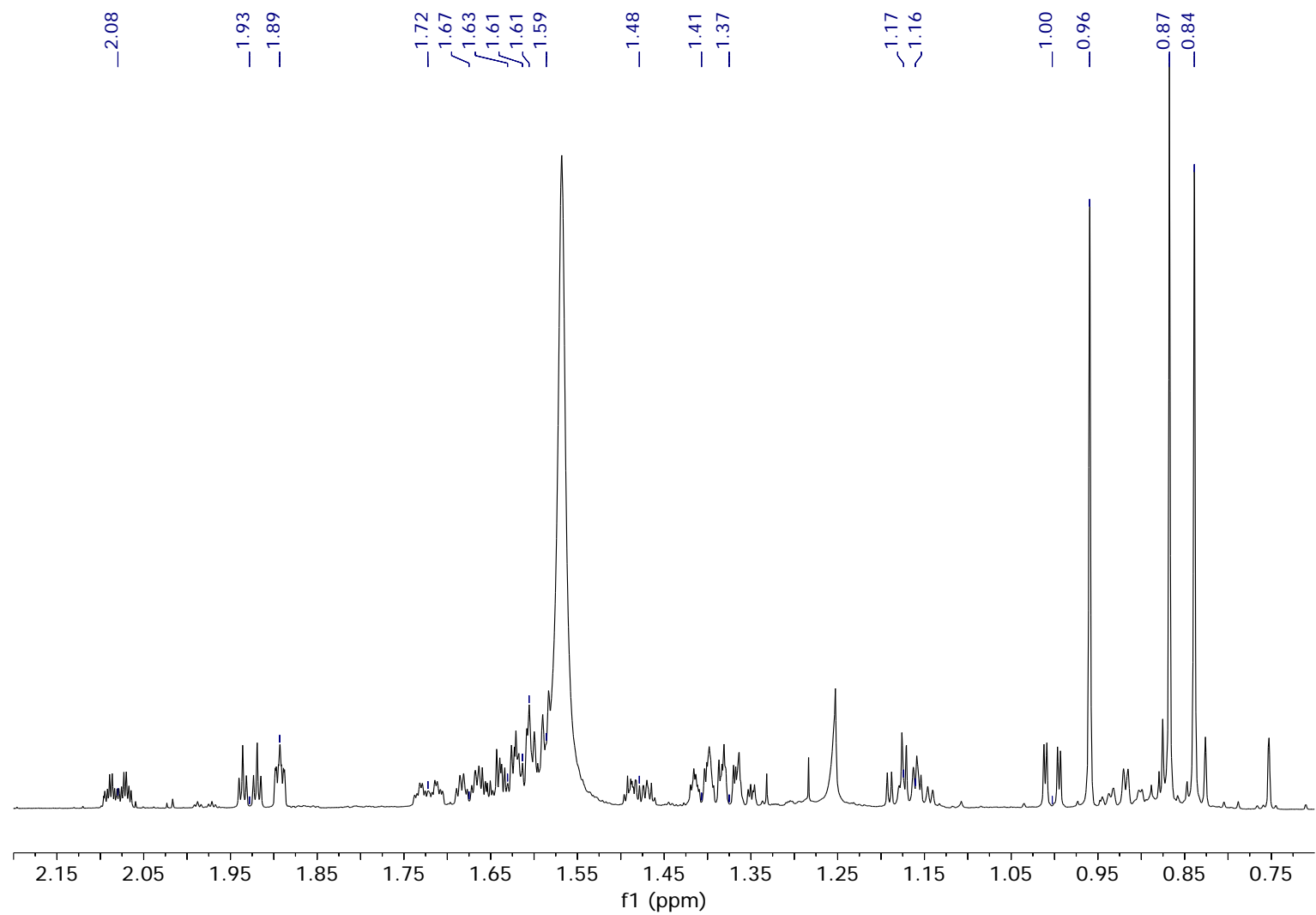


Figure S3. Expansion of the ^1H NMR (800 MHz) spectrum of aplyroseol-20 (**2**) in CDCl_3 .

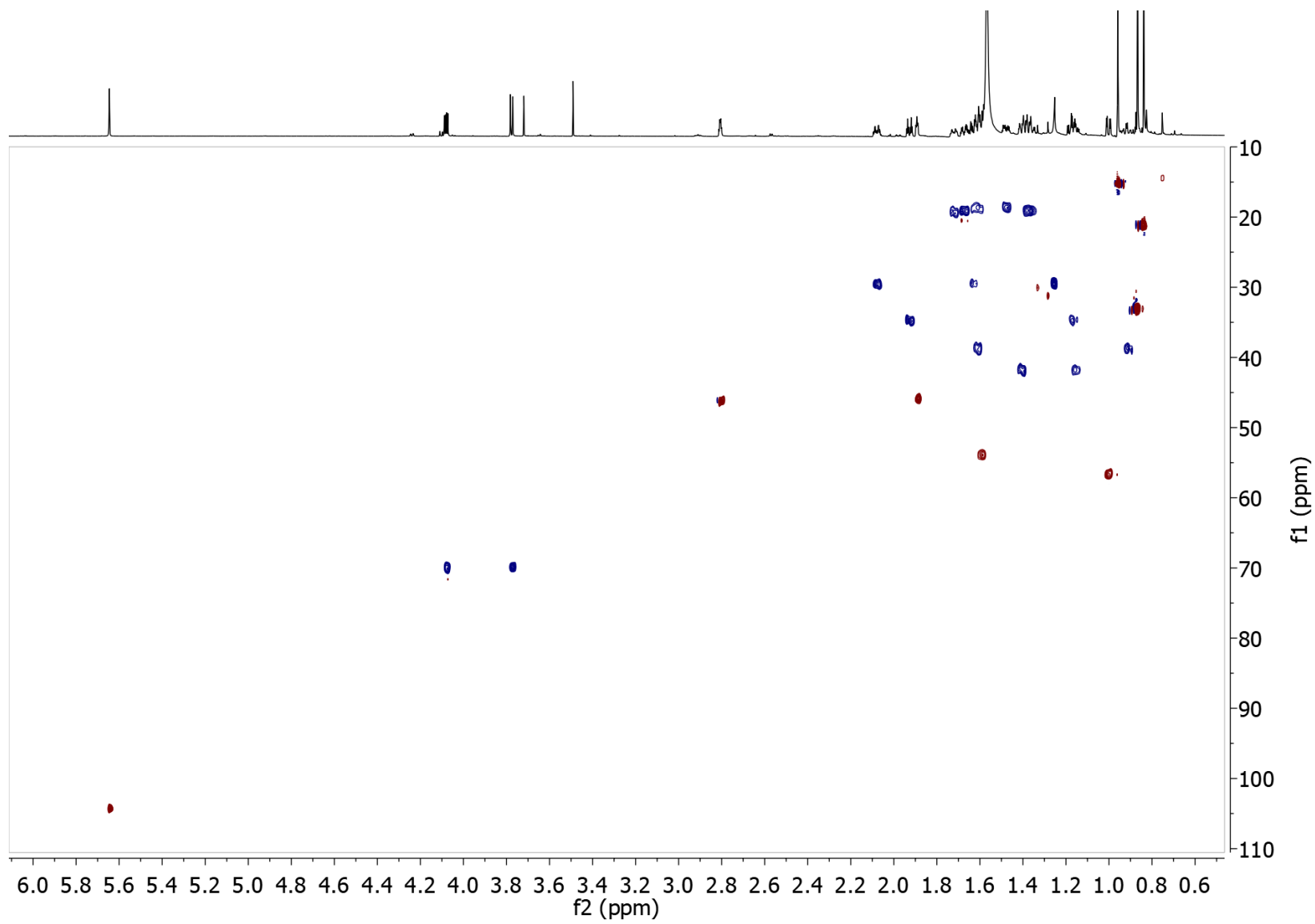


Figure S4. HSQC spectrum of aplyroseol-20 (**2**) in CDCl₃.

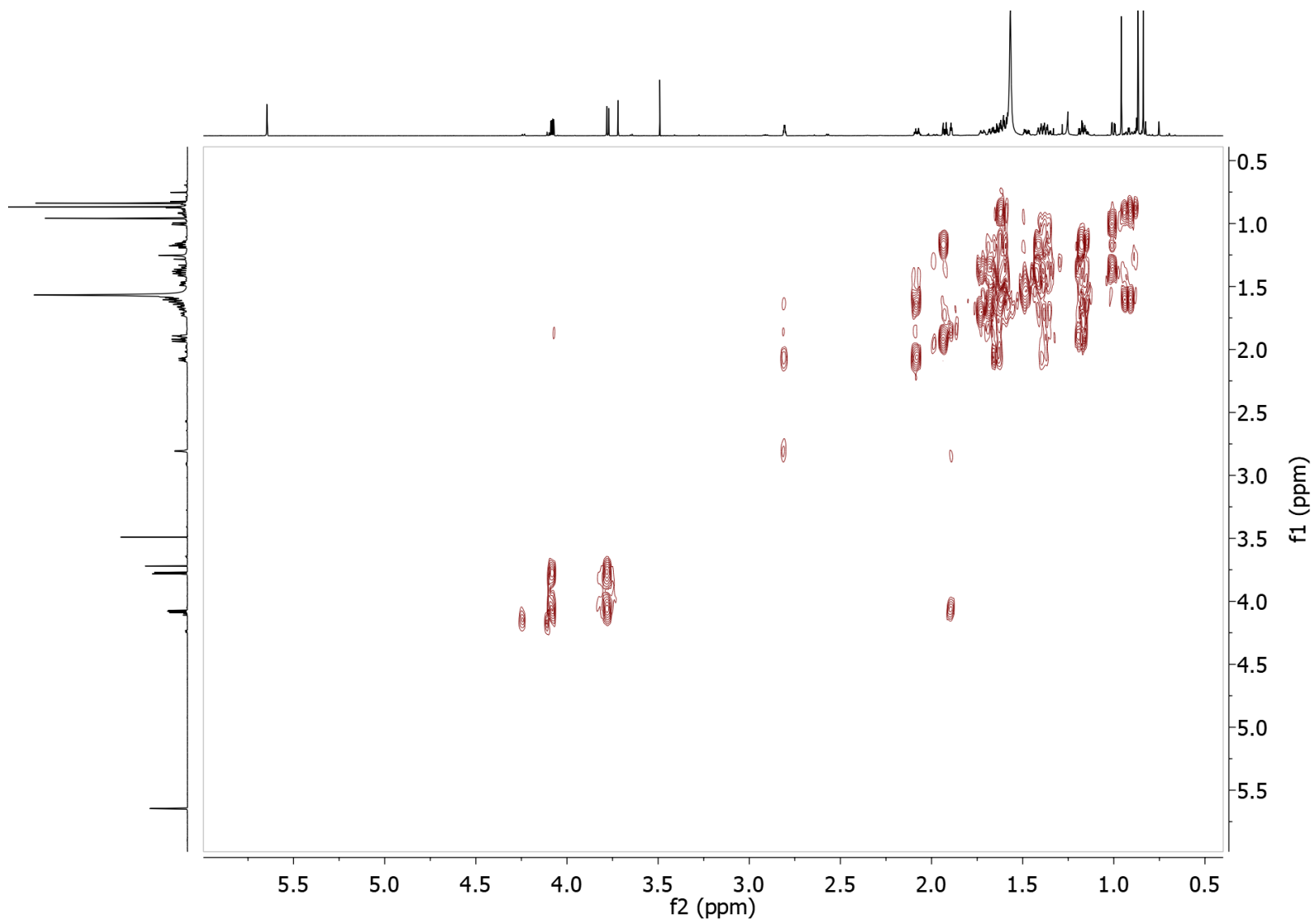


Figure S5. COSY spectrum of aplyroseol-20 (**2**) in CDCl₃.

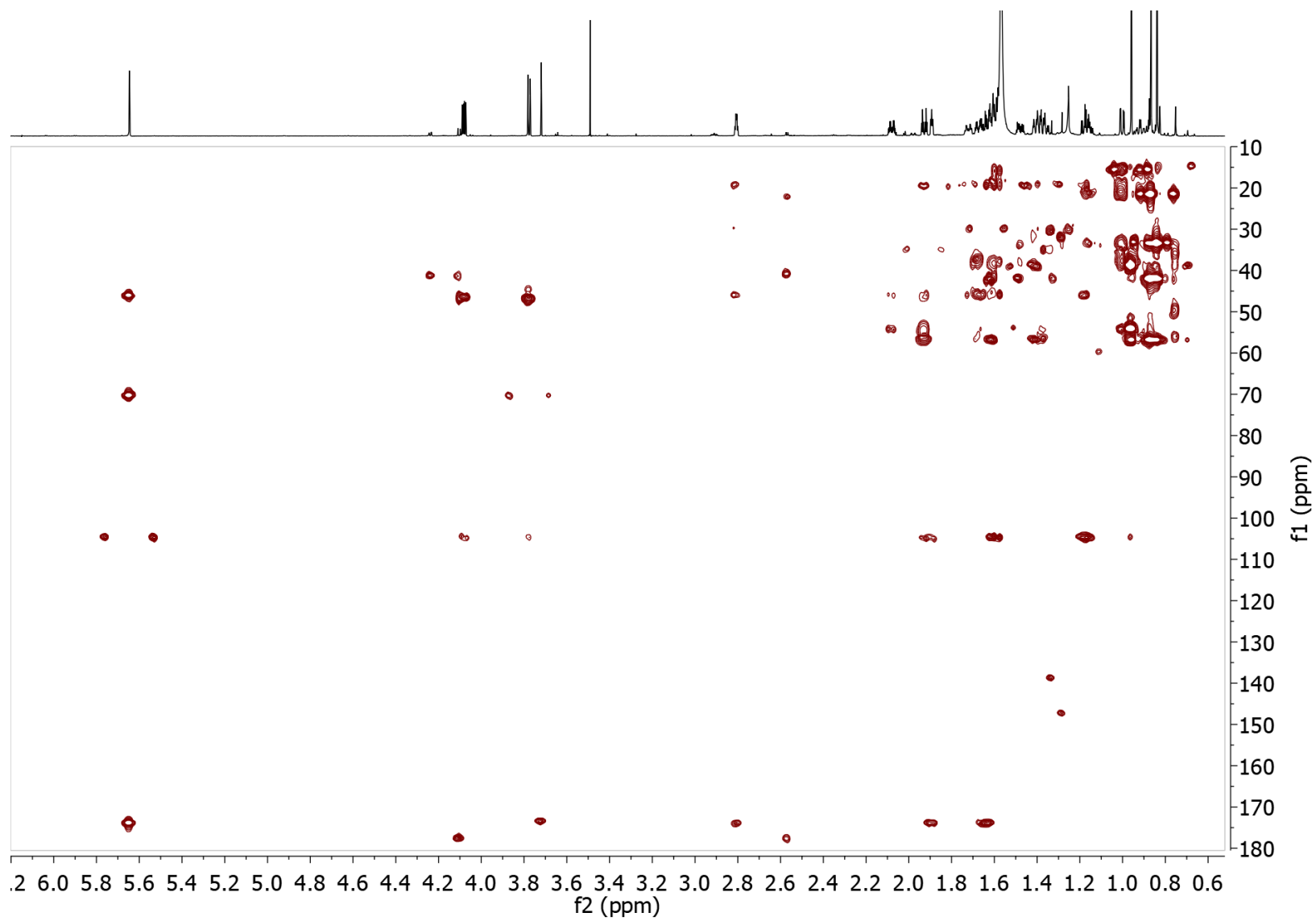


Figure S6. HMBC spectrum of alyroseol-20 (**2**) in CDCl₃.

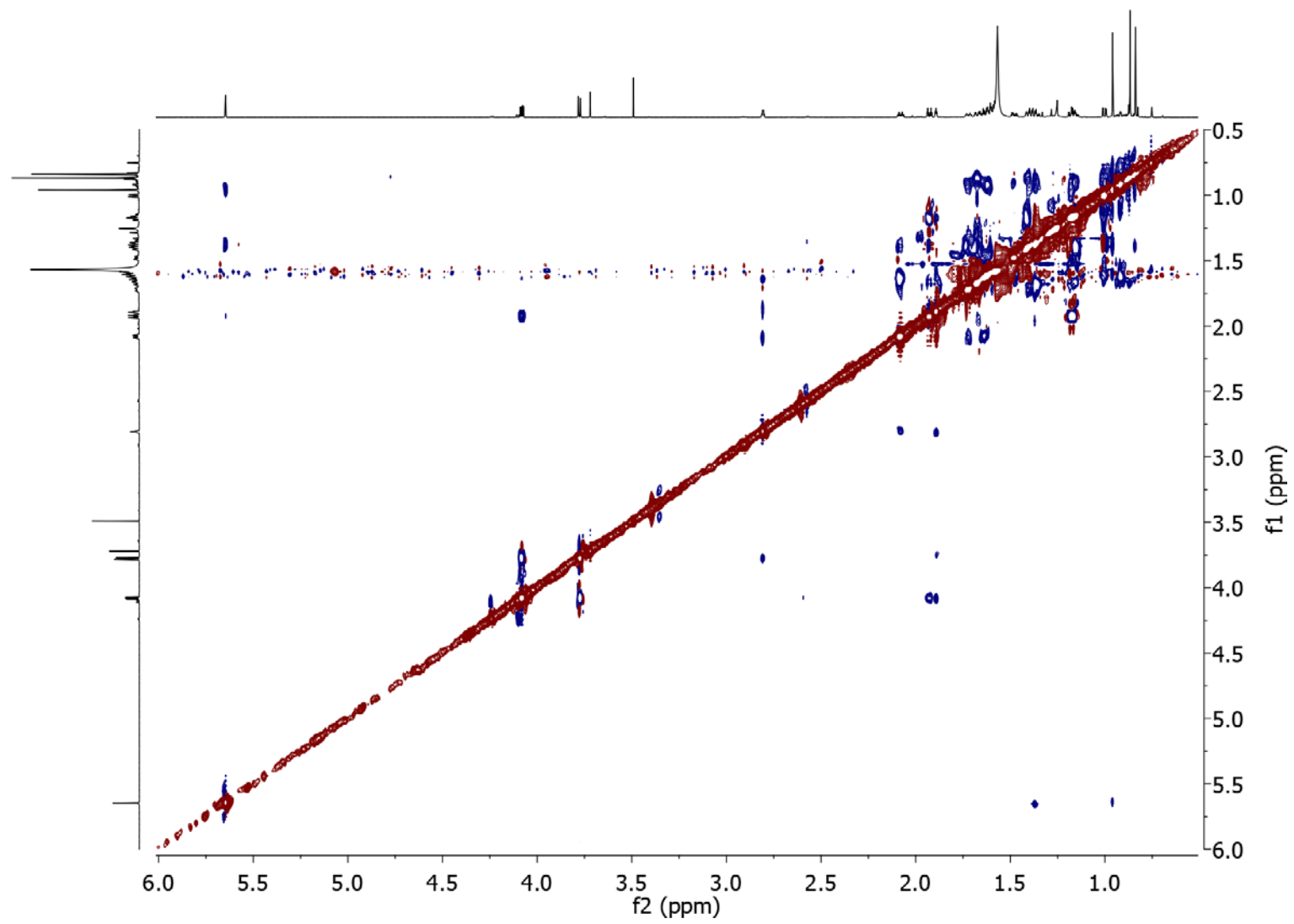


Figure S7. NOESY spectrum of alyroseol-20 (2) in CDCl₃.

Table S2. Complete NMR data for aplyroseol-21 (**3**) acquired in CDCl₃ at 25°C.

Position	¹³ C (δ , ¹ J _{CH} in Hz) ^a	¹ H (δ , mult., J in Hz) ^a	COSY ^a	HMBC ^a	NOESY ^a
1 α	38.4	0.99 (td, 12.6, 4.1)	1 β , 2 α , 2 β	3, 5, 20	1 β
1 β		1.61 (m)	1 α	3, 5	1 α
2 α	18.2	1.47 (m)	1 α , 3 α , 3 β		
2 β		1.55 (m)	1 α , 3 α	1, 3, 10	20
3 α	43.1	1.27 (m)	2 α , 2 β , 3 β	2, 18	18
3 β		1.41 (dtd, 13.6, 3.4, 1.4)	2 α , 3 α	1, 5, 18	
4	32.6				
5	50.7 (130) ^b	1.77 (d, 12.1)	6	1, 3, 4, 6, 7, 9, 18, 19, 20	1 α , 6, 19
6	70.1	5.26 (dd, 12.1, 2.4)	5, 7	5, 7, 1'	5, 17a, 19, 20
7	73.9	5.15 (d, 2.4)	6	5, 6, 8, 9, 14, 1''	14, 17a
8	46.6				
9	44.1	1.67 (dd, 12.2, 6.1)	11 β	1, 5, 7, 8, 17, 20	13
10	36.7				
11 α	16.5 (127) ^b	1.73 (m)	11 β , 12 β	8, 10, 12	11 β
11 β		1.47 (m)	9, 11 α	9, 12	11 α , 17b
12 α	20.1	1.95 (m)	12 β , 13	11, 13, 14	12 β , 13
12 β		1.55 (m)	11 α , 12 α , 13	9, 11, 14	12 α , 17b
13	38.7	2.77 (ddd, 12.3, 6.5, 4.0)	12 β , 12 α	14, 16, 17	9, 12 α
14	45.5	2.82 (dd, 6.5, 1.6)		7, 8, 12, 13, 15, 17	7
15	175.3				
16	172.4				
16-OCH ₃	52.0	3.72 (s)		16	
17a	71.0	4.27 (d, 10.1)	17b	7, 9, 14, 15	6, 7, 17b
17b		4.36 (d, 10.1)	17a	7, 9	11 β , 12 β , 17a, 20
18	36.0 (125) ^b	1.01 (s)		3, 4, 5, 18	3 α , 5
19	21.7 (128) ^b	0.85 (s)		3, 4, 5, 19	6
20	15.4 (125) ^b	0.89 (s)		1, 5, 9	2 β , 6, 17b
1'	169.9				
2'	20.9 (131) ^b	2.00 (s)		1'	
1''	169.7				
2''	21.3 (129) ^b	2.19 (s)		1''	

^aSpectra recorded in CDCl₃ (¹H, 800 MHz; ¹³C, 200 MHz) ^b¹H (δ , mult., J in Hz)^b¹J_{CH} values measured in HMBC spectrum

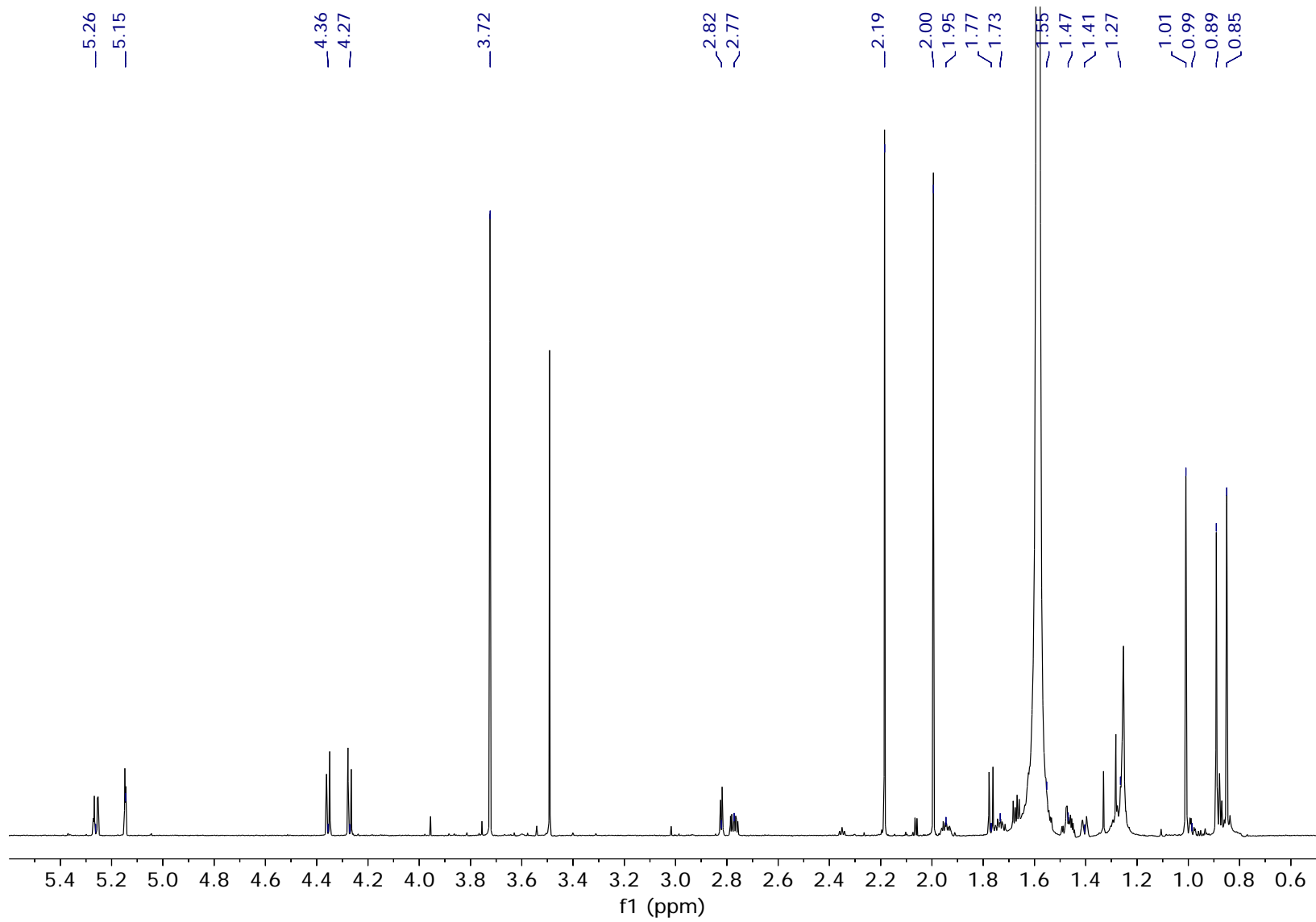


Figure S8. ¹H NMR (800 MHz) spectrum of aplyroseol-21 (**3**) in CDCl₃.

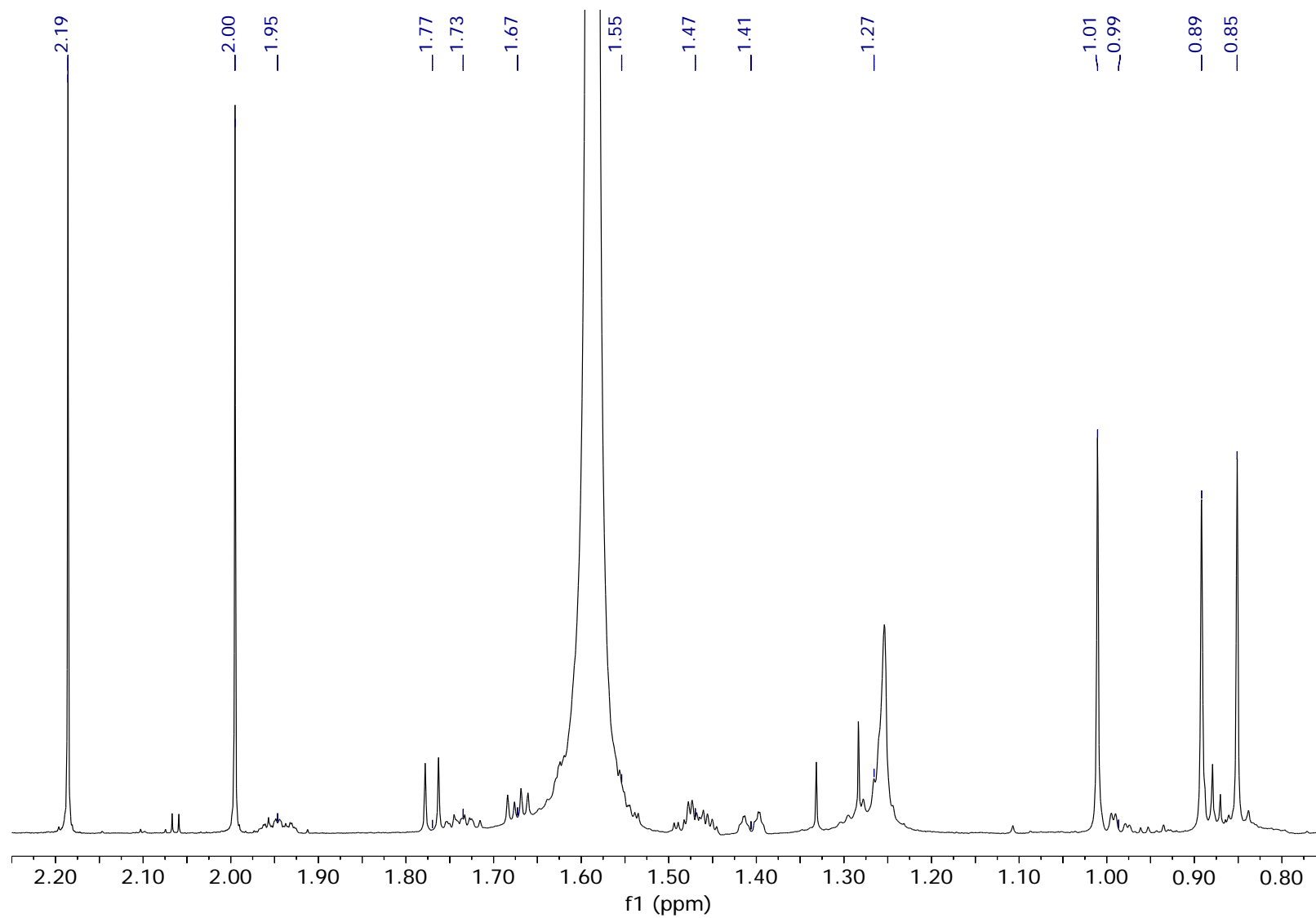


Figure S9. Expansion of the ^1H NMR (800 MHz) spectrum of aplyroseol-21 (**3**) in CDCl_3 .

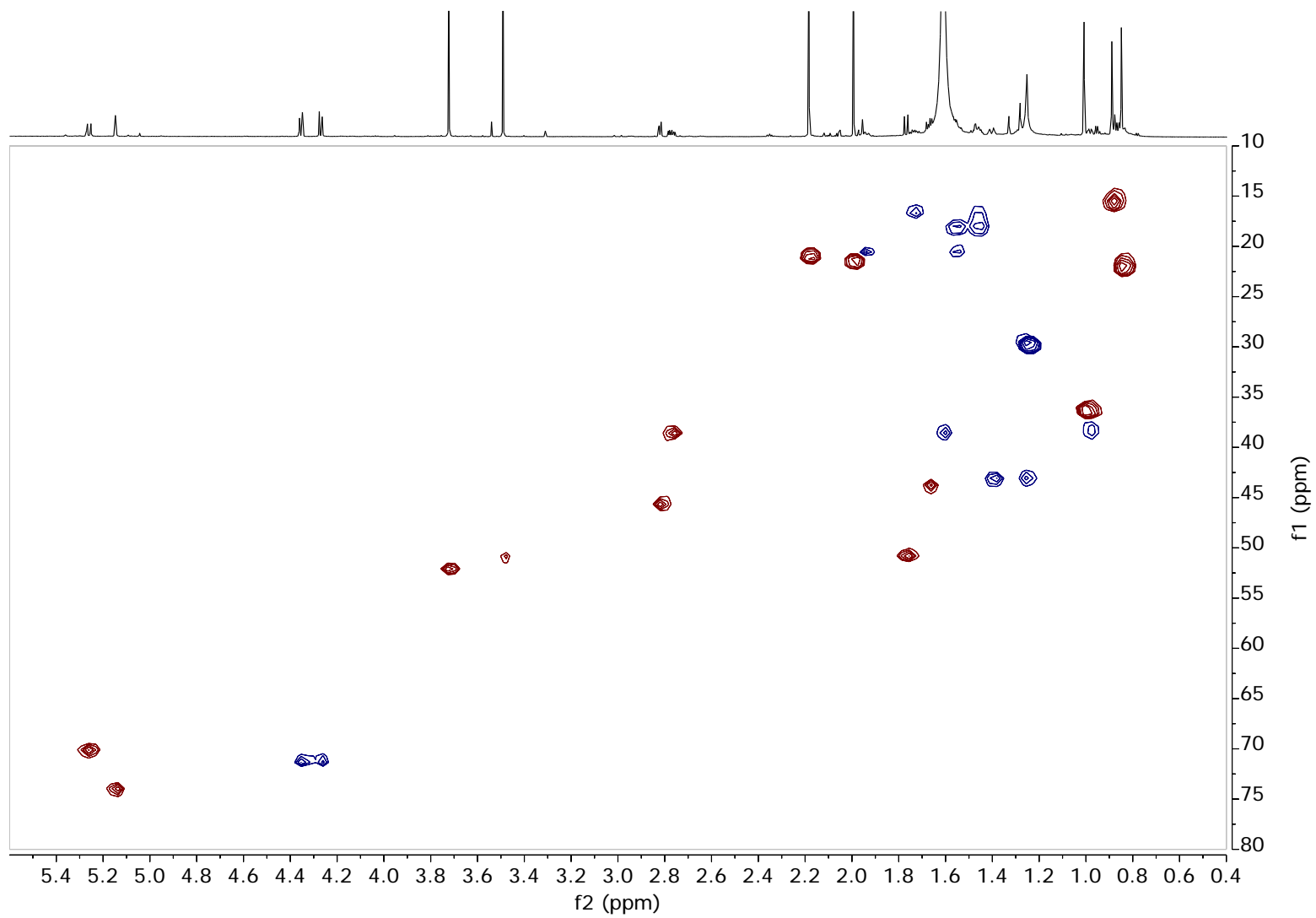


Figure S10. HSQC spectrum of alyroseol-21 (**3**) in CDCl₃.

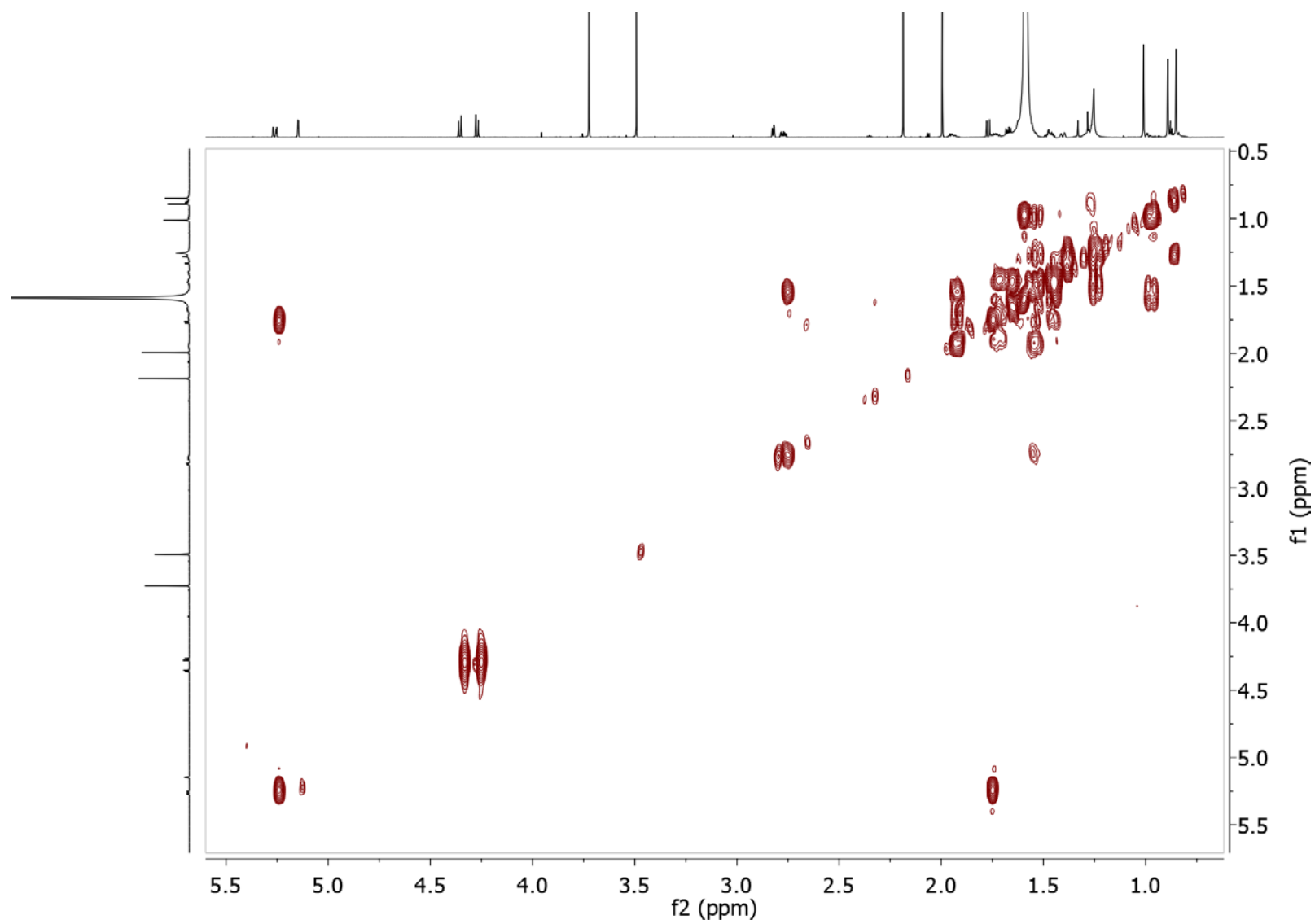


Figure S11. COSY spectrum of aplyroseol-21 (**3**) in CDCl₃.

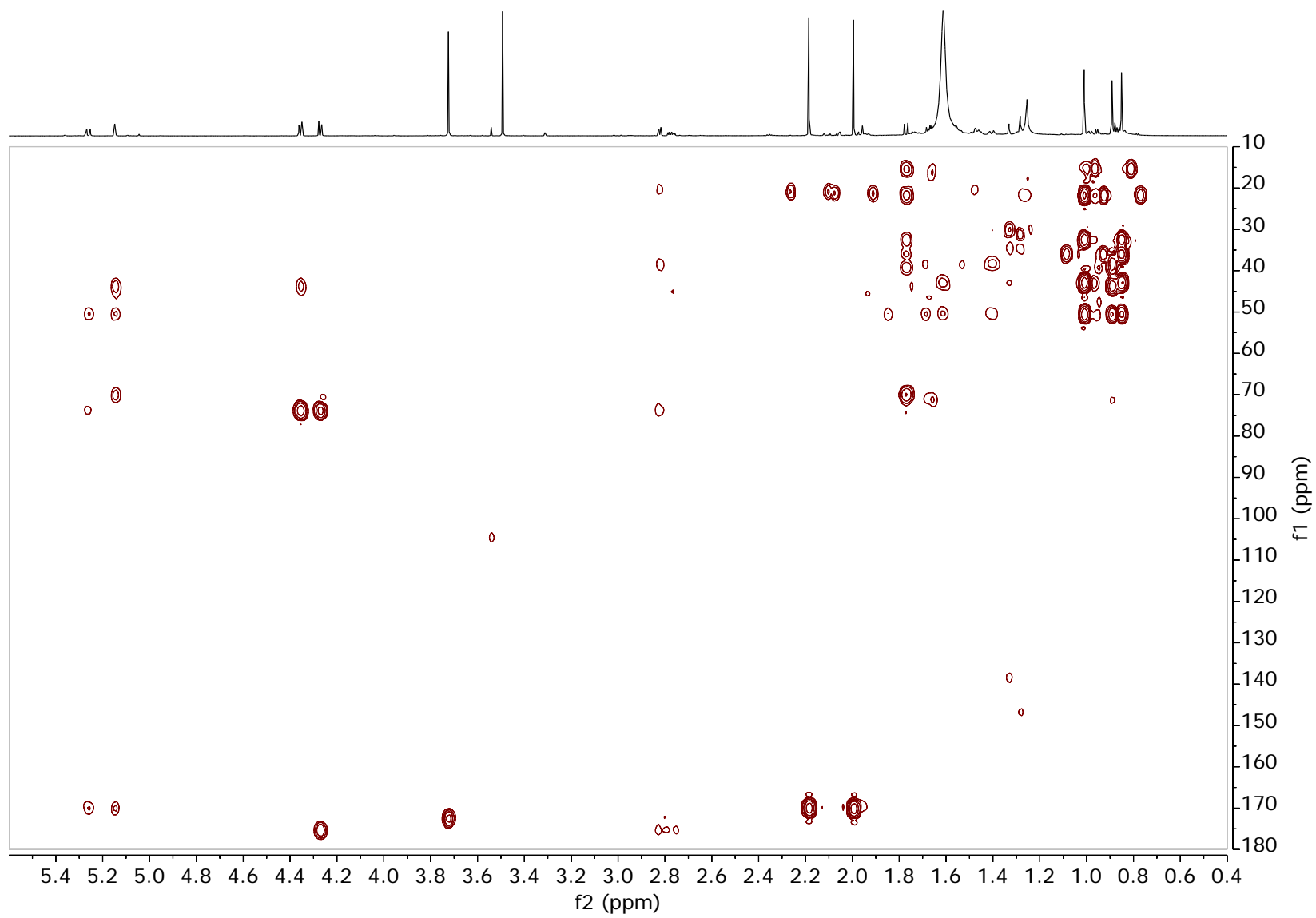


Figure S12. HMBC spectrum of alyroseol-21 (**3**) in CDCl₃.

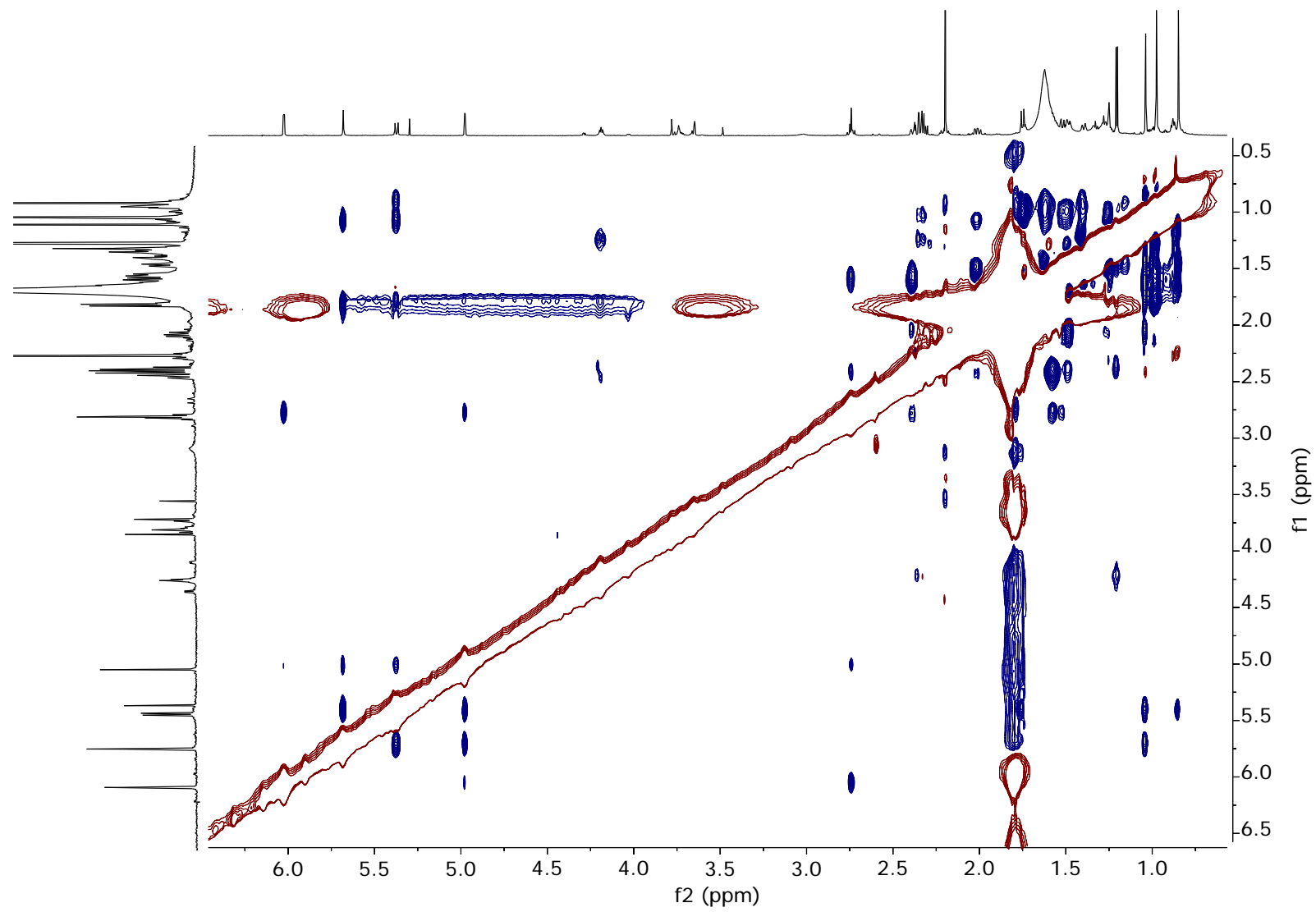


Figure S13. NOESY spectrum of alyrosciol-21 (**3**) in CDCl₃.

Table S3. Complete NMR data for aplyroseols-22 (**4**) acquired in CDCl₃ at 25°C.

Position	¹³ C (δ , ¹ J _{CH} in Hz) ^a	¹ H (δ , mult., J in Hz) ^a	COSY ^a	HMBC ^a	NOESY ^a
1 α	39.1	0.98 (m)	1 β , 2 α , 2 β	3, 20	1 β , 9
1 β		1.74 (dtd, 12.7, 4.1, 0.8)	1 α , 2 β	2, 4, 5, 10, 20	1 α , 20
2 α	18.4	1.48 (m)	1 α	1, 3, 10	
2 β		1.61 (m)	1 α , 1 β , 3a		20
3 α	43.2	1.25 (td, 13.7, 4.4)	2 β	18	18
3 β		1.40 (dtd, 13.7, 3.7, 1.2)		1, 5, 18	18, 19
4	33.1				
5	51.0 (127) ^b	1.75 (d, 12.2)	6	1, 7, 10, 18	6
6	71.6	5.37 (dd, 12.2, 2.5)	5, 7	5, 7, 8, 1'	5, 7, 17, 19, 20
7	73.4 (150) ^b	4.98 (d, 2.5)	6	5, 9, 17, 1''	6, 14, 15, 17
8	49.4				
9	49.1	1.52 (dd, 12.7, 2.9)	11 β	5, 8, 11, 12, 17	1 α , 14
10	39.1				
11 α	16.2	1.48 (m)	11 β	12	11 β , 12 β
11 β		2.02 (dddd, 13.0, 12.7, 12.7, 4.1)	9, 11 α , 12 α , 12 β	9	11 α , 12 β , 20
12 α	23.4	1.58 (m)	11 β , 12 β , 13	11, 13	12 β , 13, 14
12 β		2.39 (m)	11 β , 12 α	9, 11, 13, 14, 16	11 α , 11 β , 12 α , 13
13	37.6 (129) ^b	2.74 (m)	12 α	8, 11, 12, 14, 16, 17	12 α , 12 β , 15
14	42.7	2.74 (m)	15	7, 9, 13, 15, 16, 17	7, 9, 12 α , 15
15	103.4 (189) ^b	6.02 (d, 5.2)	14	14, 16, 17	7, 13, 14
16	177.1				
17	103.0 (172) ^b	5.68 (s)		7, 9, 14, 15	6, 7, 15, 20
17-OH		3.73 (bs)			
18	36.2 (122) ^b	0.98 (s)		3, 4, 5, 18	3 α
19	21.8 (124) ^b	0.85 (s)		3, 4, 5, 19	2 β , 3 β , 6,
20	16.3 (123) ^b	1.04 (s)		5, 9	1 β , 2 β , 6, 11 β , 17
1'	171.9				
2a'	43.7	2.32 (dd, 16.5, 9.1)	3'	1', 3', 4'	18, 4'
2b'		2.36 (dd, 16.5, 3.1)	3'	1', 4'	3', 4'
3'	63.9	4.19 (dqd, 9.3, 6.3, 3.1)	2a', 2b', 4'		2a', 2b', 4'
3'-OH		3.02 (bs)			
4'	22.5 (124) ^b	1.21 (d, 6.3)	3'	2' 3'	2a', 2b', 3'
1''	171.3''				
2''	21.2 (130) ^b	2.20 (s)		1''	

^a Spectra recorded in CDCl₃ (¹H, 800 MHz; ¹³C, 200 MHz) ^b ¹H (δ , mult., J in Hz)^b ¹J_{CH} values measured in HMBC spectrum

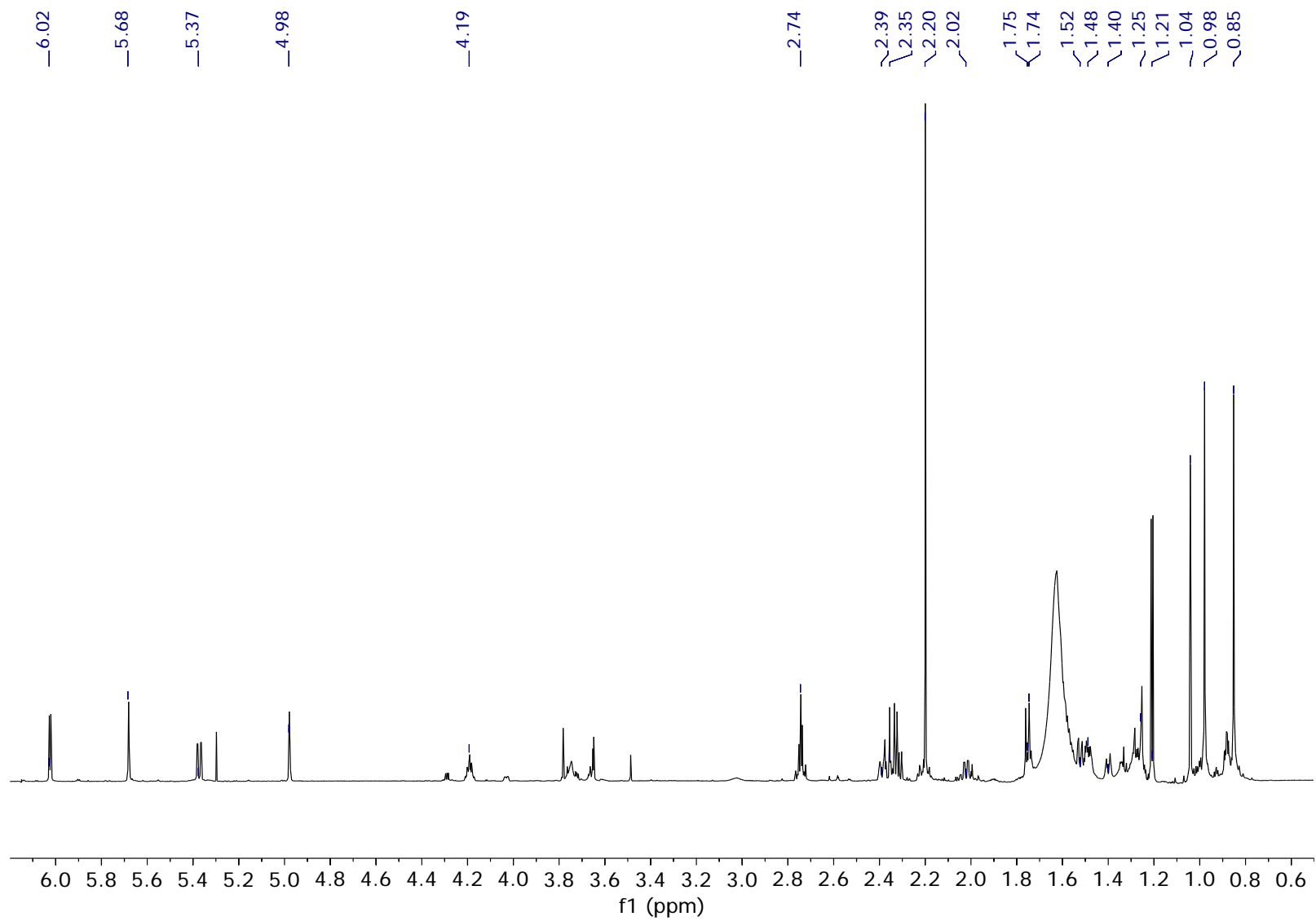


Figure S14. ¹H NMR (800 MHz) spectrum of aplyroseol-22 (**4**) in CDCl₃.

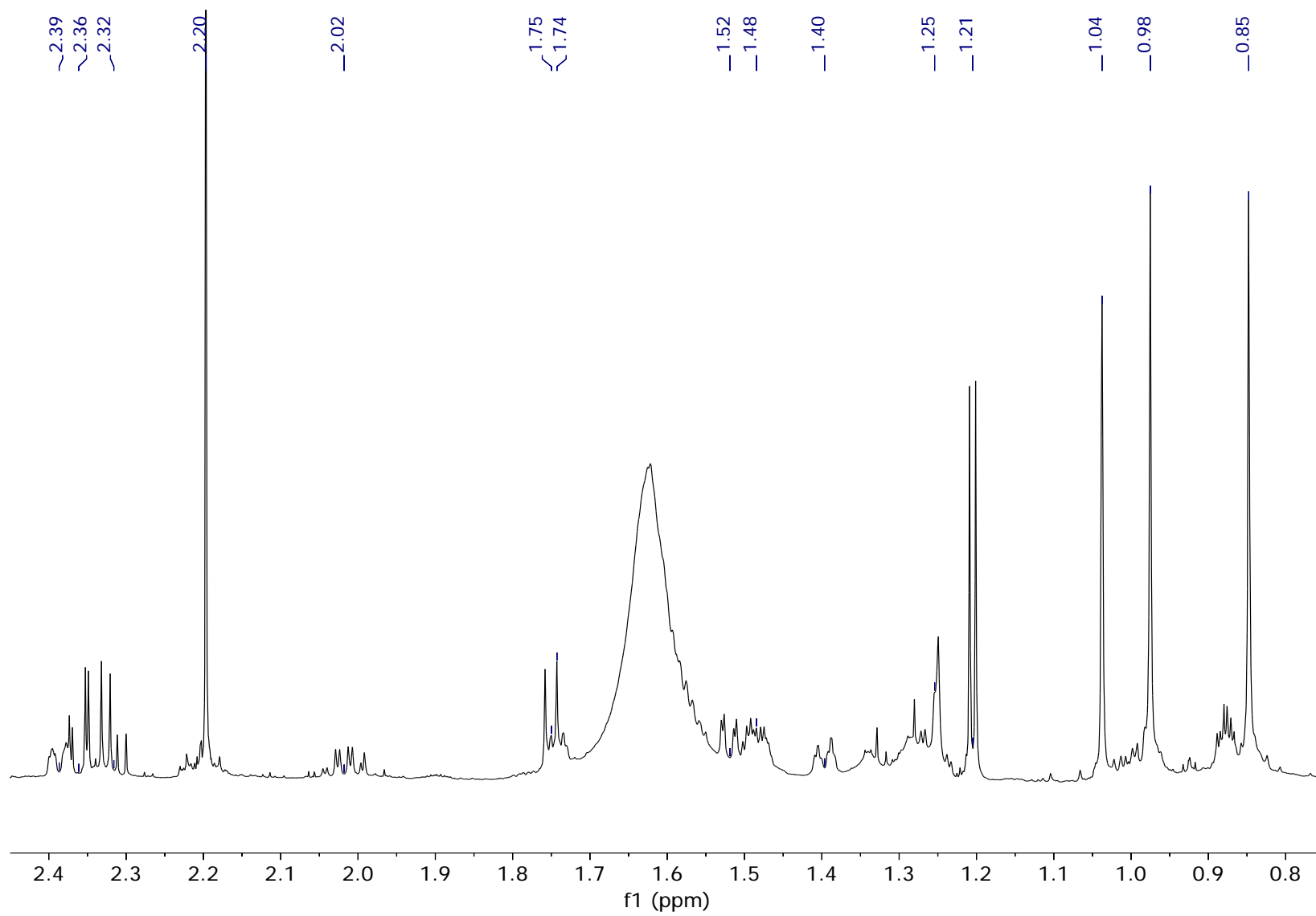


Figure S15. Expansion of the ^1H NMR (800 MHz) spectrum of aplyroseol-22 (**4**) in CDCl_3 .

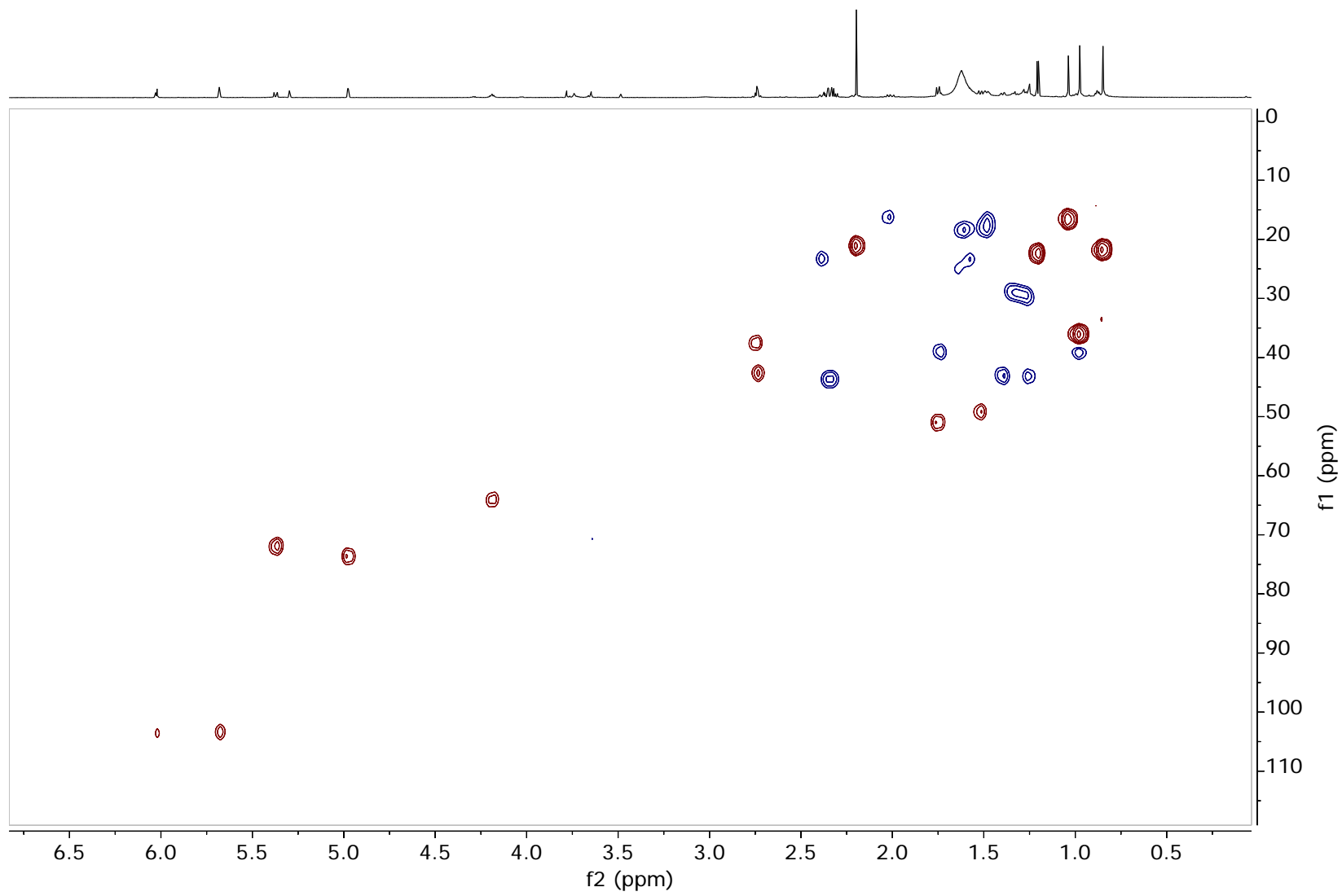


Figure S16. HSQC spectrum of aplyroseol-22 (**4**) in CDCl₃.

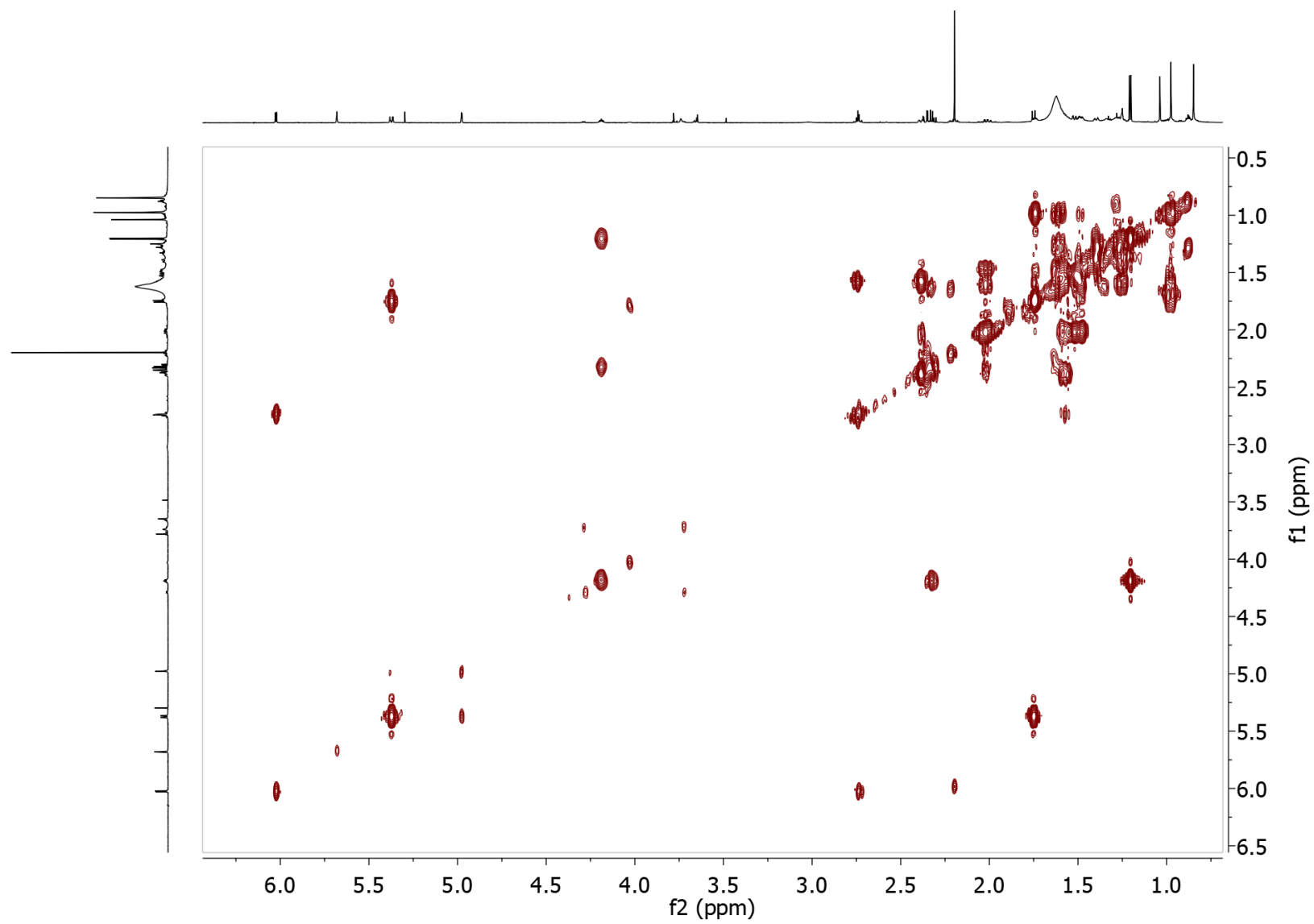


Figure S17. COSY spectrum of aplyroseol-22 (**4**) in CDCl₃.

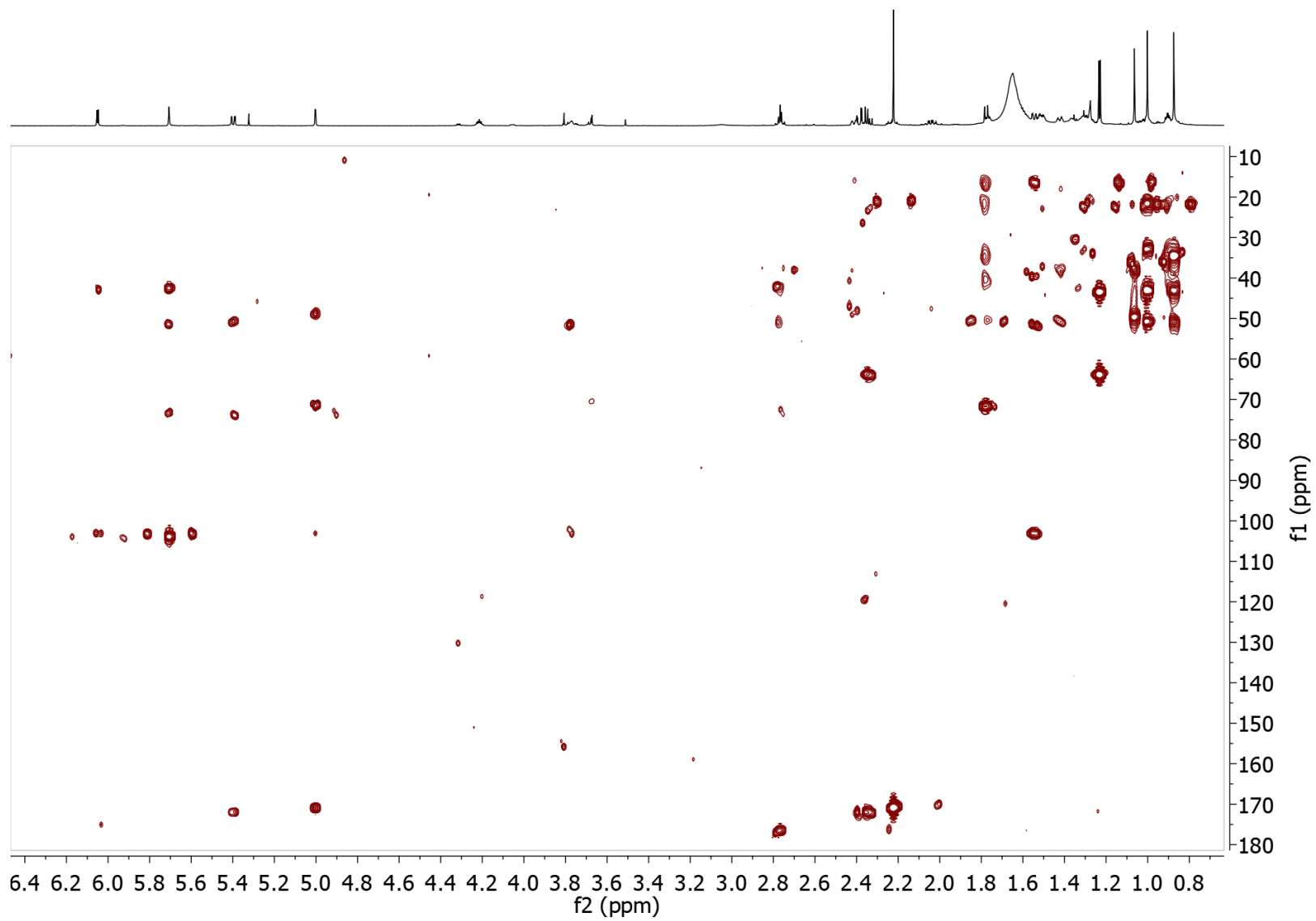


Figure S18. HMBC spectrum of alyroseol-22 (**4**) in CDCl₃.

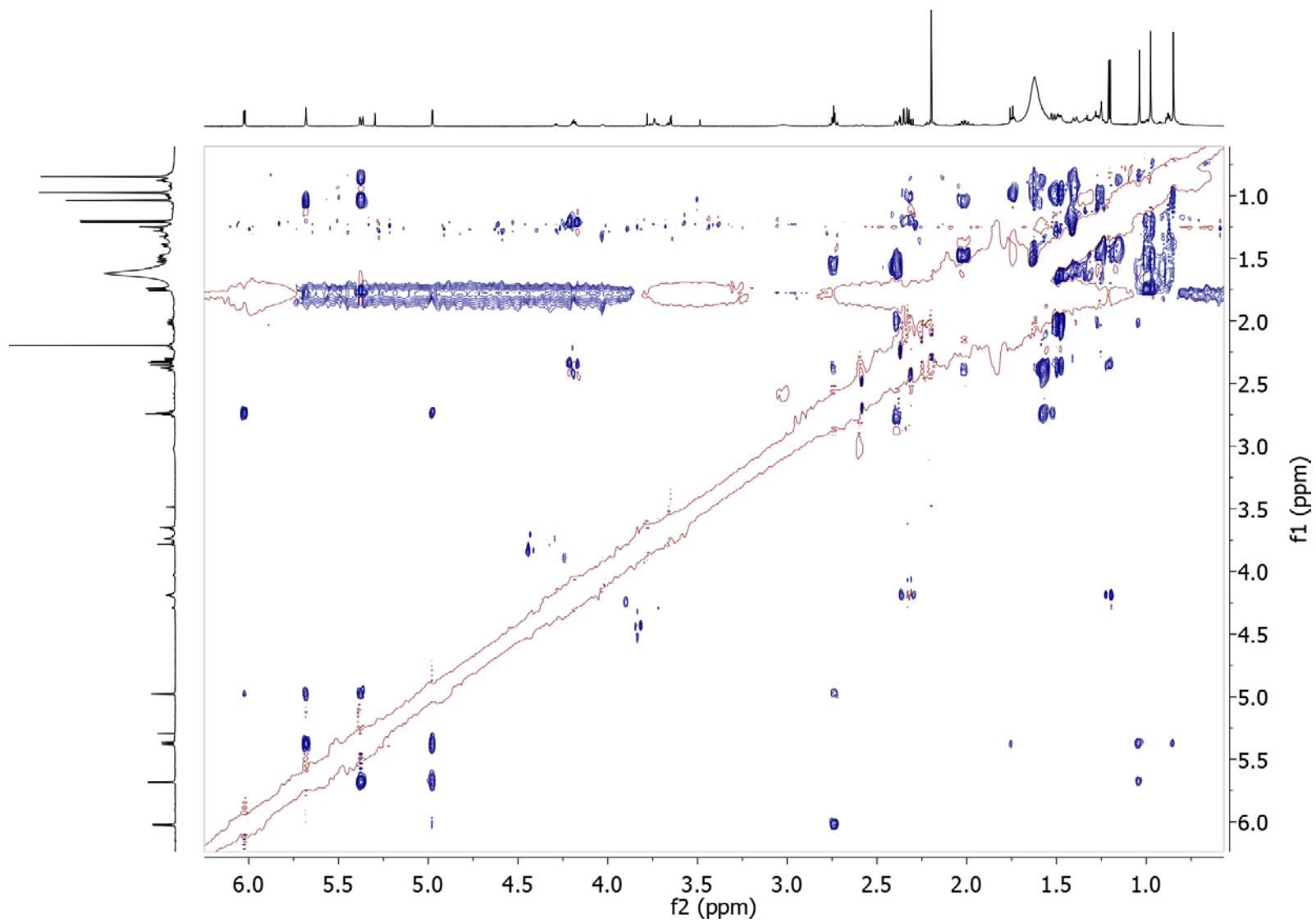


Figure S19. NOESY spectrum of aplyroseol-22 (**4**) in CDCl₃.