

Supplementary data content page

Title: **Triterpene Glycosides from the Far Eastern Sea Cucumber *Psolus chitonoides*: Chemical Structures and Cytotoxicities of Chitonoidosides E₁, F, G, and H.**

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Table S3. ^{13}C and ^1H NMR chemical shifts, HMBC and ROESY correlations of the aglycone part of chitonoidoside H (**4**)

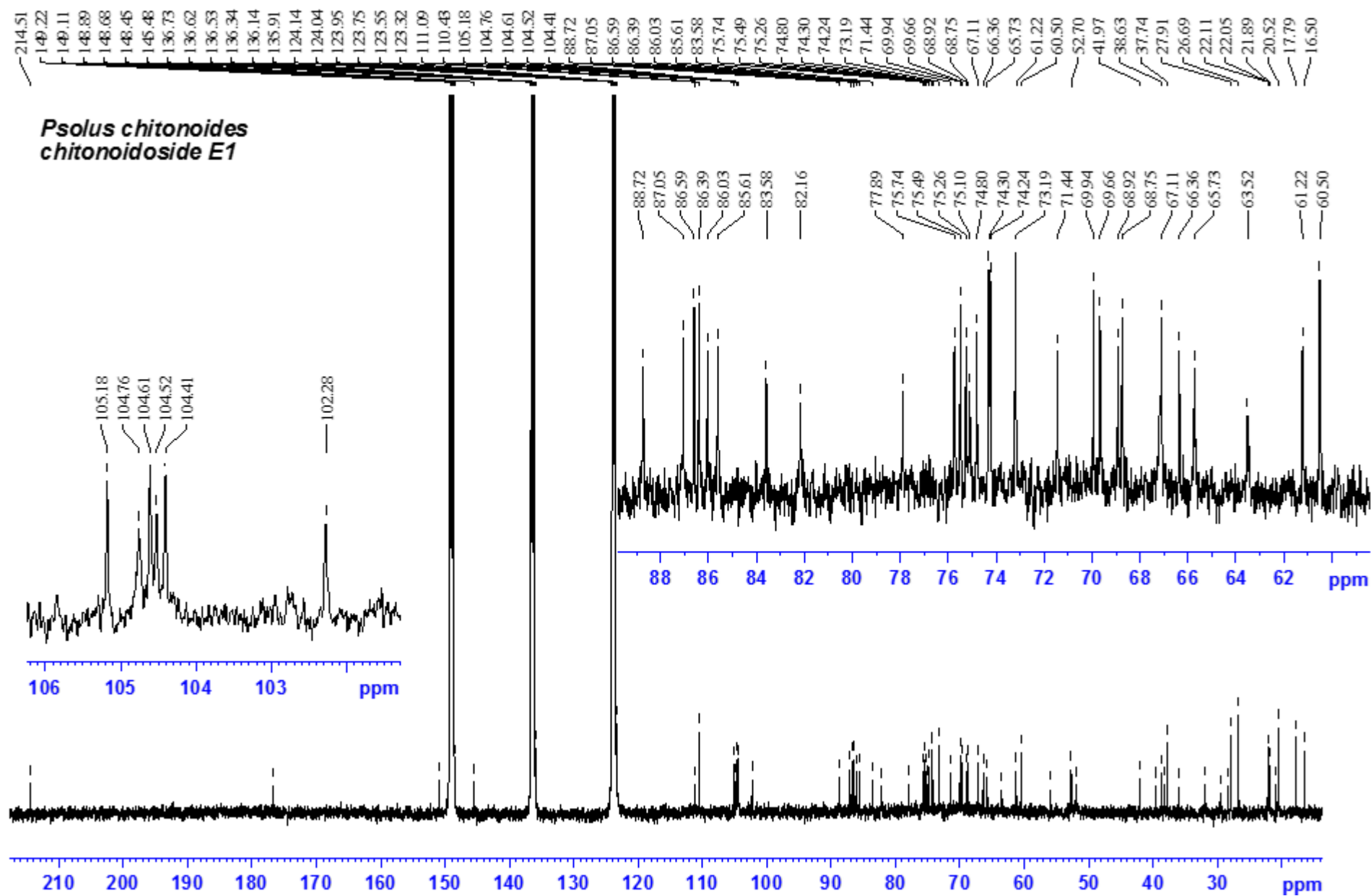


Figure S1. The ^{13}C NMR (125.67 MHz) spectrum of chitonoidoside E₁ (**1**) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1)

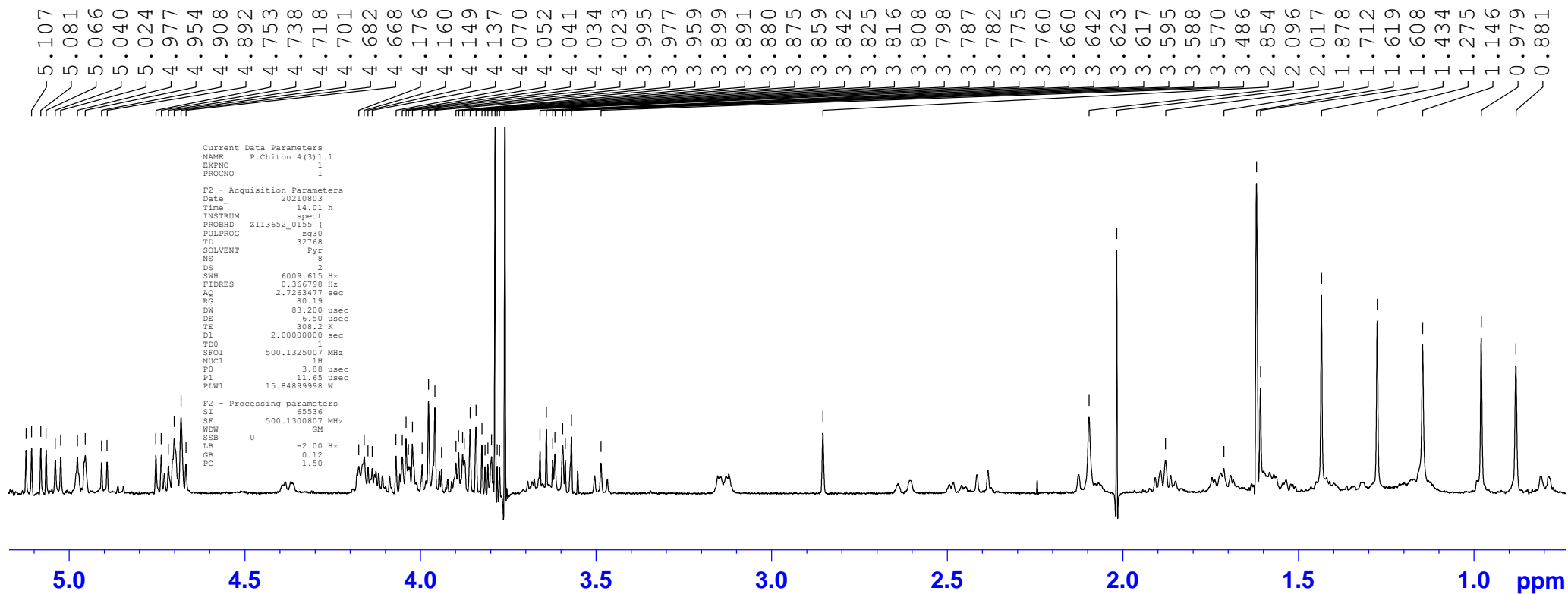


Figure S2. The ^1H NMR (500.12 MHz) spectrum of chitonoidoside E₁ (**1**) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1)

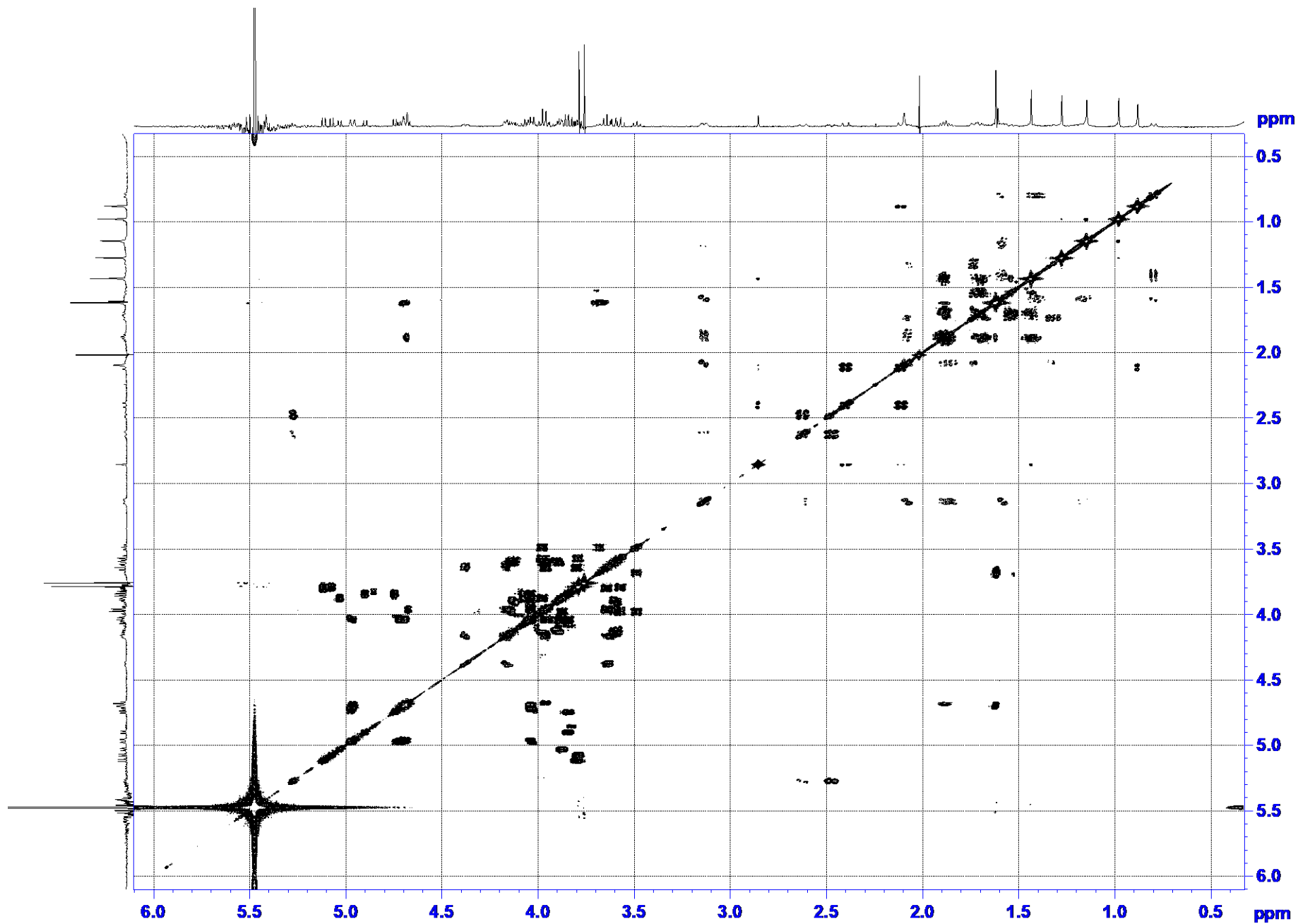


Figure S3. The COSY (500.12 MHz) spectrum of chitonoidoside E₁ (**1**) in C₅D₅N/D₂O (4/1)

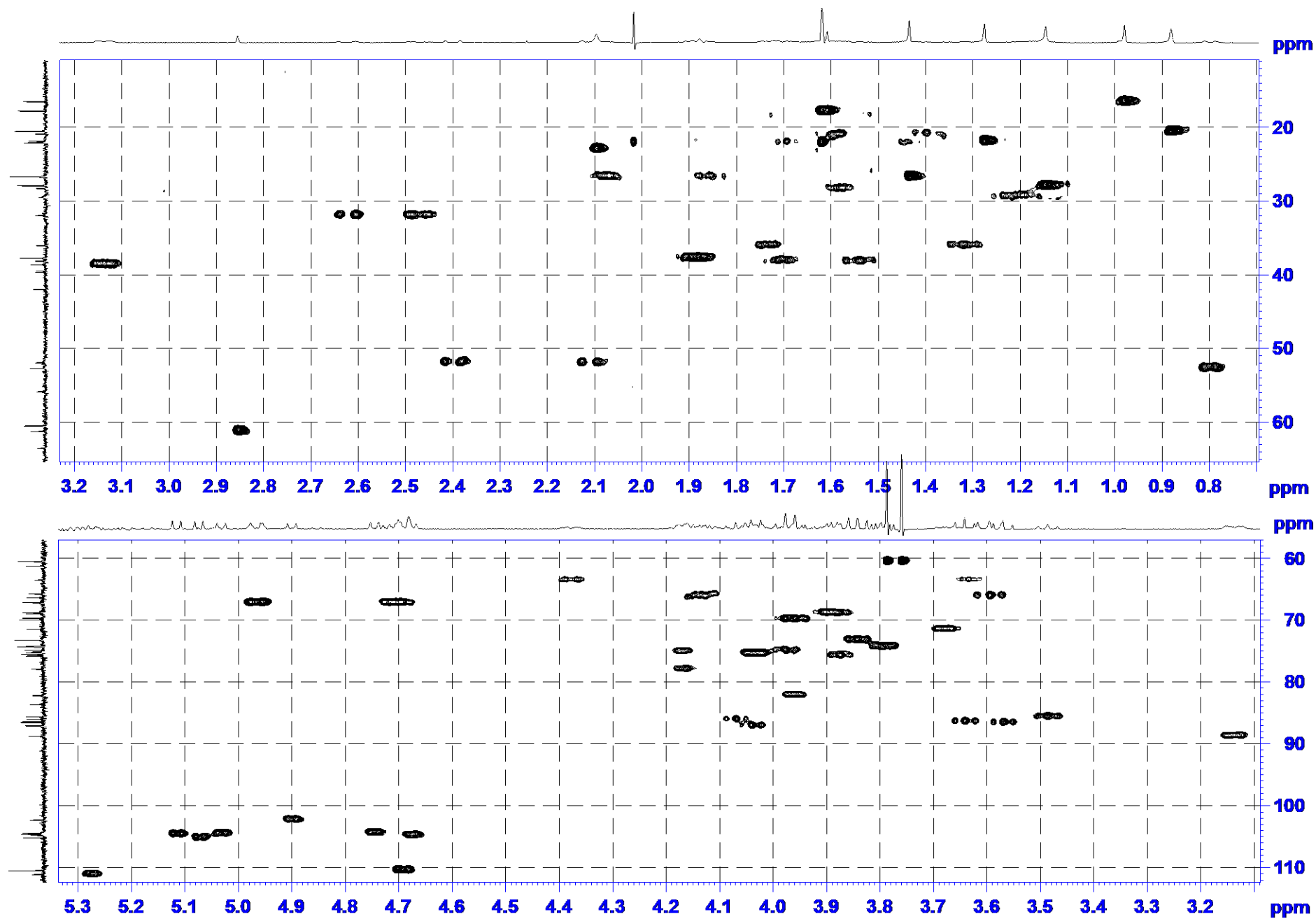


Figure S4. The HSQC (500.12 MHz) spectrum of chitonoidoside E₁ (1) in C₅D₅N/D₂O (4/1)

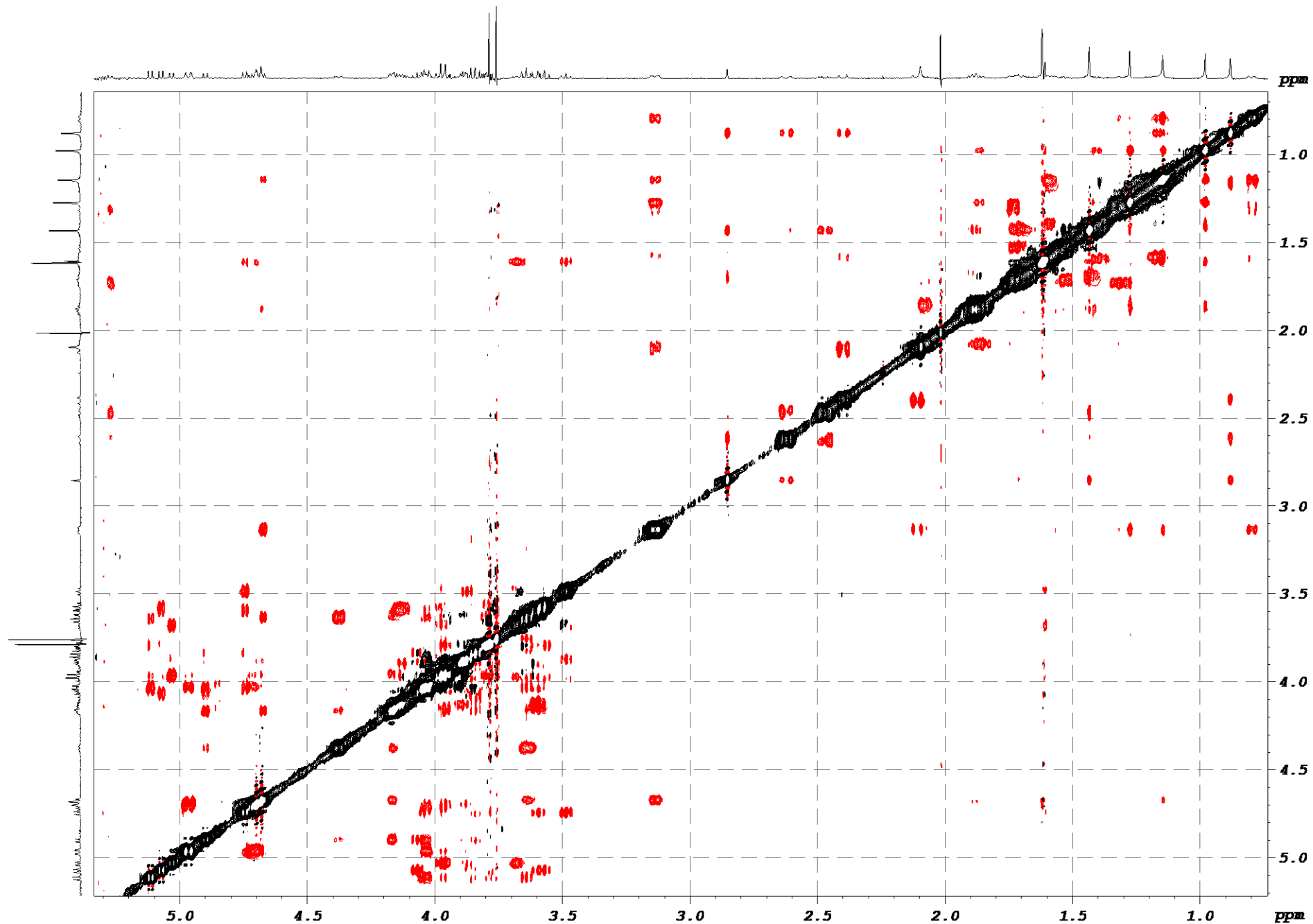


Figure S5. The ROESY (500.12 MHz) spectrum of chitonoidoside E₁ (**1**) in C₅D₅N/D₂O (4/1)

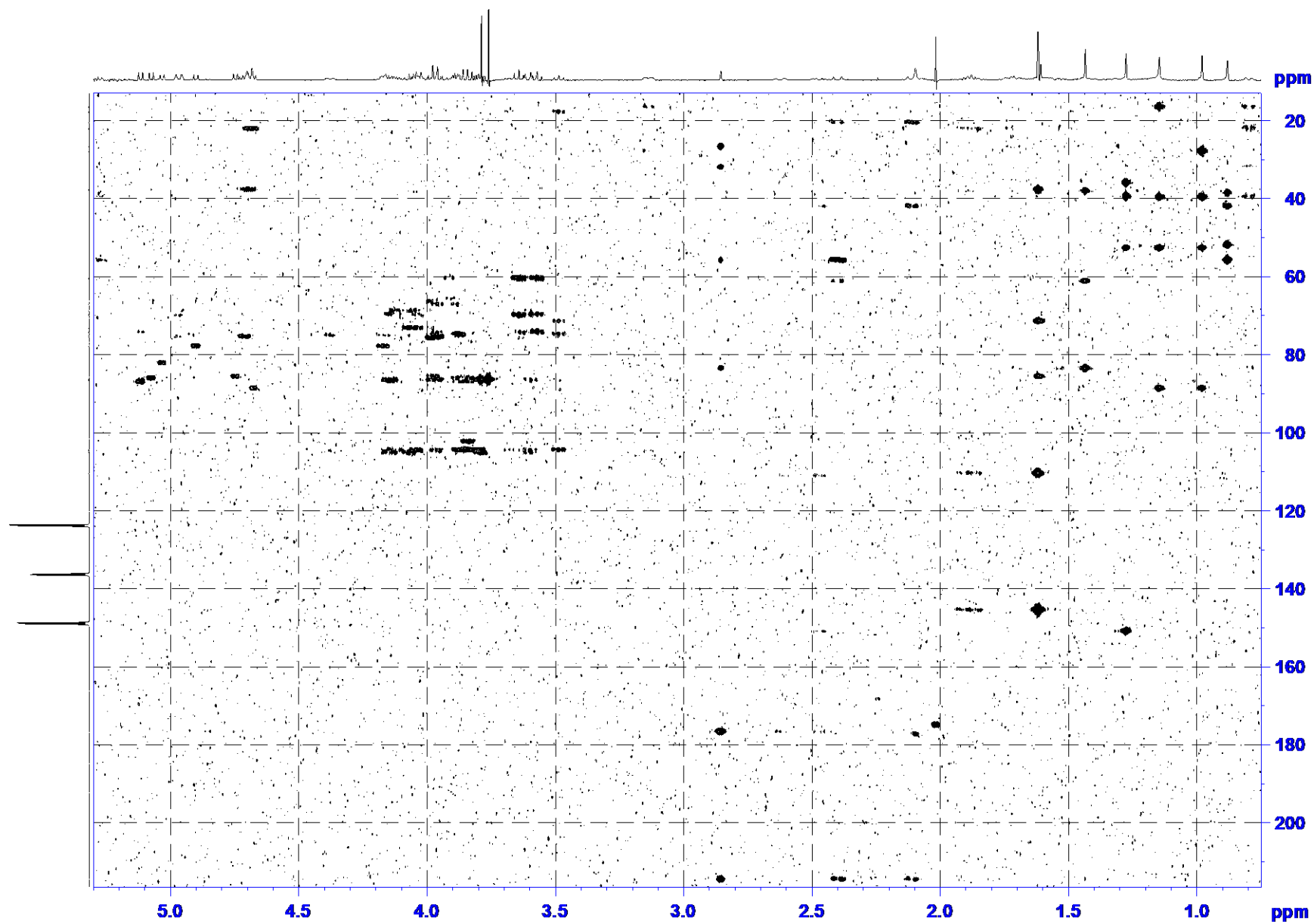


Figure S6. The HMBC (500.12 MHz) spectrum of chitonoidoside E₁ (**1**) in C₅D₅N/D₂O (4/1)

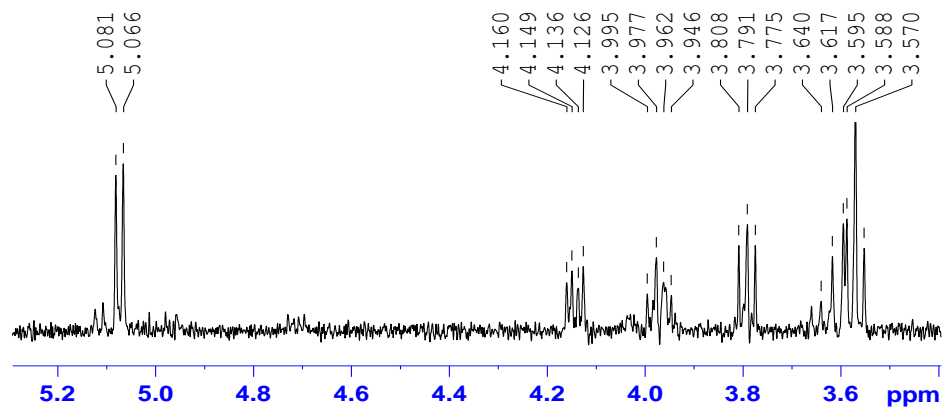
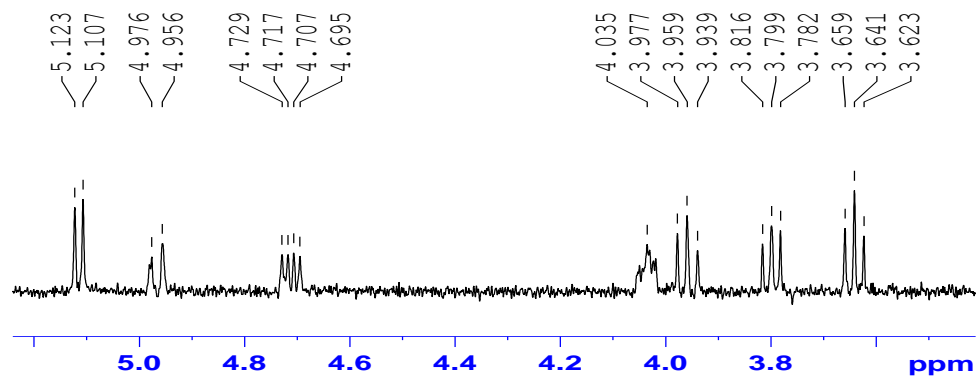
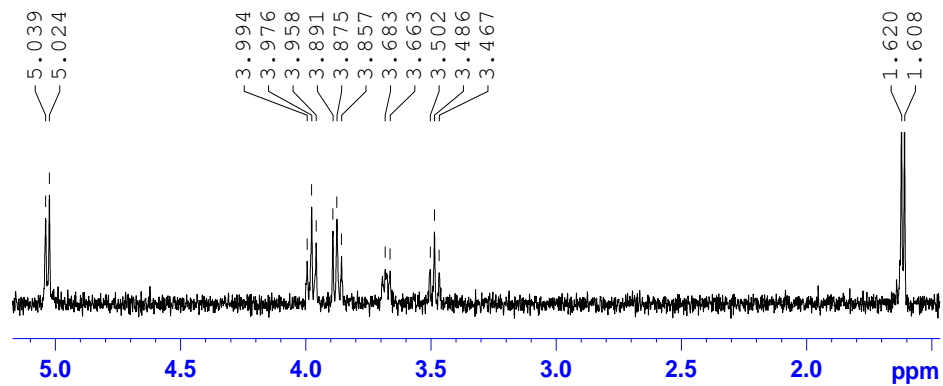
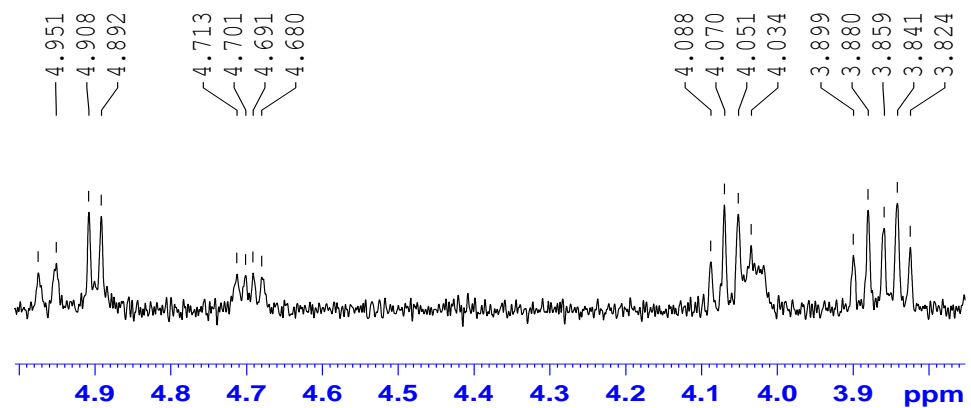
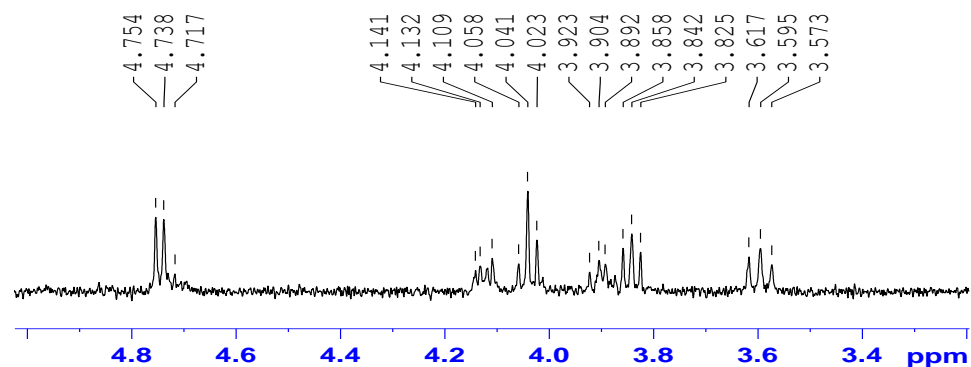
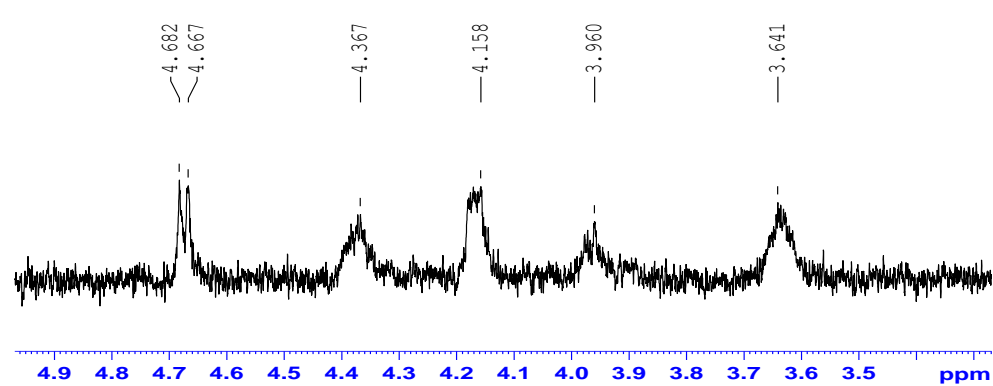


Figure S7. 1 D TOCSY (500.12 MHz) spectra of Xyl1, Qui2, Xyl3, MeGlc4, Glc5 and MeXyl6 of chitonoidoside E₁ (**1**) in C₅D₅N/D₂O (4/1)

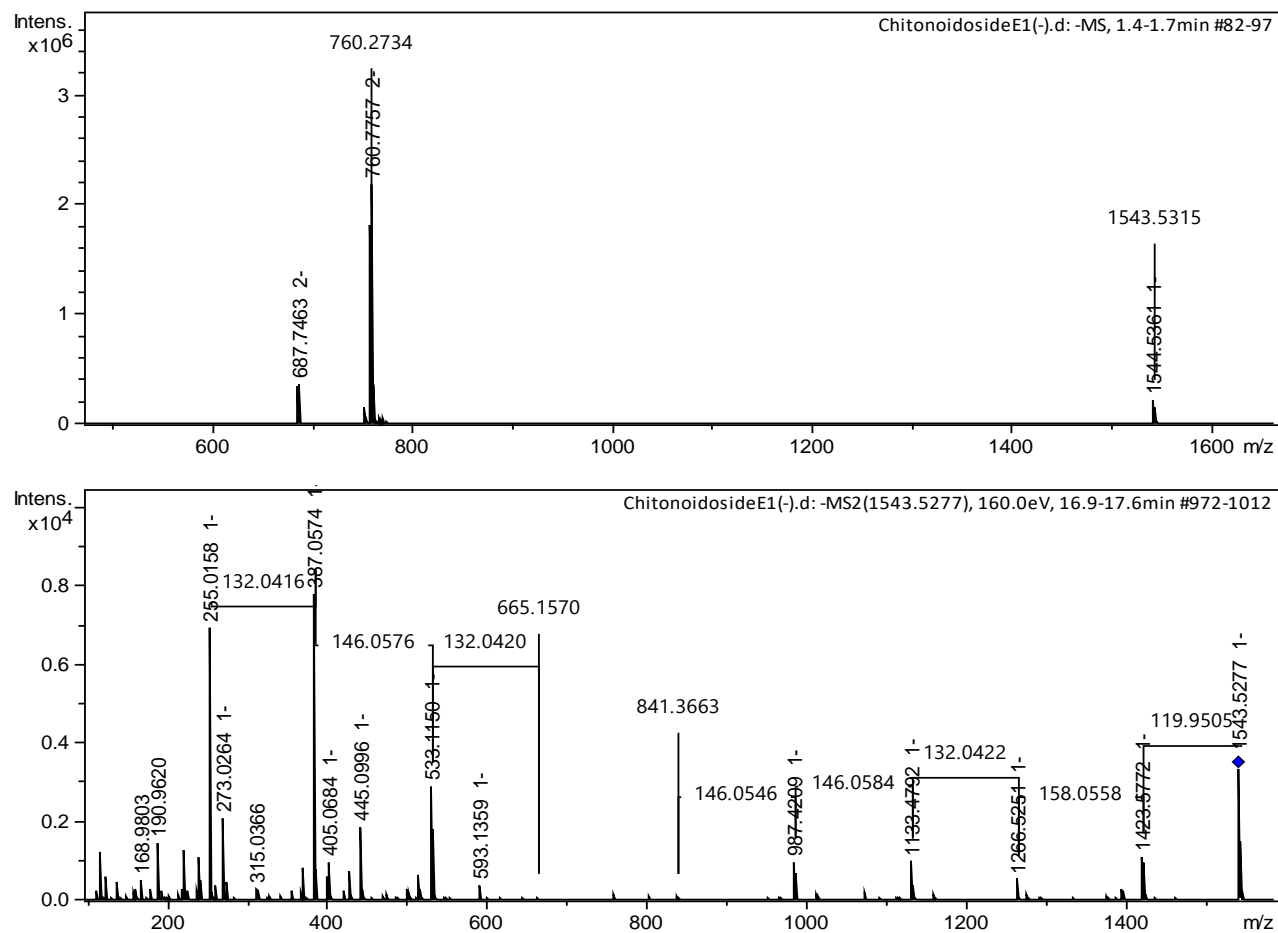


Figure S8. HR-ESI-MS (-) and ESI-MS/MS (-) spectra of chitonoidoside E₁ (**1**)

Table S1. ¹³C and ¹H NMR chemical shifts and HMBC and ROESY correlations of aglycone moiety of chitonoidoside E₁ (**1**).

Position	δ_C mult. ^a	δ_H mult. (J in Hz) ^b	HMBC	ROESY
1	36.0 CH ₂	1.73 m 1.32 m		H-11, H-19 H-3, H-5, H-11
2	27.0 CH ₂	2.08 m 1.86 m		H-19, H-30
3	88.7 CH	3.14 dd (4.1; 11.9)	C: 4, 30, 31, C:1 Xyl1	H-1, H-5, H-31, H1-Xyl1
4	39.5 C			
5	52.7 CH	0.79 brd (11.6)	C: 6, 10, 19, 30	H-1, H-3, H-31
6	20.9 CH ₂	1.59 m 1.40 m		H-31 H-19, H-30
7	28.3 CH ₂	1.58 m 1.12 m		H-32
8	38.6 CH	3.14 m		H-6, H-19
9	151.0 C			
10	39.6 C			
11	111.1 CH	5.28 m	C: 8, 10, 12, 13	H-1
12	32.0 CH ₂	2.62 d (16.6) 2.47 dd (5.0; 16.6)	C: 9, 11, 13, 18 C: 9, 11, 13, 14, 18	H-17, H-32
13	55.8 C			
14	42.0 C			
15	51.9 CH ₂	2.40 d (15.7) 2.11 d (15.7)	C: 13, 16, 17, 32 C: 8, 14, 16, 32	H-7, H-32
16	214.5 C			
17	61.2 CH	2.86 s	C: 12, 13, 16, 18, 20, 21	H-21, H-32
18	177.7 C			
19	21.9 CH ₃	1.28 s	C: 1, 5, 9, 10	H-1, H-2, H-8, H-30
20	83.6 C			
21	26.7 CH ₃	1.44 s	C: 17, 20, 22	H-12, H-17
22	38.1 CH ₂	1.70 m 1.54 m	C: 20, 21, 23 C: 17, 20, 21, 23	
23	22.0 CH ₂	1.71 m 1.45 m		
24	37.7 CH ₂	1.88 m	C: 22, 25, 26, 27	H-21
25	145.5 C			
26	110.4 CH ₂	4.70 brs 4.68 brs	C: 24, 27 C: 24, 27	
27	22.1 CH ₃	1.62 s	C: 24, 25, 26	
30	16.5 CH ₃	0.98 s	C: 3, 4, 5, 31	H-31
31	27.9 CH ₃	1.15 s	C: 3, 4, 5, 30	H-3, H-5, H-30
32	20.5 CH ₃	0.88 s	C: 8, 13, 14, 15	H-7, H-12, H-17

^a Recorded at 125.67 MHz in C₅D₅N. ^b Recorded at 500.12 MHz in C₅D₅N.

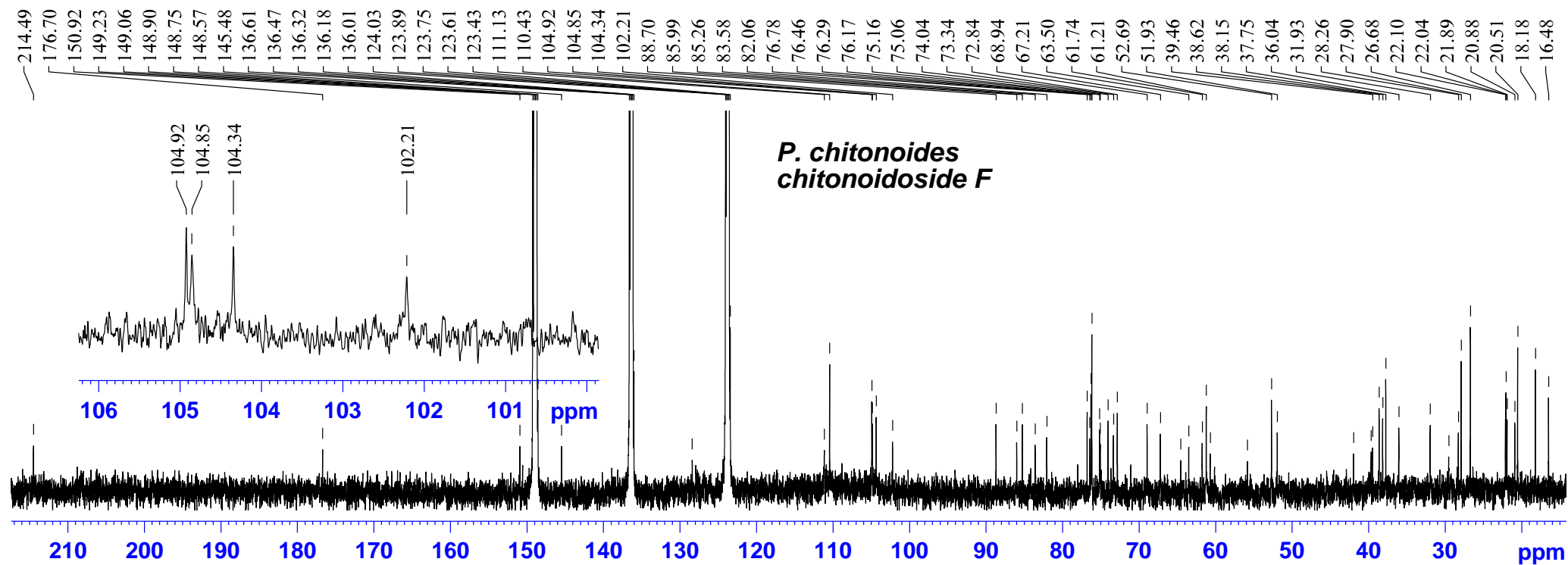


Figure S9. The ^{13}C NMR (125.67 MHz) spectrum of chitonoidoside F (2) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$
(4/1)

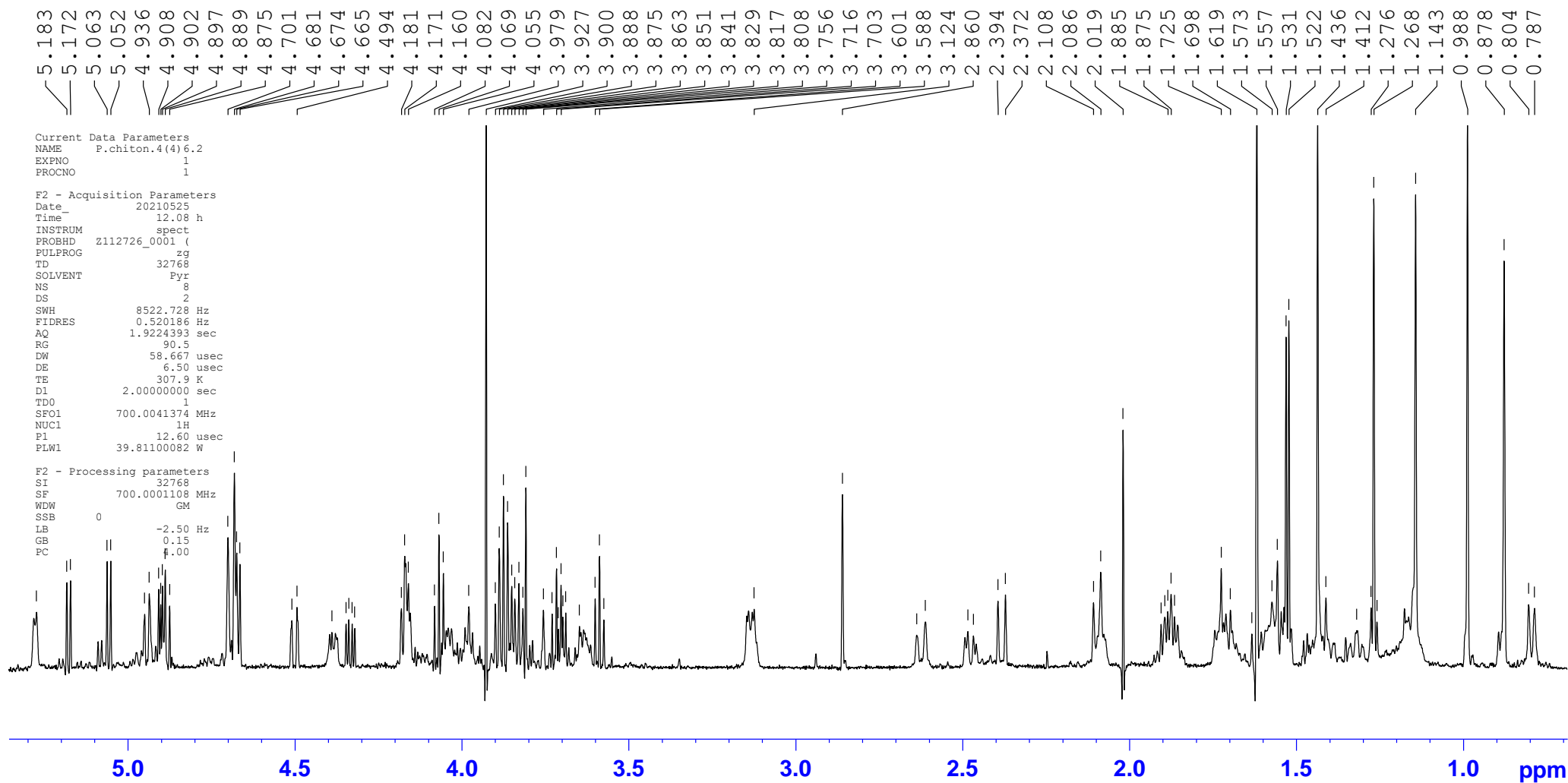


Figure S10. The ^1H NMR (500.12 MHz) spectrum of chitonoidoside F (**2**) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1).

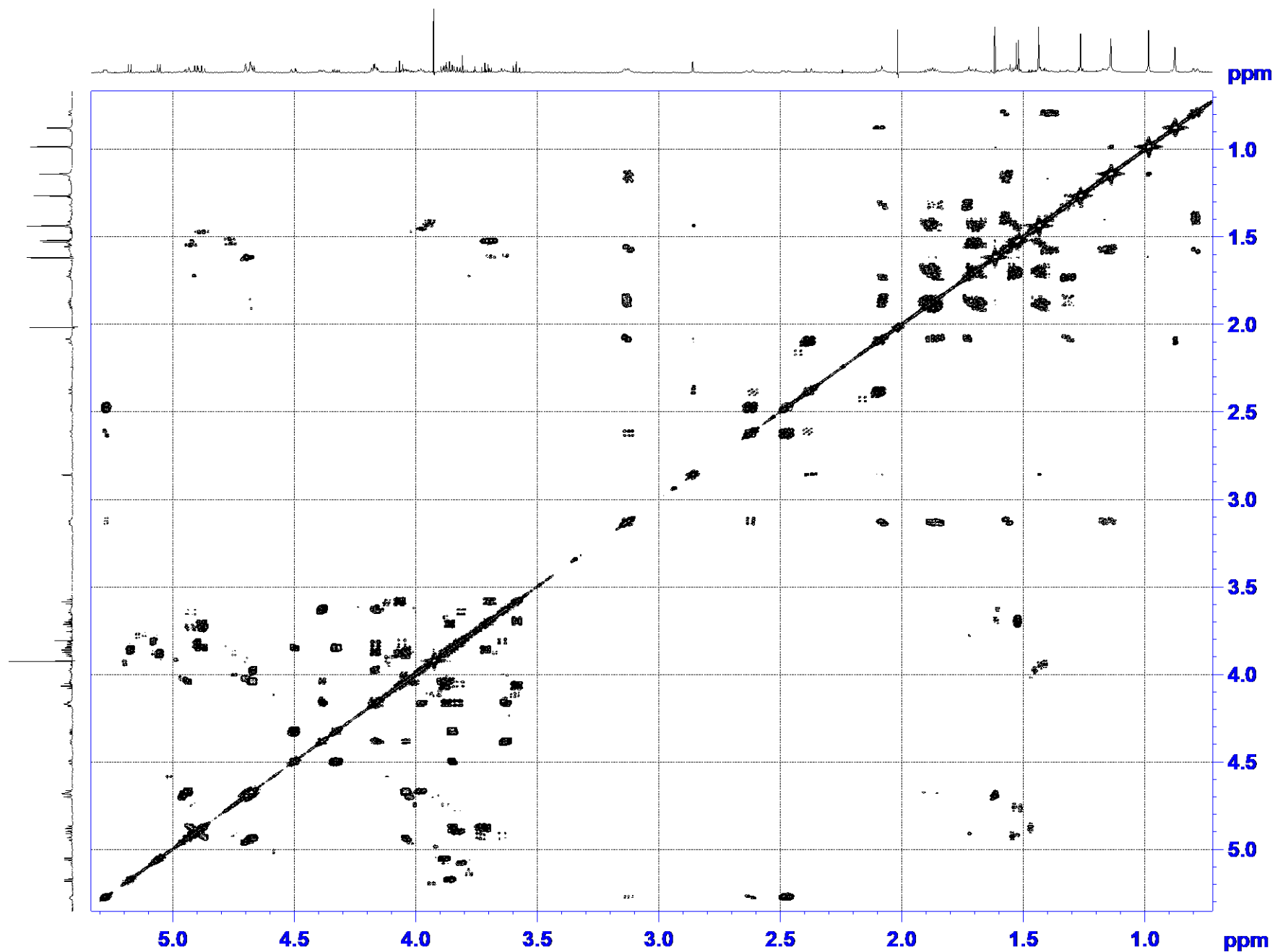


Figure S11. The COSY (500.12 MHz) spectrum of chitonoidoside F (**2**) in C₅D₅N/D₂O (4/1).

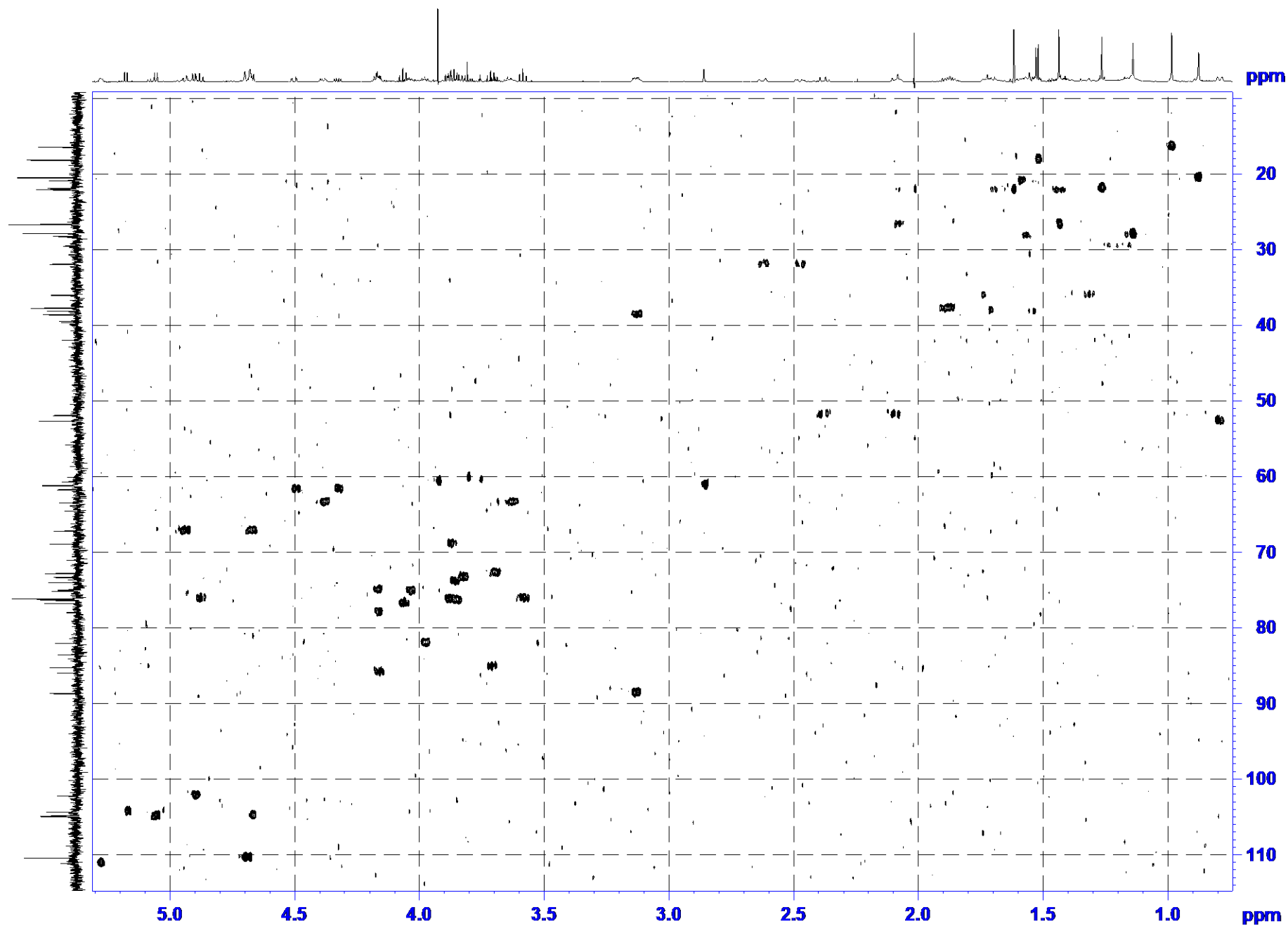


Figure S12. The HSQC (500.12 MHz) spectrum of chitonoidoside F (2) in C₅D₅N/D₂O (4/1).

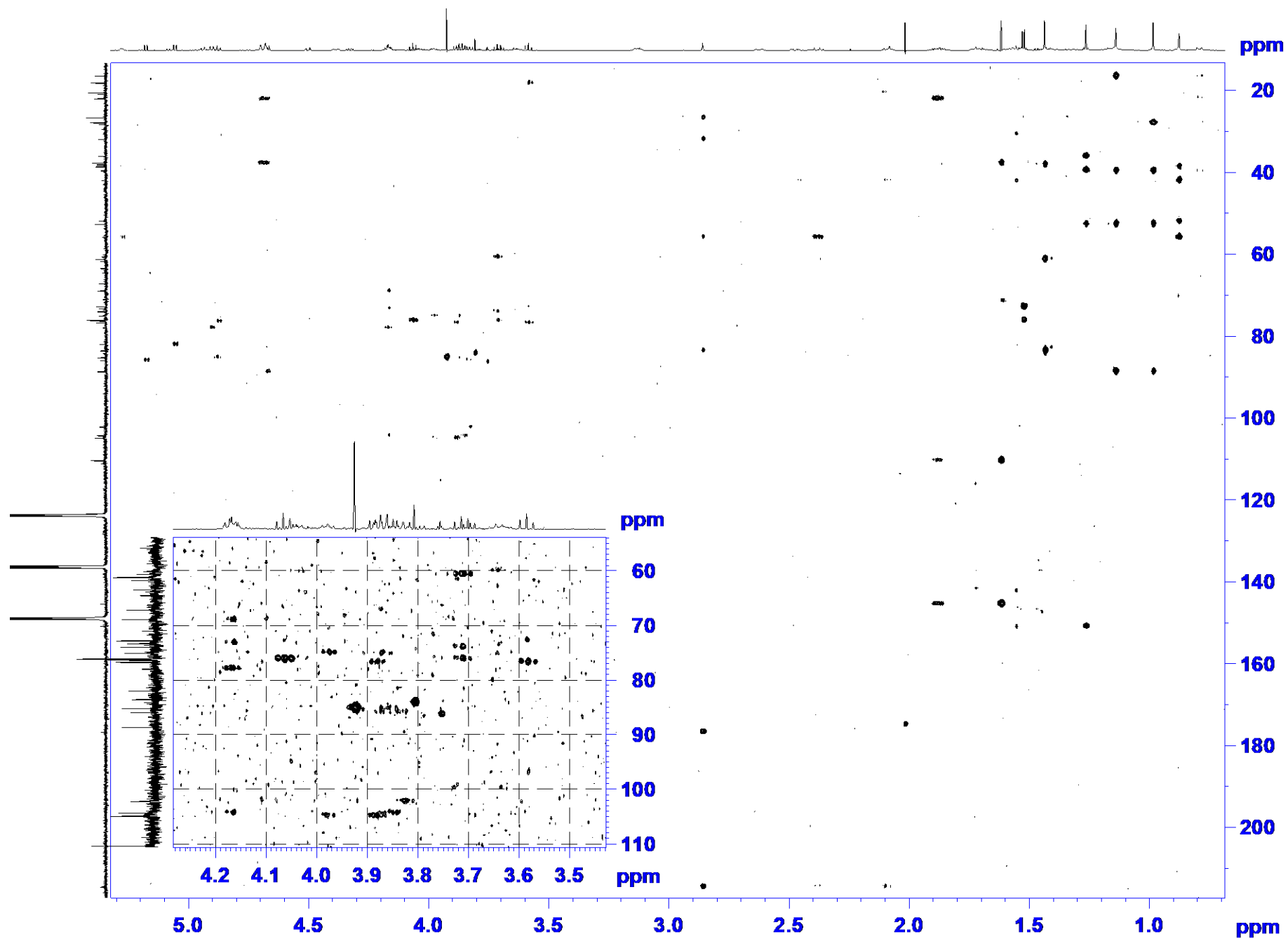


Figure S13. The HMBC (500.12 MHz) spectrum of chitonoidoside F (2) in C₅D₅N/D₂O (4/1).

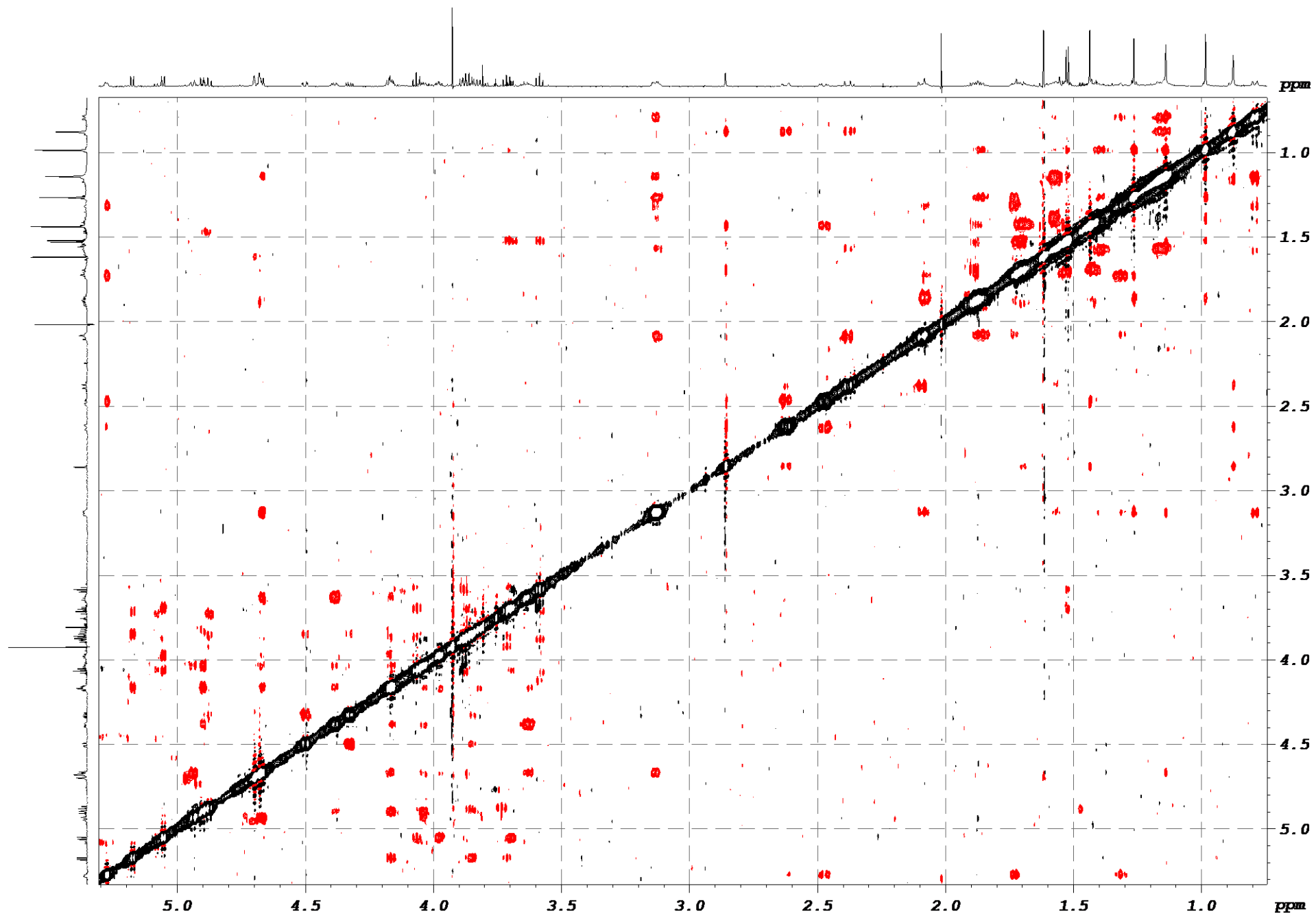


Figure S14. The ROESY (500.12 MHz) spectrum of chitonoidoside F (**2**) in C₅D₅N/D₂O (4/1).

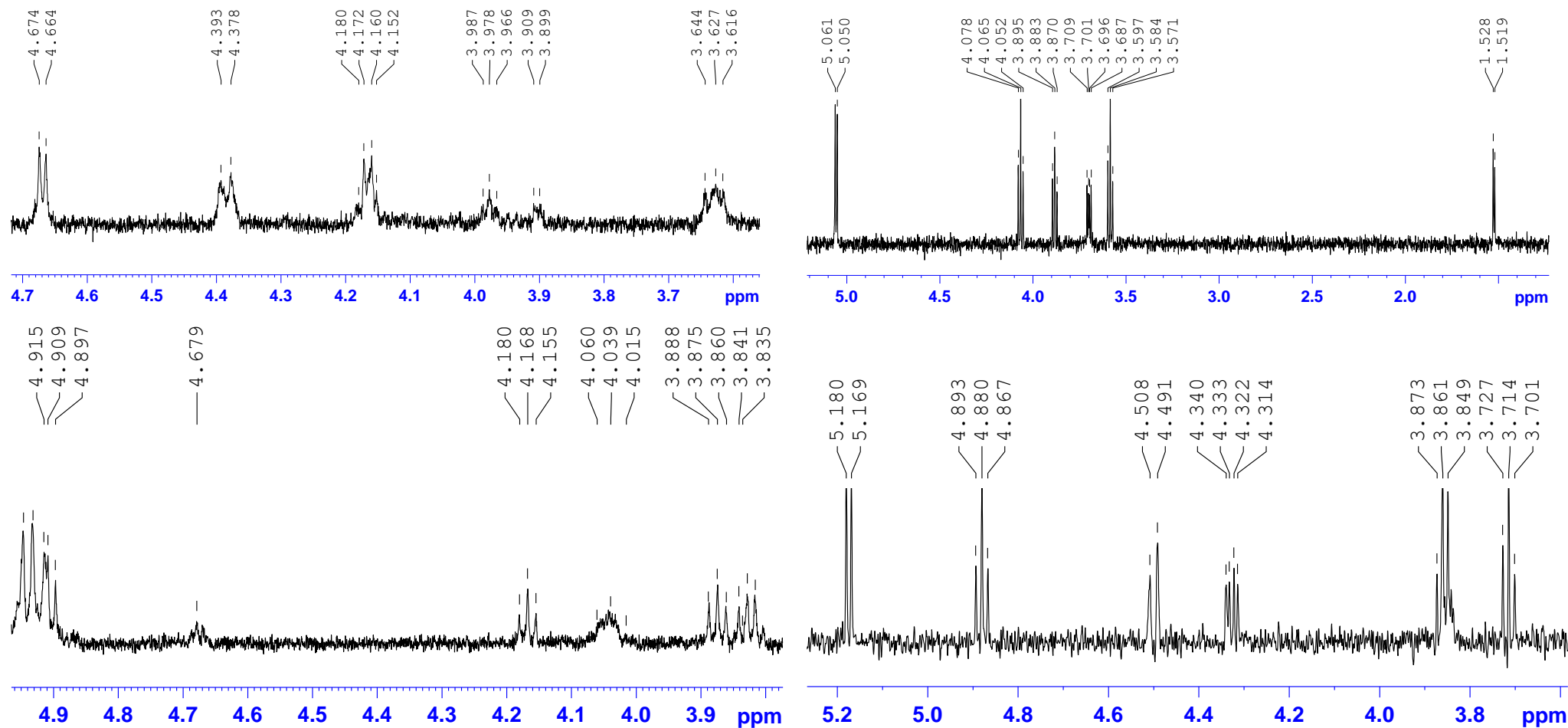


Figure S15. 1D TOCSY (500.12 MHz) spectra of Xyl1, Qui2, Glc3 and MeGlc4 of chitonoidoside F (2) in C₅D₅N/D₂O (4/1).

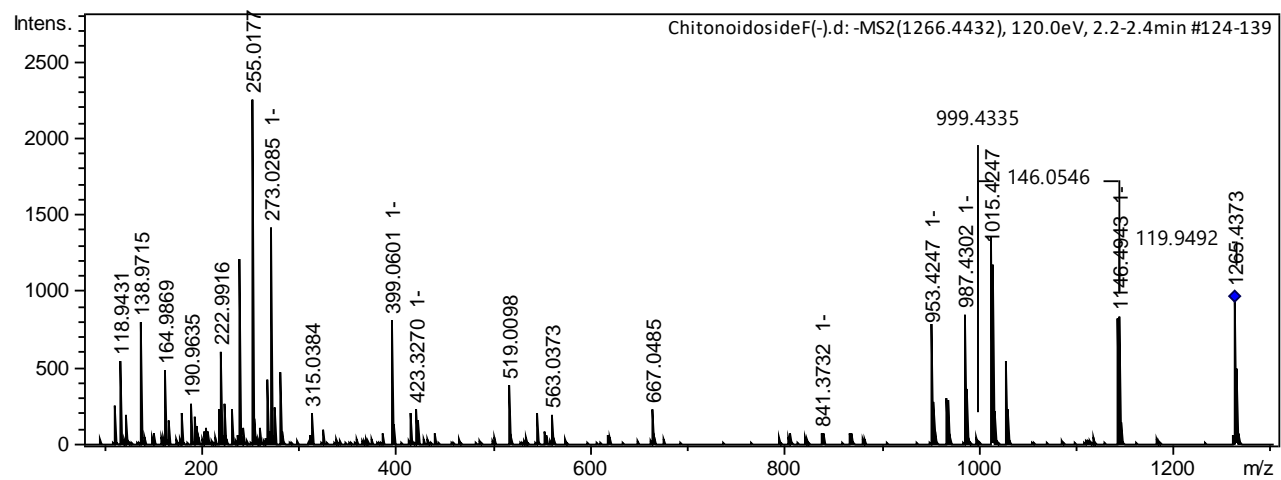
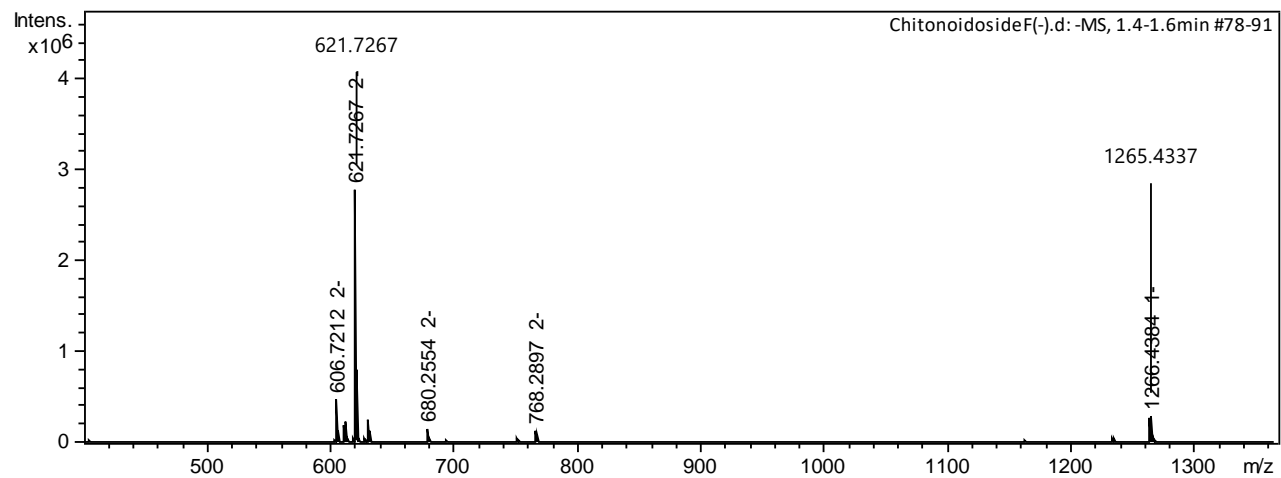


Figure S16. HR-ESI-MS and ESI-MS/MS spectra of chitonoidoside F (2).

Table S2. ¹³C and ¹H NMR chemical shifts, HMBC and ROESY correlations of the aglycone moiety of chitonoidoside F (2).

Position	δ_C mult. ^a	δ_H mult. (J in Hz) ^b	HMBC	ROESY
1	36.0 CH ₂	1.80 m		H-11, H-19
		1.32 m		H-3, H-5, H-11
2	26.7 CH ₂	2.07 m		
		1.48 m		H-19, H-30
3	88.7 CH	3.13 dd (4.2; 12.0)	C: 4, 30, 31, C:1 Xyl1	H-1, H-5, H-31, H1-Xyl1
4	39.5 C			
5	52.7 CH	0.80 brd (12.2)	C: 10, 19, 30	H-1, H-3, H-31
6	20.9 CH ₂	1.58 m		
7	28.3 CH ₂	1.56 m		
		1.17 m		H-32
8	38.6 CH	3.13 m		H-6, H-19
9	150.9 C			
10	39.7 C			
11	111.1 CH	5.28 m	C: 10, 12, 13	H-1
12	31.9 CH ₂	2.63 brd (16.9)	C: 9, 11, 13, 18	H-17, H-32
		2.48 dd (5.5; 16.9)	C: 9, 11, 13, 14, 18	
13	55.8 C			
14	42.0 C			
15	51.9 CH ₂	2.38 d (15.4)	C: 13, 16, 17, 32	H-7, H-32
		2.09 d (15.4)	C: 8, 14, 16, 32	
16	214.5 C			
17	61.7 CH	2.86 s	C: 12, 13, 16, 18, 20, 21	H-21, H-32
18	176.7 C			
19	21.9 CH ₃	1.27 s	C: 1, 5, 9, 10	H-8, H-30
20	83.6 C			
21	26.7 CH ₃	1.44 s	C: 17, 20, 22	H-12, H-17
22	38.1 CH ₂	1.71 m	C: 20, 21, 23	
		1.55 m		
23	22.0 CH ₂	1.70 m		
		1.43 m		
24	37.7 CH ₂	1.88 m	C: 25, 26, 27	
25	145.5 C			
26	110.4 CH ₂	4.70 brs	C: 24, 27	
		4.68 brs	C: 24, 27	
27	22.1 CH ₃	1.62 s	C: 24, 25, 26	
30	16.4 CH ₃	0.99 s	C: 3, 4, 5, 31	H-31
31	27.9 CH ₃	1.14 s	C: 3, 4, 5, 30	H-3, H-5, H-30
32	20.4 CH ₃	0.88 s	C: 8, 13, 14, 15	H-7, H-12, H-17

^aRecorded at 125.67 MHz in C₅D₅N/D₂O (4/1). ^bRecorded at 500.12 MHz in C₅D₅N/D₂O (4/1).

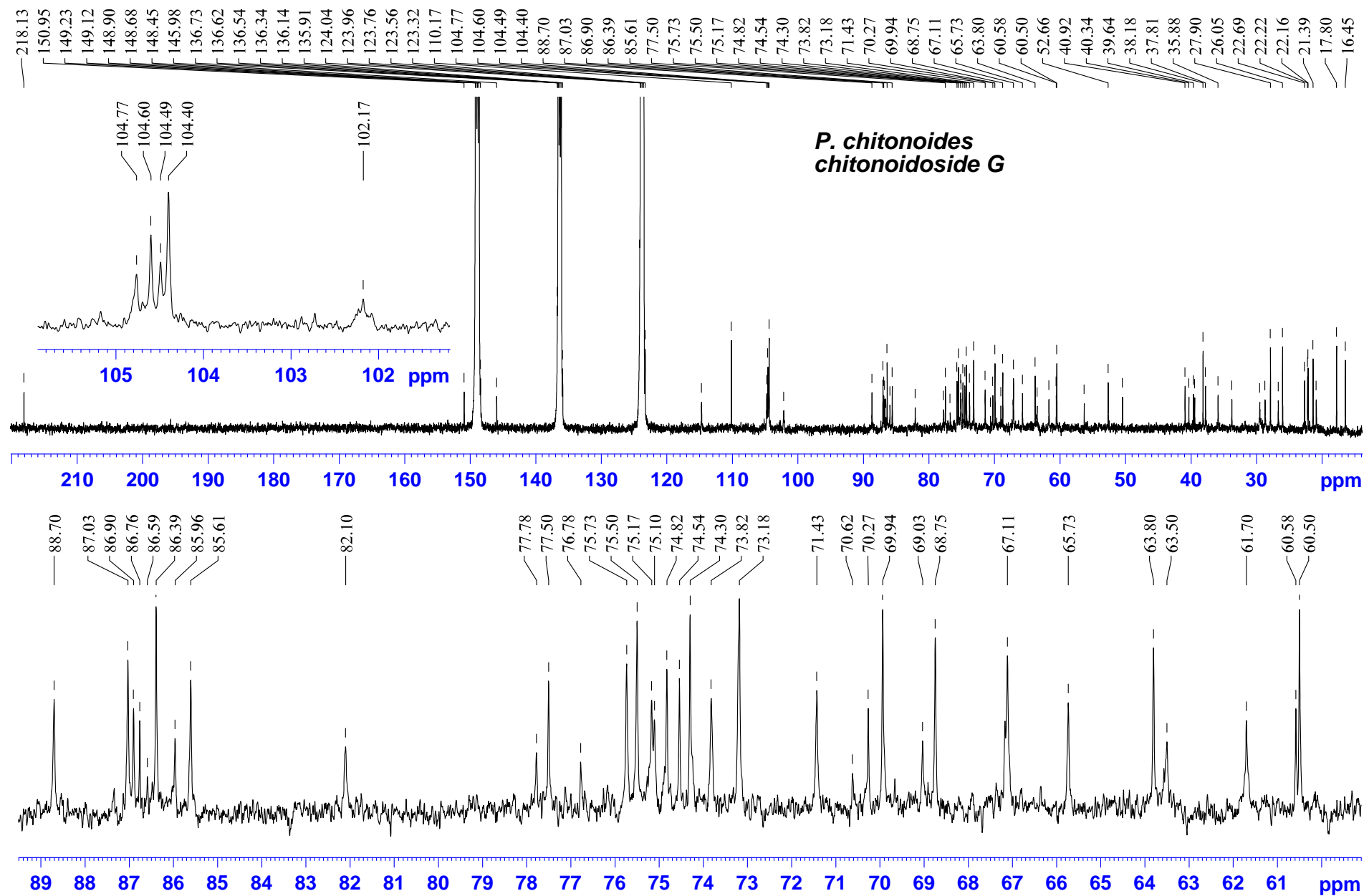


Figure S17. The ^{13}C NMR (125.67 MHz) spectrum of chitonoidoside G (**3**) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1).

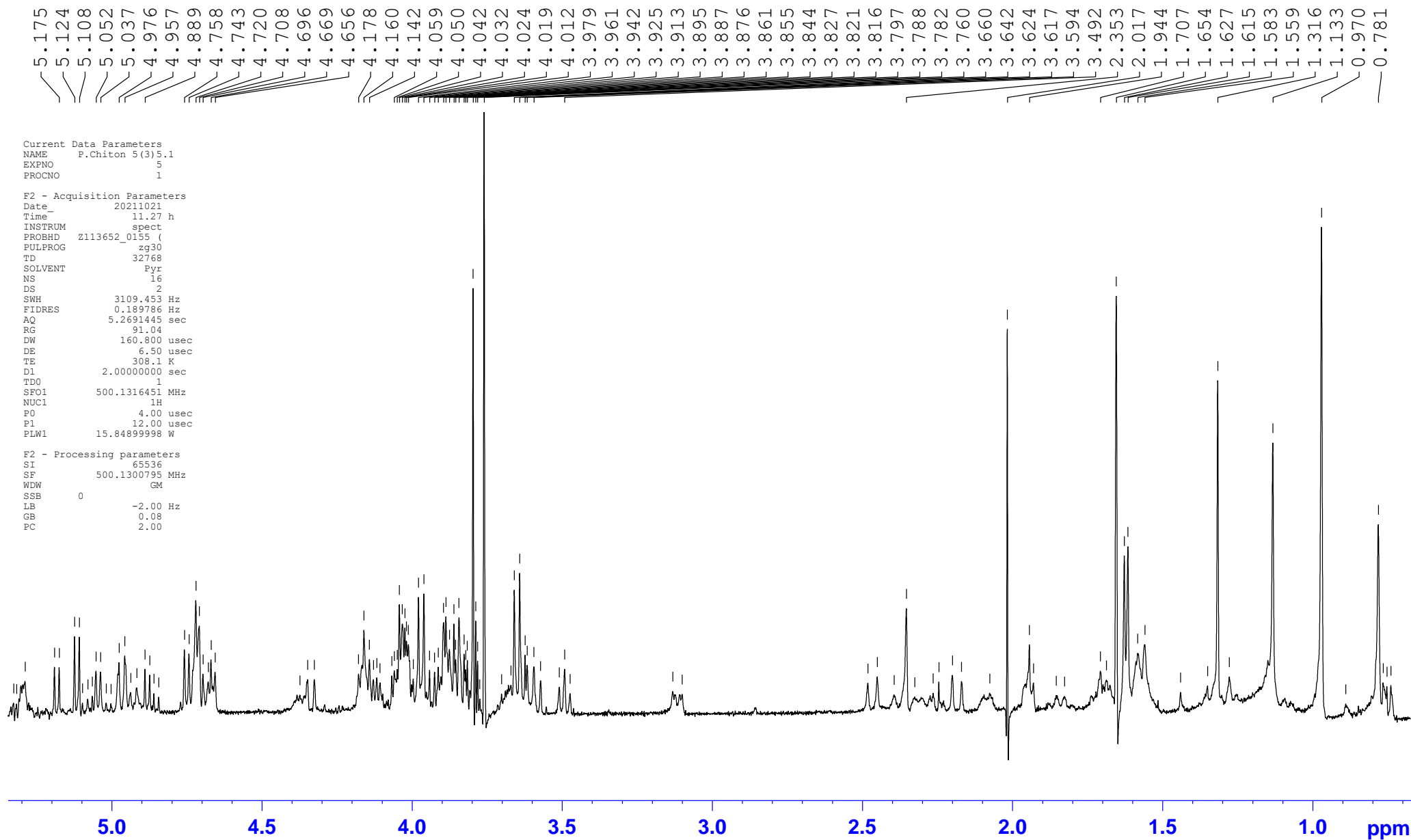


Figure S18. The ^1H NMR (500.12 MHz) spectrum of chitonoidoside G (3) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1)

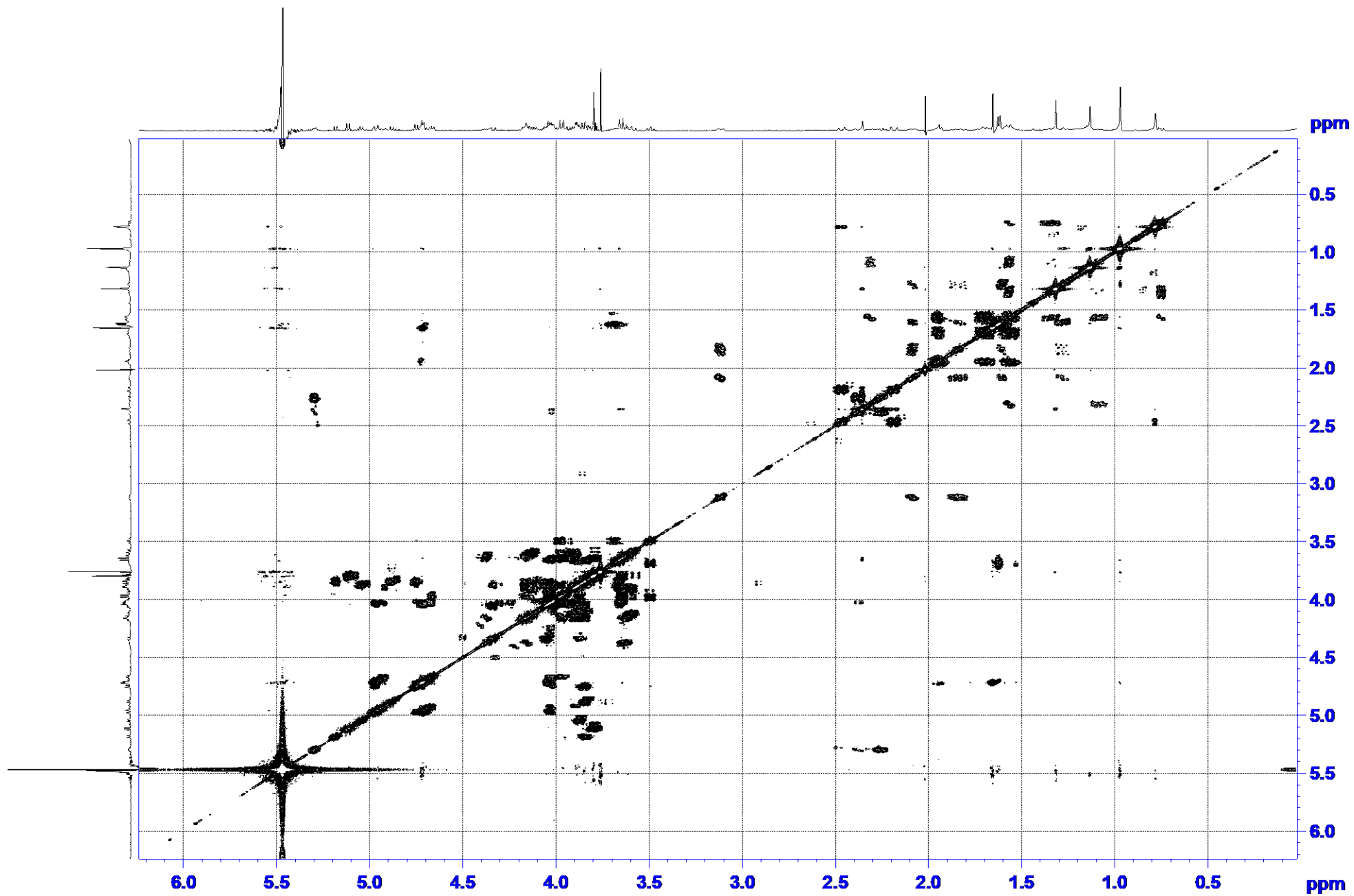


Figure S19. The COSY (500.12 MHz) spectrum of chitonoidoside G (**3**) in C₅D₅N/D₂O (4/1)

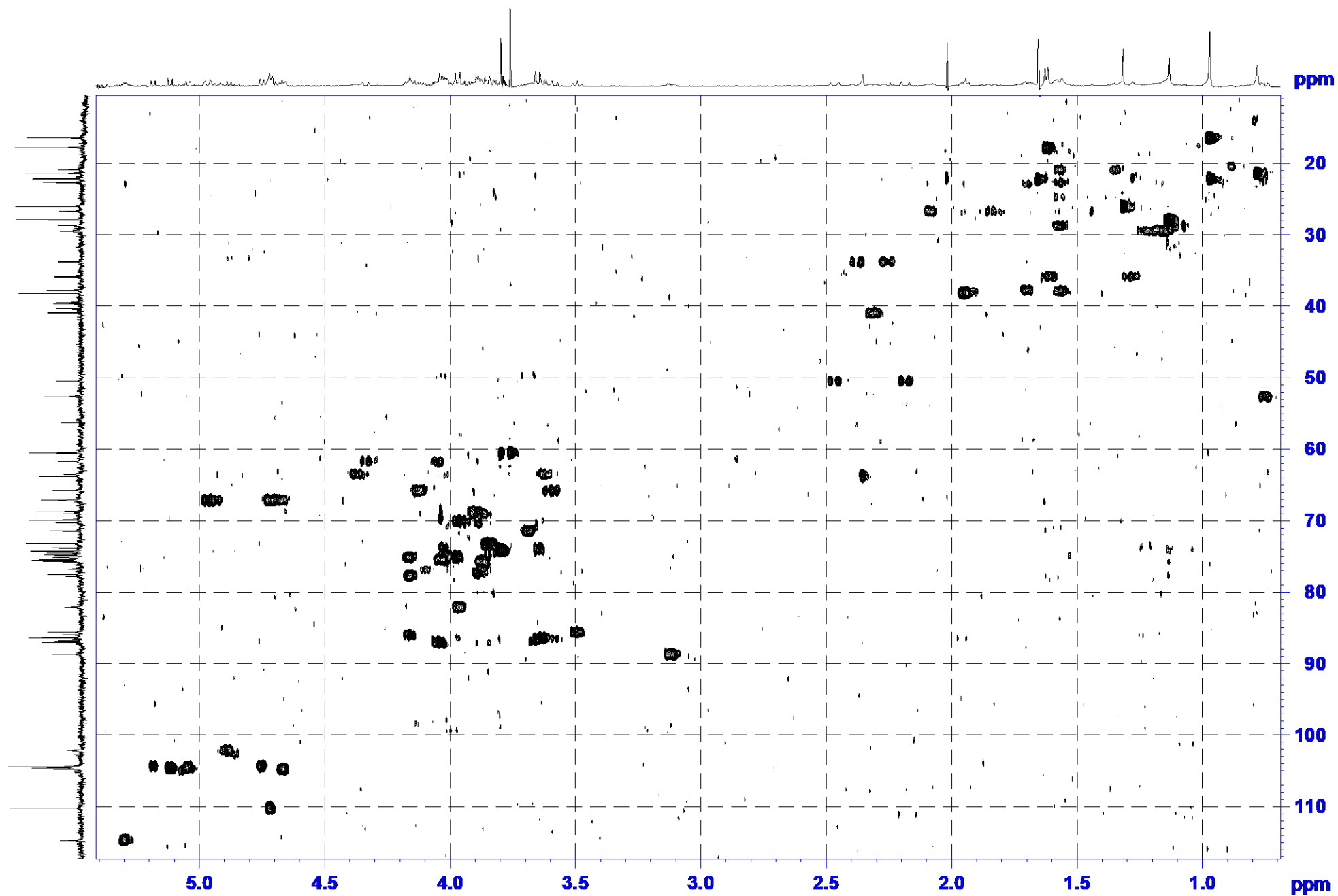


Figure S20. The HSQC (500.12 MHz) spectrum of chitonoidoside G (3) in C₅D₅N/D₂O (4/1)

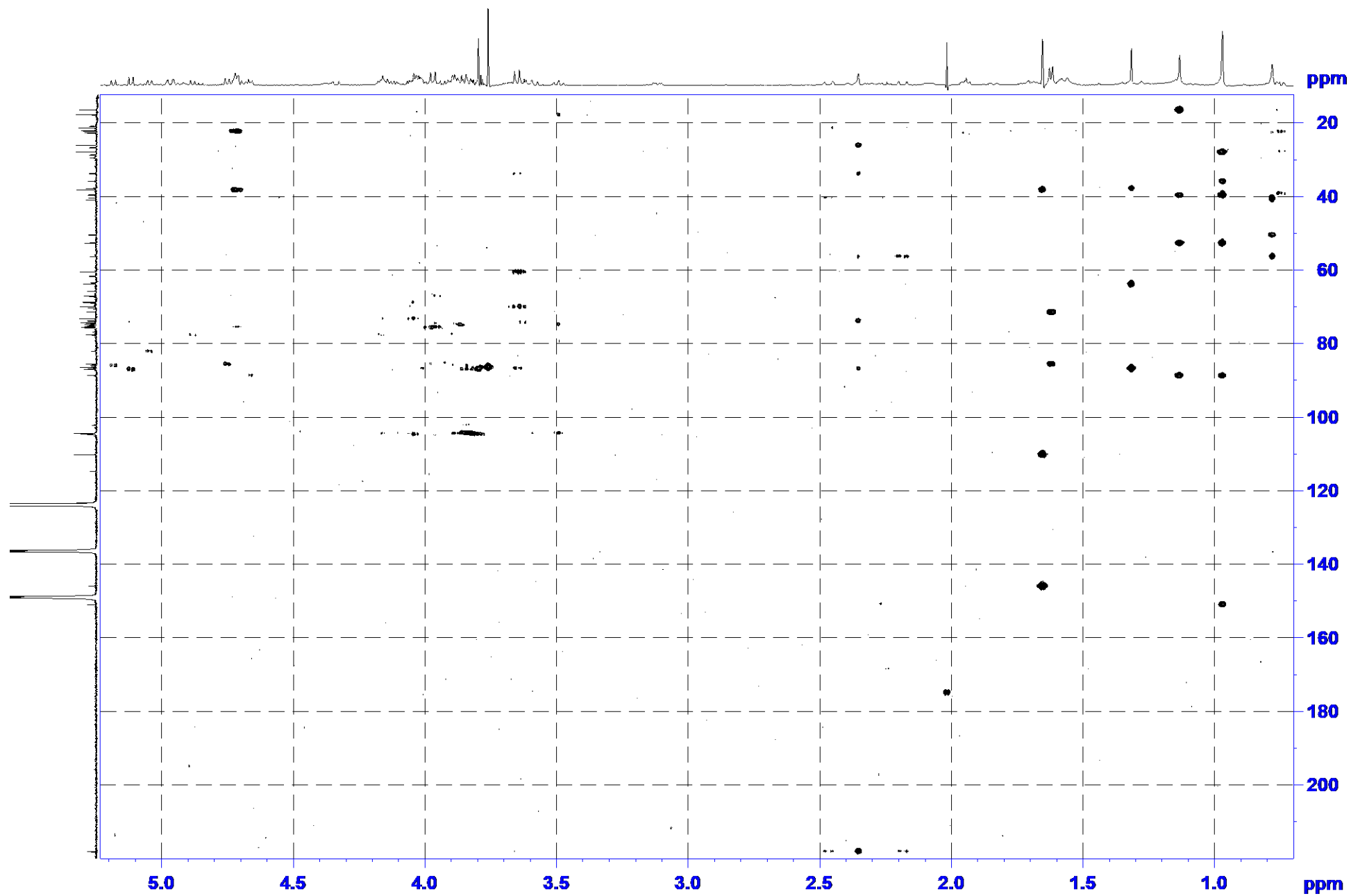


Figure S21. The HMBC (500.12 MHz) spectrum of chitonoidoside G (3) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1)

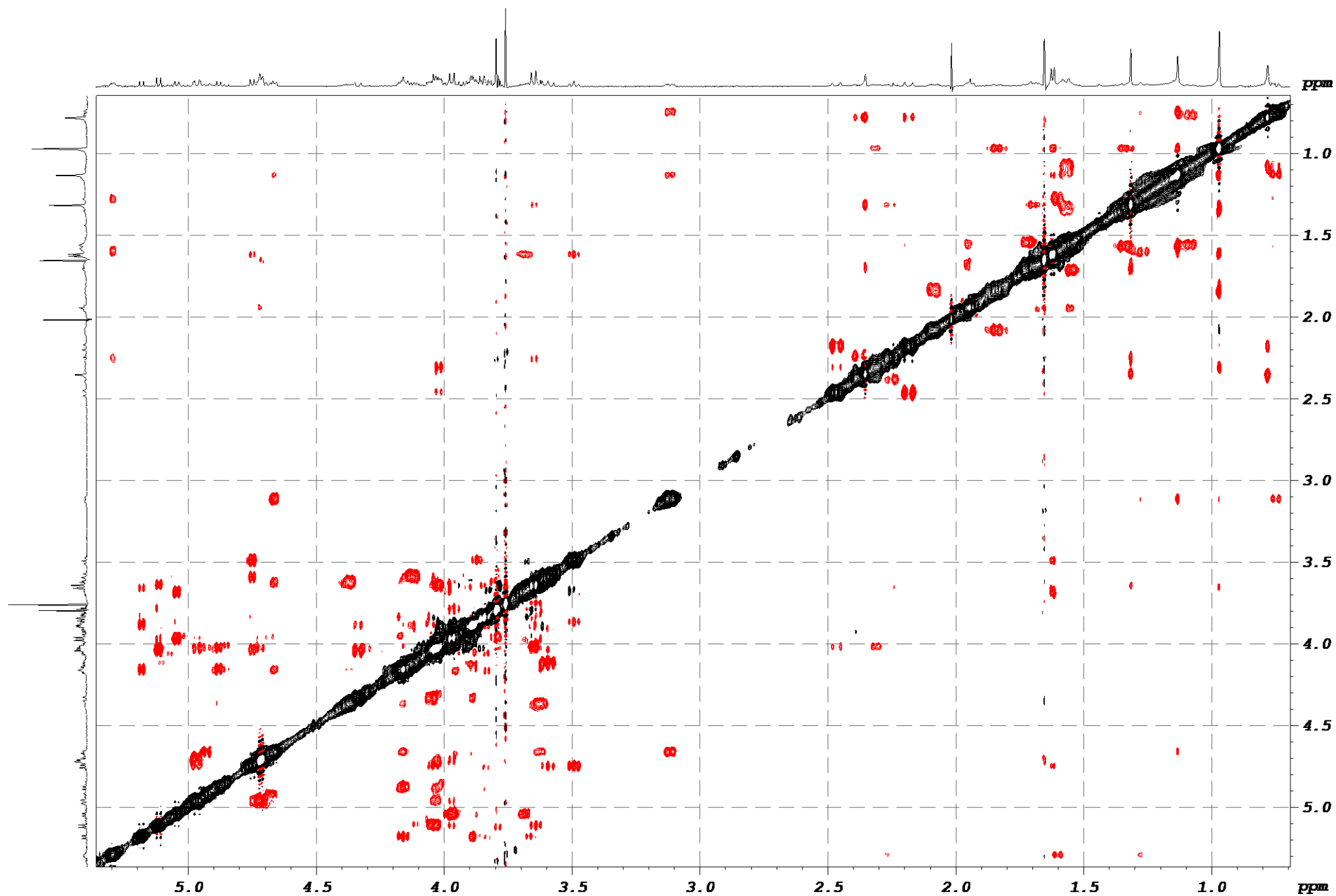


Figure S22. The ROESY (500.12 MHz) spectrum of chitonoidoside G (**3**) in C_5D_5N/D_2O (4/1)

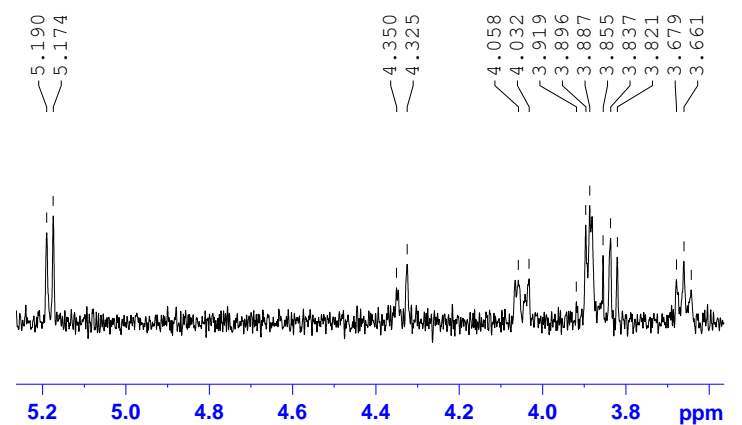
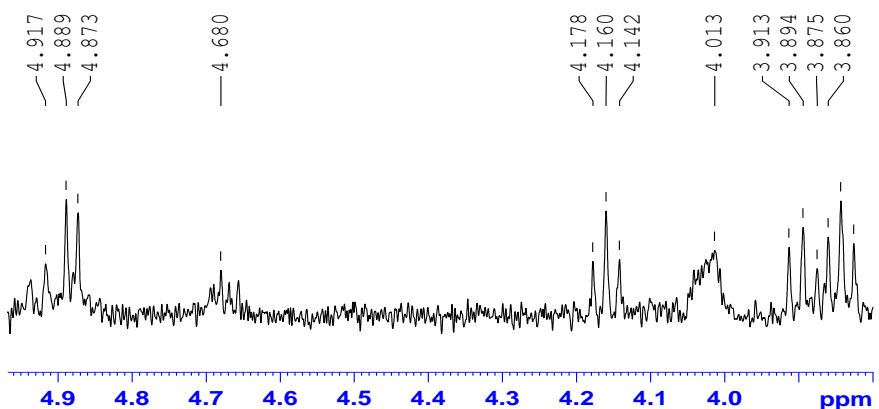
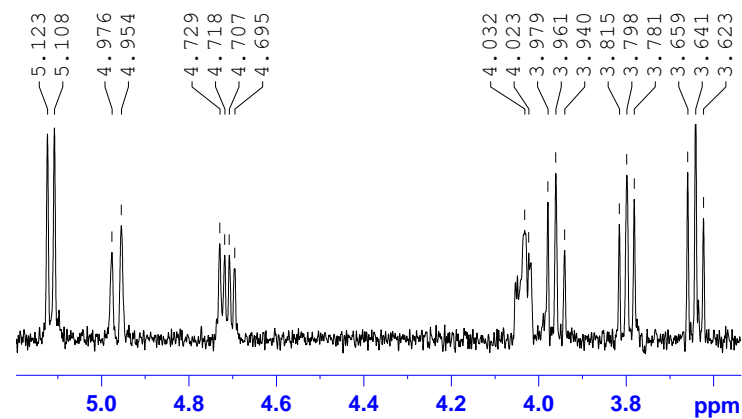
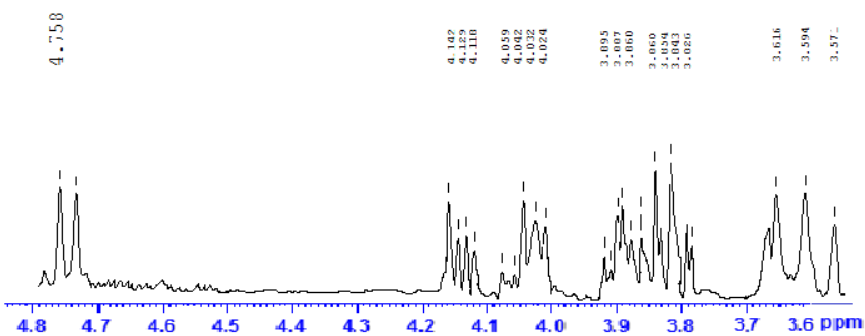
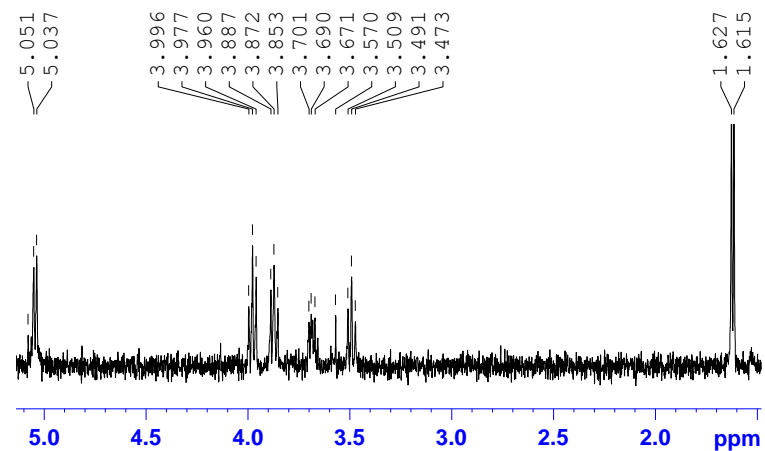
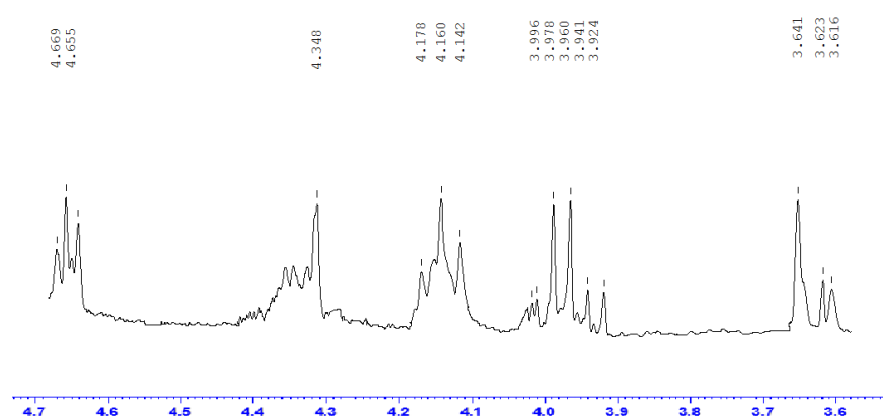


Figure S23. 1 D TOCSY (500.12 MHz) spectra of Xyl1, Qui2, Xyl3, MeGlc4, Glc5 and MeGlc6 of chitonoidoside G (**3**) in C₅D₅N/D₂O (4/1)

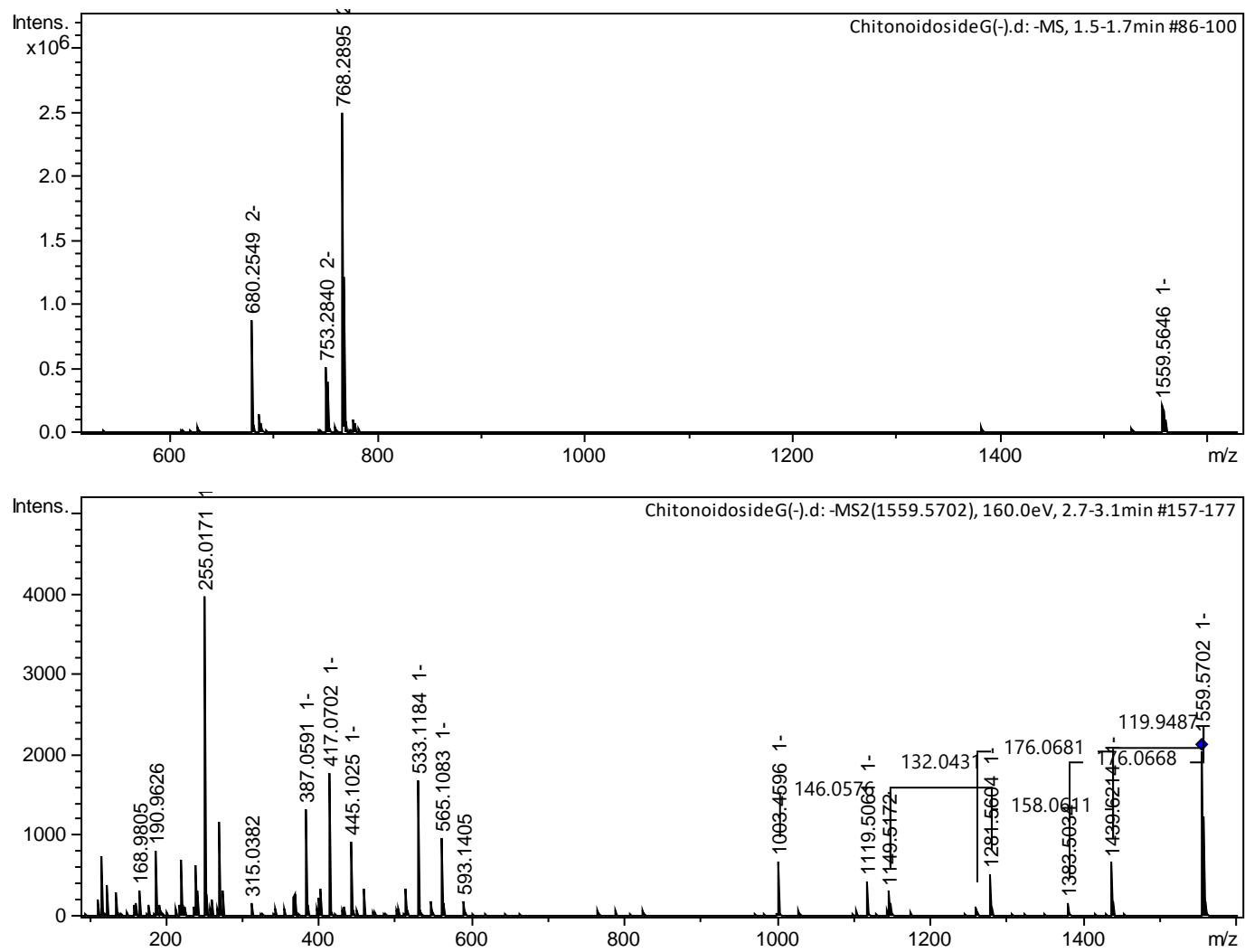


Figure S24. HR-ESI-MS and ESI-MS/MS spectra of chitonoidoside G (3)

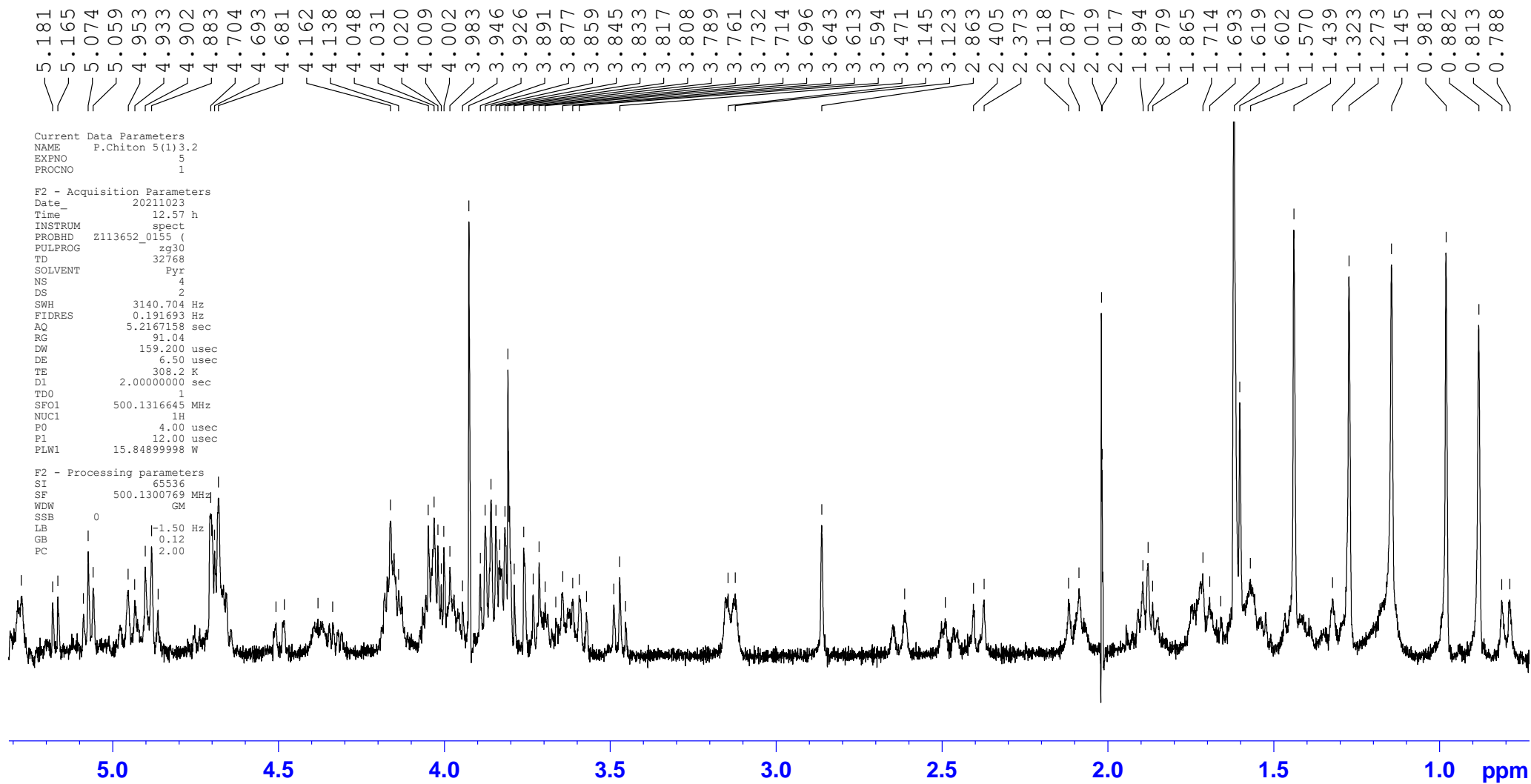


Figure S26. The ^1H NMR (500.12 MHz) spectrum of chitonoidoside H (**4**) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1)

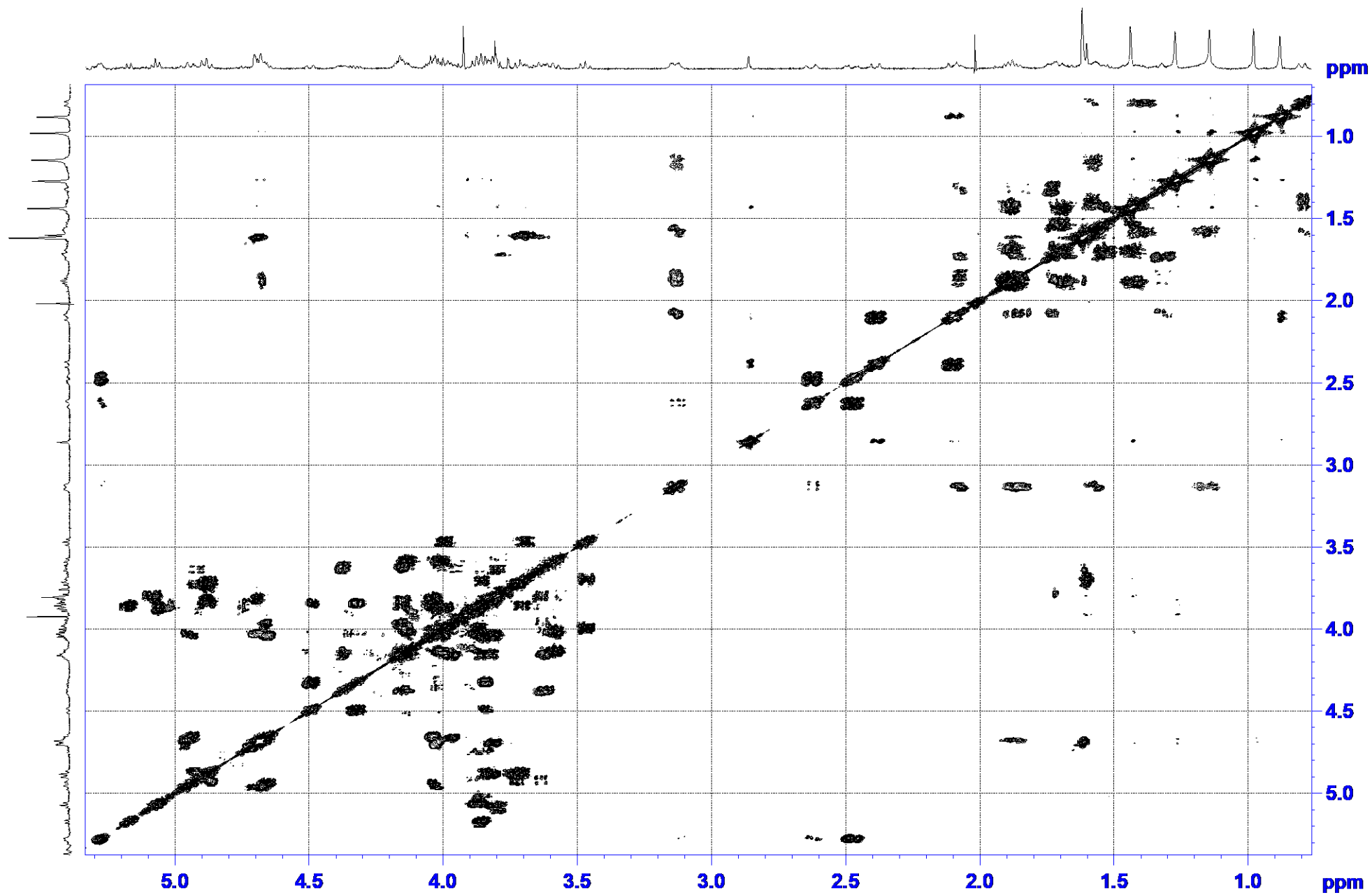


Figure S27. The COSY (500.12 MHz) spectrum of chitonoidoside H (**4**) in C₅D₅N/D₂O (4/1)

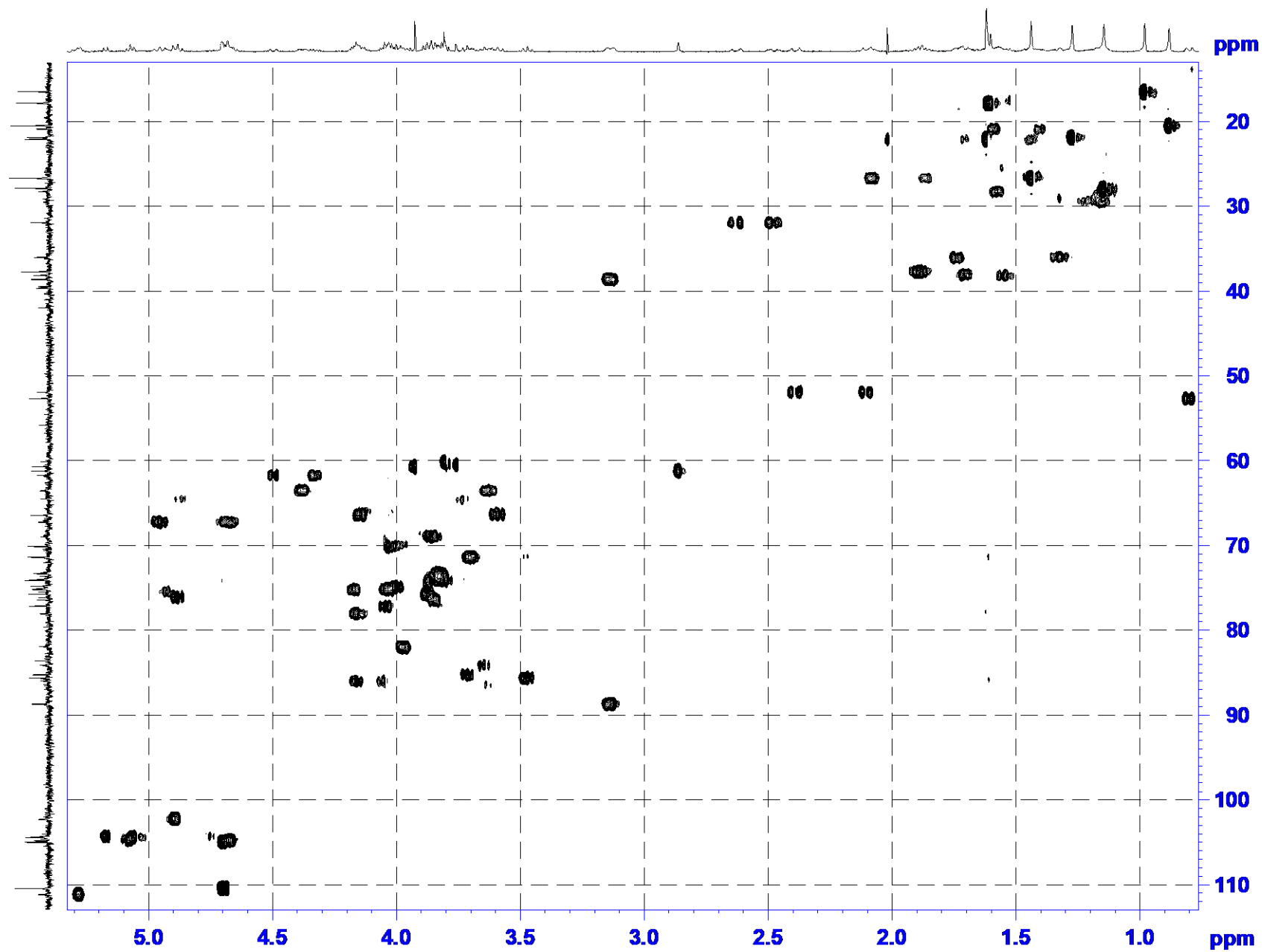


Figure S28. The HSQC (500.12 MHz) spectrum of chitonoidoside H (**4**) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1)

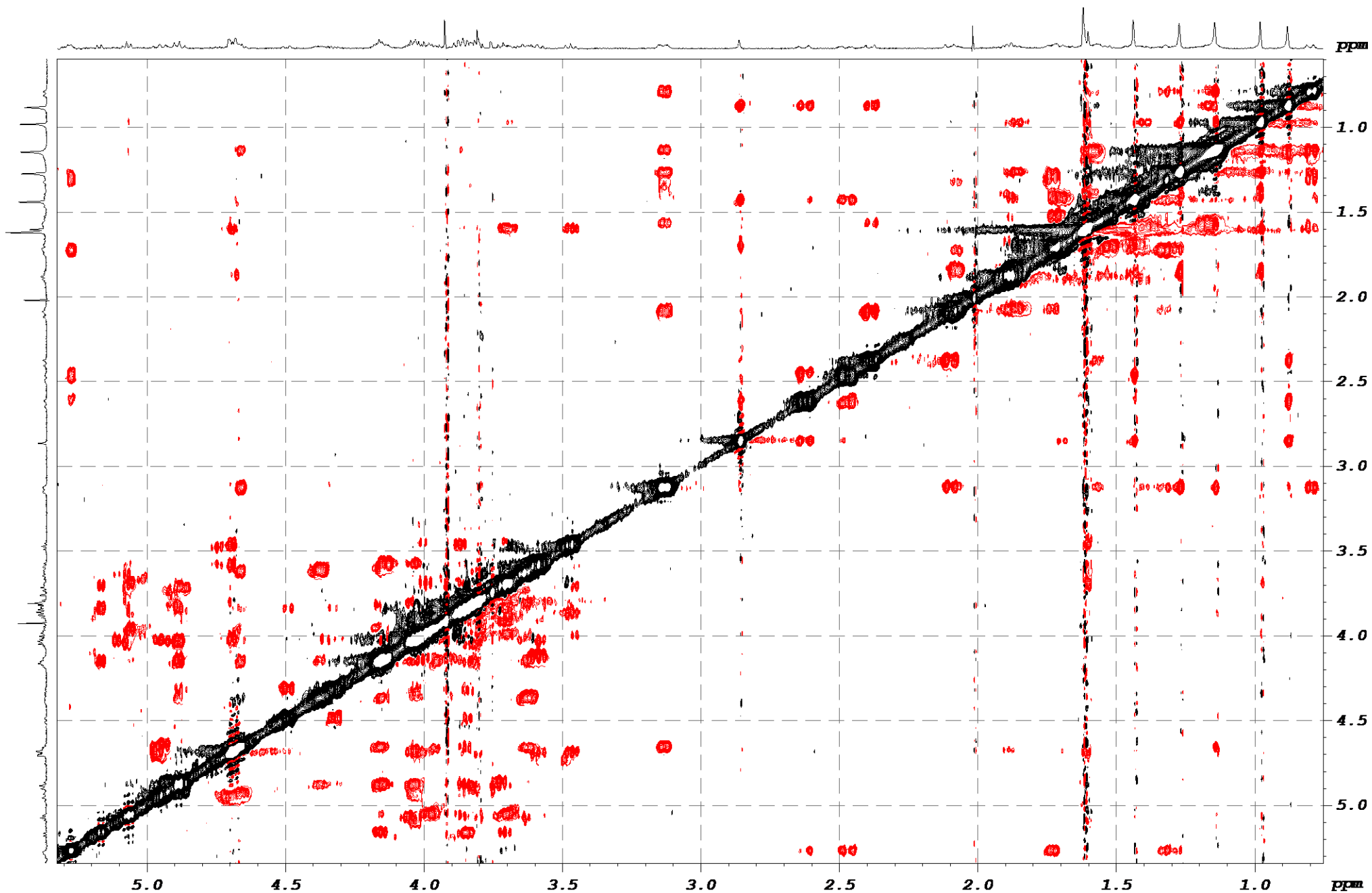


Figure S29. The ROESY (500.12 MHz) spectrum of chitonoidoside H (4) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1)

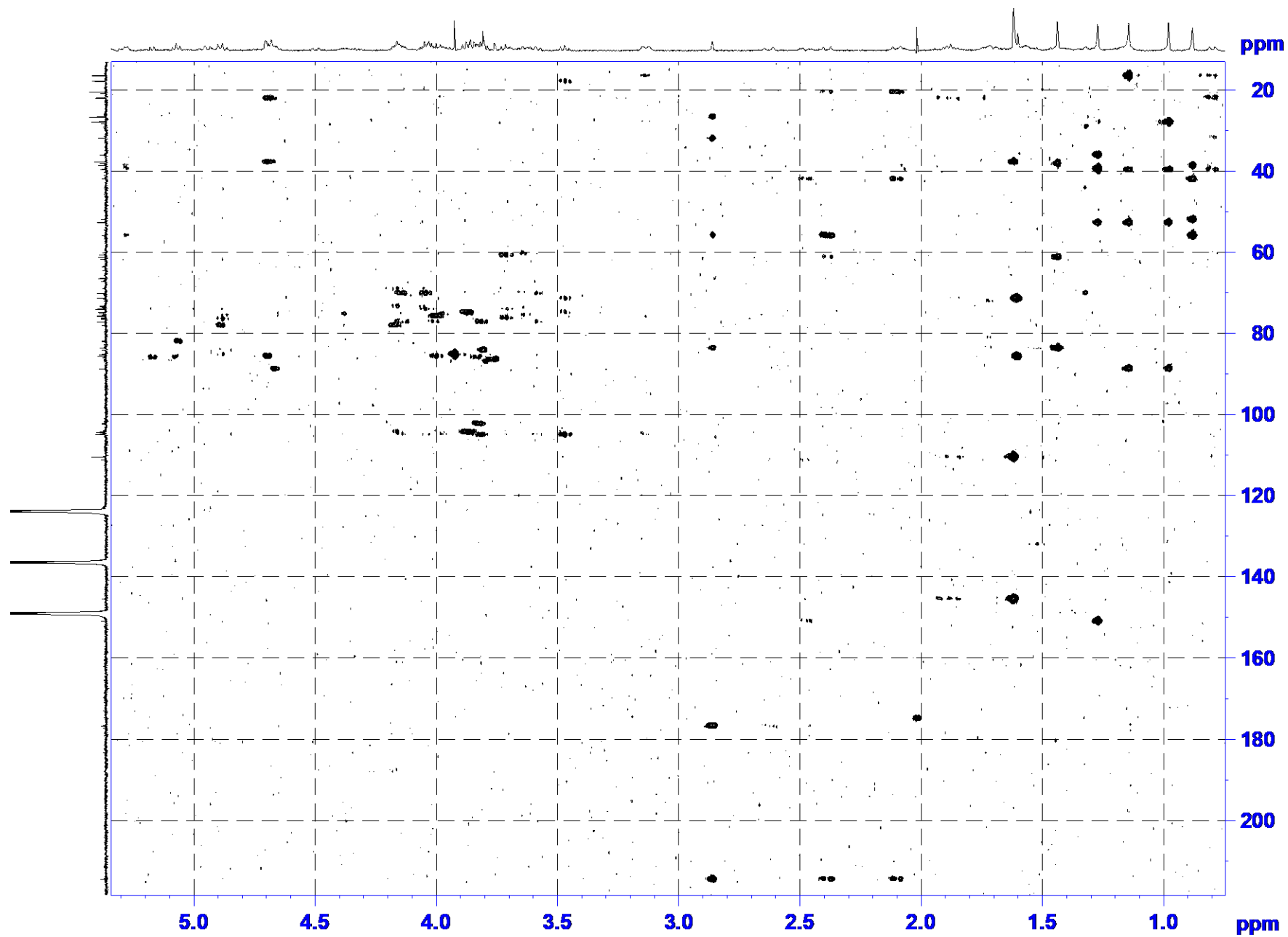


Figure S30. The HMBC (500.12 MHz) spectrum of chitonoidoside H (4) in $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ (4/1)

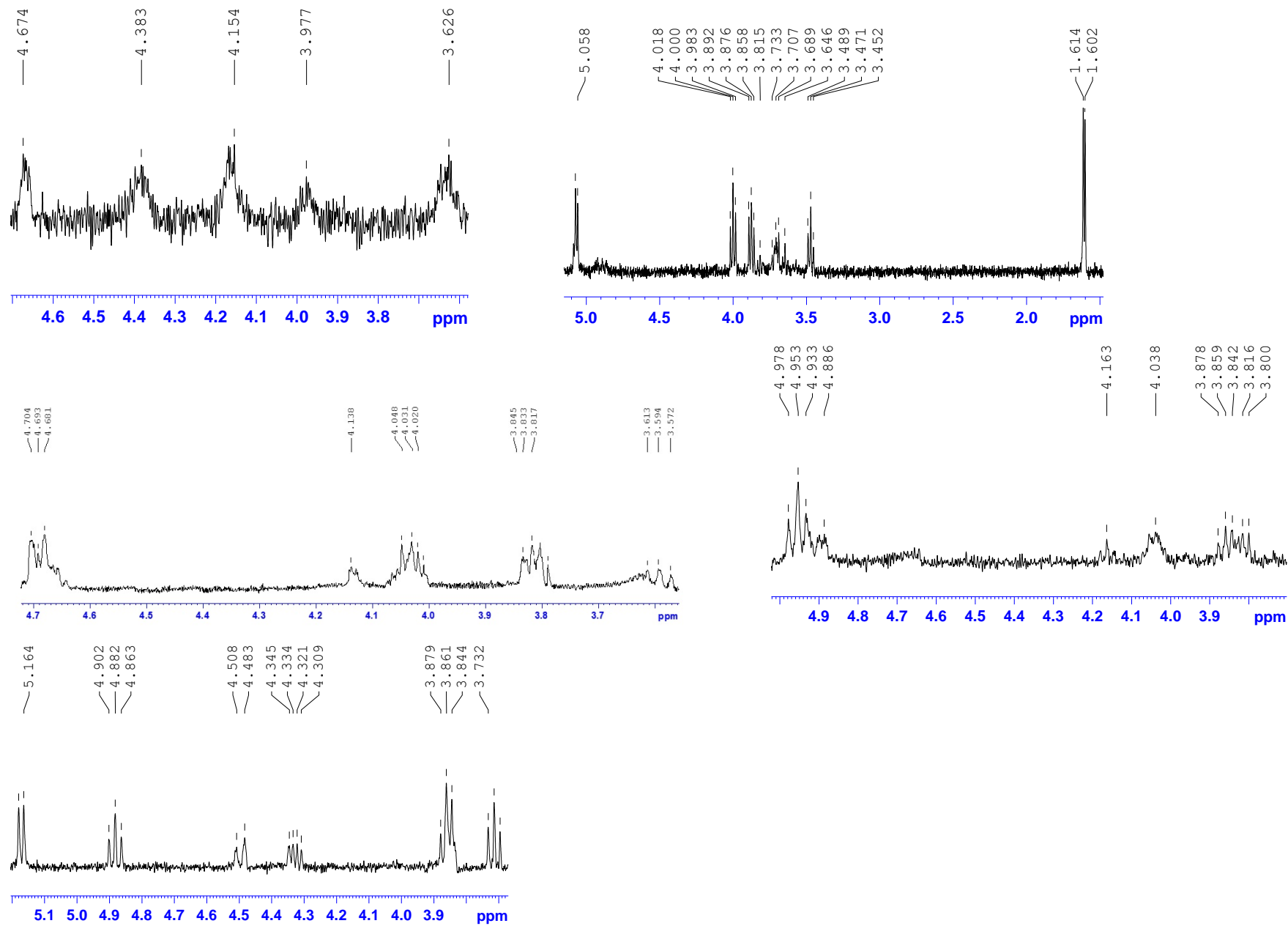


Figure S31. 1D TOCSY (500.12 MHz) spectra of Xyl1, Qui2, Xyl3, Glc4 and MeGlc5 of chitonoidoside H (**4**) in C₅D₅N/D₂O (4/1)

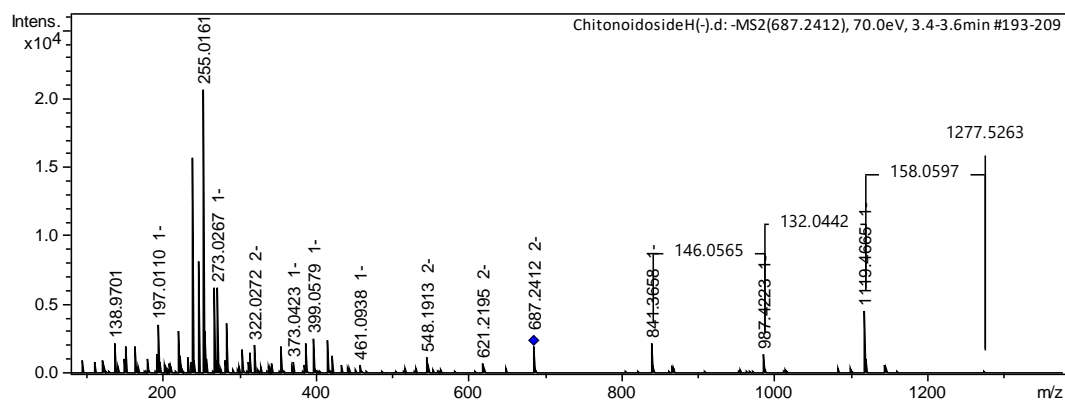
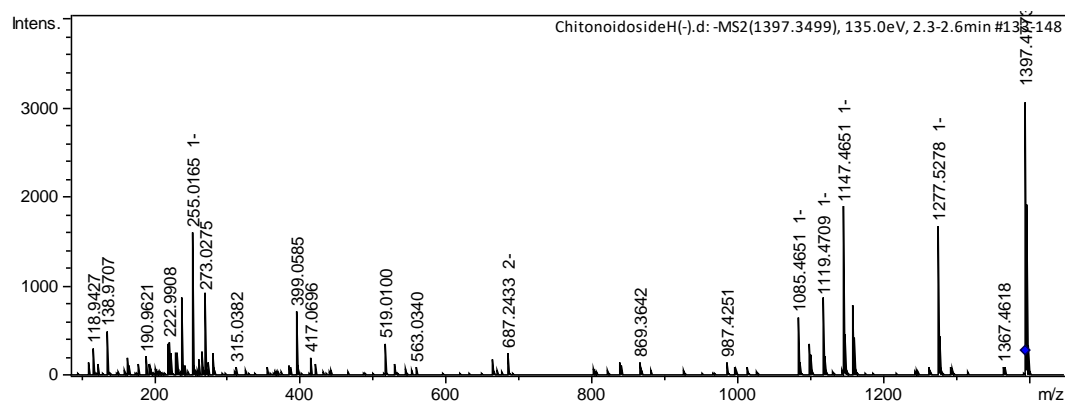
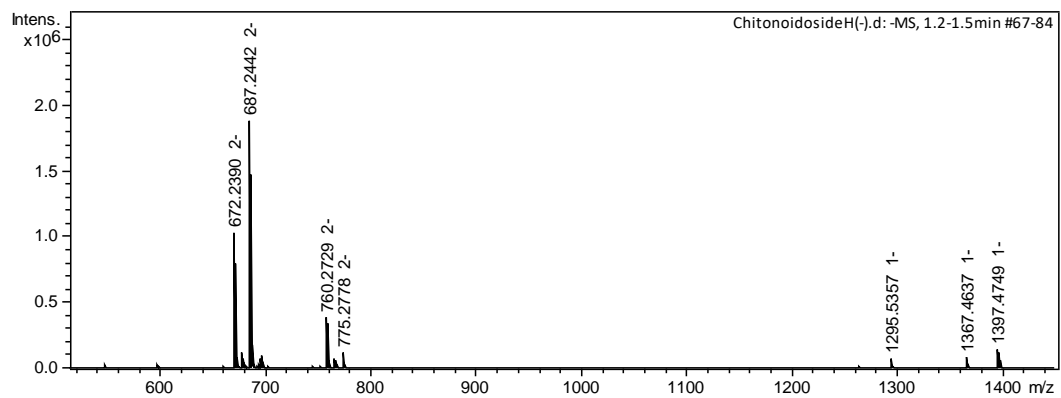


Figure S33. HR-ESI-MS and ESI-MS/MS spectra of chitonoidoside C (**4**)

Table S3. ¹³C and ¹H NMR chemical shifts, HMBC and ROESY correlations of the aglycone moiety of chitonoidoside H (4).

Position	δ_C mult. ^a	δ_H mult. (J in Hz) ^b	HMBC	ROESY
1	36.0 CH ₂	1.74 m		H-11
		1.32 m		H-11
2	26.7 CH ₂	2.08 m		
		1.87 m		
3	88.7 CH	3.14 dd (3.8; 11.9)	C: 4, 30, 31, C:1 Xyl1	H-5, H-31, H1-Xyl1
4	39.5 C			
5	52.7 CH	0.80 brd (11.0)	C: 6, 10, 30	H-3, H-31
6	20.9 CH ₂	1.57 m		H-31
		1.39 m		
7	28.3 CH ₂	1.58 m		
		1.10 m		H-32
8	38.6 CH	3.13 m		H-15, H-19
9	150.9 C			
10	39.7 C			
11	111.1 CH	5.28 m	C: 8, 13	H-1
12	31.9 CH ₂	2.63 d (17.3)	C: 9, 13, 18	H-17, H-32
		2.48 dd (5.5; 17.3)	C: 9, 11, 13, 14, 18	H-21
13	55.8 C			
14	42.0 C			
15	51.9 CH ₂	2.39 d (15.7)	C: 13, 16, 17, 32	H-32
		2.10 d (15.7)	C: 8, 14, 16, 32	H-8
16	214.5 C			
17	61.2 CH	2.87 s	C: 12, 13, 16, 18, 20, 21	H-12, H-21, H-22, H-32
18	176.7 C			
19	21.9 CH ₃	1.27 s	C: 1, 5, 9, 10	H-1, H-2, H-8, H-30
20	83.6 C			
21	26.7 CH ₃	1.44 s	C: 17, 20, 22	H-12, H-17
22	38.1 CH ₂	1.70 m	C: 20, 21, 23	
		1.54 m	C: 20, 21	
23	22.1 CH ₂	1.70 m		
		1.44 m		
24	37.7 CH ₂	1.89 m	C: 23, 25, 26, 27	
25	145.5 C			
26	110.4 CH ₂	4.71 brs	C: 24, 27	
		4.68 brs	C: 24, 27	
27	22.0 CH ₃	1.62 s	C: 24, 25, 26	
30	16.5 CH ₃	0.98 s	C: 3, 4, 5, 31	H-31
31	27.9 CH ₃	1.15 s	C: 3, 4, 5, 30	H-3, H-5, H-30
32	20.5 CH ₃	0.88 s	C: 8, 13, 14, 15	H-7, H-12, H-17

^aRecorded at 125.67 MHz in C₅D₅N/D₂O (4/1). ^bRecorded at 500.12 MHz in C₅D₅N/D₂O (4/1).

