

## Supplementary data content page

**Title:** Sulfated Triterpene Glycosides from the Far Eastern Sea Cucumber *Cucumaria djakonovi*: Djakonoviosides C<sub>1</sub>, D<sub>1</sub>, E<sub>1</sub>, and F<sub>1</sub>; Cytotoxicity Against Human Breast Cancer Cell Lines; Quantitative Structure – Activity Relationships

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### Content:

Figure S1. The <sup>13</sup>C NMR (125.67 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S2. The <sup>1</sup>H NMR (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S3. The COSY (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S4. The HSQC (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S5. The ROESY (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S6. The HMBC (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S7. 1 D TOCSY (500.12 MHz) spectra of Xyl1, Xyl2, Glc3, MeGlc4, Xyl5 of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S8. HR-ESI-MS and ESI-MS/MS spectra of djakonovioside C<sub>1</sub> (**1**)

Figure S9. The <sup>13</sup>C NMR (125.67 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S10. The <sup>1</sup>H NMR (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S11. The COSY (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S12. The HSQC (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S13. The HMBC (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S14. The ROESY (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S15. 1D TOCSY (500.12 MHz) spectra of Xyl1, Glc2, Glc3, MeGlc4, Xyl5 of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S16. HR-ESI-MS and ESI-MS/MS spectra of djakonovioside D<sub>1</sub> (**2**)

Figure S17. The <sup>13</sup>C NMR (125.67 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S18. The <sup>1</sup>H NMR (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S19. The COSY (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S20. The HSQC (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S21. The ROESY (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S22. The HMBC (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S23. 1D TOCSY (500.12 MHz) spectra of Xyl1, Glc2, Glc3, MeGlc4 of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S24. HR-ESI-MS and ESI-MS/MS spectra of djakonovioside E<sub>1</sub> (**3**)

Table S1. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of the aglycone part of djakonovioside E<sub>1</sub> (**3**)

Figure S25. The <sup>13</sup>C NMR (125.67 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S26. The <sup>1</sup>H NMR (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S27. The COSY (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S28. The HSQC (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S29. The ROESY (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S30. The HMBC (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S31. 1D TOCSY (500.12 MHz) spectra of Xyl1, Qui2, Glc3, MeGlc4, Xyl5 of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S32. HR-ESI-MS and ESI-MS/MS spectra of djakonovioside F<sub>1</sub> (**4**)

Table S2. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of the aglycone part of okhotoside A<sub>2</sub>-1 (**5**)

Table S3. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of the carbohydrate part of okhotoside A<sub>2</sub>-1 (**5**)

Figure S33. The <sup>13</sup>C NMR (125.67 MHz) spectrum of okhotoside A<sub>2</sub>-1 (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S34. The <sup>1</sup>H NMR (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S35. The COSY (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S36. The HSQC (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S37. The ROESY (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S38. The HMBC (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Table S4. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of the aglycone part of cucumarioside A<sub>2</sub>-5 (**6**)

Table S5. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of the carbohydrate part of cucumarioside A<sub>2</sub>-5 (**6**)

Figure S39. The <sup>13</sup>C NMR (125.67 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S40. The <sup>1</sup>H NMR (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S41. The COSY (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S42. The HSQC (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S43. The ROESY (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S44. The HMBC (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Table S6. <sup>13</sup>C NMR chemical shifts of frondoside A<sub>2</sub>-3 (**7**).

Figure S45. The <sup>13</sup>C NMR (125.67 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S46. The <sup>1</sup>H NMR (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S47. The COSY (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S48. The HSQC (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S49. The ROESY (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S50. The HMBC (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S51. 1D TOCSY (500.12 MHz) spectra of Xyl1, Qui2, Glc3, MeGlc4, Xyl5 of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Table S7. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of the carbohydrate part of isokoreoside A (**9**)

Table S8. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of the aglycone part of isokoreoside A (**9**)

Figure S52. The <sup>13</sup>C NMR (125.67 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S53. The <sup>1</sup>H NMR (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S54. The COSY (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S55. The HSQC (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S56. The ROESY (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Figure S57. The HMBC (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

Table S9. <sup>13</sup>C NMR chemical shifts of koreoside A (**10**)

Figure S58. The PCR QSAR model correlation plot reflecting the relationship of predicted and experimental hemolytic activity.

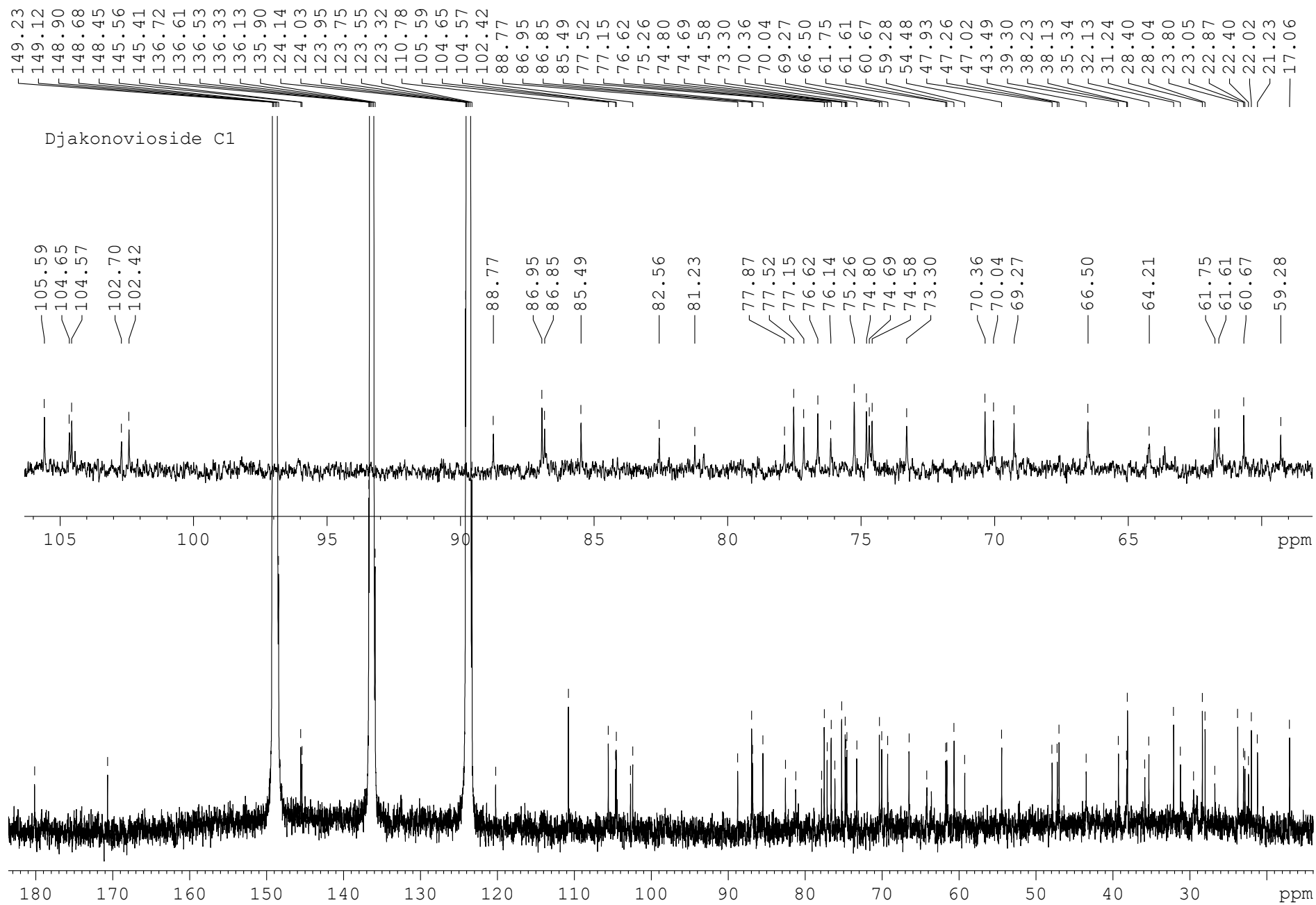


Figure S1. The  $^{13}\text{C}$  NMR (125.67 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)



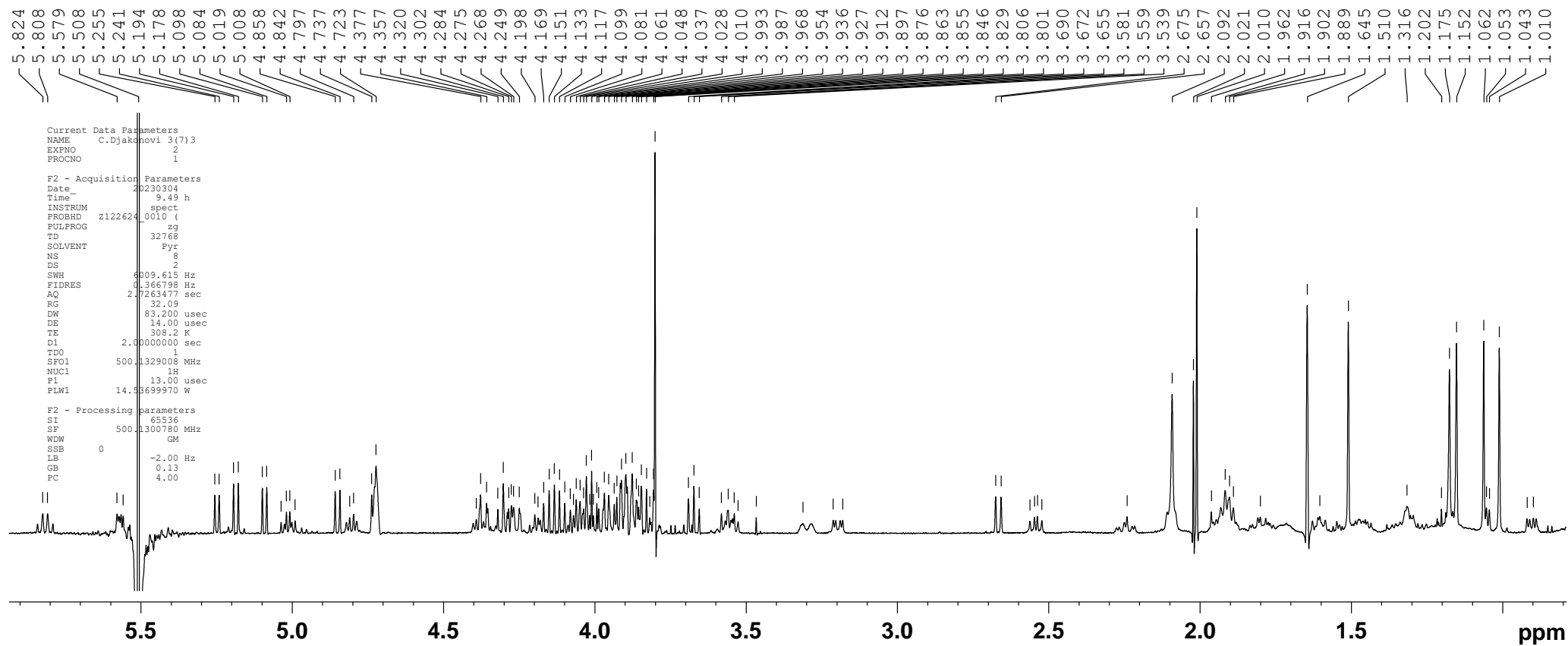


Figure S2. The  $^1\text{H}$  NMR (500.12 MHz) spectrum of djakonovioside  $\text{C}_1$  (**1**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

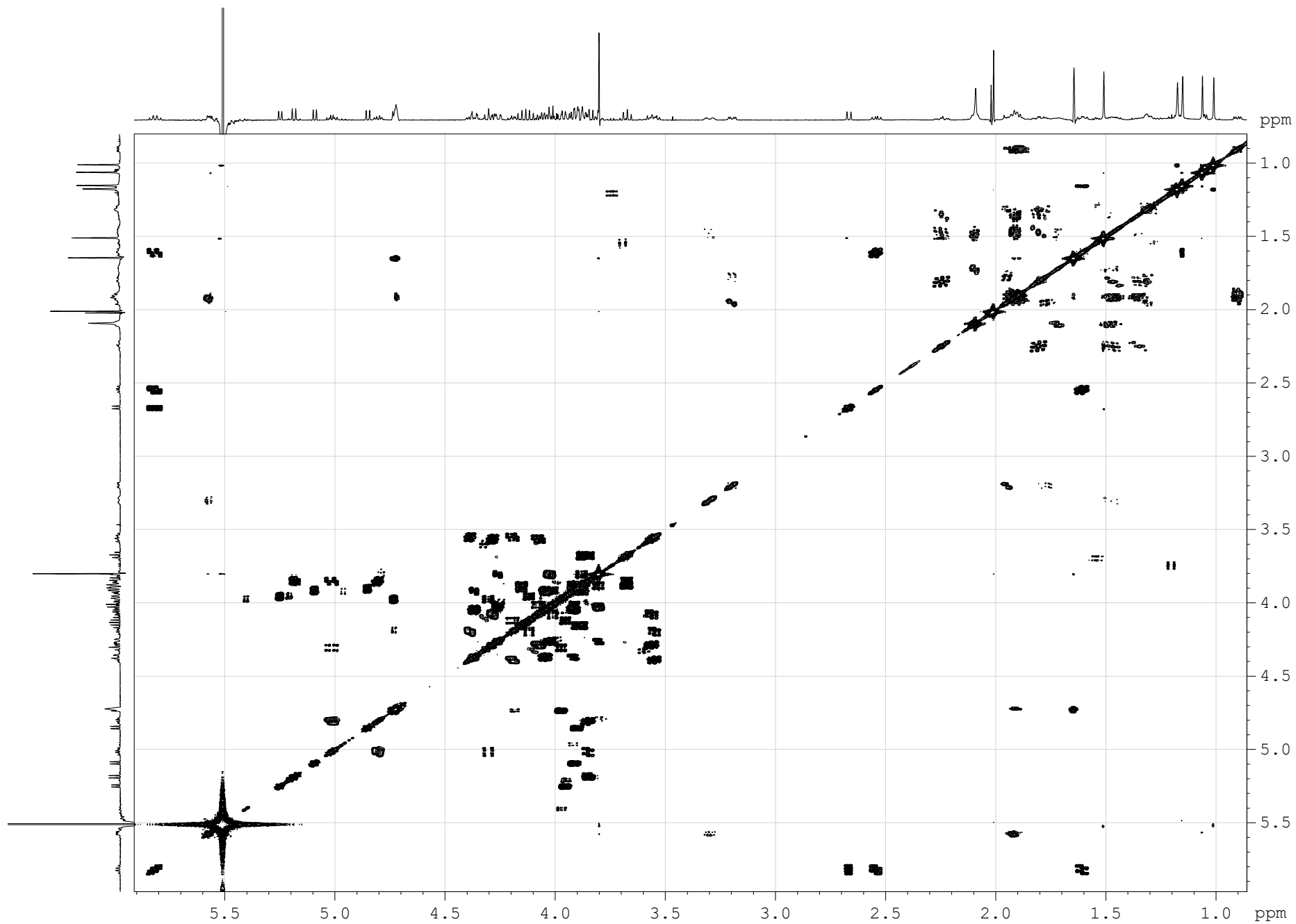


Figure S3. The COSY (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

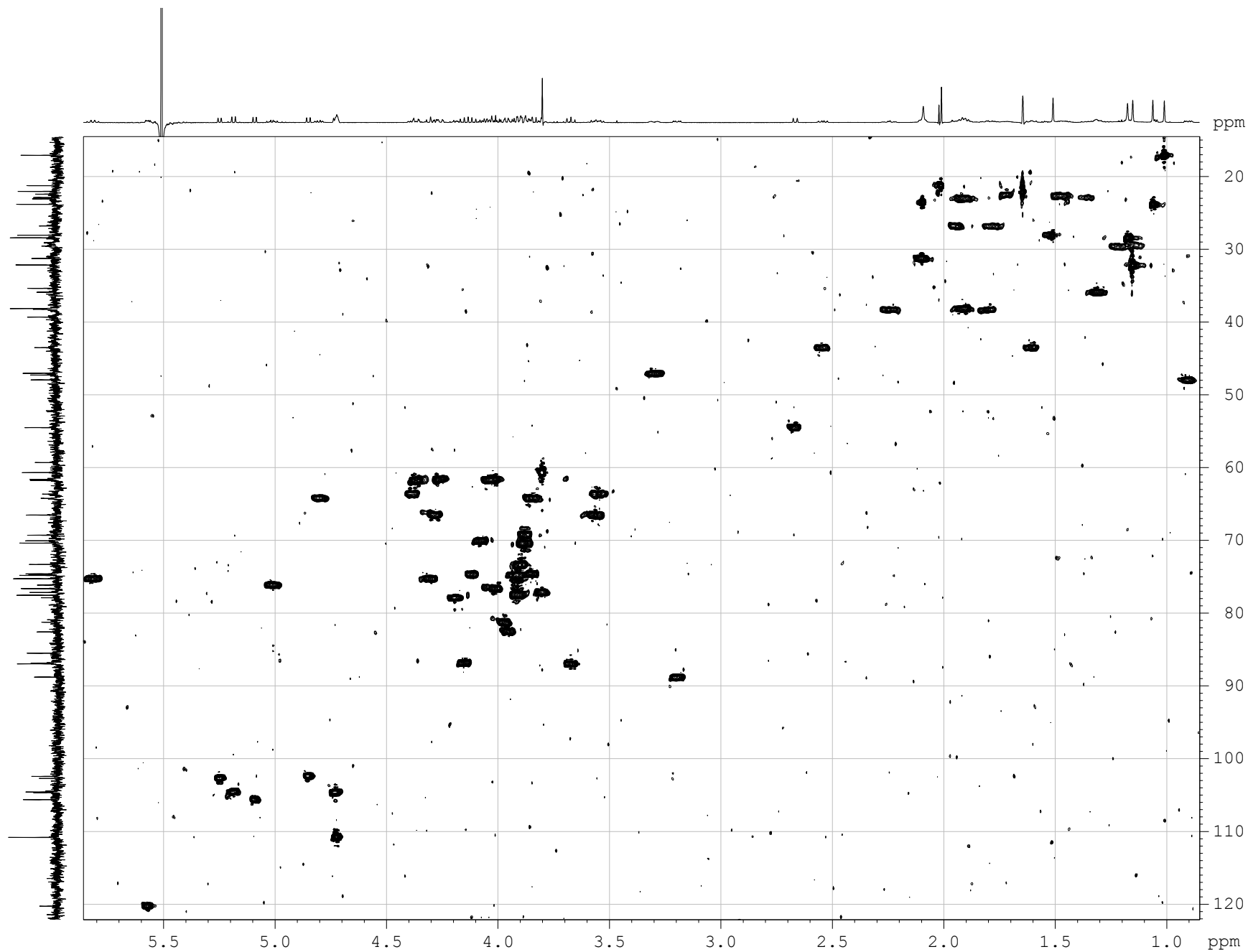


Figure S4. The HSQC (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

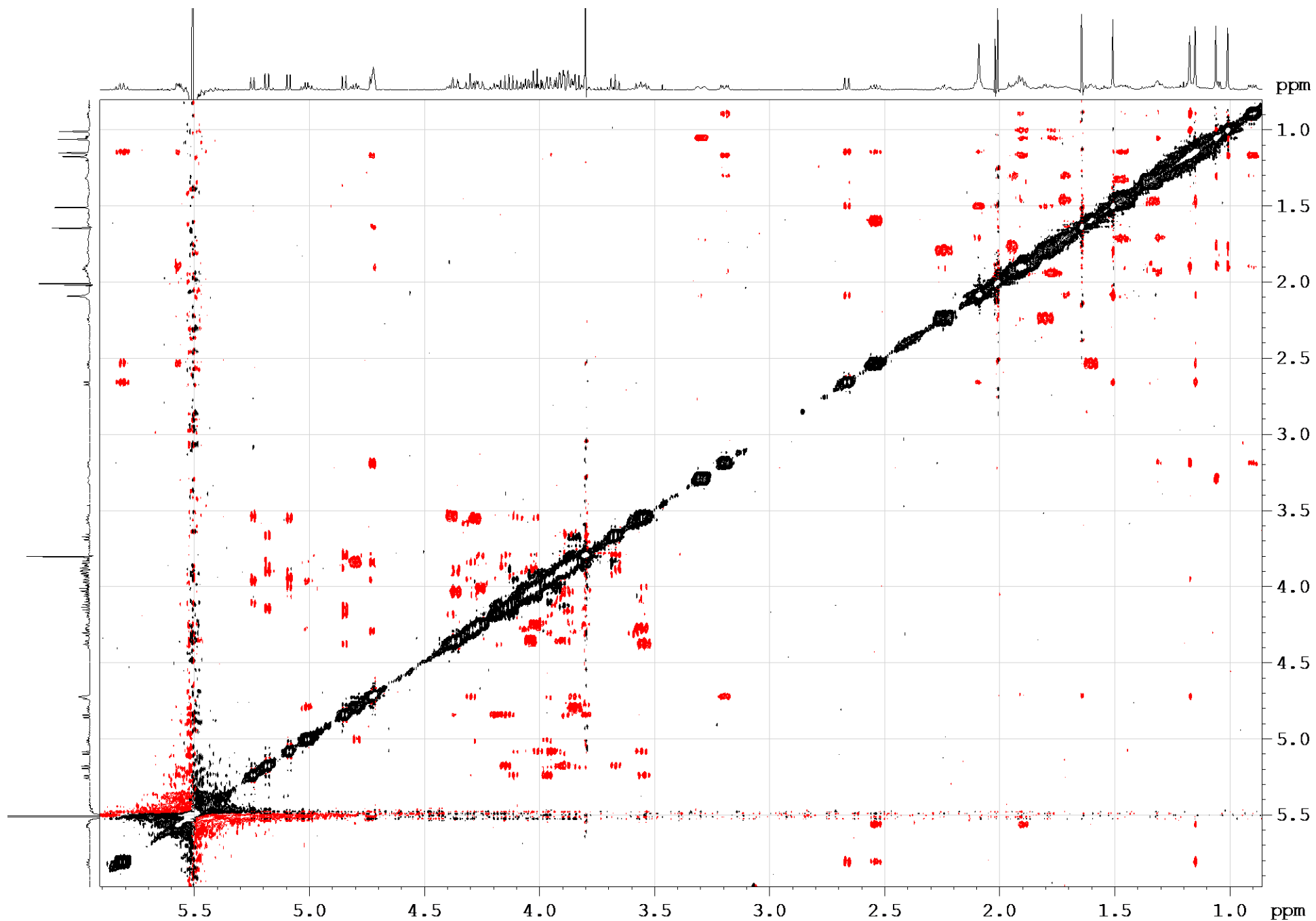


Figure S5. The ROESY (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

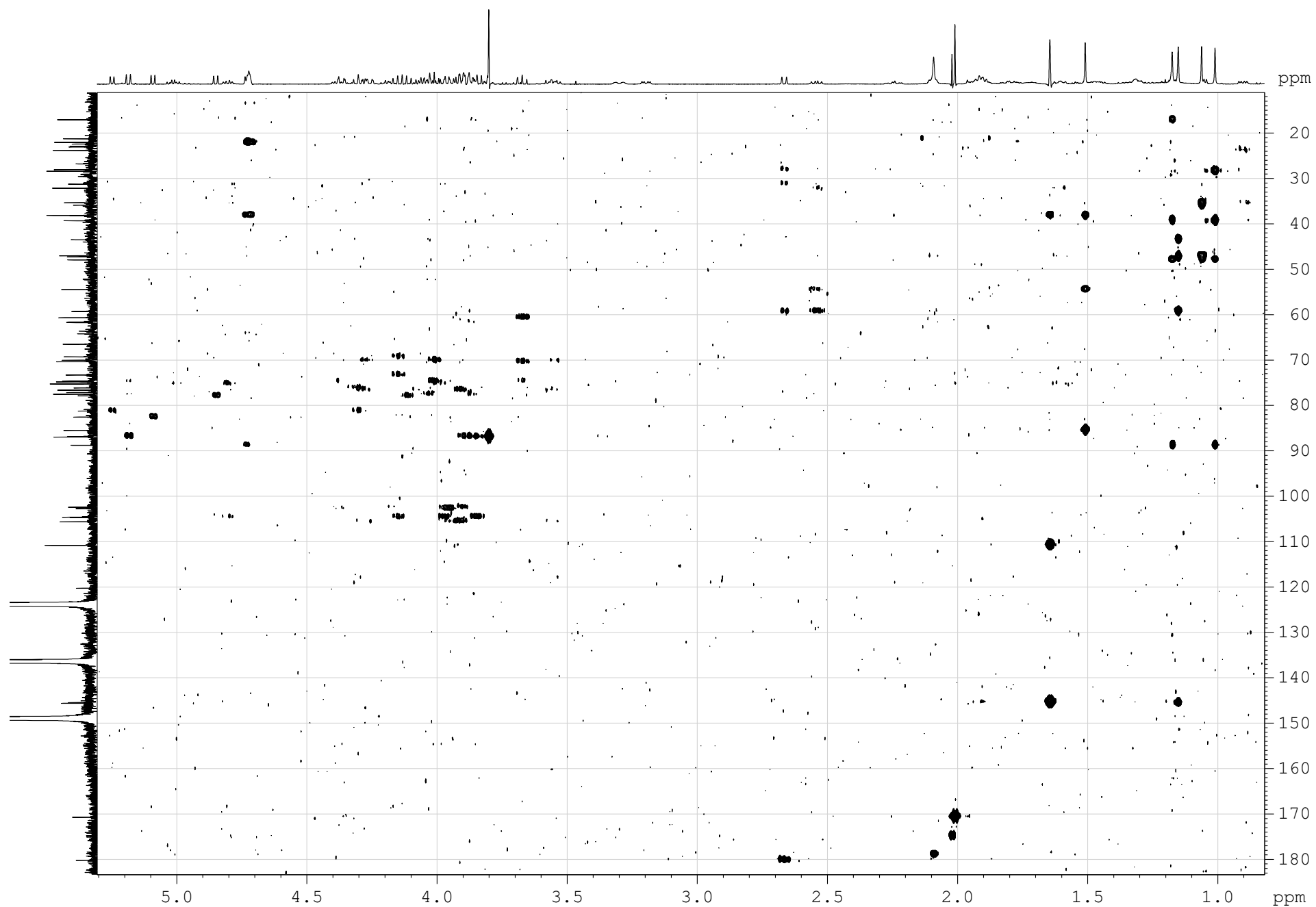


Figure S6. The HMBC (500.12 MHz) spectrum of djakonovioside C<sub>1</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

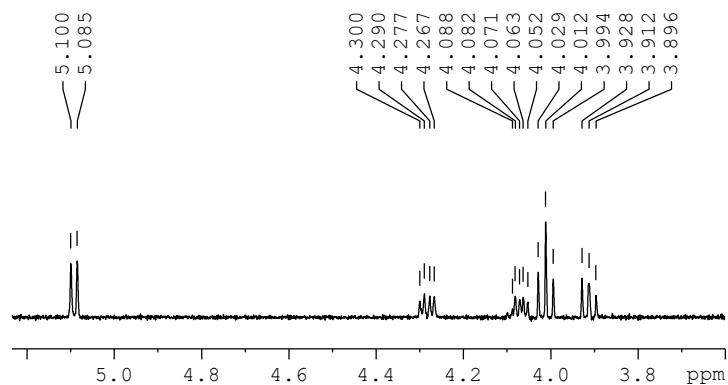
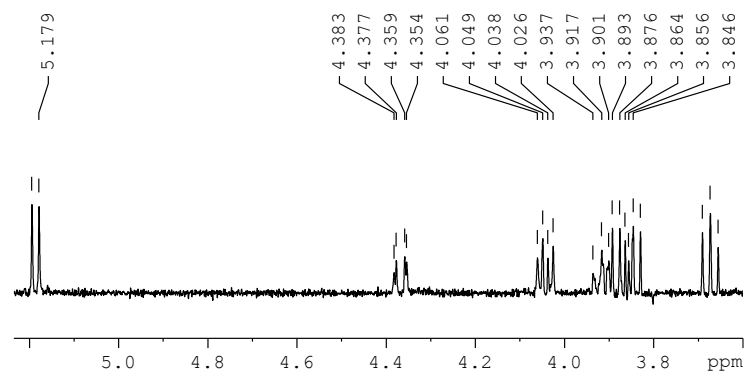
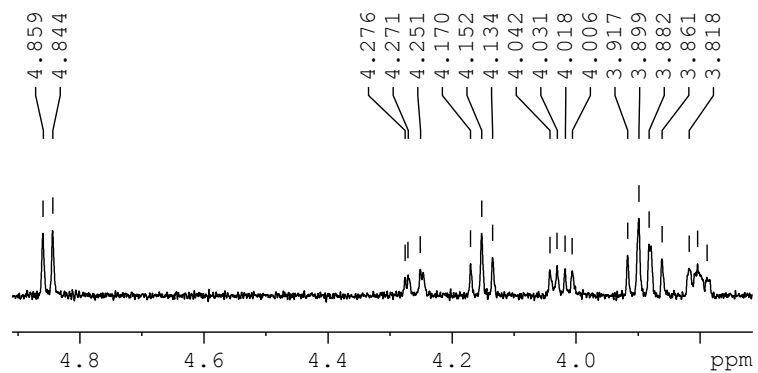
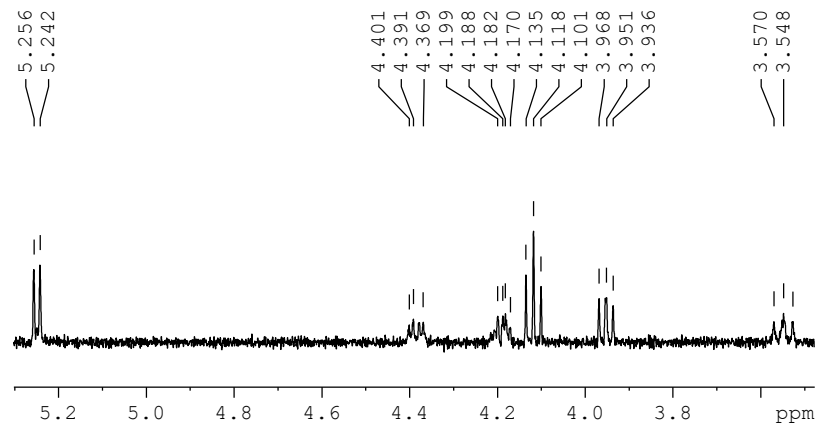
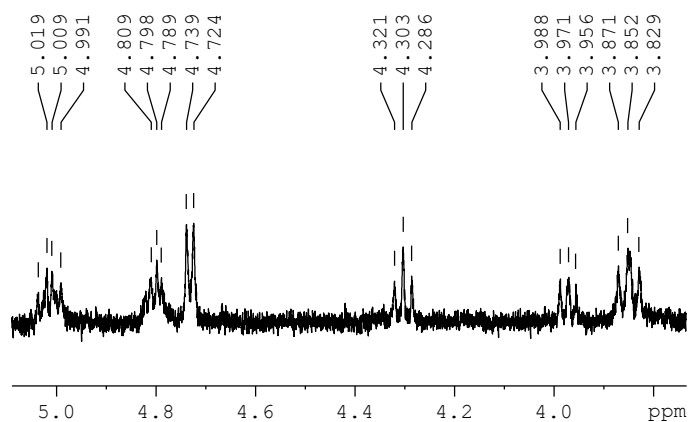


Figure S7. 1 D TOCSY (500.12 MHz) spectra of Xyl1, Xyl2, Glc3, MeGlc4, Xyl5 of djakonovioside C<sub>1</sub> (1) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

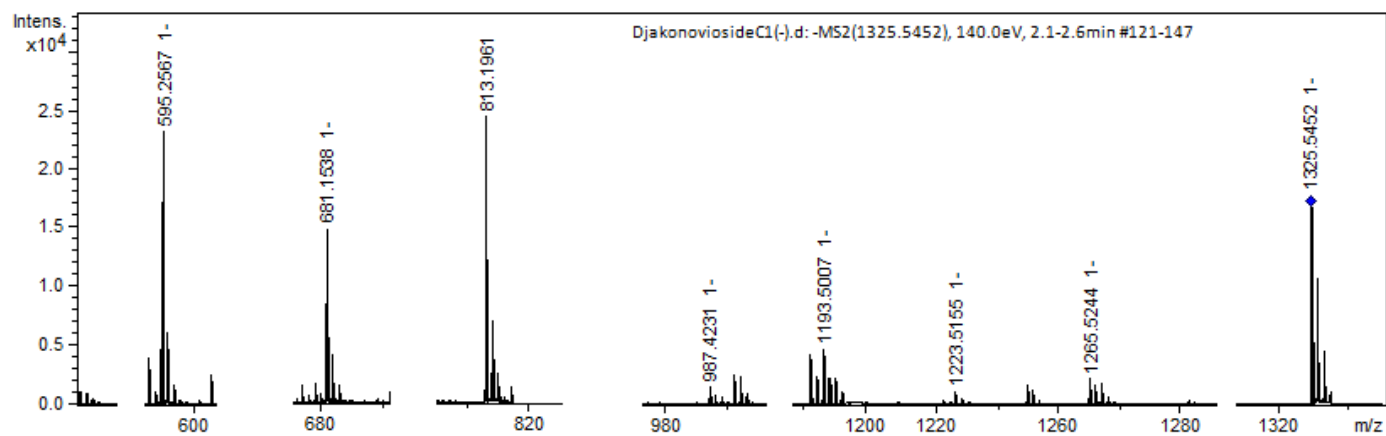
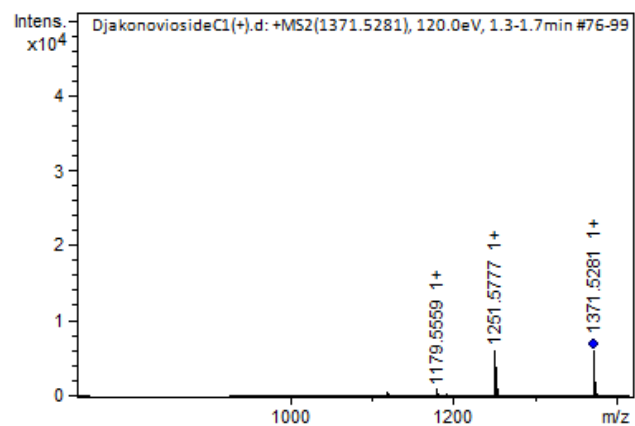
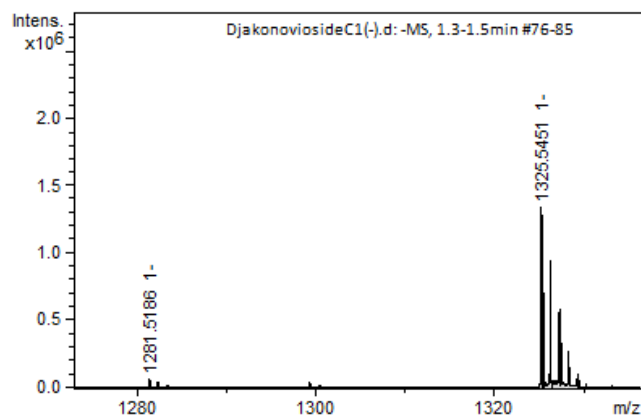


Figure S8. HR-ESI-MS and ESI-MS/MS spectra of djakonovioside C<sub>1</sub> (**1**)

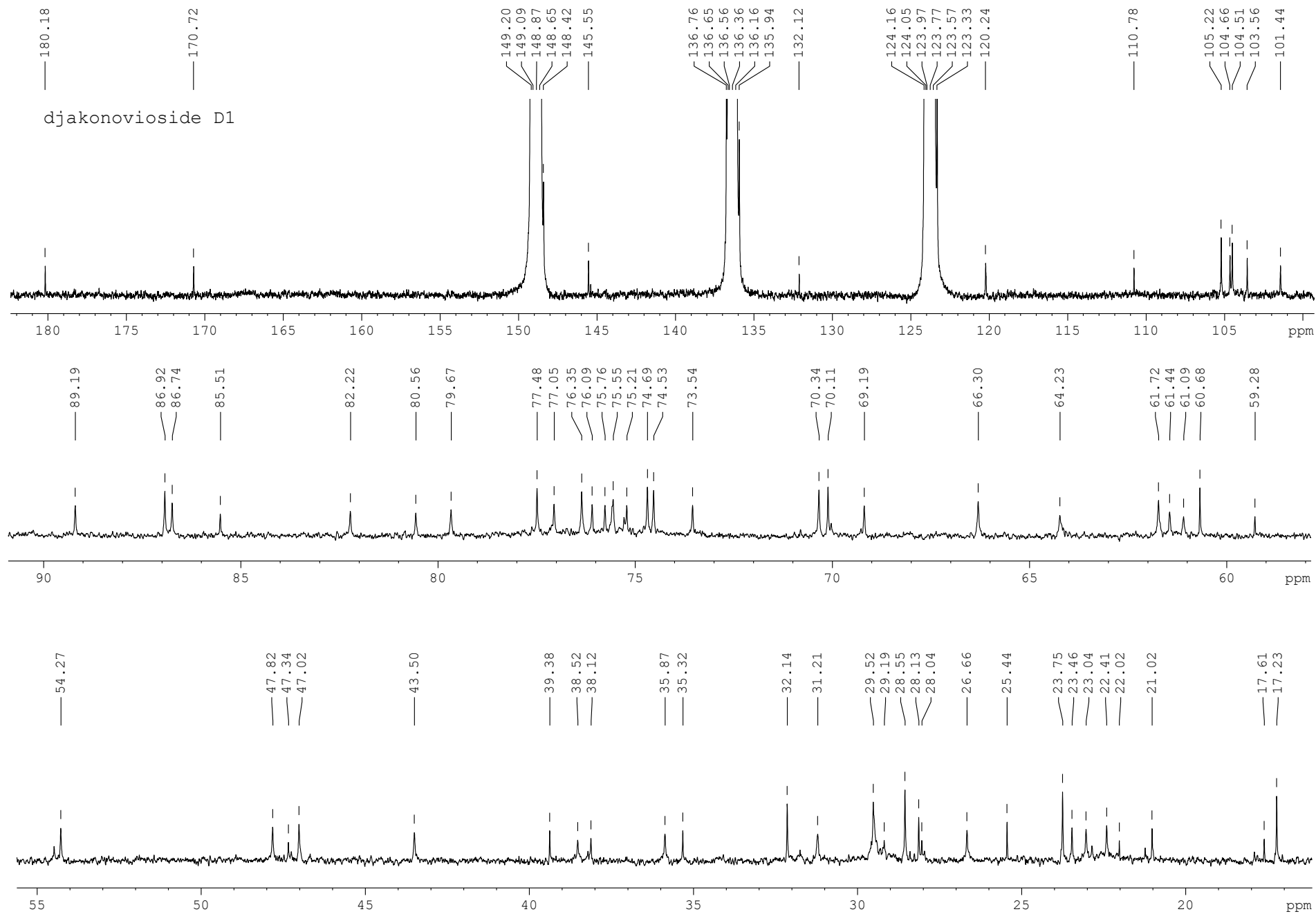


Figure S9. The  $^{13}\text{C}$  NMR (125.67 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)



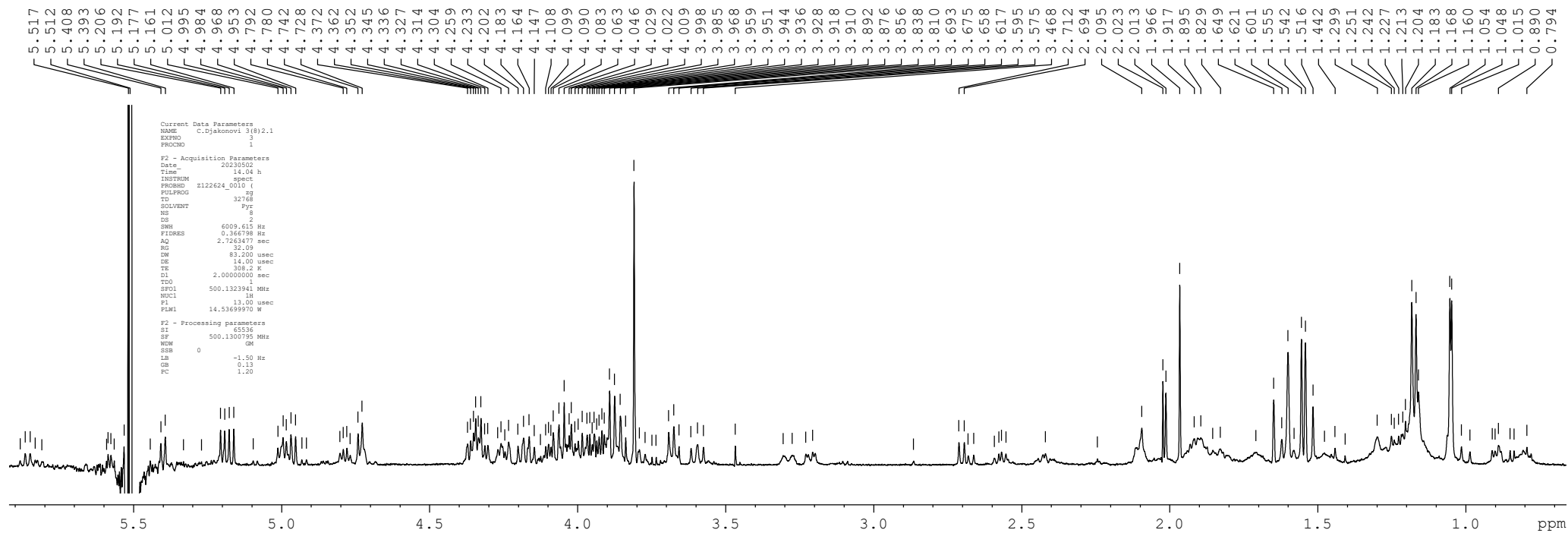


Figure S10. The  $^1\text{H}$  NMR (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

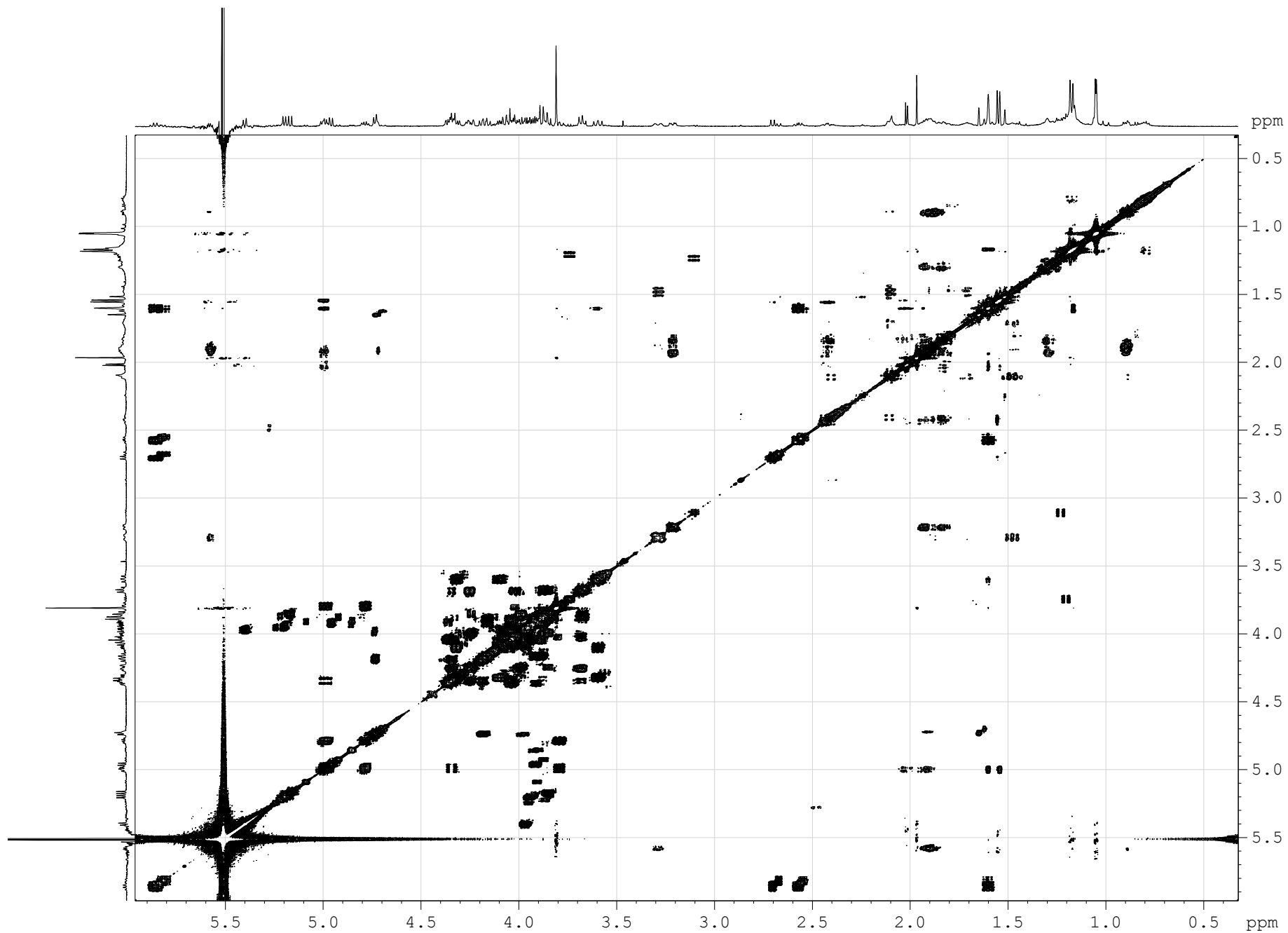


Figure S11. The COSY (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

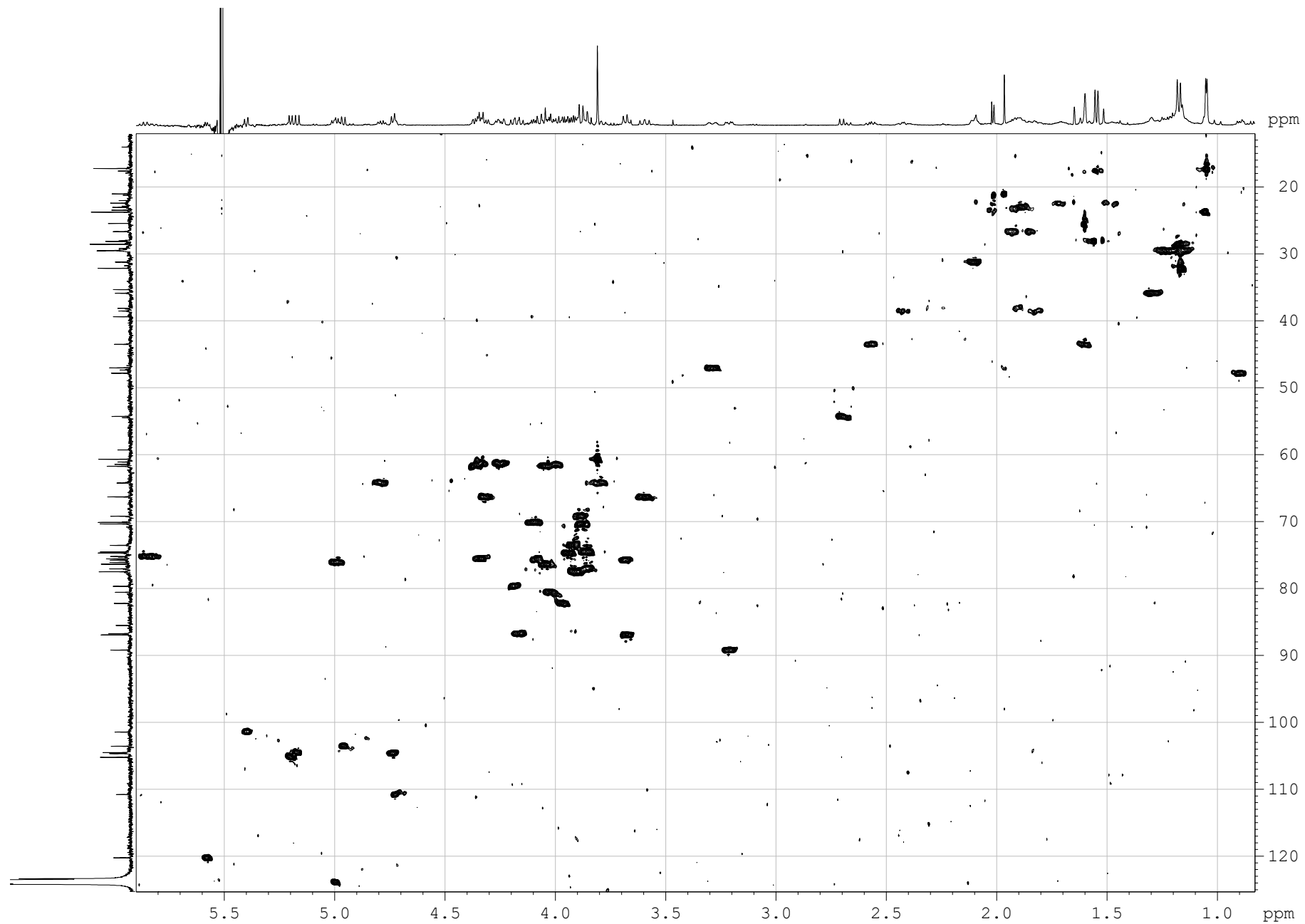


Figure S12. The HSQC (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

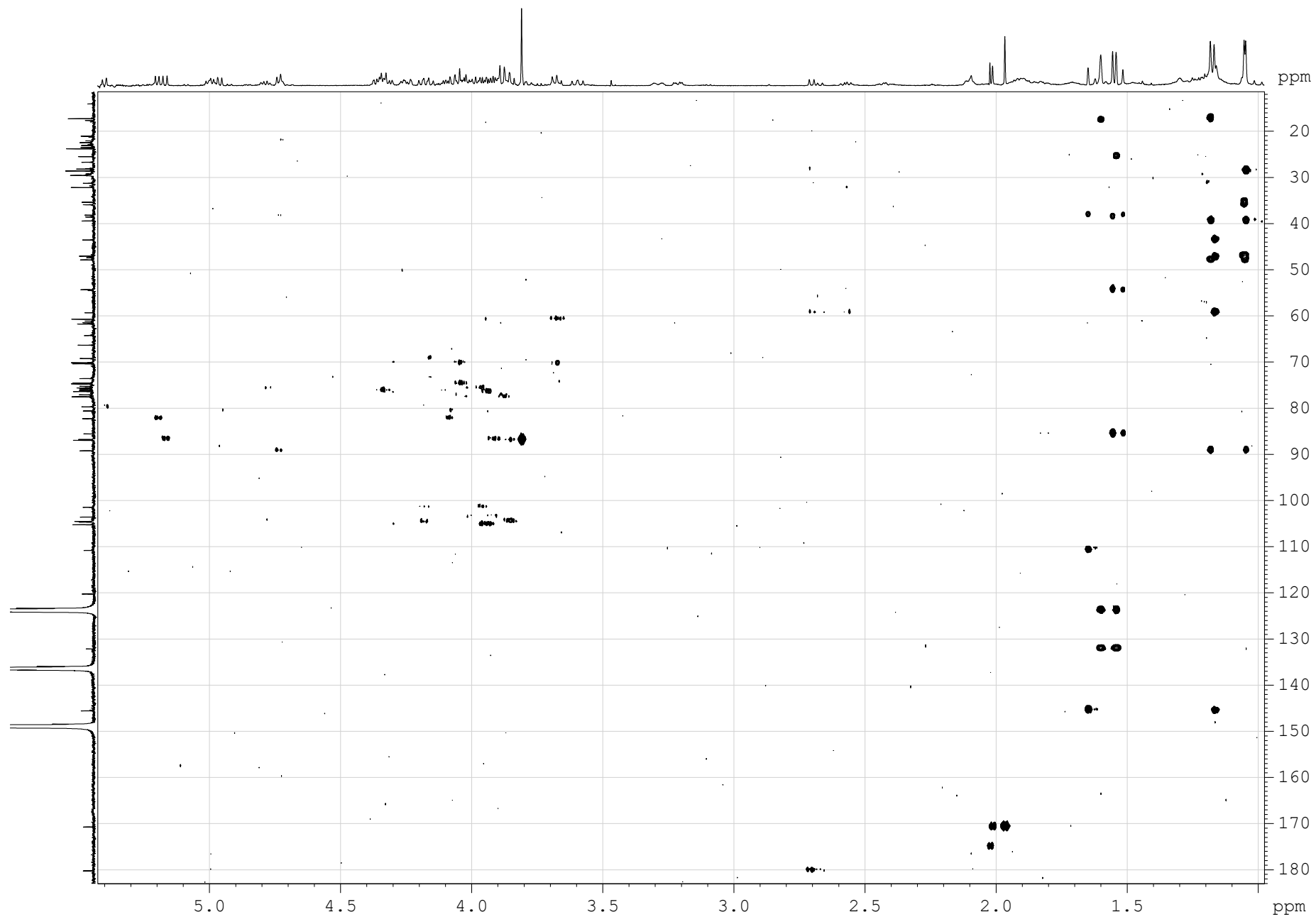


Figure S13. The HMBC (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

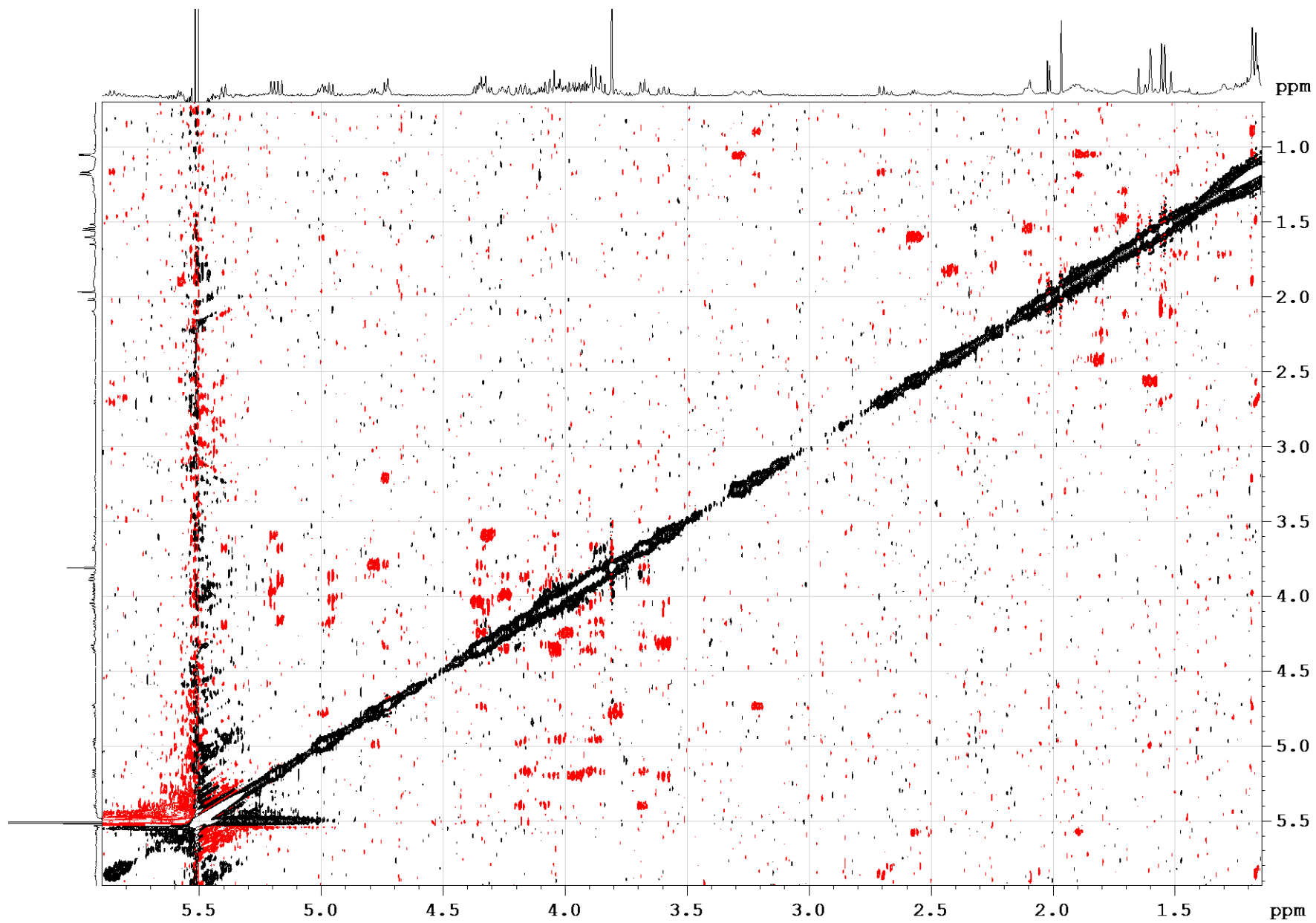


Figure S14. The ROESY (500.12 MHz) spectrum of djakonovioside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

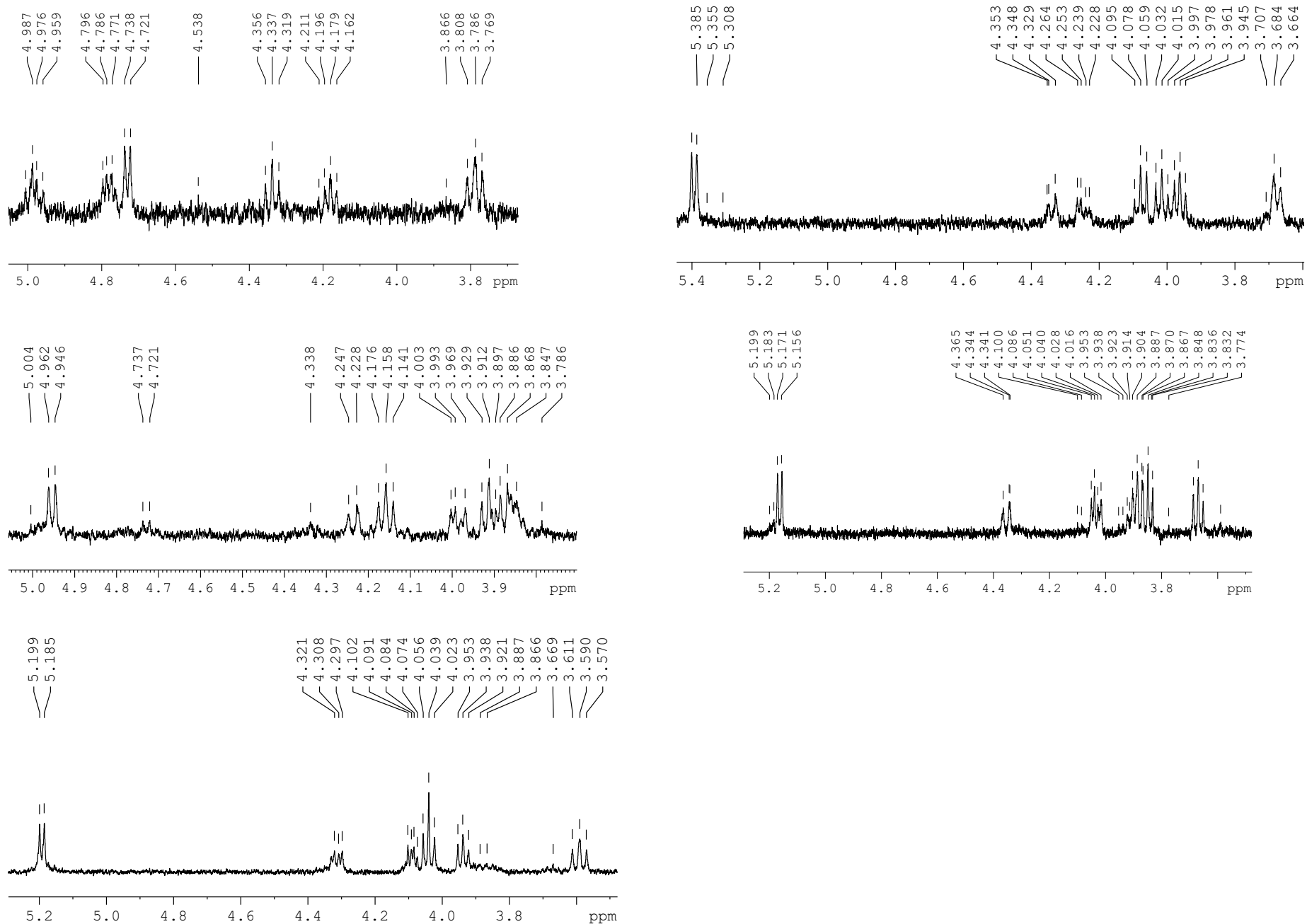


Figure S15. 1D TOCSY (500.12 MHz) spectra of Xyl1, Glc2, Glc3, MeGlc4, Xyl5 of djakonovioside D<sub>1</sub> (2) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

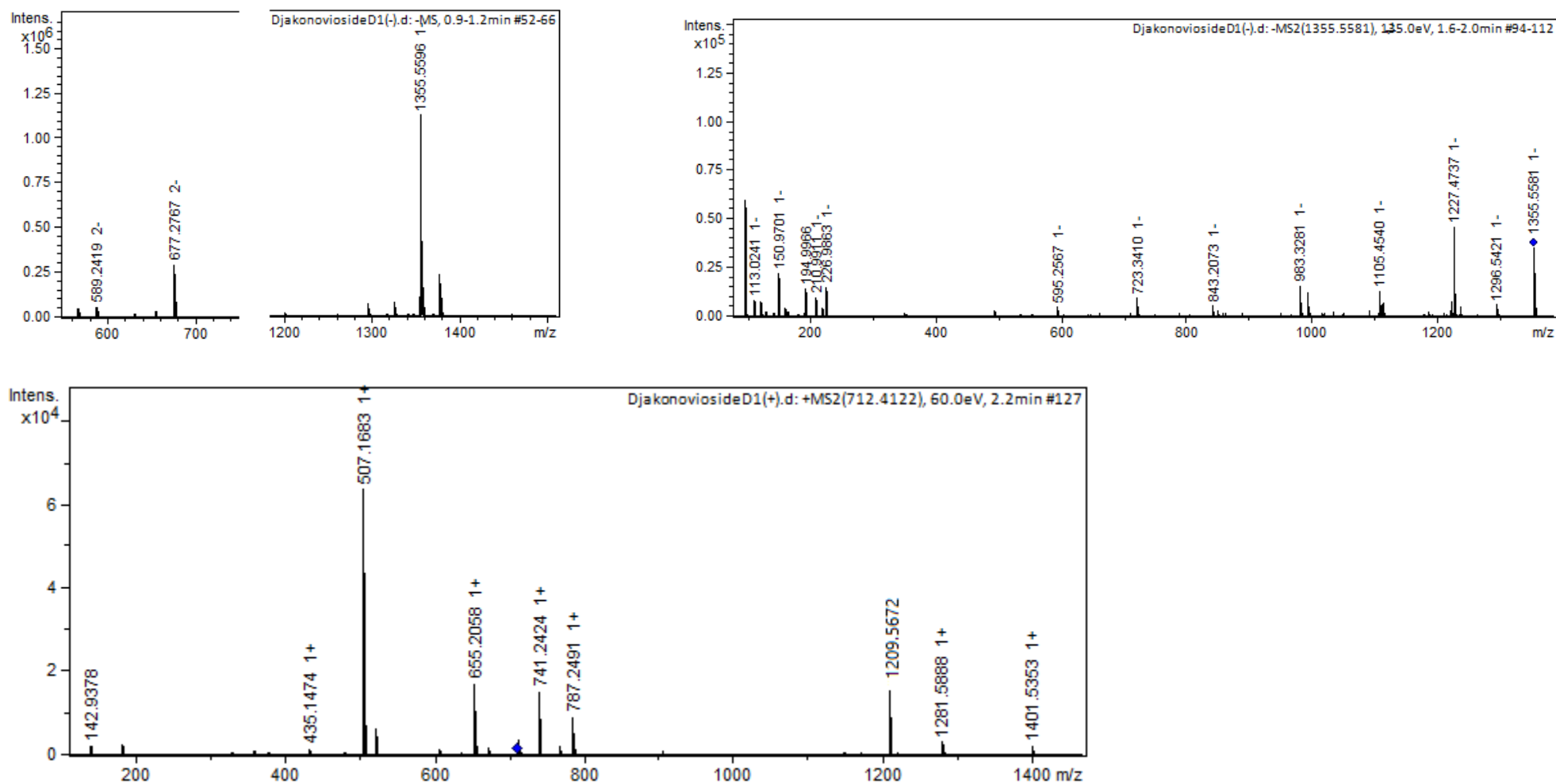


Figure S16. HR-ESI-MS and ESI-MS/MS spectra of djakonovioside D<sub>1</sub> (2)

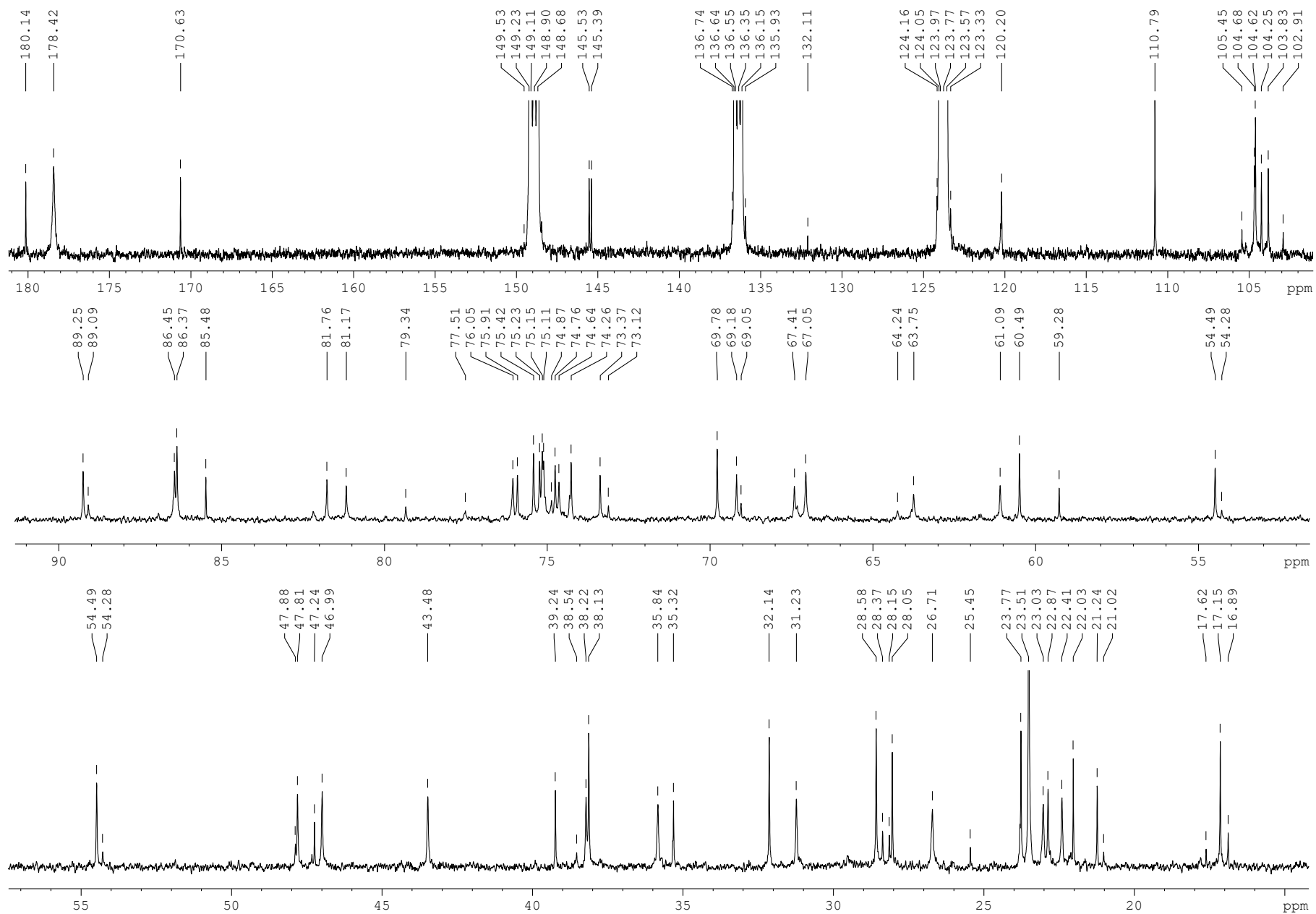


Figure S17. The  $^{13}\text{C}$  NMR (125.67 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)



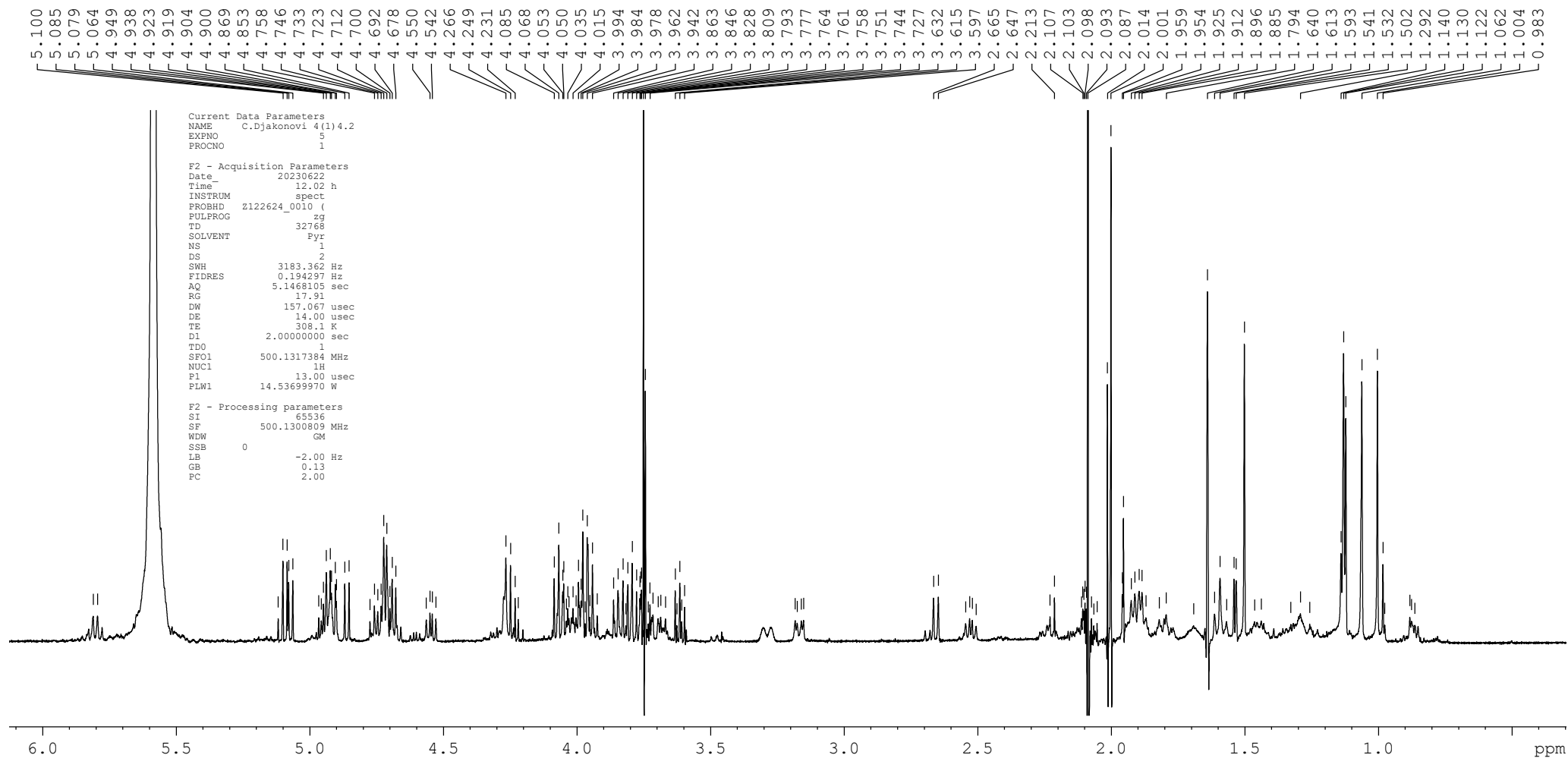


Figure S18. The  $^1\text{H}$  NMR (500.12 MHz) spectrum of djakonovioside  $\text{E}_1$  (**3**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

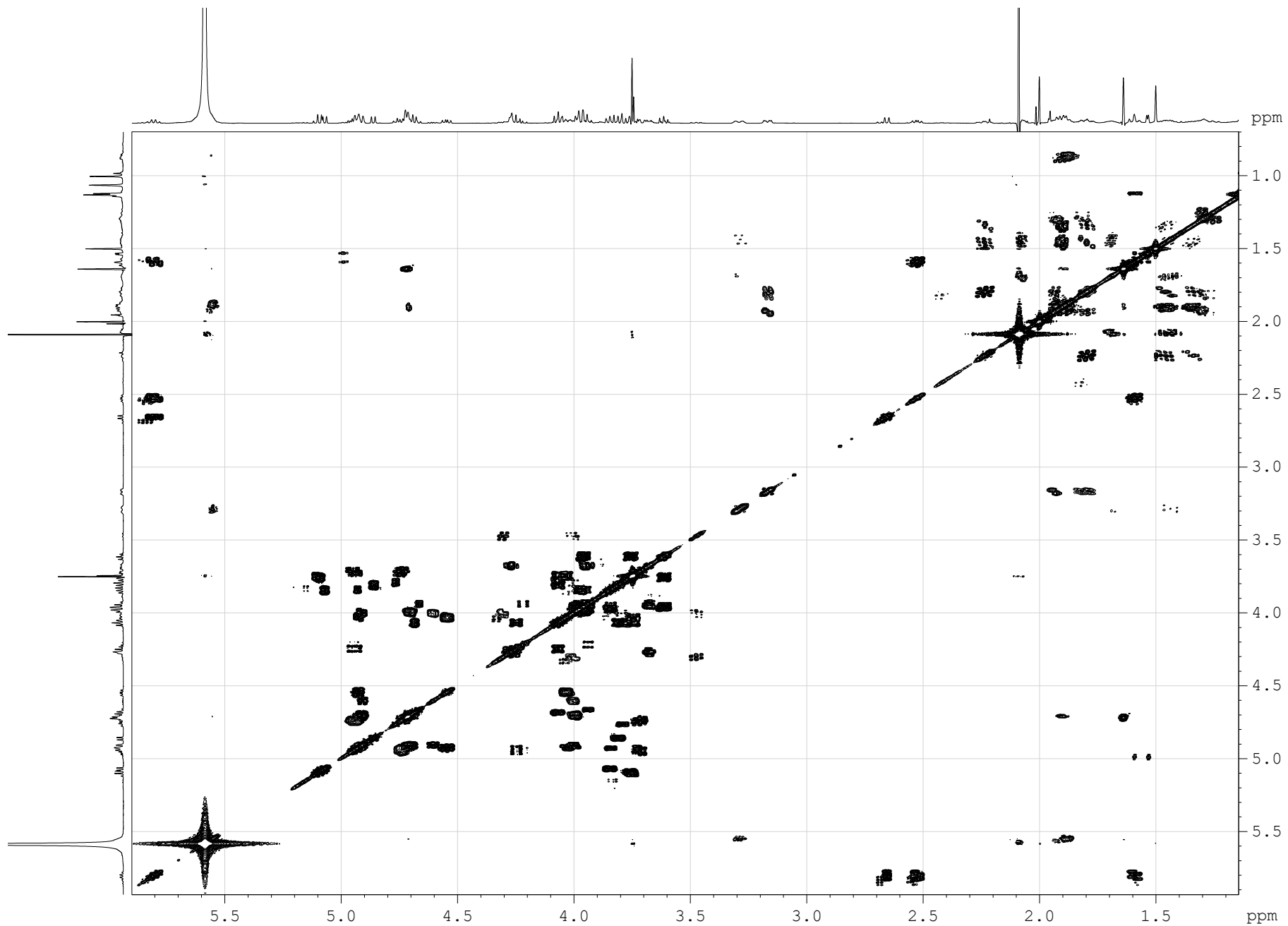


Figure S19. The COSY (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (3) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

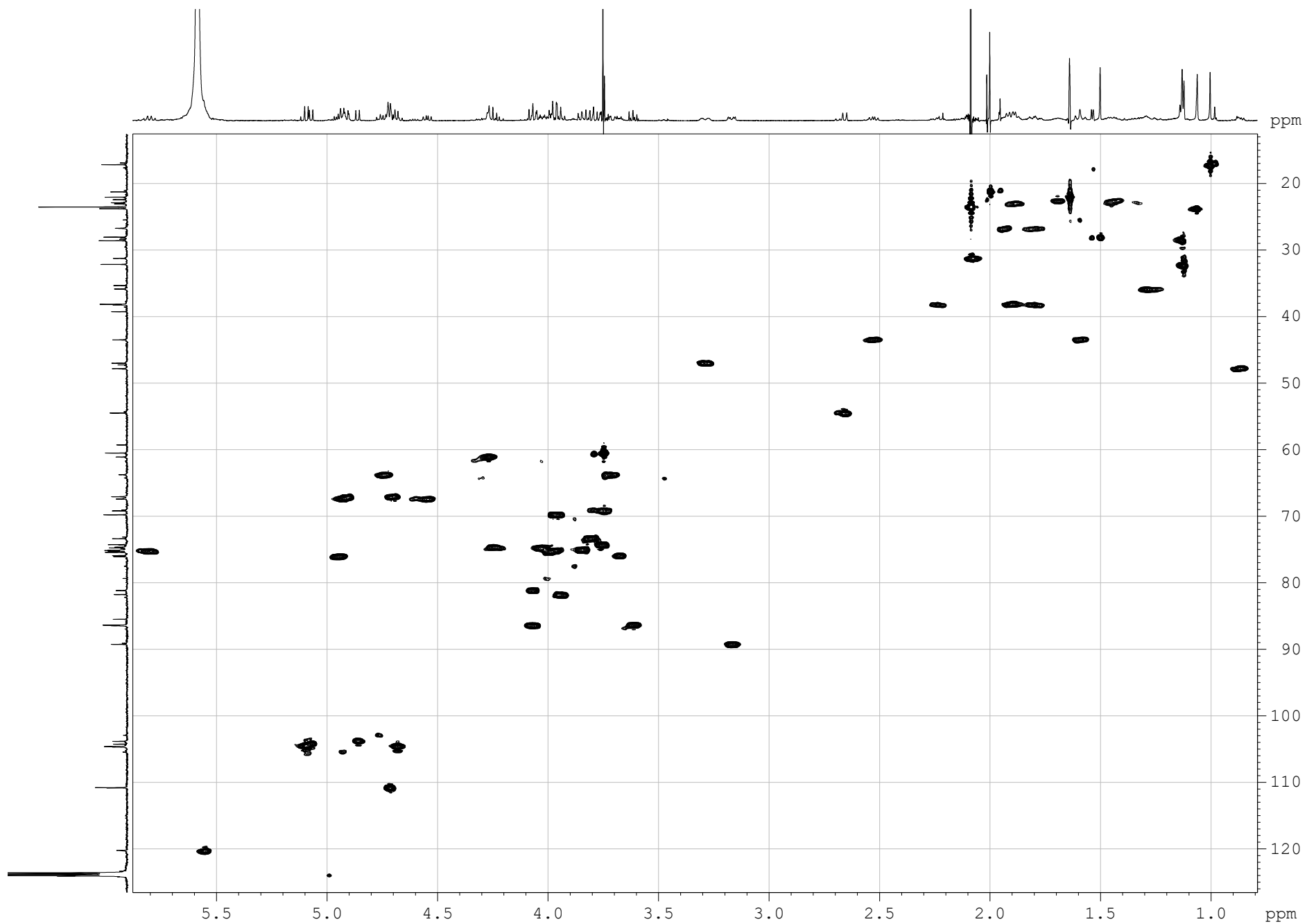


Figure S20. The HSQC (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

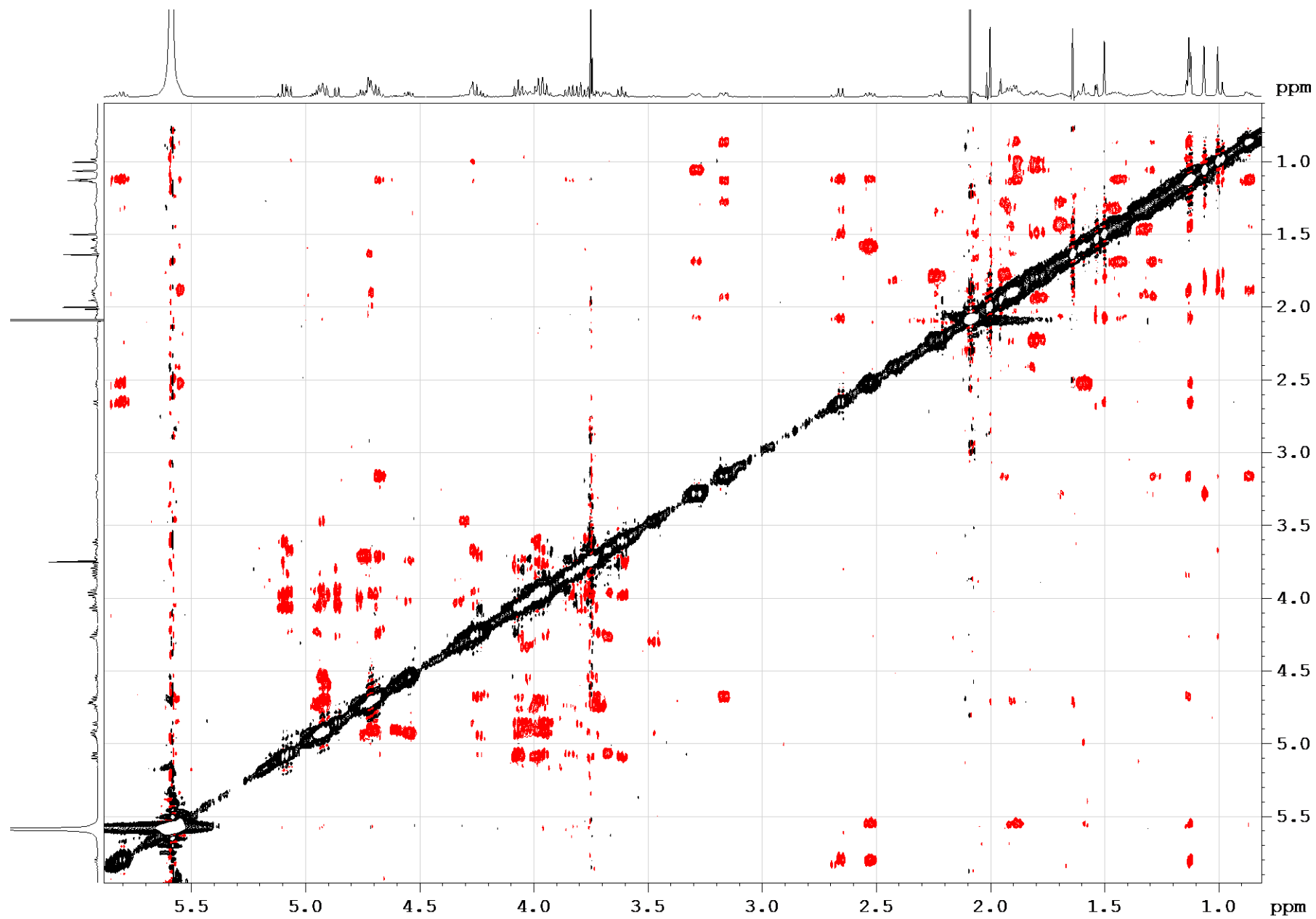


Figure S21. The ROESY (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (3) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

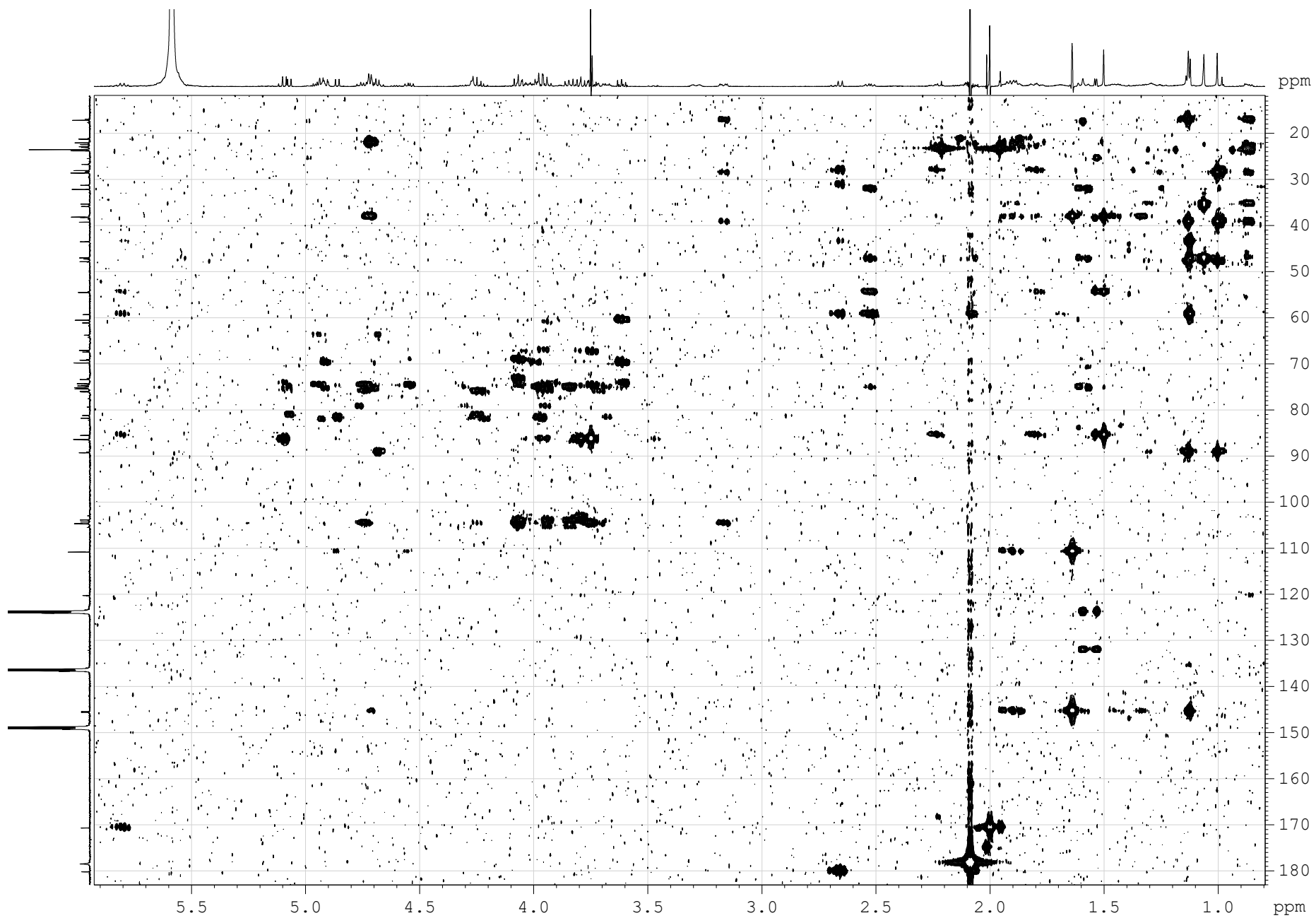


Figure S22. The HMBC (500.12 MHz) spectrum of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

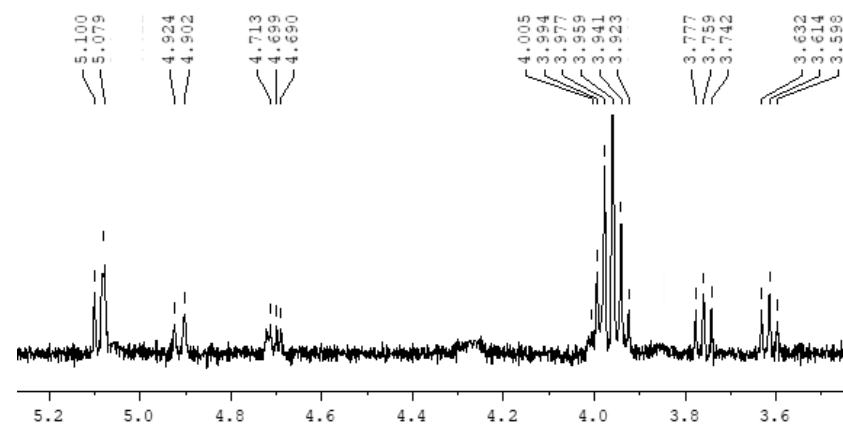
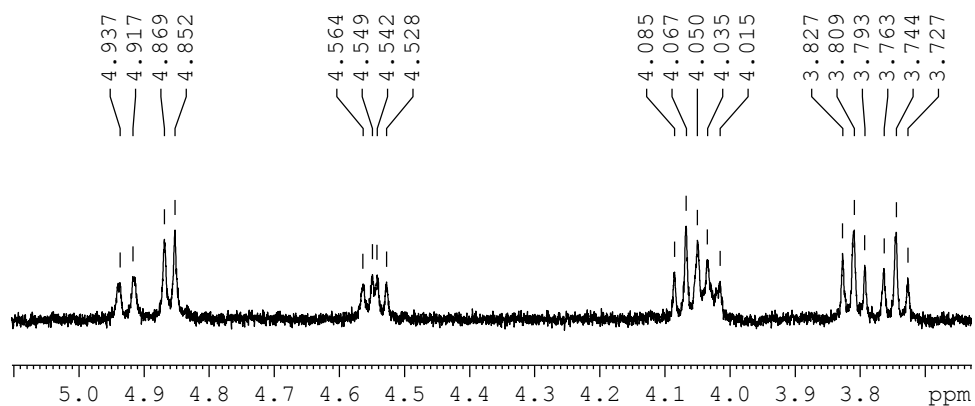
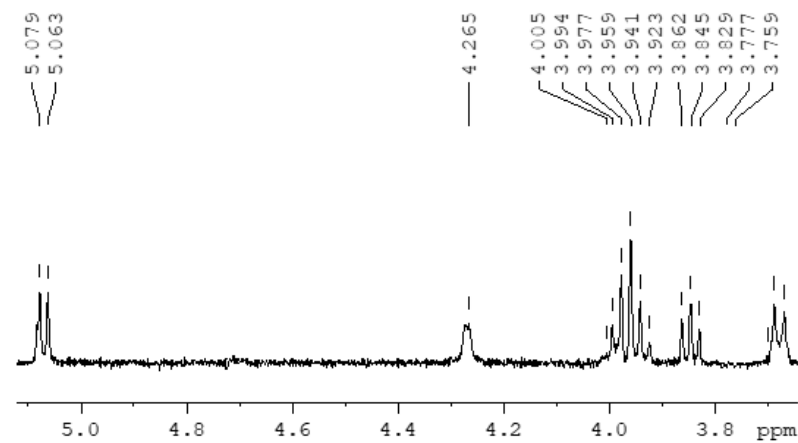
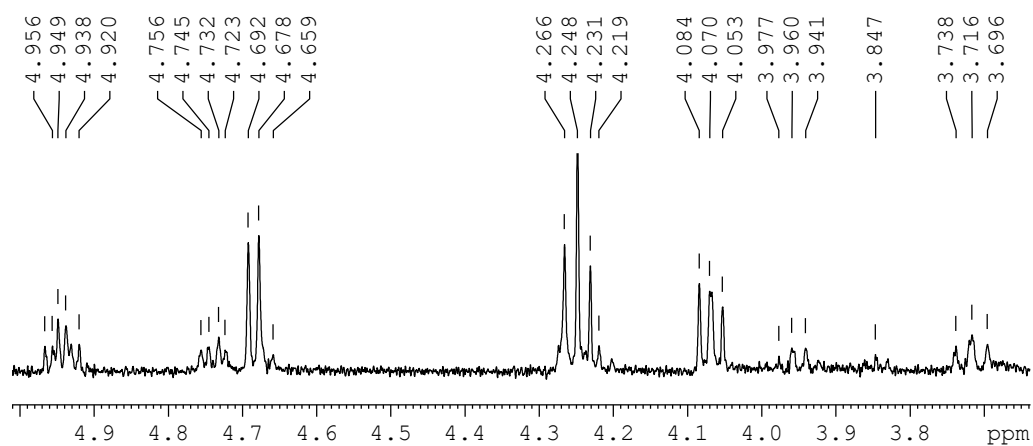


Figure S23. 1D TOCSY (500.12 MHz) spectra of Xyl1, Glc2, Glc3, MeGlc4 of djakonovioside E<sub>1</sub> (**3**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

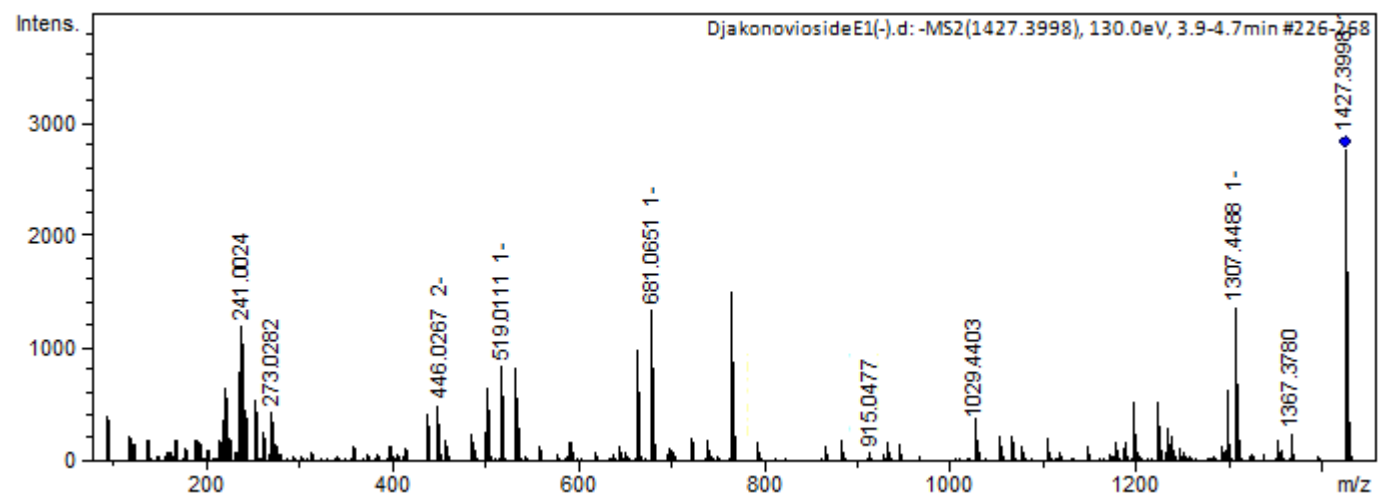
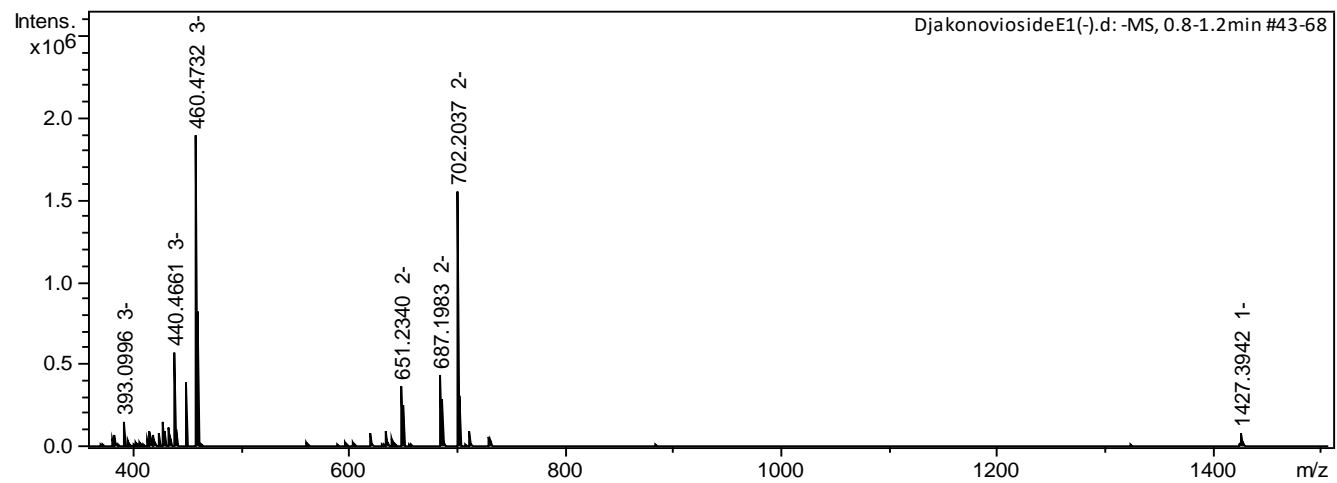


Figure S24. HR-ESI-MS and ESI-MS/MS spectra of djakonovioside E<sub>1</sub> (3)

Table S1. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of the aglycone part of djakonovioside E<sub>1</sub> (**3**)

Position	$\delta_C$ mult. <sup>a</sup>	$\delta_H$ mult. (J in Hz) <sup>b</sup>	HMBC	ROESY
1	35.8 CH <sub>2</sub>	1.29 m		H-3, H-11, H-19
2	26.7 CH <sub>2</sub>	1.93 m 1.80 m		
3	89.3 CH	3.17 dd (4.1; 11.6)		H-1, H-5, H-31, H1-Xyl1
4	39.2 C			
5	47.9 CH	0.87 dd (6.6; 12.4)	C: 19	H-1, H-3, H-31
6	23.0 CH <sub>2</sub>	1.89 m		
7	120.4 CH	5.55 m		H-15, H-32
8	145.5 C			
9	47.0 CH	3.29 brd (14.0)		H-19
10	35.3 C			
11	22.4 CH <sub>2</sub>	1.68 m 1.44 m		H-1
12	31.2 CH <sub>2</sub>	2.07 m		H-17, H-21, H-32
13	59.3 C			
14	47.2 C			
15	43.5 CH <sub>2</sub>	2.53 dd (7.4; 12.4) 1.59 brt (12.4)	C: 13, 14, 17, 32	H-7, H-32
16	75.2 CH	5.80 dd (8.5; 16.8)		H-32
17	54.5 CH	2.66 d (9.1)	C: 12, 13, 18, 21	H-12, H-16, H-21, H-32
18	180.1 C			
19	23.8 CH <sub>3</sub>	1.06 s	C: 5, 9, 10	H-1, H-2, H-6, H-9
20	85.5 C			
21	28.0 CH <sub>3</sub>	1.50 s	C: 17, 20, 22	H-12, H-17, H-22
22	38.2 CH	2.23 m 1.80 m		H-21
23	22.9 CH <sub>2</sub>	1.47 m 1.35 m		
24	38.1 CH <sub>2</sub>	1.90 m		
25	145.4 C			
26	110.8 CH <sub>2</sub>	4.72 m	C: 24, 27	H-24
27	22.0 CH <sub>3</sub>	1.64 s	C: 24, 25, 26	
30	17.1 CH <sub>3</sub>	1.00 s	C: 3, 4, 5, 31	H-2, H-6, H-31
31	28.6 CH <sub>3</sub>	1.13 s	C: 3, 4, 5, 30	H-3, H-5, H-6, H-30, H-1 Xyl1
32	32.1 CH <sub>3</sub>	1.12 s	C: 8, 13, 14, 15	H-7, H-12, H-15, H-16, H-17
OCOCH <sub>3</sub>	170.6 C			
OCOCH <sub>3</sub>	21.0 CH <sub>3</sub>	2.00 s	OAc	

<sup>a</sup> Recorded at 125.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). <sup>b</sup> Recorded at 500.12 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1).



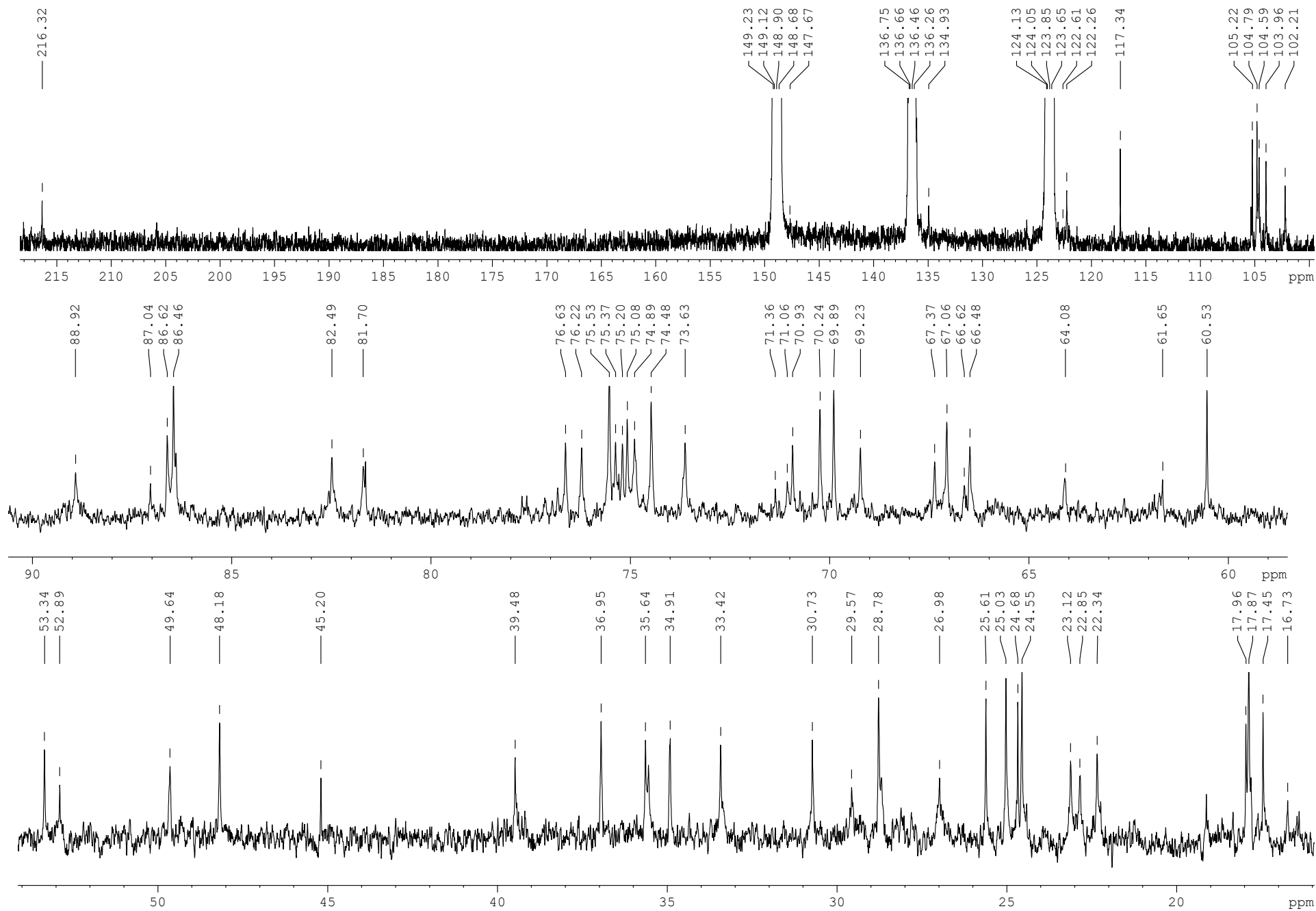


Figure S25. The  $^{13}\text{C}$  NMR (125.67 MHz) spectrum of djakonovioside  $\text{F}_1$  (**4**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

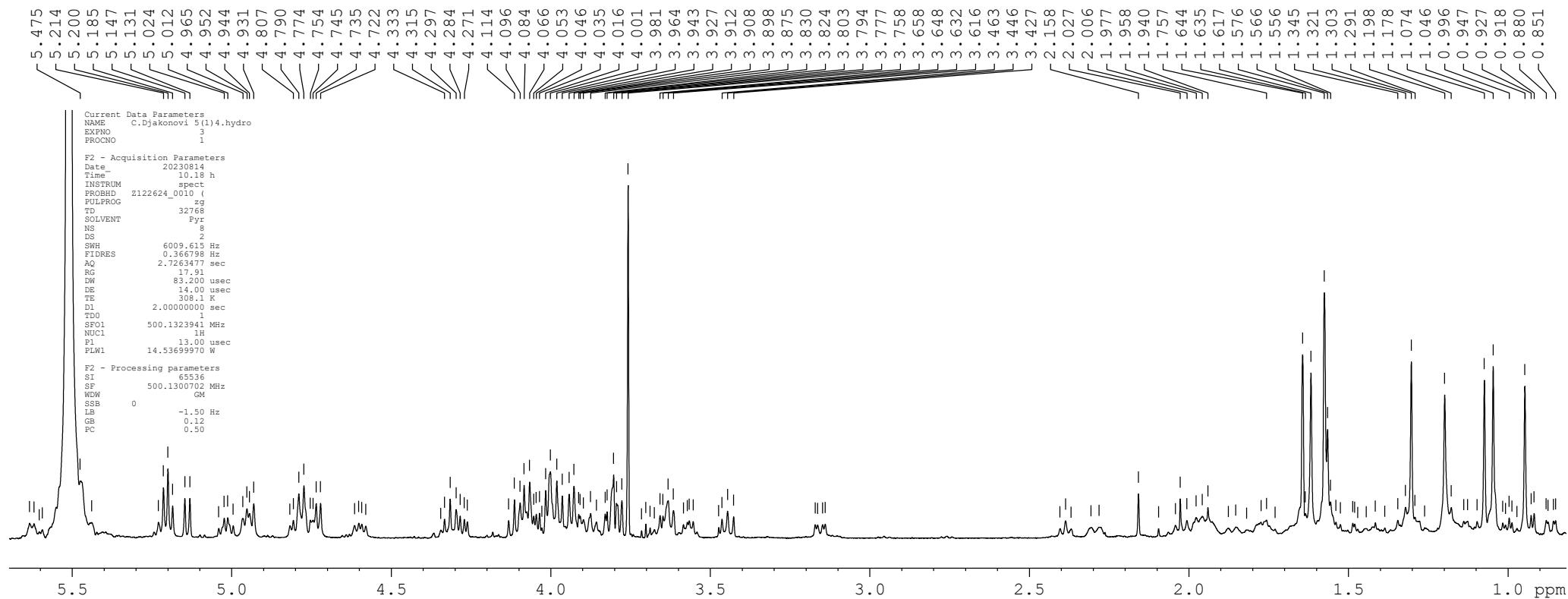


Figure S26. The  $^1\text{H}$  NMR (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

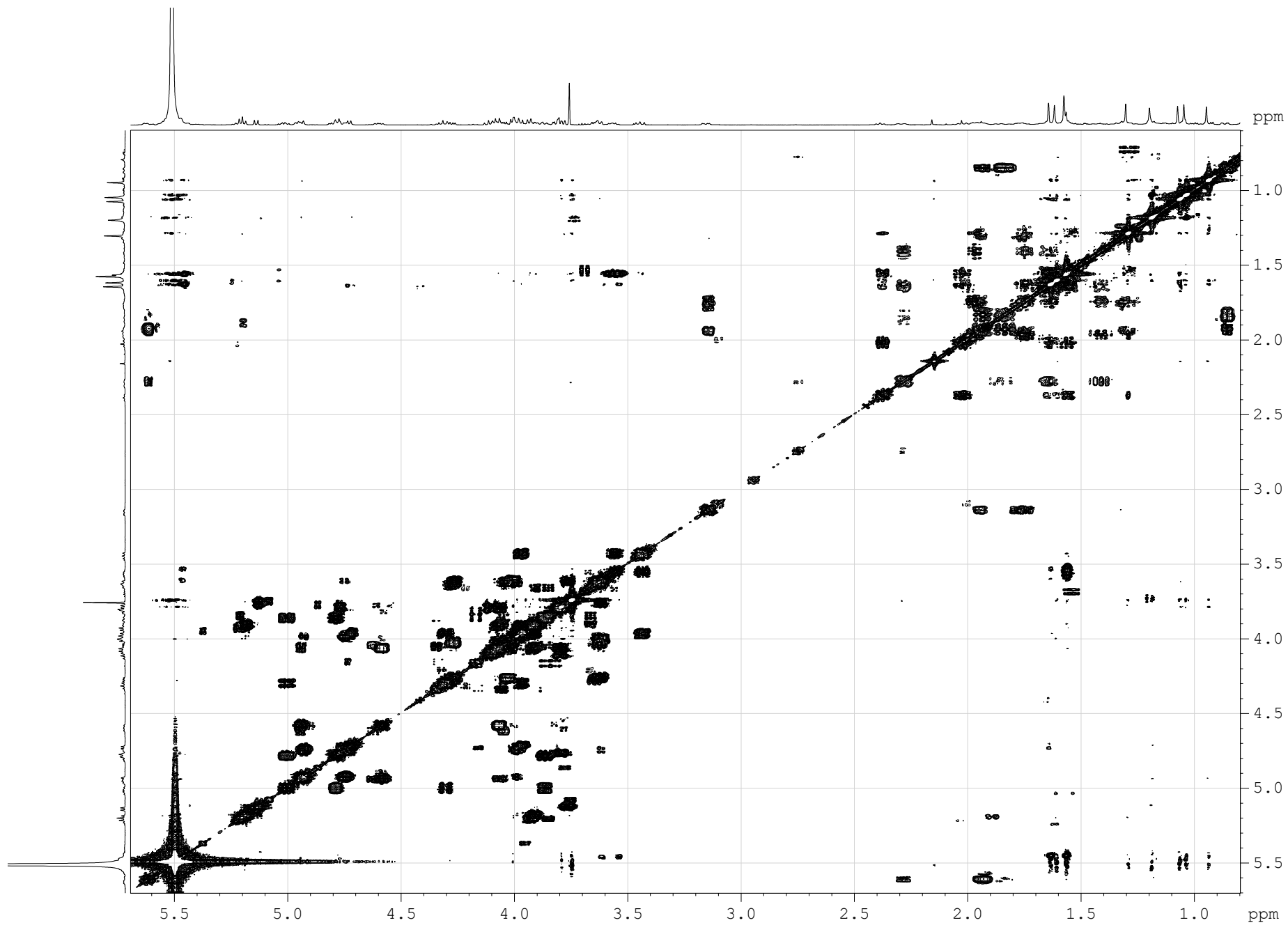


Figure S27. The COSY (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

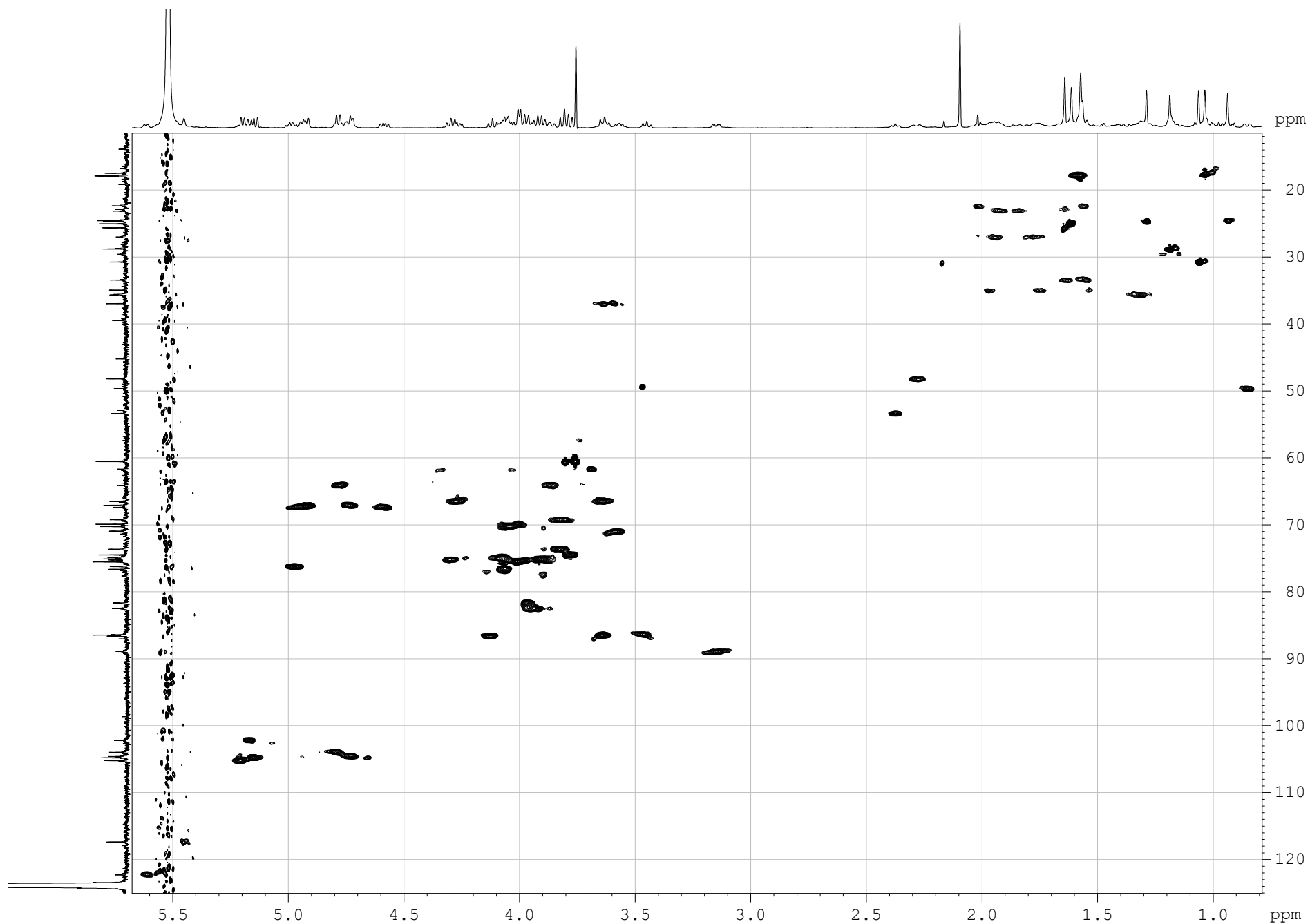


Figure S28. The HSQC (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

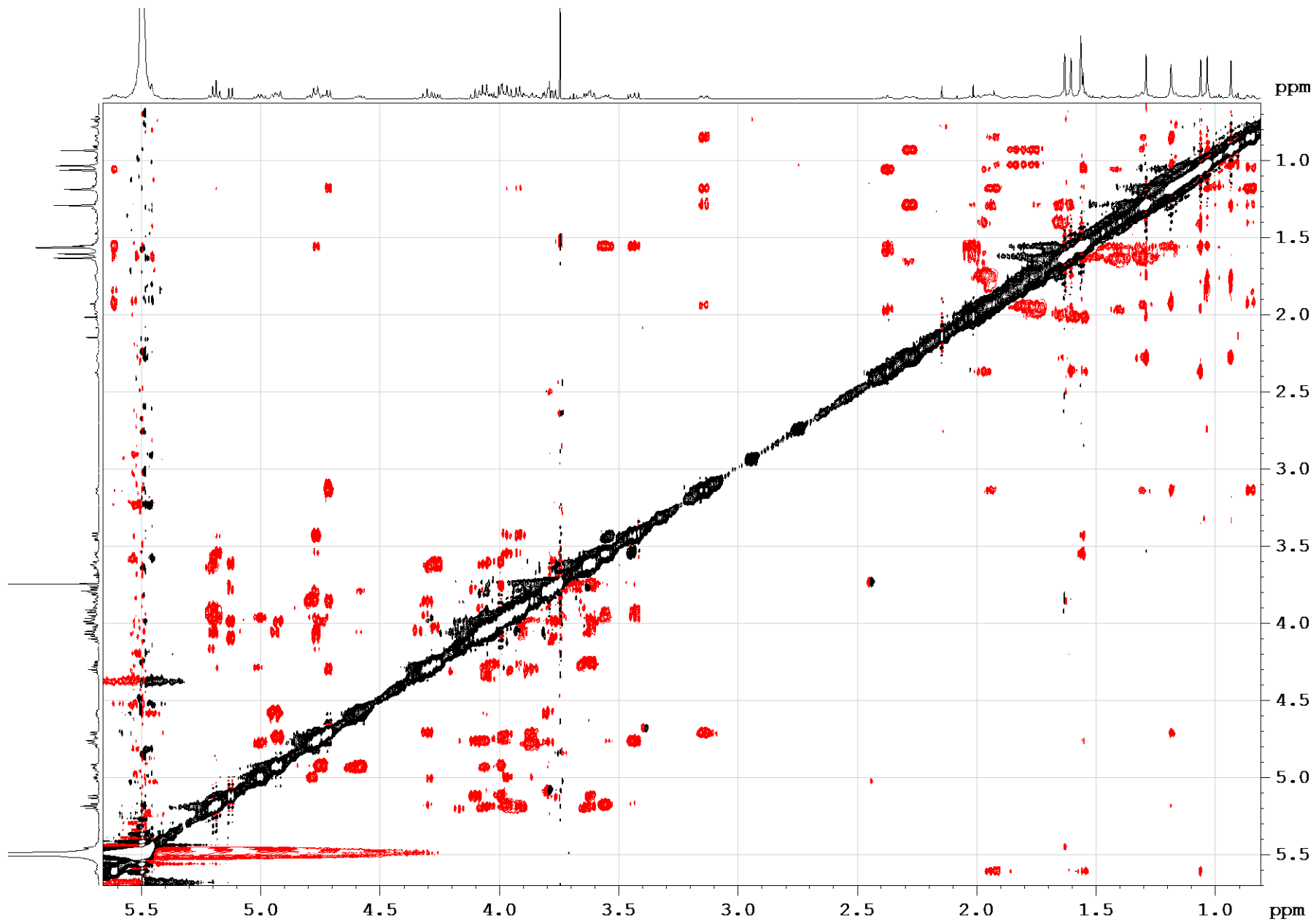


Figure S29. The ROESY (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

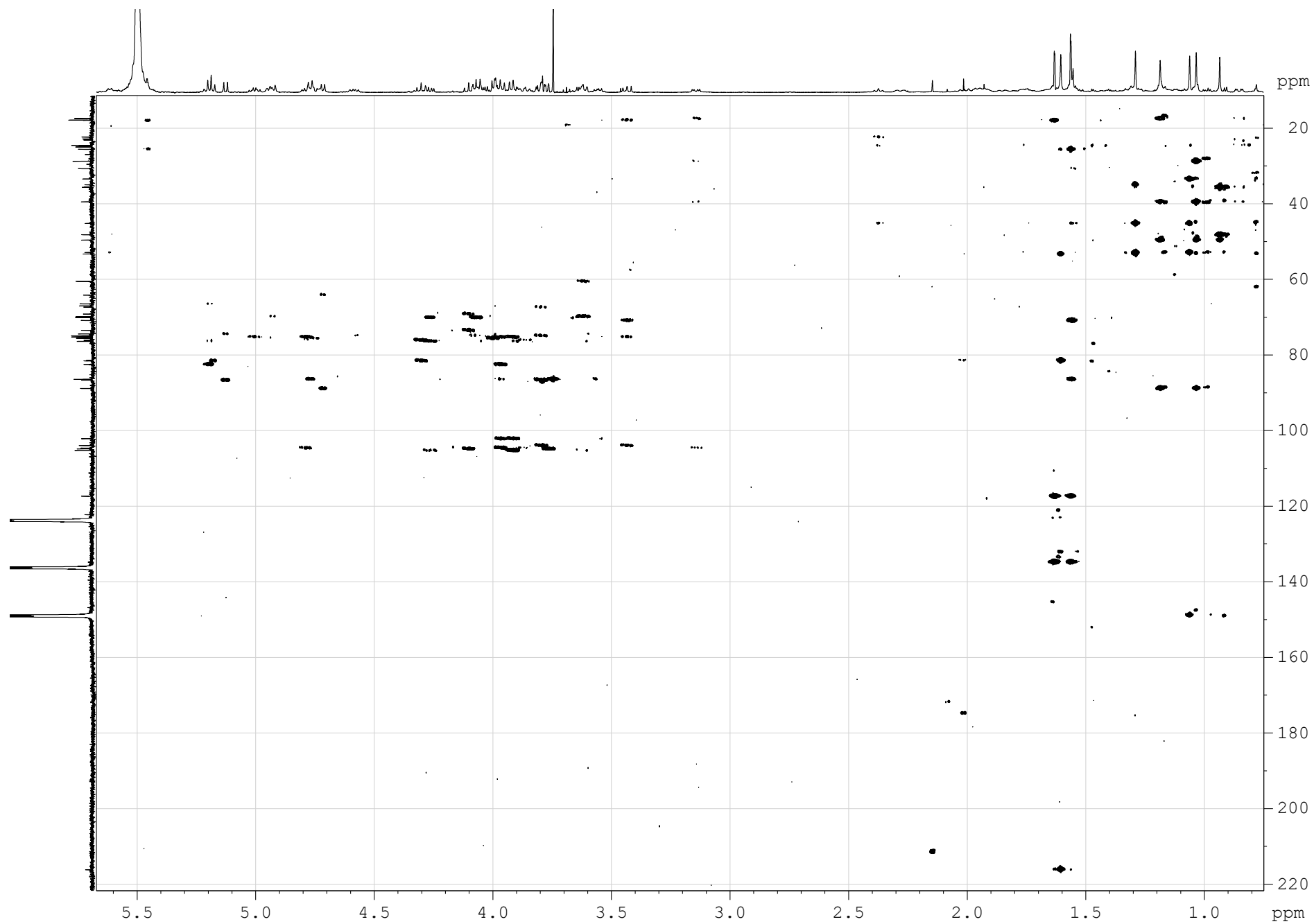


Figure S30. The HMBC (500.12 MHz) spectrum of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

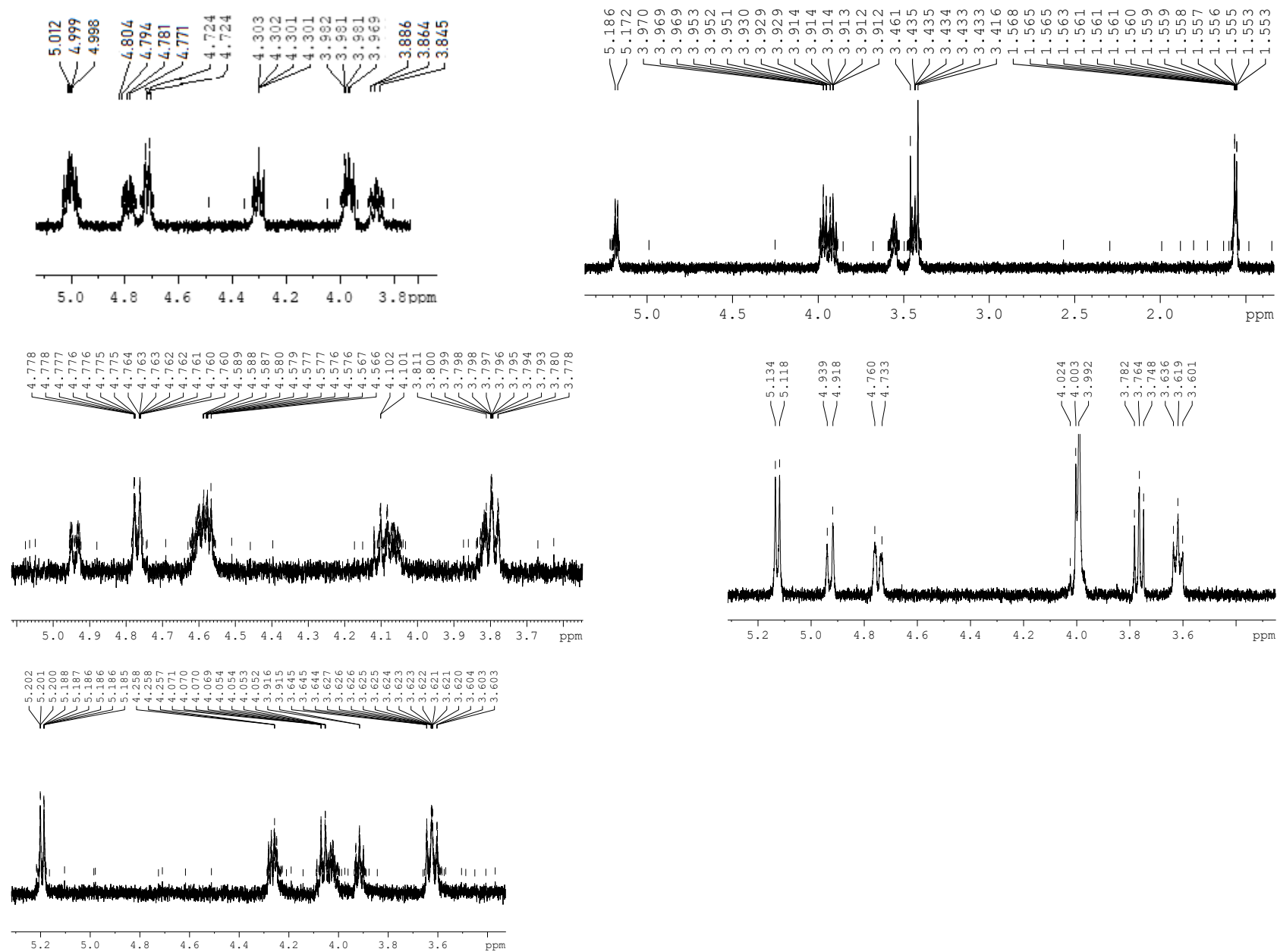


Figure S31. 1D TOCSY (500.12 MHz) spectra of Xyl1, Qui2, Glc3, MeGlc4, Xyl5 of djakonovioside F<sub>1</sub> (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

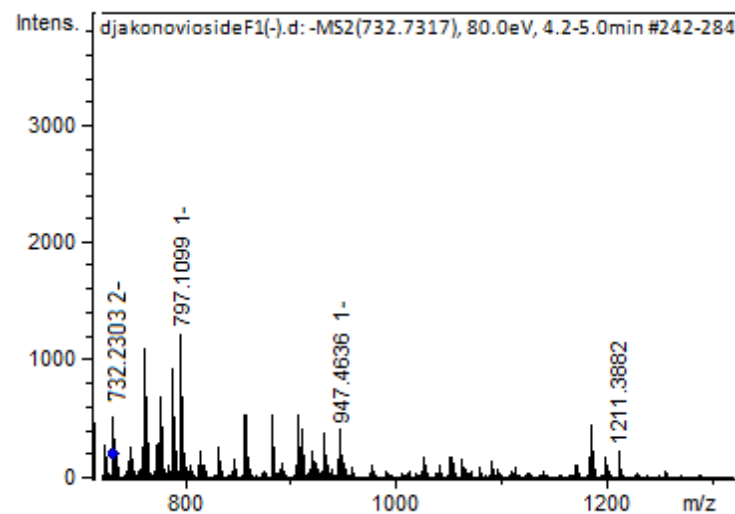
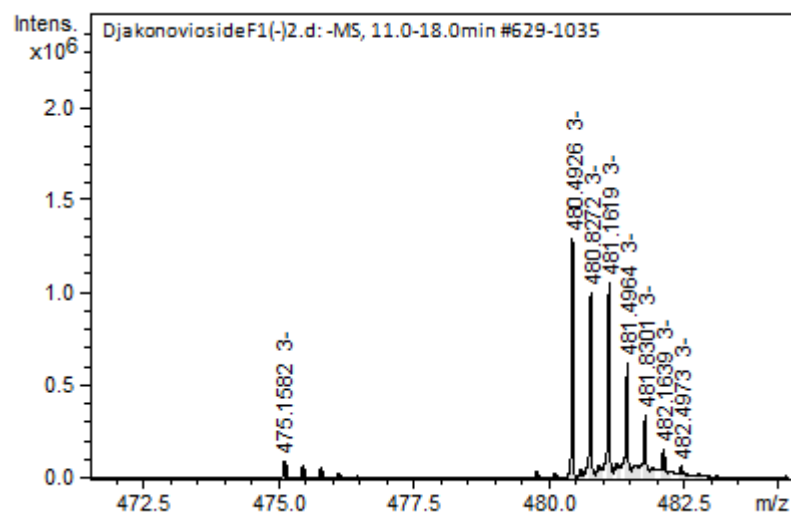
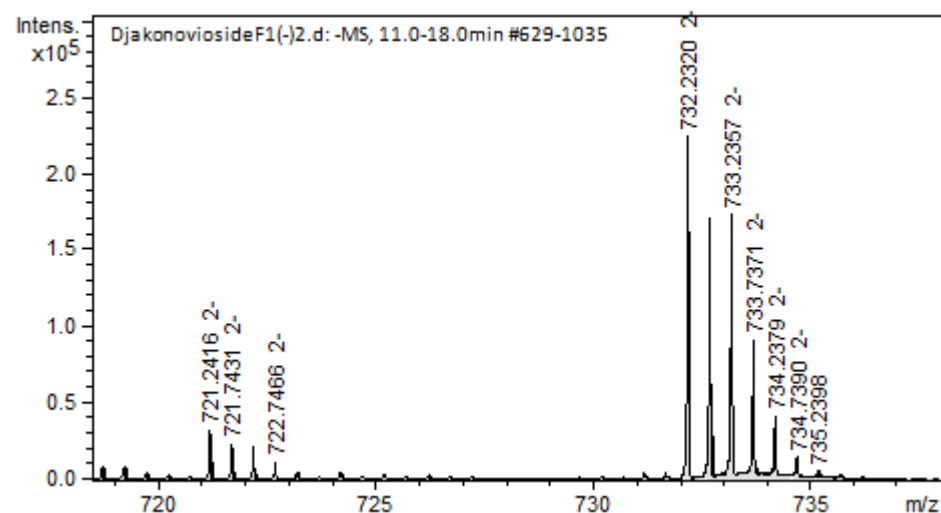
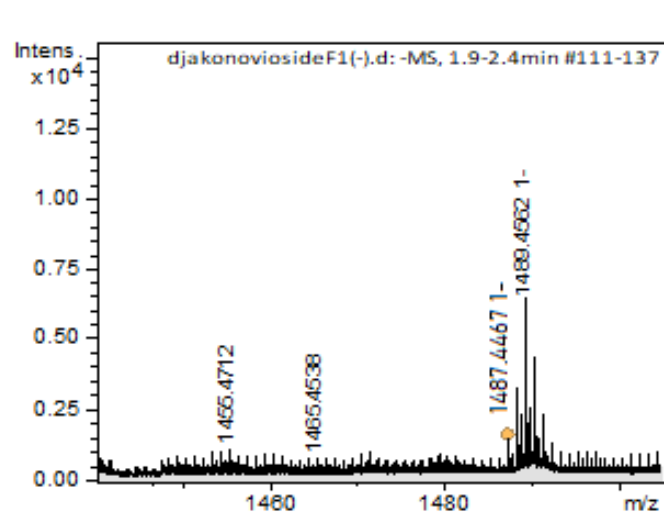


Figure S32. HR-ESI-MS and ESI-MS/MS spectra of djakonovioside F<sub>1</sub> (4)



**Table S2.** <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts and HMBC and ROESY correlations of aglycone moiety of okhotoside A2-1 (**5**).

Position	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. ( <i>J</i> in Hz) <sup>b</sup>	HMBC	ROESY
1	35.8 CH <sub>2</sub>	1.29 m		H-3, H-11, H-19
2	26.6 CH <sub>2</sub>	1.91 m 1.81 m		H-19, H-30
3	89.2 CH	3.20 dd (4.0; 11.6)		H-1, H-5, H-31, H1-Xyl1
4	39.3 C			
5	47.8 CH	0.89 dd (5.3; 9.9)	C: 19	H-1, H-3, H-31
6	23.1 CH <sub>2</sub>	1.89 m		H-19, H-30, H-31
7	120.2 CH	5.57 m		H-15, H-32
8	145.4 C			
9	47.0 CH	3.30 brd (14.5)		H-19
10	35.3 C			
11	22.4 CH <sub>2</sub>	1.70 m 1.47 m		H-1
12	31.2 CH <sub>2</sub>	2.09 m		H-17, H-21, H-32
13	59.3 C			
14	47.2 C			
15	43.5 CH <sub>2</sub>	2.55 dd (7.6; 12.2) 1.60 dd (9.2; 12.2)	C: 13, 17, 32	H-7, H-32
16	75.2 CH	5.82 q (8.4)		H-32
17	54.5 CH	2.66 d (9.2)	C: 12, 13, 18, 21	H-12, H-16, H-21, H-32
18	180.1 C			
19	23.7 CH <sub>3</sub>	1.05 s	C: 5, 9, 10	H-1, H-2, H-6, H-9
20	85.5 C			
21	28.0 CH <sub>3</sub>	1.51 s	C: 17, 20, 22	H-12, H-17, H-22
22	38.2 CH	2.24 td (4.6; 13.0) 1.80 m		
23	22.9 CH <sub>2</sub>	1.47 m 1.34 m		
24	38.1 CH <sub>2</sub>	1.91 m		
25	145.5 C			
26	110.8 CH <sub>2</sub>	4.72 m	C: 24, 27	H-24
27	22.0 CH <sub>3</sub>	1.64 s	C: 24, 25, 26	
30	17.2 CH <sub>3</sub>	1.04 s	C: 3, 4, 5, 31	H-2, H-6, H-31
31	28.5 CH <sub>3</sub>	1.17 s	C: 3, 4, 5, 30	H-3, H-5, H-6, H-30
32	32.1 CH <sub>3</sub>	1.15 s	C: 8, 13, 14, 15	H-7, H-12, H-15, H-16, H-17
OCOCH <sub>3</sub>	170.6 C			
OCOCH <sub>3</sub>	21.2 CH <sub>3</sub>	2.01 s	OAc	OAc

<sup>a</sup> Recorded at 125.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). <sup>b</sup> Recorded at 500.12 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). The original spectra of **5** are provided as Figures S33–S38.

**Table S3.** <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts and HMBC and ROESY correlations of carbohydrate moiety of okhotoside A<sub>2</sub>-1 (**5**).

Atom	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. ( <i>J</i> in Hz) <sup>b,c,d</sup>	HMBC	ROESY
Xyl1 (1→C-3)				
1	104.6 CH	4.72 d (7.4)	C: 3	H-3; H-3, 5 Xyl1
2	<b>79.7</b> CH	4.17 t (8.9)	C: 1 Glc2; C: 1 Xyl1	H-1 Glc2
3	75.5 CH	4.33 t (8.9)	C: 4 Xyl1	H-1 Xyl1
4	76.0 CH	4.98 m		
5	64.2 CH <sub>2</sub>	4.77 dd (5.2; 11.9) 3.77 brd (11.1)	C: 4 Xyl1	
Glc2 (1→2Xyl1)				
1	101.5 CH	5.39 d (7.5)	C: 2 Xyl1	H-2 Xyl1; H-5 Glc2
2	<b>82.2</b> CH	3.96 t (8.4)	C: 1 Xyl5, C: 1, 3 Glc2	H-1 Xyl5
3	75.6 CH	4.08 t (8.4)	C: 2, 4 Glc2	H-1 Glc2
4	<b>80.6</b> CH	4.02 t (9.2)	C: 1 Glc3; C: 5 Glc2	H-1 Glc3
5	75.8 CH	3.67 brd (9.2)		H-1 Glc2
6	61.4 CH <sub>2</sub>	4.34 dd (11.7; 2.5) 4.25 dd (11.7; 5.0)		
Glc3 (1→4Glc2)				
1	103.6 CH	4.96 d (8.4)	C: 4 Glc2	H-4 Glc2; H-3, 5 Glc3
2	73.5 CH	3.90 t (8.4)	C: 1, 3 Glc3	
3	<b>86.8</b> CH	4.15 t (8.4)	C: 2, 4 Glc3	H-1 MeGlc4
4	69.2 CH	3.88 t (8.4)		
5	77.1 CH	3.85 t (8.4)		H-1 Glc3
6	61.1 CH <sub>2</sub>	4.25 brd (11.9) 3.98 m		
MeGlc4 (1→3Glc3)				
1	104.5 CH	5.16 d (8.3)	C: 3 Glc3	H-3 Glc3; H-3, 5 MeGlc4
2	74.5 CH	3.85 t (9.0)	C: 1, 3 MeGlc4	
3	86.7 CH	3.66 t (9.0)	OMe	H-1 MeGlc4; OMe
4	70.3 CH	3.87 m	C: 5 MeGlc4	
5	77.5 CH	3.89 m		H-1 MeGlc4
6	61.7 CH <sub>2</sub>	4.36 dd (11.8; 2.9) 4.04 dd (11.8; 5.5)	C: 4 MeGlc4 C: 4, 5 MeGlc4	
OMe	60.7 CH <sub>3</sub>	3.80 s	C: 3 MeGlc4	
Xyl5 (1→2Glc2)				
1	105.2 CH	5.20 d (6.9)	C: 2 Glc2	H-2 Glc2; H-3, 5 Xyl5
2	74.7 CH	3.94 t (9.0)	C: 1, 3 Xyl5	
3	76.3 CH	4.04 t (9.0)	C: 2 Xyl5	H-1 Xyl5
4	70.1 CH	4.10 m		
5	66.3 CH <sub>2</sub>	4.31 dd (11.8; 4.8) 3.59 dd (11.8; 9.7)		H-1 Xyl5

<sup>a</sup> Recorded at 125.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O. <sup>b</sup> Bold = interglycosidic positions. <sup>c</sup> Italic = sulfate position. <sup>d</sup> Recorded at 500.12 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O. The original spectra of **5** are provided as Figures S33–S38.

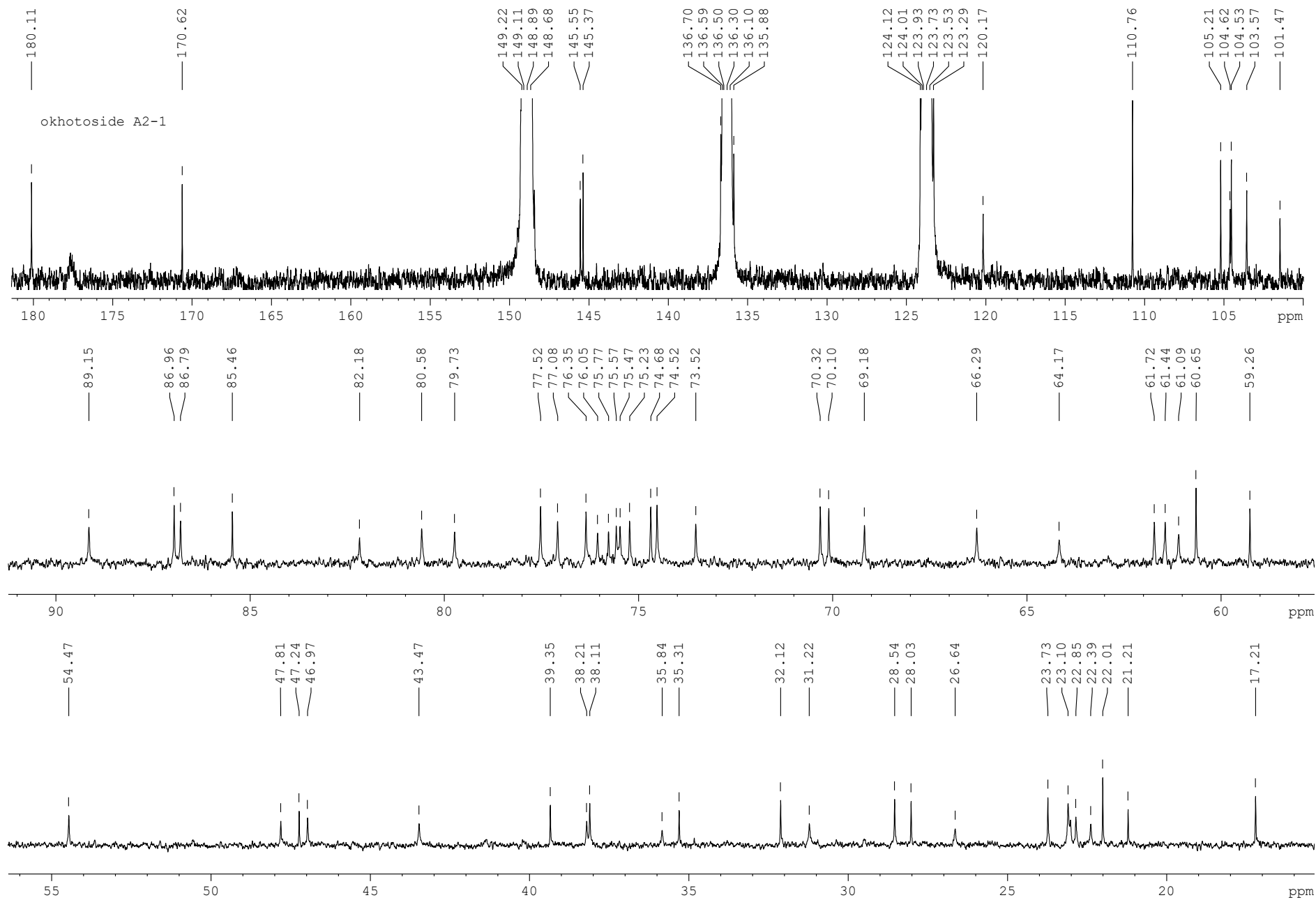


Figure S33. The  $^{13}\text{C}$  NMR (125.67 MHz) spectrum of okhotoside A2-1 (**5**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

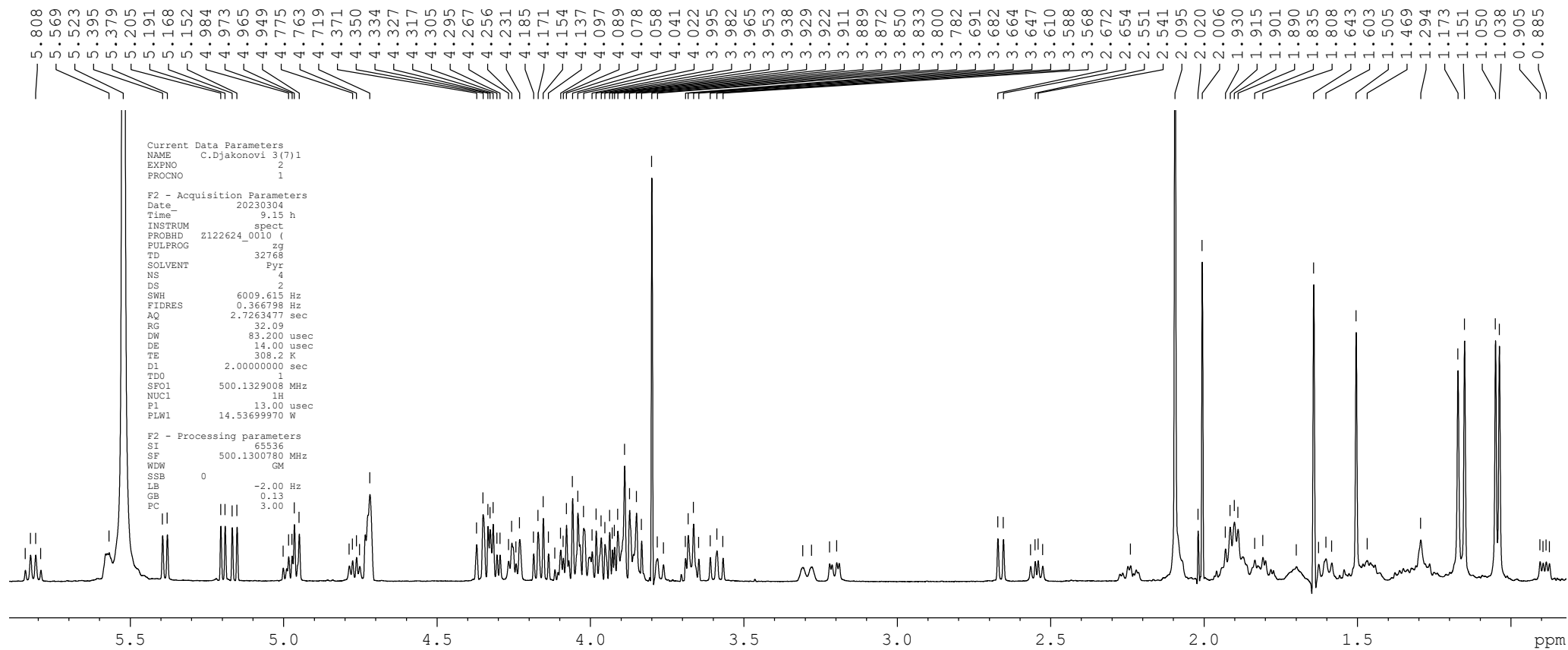


Figure S34. The  $^1\text{H}$  NMR (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (**5**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

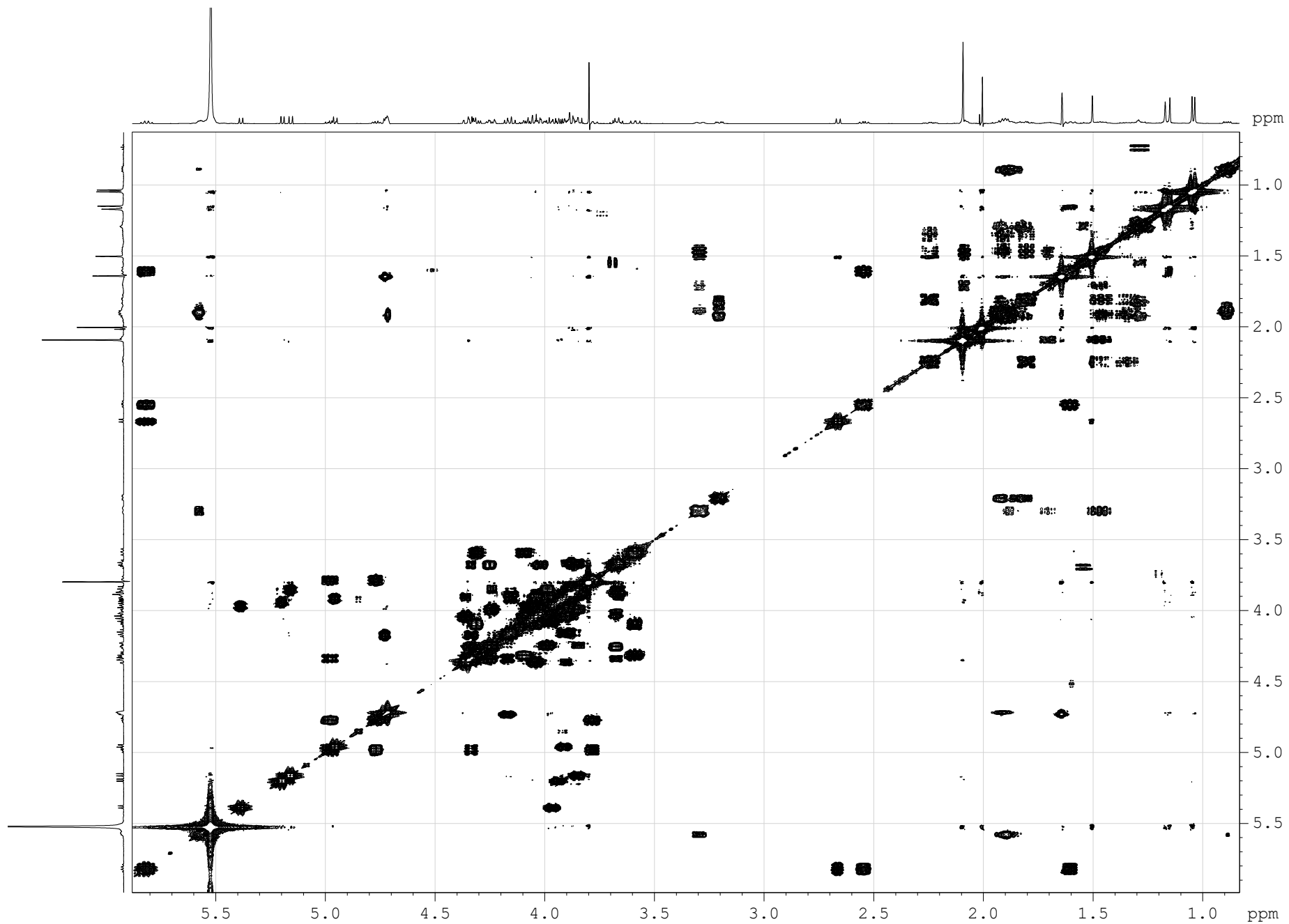


Figure S35. The COSY (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (5) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

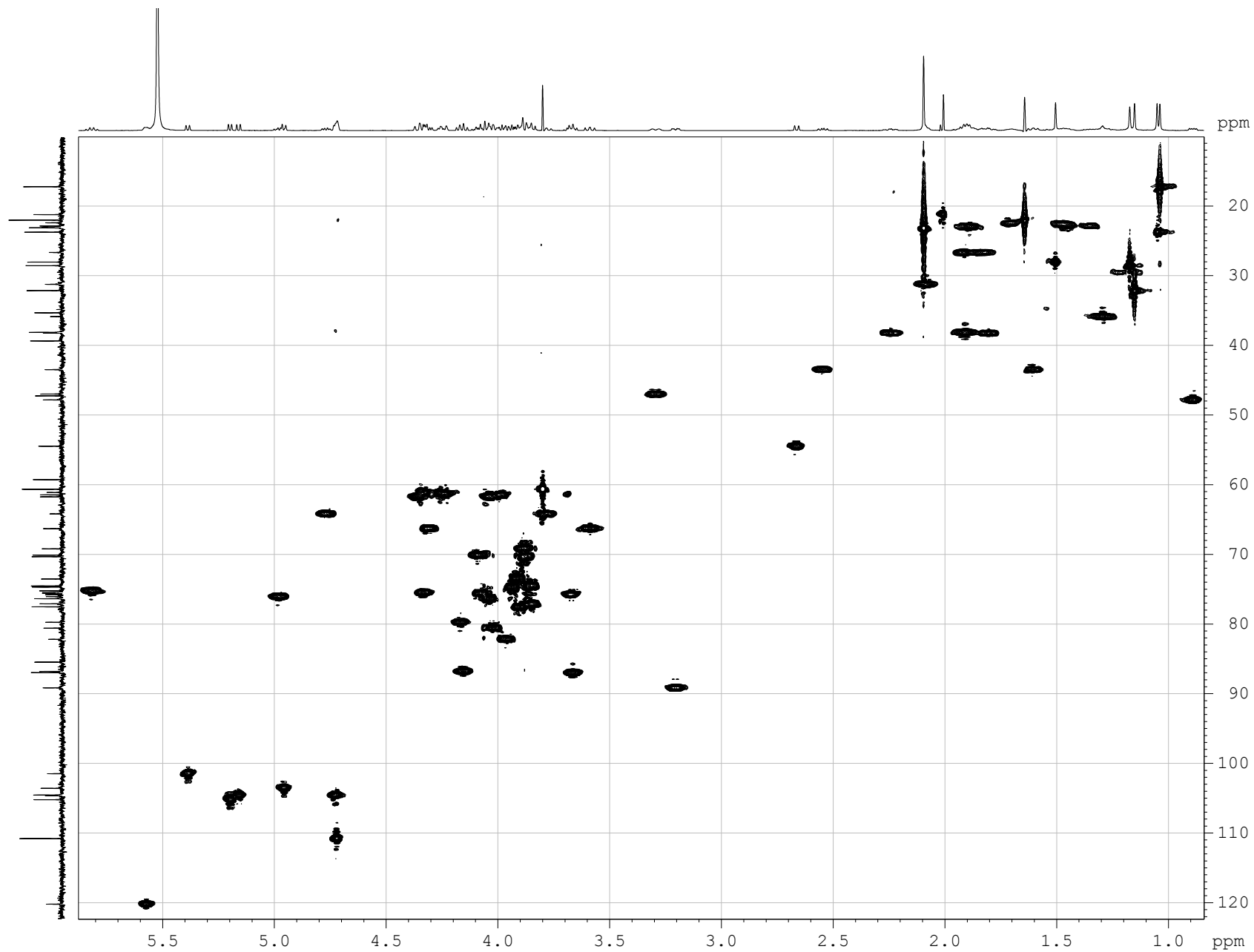


Figure S36. The HSQC (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

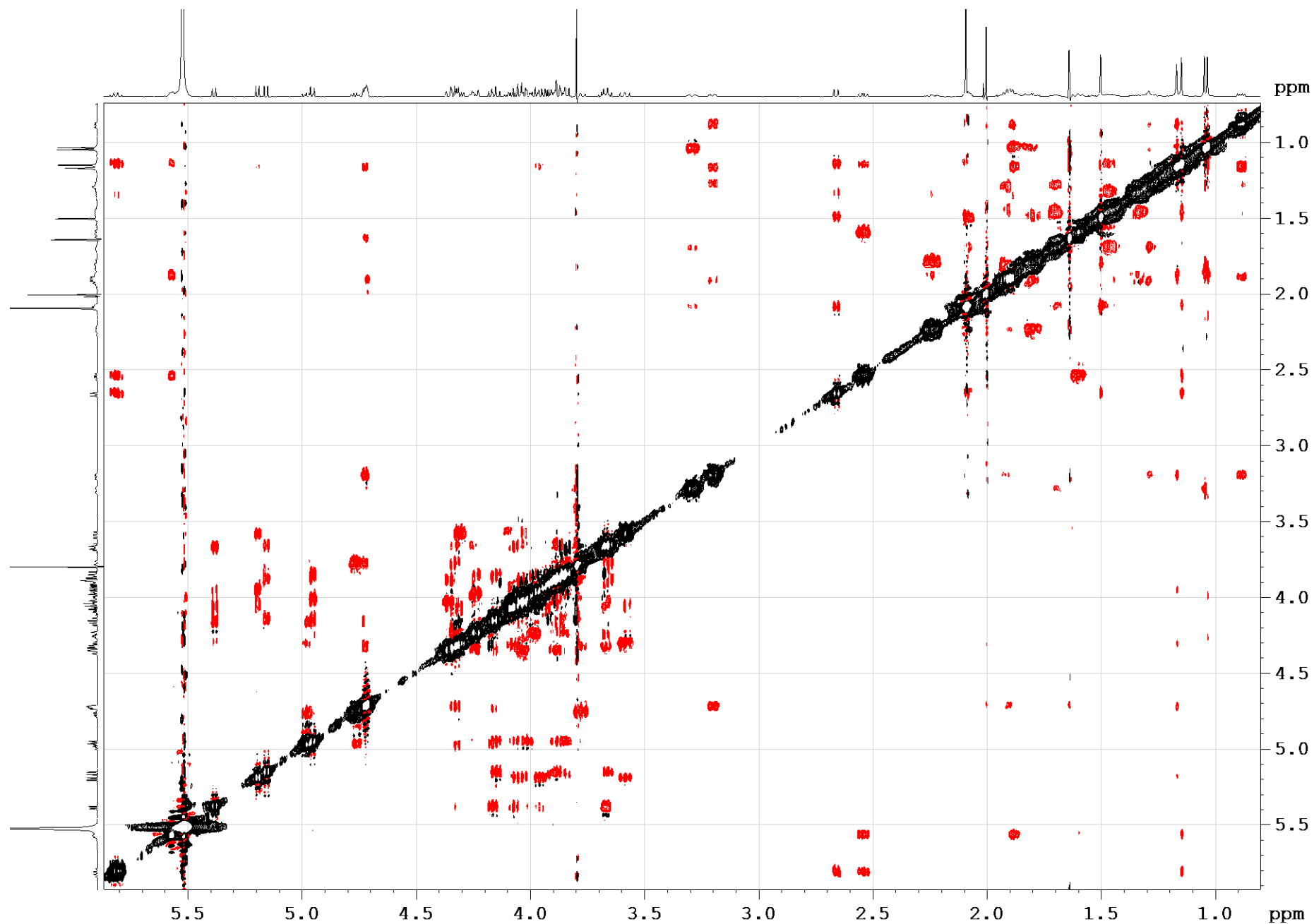


Figure S37. The ROESY (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (5) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

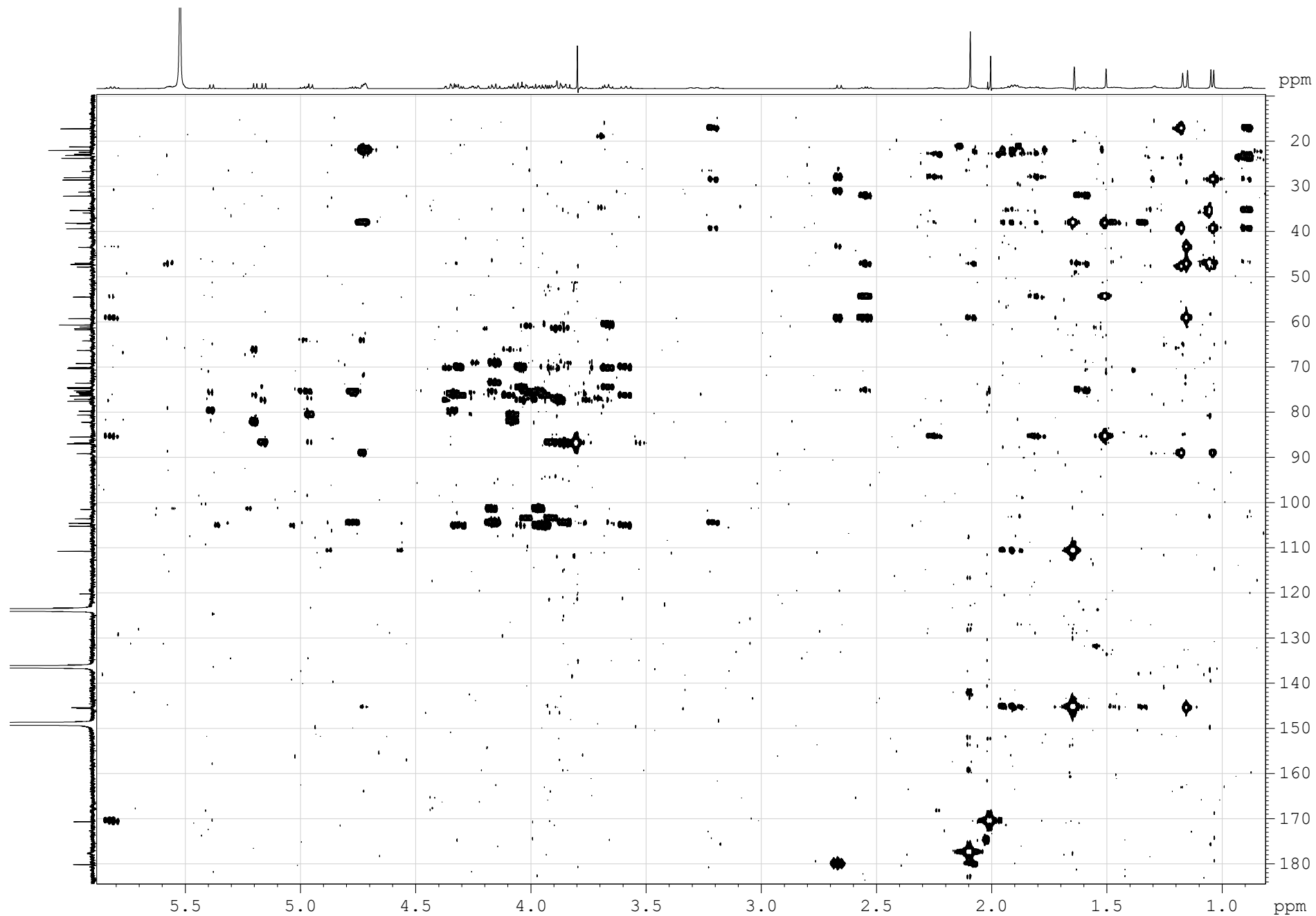


Figure S38. The HMBC (500.12 MHz) spectrum of okhotoside A<sub>2</sub>-1 (5) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)



**Table S4.** <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts and HMBC and ROESY correlations of aglycone moiety of cucumarioside A<sub>2</sub>-5 (**6**).

Position	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. (J in Hz) <sup>b</sup>	HMBC	ROESY
1	35.8 CH <sub>2</sub>	1.32 m		H-11
2	26.7 CH <sub>2</sub>	1.94 m 1.78 m		
3	88.9 CH	3.19 dd (3.8; 12.6)		H-5, H-31, H1-Xyl1
4	39.3 C			
5	47.8 CH	0.90 dd (5.1; 10.0)	C: 19	H-3, H-31
6	23.1 CH <sub>2</sub>	1.95 m 1.90 m		H-31
7	120.4 CH	5.57 m		H-15
8	145.4 C			
9	47.0 CH	3.27 brd (14.5)		H-19
10	35.4 C			
11	22.4 CH <sub>2</sub>	1.72 m 1.46 m		H-1
12	31.0 CH <sub>2</sub>	2.03 m		H-21
13	57.8 C			
14	47.4 C			
15	43.5 CH <sub>2</sub>	2.62 dd (7.0; 11.7) 1.48 dd (3.0; 11.7)	C: 12, 13, 14, 17	H-7
16	76.1 CH	5.68 q (8.5)	OAc	H-32
17	55.1 CH	3.19 m	C: 13, 18, 21	H-12, H-21, H-32
18	180.0 C			
19	23.8 CH <sub>3</sub>	1.09 s	C: 5, 9, 10	H-1, H-2, H-6, H-9
20	82.6 C			
21	29.4 CH <sub>3</sub>	1.58 s	C: 17, 20, 22	H-12, H-17
22	52.6 CH	3.82 m 3.20 m	C: 20, 23 C: 17, 20, 23	
23	209.1 C			
24	51.5 CH <sub>2</sub>	2.42 dd (5.5; 15.6) 2.24 ddd (7.8; 12.5; 15.6)	C: 23, 25, 26, 27 C: 23, 25, 26, 27	
25	24.3 CH	2.08 m	C: 26, 27	
26	22.4 CH <sub>3</sub>	0.87 d (6.7)	C: 24, 25, 27	H-25
27	22.2 CH <sub>3</sub>	0.83 d (6.7)	C: 24, 25, 26	H-25
30	17.3 CH <sub>3</sub>	1.02 s	C: 3, 4, 5, 31	H-2, H-6, H-31
31	28.6 CH <sub>3</sub>	1.18 s	C: 3, 4, 5, 30	H-3, H-5, H-6, H-30, H-1 Xyl1
32	32.0 CH <sub>3</sub>	1.06 s	C: 8, 13, 14, 15	H-15, H-16, H-17
OCOCH <sub>3</sub>	170.1 C			
OCOCH <sub>3</sub>	21.3 CH <sub>3</sub>	2.01 s	OAc	

<sup>a</sup> Recorded at 125.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). <sup>b</sup> Recorded at 500.12 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). The original spectra of **6** are provided as Figures S39–S44.

**Table S5.** <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts and HMBC and ROESY correlations of carbohydrate moiety of cucumarioside A<sub>2</sub>-5 (**6**).

Atom	$\delta_C$ mult. <sup>a</sup>	$\delta_H$ mult. ( <i>J</i> in Hz) <sup>b,c,d</sup>	HMBC	ROESY
Xyl1 (1→C-3)				
1	104.6 CH	4.74 d (6.4)	C: 3	H-3; H-3, 5 Xyl1
2	<b>81.4</b> CH	3.98 t (8.4)	C: 1 Qui2; C: 1 Xyl1	
3	75.4 CH	4.32 t (8.4)	C: 2, 4 Xyl1	
4	76.3 CH	5.00 dd (13.7; 8.4)	C: 3 Xyl1	H-2 Xyl1
5	64.1 CH <sub>2</sub>	4.79 dd (11.6; 5.8) 3.85 t (10.0)	C: 1, 3 Xyl1	
Qui2 (1→2Xyl1)				
1	101.9 CH	5.20 d (8.5)	C: 2 Xyl1	H-2 Xyl1; H-5 Qui2
2	82.4 CH	3.95 m	C: 1, 3 Qui2	
3	75.3 CH	4.00 m	C: 2, 4 Qui2	H-1 Qui2
4	<b>86.0</b> CH	3.55 t (8.8)	C: 1 Glc3; C: 3, 5 Qui2	H-1 Glc3
5	71.0 CH	3.59 m		H-1 Qui2
6	17.9 CH <sub>3</sub>	1.59 d (5.8)		
Glc3 (1→4Qui2)				
1	104.0 CH	4.86 d (7.8)	C: 4 Qui2	H-4 Qui2; H-3, 5 Glc3
2	73.6 CH	3.93 t (8.4)	C: 1 Glc3	
3	<b>86.8</b> CH	4.21 t (8.4)	C: 1 MeGlc4; C: 4 Glc3	H-1 MeGlc4
4	69.3 CH	3.90 m	C: 3 Glc3	
5	77.1 CH	3.90 m	C: 6 Glc3	H-1 Glc3
6	61.6 CH <sub>2</sub>	4.29 brd (12.0) 4.01 brd (12.0)	C: 5 Glc3	
MeGlc4 (1→3Glc3)				
1	104.6 CH	5.22 d (8.9)	C: 3 Glc3	H-3 Glc3; H-3, 5 MeGlc4
2	74.6 CH	3.87 t (8.9)	C: 1, 3 MeGlc4	
3	87.0 CH	3.69 t (8.9)	OMe; C: 2, 4 MeGlc4	H-1 MeGlc4; Ome
4	70.4 CH	3.89 m	C: 5 MeGlc4	
5	77.6 CH	3.93 m		
6	61.8 CH <sub>2</sub>	4.37 d (11.0) 4.05 dd (11.0; 4.8)	C: 5 MeGlc4	
OMe	60.6 CH <sub>3</sub>	3.81 s	C: 3 MeGlc4	
Xyl5 (1→2Qui2)				
1	105.3 CH	5.19 d (7.4)	C: 2 Qui2	H-2 Qui2; H-3,5 Xyl5
2	74.8 CH	3.92 t (8.5)	C: 1, 3 Xyl5	
3	76.3 CH	4.01 t (9.4)	C: 2, 4 Xyl5	H-1 Xyl5
4	70.0 CH	4.08 m		
5	66.4 CH <sub>2</sub>	4.31 m 3.59 m	C: 4 Xyl5	H-1 Xyl5

<sup>a</sup> Recorded at 25.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O. <sup>b</sup> Recorded at 500.12 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O. <sup>c</sup> Bold = interglycosidic positions. <sup>d</sup> Italic – sulfate positions. The original spectra of **6** are provided as Figures S39–S44.

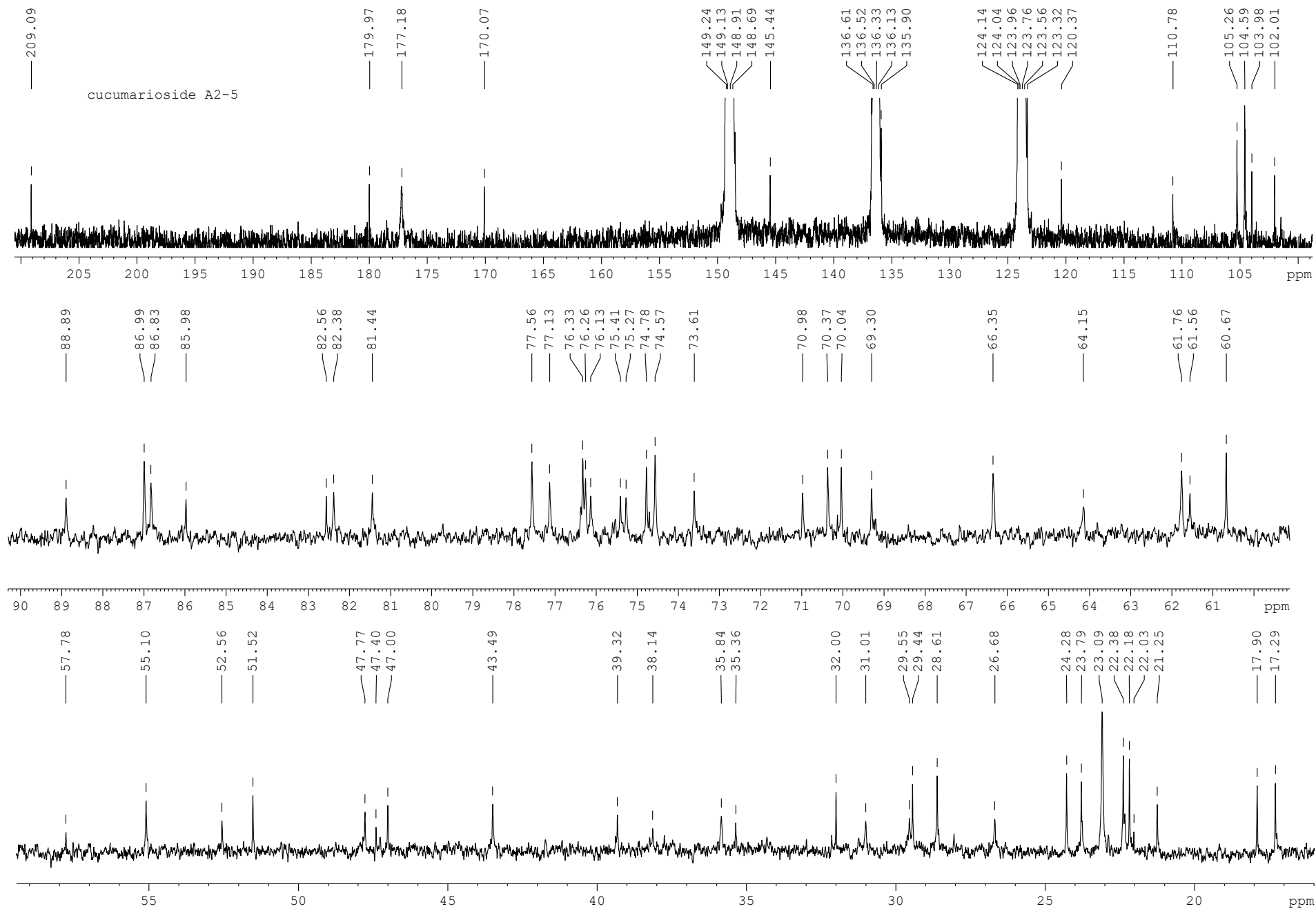


Figure S39. The  $^{13}\text{C}$  NMR (125.67 MHz) spectrum of cucumarioside A2-5 (**6**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

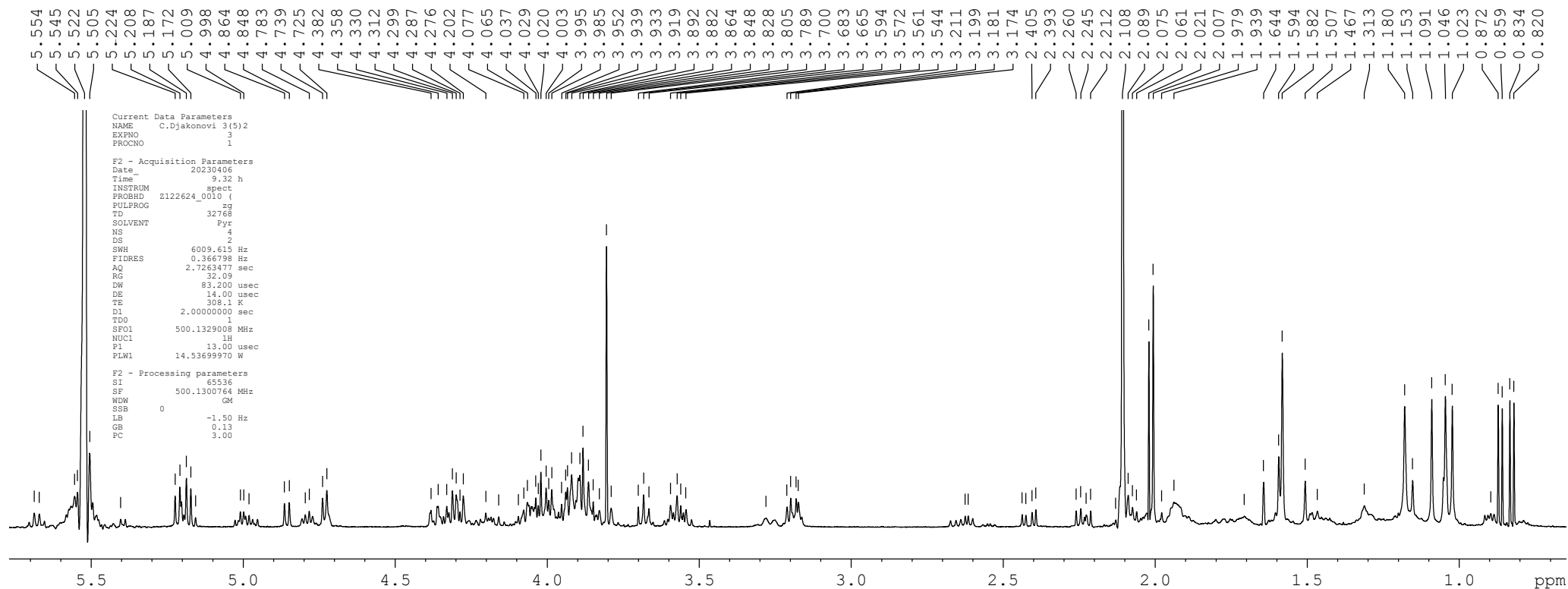


Figure S40. The  $^1\text{H}$  NMR (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

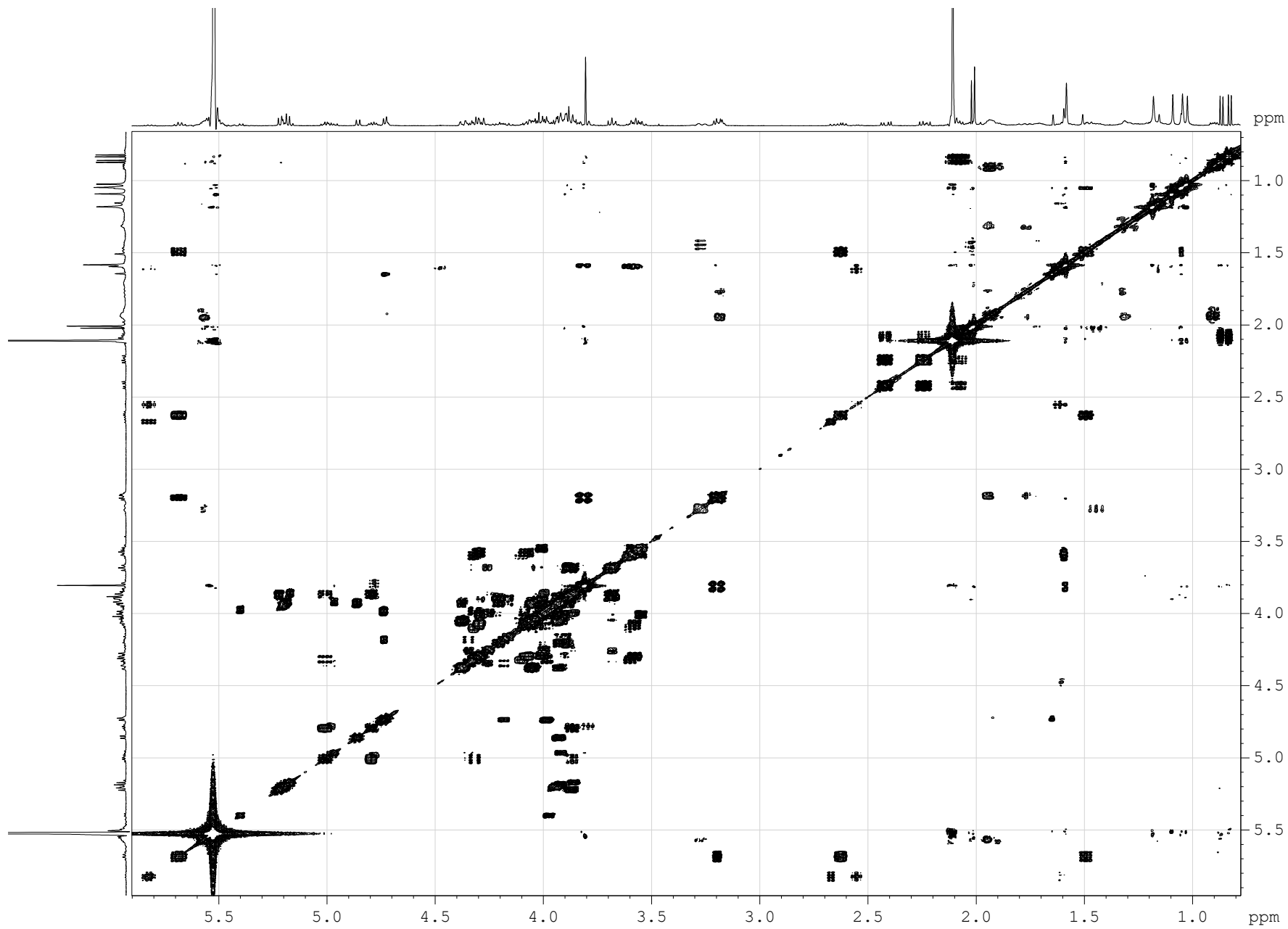


Figure S41. The COSY (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

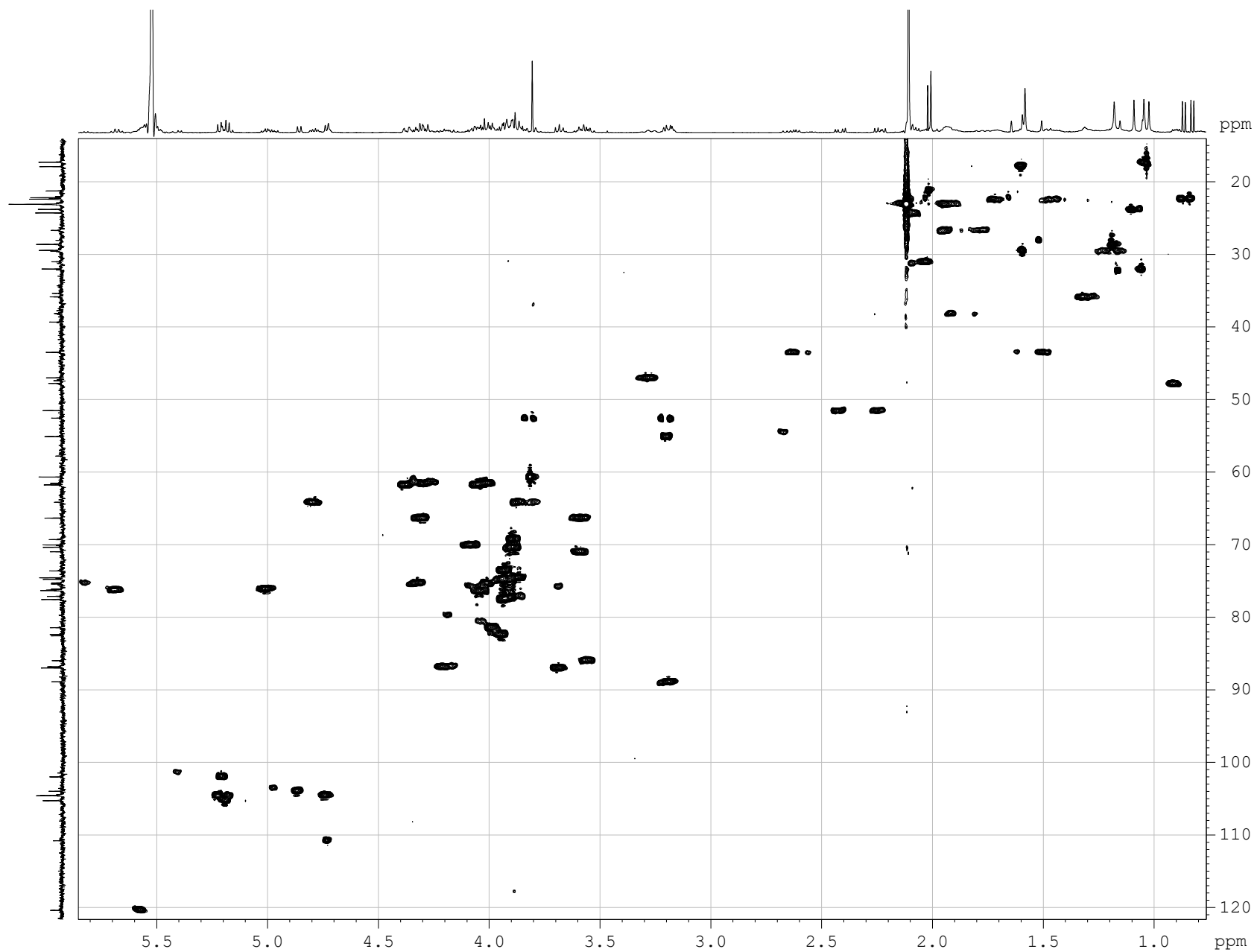


Figure S42. The HSQC (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

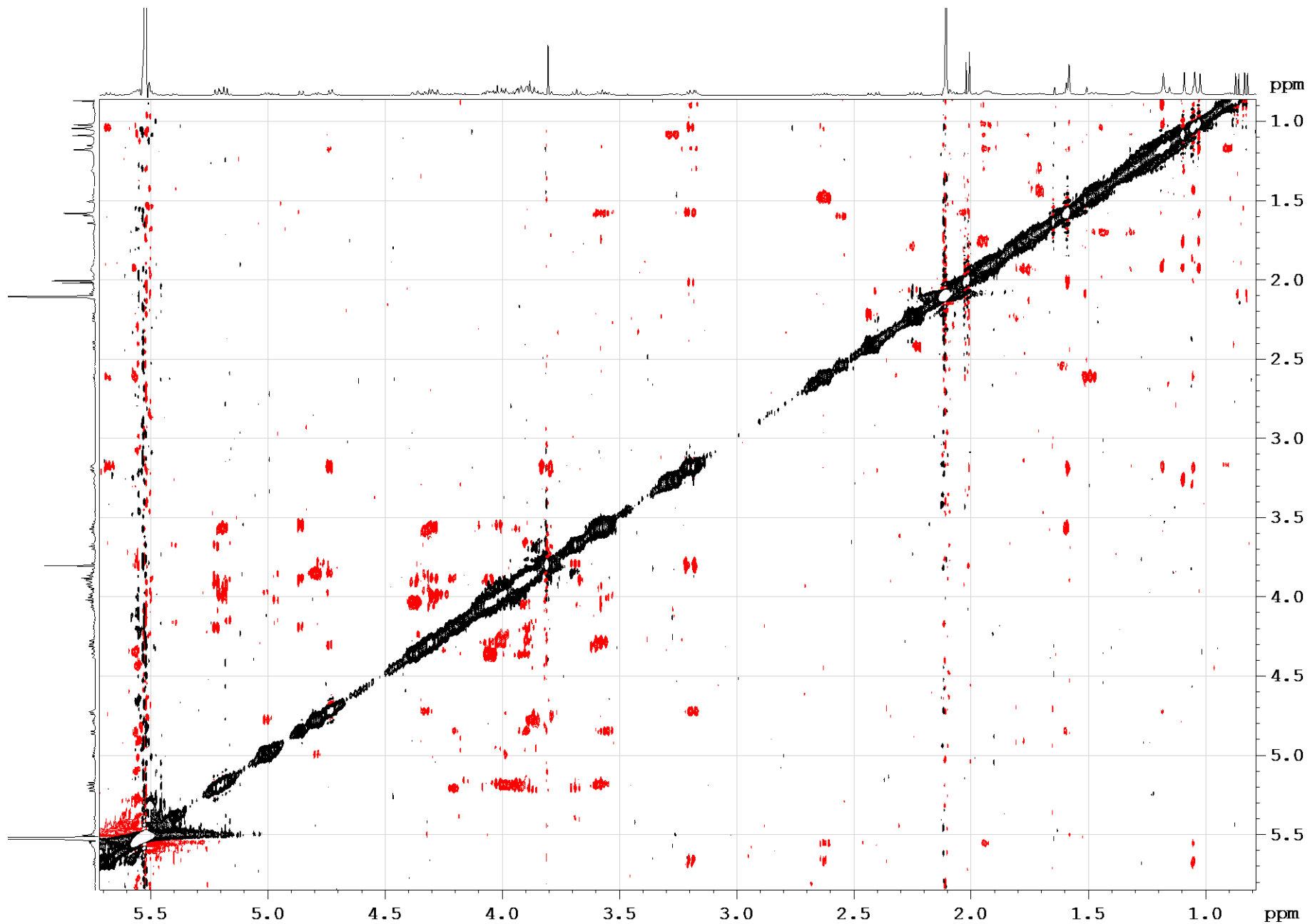


Figure S43. The ROESY (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (6) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

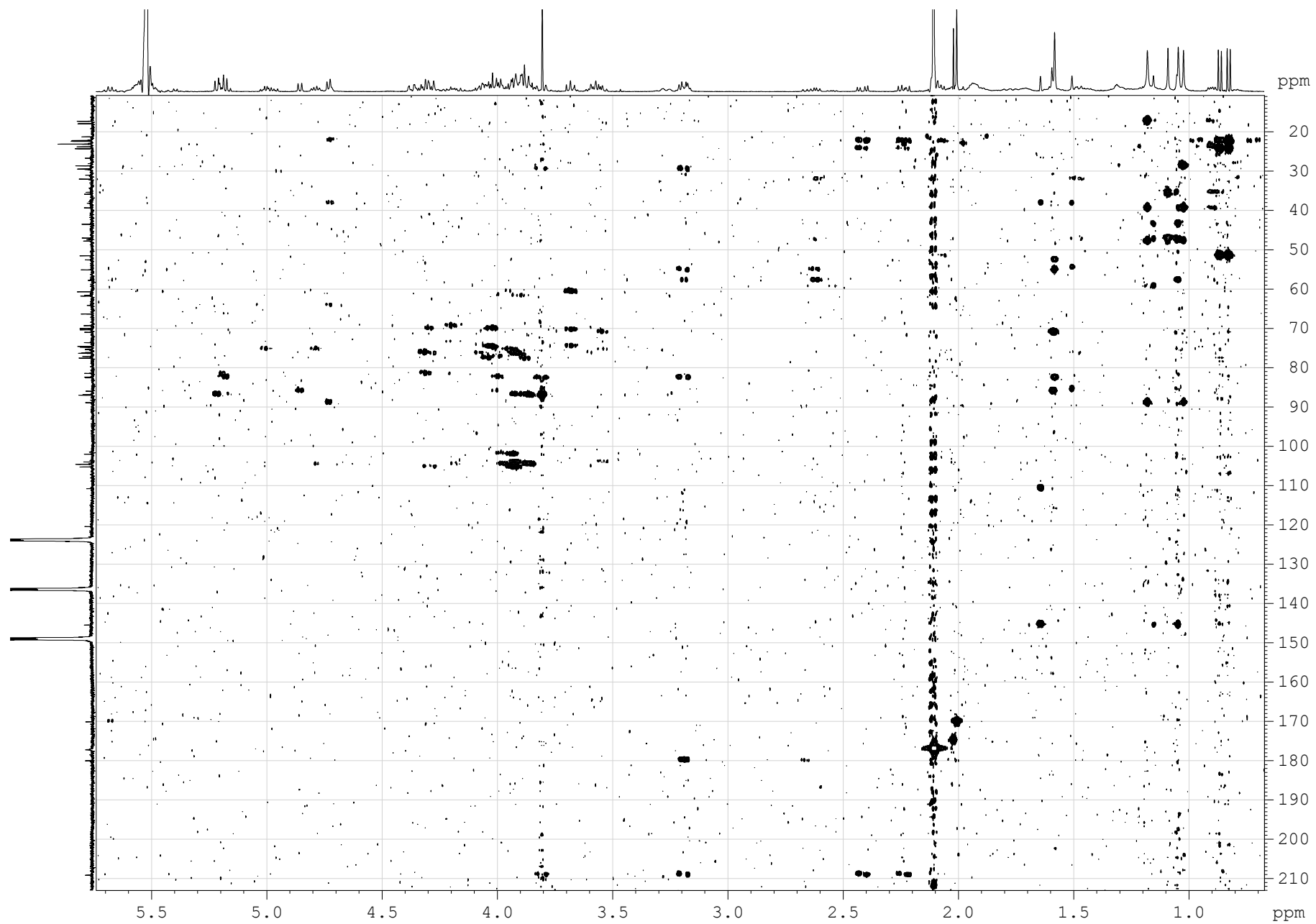


Figure S44. The HMBC (500.12 MHz) spectrum of cucumarioside A<sub>2</sub>-5 (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)



**Table S6.** <sup>13</sup>C NMR chemical shifts of frondoside A<sub>2</sub>-3 (7).

Position	δ <sub>c</sub> mult. <sup>a</sup>	Position	δ <sub>c</sub> mult. <sup>a</sup>
1	36.0 CH <sub>2</sub>	2	81.4 CH
2	26.7 CH <sub>2</sub>	3	75.4 CH
3	89.0 CH	4	76.1 CH
4	39.4 C	5	64.1 CH <sub>2</sub>
5	48.0 CH	Qui2 (1→2Xyl1)	
6	23.2 CH <sub>2</sub>	1	102.0 CH
7	120.0 CH	2	82.4 CH
8	146.7 C	3	75.3 CH
9	47.3 CH	4	86.0 CH
10	35.3 C	5	71.0 CH
11	22.7 CH <sub>2</sub>	6	17.9 CH <sub>3</sub>
12	30.1 CH <sub>2</sub>	Glc3 (1→4Qui2)	
13	58.7 C	1	104.0 CH
14	46.1 C	2	73.6 CH
15	34.1 CH <sub>2</sub>	3	86.8 CH
16	23.1 CH <sub>2</sub>	4	69.3 CH
17	53.1 CH	5	77.1 CH
18	180.9 C	6	61.5 CH <sub>2</sub>
19	23.9 CH <sub>3</sub>	MeGlc4 (1→3Glc3)	
20	84.4 C	1	104.6 CH
21	26.1 CH <sub>3</sub>	2	74.6 CH
22	42.0 CH <sub>2</sub>	3	87.0 CH
23	119.8 CH	4	70.4 CH
24	143.7 CH	5	77.5 CH
25	66.6 C	6	61.8 CH <sub>2</sub>
26	29.9 CH <sub>3</sub>	OMe	
27	29.8 CH <sub>3</sub>	Xyl5 (1→2Qui2)	
30	17.3 CH <sub>3</sub>	1	105.2 CH
31	28.7 CH <sub>3</sub>	2	74.7 CH
32	30.7 CH <sub>3</sub>	3	76.3 CH
Xyl1 (1→C-3)		4	70.0 CH
1	104.6 CH	5	66.3 CH <sub>2</sub>

<sup>a</sup> Recorded at 125.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4.1).

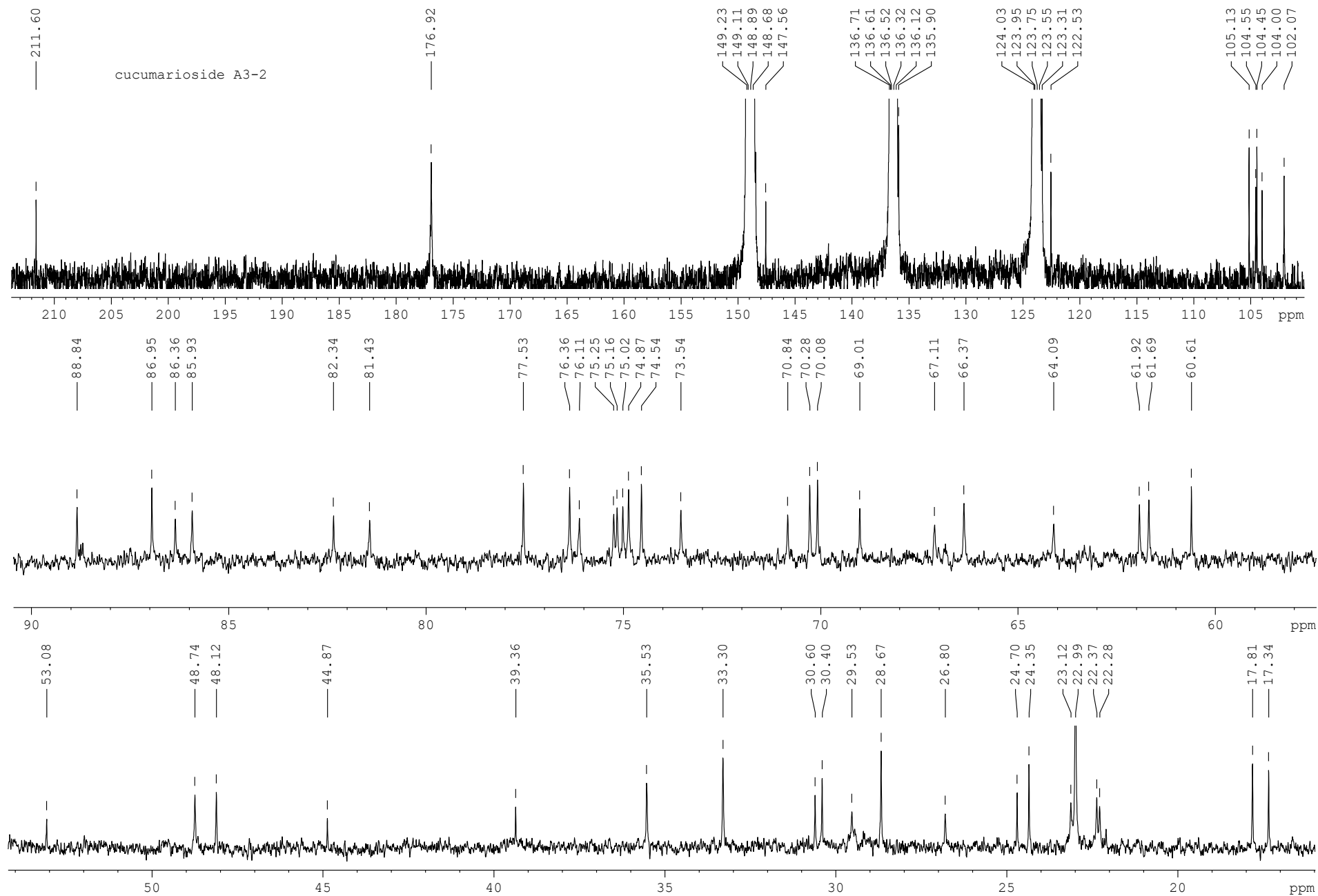


Figure S45. The  $^{13}\text{C}$  NMR (125.67 MHz) spectrum of cucumarioside A3-2 (**8**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

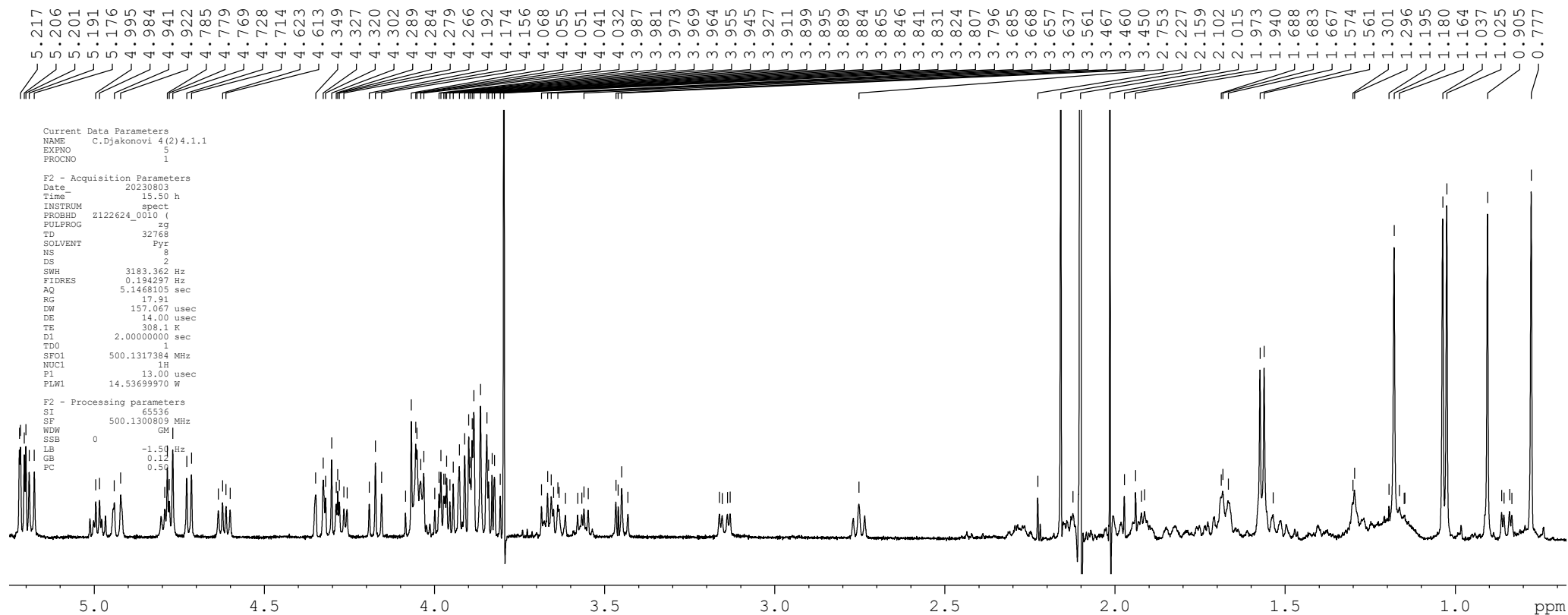


Figure S46. The  $^1\text{H}$  NMR (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (**8**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

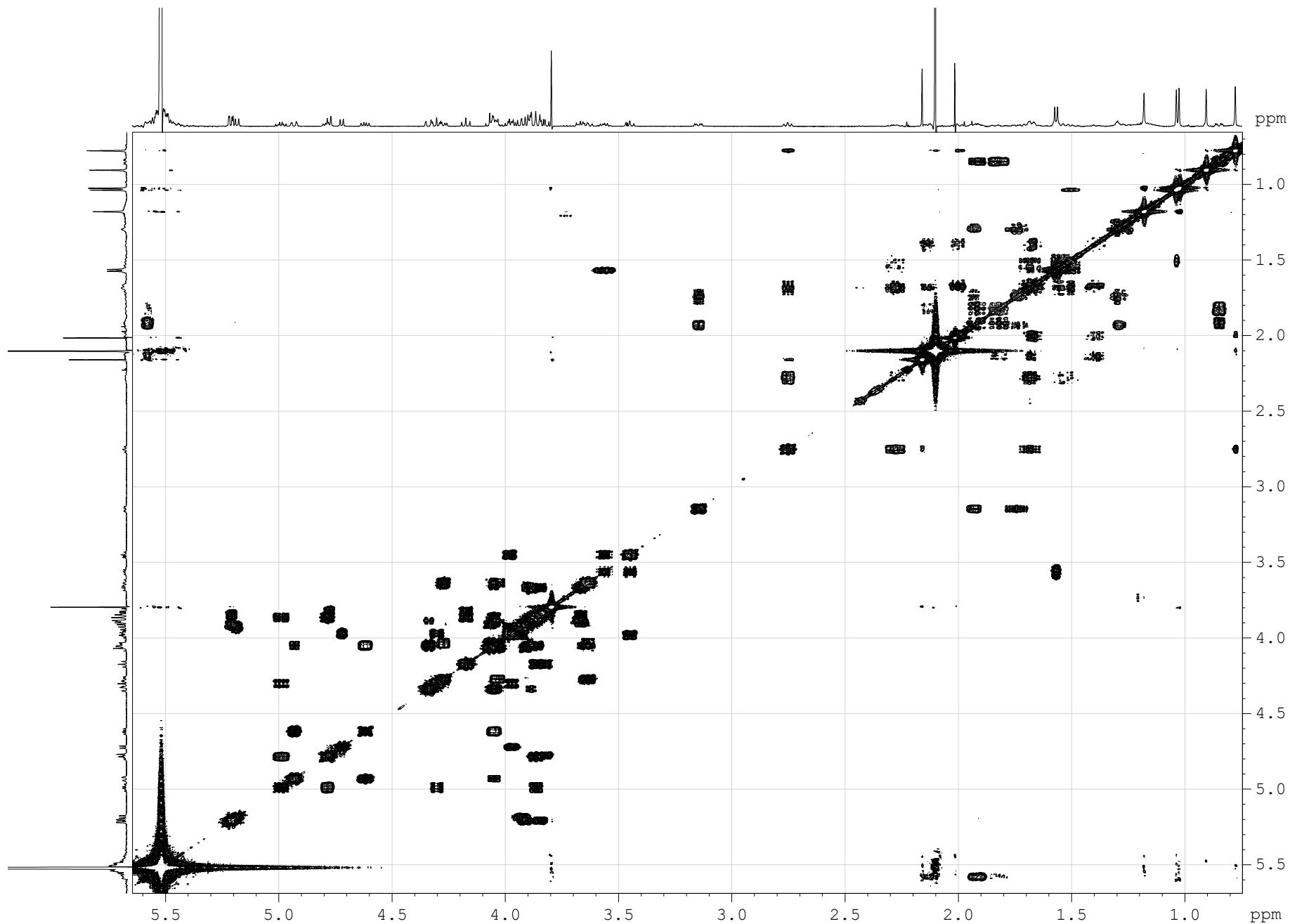


Figure S47. The COSY (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

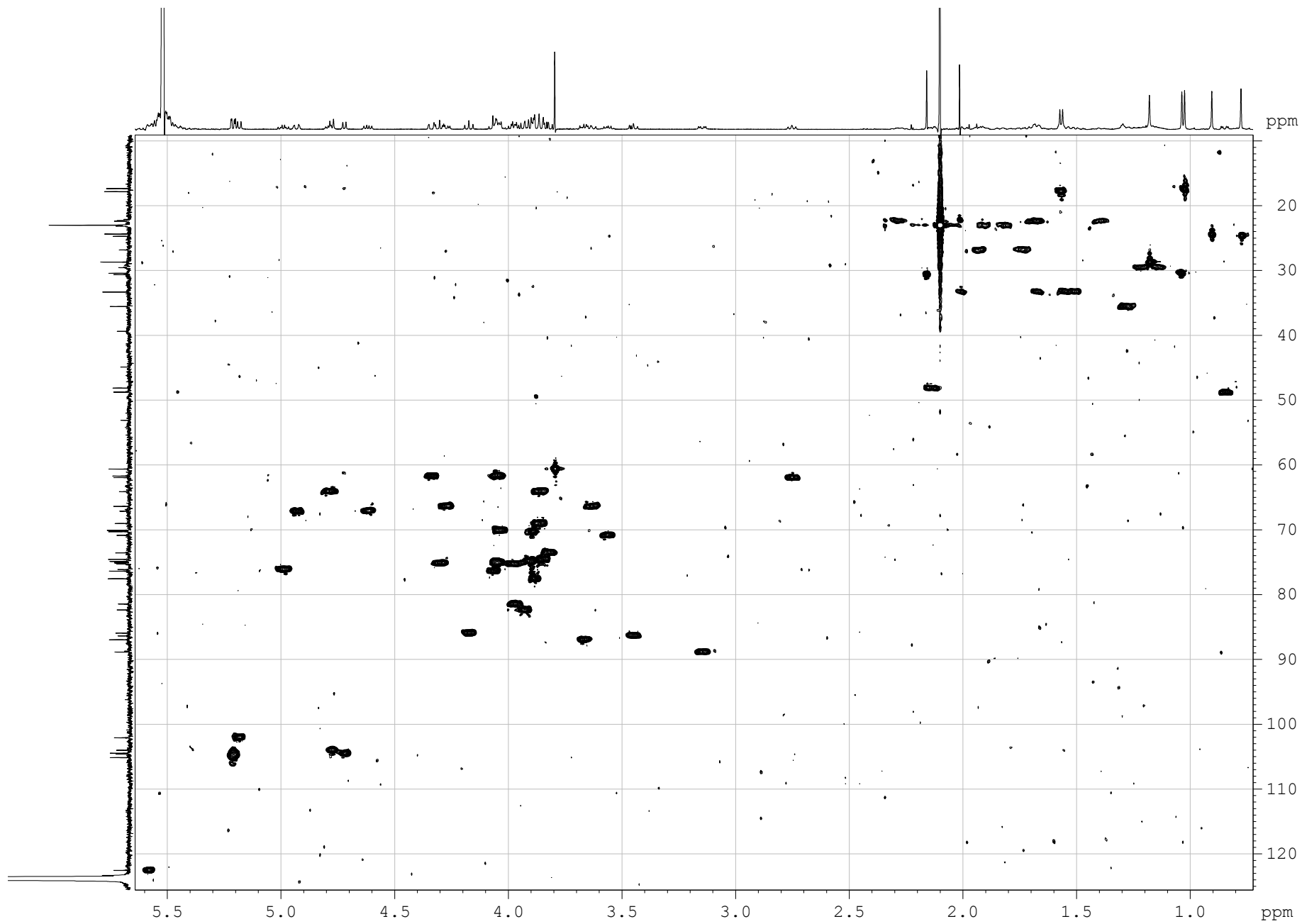


Figure S48. The HSQC (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (8) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

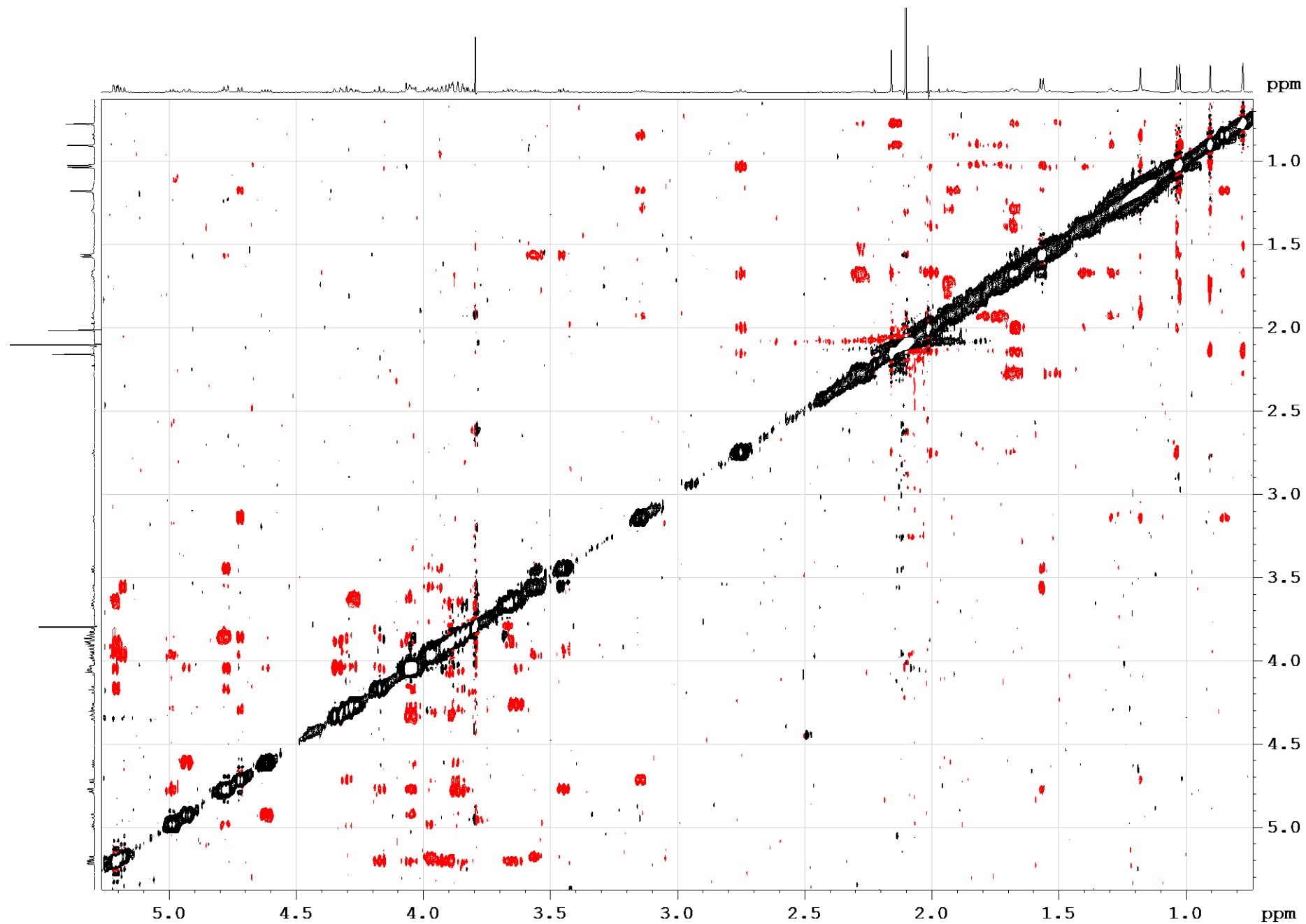


Figure S49. The ROESY (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (8) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

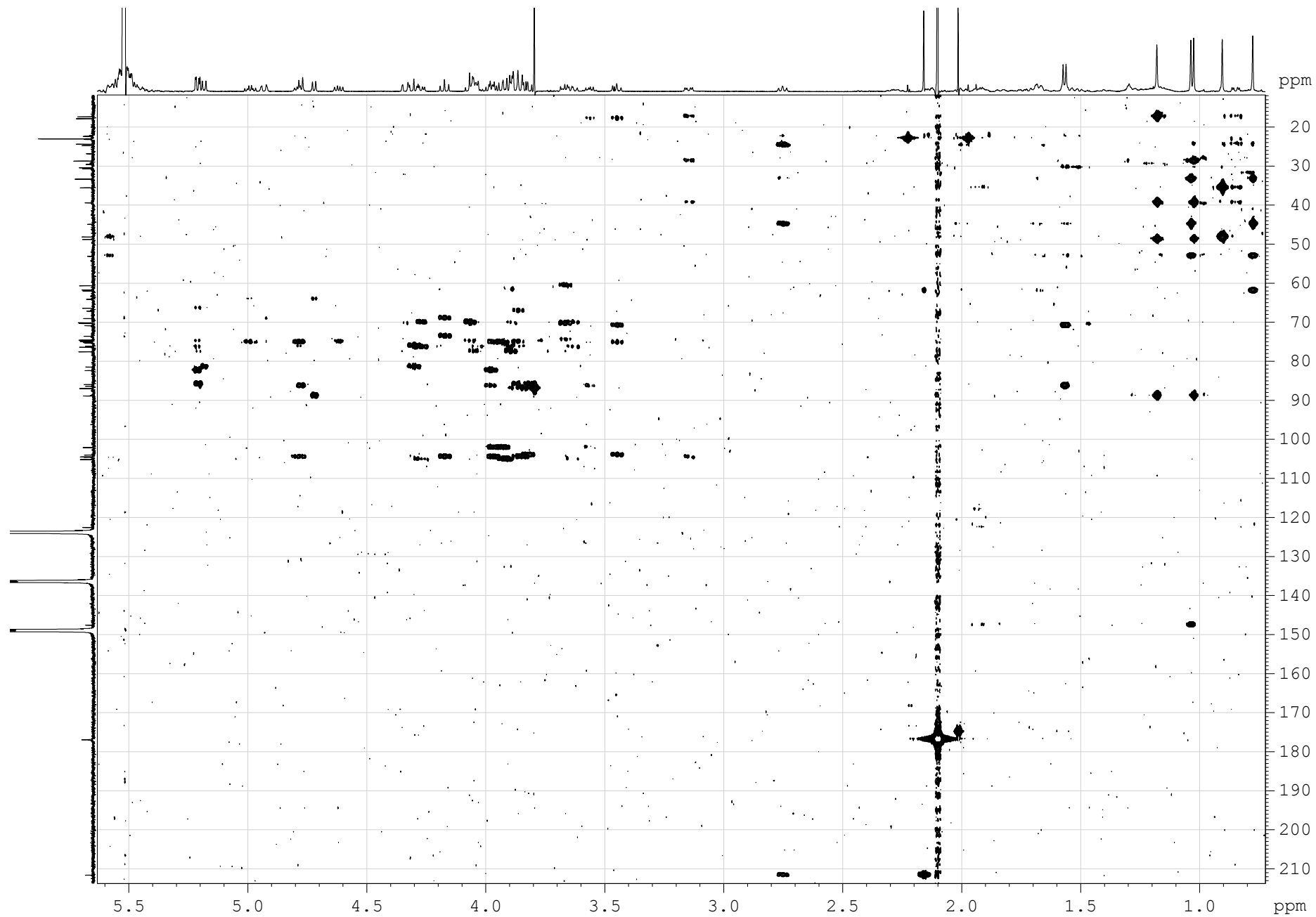


Figure S50. The HMBC (500.12 MHz) spectrum of cucumarioside A<sub>3</sub>-2 (8) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

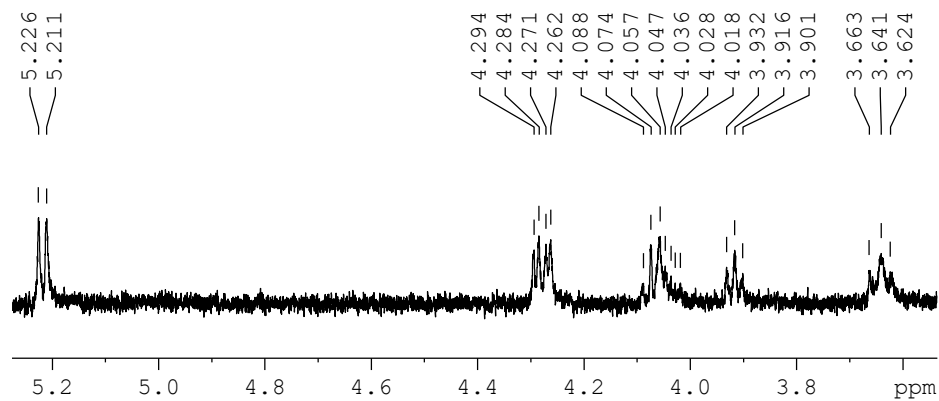
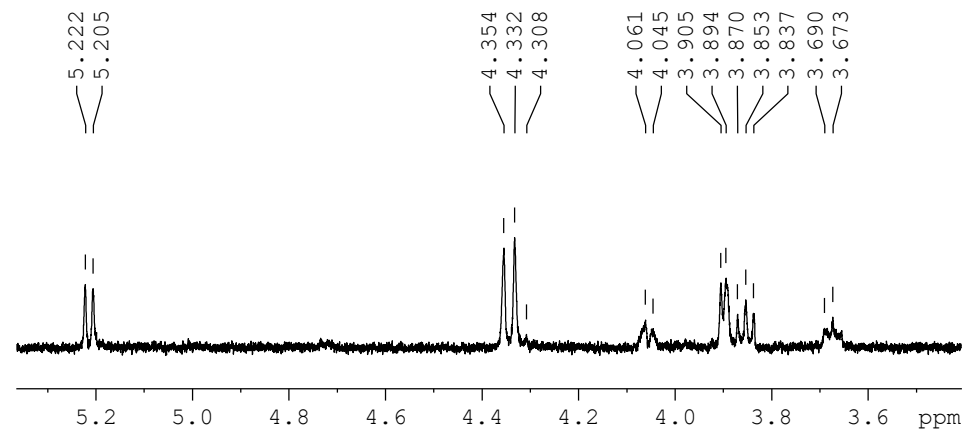
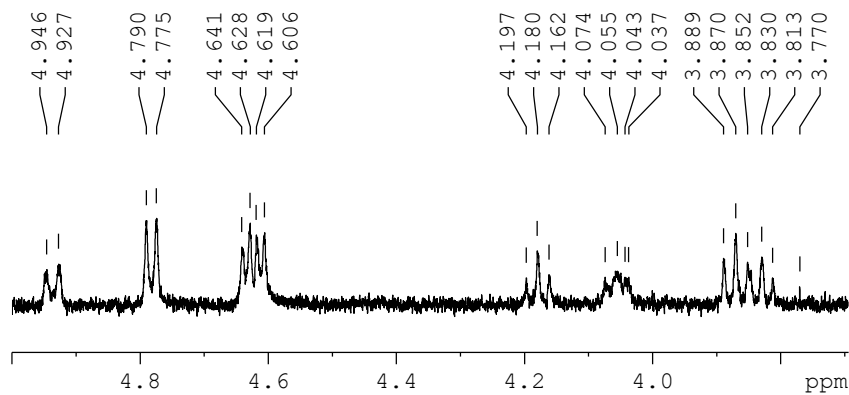
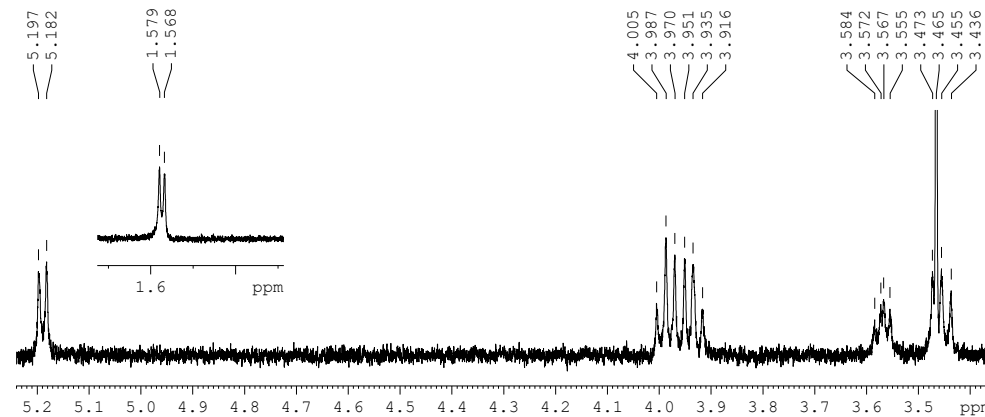
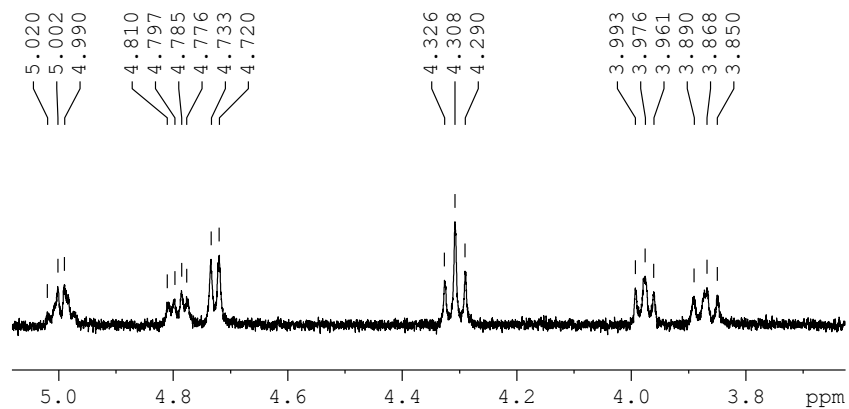


Figure S51. 1D TOCSY (500.12 MHz) spectra of Xyl1, Qui2, Glc3, MeGlc4, Xyl5 of cucumarioside A<sub>3</sub>-2 (**8**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)



**Table S7.** <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts and HMBC and ROESY correlations of carbohydrate moiety of isokoreoside A (**9**).

Atom	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. ( <i>J</i> in Hz) <sup>b,c,d</sup>	HMBC	ROESY
Xyl1 (1→C-3)				
1	104.6 CH	4.73 d (6.9)	C: 3; C: 3, 5 Xyl1	H-3; H-3, 5 Xyl1
2	<b>81.5</b> CH	3.97 dd (6.9; 9.3)	C: 1 Qui2; C: 1 Xyl1	H-4 Xyl1; H-1 Qui2
3	75.1 CH	4.31 t (9.3)	C: 2, 4 Xyl1	H-1, 5 Xyl1
4	76.1 CH	4.99 dd (8.3; 13.7)	C: 3 Xyl1	
5	64.1 CH <sub>2</sub>	4.79 dd (4.4; 11.3) 3.88 dd (8.3; 11.3)	C: 1 Xyl1	H-1, 3 Xyl1
Qui2 (1→2Xyl1)				
1	102.1 CH	5.19 d (7.5)	C: 2 Xyl1	H-2 Xyl1; H-3, 5 Qui2
2	<b>82.4</b> CH	3.95 t (8.2)	C: 1 Xyl5, C: 1, 3 Qui2	H-1 Xyl5, H-4 Qui2
3	75.2 CH	3.99 t (8.2)	C: 2, 4 Qui2	
4	<b>86.3</b> CH	3.47 t (8.2)	C: 1 Glc3; C: 3, 5 Qui2	H-1 Glc3; H-2 Qui2
5	70.9 CH	3.58 dd (6.0; 8.2)	C: 4 Qui2	H-1, 3 Qui2
6	17.8 CH <sub>3</sub>	1.58 d (6.0)	C: 4, 5 Qui2	
Glc3 (1→4Qui2)				
1	103.9 CH	4.78 d (7.8)	C: 4 Qui2	H-4 Qui2; H-5 Glc3
2	73.5 CH	3.81 t (9.6)	C: 1, 3 Glc3	
3	<b>86.5</b> CH	4.12 t (9.6)	C: 1 MeGlc4; C: 2, 4	H-1 MeGlc4; H-1 Glc3
4	69.1 CH	3.81 t (9.6)	C: 5, 6 Glc3	
5	75.5 CH	4.07 m	C: 4 MeGlc4	H-1 Glc3
6	67.3 CH <sub>2</sub>	4.95 d (10.5) 4.60 dd (6.1; 11.3)	C: 5 Glc3	H-4 Glc3
MeGlc4 (1→3Glc3)				
1	104.8 CH	5.15 d (7.9)	C: 3 Glc3	H-3 Glc3; H-3, 5 MeGlc4
2	74.3 CH	3.78 t (8.7)	C: 1 MeGlc4	H-4 MeGlc4
3	86.3 CH	3.64 t (8.7)	OMe; C: 2, 4 MeGlc4	H-1, 5 MeGlc4; OMe
4	69.8 CH	4.01 m	C: 5 MeGlc4	
5	75.5 CH	4.00 m		H-1 MeGlc4
6	67.0 CH <sub>2</sub>	4.93 d (11.3) 4.75 dd (3.8; 11.3)	C: 4 MeGlc4	
OMe	60.5 CH <sub>3</sub>	3.76 s	C: 3 MeGlc4	
Xyl5 (1→2Qui2)				
1	105.1 CH	5.23 d (7.0)	C: 2 Qui2	H-2 Qui2; H-3, 5 Xyl5
2	74.9 CH	3.92 t (8.2)	C: 1, 3 Xyl5	
3	76.4 CH	4.08 t (8.2)	C: 4 Xyl5	H-1 Xyl5
4	70.1 CH	4.06 m		
5	66.4 CH <sub>2</sub>	4.29 dd (5.1; 11.4) 3.66 brt (10.1)	C: 3, 4 Xyl5 C: 3 Xyl5	H-1 Xyl5

<sup>a</sup> Recorded at 125.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O. <sup>b</sup> Recorded at 500.12 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O. <sup>c</sup> Bold = interglycosidic positions. <sup>d</sup> Italic – sulfate positions. Multiplicity by 1D TOCSY. The original spectra of **9** are provided as Figures S51–S56.

**Table S8.** <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, HMBC and ROESY correlations of aglycone moiety of isokoreoside A (**9**).

Position	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. ( <i>J</i> in Hz) <sup>b</sup>	HMBC	ROESY
1	36.2 CH <sub>2</sub>	1.63 m 1.28 m		H-11 H-3, H-11
2	26.7 CH <sub>2</sub>	2.00 m 1.77 m		H-19, H-30
3	88.6 CH	3.11 dd (4.1; 11.4)	C: 4, 30, 31, C: 1 Xyl1	H-1, H-5, H-31, H1-Xyl1
4	39.6 C			
5	52.8 CH	0.77 brd (12.0)	C: 10, 19, 30	H-3, H-31
6	21.1 CH <sub>2</sub>	1.60 m 1.32 m		
7	28.3 CH <sub>2</sub>	1.55 m		
8	41.5 CH	2.02 m		H-15, H-18, H-19
9	148.5 C			
10	39.2 C			
11	114.1 CH	5.20 m	C: 8, 10, 13	H-1
12	35.9 CH <sub>2</sub>	2.29 brd (16.5) 1.90 brdd (6.2; 16.5)	C: 9, 11, 13, 14, 18	H-17, H-32 H-18, H-21
13	46.1 C			
14	47.5 C			
15	33.9 CH <sub>2</sub>	1.35 m		H-8, H-18, H-32
16	21.8 CH <sub>2</sub>	2.34 m 1.61 m	C: 14, 17	
17	59.8 CH	2.95 t (8.9)	C: 12, 13, 16, 18, 20	H-12, H-21, H-32
18	16.4 CH <sub>3</sub>	0.51 s	C: 12, 13, 14, 17	H-8, H-12, H-15, H-16, H-19, H-
19	22.1 CH <sub>3</sub>	0.92 s	C: 1, 5, 9, 10	H-1, H-2, H-6, H-8
20	211.9 C			
21	31.0 CH <sub>3</sub>	2.17 s	C: 17, 20	H-12, H-17, H-18
30	16.6 CH <sub>3</sub>	0.99 s	C: 3, 4, 5, 31	H-2, H-6, H-31
31	28.0 CH <sub>3</sub>	1.17 s	C: 3, 4, 5, 30	H-3, H-5, H-6
32	18.6 CH <sub>3</sub>	0.75 s	C: 8, 13, 14, 15	H-12, H-15, H-17

<sup>a</sup> Recorded at 125.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). <sup>b</sup> Recorded at 500.12 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). The original spectra of **9** are provided as Figures S51–S56.

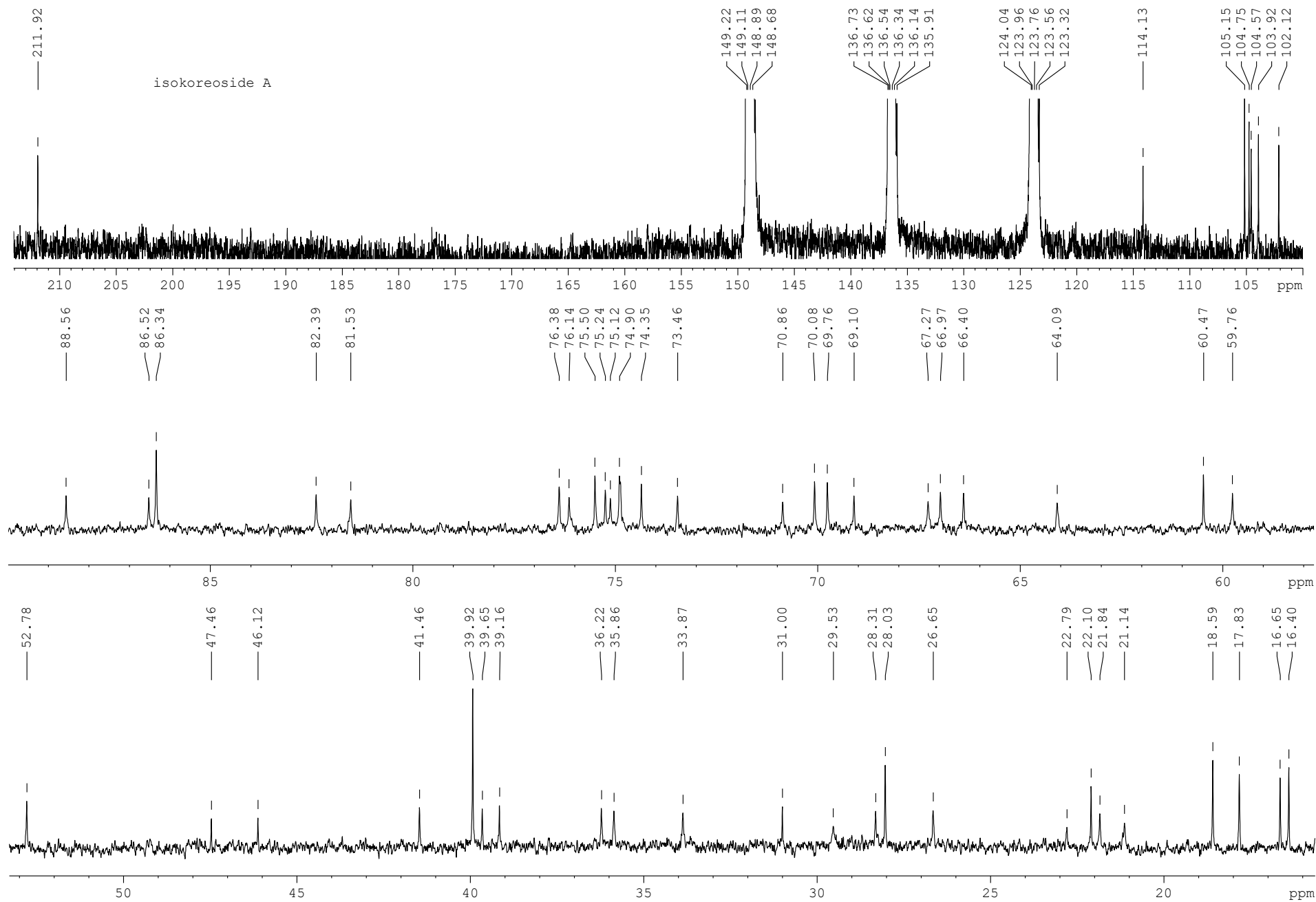


Figure S52. The  $^{13}\text{C}$  NMR (125.67 MHz) spectrum of isokoreoside A (**9**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

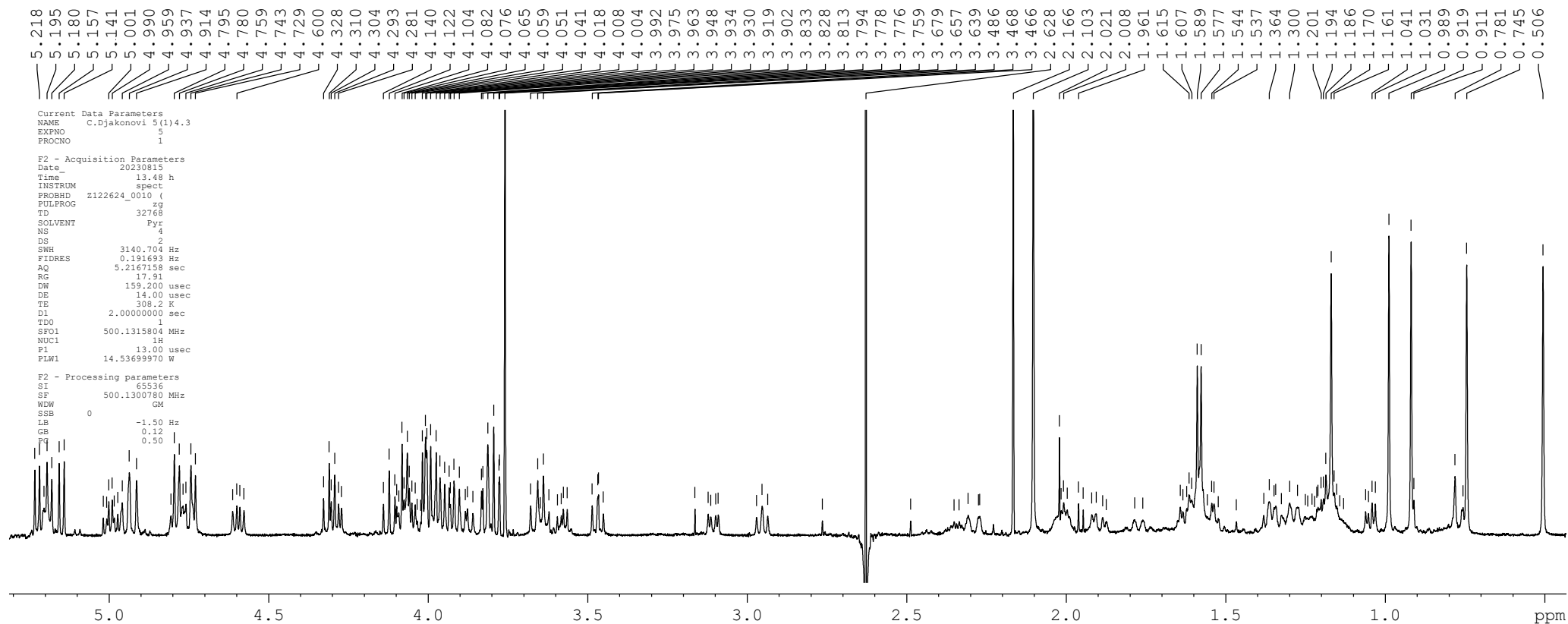


Figure S53. The  $^1\text{H}$  NMR (500.12 MHz) spectrum of isokoreoside A (**9**) in  $\text{CsD}_5\text{N}/\text{D}_2\text{O}$  (4/1)

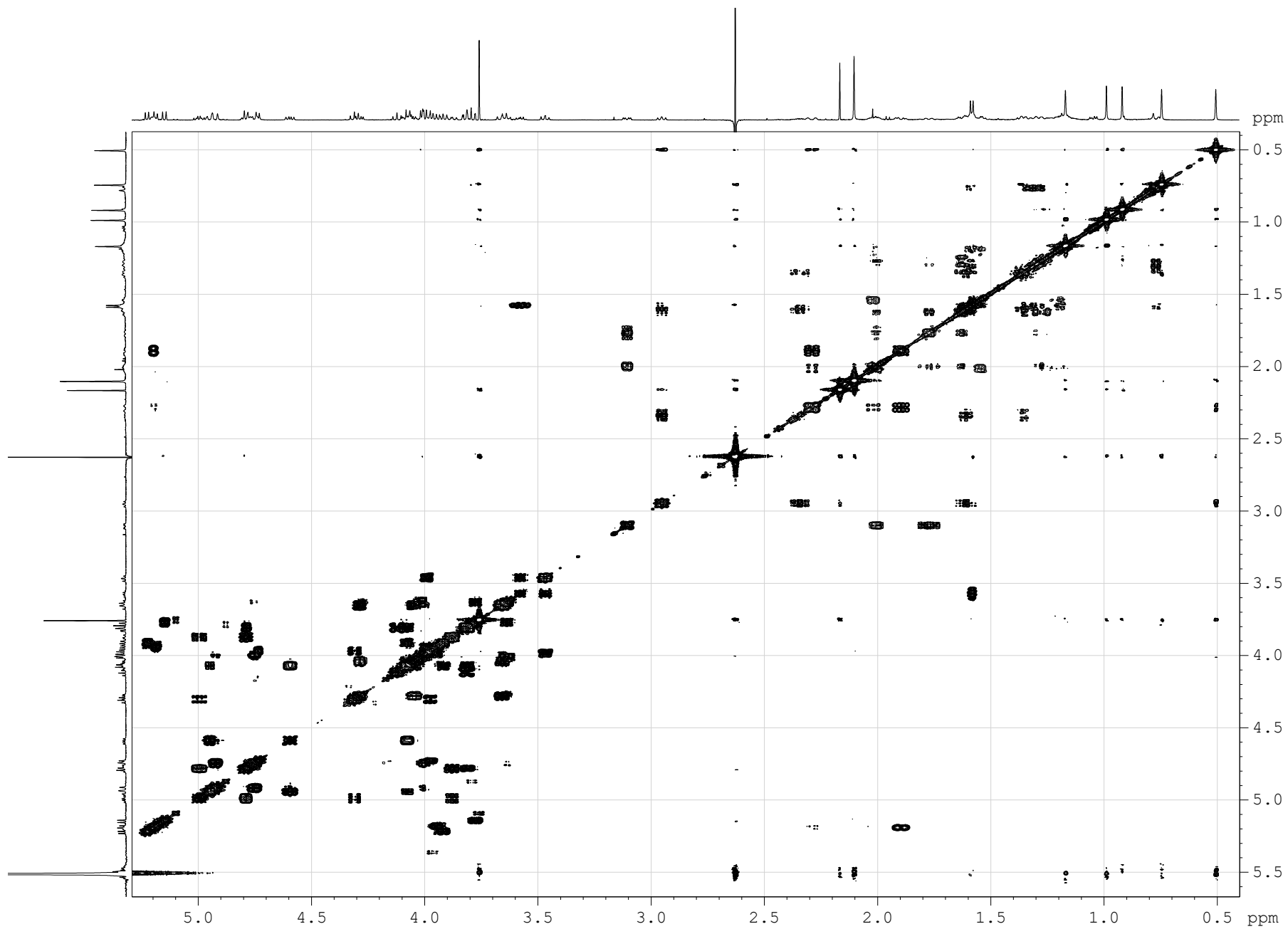


Figure S54. The COSY (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

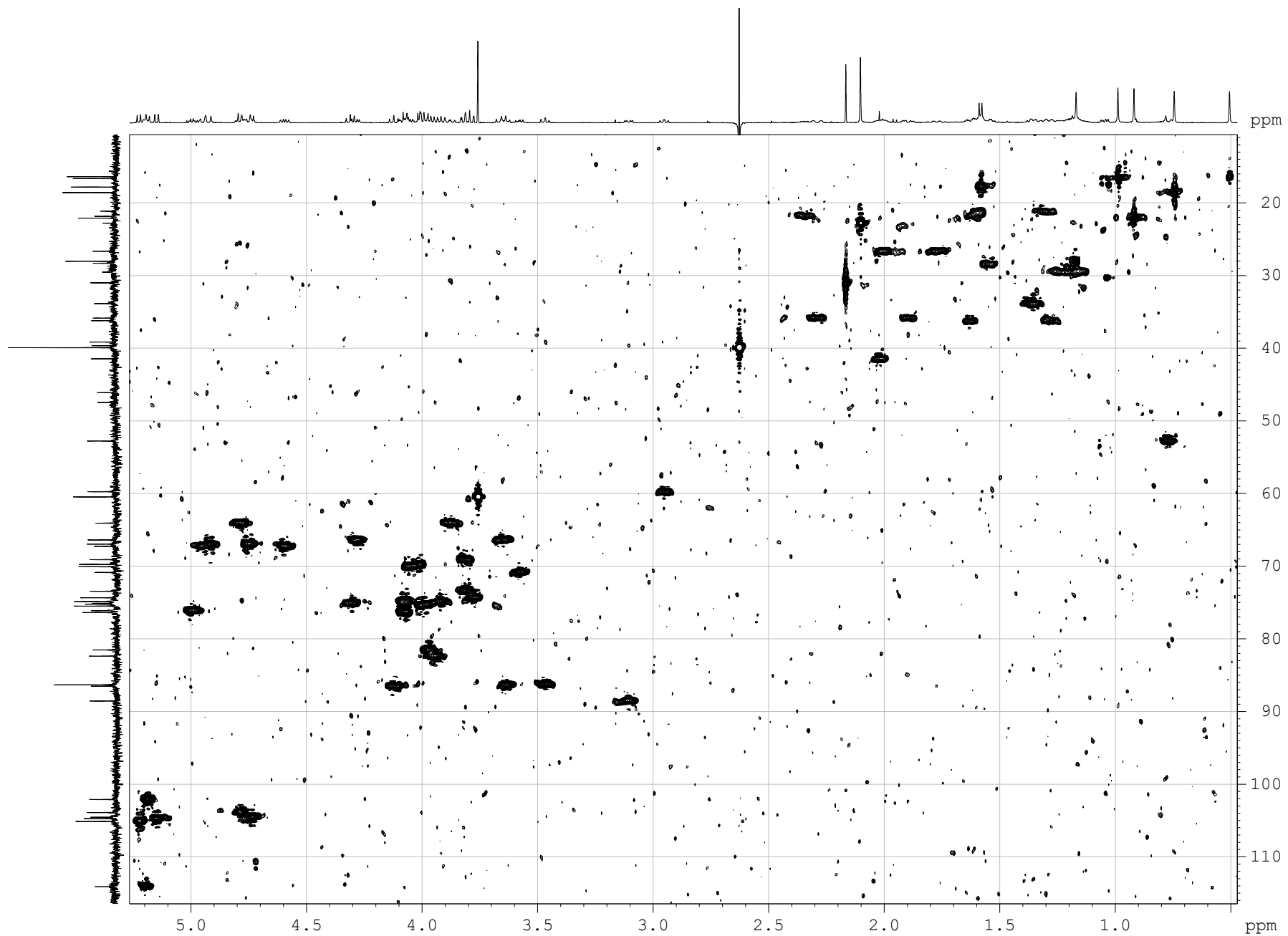


Figure S55. The HSQC (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

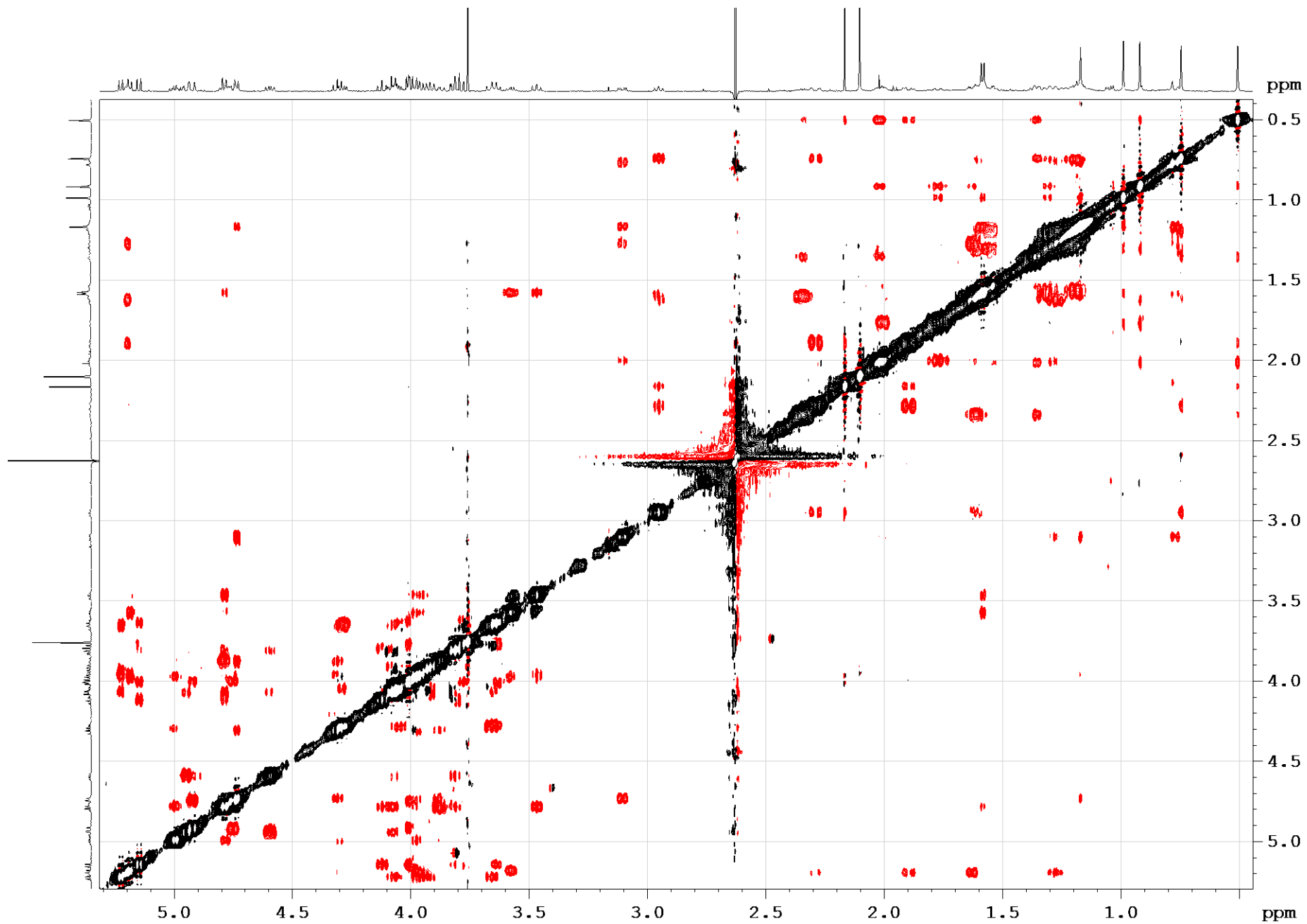


Figure S56. The ROESY (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

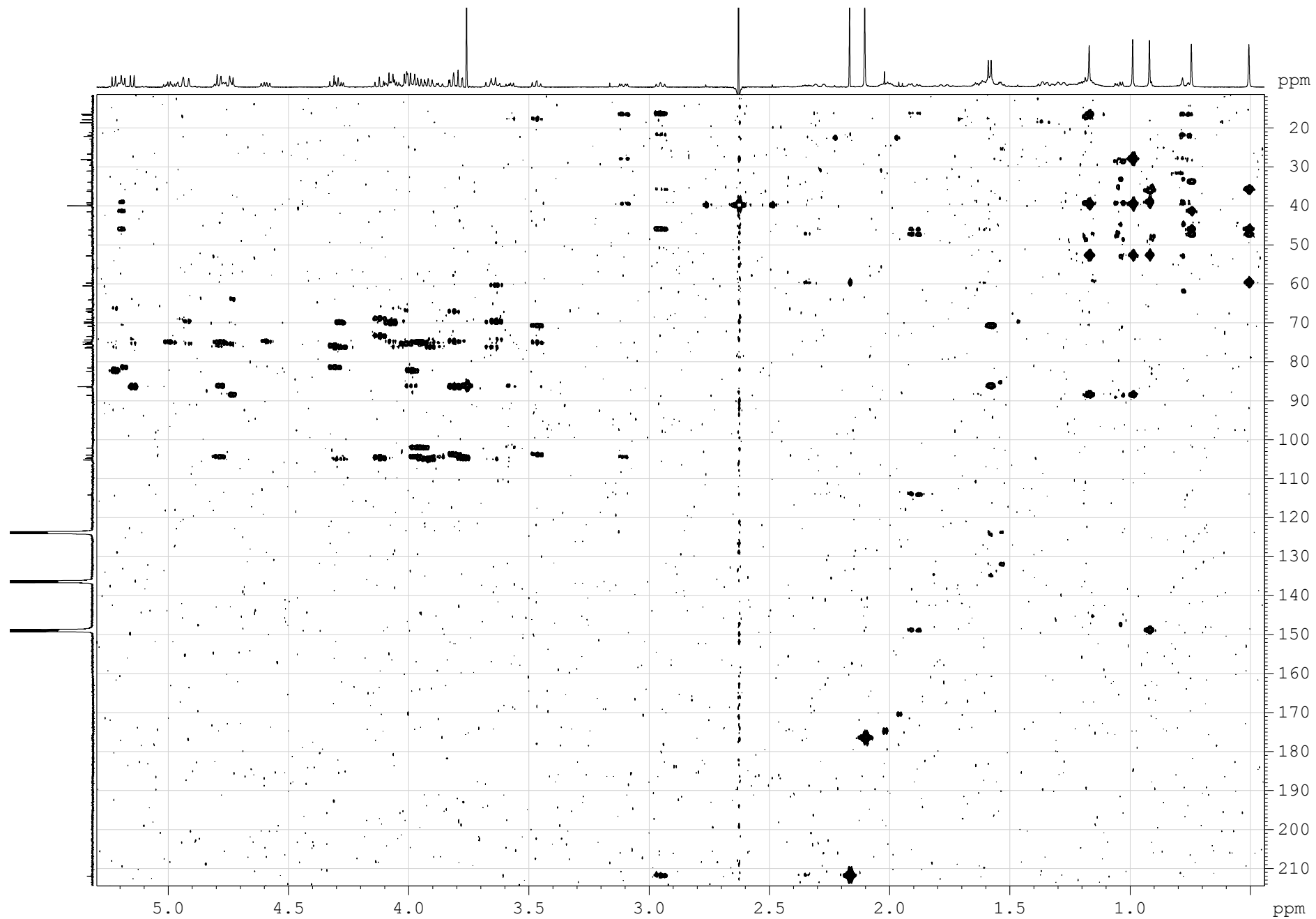


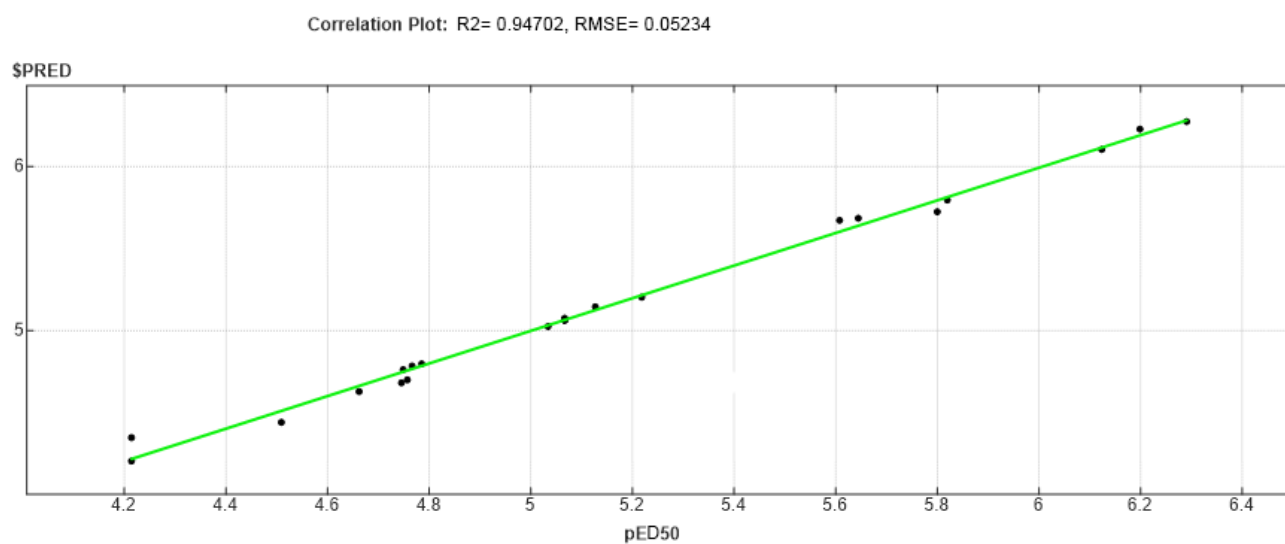
Figure S57. The HMBC (500.12 MHz) spectrum of isokoreoside A (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)



**Table S9.** <sup>13</sup>C NMR chemical shifts of koreoside A (**10**).

Position	$\delta_c$ mult. <sup>a</sup>	Position	$\delta_c$ mult. <sup>a</sup>
1	35.5 CH <sub>2</sub>	Qui2 (1→2Xyl1)	
2	26.8 CH <sub>2</sub>	1	102.1 CH
3	88.8 CH	2	82.4 CH
4	39.4 C	3	75.2 CH
5	48.7 CH	4	86.3 CH
6	23.1 CH <sub>2</sub>	5	70.9 CH
7	122.5 CH	6	17.8 CH <sub>3</sub>
8	147.6 C	Glc3 (1→4Qui2)	
9	48.1 CH	1	103.9 CH
10	35.5 C	2	73.4 CH
11	22.4 CH <sub>2</sub>	3	86.5 CH
12	33.3 CH <sub>2</sub>	4	69.1 CH
13	53.1 C	5	74.8 CH
14	44.9 C	6	67.3 CH <sub>2</sub>
15	33.3 CH <sub>2</sub>	MeGlc4 (1→3Glc3)	
16	22.3 CH <sub>2</sub>	1	104.7 CH
17	61.9 CH	2	74.3 CH
18	24.7 CH <sub>3</sub>	3	86.3 CH
19	24.4 CH <sub>3</sub>	4	69.8 CH
20	211.7 C	5	75.6 CH
21	30.4 CH <sub>3</sub>	6	67.0 CH <sub>2</sub>
30	17.3 CH <sub>3</sub>	OMe	60.5 CH <sub>3</sub>
31	28.7 CH <sub>3</sub>	Xyl5 (1→2Qui2)	
32	30.6 CH <sub>3</sub>	1	105.2 CH
Xyl1 (1→C-3)		2	74.9 CH
1	104.5 CH	3	76.4 CH
2	81.6 CH	4	70.1 CH
3	75.1 CH	5	66.4 CH <sub>2</sub>
4	76.1 CH		
5	64.1 CH <sub>2</sub>		

<sup>a</sup> Recorded at 125.67 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O.



**Figure S58.** The PCR QSAR model correlation plot reflecting the relationship of predicted and experimental hemolytic activity. The PCR analysis of 148 selected calculated for 20 glycosides tested. The membranotropic action was expressed as pED<sub>50</sub>.