

## Supplementary data content page

**Title:** Triterpene glycosides from the Far Eastern sea cucumber *Thyonidium (=Duasmodactyla) kurilensis* (Levin): the structures, cytotoxicities and biogenesis of Kurilosides A<sub>3</sub>, D<sub>1</sub>, G, H, I, I<sub>1</sub>, J, K and K<sub>1</sub>

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**Table S1.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts, HMBC and ROESY correlations of the carbohydrate moiety of kuriloside A<sub>3</sub> (**1**).

Atom.	$\delta_{\text{C}}$ mult. <sup>a, b, c</sup>	$\delta_{\text{H}}$ mult. <sup>d</sup> (J in Hz)	HMBC	ROESY
Xyl1 (1→C-3)				
1	104.7 CH	4.64 d (7.1)	C-3	H-3; H-3, 5 Xyl1
2	<b>82.0</b> CH	3.95 t (7.1)	C: 1 Qui2; C: 1, 3 Xyl1	H-1 Qui2
3	75.1 CH	4.15 t (7.9)	C: 2, 4 Xyl1	H-1 Xyl1
4	<b>78.0</b> CH	4.13 t (7.9)	C: 1 Glc4; C: 3 Xyl1	H-1 Glc4
5	63.5 CH <sub>2</sub>	4.36 dd (5.0; 11.4) 3.61 m	C: 3, 4 Xyl1	
Qui2 (1→2Xyl1)				
1	104.5 CH	5.03 d (7.6)	C: 2 Xyl1	H-2 Xyl1; H-3, 5 Qui2
2	75.6 CH	3.88 t (8.4)	C: 1, 3 Qui2	H-4 Qui2
3	75.1 CH	4.00 t (8.4)	C: 2, 4 Qui2	H-1, 5 Qui2
4	<b>86.3</b> CH	3.53 t (8.4)	C: 1 Glc3; C: 3, 5 Qui2	H-1 Glc3; H-2 Qui2
5	71.4 CH	3.70 dd (5.9; 9.3)		H-1 Qui2
6	17.9 CH <sub>3</sub>	1.62 d (5.9)	C: 4, 5 Qui2	
Glc3 (1→4Qui2)				
1	104.6 CH	4.81 d (7.5)	C: 4 Qui2	H-4 Qui2; H-3, 5 Glc3
2	74.3 CH	3.87 t (8.7)	C: 1, 3 Glc3	
3	77.6 CH	4.13 t (8.7)	C: 4 Glc3	H-1 Glc3
4	70.9 CH	3.93 t (8.7)	C: 5 Glc3	
5	77.5 CH	3.92 t (8.7)	C: 6 Glc3	H-1, 3 Glc3
6	61.8 CH <sub>2</sub>	4.39 d (12.4) 4.06 dd (5.0; 12.4)	C: 5 Glc3	
Glc4 (1→4Xyl1)				
1	102.3 CH	4.87 d (7.5)	C: 4 Xyl1	H-4 Xyl1; H-3, 5 Glc4
2	73.2 CH	3.83 t (8.7)	C: 1, 3 Glc4	
3	<b>86.0</b> CH	4.15 t (8.7)	C: 2, 4 Glc4; C: 1 MeGlc5	H-1 MeGlc5; H-1, 5 Glc4
4	69.2 CH	3.88 t (8.7)	C: 3, 5, 6 Glc4	
5	75.1 CH	4.02 t (8.7)		H-1, 3 Glc4
6	67.2 CH <sub>2</sub>	4.93 brd (11.2) 4.66 dd (6.0; 11.2)	C: 4, 5 Glc4 C: 5 Glc4	
MeGlc5 (1→3Glc4)				
1	104.4 CH	5.18 d (7.5)	C: 3 Glc4	H-3 Glc4; H-3, 5 MeGlc5
2	74.5 CH	3.83 t (8.6)	C: 1 MeGlc5	
3	86.9 CH	3.65 t (8.6)	C: 2, 4 MeGlc5, OMe	H-1, 5 MeGlc5
4	70.3 CH	3.89 t (8.6)	C: 3 MeGlc5	H-6 MeGlc6
5	77.3 CH	3.89 t (8.6)	C: 4 MeGlc5	H-1, 3 MeGlc5
6	61.7 CH <sub>2</sub>	4.34 d (12.8) 4.05 dd (6.4; 12.8)	C: 4, 5 MeGlc5 C: 5 MeGlc5	
OMe	60.6 CH <sub>3</sub>	3.79 s	C: 3 MeGlc5	

<sup>a</sup>Recorded at 176.03 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). <sup>b</sup>Bold = interglycosidic positions. <sup>c</sup>Italic = sulphate position. <sup>d</sup>Recorded at 700.00 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). Multiplicity by 1D TOCSY.

**Table S2.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts, HMBC and ROESY correlations of the aglycone of kurilosides A<sub>3</sub> (**1**) and G (**3**).

Position	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. ( $J$ in Hz) <sup>b</sup>	HMBC	ROESY
1	36.2 CH <sub>2</sub>	1.77 m 1.41 m	C: 4, 30, 31, C:1 Xyl1	H-11 H-3, H-5, H-11, H-31
2	27.0 CH <sub>2</sub>	2.19 m 1.94 m		
3	88.4 CH	3.19 dd (4.6; 12.5)	C: 4, 10, 19, 30	H-1, H-5, H-31, H1-Xyl1
4	39.7 C			
5	52.8 CH	0.92 brd (12.5)	C: 4, 10, 19, 30	H-1, H-3, H-7, H-31
6	21.2 CH <sub>2</sub>	1.70 m 1.47 m		
7	28.4 CH <sub>2</sub>	1.64 m 1.36 m		H-31 H-19
8	41.5 CH	2.16 m		
9	149.0 C			
10	39.4 C			
11	114.2 CH	5.31 brd (6.3)	C: 8, 10, 12, 13	H-1
12	35.8 CH <sub>2</sub>	2.48 brd (16.1) 1.94 dd (6.3; 16.1)	C: 9, 11, 13, 18	H-17, H-32 H-8, H-18
13	46.9 C			
14	46.8 C			
15	45.2 CH <sub>2</sub>	2.07 dd (9.2; 13.2) $\beta$ 1.79 d (13.2) $\alpha$	C: 8, 13, 32 C: 14, 16, 32	H-16, H-18 H-32
16	71.1 CH	5.40 brt (7.5)	C: 13, 14, 20	H-15 $\beta$ , H-18
17	70.0 CH	3.40 d (6.4)	C: 12, 13, 14, 16, 18, 20	H-12, H-21, H-32
18	17.3 CH <sub>3</sub>	0.71 s	C: 12, 13, 17	H-8, H-12, H-15 $\beta$ , H-16, H-19
19	22.3 CH <sub>3</sub>	1.10 s	C: 1, 5, 9, 10	H-1, H-2, H-6, H-8, H-18
20	208.8 C			
21	31.2 CH <sub>3</sub>	2.18 s	C: 17, 20	H-12, H-17
30	16.5 CH <sub>3</sub>	1.05 s	C: 3, 4, 5, 31	H-2, H-6, H-31, H-6 Qui2
31	27.9 CH <sub>3</sub>	1.24 s	C: 3, 4, 5, 30	H-3, H-5, H-6, H-30, H-1 Xyl1
32	20.0 CH <sub>3</sub>	1.24 s	C: 8, 13, 15	H-7, H-12, H-15, H-17

<sup>a</sup> Recorded at 176.04 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). <sup>b</sup> Recorded at 700.13 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1).

**Table S3.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts, HMBC and ROESY correlations of carbohydrate moiety of kuriloside D<sub>1</sub> (**2**).

Atom	$\delta_{\text{C}}$ mult. <sup>a, b, c</sup>	$\delta_{\text{H}}$ mult. ( <i>J</i> in Hz) <sup>d</sup>	HMBC	ROESY
Xyl1 (1→C-3)				
1	105.0 CH	4.70 d (7.6)	C: 3	H-3; H-3, 5 Xyl1
2	<b>83.3</b> CH	3.95 t (8.3)	C: 3 Xyl1	H-1 Qui2
3	75.4 CH	4.14 t (8.3)	C: 2 Xyl1	H-1 Xyl1
4	<b>79.7</b> CH	4.07 m		H-1 Glc5
5	63.8 CH <sub>2</sub>	4.30 dd (6.1; 12.1) 3.59 dd (9.1; 12.1)		H-1 Xyl1
Qui2 (1→2Xyl1)				
1	105.3 CH	5.02 d (7.6)	C: 2 Xyl1	H-2 Xyl1; H-3, 5 Qui2
2	75.8 CH	3.95 t (8.3)		H-4 Qui2
3	75.3 CH	4.05 t (8.3)	C: 2, 4 Qui2	H-1 Qui2
4	<b>87.1</b> CH	3.56 t (8.3)	C: 1 Glc3; C: 5 Qui2	H-1 Glc3; H-2 Qui2
5	71.6 CH	3.76 dd (6.1; 9.7)		H-1, 3 Qui2
6	17.9 CH <sub>3</sub>	1.71 d (6.1)	C: 4, 5 Qui2	
Glc3 (1→4Qui2)				
1	104.8 CH	4.90 d (7.5)	C: 4 Qui2	H-4 Qui2
2	73.6 CH	4.03 t (8.2)	C: 1, 3 Glc3	
3	<b>88.1</b> CH	4.20 m	C: 4 Glc3	H-1 Glc4; H-1 Glc3
4	69.7 CH	4.00 m	C: 3, 5 Glc3	
5	78.5 CH	4.00 m		
6	62.1 CH <sub>2</sub>	4.47 d (12.3) 4.13 m		
Glc4 (1→3Glc3)				
1	105.7 CH	5.28 d (8.2)	C: 3 Glc3	H-3 Glc3; H-3, 5 Glc4
2	75.3 CH	4.06 t (9.1)	C: 1, 3 Glc4	
3	77.9 CH	4.22 t (9.1)	C: 2, 4 Glc4	
4	71.5 CH	4.15 t (9.1)	C: 5, 6 Glc4	
5	78.1 CH	4.00 m		H-1 Glc4
6	62.4 CH <sub>2</sub>	4.51 dd (3.0; 11.5) 4.28 dd (5.4; 11.5)		
Glc5 (1→4Xyl1)				
1	103.7 CH	4.86 d (7.8)	C: 4 Xyl1	H-4 Xyl1; H-3 Glc5
2	73.2 CH	3.88 t (7.8)	C: 1, 3 Glc5	
3	<b>87.0</b> CH	4.14 t (9.2)	C: 1 MeGlc6; C: 2, 4 Glc5	H-1 MeGlc6; H-1 Glc5
4	69.6 CH	3.92 t (9.2)	C: 3, 5, 6 Glc5	
5	76.1 CH	4.11 m		
6	67.2 CH <sub>2</sub>	5.18 d (9.9) 4.76 dd (6.6; 11.2)	C: 5 Glc5	
MeGlc6 (1→3Glc4)				
1	105.3 CH	5.24 d (7.9)	C: 3 Glc5	H-3 Glc5; H-3, 5 MeGlc6
2	74.9 CH	3.95 t (8.6)	C: 1, 3 MeGlc6	
3	87.8 CH	3.68 t (8.6)	C: 2, 4 MeGlc6; OMe	H-1, 5 MeGlc6; OMe
4	70.4 CH	4.13 t (8.6)	C: 3, 6 MeGlc6	H-6 MeGlc6
5	78.2 CH	3.92 t (8.6)		H-1, 3 MeGlc6
6	61.9 CH <sub>2</sub>	4.44 dd (2.6; 11.8) 4.26 dd (5.3; 11.8)	C: 4 MeGlc6 C: 5 MeGlc6	
OMe	60.5 CH <sub>3</sub>	3.85 s	C: 3 MeGlc6	

<sup>a</sup> Recorded at 176.04 MHz in CsD<sub>5</sub>N/D<sub>2</sub>O (4/1). <sup>b</sup> Bold = interglycosidic positions. <sup>c</sup> Italic = sulfate position. <sup>d</sup> Recorded at 700.13 MHz in CsD<sub>5</sub>N/D<sub>2</sub>O (4/1). Multiplicity by 1D TOCSY.

**Table S4.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts, HMBC and ROESY correlations of the aglycone moiety of kurilosides H (4) and I<sub>1</sub> (6).

Position	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. ( $J$ in Hz) <sup>b</sup>	HMBC	ROESY
1	36.2 CH <sub>2</sub>	1.77 m 1.38 m		H-11, H-19 H-3, H-5, H-11
2	27.0 CH <sub>2</sub>	2.19 m 1.94 m		H-19 H-19, H-30
3	88.3 CH	3.18 dd (4.2; 11.9)	C: 1, 30, 31, C-1Xyl1	H-1, H-5, H-31, H-1Xyl1
4	39.7 C			
5	52.7 CH	0.87 brd (12.3)	C: 6, 10, 19, 30	H-1, H-3, H-7, H-31
6	21.1 CH <sub>2</sub>	1.70 m 1.50 m		H-30, H-31 H-19, H-30
7	28.0 CH <sub>2</sub>	1.58 m 1.27 m		H-15 H-5, H-32
8	41.2 CH	2.20 m		H-18
9	148.9 C			
10	39.3 C			
11	114.0 CH	5.23brd (5.6)	C: 8, 10, 12, 14	H-1
12	35.8 CH <sub>2</sub>	2.08m 1.78 m	C: 9, 11, 13, 15, 18	H-17, H-32 H-18, H-21
13	45.5 C			
14	43.6 C			
15	43.7 CH <sub>2</sub>	2.10dd (6.3; 13.6) 1.35dd (5.0; 13.6)	C: 32 C: 8, 13, 16, 32	H-32 H-18
16	73.8 CH	5.64 dd (5.2; 7.7; 13.4)	C: 15; OAc-16	H-32; OAc-16
17	53.3 CH	2.41dd (7.7; 10.6)	C: 12, 15, 18, 20, 21	H-12, H-21, H-32
18	15.2 CH <sub>3</sub>	0.82 s	C: 12, 13, 14, 17	H-8, H-12, H-19, H-20, H-21
19	22.3 CH <sub>3</sub>	1.14 s	C: 1, 5, 9, 10	H-1, H-2, H-6, H-8, H-18, H-30
20	69.4 CH	5.46 dd (6.1; 10.6)	C: 16, 17, 21, OAc-20	H-21, OAc-20
21	19.6 CH <sub>3</sub>	1.32d (6.0)	C: 17, 20	H-12, H-17, H-18, H-20
30	16.4 CH <sub>3</sub>	1.04 s	C: 3, 4, 5, 31	H-2, H-6, H-31
31	27.8 CH <sub>3</sub>	1.24 s	C: 3, 4, 5, 30	H-3, H-5, H-6, H-30, H-1 Xyl1
32	18.9 CH <sub>3</sub>	0.76 s	C: 8, 13, 14, 15	H-7, H-12, H-15, H-16, H-17
<u>COOCH<sub>3</sub>-16</u>	169.8 C			
<u>COOCH<sub>3</sub>-16</u>	20.2 CH <sub>3</sub>	2.12 s		H-16, H-18
<u>COOCH<sub>3</sub>-20</u>	169.9 C			
<u>COOCH<sub>3</sub>-20</u>	21.0 CH <sub>3</sub>	2.05 s		H-21

<sup>a</sup>Recorded at 176.03 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1). <sup>b</sup>Recorded at 700.00 MHz in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1).

**Table S5.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts, HMBC and ROESY correlations of carbohydrate moiety of DS-kuriloside L (**10**).

Atom	$\delta_{\text{C}}$ mult. <sup>a, b</sup>	$\delta_{\text{H}}$ mult. ( $J$ in Hz) <sup>c</sup>	HMBC	ROESY
Xyl1 (1→C-3)				
1	105.2 CH	4.75 d (7.6)	C: 3; C: 5 Xyl1	H-3; H-3, 5 Xyl1
2	<b>83.2</b> CH	4.10 dd (7.6; 8.7)	C: 1 Qui2; C: 1, 3 Xyl1	H-1 Qui2
3	75.7 CH	4.23 t (8.7)	C: 2, 4 Xyl1	H-1, 5 Xyl1
4	<b>77.5</b> CH	4.29 m	C: 1 Glc3; C: 3 Xyl1	H-1 Glc3
5	63.9 CH <sub>2</sub>	4.39 dd (4.6; 11.6) 3.63 dd (8.7; 11.6)	C: 1, 3, 4 Xyl1 C: 4 Xyl1	H-1 Xyl1 H-1, 3 Xyl1
Qui2 (1→2Xyl1)				
1	106.0 CH	5.20 d (8.0)	C: 2 Xyl1	H-2 Xyl1; H-3, 5 Qui2
2	77.0 CH	4.06 t (8.0)	C: 1, 3 Qui2	H-4 Qui2
3	77.6 CH	4.14 t (8.6)	C: 4 Qui2	H-1, 5 Qui2
4	76.5 CH	3.73 t (9.2)	C: 3, 5 Qui2	H-2 Qui2
5	73.3 CH	3.82 dd (6.3; 9.2)	C: 3, 4, 6 Qui2	H-1, 3 Qui2
6	18.4 CH <sub>3</sub>	1.70 d (6.3)	C: 4, 5 Qui2	H-4, 5 Qui2
Glc3 (1→4Xyl1)				
1	103.3 CH	5.02 d (8.4)	C: 4 Xyl1	H-4 Xyl1; H-3, 5 Glc3
2	74.2 CH	4.00 t (9.0)	C: 3 Glc3	
3	78.0 CH	4.20 t (9.0)	C: 4 Glc3	H-1 Glc3
4	71.5 CH	4.19 t (9.0)	C: 3 Glc3	
5	78.5 CH	3.98 m		H-1, 3 Glc3
6	62.4 CH <sub>2</sub>	4.54 brd (10.3) 4.32 dd (5.2; 10.3)	C: 5 Glc3	

<sup>a</sup> Recorded at 176.04 MHz in  $\text{CsD}_5\text{N}$ . <sup>b</sup> Bold = interglycosidic positions. <sup>c</sup> Recorded at 700.13 MHz in  $\text{CsD}_5\text{N}$ . Multiplicity by 1D TOCSY.

**Table S6.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts, HMBC and ROESY correlations of the aglycone moiety of DS-kuriloside L (10).

Position	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. ( $J$ in Hz) <sup>b</sup>	HMBC	ROESY
1	36.2 CH <sub>2</sub>	1.75 m 1.41 m		H-5, H-11 H-11
2	26.9 CH <sub>2</sub>	2.20 m 1.96 m		H-19, H-30
3	88.5 CH	3.23 dd (4.2; 11.7)	C: 4, 30, 31, C-1Xyl1	H-1, H-5, H-31, H-1Xyl1
4	39.8 C			
5	52.9 CH	0.94 brdd (1.9; 11.7)	C: 4, 19, 30, 31	H-1, H-3, H-31
6	21.0 CH <sub>2</sub>	1.74 m 1.53 m		H-8, H-19, H-30
7	27.9 CH <sub>2</sub>	1.67 m 1.35 m		H-5, H-32
8	39.4 CH	2.39 brd (12.2)	C: 7	
9	149.1 C			
10	39.4 C			
11	115.2 CH	5.35 brd (5.6)	C: 8, 13	H-1
12	32.1 CH <sub>2</sub>	2.61 brdd (5.6; 17.8) 2.49 brd (17.8)	C: 9, 11, 13, 14	H-18 H-32
13	49.6 C			
14	47.0 C			
15	41.7 CH <sub>2</sub>	2.26 brd (16.8) 2.06 brdd (3.7; 16.8)	C: 16, 17, 32 C: 13, 14, 16, 17, 32	H-18 H-7, H-32
16	144.3 CH	6.63 brt (2.6)		
17	152.1 C			
18	19.3 CH <sub>3</sub>	1.00 s	C: 12, 13, 14, 17	H-8, H-12, H-15
19	22.1 CH <sub>3</sub>	1.12 s	C: 1, 5, 8, 9	H-2, H-6, H-8
20	196.1 C			
21	26.7 CH <sub>3</sub>	2.29 s	C: 20	
30	16.5 CH <sub>3</sub>	1.17 s	C: 3, 4, 5, 31	H-2, H-6, H-31
31	28.0 CH <sub>3</sub>	1.32 s	C: 3, 4, 5, 30	H-3, H-6, H-30, H-1 Xyl1
32	19.8 CH <sub>3</sub>	0.88 s	C: 8, 13, 14, 15	H-7, H-12, H-15

<sup>a</sup>Recorded at 176.03 MHz in C<sub>5</sub>D<sub>5</sub>N. <sup>b</sup>Recorded at 700.00 MHz in C<sub>5</sub>D<sub>5</sub>N.

**Table S7.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts, HMBC and ROESY correlations of carbohydrate moiety of DS-kuriloside M (**11**).

Atom	$\delta_{\text{C}}$ mult. <sup>a, b</sup>	$\delta_{\text{H}}$ mult. ( $J$ in Hz) <sup>c</sup>	HMBC	ROESY
Xyl1 (1→C-3)				
1	105.1 CH	4.75 d (6.4)	C: 3	H-3; H-3, 5 Xyl1
2	<b>83.5</b> CH	4.03 t (8.9)	C: 1, 3 Xyl1	H-1 Qui2
3	75.6 CH	4.22 t (8.9)	C: 2, 4 Xyl1	H-1, 5 Xyl1
4	<b>77.2</b> CH	4.26 dd (5.1; 8.5)	C: 1 Glc4; C: 3 Xyl1	H-1 Glc4
5	63.9 CH <sub>2</sub>	4.39 dd (5.0; 11.2) 3.64 dd (9.1; 11.2)	C: 1, 3 Xyl1	H-1 Xyl1
Qui2 (1→2Xyl1)				
1	105.4 CH	5.15 d (8.1)	C: 2 Xyl1	H-2 Xyl1; H-3, 5 Qui2
2	76.2 CH	4.04 t (9.1)	C: 1, 3 Qui2	H-4 Qui2
3	75.8 CH	4.15 t (9.1)	C: 2, 4 Qui2	H-1, 5 Qui2
4	<b>87.2</b> CH	3.68 t (9.1)	C: 1 Glc3; C: 3, 5 Qui2	H-1 Glc3; H-2 Qui2
5	71.5 CH	3.82 dd (6.1; 9.1)		H-1, 3 Qui2
6	18.1 CH <sub>3</sub>	1.77 d (6.1)	C: 4, 5 Qui2	
Glc3 (1→4Qui2)				
1	105.3 CH	5.01 d (7.5)	C: 4 Qui2	H-4 Qui2; H-3, 5 Glc3
2	74.8 CH	4.05 t (8.5)	C: 1 Glc3	
3	78.1 CH	4.23 t (8.5)	C: 2, 4 Glc3	H-1 Glc3
4	71.6 CH	4.15 t (8.5)	C: 5 Glc3	H-6 Glc3
5	78.2 CH	4.08 t (8.5)		H-1, 3 Glc3
6	62.5 CH <sub>2</sub>	4.60 brd (13.2) 4.29 m		
Glc4 (1→4Xyl1)				
1	102.7 CH	4.98 d (7.5)	C: 4 Xyl1	H-4 Xyl1; H-3, 5 Glc4
2	72.9 CH	4.00 t (8.5)	C: 1 Glc4	
3	<b>88.0</b> CH	4.18 t (8.5)	C: 1 MeGlc5; C: 2 Glc4	H-1 MeGlc5; H-1 Glc4
4	69.6 CH	4.07 t (8.5)	C: 5, 6 Glc4	
5	78.3 CH	3.89 m		H-1, 3 Glc4
6	62.0 CH <sub>2</sub>	4.44 brd (13.2) 4.22 brdd (5.6; 13.2)		
MeGlc5 (1→3Glc4)				
1	105.5 CH	5.24 d (8.5)	C: 3 Glc4	H-3 Glc4; H-3, 5 MeGlc5
2	75.0 CH	3.99 t (8.5)	C: 1, 3 MeGlc5	
3	87.8 CH	3.71 t (8.5)	C: 2, 4 MeGlc5; OMe	
4	70.4 CH	4.14 t (8.5)	C: 5, 6 MeGlc5	
5	78.2 CH	3.95 m		H-1, 3 MeGlc5
6	62.1 CH <sub>2</sub>	4.46 brd (12.2) 4.27 m		
OMe	60.5 CH <sub>3</sub>	3.86 s	C: 3 MeGlc5	

<sup>a</sup> Recorded at 176.04 MHz in  $\text{CsD}_5\text{N}$ . <sup>b</sup> Bold = interglycosidic positions. <sup>c</sup> Recorded at 700.13 MHz in  $\text{C}_5\text{D}_5\text{N}$ . Multiplicity by 1D TOCSY.

**Table S8.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts, HMBC and ROESY correlations of the aglycone moiety of DS-kuriloside M (**11**).

Position	$\delta_{\text{C}}$ mult. <sup>a</sup>	$\delta_{\text{H}}$ mult. ( $J$ in Hz) <sup>b</sup>	HMBC	ROESY
1	35.7 CH <sub>2</sub>	1.45 m	C: 2, 3, 10, 19	H-3, H-5, H-11, H-19
2	27.2 CH <sub>2</sub>	2.16 m 1.94 m		H-19, H-30
3	88.7 CH	3.29 dd (4.1; 11.6)	C: 4, 30, 31, C-1Xyl1	H-1, H-5, H-31, H-1Xyl1
4	39.5 C			
5	49.2 CH	1.00 brdd (3.5; 12.3)		H-1, H-3, H-31
6	23.1 CH <sub>2</sub>	2.05 m 1.99 m	C: 7, 8, 10	H-31 H-19, H-30
7	122.8 CH	5.72 m	C: 9	
8	147.6 C			
9	47.7 CH	2.31 m		H-19
10	35.5 C			
11	22.4 CH <sub>2</sub>	1.80 m 1.61 m		H-1
12	33.3 CH <sub>2</sub>	2.18 m 1.74 m	C: 9, 14, 16, 18 C: 13, 18	H-17, H-32
13	52.4 C			
14	45.6 C			
15	45.0 CH <sub>2</sub>	2.31 m 2.06 d (12.9)	C: 13, 32 C: 13, 14, 16, 32	H-16, H-18 H-32
16	71.5 CH	5.35 m		H-18
17	71.8 CH	3.22 d (6.2)	C: 12, 14, 16, 18, 20	H-21, H-32
18	25.6 CH <sub>3</sub>	1.02 s	C: 12, 13, 14, 17	H-9
19	24.4 CH <sub>3</sub>	1.07 s	C: 1, 5, 9, 10	H-1, H-2, H-9, H-30
20	208.6 C			
21	30.78 CH <sub>3</sub>	2.20 s	C: 17, 20	H-12, H-17
30	17.2 CH <sub>3</sub>	1.17 s	C: 3, 4, 5, 31	H-2, H-6, H-19, H-31
31	28.6 CH <sub>3</sub>	1.32 s	C: 3, 4, 5, 30	H-3, H-5, H-6, H-30, H-1 Xyl1
32	31.4 CH <sub>3</sub>	1.59 s	C: 8, 13, 15	H-11, H-12, H-15, H-17

<sup>a</sup>Recorded at 176.03 MHz in C<sub>5</sub>D<sub>5</sub>N. <sup>b</sup>Recorded at 700.00 MHz in C<sub>5</sub>D<sub>5</sub>N.

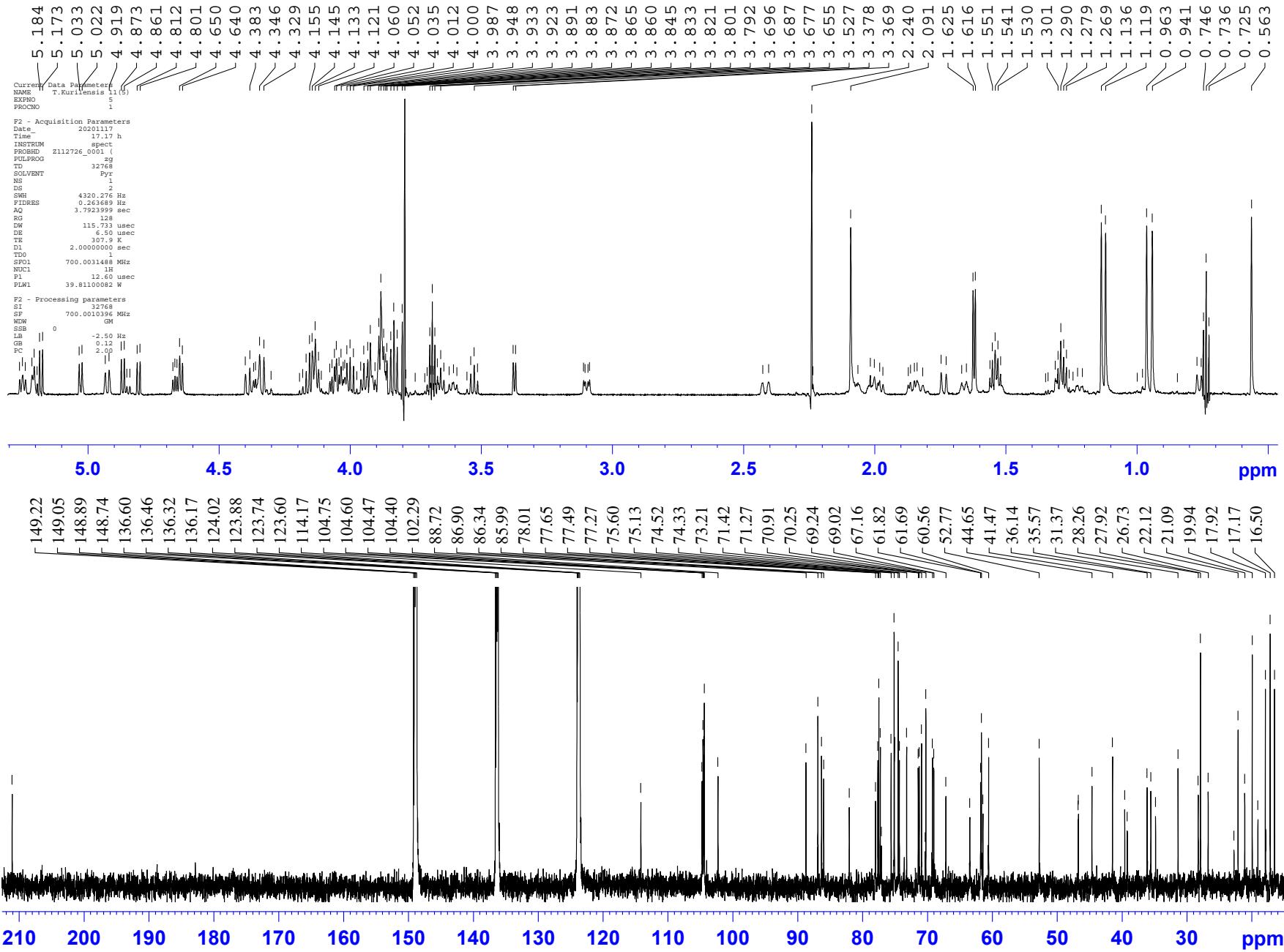


Figure S1. The  $^1\text{H}$  NMR (700.00 MHz) and  $^{13}\text{C}$  NMR (176.03 MHz) spectra of kuriloside A<sub>3</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

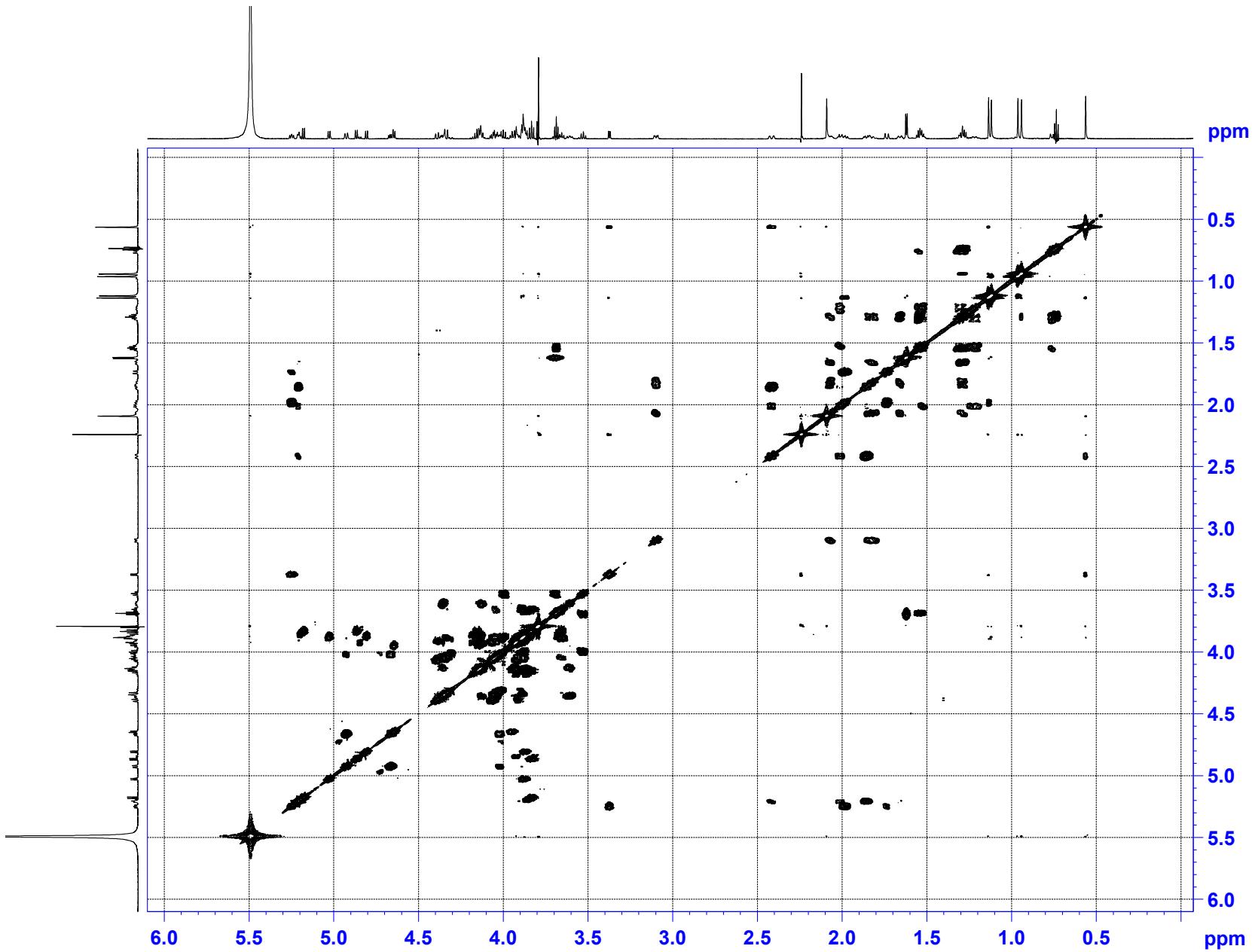


Figure S2. The COSY (700.00 MHz) spectrum of kuriloside A<sub>3</sub> (**1**) in  $C_5D_5N/D_2O$  (4/1)

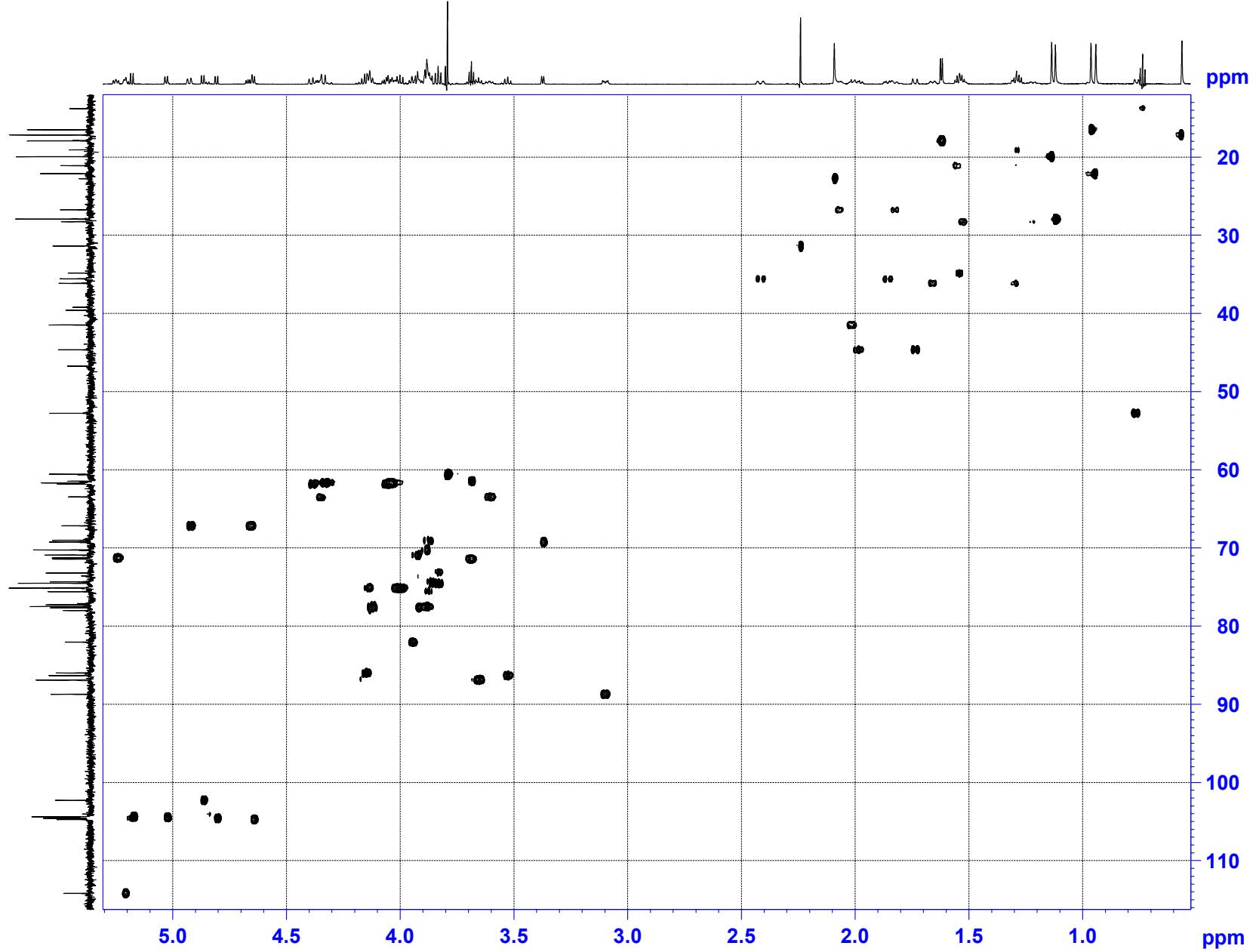


Figure S3. The HSQC (700.00 MHz) spectrum of kuriloside A<sub>3</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

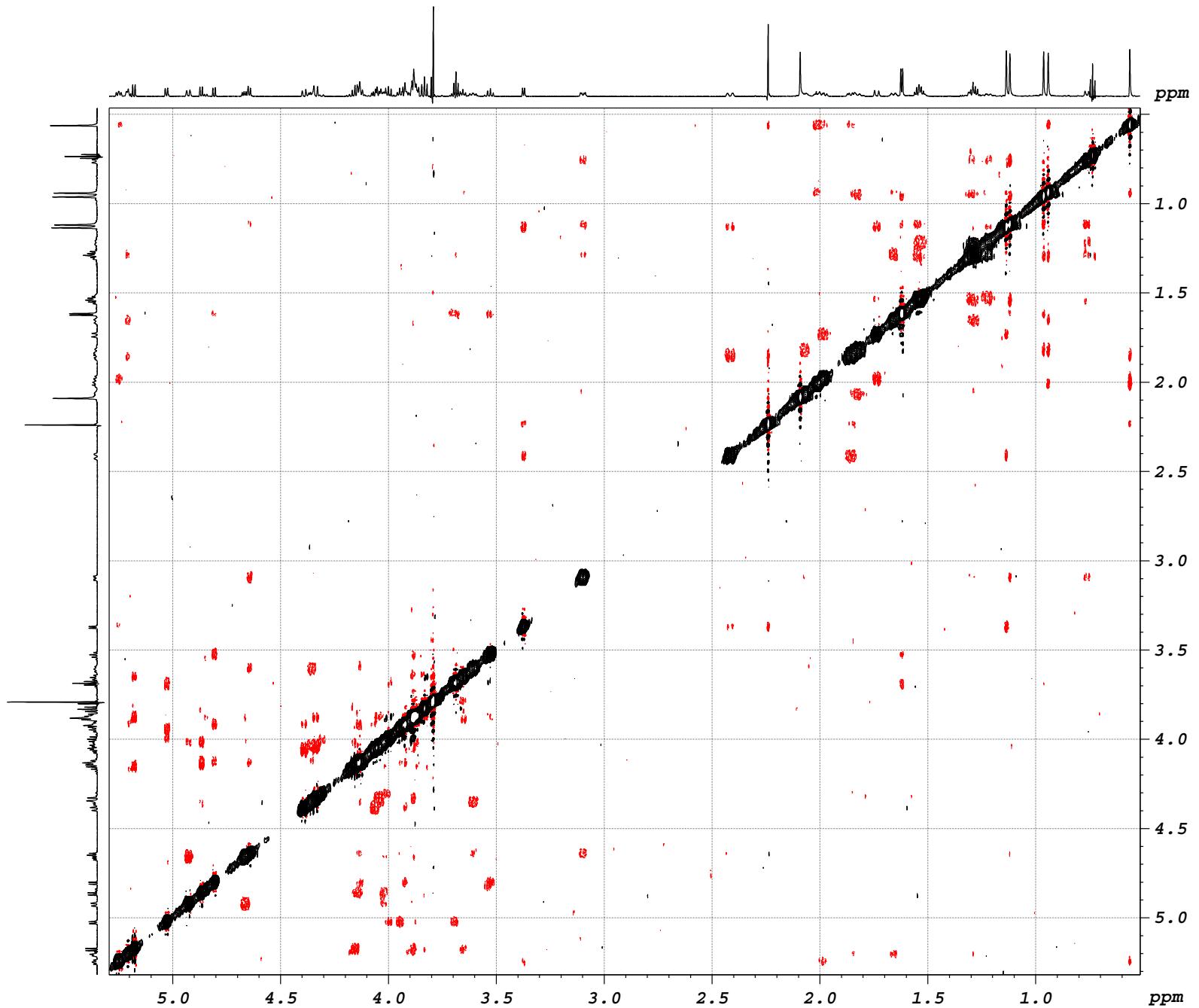


Figure S4. The ROESY (700.00 MHz) spectrum of kuriloside A<sub>3</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

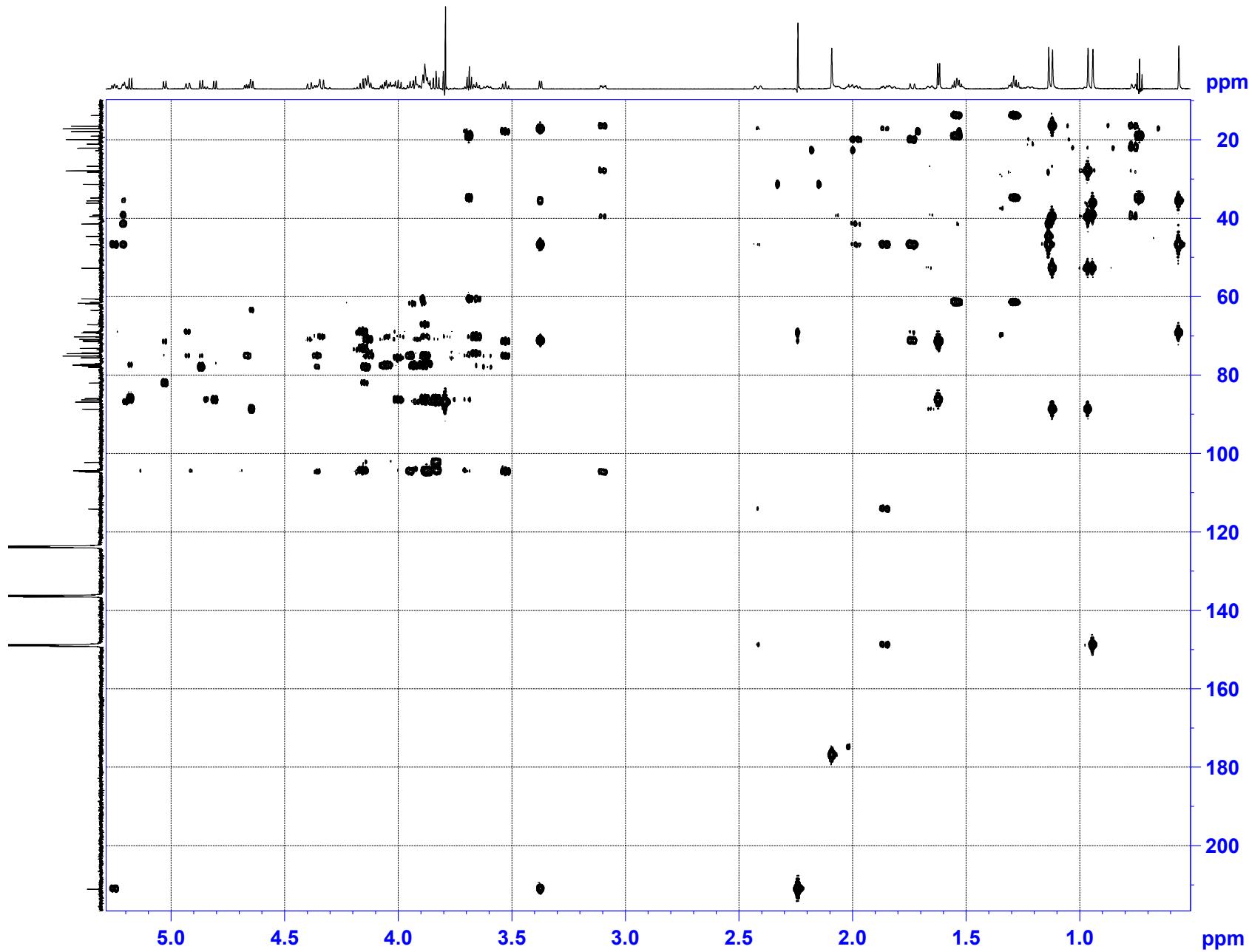


Figure S5. The HMBC (700.00 MHz) spectrum of kuriloside A<sub>3</sub> (**1**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

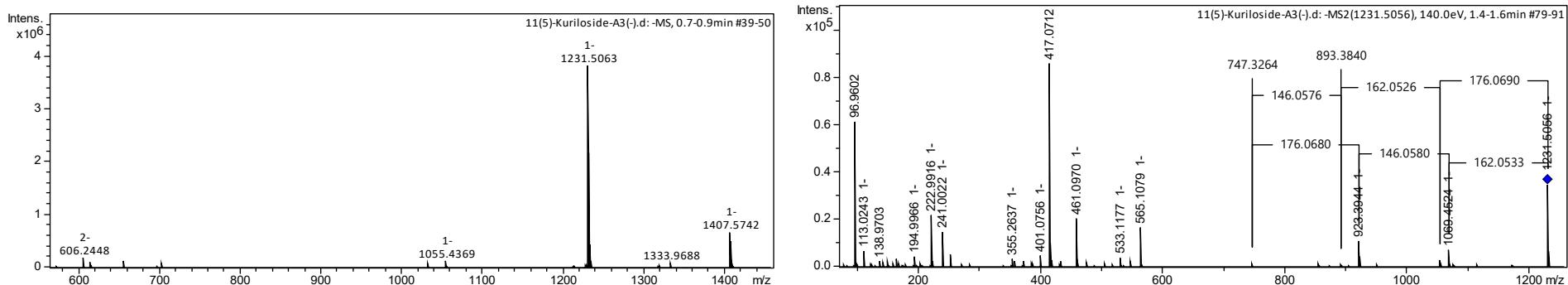


Figure S6. HR-ESI-MS and ESI-MS/MS spectra of kuriloside A<sub>3</sub> (**1**)

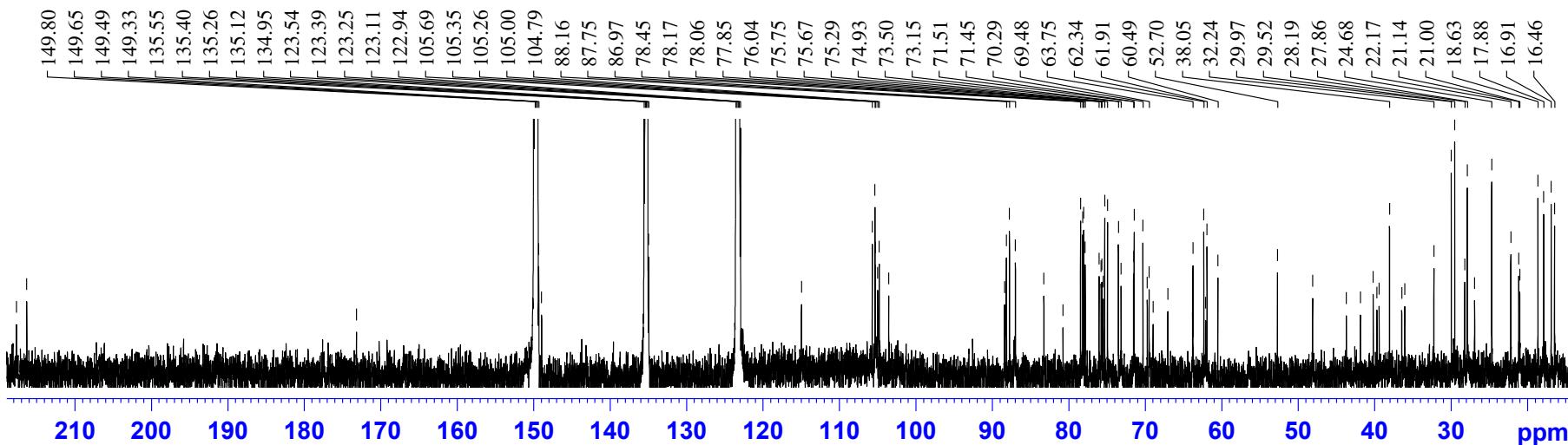
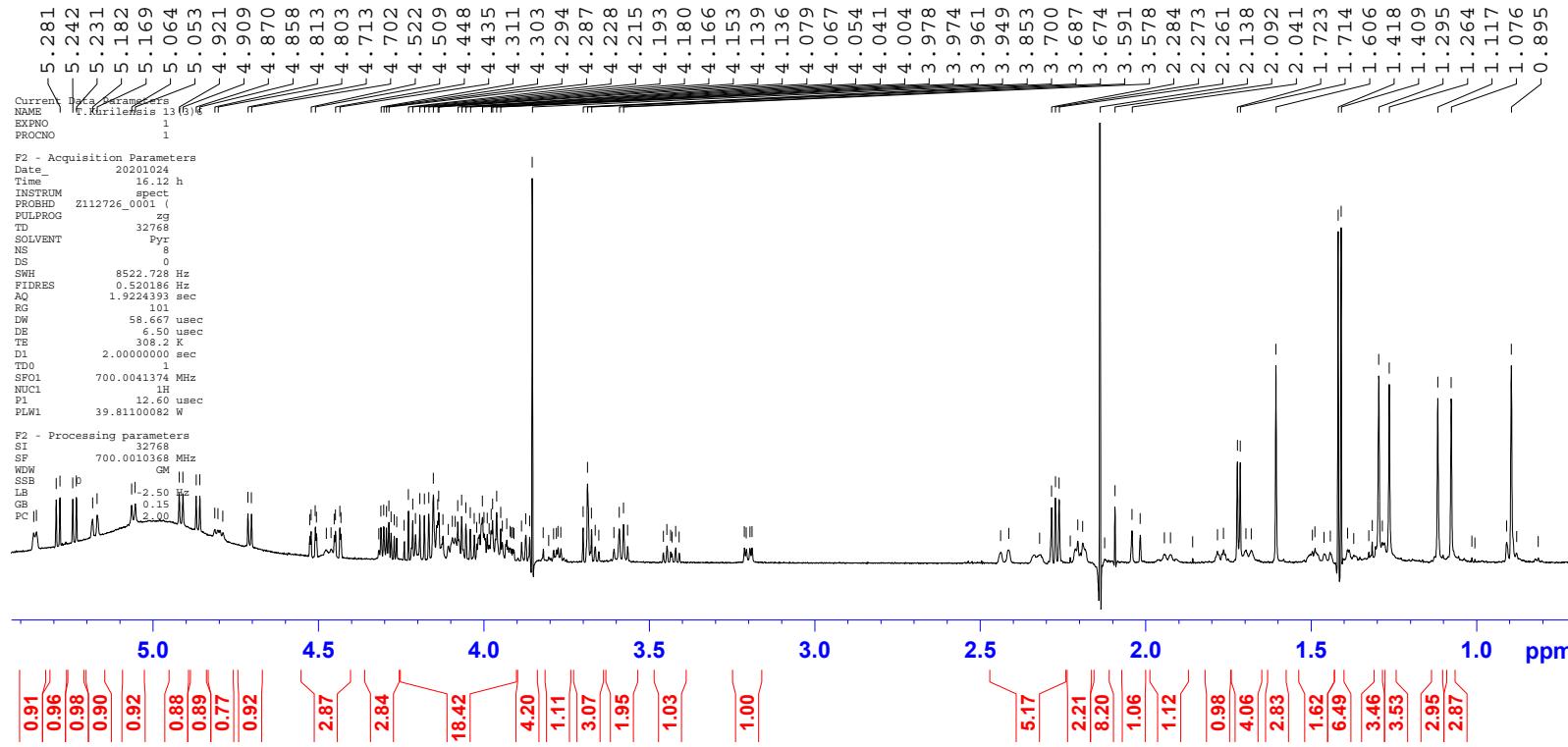


Figure S7. The <sup>13</sup>C NMR (176.03 MHz) spectrum of kuriloside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)



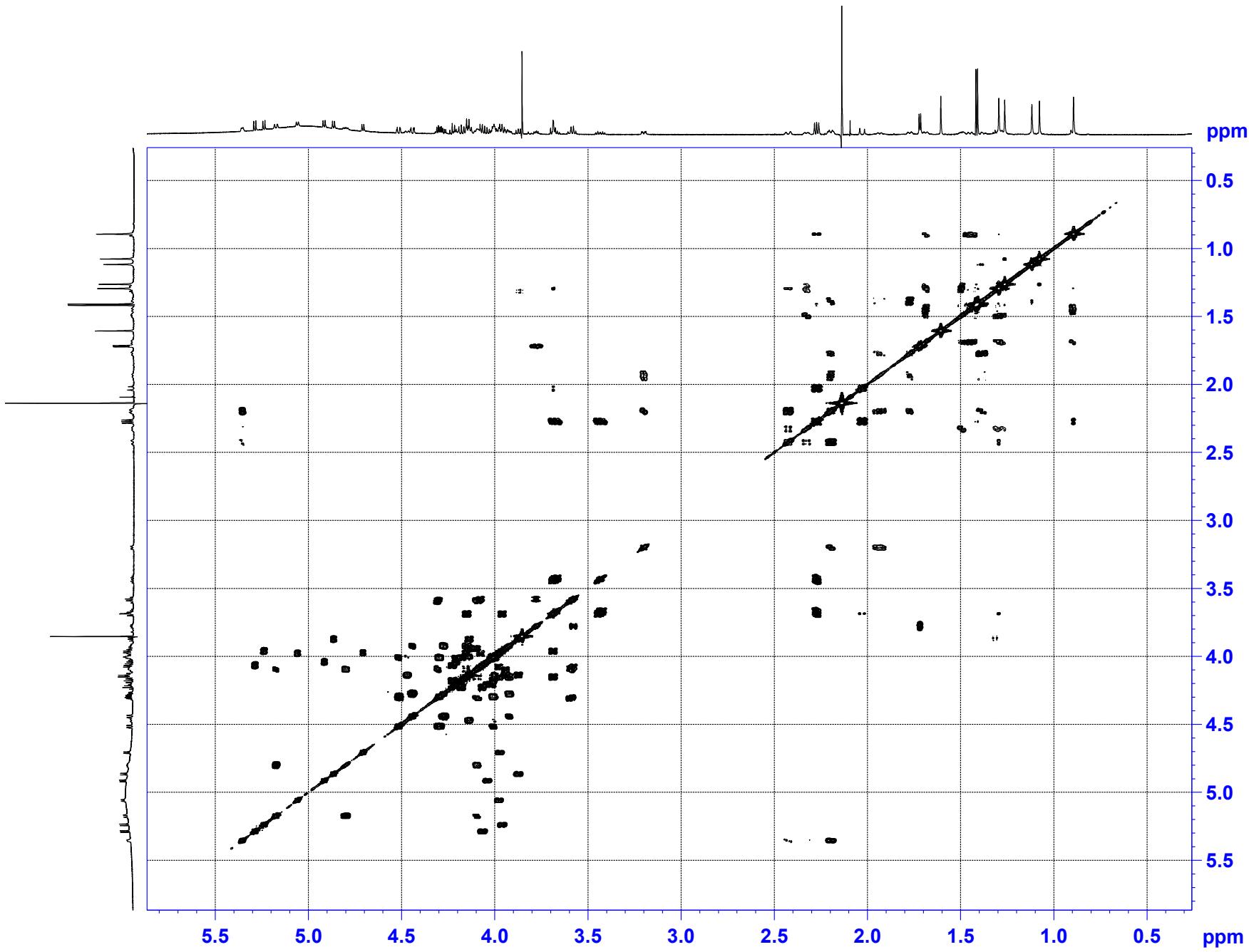


Figure S9. The COSY (700.00 MHz) spectrum of kuriloside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

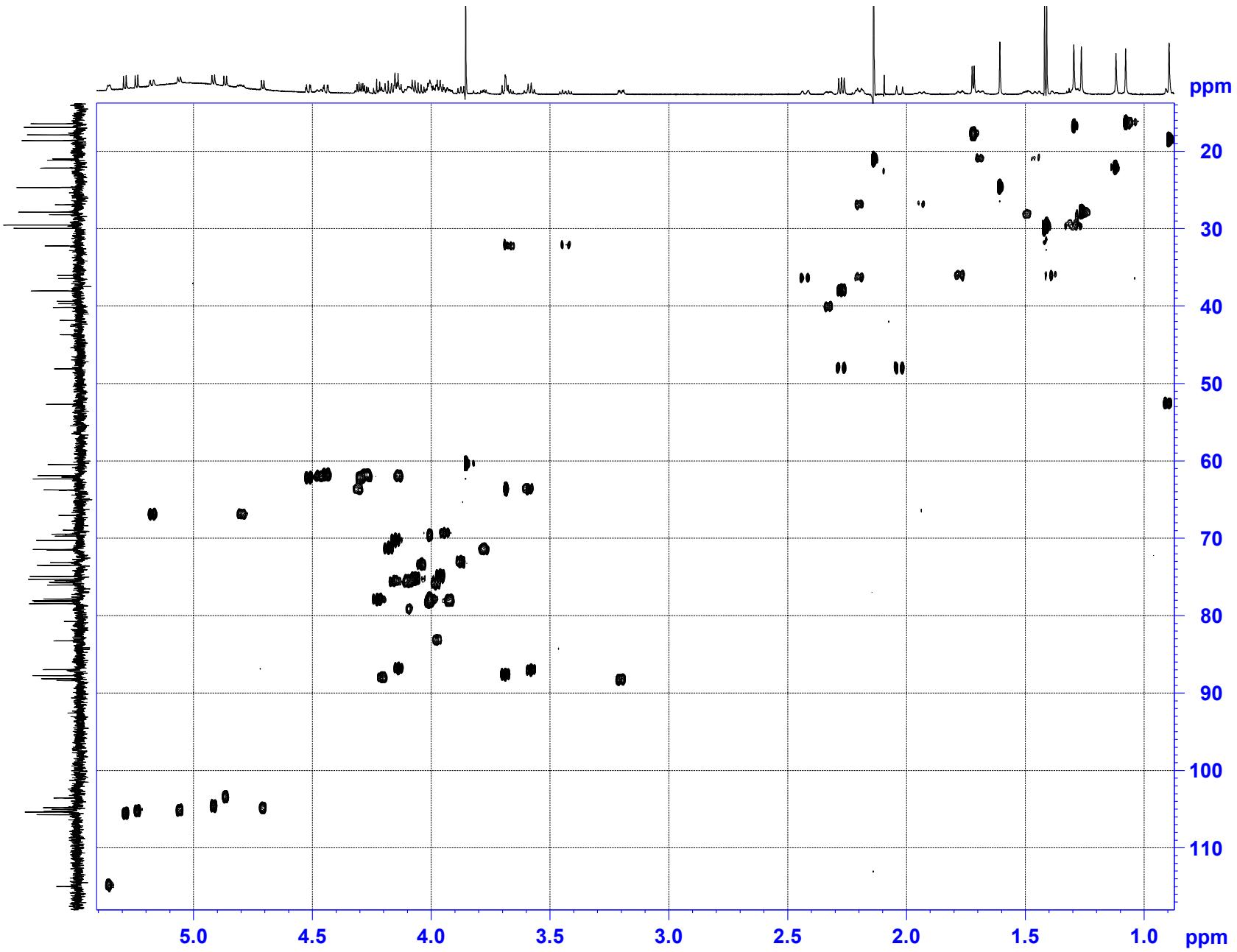


Figure S10. The HSQC (700.00 MHz) spectrum of kuriloside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

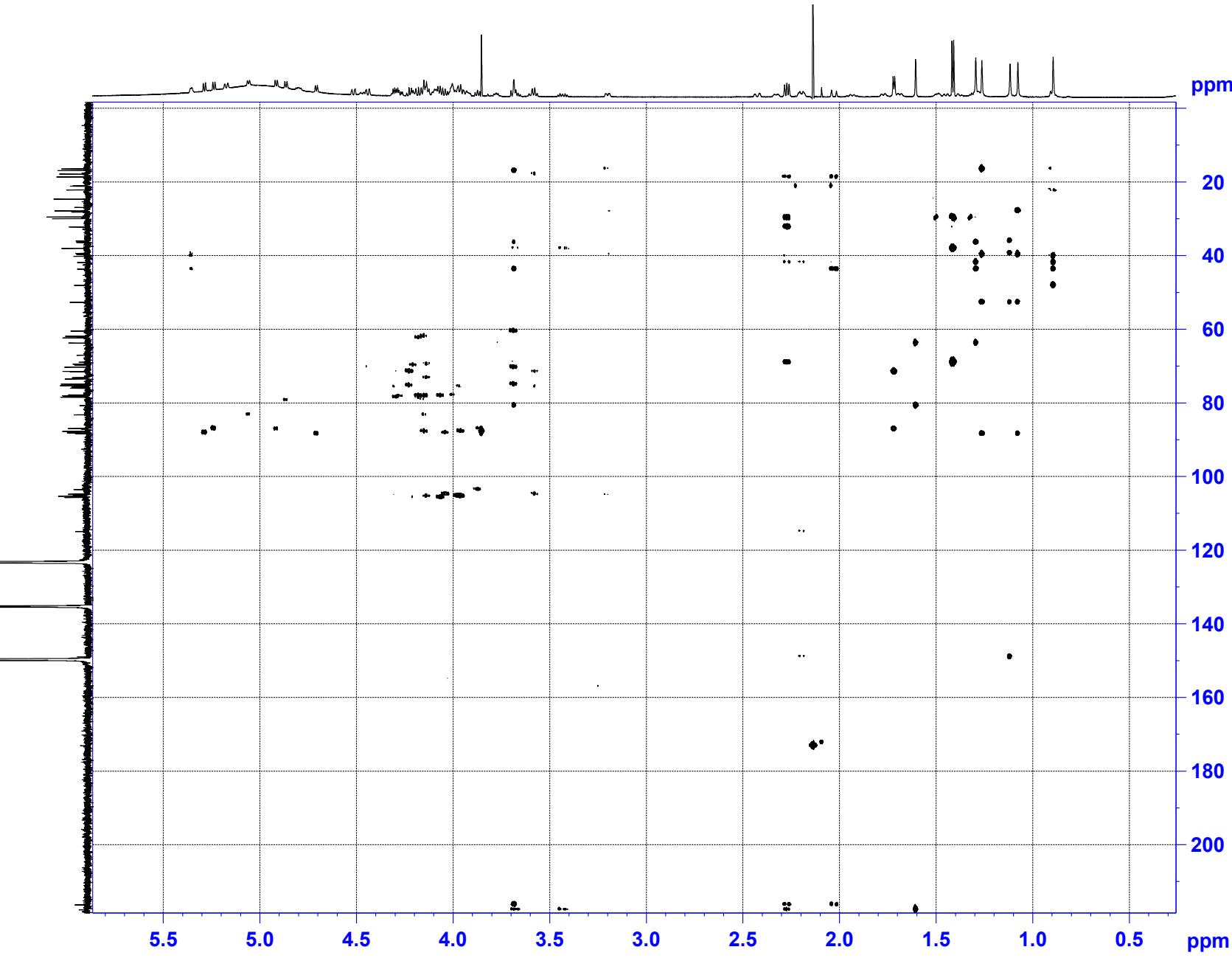


Figure S11. The HMBC (700.00 MHz) spectrum of kuriloside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

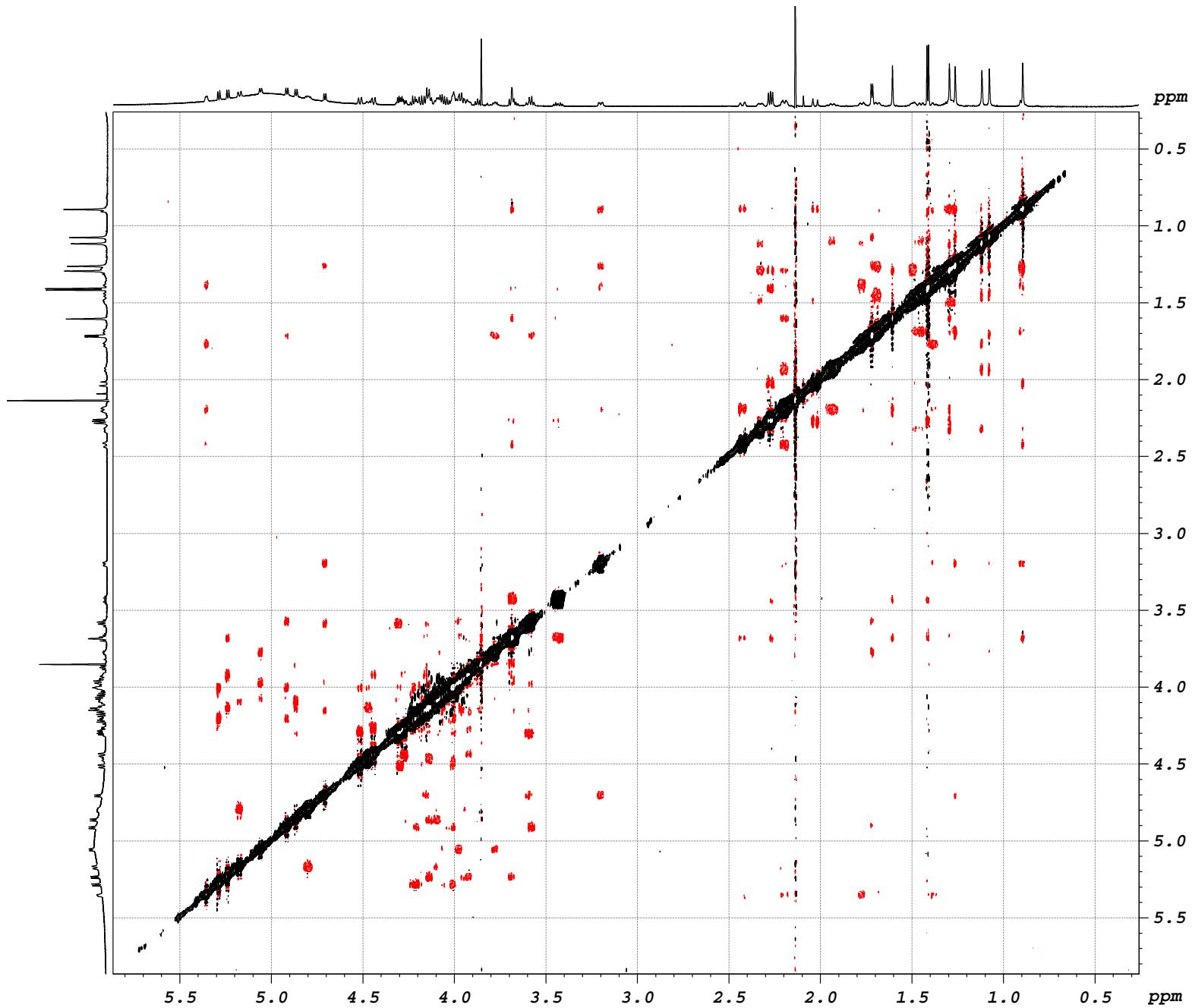


Figure S12. The ROESY (700.00 MHz) spectrum of kuriloside D<sub>1</sub> (**2**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

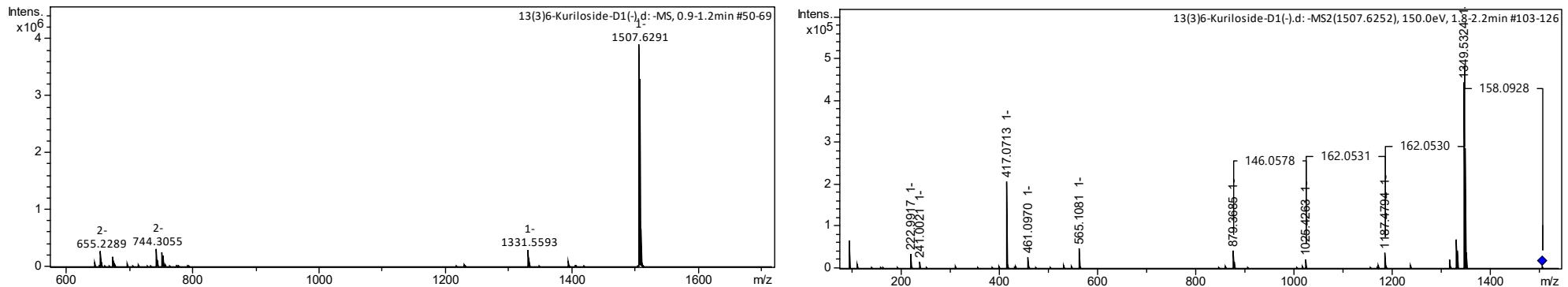
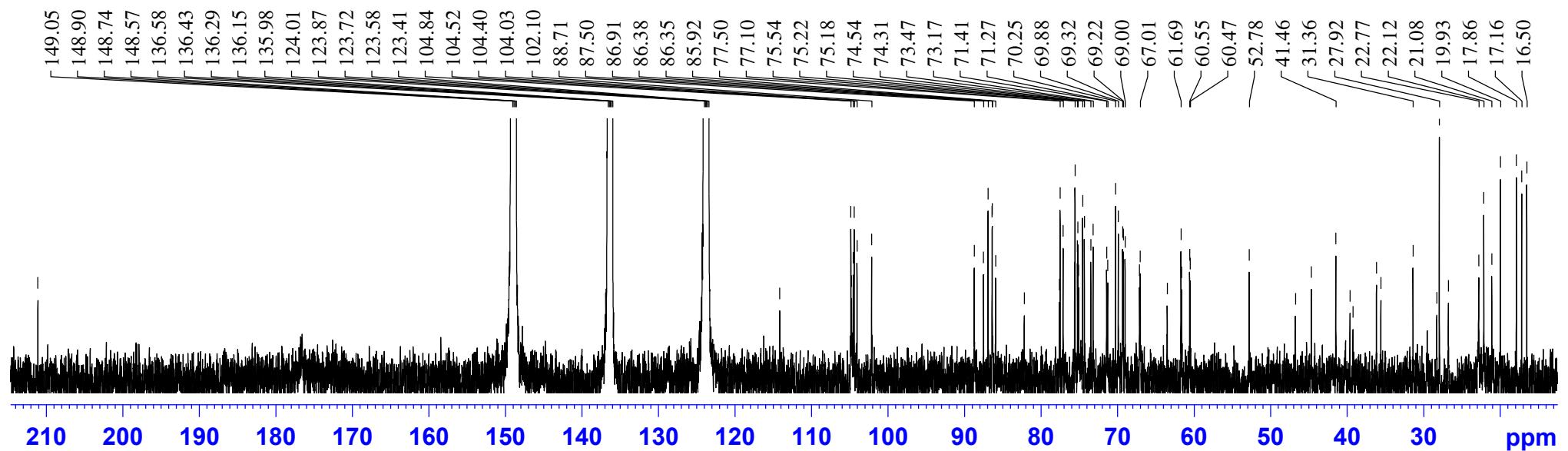


Figure S13. HR-ESI-MS and ESI-MS/MS spectra of kuriloside D<sub>1</sub> (**2**)



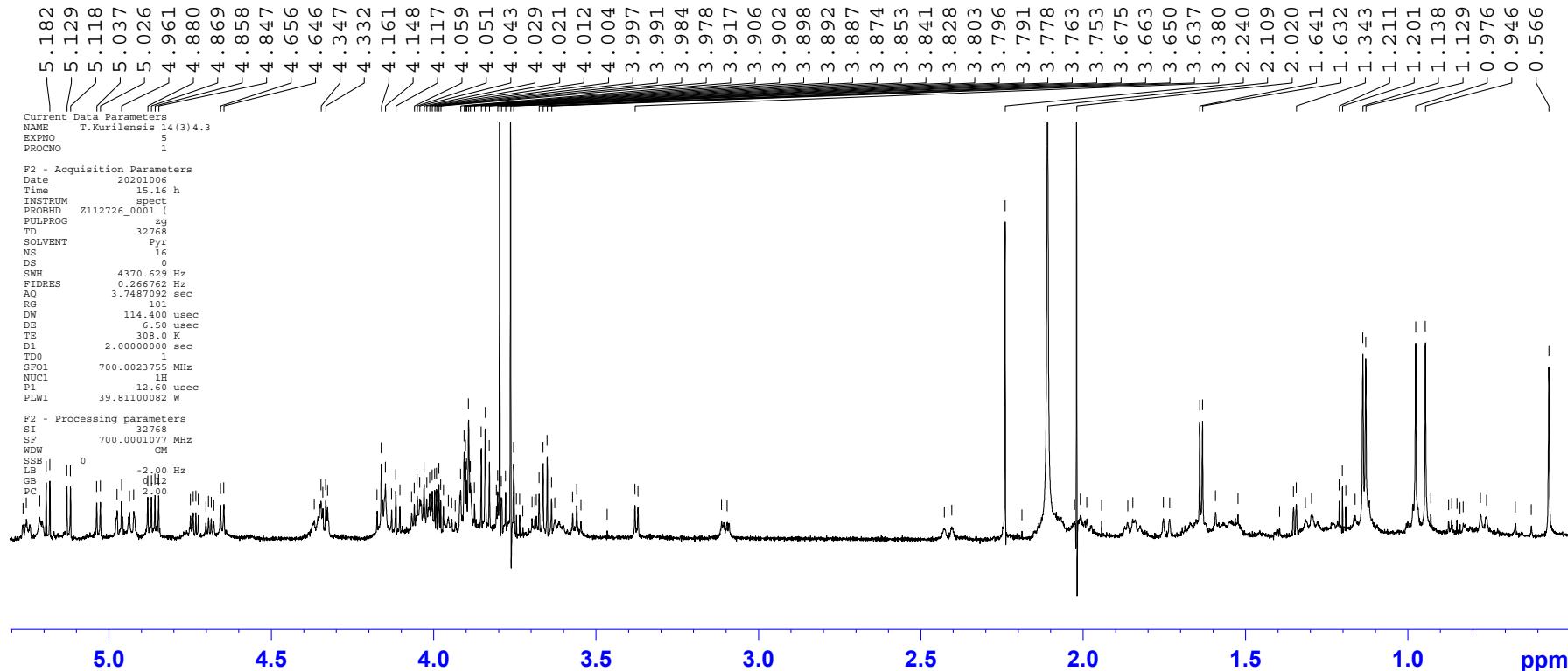


Figure S15. The  $^1\text{H}$  NMR (700.00 MHz) spectrum of kuriloside G (3) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

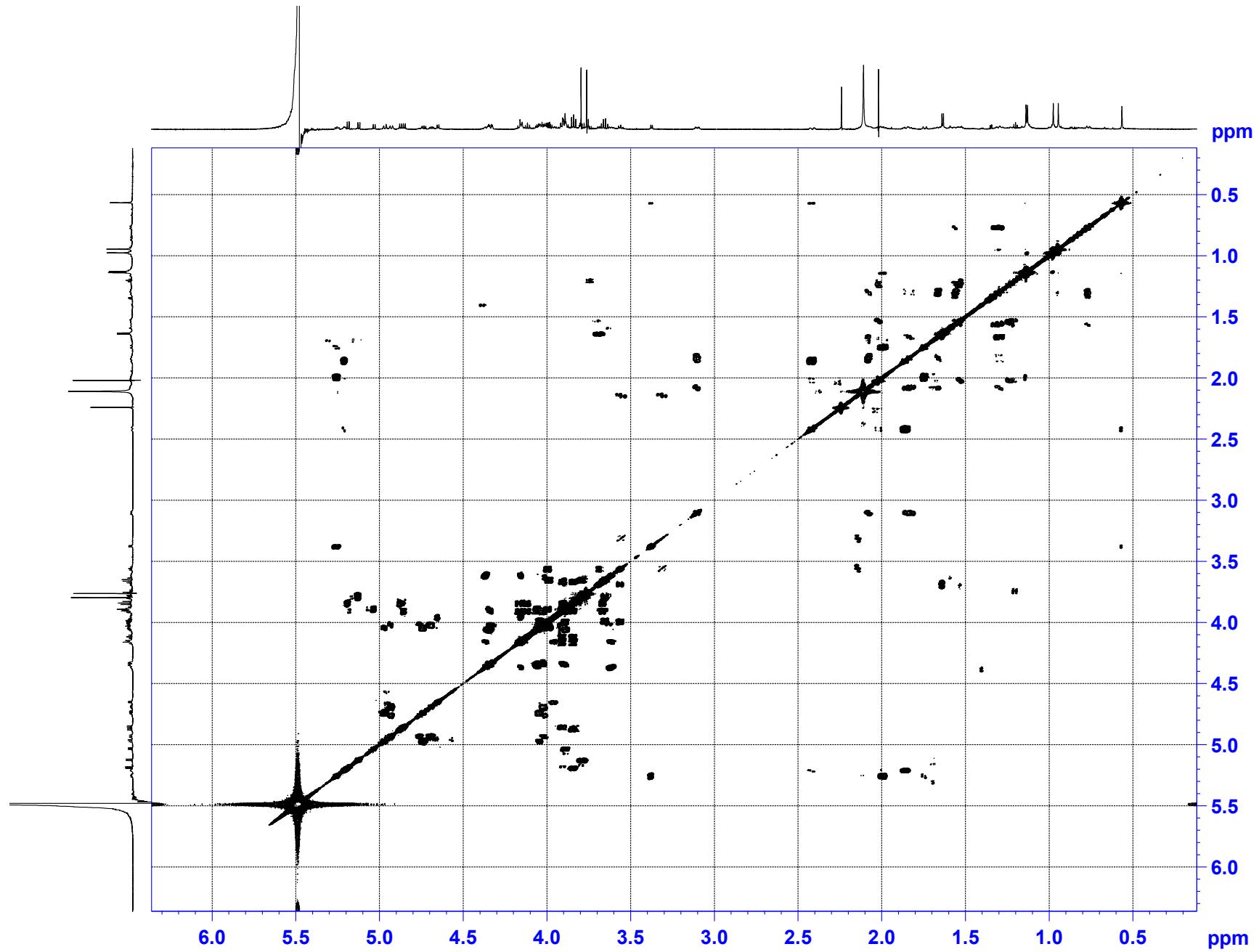


Figure S16. The COSY (700.00 MHz) spectrum of kuriloside G (3) in  $C_5D_5N/D_2O$  (4/1)

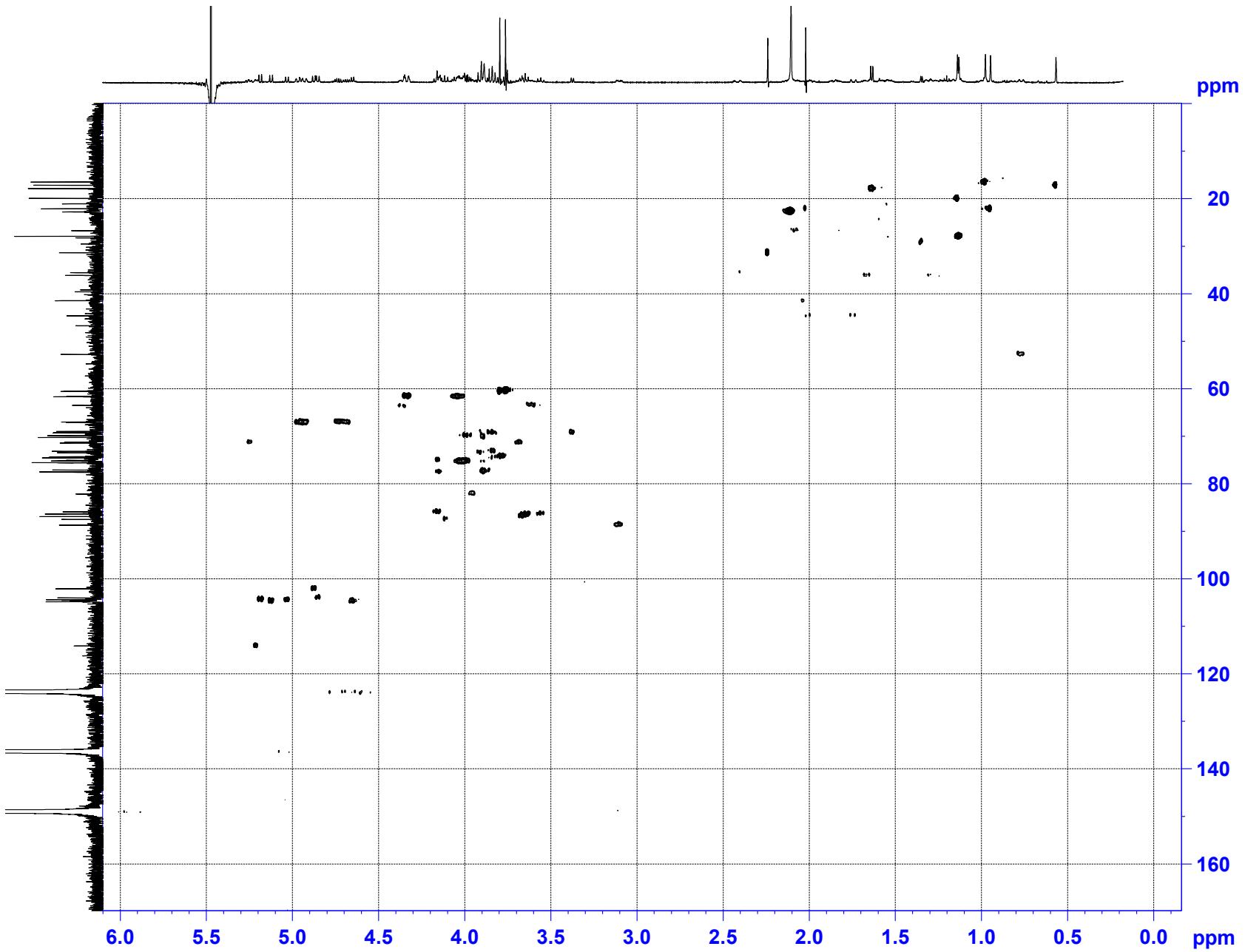


Figure S17. The HSQC (700.00 MHz) spectrum of kuriloside G (3) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

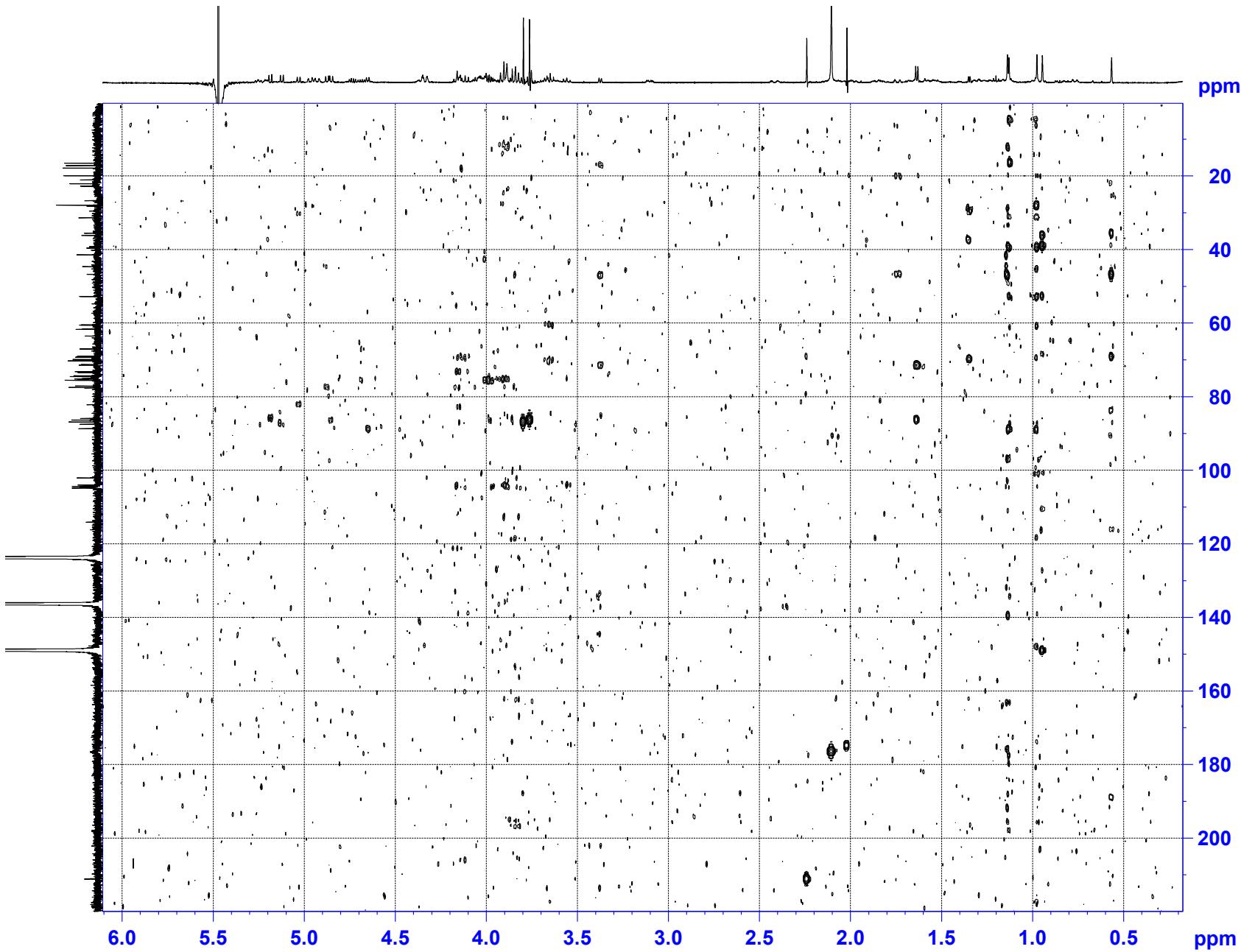


Figure S18. The HMBC (700.00 MHz) spectrum of kuriloside G (3) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

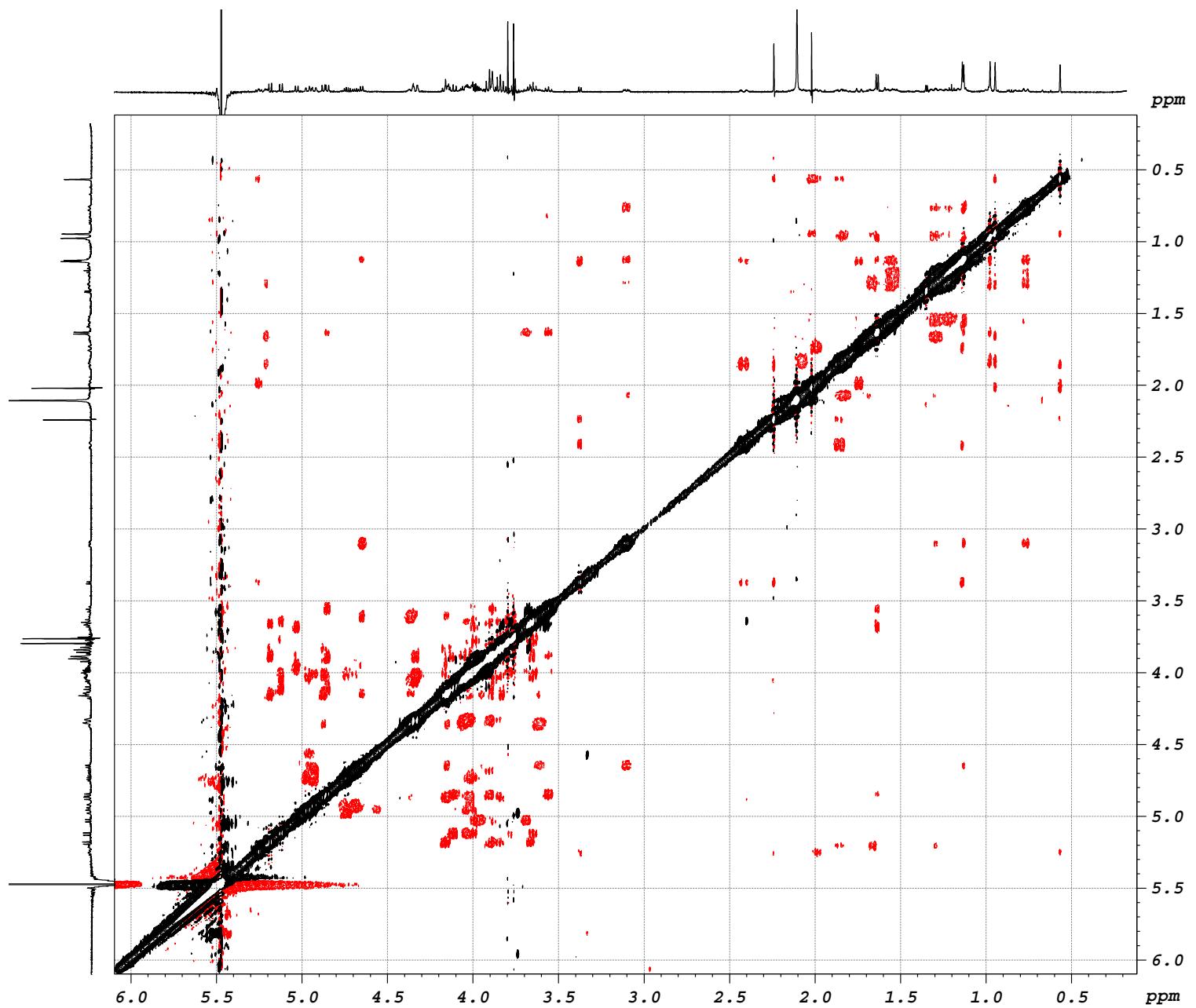


Figure S19. The ROESY (700.00 MHz) spectrum of kuriloside G (3) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

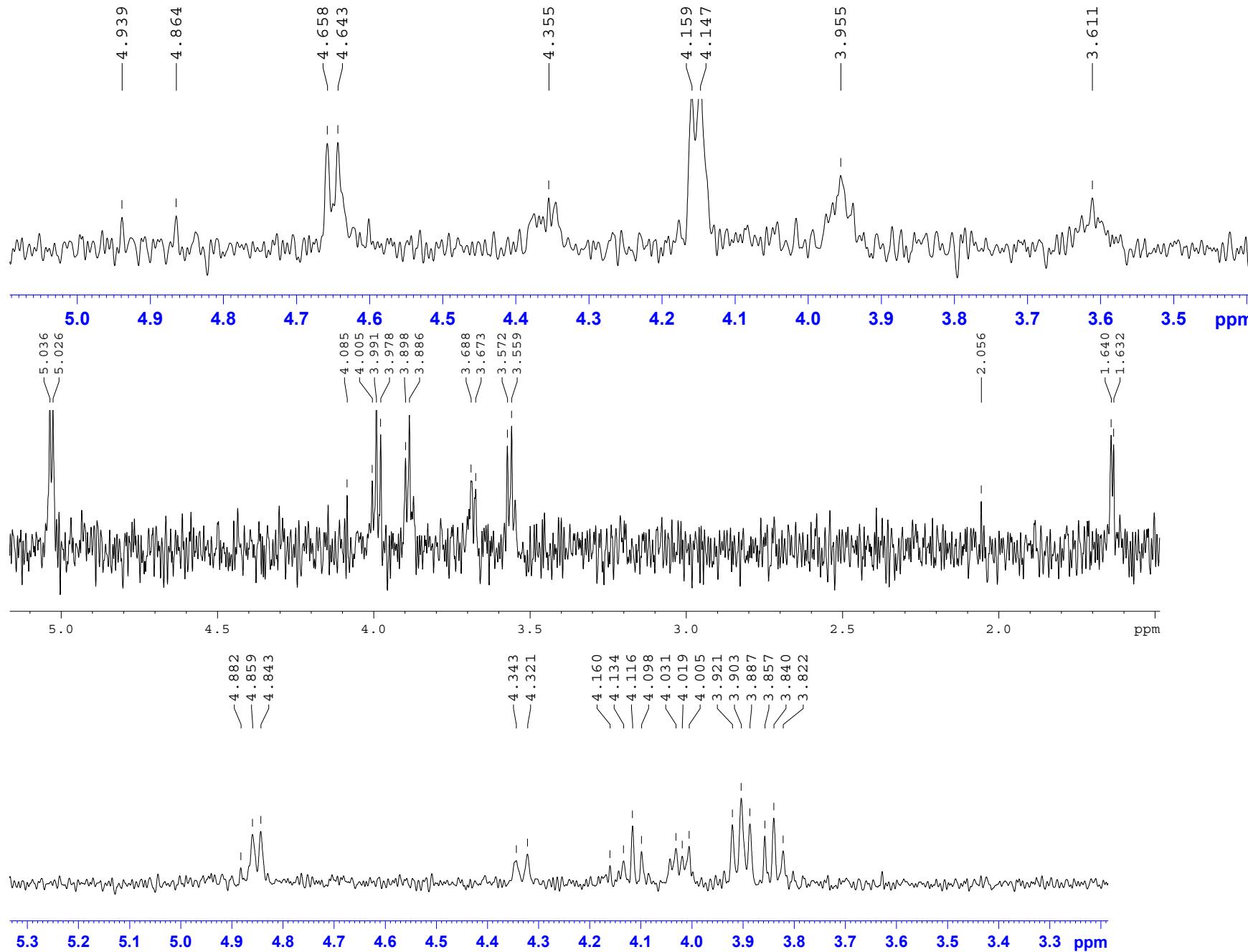


Figure S20. 1 D TOCSY (700.00 MHz) spectra of the XyloseI, QuinovoseII and GlucoseII of kuriloside G (3), C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

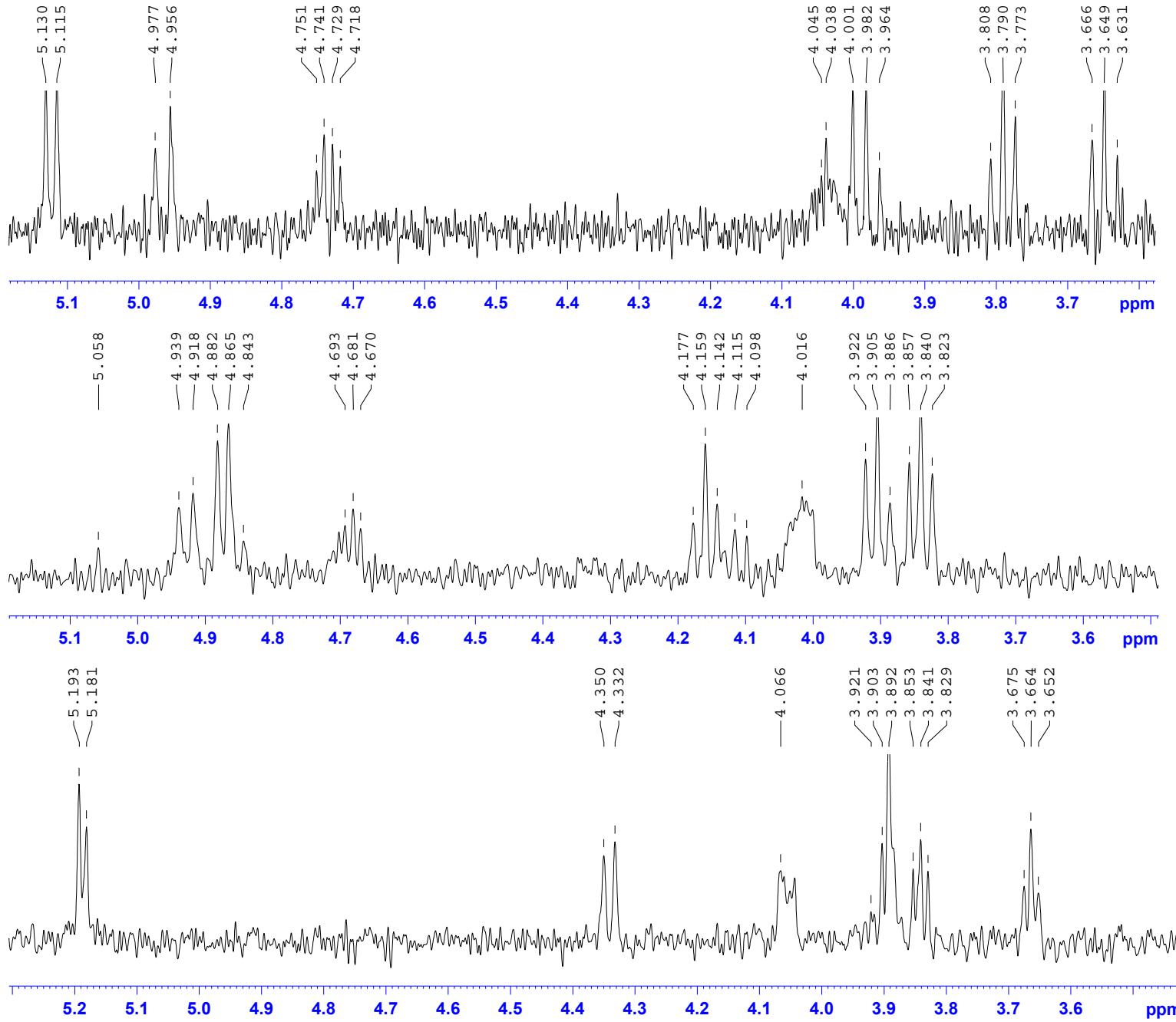


Figure S21. 1 D TOCSY (700.00 MHz) spectra of the MeGlcIV, GlucoseV and MeGlcVI of kuriloside G (3), C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

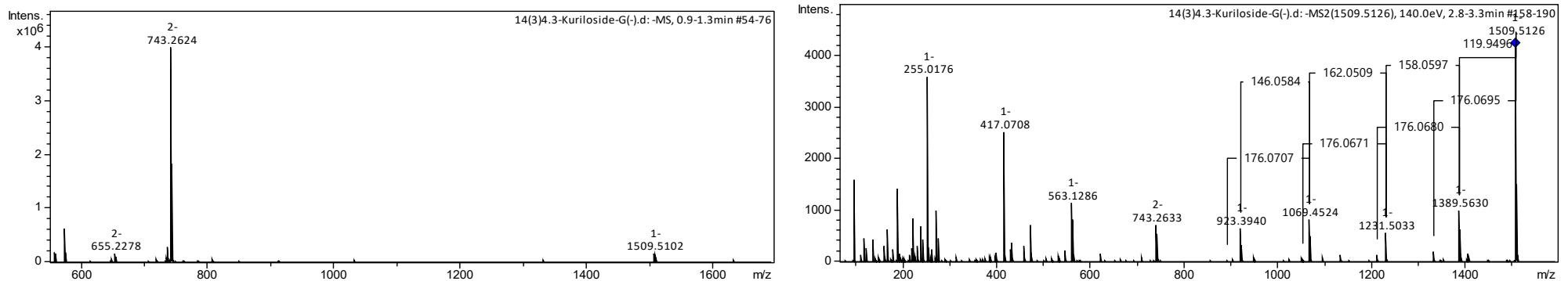


Figure S22. HR-ESI-MS and ESI-MS/MS spectra of kuriloside G (3)

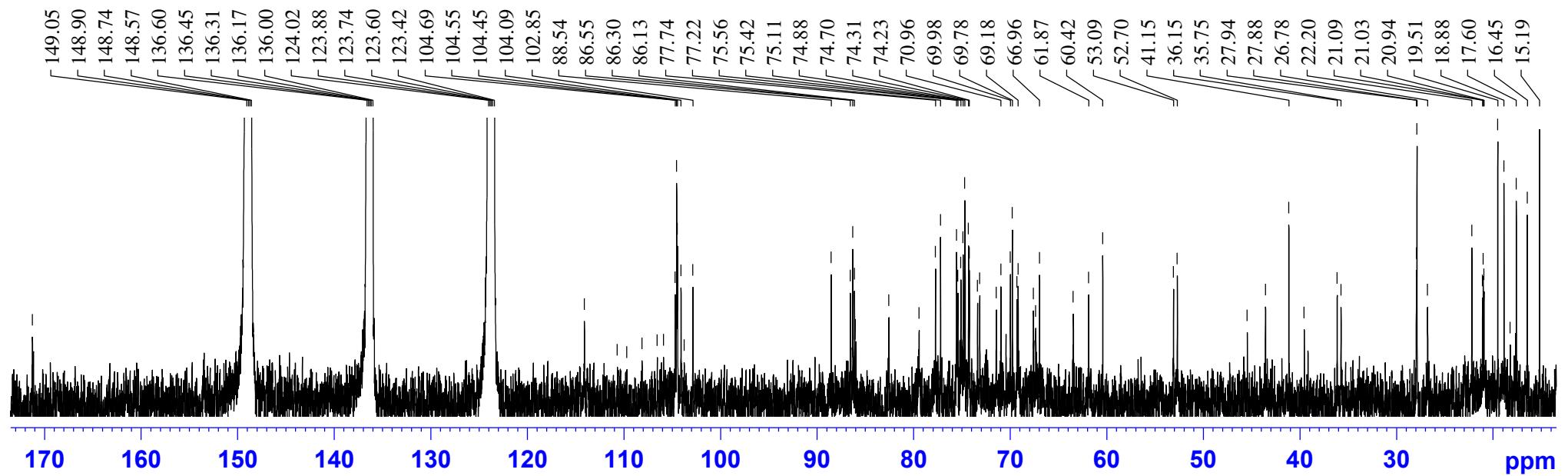


Figure S23. The  $^{13}\text{C}$  NMR (176.03 MHz) spectrum of kuriloside H (4) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

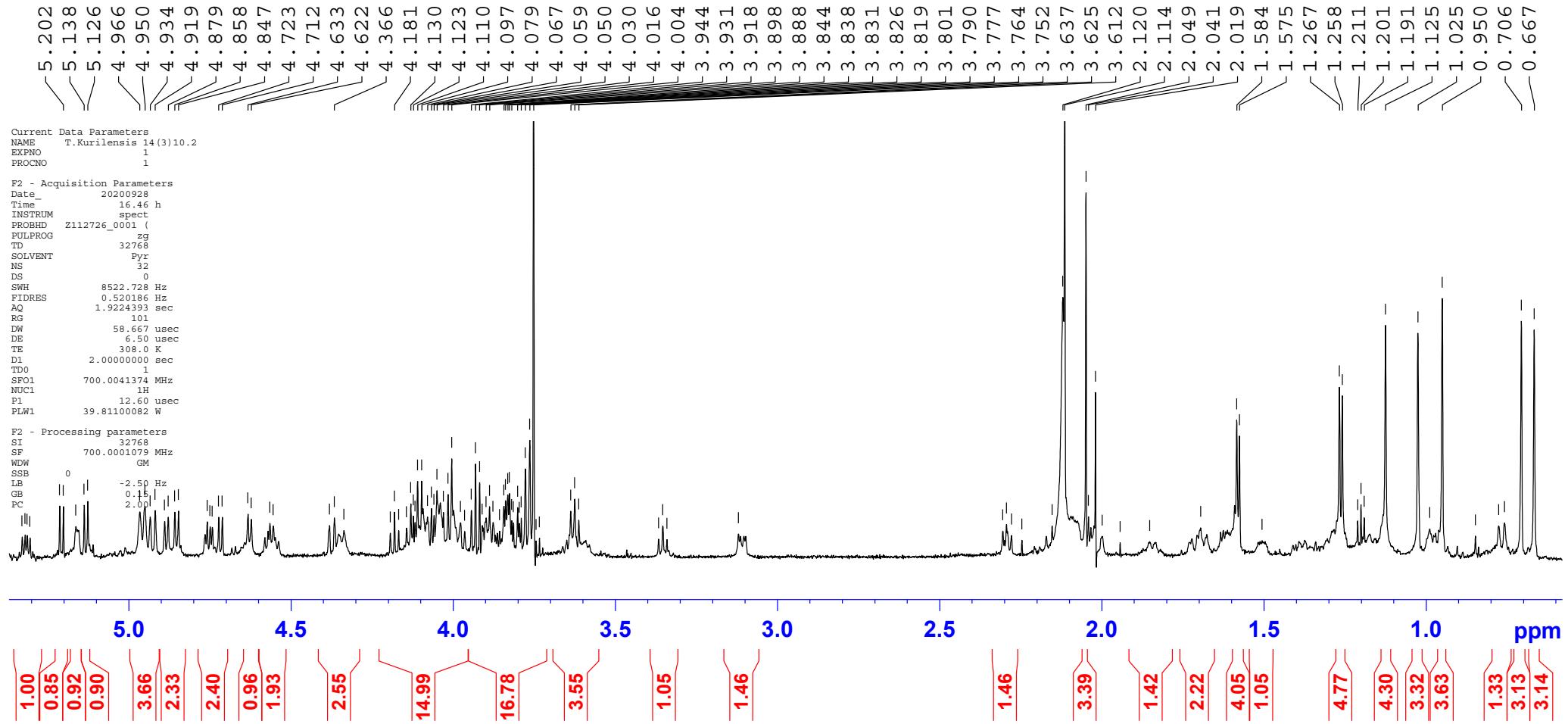


Figure S24. The  $^1\text{H}$  NMR (700.00 MHz) spectrum of kuriloside H (**4**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

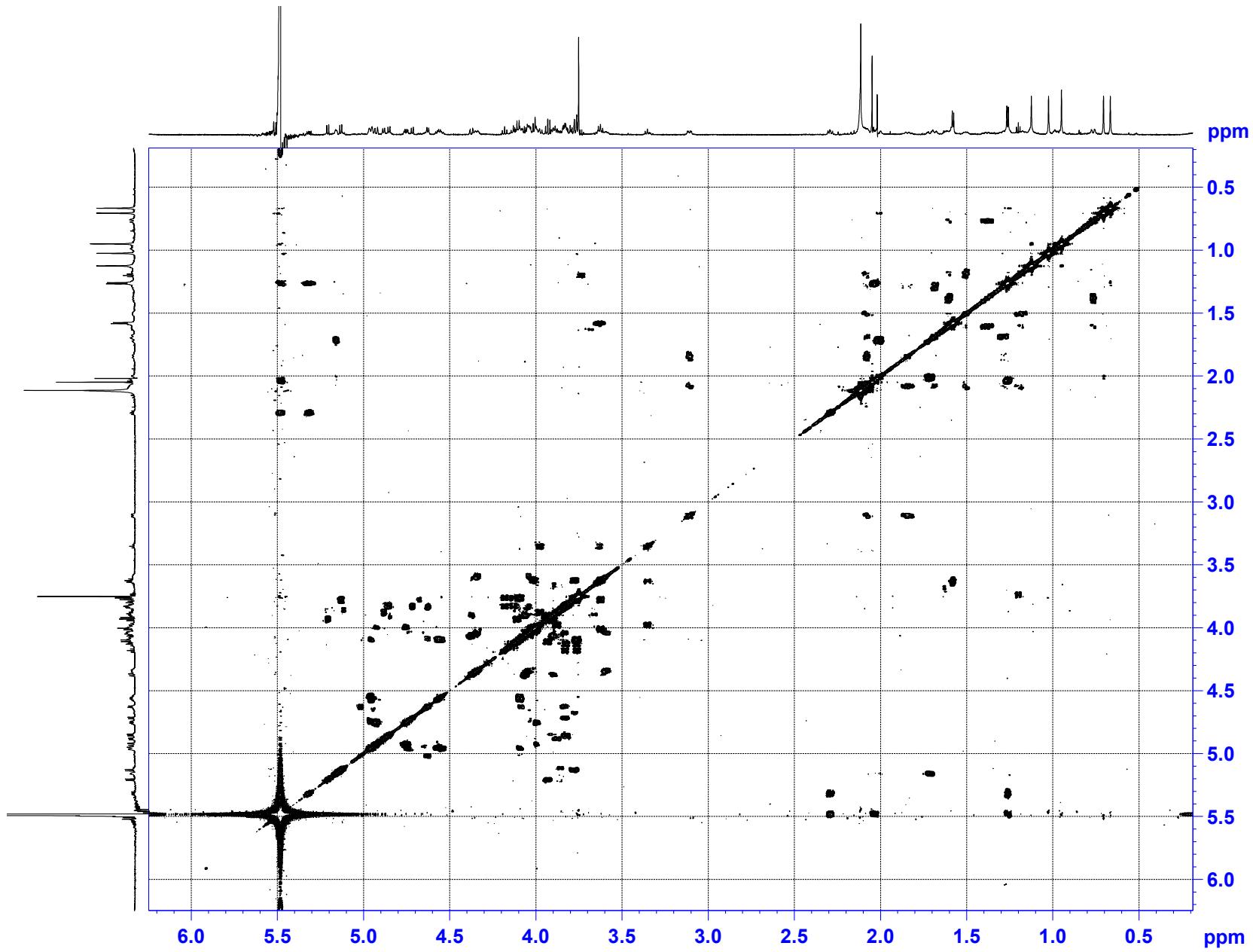


Figure S25. The COSY (700.00 MHz) spectrum of kuriloside H (4) in  $C_5D_5N/D_2O$  (4/1)

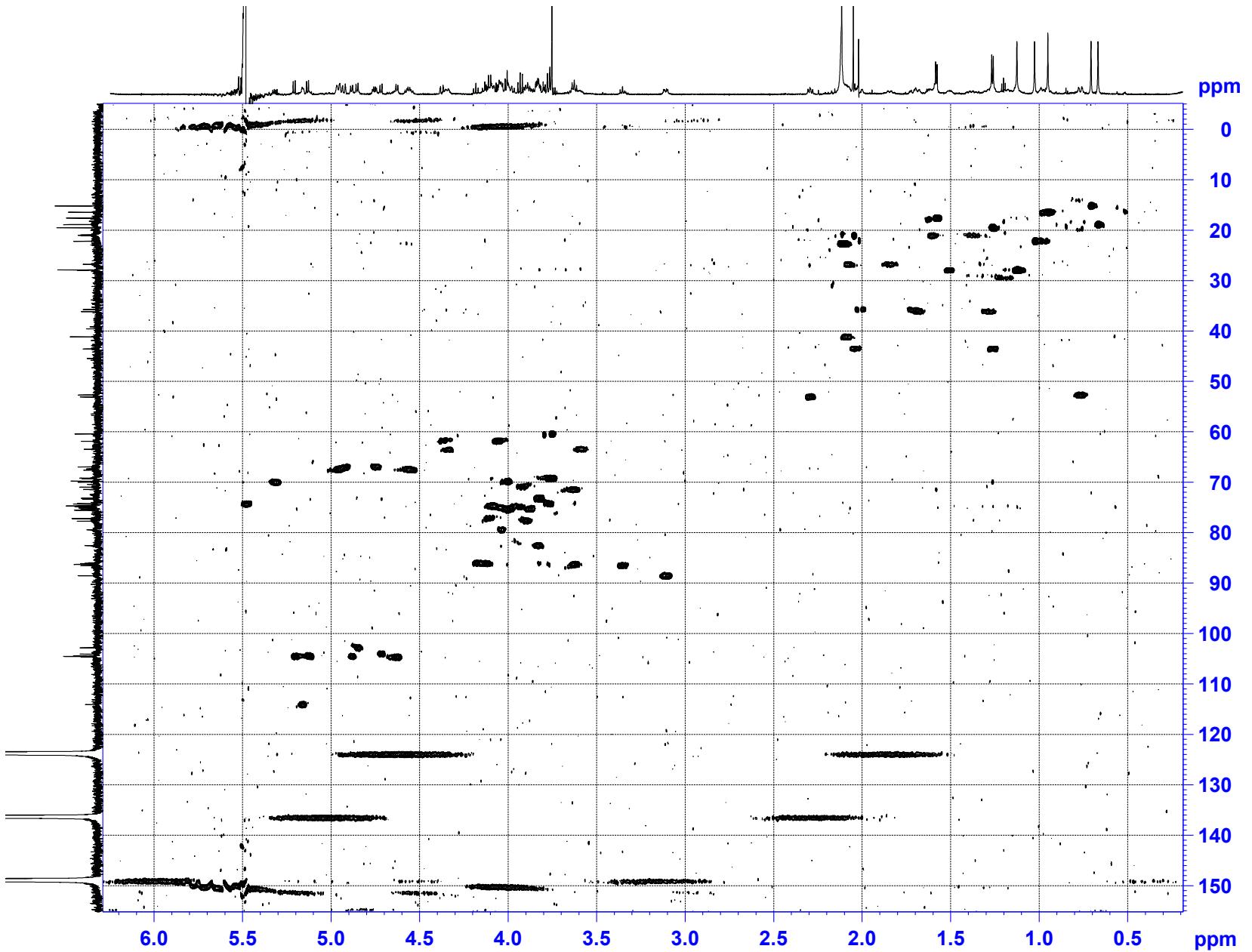


Figure S26. The HSQC (700.00 MHz) spectrum of kuriloside H (**4**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

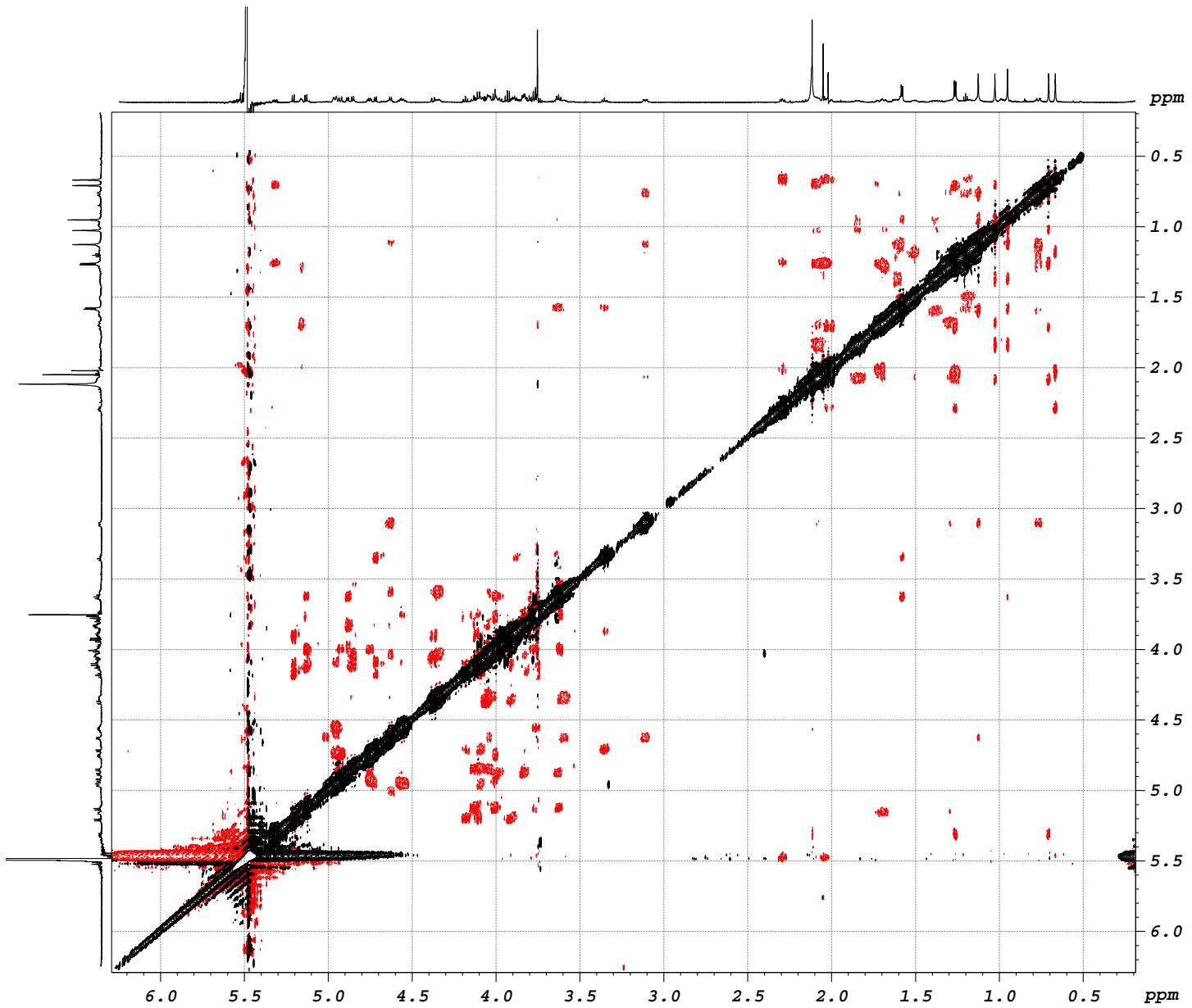


Figure S27. The ROESY (700.00 MHz) spectrum of kuriloside H (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

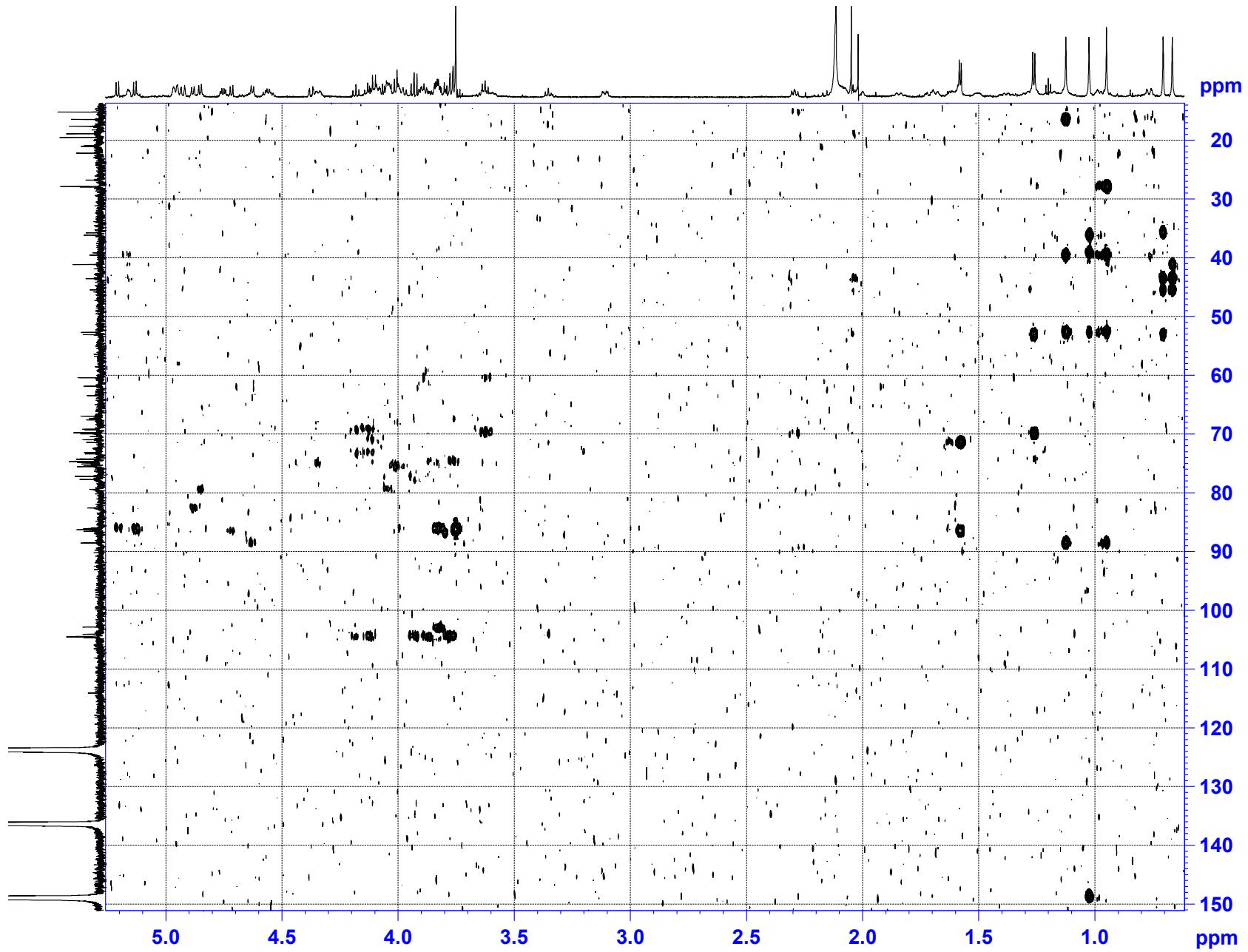


Figure S28. The HMBC (700.00 MHz) spectrum of kuriloside H (**4**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

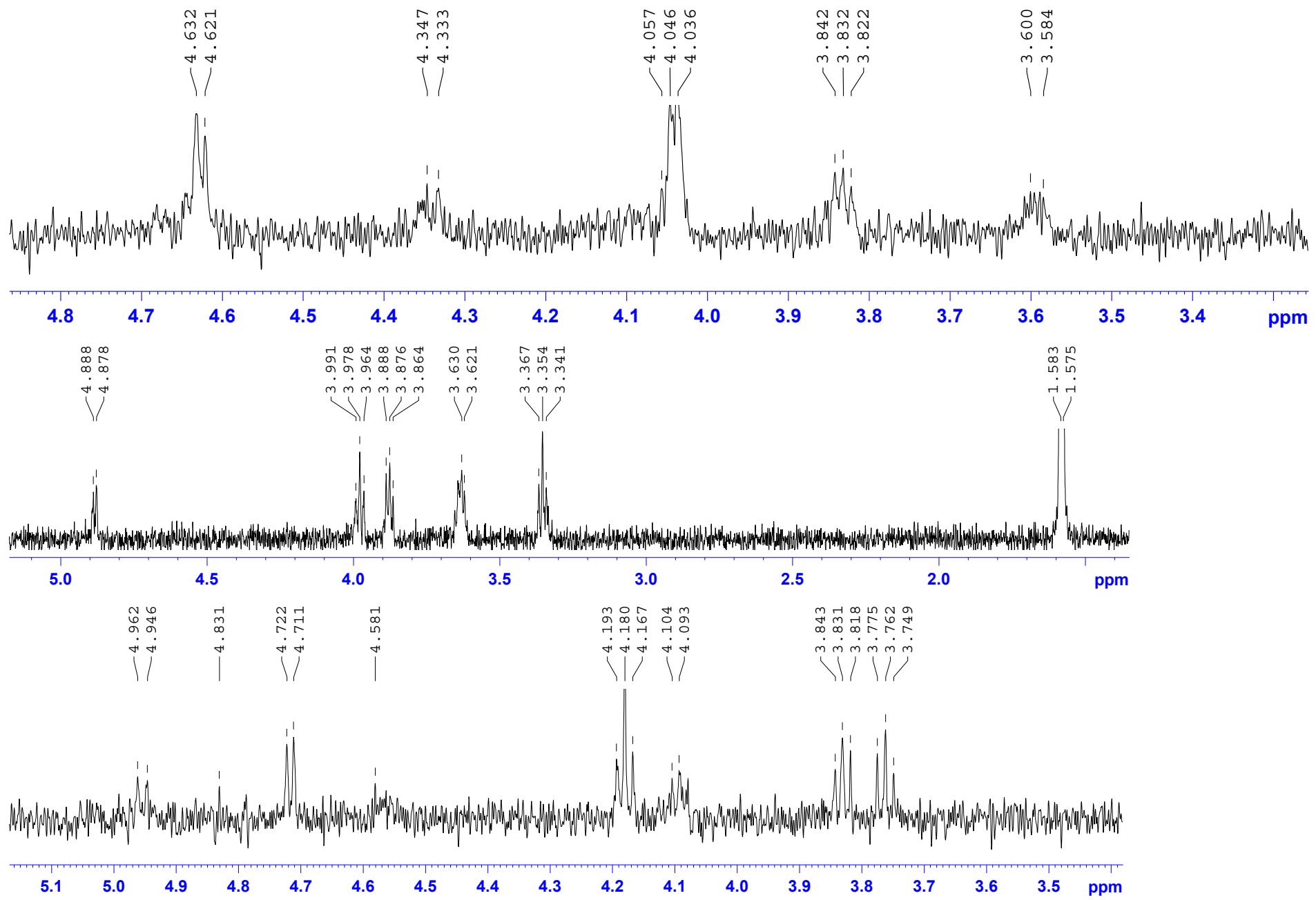


Figure S29. 1D TOCSY (700.00 MHz) spectra of XyloseI, QuinovoseII and GlucoseIII of kuriloside H (**4**), C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

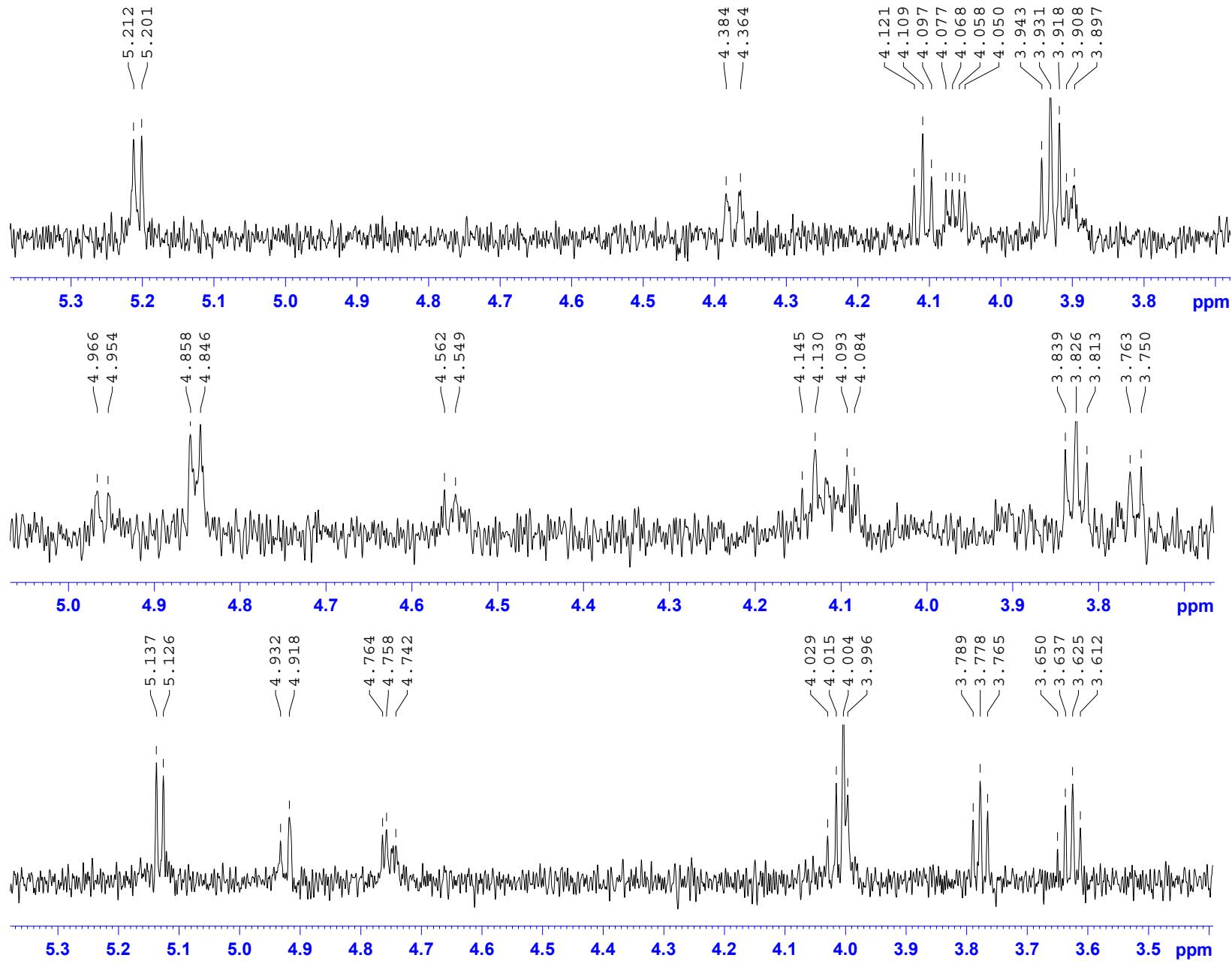


Figure S30. 1 D TOCSY (700.00 MHz) spectra of GlcIV, GlucoseV and MeGlcVI of kuriloside H (**4**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

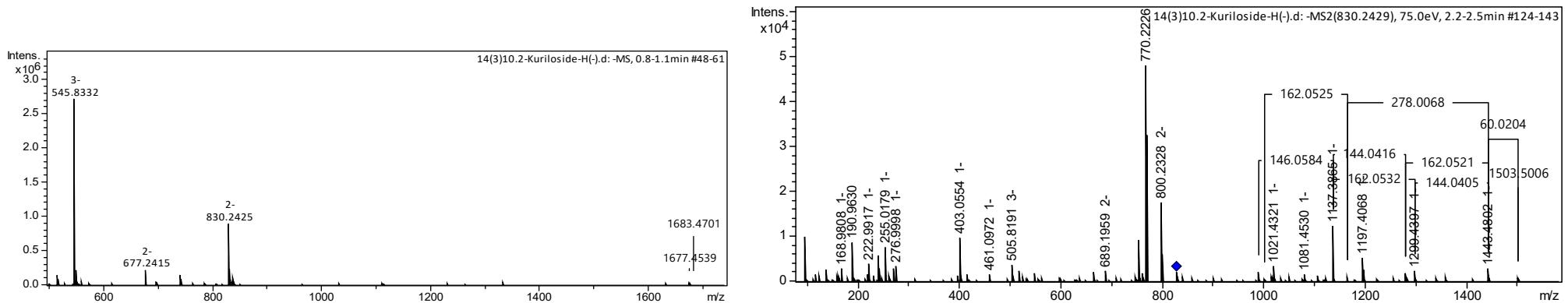


Figure S31. HR-ESI-MS and ESI-MS/MS spectra of kuriloside H (4)

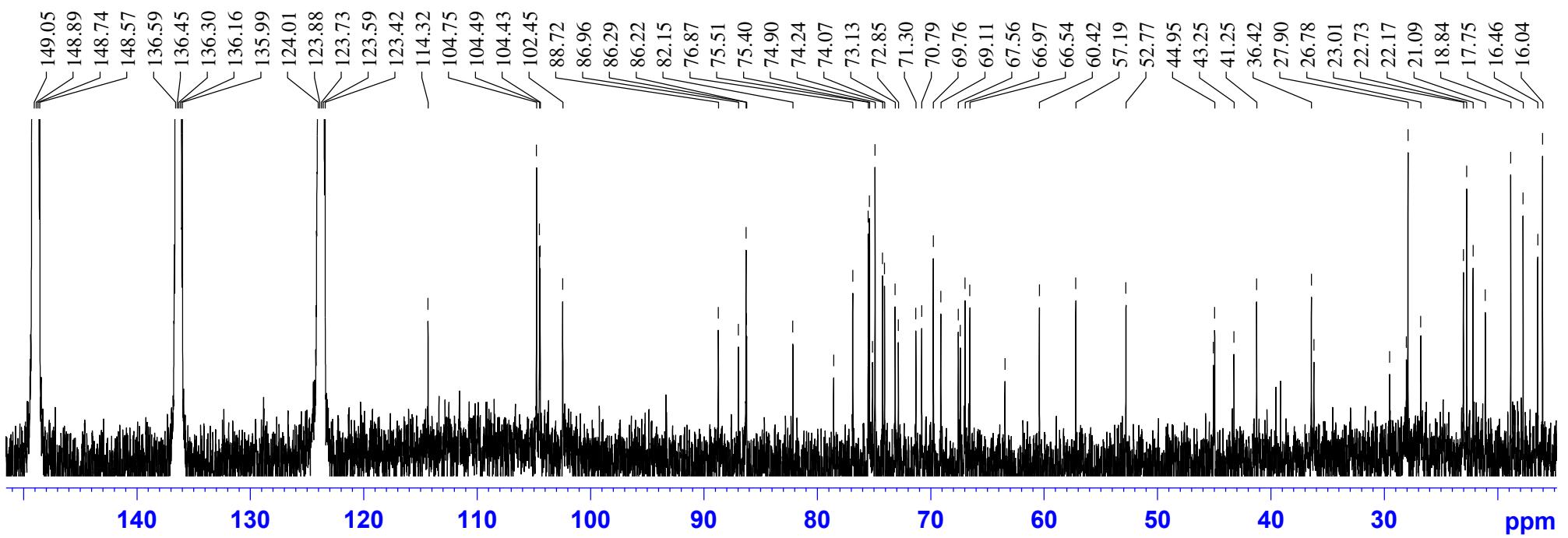


Figure S32. The  $^{13}\text{C}$  NMR (176.03 MHz) spectrum of kuriloside I (5) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

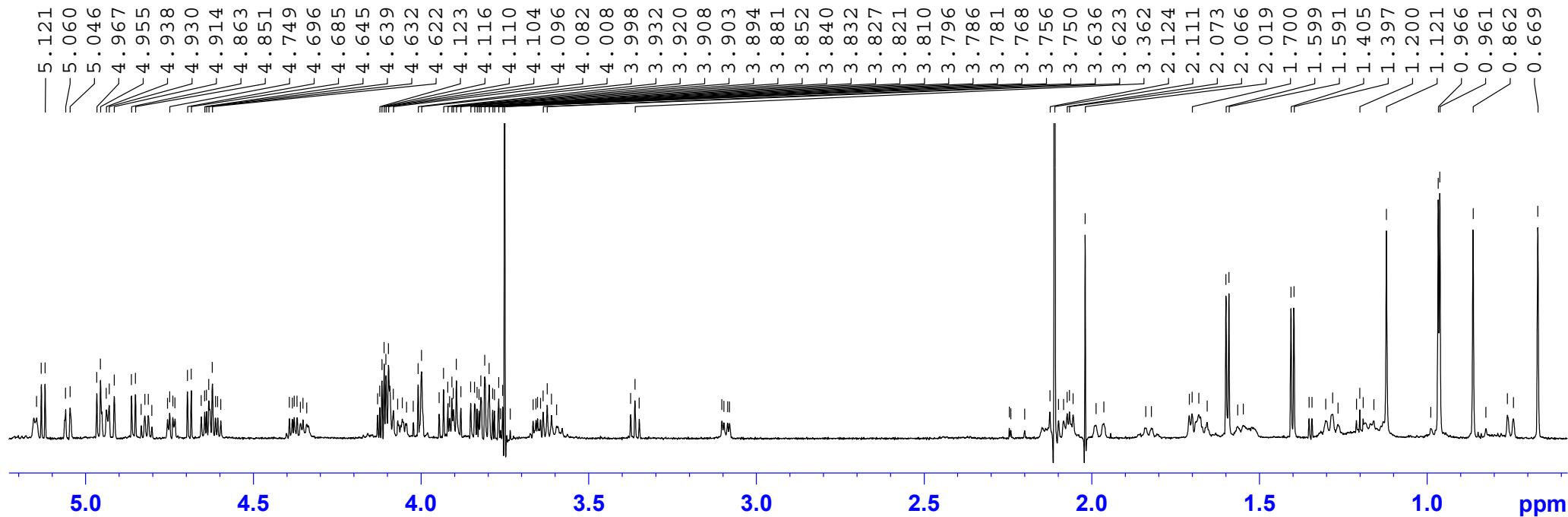


Figure S33. The  ${}^1\text{H}$  NMR (700.00 MHz) spectrum of kuriloside I (5) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

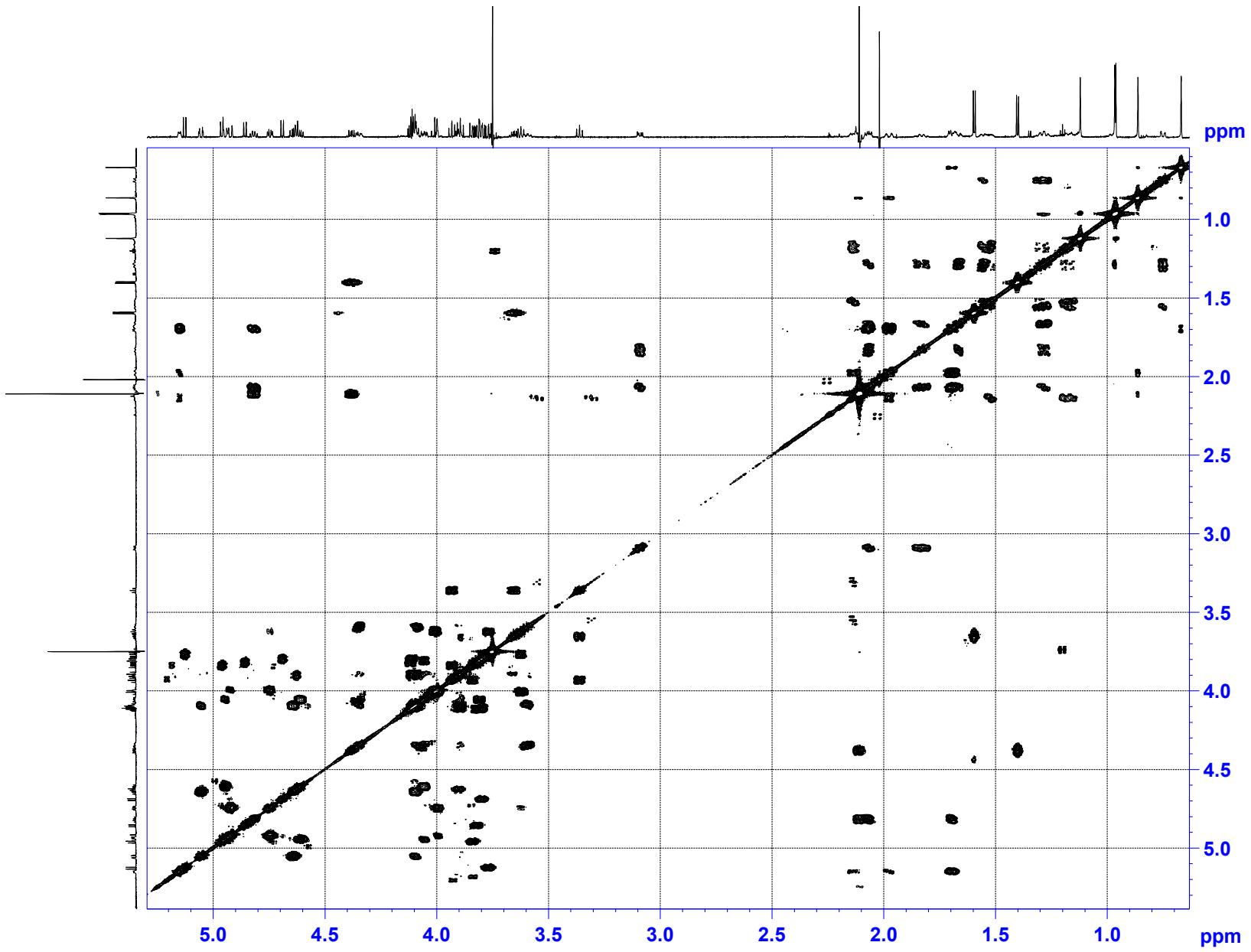


Figure S34. The COSY (700.00 MHz) spectrum of kuriloside I (5) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

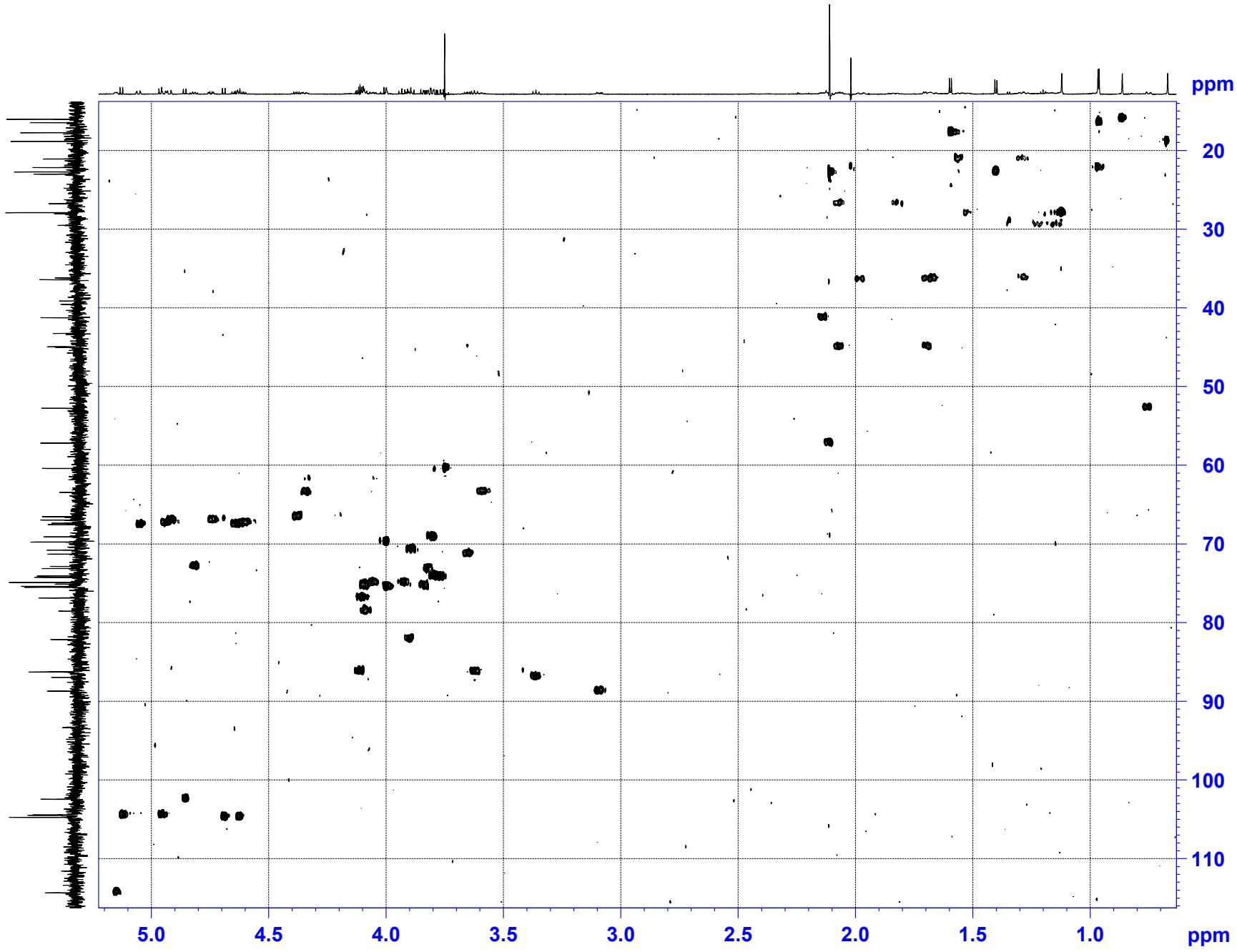


Figure S35. The HSQC (700.00 MHz) spectrum of kuriloside I (5) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

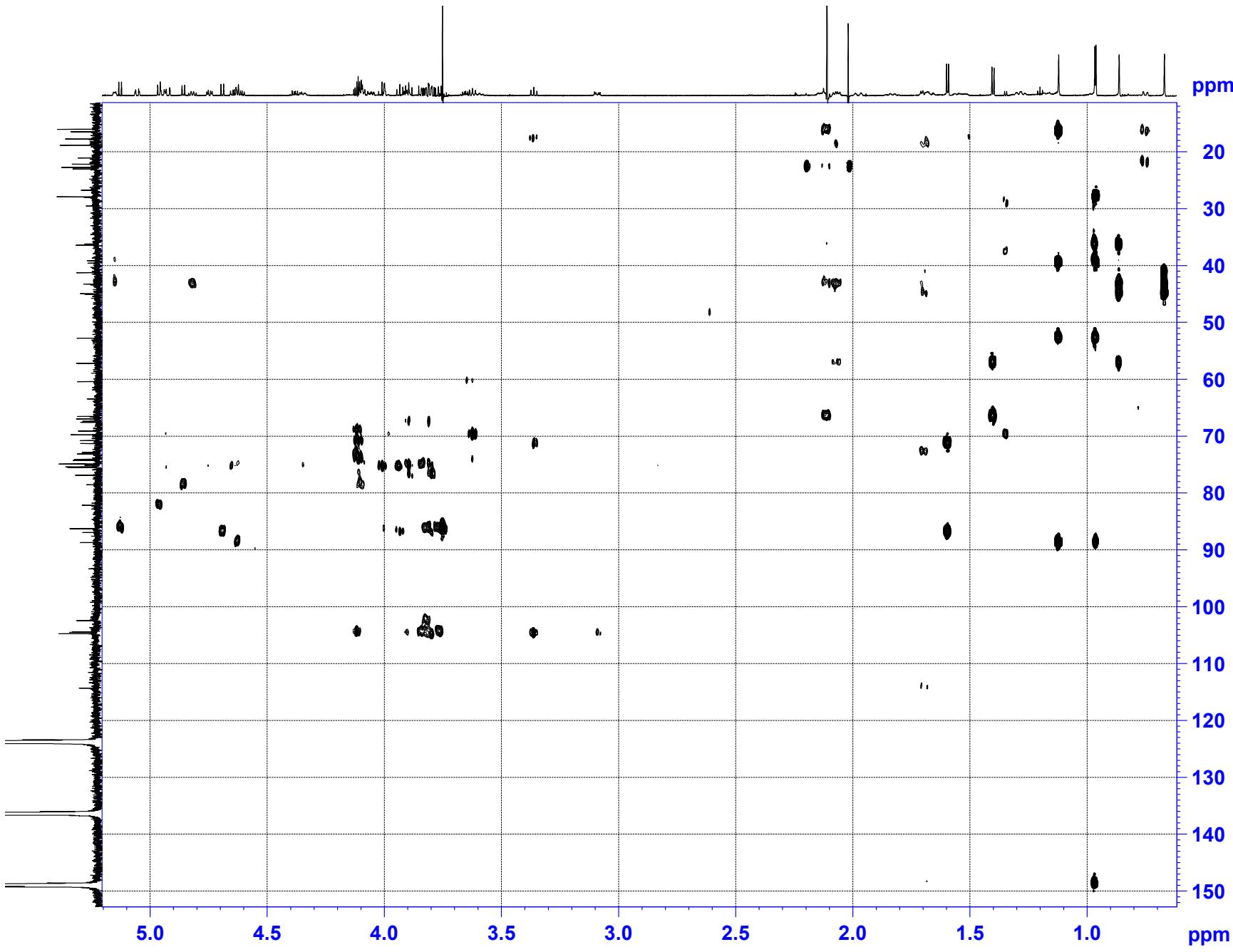


Figure S36. The HMBC (700.00 MHz) spectrum of kuriloside I (**5**) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

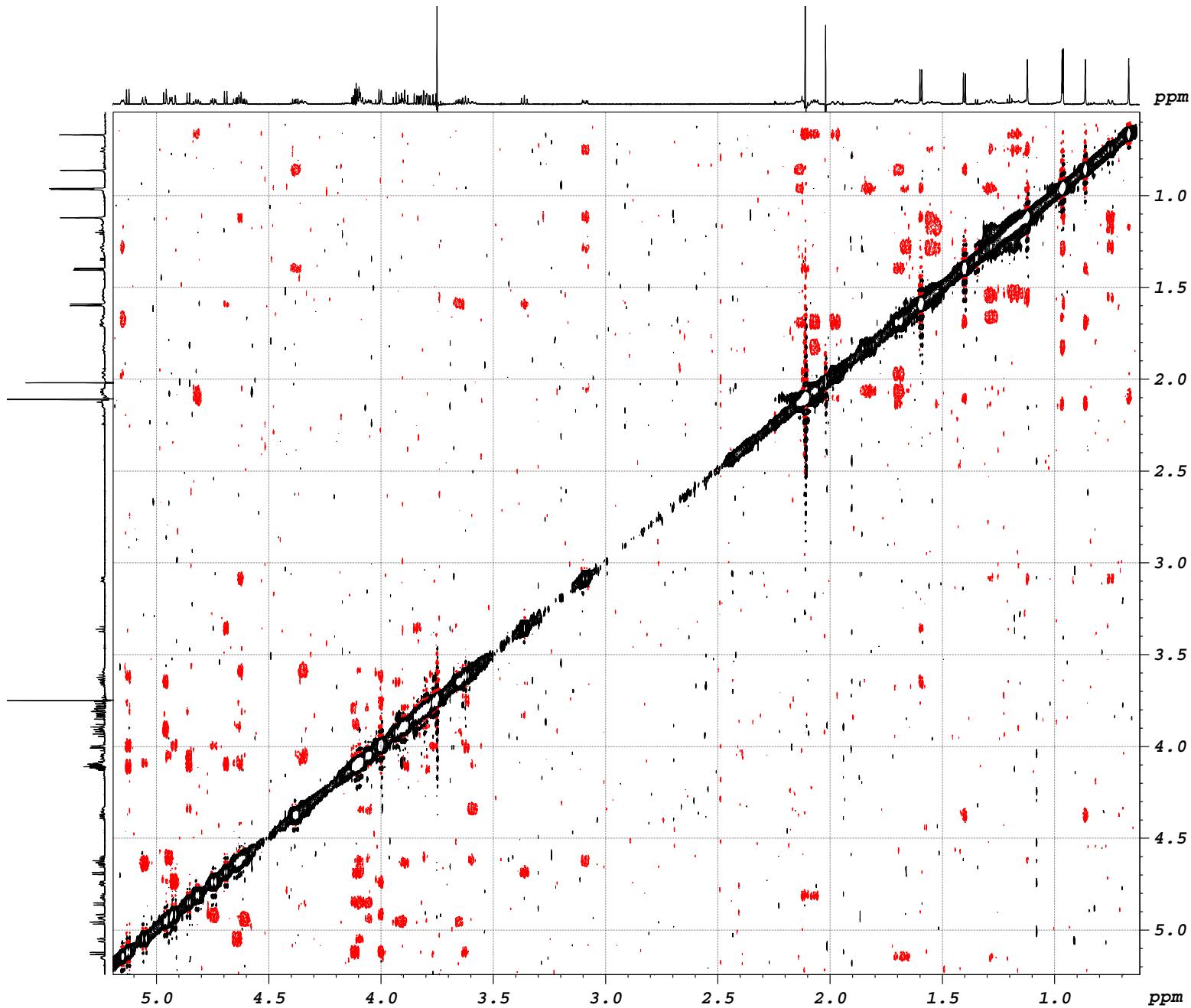


Figure S37. The ROESY (700.00 MHz) spectrum of kuriloside I (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

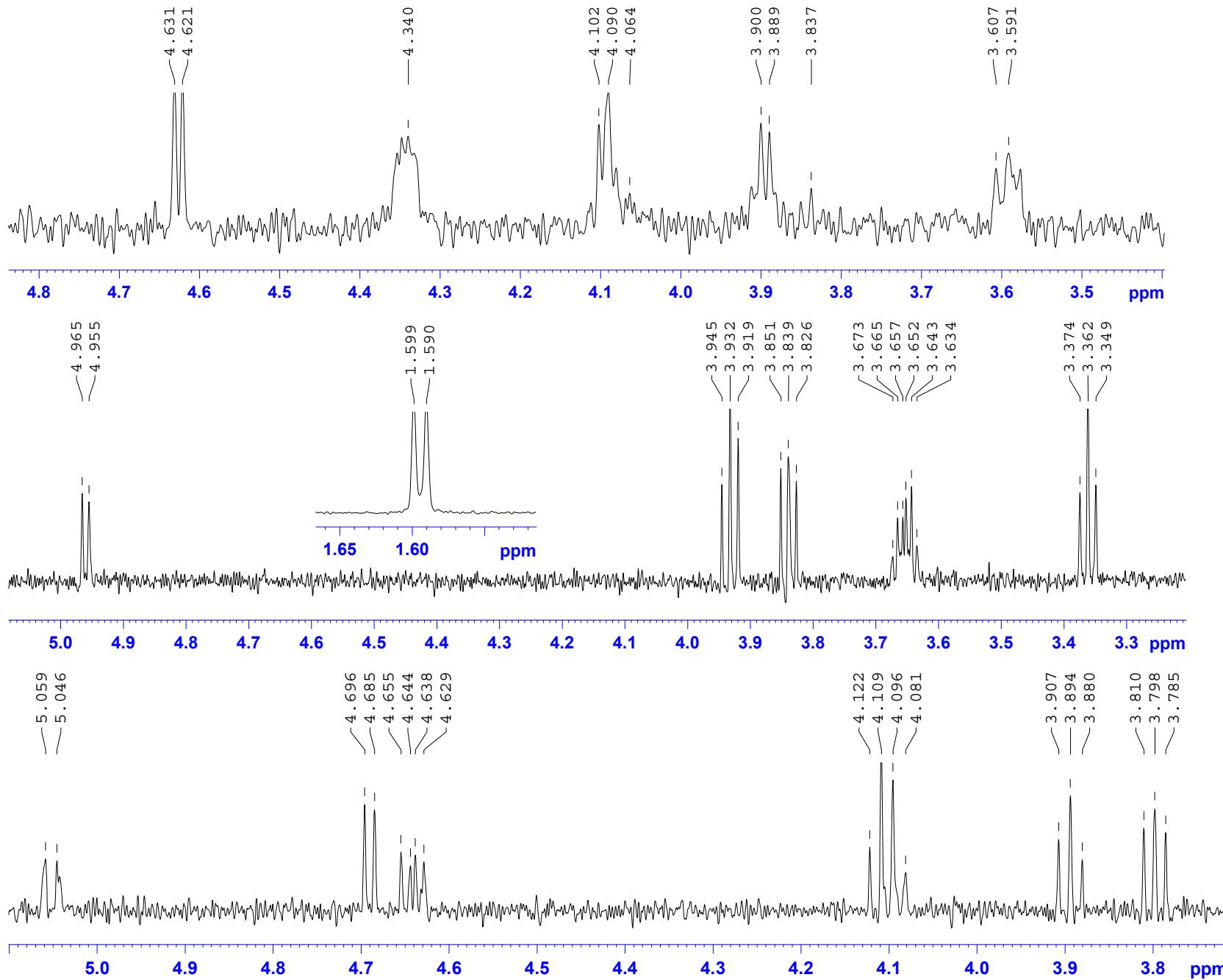


Figure S38. 1D TOCSY (700.00 MHz) spectra of XyloseI, QuinovoseII and GlucoseIII kuriloside I (**5**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

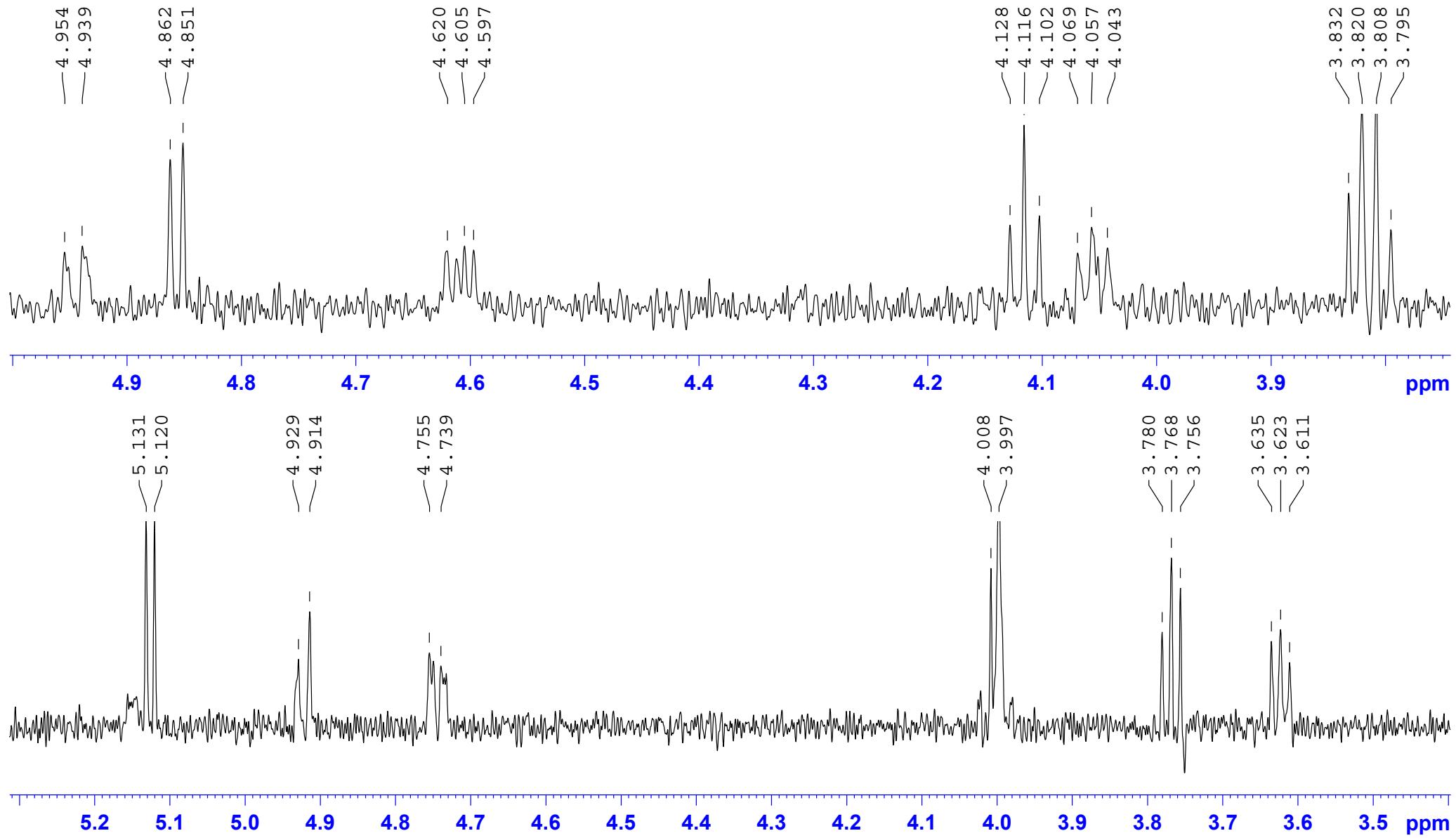


Figure S39. 1D TOCSY (700.00 MHz) spectra of GlucoseIV and MeGlcV of kuriloside I (**5**), C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

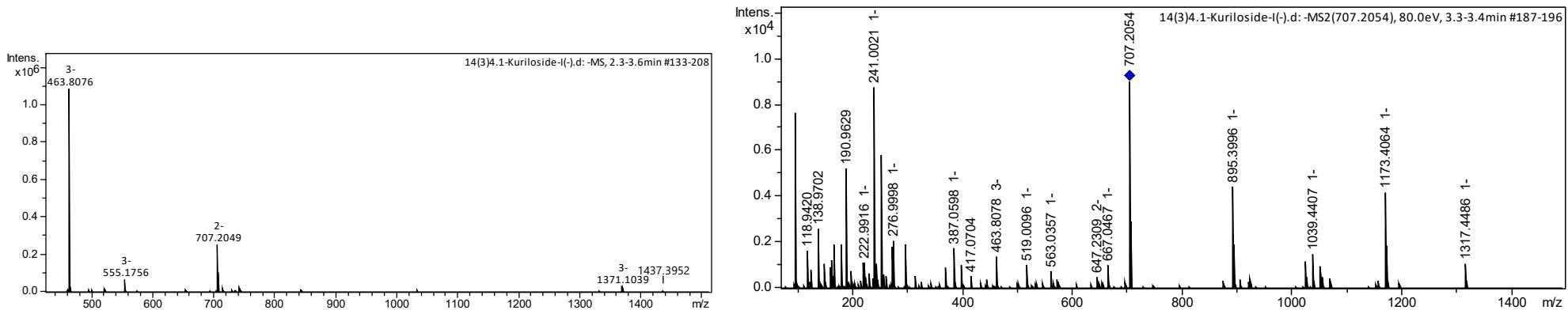


Figure S40. HR-ESI-MS and ESI-MS/MS spectra of kuriloside I (5)

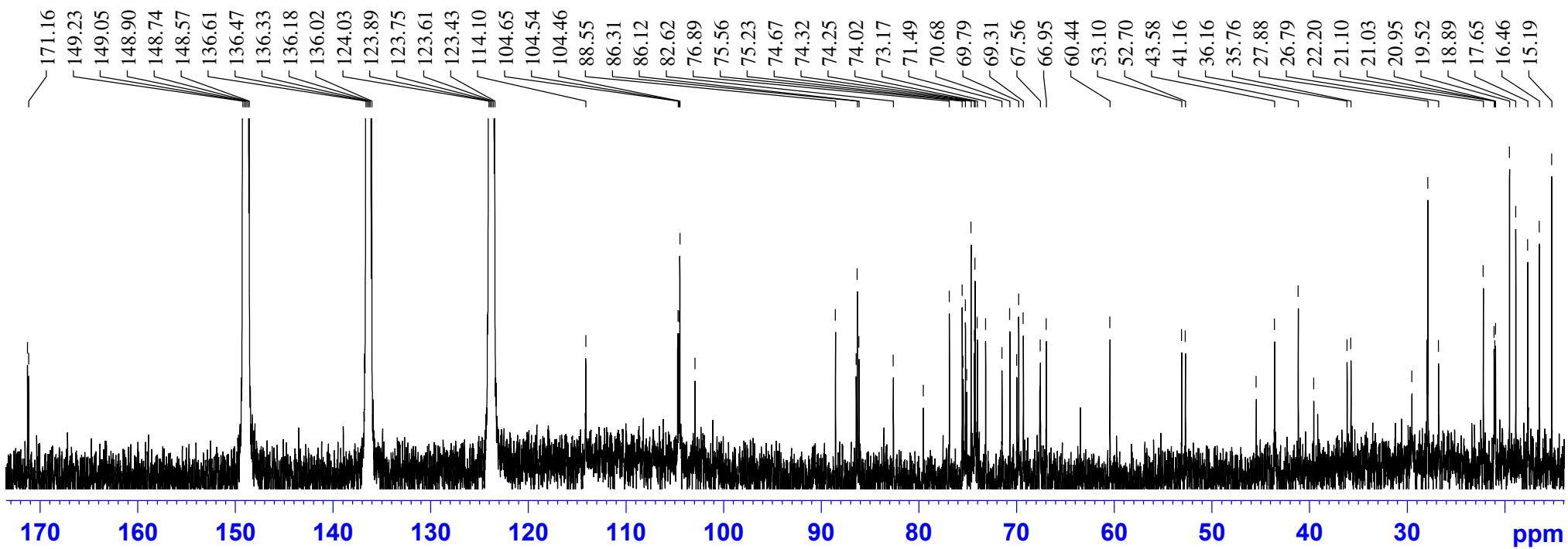


Figure S41. The  $^{13}\text{C}$  NMR (176.03 MHz) spectrum of kuriloside I<sub>1</sub> (6) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

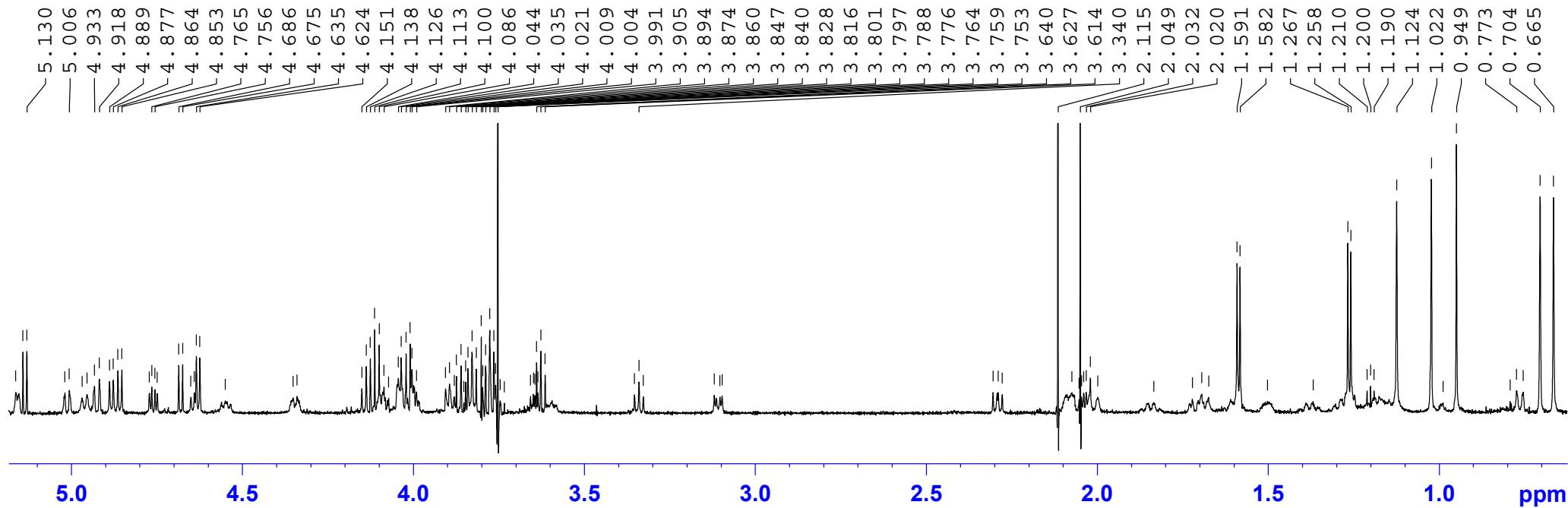


Figure S42. The  $^1\text{H}$  NMR (700.00 MHz) spectrum of kuriloside I<sub>1</sub> (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

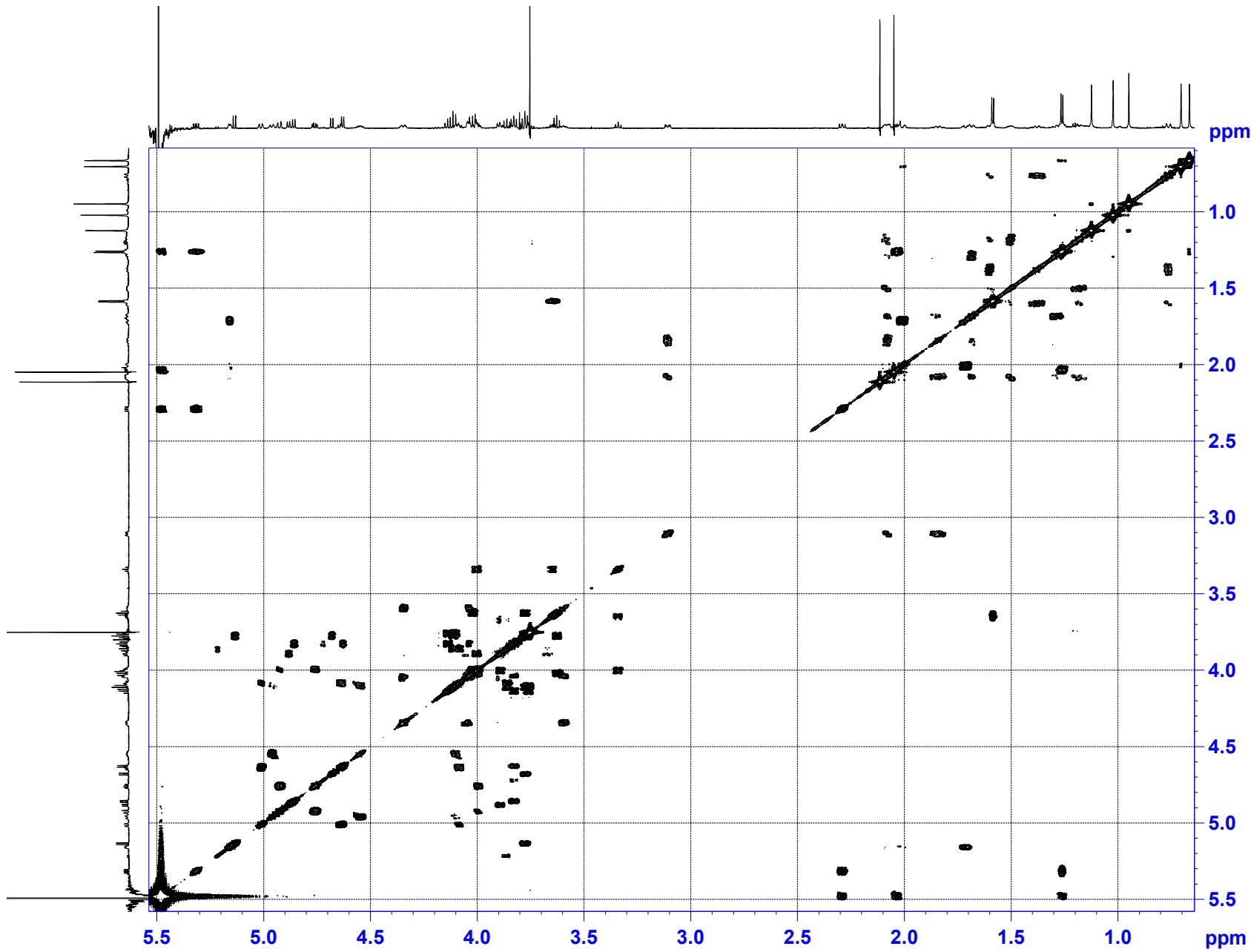


Figure S43. The COSY (700.00 MHz) spectrum of kuriloside I<sub>1</sub> (6) in  $C_5D_5N/D_2O$  (4/1)

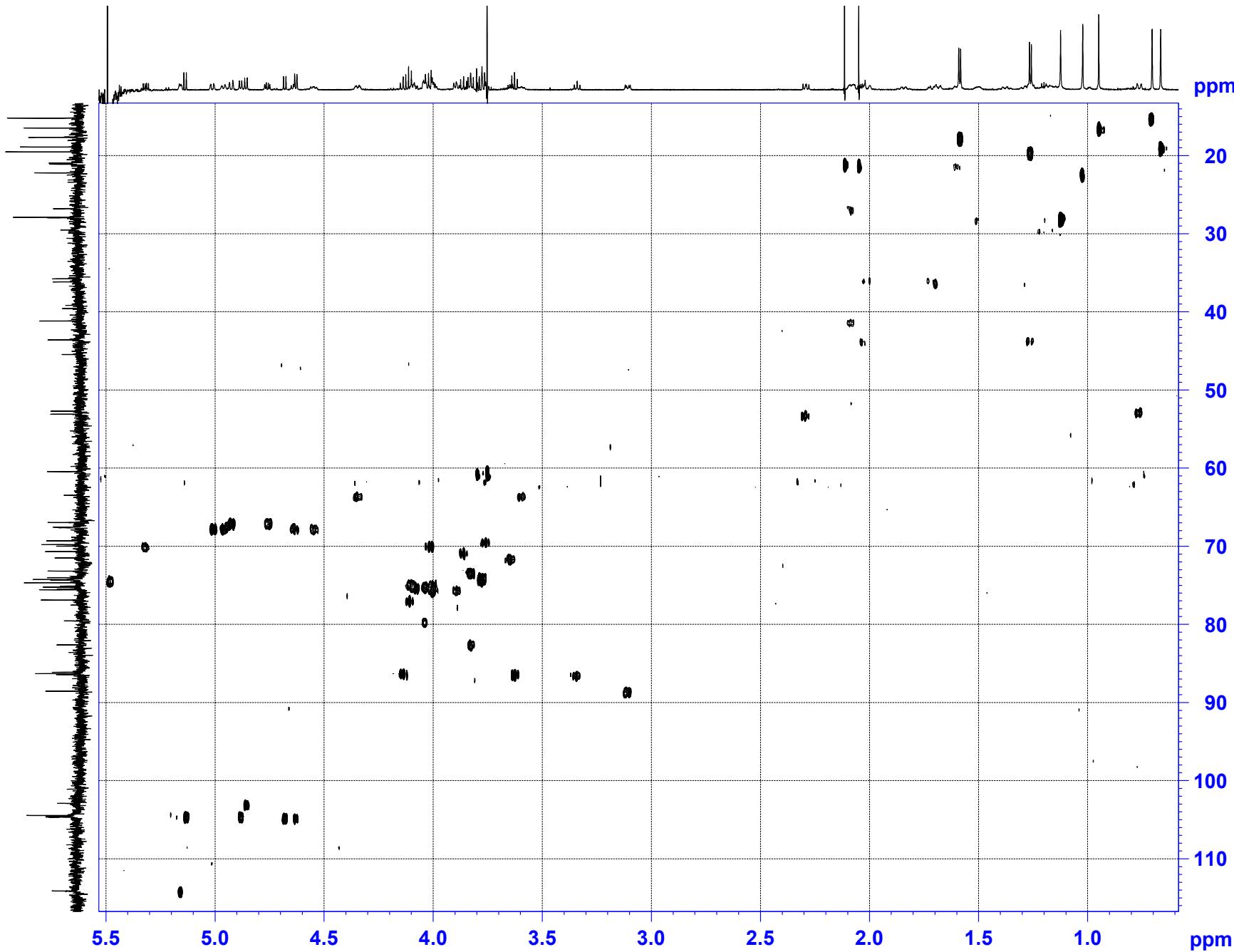


Figure S44. The HSQC (700.00 MHz) spectrum of kuriloside I<sub>1</sub> (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

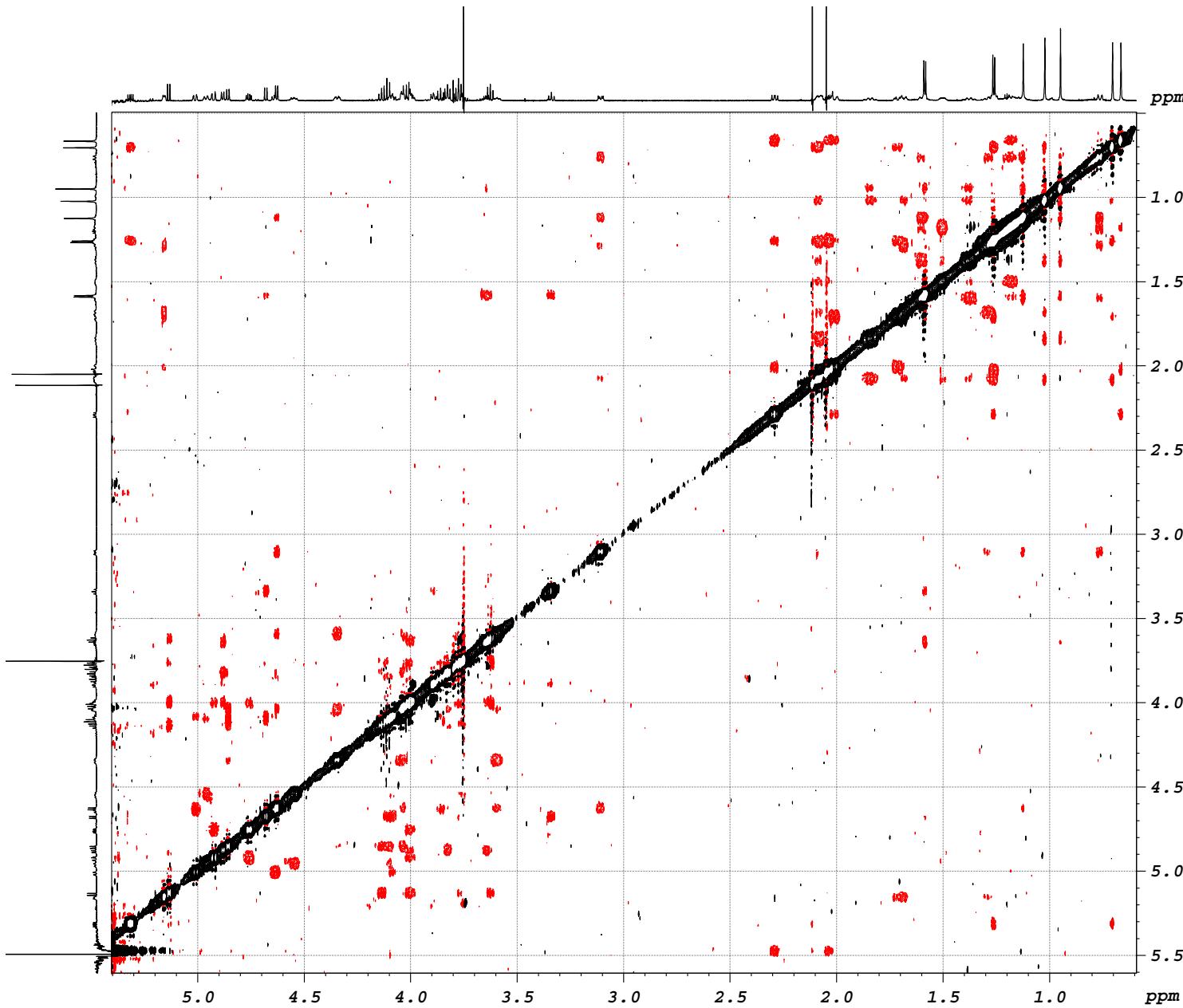


Figure S45. The ROESY (700.00 MHz) spectrum of kuriloside I<sub>1</sub> (**6**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

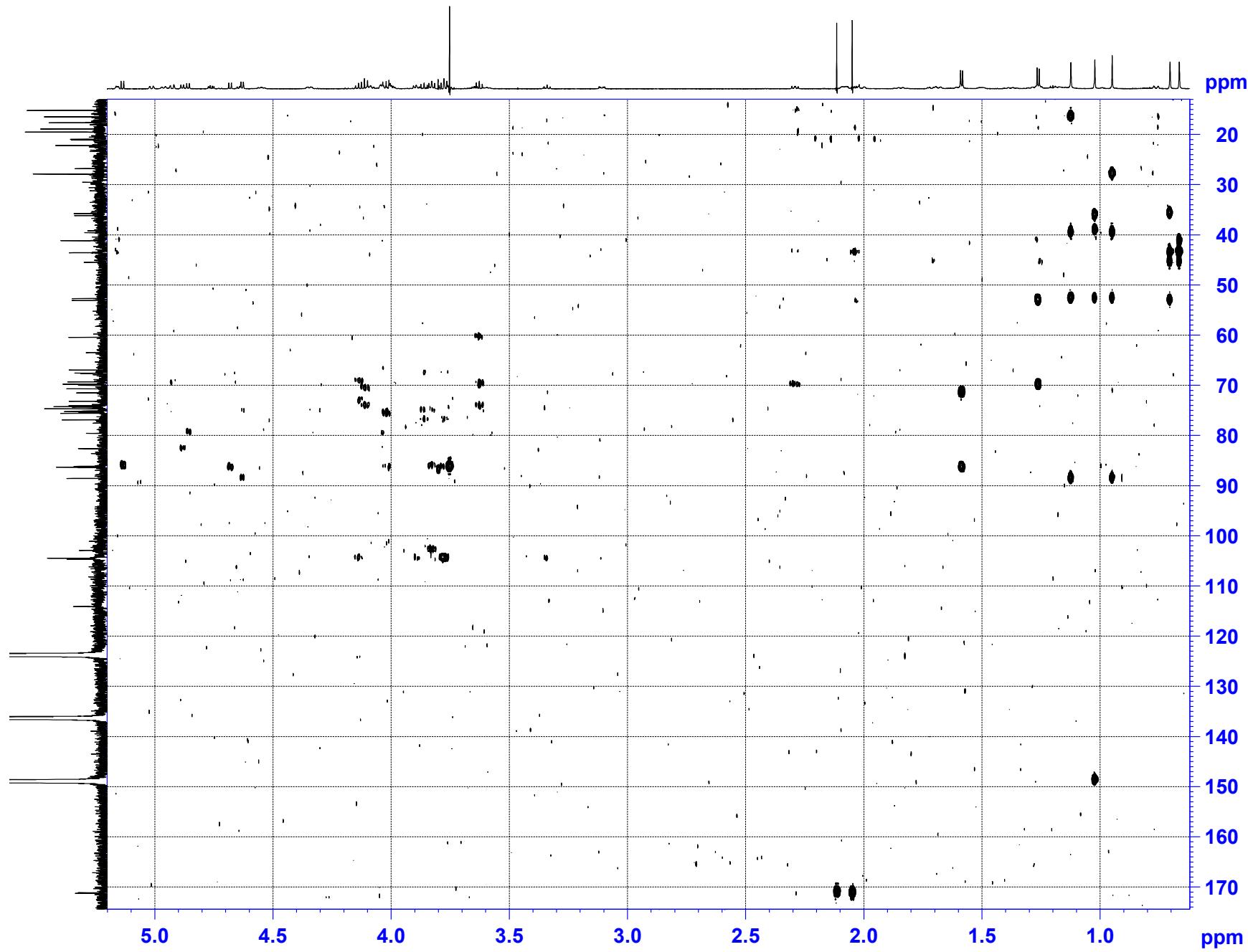


Figure S46. The HMBC (700.00 MHz) spectrum of kuriloside I (6) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

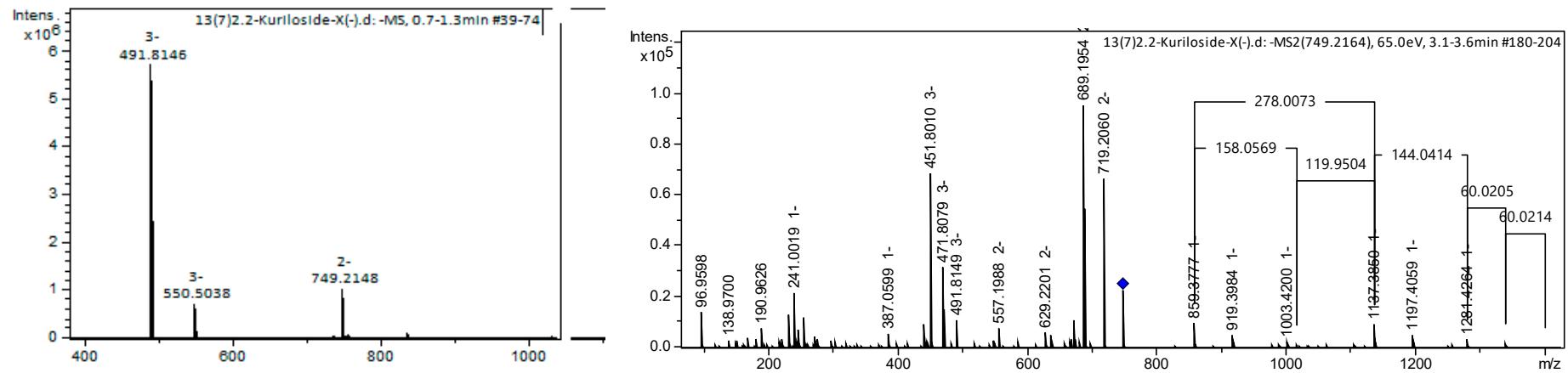


Figure S47. HR-ESI-MS and ESI-MS/MS spectra of kuriloside I<sub>1</sub> (6)

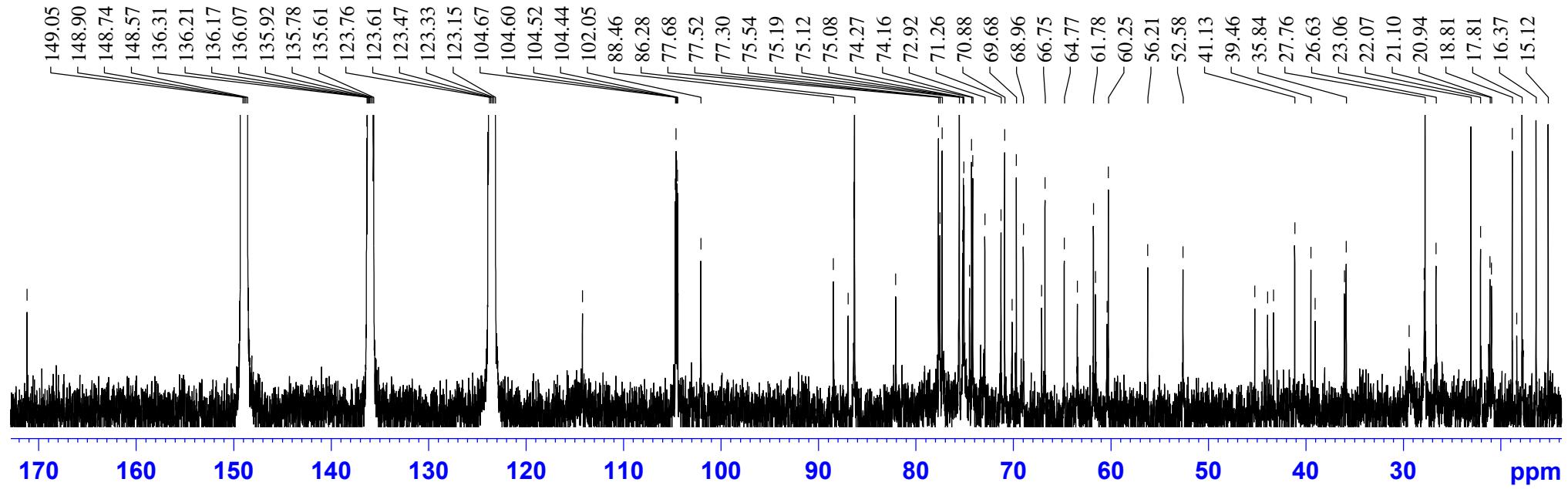


Figure S48. The <sup>13</sup>C NMR (176.03 MHz) spectrum of kuriloside J (7) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

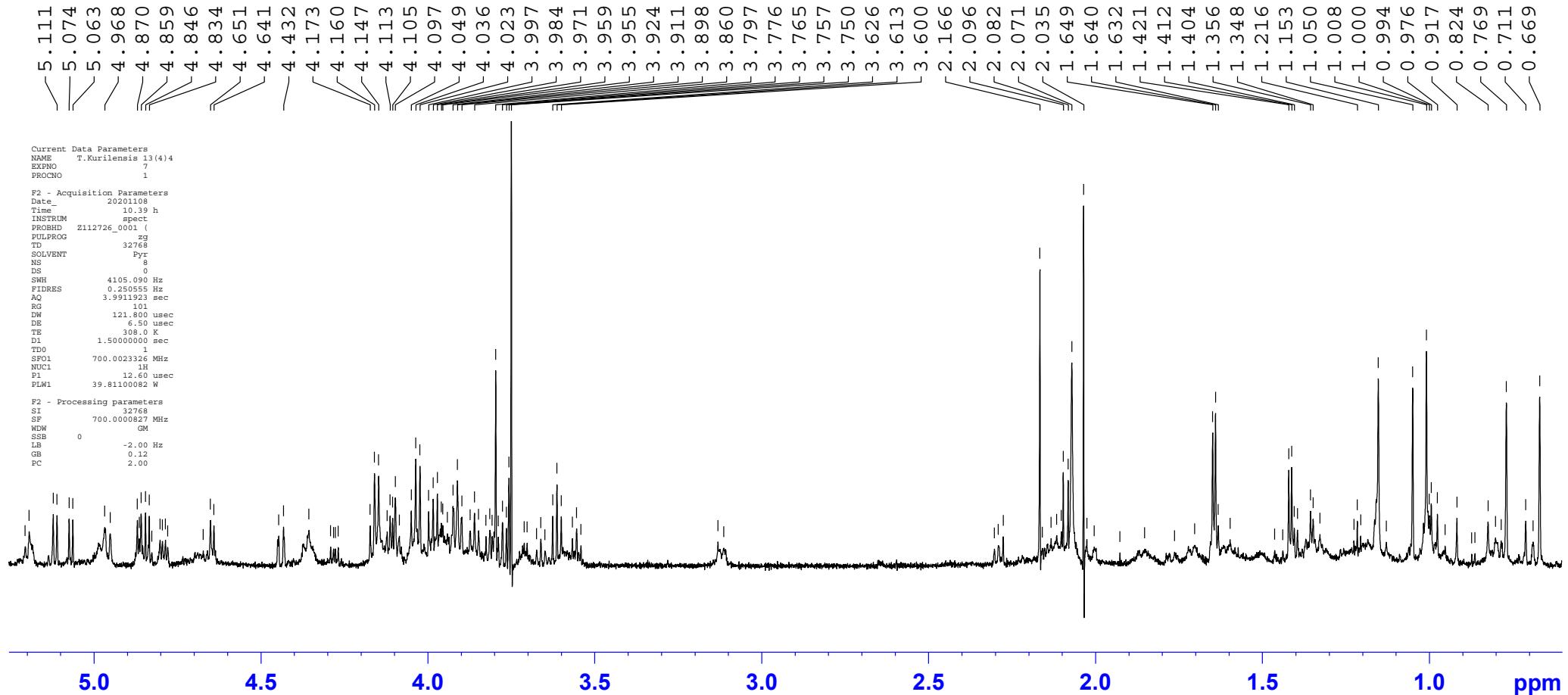


Figure S49. The  $^1\text{H}$  NMR (700.00 MHz) spectrum of kuriloside J (7) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

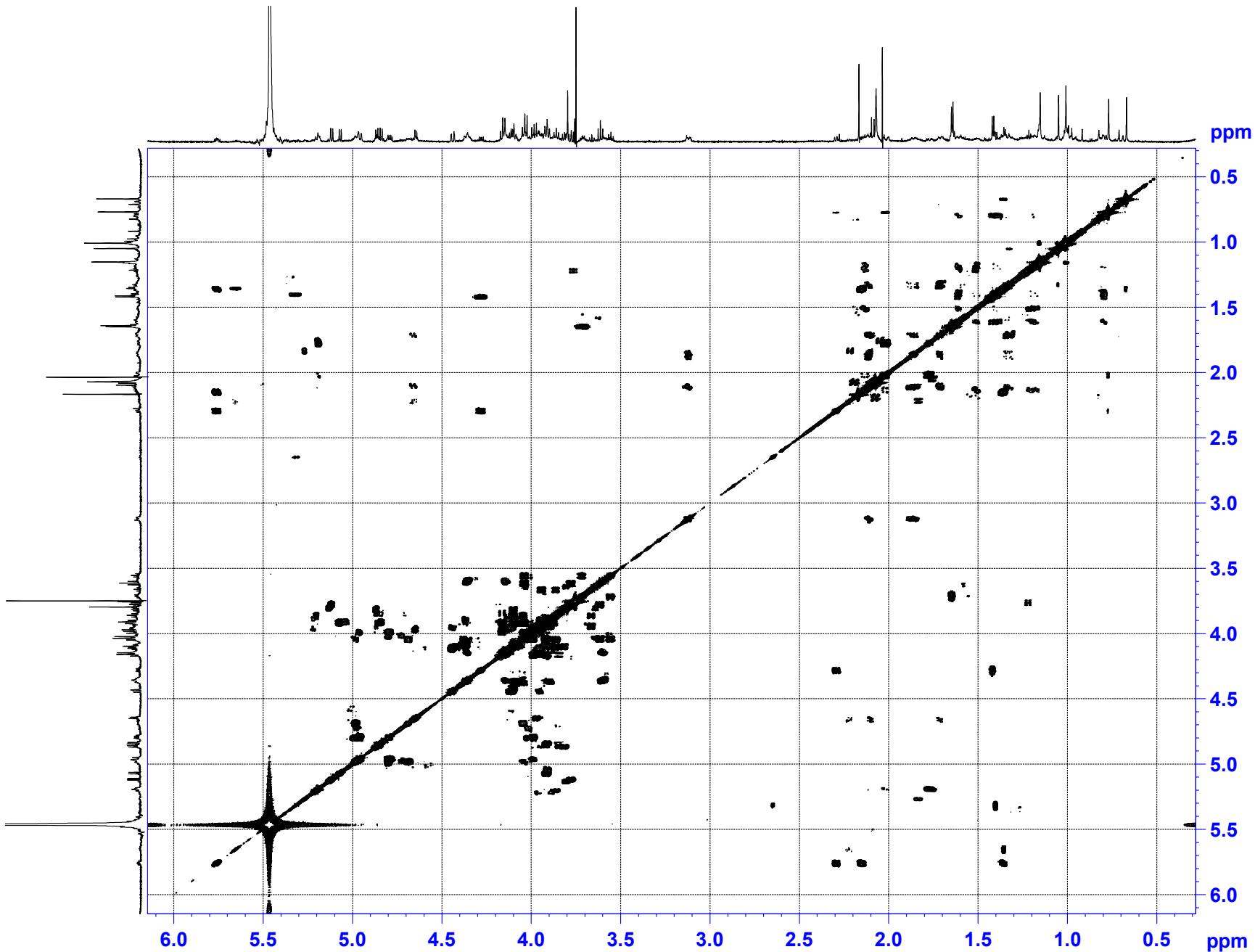


Figure S50. The COSY (700.00 MHz) spectrum of kuriloside J (7) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

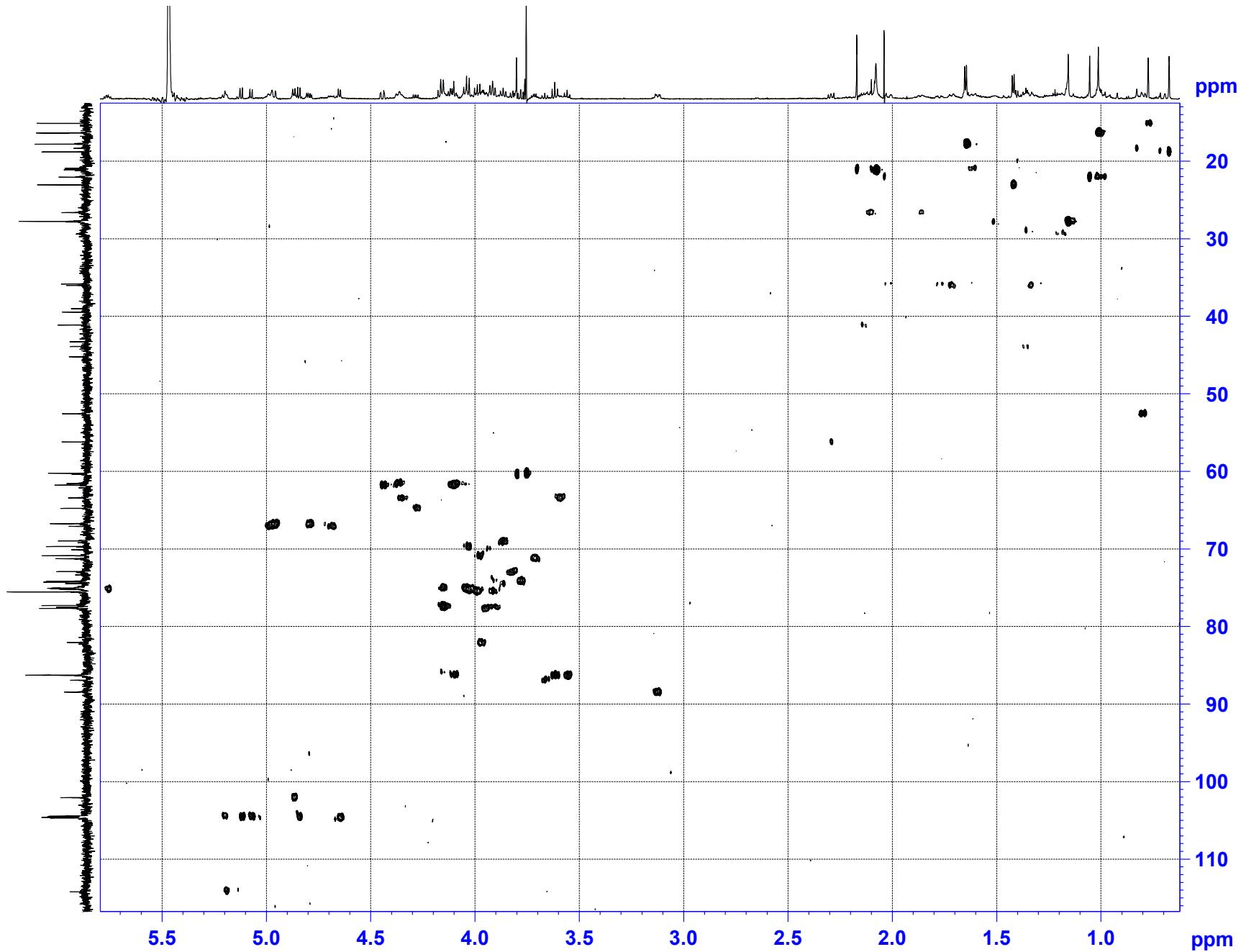


Figure S51. The HSQC (700.00 MHz) spectrum of kuriloside J (7) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

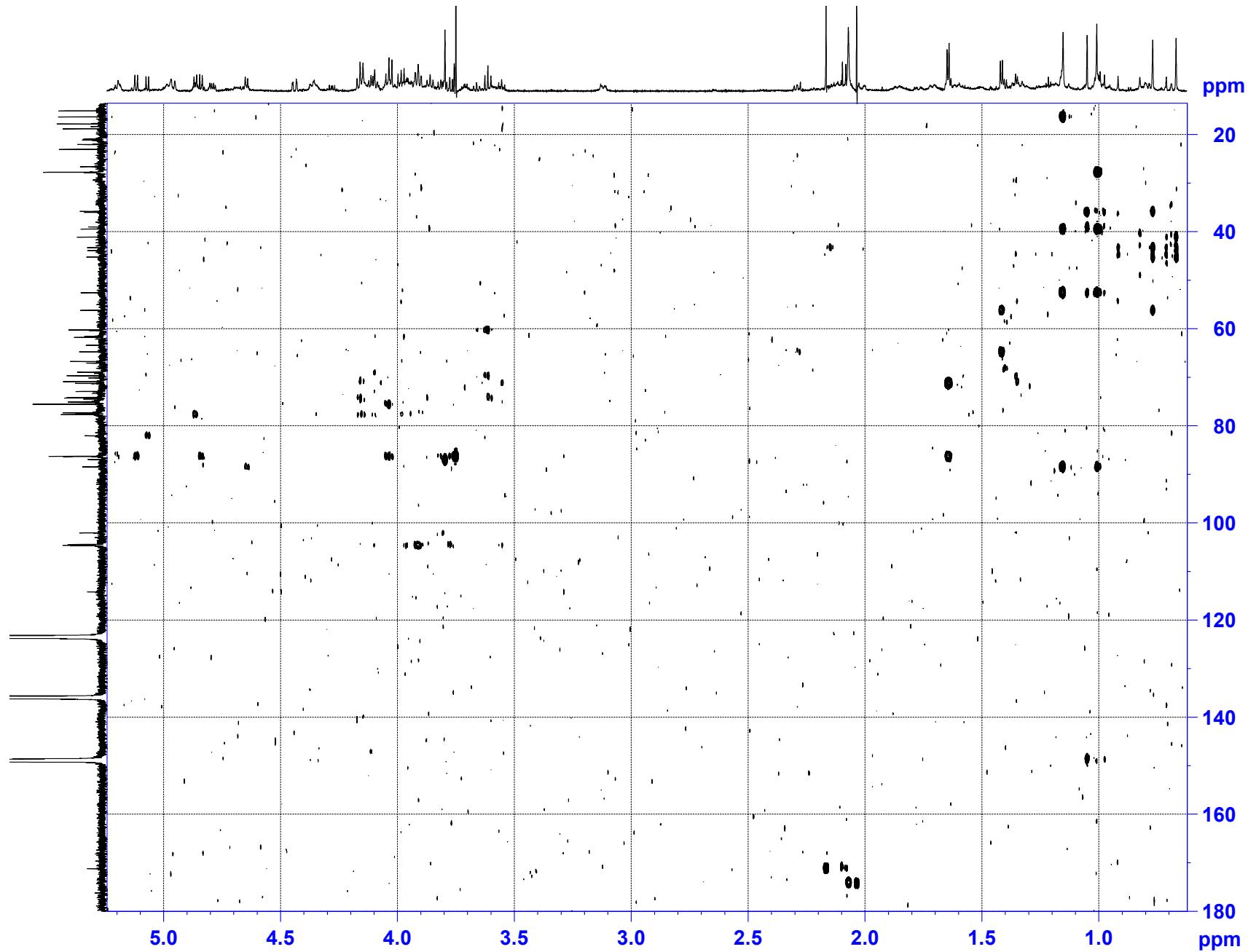


Figure S52. The HMBC (700.00 MHz) spectrum of kuriloside J (7) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

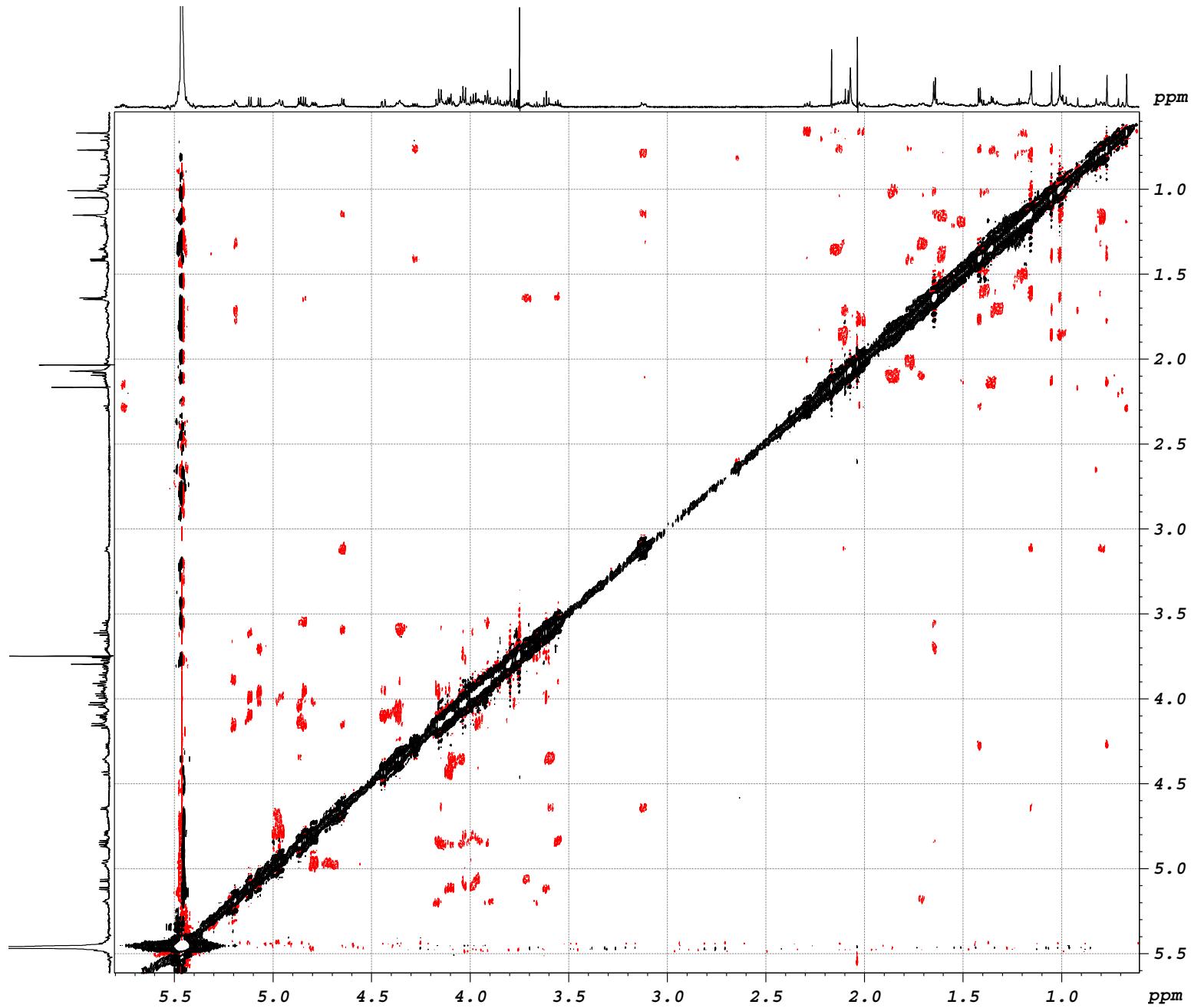


Figure S53. The ROESY (700.00 MHz) spectrum of kuriloside J (7) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

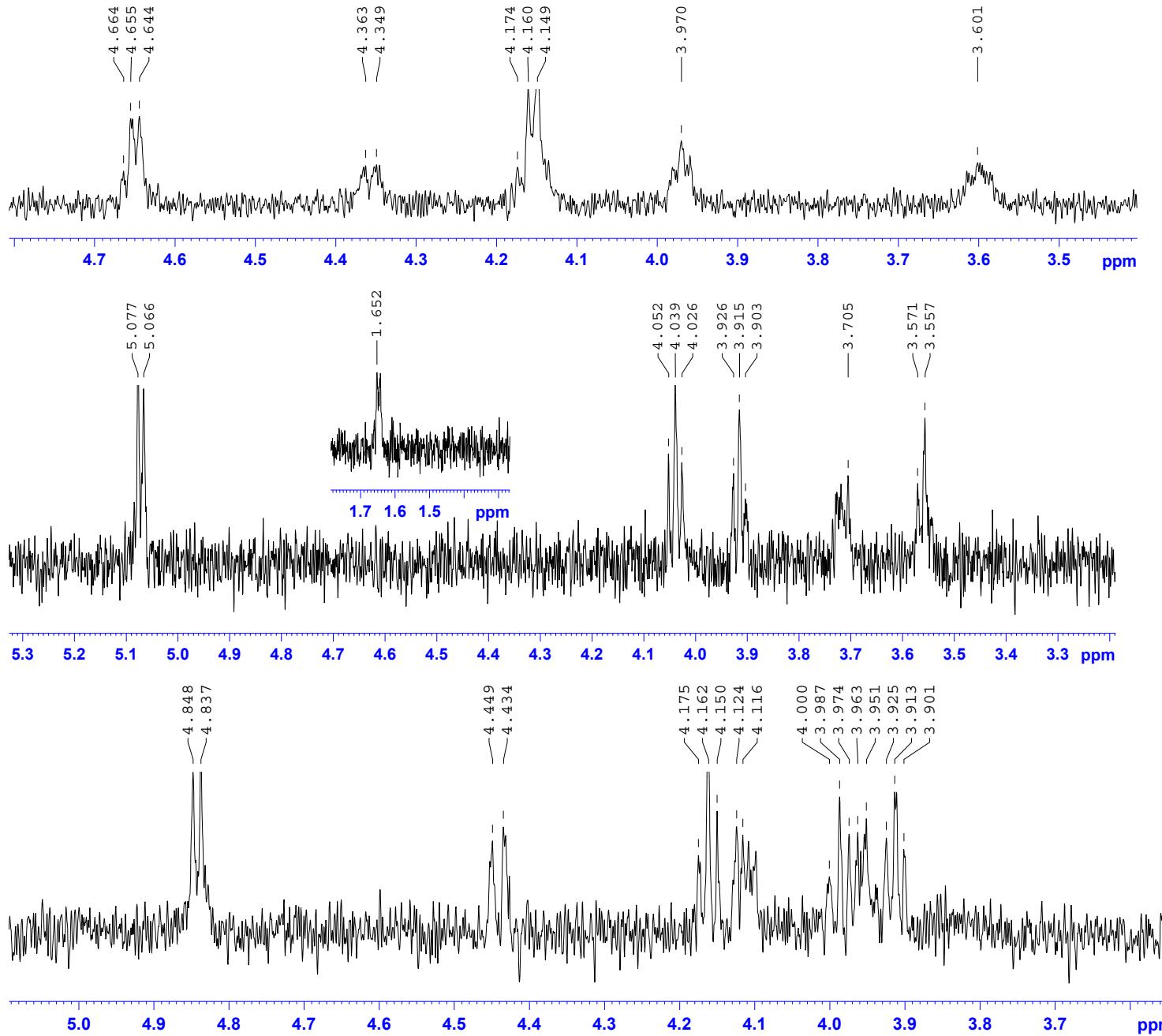


Figure S54. 1 D TOCSY (700.00 MHz) spectra of XyloseI, QuinovoseII and GlucoseIII of kuriloside J (7) in  $C_5D_5N/D_2O$  (4/1)

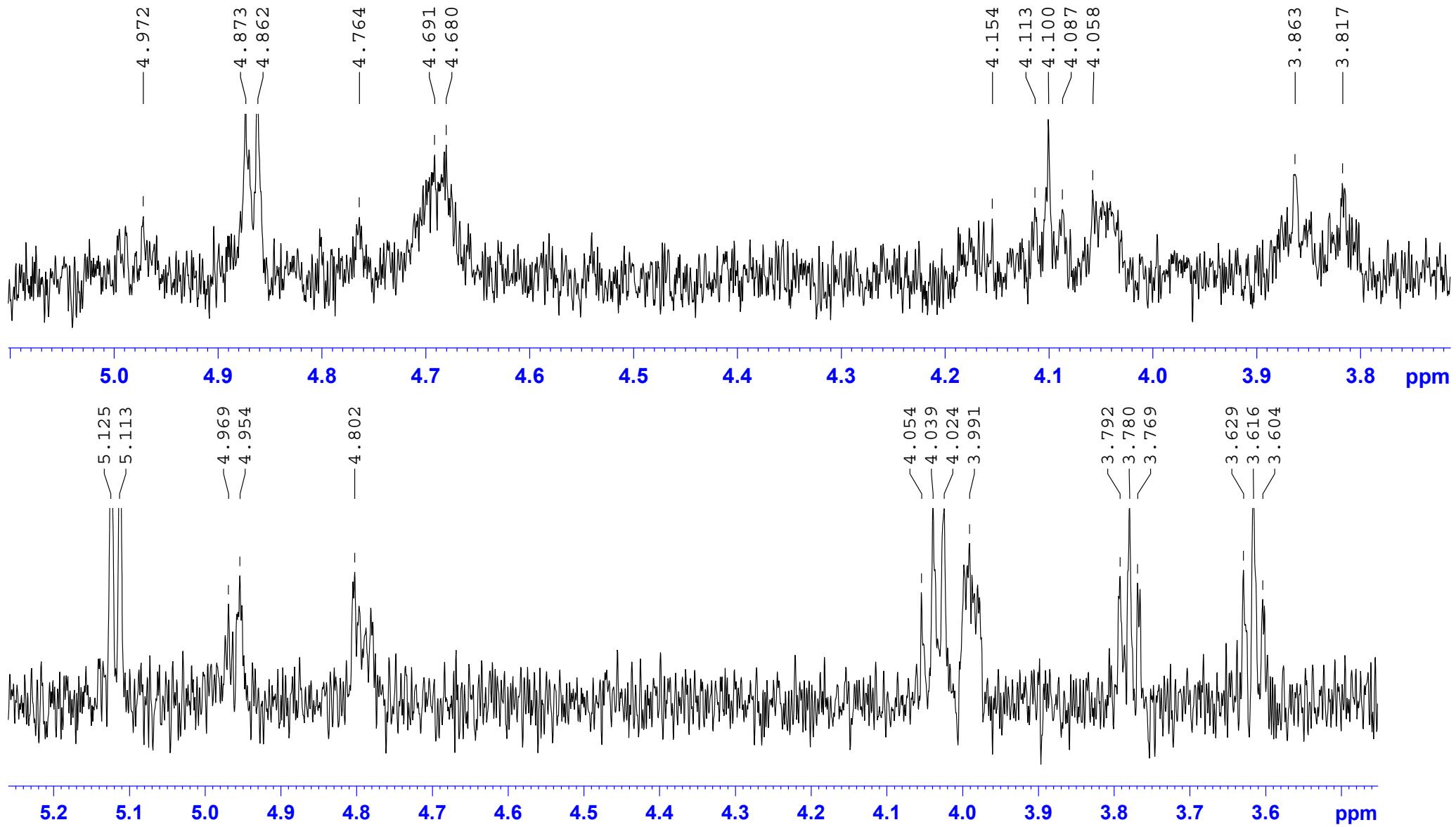


Figure S55. 1 D TOCSY (700.00 MHz) spectra of GlcIV and MeGlcV of kuriloside J (7) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

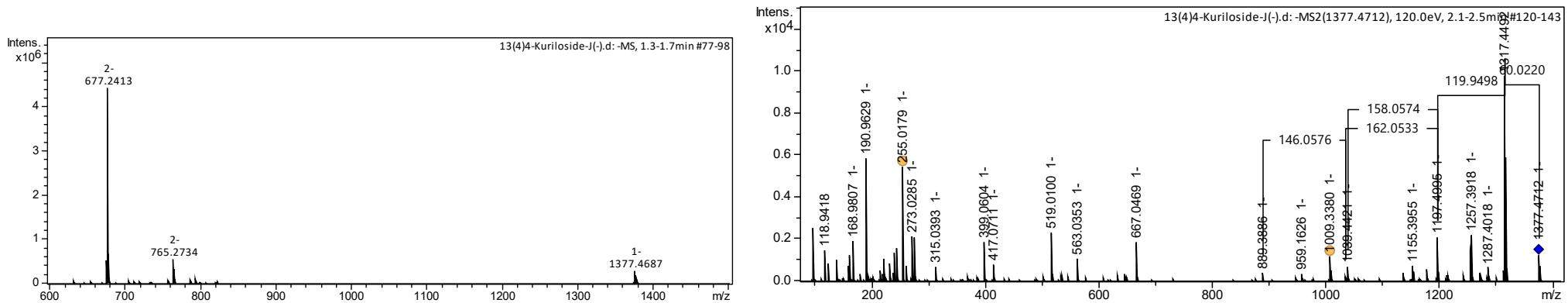


Figure S56. HR-ESI-MS and ESI-MS/MS spectra of kuriloside J (7)

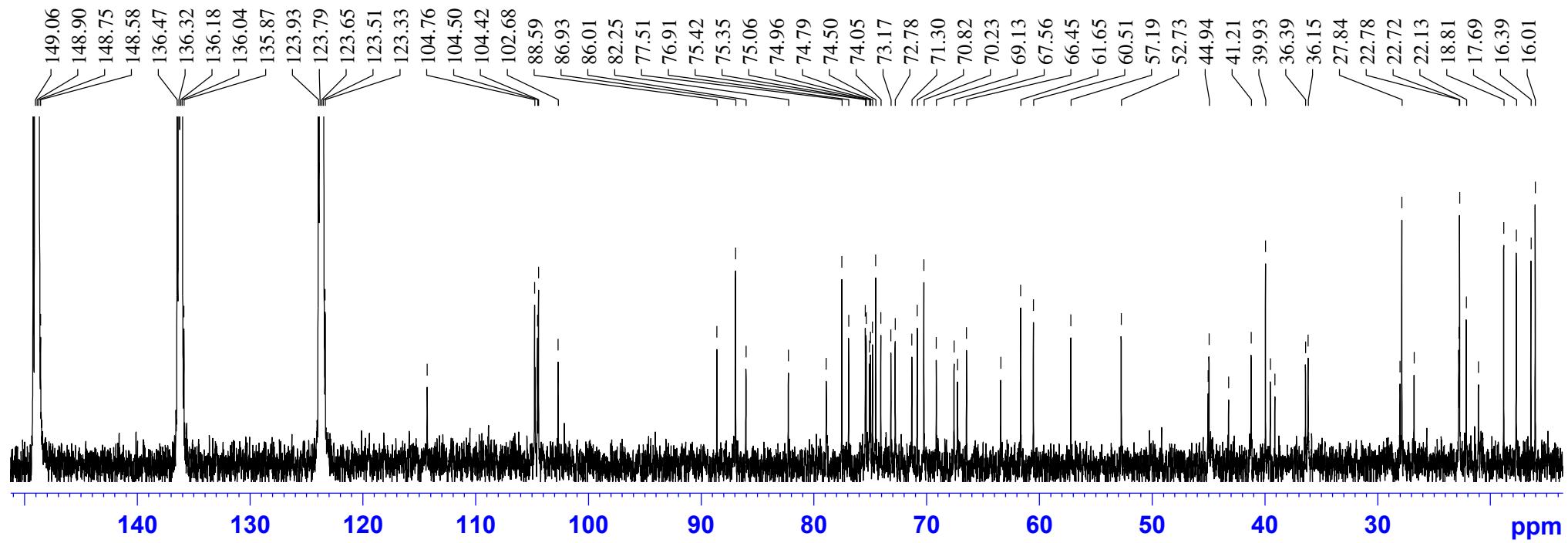


Figure S57. The <sup>13</sup>C NMR (176.03 MHz) spectrum of kuriloside K (8) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

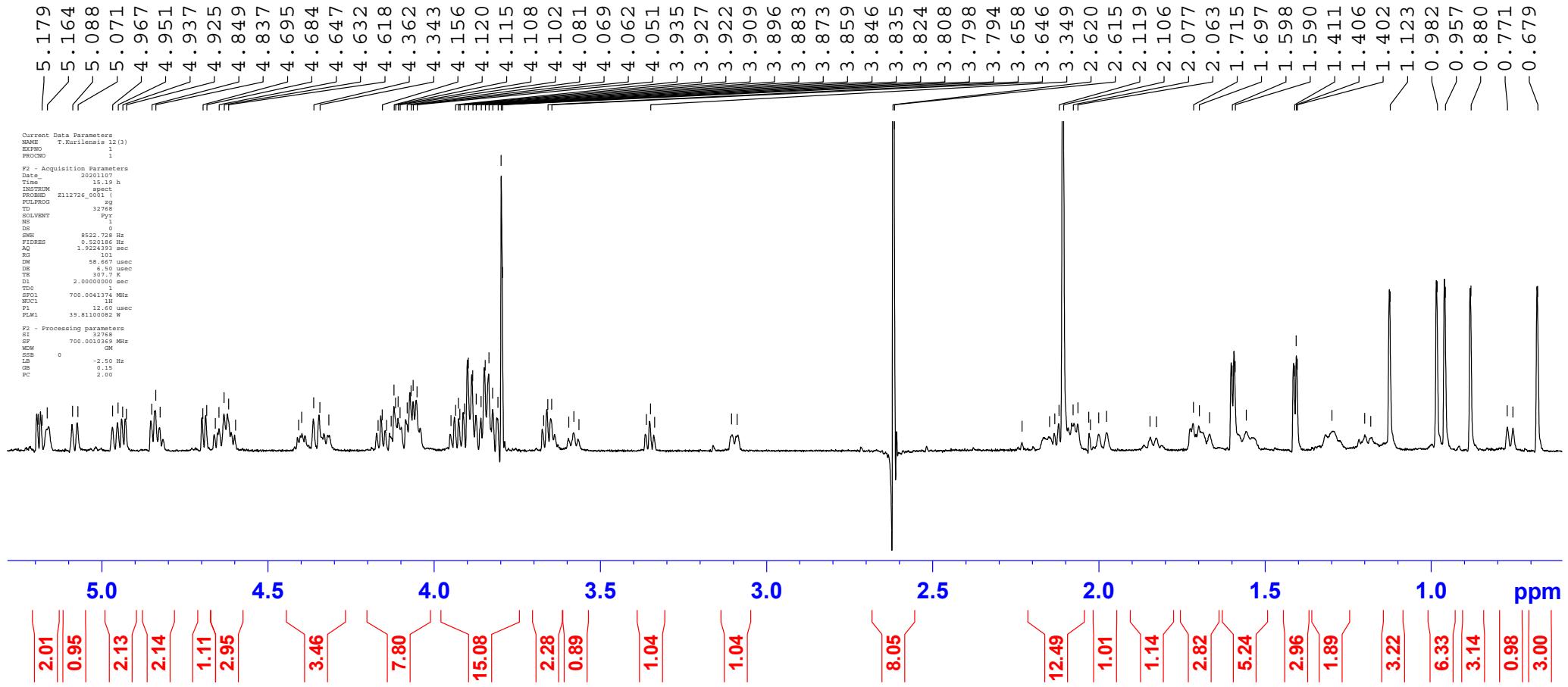


Figure S58. The  $^1\text{H}$  NMR (700.00 MHz) spectrum of kuriloside K (8) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

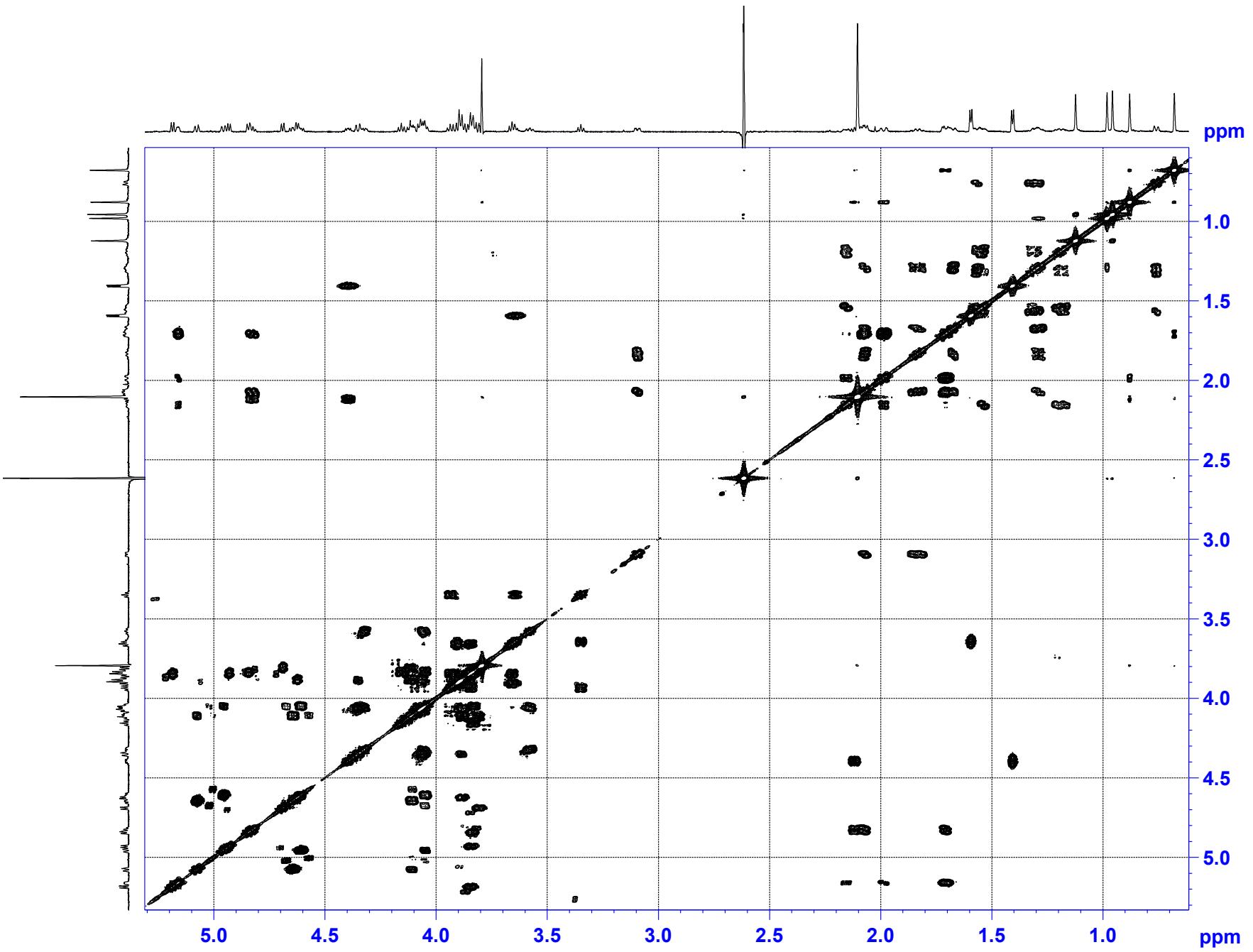


Figure S59. The COSY (700.00 MHz) spectrum of kuriloside K (8) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

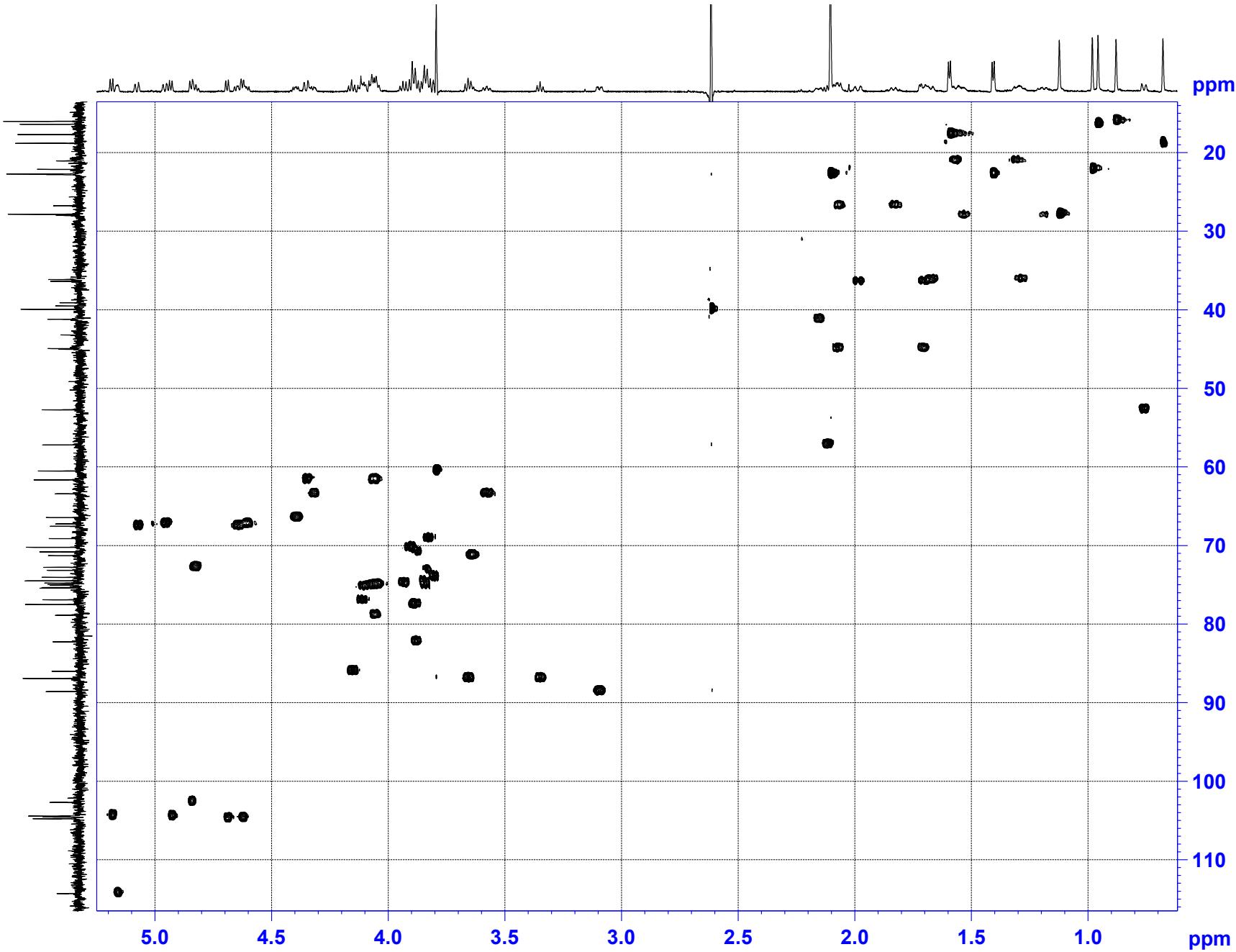


Figure S60. The HSQC (700.00 MHz) spectrum of kuriloside K (8) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

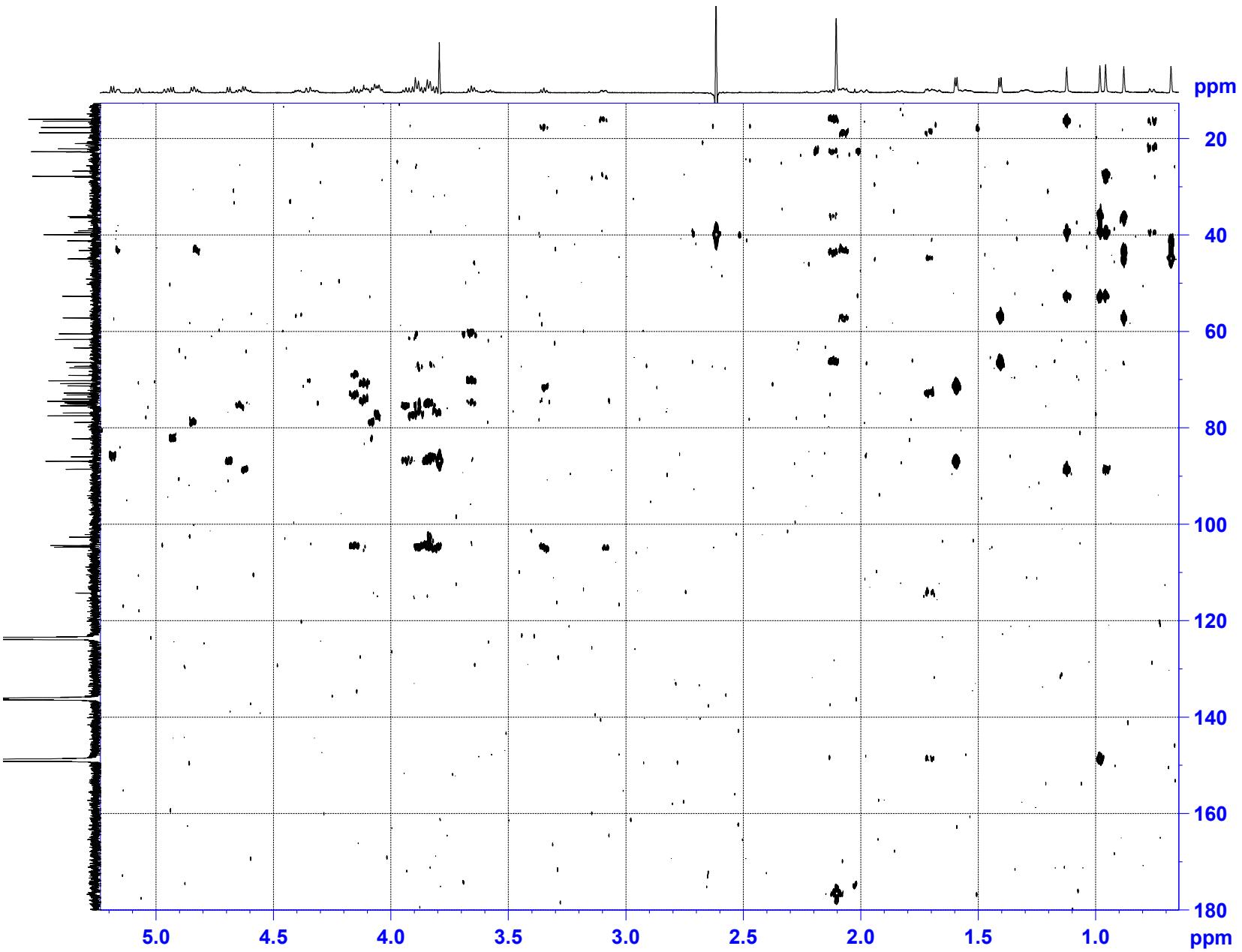


Figure S61. The HMBC (700.00 MHz) spectrum of kuriloside K (8) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

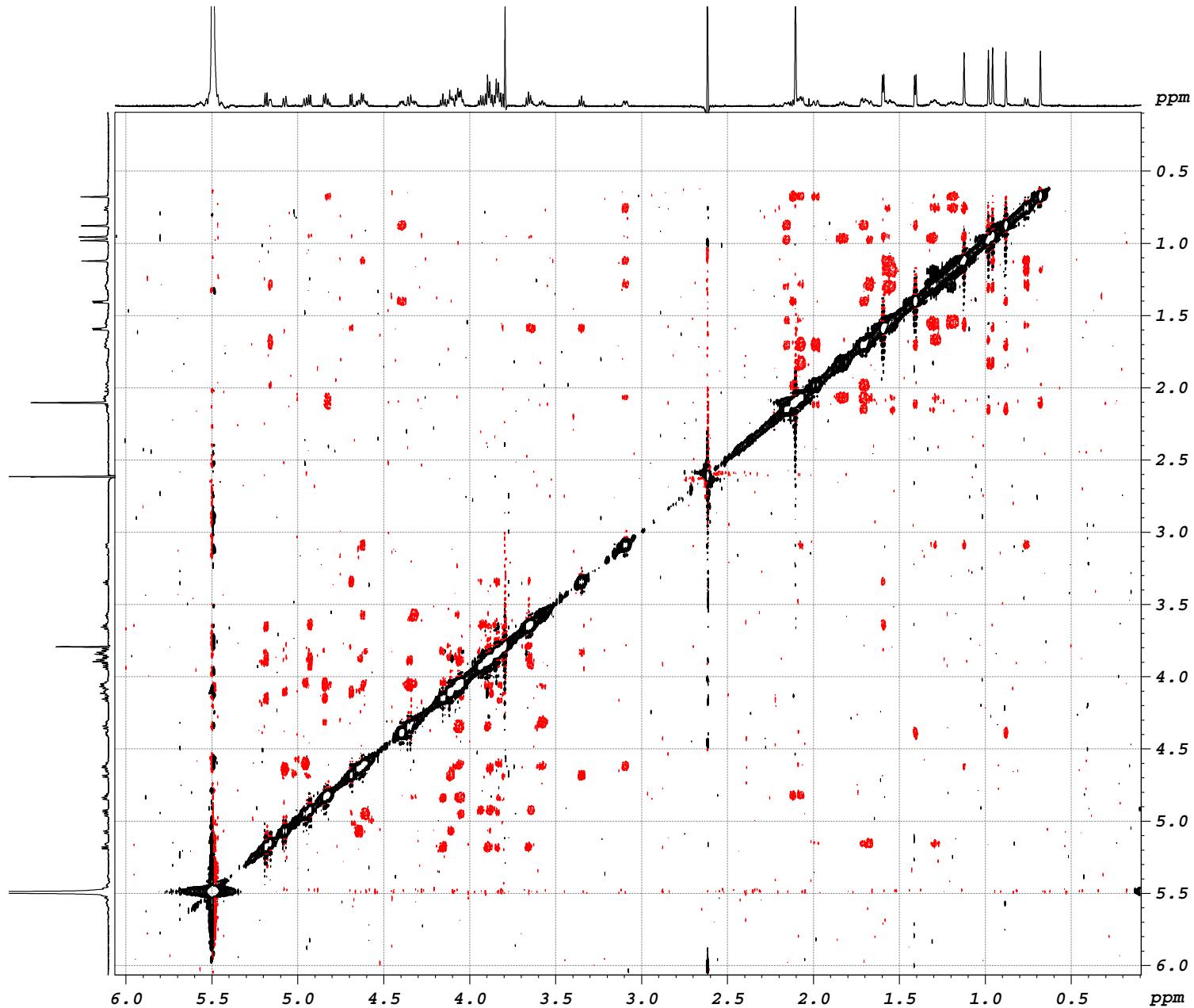


Figure S62. The ROESY (700.00 MHz) spectrum of kuriloside K (8) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

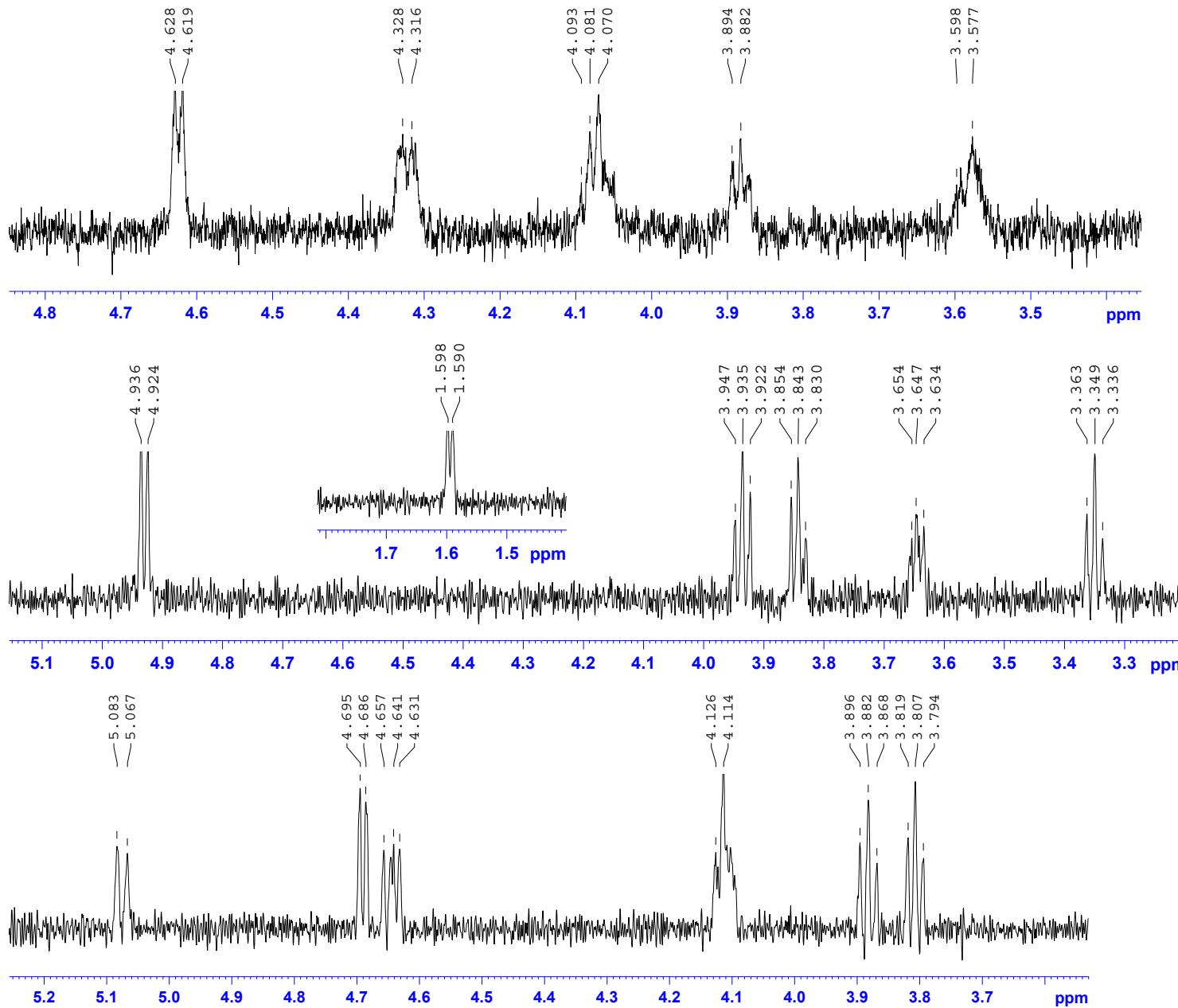


Figure S63. 1 D TOCSY (700.00 MHz) spectra of XyloseI, QuinovoseII and GlucoseIII of kuriloside K (8) in  $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$  (4/1)

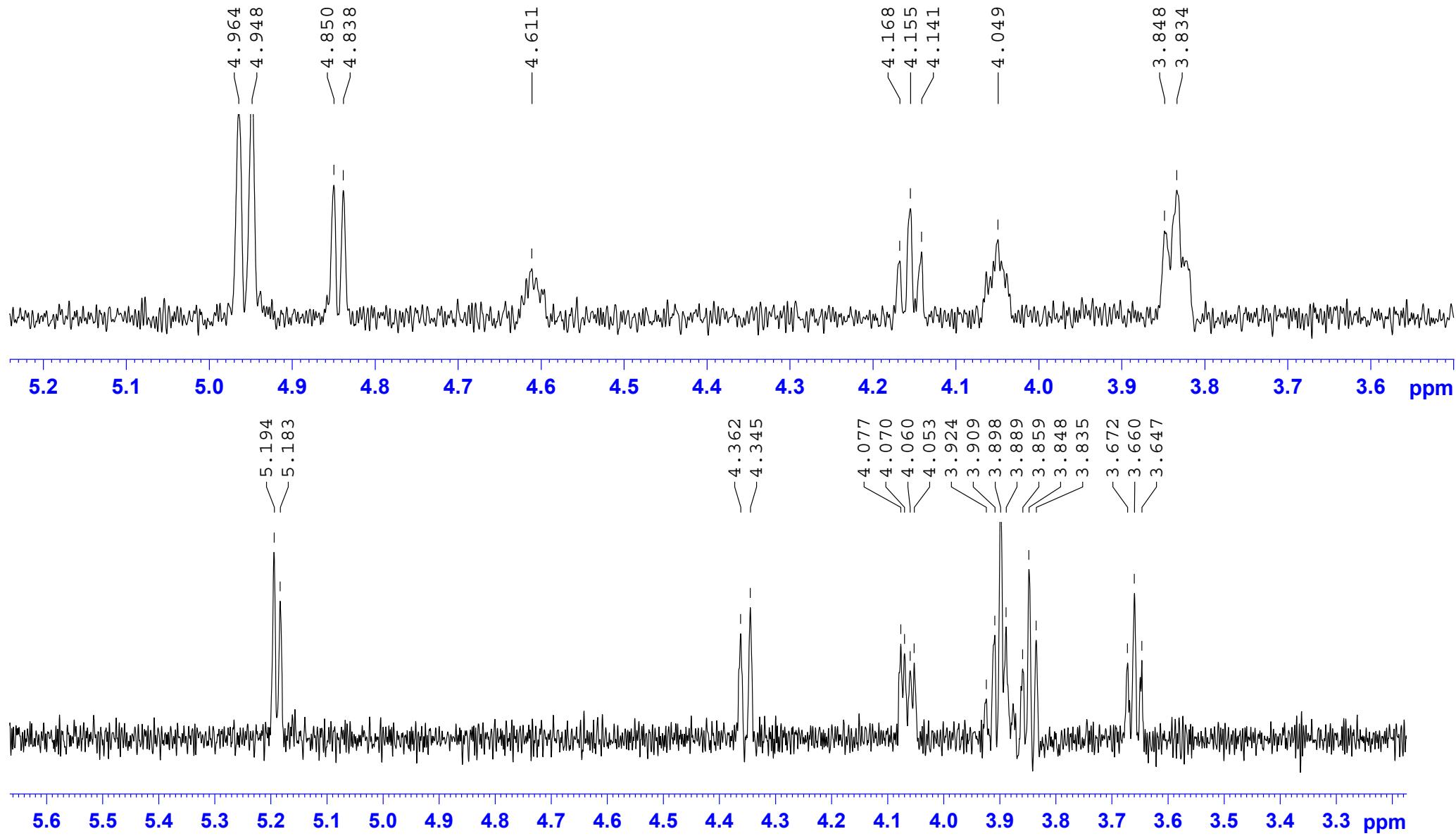


Figure S64. 1 D TOCSY (700.00 MHz) spectra of GlcIV and MeGlcV of kuriloside K (8) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

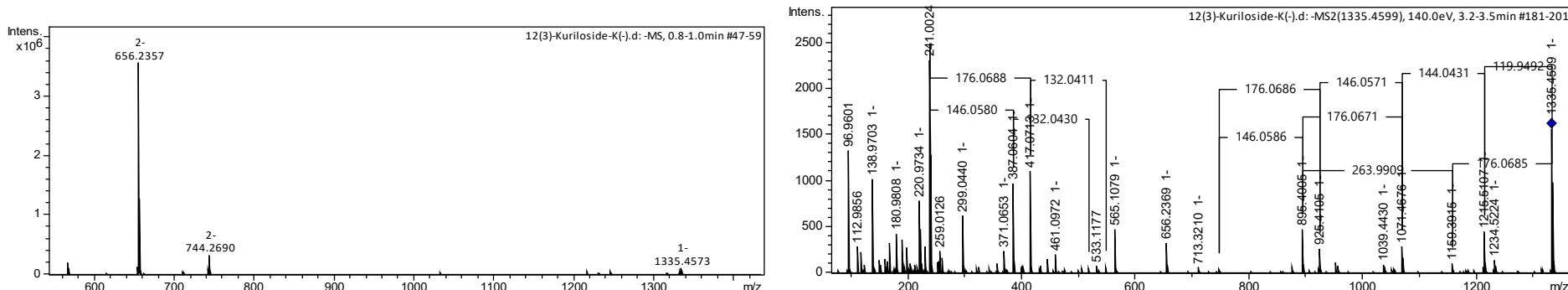


Figure S65. HR-ESI-MS and ESI-MS/MS spectra of kuriloside K (8)

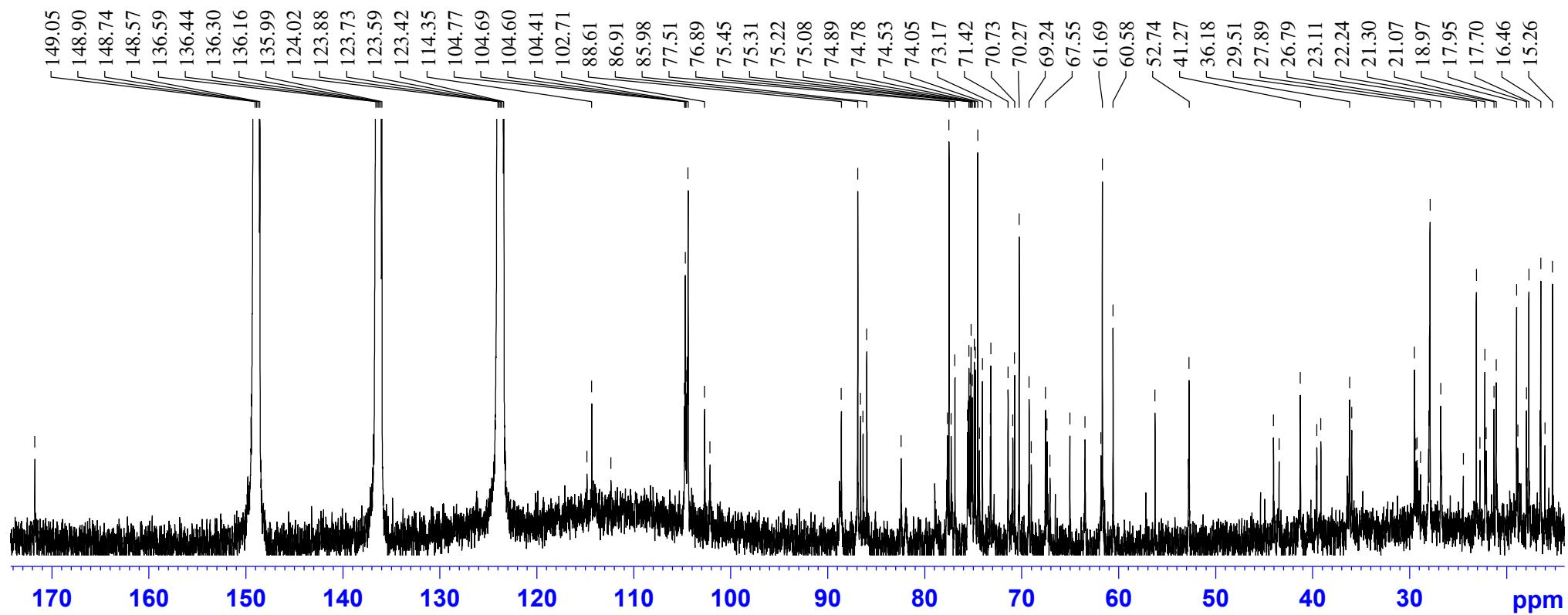


Figure S66. The  $^{13}\text{C}$  NMR (176.03 MHz) spectrum of kuriloside K<sub>1</sub> (9) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

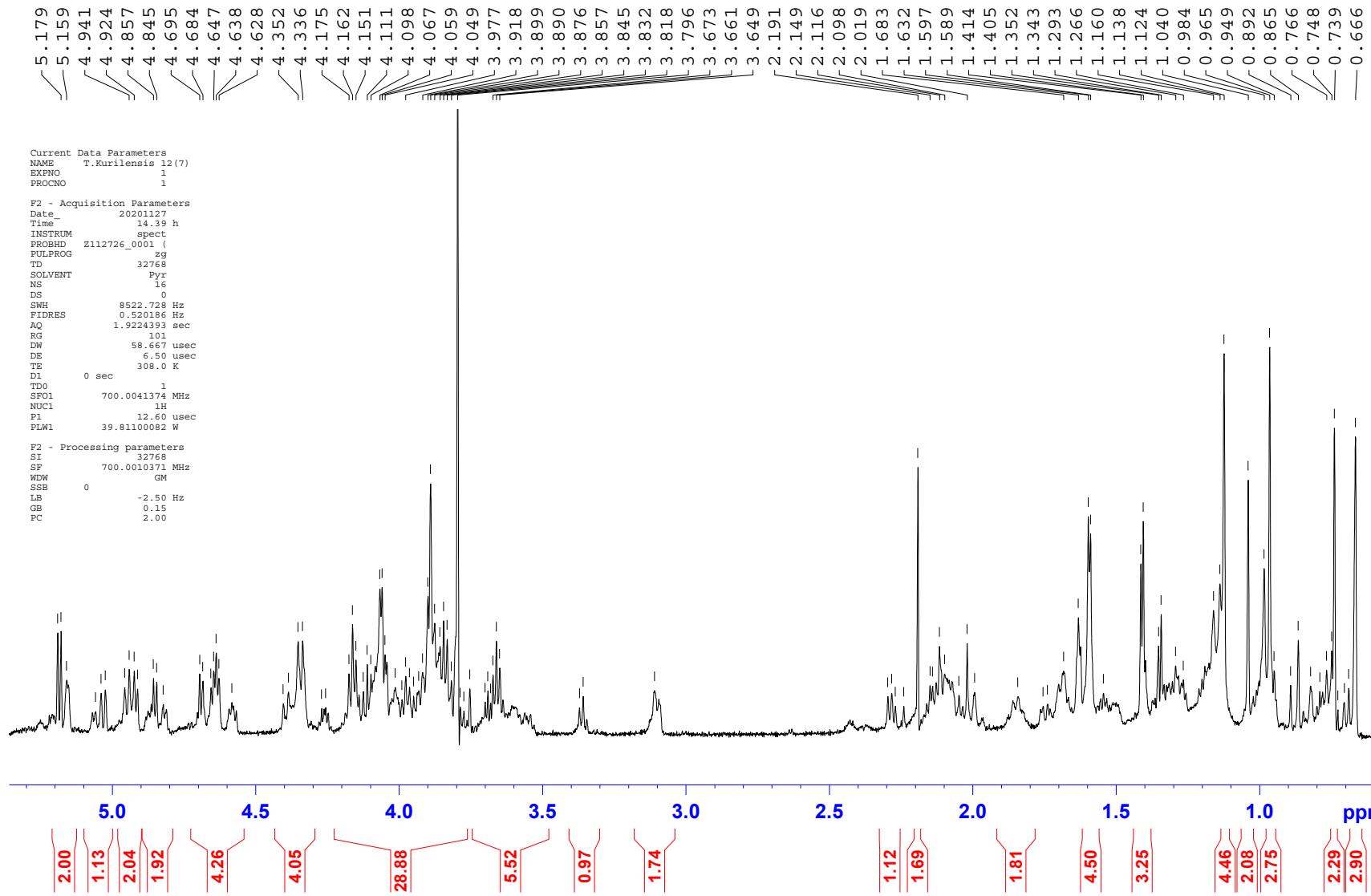


Figure S67. The  $^1\text{H}$  NMR (700.00 MHz) spectrum of kuriloside K<sub>1</sub> (**9**) in C<sub>5</sub>D<sub>5</sub>N/D<sub>2</sub>O (4/1)

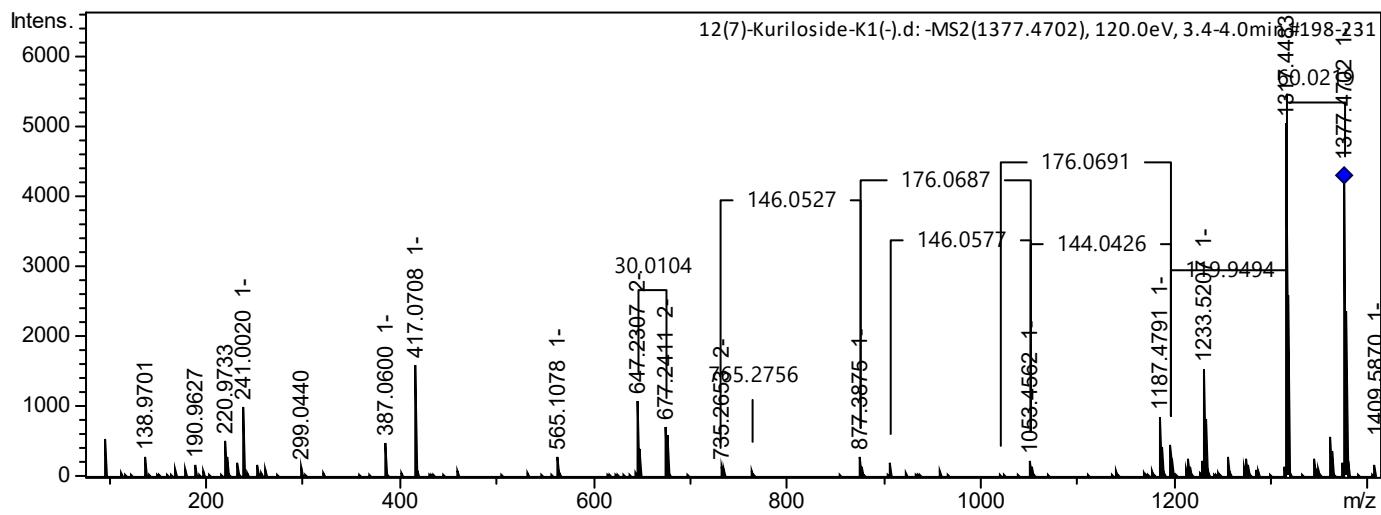
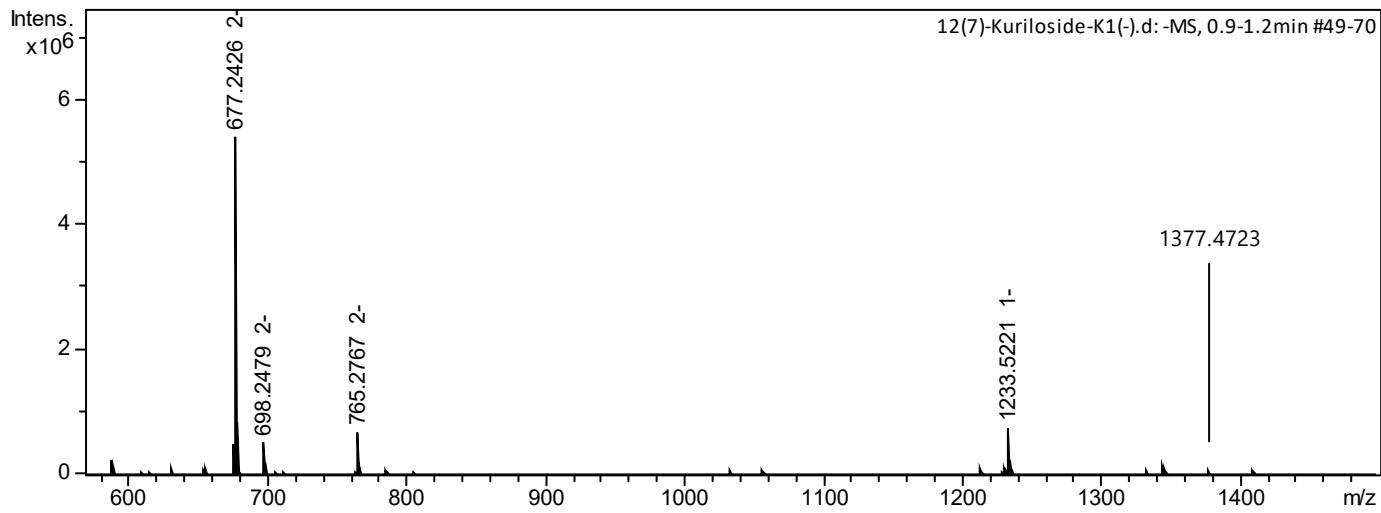


Figure S68. HR-ESI-MS and ESI-MS/MS spectra of kuriloside K<sub>1</sub> (**9**)

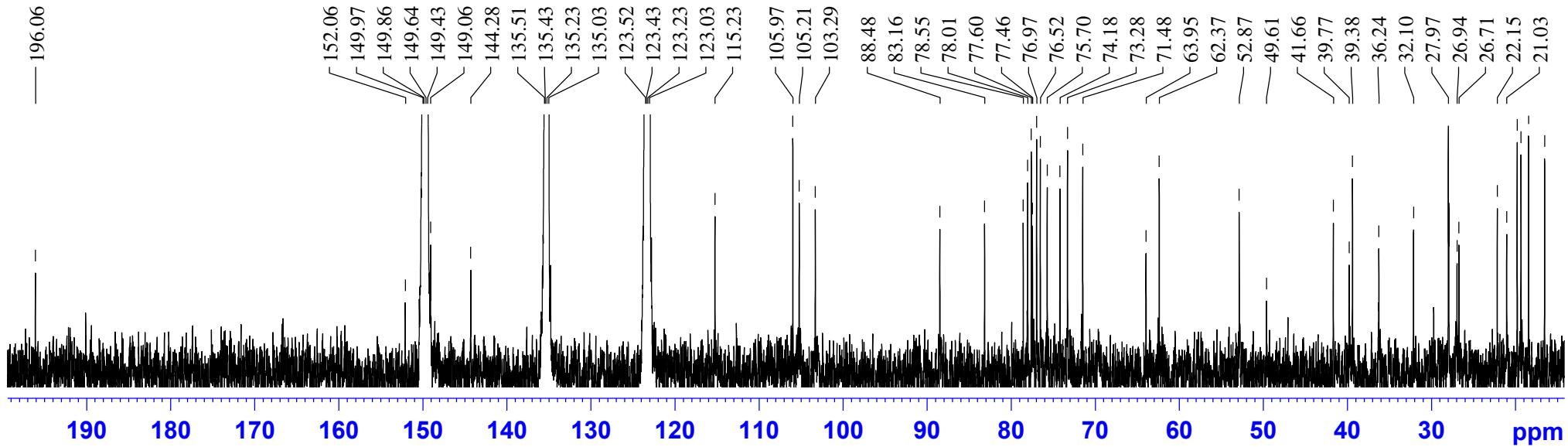


Figure S69. The  $^{13}\text{C}$  NMR (176.03 MHz) spectrum of DS-kuriloside L (**10**) in  $\text{C}_5\text{D}_5\text{N}$

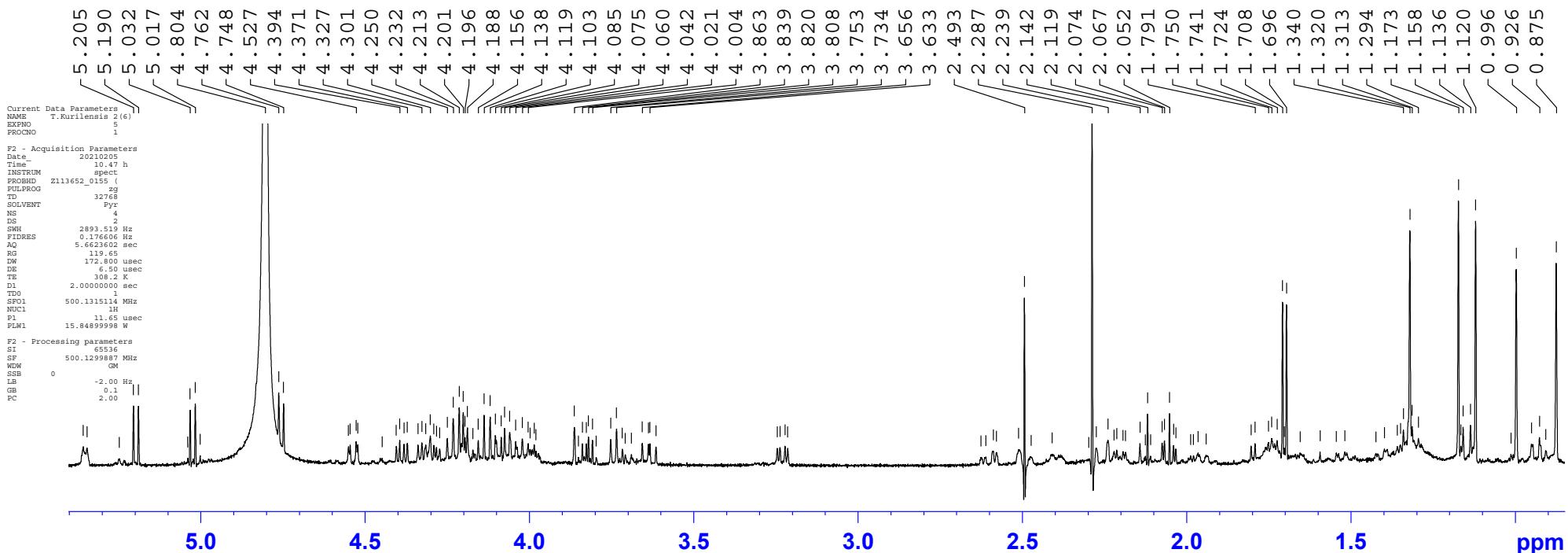


Figure S70. The  $^1\text{H}$  NMR (700.00 MHz) spectrum of DS-kuriloside L (**10**) in  $\text{C}_5\text{D}_5\text{N}$

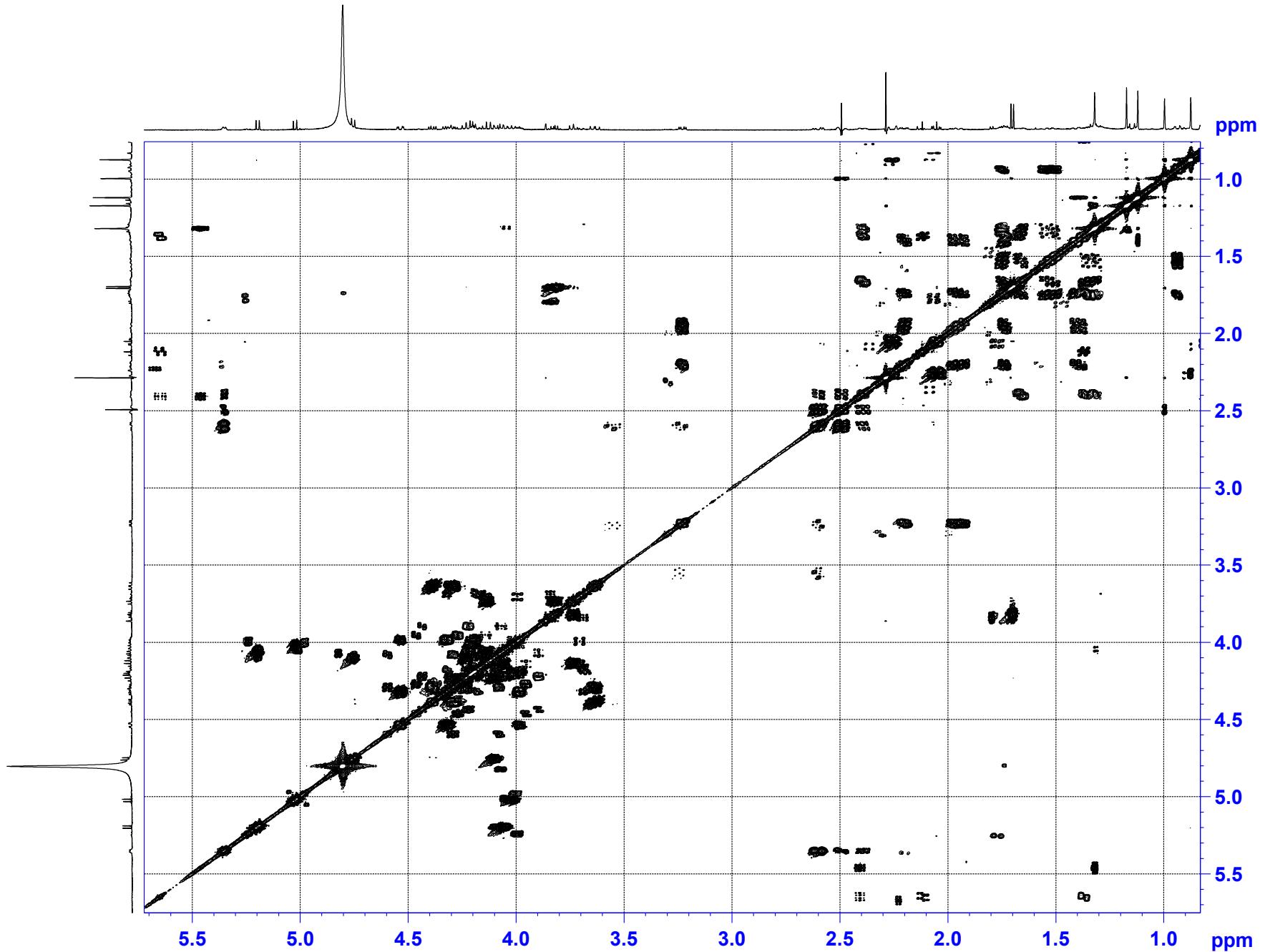


Figure S71. The COSY (700.00 MHz) spectrum of DS-kuriloside L (10) in  $C_5D_5N$

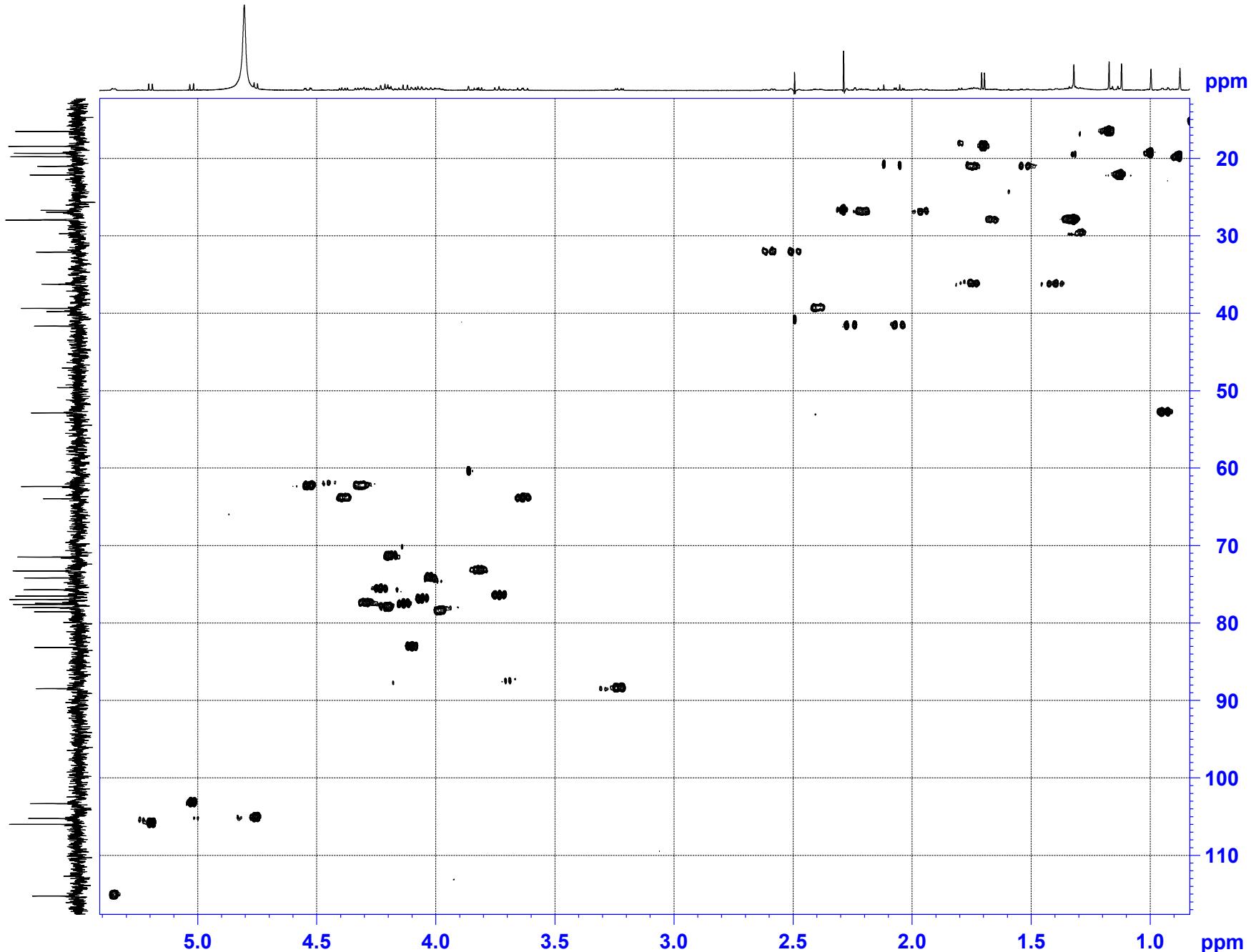


Figure S72. The HSQC (700.00 MHz) spectrum of DS-kuriloside L (**10**) in  $C_5D_5N$

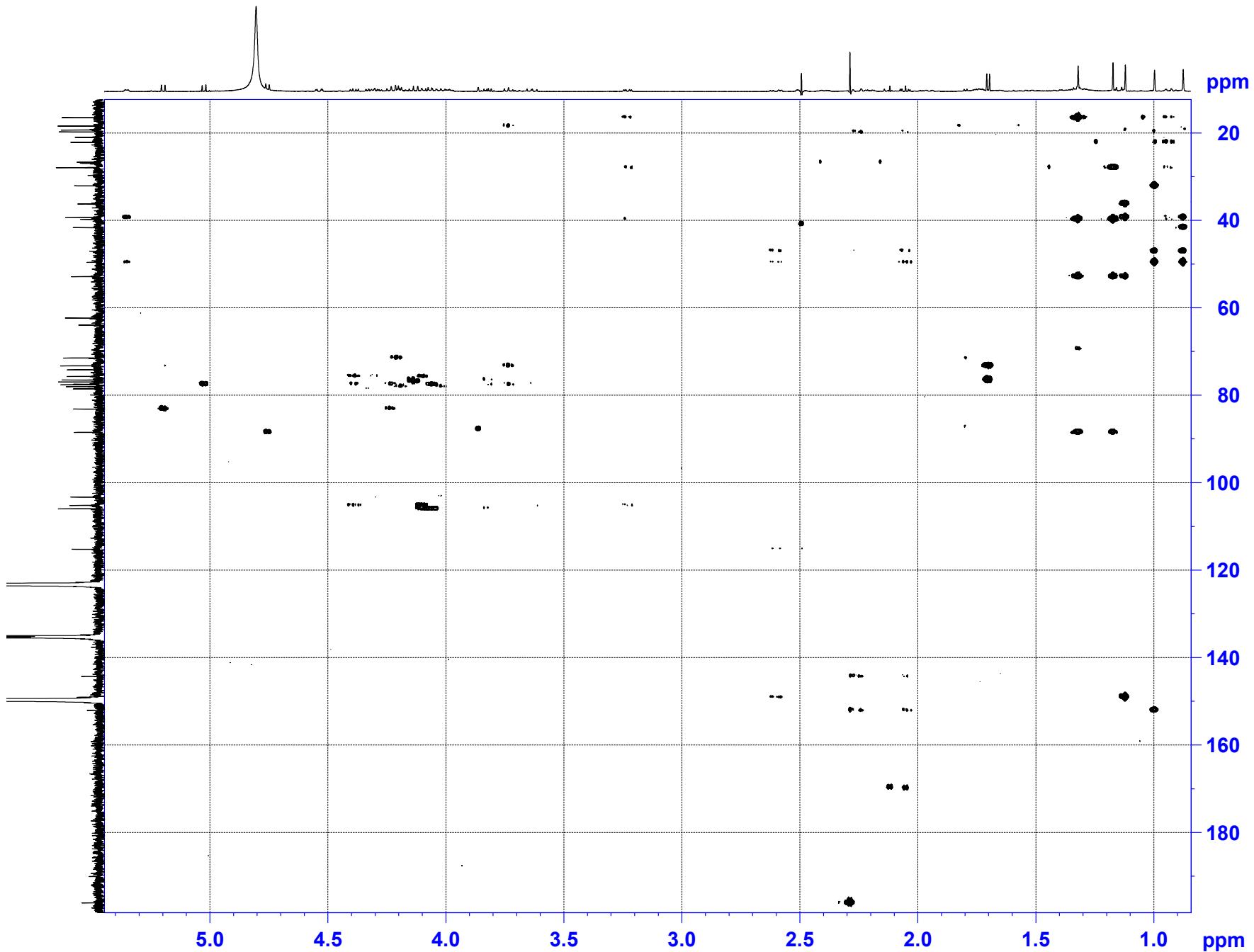


Figure S73. The HMBC (700.00 MHz) spectrum of DS-kuriloside L (10) in  $C_5D_5N$

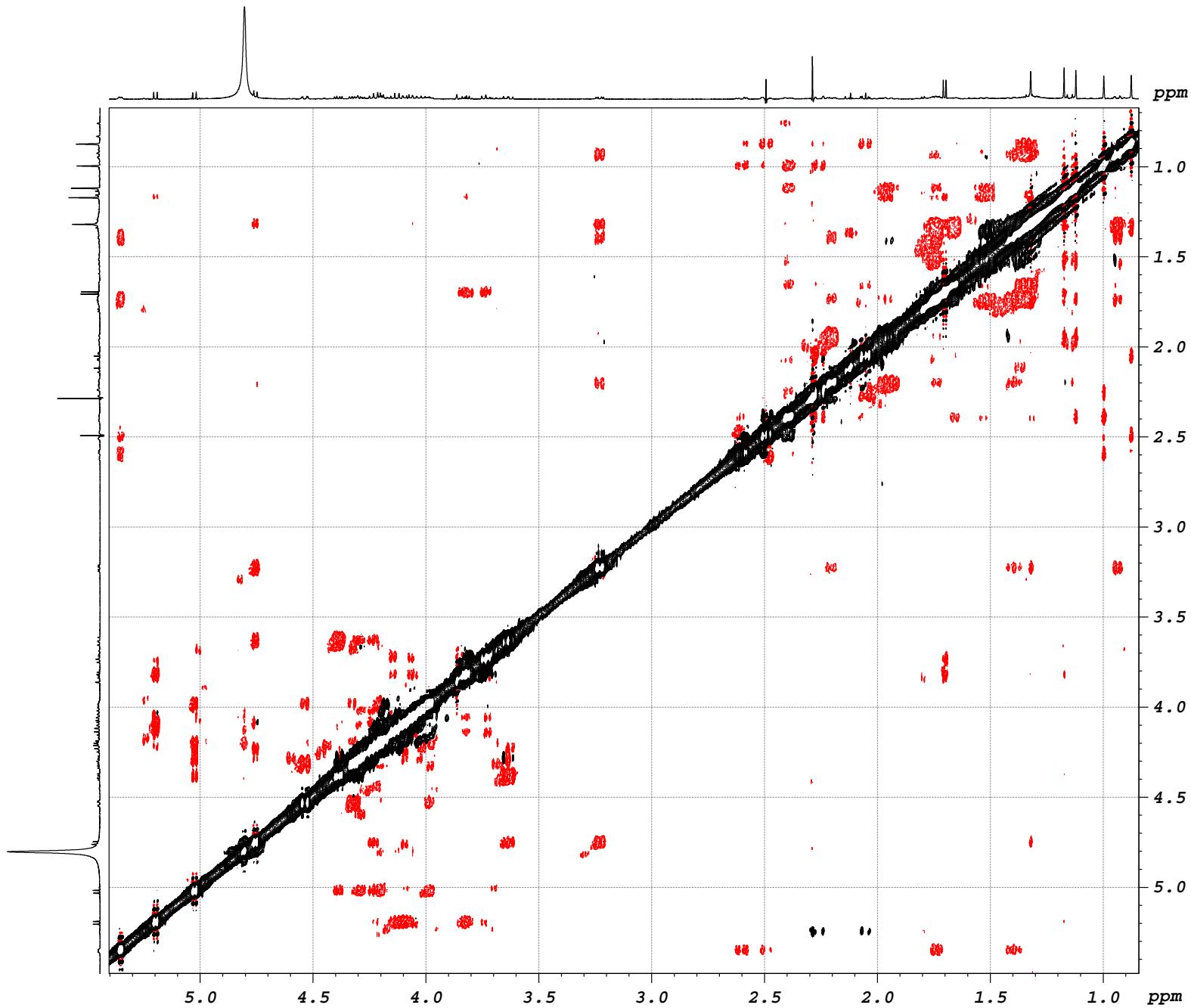


Figure S74. The ROESY (700.00 MHz) spectrum of DS-kuriloside L (**10**) in  $\text{C}_5\text{D}_5\text{N}$

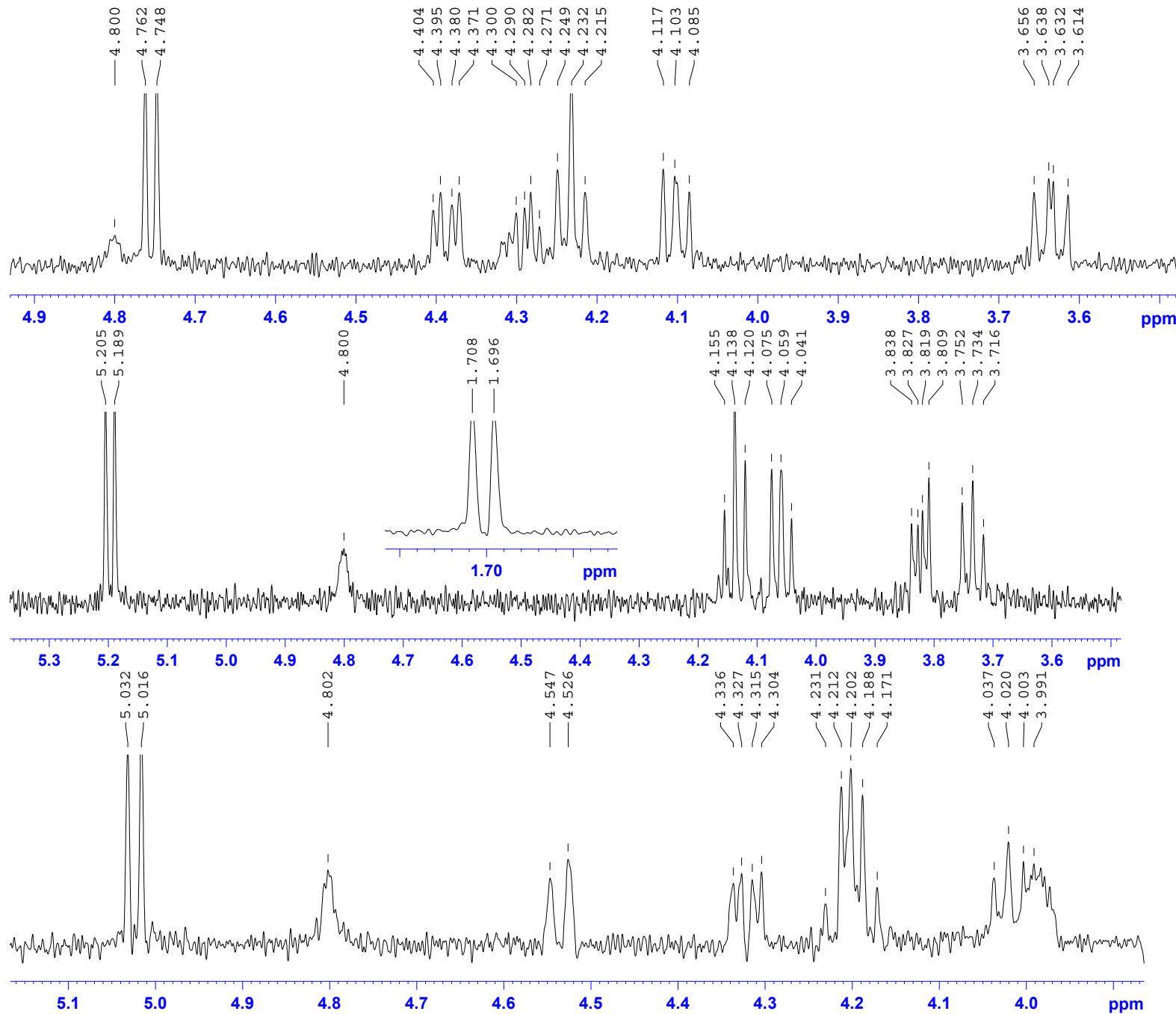


Figure S75. 1 D TOCSY (700.00 MHz) spectra of XyloseI, QuinovoseII and GlucoseIII of DS-kuriloside L (**10**) in  $C_5D_5N$

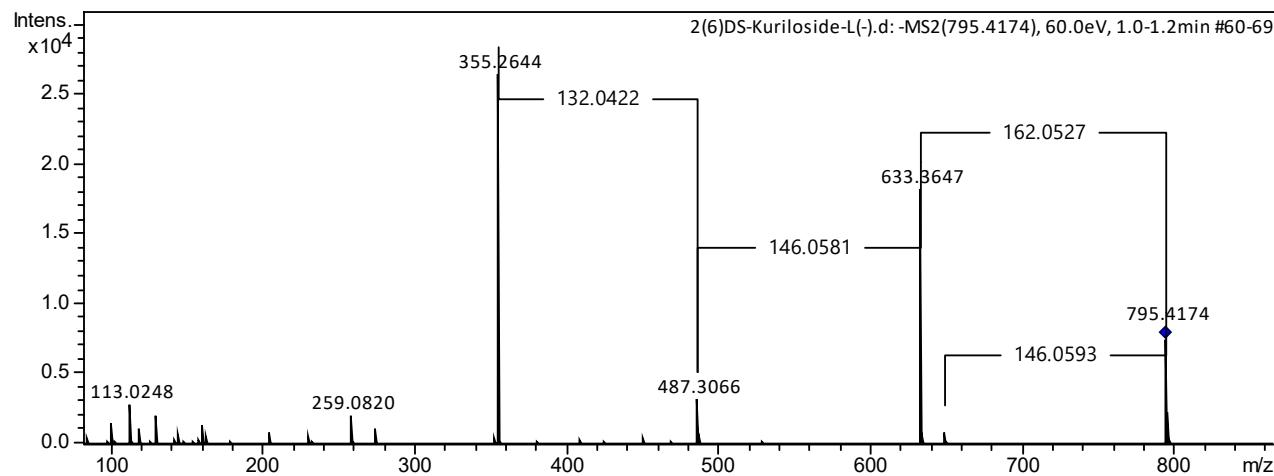
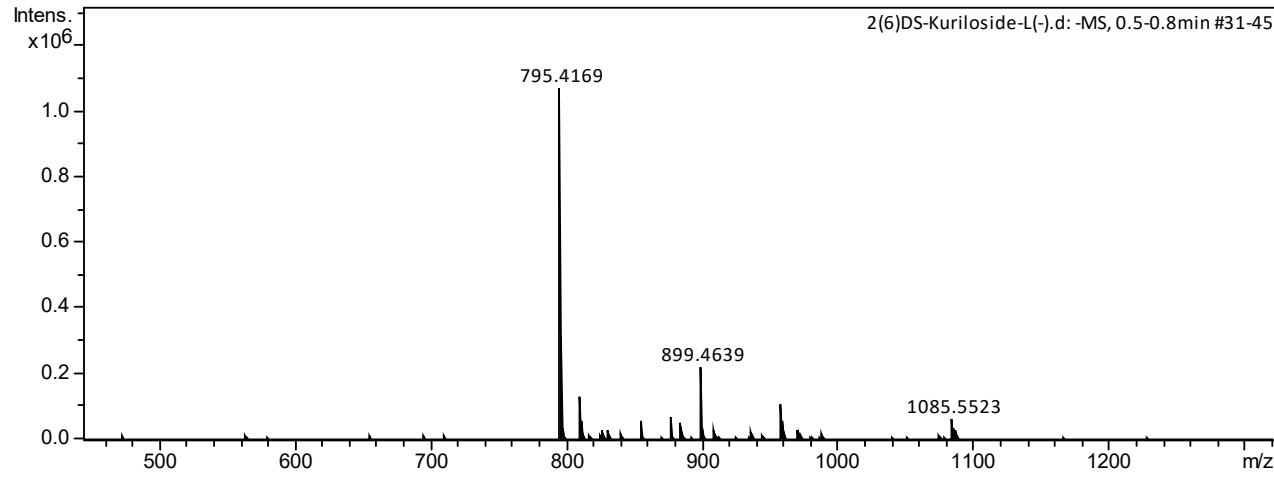


Figure S76. HR-ESI-MS (-) and ESI-MS/MS spectra of DS-kuriloside L (**10**).

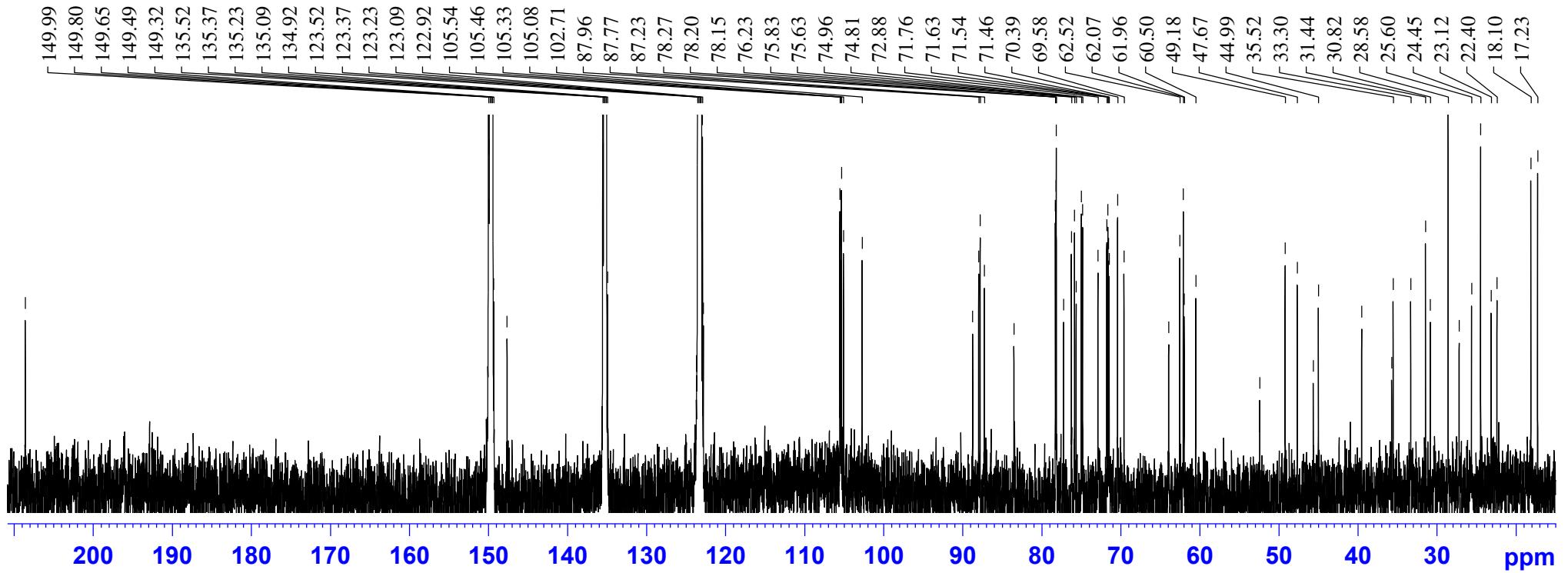


Figure S77. The  $^{13}\text{C}$  NMR (176.03 MHz) spectrum of DS-kuriloside M (11) in  $\text{C}_5\text{D}_5\text{N}$

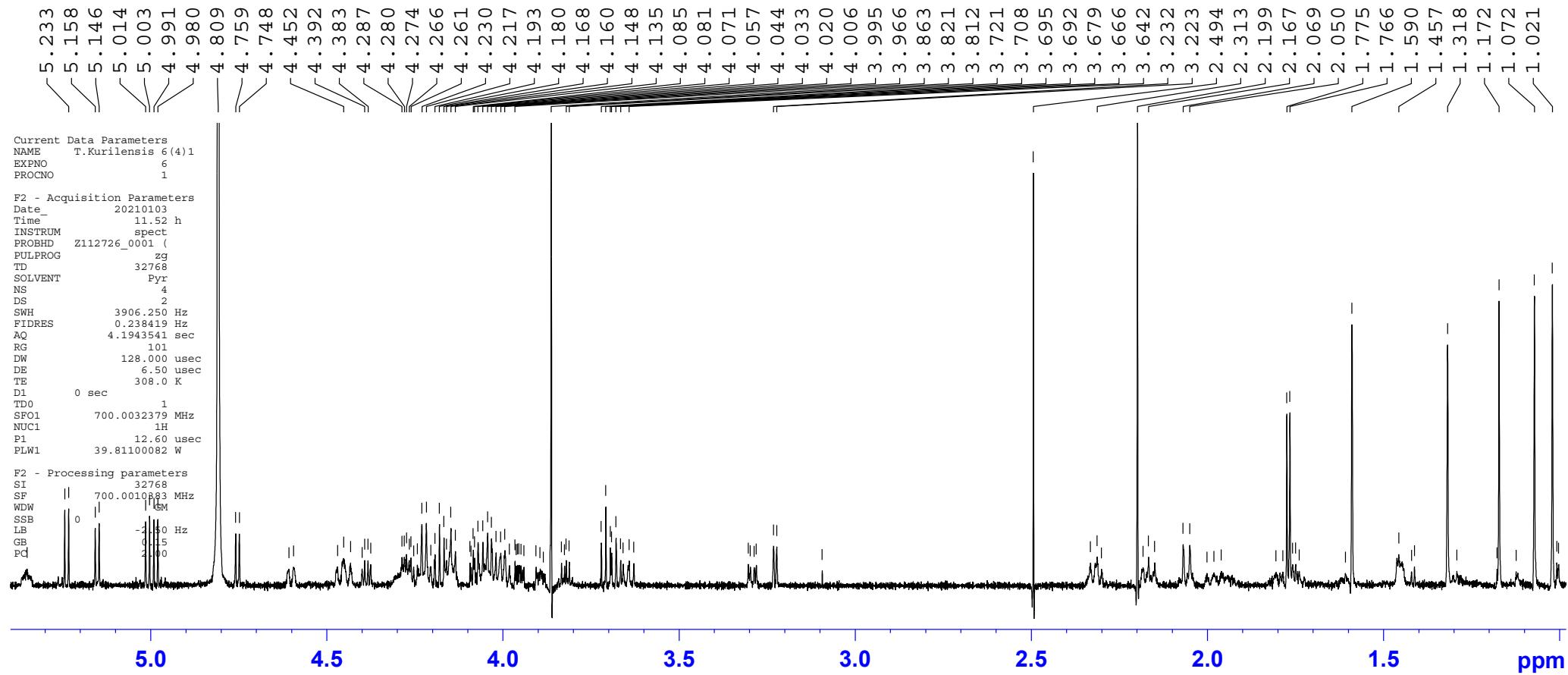


Figure S78. The  $^1\text{H}$  NMR (700.00 MHz) spectrum of DS-kuriloside M (**11**) in  $\text{C}_5\text{D}_5\text{N}$

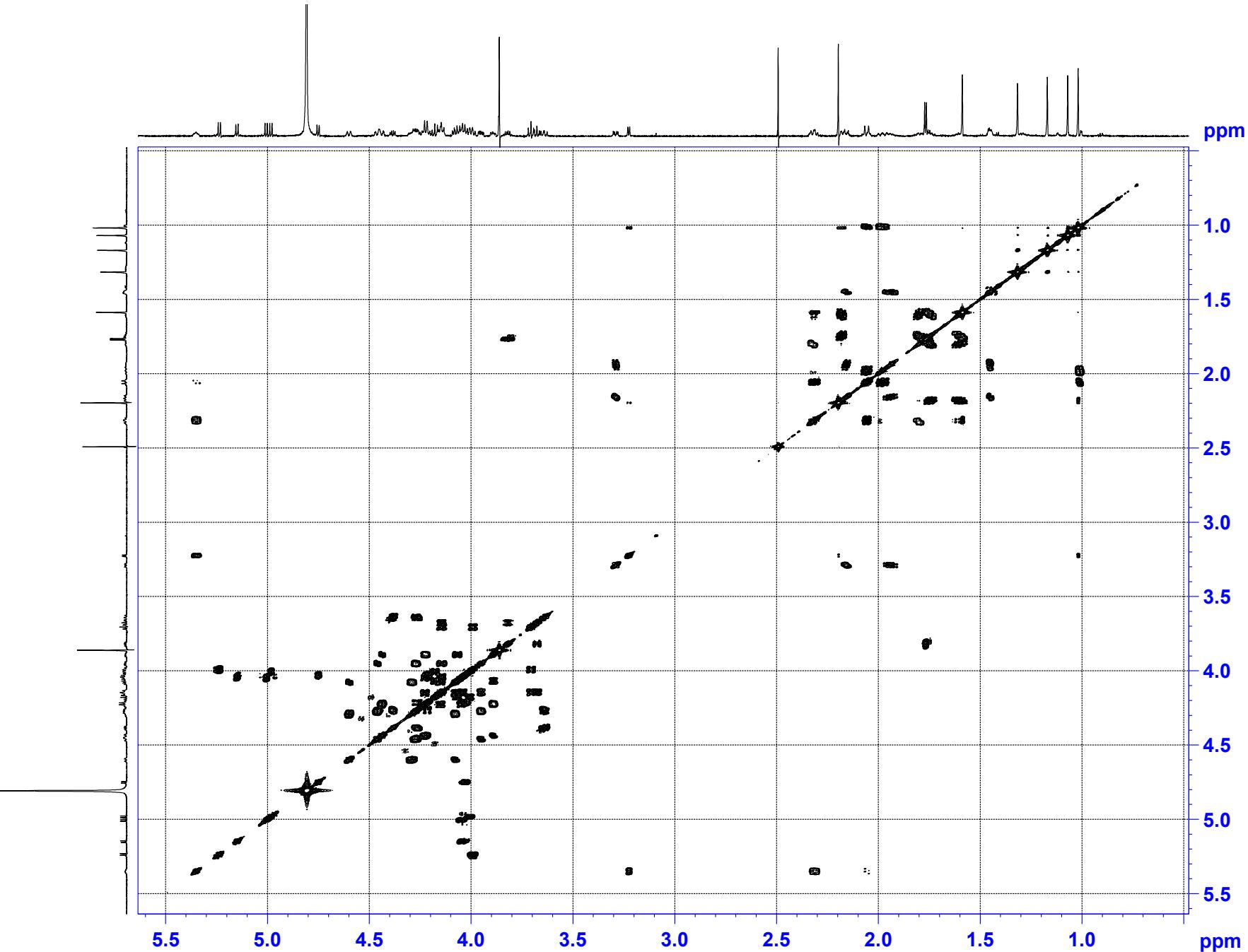


Figure S79. The COSY (700.00 MHz) spectrum of DS-kuriloside M (11) in  $C_5D_5N$

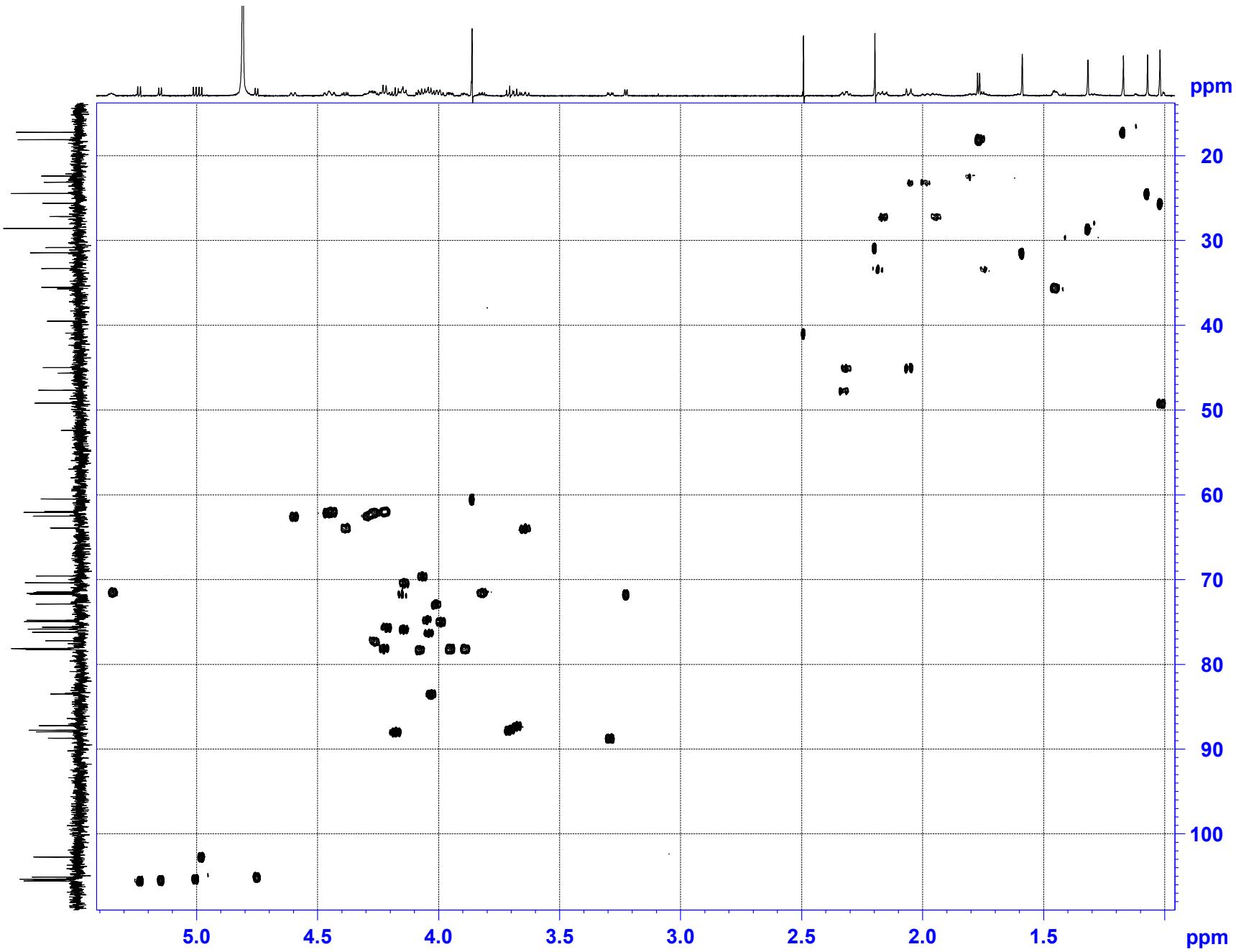


Figure S80. The HSQC (700.00 MHz) spectrum of DS-kuriloside M (11) in  $C_5D_5N$

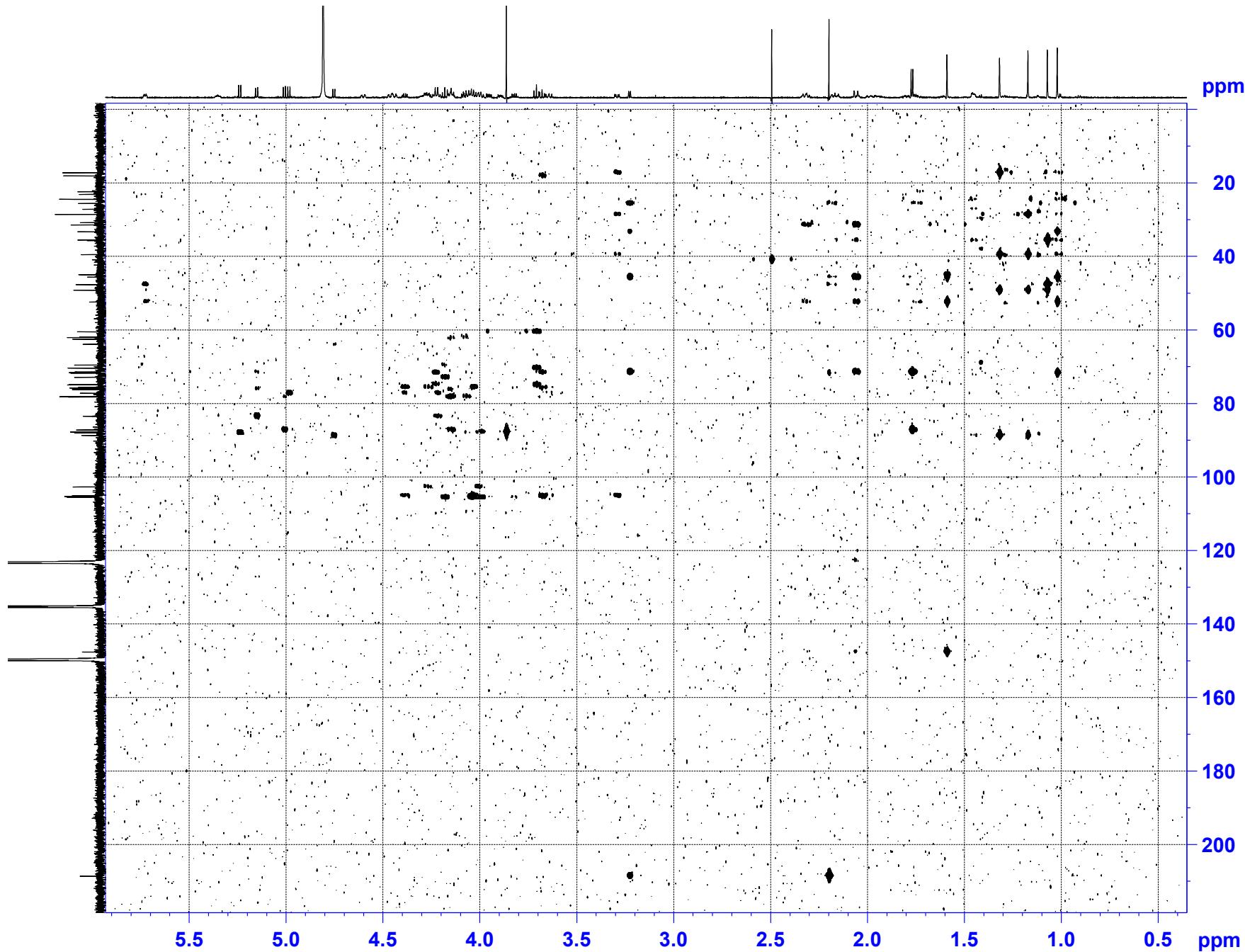


Figure S81. The HMBC (700.00 MHz) spectrum of DS-kuriloside M (**11**) in  $C_5D_5N$

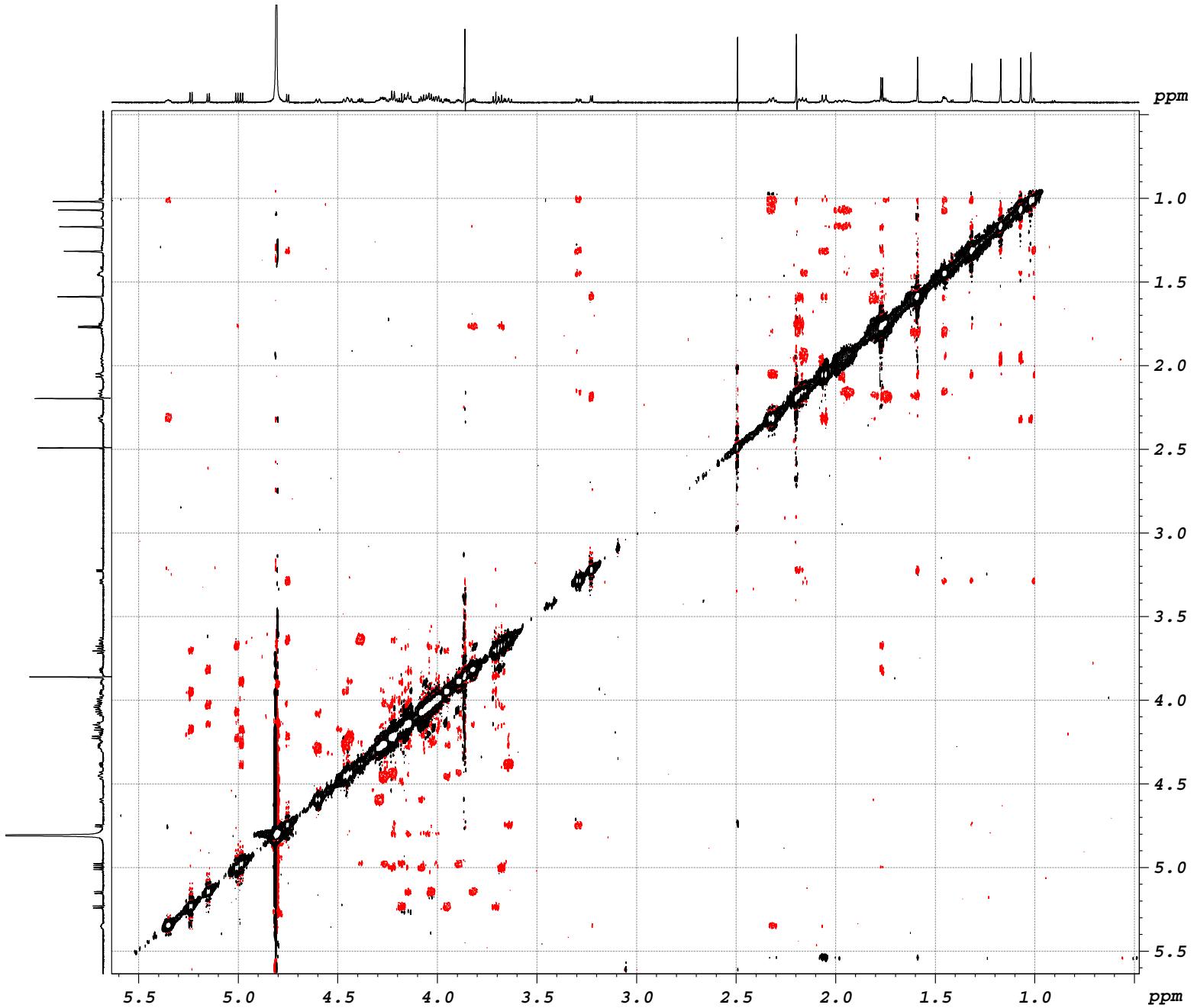


Figure S82. The ROESY (700.00 MHz) spectrum of DS-kuriloside M (11) in  $C_5D_5N$

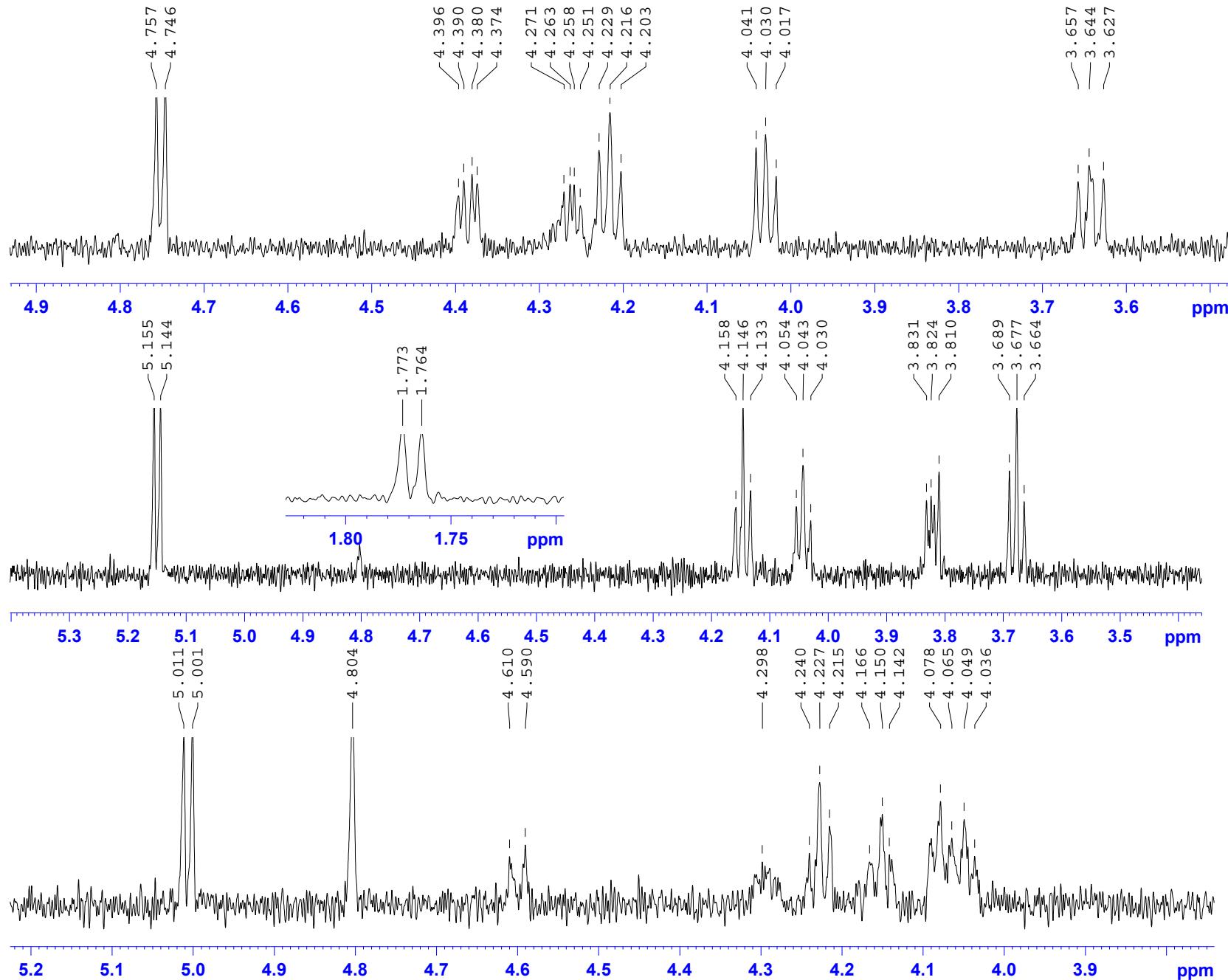


Figure S83. 1 D TOCSY (700.00 MHz) spectra of XyloseI, QuinovoseII and GlucoseIII of DS-kuriloside M (**11**) in <sup>13</sup>C<sub>5</sub>D<sub>5</sub>N

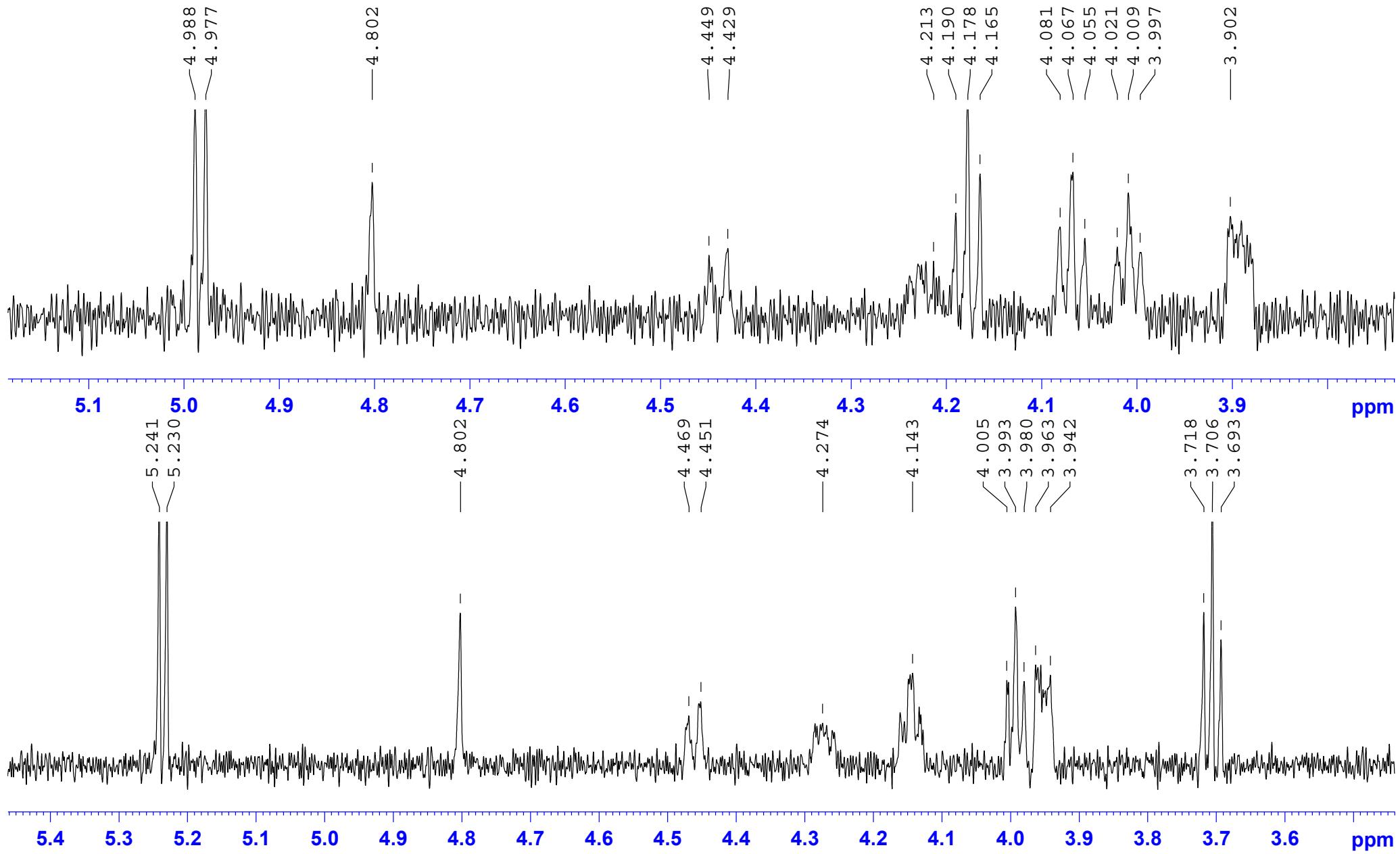


Figure S84. 1 D TOCSY (700.00 MHz) spectra of GlcIV and MeGlcV of DS-kuriloside M (**11**) in  $C_5D_5N$

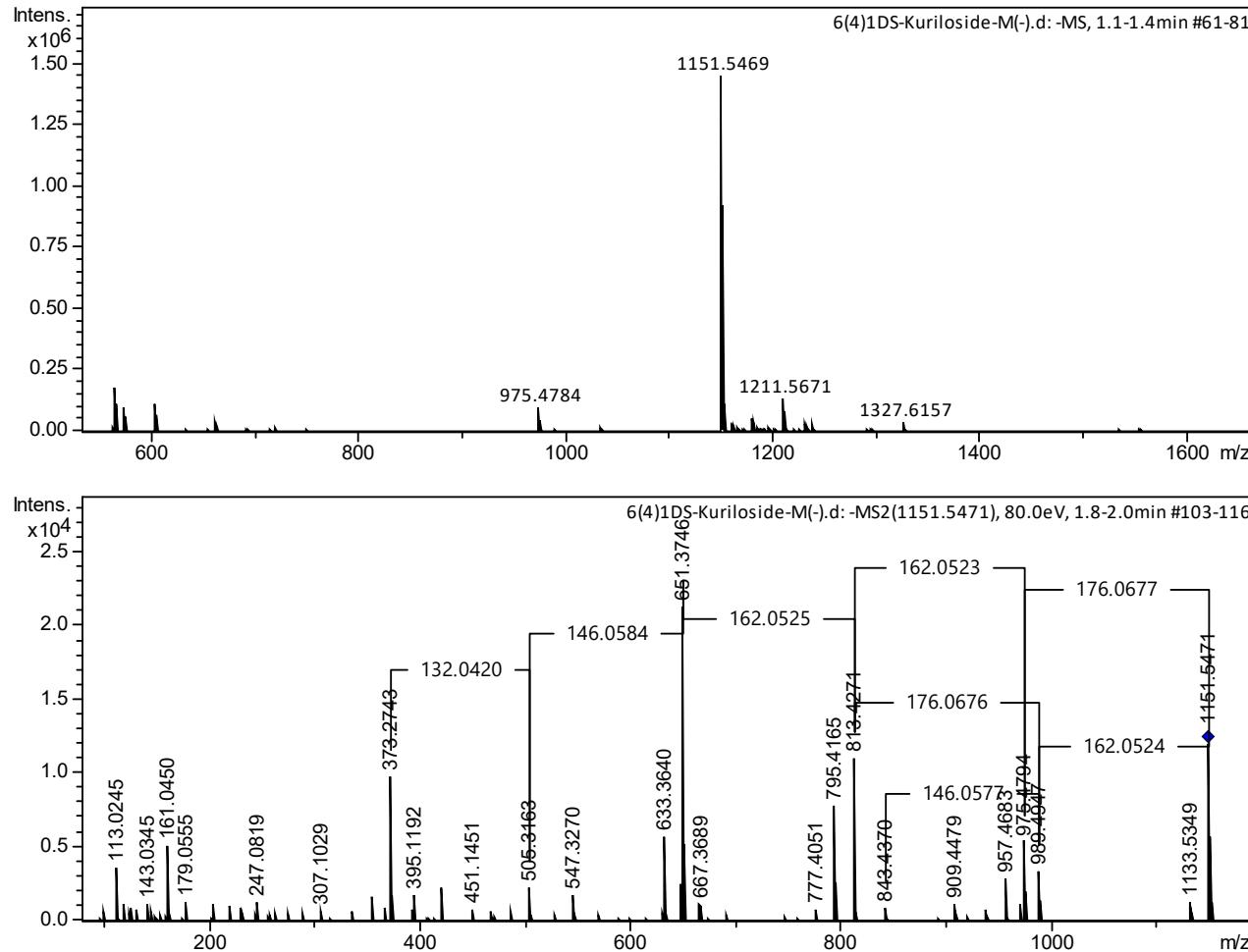


Figure S85. HR-ESI-MS(–) and ESI-MS/MS spectra of DS-kuriloside M (11).