Application of 3D NMR for Structure Determination of Peptide Natural Products

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Figure S1. ^{1}H NMR Spectrum of Eudistamide A (**1**; 500 MHz, DMSO-d_6).

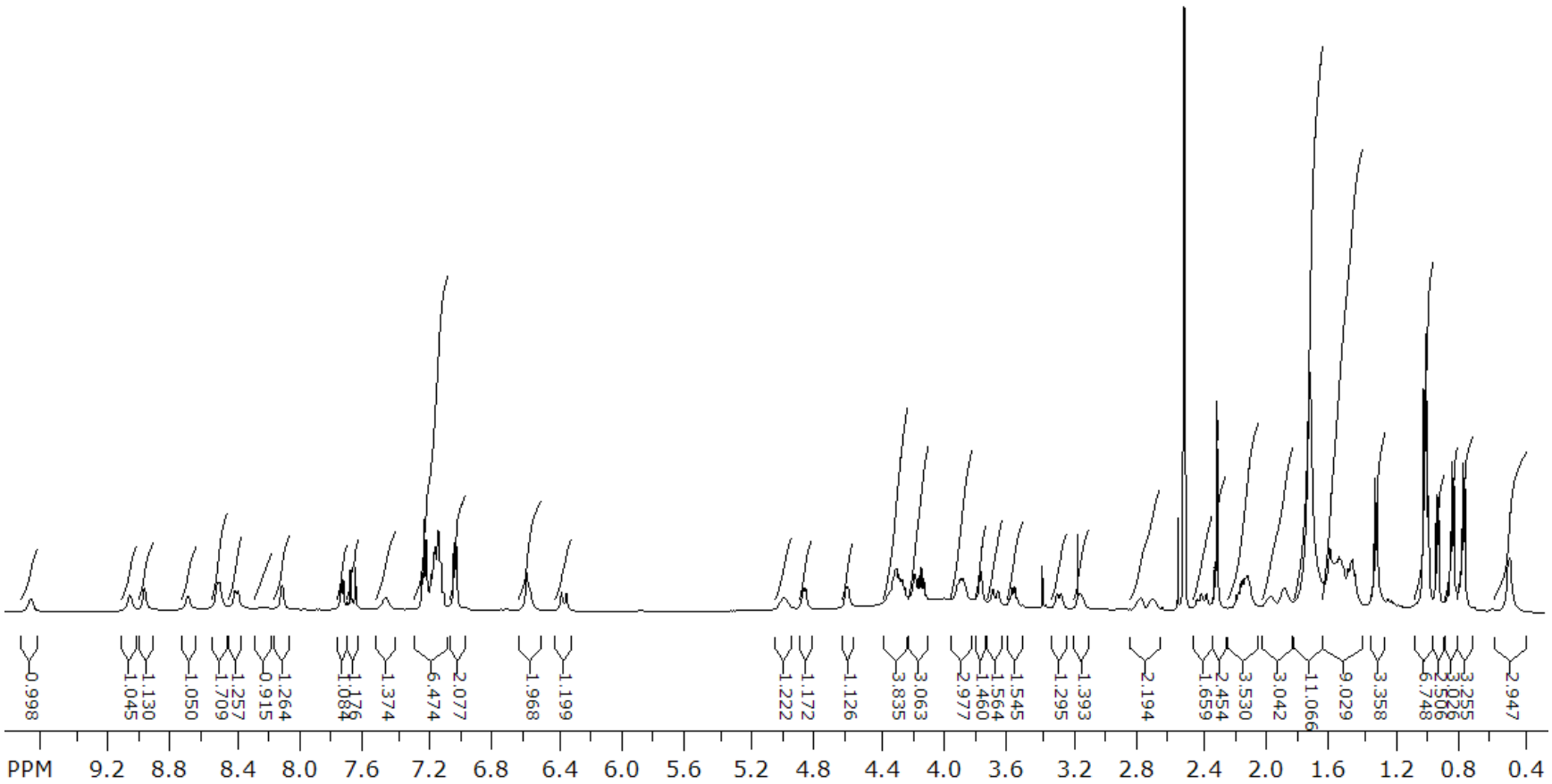

Figure S2. ^{13}C NMR Spectrum of Eudistamide A (**1**; 125 MHz, DMSO-d_6).

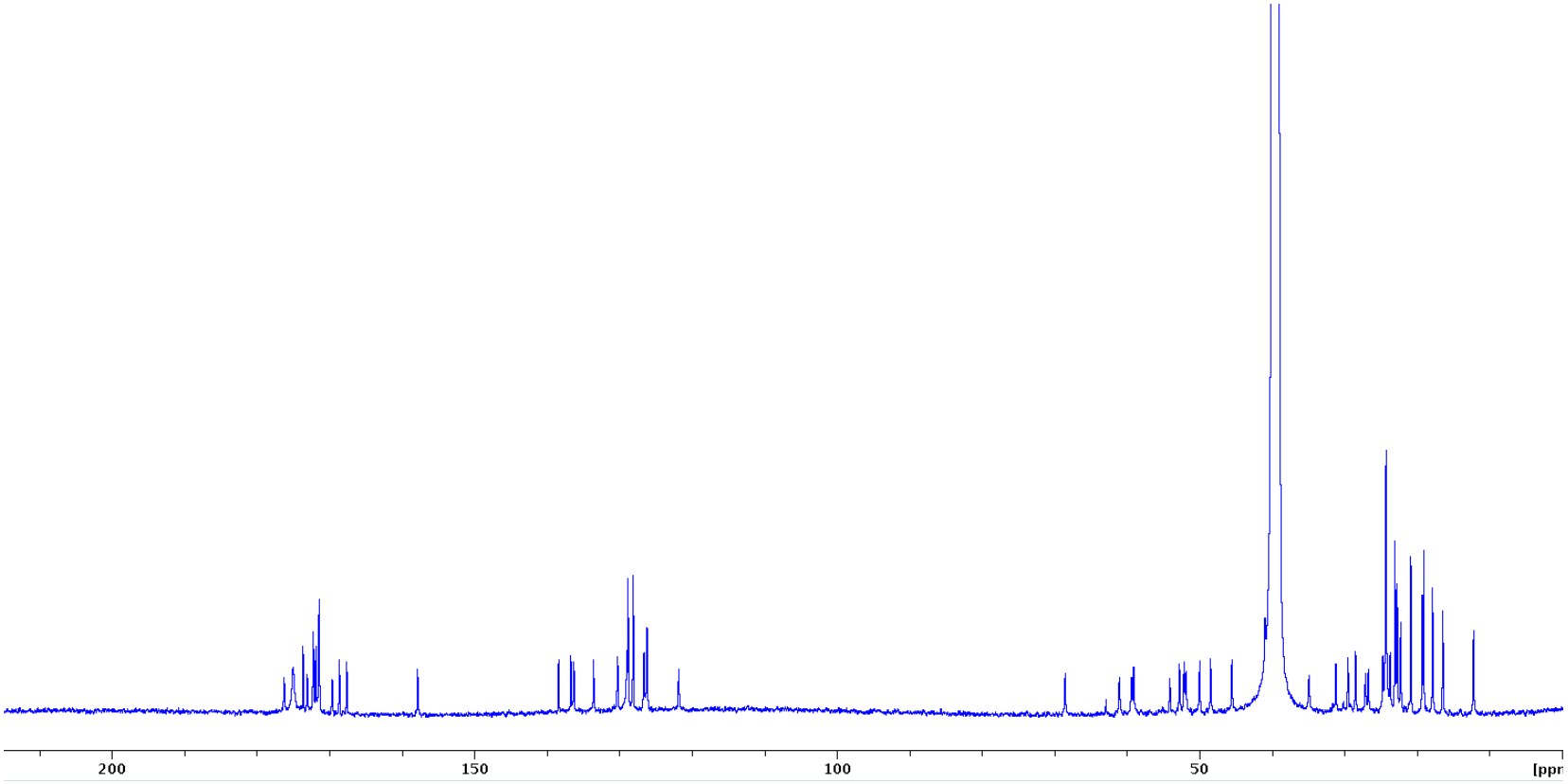

Figure S3. gCOSY Spectrum of Eudistamide A (**1**; 500 MHz, DMSO-d_6).

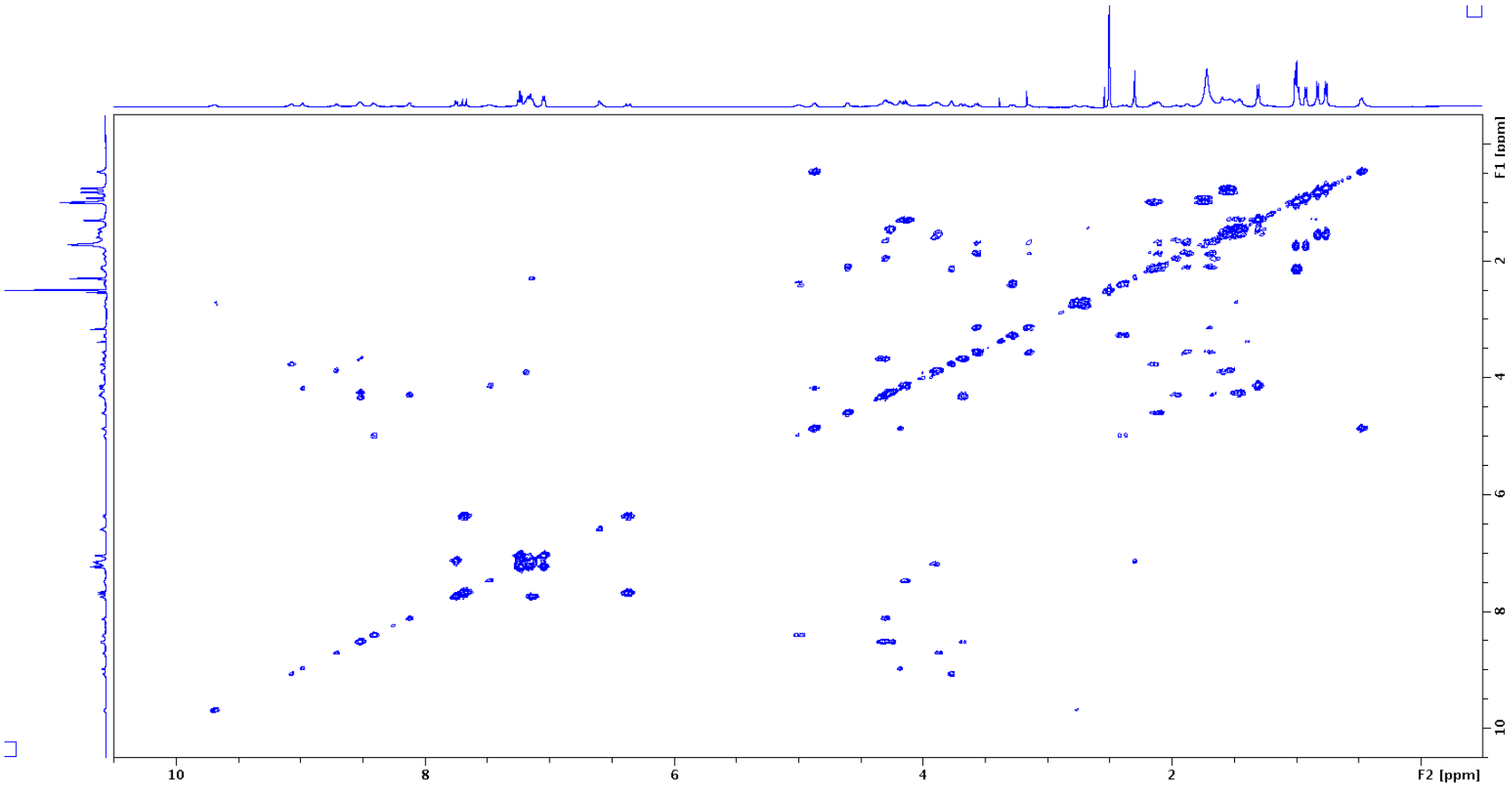

Figure S4. gHSQC Spectrum of Eudistamide A (**1**; 500 MHz, DMSO-d_6).

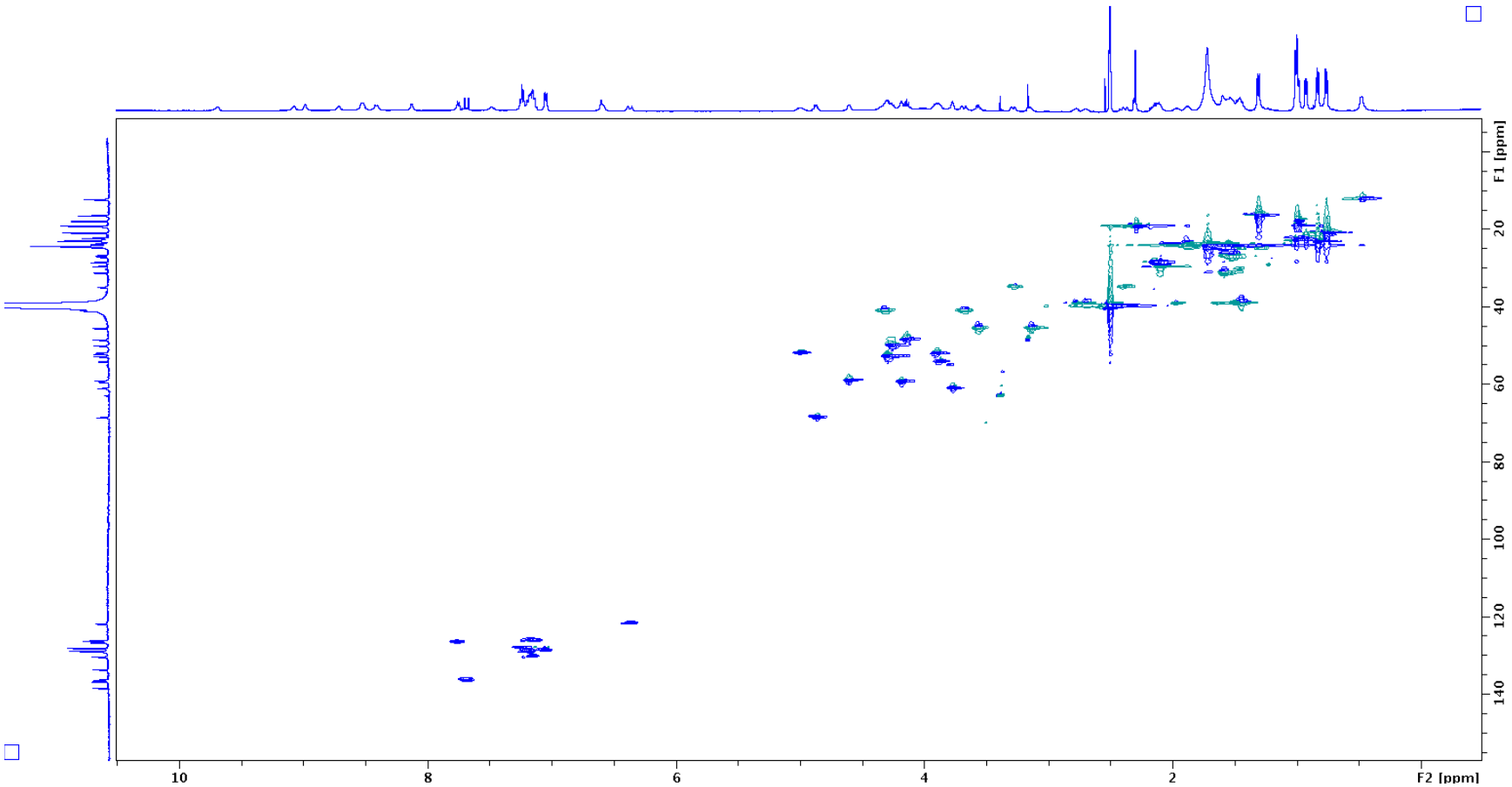

Figure S5. gHMBC Spectrum of Eudistamide A (**1**; 500 MHz, DMSO-d_6).

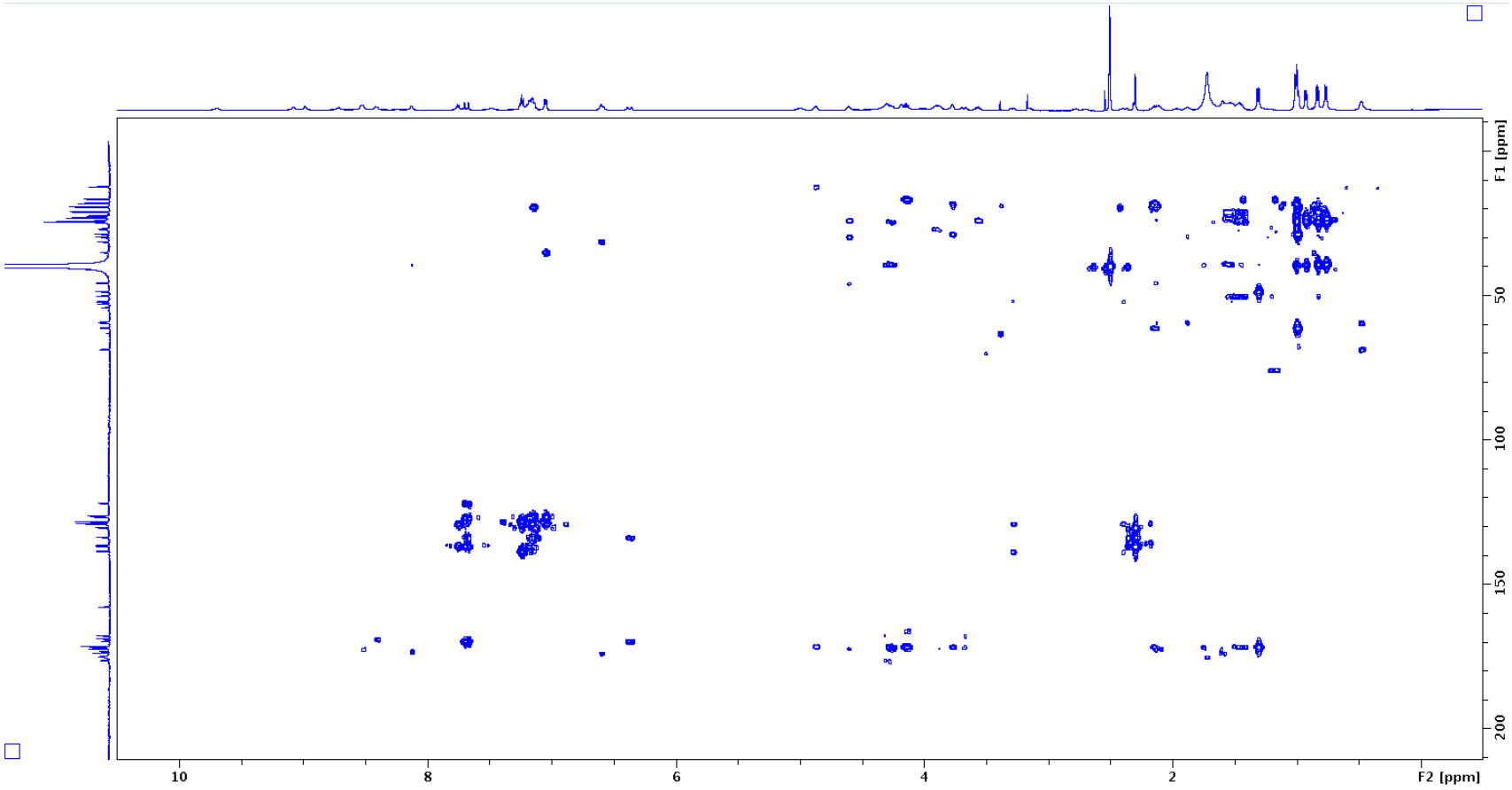

Figure S6. ROESY Spectrum of Eudistamide A (**1**; 500 MHz, DMSO-d_6).

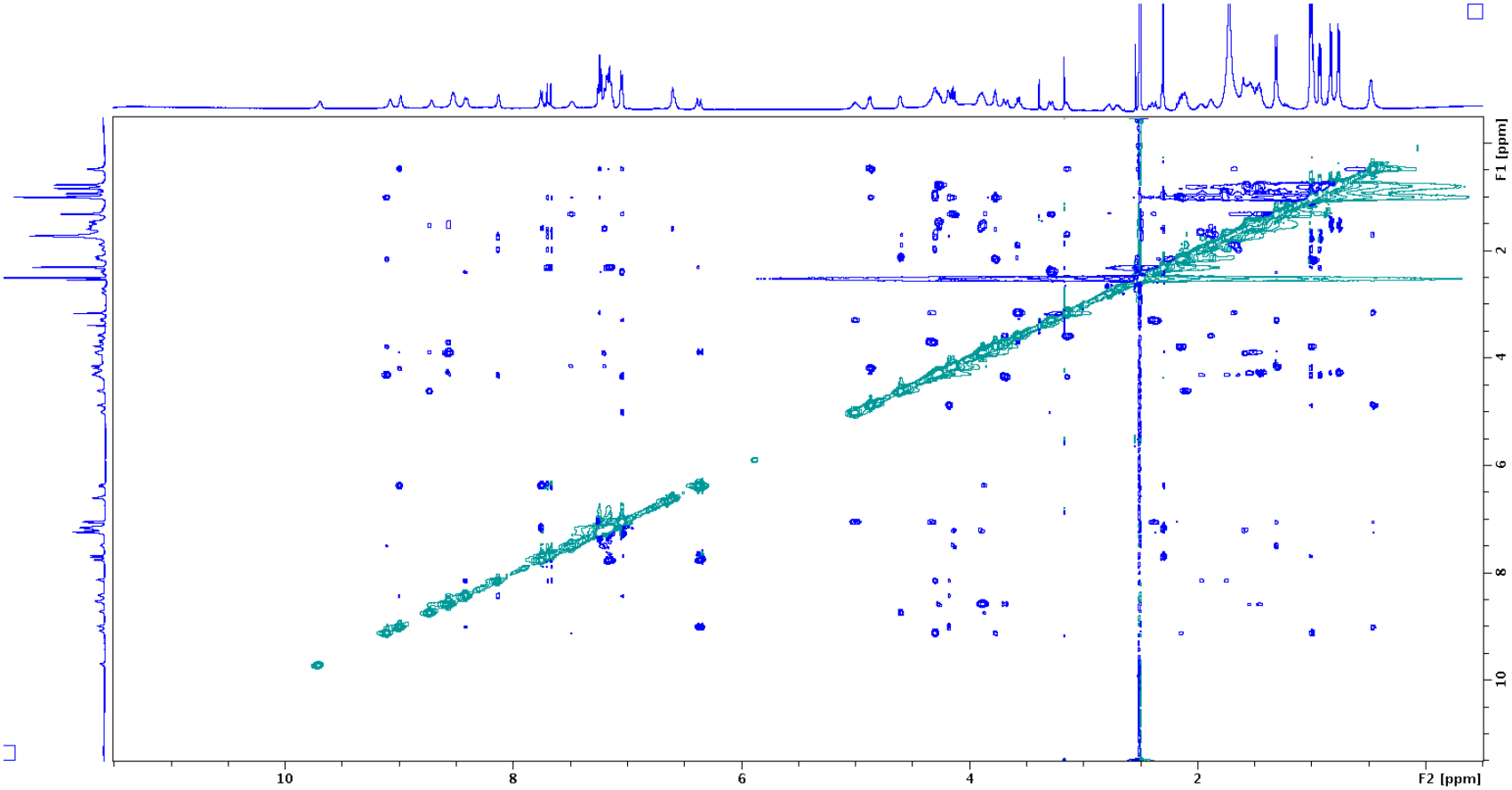

Figure S7. HRESIMS of Eudistamide A (**1**).

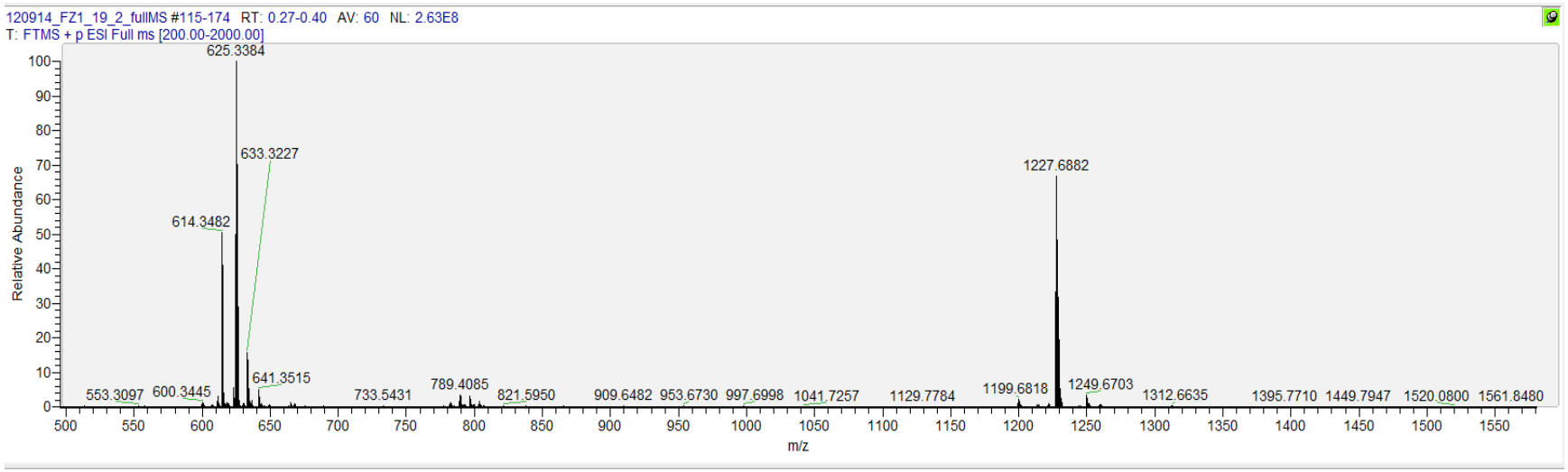

Figure S8. NHCA spectrum of ^{13}C, ^{15}N-labeled **1** (800 MHz, DMSO-d_6).

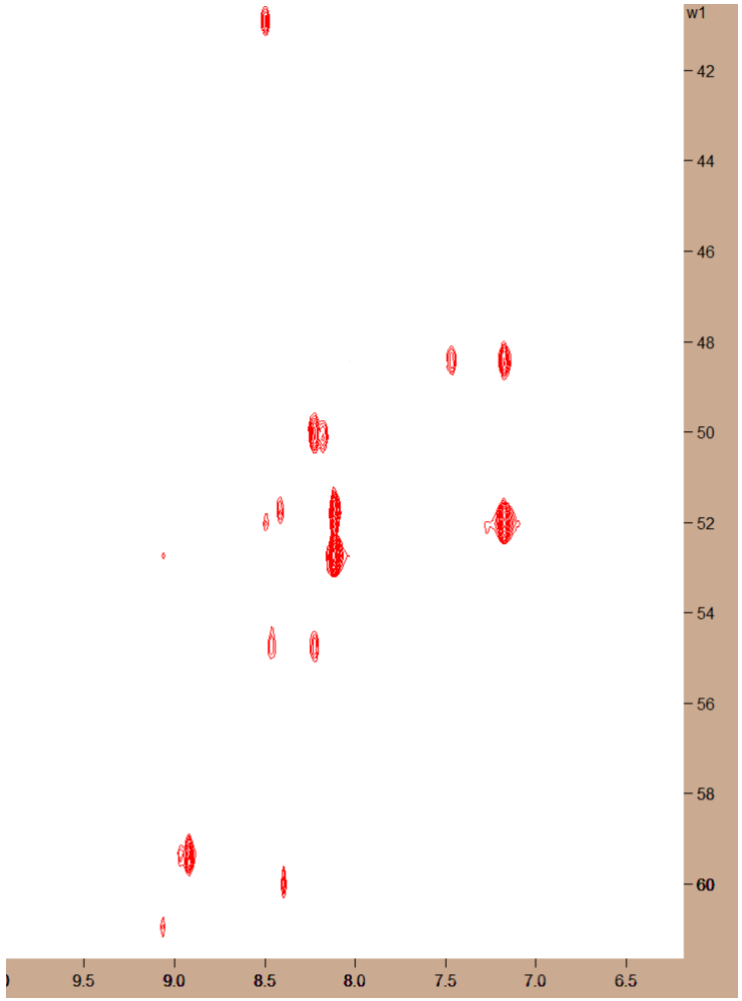

Figure S9. NH(CO)CA spectrum of ^{13}C, ^{15}N-labeled **1** (800 MHz, DMSO-d_6).

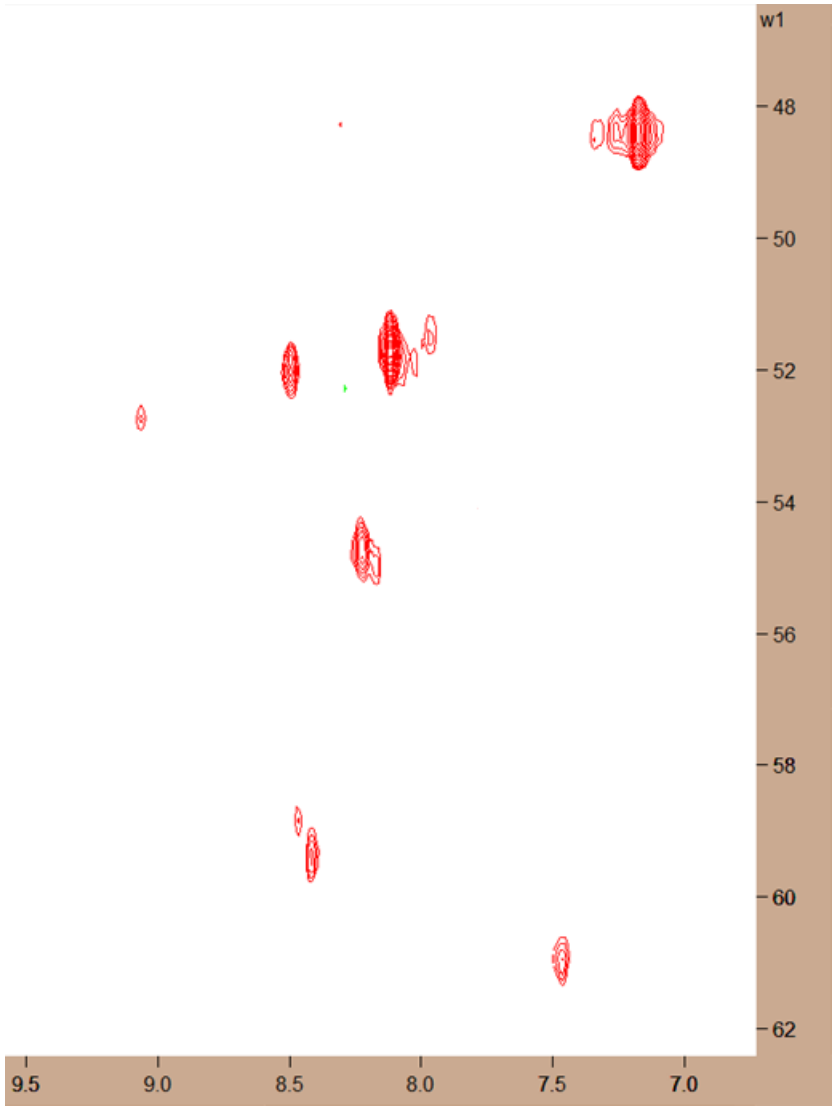

Figure S10. CBCANH spectrum of ^{13}C, ^{15}N-labeled **1** (800 MHz, DMSO-d_6).

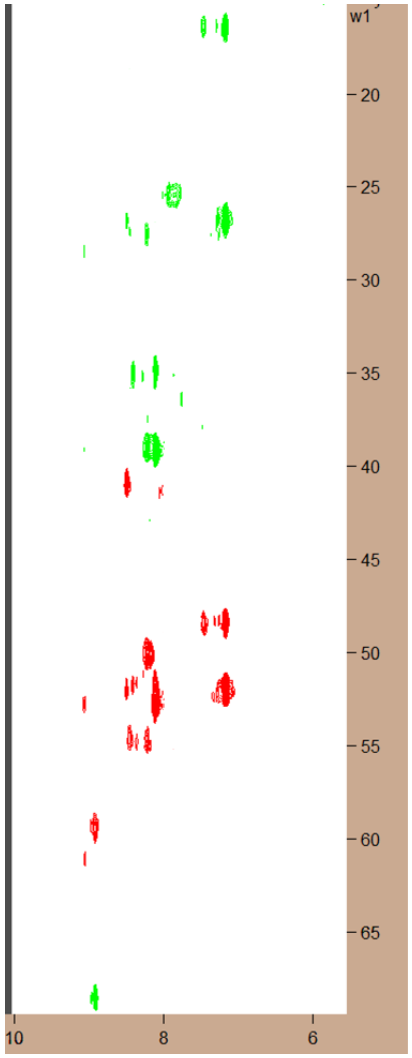

Figure S11. CBCA(CO)NH spectrum of ^{13}C, ^{15}N-labeled **1** (800 MHz, DMSO-d_6).

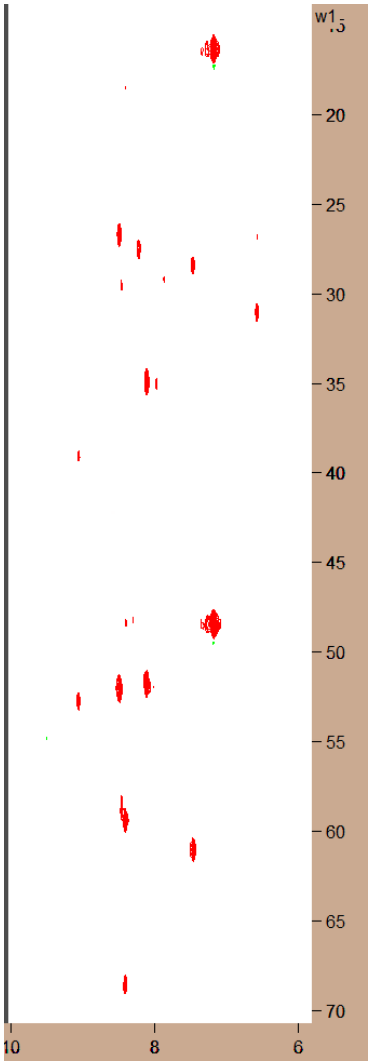

Figure S12. NHCO spectrum of ^{13}C, ^{15}N-labeled **1** (800 MHz, DMSO-d_6).

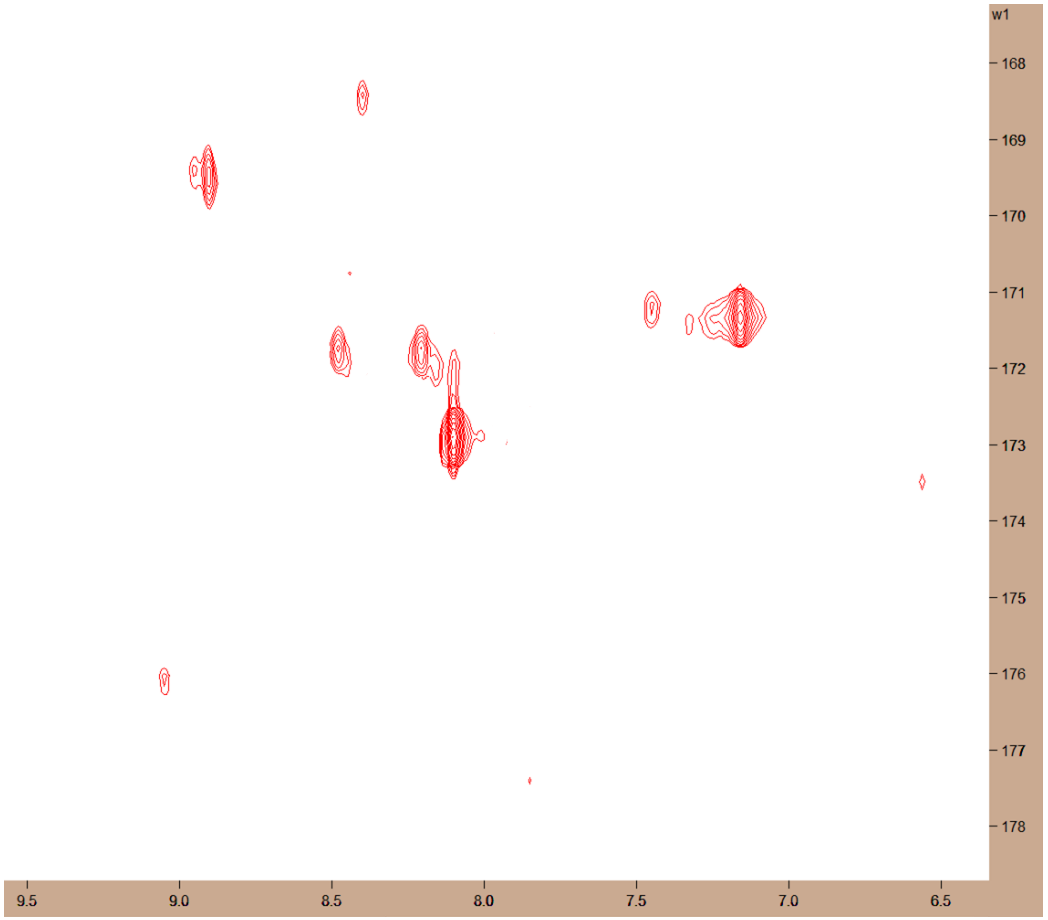

Figure S13. NH(CA)CO spectrum of ^{13}C, ^{15}N-labeled **1** (800 MHz, DMSO-d_6).

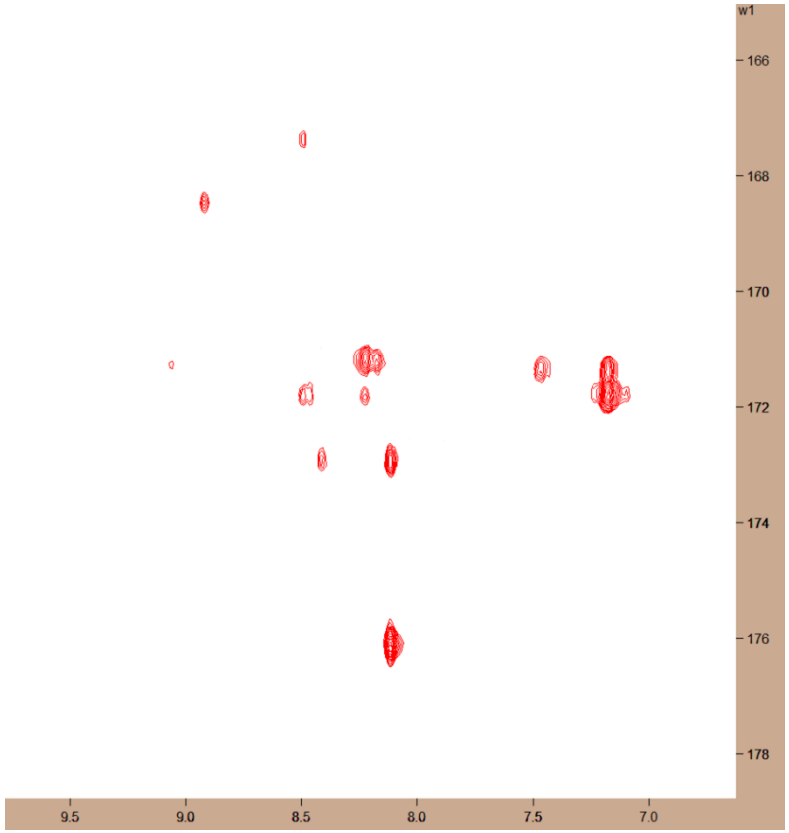

Figure S14. HCCH-TOCSY spectrum of ^{13}C, ^{15}N-labeled **1** (800 MHz, DMSO-d_6).

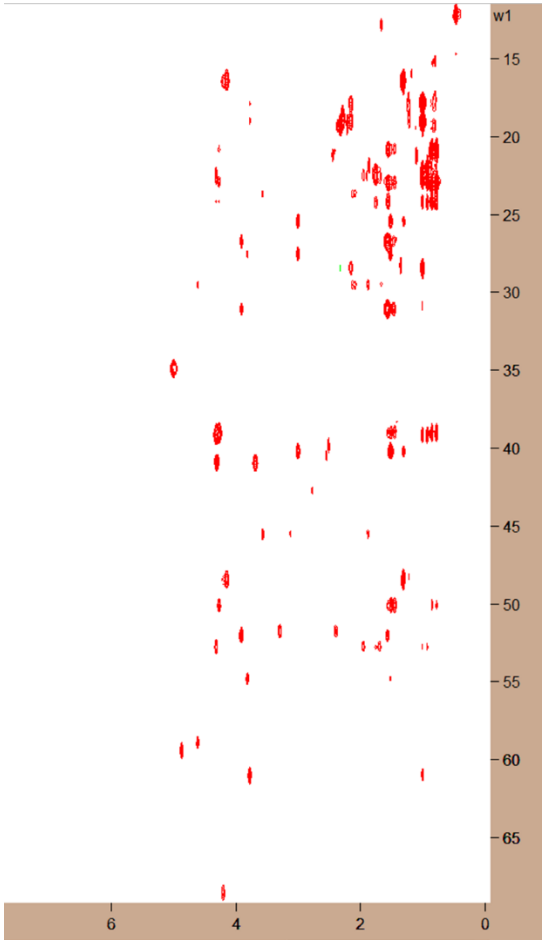

Figure S15. ^{1}H NMR Spectrum of Eudistamide B (**2**; 500 MHz, DMSO-d_6).

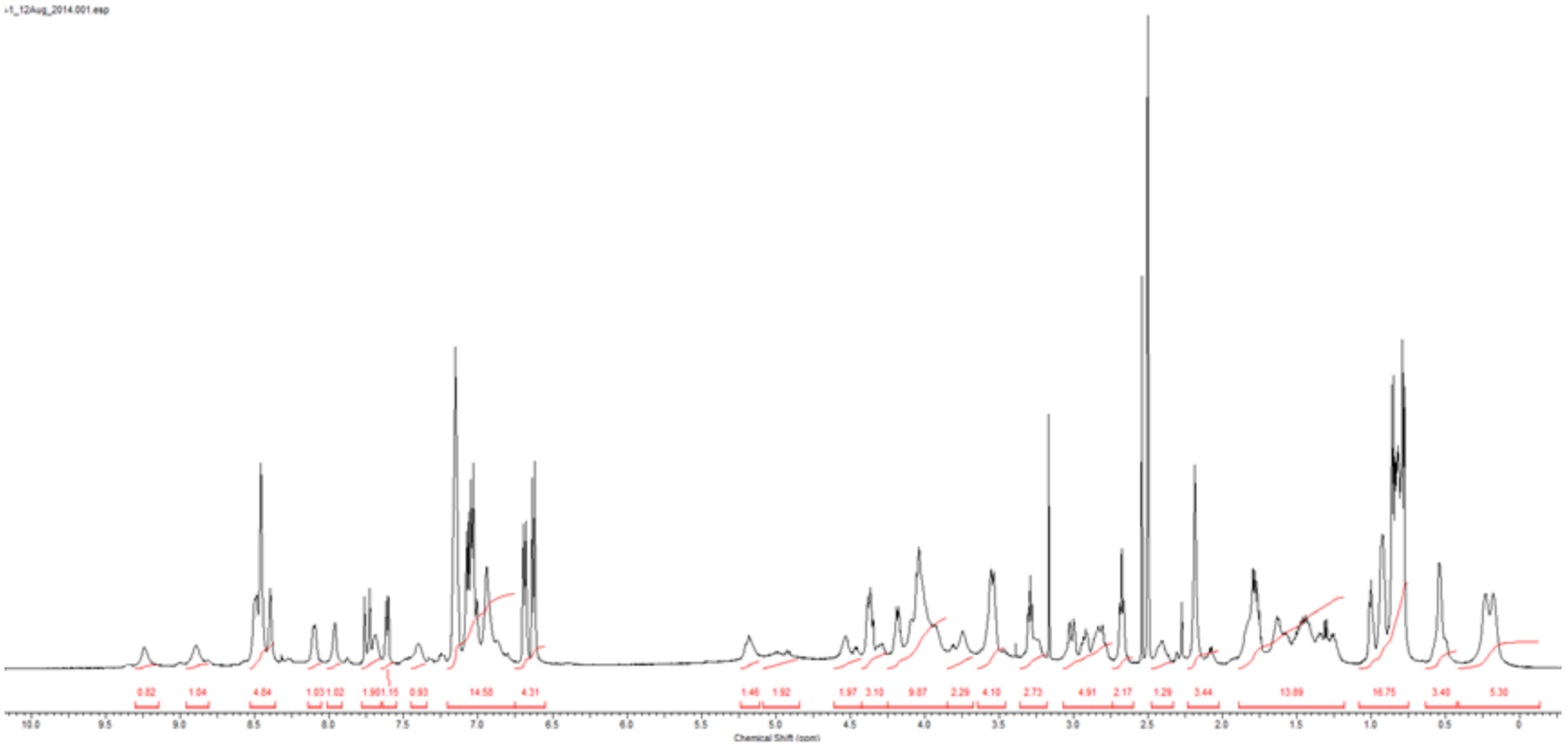

Figure S16. ^{1}H NMR Spectrum of Eudistamide B (**2**; 500 MHz, MeOD-d_3).

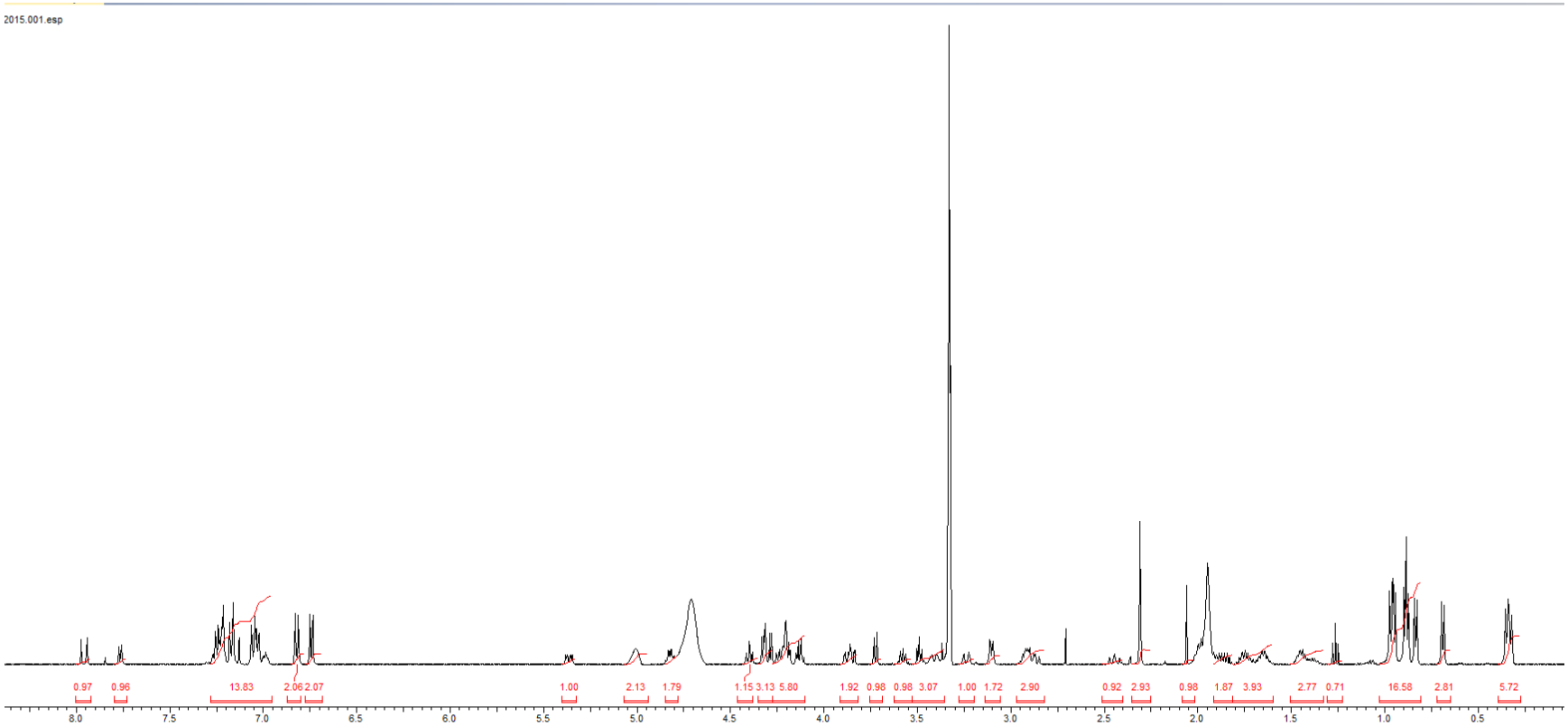

Figure S17. ^{13}C NMR Spectrum of Eudistamide B (**2**; 125 MHz, DMSO-d_6).

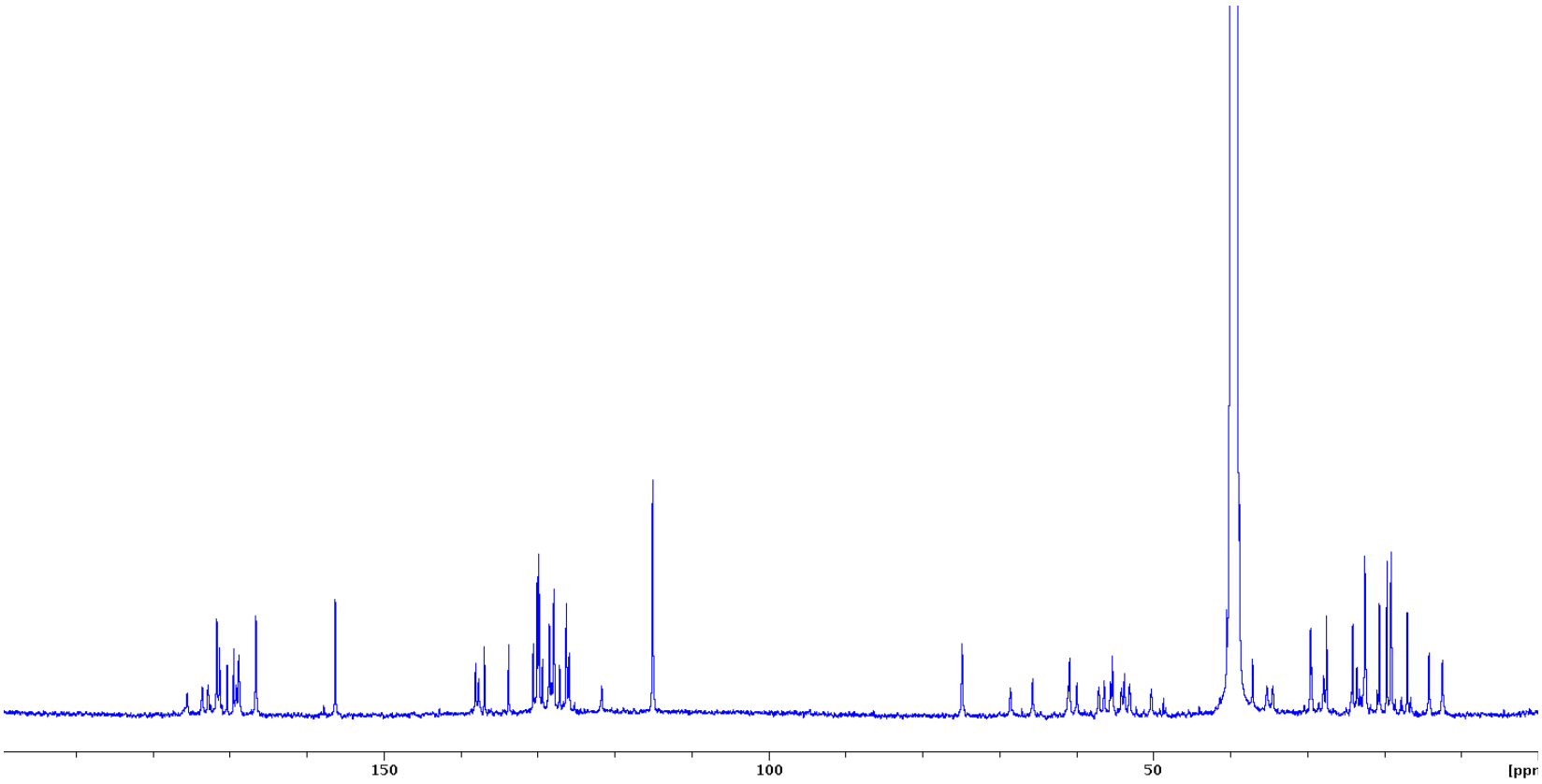

Figure S18. gCOSY Spectrum of Eudistamide B (**2**; 500 MHz, DMSO-d_6).

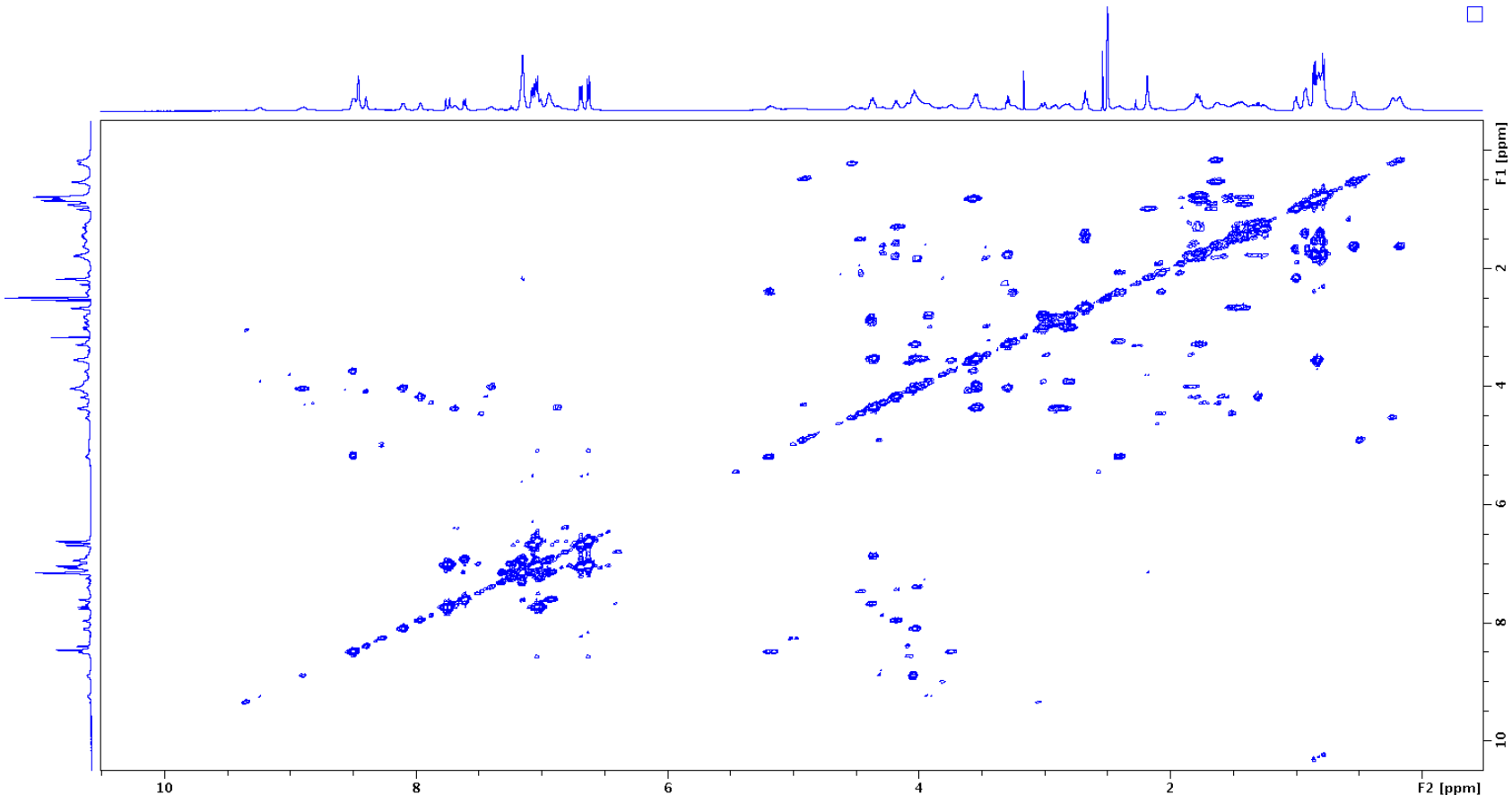

Figure S19. gHSQC NMR Spectrum of Eudistamide B (**2**; 500 MHz, DMSO-d_6).

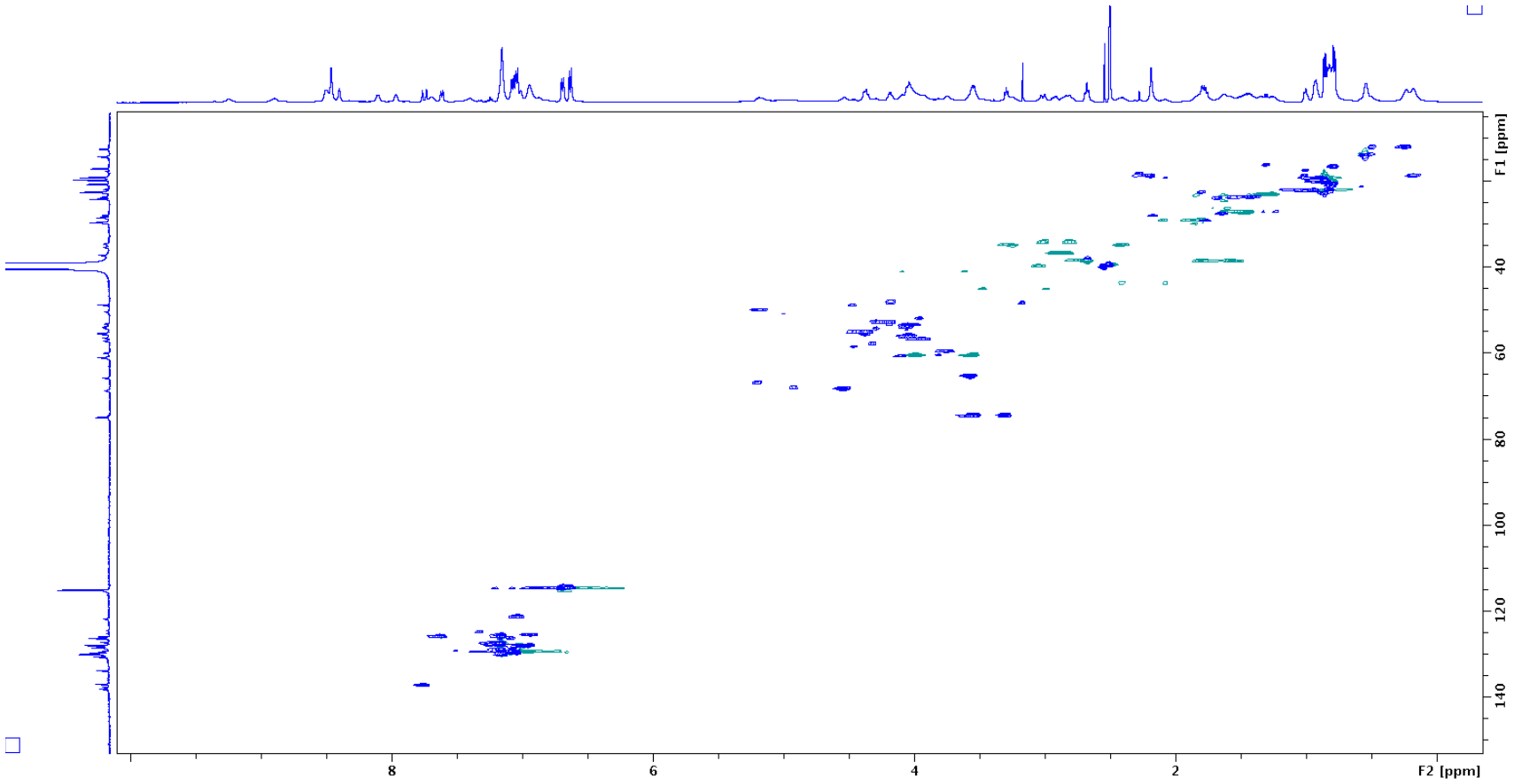

Figure S20. gHMBC NMR Spectrum of Eudistamide B (**2**; 500 MHz, DMSO-d_6).

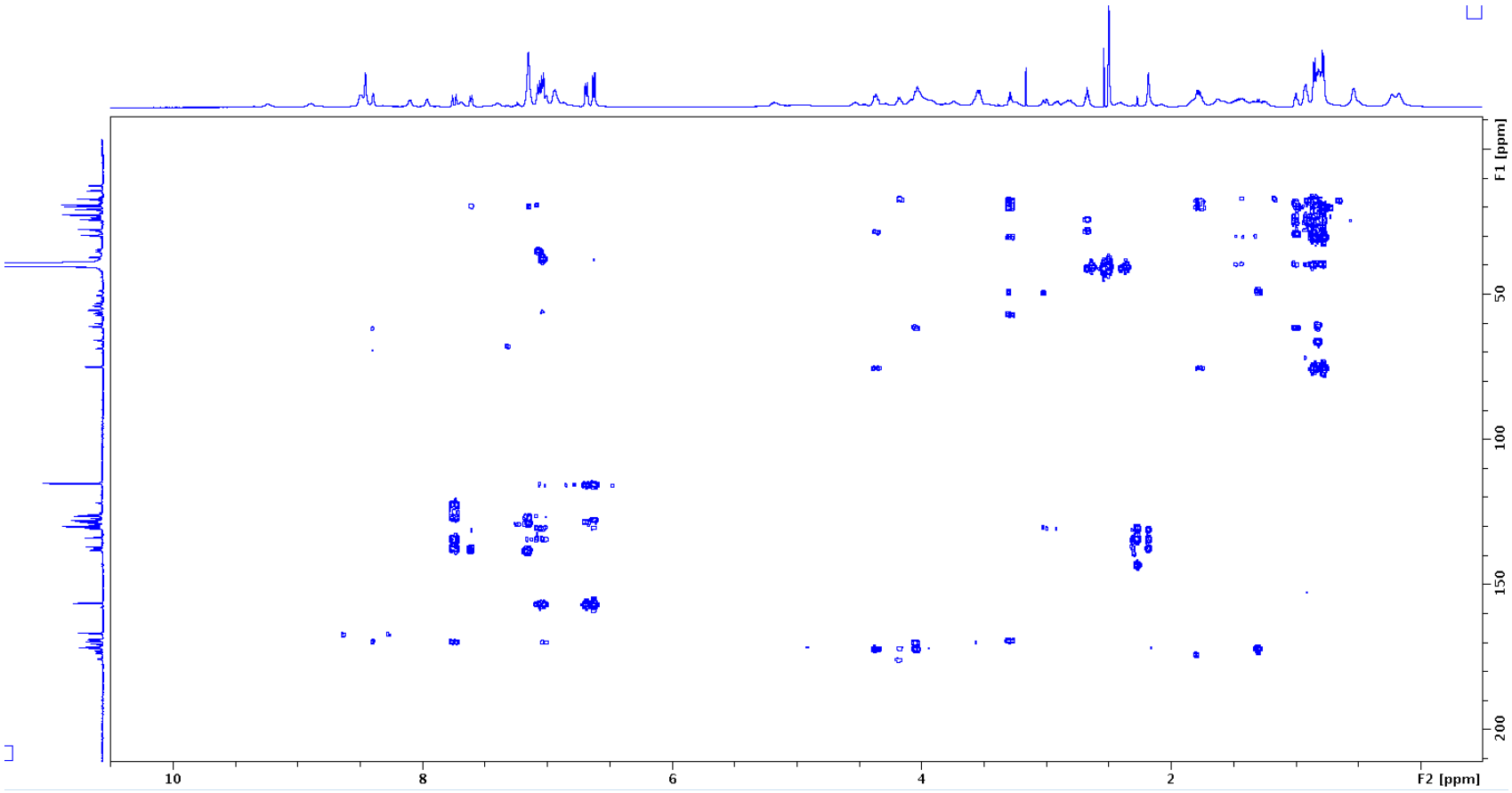

Figure S21. ROESY NMR Spectrum of Eudistamide B (**2**; 500 MHz, DMSO-d_6).

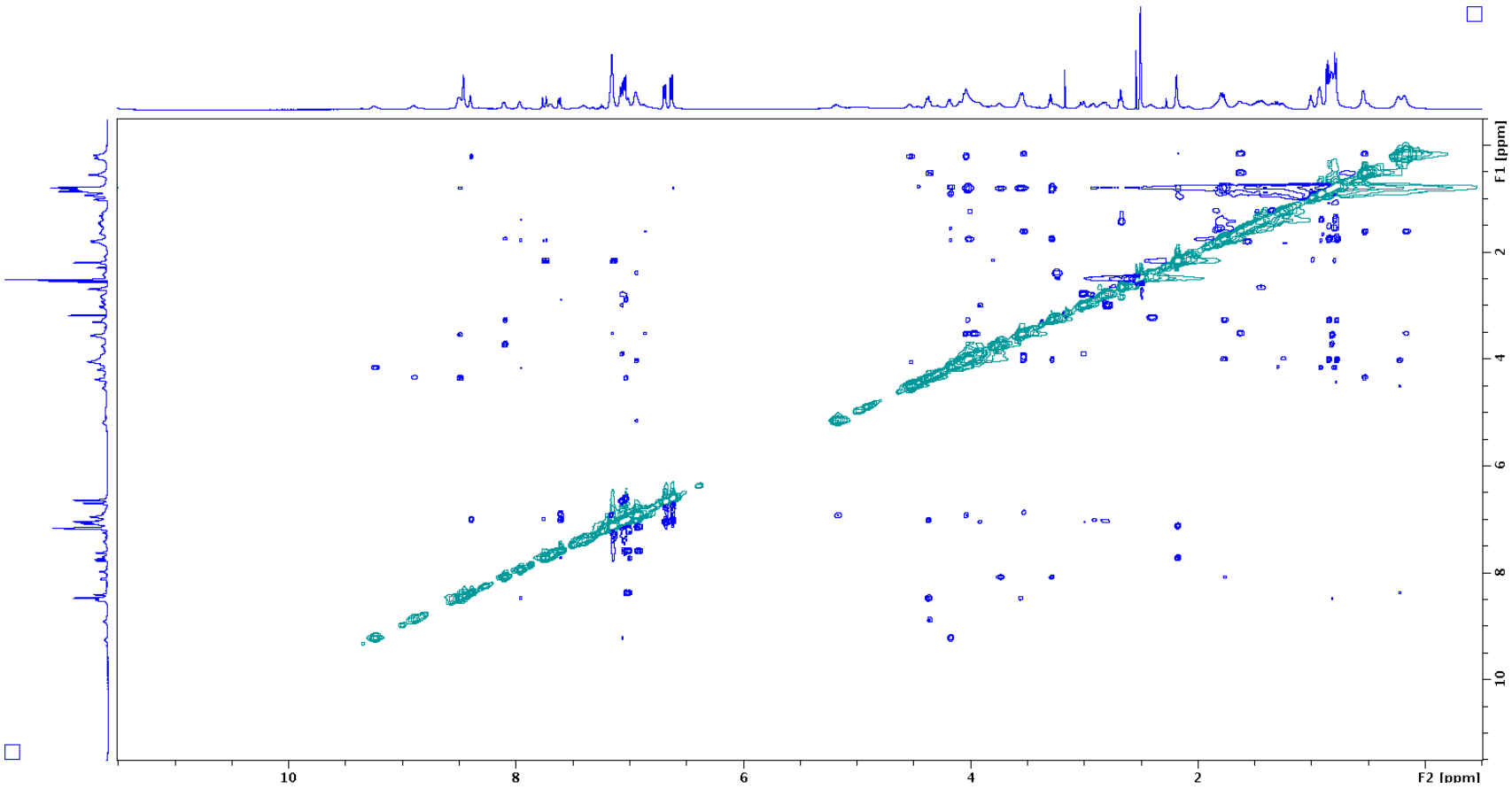

Figure S22. HRESIMS of Eudistamide B (**2**).

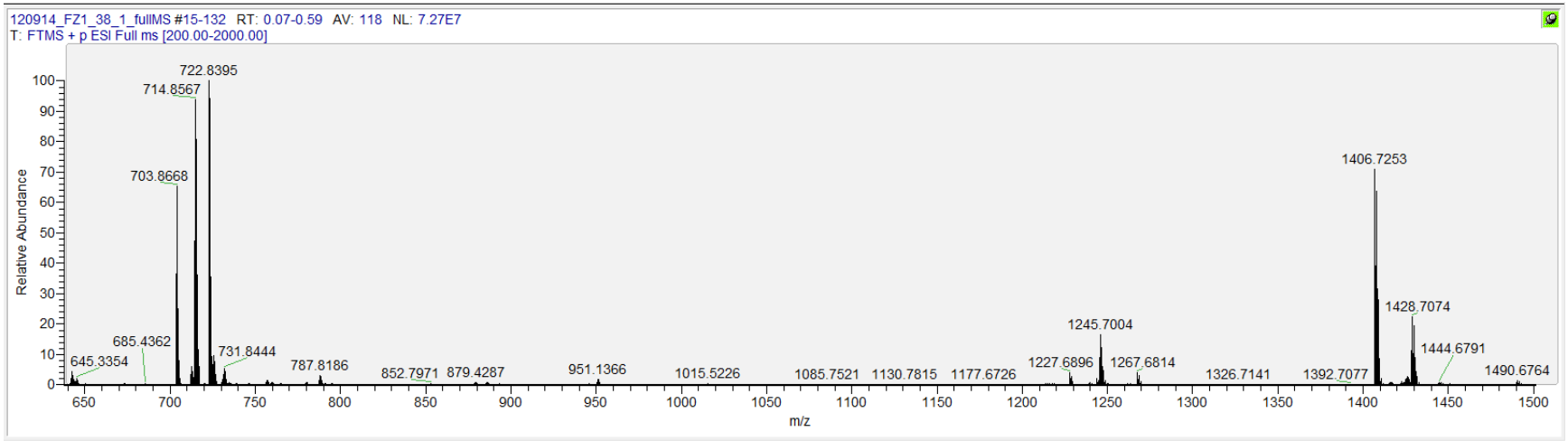

Figure S23. MS/MS spectrum of Eudistamide B (**2**).

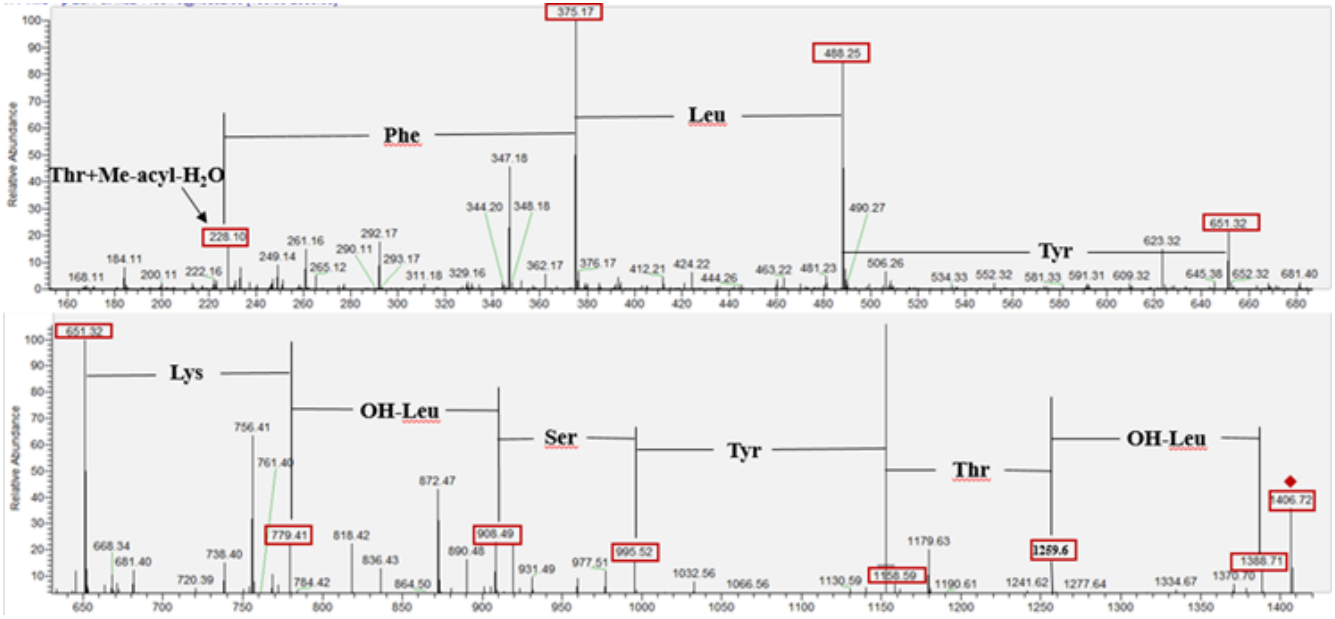

Figure S24. NHCA spectrum of ^{13}C, ^{15}N-labeled **2** (800 MHz, DMSO-d_6).

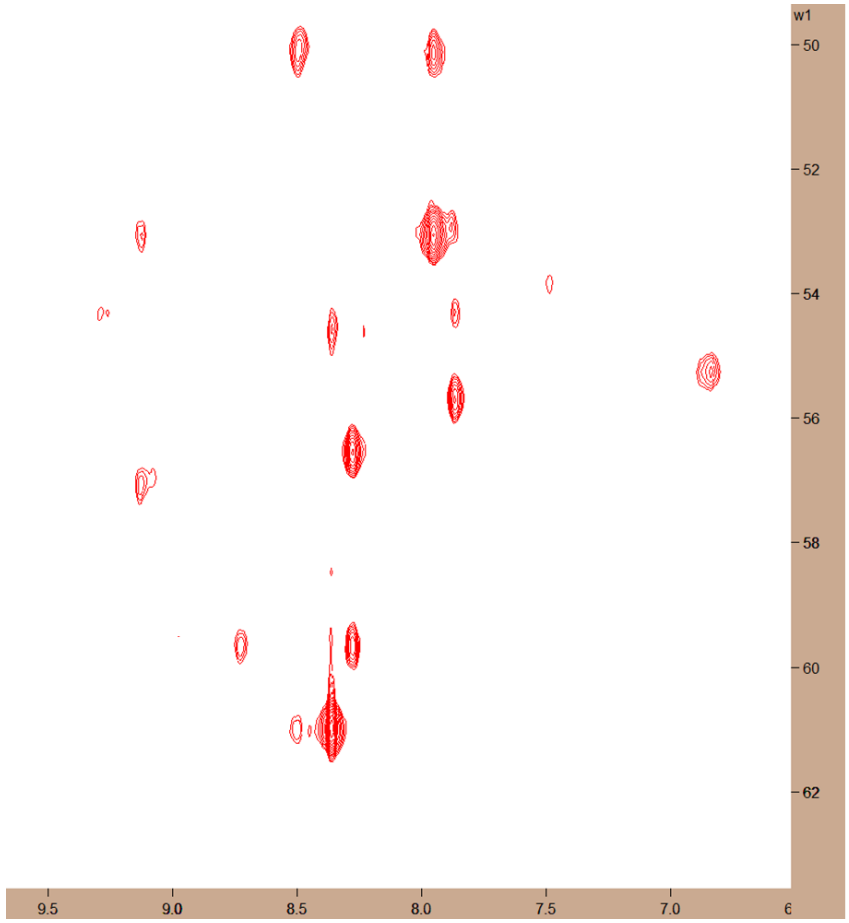

Figure S25. NH(CO)CA spectrum of ^{13}C, ^{15}N-labeled **2** (800 MHz, DMSO-d_6).

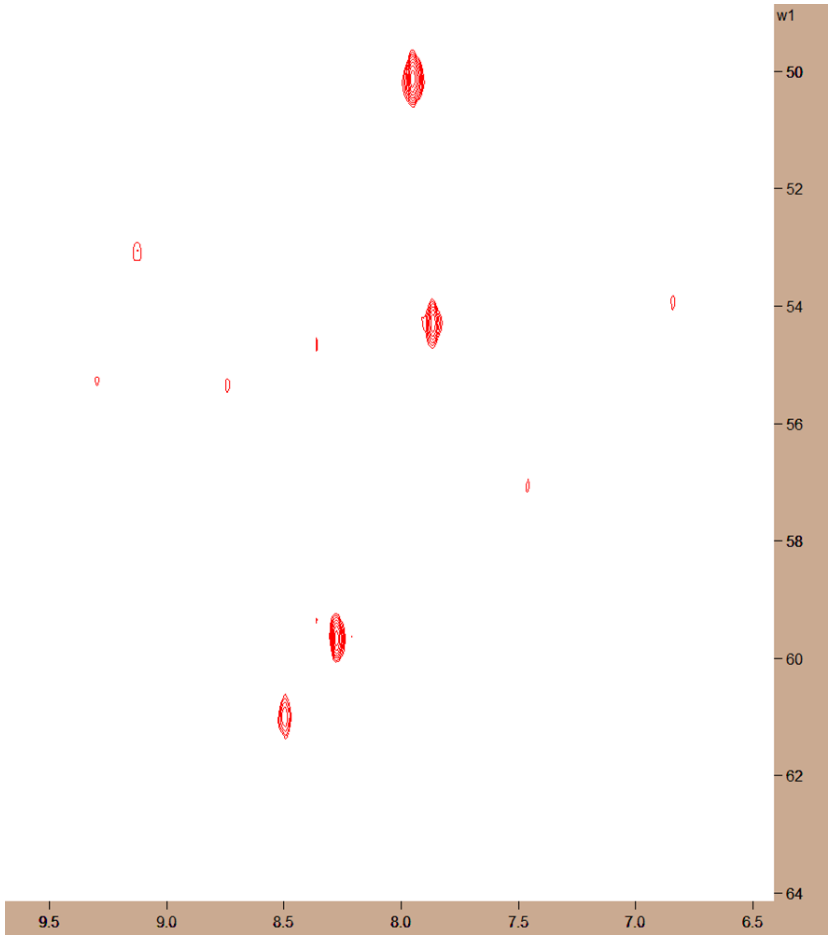

Figure S26. CBCANH spectrum of ^{13}C, ^{15}N-labeled **2** (800 MHz, DMSO-d_6).

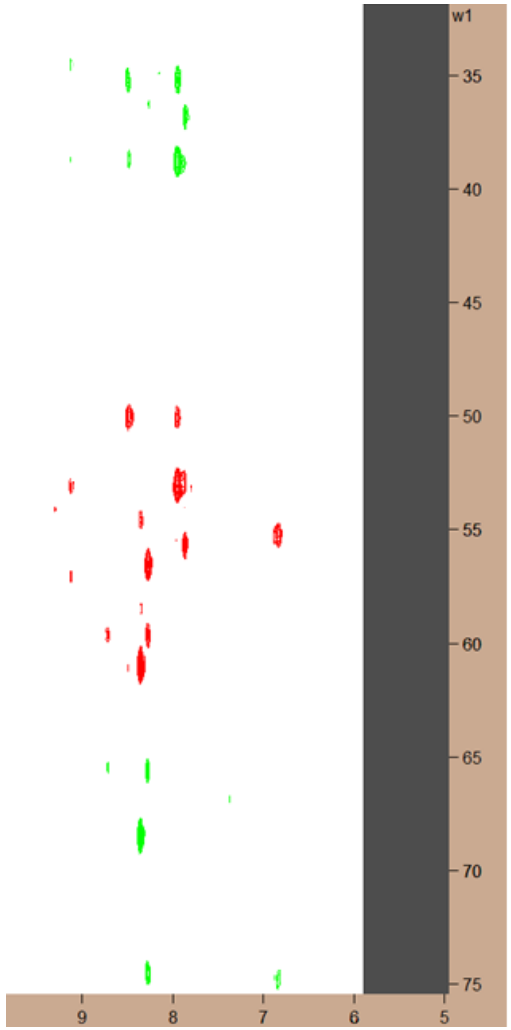

Figure S27. CBCA(CO)NH spectrum of ^{13}C, ^{15}N-labeled **2** (800 MHz, DMSO-d_6).

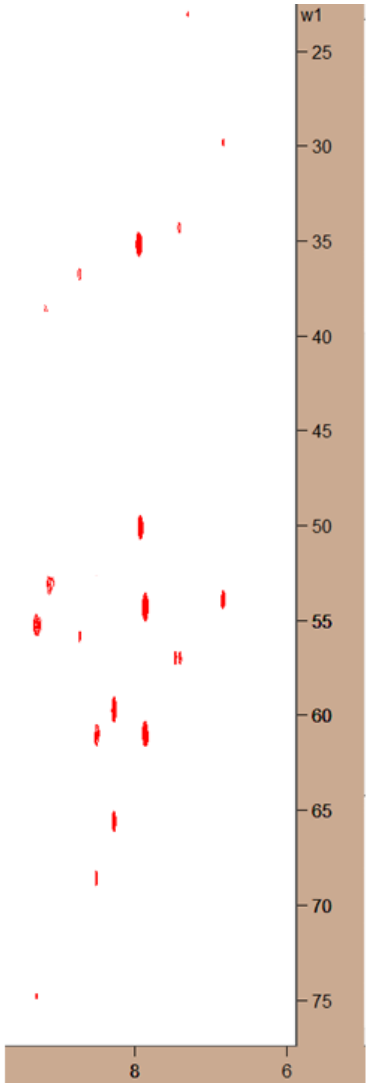

Figure S28. NHCO spectrum of ^{13}C, ^{15}N-labeled **2** (800 MHz, DMSO-d_6).

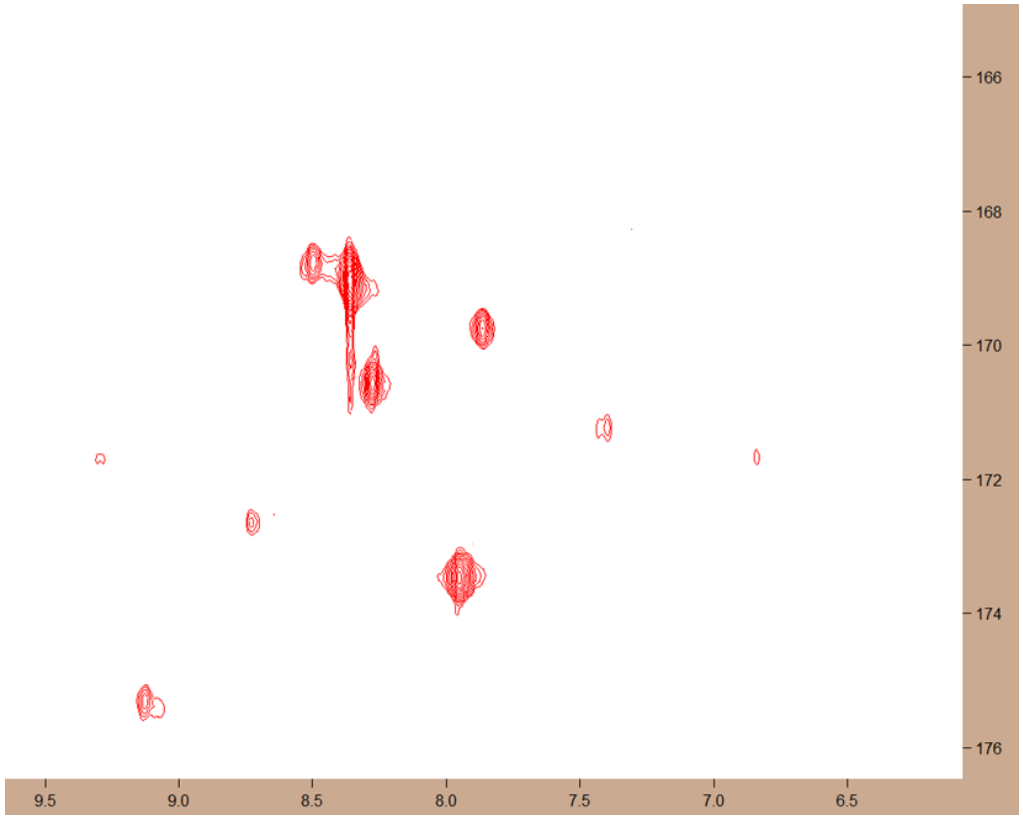

Figure S29. NH(CA)CO spectrum of ^{13}C, ^{15}N-labeled **2** (800 MHz, DMSO-d_6).

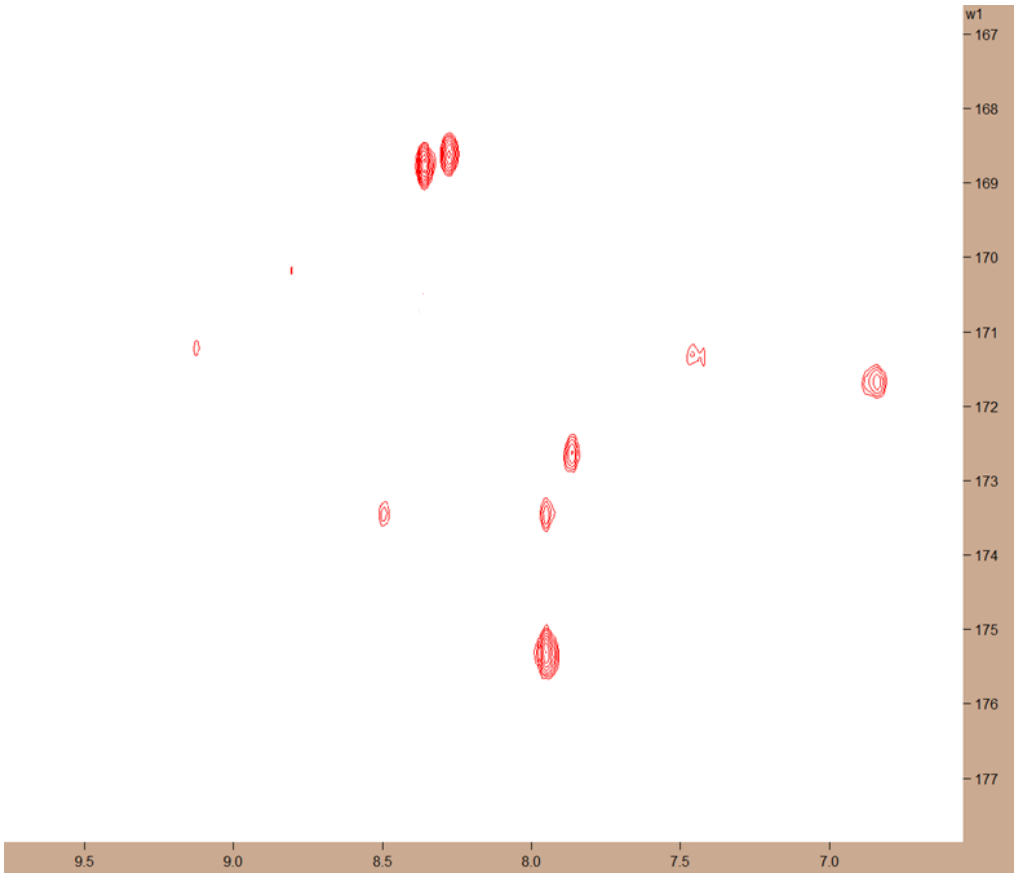

Figure S30. HCCH-TOCSY spectrum of ^{13}C, ^{15}N-labeled **2** (800 MHz, DMSO-d_6).

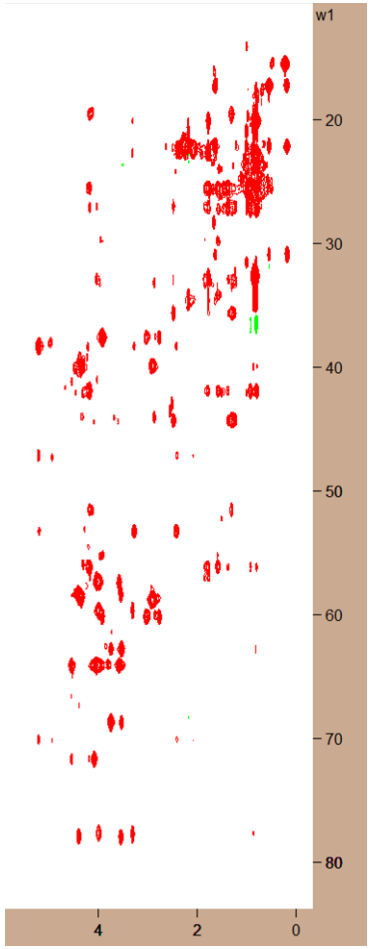

Table S1. 3D NMR data for Eudistamide A (**1**; 800 MHz, DMSO-d_6).

Position	δ_C, mult.	δ_H (J in Hz)	CBCA(CO)NH	CBCANH	NHCA	NH(CO)CA	NHCO	NH(CA)CO	HCCHTOCSY
1	171.4, C								
2	49.9, CH	4.26, m							3, 4, 5, 6
3	38.9, CH_2	1.46, m							2, 4, 5, 6
4	24.2, CH	1.55, m							2, 3, 5, 6
5	23.0, CH_3	0.83, d (6.5)							2, 3, 4, 6
6	20.8, CH_3	0.76, d (6.5)							2, 3, 4, 5
7-NH		8.23, br s	9, 10	2, 3; 9, 10	2, 9	9	8	1, 8	
8	171.8, C								
9	54.7, CH	3.87, m							10, 11b
10	27.0, CH_2	1.52, m							9, 11, 12
11	24.7, CH_2	1.46, m							9, 12
		1.30, m							
12	38.9, CH_2	2.77, m							9, 10, 11
		2.70, m							
13-NH									
14	157.8, C								
15-NH_2									
16-NH									
17-NH		8.46, br s	19, 20	9, 10	9	19	18	8	
18	171.8, C								
19	59.0, CH	4.60, d (3.7)							20, 21
20	29.5, CH_2	2.10, m							19, 21, 22
21	23.7, CH_2	1.88, m							19, 22
		1.71, m							
22	45.5, CH_2	3.57, m							19, 20, 21
		3.15, m							
23	167.5, CH								

24	40.9, CH_2	4.32, d (15.8) 3.68, d (15.8)							
25-NH		8.50, br s	27, 28	24; 27, 28	24, 27	27	26	23, 26	
26	171.8, C								
27	52.1, CH	3.90, m							28
28	26.7, CH_2	1.58, m							27, 29
29	31.1, CH_2	1.58, m							27, 28
30	173.6, C								
31-NH_2		6.60, s; 6.58, s					30		
32-NH		7.18	34, 35	34, 35; 27, 28	27, 34	34	33	26, 33	
33	171.4, C								
34	48.4, CH	4.14, m							35
35	16.4, CH_3	1.31, d (7.4)							34
36-NH		7.48, br s	38, 39	34, 35	34	38	37	33, 37	
37	171.4, C								
38	61.0, CH	3.77, br s							39, 40, 41
39	28.4, CH	2.14							38, 40, 41
40	19.0, CH_3	1.00, d (6.8)							38, 39, 41
41	17.8, CH_3	0.99, d (6.8)							38, 39, 40
42-NH		9.07, br s	44, 45	38, 39; 44, 45	38, 44	44	43	37	
43	176.2, C								
44	52.7, CH	4.30, m							45, 46, 47, 48
45	39.0, CH_2	1.97, m							44, 46, 47, 48
		1.65, m							
46	23.0, CH	1.72, m							
47	22.7, CH_3	1.00, d (6.8)							44, 45, 46, 48
48	22.2, CH_3	0.92, d (6.4)							44, 45, 46, 47
49-NH		8.12, br s	51, 52	44, 45; 51, 52	44, 51	51	50	43, 50	

50	173.0, C								
51	51.8, CH	5.00, br s							52
52	34.8, CH_2	3.28, d (10)							51
		2.39, d (10)							
53	138.3, C								
54	128.8, CH	7.04, d (7.4)							
55	128.0, CH	7.24, t (7.4)							
56	126.1, CH	7.15, t (7.4)							
57	128.0, CH	7.24, t (7.4)							
58	128.8, CH	7.04, d (7.4)							
59-NH		8.41, d (8.9)	61, 62	51, 52	51	61	60	50	
60	168.6, C								
61	59.3, CH	4.18, m							62
62	68.5, CH	4.87, m							61, 63
63	12.1, CH_3	0.48, d (5.3)							61, 62
64-NH		8.92, br s		61, 62	61		65	60	
65	169.5, C								
66	121.7, CH	6.37, d (15.5)							
67	136.2, CH	7.69, d (15.5)							
68	133.5, C								
69	136.6, C								
70	130.2, CH	7.14, m							
71	130.2, CH	7.14, m							
72	128.9, CH	7.18, m							
73	126.5, CH	7.75, d (7.4)							
74	19.2, CH_3	2.30, s							

Table S2. 3D NMR data for Eudistamide B (**2**; 800 MHz, DMSO-d_6).

Position	δ_C, mult.	δ_H (J in Hz)	CBCANH	CBCA(CO)NH	NHCA	NHCOCA	NHCO	NHCACO	HCCHTOCSY
1	168.8, C								
2	56.4, CH	4.03, m							3, 4, 5, 6
3	74.8, CH	3.29, m							2, 4, 5, 6
4	29.5, CH	1.77, m							
5	19.1, CH_3	0.86, d (7.0)							
6	16.7, CH_3	0.78, d (7.0)							
7-NH		8.28, d (6.0)	2, 3; 9, 10	9, 10	2, 9	9	8	1	
8	170.3, C								
9	59.9, CH	3.74, m							10, 11
10	65.6, CH	3.56, m							9, 11
11	20.6, CH_3	0.83, d (6.0)							
12-NH		8.74, br s	9, 10	14, 15	9	14	13	8	
13	172.8, C								
14	55.5, CH	4.34, m							15
15	37.0, CH_2	2.83, d (12.5)							14
		2.92 d (12.5)							
16	127.1, C								
17	130.0, CH	7.04, d (8.0)							
18	115.0, CH	6.63, d (8.0)							
19	156.3, C								
20	115.0, CH	6.63, d (8.0)							
21	130.0, CH	7.04, d (8.0)							
22-NH		7.86, br s	14, 15	24, 25	14, 24	24	23	13	
23	169.4, C								
24	54.1, CH	4.04, m							25
25	60.8, CH_2	3.54, m							24
		3.98, m							

26-NH		9.28, br s	24	28, 29	24	28	27		
27	168.8, C								
28	55.3, CH	4.37, m							29
29	74.8, CH	3.54, m							28, 30, 31, 32
30	27.8, CH	1.64, m							31, 32
31	14.1, CH_3	0.53, br s							30, 32
32	19.1, CH_3	0.17, br s							30, 31
33-NH		6.85, br s	28, 29	35, 36	28	35	34	27	
34	171.7, C								
35	53.71, CH	4.01, m							36
36	29.4, CH_2	1.83, m							35, 37, 38, 39
37	23.5, CH_2	1.26, m							35, 36, 38, 39
		1.34, m							
38	27.5, CH_2	1.46, m							
39	38.8, CH_2	2.68, t (7.5)							
40-NH_2									
41-NH		7.41, br s		43, 44	35	43	42		
42	171.3, C								
43	57.0, CH	3.92, m							44
44	34.4, CH_2	2.80, d (12.5)							
		3.01, d (12.5)							
45	127.8, C								
46	129.8, CH	7.07, d (7.5)							
47	115.0, CH	6.69, d (7.5)							
48	156.3, C								
49	115.0, CH	6.69, d (7.5)							
50	129.8, CH	7.07, d (7.5)							
51-NH		9.13, br s	43, 44; 53, 54	53, 54	43, 53	53	52	42	
52	175.5, C								
53	53.1, CH	4.18, m							54, 55, 56, 57
54	38.9, CH_2	1.57, m							

		1.80, m						
55	24.1, CH	1.41, m						
56	22.5, CH_3	0.93, d (6.5)						
57	22.4, CH_3	0.80, d (7.5)						
58-NH		7.95, br s	53, 54; 60, 61	60, 61	53, 60	60	59	52
59	173.6, C							
60	50.2, CH	5.18, m						
61	35.2, CH_2	2.41, m						
		3.25, m						
62	138.0, C							
63	128.4, CH	6.94, m						
64	127.8, CH	7.16, m						
65	126.2, CH	7.15, m						
66	127.8, CH	7.16, m						
67	128.4, CH	6.94, m						
68-NH		8.50, d (6.5)	60, 61	70, 71	60, 70	70	69	59
69	168.8, C							
70	61.0, CH	4.09, m						
71	68.5, CH	4.53, m						
72	12.4, CH_3	0.23, br s						
73-NH		8.36, br s	70, 71		70		74	
74	169.1, C							
75	121.6, CH	7.04, d (15.5)						
76	137.6, CH	7.75, d (15.5)						
77	133.7, C							
78	136.9, C							
79	129.3, CH	7.16, m						
80	130.5, CH	7.14, m						
81	128.4, CH	6.93, m						
82	126.2, CH	7.60, d (7.5)						
83	19.1, CH_3	2.19, s						

Table S3. ^{1}H and ^{13}C NMR data for 1. (500 MHz for ^{1}H, 125 MHz for ^{13}C, DMSO-d_6).

Position	δ_C, mult.	δ_H (J in Hz)	COSY	HMBC	ROESY
1	171.4, C				
2	49.9, CH	4.26, m	3	1	6, 7
3	38.9, CH_2	1.46, m	2	2, 4, 5, 6	5, 6
4	24.2, CH	1.55, m	3, 5, 6	2, 3, 5, 6	2
5	23.0, CH_3	0.83, d (6.5)	4	4, 6	2
6	20.8, CH_3	0.76, d (6.5)	4	3, 4, 5	2, 3
7-NH		8.53, br s	2		2, 9, 10, 11
8	171.8, C				
9	54.7, CH	3.87, m	10, 17	10, 11, 18	17
10	27.0, CH_2	1.52, m		9, 11, 12a	
11	24.7, CH_2	1.46, m			7, 9
		1.30, m			
12	38.9, CH_2	2.77, m	11	11	
		2.70, m	11		
13-NH		9.69, br s	12		9, 10, 11, 12
14	157.8, C				
15-NH_2		7.20, br s			
16-NH		7.20, br s			
17-NH		8.71, br s	9		9, 10, 19, 21
18	171.8, C				
19	59.0, CH	4.60, d (3.7)	20	18, 20, 21a, 22a	17
20	29.5, CH_2	2.10, m	19, 21	19, 21, 22a	22a
21	23.7, CH_2	1.88, m	20, 21b, 22	19, 20, 22a	19
		1.71, m	20, 21a, 22		
22	45.5, CH_2	3.57, m	21, 22b	19	20, 24
		3.15, m	21, 22a		
23	167.5, CH			24	
24	40.9, CH_2	4.32, d (15.8)	24b, 25		25
		3.68, d (15.8)	24a, 25		
25-NH		8.52, br s	24	26	24, 27
26	171.8, C				
27	52.1, CH	3.90, m	28, 32	28, 29	25, 29, 32
28	26.7, CH_2	1.58, m	27	27	
29	31.1, CH_2	1.58, m		31	27, 31, 32
30	173.6, C			29, 31	
31-NH_2		6.60, s; 6.58, s			29
32-NH		7.18, br s	27		27, 28, 29, 36
33	171.4, C				
34	48.4, CH	4.14, m	35, 36	33, 35	32, 36

35	16.4, CH_3	1.31, d (7.4)	34	33, 34	36
36-NH		7.48, br s	34		34, 38, 42
37	171.4, C				
38	61.0, CH	3.77, br s	39, 42	37, 39, 40, 41, 43	32, 36, 40, 41, 42
39	28.4, CH	2.14, m	38	37, 38, 40, 41	42
40	19.0, CH_3	1.00, d (6.8)	39	38, 39, 41	38, 42
41	17.8, CH_3	0.99, d (6.8)	39	40	38, 42
42-NH		9.07, br s	38		36, 38, 39, 40, 41, 44
43	176.2, C				
44	52.7, CH	4.30, m	45, 49	43, 49	44, 45, 46, 47, 48, 49
45	39.0, CH_2	1.97, m	44, 45b	46, 47, 48	47, 48, 49, 67
		1.65, m	45a		
46	23.0, CH	1.72, m	47, 48	47, 48	49, 67
47	22.7, CH_3	1.00, d (6.8)		48	44, 45
48	22.2, CH_3	0.92, d (6.4)		47	44, 45
49-NH		8.13, br s	44	50	44, 45, 46, 59
50	173.0, C				
51	51.8, CH	5.00, br s	52	52	44, 49, 54, 58, 59,
52	34.8, CH_2	3.28, d (10)	51, 52b	58	54, 58
		2.39, d (10)	51, 52a		
53	138.3, C			52a, 55	
54	128.8, CH	7.04, d (7.4)		52a, 58	51, 52b, 63
55	128.0, CH	7.24, t (7.4)			63
56	126.1, CH	7.15, t (7.4)	19	54, 56	
57	128.0, CH	7.24, t (7.4)	58	55	63
58	128.8, CH	7.04, d (7.4)	57	56, 58	51, 52b, 63
59-NH		8.40, d (8.9)	51	60	49, 52b, 61, 63, 64
60	168.6, C				
61	59.3, CH	4.18, m	62, 64	63	49, 59, 63, 64
62	68.5, CH	4.87, m	61, 63	1, 63	59, 64
63	12.1, CH_3	0.48, d (5.3)	62	62	2, 56, 58, 59, 62, 63
64-NH		8.98, br s	61		59, 61, 63, 66
65	169.5, C				
66	121.7, CH	6.37, d (15.5)	67	65, 67	64, 73, 74
67	136.2, CH	7.69, d (15.5)	66	65	70, 71
68	133.5, C			66, 67, 73, 74	
69	136.6, C			67, 70, 72, 74	
70	130.2, CH	7.14, m		67	66, 74
71	130.2, CH	7.14, m	73, 74	73, 74	74
72	128.9, CH	7.18, m		70	74
73	126.5, CH	7.75, d (7.4)	71, 74	71, 74	66, 70, 71
74	19.2, CH_3	2.30, s	71, 73	73	67, 72

Table S4. ^{1}H and ^{13}C NMR data for 2. (500 MHz for ^{1}H, 125 MHz for ^{13}C, DMSO-d_6).

Position	δ_C, mult.	δ_H (J in Hz)	COSY	HMBC	ROESY
1	168.8, C				
2	56.4, CH	4.03, m	3		3, 4, 5, 6, 81
3	74.8, CH	3.29, m	3, 4	4, 5, 6	2, 4, 5, 6, 7
4	29.5, CH	1.77, m	3, 4, 5	3, 5, 6	2, 3, 5, 6, 7
5	19.1, CH_3	0.86, d (7.0)	4	3, 4, 6	2, 3, 4
6	16.7, CH_3	0.78, d (7.0)	4	3, 4, 5	2, 3, 4
7-NH		8.10, d (6.0)	2	8	2, 3, 4, 6, 9
8	170.3, C				
9	59.9, CH	3.74, m	10, 12		7, 11
10	65.6, CH	3.56, m	9, 11		12
11	20.6, CH_3	0.83, d (6.0)	10	9, 10	9, 10, 12
12-NH		8.46, br s	9		4, 9, 11, 14
13	172.8, C				
14	55.5, CH	4.34, m	15	15	12, 15, 22
15	37.0, CH_2	2.83, d (12.5)	14	13, 14	14, 17
		2.92 d (12.5)			
16	127.1, C				
17	130.0, CH	7.04, d (8.0)	18	18, 19, 21	14
18	115.0, CH	6.63, d (8.0)	17	16, 19, 20	
19	156.3, C				
20	115.0, CH	6.63, d (8.0)	21	16, 18, 19	11
21	130.0, CH	7.04, d (8.0)	20	17, 19, 20	14
22-NH		7.69, br s	14		14, 24, 26
23	169.4, C				
24	54.1, CH	4.04, m	25, 26	23, 25	25b
25	60.8, CH_2	3.54, m	24	23	24
		3.98, m			
26-NH		8.90, br s	23		28
27	171.7, C				
28	55.3, CH	4.37, m	29, 33	29, 34	26, 29, 31
29	74.8, CH	3.54, m	28		25b, 30, 32, 33
30	27.8, CH	1.64, m	29, 31, 32	32	25, 28, 31, 32, 33
31	14.1, CH_3	0.53, br s	30		28, 30, 32
32	19.1, CH_3	0.17, br s	30		29, 30
33-NH		6.88, br s	28		29, 30
34	171.7, C				
35	53.71, CH	4.01, m	35, 36		29, 37
36	29.4, CH_2	1.83, m	35, 37		35
37	23.5, CH_2	1.26, m		37	39

		1.34, m			
38	27.5, CH_2	1.46, m	39		39
39	38.8, CH_2	2.68, t (7.5)	38		37, 38
40-NH_2					
41-NH		7.40, br s	35		
42	171.3, C				
43	57.0, CH	3.92, m	44	42	
44	34.4, CH_2	2.80, d (12.5)		47	46/50
		3.01, d (12.5)			
45	127.8, C				
46	129.8, CH	7.07, d (7.5)	47	48	43, 44, 51
47	115.0, CH	6.69, d (7.5)	46	45, 47, 48	
48	156.3, C				
49	115.0, CH	6.69, d (7.5)	50	45, 48, 49	56, 57
50	129.8, CH	7.07, d (7.5)	49	48	43, 44, 51, 56, 57
51-NH		9.24, br s	43		46/50, 53
52	175.5, C				
53	53.1, CH	4.18, m	54, 58	52, 54	51, 54, 55, 56, 57, 58
54	38.9, CH_2	1.57, m	55		53, 58
		1.80, m			
55	24.1, CH	1.41, m	56, 57	54, 56	53, 56, 57, 58
56	22.5, CH_3	0.93, d (6.5)	55	54, 55	52, 54, 55
57	22.4, CH_3	0.80, d (7.5)	55	55	52, 54, 55
58-NH		7.96, br s	53		53, 54, 56, 57, 58
59	173.6, C				
60	50.2, CH	5.18, m	61a, 68		58, 63/67
61	35.2, CH_2	2.41, m			63/67
		3.25, m			
62	138.0, C				
63	128.4, CH	6.94, m	64		61b, 70
64	127.8, CH	7.16, m	63	62	
65	126.2, CH	7.15, m	63	63	
66	127.8, CH	7.16, m	67	62	
67	128.4, CH	6.94, m	66		
68-NH		8.50, d (6.5)	60		58, 61b
69	168.8, C				
70	61.0, CH	4.09, m			71, 72, 73
71	68.5, CH	4.53, m	72		70, 72
72	12.4, CH_3	0.23, br s	71		2, 70, 71, 73
73-NH		8.40, br s	70	69	70, 72, 75
74	169.1, C				
75	121.6, CH	7.04, d (15.5)	76		
76	137.6, CH	7.75, d (15.5)	75	74, 75, 77, 78, 82	4, 5, 6, 81

77	133.7, C				
78	136.9, C				
79	129.3, CH	7.16, m	82		72
80	130.5, CH	7.14, m	81, 82	83	
81	128.4, CH	6.93, m	82		
82	126.2, CH	7.60, d (7.5)	81		83
83	19.1, CH_3	2.19, s		77	80, 82

Table S5. Advanced Marfey's analysis of Eudistamide A (**1**).

Amino acid	HPLC retention times;[a] L-FDLA derivative of acid hydrolysate		HPLC retention times;[a] L-FDLA derivative of acid hydrolysate	Assignment
	L-standard	D-standard		
Arg	15.8	15.2	15.8	L
Pro	17.1	17.5	17.1	L
Glu	16.9	17.6	17.6	D
Ala	17.1	18.2	17.1	L
Leu	18.2	19.9	19.9	D
Val	17.7	18.2	17.7	L
Phe	18.0	19.5	18.0	L
Thr	16.2	17.5	16.7	L–*allo*
	16.7 (*allo*)	17.0 (*allo*)		

[a]Measured by LC-MS selected ion chromatogram on a reversed-phase column (Phenomenex Kinetex C18, 100 x 4.6 mm, 2.6 μm, 0.5 mL/min) with a linear gradient from 10% to 100% aqueous MeOH containing 0.1% formic acid over 15 min, and a hold at 100% MeOH for 5 min.

Table S6. Advanced Marfey's analysis of Eudistamide B (**2**).

Amino acid	HPLC retention times (min)[a]; L-FDLA derivative of acid hydrolysate		HPLC retention times (min)[a]; L-FDLA derivative of acid hydrolysate	Assignment
	L-standard	D-standard		
Thr	18.3	20.4	19.7	D-*allo*
	18.5 (*allo*)	19.7 (*allo*)		
Tyr	15.4	21.2	21.2	D
Ser	18.5	18.9	18.5	L
Lys	13.1	12.7	12.7	D
Leu	22.8	26.5	22.8	L
Phe	23.2	26.2	26.2	D

[a]Measured by LC-MS selected ion chromatogram on a reversed-phase column (Phenomenex Luna C_{18}, 250 x 4.6 mm, 5 μm, 1.0 mL/min) with a linear gradient from 10% to 100% aqueous acetonitrile containing 0.1% formic acid over 30 min, and a hold at 100% acetonitrile for 5 min.

	L-FDLA derivatives of 3-OH-Leu				L-FDLA derivative of acid hydrolysate	Assignment
	2*S*, 3*R*	2*R*, 3*S*	2*S*, 3*S*	2*R*, 3*R*		
Retetion time (min)[b]	26.8	38.6	27.5	35.4	26.8	2*S*, 3*R*

[b]Measured by LC-MS selected ion chromatogram on a reversed-phase column (Phenomenex Luna C_{18}, 250 x 4.6 mm, 5 μm, 1.0 mL/min) with a linear gradient from 25% to 65% aqueous acetonitrile containing 0.1% formic acid over 50 min.

Media study of strain WMMB 705.

Recipes for different media

Media components	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**	**M9**
Soluble Starch	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g
Glucose	0.25 g	0.25 g	0.25 g	0.25 g	0.25 g	0.25 g	0	0.25 g ^{13}C-Glucose	0.25 g ^{13}C-Glucose
$CaCO_3$	0.125 g	0.125 g	0.125 g	0.125 g	0.125 g	0.125 g	0.125 g	0.125 g	0.125 g
Peptone	0.125 g	0	0.063 g	0	0	0.125 g	0.125 g	0.125 g	0.063 g
Yeast Extract	0.125 g	0	0.063 g	0	0.125 g	0	0.125 g	0.125 g	0.063 g
$^{15}NH_4Cl$	0	0	0.125 g	0.25	0.125 g	0.125 g	0	0	0.125 g
ASW	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml

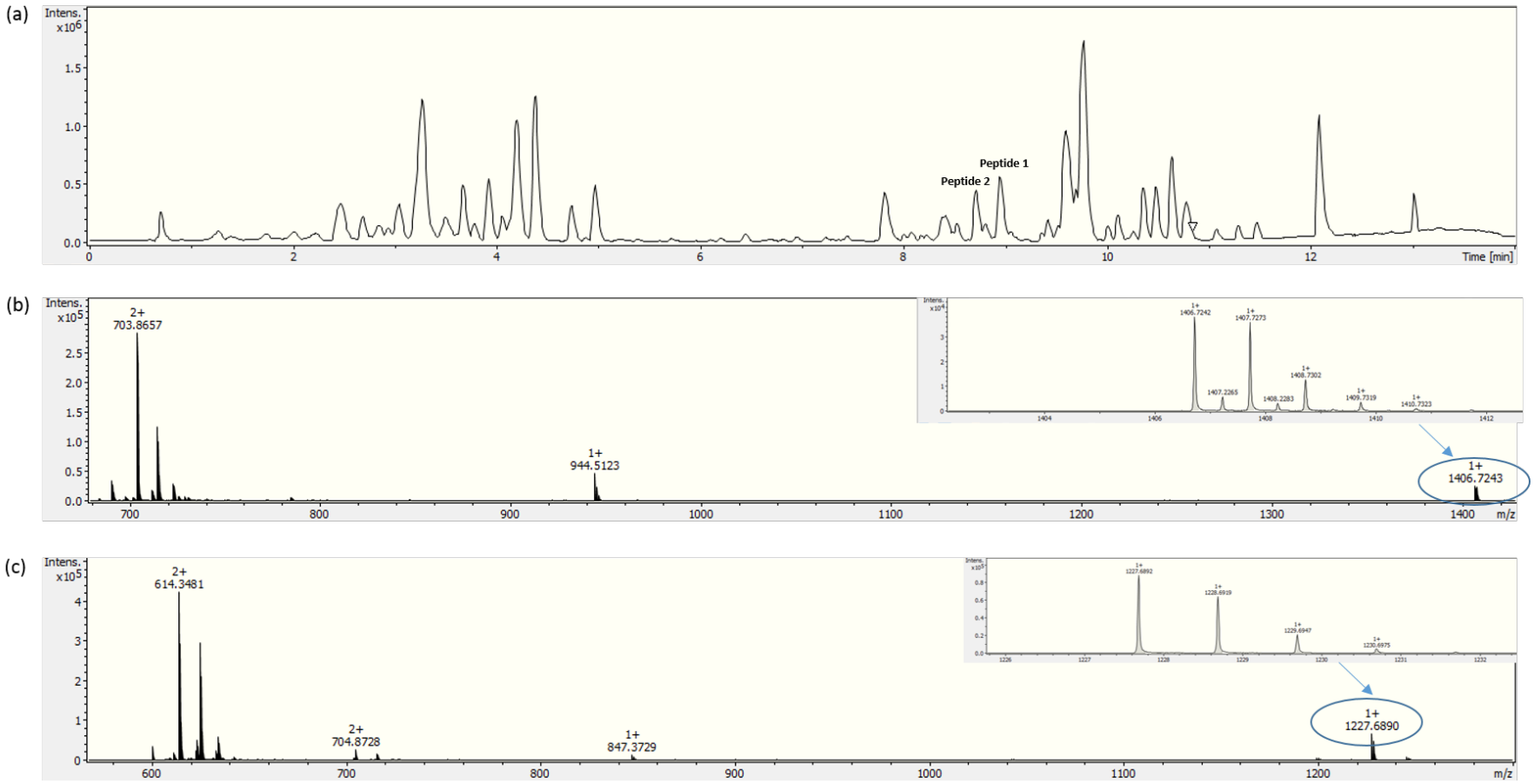

Fig 1 (a) LCMS data of crude extract of M1. (b) ESIMS of peptide **2** in M1. (b) ESIMS of peptide **1** in M1.

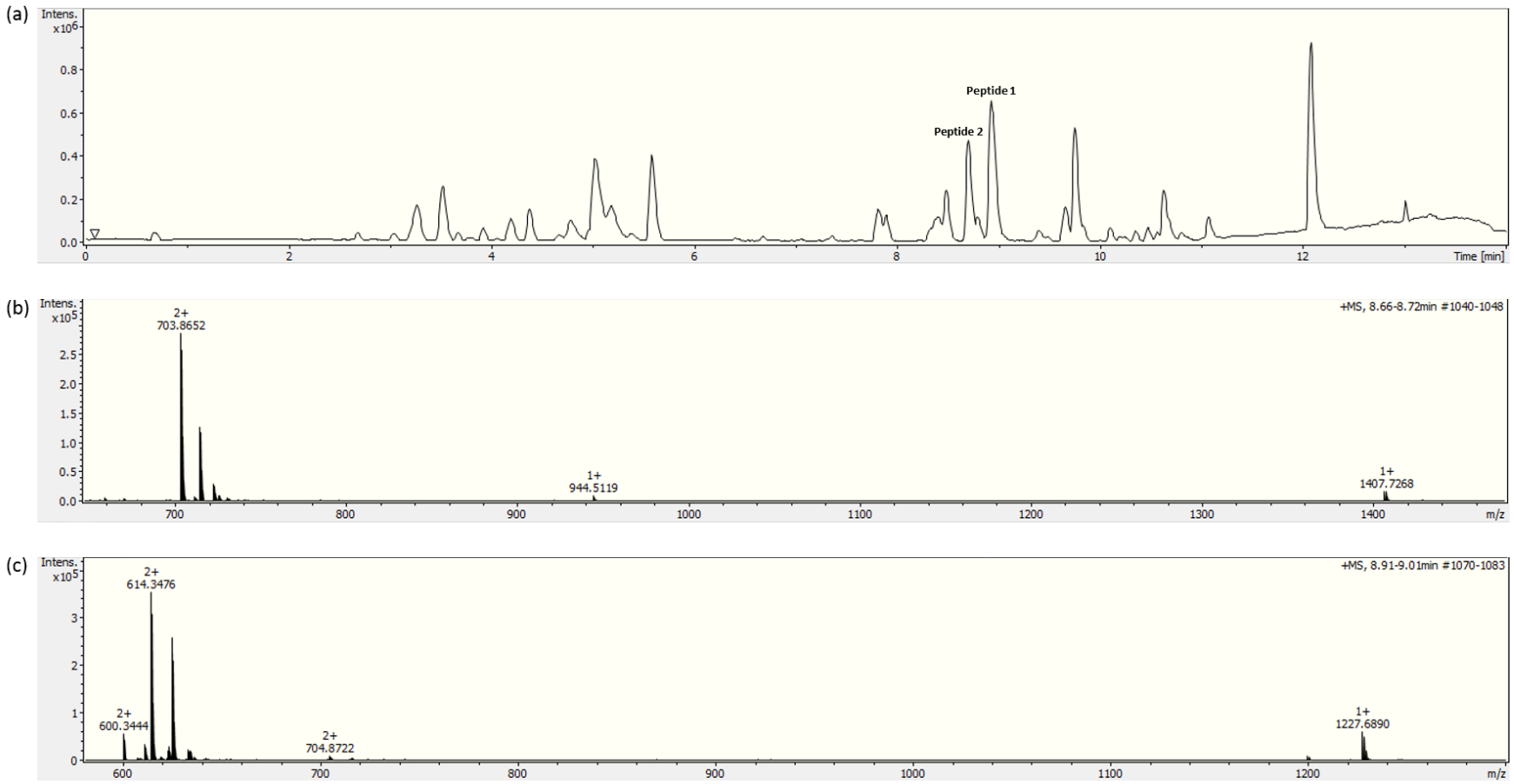

Fig 2 (a) LCMS data of crude extract of M2. (b) ESIMS of peptide **2** in M2. (b) ESIMS of peptide **1** in M2.

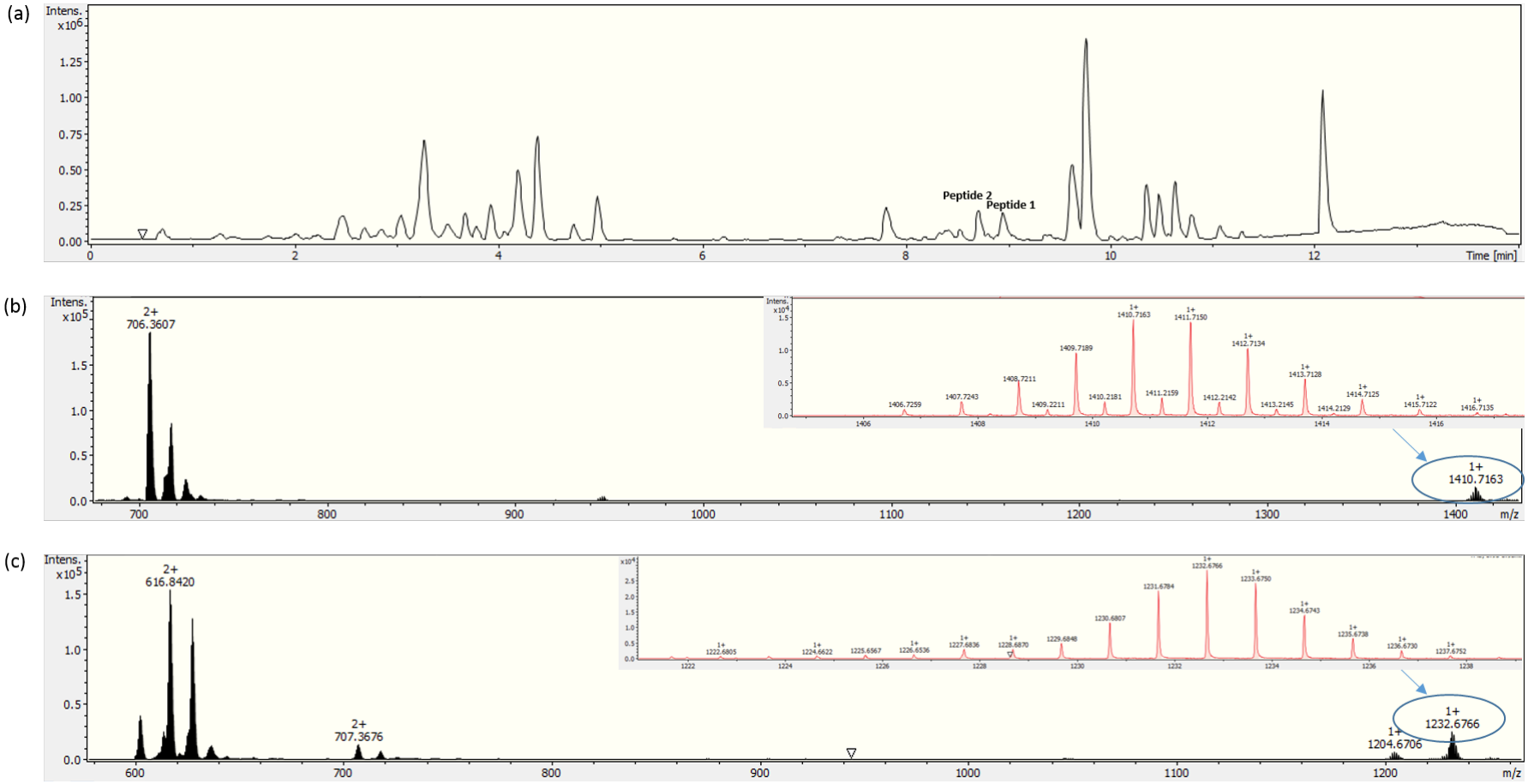

Fig 3 (a) LCMS data of crude extract of M3. (b) ESIMS of peptide **2** in M3. (b) ESIMS of peptide **1** in M3.

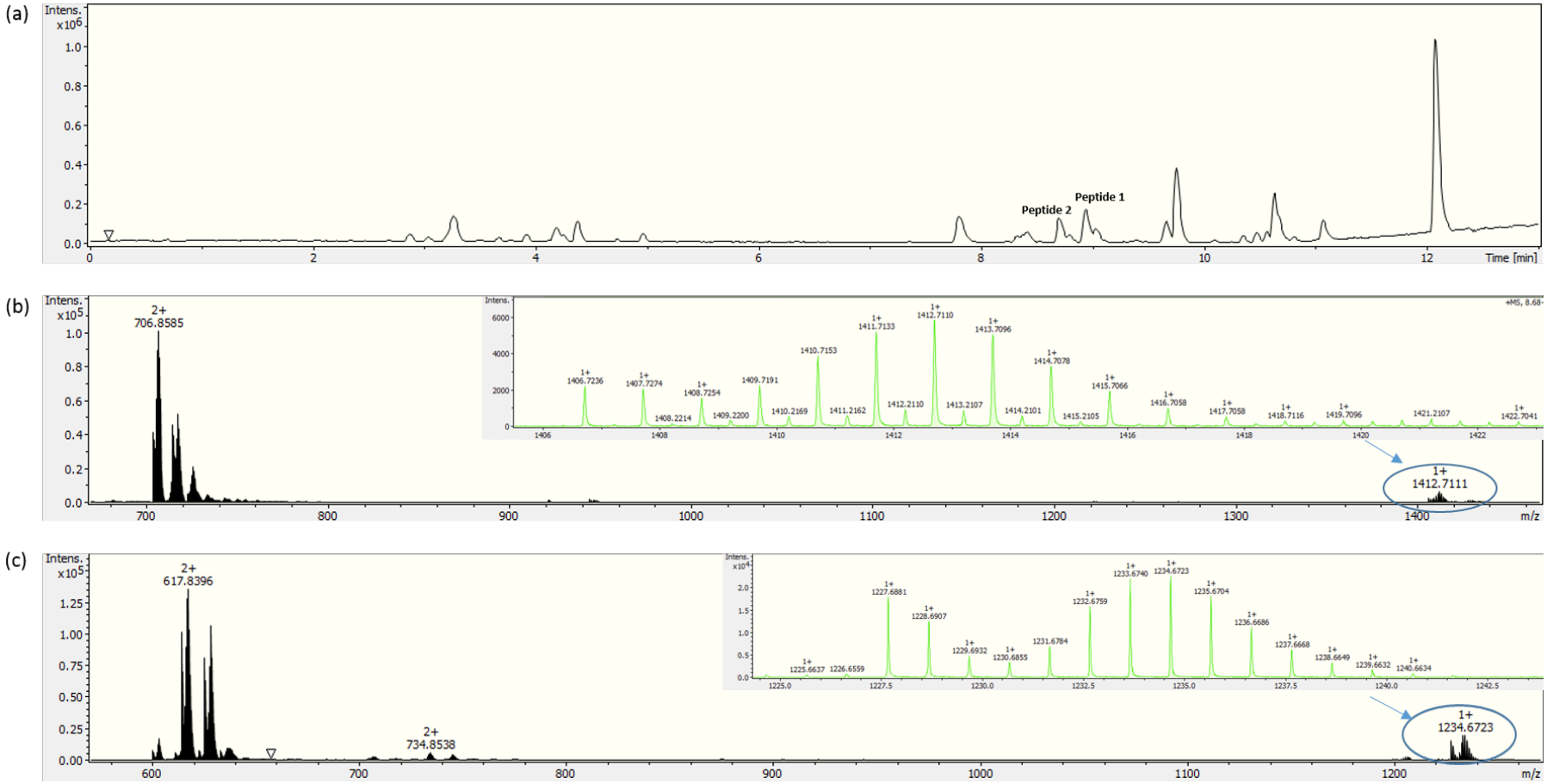

Fig 4 (a) LCMS data of crude extract of M4. (b) ESIMS of peptide **2** in M4. (b) ESIMS of peptide **1** in M4.

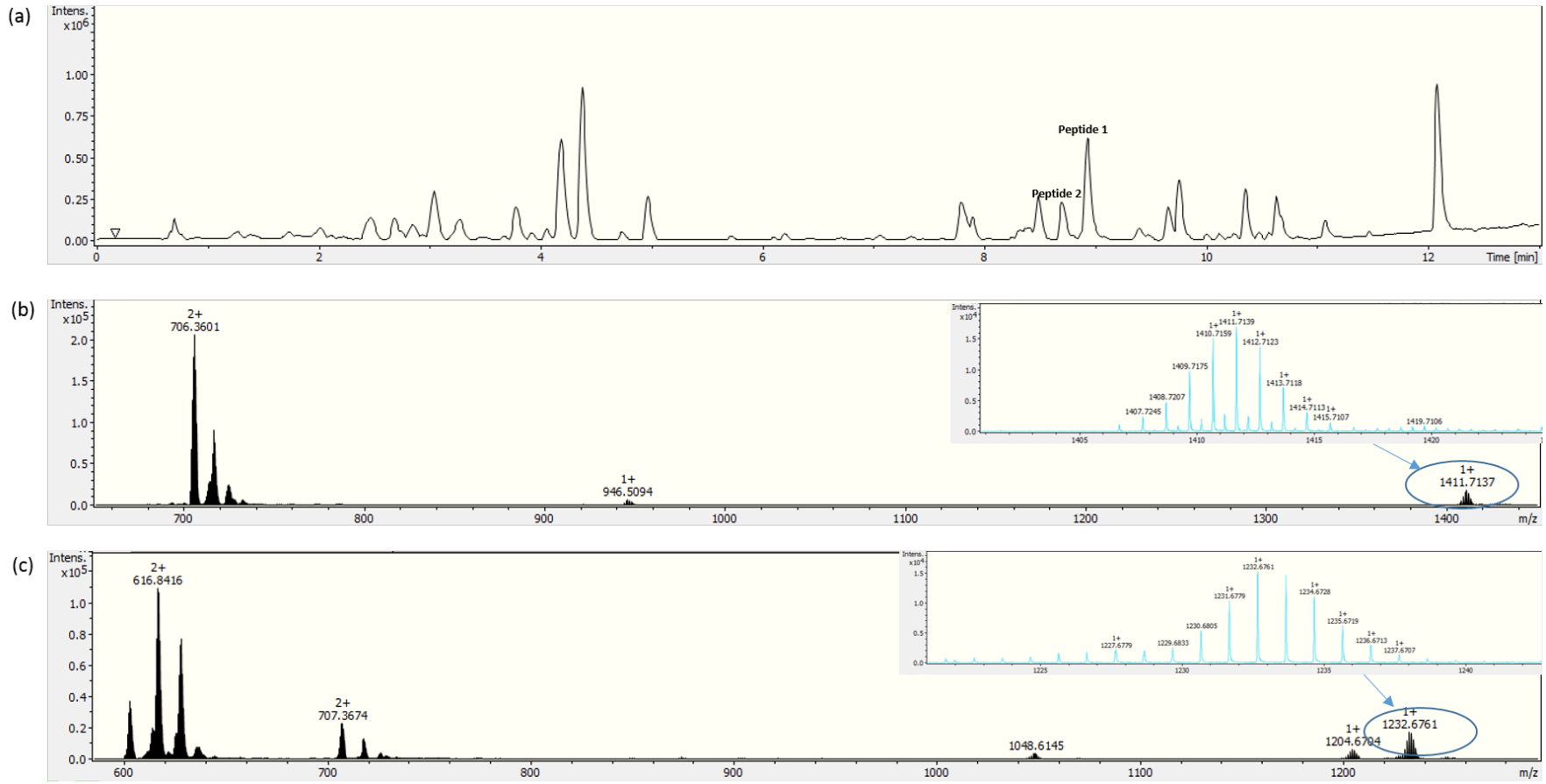

Fig 5 (a) LCMS data of crude extract of M5. (b) ESIMS of peptide **2** in M5. (b) ESIMS of peptide **1** in M5.

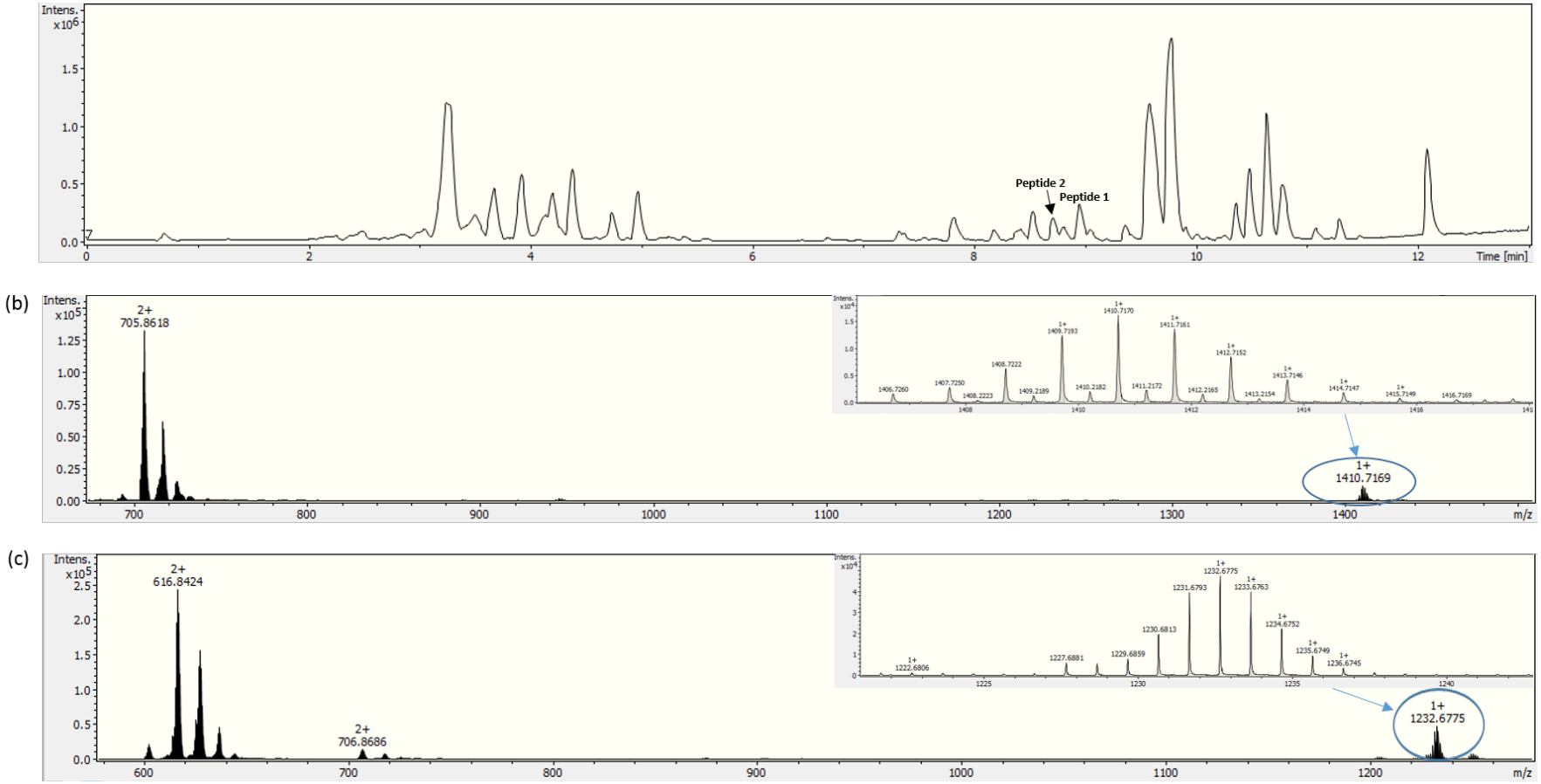

Fig 6 (a) LCMS data of crude extract of M6. (b) ESIMS of peptide **2** in M6. (b) ESIMS of peptide **1** in M6.

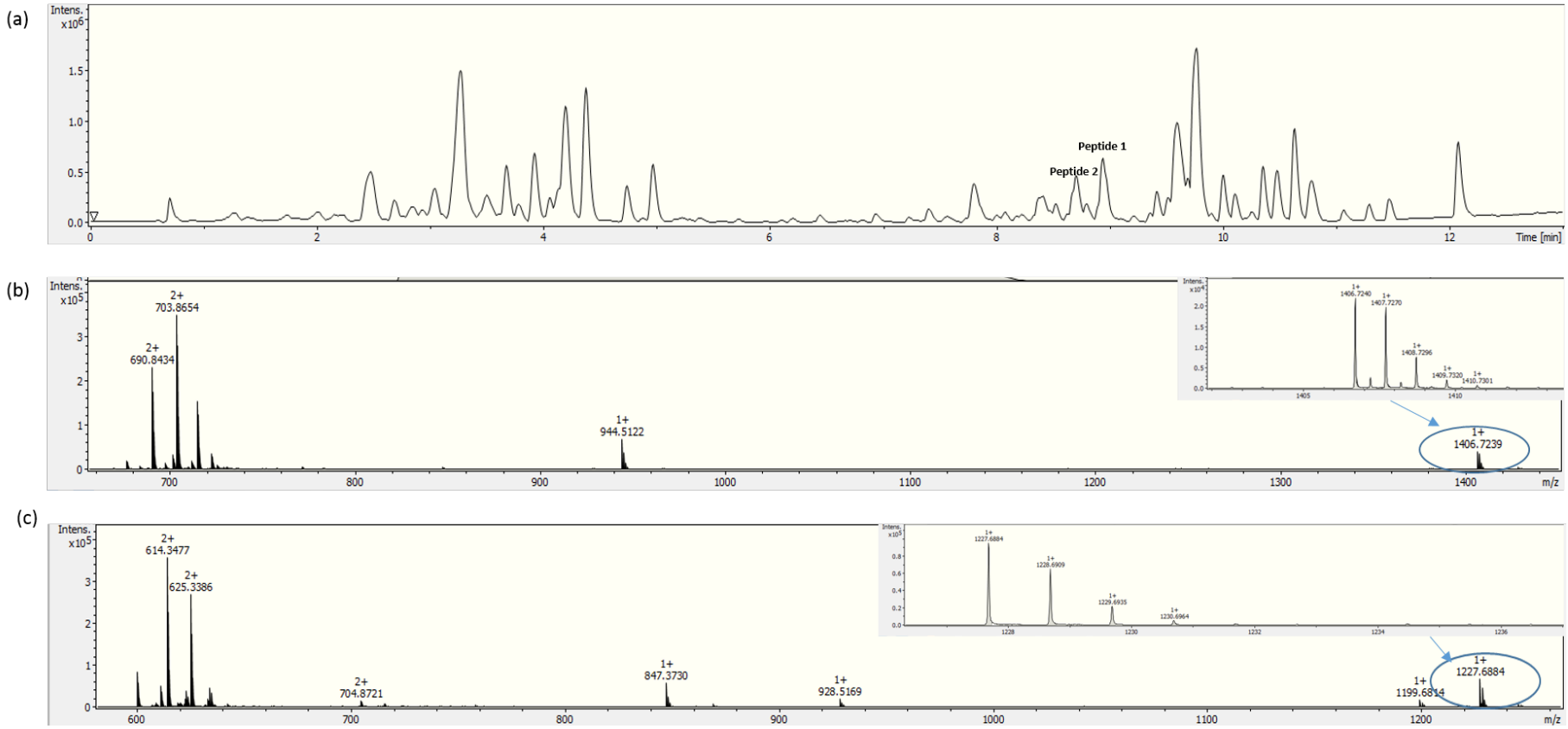

Fig 7 (a) LCMS data of crude extract of M7. (b) ESIMS of peptide **2** in M7. (b) ESIMS of peptide **1** in M7.

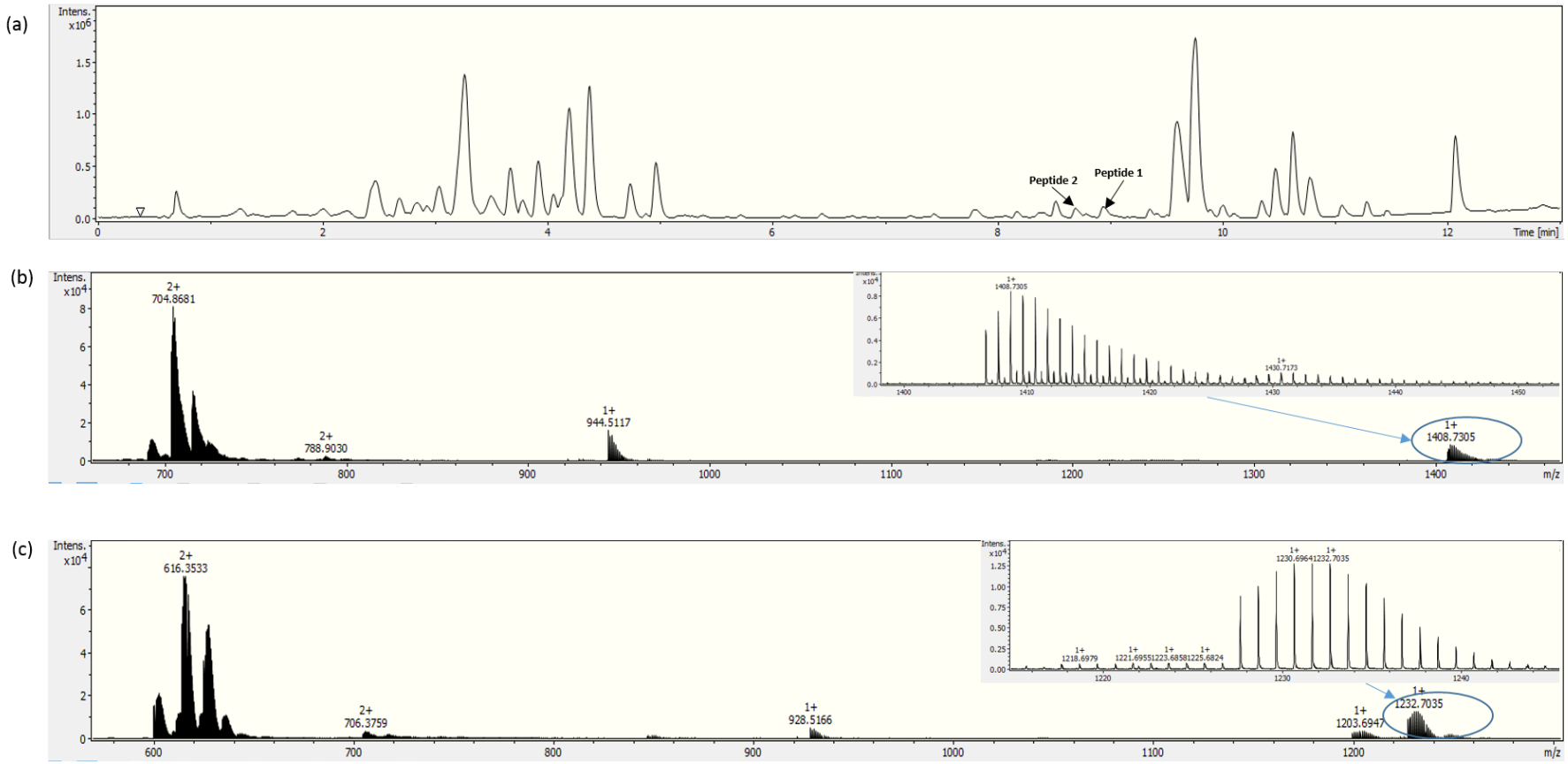

Fig 8 (a) LCMS data of crude extract of M8. (b) ESIMS of peptide **2** in M8. (b) ESIMS of peptide **1** in M8.

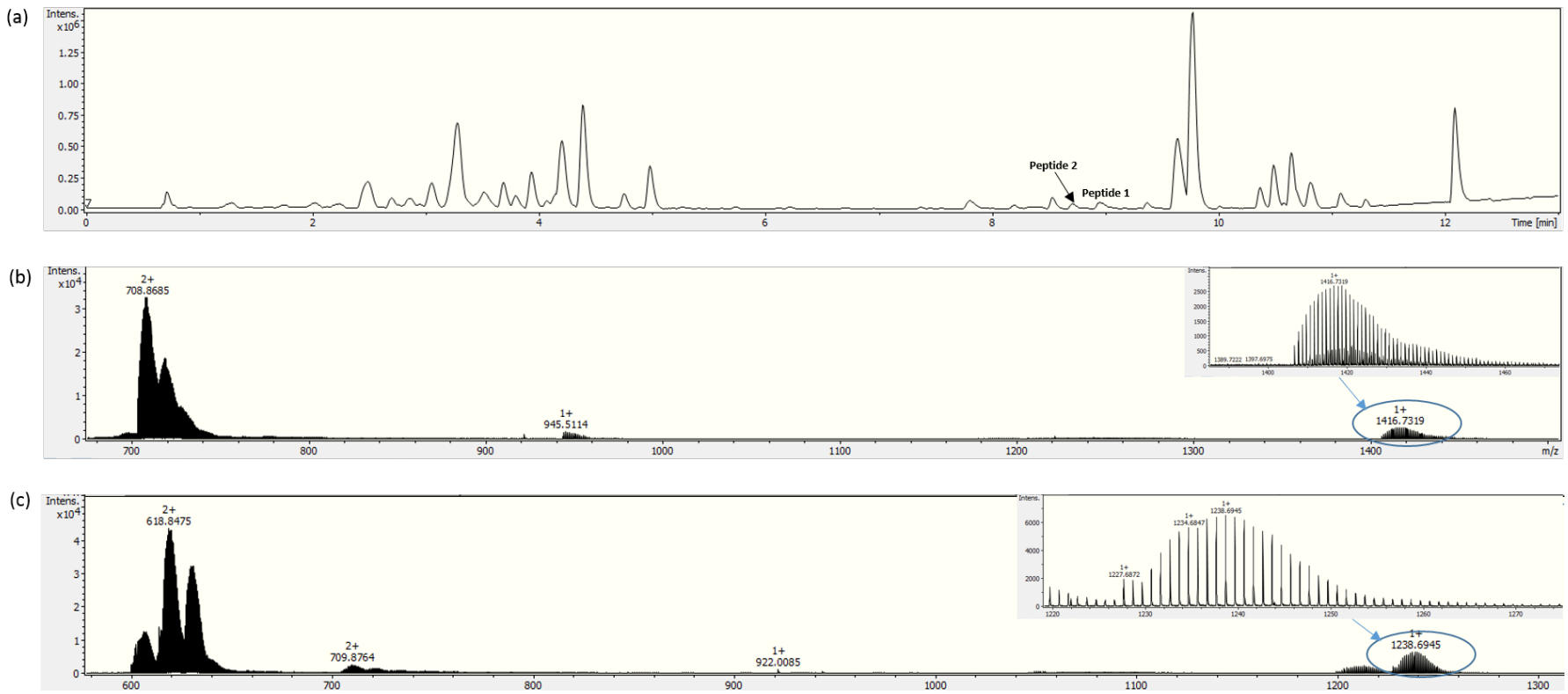

Fig 9 (a) LCMS data of crude extract of M9. (b) ESIMS of peptide **2** in M9. (b) ESIMS of peptide **1** in M9.