

# Supporting Information

## The Samholides, Swinholide Related Metabolites from a Marine Cyanobacterium cf. *Phormidium* sp.

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Table S1  $^{13}\text{C}$  NMR data comparison of samholide A (**1**), swinholide A and ankaraholide A<sup>a</sup>

No. in <b>1</b>	Compound <b>1</b> ( $\text{CDCl}_3$ ) 20-demethyl	Swinholide A ( $\text{CDCl}_3$ ) 16,20-dimethyl	$\Delta$	Ankaraholide A (( $\text{CDCl}_3$ ) 16-demethyl	$\Delta$
1	170.64	170.1	0.54	170.1	0.54
2	113.54	113.3	0.24	115	-1.46
3	153.07	153.3	-0.23	151.9	1.17
4	133.91	134.3	-0.39	134.6	-0.69
5	142.86	142.3	0.56	139.8	3.06
6	33.53	33.9	-0.37	33.6	-0.07
7	78.98	76	2.98	76.7	2.28
8	39.86	38.5	1.36	39.7	0.16
9	68.7	65.9	2.8	69.4	-0.7
10	123.27	123.3	-0.03	123.6	-0.33
11	129.67	129.9	-0.23	129.6	0.07
12	31.47	30	1.47	31.9	-0.43
13	63.36	64.6	-1.24	64.4	-1.04
14	36.41	37.4	-0.99	37.2	-0.79
15	75.02	74.4	0.62	74.8	0.22
16	41.19	40.9	0.29	40.7	0.49
17	73.48	73.9	-0.42	74.7	-1.22
18	41.39	41.1	0.29	41.7	-0.31
19	69.62	66.7	2.92	69.9	-0.28
20	42.1	41.1	1	43.6	-1.5
21	70.34	71.4	-1.06	71.4	-1.06
22	40.49	38.7	1.79	40.1	0.39
23	75.81	75.1	0.71	76.6	-0.79
24	33.43	33.3	0.13	33.5	-0.07
25	23.22	24	-0.78	24	-0.78
26	29.29	29.4	-0.11	29.7	-0.41
27	71.53	71.4	0.13	71.6	-0.07
28	35.05	34.9	0.15	35.4	-0.35
29	73.45	73.3	0.15	73.7	-0.25
30	38.88	37.7	1.18	39	-0.12
31	64.7	65.8	-1.1	65	-0.3
32	102.11	—		103	-0.89
33	73.16	—		73	0.16
34	82.43	—		84	-1.57
35	79.26	—		79.6	-0.34
36	62.32	—		62.8	-0.48
37	170.7	—		—	
38	72.37	—		—	
39	64.66	—		—	
4-Me	12.06	12.3	-0.24	12.7	-0.64
16-Me	9.32	9.1	0.22	N	
20-Me	N	9.4		9.7	
22-Me	9.69	9.2	0.49	9.8	-0.11
24-Me	17.22	17.8	-0.58	17.9	-0.68
31-Me	21.87	21.8	0.07	22.3	-0.43

<sup>a</sup> Andrianasolo, E. H.; Gross, H.; Goeger, D.; Musafija-Girt, M.; McPhail, K.; Leal, R. M.; Mooberry, S. L.; Gerwick, W. H., Isolation of Swinholide A and Related Glycosylated Derivatives from Two Field Collections of Marine Cyanobacteria. *Organic Letters* 2005, 7 (7), 1375-1378.

Table S2  $^1\text{H}$  NMR data comparison of samholide A (**1**), swinholide A and ankaraholide A<sup>a</sup>

No. in <b>1</b>	<b>Compound 1</b> ( $\text{CDCl}_3$ )	<b>Swinholide A</b> ( $\text{CDCl}_3$ )	<b>Ankaraholide A</b> ( $\text{CDCl}_3$ )
	<b>20-demethyl</b>	<b>16,20-dimethyl</b>	<b>16-demethyl</b>
2	5.78 (overlapped)	5.79 d (15.8)	5.84 d (15.6)
3	7.6 (d, 15.5)	7.58 d (15.8)	7.51 d (15.6)
5	6.34 (dd, 9.44, 3.17)	6.08 dd (9.0, 5.1)	6.25 dd (6.4, 6.3)
6	2.50 (d, 12.76)	2.46ddd (19.9, 9.7, 9.7)	2.69 m
	2.37 (m)	2.17 br d (14.9)	2.45 m
7	4.10 (m)	4.16 dd (7.2, 7.2)	4.07 m
8	2.33 (m), 1.53 (m)	1.60 m	1.60 m, 1.35 m
9	4.21 (d, 11.81)	4.52 br d (9.2)	4.38 m
10	5.68 (d, 10.26)	5.69 d (10.2)	5.74 d (10.0)
11	5.77 (m)	5.78 m	5.83 m
12	2.08 (d, 17.58), 1.96 (m)	2.28 br d (17.2), 1.89 m	2.00 m, 1.98 m
13	3.69 (m)	3.90 m	3.7 m
14	1.86 (m), 1.64 (m)	1.45 m, 2.15 m	2.22 m, 1.63 m
15	4.07 (m)	4.01 m	3.75 m
16	1.59 (m)	1.68 m	1.65 m, 1.37 m
17	3.84 (t, 9.5)	3.84 dd (9.5, 9.5)	4.11 m
18	1.80 (m), 1.62 (m)	1.63 m, 1.58 m	1.76 m
19	3.95 (m)	4.01 m	3.90 m
20	1.94 (m), 1.52 (m)	1.75 dq (9.7, 7.2)	1.69 m
21	5.84 (d, 11.37)	5.35 d (10.8)	5.38 d (10.1)
22	1.65 (m)	1.93 m	1.92 m
23	3.18 (d, 9.01)	3.13 d (9.7)	3.12 d (8.5)
24	1.65 (m)	1.66 m	1.69 m
25	1.22 (m)	1.38 m, 1.26 m	1.39 m, 1.27 m
26	1.80 (m), 1.22 (m)	1.87 m, 1.25 m	1.90 m, 1.27 m
27	3.94 (m)	4.01 m	4.02 m
28	1.76 (m), 1.55 (m)	1.82 m, 1.59 m	1.84 m, 1.62 m
29	3.50 (m)	3.54 m	3.56 m
30	1.94 (m), 1.15 (m)	1.97 m, 1.17 m	2.01 m, 1.19 m
31	3.64 (m)	3.70 m	3.66 m
32	4.78 (d, 6.09)	—	4.58 d (5.5)
33	4.76 (dd, 8.21, 6.29)	—	3.30 m
34	3.25 (t, 7.50)	—	3.26 m
35	3.33 (m)	—	3.38 m
36	4.00 (dd, 14.79, 7.83), 3.30 (m)	—	4.03 m, 3.29 m
38	4.06 (m)	—	—
39	3.70 (m), 3.50 (m)	—	—
4-Me	1.74 (s)	1.81 s	1.84 s
16-Me	0.83 (d, 6.85)	0.81 d (6.9)	—
20-Me	—	0.98 d (6.9)	0.88 d (7.0)
22-Me	0.90 (d, 6.85)	0.83 d (6.9)	0.94 d (6.7)
24-Me	0.95 (d, 6.67)	0.99 d (7.2)	1.01 d (6.3)
31-Me	1.16 (d, 6.19)	1.20 d (5.9)	1.22 d (6.3)

<sup>a</sup> Andrianasolo, E. H.; Gross, H.; Goeger, D.; Musafija-Girt, M.; McPhail, K.; Leal, R. M.; Mooberry, S. L.; Gerwick, W. H., Isolation of Swinholide A and Related Glycosylated Derivatives from Two Field Collections of Marine Cyanobacteria. *Organic Letters* 2005, 7 (7), 1375-1378.

**Table S3** NMR data for samholide B (**2**)

	$\delta_{\text{C}}$	$\delta_{\text{C}^*}$	$\delta_{\text{H}}$	$\delta_{\text{H}^*}$	COSY	HMBC(H→C)	HSQC-TOCSY	ROESY
1,1'	167.9	170.1						
2,2'	116.3	114.3	5.67 m	5.79 m	3/3'	1, 1', 4, 4', 21, 21'	3/3', 2/2'	4'-Me
3,3'	148.6	152.2	6.51 d (12.6)	7.50 d (15.6)	2/2'	1, 1', 2', 4', 4-Me, 4'-Me, 5, 5'	2/2', 3/3',	5/5'
4,4'		134.1						
4,4'-Me	15.7	12.4	1.86 s	1.77 s	5/5'	3/3', 4/4', 5/5'	4/4'-Me, 5/5'	2/2', 8/8'
5,5'	135.0	140.6	5.84 dd (7.06, 6.27)	6.14 dd (6.47)	6/6', 4/4'-Me	3/3', 4/4'-Me, 6/6', 7/7'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	3/7, 3'/7'
6,6'	33.0	33.1	2.55 dd (14.73, 5.62)	2.62 br d (13.34)	5/5', 7/7'	4/4', 5/5', 7/7', 8/8'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	9/9',
			2.38 m	2.28 m				
7,7'	77.4 <sup>b</sup>	77.7 <sup>b</sup>	4.06 m	4.10 m	6/6', 8/8'	32/32'	6/6', 8/8', 9/9', 7/7', 5/5'	32'
8,8'	39.5	39.6	2.15 m, 1.52 m	2.28 m, 1.54 m	7/7', 9/9'	6/6', 7/7', 8/8', 9/9'	5/5', 7/7', 9/9', 8/8', 6/6'	
9,9'		69.5		4.30 m	8/8', 10/10'	8/8', 10/10', 11/11', 13/13'	6/6', 12/12', 8/8', 9/9', 7/7', 10/10', 11/11', 5/5'	6a/6a'
10,10'	129.7 <sup>a</sup>	129.6 <sup>a</sup>		5.70 m	9/9', 11/11', 12/12'	9/9', 12/12'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
11,11'	123.8 <sup>a</sup>	123.7 <sup>a</sup>		5.80 m	10/10', 12/12'	9/9', 12/12', 13/13'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
12,12'	31.5 <sup>a</sup>	31.4 <sup>a</sup>		2.01 m	11/11', 13/13'	10/10', 11/11', 13/13', 14/14'	12/12', 14/14', 13/13', 7/7', 10/10', 11/11'	
13,13'	64.1	63.8		3.67 m	12/12', 14/14'a		12/12', 14/14', 15/15', 13/13'	
14,14'	36.2	35.9		1.87 m, 1.62 m	13/13', 15/15'		12/12', 14/14', 13/13', 15/15'	
15,15'		77.2 <sup>b</sup>		4.06 m	14/14'		12/12', 14/14', 13/13', 15/15',	
16,16'		41.5		1.54 m	16/16'-Me, 15/15'		13/13', 15/15', 16/16', 14/14', 16,16'-Me	
16,16'-Me	9.9 <sup>a</sup>	9.6 <sup>a</sup>	0.81 d (6.0)	0.82 d (6.0)	16/16'	15/15', 16/16', 17/17'	16,16'-Me, 16/16', 19/19', 17/17', 18/18'	
17,17'	73.9	73.6		3.85 m	18/18'		16/16'-Me, 18/18', 17/17', 19/19'	
18,18'	40.9	41.2		1.76 m, 1.63 m			17/17', 18/18', 19/19', 20/20'	
19,19'	69.3	68.8	3.93 m		3.88, m		20/20', 21/21', 19/19', 18/18'	
20,20'	41.1	41.5		1.94 m, 1.53 m	20/20'		20/20', 21/21', 19/19'	
21,21'	71.1	71.4	5.63 d (9.82)		5.71 m	1', 1,19, 19', 20', 22-Me, 22'-Me, 23, 23'	20/20', 19/19'	
22,22'	41.1	40.9		1.64 m	22/22'		22,22'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
22,22'-Me	10.0	10.2	0.87 d (6.81)		0.89 d (6.86)	22/22', 24/24'	22,22'-Me, 22/22', 23/23'	
23,23'	76.6	76.1	3.17 d (9.69)		3.12 d (9.59)	21/21', 22/22', 24/24'-Me, 25/25'	22/22'-Me, 22/22', 23/23'	22/22'-Me, 24/24'-Me
24,24'		33.5		1.67 m	24/24'		24/24'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
24,24'-Me	17.6 <sup>a</sup>	17.5 <sup>a</sup>	0.97 d (7.15)		0.95 d (7.07)	23/23', 24/24', 25/25'	24,24'-Me, 26/26', 24/24', 27/27', 25/25'	
25,25'	24.0 <sup>a</sup>	23.8 <sup>a</sup>		1.25 m			24,24'-Me, 26/26', 25/25', 24/24', 27/27'	

26,26'	29.4	29.3		1.88 m, 1.25 m		24/24'-Me, 25/25', 26/26', 27/27'
27,27'	71.6	71.5		3.99 m		24/24'-Me, 25/25', 26/26', 28/28', 30/30', 29/29'
28,28'		35.1		1.82 m, 1.59 m		31/31', 30/30', 28/28', 29/29', 27/27'
29,29'		73.4		3.53 m		28/28', 29/29', 30/30', 31/31', 31/31'-Me,
30,30'		38.9		1.99 m, 1.18 m		31/31'-Me, 28/28', 30/30', 31/31', 29/29'
31,31'		64.8		3.67 m		31/31'-Me, 28/28', 30/30', 31/31', 29/29'
31,31'-Me	22.0 <sup>a</sup>	21.9 <sup>a</sup>	1.18 d (6.36)	1.17 d (6.14)	31/31'	31,31'-Me, 30/30', 31/31', 28/28', 29/29'
32,32'	100.7	101.2	4.67 d (6.91)	4.74 d (6.80)		32/32', 33/33', 34/34', 35/35', 36/36'
33,33'		73.4		4.82 dd (8.33, 7.02)	34/34'	32/32', 34/34', 37/37'
34,34'	82.1	82.4		3.34 m	33/33'	32/32', 33/33', 34/34', 35/35', 36/36'
35,35'	79.0	79.3		3.34 m		32/32', 33/33', 34/34', 35/35', 36/36'
36,36'		62.7		4.05 m, 3.28 m	35/35'	32/32', 34/34', 35/35'
37,37'	171.4	170.9				
38,38'	72.5	72.4	4.28 m	4.20 brs	39/39'	37/37', 39/39'
39,39'	64.4	64.5		3.88 m, 3.66 m	38/38'	38/38', 39/39'
15,15'-OMe	57.1 <sup>a</sup>	57.2 <sup>a</sup>		3.34 s		15,15'-OMe
29,29'-OMe		55.4		3.32 s		29,29'-OMe
34,34'-OMe	60.2 <sup>a</sup>	60.1 <sup>a</sup>		3.48 s		34,34'-OMe
35,35'-OMe	58.6 <sup>a</sup>	58.7 <sup>a</sup>		3.44 s		35,35'-OMe

<sup>a</sup> Can be exchanged.

<sup>b</sup> Overlapped with CDCl<sub>3</sub>, assigned using HMBC, HSQC and HSQC-TOCSY.

Table S4 NMR data for samholide C (3)

	$\delta_{\text{C}}$ / $\delta_{\text{C}^*}$	$\delta_{\text{H}}$ / $\delta_{\text{H}^*}$	COSY	HMBC	HSQC-TOCSY	ROESY
1,1'	170.3					
2,2'	114.2	5.79 d (15.59)	3/3'	3/3', 1/1'	3/3', 2/2'	4/4'-Me
3,3'	152.4	7.53 d (15.56)	2/2'	1/1', 2/2', 4/4', 4/4'-Me, 5/5'	2/2', 3/3'	5/5'
4,4'	134.6					
4,4'-Me	12.4	1.82 s	5/5'	3/3', 4/4', 5/5'	4/4'-Me, 5/5'	2/2', 6/6'
5,5'	140.8	6.31 dd (7.55, 7.37)	6/6', 4/4'-Me	4/4'-Me, 3/3', 6/6', 7/7'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	7/7', 3/3'
6,6'	33.2	2.59 ddd (2.85, 6.14, 14.47) 2.37 dt (8.86, 14.34)	5/5', 7/7'	4/4', 5/5', 7/7', 8/8'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	4/4'-Me, 9/9'
7,7'	76.6 <sup>a</sup>	4.04 m	6/6', 8/8'	5/5', 6/6', 8/8', 9/9', 32/32'	6/6', 8/8', 9/9', 7/7', 5/5'	5/5', 32/32'
8,8'	39.8	2.25 ddd (5.02, 9.81, 15.0) 1.63 m	7/7', 9/9'	6/6', 7/7', 9/9', 10/10'	5/5', 7/7', 9/9', 8/8', 6/6'	4/4'-Me, 13/13'
9,9'	69.6	4.30 m	8/8', 10/10'	7/7', 8/8', 10/10', 11/11', 13/13'	6/6', 12/12', 8/8', 9/9', 7/7', 10/10', 11/11', 5/5'	6a/6a', 14/14'
10,10'	129.8	5.74 m	9/9', 11/11', 12/12'	9/9', 12/12'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
11,11'	123.5	5.74 m	10/10', 12/12'	9/9', 12/12', 13/13'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
12,12'	31.6	1.97 m	11/11', 13/13'	10/10', 11/11', 13/13', 14/14'	12/12', 14/14', 13/13', 7/7', 10/10', 11/11'	
13,13'	63.6	3.63 m	12/12', 14/14'a		12/12', 14/14', 15/15', 13/13'	5/5', 7/7', 8a/8a'
14,14'	36.9	1.78 m, 1.64 m	13/13', 15/15'	9/9', 14/14', 15/15'	12/12', 14/14', 13/13', 15/15'	
15,15'	76	4.01 m	14/14'	14/14', 15/15'-OMe, 16/16'-Me, 16/16', 17/17'	12/12', 14/14', 13/13', 15/15',	13/13'
16,16'	41.5	1.51 m	16/16'-Me, 15/15'	16/16'-Me, 15/15'	13/13', 15/15', 16/16', 14/14', 16,16'-Me	
16,16'-Me	9.3	0.78 d (6.98)	16/16'	15/15', 16/16', 17/17'	16,16'-Me, 16/16', 19/19', 17/17', 18/18'	
17,17'	74	3.84 t (9.70)	18/18'	15/15', 16/16'-Me, 16/16', 18/18', 19/19'	16/16'-Me, 18/18', 17/17', 19/19'	16/16'-Me
18,18'	40.8	1.70 m, 1.41 m		17/17', 19/19'	17/17', 18/18', 19/19', 20/20'	
19,19'	69.9	3.88 t (10.55)		17/17', 18/18', 21/21'	20/20', 21/21', 19/19', 18/18'	
20,20'	42.2	1.87 m	20/20'	21/21',	20/20', 21/21', 19/19'	
21,21'	70.6	5.56 d (11.09)		1/1', 19/19', 23/23', 20/20', 22/22', 22/22'-Me	20/20', 19/19'	22-Me, 19/19'
22,22'	40.8	1.65 m	22/22'		22,22'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
22,22'-Me	10.1	0.90 d (6.89)	22/22', 24/24'	21/21', 22/22', 23/23'	22,22'-Me, 22/22', 23/23'	
23,23'	76.3	3.19 m		21/21', 22/22', 24/24', 24/24'-Me, 25/25'	22/22'-Me, 22/22', 23/23'	22/22'-Me, 24/24'-Me, 21/21'
24,24'	33.2	1.68 m	24/24'	23/23', 24/24'-Me	24/24'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	

24,24'-Me	17.4	0.93 d (6.73)	23/23',24/24',25/25'	24,24'-Me, 26/26', 24/24', 27/27', 25/25'
25,25'	23.9	1.34 m, 1.17 m	24/24', 24/24'-Me, 26/26'	24,24'-Me, 26/26', 25/25', 24/24', 27/27'
26,26'	29.4	1.83 m, 1.26 m	25/25', 27/27'	24/24'-Me, 25/25', 26/26', 27/27'
27,27'	71	3.98 m		24/24'-Me, 25/25', 26/26', 28/28', 30/30', 29/29'
28,28'	35	1.79 m, 1.59 m	29/29'	31/31', 30/30', 28/28', 29/29',27/27'
29,29'	73.4	3.52 ddd (4.4, 9.83, 14.17)	27/27', 28/28', 31/31', 29/29'-OMe	28/28', 29/29', 30/30', 31/31', 31/31'-Me,
30,30'	38.7	1.95 m, 1.18 m		31/31'-Me, 28/28', 30/30', 31/31', 29/29'
31,31'	64.9	3.69 dddd (2.88, 6.13, 12.0, 15.0)	27/27', 29/29', 31/31'-Me	31/31'-Me, 28/28', 30/30', 31/31', 29/29'
31,31'-Me	22	1.20 d (6.18)	31/31'	31,31'-Me, 30/30', 31/31', 28/28', 29/29'
32,32'	103.3	4.43 d (6.64)	7/7', 34/34', 36/36'	32/32', 33/33', 34/34', 35/35', 36/36'
33,33'	73.4	3.28 t (7.15)	34/34'	32/32', 33/33', 34/34', 35/35', 36/36'
34,34'	83.5	3.24 m	33/33'	32/32', 33/33', 34/34', 35/35', 36/36'
35,35'	79.4	3.24 m	34/34'	32/32', 33/33', 34/34', 35/35', 36/36'
36,36'	62.5	3.98 m, 3.16 m	35/35'	32/32', 33/33', 34/34', 35/35', 36/36'
15,15'-OMe	57.5	3.35 s	15/15'	
29,29'-OMe	55.4	3.32 s	29/29'	
34,34'-OMe	60.2	3.56 s	34/34'	
35,35'-OMe	58.6	3.45 s	35/35'	

<sup>a</sup> Overlapped with CDCl<sub>3</sub>, assigned using HMBC, HSQC and HSQC-TOCSY.

Table S5 NMR data for samholide D (**4**)

	$\delta_{\text{C}}$	$\delta_{\text{C}^{\prime}}$	$\delta_{\text{H}}$	$\delta_{\text{H}^{\prime}}$	COSY	HMBC	HSQC-TOCSY	ROESY
1,1'	167.4	170.9						
2,2'	116.7	115.8	5.69 m	5.82 m	3/3'	4/4', 1/1'	3/3', 2/2'	3, 4'-Me
3,3'	148.5	150.5	6.46 d (12.41)	7.39 d (15.56)	2/2'	1, 2, 4, 4'-Me, 5	1', 4', 4'-Me	2/2', 3/3', 5/5'
4,4'		133.6						
4,4'-Me	16.2	12.7	1.84 s	1.82 s	5/5'	3/3', 4/4', 5/5'	4/4'-Me, 5/5'	6, 6', 2'
5,5'	134.8	137.9	5.98 t (6.33)	6.09 t (6.23)	6/6', 4/4'-Me	4/4'-Me, 3/3', 6/6'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	7/7', 3/3'
6,6'	33.3	33.4	2.56 m	2.64 m	5/5', 7/7'	4/4', 5/5', 7/7', 8/8'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	9/9',
			2.34 m	2.36 m				
7,7'	76.7 <sup>b</sup>	75.7 <sup>b</sup>	4.01 m	4.00 m	6/6', 8/8'		6/6', 8/8', 9/9', 7/7', 5/5'	
8,8'		39.1		2.10 m, 1.64 m	7/7', 9/9'	6/6', 7/7', 9/9'	5/5', 7/7', 9/9', 8/8', 6/6'	13/13'
9,9'	69.2	68.6		4.36 m	8/8', 10/10'		6/6', 12/12', 8/8', 9/9', 7/7', 10/10', 11/11', 5/5'	6a/6a'
10,10'	129.6 <sup>a</sup>	129.5 <sup>a</sup>		5.74 m	9/9', 11/11', 12/12'	9/9', 12/12'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
11,11'	124.0	123.2		5.80 m	10/10', 12/12'	9/9', 12/12'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
12,12'	31.4	31.3		1.96 m	11/11', 13/13'	10/10', 11/11', 13/13', 14/14'	12/12', 14/14', 13/13', 7/7', 10/10', 11/11'	
13,13'	64.4	64.3		3.64 m	12/12', 14/14'a		12/12', 14/14', 15/15', 13/13'	
14,14'	36.1	35.7		1.87 m, 1.55 m	13/13', 15/15'		12/12', 14/14', 13/13', 15/15'	
15,15'		78.0 <sup>b</sup>		3.78 m	14/14'	15/15'-OMe	12/12', 14/14', 13/13', 15/15',	16/16'-Me, 15/15'-OMe
16,16'	41.0	41.2		1.55 m	16/16'-Me, 15/15'		13/13', 15/15', 16/16', 14/14', 16,16'-Me	
16,16'-Me	10.0	10.2	0.83 d (6.54)	0.84 d (6.32)	16/16'	15/15', 16/16', 17/17'	16,16'-Me, 16/16', 19/19', 17/17', 18/18'	
17,17'	73.8	74.2		3.80 m	18/18'		16/16'-Me, 18/18', 17/17', 19/19'	16/16'-Me
18,18'		41.7		1.79 m, 1.41 m			17/17', 18/18', 19/19', 20/20'	
19,19'		69.5		3.85 m			20/20', 21/21', 19/19', 18/18'	
20,20'	41.9	42.1		1.87 m, 1.53 m	20/20'		20/20', 21/21', 19/19'	
21,21'	71.1	70.7	5.64 m	5.66 m		1'/1, 22/22'-Me, 19/19'	20/20', 19/19'	19/19', 23/23'
22,22'		40.5		1.64 m	22/22'		22,22'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
22,22'-Me	10.3	10.5	0.87 d (8.45)	0.89 d (7.47)	22/22', 24/24'	21/21', 22/22', 23/23'	22,22'-Me, 22/22', 23/23'	
23,23'		76.5		3.09 m		21/21', 24/24'-Me, 25/25'	22/22'-Me, 22/22', 23/23'	22/22'-Me, 24/24'-Me, 21/21'
24,24'	33.0	32.8		1.69 m	24/24'		24/24'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
24,24'-Me	17.7	17.6		0.97 d (6.10)		23/23', 24/24', 25/25'	24,24'-Me, 26/26', 24/24', 27/27', 25/25'	
25,25'	24.2	23.9		1.37 m, 1.25 m			24,24'-Me, 26/26', 25/25', 24/24', 27/27'	
26,26'	29.8	29.3		1.86 m, 1.25 m			24/24'-Me, 25/25', 26/26', 27/27'	

27,27'	71.7		3.98 m		24/24'-Me, 25/25', 26/26', 28/28', 30/30', 29/29'	
28,28'	35		1.82 m, 1.56 m		31/31', 30/30', 28/28', 29/29', 27/27'	
29,29'	73.4		3.52 m	OMe, 31/31'	28/28', 29/29', 30/30', 31/31', 31/31'-Me,	
30,30'	38.9		1.97 m, 1.16 m		31/31'-Me, 28/28', 30/30', 31/31', 29/29'	
31,31'	64.7		3.68 m	31/31'-Me	31/31'-Me, 28/28', 30/30', 31/31', 29/29'	
31,31'-Me	22		1.20 d (5.9)	31/31'	31,31'-Me, 30/30', 31/31', 28/28', 29/29'	
32,32'	101.9	102.6	4.46 d (6.6)	4.39 m	7/7', 36/36'	32/32', 33/33', 34/34', 35/35', 36/36' 7/7', 34/34'
33,33'		73.4		3.29 m	34/34'	32/32', 33/33', 34/34', 35/35', 36/36'
34,34'	83.4	83.5		3.20 m	33/33'	33/33', 35/35', OMe,
35,35'	79.0	79.3		3.25 m		32/32', 33/33', 34/34', 35/35', 36/36'
36,36'		62.6		3.99 m, 3.21 m	35/35'	34/34', 36/36', OMe
15,15'-OMe		57.1		3.35 s		32/32', 33/33', 34/34', 35/35', 36/36'
29,29'-OMe		55.4		3.34 s		15,15'-OMe
34,34'-OMe	60.3	60.2		3.59 s		29,29'-OMe
35,35'-OMe		58.5	3.45 s	3.44 s		34,34'-OMe
						35,35'-OMe

<sup>a</sup> Can be exchanged.

<sup>b</sup> Overlapped with CDCl<sub>3</sub>, assigned using HMBC, HSQC and HSQC-TOCSY.

Table S6 NMR data for samholide E (**5**)

	$\delta_{\text{C}}$	$\delta_{\text{C}'}$	$\delta_{\text{H}}$	$\delta_{\text{H}'}$	COSY	HMBC	ROESY
1,1'	170.5	169.9					
2,2'	113.5	114.4		5.79 d (15.48)	3/3'	1/1', 4/5'	4/4'-Me, 22/22'-Me
3,3'	153.1	152.1	7.57 d (15.55)	7.52 d (15.56)	2/2'	1/1', 2/2', 4/4', 4/4'-Me, 5/5'	5/5', 38
4,4'	133.7	134.5					
4,4'-Me	12.1	12.4	1.75 s	1.82 s	5/5'	3/3', 4/4', 5/5'	2/2', 6/6'
5,5'	142.7	140.3	6.32 m	6.33 m	6/6', 4/4'-Me	4/4'-Me, 3/3', 6/6', 7/7'	7/7', 3/3'
6,6'	33.6	33.2	2.50 d (13.39)	2.67 d (12.99)	5/5', 7/7'(weak)	4/4', 5/5', 7/7',	7/7', 9/9'
			2.35 m	2.35 m			
7,7'	78.6	76.6	4.15 m	4.07 m	6/6', 8/8'		5/5', 32
8,8'	39.8	39.7		2.29 m, 1.67 m	7/7', 9/9'	6/6', 7/7', 9/9', 10/10'	13/13'
9,9'	68.9	69.2	4.21 d (11.37)	4.31 brs	8/8', 10	8/8', 10, 13/13'	6a/6a'
10,10'	129.7	129.8	5.72 m	5.78 m	9/9', 11/11', 12/12'	9/9', 12/12'	
11,11'	123.4	123.7	5.80 m	5.71 m	10/10', 12/12'	9/9', 12/12', 13/13'	
12,12'		31.5		2.08 d (17.61), 1.98 m	11/11', 13/13'	10/10', 11/11', 13/13', 14/14'	
13,13'	63.5	64.1		3.69 m	12/12', 14/14'a		8/8', 7/7'
14,14'	36.2	36.7		1.84 m, 1.63 m	13/13', 15/15'		15/15'-OMe
15,15'	75.7	75.4		4.05 m	14/14'	14/14', 15/15'-OMe, 16/16'-Me, 16/16'	16/16'-Me
16,16'		41.6		1.59 m	16/16'-Me, 15/15'		
16,16'-Me	9.2	9.0	0.80 d (7.14)	0.78 d (7.02)	16/16'	15/15', 16/16', 17/17'	17/17'
17,17'	73.6	73.8		3.88 m	18/18'	15/15', 16/16', 18/18', 19/19'	16/16'-Me
18,18'	40.9	40.6		1.74 m, 1.55 m			
19,19'	70.0	69.4	3.99 m	3.88 m			
20,20'		42.4		1.90 m, 1.55 m	20/20'		
21,21'	70.3	70.5		5.71 m		1/1'	
22,22'	41.2	40.9		1.69 m	22/22'	22/22'-Me, 23/23'	
22,22'-Me	9.9	10.1	0.91 d (6.92)	0.89 d (7.13)	22/22', 24/24'	21/21', 22/22', 23/23'	
23,23'	76.1	76.5		3.20 m		21/21', 22/22', 24/24'-Me, 25/25'	
24,24'	33.4	33.0		1.69 m	24/24'	23/23', 24/24'-Me	
24,24'-Me		17.5	0.96 d (7.17)	0.95 d (7.23)		23/23', 24/24', 25/25'	
25,25'	23.6	24.0		1.35 m, 1.20 m			
26,26'		29.8		1.86 m, 1.27 m			

27,27'	71.4	71.3		3.98 m		
28,28'	35.1	35.0		1.81 m, 1.59 m	29/29', 30/30'	
29,29'		73.4		3.52 m	29/29'-OMe	
30,30'		38.8		1.98 m, 1.19 m	,	
31,31'	64.8	64.9		3.69 m	29/29', 31/31'-Me	
31,31'-Me	21.9	22.0	1.17 d (5.90)	1.19 d (6.44)	31/31'	30/30',31/31'
32,32'	101.4	102.9	4.81 d (4.98)	4.46 d (5.45)		7/7', 33, 36/36'
33,33'	73.1	73.3	4.74 t (6.11)	3.27 m	34/34'	32/32',34/34',35,37
34,34'	82.1	83.3	3.32 m	3.25 m	33/33'	33', 34/34'-OMe, 35/35'
35,35'		79.2		3.31 m		32/32', 34/34'
36,36'	62.2	62.5	4.01 m, 3.25 m	4.00 m, 3.23 m	35/35'	
37,37'	170.5	/N				
38,38'	72.6	/N	4.13 m	N	39/39'	37, 39
39,39'	64.6	/N	3.77 m, 3.63 m	N	38/38'	37
15,15'-OMe	57.6	57.5	3.35 s	3.33 s		
29,29'-OMe		55.4		3.32 s		
34,34'-OMe		60.1	3.47 s	3.56 s		
35,35'-OMe		58.5	3.43 s	3.45 s		

Table S7 NMR data for samholide F (**6**)

	$\delta_{\text{C}}$	$\delta_{\text{C}^{\prime}}$	$\delta_{\text{H}}$	$\delta_{\text{H}^{\prime}}$	COSY	HMBC	HSQC-TOCSY	ROESY
1,1'	167.6	169.5						
2,2'	116.5	115.3	5.68 d (12.47)	5.81 d (15.68)	3/3'	1'/1,4/4'	3/3', 2/2'	4/4'-Me,
3,3'	148.7	151.1	6.52 d (12.62)	7.44 d (15.54)	2/2'	1'/1, 2/2', 4/4', 4/4'-Me, 5/5'	2/2', 3/3',	5/5'
4,4'		134.7						
4,4'-Me	15.8	12.6	1.86 s	1.81 s	5/5' (weak)	3/3', 4/4', 5/5'	4/4'-Me, 5/5'	2/2', 6/6'
5,5'	134.1	138.5	5.86 t (7.00)	6.14 t (6.87)	6/6', 4/4'-Me	4/4'-Me, 3/3', 6/6', 7/7'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	7/7', 3/3', 8/8'
6,6'		33	2.57 ddd (4.06, 6.48, 13.87)	2.69 ddd (4.38, 6.03, 11.73)	5/5', 7/7'	4/4', 5/5', 7/7', 8/8'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	9/9', 4/4'-Me
				2.40 dt (7.02, 15.36)	2.28 dt (7.45, 15.12)			
7,7'	77.0	75.7	4.00 m	3.97 m	6/6', 8/8'	5/5', 32/32'	6/6', 8/8', 9/9', 7/7', 5/5'	5/5', 32/32'
8,8'	39.6	39.3	2.10 m	2.10 m	7/7', 9/9'	6/6', 7/7', 9/9', 10/10'	5/5', 7/7', 9/9', 8/8', 6/6'	13/13'
			1.55 m	1.67 m				
9,9'	69.0	69.6	4.29 m	4.39 m	8/8', 10/10' (weak)	8/8', 10/10', 11/11', 13/13',	6/6', 12/12', 8/8', 9/9', 7/7', 10/10', 11/11', 5/5'	6a/6a', 7/7'
10,10'		129.6	5.69 m	5.78 m	9/9', 11/11'	9/9', 12/12'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
11,11'	124.0	123.8	5.80 m	5.69 m	10/10', 12/12'	9/9', 12/12', 13/13'(weak)	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
12,12'	31.3	31.2		1.97 m	11/11', 13/13'	11/11', 13/13', 14/14'	12/12', 14/14', 13/13', 7/7', 10/10', 11/11'	
13,13'	64.4	64.3		3.68 m	12/12', 14/14'a		12/12', 14/14', 15/15', 13/13'	8/8'
14,14'	35.7	35.6		1.88 m, 1.56 m	13/13', 15/15'	12/12', 13/13', 15/15', 16/16'	12/12', 14/14', 13/13', 15/15'	
15,15'		77.0 <sup>a</sup>	3.78 ma	3.82 ma	14/14'	15/15'-OMe, 16/16'-Me, 16/16'	12/12', 14/14', 13/13', 15/15',	
16,16'	40.9	40.5		1.65 m	16/16'-Me, 15/15'	16/16'-Me, 17/17'	13/13', 15/15', 16/16', 14/14', 16,16'-Me	
16,16'-Me	10.2	9.9	0.82 d (6.91)	0.81 d (7.13)	16/16'	15/15', 16/16', 17/17'	16,16'-Me, 16/16', 19/19', 17/17', 18/18'	
17,17'	74.3	74.2	3.76 m	3.86 m	18/18'	15/15', 16/16'-Me, 18/18', 19/19'	16/16'-Me, 18/18', 17/17', 19/19'	16/16'-Me
18,18'	41.7	41.4		1.70 m, 1.55 m	17/17', 19/19'	17/17', 19/19'	17/17', 18/18', 19/19', 20/20'	
19,19'		69		3.88 m	18/18', 20/20'	17/17', 18/18'	20/20', 21/21', 19/19', 18/18'	
20,20'		41.8		1.87 m, 1.53 m	19/19', 21/21'	21/21'	20/20', 21/21', 19/19'	

21,21'	71.3	70.8	5.60 d (10.39)	5.63 d (10.00)	20/20', 22/22'	1/1', 19/19', 23/23', 20/20', 22/22', 22/22'-Me	20/20', 19/19'	19/19', 23/23'
22,22'	41.1	40.9		1.76 m	22/22'-Me, 21/21', 23/23'	22/22'-Me, 23/23'	22,22'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
22,22'-Me	10.3		0.89 d (6.78)	0.88 d (6.78)	22/22'	21/21', 22/22', 23/23'	22,22'-Me, 22/22', 23/23'	
23,23'	76.7		3.15 d (9.39)	3.12 d (9.83)	22/22', 24/24'	21/21', 22/22', 22/2'-Me, 24/24'-Me, 24/24', 25/25'	22/22'-Me, 22/22', 23/23'	22/22'-Me, 24/24'-Me, 21/21'
24,24'	33.4			1.68 m	24/24'-Me,	22/22'-Me, 24/24'-Me	24/24'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
24,24'-Me	17.6		0.98 d (6.80)	0.96 d (6.80)	24/24'	23/23', 24/24', 25/25'	24,24'-Me, 26/26', 24/24', 27/27', 25/25'	
25,25'	24			1.39 m, 1.24 m	26/26',		24,24'-Me, 26/26', 25/25', 24/24', 27/27'	
26,26'	29.3			1.87 m, 1.25 m	25/25', 27/27'		24/24'-Me, 25/25', 26/26', 27/27'	
27,27'	71.5			3.99 m	26/26', 28/28'	29/29', 31/31'	24/24'-Me, 25/25', 26/26', 28/28', 30/30', 29/29'	29/29'-OMe, 31/31'
28,28'	35			1.82 m, 1.58 m	29/29', 30/30'		31/31', 30/30', 28/28', 29/29', 27/27'	
29,29'	73.4			3.52 m	28/28', 31/31'	27/27', 28/28', 31/31'	28/28', 29/29', 30/30', 31/31', 31/31'-Me,	31/31'
30,30'	38.9			1.99 m, 1.18 m	29/29',		31/31'-Me, 28/28', 30/30', 31/31', 29/29'	
31,31'	64.7			3.69 m	31/31'-Me	29/29', 31/31-Me	31/31'-Me, 28/28', 30/30', 31/31', 29/29'	
31,31'-Me	22			1.19 d (6.25)	31/31'	30/30', 31/31'	31,31'-Me, 30/30', 31/31', 28/28', 29/29'	
32,32'	100.4	102.1	4.65 d (6.77)	4.39 d (6.72)		7/7', 34/34', 36/36'	32/32', 33/33', 34/34', 35/35', 36/36'	7/7', 34/34', 5/5', 6/6'
33,33'	73.4		4.83 dd (6.85, 8.39)	3.52 m	34/34'	32/32', 34/34', 37/37', 35/35'	32/32', 33/33', 34/34', 35/35', 36/36'	34-OMe, 36
34,34'	82.0	83.5	3.35 m	3.21 m	33/33'		32/32', 33/33', 34/34', 35/35', 36/36'	
35,35'	79.1			3.30 m		34/34', 36/36', 35/35'-OMe	32/32', 33/33', 34/34', 35/35', 36/36'	

36,36'	62.6		3.99 m, 3.25 m	35/35'	32/32', 34/34', 35/35'	32/32', 33/33', 34/34', 35/35', 36/36'
37,37'	171.5	N				
38,38'	72.4	N	4.27 m	N	39/39'	38/38', 39/39'
39,39'	64.3	N	3.80 m	N	38/38'	38/38', 39/39'
15,15'-OMe	57.2	57.1	3.34 s	3.32 s		15,15'
29,29'-OMe		55.4		3.32 s		29,29'
34,34'-OMe	60.2	60.3		3.48 s		34
35,35'-OMe	58.7	58.5 <sup>a</sup>		3.44 s		35

<sup>a</sup> Overlapped with CDCl<sub>3</sub>, assigned using HMBC, HSQC and HSQC-TOCSY.

Table S8 NMR data for samholide G (7)

	$\delta_{\text{C}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{H}'}$	COSY	HMBC	HSQC-TOCSY	ROESY
1,1'	169.5	167.4						
2,2'	114.5	116.2	5.80 m	5.66 d (12.72)	3/3'	1/1', 3/3', 4/4'	3/3', 2/2'	4-Me
3,3'	153.9	148.3	7.47 d (15.63)	6.46 d (12.69)	2/2'	1.1', 2/2', 4, 4/4'-Me, 5/5'	2/2', 3/3',	5/5', 38, 4'-Me
4,4'	134.1							
4,4'-Me	12.5	16.1	1.78 s	1.86 s	5/5'	3/3', 4/4', 5/5'	4/4'-Me, 5/5'	2/2', 6/6'
5,5'	140	134	6.11 t (6.88)	5.97 brs	6/6', 4/4'-Me	4/4'-Me, 3, 6, 7	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	7/7', 3/3'
6,6'	33.6	33.2	2.59 m	2.57 m	5/5', 7/7'	4/4', 5/5', 7/7', 8/8'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	9/9'
			2.34 m	2.41 dt (7.38, 14.56)				
7,7'	77.2	76.7 <sup>b</sup>	4.03 m	3.97 m	6/6', 8/8'	32/32'	6/6', 8/8', 9/9', 7/7', 5/5'	5/5', 32/32'
8,8'	39.5	39.1	2.19 m	2.05 m	7/7', 9/9'	7/7'	5/5', 7/7', 9/9', 8/8', 6/6'	13/13'
			1.54 m	1.64 m				
9,9'	69.4	69.7	4.28 m	4.38 m	8/8', 10/10'		6/6', 12/12', 8/8', 9/9', 7/7', 10/10', 11/11', 5/5'	6a/6a'
10,10'	129.5	129.6		5.71 m	9/9', 11/11', 12/12'	9/9', 12/12'		12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'
11,11'	123.9	123.6		5.74 m	10/10', 12/12'	9/9', 12/12', 13/13'		12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'
12,12'	31.4			1.95 m	11/11', 13/13'	10/10', 11/11', 13/13', 14/14'		12/12', 14/14', 13/13', 7/7', 10/10', 11/11'
13,13'	64.5			3.79 m	12/12', 14/14'a			12/12', 14/14', 15/15', 13/13'
14,14'	36.1	35.9		1.84 m, 1.58 m	13/13', 15/15'	16/16'		12/12', 14/14', 13/13', 15/15'
15,15'	77.0 <sup>b</sup>			3.82 m	14/14'			12/12', 14/14', 13/13', 15/15',
16,16'	40.8	40.6		1.63 m	16/16'-Me, 15/15'			16/16'-Me
16,16'-Me	9.9		0.83 d (7.13)	0.84 d (7.75)	16/16'	15/15', 16/16', 17/17'		13/13', 15/15', 16/16', 14/14', 16,16'-Me
17,17'	74.3	74.1		3.79 m	18/18'			16/16'-Me, 16/16', 19/19', 17/17', 18/18'
18,18'	41.7	41.5		1.85 m, 1.50 m				17/17', 18/18', 19/19', 20/20'
19,19'	69.8	68.3	3.87 m	3.85 m		17/17'		20/20', 21/21', 19/19', 18/18'
20,20'	42.1			1.87 m, 1.57 m	20/20'			20/20', 21/21', 19/19'
21,21'	70.9	71.3	5.65 m	5.69 m		1/1', 19/19', 23/23', 20/20', 22/22', 22/22'-Me	20/20', 19/19'	19/19', 23/23'
22,22'	41.3	40.9		1.73 m	22/22'	22/22'-Me, 23/23'		22,22'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'

22,22'-Me	10.3	10.2	0.86 d (7.03)	0.90 d (6.95)	22/22', 24/24'	21/21', 22/22', 23/23'	22,22'-Me, 22/22', 23/23'		
23,23'	76.3			3.12 m		21/21', 22/22', 24/24', 24/24'-Me, 25/25'	22/22'-Me, 22/22', 23/23'	22/22'-Me,	24/24'-Me, 21/21',
24,24'	33			1.66 m	24/24'		24/24'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'		
24,24'-Me	17.6		0.97 d (6.18)	0.96 d (6.3)		23/23', 24/24', 25/25'	24,24'-Me, 26/26', 24/24', 27/27', 25/25'		
25,25'	24.2	23.6		1.35 m, 1.24 m		24/24'-Me, 26/26', 25/25', 24/24', 27/27'	24,24'-Me, 26/26', 25/25', 24/24', 27/27'		
26,26'	29.3	29.2		1.86 m, 1.22 m		25/25', 27/27'	24/24'-Me, 25/25', 26/26', 27/27'		
27,27'	71.5	71.7		3.97 m		29/29', 31/31'	24/24'-Me, 25/25', 26/26', 28/28', 30/30', 29/29'	29/29'-OMe	
28,28'	35			1.80 m, 1.57 m		29/29', 30/30'	31/31', 30/30', 28/28', 29/29', 27/27'		
29,29'	73.4			3.52 m		27/27', 28/28', 31/31', 29/29'-OMe	28/28', 29/29', 30/30', 31/31', 31/31'-Me,		
30,30'	38.9			1.94 m, 1.17 m		29/29'	31/31'-Me, 28/28', 30/30', 31/31', 29/29'		
31,31'	64.7			3.67 m		29/29'	31/31'-Me, 28/28', 30/30', 31/31', 29/29'		
31,31'-Me	21.9		1.18 d (6.24)	1.20 d (6.3)	31/31'	30/30', 31/31'	31,31'-Me, 30/30', 31/31', 28/28', 29/29'		
32,32'	100.8	102.5	4.71 m	4.43 d (6.29)			32/32', 33/33', 34/34', 35/35', 36/36'	7/7', 34/34', 5/5'	
33,33'	73.4	72.9	4.83 dd (7.18,	3.37 m	34/34'	32/32', 34/34', 37	32/32', 33/33', 34/34', 35/35', 36/36'	35, 35-OMe	
			8.13)						
34,34'	82.4	83.6	3.31 m	3.21 m	33/33'	32/32', 34/34'-OMe, 35/35'	32/32', 33/33', 34/34', 35/35', 36/36'	32/32'	
35,35'	79.3		3.31 m	3.26 m		33/33', 35/35'-OMe	32/32', 33/33', 34/34', 35/35', 36/36'		
36,36'	62.7			3.99 m, 3.23 m	35/35'	32/32', 34/34'	32/32', 33/33', 34/34', 35/35', 36/36'		
37,37'	170.8	N							
38,38'	72.4	N	4.21 m	N	39/39'		38/38', 39/39'	3	
39,39'	64.5	N	3.81 m	N	38/38'		38/38', 39/39'		
15,15'-OMe	57.3	56.9	3.34 s	3.32 s		15/15'			
29,29'-OMe	55.4			3.34 s		29/29'			
34,34'-OMe	60.2	60.1	3.48 s	3.58 s		34			
35,35'-OMe	58.6	58.5 <sup>a</sup>	3.44 s	3.45s		35			

Table S9 NMR data for samholide H (**8**)

	$\delta_{\text{C}}$	$\delta_{\text{C}'}$	$\delta_{\text{H}}$	$\delta_{\text{H}'}$	COSY	HMBC	HSQC-TOCSY	ROESY
1,1'		170.3						
2,2'	114.3	113.9	5.80 d (15.6)		3/3'	1/1', 4/4'	3/3', 2/2'	4/4'-Me
3,3'	152.2	152.1	7.55 d (15.6)		2/2'	1/1', 2/2', 4/4', 4/4'-Me, 5/5'	2/2', 3/3',	5/5'
4,4'		134.4						
4,4'-Me	12.5	12.4	1.83 s		5/5'	3/3', 4/4', 5/5'	4/4'-Me, 5/5'	2/2', 6/6'
5,5'	141	134	6.35 m		6/6', 4/4'-Me	4/4'-Me, 3/3'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	7/7', 3/3'
6,6'	33.6	33.3	2.60 m, 2.38 m		5/5', 7/7'	4/4', 5/5', 7/7'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	5/5', 9/9'
7,7'	76.0	76.3	4.08 m		6/6', 8/8'		6/6', 8/8', 9/9', 7/7', 5/5'	5/5', 32/32'
8,8'	39.8	39.7	2.26 m, 1.62 m		7/7', 9/9'	6/6', 7/7', 9/9'	5/5', 7/7', 9/9', 8/8', 6/6'	13/13'
9,9'		69.6	4.29 m		8/8', 10/10'		6/6', 12/12', 8/8', 9/9', 7/7', 10/10', 11/11', 5/5'	6a/6a', 10/10', 14/14'
10,10'		129.8	5.74 m		9/9', 11/11', 12/12'	9/9', 12/12'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
11,11'		123.6	5.77 m		10/10', 12/12'	9/9', 12/12'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
12,12'	31.4	31.6	1.97 m		11/11', 13/13'	10/10', 11/11', 13/13', 14/14'	12/12', 14/14', 13/13', 7/7', 10/10', 11/11'	
13,13'	63.7	63.5	3.64 m		12/12', 14/14'a		12/12', 14/14', 15/15', 13/13'	
14,14'	36.9	36.8	1.77 m, 1.64 m		13/13', 15/15'	15/15'	12/12', 14/14', 13/13', 15/15'	
15,15'	75.8	76.0	4.08 m		14/14'		12/12', 14/14', 13/13', 15/15',	6a/6a', 5/5', 14/14', 8/8'
16,16'	41.5	41.4	1.66 m		16/16'-Me, 15/15'	16/16'-Me	13/13', 15/15', 16/16', 14/14', 16,16'-Me	
16,16'-Me	9.4	9.3	0.79 d (6.36)	0.78 d (6.35)	16/16'	15/15', 16/16', 17/17'	16,16'-Me, 16/16', 19/19', 17/17', 18/18'	
17,17'	74.0	74.1	3.85 m		18/18'		16/16'-Me, 18/18', 17/17', 19/19'	16/16'-Me,
18,18'		40.8	1.72 m, 1.41 m			17/17'	17/17', 18/18', 19/19', 20/20'	
19,19'		69.8	3.90 m				20/20', 21/21', 19/19', 18/18'	
20,20'	42.1	42.0	1.85 m, 1.53 m		20/20'		20/20', 21/21', 19/19'	
21,21'	70.7	70.6	5.55 d (11.17)			1/1', 19/19', 22/22', 22/22'-Me	20/20', 19/19'	19/19'
22,22'	40.8	40.7	1.76 m		22/22'		22,22'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
22,22'-Me	10.3	10.2	0.91 m		22/22', 24/24'	21/21', 22/22', 23/23'	22,22'-Me, 22/22', 23/23'	
23,23'		76.8 <sup>a</sup>	3.20 m				22/22'-Me, 22/22', 23/23'	22/22'-Me, 24/24'-Me
24,24'	33.2	33.3	1.68 m		24/24'	23/23', 24/24'-Me	24/24'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
24,24'-Me	17.5	17.4	0.93 m			23/23', 24/24', 25/25'	24,24'-Me, 26/26', 24/24', 27/27', 25/25'	
25,25'		24	1.36 m, 1.21 m			24/24'-Me	24,24'-Me, 26/26', 25/25', 24/24', 27/27'	
26,26'	29.4	29.5	1.84 m, 1.26 m			27/27'	24/24'-Me, 25/25', 26/26', 27/27'	
27,27'	71.1	71.0	3.97 m				24/24'-Me, 25/25', 26/26', 28/28', 30/30', 29/29'	29/29'-OMe

28,28'	35		1.79 m, 1.58 m			31/31', 30/30', 28/28', 29/29', 27/27'
29,29'	73.4		3.52 m	29/29'-OMe		28/28', 29/29', 30/30', 31/31', 31/31'-Me,
30,30'	38.7		1.97 m, 1.17 m	29/29', 31/31'		31/31'-Me, 28/28', 30/30', 31/31', 29/29'
31,31'	64.9		3.70 m			31/31'-Me, 28/28', 30/30', 31/31', 29/29'
31,31'-Me	21.9		1.21 d (6.6)	31/31'		31,31'-Me, 30/30', 31/31', 28/28', 29/29'
32,32'	103.2	102.9	4.47 d (6.69)	4.53 d (5.45)	7/7', 36/36'	32/32', 33/33', 34/34', 35/35', 36/36' 7/7', 34/34', 5/5', 20/20'
33,33'	73.1	72.1	3.36 m	3.29 m	34/34'	32/32', 33/33', 34/34', 35/35', 36/36'
34,34'	83.2	83.3	3.20 m	3.26 m	33/33'	33/33', 34/34'-OMe, 35/35'
35,35'	79.3	68.9	3.29 m	3.36 m		32/32', 33/33', 34/34', 35/35', 36/36'
36,36'	62.5	64.2	3.99 m 3.18 m	3.96 m 3.31 m	35/35'	32/32', 34/34', 35/35' 32/32', 33/33', 34/34', 35/35', 36/36'
15,15'-OMe	57.5		3.35 s	3.36 s	15,15'	
29,29'-OMe	55.5			3.34 s	29,29'	
34,34'-OMe	60.1	59.8		3.55 s	34,34'	
35,35'-OMe	58.5	N	3.45	N	35	

<sup>a</sup> Overlapped with CDCl<sub>3</sub>, assigned using HMBC, HSQC and HSQC-TOCSY.

Table S10 NMR data for samholide I (9)

	$\delta_{\text{C}}/\delta_{\text{C}^{\prime}}$	$\delta_{\text{H}}/\delta_{\text{H}^{\prime}}$	COSY	HMBC	HSQC-TOCSY	ROESY
1,1'	169.6					
2,2'	114.5	5.80 d (15.62)	3/3'	1/1', 4/4'	3/3', 2/2'	4/4'-Me
3,3'	152	7.47 d (15.62)	2/2'	1/1', 2/2', 4/4', 4/4'-Me, 5/5'	2/2', 3/3',	5/5'
4,4'	134.2					
4,4'-Me	12.5	1.80 s		3/4', 4/4', 5/5'	4/4'-Me, 5/5'	2/2'
5,5'	140.3	6.19 t (7.03)	6/6'	4/4'-Me, 3/3', 6/6', 7/7'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	7/7', 3/3'
6,6'	36.7	2.47 ddd (3.24, 7.14, 14.94)	5/5', 7/7'	4/4', 5/5', 7/7', 8/8'	4/4'-Me, 6/6', 8/8', 9/9', 7/7', 5/5'	8/8', 9/9'
		2.31 dt (7.56, 15.19)				
7,7'	69.8	4.04 m	6/6', 8/8'		6/6', 8/8', 9/9', 7/7', 5/5'	9/9'
8,8'	40.7 <sup>a</sup>	1.89 m, 1.52 m	7/7'	7/7', 9/9'	5/5', 7/7', 9/9', 8/8', 6/6'	7/7'
9,9'	72.6	4.34 d (10.74)	8/8', 10/10'	10/10', 13/13'	6/6', 12/12', 8/8', 9/9', 7/7', 10/10', 11/11', 5/5'	6a/6a', 7/7'
10,10'	129.4	5.65 m	9/9', 11/11', 12/12'	9/9', 12/12'	12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
11,11'	124.2	5.81 m	10/10', 12/12'		12/12', 14/14', 8/8', 13/13', 9/9', 10/10', 11/11'	
12,12'	31.3	1.98 m	11/11', 13/13'	10/10', 11/11', 14/14'	12/12', 14/14', 13/13', 7/7', 10/10', 11/11'	
13,13'	64.5	3.68 m	12/12', 14/14'		12/12', 14/14', 15/15', 13/13'	
14,14'	35.9	1.86 m, 1.59 m	13/13', 15/15'	13/13', 16/16'	12/12', 14/14', 13/13', 15/15'	
15,15'	77.6	3.83 m	14/14'	15/15'-OMe, 16/16'-Me, 16/16', 17/17'	12/12', 14/14', 13/13', 15/15',	16/16'-Me
16,16'	40.5 <sup>a</sup>	1.68 m	16/16'-Me, 15/15'	16/16'-Me, 18/18', 17/17'	13/13', 15/15', 16/16', 14/14', 16,16'-Me	
16,16'-Me	9.8	0.83 d (7.02)	16/16'	15/15', 16/16', 17/17'	16,16'-Me, 16/16', 19/19', 17/17', 18/18'	
17,17'	75	3.84 m	18/18'	15/15', 16/16', 17/17'	16/16'-Me, 18/18', 17/17', 19/19'	16/16'-Me
18,18'	40.8 <sup>a</sup>	1.87 m, 1.50 m		17/17', 19/19'	17/17', 18/18', 19/19', 20/20'	
19,19'	69.2	3.84 m	18/18', 20/20'		20/20', 21/21', 19/19', 18/18'	21/21'
20,20'	41.7	1.89 m, 1.55 m		21/21'	20/20', 21/21', 19/19'	
21,21'	70.4	5.65 m	20/20'	1/1', 22/22'-Me	20/20', 19/19'	19/19', 23/23', 22/22'-Me
22,22'	40.9 <sup>a</sup>	1.74 m		22/22'-Me, 23/23'	22,22'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
22,22'-Me	10.2	0.91 d (6.93)	22/22'	21/21', 22/22', 23/23'	22,22'-Me, 22/22', 23/23'	21/21'
23,23'	76.6 <sup>b</sup>	3.14 dd (1.52, 9.66)		24/24', 24/24'-Me, 25/25'	22/22'-Me, 22/22', 23/23'	24/24'-Me, 21/21'
24,24'	33.3	1.66 m			24/24'-Me, 25/25', 26/26', 24/24', 22/22', 23/23'	
24,24'-Me	17.7	0.98 d (6.74)	24/24'	23/23', 24/24', 25/25'	24,24'-Me, 26/26', 24/24', 27/27', 25/25'	
25,25'	24.2	1.37 m, 1.23 m		24/24'-Me	24,24'-Me, 26/26', 25/25', 24/24', 27/27'	
26,26'	29.4	1.87 m, 1.24 m		27/27', 28/28'	24/24'-Me, 25/25', 26/26', 27/27'	

27,27'	71.6	3.98 m	26/26', 28/28'	31/31'	24/24'-Me, 25/25', 26/26', 28/28', 30/30', 29/29'	31/31'-Me, 29/29'-OMe
28,28'	35	1.81 m, 1.58 m		29/29', 30/30'	31/31', 30/30', 28/28', 29/29', 27/27'	
29,29'	73.4	3.52 m	28/28', 30/30'	31/31', 29/29'-OMe	28/28', 29/29', 30/30', 31/31', 31/31'-Me,	26/26'
30,30'	38.8	1.98 m, 1.16 m		29/29',	31/31'-Me, 28/28', 30/30', 31/31', 29/29'	
31,31'	64.8	3.69 m	31/31'-Me	29/29'	31/31'-Me, 28/28', 30/30', 31/31', 29/29'	26/26'
31,31'-Me	22	1.20 d (6.18)	31/31'	30/30', 31/31'	31,31'-Me, 30/30', 31/31', 28/28', 29/29'	27/27'
15,15'-OMe	57.2	3.35 s		15,15'		
29,29'-OMe	55.5	3.34 s		29,29'		

<sup>a</sup> Can be exchanged.

<sup>b</sup> Overlapped with CDCl<sub>3</sub>, assigned using HMBC, HSQC and HSQC-TOCSY.

F4-a #12-18 RT: 0.29-0.44 AV: 7 SB: 1 0.17 NL: 2.81E7

T: + c Full ms [ 300.00-2000.00]

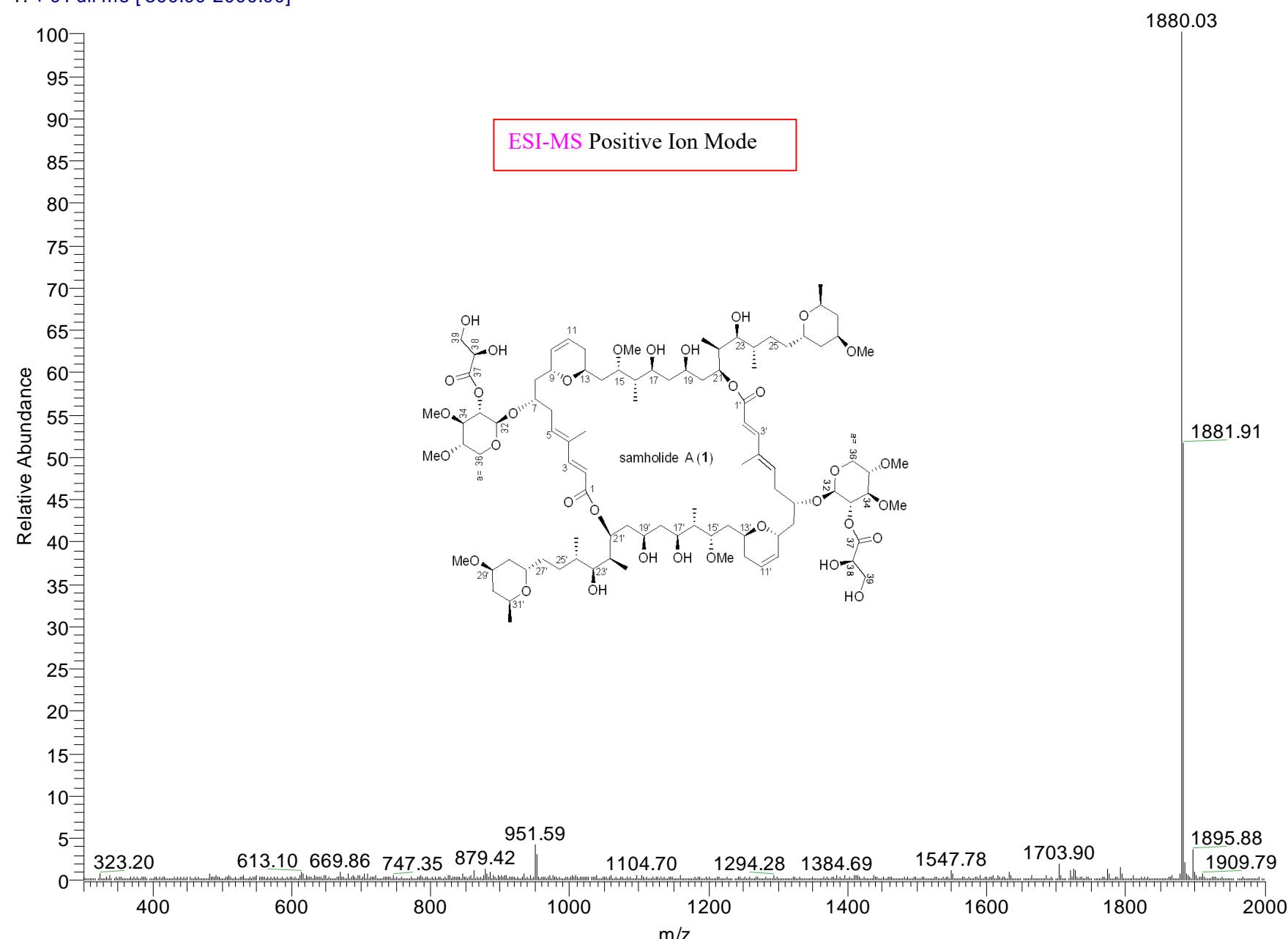


Figure S1 The ESI MS spectrum of samholide A (1)

F4-a #29-34 RT: 0.66-0.74 AV: 6 SB: 3 0.80-0.84 NL: 2.67E6

T: + c Full ms2 1880.00@35.00 [ 515.00-2000.00]

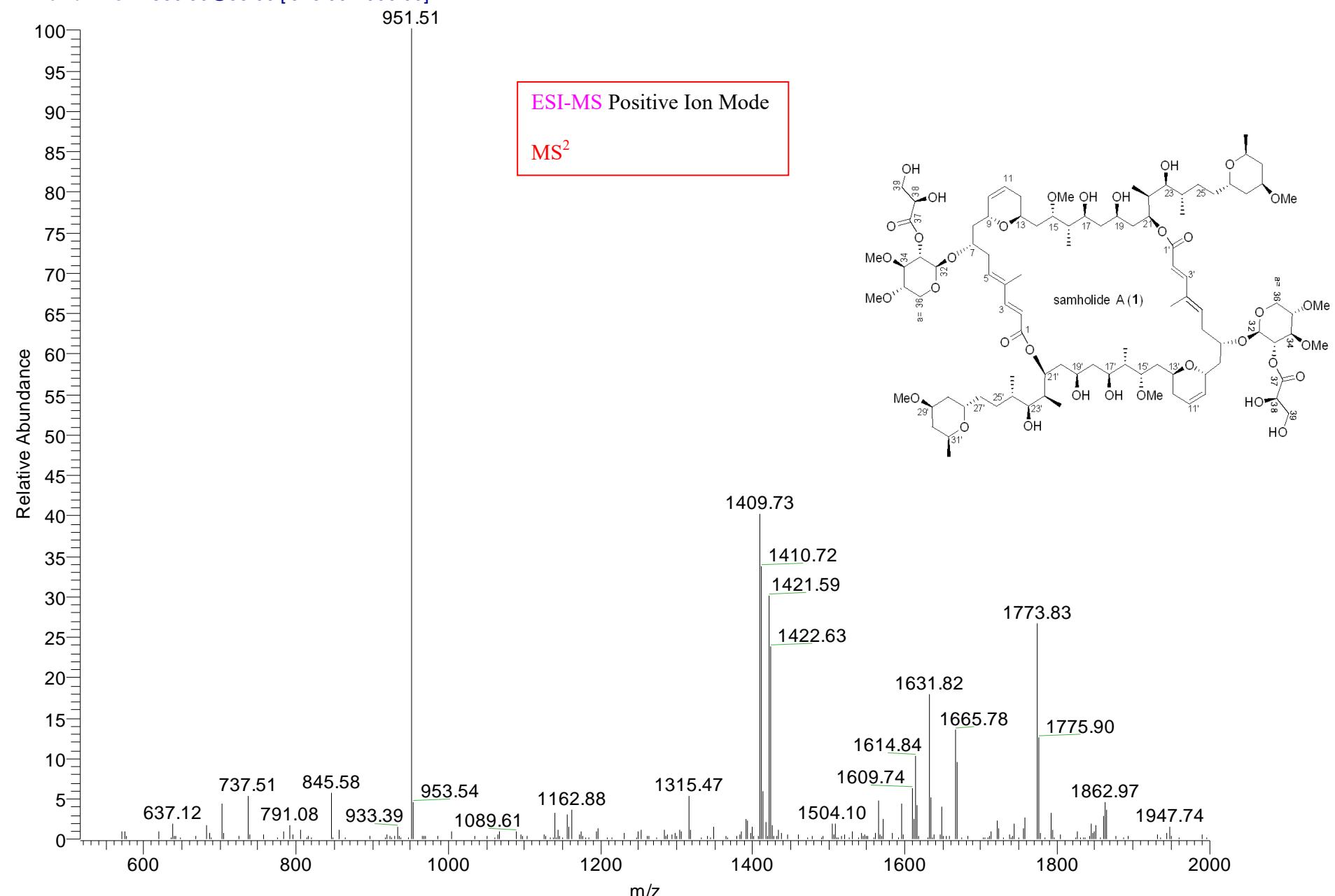


Figure S2 The ESI MS<sup>2</sup> spectrum of samholide A (1)

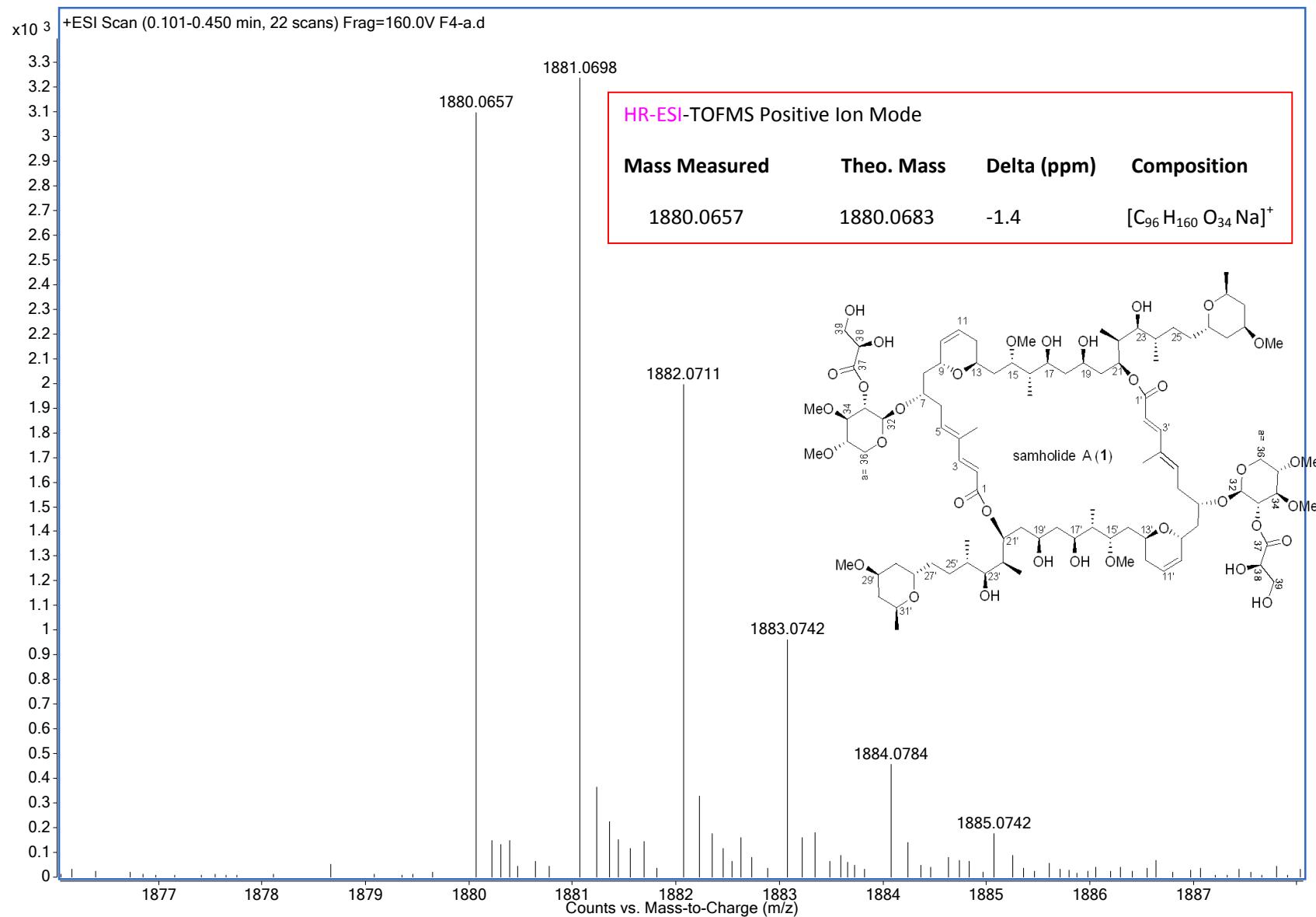
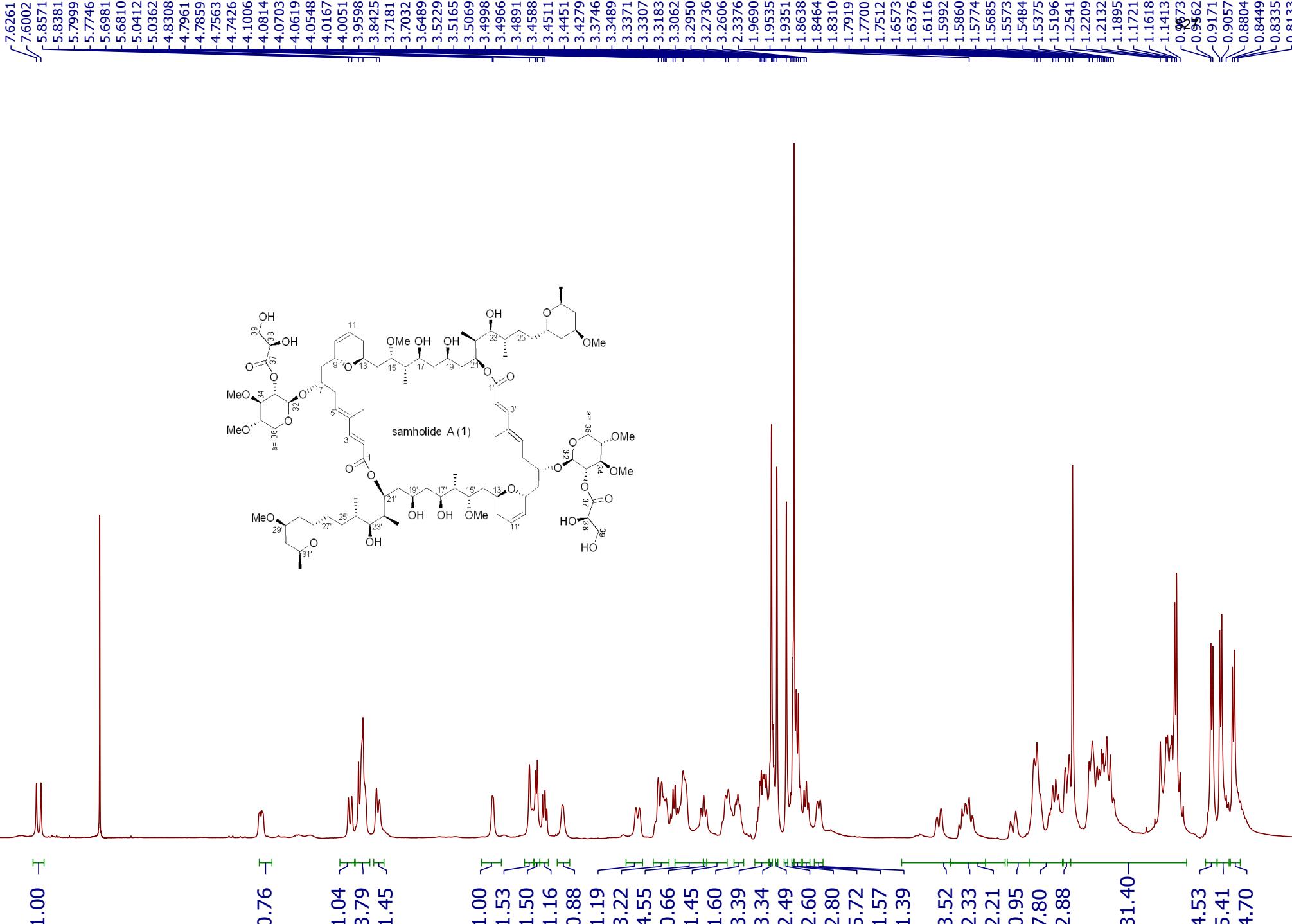
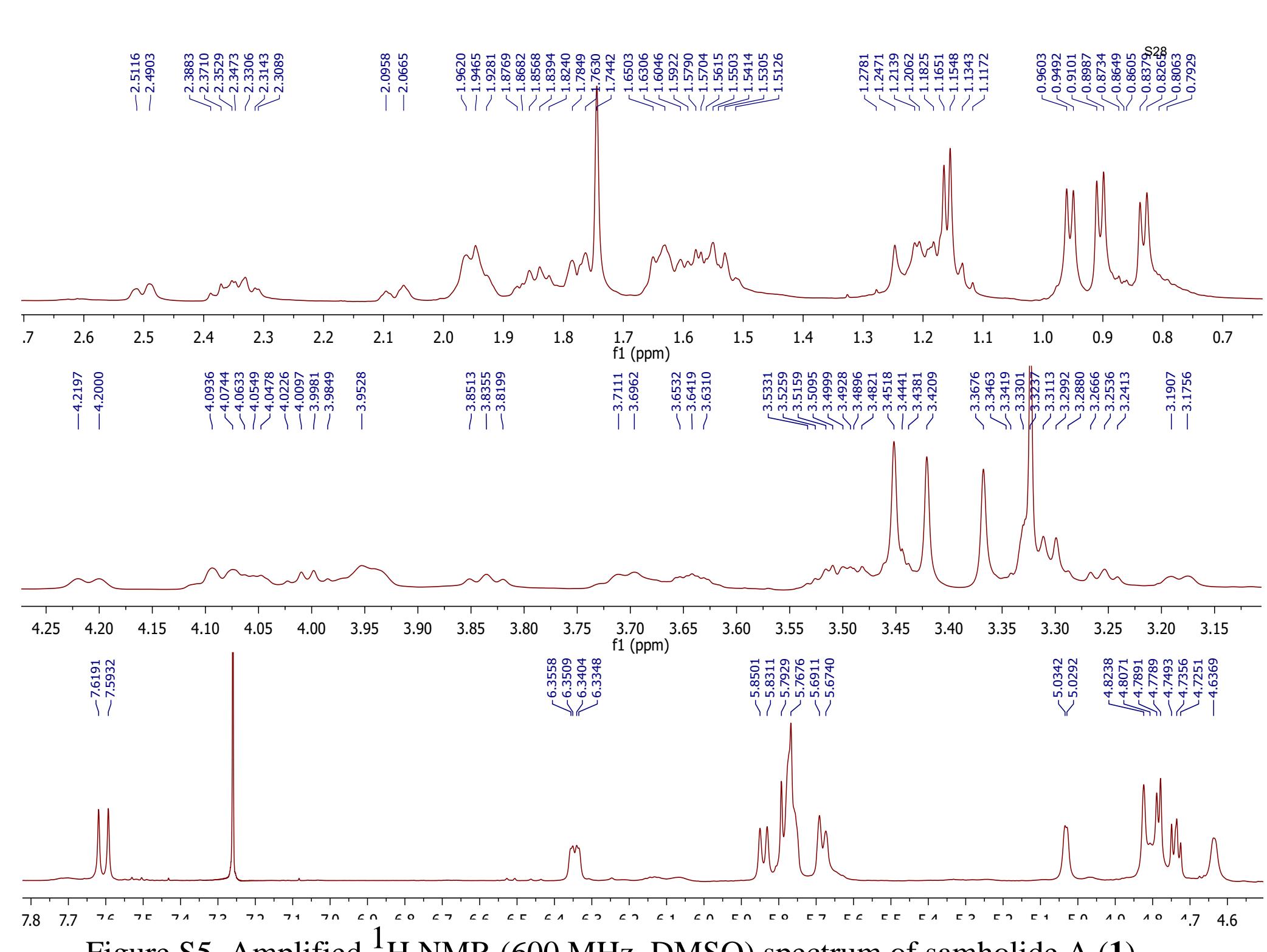


Figure S3 The positive HRESIMS spectrum of samholide A (**1**)





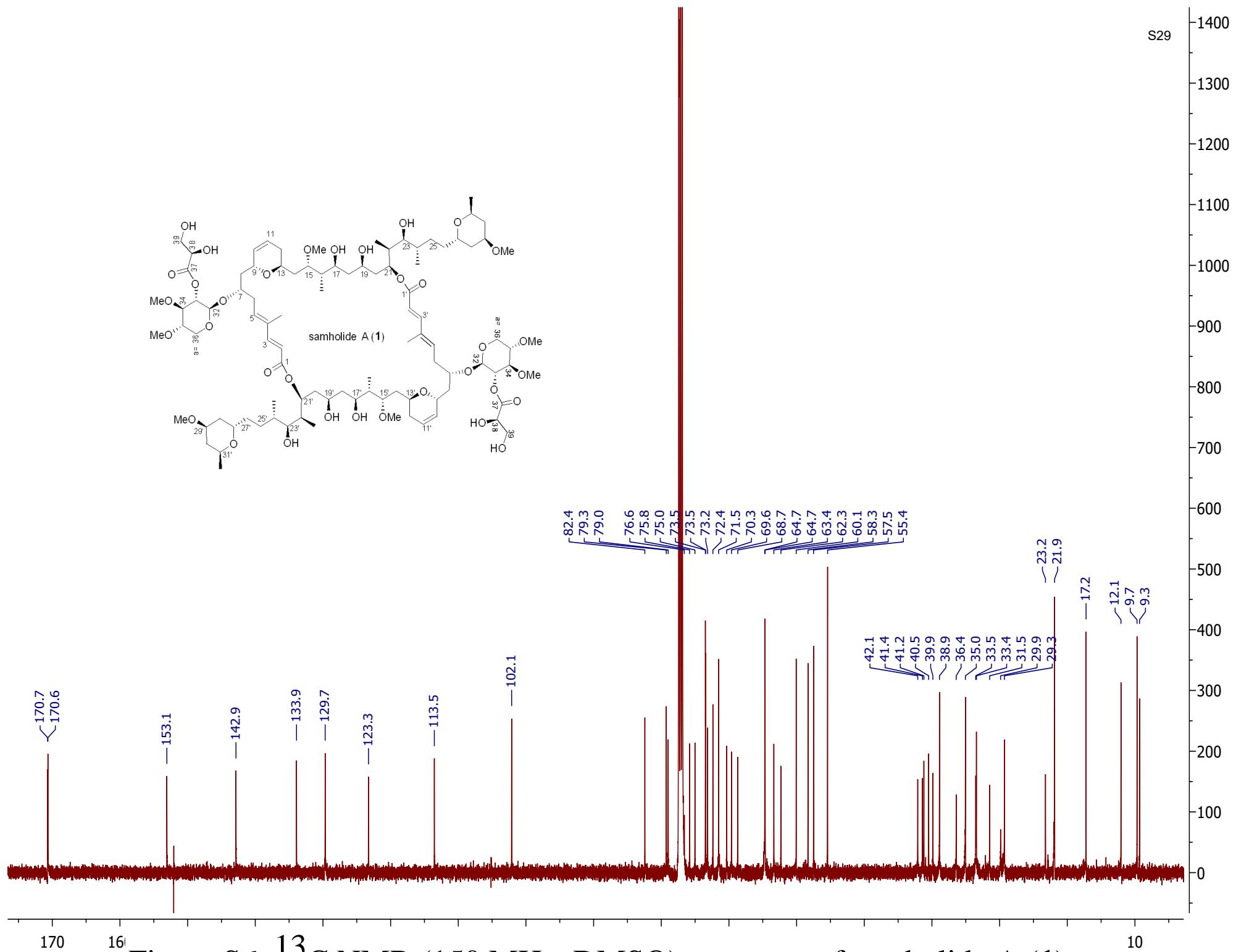
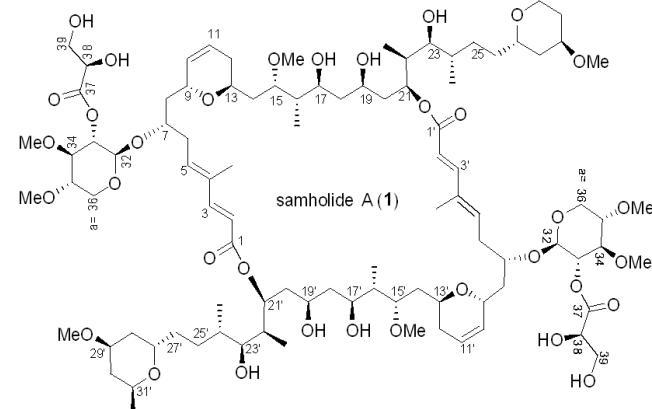


Figure S6  $^{13}\text{C}$  NMR (150 MHz, DMSO) spectrum of samholide A (1)

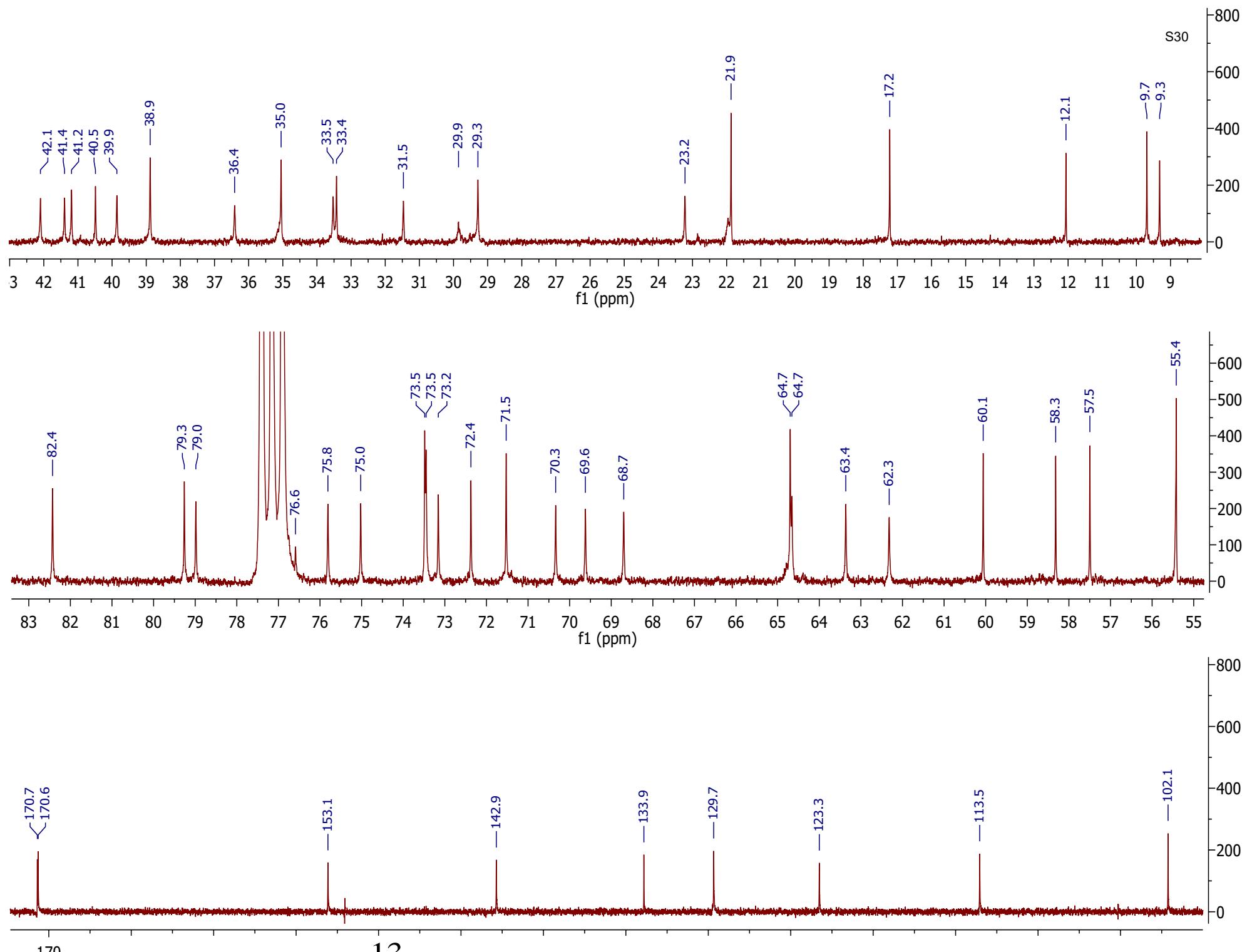


Figure S7 Amplified  $^{13}\text{C}$  NMR (150 MHz, DMSO) spectrum of samholide A (1)

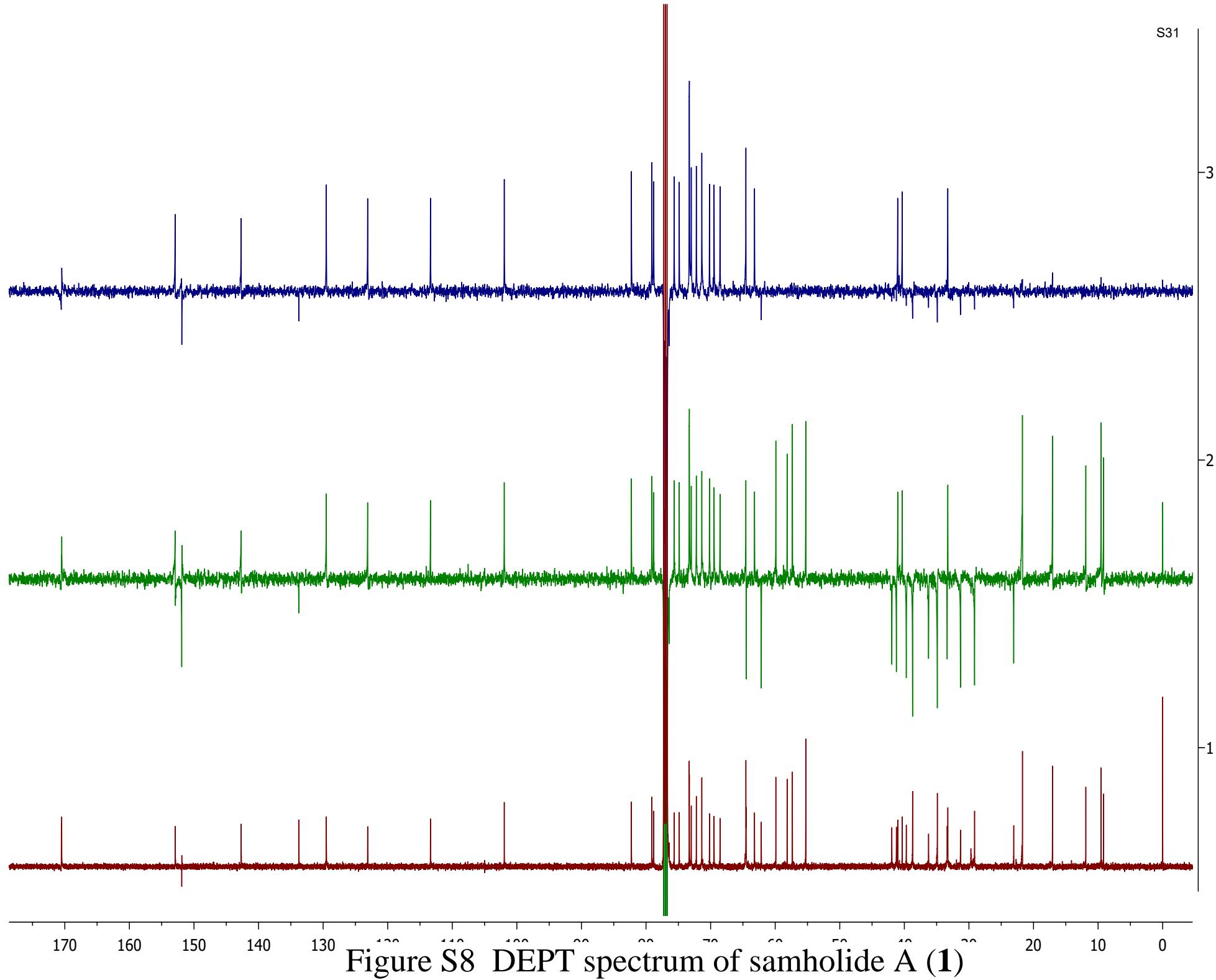
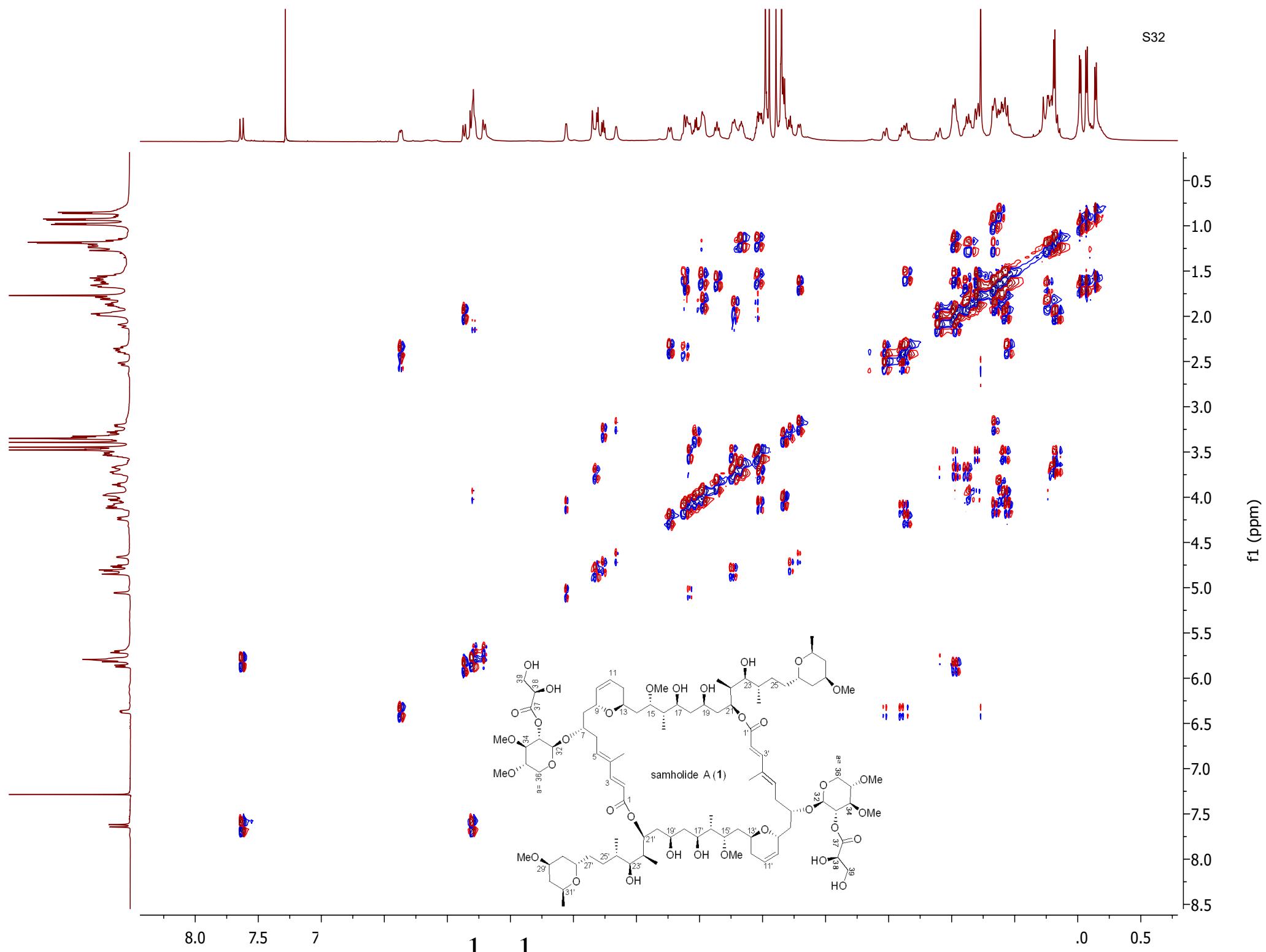


Figure S8 DEPT spectrum of sâmholide A (1)

S32

Figure S9  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of samholide A (**1**)

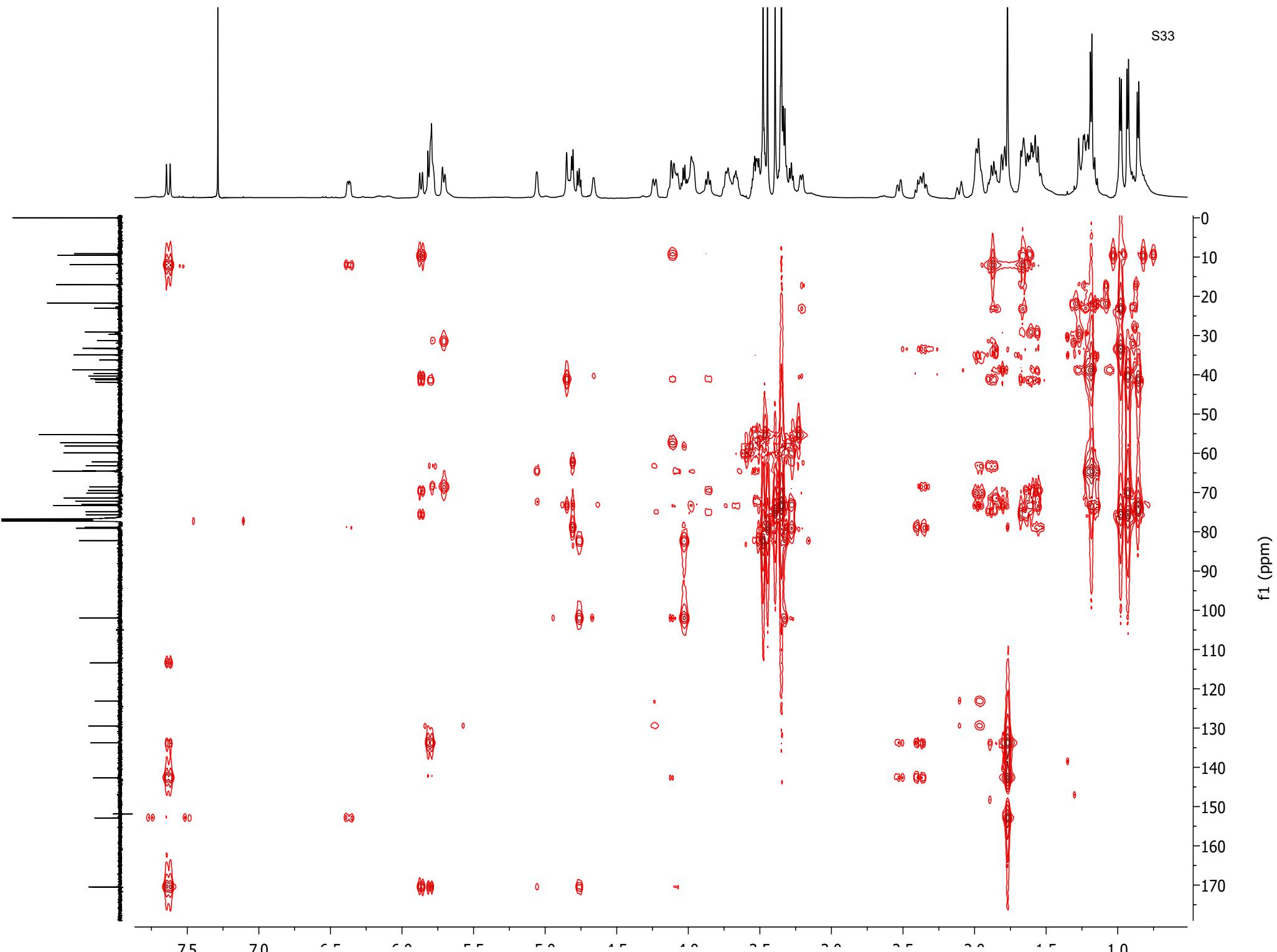


Figure S10 HMBC spectrum of samholide A (1)

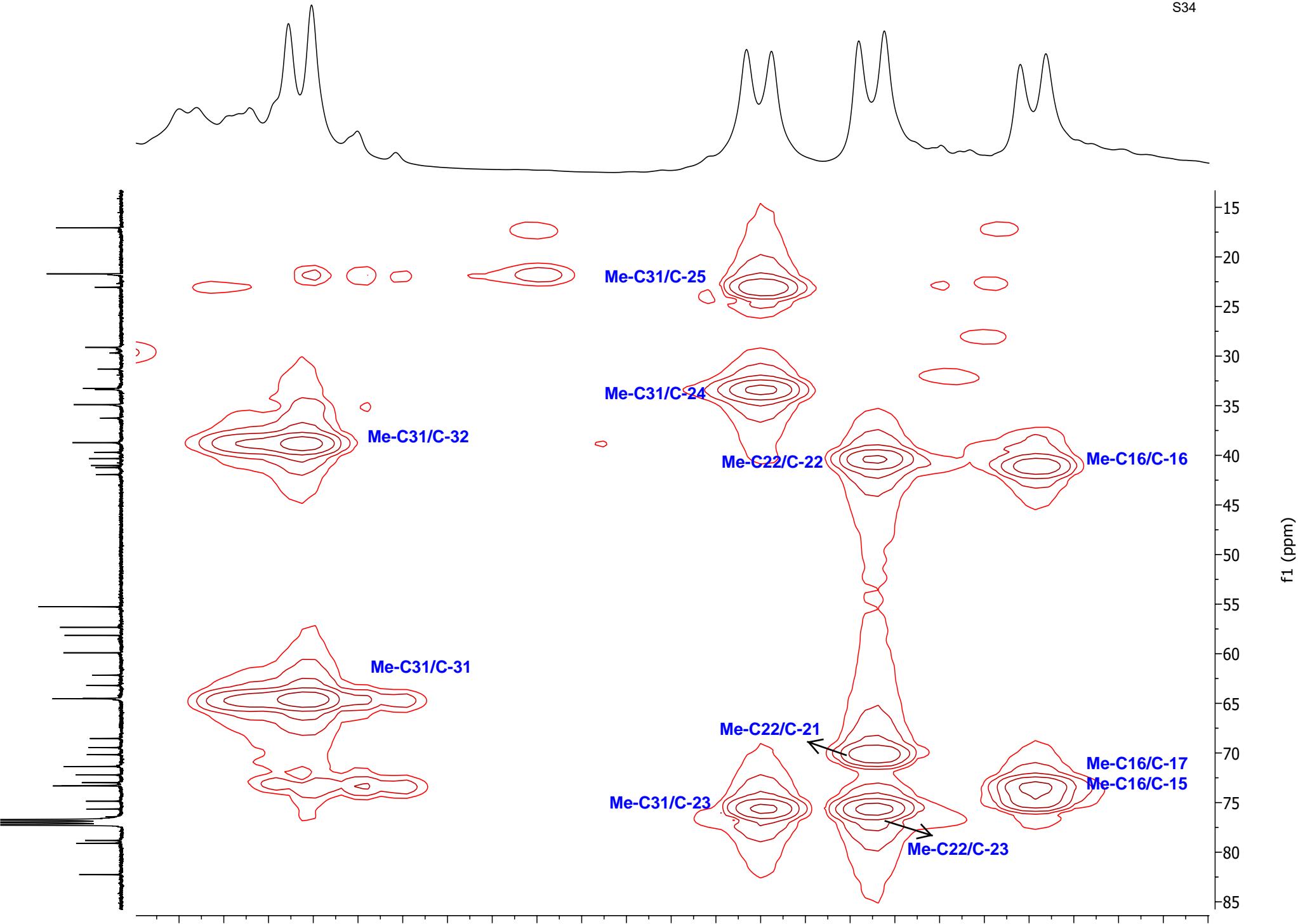


Figure S11 Amplified HMBC spectrum of samholide A (1)

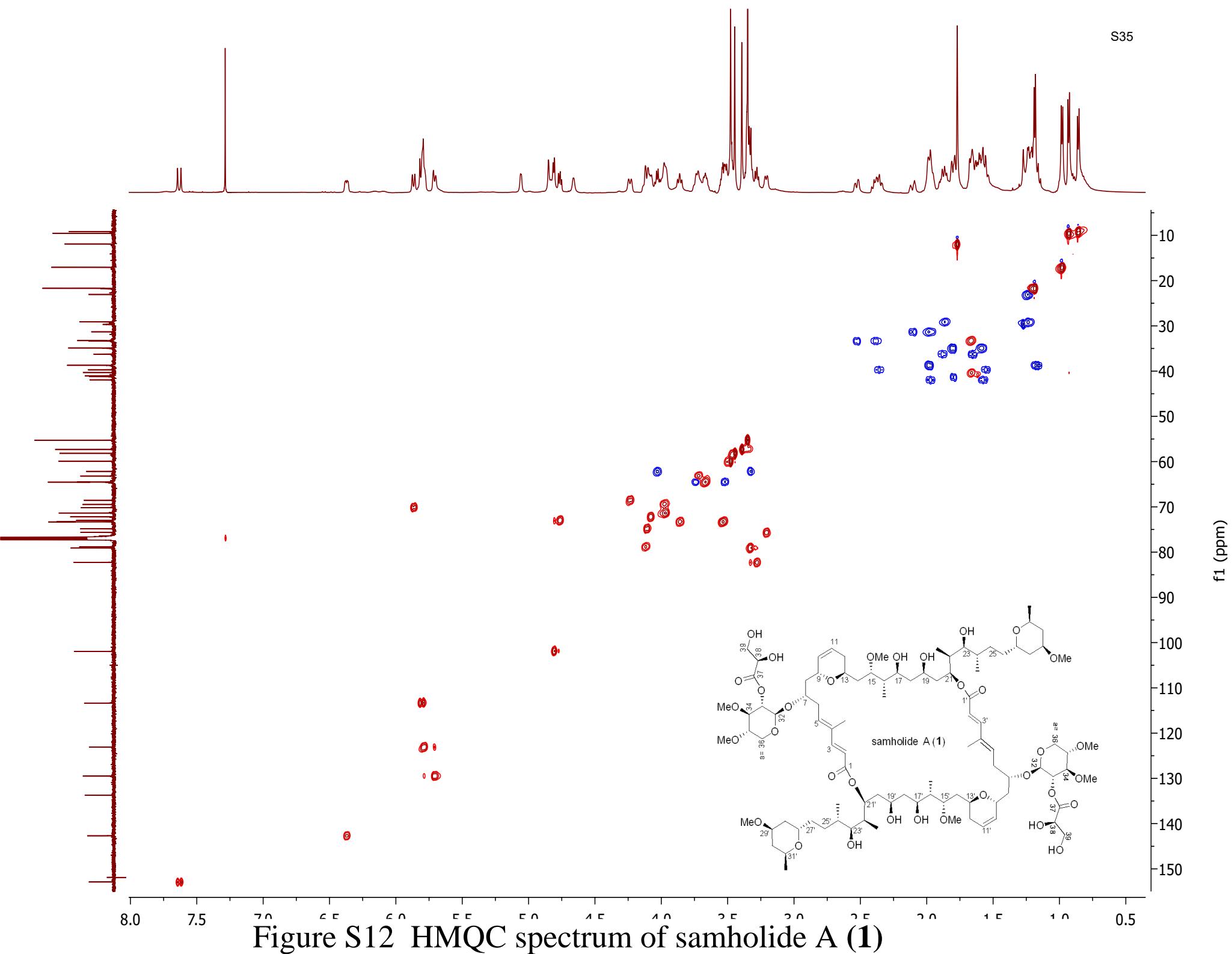


Figure S12 HMQC spectrum of samholide A (1)

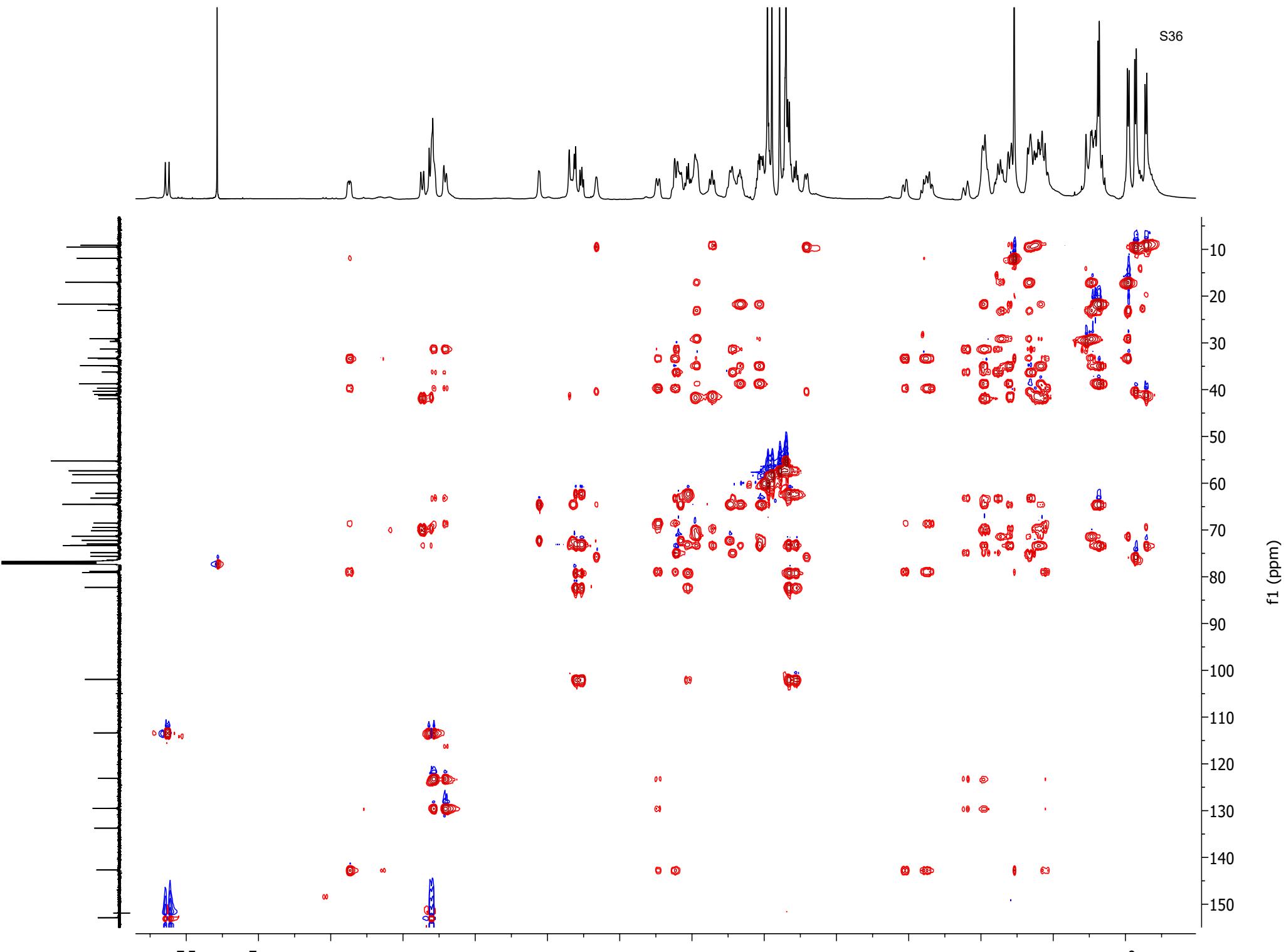


Figure S13 HSQC-TOCSY spectrum of samholide A (1)

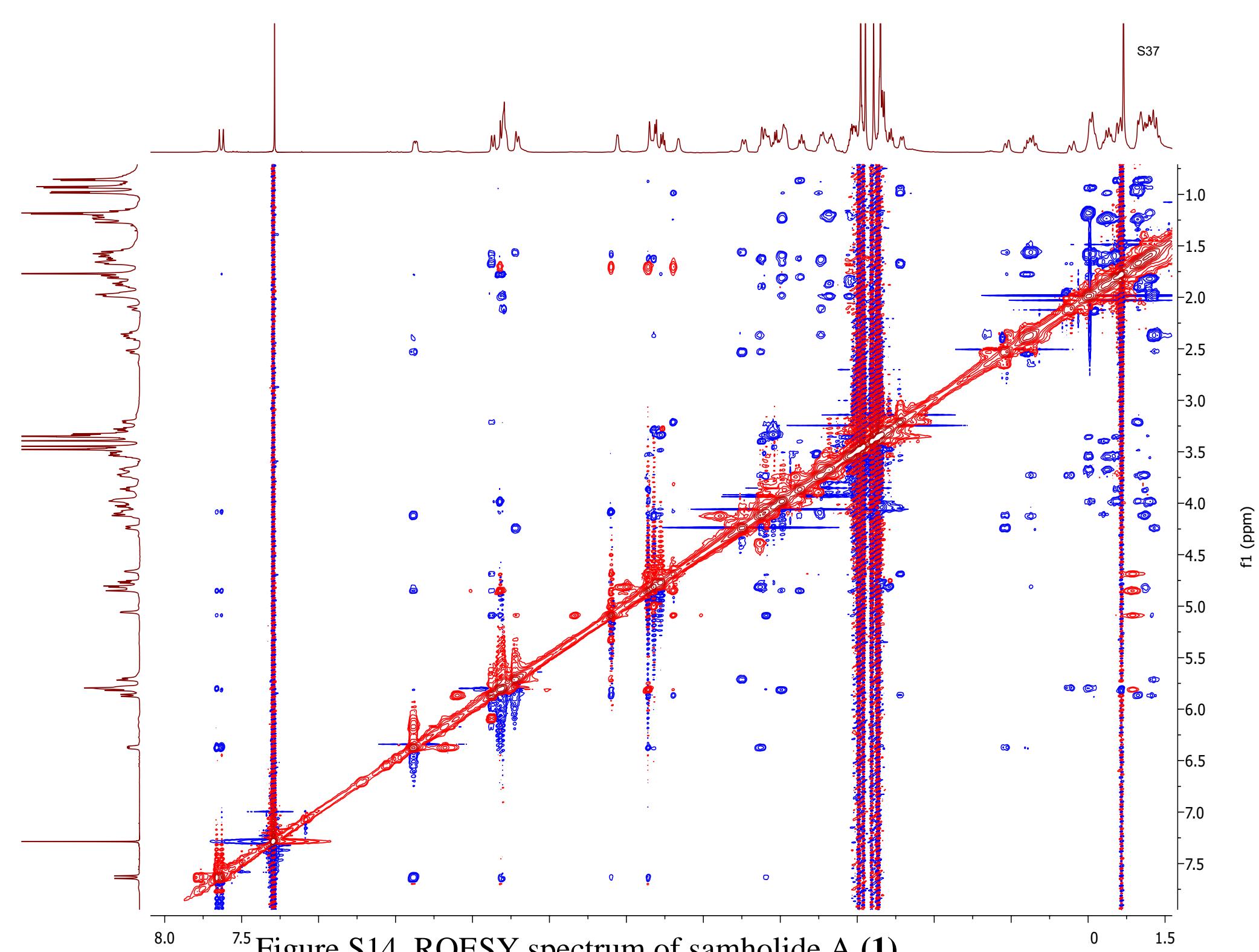


Figure S14 ROESY spectrum of samholide A (1)

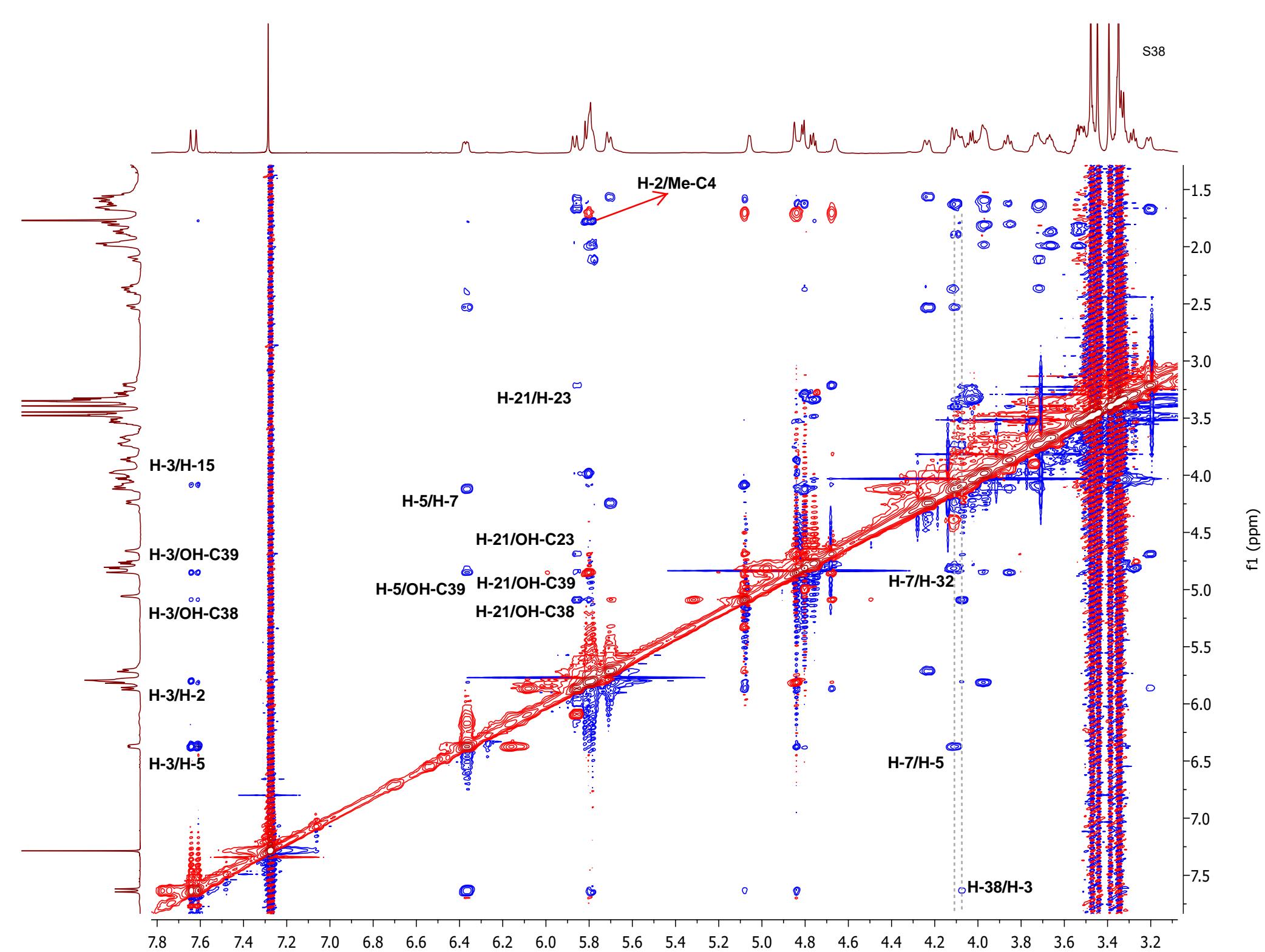


Figure S15 Amplified ROESY spectrum of samholide A (1)

C7-a #44-52 RT: 1.06-1.25 AV: 9 SB: 7 0.74-0.89 NL: 2.70E7

T: + c Full ms [300.00-2000.00]

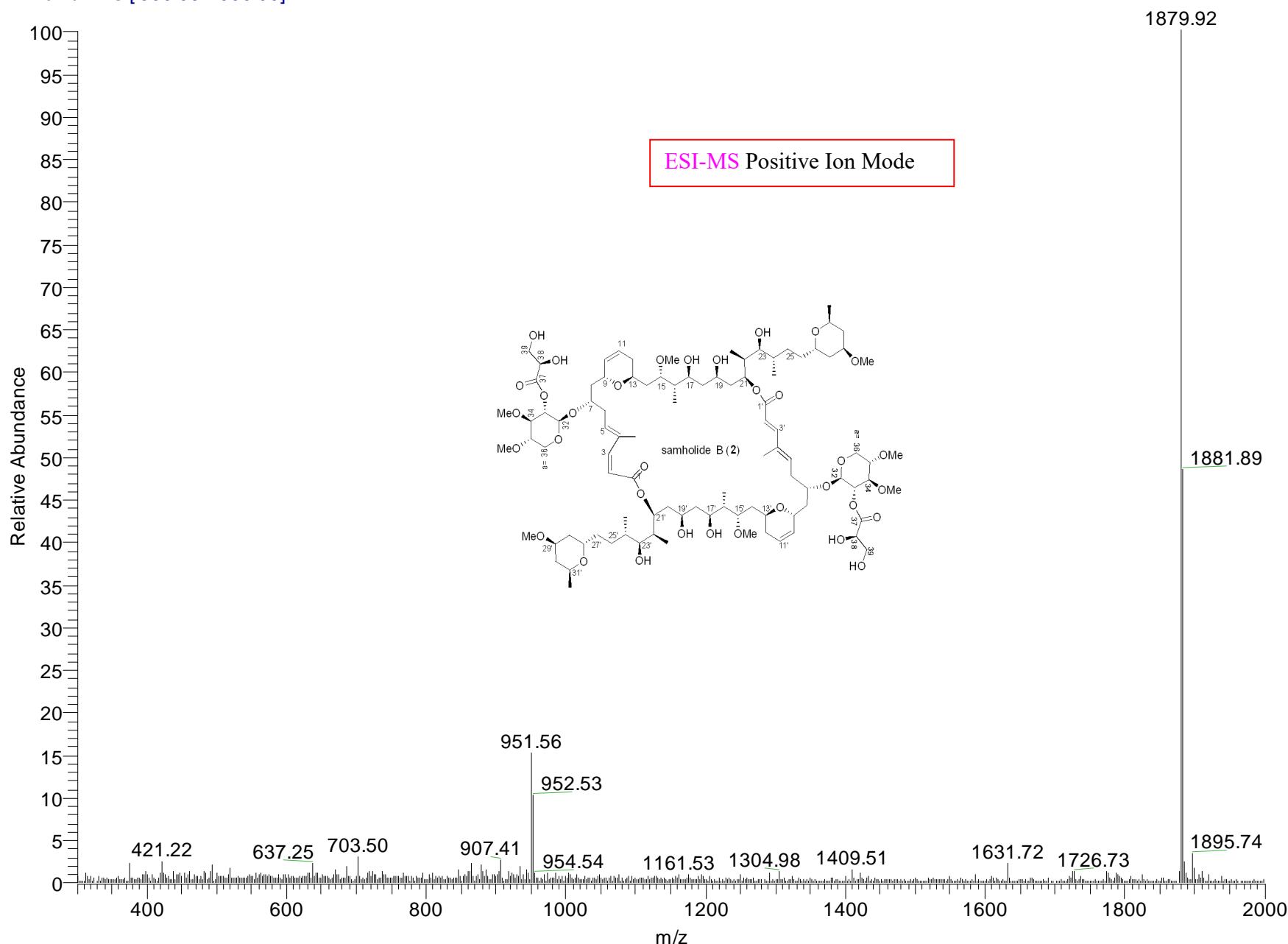


Figure S16 The ESI MS spectrum of samholide B (2)

C7-a #162-172 RT: 3.96-4.13 AV: 11 SB: 7 3.62-3.79 NL: 1.10E7

T: + c Full ms2 1880.00@35.00 [ 515.00-2000.00]

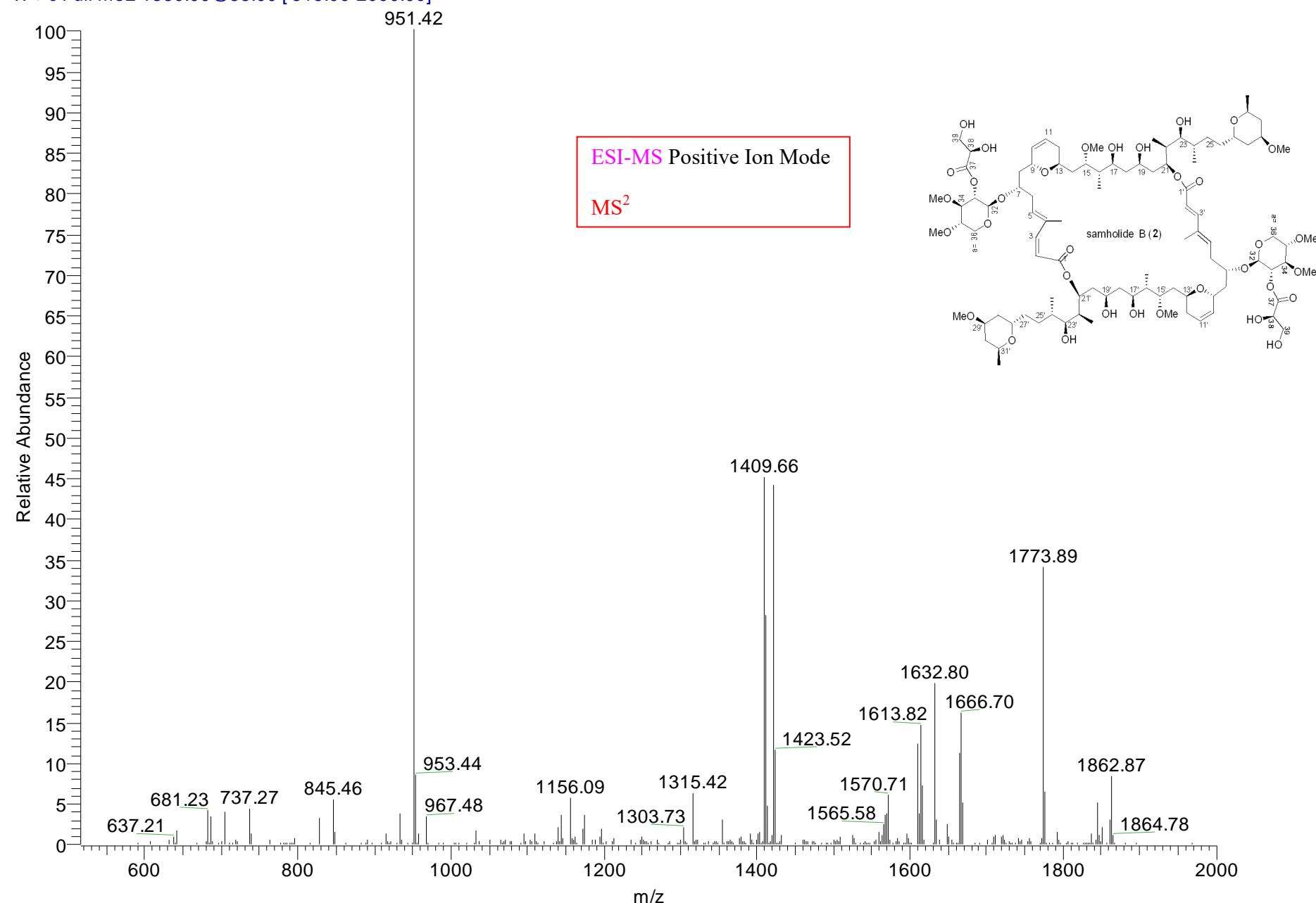


Figure S17 The ESI MS<sup>2</sup> spectrum of samholide B (2)

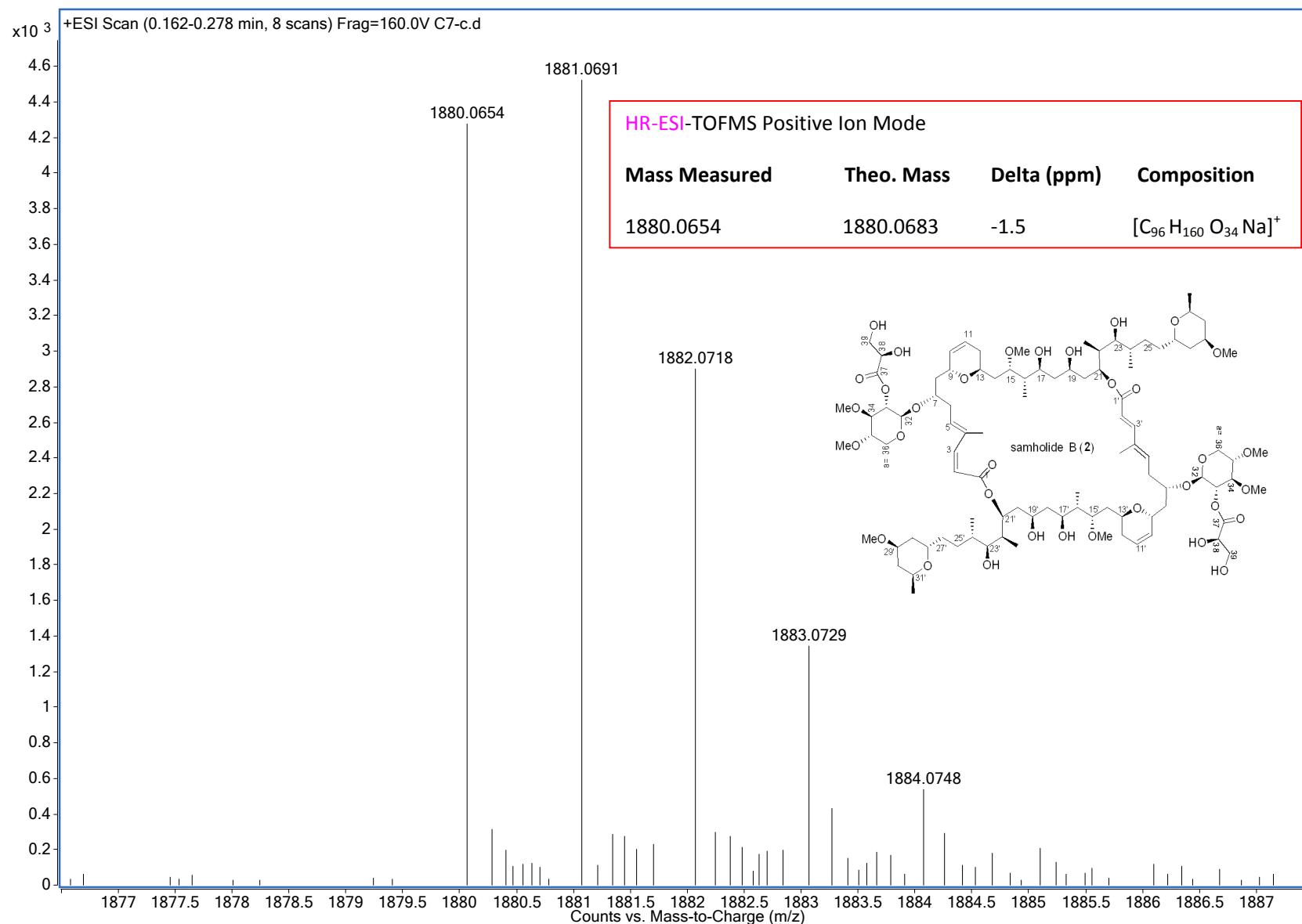


Figure S18 The positive HRESIMS spectrum of samholide B (2)

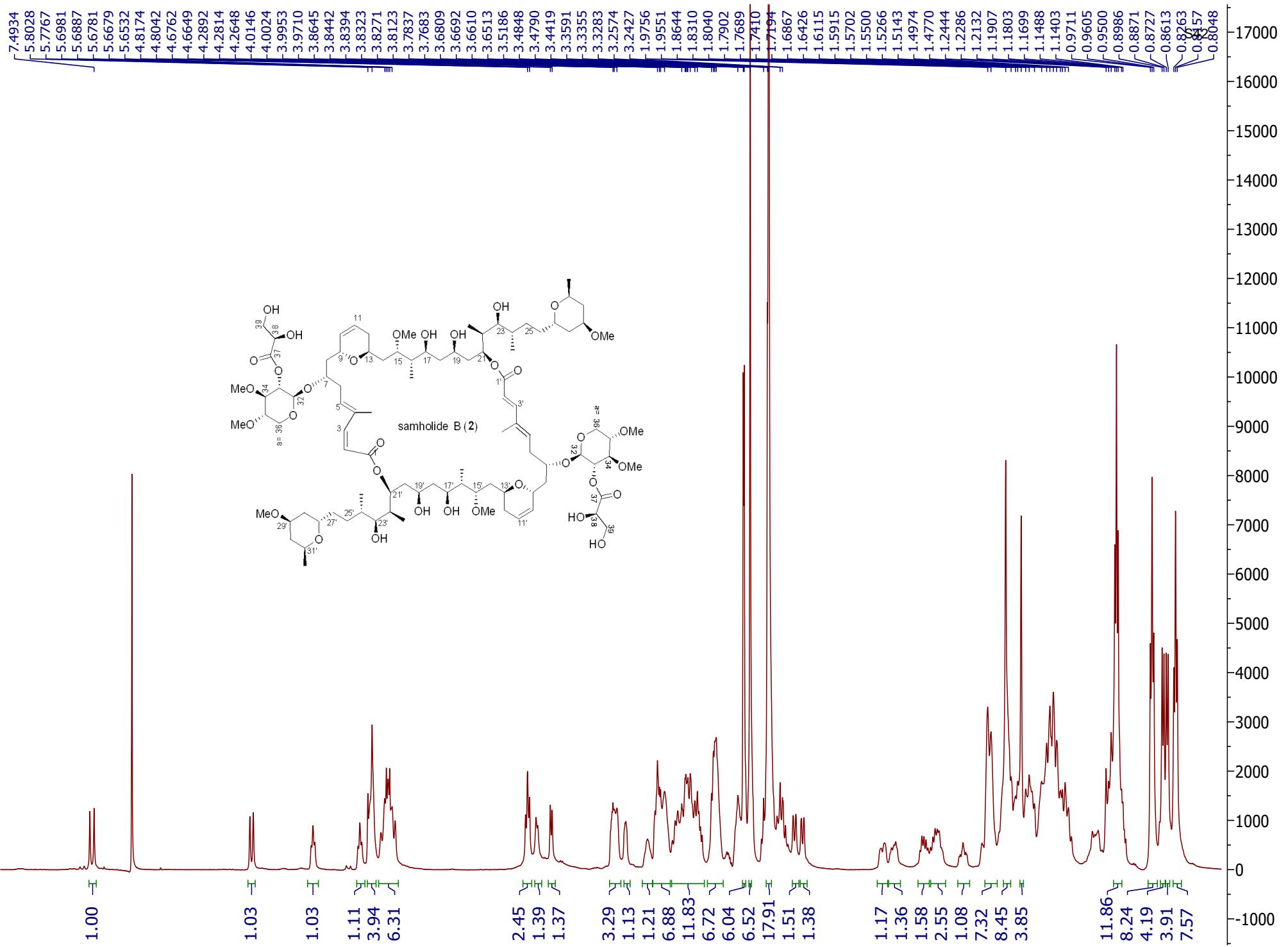
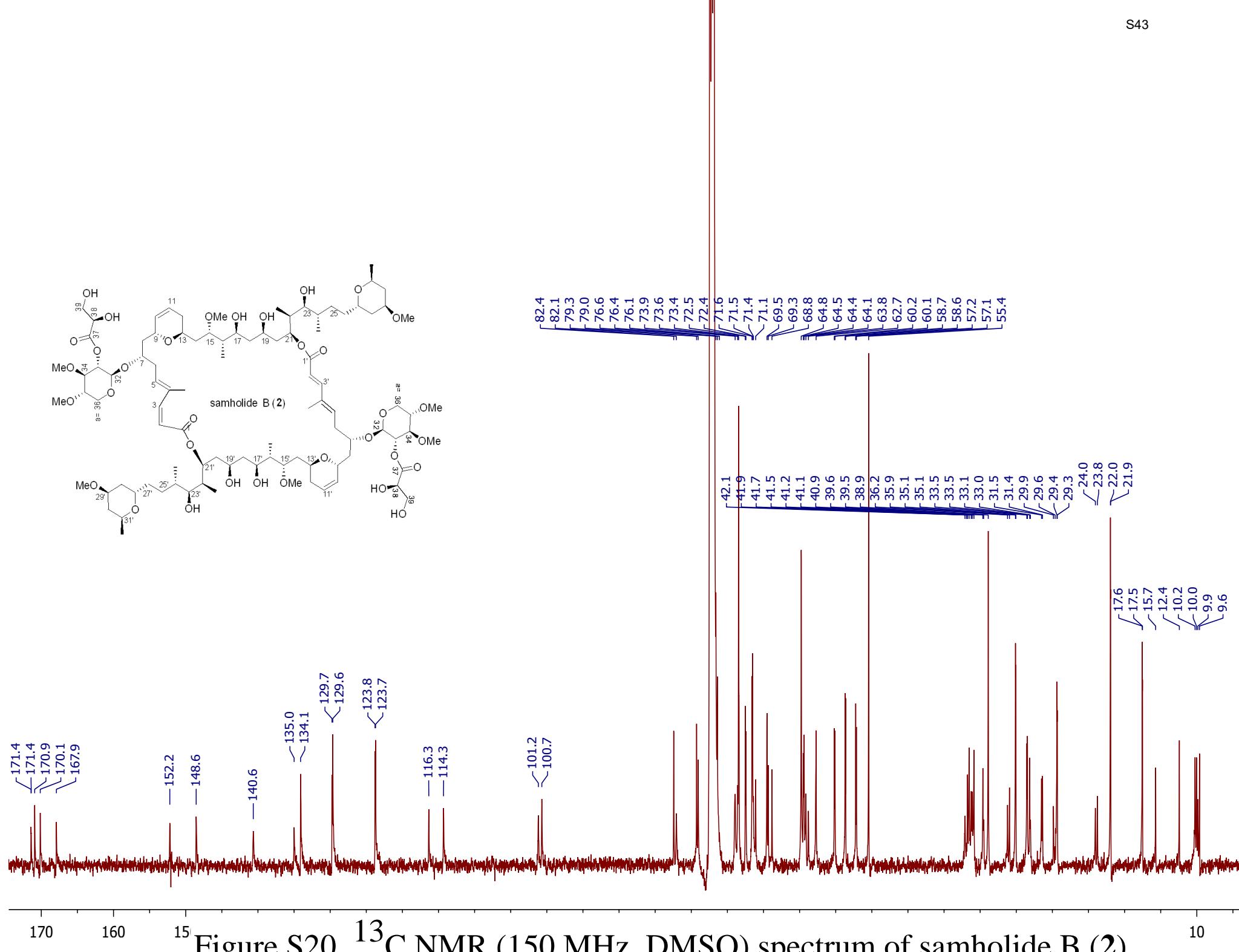


Figure S19  $^1\text{H}$  NMR (600 MHz, DMSO) spectrum of samholide B (**2**)



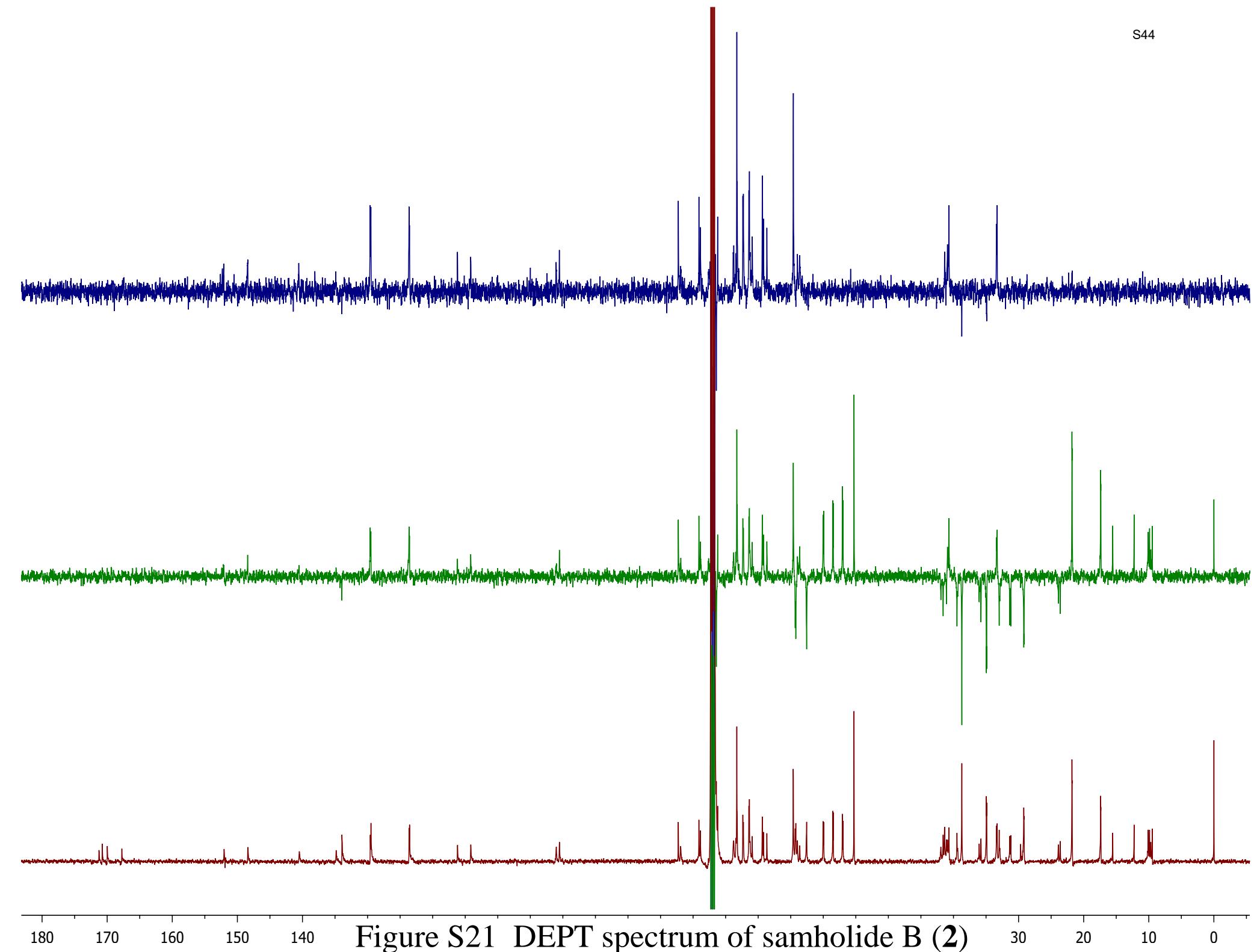
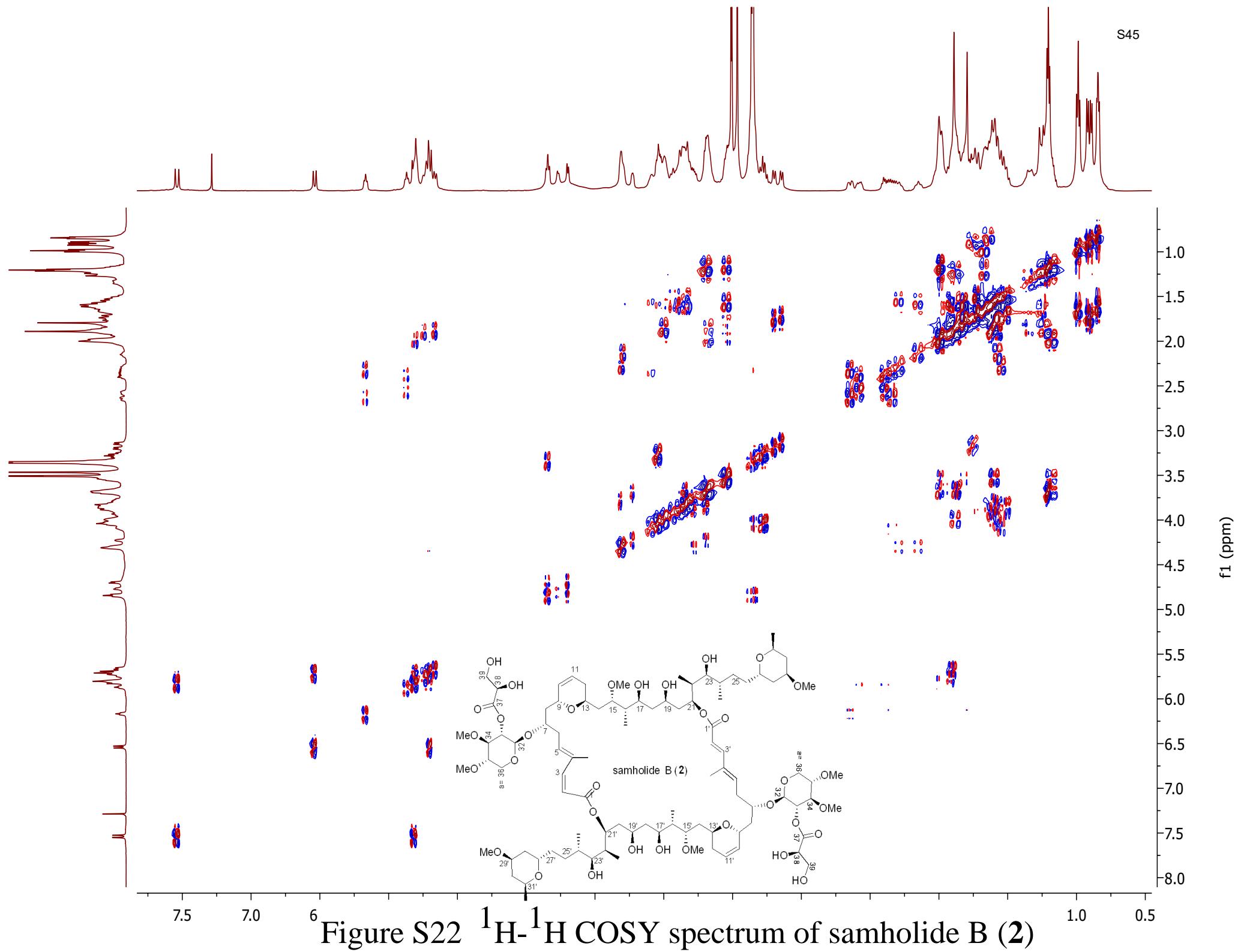


Figure S21 DEPT spectrum of samholide B (2)

S45



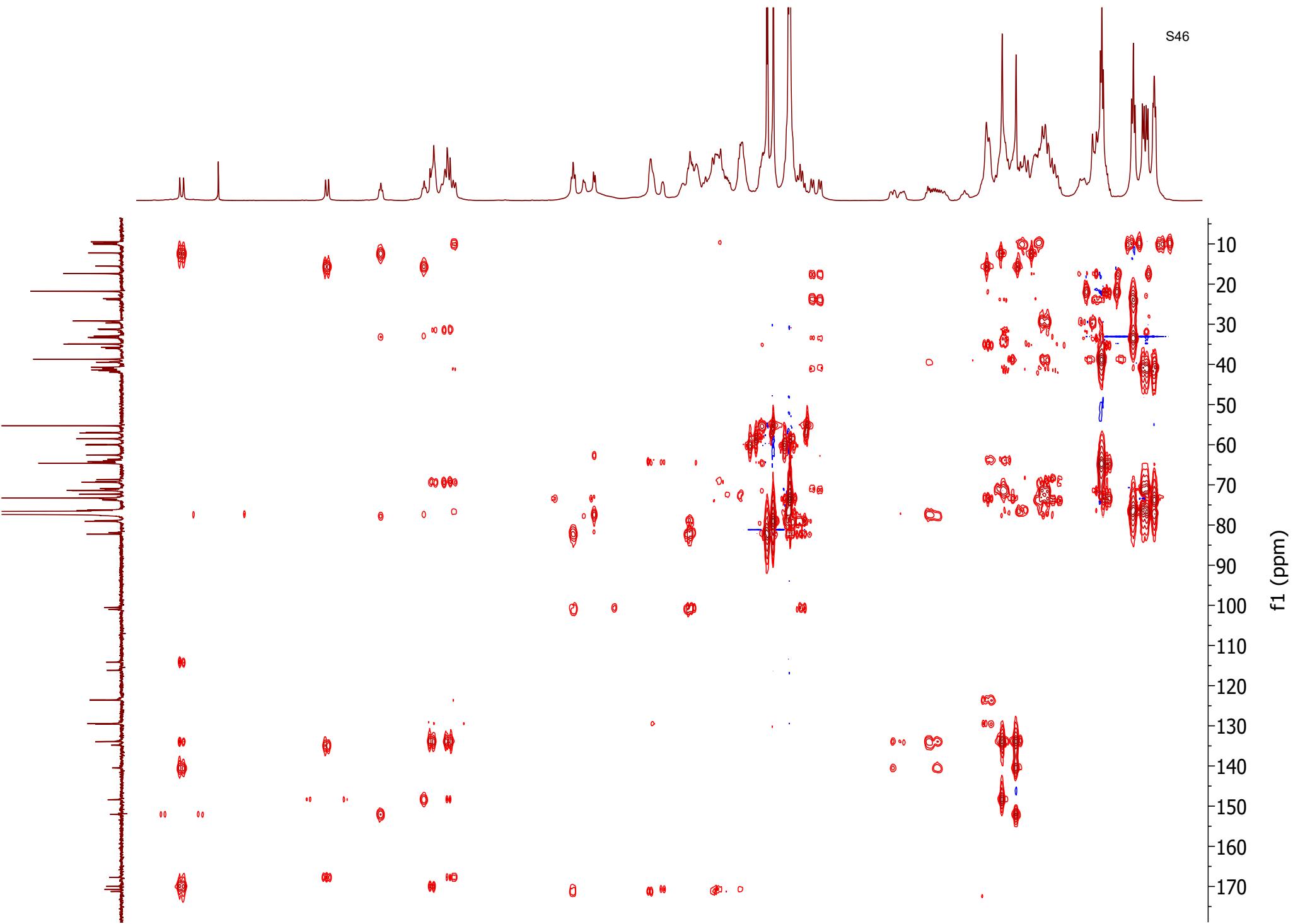
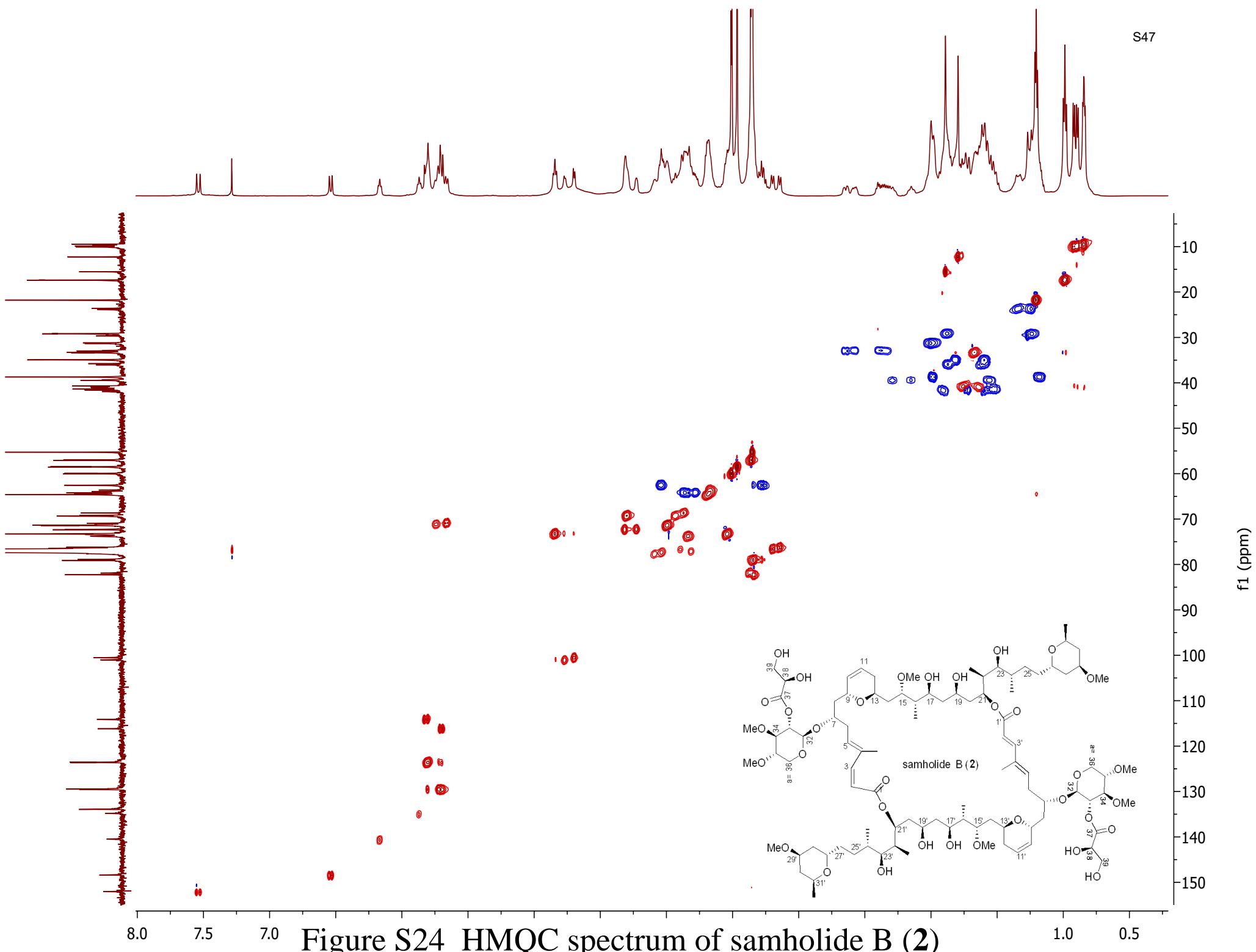


Figure S23 HMBC spectrum of samholide B (2)



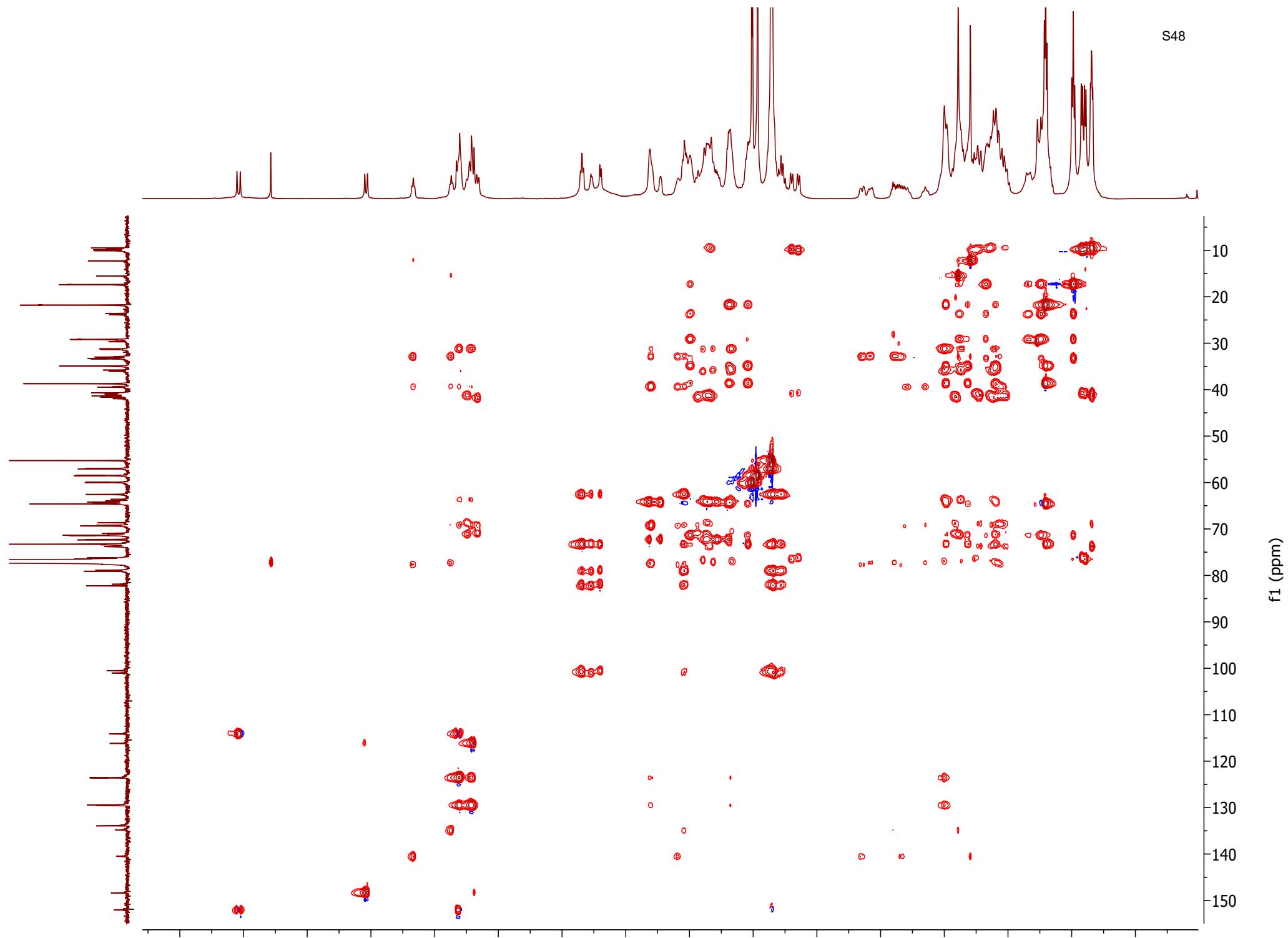


Figure S25 HSQC-TOCSY spectrum of samholide B (2)

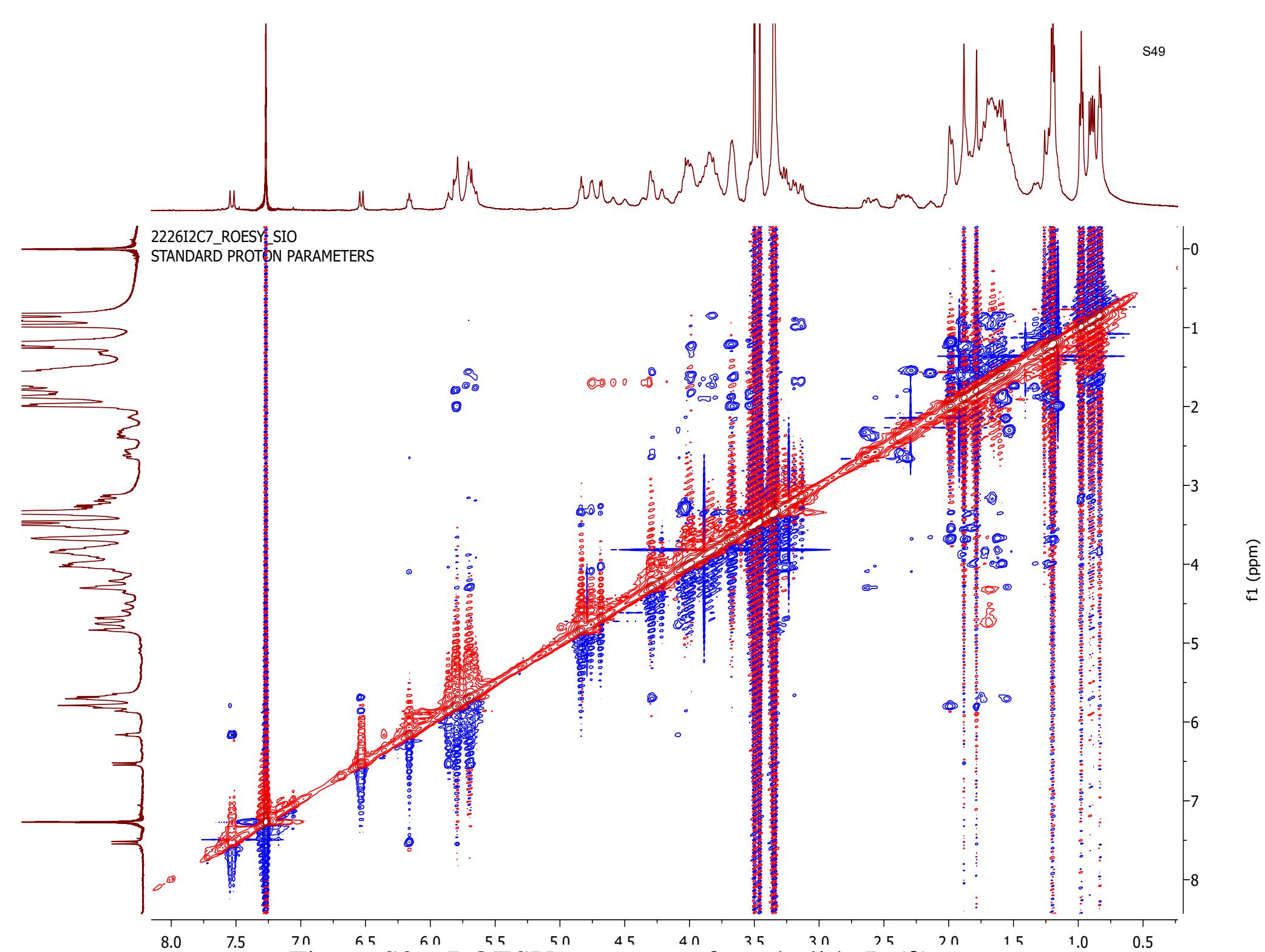


Figure S26 ROESY spectrum of samholide B (2)

F5-a #13-18 RT: 0.30-0.42 AV: 6 SB: 3 0.06-0.11 NL: 4.11E7

T: + c Full ms [ 300.00-2000.00]

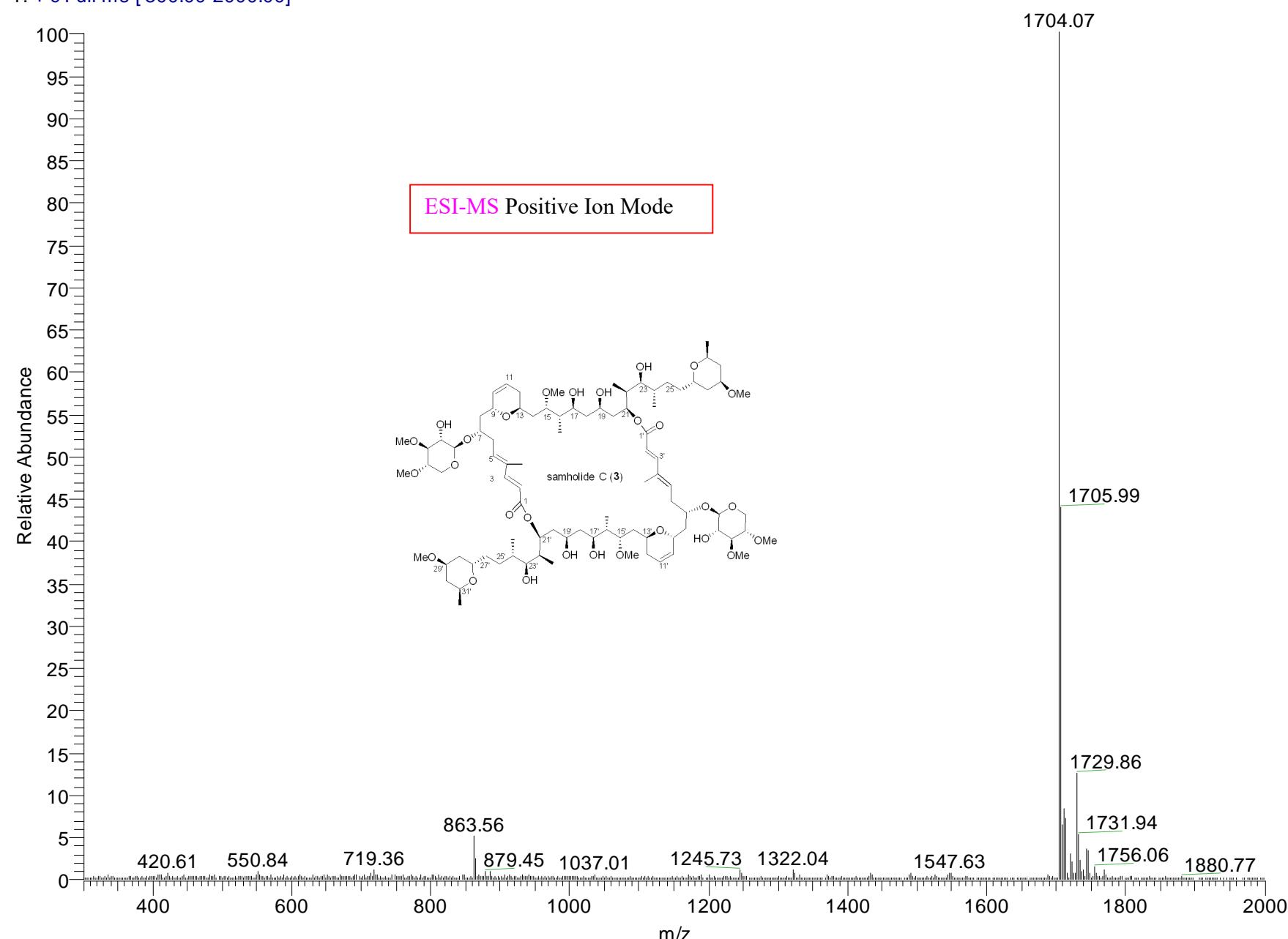


Figure S27 The ESI MS spectrum of samholide C (**3**)

F5-a #51-56 RT: 1.10-1.18 AV: 6 SB: 5 0.93-1.01 NL: 3.45E7

T: + c Full ms2 1704.00@35.00 [ 465.00-2000.00]

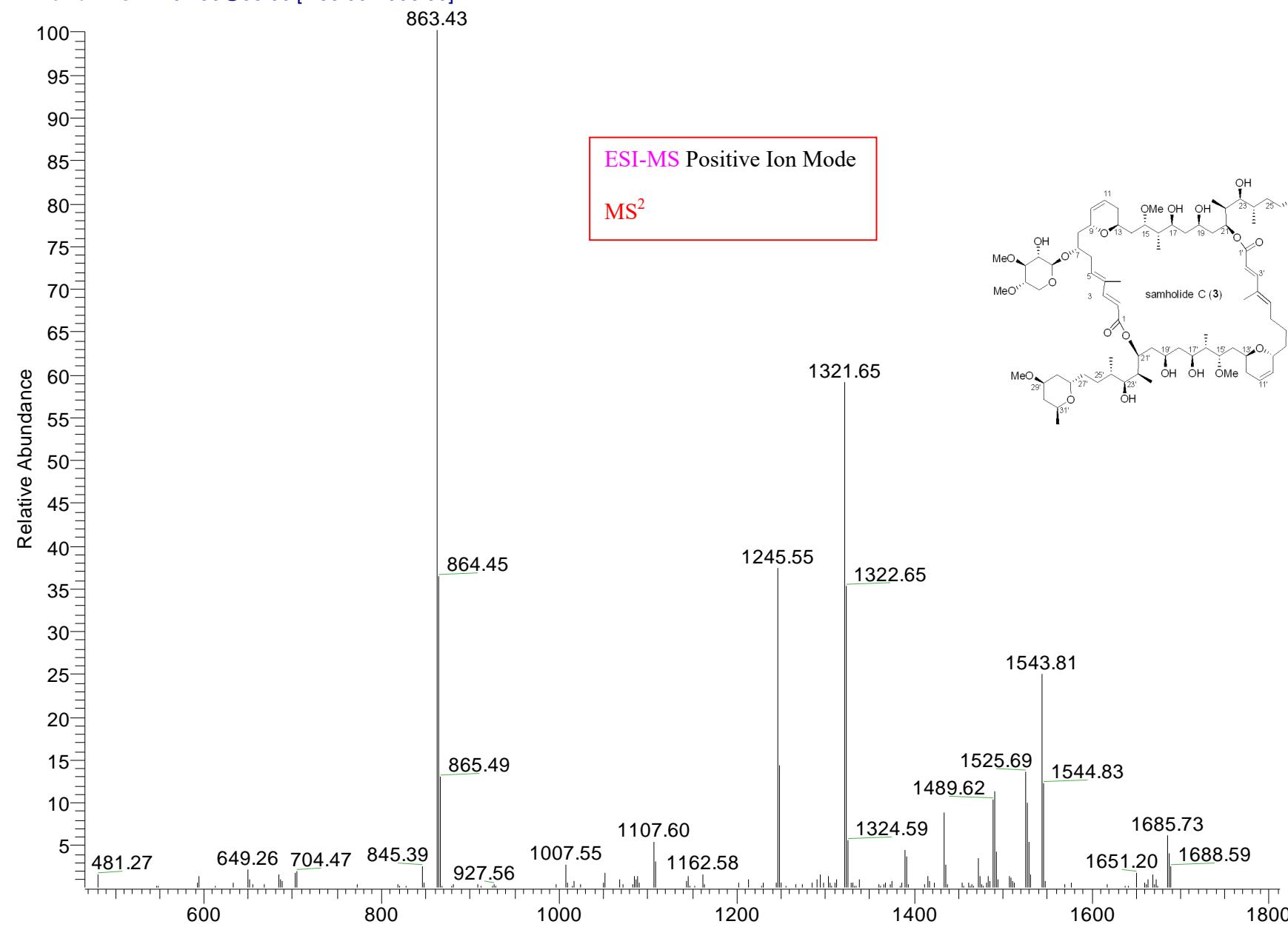
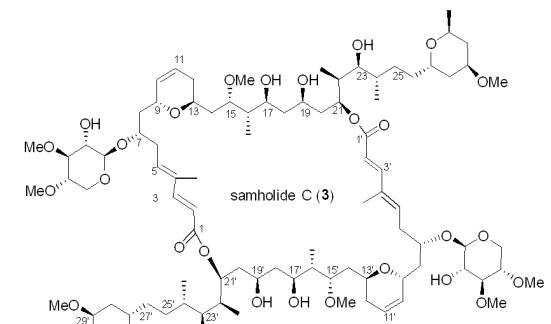


Figure S28 The ESI MS<sup>2</sup> spectrum of samholide C (3)



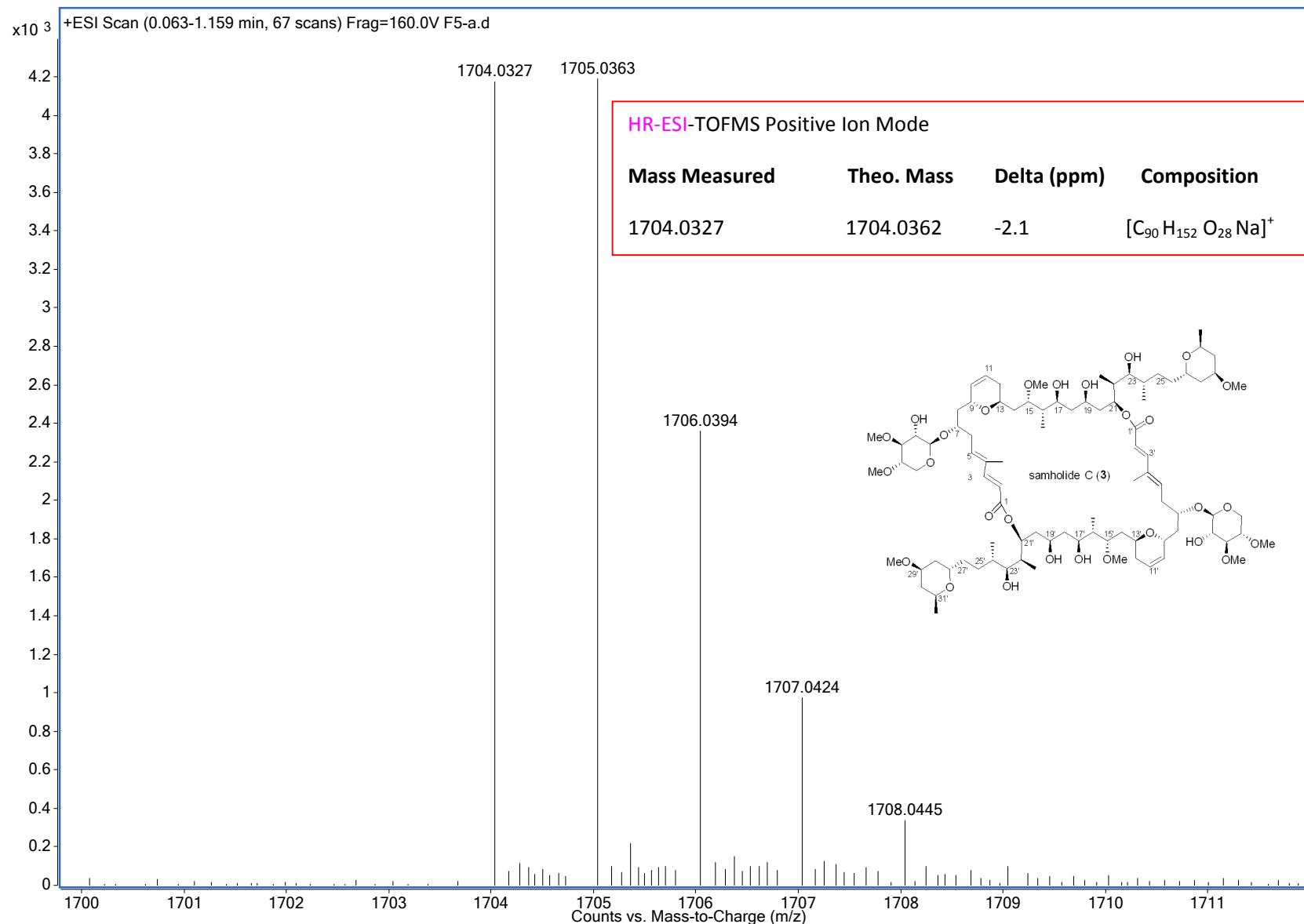
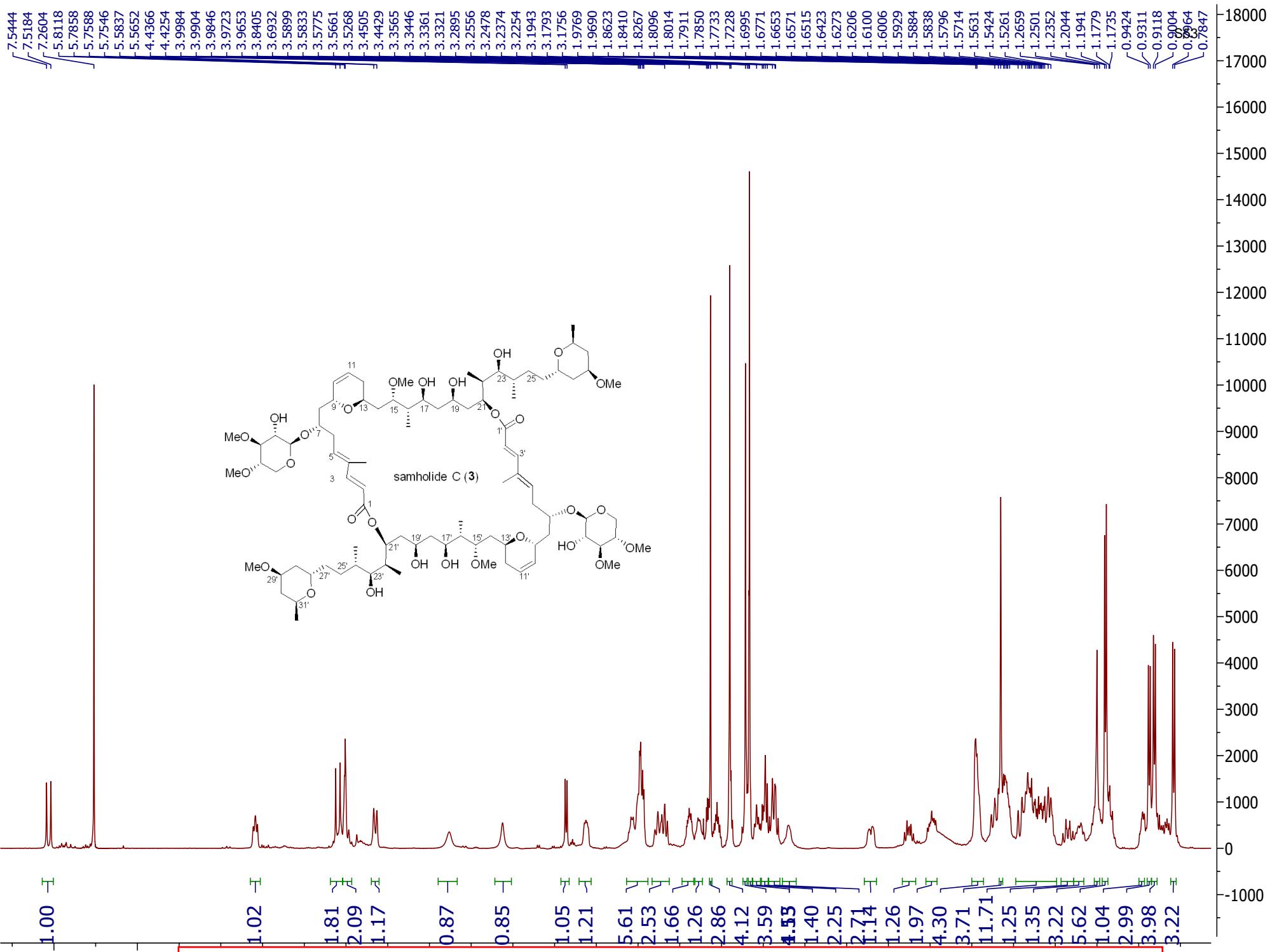
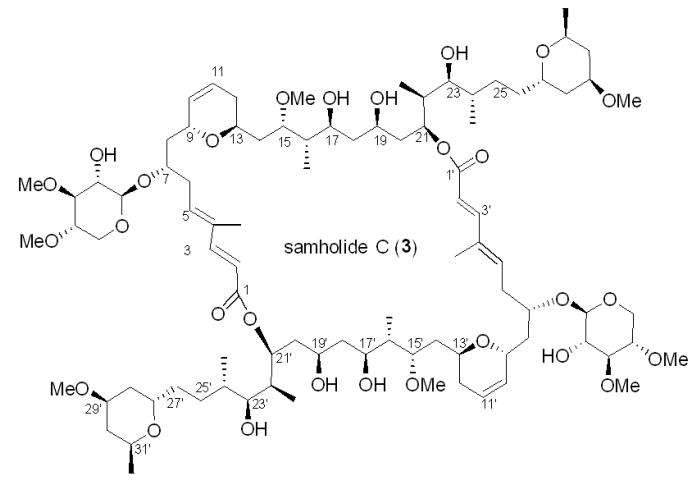


Figure S29 The positive HRESIMS spectrum of samholide C (3)





samholide C (3)

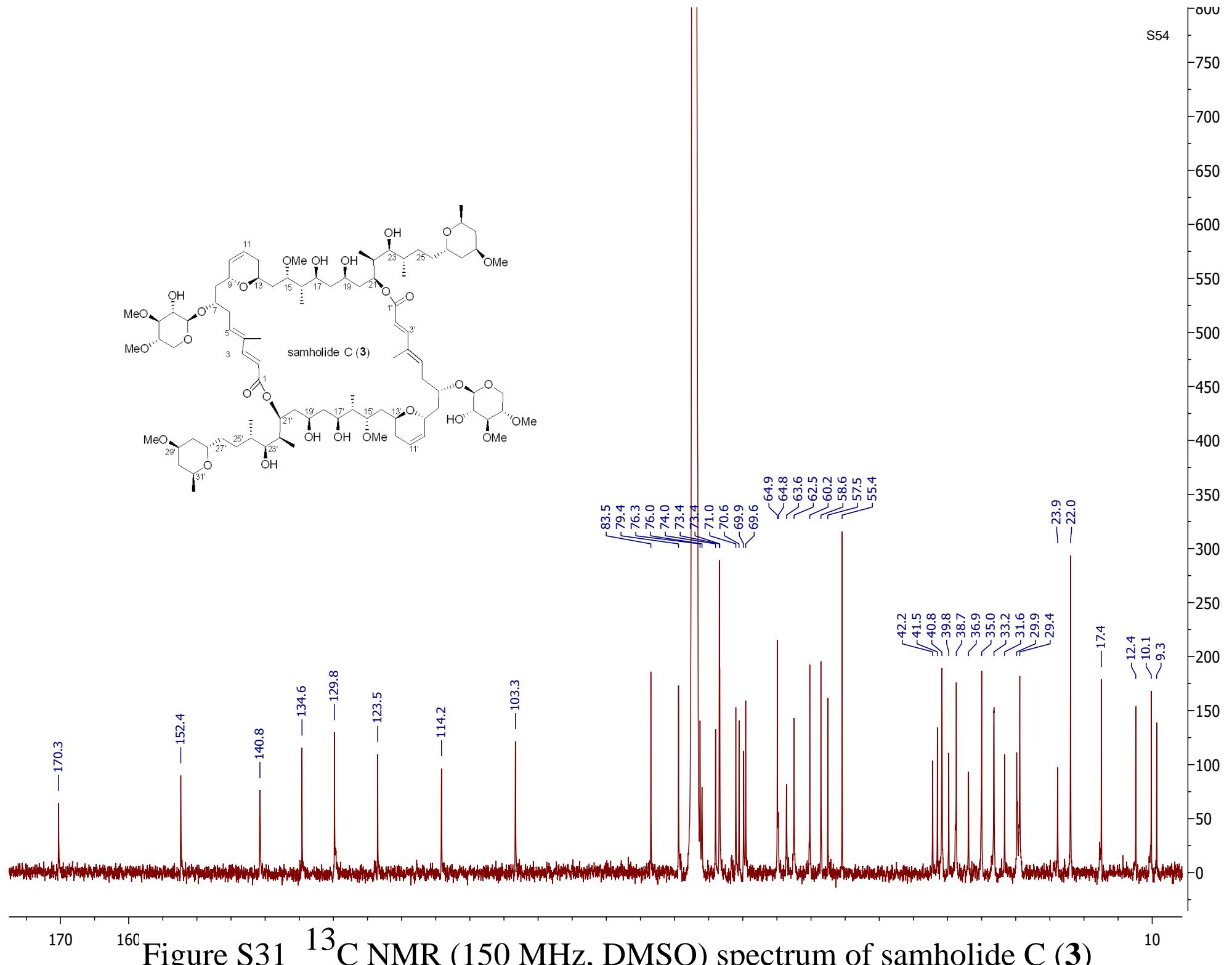


Figure S31 <sup>13</sup>C NMR (150 MHz, DMSO) spectrum of samholide C (3)

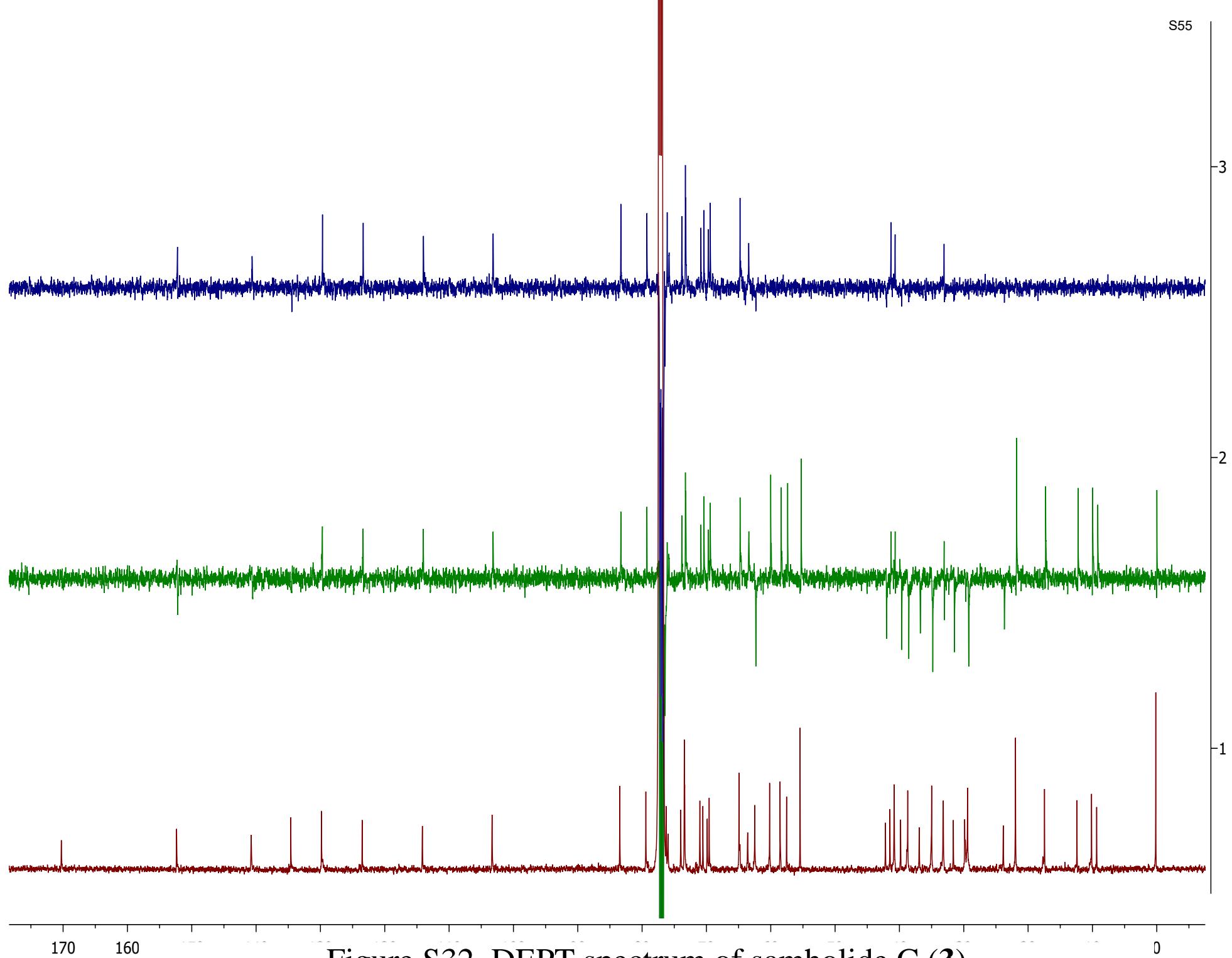


Figure S32 DEPT spectrum of samholide C (3)

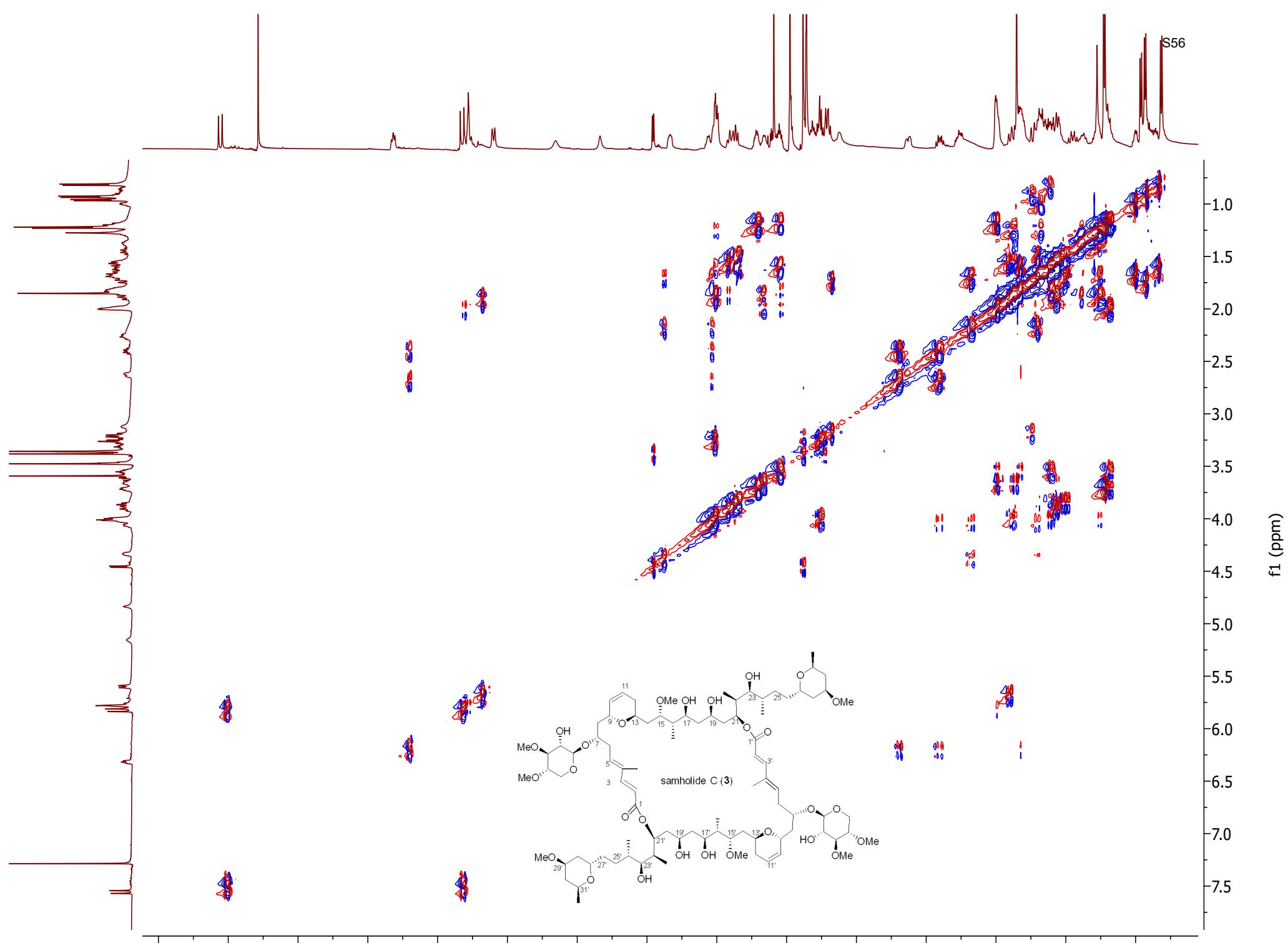


Figure S33  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of samholide C (3)

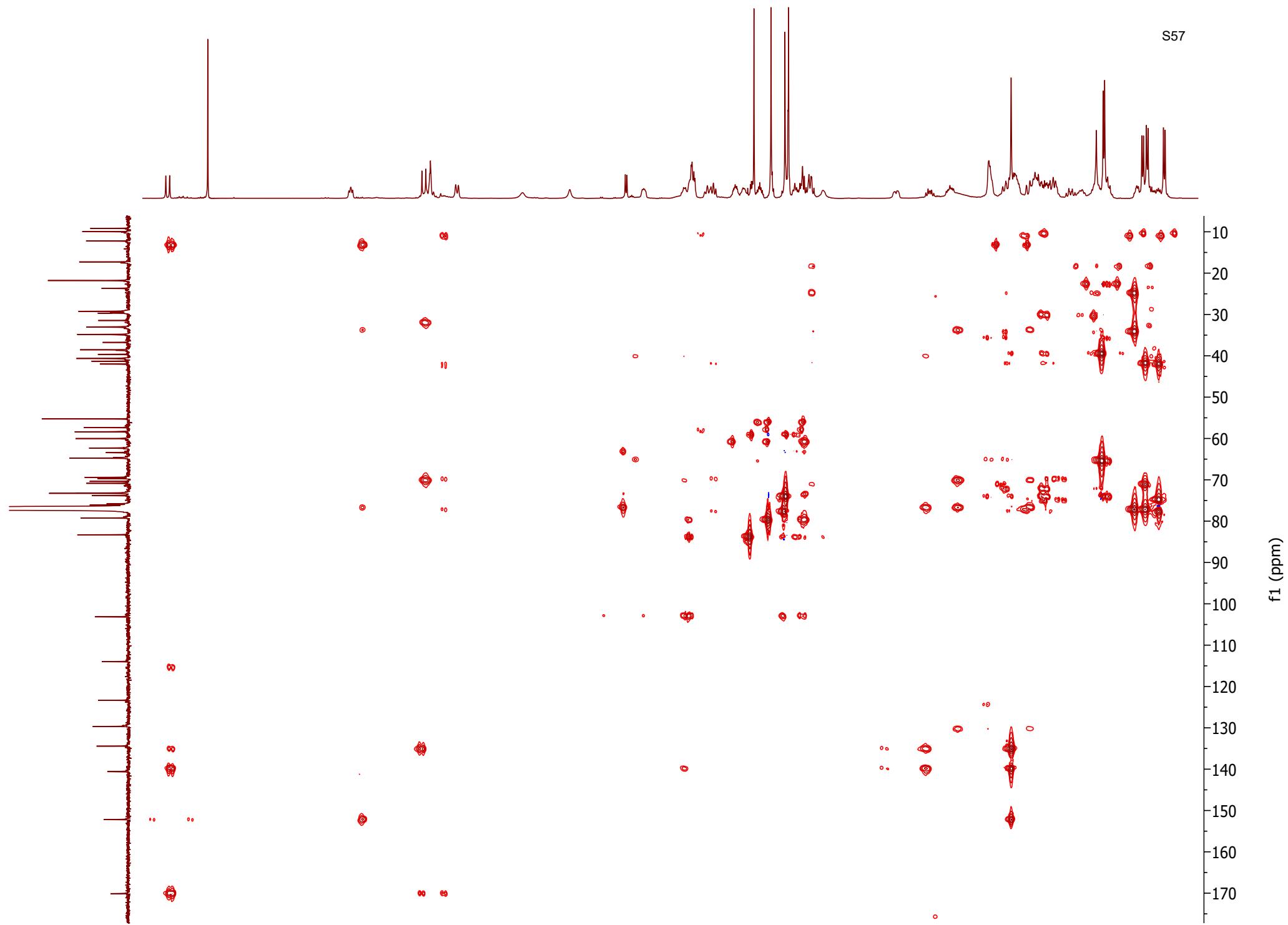


Figure S34 HMBC spectrum of samholide C (3)

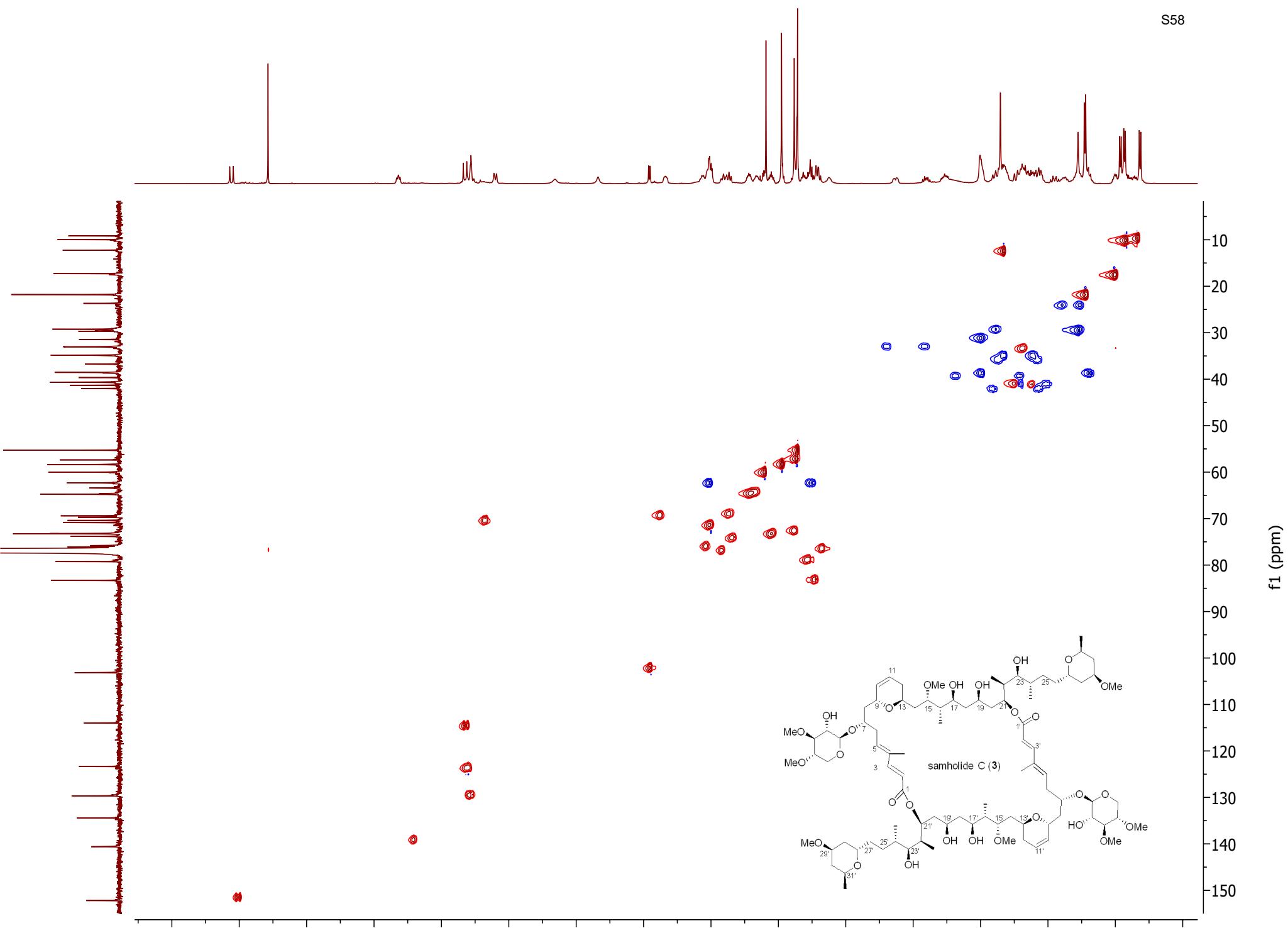


Figure S35 HMQC spectrum of samholide C (3)

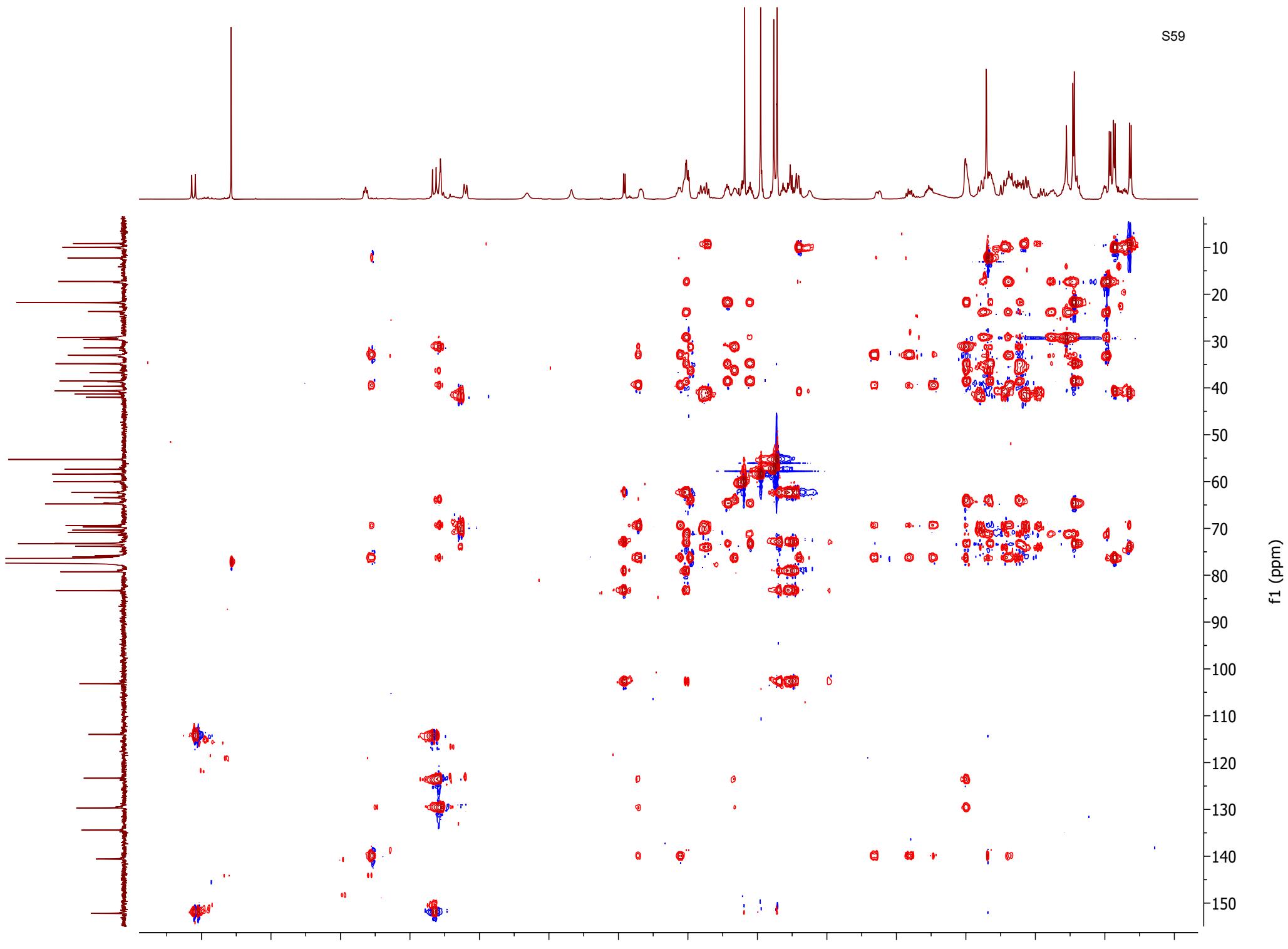
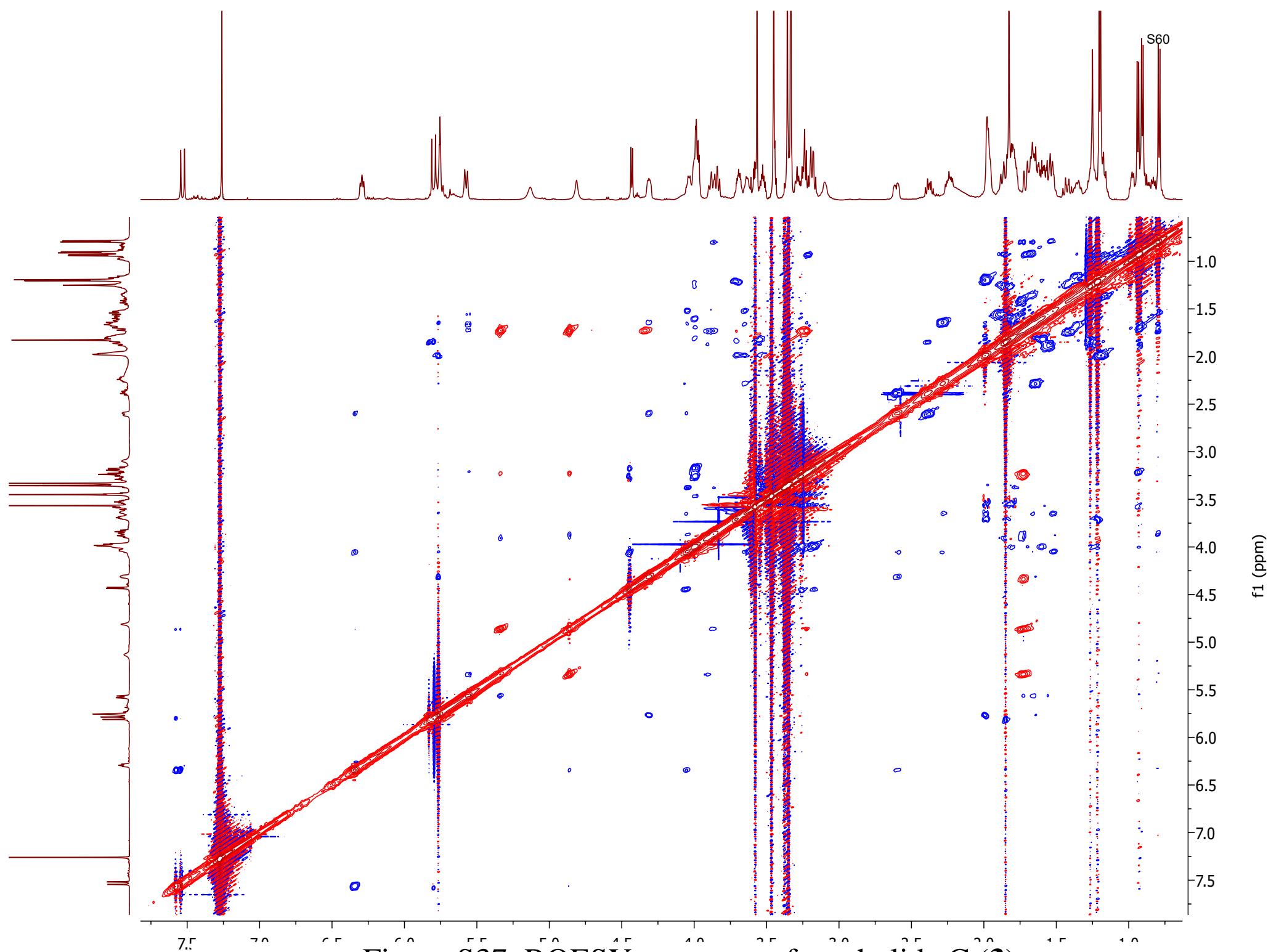


Figure S36 HSQC-TOCSY spectrum of samholide C (3)



2226H3D2B-a #20-22 RT: 0.48-0.53 AV: 3 SB: 6 0.07-0.19 NL: 2.71E8

T: + c Full ms [200.00-2000.00]

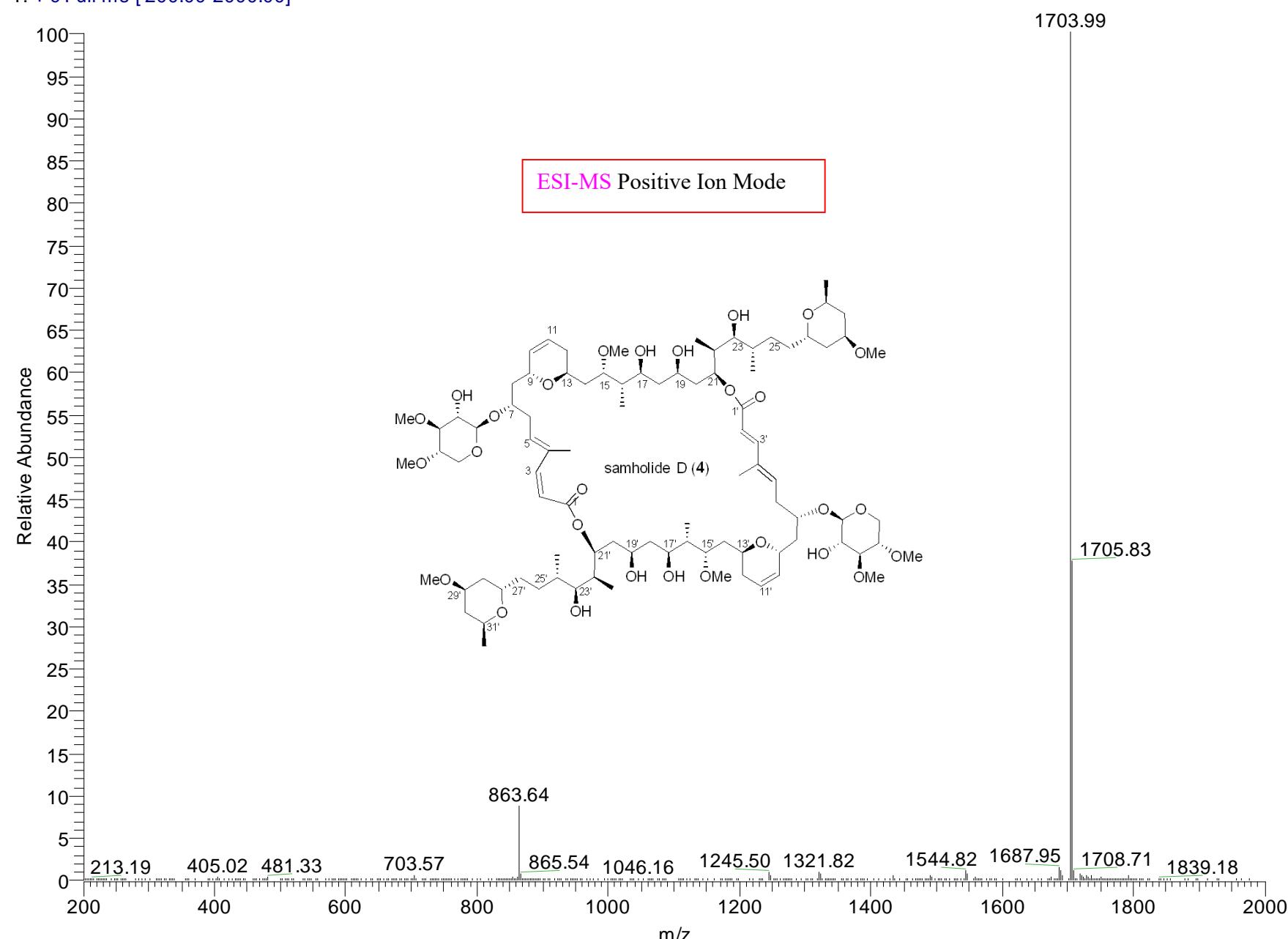


Figure S38 The ESI MS spectrum of samholide D (4)

2226H3D2B-a #24-33 RT: 0.58-0.72 AV: 10 NL: 3.76E7

F: + c Full ms2 1704.00@35.00 [ 490.00-2000.00]

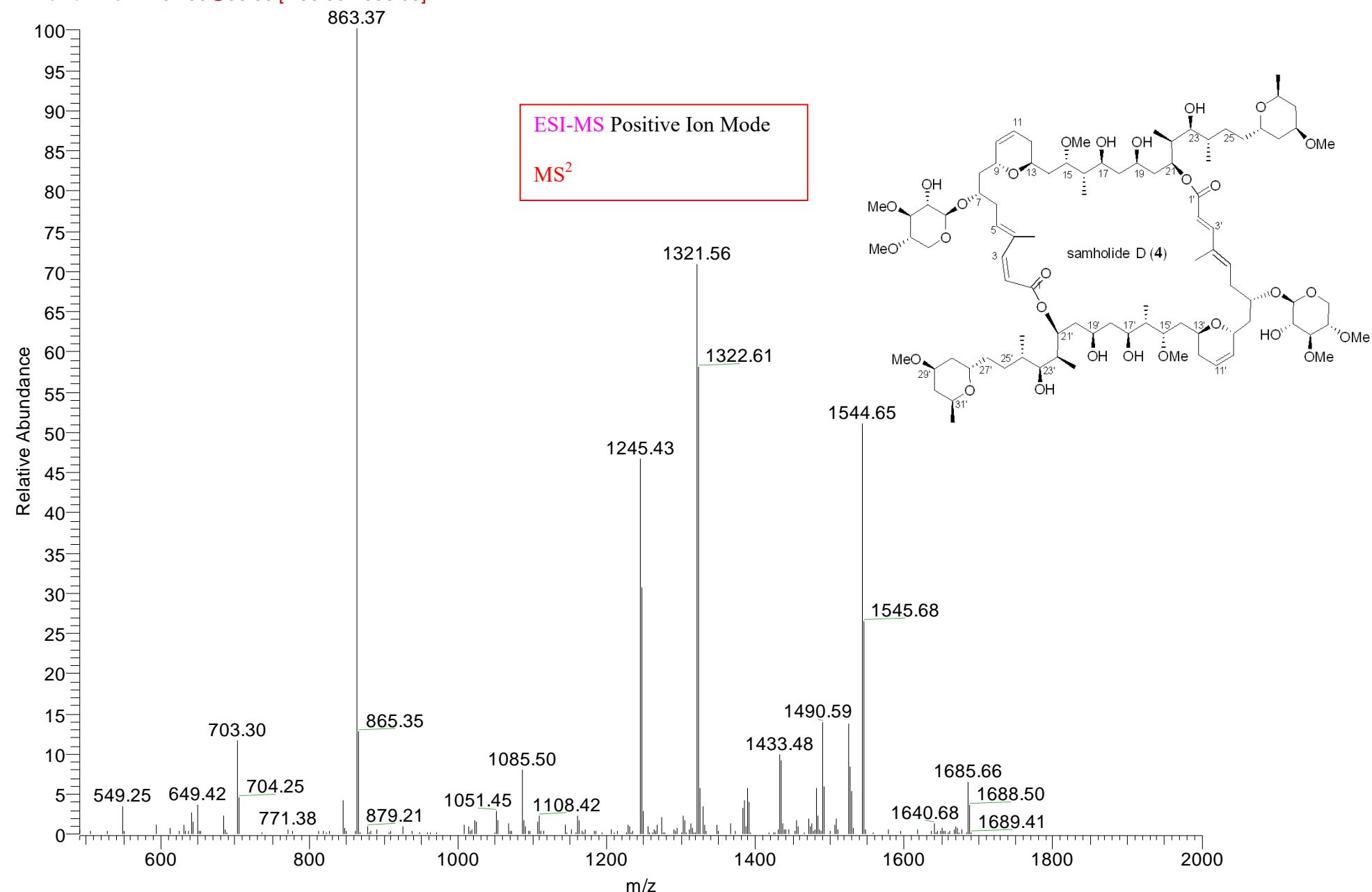


Figure S39 The ESI  $\text{MS}^2$  spectrum of samholide D (4)

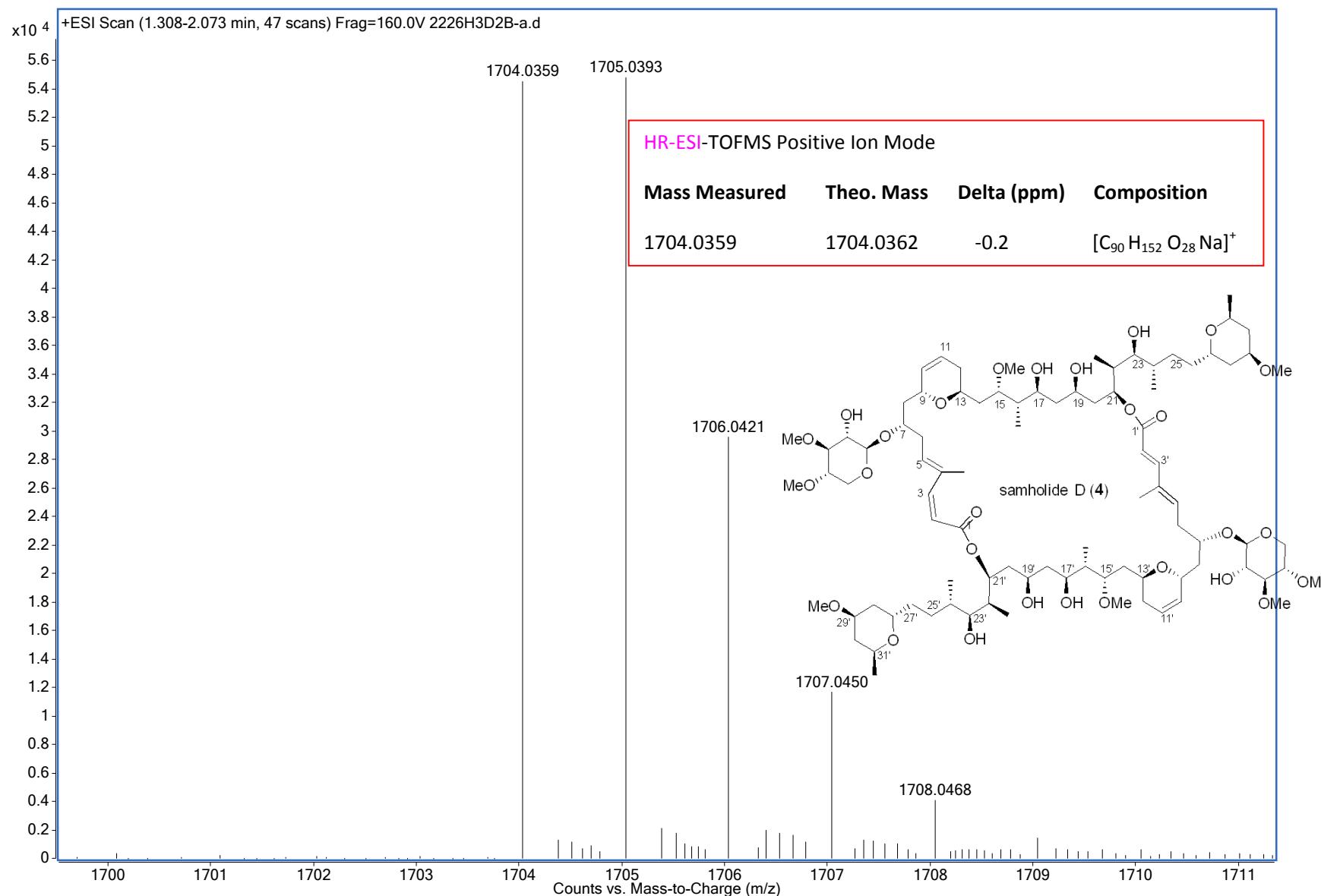
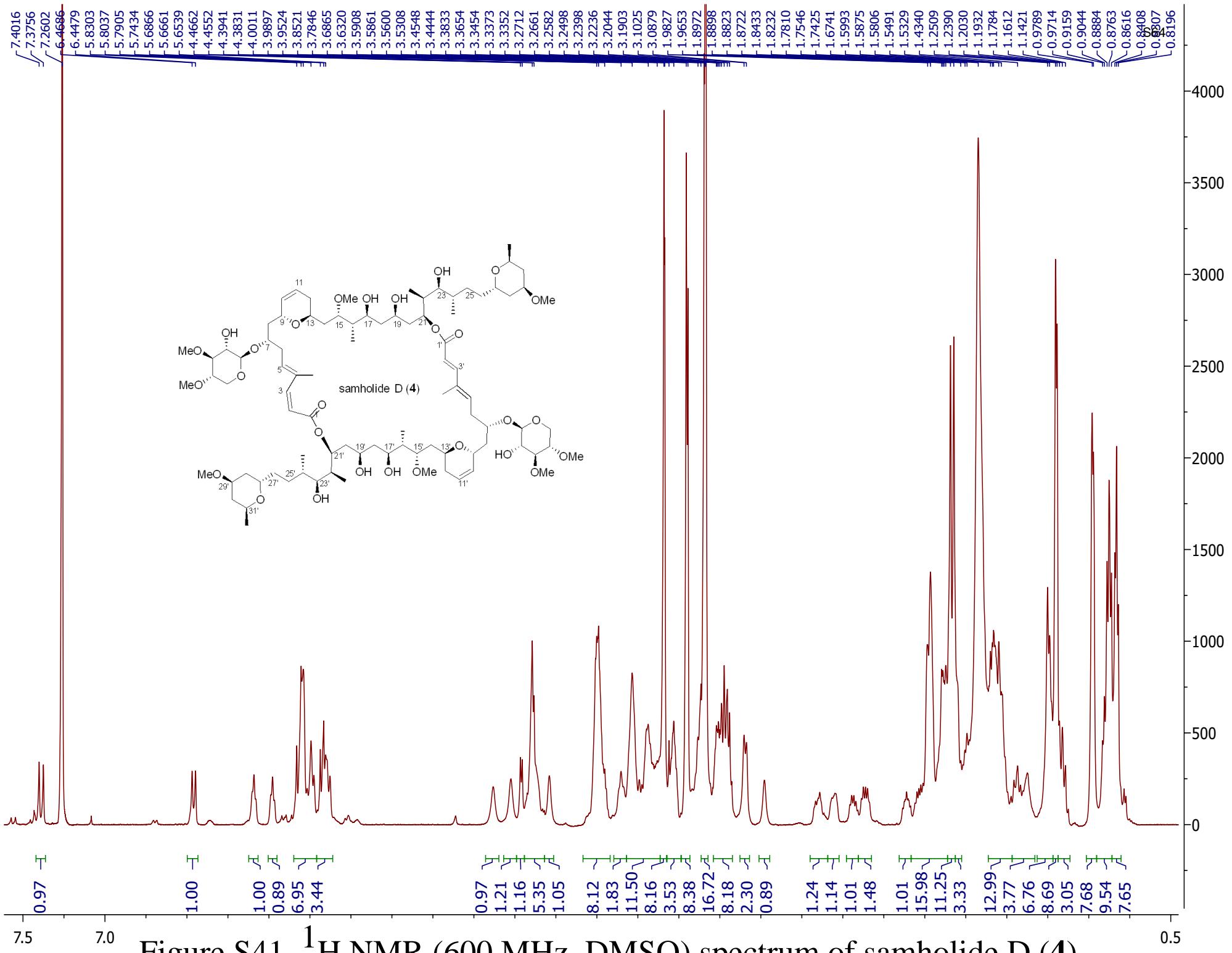


Figure S40 The positive HRESIMS spectrum of samholide D (4)



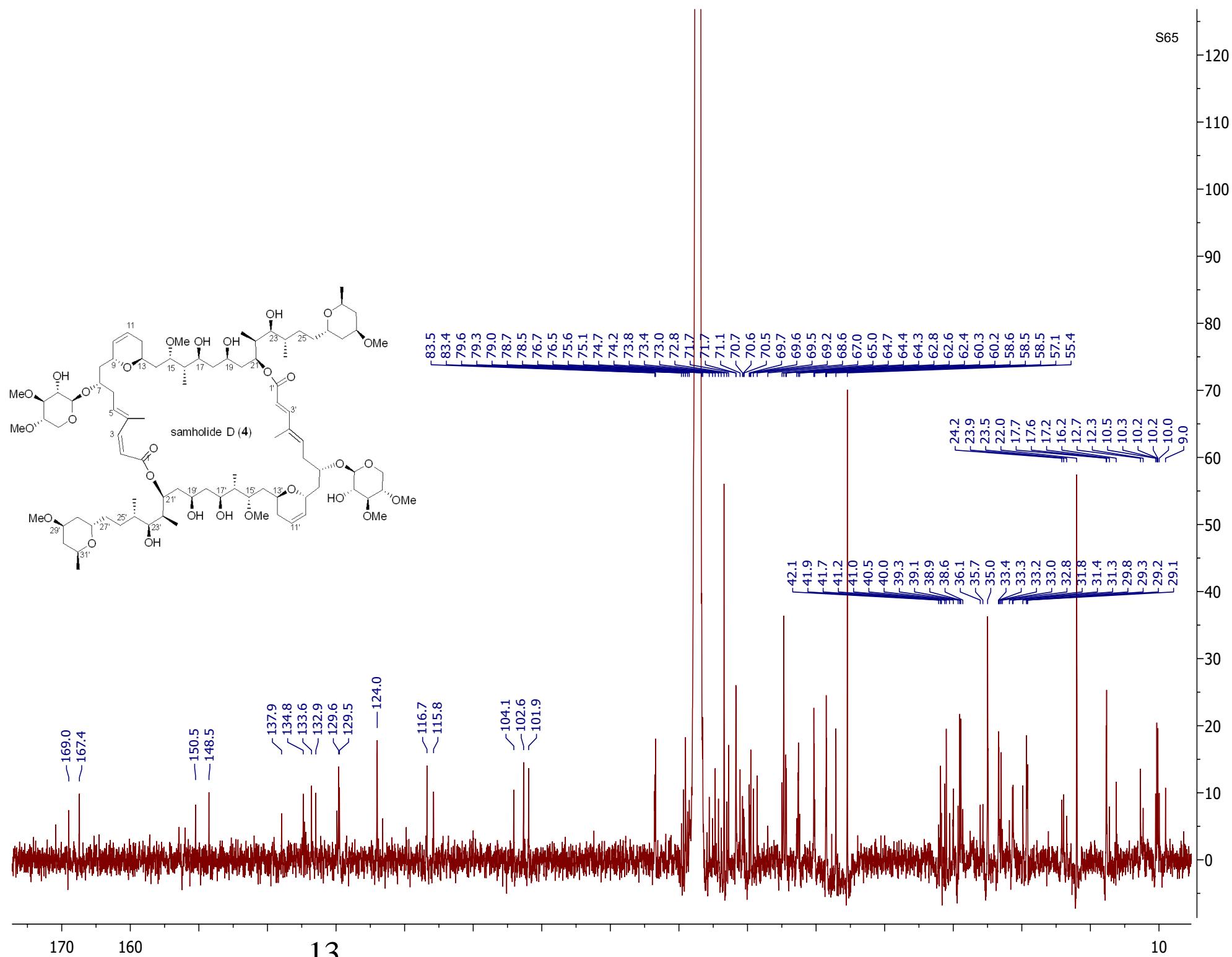
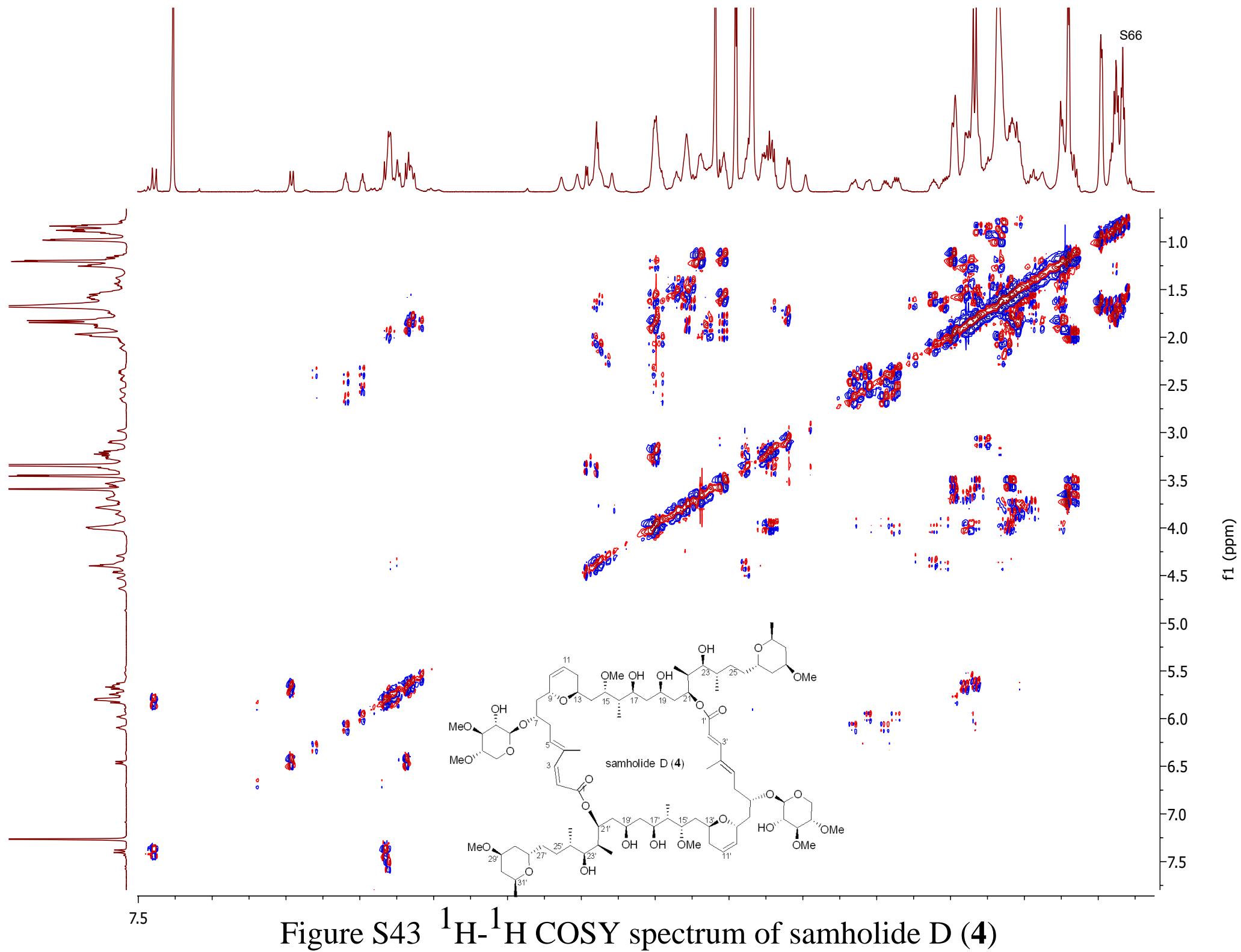


Figure S42  $^{13}\text{C}$  NMR (150 MHz, DMSO) spectrum of samholide D (4)



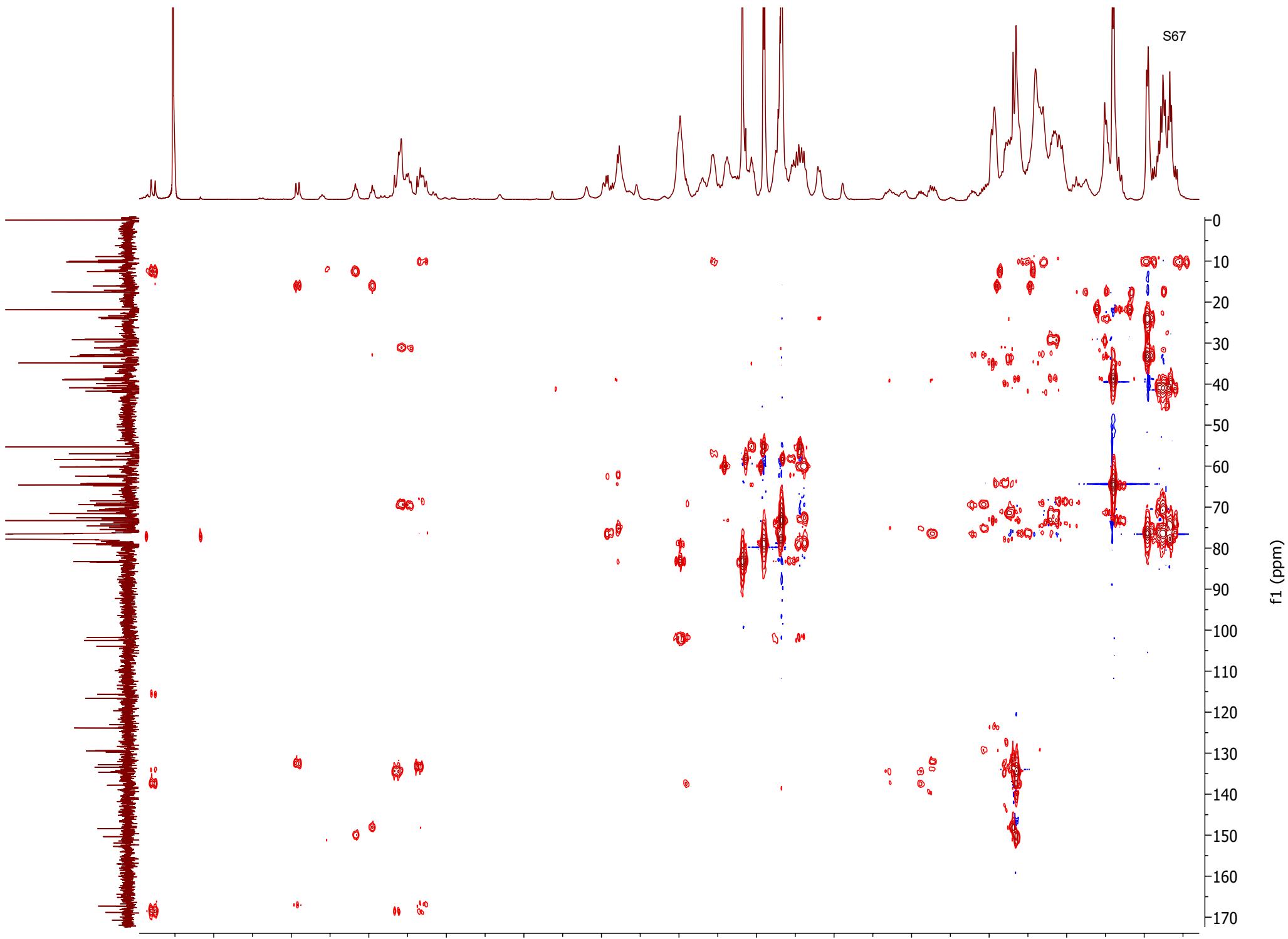


Figure S44 HMBC spectrum of samholide D (4)

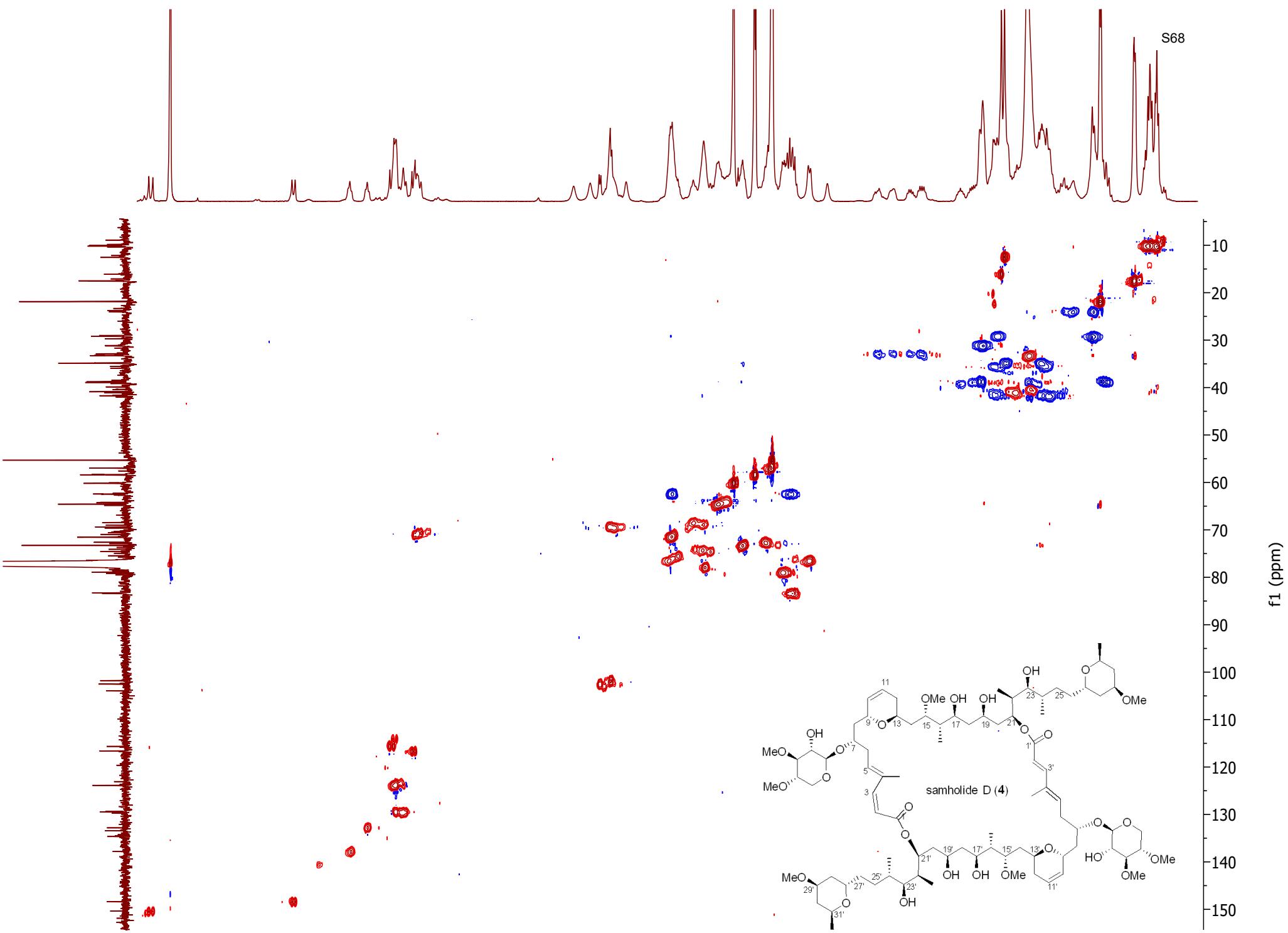
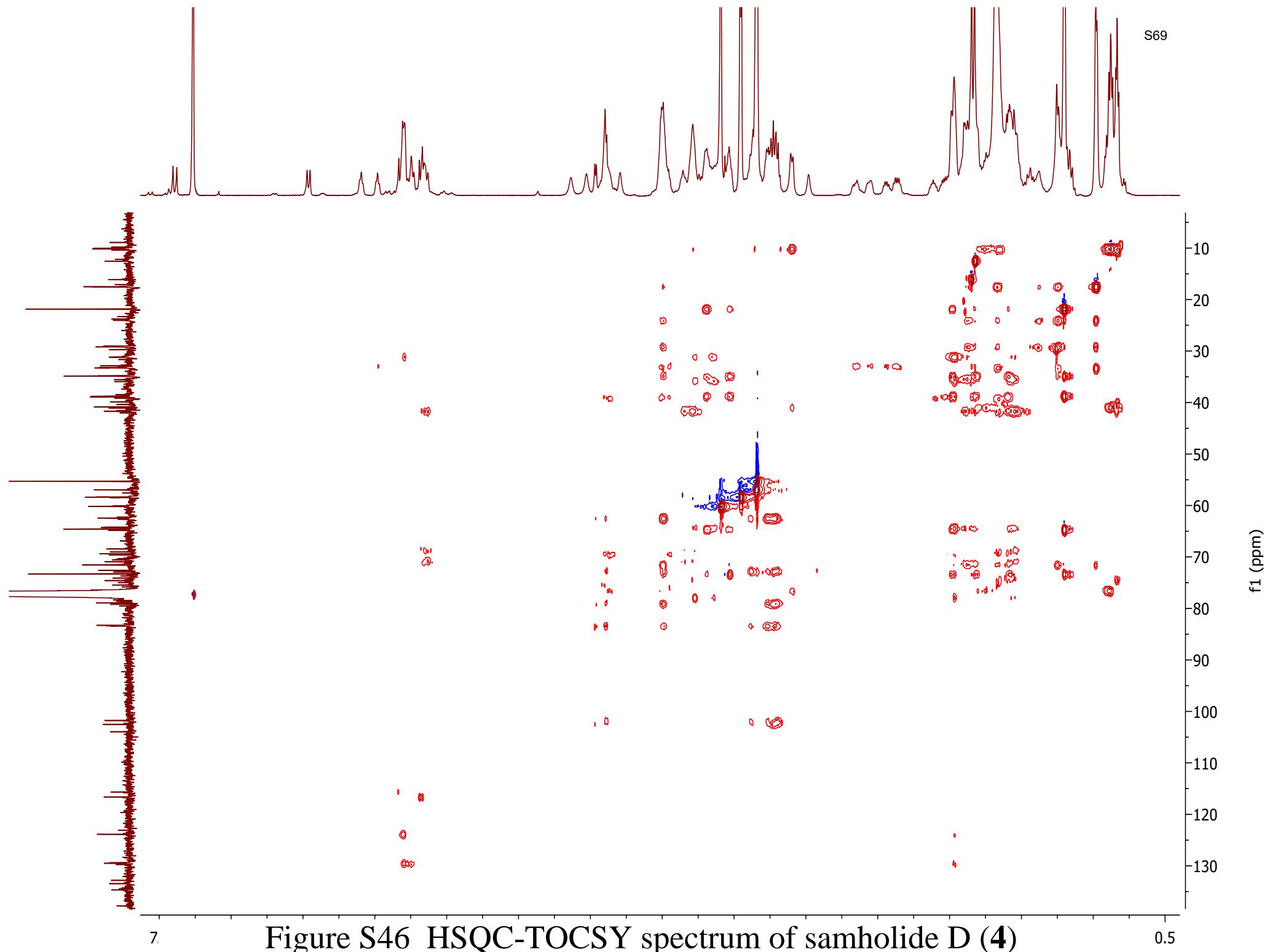


Figure S45 HMQC spectrum of samholide D (4)



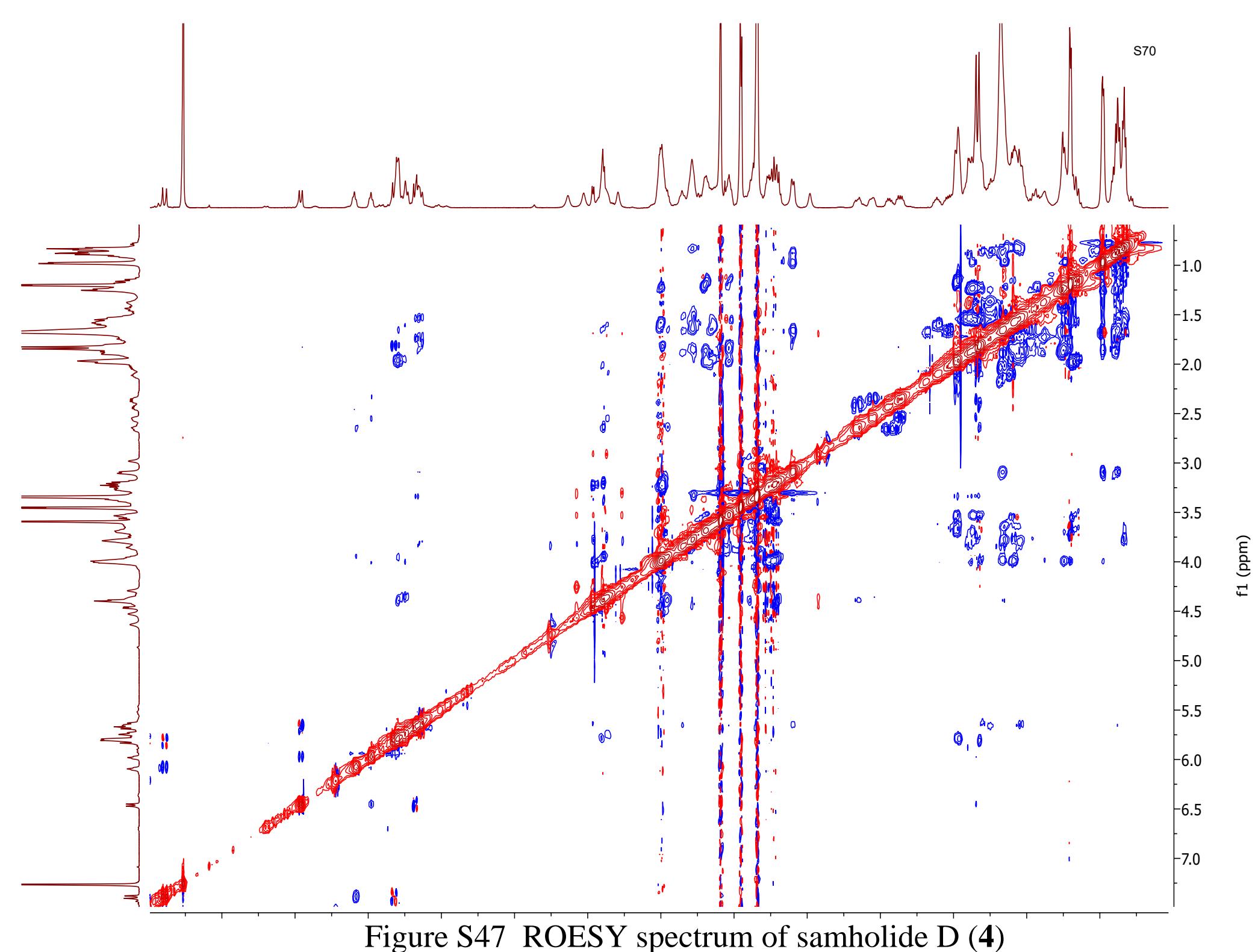


Figure S47 ROESY spectrum of samholide D (4)

E4-a #68-77 RT: 1.79-2.01 AV: 10 SB: 4 1.41-1.49 NL: 7.68E6

T: + c Full ms [ 300.00-2000.00]

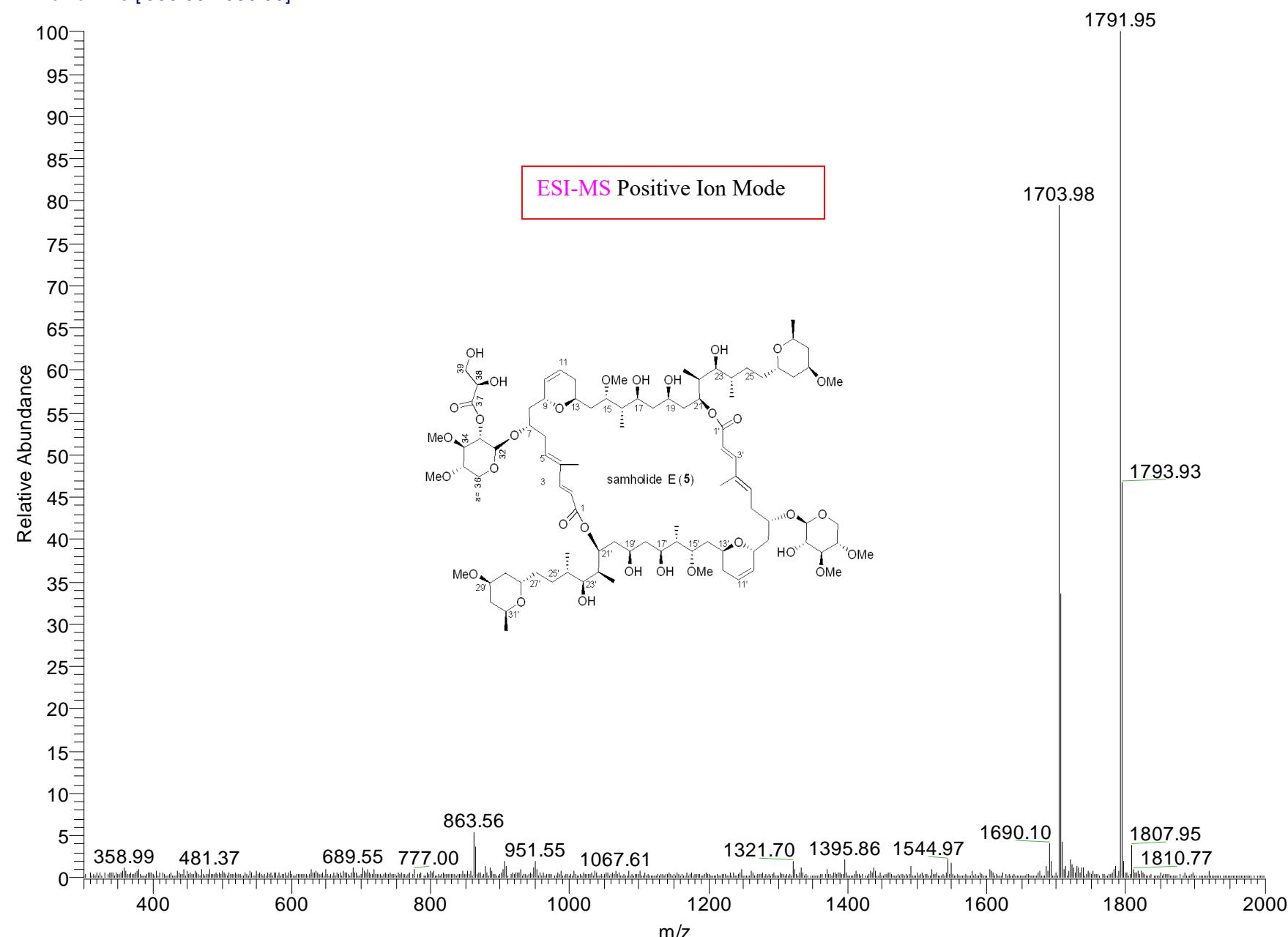


Figure S48 The ESI MS spectrum of samholide E (5)

E4-a #89-97 RT: 2.27-2.40 AV: 9 SB: 6 2.13-2.23 NL: 3.31E6

T: + c Full ms2 1792.00@35.00 [ 490.00-2000.00]

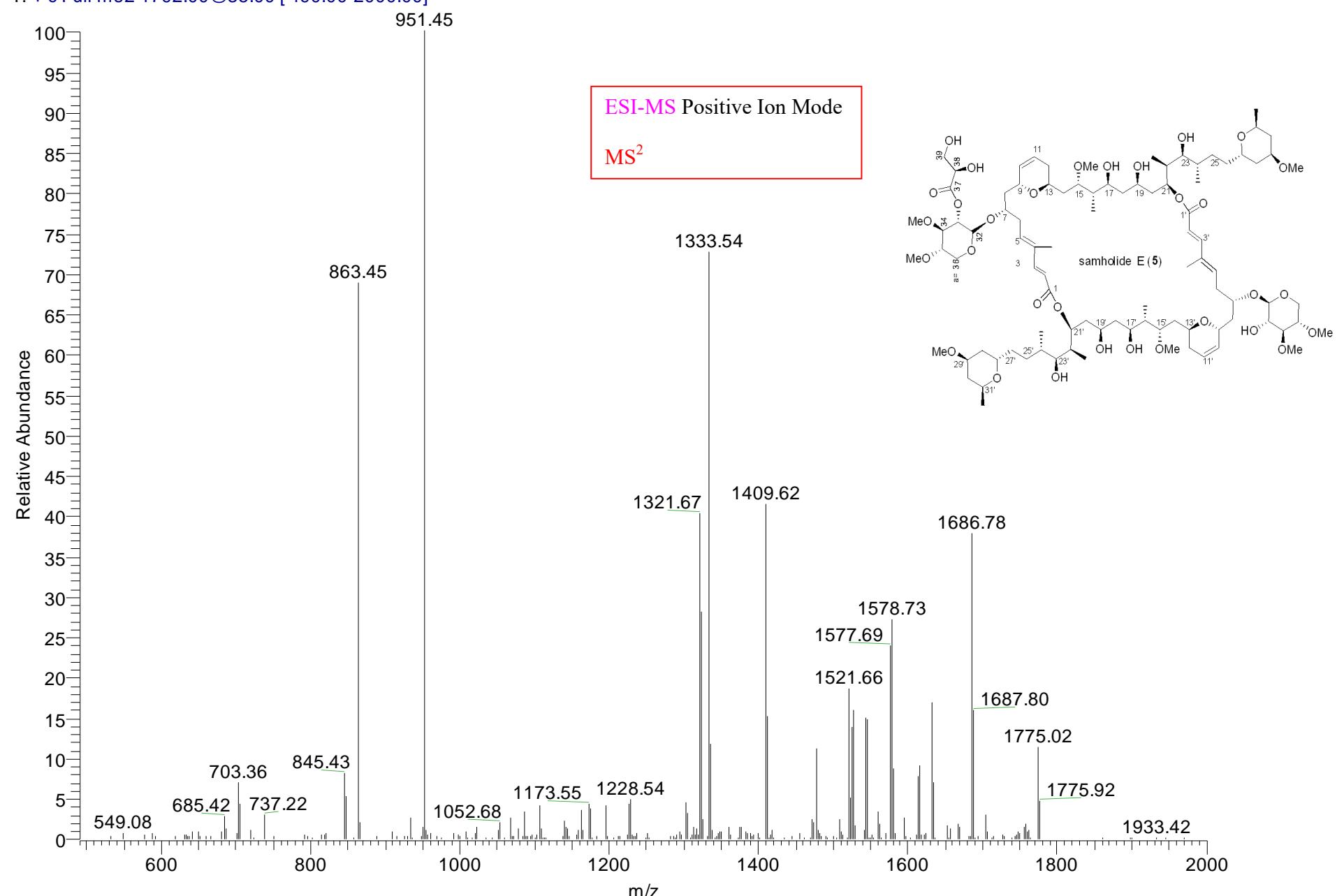


Figure S49 The ESI MS<sup>2</sup> spectrum of samholide E (5)

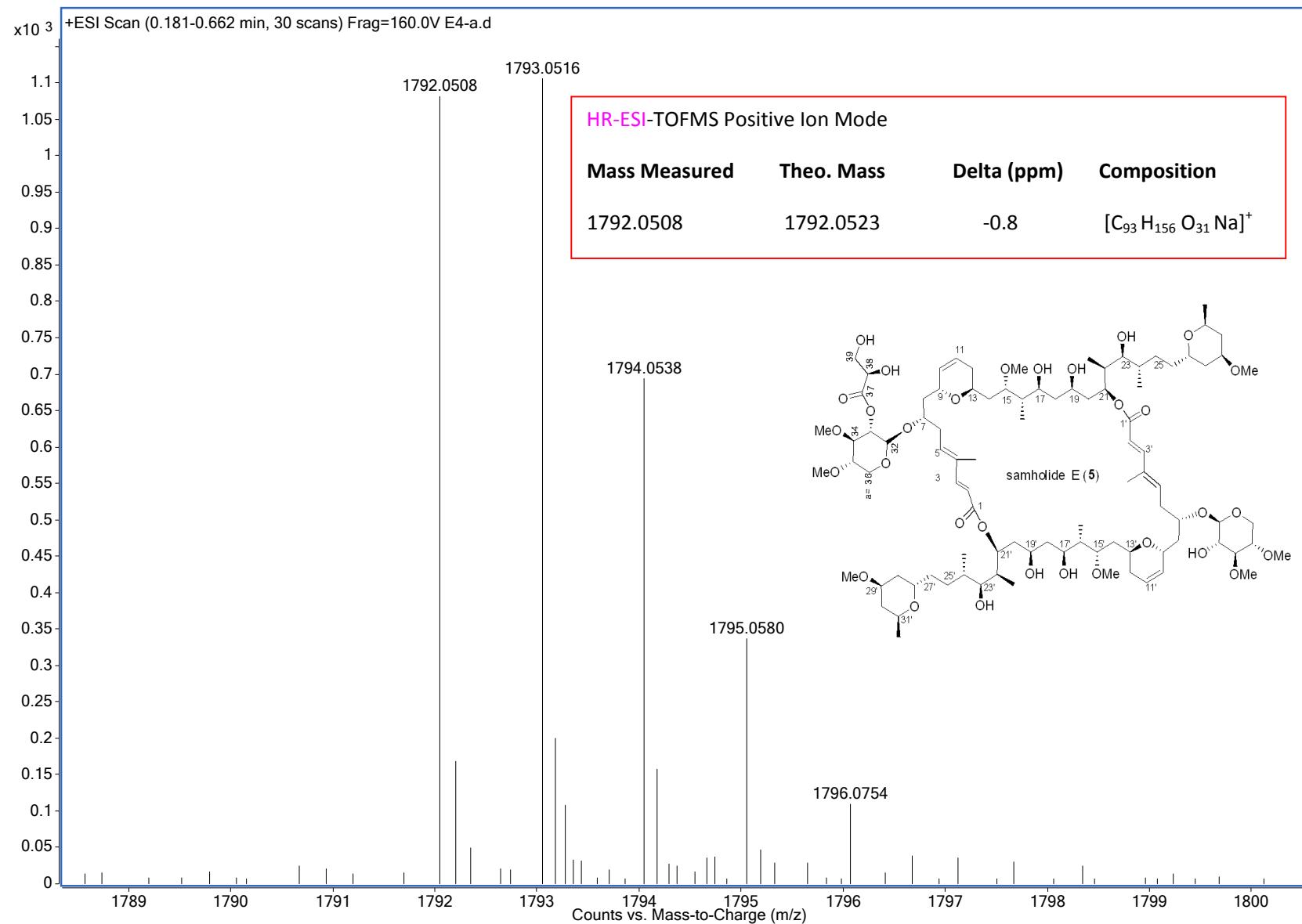


Figure S50 The positive HRESIMS spectrum of samholide E (**5**)

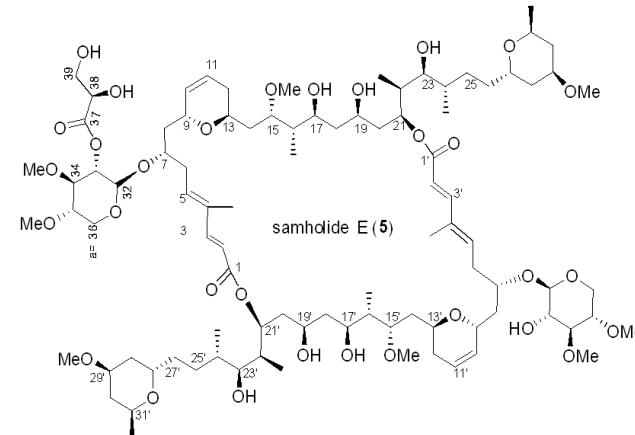


Figure S51  $^1\text{H}$  NMR (600 MHz, DMSO) spectrum of samholide E (5)

1.01  
0.99

1.53

9.07

1.54

0.82

1.10

1.00

1.173

1.58

6.88

3.00

4.10

3.41

11.26

16.92

6.38

1.03

0.97

4.38

0.83

13.56

6.01

4.65

1.69

22.80

7.51

12.80

8.19

11.09

15.63

1.0

0.87

0.8602

0.8359

0.8253

0.8076

0.7957

0.7890

0.7773

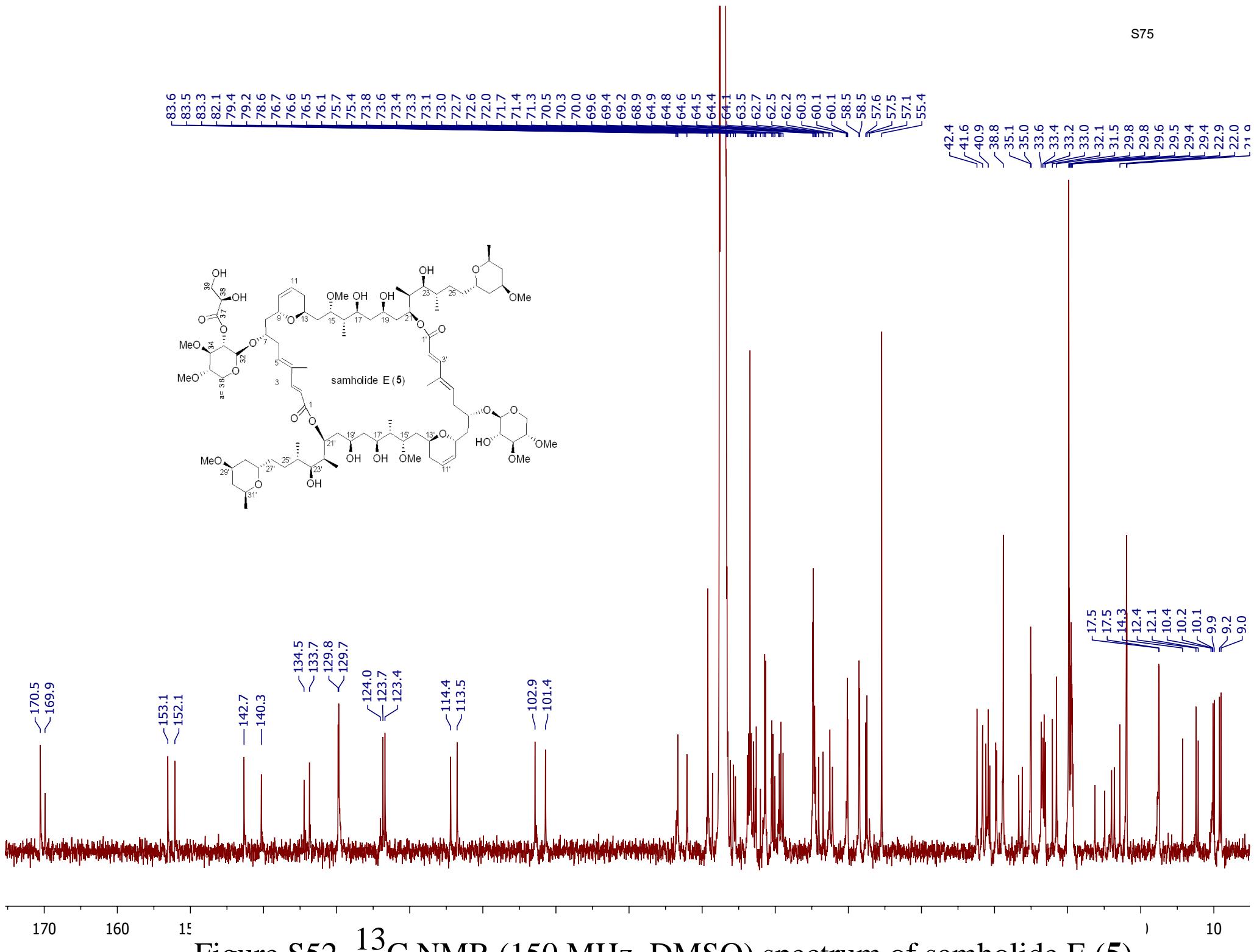


Figure S52 <sup>13</sup>C NMR (150 MHz, DMSO) spectrum of samholide E (**5**)

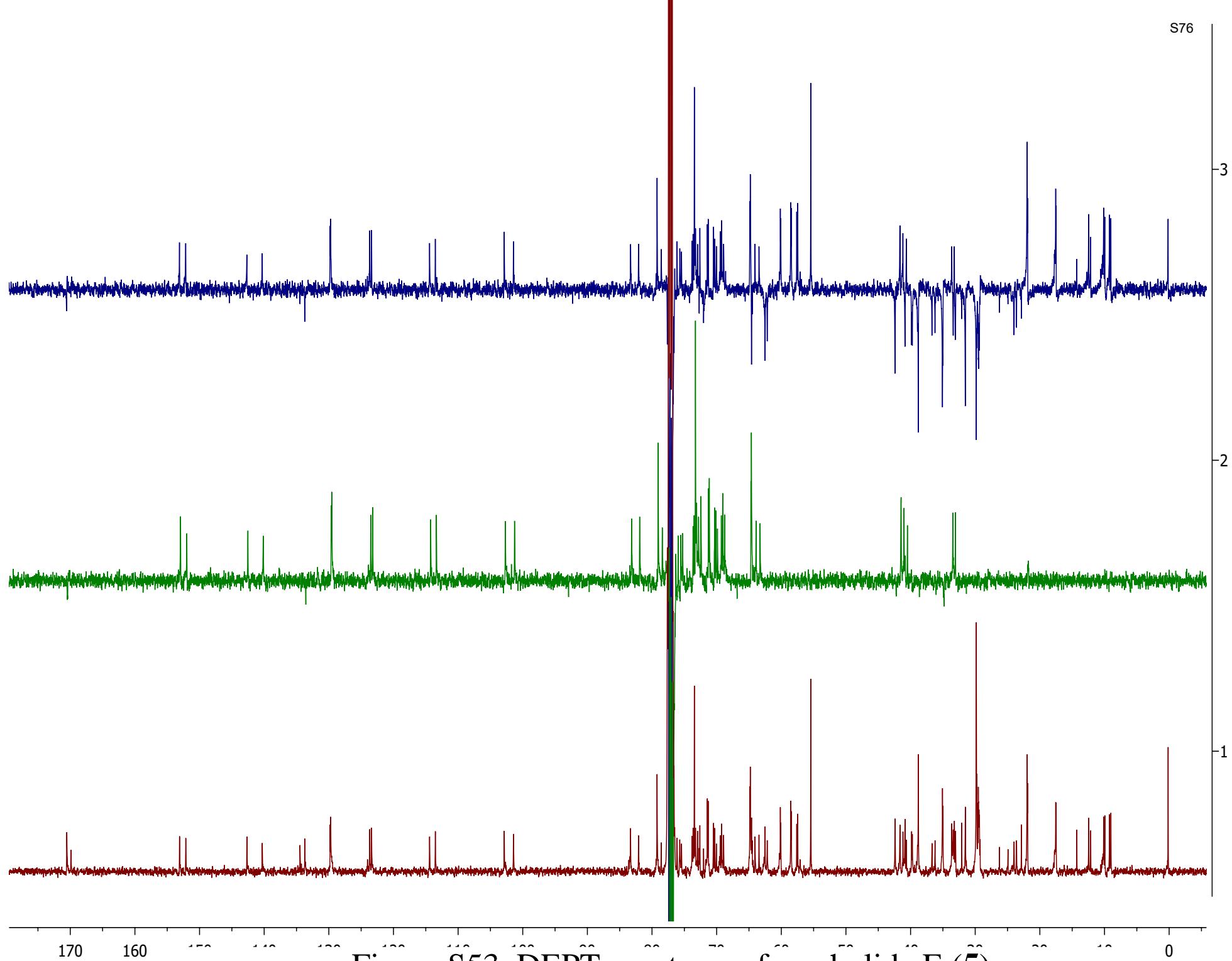
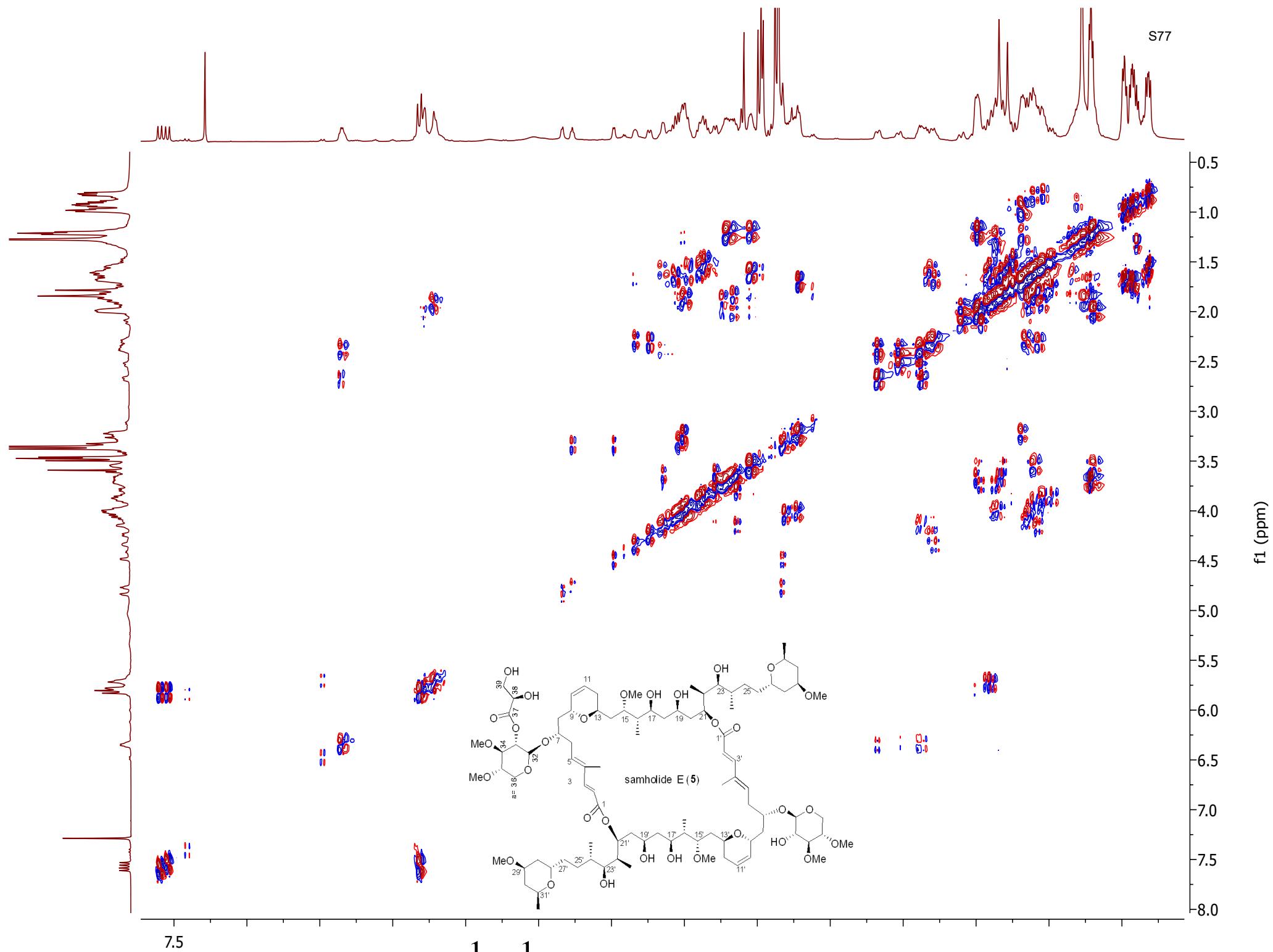


Figure S53 DEPT spectrum of samholide E (5)



S78

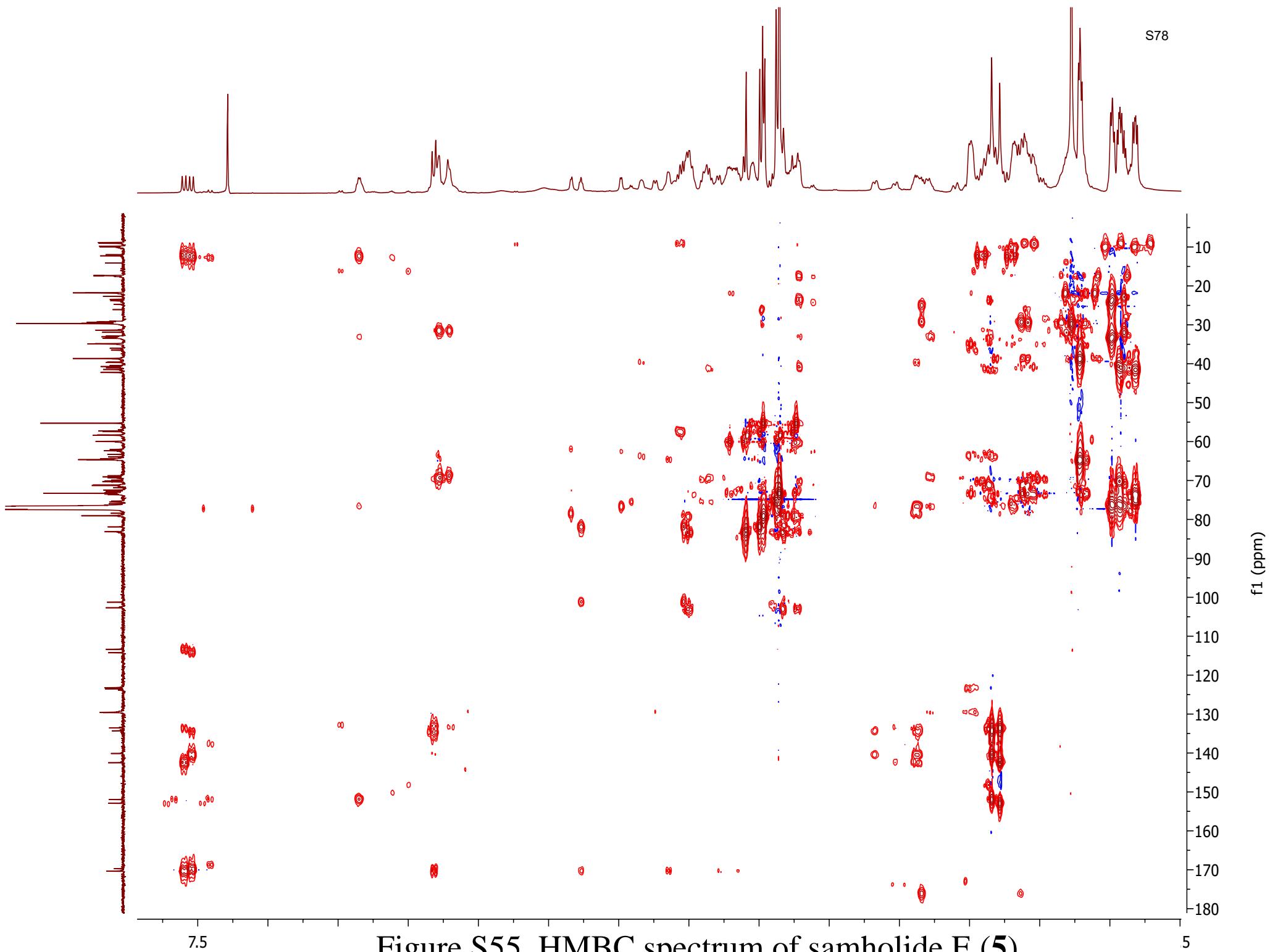


Figure S55 HMBC spectrum of samholide E (5)

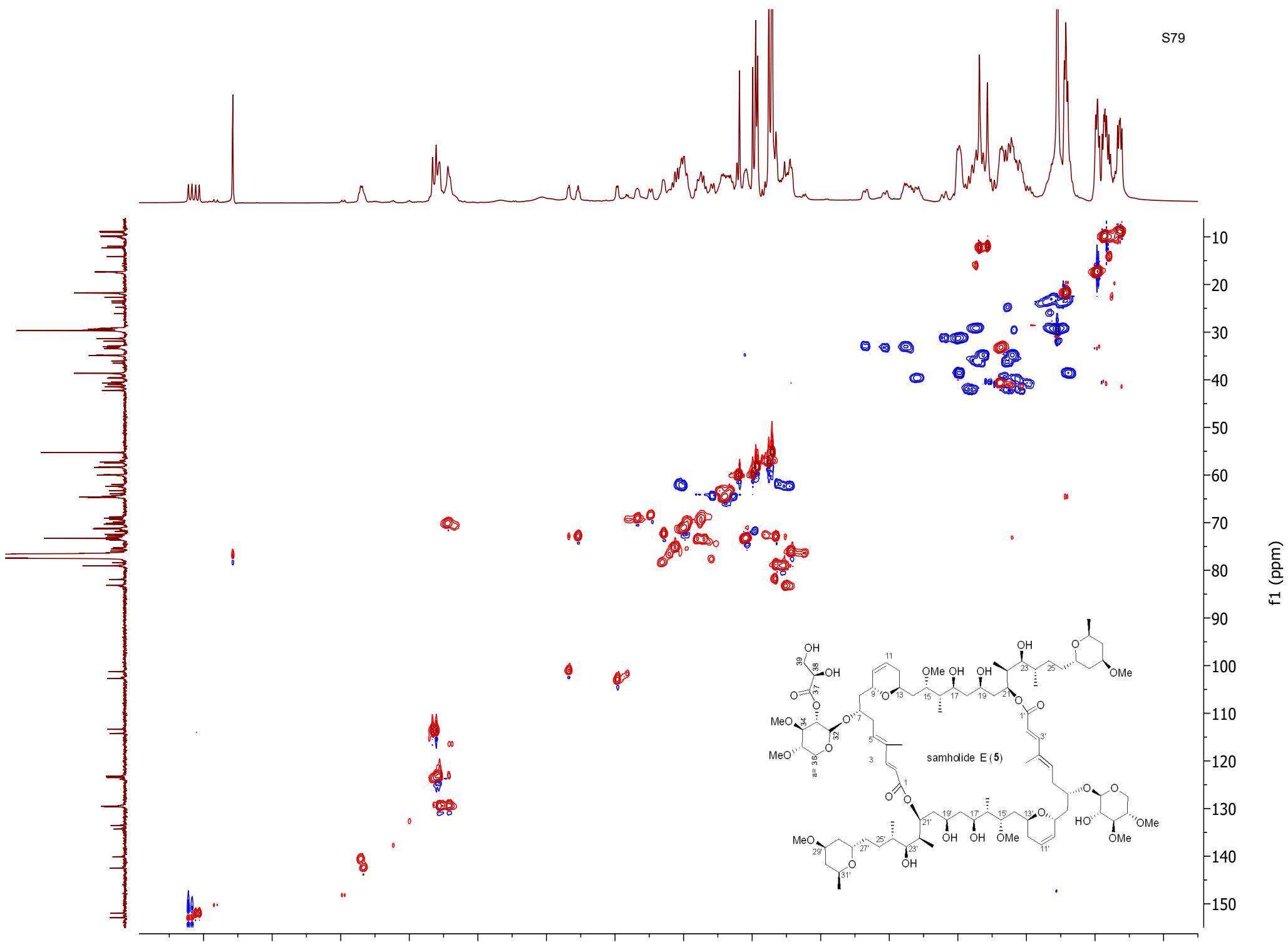


Figure S56 HMQC spectrum of samholide E (5)

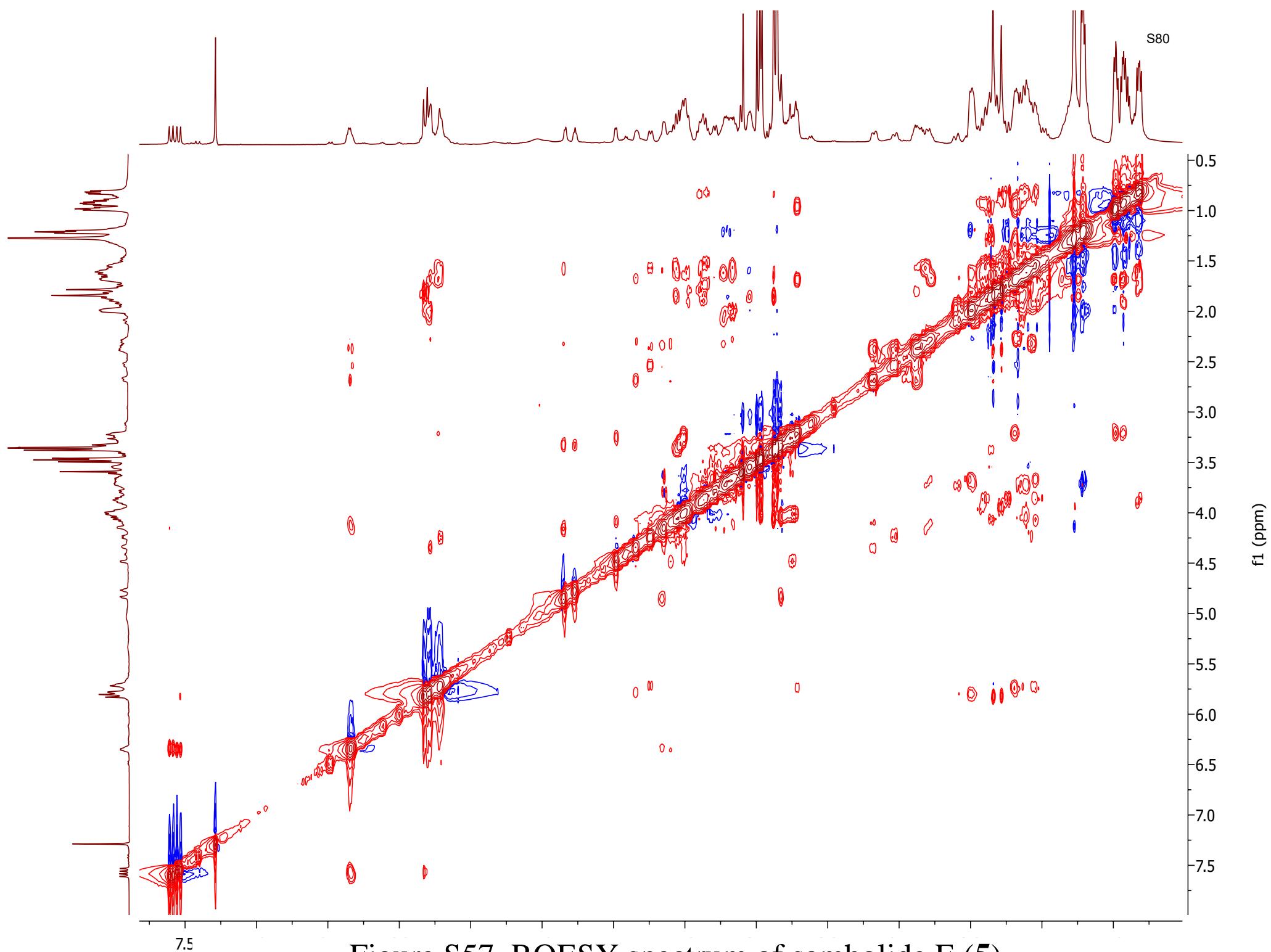


Figure S57 ROESY spectrum of samholide E (5)

2226H3C7A1-a #9-13 RT: 0.23-0.33 AV: 5 SB: 3 0.08-0.13 NL: 2.09E6  
T: + c Full ms [200.00-2000.00]

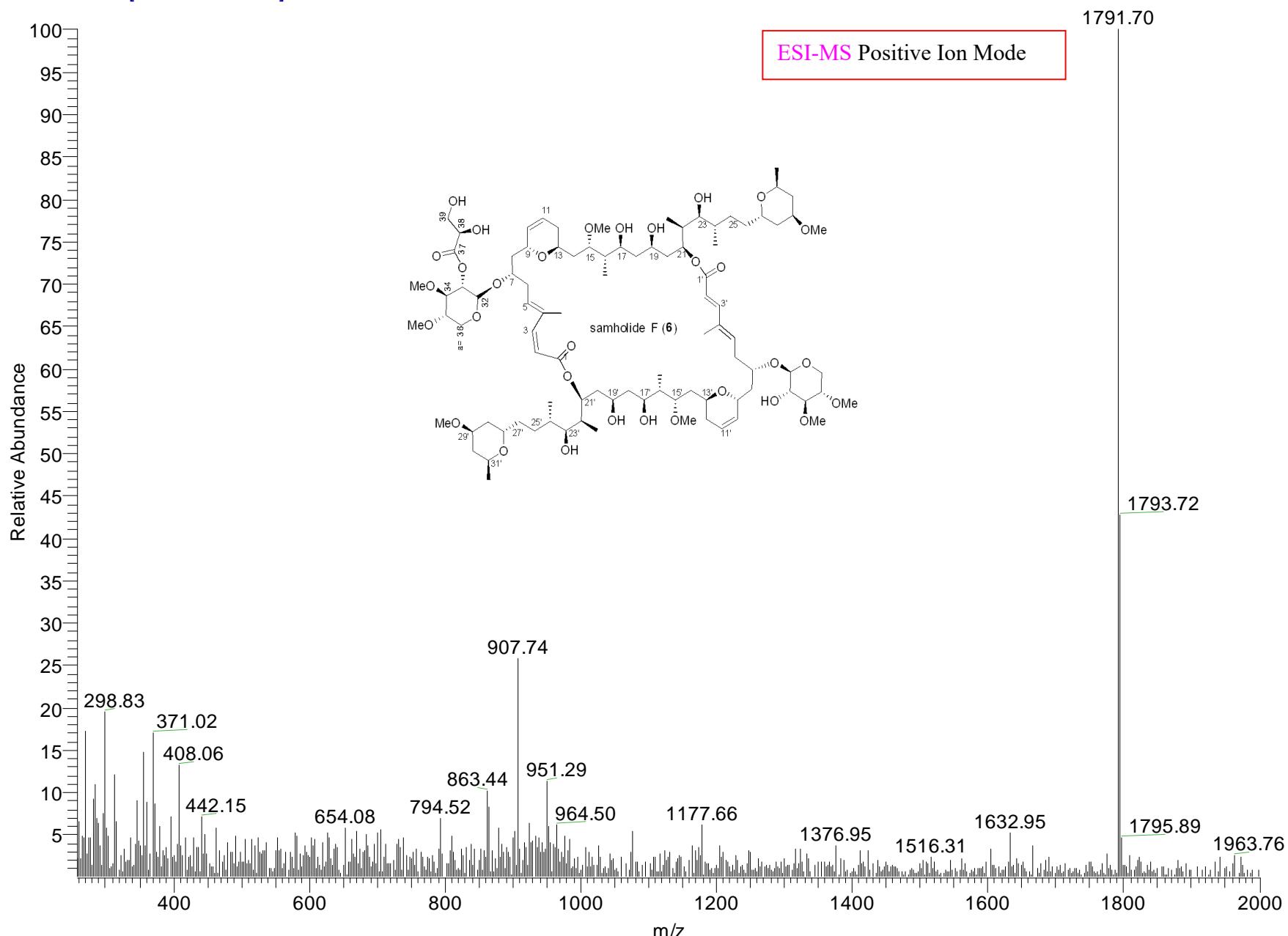


Figure S58 The ESI MS spectrum of samholide F (**6**)

2226H3C7A1-a #25-28 RT: 0.61-0.66 AV: 4 NL: 1.93E6

F: + c Full ms2 1792.00@35.00 [ 490.00-2000.00]

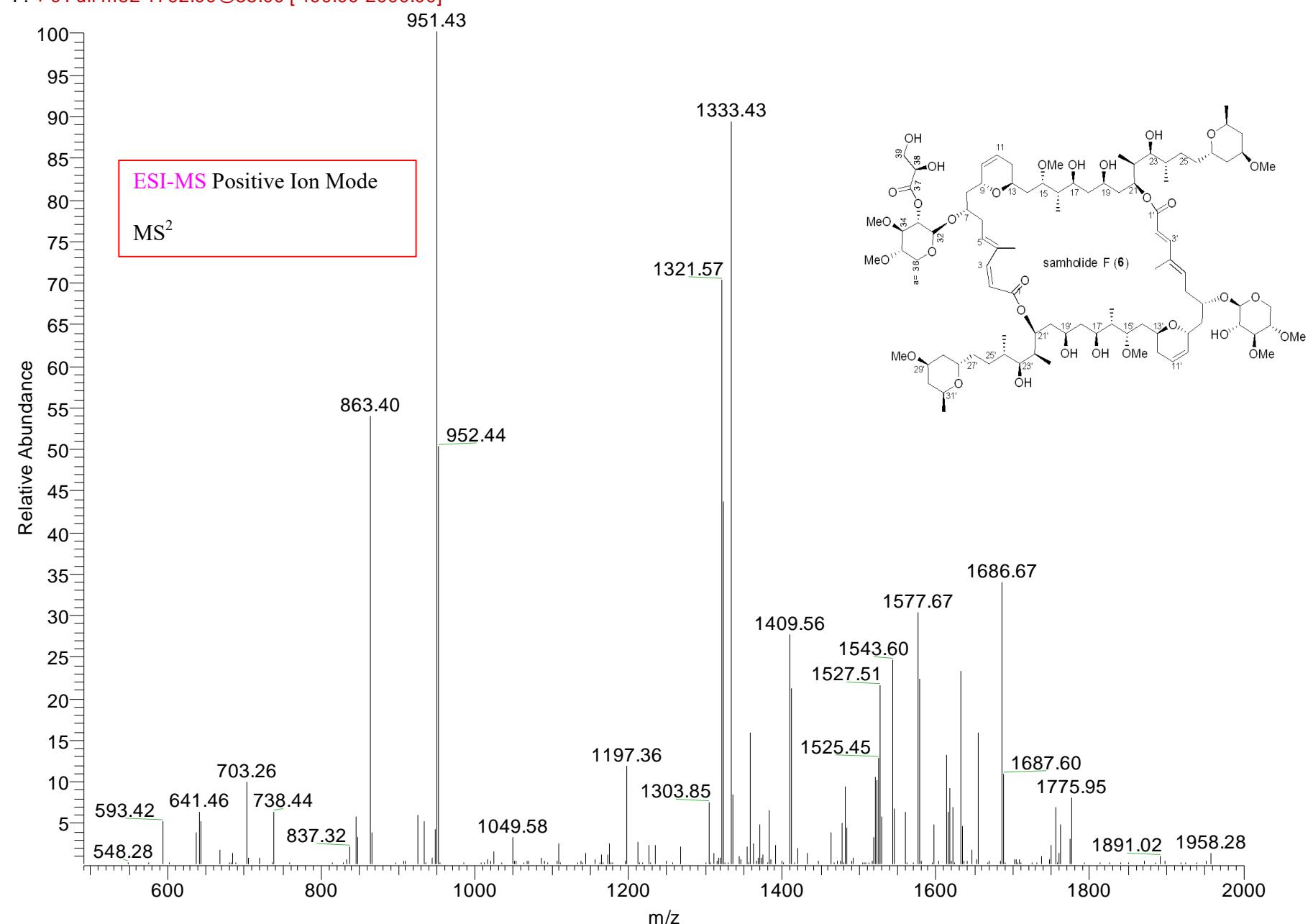


Figure S59 The ESI MS<sup>2</sup> spectrum of samholide F (6)

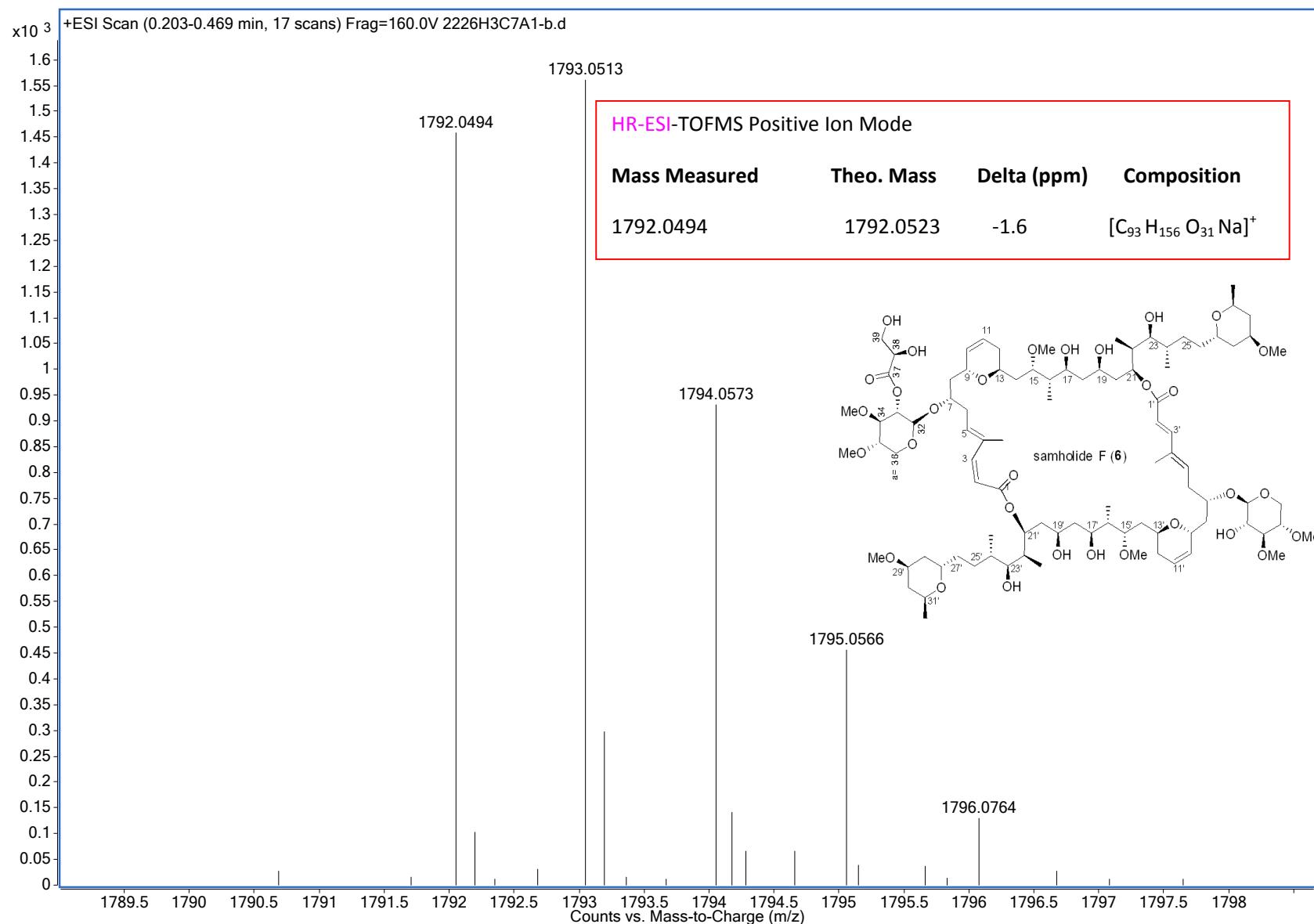


Figure S60 The positive HRESIMS spectrum of samholide F (**6**)

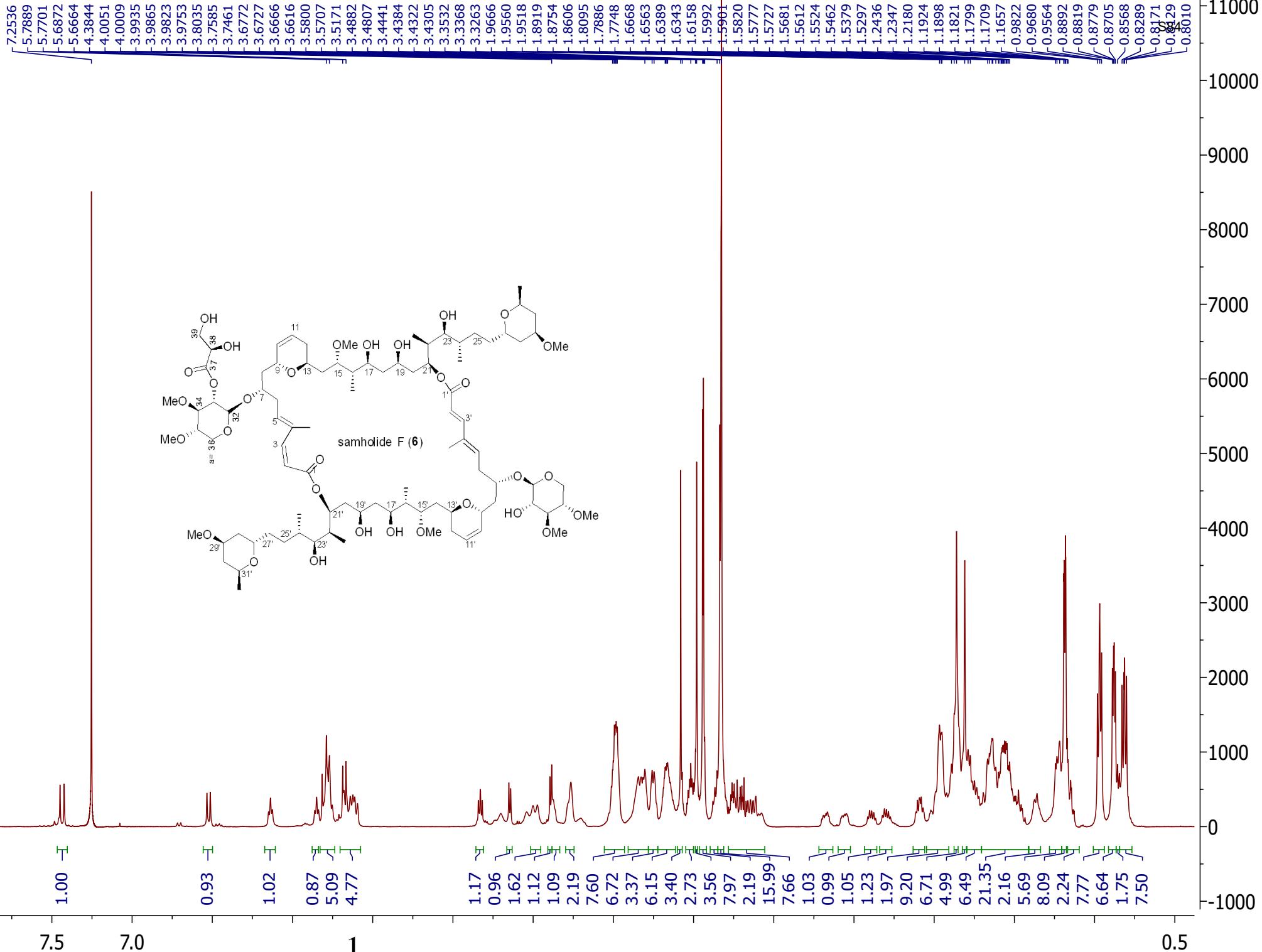
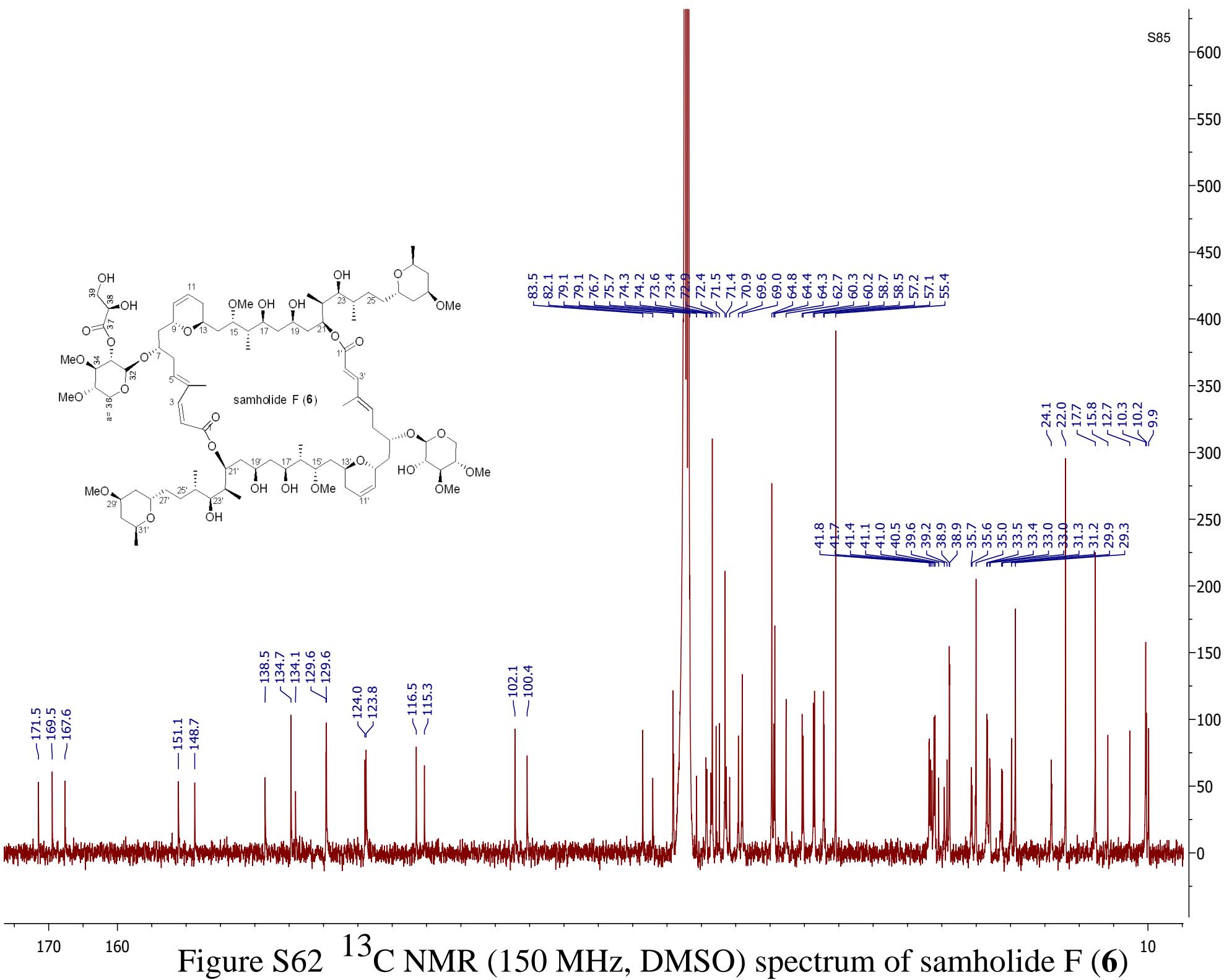
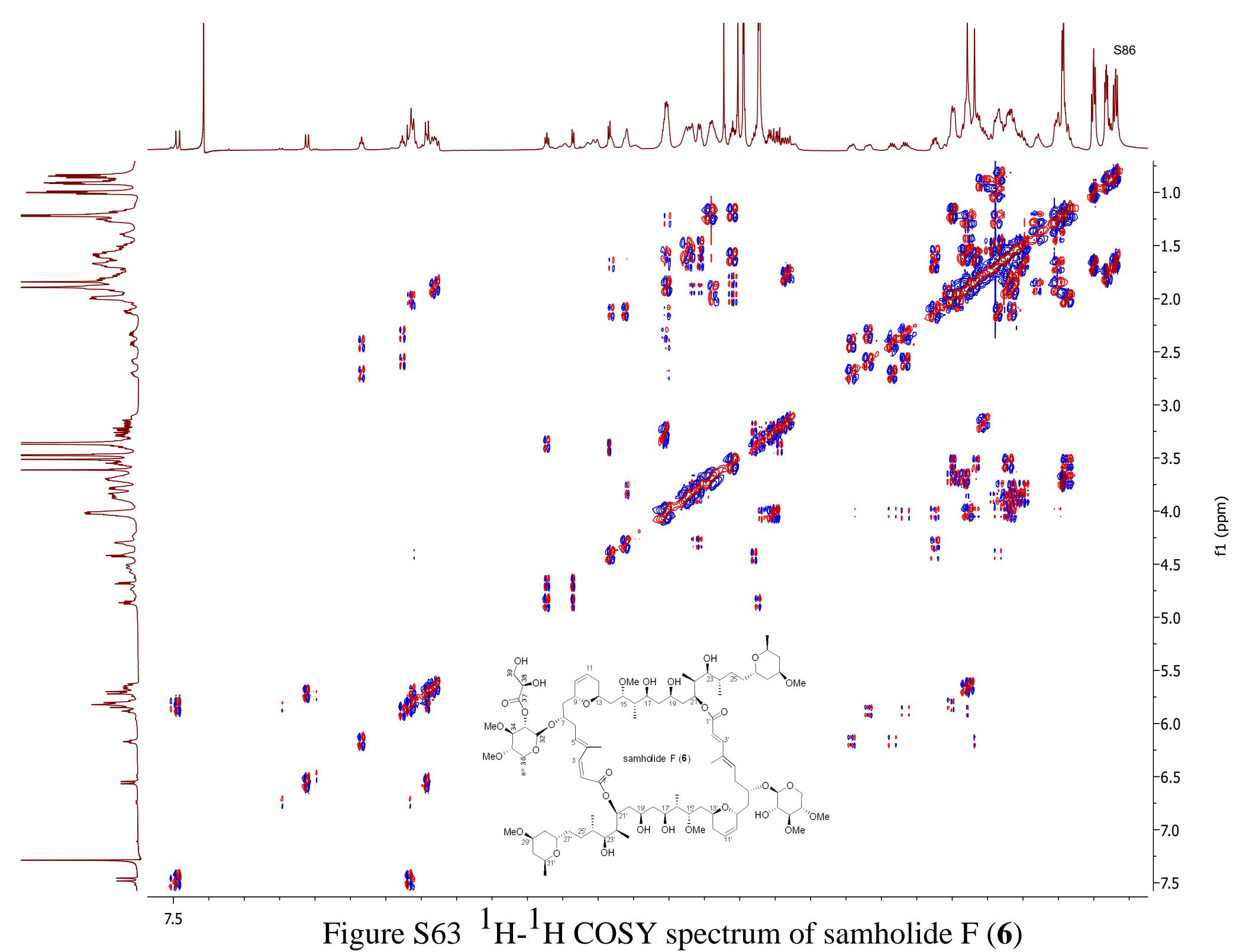


Figure S61  $^1\text{H}$  NMR (600 MHz, DMSO) spectrum of samholide F (**6**)





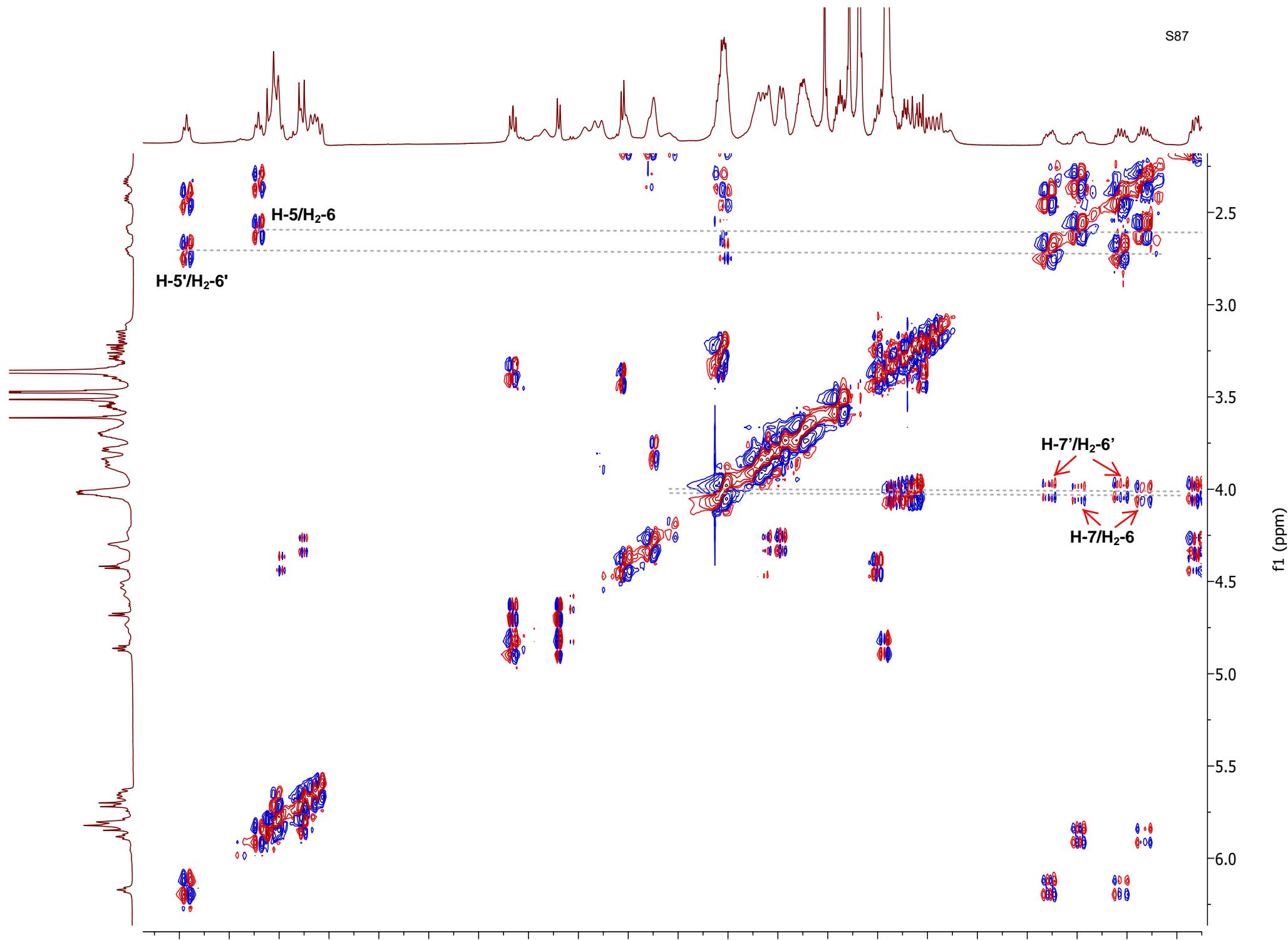


Figure S64 Amplified  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of samholide F (**6**)

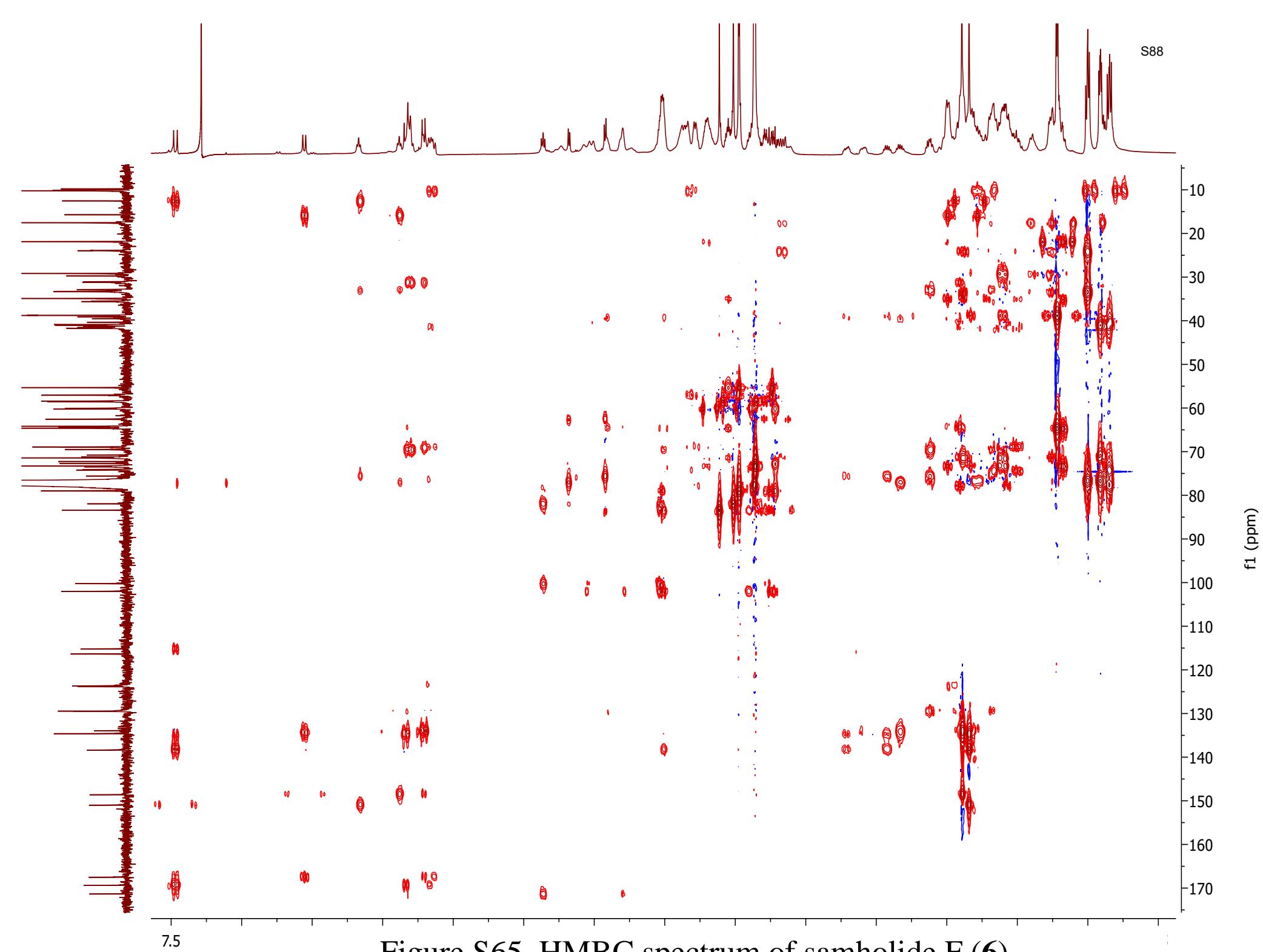


Figure S65 HMBC spectrum of samholide F (**6**)

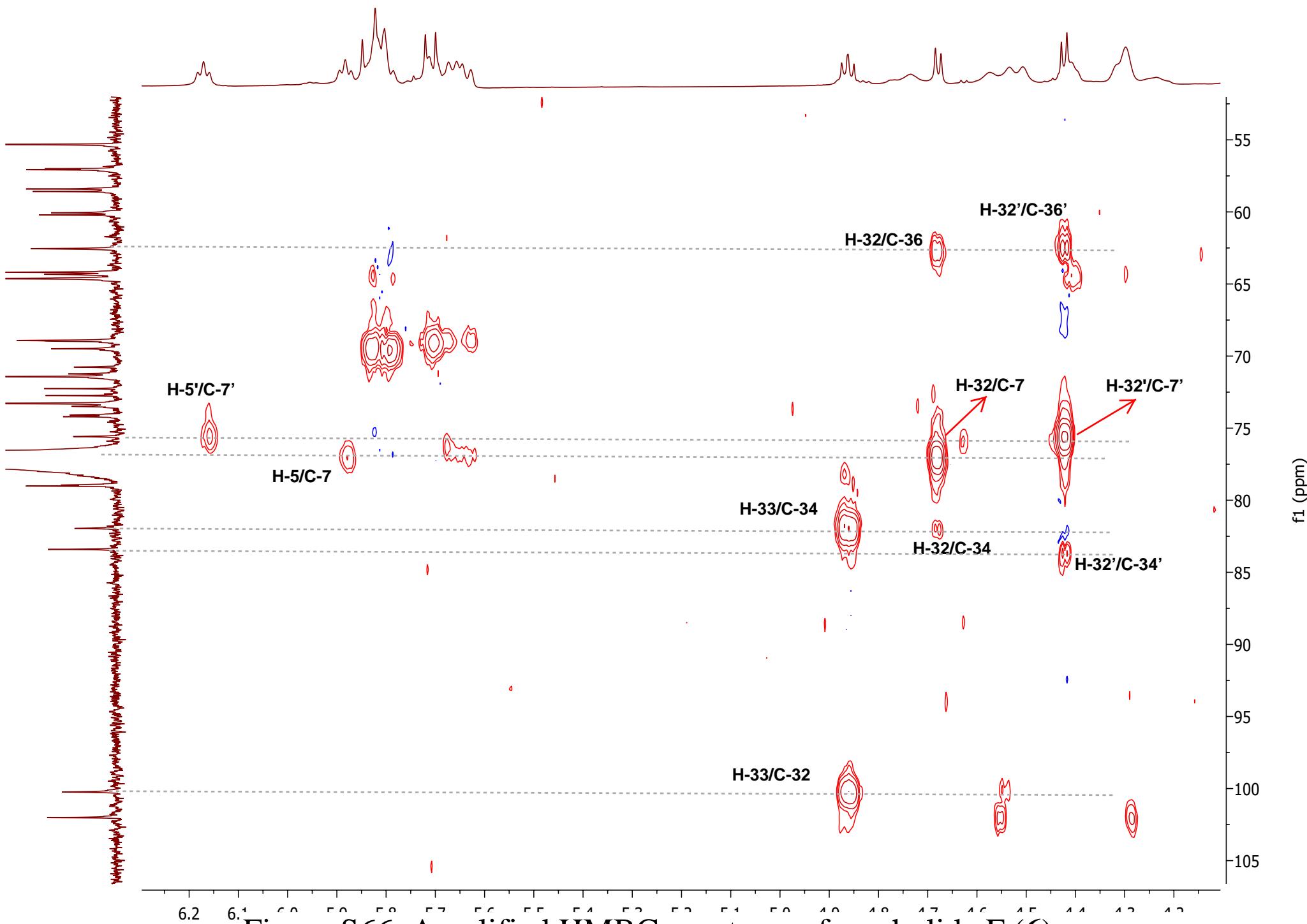


Figure S66 Amplified HMBC spectrum of samholide F (6)

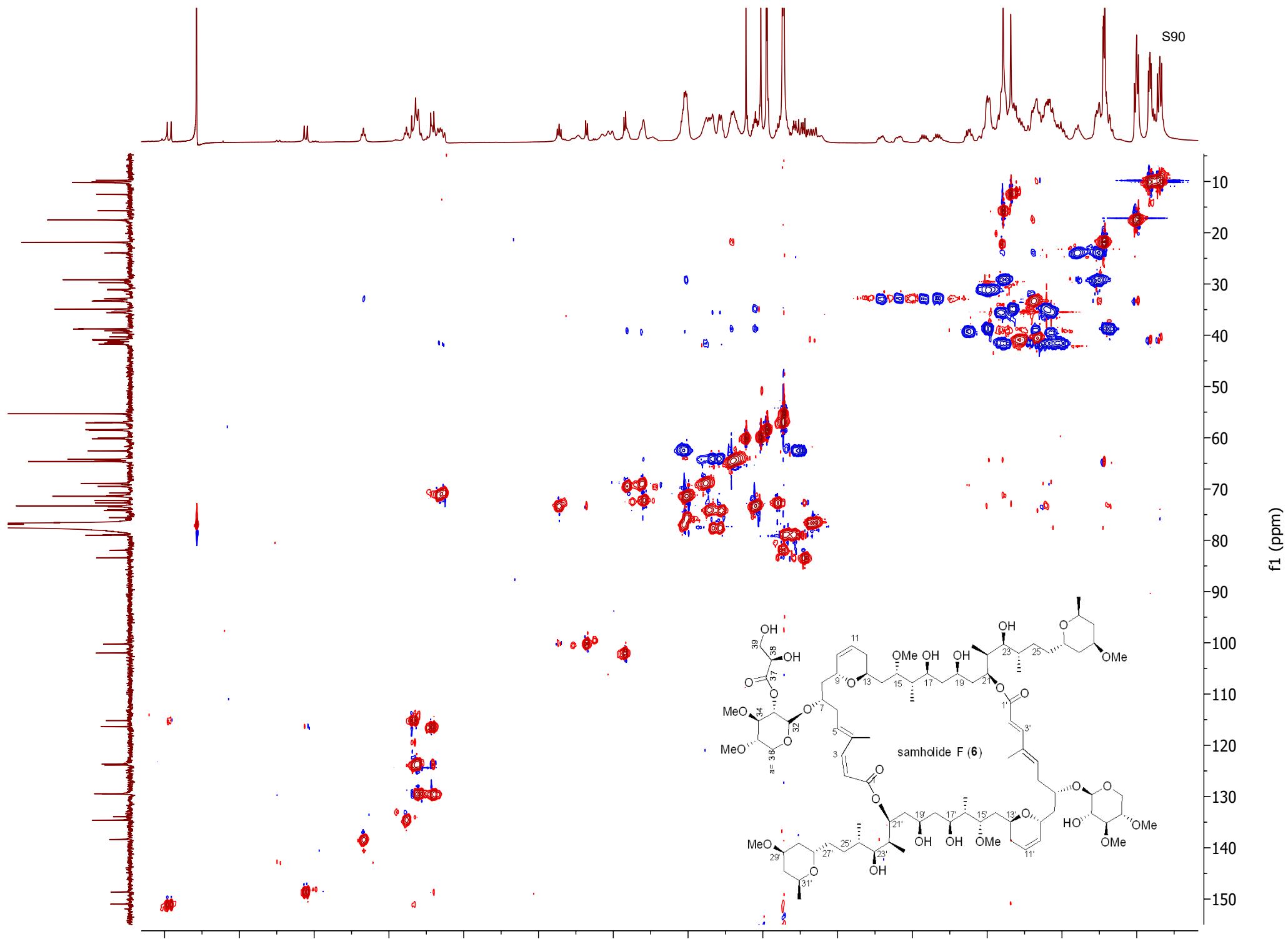


Figure S67 HMQC spectrum of samholide F (**6**)

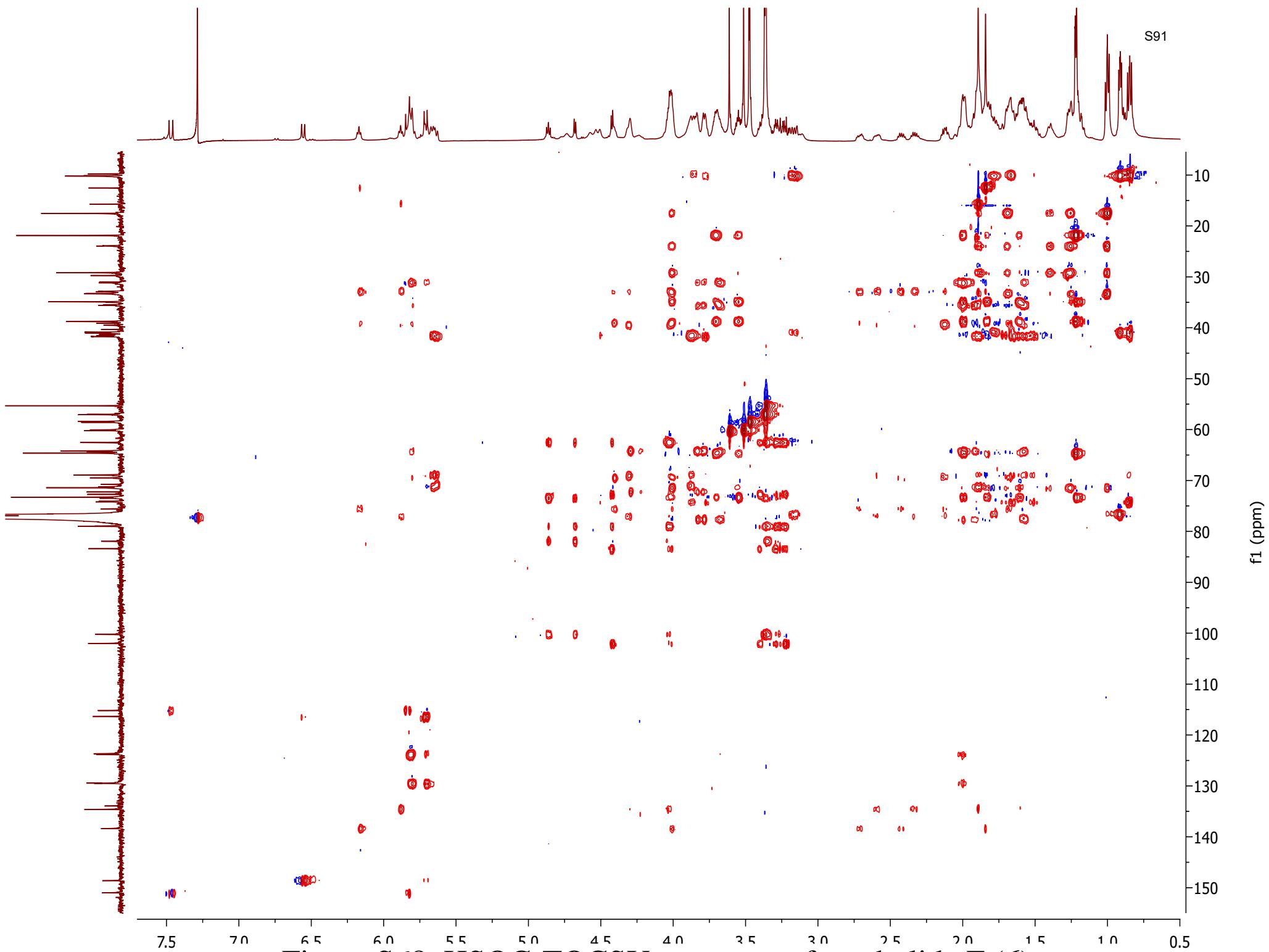


Figure S68 HSQC-TOCSY spectrum of samholide F (**6**)

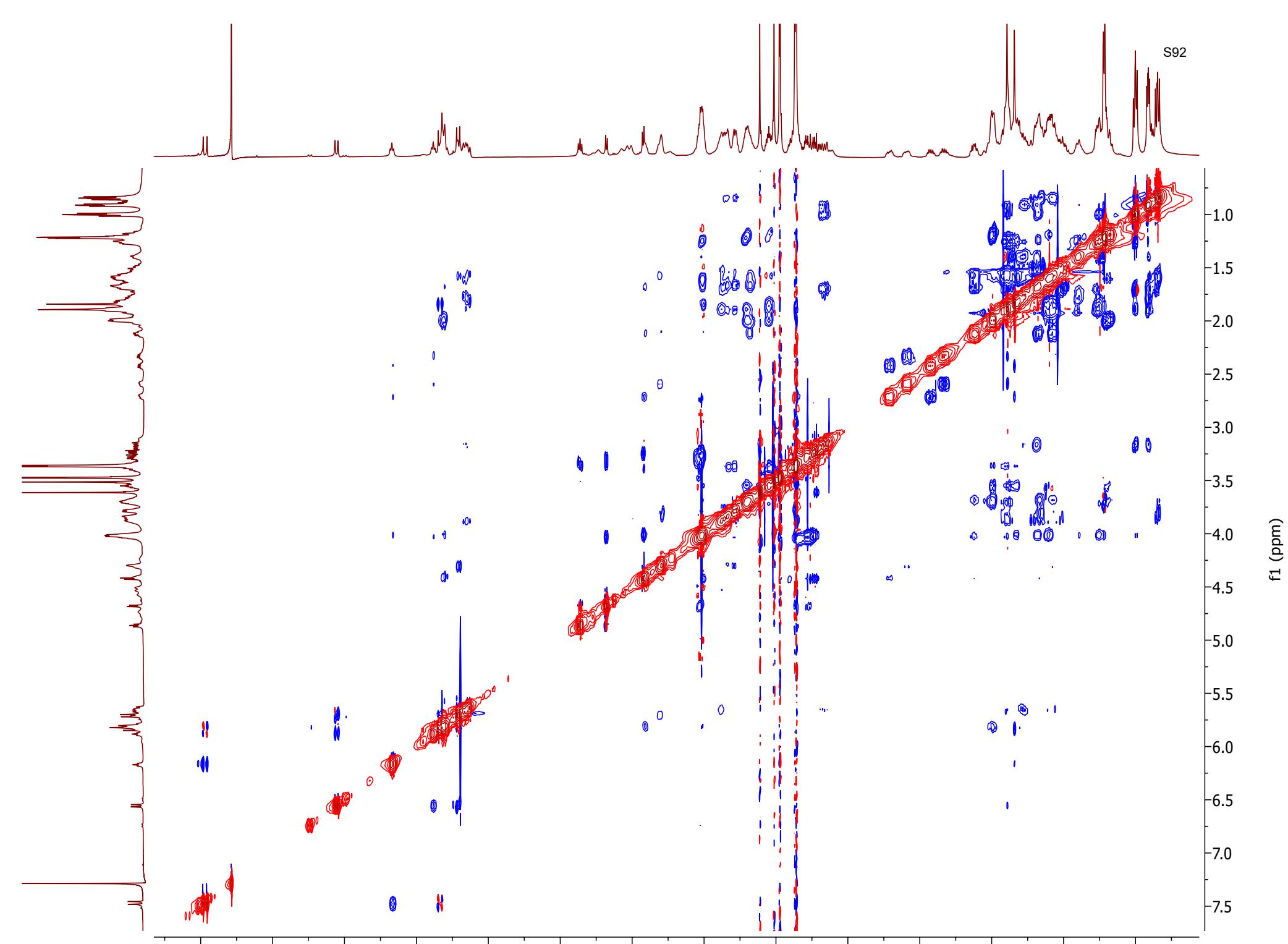
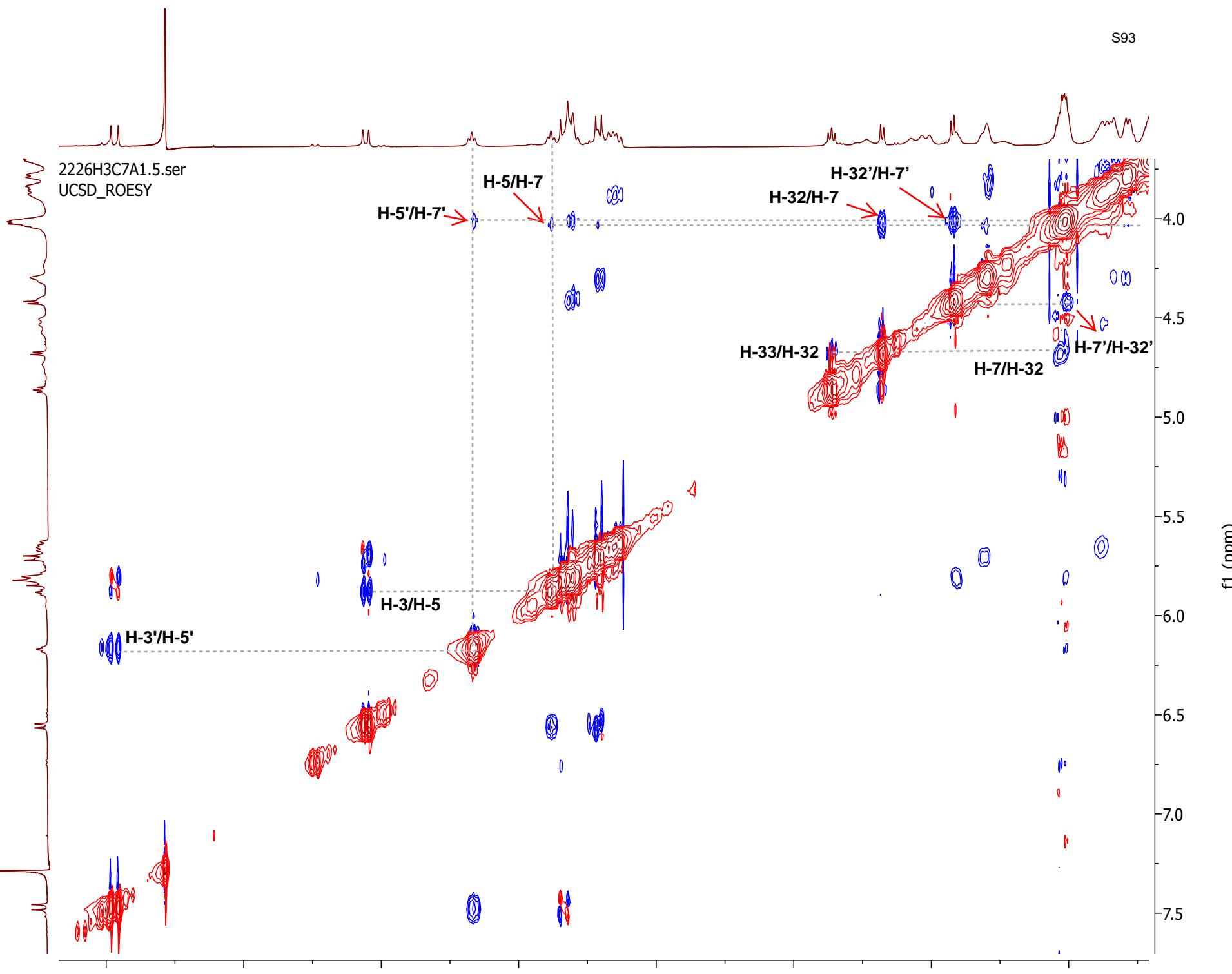


Figure S69 ROESY spectrum of samholide F (6)

Figure S70 Amplified ROESY spectrum of samholide F (**6**)

2226H3C9A-a #17-21 RT: 0.41-0.50 AV: 5 SB: 4 0.26-0.33 NL: 9.29E7

T: + c Full ms [300.00-2000.00]

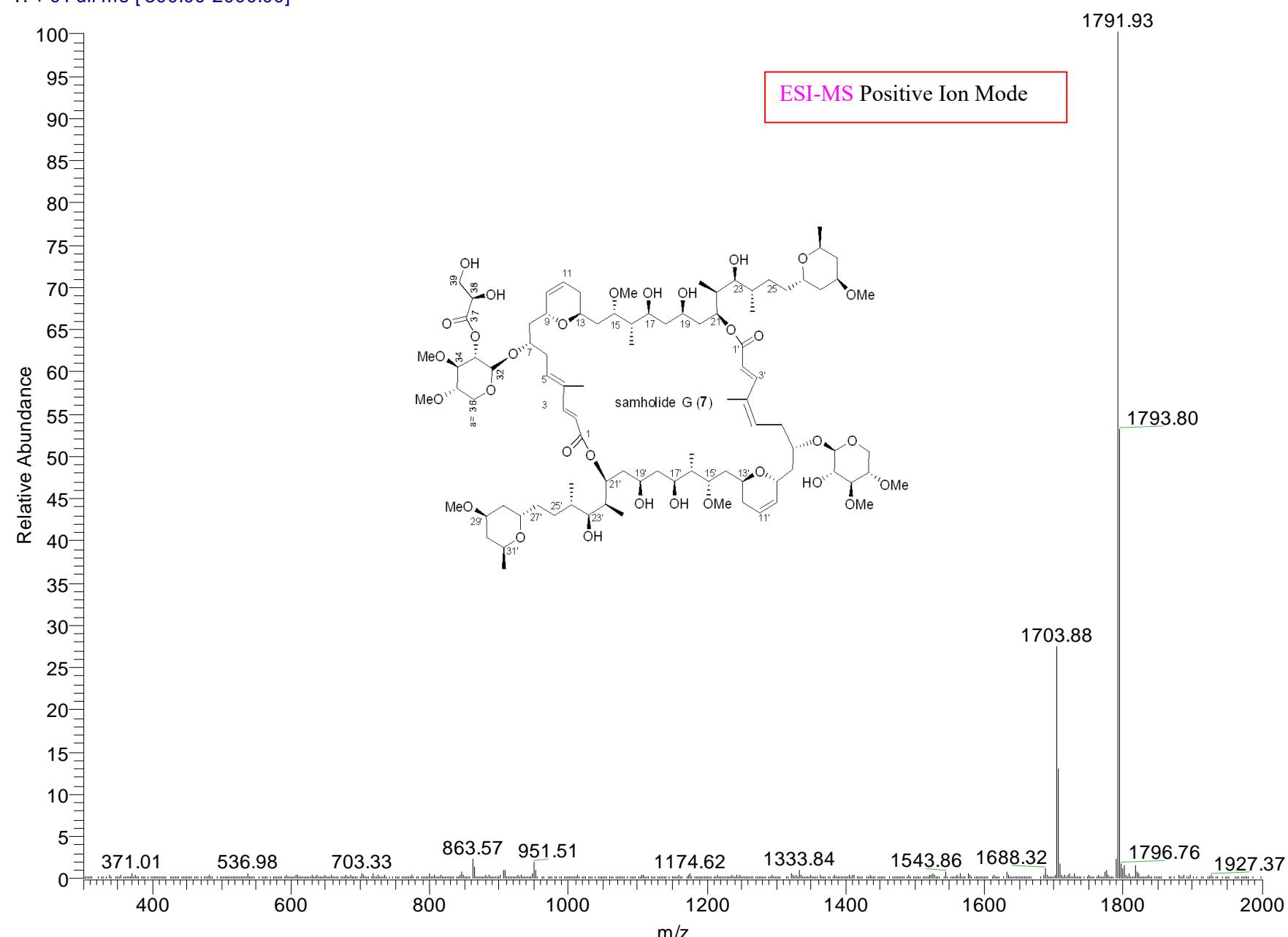


Figure S71 The ESI MS spectrum of samholide G (7)

2226H3C9A-a #33-36 RT: 0.75-0.80 AV: 4 NL: 2.96E7

F: + c Full ms2 1792.00@35.00 [ 490.00-2000.00]

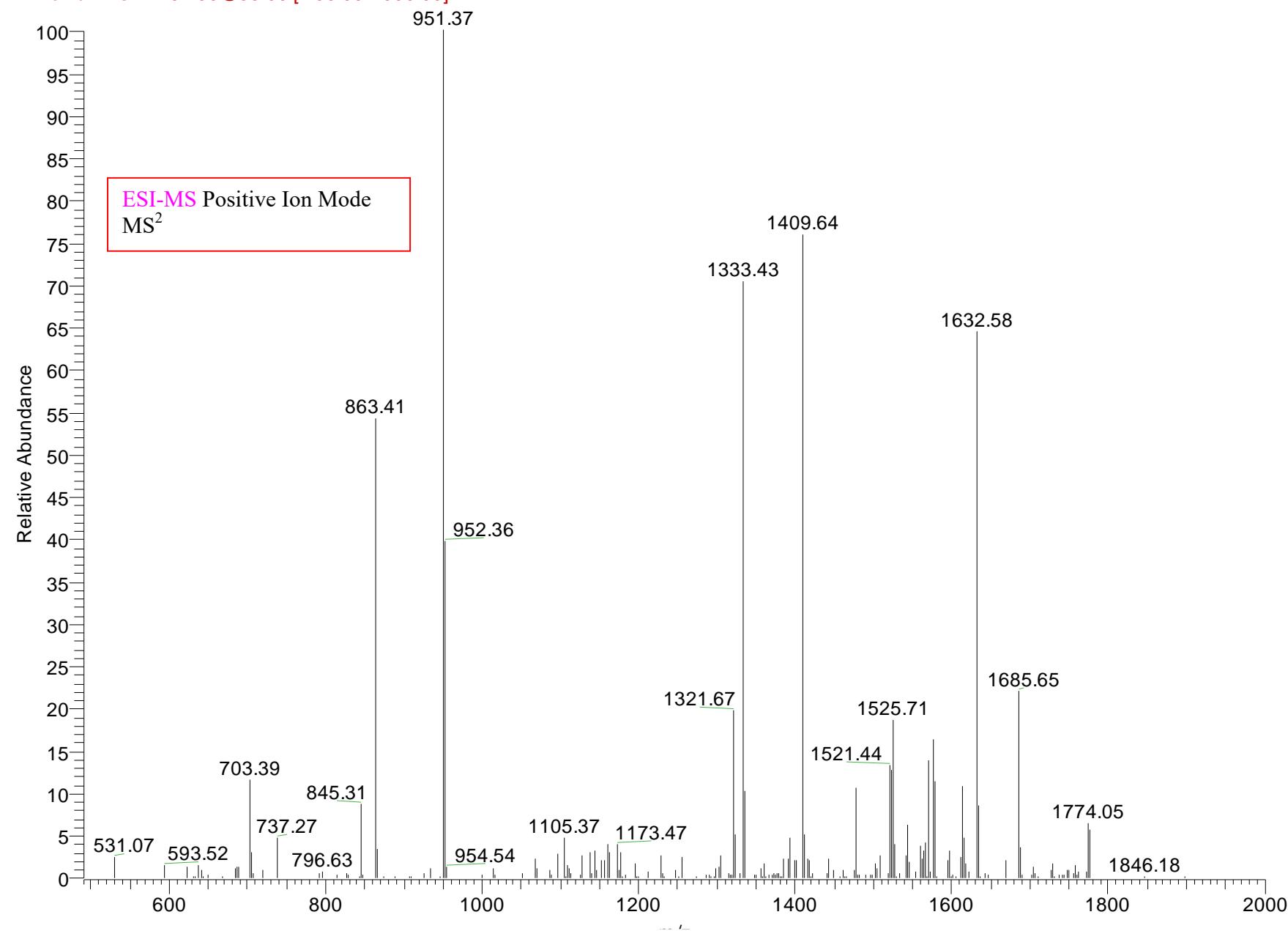


Figure S72 The ESI MS<sup>2</sup> spectrum of samholide G (7)

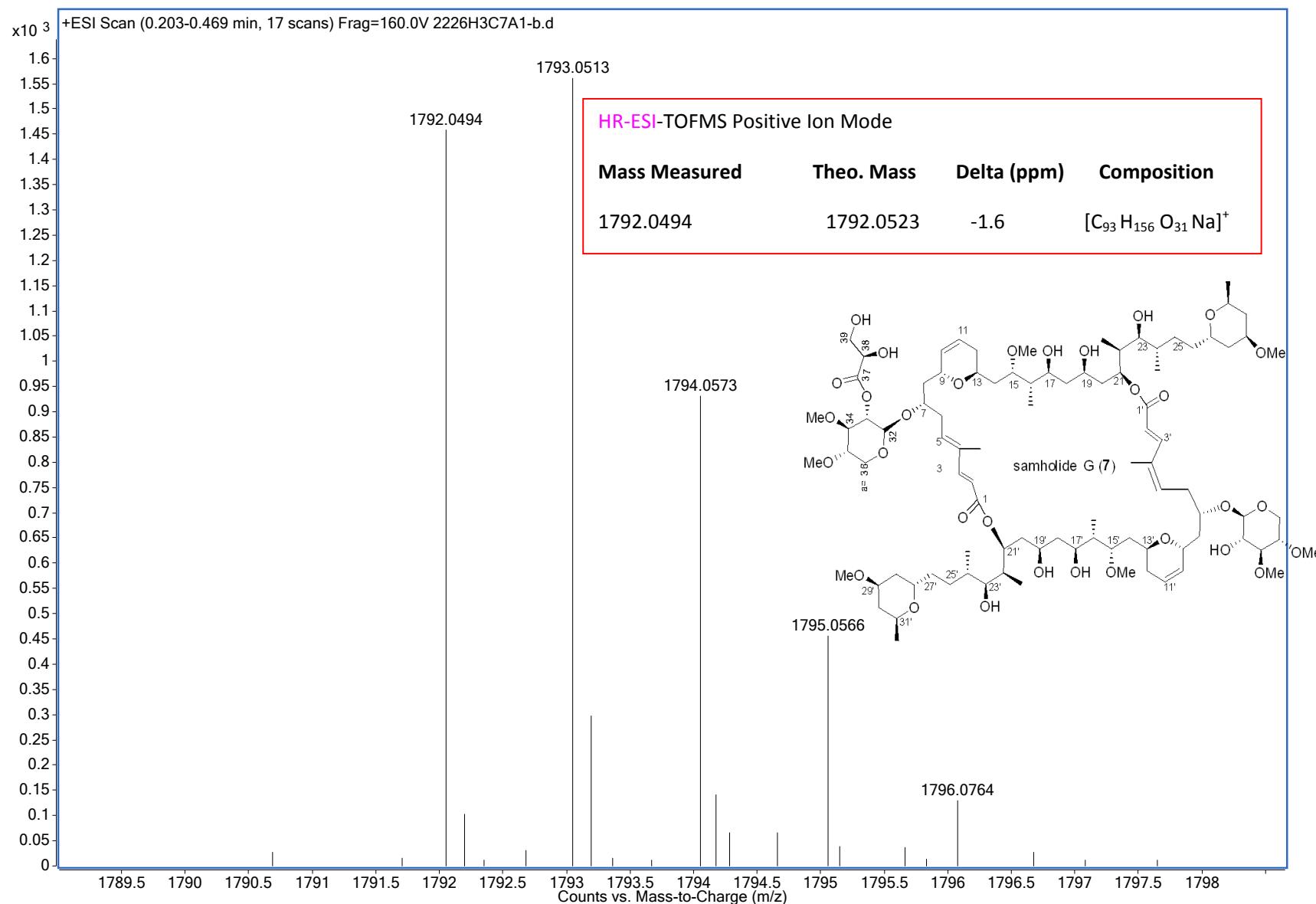
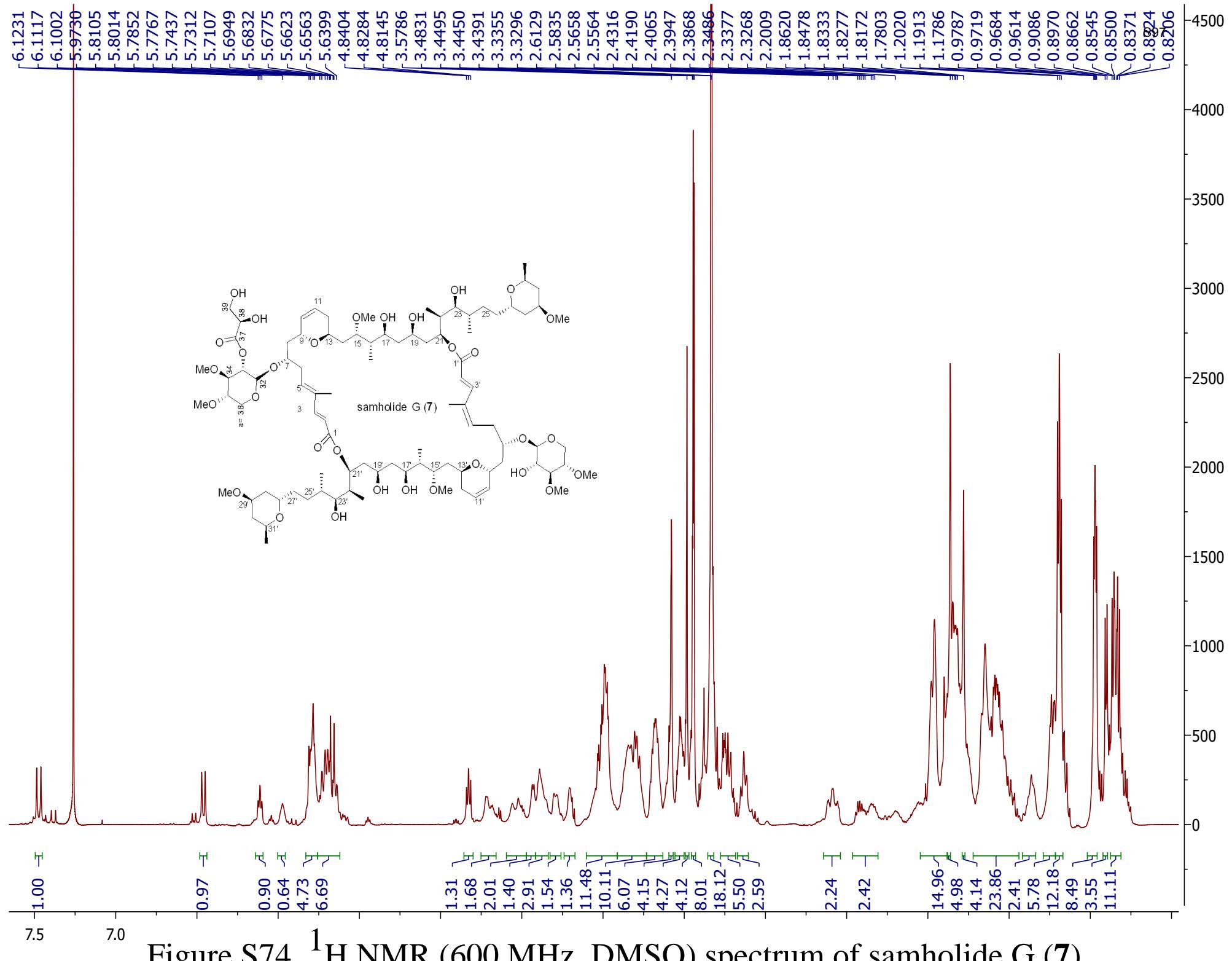


Figure S73 The positive HRESIMS spectrum of samholide G (7)



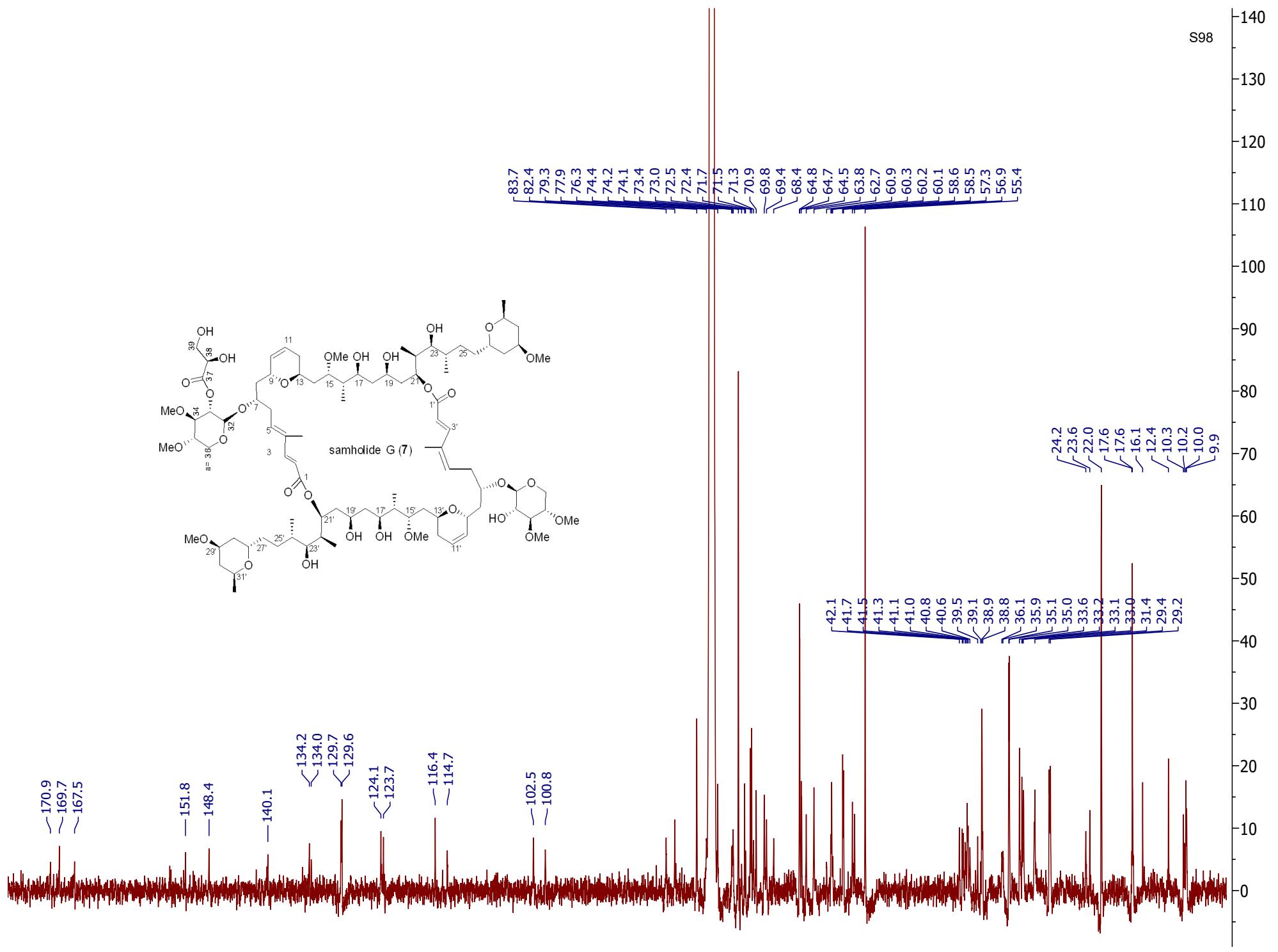


Figure S75  $^{13}\text{C}$  NMR (150 MHz, DMSO) spectrum of samholide G (7)

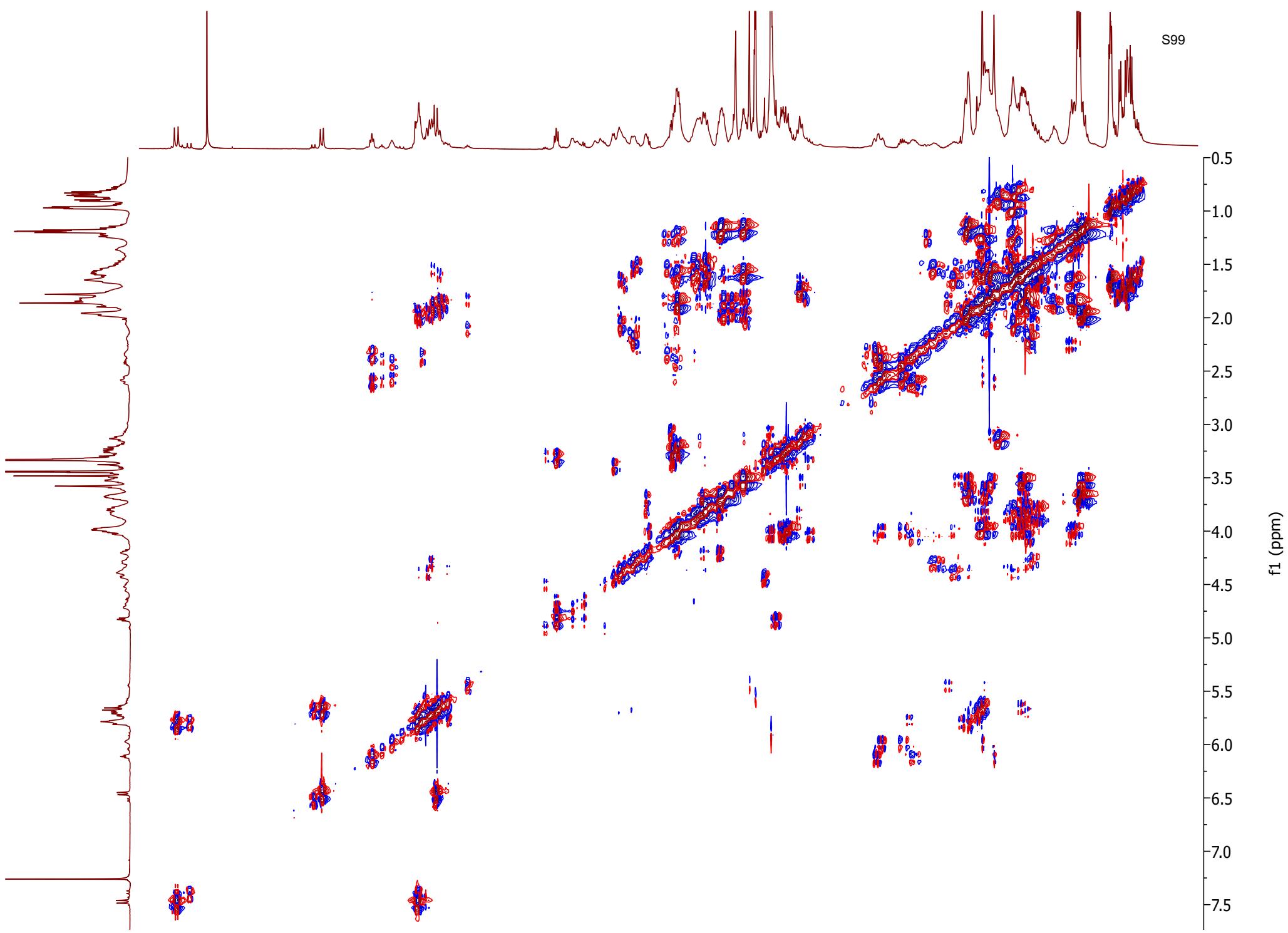


Figure S76  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of samholide G (7)

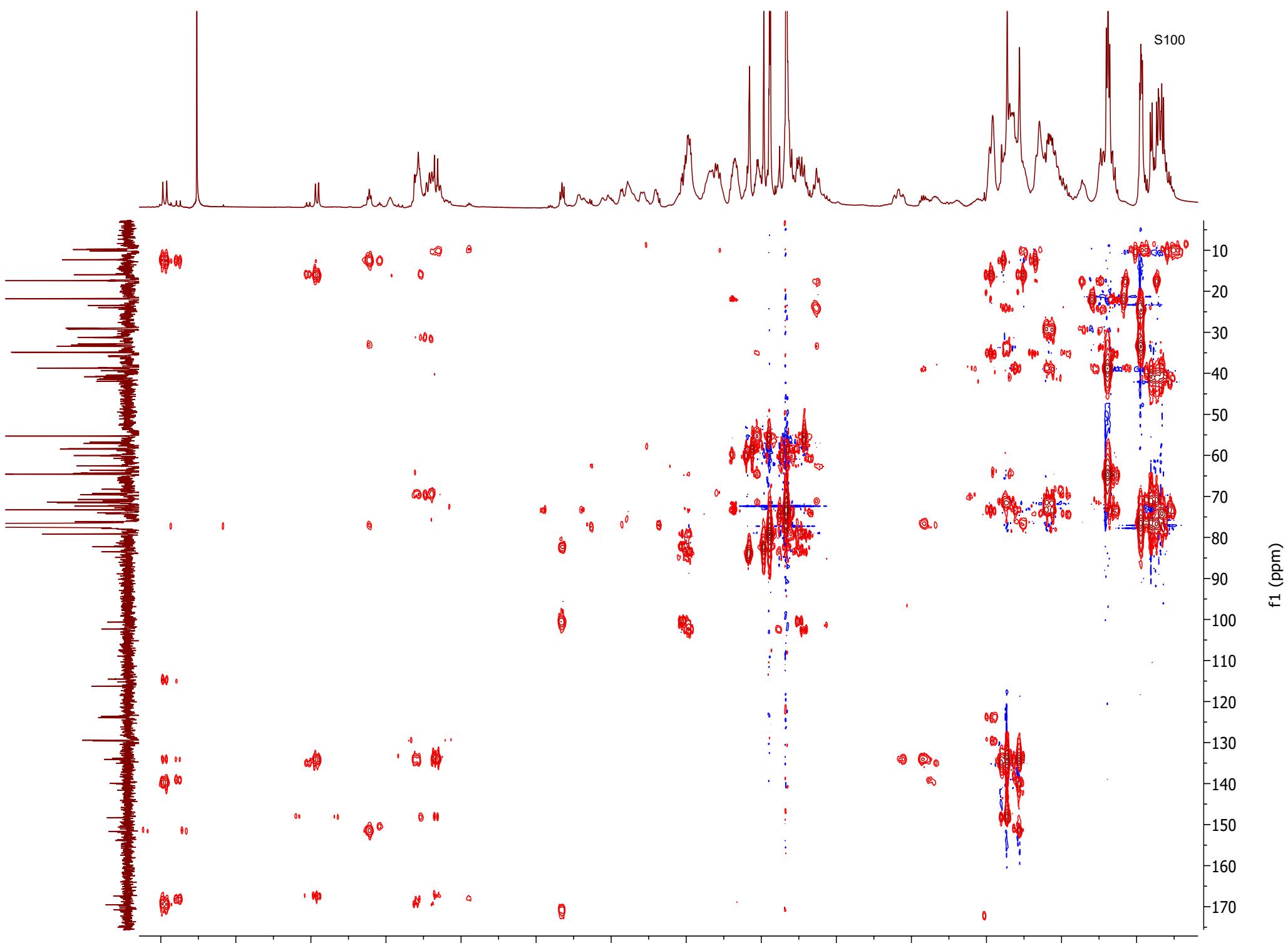


Figure S77 HMBC spectrum of samholide G (7)

S101

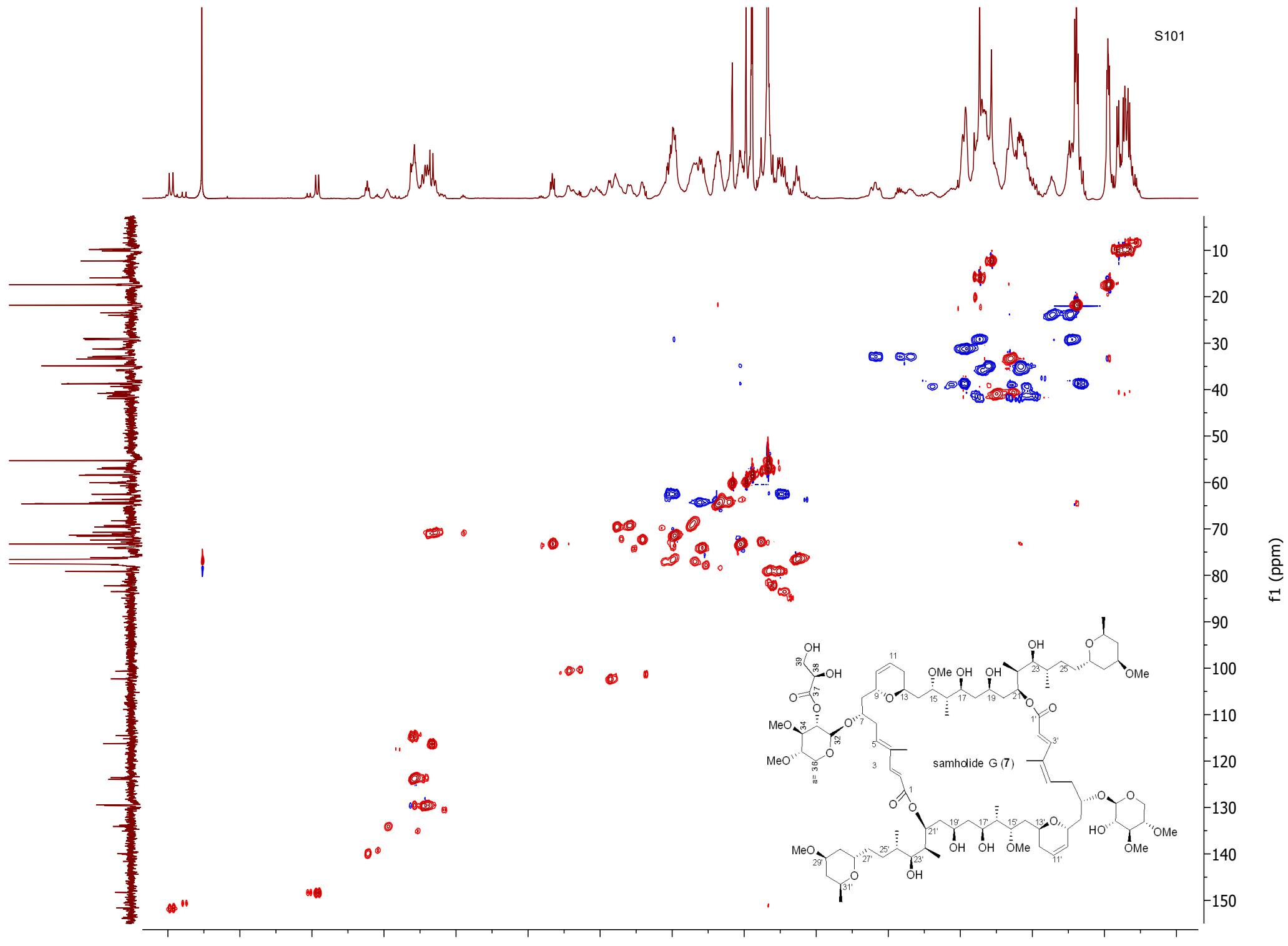


Figure S78 HMQC spectrum of samholide G (7)

S102

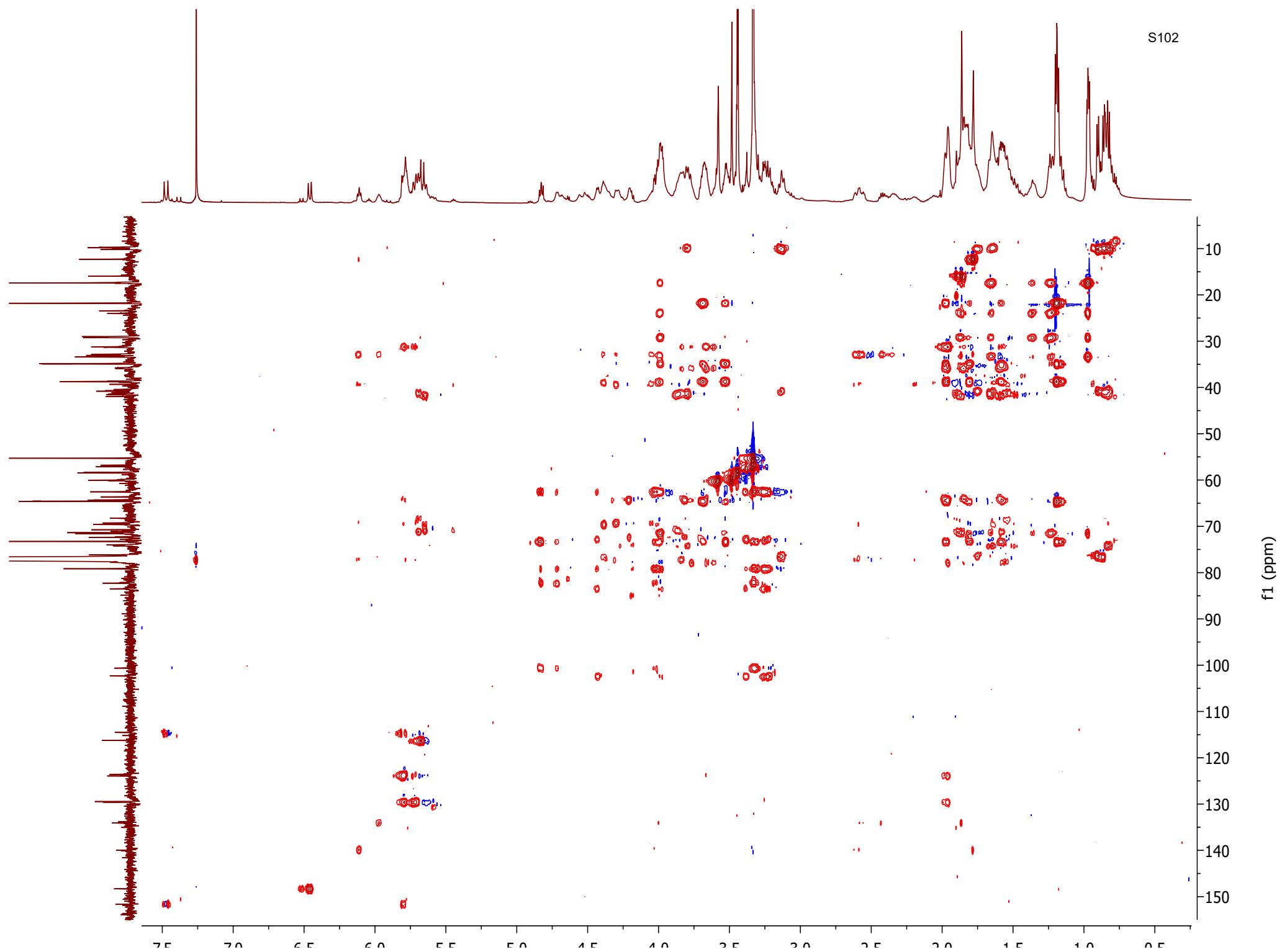


Figure S79 HSQC-TOCSY spectrum of samholide G (7)

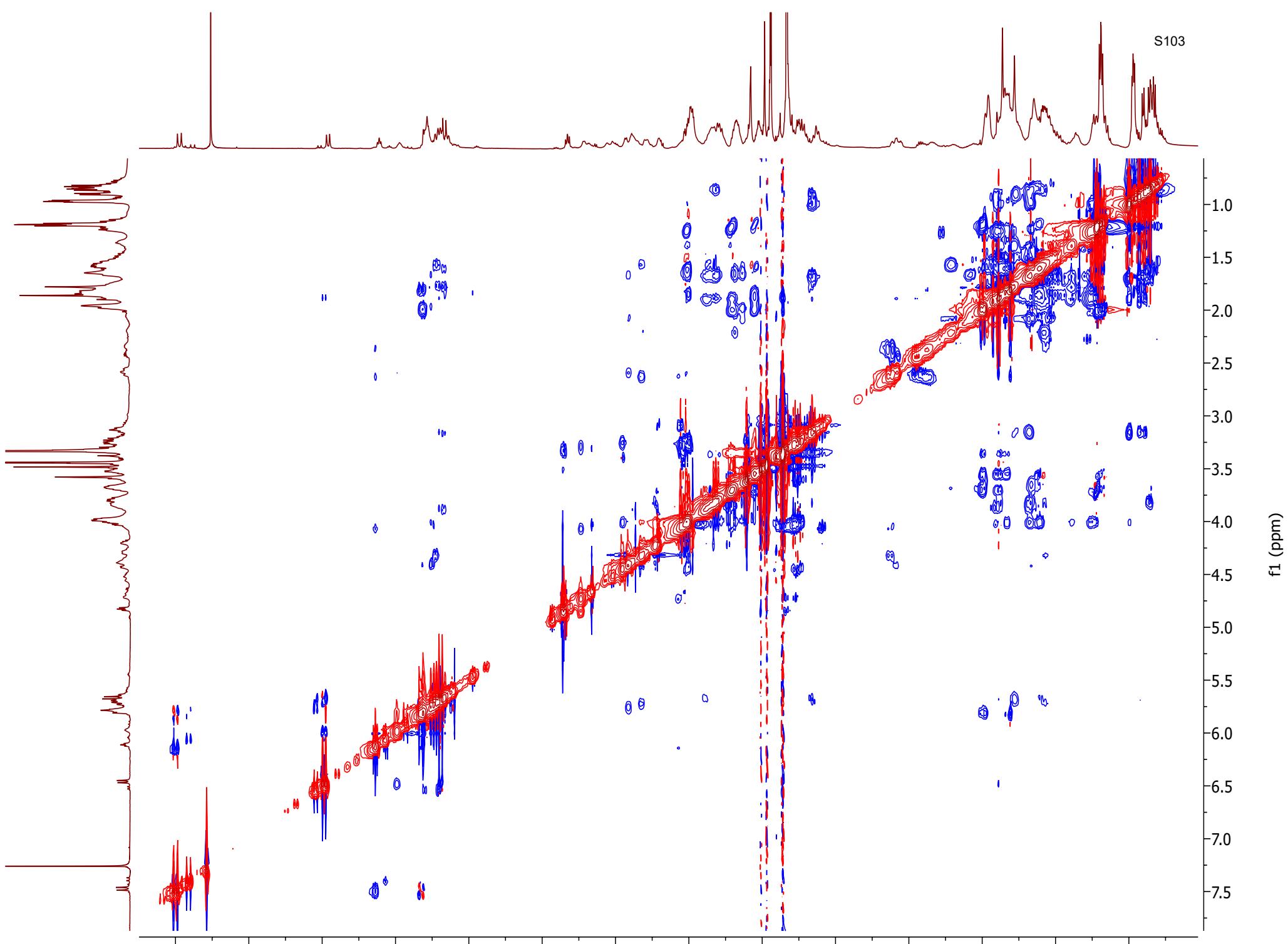


Figure S80 ROESY spectrum of samholide G (7)

2226H3CB4A-a #12-15 RT: 0.28-0.35 AV: 4 SB: 3 0.18-0.23 NL: 1.72E6

T: + c Full ms [ 300.00-2000.00]

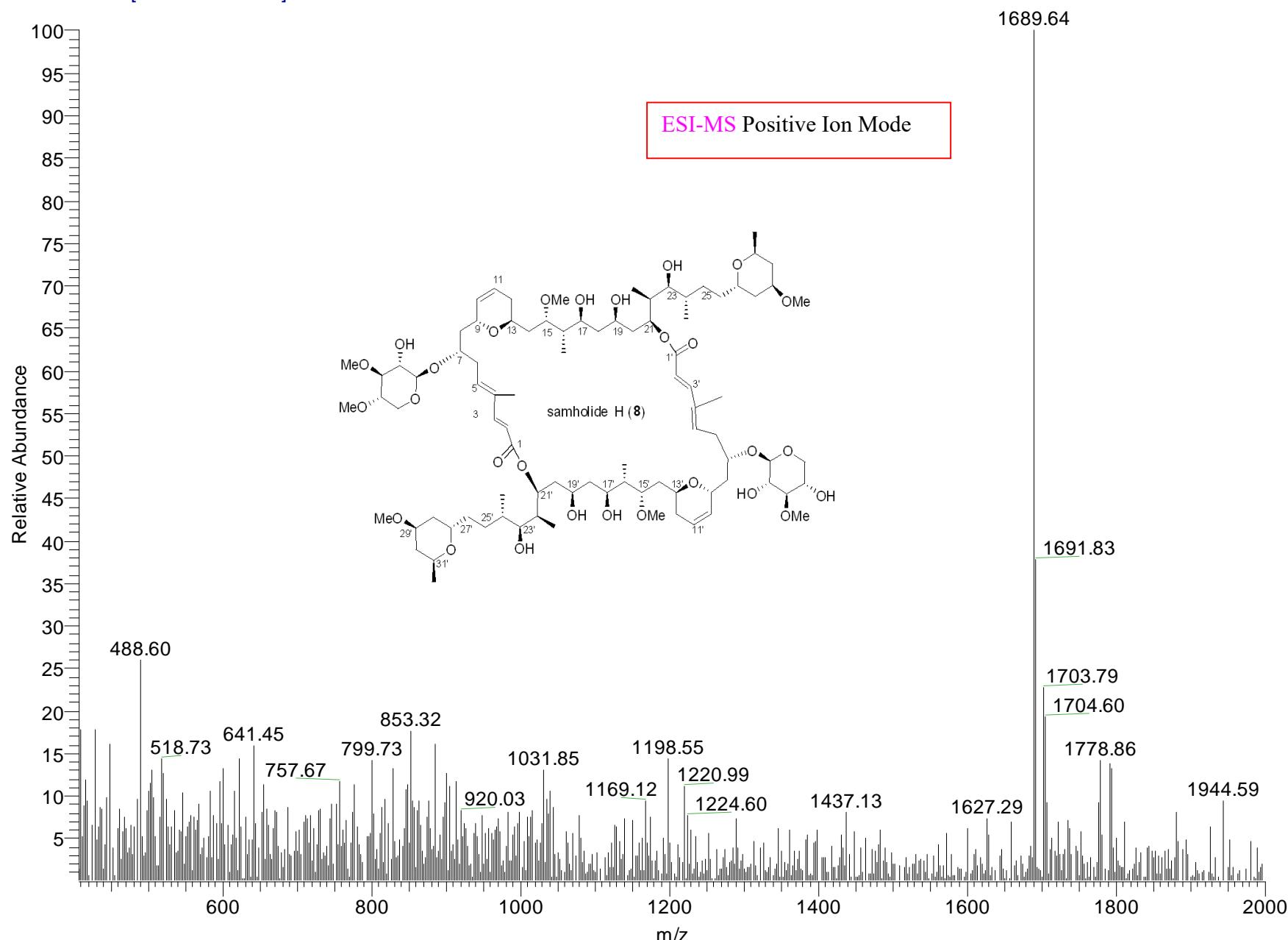


Figure S81 The ESI MS spectrum of samholide H (8)

2226H3CB4A-a #55-73 RT: 1.30-1.62 AV: 19 NL: 3.56E5

F: + c Full ms2 1690.00@35.00 [ 465.00-2000.00]

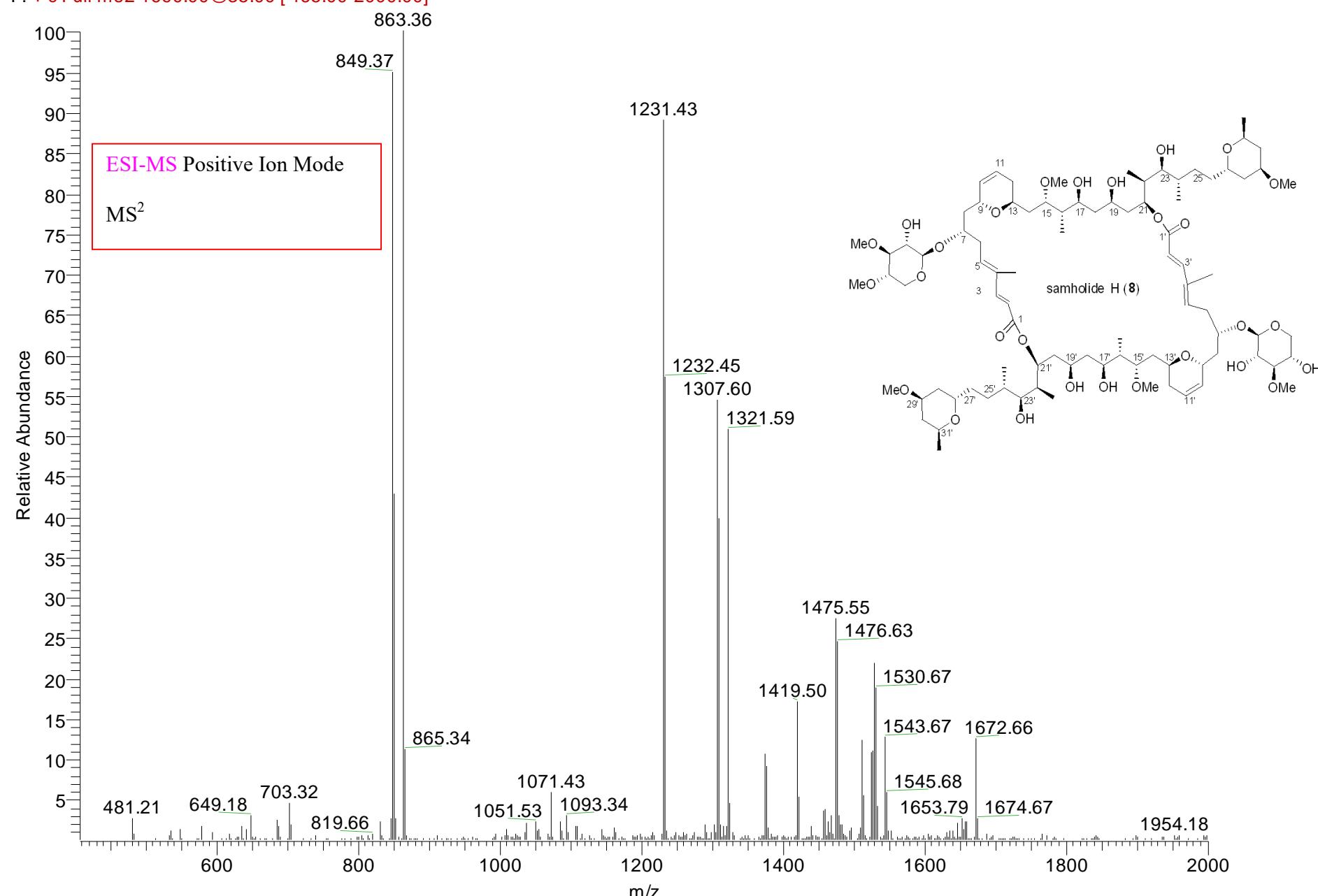


Figure S82 The ESI MS<sup>2</sup> spectrum of samholide H (8)

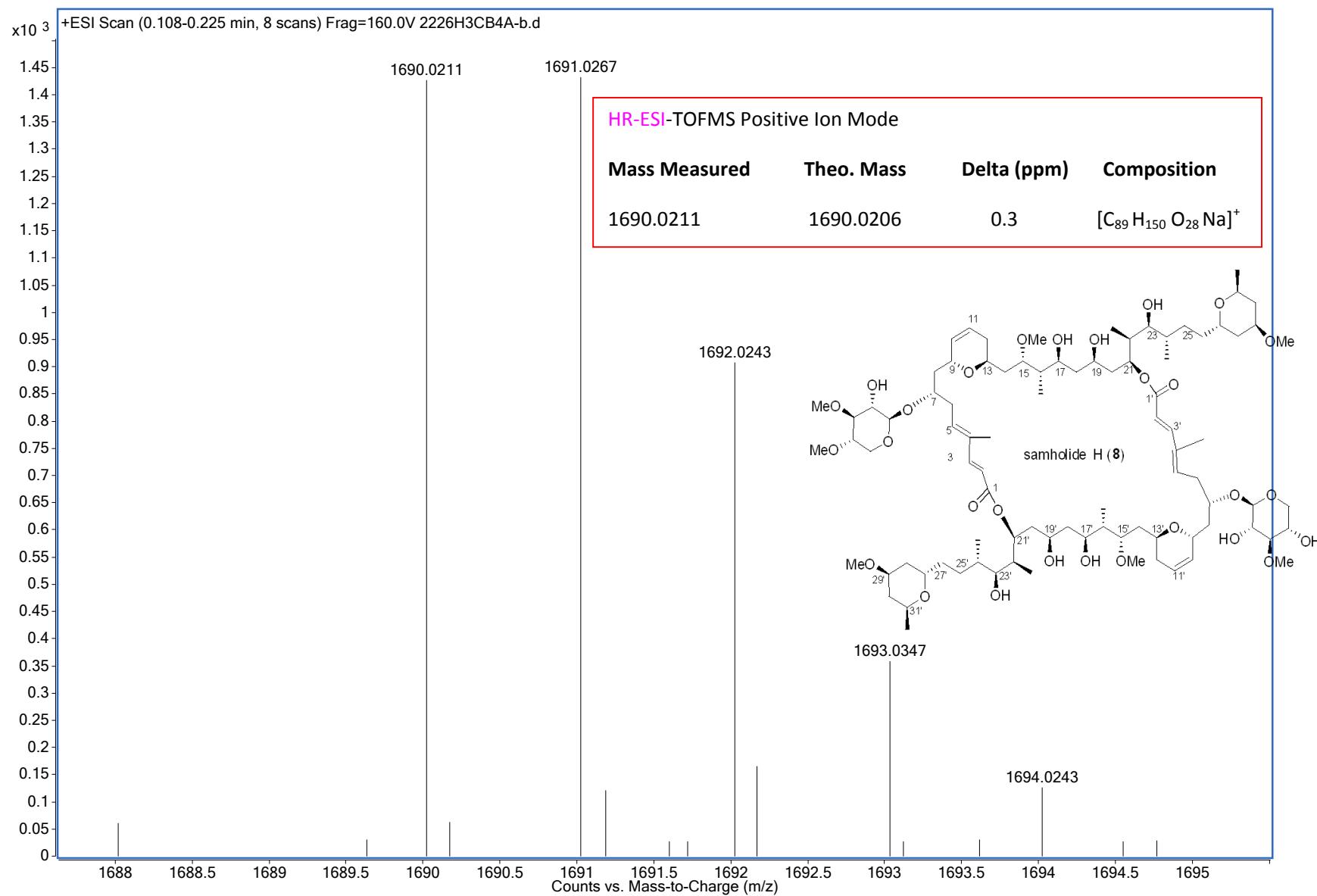


Figure S83 The positive HRESIMS spectrum of samholide H (8)

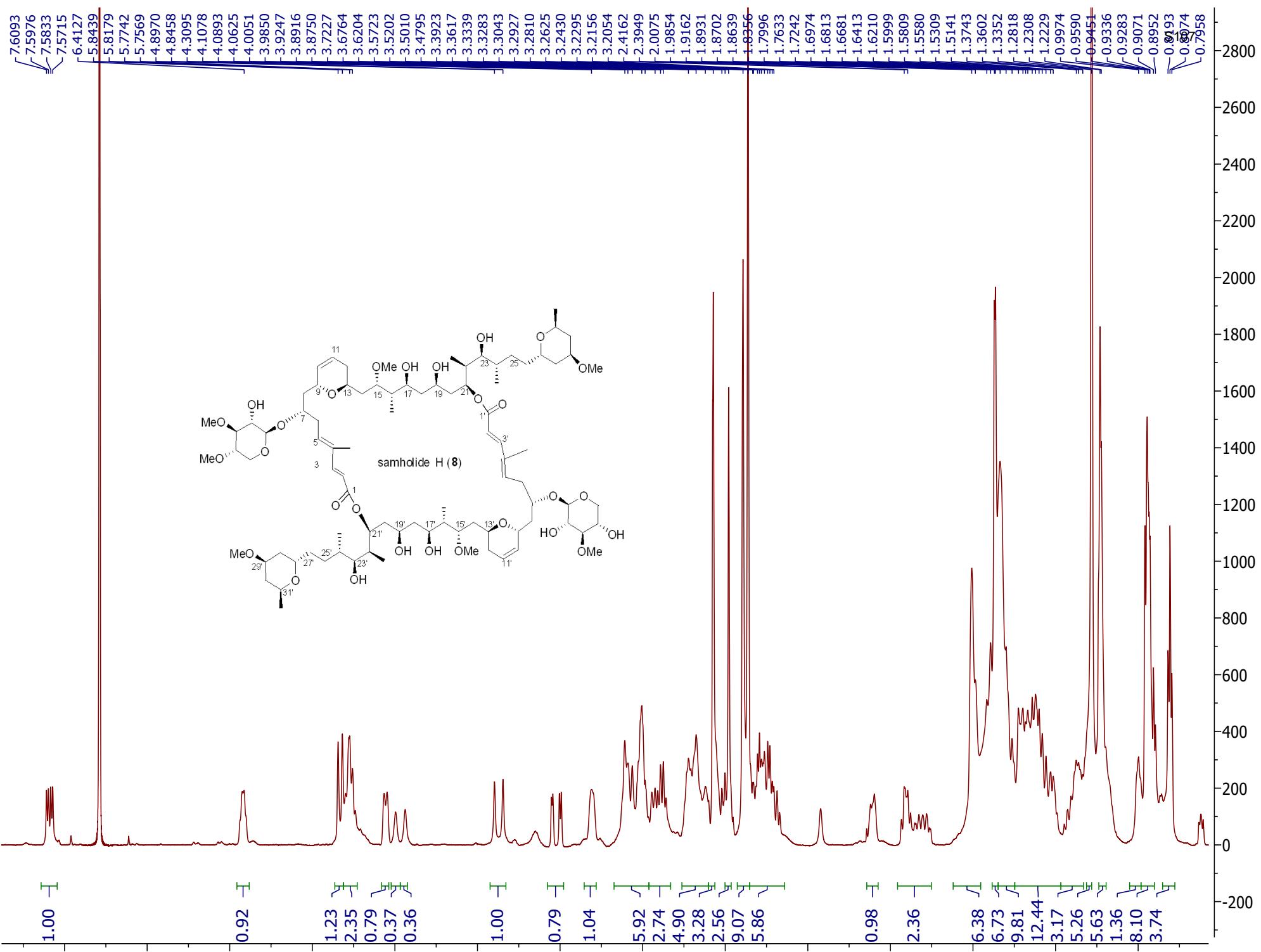
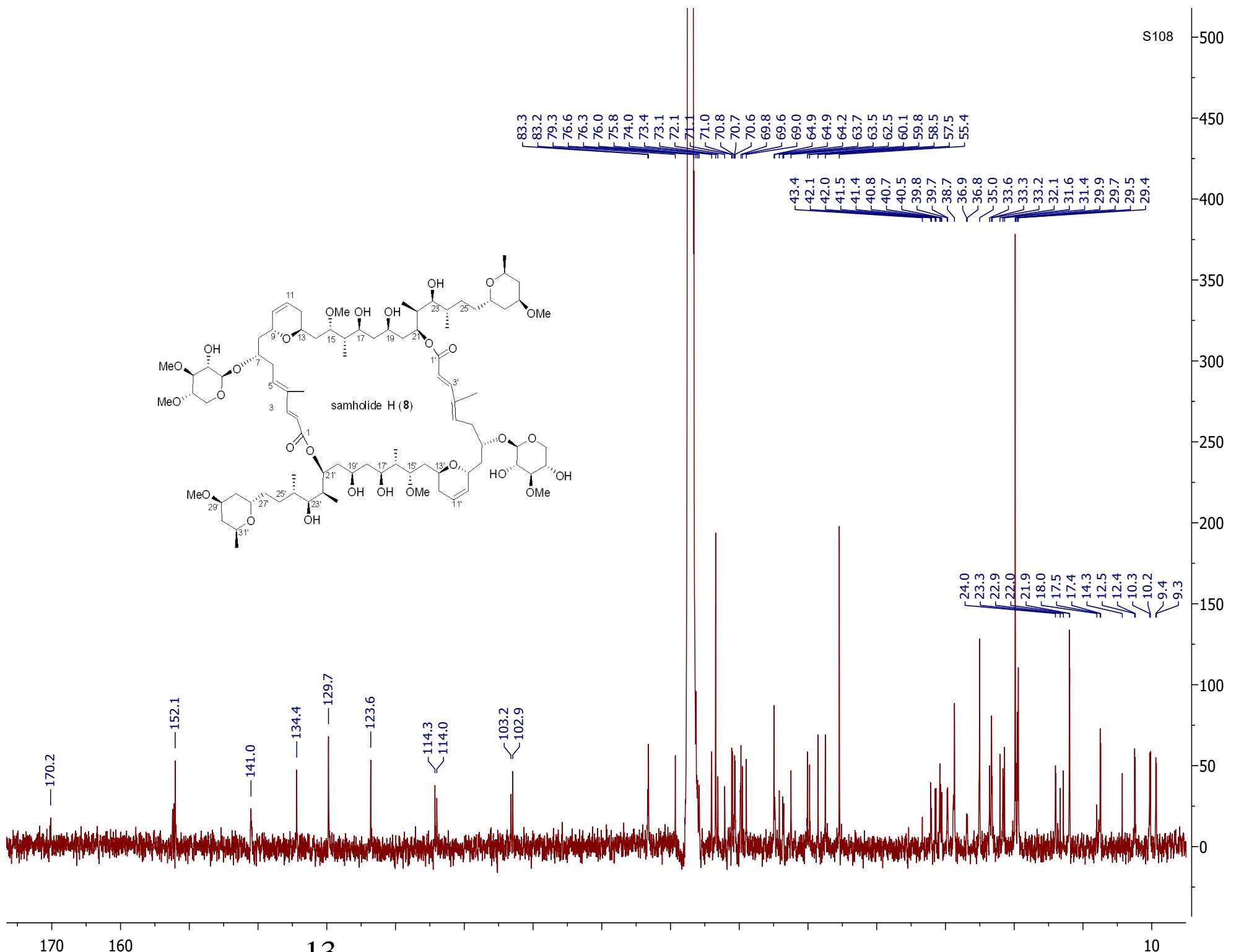
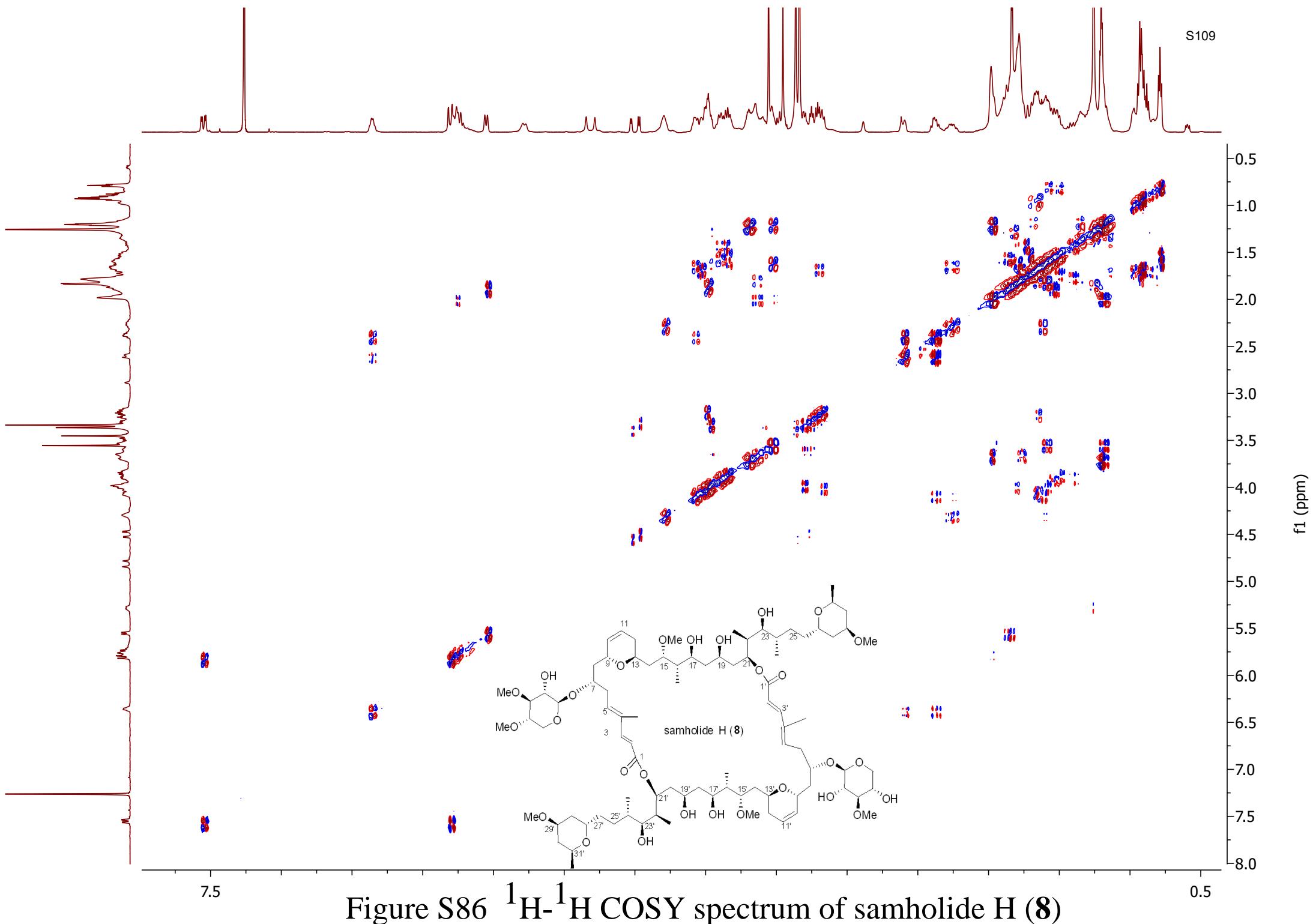


Figure S84  $^1\text{H}$  NMR (600 MHz, DMSO) spectrum of samholide H (**8**)





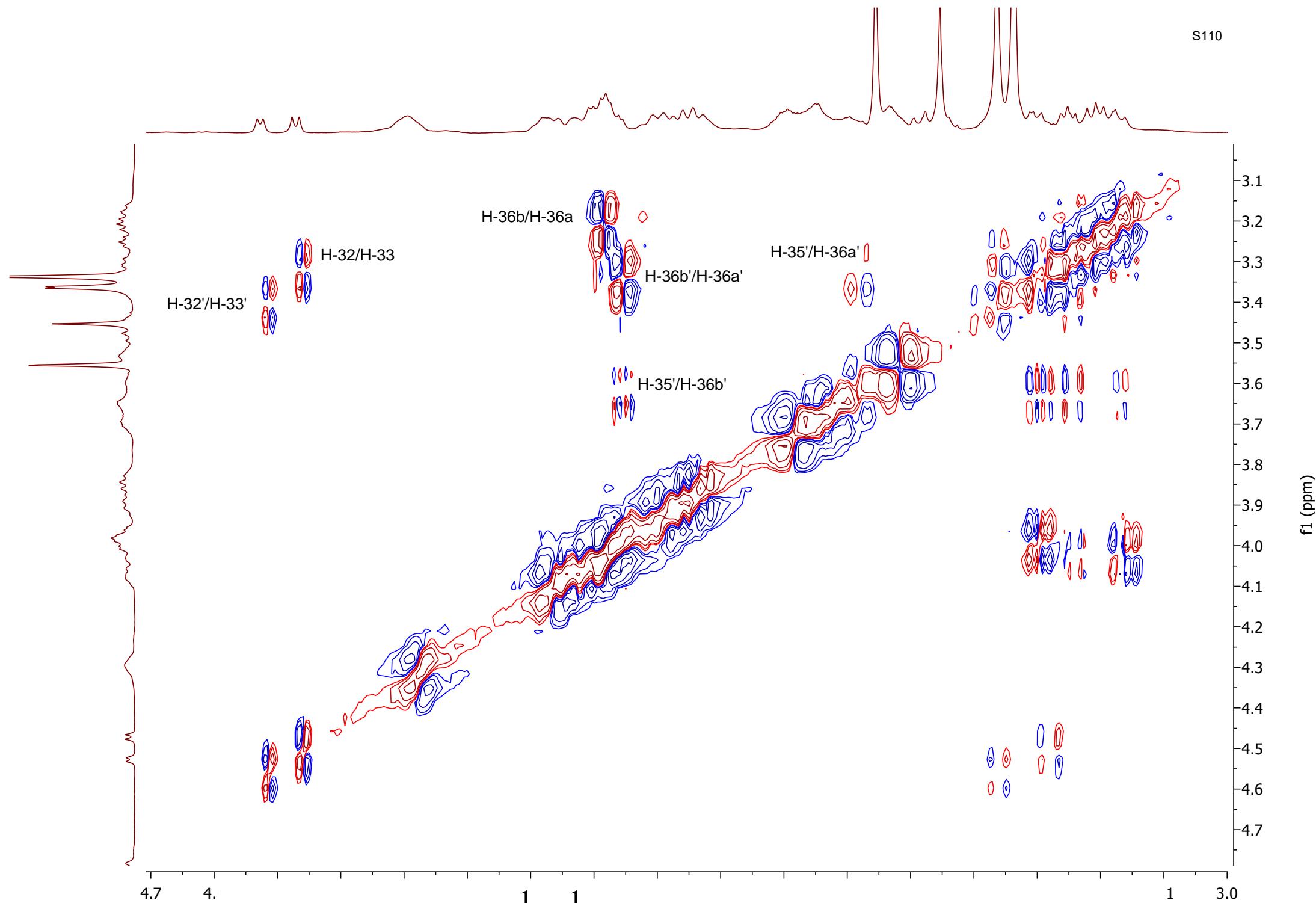


Figure S87 Amplified  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of samholide H (8)

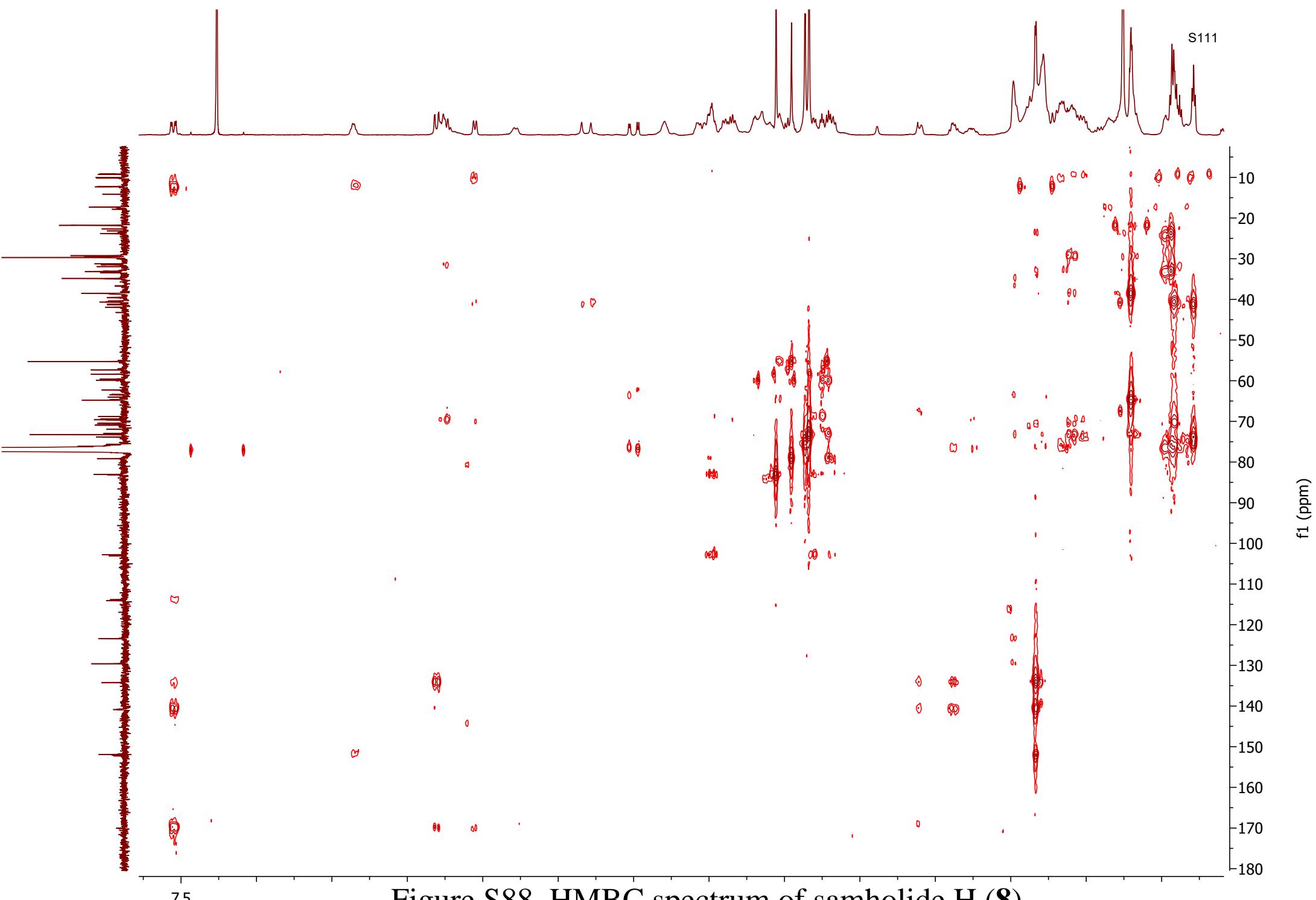


Figure S88 HMBC spectrum of samholide H (8)

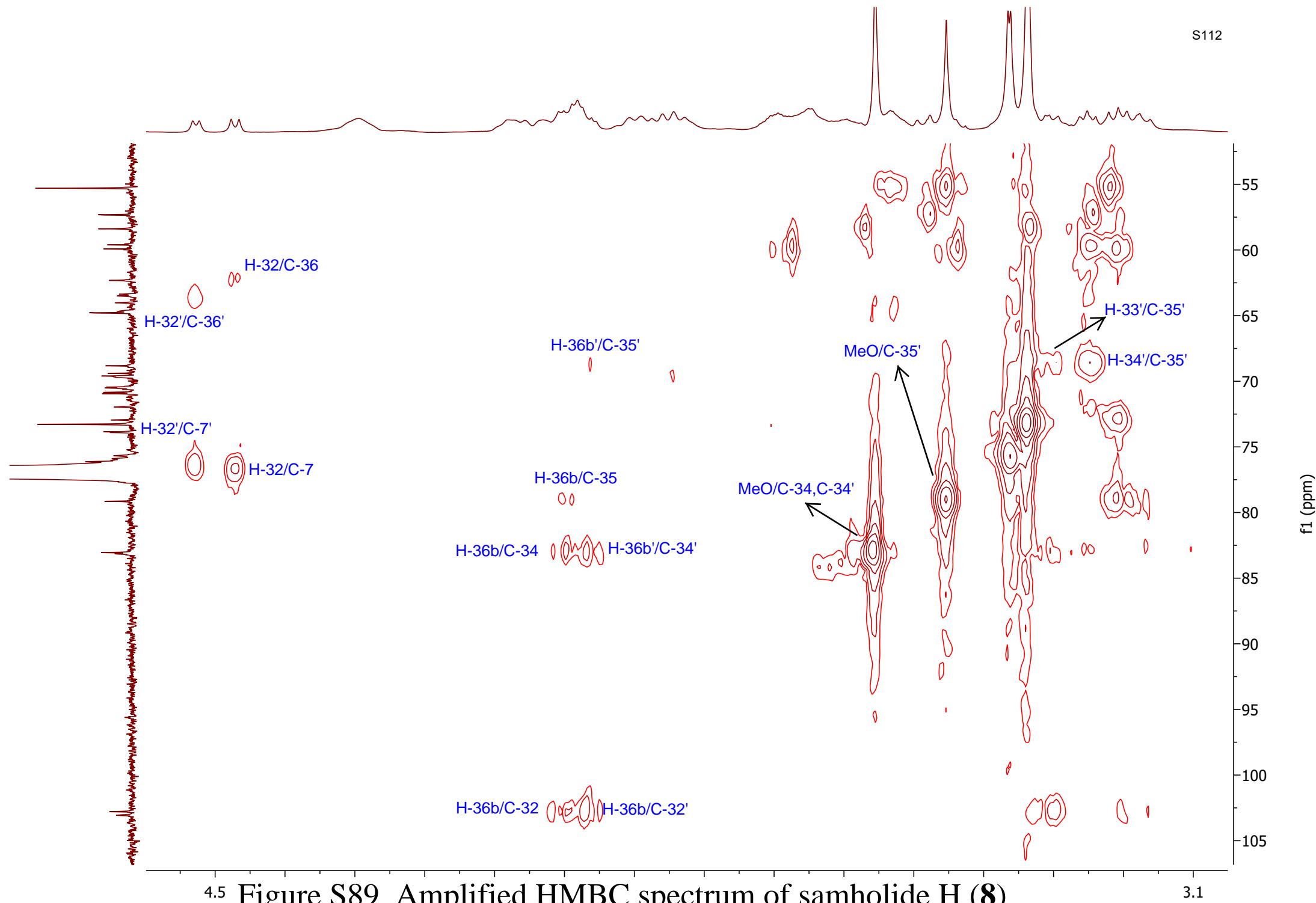
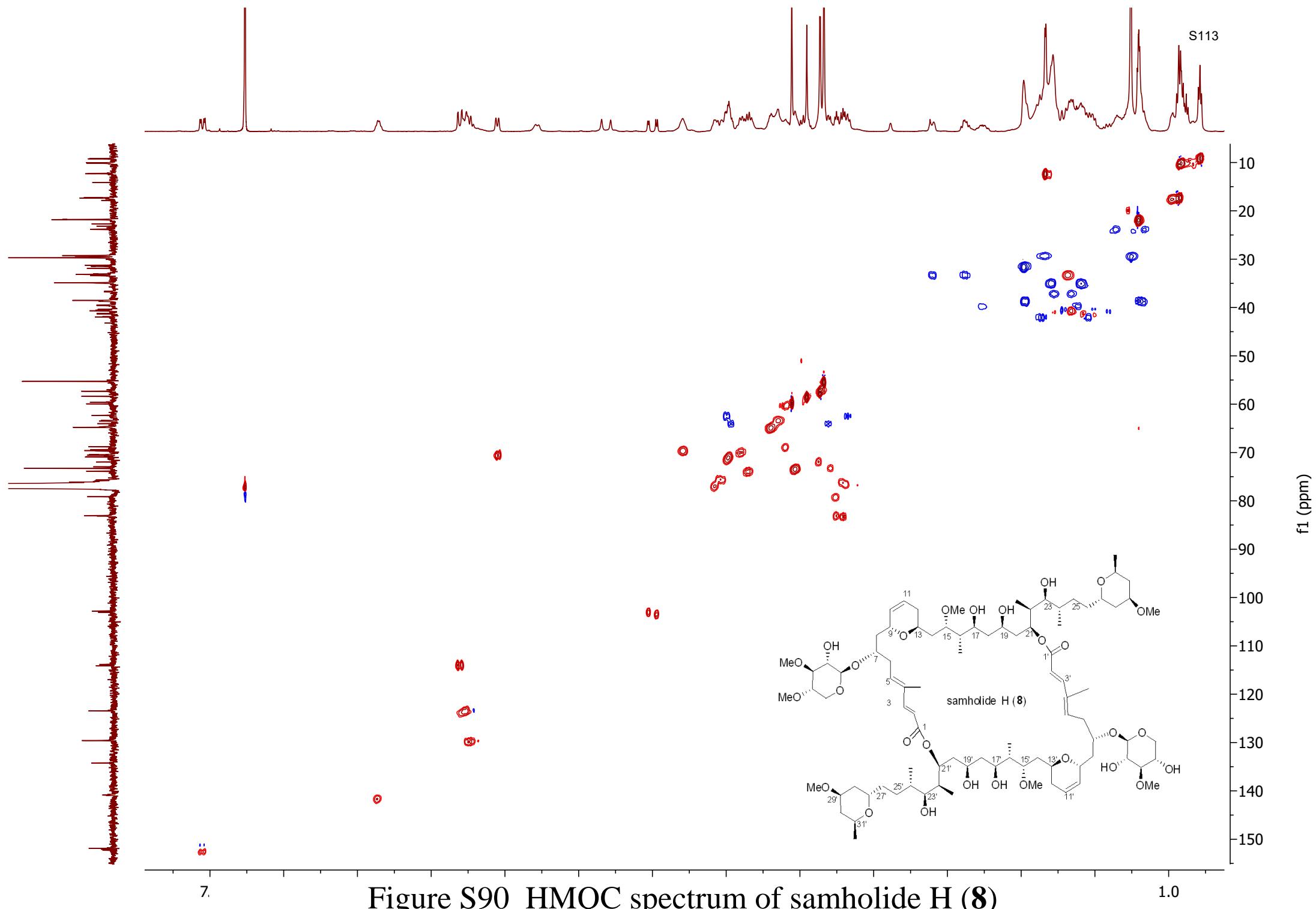


Figure S89 Amplified HMBC spectrum of samholide H (8)



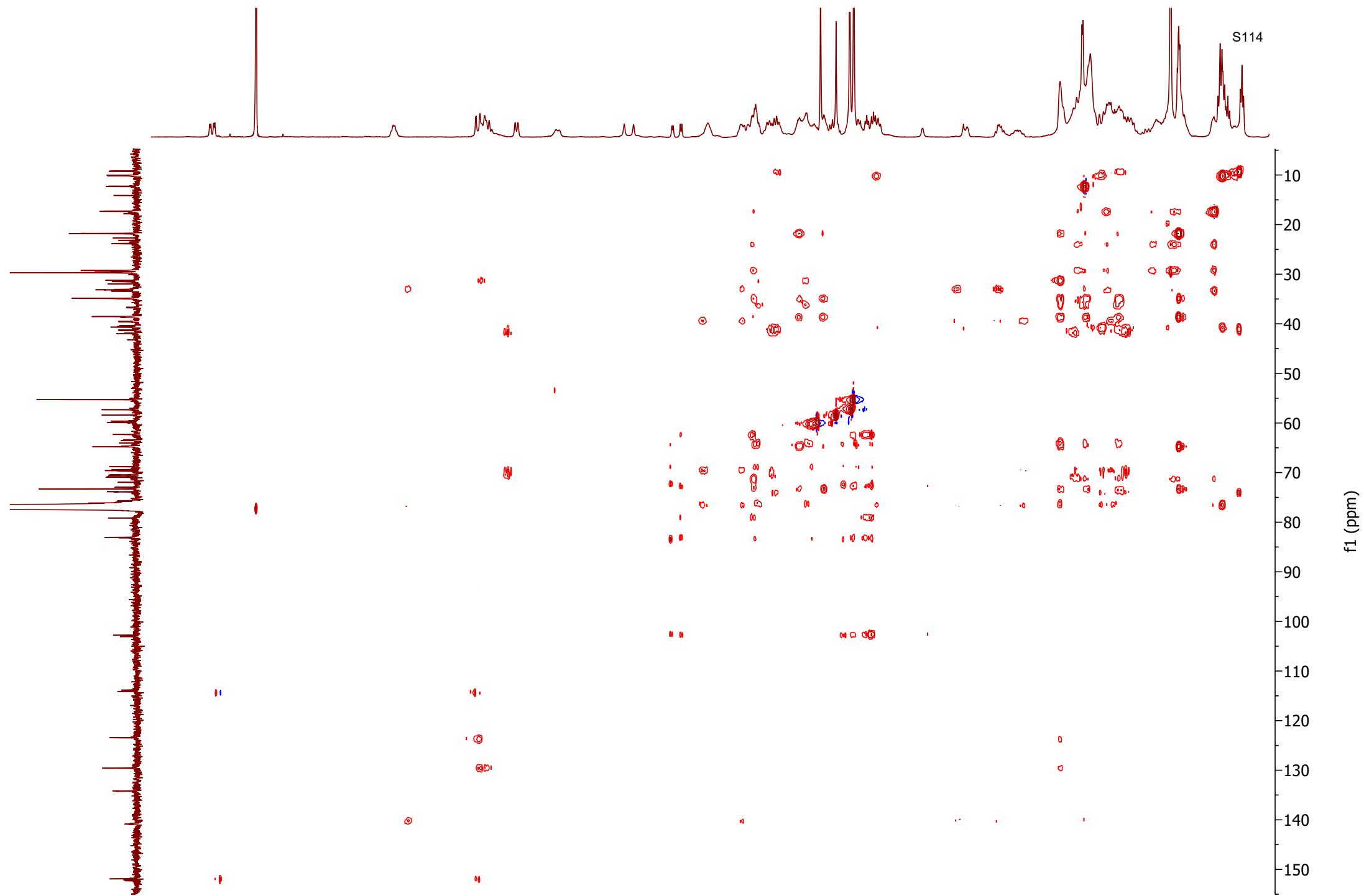


Figure S91 HSQC-TOCSY spectrum of samholide H (8)

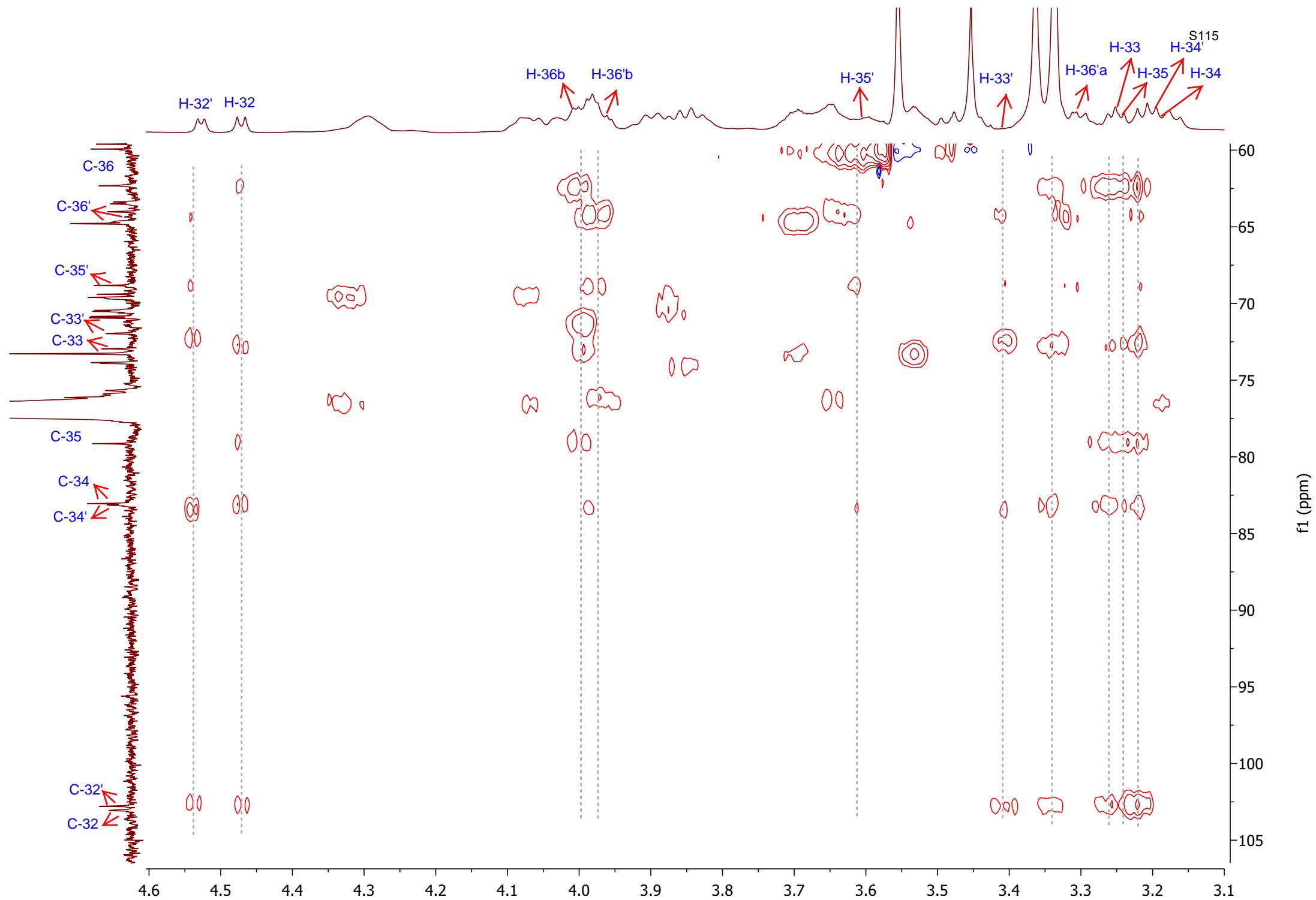
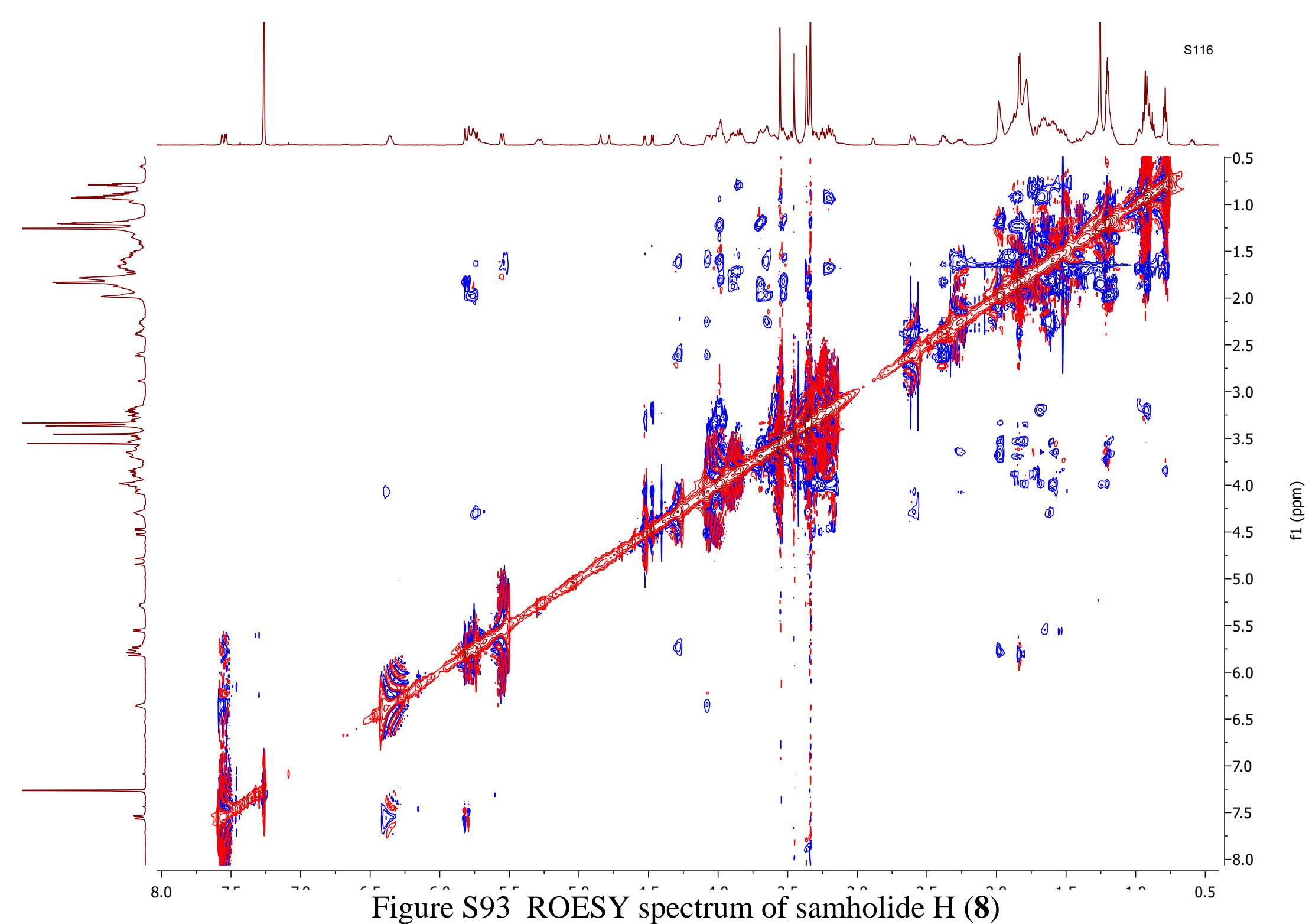


Figure S92 Amplified HSQC-TOCSY spectrum of samholide H (8)



2226H3C3-a #13-15 RT: 0.34-0.39 AV: 3 SB: 2 0.27-0.29 NL: 1.71E7

F: + c Full ms [200.00-2000.00]

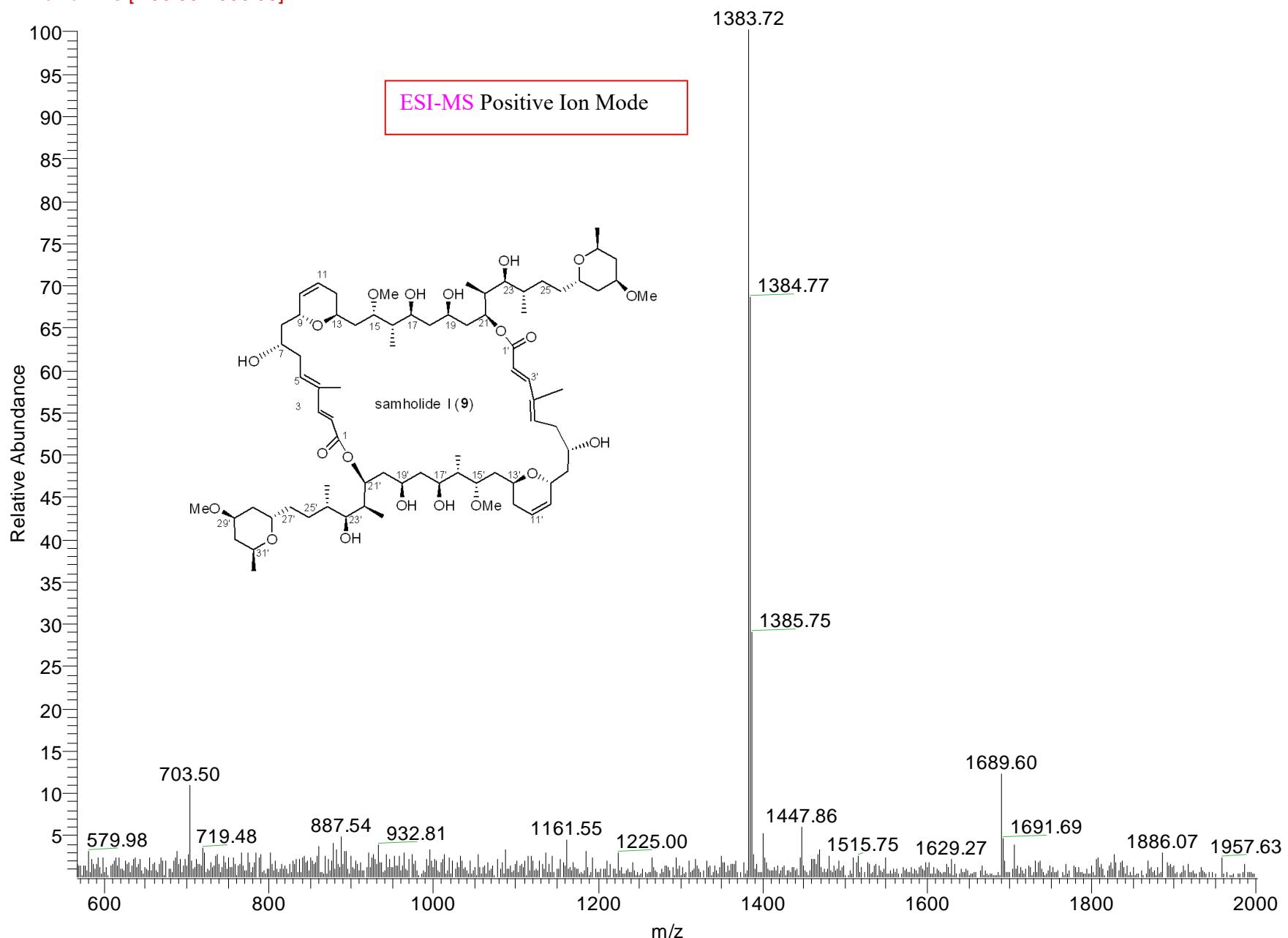


Figure S94 The ESI MS spectrum of samholide I (**9**)

2226H3C3-a #31-34 RT: 0.73-0.77 AV: 4 NL: 8.51E6

F: + c Full ms2 1384.00@35.00 [ 380.00-1400.00]

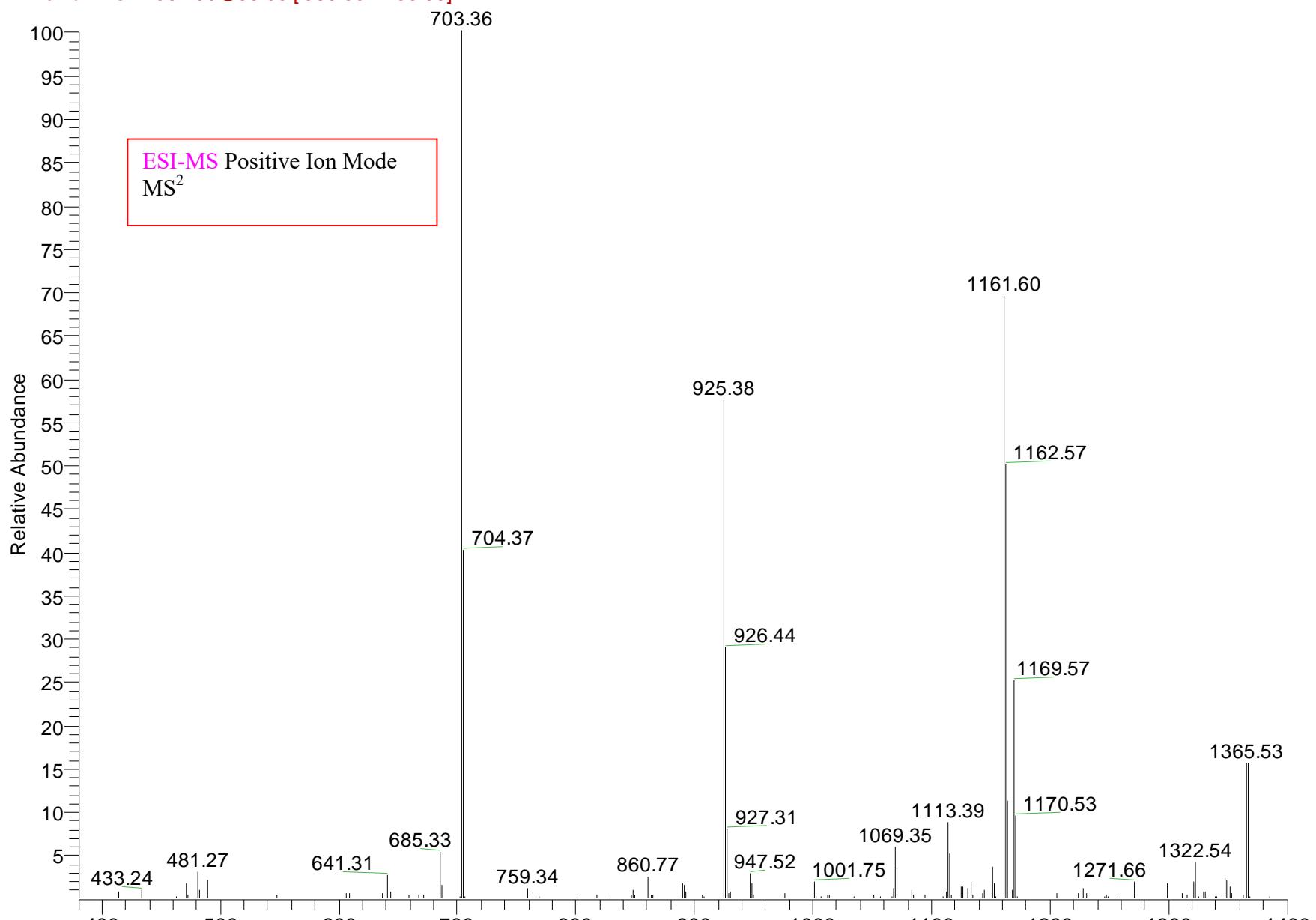


Figure S95 The ESI MS<sup>2</sup> spectrum of samholide I (9)

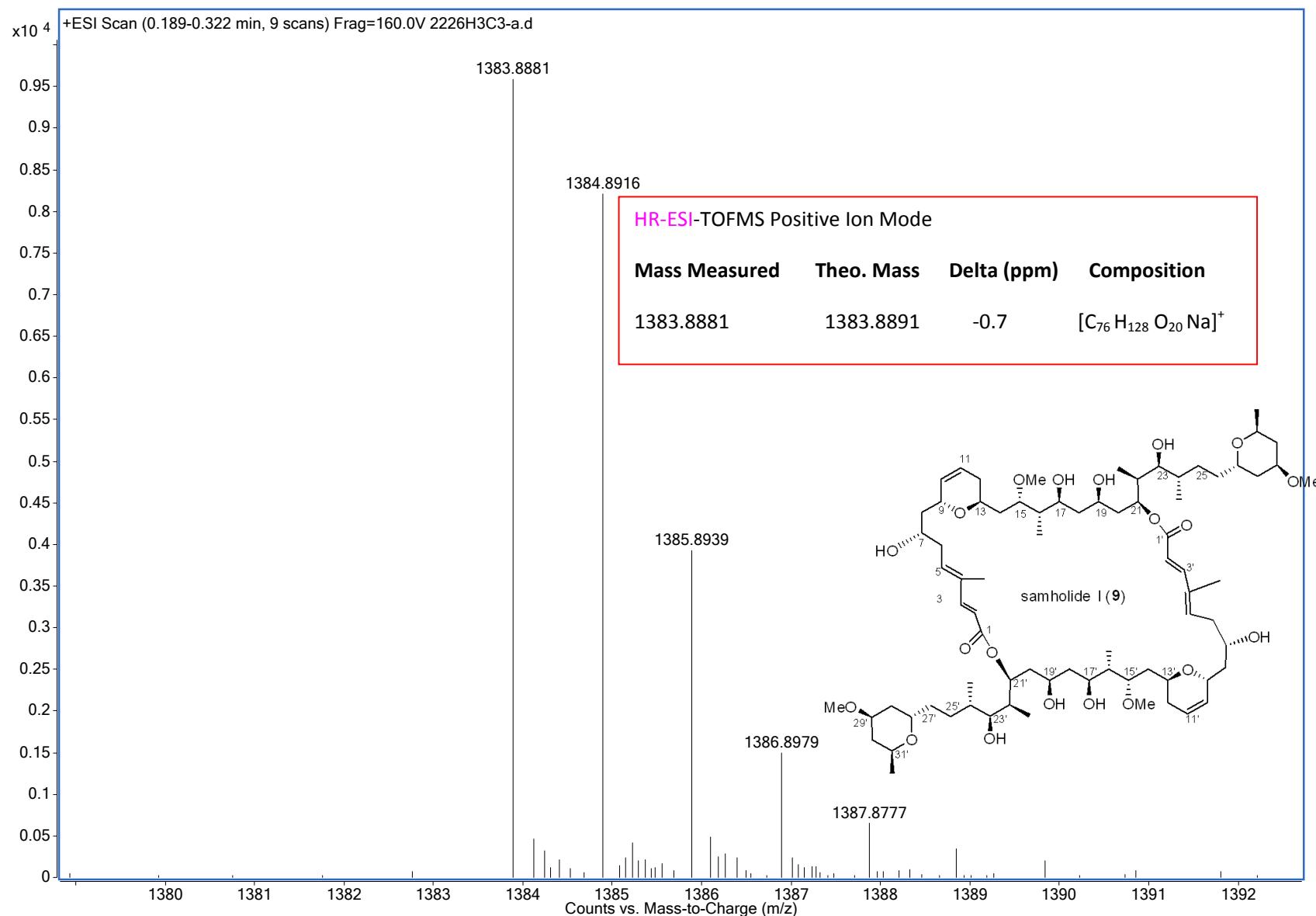


Figure S96 The positive HRESIMS spectrum of samholide I (**9**)

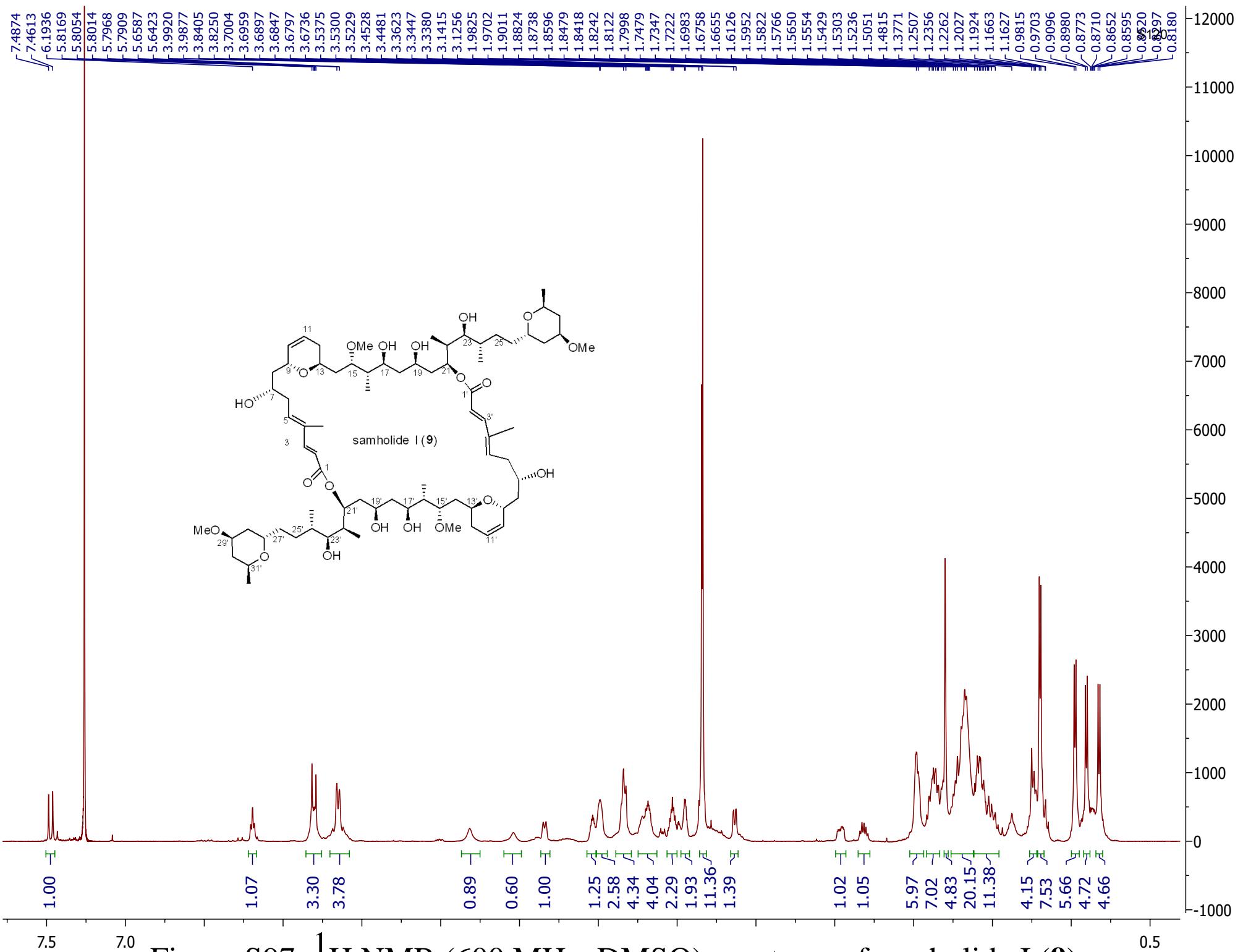
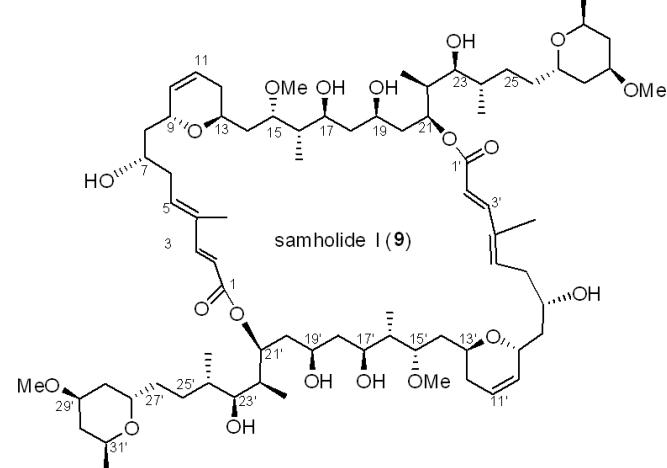


Figure S97  $^1\text{H}$  NMR (600 MHz, DMSO) spectrum of samholide I (**9**)



—169.6  
—152.0  
—140.3  
—134.2  
—129.4  
—124.2  
—114.5

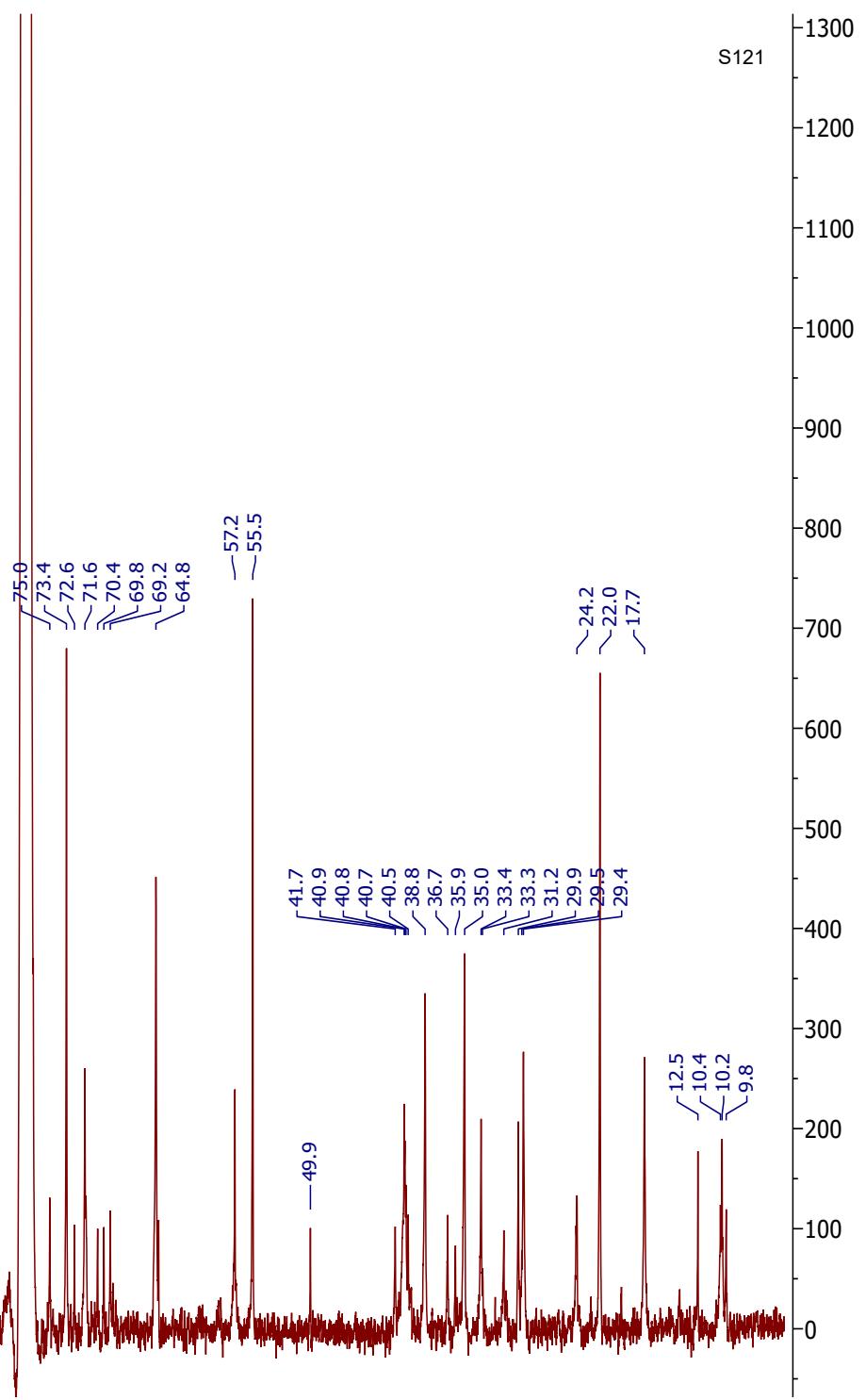


Figure S98  $^{13}\text{C}$  NMR (150 MHz, DMSO) spectrum of samholide I (**9**)

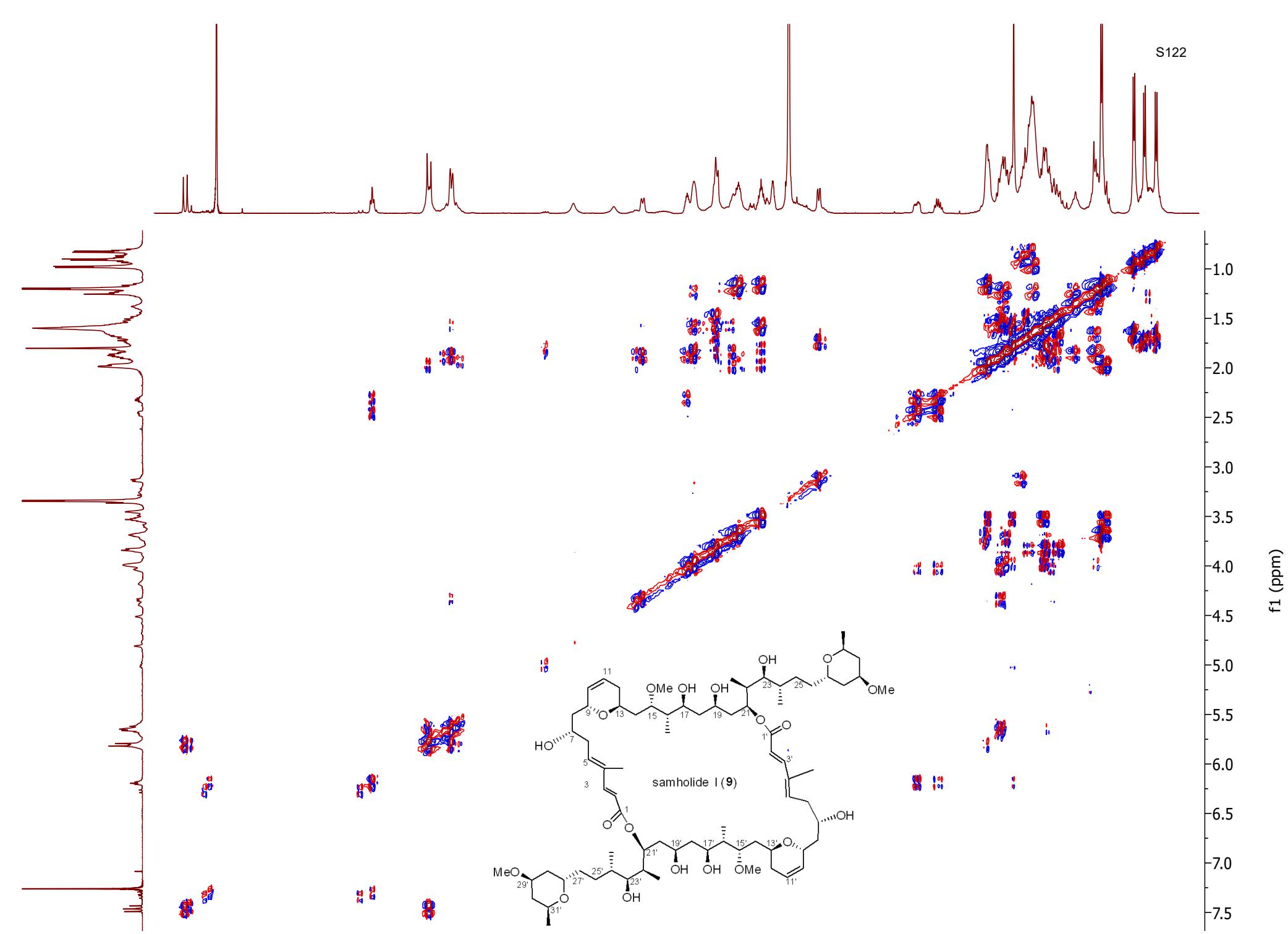


Figure S99  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of samholide I (9)

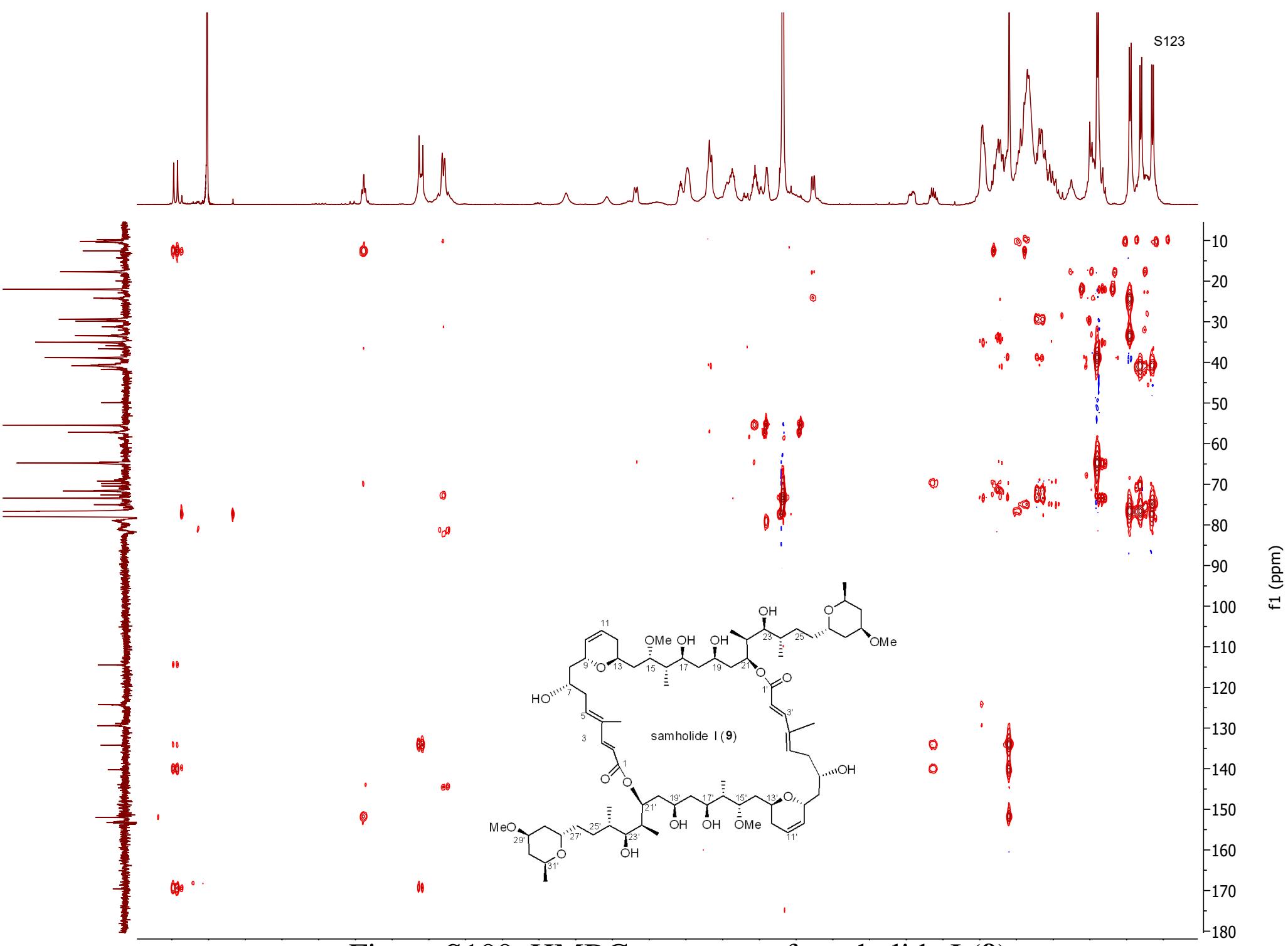
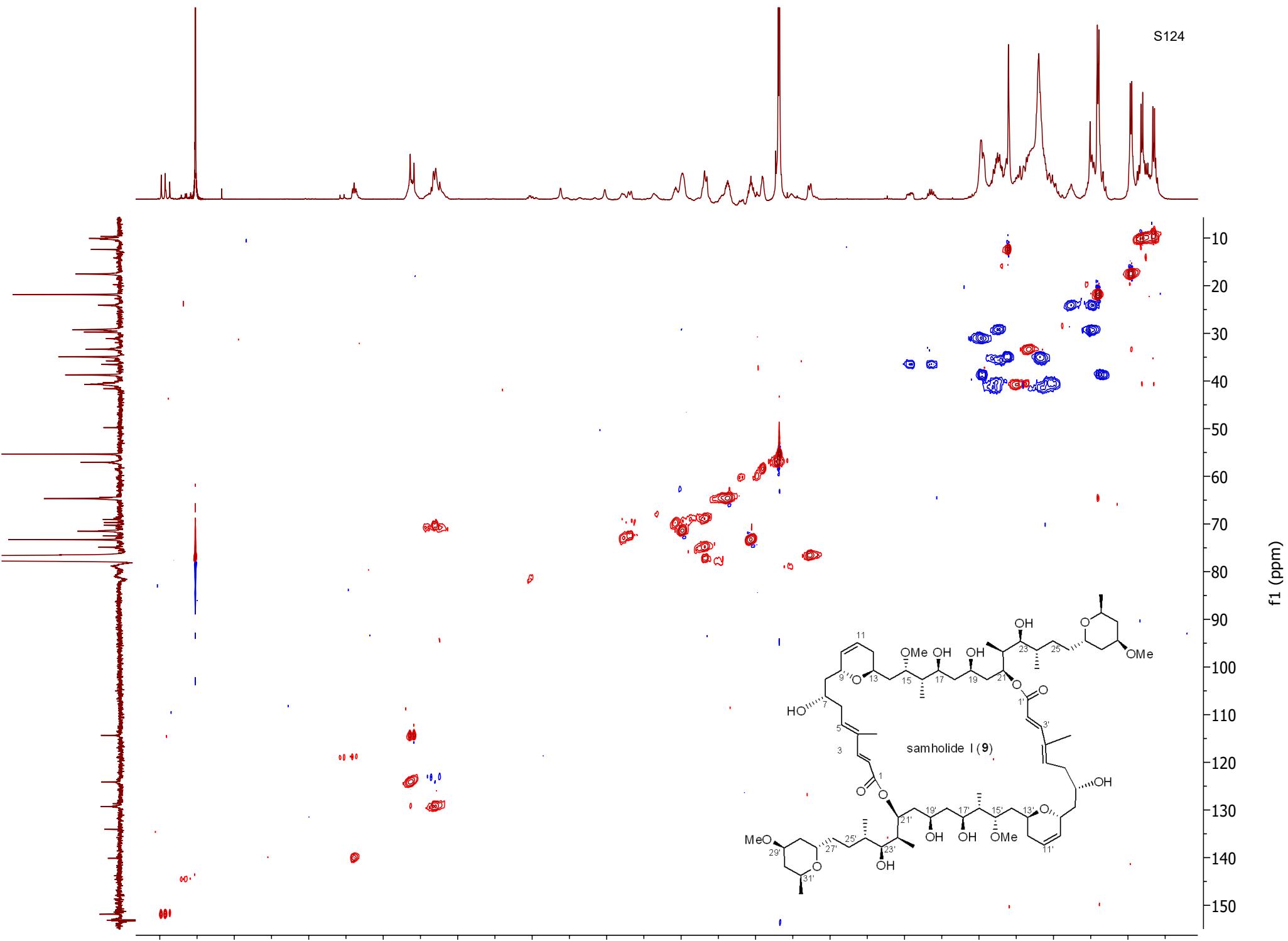


Figure S100 HMBC spectrum of samholide I (**9**)



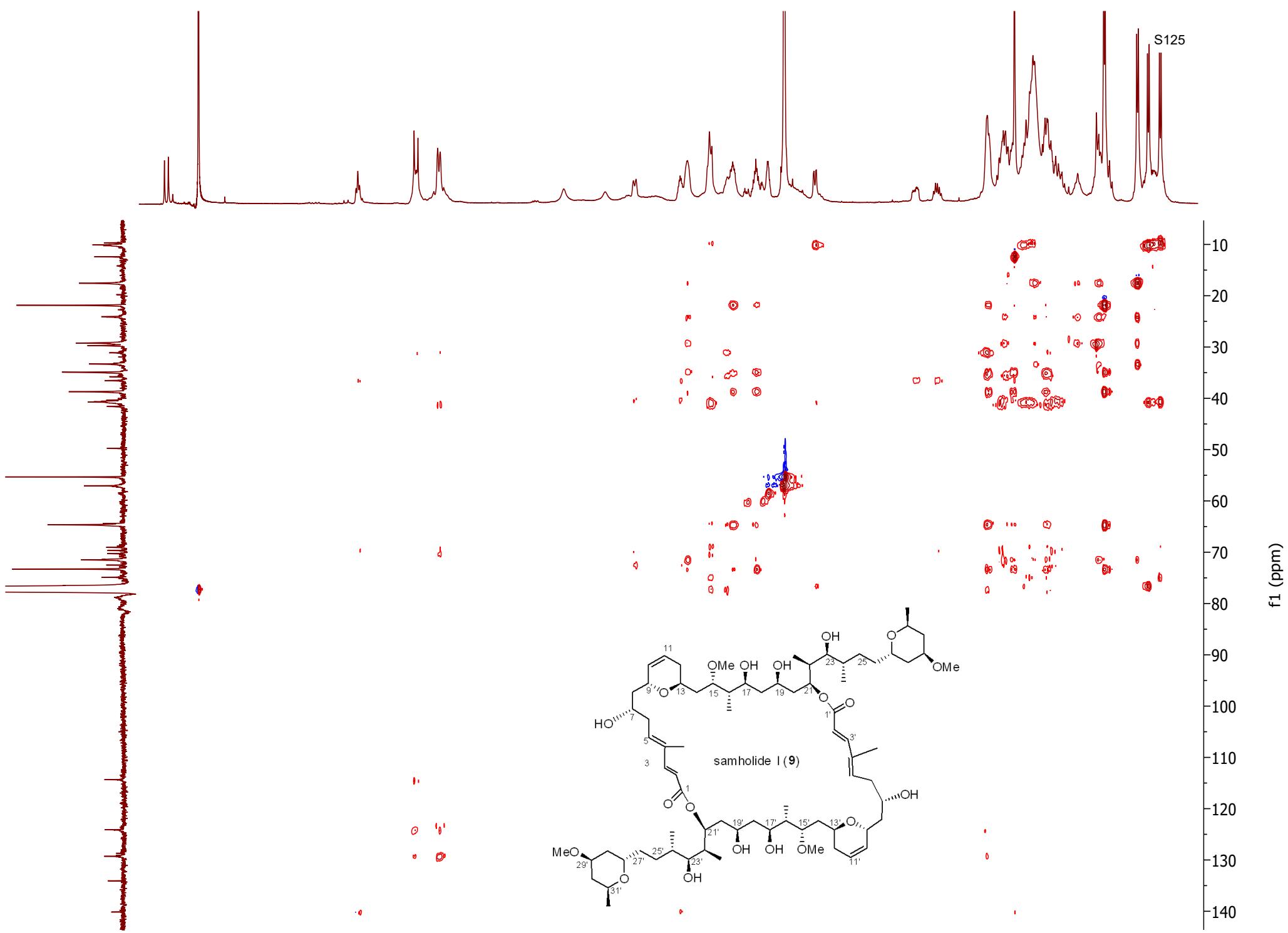


Figure S102 <sup>1</sup>HSQC-TOCSY spectrum of samholide I (9)

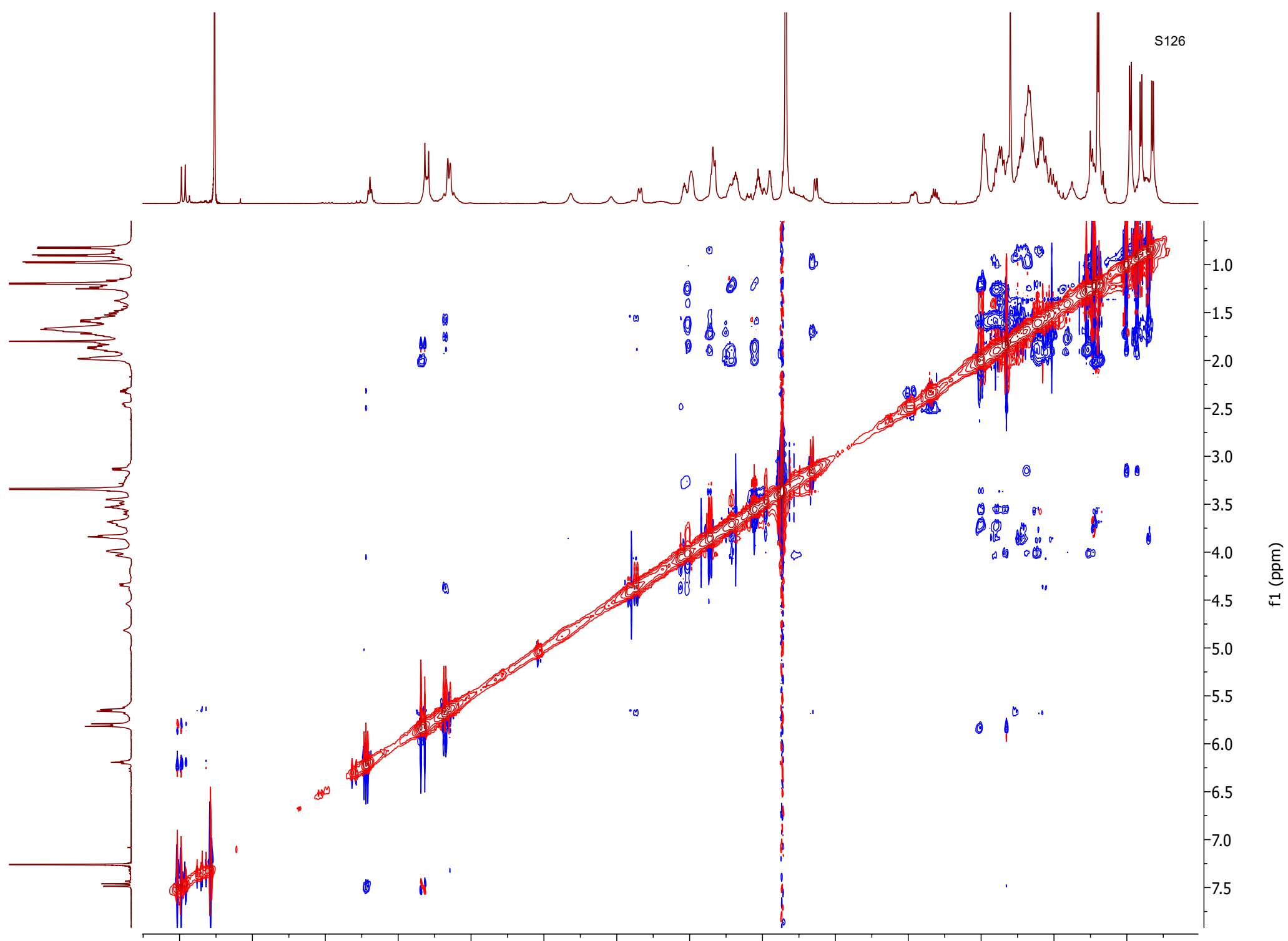


Figure S103 ROESY spectrum of samholide I (9)

Figure S104  $\text{MS}^2$ -based molecular networking of fractions D-I of cf. *Phormidium* sp.

