Supplementary Note

Automated structure prediction of *trans*-acyltransferase polyketide synthase products

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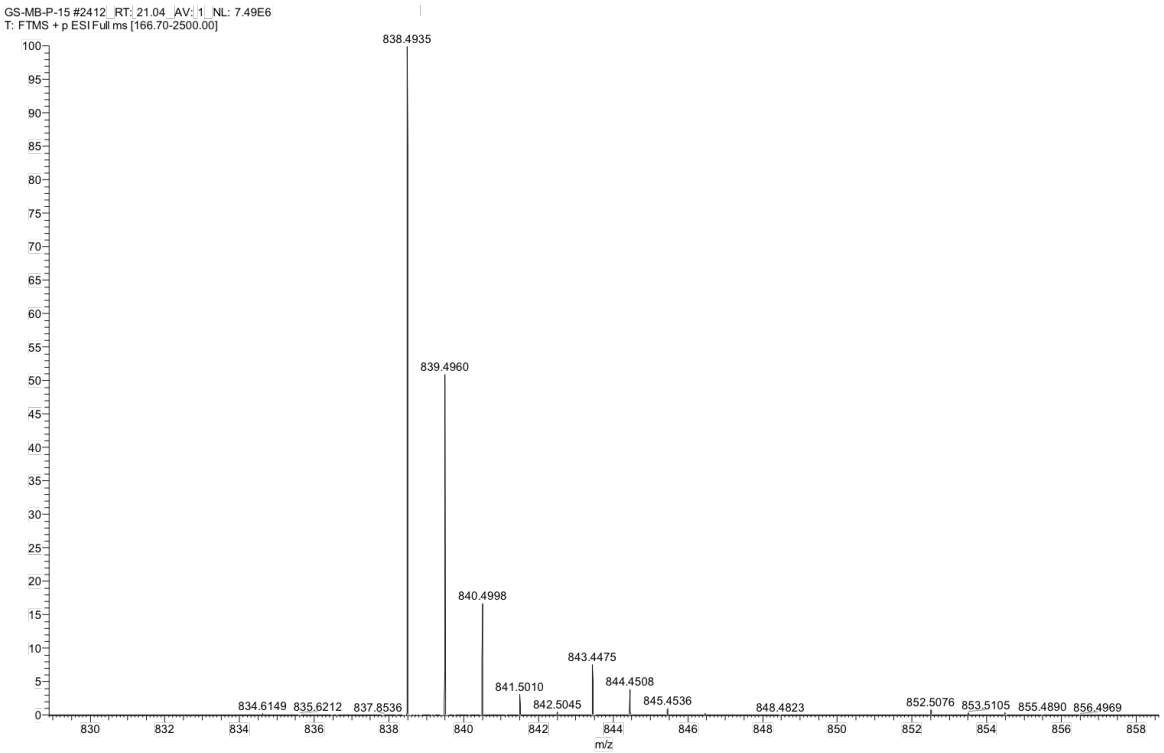
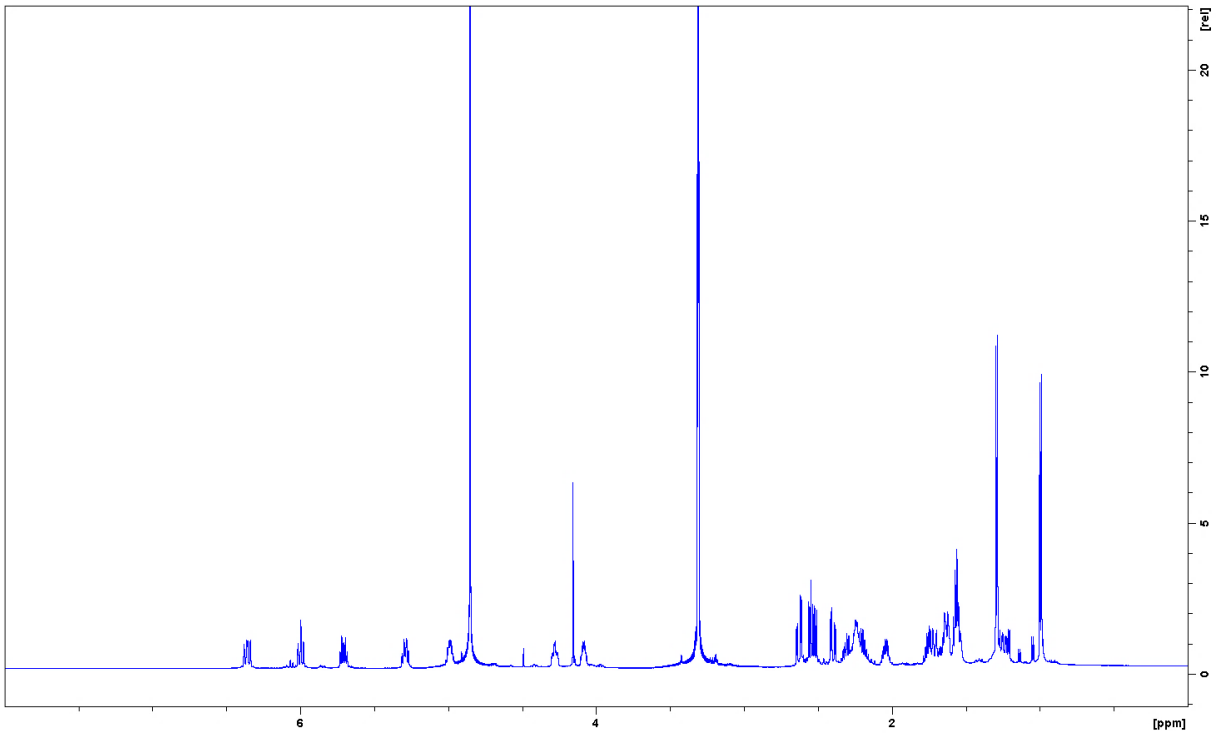
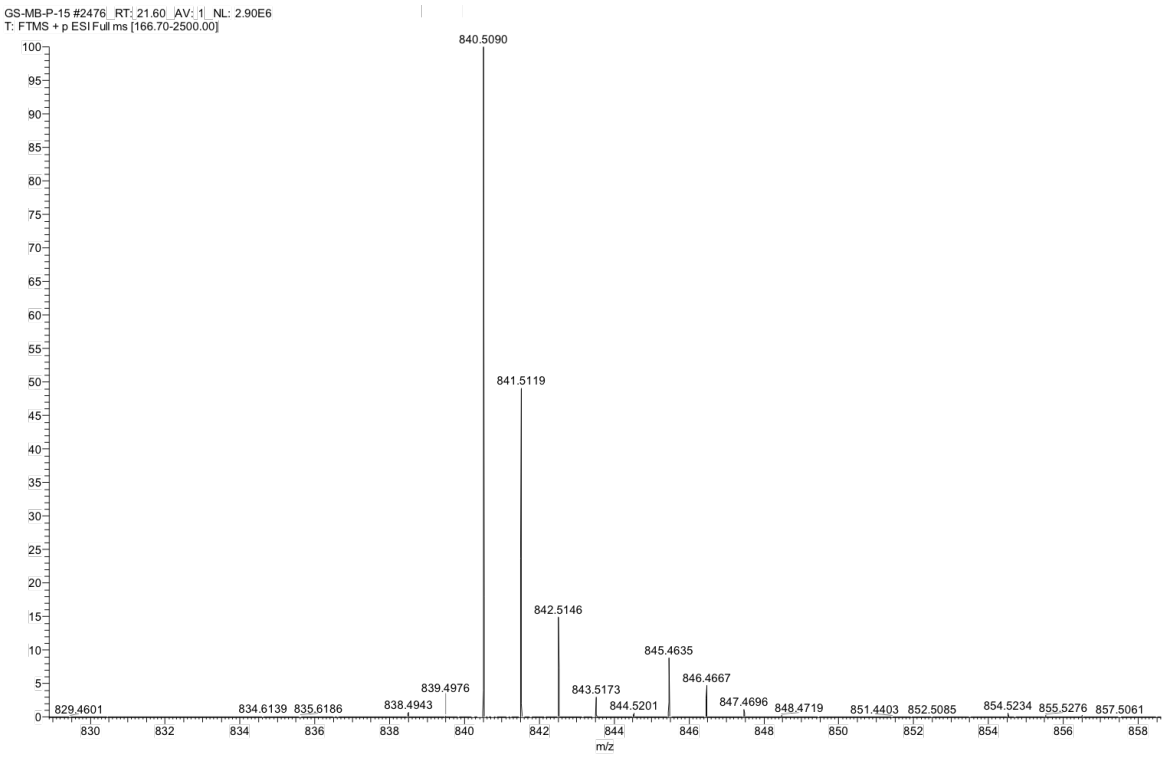
*Authors contributed equally to this work



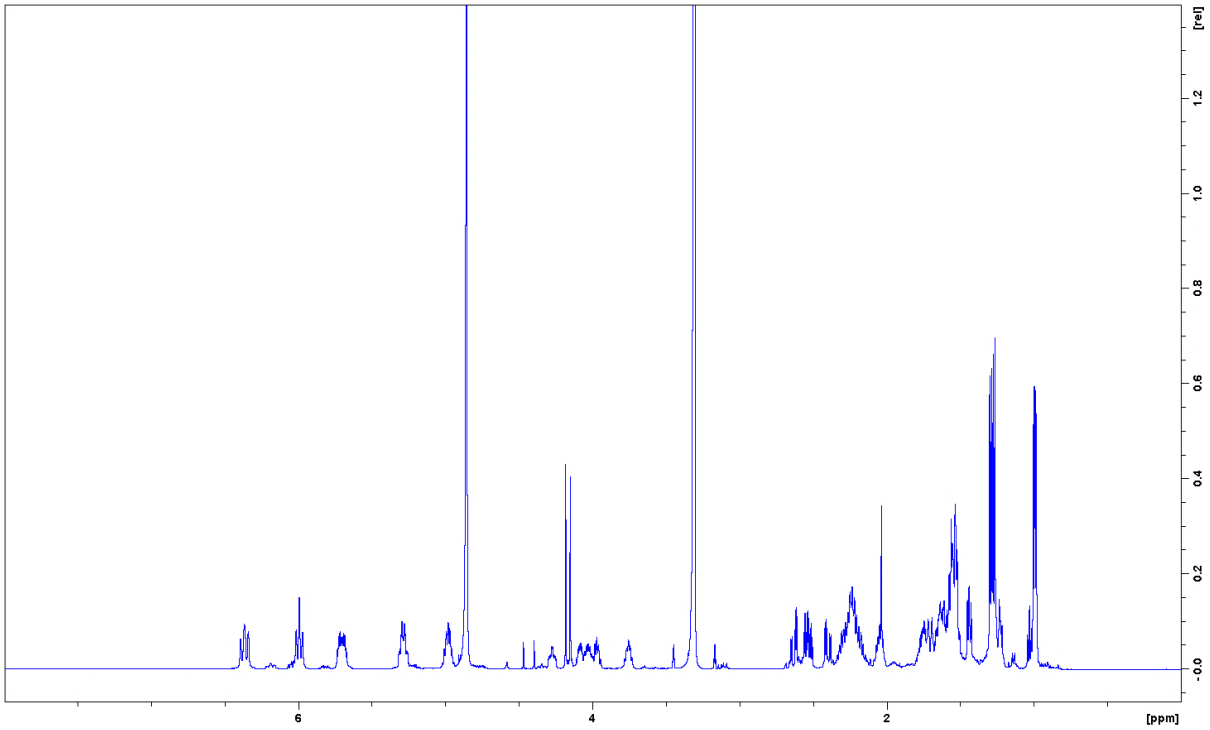
Supplementary Note Figure 1: HR-ESI-MS spectrum of tartrolon D (4) from *Gynuella sunshinyii* (*m*/*z* 838.4935 $[M+NH_4]^+$, *m*/*z* 843.4475 $[M+Na]^+$) (n = 1).



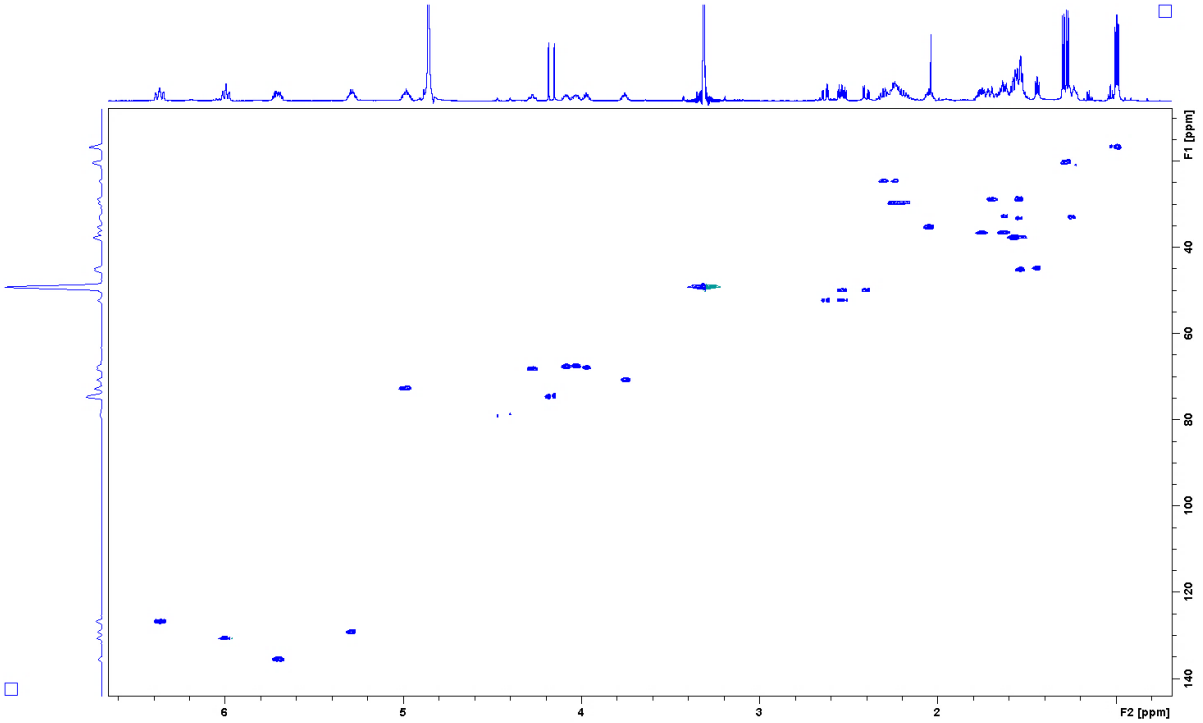
Supplementary Note Figure 2: ^{1}H NMR spectrum of tartrolon D (4) from *Gynuella sunshinyii* in CD_3OD (n = 1).



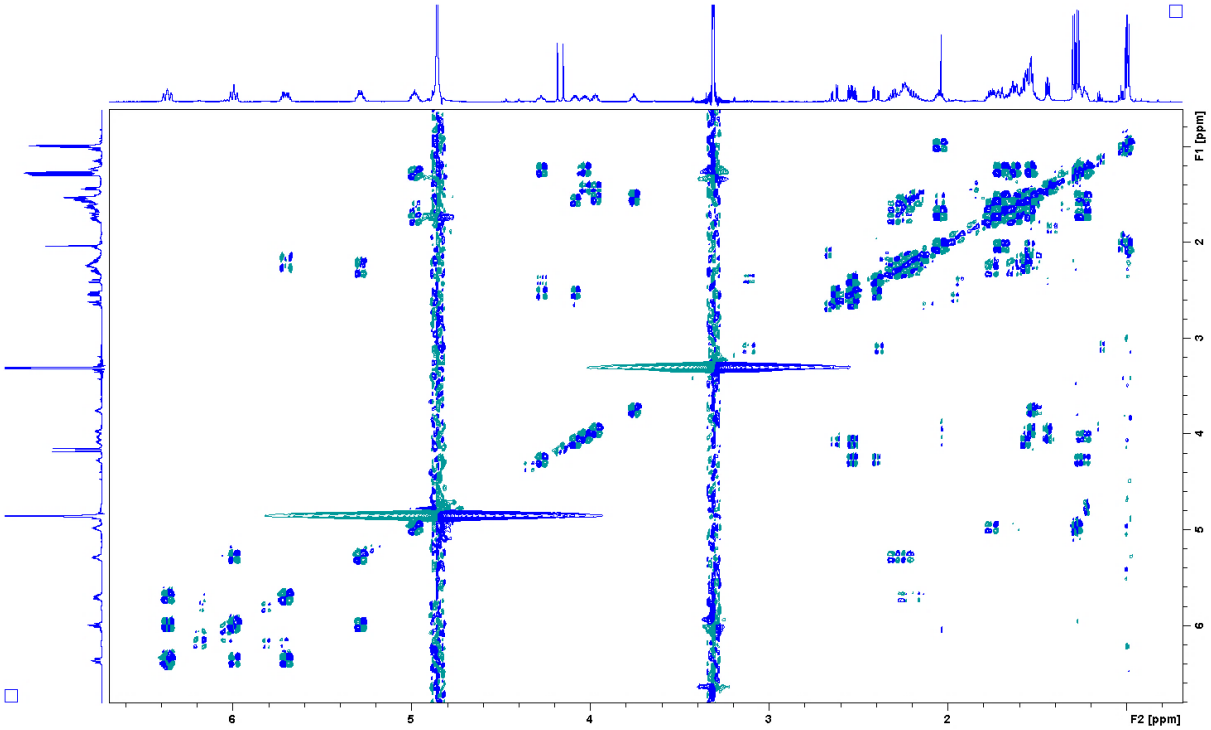
Supplementary Note Figure 3: HR-ESI-MS spectrum of tartrolon F (5) from *Gynuella sunshinyii* (*m*/*z* 840.5090 $[M+NH_4]^+$, *m*/*z* 845.4635 $[M+Na]^+$) (n = 1).



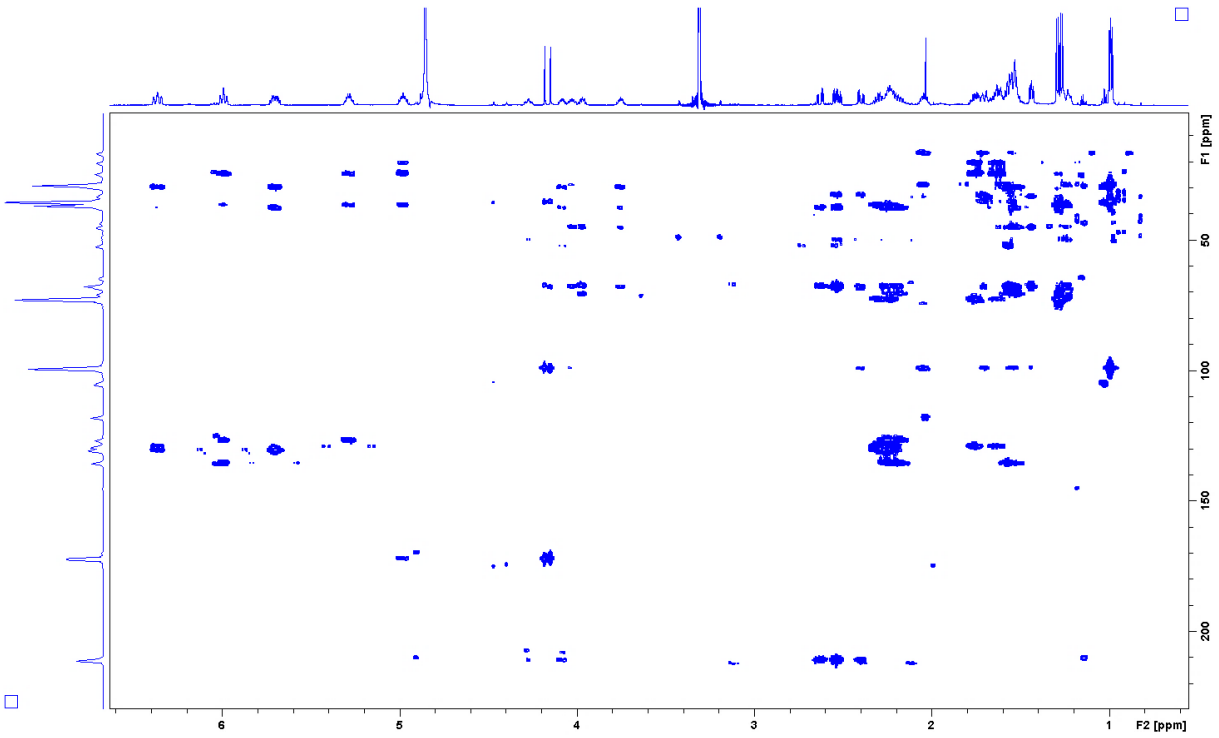
Supplementary Note Figure 4: ^{1}H NMR spectrum of tartrolon F (5) from *Gynuella sunshinyii* in CD_3OD (n = 1).



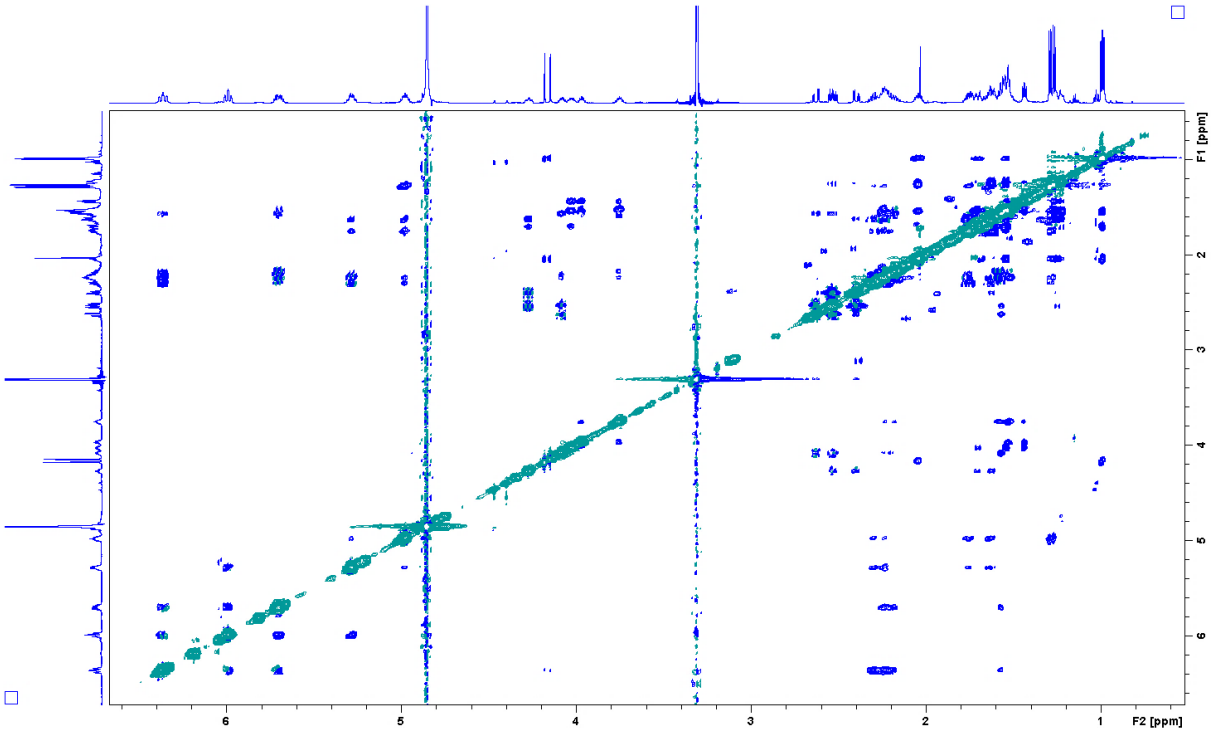
Supplementary Note Figure 5: HSQC spectrum of tartrolon F (5) from *Gynuella sunshinyii* in CD_3OD (n = 1).



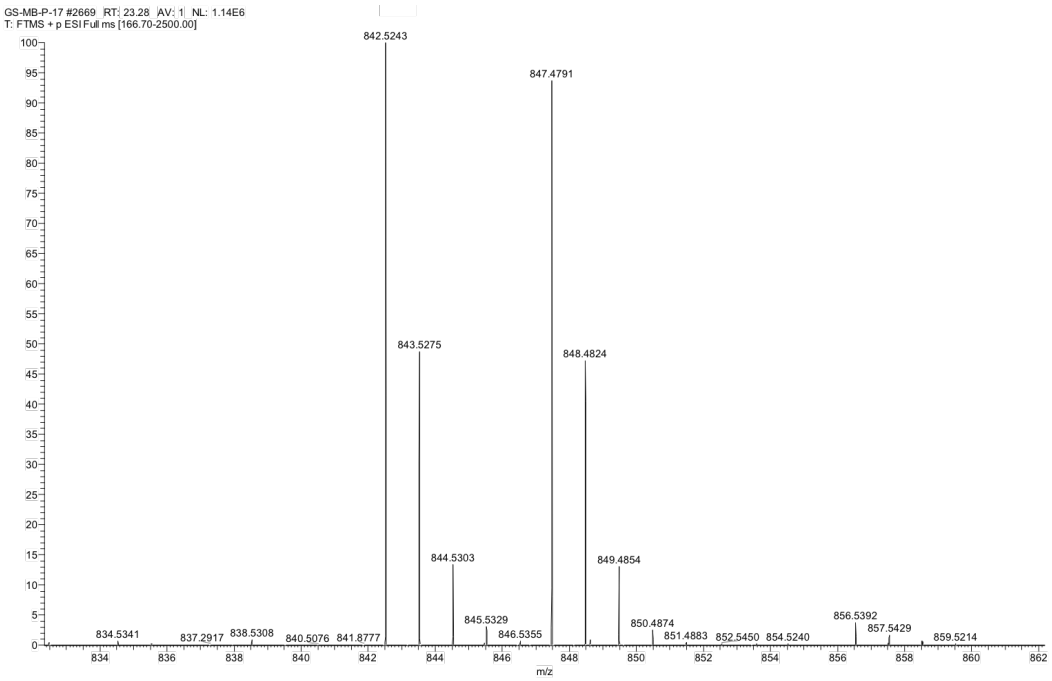
Supplementary Note Figure 6: COSY spectrum of tartrolon F (5) from *Gynuella sunshinyii* in CD_3OD (n = 1).



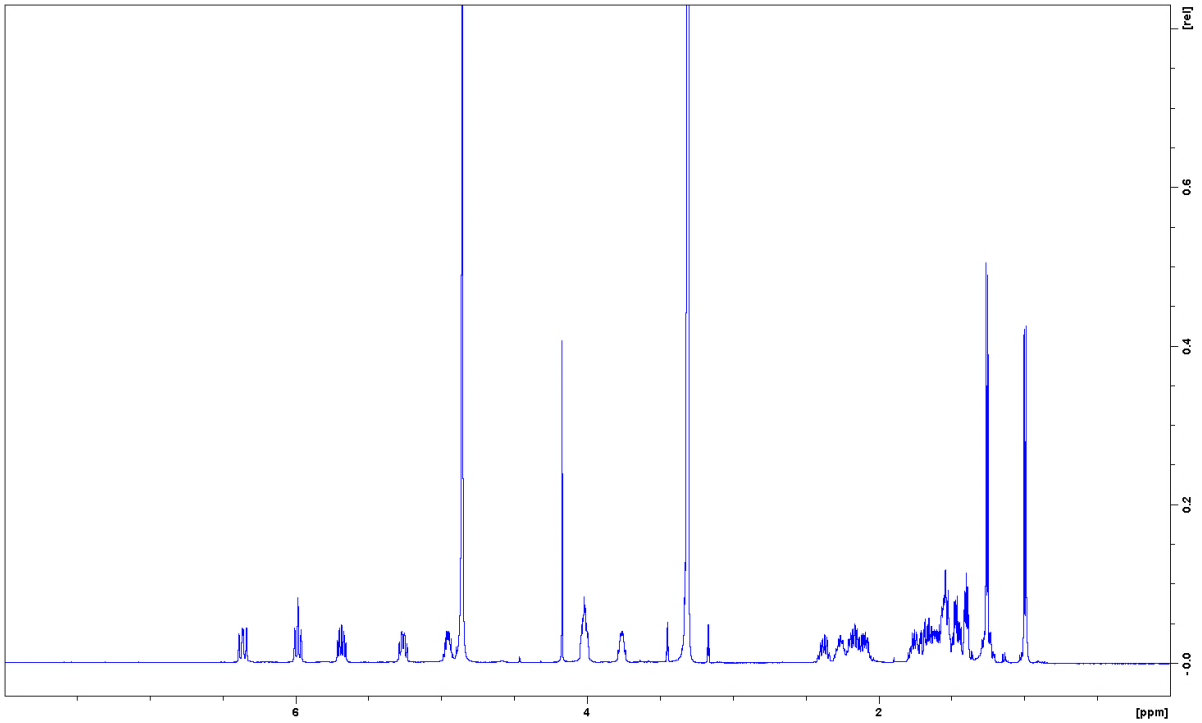
Supplementary Note Figure 7: HMBC spectrum of tartrolon F (5) from *Gynuella sunshinyii* in CD_3OD (n = 1).



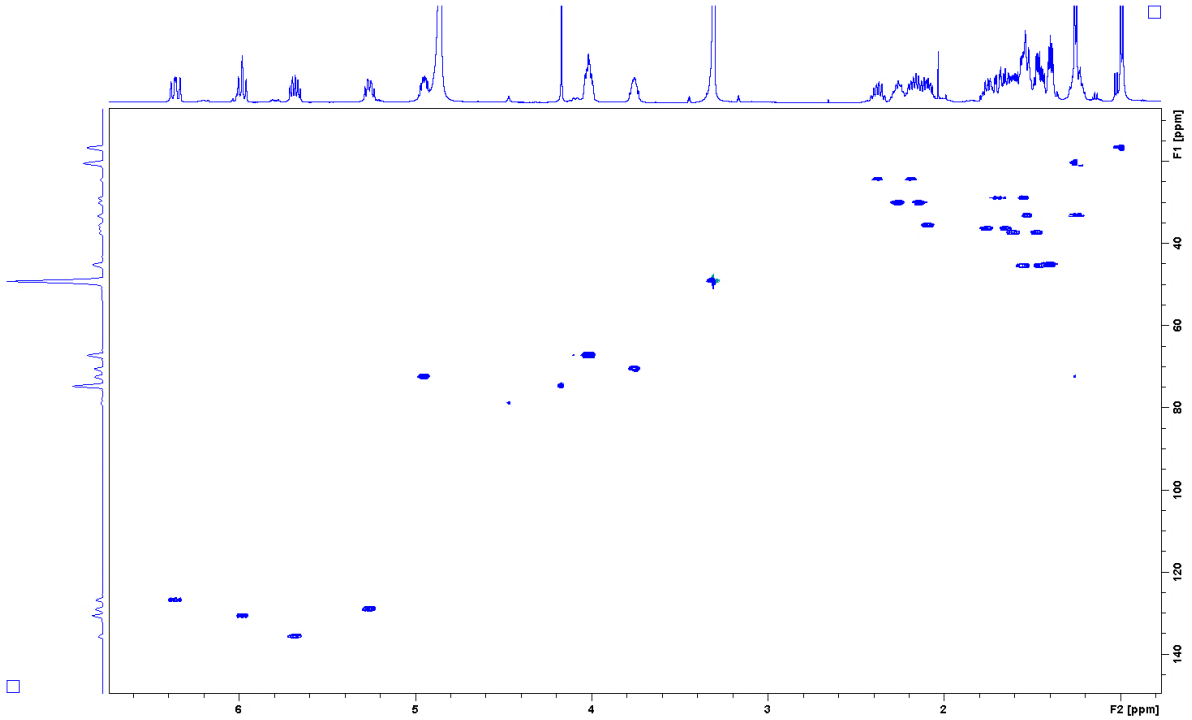
Supplementary Note Figure 8: NOESY spectrum of tartrolon F (5) from *Gynuella sunshinyii* in CD_3OD (n = 1).



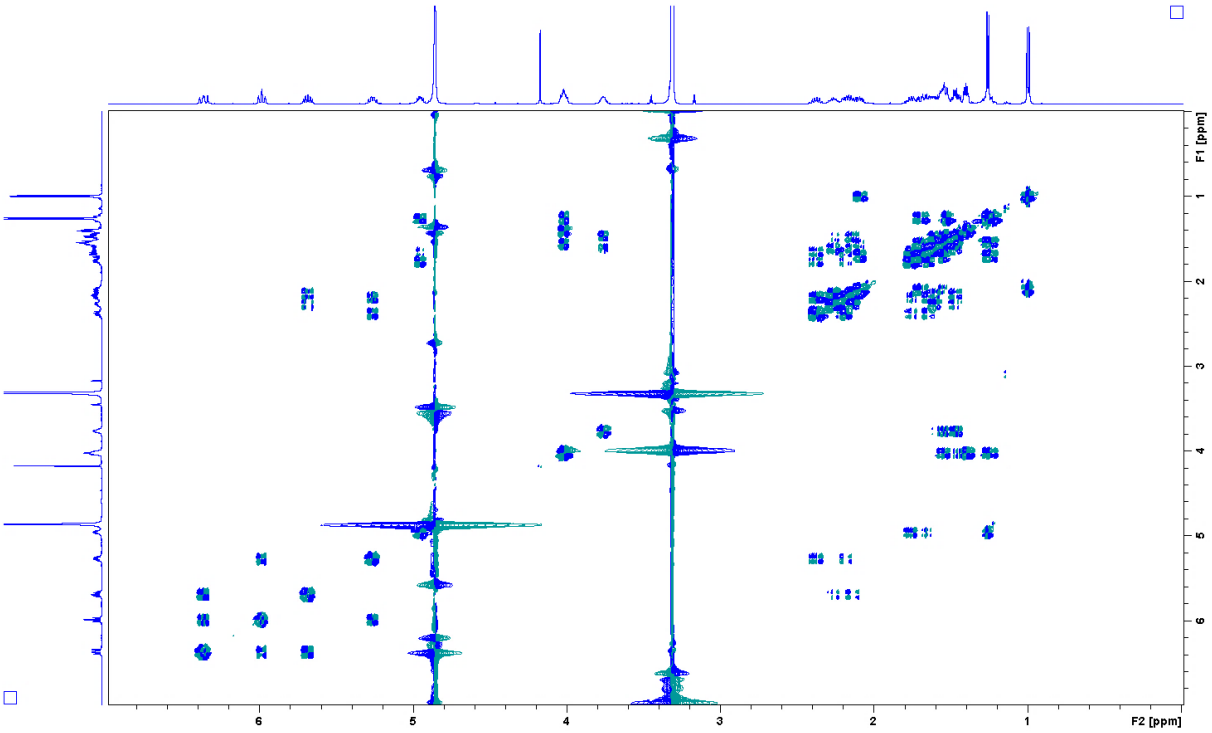
Supplementary Note Figure 9: HR-ESI-MS spectrum of tartrolon G (6) from *Gynuella sunshinyii* (*m/z* 842.5243 $[M+NH_4]^+$, *m/z* 847.4791 $[M+Na]^+$) (n = 1).



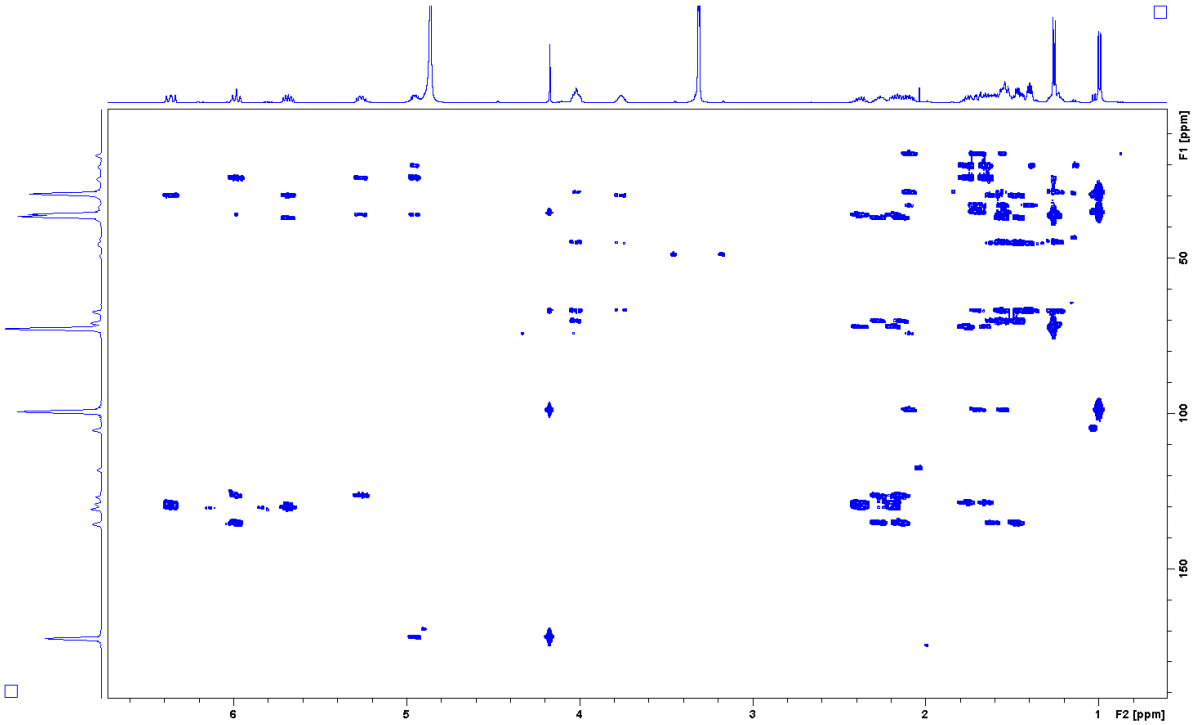
Supplementary Note Figure 10: ^{1}H NMR spectrum of tartrolon G (6) from *Gynuella sunshinyii* in CD_3OD (n = 1).



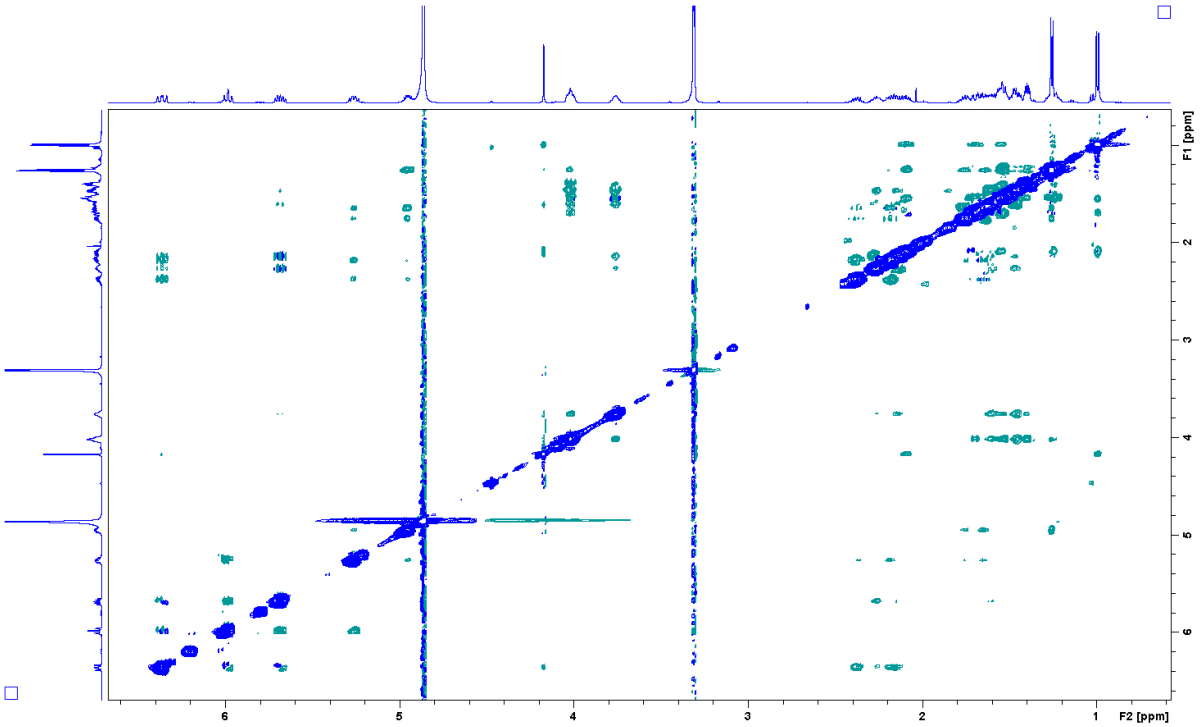
Supplementary Note Figure 11: HSQC spectrum of tartrolon G (6) from *Gynuella sunshinyii* in CD_3OD (n = 1).



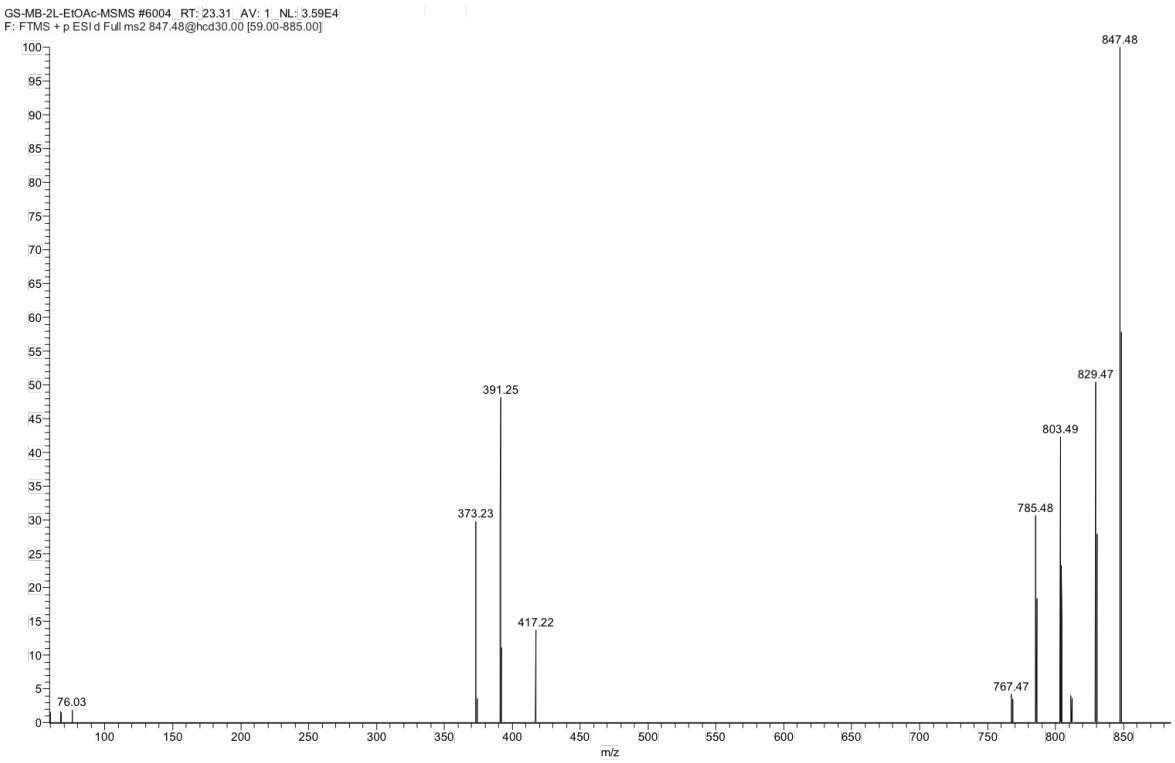
Supplementary Note Figure 12: COSY spectrum of tartrolon G (6) from *Gynuella sunshinyii* in CD_3OD (n = 1).



Supplementary Note Figure 13: HMBC spectrum of tartrolon G (6) from *Gynuella sunshinyii* in CD_3OD (n = 1).

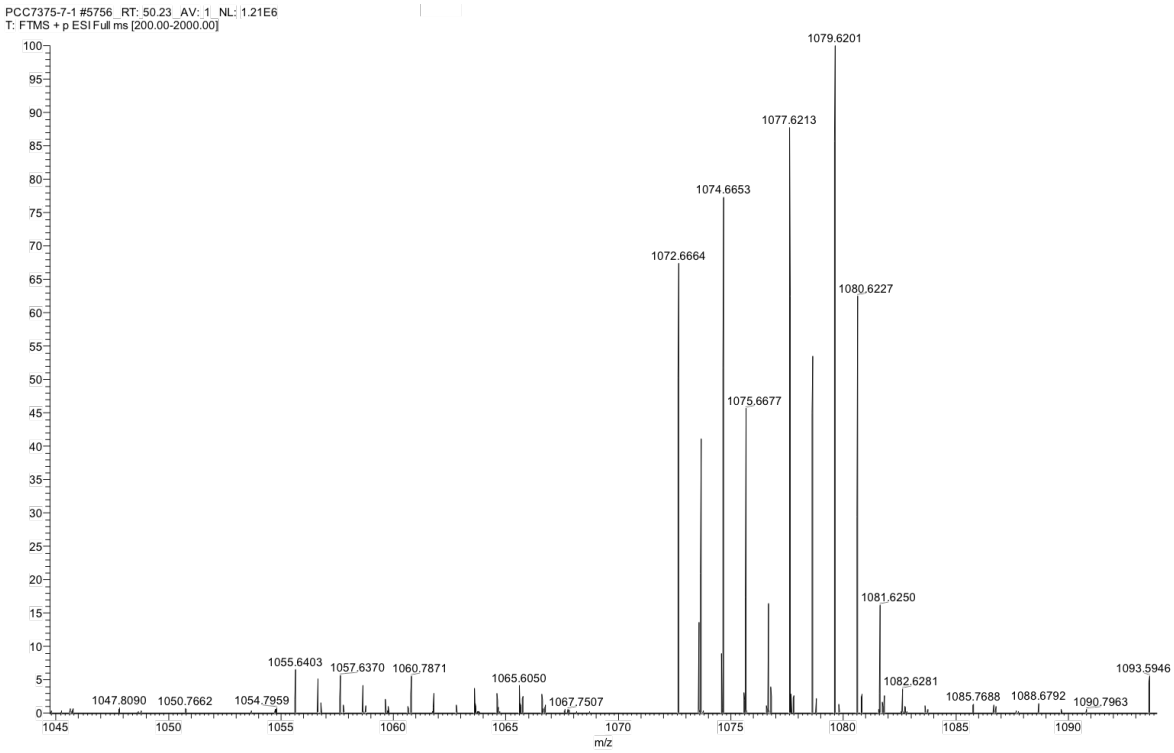


Supplementary Note Figure 14: NOESY spectrum of tartrolon G (6) from *Gynuella sunshinyii* in CD_3OD (n = 1).



Supplementary Note Figure 15: ESI-MS^2 spectrum of tartrolon G (6) from *Gynuella sunshinyii* (n = 1).

A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1077.6213
1074.6653
1072.6664
1080.6227
1075.6677
1081.6250
1082.6281
1093.5946
1055.6403
1057.6370
1060.7871
1065.6050
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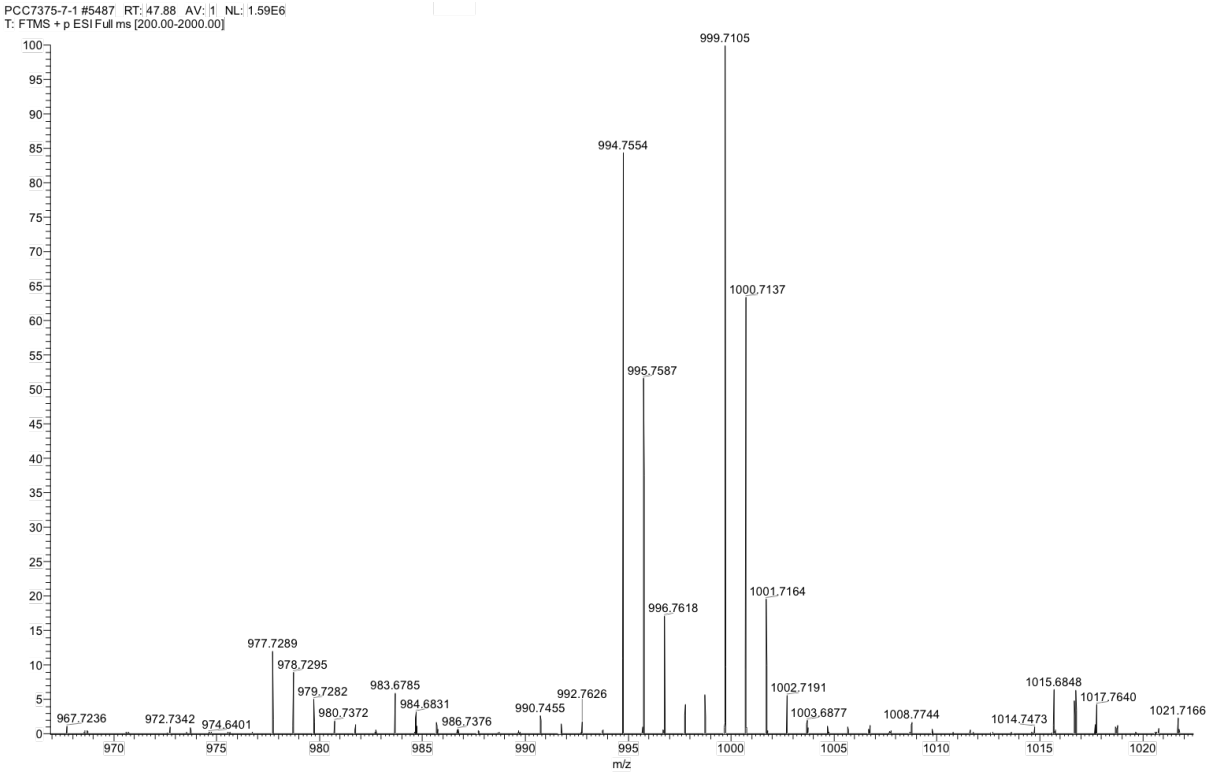
1088.6792
1090.7963
m/z

B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T: FTMS + p ESI Full ms [200.00-2000.00]
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995.7587
1001.7164
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978.7295
979.7282
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984.6831
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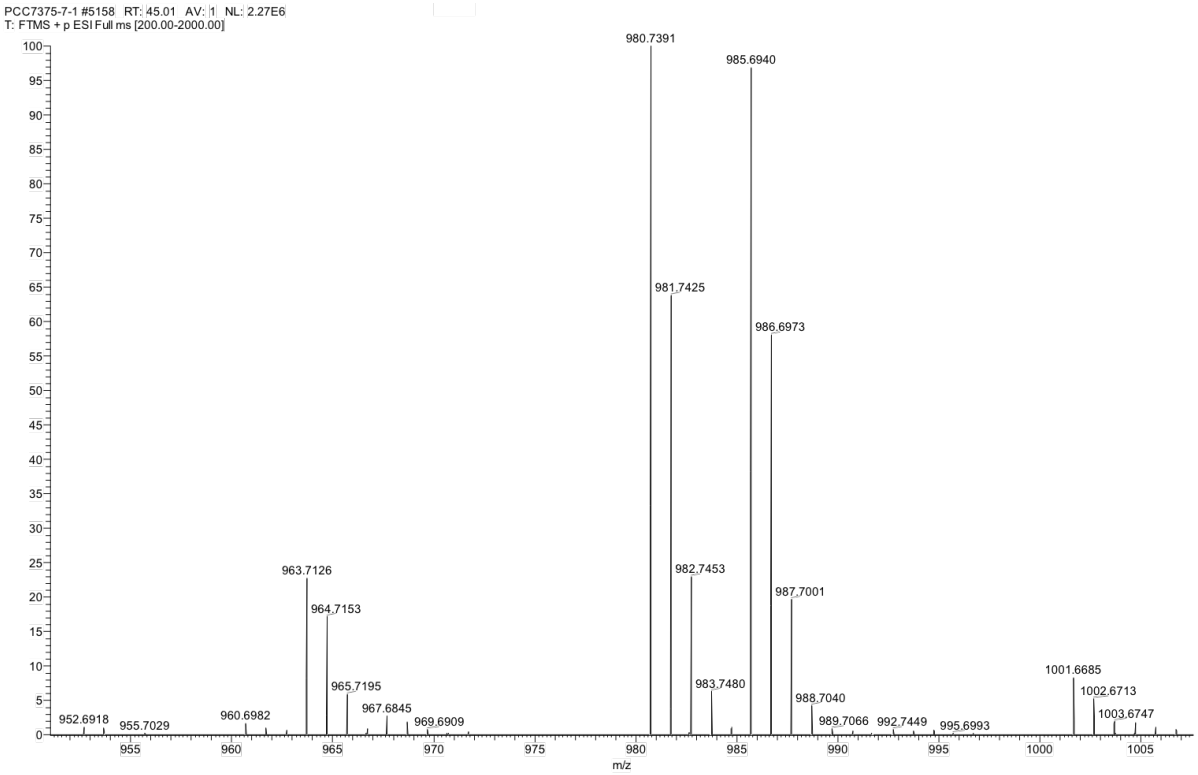
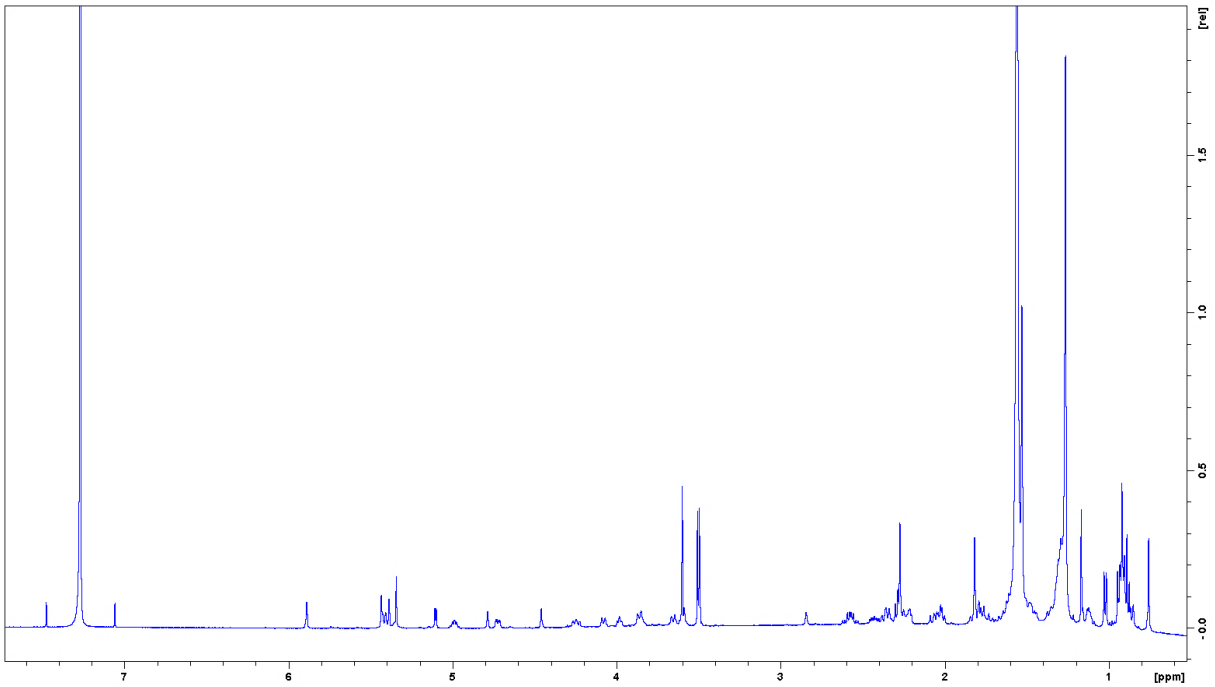
m/z

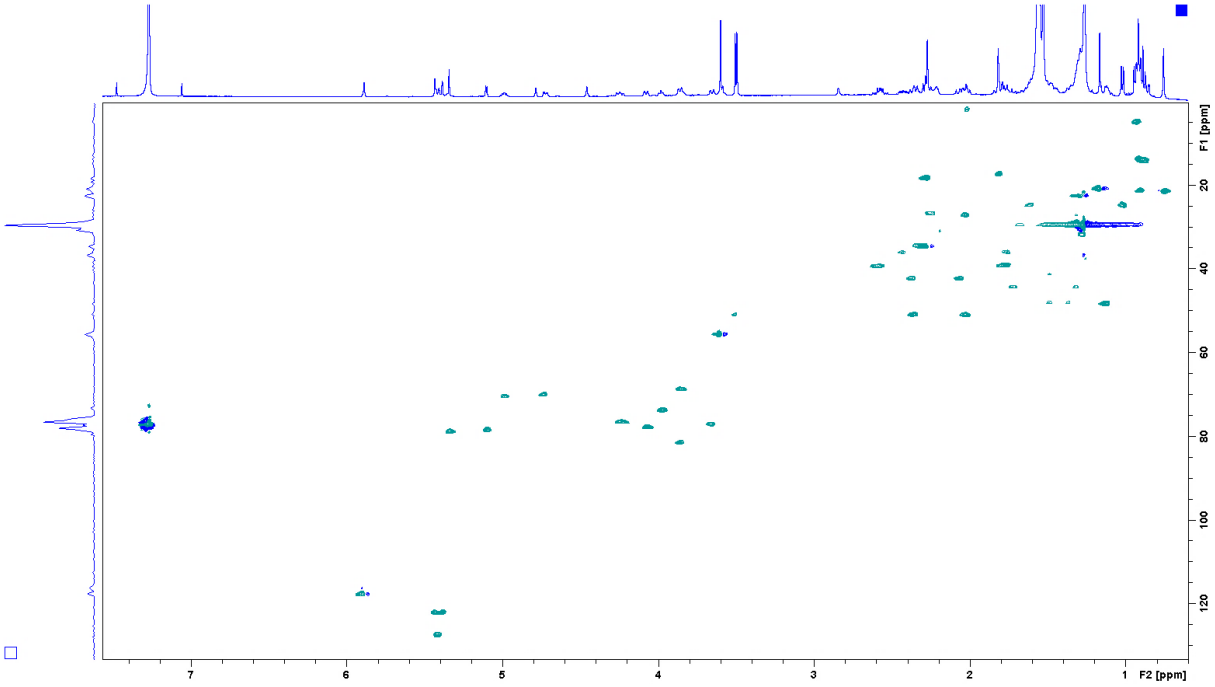
C



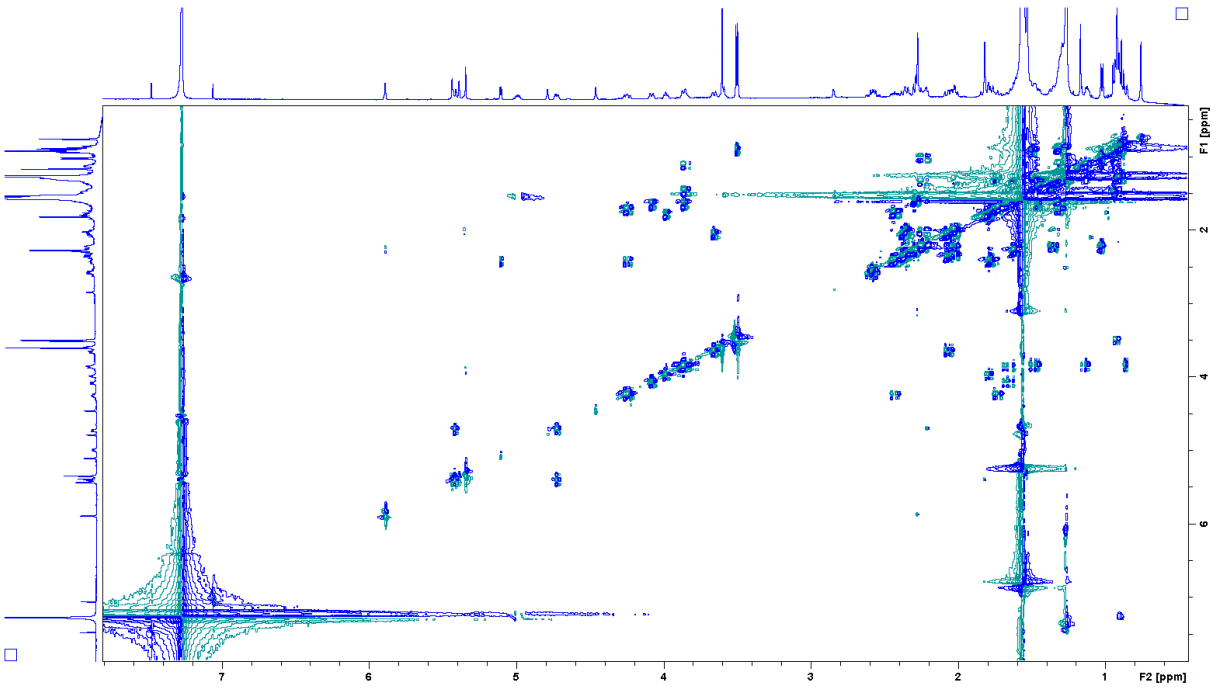
Supplementary Note Figure 16: HR-ESI-MS spectra of 10-12. A: leptolyngbyalide A (**10**) (*m/z* 1055.6403, 1057.6370 $[M+H]^+$, *m/z* 1072.6664, 1074.6653 $[M+NH_4]^+$, *m/z* 1077.6213, 1.79.6201 $[M+Na]^+$), B: leptolyngbyalide B (**11**) (*m/z* 977.7289 $[M+H]^+$, *m/z* 994.7554 $[M+NH_4]^+$, *m/z* 999.7105 $[M+Na]^+$) and C: leptolyngbyalide C (**12**) (*m/z* 963.7126 $[M+H]^+$, *m/z* 980.7391 $[M+NH_4]^+$, *m/z* 985.6940 $[M+Na]^+$) from *Leptolyngbya* sp. PCC 7375 (n = 1).



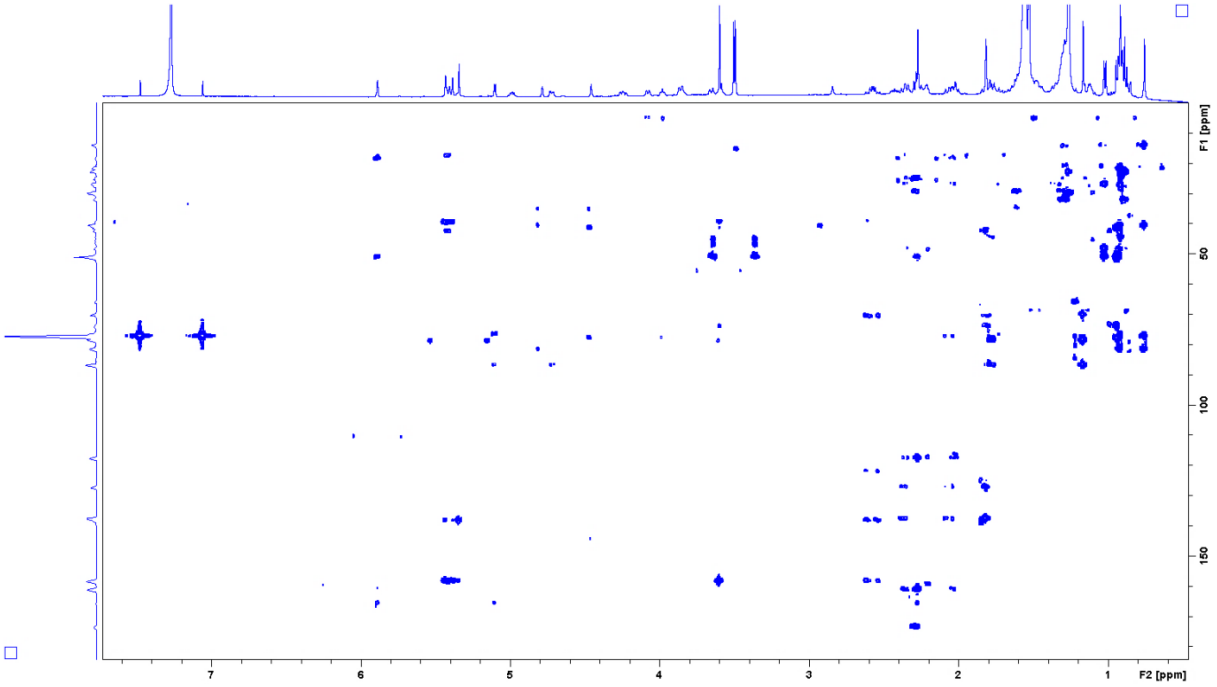
Supplementary Note Figure 17: ^{1}H NMR spectrum of leptolyngbyalide A (10) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



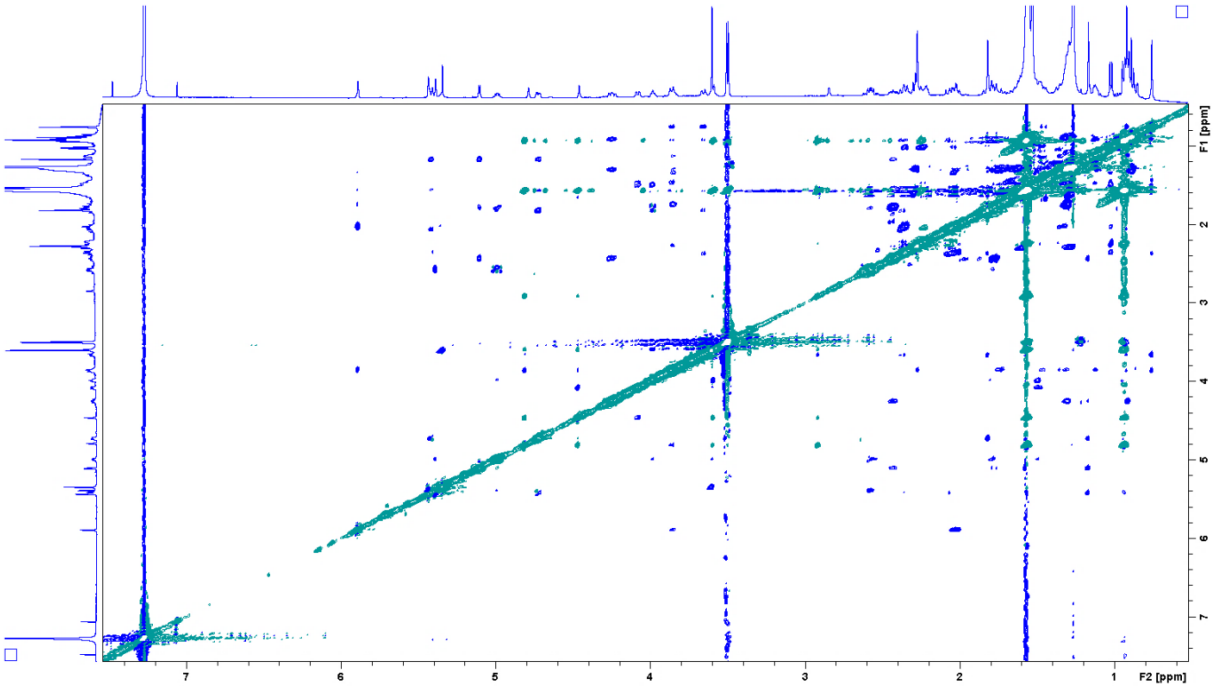
Supplementary Note Figure 18: HSQC spectrum of leptolyngbyalide A (10) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



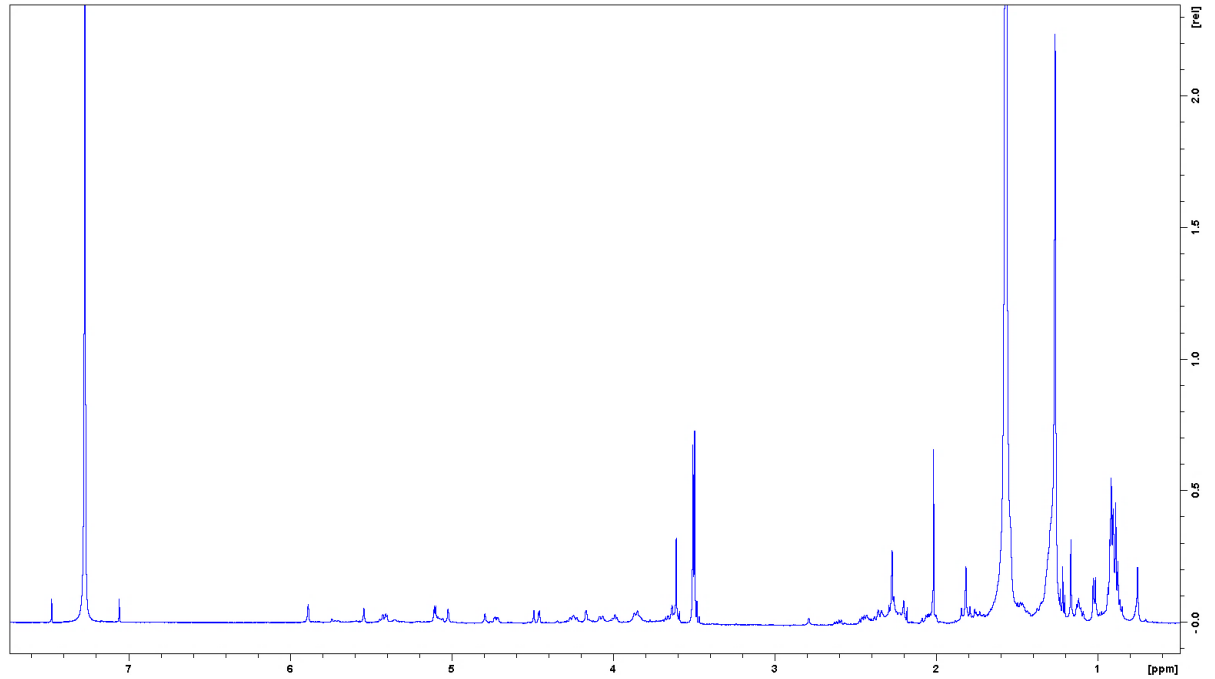
Supplementary Note Figure 19: COSY spectrum of leptolyngbyalide A (10) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



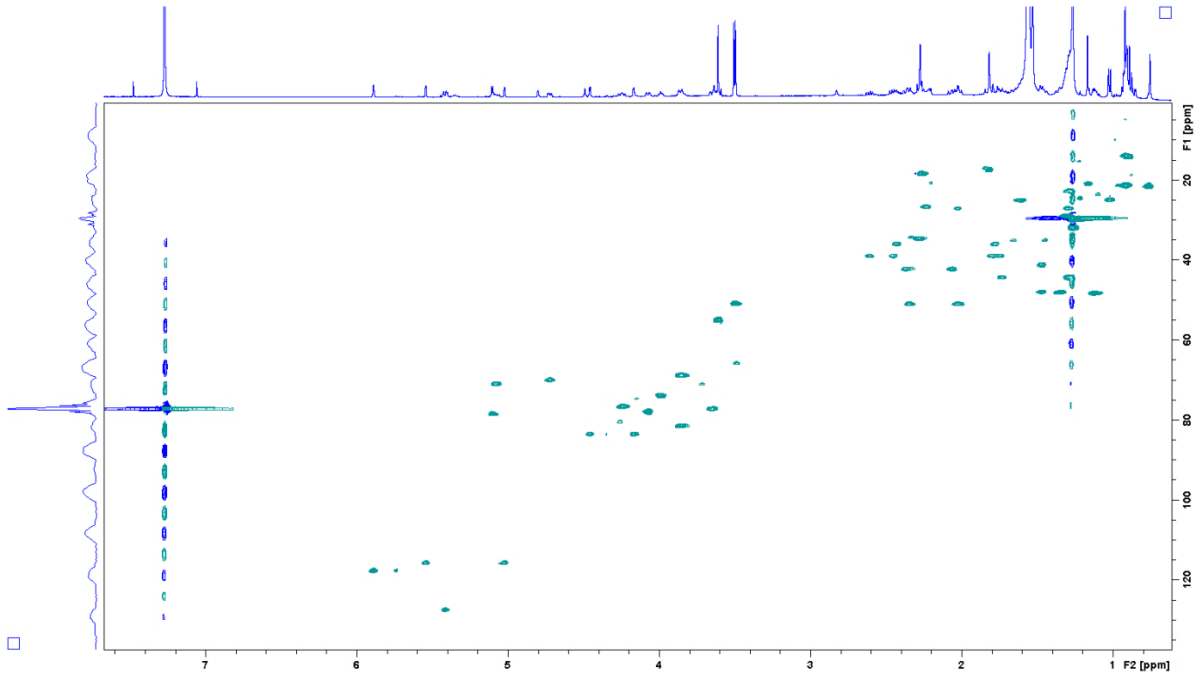
Supplementary Note Figure 20: HMBC spectrum of leptolyngbyalide A (10) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



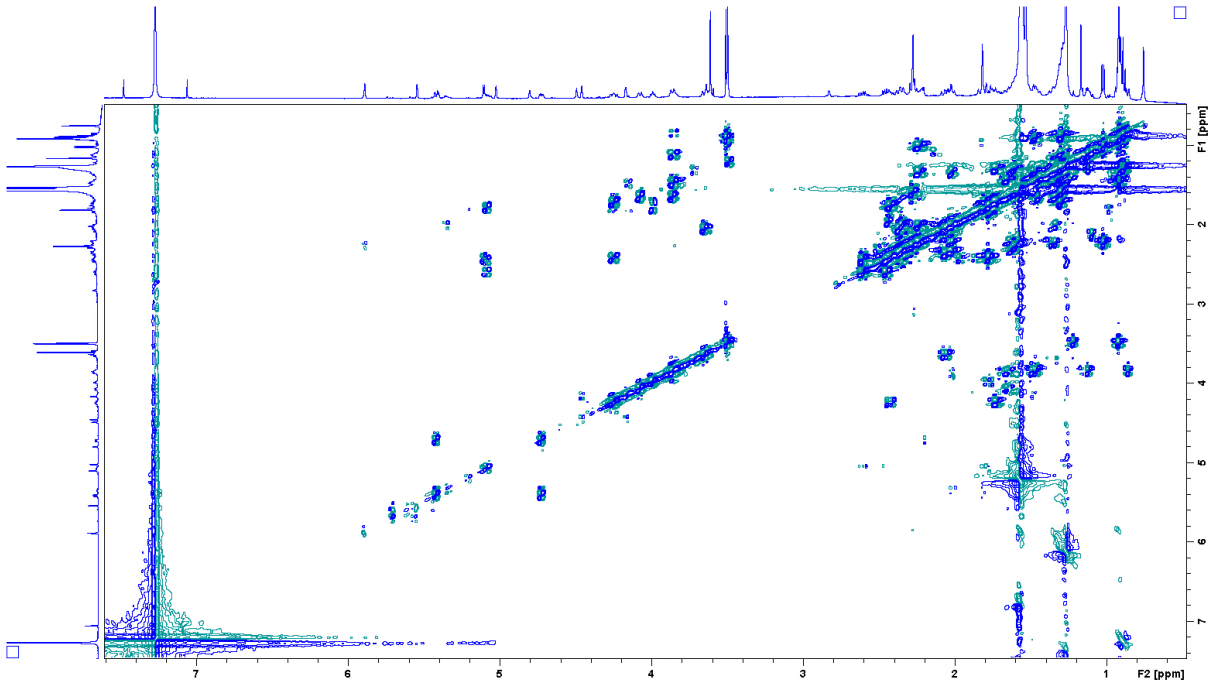
Supplementary Note Figure 21: NOESY spectrum of leptolyngbyalide A (10) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



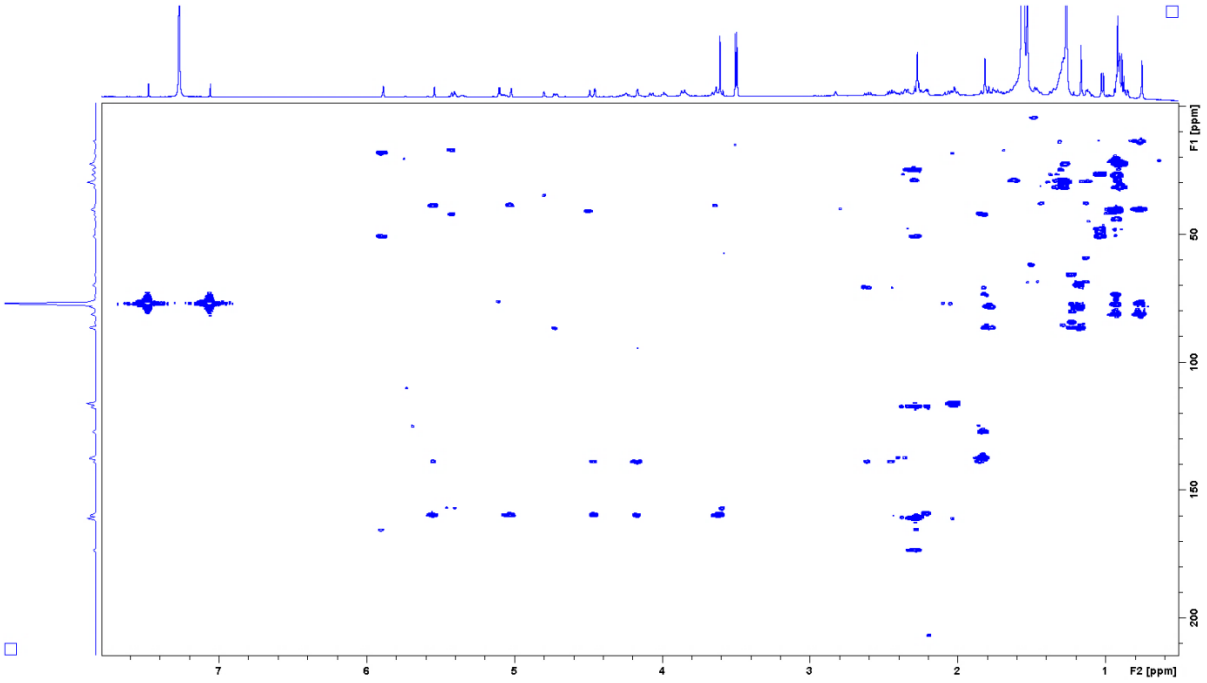
Supplementary Note Figure 22: ^{1}H NMR spectrum of leptolyngbyalide B (11) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



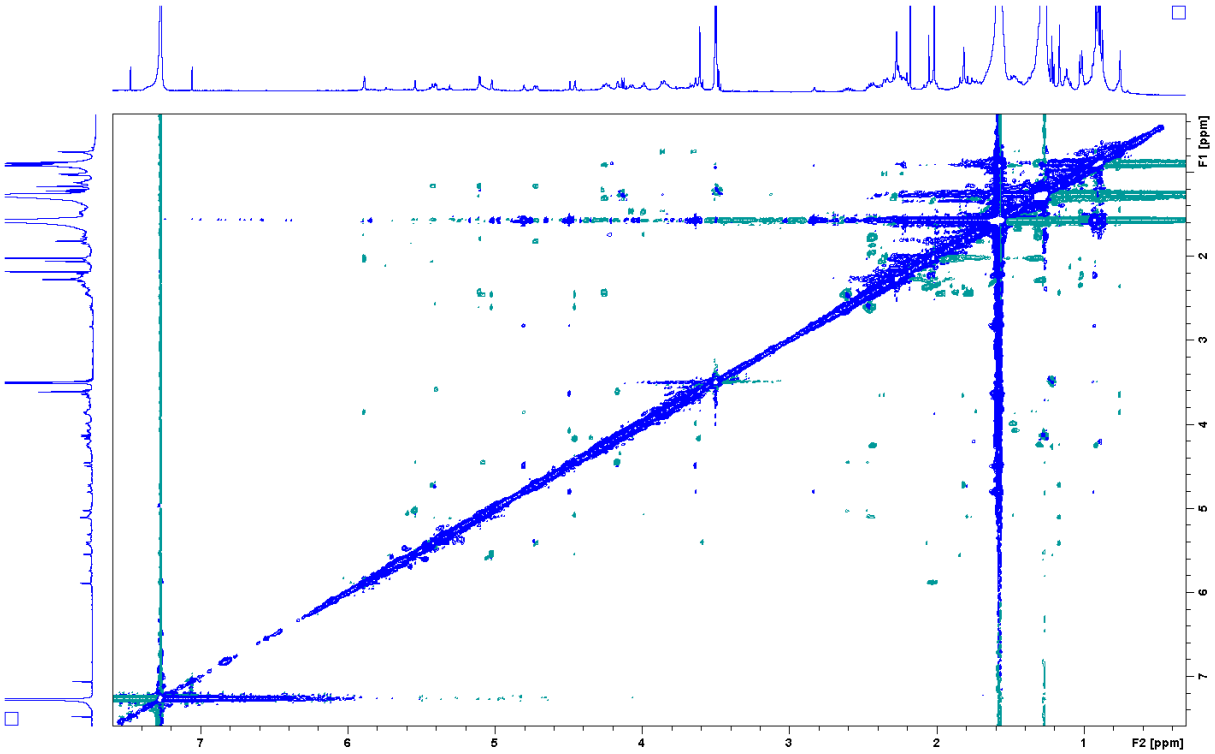
Supplementary Note Figure 23: HSQC spectrum of leptolyngbyalide B (11) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



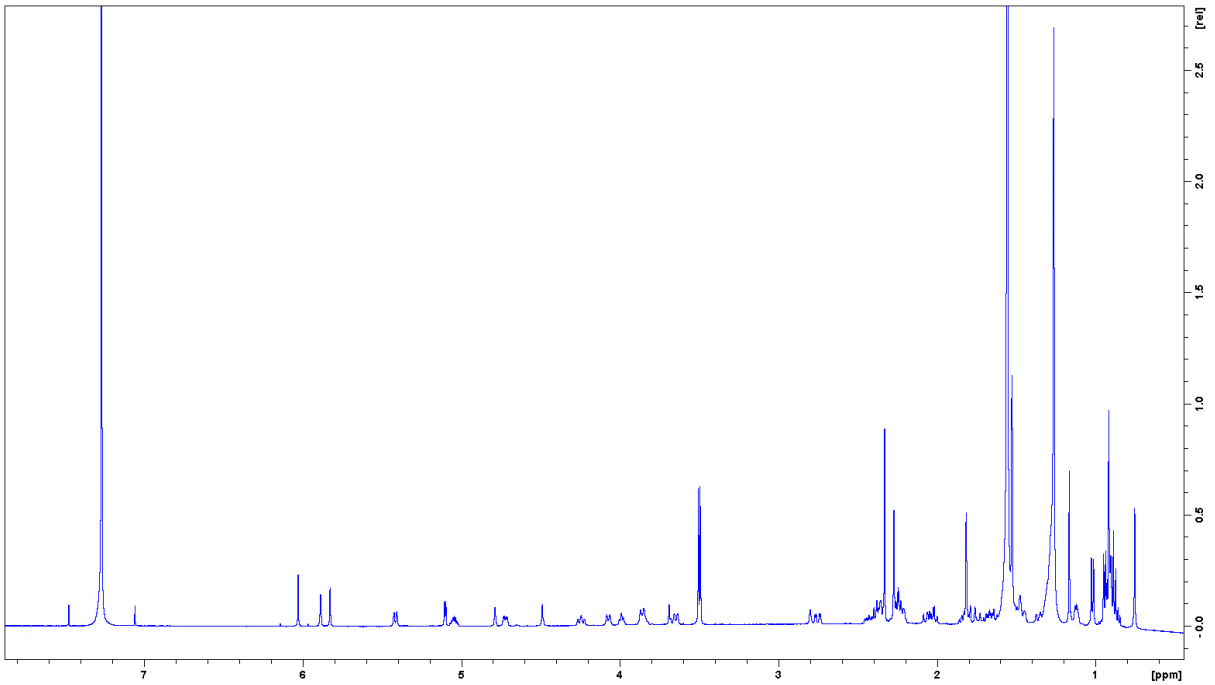
Supplementary Note Figure 24: COSY spectrum of leptolyngbyalide B (11) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



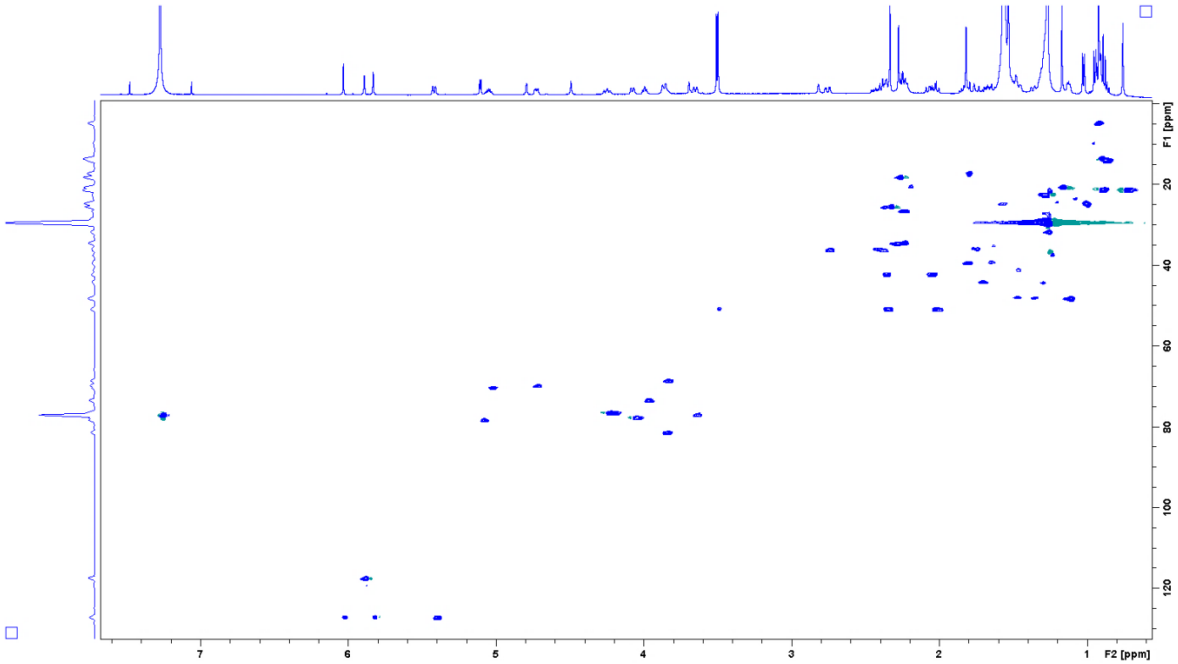
Supplementary Note Figure 25: HMBC spectrum of leptolyngbyalide B (11) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



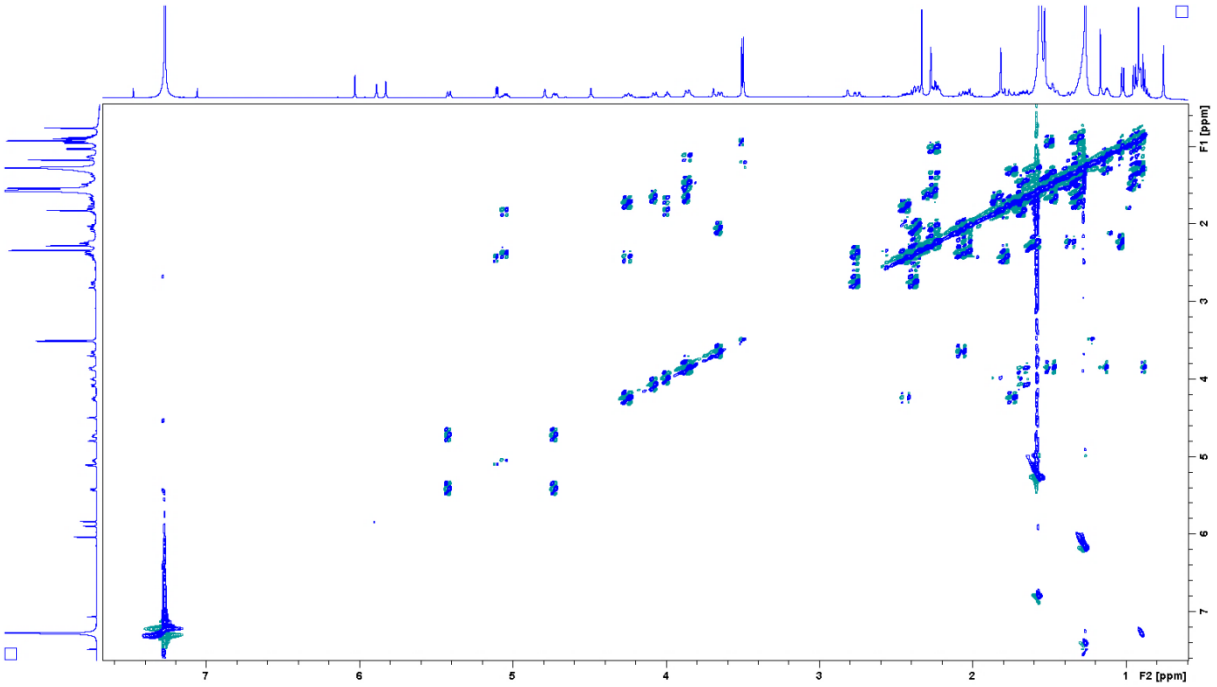
Supplementary Note Figure 26: NOESY spectrum of leptolyngbyalide B (11) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



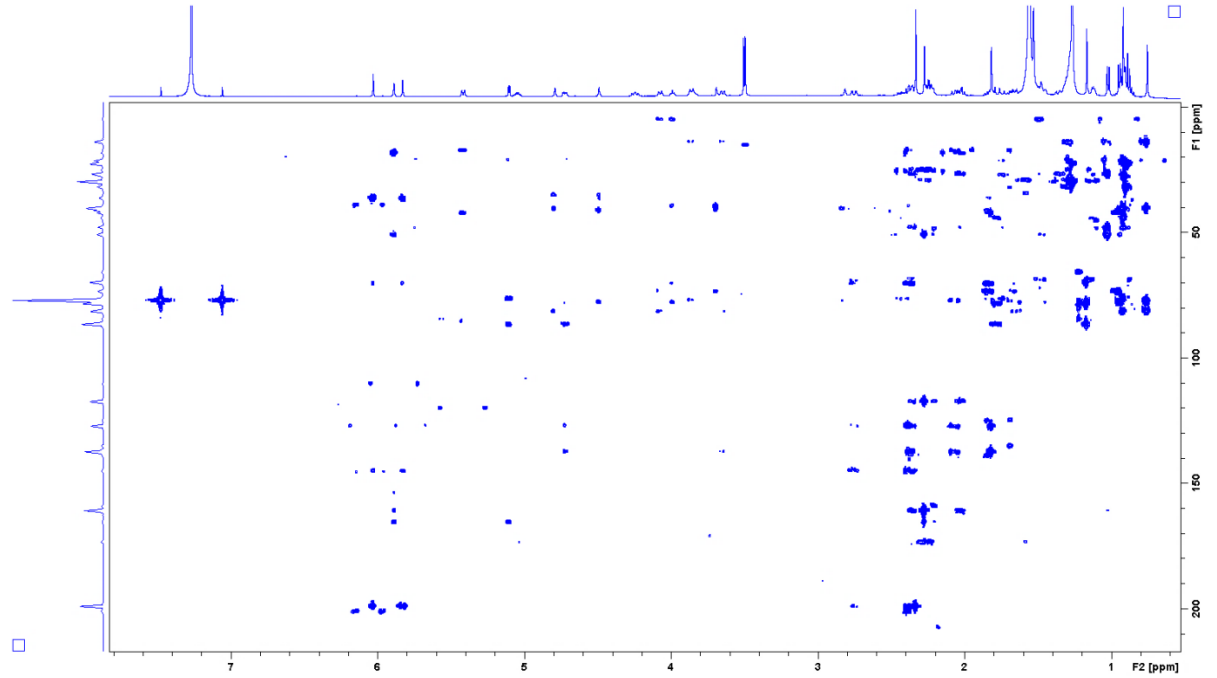
Supplementary Note Figure 27: ^{1}H NMR spectrum of leptolyngbyalide C (12) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



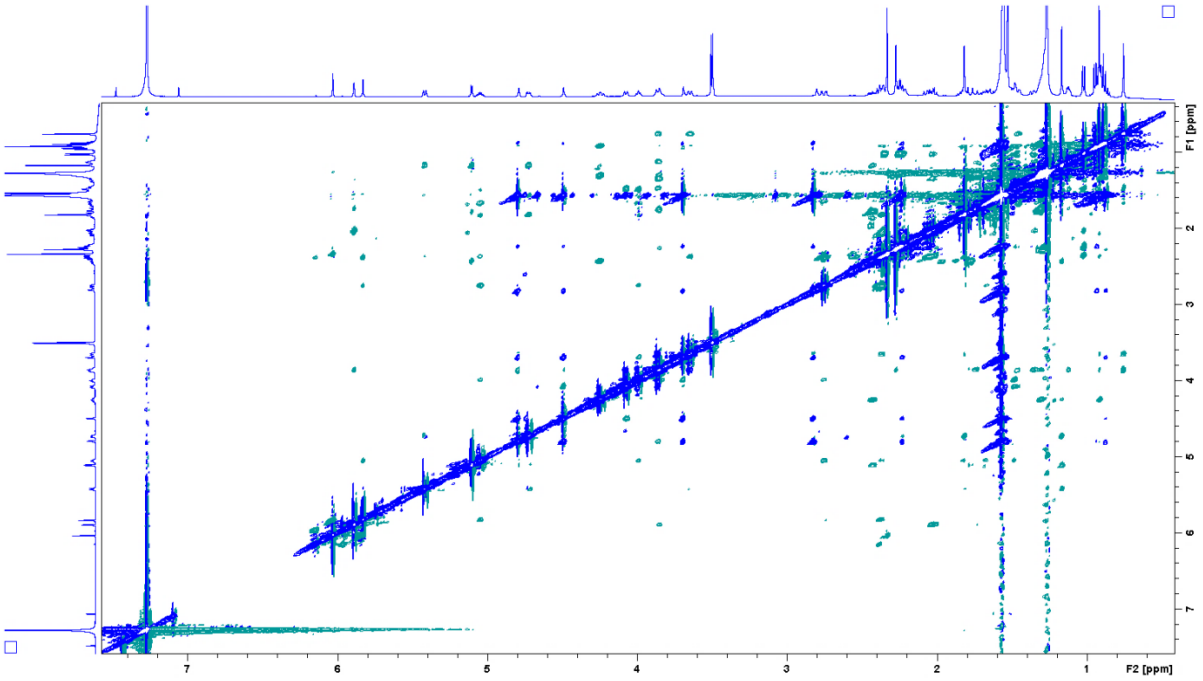
Supplementary Note Figure 28: HSQC spectrum of leptolyngbyalide C (12) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



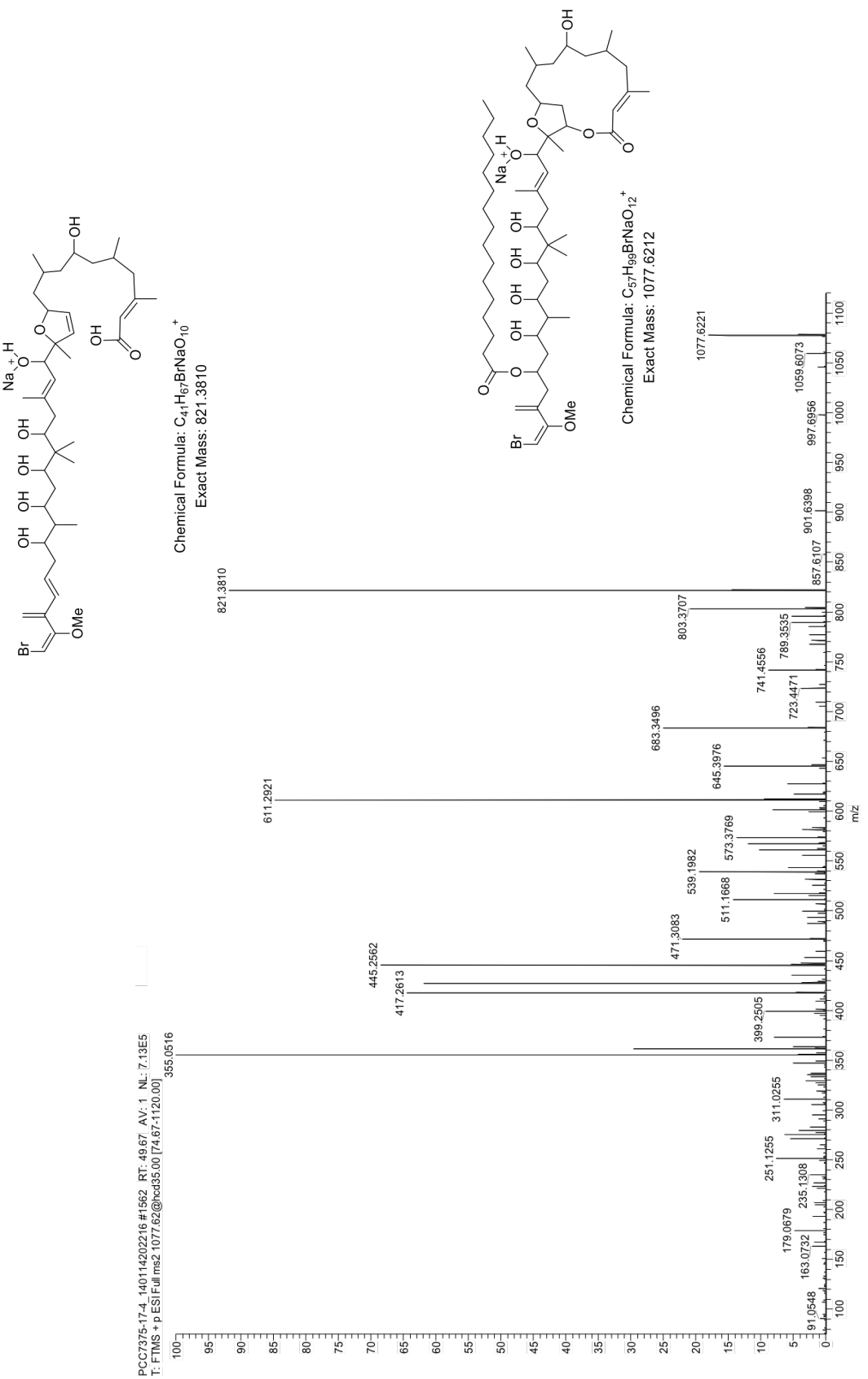
Supplementary Note Figure 29: COSY spectrum of leptolyngbyalide C (12) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



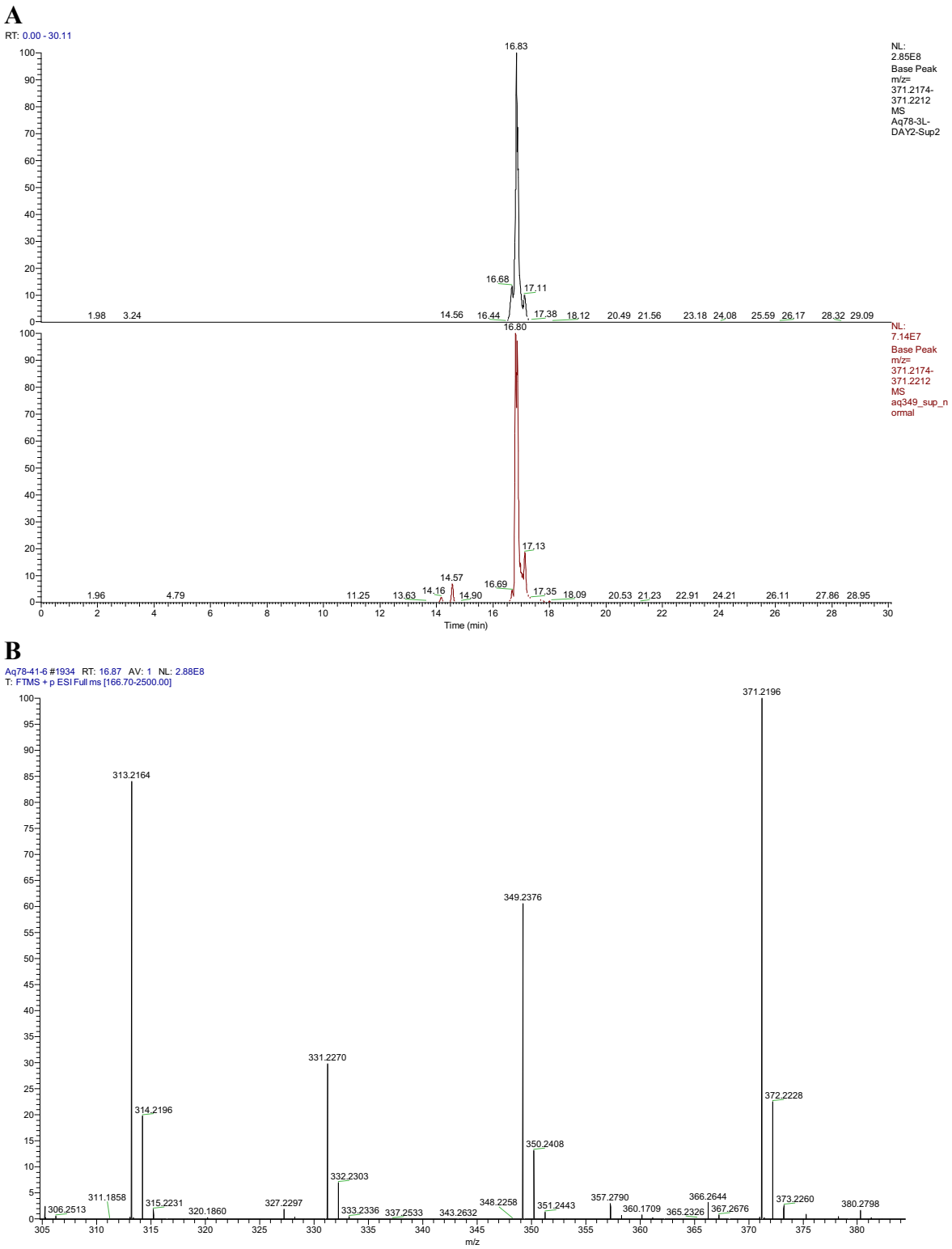
Supplementary Note Figure 30: HMBC spectrum of leptolyngbyalide C (12) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



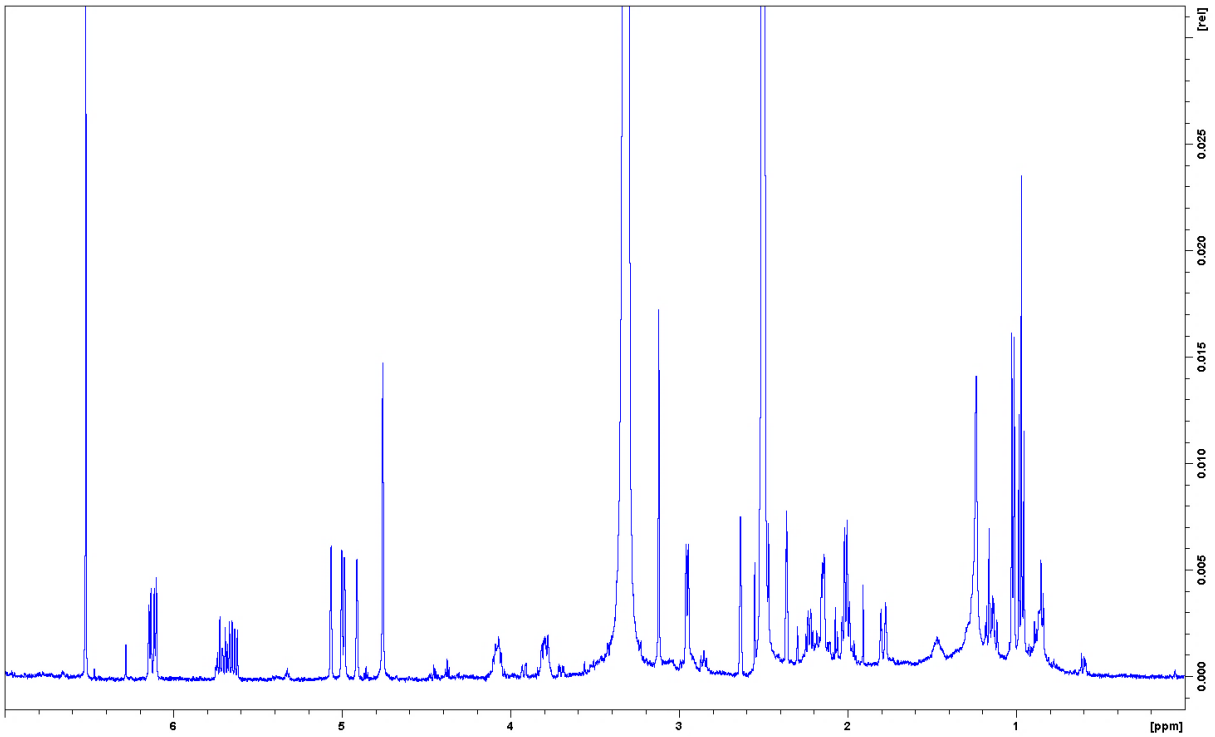
Supplementary Note Figure 31: NOESY spectrum of leptolyngbyalide C (12) from *Leptolyngbya* sp. PCC 7375 in $CDCl_3$ (n = 1).



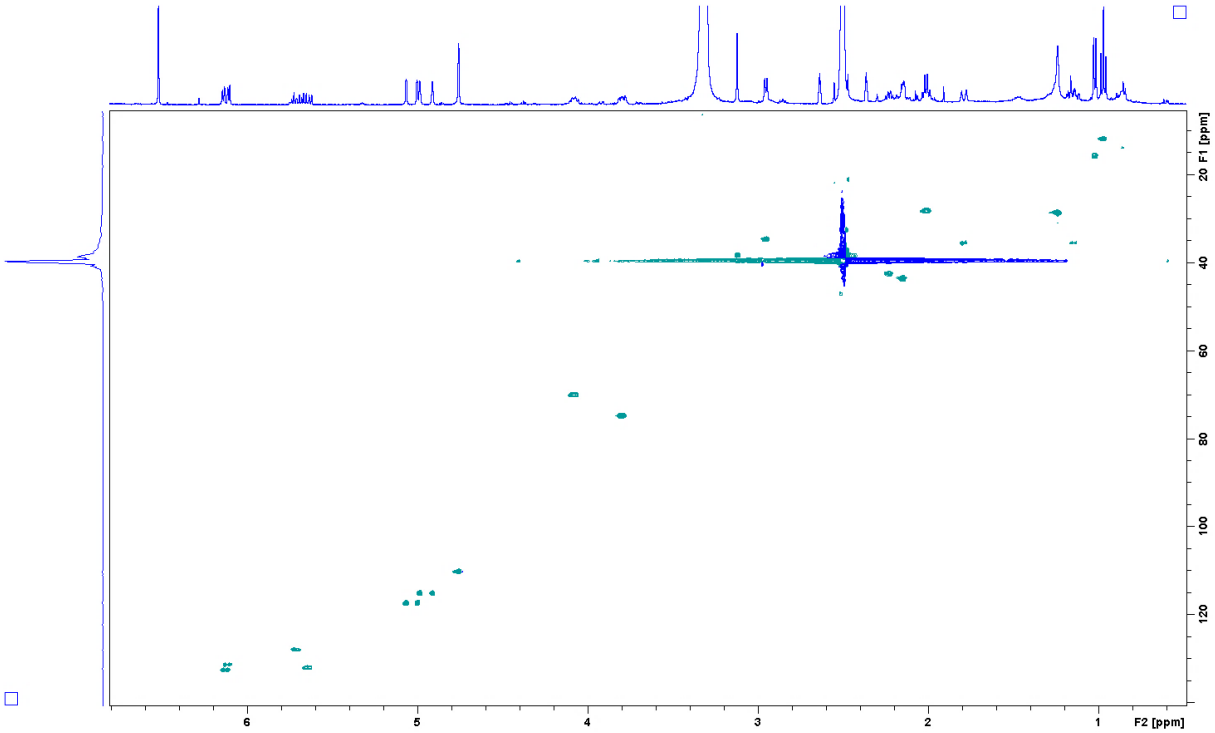
Supplementary Note Figure 32: HR-ESI-MS^2 spectrum of leptolynbyalide A (10) (n = 1).



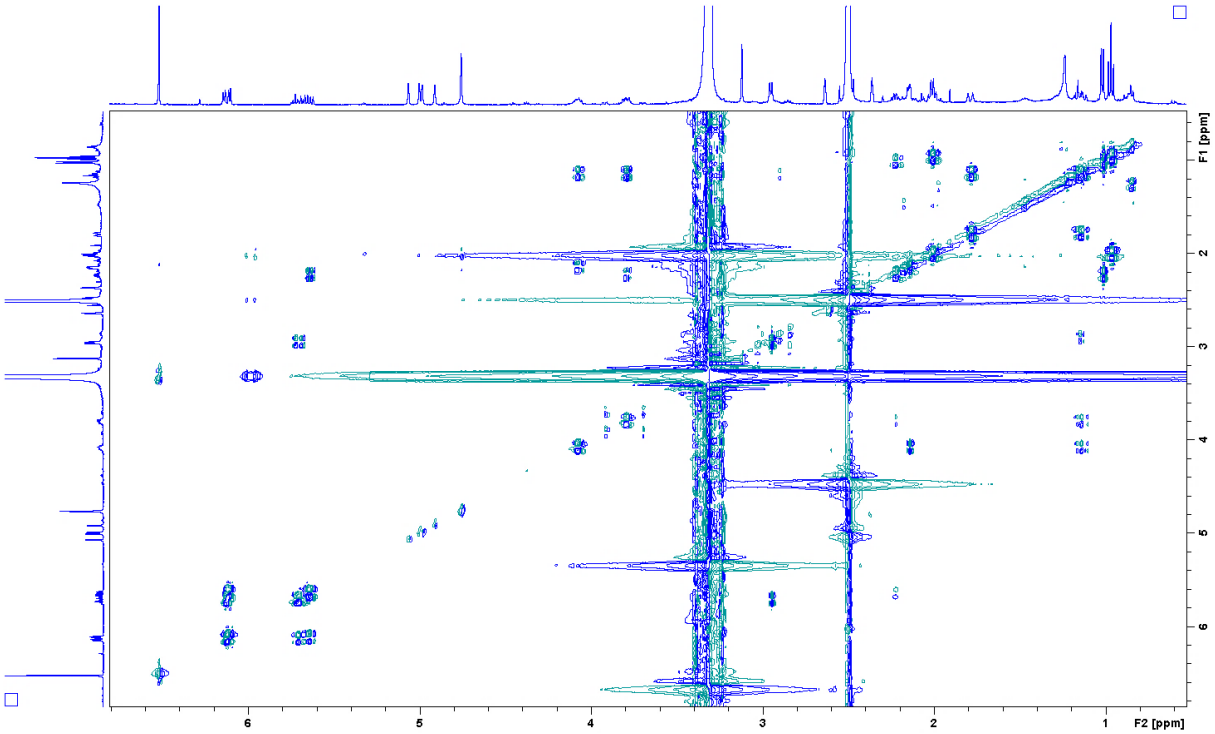
Supplementary Note Figure 33: HR-ESI-MS spectra of cuniculene 6A from *Aquimarina* sp. Aq78 and *Aquimarina* sp. Aq349. A: Extracted ion chromatogram (*m/z* 371.2174-371.2212) of the extract from *Aquimarina* sp. Aq78 (upper) and *Aquimarina* sp. Aq349 (lower). **B**: HR-ESI-MS spectrum of cuniculene 6A (**14**) from *Aquimarina* sp. Aq78 (*m/z* 349.2376 $[M+H]^+$, *m/z* 371.2196 $[M+Na]^+$, *m/z* 331.2270 $[M+H-H_2O]^+$, *m/z* 313.2164 $[M+H-2H_2O]^+$) (n = 1).



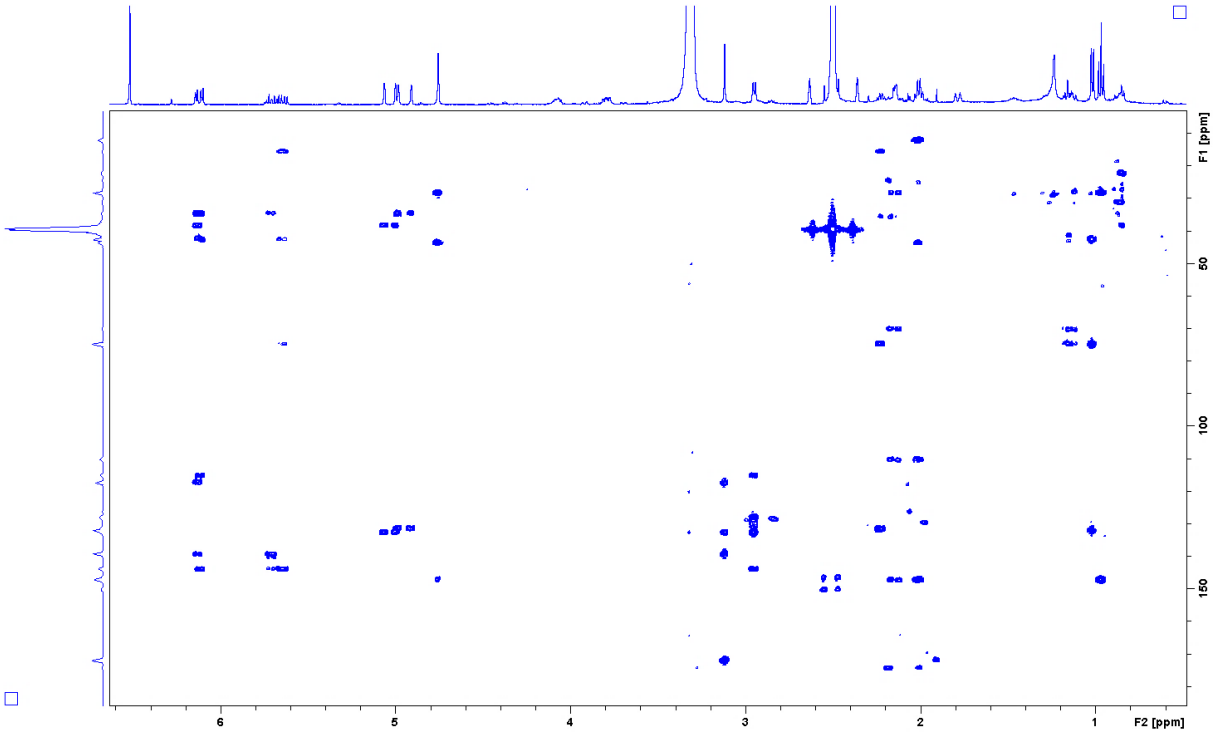
Supplementary Note Figure 34: ^{1}H NMR spectrum of cuniculene 6A (14) from *Aquimarina* sp. Aq78 in DMSO-d_6 (n = 1).



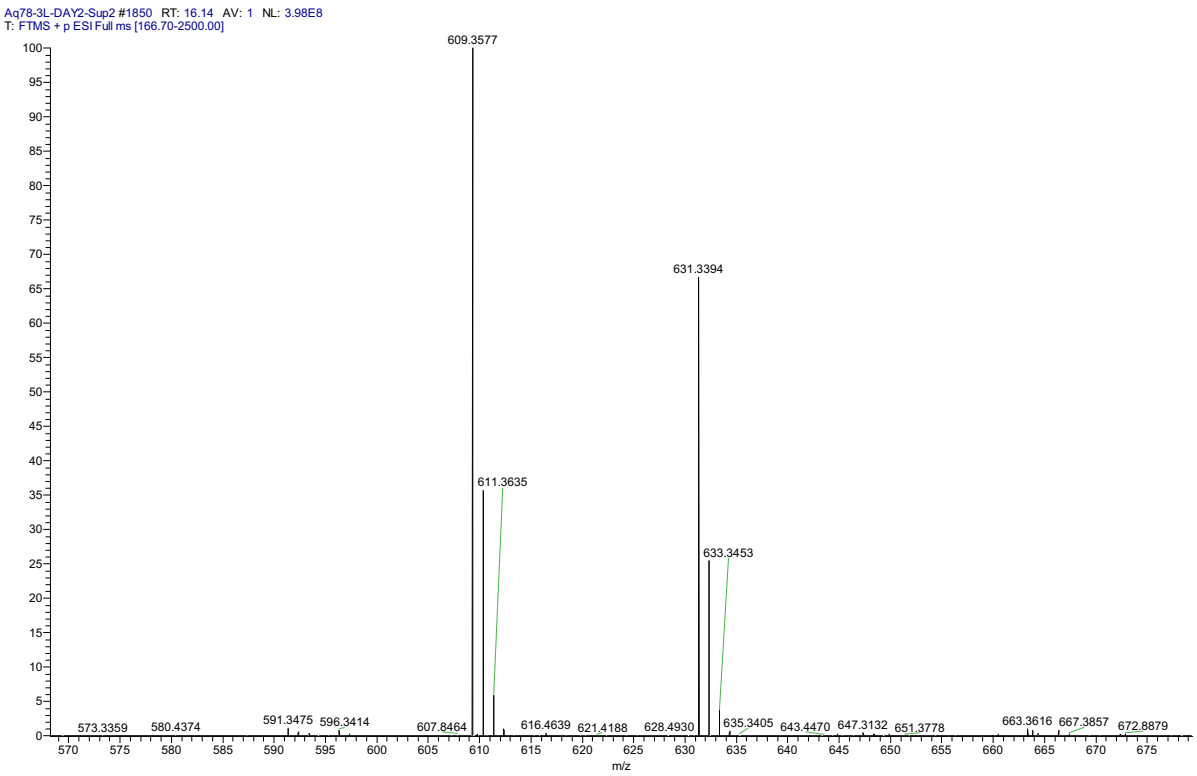
Supplementary Note Figure 35: HSQC spectrum of cuniculene 6A (14) from *Aquimarina* sp. Aq78 in DMSO-d_6 (n = 1).



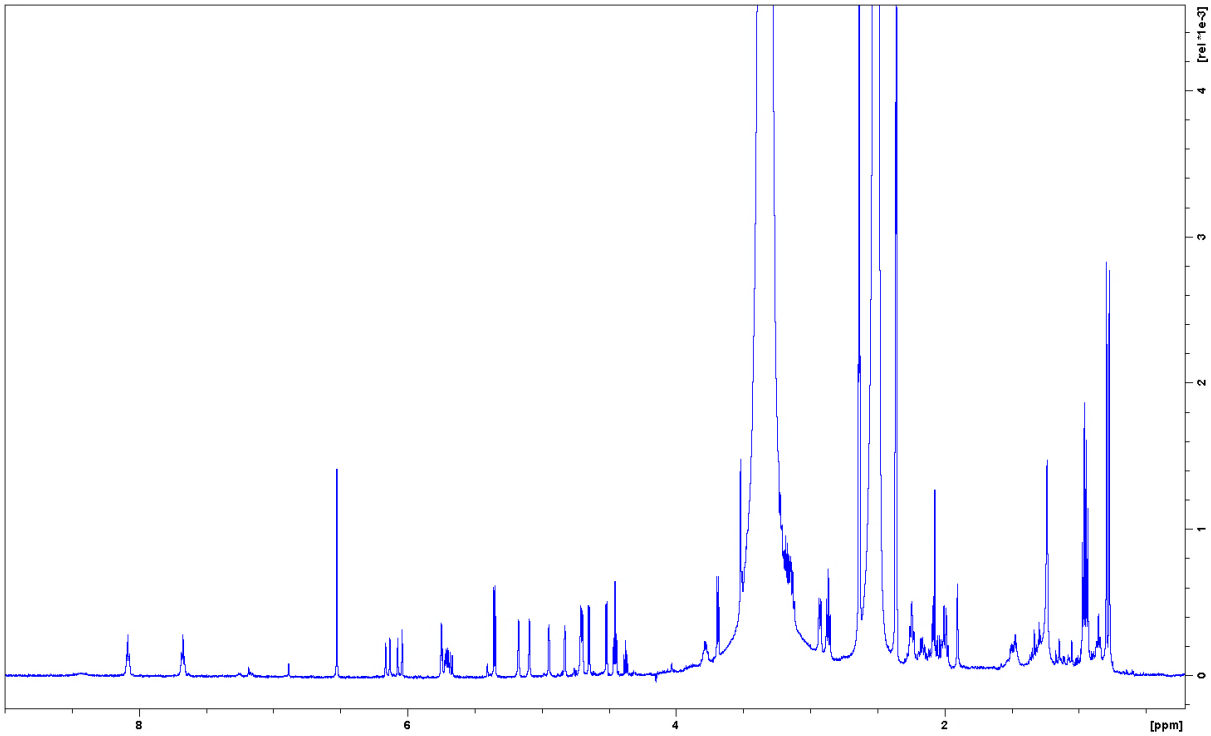
Supplementary Note Figure 36: COSY spectrum of cuniculene 6A (14) from *Aquimarina* sp. Aq78 in DMSO-d_6 (n = 1).



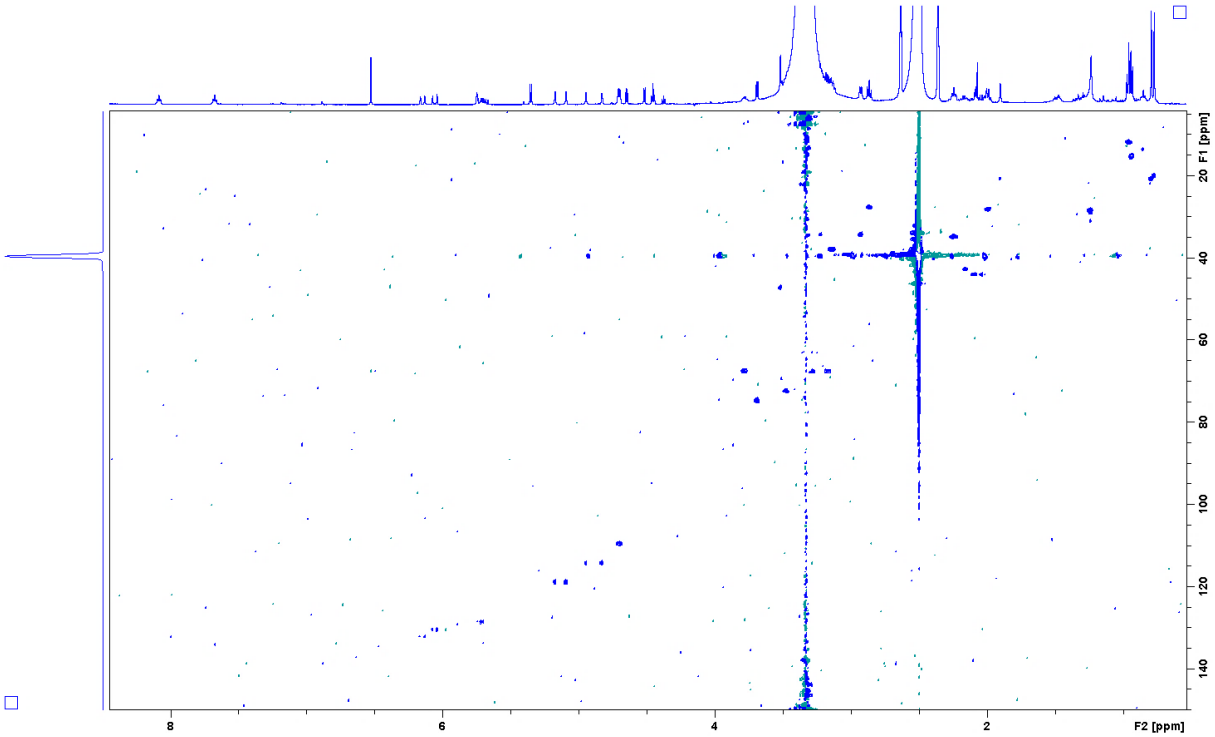
Supplementary Note Figure 37: HMBC spectrum of cuniculene 6A (14) from *Aquimarina* sp. Aq78 in DMSO-d_6 (n = 1).



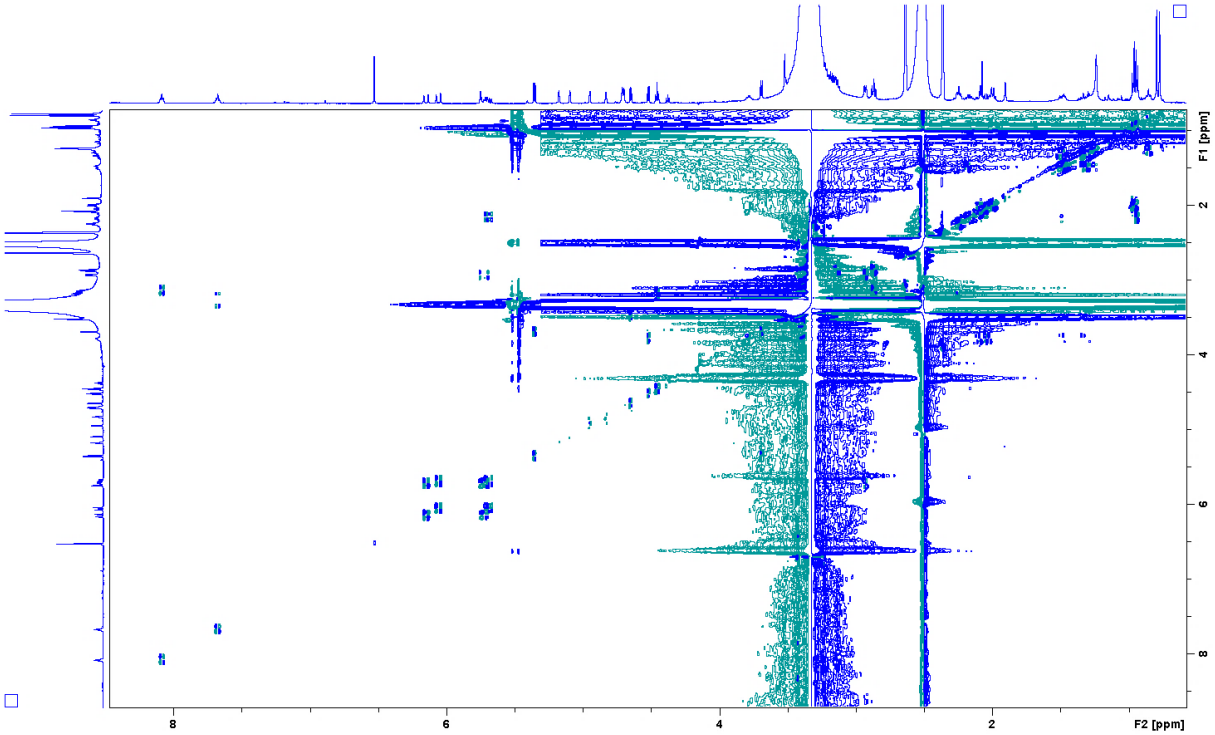
Supplementary Note Figure 38: HR-ESI-MS spectrum of cuniculene 6B (15) from *Aquimarina* sp. Aq78 (*m*/*z* 609.3577 $[M+H]^+$, *m*/*z* 631.3394 $[M+Na]^+$) (n = 1).



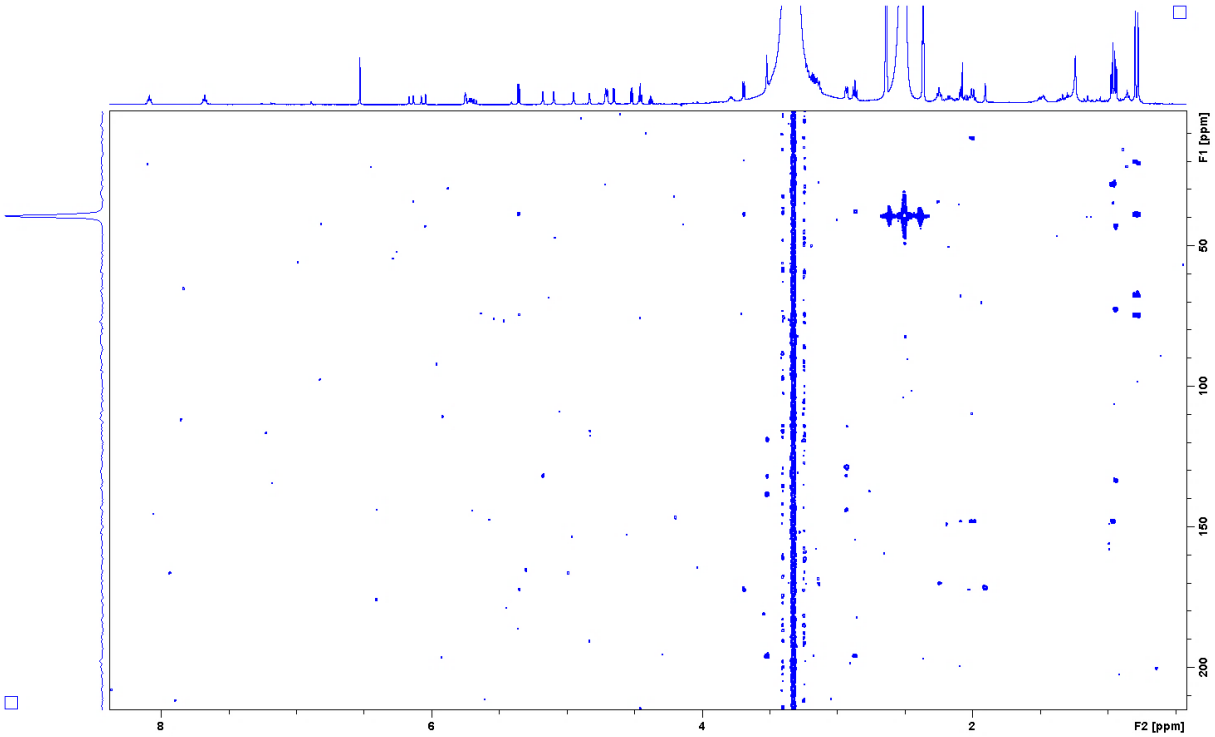
Supplementary Note Figure 39: ^{1}H NMR spectrum of cuniculene 6B (15) from *Aquimarina* sp. Aq78 in DMSO-d_6 (n = 1).



Supplementary Note Figure 40: HSQC spectrum of cuniculene 6B (15) from *Aquimarina* sp. Aq78 in DMSO-d_6 (n = 1).



Supplementary Note Figure 41: COSY spectrum of cuniculene 6B (15) from *Aquimarina* sp. Aq78 in DMSO-d_6 (n = 1).



Supplementary Note Figure 42: HMBC spectrum of cuniculene 6B (15) from *Aquimarina* sp. Aq78 in DMSO-d_6 (n = 1).

Supplementary Note Table 1: NMR chemical shifts of tartrolons F (5) and G (6) in CD_3OD.

	Compound **5**					Compound **6**	
No.	δ_C	δ_H, mult.	No.	δ_C	δ_H, mult.	δ_C	δ_H, mult.
1	172.2		1'	172.4		172.5	
2	74.5	4.15 s	2'	74.7	4.18 s	74.6	4.17 s
3	99.3		3'	99.1		99.2	
4	35.3	2.05 ovlp	4'	35.4	2.05 ovlp	35.5	2.09 m
5	28.9	1.54 ovlp	5'	28.9	1.54 ovlp	28.9	1.55 ovlp
		1.70 ovlp			1.70 ovlp		1.70 ovlp
6	33.0	1.24 m	6'	33.0	1.24 m	33.2	1.24 ovlp
							1.53 ovlp
7	68.2	4.27 m	7'	67.5	4.03 m	67.1	4.02 ovlp
8	49.9	2.40 (dd, 4.2, 14.9)	8'	44.8	1.44 (dd, 6.1, 6.1)	45.1	1.40 m
		2.54 (dd, 8.8, 14.9)					
9	211.3		9'	67.9	3.97 m	67.1	4.02 ovlp
10	52.3	2.53 (dd, 8.8, 15.8)	10'	45.2	1.53 ovlp	45.4	1.46 ovlp
		2.63 (dd, 3.9, 15.8)					1.55 ovlp
11	67.7	4.08 m	11'	70.8	3.75 m	70.5	3.76 m
12	37.7	1.52 ovlp	12'	37.7	1.52 ovlp	37.3	1.48 ovlp
		1.57 ovlp			1.57 ovlp		1.61 m
13	29.7	2.18 ovlp	13'	29.7	2.18 ovlp	30.0	2.14 ovlp
		2.25 ovlp			2.25 ovlp		2.26 m
14	135.6	5.70 ovlp	14'	135.6	5.70 ovlp	135.6	5.68 (ddd, 7.8, 7.8, 15.0)
15	126.8	6.36 ovlp	15'	126.8	6.36 ovlp	126.8	6.36 (dd, 11.0, 15.0)
16	130.7	5.99 (dd, 10.8, 10.8)	16'	130.7	5.99 (dd, 10.8, 10.8)	130.6	5.98 (dd, 11.0, 11.0)
17	129.2	5.29 ovlp	17'	129.2	5.29 ovlp	129.0	5.26 m
18	24.6	2.24ovlp	18'	24.6	2.24 ovlp	24.4	2.19 m
		2.30 ovlp			2.30 ovlp		2.38 m
19	36.7	1.63 ovlp	19'	36.7	1.63 ovlp	36.3	1.65 m
		1.75 ovlp			1.75 ovlp		1.76 m
20	72.7	4.99 ovlp	20'	72.7	4.97 ovlp	72.4	4.95 m
21	20.4	1.29 (d, 6.2)	21'	20.3	1.27 (d, 6.3)	20.4	1.26 (d, 6.1)
22	16.7	0.99 (d, 6.7)	22'	16.7	1.00 (d, 6.7)	16.6	0.99 (d, 6.7)

Supplementary Note Table 2: NMR chemical shifts of leptolyngbyalides A-C (10-12) in $CDCl_3$.

	Compound 10		Compound 11		Compound 12	
No.	δ_C	δ_H, mult.	δ_C	δ_H, mult.	δ_C	δ_H, mult.
1	165.9		165.9		166.0	
2	117.7	5.89 s	117.7	5.89 s	117.7	5.89 s
3	161.3		161.3		161.3	
4	51.0	2.03 (dd, 11.8, 11.8)	51.1	2.02 (dd, 11.7, 11.7)	51.0	2.03 ovlp
		2.37 ovlp		2.35 ovlp		2.37 ovlp
5	26.8	2.26 ovlp	26.8	2.24 m	26.8	2.26 ovlp
6	48.2	1.37 ovlp	48.2	1.36 ovlp	48.2	1.37 ovlp
		1.49 ovlp		1.48 ovlp		1.49 ovlp
7	68.8	3.86 ovlp	68.9	3.86 ovlp	68.8	3.86 ovlp
8	48.4	1.12 m	48.4	1.12 m	48.4	1.12 m
9	27.3	1.29 ovlp	27.2	1.30 ovlp	27.2	1.32 ovlp
10	44.4	1.32 ovlp	44.4	1.29 ovlp	44.4	1.32 ovlp
		1.73 m		1.74 ovlp		1.73 m
11	76.7	4.25 (dd, 10.3, 10.3)	76.7	4.27 br	76.7	4.25 br
12	36.1	1.78 m	36.1	1.78 ovlp	36.1	1.76 ovlp
		2.43 (ddd, 4.4, 8.7, 13.1)		2.44 m		2.43 (ddd, 4.5, 8.9, 14.4)
13	78.6	5.10 (d, 4.3)	78.6	5.10 (d, 4.3)	78.6	5.10 (d, 4.3)
14	87.0		86.8		86.9	
15	70.1	4.73 (dd, 3.7, 9.0)	70.1	4.72 (dd, 3.4, 8.9)	70.0	4.73 (dd, 3.7, 8.9)
16	127.5	5.42 (d, 9.0)	127.5	5.42 (d, 8.9)	127.4	5.42 (d, 8.9)
17	137.7		137.7		137.8	
18	42.3	2.06 (dd, 10.9, 13.1)	42.4	2.06 (dd, 10.9, 13.2)	42.3	2.06 (dd, 11.1, 13.1)
		2.37 ovlp		2.37 ovlp		2.38 ovlp
19	77.3	3.65 (d, 10.9)	77.2	3.65 ovlp	77.2	3.66 (d, 10.6)
20	40.6		40.5		40.6	
21	81.6	3.86 ovlp	81.6	3.86 ovlp	81.5	3.86 ovlp
22	35.1	1.48 ovlp	35.2	1.46 ovlp	35.0	1.47 ovlp
		1.65 ovlp		1.66 ovlp		1.66 ovlp
23	78.0	4.08 (d, 9.7)	78.0	4.07 (d, 9.8)	77.9	4.08 (d, 9.9)
24	41.3	1.48 ovlp	41.3	1.48 ovlp	41.3	1.49 ovlp
25	73.7	3.99 (dd, 6.4, 6.4)	73.9	3.99 (dd, 6.7, 6.7)	73.9	3.98 (dd, 6.2, 6.2)
26	39.5	1.66 ovlp	39.1	1.75 ovlp	39.2	1.78 ovlp
		1.82 ovlp		1.80 ovlp		
27	70.5	5.05 m	71.1	5.07 m	70.5	4.99 m
28	36.4	2.39 ovlp	39.1	2.45	39.4	2.55 (dd, 6.2, 14.3)
		2.76 (dd, 3.4, 13.9)		2.61 (dd, 6.9, 14.1)		2.60 (dd, 6.8, 14.3)
29	145.4		139.2		138.4	
30	199.5		160.1		158.6	
31	25.7	2.33 s	83.6	4.17 brd	78.9	5.34 s

				4.46 (d, 2.7)		
32	18.5	2.27 brs	18.5	2.27 brs	18.4	2.27 brs
33	24.9	1.02 (d, 6.9)	25.0	1.02 (d, 6.8)	24.9	1.02 (d, 6.8)
34	21.4	0.91 ovlp	21.4	0.92 ovlp	21.4	0.91 ovlp
35	20.9	1.17 s	21.0	1.17 s	20.9	1.17 s
36	17.4	1.82 brs	17.5	1.82 brs	17.5	1.82 brs
37	21.5	0.76 s	21.6	0.75 s	21.5	0.76 s
38	13.8	0.92 s	14.0	0.92 s	13.9	0.92 s
39	5.0	0.94 (d, 7.0)	4.9	0.92 ovlp	4.9	0.94 (d, 7.2)
40	127.3	5.83 s	115.8	5.02 brs	122.2	5.39 brs
		6.03 s		5.54 brd		5.43 brs
41	173.8		173.8		173.8	
42	34.7	2.24 m	34.8	2.28 ovlp	34.8	2.29 ovlp
43	25.1	1.59 ovlp	25.2	1.62 ovlp	24.9	1.62 ovlp
44	29.4	1.31 ovlp	29.2	1.30 ovlp	29.3	1.31 ovlp
45-53	28.4-30.5	1.28 ovlp	29.2-30.2	1.27 ovlp	28.7-30.7	1.28 ovlp
54	31.9	1.28 ovlp	32.0	1.27 ovlp	31.9	1.29 ovlp
55	22.7	1.29 ovlp	22.8	1.29 ovlp	22.7	1.29 ovlp
56	14.1	0.88 (t, 7.3)	14.2	0.89 (t, 7.1)	14.2	0.89 (t, 7.2)
57			55.1	3.61 s	55.7	3.60 s
19-OH		2.80 br				
21-OH		4.79 br		4.80 br		4.79 br
23-OH		4.49 br		4.49 br		4.46 br
25-OH		3.69 br		3.64 br		3.59 br

Supplementary Note Table 3: NMR chemical shifts of cuniculene 6A (14) in DMSO-*d*$_6$.

Compound **14**		
No.	δ_C	δ_H, mult.
1	172.1	
2	38.3	3.12 s
3	139.3	
4	132.6	6.13 (d, 15.8)
5	127.9	5.71 (dt, 6.8, 15.8)
6	34.6	2.95 (d, 6.8)
7	143.9	
8	131.3	6.12 (d, 15.8)
9	132.1	5.64 (dd, 8.0, 15.8)
10	42.4	2.23 m
11	74.7	3.80 m
12	35.5	1.14 m
		1.79 brddd
13	70.1	4.08 m
14	43.5	2.15 m
15	147.0	
16	28.2	2.01 (q, 7.4)
17	11.9	0.97 (t, 7.4)
18	117.3	5.00 brs
		5.07 brs
19	115.1	4.91 brs
		4.98 brs
20	15.6	1.02 (d, 6.7)
21	110.2	4.76 brs

Supplementary Note Table 4: NMR chemical shifts of cuniculene 6B (15) in DMSO-*d*$_6$.

Compound **15**					
No.	δ_C	δ_H, mult.	No.	δ_C	δ_H, mult.
1	196.2		1'	67.7	3.17 m
2	47.2	3.52 s			3.28 ovlp.
3	138.6		1'-OH		4.45 (dd, 5.6, 5.6)
4	132.1	6.15 (d, 15.9)	2'	39.0	
5	128.5	5.72 (dt, 6.7, 15.9)	3'	74.7	3.69 (d, 5.6)
6	34.3	2.93 (d, 6.7)	3'-OH		5.35 (d, 5.6)
7	144.1		4'	172.6	
8	130.4	6.06 (d, 15.9)	5'-NH		7.67 brt
9	133.7	5.69 (dd, 8.0, 15.9)	6'	34.4	3.27 ovlp.
10	42.8	2.16 m	7'	34.8	2.24 m
11	72.4	3.48 m	8'	170.4	
12		1.32 m	9'-NH		8.08 brt
		1.48 m	10'	37.8	3.14 m
13	67.6	3.78 m	11'	27.7	2.87 (t, 7.0)
14	44.1	2.04 m	12'	20.0	0.77 s
		2.09 m	13'	20.7	0.79 s
15					
16	28.2	2.00 (q, 7.4)			
17	11.8	0.96 (t, 7.4)			
18	118.8	5.09 brs			
		5.17 brs			
19	114.2	4.83 brs			
		4.95 brs			
20	15.2	0.94 (d, 6.3)			
21	109.5	4.70 brd			
11-OH		4.65 (d, 4.7)			
13-OH		4.52 (d, 4.5)			