Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Biosynthetic studies of novel polyketides from the marine sponge-derived fungus *Stachylidium* sp. 293K04

Fayrouz El Maddah,[1,2] Ekaterina Eguereva,[1] Stefan Kehraus,[1] Gabriele M. König[1]

[1]Institute for Pharmaceutical Biology, University of Bonn, Nussallee 6, 53115 Bonn
[2]Department of Pharmacognosy and Tissue Culture,National Organization for Drug Control and Research, Cairo, Egypt

Table S1. ^{13}C NMR data of marilone A (**1**) and mariline B (**5**) and relative % ^{13}C enrichment after feeding [1-^{13}C]sodium acetate and [2-^{13}C]sodium acetate.

Table S2. ^{13}C NMR data of marilone A (**1**) and mariline B (**5**) and relative % ^{13}C enrichment after feeding of [1-^{13}C]sodium propionate

Figure S1. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of marilone A (**1**) (taken from literature).[1]

Figure S2. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of mariline B (**5**) (taken from literature).[2]

Figure S3. ^{13}C NMR (75 MHz, acetone-d_6) spectrum of marilone A (**1**) after feeding [1-^{13}C]sodium acetate.

Figure S4. ^{13}C NMR (75 MHz, acetone-d_6) spectrum of mariline B (**5**) after feeding [1-^{13}C]sodium acetate.

Figure S5. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of marilone A (**1**) after feeding [2-^{13}C]sodium acetate.

Figure S6. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of mariline B (**5**) after feeding [2-^{13}C]sodium acetate.

Figure S7. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of marilone A (**1**) after feeding [1-^{13}C]sodium propionate.

Figure S8. ^{13}C NMR (75 MHz, acetone-d_6) spectrum of mariline B (**5**) after feeding [1-^{13}C]sodium propionate.

Figure S9. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of marilone A (**1**) after feeding L-[*Me*-^{13}C]methionine.

Figure S10. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of mariline B (**5**) after feeding L-[*Me*-^{13}C]methionine.

Figure S11. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [1-^{13}C]sodium acetate.

Figure S12. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [1-^{13}C]sodium acetate.

Figure S13. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [2-^{13}C]sodium acetate.

Figure S14. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [2-^{13}C]sodium acetate.

Figure S15. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [1-^{13}C]sodium propionate.

Figure S16. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [1-^{13}C]sodium propionate.

Figure S17. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture supplemented with L-[*Me*-^{13}C]methionine.

Figure S18. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture supplemented with L-[*Me*-^{13}C]methionine.

Figure S19. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture.

Figure S20. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture.

Figure S21.HPLC isolation chromatogram of marilone A (**1**).

Figure S22.HPLC isolation chromatogram of mariline B (**5**).

TableS1. ^{13}C NMR data of marilone A (**1**) and mariline B (**5**) and relative % ^{13}C enrichment after feeding [1-^{13}C]sodium acetate and [2-^{13}C]sodium acetate.

	Marilone A (**1**)			Mariline B (**5**)		
		% ^{13}C enrichment[b]			% ^{13}C enrichment[b]	
C	δ_C(ppm)[a]	[1-^{13}C] acetate[c]	[2-^{13}C] acetate[d], J_{cc}(Hz)	δ_C(ppm)[a]	[1-^{13}C] acetate[c]	[2-^{13}C] acetate[d], J_{cc}(Hz)
1	168.2, qC	7.5	-	167.3, qC	7.8	-
2	110.0, qC	-	8.0	116.3, qC	-	8.0
3	158.0, qC	7.4	-	156.9, qC	8.5	-
4	120.4, qC	-	7.4, $J_{(4,11)}$=23.0	119.3, qC	-	8.0, $J_{(4,11)}$=23.0
5	164.2, qC	7.0	-	161.7, qC	7.9	-
6	100.8, CH	-	8.3	101.8, CH	-	7.5
7	154.2, qC	8.0	-	150.0, qC	8.1	-
8	77.0, CH	-	9.1, $J_{(8,9)}$=20.0	56.9, CH	-	7.6, $J_{(8,9)}$=20.0
9	20.9, CH_3	-	2.5, $J_{(9,8)}$=20.0	18.9, CH_3	-	2.0, $J_{(9,8)}$=20.0
10	62.1, CH_3	-	2.8	62.1, CH_3	-	2.4
11	8.8, CH_3	-	2.5, $J_{(4,11)}$=23.0	8.8, CH_3	-	2.0, $J_{(11,4)}$=23.0
12				43.6, CH_2	-	2.5, $J_{(12,13)}$=20.0
13				61.7, CH_2	-	2.5, $J_{(13,12)}$=20.0
1'	66.5, CH_2	5.5	-	66.2, CH_2	6.5	-
2'	120.1, CH	-	6.7	120.6, CH	-	6.5
3'	142.1, qC	6.3	-	141.5, qC	7.0	-
4'	40.1, CH_2	-	6.6	40.1, CH_2	-	5.7
5'	26.9, CH_2	6.6	-	27.0, CH_2	6.7	-
6'	124.6, CH	-	5.9	124.6, CH	-	6.6
7'	132.1, qC	6.5	-	132.1, qC	6.5	_-
8'	25.8, CH_3	-	6.4	25.8, CH_3	-	5.5
9'	16.7, CH_3	-	6.9	16.7, CH_3	-	6.5
10'	17.7, CH_3	-	6.6	17.7, CH_3	-	6.6

[a] Referenced to acetone-d_6. [b] % ^{13}C-enrichment was calculated according to Scott et al.,[35c] % ^{13}C-enrichment relative to the natural abundance of C-11, [d]% ^{13}C-enrichment relative to the natural abundance of C-1', J_{cc}(Hz)= coupling constant in Hertz. % ^{13}C enrichment= 1.1% X [Integrated Intensity *I* (labeled)/Integrated Intensity *I* (unlabeled)] – 1.1%

Table S2. ^{13}C NMR data of marilone A (**1**) and mariline B (**5**) and relative % ^{13}C enrichment after feeding [1-^{13}C]sodium propionate

	Marilone A (**1**)				Mariline B (**5**)			
C	δ_C(ppm)[a]	*I* (labeled)	*I* (unlabeled)	%^{13}C enrichment	δ_C(ppm)[a]	*I* (labeled)	*I* (unlabeled)	%^{13}C enrichment
1	168.2, qC	0.35	0.25	0.44	167.3, qC	0.27	0.15	0.88
2	110.0, qC	0.35	0.19	0.92	116.3, qC	0.52	0.30	0.81
3	158.0, qC	0.31	0.20	0.61	156.9, qC	0.75	0.46	0.69
4	120.4, qC	0.47	0.27	0.81	119.3, qC	n.d	0.11	n.d
5	164.2, qC	0.60	0.32	0.96	161.7, qC	n.d	0.30	n.d
6	100.8, CH	2.59	1.64	0.63	101.8, CH	1.25	0.77	0.69
7	154.2, qC	0.48	0.29	0.72	150.0, qC	0.95	0.61	0.61
8	77.0, CH	2.42	1.52	0.65	56.9, CH	1.08	0.80	0.39
9	20.9, CH_3	2.56	1.49	0.79	18.9, CH_3	2.25	1.43	0.63
10	62.1, CH_3	2.00	1.12	0.86	62.1, CH_3	1.58	0.96	0.71
11	8.8, CH_3	1.00	1.00	Internal reference	8.8, CH_3	1.00	1.00	Internal reference
12					43.6, CH_2	1.89	1.06	0.86
13					61.7, CH_2	1.11	0.72	0.60
1’	66.5, CH_2	2.89	1.79	0.68	66.2, CH_2	1.46	0.91	0.66
2’	120.1, CH	2.58	1.62	0.65	120.6, CH	1.72	1.11	0.60
3’	142.1, qC	1.12	0.66	0.76	141.5, qC	0.18	0.13	0.42
4’	40.1, CH_2	2.54	1.50	0.76	40.1, CH_2	2.74	1.83	0.54
5’	26.9, CH_2	2.90	1.80	0.67	27.0, CH_2	2.89	1.98	0.51
6’	124.6, CH	1.89	1.29	0.51	124.6, CH	1.21	0.71	0.77
7’	132.1, qC	0.54	0.30	0.88	132.1, qC	n.d.	0.10	n.d
8’	25.8, CH_3	2.76	1.62	0.77	25.8, CH_3	2.58	1.59	0.68
9’	16.7, CH_3	2.52	1.50	0.75	16.7, CH_3	1.87	1.32	0.46
10’	17.7, CH_3	1.98	1.10	0.88	17.7, CH_3	1.78	1.14	0.62

[a] Referenced to acetone-d_6. [b] % ^{13}C-enrichment was calculated according to Scott et al.,[35c] % ^{13}C-enrichment relative to the natural abundance of C-11, *I* = integrated intensity of ^{13}C signal, n.d. = not determined, %^{13}C enrichment= 1.1% X [Integrated Intensity *I* (labeled)/Integrated Intensity *I* (unlabeled)] – 1.1%

Figure S1. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of mariloneA(**1**) (taken from literature).[1]

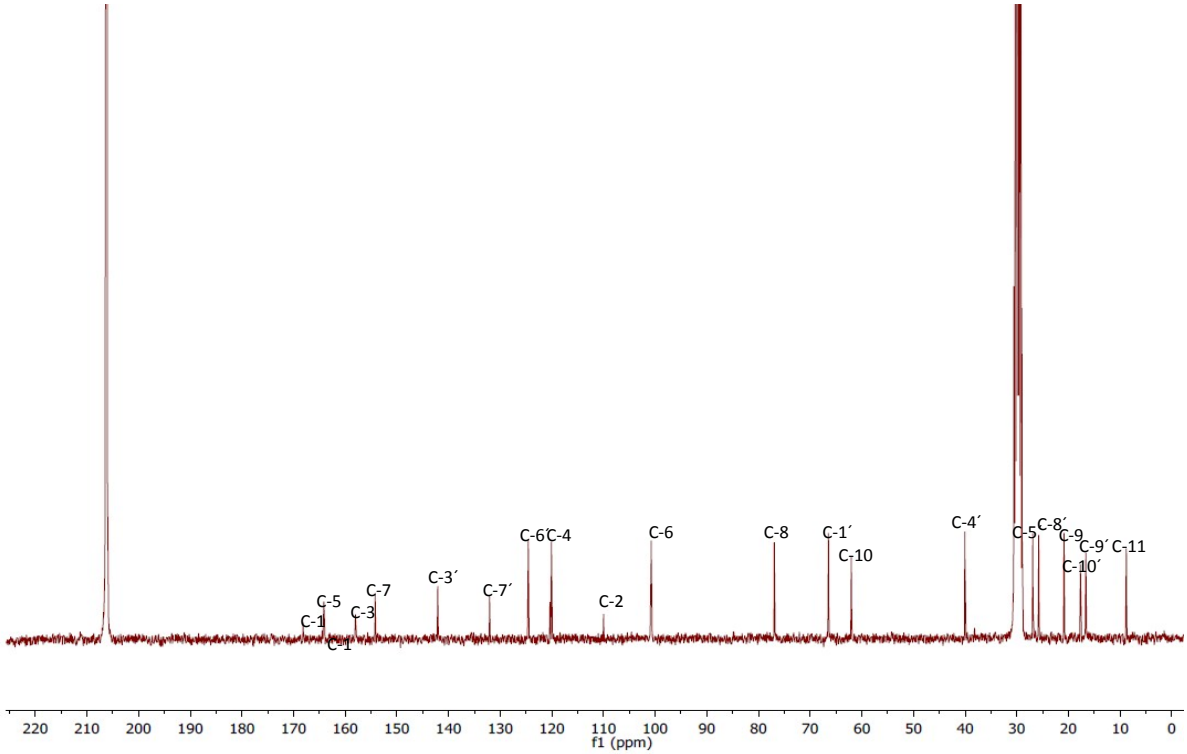


Figure S2. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of mariline B (**5**) (taken from literature).[2]

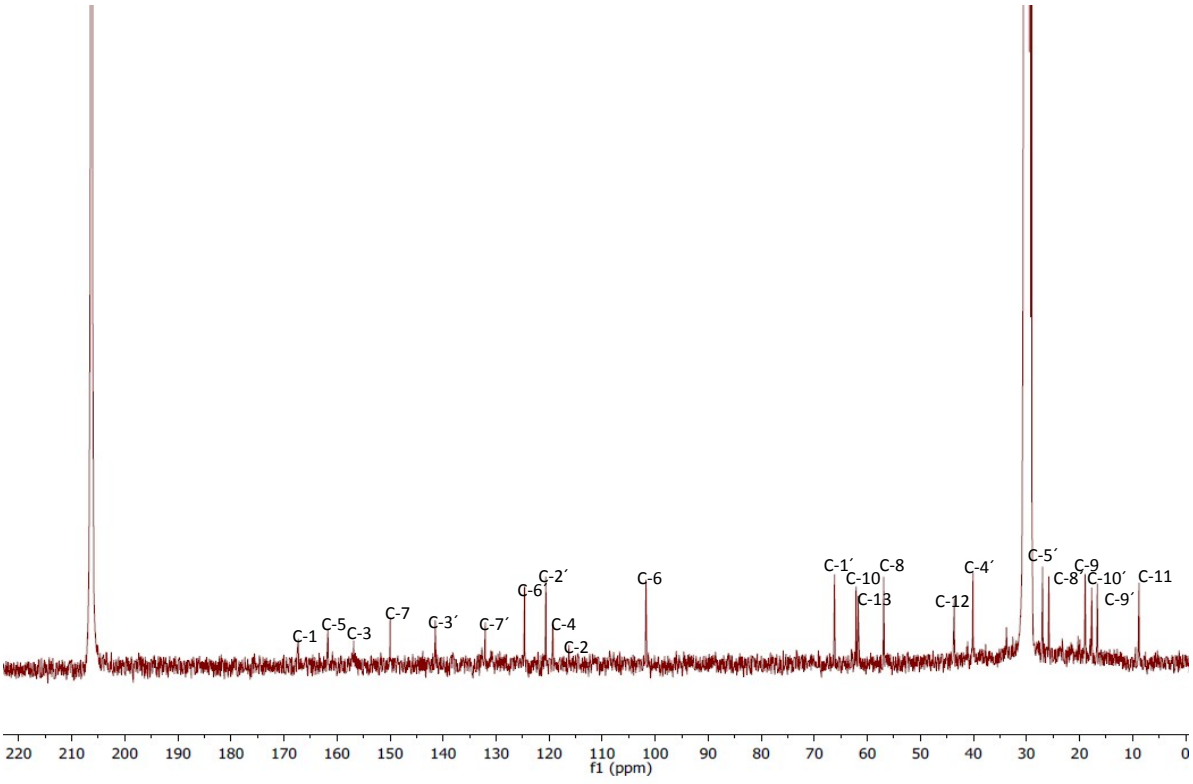


Figure S3. ^{13}C NMR (75 MHz, acetone-d_6) spectrum of marilone A (**1**) after feeding [1-^{13}C]sodium acetate.

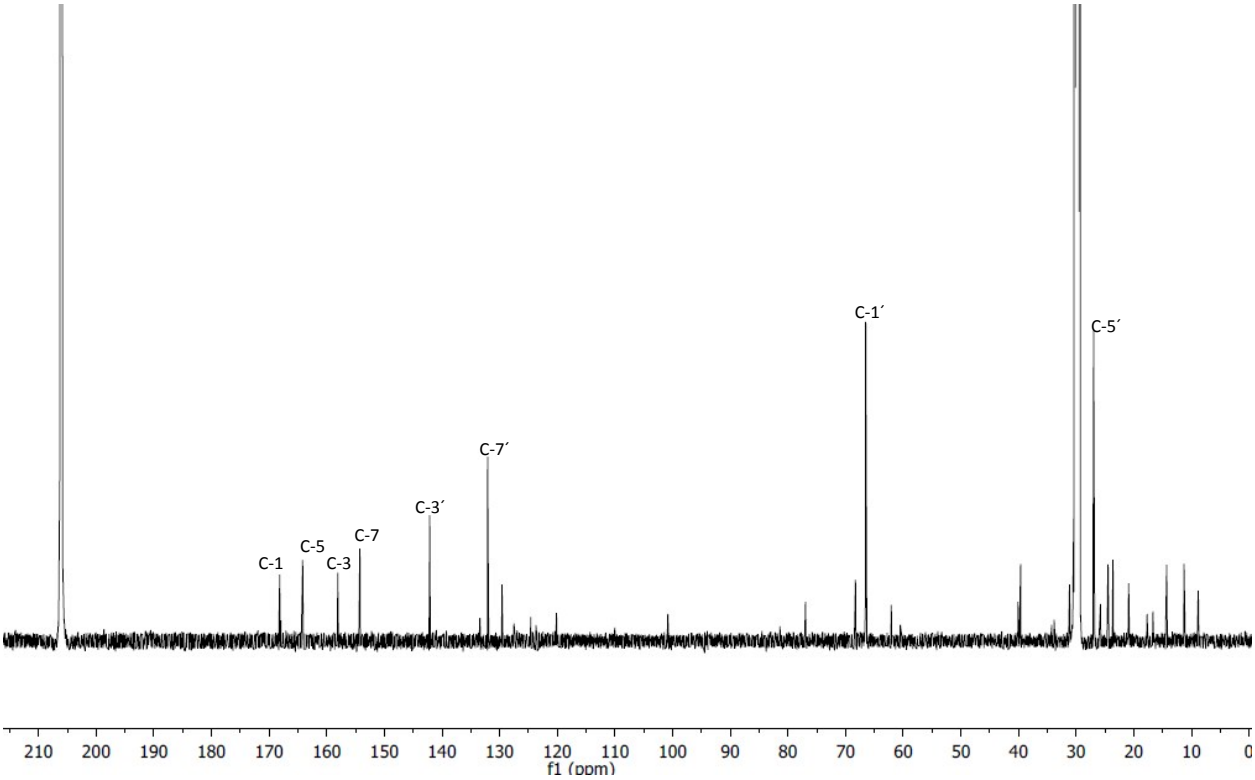


Figure S4. ^{13}C NMR (75 MHz, acetone-d_6) spectrum of mariline B(**5**) after feeding [1-^{13}C]sodium acetate.

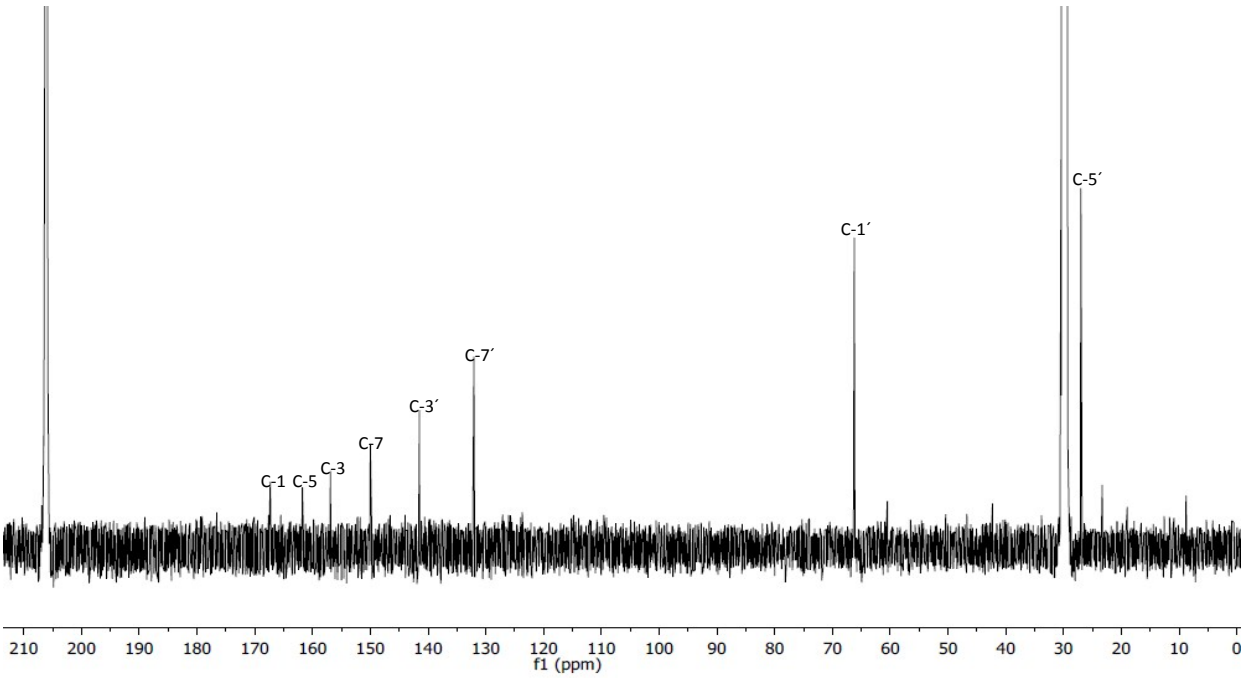


Figure S5. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of marilone A (**1**) after feeding [2-^{13}C]sodiumacetate.

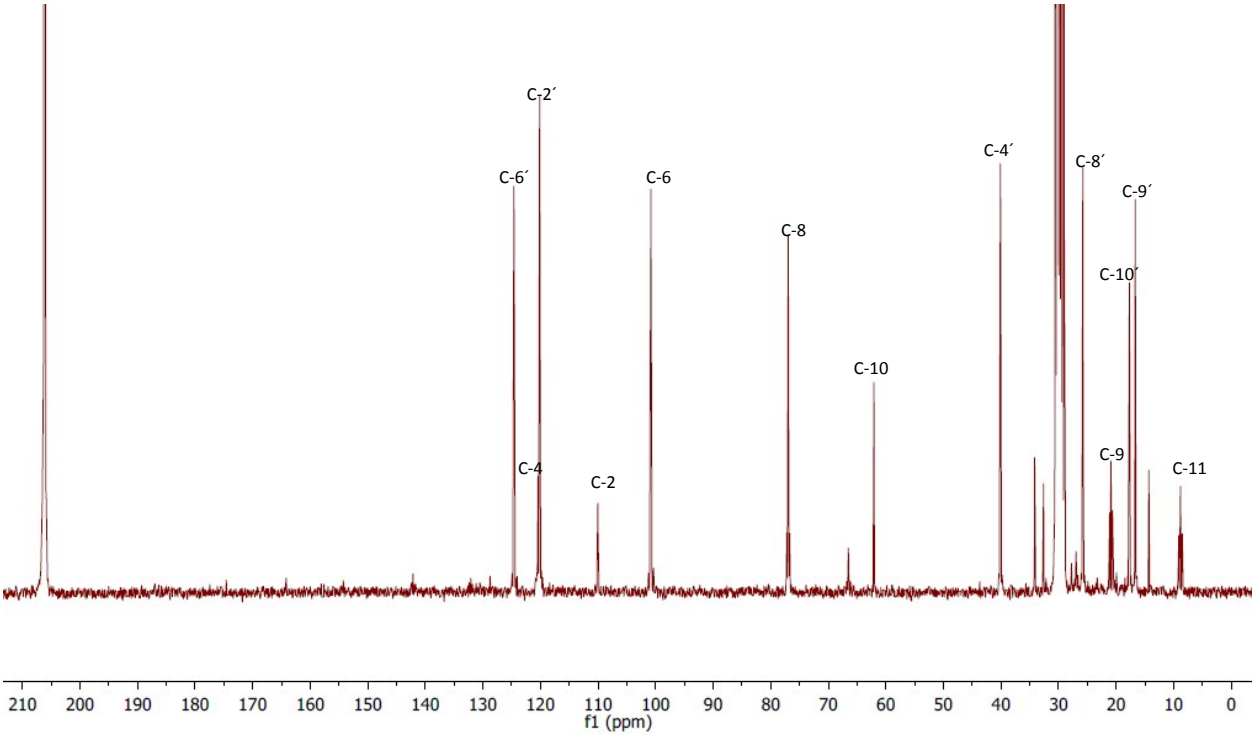


Figure S6. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of marilineB(**5**) after feeding [2-^{13}C]sodium acetate.

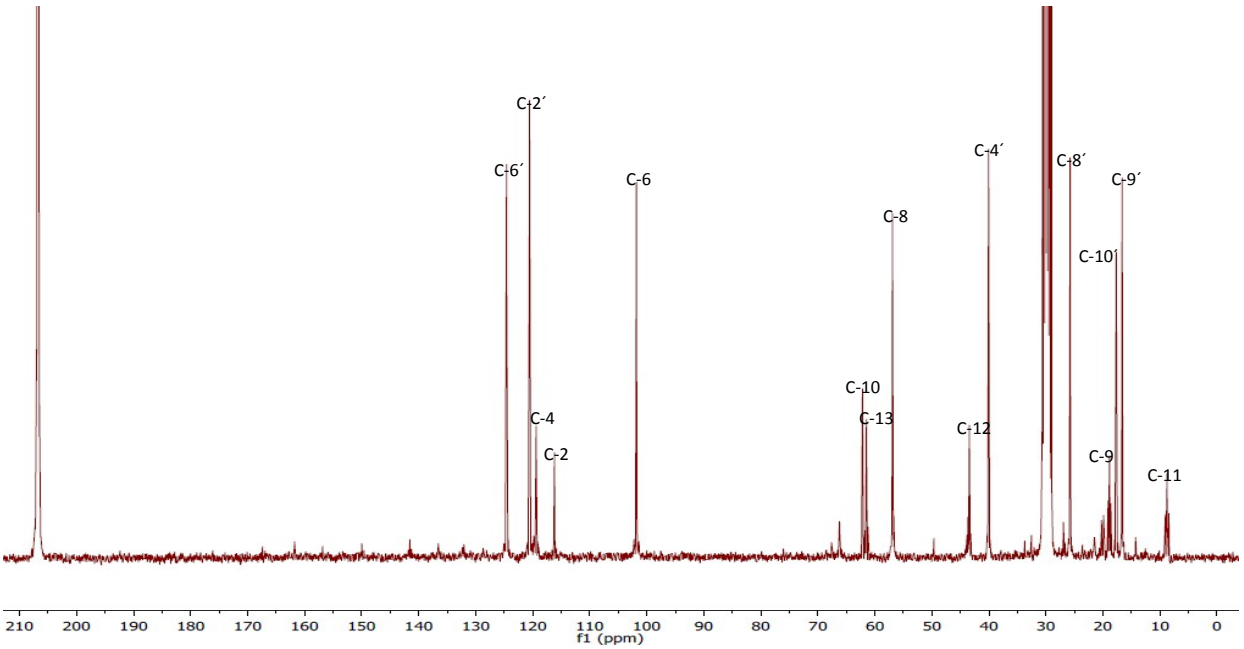


Figure S7. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of mariloneA (**1**) after feeding [1-^{13}C]sodiumpropionate.

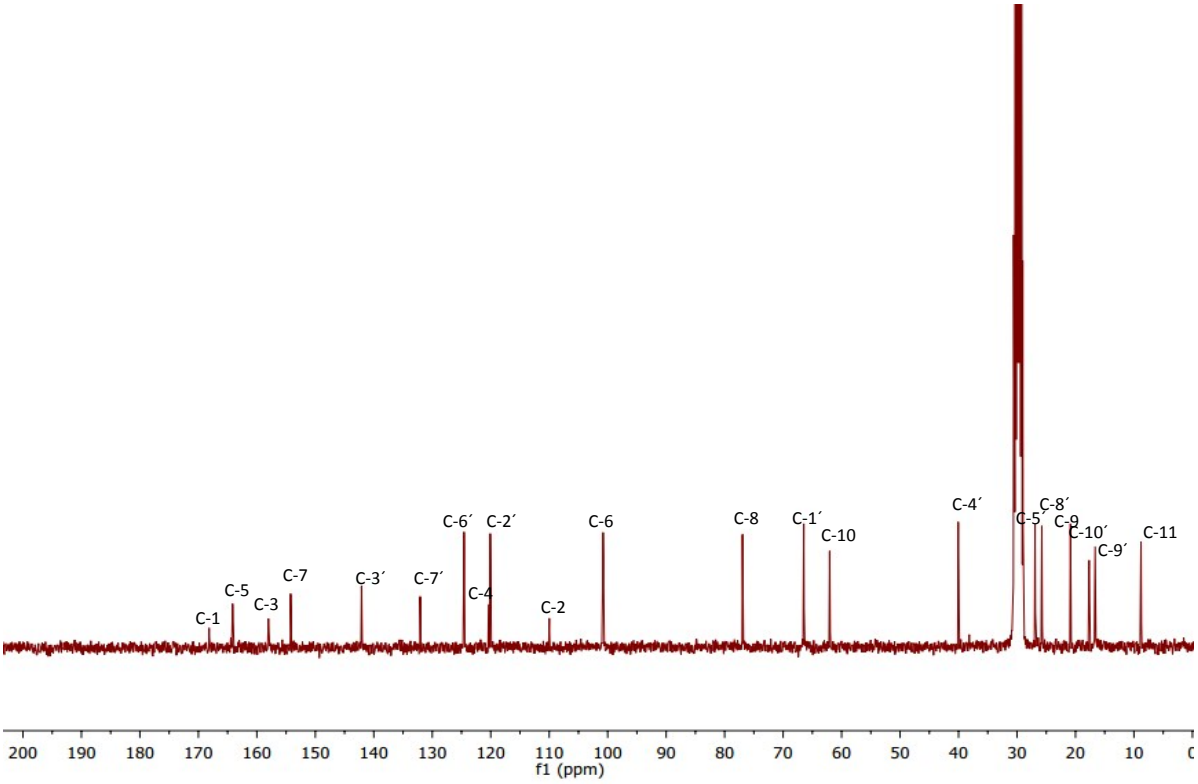


Figure S8. ^{13}C NMR (75 MHz, acetone-d_6) spectrum of mariline B (**5**) after feeding [1-^{13}C]sodium propionate.

Figure S9. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of marilone A (**1**) after feeding L-[*Me*-^{13}C]methionine.

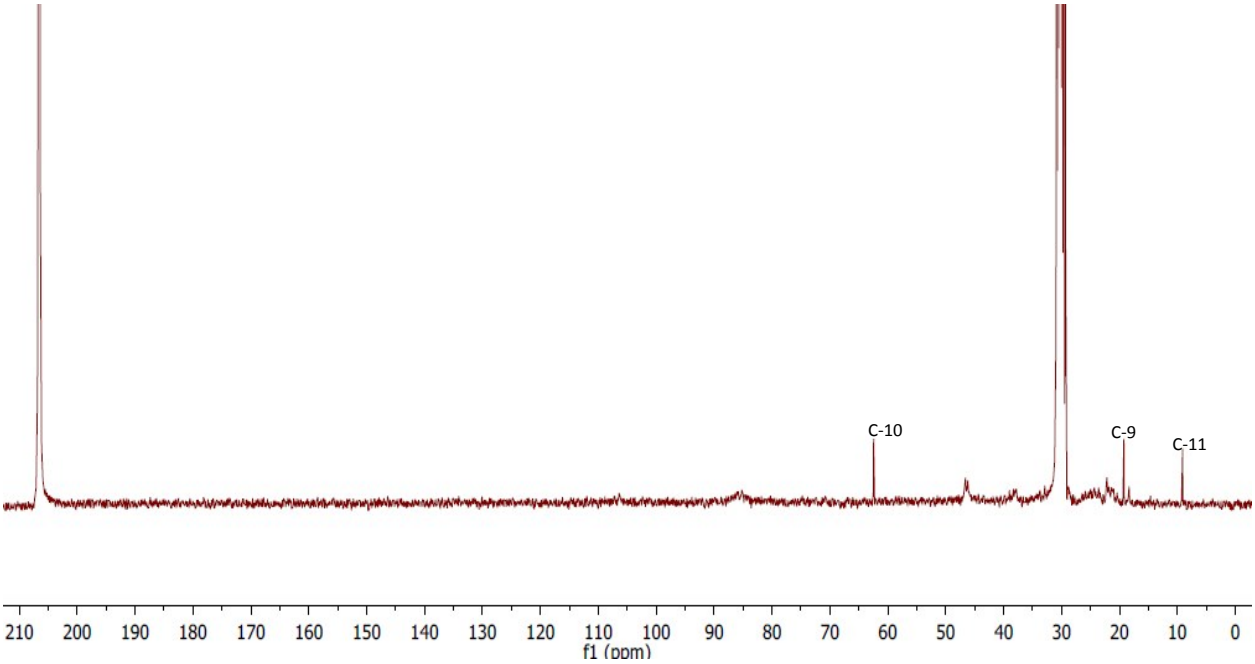
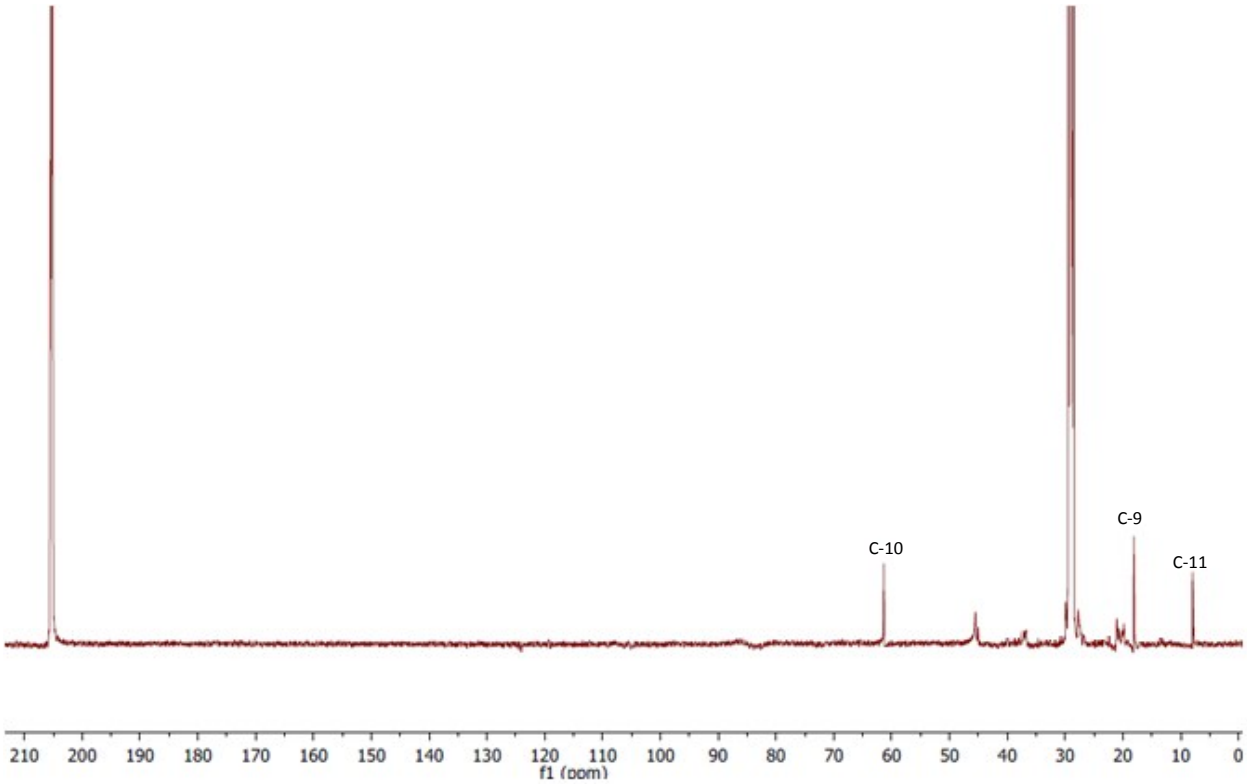


Figure S10. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of mariline B (**5**) after feeding L-[*Me*-^{13}C]methionine.



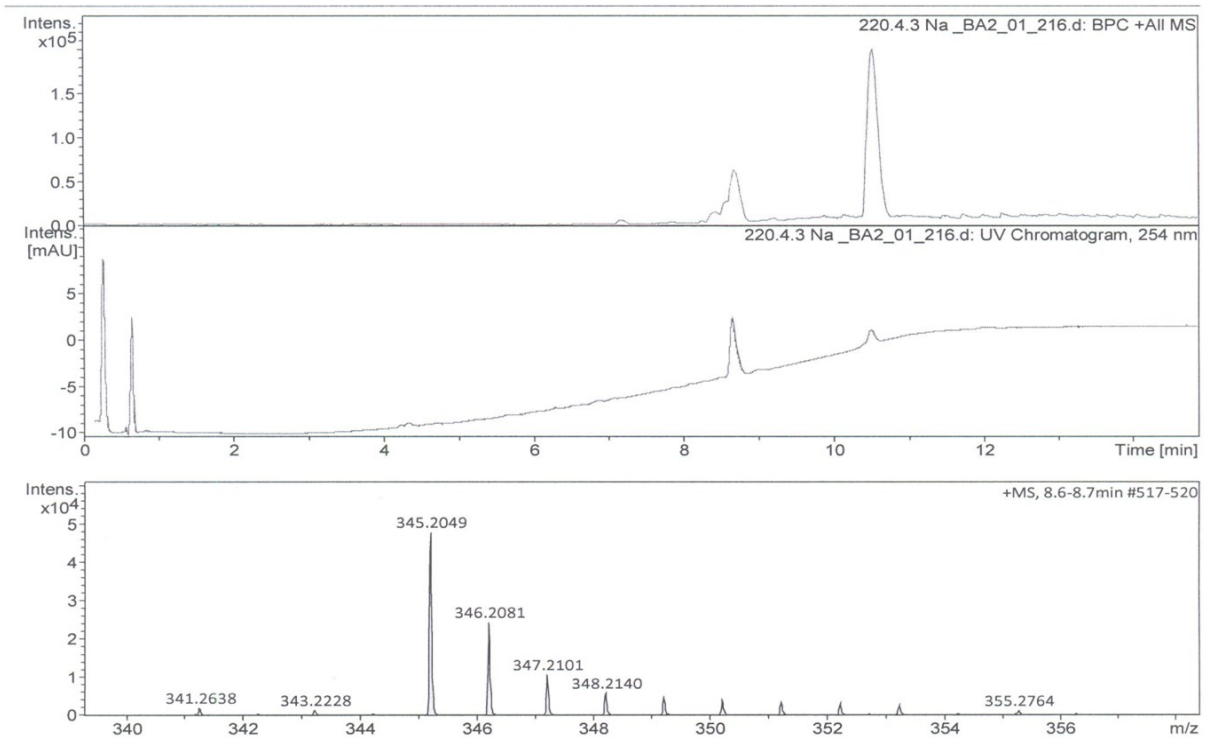


Figure S11. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [1-^{13}C]sodium acetate.

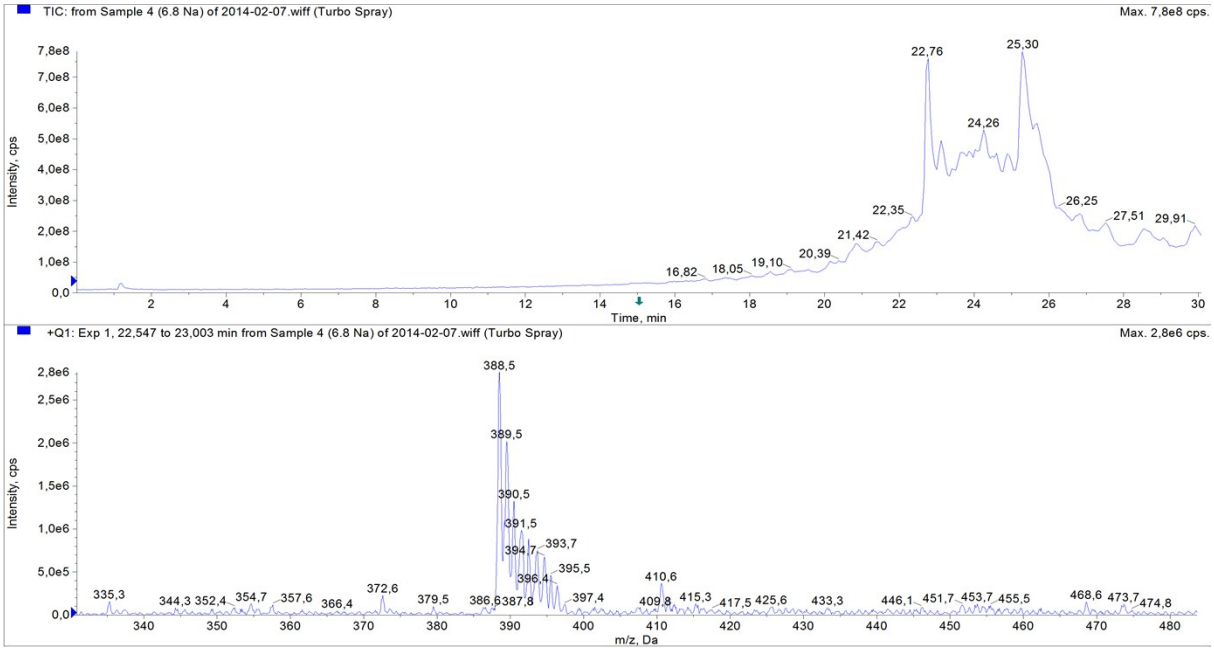


Figure S12. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [1-^{13}C]sodium acetate.

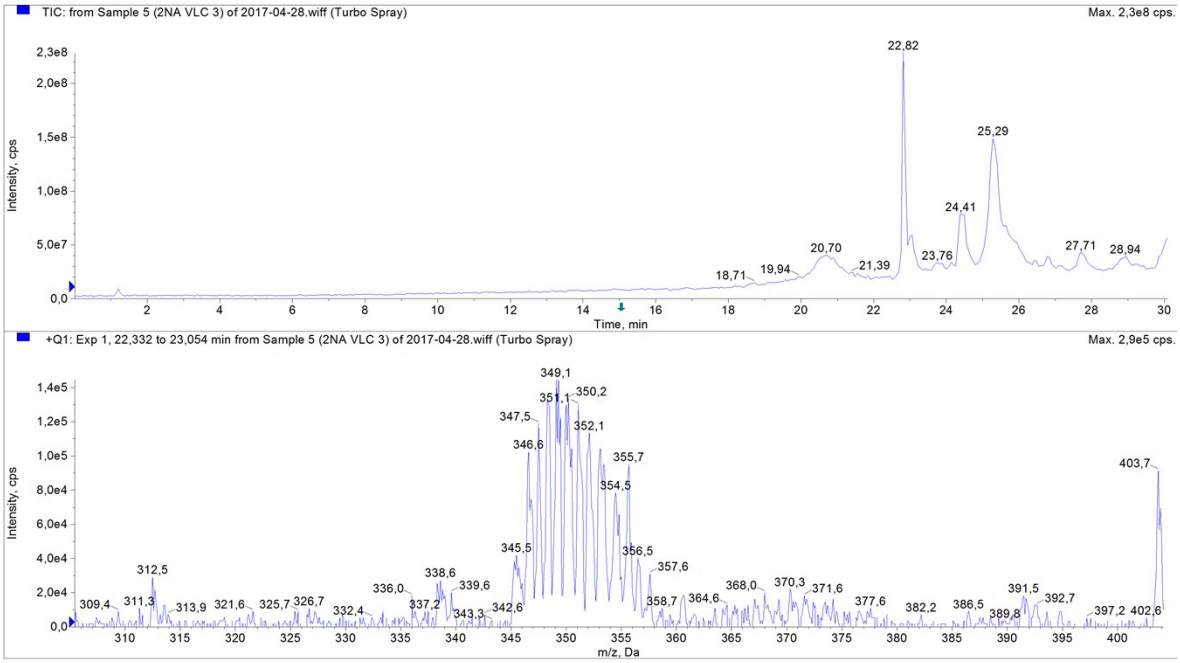


Figure S13. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [2-^{13}C]sodium acetate.

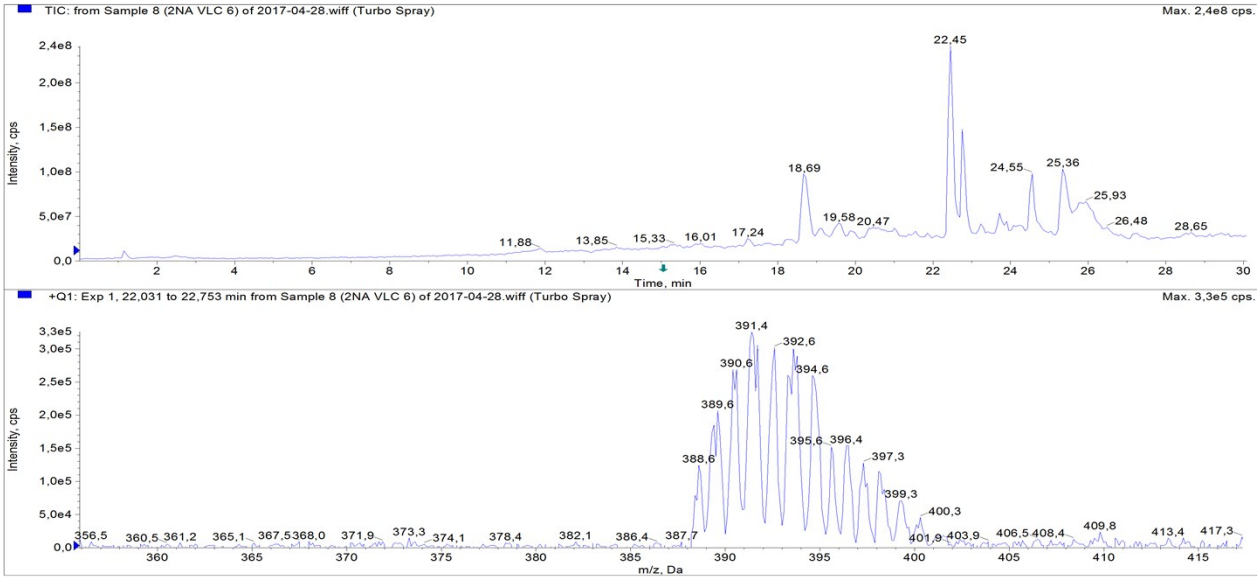


Figure S14. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [2-^{13}C]sodium acetate.

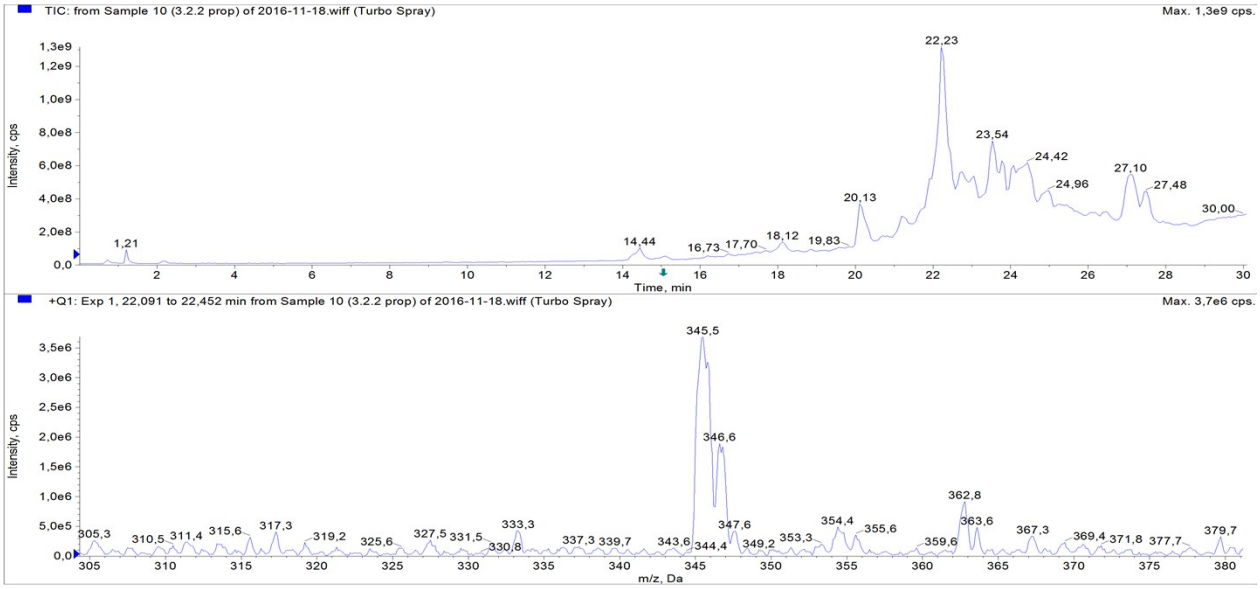


Figure S15. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [1-^{13}C]sodium propionate.

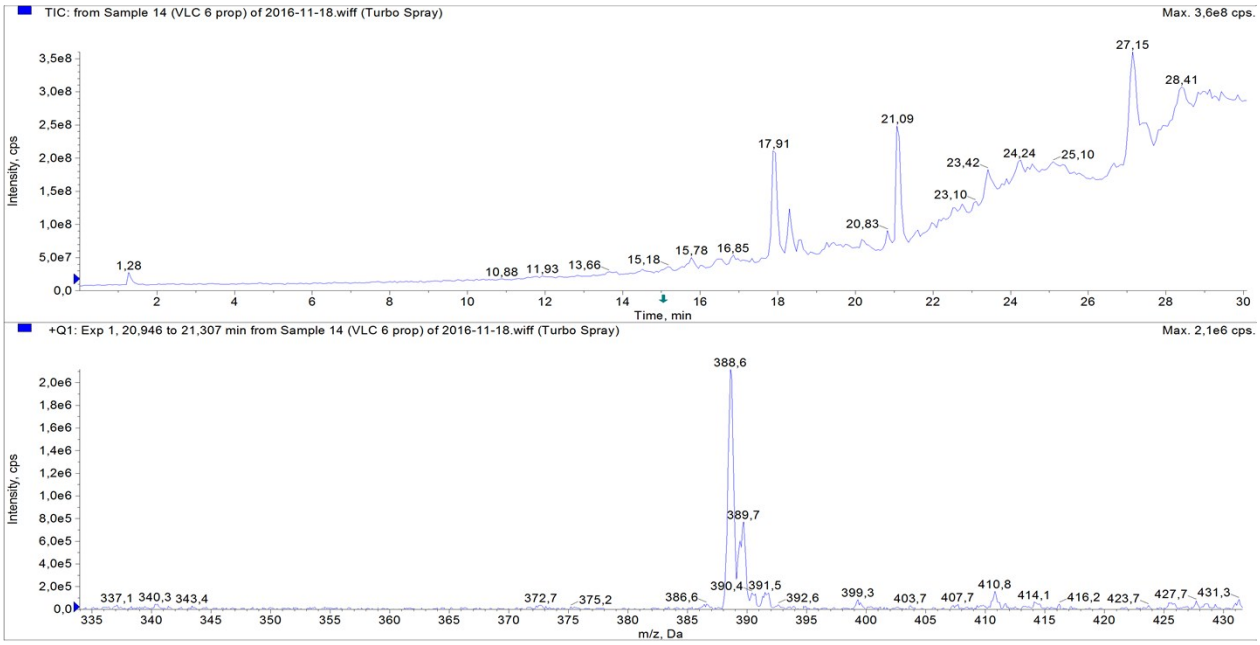


Figure S16. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture supplemented with [1-^{13}C]sodium propionate.

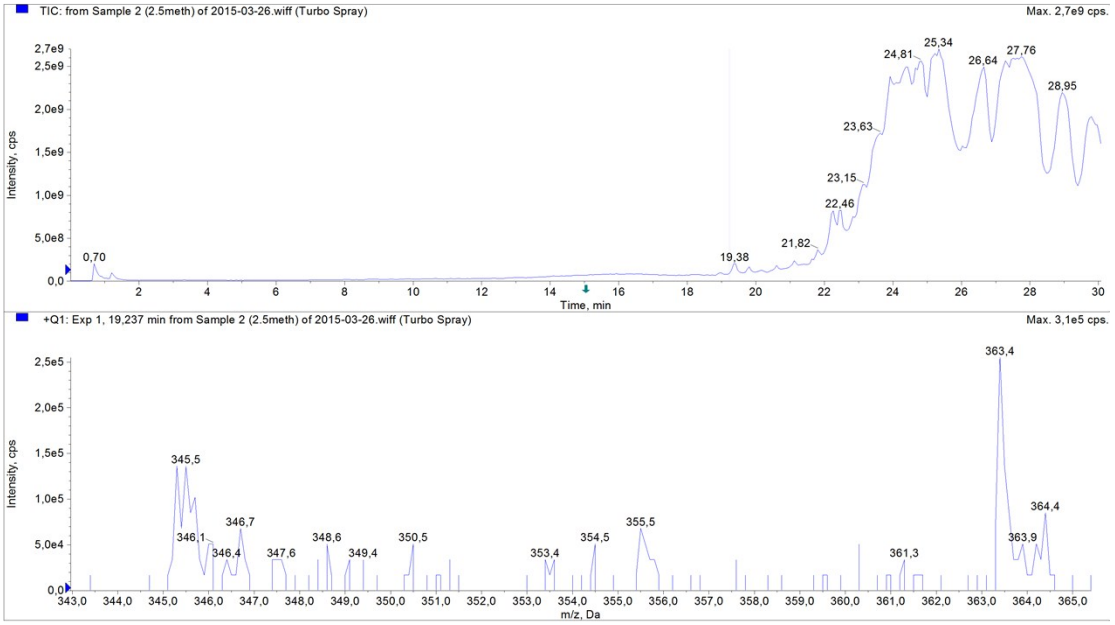


Figure S17. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture supplemented with L-[*Me*-^{13}C]methionine.

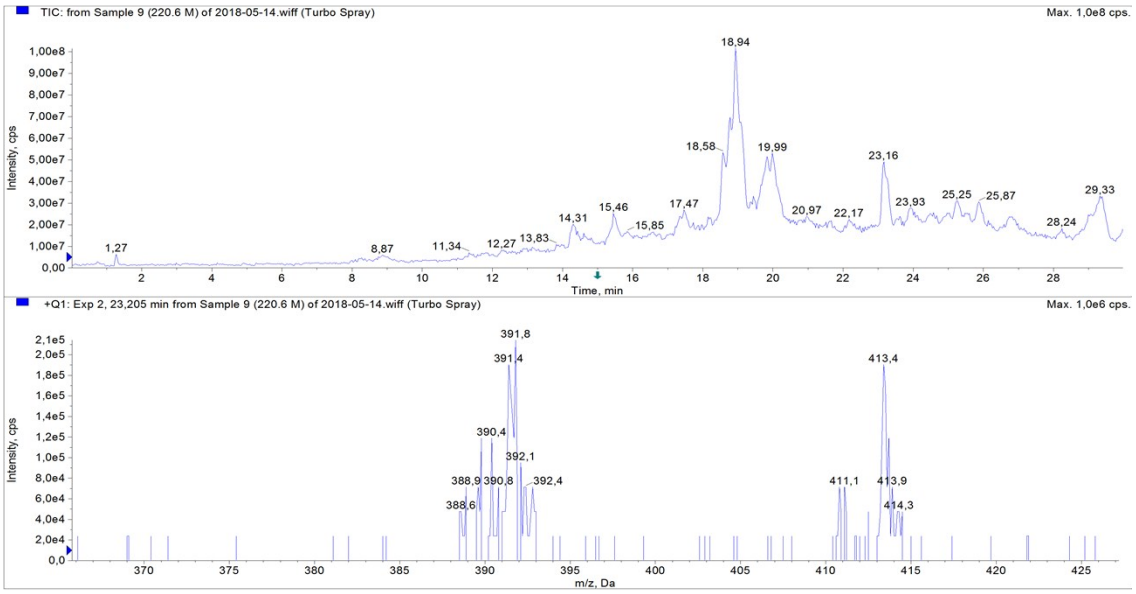


Figure S18. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture supplemented with L-[*Me*-^{13}C]methionine.

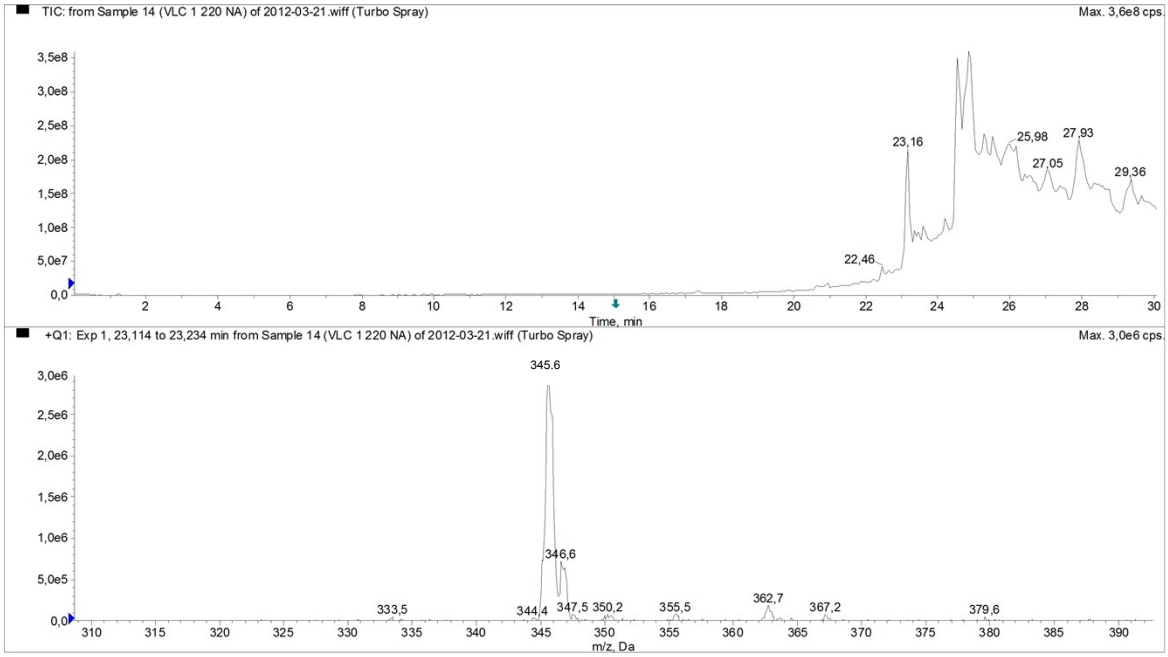


Figure S19. LC-ESIMS spectrum of marilone A (**1**) isolated from *Stachylidium* sp. BMS agar culture.

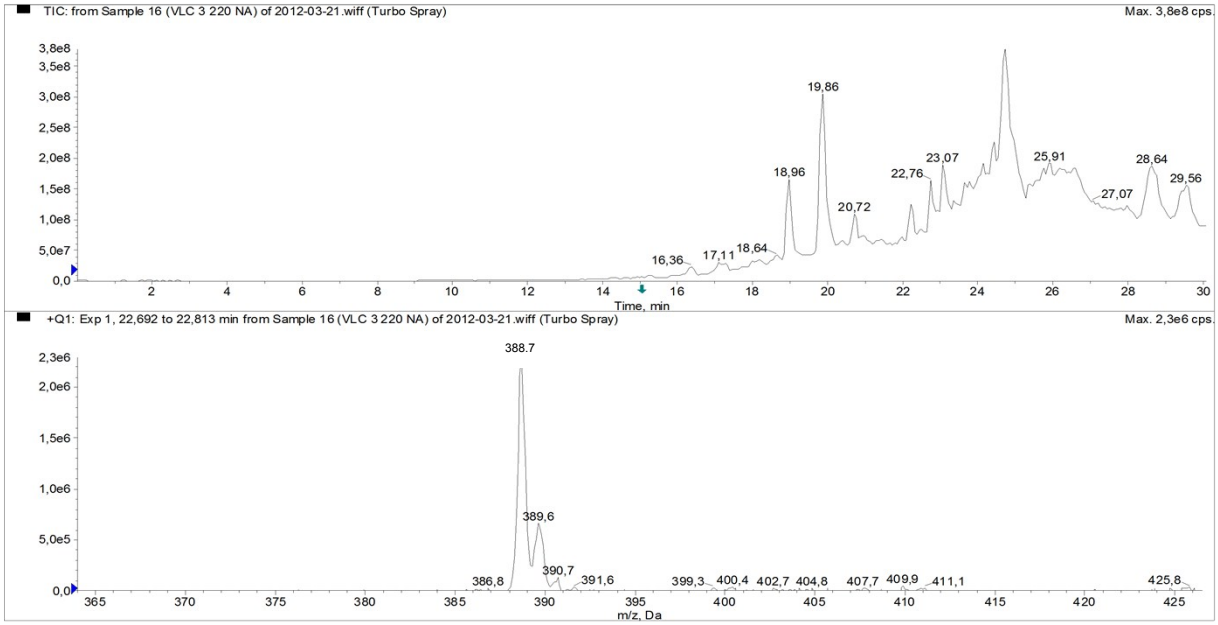


Figure S20. LC-ESIMS spectrum of mariline B (**5**) isolated from *Stachylidium* sp. BMS agar culture.

Figure S21.HPLC isolation chromatogram of marilone A (**1**)

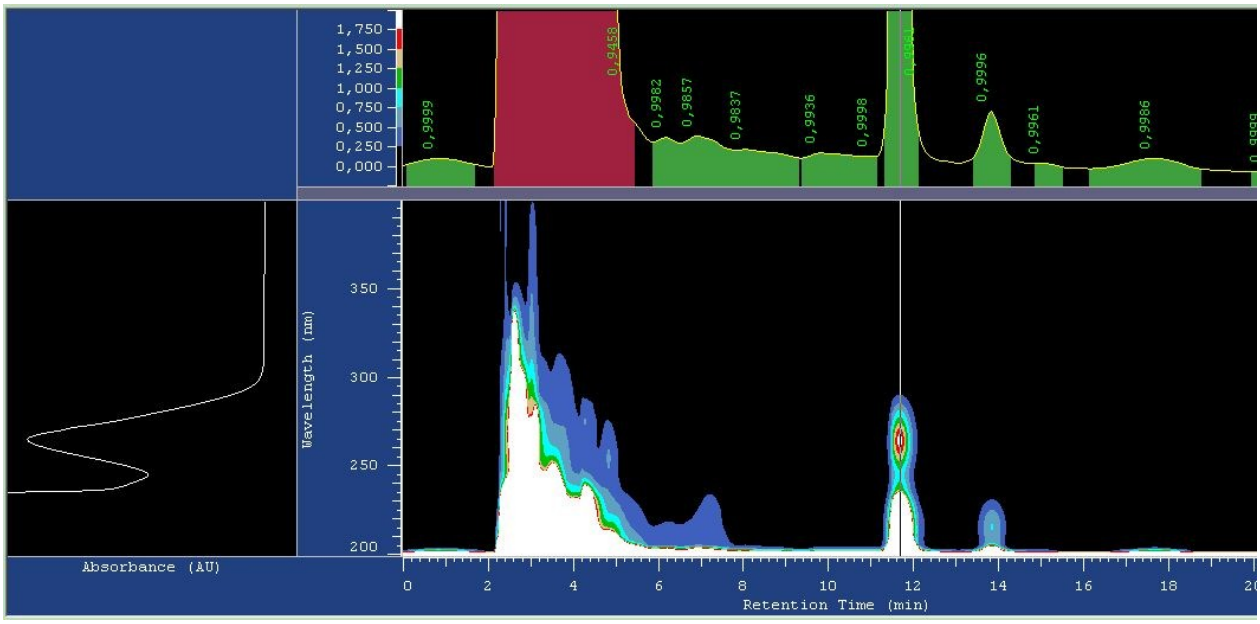


Figure S22.HPLC isolation chromatogram of mariline B (**5**)