Supplementary Material

Article

Identification of antimycobacterial natural products from a library of marine invertebrate extracts

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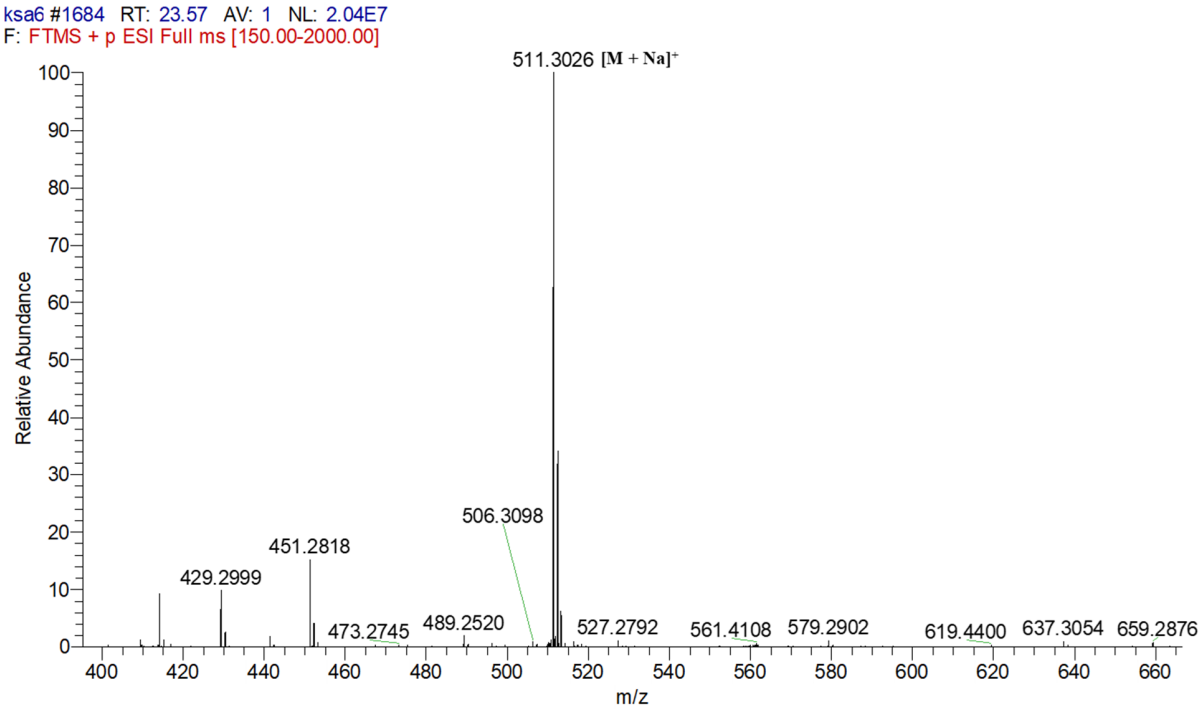

Figure S1. HR-ESI-MS spectrum of heteronemin **1**

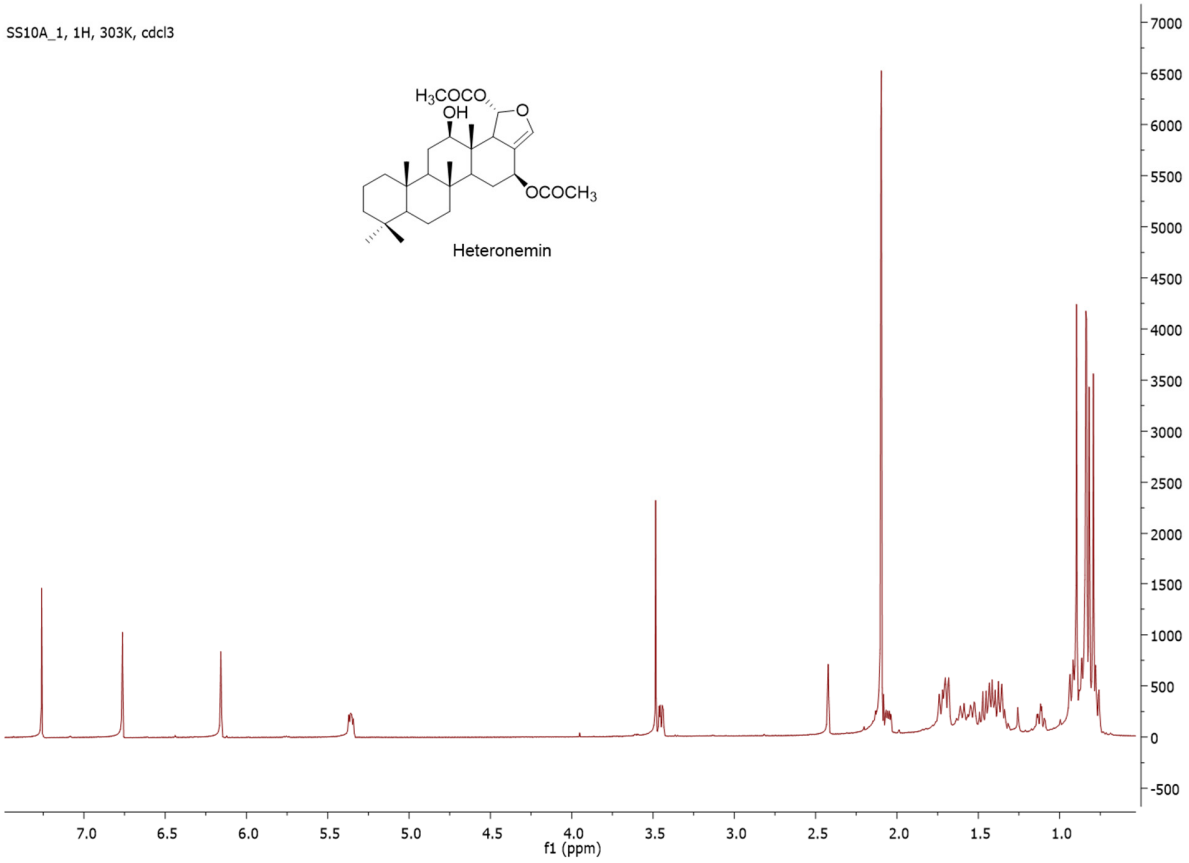

Figure S2. ^{1}H-NMR spectrum (600MHz, $CDCl_3$, 303K) of heteronemin **1**

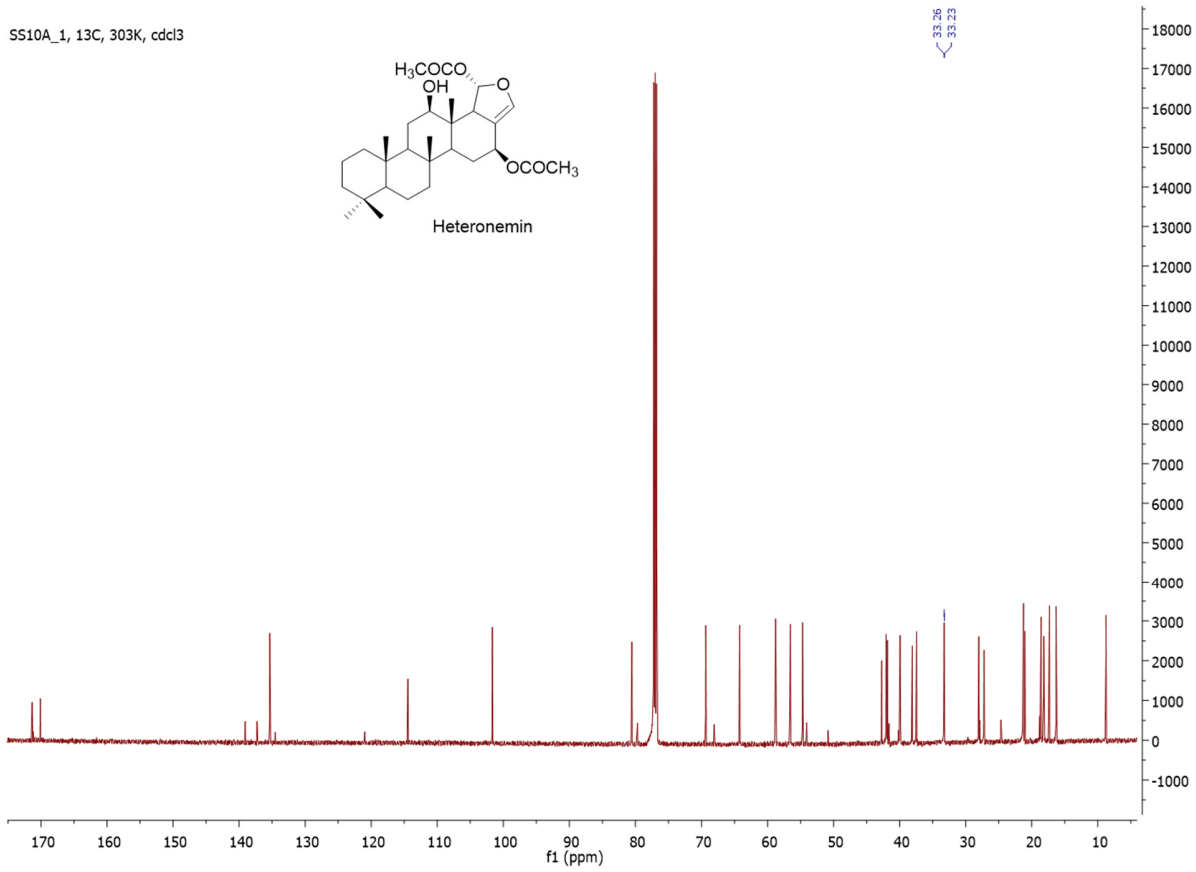

Figure S3. ^{13}C-NMR spectrum (150MHz, $CDCl_3$, 303K) of heteronemin **1**

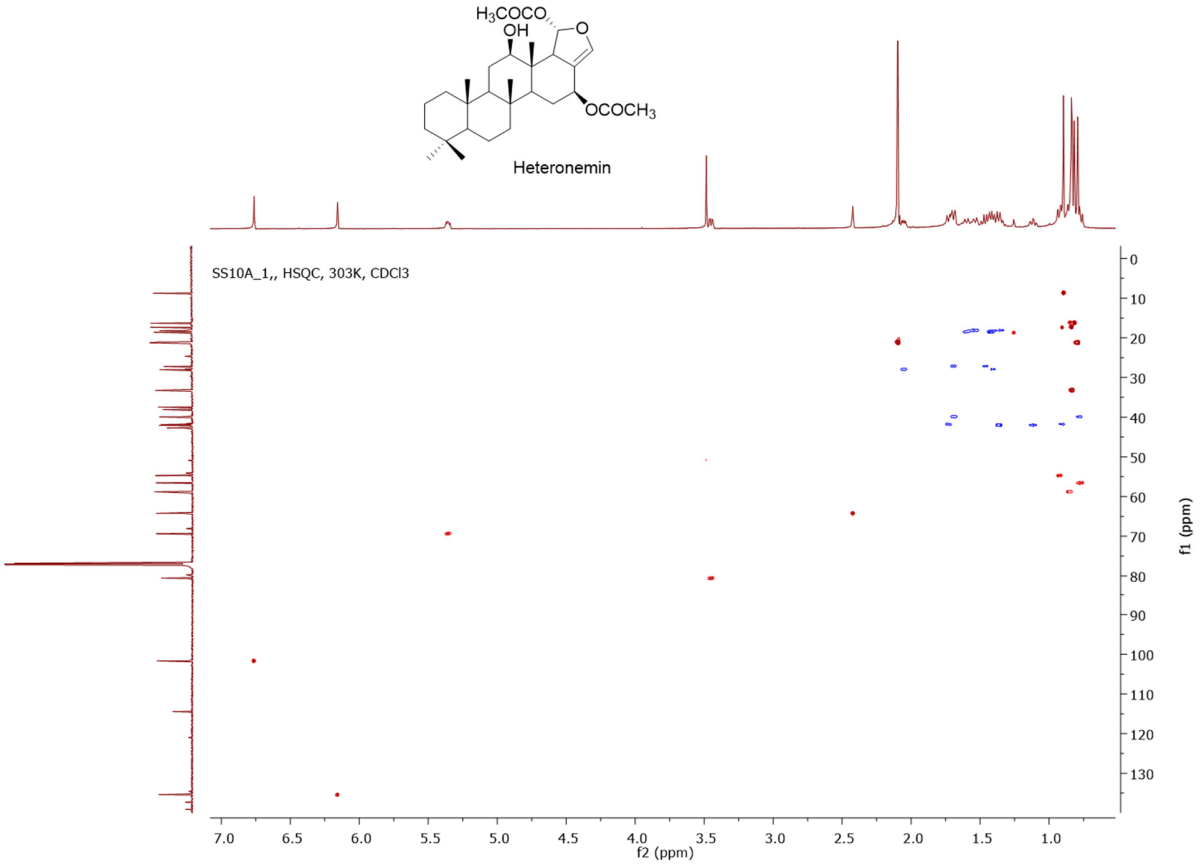

Figure S4. HSQC NMR spectrum (600MHz, $CDCl_3$, 303K) of heteronemin **1**

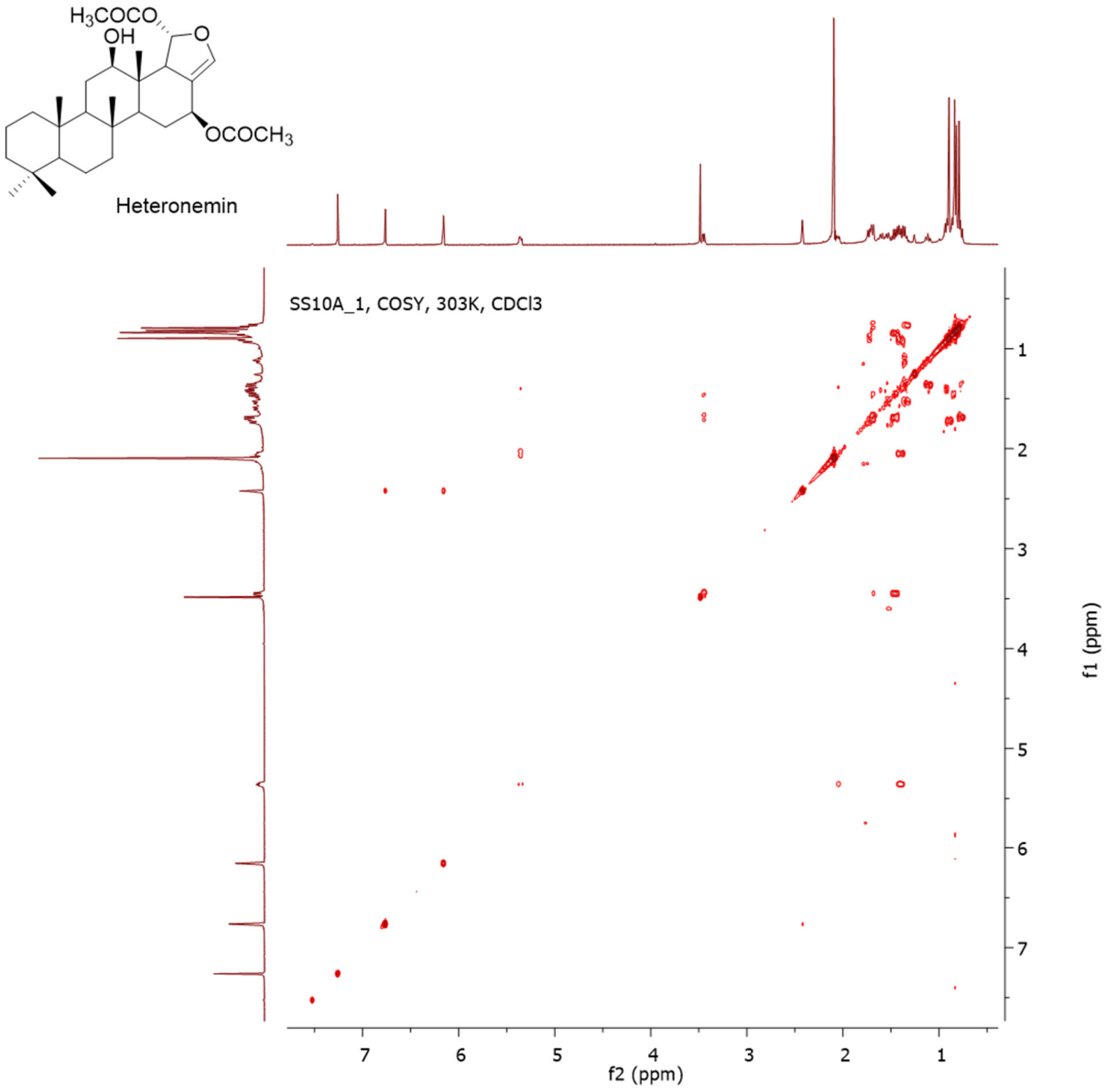

Figure S5. ^{1}H-^{1}H COSY spectrum (600MHz, $CDCl_3$, 303K) of heteronemin **1**

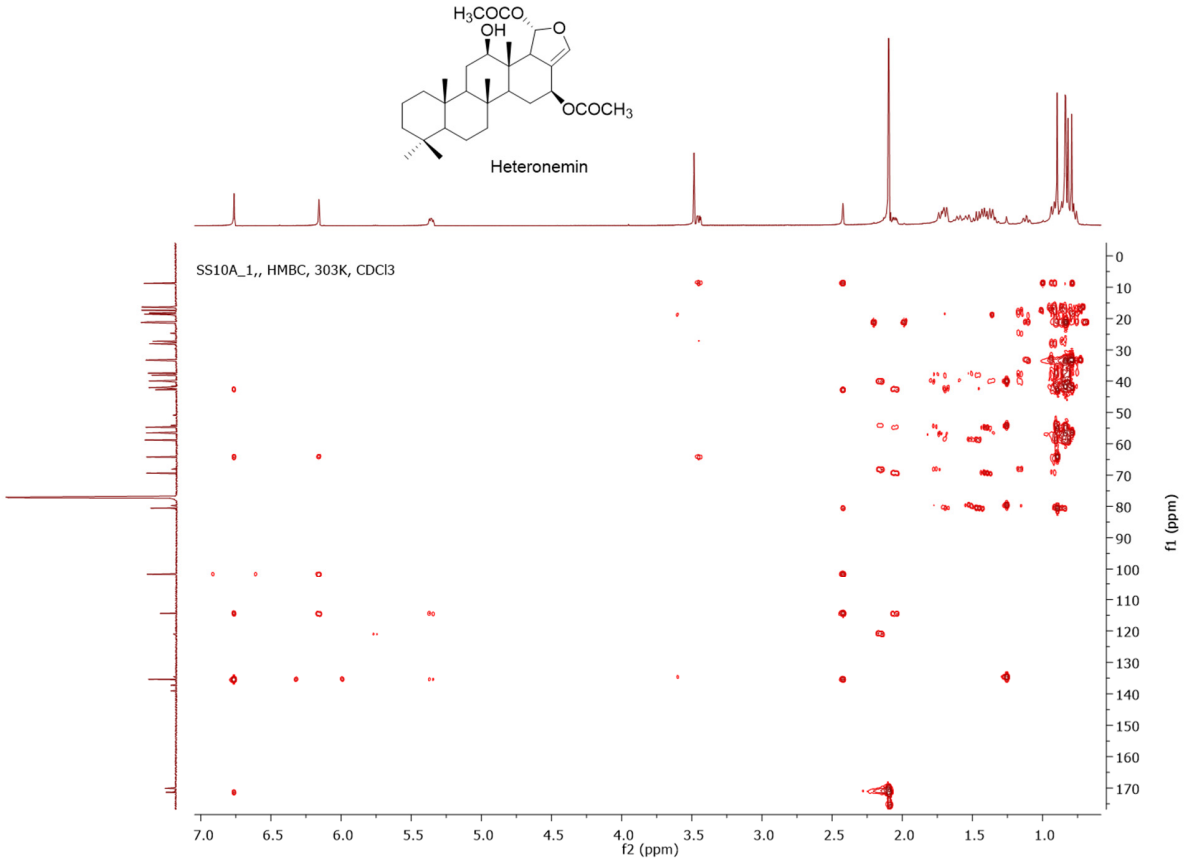

Figure S6. HMBC NMR spectrum (600MHz, $CDCl_3$, 303K) of heteronemin **1**

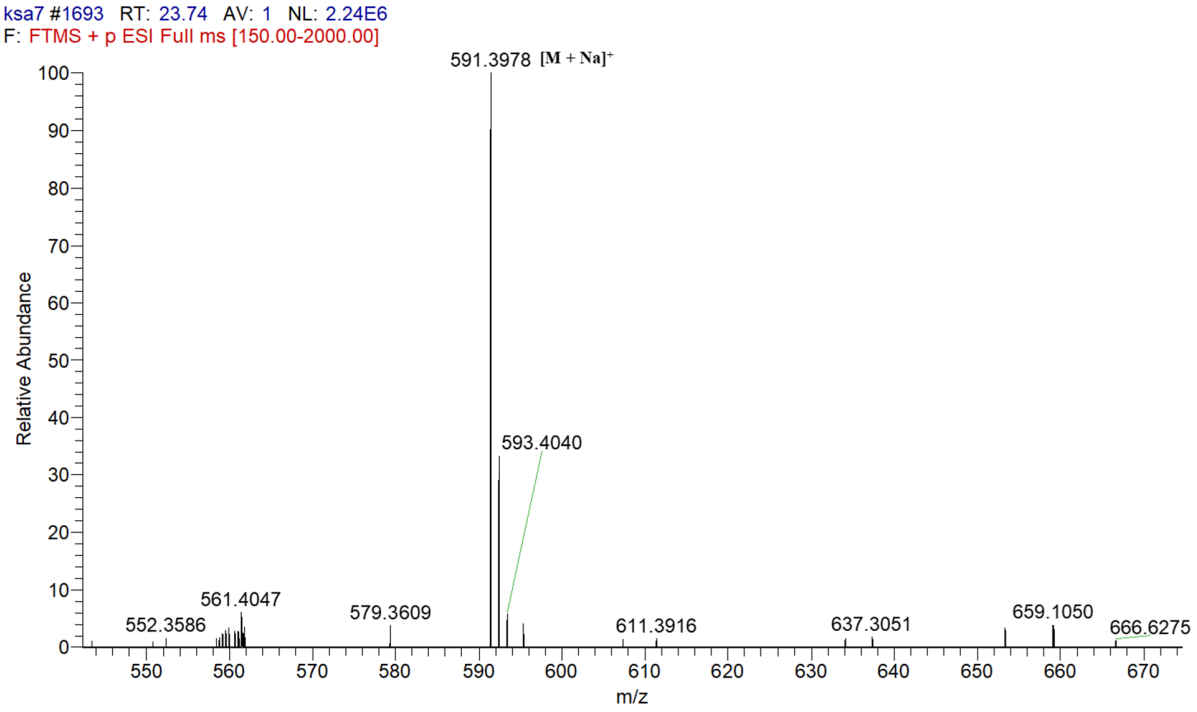

Figure S7. HR-ESI-MS spectrum of bengamide P **2**

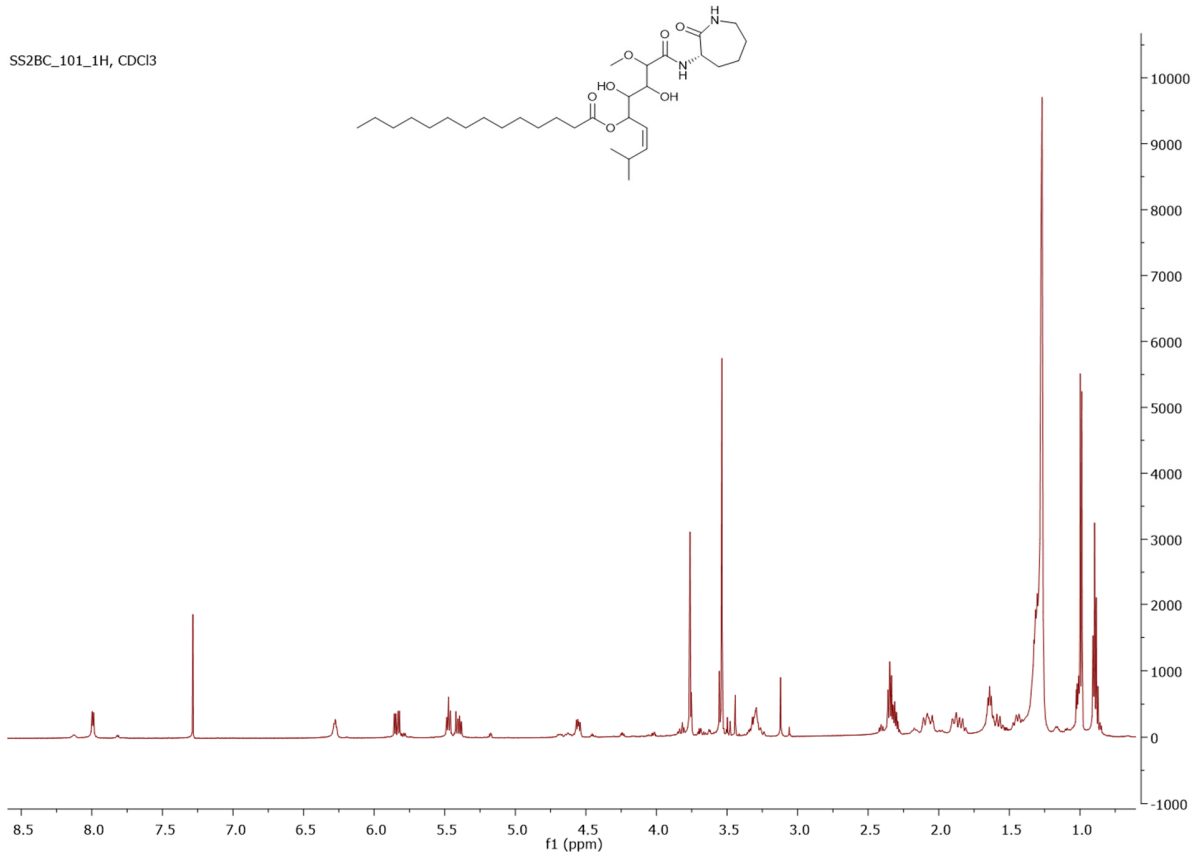

Figure S8. ^{1}H-NMR spectrum (600MHz, $CDCl_3$, 303K) of bengamide P **2**

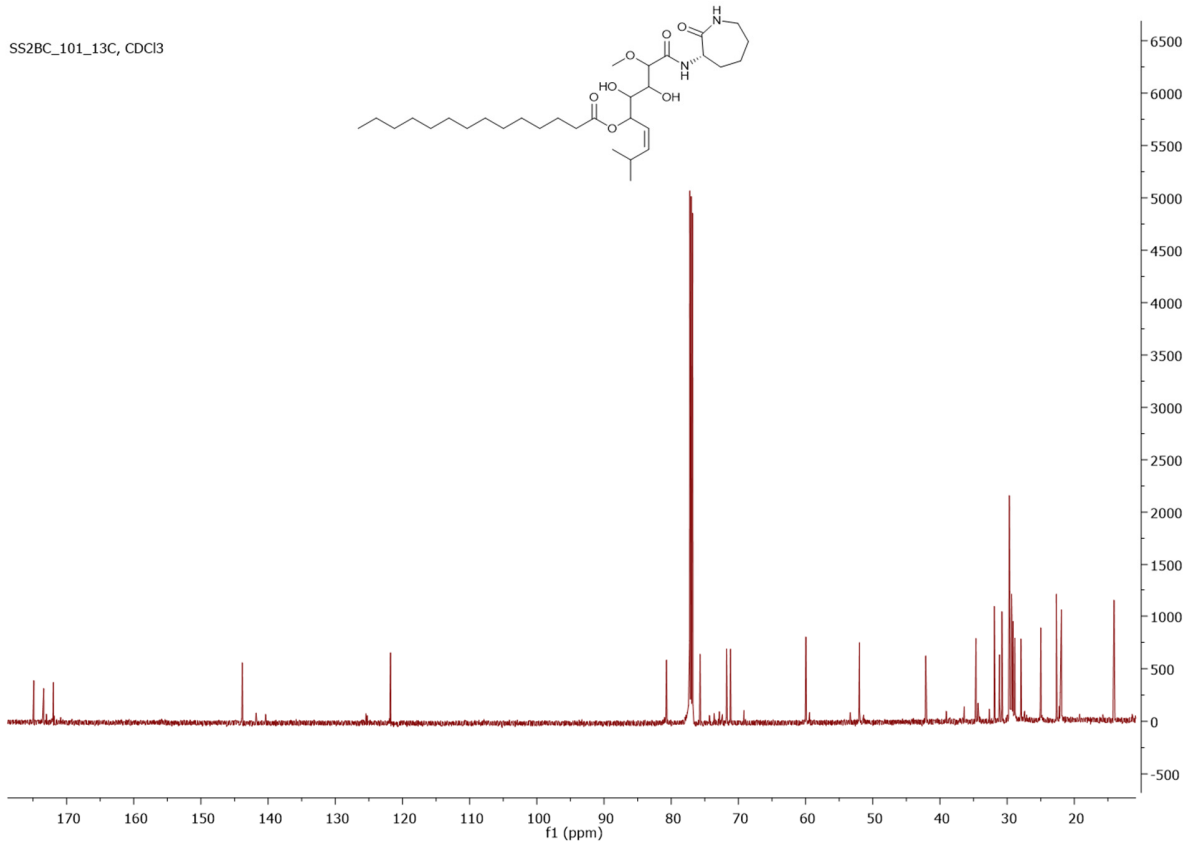

Figure S9. ^{13}C-NMR spectrum (150MHz, $CDCl_3$, 303K) of bengamide P **2**

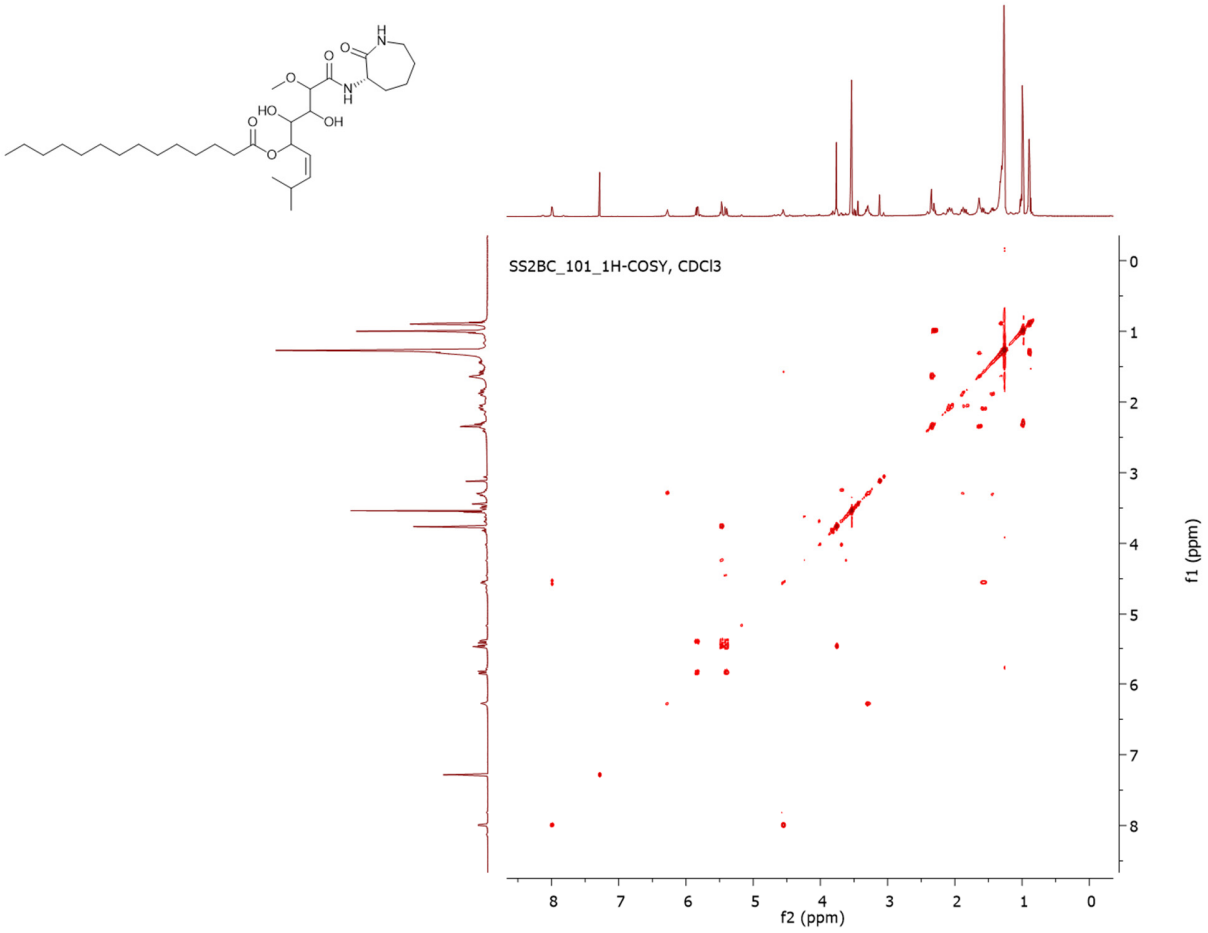

Figure S10. ^{1}H-^{1}H COSY spectrum (600MHz, $CDCl_3$, 303K) of bengamide P **2**

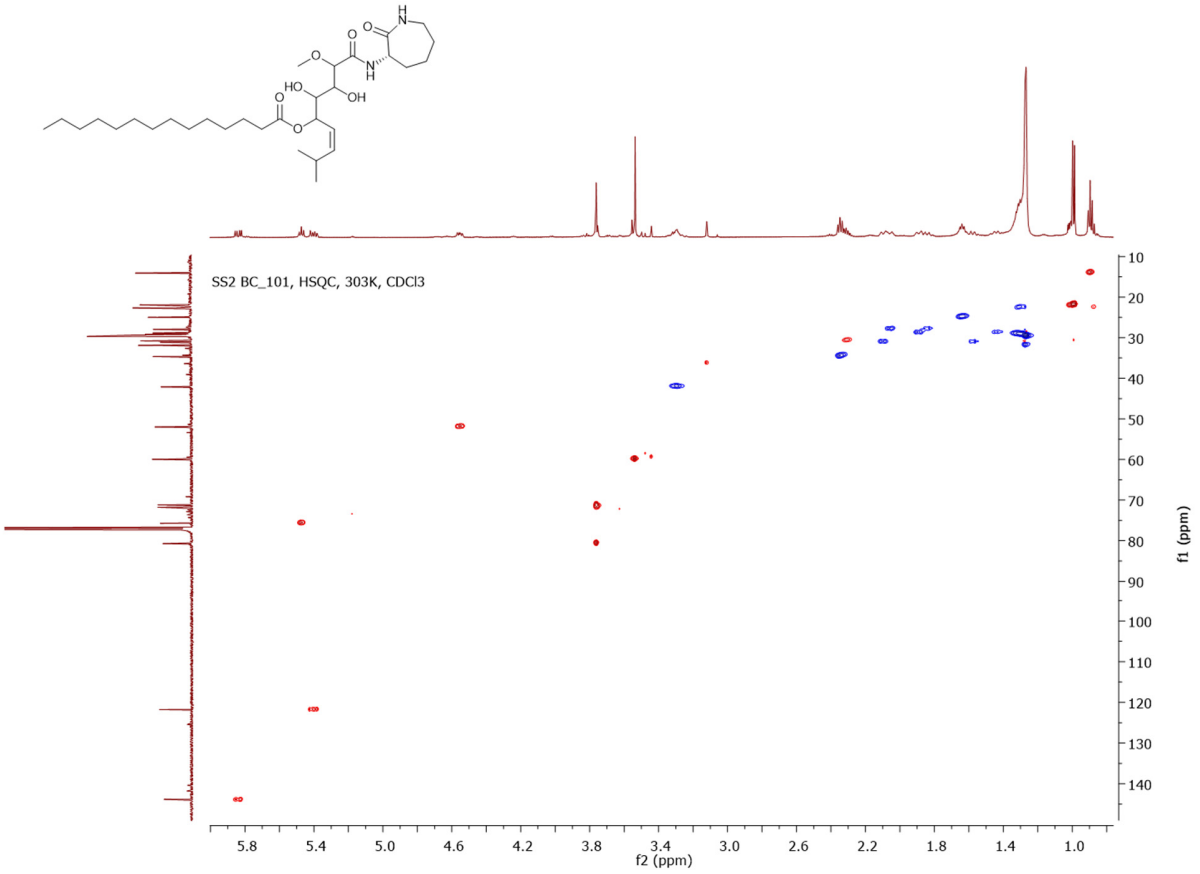

Figure S11. HSQC NMR spectrum (600MHz, $CDCl_3$, 303K) of bengamide P **2**

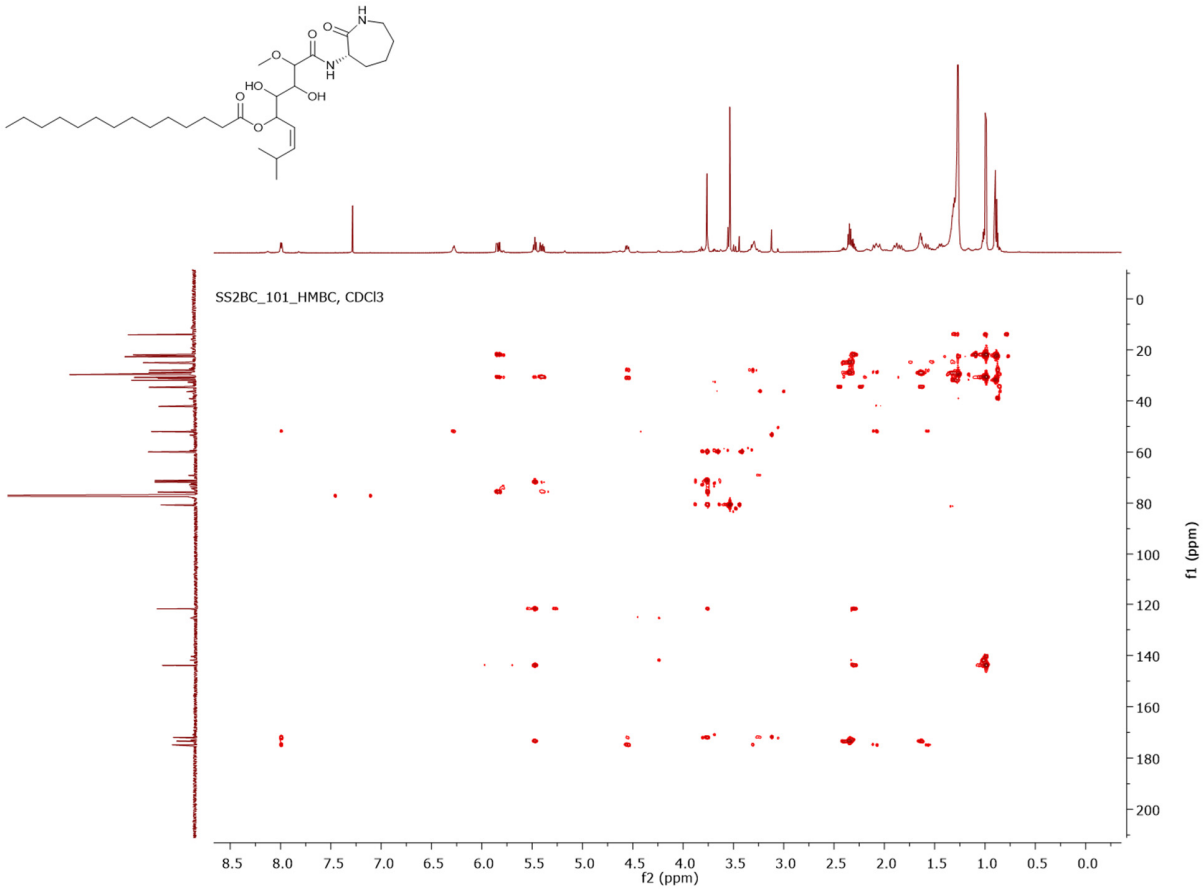

Figure S12. HMBC NMR spectrum (600MHz, $CDCl_3$, 303K) of bengamide P **2**

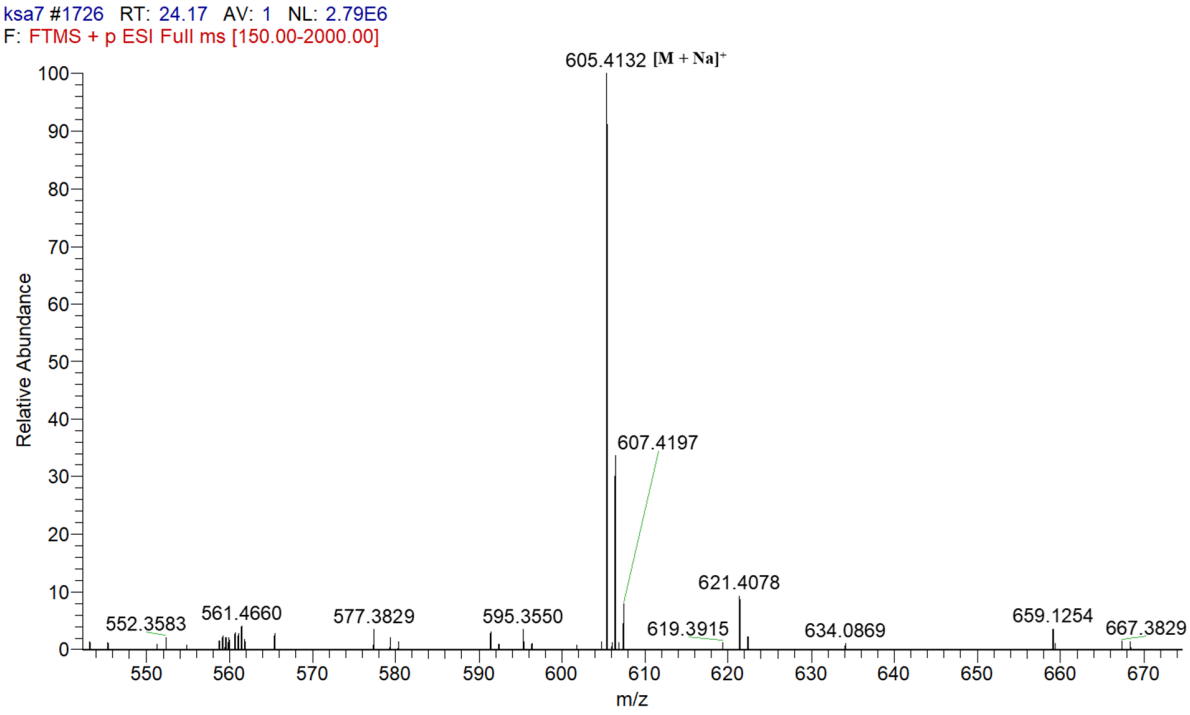

Figure S13. HR-ESI-MS spectrum of bengamide Q **3**

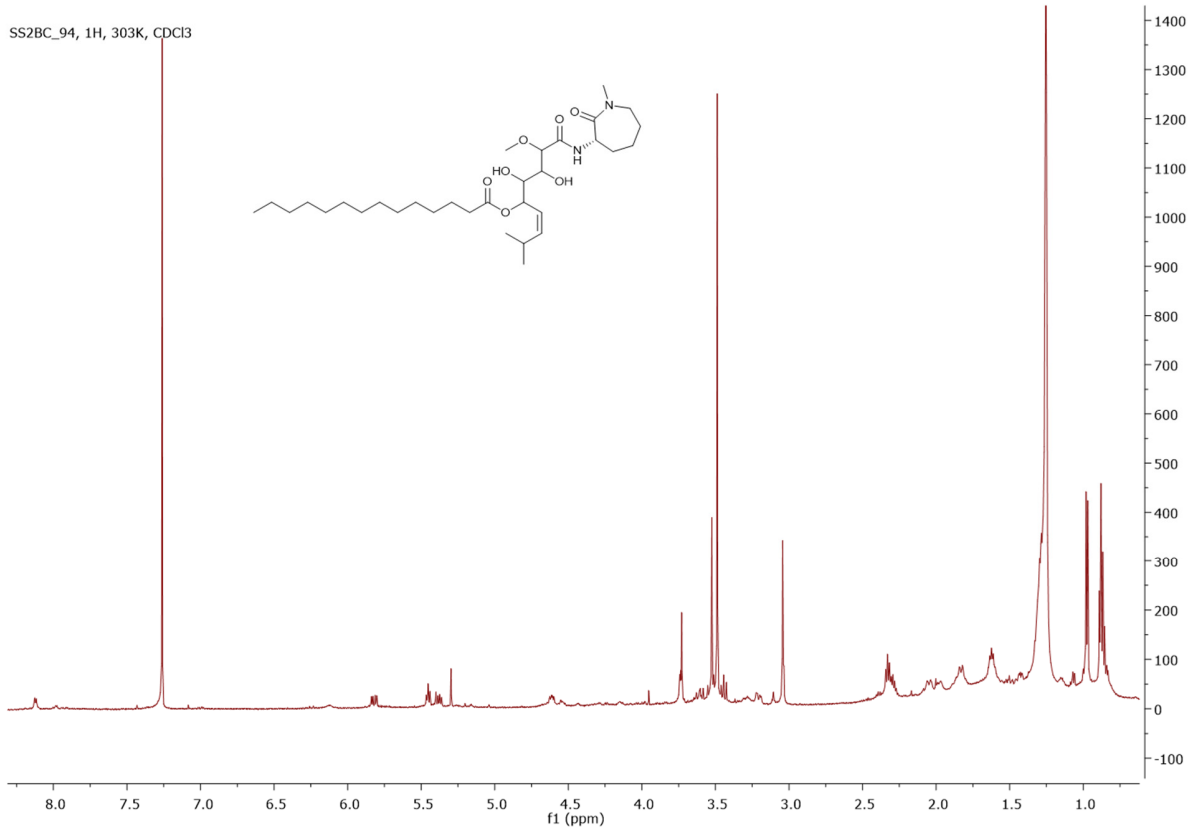

Figure S14. ^{1}H-NMR spectrum (600MHz, $CDCl_3$, 303K) of bengamide Q **3**

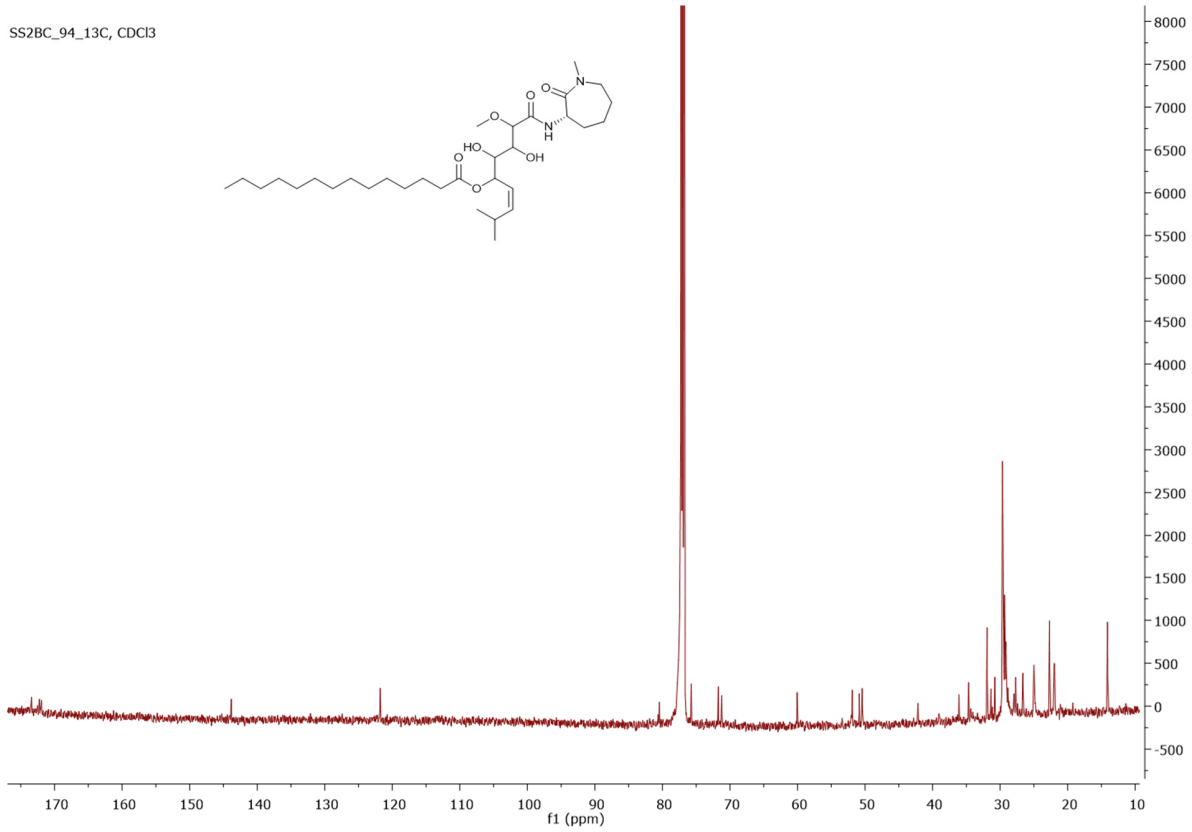

Figure S15. ^{13}C-NMR spectrum (150MHz, $CDCl_3$, 303K) of bengamide Q **3**

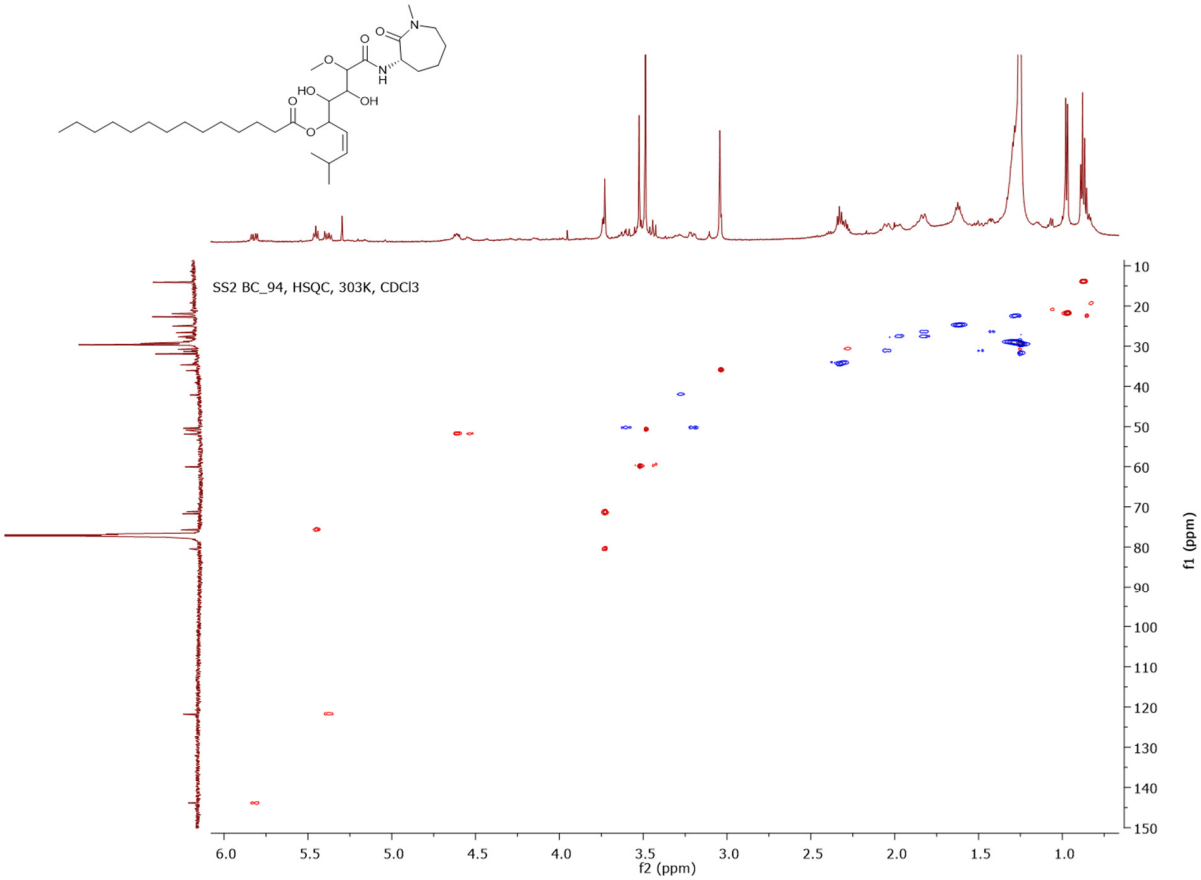

Figure S16. HSQC NMR spectrum (600MHz, $CDCl_3$, 303K) bengamide Q **3**

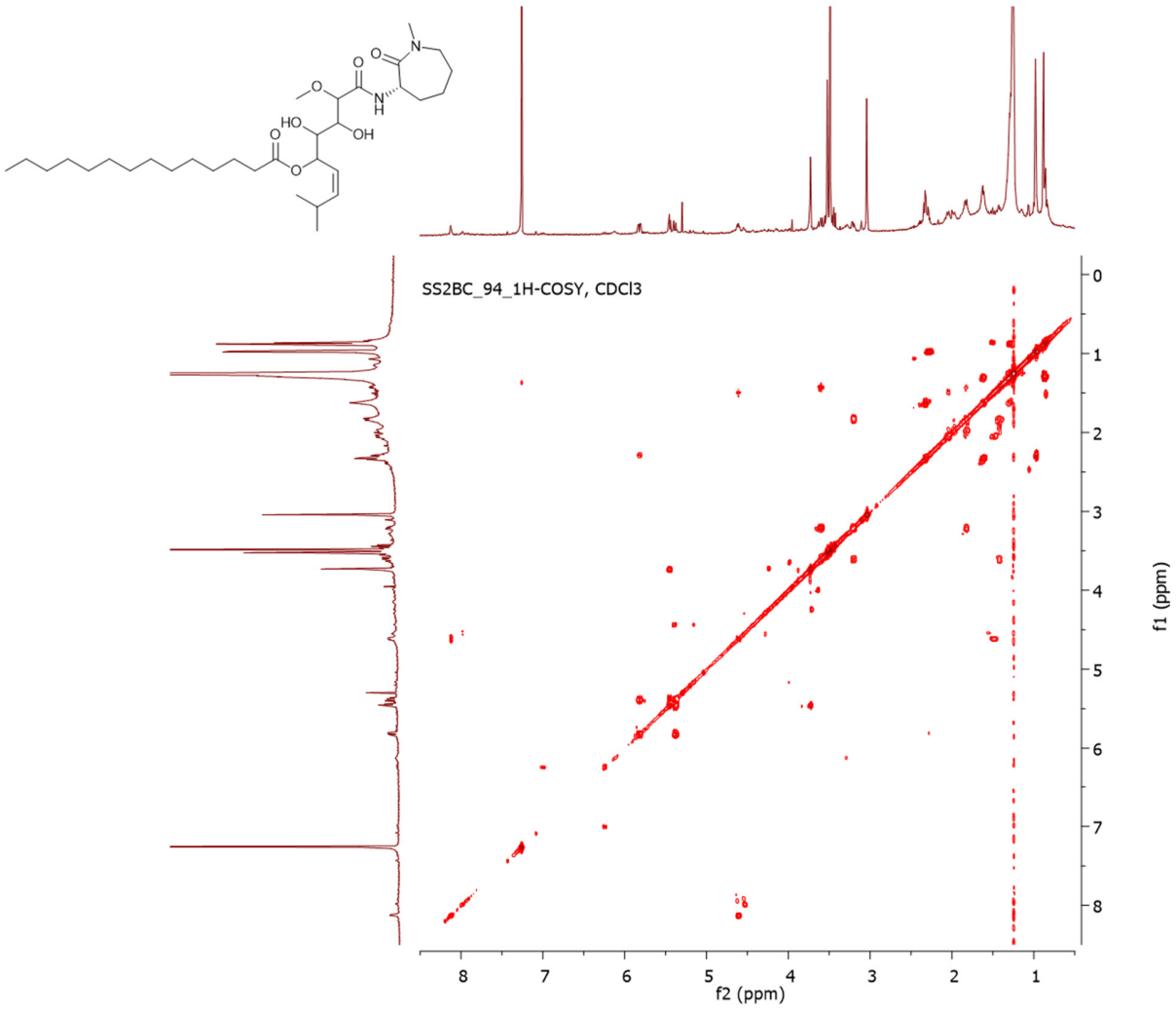

Figure S17. ^{1}H-^{1}H COSY spectrum (600MHz, $CDCl_3$, 303K) of bengamide Q **3**

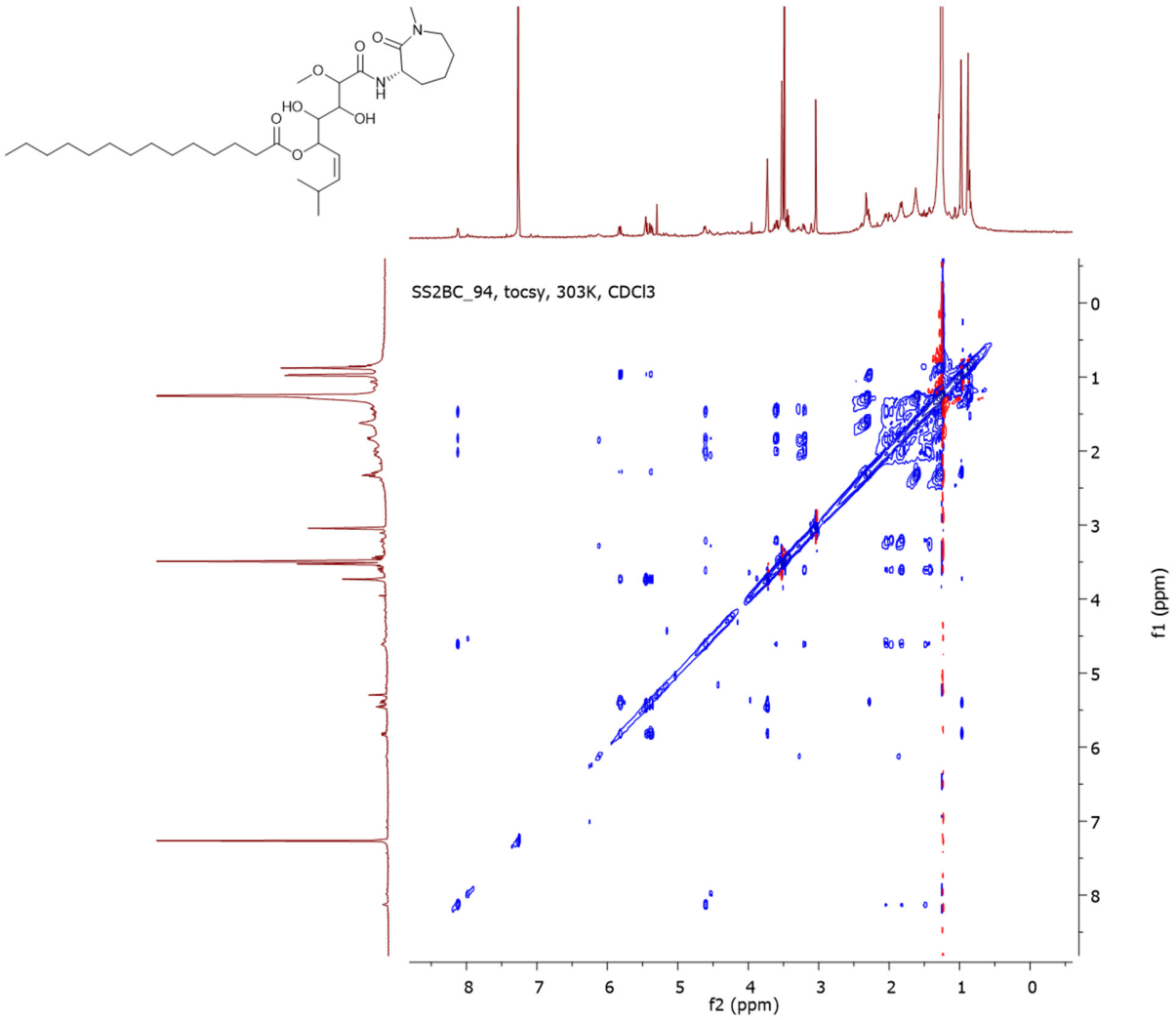

Figure S18. ^{1}H-^{1}H TOCSY spectrum (600MHz, $CDCl_3$, 303K) of bengamide Q **3**

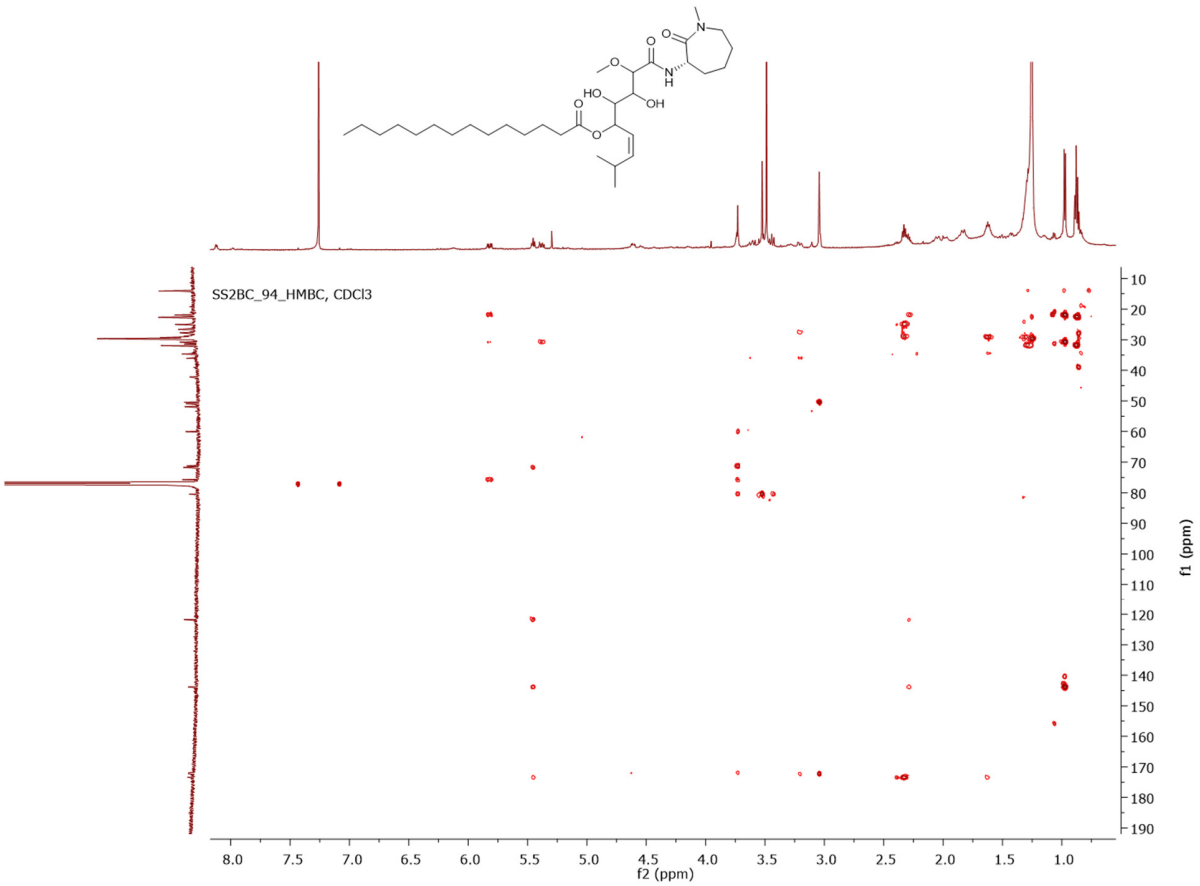

Figure S19. HMBC NMR spectrum (600MHz, $CDCl_3$, 303K) of bengamide Q **3**

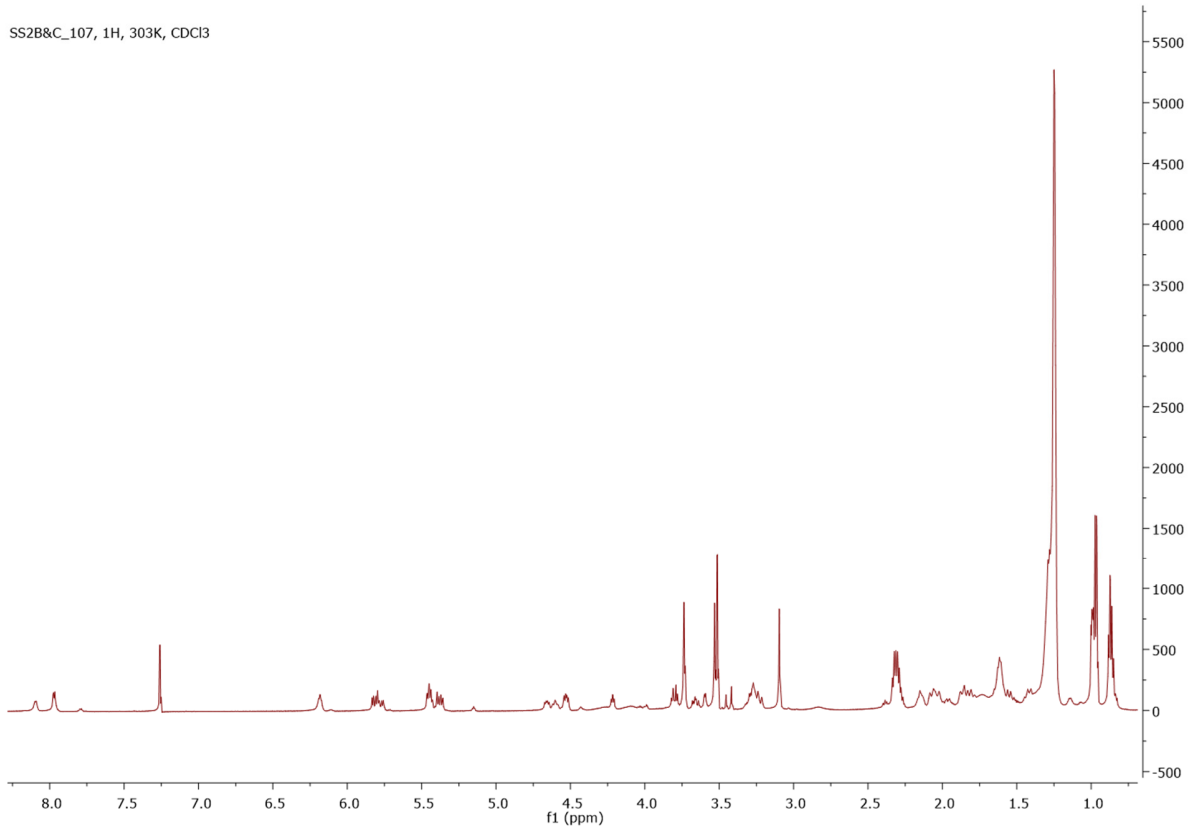

Figure S20. ^{1}H-NMR spectrum (600MHz, $CDCl_3$, 303K) of F107

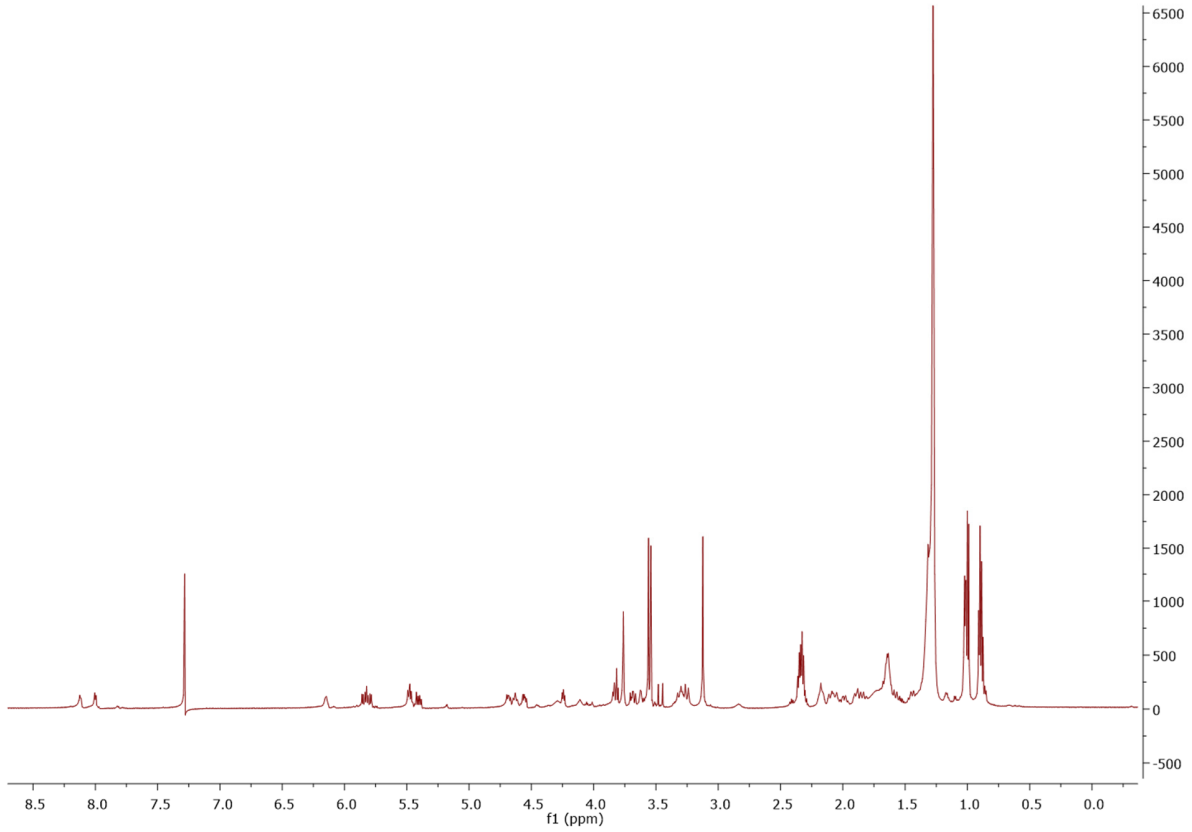

Figure S21. ^{1}H-NMR spectrum (600MHz, $CDCl_3$, 303K) of F114

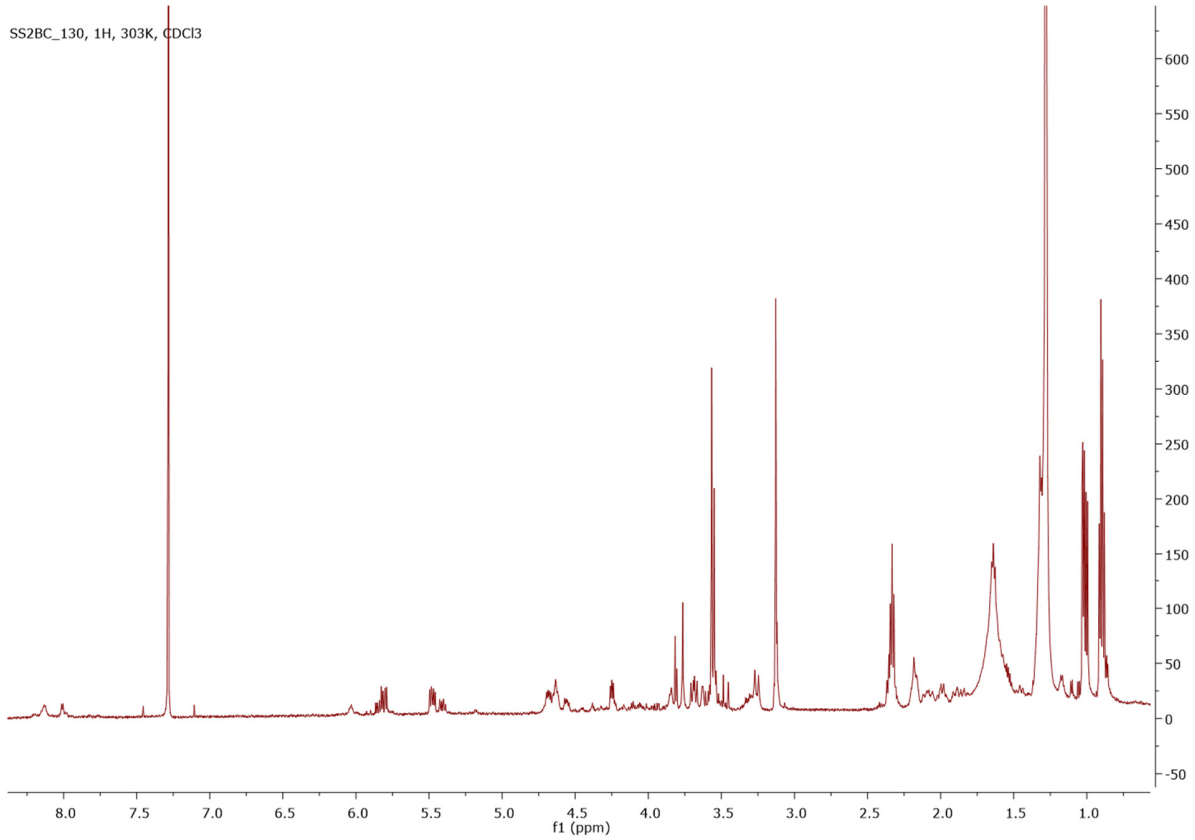

Figure S22. ^{1}H-NMR spectrum (600MHz, $CDCl_3$, 303K) of F130

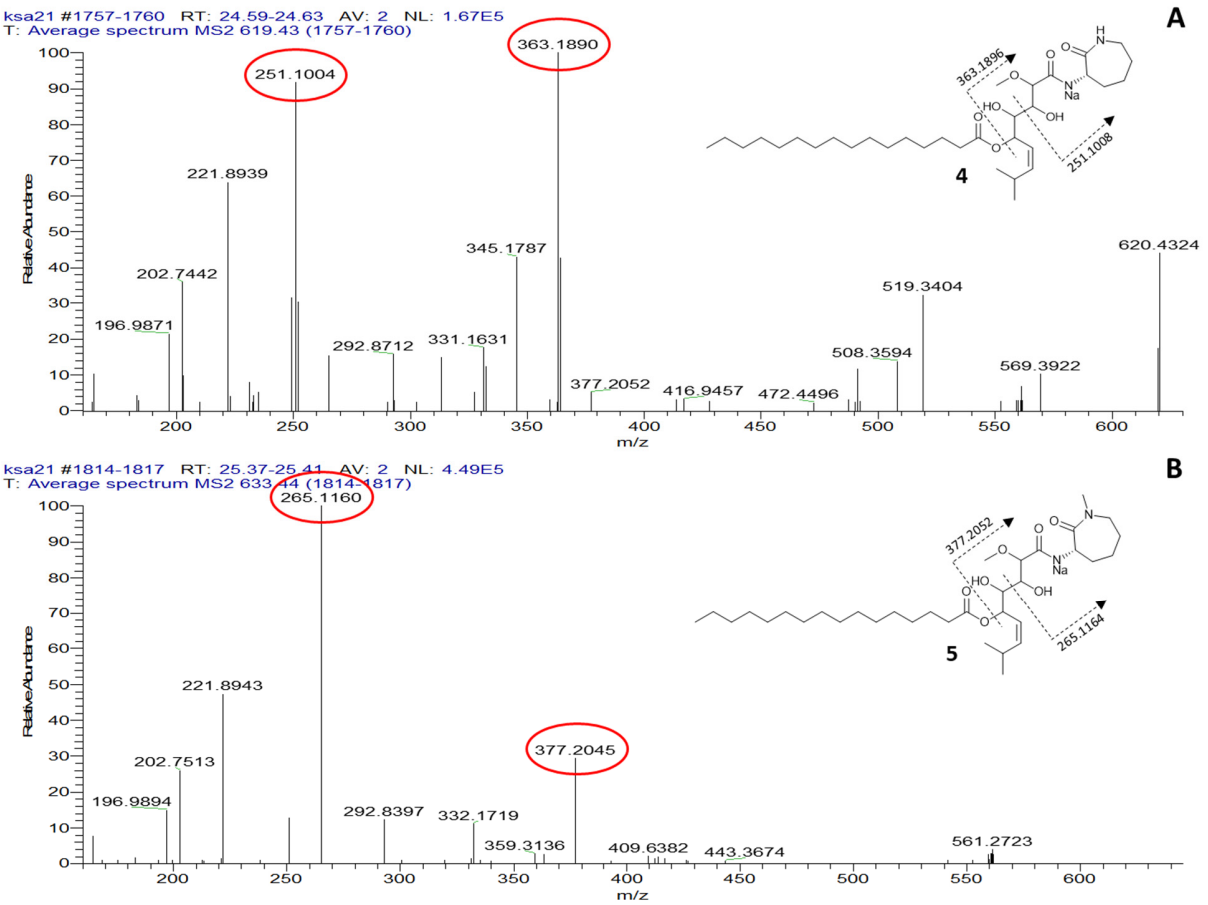

Figure S23. MS/MS fragmentation pattern of bengamide R **4** (A) and bengamide S **5** (B) with fragment ions circled in red showing methylation is on the nitrogen of the caprolactam ring.

Table S1. ^{13}C and ^{1}H chemical shifts of Heteronemin **1** isolated and that reported in literature.

	Isolated		Literature[1]	
Position	^{13}C	^{1}H, mult. (*J*, Hz)	^{13}C	^{1}H, mult. (*J*, Hz)
1	39.9	1.69 0.78	39.9	
2	18.2	1.53 1.36	18.2	
3	42.1	1.37 td J=4.03, 13.45, 13.51 1.11	42.0	
4	33.2		33.2	
5	56.5	0.78	56.5	
6	18.6	1.60 1.42	18.6	
7	41.9	1.73 0.91	41.8	
8	37.4		37.4	
9	58.8	0.78	58.8	
10	38.1		38.1	
11	27.2	1.69 1.46	27.2	
12	80.6	3.45 dd *J*=3.99, 11.37	80.5	3.44, dt, J =3.8.11.3
13	42.7		42.7	
14	54.8	0.92	54.7	
15	28.0	2.05 1.40	28.0	
16	69.4	5.36 dd J=6.06, 10.43	69.3	5.38 (dd,J = 4,10Hz)
17	114.4		114.4	
18	64.2	2.42	64.2	2.42
19	101.7	6.76 d *J*=1.38	101.6	6.77 (d, J= 1.3 Hz)
20	135.4	6.15 t *J*=1.93	135.3	6.17 (t, J = 2 Hz)
21	33.3	0.84	33.2	0.87
22	21.3	0.79	21.3	0.77
23	16.3	0.82	16.3	0.79
24	17.3	0.82	17.3	0.81
25	8.8	0.90	8.8	0.81
OAc	21.4	2.09	21.2	2.07
OAc	21.0	2.09	21.0	2.07
CO	171.3		171.3	
CO	170.1		170.1	

Table S2. ^{13}C and ^{1}H chemical shifts of bengamide P **2** isolated and that reported in literature.

	Isolated		Literature[2]	
Position	^{13}C	^{1}H, mult. (*J*, Hz)	^{13}C	^{1}H, mult. (*J*, Hz)
17	174.9		175.1	
16	173.3		173.6	
9	172.0		172.2	
3	143.8	5.84 (1H, dd, J= 6.47, 15.42 Hz)	144.1	5.83 (1H, dd, J= 6.5, 16.0 Hz)
4	121.8	5.40 (1H, dd, J= 7.84, 15.41 Hz)	122.0	5.39 (1H, dd, J= 7.5, 16.0 Hz)
8	80.7	3.76 (1H, bs)	80.8	3.74 (1H, bs)
5	75.7	5.47 (1H, t= 7.60 Hz)	75.9	5.47 (1H, t= 7.5 Hz)
7	71.8	3.75 (1H, bs)	72.0	3.74 (1H, bs)
6	71.2	3.75 (1H, bs)	71.4	3.74 (1H, bs)
13	28.8	1.88 (1H, m) 1.43 (1H, m)	29.1	1.86 (1H, m) 1.43 (1H, m)
OMe	60.0	3.53 (3H, s)	60.2	3.53 (3H, s)
10	52.0	4.55 (1H, m)	52.2	4.54 (1H, m)
14	42.1	3.29 (2H, m)	42.3	3.29 (2H, m)
18	34.6	2.34 (2H, t, J=7.32)	34.9	2.34 (2H, t, J=7.5)
12	27.9	2.05 (1H, m) 1.84 (1H, m)	28.2	2.07 (1H, m) 1.86 (1H, m)
28	31.9	1.27 (2H, m)	32.1	1.26 (2H, m)
2	30.9	2.30 (1H, m)	30.0	2.34 (1H, m)
20-27	30.8-29.1	1.27 (16H, m)	30.0-29.3	1.26 (16H, m)
11	31.1	2.09 (1H, m) 1.56 (1H, m)	31.4	2.07 (1H, m) 1.60 (1H, m)
19	25.0	1.64 (2H, m)	25.2	1.60 (2H, m)
29	22.8	1.28 (2H, m)	22.9	1.26 (2H, m)
1,15	21.9, 22.0	0.99 (6H, d J=6.88 Hz)	22.1,22.2	0.98 (6H, d J=7.0 Hz)
30	14.1	0.88 (3H, t J=7.08 Hz)	14.3	0.89 (3H, t J=7.0 Hz)

Table S3. ^{13}C and ^{1}H chemical shifts of bengamide Q **3** isolated and that reported in literature.

	Isolated		Literature[3]	
Position	^{13}C	^{1}H, mult. (J, Hz)	^{13}C	^{1}H, mult. (J, Hz)
17	173.4		173.6	
16	172.2		172.4	
9	171.9		172.1	
3	143.8	5.82 (1H, dd, J=6.47, 15.42 Hz)	144.0	5.83 (1H, dd, J=6.5, 16.0 Hz)
4	121.8	5.38 (1H, dd, J=7.92, 15.39 Hz)	122.0	5.39 (1H, dd, J=7.5, 16.0 Hz)
8	80.4	3.74 (1H, bs)	80.6	3.74 (1H, bs)
5	75.7	5.45 (1H, t, J=7.64 Hz)	75.9	5.46 (1H, t, J=7.5 Hz)
7	71.7	3.72 (1H, bs)	71.9	3.74 (1H, bs)
6	71.2	3.72 (1H, bs)	71.4	3.74 (1H, bs)
13	26.6	1.82 (1H, m) 1.42 (1H, m)	27.9	1.84 (1H, m) 1.47 (1H, m)
OMe	60.1	3.50 (3H, s)	60.3	3.54 (3H, s)
10	51.6	4.61 (1H, m)	50.6	4.62 (1H, m)
NMe	36.1	3.03 (3H, s)	36.3	3.05 (3H, s)
14	50.4	3.60 (1H, dd, J=15.50, 11.51) 3.21 (1H, dd, J=5.45, 15.53)	52.1	3.62 (1H, dd, J=15.5, 11.5) 3.22 (1H, dd, J=5.5, 15.5)
18	34.7	2.32 (2H, m)	34.9	2.34 (2H, t, J=7.5)
12	27.7	1.97 (1H, m) 1.82 (1H, m)	26.8	2.02 (1H, m) 1.84 (1H, m)
28	31.9	1.25 (2H, m)	32.1	1.26 (2H, m)
2	30.8	2.28 (1H, m)	31.0	2.34 (1H, m)
20-27	29.7-29.2	1.26 (16H, m)	29.9-29.3	1.26 (16H, m)
11	31.4	2.04 (1H, m) 1.49 (1H, m)	31.5	2.02 (1H, m) 1.63 (1H, m)
19	25.0	1.62 (2H, m)	25.2	1.63 (2H, m)
29	22.7	1.27 (2H, m)	22.9	1.26 (2H, m)
1,15	22.0, 21.9	0.97 (6H, d J=6.74 Hz)	22.2-22.1	0.98 (6H, d J=6.5 Hz)
30	14.3	0.87 (3H, t J=6.81 Hz)	14.3	0.89 (3H, t J=6.5 Hz)

Table S4. Compounds isolated and tentatively identified in the molecular cluster of the crude extract (SS2) of the sponge Jaspis splendens with their corresponding masses (observed and calculated), molecular formulae (MF), and mass error (ID (Δ ppm))

Compound	m/z ($[M+Na]^+$) Observed	m/z ($[M+Na]^+$) Calculated	MF	ID Δ ppm
Bengamide P	591.3978	591.3966	$C_{31}H_{56}N_2O_7$	2.03
Bengamide Q	605.4133	605.4122	$C_{32}H_{58}N_2O_7$	1.82
Bengamide A Bengamide N Bengamide H	607.3928	607.3915	$C_{31}H_{56}N_2O_8$	2.14
Bengamide R	619.4286	619.4279	$C_{33}H_{60}N_2O_7$	1.13
Bengamide B Bengamide I Bengamide L Bengamide O	621.4084	621.4071	$C_{32}H_{59}N_2O_8$	2.09
Bengamide J Bengamide M	635.4233	635.4228	$C_{33}H_{60}N_2O_8$	0.78
Bengamide S	633.4446	633.4455	$C_{34}H_{62}N_2O_7$	-1.42

References

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3. Thale, Z. *et al.* Bengamides Revisited : New Structures and Antitumor Studies. *J. Org. Chem.* 2001, 66, 1733–1741.