Supporting Information

for

A dereplication and bioguided discovery approach to reveal new compounds from a marine-derived fungus *Stilbella fimetaria*

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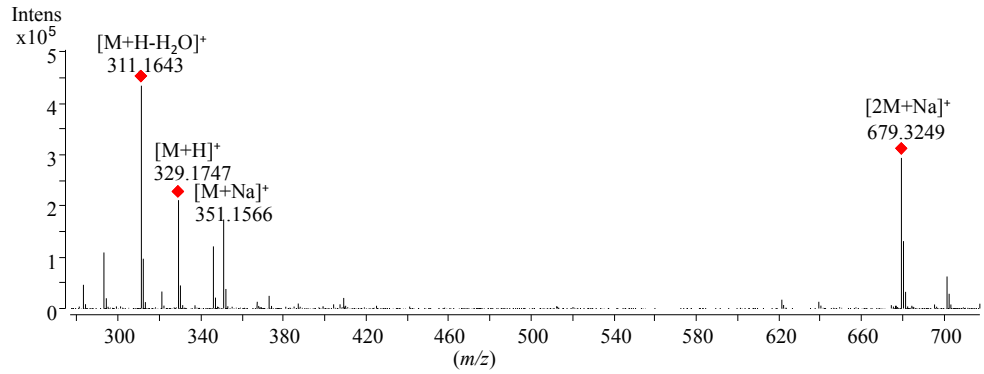
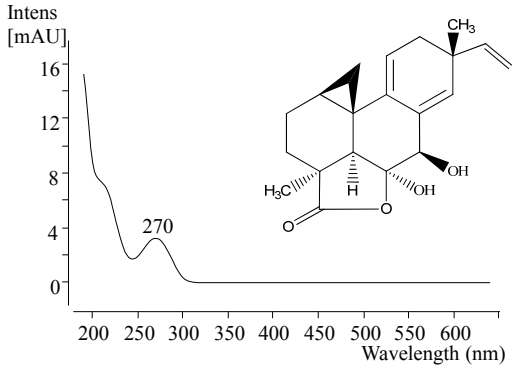
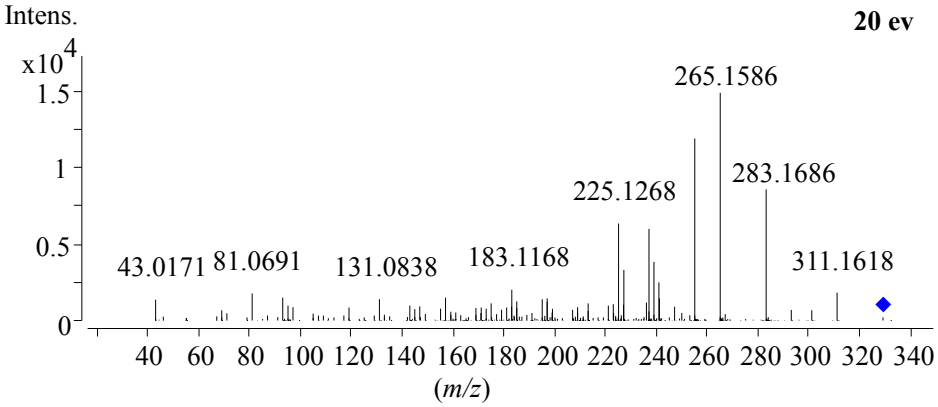
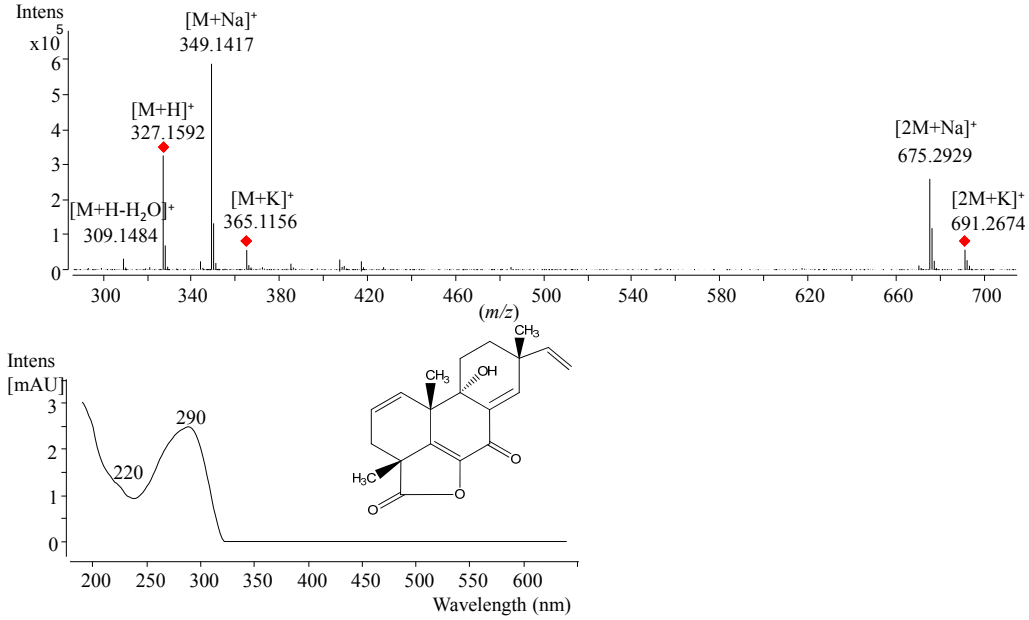
S1: MS and UV and MS/HRMS (20 eV) spectra of myrocin F

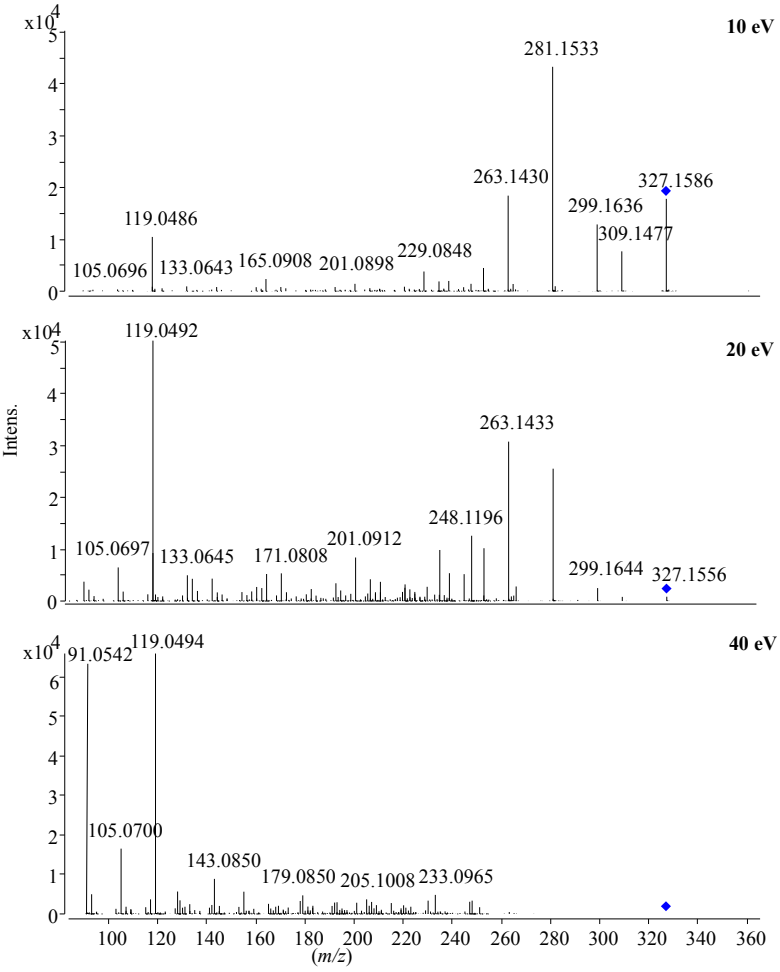




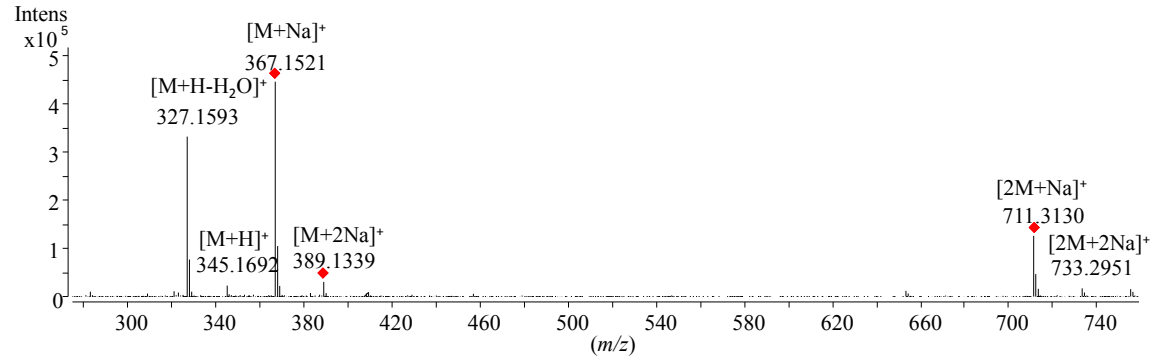


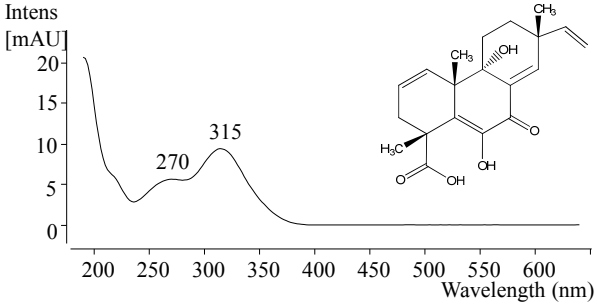
S2: MS, MS/HRMS (10, 20 and 40 eV) and UV spectra of libertellenone M

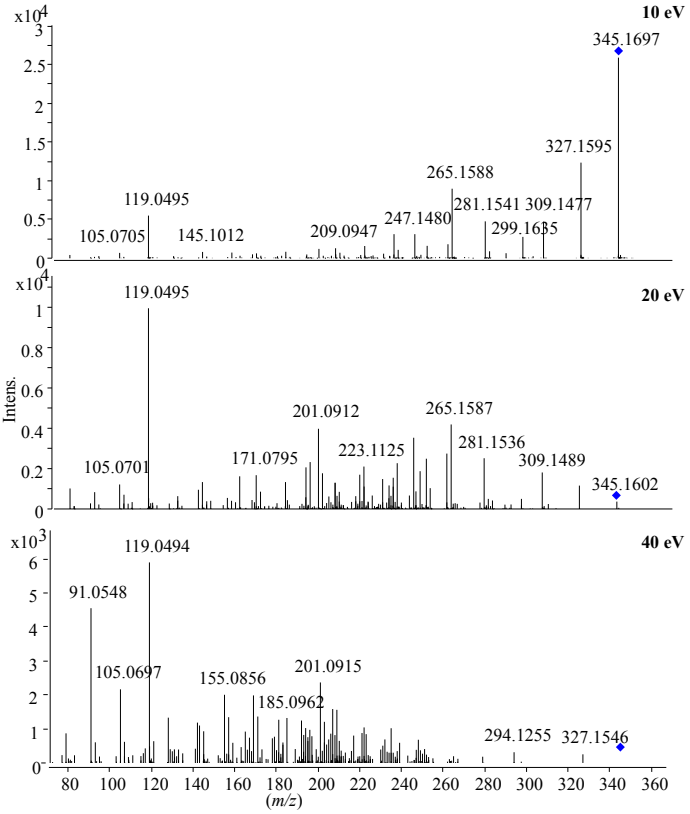




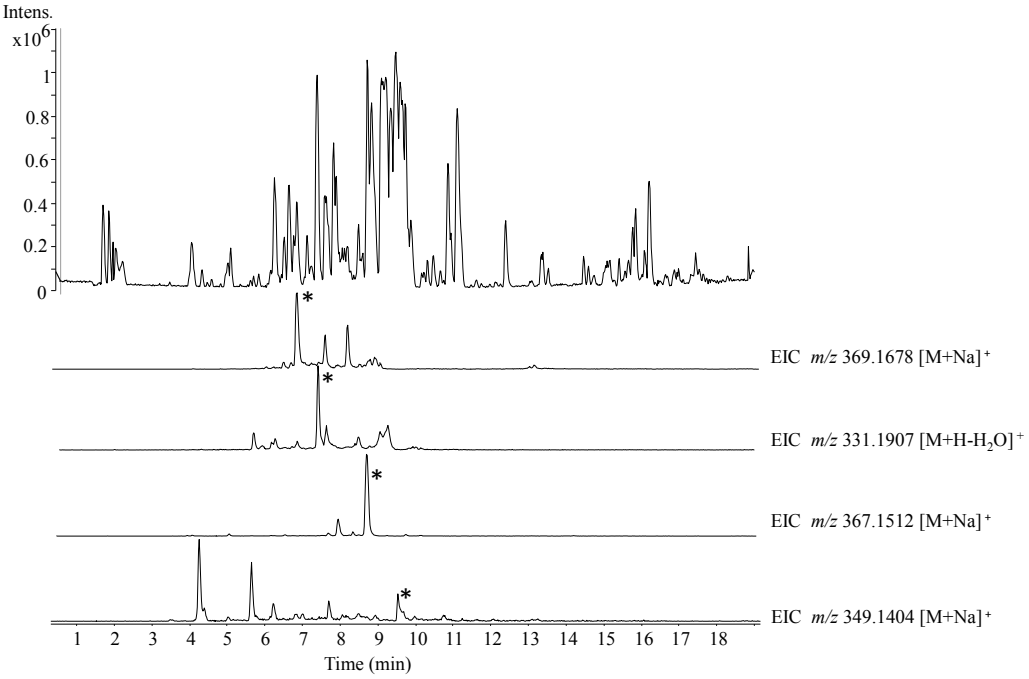
S3: MS, MS/HRMS (10, 20 and 40 eV) and UV spectra of opened γ-lactam libertellenone M



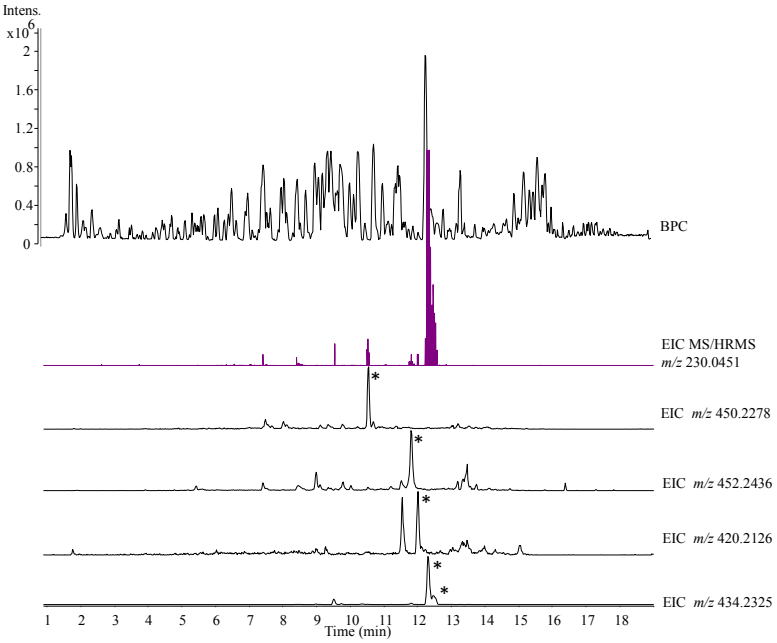




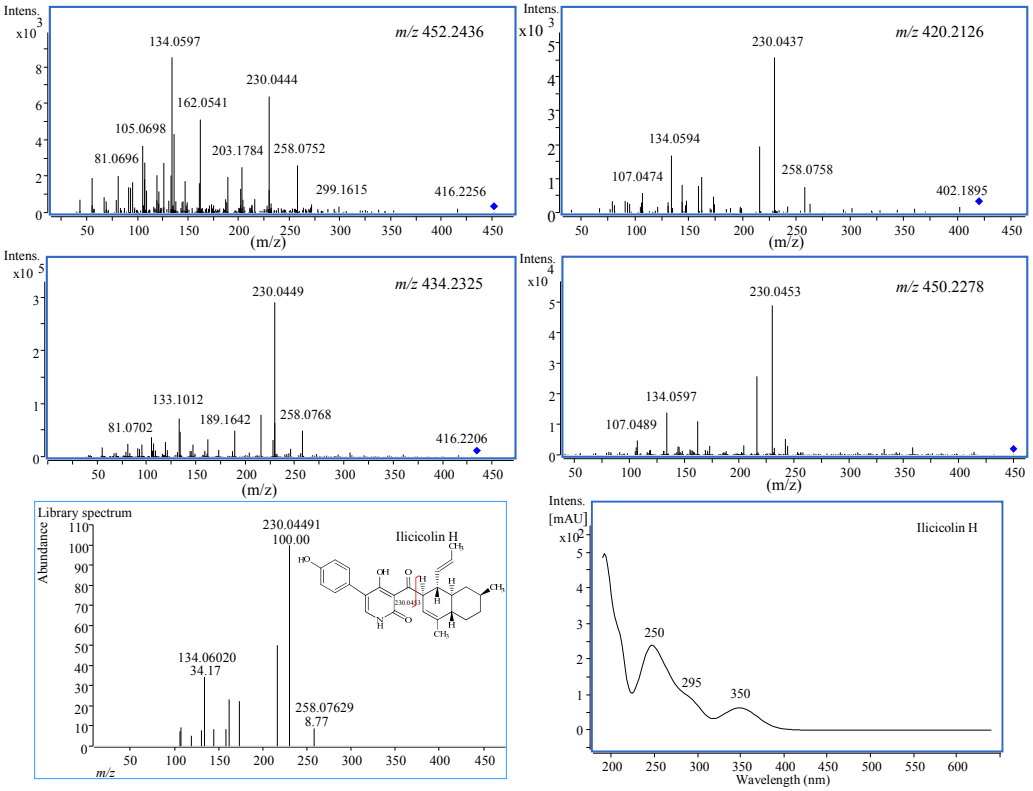
S4: BPC of the rice crude extract with EIC from HRMS showing the most abundant ion of the diterpenes: libertellenone E (*m/z* 369.1678 $[M+Na]^+$), libertellenone C (*m/z* 331.1907 $[M+H-H_2O]^+$), opened γ-lactone ring of libertellenone M libertellenone M (*m/z* 367.1512 $[M+Na]^+$) and libertellenone M (*m/z* 349.1404 $[M+Na]^+$).



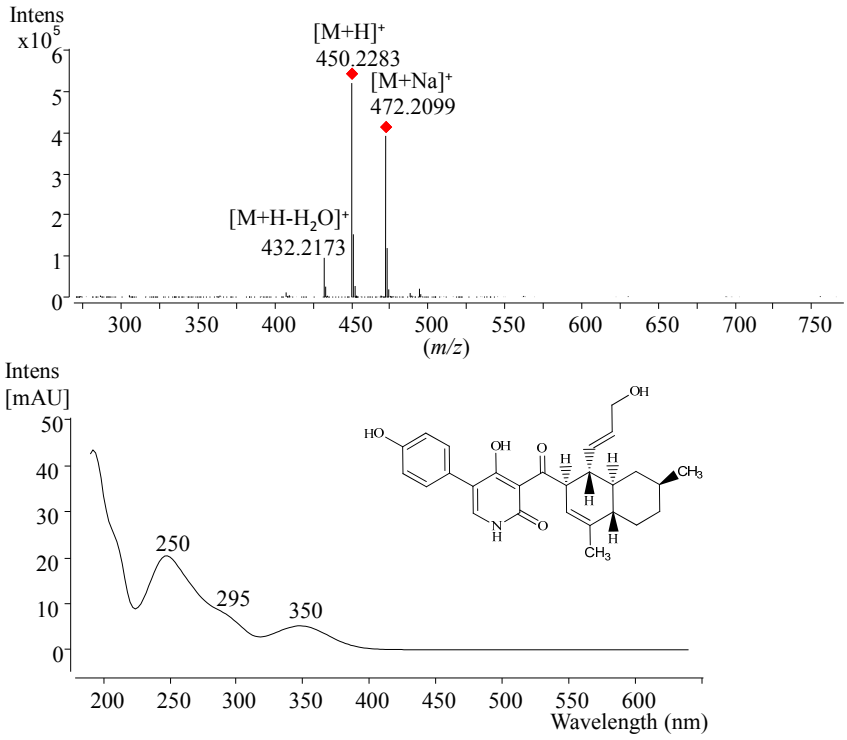
S5: BPC of the rice crude extract with EIC from MS/HRMS showing the fragment ion *m/z* 230.0451 and EIC from MS of *m/z* 450.2278, *m/z* 452.2436, *m/z* 420.2126 and *m/z* 434.2325 displaying ilicicolin H and the tentatively identified analogues and their position in the chromatogram



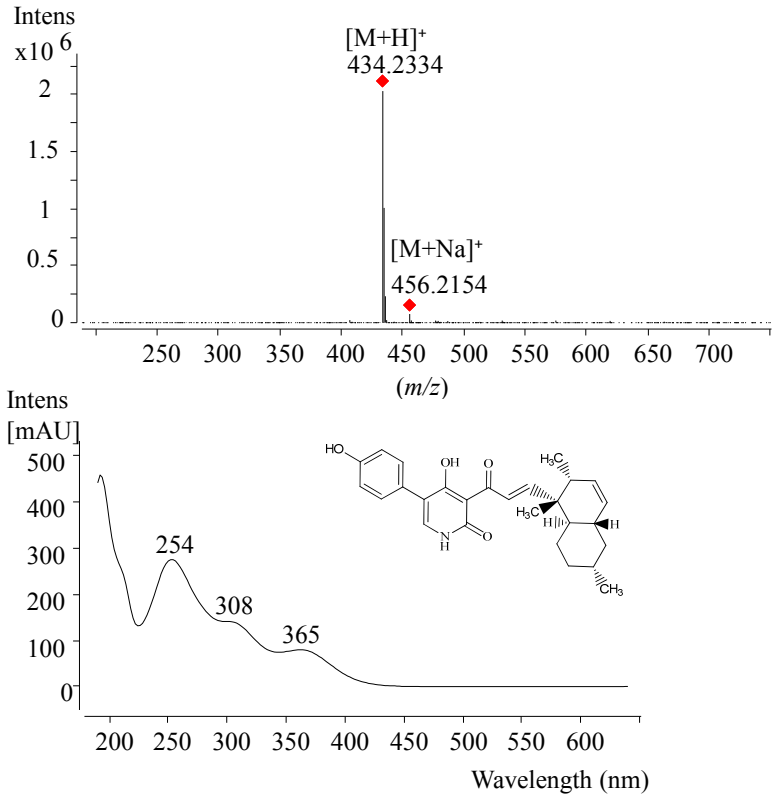
S6: MS/HRMS spectra, 40 eV of *m/z* 450.2278, *m/z* 452.2436, *m/z* 420.2126 and *m/z* 434.2325 compared to the library spectrum of ilicicolin H. UV spectrum of ilicicolin H.



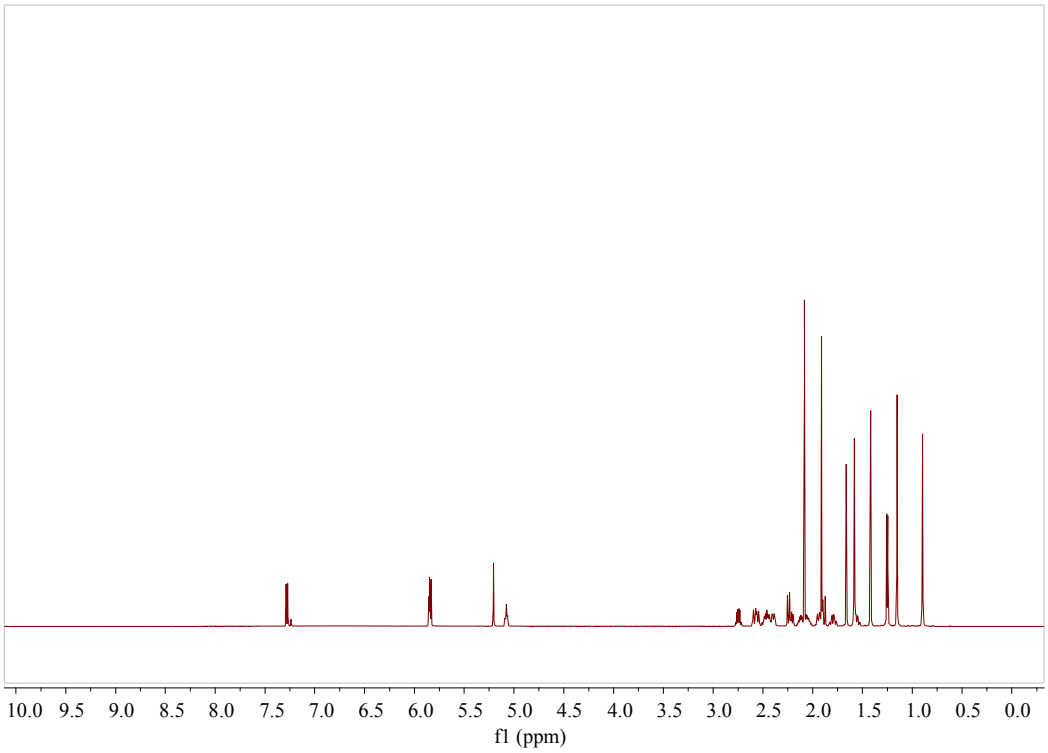
S7: MS and UV spectra of hydroxyl ilicicolin H ($C_{27}H_{31}NO_5$)



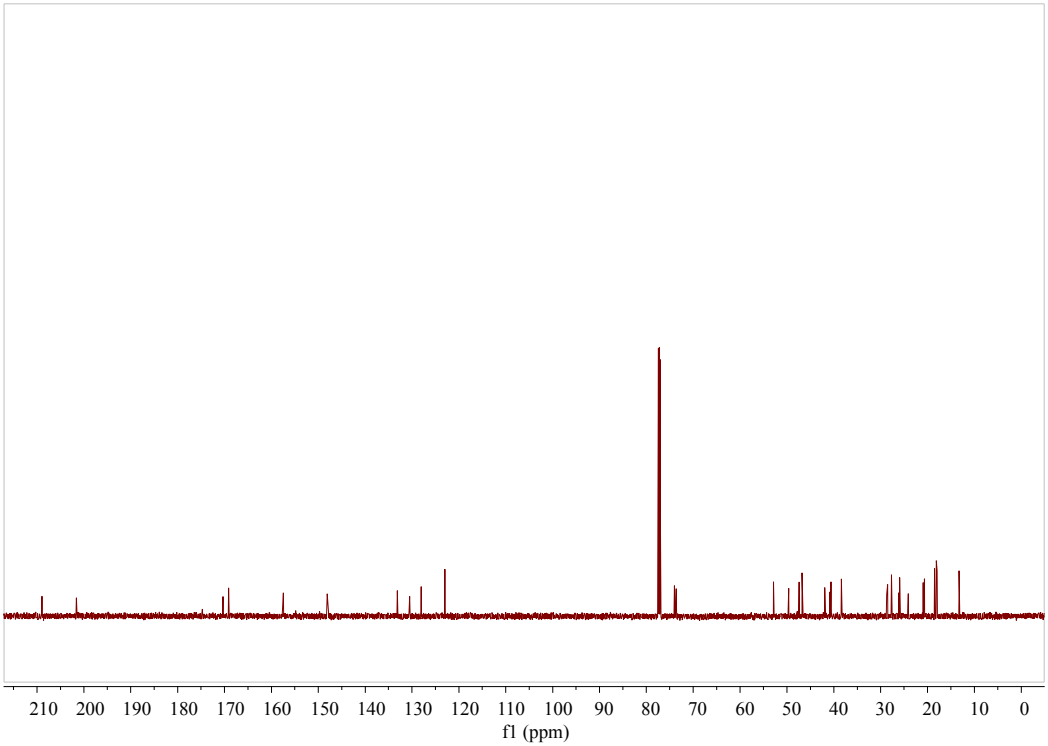
S8: MS and UV spectra of ilicicolin I ($C_{27}H_{31}NO_4$)



S9: ^{1}H NMR (600 MHz $CDCl_3$) of helvolic acid



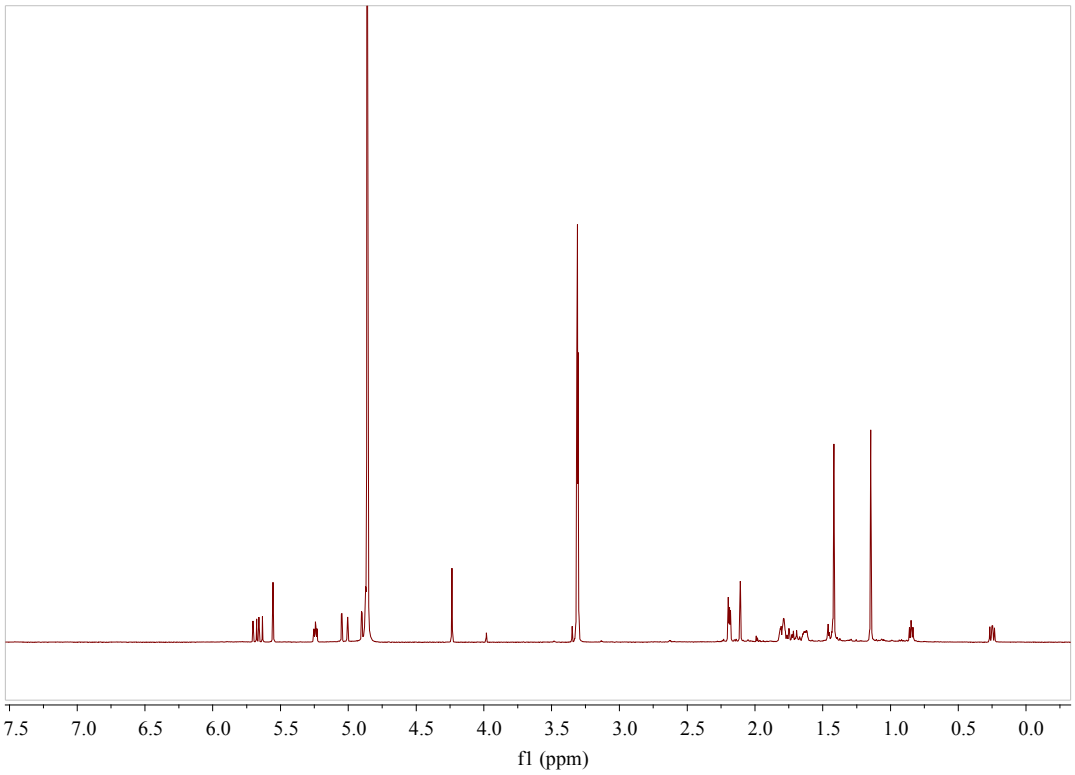
S10: ^{13}C NMR (600 MHz $CDCl_3$) of helvolic acid



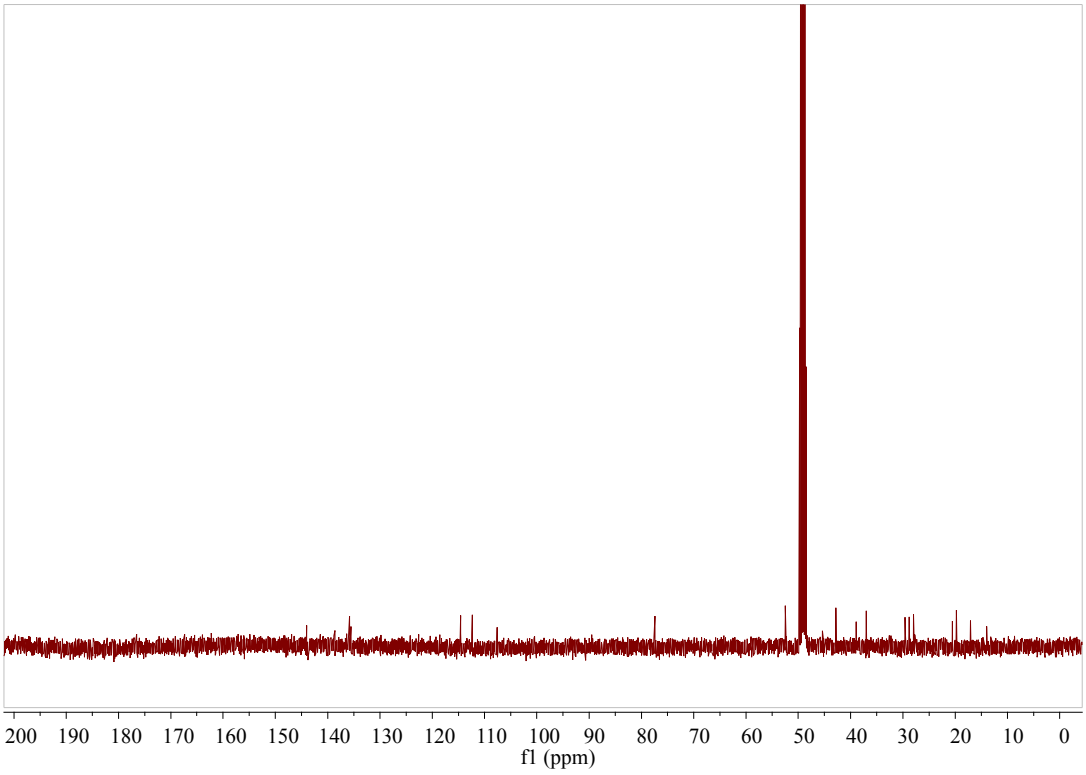
S11: Table 1. ^{13}C-NMR Spectroscopic Data (600 MHz CD_3Cl, δ in ppm) for helvolic acid

Position	δ ^{13}C
1	157.5
2	128.0
3	201.6
4	40.9
5	47.4
6	73.7
7	209.0
8	52.9
9	41.9
10	38.4
11	24.1
12	26.1
13	49.6
14	46.8
15	40.6
16	74.0
17	148.1
18	18.1
19	27.7
20	130.5
21	174.7
22	28.7
23	28.5
24	122.9
25	133.1
26	17.9
27	26.0
28	13.3
29	18.5
30/32	169.1/170.3
31/33	20.9/20.7

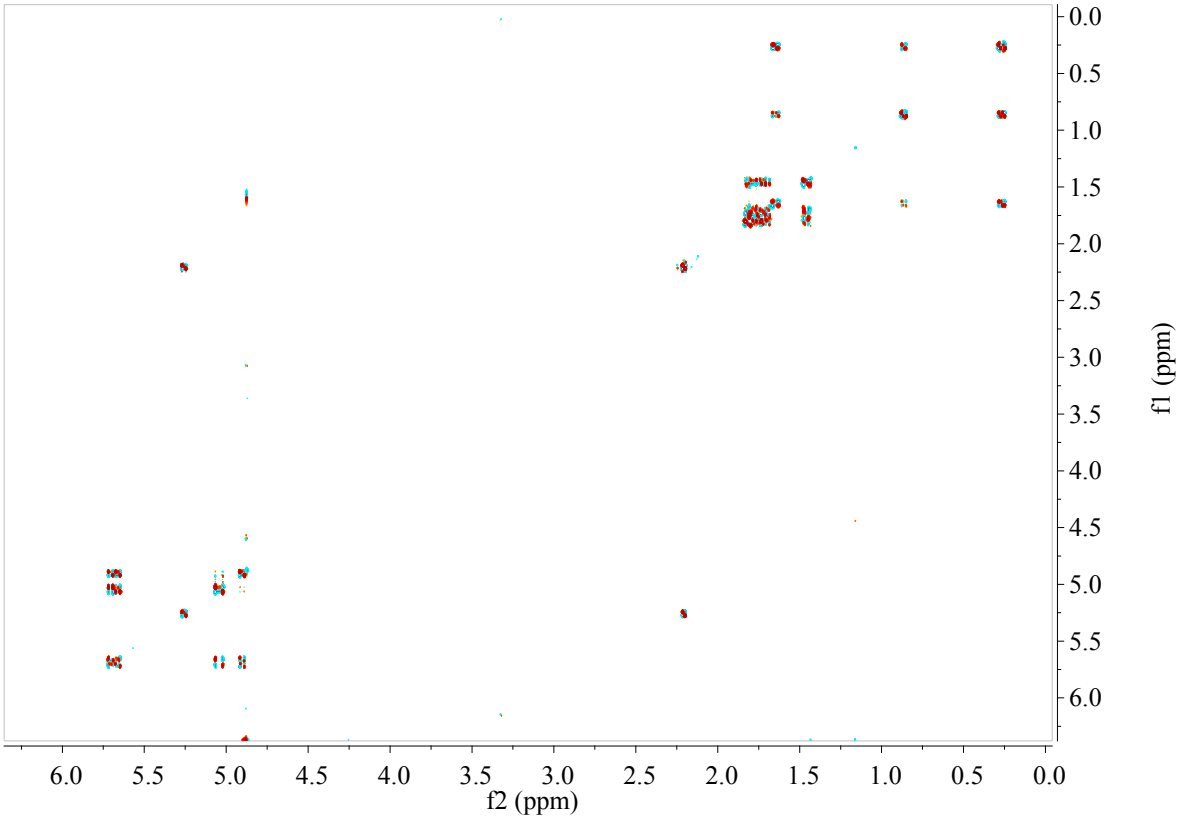
S12: ^{1}H-NMR 400 MHz MeOD of myrocin F



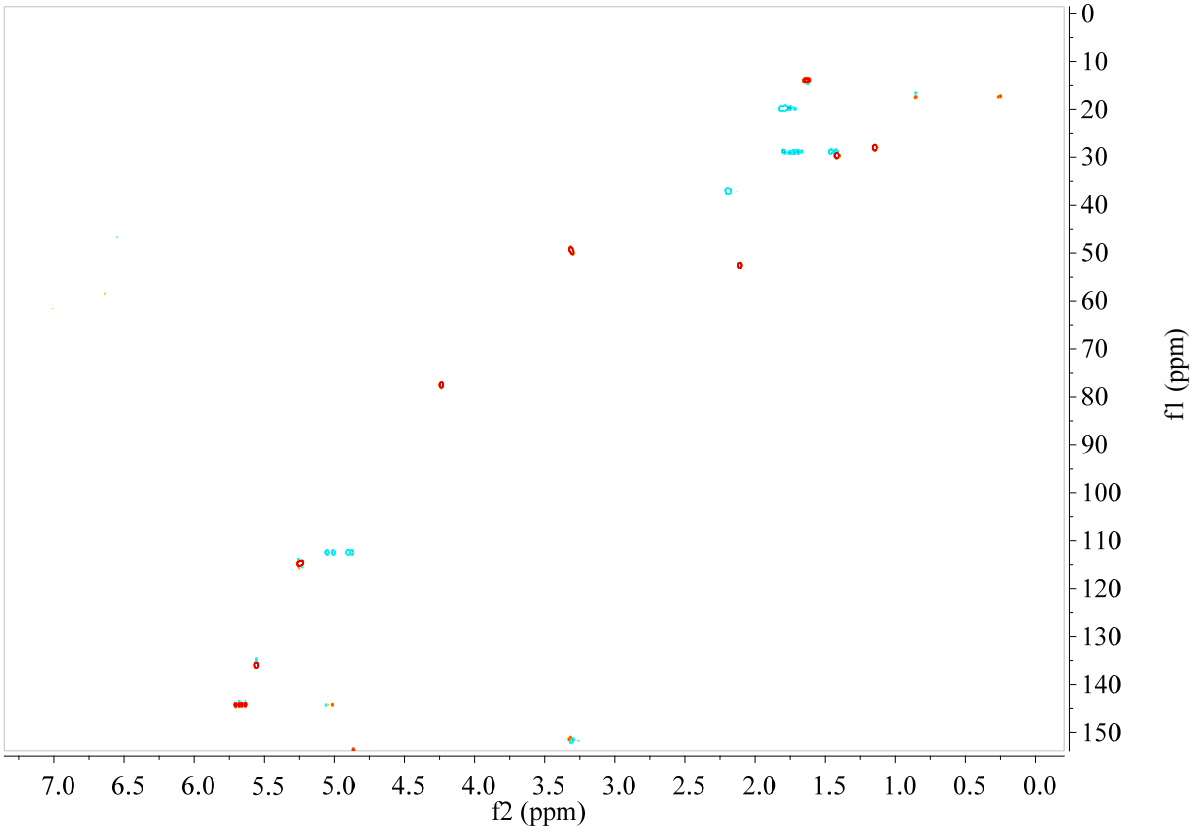
S13: ^{13}C NMR 400 MHz MeOD of myrocin F



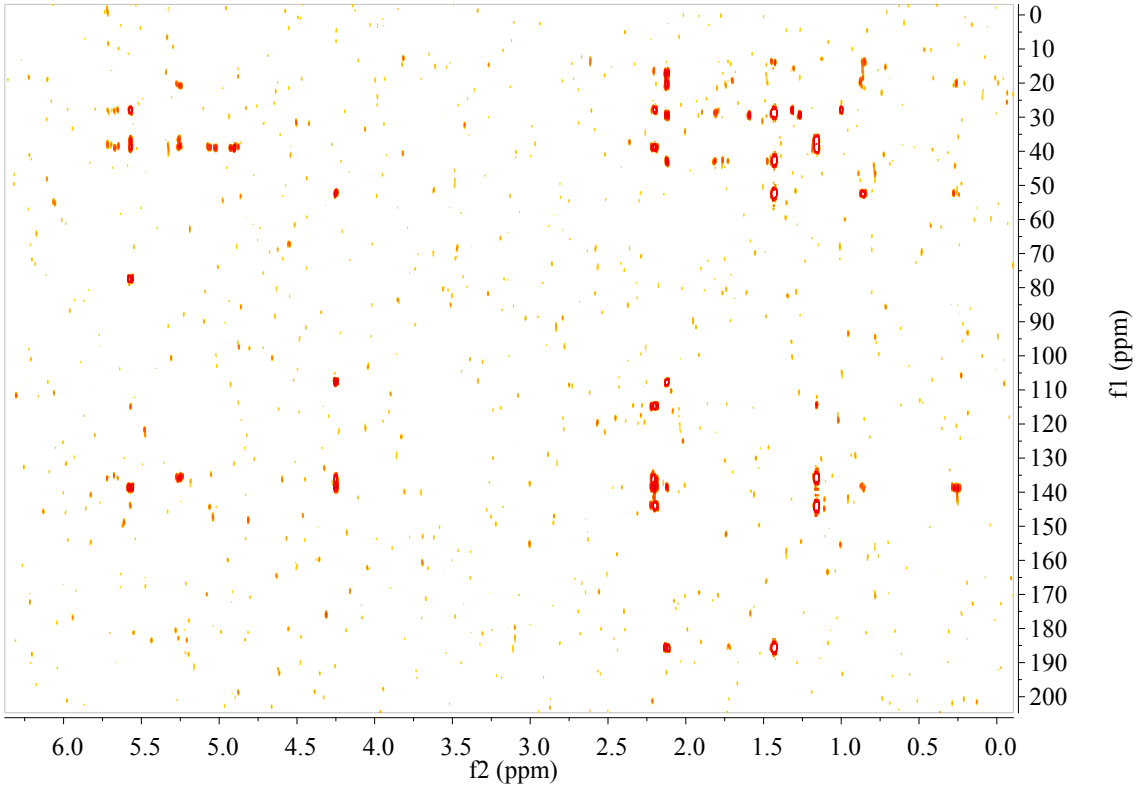
S14: COSY spectrum (400 MHz MeOD) of myrocin F



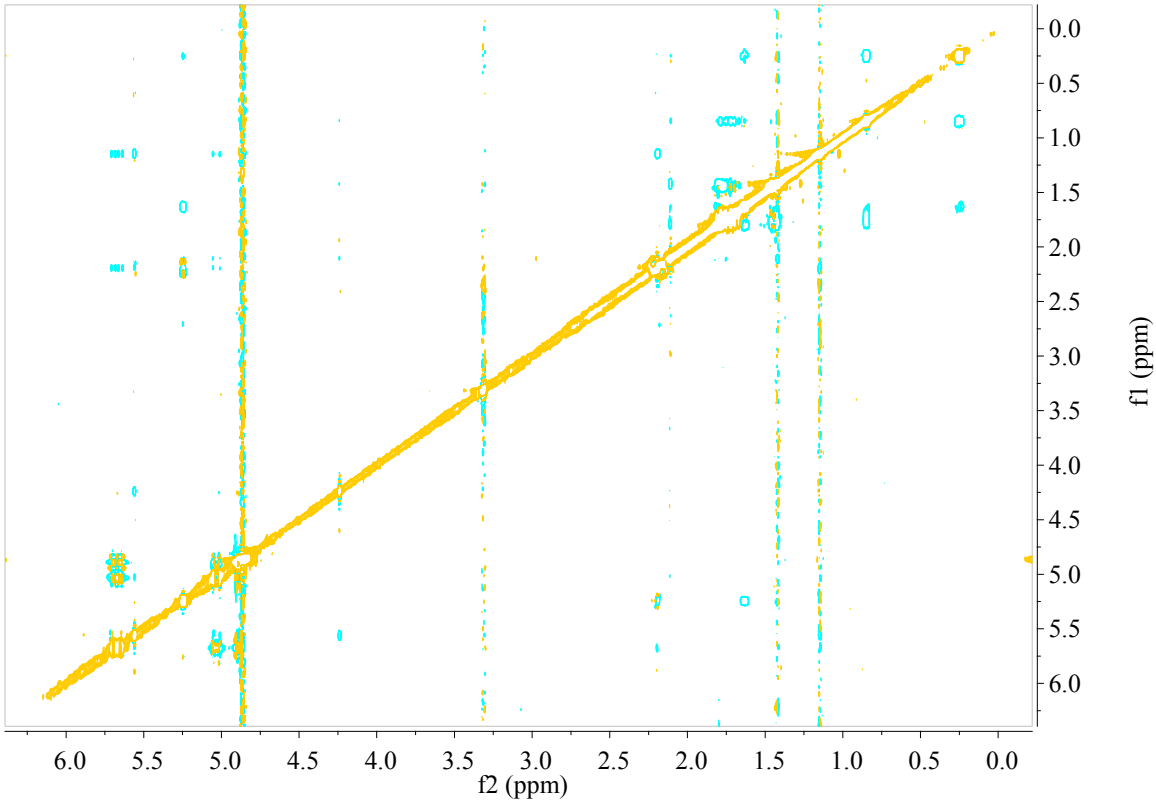
S15: Edited HSQC spectrum (400 MHz MeOD) of myrocin F



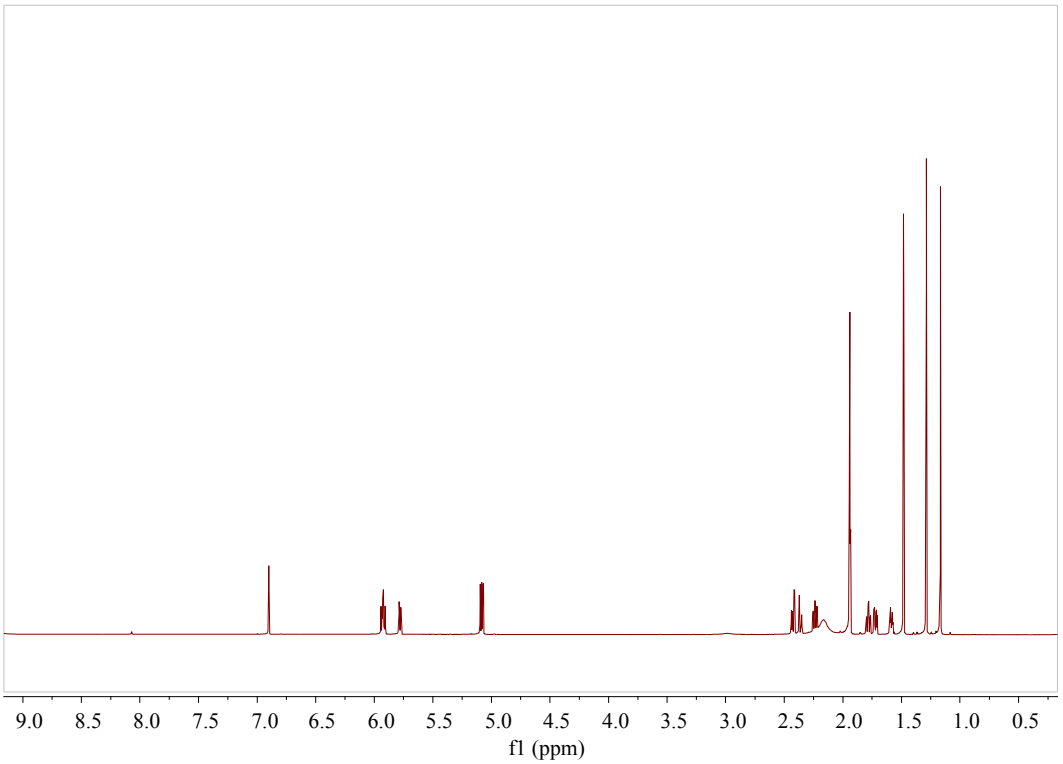
S16: HMBC spectrum (400 MHz MeOD) of myrocin F



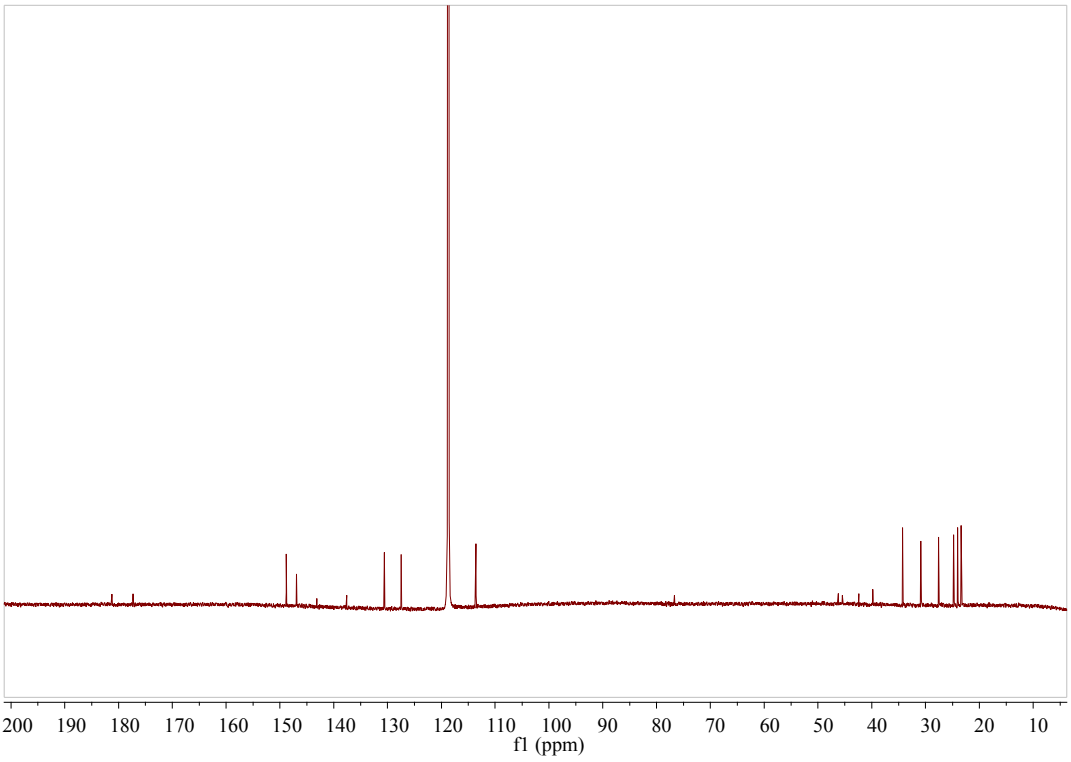
S17: NOESY spectrum (400 MHz MeOD) of myrocin F



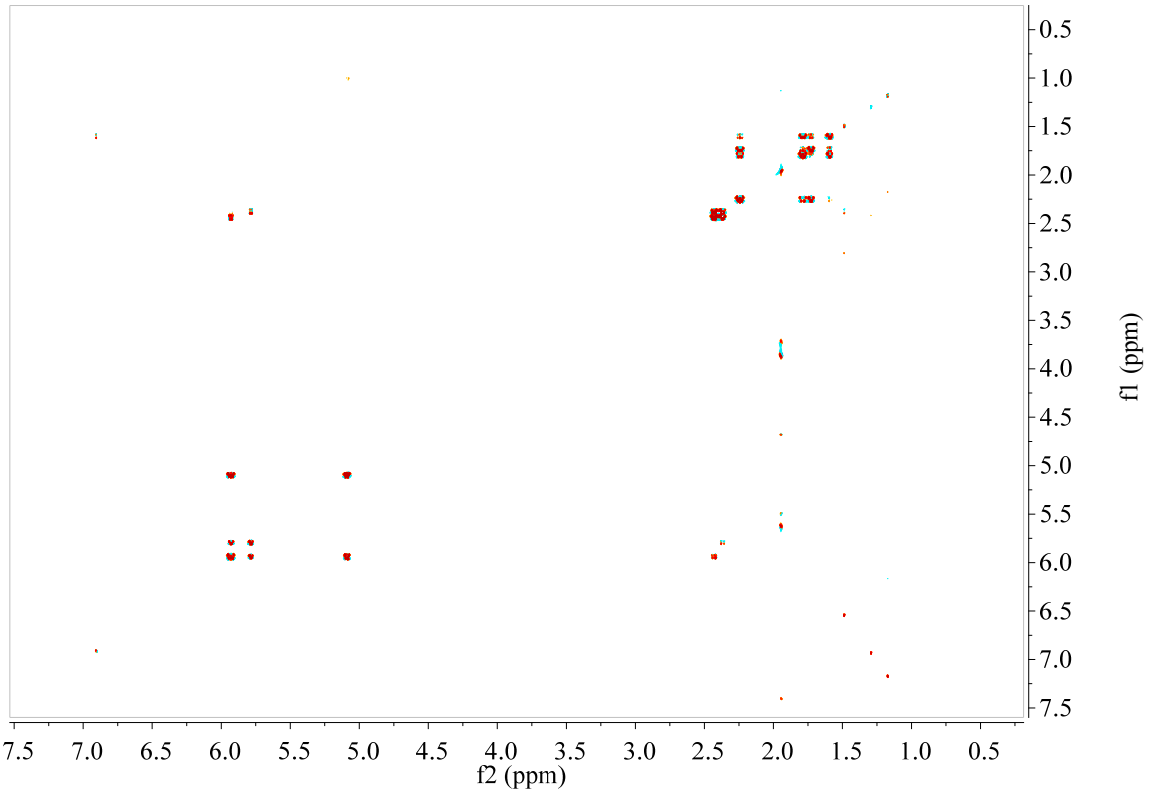
S18: ^{1}H-NMR (800 MHz CD_3CN) of libertellenone M



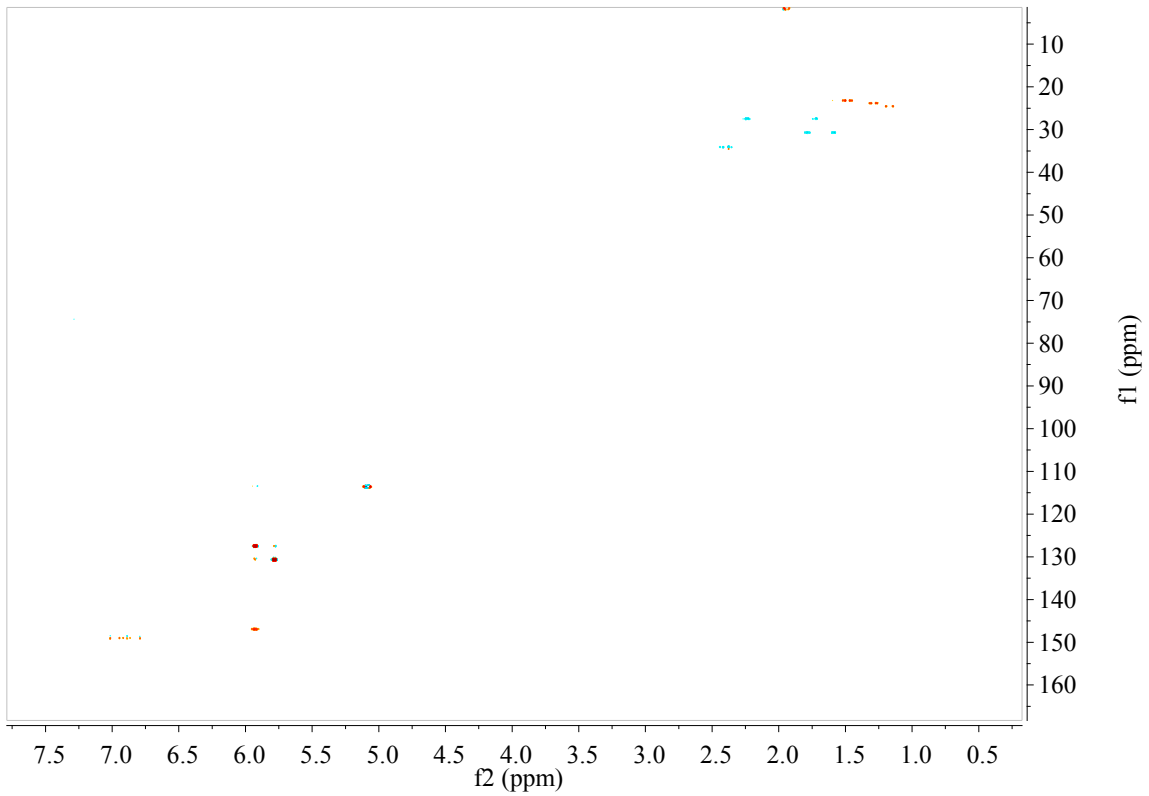
S19: ^{13}C-NMR (800 MHz CD_3CN) of libertellenone M



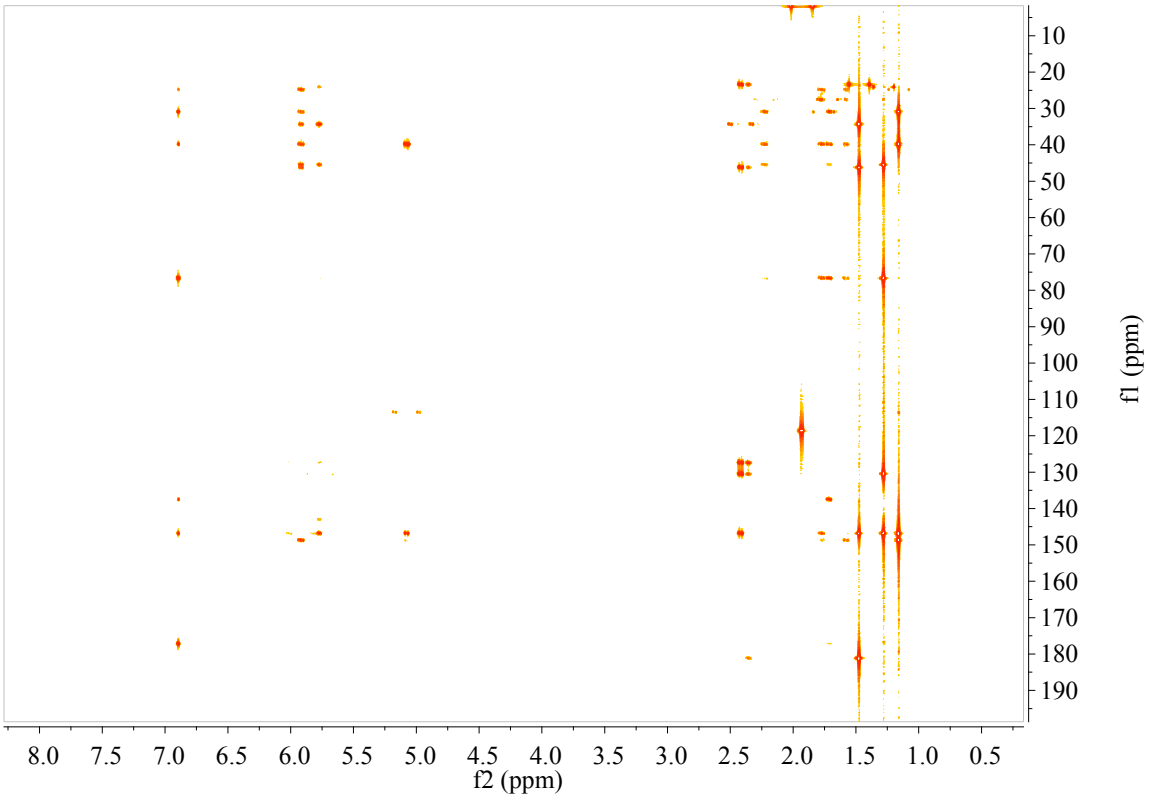
S20: DQF-COSY spectrum (800 MHz CD_3CN) of libertellenone M



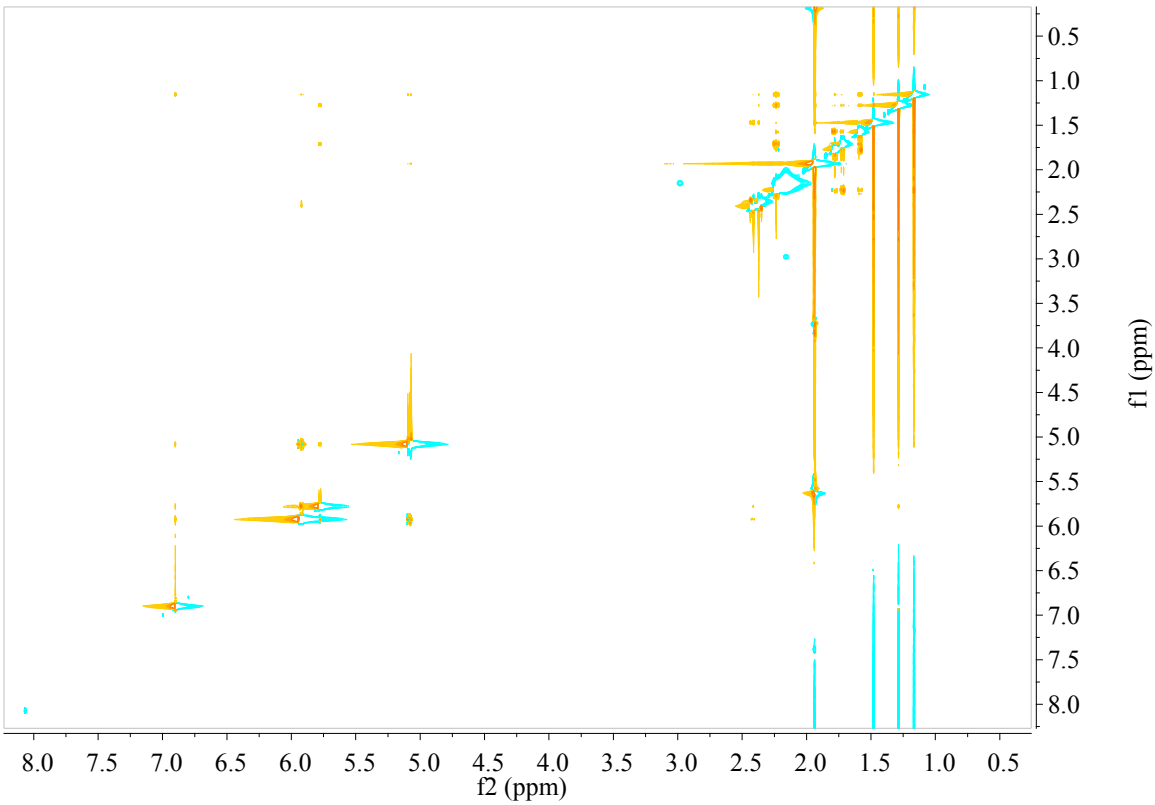
S21: Edited HSQC (800 MHz CD_3CN) of libertellenone M



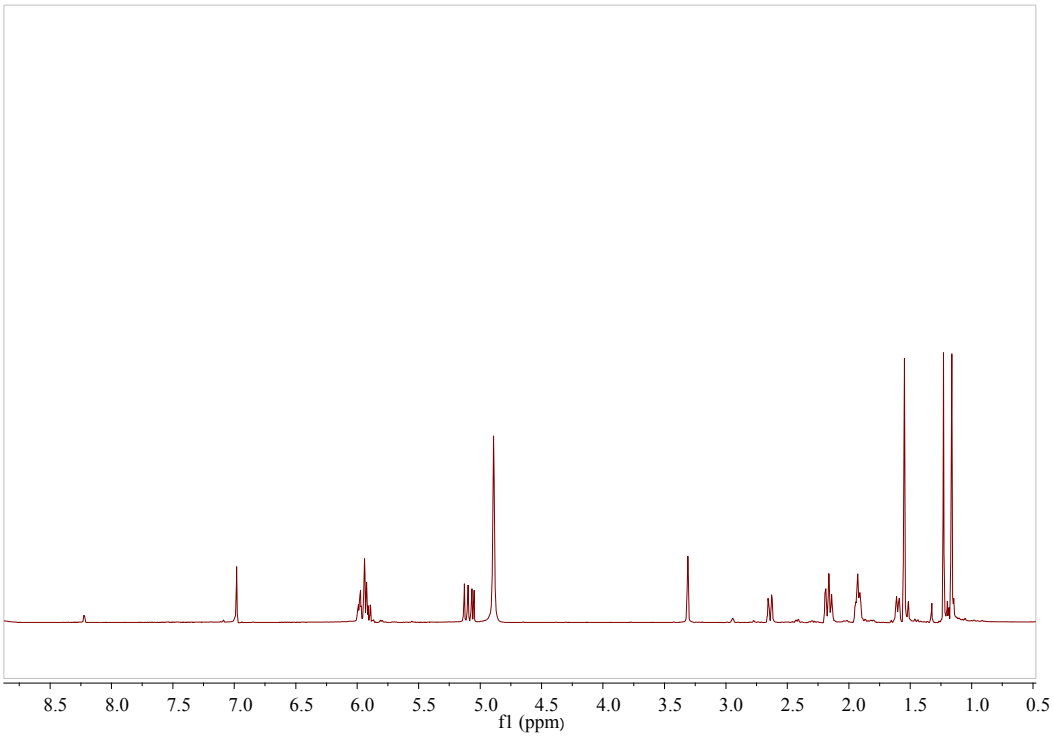
S22: HMBC spectrum (800 MHz CD_3CN) of libertellenone M



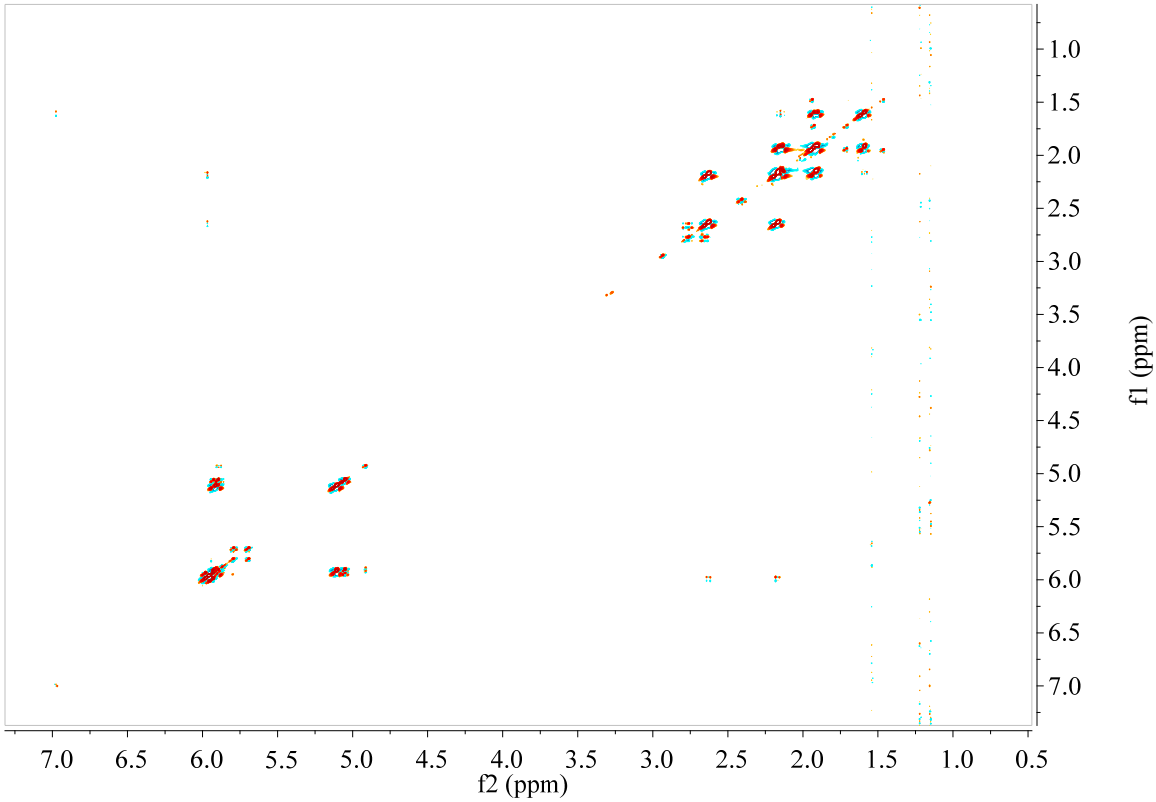
S23: NOESY spectrum (400 MHz CD_3CN) of libertellenone M



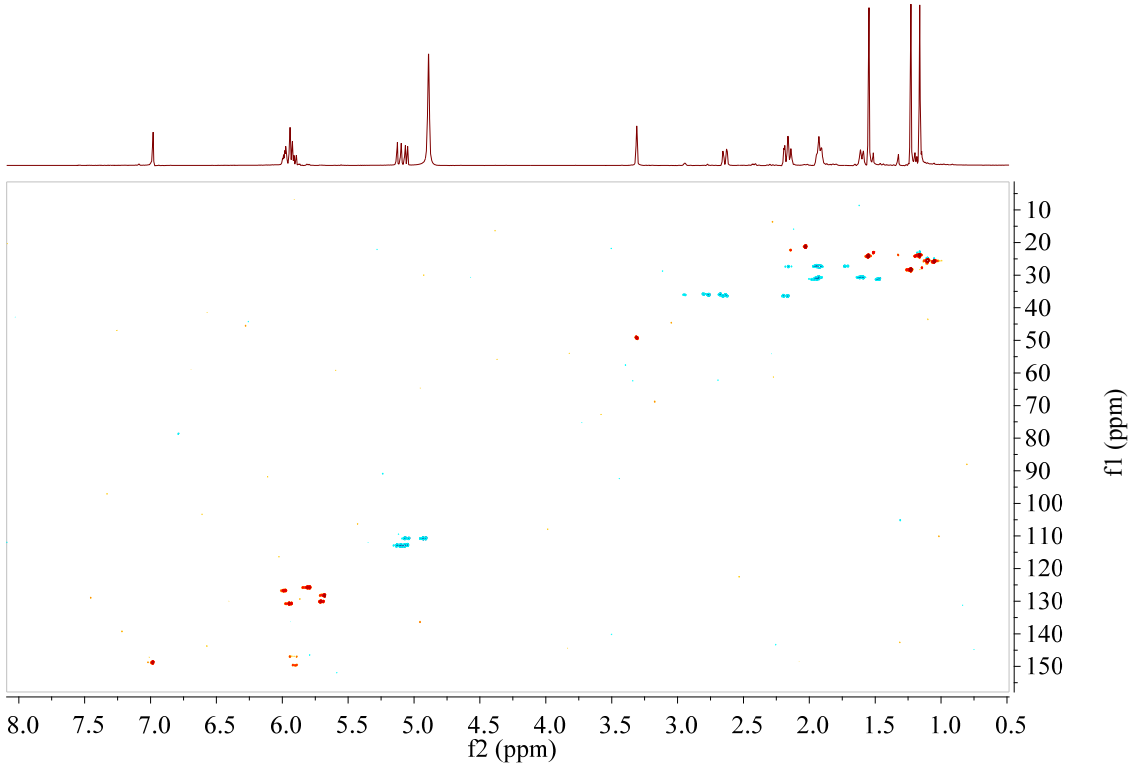
S24: ^{1}H-NMR (800 MHz MeOD) of opened γ-lactam libertellenone M



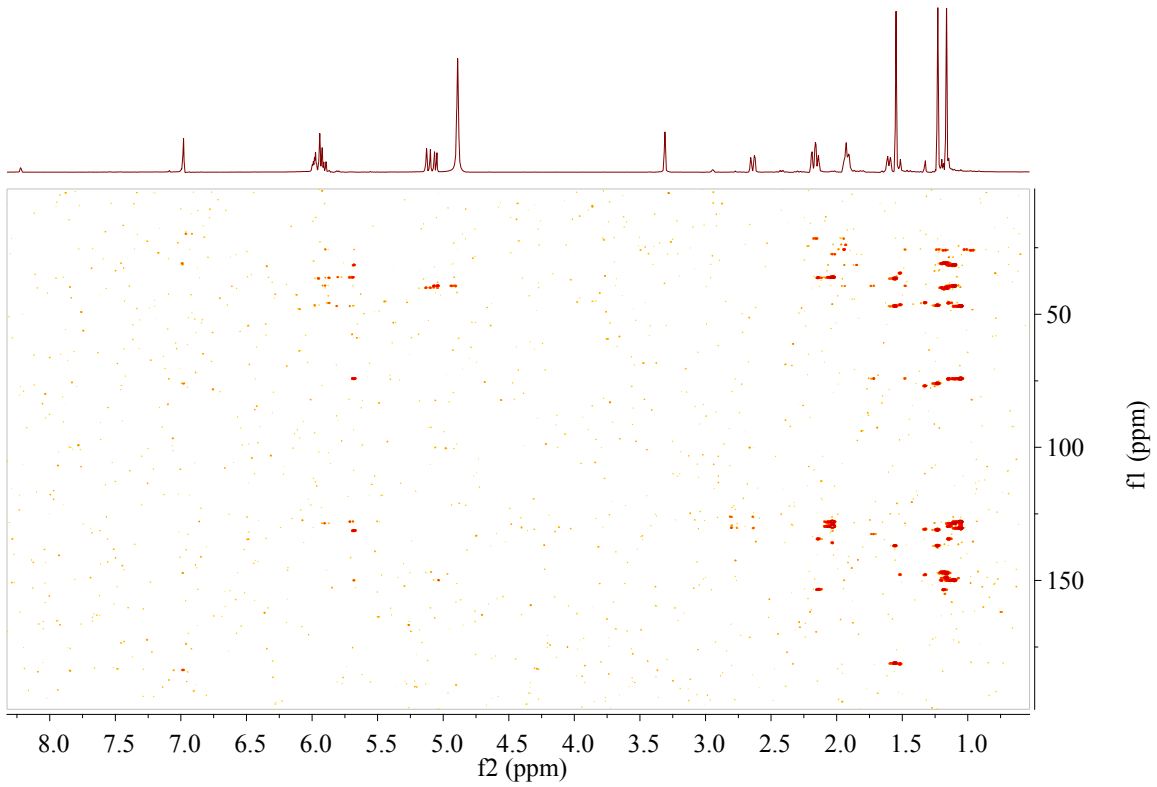
S25: DQF-COSY (800 MHz MeOD) of opened γ-lactam libertellenone M



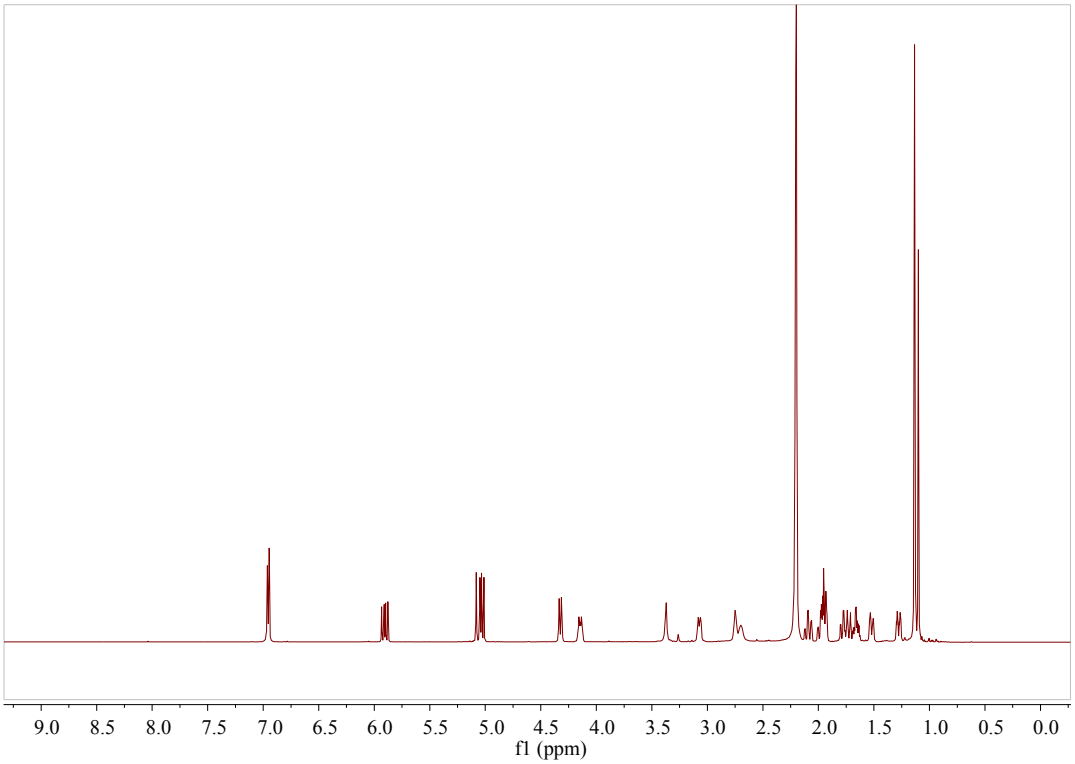
S26: Edited-HSQC (800 MHz MeOD) of opened γ-lactam libertellenone M



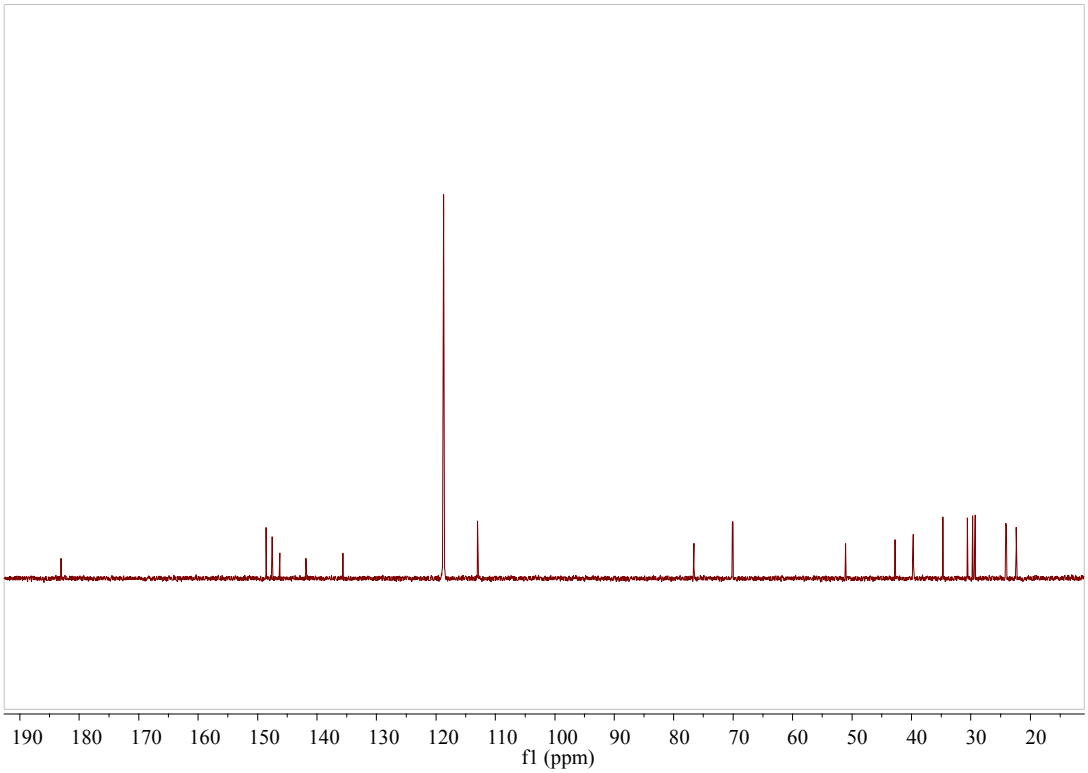
S27: HMBC (800 MHz MeOD) of opened γ-lactam libertellenone M



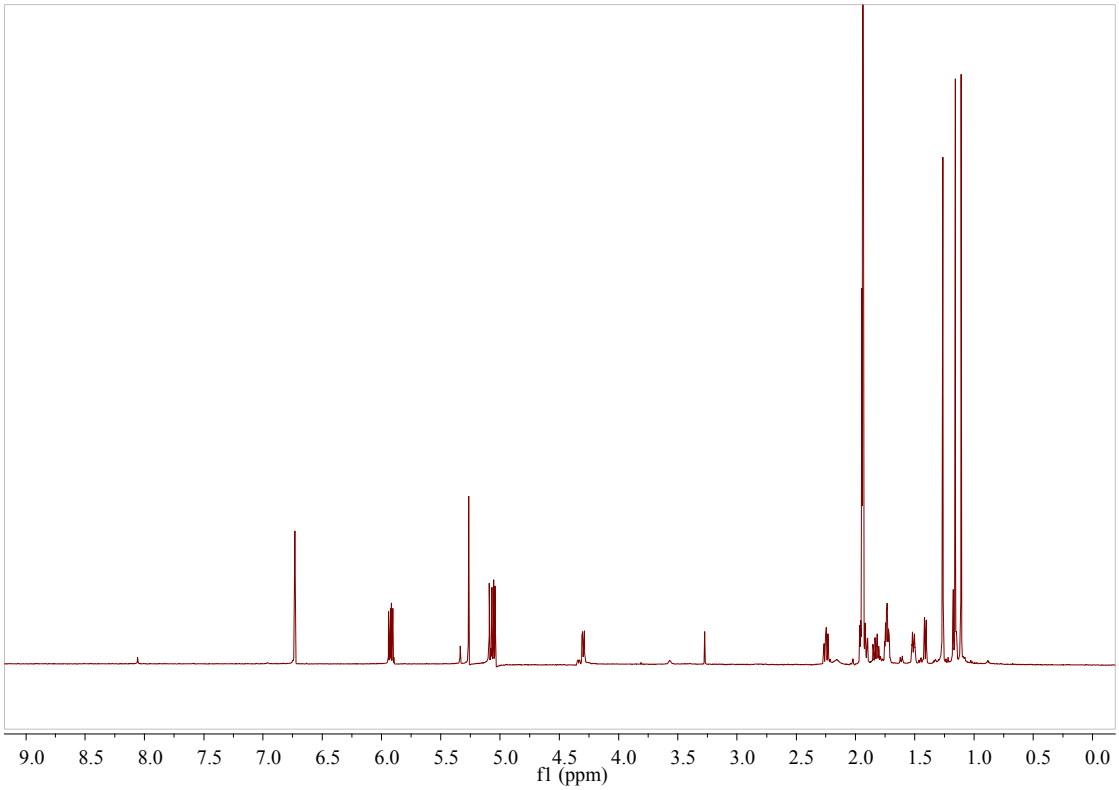
S28: ^{1}H-NMR (800 MHz CD_3CN) of libertellenone C



S29: ^{13}C-NMR (800 MHz CD_3CN) of libertellenone C



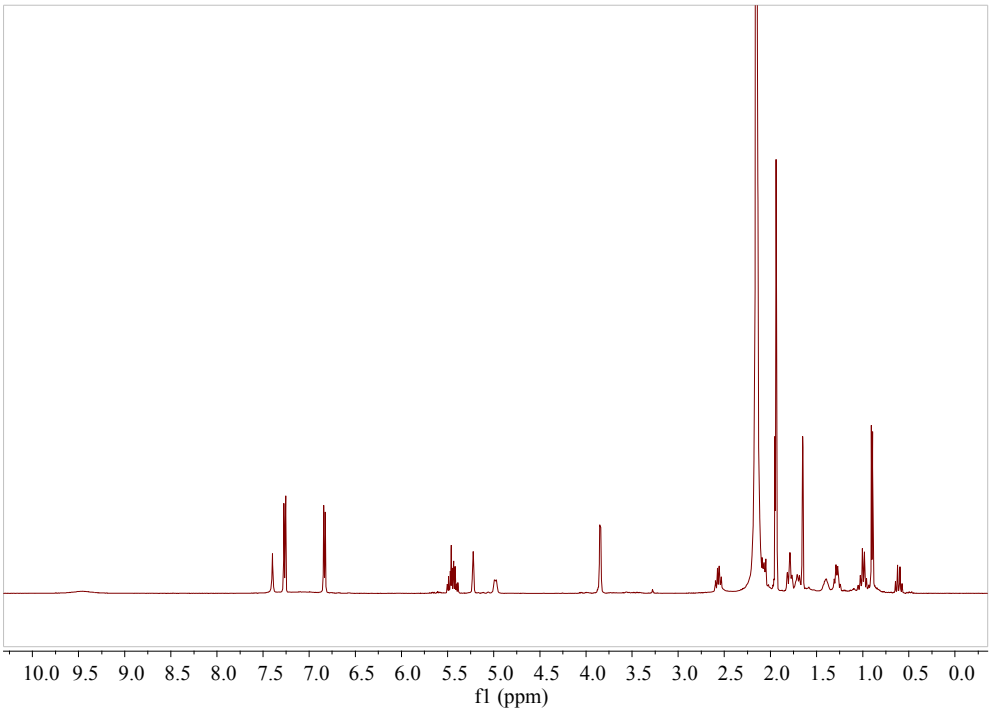
S30: ^{1}H-NMR (800 MHz CD_3CN) of libertellenone E



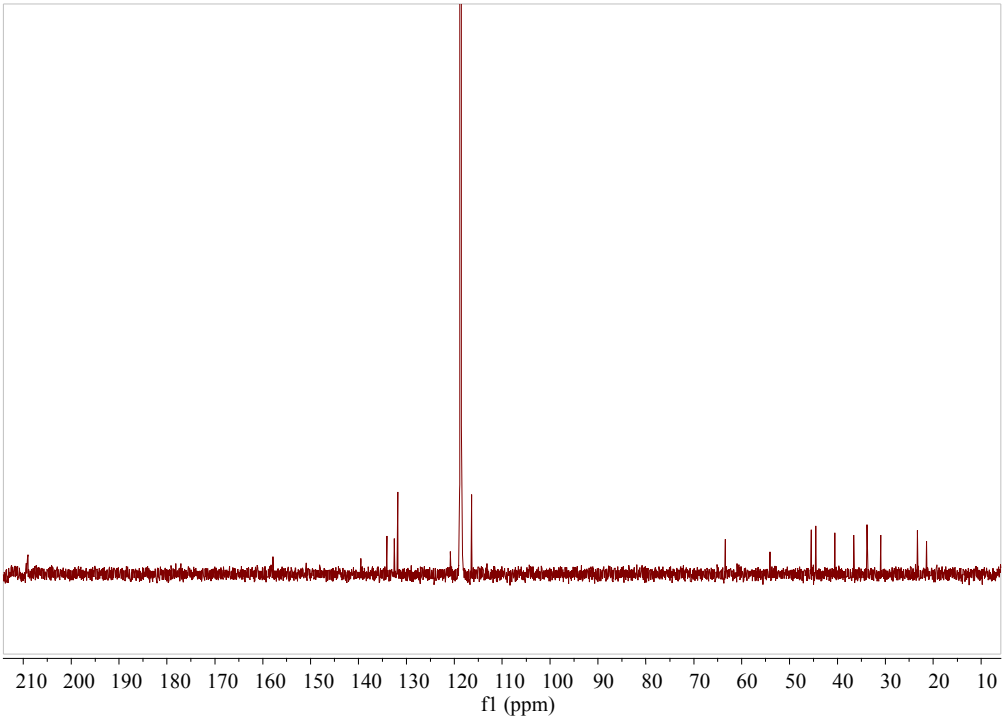
S31: Table 2. NMR Spectroscopic Data (400 MHz, MeCN-d3, δ in ppm, *J* in Hz) for libertellenone C and libertellenone E.

		Libertellenone C		**Libertellenone E**
	δ ^{13}C	δ ^{1}H (mult, *J*)	δ ^{13}C	δ ^{1}H (mult, *J*)
1	70.1	4.15 m	69.8	4.30 dd(11.6,4.5)
2a	29.3	1.66 m	29.2	1.73 m
2b		1.72 m		1.81 m
3a	34.7	1.28 m	27.4	1.41 dt(13.4,3.5)
3b		1.98 m		1.91 dd(13.5,3.5)
4	42.8	-	49.7	-
5	141.9	-	146.7	-
6	146.3	-	146.0	-
7	183.0	-	179.6	-
8	135.7	-	138.5	-
9	76.6	-	75.9	-
10	51.1	-	48.4	-
11a	29.7	2.09 td(14.4,3.3)	29.3	2.25 td(14.4,3.4)
11b		1.96 m		1.96 m
12a	30.6	1.52 m	30.9	1.51 m
12b		1.78 m		1.74 m
13	39.7	-	39.3	-
14	148.6	6.96 d(1.6)	146.1	6.73 s
15	147.6	5.90dd(17.6,10.7)	147.7	5.92 dd(17.3,10.9)
16a	113.0	5.07 d(17.6)	113.0	5.08 d(17.3)
16b		5.02 d(10.7)		5.05 d(10.9)
17	24.0	1.10 s	24.4	1.11 s
18	22.4	1.13s	25.6	1.26 s
19a	70.2	4.32 d(10.4)	108.0	5.26 s
19b		3.07 d(10.4)	-	-
20	24.1	1.13 s	18.1	1.16 s

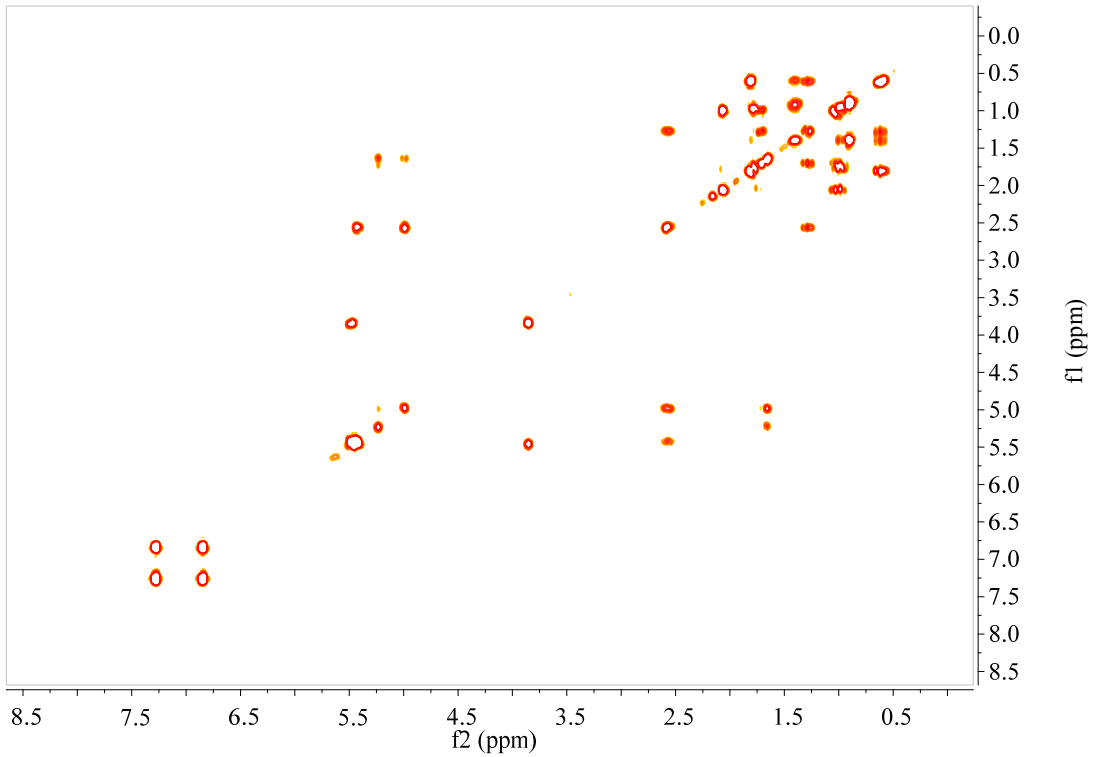
S32: ^{1}H-NMR (500 MHz CD_3CN) of hydroxyl-ilicicolin H



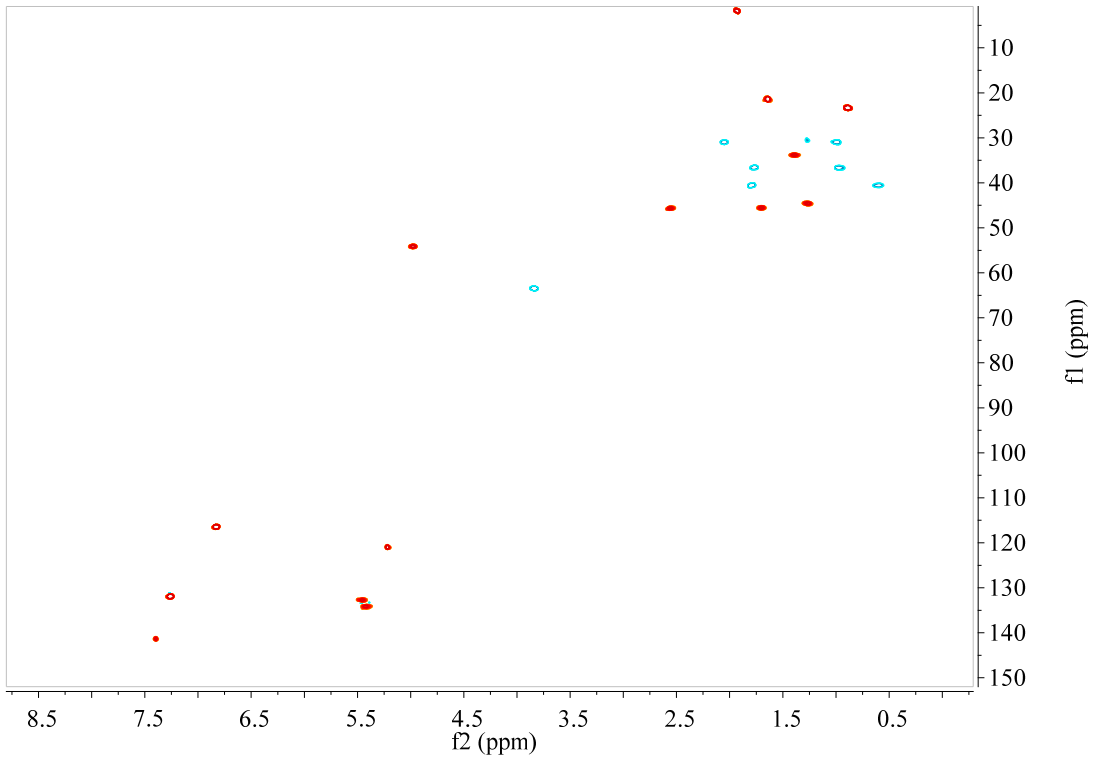
S33: ^{13}C-NMR (500 MHz CD_3CN) of hydroxyl-ilicicolin H



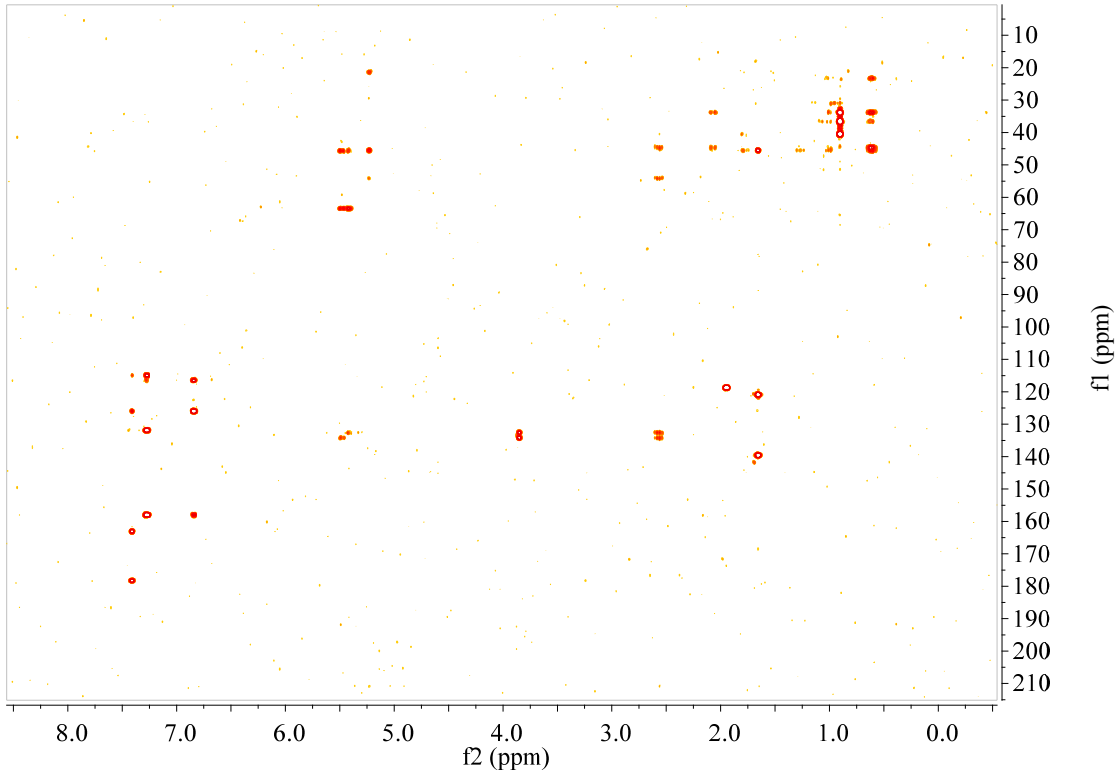
S34: COSY spectrum (500 MHz CD_3CN) of hydroxyl-ilicicolin H



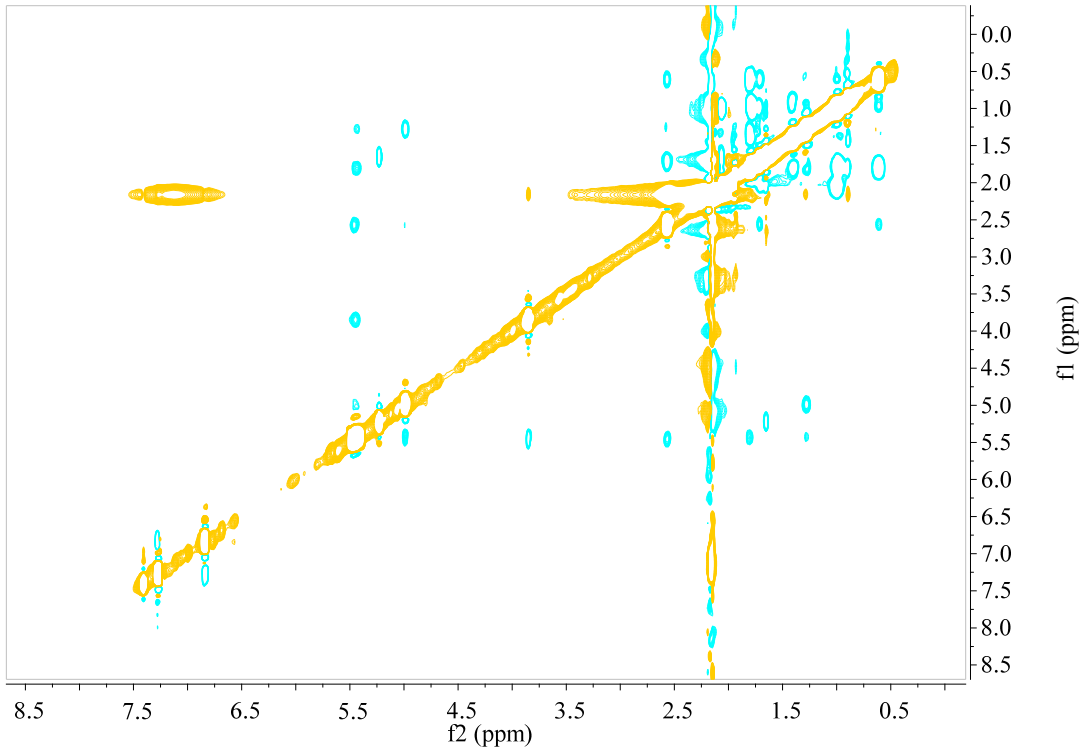
S35: Edited HSQC spectrum (500 MHz CD_3CN) of hydroxyl-ilicicolin H



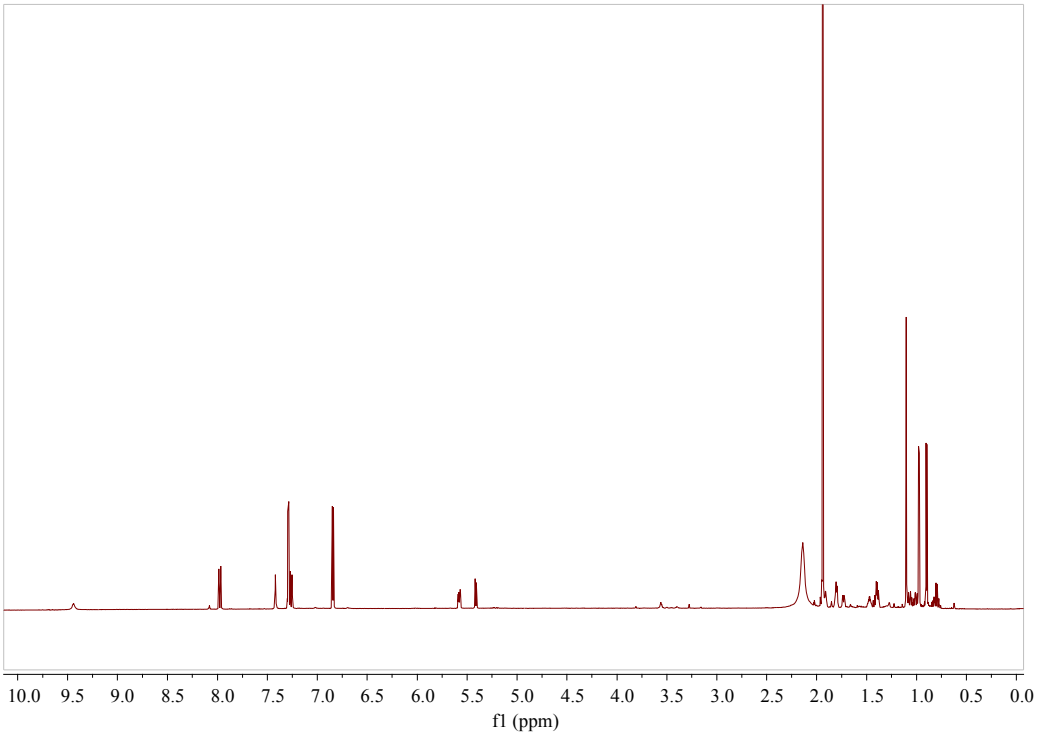
S36: HMBC spectrum (500 MHz CD_3CN) of hydroxyl-ilicicolin H



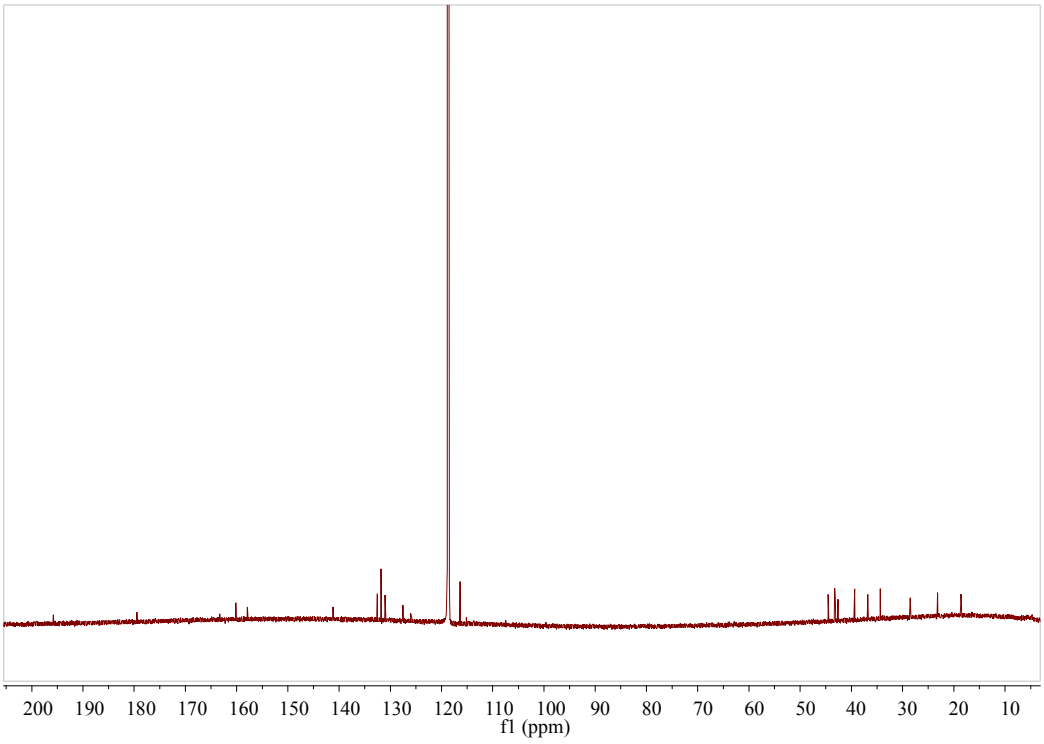
S37: NOESY spectrum (500 MHz CD_3CN) of hydroxyl-ilicicolin H



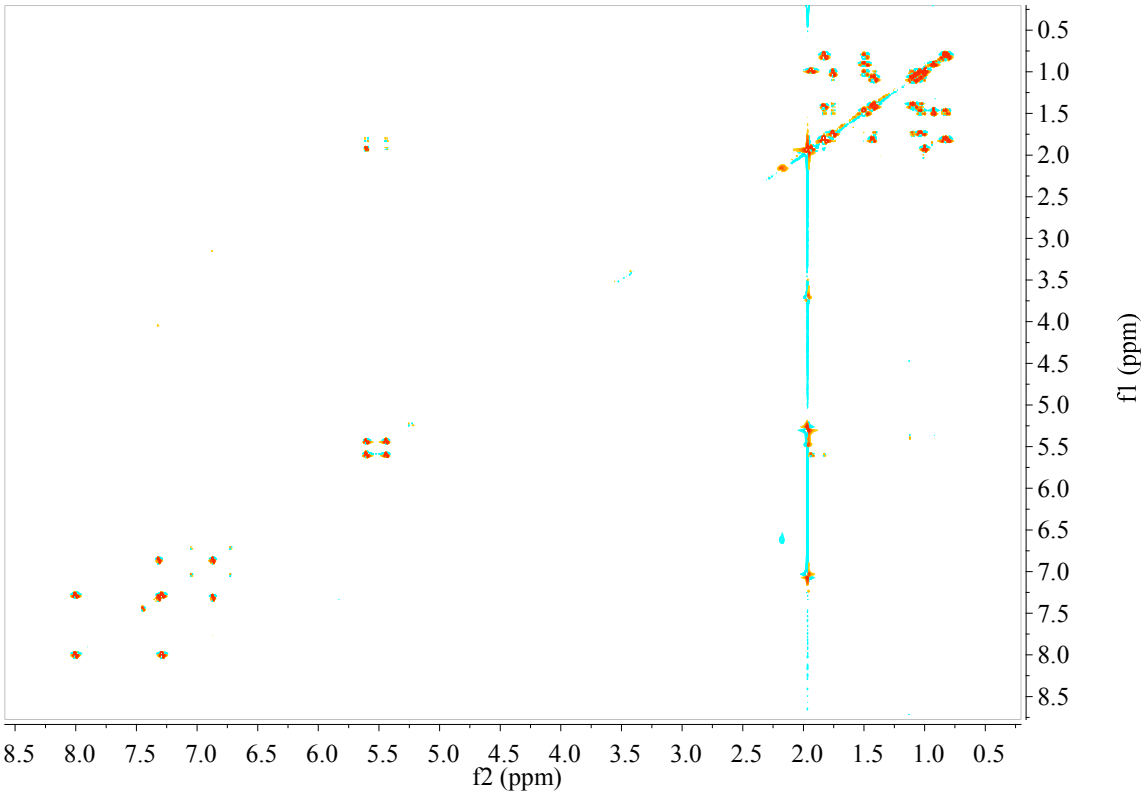
S38: ^{1}H-NMR (800 MHz CD_3CN) of ilicicolin I



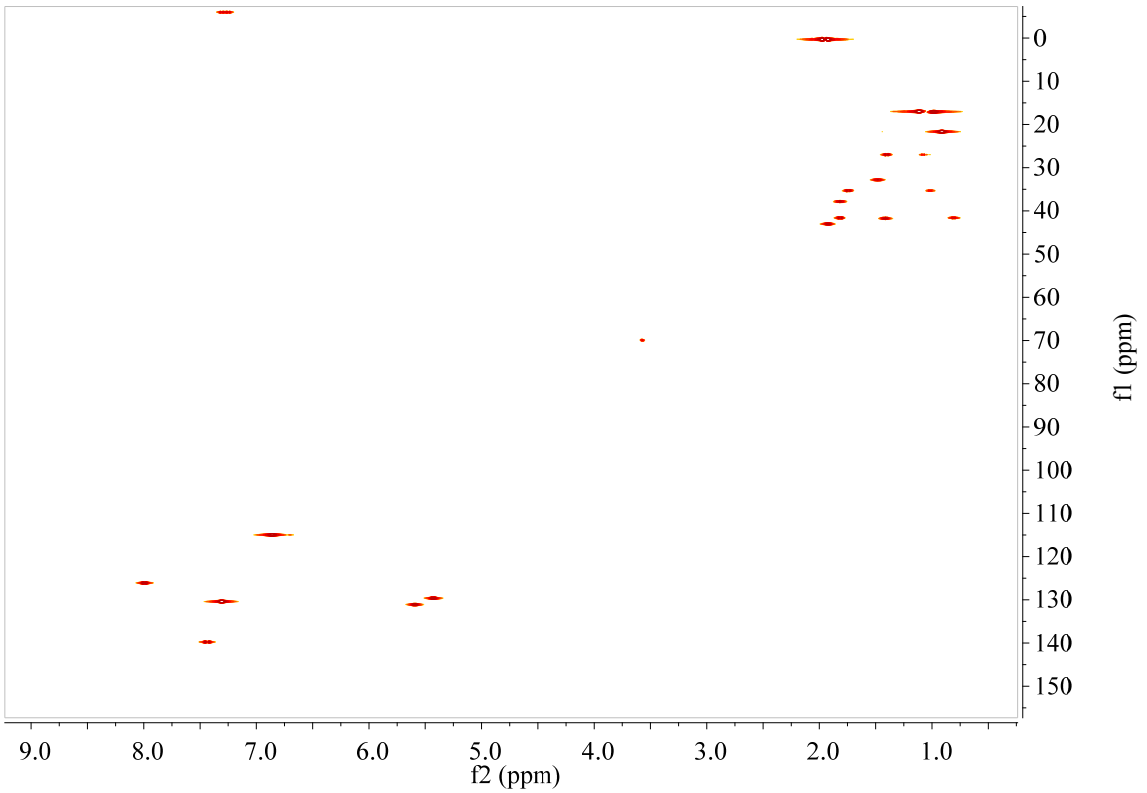
S39: ^{13}C-NMR (800 MHz CD_3CN) of ilicicolin I



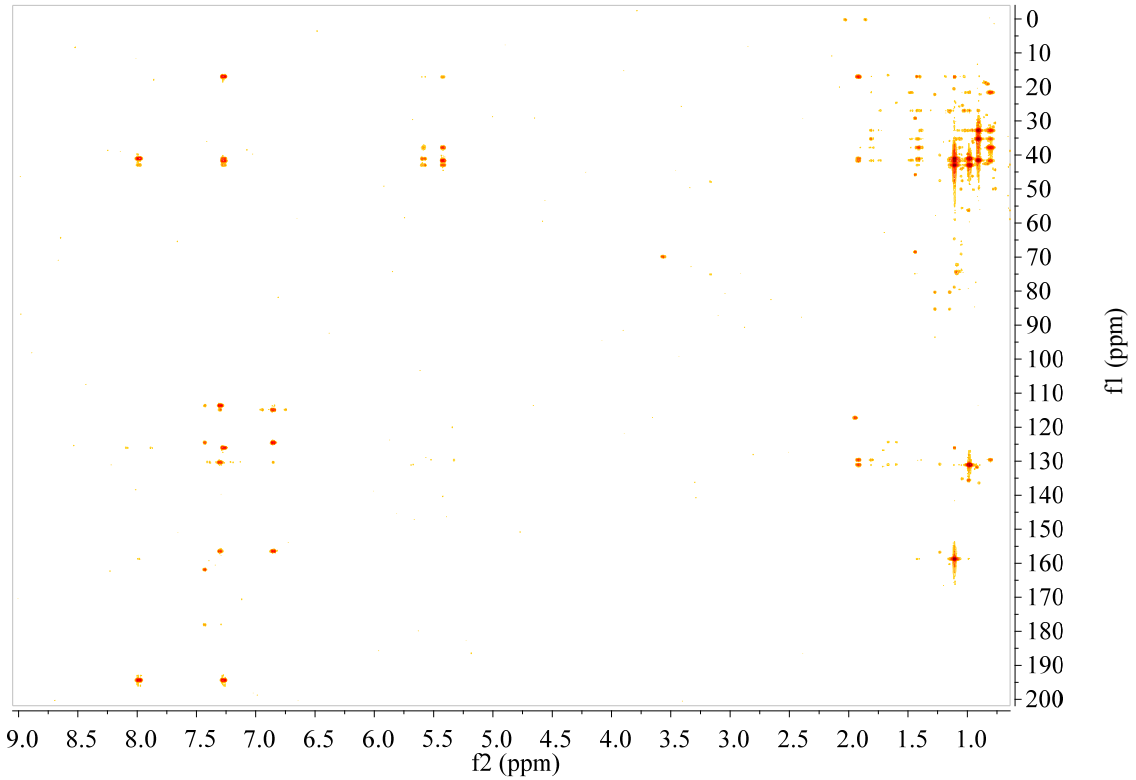
S40: COSY spectrum (800 MHz CD_3CN) of ilicicolin I



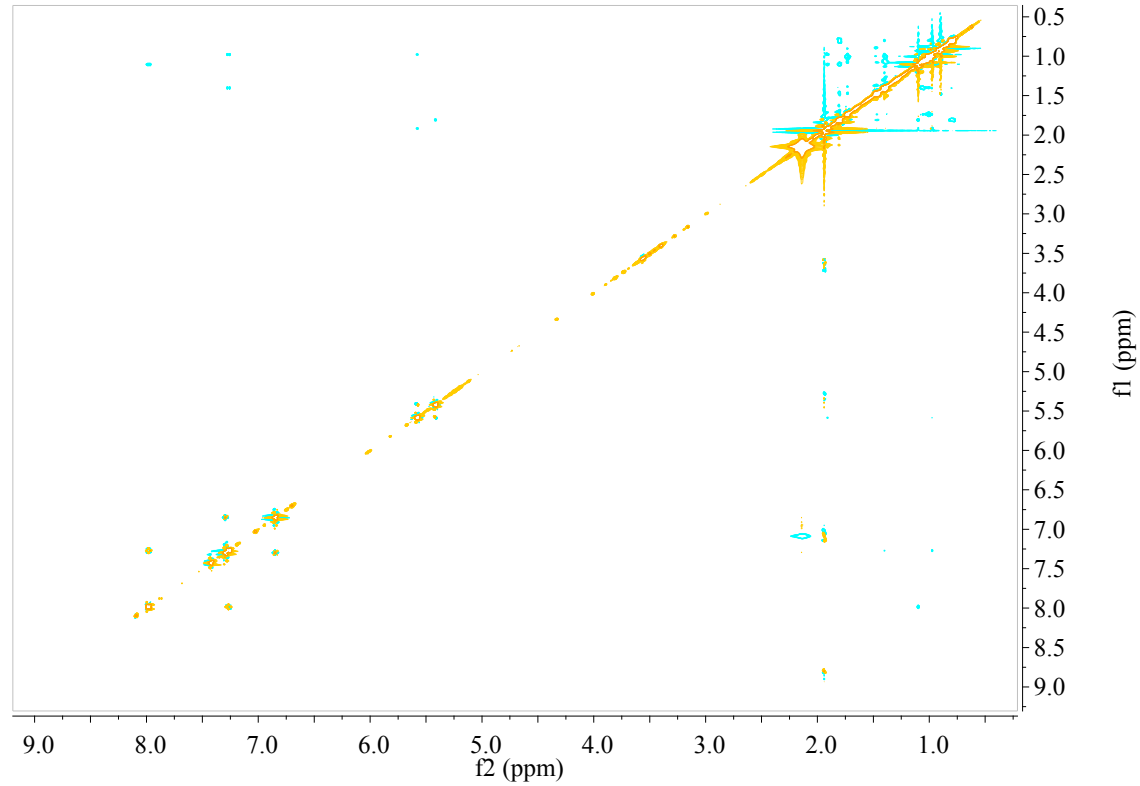
S41: HSQC spectrum (800 MHz CD_3CN) of ilicicolin I



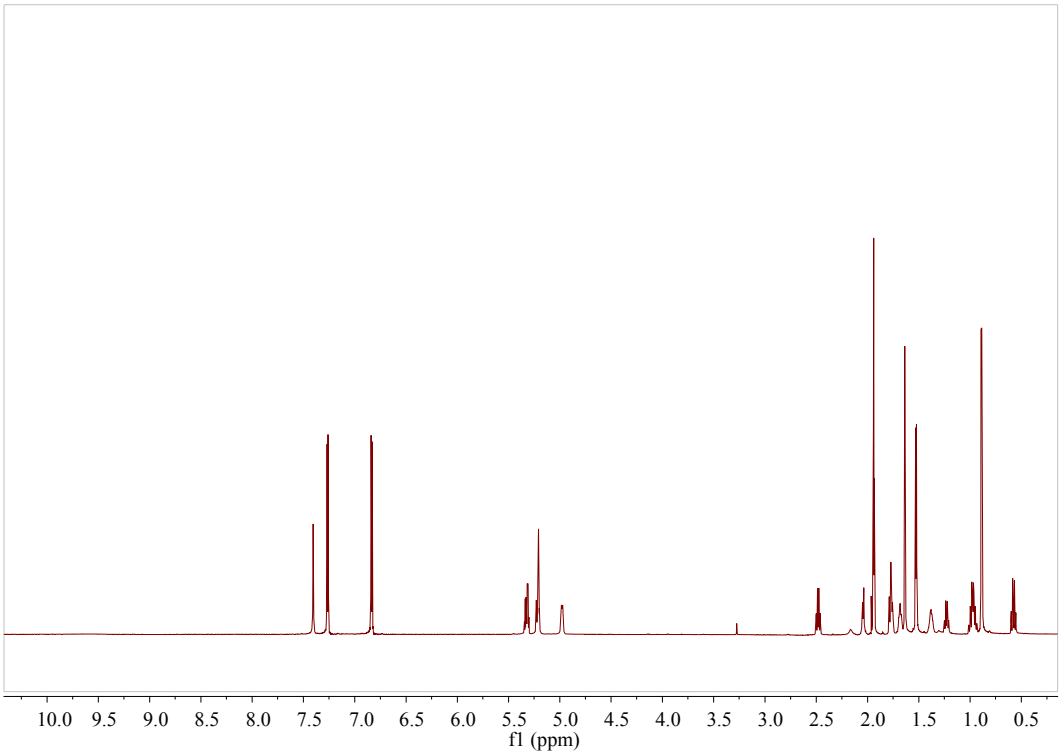
S42: HMBC spectrum (800 MHz CD_3CN) of ilicicolin I



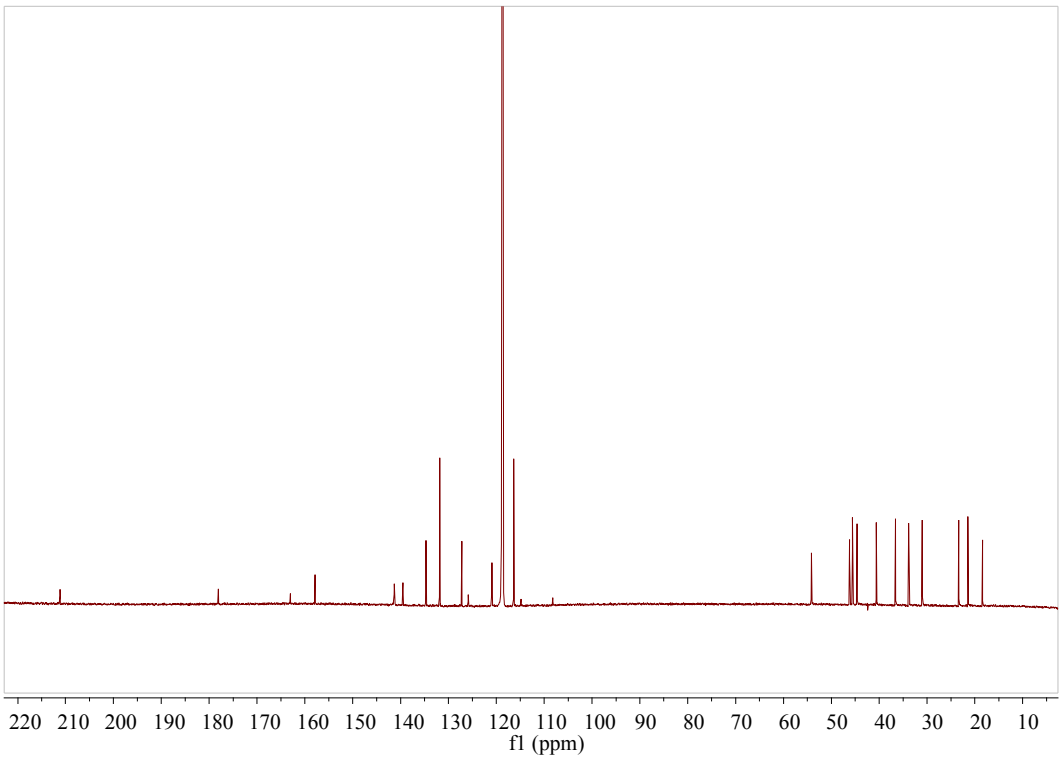
S43: NOESY spectrum (800 MHz CD_3CN) of ilicicolin I



S44: ^{1}H-NMR (800 MHz CD_3CN) of ilicicolin H



S45: ^{13}C-NMR (800 MHz CD_3CN) of ilicicolin H



S46: Table 3. Anticancer activity of pimarane-diterpenes**.** IC_{50} values (μM) of myrocin F, libertellenone M, libertellenone C and libertellenone E against cell lines NCH421k (glioblastoma), A549 (lung carcinoma), MCF7 (breast carcinoma), SW480 (colorectal adenocarcinoma), DU 145 (prostate carcinoma) after incubation of each compound at (0 – 300 μM) for 48 hours.

	NCH421k	**A549**	**MCF7**	**SW480**	**DU 145**
Myrocin F	40	50	24	20	30
Libertellenone M	18	75	49	110	270
Libertellenone C	40	150	70	65	130
Libertellenone E	>300	>300	>300	>300	>300

S47: Dose response curves of pimarane-diterpenes in glioblastoma stem-like cells**.** Myrocin F (A), libertellenone M (B), libertellenone C (C) and libertellenone E (D) were incubated at various concentrations with GSC line NCH421k for 48 hours. The IC_{50} is shown for each compound. (n = 3, biological replicates, error bars represent SEM).