Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Clavipines A-C, antiproliferative meroterpenoids with a fused azepine skeleton from the basidiomycete *Clitocybe clavipes*

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List of contents

Table 4. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data of **4**-**6** in $CDCl_3$

	4		**5**		**6**	
no.	δ_H, (J, Hz)	δ_C	δ_H, (J, Hz)	δ_C	δ_H, (J, Hz)	δ_C
1		184.1, C_q		184.0, C_q		151.0, C_q
2		146.4, C_q	5.90, s	103.0, CH	6.76, d (8.4)	118.8,CH
3	5.87, s	102.4, CH		146.0, C_q	6.65, d (8.4)	115.6, CH
4		183.1, C_q		182.2, C_q		151.0, C_q
5		145.1, C_q		152.2, C_q		121.1, C_q
6	6.20, s	72.1, CH	6.07, s	71.9, CH	6.28, s	77.2, CH
7	3.95, s	63.0, CH	3.97, s	62.9, CH	4.08, s	65.2, CH
8		60.8, C_q		60.8, C_q		62.9, C_q
9	1.29, m, b 2.70, d (12.0), a	24.8, CH_2	1.28, m, b 2.70, d (12.6), a	24.7, CH_2	1.26,dd (3.0, 14.4), b 2.59, dd (2.4, 14.4), a	26.3, CH_2
10	2.24, m, b 2.38, m, a	22.9, CH_2	2.24, m, b 2.38, m, a	22.9,CH_2	2.15, m, b 2.42, m, a	23.6, CH_2
11	5.33, t (7.2)	124.2, CH	5.30, t (7.2)	123.7, CH	5.25, t (7.8)	122.8, CH
12		135.1, C_q		135.6, C_q		139.9, C_q
13	2.93, d (14.4), b 3.58, d (14.4), a	26.6, CH_2	2.86, d (13.8), b 3.75, d (13.8), a	27.2, CH_2	2.94, d (15.6), b 3.65, d (15.0), a	28.4, CH_2
14		137.8, C_q		133.6, C_q		128.4, C_q
15	1.51, s	23.0, CH_3	1.51, s	23.2, CH_3	1.56, s	21.9, CH_3
16		171.8, C_q		171.6, C_q		174.9, C_q

Table 5. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data of **5**.

	5^{a,natural}		**5**^{b,natural}		**5**^{c,synthetic}	
no.	δ_H, (J, Hz)	δ_C	δ_H, (J, Hz)	δ_C	δ_H, (J, Hz)	δ_C
1		184.2, C_q		184.0, C_q		184.2, C_q
2	5.90	101.8, CH	5.90	103.0, CH	5.90	101.8, CH
3		148.9, CH		146.0, C_q		148.9, CH
4		183.2, C_q		182.2, C_q		183.3, C_q
5		151.3., C_q		152.2, C_q		151.3., C_q
6	5.99	73.1, CH	6.07	71.9, CH	5.99	73.2, CH
7	4.42	63.6, CH	3.97	62.9, CH	4.42	63.6, CH
8		61.1, C_q		60.8, C_q		61.2, C_q
9	1.36, 2.62	24.8, CH_2	1.28, 2.70	24.7, CH_2	1.35, 2.62	25.2, CH_2
10	2.27, 2.37	22.9, CH_2	2.24, 2.38	22.9,CH_2	2.28, 2.37	23.2, CH_2
11	5.38	124.0, CH	5.30	123.7, CH	5.38	124.1, CH
12		136.4, C_q		135.6, C_q		136.5, C_q
13	2.86, 3.76	27.2, CH_2	2.86, 3.75	27.2, CH_2	2.86, 3.76	27.3, CH_2
14		134.4, C_q		133.6, C_q		134.5, C_q
15	1.57	23.0, CH_3	1.51, s	23.2, CH_3	1.57	23.0, CH_3
16		171.8, C_q		171.6, C_q		172.6, C_q

5^{a} measured in acetone-d_6;[1] 5^{b} of this article measured in $CDCl_3$; 5^{c} mesured in acetone-d_6.[8c]

Labeled Precursors

L-Phenylalanine-^{13}C9,^{15}N(^{13}C,98%, ^{15}N,98%) was purchased from Sigma (USA, TA1002V).

Identification of clavilactone D from feeding of [U-^{13}C]-Phe

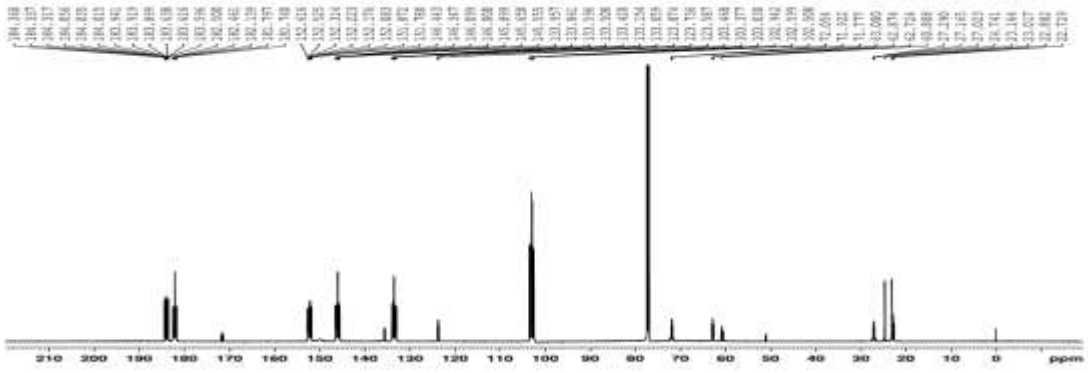

Figure. The ^{13}C NMR of clavilactone D from feeding of [U- ^{13}C]-Phe

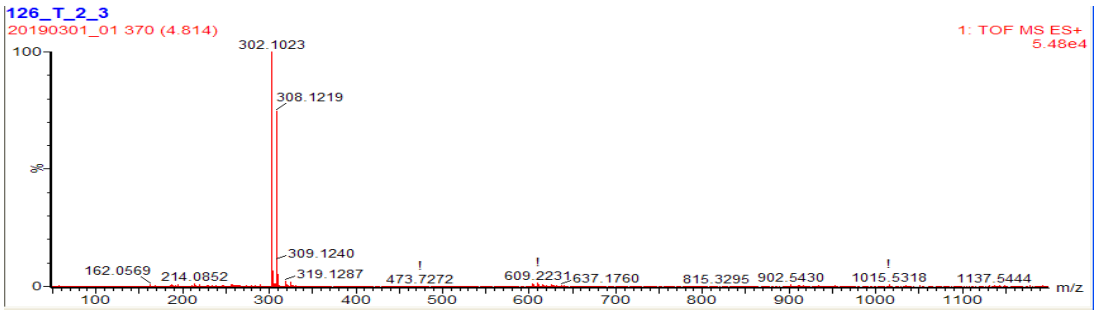

Figure. HRESIMS spectrum of clavilactone D from feeding of [U-^{13}C]-Phe

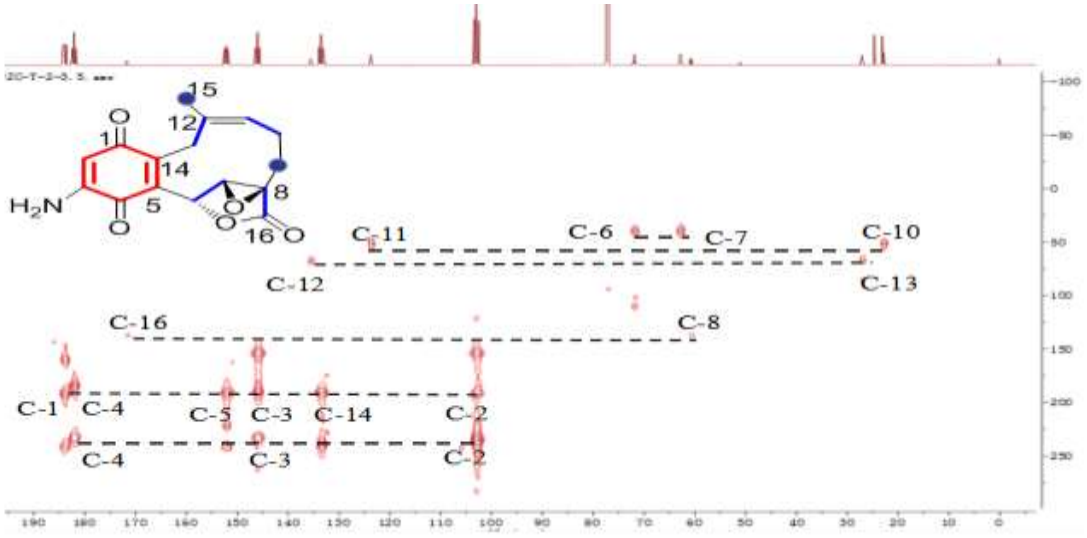

Figure. The INADEQUATE of clavilactone D from feeding of [U-^{13}C]-Phe

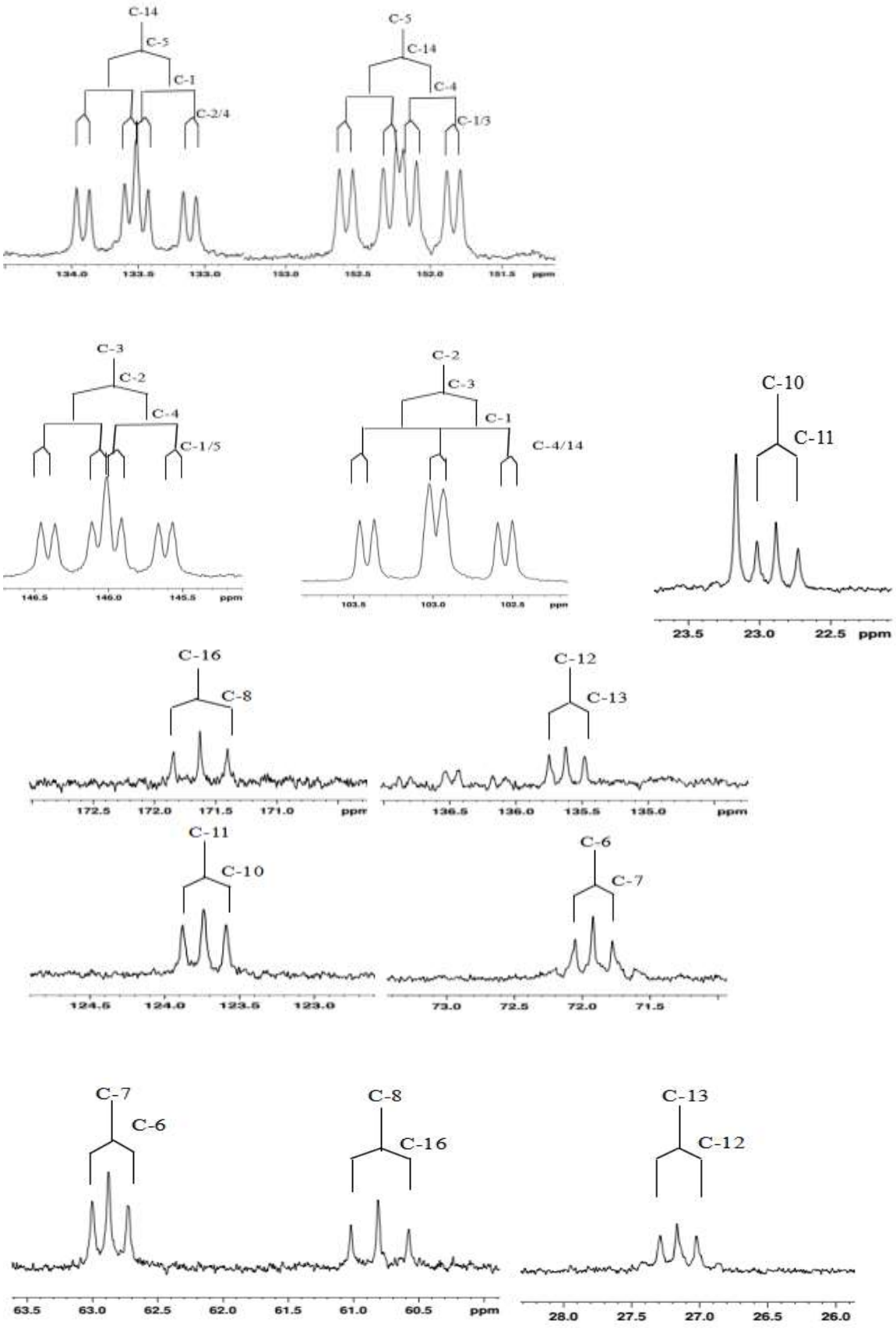

Figure. Analyses of ^{13}C NMR signals of clavilactone D

The ITS sequences data of *Clitocybe clavipes* (CBS 126.44)

ACTGGCTGTCTACCTGATTTGAGGTCACATTAAAATGAAGATTTGTCCCAG
AGAGGGACAGGTTATAAGCCAAACCCTGGTGCTTGTTAGGCTTGCTTCACG
ATCACTGGGATAGATAATTATCACGCCAATAATGATCCACAAAGGGTTCCAC
TAATGCATTTAAGGGGAGCCGATCTCTGAGAGACCCGCAGCCCCCACATCC
AAGCCTGATCAATCATTACAAAAGAAAAGGTTGATAATTTAATGACACTCA
AACAGGCATGCCCTTTGGAATACCAAAGGGCGCAAGGTGCGTTCAAAGAT
TCGATGATTCACTGAATTCTGCAATTCACATTACATATCGCGTTTCGCTGCGT
TCTTCATCGATGCGAGAGCCAAGAGATCCATTGTTGAAAGTTGTATAAATTT
ATAGCTATGCTAGGCAAAGCCATTGATGACATTCTGTGACATACAAAAGGG
GTGTGTAAACATAGACTGGAAAGCAGGGGCAGCCAACCTCCTCCAAAAAA
AGAAGGAGGTCCCAACCCCCACACCAAAAGCAAGCTGTTGAAGAGGTGA
CCAAGTGGTGAGACTCAGAAAAACAGGAAAAGAAACAATTTGCATATCCC
CGTGCCCAAACCCATTTACATCCCCCCCCAAAGGGGAGAGTGCGTTCTTTG
AATGACTTTGAACCCAAGCAGCCTGACATGCGTAGAAGGGTGACCGTATTT
CAGGACATGTAAGGAAAGCAGGACAAAAAAAAACCCCTGCAAGCCTCTTT
TCCTACGCATGTTTGTAAAAAAAACCCAATCCCCAAAAAG

Crystal data section

Table S1. X-ray crystallographic data for compound **1**.

Identification code	exp_5894
Empirical formula	$C_{20}H_{19}NO_5$
Formula weight	353.36
Temperature / K	109.2(5)
Crystal system	monoclinic
Space group	$P2_1$
a / Å, b / Å, c / Å	10.0737(5), 6.13340(19), 13.8766(6)
α/°, β/°, γ/°	90, 107.776(5), 90
Volume / Å^3	816.45(6)
Z	2
ρ_{calc} / mg mm^{-3}	1.437
μ / mm^{-1}	0.858

F(000)	372
Crystal size / mm^3	0.240 × 0.230 × 0.200
2Θ range for data collection	9.22 to 142.294°
Index ranges	$-12 \leq h \leq 10$, $-7 \leq k \leq 7$, $-10 \leq l \leq 16$
Reflections collected	5154
Independent reflections	3091[R(int) = 0.0231 (inf-0.9Å)]
Data/restraints/parameters	3091/1/236
Goodness-of-fit on F^2	1.047
Final R indexes [$I>2\sigma(I)$ i.e. $F_o>4\sigma(F_o)$]	$R_1 = 0.0370$, $wR_2 = 0.0938$
Final R indexes [all data]	$R_1 = 0.0376$, $wR_2 = 0.0945$
Largest diff. peak/hole / e $Å^{-3}$	0.209/-0.353
Flack Parameters	0.05(8)
Completeness	0.9988

Table S2. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacem--ent Parameters (Å2×103) for compound **1**. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	-4272.6(18)	-2658(3)	-6326.8(13)	21.4(4)
O4	-1490.3(19)	-10575(3)	-8555.8(13)	21.6(4)
O2	-5414.2(16)	-5881(3)	-7759.5(12)	18.3(4)
O5	-4235.2(17)	-3218(3)	-9756.6(12)	20.7(4)
O3	-6225.7(18)	-7149(3)	-6532.9(13)	25.0(4)
C1	-2056(2)	-8819(4)	-8845.3(16)	15.2(4)
C6	-4243(2)	-4570(4)	-7857.7(17)	16.8(5)
C14	-2712(2)	-7647(4)	-8141.2(16)	14.4(4)
N1	-2877(2)	-4775(4)	-10937.5(15)	19.0(4)
C2	-2114(2)	-7892(4)	-9827.2(17)	14.3(4)
C17	-1504(2)	-9260(4)	-10446.6(18)	17.4(5)
C3	-2781(2)	-5926(4)	-10100.4(16)	15.2(5)
C9	-3465(2)	-5735(4)	-5026.4(17)	18.8(5)
C7	-3436(2)	-3971(4)	-6780.5(17)	16.5(5)
C4	-3555(2)	-4868(4)	-9454.5(16)	15.0(5)
C11	-1408(2)	-7604(4)	-5334.4(18)	19.4(5)
C5	-3454(2)	-5814(4)	-8446.5(17)	14.5(4)
C13	-2512(2)	-8759(4)	-7136.0(17)	15.7(4)
C16	-5368(2)	-6131(4)	-6774.0(18)	17.4(5)
C18	-1420(3)	-8944(4)	-11386.3(18)	20.3(5)

C20	-1879(2)	-4884(4)	-11509.0(17)	19.0(5)
C12	-1314(2)	-7879(4)	-6264.5(17)	17.7(5)
C10	-2686(3)	-7902(4)	-4993.2(17)	20.4(5)
C15	18(2)	-7394(5)	-6503.9(19)	24.5(5)
C19	-1902(3)	-7032(5)	-12064.5(17)	21.3(5)
C8	4106(2))	4984(4)	-6090.7(18)	17.0(5)

Table S3. Anisotropic Displacement Parameters (Å2×103) for compound 2. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+... +2hka×b×U12]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	29.6(9)	14.9(8)	24.3(9)	-0.4(7)	15.0(7)	2.3(7)
O4	27.9(9)	17.9(9)	21.0(8)	3.3(7)	10.5(7)	6.9(7)
O2	14.0(7)	24.3(8)	17.0(8)	-0.2(7)	5.4(6)	0.3(7)
O5	20.9(8)	21.3(9)	20.2(8)	6.3(7)	6.9(6)	6.1(7)
O3	22.4(8)	32(1)	22.8(8)	-0.1(8)	9.9(7)	-7.8(8)
C1	13.3(10)	15.6(10)	16.5(10)	-1.1(9)	4.2(8)	-0.7(8)
C6	17.4(10)	16.1(11)	18.3(11)	3.4(9)	7.4(8)	2.1(9)
C14	13.9(9)	16.8(11)	12.7(10)	-0.4(9)	4.2(8)	-4.1(9)
N1	18.8(9)	22(1)	16.5(9)	4.4(8)	5.7(7)	3.8(8)
C2	12.7(9)	17.2(11)	13.6(9)	-2.3(9)	4.8(8)	-3.4(8)
C17	16.2(10)	16.3(11)	19.2(11)	-1.9(9)	4.6(8)	-0.7(8)
C3	10.9(9)	19.5(11)	13.6(10)	-0.5(9)	1.6(8)	-3.2(9)
C9	20.4(11)	22.4(12)	15.5(10)	-2.4(9)	8.3(9)	-2.8(9)
C7	19.5(11)	12.3(10)	19.3(10)	-1.2(8)	8.4(9)	-0.5(9)
C4	12.3(9)	15.1(11)	16.9(10)	0.1(9)	3.3(8)	-2.4(9)
C11	19.7(11)	20.0(11)	16.8(10)	1.1(9)	2.9(8)	2.0(9)
C5	13(1)	15.6(11)	14.8(10)	0.2(9)	4.0(8)	-1.8(8)
C13	18.9(11)	12.5(10)	17.2(10)	1.4(9)	7.7(9)	1.1(9)
C16	19.1(11)	17.1(10)	17.8(11)	0.2(9)	8.1(9)	2.9(9)
C18	20.7(11)	23.0(12)	19.8(11)	-6.2(10)	10.0(9)	-3.8(9)
C20	18.9(10)	23.1(12)	15.7(10)	2.8(9)	6.4(8)	-0.4(10)
C12	17.3(10)	16.6(11)	18.4(10)	2.3(9)	4.2(8)	4.3(9)
C10	26.8(11)	22.4(12)	12.7(10)	0.1(9)	7.0(9)	-0.3(10)
C15	18.3(11)	33.9(14)	21.5(11)	0.3(11)	6.5(9)	0(1)
C19	21.7(11)	28.4(13)	15.1(10)	-0.9(10)	7.5(9)	-4.1(10)
C8	19.4(10)	14.7(11)	19.9(11)	-2.8(9)	10.3(9)	-0.1(9)

Table S4. Bond Lengths for compound **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

O1	C7	1.442(3)	C2	C17	1.464(3)
O1	C8	1.462(3)	C2	C3	1.376(3)
O4	C1	1.227(3)	C17	C18	1.346(3)
O2	C6	1.468(3)	C3	C4	1.503(3)
O2	C16	1.363(3)	C9	C10	1.537(3)
O5	C4	1.222(3)	C9	C8	1.493(3)
O3	C16	1.194(3)	C7	C8	1.468(3)
C1	C14	1.517(3)	C4	C5	1.489(3)
C1	C2	1.461(3)	C11	C12	1.333(3)
C6	C7	1.513(3)	C11	C10	1.512(3)
C6	C5	1.510(3)	C13	C12	1.523(3)
C14	C5	1.345(3)	C16	C8	1.508(3)
C14	C13	1.510(3)	C18	C19	1.489(4)
N1	C3	1.337(3)	C20	C19	1.523(4)
N1	C20	1.460(3)	C12	C15	1.507(3)

Table S5. Bond Angles for compound **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O1	C8	60.71(14)	O5	C4	C5	121.0(2)
C16	O2	C6	111.87(18)	C5	C4	C3	119.5(2)
O4	C1	C14	117.1(2)	C12	C11	C10	127.3(2)
O4	C1	C2	122.0(2)	C14	C5	C6	125.9(2)
C2	C1	C14	121.0(2)	C14	C5	C4	119.6(2)
O2	C6	C7	104.27(17)	C4	C5	C6	114.5(2)
O2	C6	C5	110.14(19)	C14	C13	C12	115.01(19)
C5	C6	C7	116.36(19)	O2	C16	C8	110.04(19)
C5	C14	C1	120.2(2)	O3	C16	O2	122.3(2)
C5	C14	C13	124.9(2)	O3	C16	C8	127.7(2)
C13	C14	C1	114.82(19)	C17	C18	C19	128.4(2)
C3	N1	C20	124.7(2)	N1	C20	C19	114.1(2)
C1	C2	C17	114.8(2)	C11	C12	C13	122.7(2)
C3	C2	C1	118.4(2)	C11	C12	C15	121.3(2)
C3	C2	C17	126.7(2)	C15	C12	C13	116.0(2)
C18	C17	C2	130.4(2)	C11	C10	C9	111.2(2)
N1	C3	C2	127.0(2)	C18	C19	C20	114.19(19)
N1	C3	C4	112.2(2)	O1	C8	C9	120.54(19)
C2	C3	C4	120.8(2)	O1	C8	C7	58.98(14)
C8	C9	C10	111.05(18)	O1	C8	C16	107.30(19)
O1	C7	C6	110.92(19)	C9	C8	C16	120.4(2)
O1	C7	C8	60.32(14)	C7	C8	C9	129.0(2)
C8	C7	C6	109.0(2)	C7	C8	C16	104.8(2)
O5	C4	C3	119.4(2)				

Table S6.Torsion Angles for compound **1**.

A	B	C	D	Angle/°
O1	C7	C8	C9	-106.0(3)
O1	C7	C8	C16	101.56(19)
O4	C1	C14	C5	-174.1(2)
O4	C1	C14	C13	3.1(3)
O4	C1	C2	C17	2.5(3)
O4	C1	C2	C3	179.3(2)
O2	C6	C7	O1	-62.6(2)
O2	C6	C7	C8	2.0(2)
O2	C6	C5	C14	-66.5(3)
O2	C6	C5	C4	112.8(2)
O2	C16	C8	O1	63.3(2)
O2	C16	C8	C9	-153.6(2)
O2	C16	C8	C7	1.7(2)
O5	C4	C5	C6	-0.2(3)
O5	C4	C5	C14	179.2(2)
O3	C16	C8	O1	-117.4(3)
O3	C16	C8	C9	25.7(4)
O3	C16	C8	C7	-179.0(2)
C1	C14	C5	C6	175.5(2)
C1	C14	C5	C4	-3.7(3)
C1	C14	C13	C12	97.4(2)
C1	C2	C17	C18	177.8(2)
C1	C2	C3	N1	176.2(2)
C1	C2	C3	C4	-6.1(3)
C6	O2	C16	O3	-179.9(2)
C6	O2	C16	C8	-0.5(3)
C6	C7	C8	O1	-103.8(2)
C6	C7	C8	C9	150.2(2)
C6	C7	C8	C16	-2.2(2)
C14	C1	C2	C17	-176.82(18)
C14	C1	C2	C3	0.0(3)
C14	C13	C12	C11	139.5(2)
C14	C13	C12	C15	-42.4(3)
N1	C3	C4	O5	4.2(3)
N1	C3	C4	C5	-174.36(19)
N1	C20	C19	C18	-66.7(3)
C2	C1	C14	C5	5.2(3)
C2	C1	C14	C13	-177.51(19)
C2	C17	C18	C19	2.0(4)

C2	C3	C4	O5	-173.9(2)
C16	O2	C6	C7	-0.9(2)
C16	O2	C6	C5	124.7(2)
C20	N1	C3	C2	-25.8(4)
C20	N1	C3	C4	156.4(2)
C12	C11	C10	C9	-93.7(3)
C10	C9	C8	O1	-149.2(2)
C10	C9	C8	C7	-76.2(3)
C10	C9	C8	C16	72.6(3)
C10	C11	C12	C13	-5.5(4)
C10	C11	C12	C15	176.4(2)
C8	O1	C7	C6	100.6(2)
C8	C9	C10	C11	68.1(2)

Table S7. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for compound **1**.

Atom	*x*	*y*	*z*	U(eq)
H6	-4615	-3232	-8228	20
H1	-3576	-3910	-11155	23
H17	-1112	-10556	-10142	21
H9A	-4187	-5921	-4705	23
H9B	-2820	-4636	-4652	23
H7	-2421	-3789	-6579	20
H11	-596	-7181	-4840	23
H13A	-2356	-10301	-7214	19
H13B	-3368	-8621	-6958	19
H18	-1007	-10064	-11645	24
H20A	-949	-4656	-11048	23
H20B	-2073	-3706	-11999	23
H10A	-2408	-8470	-4308	25
H10B	-3304	-8955	-5429	25
H15A	-150	-6276	-7011	37
H15B	337	-8691	-6751	37
H15C	715	-6906	-5902	37
H19A	-2846	-7306	-12493	26
H19B	-1315	-6892	-12500	26

Table S8. X-ray crystallographic data for compound **6**.

Identification code	exp_5895
Empirical formula	$C_{16}H_{14}O_5$
Formula weight	286.27
Temperature / K	109.65(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a / Å, b / Å, c / Å	8.5940(3), 11.8962(8), 13.1105(5)
α/°, β/°, γ/°	90, 90, 90
Volume / $Å^3$	1340.37(12)
Z	4
ρ_{calc} / mg mm^{-3}	1.419
μ / mm^{-1}	0.886
F(000)	600
Crystal size / mm^3	0.250 × 0.200 × 0.200
2Θ range for data collection	10.04 to 141.962°
Index ranges	$-5 \leq h \leq 10$, $-13 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	4265
Independent reflections	2530[R(int) = 0.0193 (inf-0.9Å)]
Data/restraints/parameters	2530/0/191
Goodness-of-fit on F^2	1.090
Final R indexes [$I>2\sigma(I)$ i.e. $F_o>4\sigma(F_o)$]	$R_1 = 0.0384$, $wR_2 = 0.0986$
Final R indexes [all data]	$R_1 = 0.0389$, $wR_2 = 0.0991$
Largest diff. peak/hole / e $Å^{-3}$	0.456/-0.294
Flack Parameters	-0.08(8)
Completeness	0.9986

Spectroscopic data section

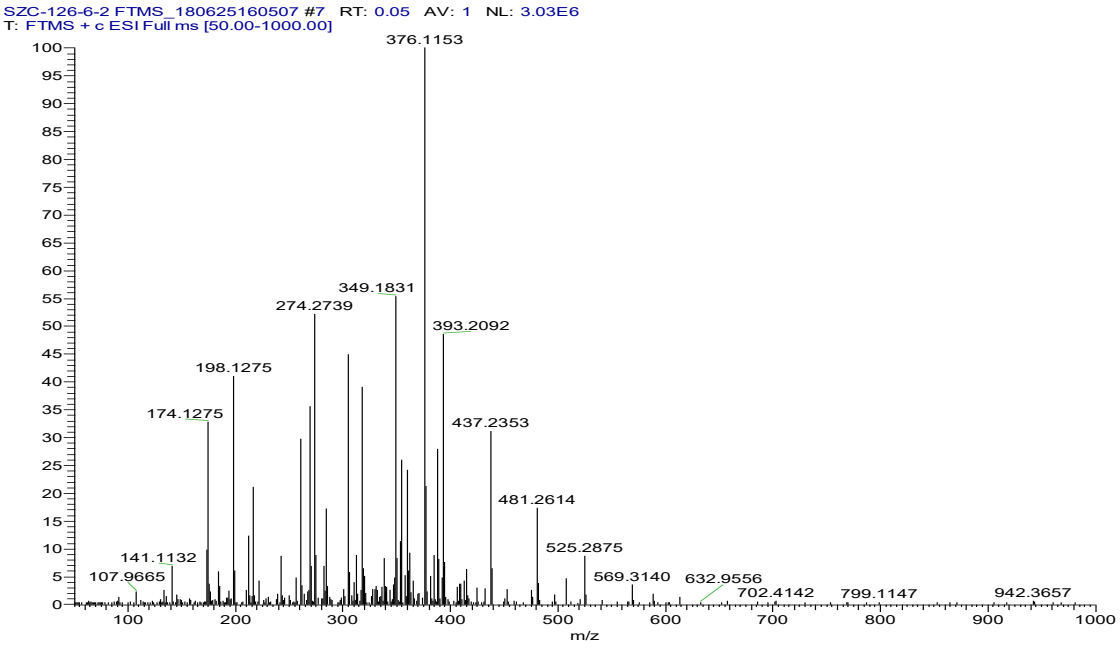

Figure S1. HRESIMS spectrum of clavipine A (**1**)

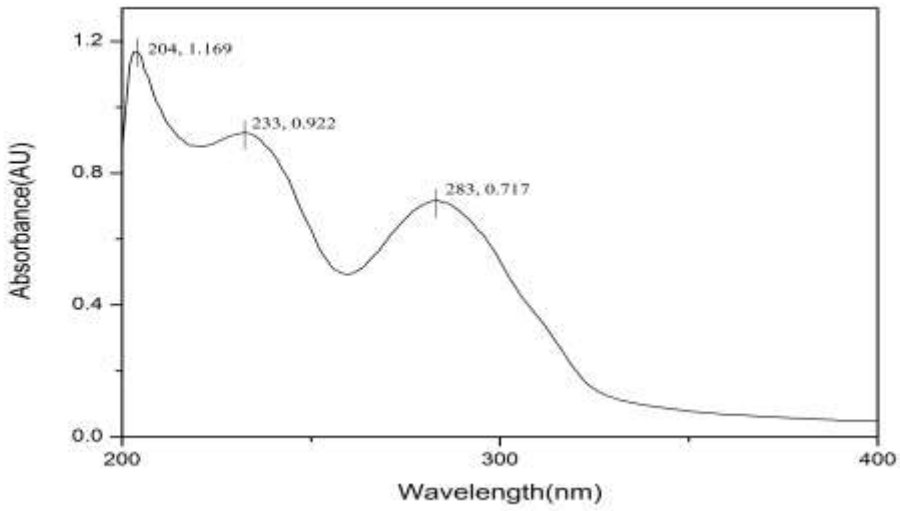

Figure S2. UV spectrum of clavipine A (**1**)

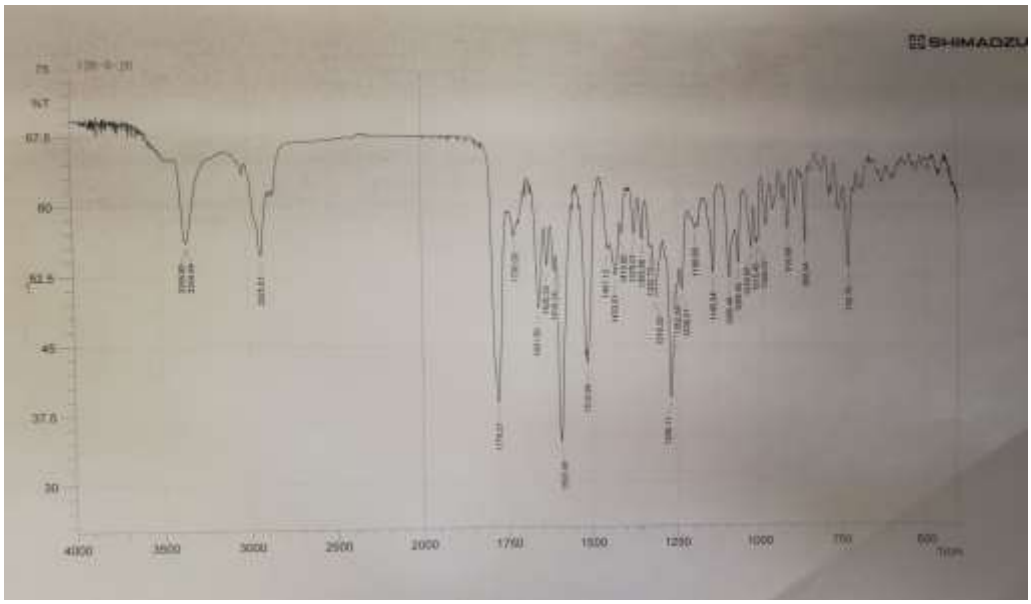

Figure S3. IR spectrum of clavipine A (**1**)

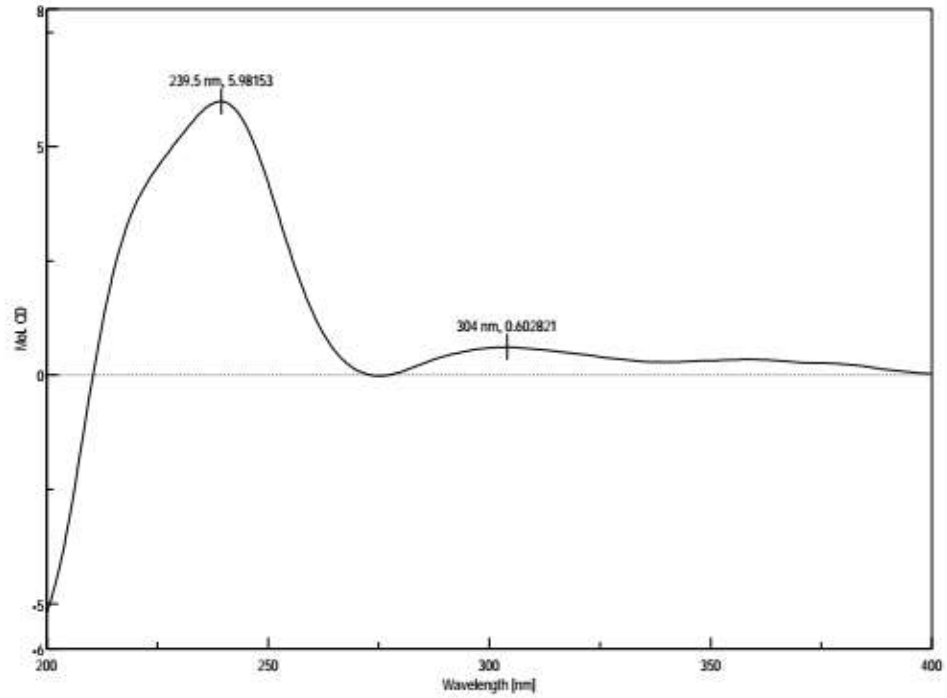

Figure S4. CD spectrum of clavipine A (**1**) (MeOH)

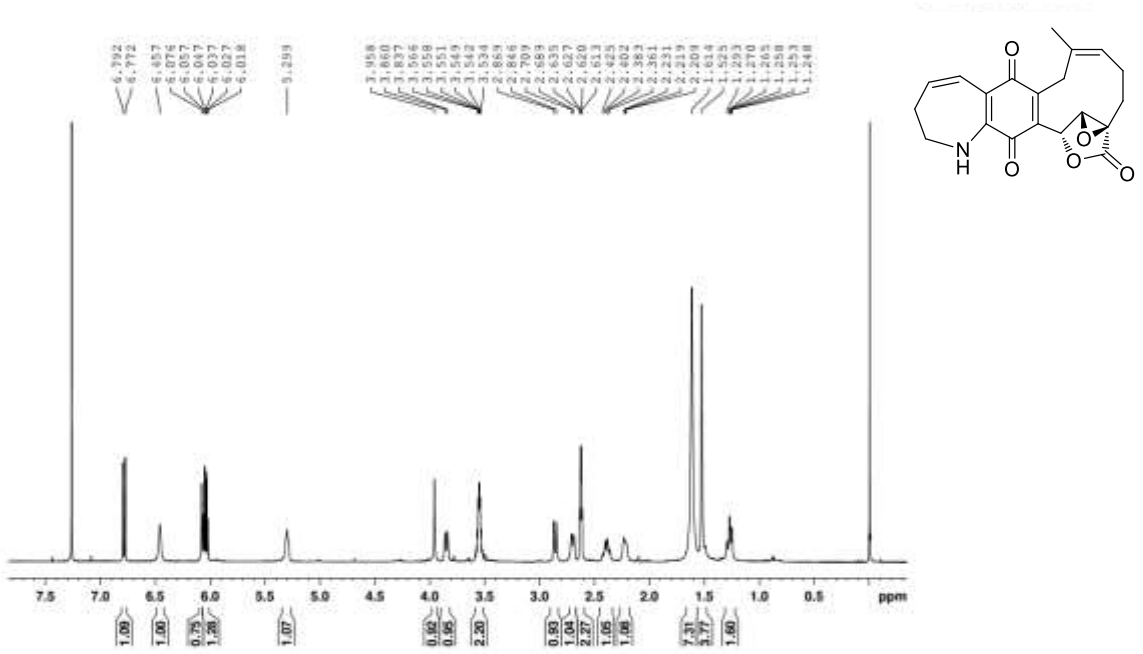

Figure S5. ^{1}HNMR spectrum of clavipine A (**1**)($CDCl_3$, 600MHz)

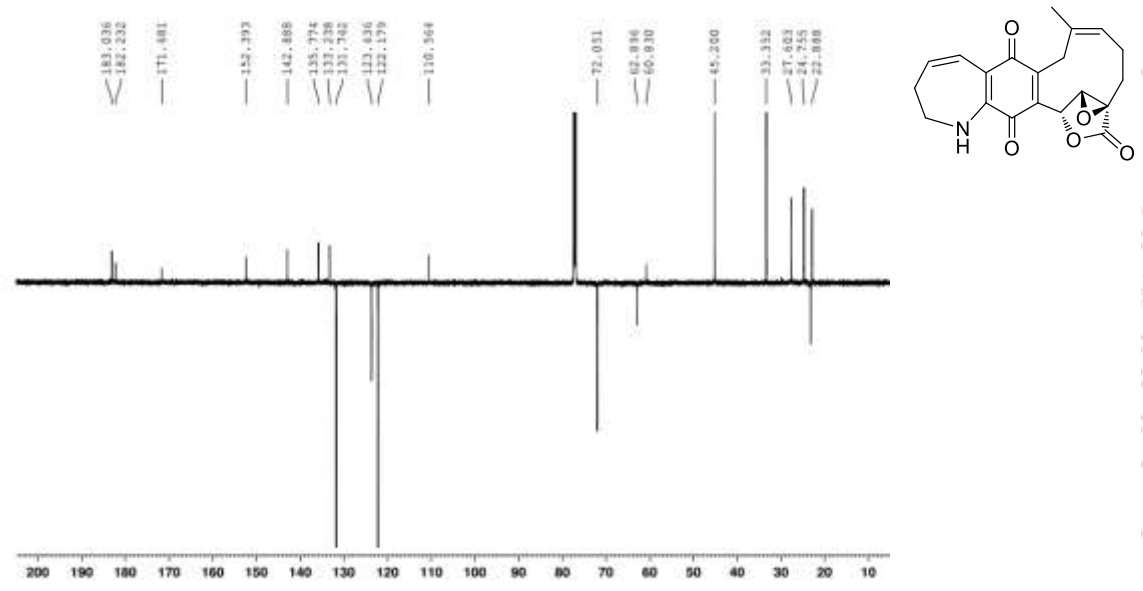

Figure S6. ^{13}C APT spectrum of clavipine A (**1**)($CDCl_3$, 150MHz)

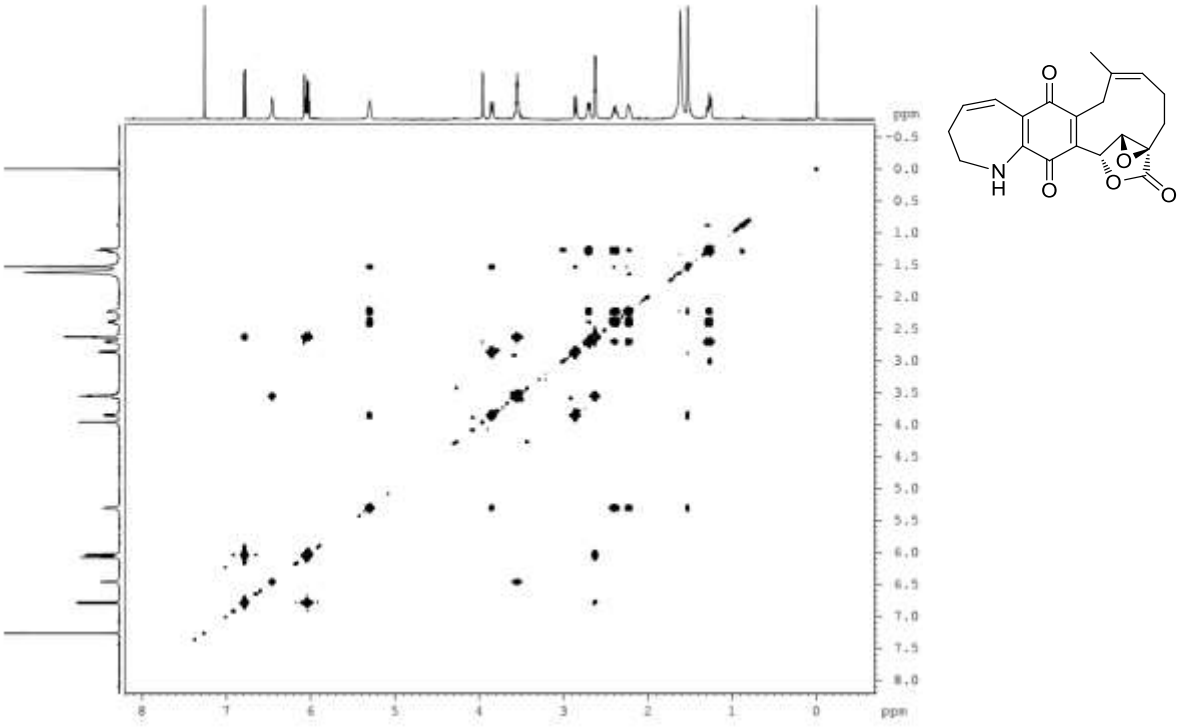

Figure S7. $^{1}H-^{1}H$ COSY spectrum of clavipine A (**1**)($CDCl_3$)

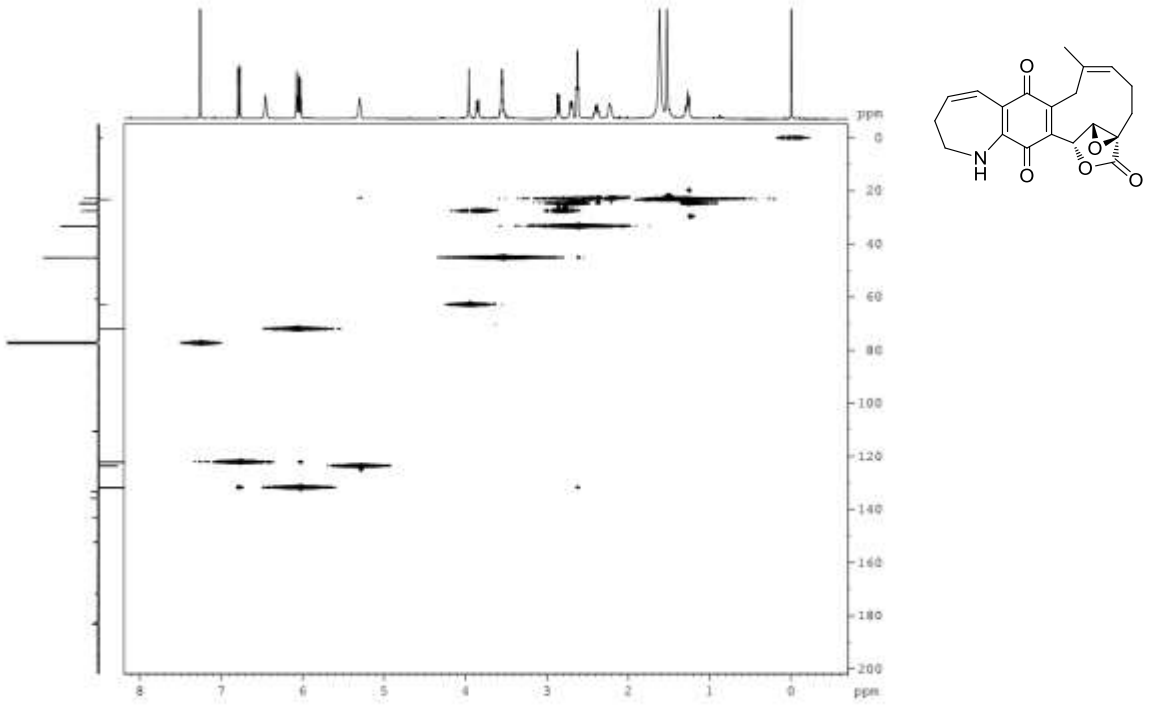

Figure S8. HSQC spectrum of clavipine A (**1**)($CDCl_3$)

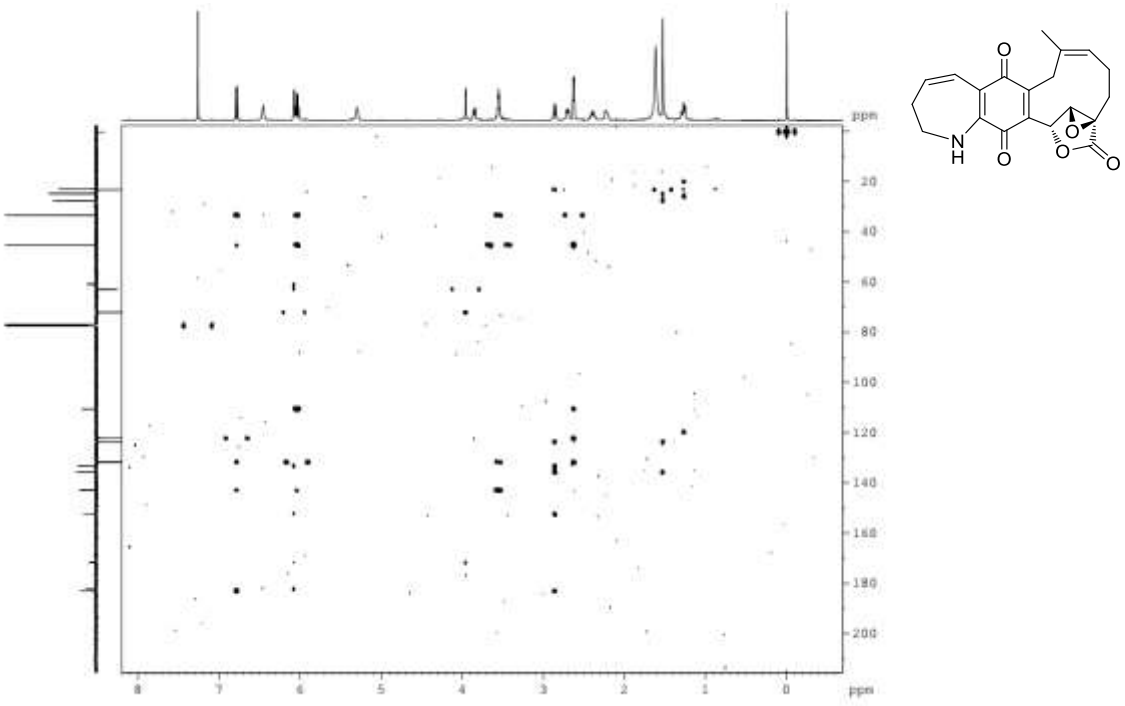

Figure S9. HMBC spectrum of clavipine A (**1**)($CDCl_3$)

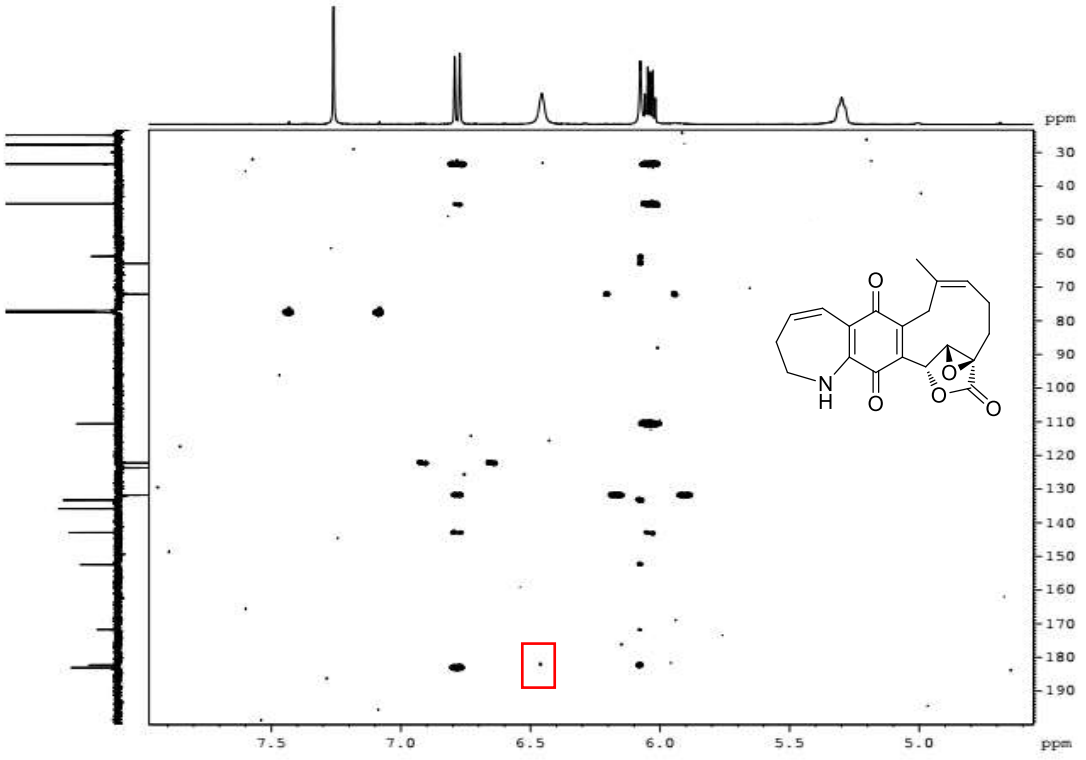

Figure S10. HMBC spectrum of clavipine A (**1**)($CDCl_3$)

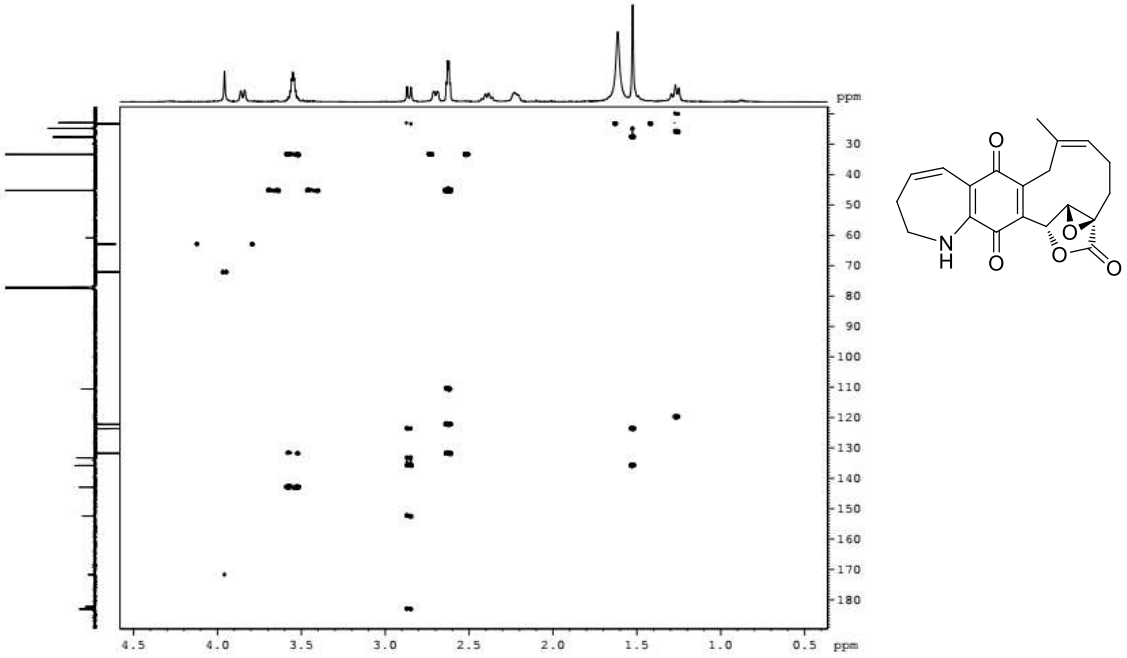

Figure S11. HMBC spectrum of clavipine A (**1**)($CDCl_3$)

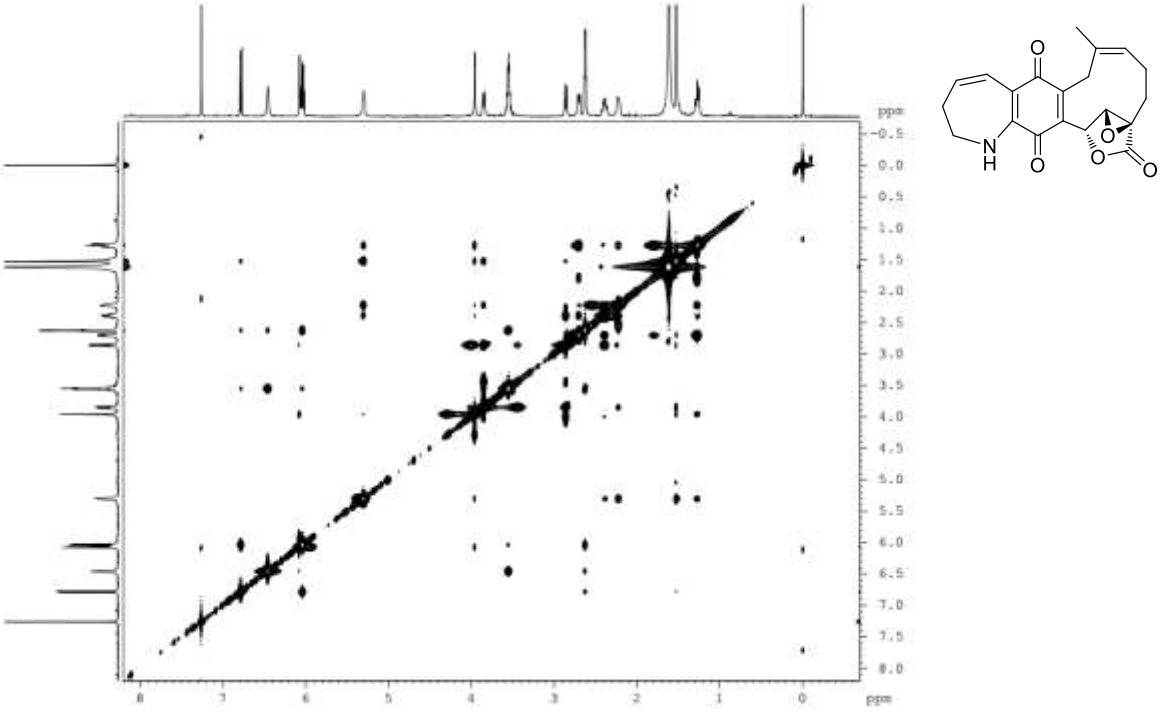

Figure S12. NOESY spectrum of clavipine A (**1**)($CDCl_3$)

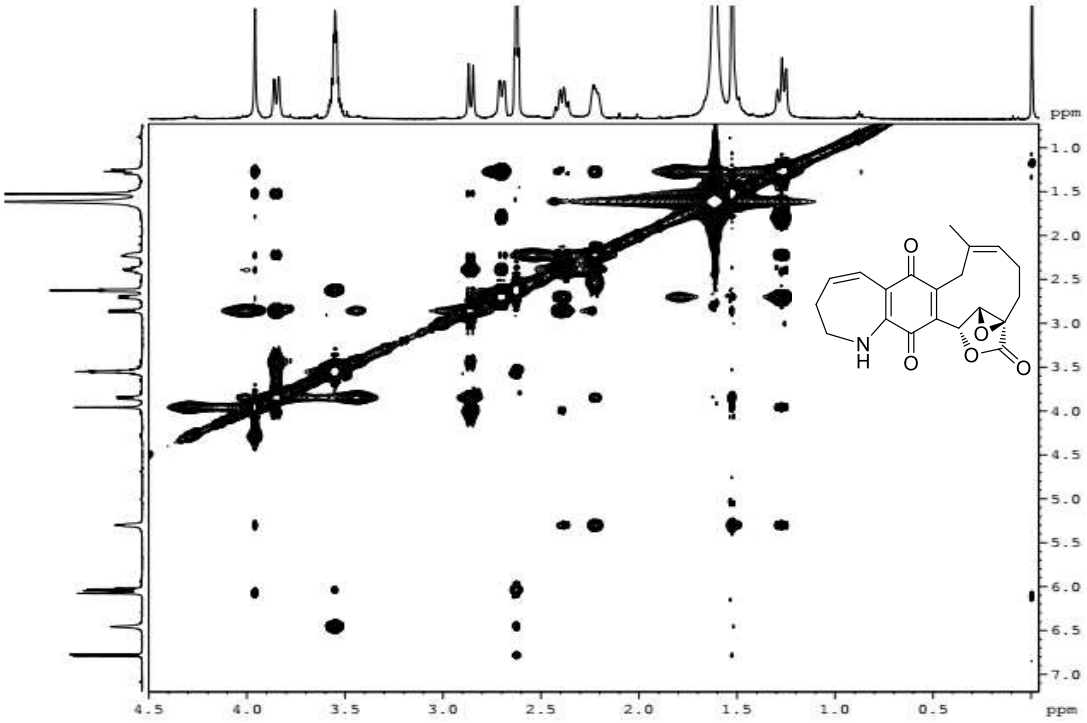

Figure S13. NOESY spectrum of clavipine A (**1**)($CDCl_3$)

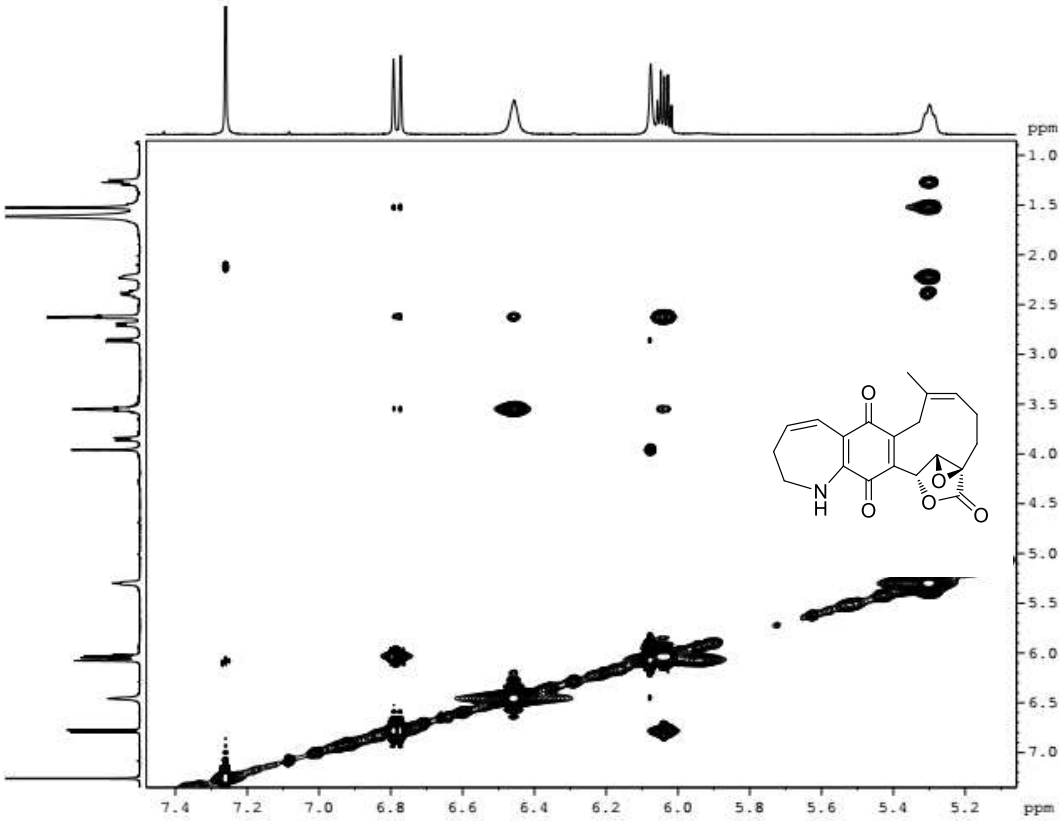

Figure S14. NOESY spectrum of clavipine A (**1**)($CDCl_3$)

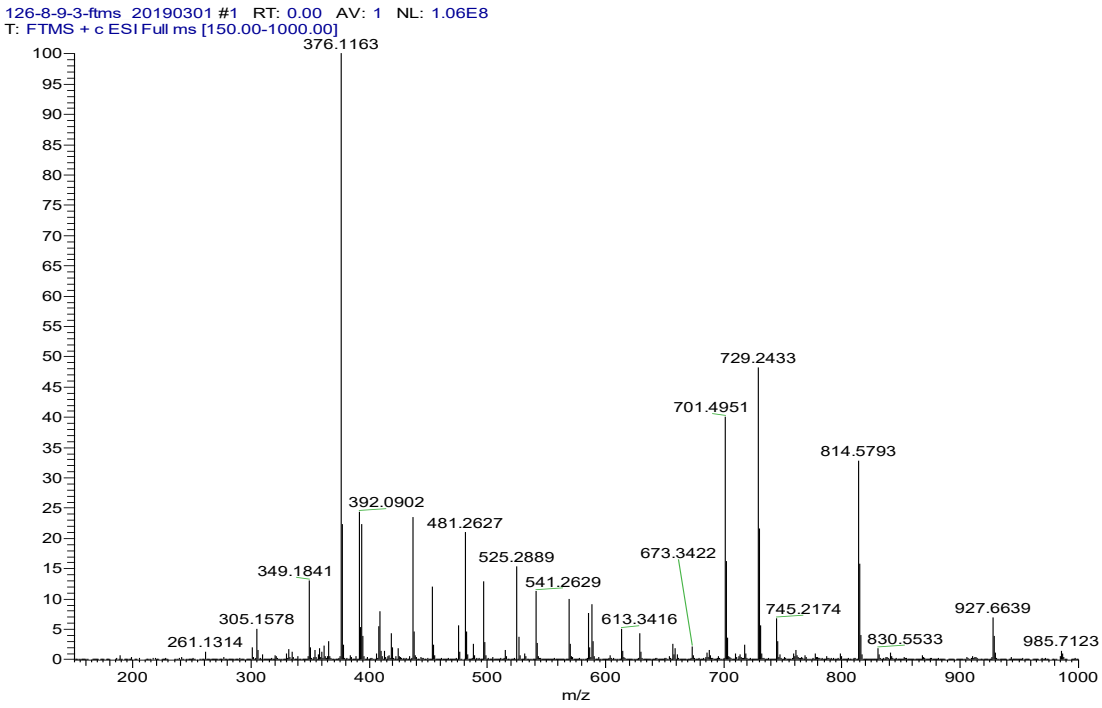

Figure S15. HRESIMS spectrum of clavipine B (**2**)

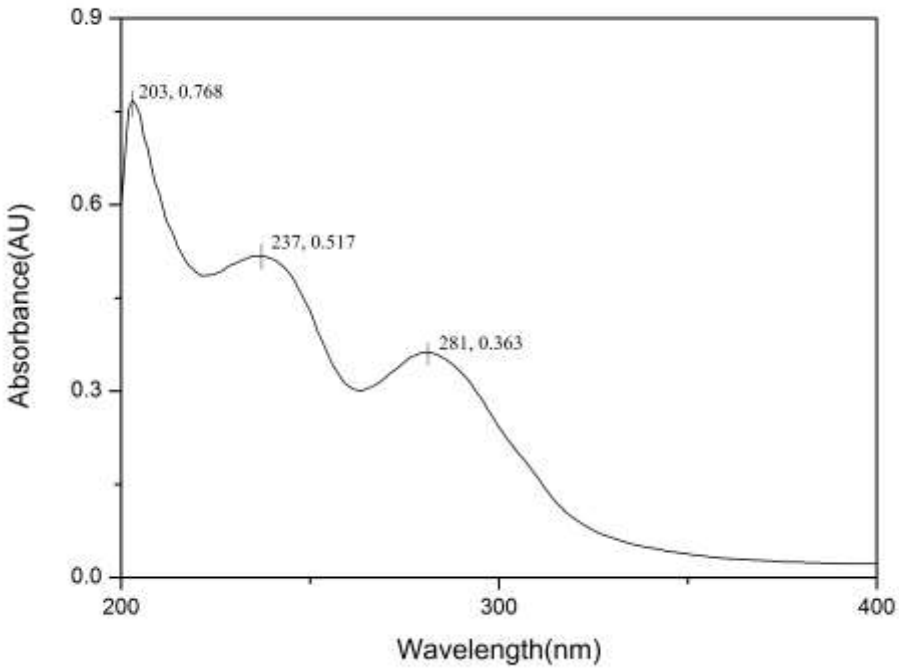

Figure S16. UV spectrum of clavipine B (**2**)

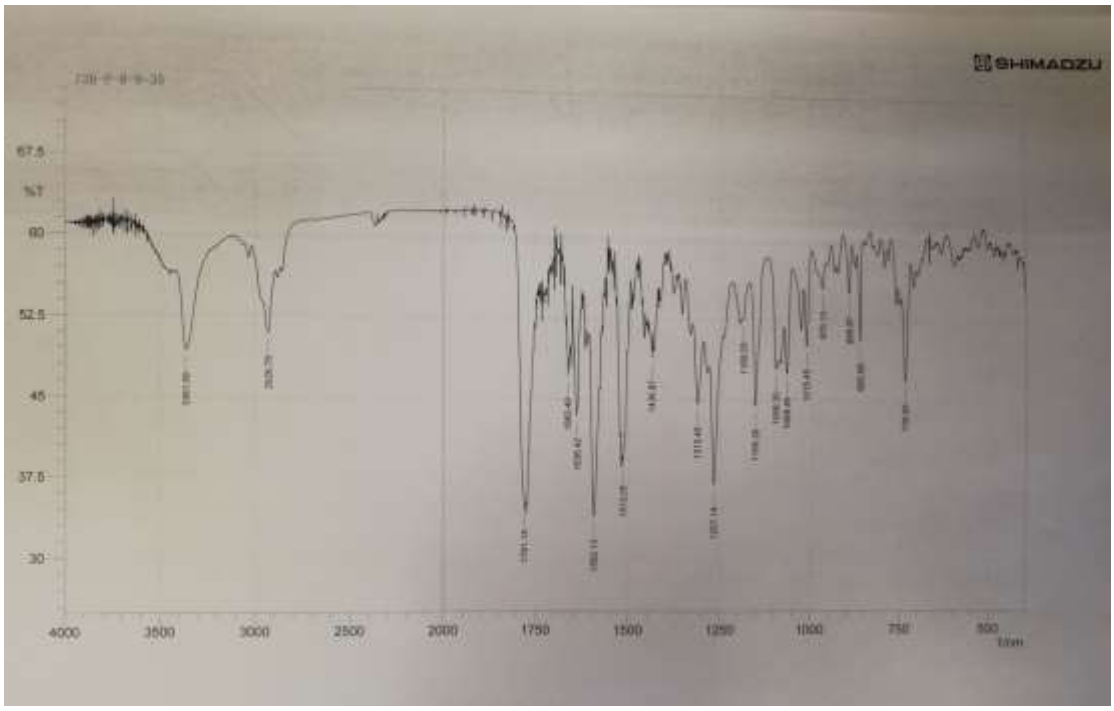

Figure S17. IR spectrum of clavipine B (**2**)

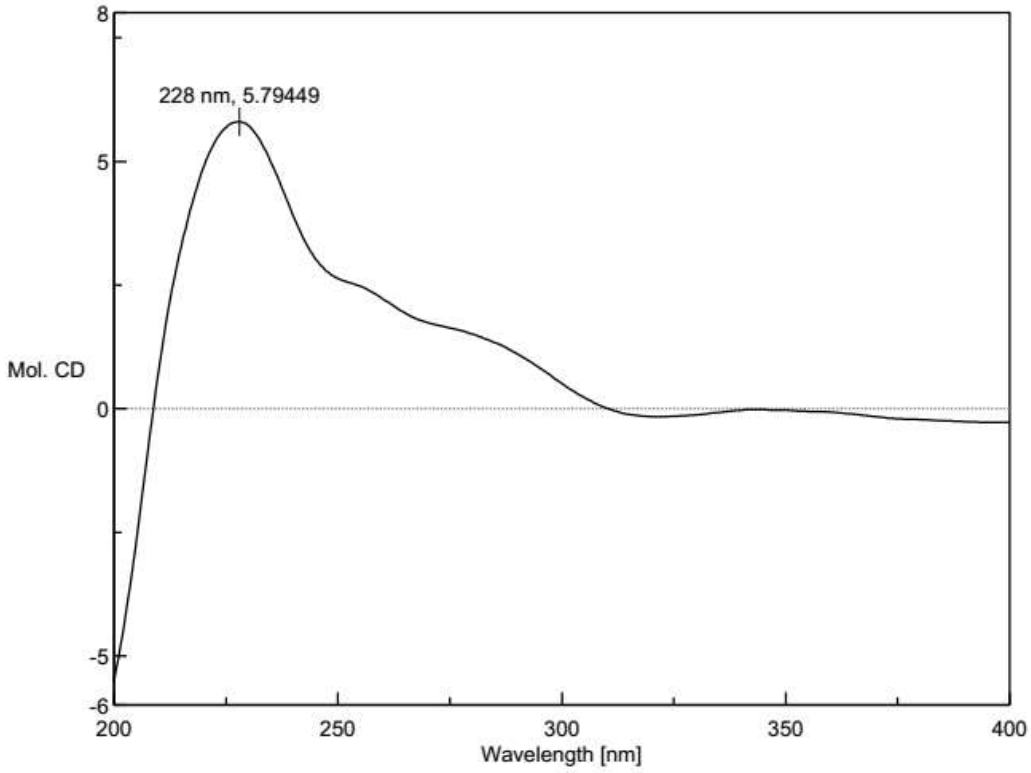

Figure S18. CD spectrum of clavipine B (**2**)(MeOH)

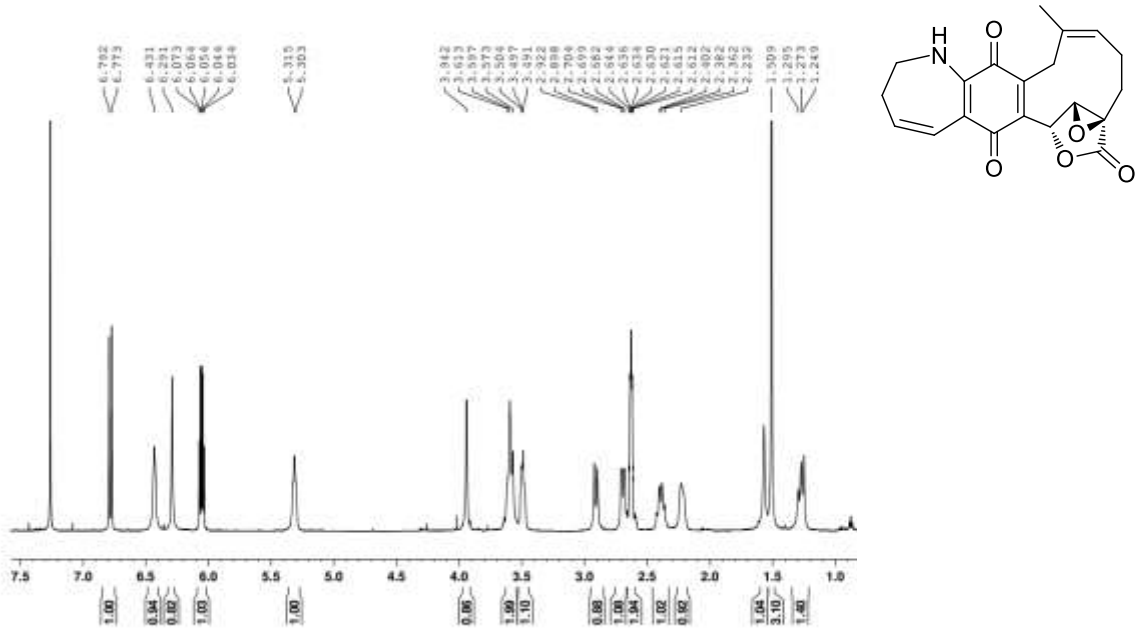

Figure S19. ^{1}HNMR spectrum of clavipine B (**2**)($CDCl_3$, 600MHz)

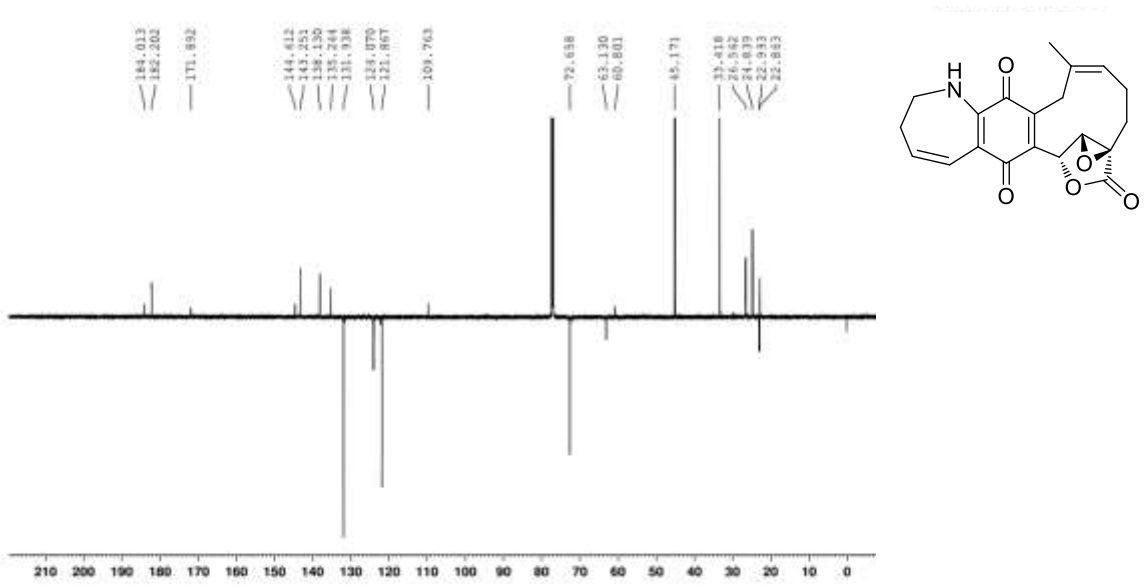

Figure S20. ^{13}C APT spectrum of clavipine B (**2**)($CDCl_3$, 150MHz)

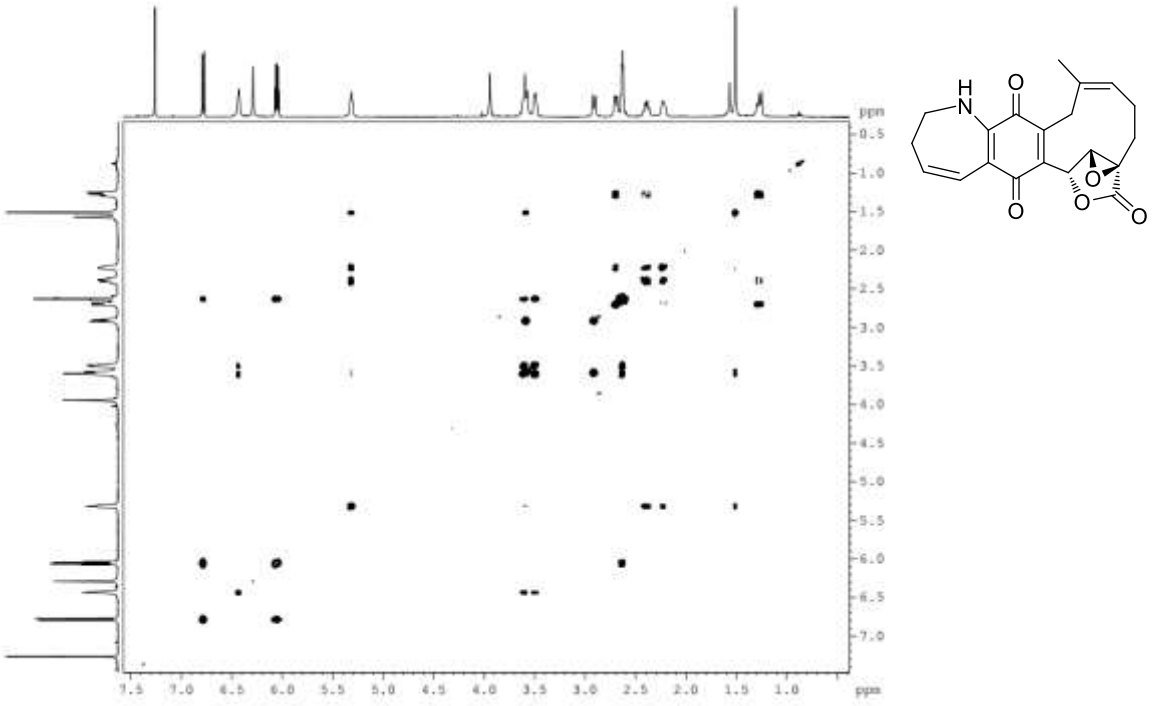

Figure S21. $^{1}H-^{1}H$ COSY spectrum of clavipine B (**2**)($CDCl_3$)

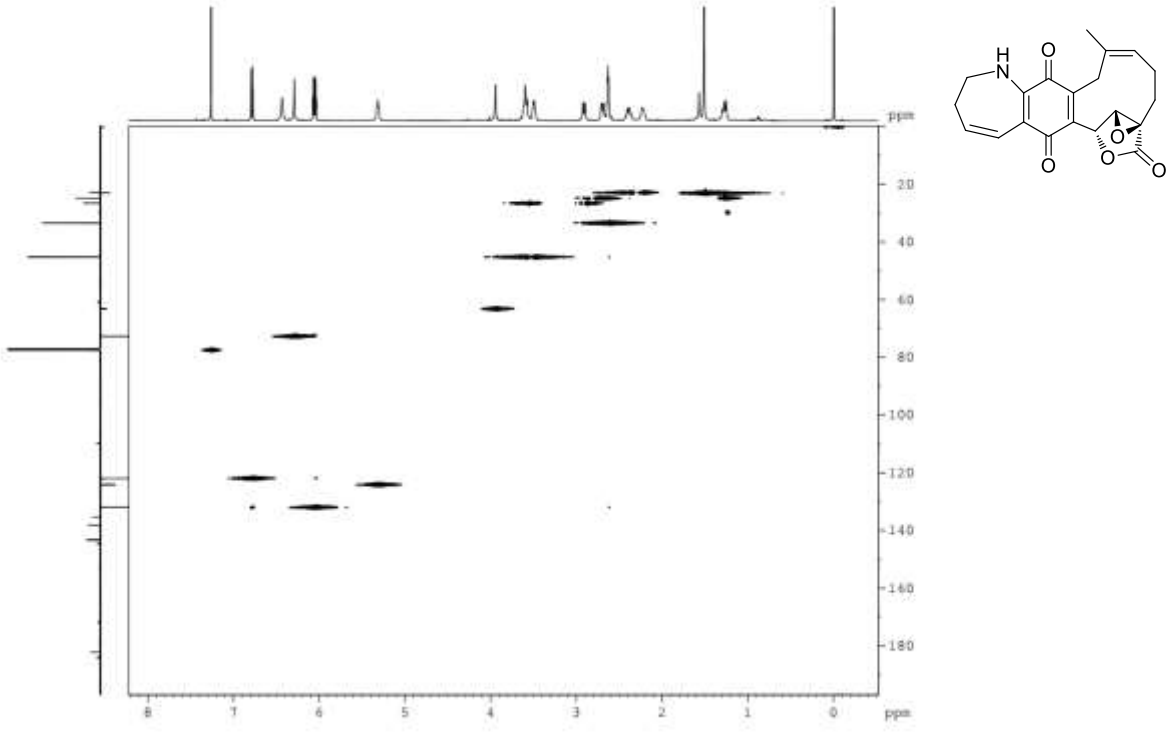

Figure S22. HSQC spectrum of clavipine B (**2**)($CDCl_3$)

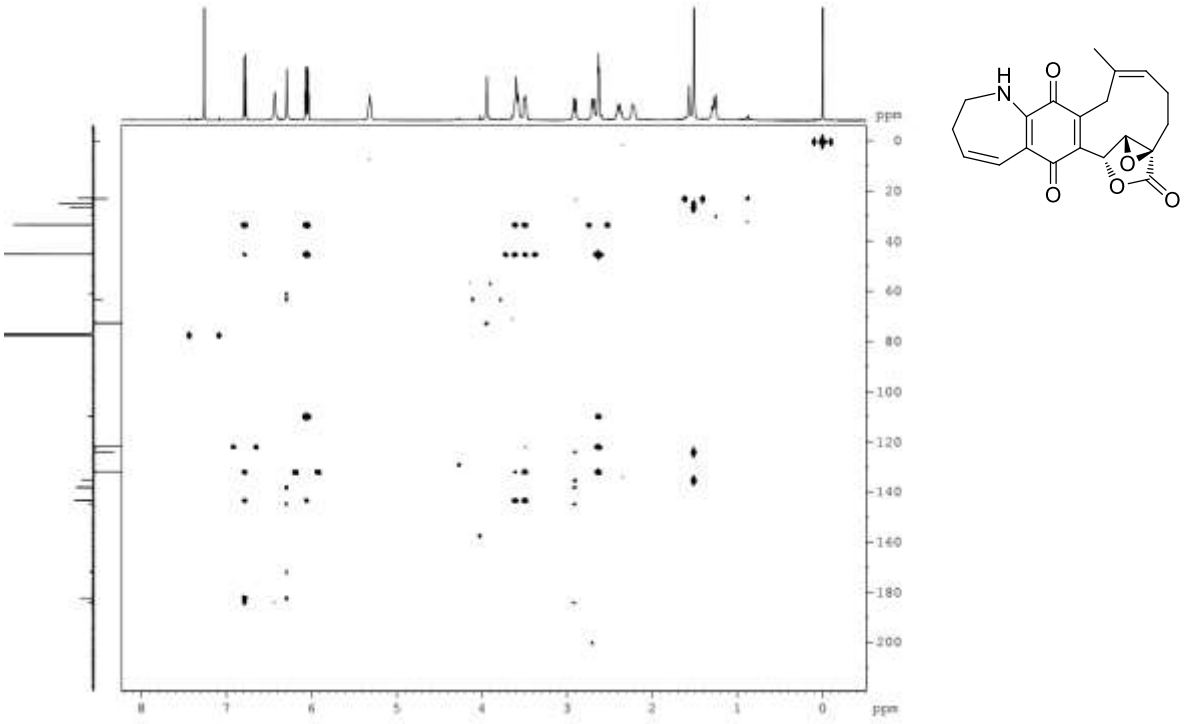

Figure S23. HMBC spectrum of clavipine B (**2**)($CDCl_3$)

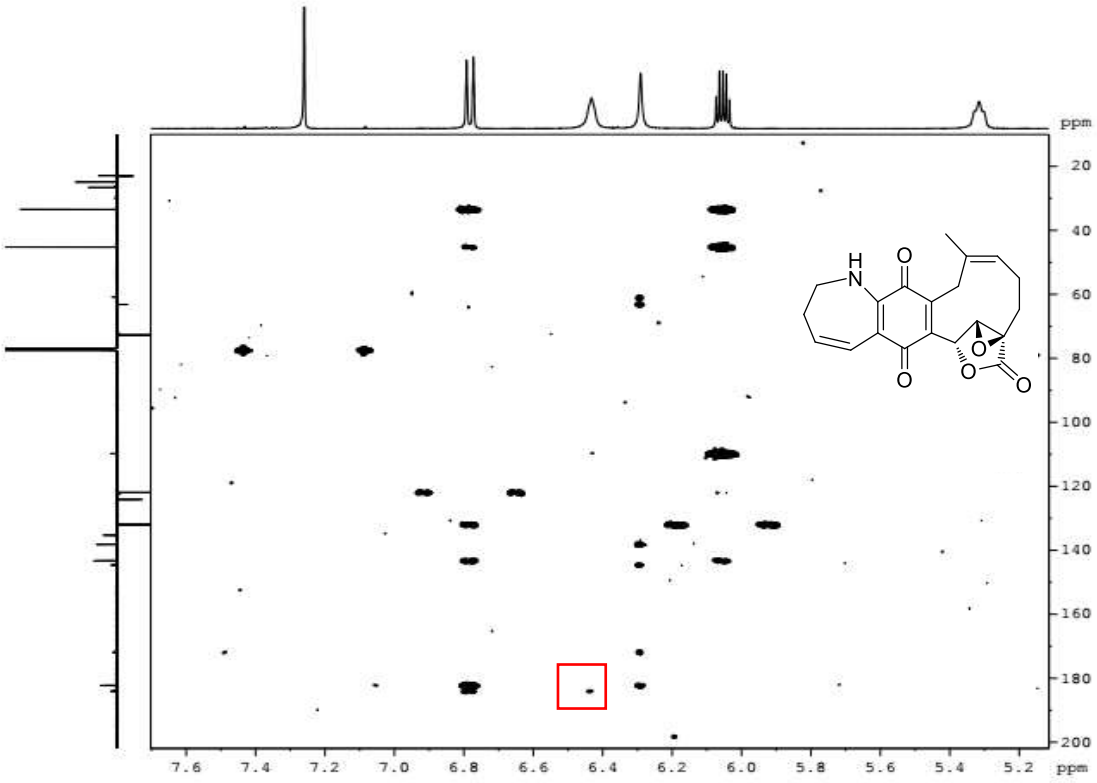

Figure S24. HMBC spectrum of clavipine B (**2**)($CDCl_3$)

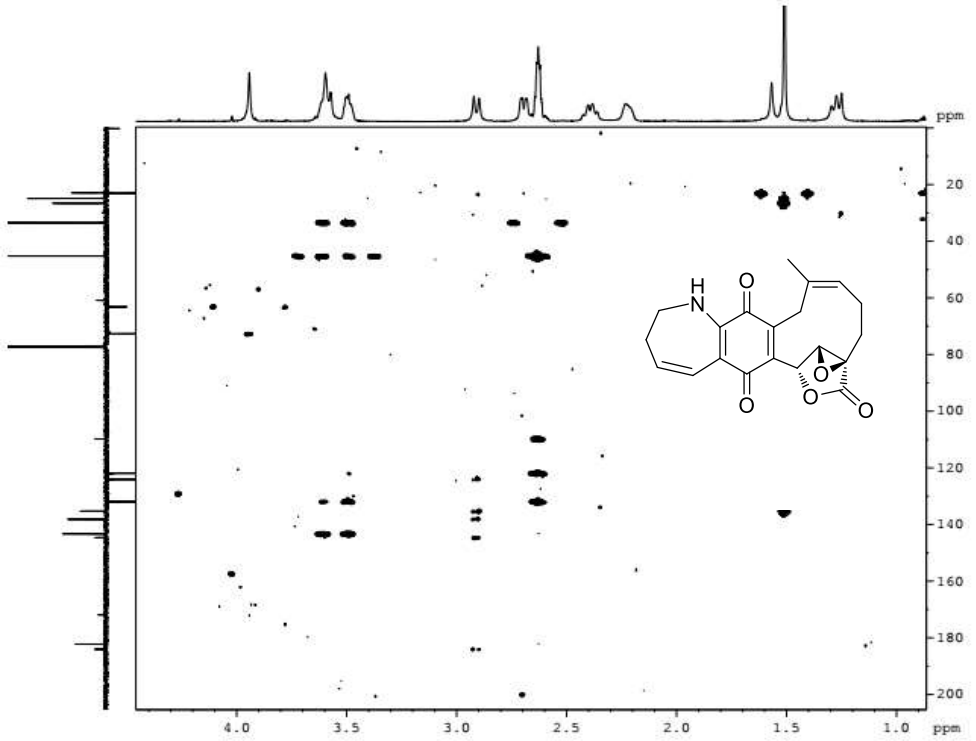

Figure S25. HMBC spectrum of clavipine B (**2**)($CDCl_3$)

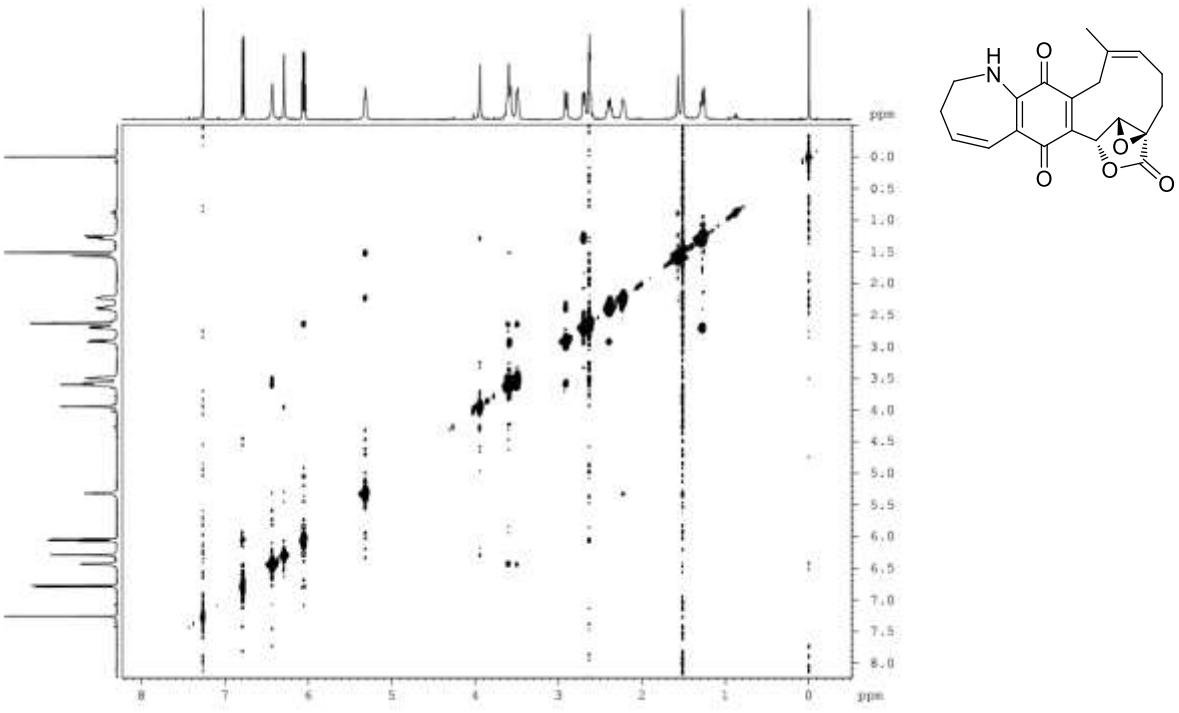

Figure S26. NOESY spectrum of clavipine B (**2**)($CDCl_3$)

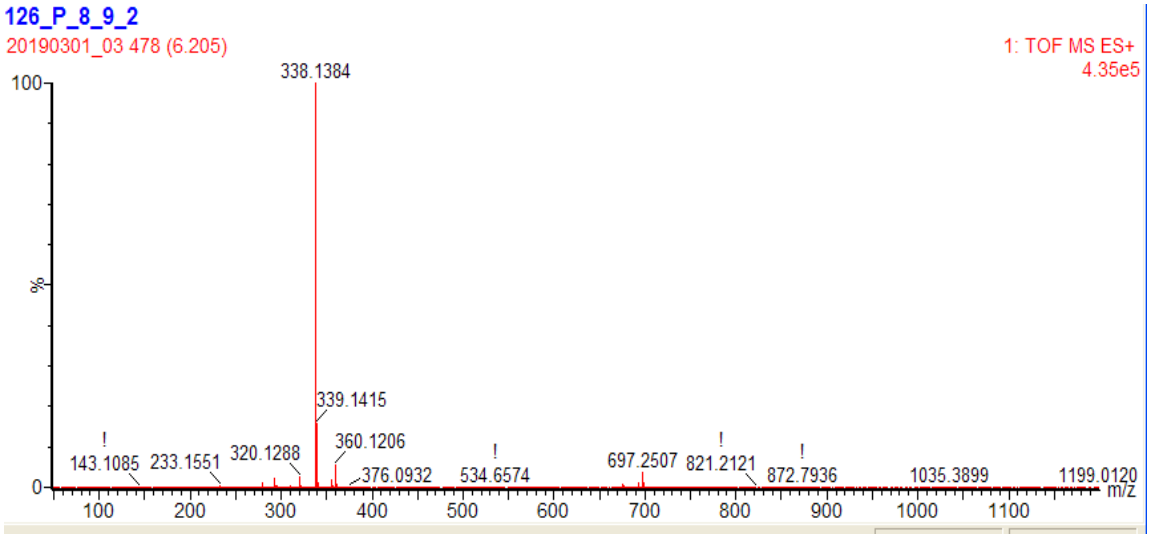

Figure S27. HRESIMS spectrum of clavipine C (**3**)

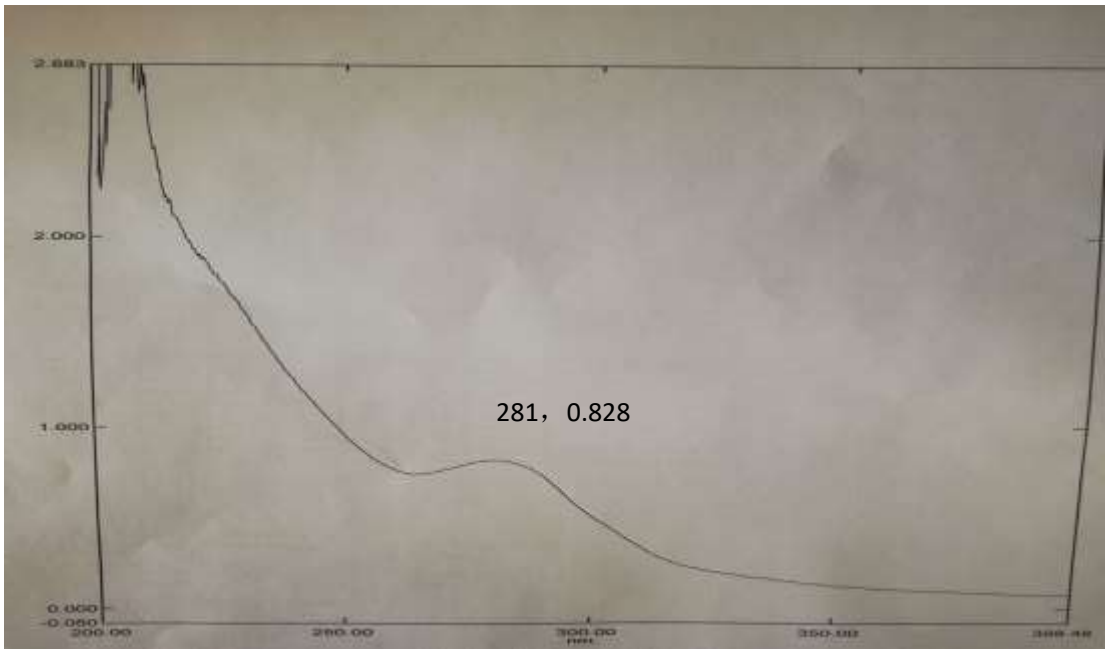

Figure S28. UV spectrum of clavipine C (**3**)

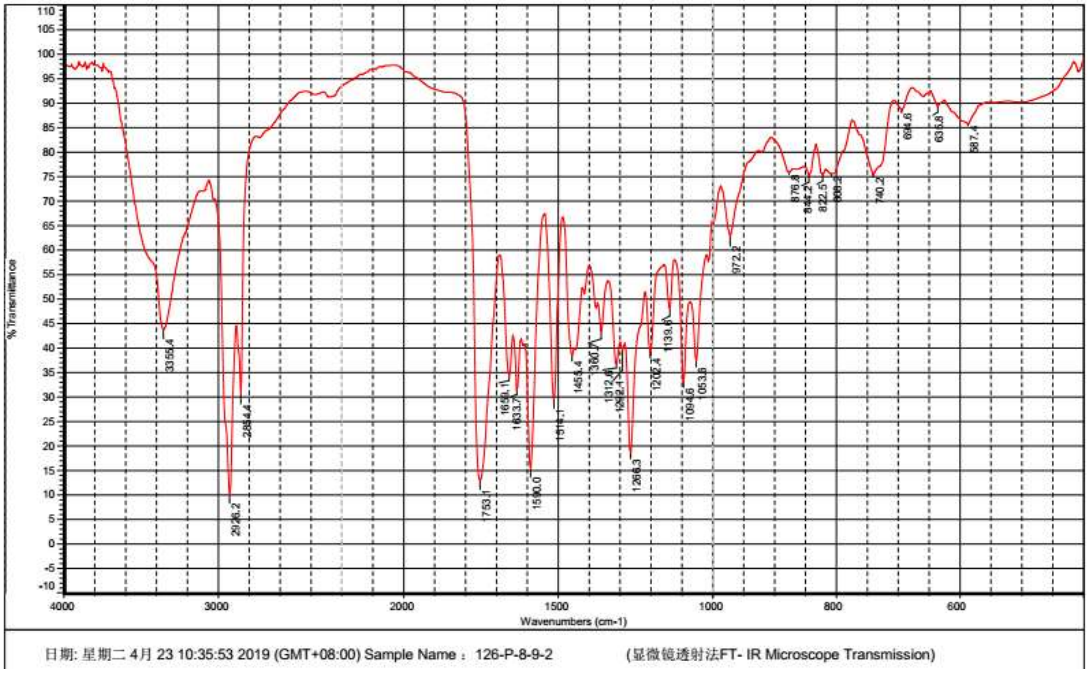

Figure S29. IR spectrum of clavipine C (**3**)

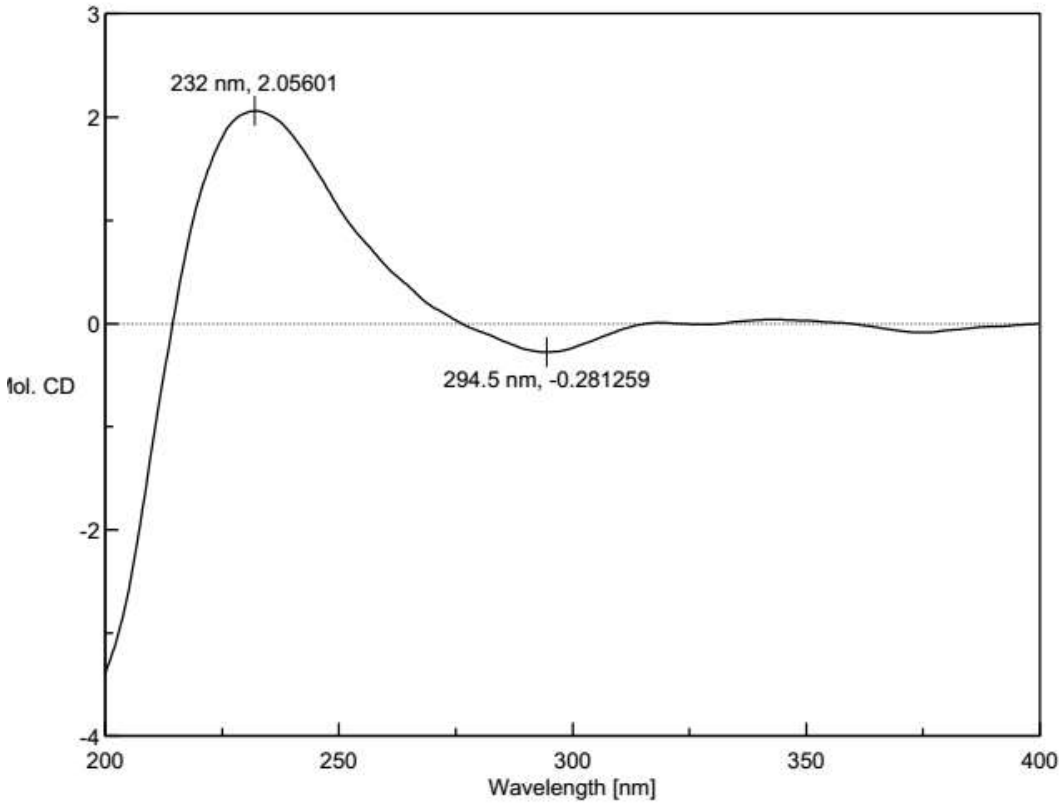

Figure S30. CD spectrum of clavipine C (**3**)(MeOH)

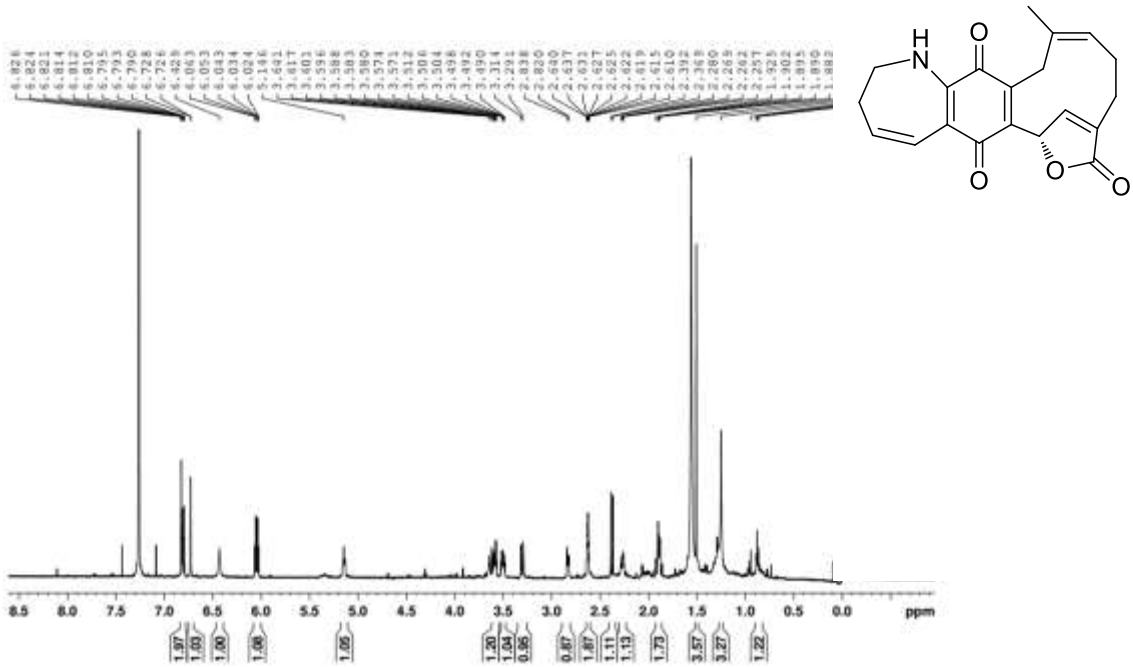

Figure S31. ^{1}HNMR spectrum of clavipine C (**3**)($CDCl_3$, 600MHz)

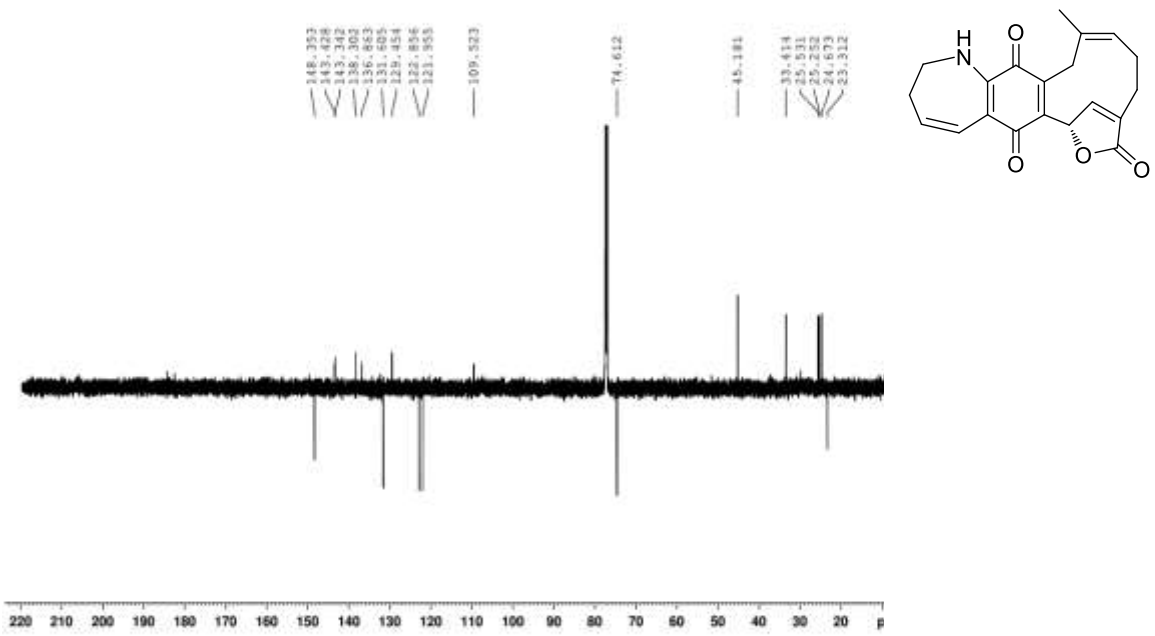

Figure S32. ^{13}C APT spectrum of clavipine C (**3**)($CDCl_3$, 150MHz)

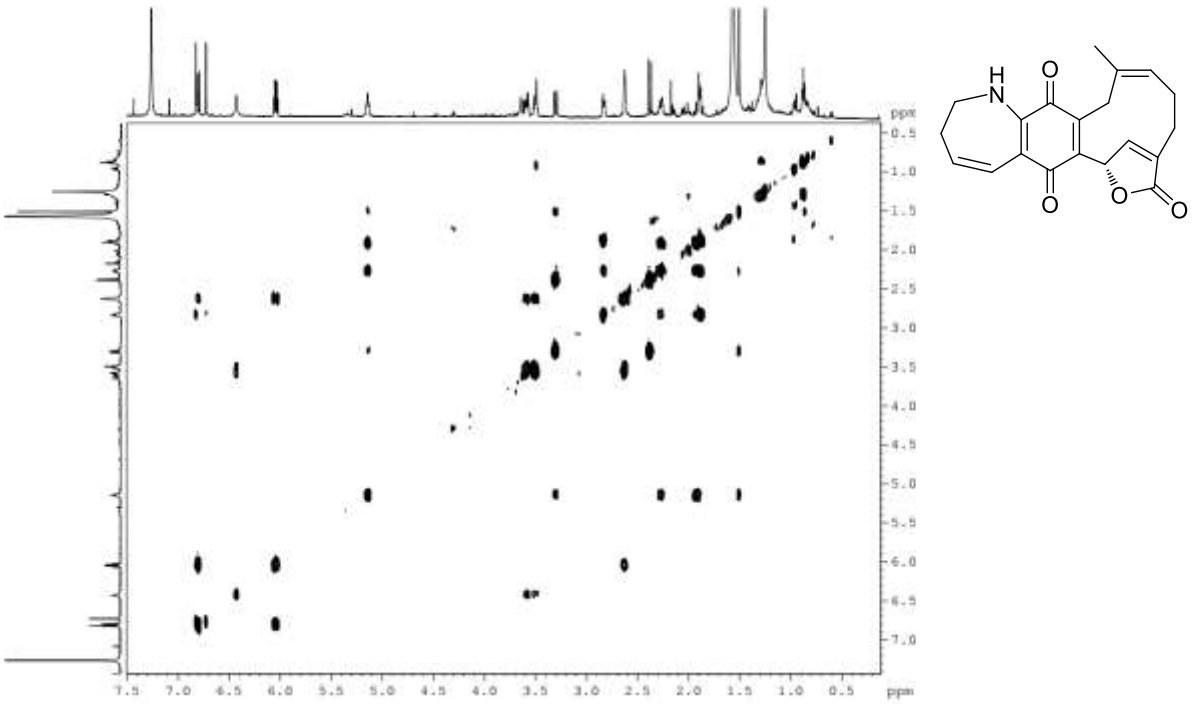

Figure S33. $^{1}H-^{1}H$ COSY spectrum of clavipine C (**3**)($CDCl_3$)

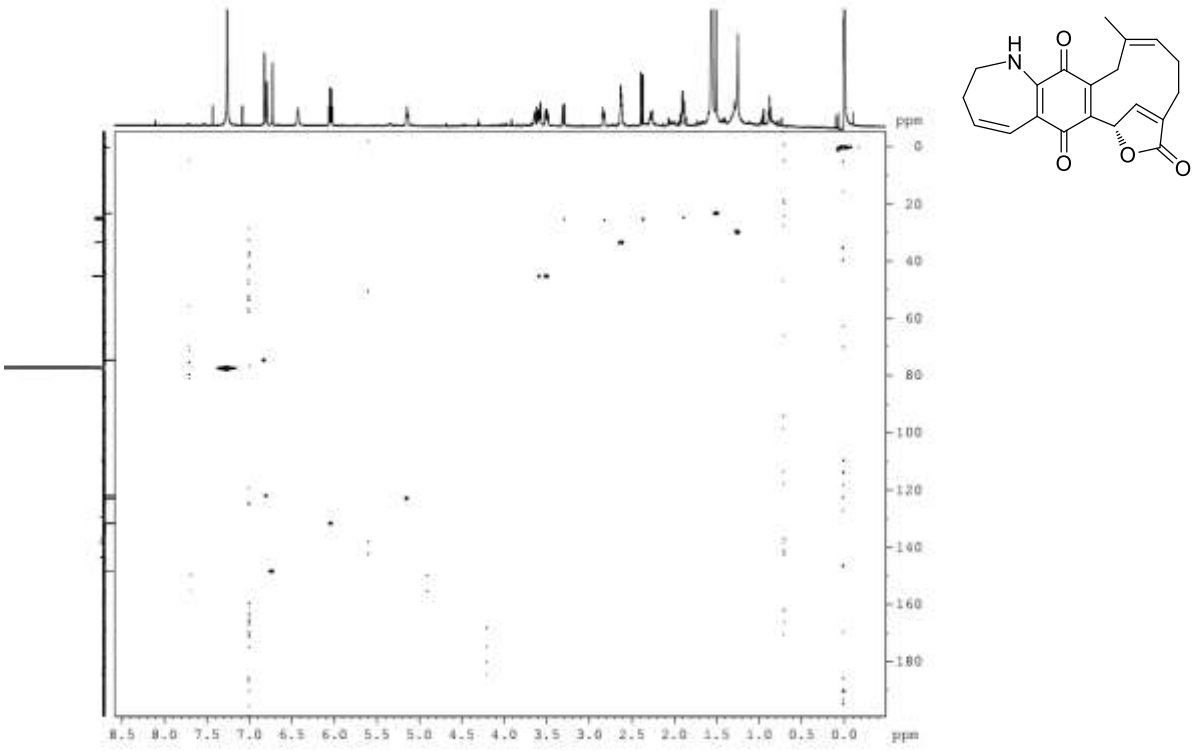

Figure S34. HSQC spectrum of clavipine C (**3**)($CDCl_3$)

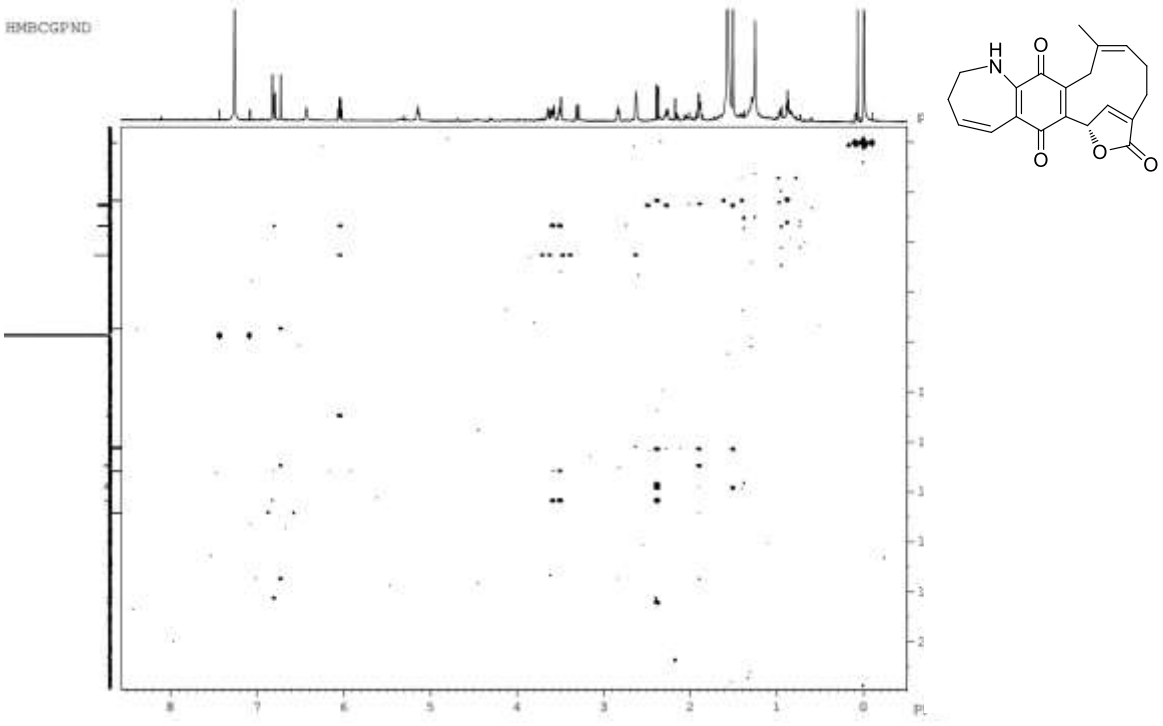

Figure S35. HMBC spectrum of clavipine C (**3**)($CDCl_3$)

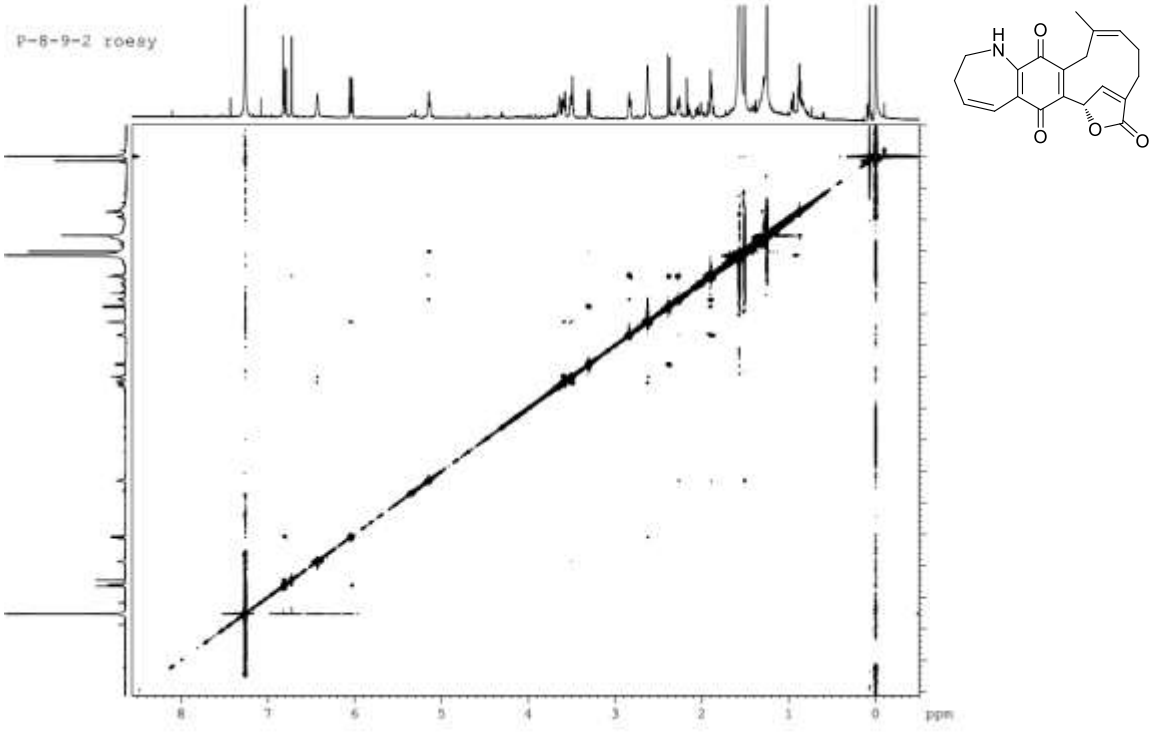

Figure S36. ROESY spectrum of clavipine C (**3**)($CDCl_3$)

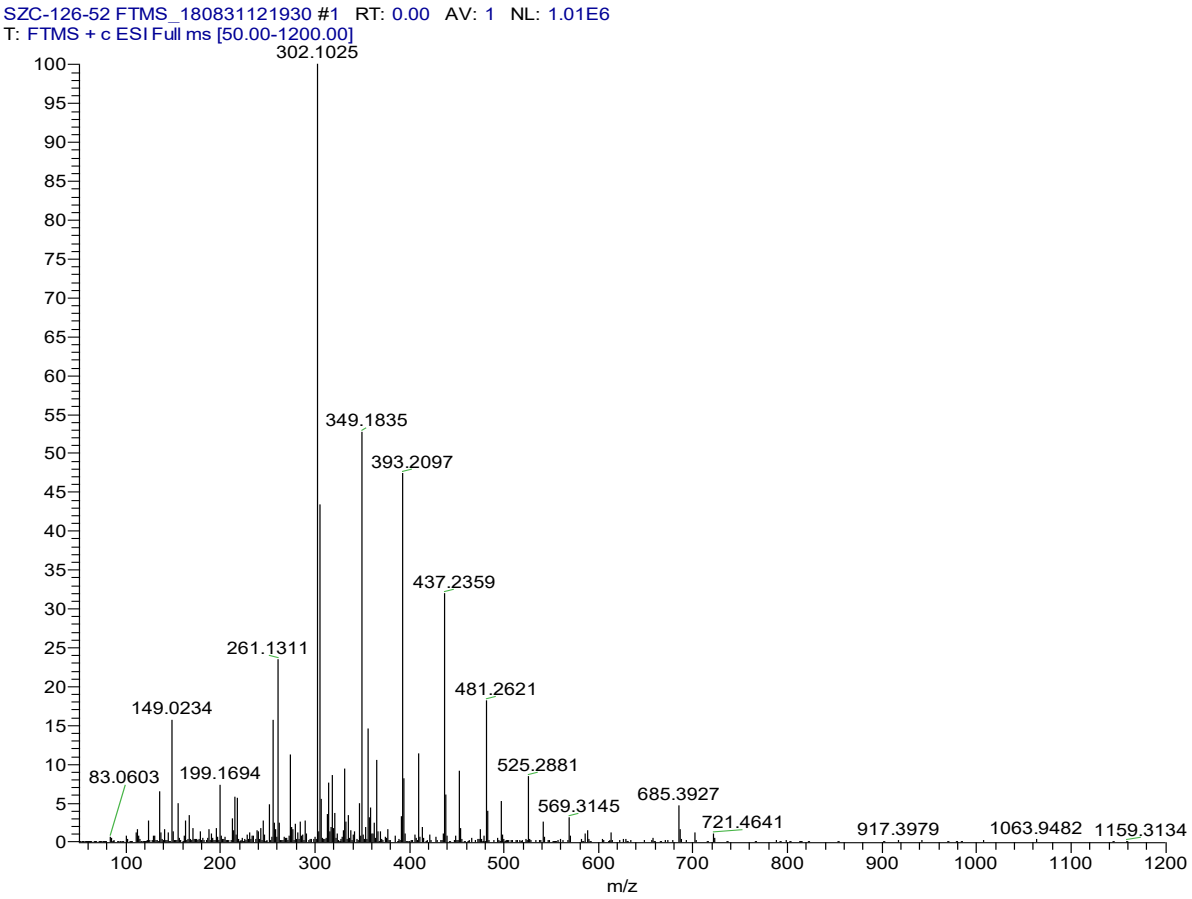

Figure S37. HRESIMS spectrum of clavilactone F (**4**)

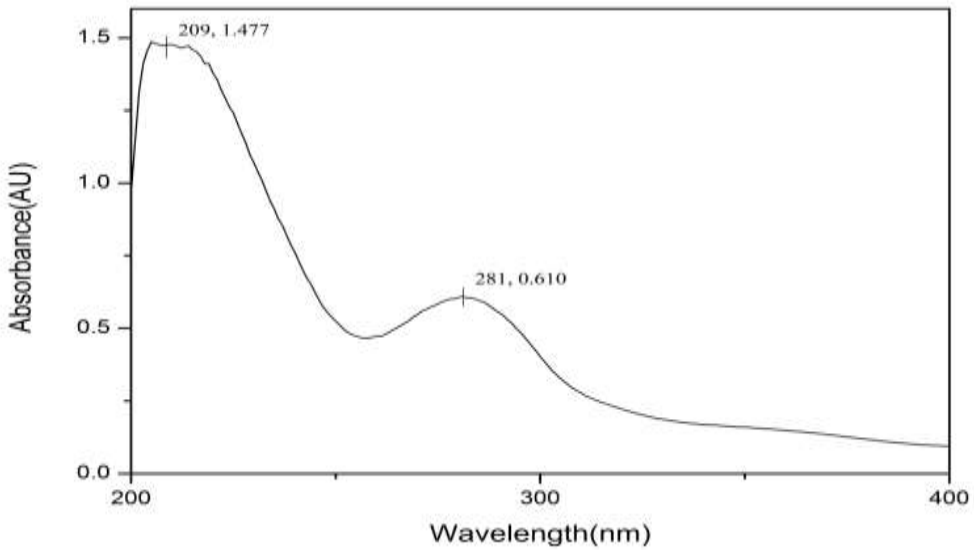

Figure S38. UV spectrum of clavilactone F (**4**)

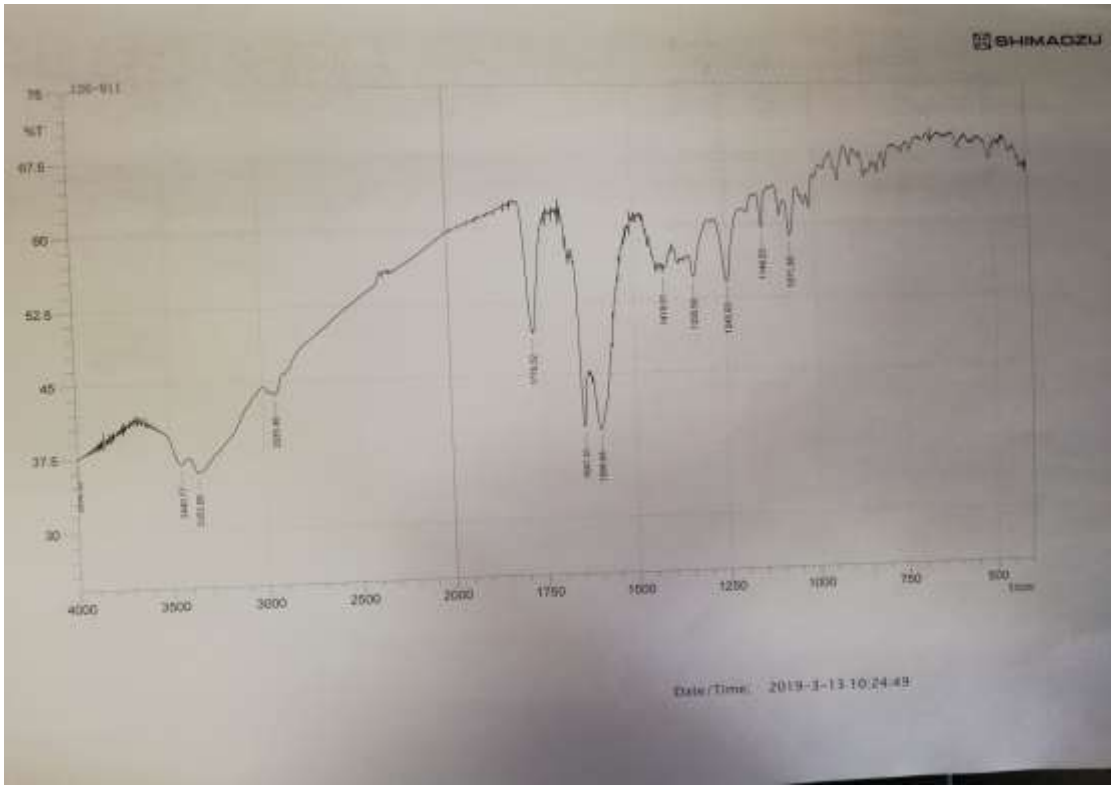

Figure S39. IR spectrum of clavilactone F (**4**)

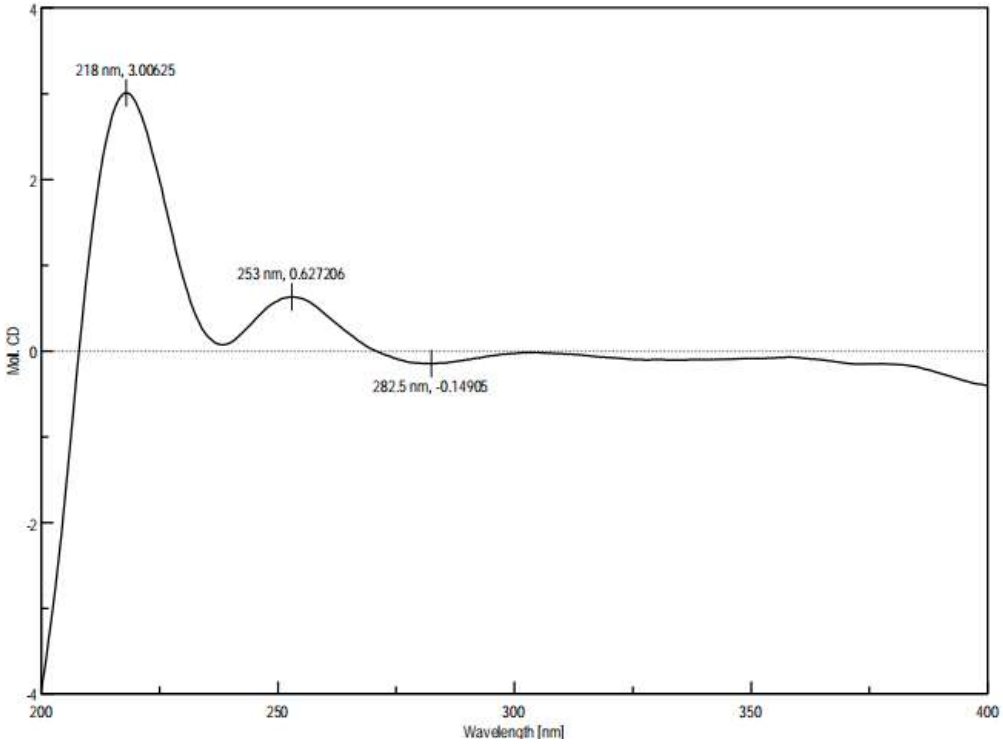

Figure S40. CD spectrum of clavilactone F (**4**)(MeOH)

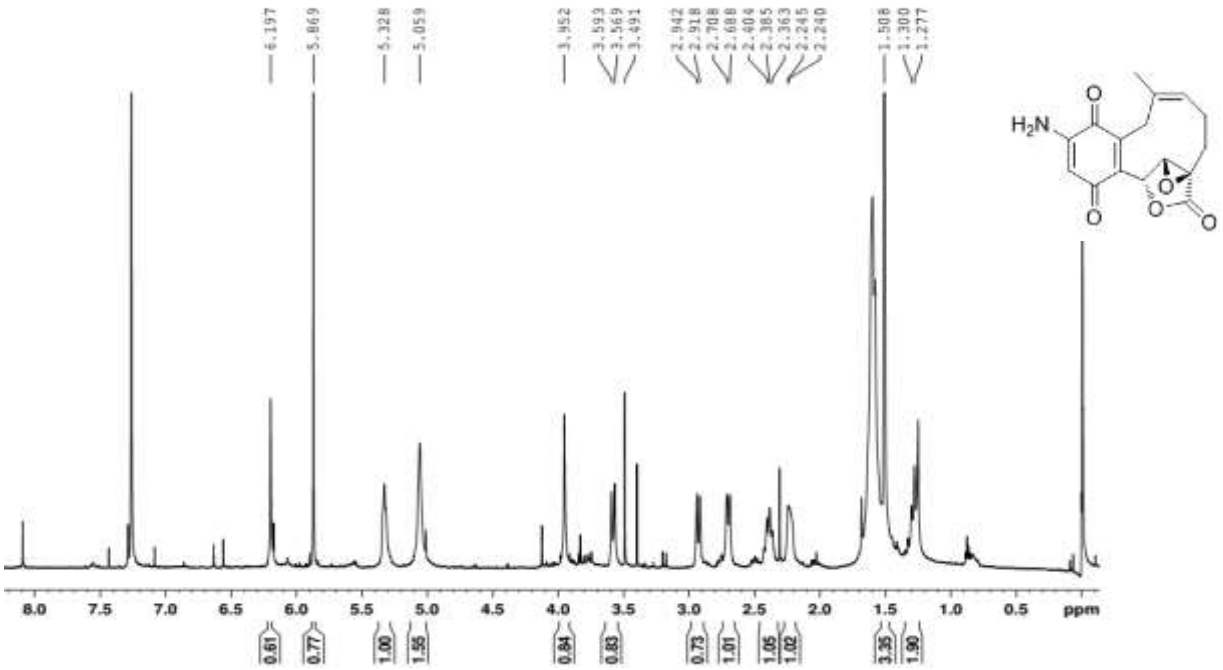

Figure S41. [1]HNMR spectrum of clavilactone F (**4**) ($CDCl_3$, 600MHz)

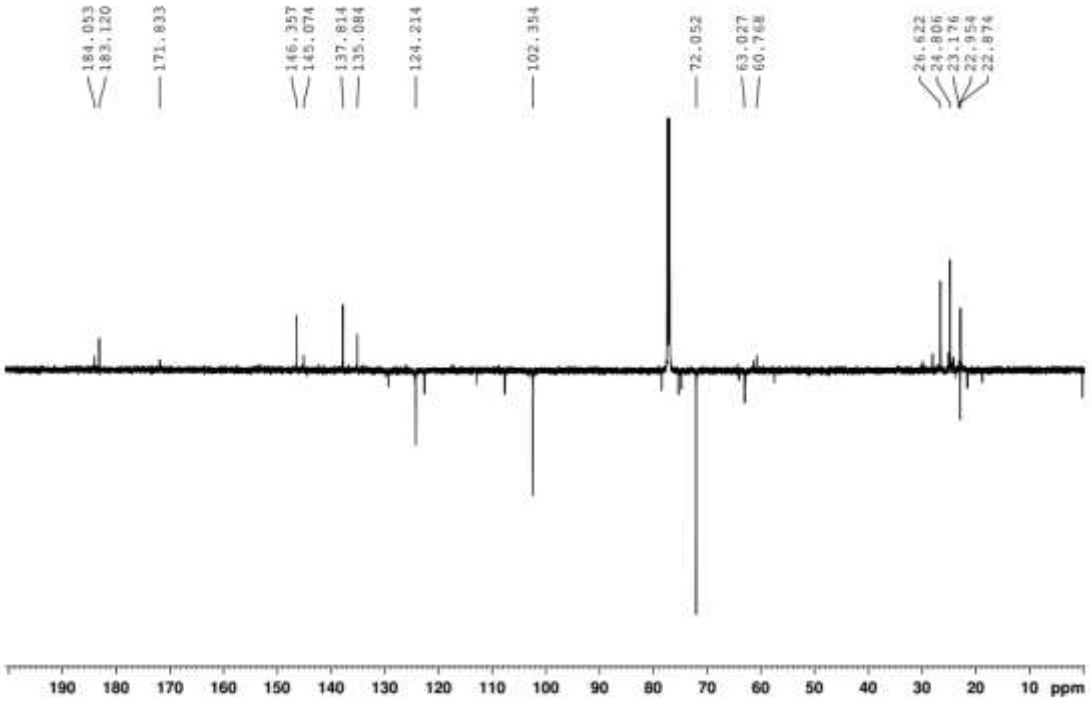

Figure S42. [13]C APT spectrum of clavilactone F (**4**)($CDCl_3$, 150MHz)

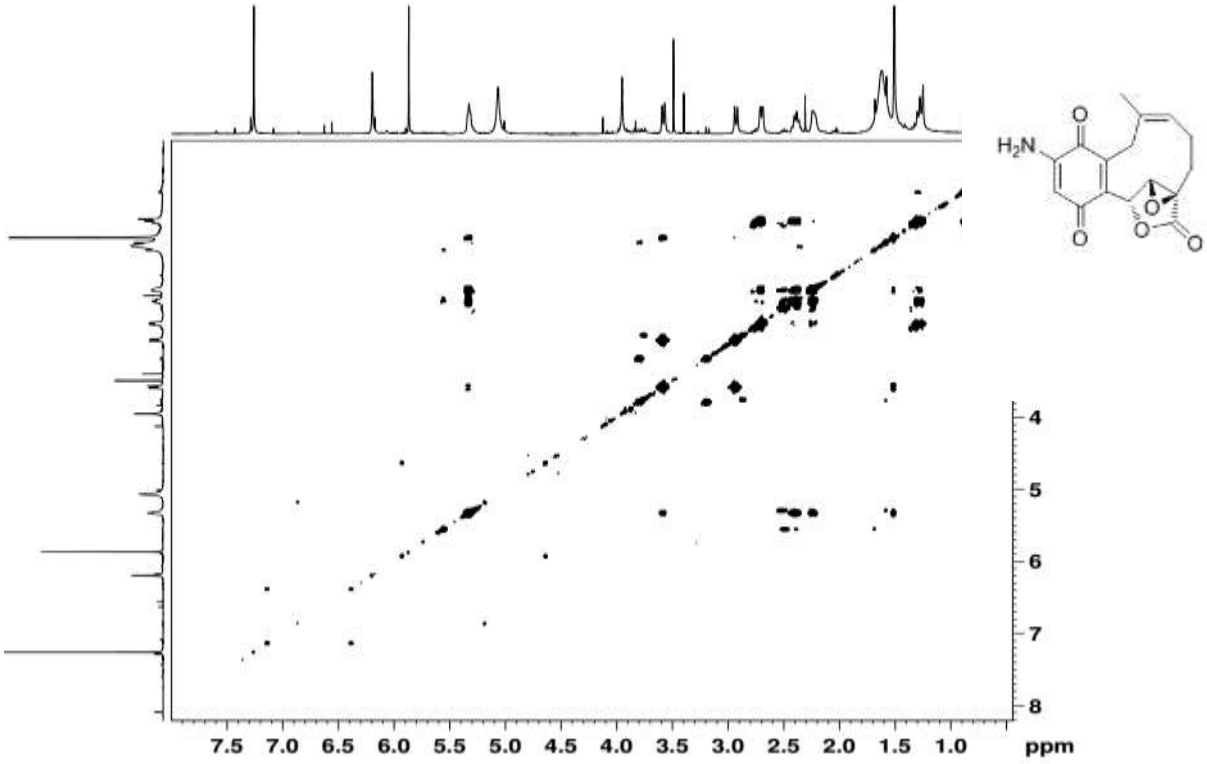

Figure S43. $^{1}H-^{1}H$ COSY spectrum of clavilactone F (**4**)($CDCl_3$)

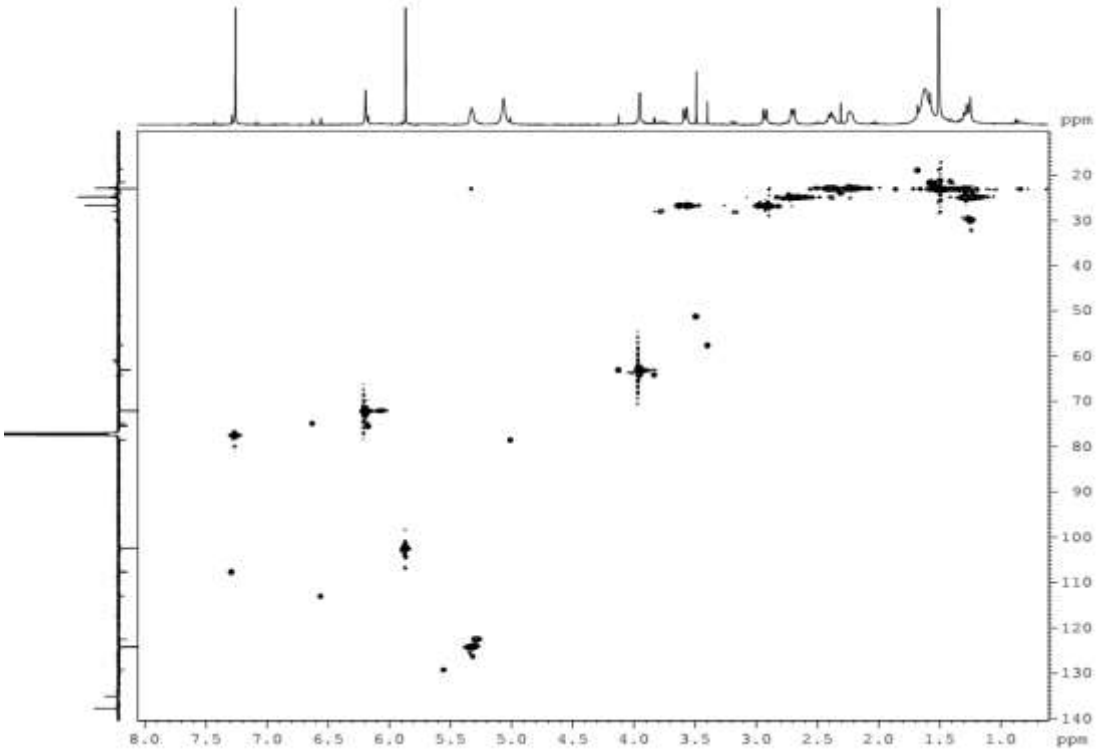

Figure S44. HSQC spectrum of clavilactone F (**4**)($CDCl_3$)

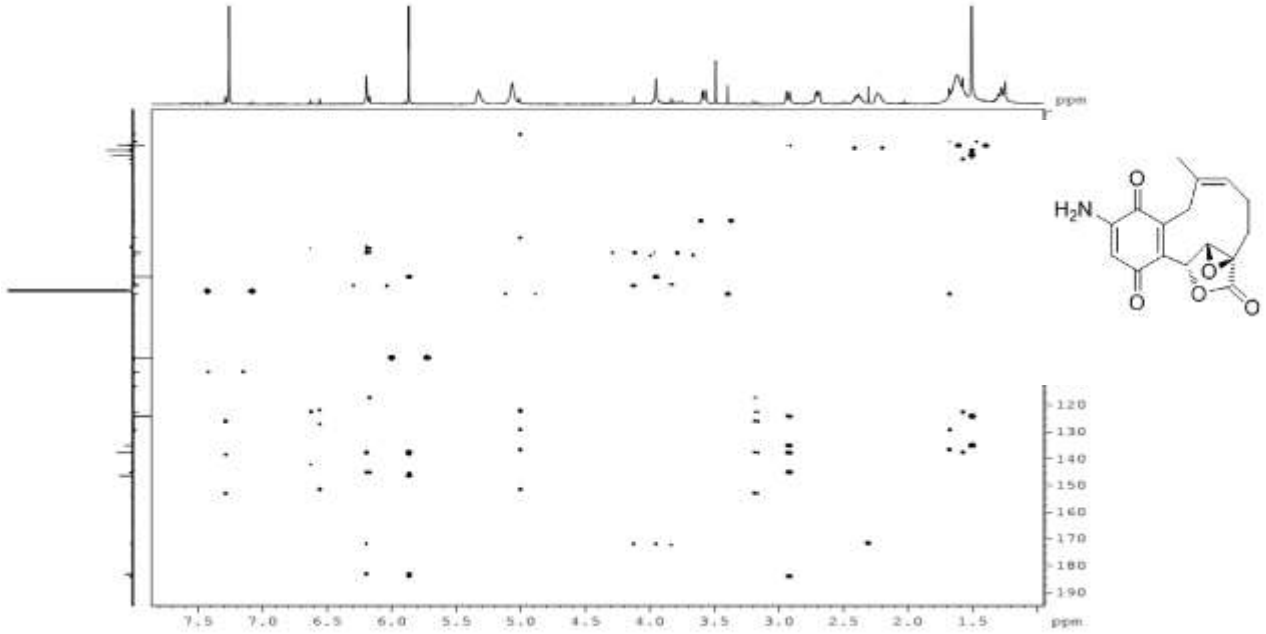

Figure S45. HMBC spectrum of clavilactone F (**4**)($CDCl_3$)

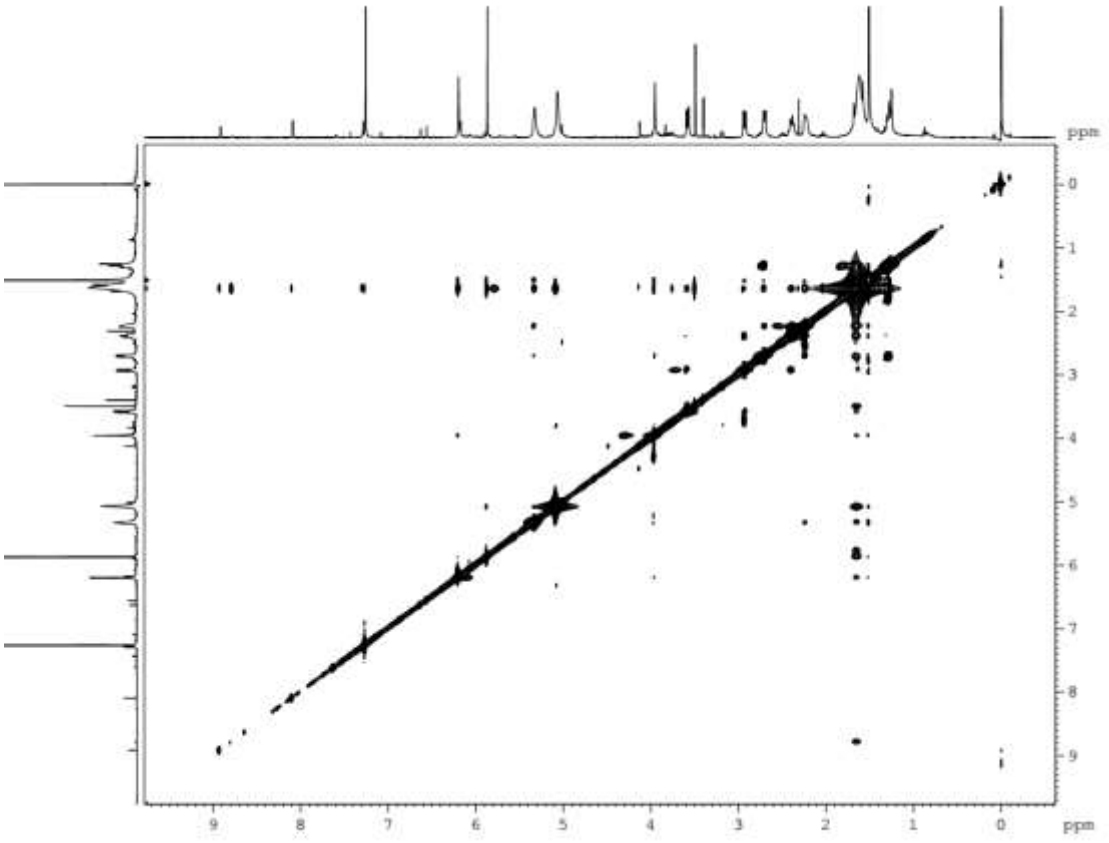

Figure S46. ROESY spectrum of clavilactone F (**4**)($CDCl_3$)

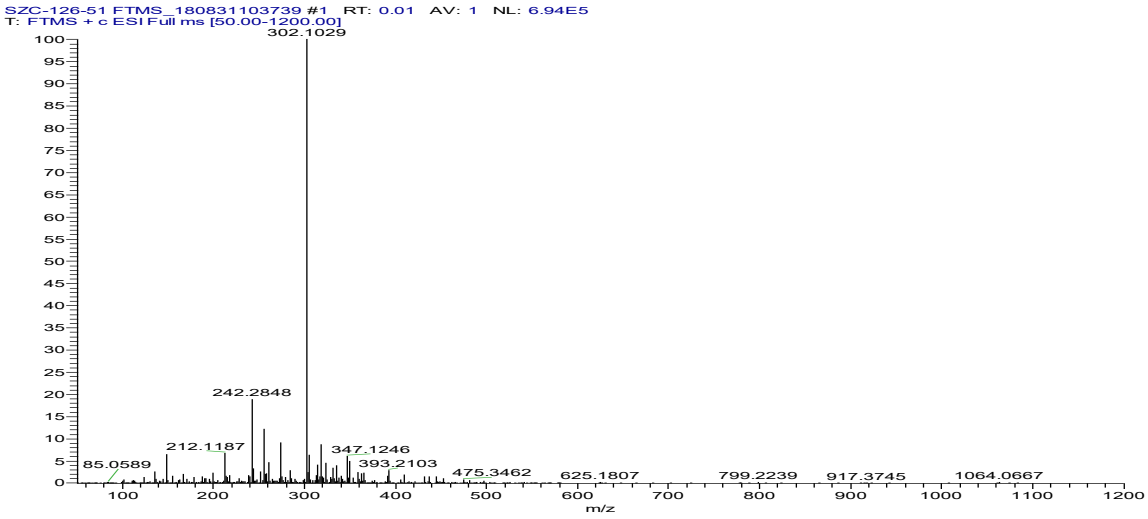

Figure S47. HRESIMS spectrum of clavilactone D (**5**)

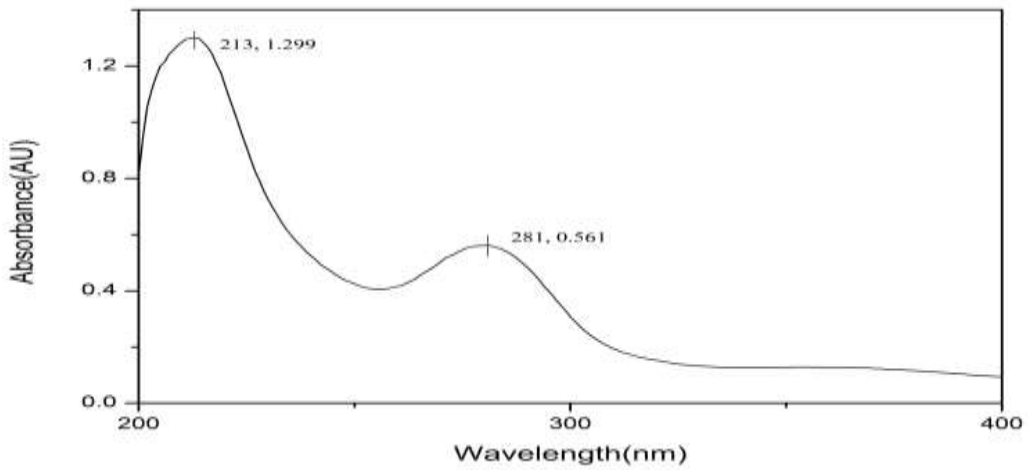

Figure S48. UV spectrum of clavilactone D (**5**)

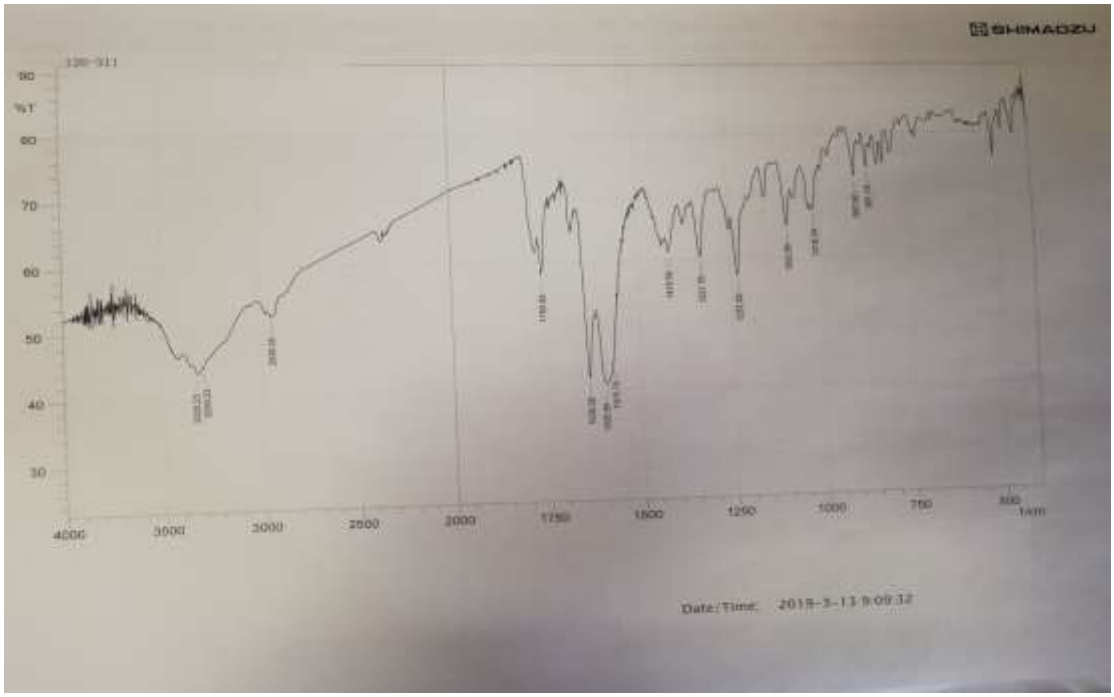

Figure S49. IR spectrum of clavilactone D(**5**)

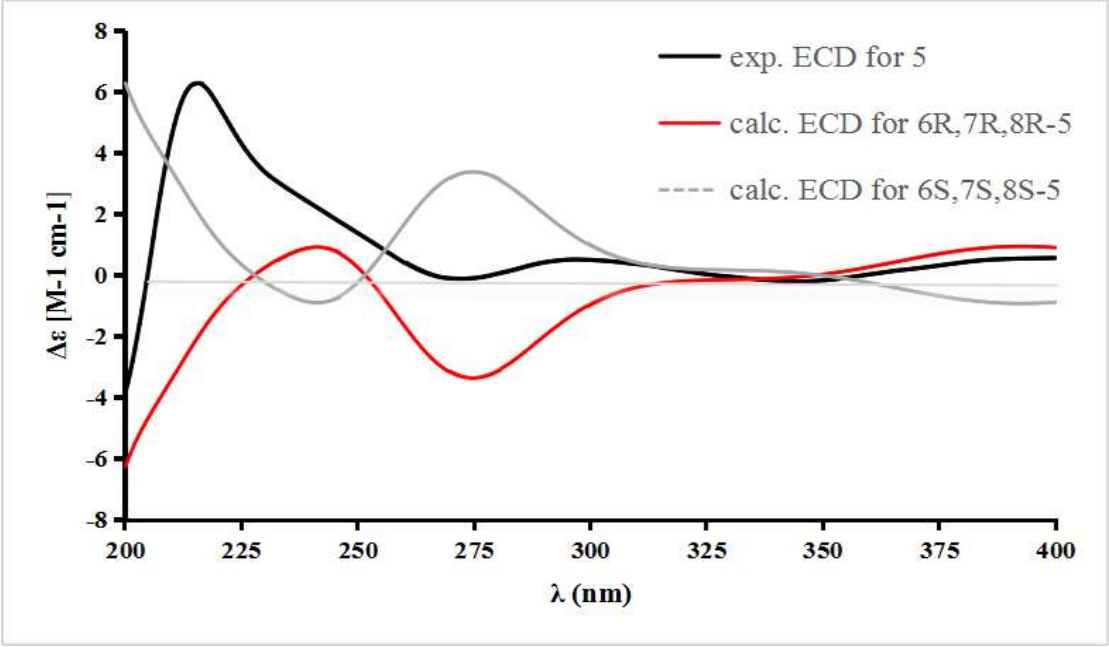

Figure S50. Experimental and calculated ECD spectra of **5**. (MeOH)

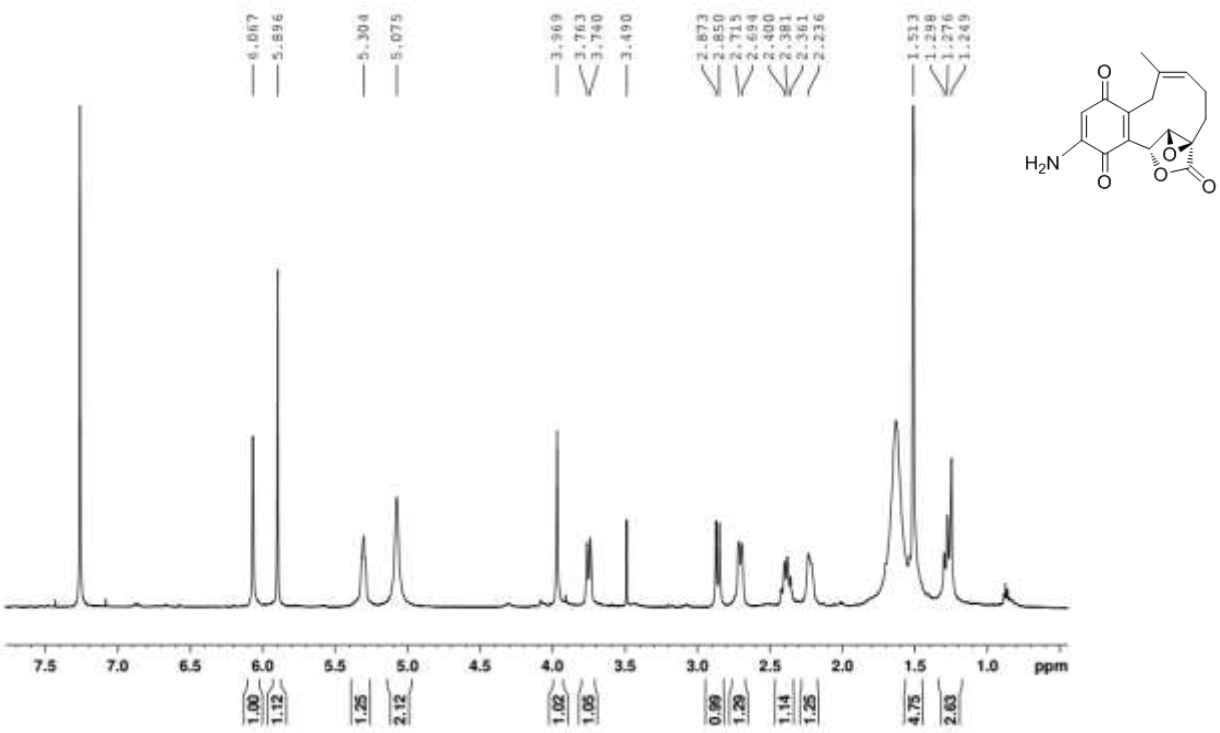

Figure S51. [1]HNMR spectrum of clavilactone D (**5**) ($CDCl_3$, 600MHz)

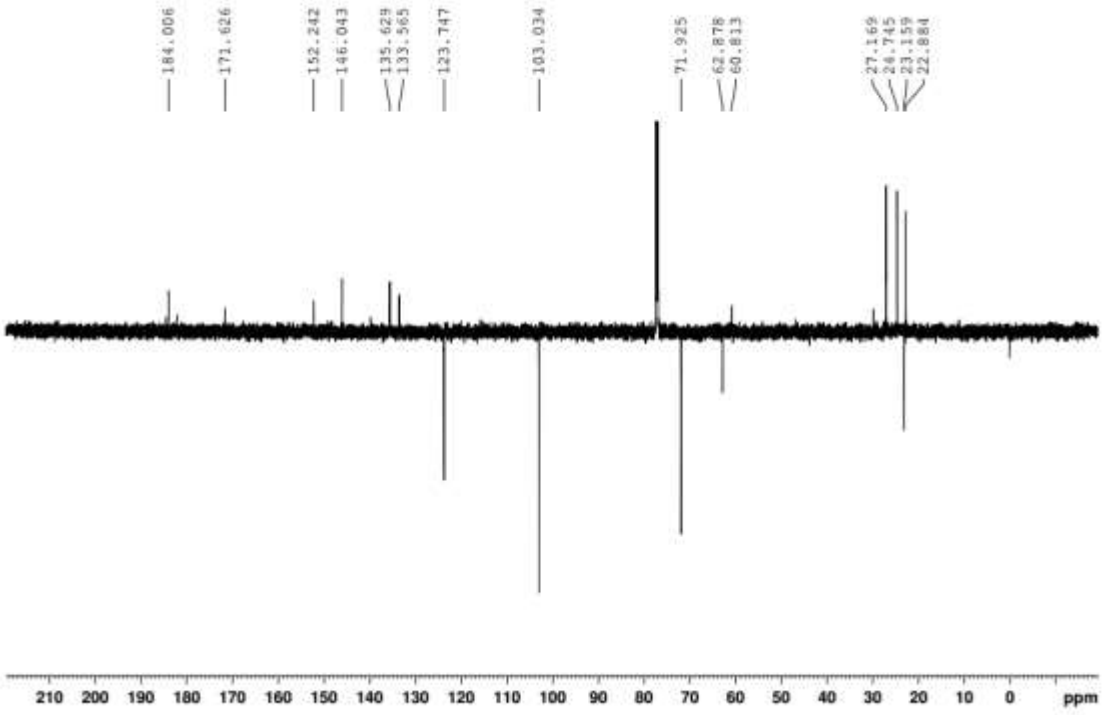

Figure S52. [13]C APT spectrum of clavilactone D (**5**)($CDCl_3$, 150MHz)

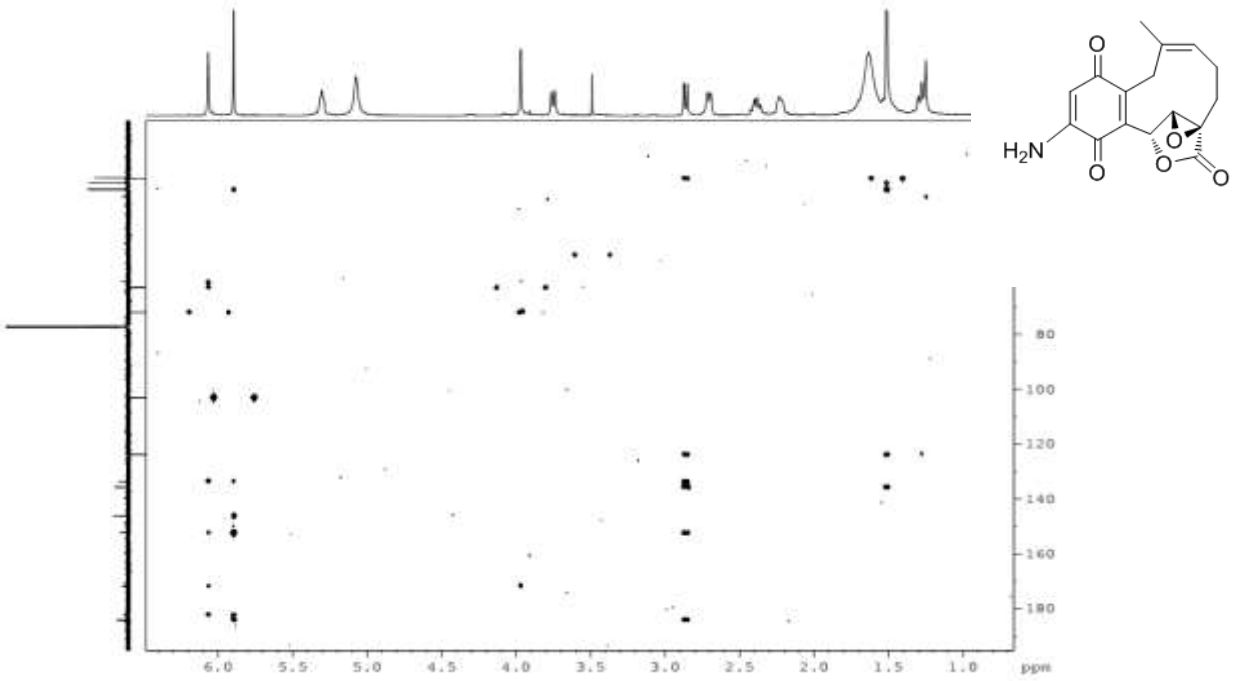

Figure S53. HMBC spectrum of clavilactone D (**5**)($CDCl_3$)

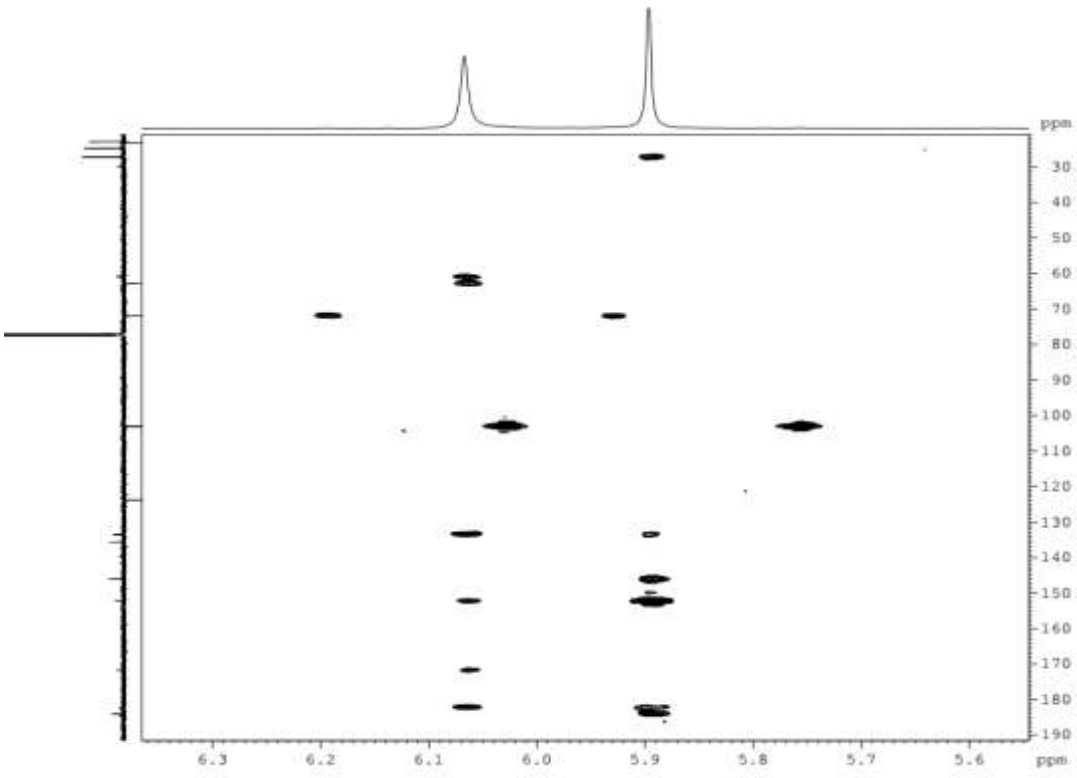

Figure S54. HMBC spectrum of clavilactone D (**5**)($CDCl_3$)

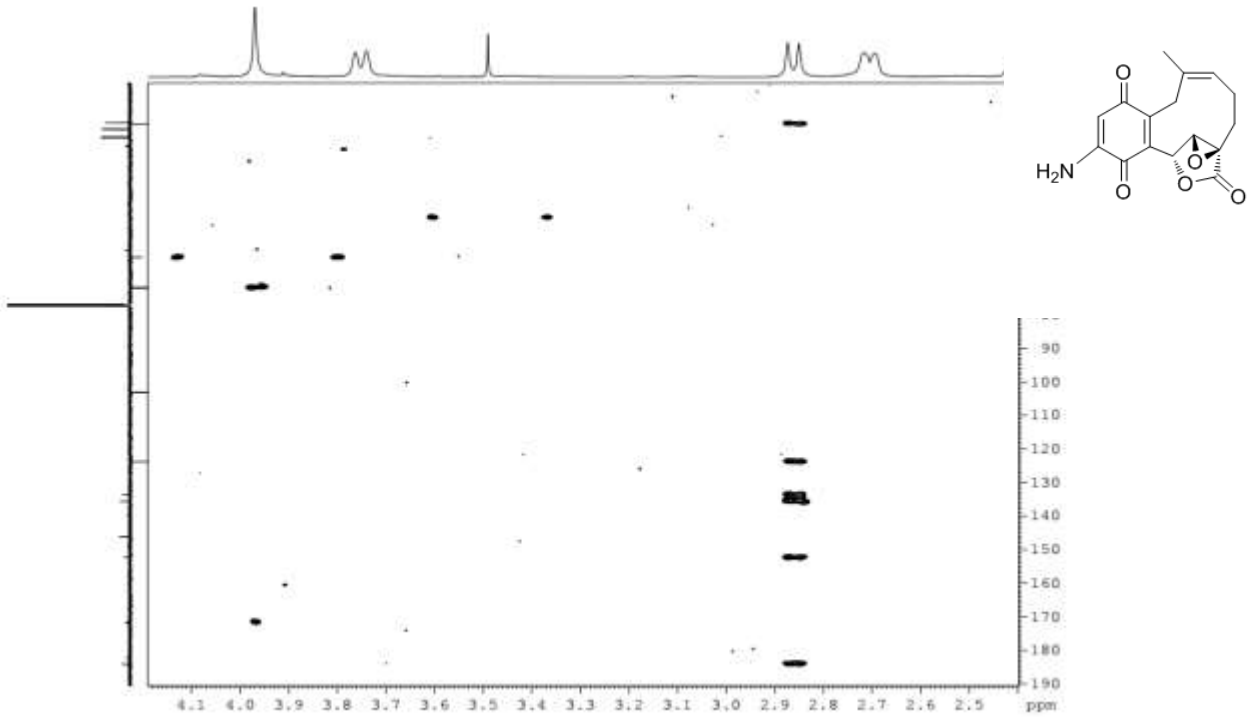

Figure S55. HMBC spectrum of clavilactone D (**5**)($CDCl_3$)

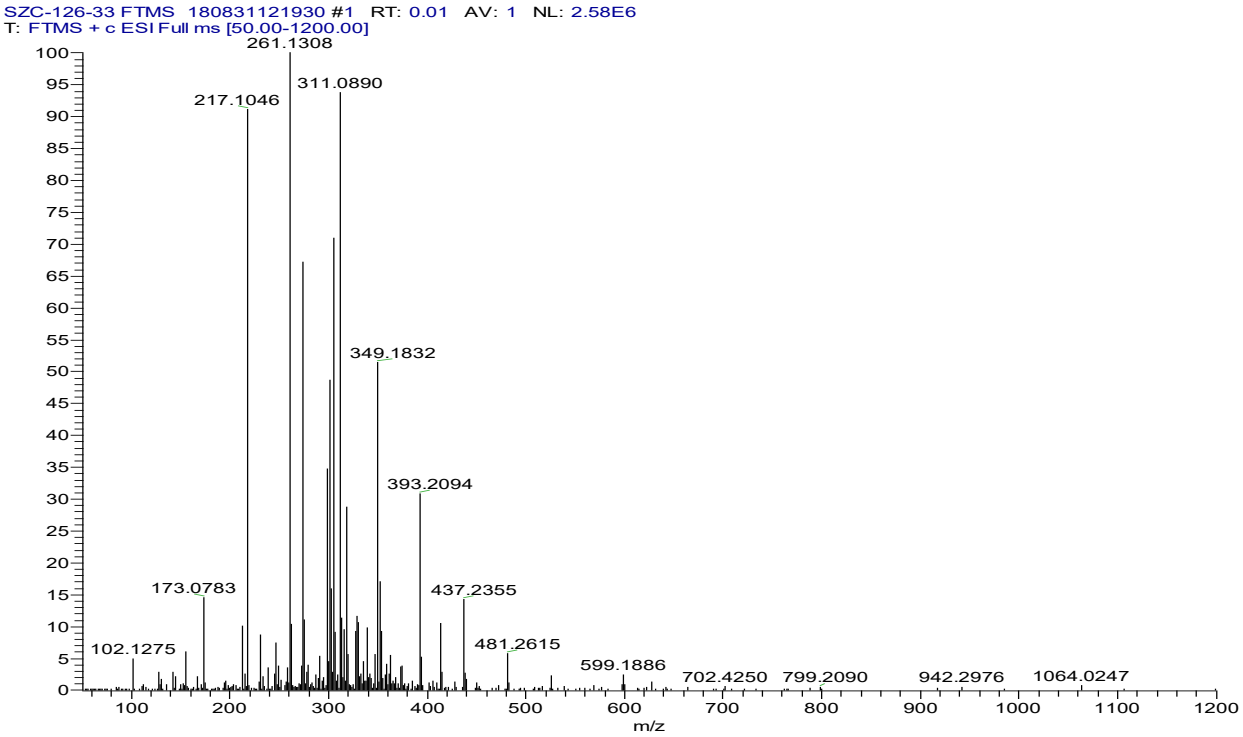

Figure S56. HRESIMS spectrum of clavilactone A (**6**)

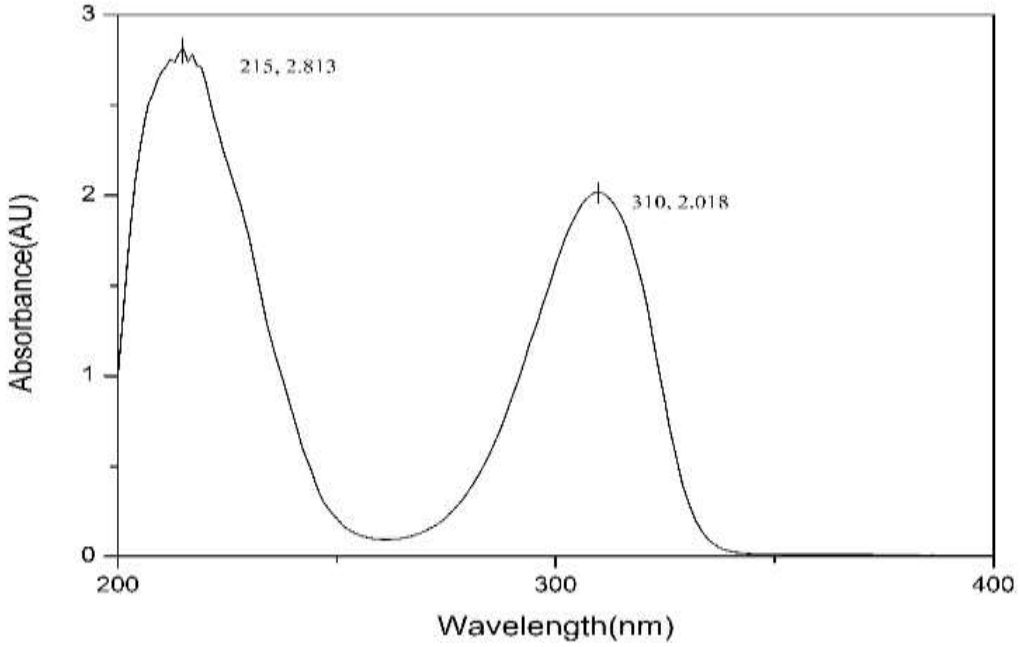

Figure S57. UV spectrum of clavilactone A (**6**)

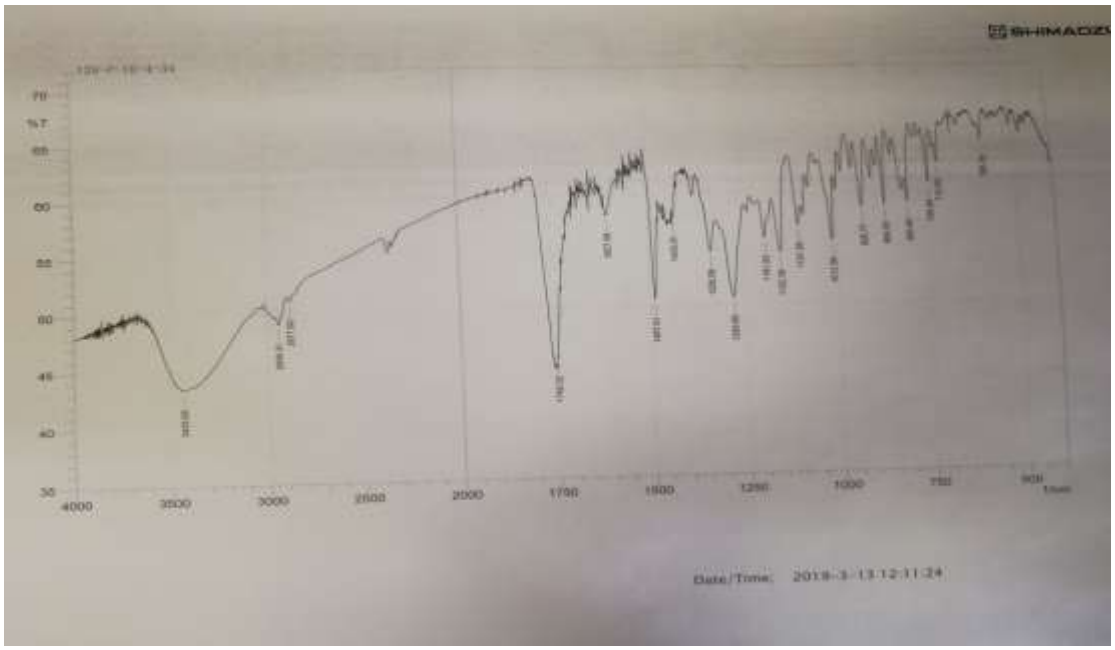

Figure S58. IR spectrum of clavilactone A(**6**)

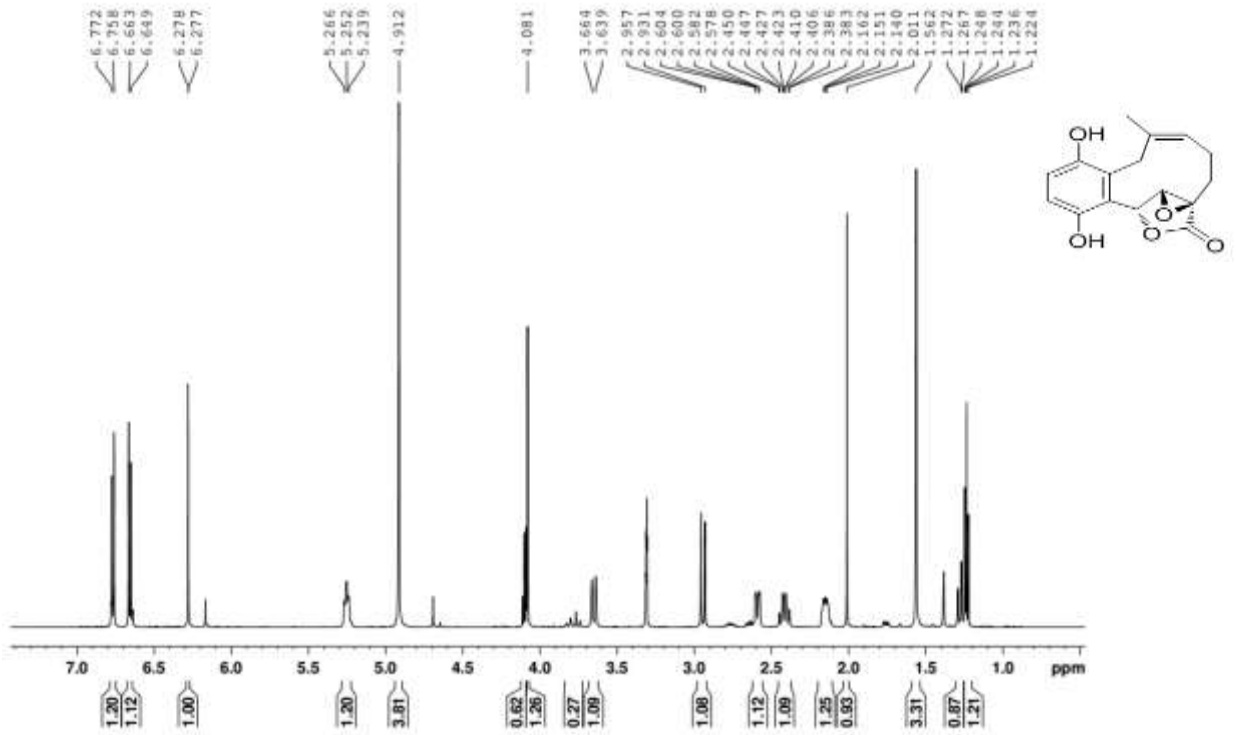

Figure S59. [1]HNMR spectrum of clavilactone A(**6**) ($CDCl_3$, 600MHz)

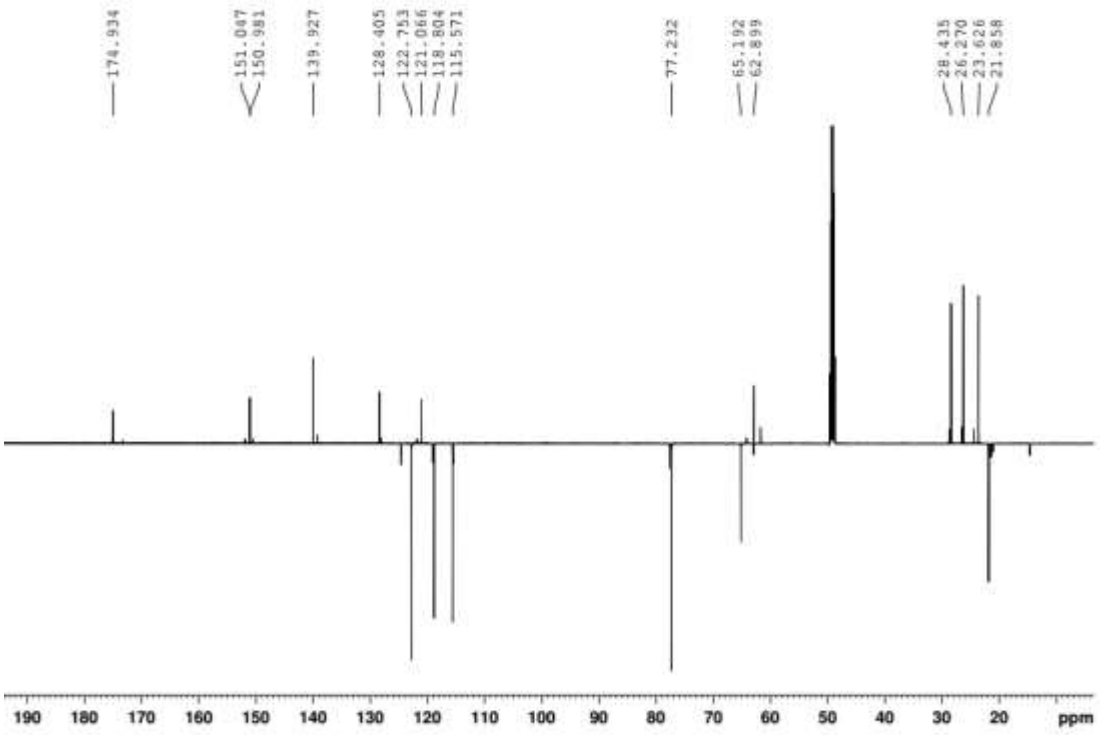

Figure S60. [13]C APT spectrum of clavilactone A (**6**)($CDCl_3$, 150MHz)