Supporting Information

for

Bromotyrosine-derived alkaloids from the Caribbean sponge *Aplysina lacunosa*

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1D, 2D NMR, and CD spectra of three new compounds. 1D NMR, mass and CD spectra of all known isolated compounds

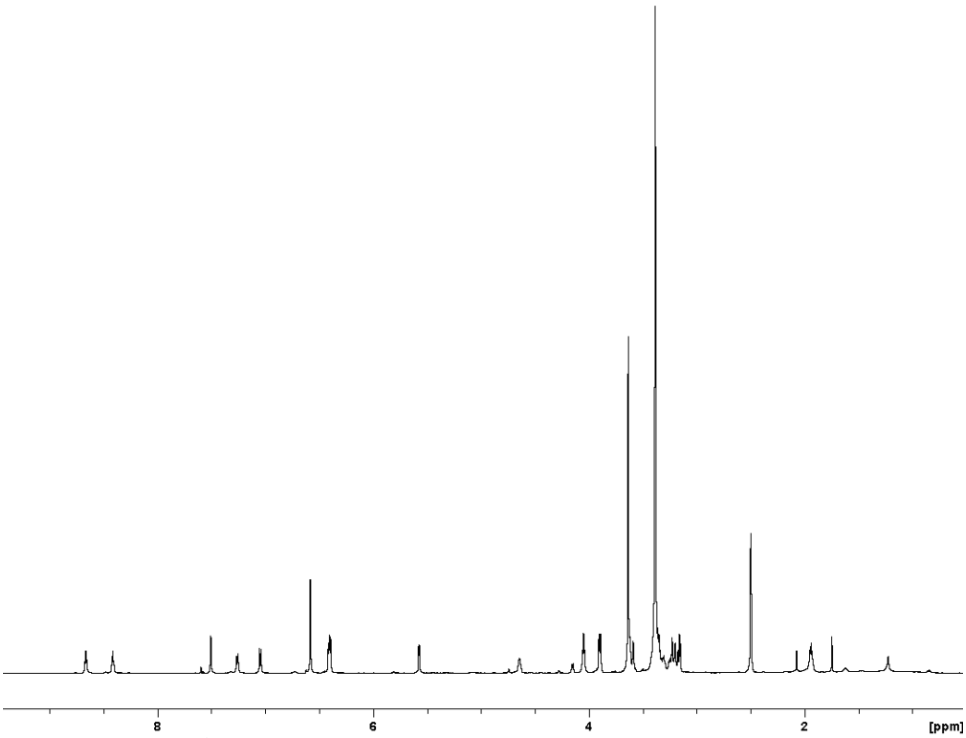

Figure S1: 1D ^{1}H-NMR spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6, 303 K, 600 MHz.

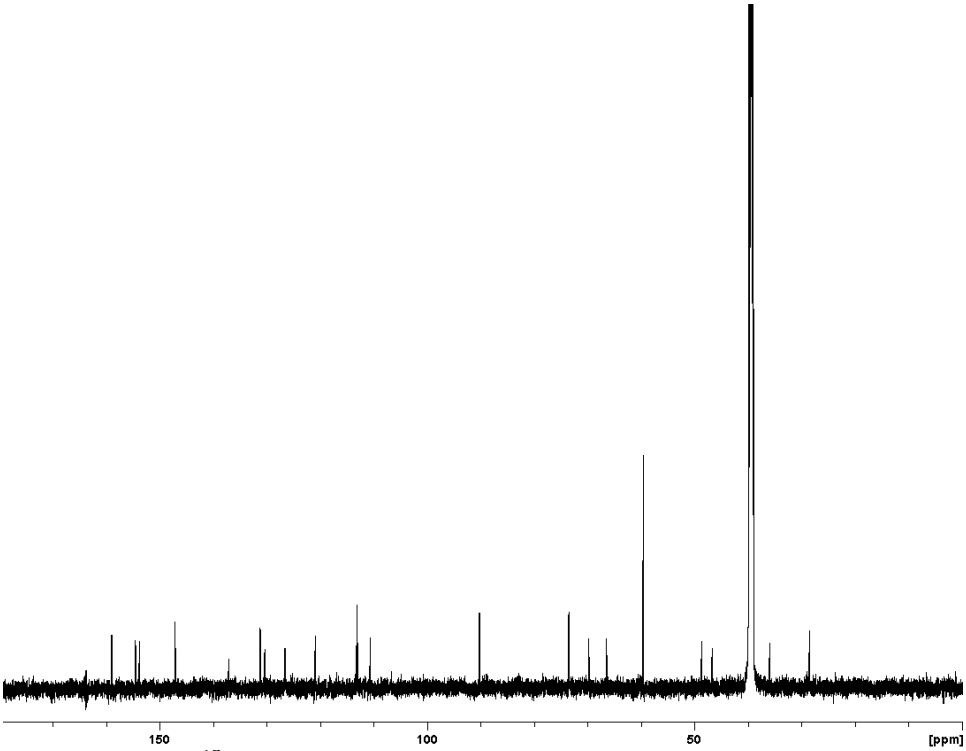

Figure S2: 1D ^{13}C-NMR spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6, 303 K, 150 MHz.

Table S1: NMR data (^{13}C, ^{1}H, ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMBC, 1,1-ADEQUATE, and ^{1}H,^{1}H-NOESY) of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6

position	δ_C	δ_H	^{1}H,^{1}H-COSY	^{1}H,^{13}C-HMBC	1,1-ADEQ	^{1}H,^{1}H-NOESY
1/1´	73.6 73.5	3.92	---	2/2´, 3/3´, 5/5´, 6/6´	2/2´, 6/6´	--- ---
2/ 2´	113.6, 2C	---	---	---	---	---
3/ 3´	147.1, 2C	---	---	---	---	---
4/ 4´	120.9, 120.8	---	---	---	---	---
5/5´	131.2, 131.1	6.57	---	1/1´, 6/6´, 7/7´	6/ 6´	---
6/ 6´	90.3 90.2	---	---	---	---	7/ 7´
7/	40.0	3.21 3.63	--- ---	1/1´, 5/5´, 6/6´, 8/8´, 9/9´	6/6´, 8/8´	6
7´	39.9	3.19 3.62	---			6´
8/ 8´	154.5 154.6	---	---	---	---	---
9/ 9´	159.1 159.0	---	---	---	---	---
10	36.1	3.36	9-NH, 11	9	11	---
11	28.6	1.95	10, 12	---	10, 12	---
12	66.5	4.06	11	10, 11, 13	11	---
13	153.8	---	---	---	---	---
14	113.3	7.05	15	13, 15	13, 15	---
15	126.7	7.28	14	---	---	---
16	137.2	---	---	---	---	---
17	130.5	7.52	---	---	---	---
18	110.8	---	---	---	---	---
19	69.9	4.65	20	15, 16, 17, 20	16, 20	15, 17, 9´-NH
20	46.8	3.35	19, 9´-NH	9´	---	---
3/ 3´-OMe	59.7, 2C	3.64	---	---	---	---
9-NH	---	8.60	10	9, 10	---	---
9´-NH	---	8.35	20	20	---	---
1-OH	---	6.36	---	---	---	7
1´-OH	---	6.37	---	---	---	7´, 19-OH
19-OH	---	5.54	---	---	---	1´-OH

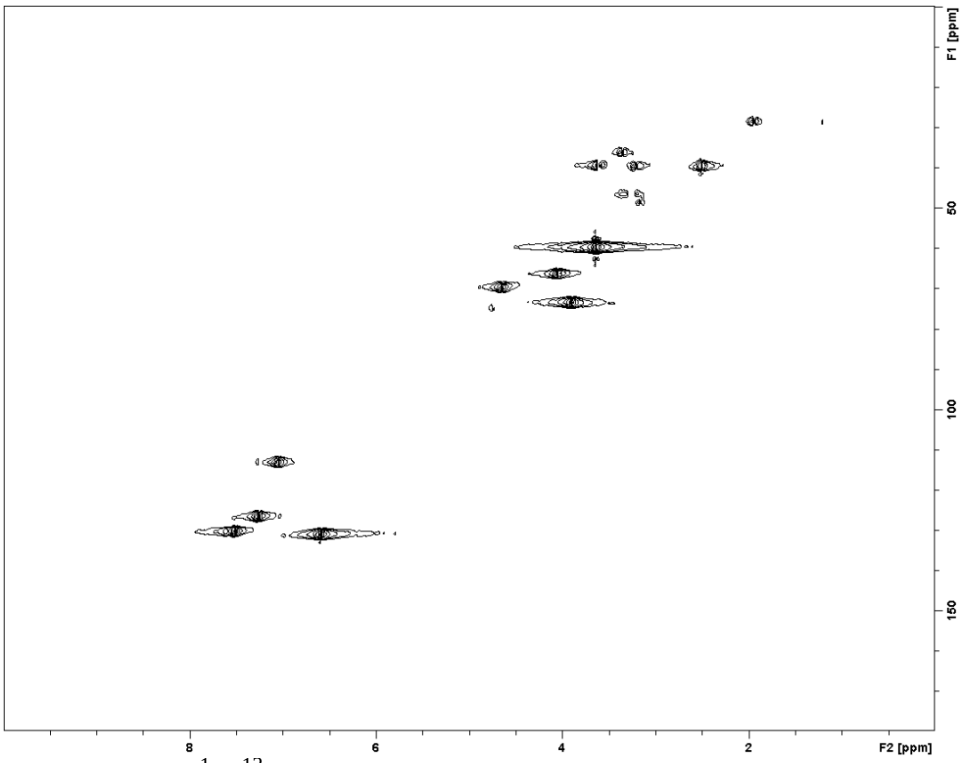

Figure S3: 2D $^{1}H,^{13}C$-HSQC spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6, 303 K.

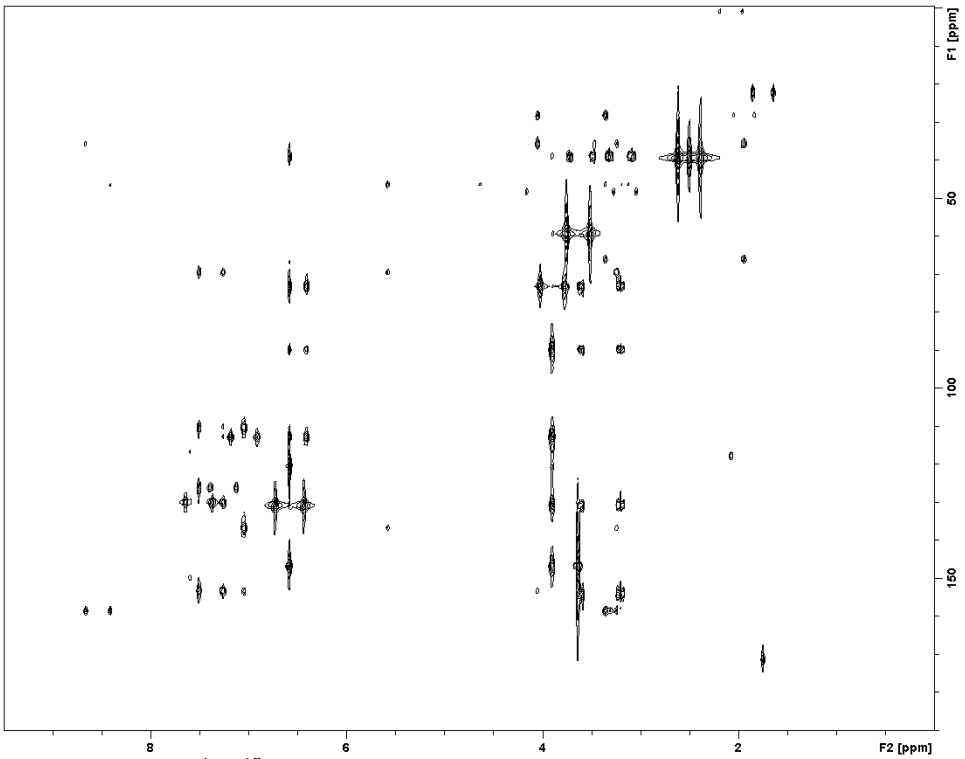

Figure S4: 2D $^{1}H,^{13}C$-HMBC spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6, 303 K.

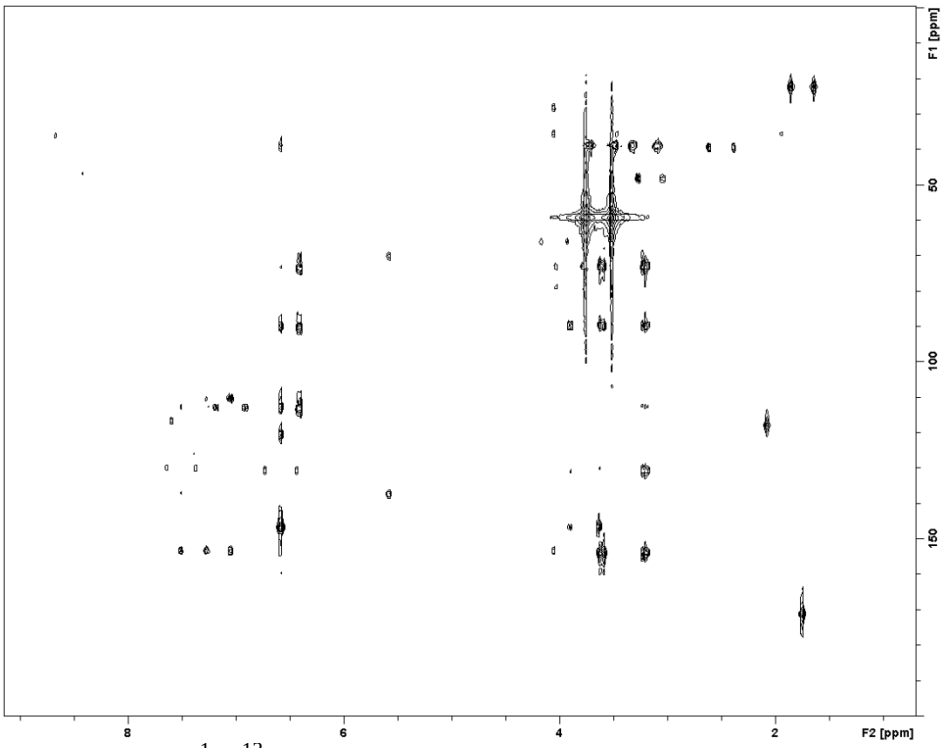

Figure S5: 2D $^{1}H,^{13}C$-HMBC spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6, D6 = 0.2500, 303 K.

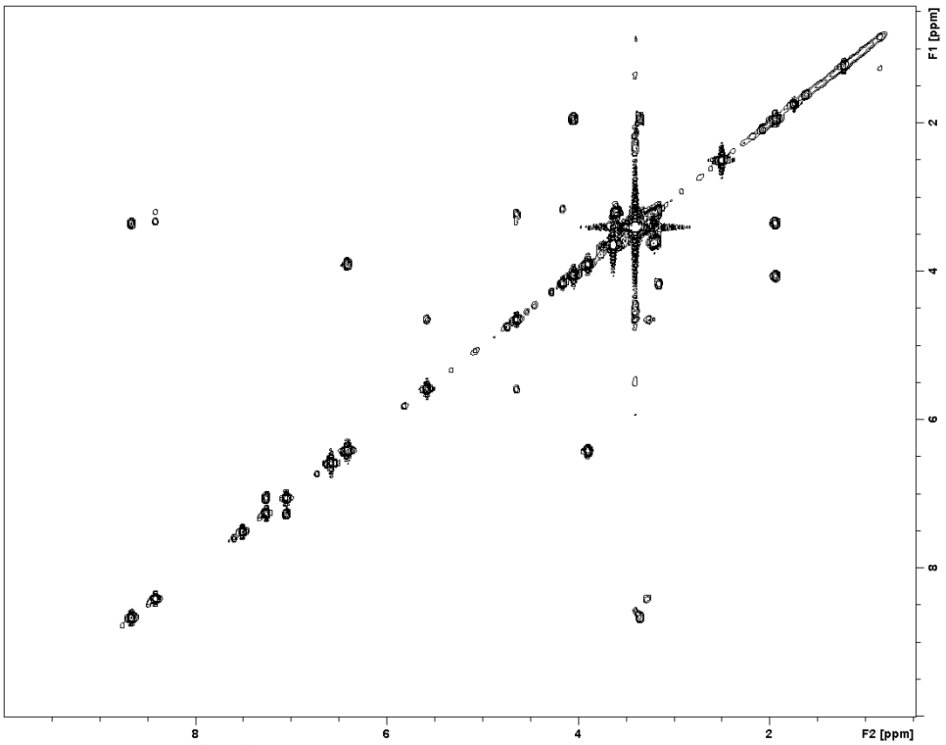

Figure S6: 2D $^{1}H,^{1}H$-COSY spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6, 303 K.

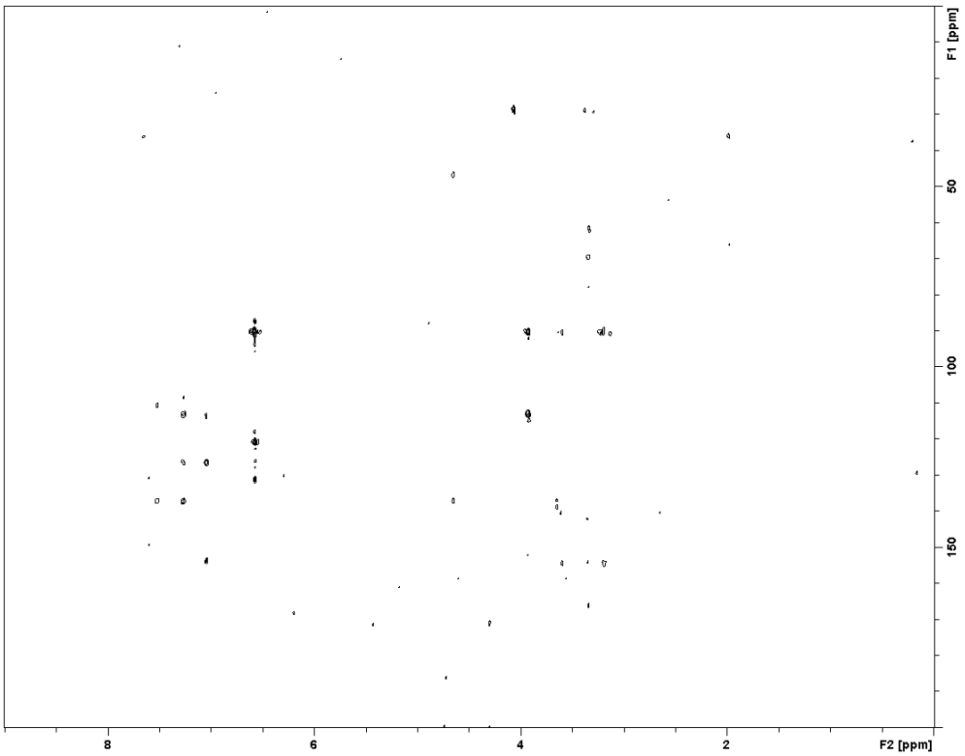

Figure S7: 2D 1,1-ADEQUATE spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6, 303 K.

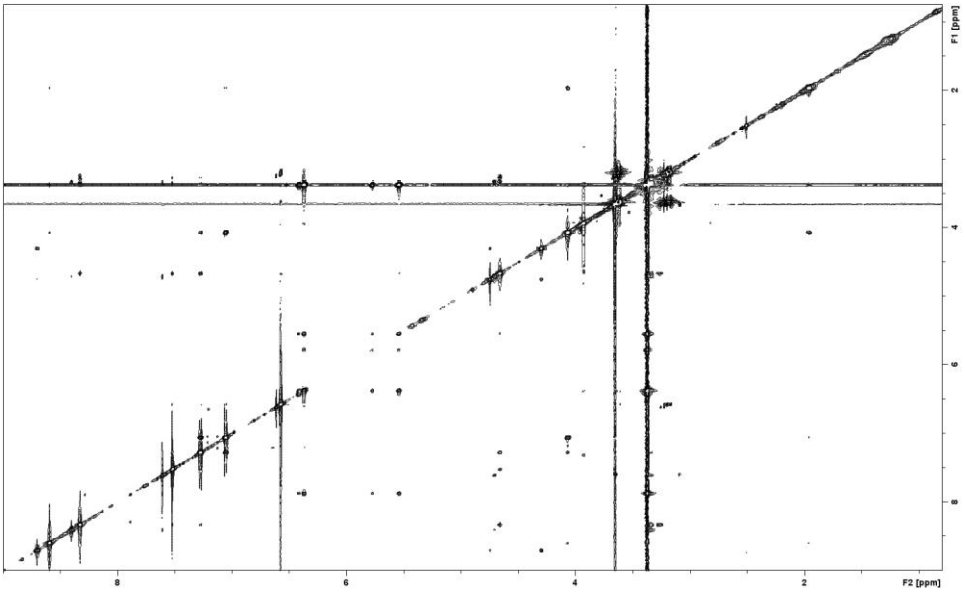

Figure S8: 2D ^{1}H,^{1}H-NOESY spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) in DMSO-d_6, 303 K.

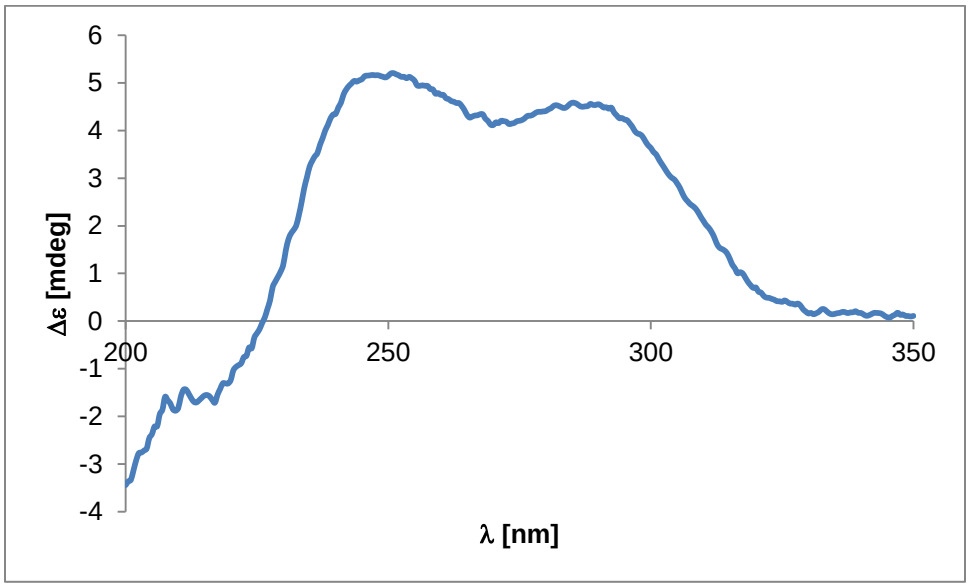

Figure S9: Circular dichroism spectrum of 14-debromo-11-deoxyfistularin-3 (**1**) (c = 2.0 × 10^{-4} M, MeOH, 25 °C).

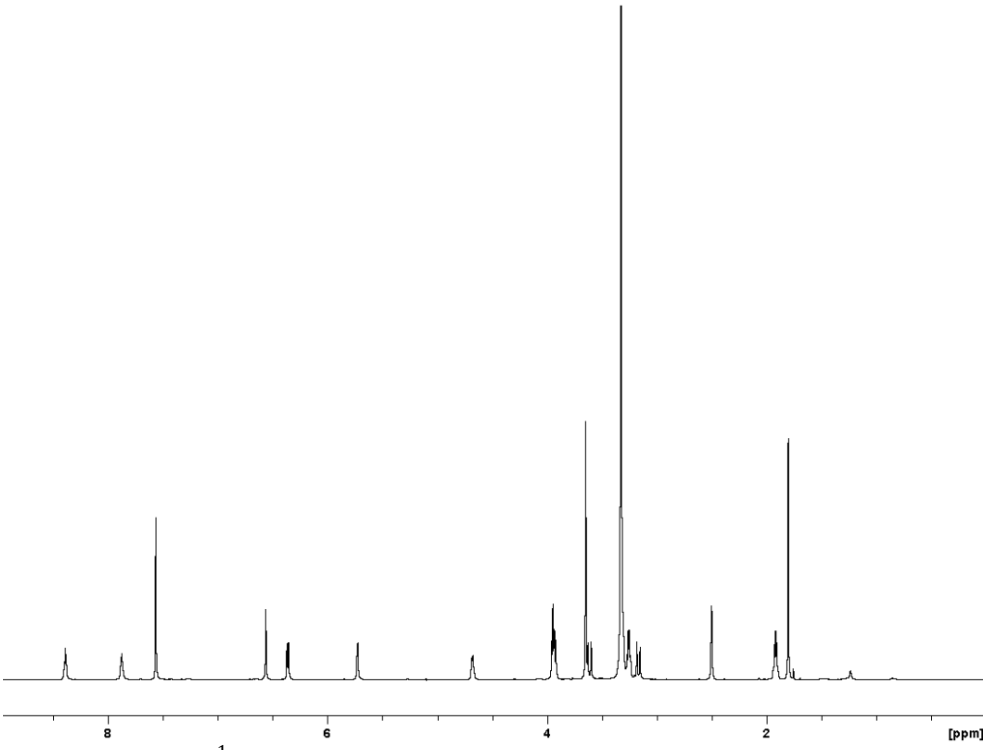

Figure S10: 1D ^{1}H-NMR spectrum of aplysinin A (**2**) in DMSO-d_6, 303 K, 600 MHz.

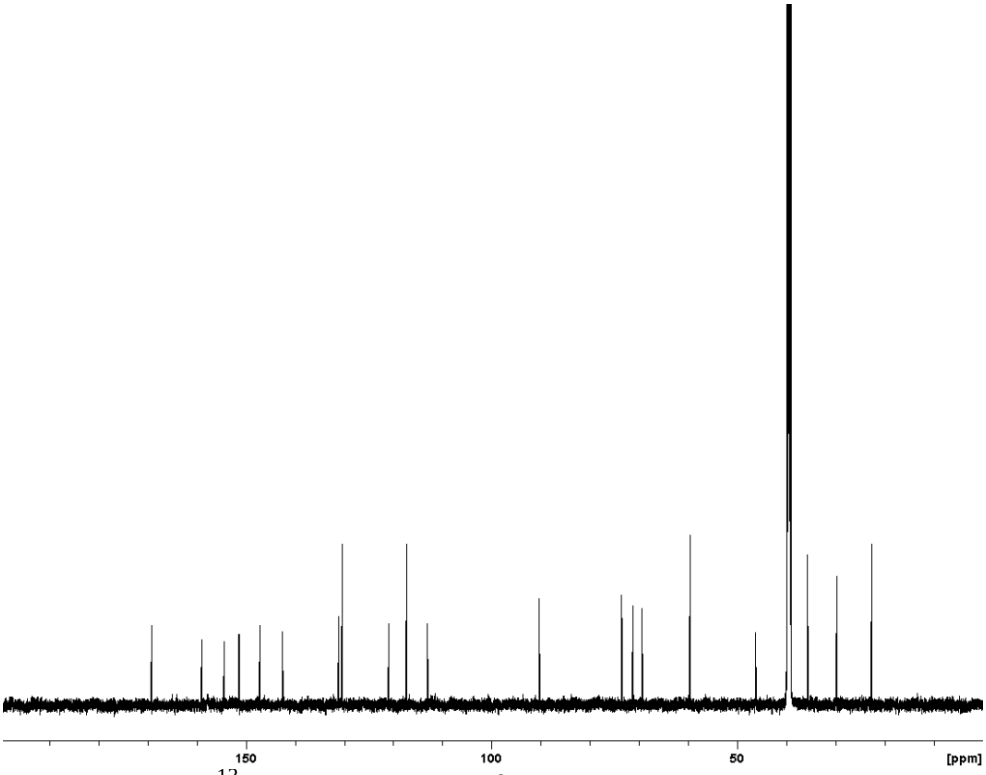

Figure S11: 1D ^{13}C-NMR spectrum of aplysinin A (**2**) in DMSO- d_6, 303 K, 150 MHz.

Table S2: NMR data (^{13}C, ^{1}H, ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMBC, 1,1-ADEQUATE, and ^{1}H,^{1}H-NOESY) of aplysinin A (**2**) in DMSO-d_6

position	δ_C	δ_H	^{1}H,^{1}H-COSY	^{1}H,^{13}C-HMBC	1,1-ADEQ	^{1}H,^{1}H-NOESY
1	73.5	3.93	1-OH	2, 3, 5, 6	---	---
2	113.1	---	---	---	---	---
3	147.1	---	---	---	---	---
4	120.9	---	---	---	---	---
5	131.1	6.56	---	4, 6	6	7
6	90.3	---	---	---	---	---
7	39.7	3.17	---	1, 5, 6, 8, 9	---	5
		3.61	---	---	---	---
8	154.3	--	---	---	---	---
9	159.0	---	---	---	---	---
10	46.3	3.33, 2H	9-NH	9, 12	---	---
11	69.3	4.67	10, 11-OH	10, 12, 13, 17	---	10, 13, 17
12	142.5	---	---	---	---	---
13/17	130.4, 2C	7.57, 2H	---	11, 12, 14/16	12, 16, 14	---
14/16	117.3, 2C	---	---	---	---	---
15	151.4	---	---	---	---	---
18	71.3	3.96, 2H	19	15, 19, 20	---	---
19	29.8	1.91, 2H	20	---	---	---
20	35.7	3.25, 2H	20-NH	21	---	---
21	169.1	---	---	---	---	---
22	22.6	1.80, 3H	---	21	---	---
3-OMe	59.6	3.65, 3H	---	3	---	---
9-NH	---	8.39	10	9	---	11
1-OH	---	6.36	1	1, 2, 6	---	11-OH
11-OH	---	5.72	11	---	---	---
20-NH	---	7.86	20	21	---	---

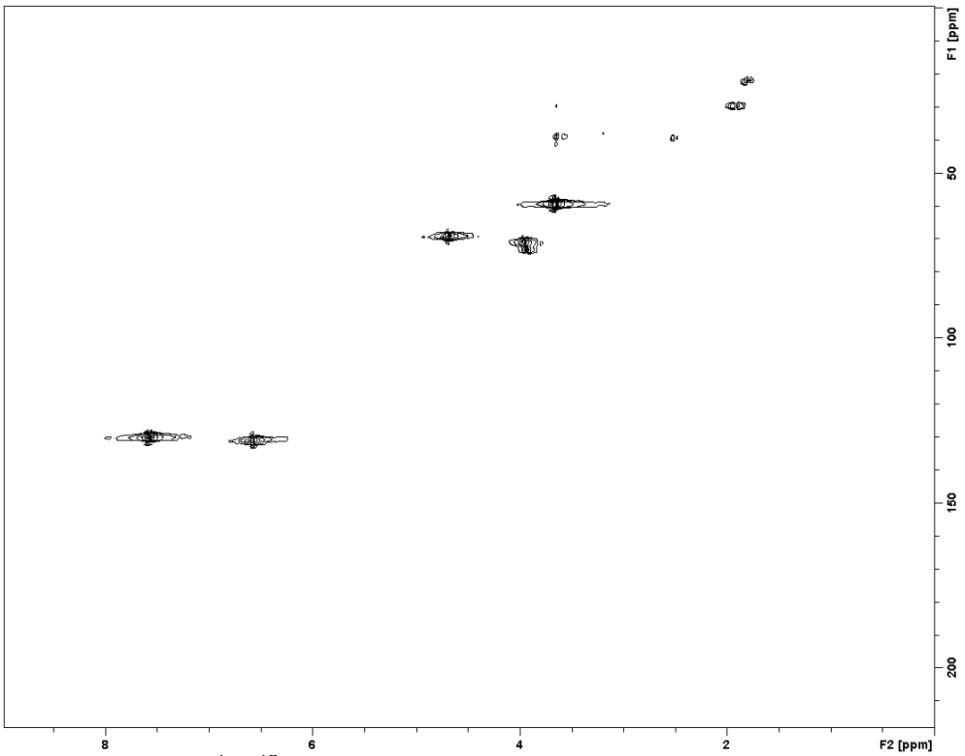

Figure S12: 2D $^{1}H,^{13}C$-HSQC spectrum of aplysinin A (**2**) in DMSO- d_6, 303 K.

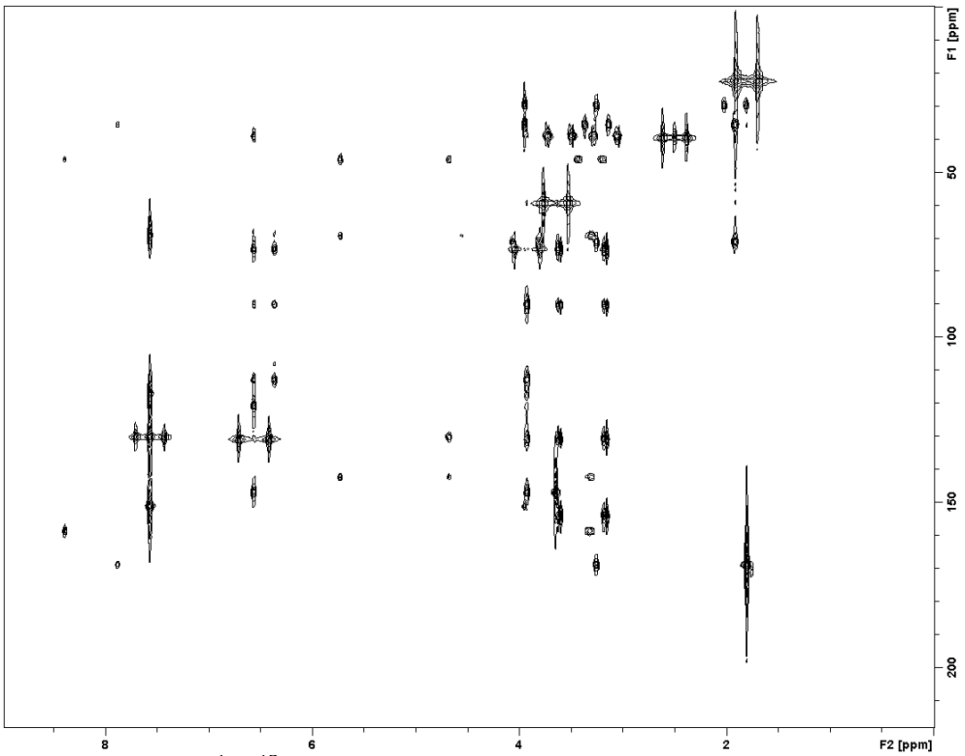

Figure S13: 2D $^{1}H,^{13}C$-HMBC spectrum of aplysinin A (**2**) in DMSO- d_6, 303 K.

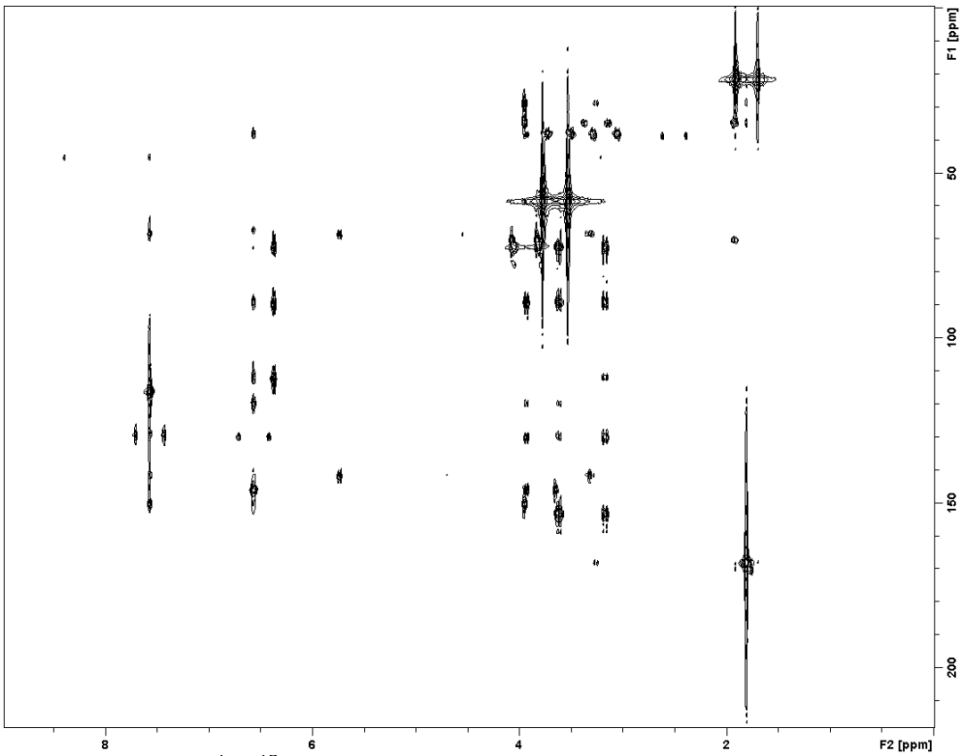

Figure S14: 2D $^{1}H,^{13}C$-HMBC spectrum of aplysinin A (**2**) in DMSO- d_6, D6 = 0.2500, 303 K.

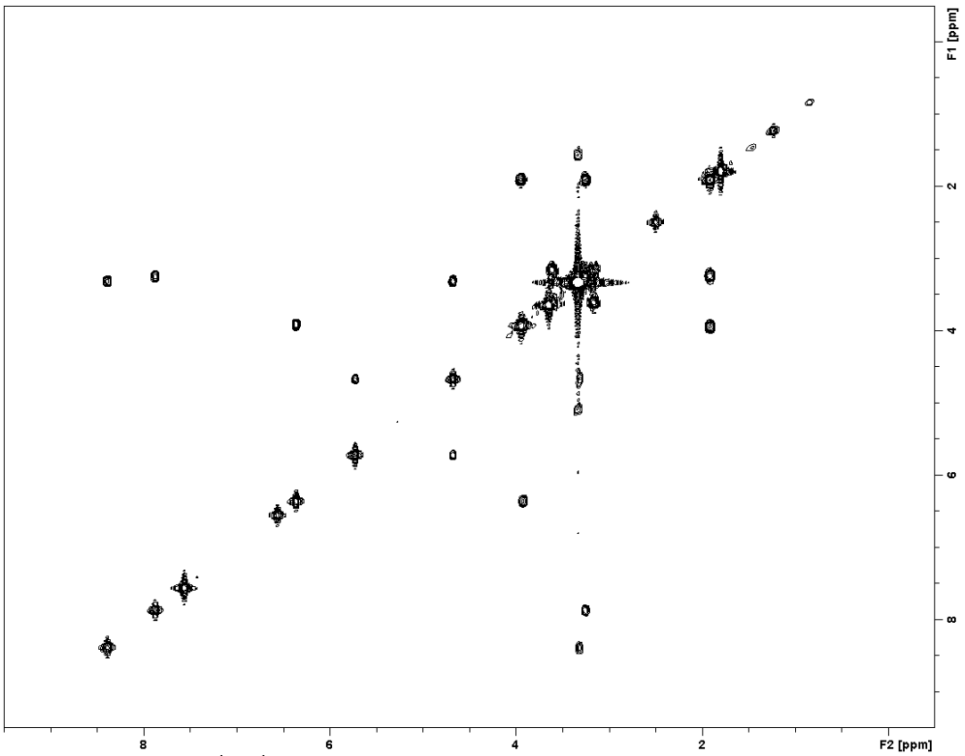

Figure S15: 2D $^{1}H,^{1}H$-COSY spectrum of aplysinin A (**2**) in DMSO- d_6, 303 K.

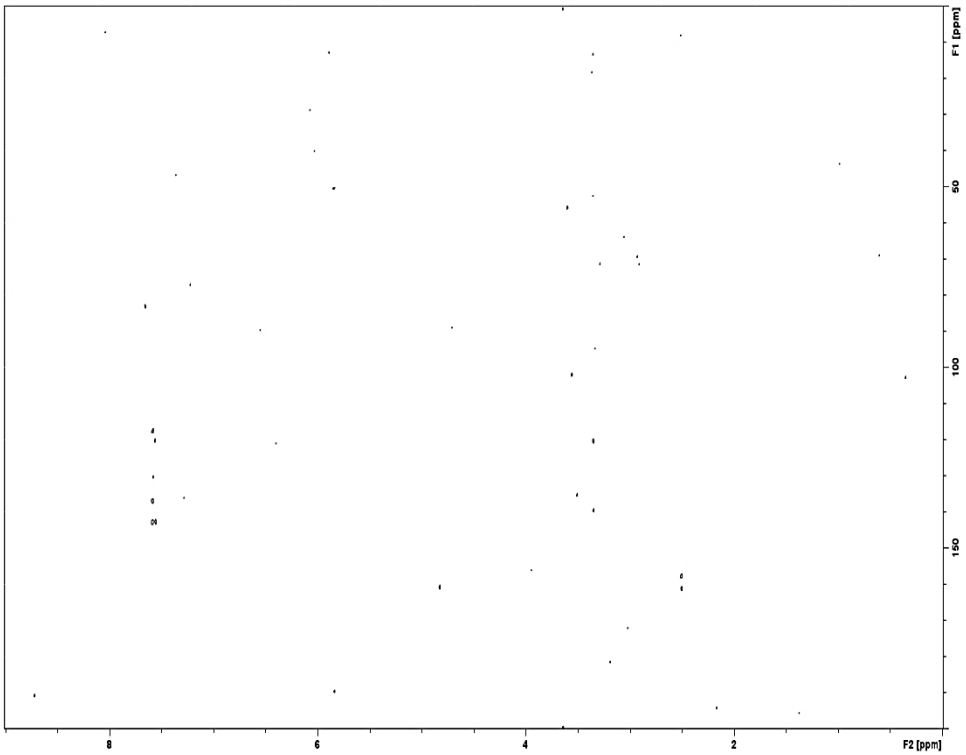

Figure S16: 2D 1,1-ADEQUATE spectrum of aplysinin A (**2**) in DMSO-d_6, 303 K.

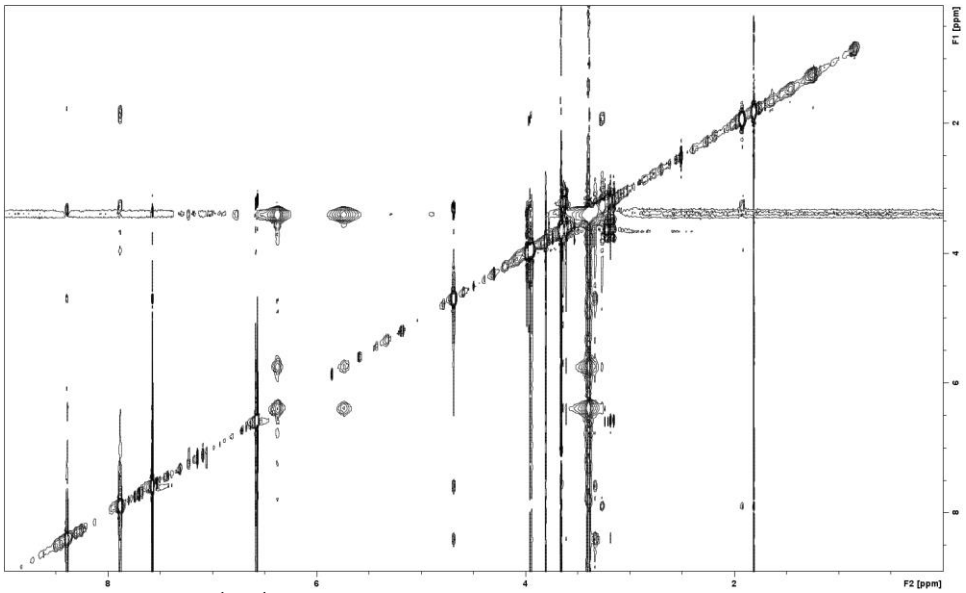

Figure S17: 2D ^{1}H,^{1}H-NOESY spectrum of aplysinin A (**2**) in DMSO-d_6, 303 K.

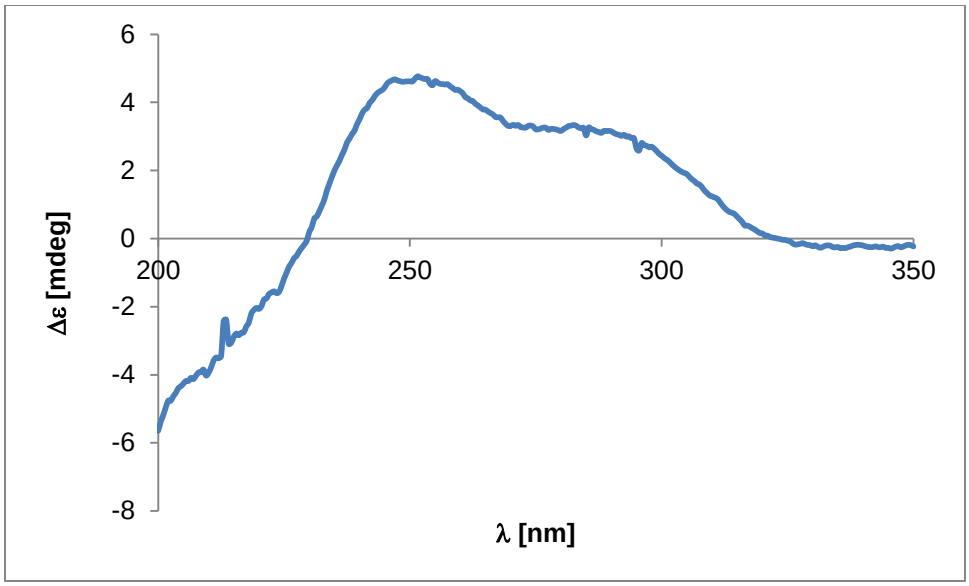

Figure S18: Circular dichroism spectrum of aplysinin A (**2**) (c = 2.6 × 10^{-4} M, MeOH, 25 °C).

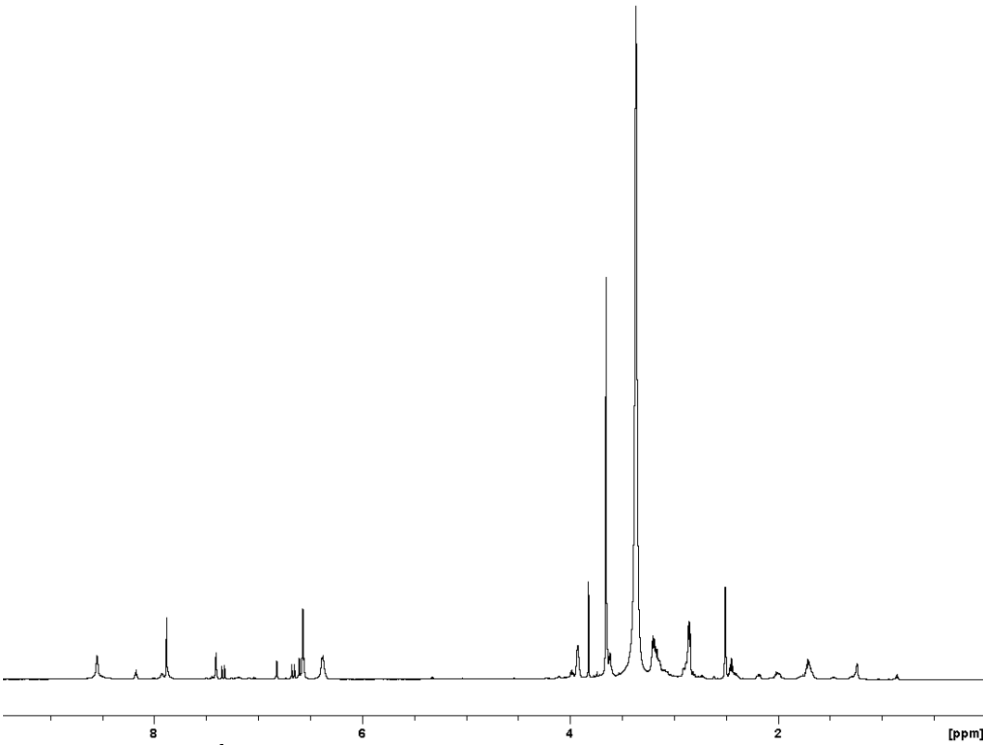

Figure S19: 1D ^{1}H-NMR spectrum of aplysinin B (**3**) in DMSO-d_6, 303 K, 600 MHz.

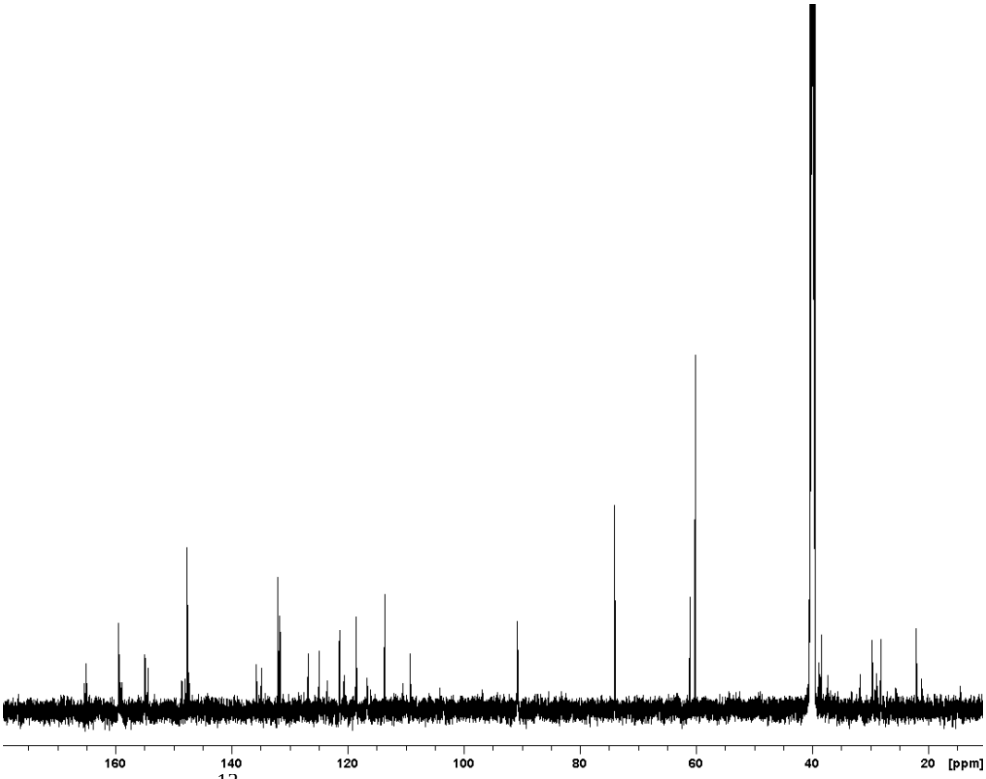

Figure S20: 1D ^{13}C-NMR spectrum of aplysinin B (**3**) in DMSO- d_6, 303 K, 150 MHz.

Table S3: NMR data (^{13}C, ^{1}H, ^{1}H,^{1}H-COSY, and ^{1}H,^{13}C-HMBC) of aplysinin B (**3**) in DMSO-d_6

position	δ_C	δ_H	^{1}H,^{1}H-COSY	^{1}H,^{13}C-HMBC
1	134.9	---	---	---
2/6	131.7, 2C	7.88, 2H	---	3, 4, 5, 7
3/5	118.5, 2C	---	---	---
4	154.4	---	---	---
7	135.7	7.33	---	1, 2, 6, 8, 9
8	124.9	6.66	---	1, 9
9	165.0	---	---	---
10	38.4	3.20	---	9, 11
11	28.1	1.71, 2H	11	10, 12, 13
12	22.0	2.45, 2H	12	13, 14
13	126.8	---	---	---
14	109.2	6.60	---	13, 15
15	147.4	---	---	---
4-OMe	61.0	3.82, 3H	---	4
9-NH	---	8.17	10	9, 10

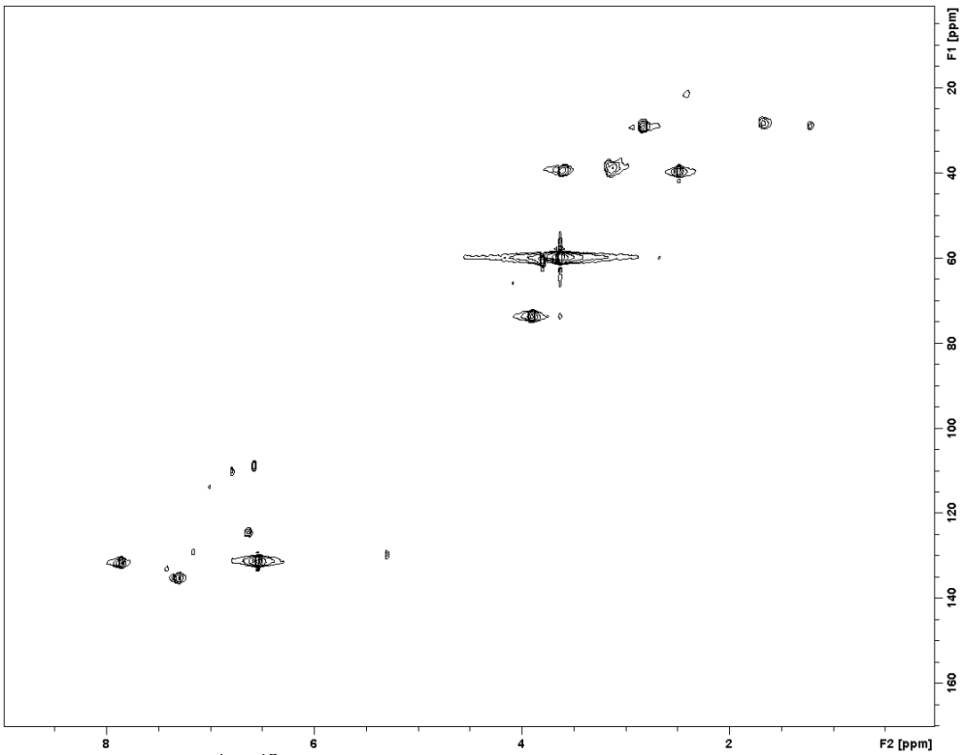

Figure S21: 2D ^{1}H,^{13}C-HSQC spectrum of aplysinin B (**3**) in DMSO-d_6, 303 K.

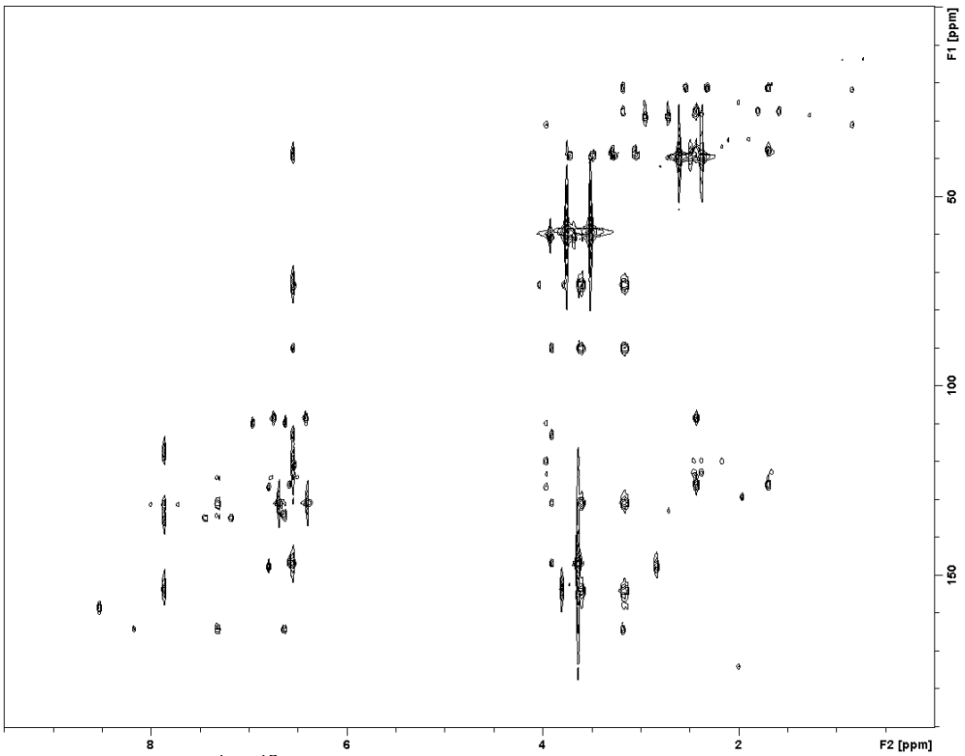

Figure S22: 2D $^{1}H,^{13}C$-HMBC spectrum of aplysinin B (**3**) in DMSO-d_6, 303 K.

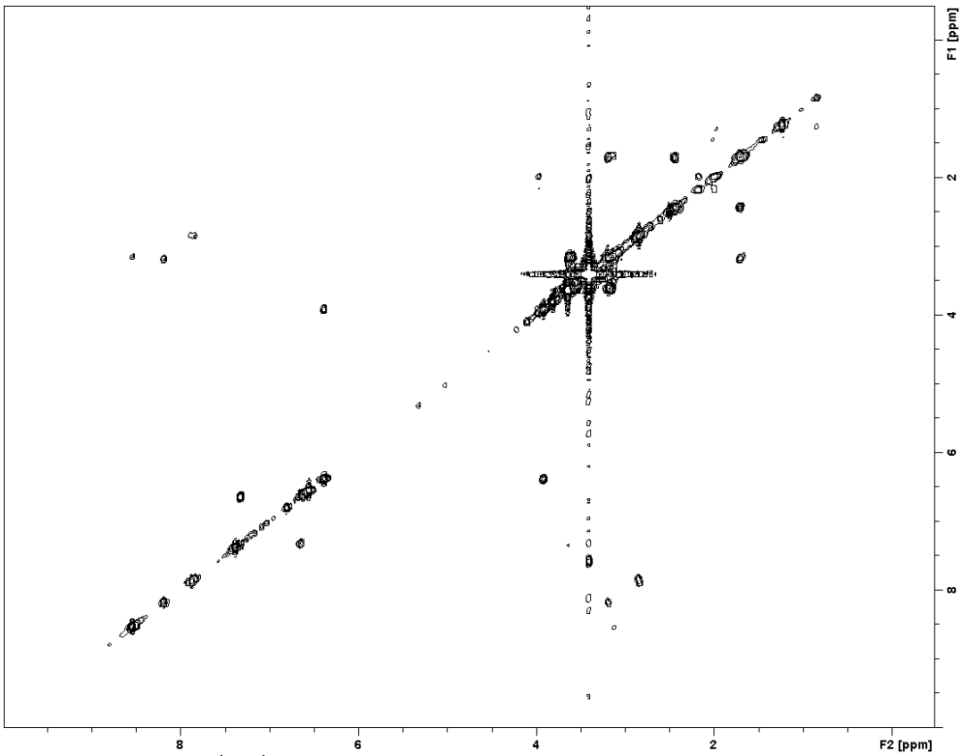

Figure S23: 2D $^{1}H,^{1}H$-COSY spectrum of aplysinin B (**3**) in DMSO-d_6, 303 K.

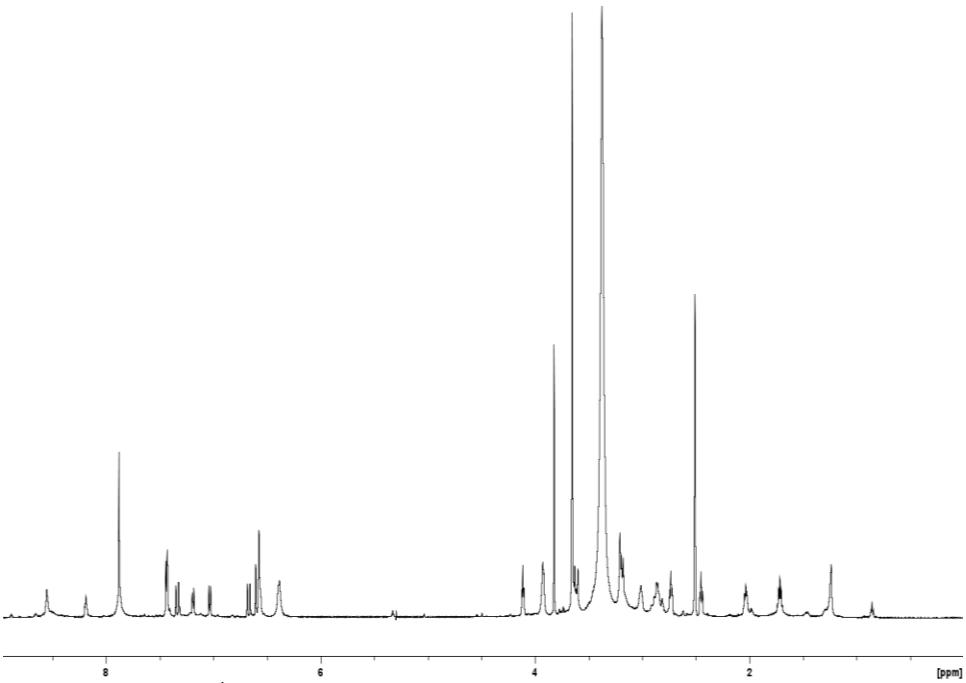

Figure S24: 1D ^{1}H-NMR spectrum of 14-debromoaraplysillin I (**4**) in DMSO-d_6, 303 K, 600 MHz.

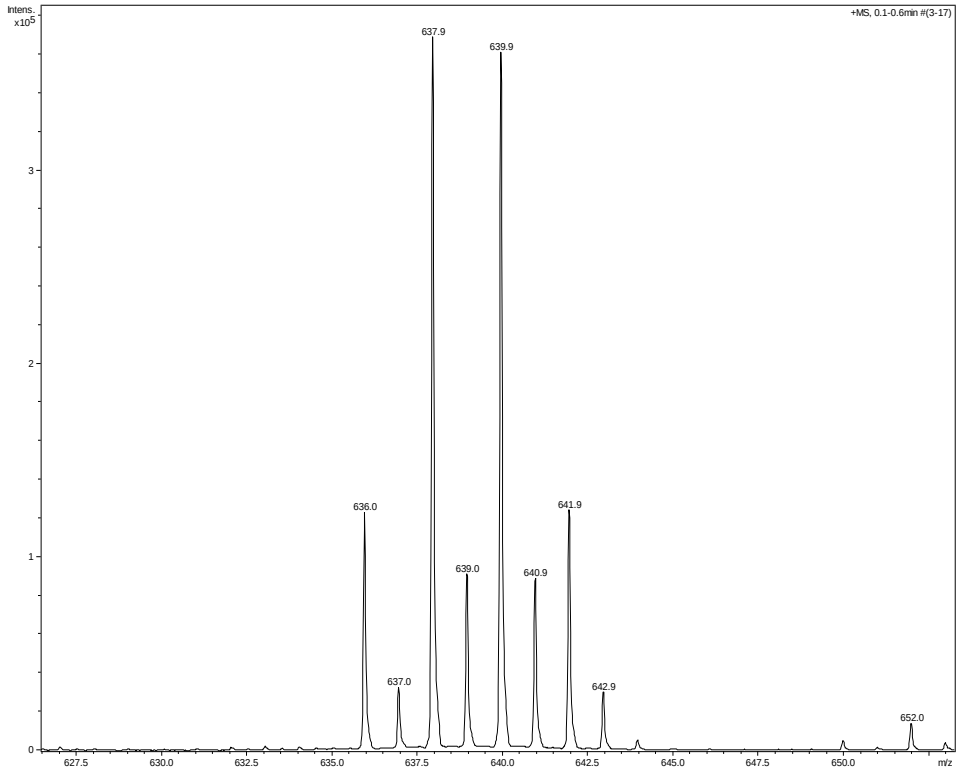

Figure S25: ESI–MS(+) spectral data of 14-debromoaraplysillin I (**4**).

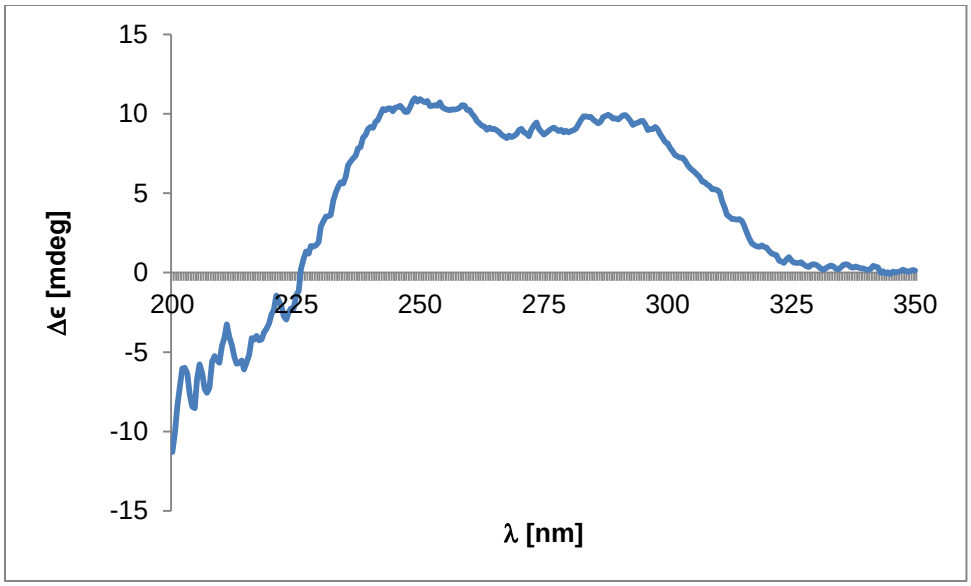

Figure S26: Circular dichroism spectrum of 14-debromoaraplysillin I (**4**) (c = 3.1 × 10^{-4} M, MeOH, 25 °C).

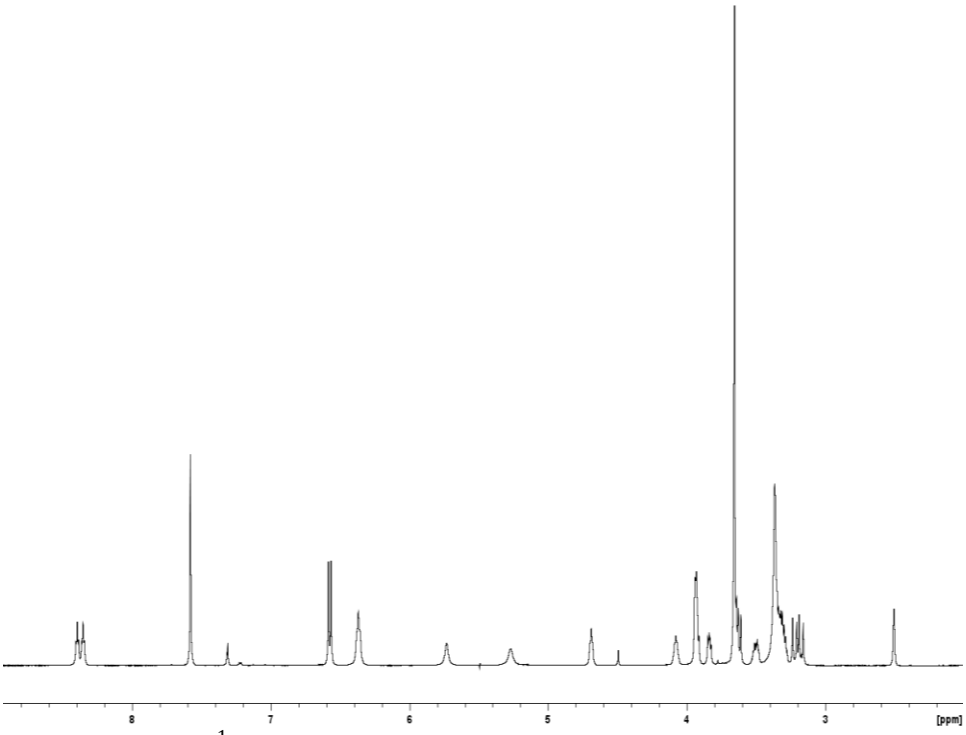

Figure S27: 1D ^{1}H-NMR spectrum of fistularin-3 (**5**) in DMSO-d_6, 303 K, 600 MHz.

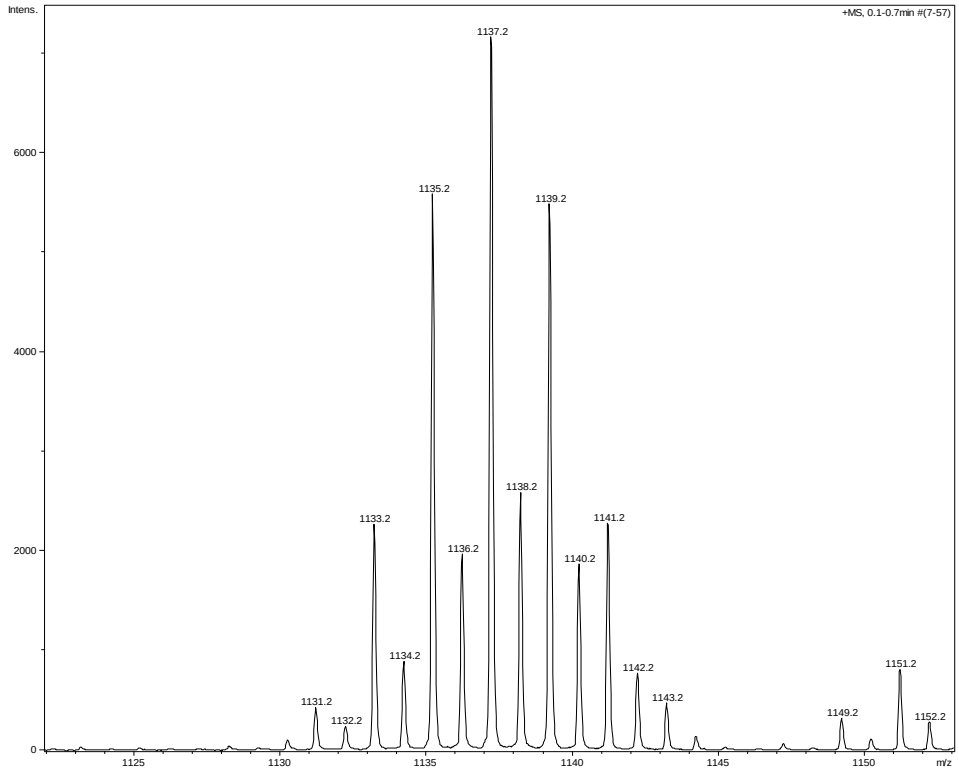

Figure S28: ESI–MS(+) spectral data of fistularin-3 (**5**).

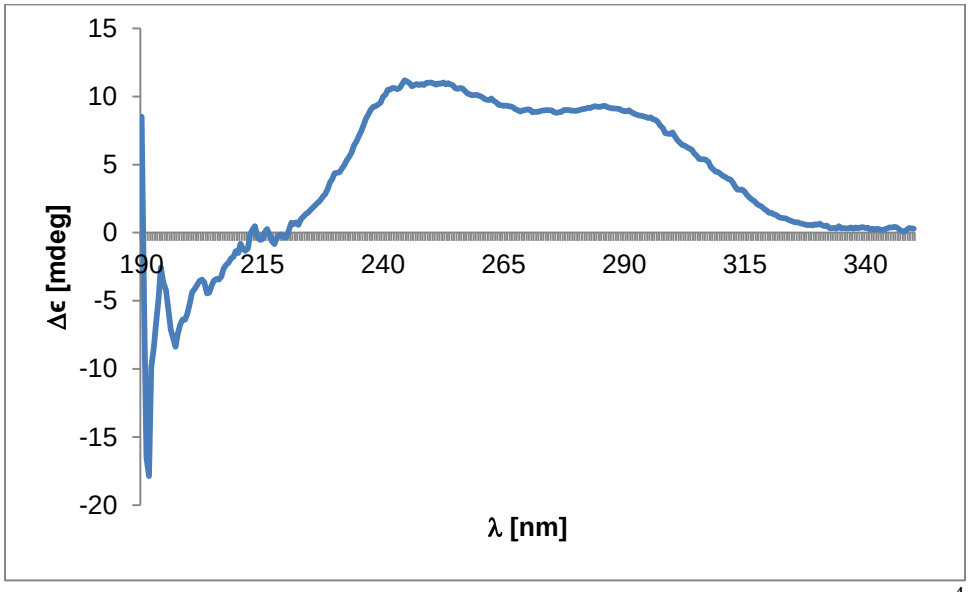

Figure S29: Circular dichroism spectrum of fistularin-3 (**5**) (c = 1.7 × 10^{-4} M, MeOH, 25 °C).

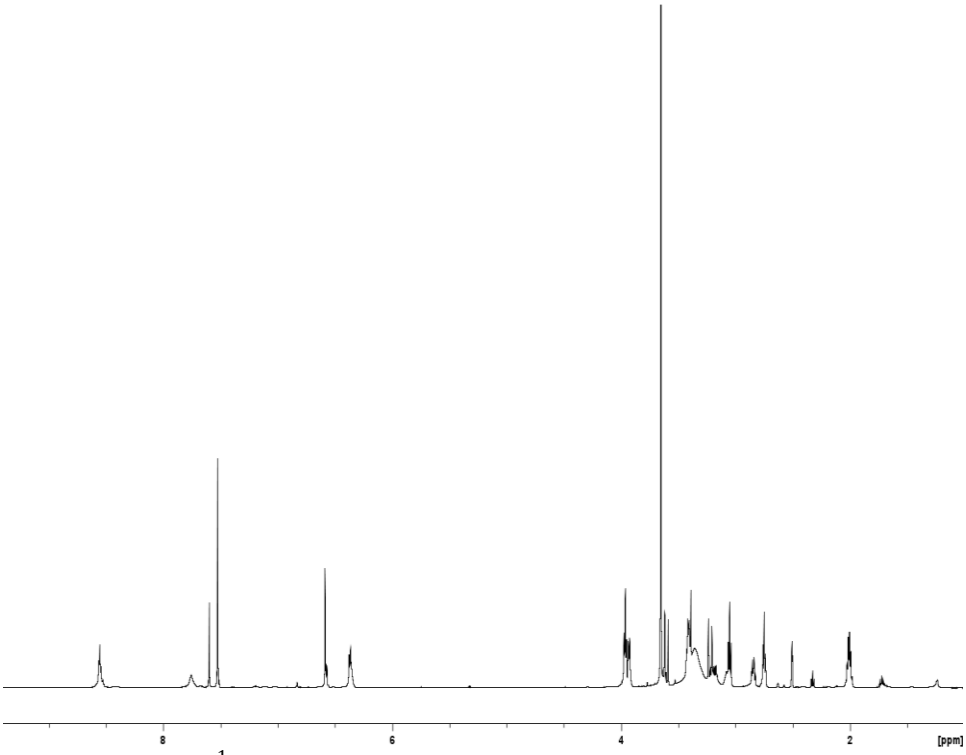

Figure S30: 1D ^{1}H-NMR spectrum of 11,19-dideoxyfistularin-3 (**6**) in DMSO-d_6, 303 K, 600 MHz.

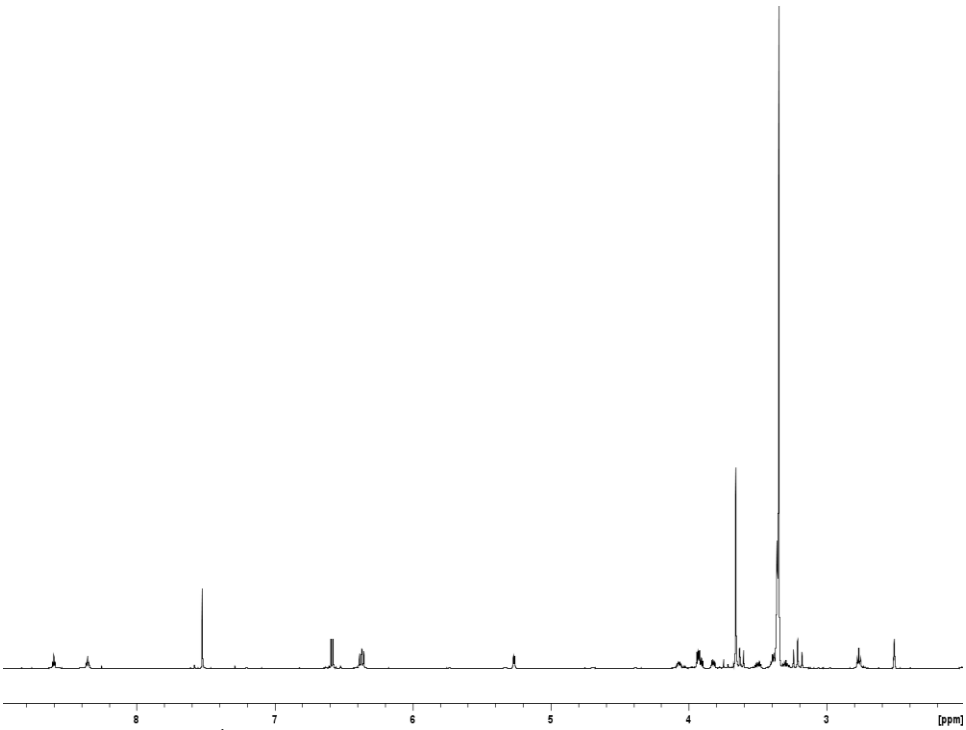

Figure S31: 1D ^{1}H-NMR spectrum of 19-deoxyfistularin-3 (**7**) in DMSO-d_6, 303 K, 600 MHz.

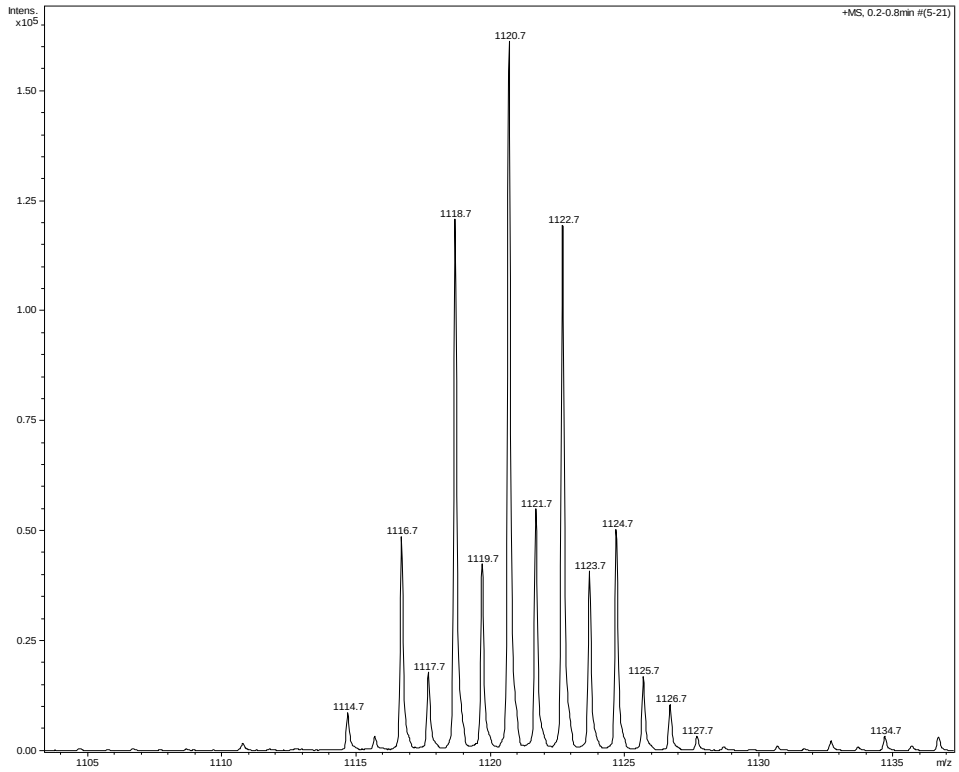

Figure S32: ESI–MS(+) spectral data of 19-deoxyfistularin-3 (**7**).

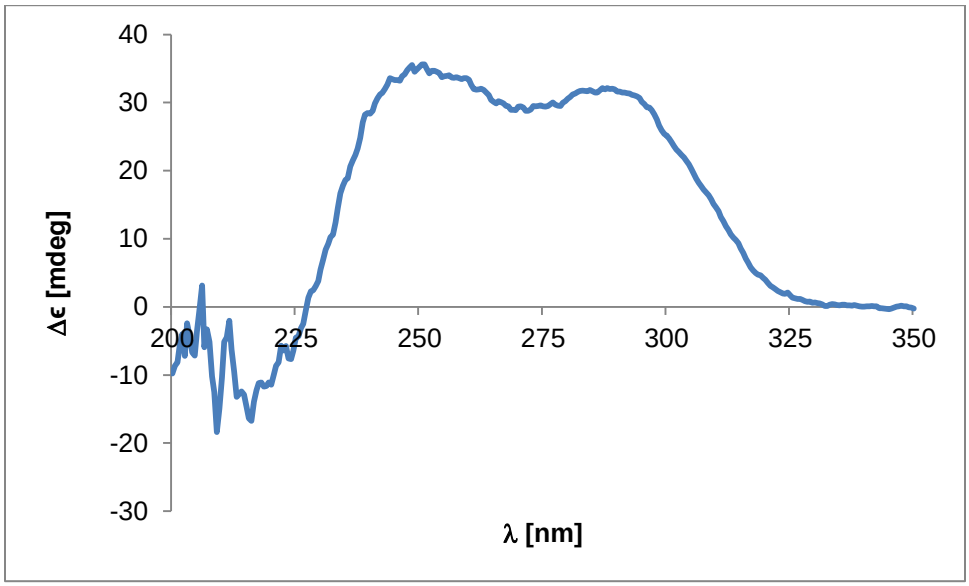

Figure S33: Circular dichroism spectrum of 19-deoxyfistularin-3 (**7**) (c = 1.8 × 10^{-4} M, MeOH, 25 °C).

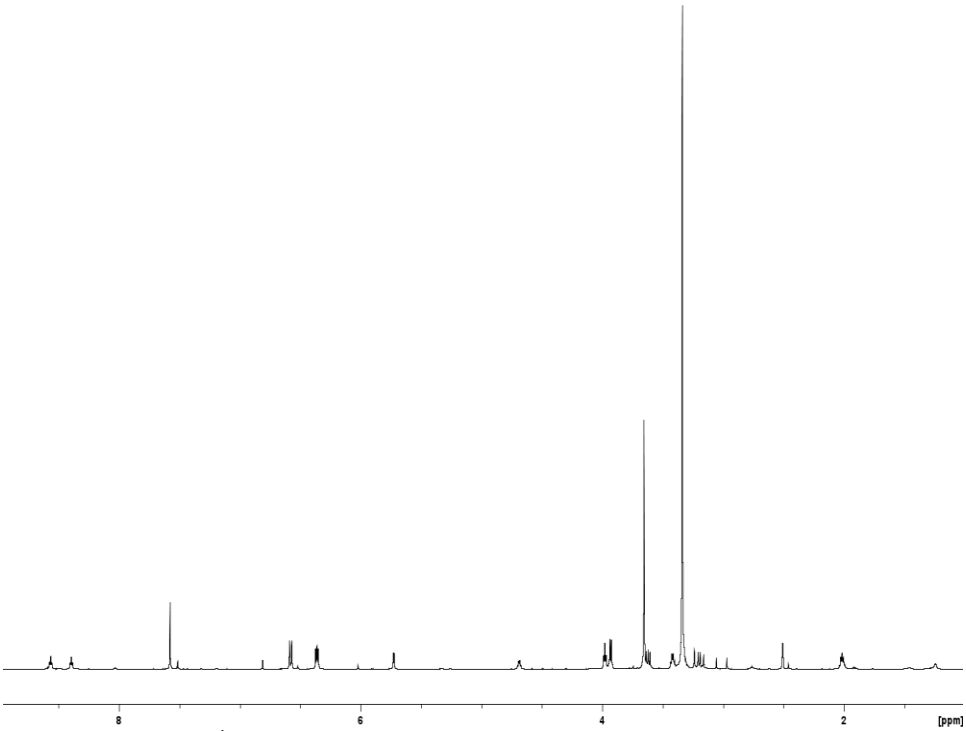

Figure S34: 1D ^{1}H-NMR spectrum of 11-deoxyfistularin-3 (**8**) in DMSO-d_6, 303 K, 600 MHz.

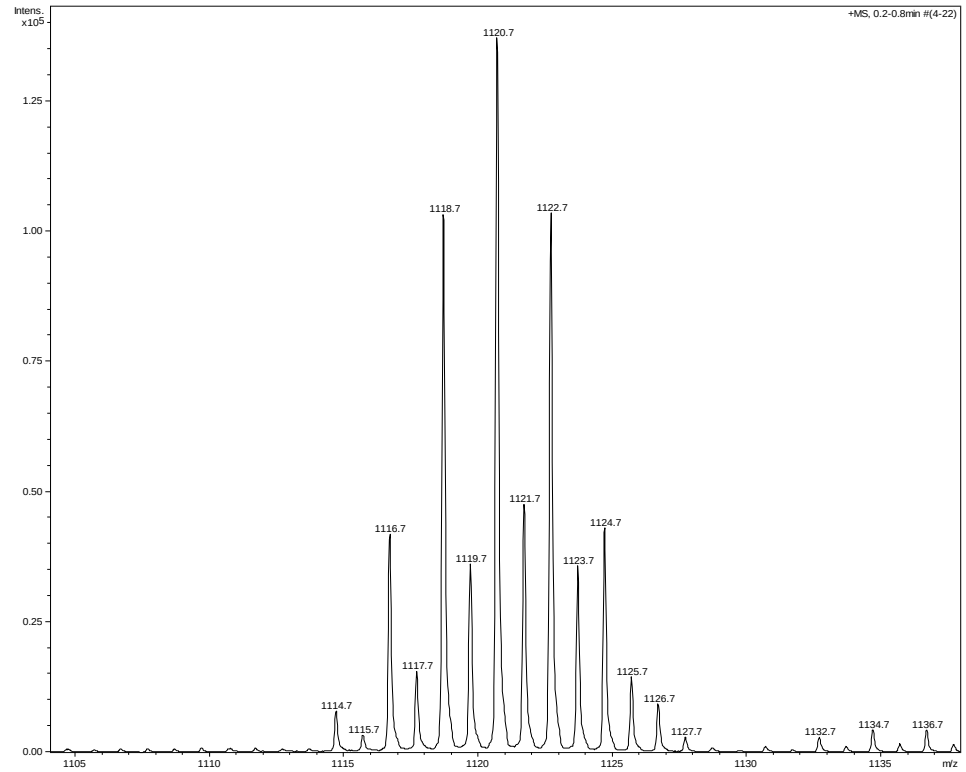

Figure S35: ESI–MS(+) spectral data of 11-deoxyfistularin-3 (**8**).

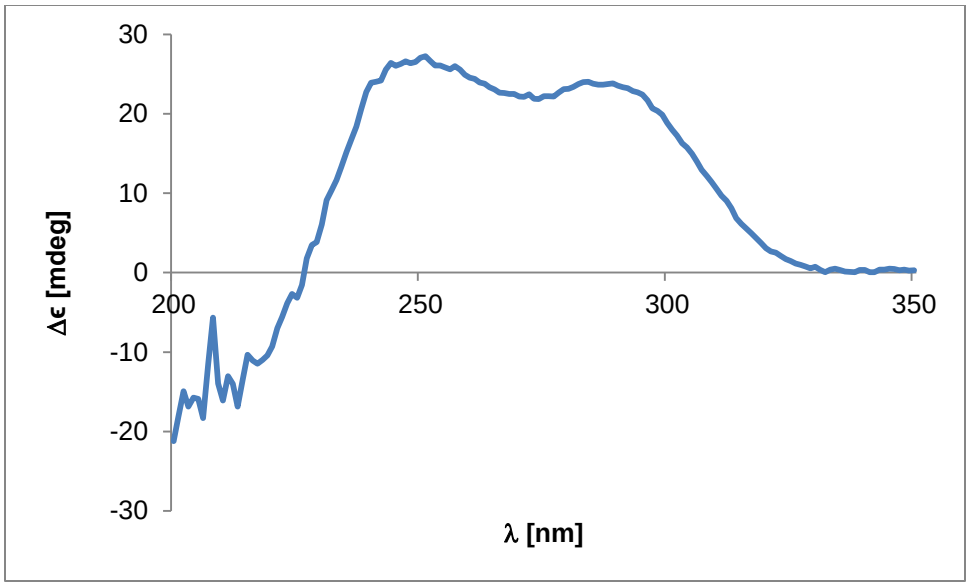

Figure S36: Circular dichroism spectrum of 11-deoxyfistularin-3 (**8**) (c = 1.8 × 10^{-4} M, MeOH, 25 °C).

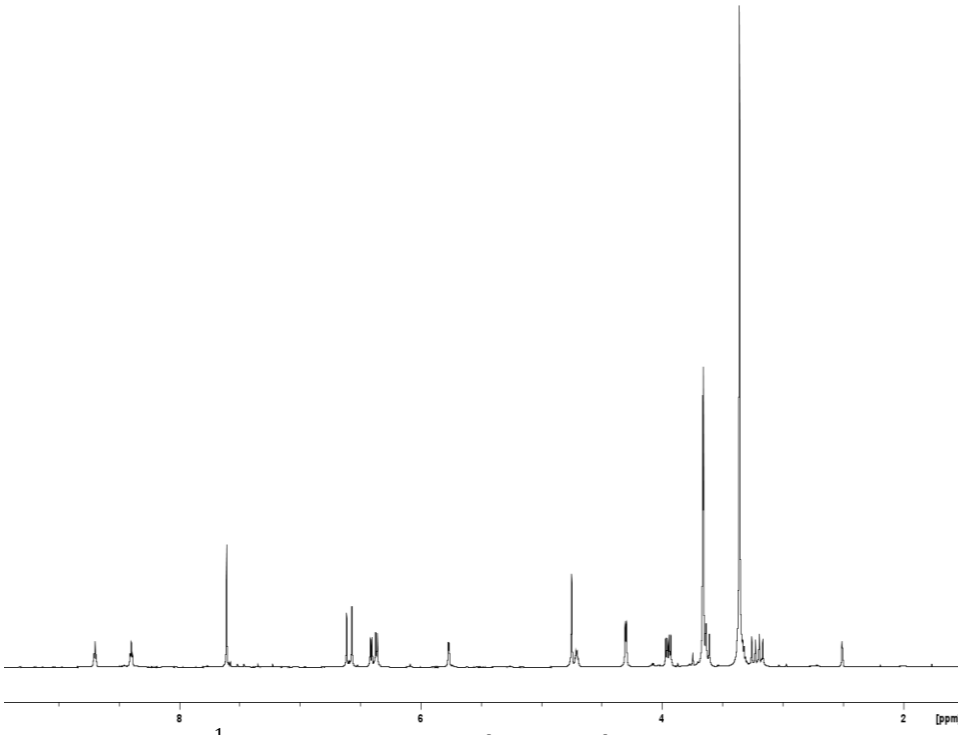

Figure S37: 1D ^{1}H-NMR spectrum of 11-ketofistularin-3 (**9**) in DMSO-d_6, 303 K, 600 MHz.

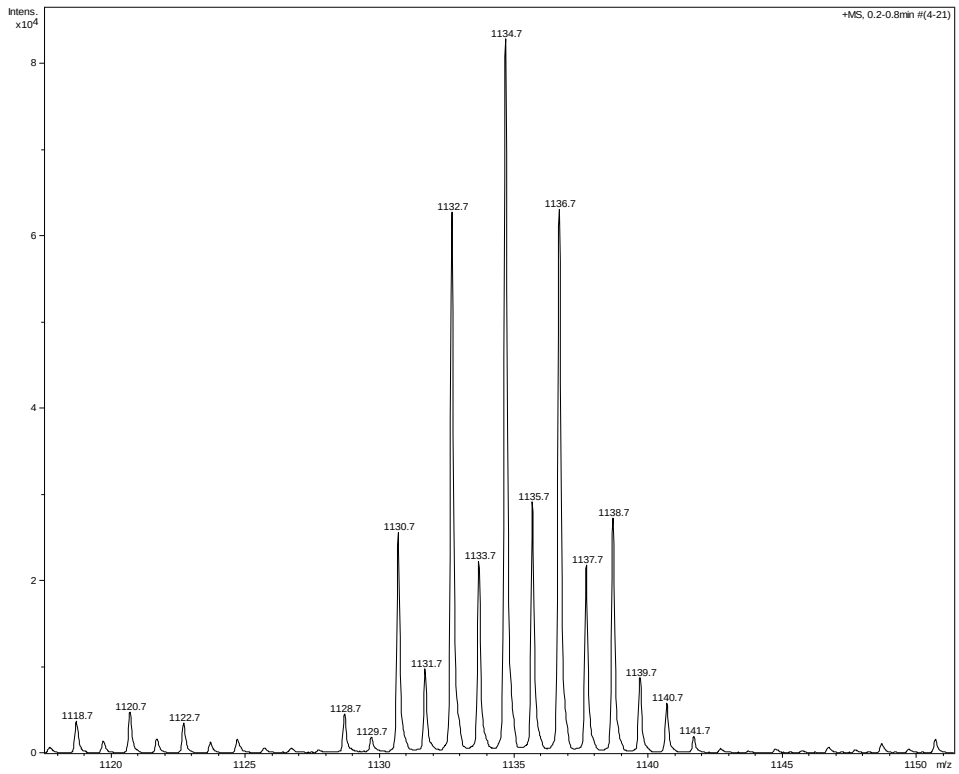

Figure S38: ESI–MS(+) spectral data of 11-ketofistularin-3 (**9**).

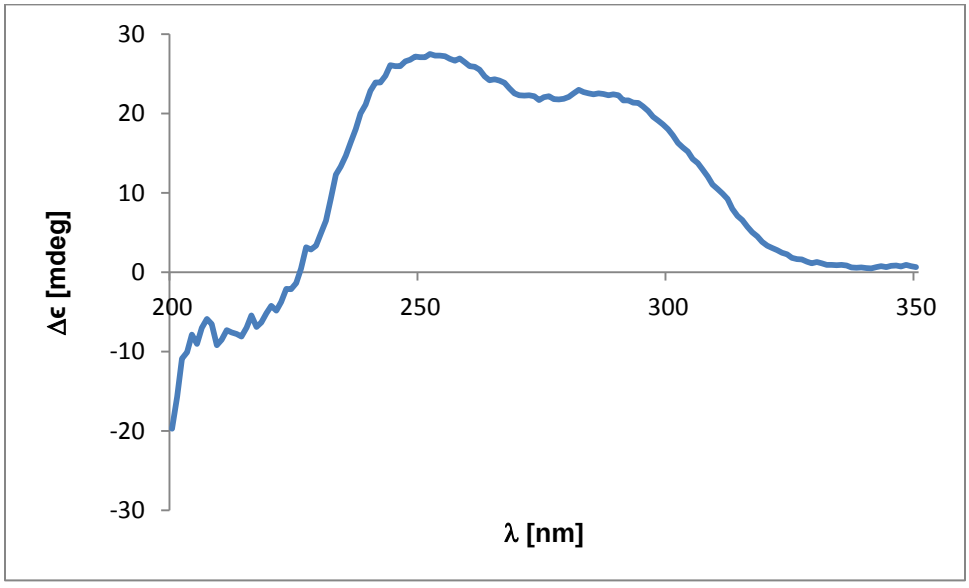

Figure S39: Circular dichroism spectrum of 11-ketofistularin-3 (**9**) (c = 1.8 × 10^{-4} M, MeOH, 25 °C).

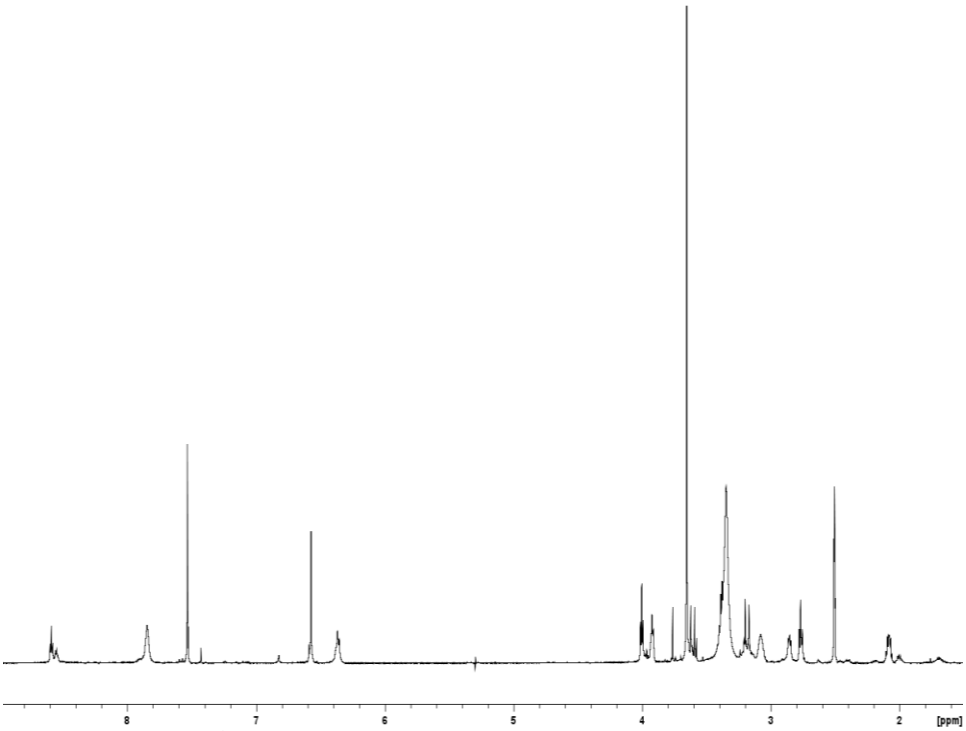

Figure S40: 1D ^{1}H-NMR spectrum of hexadelin B (**10**) in DMSO-d_6, 303 K, 600 MHz.

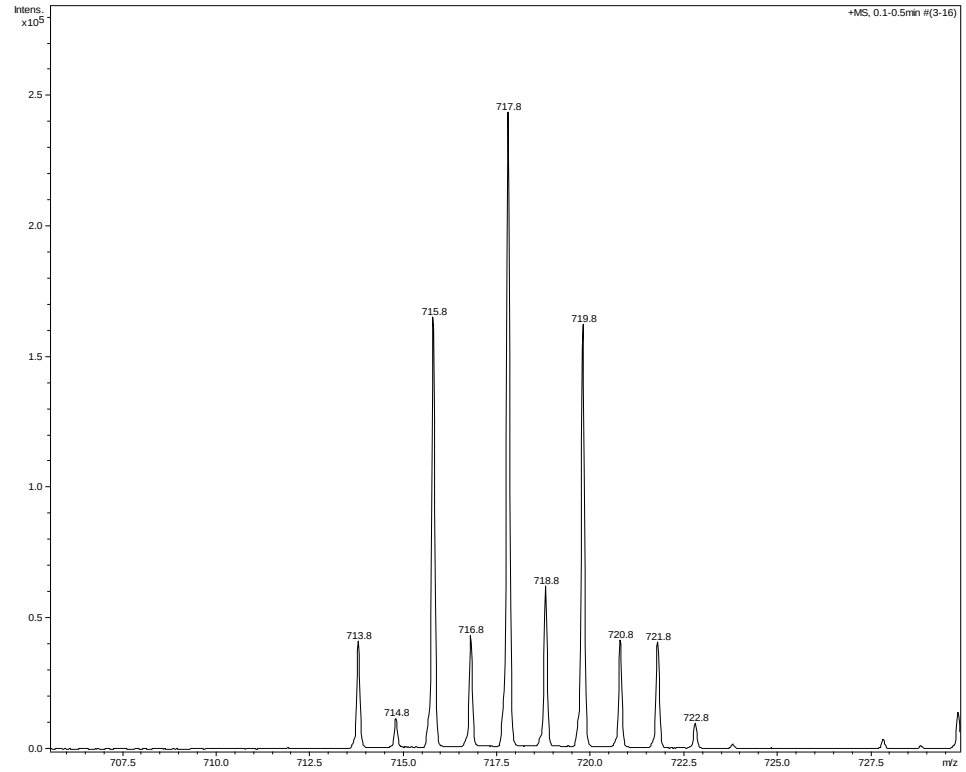

Figure S41: ESI–MS(+) spectral data of hexadelin B (**10**).

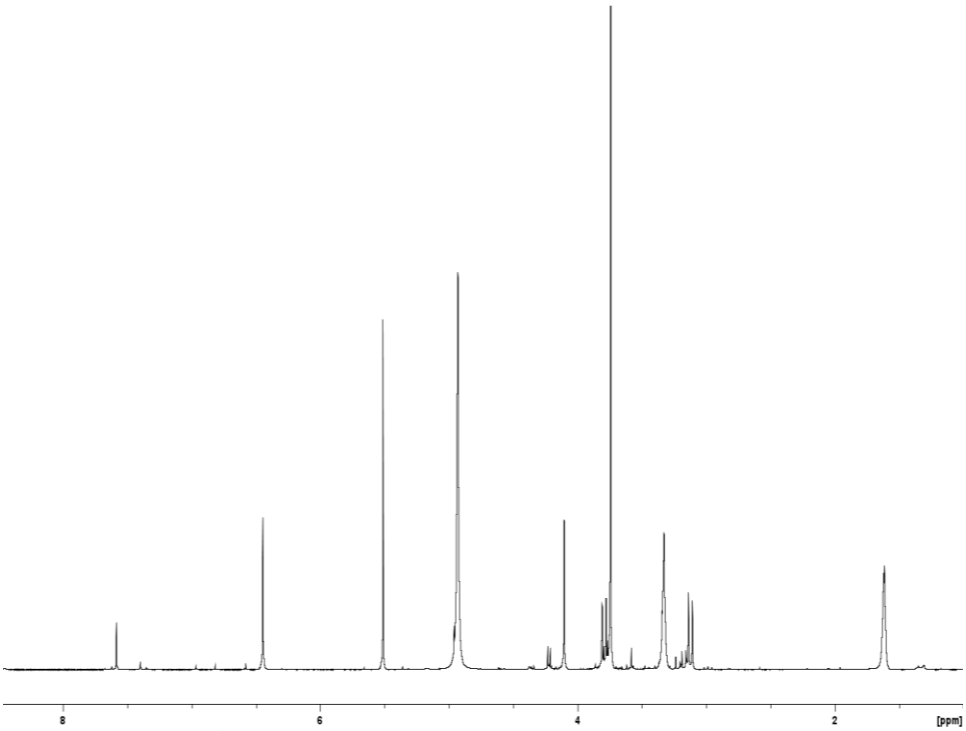

Figure S42: 1D ^{1}H-NMR spectrum of aerothionin (**11**) in DMSO-d_6, 303 K, 600 MHz.

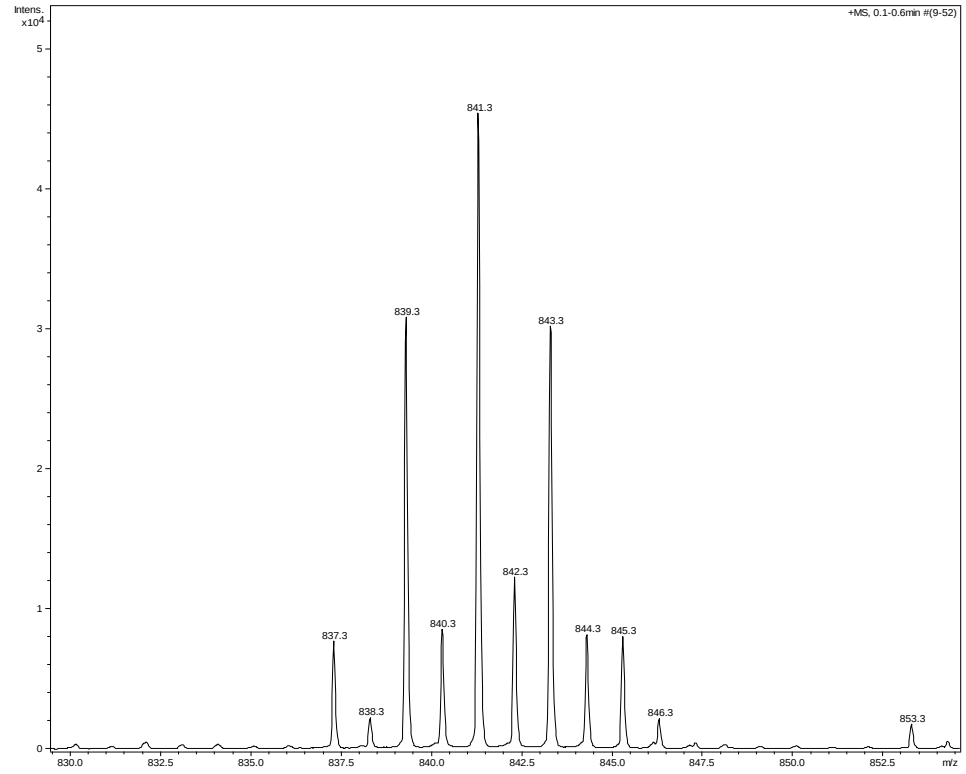

Figure S43: ESI–MS(+) spectral data of aerothionin (**11**).

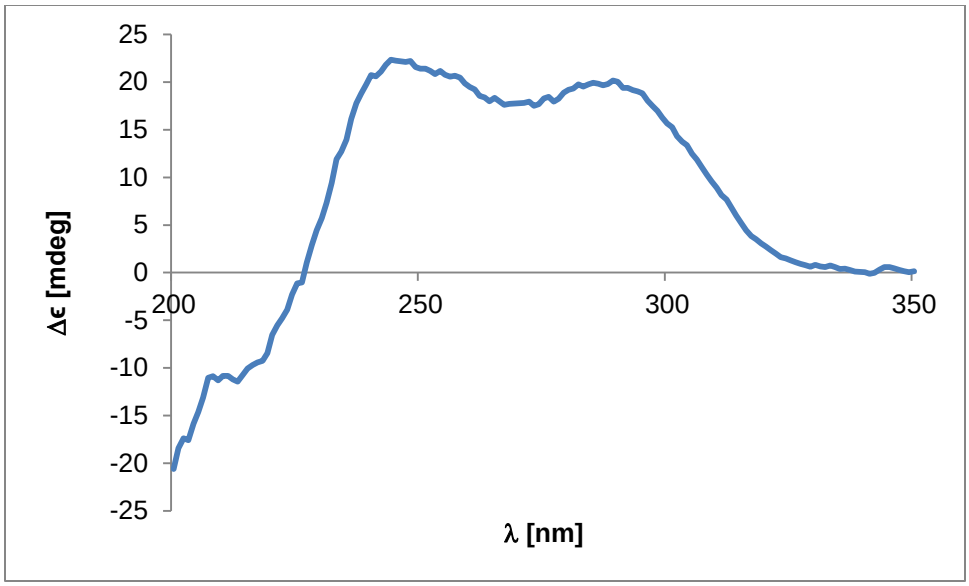

Figure S44: Circular dichroism spectrum of aerothionin (**11**) (c = 2.4 × 10^{-4} M, MeOH, 25 °C).

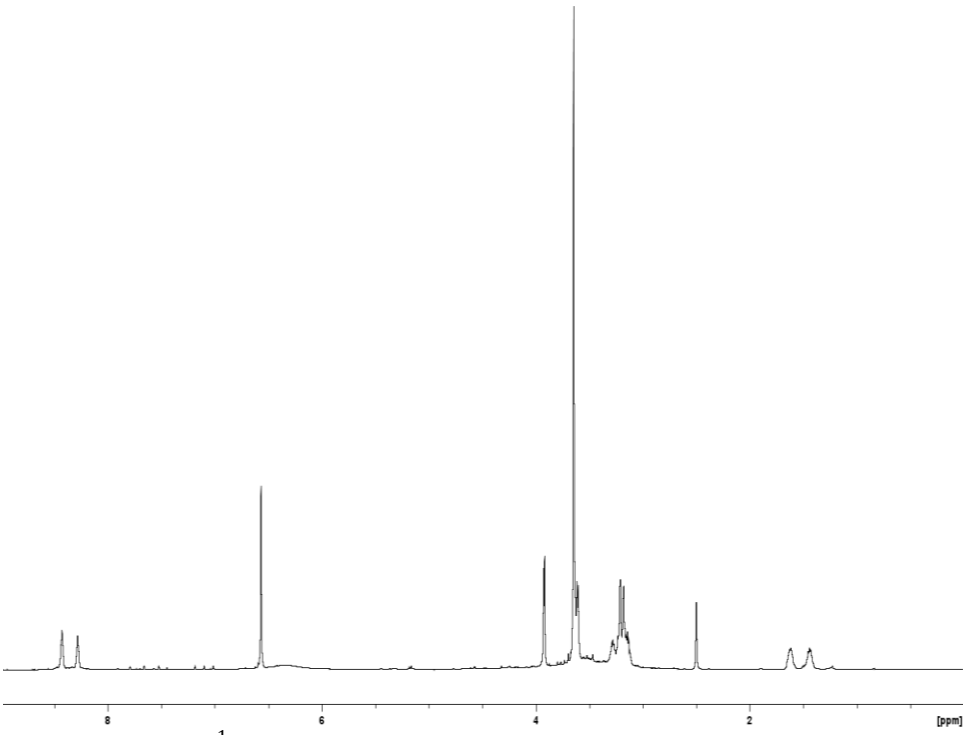

Figure S45: 1D ^{1}H-NMR spectrum of 11-hydroxyaerothionin (**12**) in DMSO-d_6, 303 K, 600 MHz.

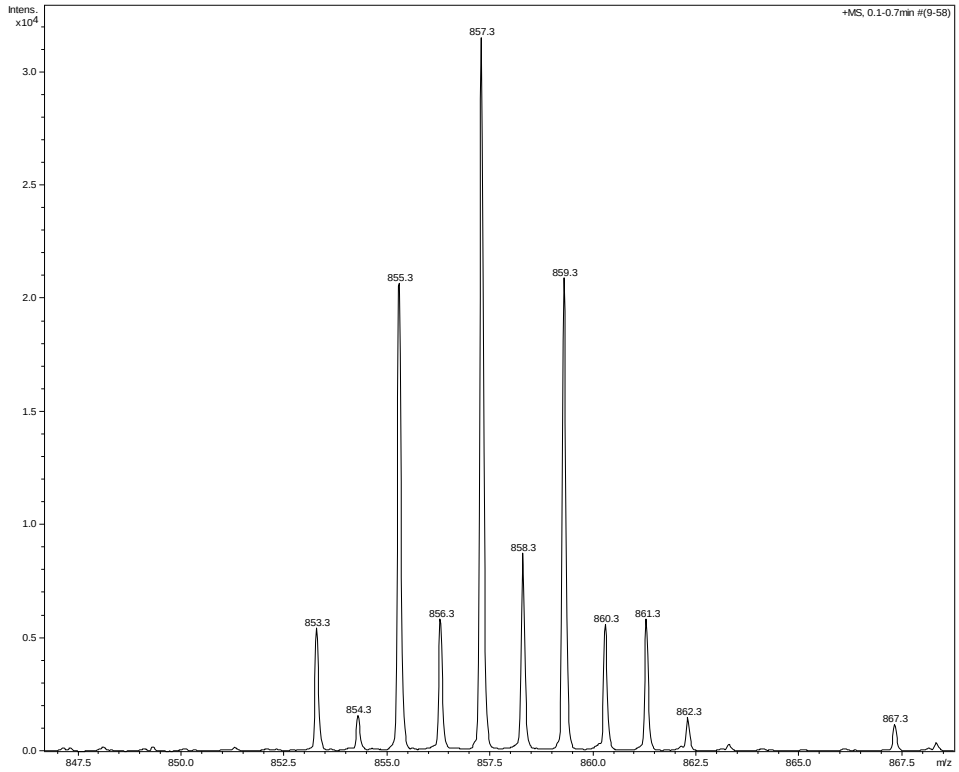

Figure S46: ESI–MS(+) spectral data of 11-hydroxyaerothionin (**12**).

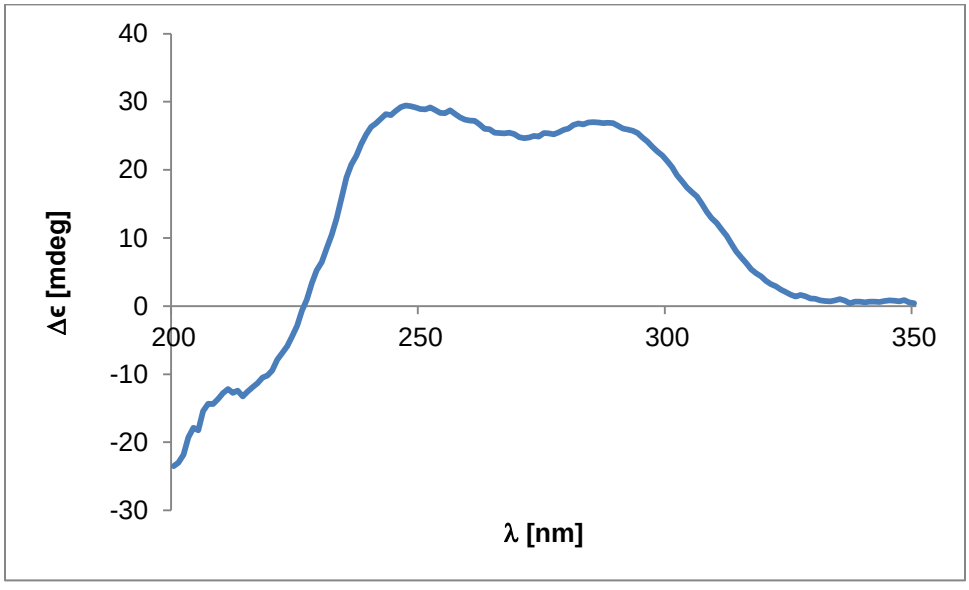

Figure S47: Circular dichroism spectrum of 11-hydroxyaerothionin (**12**) (c = 2.4 × 10^{-4} M, MeOH, 25 °C).

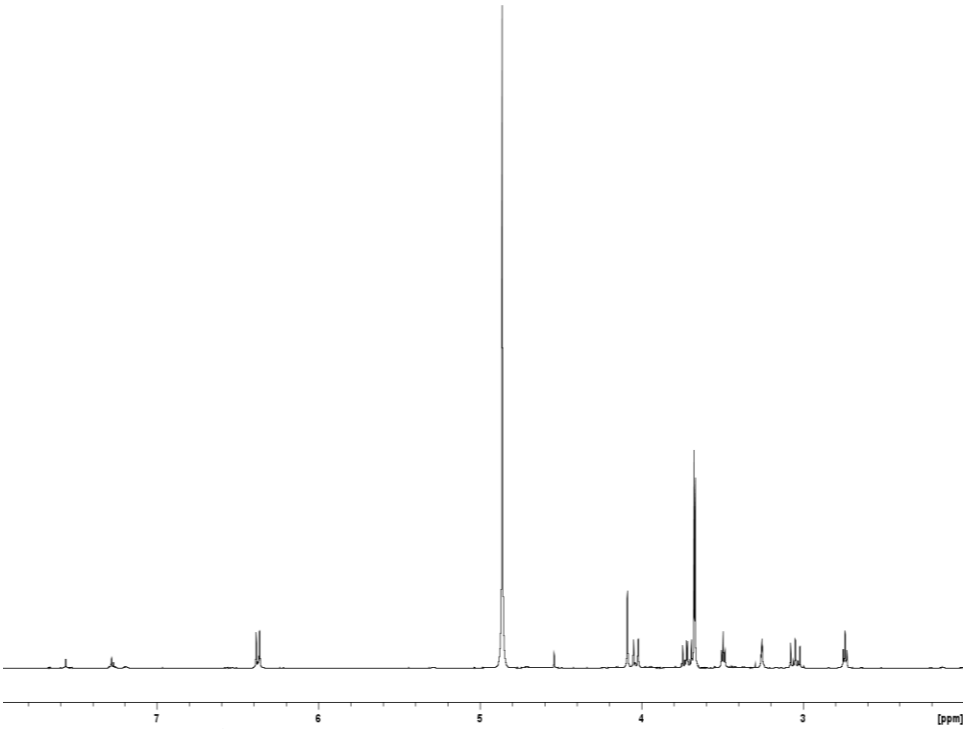

Figure S48: 1D ^{1}H-NMR spectrum of 11-oxoaerothionin (**13**) in CD_3OD, 303 K, 600 MHz.

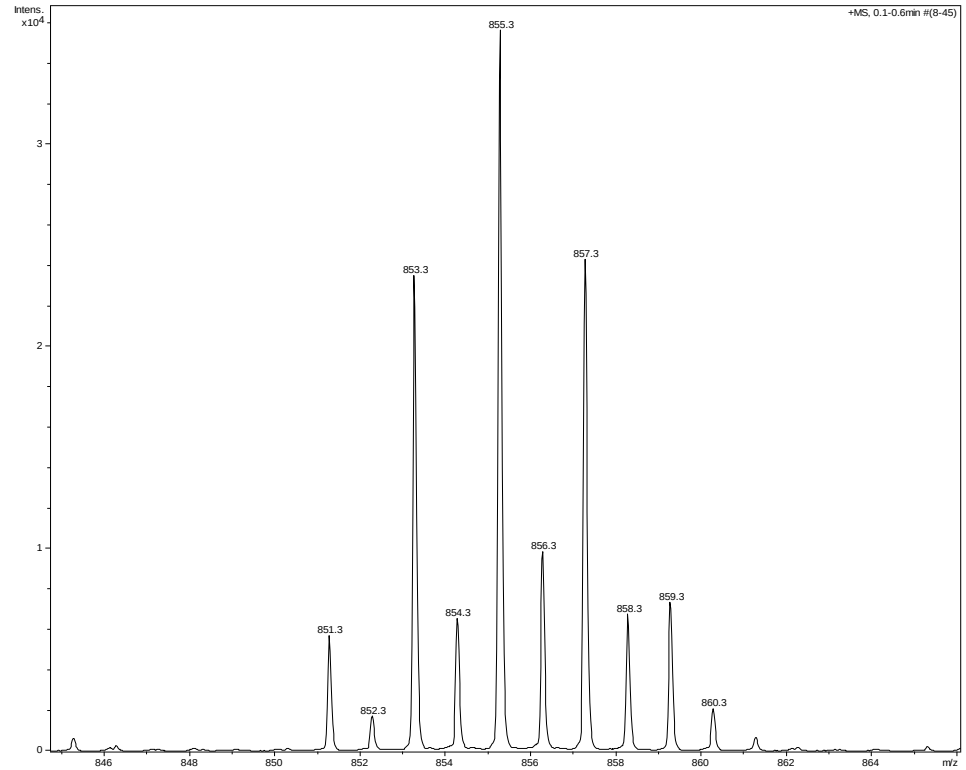

Figure S49: ESI–MS(+) spectral data of 11-oxoaerothionin (**13**).

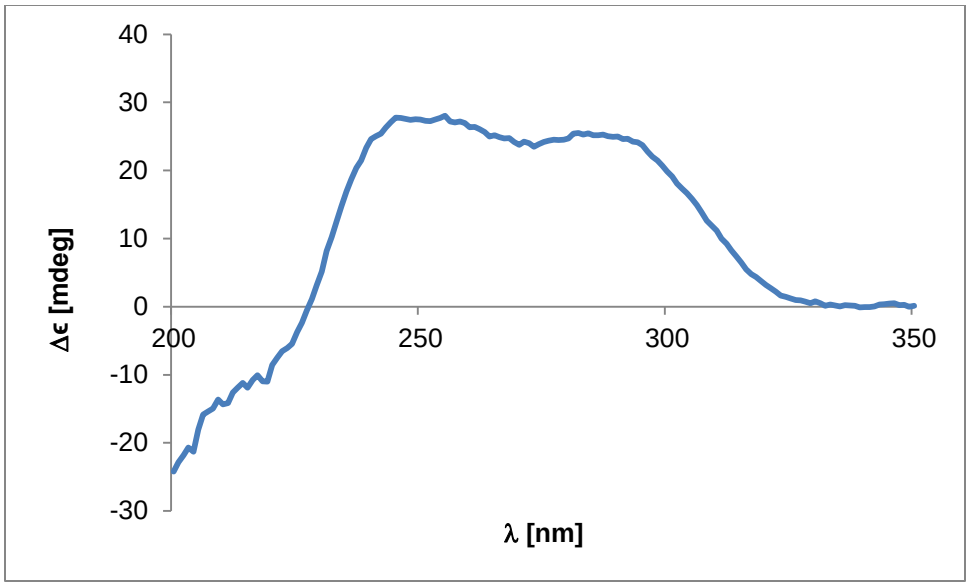

Figure S50: Circular dichroism spectrum of 11-oxoaerothionin (**13**) (c = 2.4 × 10^{-4} M, MeOH, 25 °C).

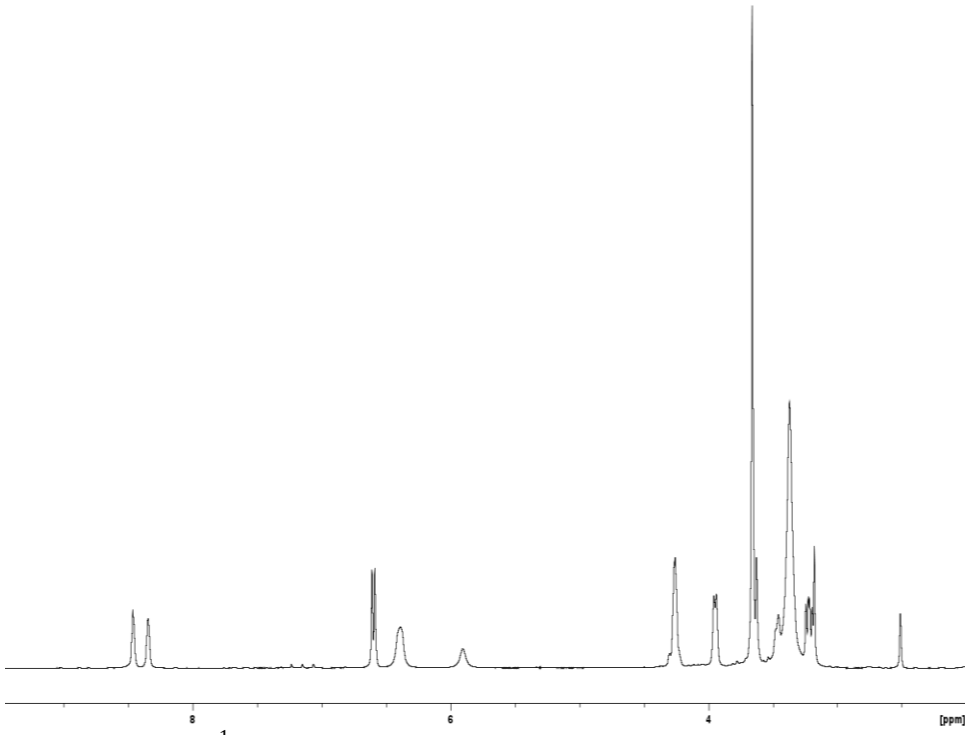

Figure S51: 1D ^{1}H-NMR spectrum of 11-oxo-12-hydroxyaerothionin (**14**) in DMSO-d_6, 303 K, 600 MHz.

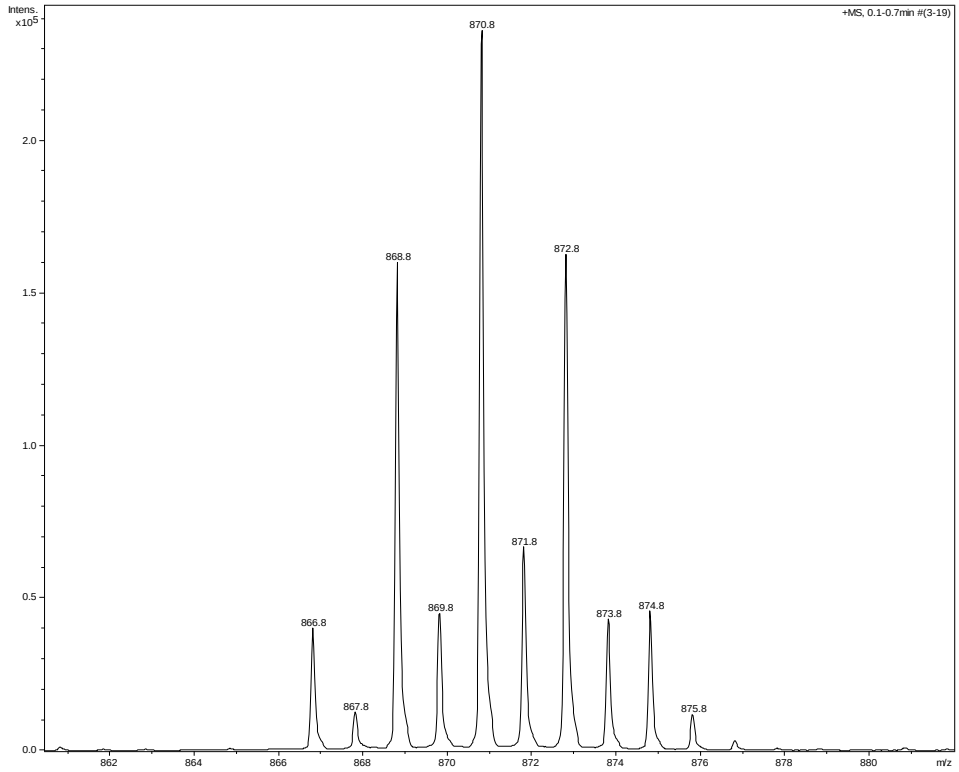

Figure S52: ESI–MS(+) spectral data of 11-oxo-12-hydroxyaerothionin (**14**).

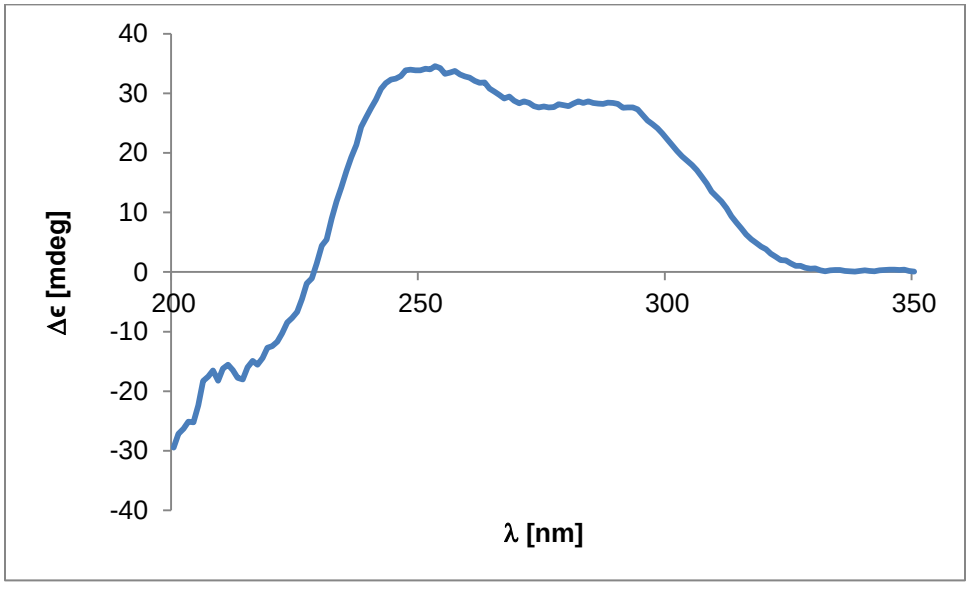

Figure S53: Circular dichroism spectrum of 11-oxo-12-hydroxyaerothionin (**14**) (c = 2.3 × 10^{-4} M, MeOH, 25 °C)

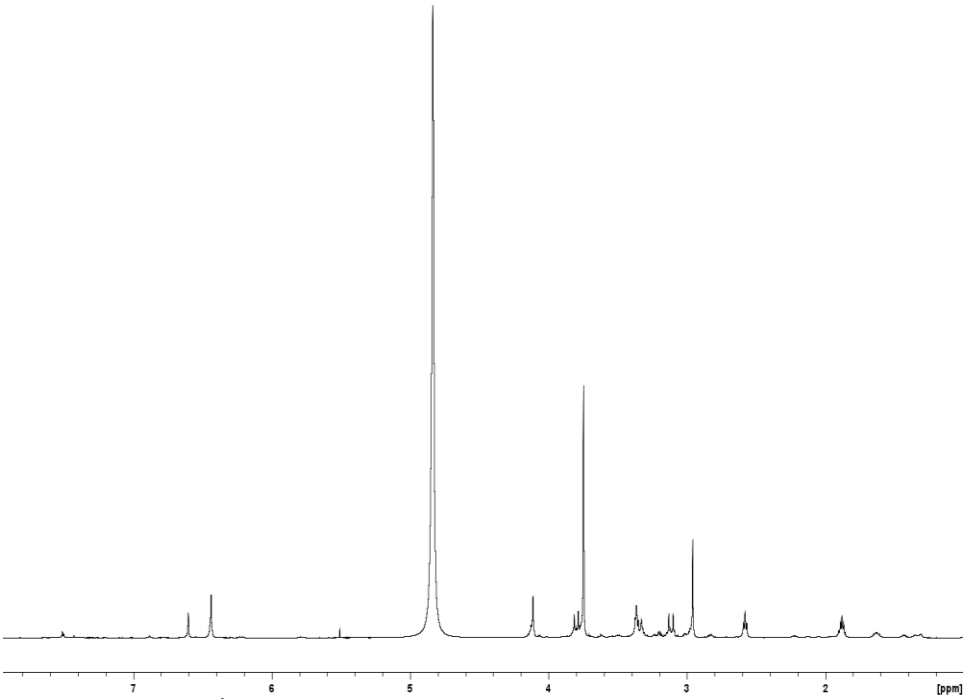

Figure S54: 1D ^{1}H-NMR spectrum of *N*-methyl-aerophobin-2 (**15**) in CD_3OD-d_4, 303 K, 600 MHz.

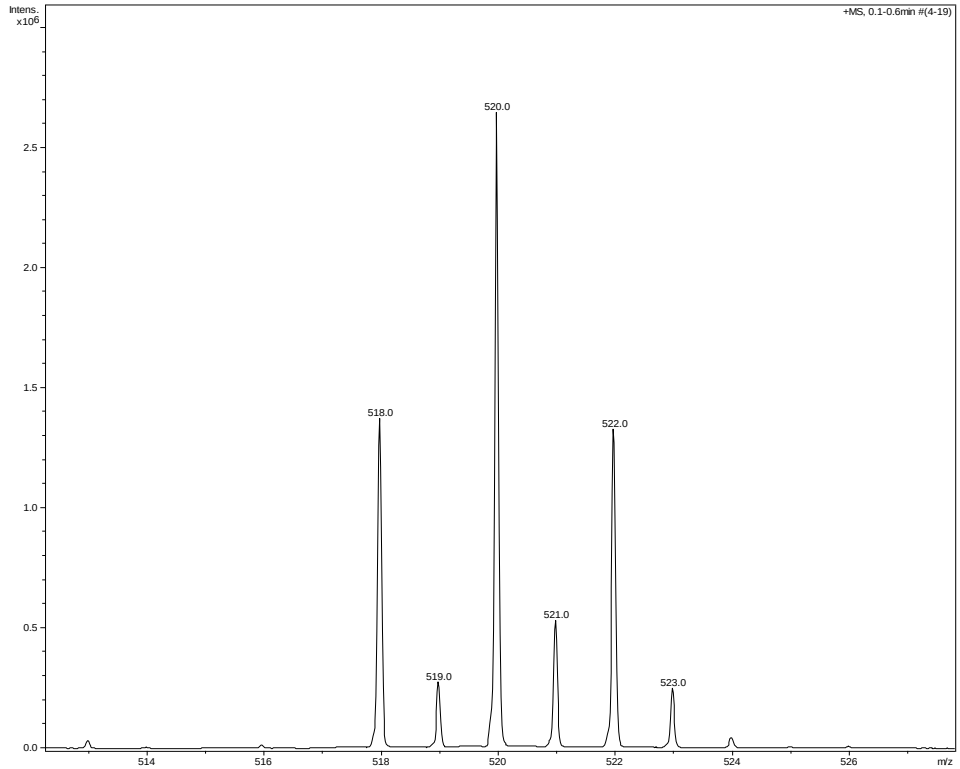

Figure S55: ESI–MS(+) spectral data of *N*-methyl-aerophobin-2 (**15**).

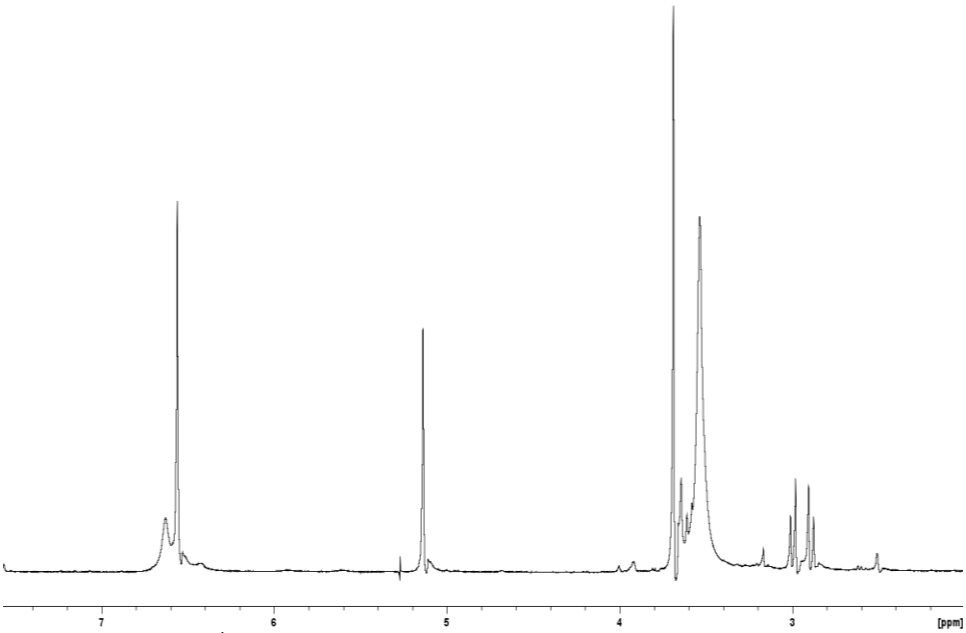

Figure S56: 1D ^{1}H-NMR spectrum of aeroplysinin-2 (**16**) in DMSO-d_6, 303 K, 600 MHz.

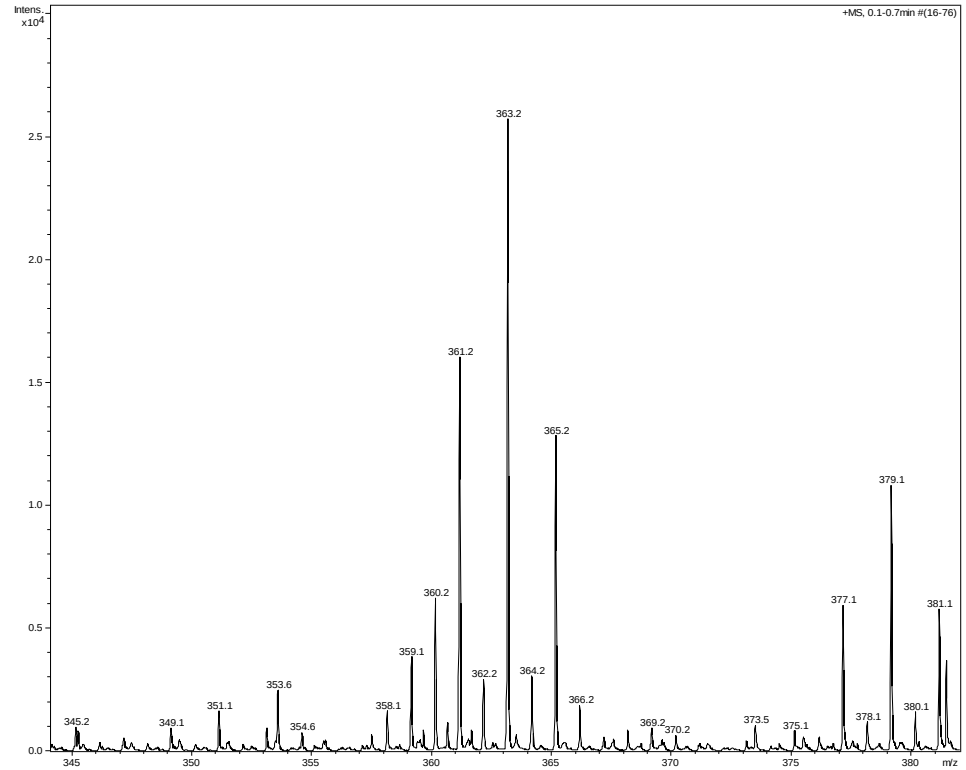

Figure S57: ESI–MS(+) spectral data of aeroplysinin-2 (**16**).

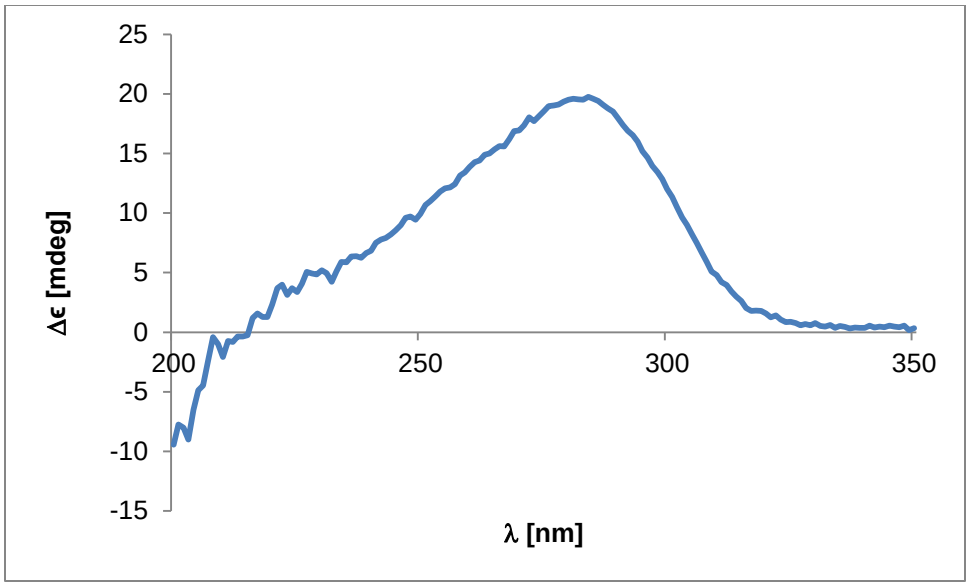

Figure S58: Circular dichroism spectrum of aeroplysinin-2 (**16**) (c = 5.5 × 10^{-4} M, MeOH, 25 °C)

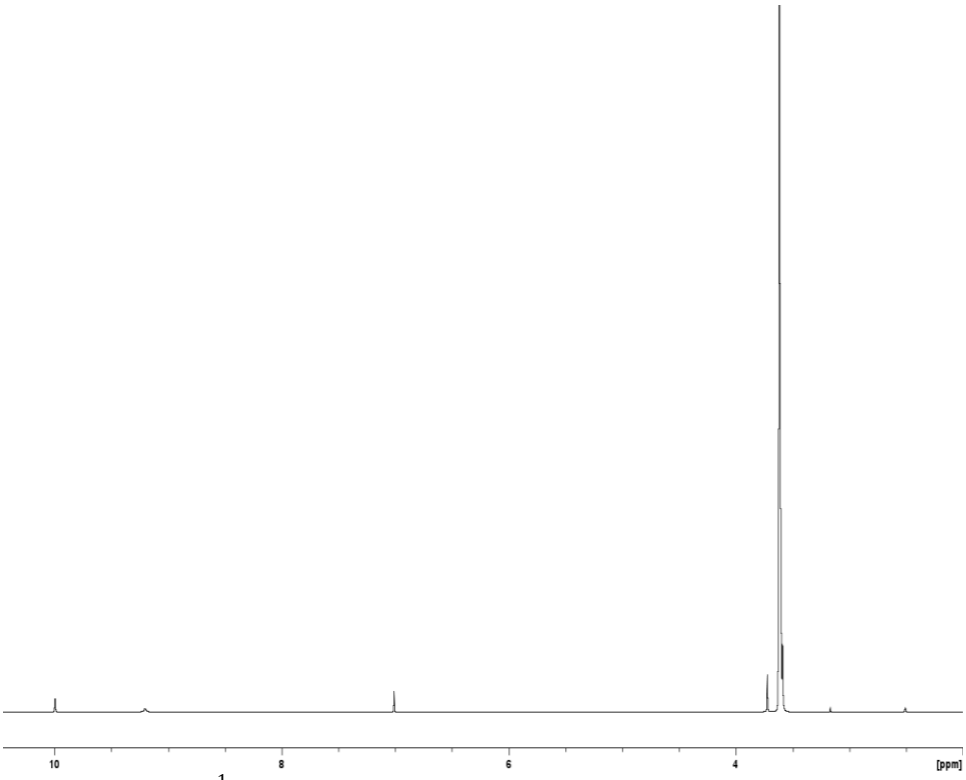

Figure S59: 1D ^{1}H-NMR spectrum of subereaphenol B (**17**) in DMSO-d_6, 303 K, 600 MHz.

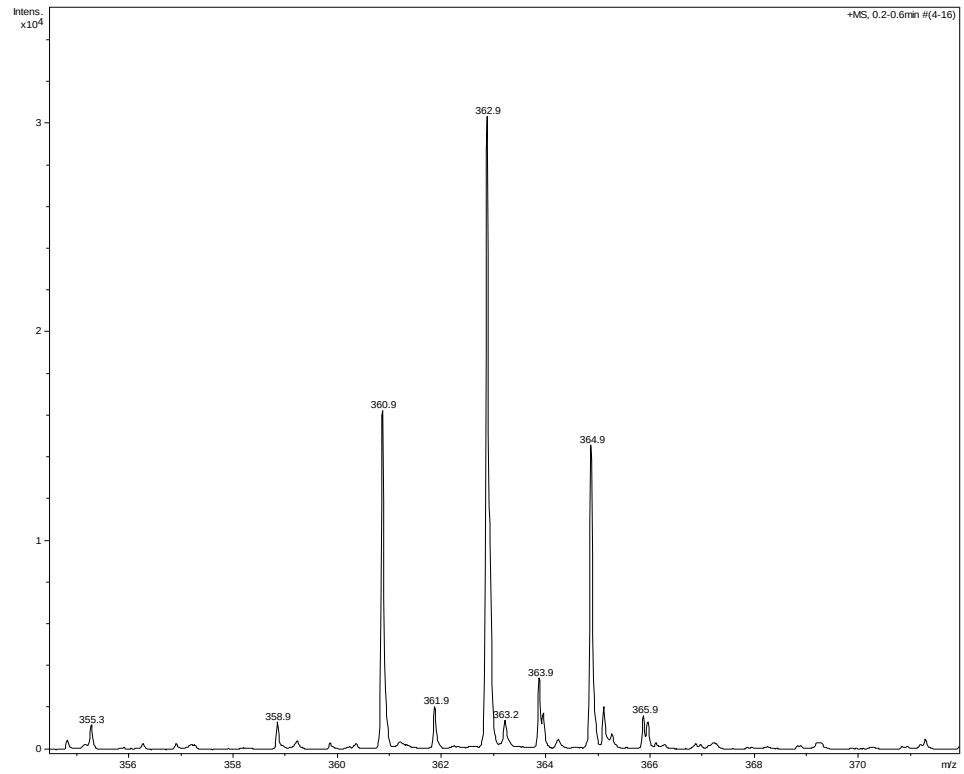

Figure S60: ESI–MS(+) spectral data of subereaphenol B (**17**).

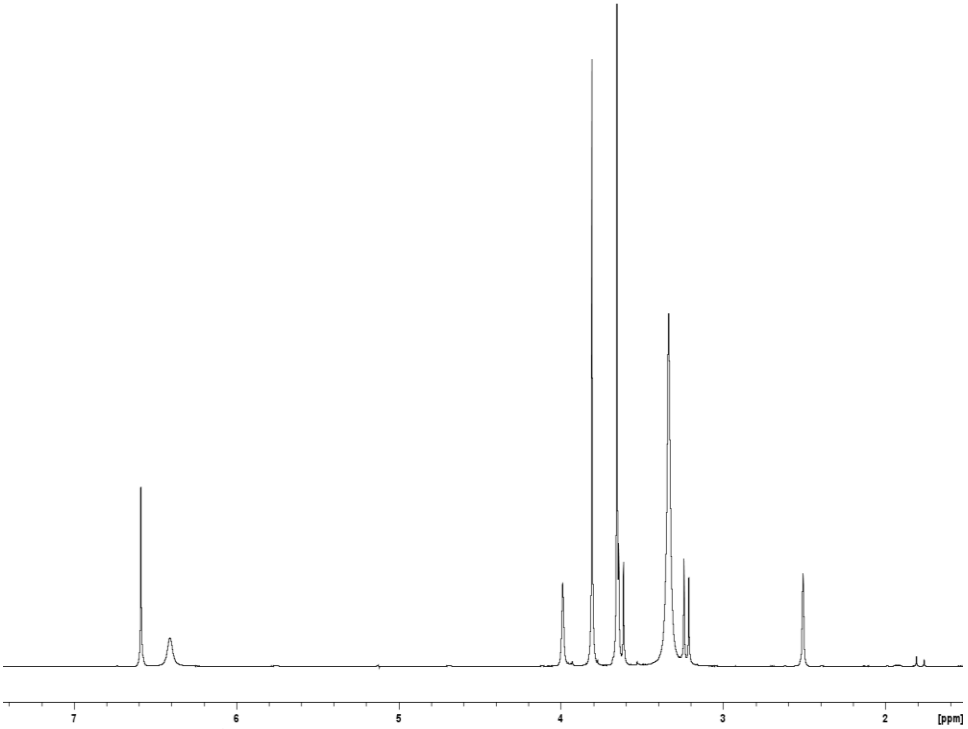

Figure S61: 1D ^{1}H-NMR spectrum of unnamed bromytyrosine (**18**) in DMSO-d_6, 303 K, 600 MHz.

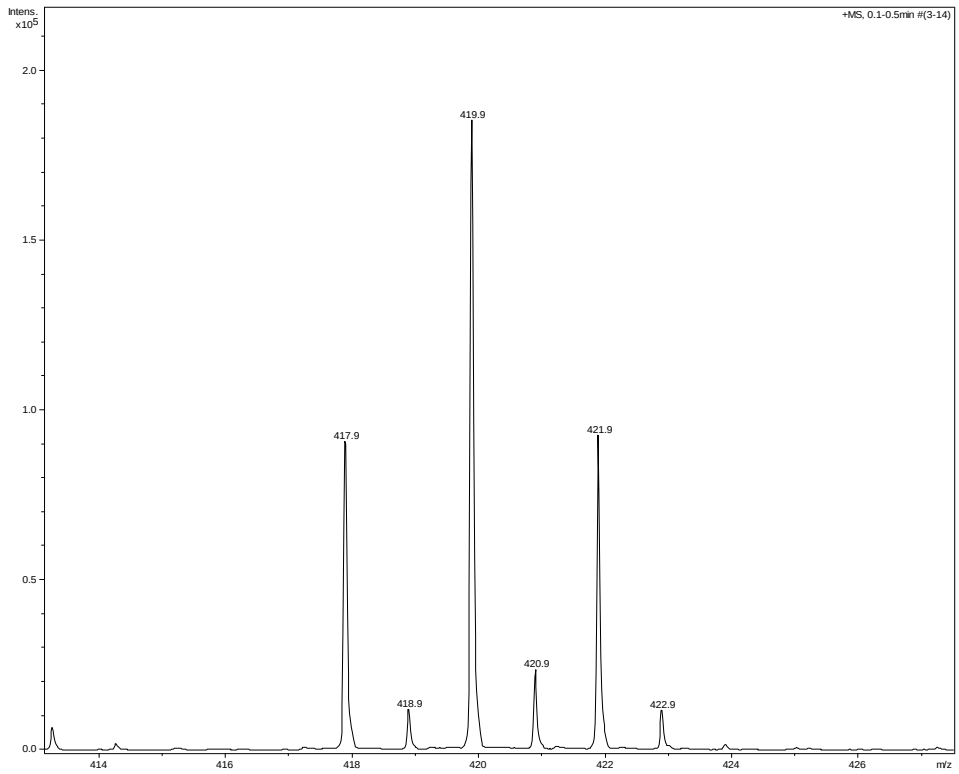

Figure S62: ESI–MS(+) spectral data of unnamed bromytyrosine (**18**).

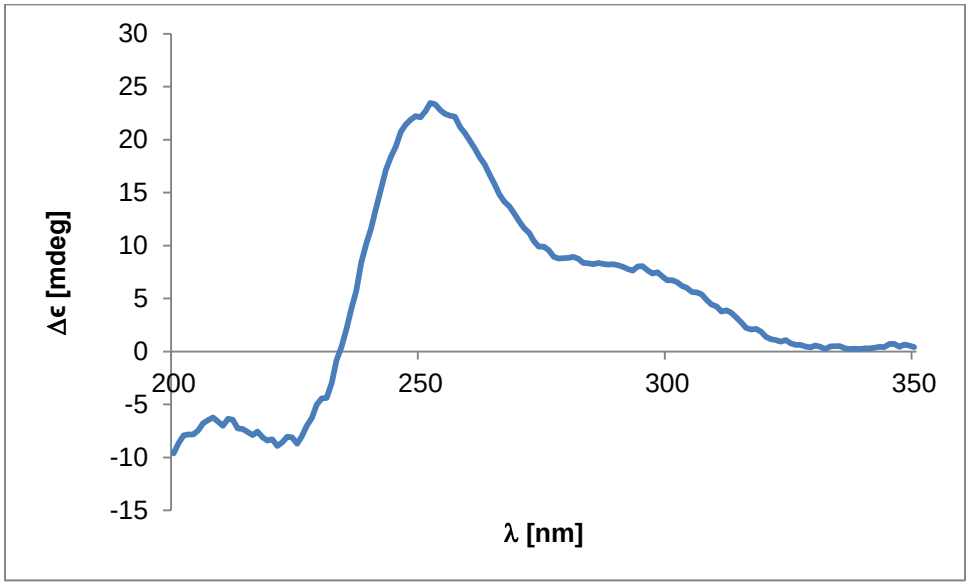

Figure S63: Circular dichroism spectrum of unnamed bromytyrosine (**18**) (c = 4.8 × 10^{-4} M, MeOH, 25 °C)