SUPPORTING INFORMATION

The Chemical Gymnastics of Enterocin: Evidence for Stereodivergence in Nature

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A. NMR Tables

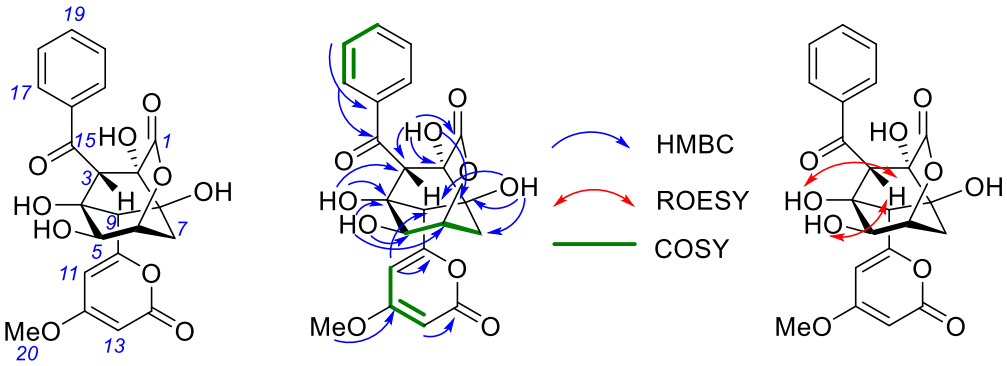


Table S1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for enterocin (**1**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		173.6			
2		79.8			
3	4.459, s	53.0	1, 2, 4, 5, 8, 9, 15		4-OH, 5-OH, 17
4		78.2			
5	4.462, dd (5.7, 4.6)	69.3	3, 6	5-OH, 6	7a
6	4.64, ddd (4.6, 3.0, 3.0)	75.4	1	5, 7a/b	7a/b
7a	2.29, dd (14.5, 3.0)	35.6	2, 8, 9	6, 7b, 9	5, 6, 7b
7b	1.66, ddd (14.5, 3.0, 2.7)		5, 6, 8, 9	6, 7a	6, 7a, 8-OH, 20
8		76.4			
9	4.65, d (2.7)	54.6	3, 4, 5, 7, 8, 11, 14	7a, 11	4-OH, 11, 8-OH
10		161.5			
11	6.28, d (2.3)	104.7	9, 10, 12, 13	9, 13	9, 20
12		170.7			
13	5.61, d (2.3)	87.8	11, 12, 14	11, 20	20
14		163.3			
15		194.9			
16		139.6			
17	7.77, dd (7.8, 7.4)	127.9	15, 17, 19	18	
18	7.50, d (7.4)	128.4	16, 17	19, 20	3
19	7.59, t (7.8)	132.5	18	18	
20	3.82, s	56.3	12	13	5-OH, 7b, 11, 13
2-OH	5.82, s		1, 2, 3, 8		
4-OH	5.46, s		3, 4, 5, 9		3, 9
5-OH	5.64, d (5.7)		4, 5, 6	5	3, 20
8-OH	5.89, s		7, 8, 9		7b, 9

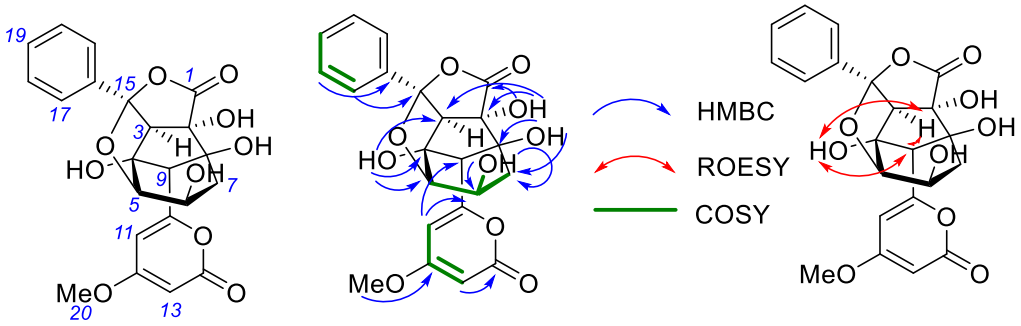


Table S2. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for isoenterocin A (**2**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		174.1			
2		82.9			
3	3.09, d (0.7)	68.2	1, 2, 4, 5, 8, 16	5	4-OH, 9, 17
4		83.7			
5	4.58, dd (5.4, 0.7)	90.0	3, 4, 6, 7, 15	3, 6, 6-OH, 7a	6, 7a
6	3.97, ddd (9.6, 9.6, 5.4)	62.4		5, 7a/b	5, 7a
7a	2.24, dd (15.1, 9.6)	37.1	2, 5, 6, 8	5, 6, 7b	5, 6, 7b
7b	1.49, dd (15.1, 9.6)		2, 6, 8, 9	6, 7a, 9	7a
8		77.4			
9	3.60, s	53.4	4, 5, 7, 8, 9, 10, 11	7b, 11	3, 4-OH, 8-OH, 11
10		160.9			
11	6.35, dd (2.2, 1.4)	102.0	9, 10, 12, 13	9, 13	8-OH, 9
12		170.5			
13	5.61, m	88.1	11, 12, 14	11	15
14		163.1			
15		112.0			
16		140.2			
17	7.53, d (7.0)	125.4	15, 17, 19		3
18	7.45, dd (7.2, 7.0)	128.3	16, 18		
19	7.40, t (7.2)	128.8	17		
20	3.81, s	56.3	12		13
2-OH	6.69, s		1, 2, 3, 8		
4-OH	6.11, s		3, 4, 5		3, 9
6-OH	4.86, d (5.9)		5, 6, 7	6	6
8-OH	5.63, m		2, 7, 8, 9		9, 11

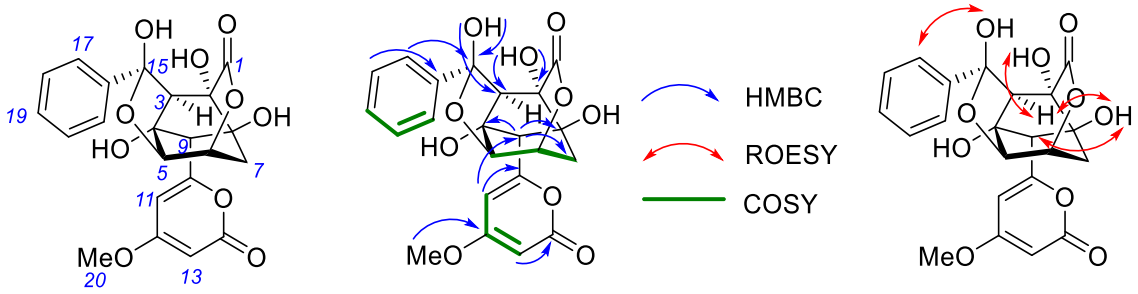


Table S3. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for isoenterocin B (**3**) in DMSO-d_6

Position	δ_H, mult (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		170.8			
2		81.8			
3	2.69, d (2.3)	66.0	1, 4, 8, 15, 16		2-OH, 8-OH, 9, 17
4		80.2			
5	4.82, dd (4.5, 2.3)	81.5	6	6	6
6	4.28, dt (4.5, 2.6)	72.0	5, 8	5, 7a/b	5, 7a/b
7a	2.59, dt (14.5, 2.2)	32.7	5, 6, 8, 9	6, 7b, 9	6, 7b
7b	1.74, dd (14.5, 3.2)		4, 8, 9	7, 7a	5, 6, 7a
8		78.7			
9	3.62, d (2.1)	53.1	2, 4, 7, 8, 11	7a	2-OH, 3, 8-OH, 11
10		161.9			
11	6.16, d (2.4)	104.2	9, 10, 12, 13	13	9
12		170.8			
13	5.62, m	87.6	11, 12, 14	11	
14		163.1			
15		107.2			
16		136.2			
17	7.33, m	126.8	15		3
18	7.53, m	128.3			
19	7.33, m	127.1			
20	3.82, s	56.3	12		
2-OH	5.91, br s[\]		3, 16		3, 9
4-OH	4.82, dd (4.5, 2.3)[a]				
8-OH	5.84, br s				3, 9
15-OH	4.82, dd (4.5, 2.3)[a]		3, 15		17

[a] overlapping

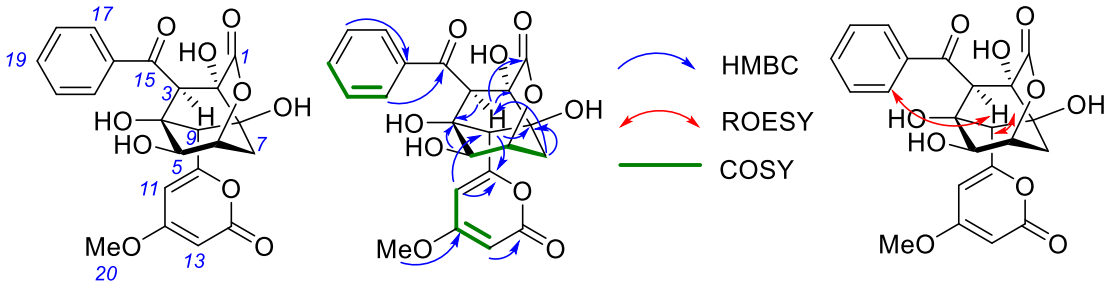


Table S4. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for 3-*epi*-enterocin (**4**) in D_2O

Position	δ_H, mult (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY[b]
1		174.4			
2		82.2			
3	4.48, s	51.4	1, 2, 4, 5, 8, 9, 10, 15		9, 17
4		79.9			
5	4.64, d (4.4)	67.0	3, 4, 6	6	
6	4.81, m	75.5	5	5, 7a/b	
7a	2.54, dd (14.8, 2.9)	33.2	2, 4, 9	6, 7b	
7b	1.79, m		4, 6, 6, 9	6, 7a, 9	
8		78.4			
9	4.56, d (2.9)	52.8	4, 5, 7, 8, 10, 11	7b	3
10		166.7			
11	6.77, d (2.3)	104.5	9, 10, 12, 13	9, 13	
12		171.5			
13	5.72, d (2.3)	86.7	11, 12, 14	11	
14		160.2			
15		195.2			
16		136.8			
17	7.68, m	127.0	18	18	3
18	7.88, m	126.8	15, 17, 19	17	
19	7.77, t (7.8)	132.1	16, 18		
20	3.93, s	54.8	12		
2-OH	[a]				
4-OH	[a]				
5-OH	[a]				
8-OH	[a]				

[a] exchanged with D_2O. [b] Most ROESY correlations too weak to observe.

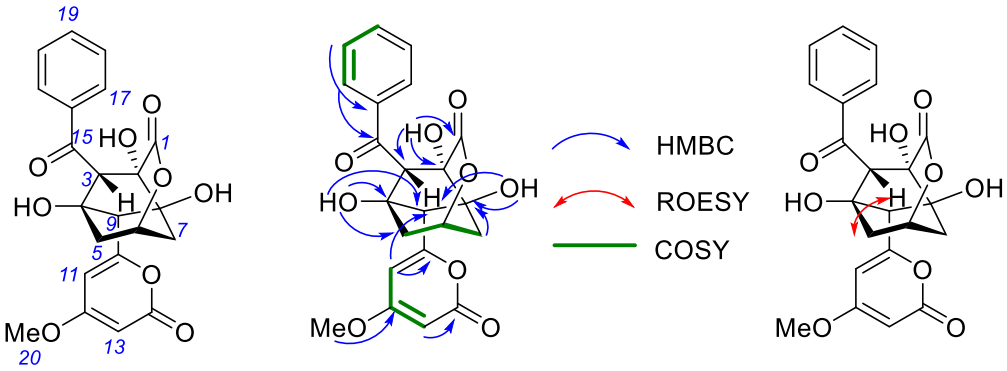


Table S5. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for 5-deoxyenterocin (**5**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		174.0			
2		79.7			
3	4.02, s	60.9	1, 2, 4, 7, 8, 9, 10, 15	17	7b, 17
4		77.0			
5a	2.24, dd (14.2, 3.3)	36.7	2, 4, 9	5b, 6	5b, 6
5b	1.64, ddd (14.2, 2.5, 2.2)		4, 6, 7, 9	5a, 6, 7b, 9	5a, 6
6	4.84, ddd (4.4, 2.5, 1.9)	72.6	1, 4, 8	5a/b, 7a/b, 4-OH	5a/b, 7a/b
7a	2.66, dd (14.8, 4.4)	40.0	3, 8	6, 7b	6, 7b
7b	2.08, ddd (14.8, 1.9, 1.7)		3, 5, 6, 8, 9	5b, 6, 7a, 9	6, 7a
8		75.8			
9	4.62, t (1.7)	54.3	3, 4, 5, 6, 8, 10, 11	5b, 5b,7b, 11	4-OH, 8-OH, 11, 13
10		161.9			
11	6.27, d (2.3)	104.5	9, 10, 12, 13	9, 13, 15	9
12		170.7			
13	5.62, d (2.3)	87.8	11, 12, 14	11, 15	9, 15
14		163.4			
15		195.0			
16		139.4			
17	7.80, d (1.4)	128.4	15, 18, 19	3, 18	3
18	7.51, dd (7.4, 1.4)	127.9	16, 17	17, 19	
19	7.60, t (7.4)	132.6	18	18	
20	3.83, s	56.3	12	11, 13	13
2-OH	5.78, s		1, 2, 3		
4-OH	5.90, s		4, 5, 9		9
8-OH	5.49, s		8, 9		7a/b, 9

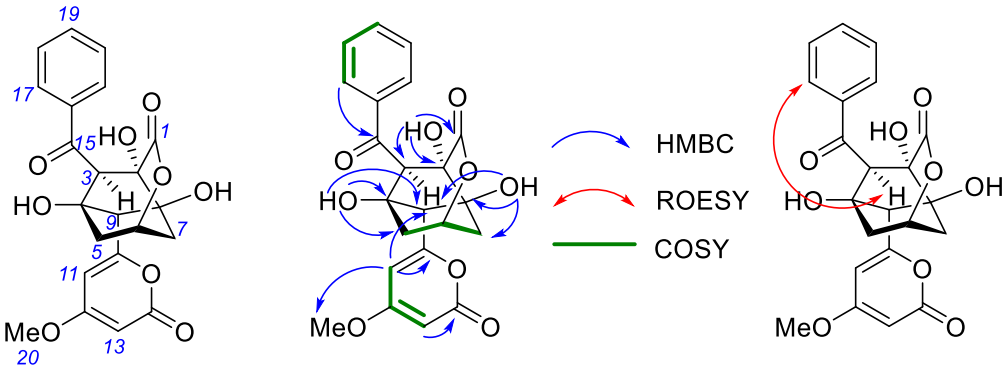


Table S6. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for 3-*epi*-5-deoxyenterocin (**6**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		171.8			
2		80.2			
3	4.16, d (1.6)	64.2	1, 2, 4, 5, 9, 15	5	17
4		75.2			
5a	2.79, dd (14.9, 1.5)	32.3	6, 7, 8, 9	5b, 6, 7b, 9	6
5b	2.40, ddd (14.9, 4.5, 1.8)		3, 8	3, 5a, 6	6
6	4.80, m	71.6		5a,/b, 7a/b	5a/b, 7a/b
7a	2.23, dd (14.0, 3.4)	35.9		6, 7b, 9	6
7b	1.56, ddd (14.0, 4.2, 1.8)		6, 8, 9	5a, 6, 7a	6
8		76.3			
9	3.43, s	59.4	3, 4, 5, 7, 8, 10, 11	5a, 7a	
10		161.3			
11	6.21, d (2.3)	104.6	9, 10, 12, 13	13, 20	
12		170.6			
13	5.63, d (2.3)	87.9		11	
14		163.3			
15		197.6			
16		138.6			
17	8.00, m	128.6	15, 18, 19	18	3
18	7.51, m	128.3		17, 19	
19	7.63, m	133.1	18	18	
20	3.82, s	56.3		11	
2-OH	5.73, s		1, 2, 3		
4-OH	6.11, s		3, 4, 5, 9		
8-OH	5.81, s		7, 8, 9		

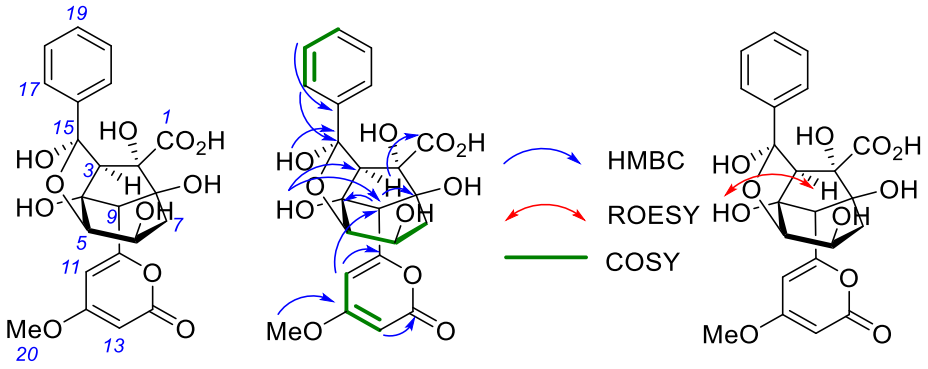


Table S7. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for enterocinic acid A (**7**) in DMSO-d_6

Position	δ_H, mult (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		174.3			
2		82.6			
3	2.79 (2.2)	61.8	1, 2, 4, 8, 16	5	4-OH, 9, 17
4		81.7			
5	4.97, dd (4.6, 2.2)	82.2	4, 6, 15	3, 6	6
6	4.34, ddd (4.6, 3.8, 2.0)	71.1	4, 8	6, 7a/b	5, 7a/b
7a	2.31 (14.8, 2.0)	33.8	5, 6, 8, 9	6, 7b, 9	6, 7b
7b	1.82 (14.8, 3.8)		1, 8, 9	6, 7a	6, 7a
8		80.2			
9	3.71, d (2.2)	51.8	4, 7, 8, 10, 11	7a	3
10		161.2			
11	6.06, d (2.2)	104.2	9, 10, 12, 13	13	
12		170.8			
13	5.64, d (2.2)	87.8	11, 12, 14	11	20
14		163.1			
15		108.4			
16		135.4			
17	7.62, m	126.7	15, 18, 19	18	3, 18
18	7.41, m[b]	128.0	16, 17, 19	18	18
19	7.41, m[b]	129.0	17, 18		
20	3.82, s	56.3	12		
2-OH	[a]				
4-OH	5.94, s		3, 4, 9		3
6-OH	[a]				
8-OH	[a]				
15-OH	4.84, m		15		
1-CO_2H	12.81, br s				

[a] not observed; [b] overlapping.

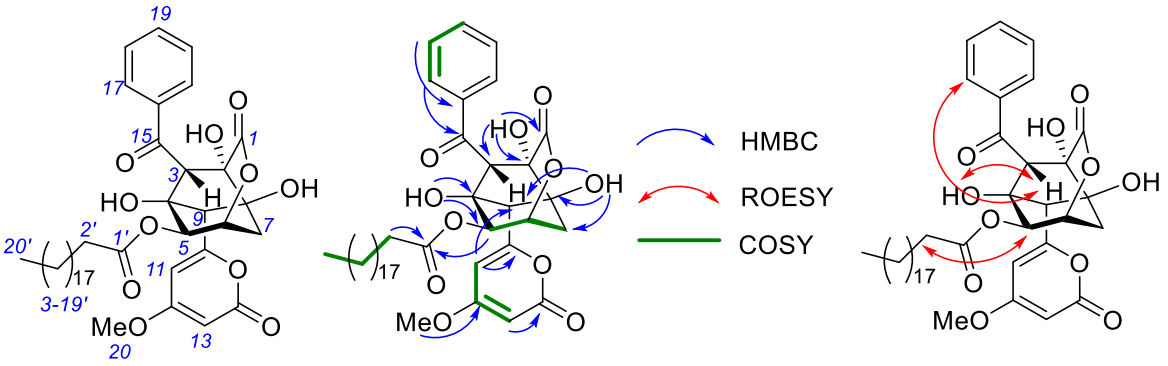


Table S8. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for 5-*O*-arachidoylenterocin (**8**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		173.2			
2		79.9			
3	4.42, s	54.0	1, 2, 4, 5, 9, 10, 15		4-OH, 17
4		76.8			
5	5.73, d (4.4)	71.7	3, 4, 6, 1’	6	6, 2’
6	4.83, m	72.4	1, 8	5, 7a/b	5, 7a/b
7a	2.36, m	35.4	2, 8	5, 7b	6
7b	1.74, ddd (14.5, 2.8, 2.8)		6	5, 7a, 9	5, 8-OH
8		76.3			
9	4.75, d (2.6)	54.8	3, 4, 5, 7, 10, 11	7b	2-OH, 4-OH, 11
10		160.6			
11	6.31, d (2.2)	105.0	9, 10, 12, 13	13	4-OH, 8-OH, 9
12		170.6			
13	5.65, d (2.2)	88.0	11, 12, 14	11	20
14		163.0			
15		193.9			
16		139.3			
17	7.78, d (8.5)	127.8	15, 17, 19	18	3, 18
18	7.53, dd (8.5, 7.4)	128.5	16, 18	17, 19	17, 19
19	7.62, t (7.4)	132.8	17	18	18
20	3.84, s	56.3	12		13
1′		172.1			
2′	2.39, m	33.5	1’, 3’, 4’-19’	3’	5
3′	1.52, m	33.5	1’, 2’, 4’-19’	2’, 4’-19’	
4′-19′	1.23, m	29.0	2’, 3’, 4’-19’	2’, 20’	
20′	0.85, t (7.1)	13.9	4’-19’	4’-19’	4’-19’
2-OH	6.08, s		1, 2, 3		9
4-OH	5.89, s		4, 5, 9		3, 9, 11
8-OH	6.07, s		7, 8, 9		7b, 11

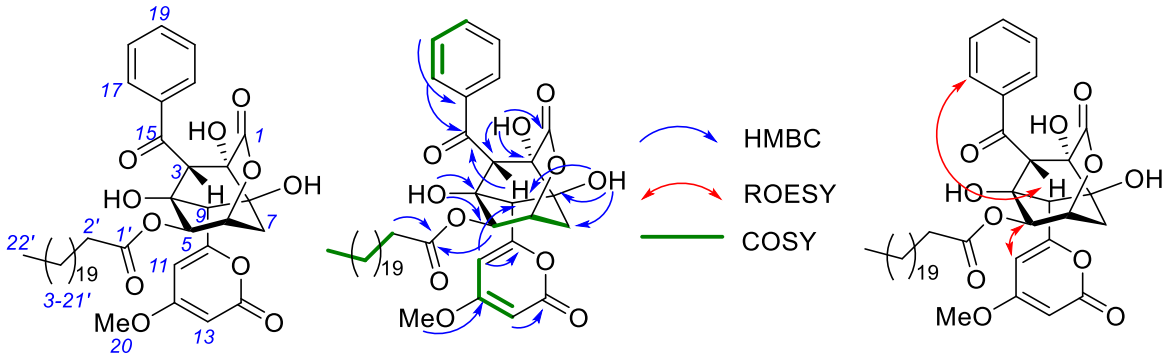


Table S9. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for 5-*O*-behenoylenterocin (**9**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		173.2			
2		79.9			
3	4.42, s	54.0	1, 2, 4, 5, 9, 15		17
4		76.8			
5	5.73, d (4.5)	71.7	3, 4, 2’	6	6, 7a
6	4.83, m	72.3	1, 4	5, 7a/b	5, 7a/b
7a	2.39, m	35.4	2, 8	6, 7b	5, 6
7b	1.74, ddd (14.5, 3.0, 2.8)		5, 8, 9	6, 7a, 9	6
8		76.3			
9	4.75, d (2.5)	54.8	4, 5, 7, 10, 11	7b	2-OH, 4-OH, 11
10		160.6			
11	6.31, d (2.2)	105.0	9, 10, 12, 13	13	9
12		170.6			
13	5.65, d (2.2)	88.0	11, 12, 14	11	20
14		163.0			
15		193.9			
16		139.3			
17	7.78, d (7.3)	127.7	15, 17, 19	18	3
18	7.30, dd (7.4, 7.3)	128.5	16, 18	17, 19	
19	7.62, t (7.4)	132.8	17	18	
20	3.84, s	56.3	12		13
1′		172.0			
2′	2.36, m	33.5	1’, 3’, 4’-21’	3’	
3′	1.53, m	24.4	1’, 3’, 4’-21’	2’, 4’-21’	4’-21’
4′-21′	1.24, m	30.0	3’, 4’-21’, 22	3’, 22’	
22′	0.85, t (6.9)	13.9	4’-21’	4’-21’	4’-21’
2-OH	6.08, s		1, 2, 3		9
4-OH	5.88, s		3, 4, 5		3, 9
8-OH	6.07, s		7, 8, 9		

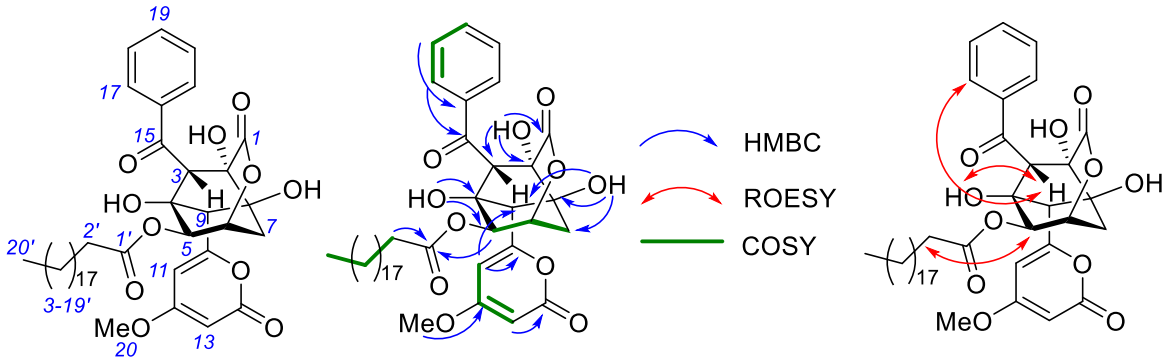


Table S10. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for 5-*O*-palmitoylenterocin (**10**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		173.2			
2		79.9			
3	4.41, s	54.0	1, 2, 4, 5, 8, 9, 15		17
4		76.8			
5	5.73, d (4.5)	71.7	3, 4, 6, 1’	6	4-OH, 6, 7a, 11
6	4.83, m	72.4	4	5, 7a/b	5
7a	2.39, m	35.4	2, 8, 9	6, 7b	5, 8-OH
7b	1.74, ddd (14.8, 2.8, 2.6)			6, 7a, 9	8-OH, 2’
8		76.3			
9	4.75, d (2.6)	54.8	4, 5, 7, 10, 11	7a	2-OH, 4-OH, 8-OH, 11
10		160.6			
11	6.31, d (2.3)	105.0	9, 10, 12, 13	13	5, 8-OH, 9, 20
12		170.6			
13	5.65, d (2.3)	88.0	11, 12	11	20
14		163.1			
15		193.9			
16		139.3			
17	7.78, d (7.2)	127.8	15, 19	18	3
18	7.53, dd (7.5, 7.2)	128.5	16, 19	17, 19	
19	7.63, t (7.5)	132.8	17	18	
20	3.84, s	56.3	12		11, 13
1′		172.1			
2′	2.39, m	33.5	1’, 3’, 4’-15’	3’	7b, 3’-15’
3′	1.53, m	24.4	1’, 2’, 4’-15’	2’, 4’-14’	
4′-15′	1.23, m	29.0	2’, 16’	2’, 16’	16’
16′	0.85, t (7.0)	13.9	2’-15’	3’-15’	3’-15’
2-OH	6.10, s		1, 2, 3		9
4-OH	5.89, s		4, 5, 9		5, 9
8-OH	6.08, s		7, 8, 9		7a/b, 9, 11

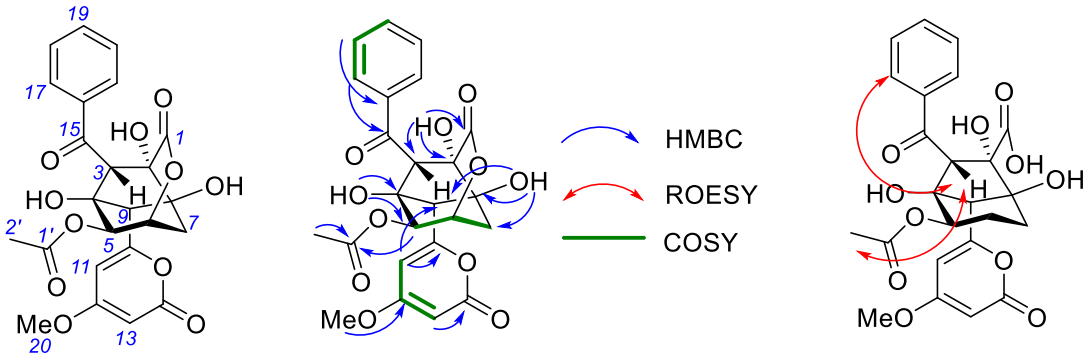


Table S11. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for 5-*O*-acetylenterocin (**11**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		173.3			
2		79.9			
3	4.40, s	54.1	1, 2, 4, 5, 8, 9, 15		4-OH, 5, 17, 2’
4		76.7			
5	5.73, d (4.4)	71.8	3, 4, 6, 1’	6, 9	3, 6, 7a
6	4.83 ddd (4.4, 3.0, 2.9)	72.4	1, 3, 5	5, 7a/b	5, 7a/b
7a	2.38, dd (14.7, 3.0)	35.4	2, 8, 9	6, 7b	5, 8-OH, 11
7b	1.74, ddd (14.7, 2.9, 2.6)		6, 8, 9	6, 7a, 9	2-OH, 5, 8-OH
8		76.3			
9	4.77, d (2.6)	54.7	4, 5, 8, 10, 11	5, 7b, 11	2-OH, 4-OH, 8-OH, 11, 17
10		160.6			
11	6.31, d (2.3)	105.0	9, 10, 12, 13	9, 13, 20	7a, 9, 20
12		170.6			
13	5.65, d (2.3)	88.0	11, 12, 14	11, 20	20
14		163.1			
15		193.9			
16		139.3			
17	7.79, d (7.3)	128.6	15, 18, 19	18, 19	2-OH, 3, 4-OH, 9
18	7.54, dd (7.4, 7.3)	127.8	17, 19	17, 19	
19	7.62, t (7.4)	132.8	18	17, 18	
20	3.84, s	56.3	12	11, 13	11, 13
1′		169.8			
2′	2.11, s	20.9	1’		3, 4-OH
2-OH	6.11, s		1, 2, 3, 8		7b, 9, 17
4-OH	5.93, s		4, 5, 9		3, 9, 18, 2’
8-OH	6.08, s		7, 8, 9		7a/b, 9

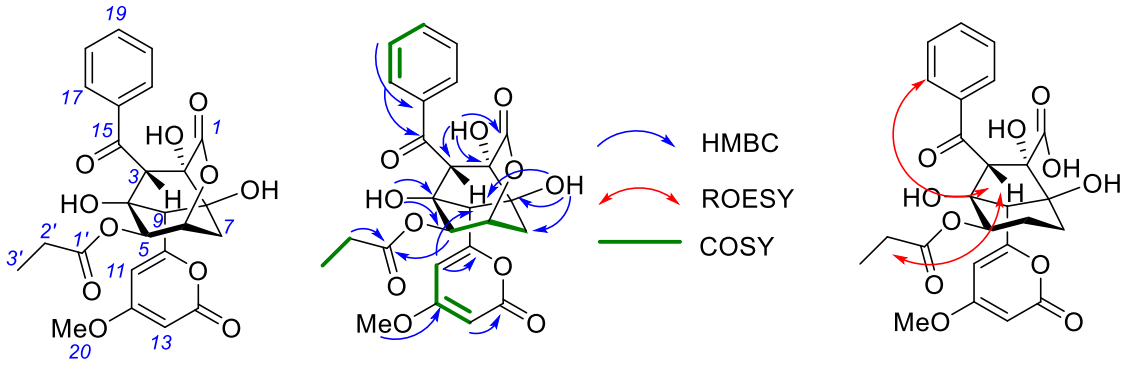


Table S12. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for 5-*O*-propionylenterocin (**12**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		173.3			
2		79.9			
3	4.42, s	54.0	1, 2, 4, 5, 8, 9, 15		4-OH, 17, 2’
4		76.8			
5	5.75, d (4.5)	71.7	3, 4, 15, 1’	6	4-OH, 6, 11
6	4.83, ddd (4.5, 3.1, 2.8)	72.4	1, 5, 8	5, 7a/b	5, 7a/b
7a	2.83, dd (14.5, 3.1)	35.4	2, 8, 9	6, 7b	5, 6, 7b, 8-OH, 11
7b	1.73, ddd (14.5, 2.8, 2.6)		5, 6, 8, 9	6, 7a, 9	6, 7a, 8-OH
8		76.3			
9	4.76, d (2.6)	54.7	4, 5, 7, 8, 10	7b, 11	4-OH, 8-OH, 11
10		160.6			
11	6.32, d (2.3)	105.0	10, 12, 13	9, 13	5, 7a, 8-OH, 9, 20
12		170.6			
13	5.65, d (2.3)	88.0	11, 12, 14	11, 20	20
14		163.1			
15		193.9			
16		139.3			
17	7.78, d (7.2)	127.8	15, 17, 19	18, 19	3
18	7.54, dd (7.4, 7.2)	128.6	16, 17	17, 19	
19	7.63, t (7.4)	132.8	18	17, 18	
20	3.84, s	56.3	12	13	2, 11
1′		172.9			
2′	2.43, q (7.5)	26.8	1’, 3’	3’	3, 4-OH, 3’
3′	1.04, t (7.5)	8.8	1’, 2’	2’	2’
2-OH	6.11, s		1, 2, 3		
4-OH	5.91, s		4, 5, 9		3, 5, 8, 2’
8-OH	6.09, s		7, 8, 9		7a/b, 9, 11

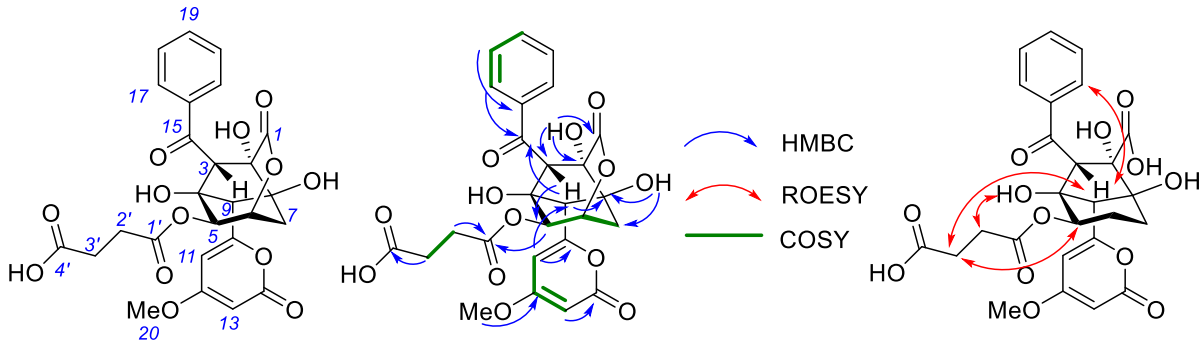


Table S13. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for 5-*O*-carboxypropionylenterocin (**13**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		173.2			
2		79.9			
3	4.42, s	53.9	1, 2, 5, 8, 9, 15	9	17, 3’
4		76.8			
5	5.75, d (4.4)	72.0	3, 4	6, 7a	7a, 11, 3’
6	4.80, ddd (4.4, 3.0, 2.8)	72.4		5	5, 7a/b, 11
7a	2.37, dd (14.7, 3.0)	35.5	2, 8	6, 7b	5, 6
7b	1.74, ddd (14.7, 8.2, 2.6)		5, 8, 9	7a, 9	6
8		76.3			
9	4.76, d (2.6)	54.7	5, 7, 8, 10, 11	3, 7b	11
10		160.6			
11	6.31, d (2.2)	105.0	9, 10, 12, 13	13	5, 6, 9, 20
12		170.5			
13	5.65, d (2.2)	87.9	11, 12, 14	11	11, 20
14		163.0			
15		193.8			
16		139.3			
17	7.79, d (7.9)	127.8	15, 19	18	3
18	7.54, dd (7.9, 7.3)	128.5	16, 17	17, 19	
19	7.63, t (7.3)	132.7	18	18	
20	3.84, s	56.3	12		11, 13
1′		173.0			
2′	2.47, m	28.9	1’, 3’, 4’	3’	4-OH
3′	2.63, m	28.7	1’, 2’, 4’	2’	3, 4-OH, 5
4′		171.6			
2-OH	6.07[a], br s		1, 2, 3		
4-OH	5.97, br s				2’-3’
8-OH	6.08[a], br s		7, 8		
4′-COOH	12.23, br s				

[a] Assignments interchangeable

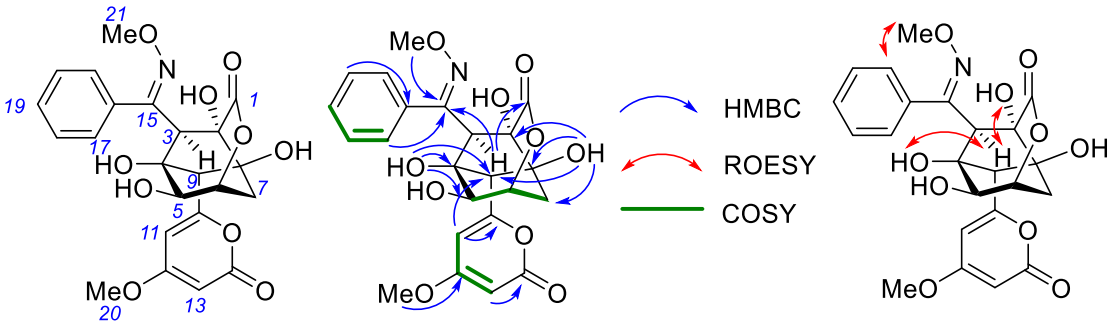


Table S14. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**) in DMSO-d_6

Position	δ_H, mult. (*J* in Hz)	δ_C	^{1}H-^{13}C HMBC	COSY	ROESY
1		173.9			
2		80.0			
3	3.64, s	55.4	1, 2, 4, 5, 8, 9, 10, 15, 16		2-OH, 4-OH, 17
4		78.7			
5	4.40, dd (4.6, 4.6)	69.1	3, 4, 6, 15	6	5-OH, 6, 7a
6	4.59, ddd (4.6, 3.0, 2.8)	75.2	1, 3, 5, 7	5, 7a/b	5, 7a/b
7a	2.37, dd (14.5, 3.0)	35.5	2, 8, 9	6, 7b	5, 6, 7b
7b	1.67, ddd (14.5, 2.8, 2.5)		5, 8, 9	6, 7a	6, 7a
8		75.7			
9	4.25, br s	55.6	5		
10		161.4			
11	5.94, br s	104.6	10, 13	13	
12		170.5			
13	5.61, d (2.3)	87.7	11, 12, 14	11	20
14		163.3			
15		153.1			
16		136.0			
17	7.41, d (7.9)	128.4	15, 18	18	3, 21
18	7.35, dd (7.9, 7.4)	127.9	16, 19	17, 19	
19	7.30, t (7.4)	127.4	17, 18	18	
20	3.81, s	56.2	11, 12, 13		13
21	3.80, s	61.6	15		17
2-OH	5.57[a]				3
4-OH	5.29, s		4, 5, 9		3
5-OH	5.57[a]				
8-OH	5.71, s		2, 7, 8, 9		

[a] Overlapping

B. NMR Spectra

Figures S1-6. NMR spectra of enterocin (**1**)

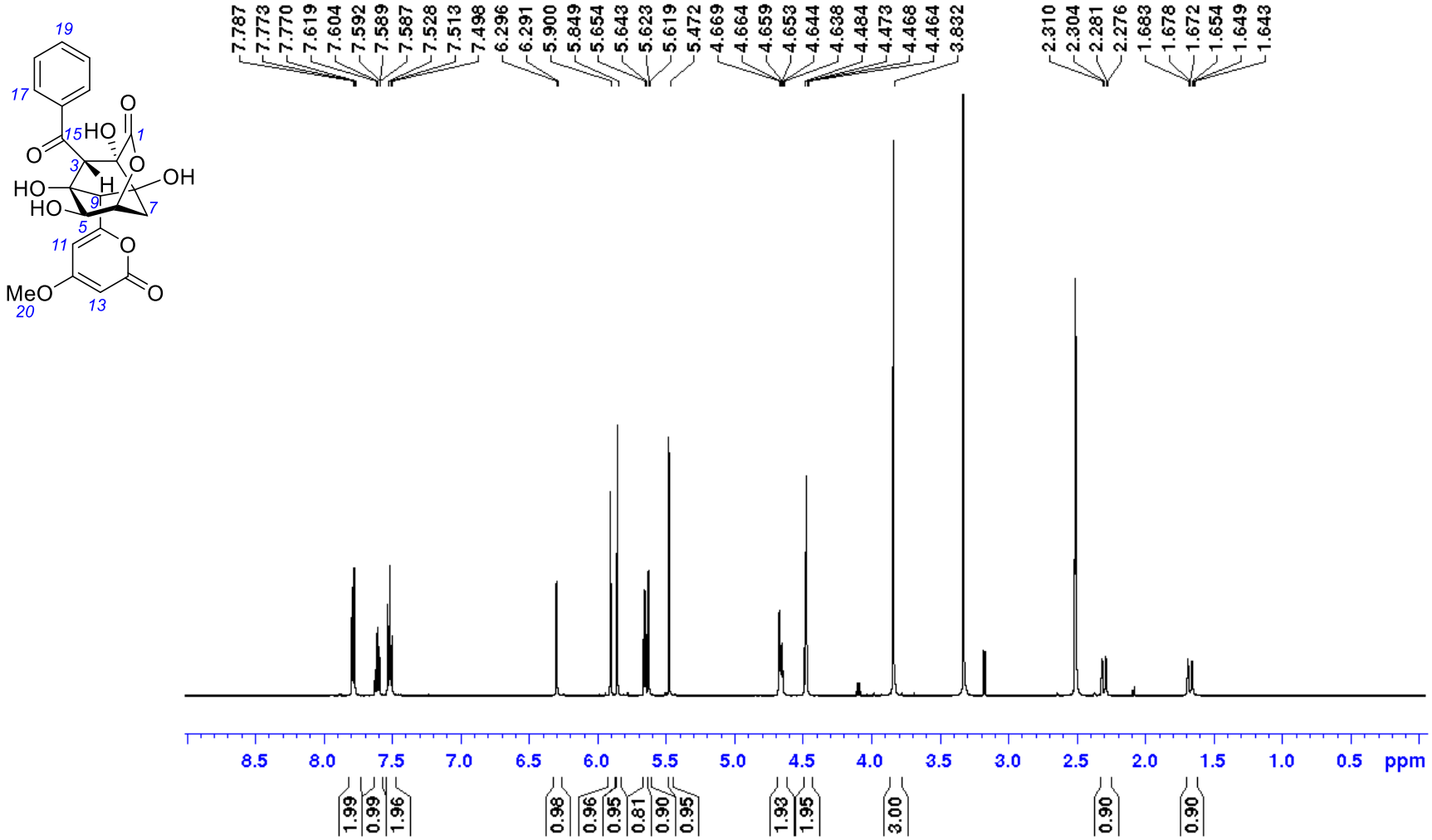


Figure S1. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of enterocin (**1**)

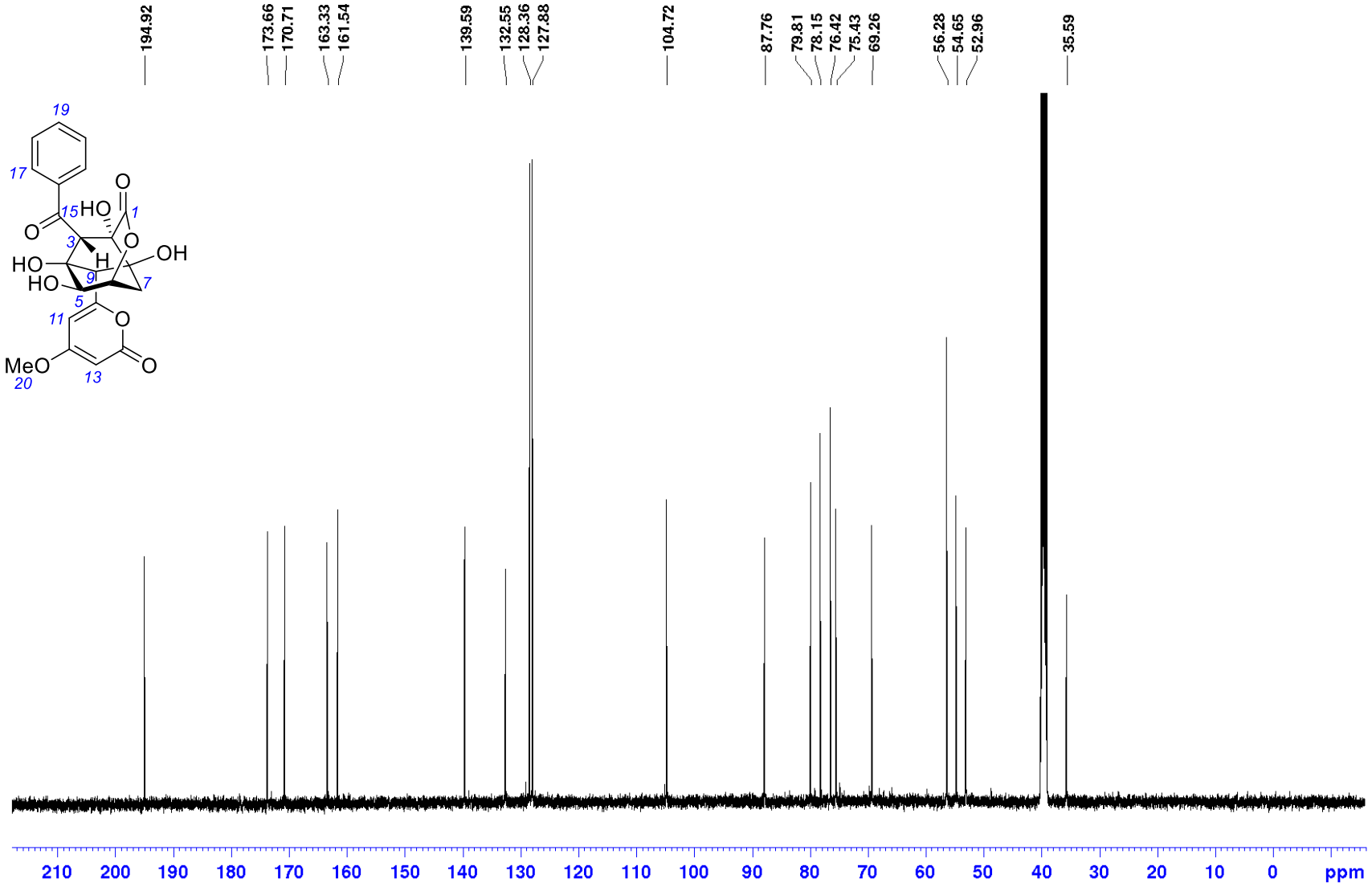


Figure S2. ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of enterocin (**1**)

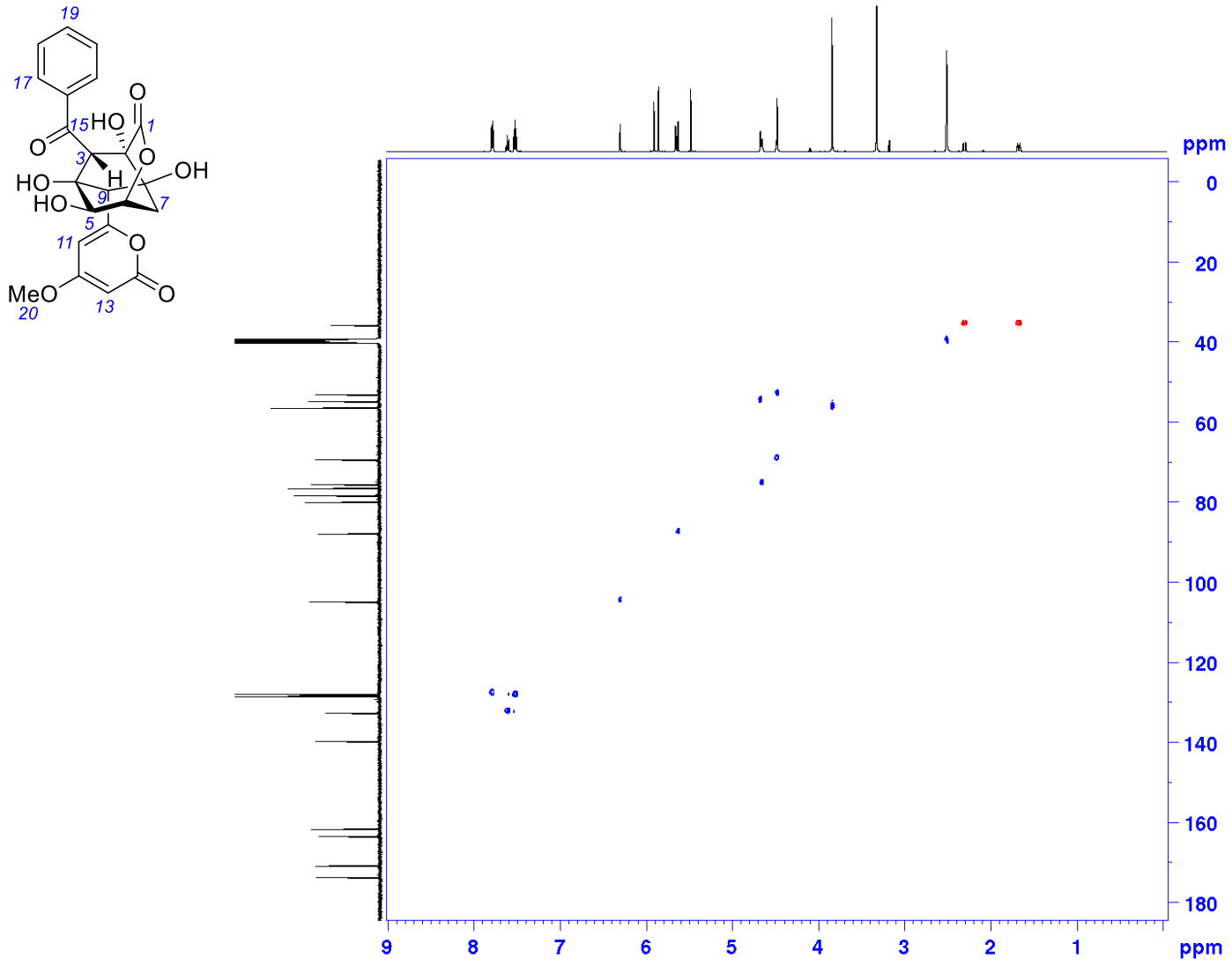


Figure S3. ^{1}H-^{13}C HSQC spectrum (500 MHz, DMSO-d_6) of enterocin (**1**)

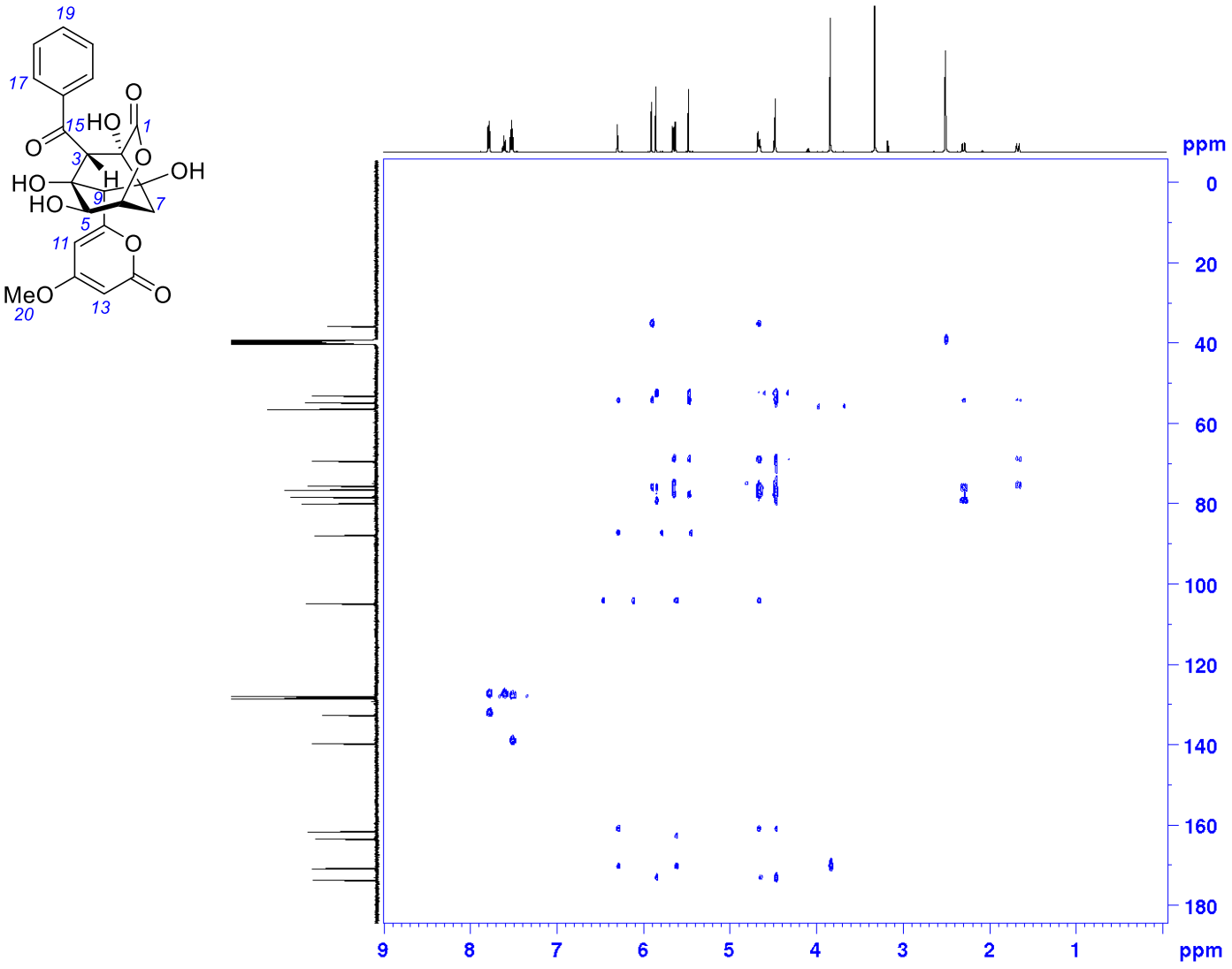


Figure S4. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz, DMSO-d_6) of enterocin (**1**)

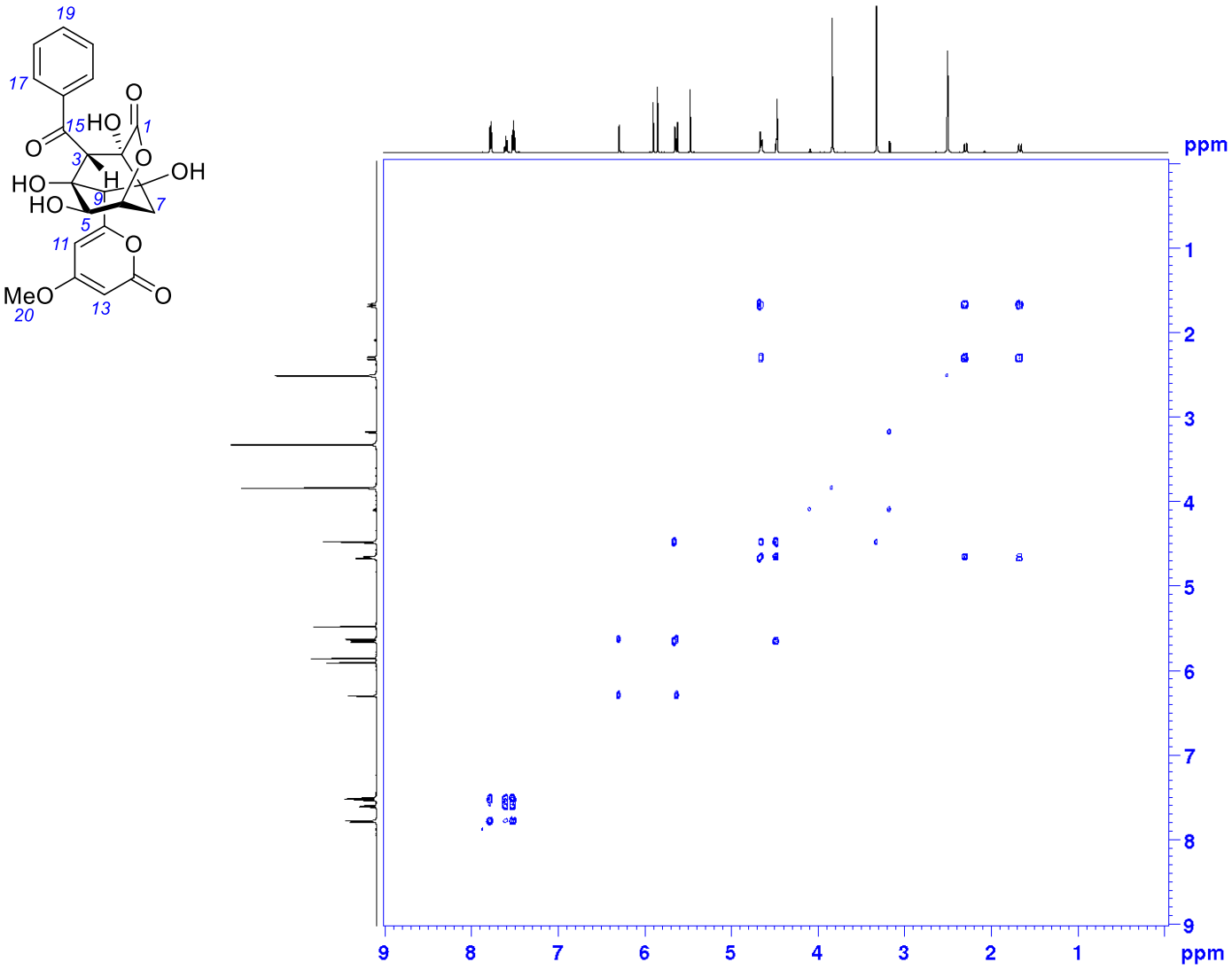


Figure S5. ^{1}H-^{1}H COSY spectrum (500 MHz, DMSO-*d*$_6$) of enterocin (**1**)

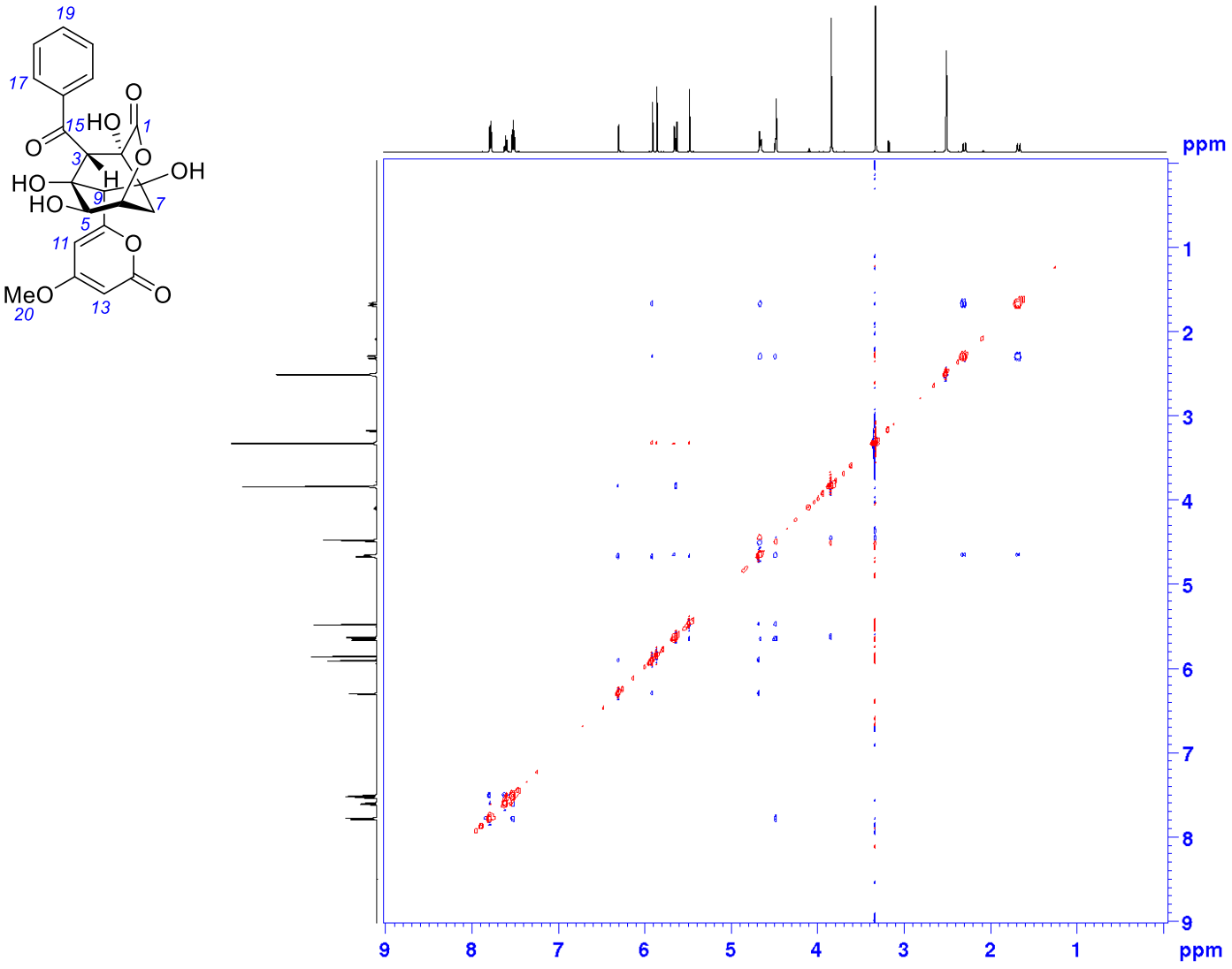
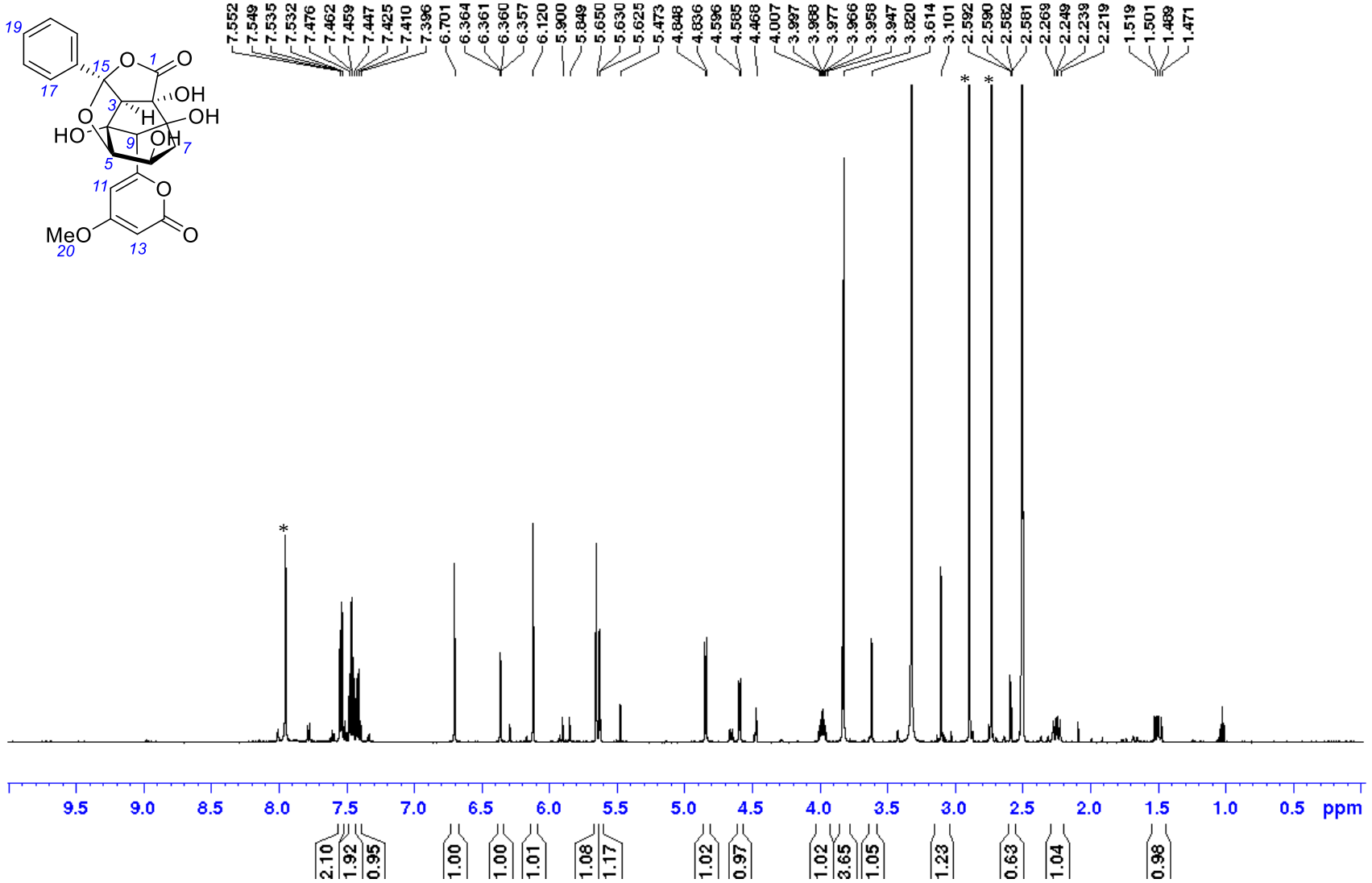


Figure S6. ^{1}H-^{1}H ROESY spectrum (500 MHz, DMSO-d_6) of enterocin (**1**)

Figure S7-14. NMR spectra of isoenterocin A (**2**)



* - Residual DMF

Figure S7. ^{1}H NMR spectrum (500 MHz, DMSO-*d*$_6$) of isoenterocin A (**2**)

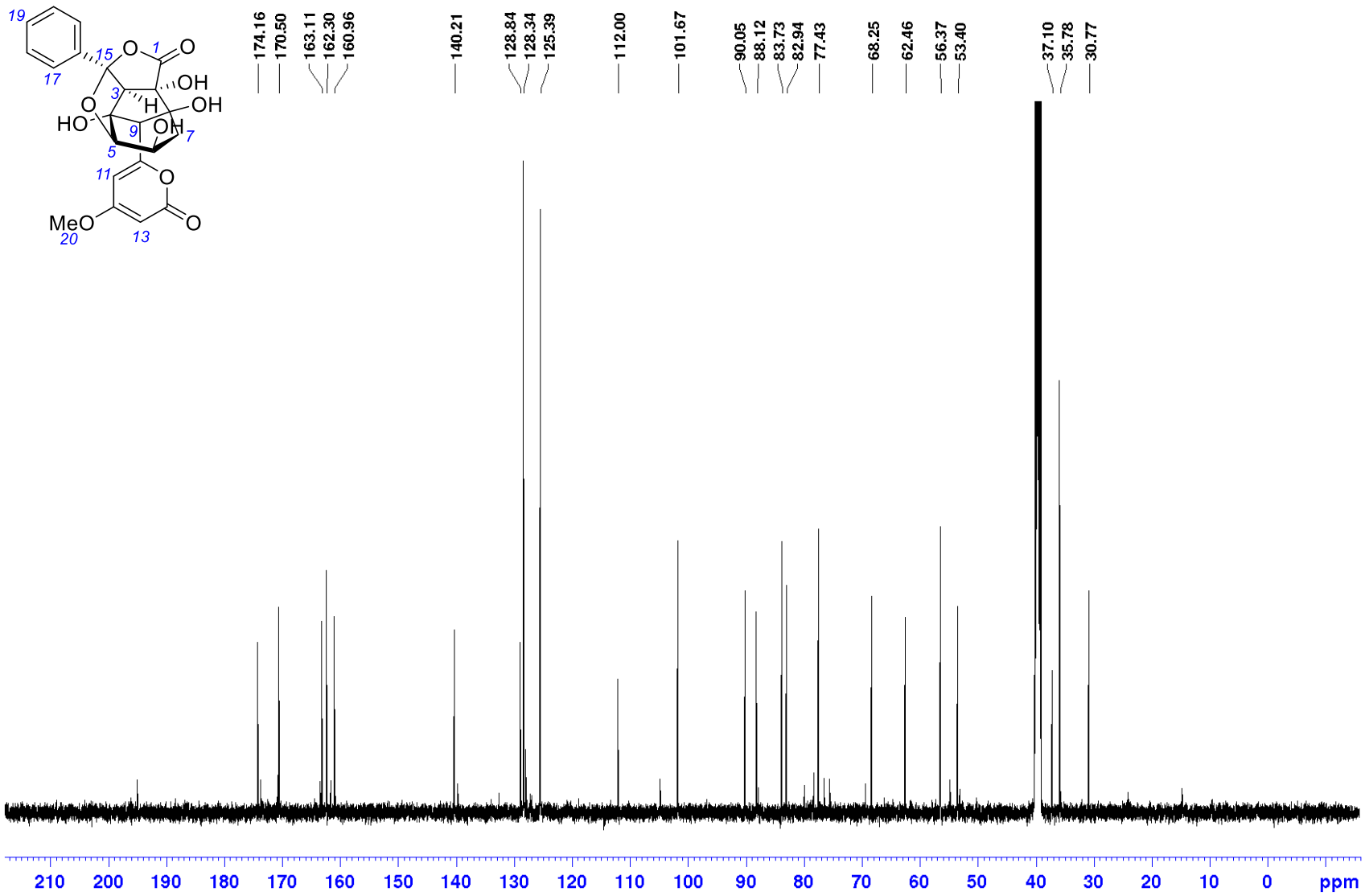


Figure S8. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of isoenterocin A (**2**)

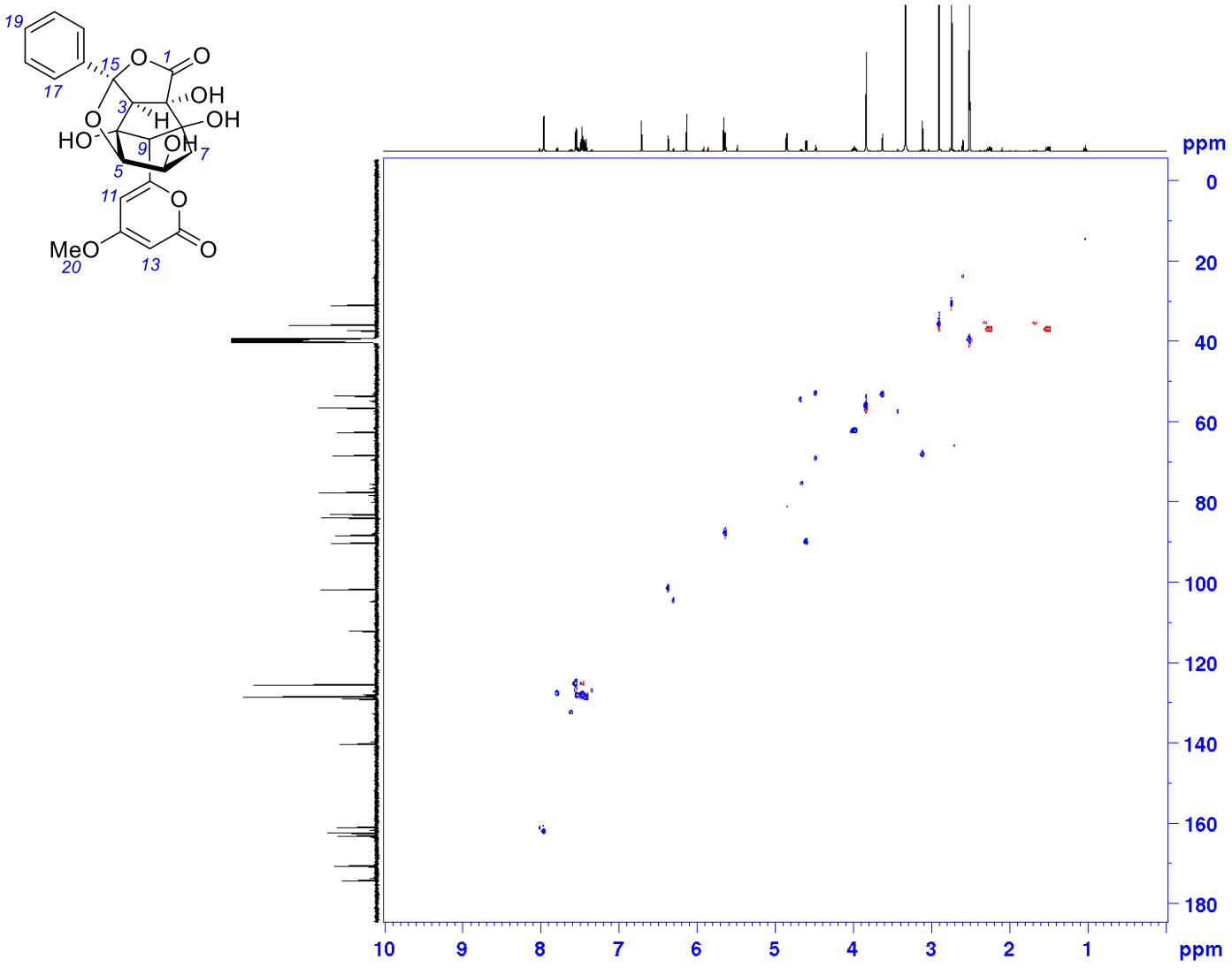


Figure S9. ^{1}H-^{13}C HSQC spectrum (500 MHz, DMSO-d_6) of isoenterocin A (**2**)

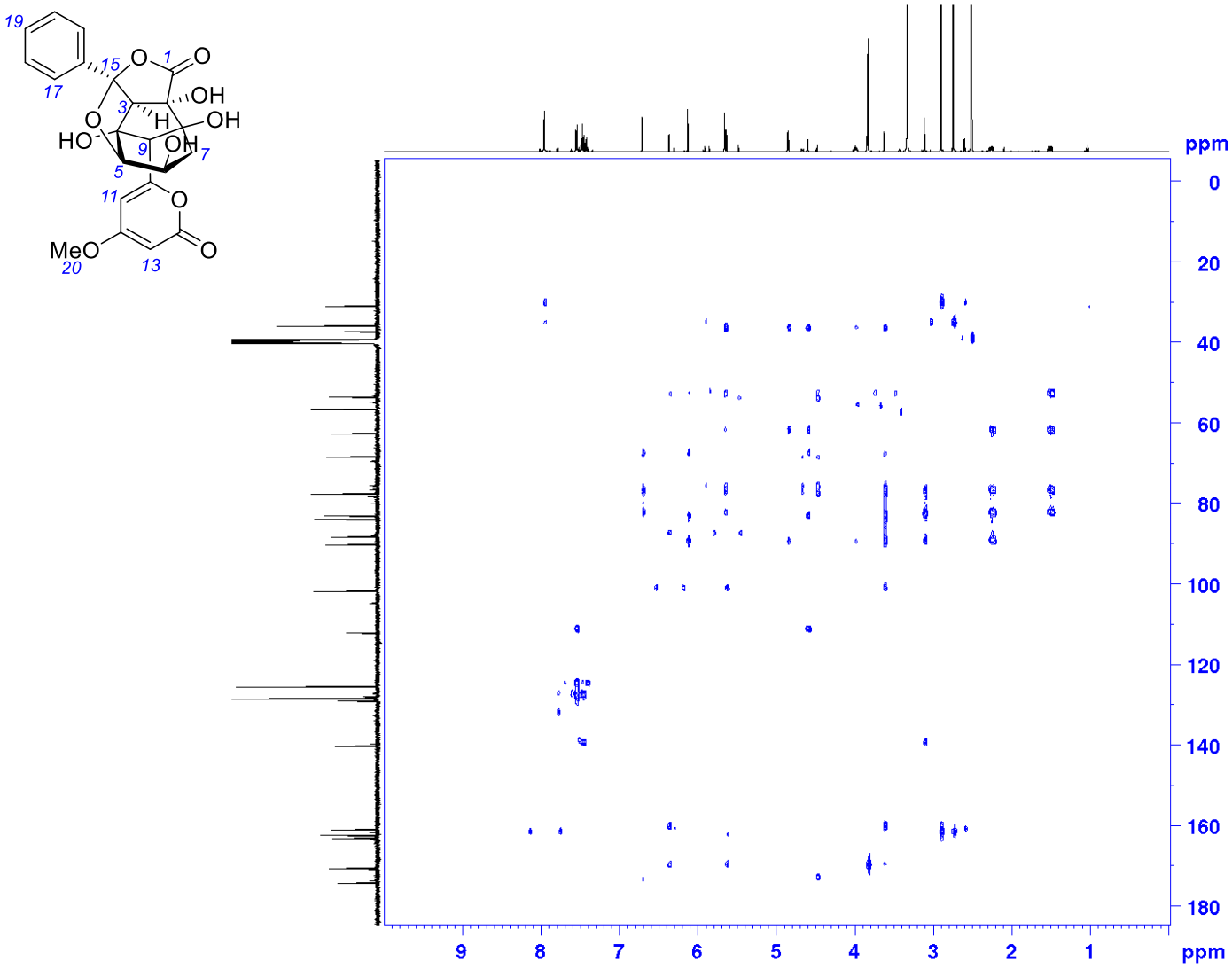


Figure S10. ^{1}H-^{13}C HMBC spectrum (500 MHz, DMSO-d_6) of isoenterocin A (**2**)

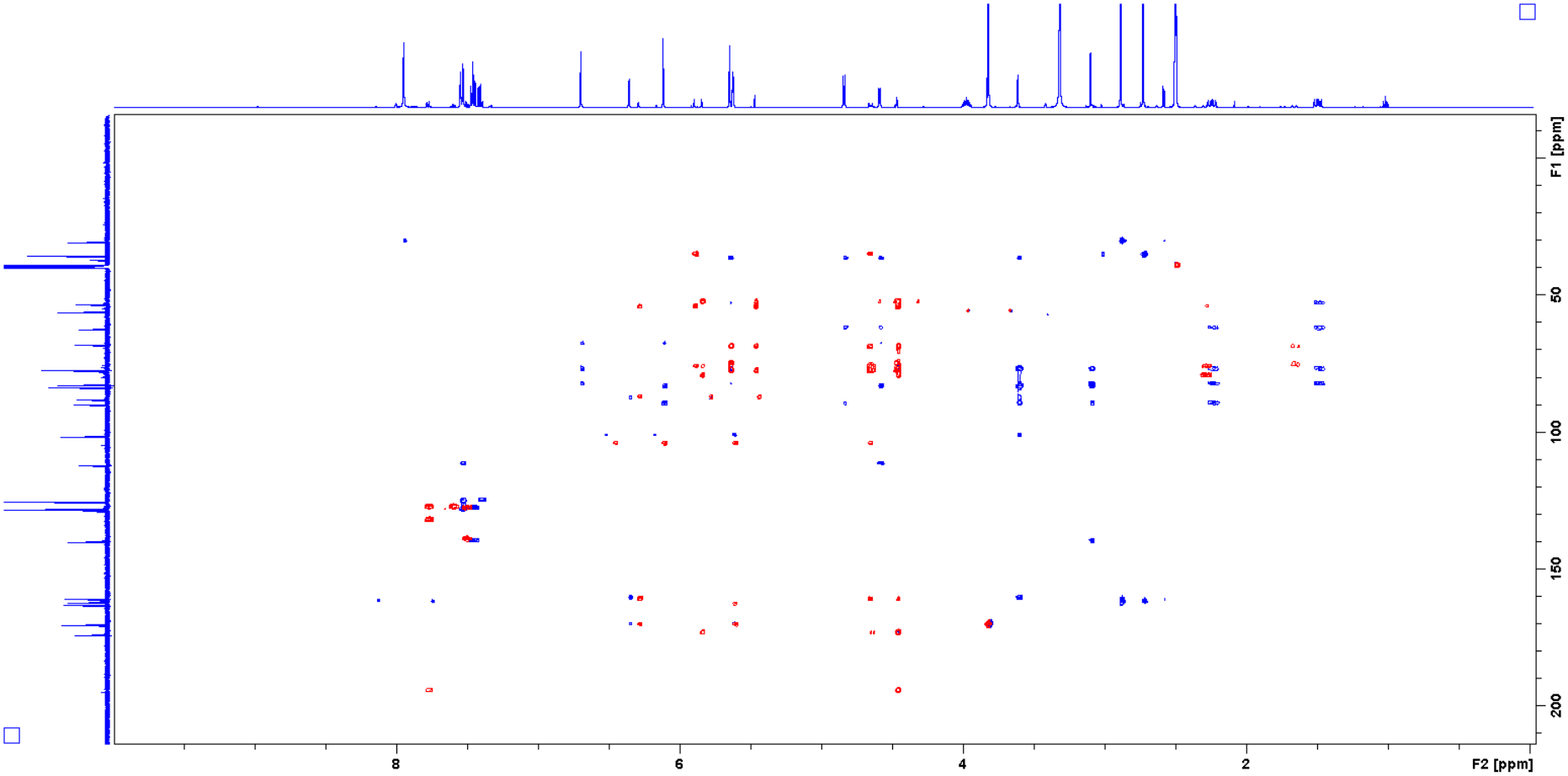


Figure S11. Overlay of ^{1}H-^{13}C HMBC spectrum of isoenterocin A (**2**) (blue) compared to enterocin (**1**) (red).

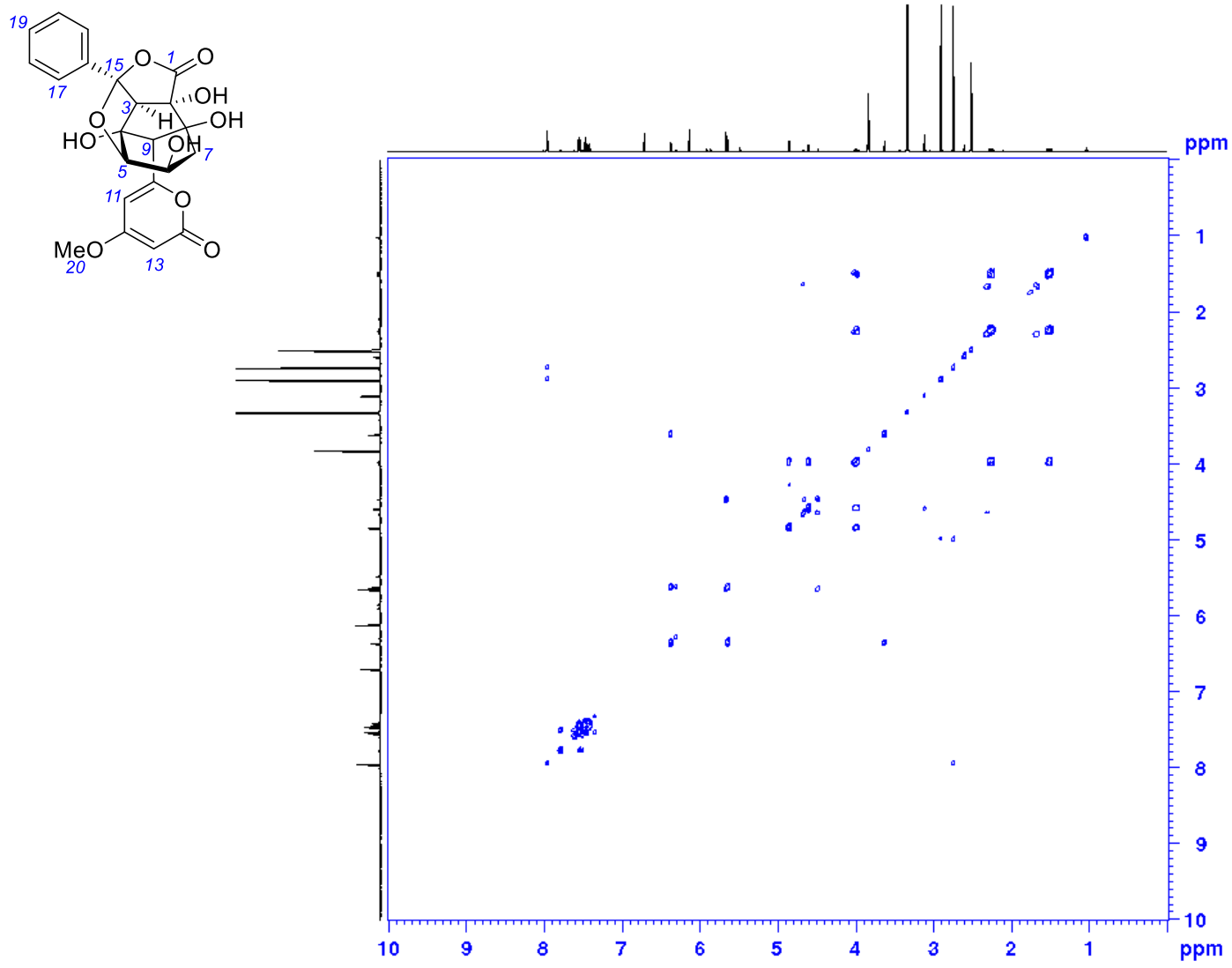


Figure S12. ^{1}H-^{1}H COSY spectrum (500 MHz, DMSO-*d*$_6$) of isoenterocin A (**2**)

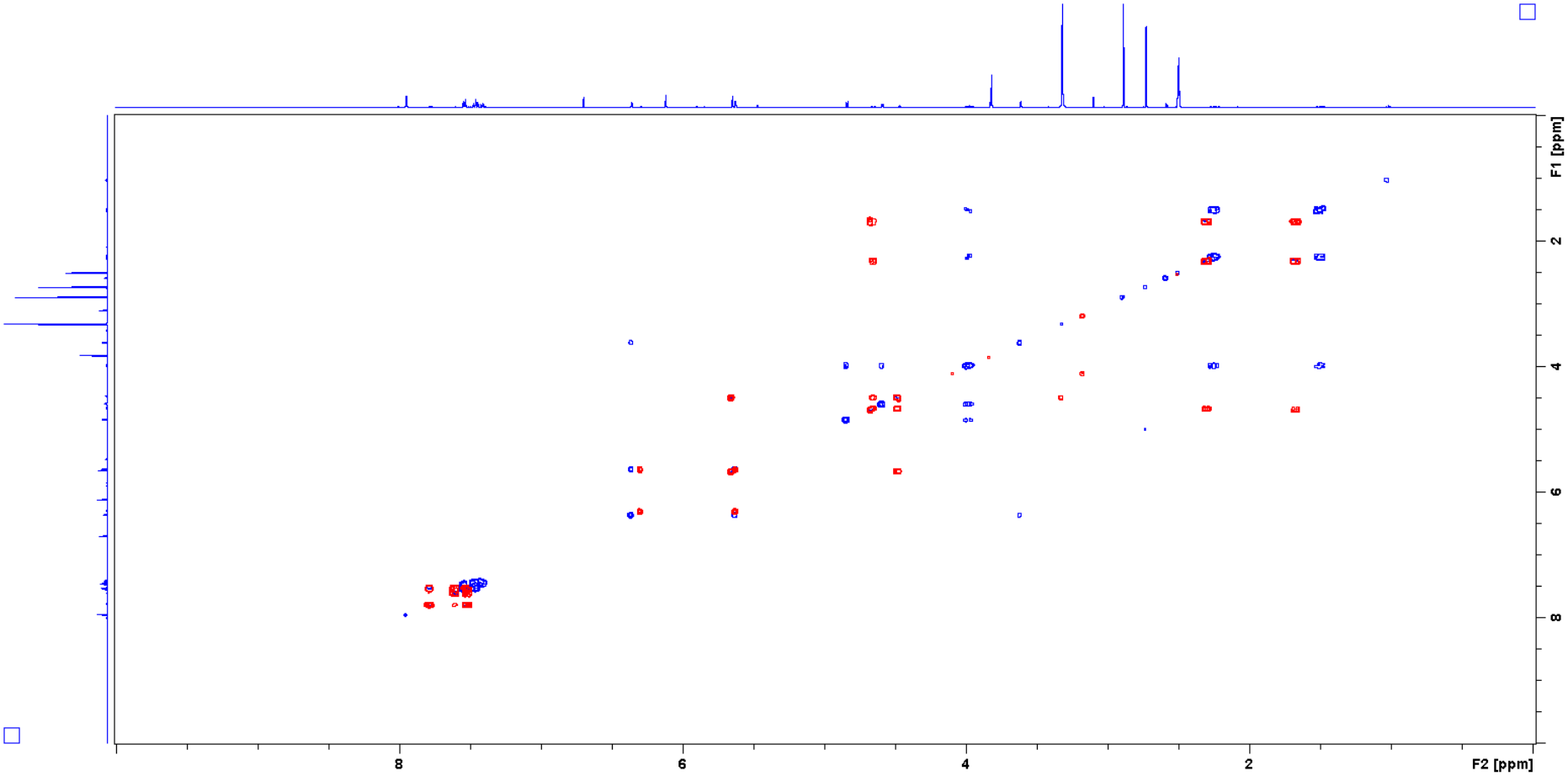


Figure S13. Overlay of ^{1}H-^{1}H COSY spectrum of isoenterocin A (**2**) (blue) compared to enterocin (**1**) (red).

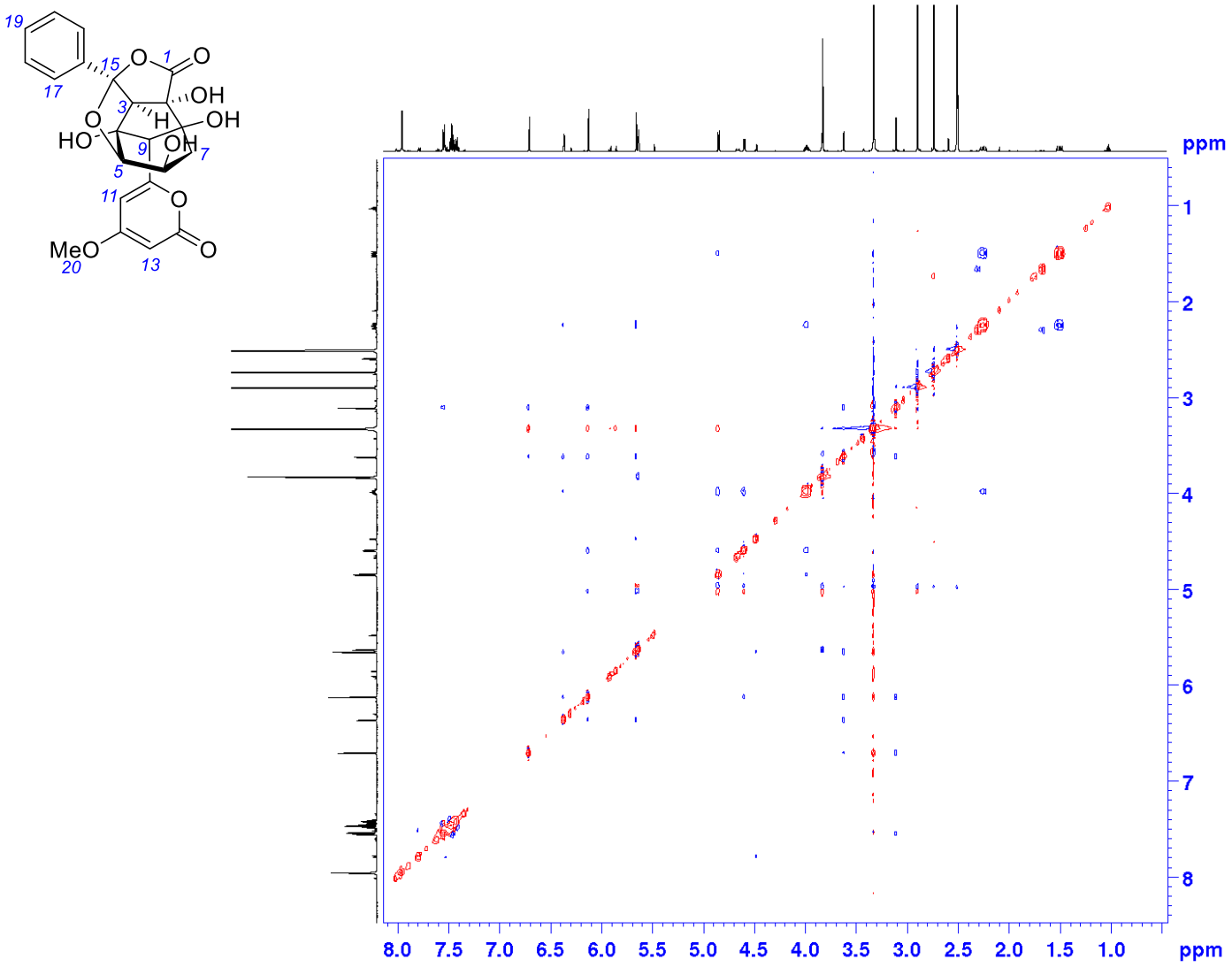


Figure S14. ^{1}H-^{1}H ROESY spectrum (500 MHz, DMSO-d_6) of isoenterocin A (**2**)

Figure S15-21. NMR spectra of isoenterocin B (**3**)

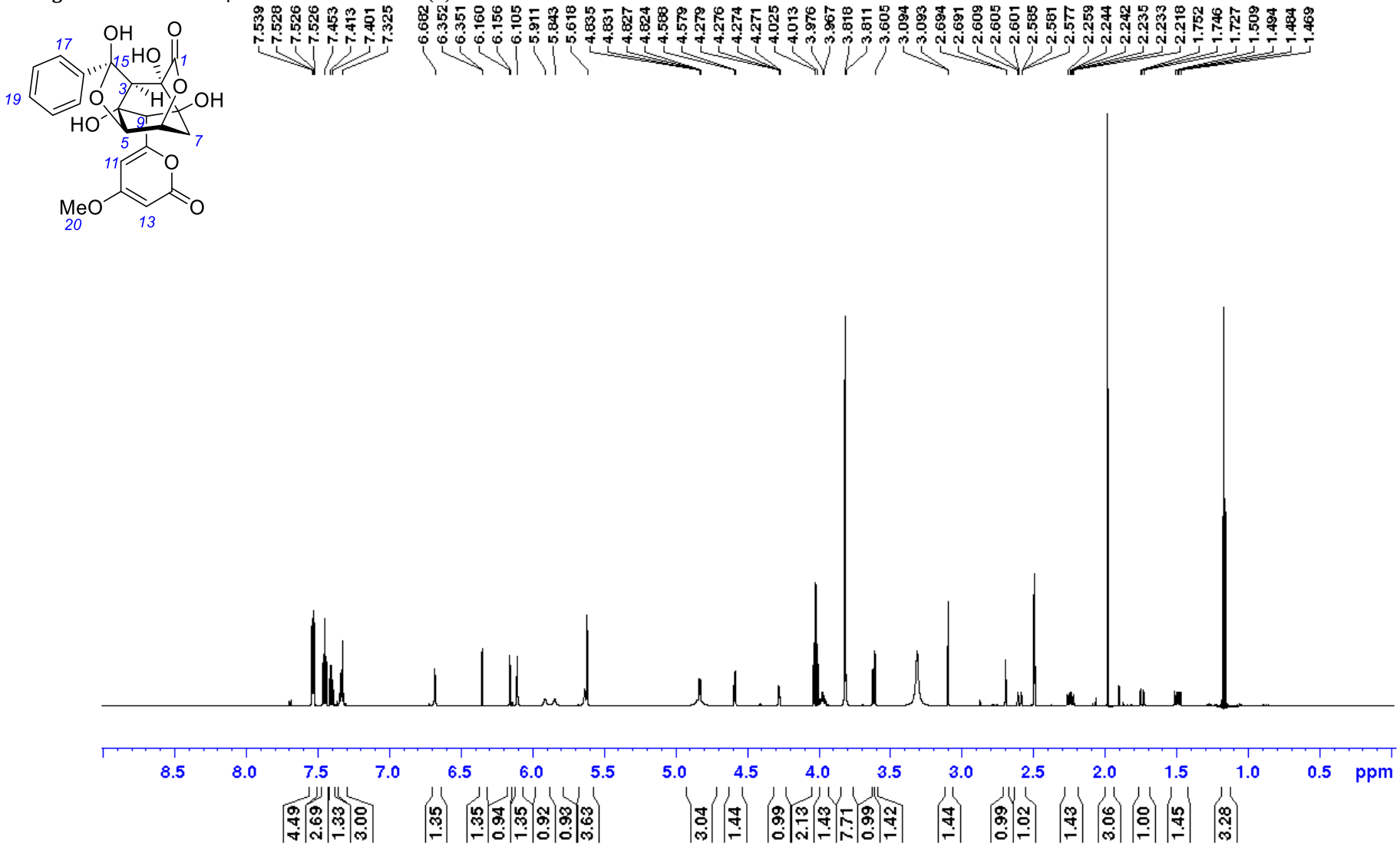


Figure S15. ^{1}H NMR spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of isoenterocin A (**2**) (major) and isoenterocin B (**3**) (minor)

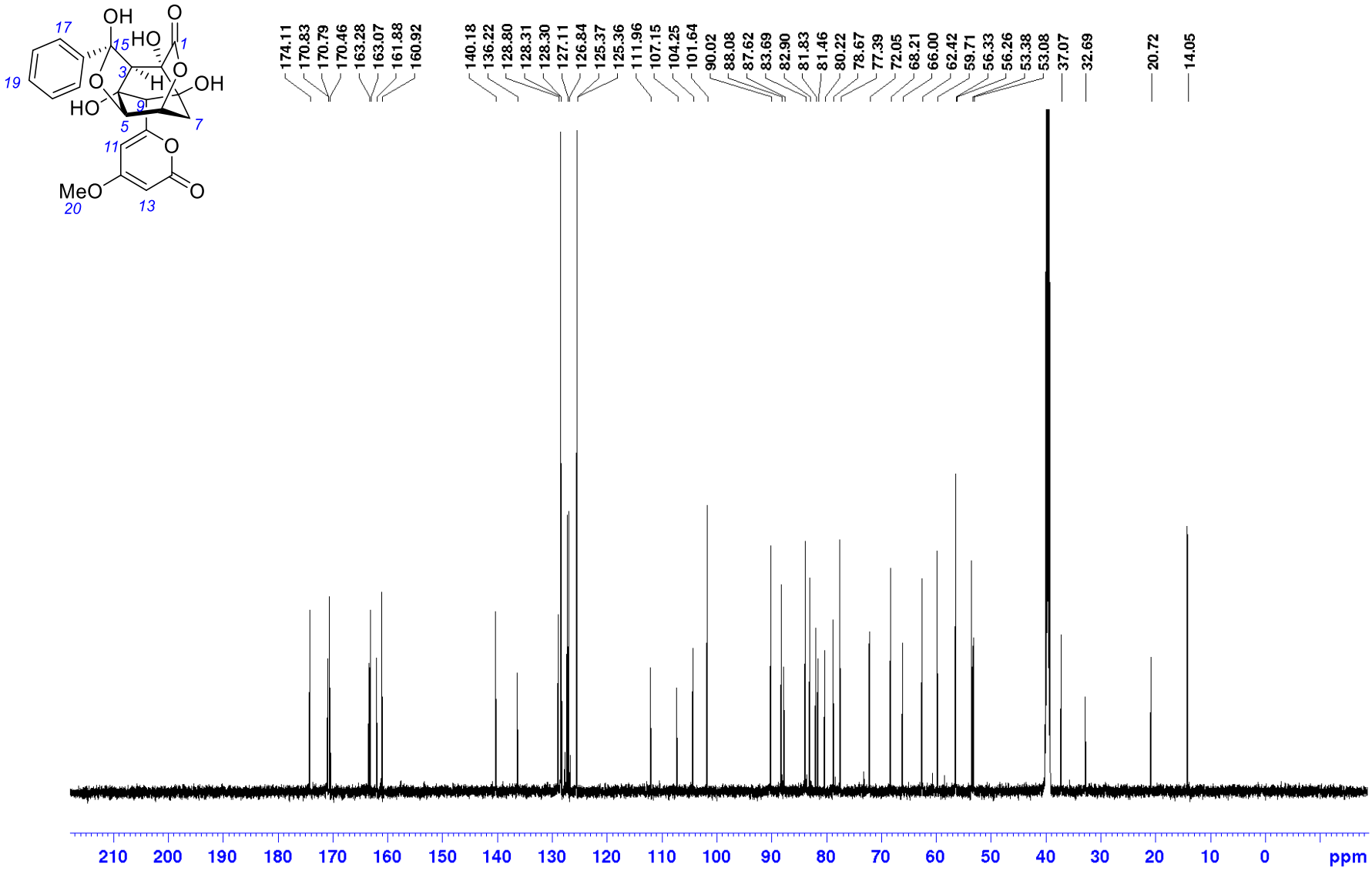


Figure S16. ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of a mixture of isoenterocin A (**2**) (major) and isoenterocin B (**3**) (minor)

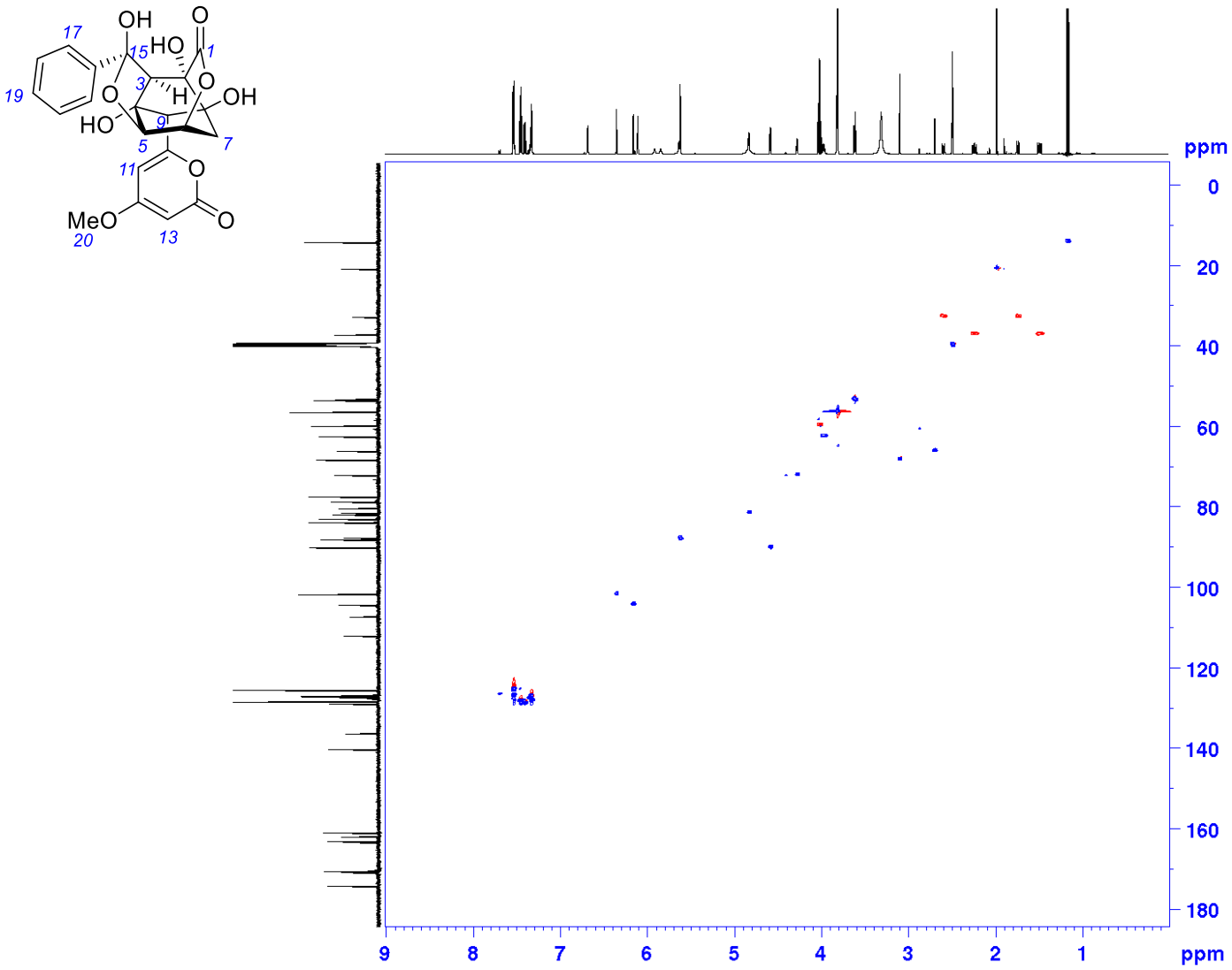


Figure S17. ^{1}H-^{13}C HSQC spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of isoenterocin A (**2**) (major) and isoenterocin B (**3**) (minor)

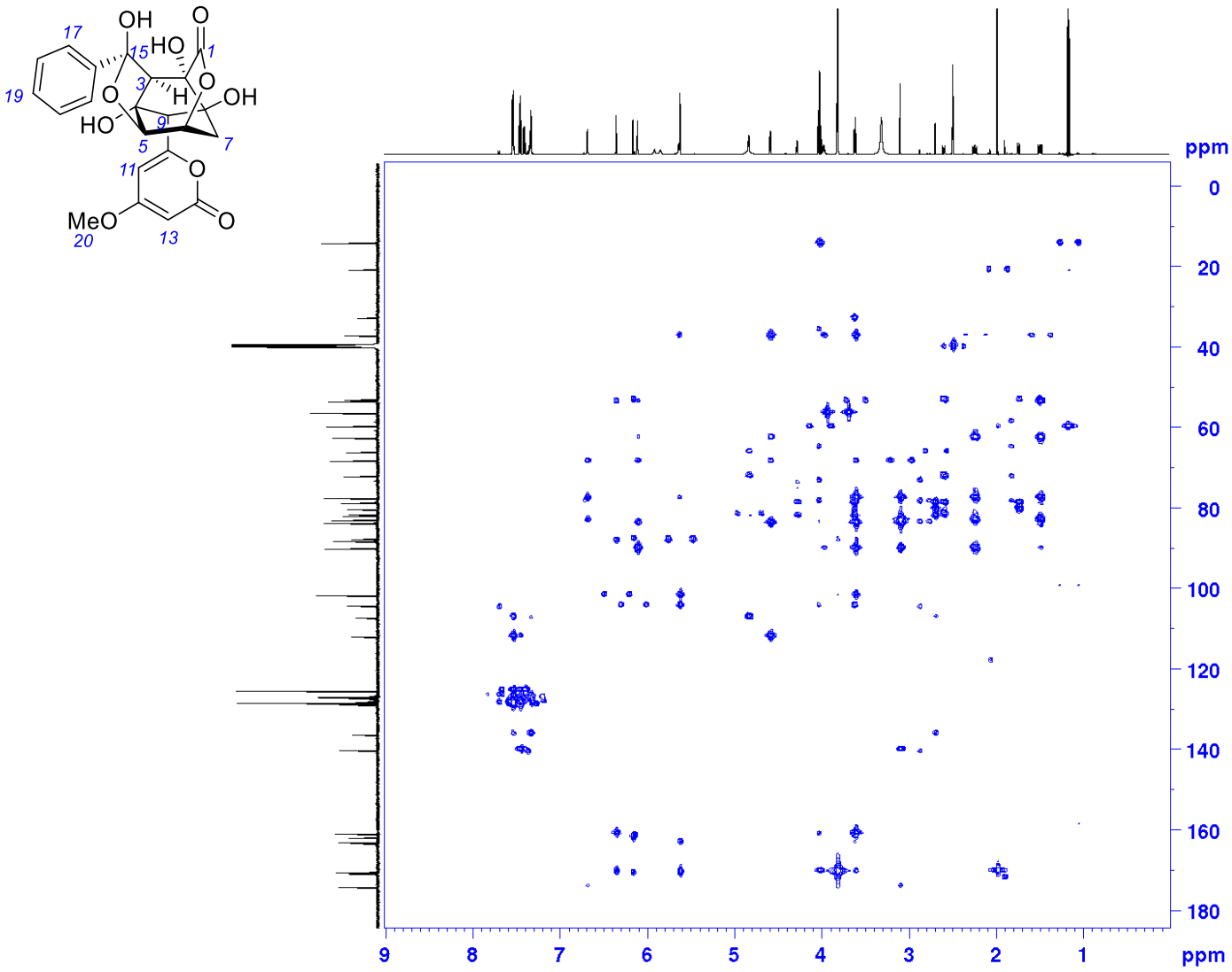


Figure S18. ^{1}H-^{13}C HMBC spectrum (600 MHz, DMSO-d_6) of a mixture of isoenterocin A (**2**) (major) and isoenterocin B (**3**) (minor)

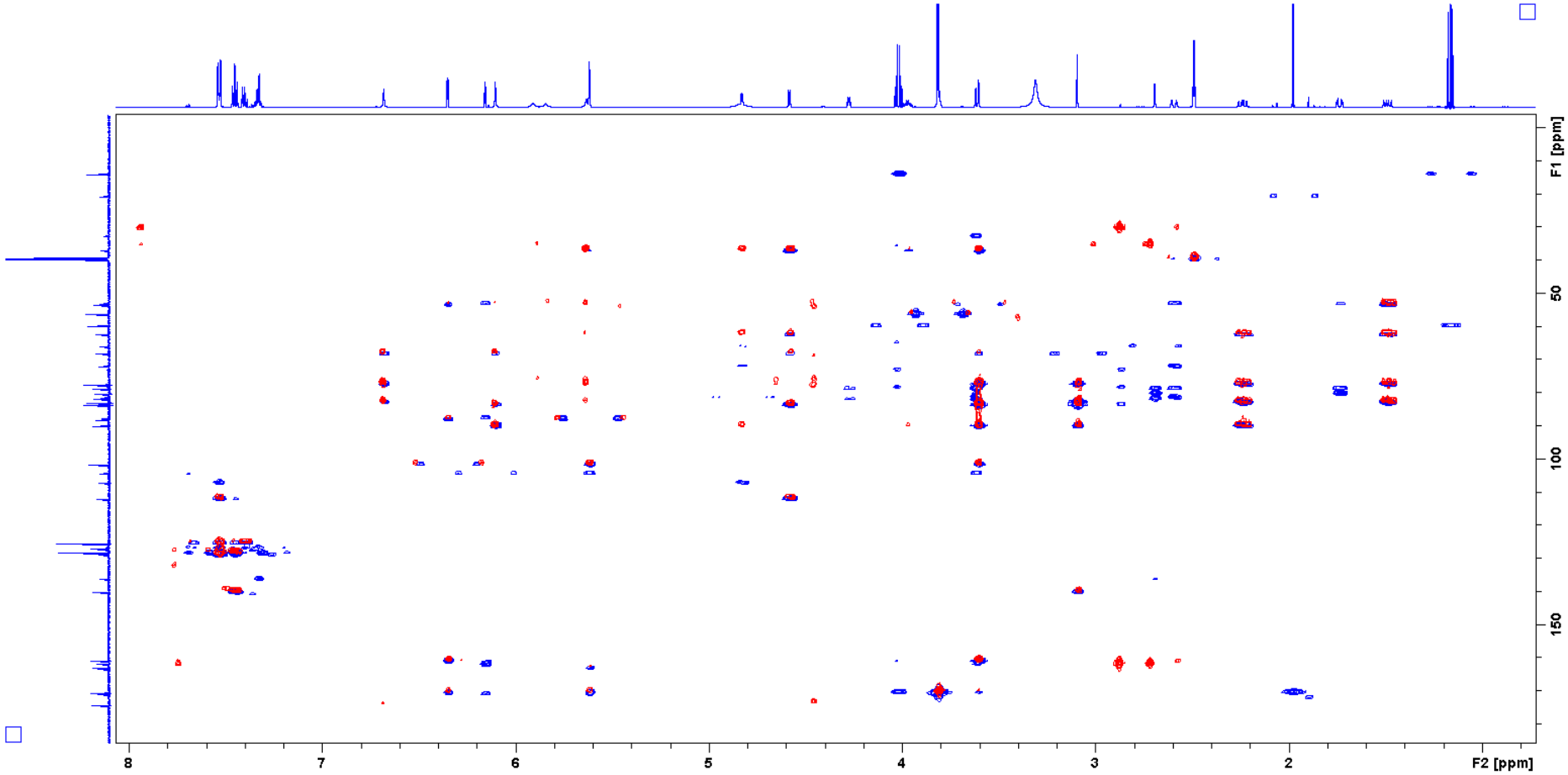


Figure S19. Overlay of ^{1}H-^{13}C HMBC spectrum of isoenterocin B (**3**) (blue) compared to isoenterocin A (**2**) (red).

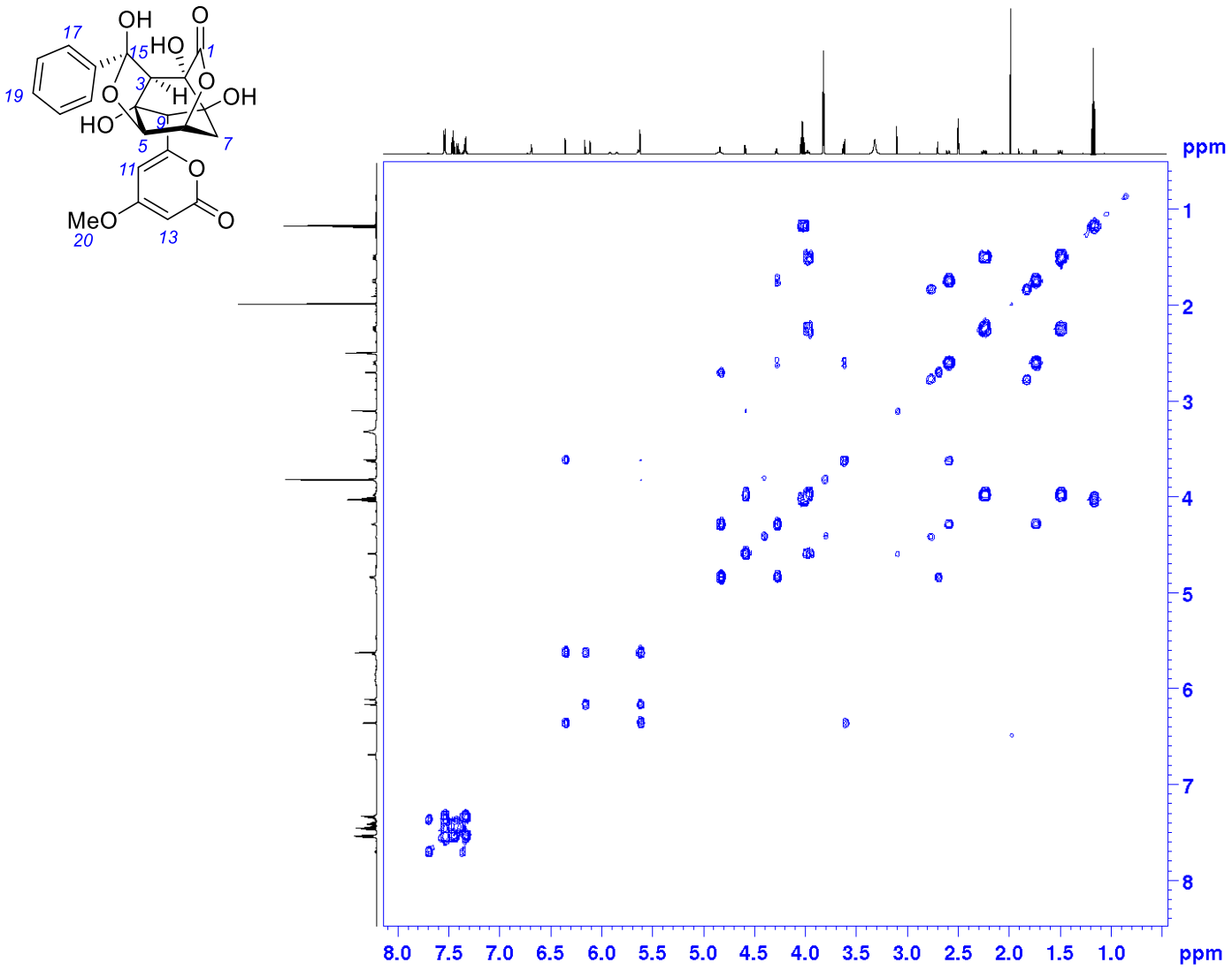


Figure S20. ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of isoenterocin A (**2**) (major) and isoenterocin B (**3**) (minor)

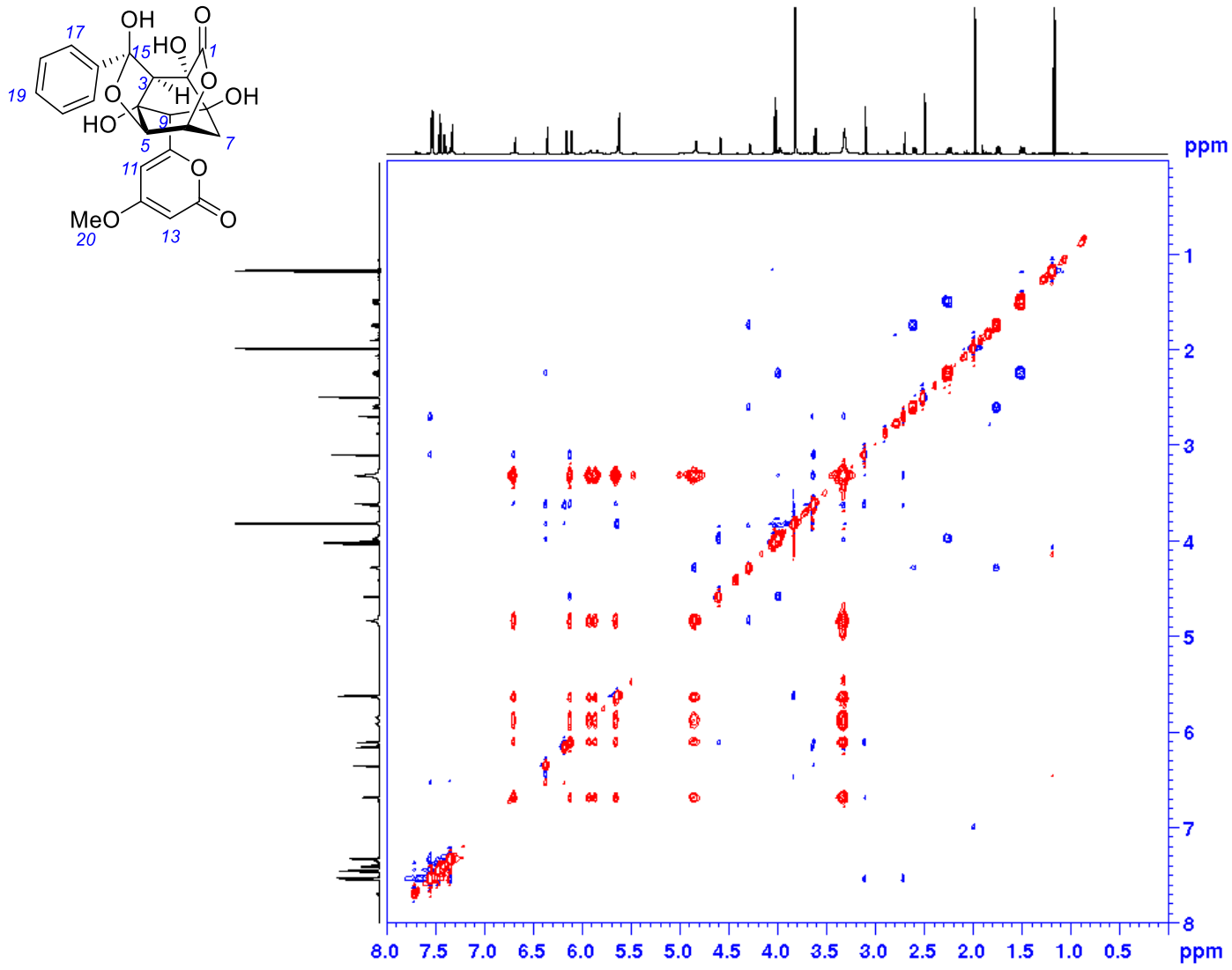


Figure S21. ^{1}H-^{1}H ROESY spectrum (600 MHz, DMSO-*d*$_6$) of of a mixture isoenterocin A (**2**) (major) and isoenterocin B (**3**) (minor)

Figures S22-29. NMR spectra of 3-*epi*-enterocin (**4**)

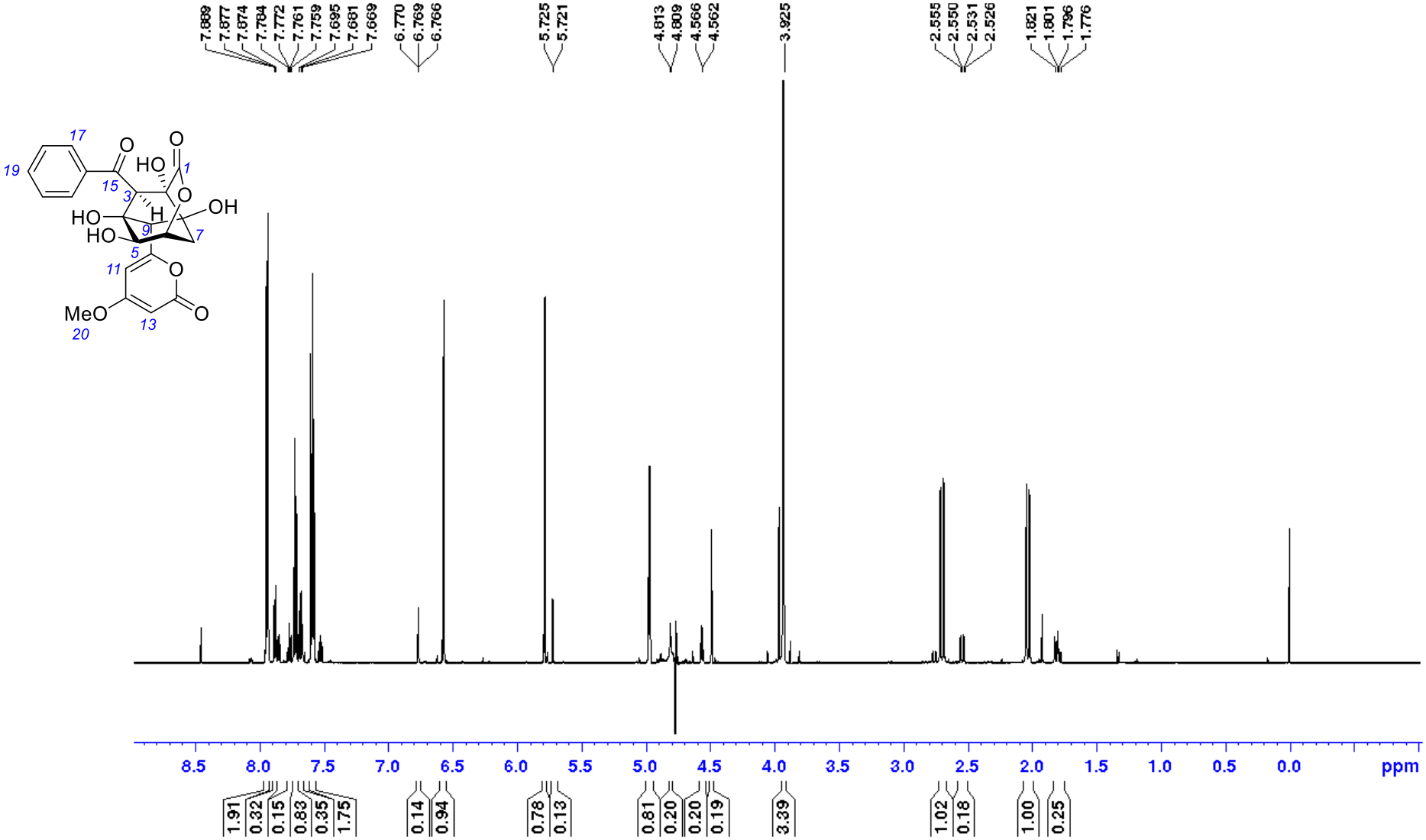


Figure S22. ^{1}H NMR spectrum (600 MHz, D_2O) of a mixture of enterocin (**1**) (major) and 3-*epi*-enterocin (**4**) (minor) with water suppression (pre-saturation)

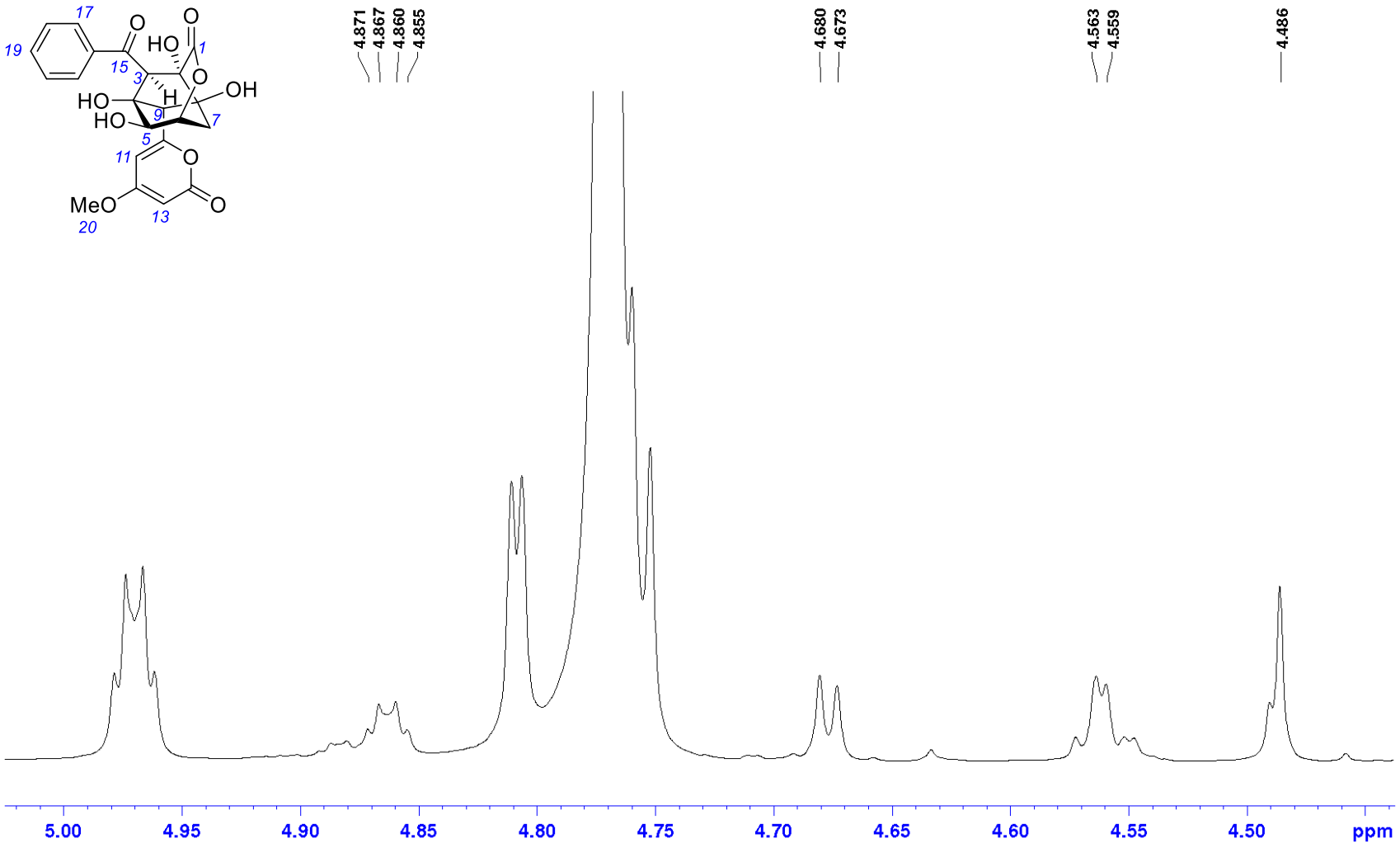


Figure S23. Expansion of ^{1}H NMR spectrum (600 MHz, D_2O) of a mixture of enterocin (**1**) (major) and 3-*epi*-enterocin (**4**) (minor) without water suppression

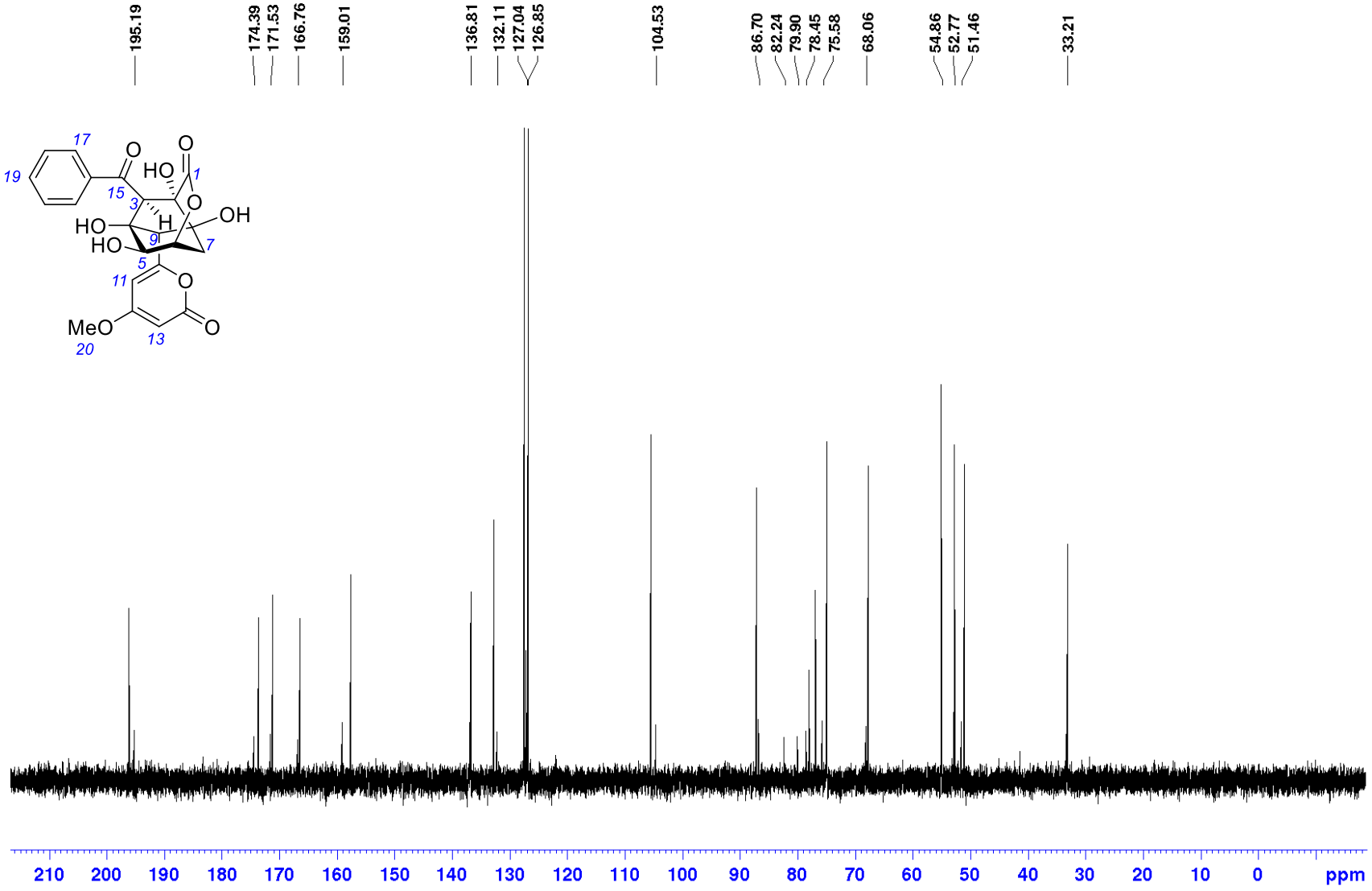


Figure S24. ^{13}C NMR spectrum (150 MHz, D_2O) of a mixture of enterocin (**1**) (major) and 3-*epi*-enterocin (**4**) (minor)

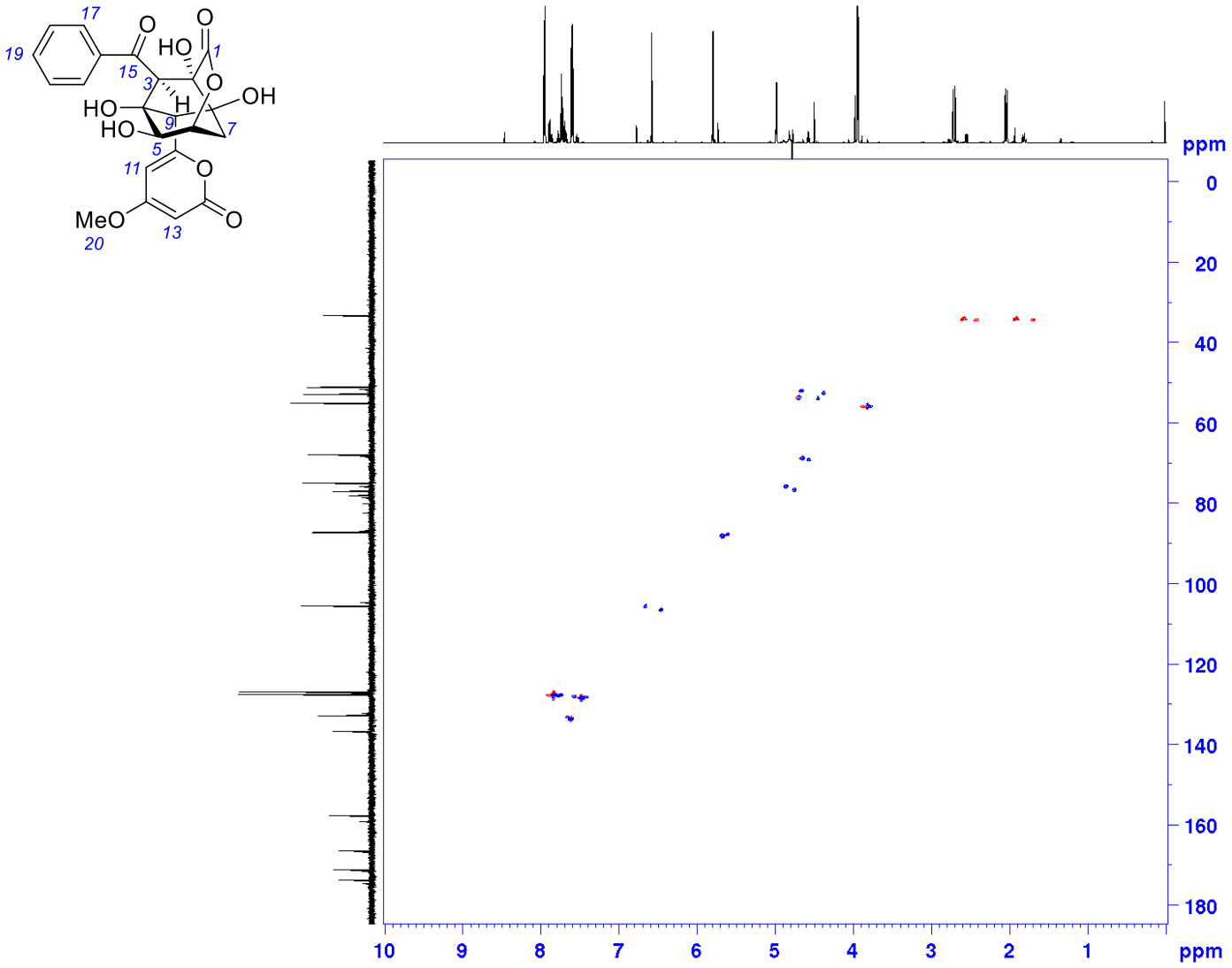


Figure S25. ^{1}H-^{13}C HSQC spectrum (600 MHz, D_2O) of a mixture of enterocin (**1**) (major) and 3-*epi*-enterocin (**4**) (minor)

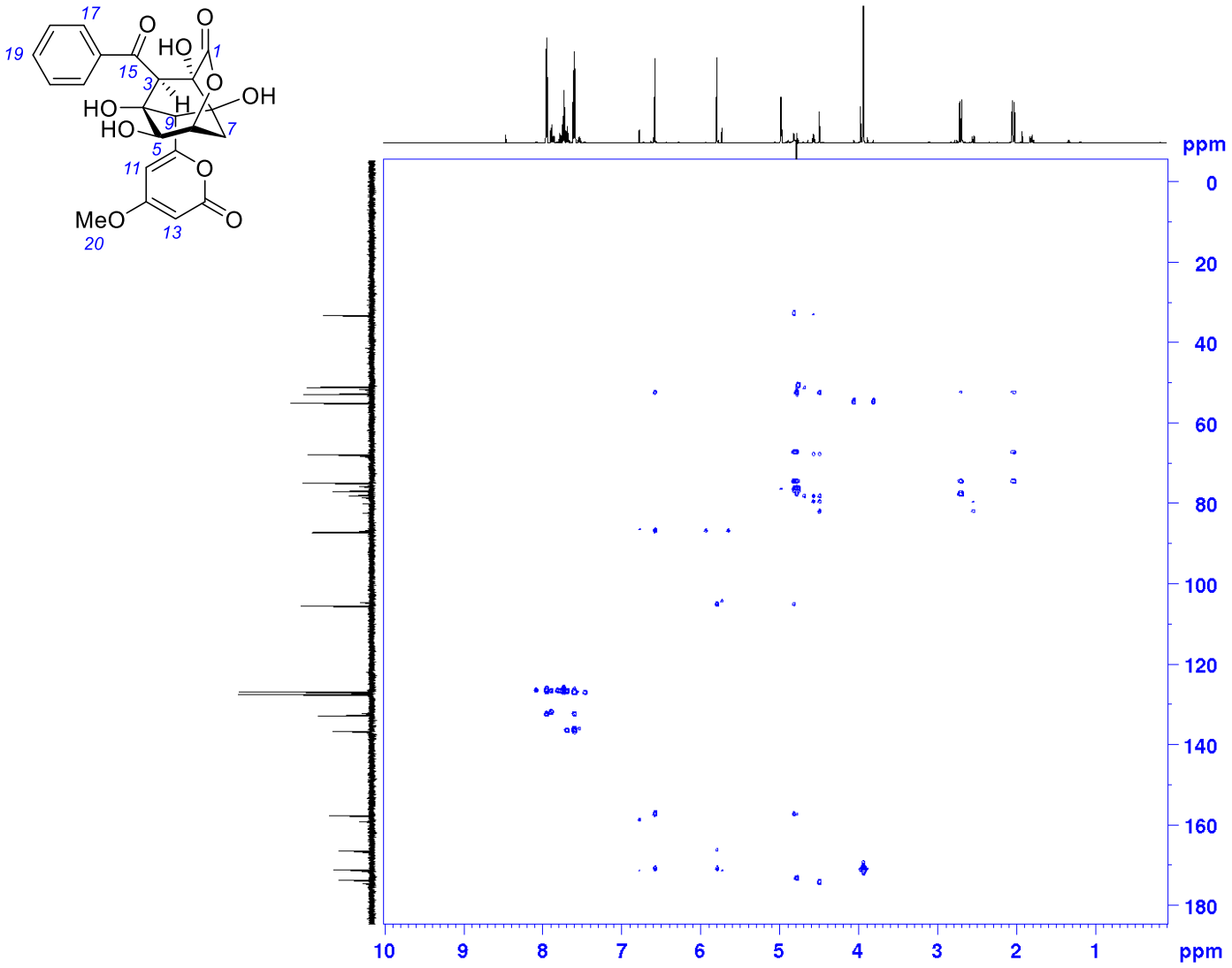


Figure S26. ^{1}H-^{13}C HMBC spectrum (600 MHz, D_2O) of a mixture of enterocin (**1**) (major) and 3-*epi*-enterocin (**4**) (minor)

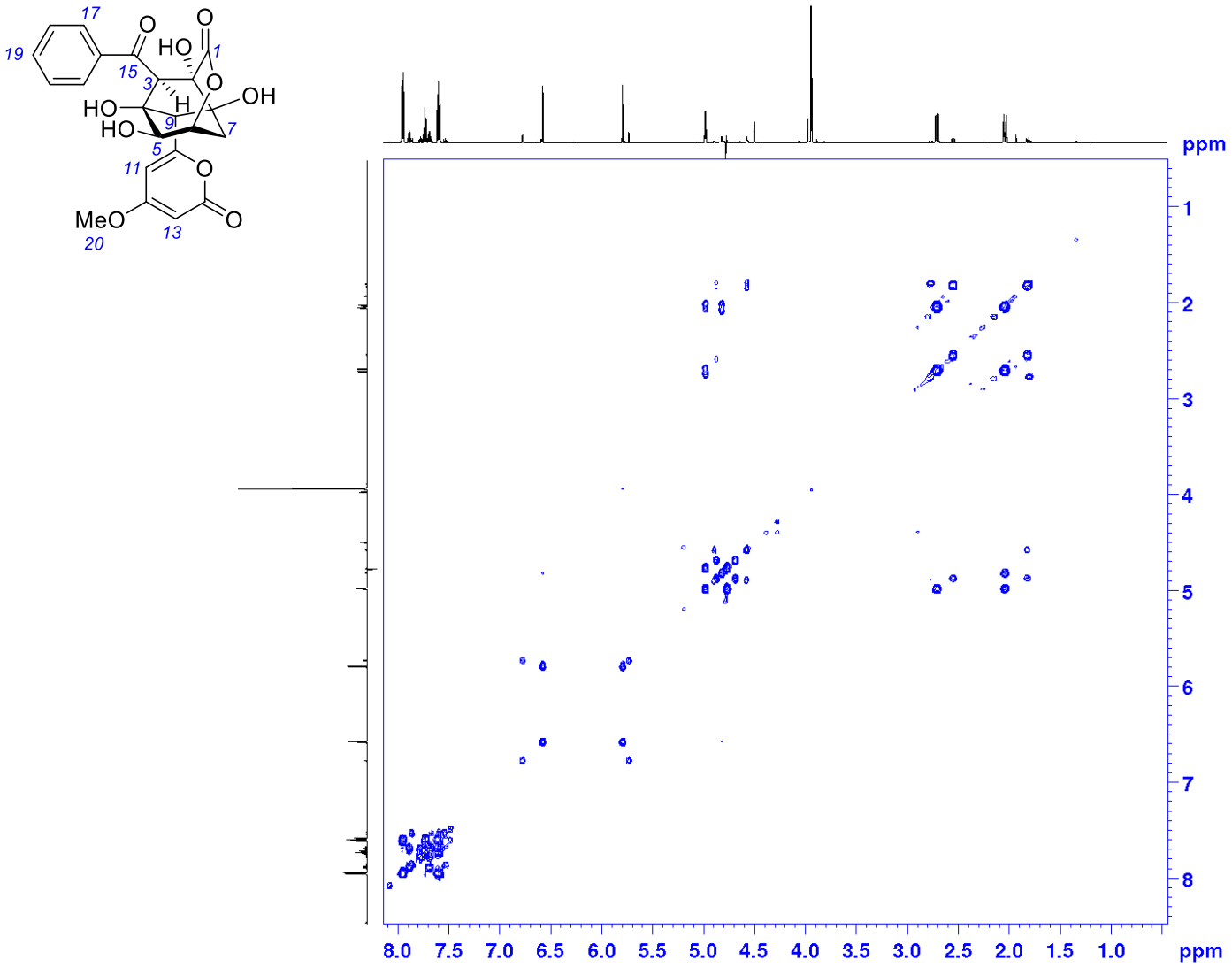


Figure S27. ^{1}H-^{1}H COSY spectrum (600 MHz, D_2O) of a mixture of enterocin (**1**) (major) and 3-*epi*-enterocin (**4**) (minor)

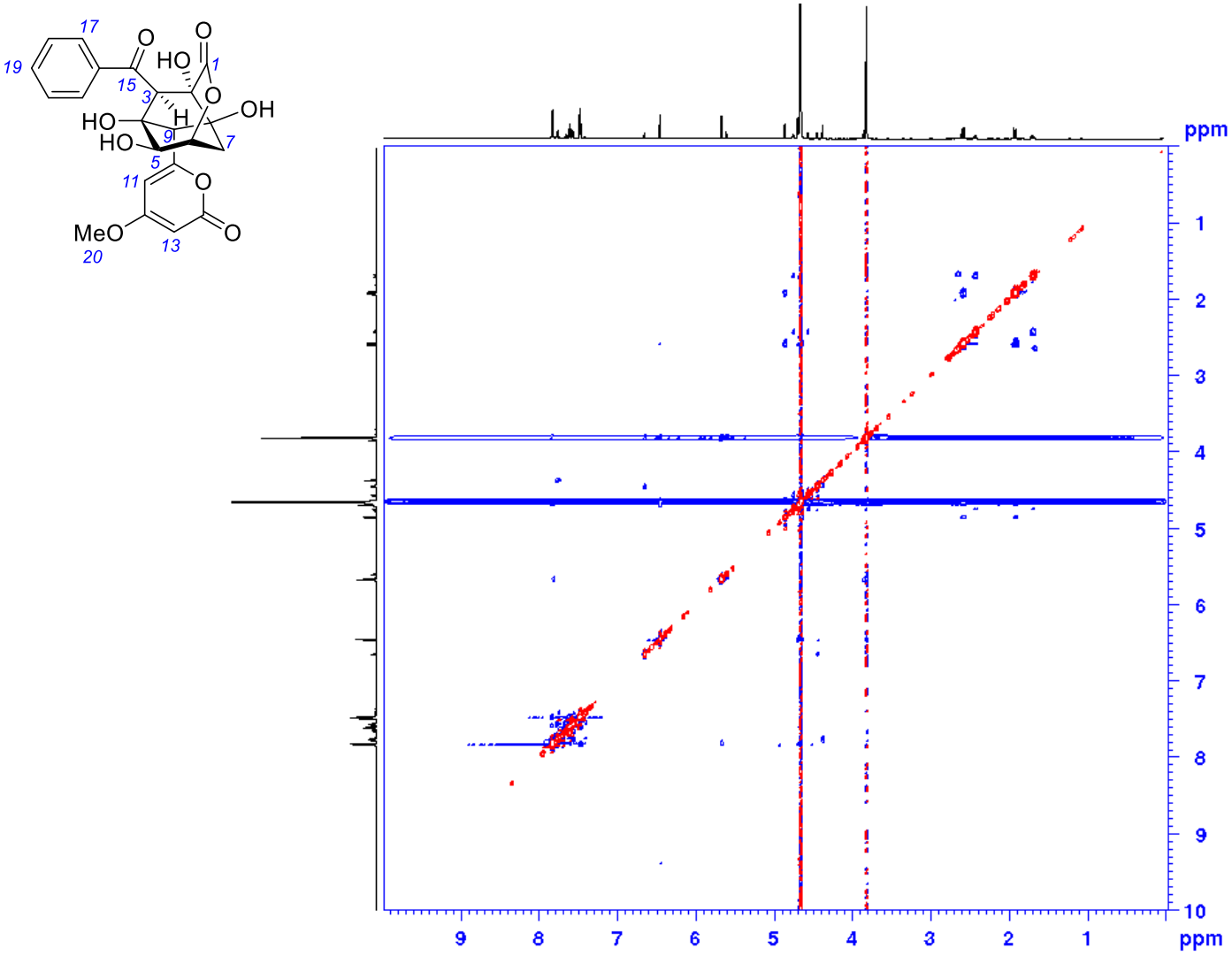


Figure S28. ^{1}H-^{1}H ROESY spectrum (600 MHz, D_2O) of a mixture of enterocin (**1**) (major) and 3-*epi*-enterocin (**4**) (minor)

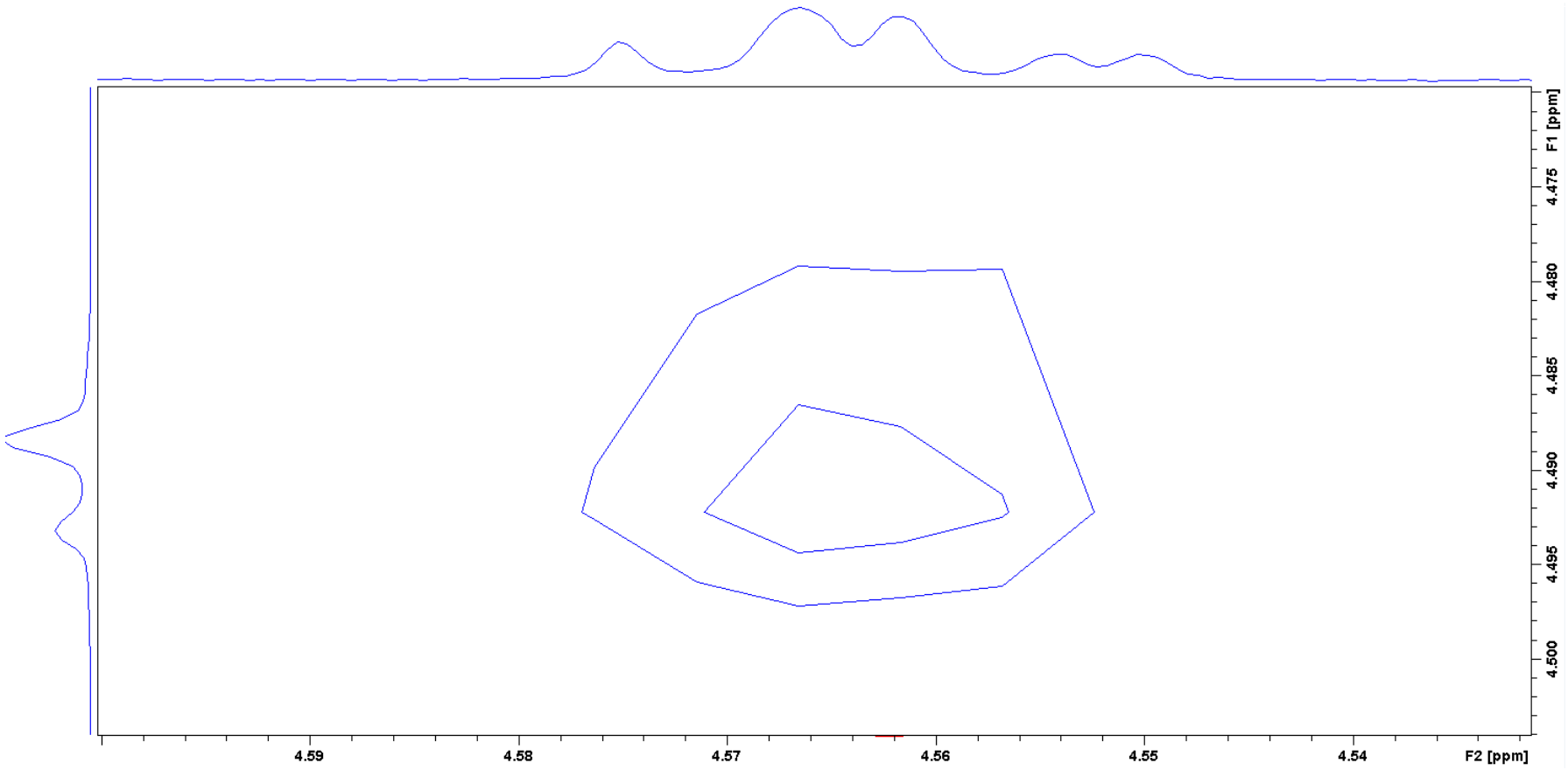


Figure S29. Expansion of ^{1}H-^{1}H ROESYNMR spectrum (600 MHz, D_2O) of a mixture of enterocin (**1**) (major) and 3-*epi*-enterocin (**4**) (minor) with water suppression, indicating the key ROESY correlation between H-3 and H-9.

Figure S30-35. NMR spectra of 5-deoxyenterocin (**5**)

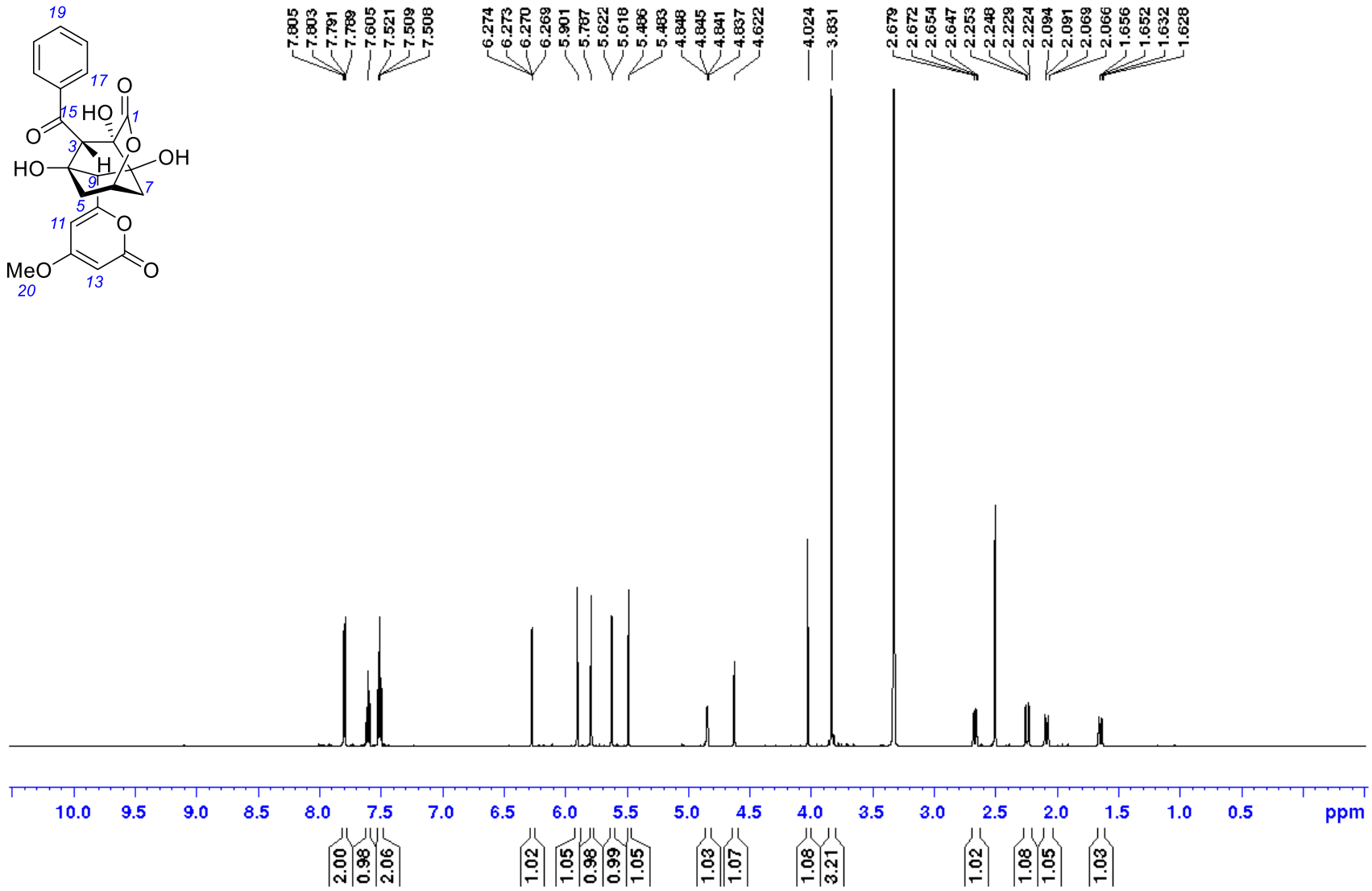


Figure S30. [1]H NMR spectrum (600 MHz, DMSO-*d*6) of 5-deoxyenterocin (**5**)

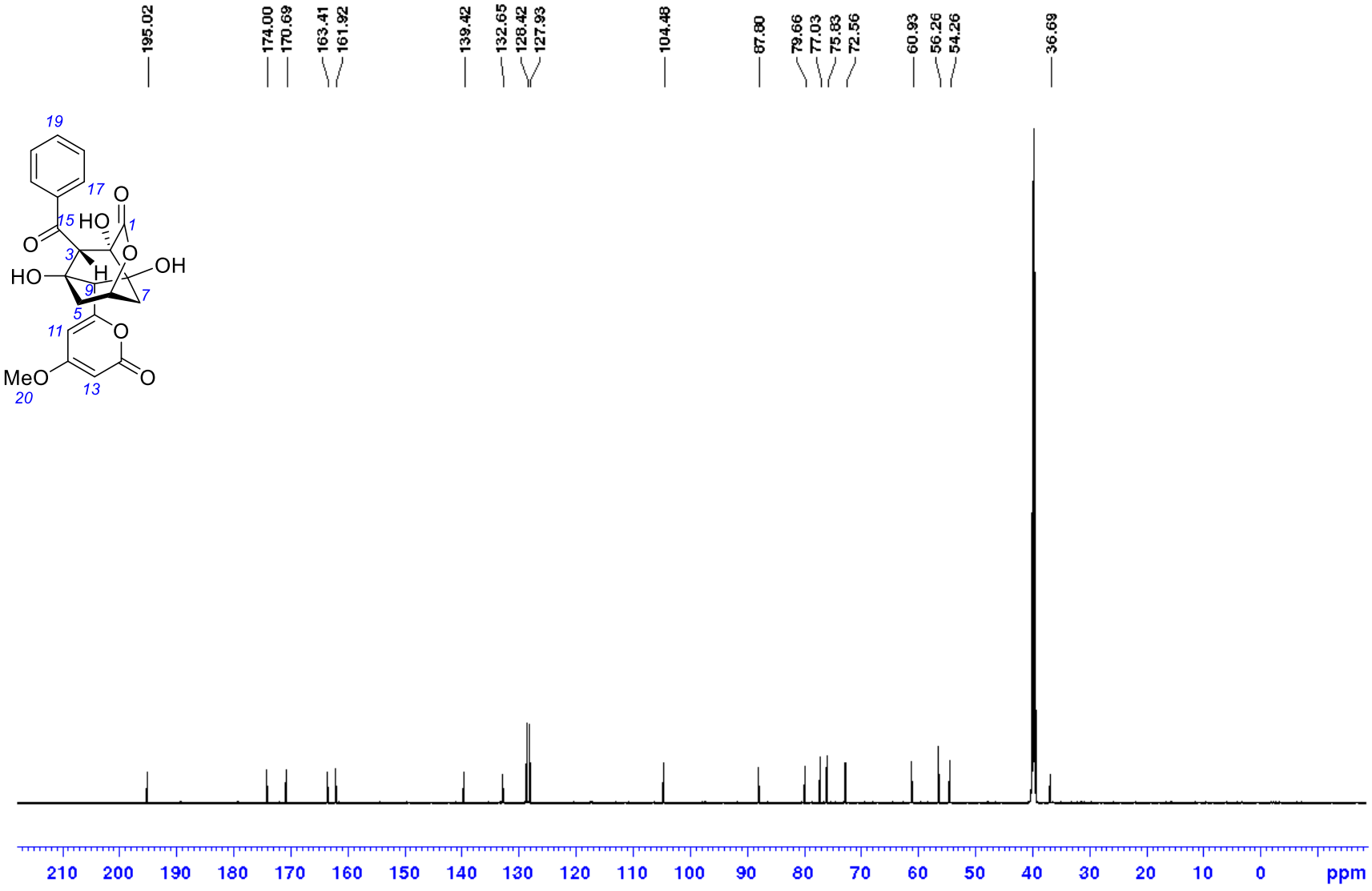


Figure S31. ^{13}C NMR spectrum (150 MHz, DMSO-*d*6) of 5-deoxyenterocin (**5**)

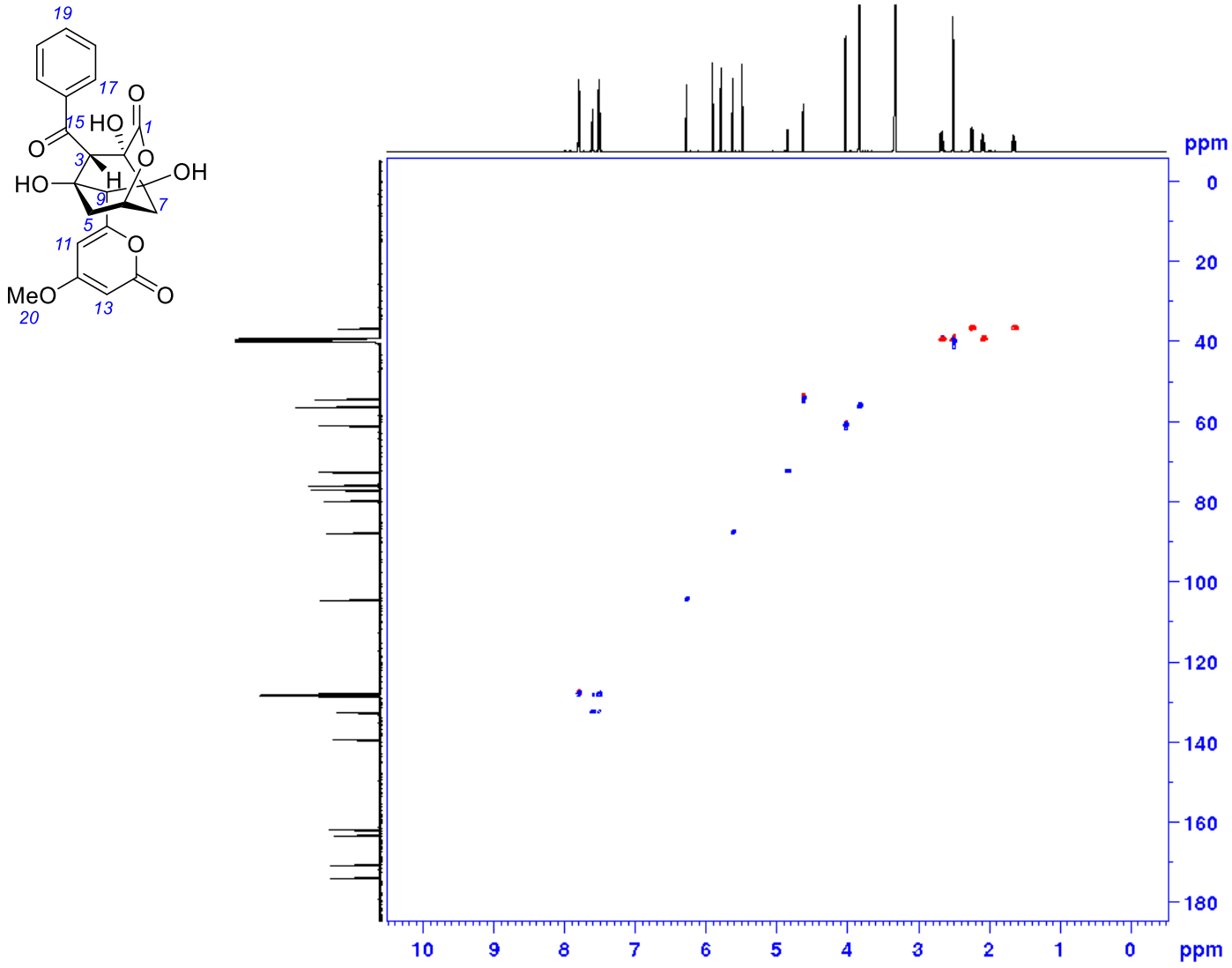


Figure S32. ^{1}H-^{13}C HSQC spectrum (600 MHz, DMSO-d_6) of 5-deoxyenterocin (**5**)

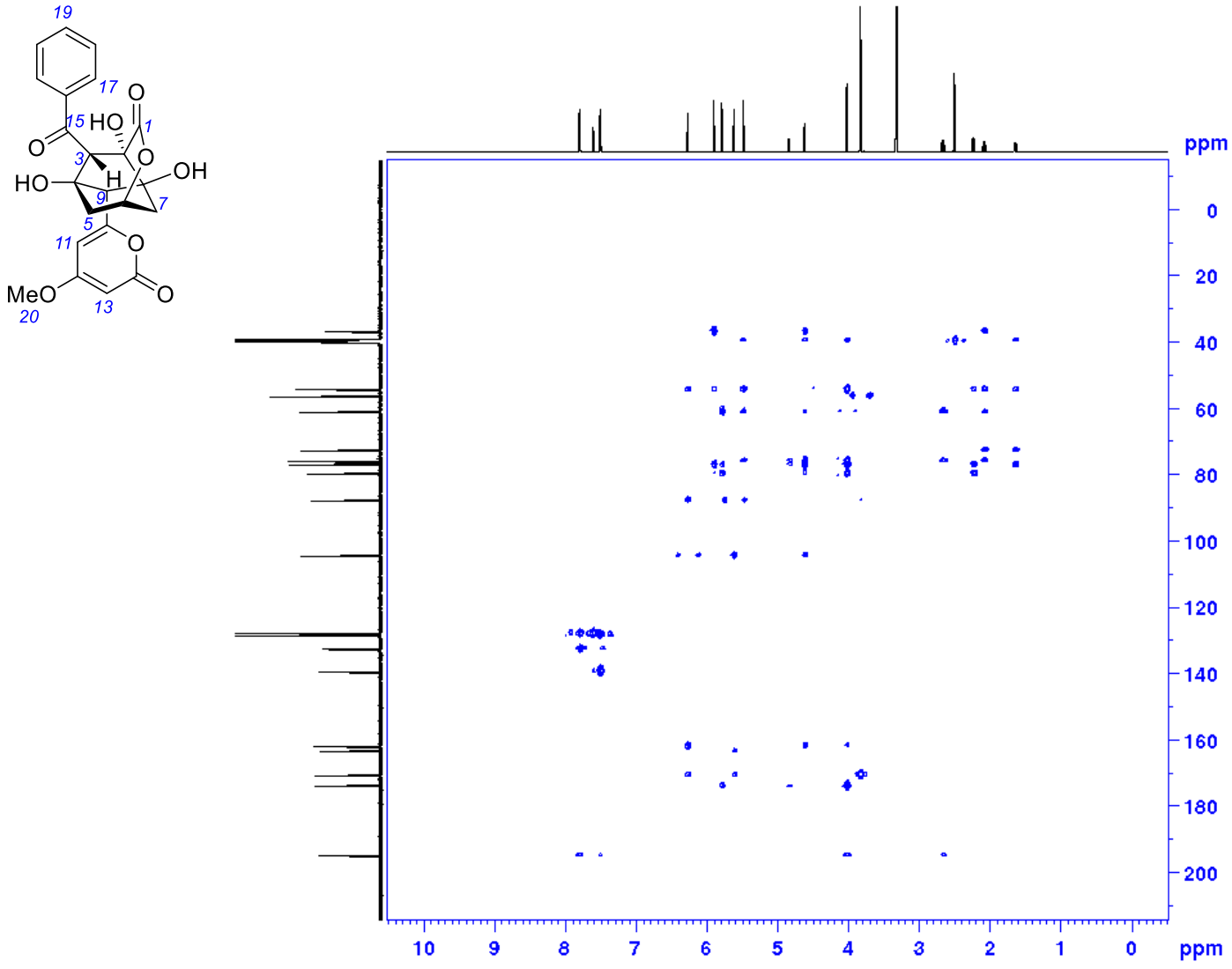


Figure S33. ^{1}H-^{13}C HMBC spectrum (600 MHz, DMSO-*d*$_6$) of 5-deoxyenterocin (**5**)

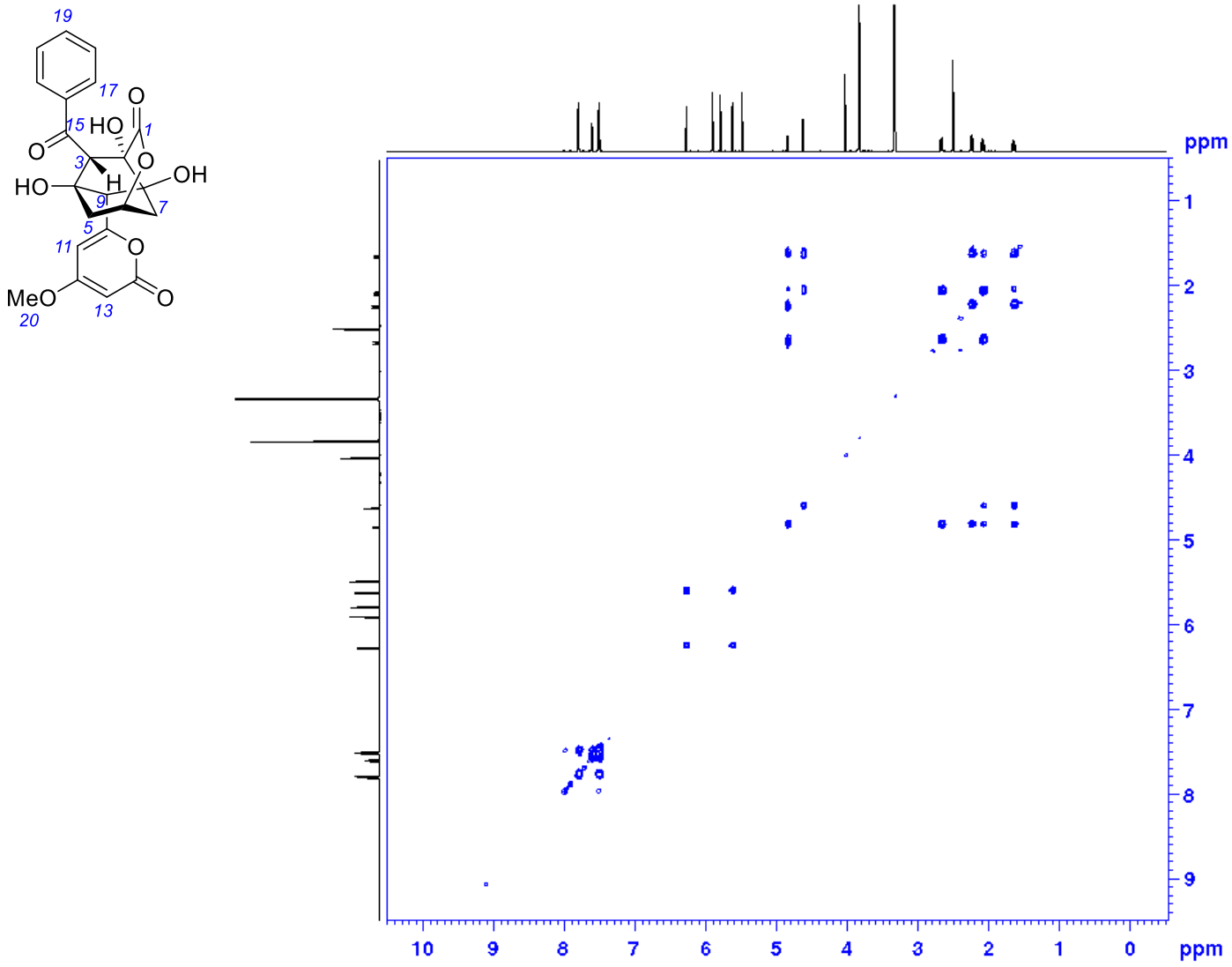


Figure S34. ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-*d*$_6$) of 5-deoxyenterocin (**5**)

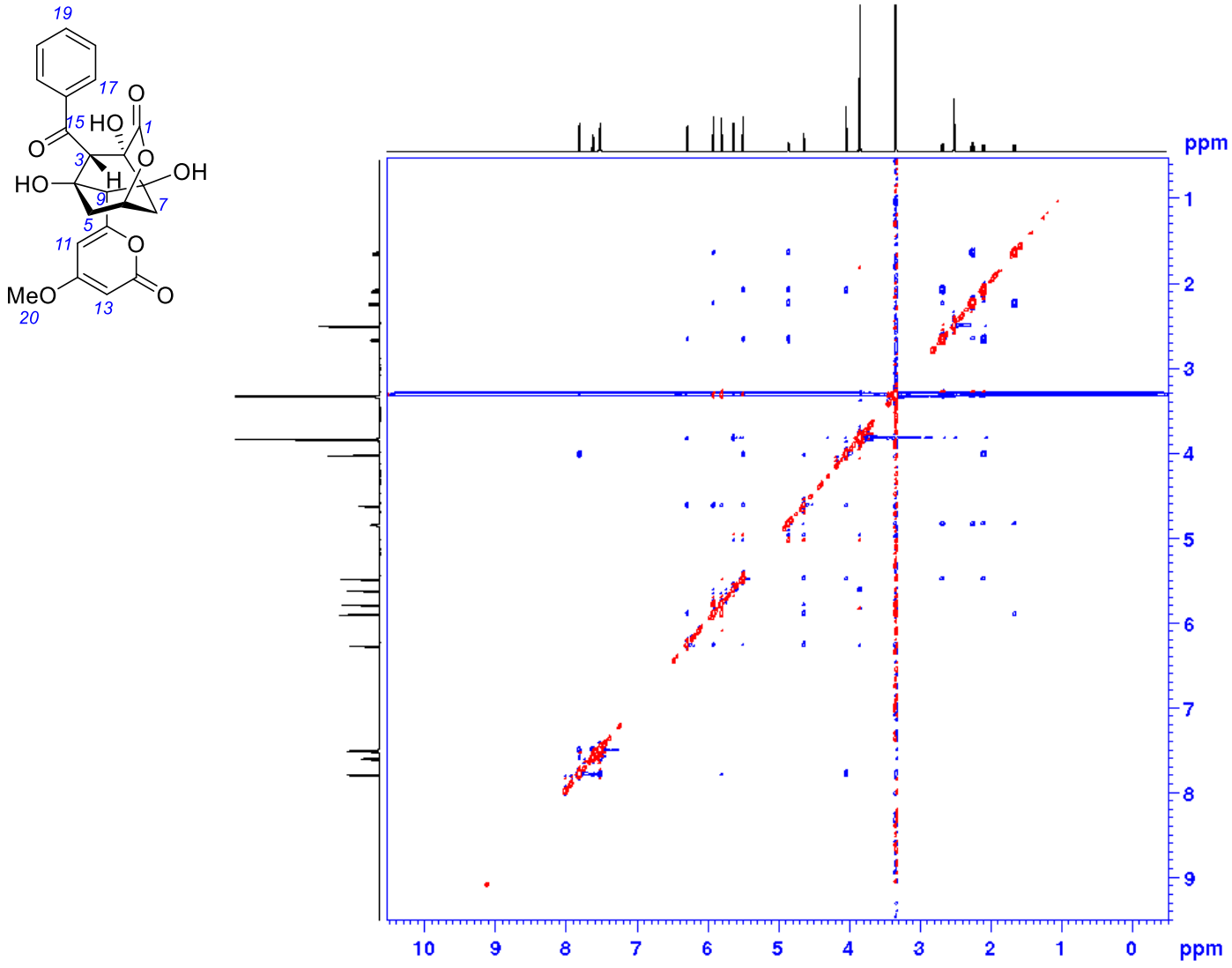


Figure S35. ^{1}H-^{1}H ROESY spectrum (600 MHz, DMSO-*d*$_6$) of 5-deoxyenterocin (**5**)

Figure S36-41. NMR spectra of 3-*epi*-5-deoxyenterocin (**6**)

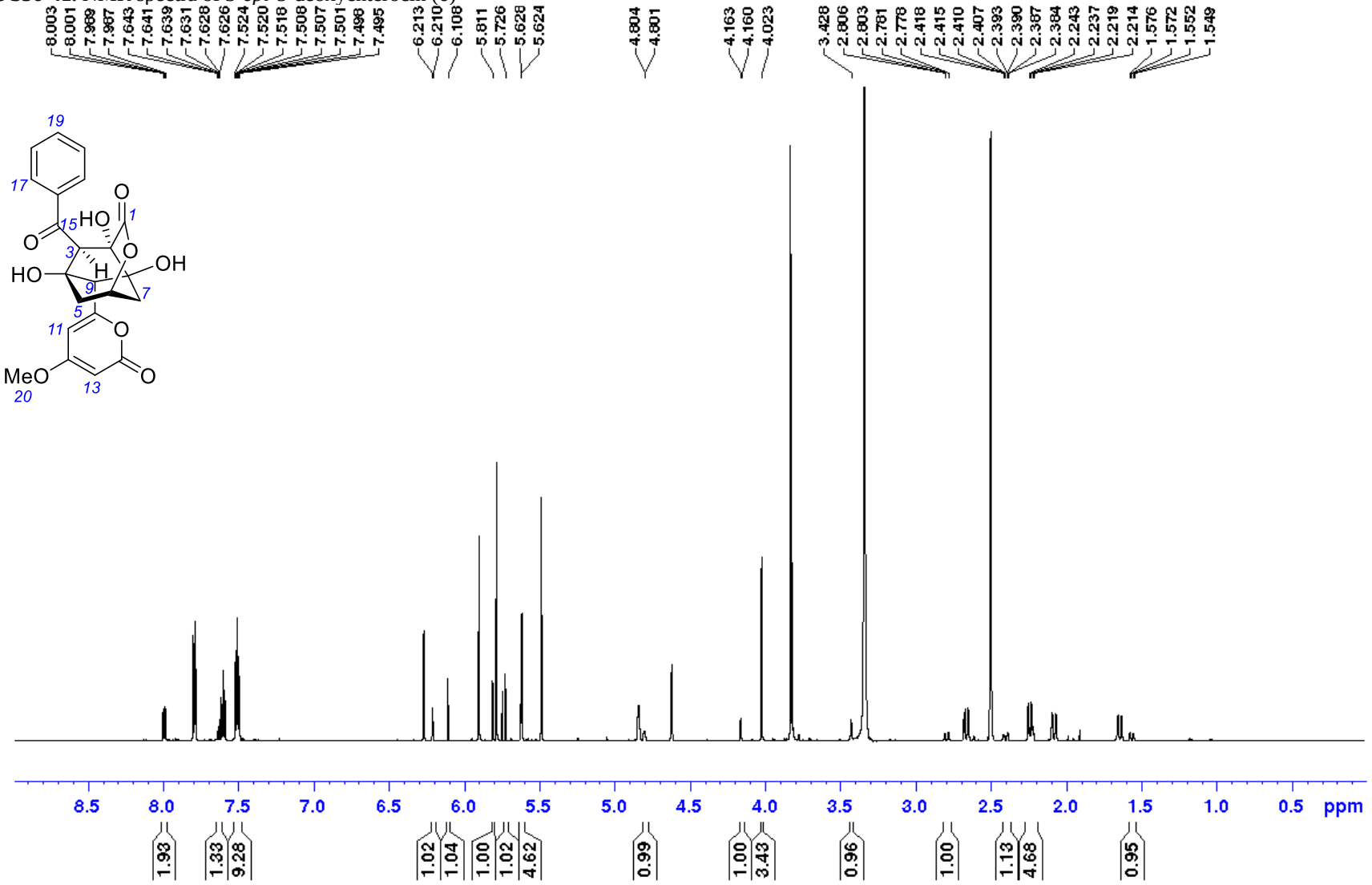


Figure S36. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of a mixture of 5-deoxyenterocin (**5**) (major) and 3-*epi*-5-deoxyenterocin (**6**) (minor)

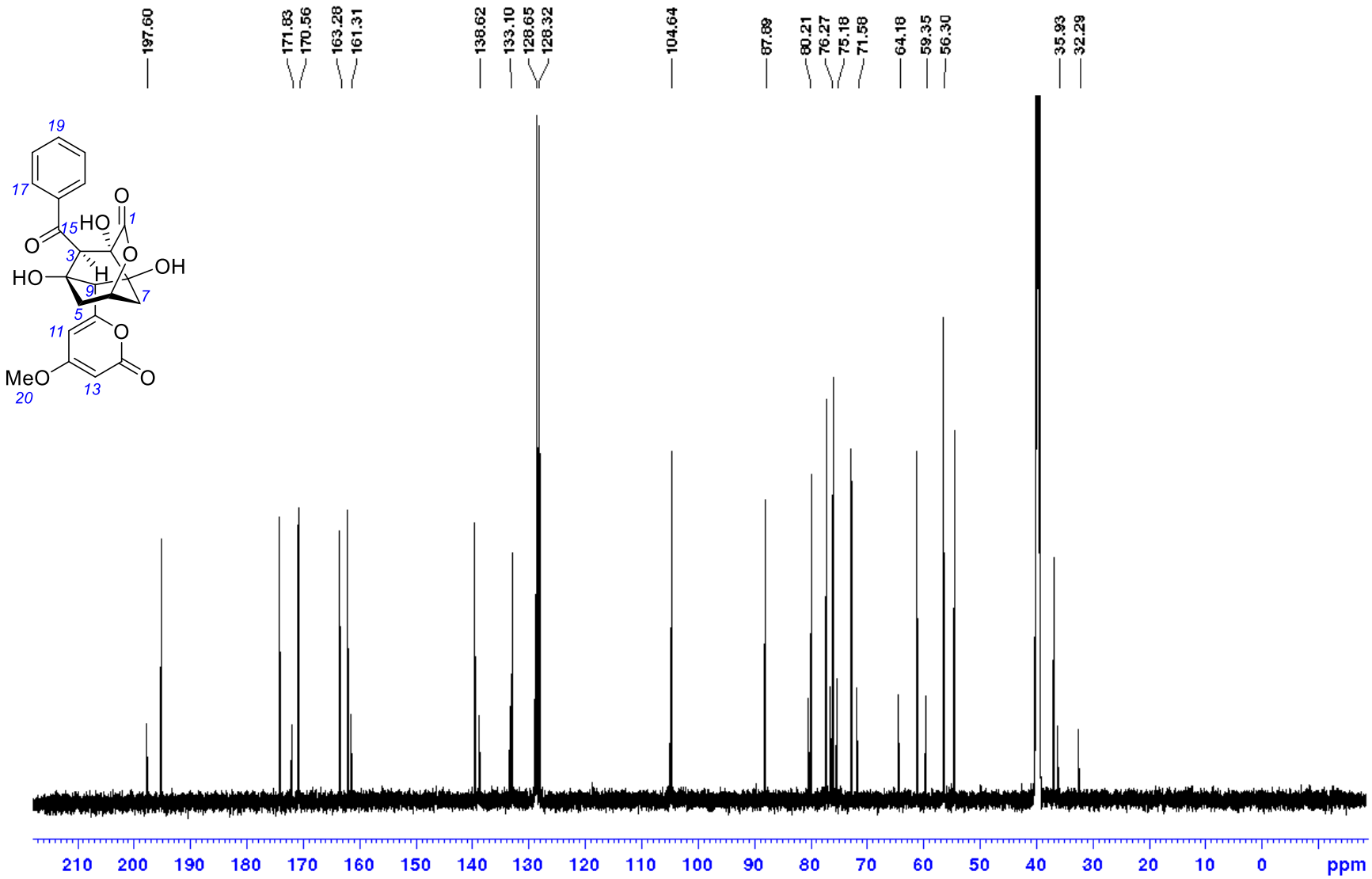


Figure S37. ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of a mixture of 5-deoxyenterocin (**5**) (major) and 3-*epi*-5-deoxyenterocin (**6**) (minor)

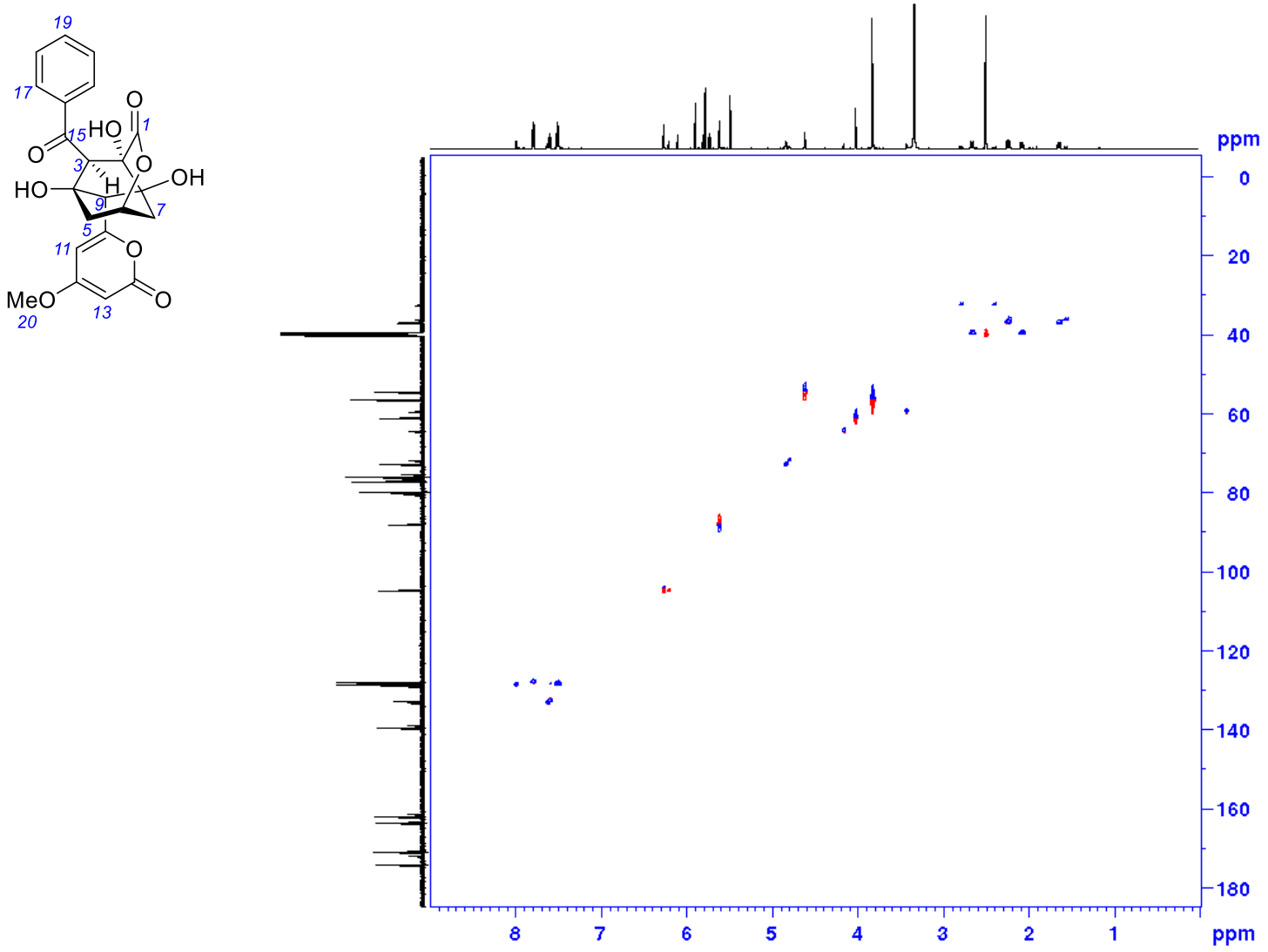


Figure S38. ^{1}H-^{13}C HSQC spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-deoxyenterocin (**5**) (major) and 3-*epi*-5-deoxyenterocin (**6**) (minor)

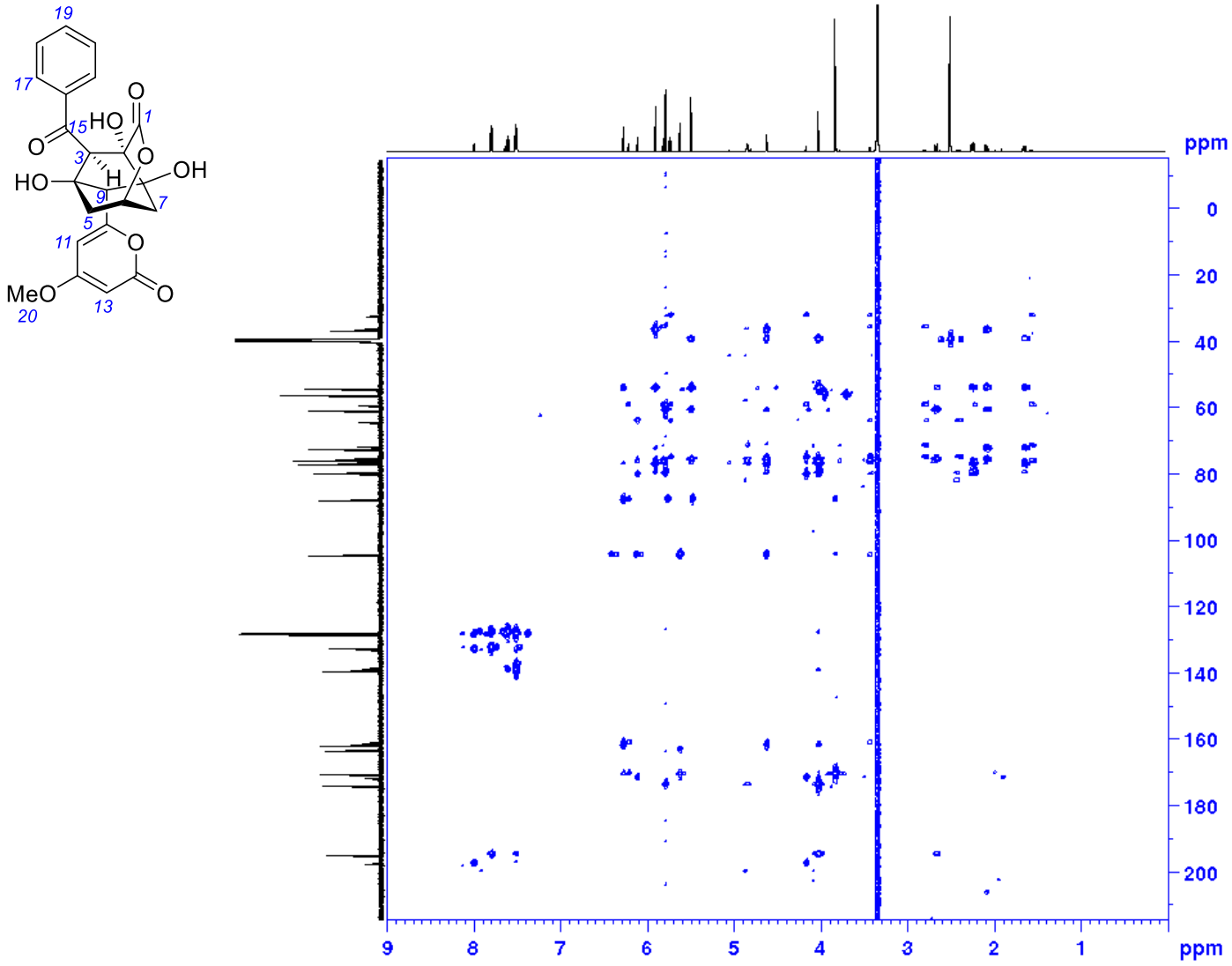


Figure S39. ^{1}H-^{13}C HMBC spectrum (600 MHz, DMSO-d_6) of a mixture of 5-deoxyenterocin (**5**) (major) and 3-*epi*-5-deoxyenterocin (**6**) (minor)

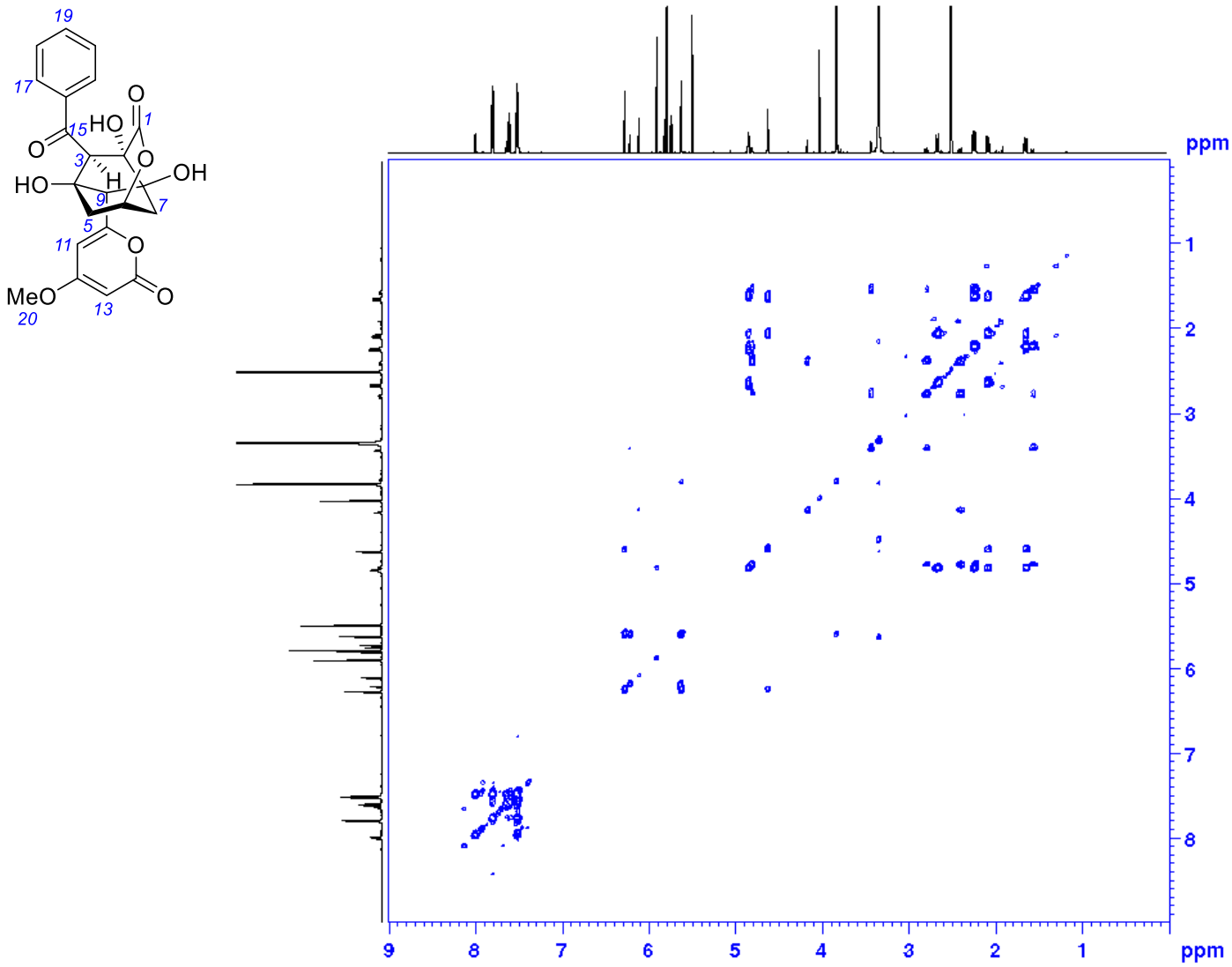


Figure S40. ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-deoxyenterocin (**5**) (major) and 3-*epi*-5-deoxyenterocin (**6**) (minor)

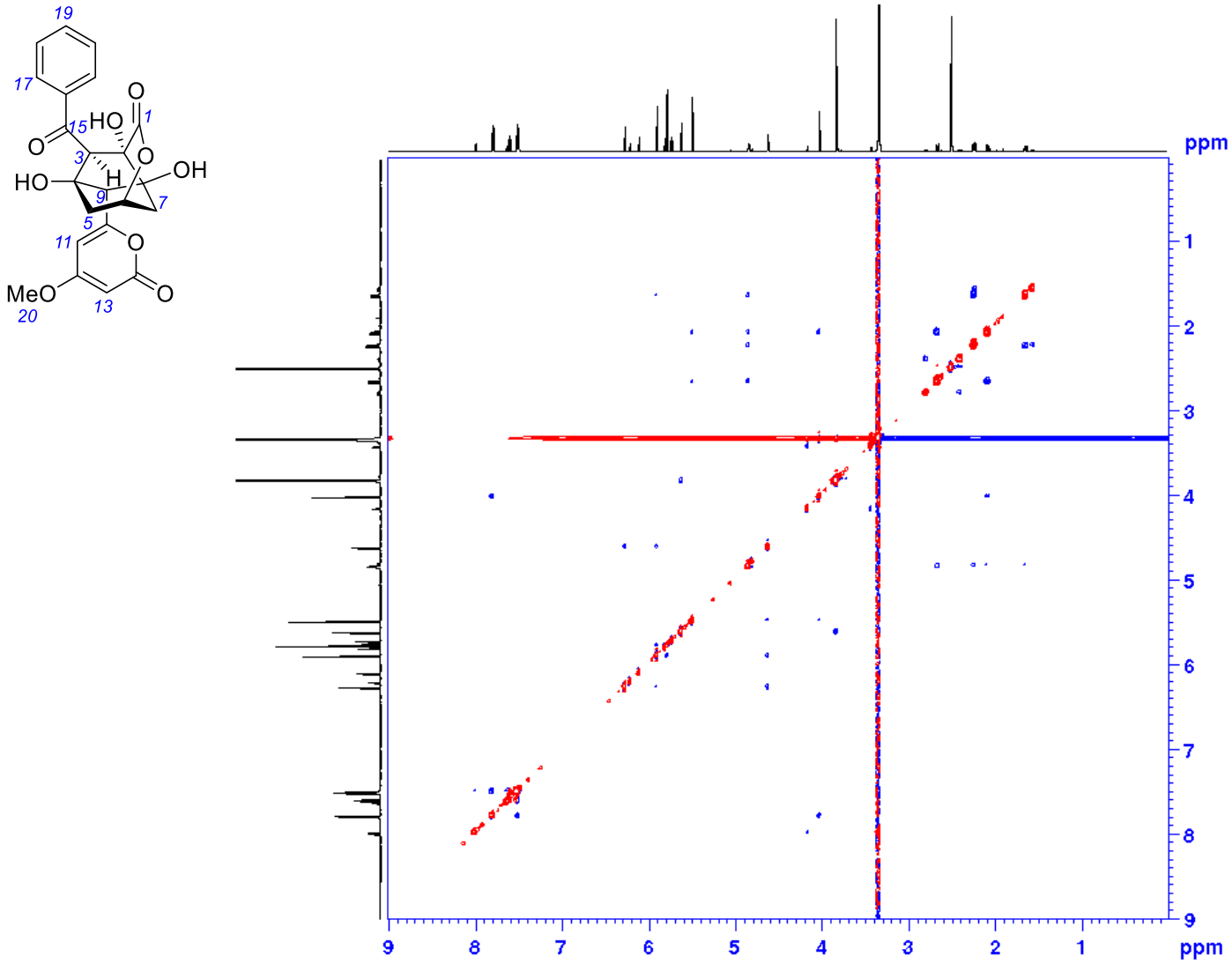


Figure S41. ^{1}H-^{1}H ROESY spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-deoxyenterocin (**5**) (major) and 3-*epi*-5-deoxyenterocin (**6**) (minor)

Figures S42-48. NMR spectra of enterocinic acid A (**7**)

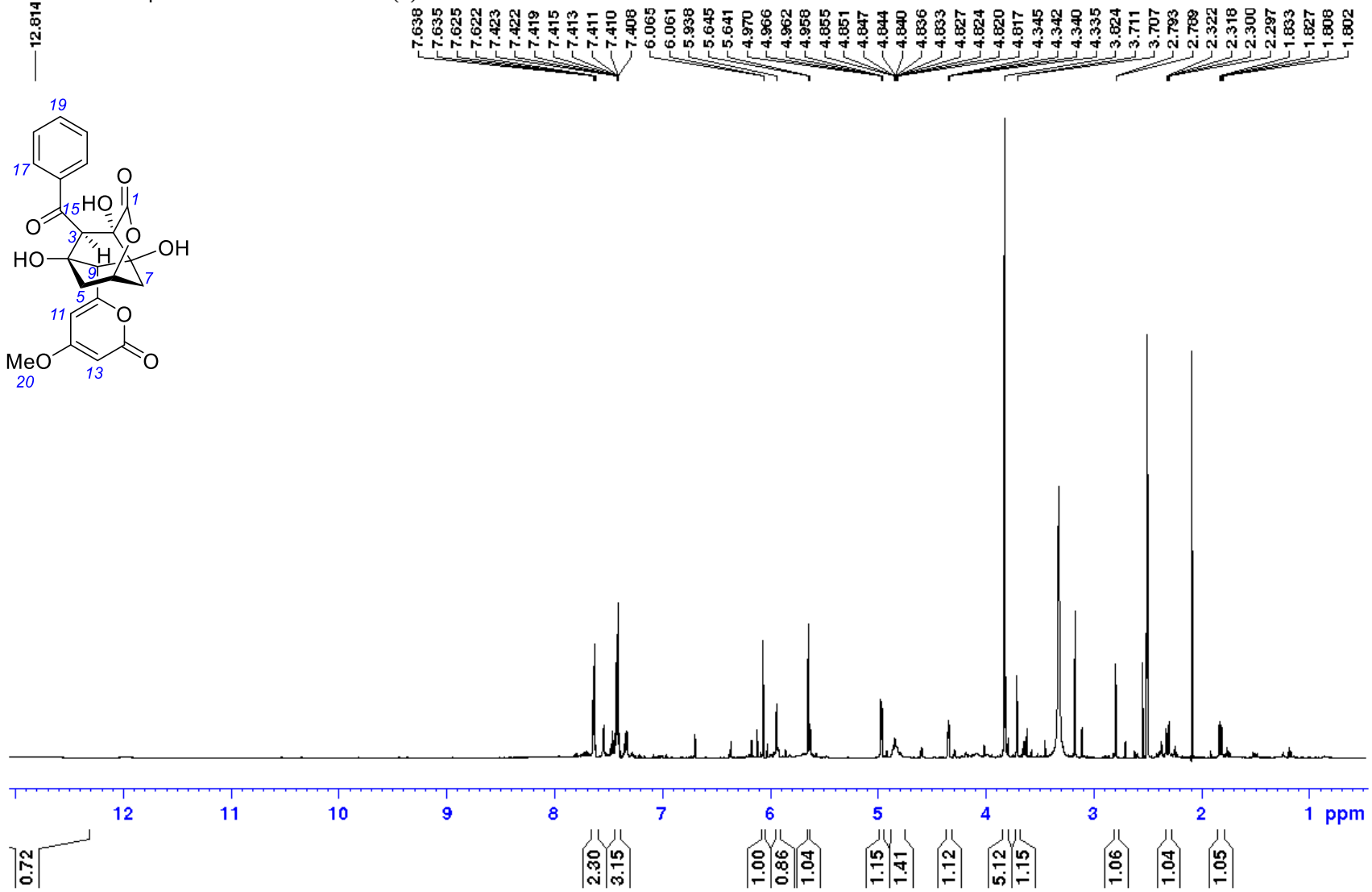


Figure S42. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of a mixture of enterocinic acid A (**7**) (major) and isoenterocin B (**3**) (minor)

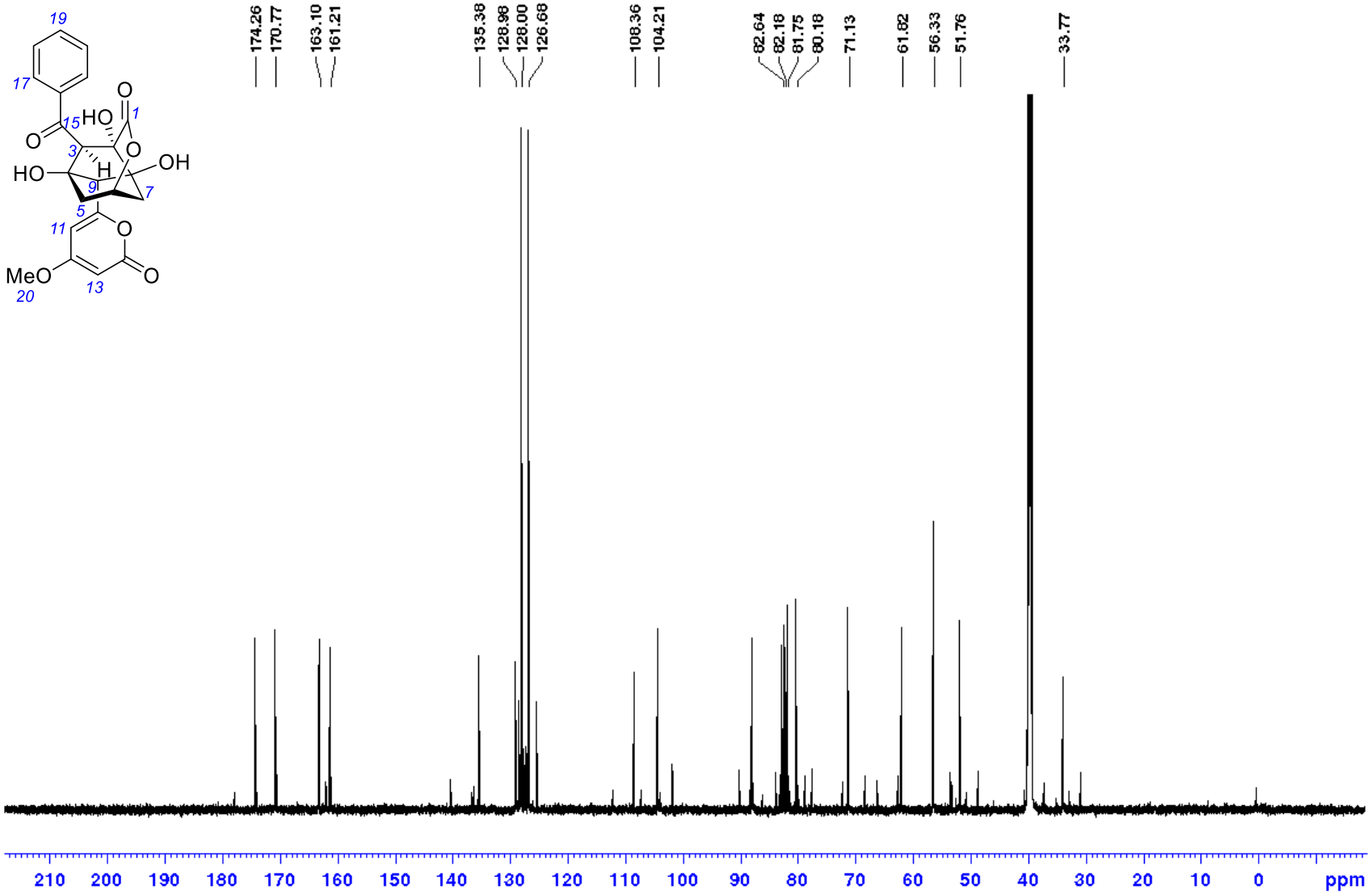


Figure S43. ^{13}C NMR spectrum (150 MHz, DMSO-*d*$_6$) of a mixture of enterocinic acid A (**7**) (major) and isoenterocin B (**3**) (minor)

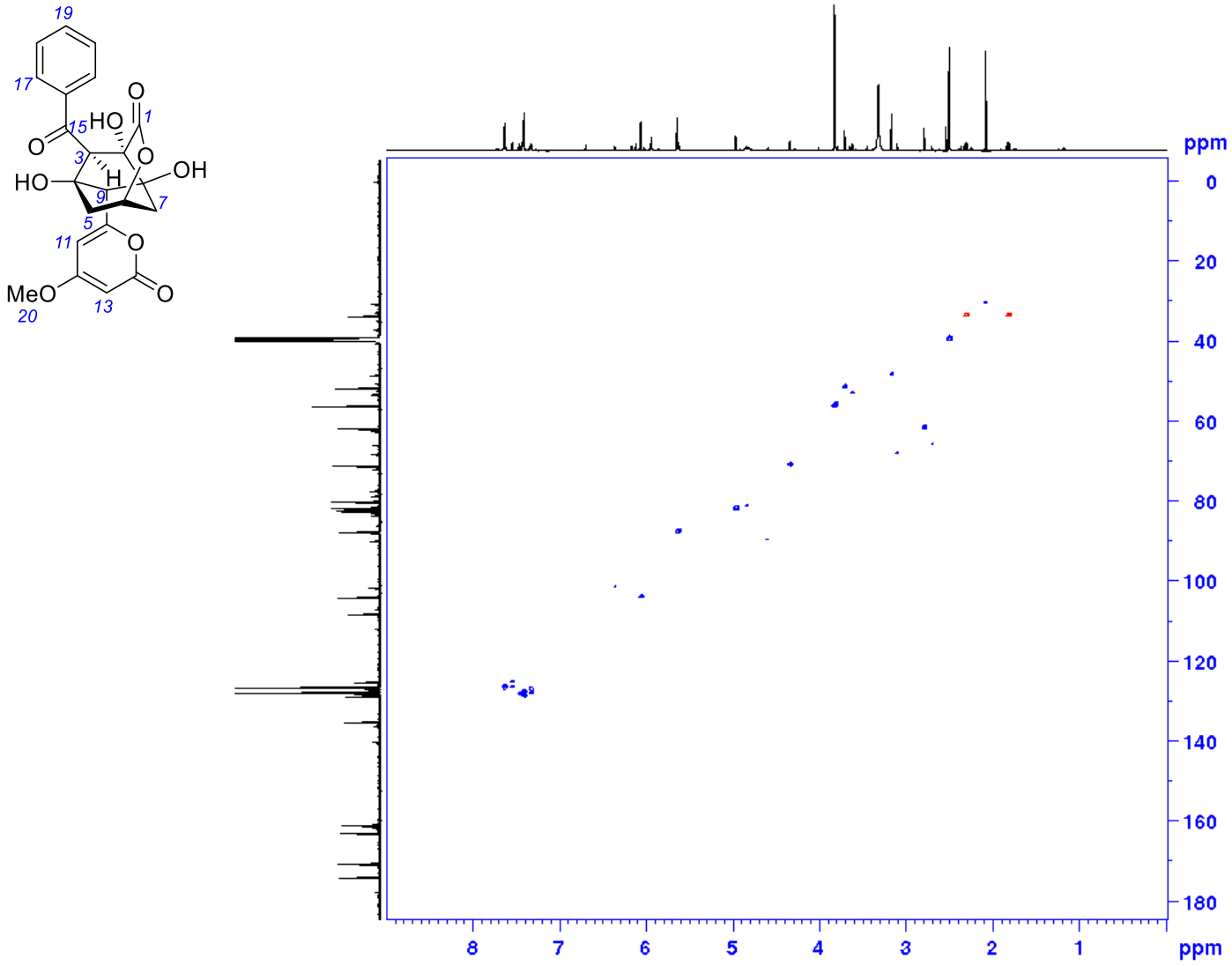


Figure S44. ^{1}H-^{13}C HSQC spectrum (600 MHz, DMSO-*d*6) of a mixture of enterocinic acid A (**7**) (major) and isoenterocin B (**3**) (minor)

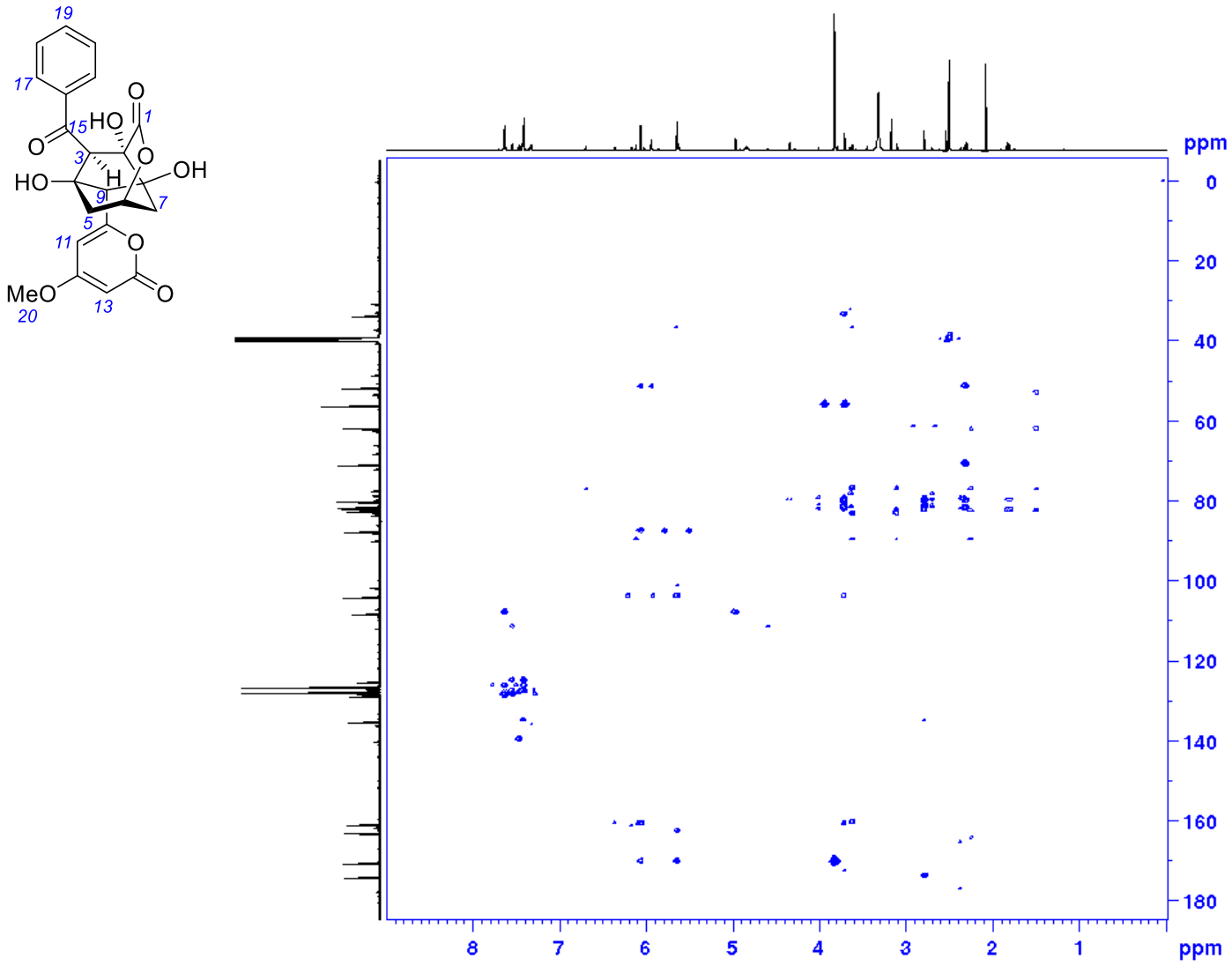


Figure S45. ^{1}H-^{13}C HMBC spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of enterocinic acid A (**7**) (major) and isoenterocin B (**3**) (minor)

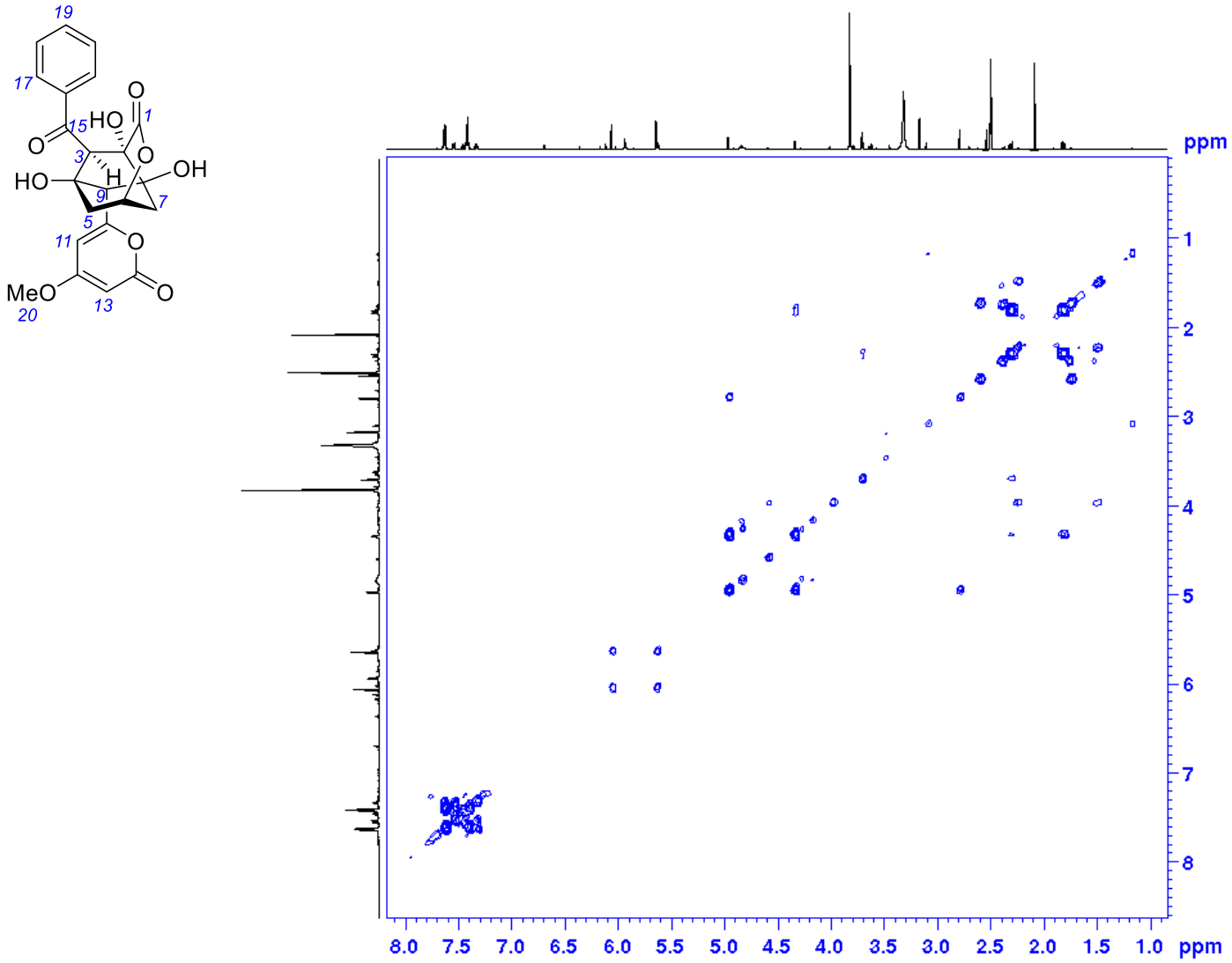


Figure S46. ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-d_6) of a mixture of enterocinic acid A (**7**) (major) and isoenterocin B (**3**) (minor)

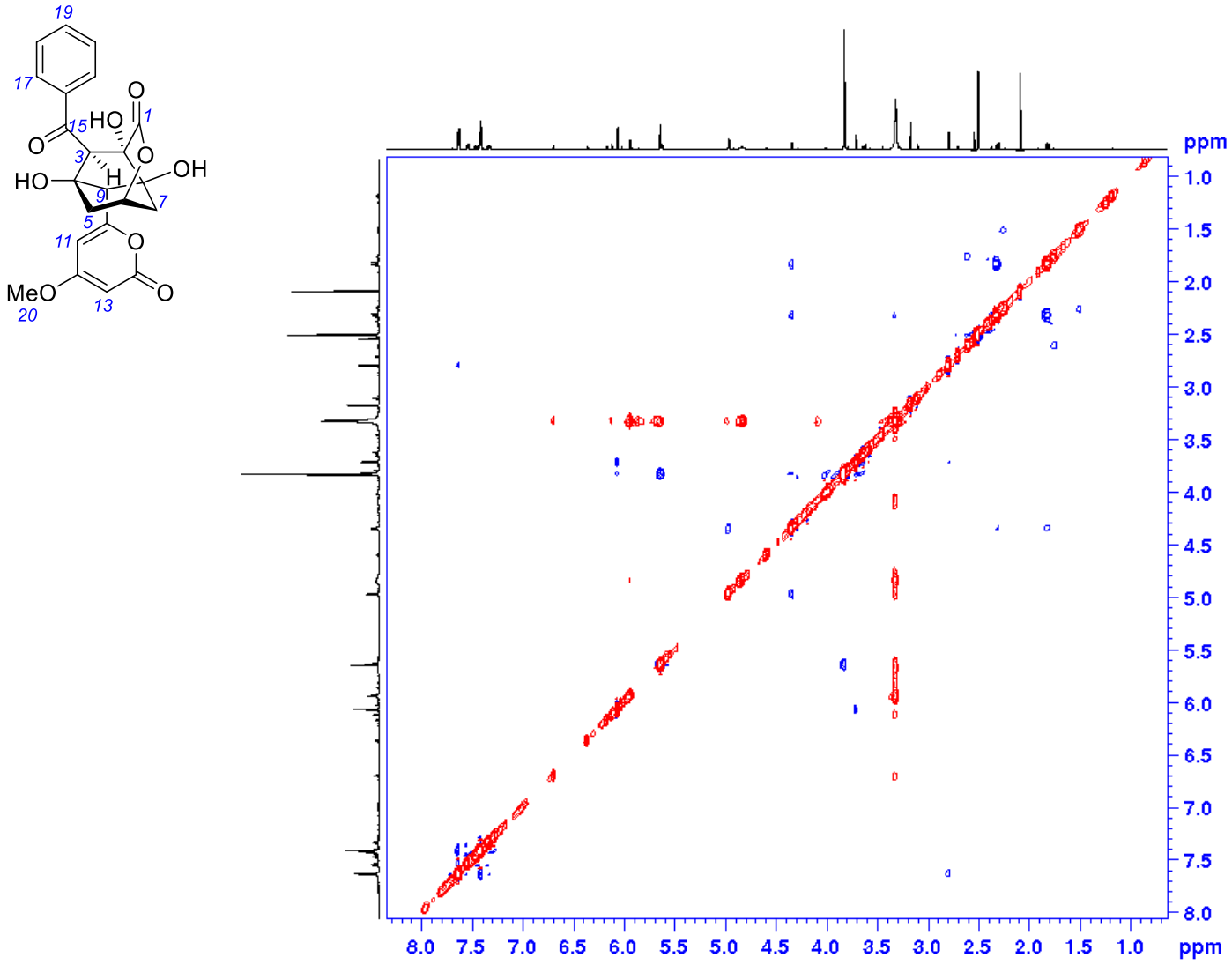


Figure S47. ^{1}H-^{1}H ROESY spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of enterocinic acid A (**7**) (major) and isoenterocin B (**3**) (minor)

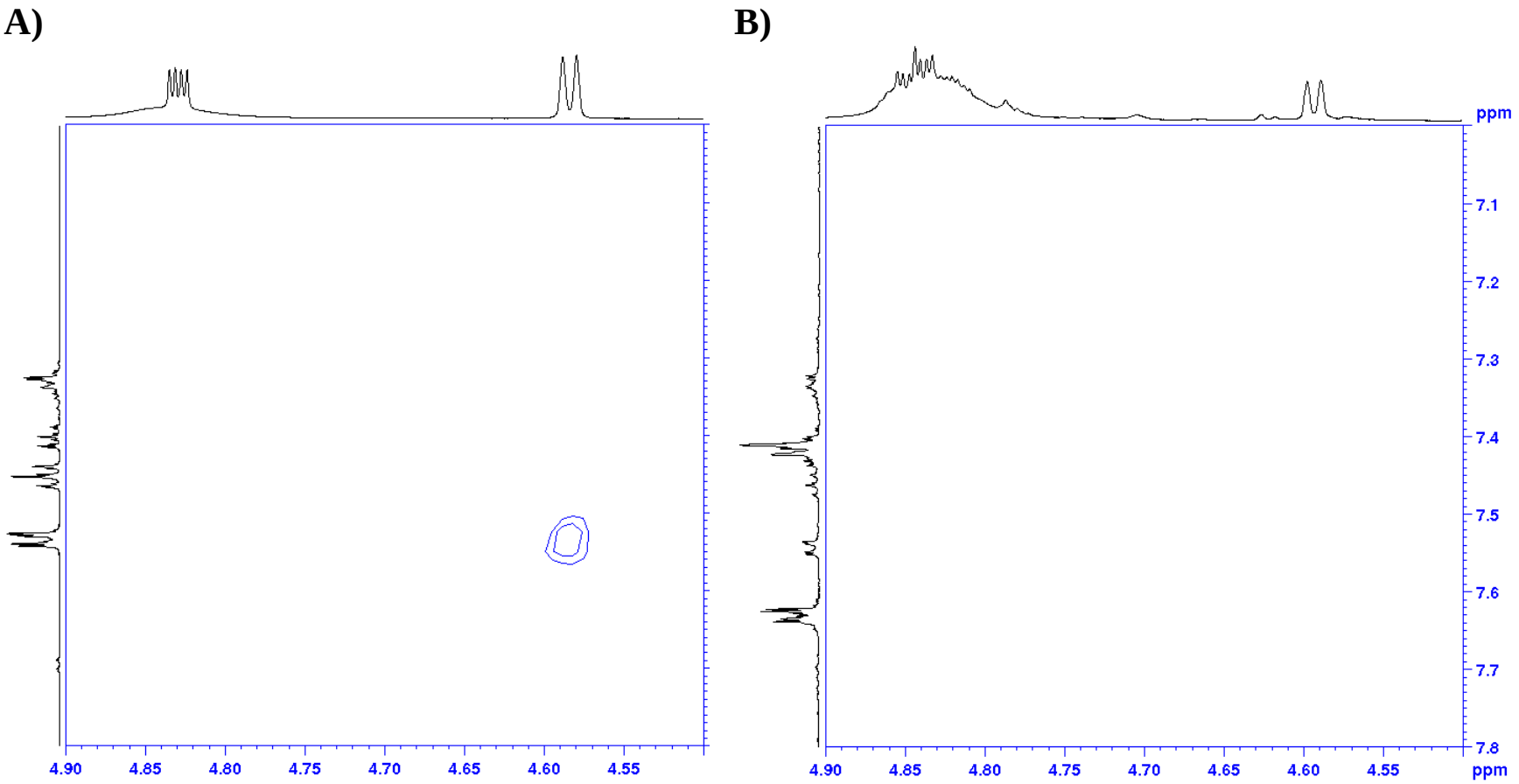


Figure S48. Expansion of ^{1}H-^{1}H ROESYNMR spectrum (600 MHz, D_2O) of A) isoenterocin A (**2**) in mixture with isoenterocin B (**3**) and B) enterocinic acid A (**7**), indicating the presence or absence of the key ROESY correlation between H-5 and H-17.

Figures S49-54. NMR spectra of 5-*O*-arachidoylenterocin (**8**)

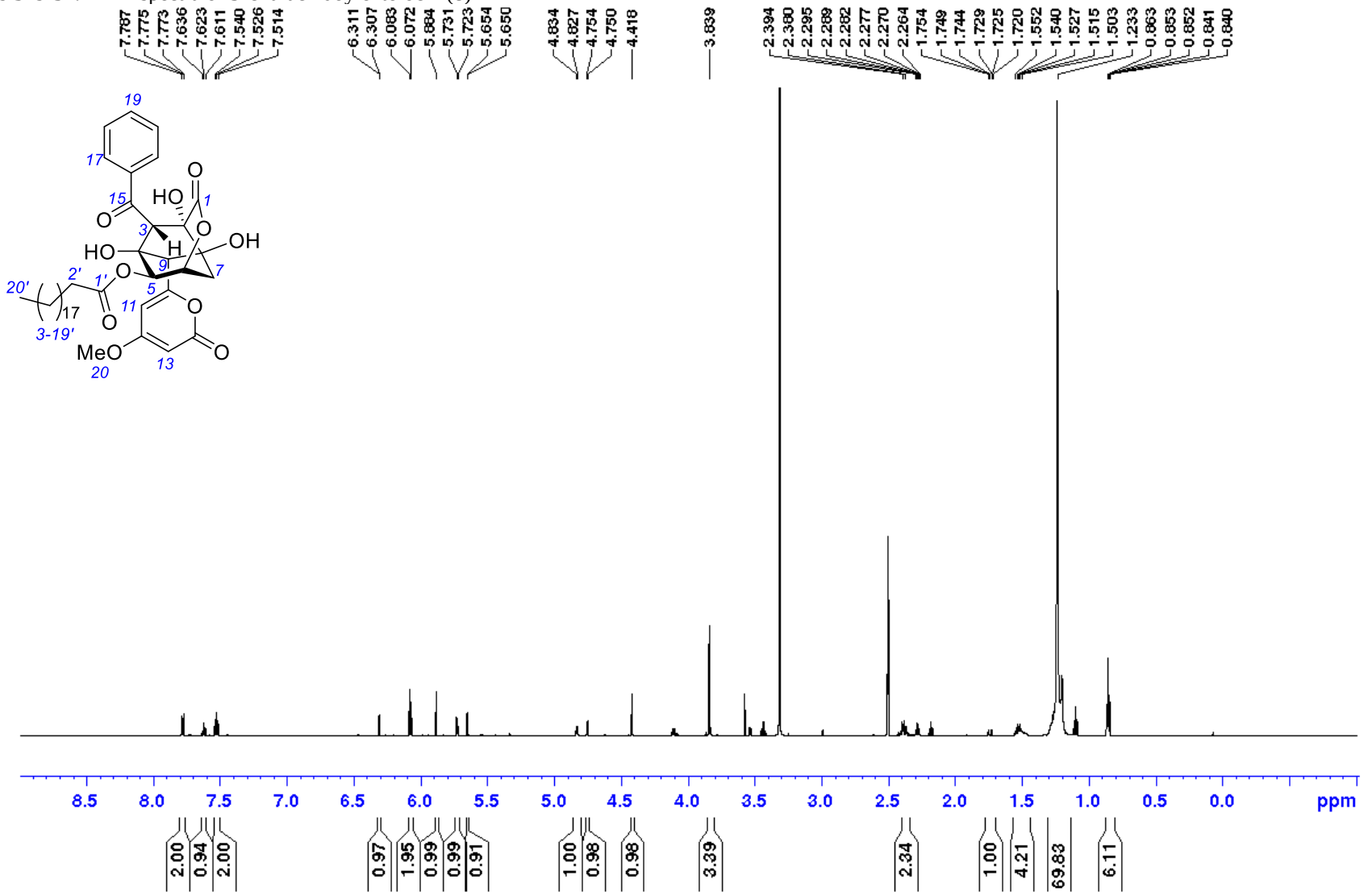


Figure S49. ^{1}H NMR spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-*O*-arachidoylenterocin (**8**) and arachidic acid

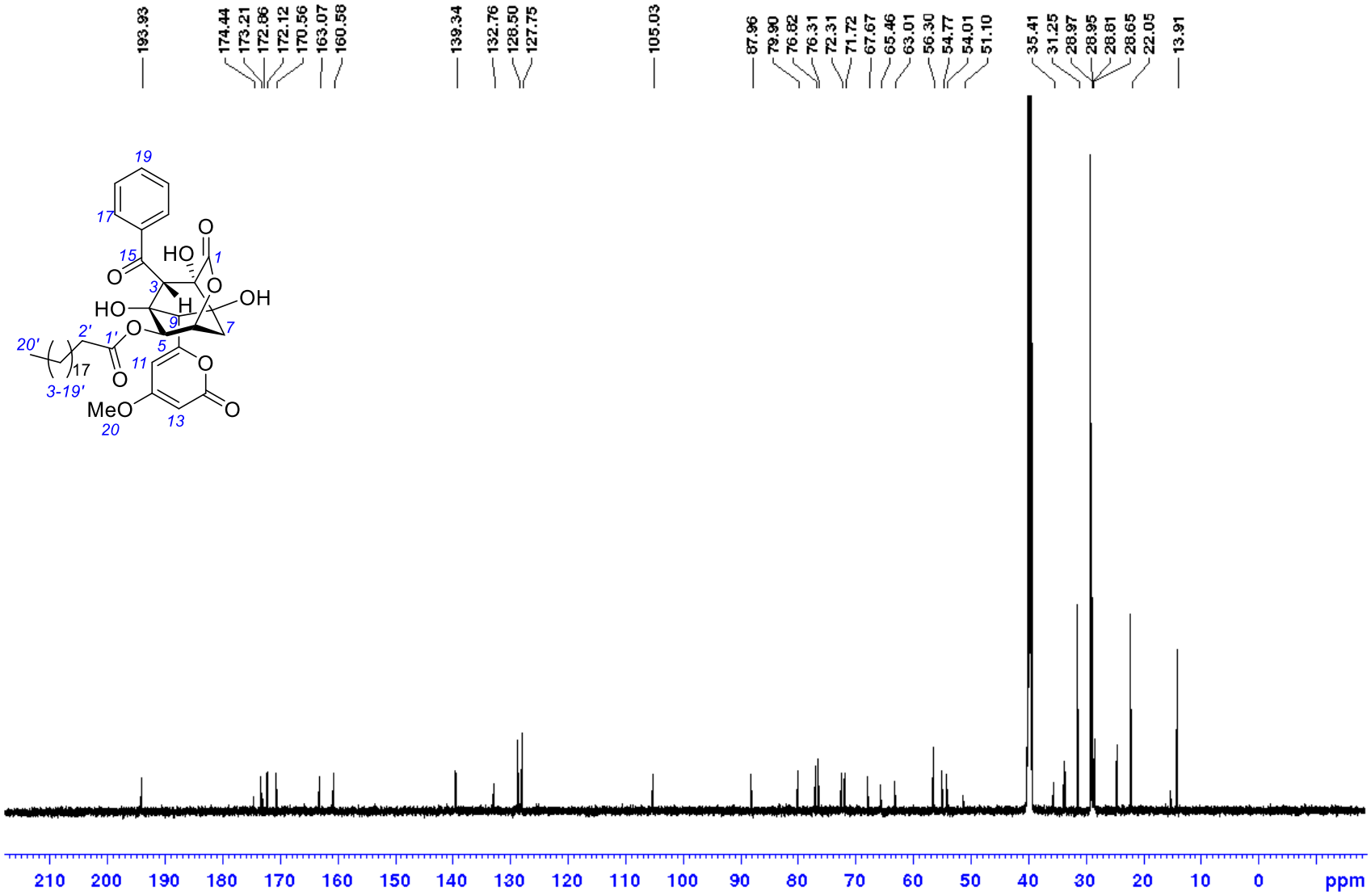


Figure S50. ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of a mixture of 5-*O*-arachidoylenterocin (**8**) and arachidic acid

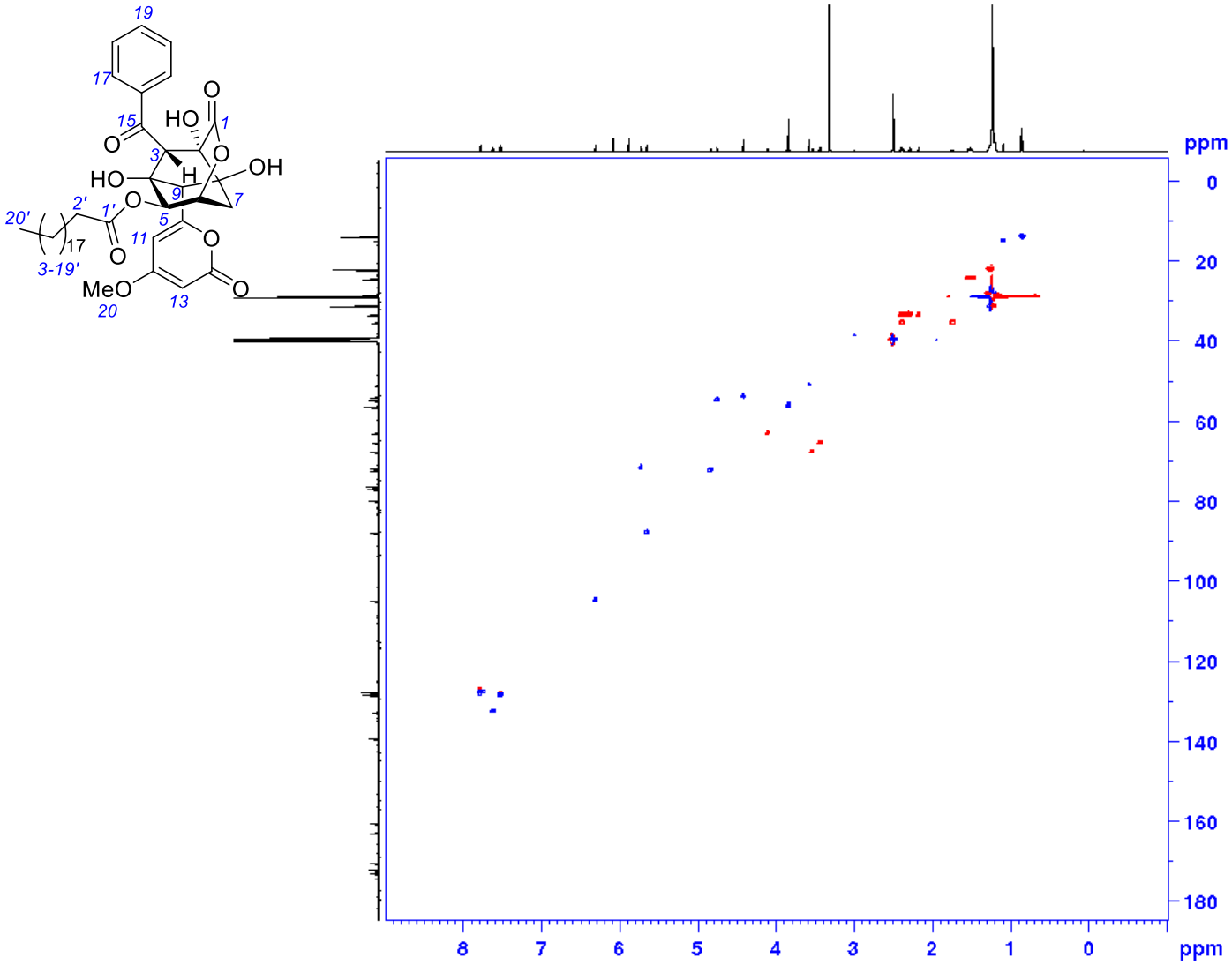


Figure S51. ^{1}H-^{13}C HSQC spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-*O*-arachidoylenterocin (**8**) and arachidic acid

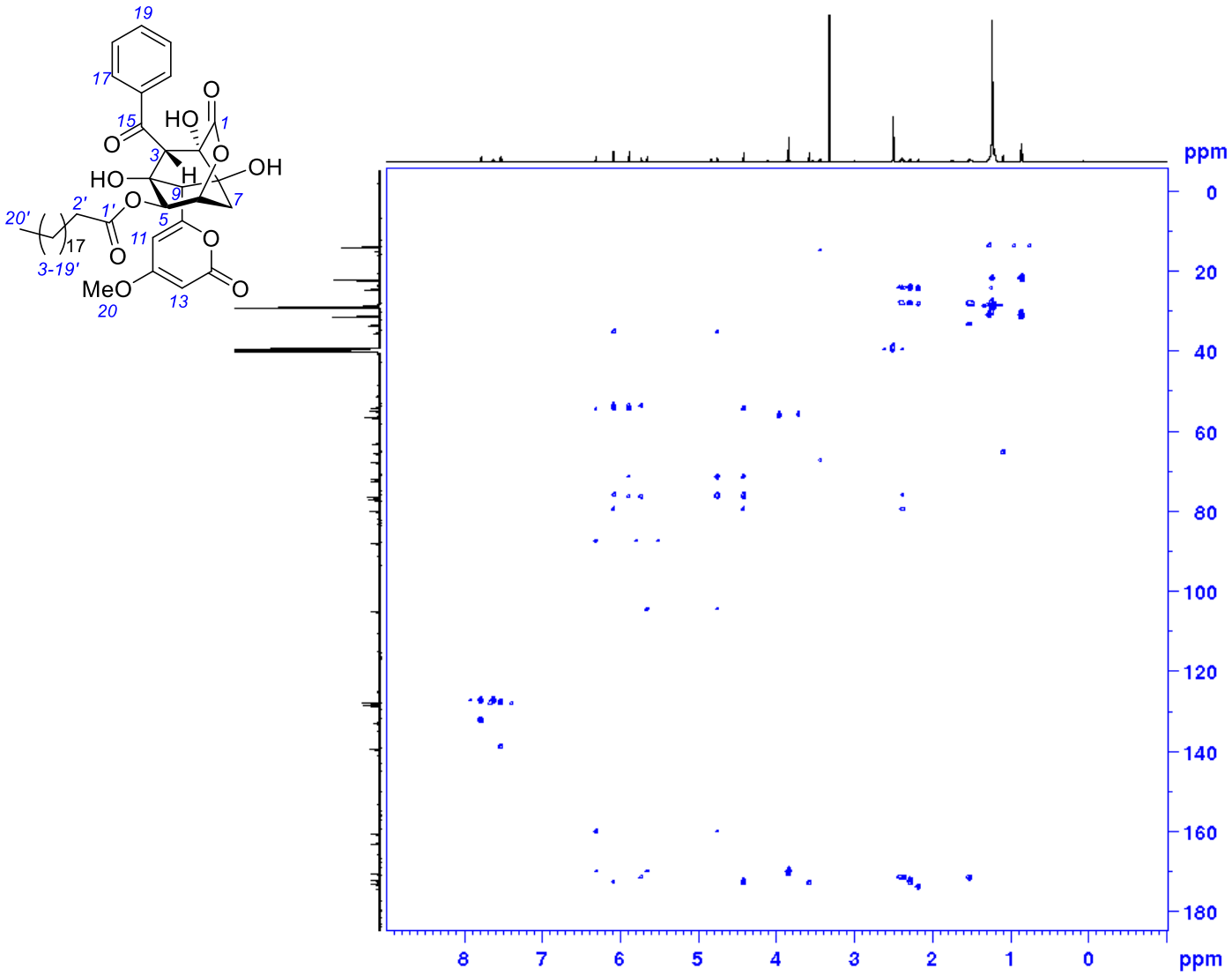


Figure S52. ^{1}H-^{13}C HMBC spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-*O*-arachidoylenterocin (**8**) and arachidic acid

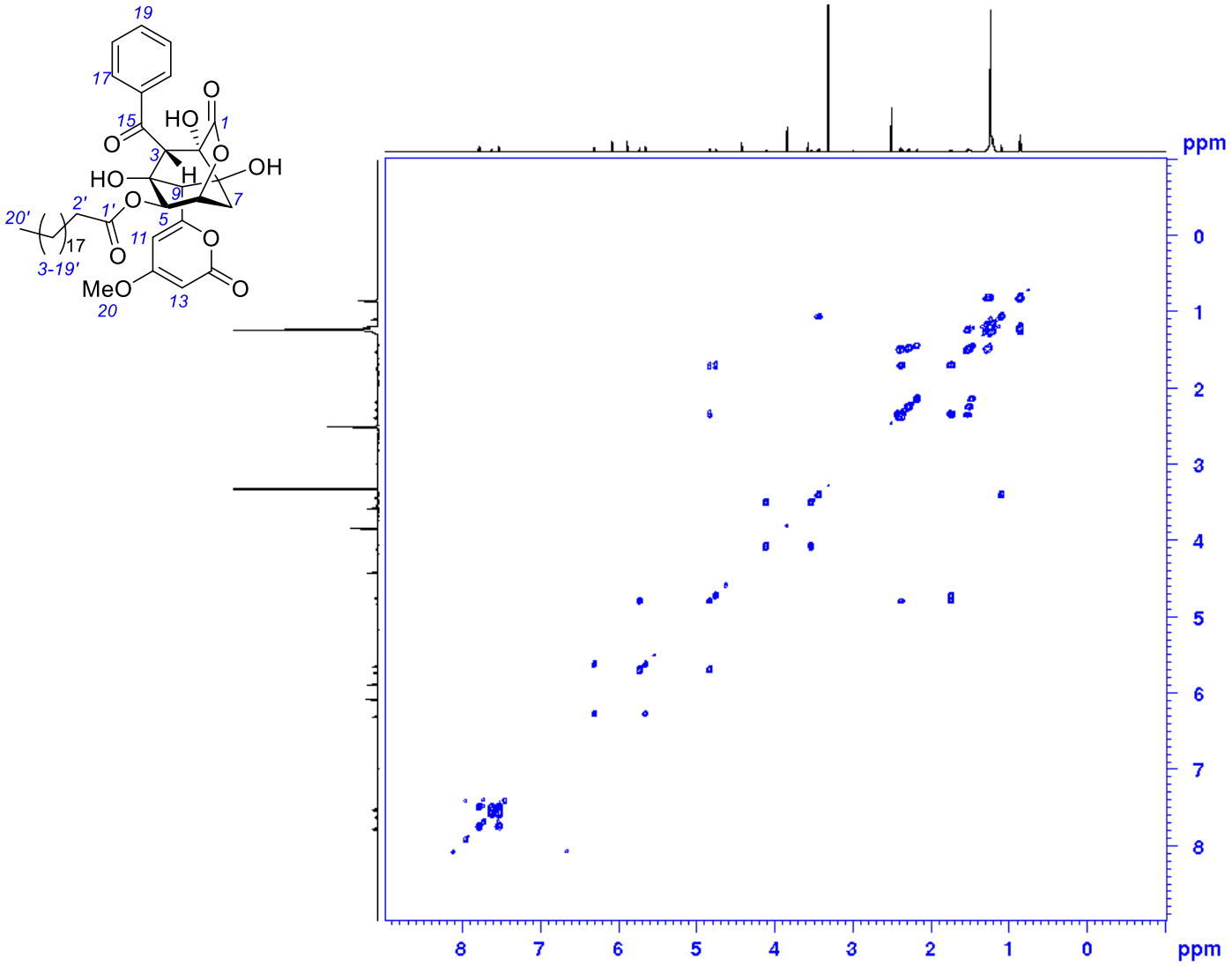


Figure S53. ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-d_6) of a mixture of 5-*O*-arachidoylenterocin (**8**) and arachidic acid

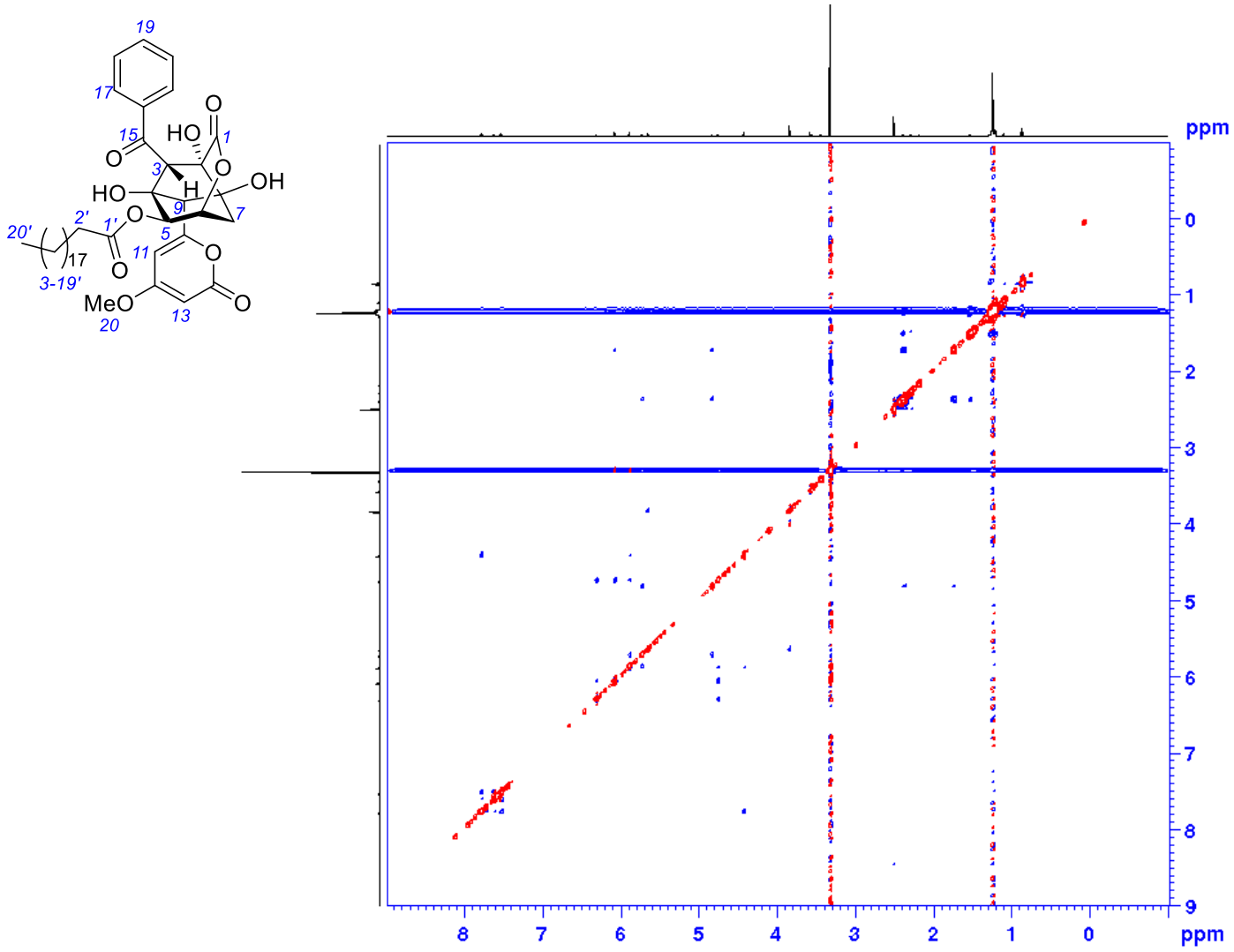


Figure S54. ^{1}H-^{1}H ROESY spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-*O*-arachidoylenterocin (**8**) and arachidic acid

Figure S55-60. NMR spectra of 5-*O*-behenoylenterocin (**9**)

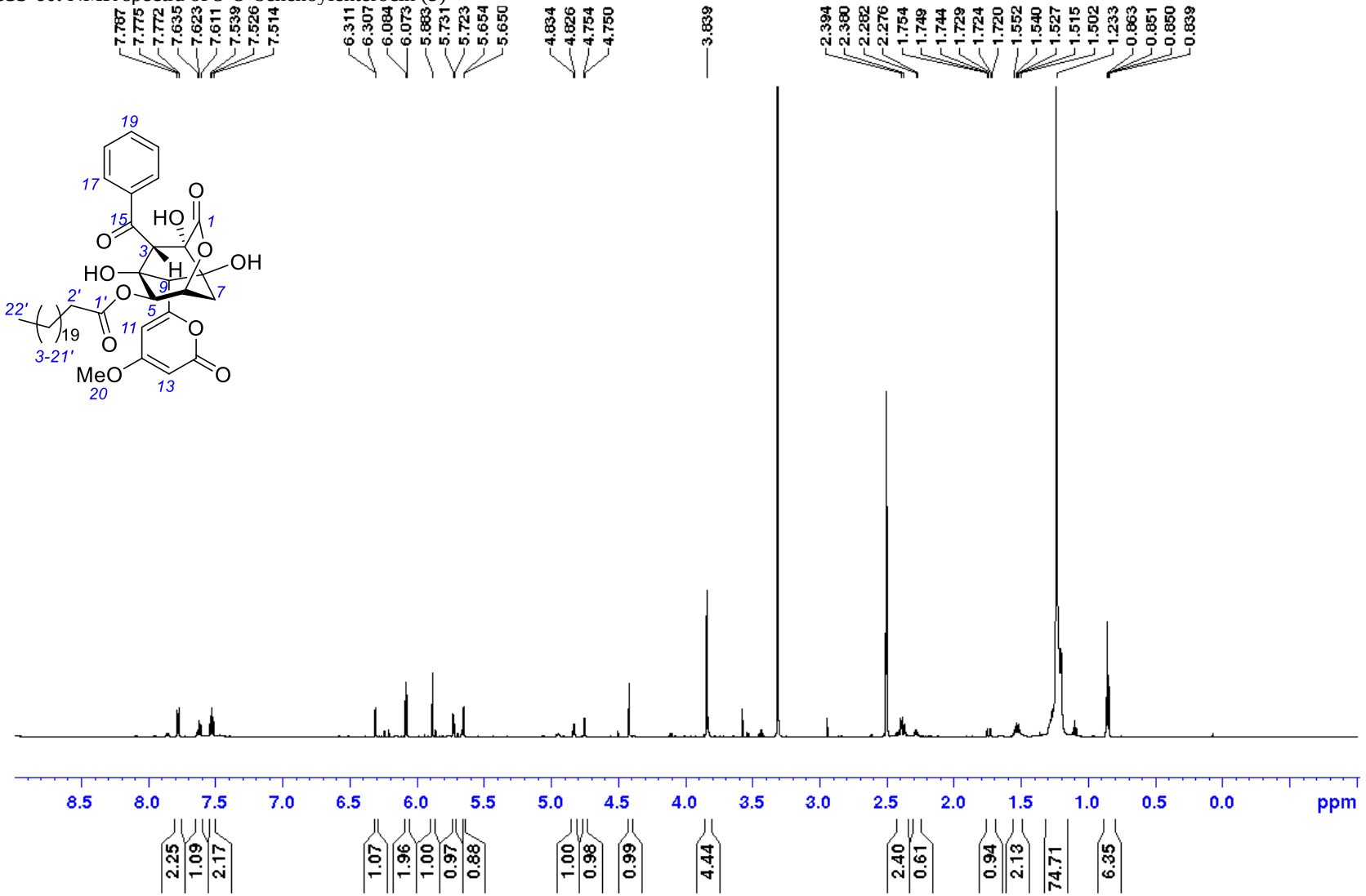


Figure S55. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of a mixture of 5-*O*-behenoylenterocin (**9**) with behenic acid

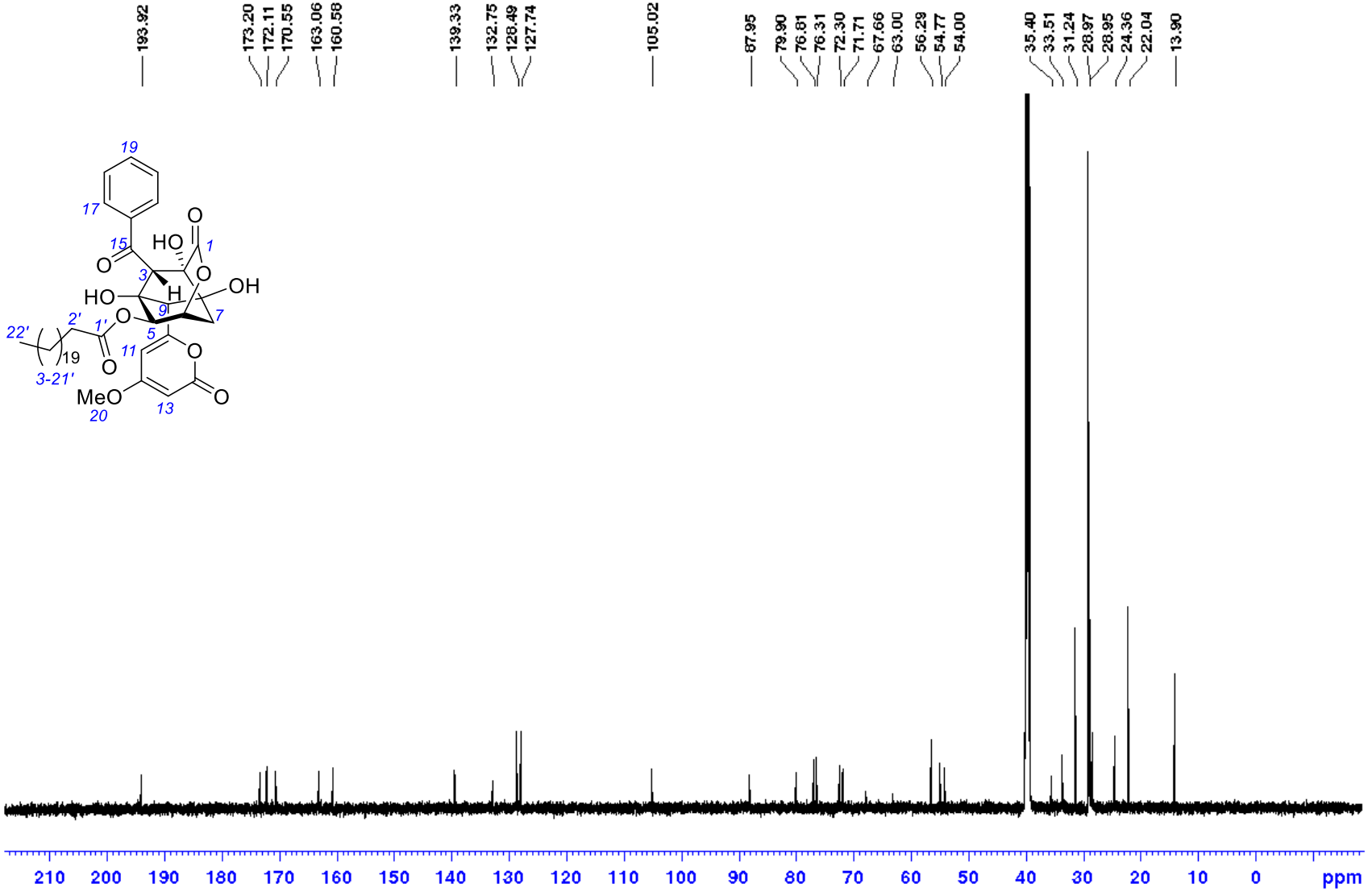


Figure S56. ^{13}C NMR spectrum (150 MHz, DMSO-*d*$_6$) of a mixture of 5-*O*-behenoylenterocin (**9**) with behenic acid

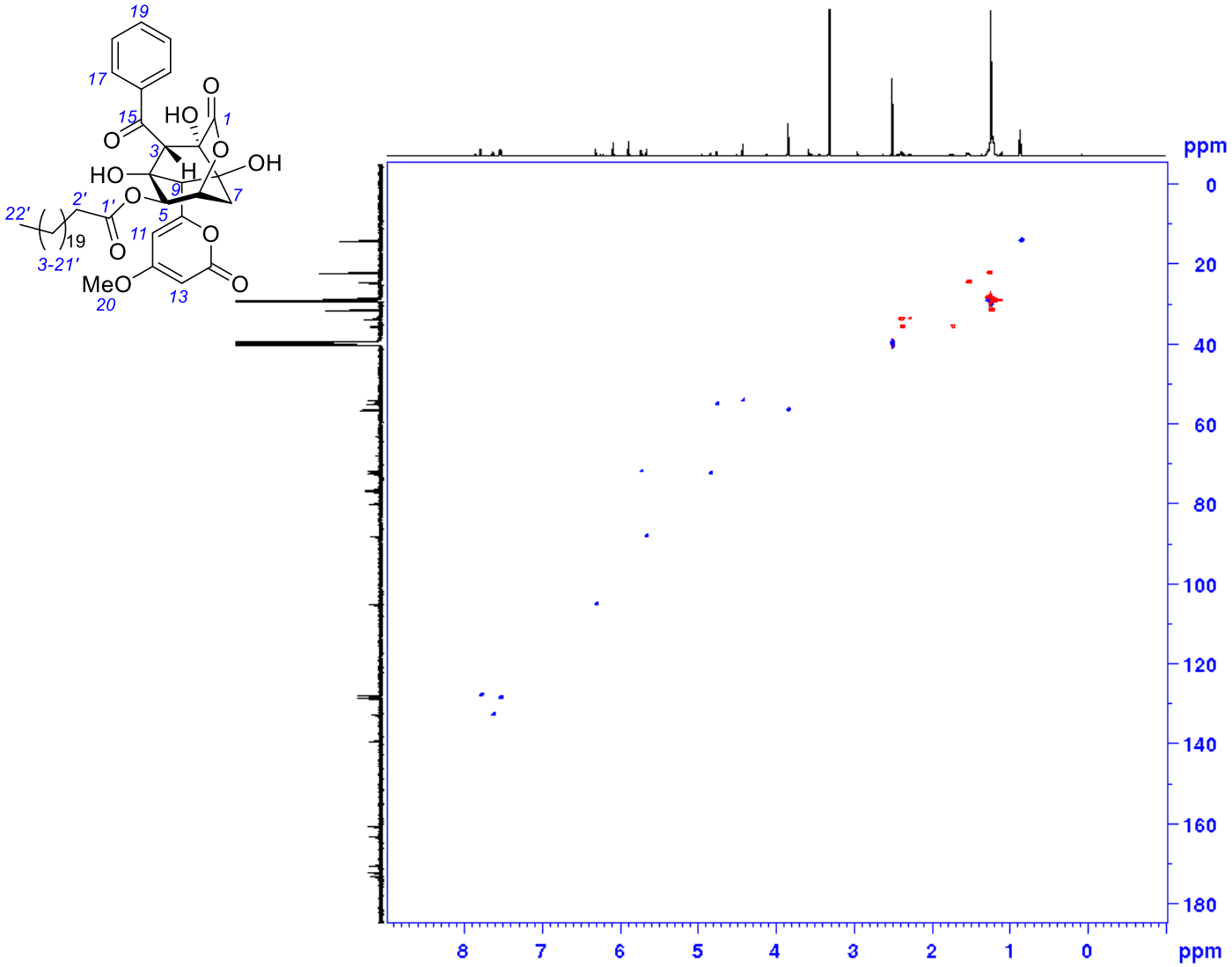


Figure S57. ^{1}H-^{13}C HSQC spectrum (600 MHz, DMSO-d_6) of a mixture of 5-*O*-behenoylenterocin (**9**) with behenic acid

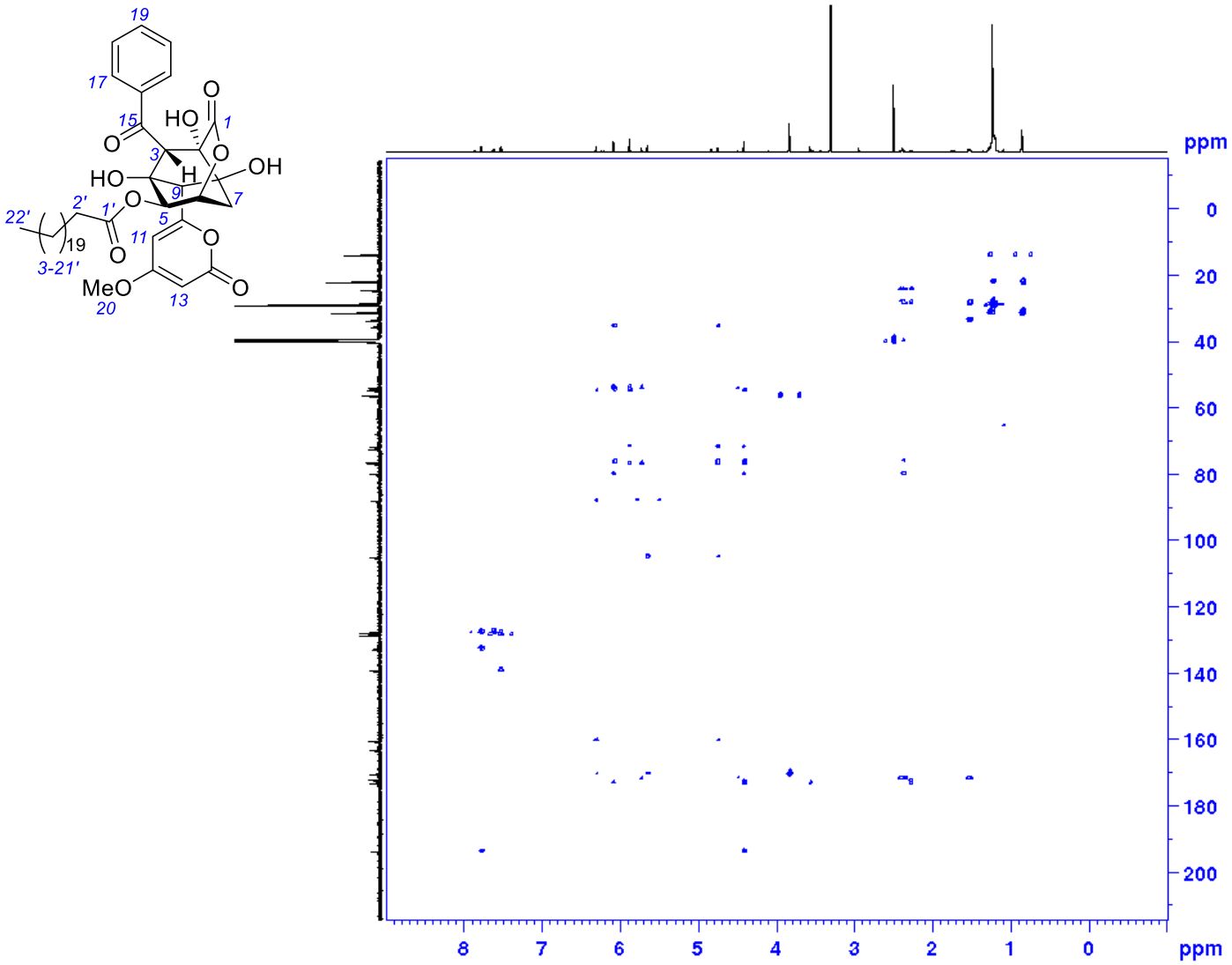


Figure S58. ^{1}H-^{13}C HMBC spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-*O*-behenoylenterocin (**9**) with behenic acid

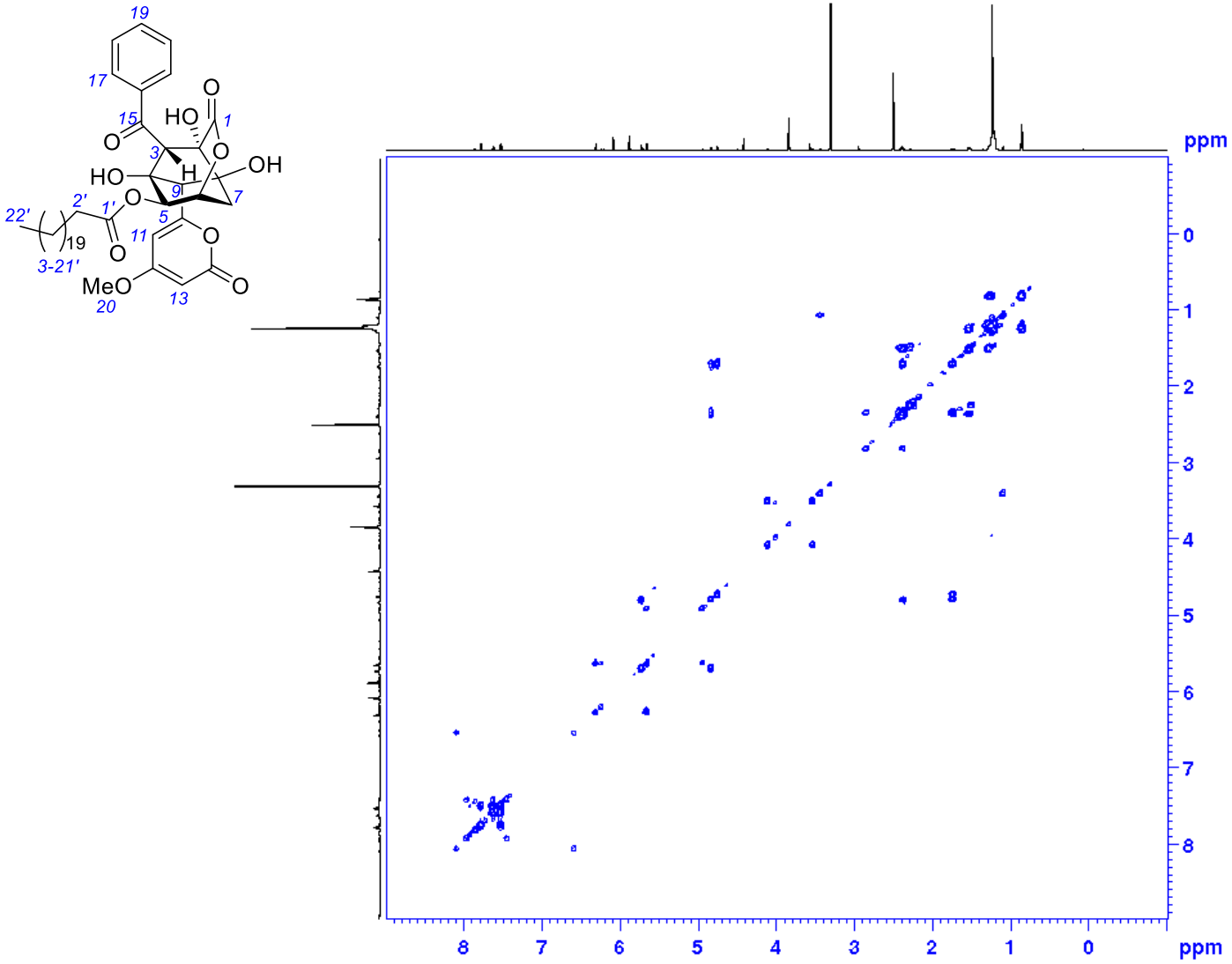


Figure S59. ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-*d*$_6$) of a mixture of 5-*O*-behenoylenterocin (**9**) with behenic acid

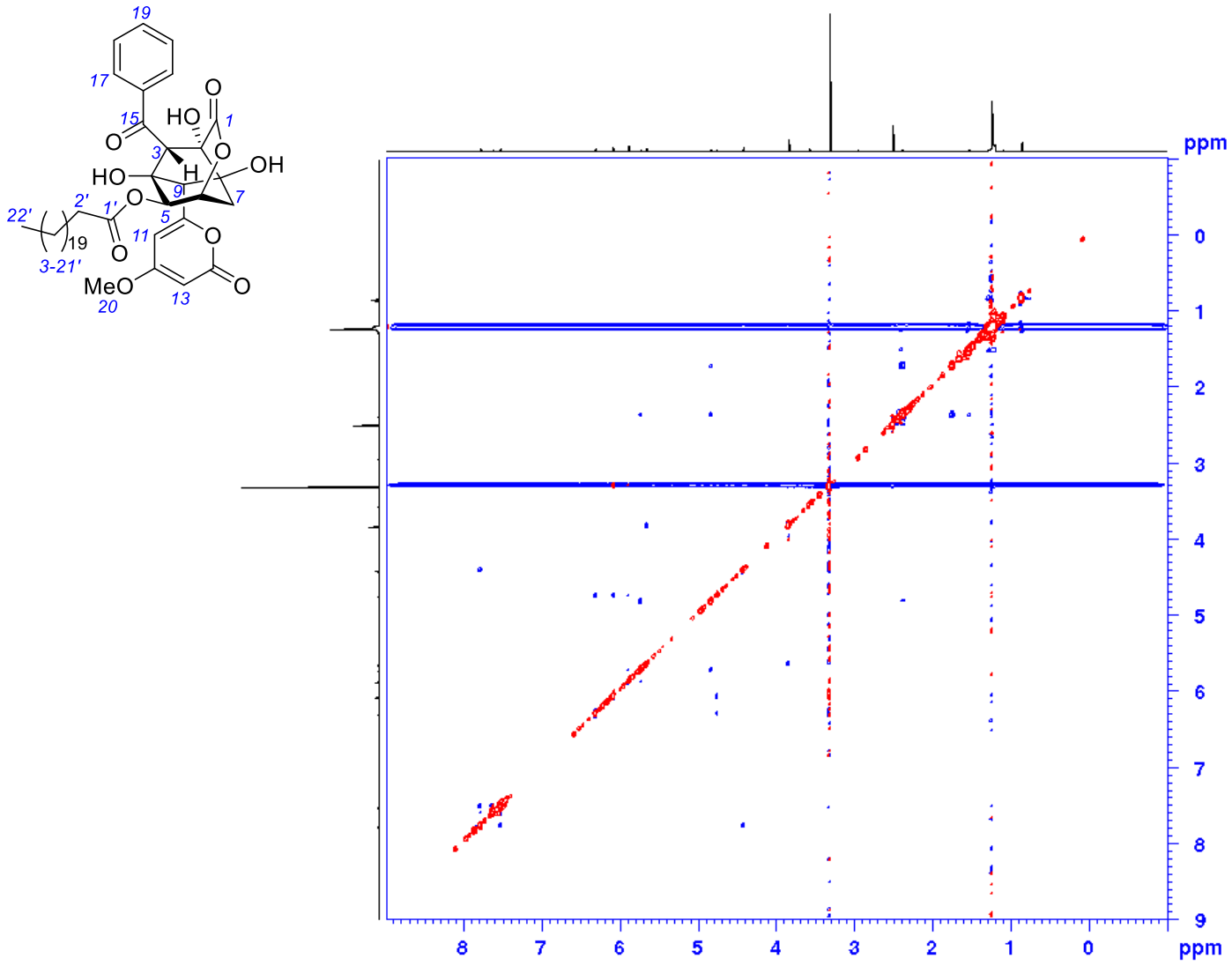


Figure S60. ^{1}H-^{1}H ROESY spectrum (600 MHz, DMSO-*d*6) of a mixture of 5-*O*-behenoylenterocin (**9**) with behenic acid

Figure S61-66. NMR spectra of 5-*O*-palmitylenterocin (**10**)

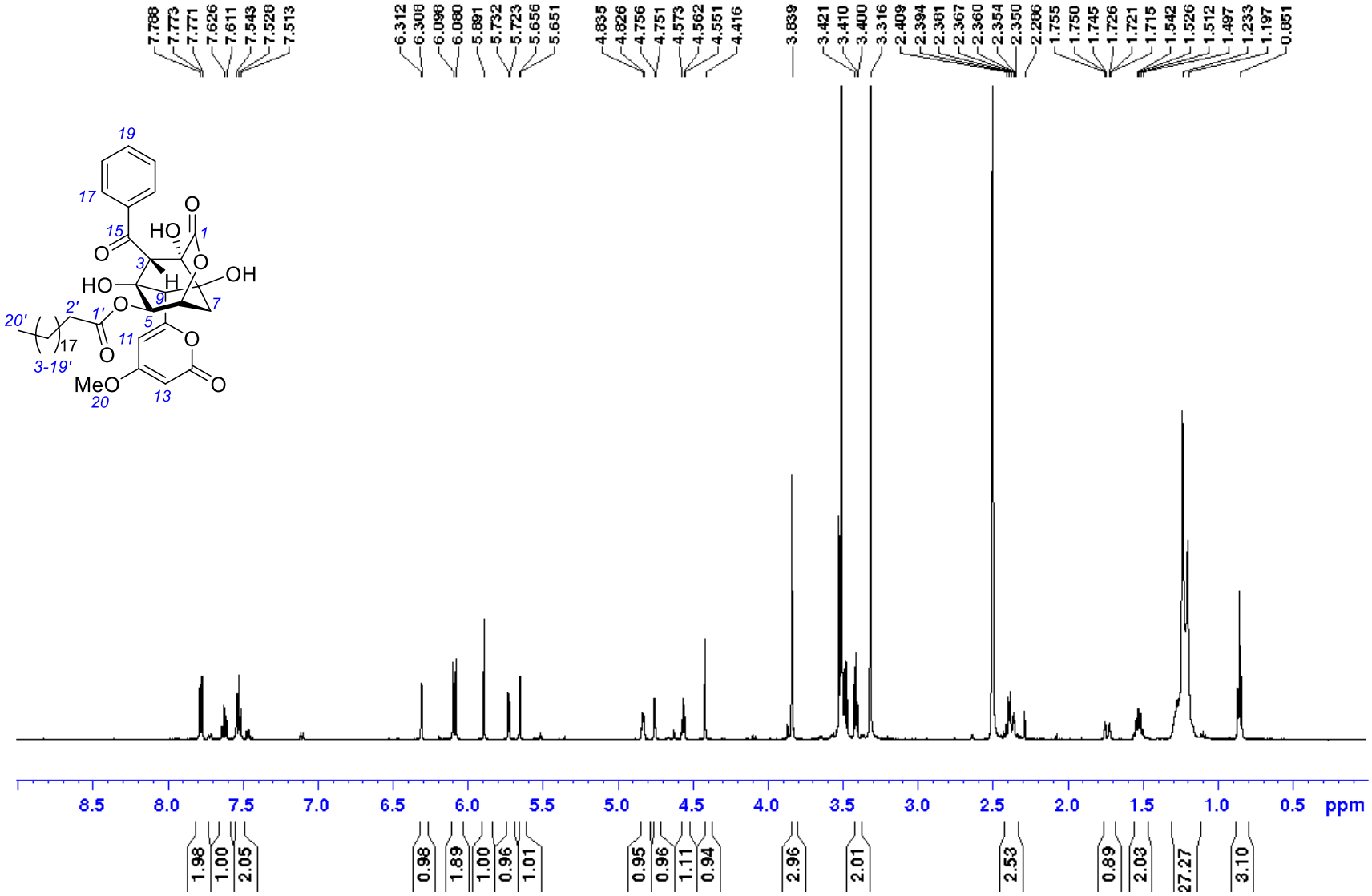


Figure S61. ^{1}H NMR spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-palmitoylenterocin (**10**)

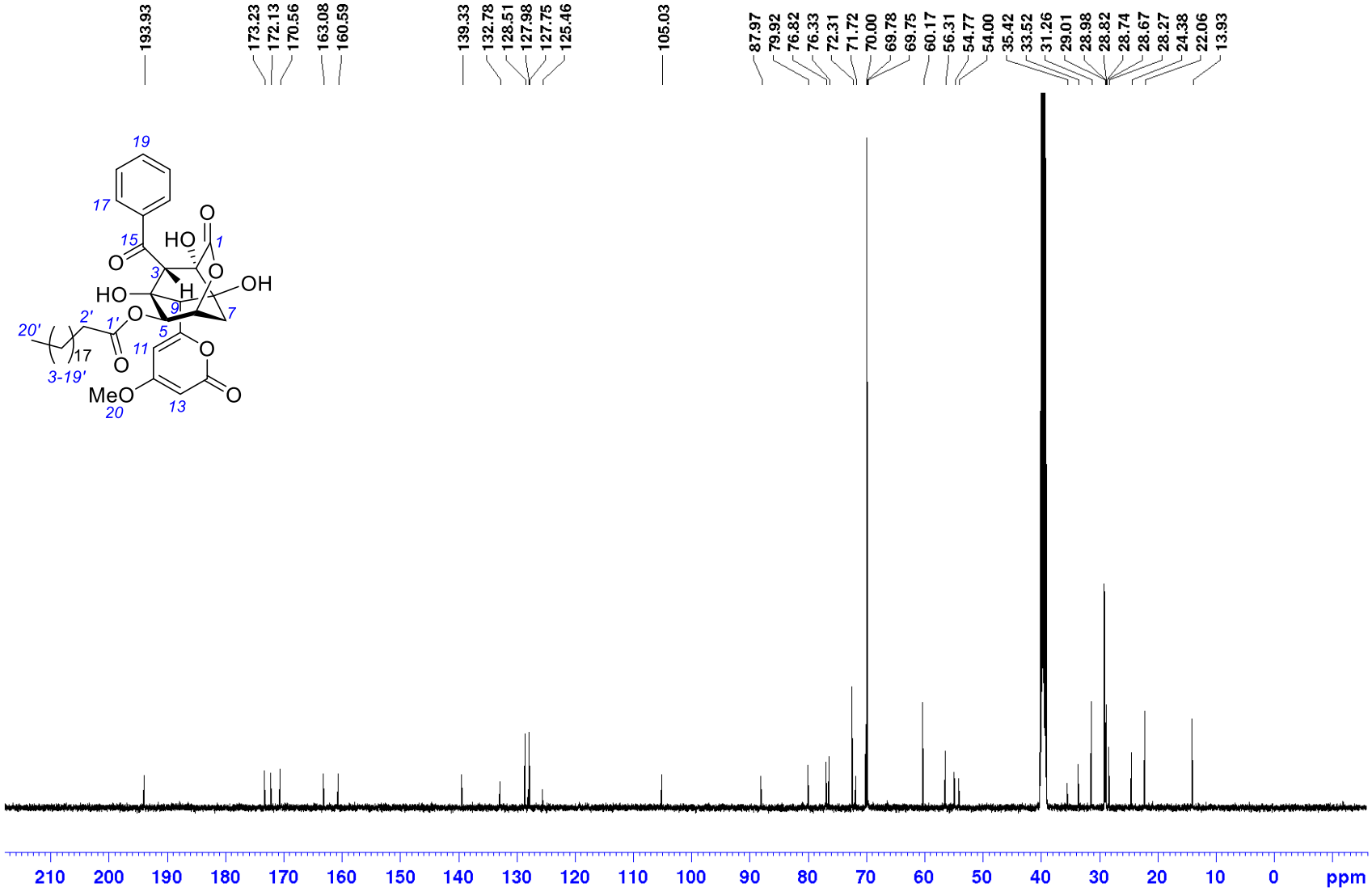


Figure S62. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of 5-*O*-palmitoylenterocin (**10**)

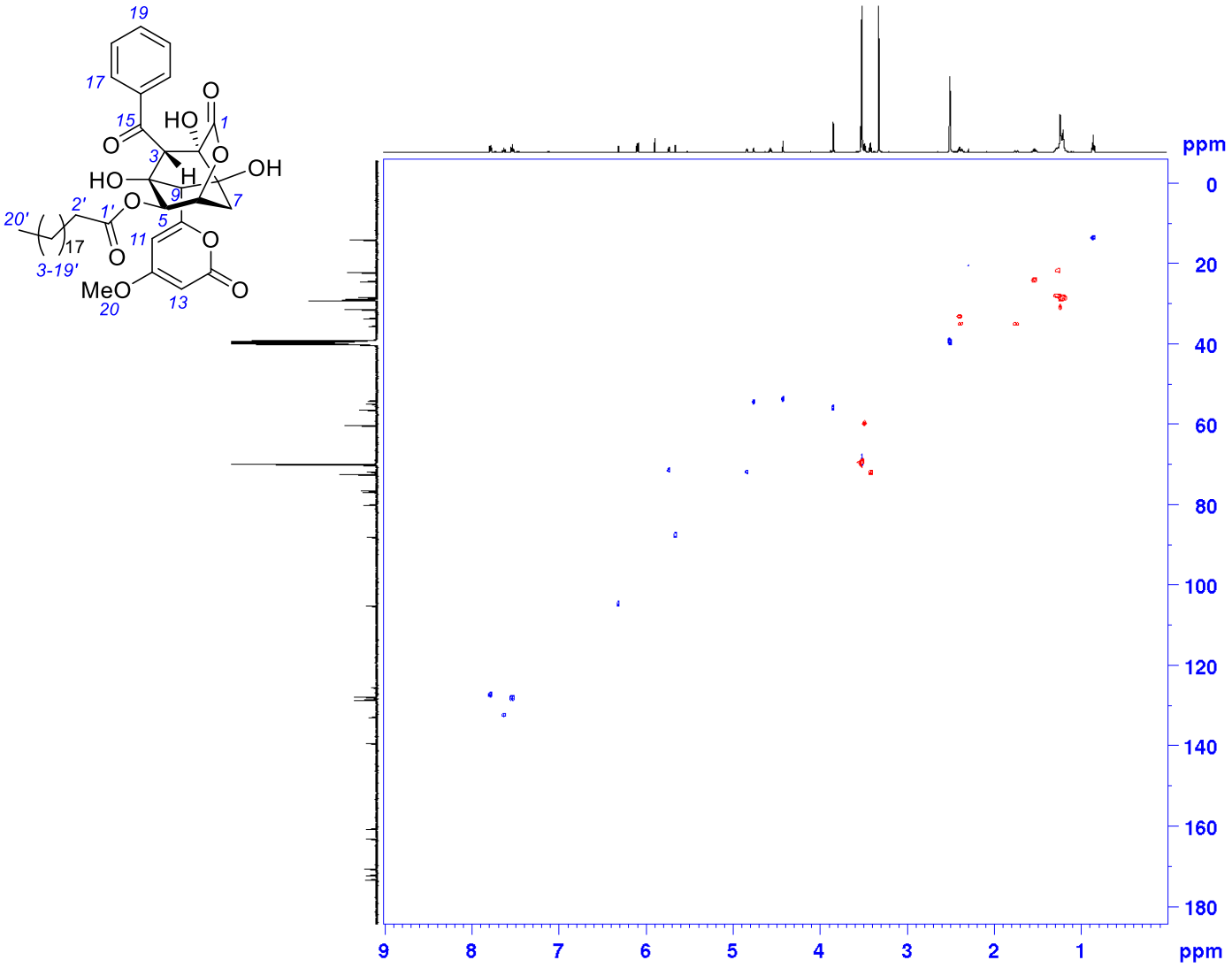


Figure S63. ^{1}H-^{13}C HSQC spectrum (500 MHz, DMSO-*d*6) of 5-*O*-palmitoylenterocin (**10**)

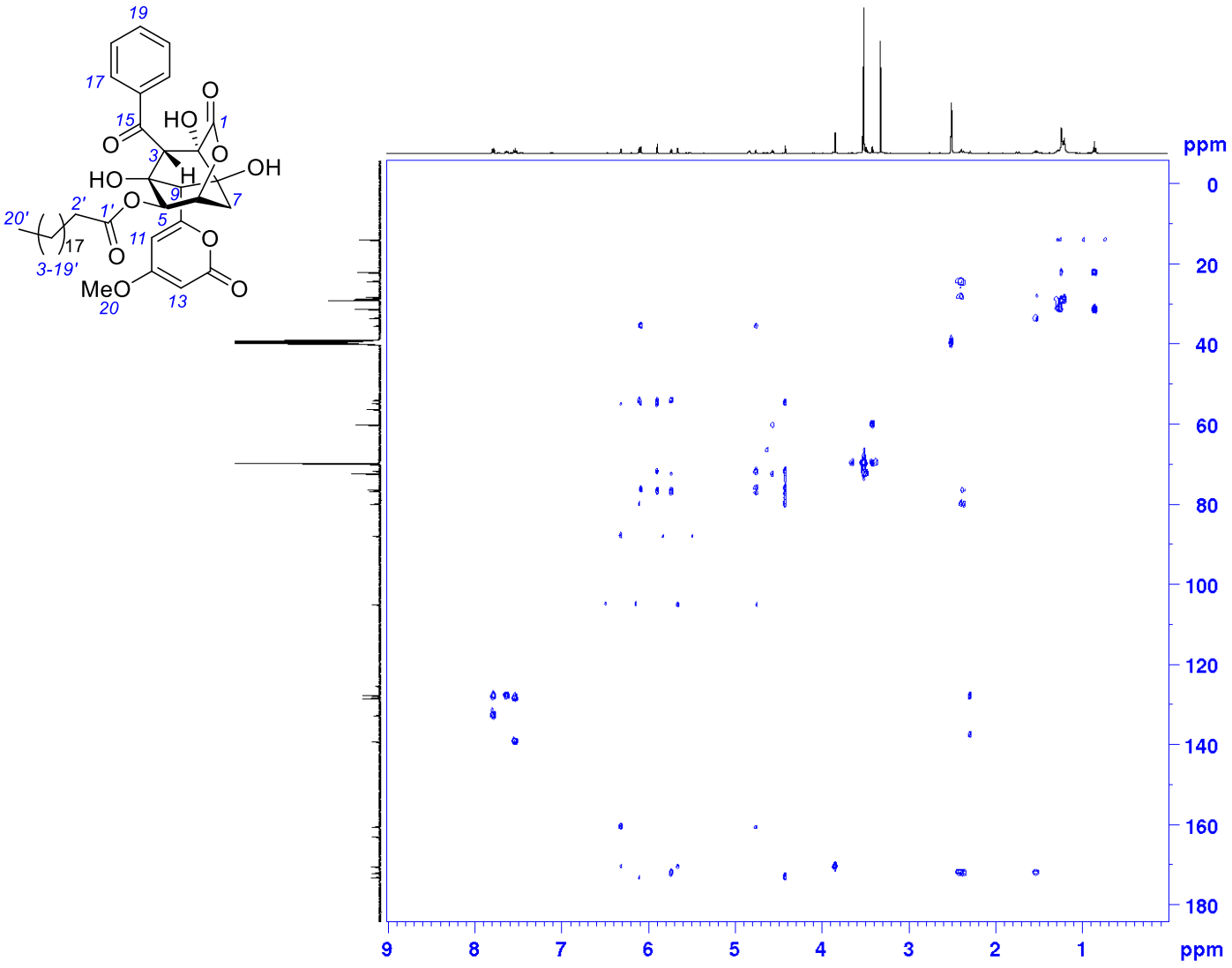


Figure S64. ^{1}H-^{13}C HMBC spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-palmitoylenterocin (**10**)

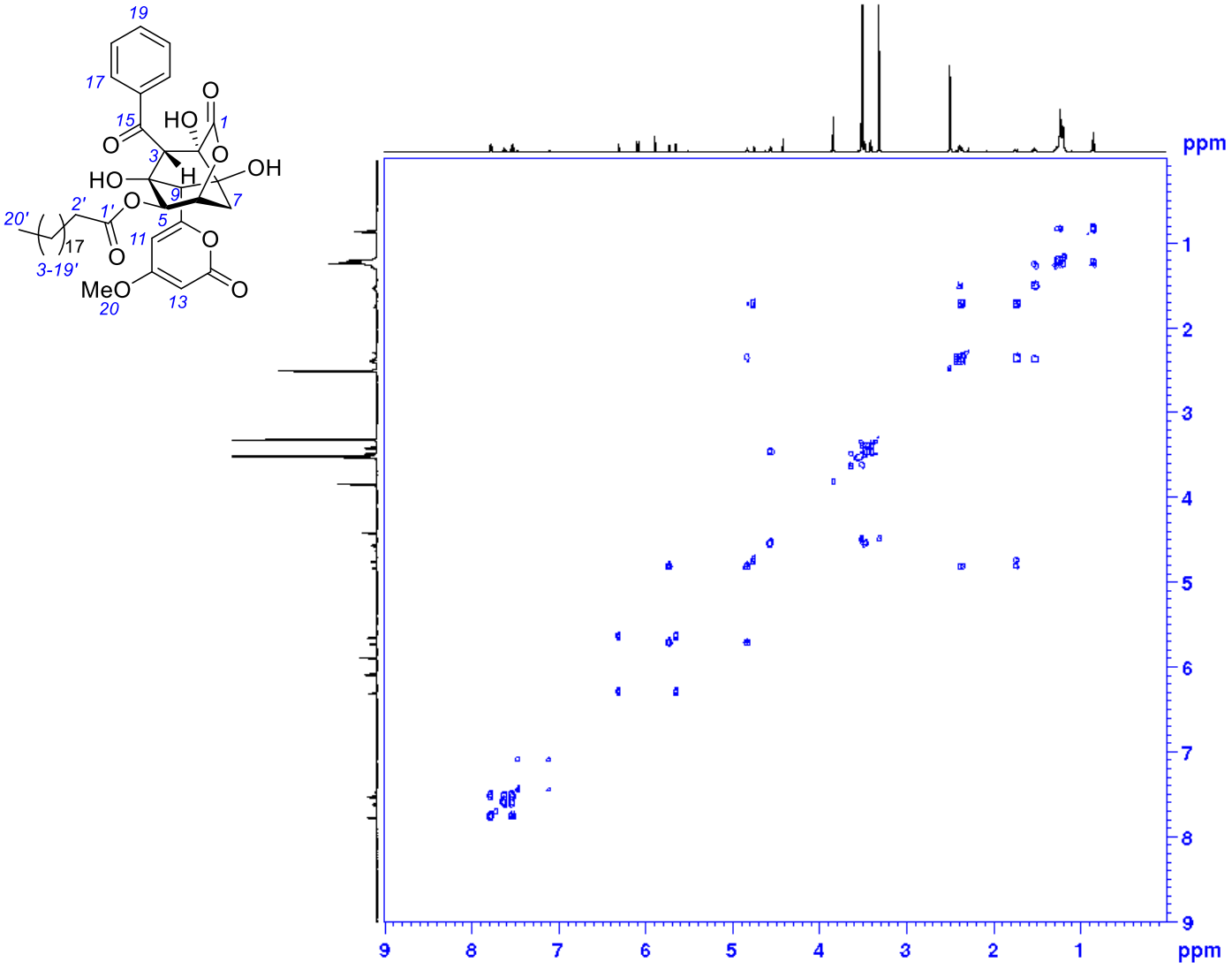


Figure S65. ^{1}H-^{1}H COSY spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-palmitoylenterocin (**10**)

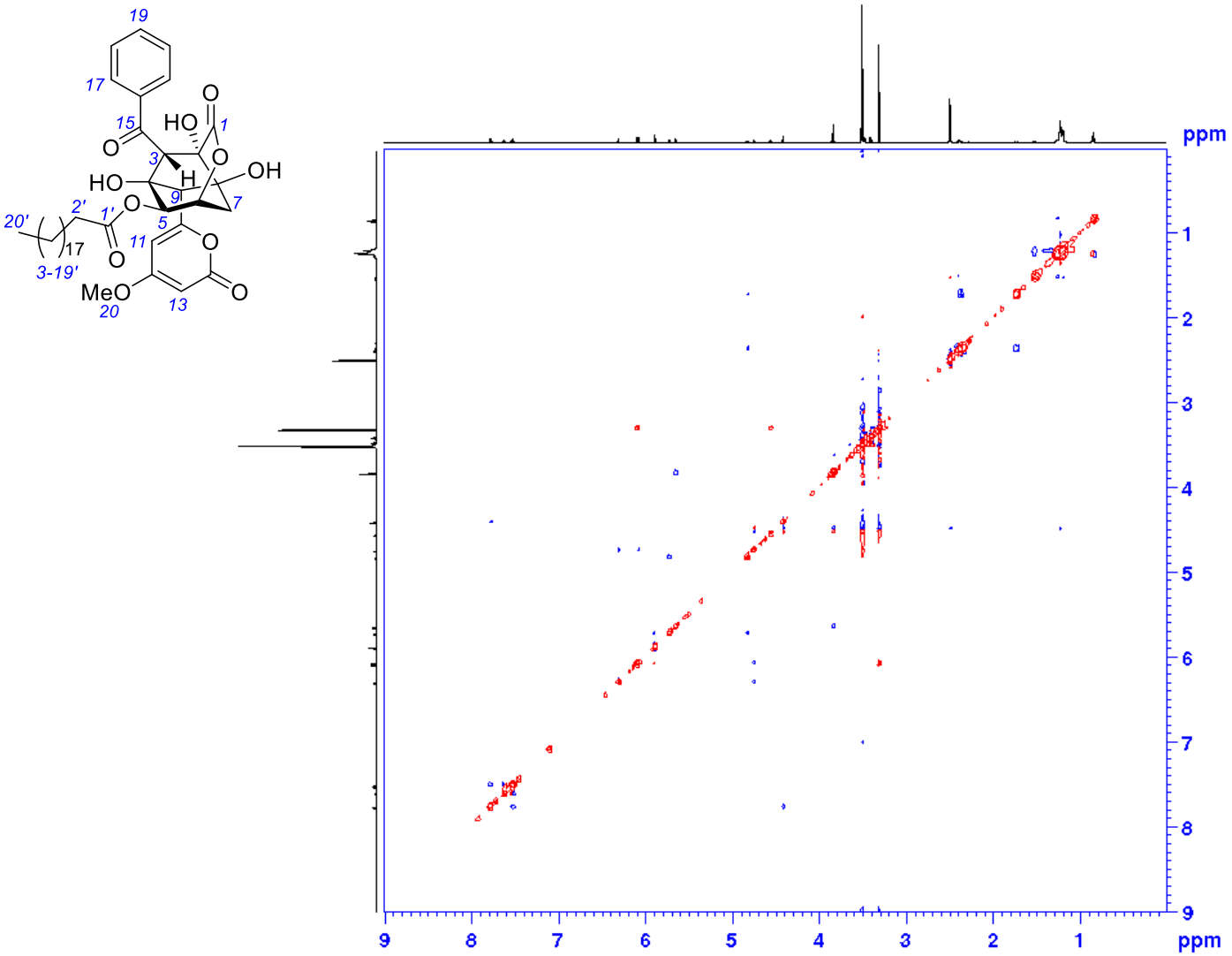


Figure S66. ^{1}H-^{1}H ROESY spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-palmitoylenterocin (**10**)

Figures S67-72. NMR spectra of 5-*O*-acetylenterocin (**11**)

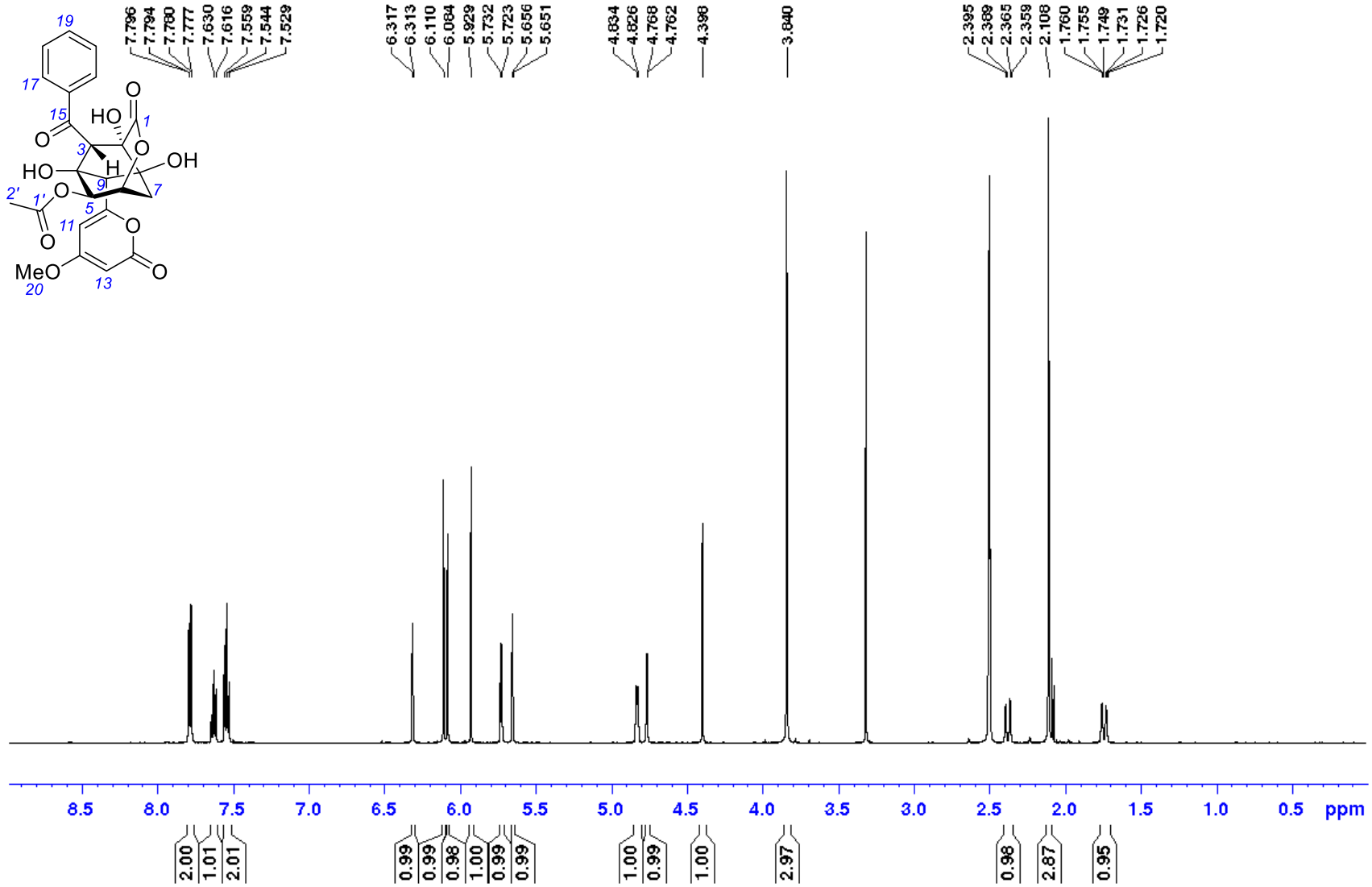


Figure S67. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of 5-*O*-acetylenterocin (**11**)

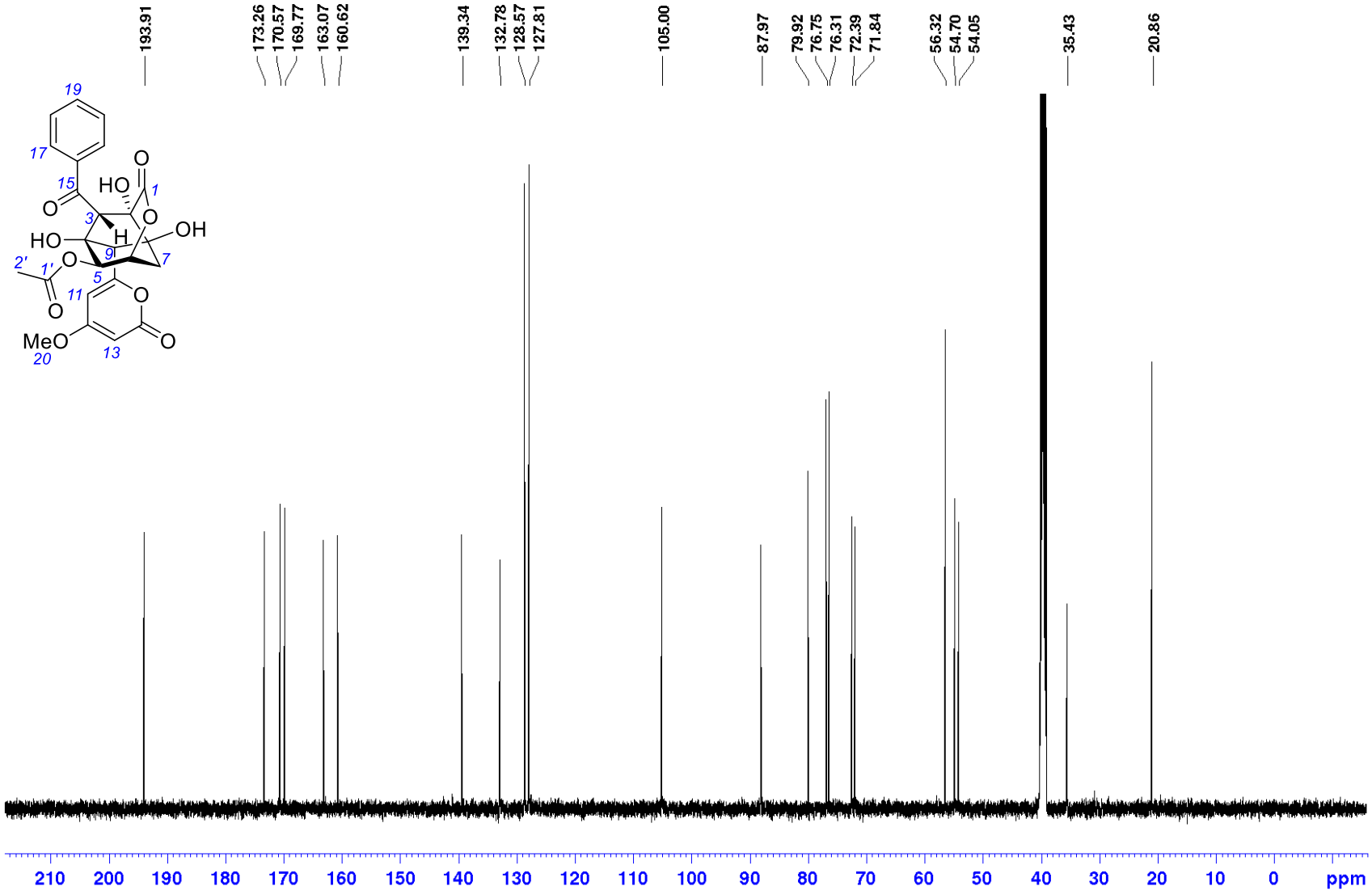


Figure S68. ^{13}C NMR spectrum (125 MHz, DMSO-*d*$_6$) of 5-*O*-acetylenterocin (**11**)

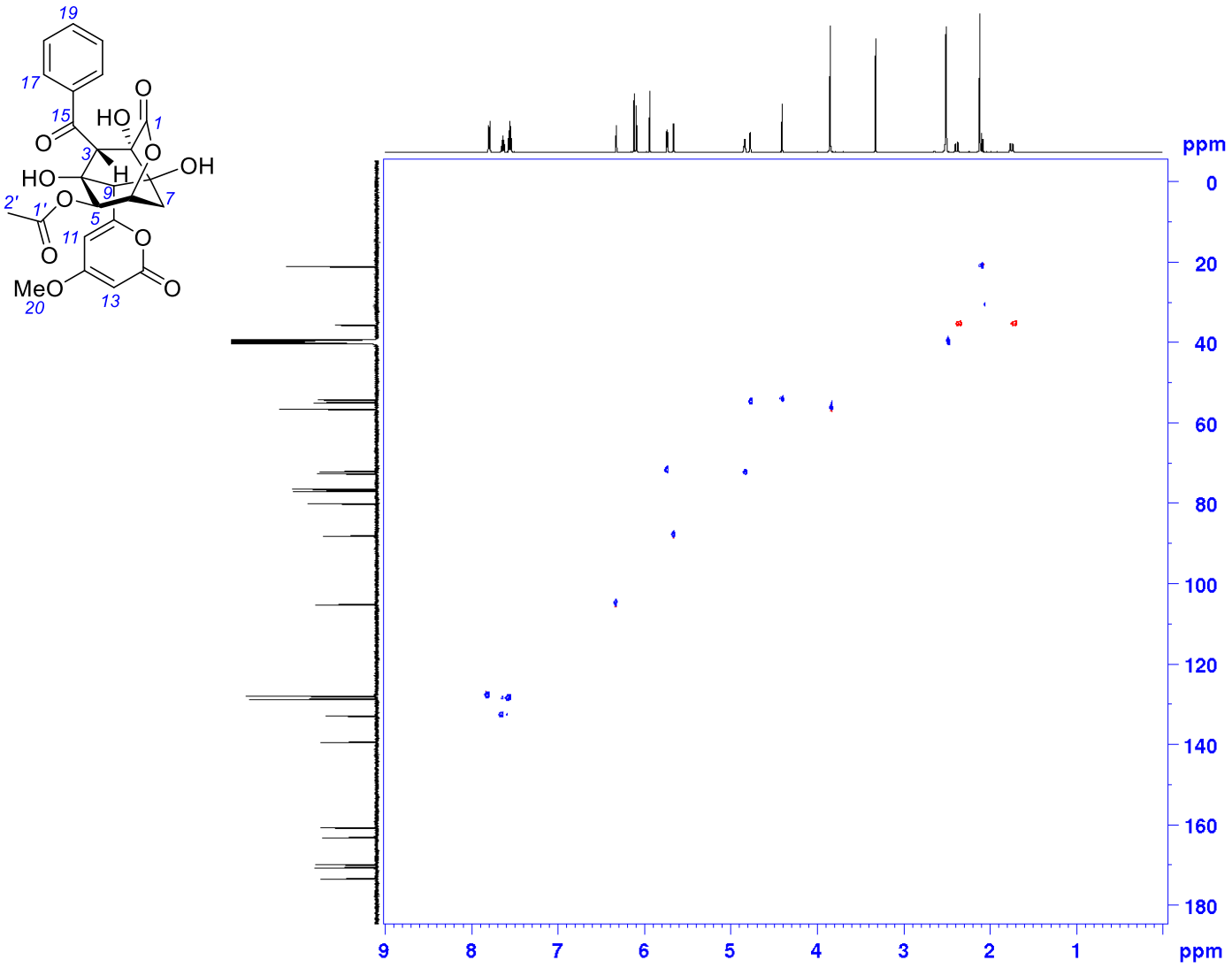


Figure S69. ^{1}H-^{13}C HSQC spectrum (500 MHz, DMSO-*d*6) of 5-*O*-acetylenterocin (**11**)

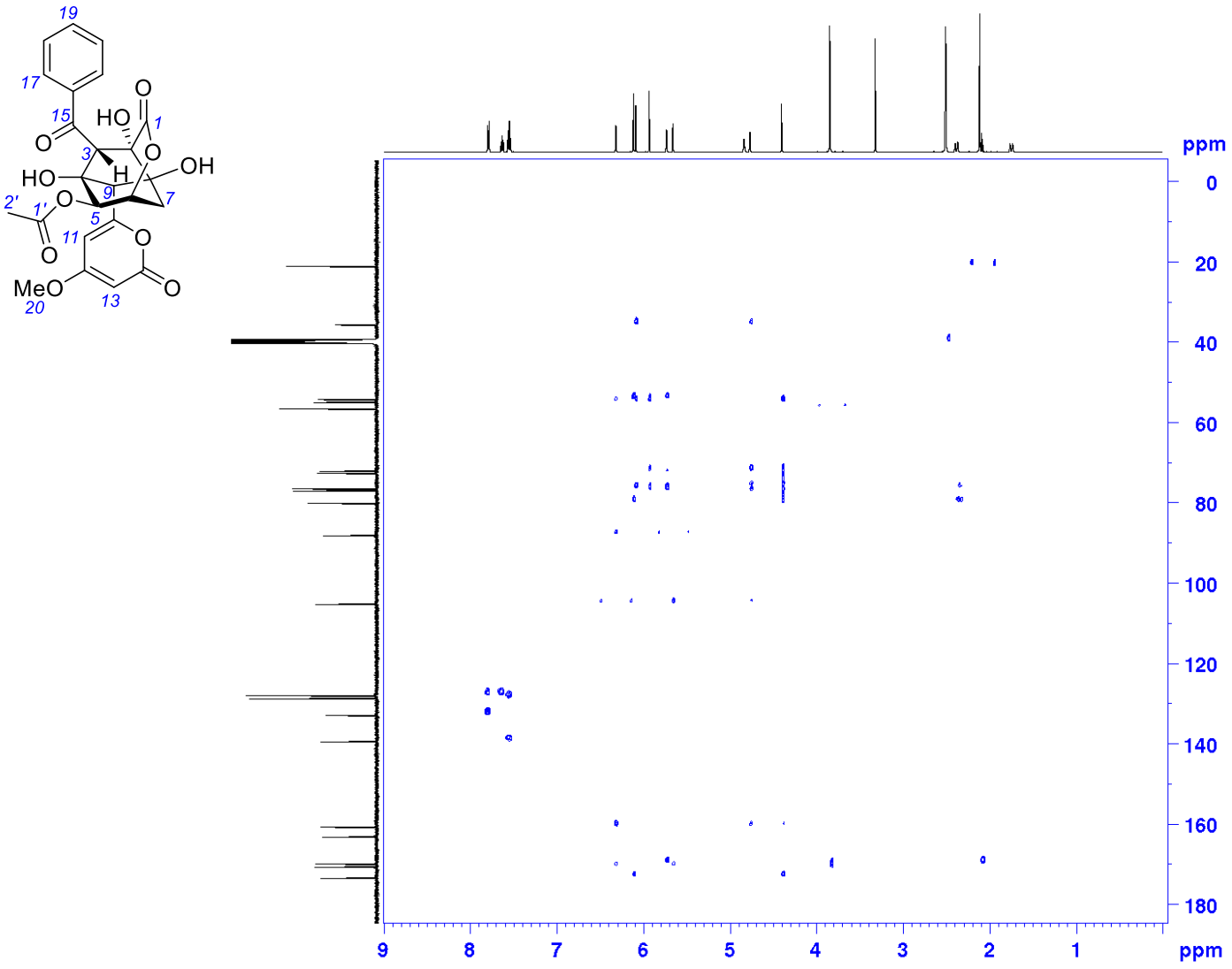


Figure S70. ^{1}H-^{13}C HMBC spectrum (500 MHz, DMSO-*d*6) of 5-*O*-acetylenterocin (**11**)

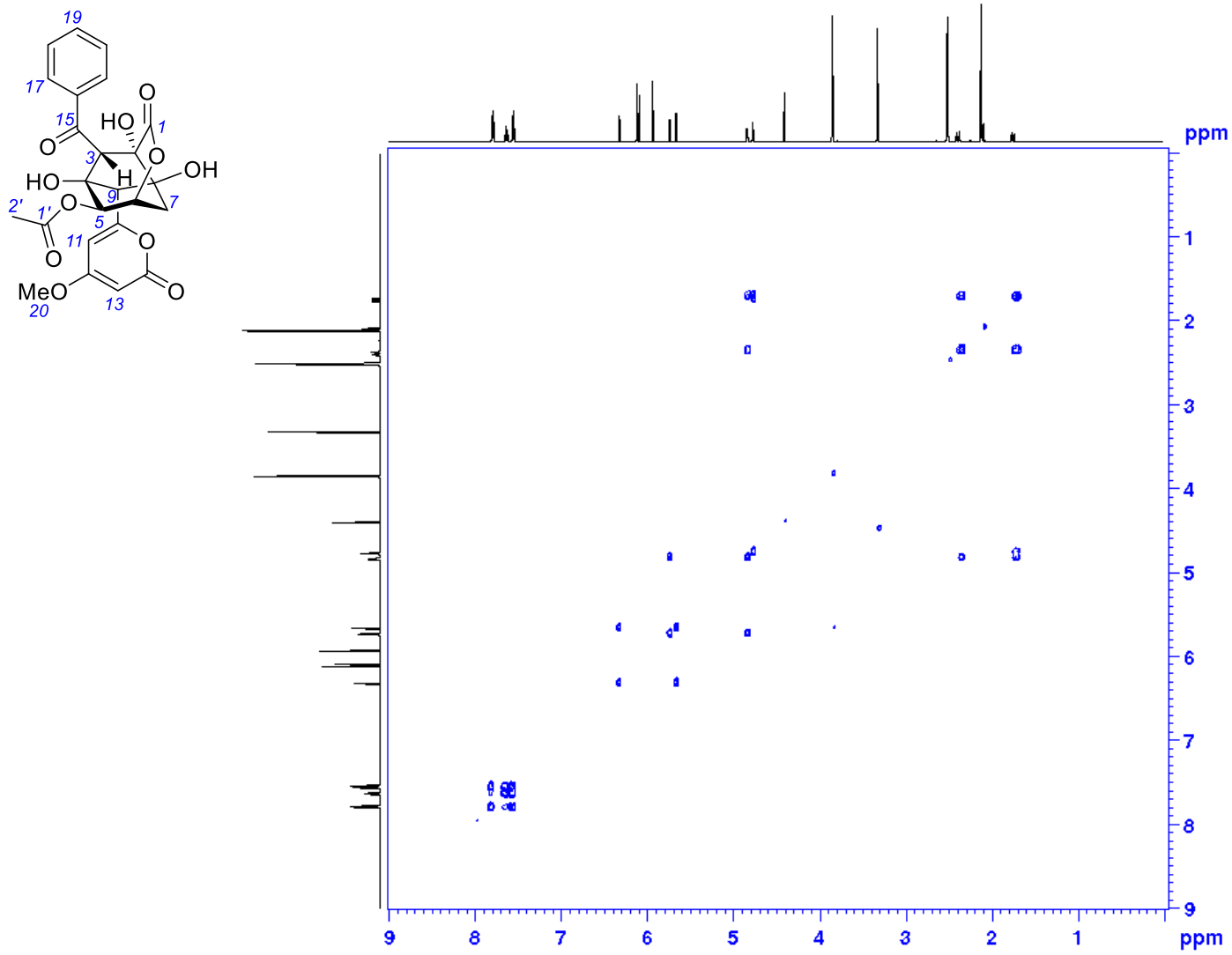


Figure S71. ^{1}H-^{1}H COSY spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-acetylenterocin (**11**)

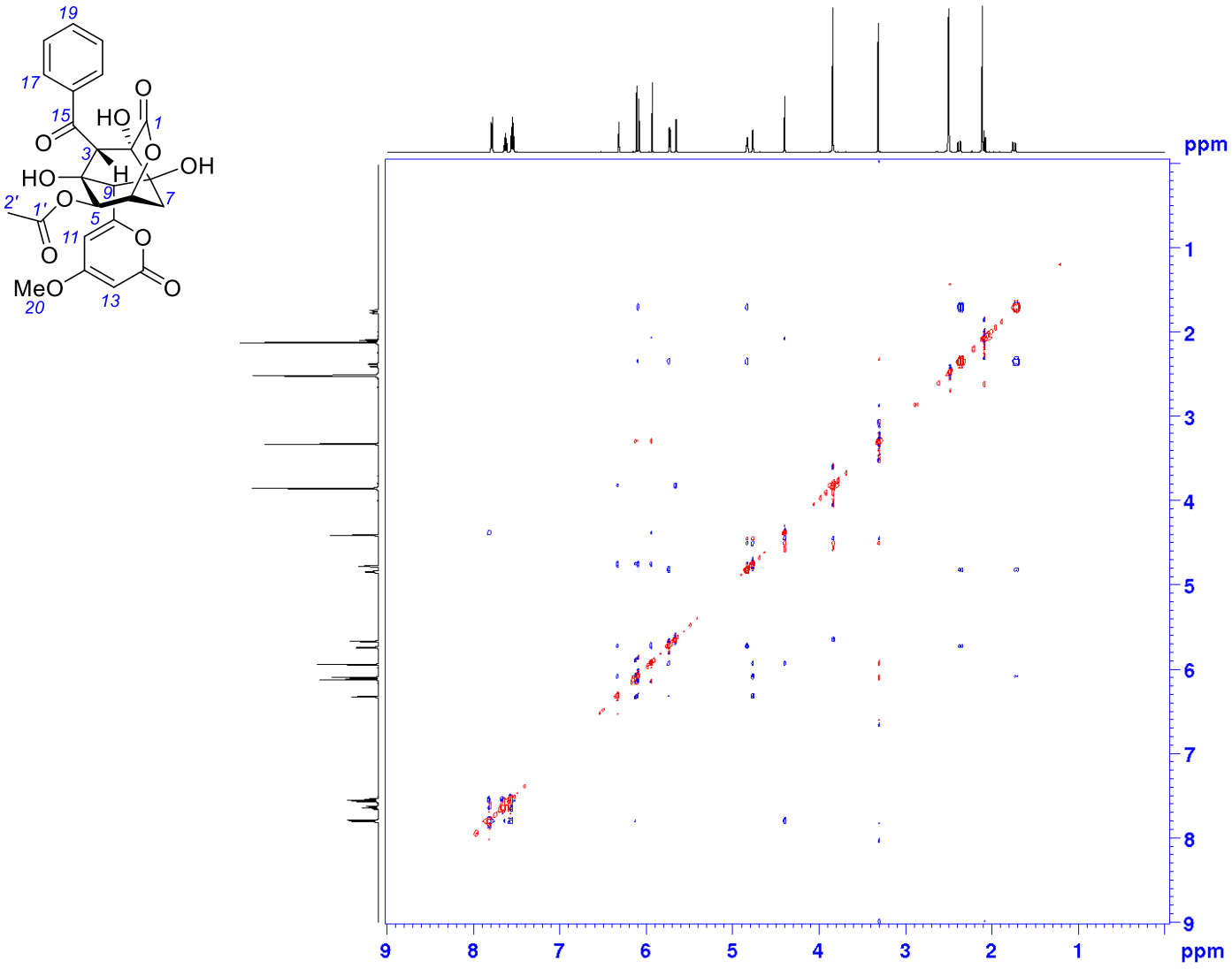


Figure S72. ^{1}H-^{1}H ROESY spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-acetylenterocin (**11**)

Figures S73-78. NMR spectra of 5-*O*-propionylenterocin (**12**)

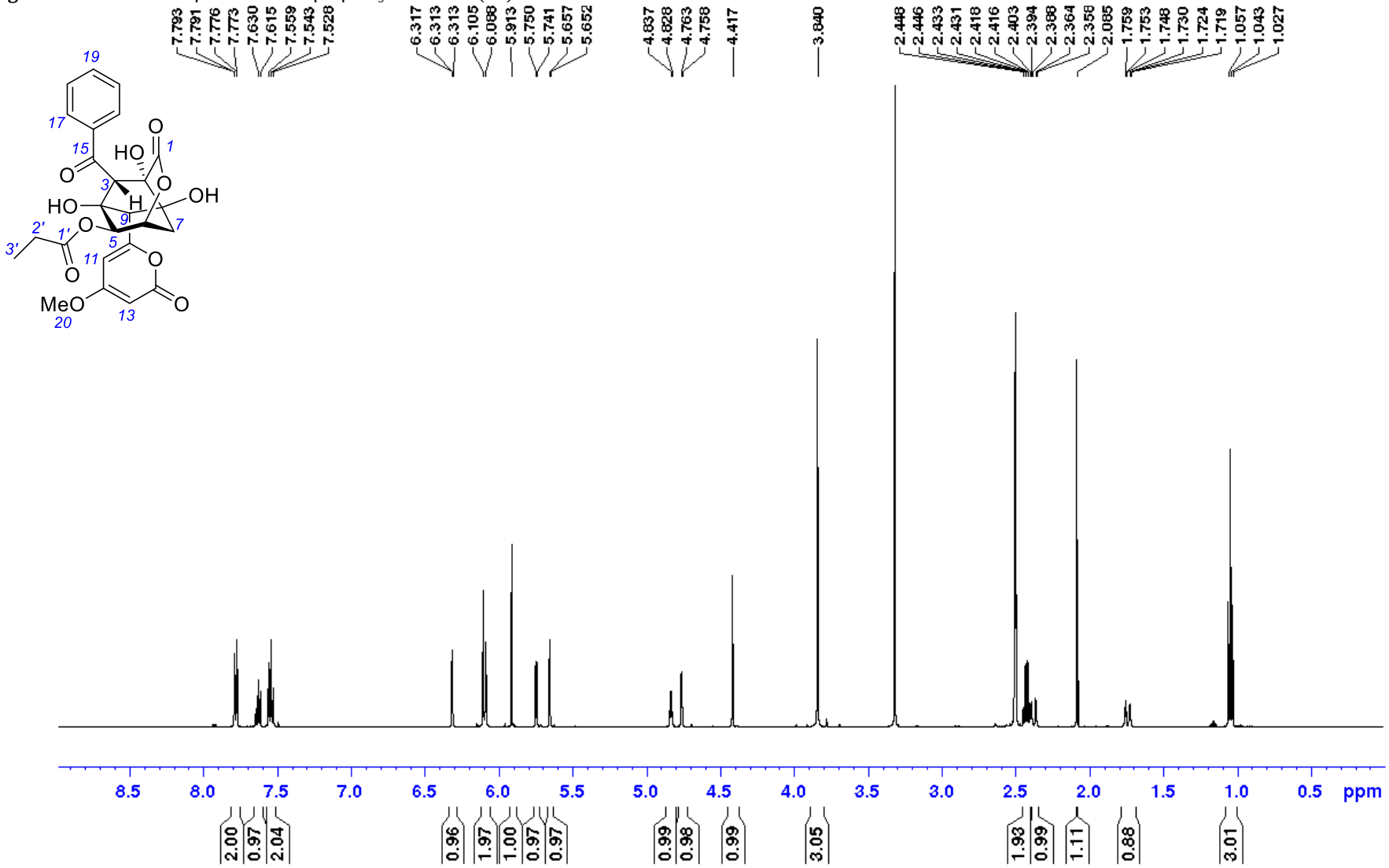


Figure S73. ^{1}H NMR spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-propionylenterocin (**12**)

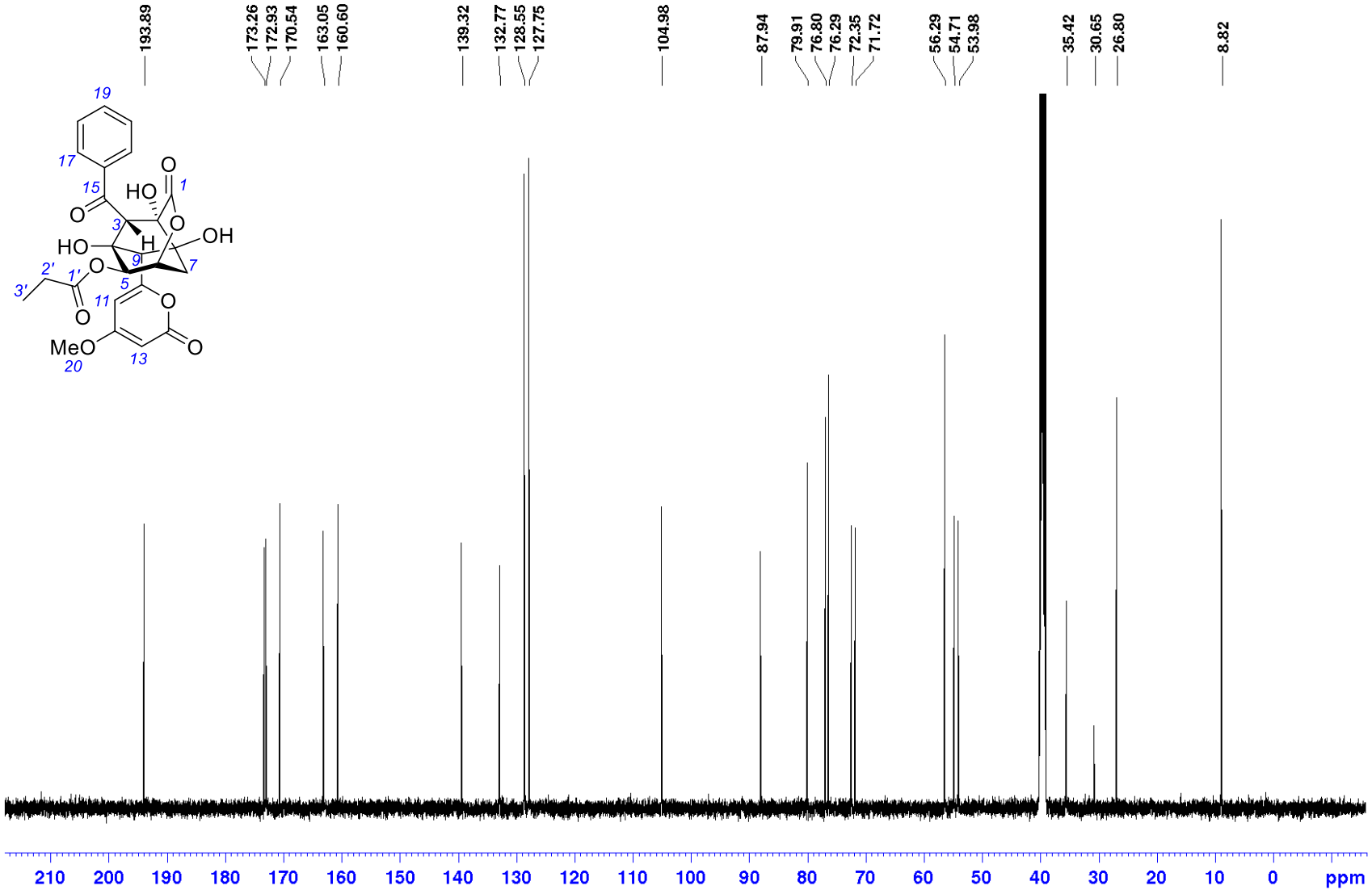


Figure S74. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of 5-*O*-propionylenterocin (**12**)

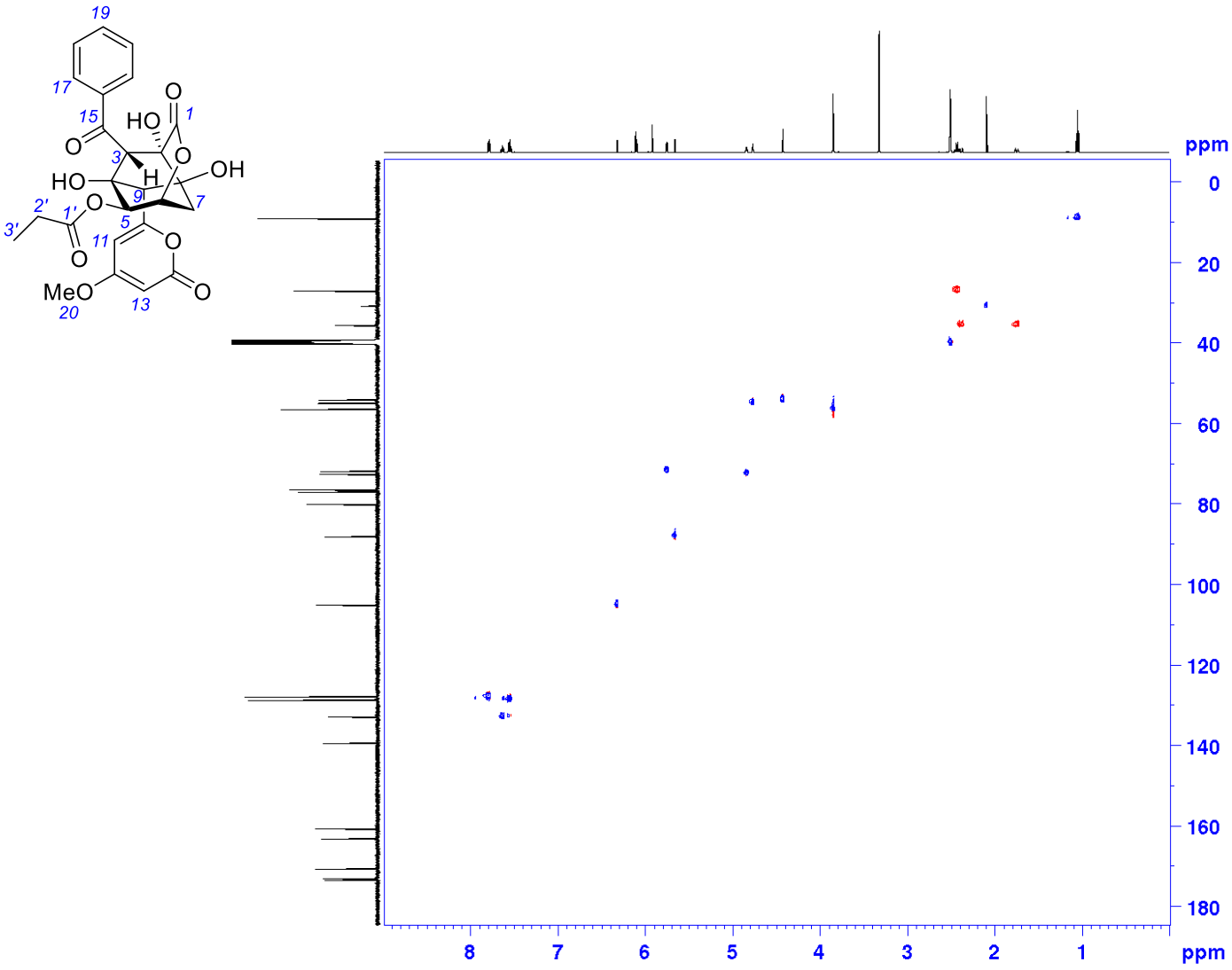


Figure S75. ^{1}H-^{13}C HSQC spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-propionylenterocin (**12**)

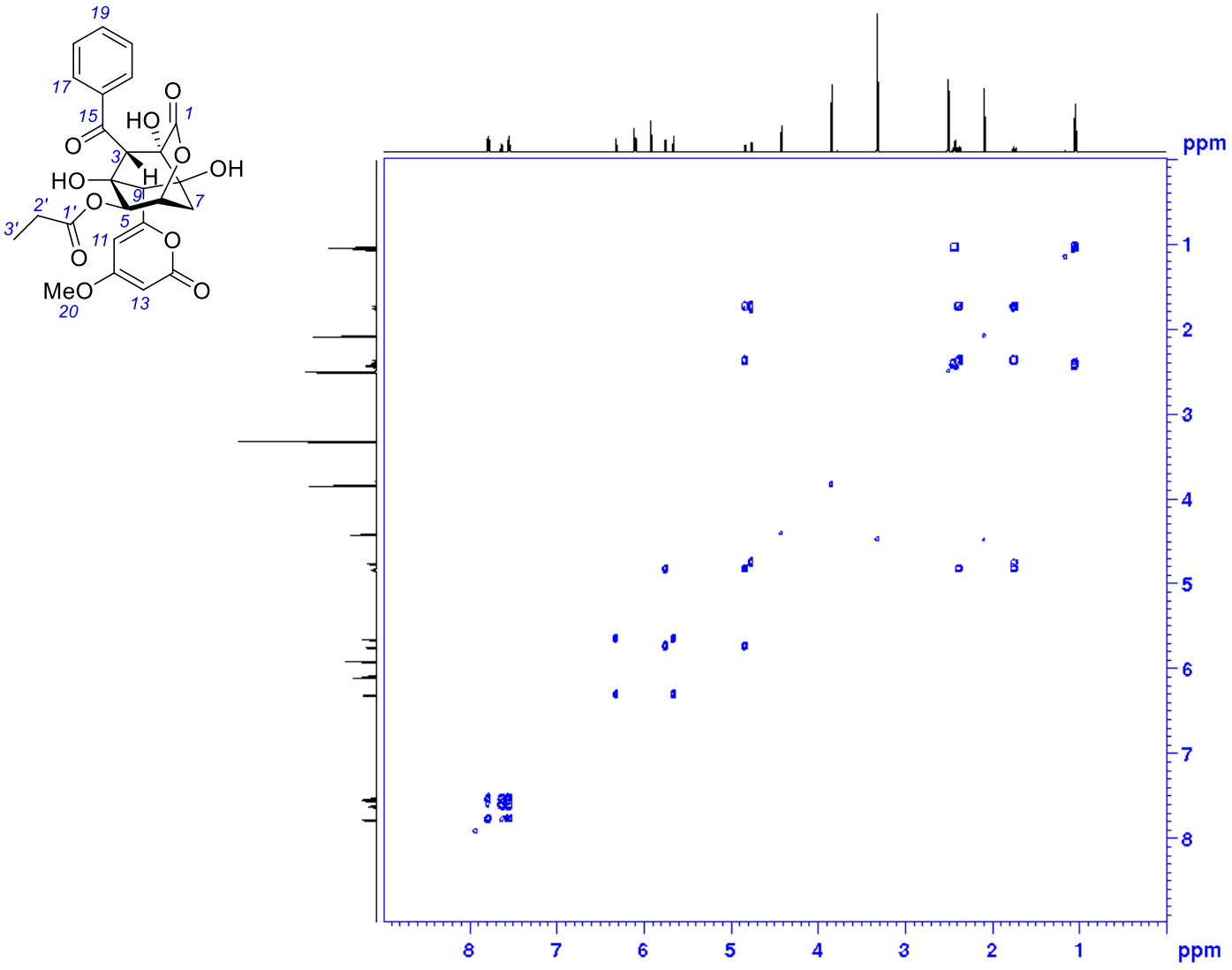


Figure S76. ^{1}H-^{13}C HMBC spectrum (500 MHz, DMSO-d_6) of 5-*O*-propionylenterocin (**12**)

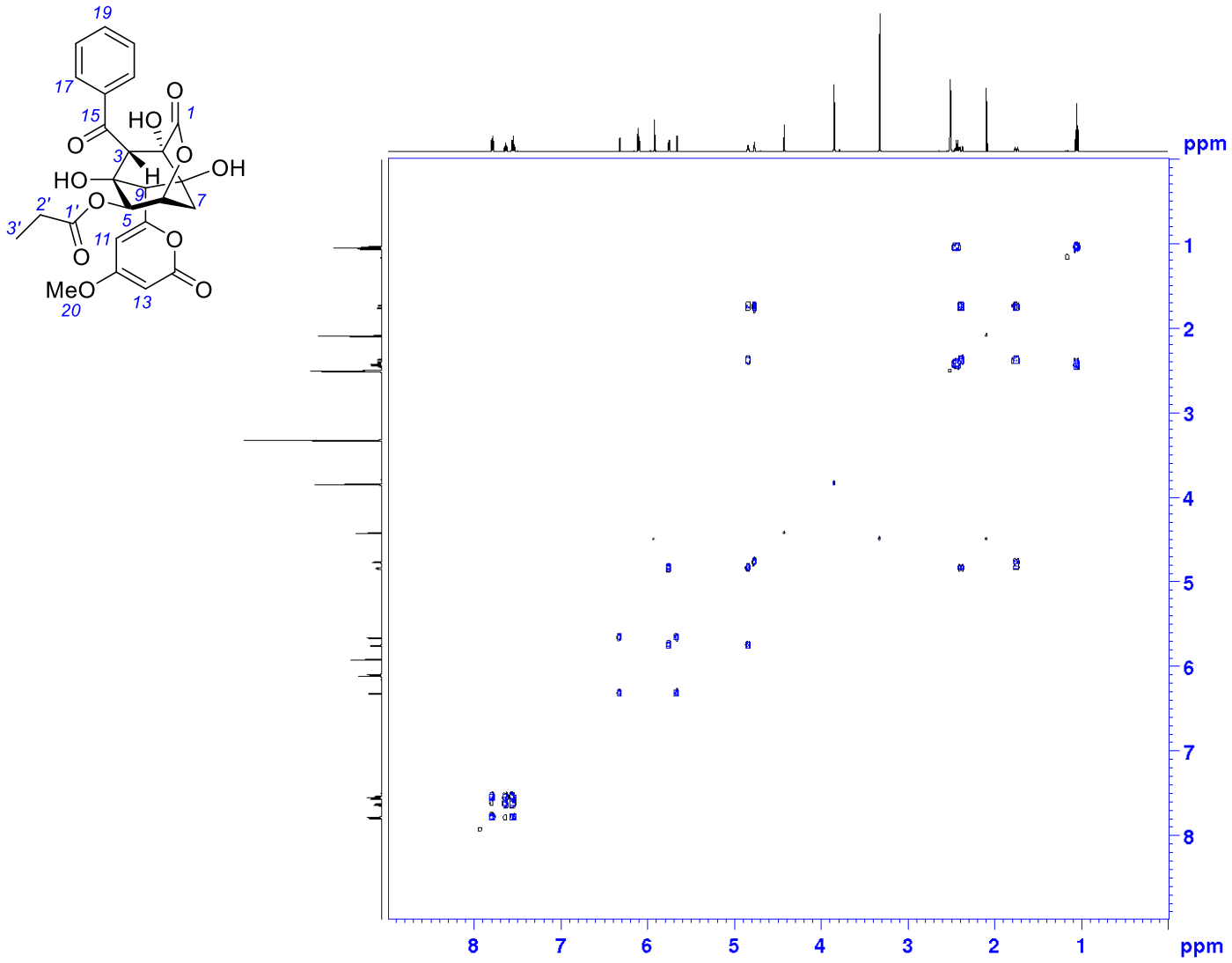


Figure S77. ^{1}H-^{1}H COSY spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-propionylenterocin (**12**)

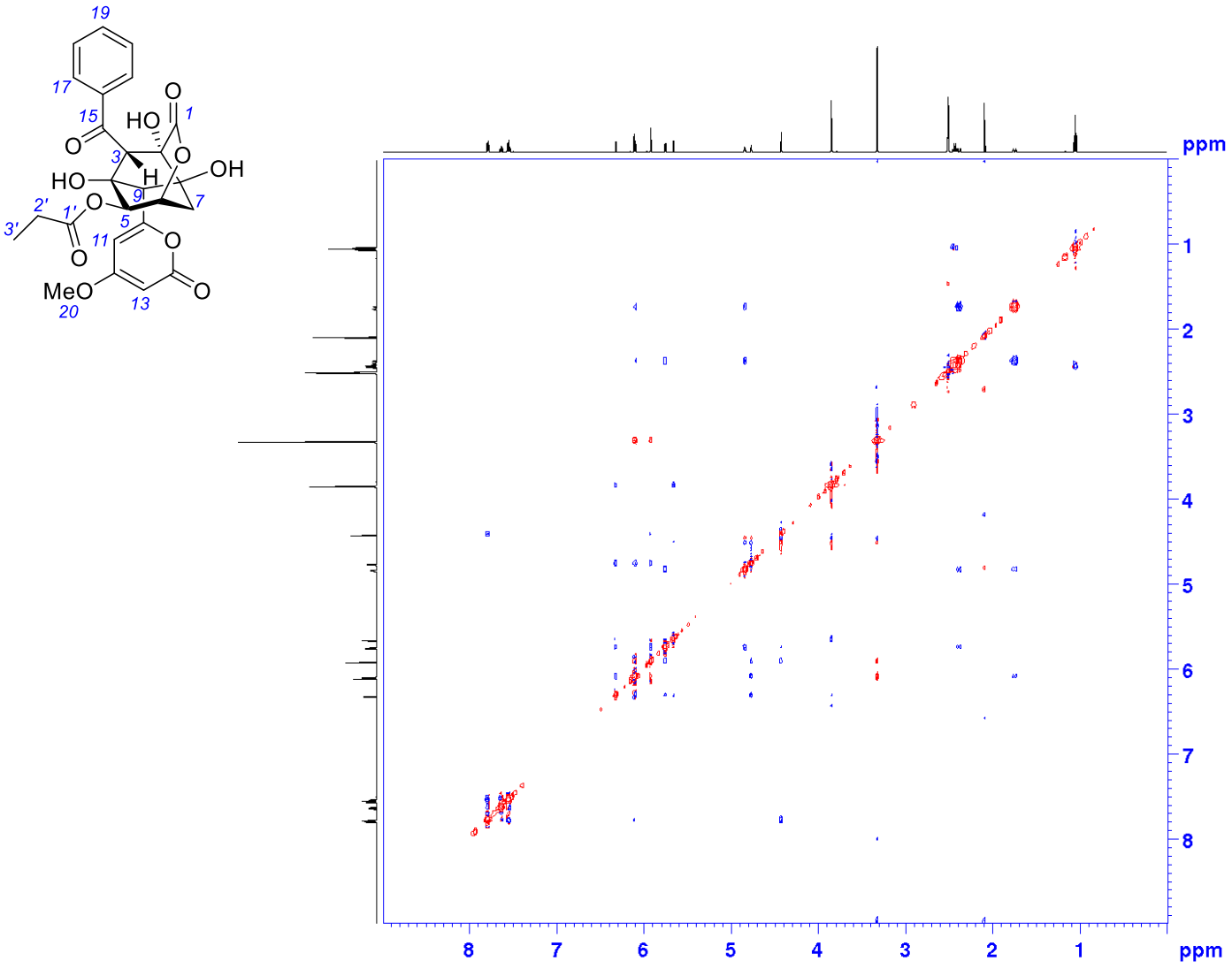


Figure S78. ^{1}H-^{1}H ROESY spectrum (500 MHz, DMSO-*d*$_6$) of 5-*O*-propionylenterocin (**12**)

Figures S79-84. NMR spectra of 5-*O*-carboxypropionylenterocin (**13**)

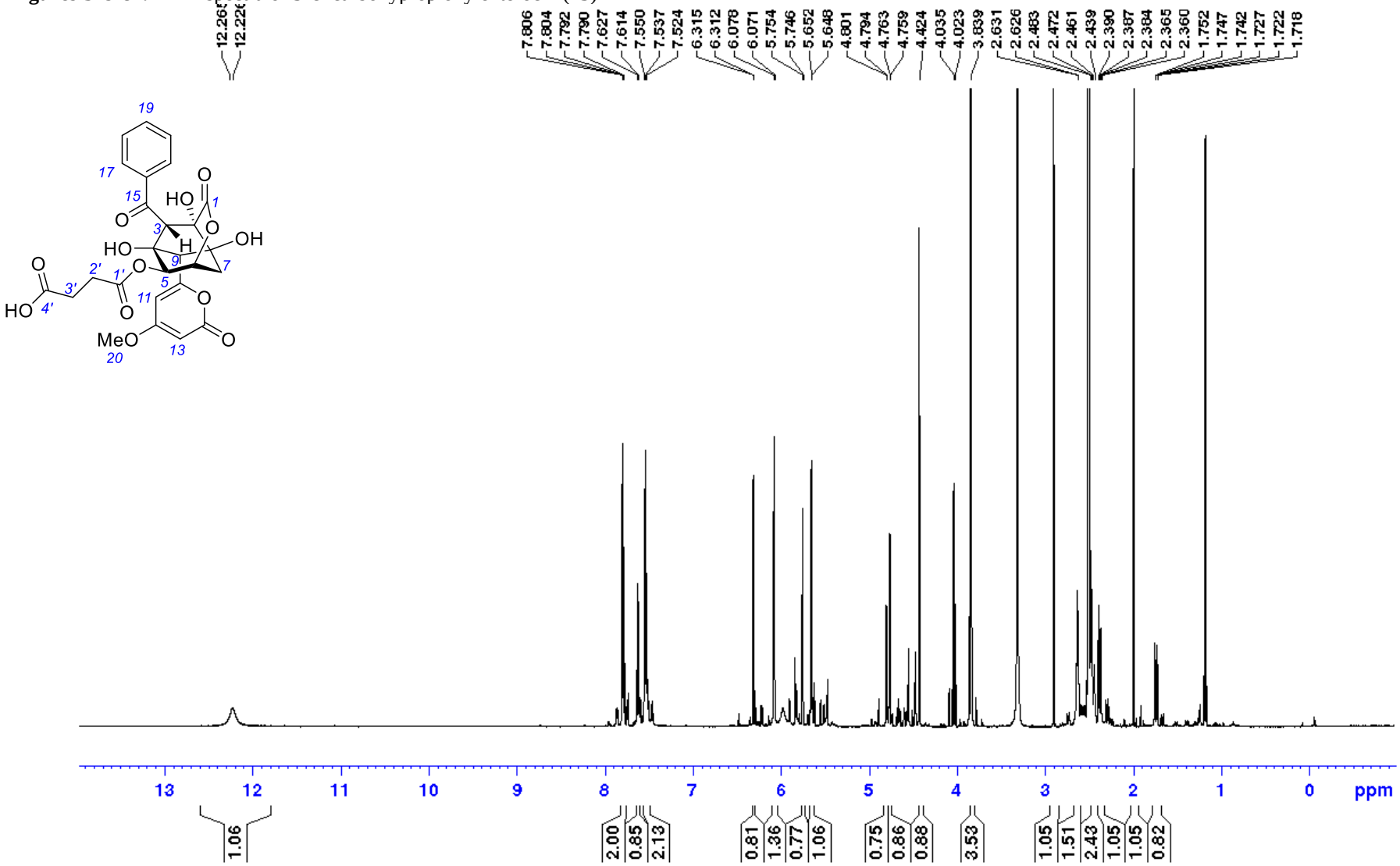


Figure S79. ^{1}H NMR spectrum (600 MHz, DMSO-*d*$_6$) of 5-*O*-carboxypropionylenterocin (**13**)

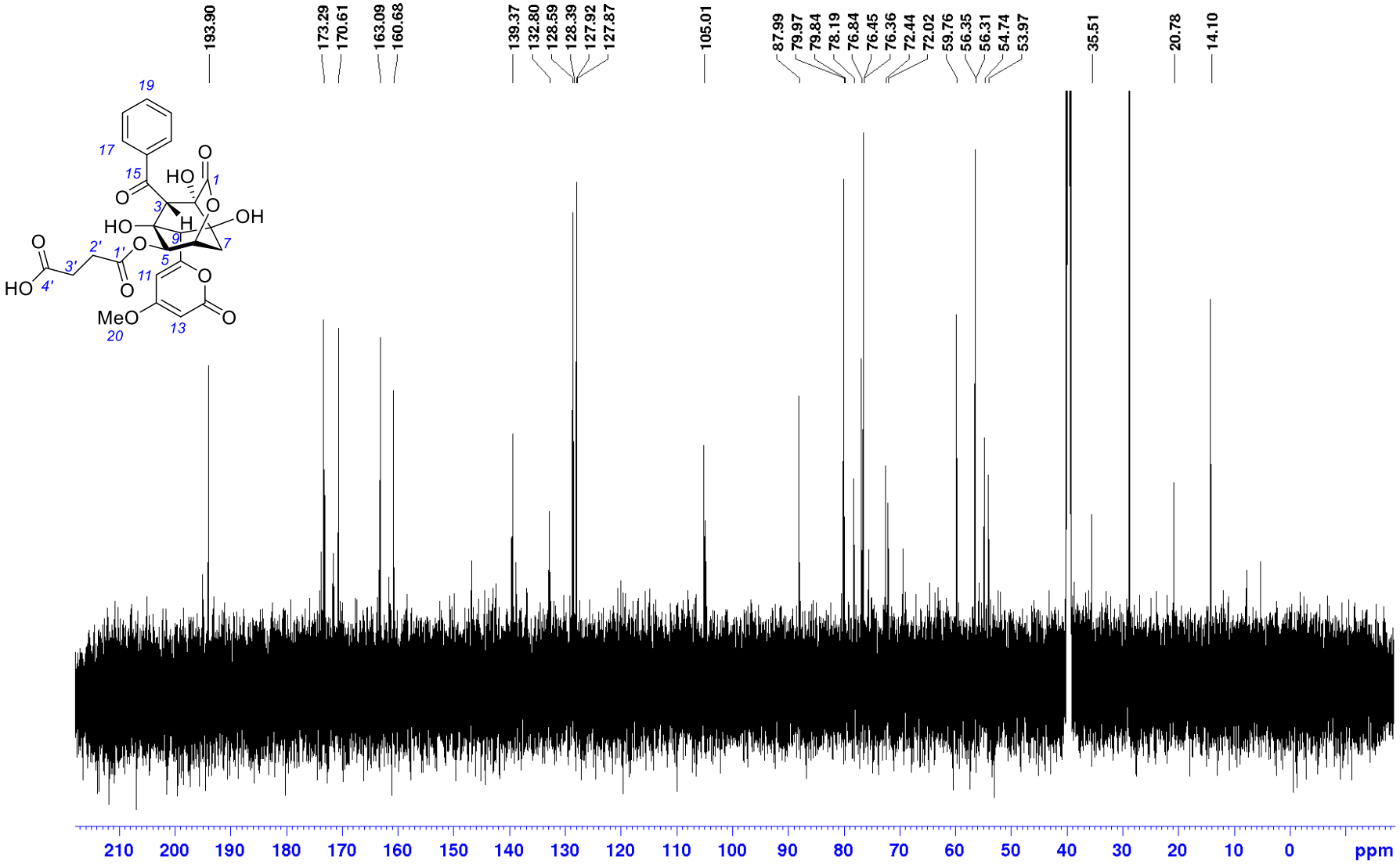


Figure S80. ^{13}C NMR spectrum (150 MHz, DMSO-*d*$_6$) of 5-*O*-carboxypropionylenterocin (**13**)

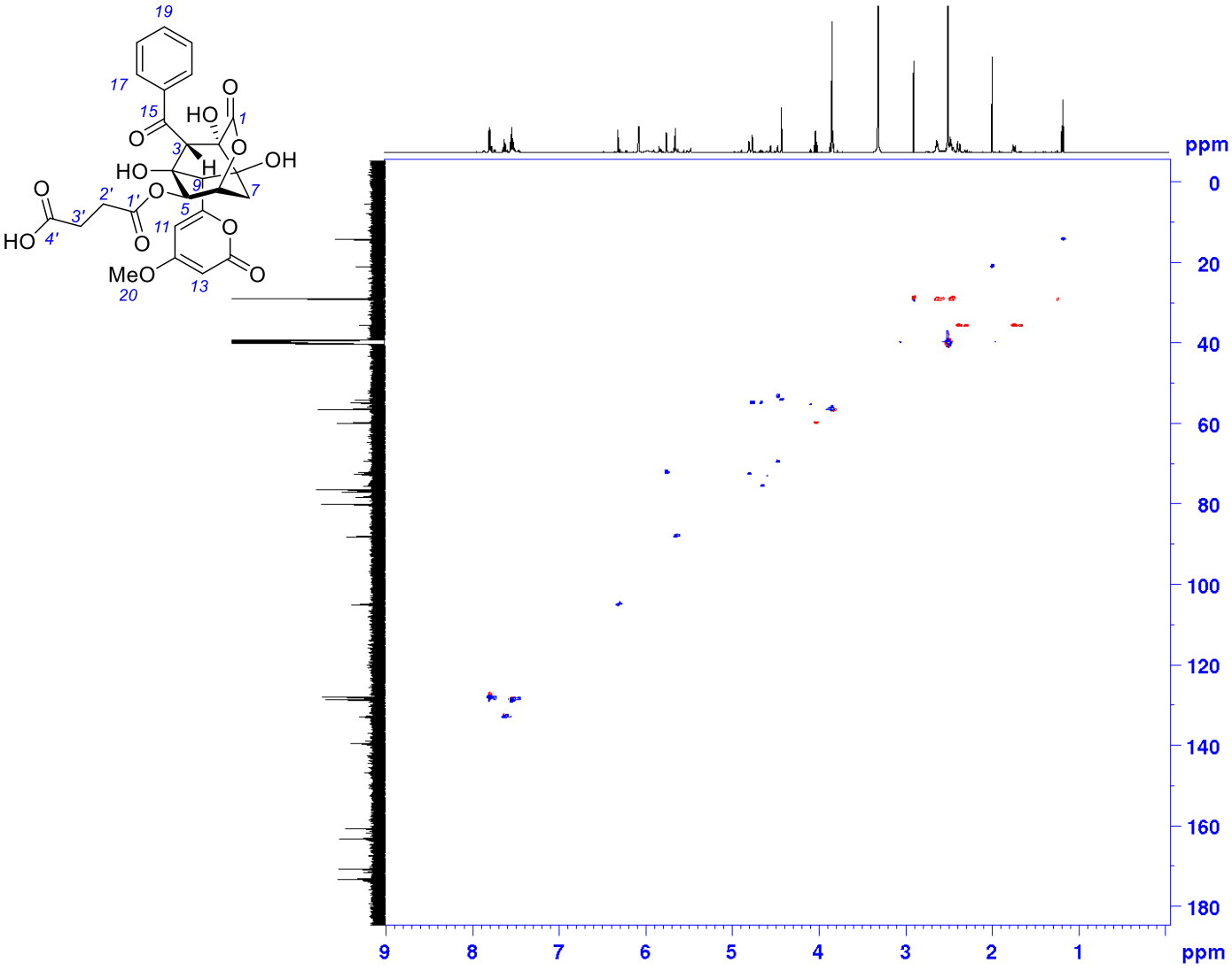


Figure S81. ^{1}H-^{13}C HSQC spectrum (600 MHz, DMSO-d_6) of 5-*O*-carboxypropionylenterocin (**13**)

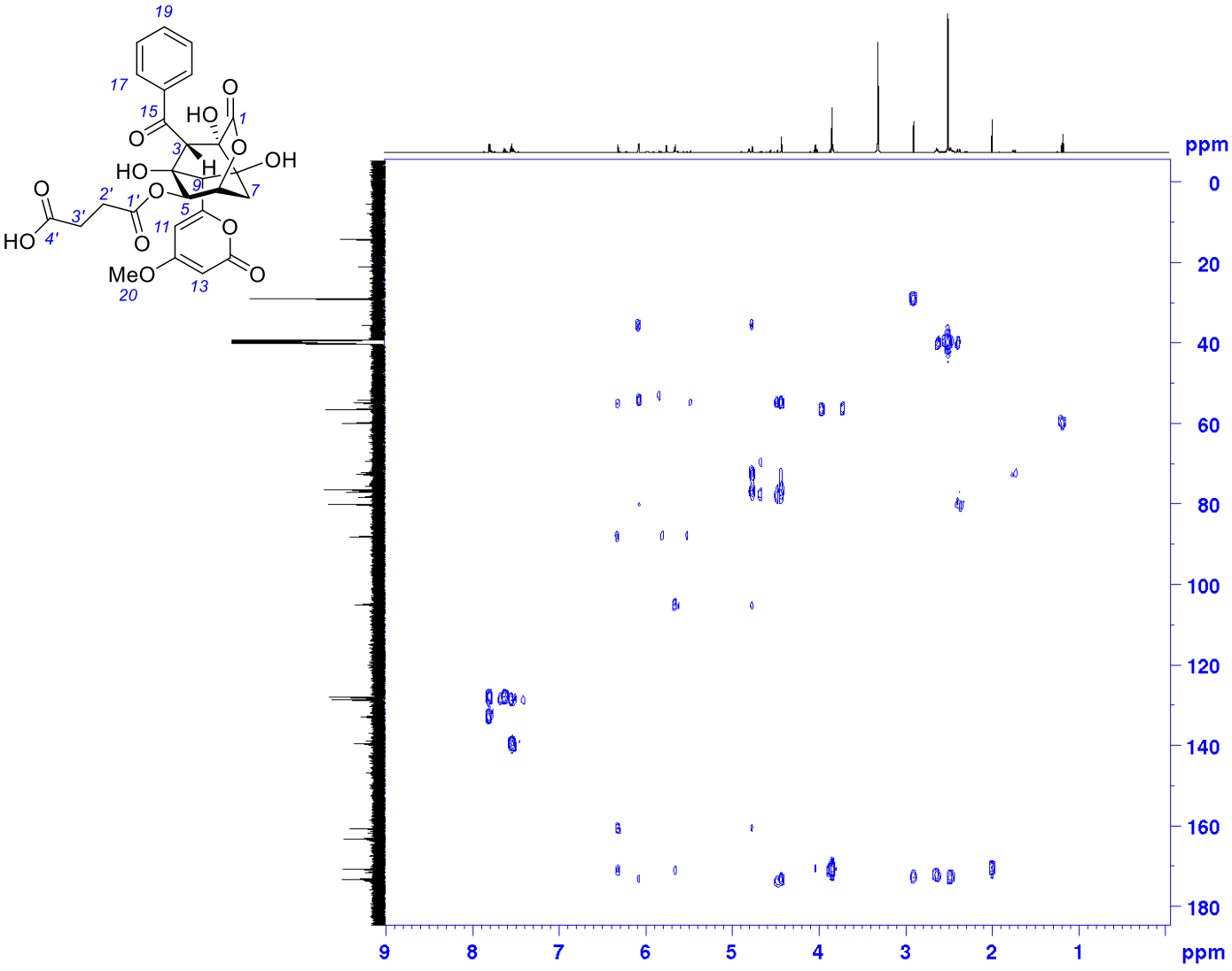


Figure S82. ^{1}H-^{13}C HMBC spectrum (600 MHz, DMSO-*d*$_6$) of 5-*O*-carboxypropionylenterocin (**13**)

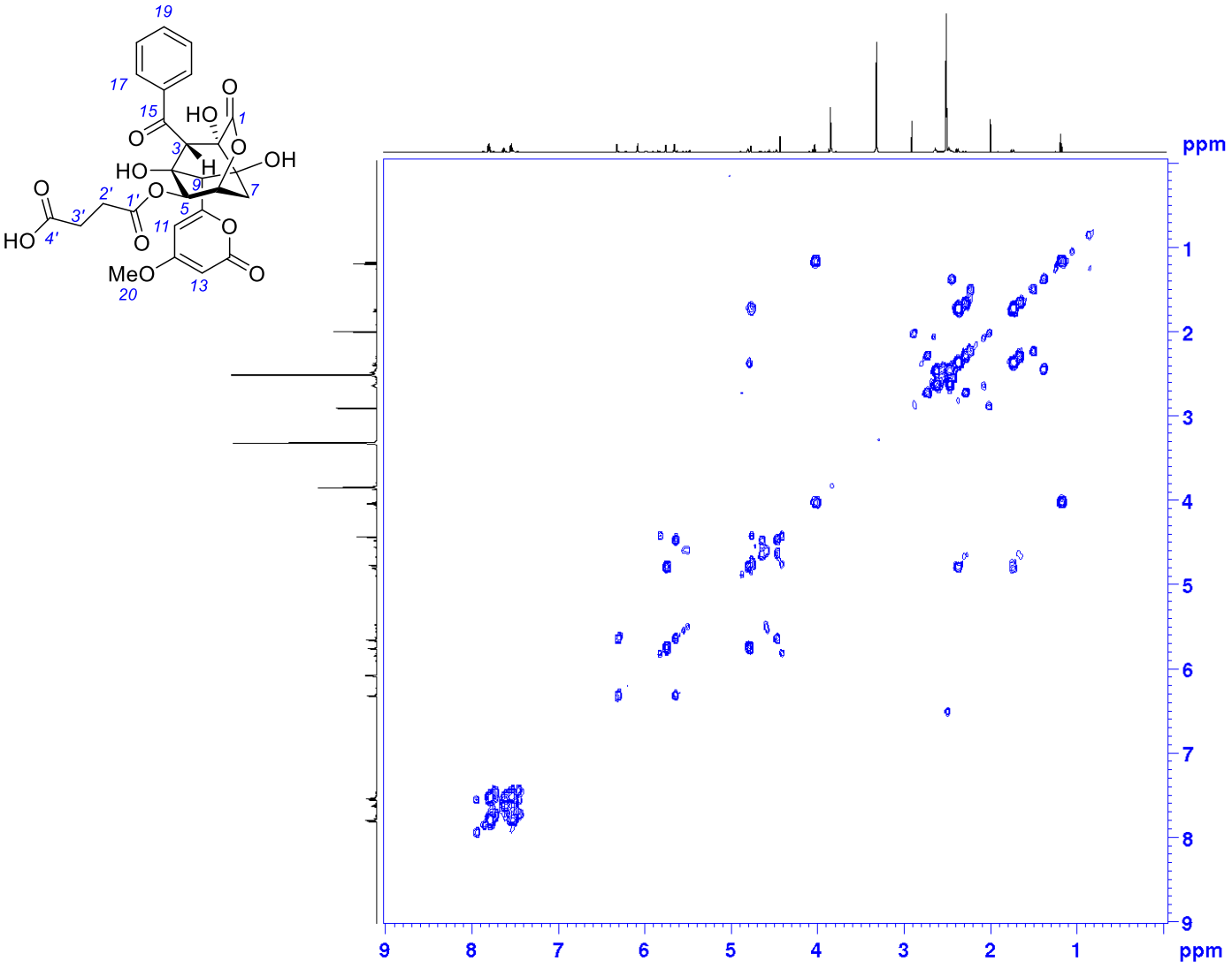


Figure S83. ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-*d*$_6$) of 5-*O*-carboxypropionylenterocin (**13**)

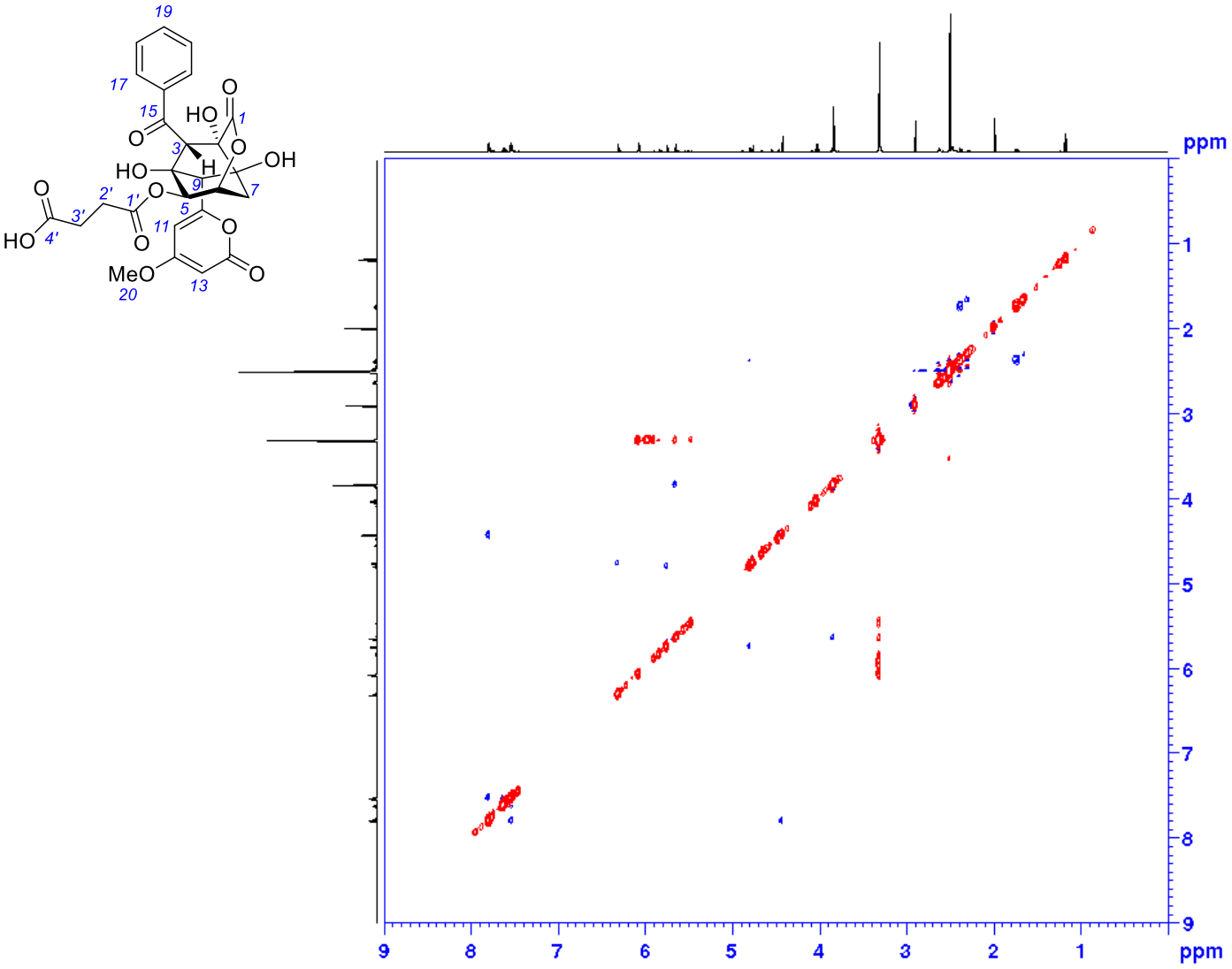


Figure S84. ^{1}H-^{1}H ROESY spectrum (600 MHz, DMSO-*d*$_6$) of 5-*O*-carboxypropionylenterocin (**13**)

Figures S85-90. NMR spectra of 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**)

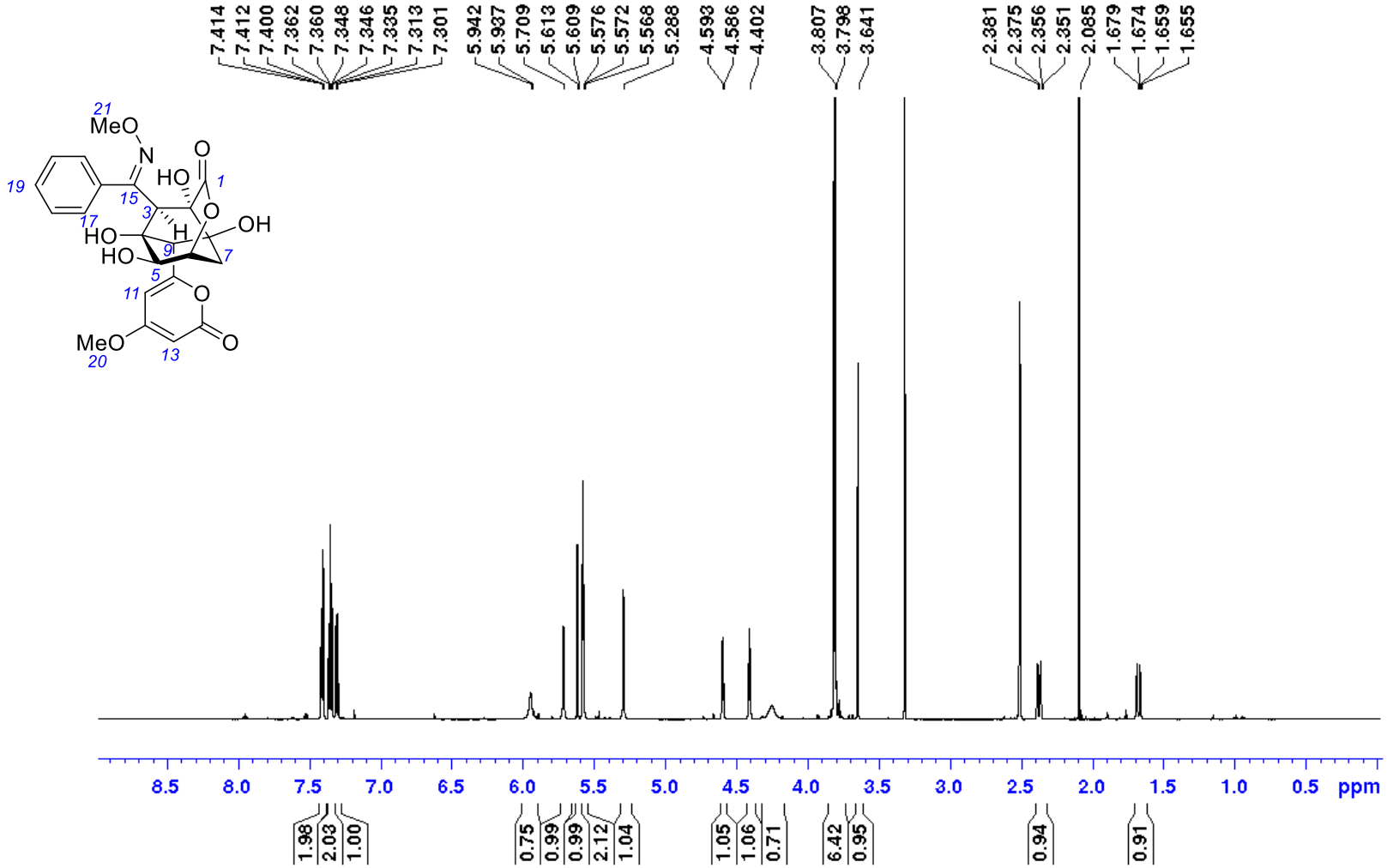


Figure S85. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**)

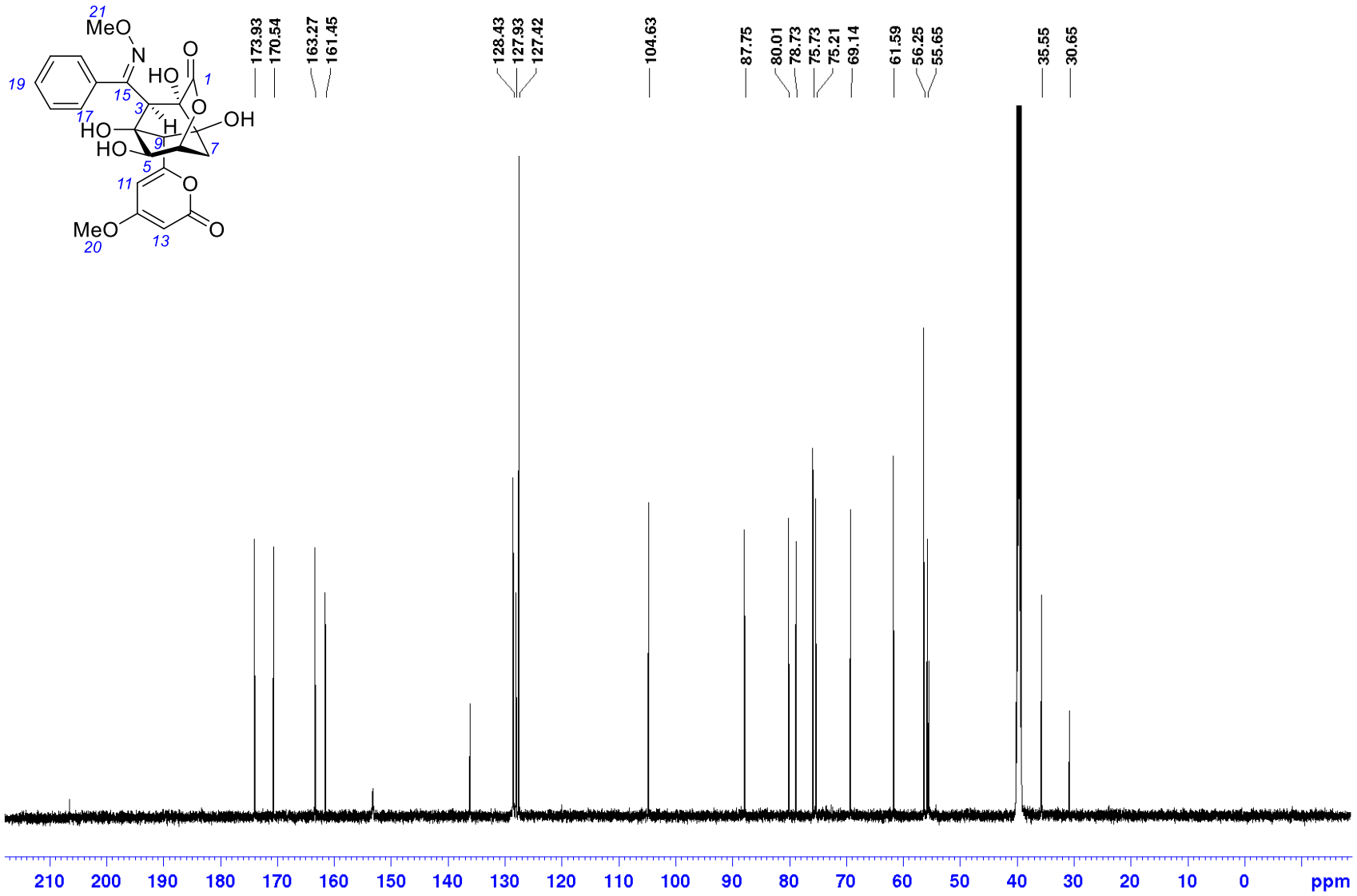


Figure S86. ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**)

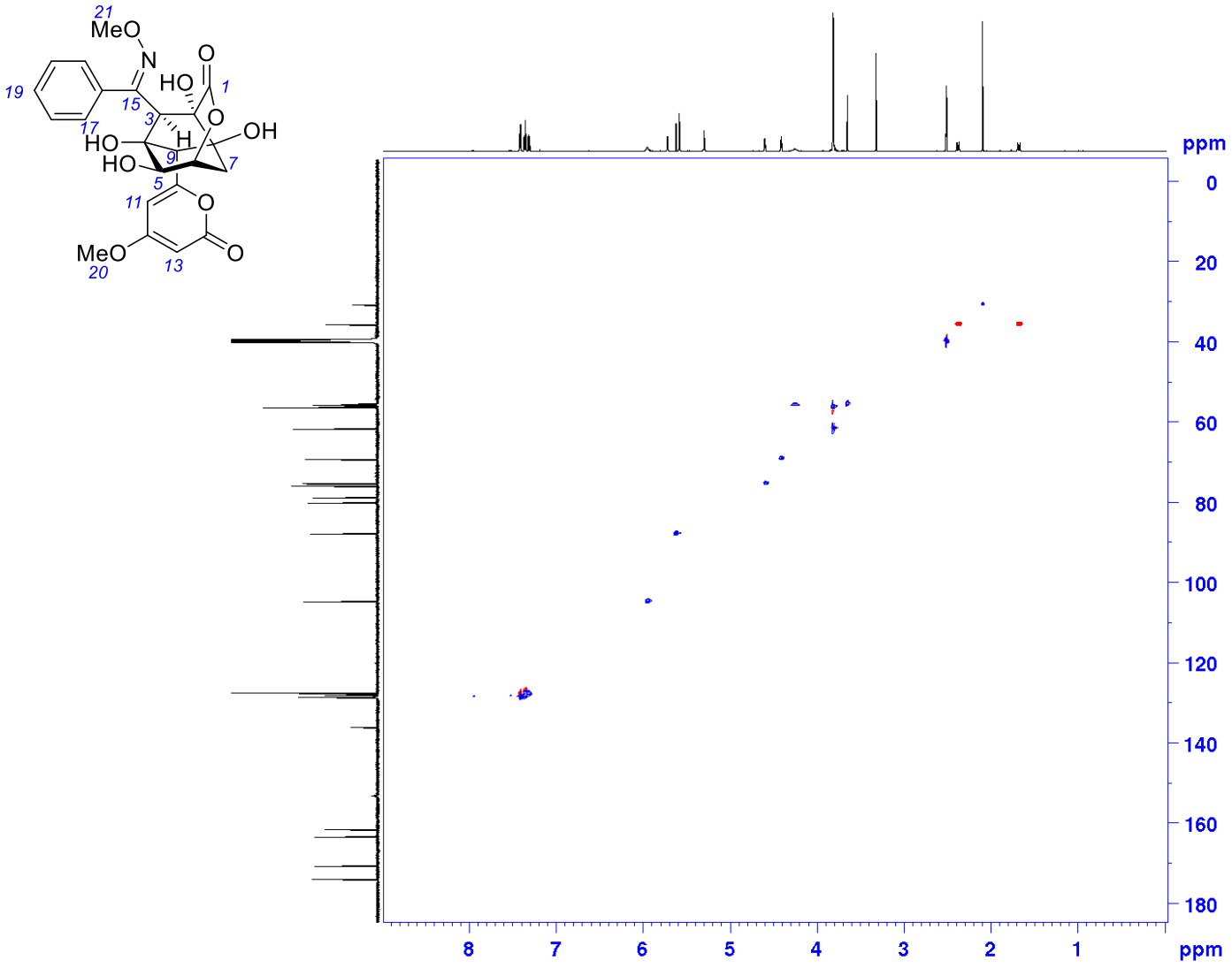


Figure S87. ^{1}H-^{13}C HSQC spectrum (600 MHz, DMSO-*d*6) of 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**)

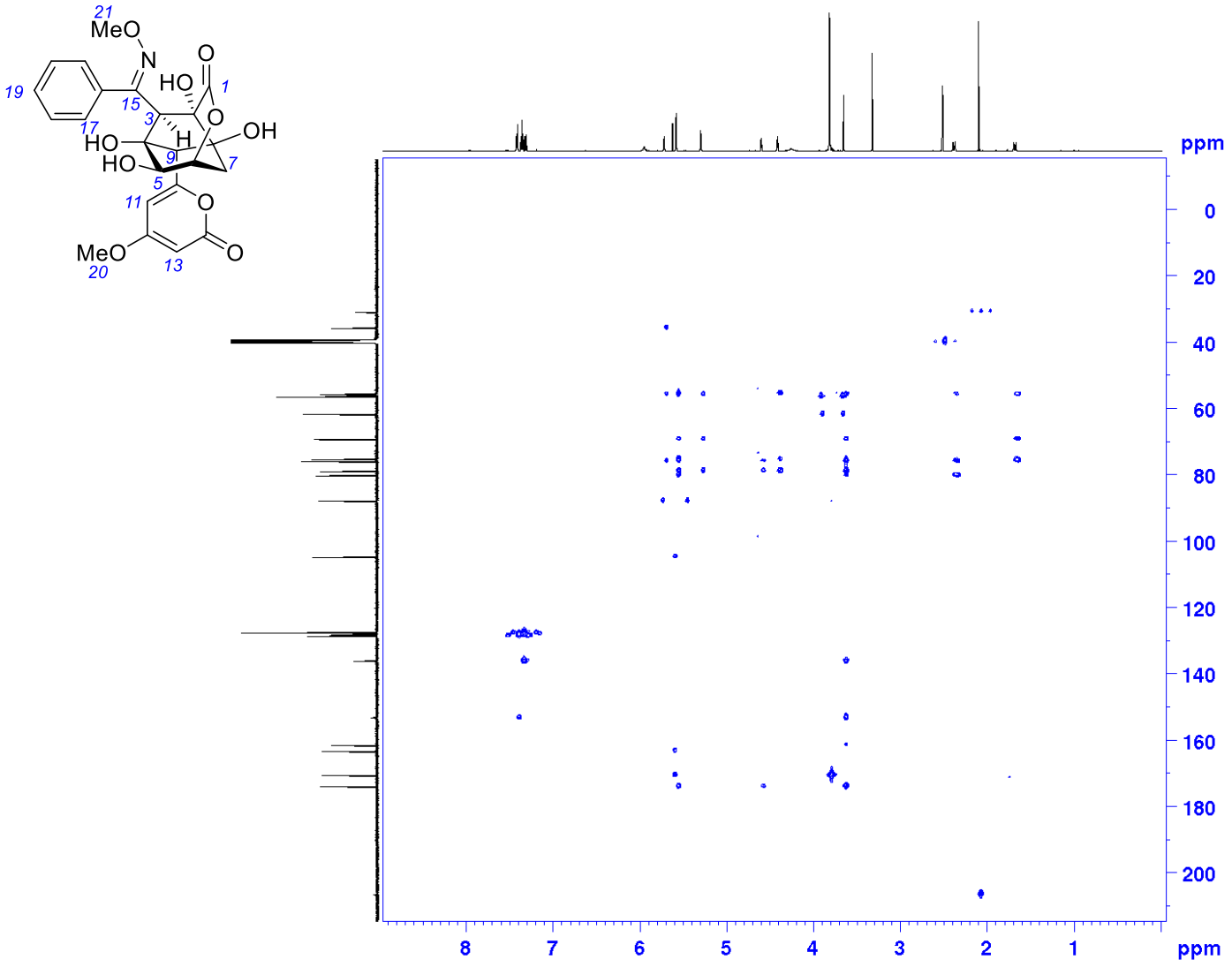


Figure S88. ^{1}H-^{13}C HMBC spectrum (600 MHz, DMSO-d_6) of 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**)

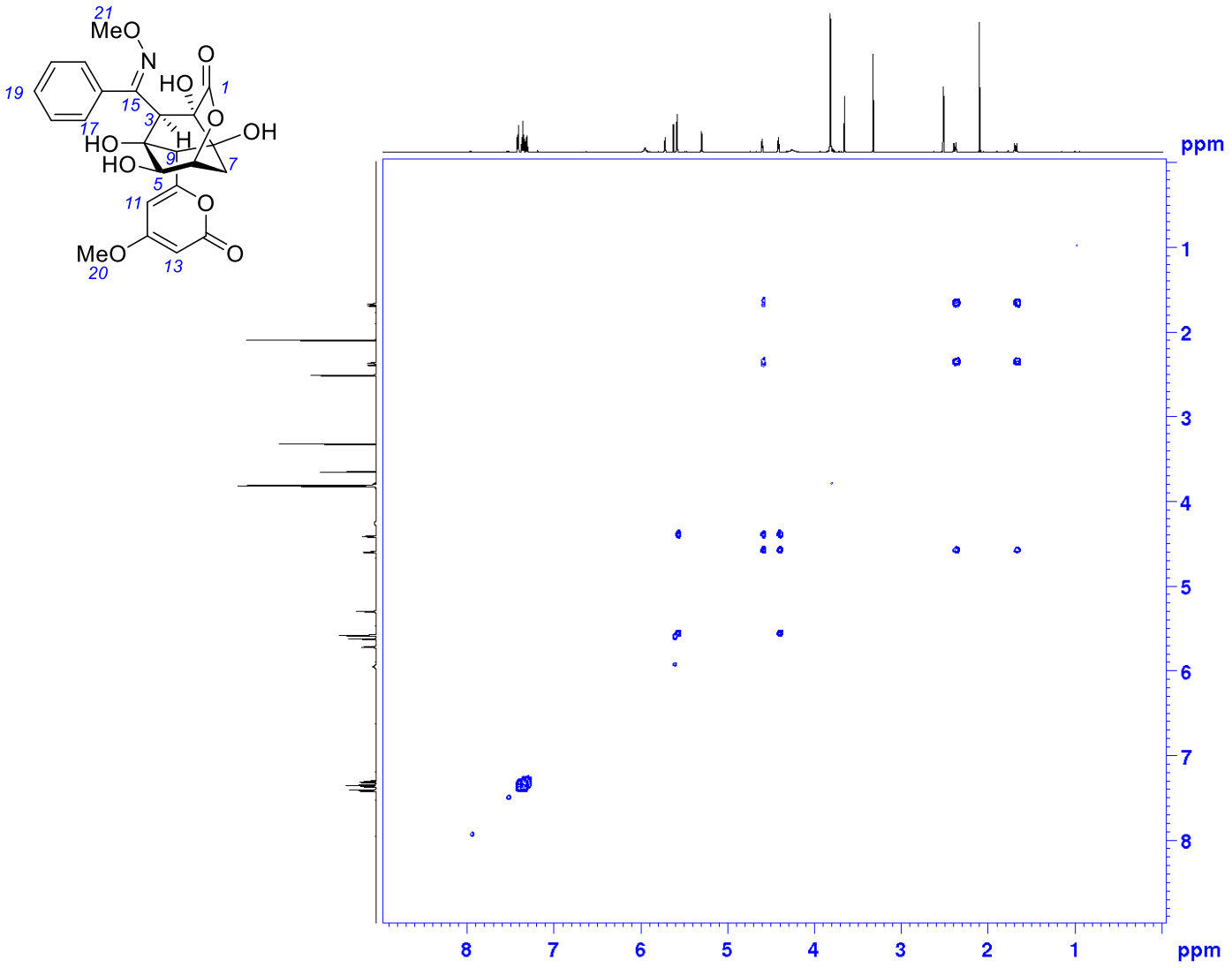


Figure S89. ^{1}H-^{1}H COSY spectrum (600 MHz, DMSO-*d*$_6$) of 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**)

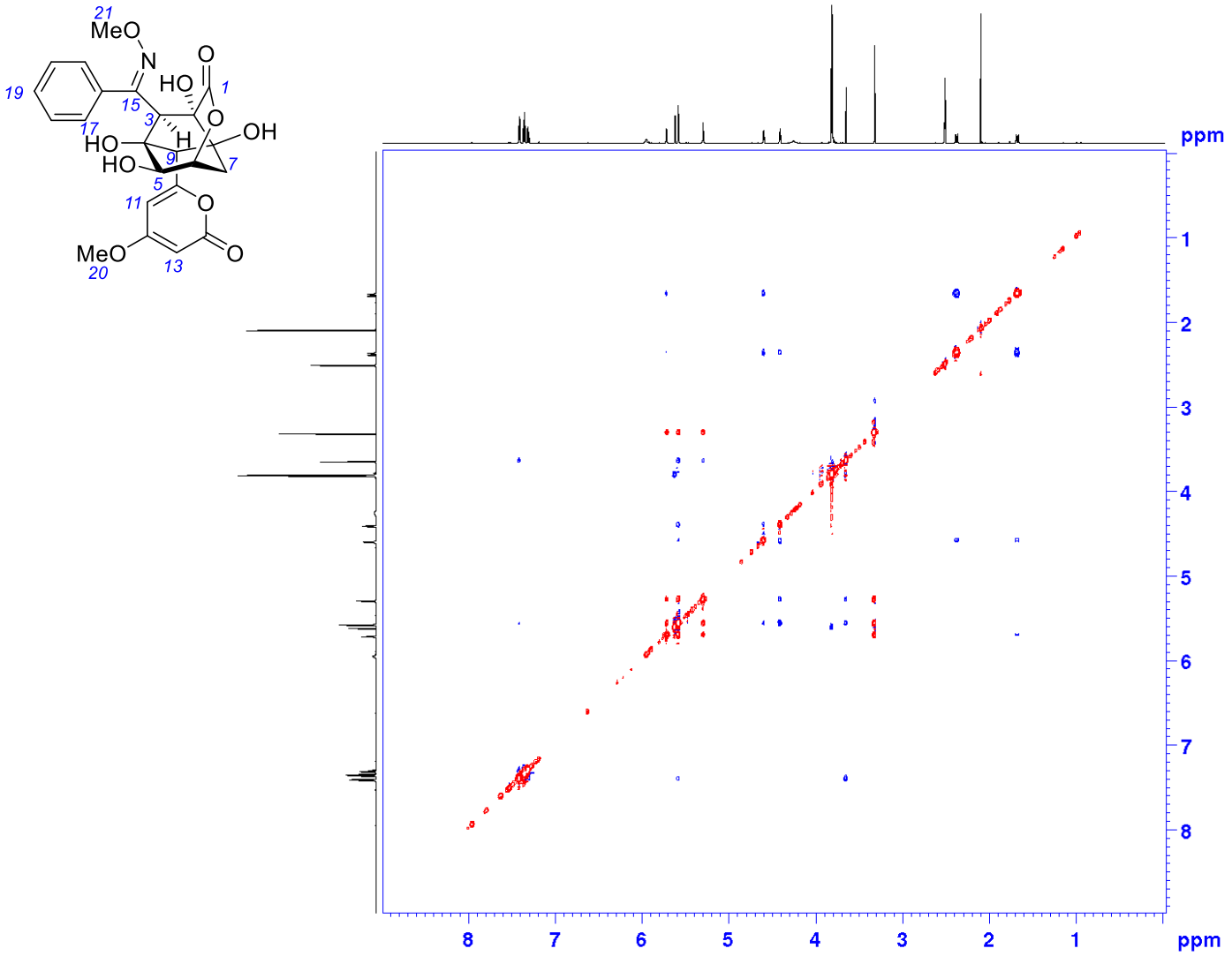


Figure S90. ^{1}H-^{1}H ROESY spectrum (600 MHz, DMSO-d_6) of 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**)

C. UV-visible Spectra

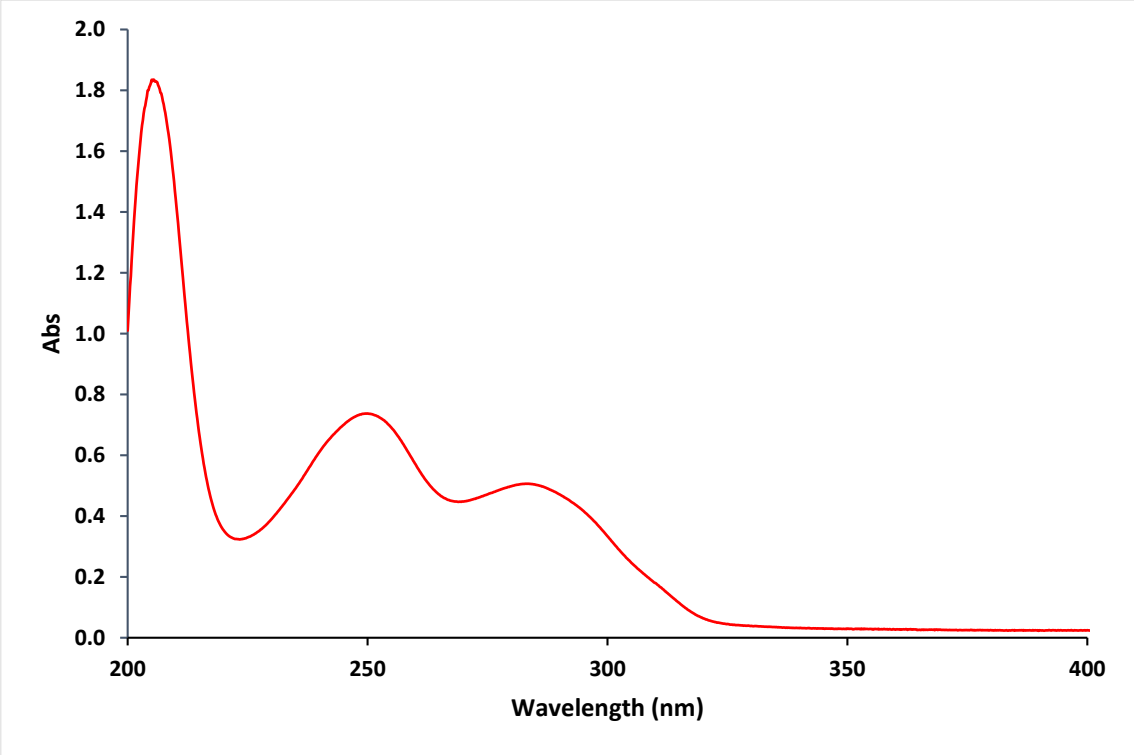


Figure S91. UV-vis spectrum of enterocin (**1**) in MeOH

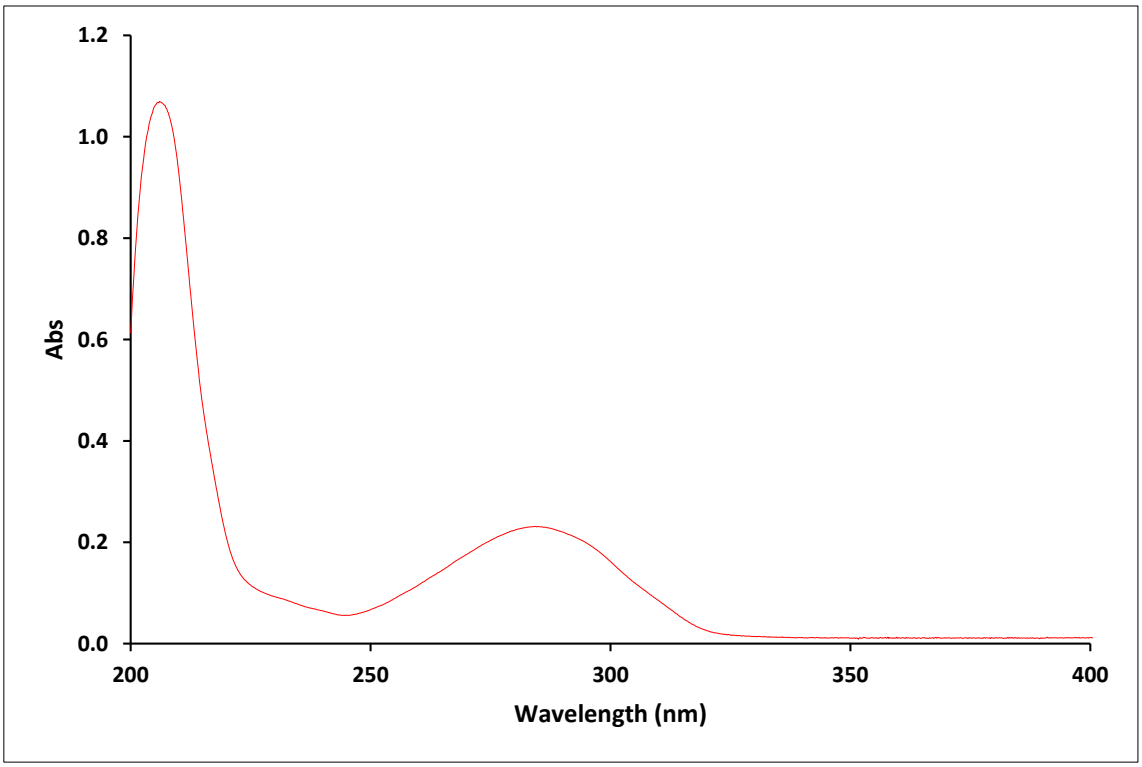


Figure S92. UV-vis spectrum of isoenterocin A (**2**) in MeOH

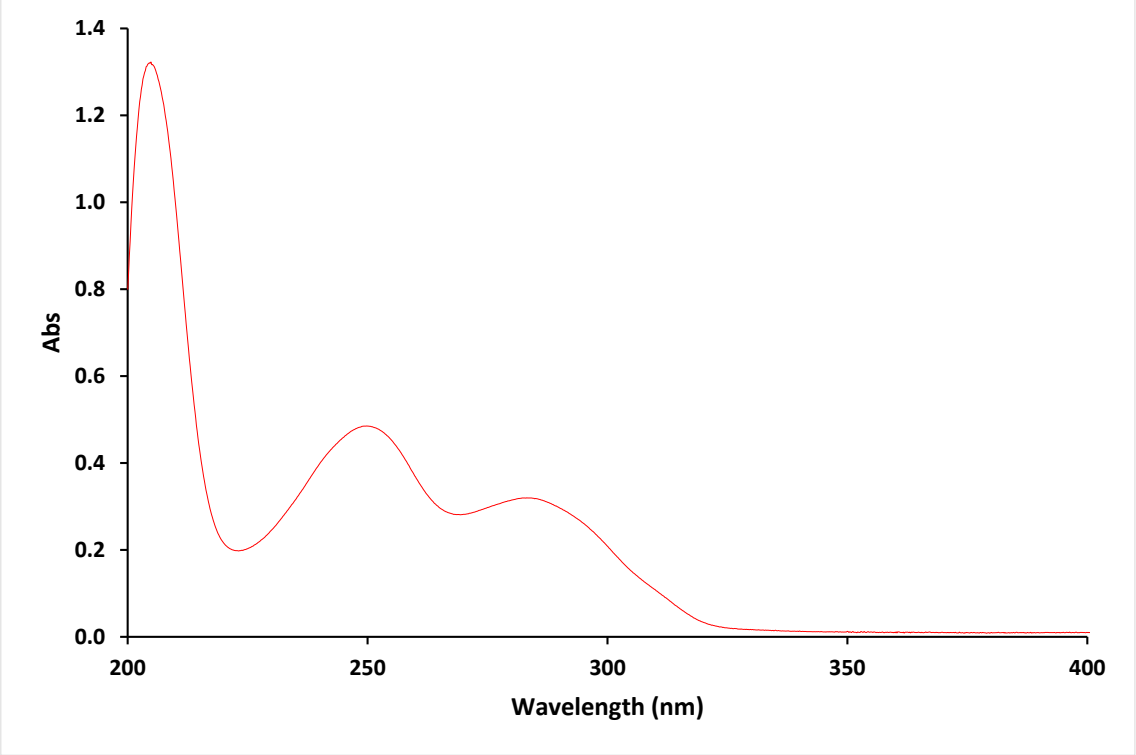


Figure S93. UV-vis spectrum of 5-*O*-palmitoylenterocin (**10**) in MeOH

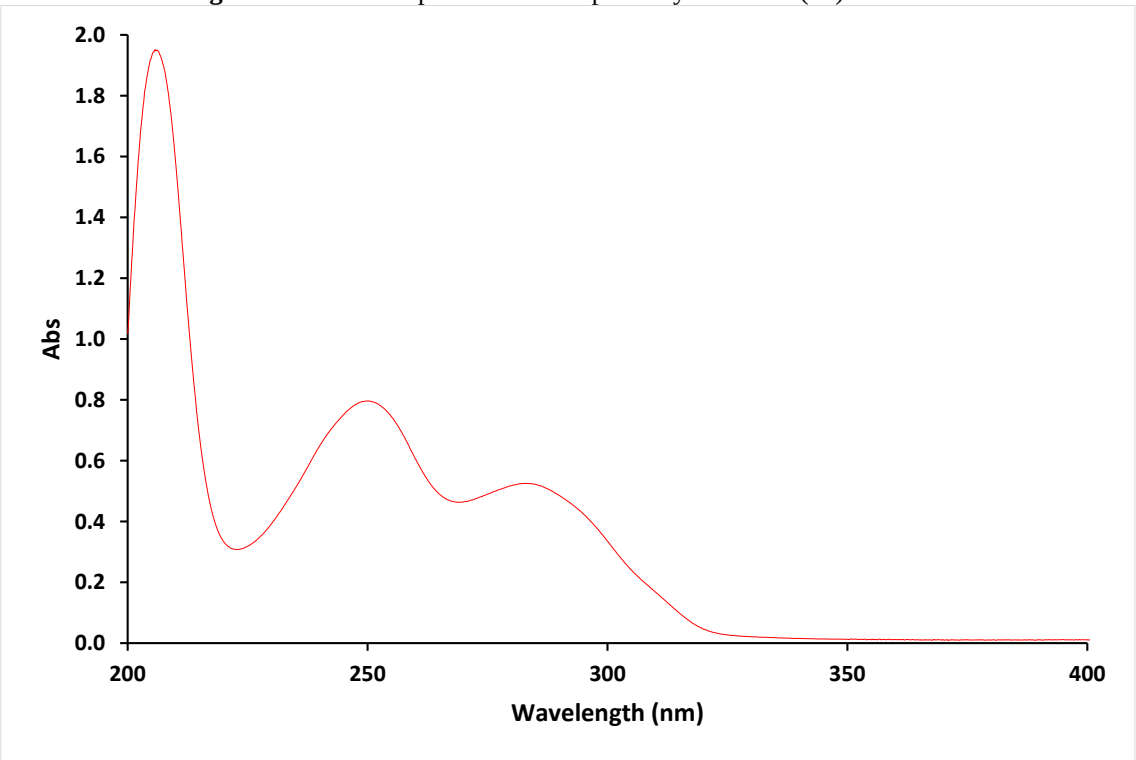


Figure S94. UV-vis spectrum of 5-*O*-acetylenterocin (**11**) in MeOH

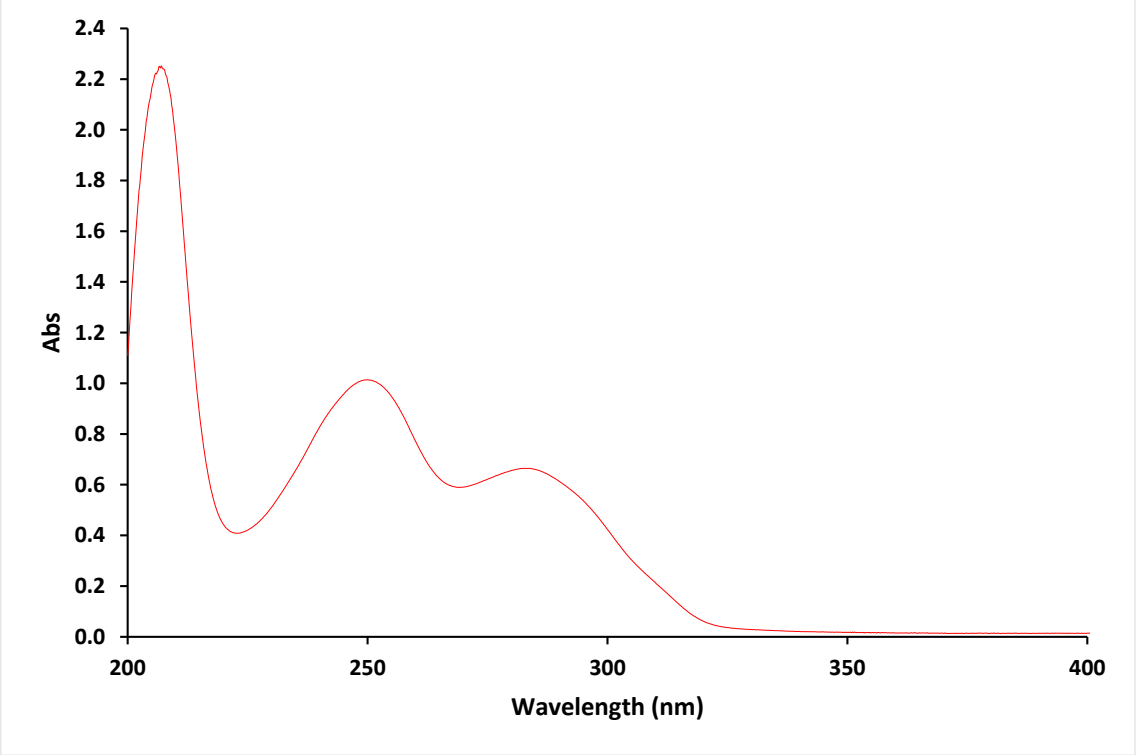


Figure S95. UV-vis spectrum of 5-*O*-propionylenterocin (**12**) in MeOH

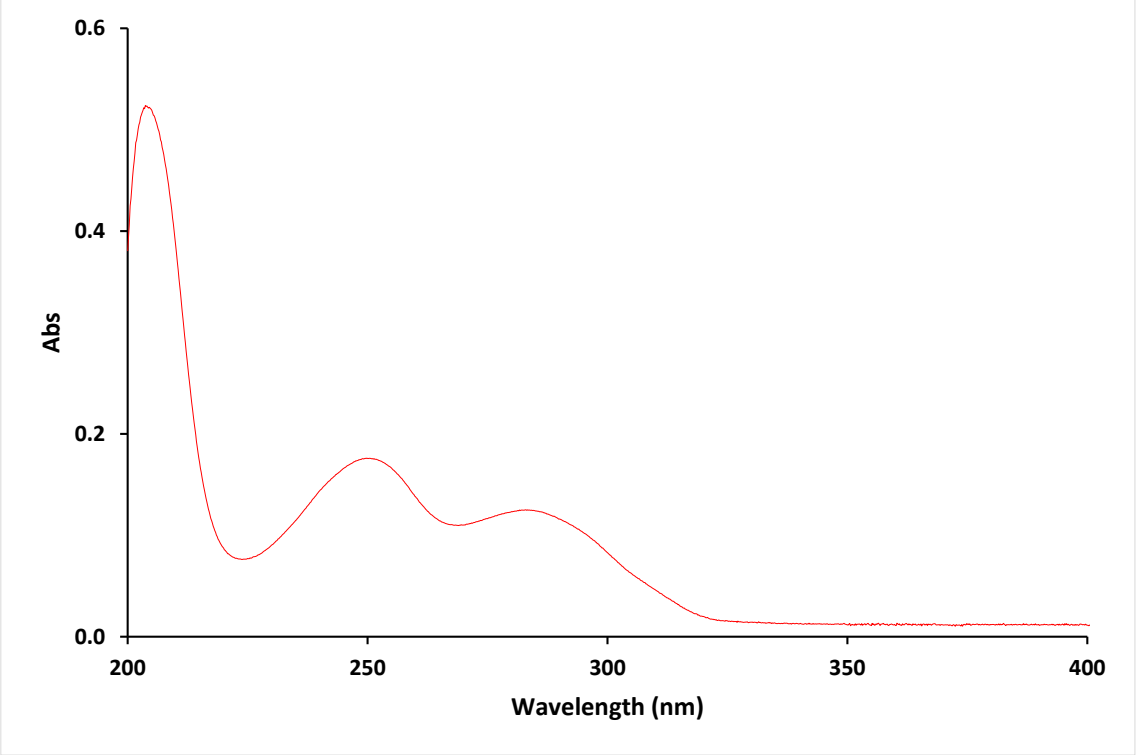


Figure S96. UV-vis spectrum of 5-*O*-carboxypropionylenterocin (**13**) in MeOH

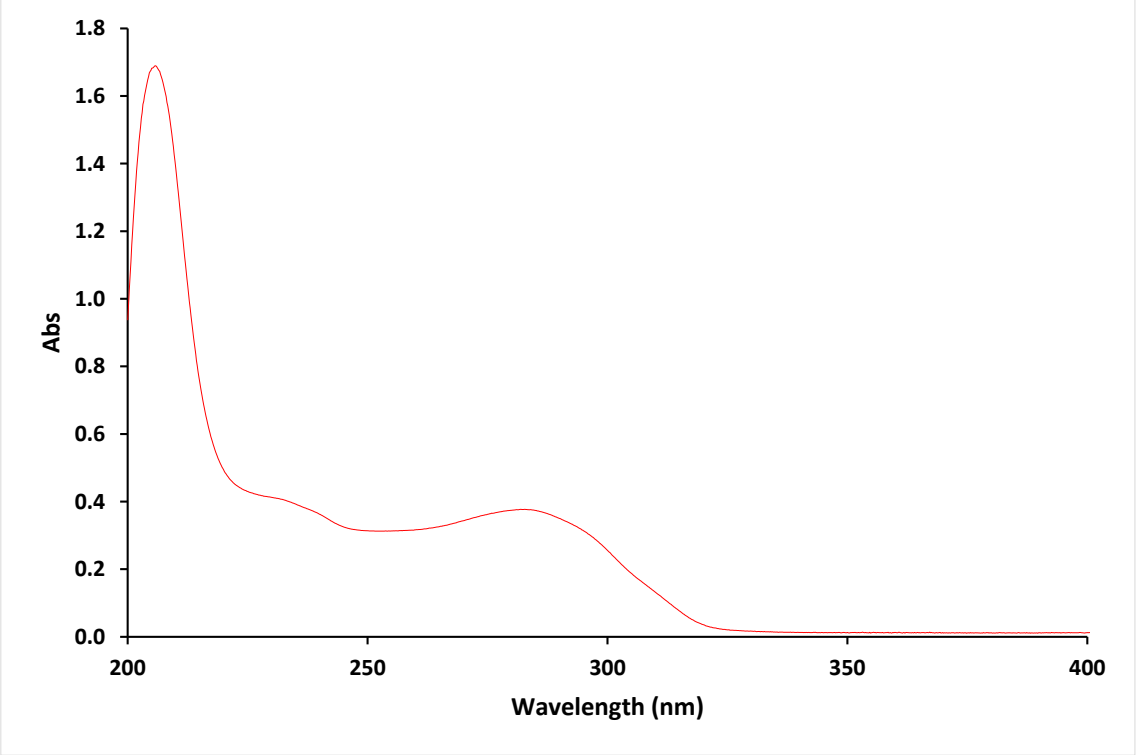


Figure S97. UV-vis spectrum of 3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**) in MeOH

D. HRMS Spectra

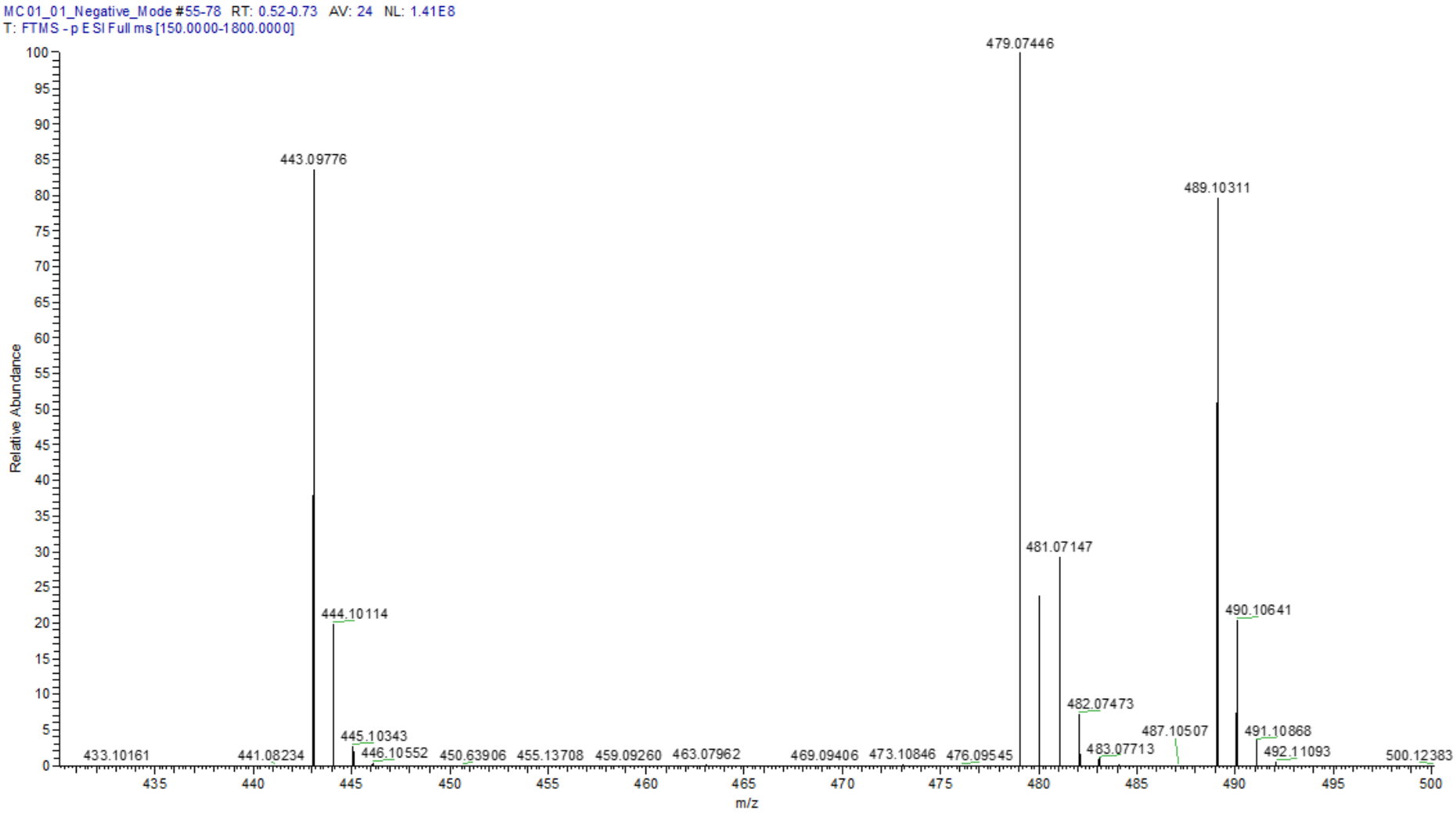


Figure S98. HR-ESI(–)-MS spectrum of enterocin (**1**)

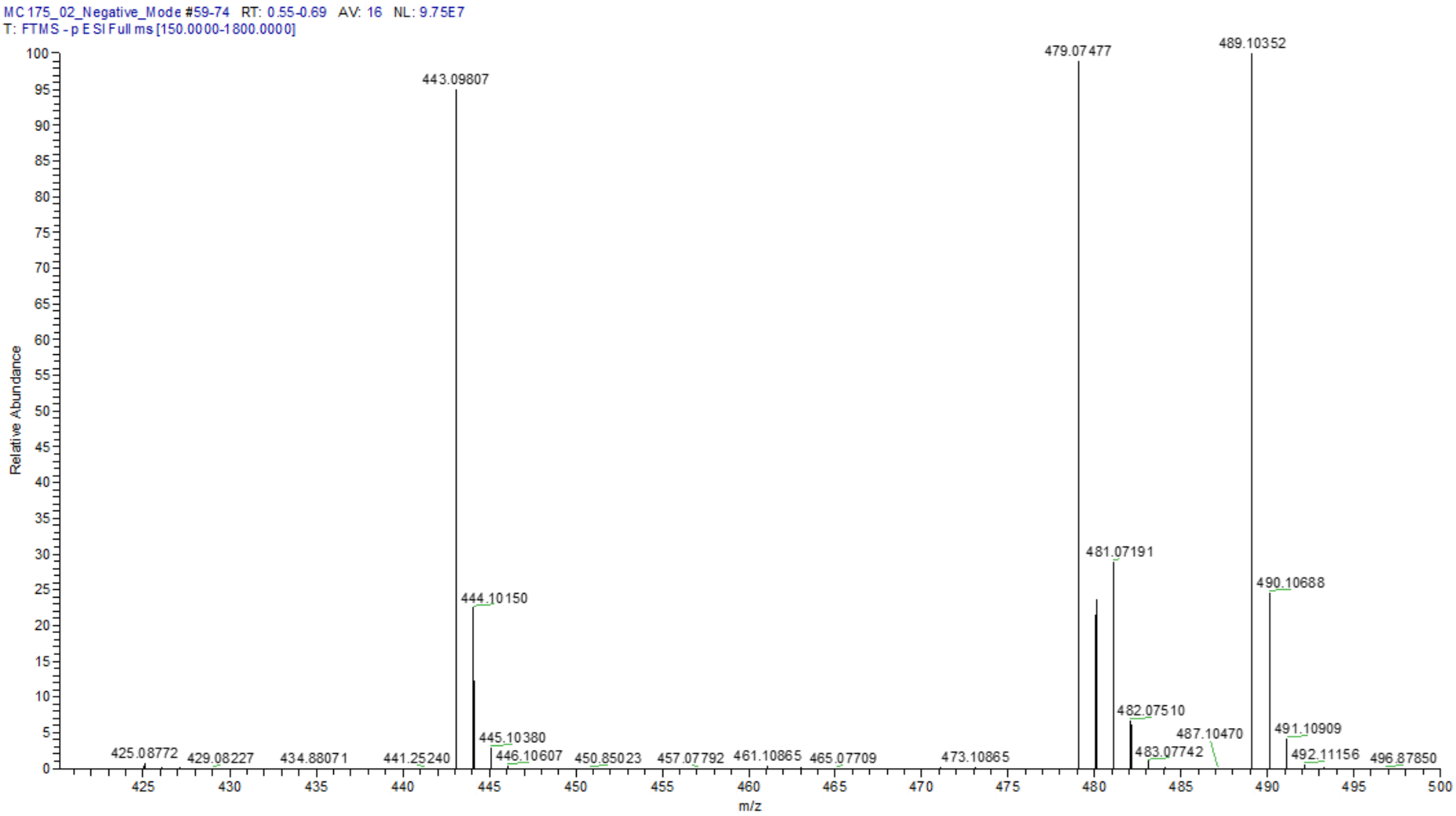


Figure S99. HR-ESI(–)-MS spectrum of isoenterocin A (**2**)

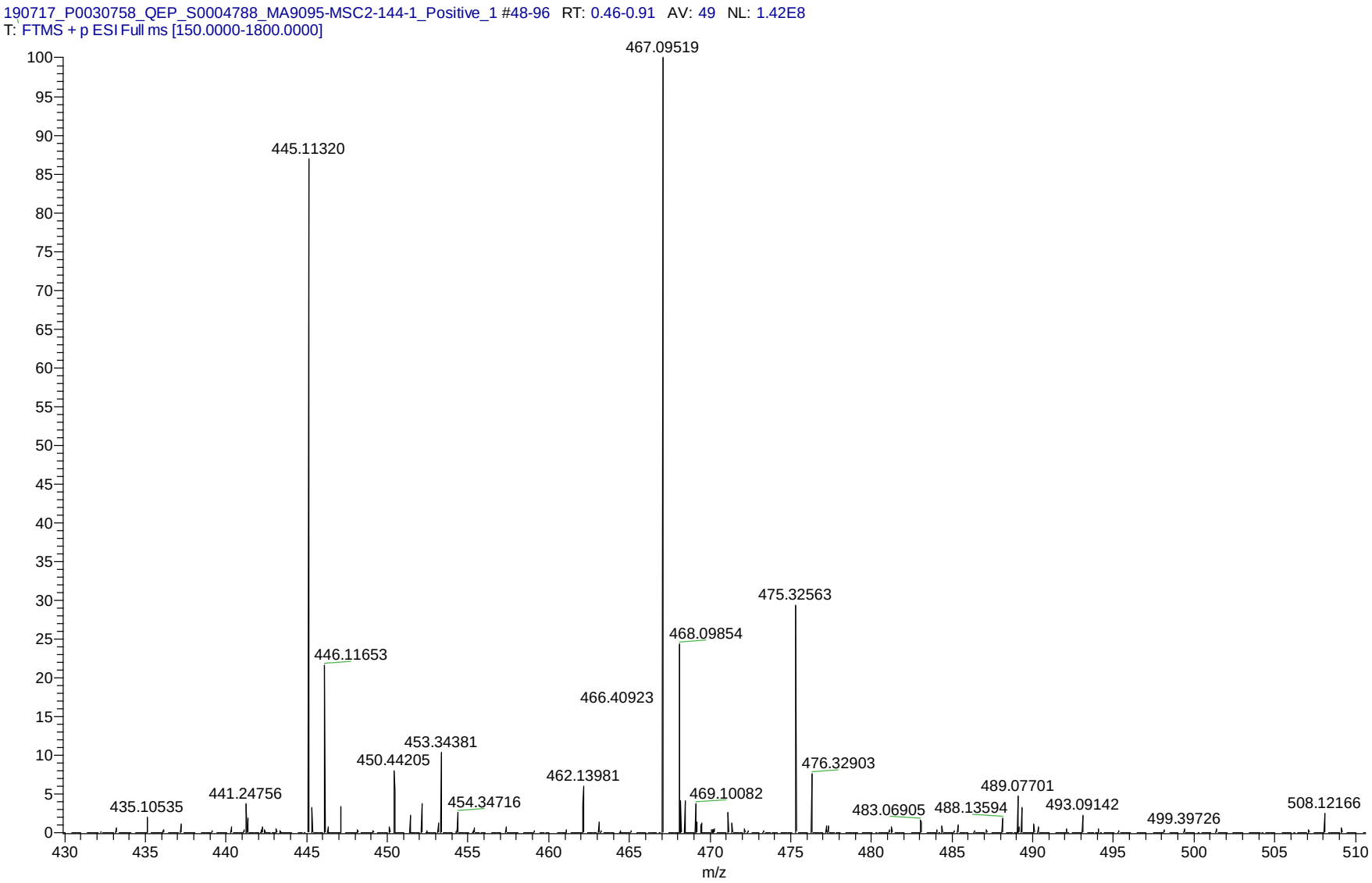


Figure S100. HR-ESI(+)-MS spectrum of isoenterocin B (**3**)

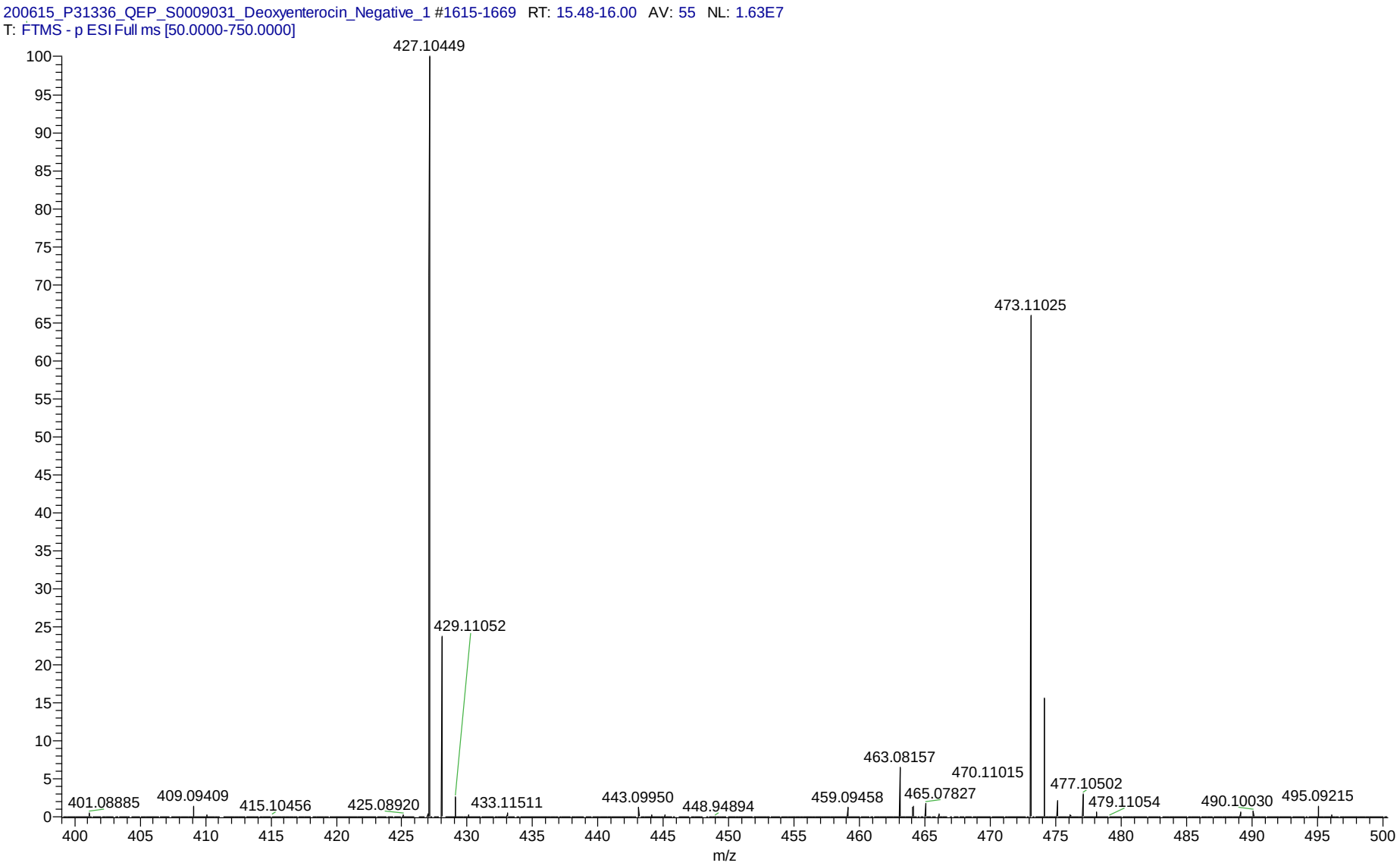


Figure S101. HR-ESI(–)-MS spectrum of 5-*O*-deoxyenterocin (**5**)

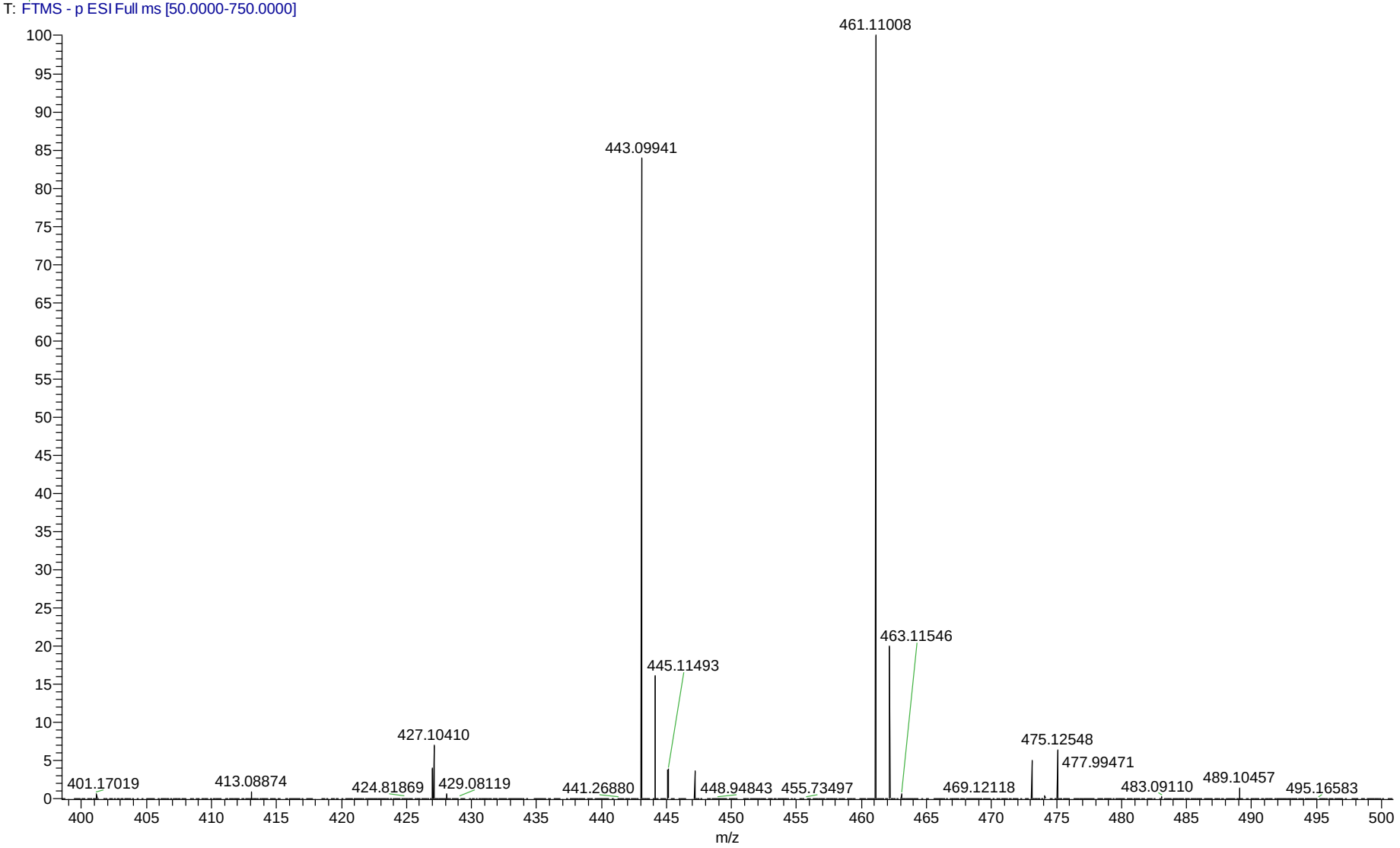


Figure S102. HR-ESI(–)-MS spectrum of enterocinic acid A (**7**)

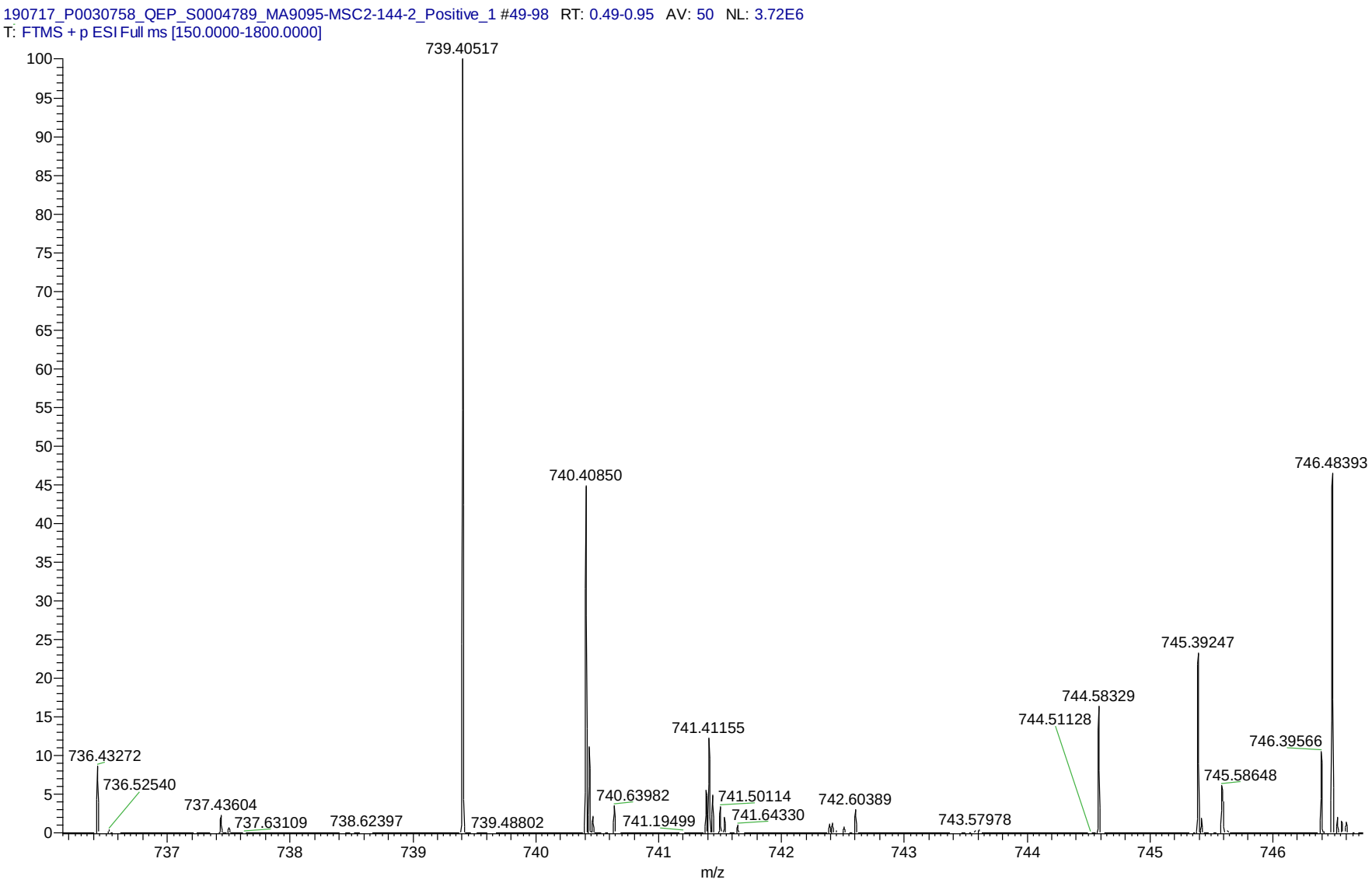


Figure S103. HR-ESI(+)-MS spectrum of 5-*O*-arachidoylenterocin (**8**)

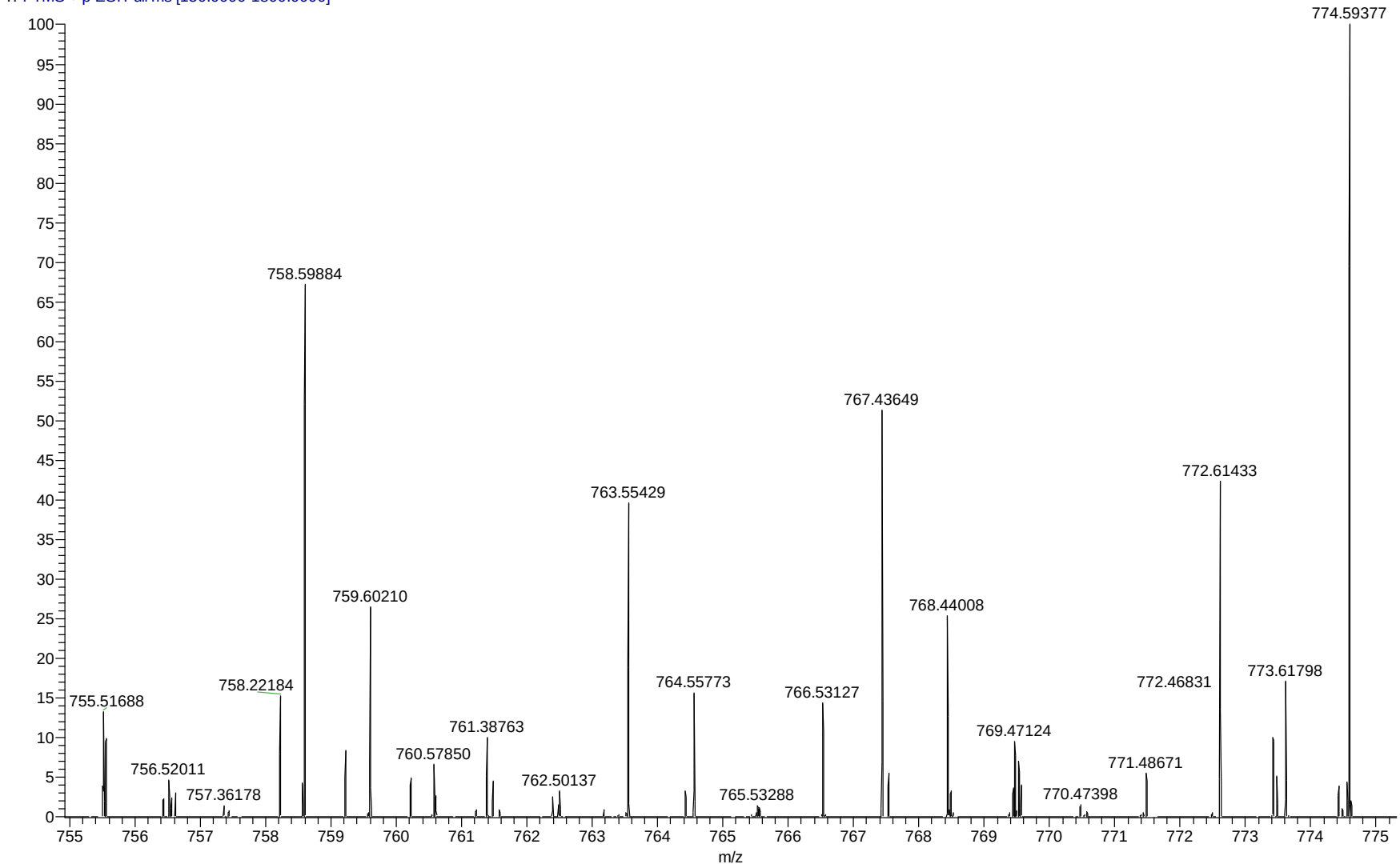


Figure S104. HR-ESI(+)-MS spectrum of 5-*O*-behenoylenterocin (**9**)

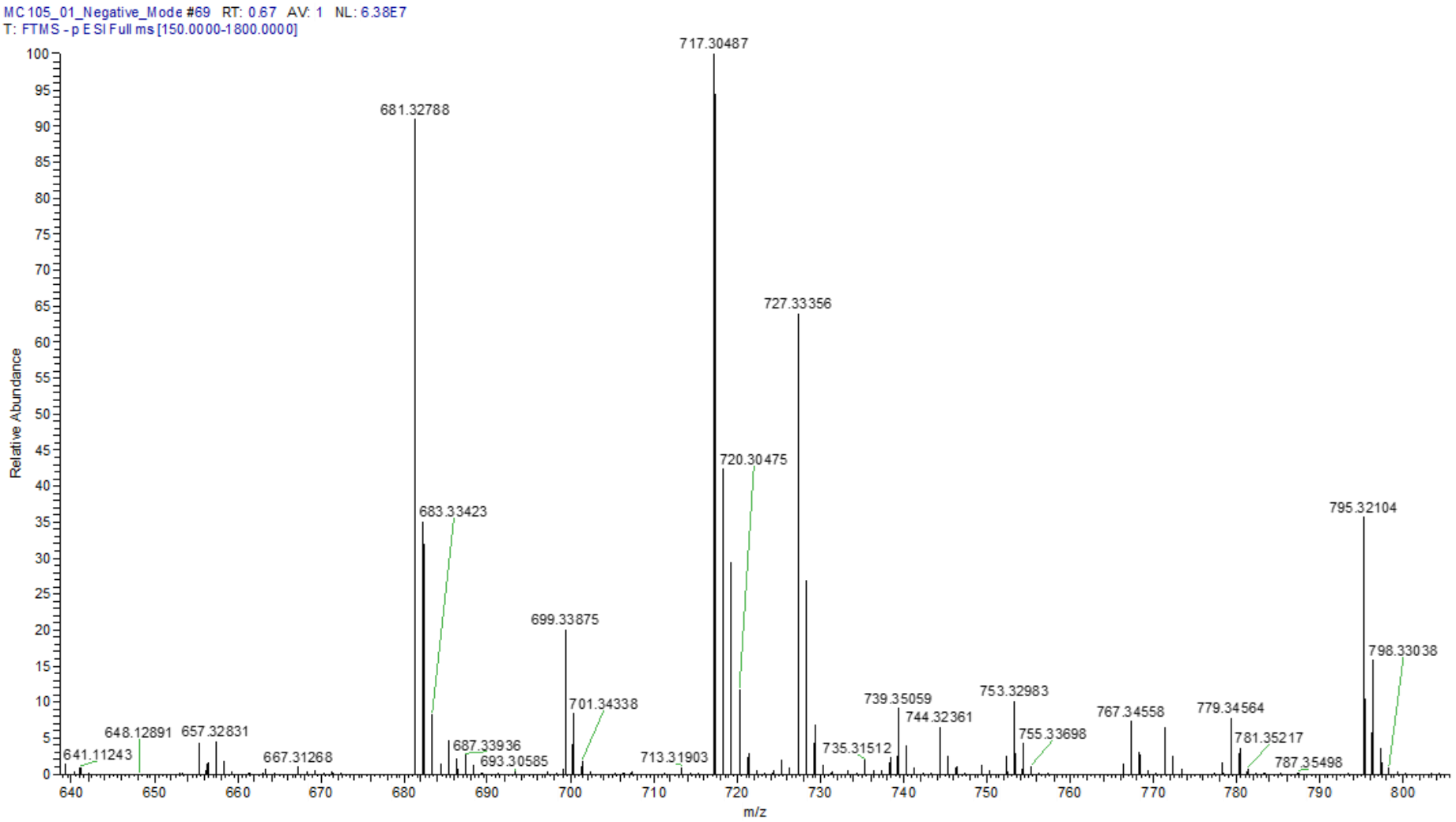


Figure S105. HR-ESI(–)-MS spectrum of 5-*O*-palmitoylenterocin (**10**)

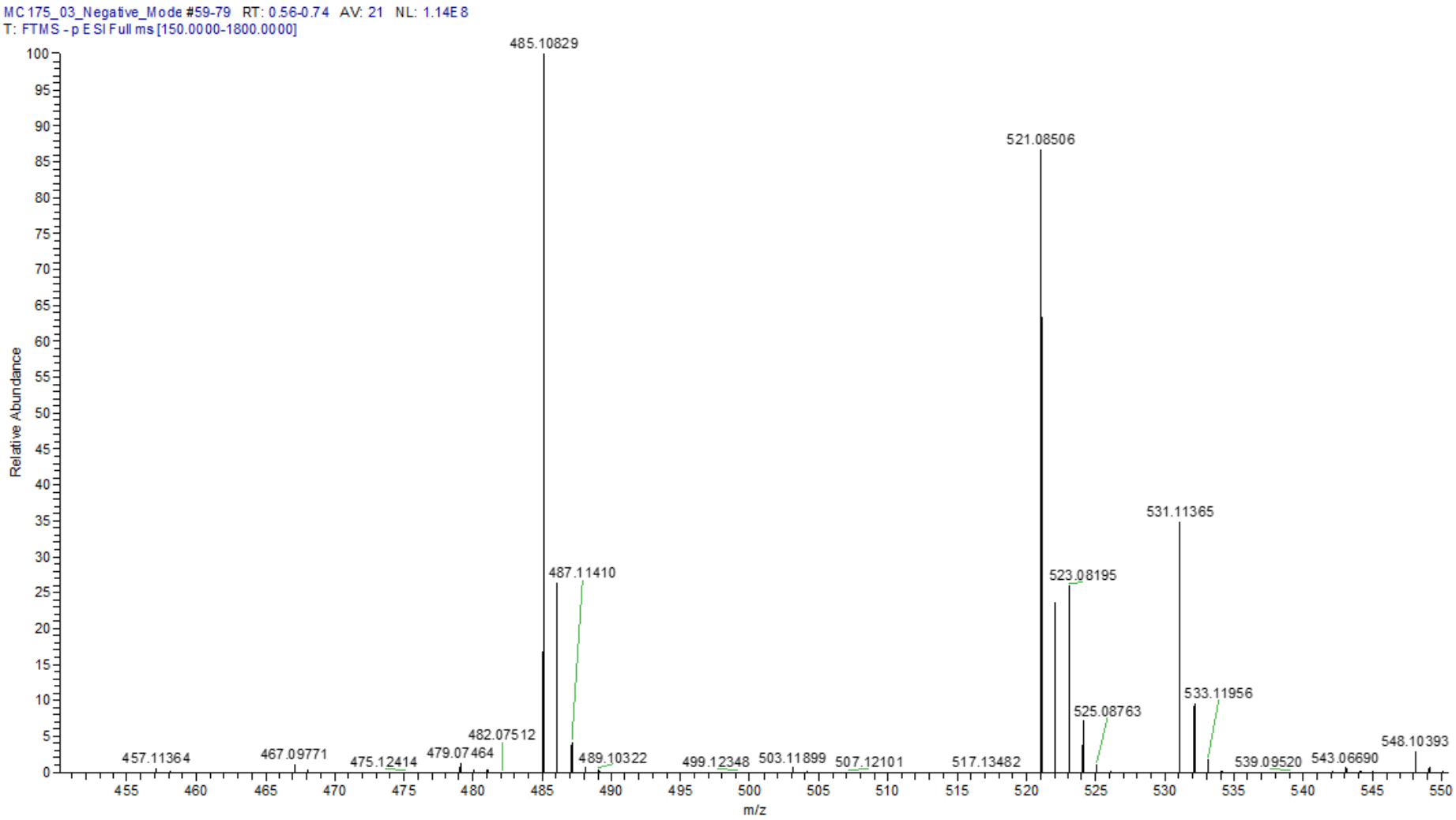


Figure S106. HR-ESI(–)-MS spectrum of 5-*O*-acetylenterocin (**11**)

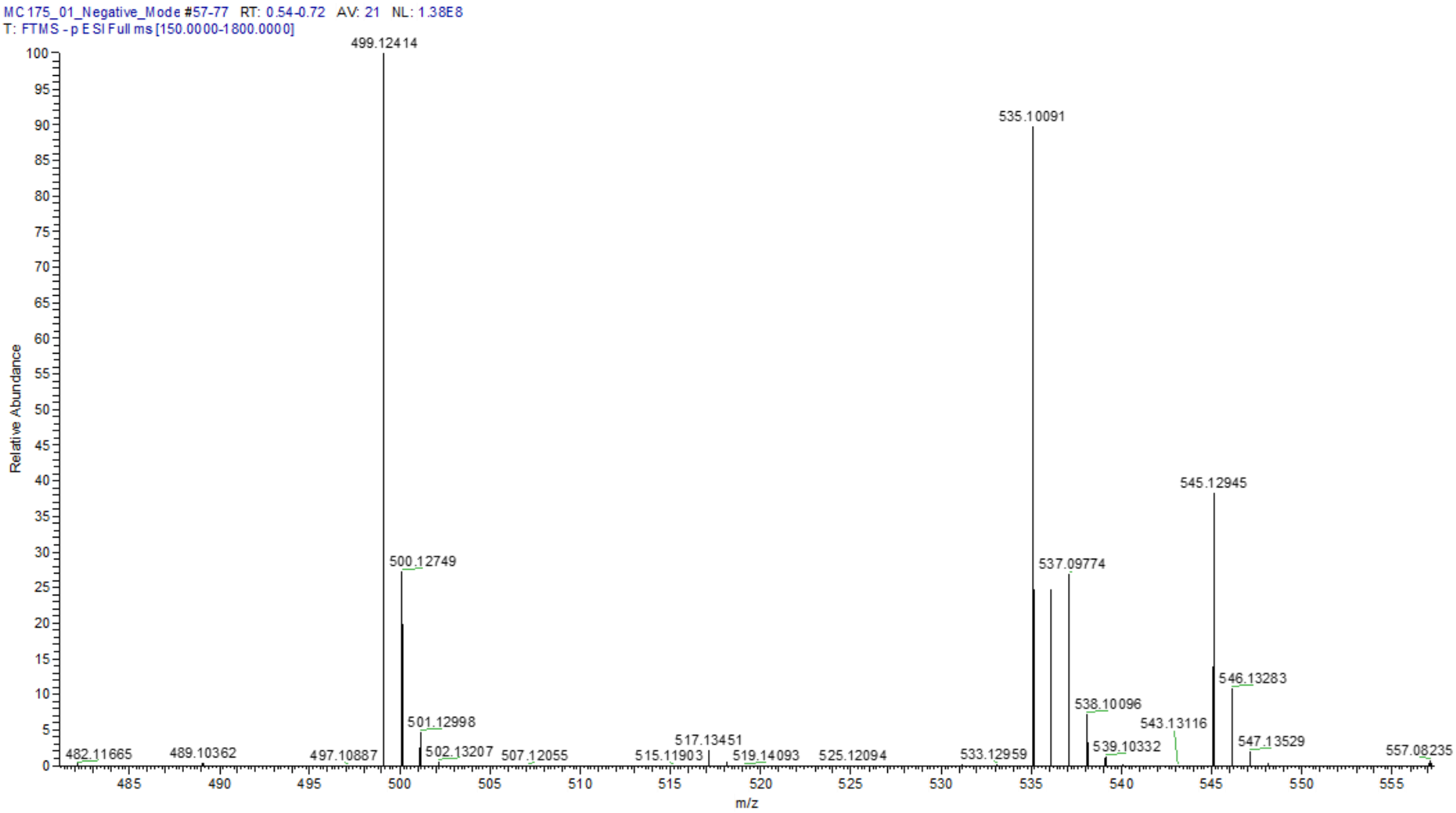


Figure S107. HR-ESI(–)-MS spectrum of 5-*O*-propionylenterocin (**12**)

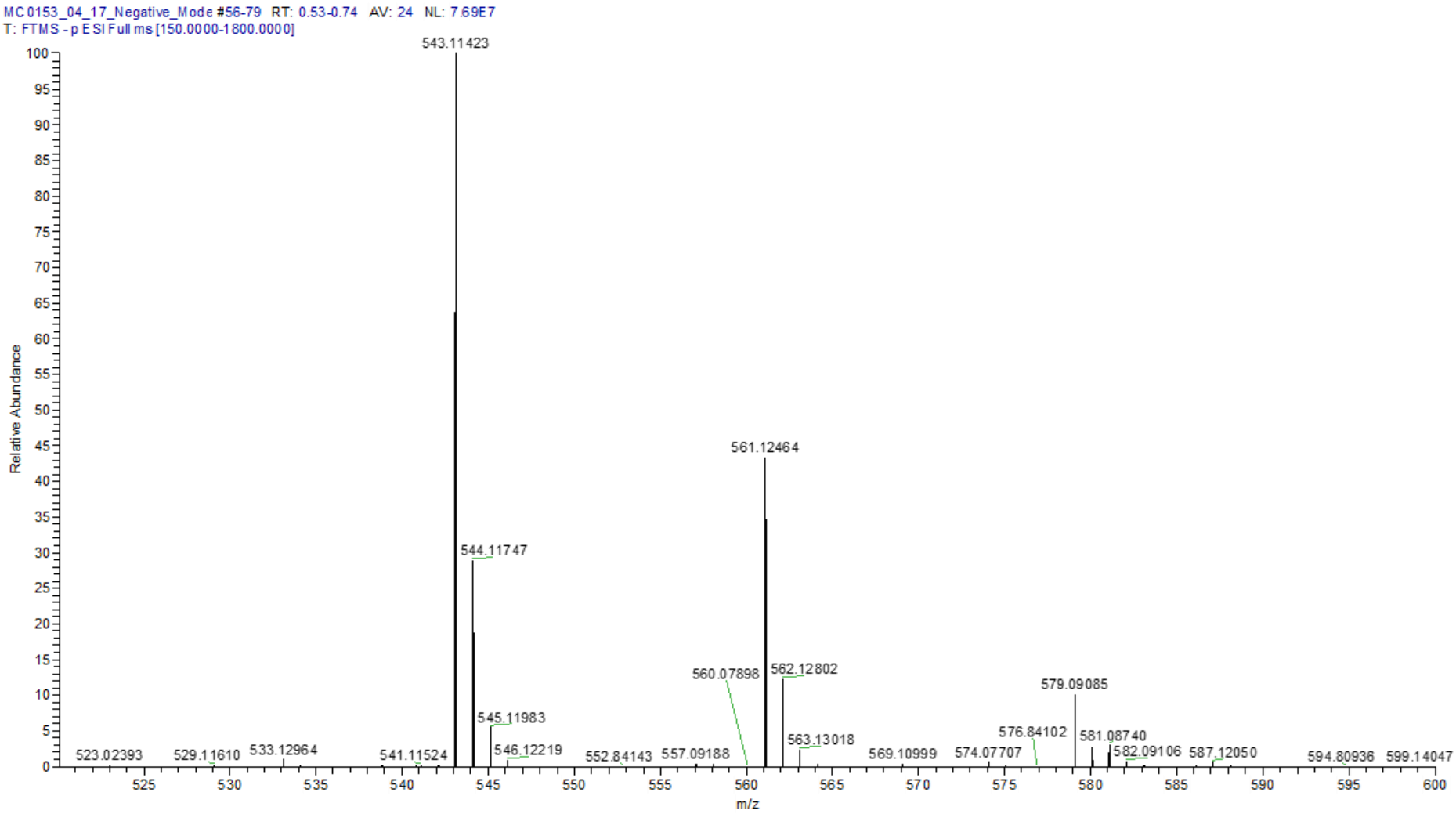


Figure S108. HR-ESI(–)-MS spectrum of 5-*O*-carboxypropionylenterocin (**13**)

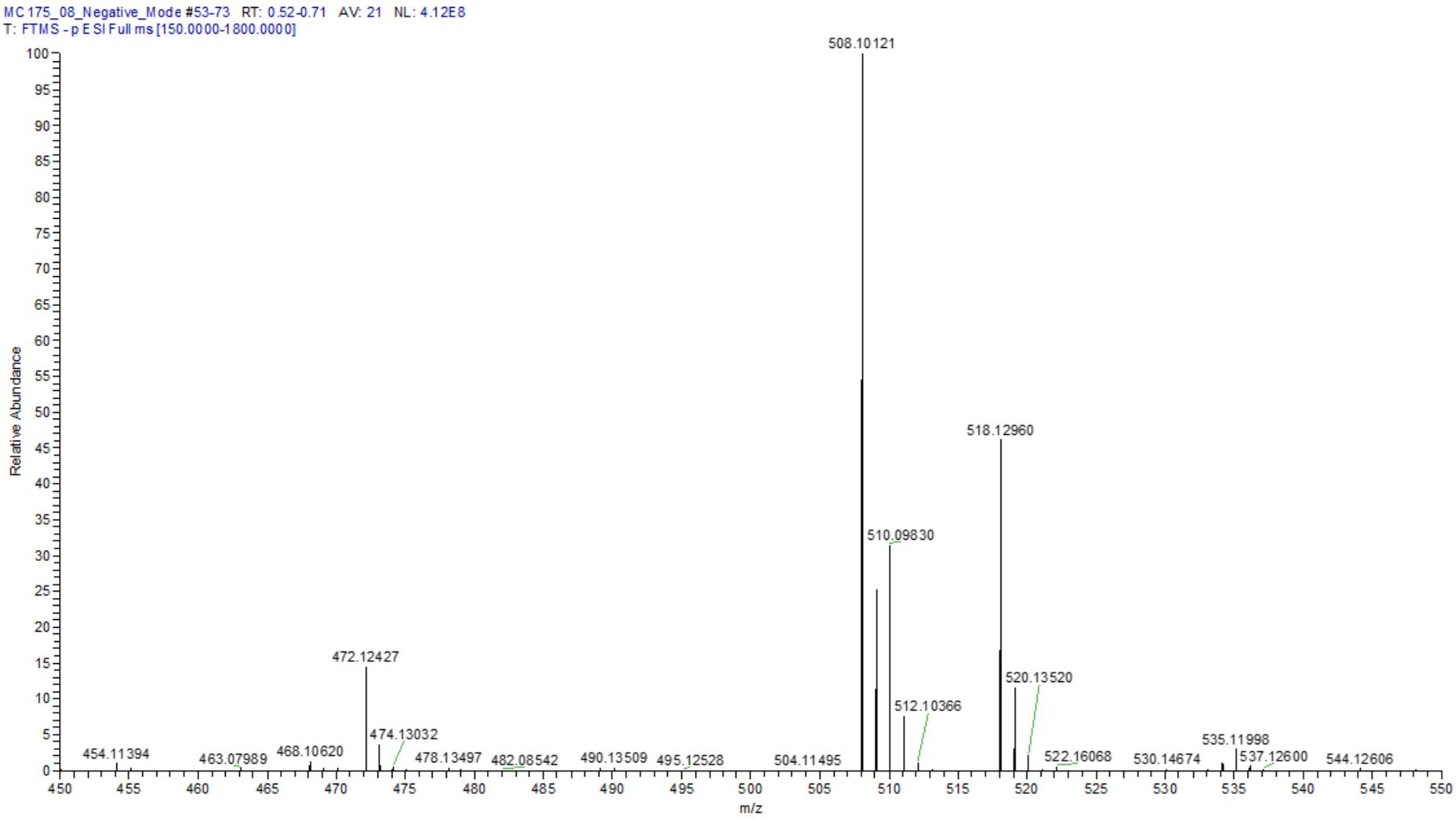


Figure S109. HR-ESI(–)-MS spectrum of 3-*epi*-(*Z*)-15-*O*-methyloxime (**14**)

E. HPLC Traces for Kinetic and Stability Studies

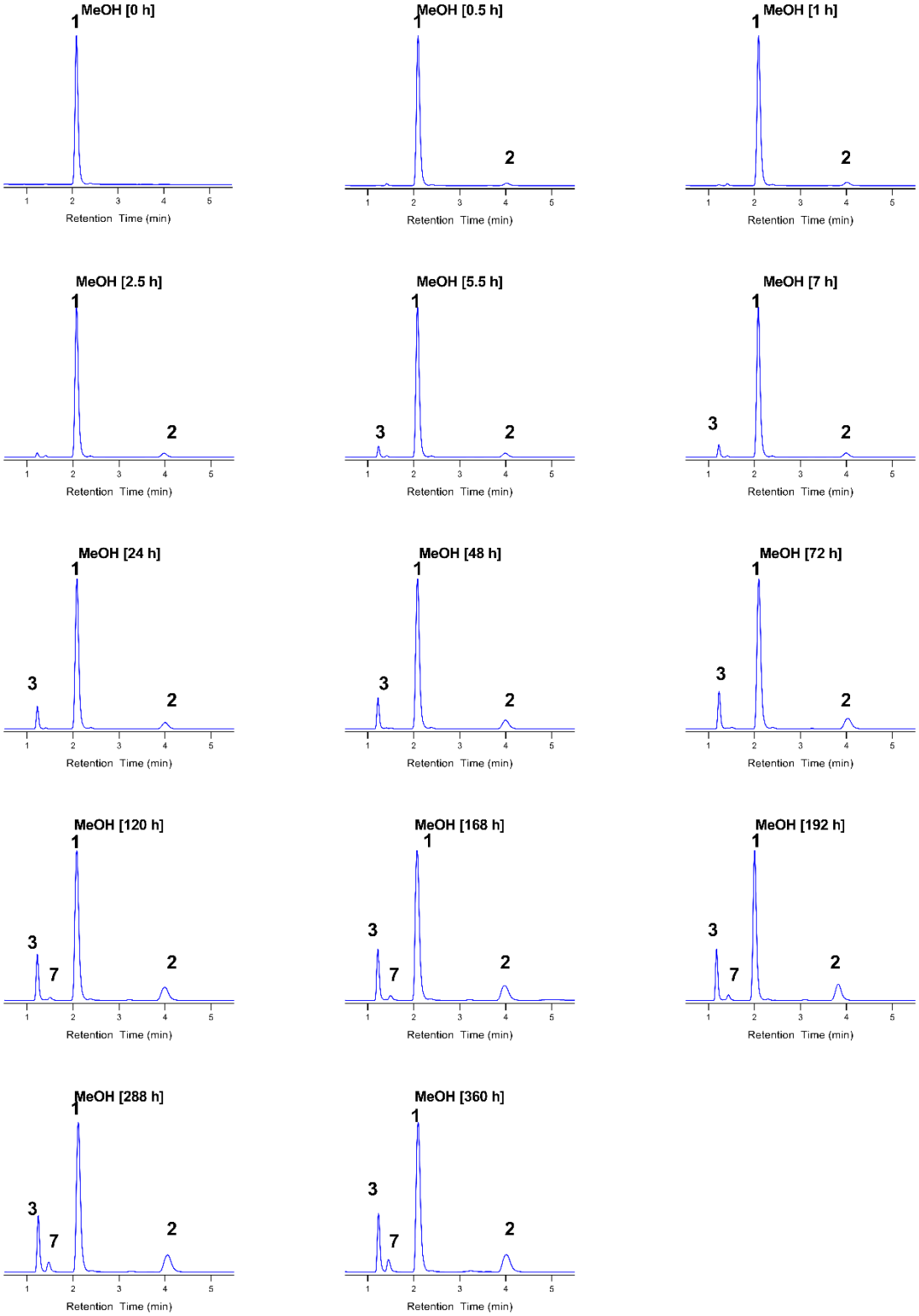


Figure S110. HPLC traces (210 nm) of enterocin (**1**) in MeOH following incubation at 50 °C.

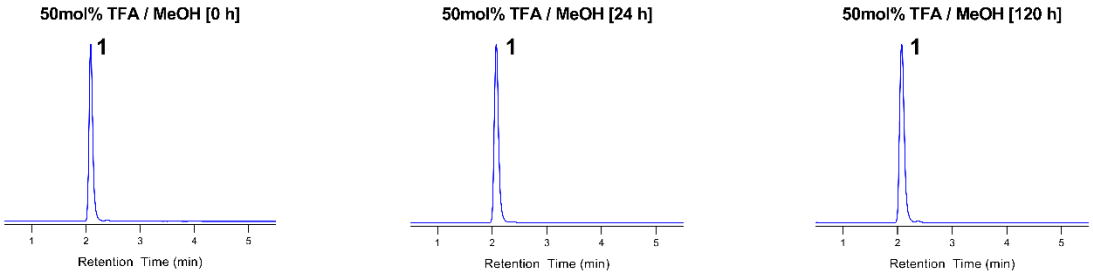


Figure S111. HPLC traces (210 nm) of enterocin (**1**) in 50 mol% TFA/MeOH following incubation at 50 °C.

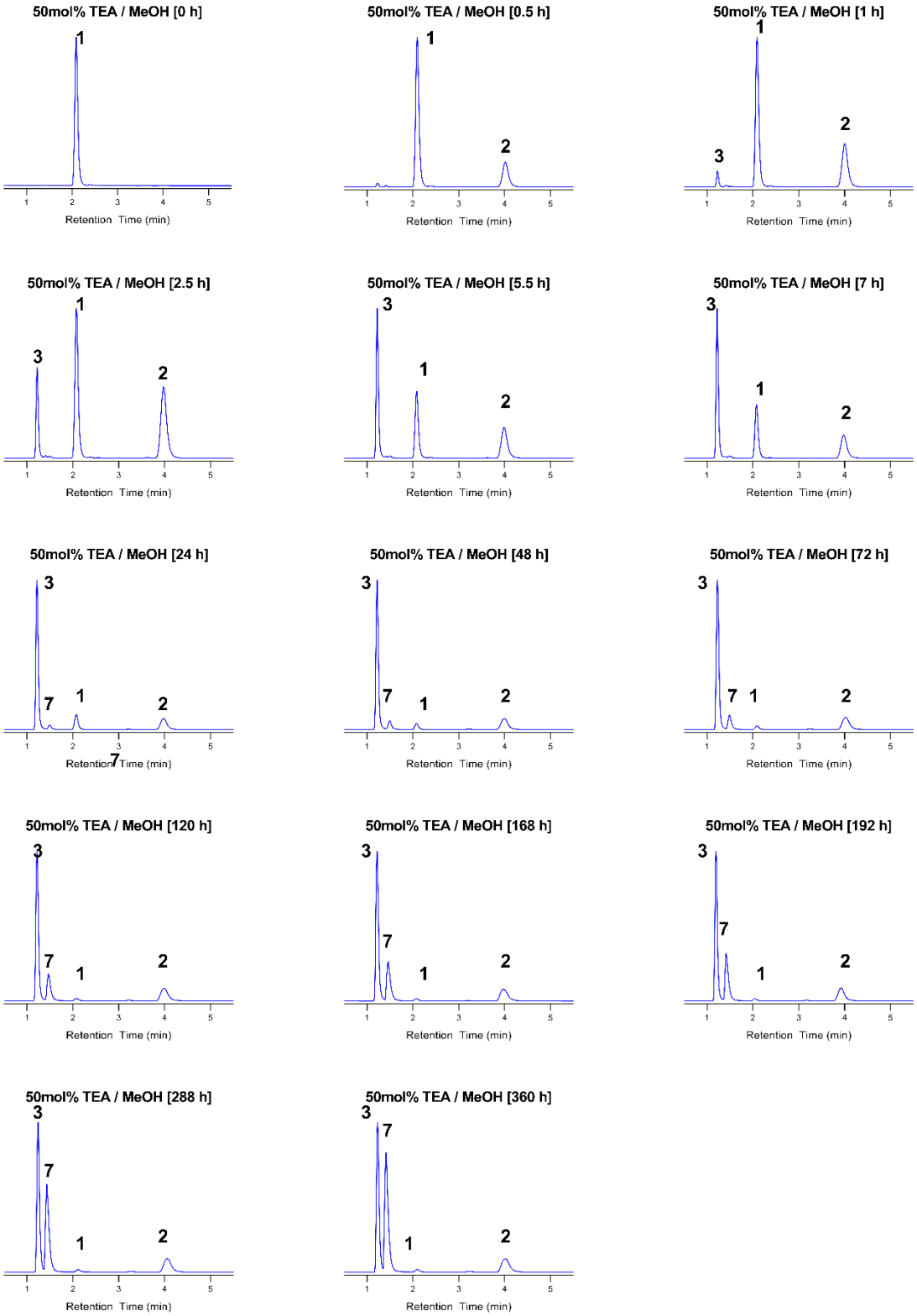


Figure S112. HPLC traces (210 nm) of enterocin (**1**) in 50 mol% TEA/MeOH following incubation at 50 °C.

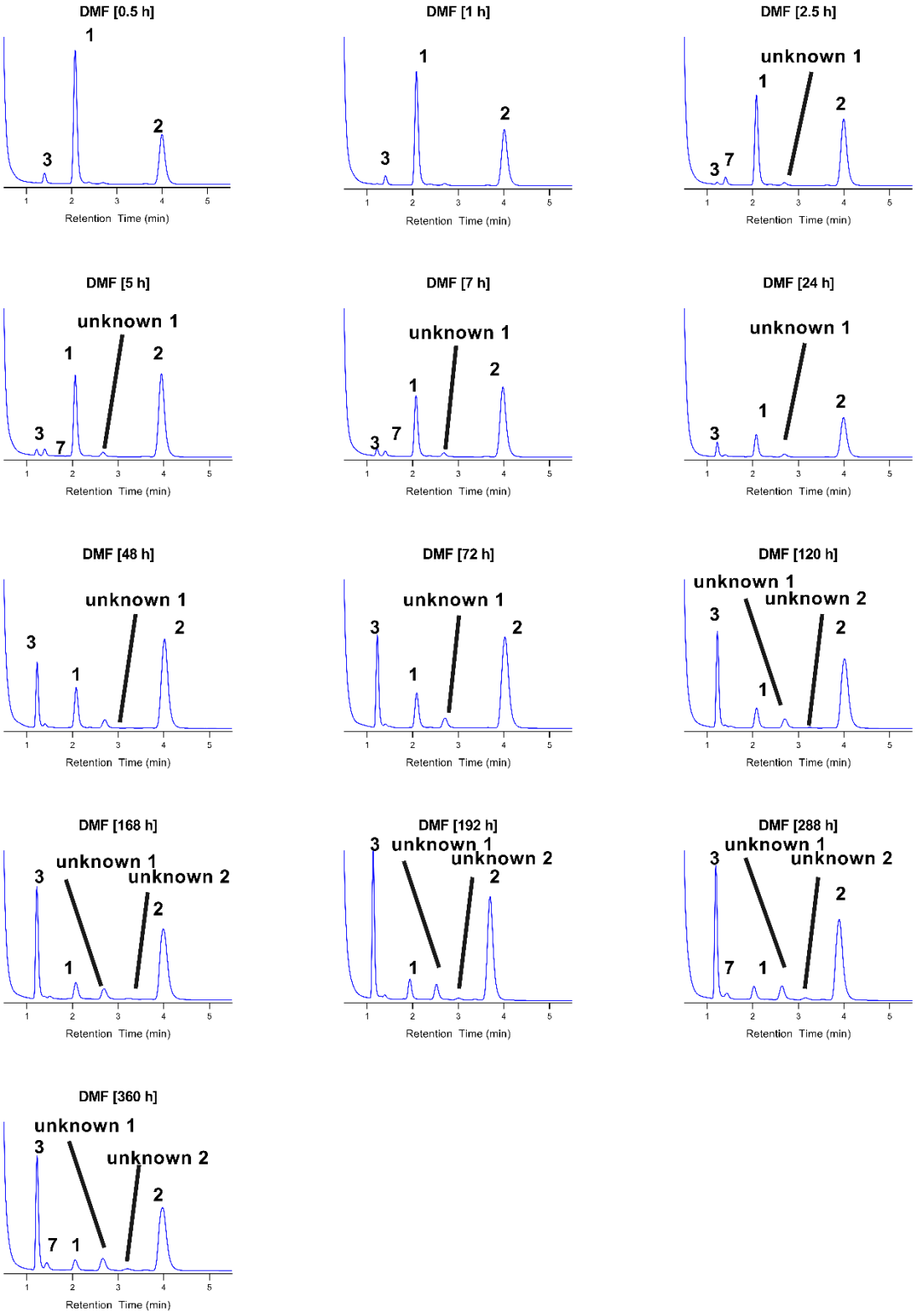


Figure S113. HPLC traces (210 nm) of enterocin (**1**) in DMF following incubation at 50 °C.

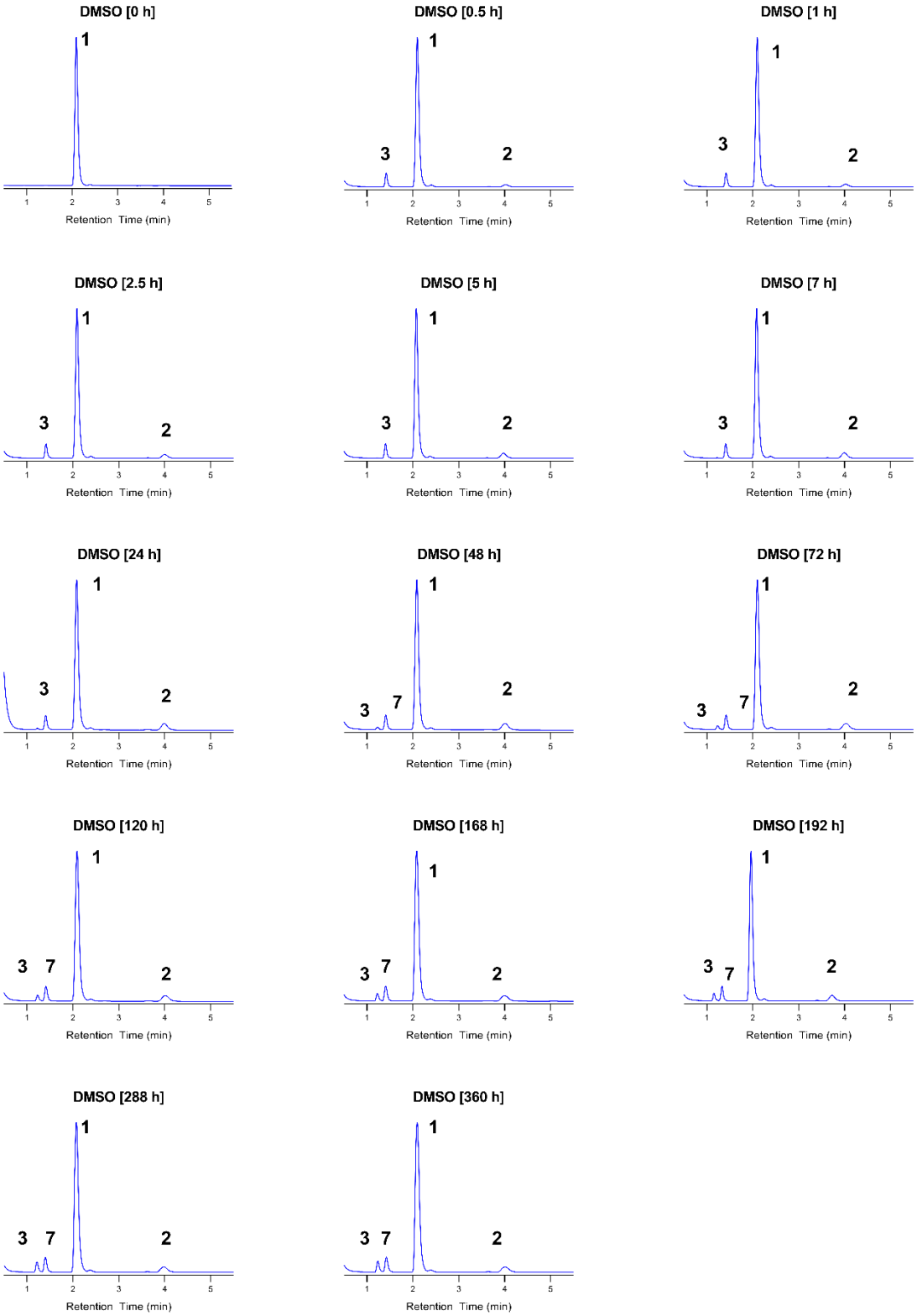


Figure S114. HPLC traces (210 nm) of enterocin (**1**) in 50 mol% TFA/DMSO following incubation at 50 °C.

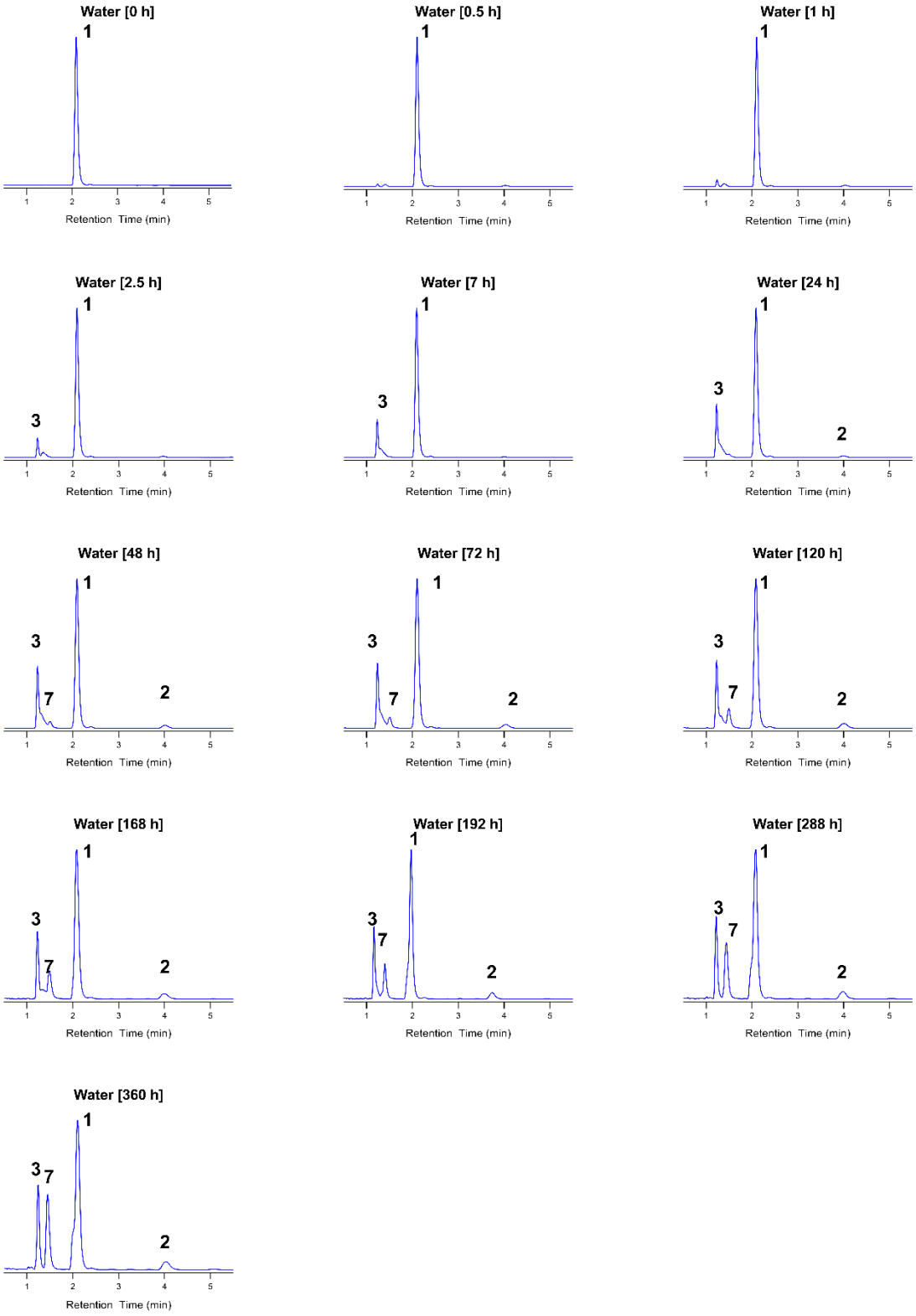


Figure S115. HPLC traces (210 nm) of enterocin (**1**) in water following incubation at 50 °C.

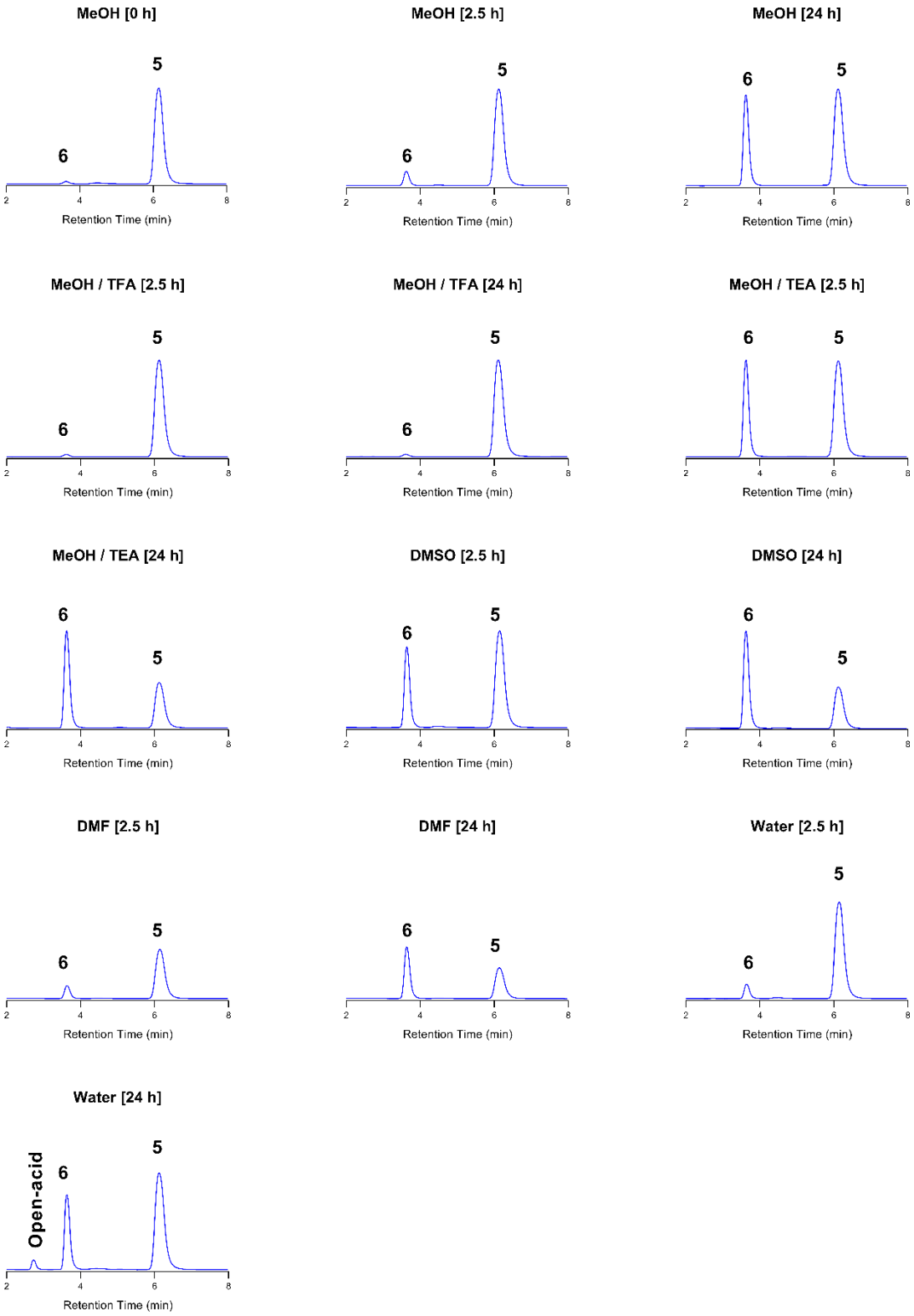


Figure S116. HPLC traces (210 nm) of 5-deoxyenterocin (**5**) in various solvents following incubation at 50 °C.

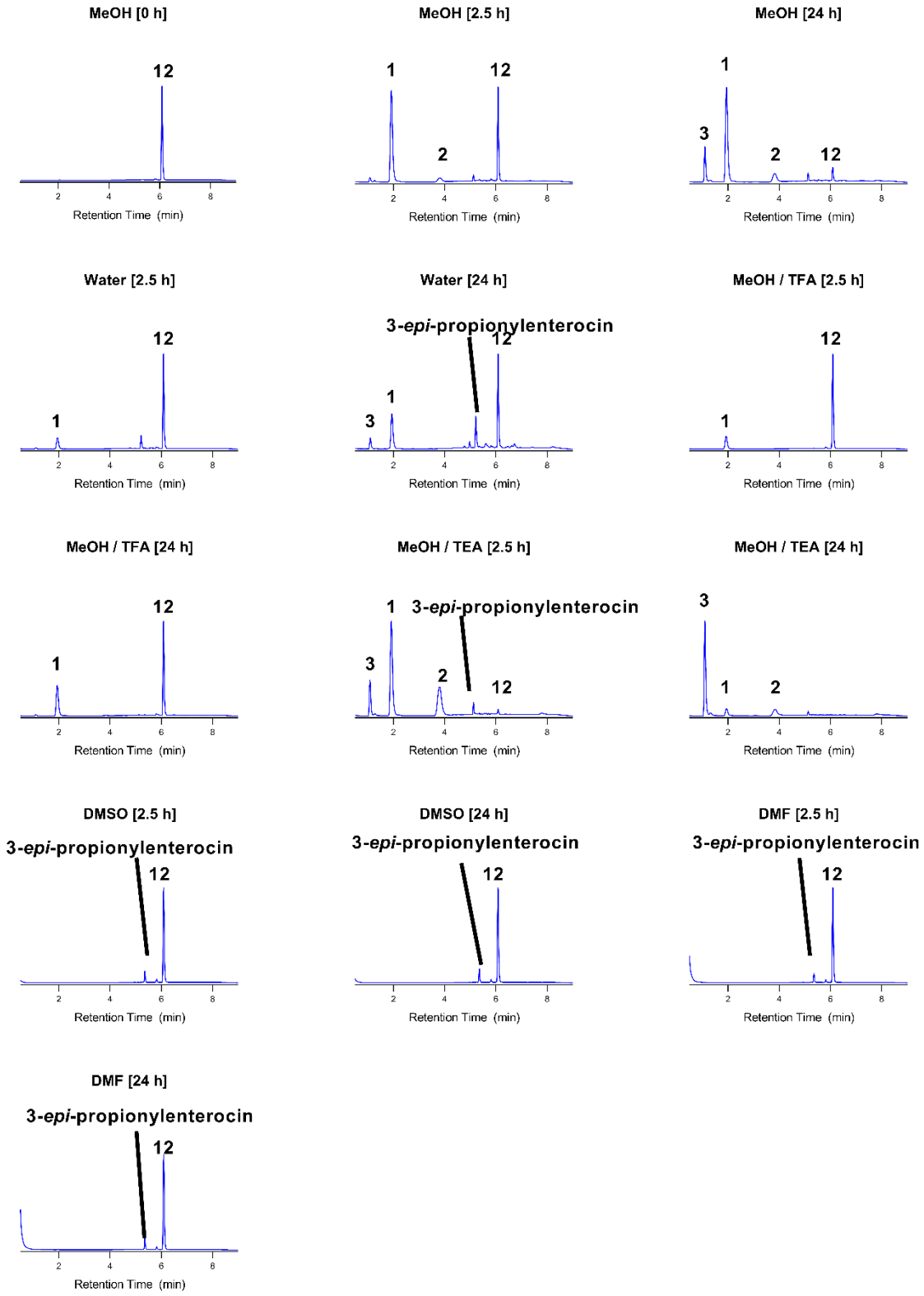


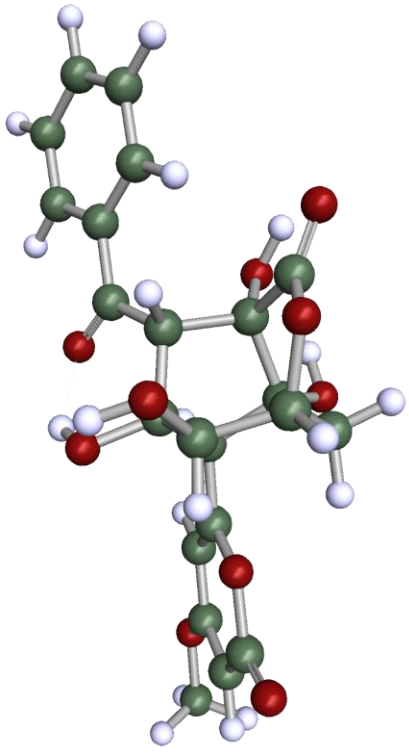
Figure S117. HPLC traces (210 nm) of 5-*O*-propionylenterocin (**12**) following incubation at 50 °C.

F. DFT Calculations

Table S15. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of enterocin (**1**).

Enterocin
52

C 1.531229 0.493382 0.557525
O 2.430813 0.577481 1.635034
H 3.082612 -0.140019 1.491773
C 2.154364 -0.347198 -0.657302
O 3.258972 -1.094686 -0.188191
H 3.985500 -0.900451 -0.821437
C 2.596095 0.545593 -1.807361
O 1.681227 1.405813 -2.266801
O 3.688177 0.414163 -2.332008
C 1.183728 1.896148 0.051773
H 2.100466 2.490906 -0.020023
H 0.489485 2.396456 0.728259
C 0.573442 1.746321 -1.338231
H 0.211190 2.688487 -1.749334
C -0.576696 0.729265 -1.348457
O -0.911212 0.443372 -2.704840
H -1.636266 -0.204651 -2.664478
H -1.413893 1.216911 -0.835239
C -0.268244 -0.579689 -0.580289
C 0.975751 -1.233775 -1.223971
H 0.909009 -1.131381 -2.313328
C 1.137255 -2.724532 -0.916869
O 0.409939 -3.274323 -0.085748
O -1.456535 -1.350082 -0.662152
H -1.219499 -2.230076 -0.303242
C 0.243875 -0.320041 0.863034
H 0.568502 -1.288267 1.259777
C 4.029265 -5.027498 -3.074383
H 4.760661 -5.621911 -3.615479
C 3.243286 -5.621872 -2.080490
H 3.365594 -6.676253 -1.848853
C 2.306840 -4.862055 -1.388377
H 1.687634 -5.301412 -0.612282
C 2.145521 -3.496461 -1.681513
C 2.937598 -2.908190 -2.680866
H 2.837581 -1.854885 -2.919216
C 3.875353 -3.671250 -3.372909
H 4.484991 -3.207309 -4.142786
C -2.557346 1.391447 3.603481
H -3.280085 1.873220 4.248565
C -1.863131 0.261116 3.968015
O -1.995525 -0.375063 5.152522
C -2.935507 0.183116 6.089747
H -2.642844 1.206787 6.353551
H -2.892769 -0.466267 6.964829
H -3.943836 0.183918 5.657972
C -0.919366 -0.337535 3.077623
H -0.376941 -1.227249 3.370970
C -0.715901 0.228712 1.861356
O -1.388541 1.339357 1.477173
C -2.352457 2.001965 2.325839
O -2.868357 2.991448 1.857636



VIBRATIONAL SPECTRUM :

mode	symmetry	wave number cm**(-1)	intensity km/mol	selection rules	
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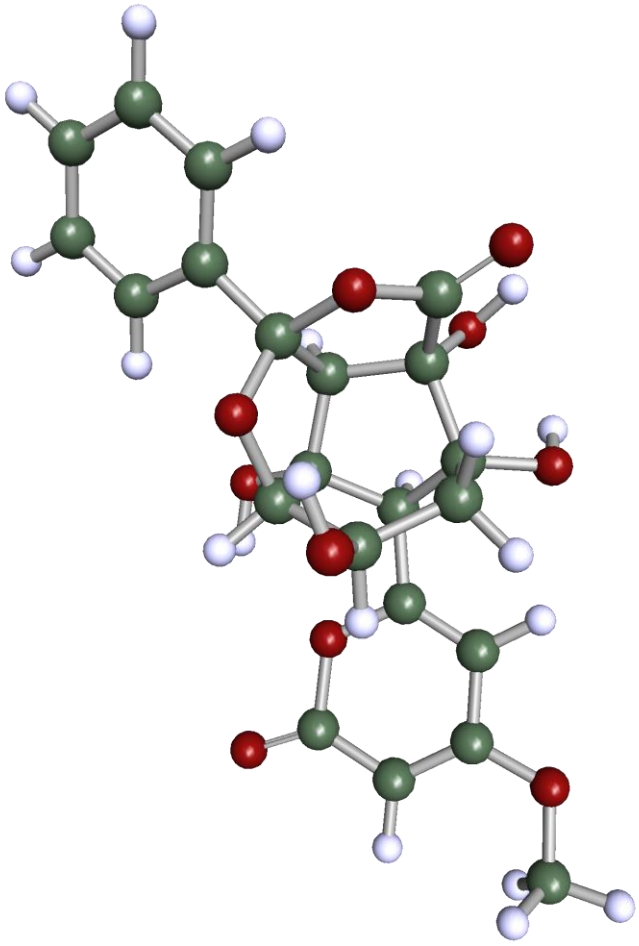
2		0.00	0.0000000	-	-
3		0.00	0.0000000	-	-
4		0.00	0.0000000	-	-
5		0.00	0.0000000	-	-
6		0.00	0.0000000	-	-
7	a	19.48	1.5691400	YES	YES
8	a	27.87	1.1751500	YES	YES
9	a	33.88	0.6398600	YES	YES
10	a	41.57	0.0691300	YES	YES
11	a	56.46	0.9744100	YES	YES
12	a	71.35	0.3814200	YES	YES
13	a	100.94	2.3066600	YES	YES
14	a	109.89	1.3787200	YES	YES
15	a	126.77	1.5868900	YES	YES
16	a	133.91	0.9890800	YES	YES
17	a	143.87	0.6790800	YES	YES
18	a	149.30	1.3375400	YES	YES
19	a	152.26	0.3107700	YES	YES
20	a	173.86	3.8024600	YES	YES
21	a	190.20	1.3802600	YES	YES
22	a	193.85	2.7703600	YES	YES
23	a	206.03	3.5898400	YES	YES
24	a	223.00	1.1020100	YES	YES
25	a	236.04	11.2547700	YES	YES
26	a	241.05	2.2120400	YES	YES
27	a	245.36	5.0390900	YES	YES
28	a	259.11	0.1348900	YES	YES
29	a	297.51	15.6826900	YES	YES
30	a	307.65	16.7889400	YES	YES
31	a	328.54	6.0714200	YES	YES
32	a	333.20	25.9171300	YES	YES
33	a	351.07	6.1473600	YES	YES
34	a	381.77	3.9693100	YES	YES
35	a	386.82	1.0005200	YES	YES
36	a	396.53	1.3691900	YES	YES
37	a	414.59	2.6716300	YES	YES
38	a	420.95	0.1717300	YES	YES
39	a	445.04	1.5514400	YES	YES
40	a	454.81	23.7325500	YES	YES
41	a	458.86	23.1921500	YES	YES
42	a	468.58	83.4708300	YES	YES
43	a	473.11	1.2329300	YES	YES
44	a	490.63	18.3755700	YES	YES
45	a	499.87	27.3183700	YES	YES
46	a	525.60	3.2843700	YES	YES
47	a	534.06	3.3057000	YES	YES
48	a	541.86	3.3190400	YES	YES
49	a	563.14	16.7173500	YES	YES
50	a	577.60	2.6375000	YES	YES
51	a	595.44	24.2364400	YES	YES
52	a	602.02	42.1322300	YES	YES
53	a	609.89	15.0598100	YES	YES
54	a	613.34	15.1246600	YES	YES
55	a	625.97	128.0789800	YES	YES
56	a	635.57	32.5826100	YES	YES
57	a	647.48	25.6943000	YES	YES
58	a	654.78	23.9232000	YES	YES
59	a	669.60	24.5465300	YES	YES
60	a	674.42	16.8714700	YES	YES
61	a	684.27	30.8178700	YES	YES
62	a	686.11	24.2167000	YES	YES
63	a	717.86	6.7659500	YES	YES
64	a	735.61	62.3671500	YES	YES
65	a	750.21	16.1038600	YES	YES
66	a	771.52	42.5135100	YES	YES
67	a	790.16	2.6520000	YES	YES
68	a	814.13	13.0167800	YES	YES
69	a	819.11	32.6519200	YES	YES
70	a	822.78	20.3037500	YES	YES
71	a	826.57	1.9212800	YES	YES
72	a	840.49	9.5057900	YES	YES
73	a	850.21	10.2273100	YES	YES
74	a	877.05	74.3924100	YES	YES
75	a	909.68	0.6374700	YES	YES
76	a	918.09	26.4395000	YES	YES
77	a	935.57	0.8215400	YES	YES
78	a	940.90	1.2667700	YES	YES
79	a	950.96	22.3143600	YES	YES
80	a	953.90	15.7959000	YES	YES
81	a	956.06	3.1887500	YES	YES
82	a	962.72	7.0698200	YES	YES
83	a	977.15	32.7251500	YES	YES
84	a	990.37	8.5276100	YES	YES
85	a	1000.06	48.8803900	YES	YES
86	a	1019.66	32.9219400	YES	YES
87	a	1025.78	14.4122000	YES	YES
88	a	1032.87	52.9262900	YES	YES
89	a	1059.03	53.4106200	YES	YES
90	a	1065.11	29.8660100	YES	YES
91	a	1079.08	129.8802500	YES	YES
92	a	1084.01	13.5450700	YES	YES
93	a	1092.36	23.4962200	YES	YES
94	a	1103.35	78.0446500	YES	YES
95	a	1115.58	58.1467600	YES	YES
96	a	1124.90	69.9948500	YES	YES
97	a	1126.65	0.2672200	YES	YES
98	a	1140.44	27.2402900	YES	YES
99	a	1155.11	95.8447500	YES	YES
100	a	1158.74	7.8732300	YES	YES
101	a	1174.14	73.4744300	YES	YES
102	a	1180.06	55.7339700	YES	YES
103	a	1190.85	55.5392000	YES	YES
104	a	1196.42	116.1395600	YES	YES
105	a	1209.31	100.3920800	YES	YES
106	a	1212.39	121.8065200	YES	YES
107	a	1232.06	170.6246200	YES	YES
108	a	1235.54	30.8626800	YES	YES
109	a	1242.06	10.5691700	YES	YES
110	a	1260.04	25.3006900	YES	YES
111	a	1291.58	42.7200200	YES	YES
112	a	1294.54	31.9076200	YES	YES
113	a	1308.63	21.7353500	YES	YES
114	a	1314.83	47.3707000	YES	YES
115	a	1326.50	37.2416400	YES	YES
116	a	1334.51	11.0265100	YES	YES
117	a	1346.17	45.5506500	YES	YES
118	a	1346.35	28.3615400	YES	YES
119	a	1359.86	31.9577700	YES	YES
120	a	1382.69	108.2632500	YES	YES
121	a	1386.63	76.6589000	YES	YES
122	a	1388.25	72.2642700	YES	YES
123	a	1419.50	12.9723000	YES	YES
124	a	1437.99	24.1830600	YES	YES
125	a	1438.07	4.7527000	YES	YES
126	a	1441.68	10.0142700	YES	YES
127	a	1447.39	78.0062000	YES	YES
128	a	1456.95	4.0989800	YES	YES
129	a	1477.51	2.5483600	YES	YES
130	a	1546.58	210.2319500	YES	YES
131	a	1568.83	32.7115200	YES	YES
132	a	1588.22	63.4267800	YES	YES
133	a	1620.05	366.2368600	YES	YES
134	a	1636.17	85.2846900	YES	YES
135	a	1718.52	334.5079200	YES	YES
136	a	1767.70	578.4441900	YES	YES
137	a	2954.59	38.2018100	YES	YES
138	a	2969.19	4.1151700	YES	YES
139	a	2986.72	15.4145300	YES	YES
140	a	3001.77	2.6407800	YES	YES
141	a	3002.63	10.0836200	YES	YES
142	a	3023.21	21.2213600	YES	YES
143	a	3055.58	8.5667800	YES	YES
144	a	3070.67	0.8006000	YES	YES
145	a	3087.77	12.7266600	YES	YES
146	a	3101.87	0.5834900	YES	YES
147	a	3113.30	6.3901700	YES	YES
148	a	3121.34	12.4810500	YES	YES
149	a	3131.31	8.9820300	YES	YES
150	a	3133.76	4.0099800	YES	YES
151	a	3161.16	1.5139200	YES	YES
152	a	3165.80	0.5120600	YES	YES
153	a	3448.41	124.4280200	YES	YES
154	a	3510.89	58.2059900	YES	YES
155	a	3516.72	237.7369700	YES	YES
156	a	3647.62	40.1093600	YES	YES

Table S16. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of isoenterocin A (**2**).

52

C 1.585585 -0.934268 1.052058
O 2.585073 -1.674193 1.723508
H 2.463868 -2.600593 1.435125
C 1.410695 -1.455837 -0.440382
O 1.663322 -2.858282 -0.477513
H 2.568618 -2.955745 -0.833255
C 2.288924 -0.722975 -1.437901
O 1.109242 2.815037 0.673682
O 3.439143 -0.985406 -1.696762
C 1.959172 0.556202 1.137594
H 2.646731 0.828066 0.331033
H 2.499314 0.705196 2.076379
C 0.743292 1.514071 1.121548
H 0.403753 1.650154 2.152950
C -0.476156 0.992032 0.335693
O -0.334914 1.266670 -1.083120
H 1.125801 2.773683 -0.299949
H -1.365569 1.540470 0.653022
C -0.695085 -0.538957 0.442487
C -0.011195 -1.072334 -0.826460
H -0.565933 -1.895806 -1.274637
C 0.141007 0.142866 -1.775245
O 1.595384 0.291061 -2.011728
O -2.067167 -0.898888 0.414516
H -2.456758 -0.567613 1.243998
C 0.138230 -1.174920 1.579940
H -0.057092 -2.256419 1.553949
C -2.003769 -0.243648 -5.484603
H -2.562525 -0.348988 -6.410616
C -0.612588 -0.148070 -5.514304
H -0.084084 -0.176500 -6.463216
C 0.110975 -0.013740 -4.325673
H 1.192695 0.063563 -4.348182
C -0.565364 0.031292 -3.105468
C -1.962498 -0.067881 -3.073281
H -2.475102 -0.040966 -2.114746
C -2.678432 -0.204879 -4.260002
H -3.761891 -0.281104 -4.231021
C -0.974216 0.445328 5.381839
H -1.328643 0.882689 6.305849
C 0.293372 -0.071890 5.236758
O 1.228811 -0.092550 6.207958
C 0.864645 0.476573 7.481168
H 0.608107 1.535906 7.360145
H 1.747557 0.363958 8.110936
H 0.013333 -0.067891 7.907286
C 0.723835 -0.638101 3.994784
H 1.724438 -1.033755 3.875826
C -0.144209 -0.652631 2.956511
O -1.403936 -0.153013 3.070152
C -1.908000 0.430429 4.299121
O -3.046867 0.832464 4.253671



VIBRATIONAL SPECTRUM :

mode	symmetry	wave number cm**(-1)	intensity km/mol	selection rules	
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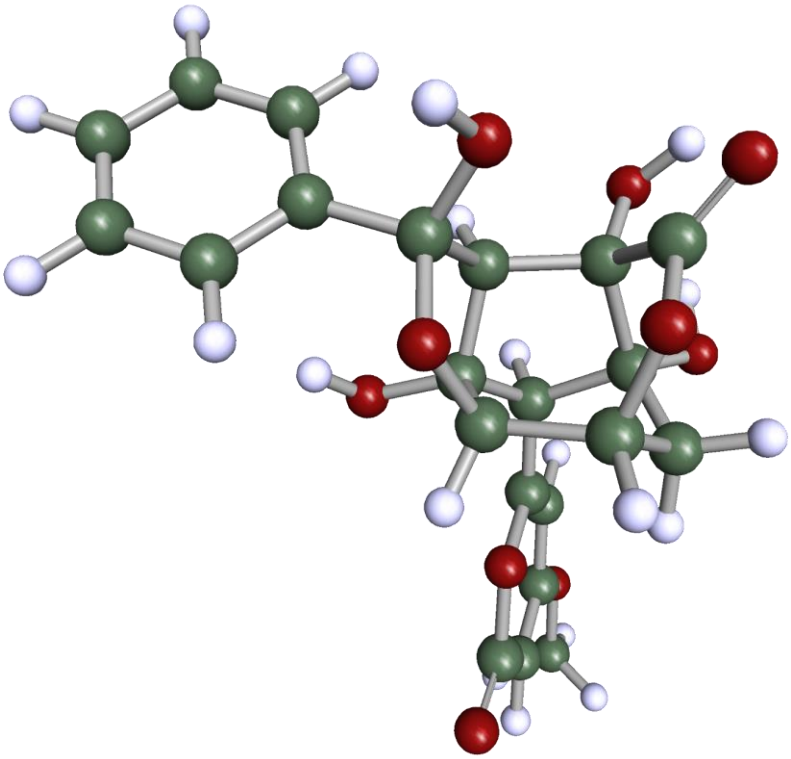
2		0.00	0.0000000	-	-
3		0.00	0.0000000	-	-
4		0.00	0.0000000	-	-
5		0.00	0.0000000	-	-
6		0.00	0.0000000	-	-
7	a	13.81	0.0222000	YES	YES
8	a	22.79	2.4221900	YES	YES
9	a	37.71	0.3385400	YES	YES
10	a	40.74	0.6909600	YES	YES
11	a	59.39	0.1557100	YES	YES
12	a	72.78	1.5934700	YES	YES
13	a	81.92	0.9471800	YES	YES
14	a	103.36	1.8185700	YES	YES
15	a	132.06	0.5669300	YES	YES
16	a	144.58	1.0698600	YES	YES
17	a	155.37	2.3474000	YES	YES
18	a	170.77	0.4498700	YES	YES
19	a	181.67	2.6038200	YES	YES
20	a	201.64	2.5484000	YES	YES
21	a	213.42	1.5340400	YES	YES
22	a	220.70	0.7220100	YES	YES
23	a	240.07	6.6121100	YES	YES
24	a	241.93	2.0009600	YES	YES
25	a	248.41	0.9835200	YES	YES
26	a	249.56	1.3052200	YES	YES
27	a	251.45	8.6315600	YES	YES
28	a	265.34	5.4276900	YES	YES
29	a	289.29	5.9321900	YES	YES
30	a	301.62	11.1302100	YES	YES
31	a	318.10	24.0312000	YES	YES
32	a	342.93	12.2505500	YES	YES
33	a	358.79	6.8728100	YES	YES
34	a	377.44	8.9778600	YES	YES
35	a	385.79	44.1706400	YES	YES
36	a	396.46	0.5498100	YES	YES
37	a	402.07	38.3315700	YES	YES
38	a	411.13	22.3137000	YES	YES
39	a	414.45	8.5019800	YES	YES
40	a	427.81	23.6515900	YES	YES
41	a	452.44	6.4400400	YES	YES
42	a	471.30	4.9766200	YES	YES
43	a	475.47	3.6980400	YES	YES
44	a	490.63	82.1166300	YES	YES
45	a	504.41	37.2110300	YES	YES
46	a	511.95	2.0365300	YES	YES
47	a	523.88	1.5272000	YES	YES
48	a	546.89	9.9703700	YES	YES
49	a	566.56	1.3469500	YES	YES
50	a	583.32	7.8239100	YES	YES
51	a	611.75	2.0139600	YES	YES
52	a	613.17	6.8104100	YES	YES
53	a	621.03	33.2170800	YES	YES
54	a	623.07	8.0097700	YES	YES
55	a	638.60	18.9844000	YES	YES
56	a	659.44	10.0674800	YES	YES
57	a	670.56	2.3053400	YES	YES
58	a	677.12	4.3752300	YES	YES
59	a	688.49	23.6219600	YES	YES
60	a	691.15	11.6727000	YES	YES
61	a	717.19	54.4770000	YES	YES
62	a	719.78	101.3173300	YES	YES
63	a	755.34	10.3590700	YES	YES
64	a	758.03	23.9754600	YES	YES
65	a	769.21	33.2885400	YES	YES
66	a	791.36	27.6241200	YES	YES
67	a	796.56	14.0898400	YES	YES
68	a	828.08	2.8517300	YES	YES
69	a	831.67	29.2492700	YES	YES
70	a	836.78	31.1339900	YES	YES
71	a	853.56	13.1208700	YES	YES
72	a	871.41	18.6102700	YES	YES
73	a	872.11	3.6799700	YES	YES
74	a	888.05	158.4463000	YES	YES
75	a	903.84	2.1506200	YES	YES
76	a	914.37	5.5834400	YES	YES
77	a	938.59	0.0815900	YES	YES
78	a	945.14	23.8444000	YES	YES
79	a	948.05	58.8352600	YES	YES
80	a	952.97	0.1227800	YES	YES
81	a	959.19	5.6269100	YES	YES
82	a	978.59	51.1303200	YES	YES
83	a	991.85	2.3367600	YES	YES
84	a	1002.04	18.8844500	YES	YES
85	a	1019.88	111.0029200	YES	YES
86	a	1028.50	2.7769400	YES	YES
87	a	1032.23	36.1333300	YES	YES
88	a	1038.00	40.9417000	YES	YES
89	a	1051.35	123.1909600	YES	YES
90	a	1059.04	7.2383900	YES	YES
91	a	1074.36	84.1494300	YES	YES
92	a	1080.40	6.6395500	YES	YES
93	a	1087.77	4.8214200	YES	YES
94	a	1091.12	66.7817400	YES	YES
95	a	1104.85	64.9942700	YES	YES
96	a	1115.22	75.5085900	YES	YES
97	a	1124.63	29.3063000	YES	YES
98	a	1127.12	0.4954200	YES	YES
99	a	1139.56	4.4192000	YES	YES
100	a	1147.16	43.4743700	YES	YES
101	a	1153.07	0.1228800	YES	YES
102	a	1164.13	32.9703300	YES	YES
103	a	1173.27	54.0788700	YES	YES
104	a	1176.24	40.9002100	YES	YES
105	a	1180.05	73.9327300	YES	YES
106	a	1196.07	50.1314900	YES	YES
107	a	1199.44	4.0220700	YES	YES
108	a	1229.99	172.5920200	YES	YES
109	a	1243.53	12.8047500	YES	YES
110	a	1245.36	178.0634400	YES	YES
111	a	1257.70	35.2668500	YES	YES
112	a	1266.72	81.8292100	YES	YES
113	a	1286.26	14.6021000	YES	YES
114	a	1294.32	35.3645100	YES	YES
115	a	1304.40	17.5495800	YES	YES
116	a	1307.19	6.0021900	YES	YES
117	a	1310.28	6.3918600	YES	YES
118	a	1336.11	18.4386600	YES	YES
119	a	1340.13	8.0441600	YES	YES
120	a	1343.47	28.7536800	YES	YES
121	a	1357.28	25.2289700	YES	YES
122	a	1367.80	30.7856700	YES	YES
123	a	1388.59	48.6885200	YES	YES
124	a	1392.83	139.4458200	YES	YES
125	a	1436.55	78.0942600	YES	YES
126	a	1437.70	9.9090600	YES	YES
127	a	1442.98	10.2558700	YES	YES
128	a	1447.47	18.1451600	YES	YES
129	a	1452.15	9.1435400	YES	YES
130	a	1483.48	7.3239200	YES	YES
131	a	1546.44	178.7613200	YES	YES
132	a	1580.94	0.2251800	YES	YES
133	a	1597.59	1.4654700	YES	YES
134	a	1620.44	299.6529700	YES	YES
135	a	1763.52	381.0897600	YES	YES
136	a	1768.91	517.1795400	YES	YES
137	a	2940.48	2.1265400	YES	YES
138	a	2956.76	35.2647800	YES	YES
139	a	2978.06	18.9736300	YES	YES
140	a	2999.42	7.8932100	YES	YES
141	a	3019.18	13.4114400	YES	YES
142	a	3025.34	19.2733600	YES	YES
143	a	3038.44	15.5138500	YES	YES
144	a	3065.95	0.1123700	YES	YES
145	a	3086.77	11.2767200	YES	YES
146	a	3098.86	0.0231800	YES	YES
147	a	3109.13	8.3030700	YES	YES
148	a	3119.54	17.8505500	YES	YES
149	a	3128.96	6.9989800	YES	YES
150	a	3135.26	4.5592000	YES	YES
151	a	3159.17	7.2568000	YES	YES
152	a	3164.78	0.7207500	YES	YES
153	a	3537.55	90.2503900	YES	YES
154	a	3553.38	46.9420200	YES	YES
155	a	3614.81	151.2609300	YES	YES
156	a	3615.30	22.8528300	YES	YES

Table S17. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of isoenterocin B (**3**).

52

C 1.886341 -0.321940 2.242749
O 2.451535 -1.330675 3.016853
H 2.393212 -2.139179 2.433244
C 1.843388 -0.782317 0.683350
O 2.012597 -2.178952 0.614484
H 2.834860 -2.287265 0.049917
C 3.023159 -0.135004 -0.054901
O 3.101222 1.202618 0.017952
O 3.866744 -0.820660 -0.606439
C 2.662256 0.999244 2.355293
H 3.752022 0.792993 2.380102
H 2.402810 1.545224 3.282949
C 2.333466 1.810659 1.101141
H 2.731215 2.841297 1.144101
C 0.796408 1.873652 0.774925
O 0.603170 1.873567 -0.647416
H 0.374341 2.809347 1.186466
C -0.049905 0.640393 1.239192
C 0.436490 -0.339508 0.159717
H -0.194085 -1.244734 0.090967
C 0.377839 0.526358 -1.117218
O 1.378661 0.102578 -2.007290
O -1.432170 0.894769 1.261012
H -1.720407 1.167664 0.358109
C 0.381692 -0.026383 2.542080
H -0.142833 -1.001756 2.611026
C -3.499167 0.334805 -3.089350
H -4.482226 0.275931 -3.584261
C -3.044009 1.555677 -2.568537
H -3.663828 2.462494 -2.660181
C -1.792260 1.629832 -1.930631
H -1.417838 2.585165 -1.531920
C -0.989503 0.478834 -1.807961
C -1.444901 -0.741597 -2.348312
H -0.805708 -1.636563 -2.276867
C -2.693430 -0.814077 -2.981319
H -3.043074 -1.774235 -3.394622
C -0.280954 2.379884 6.019801
H -0.429873 3.072171 6.857795
C -0.282040 1.000380 6.166282
O -0.458920 0.345218 7.331007
C -0.655891 1.109774 8.515429
H 0.221634 1.764268 8.721516
H -0.772794 0.375549 9.336339
H -1.574140 1.736182 8.441317
C -0.086307 0.150588 5.023826
H -0.075539 -0.940440 5.141062
C 0.105188 0.731723 3.800788
O 0.117394 2.073071 3.645000
C -0.075333 2.999996 4.734691
O -0.035240 4.176613 4.445772
H 1.390630 0.725373 -2.768718



VIBRATIONAL SPECTRUM :

mode	symmetry	wave number cm**(-1)	intensity km/mol	selection rules	
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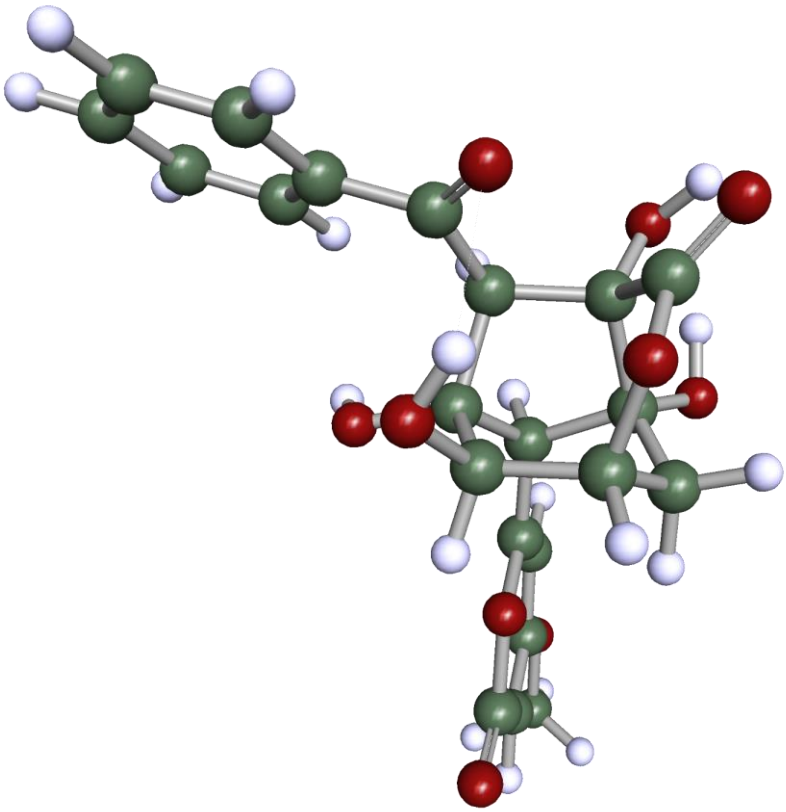
2		0.00	0.0000000	-	-
3		0.00	0.0000000	-	-
4		0.00	0.0000000	-	-
5		0.00	0.0000000	-	-
6		0.00	0.0000000	-	-
7	a	13.81	0.0222000	YES	YES
8	a	22.79	2.4221900	YES	YES
9	a	37.71	0.3385400	YES	YES
10	a	40.74	0.6909600	YES	YES
11	a	59.39	0.1557100	YES	YES
12	a	72.78	1.5934700	YES	YES
13	a	81.92	0.9471800	YES	YES
14	a	103.36	1.8185700	YES	YES
15	a	132.06	0.5669300	YES	YES
16	a	144.58	1.0698600	YES	YES
17	a	155.37	2.3474000	YES	YES
18	a	170.77	0.4498700	YES	YES
19	a	181.67	2.6038200	YES	YES
20	a	201.64	2.5484000	YES	YES
21	a	213.42	1.5340400	YES	YES
22	a	220.70	0.7220100	YES	YES
23	a	240.07	6.6121100	YES	YES
24	a	241.93	2.0009600	YES	YES
25	a	248.41	0.9835200	YES	YES
26	a	249.56	1.3052200	YES	YES
27	a	251.45	8.6315600	YES	YES
28	a	265.34	5.4276900	YES	YES
29	a	289.29	5.9321900	YES	YES
30	a	301.62	11.1302100	YES	YES
31	a	318.10	24.0312000	YES	YES
32	a	342.93	12.2505500	YES	YES
33	a	358.79	6.8728100	YES	YES
34	a	377.44	8.9778600	YES	YES
35	a	385.79	44.1706400	YES	YES
36	a	396.46	0.5498100	YES	YES
37	a	402.07	38.3315700	YES	YES
38	a	411.13	22.3137000	YES	YES
39	a	414.45	8.5019800	YES	YES
40	a	427.81	23.6515900	YES	YES
41	a	452.44	6.4400400	YES	YES
42	a	471.30	4.9766200	YES	YES
43	a	475.47	3.6980400	YES	YES
44	a	490.63	82.1166300	YES	YES
45	a	504.41	37.2110300	YES	YES
46	a	511.95	2.0365300	YES	YES
47	a	523.88	1.5272000	YES	YES
48	a	546.89	9.9703700	YES	YES
49	a	566.56	1.3469500	YES	YES
50	a	583.32	7.8239100	YES	YES
51	a	611.75	2.0139600	YES	YES
52	a	613.17	6.8104100	YES	YES
53	a	621.03	33.2170800	YES	YES
54	a	623.07	8.0097700	YES	YES
55	a	638.60	18.9844000	YES	YES
56	a	659.44	10.0674800	YES	YES
57	a	670.56	2.3053400	YES	YES
58	a	677.12	4.3752300	YES	YES
59	a	688.49	23.6219600	YES	YES
60	a	691.15	11.6727000	YES	YES
61	a	717.19	54.4770000	YES	YES
62	a	719.78	101.3173300	YES	YES
63	a	755.34	10.3590700	YES	YES
64	a	758.03	23.9754600	YES	YES
65	a	769.21	33.2885400	YES	YES
66	a	791.36	27.6241200	YES	YES
67	a	796.56	14.0898400	YES	YES
68	a	828.08	2.8517300	YES	YES
69	a	831.67	29.2492700	YES	YES
70	a	836.78	31.1339900	YES	YES
71	a	853.56	13.1208700	YES	YES
72	a	871.41	18.6102700	YES	YES
73	a	872.11	3.6799700	YES	YES
74	a	888.05	158.4463000	YES	YES
75	a	903.84	2.1506200	YES	YES
76	a	914.37	5.5834400	YES	YES
77	a	938.59	0.0815900	YES	YES
78	a	945.14	23.8444000	YES	YES
79	a	948.05	58.8352600	YES	YES
80	a	952.97	0.1227800	YES	YES
81	a	959.19	5.6269100	YES	YES
82	a	978.59	51.1303200	YES	YES
83	a	991.85	2.3367600	YES	YES
84	a	1002.04	18.8844500	YES	YES
85	a	1019.88	111.0029200	YES	YES
86	a	1028.50	2.7769400	YES	YES
87	a	1032.23	36.1333300	YES	YES
88	a	1038.00	40.9417000	YES	YES
89	a	1051.35	123.1909600	YES	YES
90	a	1059.04	7.2383900	YES	YES
91	a	1074.36	84.1494300	YES	YES
92	a	1080.40	6.6395500	YES	YES
93	a	1087.77	4.8214200	YES	YES
94	a	1091.12	66.7817400	YES	YES
95	a	1104.85	64.9942700	YES	YES
96	a	1115.22	75.5085900	YES	YES
97	a	1124.63	29.3063000	YES	YES
98	a	1127.12	0.4954200	YES	YES
99	a	1139.56	4.4192000	YES	YES
100	a	1147.16	43.4743700	YES	YES
101	a	1153.07	0.1228800	YES	YES
102	a	1164.13	32.9703300	YES	YES
103	a	1173.27	54.0788700	YES	YES
104	a	1176.24	40.9002100	YES	YES
105	a	1180.05	73.9327300	YES	YES
106	a	1196.07	50.1314900	YES	YES
107	a	1199.44	4.0220700	YES	YES
108	a	1229.99	172.5920200	YES	YES
109	a	1243.53	12.8047500	YES	YES
110	a	1245.36	178.0634400	YES	YES
111	a	1257.70	35.2668500	YES	YES
112	a	1266.72	81.8292100	YES	YES
113	a	1286.26	14.6021000	YES	YES
114	a	1294.32	35.3645100	YES	YES
115	a	1304.40	17.5495800	YES	YES
116	a	1307.19	6.0021900	YES	YES
117	a	1310.28	6.3918600	YES	YES
118	a	1336.11	18.4386600	YES	YES
119	a	1340.13	8.0441600	YES	YES
120	a	1343.47	28.7536800	YES	YES
121	a	1357.28	25.2289700	YES	YES
122	a	1367.80	30.7856700	YES	YES
123	a	1388.59	48.6885200	YES	YES
124	a	1392.83	139.4458200	YES	YES
125	a	1436.55	78.0942600	YES	YES
126	a	1437.70	9.9090600	YES	YES
127	a	1442.98	10.2558700	YES	YES
128	a	1447.47	18.1451600	YES	YES
129	a	1452.15	9.1435400	YES	YES
130	a	1483.48	7.3239200	YES	YES
131	a	1546.44	178.7613200	YES	YES
132	a	1580.94	0.2251800	YES	YES
133	a	1597.59	1.4654700	YES	YES
134	a	1620.44	299.6529700	YES	YES
135	a	1763.52	381.0897600	YES	YES
136	a	1768.91	517.1795400	YES	YES
137	a	2940.48	2.1265400	YES	YES
138	a	2956.76	35.2647800	YES	YES
139	a	2978.06	18.9736300	YES	YES
140	a	2999.42	7.8932100	YES	YES
141	a	3019.18	13.4114400	YES	YES
142	a	3025.34	19.2733600	YES	YES
143	a	3038.44	15.5138500	YES	YES
144	a	3065.95	0.1123700	YES	YES
145	a	3086.77	11.2767200	YES	YES
146	a	3098.86	0.0231800	YES	YES
147	a	3109.13	8.3030700	YES	YES
148	a	3119.54	17.8505500	YES	YES
149	a	3128.96	6.9989800	YES	YES
150	a	3135.26	4.5592000	YES	YES
151	a	3159.17	7.2568000	YES	YES
152	a	3164.78	0.7207500	YES	YES
153	a	3537.55	90.2503900	YES	YES
154	a	3553.38	46.9420200	YES	YES
155	a	3614.81	151.2609300	YES	YES
156	a	3615.30	22.8528300	YES	YES
129	a	1452.15	9.1435400	YES	YES
130	a	1483.48	7.3239200	YES	YES
131	a	1546.44	178.7613200	YES	YES
132	a	1580.94	0.2251800	YES	YES
133	a	1597.59	1.4654700	YES	YES
134	a	1620.44	299.6529700	YES	YES
135	a	1763.52	381.0897600	YES	YES
136	a	1768.91	517.1795400	YES	YES
137	a	2940.48	2.1265400	YES	YES
138	a	2956.76	35.2647800	YES	YES
139	a	2978.06	18.9736300	YES	YES
140	a	2999.42	7.8932100	YES	YES
141	a	3019.18	13.4114400	YES	YES
142	a	3025.34	19.2733600	YES	YES
143	a	3038.44	15.5138500	YES	YES
144	a	3065.95	0.1123700	YES	YES
145	a	3086.77	11.2767200	YES	YES
146	a	3098.86	0.0231800	YES	YES
147	a	3109.13	8.3030700	YES	YES
148	a	3119.54	17.8505500	YES	YES
149	a	3128.96	6.9989800	YES	YES
150	a	3135.26	4.5592000	YES	YES
151	a	3159.17	7.2568000	YES	YES
152	a	3164.78	0.7207500	YES	YES
153	a	3537.55	90.2503900	YES	YES
154	a	3553.38	46.9420200	YES	YES
155	a	3614.81	151.2609300	YES	YES
156	a	3615.30	22.8528300	YES	YES

Table S18. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of 3-*epi*-enterocin (**4**).

52

C 1.153784 1.421089 0.719599
O 2.333227 1.727035 1.394434
H 3.047433 1.667126 0.698210
C 1.394987 1.526340 -0.886891
O 2.776957 1.598346 -1.149795
H 2.922029 2.485151 -1.583549
C 0.728562 2.796544 -1.430120
O -0.576999 2.966153 -1.134730
O 1.371838 3.654039 -2.013543
C 0.003067 2.349368 1.122447
H 0.360425 3.399328 1.171918
H -0.401641 2.087340 2.119465
C -1.071484 2.235423 0.046315
H -1.993796 2.786750 0.307462
C -1.456323 0.784301 -0.329117
O -2.186012 0.759235 -1.544545
H -1.791408 1.437528 -2.142986
H -2.136154 0.411904 0.461978
C -0.250895 -0.209331 -0.364279
C 0.783015 0.225627 -1.463509
H 1.603227 -0.521109 -1.431228
C 0.273554 0.296626 -2.893969
O 0.055414 1.391058 -3.429860
O -0.802095 -1.490164 -0.527906
H -0.088122 -2.160392 -0.433801
C 0.674823 -0.059880 0.876312
H 1.567033 -0.696181 0.700394
C -0.512216 -3.309544 -5.116022
H -0.726845 -4.223234 -5.694101
C -1.049129 -2.073459 -5.526940
H -1.687106 -2.019189 -6.423977
C -0.771685 -0.913799 -4.794454
H -1.183002 0.060309 -5.101306
C 0.031503 -0.973321 -3.630537
C 0.570536 -2.217641 -3.230391
H 1.231110 -2.291416 -2.354064
C 0.302583 -3.377613 -3.972231
H 0.736302 -4.340104 -3.657143
C -0.982449 -1.044573 4.703583
H -1.474788 -1.255126 5.661715
C 0.350514 -1.353377 4.455977
O 1.184561 -1.928893 5.333865
C 0.689578 -2.263384 6.637824
H 0.349424 -1.351213 7.175747
H 1.542257 -2.720299 7.175202
H -0.146107 -2.993608 6.565802
C 0.930474 -1.059221 3.173773
H 1.981055 -1.308519 2.974242
C 0.154868 -0.459231 2.219652
O -1.141675 -0.151160 2.457634
C -1.799446 -0.429135 3.697905
O -2.976897 -0.107593 3.752714



VIBRATIONAL SPECTRUM :

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5		0.00	0.0000000	-	-
6		0.00	0.0000000	-	-
7	a	17.76	1.1686700	YES	YES
8	a	20.21	0.6572500	YES	YES
9	a	42.03	0.3526700	YES	YES
10	a	47.61	0.0730200	YES	YES
11	a	59.03	0.8884500	YES	YES
12	a	77.03	1.1494000	YES	YES
13	a	101.69	2.4900200	YES	YES
14	a	105.00	0.2171600	YES	YES
15	a	122.84	0.3420400	YES	YES
16	a	135.64	0.7012300	YES	YES
17	a	147.31	0.8853600	YES	YES
18	a	155.05	0.8810700	YES	YES
19	a	164.74	0.2825100	YES	YES
20	a	184.68	1.5615600	YES	YES
21	a	191.06	0.4376200	YES	YES
22	a	212.93	3.6200200	YES	YES
23	a	219.55	2.3951500	YES	YES
24	a	224.05	2.4230000	YES	YES
25	a	232.85	12.1733300	YES	YES
26	a	240.30	1.7990900	YES	YES
27	a	243.09	2.5537700	YES	YES
28	a	251.63	7.2431300	YES	YES
29	a	288.00	8.4055600	YES	YES
30	a	301.51	21.9855000	YES	YES
31	a	323.09	10.9181500	YES	YES
32	a	334.70	7.3068600	YES	YES
33	a	355.19	23.5629100	YES	YES
34	a	367.42	5.1156800	YES	YES
35	a	386.99	0.4680600	YES	YES
36	a	397.76	2.1536200	YES	YES
37	a	418.19	4.2167600	YES	YES
38	a	422.31	0.7990100	YES	YES
39	a	441.42	7.2676200	YES	YES
40	a	448.65	2.7883300	YES	YES
41	a	456.55	12.7874700	YES	YES
42	a	468.99	15.0713300	YES	YES
43	a	489.95	1.8947300	YES	YES
44	a	496.06	23.9438700	YES	YES
45	a	506.92	19.0493500	YES	YES
46	a	526.00	12.4283900	YES	YES
47	a	526.54	1.0998300	YES	YES
48	a	546.64	5.2960600	YES	YES
49	a	557.97	5.3176900	YES	YES
50	a	582.40	3.2846500	YES	YES
51	a	599.94	8.1028000	YES	YES
52	a	611.02	2.8113700	YES	YES
53	a	614.38	7.6346700	YES	YES
54	a	618.13	39.9554100	YES	YES
55	a	647.42	22.3915700	YES	YES
56	a	648.08	12.8419600	YES	YES
57	a	655.59	12.9569300	YES	YES
58	a	663.27	97.7440100	YES	YES
59	a	673.85	9.3976800	YES	YES
60	a	683.43	3.8185400	YES	YES
61	a	688.00	3.2764200	YES	YES
62	a	731.46	18.9275000	YES	YES
63	a	736.61	54.0812300	YES	YES
64	a	745.74	44.7788500	YES	YES
65	a	773.56	44.7884500	YES	YES
66	a	788.13	8.2398600	YES	YES
67	a	798.18	22.0169000	YES	YES
68	a	802.17	168.4463000	YES	YES
69	a	823.62	11.2416600	YES	YES
70	a	828.24	1.0348100	YES	YES
71	a	830.49	3.2293300	YES	YES
72	a	838.57	6.2645000	YES	YES
73	a	848.26	23.8297000	YES	YES
74	a	880.94	37.6239800	YES	YES
75	a	914.28	2.6848100	YES	YES
76	a	915.94	0.6700900	YES	YES
77	a	930.44	12.9965700	YES	YES
78	a	940.87	2.2329400	YES	YES
79	a	946.68	5.6319400	YES	YES
80	a	955.48	0.3580200	YES	YES
81	a	961.85	6.5901400	YES	YES
82	a	982.13	32.3703800	YES	YES
83	a	989.65	6.0189300	YES	YES
84	a	995.54	6.6857600	YES	YES
85	a	1001.48	42.4920600	YES	YES
86	a	1018.64	30.1901600	YES	YES
87	a	1027.84	2.9111500	YES	YES
88	a	1038.64	54.4830000	YES	YES
89	a	1047.70	201.8830100	YES	YES
90	a	1064.39	6.2661700	YES	YES
91	a	1076.18	86.1538300	YES	YES
92	a	1086.32	37.7129800	YES	YES
93	a	1091.98	75.7902900	YES	YES
94	a	1098.86	7.7982600	YES	YES
95	a	1120.11	23.9937700	YES	YES
96	a	1124.52	62.2088800	YES	YES
97	a	1127.05	0.2459100	YES	YES
98	a	1134.51	61.9565100	YES	YES
99	a	1149.95	93.4283600	YES	YES
100	a	1158.19	11.7215200	YES	YES
101	a	1166.81	85.9290000	YES	YES
102	a	1179.97	57.8286000	YES	YES
103	a	1182.92	34.2432800	YES	YES
104	a	1203.25	73.9798100	YES	YES
105	a	1213.28	12.8588000	YES	YES
106	a	1219.90	157.1380600	YES	YES
107	a	1230.00	12.7172100	YES	YES
108	a	1233.51	159.3126300	YES	YES
109	a	1251.06	10.1465500	YES	YES
110	a	1285.47	99.9073500	YES	YES
111	a	1300.61	33.4807900	YES	YES
112	a	1304.64	7.7115600	YES	YES
113	a	1311.04	26.7031500	YES	YES
114	a	1319.16	12.2309700	YES	YES
115	a	1329.82	84.6113900	YES	YES
116	a	1336.65	80.6971300	YES	YES
117	a	1347.00	2.9978100	YES	YES
118	a	1350.71	48.5684300	YES	YES
119	a	1365.86	95.2917300	YES	YES
120	a	1384.59	59.5718500	YES	YES
121	a	1385.68	25.1802400	YES	YES
122	a	1416.74	29.4074600	YES	YES
123	a	1437.99	21.9309600	YES	YES
124	a	1442.14	26.3034800	YES	YES
125	a	1442.83	17.5050000	YES	YES
126	a	1447.25	75.6010900	YES	YES
127	a	1456.37	2.0334200	YES	YES
128	a	1467.29	85.9789600	YES	YES
129	a	1478.78	3.3633400	YES	YES
130	a	1546.72	184.0965100	YES	YES
131	a	1567.79	26.4837900	YES	YES
132	a	1588.47	62.1988700	YES	YES
133	a	1619.93	318.0290800	YES	YES
134	a	1635.55	134.5577800	YES	YES
135	a	1723.73	306.2999800	YES	YES
136	a	1772.71	575.1024500	YES	YES
137	a	2955.58	37.6381900	YES	YES
138	a	2978.95	7.8631600	YES	YES
139	a	2997.63	12.6265800	YES	YES
140	a	3009.30	5.5020200	YES	YES
141	a	3012.65	1.1961900	YES	YES
142	a	3024.48	20.8559800	YES	YES
143	a	3052.93	7.7166500	YES	YES
144	a	3070.41	0.5807400	YES	YES
145	a	3088.36	12.6889300	YES	YES
146	a	3101.49	0.1322700	YES	YES
147	a	3112.47	8.6534900	YES	YES
148	a	3121.52	13.3272700	YES	YES
149	a	3133.24	8.4755100	YES	YES
150	a	3136.81	5.0445000	YES	YES
151	a	3162.22	1.5432600	YES	YES
152	a	3165.57	0.5266700	YES	YES
153	a	3280.69	717.6294900	YES	YES
154	a	3411.43	137.2507100	YES	YES
155	a	3510.24	118.9023800	YES	YES
156	a	3549.70	74.9446600	YES	YES

Table S19. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of enterocinic acid A (**7**).

```
55

C -1.325547 -0.771270 -0.064528
O -2.416487 -1.615610 -0.220924
H -3.225713 -1.129143 -0.057009
C -1.581956 0.614668 -0.807806
O -2.916344 0.960349 -0.556296
H -3.394739 0.975868 -1.390757
C -1.445829 0.502936 -2.328304
O -0.254413 0.188447 -2.760222
H -0.238278 0.125489 -3.720858
O -2.397259 0.656253 -3.043800
C -0.103544 -1.588983 -0.471988
H -0.121270 -1.814050 -1.534189
H -0.227100 -2.556124 0.018191
C 1.274745 -1.029922 -0.064133
H 1.649845 -1.646655 0.747269
O 2.236894 -1.179270 -1.076252
H 2.030044 -0.588486 -1.799072
C 1.250959 0.410475 0.479447
O 1.482422 1.308555 -0.601957
H 2.061844 0.519043 1.204071
C -0.091095 0.853427 1.133992
C -0.713001 1.654693 -0.032796
H -1.402191 2.410159 0.338372
C 0.517994 2.307414 -0.650560
O 0.846988 3.351199 0.243476
O 0.081408 1.560775 2.322517
H 0.588994 2.355784 2.156216
C -1.119615 -0.241446 1.370147
H -2.042309 0.259916 1.675453
C 0.194480 4.129287 -4.516131
H 0.111487 4.603968 -5.483480
C 1.339482 3.429813 -4.180424
H 2.155688 3.357573 -4.885191
C 1.447469 2.815321 -2.947131
H 2.346352 2.266025 -2.709477
C 0.406700 2.896183 -2.035526
C -0.732264 3.611600 -2.369745
H -1.548678 3.703229 -1.666087
C -0.841562 4.219257 -3.606306
H -1.739911 4.765116 -3.856746
C -0.200987 -3.090183 4.363788
H 0.119228 -3.798386 5.110698
C -1.507989 -2.887397 4.038110
O -2.530116 -3.516373 4.580338
C -2.285136 -4.488387 5.585951
H -1.679009 -5.309886 5.203119
H -3.254416 -4.871023 5.886351
H -1.790893 -4.046518 6.451542
C -1.852220 -1.928083 3.042146
H -2.883730 -1.746360 2.785670
C -0.869060 -1.253577 2.434667
O 0.407448 -1.446803 2.762890
C 0.815320 -2.344510 3.711810
O 2.005072 -2.412358 3.899970
H 1.609795 3.829979 -0.082507
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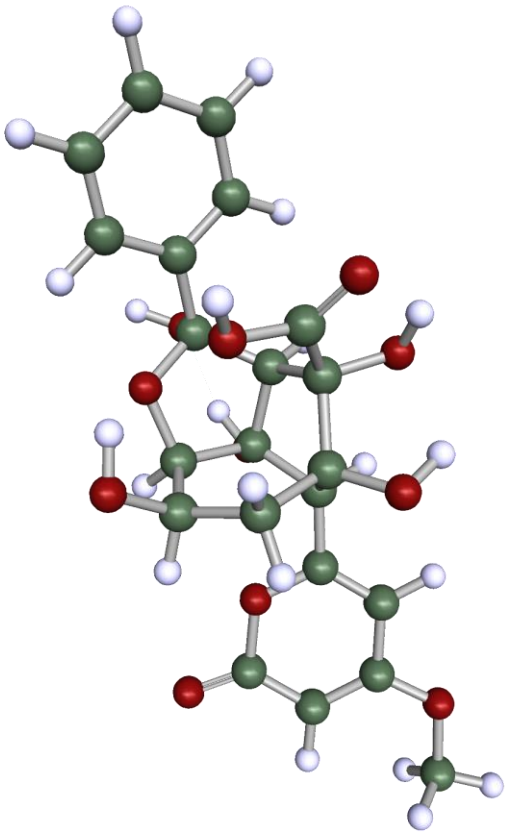

VIBRATIONAL SPECTRUM :

mode	symmetry	wave number cm**(-1)	intensity km/mol	selection rules	
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2		0.00	0.0000000	-	-
3		0.00	0.0000000	-	-
4		0.00	0.0000000	-	-
5		0.00	0.0000000	-	-
6		0.00	0.0000000	-	-
7	a	13.40	2.4481100	YES	YES
8	a	34.08	0.4667500	YES	YES
9	a	37.02	0.7561100	YES	YES
10	a	45.45	0.4242000	YES	YES
11	a	57.35	0.1876900	YES	YES
12	a	61.94	0.6231700	YES	YES
13	a	85.17	0.4298600	YES	YES
14	a	93.27	0.5281800	YES	YES
15	a	101.99	1.5480400	YES	YES
16	a	132.81	0.1965500	YES	YES
17	a	146.80	1.1451800	YES	YES
18	a	162.43	0.7747300	YES	YES
19	a	163.21	1.0809300	YES	YES
20	a	166.95	0.1597900	YES	YES
21	a	184.42	2.9068600	YES	YES
22	a	194.74	0.9279700	YES	YES
23	a	200.70	4.7597400	YES	YES
24	a	213.41	0.1100900	YES	YES
25	a	227.42	3.4357500	YES	YES
26	a	235.85	4.1286700	YES	YES
27	a	241.14	2.7422900	YES	YES
28	a	251.67	0.8594500	YES	YES
29	a	255.91	4.2477800	YES	YES
30	a	289.79	7.0979500	YES	YES
31	a	302.89	2.0057100	YES	YES
32	a	309.91	11.1259200	YES	YES
33	a	314.34	6.5050700	YES	YES
34	a	329.57	10.1012300	YES	YES
35	a	343.91	14.1530800	YES	YES
36	a	366.17	71.7755500	YES	YES
37	a	369.78	14.3761200	YES	YES
38	a	385.38	10.5960700	YES	YES
39	a	393.37	1.9319800	YES	YES
40	a	394.66	4.0349600	YES	YES
41	a	413.16	8.1232700	YES	YES
42	a	422.46	52.7527800	YES	YES
43	a	448.47	11.3495800	YES	YES
44	a	464.81	4.3420900	YES	YES
45	a	483.26	3.0846500	YES	YES
46	a	491.77	14.4625600	YES	YES
47	a	499.28	22.2529800	YES	YES
48	a	508.55	7.4078200	YES	YES
49	a	523.27	67.4673400	YES	YES
50	a	525.43	12.8065900	YES	YES
51	a	538.95	13.3168500	YES	YES
52	a	548.58	26.4312600	YES	YES
53	a	562.83	6.4739000	YES	YES
54	a	570.18	67.1800200	YES	YES
55	a	590.07	51.0179900	YES	YES
56	a	596.95	22.4931900	YES	YES
57	a	615.01	2.9068200	YES	YES
58	a	622.02	24.1022400	YES	YES
59	a	645.96	40.0578200	YES	YES
60	a	649.52	22.0352300	YES	YES
61	a	658.46	17.7021900	YES	YES
62	a	671.69	62.3226700	YES	YES
63	a	675.07	65.5708300	YES	YES
64	a	676.83	12.1857800	YES	YES
65	a	685.99	8.1884600	YES	YES
66	a	689.79	16.9014000	YES	YES
67	a	709.40	49.8791700	YES	YES
68	a	750.10	60.9514300	YES	YES
69	a	751.21	12.9700900	YES	YES
70	a	766.62	11.1240000	YES	YES
71	a	768.64	52.7046000	YES	YES
72	a	784.80	13.9740000	YES	YES
73	a	810.84	36.1633600	YES	YES
74	a	833.19	0.4700900	YES	YES
75	a	837.23	4.2944000	YES	YES
76	a	839.20	8.7523100	YES	YES
77	a	863.68	9.5786700	YES	YES
78	a	865.59	6.8365900	YES	YES
79	a	874.26	100.8434300	YES	YES
80	a	903.34	47.3872400	YES	YES
81	a	909.40	12.6943900	YES	YES
82	a	921.75	47.8257700	YES	YES
83	a	939.79	0.1604500	YES	YES
84	a	940.78	21.5686700	YES	YES
85	a	953.13	0.5646700	YES	YES
86	a	965.71	3.2725200	YES	YES
87	a	969.38	11.1689300	YES	YES
88	a	983.82	81.2268400	YES	YES
89	a	991.56	1.0174100	YES	YES
90	a	1010.38	9.4589700	YES	YES
91	a	1015.82	109.7941800	YES	YES
92	a	1023.11	53.2516000	YES	YES
93	a	1028.28	10.2468900	YES	YES
94	a	1033.43	29.4527900	YES	YES
95	a	1049.14	81.7917100	YES	YES
96	a	1066.02	79.8291400	YES	YES
97	a	1068.45	39.9693200	YES	YES
98	a	1080.65	11.0639100	YES	YES
99	a	1089.46	5.1089800	YES	YES
100	a	1094.89	92.2422500	YES	YES
101	a	1102.78	80.0941800	YES	YES
102	a	1123.40	23.6714900	YES	YES
103	a	1127.93	0.1223200	YES	YES
104	a	1131.70	96.2570300	YES	YES
105	a	1141.21	87.7626600	YES	YES
106	a	1151.96	14.3182800	YES	YES
107	a	1156.48	0.4401300	YES	YES

108	a	1170.76	23.0819700	YES	YES
109	a	1172.72	8.7345200	YES	YES
110	a	1185.83	64.3860500	YES	YES
111	a	1196.91	13.3416700	YES	YES
112	a	1208.39	26.1800100	YES	YES
113	a	1214.37	69.5121400	YES	YES
114	a	1230.39	137.2601600	YES	YES
115	a	1258.13	10.5130900	YES	YES
116	a	1260.47	65.0346600	YES	YES
117	a	1272.82	52.0770500	YES	YES
118	a	1290.78	16.8679800	YES	YES
119	a	1299.22	19.4212900	YES	YES
120	a	1306.31	27.1803700	YES	YES
121	a	1310.27	32.6696600	YES	YES
122	a	1315.87	49.1877800	YES	YES
123	a	1326.56	68.4328000	YES	YES
124	a	1330.74	9.3266200	YES	YES
125	a	1341.30	46.1553900	YES	YES
126	a	1346.39	8.3546900	YES	YES
127	a	1370.97	85.2822600	YES	YES
128	a	1383.14	125.0224100	YES	YES
129	a	1398.05	87.6708000	YES	YES
130	a	1412.00	10.7720600	YES	YES
131	a	1415.15	26.0573400	YES	YES
132	a	1438.44	11.6991100	YES	YES
133	a	1442.24	10.1782700	YES	YES
134	a	1442.84	80.7054600	YES	YES
135	a	1451.61	4.3596300	YES	YES
136	a	1456.85	7.7170100	YES	YES
137	a	1482.78	5.8273100	YES	YES
138	a	1544.59	179.5622200	YES	YES
139	a	1576.93	0.6683100	YES	YES
140	a	1596.02	1.2965100	YES	YES
141	a	1618.39	323.2464400	YES	YES
142	a	1708.69	237.6760200	YES	YES
143	a	1766.45	542.6795500	YES	YES
144	a	2954.20	39.7875200	YES	YES
145	a	2991.01	2.2725000	YES	YES
146	a	2996.14	11.6207300	YES	YES
147	a	3022.45	21.8008300	YES	YES
148	a	3027.98	9.1466800	YES	YES
149	a	3050.90	0.3765300	YES	YES
150	a	3058.67	2.7498400	YES	YES
151	a	3069.29	9.8367400	YES	YES
152	a	3086.38	14.0980100	YES	YES
153	a	3098.66	0.8454000	YES	YES
154	a	3105.95	3.1409400	YES	YES
155	a	3114.22	14.9809200	YES	YES
156	a	3123.74	11.7009000	YES	YES
157	a	3130.51	4.7468100	YES	YES
158	a	3162.45	1.2512000	YES	YES
159	a	3164.59	0.6398100	YES	YES
160	a	3435.04	168.6523100	YES	YES
161	a	3536.94	51.6286500	YES	YES
162	a	3544.42	181.4366600	YES	YES
163	a	3599.77	66.4228200	YES	YES
164	a	3629.88	60.2906100	YES	YES
165	a	3661.21	26.5296800	YES	YES

Table S20. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of intermediate A.

```
55

C -0.403260 1.449192 0.994503
O -0.947598 2.541667 1.758130
H -1.073503 3.276817 1.130730
C 1.097275 1.735476 0.654926
O 1.748385 2.156823 1.872853
H 1.091002 2.725259 2.324428
C 1.411339 2.884936 -0.315267
O 0.314974 3.684183 -0.538127
H 0.630144 4.438335 -1.073830
O -1.691042 -0.626444 -1.936483
O 2.509693 3.178043 -0.719925
C -1.261113 1.099075 -0.244114
H -0.888762 1.622958 -1.123908
H -2.278430 1.454312 -0.054634
C -1.341810 -0.417794 -0.572048
H -2.164763 -0.850049 0.005503
C -0.073707 -1.234136 -0.207754
O 0.886379 -1.244234 -1.278255
H -0.849457 -0.577821 -2.428331
H -0.352964 -2.277794 -0.049022
C 0.693789 -0.654679 0.996875
C 1.670188 0.345709 0.313731
H 2.658387 0.263810 0.765163
C 1.736383 -0.103167 -1.183148
O 1.202265 0.935377 -2.016750
H 1.653550 0.883710 -2.875673
O 1.452968 -1.635071 1.686849
H 0.818728 -2.263768 2.075762
C -0.220989 0.213117 1.901414
H 0.378520 0.505029 2.771201
C 5.715668 -1.185435 -2.470882
H 6.718151 -1.454501 -2.792323
C 5.343341 0.157010 -2.386652
H 6.056245 0.938439 -2.635073
C 4.057246 0.503994 -1.973607
H 3.777237 1.549204 -1.878283
C 3.131199 -0.495578 -1.645366
C 3.510433 -1.839245 -1.716138
H 2.795045 -2.606900 -1.444275
C 4.797766 -2.180159 -2.131719
H 5.083146 -3.227027 -2.188827
C -3.569435 -2.045463 3.319822
H -4.360538 -2.696243 3.667112
C -3.705838 -0.680494 3.215554
O -4.824906 0.010033 3.526309
C -5.962230 -0.734060 4.002611
H -6.734947 0.011680 4.187065
H -5.715856 -1.260380 4.931617
H -6.300007 -1.448226 3.243299
C -2.629035 0.135644 2.747215
H -2.740342 1.208705 2.668315
C -1.465263 -0.462969 2.397928
O -1.300665 -1.808678 2.499910
C -2.344146 -2.693096 2.969643
O -2.054841 -3.867104 3.004967
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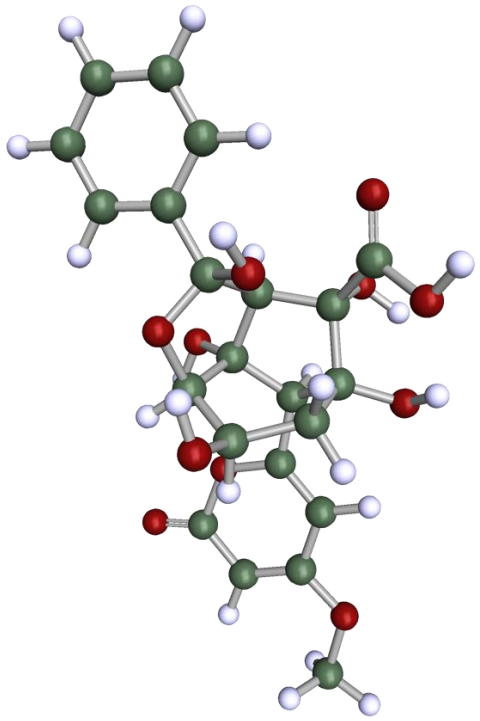

VIBRATIONAL SPECTRUM :

mode	symmetry	wave number cm**(-1)	intensity km/mol	selection rules	
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2		0.00	0.0000000	-	-
3		0.00	0.0000000	-	-
4		0.00	0.0000000	-	-
5		0.00	0.0000000	-	-
6		0.00	0.0000000	-	-
7	a	24.37	1.9321800	YES	YES
8	a	29.77	0.1453200	YES	YES
9	a	35.14	0.1167700	YES	YES
10	a	41.90	0.7800600	YES	YES
11	a	62.99	0.4632300	YES	YES
12	a	73.95	4.2264800	YES	YES
13	a	85.01	1.6212200	YES	YES
14	a	99.80	1.4304500	YES	YES
15	a	104.25	1.4139600	YES	YES
16	a	140.84	0.4745900	YES	YES
17	a	143.07	1.1013900	YES	YES
18	a	150.02	0.7292600	YES	YES
19	a	168.66	1.4838000	YES	YES
20	a	174.85	2.2306800	YES	YES
21	a	182.87	1.4742600	YES	YES
22	a	205.10	0.0580300	YES	YES
23	a	210.25	8.8158300	YES	YES
24	a	215.03	3.2168400	YES	YES
25	a	225.19	10.5679200	YES	YES
26	a	233.51	3.7764300	YES	YES
27	a	239.40	4.6962800	YES	YES
28	a	246.35	11.4416300	YES	YES
29	a	249.13	3.5492700	YES	YES
30	a	262.57	13.0060400	YES	YES
31	a	269.26	15.2710500	YES	YES
32	a	287.60	0.0825700	YES	YES
33	a	298.02	40.1188500	YES	YES
34	a	310.48	2.4872500	YES	YES
35	a	329.66	2.4822200	YES	YES
36	a	338.52	1.7367100	YES	YES
37	a	348.32	7.2499200	YES	YES
38	a	364.26	2.0913300	YES	YES
39	a	383.24	15.2168500	YES	YES
40	a	391.52	0.6456800	YES	YES
41	a	409.20	12.2603200	YES	YES
42	a	415.70	11.8805900	YES	YES
43	a	434.79	9.1983400	YES	YES
44	a	457.83	23.8180400	YES	YES
45	a	464.28	27.0817400	YES	YES
46	a	474.34	78.8993200	YES	YES
47	a	482.52	12.4077000	YES	YES
48	a	496.19	2.3774300	YES	YES
49	a	498.58	4.9212700	YES	YES
50	a	518.45	3.6669700	YES	YES
51	a	525.81	0.7451300	YES	YES
52	a	540.20	4.3813000	YES	YES
53	a	552.05	41.4357900	YES	YES
54	a	574.80	11.5697100	YES	YES
55	a	585.82	67.0757900	YES	YES
56	a	596.13	23.1927500	YES	YES
57	a	601.16	118.8011900	YES	YES
58	a	614.17	2.3671600	YES	YES
59	a	621.16	12.4511000	YES	YES
60	a	637.11	23.2318400	YES	YES
61	a	652.25	66.7822100	YES	YES
62	a	662.09	39.7980700	YES	YES
63	a	668.17	15.4891900	YES	YES
64	a	680.06	3.9726300	YES	YES
65	a	681.76	11.4767400	YES	YES
66	a	699.01	29.2475400	YES	YES
67	a	720.70	71.4148500	YES	YES
68	a	742.91	3.7810200	YES	YES
69	a	756.43	51.4458800	YES	YES
70	a	767.43	50.8186900	YES	YES
71	a	770.98	44.1807200	YES	YES
72	a	788.74	15.6412400	YES	YES
73	a	816.37	51.5311300	YES	YES
74	a	828.74	5.5938400	YES	YES
75	a	836.94	0.0025500	YES	YES
76	a	845.29	4.1099600	YES	YES
77	a	859.15	10.3702100	YES	YES
78	a	877.18	12.7195900	YES	YES
79	a	905.49	4.9339400	YES	YES
80	a	914.00	12.7556500	YES	YES
81	a	926.07	7.0428600	YES	YES
82	a	939.47	25.3987400	YES	YES
83	a	942.61	0.6560300	YES	YES
84	a	943.82	0.9997400	YES	YES
85	a	949.93	141.7522200	YES	YES
86	a	957.27	12.8825900	YES	YES
87	a	981.70	22.8990300	YES	YES
88	a	989.17	10.9795700	YES	YES
89	a	992.84	19.6719800	YES	YES
90	a	1009.09	33.5686900	YES	YES
91	a	1017.33	178.9714100	YES	YES
92	a	1025.50	69.3943400	YES	YES
93	a	1029.49	39.6480400	YES	YES
94	a	1033.40	44.3976700	YES	YES
95	a	1037.55	28.7960800	YES	YES
96	a	1052.80	174.2356300	YES	YES
97	a	1060.32	14.2440200	YES	YES
98	a	1076.55	44.3287400	YES	YES
99	a	1081.60	17.4998400	YES	YES
100	a	1093.24	15.3155900	YES	YES
101	a	1107.09	64.8748100	YES	YES
102	a	1122.42	34.3047600	YES	YES
103	a	1125.62	0.2062300	YES	YES
104	a	1139.81	6.6378100	YES	YES
105	a	1140.78	66.2192700	YES	YES
106	a	1151.99	104.6565600	YES	YES
107	a	1156.77	0.7870300	YES	YES
108	a	1171.05	9.8917200	YES	YES
109	a	1176.51	0.1862500	YES	YES
110	a	1184.21	13.7450600	YES	YES
111	a	1193.39	30.0921500	YES	YES
112	a	1203.58	14.5523100	YES	YES
113	a	1216.87	26.2071500	YES	YES
114	a	1227.85	196.3138100	YES	YES
115	a	1246.29	26.4948500	YES	YES
116	a	1258.61	2.6614000	YES	YES
117	a	1268.61	38.1933000	YES	YES
118	a	1270.80	10.2782600	YES	YES
119	a	1290.35	14.5521900	YES	YES
120	a	1297.76	77.1525500	YES	YES
121	a	1306.58	1.0888500	YES	YES
122	a	1310.12	26.3496400	YES	YES
123	a	1317.69	7.6747600	YES	YES
124	a	1324.68	70.4406500	YES	YES
125	a	1332.60	77.8693600	YES	YES
126	a	1337.12	89.3979200	YES	YES
127	a	1340.76	12.9071700	YES	YES
128	a	1352.24	12.8983300	YES	YES
129	a	1369.10	25.9981300	YES	YES
130	a	1395.45	140.7906100	YES	YES
131	a	1407.01	46.9818100	YES	YES
132	a	1437.62	50.9482000	YES	YES
133	a	1437.90	26.3216700	YES	YES
134	a	1441.84	10.6130600	YES	YES
135	a	1454.44	11.6748900	YES	YES
136	a	1460.73	20.3842400	YES	YES
137	a	1481.84	12.9720200	YES	YES
138	a	1544.83	199.8277000	YES	YES
139	a	1577.95	0.3691700	YES	YES
140	a	1596.12	2.4945200	YES	YES
141	a	1618.69	332.7200700	YES	YES
142	a	1764.56	258.8311000	YES	YES
143	a	1773.86	584.0475800	YES	YES
144	a	2954.52	36.8253300	YES	YES
145	a	2980.50	11.8544500	YES	YES
146	a	2991.55	21.4094500	YES	YES
147	a	3002.27	18.8106200	YES	YES
148	a	3023.32	20.4810700	YES	YES
149	a	3026.63	22.3009200	YES	YES
150	a	3058.57	0.5067800	YES	YES
151	a	3072.41	3.6794200	YES	YES
152	a	3088.61	12.3267300	YES	YES
153	a	3094.94	2.4806500	YES	YES
154	a	3101.99	9.5734200	YES	YES
155	a	3110.13	5.5925900	YES	YES
156	a	3120.22	29.1170700	YES	YES
157	a	3143.86	3.4283800	YES	YES
158	a	3165.35	3.6989800	YES	YES
159	a	3166.27	4.6249500	YES	YES
160	a	3542.69	51.0248000	YES	YES
161	a	3597.88	73.2557400	YES	YES
162	a	3600.73	60.4890800	YES	YES
163	a	3617.88	41.4449500	YES	YES
164	a	3627.26	100.3305000	YES	YES
165	a	3667.87	47.7564600	YES	YES

Table S21. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of intermediate B.

```
55

C -0.170334 0.834431 1.362303
O 0.347572 1.218350 2.622257
H 1.264704 0.877087 2.651268
C 0.927128 1.073427 0.238069
O 2.155302 0.601275 0.801916
H 2.717296 1.411659 0.866567
C 1.186248 2.557959 -0.116860
O 0.297917 3.252761 -0.796391
H -0.577312 2.749923 -0.987650
O 2.235822 3.070628 0.256978
C -1.501932 1.584964 1.208204
H -1.332009 2.665031 1.252172
H -2.099724 1.333811 2.087604
C -2.326054 1.241351 -0.033659
H -3.386199 1.415829 0.174083
O -1.950994 2.154096 -1.098813
H -2.289011 1.779327 -1.936374
C -2.156919 -0.212399 -0.521830
O -2.684029 -0.347956 -1.839237
H -1.918233 -0.211249 -2.455349
H -2.786492 -0.840966 0.117907
C 0.498439 0.082861 -0.905804
C -0.706993 -0.744992 -0.354668
H 1.311230 -0.655423 -0.894917
O -0.573595 -2.035362 -0.945827
C 0.495933 0.572372 -2.347215
H -1.221523 -2.625454 -0.519018
C -0.379677 -0.695396 1.172087
H 0.591607 -1.191488 1.304197
C -3.079439 -3.009101 3.557044
H -3.755051 -3.664404 4.090399
C -2.608129 -1.825248 4.083728
O -2.918174 -1.345133 5.298691
C -3.817073 -2.124862 6.130653
H -3.919790 -1.549794 7.049271
H -3.378987 -3.105364 6.339422
H -4.786933 -2.232781 5.636000
C -1.716899 -0.993846 3.333391
H -1.334017 -0.077884 3.763193
C -1.344665 -1.384235 2.093196
O -1.793237 -2.559798 1.561698
C -2.685032 -3.428561 2.257028
O -3.006987 -4.438103 1.645836
O -0.485427 0.431810 -3.087032
C 4.007387 2.386004 -3.990858
H 4.890061 2.852204 -4.419546
C 4.128212 1.567664 -2.866034
H 5.103331 1.388712 -2.423076
C 2.996902 0.976781 -2.306792
H 3.106833 0.339519 -1.435832
C 1.732861 1.189038 -2.883743
C 1.622259 2.005925 -4.025014
H 0.642344 2.171243 -4.461569
C 2.751025 2.606675 -4.568329
H 2.657460 3.248087 -5.439728
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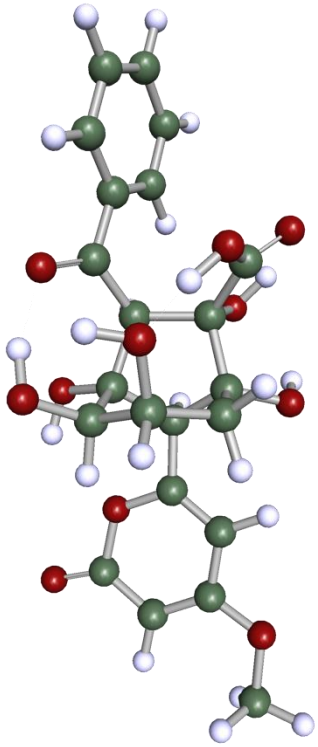

VIBRATIONAL SPECTRUM :

mode	symmetry	wave number cm**(-1)	intensity km/mol	selection rules	
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2		0.00	0.0000000	-	-
3		0.00	0.0000000	-	-
4		0.00	0.0000000	-	-
5		0.00	0.0000000	-	-
6		0.00	0.0000000	-	-
7	a	22.22	2.3388600	YES	YES
8	a	26.46	0.7742100	YES	YES
9	a	38.93	0.1146300	YES	YES
10	a	44.90	0.4263200	YES	YES
11	a	63.34	0.4557200	YES	YES
12	a	69.25	3.4634500	YES	YES
13	a	94.32	0.9902400	YES	YES
14	a	99.97	1.1174100	YES	YES
15	a	110.31	1.1491900	YES	YES
16	a	117.16	0.2684000	YES	YES
17	a	142.52	0.8929300	YES	YES
18	a	149.76	1.4190000	YES	YES
19	a	155.30	2.2821000	YES	YES
20	a	172.35	0.3389200	YES	YES
21	a	175.78	1.5957500	YES	YES
22	a	190.98	1.0134800	YES	YES
23	a	204.07	0.7582600	YES	YES
24	a	209.02	1.0129800	YES	YES
25	a	211.20	10.9584400	YES	YES
26	a	227.39	6.6287300	YES	YES
27	a	238.55	0.5794500	YES	YES
28	a	242.17	1.9099600	YES	YES
29	a	247.54	2.5732400	YES	YES
30	a	272.09	16.9460100	YES	YES
31	a	289.51	3.7218400	YES	YES
32	a	300.37	7.7505400	YES	YES
33	a	314.90	15.3326400	YES	YES
34	a	331.66	13.1166800	YES	YES
35	a	345.38	21.8516000	YES	YES
36	a	370.20	7.5290300	YES	YES
37	a	388.01	2.4967300	YES	YES
38	a	390.93	30.8226300	YES	YES
39	a	404.45	13.3654100	YES	YES
40	a	410.90	7.1993500	YES	YES
41	a	416.82	14.5138500	YES	YES
42	a	421.74	9.4952600	YES	YES
43	a	437.19	88.2386100	YES	YES
44	a	457.34	1.0729400	YES	YES
45	a	477.20	0.1862800	YES	YES
46	a	487.71	9.3872200	YES	YES
47	a	506.96	3.9160000	YES	YES
48	a	510.75	3.9573400	YES	YES
49	a	524.99	4.3105300	YES	YES
50	a	536.58	6.9670900	YES	YES
51	a	547.40	55.5539600	YES	YES
52	a	563.13	63.2543500	YES	YES
53	a	573.19	99.8036400	YES	YES
54	a	583.31	12.8079300	YES	YES
55	a	595.33	9.3432400	YES	YES
56	a	612.95	0.4832500	YES	YES
57	a	628.67	31.5037700	YES	YES
58	a	641.73	3.8892800	YES	YES
59	a	644.81	10.0671600	YES	YES
60	a	653.81	26.3125600	YES	YES
61	a	663.68	33.2866700	YES	YES
62	a	673.19	22.0705700	YES	YES
63	a	686.82	11.0031700	YES	YES
64	a	700.78	15.2679400	YES	YES
65	a	709.88	61.3819900	YES	YES
66	a	731.72	84.4465700	YES	YES
67	a	753.46	23.2145800	YES	YES
68	a	767.52	38.2955600	YES	YES
69	a	775.51	52.8452900	YES	YES
70	a	779.48	39.8665600	YES	YES
71	a	787.13	39.2859600	YES	YES
72	a	793.91	6.5507600	YES	YES
73	a	814.83	2.3930800	YES	YES
74	a	832.06	2.9801800	YES	YES
75	a	834.99	10.5237500	YES	YES
76	a	845.99	13.2472500	YES	YES
77	a	858.97	42.1588500	YES	YES
78	a	874.64	4.5669800	YES	YES
79	a	899.51	11.3813800	YES	YES
80	a	918.49	4.1173100	YES	YES
81	a	931.14	23.1078700	YES	YES
82	a	941.64	1.7297100	YES	YES
83	a	951.96	4.2251800	YES	YES
84	a	953.56	19.8263900	YES	YES
85	a	956.10	2.4240300	YES	YES
86	a	980.95	85.2183100	YES	YES
87	a	990.29	8.1577700	YES	YES
88	a	991.42	43.7771900	YES	YES
89	a	1003.68	60.2452400	YES	YES
90	a	1015.93	11.7526100	YES	YES
91	a	1027.38	4.0244700	YES	YES
92	a	1031.63	26.0305900	YES	YES
93	a	1040.57	60.0271900	YES	YES
94	a	1054.60	94.9875400	YES	YES
95	a	1066.52	124.3174600	YES	YES
96	a	1072.24	16.9923900	YES	YES
97	a	1079.98	26.0826200	YES	YES
98	a	1089.32	4.6749100	YES	YES
99	a	1093.11	46.7675600	YES	YES
100	a	1099.72	40.3547900	YES	YES
101	a	1123.38	77.1494800	YES	YES
102	a	1126.13	0.3699500	YES	YES
103	a	1139.21	55.4334600	YES	YES
104	a	1148.52	52.4073600	YES	YES
105	a	1159.51	4.0434900	YES	YES
106	a	1171.98	12.8819400	YES	YES
107	a	1180.55	47.7635200	YES	YES
108	a	1181.34	8.4313900	YES	YES
109	a	1210.08	99.8219600	YES	YES
110	a	1215.36	15.3199400	YES	YES
111	a	1223.88	29.4085900	YES	YES
112	a	1230.33	219.5233200	YES	YES
113	a	1243.05	59.5810200	YES	YES
114	a	1275.41	87.9507100	YES	YES
115	a	1282.45	115.4251000	YES	YES
116	a	1283.37	47.0928400	YES	YES
117	a	1289.54	29.6403000	YES	YES
118	a	1305.67	22.5596700	YES	YES
119	a	1312.38	6.3050700	YES	YES
120	a	1322.66	86.9748100	YES	YES
121	a	1336.70	64.4019200	YES	YES
122	a	1343.26	15.6391200	YES	YES
123	a	1347.96	6.3337200	YES	YES
124	a	1353.27	9.5939100	YES	YES
125	a	1367.53	122.9500100	YES	YES
126	a	1370.09	56.3327200	YES	YES
127	a	1386.32	104.6933600	YES	YES
128	a	1393.50	127.7055900	YES	YES
129	a	1423.54	39.4283000	YES	YES
130	a	1434.75	36.3835900	YES	YES
131	a	1438.30	8.4717000	YES	YES
132	a	1438.90	48.8375200	YES	YES
133	a	1442.50	12.6312400	YES	YES
134	a	1454.58	9.5381700	YES	YES
135	a	1458.96	72.3949900	YES	YES
136	a	1479.53	1.9982400	YES	YES
137	a	1546.57	193.8329800	YES	YES
138	a	1568.83	27.4883600	YES	YES
139	a	1589.57	63.3519900	YES	YES
140	a	1618.37	316.5750400	YES	YES
141	a	1634.13	133.6209300	YES	YES
142	a	1710.14	235.3728500	YES	YES
143	a	1777.42	596.8044400	YES	YES
144	a	2668.09	1151.6866500	YES	YES
145	a	2943.07	1.5209700	YES	YES
146	a	2955.10	35.9383800	YES	YES
147	a	2960.67	12.1249600	YES	YES
148	a	2970.93	5.7203100	YES	YES
149	a	2981.53	41.4398700	YES	YES
150	a	3002.30	12.5454700	YES	YES
151	a	3024.21	20.0312600	YES	YES
152	a	3038.14	7.4307000	YES	YES
153	a	3089.92	11.4072600	YES	YES
154	a	3102.13	0.2446000	YES	YES
155	a	3113.16	8.4559800	YES	YES
156	a	3121.07	9.4078900	YES	YES
157	a	3130.06	7.1058600	YES	YES
158	a	3134.30	9.5498000	YES	YES
159	a	3161.38	9.7169900	YES	YES
160	a	3165.68	1.0054200	YES	YES
161	a	3216.31	258.0573500	YES	YES
162	a	3253.50	942.1542900	YES	YES
163	a	3435.70	94.3092900	YES	YES
164	a	3511.30	87.8415100	YES	YES
165	a	3621.77	118.8597200	YES	YES

Table S22. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of enterocin trans enol.

```
52

C -1.355967 -0.252367 0.263955
O -2.588045 0.441973 0.366854
H -2.687079 0.741060 1.289435
C -0.987291 -0.322073 -1.297767
O -1.702822 0.633884 -2.031934
H -2.502697 0.836413 -1.508003
C -1.240347 -1.750284 -1.833191
O -0.560145 -2.738624 -1.143144
O -1.873963 -2.043830 -2.810806
C -1.450633 -1.670910 0.839582
H -2.399968 -2.125065 0.539043
H -1.415926 -1.651182 1.933981
C -0.293603 -2.480867 0.267495
H -0.224847 -3.480586 0.702668
C 1.041860 -1.756072 0.483217
O 2.124400 -2.368391 -0.220731
H 2.908139 -0.482216 0.248480
H 1.298358 -1.843559 1.544924
C 0.996986 -0.248458 0.111875
C 0.520093 -0.058373 -1.321039
H 1.858170 -2.401790 -1.160153
C 1.217285 0.547467 -2.319522
O 2.470610 1.058905 -2.124881
O 2.310380 0.281303 0.400489
H 2.651742 1.009023 -1.155467
C -0.129840 0.483796 0.873991
H -0.157550 1.520633 0.510372
C -0.081330 1.392183 -6.309336
H -0.409806 1.618069 -7.320277
C -0.286473 0.120616 -5.774068
H -0.770340 -0.651277 -6.365481
C 0.128775 -0.169091 -4.476196
H -0.025265 -1.163533 -4.076837
C 0.750306 0.812591 -3.697341
C 0.977423 2.083208 -4.250027
H 1.477177 2.838811 -3.652332
C 0.555287 2.372393 -5.544069
H 0.722339 3.363465 -5.957204
C -0.482421 0.738726 5.134454
H -0.670851 0.831481 6.195589
C 0.756043 0.453236 4.610562
O 1.877473 0.256970 5.334981
C 1.779626 0.362982 6.769188
H 1.451091 1.367521 7.057533
H 2.787307 0.175926 7.138469
H 1.086694 -0.388824 7.163089
C 0.952367 0.337950 3.196114
H 1.938043 0.146652 2.794838
C -0.107164 0.516843 2.373791
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C -1.616477 0.932914 4.285258
O -2.763592 1.179033 4.573522
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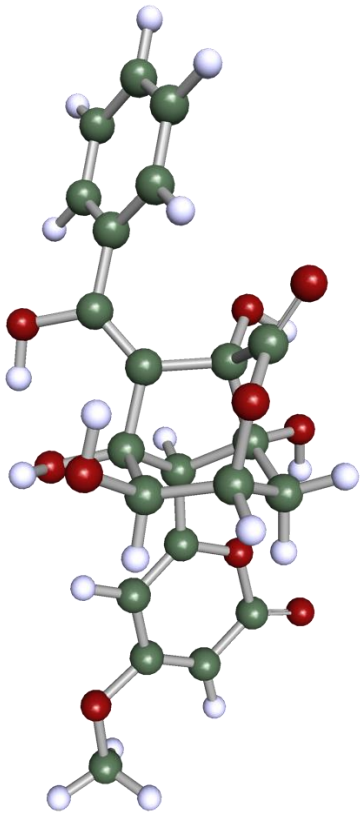

VIBRATIONAL SPECTRUM :

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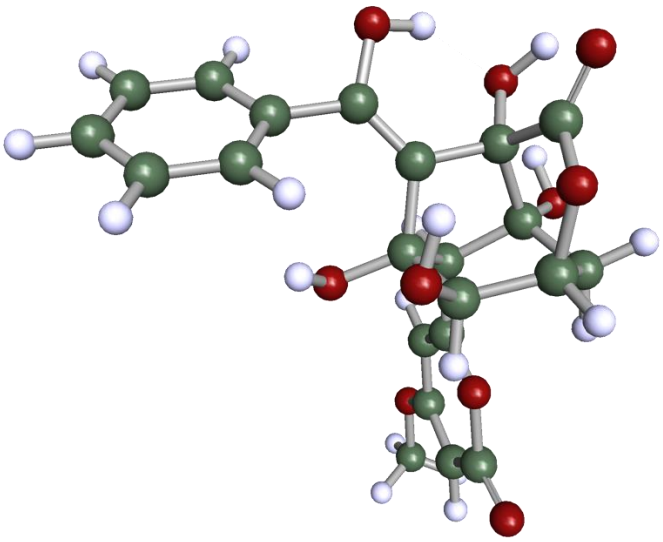
2		0.00	0.0000000	- -
3		0.00	0.0000000	- -
4		0.00	0.0000000	- -
5		0.00	0.0000000	- -
6		0.00	0.0000000	- -
7	a	17.38	1.8200000	YES YES
8	a	29.85	0.3363300	YES YES
9	a	41.85	0.1155200	YES YES
10	a	57.16	0.8549100	YES YES
11	a	62.63	0.6596500	YES YES
12	a	78.53	0.1011700	YES YES
13	a	86.54	0.5667000	YES YES
14	a	100.34	3.3880200	YES YES
15	a	109.82	0.0240000	YES YES
16	a	137.68	0.6750600	YES YES
17	a	144.49	0.6728900	YES YES
18	a	151.71	1.2014200	YES YES
19	a	174.65	2.4997300	YES YES
20	a	192.95	1.2378200	YES YES
21	a	203.02	1.7673300	YES YES
22	a	216.09	1.3835900	YES YES
23	a	219.40	5.3886800	YES YES
24	a	227.62	5.9391100	YES YES
25	a	234.99	7.0343300	YES YES
26	a	240.80	4.1701400	YES YES
27	a	246.19	9.5309600	YES YES
28	a	256.73	4.7455700	YES YES
29	a	269.97	42.1925700	YES YES
30	a	286.78	28.3345600	YES YES
31	a	309.09	2.7068700	YES YES
32	a	332.19	0.6443800	YES YES
33	a	335.22	44.2076000	YES YES
34	a	348.47	9.5529200	YES YES
35	a	373.39	10.7015000	YES YES
36	a	384.43	61.3068300	YES YES
37	a	390.86	100.1715300	YES YES
38	a	399.67	48.7565600	YES YES
39	a	405.66	3.1918700	YES YES
40	a	419.30	2.7193000	YES YES
41	a	428.28	25.2834600	YES YES
42	a	438.65	1.0966200	YES YES
43	a	457.42	5.6359400	YES YES
44	a	481.84	5.4776400	YES YES
45	a	491.30	0.8013100	YES YES
46	a	507.35	3.5611200	YES YES
47	a	525.59	1.1872700	YES YES
48	a	540.56	11.3535800	YES YES
49	a	551.95	14.9583100	YES YES
50	a	567.68	2.6630800	YES YES
51	a	581.36	0.4116400	YES YES
52	a	587.61	4.4860600	YES YES
53	a	600.04	5.7852600	YES YES
54	a	614.04	0.4674100	YES YES
55	a	633.29	34.3924900	YES YES
56	a	638.42	15.8339600	YES YES
57	a	646.81	2.3469400	YES YES
58	a	654.95	17.0175800	YES YES
59	a	664.10	5.5806400	YES YES
60	a	669.14	35.4663300	YES YES
61	a	680.63	9.7091200	YES YES
62	a	682.74	12.4817600	YES YES
63	a	709.91	34.4994000	YES YES
64	a	735.38	27.0127600	YES YES
65	a	753.13	36.1960100	YES YES
66	a	756.23	30.9419300	YES YES
67	a	767.92	47.2282600	YES YES
68	a	790.13	23.3718700	YES YES
69	a	797.28	24.7365900	YES YES
70	a	818.77	18.4496800	YES YES
71	a	830.64	9.6909600	YES YES
72	a	832.23	13.7637100	YES YES
73	a	846.99	82.0945400	YES YES
74	a	860.48	9.6458600	YES YES
75	a	877.22	26.9771100	YES YES
76	a	903.61	10.1777600	YES YES
77	a	922.00	4.2036600	YES YES
78	a	930.49	2.0516700	YES YES
79	a	940.16	1.2169200	YES YES
80	a	949.69	0.6842500	YES YES
81	a	955.70	30.6302400	YES YES
82	a	961.93	7.7403400	YES YES
83	a	979.02	3.9237100	YES YES
84	a	987.77	11.9833900	YES YES
85	a	990.40	1.1990100	YES YES
86	a	999.22	87.2534800	YES YES
87	a	1018.20	15.2039500	YES YES
88	a	1028.79	25.9141700	YES YES
89	a	1033.59	49.4352000	YES YES
90	a	1042.09	83.0786400	YES YES
91	a	1065.49	21.8682500	YES YES
92	a	1075.86	4.5340600	YES YES
93	a	1078.75	110.8983900	YES YES
94	a	1103.95	101.0920900	YES YES
95	a	1111.25	5.7255500	YES YES
96	a	1121.96	48.1519300	YES YES
97	a	1126.91	0.2663100	YES YES
98	a	1137.19	69.0211900	YES YES
99	a	1145.39	105.8163300	YES YES
100	a	1157.84	0.6100200	YES YES
101	a	1170.28	15.9766000	YES YES
102	a	1175.33	9.1453100	YES YES
103	a	1177.60	35.5746700	YES YES
104	a	1180.07	91.5397100	YES YES
105	a	1205.32	31.8617100	YES YES
106	a	1215.17	11.9702600	YES YES
107	a	1228.42	153.2535400	YES YES
108	a	1231.97	42.3288000	YES YES
109	a	1245.87	132.7367400	YES YES
110	a	1261.03	27.7580500	YES YES
111	a	1292.52	49.3072800	YES YES
112	a	1302.41	4.6606700	YES YES
113	a	1305.69	16.8562800	YES YES
114	a	1308.36	28.9312800	YES YES
115	a	1319.16	32.6654200	YES YES
116	a	1325.42	34.1676400	YES YES
117	a	1337.95	4.2705900	YES YES
118	a	1342.89	67.6003000	YES YES
119	a	1353.57	30.9330000	YES YES
120	a	1373.86	86.5611900	YES YES
121	a	1385.43	13.3989400	YES YES
122	a	1405.75	64.9151600	YES YES
123	a	1408.60	14.7192000	YES YES
124	a	1434.27	5.7058500	YES YES
125	a	1440.24	63.5287100	YES YES
126	a	1442.05	11.4463800	YES YES
127	a	1450.44	36.3510200	YES YES
128	a	1456.86	6.1504200	YES YES
129	a	1480.96	14.5335200	YES YES
130	a	1544.22	223.0739600	YES YES
131	a	1569.15	5.4345100	YES YES
132	a	1593.43	5.3519000	YES YES
133	a	1614.82	402.7346800	YES YES
134	a	1622.82	152.0865700	YES YES
135	a	1723.33	356.6579200	YES YES
136	a	1767.85	567.7158800	YES YES
137	a	2955.23	37.7163900	YES YES
138	a	2988.52	6.0273300	YES YES
139	a	2998.90	12.0626100	YES YES
140	a	3024.17	20.6586300	YES YES
141	a	3038.55	0.5562200	YES YES
142	a	3048.16	8.9429600	YES YES
143	a	3066.98	0.7250700	YES YES
144	a	3087.71	12.8327800	YES YES
145	a	3098.43	0.0316800	YES YES
146	a	3105.92	7.3284300	YES YES
147	a	3113.65	4.0395400	YES YES
148	a	3122.48	18.1539000	YES YES
149	a	3130.85	7.9588600	YES YES
150	a	3163.68	0.9393600	YES YES
151	a	3164.31	0.9732100	YES YES
152	a	3368.51	242.7536700	YES YES
153	a	3406.18	119.1475000	YES YES
154	a	3559.13	74.2554600	YES YES
155	a	3608.10	97.2358100	YES YES
156	a	3623.05	29.1206500	YES YES

Table S23. Coordinates (XYZ format) of optimized (DFT TPPS-D/def2-TZVP) ground state structure of enterocin cis enol.

```
52

C -1.119950 0.128241 -1.042195
O -1.970941 1.142674 -1.516752
H -1.398411 1.904440 -1.733884
C 0.366876 0.275282 -1.625169
O 0.556243 1.574084 -2.213149
H 0.672418 1.383695 -3.173877
C 0.656671 -0.764396 -2.703724
O 0.425735 -2.047274 -2.364826
O 1.120888 -0.457390 -3.784654
C -1.671099 -1.238043 -1.448377
H -1.966875 -1.211353 -2.503056
H -2.539868 -1.507330 -0.846026
C -0.553773 -2.258314 -1.263751
H -0.882041 -3.283231 -1.437815
C 0.134067 -2.178131 0.113893
O 1.339600 -2.943828 0.115562
H 1.674871 -1.243097 1.976438
H -0.526884 -2.647648 0.843625
C 0.421787 -0.719340 0.584674
C 1.287282 -0.009641 -0.447467
H 1.844634 -2.659527 -0.668591
C 2.546038 0.483019 -0.334535
O 3.074267 1.347494 -1.253207
O 0.865439 -0.703159 1.922449
H 2.326972 1.671026 -1.807709
C -0.845862 0.178763 0.487028
H -0.513315 1.196762 0.722269
C 5.330595 -0.143453 2.862961
H 6.036713 -0.289964 3.675669
C 5.080094 1.141866 2.373761
H 5.589692 1.997745 2.807980
C 4.177681 1.332260 1.329899
H 3.984436 2.327083 0.941119
C 3.496510 0.238894 0.771327
C 3.774954 -1.050612 1.247622
H 3.288562 -1.907627 0.792395
C 4.680499 -1.239214 2.292776
H 4.885866 -2.244532 2.650087
C -4.105464 -0.838810 3.062993
H -4.922839 -1.162894 3.693384
C -3.672055 0.465896 3.009117
O -4.203266 1.483413 3.721497
C -5.299724 1.161726 4.597964
H -4.979785 0.429532 5.349361
H -6.139798 0.758532 4.019274
H -5.577231 2.103411 5.072800
C -2.584530 0.842168 2.162285
H -2.245054 1.869502 2.131351
C -1.984164 -0.110691 1.406031
O -2.391927 -1.401253 1.439313
C -3.484600 -1.854730 2.269880
O -3.745094 -3.033914 2.192332
```



VIBRATIONAL SPECTRUM :

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2		0.00	0.0000000	-	-
3		0.00	0.0000000	-	-
4		0.00	0.0000000	-	-
5		0.00	0.0000000	-	-
6		0.00	0.0000000	-	-
7	a	17.38	1.8200000	YES	YES
8	a	29.85	0.3363300	YES	YES
9	a	41.85	0.1155200	YES	YES
10	a	57.16	0.8549100	YES	YES
11	a	62.63	0.6596500	YES	YES
12	a	78.53	0.1011700	YES	YES
13	a	86.54	0.5667000	YES	YES
14	a	100.34	3.3880200	YES	YES
15	a	109.82	0.0240000	YES	YES
16	a	137.68	0.6750600	YES	YES
17	a	144.49	0.6728900	YES	YES
18	a	151.71	1.2014200	YES	YES
19	a	174.65	2.4997300	YES	YES
20	a	192.95	1.2378200	YES	YES
21	a	203.02	1.7673300	YES	YES
22	a	216.09	1.3835900	YES	YES
23	a	219.40	5.3886800	YES	YES
24	a	227.62	5.9391100	YES	YES
25	a	234.99	7.0343300	YES	YES
26	a	240.80	4.1701400	YES	YES
27	a	246.19	9.5309600	YES	YES
28	a	256.73	4.7455700	YES	YES
29	a	269.97	42.1925700	YES	YES
30	a	286.78	28.3345600	YES	YES
31	a	309.09	2.7068700	YES	YES
32	a	332.19	0.6443800	YES	YES
33	a	335.22	44.2076000	YES	YES
34	a	348.47	9.5529200	YES	YES
35	a	373.39	10.7015000	YES	YES
36	a	384.43	61.3068300	YES	YES
37	a	390.86	100.1715300	YES	YES
38	a	399.67	48.7565600	YES	YES
39	a	405.66	3.1918700	YES	YES
40	a	419.30	2.7193000	YES	YES
41	a	428.28	25.2834600	YES	YES
42	a	438.65	1.0966200	YES	YES
43	a	457.42	5.6359400	YES	YES
44	a	481.84	5.4776400	YES	YES
45	a	491.30	0.8013100	YES	YES
46	a	507.35	3.5611200	YES	YES
47	a	525.59	1.1872700	YES	YES
48	a	540.56	11.3535800	YES	YES
49	a	551.95	14.9583100	YES	YES
50	a	567.68	2.6630800	YES	YES
51	a	581.36	0.4116400	YES	YES
52	a	587.61	4.4860600	YES	YES
53	a	600.04	5.7852600	YES	YES
54	a	614.04	0.4674100	YES	YES
55	a	633.29	34.3924900	YES	YES
56	a	638.42	15.8339600	YES	YES
57	a	646.81	2.3469400	YES	YES
58	a	654.95	17.0175800	YES	YES
59	a	664.10	5.5806400	YES	YES
60	a	669.14	35.4663300	YES	YES
61	a	680.63	9.7091200	YES	YES
62	a	682.74	12.4817600	YES	YES
63	a	709.91	34.4994000	YES	YES
64	a	735.38	27.0127600	YES	YES
65	a	753.13	36.1960100	YES	YES
66	a	756.23	30.9419300	YES	YES
67	a	767.92	47.2282600	YES	YES
68	a	790.13	23.3718700	YES	YES
69	a	797.28	24.7365900	YES	YES
70	a	818.77	18.4496800	YES	YES
71	a	830.64	9.6909600	YES	YES
72	a	832.23	13.7637100	YES	YES
73	a	846.99	82.0945400	YES	YES
74	a	860.48	9.6458600	YES	YES
75	a	877.22	26.9771100	YES	YES
76	a	903.61	10.1777600	YES	YES
77	a	922.00	4.2036600	YES	YES
78	a	930.49	2.0516700	YES	YES
79	a	940.16	1.2169200	YES	YES
80	a	949.69	0.6842500	YES	YES
81	a	955.70	30.6302400	YES	YES
82	a	961.93	7.7403400	YES	YES
83	a	979.02	3.9237100	YES	YES
84	a	987.77	11.9833900	YES	YES
85	a	990.40	1.1990100	YES	YES
86	a	999.22	87.2534800	YES	YES
87	a	1018.20	15.2039500	YES	YES
88	a	1028.79	25.9141700	YES	YES
89	a	1033.59	49.4352000	YES	YES
90	a	1042.09	83.0786400	YES	YES
91	a	1065.49	21.8682500	YES	YES
92	a	1075.86	4.5340600	YES	YES
93	a	1078.75	110.8983900	YES	YES
94	a	1103.95	101.0920900	YES	YES
95	a	1111.25	5.7255500	YES	YES
96	a	1121.96	48.1519300	YES	YES
97	a	1126.91	0.2663100	YES	YES
98	a	1137.19	69.0211900	YES	YES
99	a	1145.39	105.8163300	YES	YES
100	a	1157.84	0.6100200	YES	YES
101	a	1170.28	15.9766000	YES	YES
102	a	1175.33	9.1453100	YES	YES
103	a	1177.60	35.5746700	YES	YES
104	a	1180.07	91.5397100	YES	YES
105	a	1205.32	31.8617100	YES	YES
106	a	1215.17	11.9702600	YES	YES
107	a	1228.42	153.2535400	YES	YES
108	a	1231.97	42.3288000	YES	YES
109	a	1245.87	132.7367400	YES	YES
110	a	1261.03	27.7580500	YES	YES
111	a	1292.52	49.3072800	YES	YES
112	a	1302.41	4.6606700	YES	YES
113	a	1305.69	16.8562800	YES	YES
114	a	1308.36	28.9312800	YES	YES
115	a	1319.16	32.6654200	YES	YES
116	a	1325.42	34.1676400	YES	YES
117	a	1337.95	4.2705900	YES	YES
118	a	1342.89	67.6003000	YES	YES
119	a	1353.57	30.9330000	YES	YES
120	a	1373.86	86.5611900	YES	YES
121	a	1385.43	13.3989400	YES	YES
122	a	1405.75	64.9151600	YES	YES
123	a	1408.60	14.7192000	YES	YES
124	a	1434.27	5.7058500	YES	YES
125	a	1440.24	63.5287100	YES	YES
126	a	1442.05	11.4463800	YES	YES
127	a	1450.44	36.3510200	YES	YES
128	a	1456.86	6.1504200	YES	YES
129	a	1480.96	14.5335200	YES	YES
130	a	1544.22	223.0739600	YES	YES
131	a	1569.15	5.4345100	YES	YES
132	a	1593.43	5.3519000	YES	YES
133	a	1614.82	402.7346800	YES	YES
134	a	1622.82	152.0865700	YES	YES
135	a	1723.33	356.6579200	YES	YES
136	a	1767.85	567.7158800	YES	YES
137	a	2955.23	37.7163900	YES	YES
138	a	2988.52	6.0273300	YES	YES
139	a	2998.90	12.0626100	YES	YES
140	a	3024.17	20.6586300	YES	YES
141	a	3038.55	0.5562200	YES	YES
142	a	3048.16	8.9429600	YES	YES
143	a	3066.98	0.7250700	YES	YES
144	a	3087.71	12.8327800	YES	YES
145	a	3098.43	0.0316800	YES	YES
146	a	3105.92	7.3284300	YES	YES
147	a	3113.65	4.0395400	YES	YES
148	a	3122.48	18.1539000	YES	YES
149	a	3130.85	7.9588600	YES	YES
150	a	3163.68	0.9393600	YES	YES
151	a	3164.31	0.9732100	YES	YES
152	a	3368.51	242.7536700	YES	YES
153	a	3406.18	119.1475000	YES	YES
154	a	3559.13	74.2554600	YES	YES
155	a	3608.10	97.2358100	YES	YES
156	a	3623.05	29.1206500	YES	YES

Figures S118-121. DFT-calculated energy diagrams for the conversion of **1** to **4**, **4** to **2**, **4** to **3**, and intermediate A to intermediate B, and **2** to **3**.

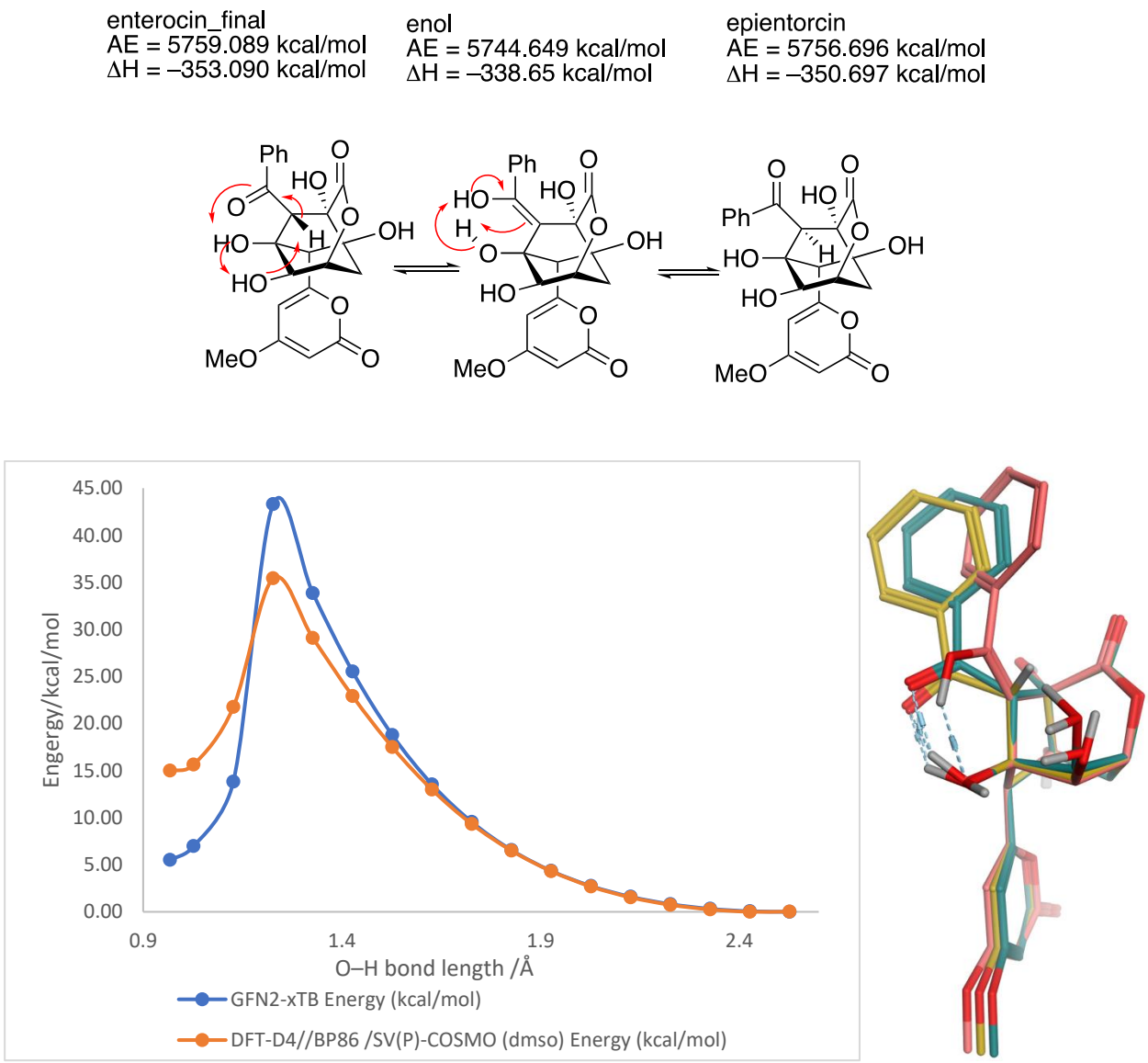
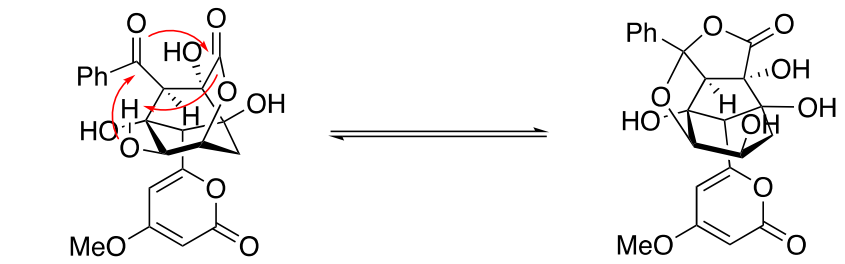
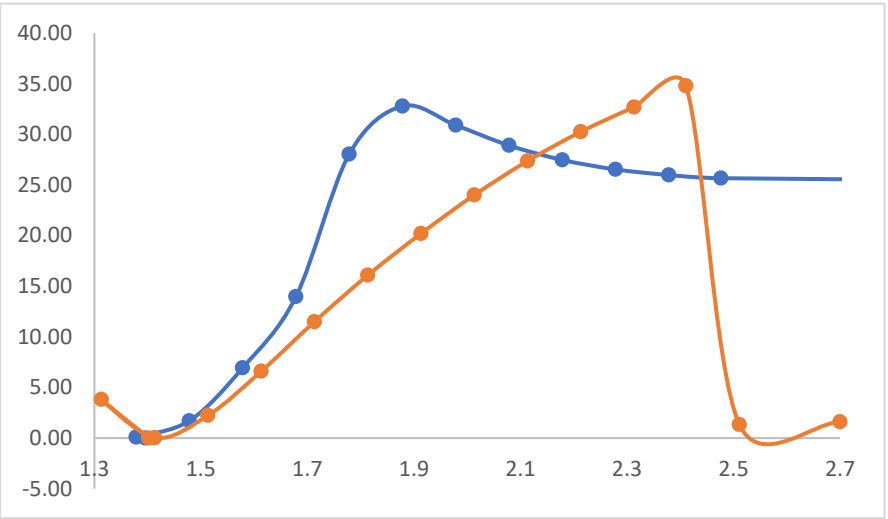


Figure S118. Enolisation of enterocin (**1**) to 3-*epi*-enterocin (**4**) modelled via a reaction trajectory calculated at the semiempirical (GFN2-xTB; blue) or DFT (BP86-D4/SV(P)-COSMO; orange) level of theory. A bondscan was generated from 4 by decreasing the C-5O to H-3 distance by 0.1 Å at a time followed by full structure optimisation (see enterocin_enolisation_2.avi). Inset are three structure along the trajectory. Enol (pink), epienterocin (gold) and the transition state (green).



epienterocin_DFT_SVP_scan0000
AE= 5754.520 kcal/mol
ΔH= –348.521 kcal/mol

epienterocin_DFT_SVP_scan0011
AE= 5751.754 kcal/mol
ΔH= –345.755 kcal/mol



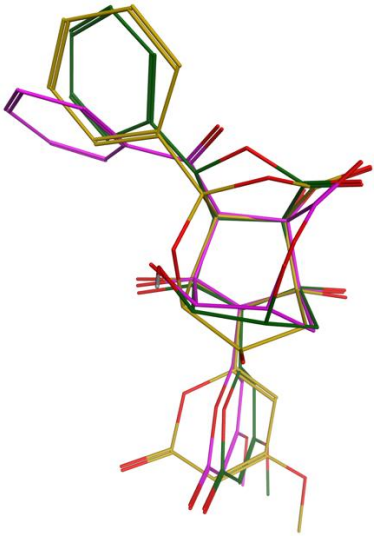
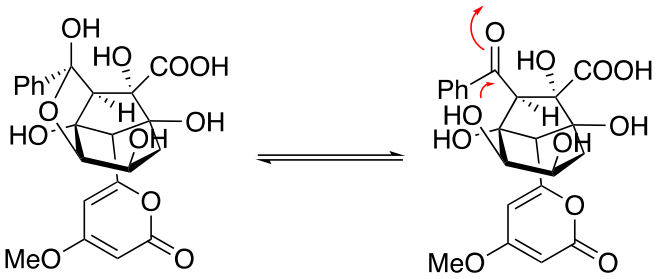


Figure S119. Concerted conversion of 3-*epi*-enterocin (**4**) to isoenterocin A (**2**) formation modelled via a reaction trajectory calculated at the semiempirical (GFN2-xTB; blue) or DFT (BP86-D4/SV(P)-COSMO; orange) level of theory. A bondscan was generated from **4** by decreasing the C-5OH to C-1 distance by 0.1 Å at a time followed by full structure optimisation (see epienterocin_to_isoenterocin_DFT.avi). Inset are three structure along the trajectory. 3-*epi*-enterocin (pink), to isoenterocin A (gold) and a transition state (green).



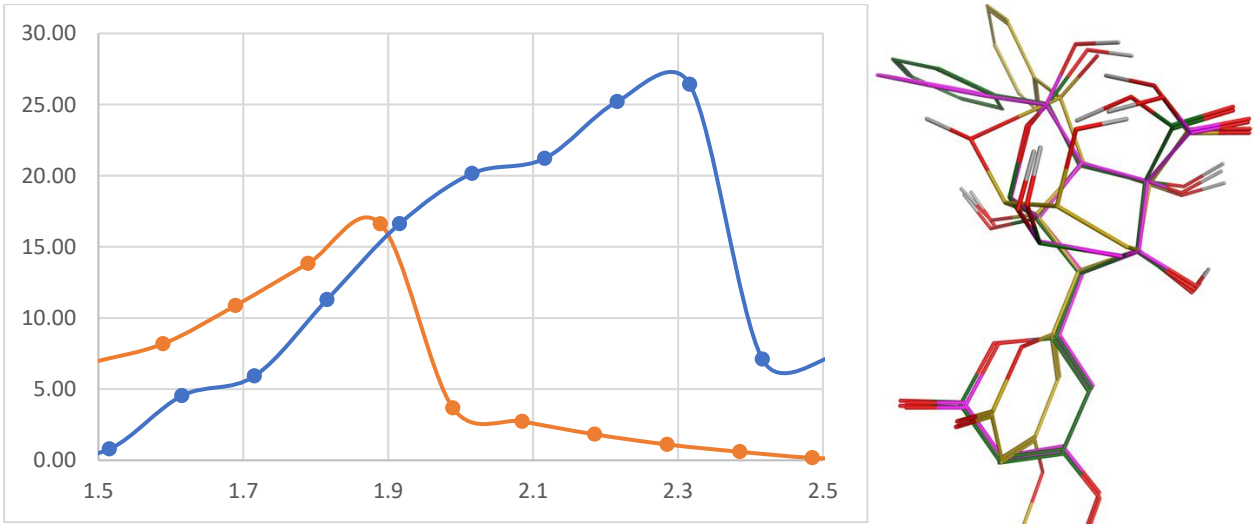


Figure S120. Concerted conversion of intermediate acid A to intermediate acid B modelled via a reaction trajectory calculated at the semiempirical (GFN2-xTB; blue) or DFT (BP86-D4/SV(P)-COSMO; orange) level of theory. A bondscan was generated from intermediate B by decreasing the C-5OH to C-16 distance by 0.1 Å at a time followed by full structure optimisation. Inset are three structure along the DFT trajectory. Intermediate A (pink), to intermediate B (gold) and the transition state (green) showing the boat to chair conversion of the central ring upon hemiketal formation.

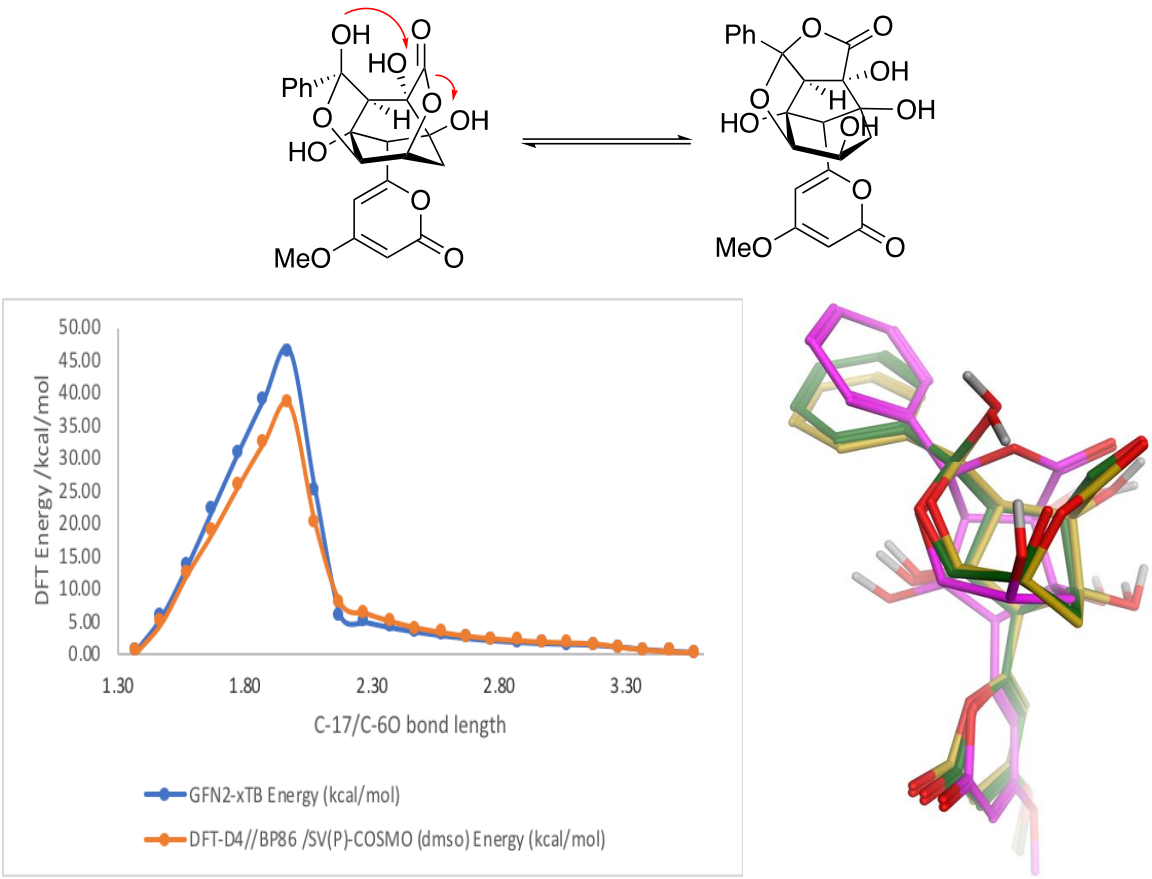


Figure S121. Concerted conversion of isoenterocin A (**2**) to isoenterocin B (**3**) modelled via a reaction trajectory calculated at the semiempirical (GFN2-xTB; blue) or DFT (BP86-D4/SV(P)-COSMO; orange) level of theory. A bondscan was generated from intermediate B by decreasing the C-6O to C-17 distance by 0.1 Å at a time followed by full structure optimisation. Inset are three structure along the DFT trajectory. isoenterocin A (pink), to isoenterocin B (gold) and transition state(green) showing the boat to chair conversion of the central ring upon hemiketal formation.

Table S24. Thermochemical data for all isolated compounds and proposed intermediates (DFT TPPS-D/def2-TZVP//sos-MP2/def2-QZVPP)

	T	p	ln(qtrans)	ln(qrot)	ln(qvib)	Chem. Pot.	energy	ΔS	Cv	Cp	enthalpy	AE	corr. AE	$\Delta H_{(f)}$	relative	relative $\Delta H_{(f)}$	ΔΔH
	(K)	(MPa)				(kJ/mol)	(kJ/mol)	(kJ/mol/K)	(kJ/mol-K)	(kJ/mol-K)	(kJ/mol)	(kcal/mol)	(kcal/mol)	**(kcal/mol)**	enthalpy	**(kcal/mol)**	(kcal/mol)
enterocin (**1**) + water	298.15	0.10	19.75	16.82	24.22	865.91	1088.85	0.75606	0.46337	0.47169	1091.33	5681.73	5759.09	**-353.09**	1.89	-413.31	0.00
cis-enol + water	298.15	0.10	19.75	16.85	23.96	864.54	1087.54	0.75698	0.46896	0.47727	1090.23	5670.21	5744.81	**-338.81**	0.79	-399.03	14.28
trans-enol + water	298.15	0.10	19.75	16.81	24.48	862.69	1087.03	0.76075	0.46825	0.47657	1089.51	5665.90	5744.34	**-338.35**	0.07	-398.56	14.74
3-epienterocin (**4**) + water	298.15	0.10	19.75	16.84	24.02	867.11	1089.12	0.75295	0.46104	0.46935	1091.60	5679.49	5756.70	**-350.70**	2.16	-410.91	2.39
isoenterocin A (**2**) + water	298.15	0.10	19.75	16.76	24.05	866.59	1087.97	0.75082	0.46070	0.46901	1090.45	5682.621	5757.85	-351.851	1.01	-412.07	1.24
intermediate A	298.15	0.10	19.81	16.80	26.51	927.04	1161.26	0.79389	0.49733	0.50564	1163.74	5898.91	5981.22	**-411.46**	3.18	-411.46	1.85
isoenterocin B (**3**) + water	298.15	0.10	19.75	16.81	22.23	870.86	1086.97	0.73314	0.46033	0.46865	1089.44	5675.66	5750.89	**-344.89**	0.00	-405.11	8.20
intermediate A	298.15	0.10	19.81	16.86	25.46	929.38	1161.09	0.78549	0.49839	0.50670	1163.57	5898.495	5981.272	-411.512	3.01	-411.51	1.79
intermediate B	298.15	0.10	19.81	16.86	25.34	928.33	1158.48	0.78022	0.48918	0.49750	1160.96	5901.773	5981.154	-411.394	0.40	-411.39	1.91
enterocinic acid (**7**)	298.15	0.10	19.81	16.79	25.75	930.58	1161.98	0.78444	0.49477	0.50308	1164.46	5898.06	5975.55	**-405.79**	3.90	-405.79	7.51
water	298.15	0.10	14.94	4.51	0.00	5.95	61.60	0.19497	0.02518	0.03349	64.08	221.87	223.98	**-60.22**			
MeOH	298.15	0.10	15.80	8.09	0.26	70.47	139.12	0.23859	0.03747	0.04578	141.60	484.38	490.09	**-50.83**			

energy=ZPE+3RT+sum(i) e(i)*(1+exp(-e(i)/kT))/2*(1-exp(-e(i)/kT))

qtrans=(m*k*T/(2*pi))^1.5*v h/(2*pi) — e(i)=frequency of i-th v — Cv=d(energy)/dT

m=mol. mass in a.u. v=vol. per mol. of ideal gas — Cp=d(enthalpy)/dT

qrot=((2*pi*kT)^3*A*B*C)^0.5/(sigma*p — entropy=(energy+RT-chem.pot.)/T — enthalpy=energy+RT

A,B,C=moments of inertia in a.u.

chem.pot.=ZPE-RT*ln(qtrans*qrot*qvib)

ZPE=zero point vibrational energy

qvib=product(i) 1/(1-exp(-e(i)/kT)

e(i)=frequency of i-th vibrational mode

Calculations were all normalised (column relative ΔH_f) to a molecular formula of $C_{22}H_{22}O_{11}$ by the addition of the ΔH_f for water where appropriate.

G. Biological Screening

Biological Screening

The compounds used in this study were dissolved in DMSO to give stock solutions with a concentration of 25 mg/mL. From each of these stock solutions, an aliquot was transferred to the first column of a 96-well microtitre plate in rows B to G, which was two-fold serially diluted across the 12 columns of the plate. Bioassay media was added to each well to provide a 100-fold dilution of each test solution in the final bioassay. After dilution, the final concentration in each well ranged from 250-0.12 μg/mL in 0.1% DMSO. In each assay, row A contained no test compound (0% inhibition) and row H was left uninoculated (100% inhibition). The absorbance of each well was measured using a Spectromax plate reader (see individual assay for wavelength and time of measurement) and MIC and LD_{99} values determined visually. Experiments were performed in duplicate due to the limited amount of test compound in some cases.

Antibacterial assay

The antibacterial activity of selected analogues of enterocin, was evaluated using the Gram-positive bacteria *Micrococcus luteus* (ACM 2644), *Staphylococcus aureus* (ATCC 25923), and *Bacillus subtilis* (ATCC 6633), as well as the Gram-negative bacterium *Escherichia coli* (ATCC 25922) as indicative species. Gentamicin (BioAustralis, MIC 1.7 μM against *M. luteus* and *E. coli*; MIC 0.8 μM against *B. subtilis* and *S. aureus*) was used as a positive control. A bacterial suspension (50 mL in a 250 mL Erlenmeyer flask) was prepared in nutrient broth (Amyl) by cultivation for 24 h at 28 °C, swirling at 250 rpm. The suspension was diluted to a standardised absorbance of 0.01 absorbance units/mL. To each well of the prepared microtitre plates, 10 μL aliquots were added to the wells of a 96-well microtitre plate, which contained the test compounds dispersed in nutrient broth (Amyl) and resazurin (10 μL, 120 μg/mL). The plates were incubated at 28 °C for 48 h during which time the uninhibited control wells changed from a blue to light pink colour. The MIC end points were determined visually. The absorbance was measured using Spectromax plate reader (Molecular Devices) at 605 nm.

Antifungal assay

The antifungal activity of selected analogues of enterocin, was evaluated using the yeasts *Candida albicans* (ATCC 10231) and *Saccharomyces cerevisiae* (ATCC 9763) were used as indicative species. Amphoterocin B (BioAustralis, MIC 0.1 μM against *C. albicans* and MIC 0.3 μM against *S. cerevisiae*) was used as a positive control. A yeast suspension (50 mL in 250 mL flask) was prepared in 1% malt extract broth by cultivation for 24 h at 250 rpm, 24 °C. The suspension was diluted to an absorbance of 0.005 and 0.03 absorbance units per mL for *C. albicans* and *S. cerevisiae*, respectively. Aliquots (20 μL and 30 μL) of *C. albicans* and *S. cerevisiae*, respectively were applied to the wells of a 96-well microtitre plate, which contained the test compounds dispersed in malt extract agar containing bromocresol green (50 μg/mL) as the indicator. The plates were incubated at 24 °C for 48 h during which time the positive control wells change colour from a blue to yellow colour. MIC end points were determined visually. The absorbance was measured using Spectromax plate reader (Molecular Devices) at 620 nm.

Cytotoxicity assay

The cytotoxicity activity of selected analogues of enterocin was evaluated. NS-1 (ATCC TIB-18) mouse myeloma cells were used as the cell-line for cytotoxicity in myeloma cells, and Neonatal Foreskin Fibroblast (NFF) cells were used as the cell-line for cytotoxicity in human cells. These cells were cultured in (DMEM) (Dulbecco's Modified Eagle IS Medium +10% foetal bovine serum (FBS) +1% penicillin/streptomycin (Life Technologies)) and incubated at 37 °C (5% CO_2) for 72 h. Mitomycin C (BioAustralis, MIC 0.93 μM) was used as a positive control against NS-1 cells. To standardise the concentration used, cells were counted under the microscope after staining with erythrosin B and diluted with DMEM to the required concentration. Once standardised, the cells (190 μL, 50,000 cells/mL (NS-1), 25,000 cells/mL (NFF)) were loaded in 96-well microtitre plates with resazurin (10 μL, 120 μg/mL) and the test compound and incubated for 72 h at 37 °C (5% CO_2). The LD_{99} end points were determined visually. The absorbance was measured using Spectromax plate reader (Molecular Devices) at 605 nm.

Germination Inhibition assay

The germination inhibitory activity of selected analogues of enterocin, was evaluated using *Eragrostis tef* (teff) seeds as the indicative species. Teff seeds were dispensed by hand into the wells of a 96-well microtitre plate to achieve a coverage of at least 10 seeds per well, which contained the test compounds dispersed in 200 μL of agar (1% w/v) per well. The plates were placed in a tray wrapped with a semi-opaque bag, exposed to 1600 lux (within the tray) using Power-GLO (20 W) and SunGLO (20 W) tubes, and incubated for 72 h at 24 °C. MIC end points were determined visually. Cycloheximide (BioAustralis, MIC 11 μM) was used as a positive control against teff.

Table S25. *In vitro* biological activities of enterocin rearrangement products and semisynthetic enterocin analogues. Note: no biological activity observed in other assays tested. [Note: the highest concentration for compounds **8** and **9** was 100 μg/mL, else 250 μg/mL was used.]

Compound	**Minimum inhibitory concentration (μM)**	**Inhibition at highest concentration (%)**
	Eragrostis tef	***Micrococcus luteus***
enterocin (**1**)	28	58
5-deoxyenterocin (**5**)	>200	47
isoenterocin A (**2**)	>200	0
5-*O*-arachidoylenterocin (**8**)	>200	53
5-*O*-behenoylenterocin (**9**)	>200	6
5-*O*-palmitoylenterocin (**10**)	>200	5
5-*O*-acetylenterocin (**11**)	200	39
5-*O*-propionylenterocin (**12**)	200	37
5-*O*-carboxypropionylenterocin (**13**)	>200	38
3-*epi*-enterocin-(*Z*)-15-*O*-methyloxime (**14**)	>200	0

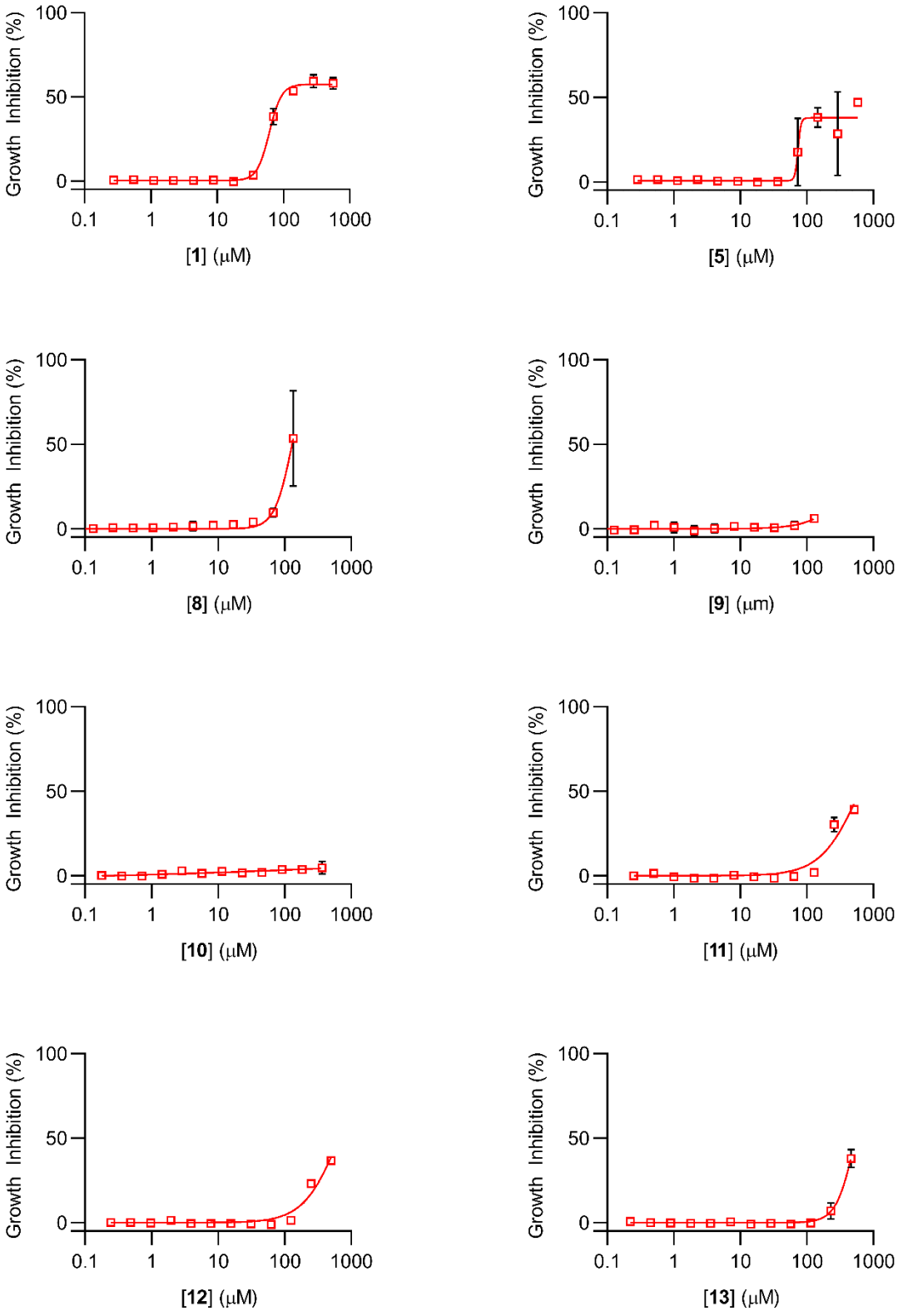


Figure S122. Growth inhibition curves for enterocin analogues with at least 5% inhibition recorded against *M. luteus*. No other significant biological activity was observed.