Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Phenazinolins A-E: Novel Diphenazines from a Tin Mine Tailings-Derived *Streptomyces* Species

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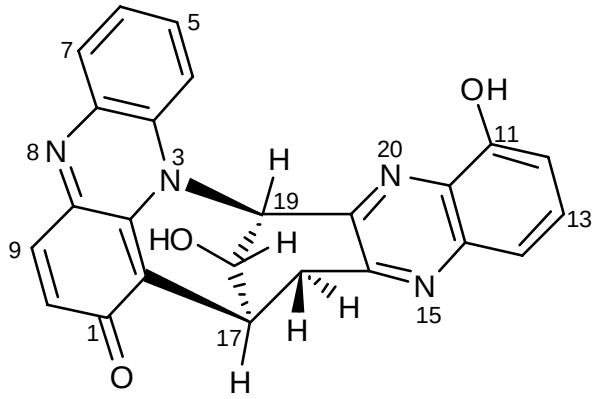


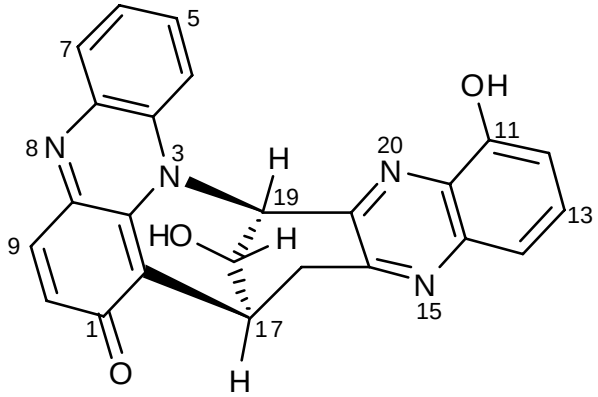
Structure of Phenazinolin A (**1**)

Table S1. 1D & 2D NMR (500 MHz, DMSO-d_6) Data for Phenazinolin A (**1**).[a]

Position	δ_C [ppm]	δ_N [ppm]	δ_H [ppm]	^{1}H-^{13}C HMBC	^{1}H-^{15}N HMBC	ROESY
1	180.1 (s)					
2	109.4 (s)					
2a	131.7 (s) [b]					
3		137.9 (s)				
3a	130.3 (s)					
4	116.4 (d)		8.88 (d, *J* = 8.6 Hz, 1H)	C-3a, C-5, C-6, C-7, C-7a	N-3	H-18, H-19
5	132.7 (d)		7.87 (dd, *J* = 7.5, 8.6 Hz, 1H) [d]	C-3a, C-4, C-7, C-7a		H-19
6	124.1 (d)		7.47 (t, *J* = 7.5 Hz, 1H)	C-3a, C-4, C-5, C-7, C-7a		
7	130.5 (d)		7.88 (d, *J* = 7.5 Hz, 1H) [d]	C-3a, C-4, C-5, C-7a	N-8	
7a	135.1 (s)					
8		330.8 (s)				
8a	146.4 (s) [c]					
9	133.0 (d)		7.54 (d, *J* = 9.8 Hz, 1H)	C-1, C-2, C-2a, C-8a	N-3, N-8	
10	135.3 (d)		7.00 (d, *J* = 9.8 Hz, 1H)	C-2, C-2a, C-8a, C-9, C-17		
11	153.1 (s)					

12	111.5 (d)		7.04 (d, *J* = 7.6 Hz, 1H)	C-11, C-13, C-14, C-14a, C-20a		
13	131.3 (d)		7.58 (t, *J* = 10.1 Hz, 1H)	C-11, C-12, C-14a, C-20a		
14	117.9 (d)		7.35 (d, *J* = 8.3 Hz, 1H)	C-11, C-12, C-13, C-20a	N-15	
14a	142.0(s)					
15		325.8 (s)				
15a	152.7 (s)					
16_{ax}	33.7 (t)		3.59 (dd, *J* = 17.7, 5.5 Hz, 1H)	C-2, C-2a, C-14a, C-15a, C-17, C-19a	N-15	H-18
16_{eq}			3.15 (dd, *J* = 17.7, 0.6 Hz, 1H)	C-2, C-14a, C-15a, C-17, C-18, C-19a	N-15	H-17, H-18
17	30.2 (d)		3.70 (m, 1H)	C-1, C-2, C-2a, C-15a, C-16, C-18, C-19		H-16, H-18, H-19
18	62.8 (d)		4.62 (dd, *J* = 4.0, 3.1 Hz, 1H)	C-16, C-19, C-19a		H-4, H-16, H-17, H-19
19	56.9 (d)		6.23 (dd, *J* = 4.0, 2.8 Hz, 1H)	C-2a, C-3a, C-15a, C-17, C-18, C-19a, C-20a		H-4, H-5, H-17, H-18
19a	146.4 (s) [c]					
20		325.8 (s)				
20a	131.6(s) [b]					
11-OH			10.06 (s, 1H)	C-12, C-20a		
18-OH			6.15 (br s, 1H)	C-17		H-18

[a] The ^{1}H NMR spectrum was recorded at 500 MHz, the ^{13}C NMR spectrum at 125 MHz, ^{15}N NMR spectrum at 50 MHz. [b] [c] The two sets of signal were interchangeable in terms of their assignments.
[d] The signals of H-5 and H-7 overlapped.



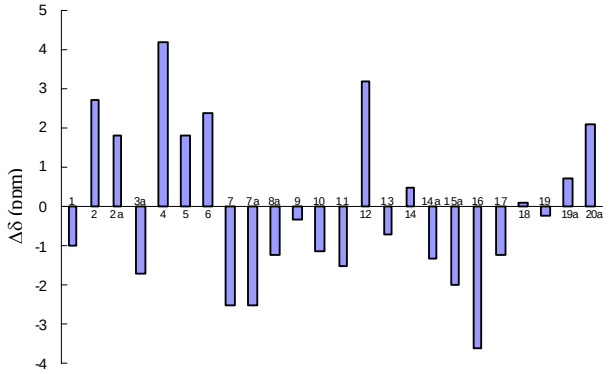
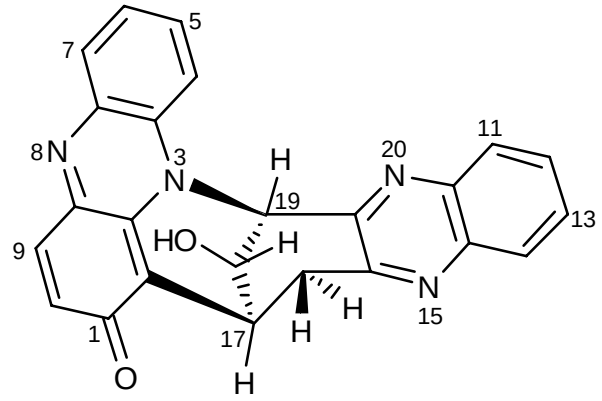


Table S2. The Errors between the Experimental ^{13}C NMR and the Computed Data for Phenazinolin A (**1**)

Position	δ (C_{exp})	Shielding	δ (C_{calcd})	Δδ (C_{error})	Position	δ (C_{exp})	Shielding	δ (C_{calcd})	Δδ (C_{error})
1	180.1	-5.1	181.1	-1.0	11	153.1	21.5	154.6	-1.5
2	109.4	69.5	106.7	2.7	12	111.5	67.9	108.3	3.2
2a	131.7	46.2	129.9	1.8	13	131.3	44.1	132.0	-0.7
3a	130.3	44.1	132.0	-1.7	14	117.9	58.8	117.4	0.5
4	116.4	64.0	112.2	4.2	14a	142.0	32.8	143.3	-1.3
5	132.7	45.2	130.9	1.8	15a	152.7	21.4	154.7	-2.0
6	124.1	54.5	121.7	2.4	16	33.7	139.1	37.3	-3.6
7	130.5	43.1	133.0	-2.5	17	30.2	145.0	31.4	-1.2
7a	135.1	38.5	137.6	-2.5	18	62.8	113.6	62.7	0.1
8a	146.4	28.5	147.6	-1.2	19	56.9	119.3	57.1	-0.2
9	133.0	42.8	133.3	-0.3	19a	146.4	30.4	145.7	0.7
10	135.3	39.7	136.4	-1.1	20a	131.6	46.6	129.5	2.1



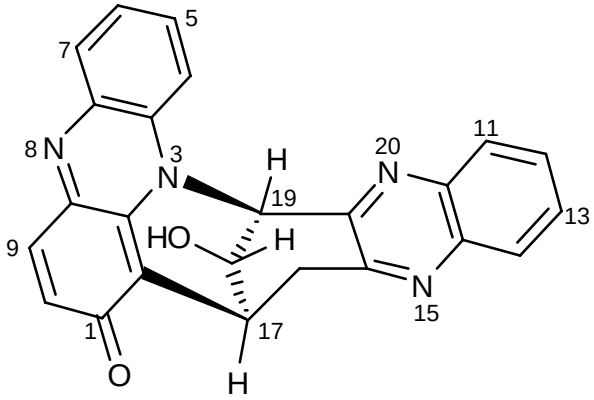
Structure of Phenazinolin B (**2**)

Table S3. 1D & 2D NMR (500 MHz, DMSO-d_6) Data for Phenazinolin B (**2**) [a]

Position	δ_C [ppm]	δ_H [ppm]	^{1}H-^{13}C HMBC	ROESY
1	180.1 (s)			
2	109.4 (s)			
2a	131.6 (s)			
3a	130.3 (s)			
4	115.6 (d)	8.68 (d, *J* = 8.5 Hz, 1H)	C-6, C-7a	H-18, H-19
5	132.4 (d)	7.92 (m, 1H) [c]	C-3a, C-7	H-19
6	124.0 (d)	7.49 (t, *J* = 7.9 Hz, 1H)	C-4, C-7a	
7	130.5 (d) [b]	7.91 (d, *J* = 7.9 Hz, 1H) [c]	C-3a, C-5	
7a	135.1 (s)			
8a	146.4 (s)			
9	133.0 (d)	7.55 (d, *J* = 9.8 Hz, 1H)	C-1, C-2a	
10	135.3 (d)	7.00 (d, *J* = 9.8 Hz, 1H)	C-2, C-8a	
11	128.1 (d)	7.95 (d, *J* = 8.0 Hz, 1H) [c]	C-13, C-14a	
12	130.6 (d) [b]	7.78 (m, 1H)	C-14, C-20a	
13	129.5 (d)	7.72 (t, *J* = 8.6 Hz, 1H)	C-11, C-14a	

14	128.5 (d)	7.93 (d, *J* = 8.6 Hz, 1H) [c]	C-12, C-13, C-14a, C-20a	
14a	140.3 (s)			
15a	152.6 (s)			
16_{ax}	33.4 (t)	3.65 (dd, *J* = 17.7, 5.0 Hz, 1H)	C-2, C-17, C-15a	
16_{eq}		3.18 (dd, *J* = 17.7, 0.5 Hz, 1H)	C-2, C-15a, C-17, C-18, C-19a	
17	30.3 (d)	3.70 (t, *J* = 5.0 Hz, 1H)	C-2, C-18, C-15a	H-18, H-19
18	62.7 (d)	4.63 (m, 1H)		H-4, H-17, H-19
19	56.6 (d)	6.34 (m, 1H)	C-19a	H-4, H-5, H-17, H-18
19a	148.9 (s)			
20a	141.1(s)			
18-OH		6.11 (d, *J* = 2.4 Hz, 1H)	C-17, C-19	H-18

[a] The ^{1}H NMR spectrum was recorded at 500 MHz, the ^{13}C NMR spectrum at 125 MHz, ^{15}N NMR spectrum at 50 MHz. [b] The two signals were interchangeable in terms of their assignments. [c] The signals of H-5, H-7, H-11, and H-14 overlapped.



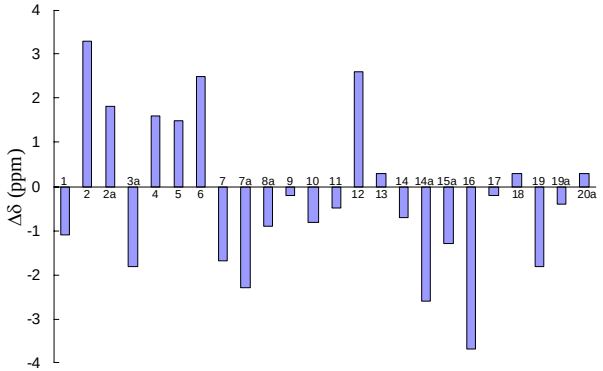
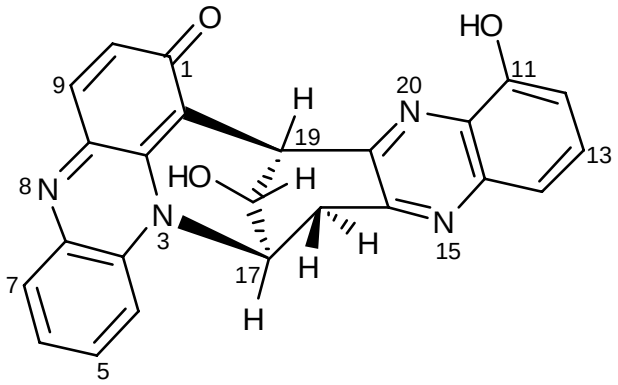


Table S4. The Errors between the Experimental ^{13}C NMR and the Computed Data for Phenazinolin B (**2**)

Position	δ (C_{exp})	Shielding	δ (C_{calcd})	Δδ (C_{error})	Position	δ (C_{exp})	Shielding	δ (C_{calcd})	Δδ (C_{error})
1	180.1	-5.2	181.2	-1.1	11	128.1	47.4	128.6	-0.5
2	109.4	69.9	106.1	3.3	12	130.6	48.0	128	2.6
2a	131.6	46.2	129.8	1.8	13	129.5	46.8	129.2	0.3
3a	130.3	43.9	132.1	-1.8	14	128.5	46.8	129.2	-0.7
4	115.6	62.0	114	1.6	14a	140.3	33.1	142.9	-2.6
5	132.4	45.1	130.9	1.5	15a	152.6	22.1	153.9	-1.3
6	124.0	54.5	121.5	2.5	16	33.4	138.9	37.1	-3.7
7	130.5	43.8	132.2	-1.7	17	30.3	145.5	30.5	-0.2
7a	135.1	38.6	137.4	-2.3	18	62.7	113.6	62.4	0.3
8a	146.4	28.7	147.3	-0.9	19	56.6	117.6	58.4	-1.8
9	133.0	42.8	133.2	-0.2	19a	148.9	26.7	149.3	-0.4
10	135.3	39.9	136.1	-0.8	20a	141.1	35.2	140.8	0.3



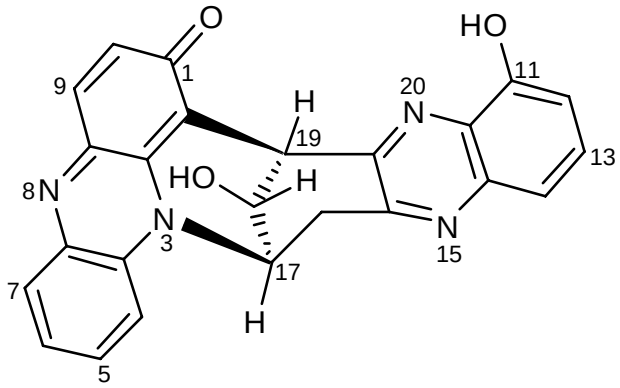
Structure of Phenazinolin C (**3**)

Table S5. 1D & 2D NMR (500 MHz, DMSO-d_6) Data for Phenazinolin C (**3**).[a]

Position	δ_C [ppm]	δ_N [ppm]	δ_H [ppm]	^{1}H-^{13}C HMBC	^{1}H-^{15}N HMBC	ROESY
1	178.9 (s)					
2	106.4 (s)					
2a	132.3 (s)					
3		140.4 (s)				
3a	130.5 (s)					
4	114.2 (d)		8.02 (d, *J* = 8.8 Hz, 1H)	C-3a, C-6, C-7a	N-3	H-16, H-17, H-18
5	133.2 (d)		7.85 (m, 1H)	C-3a, C-4, C-7		H-17
6	124.3 (d)		7.52 (m, 1H) [b]	C-4, C-7, C-7a		
7	131.0 (d)		7.98 (d, *J* = 8.0 Hz, 1H)	C-3a, C-5, C-7a	N-8	
7a	135.6 (s)					
8		332.0 (s)				
8a	146.7 (s)					
9	132.7 (d)		7.54 (m, 1H) [b]	C-1, C-2a, C-10	N-8	
10	135.5 (d)		6.94 (d, *J* = 9.6 Hz, 1H)	C-2, C-8a		
11	153.2 (s)					

12	111.4 (d)		7.03 (d, *J* = 7.6 Hz, 1H)	C-11, C-14, C-20a		
13	129.9 (d)		7.49 (m, 1H) [b]	C-11, C-14a		
14	117.7 (d)		7.27 (d, *J* = 8.4 Hz, 1H)	C-12, C-20a	N-15	
14a	141.2(s)					
15		325.8 (s)				
15a	150.6 (s)					
16_{ax}	34.6 (t)		3.93 (dd, *J* = 19.2, 5.9 Hz, 1H)	C-14a, C-15a, C-17, C-19a	N-3, N-15	H-4, H-17, H-18
16_{eq}			3.46 (dd, obscured, 1H) [c]	C-15a, C-17, C-18, C-19a	N-3, N-15	H-4, H-17, 18-OH
17	52.5 (d)		5.40 (m, 1H)	C-2a, C-3a, C-15a, C-18, C-19		H-4, H-5, H-16, H-18, H-19
18	62.8 (d)		4.60 (dd, *J* = 4.4, 3.3 Hz, 1H)	C-16, C-19 a		H-4, H-16, H-17, 18-OH
19	39.7 (d)		4.96 (dd, *J* = 4.4, 2.3 Hz, 1H)	C-1, C-2, C-2a, C-15a, C-17, C-18, C-19a		H-17, 18-OH
19a	151.4 (s)					
20		325.8 (s)				
20a	131.8(s)					
11-OH			10.34 (s, 1H)	C-11, C-12, C-20a		
18-OH			6.18 (d, *J* = 3.3 Hz,1H)	C-17, C-18, C-19		H-16, H-18, H-19

[a] The ^{1}H NMR spectrum was recorded at 500 MHz, the ^{13}C NMR spectrum at 125 MHz, ^{15}N NMR spectrum at 50 MHz. [b] The signals of H-6, H-9, and H-13 overlapped. [c] The signal was obscured by a signal due to water. After addition of D_2O in DMSO-d_6, δ = 3.40 (d, *J* =19.2 Hz).



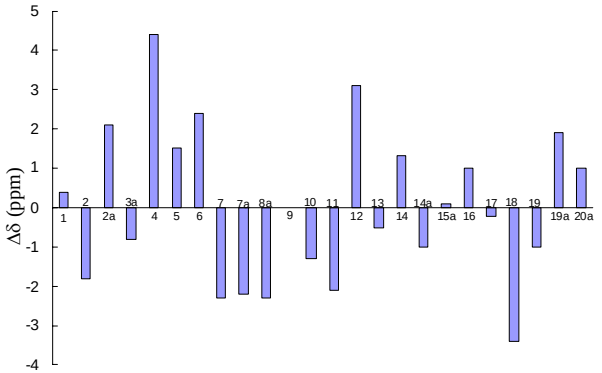
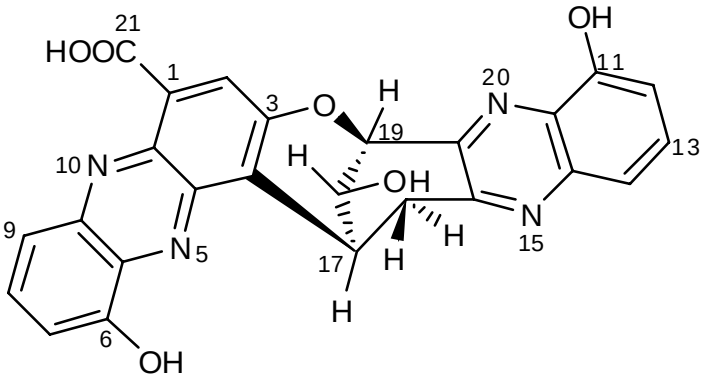


Table S6. The Errors between the Experimental ^{13}C NMR and the Computed Data for Phenazinolin C (**3**)

Position	δ (C_{exp})	Shielding	δ (C_{calcd})	Δδ (C_{error})	Position	δ (C_{exp})	Shielding	δ (C_{calcd})	Δδ (C_{error})
1	178.9	-2.7	178.5	0.4	11	153.2	20.8	155.3	-2.1
2	106.4	68.3	108.2	-1.8	12	111.4	68.2	108.3	3.1
2a	132.3	46.1	130.2	2.1	13	129.9	45.9	130.4	-0.5
3a	130.5	45.0	131.3	-0.8	14	117.7	60.0	116.4	1.3
4	114.2	66.7	109.8	4.4	14a	141.2	34.0	142.2	-1.0
5	133.2	44.6	131.7	1.5	15a	150.6	25.6	150.5	0.1
6	124.3	54.5	121.9	2.4	16	34.6	143.6	33.6	1.0
7	131.0	43.0	133.3	-2.3	17	52.5	124.3	52.7	-0.2
7a	135.6	38.4	137.8	-2.2	18	62.8	110.7	66.2	-3.4
8a	146.7	27.1	149.0	-2.3	19	39.7	136.4	40.7	-1.0
9	132.7	43.6	132.7	0.0	19a	151.4	26.6	149.5	1.9
10	135.5	39.4	136.8	-1.3	20a	131.8	45.5	130.8	1.0



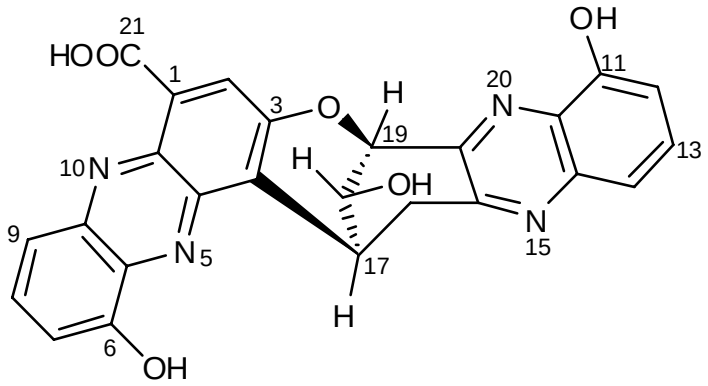
Structure of Phenazinolin D (**4**)

Table S7. 1D & 2D NMR (500 MHz, DMSO-d_6) Data for Phenazinolin D (**4**) [a]

Position	δ_C [ppm]	δ_N [ppm]	δ_H [ppm]	HMBC (^{1}H-^{13}C)	HMBC (^{1}H-^{15}N)	ROESY
1	127.5 (s)					
2	127.8 (d)		7.92 (s, 1H)	C-1, C-3, C-4, C-10a, C-21	N-10	H-17, H-18, H-19
3	151.1 (s)					
4	122.3 (s)					
4a	140.0 (s)					
5-N		308.2 (s)				
5a	135.2 (s)					
6	153.3 (s)					
7	111.6 (d) [b]		7.29 (d, *J* = 8.0 Hz, 1H) [d]	C-5a, C-6, C-8, C-9		6-OH
8	132.5 (d)		7.80 (t, *J* = 8.0 Hz, 1H)	C-5a, C-6, C-9a		
9	118.0 (d) [c]		7.67 (d, *J* = 8.8 Hz, 1H)	C-5a, C-6, C-7	N-10	
9a	139.3 (s)					
10-N		297.0 (s)				
10a	137.0 (s)					
11	153.7 (s)					
12	111.6 (d) [b]		7.08 (d, *J* = 7.3 Hz, 1H)	C-11, C-14, C-20a	N-20	11-OH

13	131.5 (d)		7.58 (t, *J* = 8.0 Hz, 1H)	C-11, C-14a		11-OH
14	117.9 (d) [c]		7.27 (d, *J* = 7.3 Hz, 1H) [d]	C-11, C-12, C-20a	N-15	
14a	142.8(s)					
15-N		324.5 (s)				
15a	152.9 (s)					
16_{ax}	34.6 (t)		3.86 (dd, *J* = 17.5, 5.1 Hz, 1H)	C-4, C-17, C-19a	N-15	
16_{eq}			3.43 (dd, obscured, 1H) [e]	C-4, C-15a, C-17, C-18, C-19a	N-15	
17	30.9 (d)		4.83 (m, 1H)	C-3, C-4, C-18, C-15a		H-2, H-19, 18-OH
18	62.7 (d)		4.77 (m, 1H)			H-2
19	76.1 (d)		5.59 (dd, *J* = 3.3, 1.8 Hz, 1H)	C-3, C-17		H-2, H-17, 18-OH
19a	146.4 (s)					
20-N		325.8 (s)				
20a	132.7 (s)					
21	165.3 (s)					
6-OH			10.68 (s, 1H)			H-7
11-OH			10.54 (s, 1H)	C-11, C-12, C-20a		H-12, H-13
18-OH			6.19 (d, *J* = 2.9 Hz, 1H)	C-17		H-17, H-19
21-OH			14.75 (br s, 1H)			

[a] The ^{1}H NMR spectrum was recorded at 500 MHz, the ^{13}C NMR spectrum at 125 MHz, ^{15}N NMR spectrum at 50 MHz. [b] [c] The two sets of signal were interchangeable in terms of their assignments. [d] The signals of H-7 and H-14 overlapped. [e] The signal was obscured by a signal due to water. After addition of D_2O in DMSO-d_6, δ = 3.14 (d, *J* =17.5 Hz).



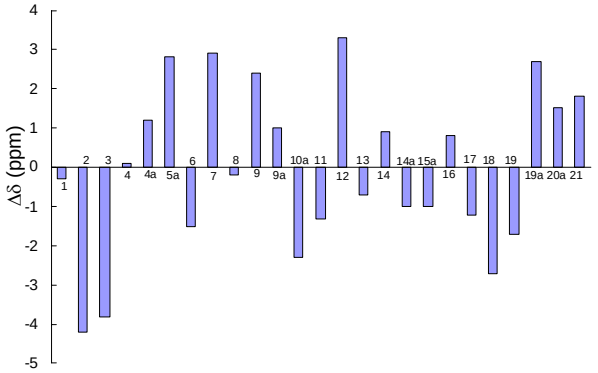
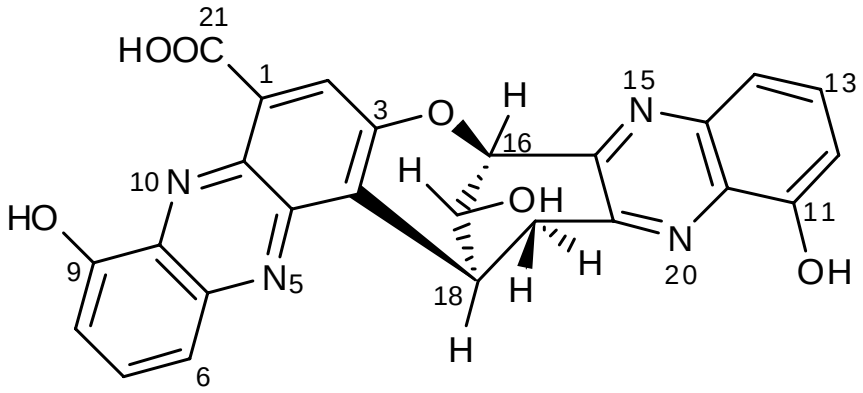


Table S8. The Errors between the Experimental ^{13}C NMR and the Computed Data for Phenazinolin D (**4**)

Position	δ (C exp)	Shielding	δ (C calcd)	Δδ (C error)	Position	δ (C exp)	Shielding	δ (C calcd)	Δδ (C error)
1	127.5	48.3	127.8	-0.3	12	111.6	68	108.3	3.3
2	127.8	44.1	132.0	-4.2	13	131.5	43.9	132.2	-0.7
3	151.1	21	154.9	-3.8	14	117.9	59.2	117.0	0.9
4	122.3	54	122.2	0.1	14a	142.8	32.2	143.8	-1.0
4a	140.0	37.3	138.8	1.2	15a	152.9	22	153.9	-1.0
5a	135.2	43.7	132.4	2.8	16	34.6	143.1	33.8	0.8
6	153.3	21.1	154.8	-1.5	17	30.9	144.8	32.1	-1.2
7	111.6	67.6	108.7	2.9	18	62.7	111.2	65.4	-2.7
8	132.5	43.4	132.7	-0.2	19	76.1	98.7	77.8	-1.7
9	118.0	60.6	115.6	2.4	19a	146.4	32.3	143.7	2.7
9a	139.3	37.8	138.3	1.0	20a	132.7	44.9	131.2	1.5
10a	137.0	36.8	139.3	-2.3	21	165.3	12.4	163.5	1.8
11	153.7	20.9	155.0	-1.3					



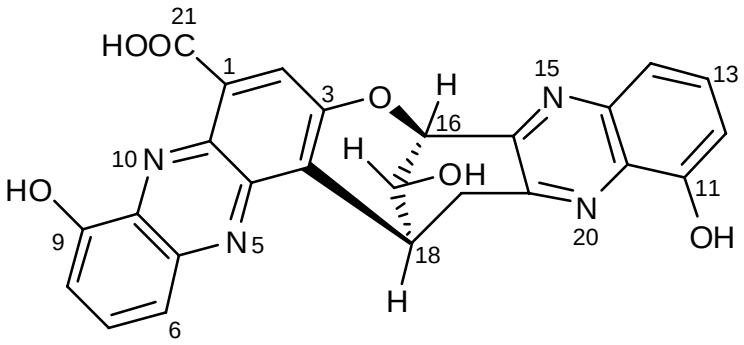
Structure of Phenazinolin E (**5**)

Table S9. 1D & 2D NMR (500 MHz, DMSO-d_6) Data for Phenazinolin E (**5**) [a]

Position	δ_C [ppm]	δ_N [ppm]	δ_H [ppm]	HMBC (^{1}H-^{13}C)	HMBC (^{1}H-^{15}N)	ROESY
1	127.1 (s)					
2	127.9 (d)		7.90 (s, 1H)	C-1, C-3, C-4, C-10a, C-21		H-16, H-17, H-18
3	151.0 (s)					
4	122.4 (s)					
4a	140.0 (s)					
5-N		307.8 (s)				
5a	142.7 (s)					
6	117.8 (d) [b]		7.28 (d, *J* = 7.9 Hz, 1H) [d]	C-7, C-8, C-9, C-9a	N-5	
7	131.4 (d)		7.57 (t, *J* = 7.9 Hz, 1H)	C-5a, C-8, C-9, C-9a		
8	111.6 (d) [c]		7.08 (d, *J* = 7.3 Hz, 1H)	C-5a, C-6, C-9, C-9a	N-10	9-OH
9	153.6 (s)					
9a	132.7 (s)					
10-N		325.8 (s)				
10a	136.9 (s)					
11	153.2 (s)					

12	111.6 (d) [c]		7.27 (d, *J* = 7.3 Hz, 1H) [d]	C-11, C-13, C-14, C-20a	N-20	11-OH
13	132.5 (d)		7.77 (t, *J* = 8.6 Hz, 1H)	C-11, C-12, C-14, C-14a, C-20a		11-OH
14	117.8 (d) [b]		7.62 (d, *J* = 8.6 Hz, 1H)	C-11, C-12, C-13, C-20a	N-15	
14a	139.1 (s)					
15-N		296.9 (s)				
15a	152.8 (s)					
16	76.0 (d)		5.60 (dd, *J* = 3.4, 2.1 Hz, 1H)	C-3, C-15a, C-17, C-18, C-19a		H-2, H-18, 17-OH
17	62.6 (d)		4.78 (m, 1H)	C-15a, C-19		H-2, H-19_{ax}
18	30.9 (d)		4.82 (m, 1H)	C-4, C-16, C-19, C-19a		H-2, H-19_{ax}, H-16
19_{ax}	34.5 (t)		3.86 (dd, *J* = 17.4, 5.2 Hz, 1H)	C-4, C-15a, C-18, C-19a	N-20	H-17, H-18
19_{eq}			3.44 (dd, obscured, 1H) [e]	C-4, C-15a, C-17, C-18, C-19a	N-20	
19a	146.4 (s)					
20-N		324.5 (s)				
20a	135.1 (s)					
21	165.1 (s)					
9-OH			10.48 (s, 1H)	C-8, C-9, C-9a		C-8
11-OH			10.62 (s, 1H)	C-11, C-12, C-20a		H-12, H-13
17-OH			6.16 (d, *J* = 2.4 Hz, 1H)	C-16, C-18		H-16
21-OH			14.71 (br s, 1H)			

[a] The ^{1}H NMR spectrum was recorded at 500 MHz, the ^{13}C NMR spectrum at 125 MHz, ^{15}N NMR spectrum at 50 MHz. [b] [c] The two sets of signal were interchangeable in terms of their assignments. [d] The signals of H-8 and H-14 overlapped. [e] The signal is obscured by a signal due to water. After addition of D_2O in DMSO-d_6, δ = 3.22 (d, *J* =17.4 Hz).



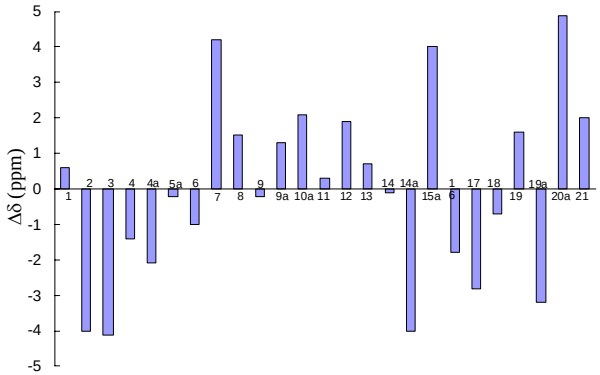
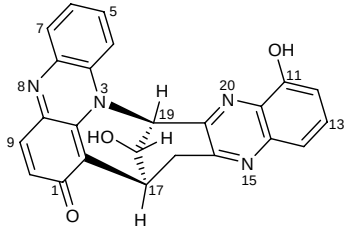
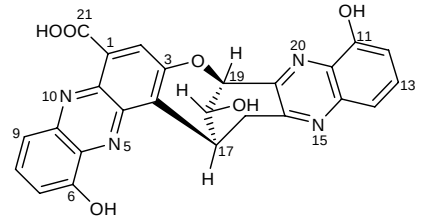
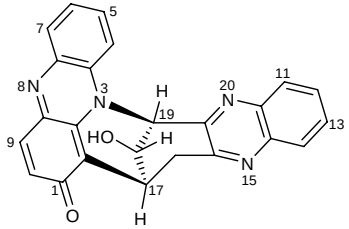
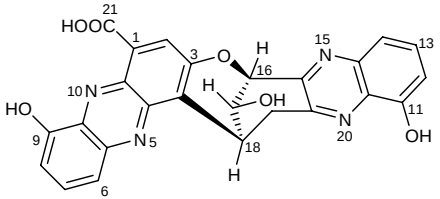
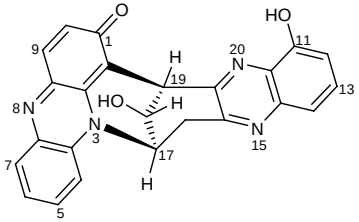


Table S10. The Errors between the Experimental ^{13}C NMR and the Computed Data for Phenazinolin E (**5**)

Position	δ (C $_{exp}$)	Shielding	δ (C $_{calcd}$)	Δδ (C $_{error}$)	Position	δ (C $_{exp}$)	Shielding	δ (C $_{calcd}$)	Δδ (C $_{error}$)
1	127.1	49.4	126.5	0.6	12	111.6	67.7	109.7	1.9
2	127.9	43.8	131.9	-4.0	13	132.5	43.5	131.8	0.7
3	151.0	20.8	155.1	-4.1	14	117.8	58.6	117.9	-0.1
4	122.4	51.5	123.8	-1.4	14a	139.1	32.5	143.1	-4.0
4a	140.0	33.4	142.1	-2.1	15a	152.8	21.3	148.8	4.0
5a	142.7	31.9	142.9	-0.2	16	76.0	98.4	77.8	-1.8
6	117.8	56.8	118.8	-1.0	17	62.6	110.7	65.4	-2.8
7	131.4	44.0	127.2	4.2	18	30.9	145.2	31.6	-0.7
8	111.6	65.6	110.1	1.5	19	34.5	142.9	32.9	1.6
9	153.6	20.9	153.8	-0.2	19a	146.4	32	149.6	-3.2
9a	132.7	44.9	131.4	1.3	20a	135.1	48.5	130.2	4.9
10a	136.9	40.8	134.8	2.1	21	165.1	12.3	163.1	2.0
11	153.2	22.7	152.9	0.3					

Table S11. Experimental and Computed Optical Rotation (OR) of Phenazinolins A–E (**1**–**5**)

Compounds	Structure	OR	Compounds	Structure	OR
Phenazinolin A (**1**)		– 378 [a] +331 (low) [b] +339 (hi) [c]	Phenazinolin D (**4**)		– 1559 [a] +1314 (low) [b] +1314 (hi) [c]
Phenazinolin B (**2**)		– 259 [a] +226 (low) [b] +216 (hi) [c]	Phenazinolin E (**5**)		– 1155 [a] +969 (low) [b] +971 (hi) [c]
Phenazinolin C (**3**)		– 1288 [a] +1091 (low) [b] +1010 (hi) [c]			

[a] Experimental optical rotation (OR). [b] B3LYP/6-31G(d)-optimized geometries were used in OR computations. [c] B3LYP/6-31+G(d,p)-optimized geometries were used in OR computations.

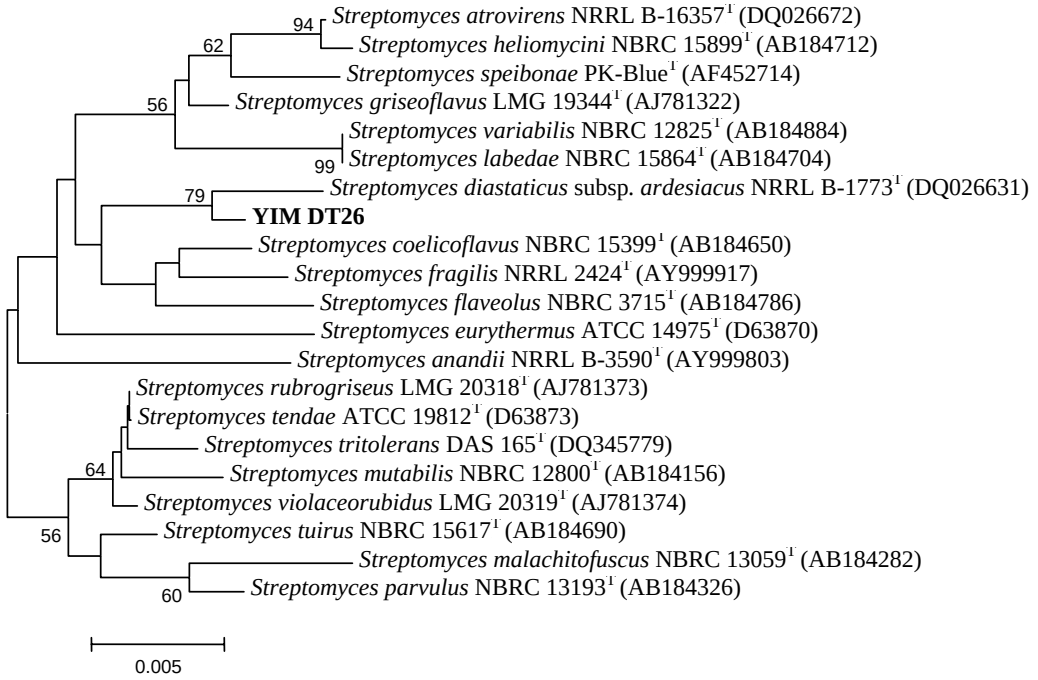


Fig. S1. Phylogenetic Analysis of Strain YIM DT26 [a]

[a] The neighbour-joining tree based on 16S rDNA sequences, showing the phylogenetic relationship of strain YIM DT26 with recognized members of the genus *Streptomyces* and the type strain *Streptomyces diastaticus*. Bar, 2 nucleotide substitution per 1000 nucleotides of 16S rDNA sequence. Phylogenetic tree was reconstructed using the neighbor-joining method of N. Saitou and M. Nei (1987) from K_{nuc} values (M. Kimura, 1980; 1983) by Mega 4.0. The topology of the neighbor-joining phylogenetic tree was evaluated by using the bootstrap resampling method of J. Felsenstein (1985) with 1000 replicates.
(J. Felsenstein, Confidence limits on phylogenies: an approach using the bootstrap. *Evolution* **1985**, *39*, 783 – 791.
M. Kimura, A simple method for estimating evolutionary rates of base substitutions through comparative studies of nucleotide sequences. *J. Mol. Evol.* 1980, **16**, 111 – 120.
M. Kimura, *The neutral theory of molecular evolution*, Cambridge University Press, Cambridge, **1983**.
N. Saitou, M. Nei, The neighbor-joining method: a new method for reconstructing phylogenetic trees. *Mol. Biol. Evol*. **1987**, *4*, 406 – 425.)

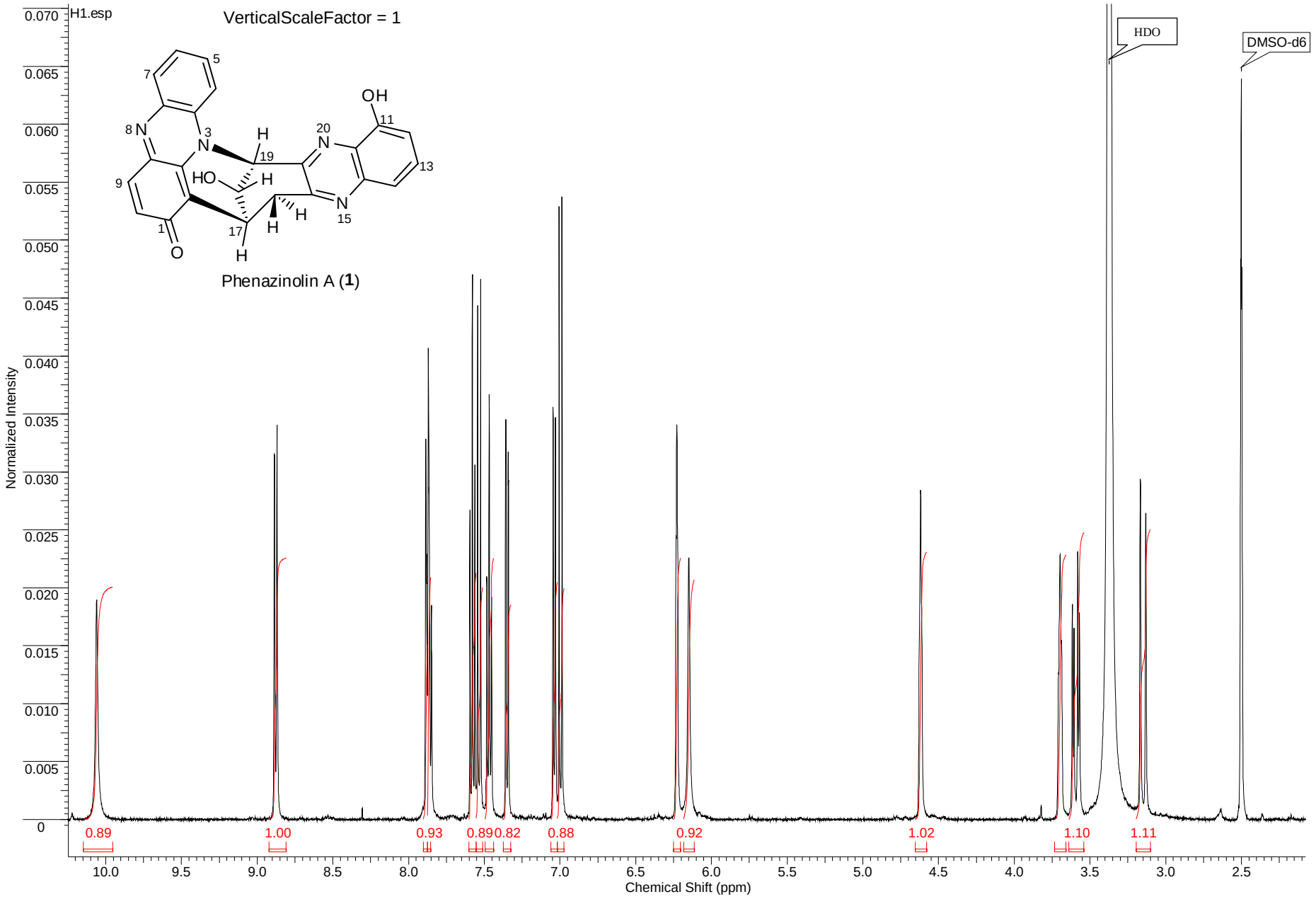
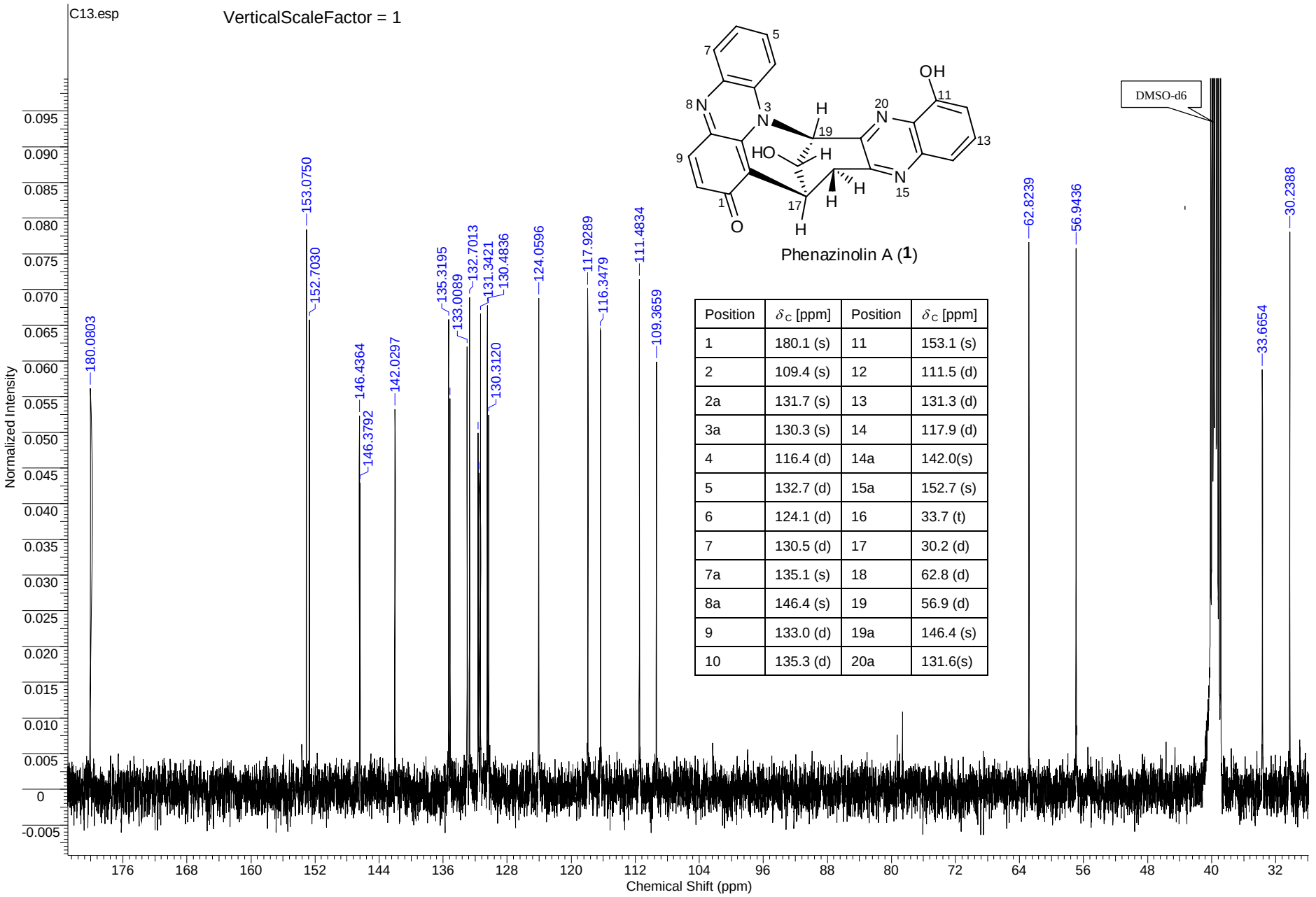


Fig. S2. ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin A (**1**)



Phenazinolin A (**1**)

Position	δ_C [ppm]	Position	δ_C [ppm]
1	180.1 (s)	11	153.1 (s)
2	109.4 (s)	12	111.5 (d)
2a	131.7 (s)	13	131.3 (d)
3a	130.3 (s)	14	117.9 (d)
4	116.4 (d)	14a	142.0(s)
5	132.7 (d)	15a	152.7 (s)
6	124.1 (d)	16	33.7 (t)
7	130.5 (d)	17	30.2 (d)
7a	135.1 (s)	18	62.8 (d)
8a	146.4 (s)	19	56.9 (d)
9	133.0 (d)	19a	146.4 (s)
10	135.3 (d)	20a	131.6(s)

Fig. S3. ^{13}C NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin A (**1**)

HSQC.esp

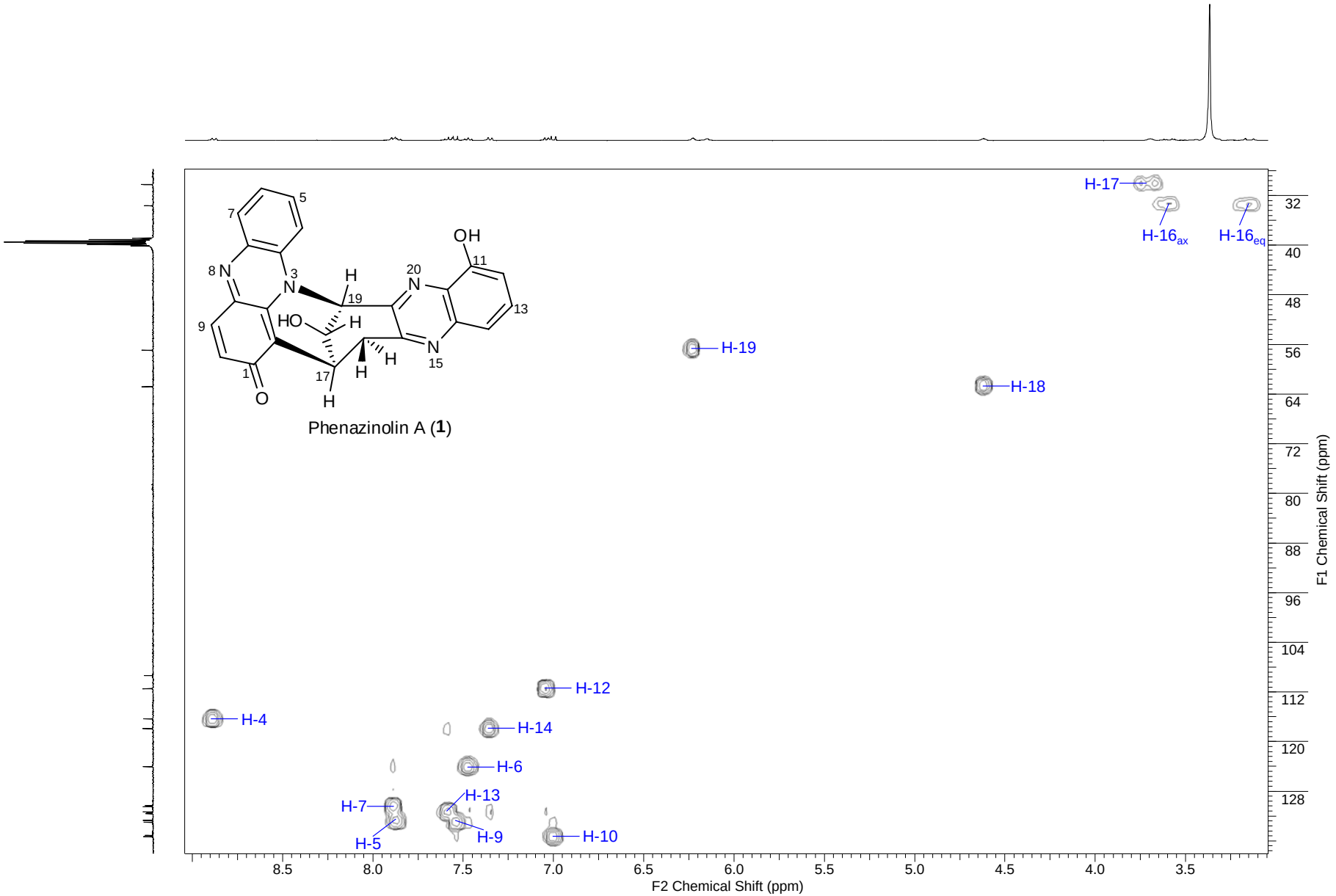


Fig. S4. HSQC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin A (**1**)

COSY.esp

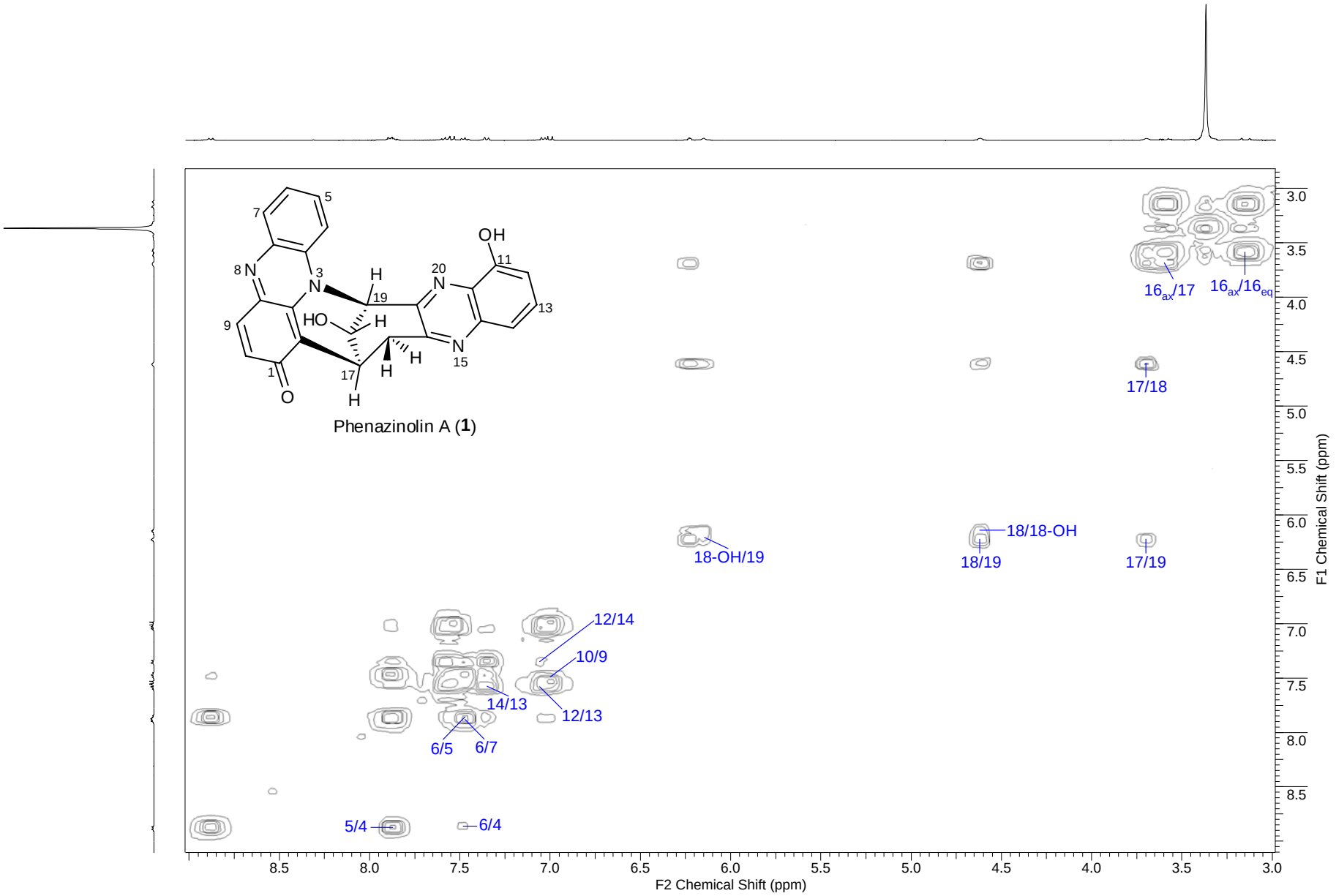


Fig. S5. ^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin A (**1**)

HMQC-TOCSY.esp

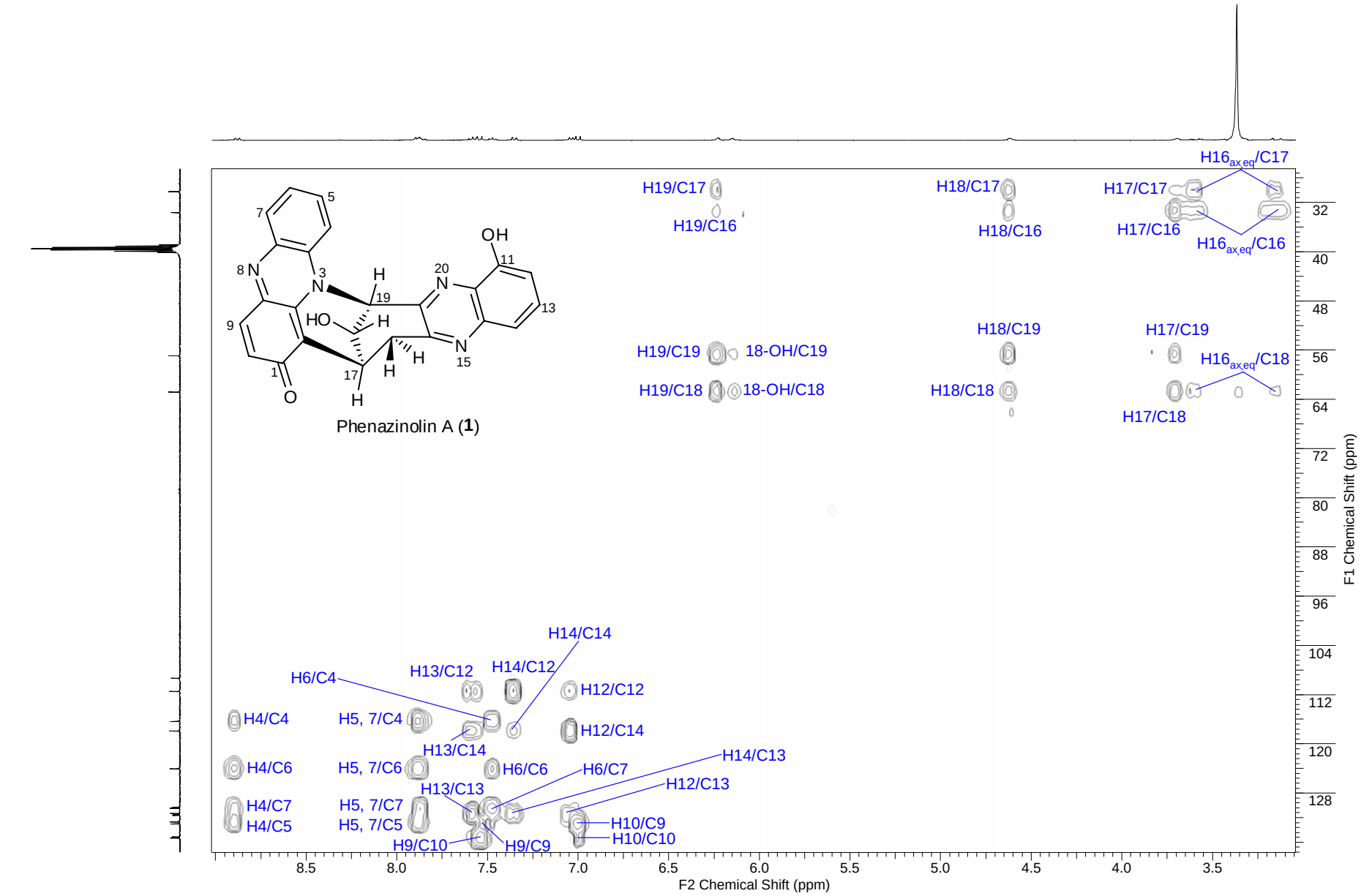


Fig. S6. HMQC-TOCSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin A (**1**)

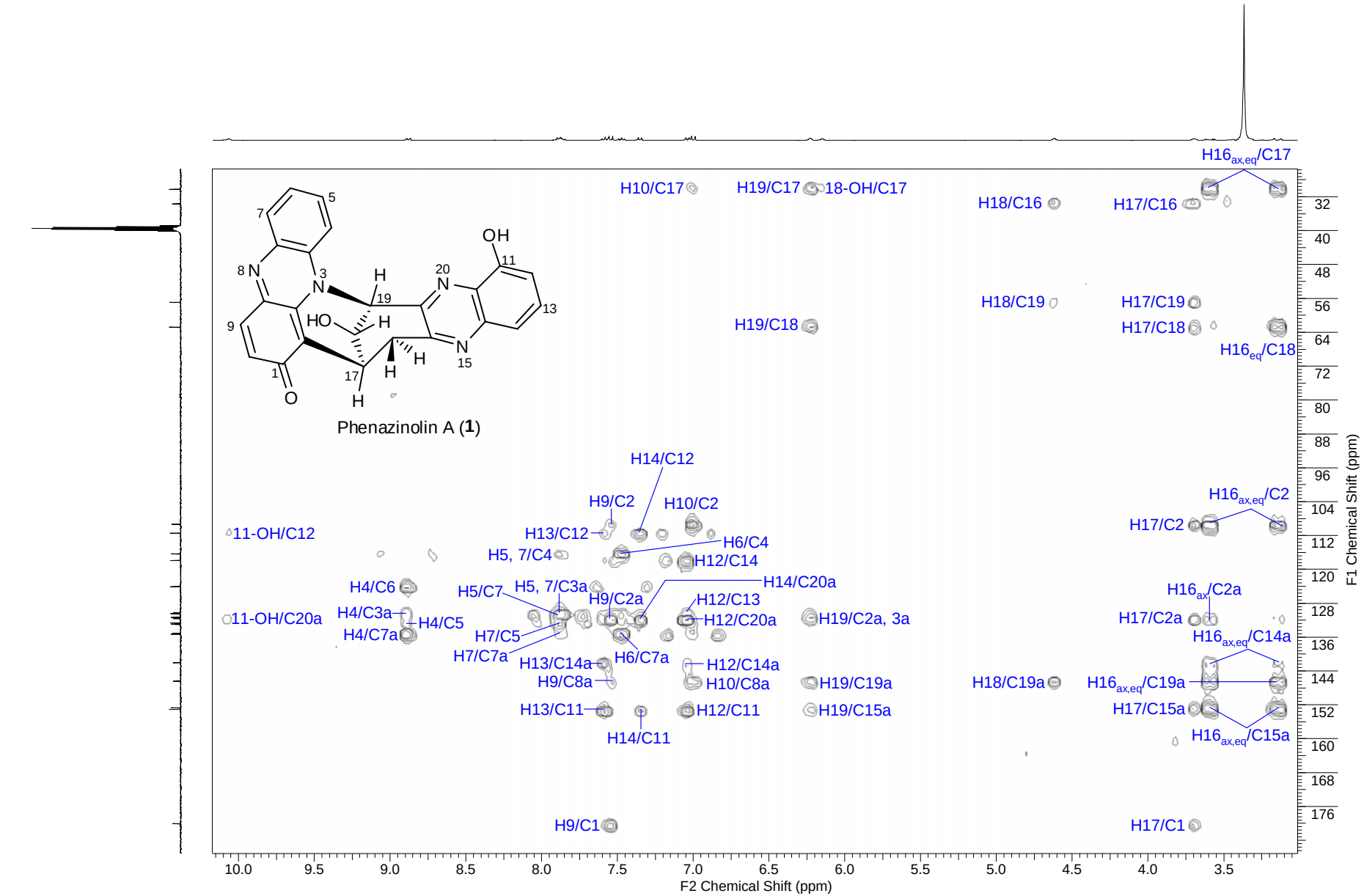


Fig. S7. ^{1}H-^{13}C HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin A (**1**)

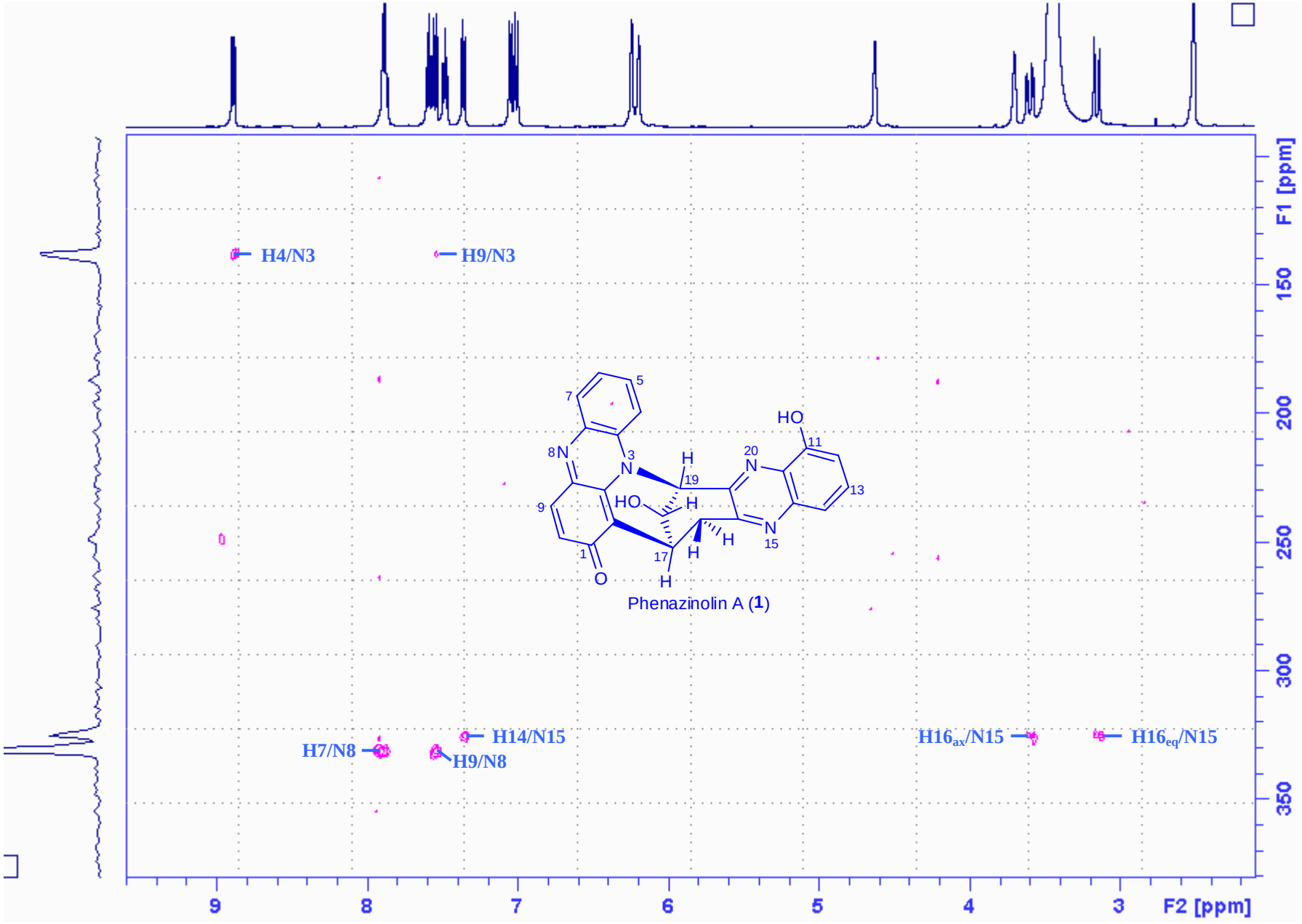


Fig. S8. ^{1}H-^{15}N HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin A (**1**)

ROESY.esp

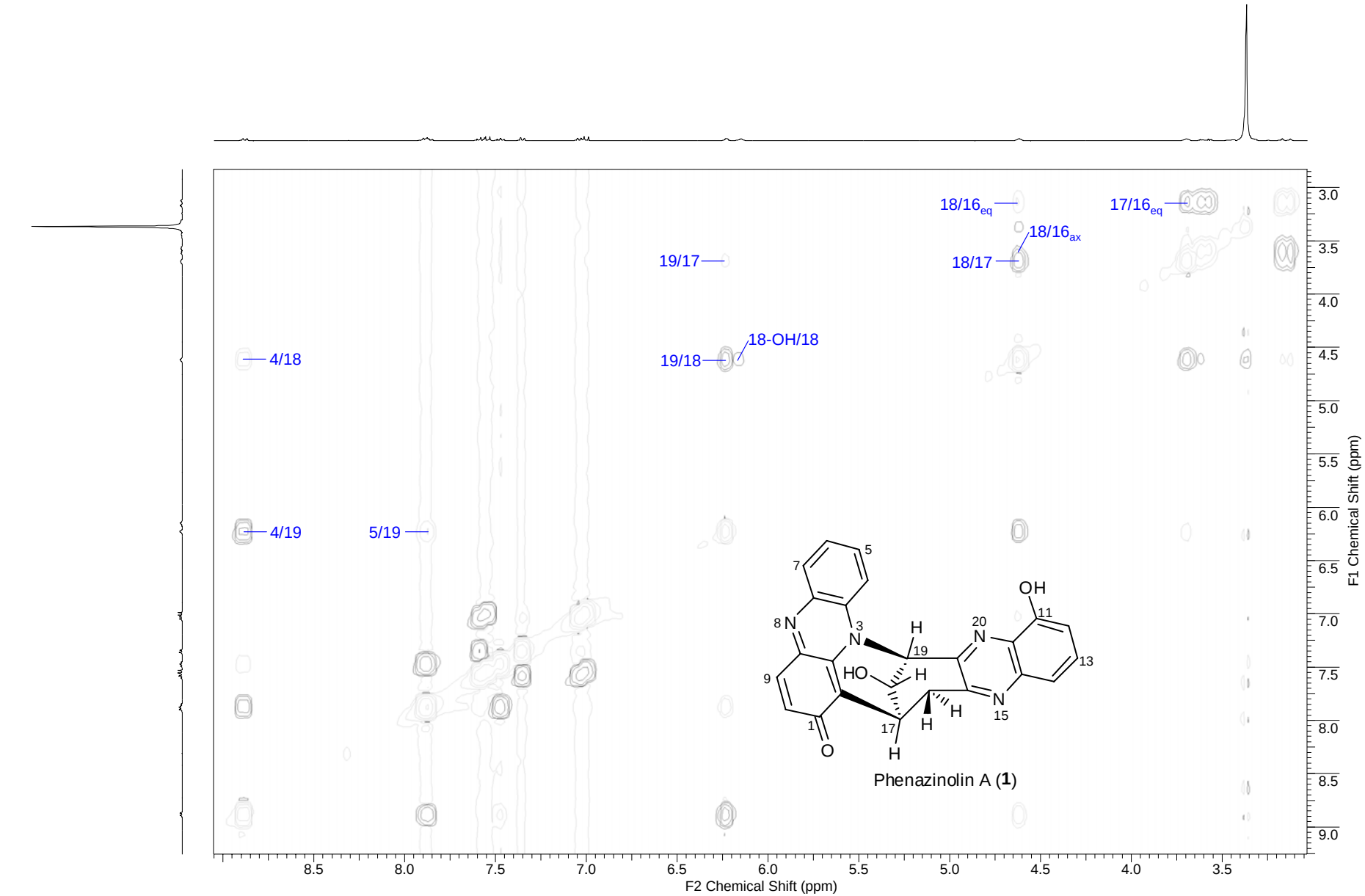


Fig. S9. ROESY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin A (**1**)

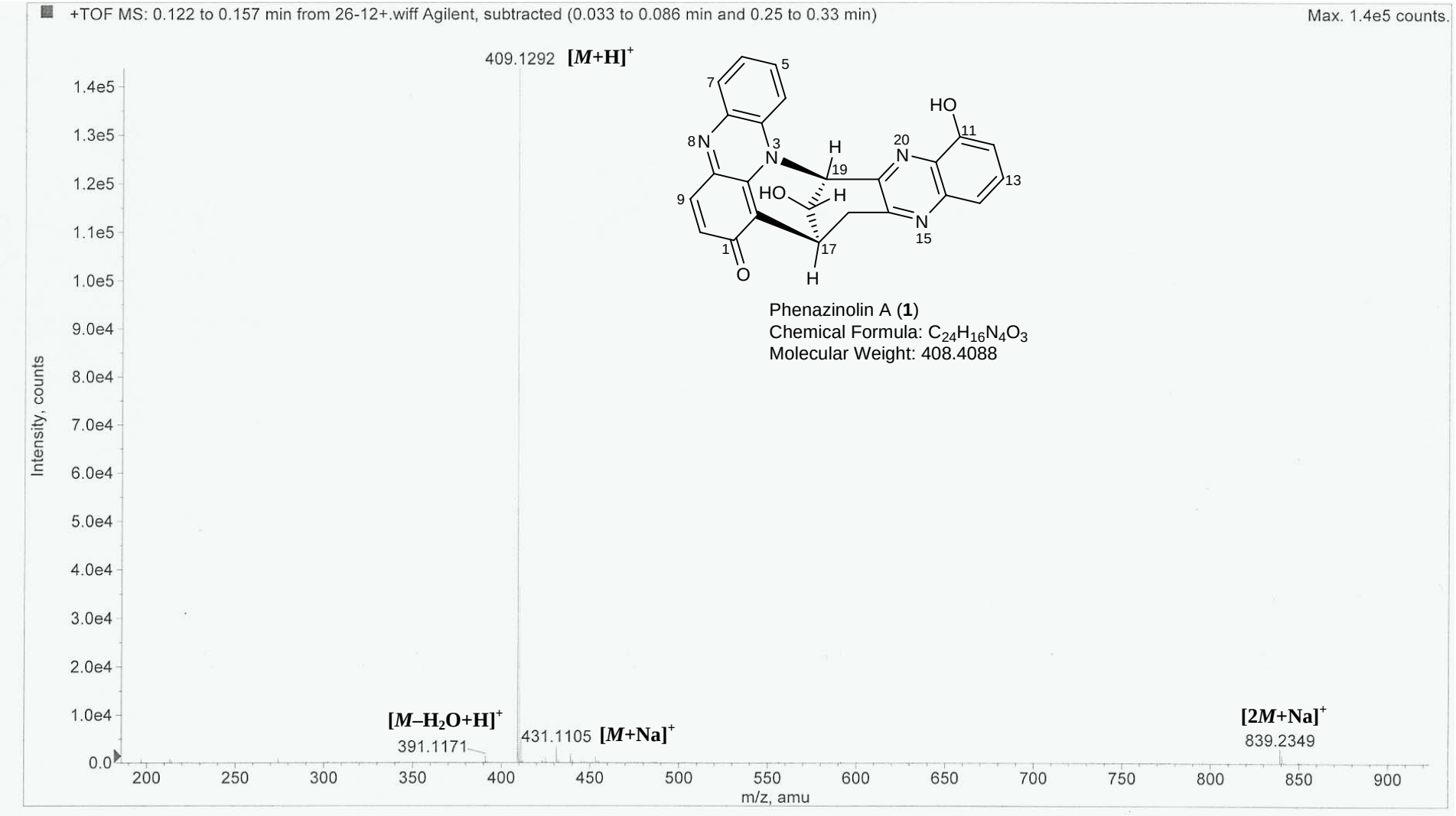


Fig. S10. HR-ESIMS(+) Spectrum of Phenazinolin A (**1**)

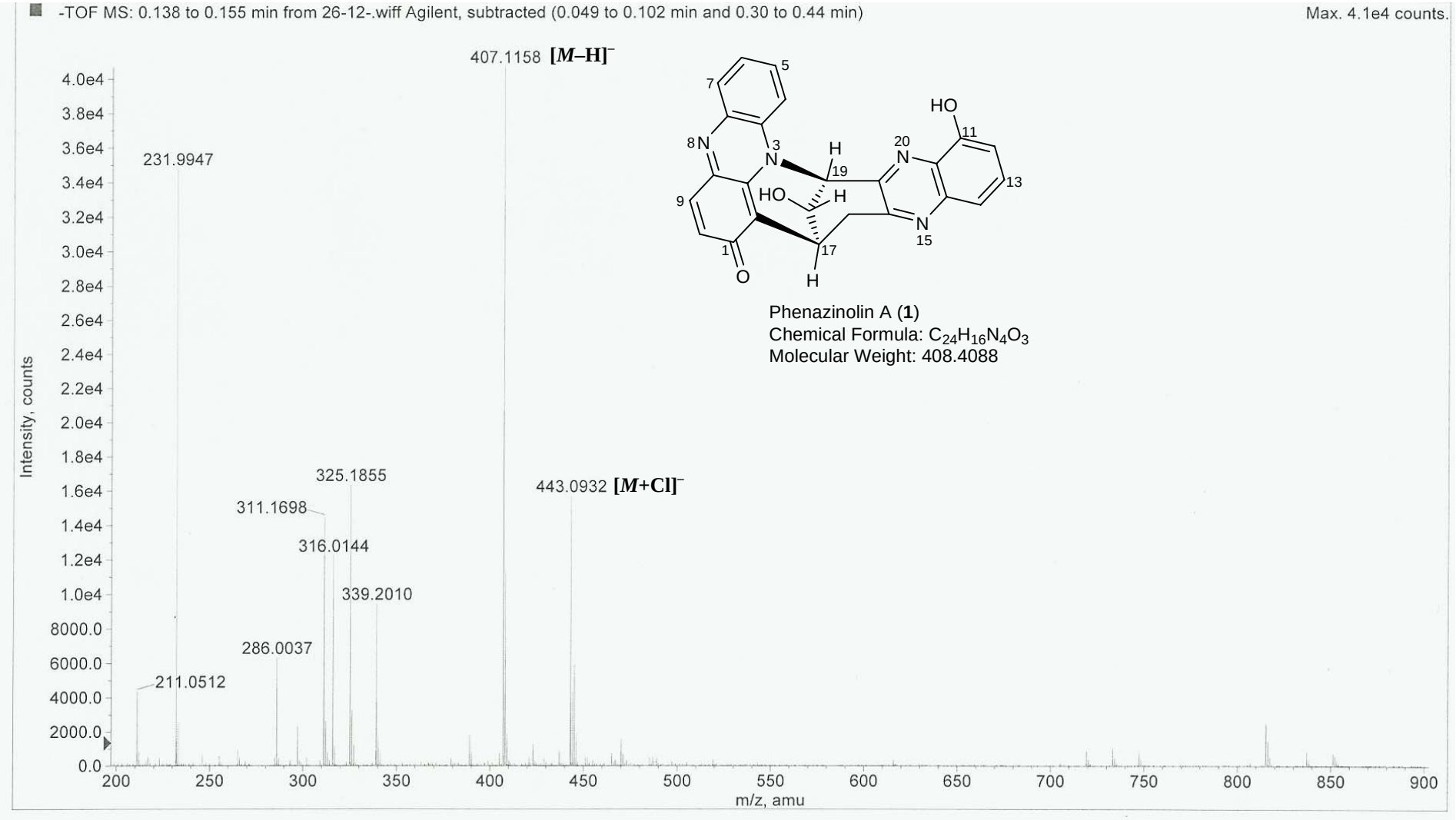
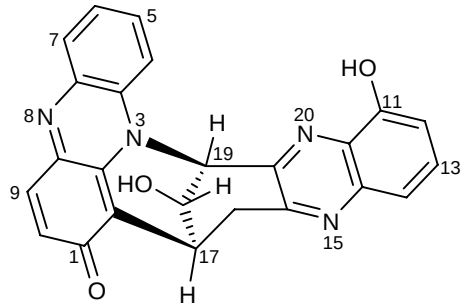


Fig. S11. HR-ESIMS(–) Spectrum of Phenazinolin A (**1**)

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
1	C10 H22 N6 O10 Na	409.1289	0.2375	0.5806	2.5
2	C24 H17 N4 O3	409.1295	-0.3170	-0.7749	18.5
3	C9 H23 N5 O13	409.1286	0.5123	1.2521	1.0
4	C25 H16 N5 Na	409.1297	-0.5917	-1.4464	20.0
5	C24 H20 N O4 Na	409.1284	0.7455	1.8221	15.0
6	C11 H25 N2 O14	409.1300	-0.8303	-2.0296	0.5
7	C23 H21 O7	409.1281	1.0202	2.4937	13.5
8	C12 H24 N3 O11 Na	409.1303	-1.1051	-2.7012	2.0
9	C26 H19 N O4	409.1308	-1.6597	-4.0567	18.0
10	C27 H18 N2 O Na	409.1311	-1.9344	-4.7283	19.5



Phenazinolin A (**1**)
Chemical Formula: $C_{24}H_{16}N_4O_3$
Molecular Weight: 408.4088

Fig. S12. HR-ESIMS(+) Data for Phenazinolin A (**1**)

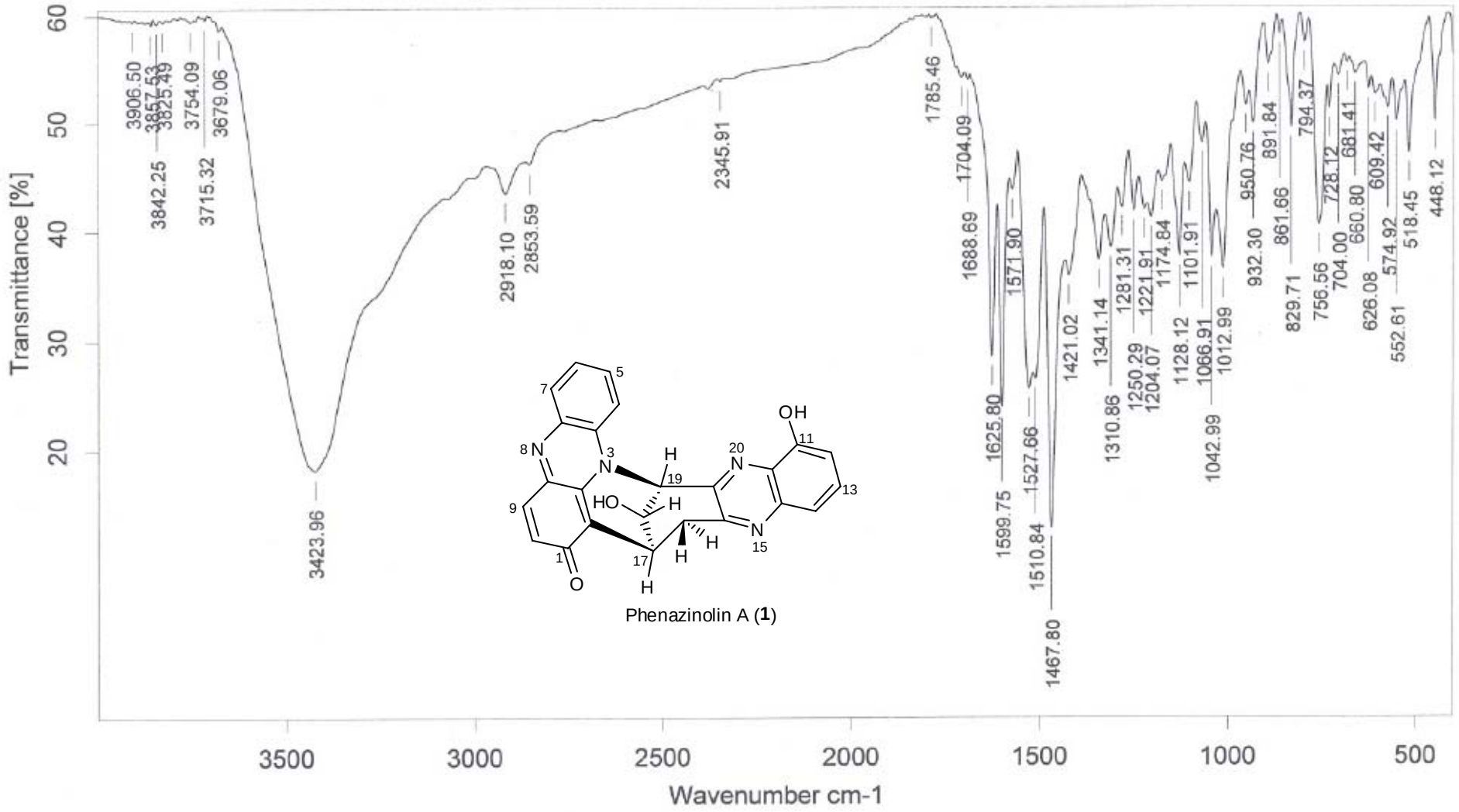


Fig. S13. IR Spectrum of Phenazinolin A (**1**)

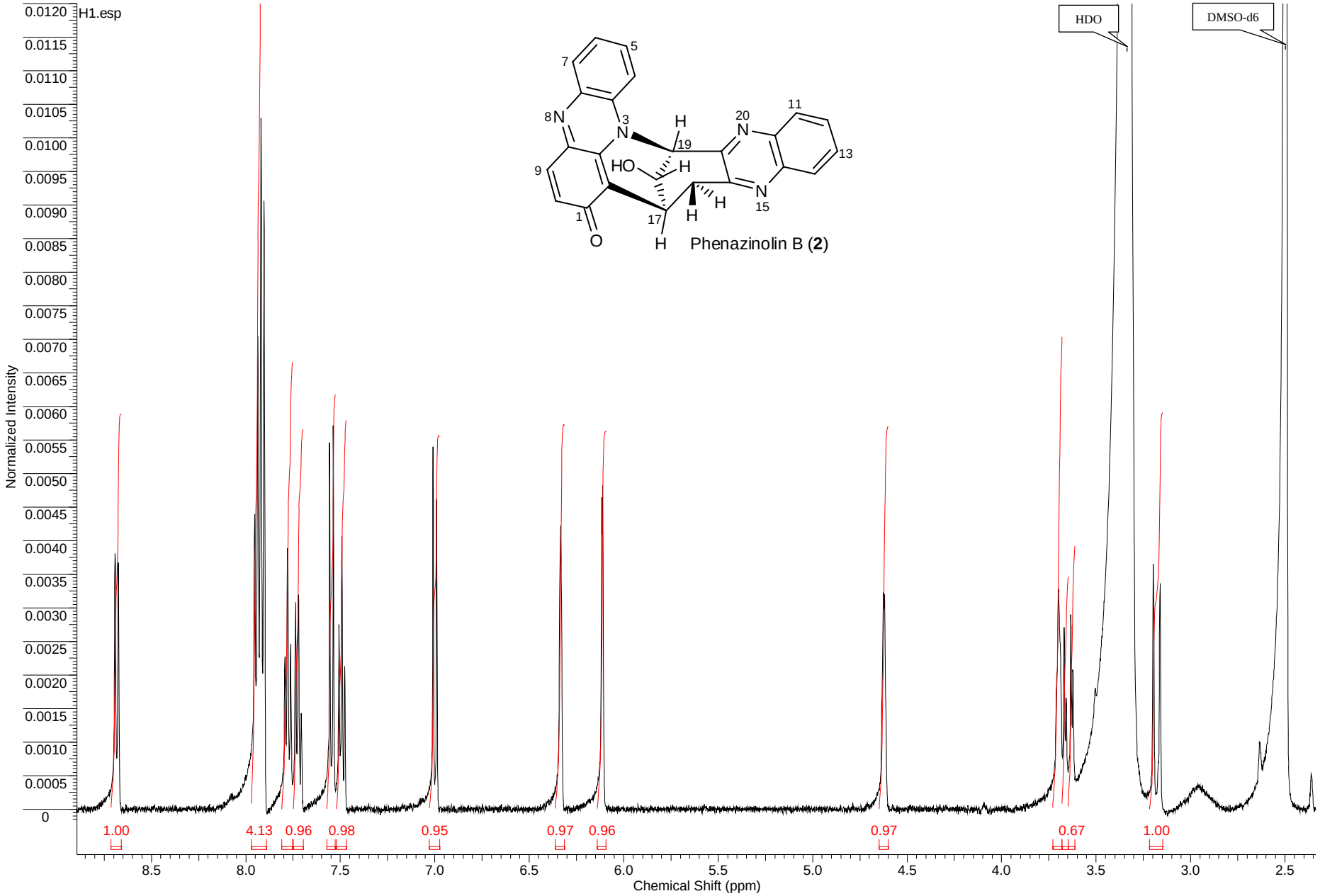
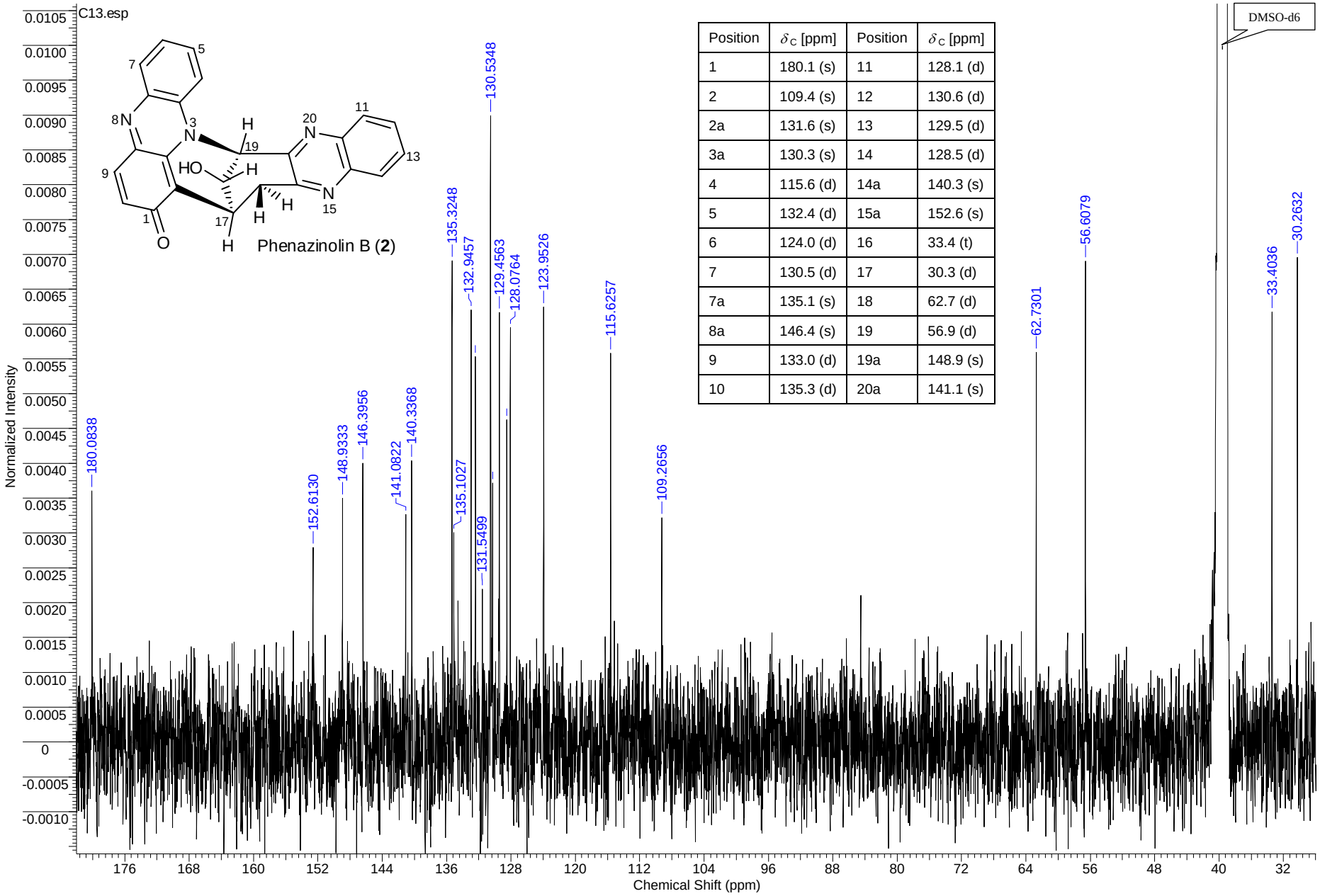


Fig. S14. ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin B (**2**)



Position	δ_C [ppm]	Position	δ_C [ppm]
1	180.1 (s)	11	128.1 (d)
2	109.4 (s)	12	130.6 (d)
2a	131.6 (s)	13	129.5 (d)
3a	130.3 (s)	14	128.5 (d)
4	115.6 (d)	14a	140.3 (s)
5	132.4 (d)	15a	152.6 (s)
6	124.0 (d)	16	33.4 (t)
7	130.5 (d)	17	30.3 (d)
7a	135.1 (s)	18	62.7 (d)
8a	146.4 (s)	19	56.9 (d)
9	133.0 (d)	19a	148.9 (s)
10	135.3 (d)	20a	141.1 (s)

Fig. S15. ^{13}C NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin B (2)

HMQC.esp

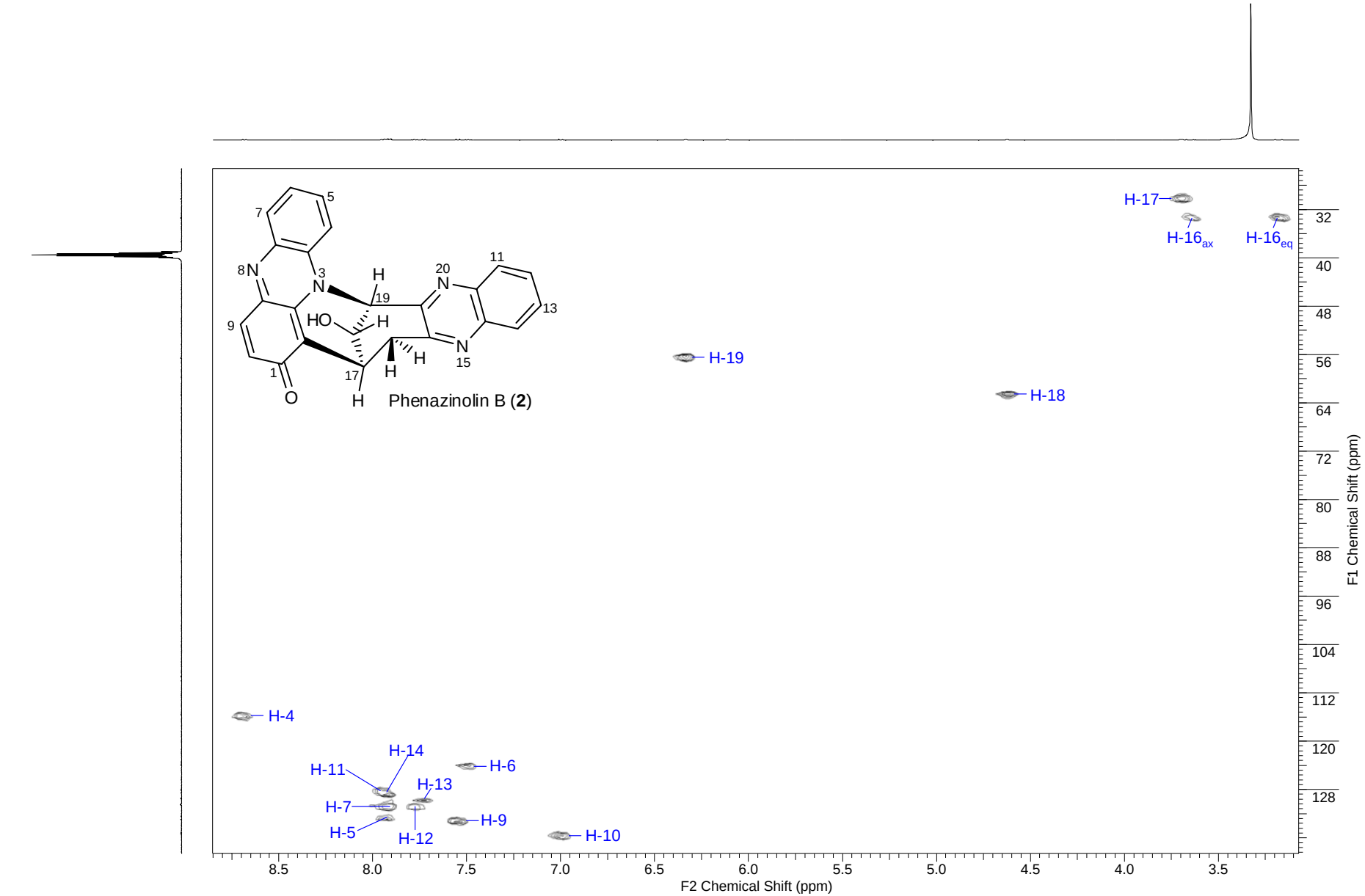


Fig. S16. HMQC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin B (**2**)

COSY.esp

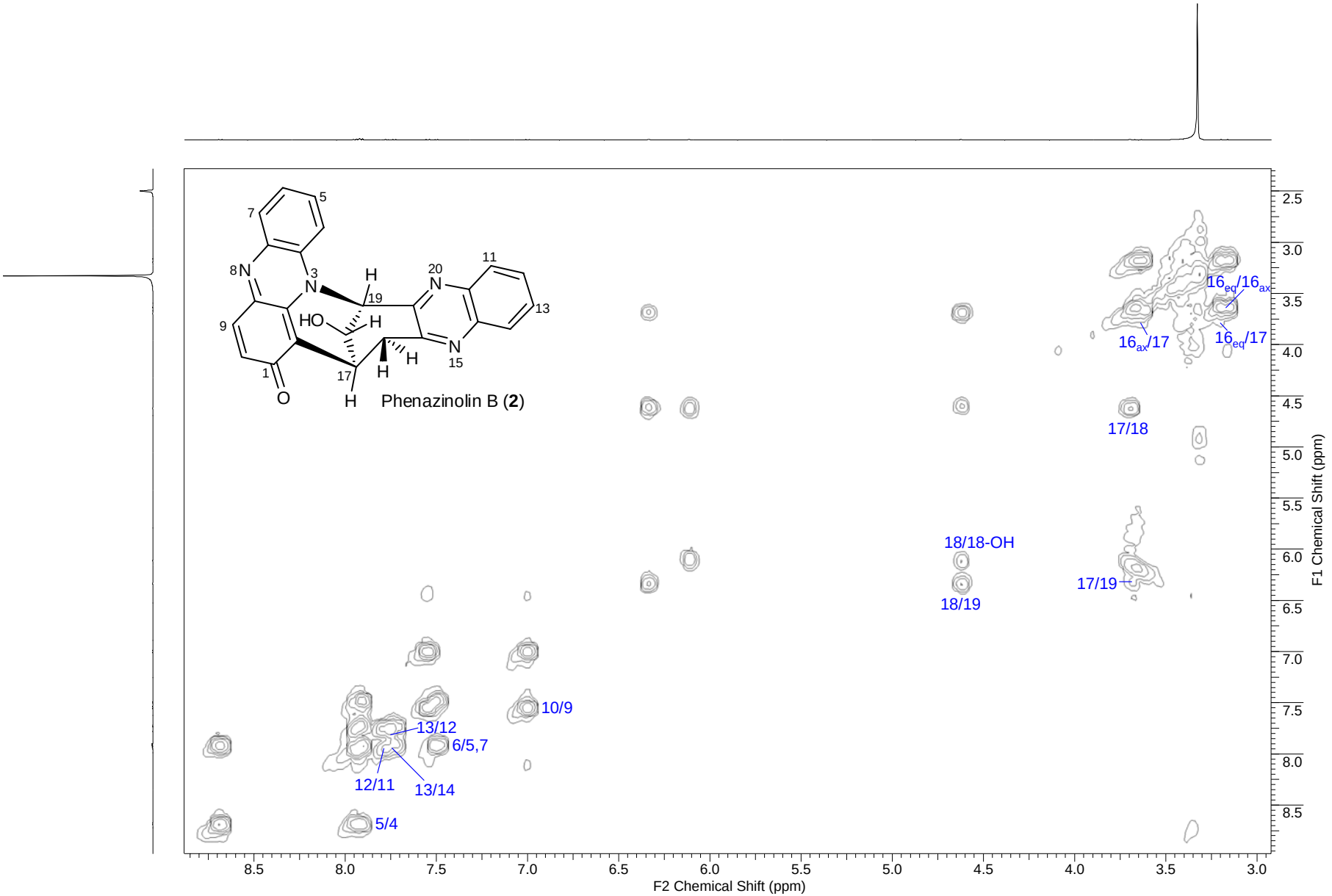


Fig. S17. ^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin B (**2**)

HMBC.esp

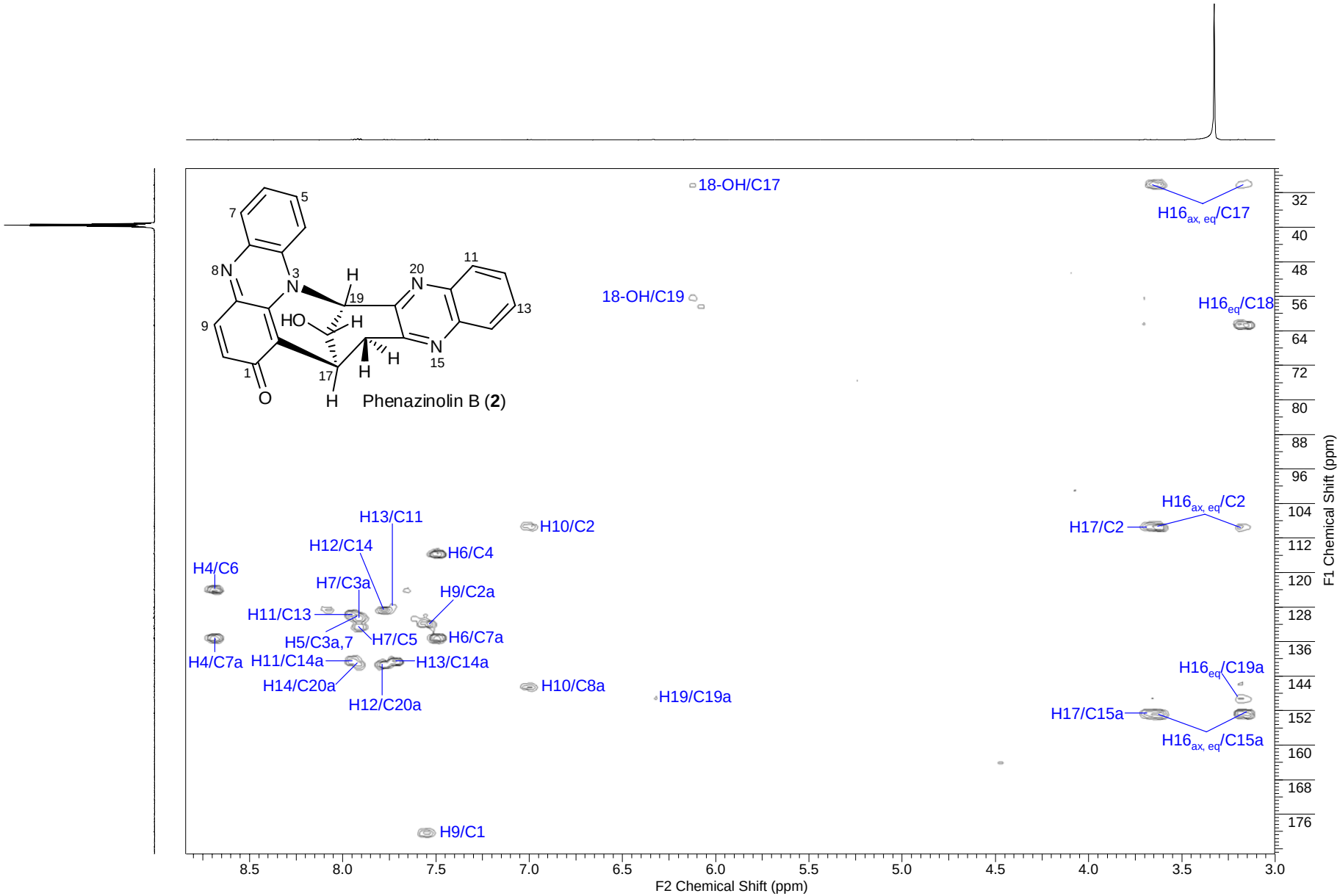


Fig. S18. ^{1}H-^{13}C HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin B (**2**)

ROESY.esp

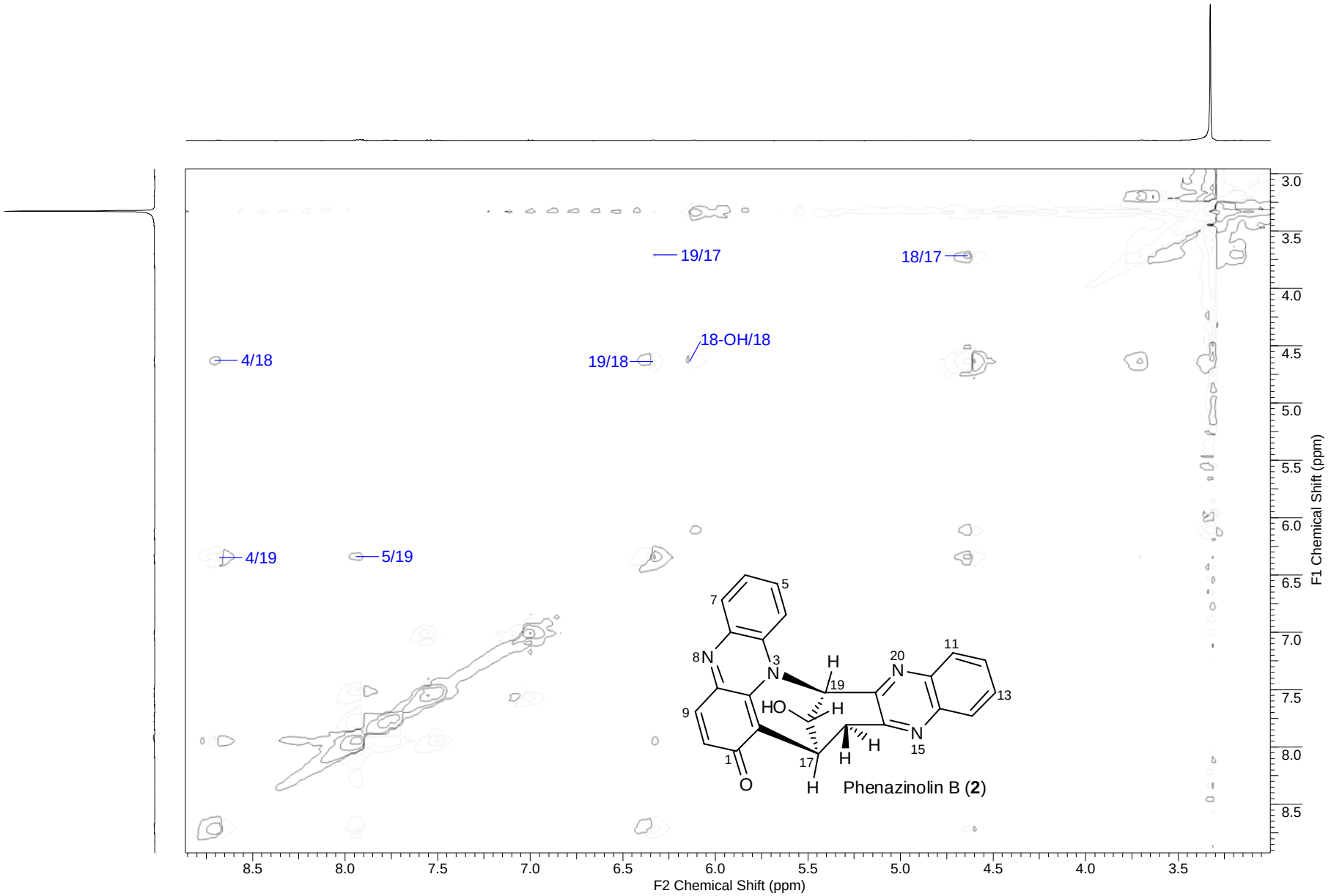


Fig. S19. ROESY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin B (**2**)

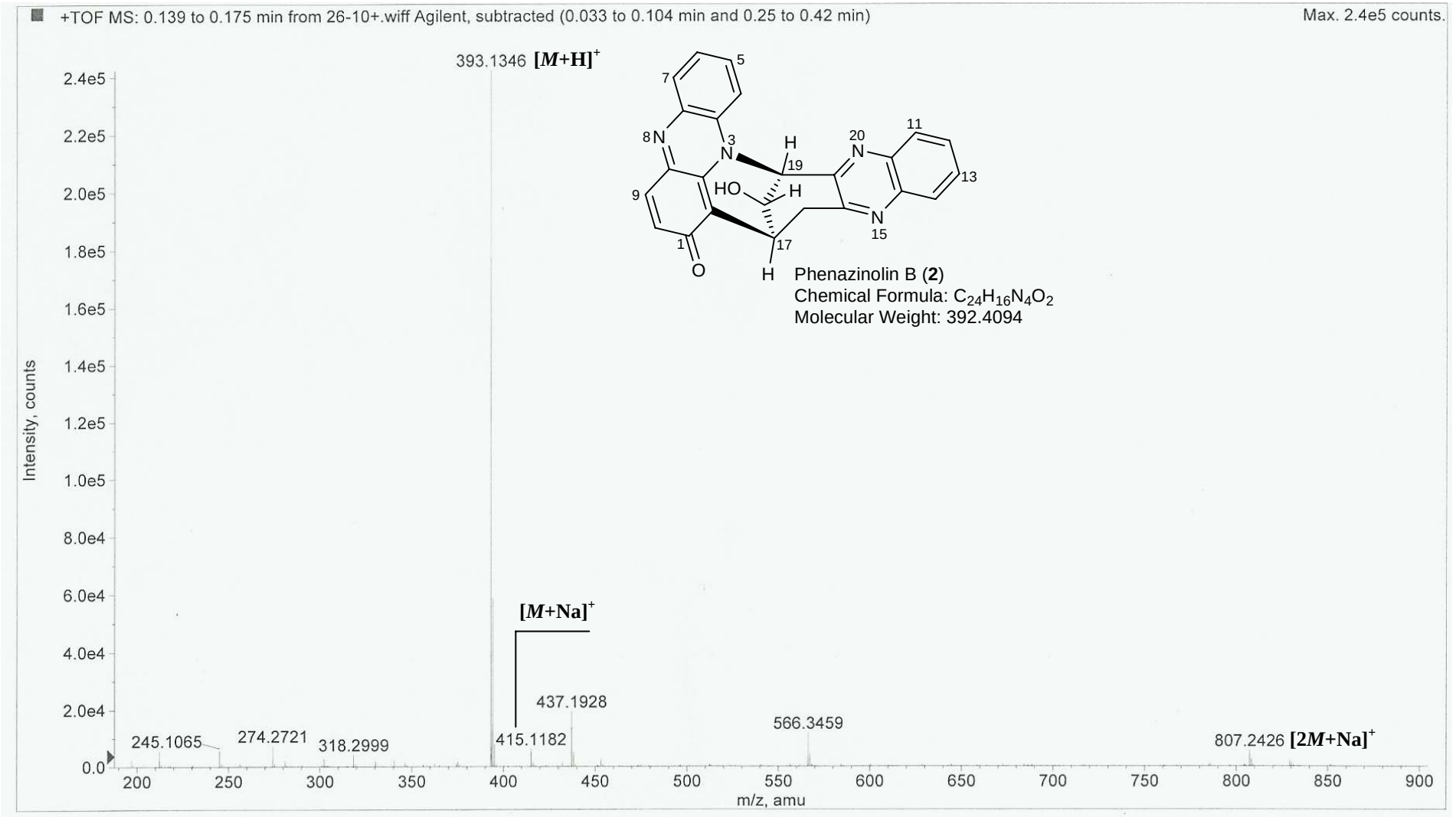


Fig. S20. HR-ESIMS(+) Spectrum of Phenazinolin B (**2**)

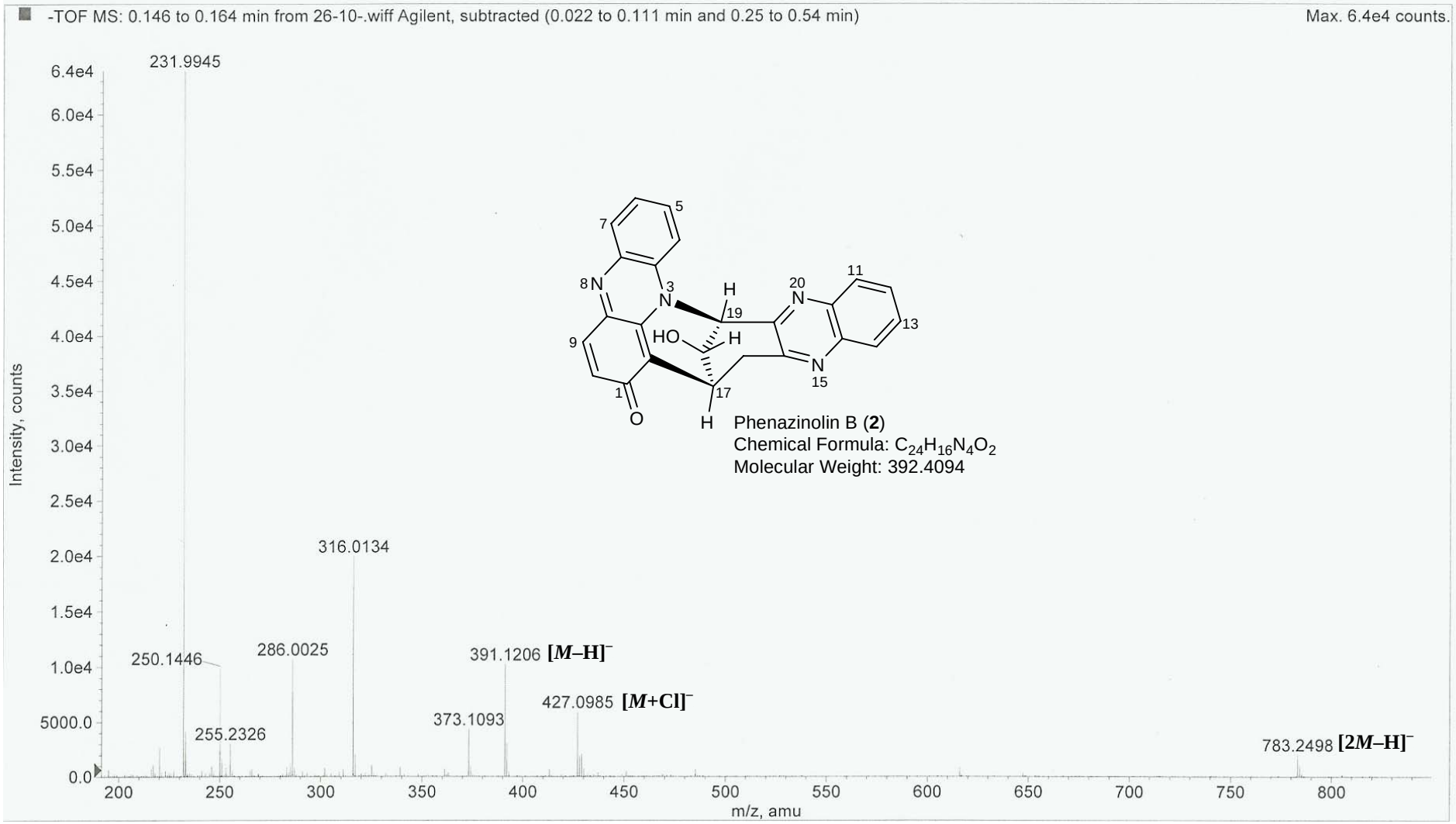
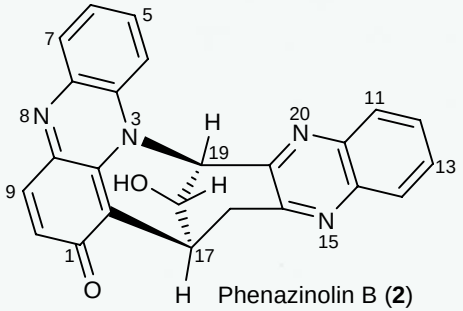


Fig. S21. HR-ESIMS(–) Spectrum of Phenazinolin B (**2**)

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
1	C24 H17 N4 O2	393.1346	-0.0024	-0.0061	18.5
2	C11 H25 N2 O13	393.1351	-0.5157	-1.3119	0.5
3	C10 H22 N6 O9 Na	393.1340	0.5521	1.4045	2.5
4	C12 H24 N3 O10 Na	393.1353	-0.7905	-2.0107	2.0
5	C9 H23 N5 O12	393.1337	0.8269	2.1034	1.0
6	C24 H20 N O3 Na	393.1335	1.0601	2.6966	15.0



Phenazinolin B (**2**)
Chemical Formula: $C_{24}H_{16}N_4O_2$
Molecular Weight: 392.4094

Fig. S22. HR-ESIMS(+) Data for Phenazinolin B (**2**)

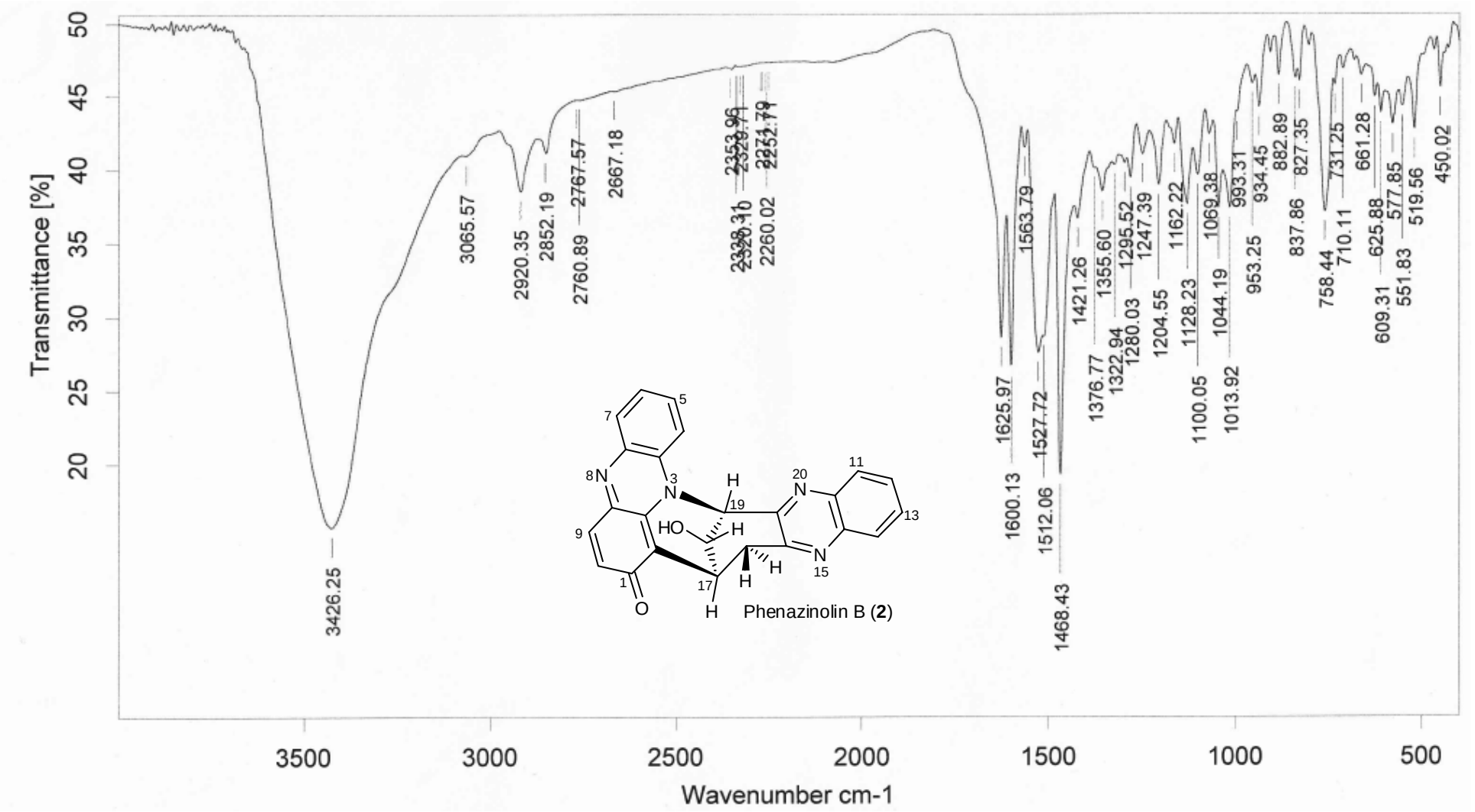


Fig. S23. IR Spectrum of Phenazinolin B (**2**)

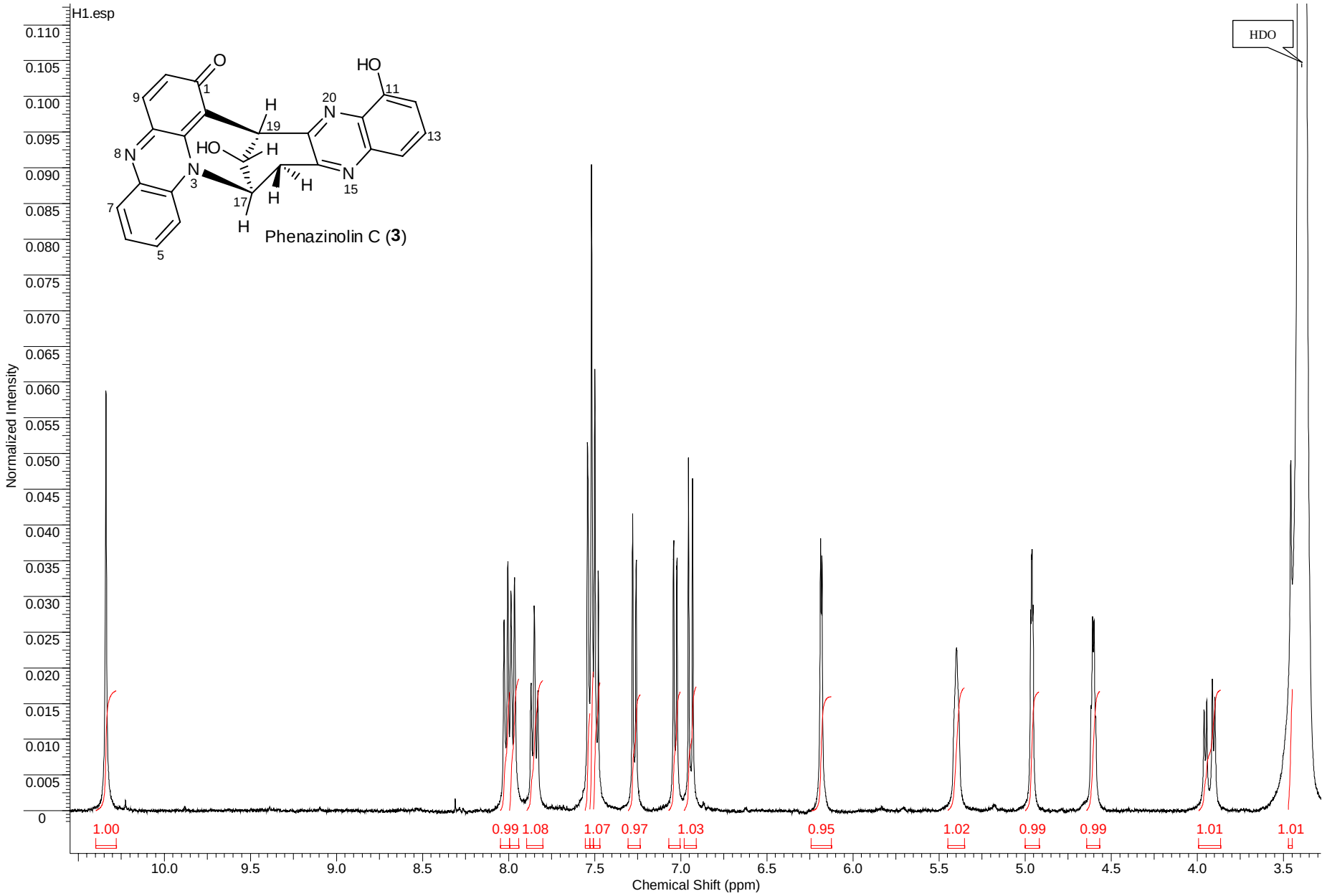
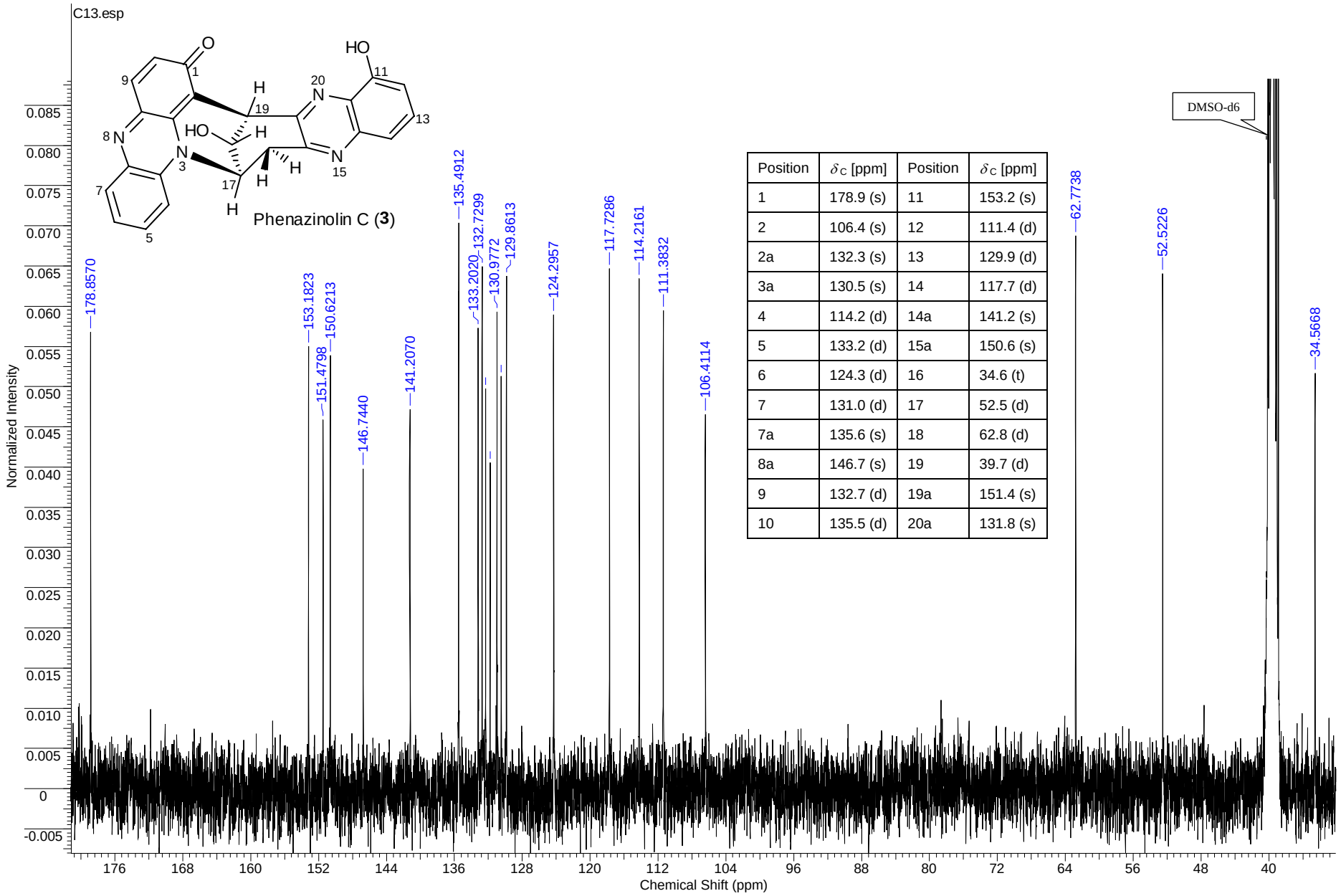


Fig. S24. ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin C (**3**)



Position	δ_C [ppm]	Position	δ_C [ppm]
1	178.9 (s)	11	153.2 (s)
2	106.4 (s)	12	111.4 (d)
2a	132.3 (s)	13	129.9 (d)
3a	130.5 (s)	14	117.7 (d)
4	114.2 (d)	14a	141.2 (s)
5	133.2 (d)	15a	150.6 (s)
6	124.3 (d)	16	34.6 (t)
7	131.0 (d)	17	52.5 (d)
7a	135.6 (s)	18	62.8 (d)
8a	146.7 (s)	19	39.7 (d)
9	132.7 (d)	19a	151.4 (s)
10	135.5 (d)	20a	131.8 (s)

Fig. S25. ^{13}C NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin C (**3**)

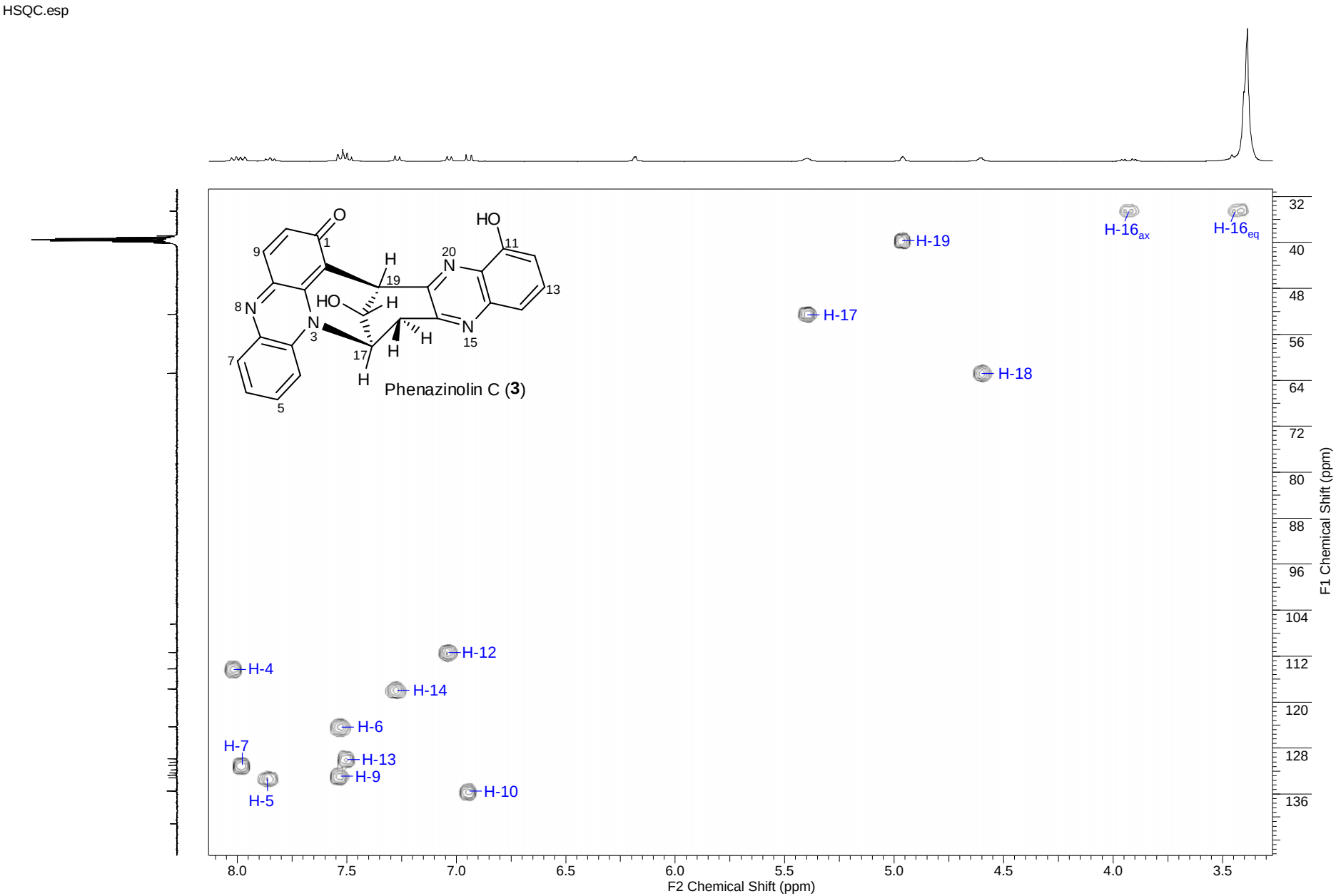


Fig. S26. HSQC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin C (**3**)

COSY.esp

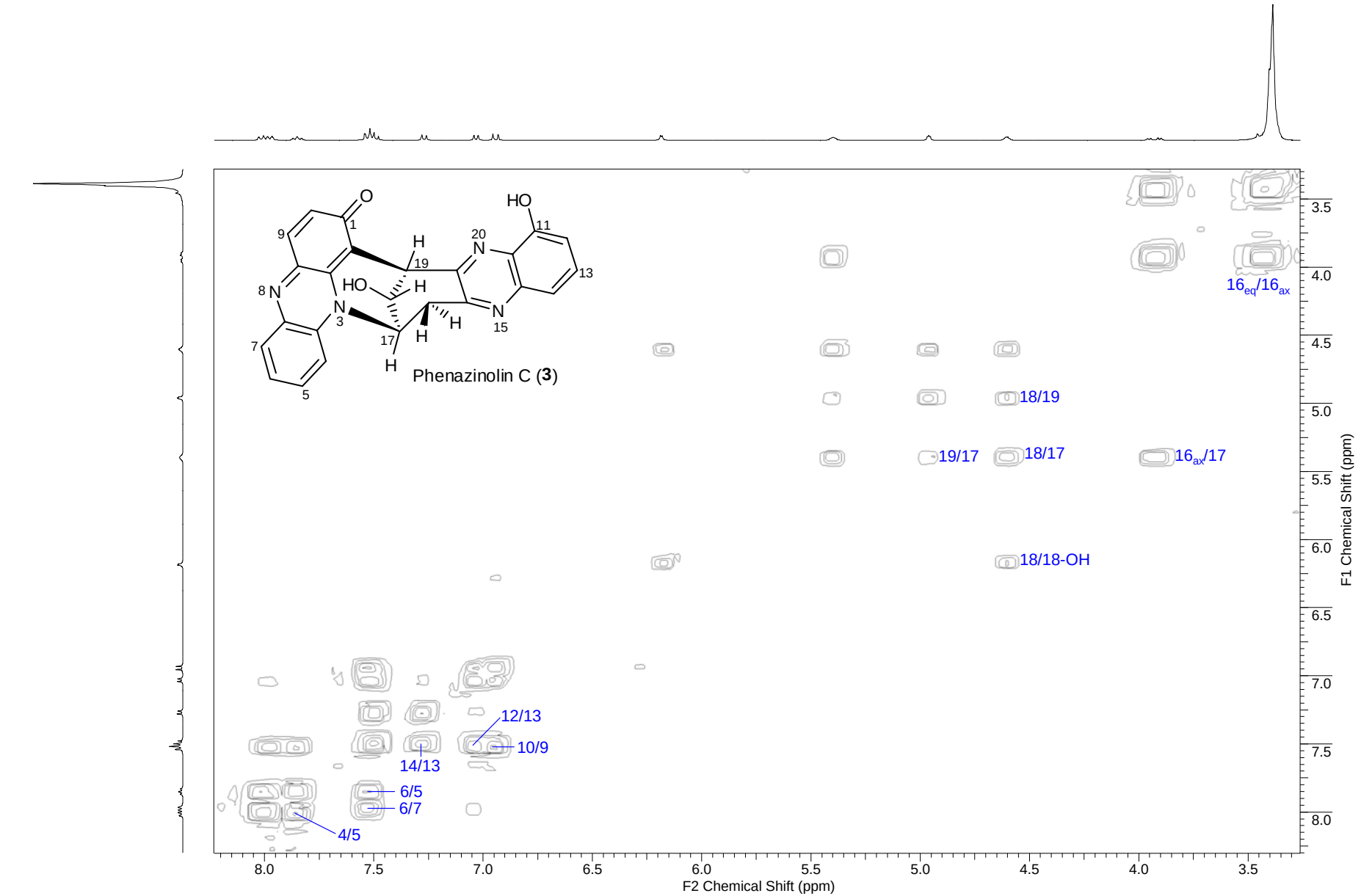


Fig. S27. ^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin C (**3**)

HMQC-TOCSY.esp

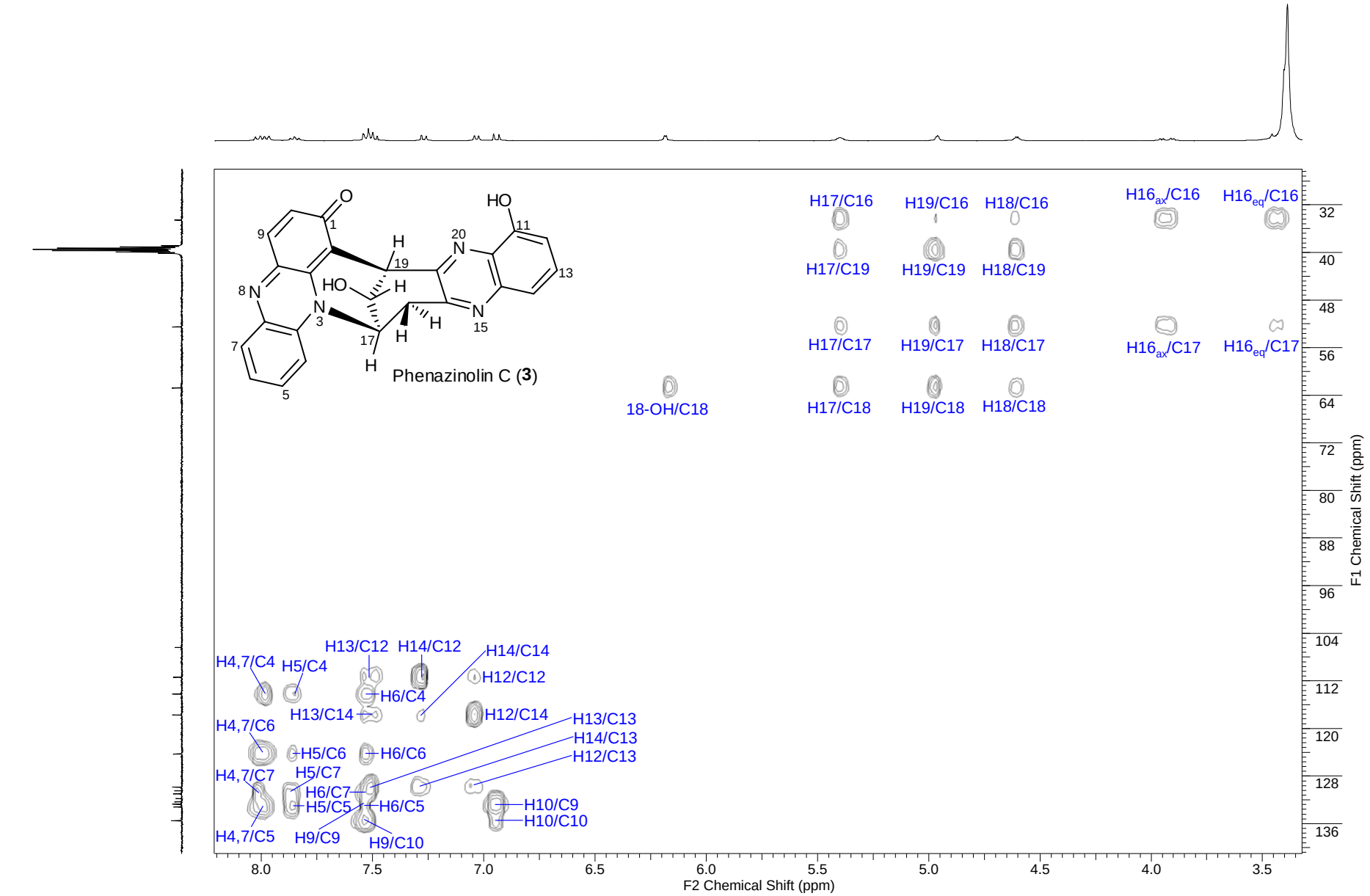


Fig. S28. HMQC-TOCSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin C (**3**)

HMBC.esp

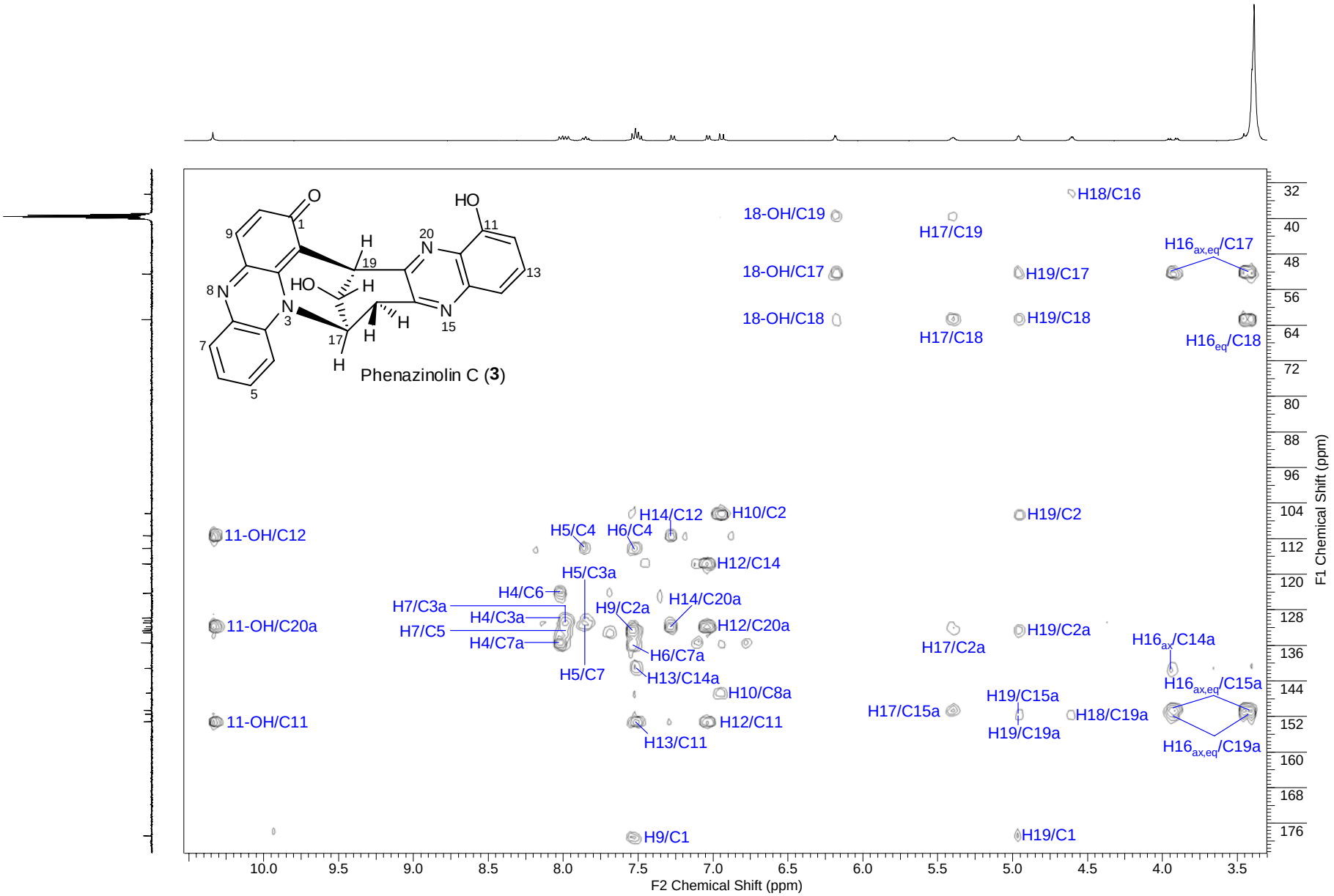


Fig. S29. ^{1}H-^{13}C HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin C (**3**)

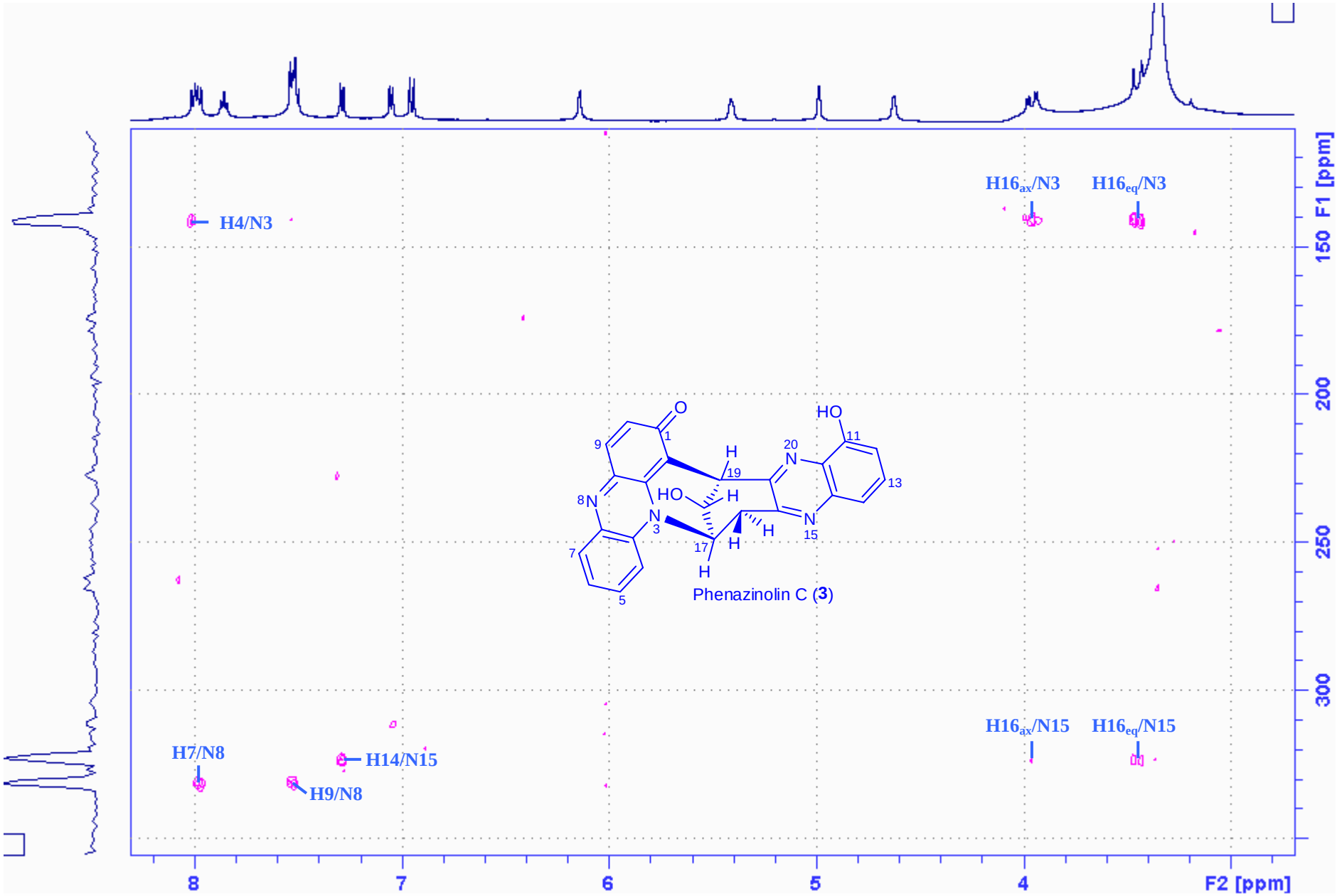


Fig. S30. ^{1}H-^{15}N HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin C (**3**)

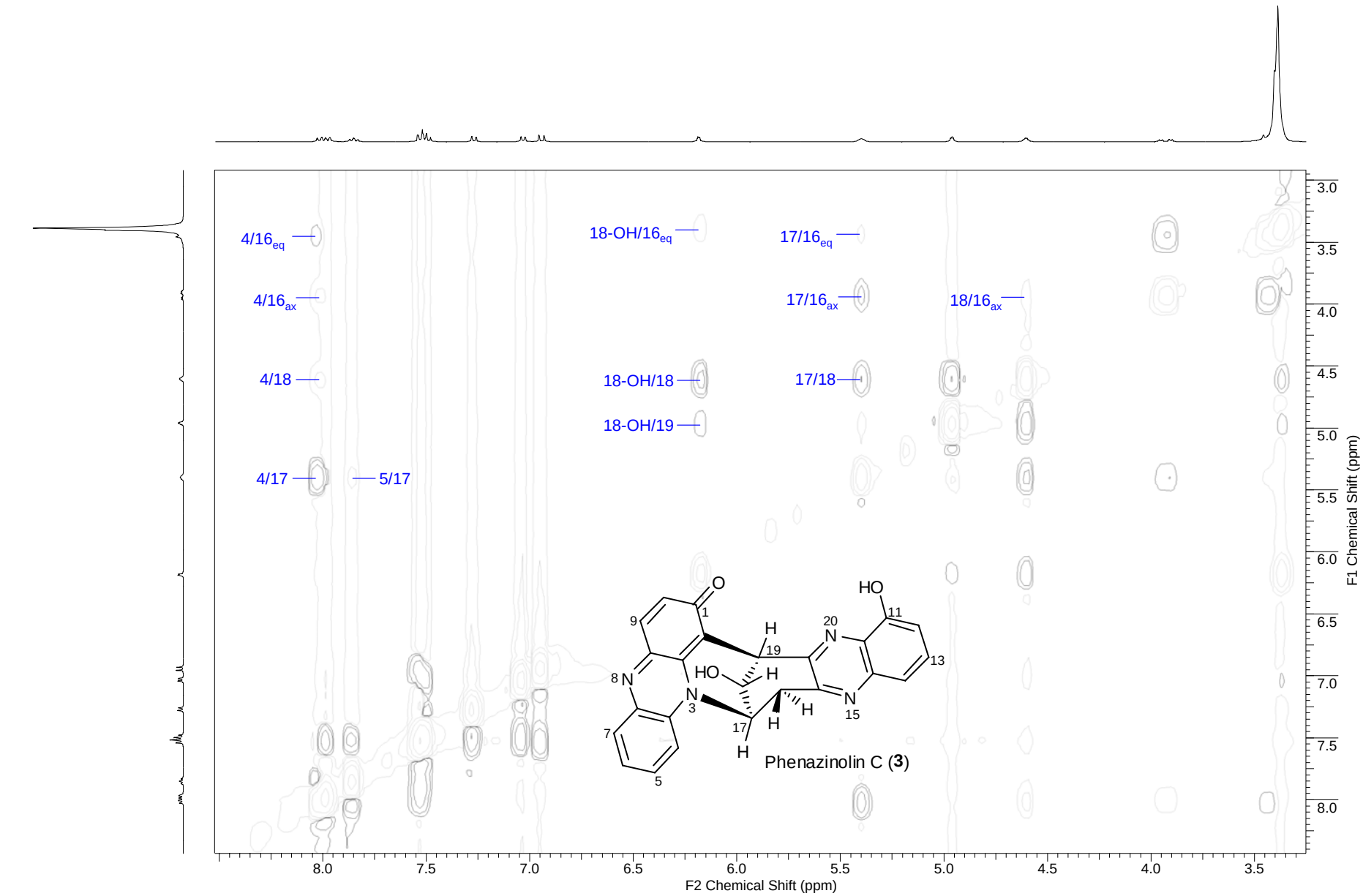


Fig. S31. ROESY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin C (**3**)

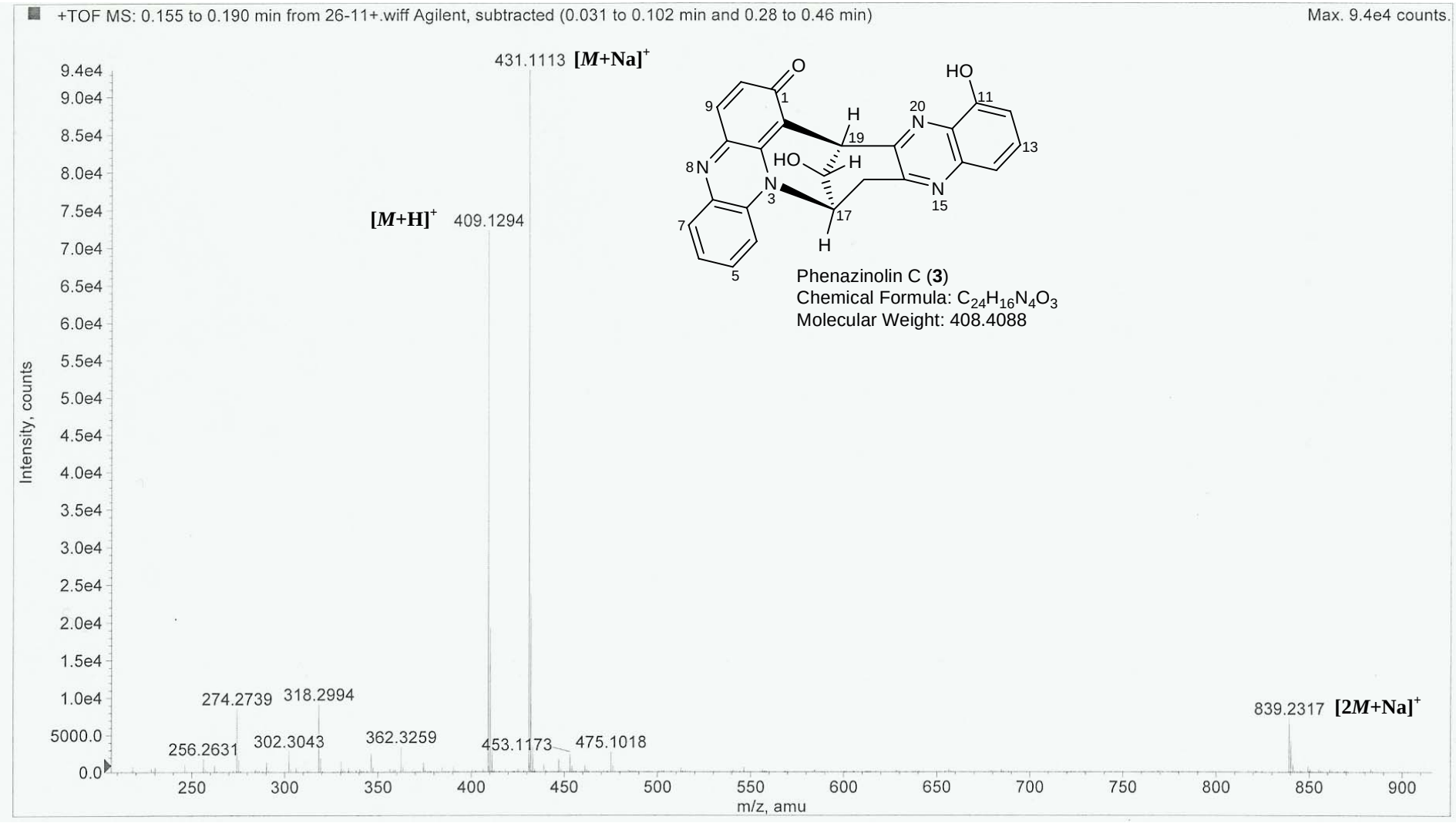


Fig. S32. HR-ESIMS(+) Spectrum of Phenazinolin C (**3**)

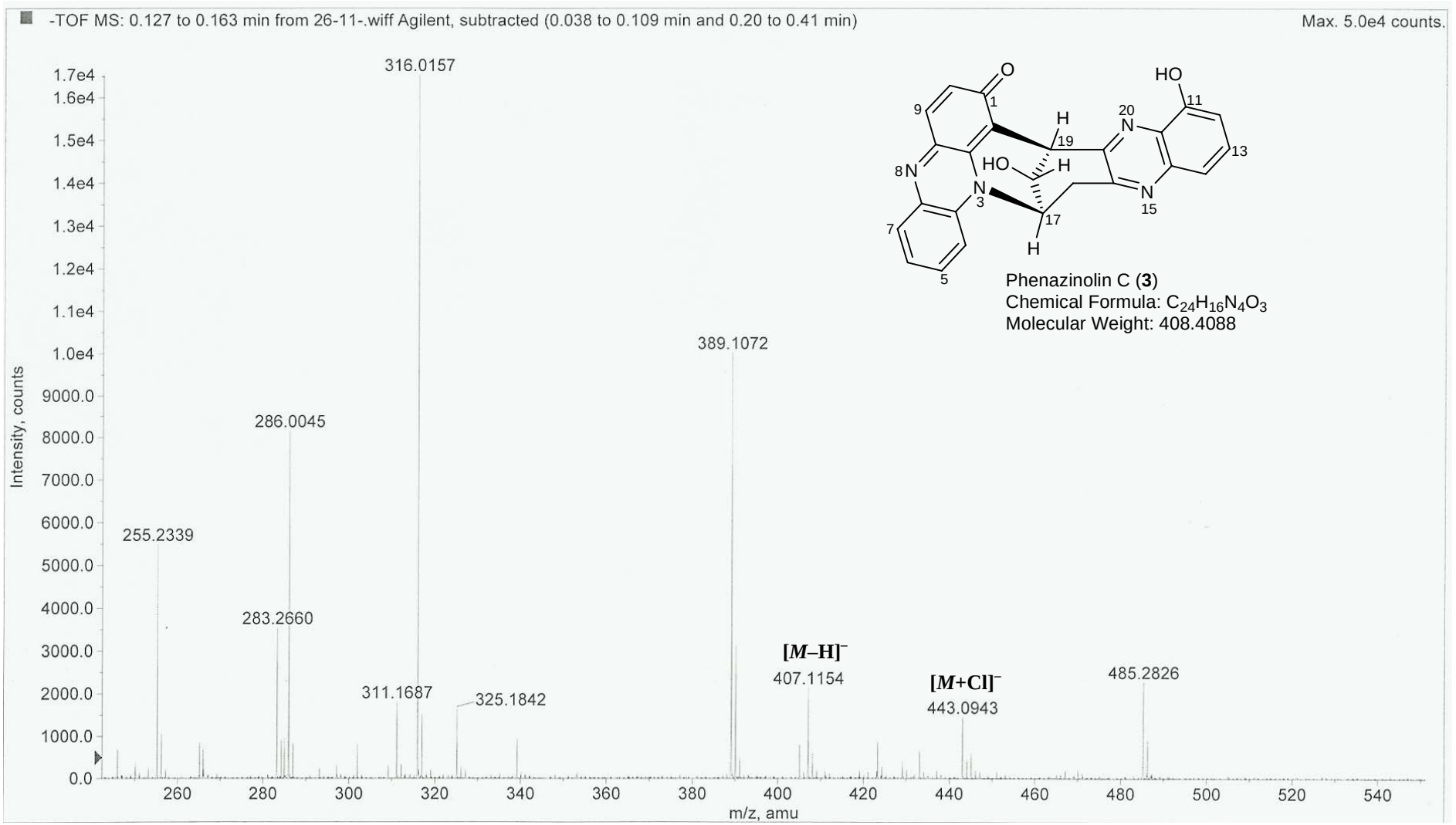
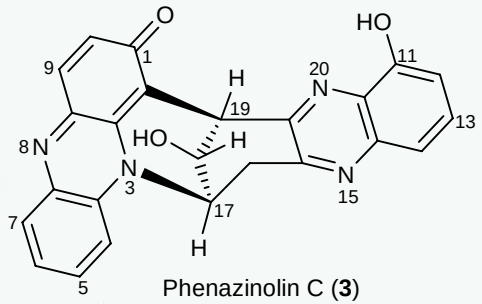


Fig. S33. HR-ESIMS(–) Spectrum of Phenazinolin C (**3**)

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
1	C24 H17 N4 O3	409.1295	-0.1170	-0.2860	18.5
2	C25 H16 N5 Na	409.1297	-0.3918	-0.9576	20.0
3	C10 H22 N6 O10 Na	409.1289	0.4375	1.0694	2.5
4	C11 H25 N2 O14	409.1300	-0.6303	-1.5408	0.5
5	C9 H23 N5 O13	409.1286	0.7123	1.7410	1.0
6	C12 H24 N3 O11 Na	409.1303	-0.9051	-2.2123	2.0
7	C24 H20 N O4 Na	409.1284	0.9455	2.3110	15.0
8	C23 H21 O7	409.1281	1.2202	2.9825	13.5



Phenazinolin C (**3**)
Chemical Formula: $C_{24}H_{16}N_4O_3$
Molecular Weight: 408.4088

Fig. S34. HR-ESIMS(+) Data for Phenazinolin C (**3**)

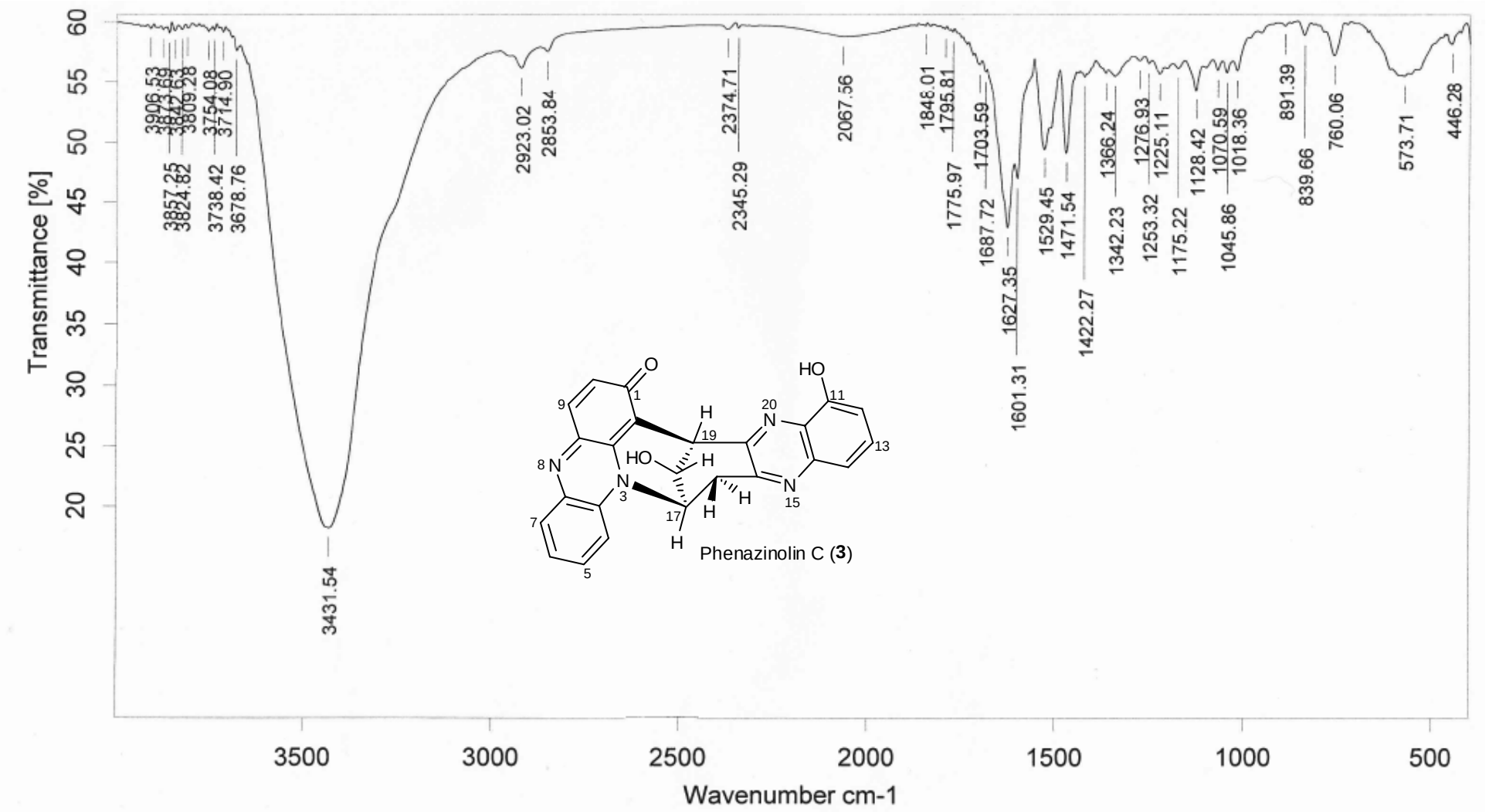


Fig. S35. IR Spectrum of Phenazinolin C (**3**)

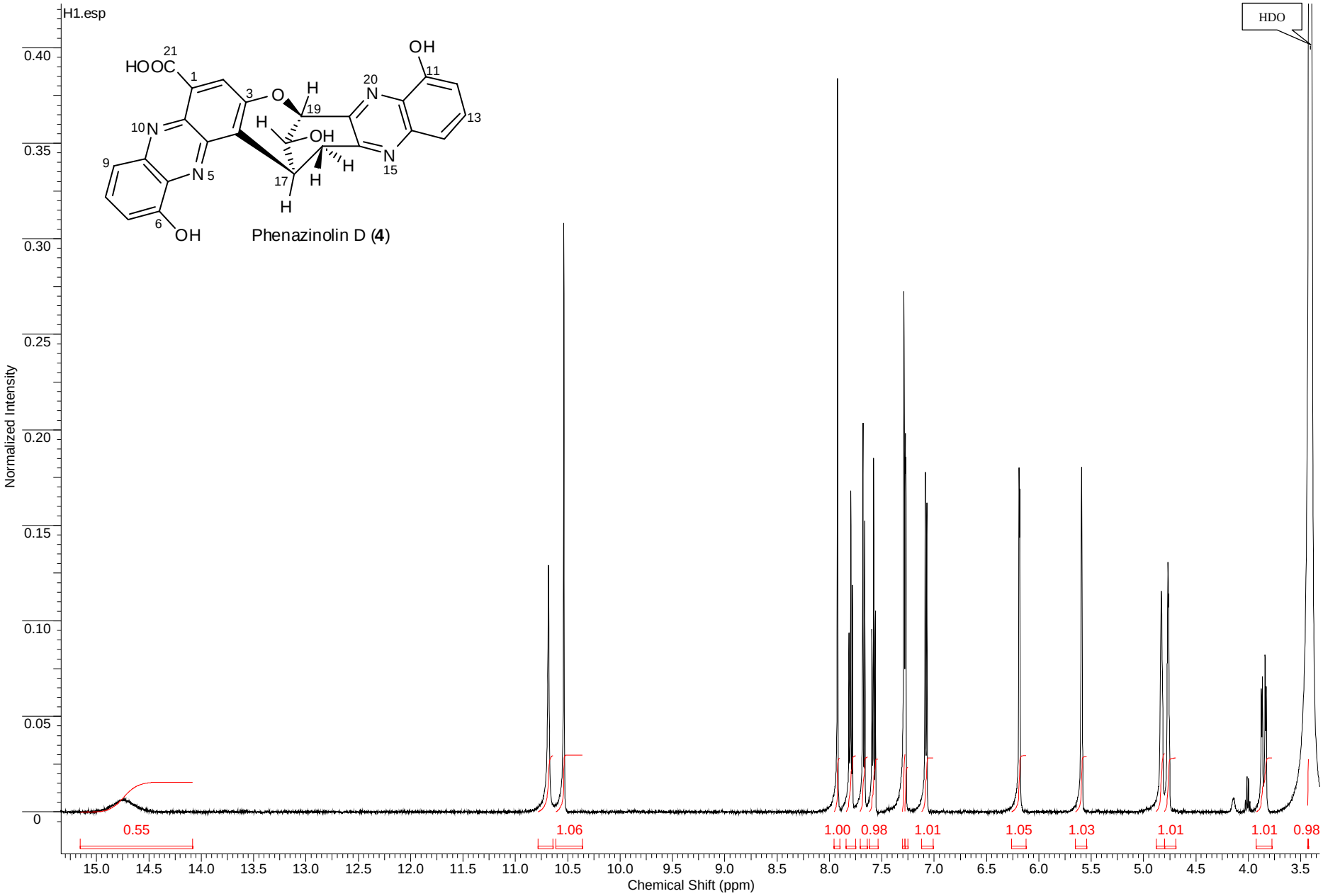
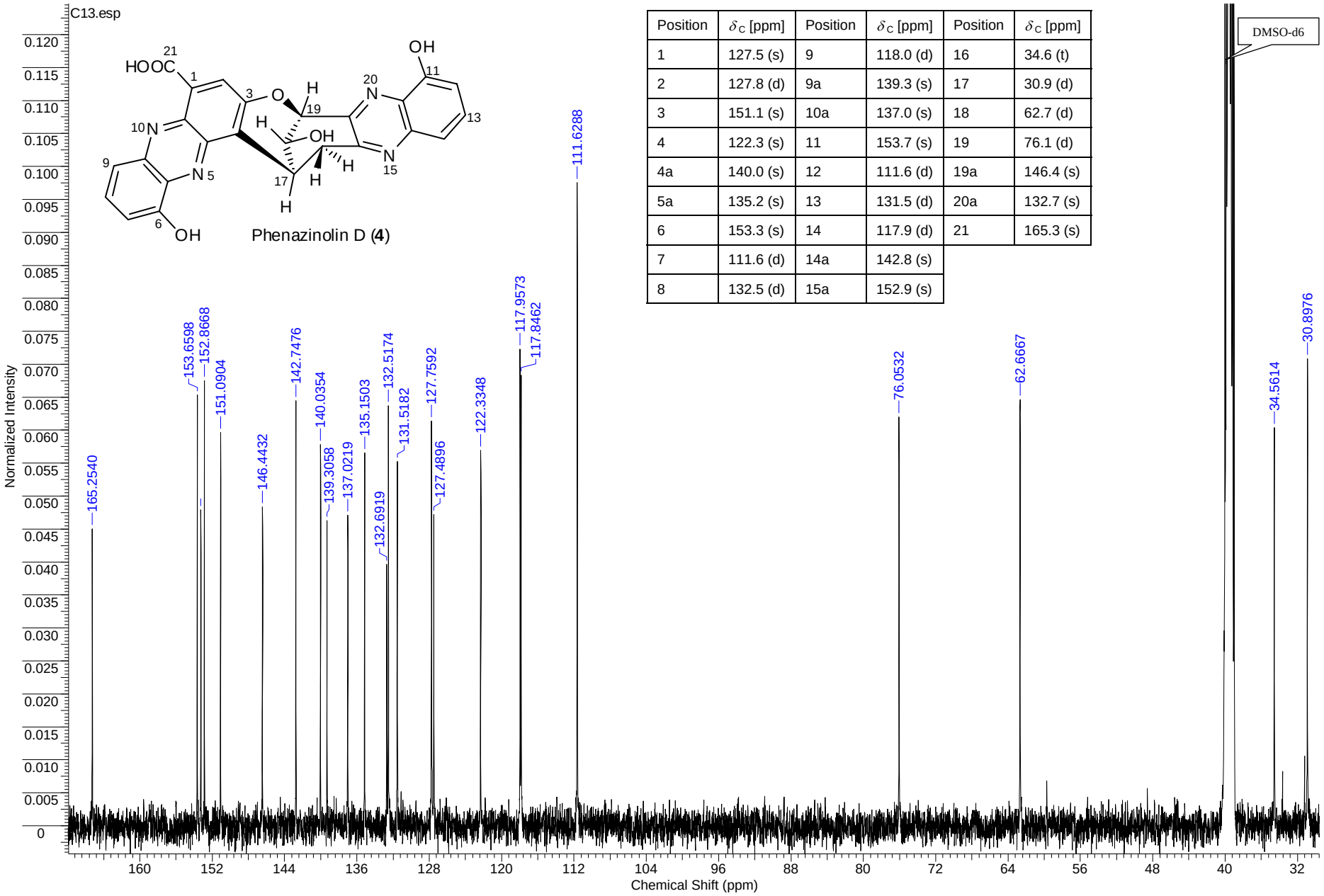


Fig. S36. ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin D (**4**)



Position	δ_C [ppm]	Position	δ_C [ppm]	Position	δ_C [ppm]
1	127.5 (s)	9	118.0 (d)	16	34.6 (t)
2	127.8 (d)	9a	139.3 (s)	17	30.9 (d)
3	151.1 (s)	10a	137.0 (s)	18	62.7 (d)
4	122.3 (s)	11	153.7 (s)	19	76.1 (d)
4a	140.0 (s)	12	111.6 (d)	19a	146.4 (s)
5a	135.2 (s)	13	131.5 (d)	20a	132.7 (s)
6	153.3 (s)	14	117.9 (d)	21	165.3 (s)
7	111.6 (d)	14a	142.8 (s)		
8	132.5 (d)	15a	152.9 (s)		

Fig. S37. ^{13}C NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin D (**4**)

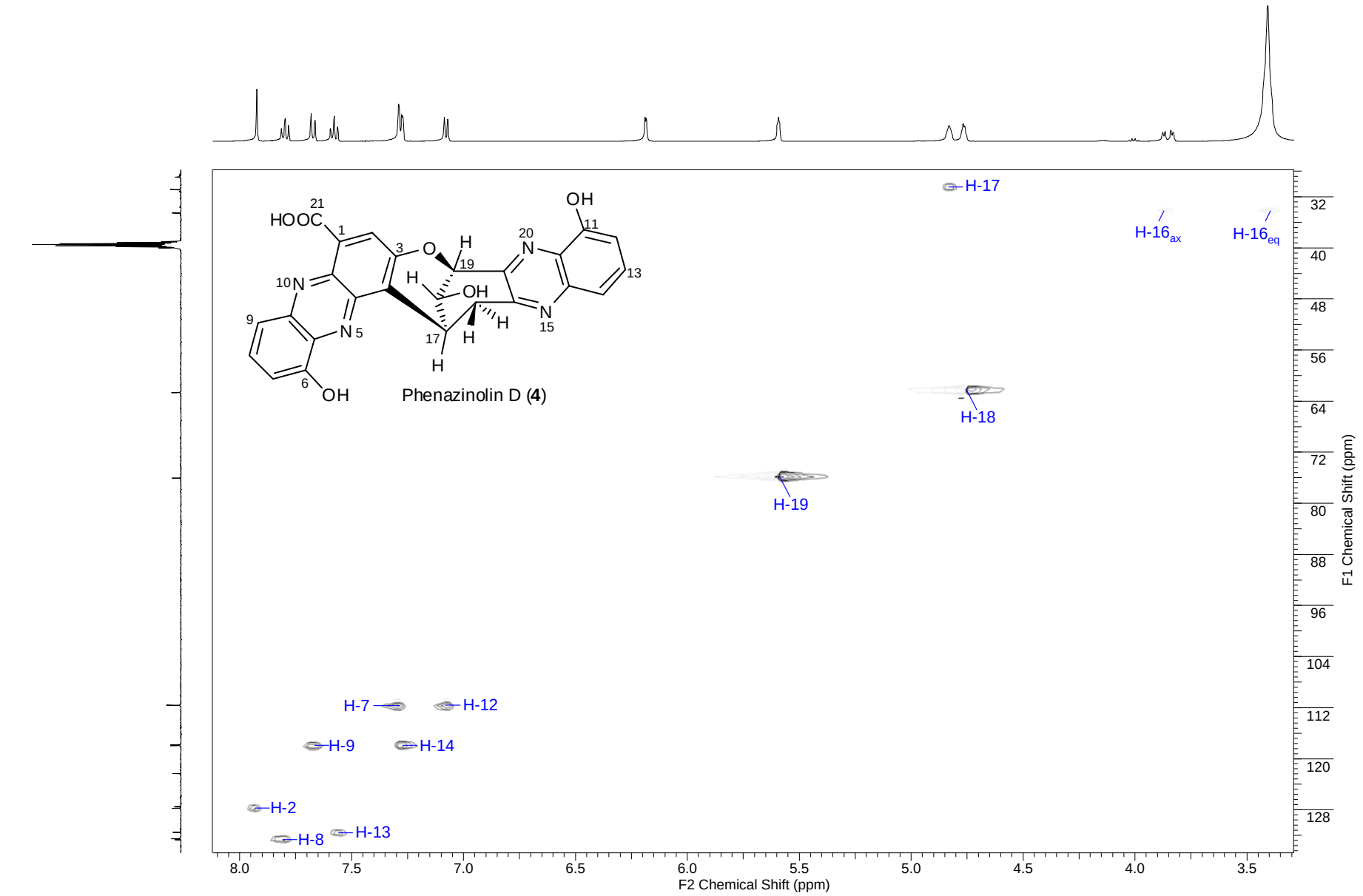


Fig. S38. HSQC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin D (**4**)

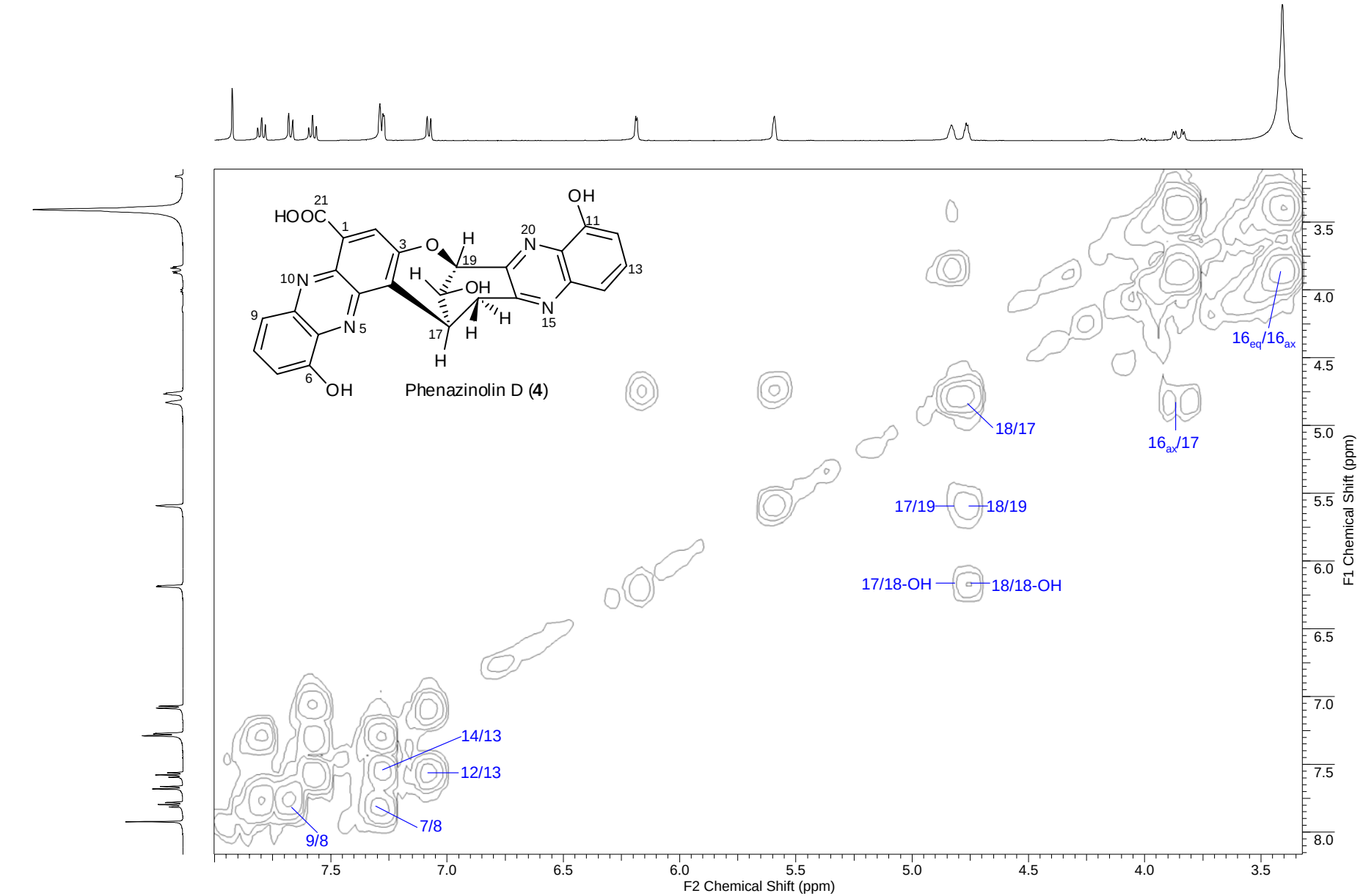


Fig. S39. ^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin D (**4**)

HMQC-TOCSY.esp

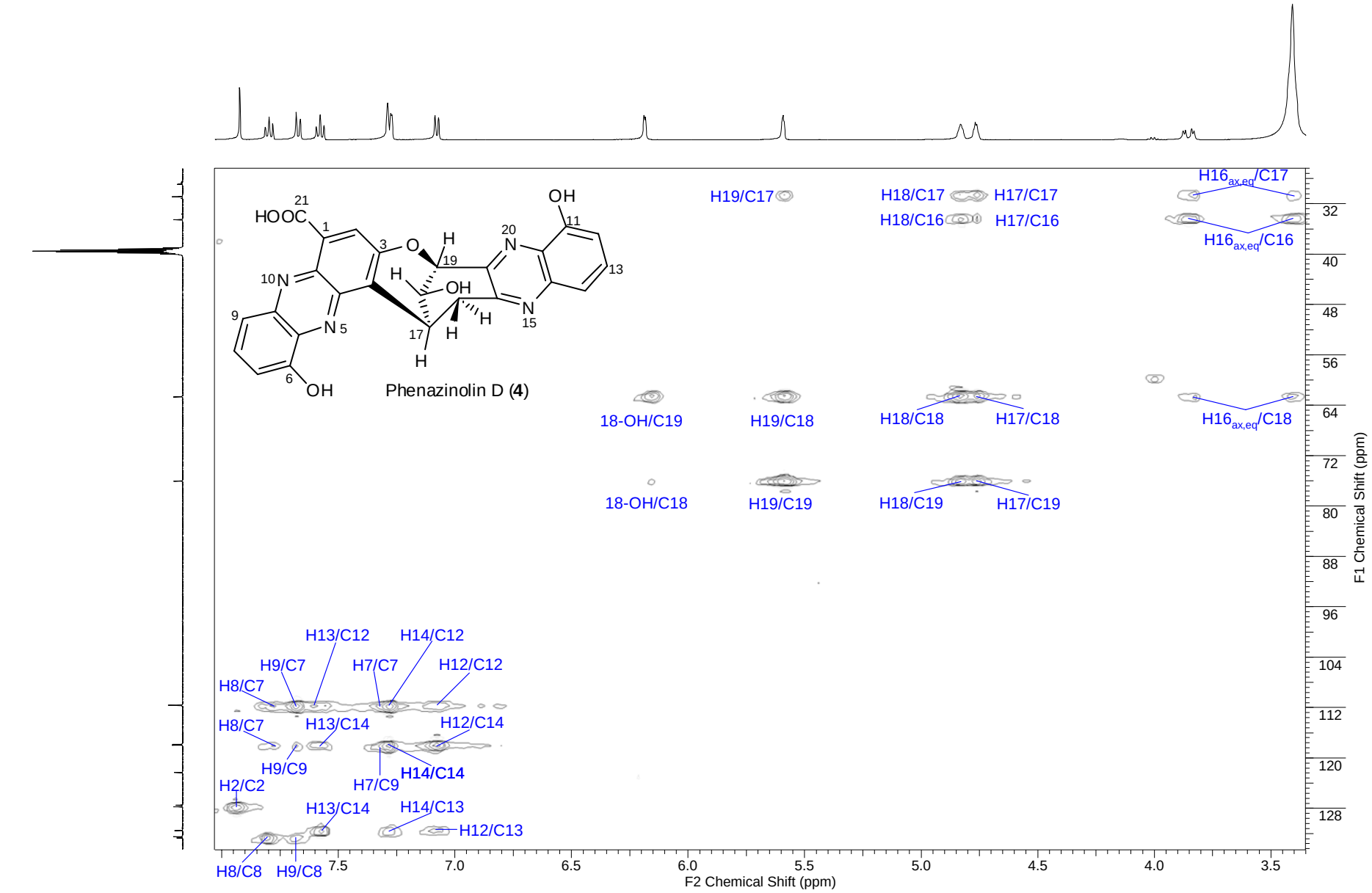


Fig. S40. HMQC-TOCSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin D (**4**)

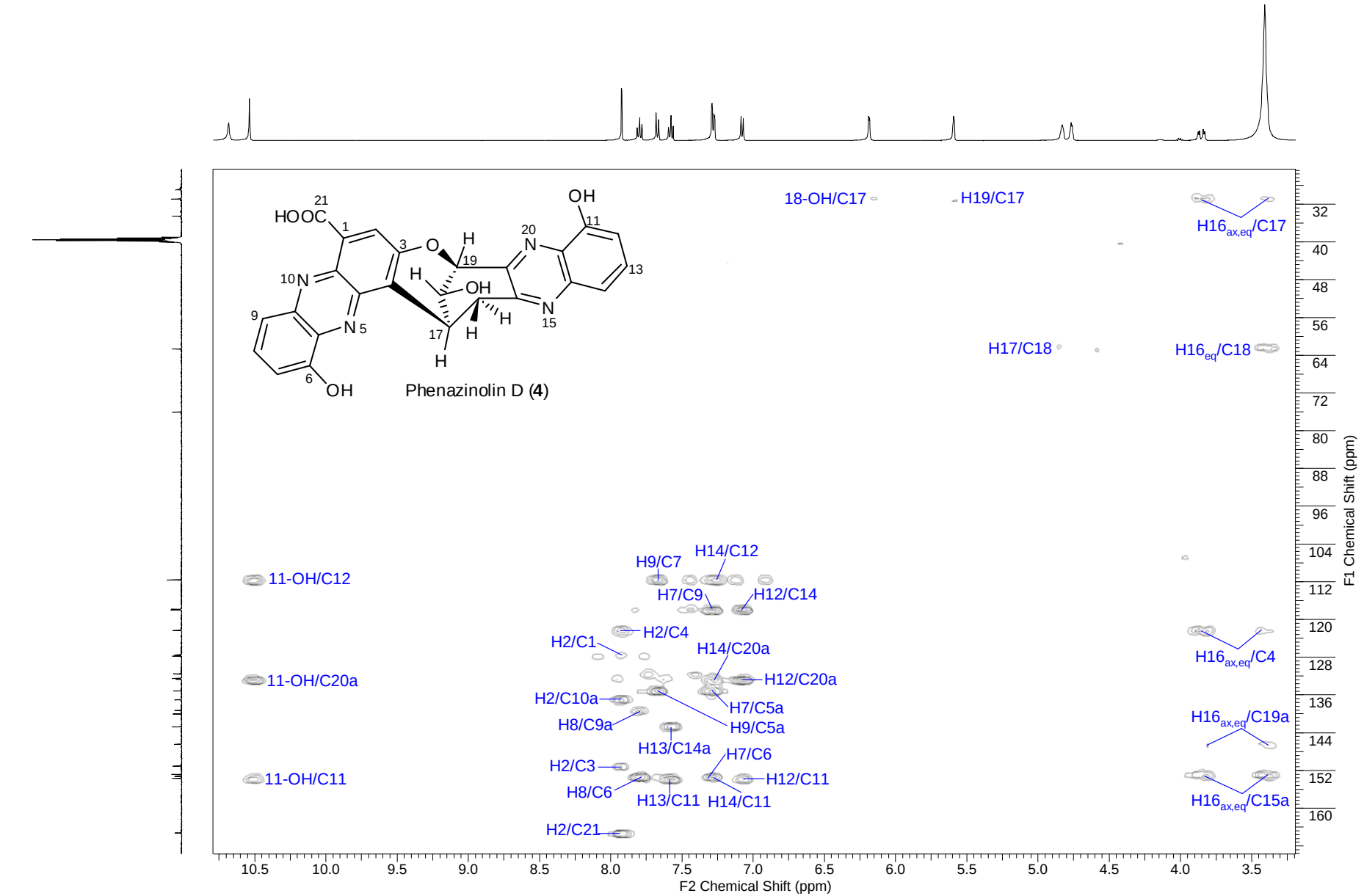


Fig. S41. ^{1}H-^{13}C HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin D (**4**)

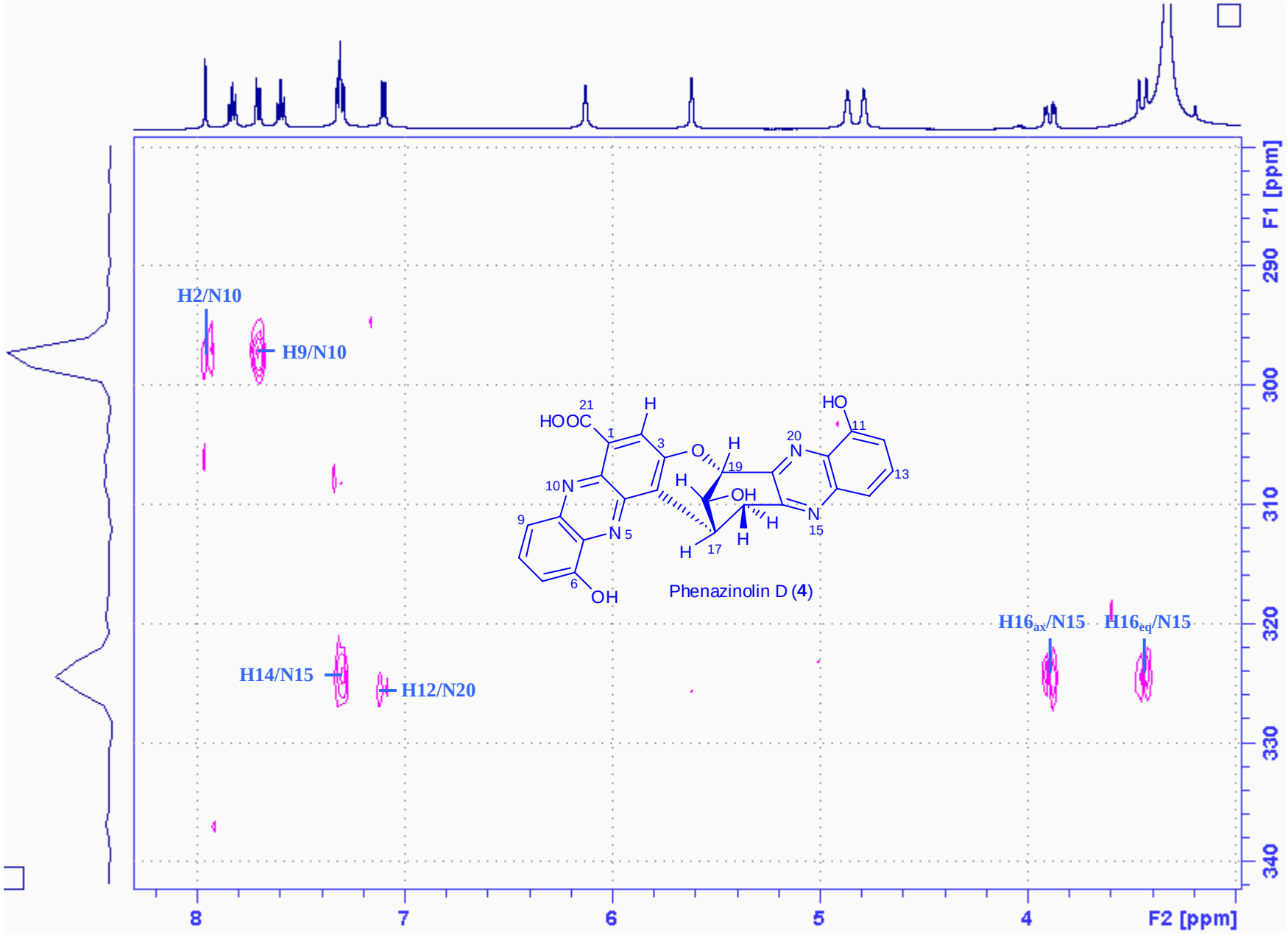


Fig. S42. ^{1}H-^{15}N HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Pheazinolin D (**4**)

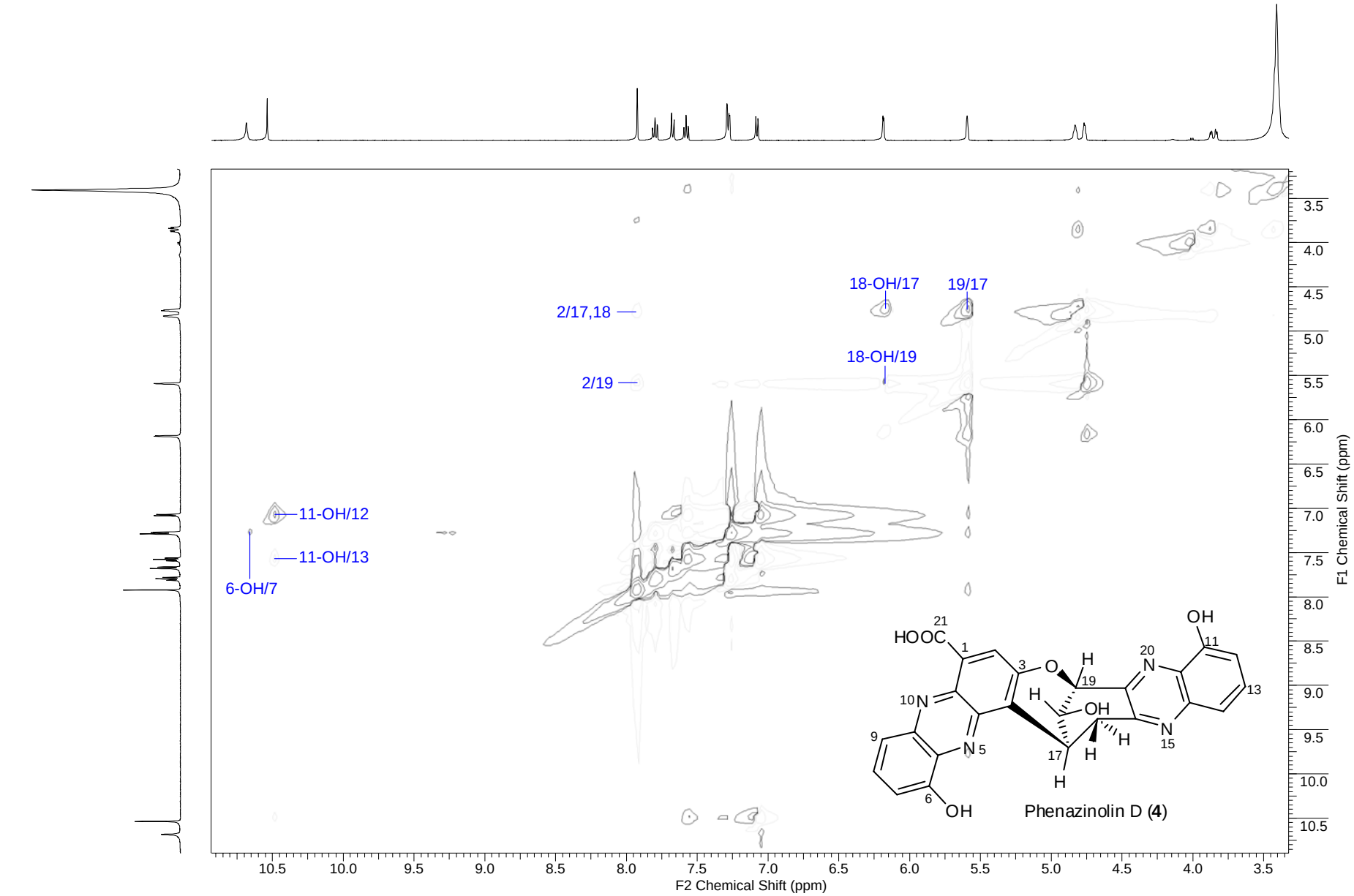


Fig. S43. ROESY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin D (**4**)

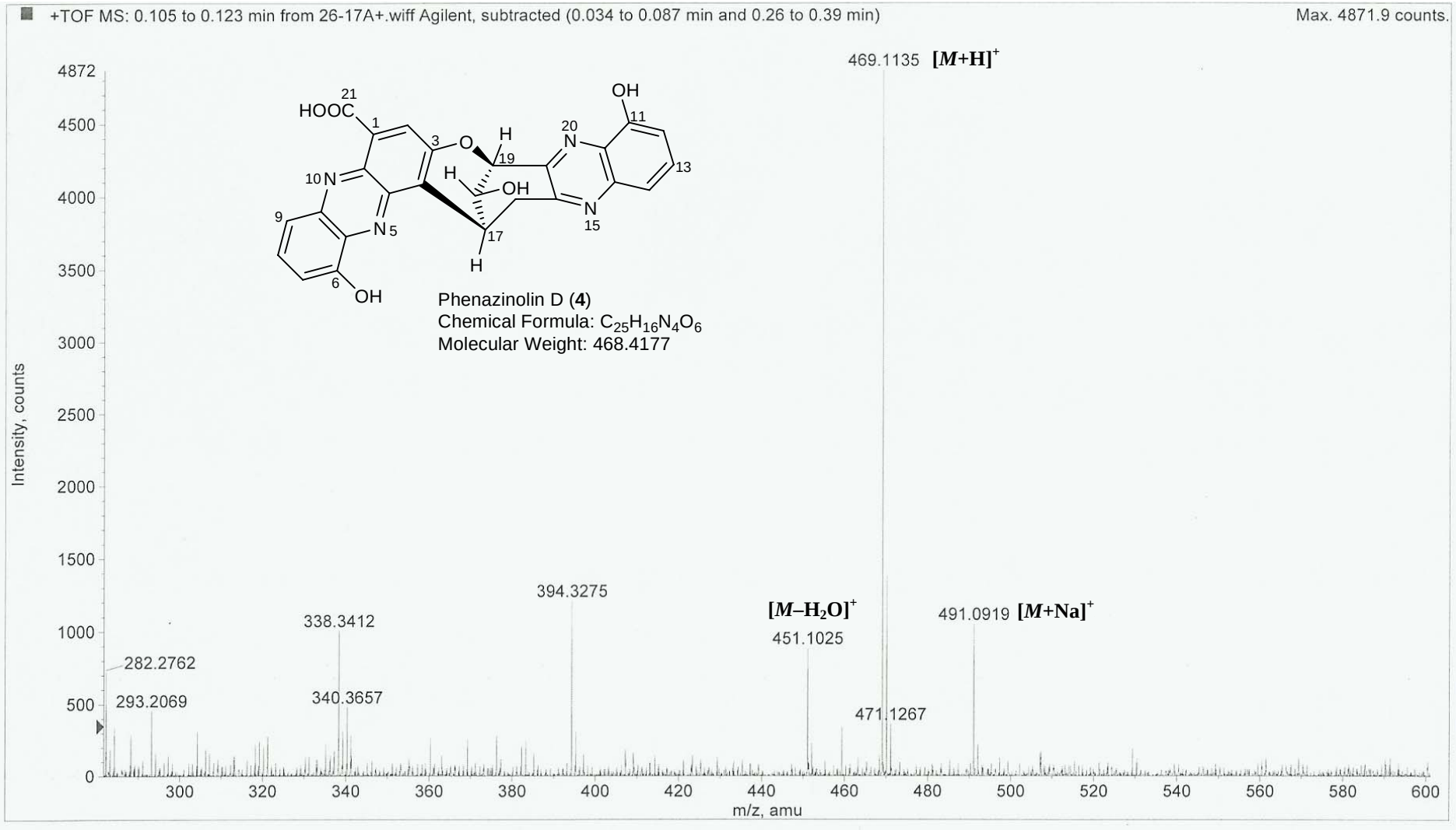


Fig. S44. HR-ESIMS(+) Spectrum of Phenazinolin D (**4**)

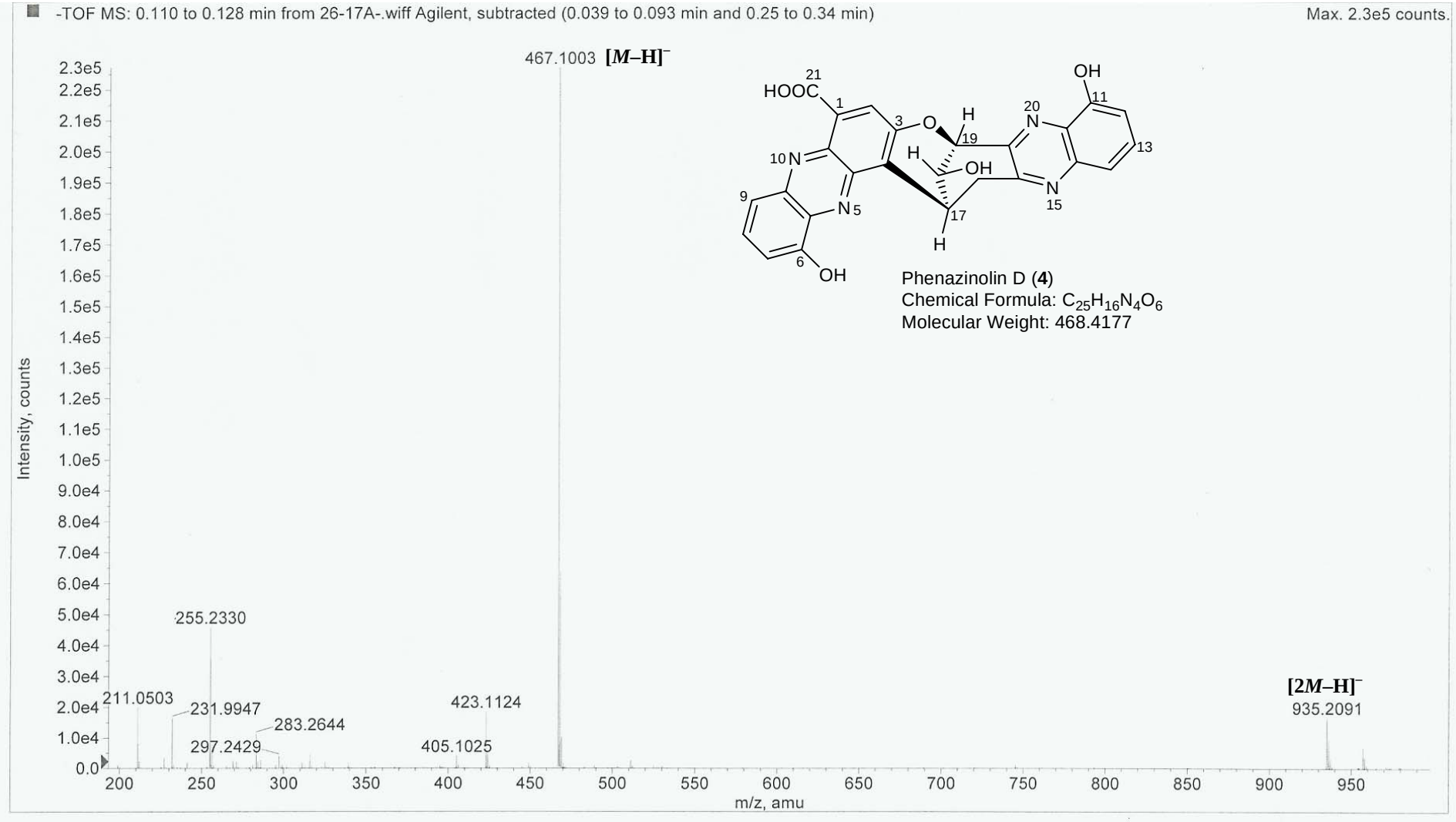
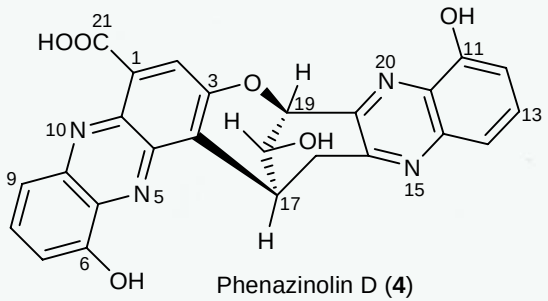


Fig. S45. HR-ESIMS(–) Spectrum of Phenazinolin D (**4**)

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
1	C10 H23 N5 O16	469.1134	0.0683	0.1457	2.0
2	C11 H22 N6 O13 Na	469.1137	-0.2063	-0.4399	3.5
3	C25 H20 N O7 Na	469.1131	0.3015	0.6428	16.0
4	C24 H21 O10	469.1129	0.5763	1.2285	14.5
5	C25 H17 N4 O6	469.1142	-0.7609	-1.6221	19.5
6	C26 H16 N5 O3 Na	469.1145	-1.0357	-2.2078	21.0
7	C12 H25 N2 O17	469.1147	-1.2743	-2.7164	1.5



Phenazinolin D (**4**)
Chemical Formula: $C_{25}H_{16}N_4O_6$
Molecular Weight: 468.4177

Fig. S46. HR-ESIMS(+)Data for Phenazinolin D (**4**)

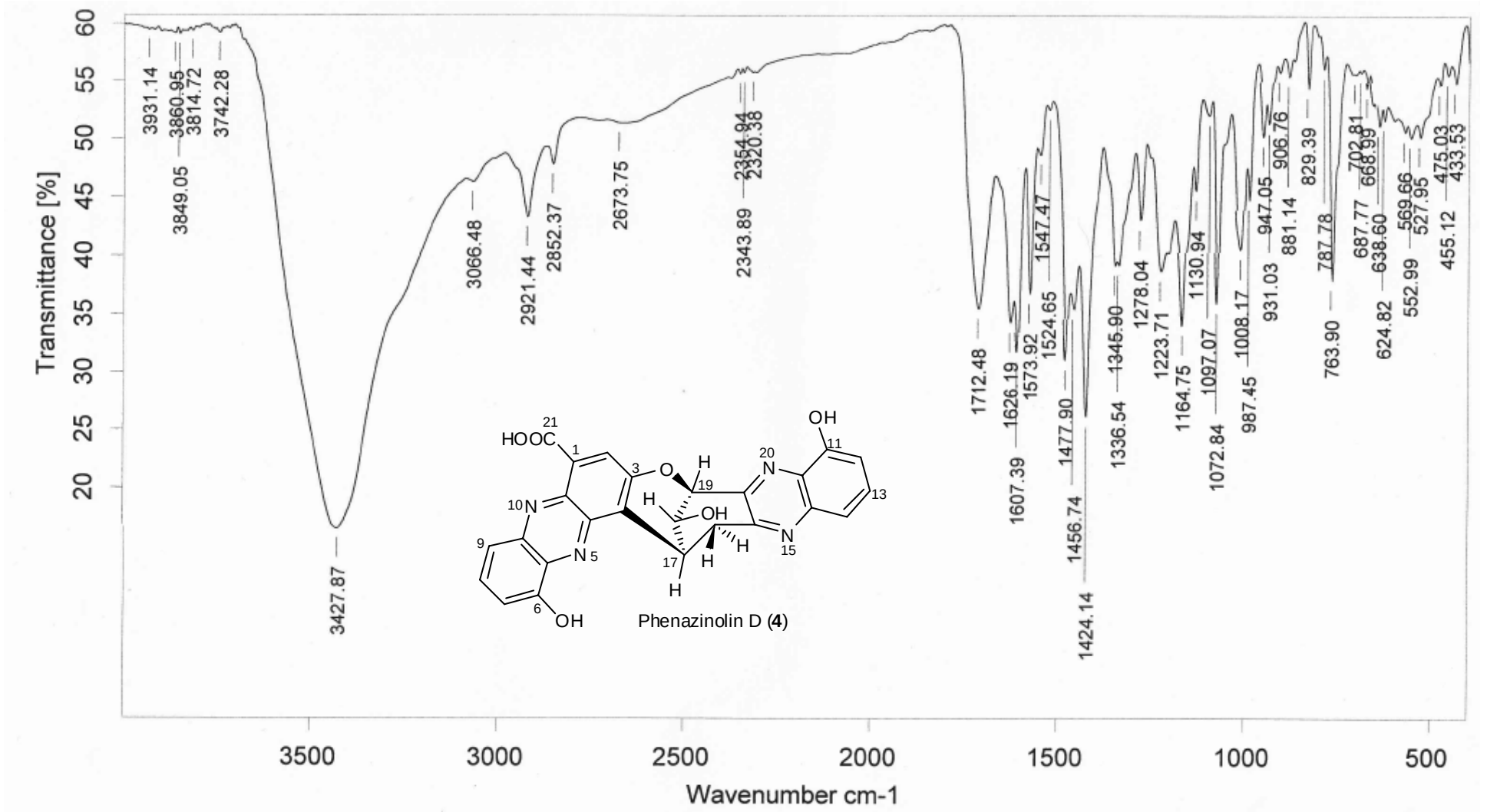


Fig. S47. IR Spectrum of Phenazinolin D (**4**)

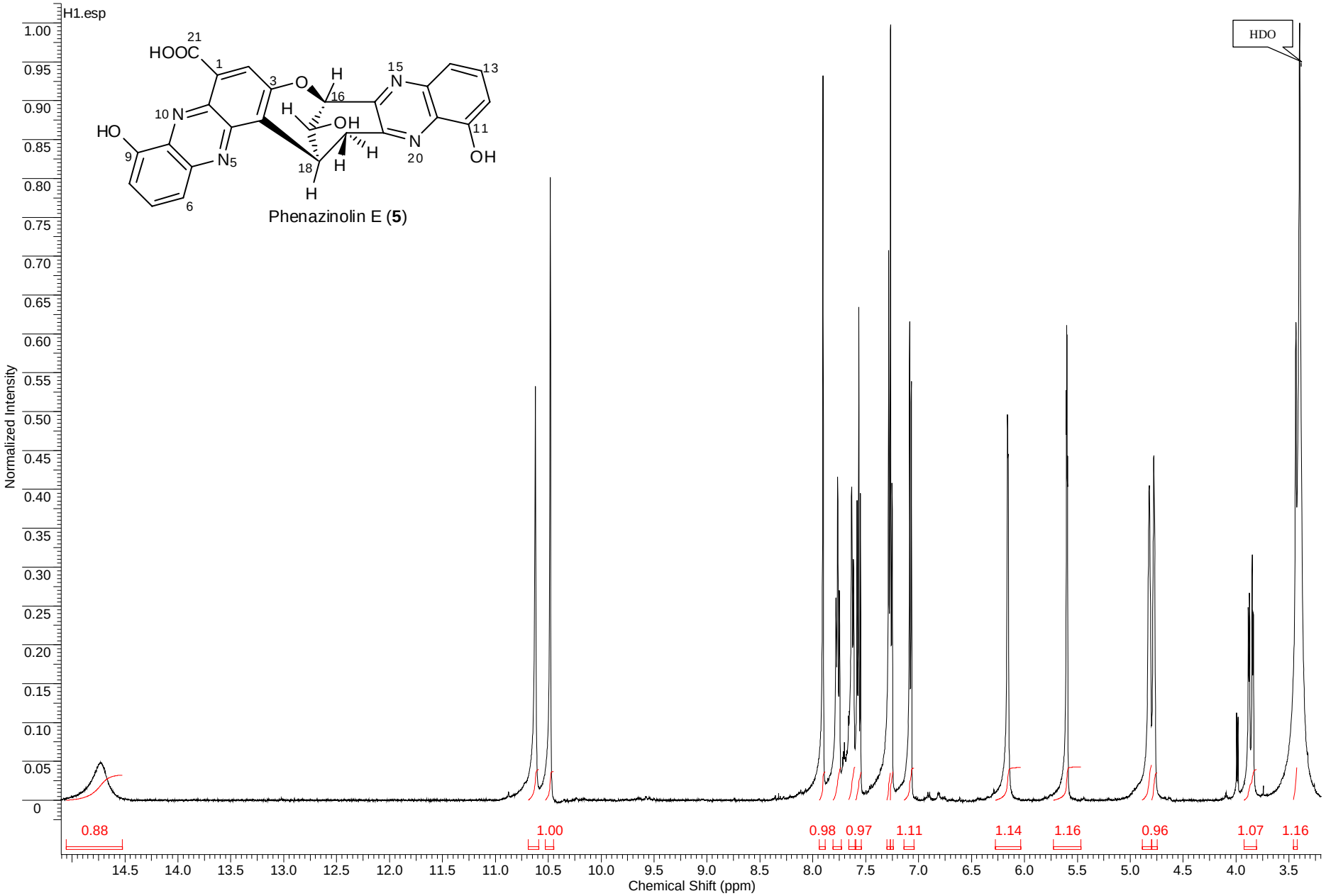
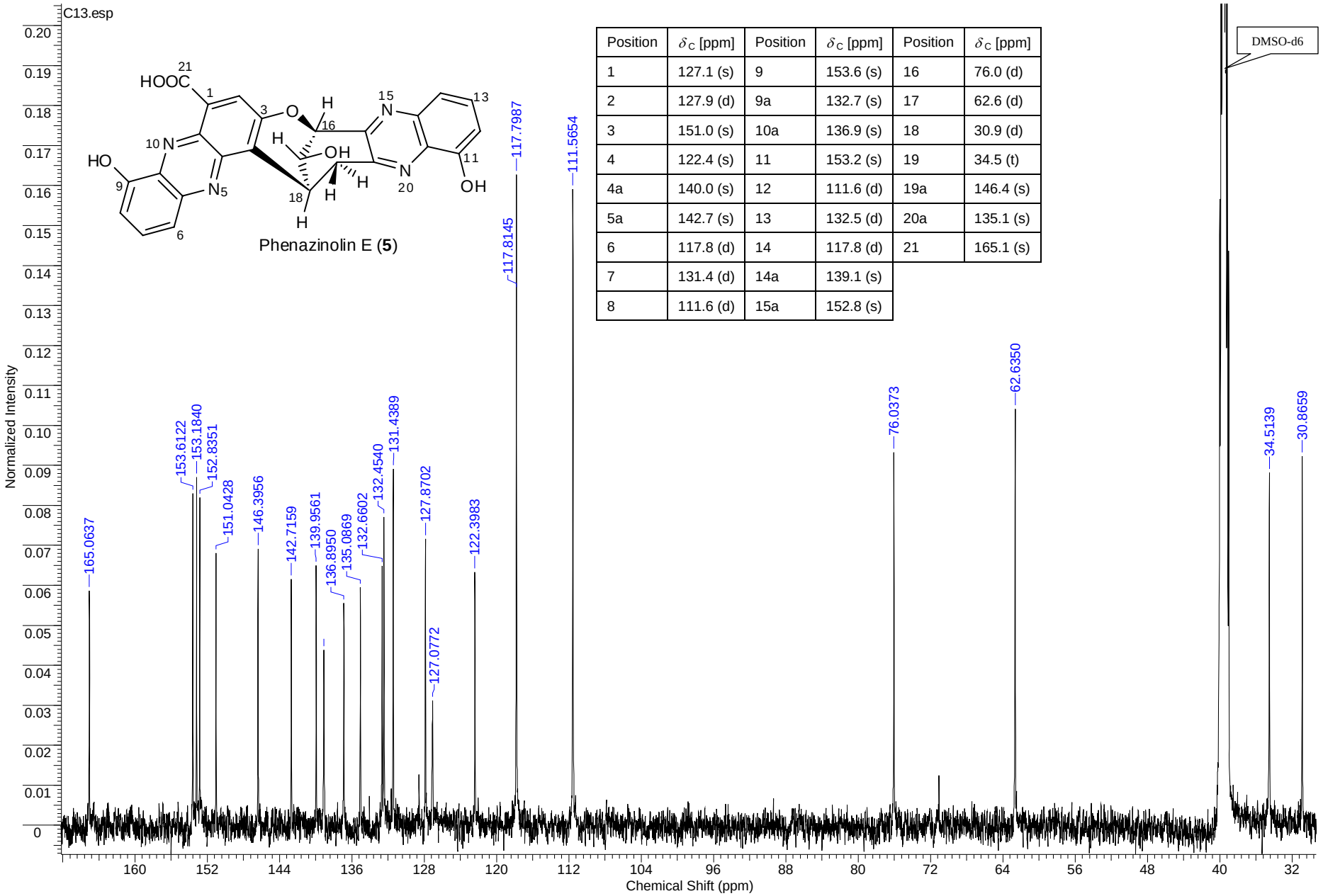


Fig. S48. ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin E (**5**)



Position	δ_C [ppm]	Position	δ_C [ppm]	Position	δ_C [ppm]
1	127.1 (s)	9	153.6 (s)	16	76.0 (d)
2	127.9 (d)	9a	132.7 (s)	17	62.6 (d)
3	151.0 (s)	10a	136.9 (s)	18	30.9 (d)
4	122.4 (s)	11	153.2 (s)	19	34.5 (t)
4a	140.0 (s)	12	111.6 (d)	19a	146.4 (s)
5a	142.7 (s)	13	132.5 (d)	20a	135.1 (s)
6	117.8 (d)	14	117.8 (d)	21	165.1 (s)
7	131.4 (d)	14a	139.1 (s)		
8	111.6 (d)	15a	152.8 (s)		

Fig. S49. ^{13}C NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin E (**5**)

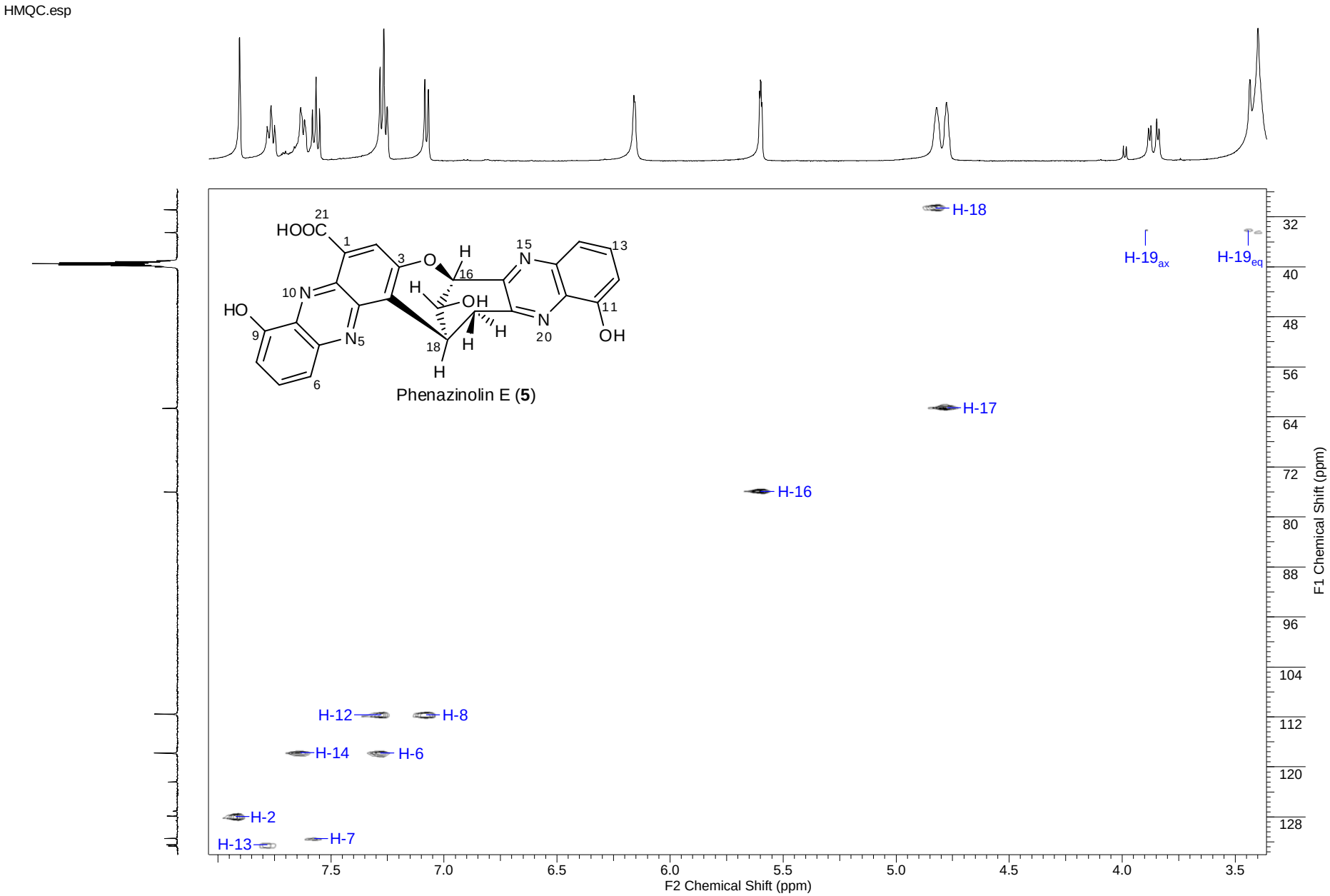


Fig. S50. HMQC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin E (**5**)

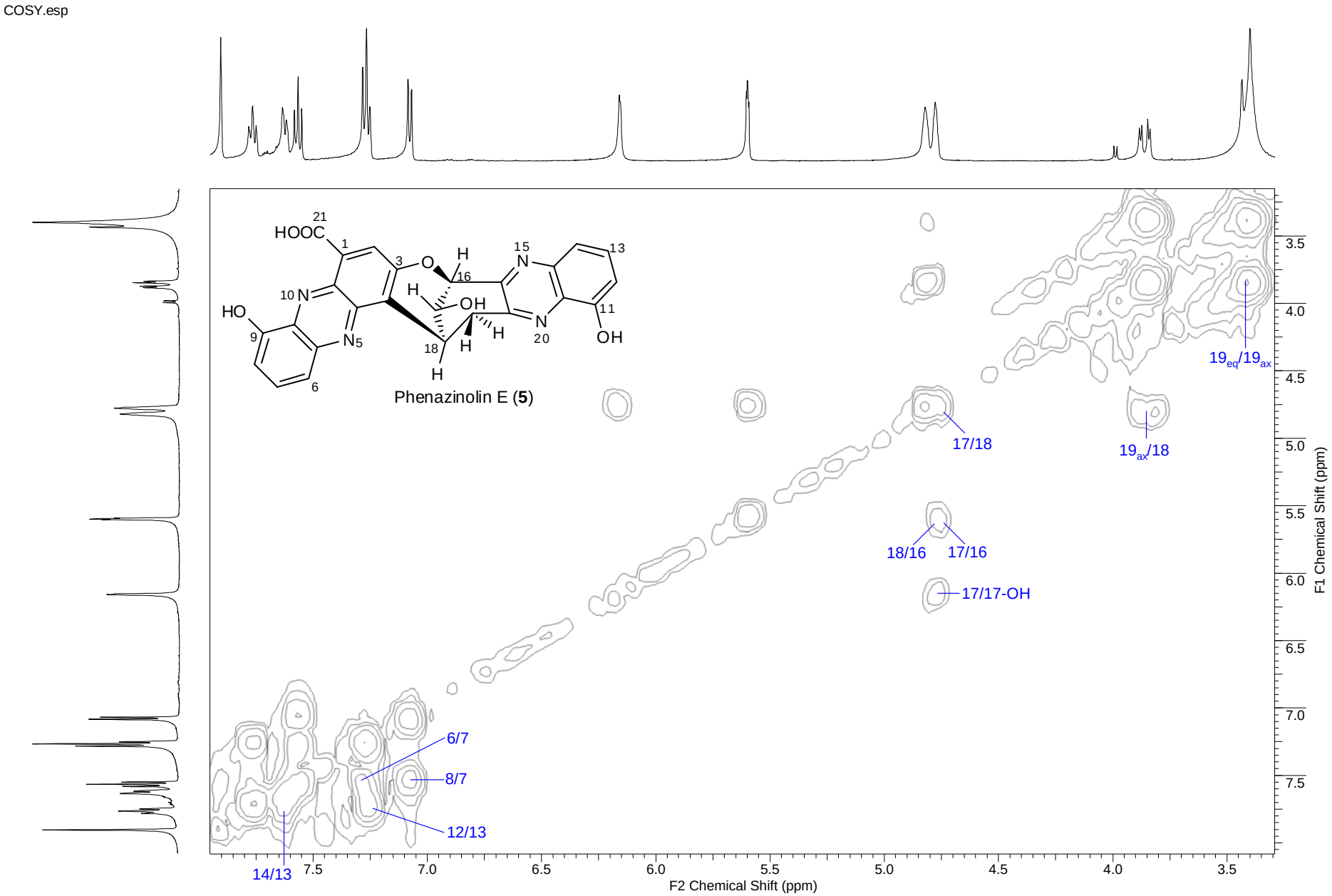


Fig. S51. ^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin E (**5**)

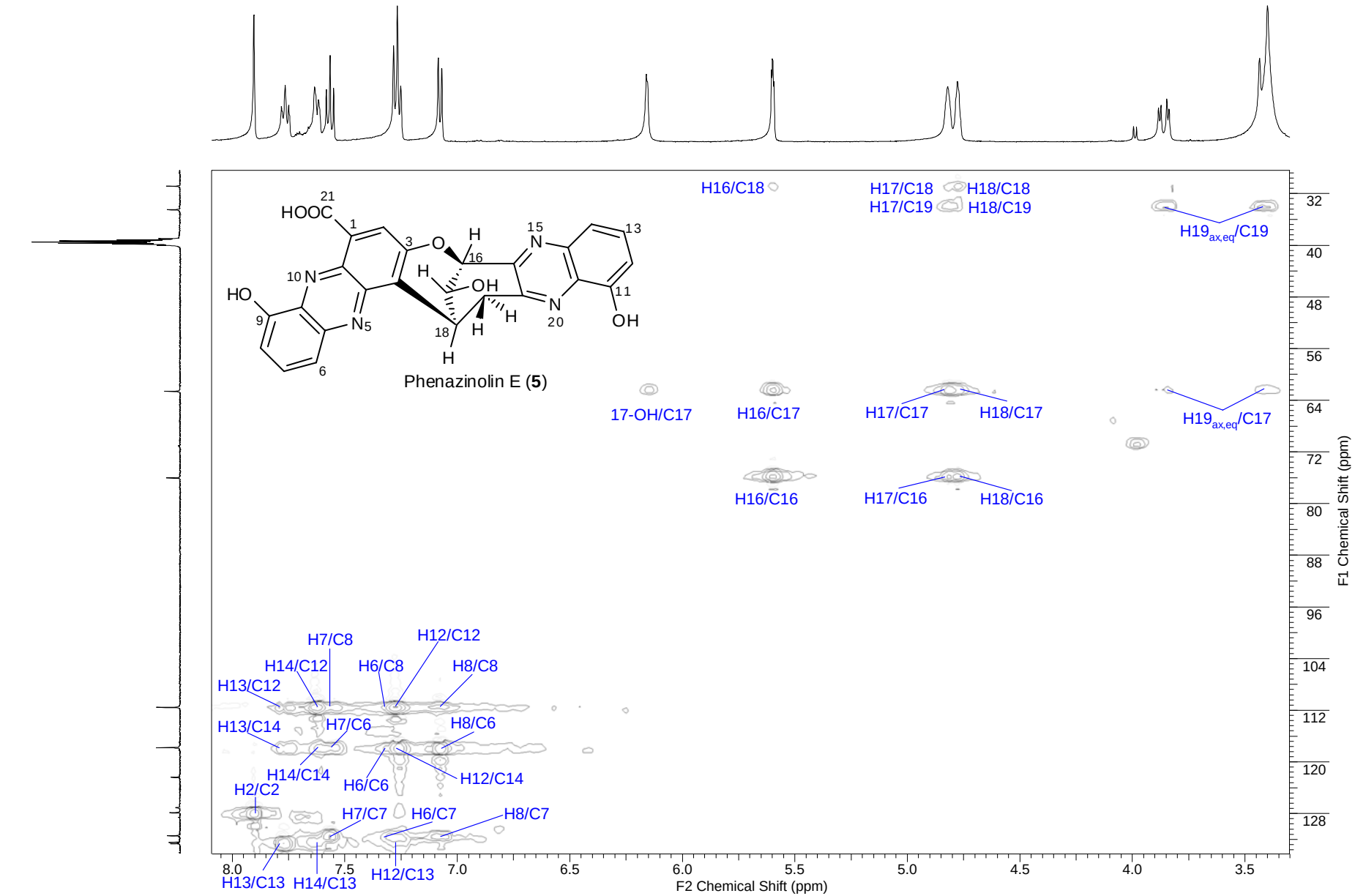


Fig. S52. HMQC-TOCSY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin E (**5**)

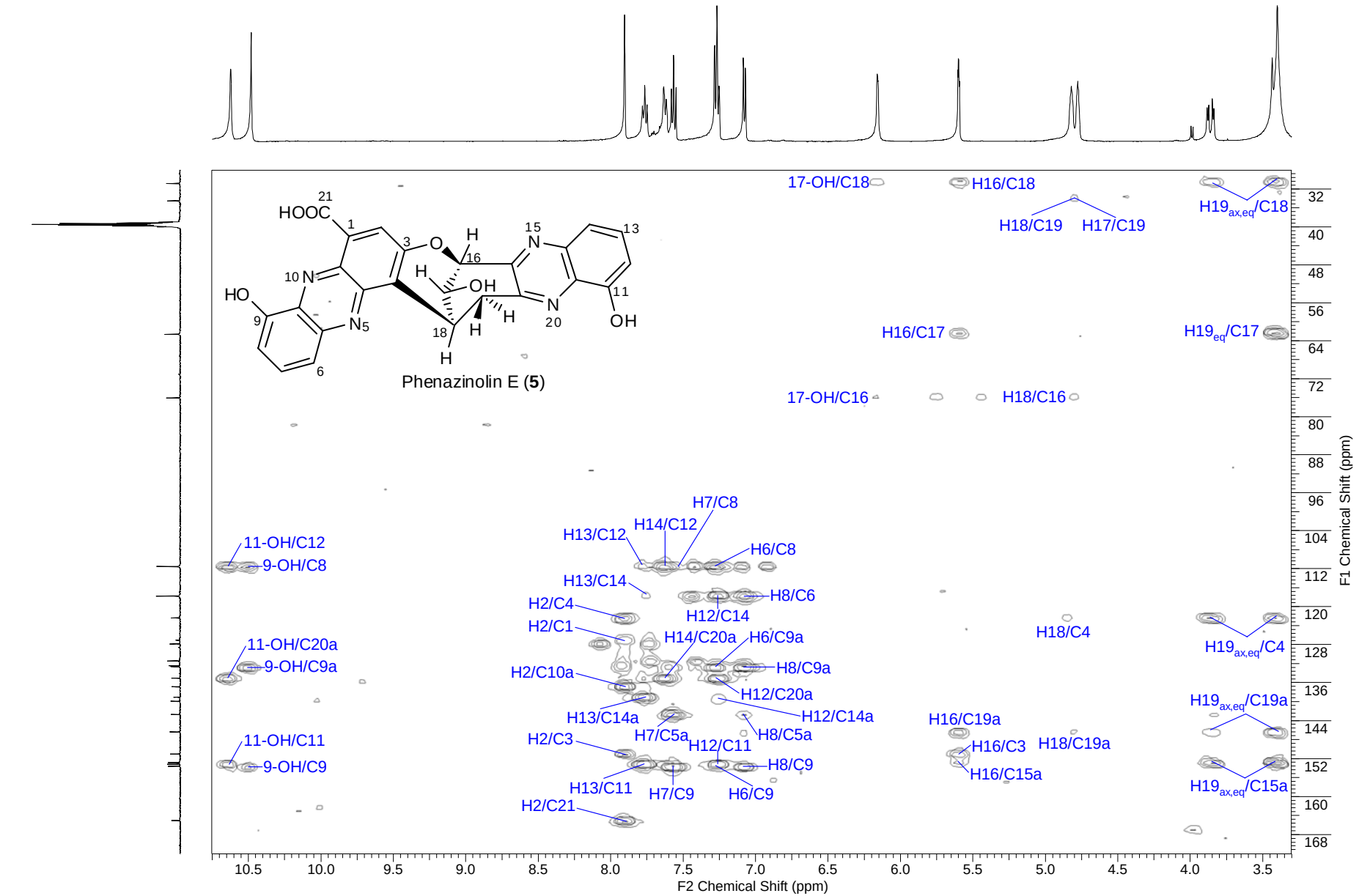


Fig. S53. ^{1}H-^{13}C HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin E (**5**)

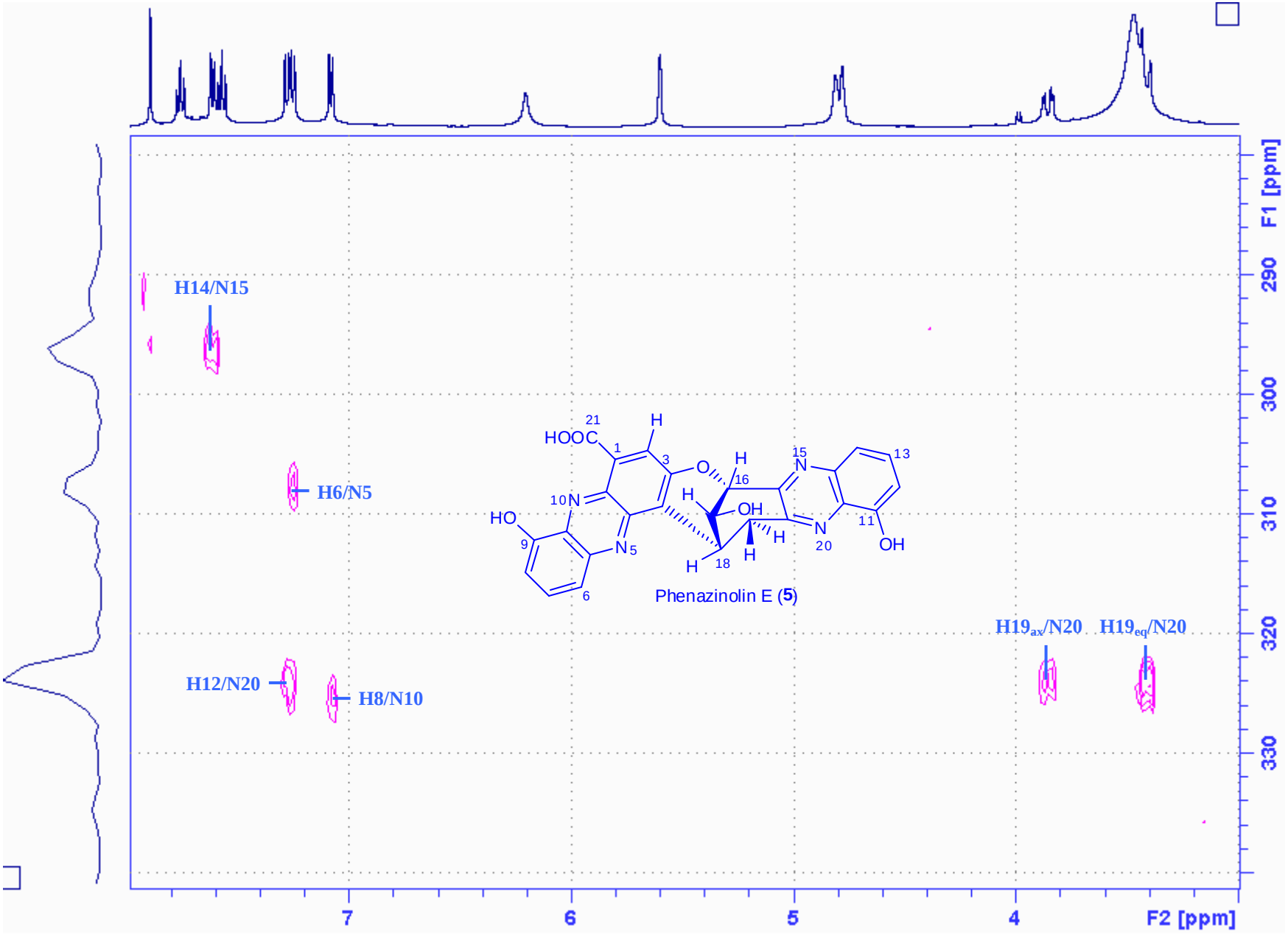


Fig. S54. ^{1}H-^{15}N HMBC NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin E (**5**)

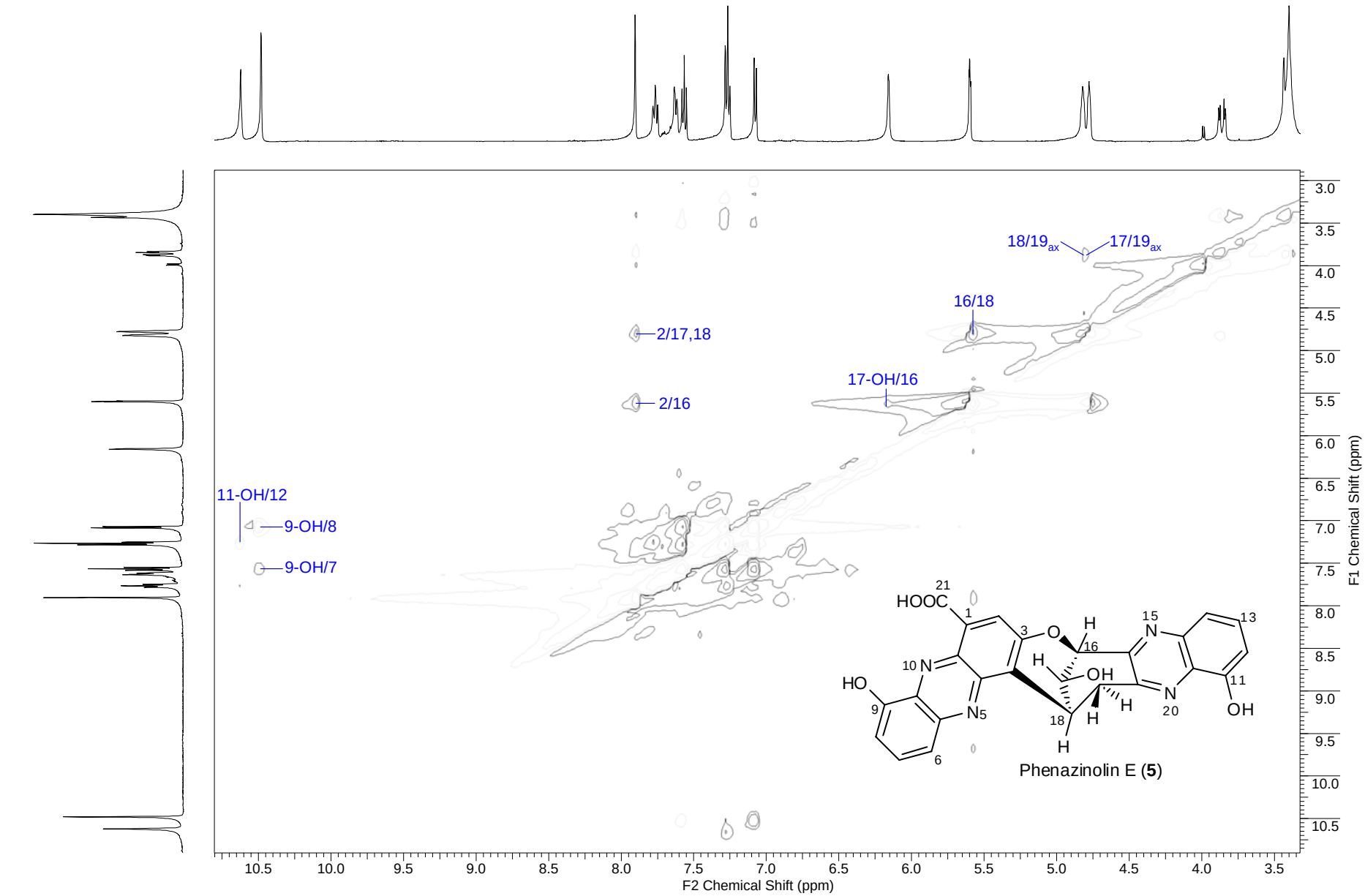


Fig. S55. ROESY NMR (500 MHz, DMSO-d_6) Spectrum of Phenazinolin E (**5**)

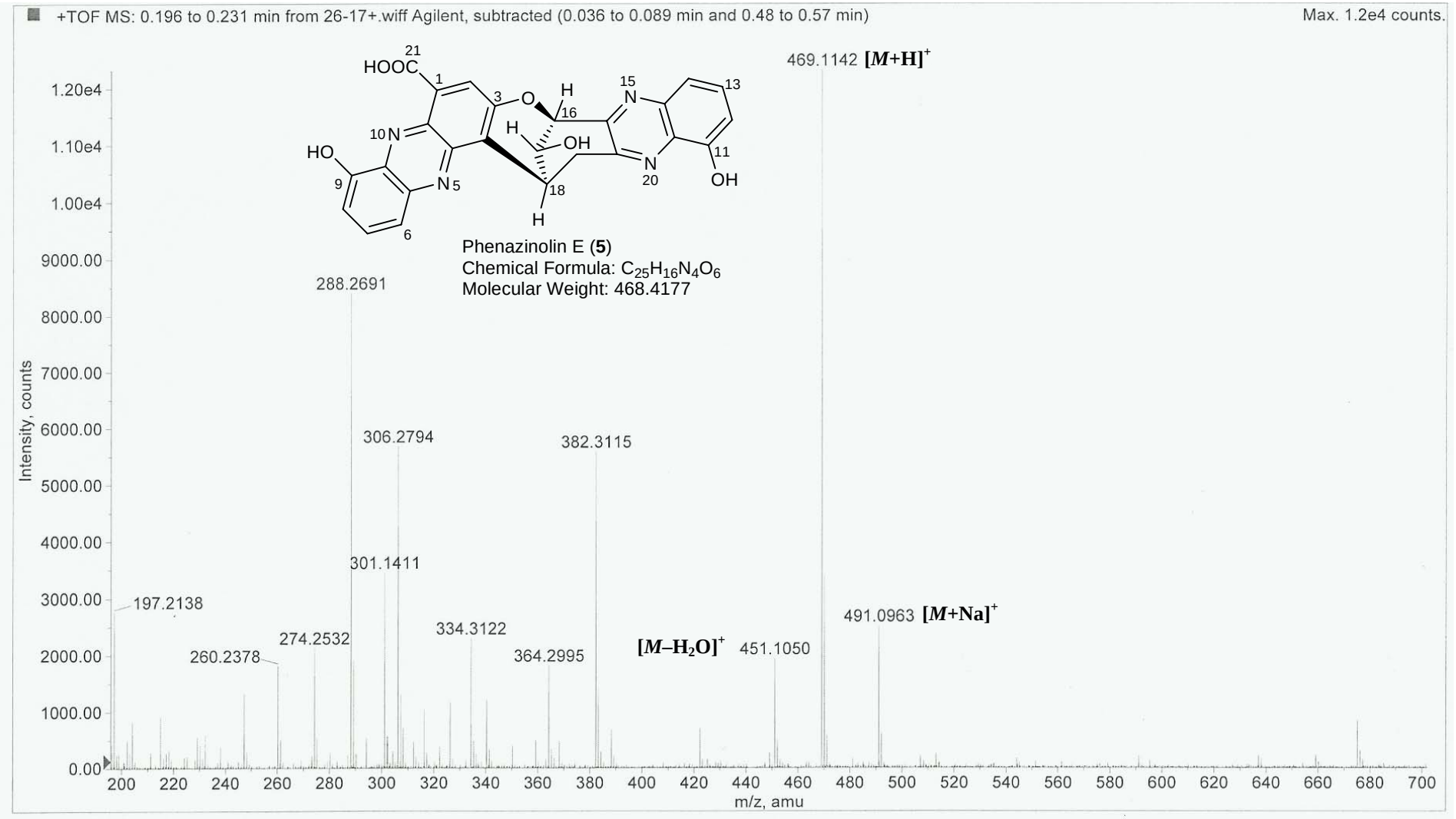


Fig. S56. HR-ESIMS(+) Spectrum of Phenazinolin E (**5**)

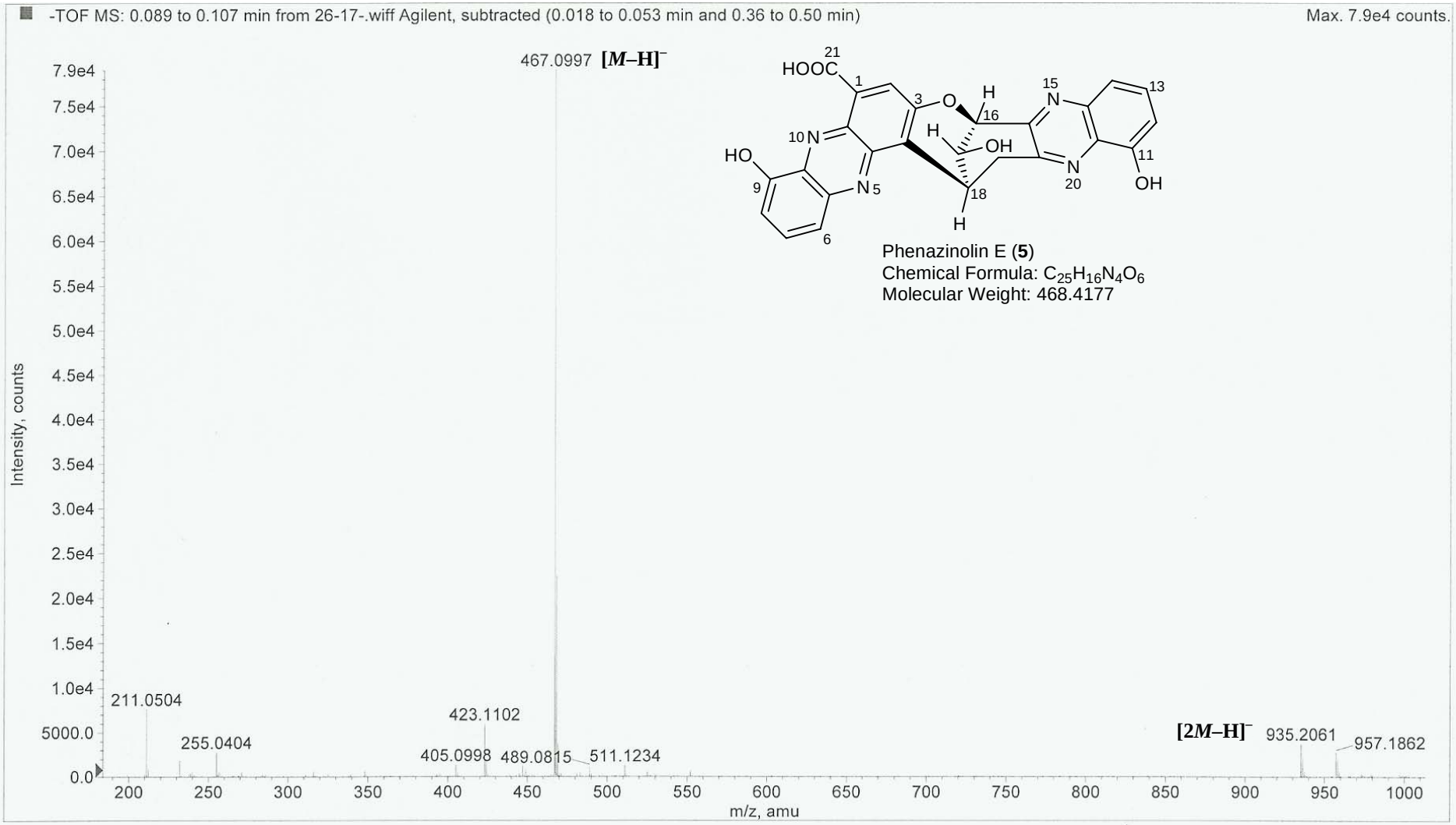
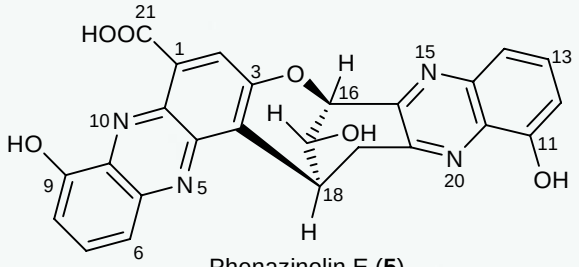


Fig. S57. HR-ESIMS(–) Spectrum of Phenazinolin E (**5**)

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
1	C25 H17 N4 O6	469.1142	-0.0609	-0.1299	19.5
2	C26 H16 N5 O3 Na	469.1145	-0.3357	-0.7156	21.0
3	C11 H22 N6 O13 Na	469.1137	0.4936	1.0522	3.5
4	C12 H25 N2 O17	469.1147	-0.5743	-1.2242	1.5
5	C10 H23 N5 O16	469.1134	0.7683	1.6379	2.0
6	C13 H24 N3 O14 Na	469.1150	-0.8490	-1.8099	3.0
7	C25 H20 N O7 Na	469.1131	1.0015	2.1350	16.0
8	C24 H21 O10	469.1129	1.2763	2.7207	14.5
9	C27 H19 N O7	469.1156	-1.4036	-2.9921	19.0



Phenazinolin E (**5**)
Chemical Formula: $C_{25}H_{16}N_4O_6$
Molecular Weight: 468.4177

Fig. S58. HR-ESIMS(+) Data for Phenazinolin E (**5**)

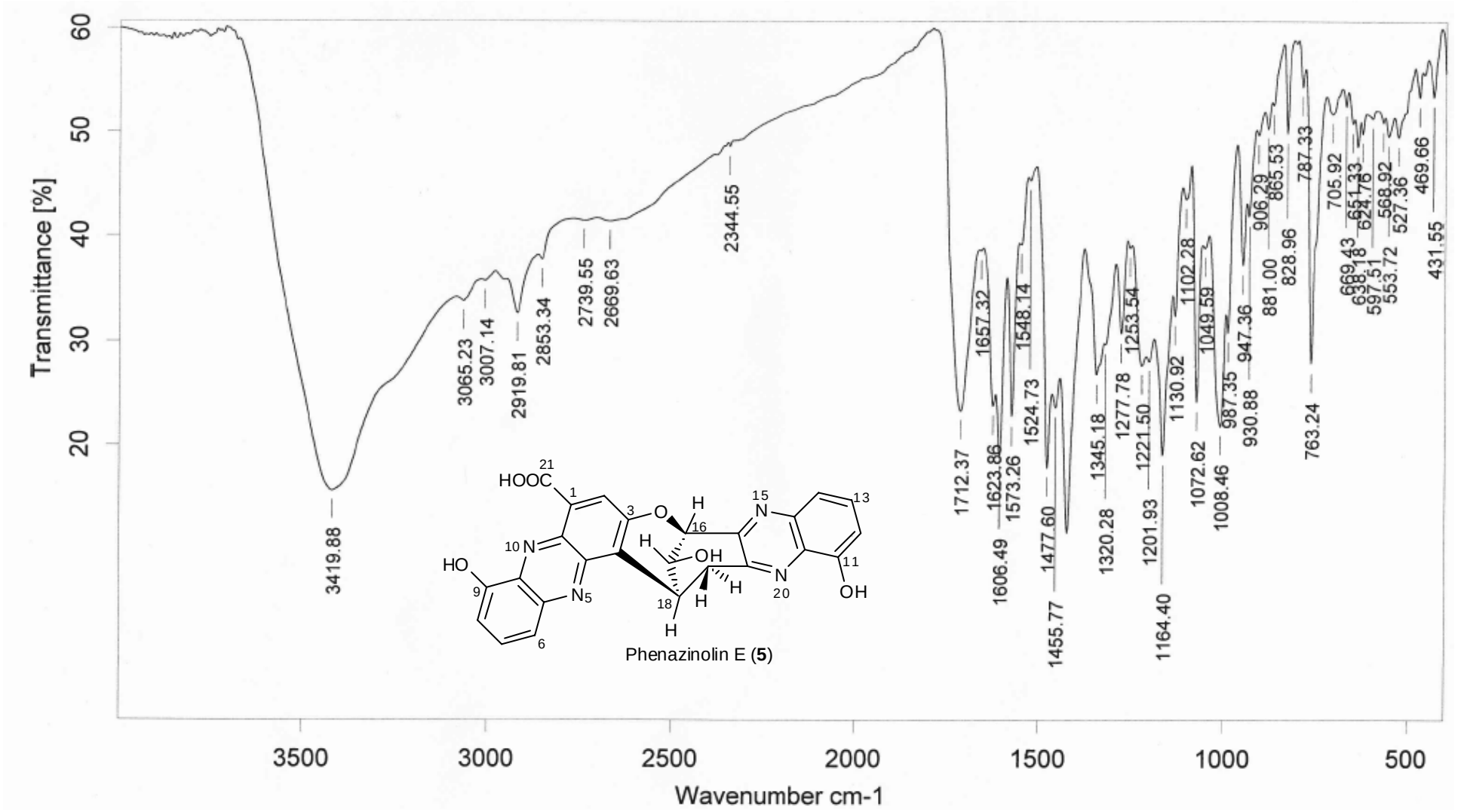


Fig. S59. IR Spectrum of Phenazinolin E (**5**)