Supplementary Material for: Metathramycin, a new bioactive aureolic acid discovered by heterologous expression of a metagenome derived biosynthetic pathway.

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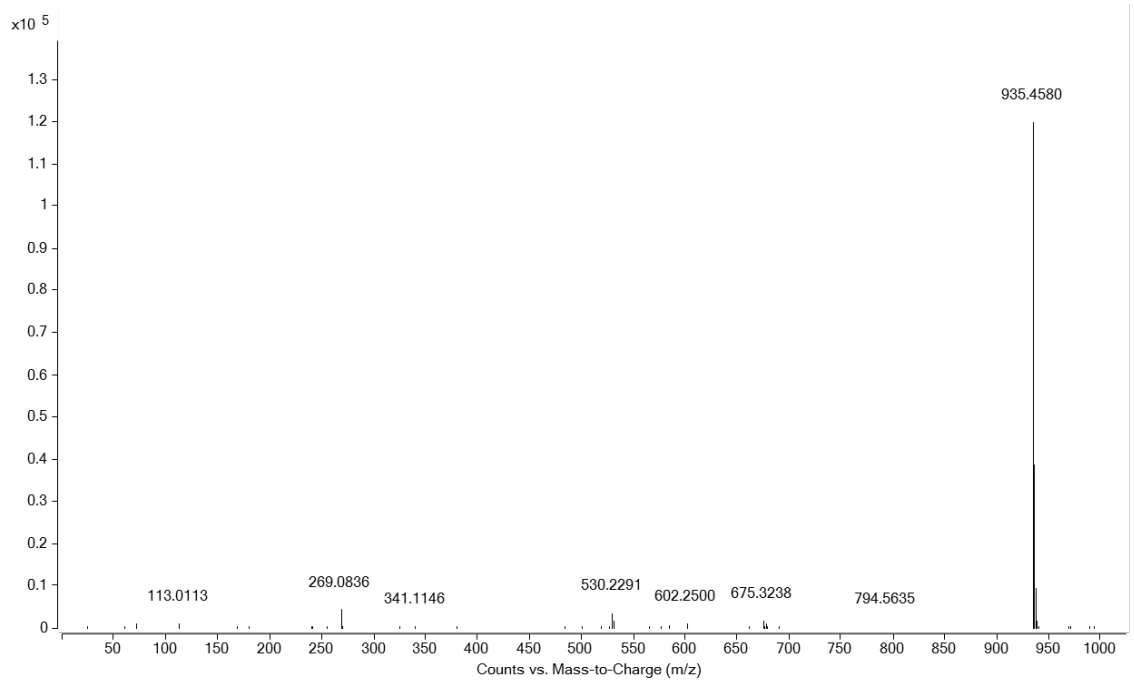
Figures

Tables

Figure S1 – MS/MS spectra for mithramycin (1) standard ($[M-H]^-$ = 1083.4647):

CID = 20.0 eV



CID = 60.0 eV

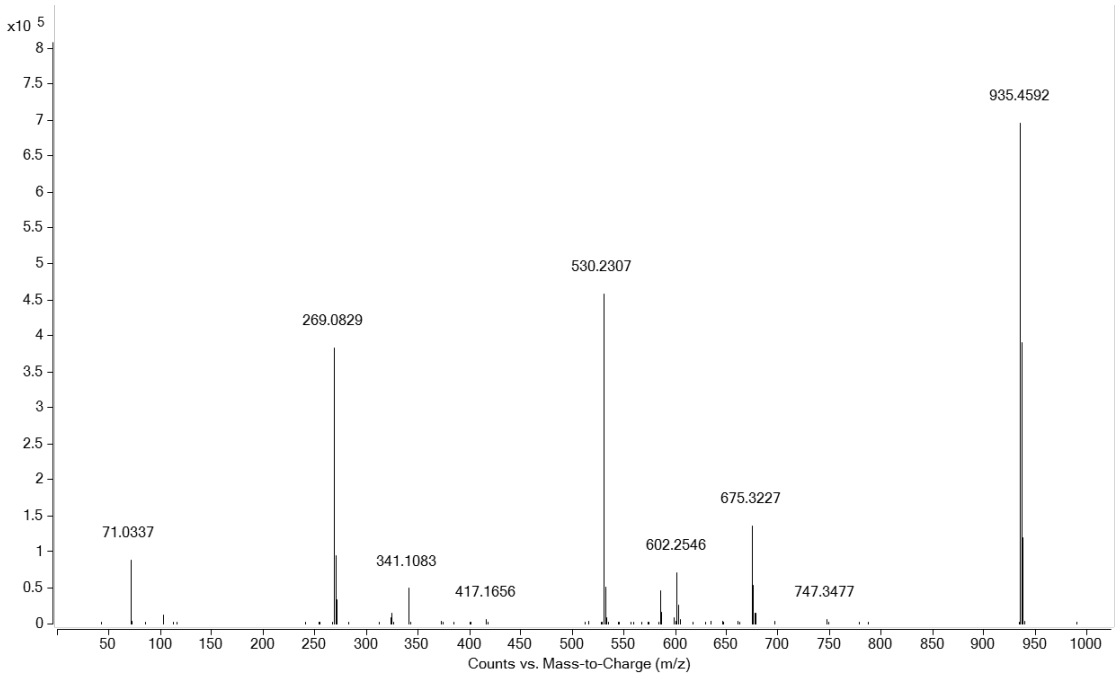
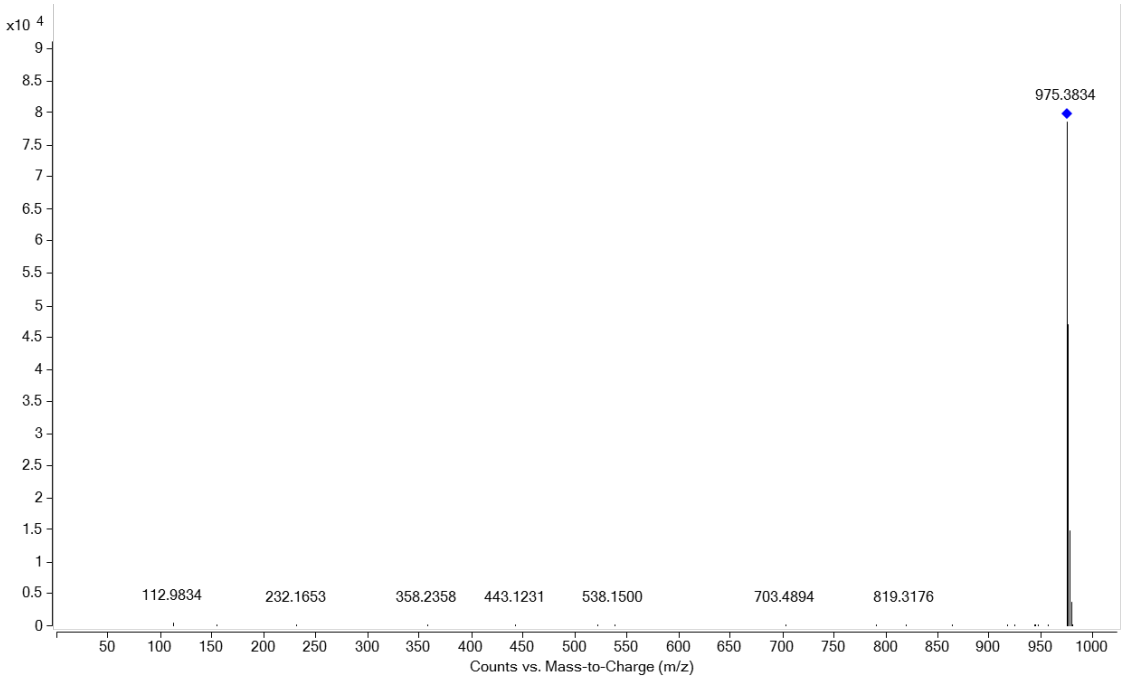


Figure S2 – MS/MS spectra for premetathramycin (5) ([M-H]$^-$ = 975.3848):

CID = 20.0 eV



CID = 60.0 eV

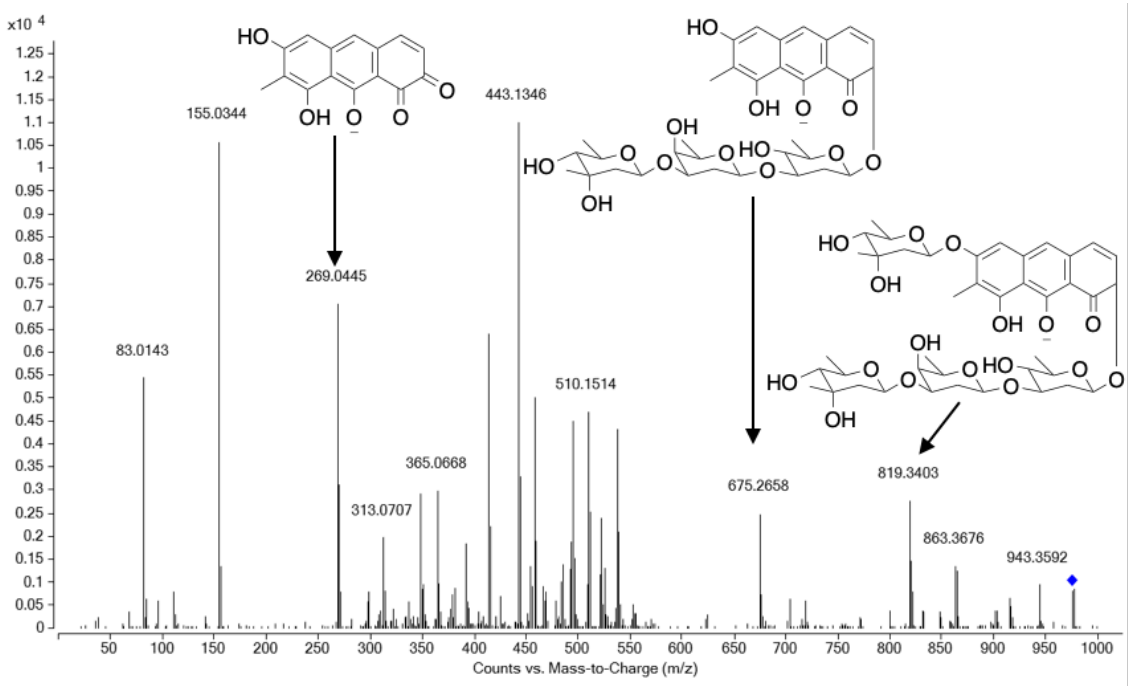
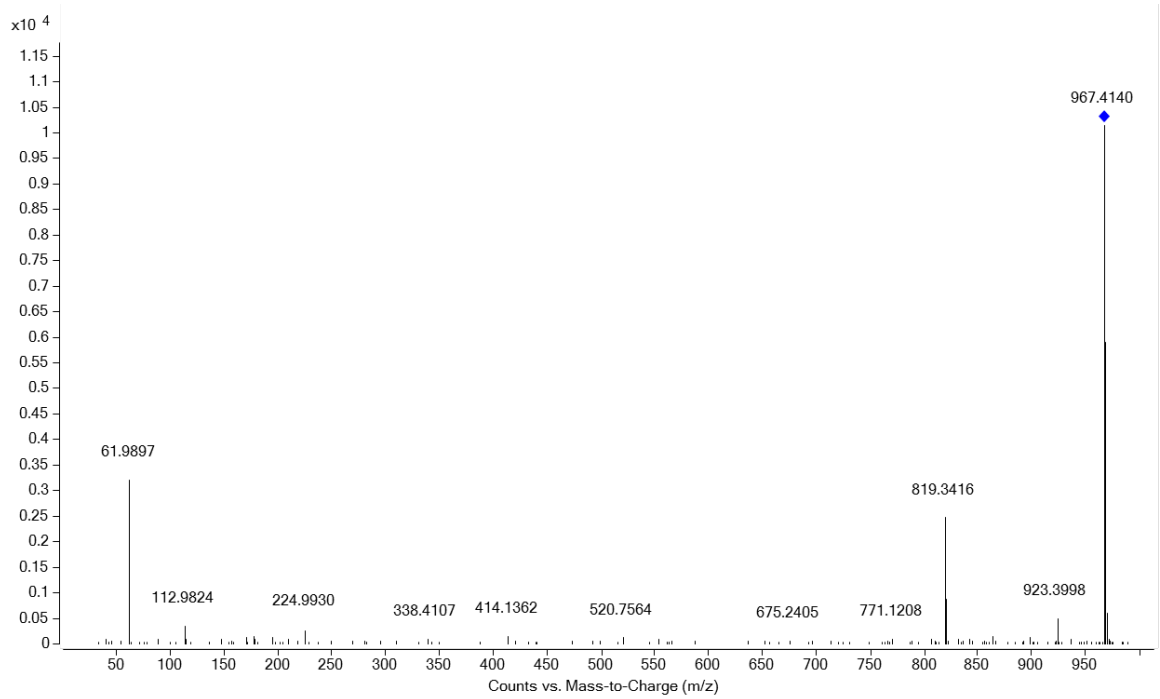


Figure S3 – MS/MS spectra for metathramycin (6) ([M-H]$^-$ = 967.4186):

CID = 20.0 eV



CID = 60.0 eV

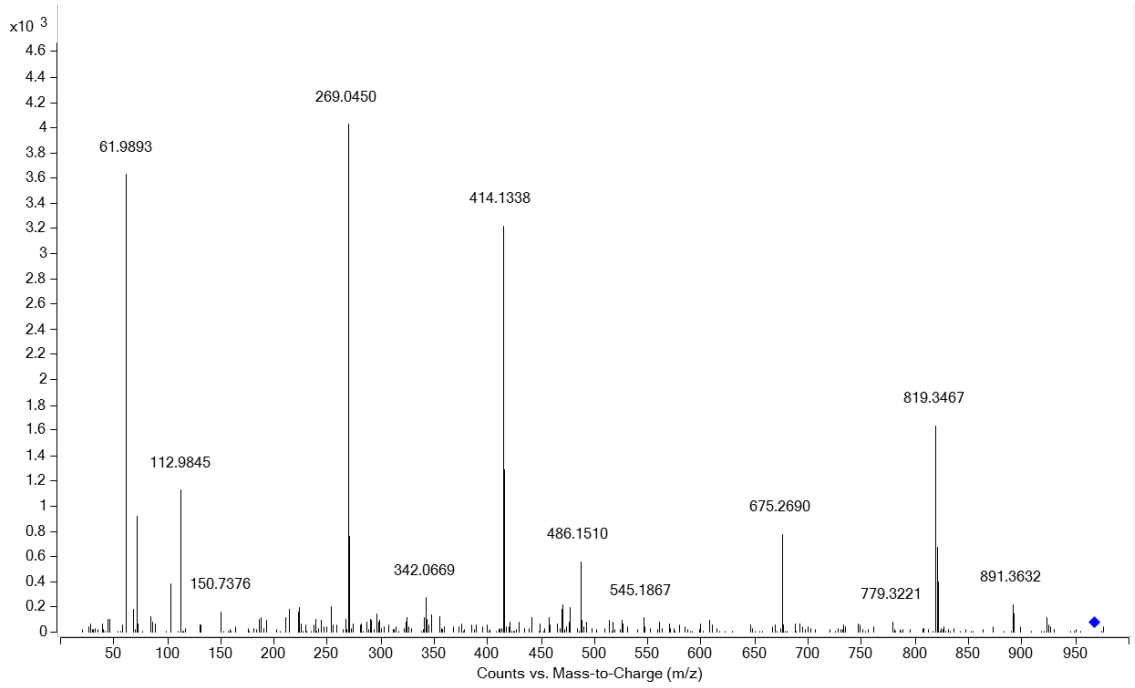


Figure S4 – ^{1}H spectrum of premetathramycin (5) (600 MHz, 1:1 $CDCl_3$: CD_3OD):

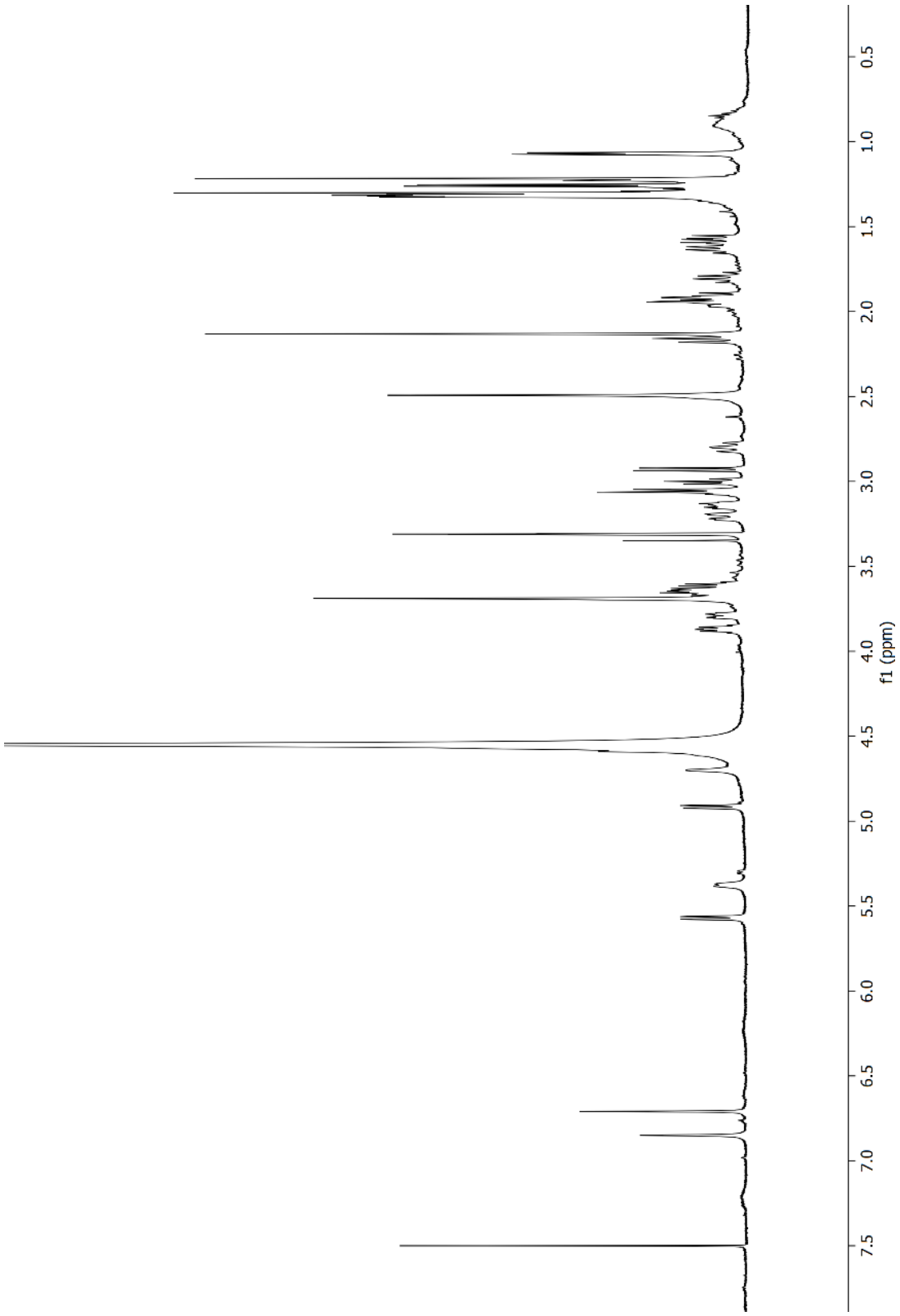


Figure S5 – ^{13}C spectrum of premetathramycin (5) (150 MHz, 1:1 $CDCl_3$: CD_3OD):

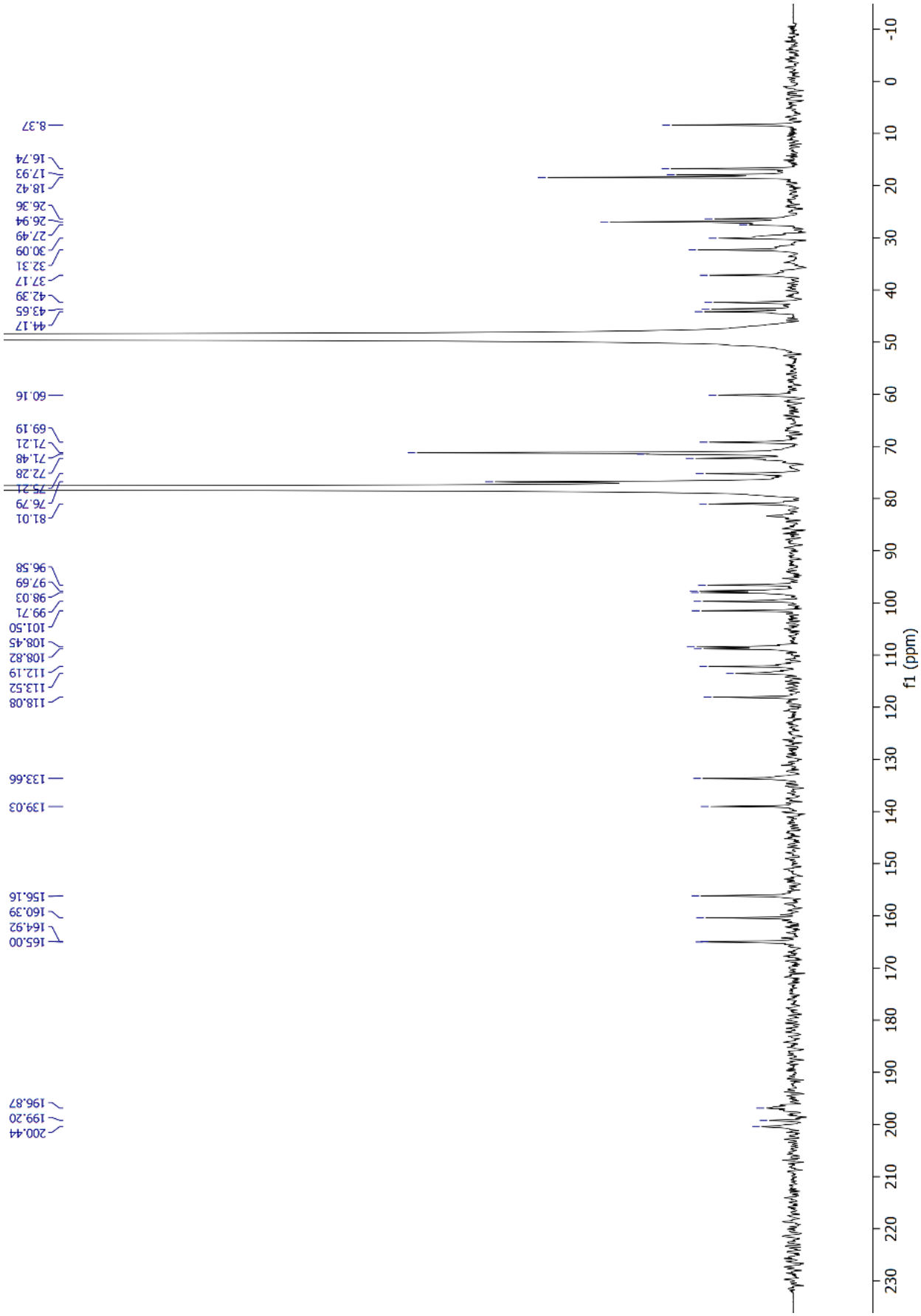


Figure S6 – COSY spectrum of premetathramycin (5) (600 MHz, 1:1 $CDCl_3$: CD_3OD):

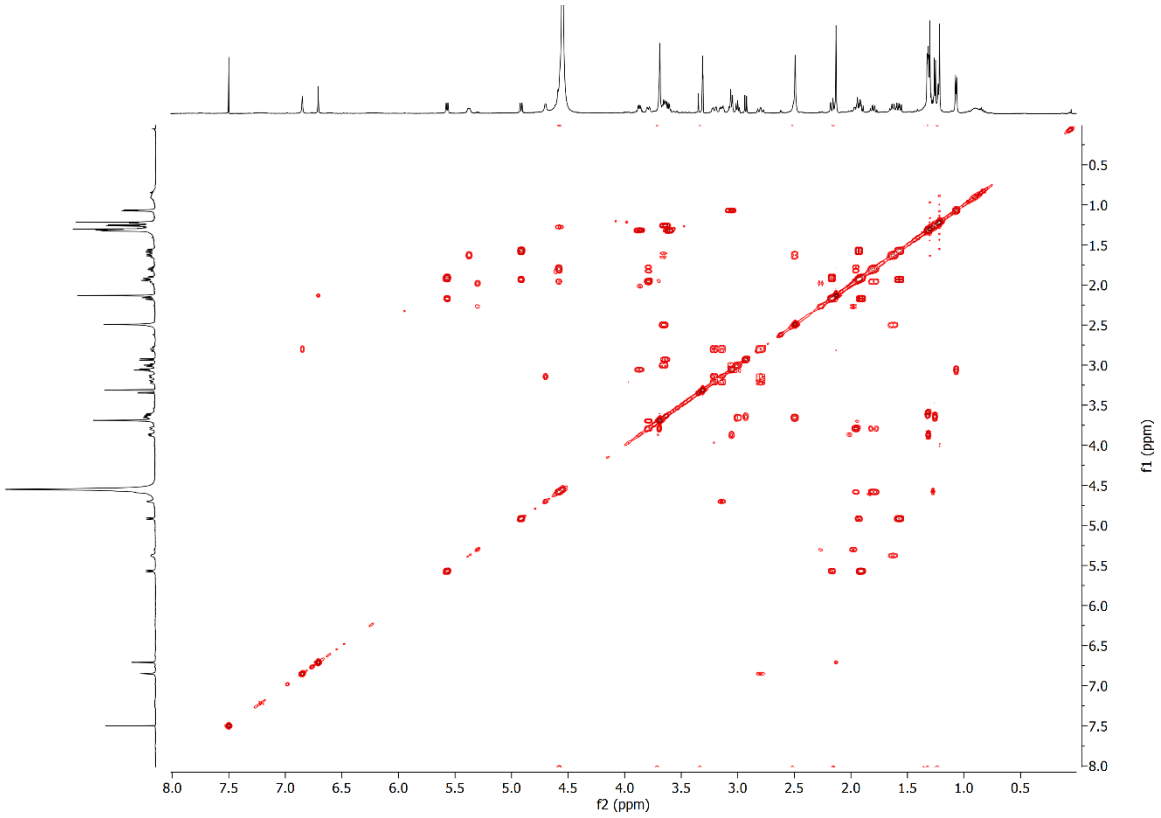


Figure S7 – HSQC spectrum of premetathramycin (5) (600 MHz, 1:1 $CDCl_3$: CD_3OD):

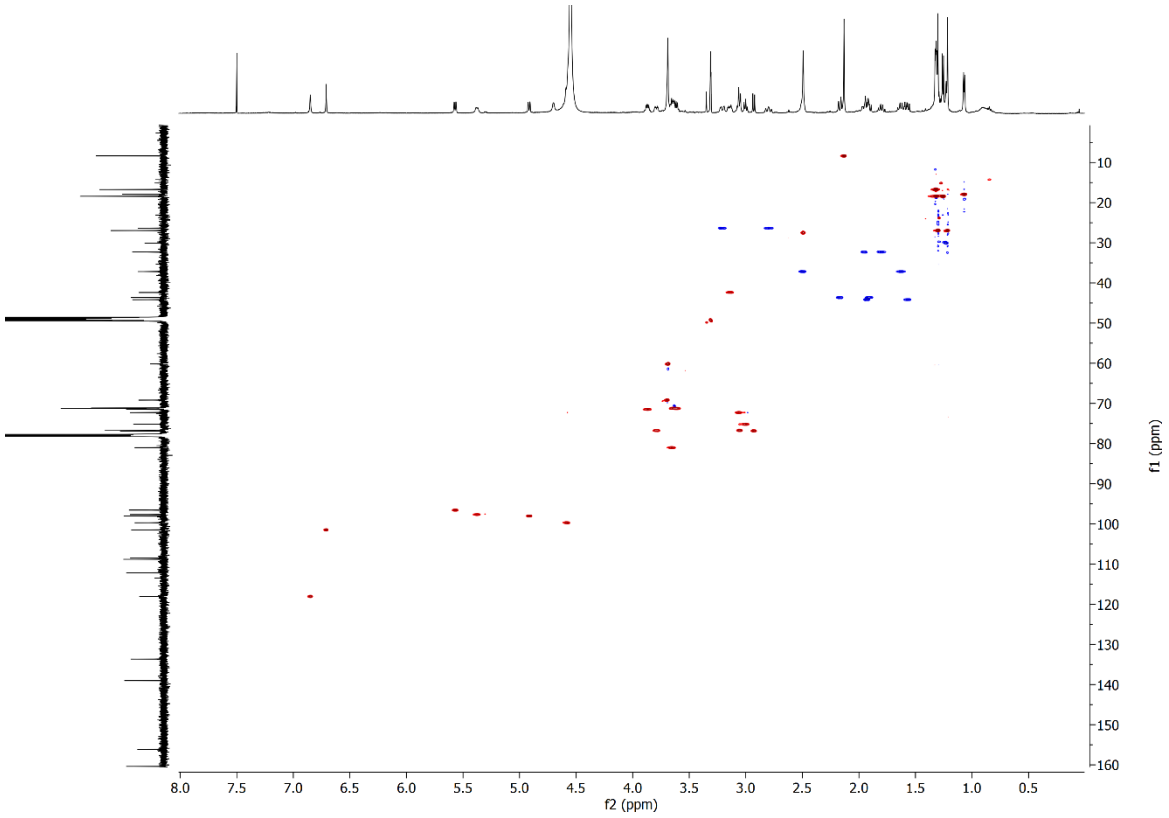


Figure S8 – HMBC spectrum of premetathramycin (5) (600 MHz, 1:1 $CDCl_3$: CD_3OD):

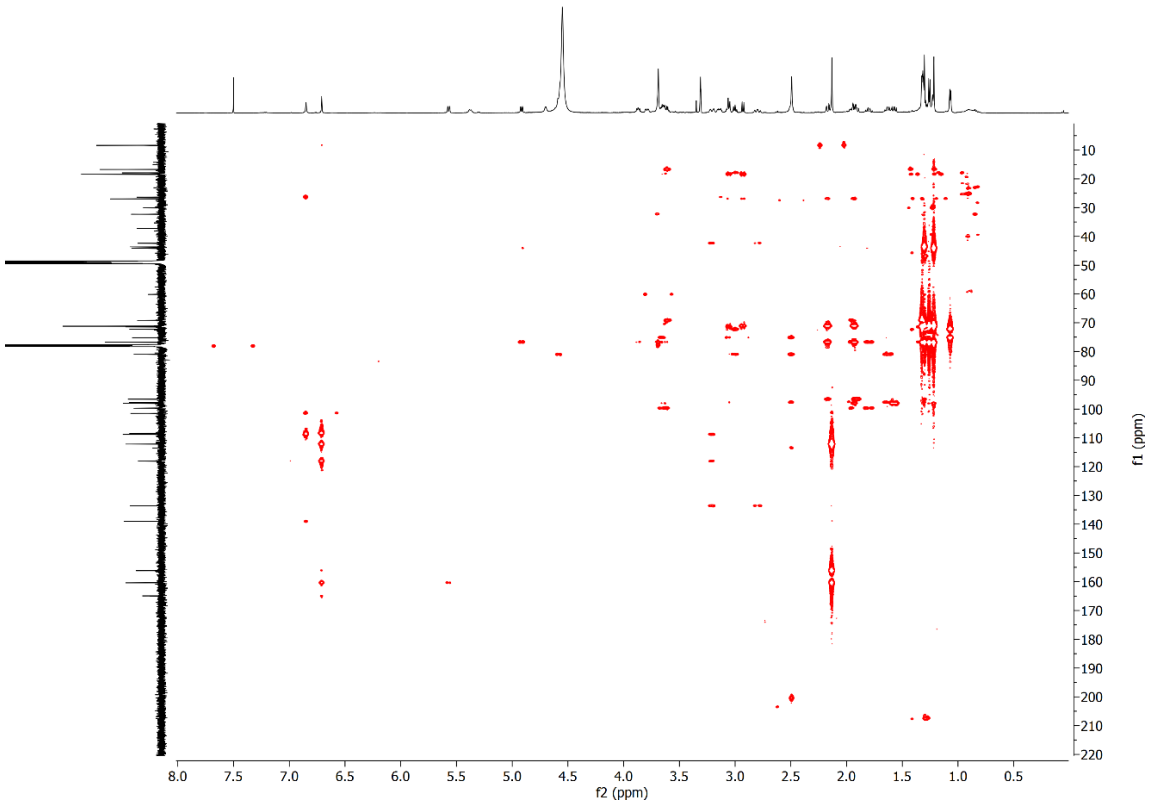


Figure S9 – HSQC-TOCSY spectrum of premetathramycin (5) (600 MHz, 1:1 $CDCl_3$: CD_3OD):

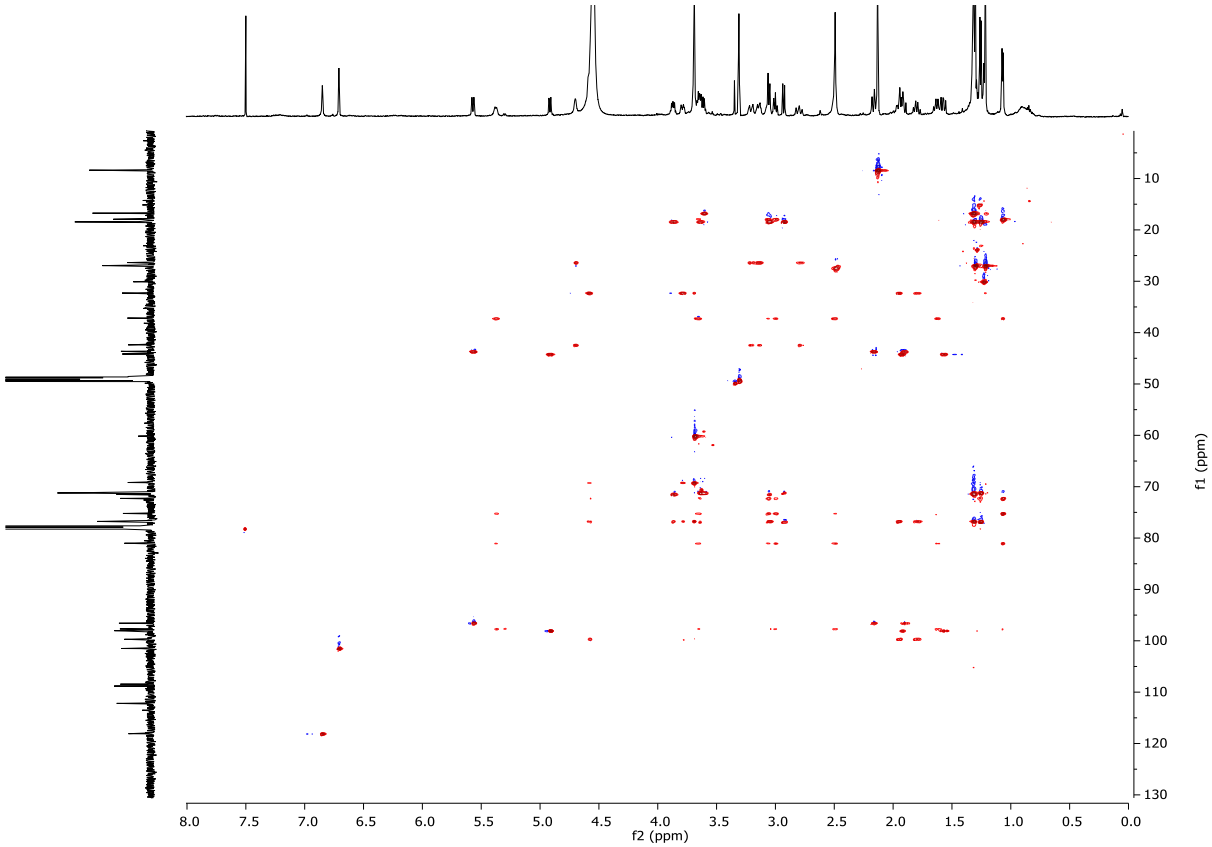


Figure S10 – ROSEY spectrum of premetathramycin (5) (600 MHz, 1:1 $CDCl_3$: CD_3OD):

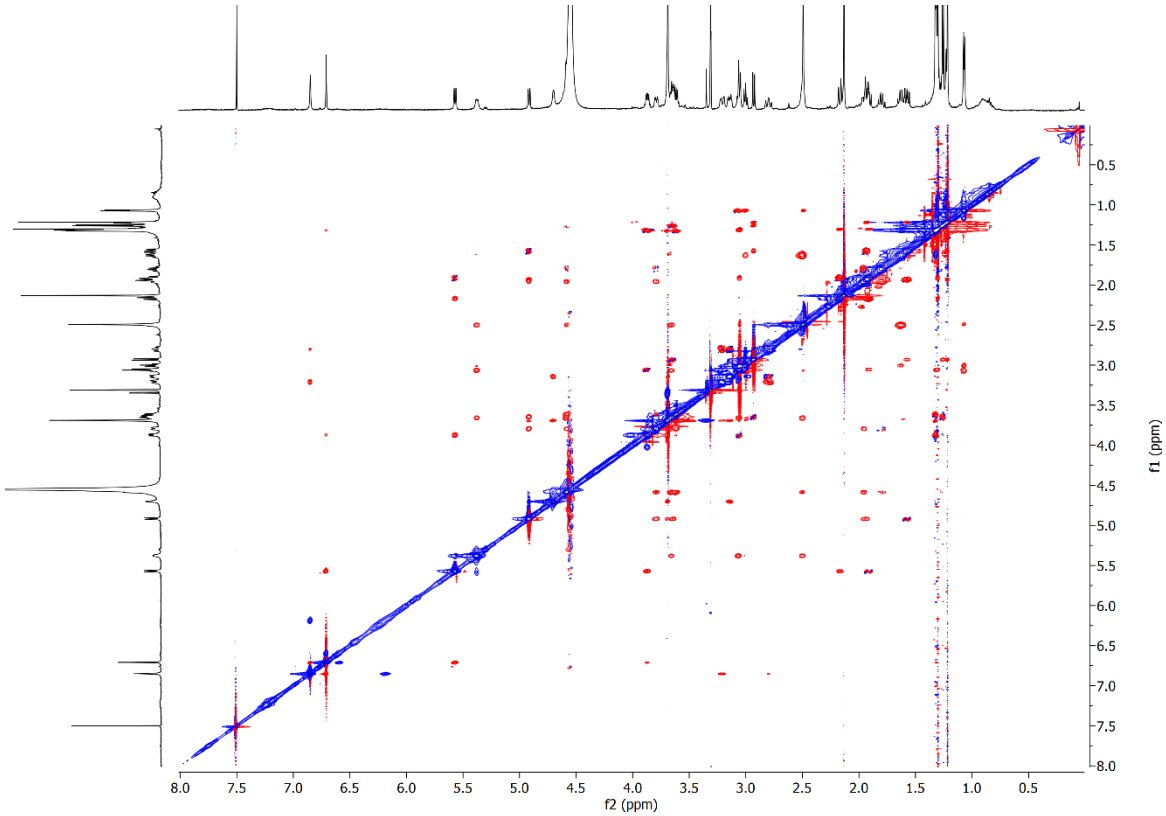


Figure S11 – IR spectrum of premetathramycin (5):

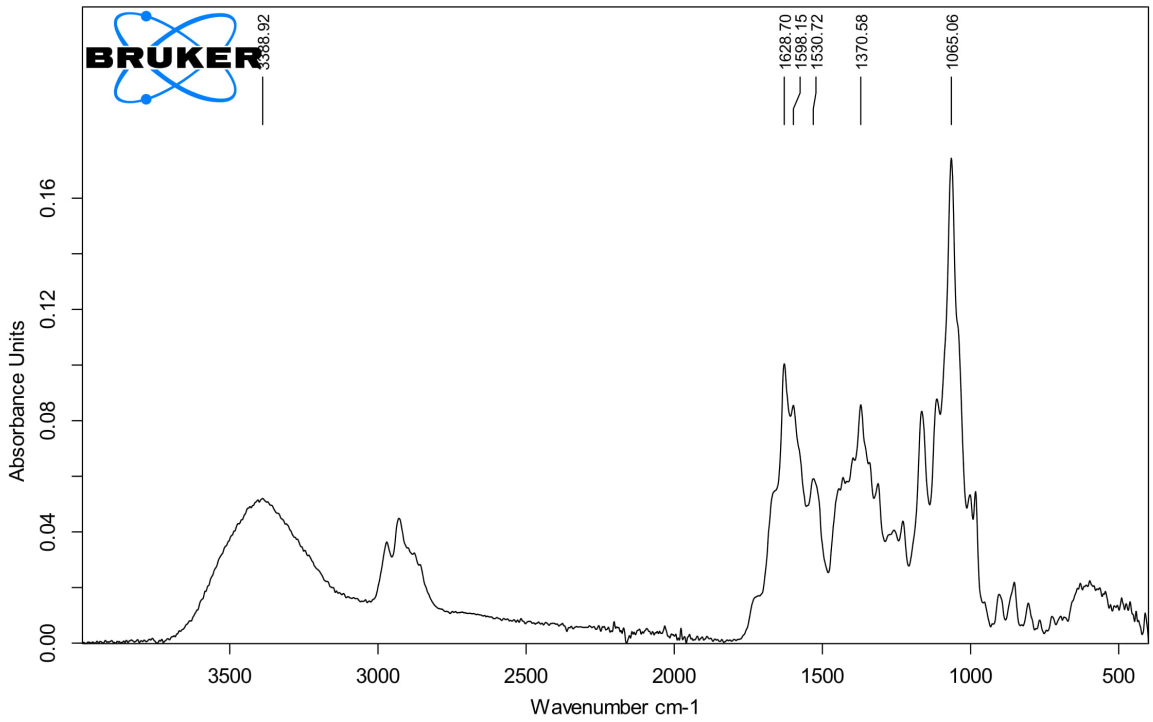


Table S1 - Chemical shifts and correlations for aglycone of Compound 5. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data in 1:1 $CDCl_3$:CD_3OD.

position	^{13}C (δ)		^{1}H (δ, mult., *J in Hz)*	COSY	HMBC	ROESY
1	196.9	CO				
2	113.5	C				
3	164.9	C				
4	77.6	CH	4.70 (br s)	5		5, 6b, 21
5	42.1	CH	3.14 (dt, 10.0, 4.7)	4, 6	6	4, 6a, 6b, 21
6a	26.4	CH_2	2.80 (dd, 11.0, 17.0)	5, 8	5, 7	5, 8, 21
6b			3.21 (dd, 17.4, 4.2)	5, 8	5, 7	4, 8
7	133.5	C				
8	117.8	CH	6.85 (s)	6	6, 9, 10, 14, 16	6a, 6b, 10
9	139.1	C				
10	101.2	CH	6.71 (s)	22	8, 11, 12, 14	8, A1, D6, D7
11	160.4	C				
12	112.2	C				
13	156.2	C				
14	108.5	C				
15	165	C				
16	108.8	C				
17	199.2	CO				
18	nd	C				
19	200.4	CO				
20	27.4	CH_3	2.49 (s)		2, 19	
21	59.8	OCH_3	3.69 (s)		4	4, 5, 6a
22	8.4	CH_3	2.13 (s)	10	11, 12, 13	

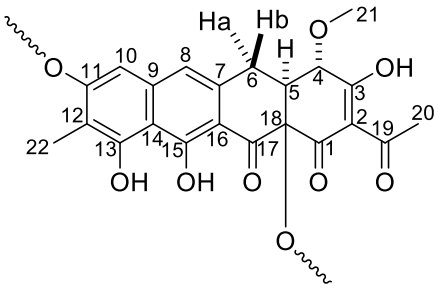


Table S2 - Chemical shifts and correlations for sugars in compound 5 (ol = overlapped). ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data in 1:1 $CDCl_3$:CD_3OD.

position	^{13}C (δ)		^{1}H (δ, mult., *J in Hz)*	COSY	HMBC	ROESY
A1	96.5	CH	5.57 (dd, 9.6, 2.2)	A2	11	10, D6, A2b
A2a	43.6	CH_2	1.91 (d, 13.2, 9.6)	A1	A1, A3, A3-Me, A4,	A3-Me
A2b			2.17 (dd, 2.2, 13.0)			A1, A3-Me
A3	71.2					
A3-Me	26.9	CH_3	1.30 (s)		A1, A2, A3, A4,	A2
A4	76.8	CH	2.93 (d, 9.4)	A5	A3, A3-Me, A5, A6	A6, D2a, D4
A5	71.2	CH	3.64 (ol.)	A4, A6	A4, A6	A6
A6	18.4	CH_3	1.26 (d, 6.2)	A5	A4, A5	A4
B1	97.6	CH	5.37 (d, 9.7)	B2		B2b, B3, B5,
B2a	37.2	CH_2	1.62 (q, 11.7)	B1, B3	B1, B3, B4	B4
B2b			2.50 (ol.)		B1, B3, B4	B1
B3	81.0	CH	3.66 (ol.)	B2, B4	B4, C1	B1
B4	75.5	CH	3.01 (t, 8.8)	B3, B5	B3, B5, B6	B2a, B6
B5	72.2	CH	3.05 (ol.)	B4, B6	B1, B4, B6	B1
B6	17.9	CH_3	1.07 (d, 6.0)	B5	B4, B5	B4
C1	99.7	CH	4.58 (ol.)	C2	B3, C2	C2b, C3, C5
C2a	32.3	CH_2	1.80 (q, 12.0)	C1, C3	C1, C3, C4	
C2b			1.95 (ol.)		C1, C3, C4	C1, C3
C3	76.8	CH	3.79 (dt, 12.0, 4.0)	C2, C4	D1	C1, C4, C5, D1
C4	69.1	CH	3.69 (ol.)	C3, C5	C2, C3	D1, C5
C5	71.1	CH	3.61 (ol.)	C4, C6	C1, C3, C4, C6	C1, C3, C4
C6	16.8	CH_3	1.32 (d, 6.7)	C5	C3, C4, C5	
D1	98	CH	4.91 (dd, 9.7, 2.1)	D2	C3, D2	C3, C4, D2b
D2a	44.2	CH_2	1.57 (dd, 13.8, 9.7)	D1	D1	A4, D3-Me
D2b			1.93 (ol.)		D1, D3, D3-Me, D4	D1, D3-Me
D3	76.7	C				
D3-Me	26.9	CH_3	1.22 (s)		D1, D2, D3, D4	D2a, D2b
D4	76.8	CH	3.05 (ol.)	D5	D3, D3-Me, D5, D6	A4, D6
D5	71.5	CH	3.87 (dq, 8.3, 6.0)	D4, D6	D3, D4, D6	
D6	18.3	CH_3	1.31 (d, 5.8)	D5	D4, D5	A1, D4