Supporting Information for:

Bridged Epipolythiodiketopiperazines from *Penicillium raciborskii*, an endophytic fungus of *Rhododendron tomentosum* Harmaja

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Full reference #38

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision B.1;* Gaussian Inc. Wallingford CT 2009.

Figure S1 HRESIMS spectra of outovirin A (1), outovirin B (2), outovirin C (3), and MSMS spectrum of the *m/z* 283 fragment ion common to the three compounds.

Figure S2 500 MHz ^{1}H spectra of outovirin A (1), outovirin B (2), and outovirin C (3) in CD_3OD.

Figure S3 500 MHz ^{1}H-^{1}H COSY-45 spectrum of outovirin B (2) in CD_3OD.

Figure S4 500 MHz ^{1}H-^{1}H NOESY spectrum of outovirin B (2) in CD_3OD. Red indicates positive signal intensity and green indicates negative signal intensity.

Figure S5 500 MHz ^{1}H-^{13}C HSQC spectrum of outovirin B (2) in CD_3OD.

Figure S6 500 MHz ^{1}H-^{13}C HMBC spectra of outovirin B (2) in CD_3OD. Two independently acquired spectra are overlaid, as denoted by red and cyan.

Figure S7 500 MHz ^{1}H-^{1}H COSY-45 spectrum of outovirin A (1) in CD_3OD.

Figure S8 500 MHz ^{1}H-^{13}C HSQC spectrum of outovirin A (1) in CD_3OD.

Figure S9 500 MHz ^{1}H-^{13}C HMBC spectrum of outovirin A (1) in CD_3OD.

Figure S10 500 MHz ^{1}H-^{1}H COSY-45 spectrum of outovirin C (3) in CD_3OD.

Figure S11 500 MHz ^{1}H-^{13}C HSQC spectrum of outovirin C (3) in CD_3OD.

Figure S12 500 MHz ^{1}H-^{13}C HMBC spectrum of outovirin C (3) in CD_3OD.

Table S1 Chemical shifts (in ppm) of outovirin A (1), outovirin B (2) and outovirin C (3) in CD_3OD (exp) and *ab initio* simulations (calc)

Scheme S1 Outovirin B (2) labeled according to the numbering schemes based on Gliovirin[22] and Pretrichodermamide A[24].

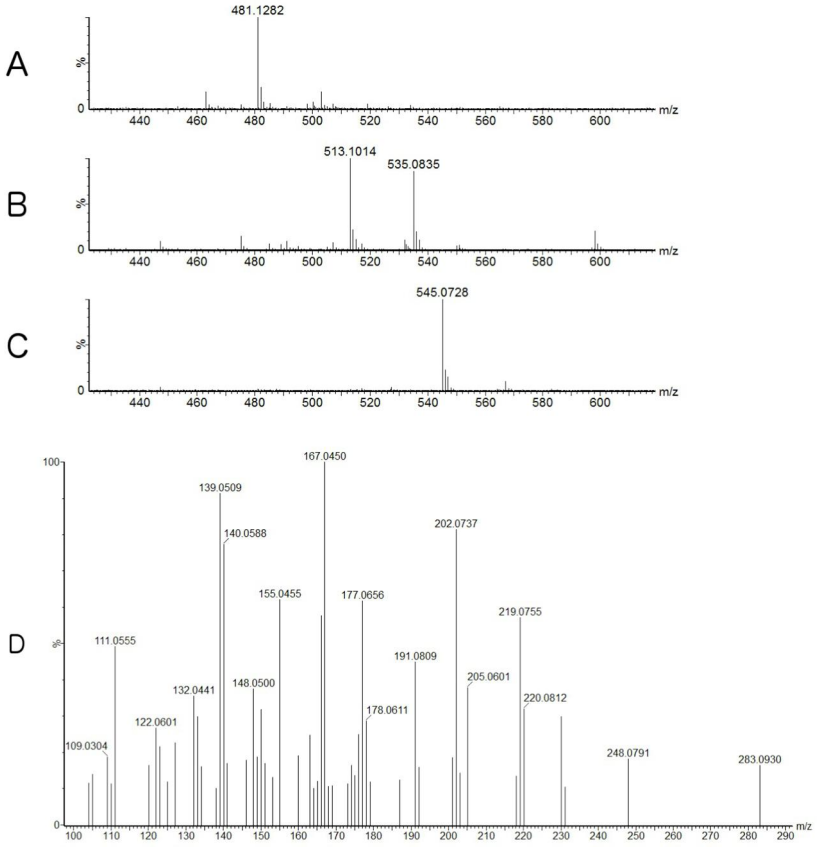


Figure S1 HRESIMS spectra of A) outovirin A (1) (*m/z* 481.1282), B) outovirin B (2) (*m/z* 513.1014), C) outovirin C (3) (*m/z* 545.0728), and D) MSMS spectrum of the *m/z* 283.0930 fragment ion common to the three outovirin compounds. The sodium adduct of outovirin B is observed at *m/z* 535.0835 in B.

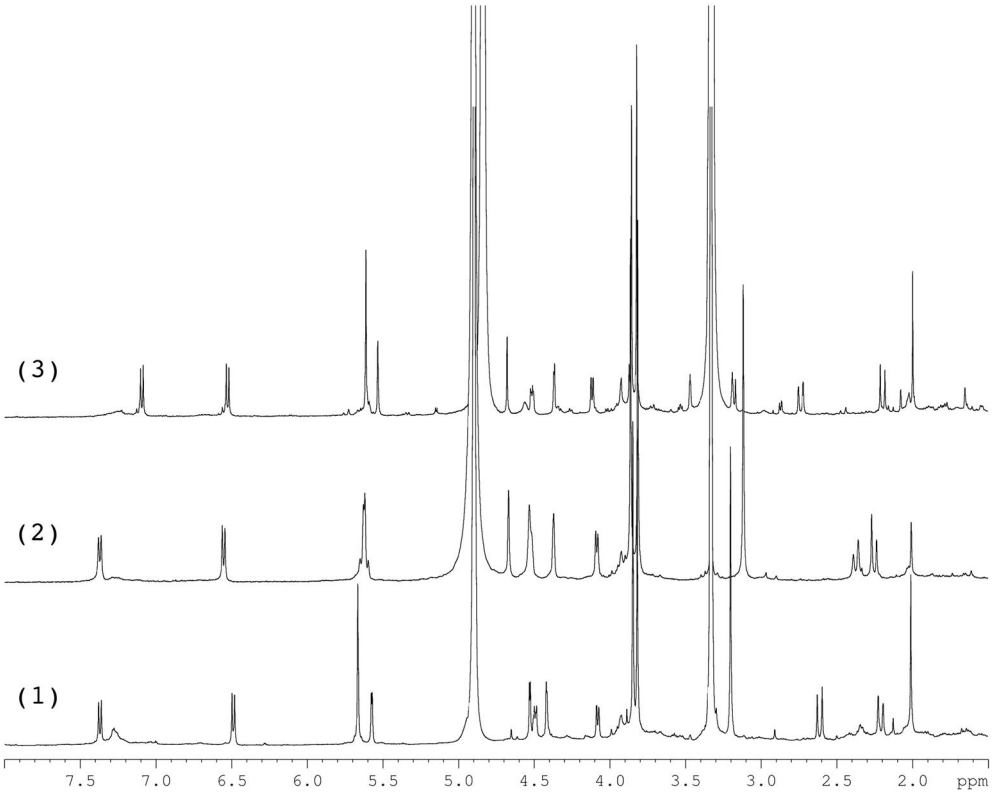


Figure S2 500 MHz ^{1}H spectra of outovirin A (**1**), outovirin B (**2**), and outovirin C (**3**) in CD_3OD.

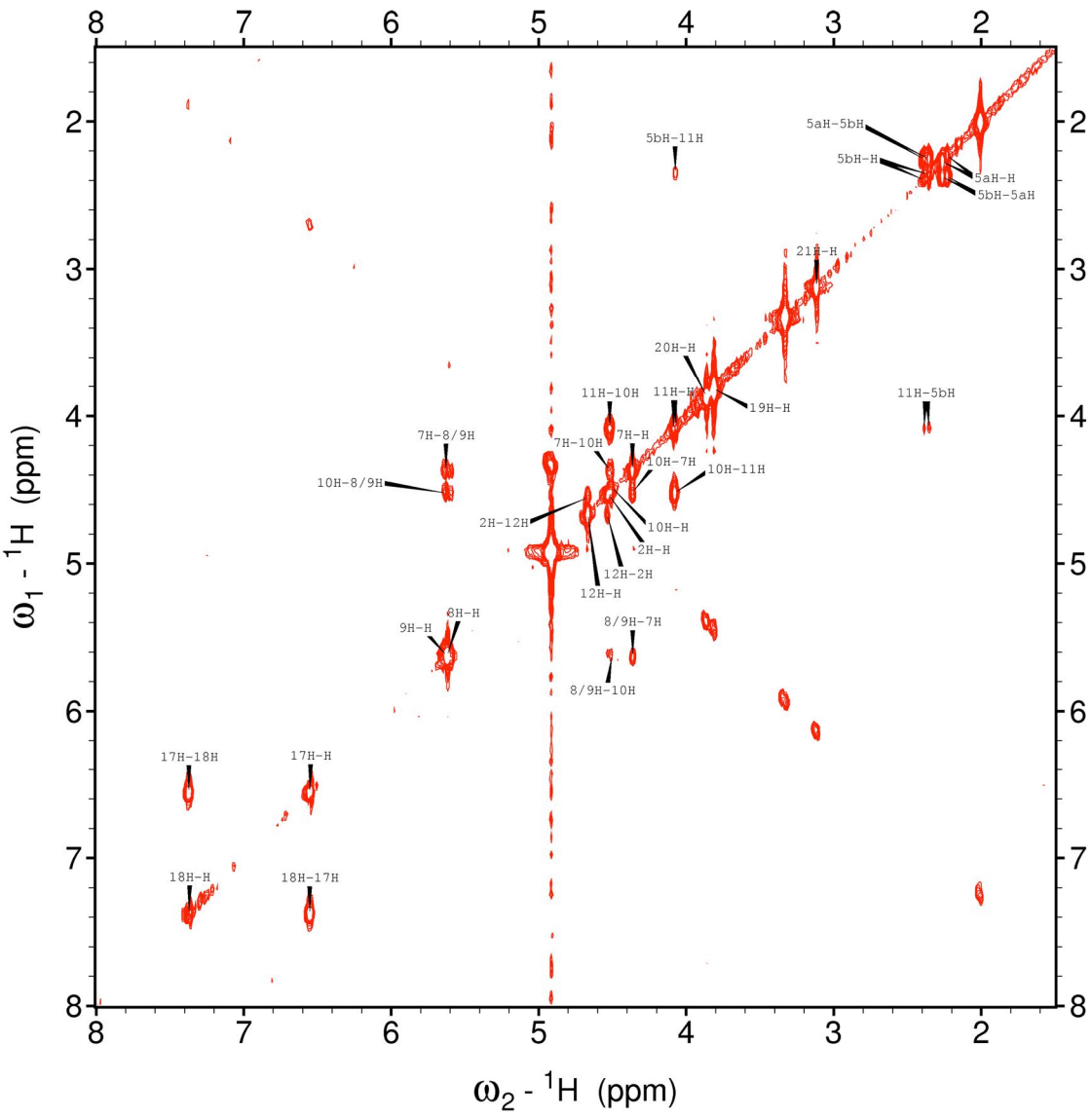


Figure S3 500 MHz ^{1}H-^{1}H COSY-45 spectrum of outovirin B (**2**) in CD_3OD.

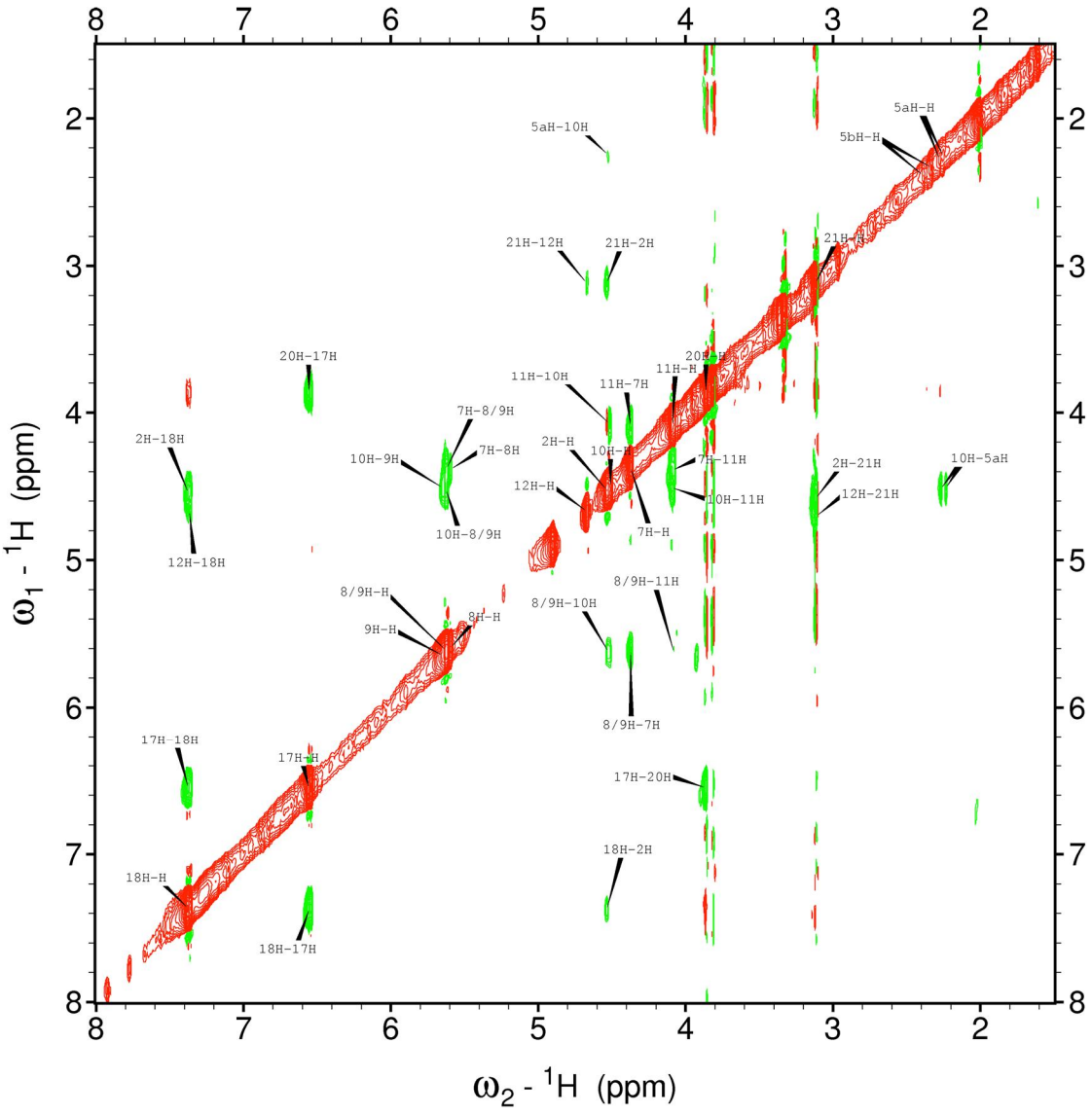


Figure S4 500 MHz ^{1}H-^{1}H NOESY spectrum of outovirin B (**2**) in CD_3OD. Red indicates positive signal intensity and green indicates negative signal intensity.

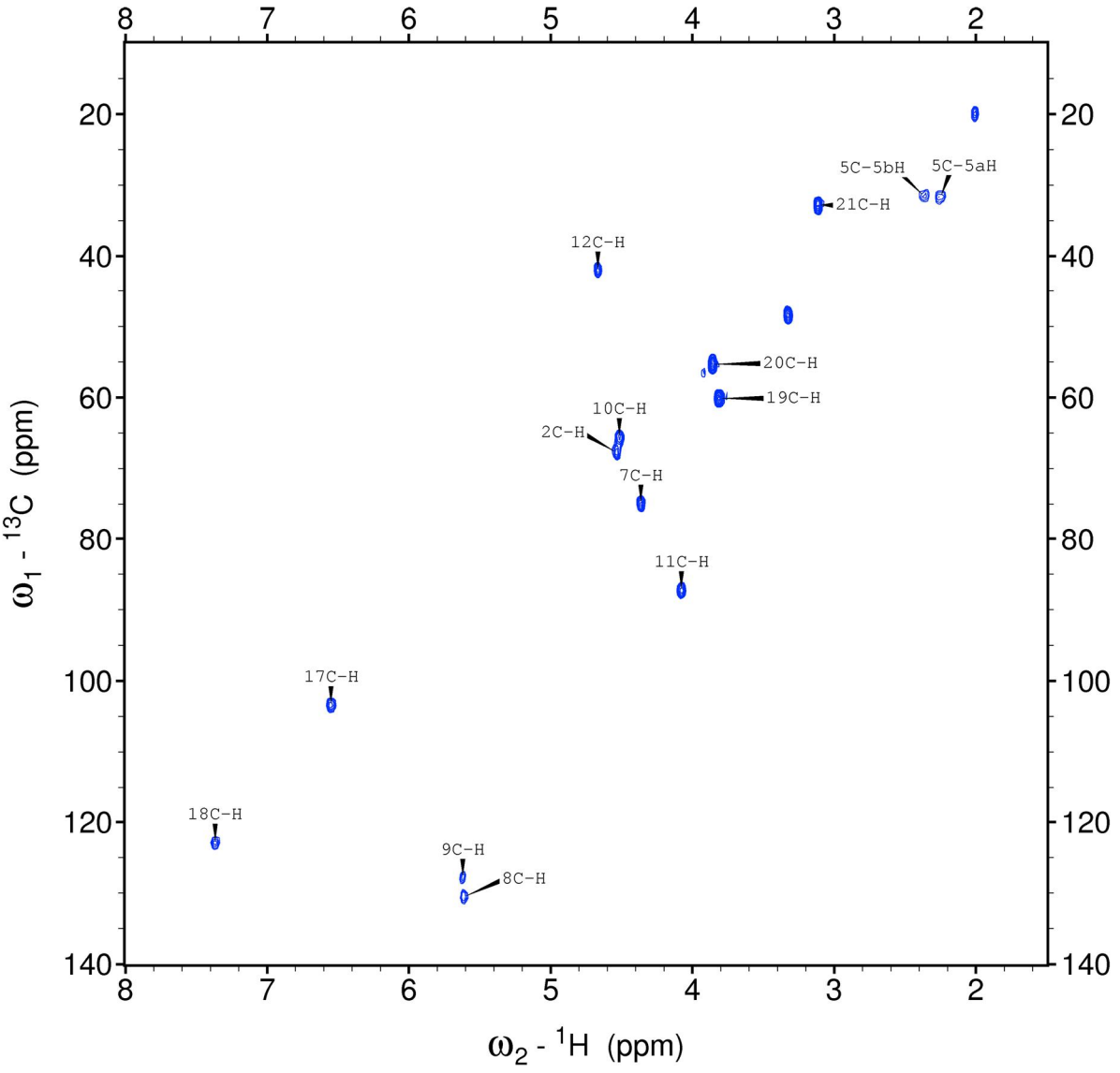


Figure S5 500 MHz ^{1}H-^{13}C HSQC spectrum of outovirin B (**2**) in CD_3OD.

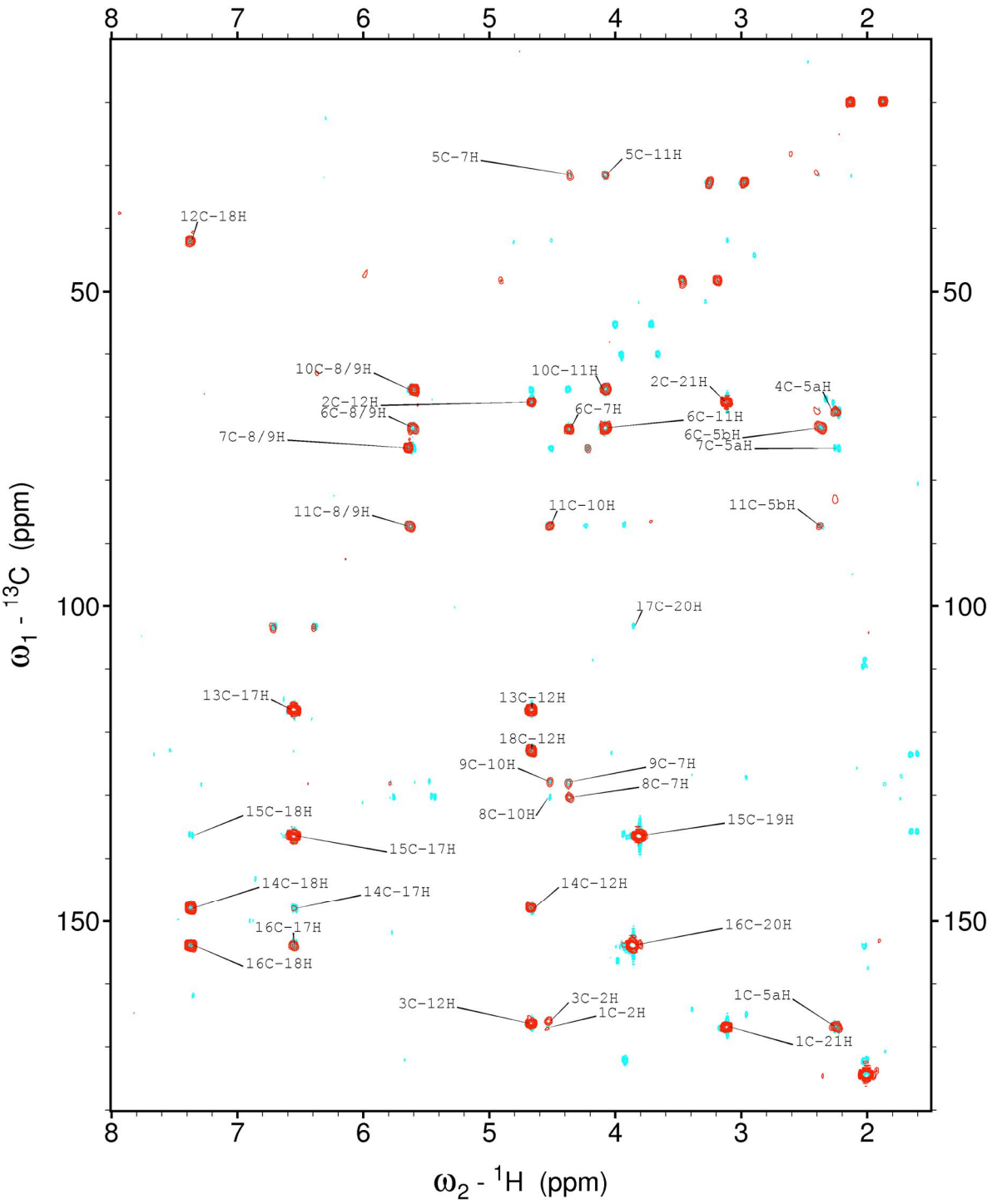


Figure S6 500 MHz ^{1}H-^{13}C HMBC spectra of outovirin B (**2**) in CD_3OD. Two independently acquired spectra are overlaid, as denoted by red and cyan.

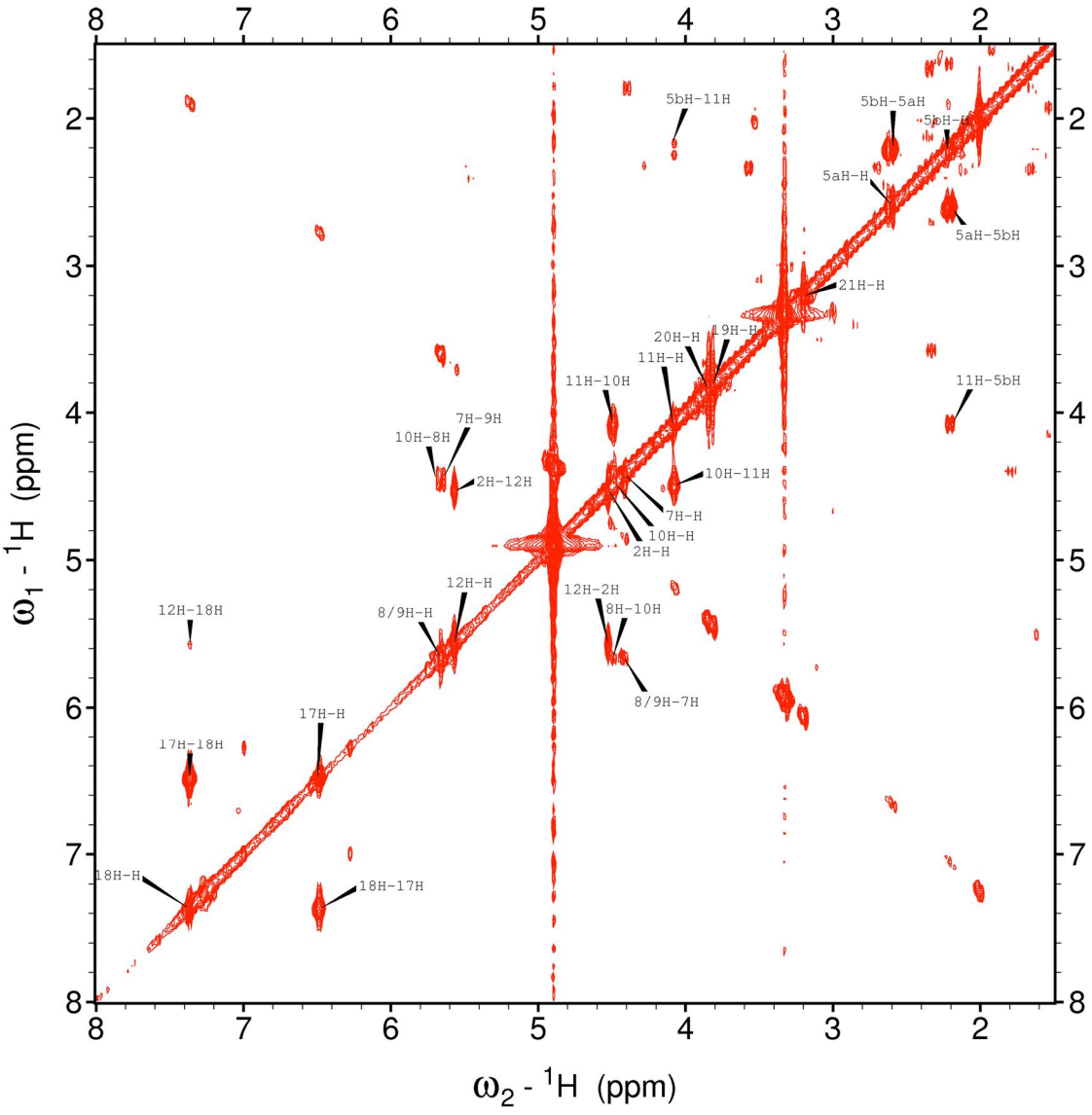


Figure S7 500 MHz ^{1}H-^{1}H COSY-45 spectrum of outovirin A (**1**) in CD_3OD.

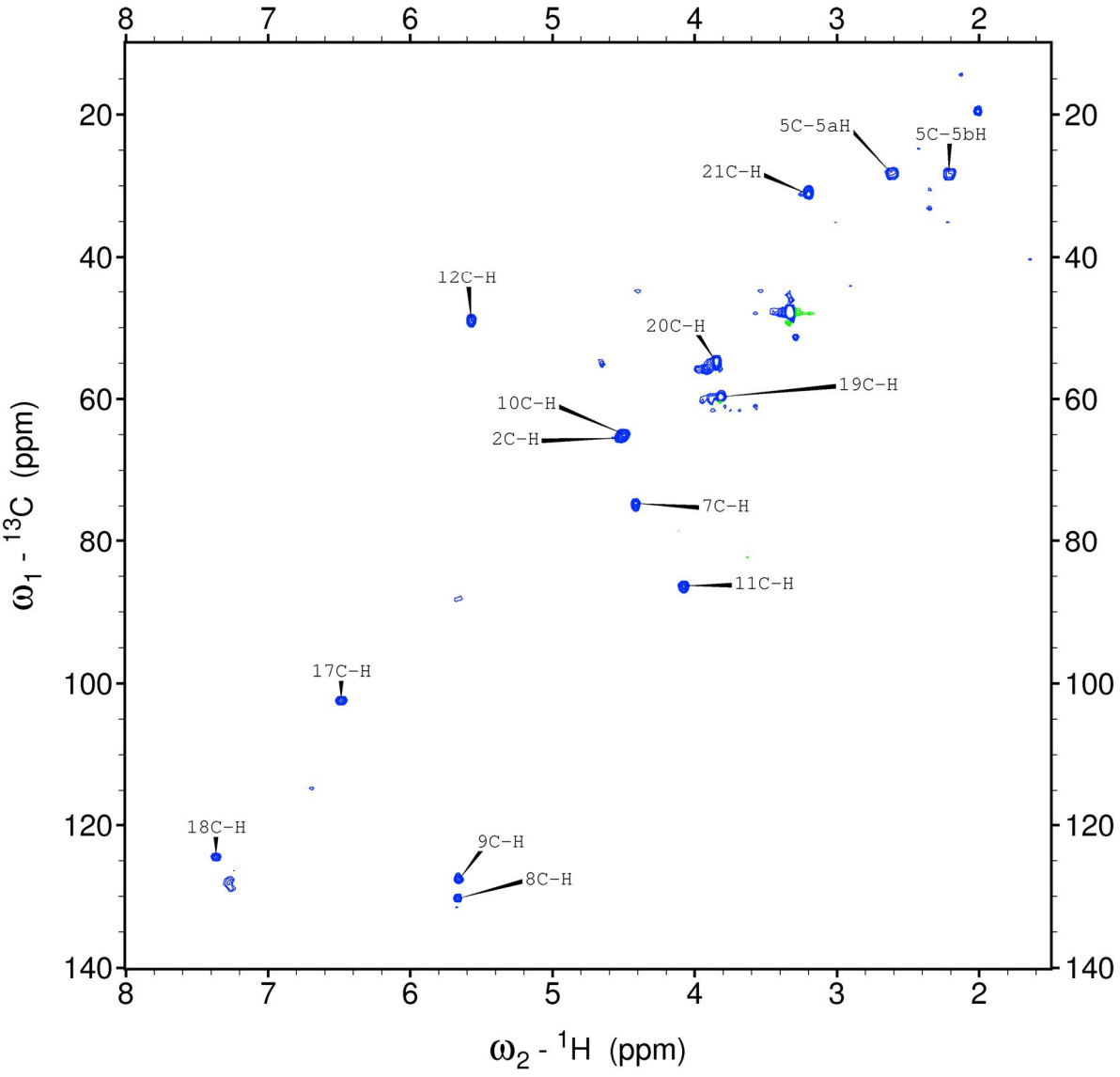


Figure S8 500 MHz ^{1}H-^{13}C HSQC spectrum of outovirin A (**1**) in CD_3OD.

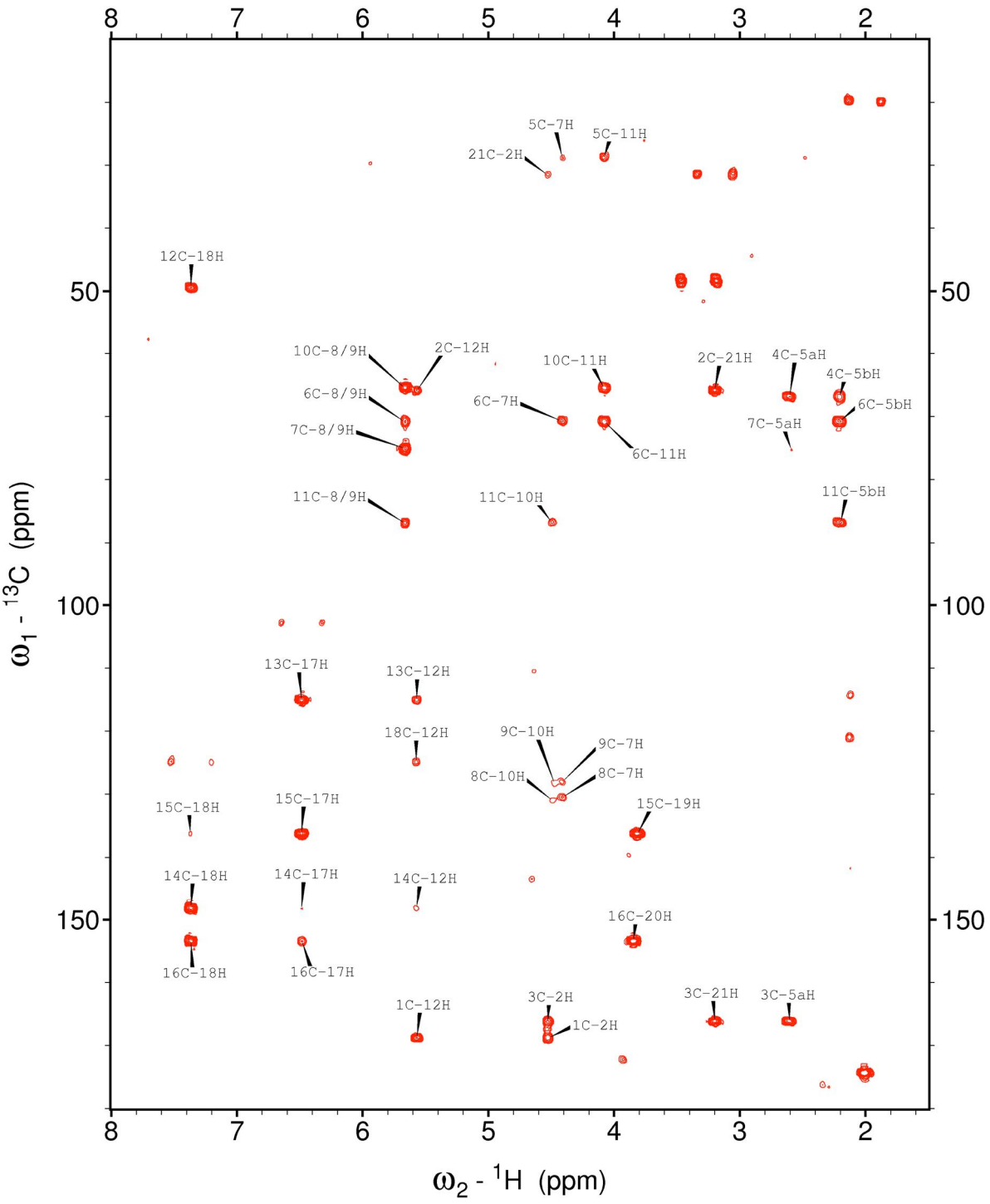


Figure S9 500 MHz ^{1}H-^{13}C HMBC spectrum of outovirin A (**1**) in CD_3OD.

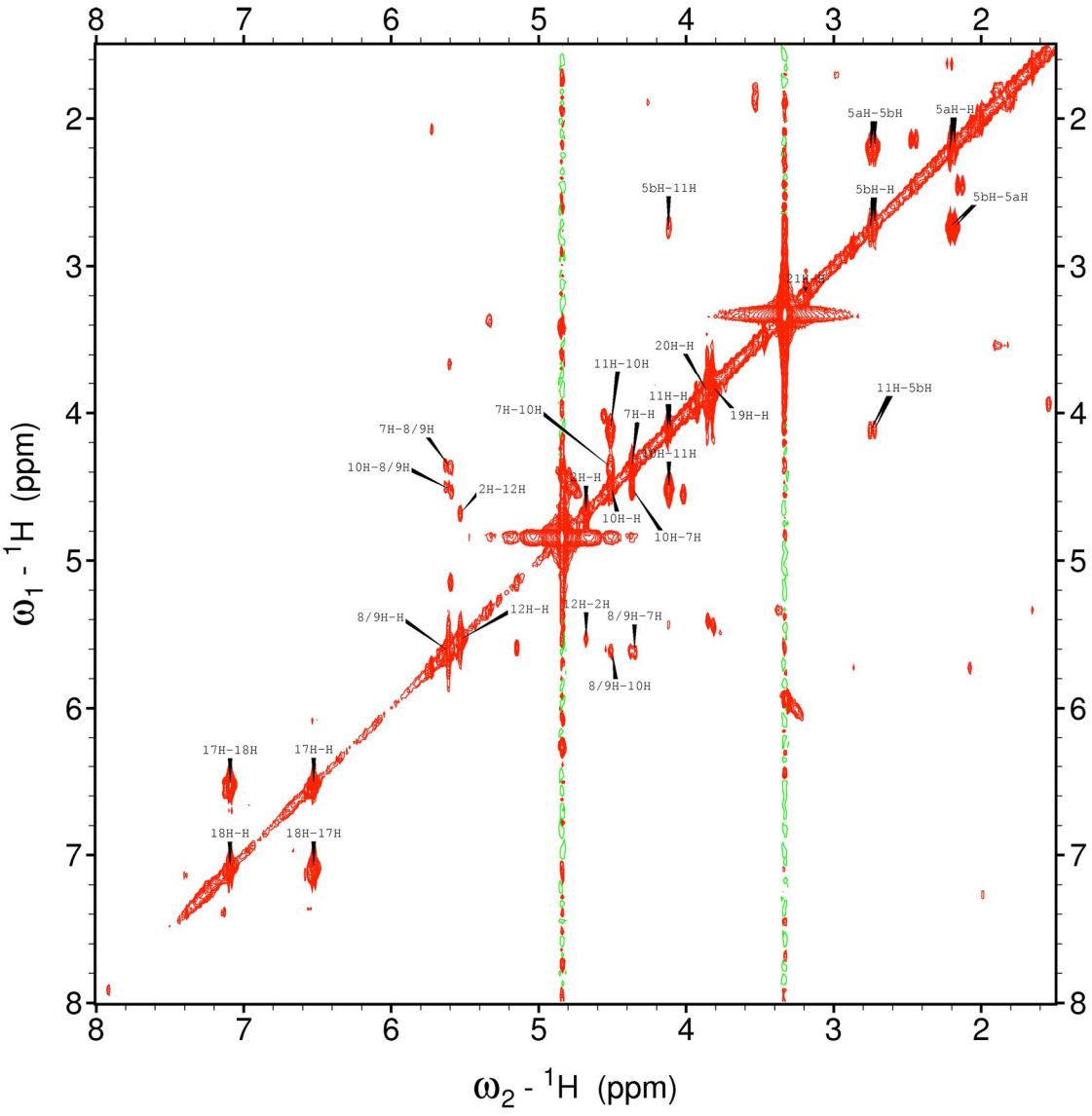


Figure S10 500 MHz ^{1}H-^{1}H COSY-45 spectrum of outovirin C (**3**) in CD_3OD.

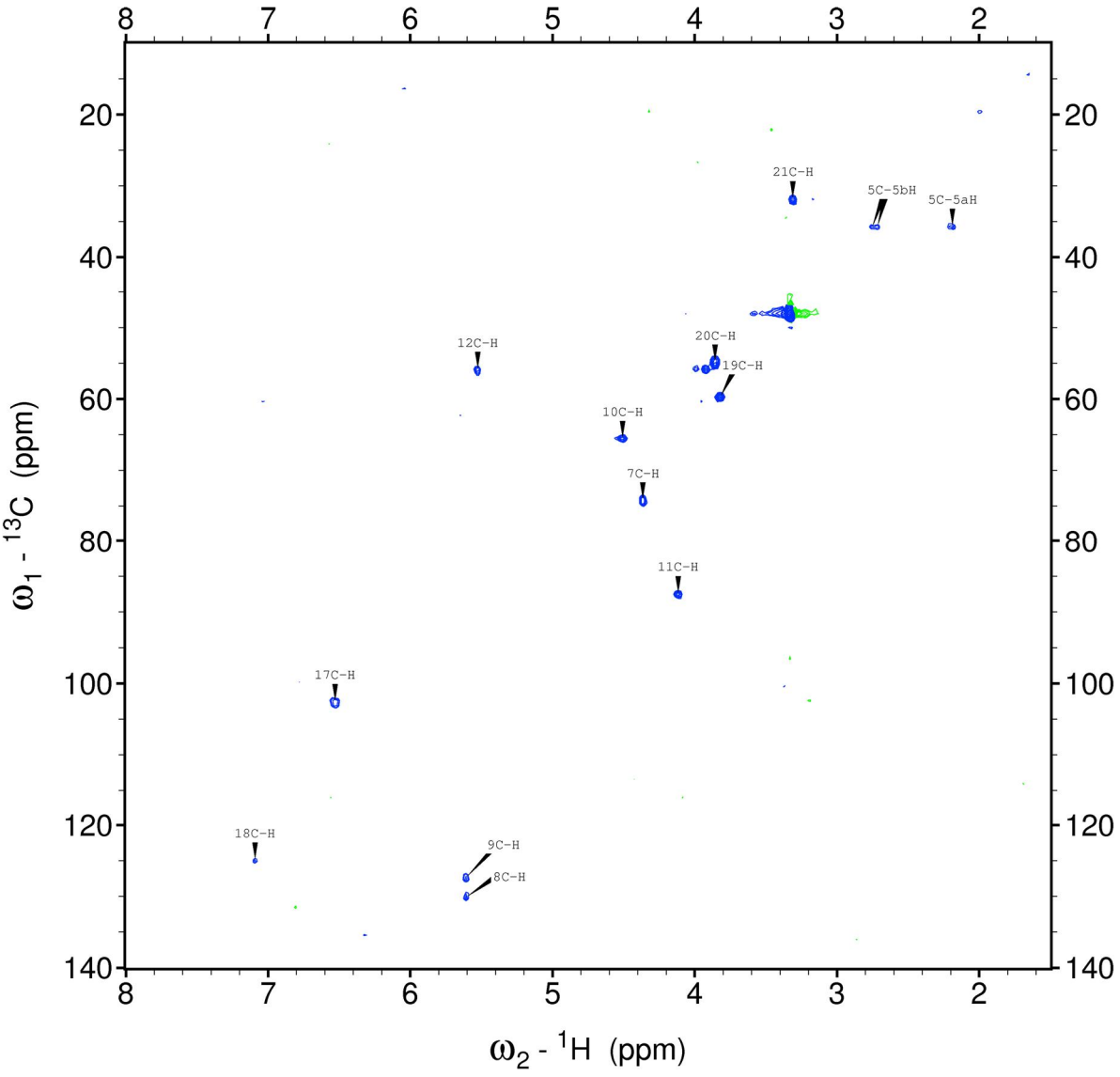


Figure S11 500 MHz ^{1}H-^{13}C HSQC spectrum of outovirin C (**3**) in CD_3OD.

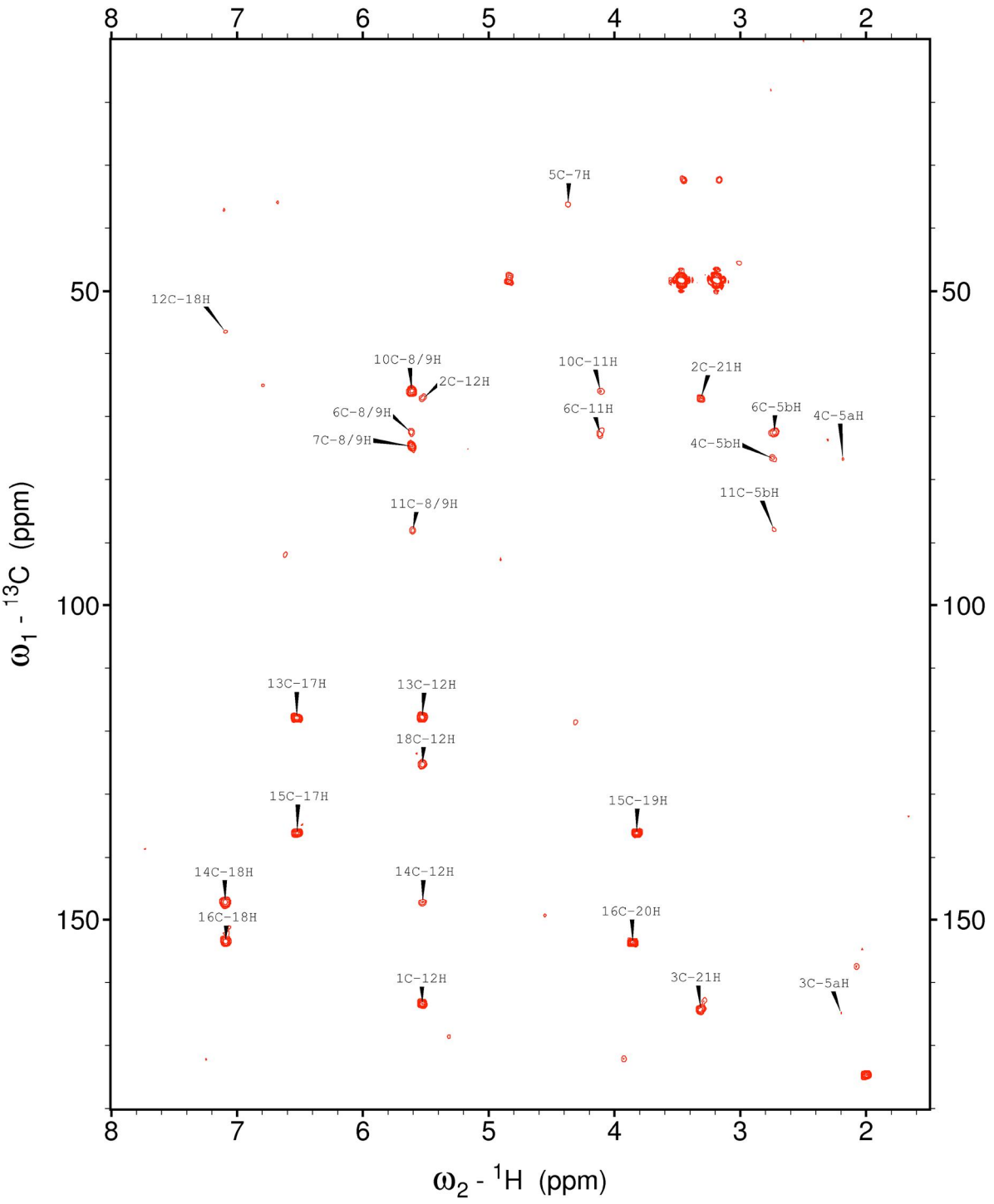
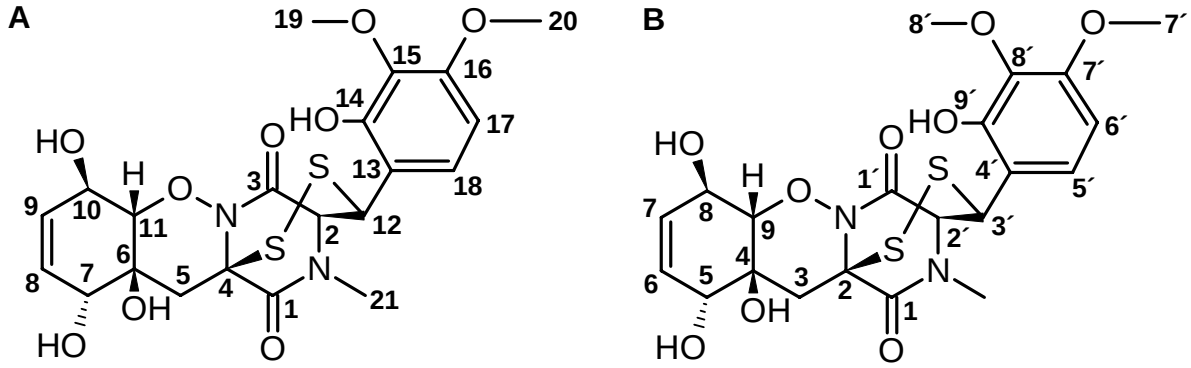


Figure S12 500 MHz ^{1}H-^{13}C HMBC spectrum of outovirin C (**3**) in CD_3OD.

Table S1 Chemical shifts (in ppm) of outovirin A (**1**), outovirin B (**2**) and outovirin C (**3**) in CD_3OD (exp) and *ab initio* simulations (calc)

	(1) 13C		(1) 1H		(2) 13C		(2) 1H		(3) 13C		(3) 1H	
	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc
1	166.1	162.8			166.8	163.5			164.5	163.2		
2	65.7	68.3	4.53	3.84	67.6	69.9	4.54	4.09	67.1	67.5	4.68	4.77
3	168.8	167.0			166.1	165.1			163.4	160.2		
4	66.8	75.5			69.1	77.6			76.7	79.1		
5	28.6	32.6			31.5	34.6			35.9	37.1		
5a			2.61	2.72			2.25	2.42			2.20	2.17
5b			2.21	2.33			2.37	2.48			2.74	2.65
6	70.8	74.6			71.7	74.7			72.6	75.5		
7	75.0	77.7	4.42	4.77	74.9	78.0	4.37	4.75	74.5	78.6	4.37	4.69
8	130.5	130.6	5.68	5.93	130.4	130.3	5.61	5.96	130.1	129.4	5.61	5.88
9	128.0	128.1	5.65	5.95	127.9	128.8	5.64	6.00	127.4	129.7	5.61	5.89
10	65.3	68.7	4.48	4.90	65.6	69.1	4.52	4.83	65.9	68.3	4.51	4.61
11	86.7	90.4	4.08	4.00	87.3	89.3	4.08	4.00	87.8	89.2	4.12	3.84
12	49.3	56.6	5.57	5.73	41.9	50.5	4.67	4.83	56.3	70.3	5.53	5.37
13	115.1	113.7			116.4	115.3			117.8	116.4		
14	148.2	148.3			147.9	149.2			147.2	146.2		
15	136.2	134.5			136.4	134.9			136.1	133.5		
16	153.4	152.8			153.8	153.4			153.5	151.8		
17	102.4	100.3	6.49	6.38	103.3	101.0	6.55	6.50	102.7	101.5	6.53	6.44
18	124.6	127.0	7.37	7.36	122.9	125.7	7.37	8.08	125.1	124.5	7.09	7.34
19	59.7	58.4	3.82	4.01	60.1	58.2	3.81	4.00	59.7	58.4	3.82	4.08
20	54.7	53.3	3.85	3.93	55.3	53.0	3.86	3.93	54.9	53.3	3.86	3.96
N	31.3	29.2	3.20	3.29	32.8	31.3	3.12	3.11	31.9	33.2	3.26	3.25
RMSD		3.5		.27		3.4		.31		3.7		.20
CMAE		2.7		.21		2.6		.24		2.3		.18

Scheme S1 Outovirin B (2) labeled according to the numbering schemes based on Gliovirin[22] (A) and Pretrichodermamide A[24] (B).



A	B
1	1
2	2´
3	1´
4	2
5	3
6	4
7	5
8	6
9	7
10	8
11	9
12	3´
13	4´
14	9´
15	8´
16	7´
17	6´
18	5´
19	8´ -OCH3
20	9´ -OCH3
21	-