Electronic Supplementary Information

Mutanobactin A from the human oral pathogen *Streptococcus mutans* is a cross-kingdom regulator of the yeast-mycelium transition

P. Matthew Joyner,[a] Jinman Liu,[b] Zhijun Zhang,[b] Justin Merritt,[b] Fengxia Qi,[b] and Robert H. Cichewicz*[,a,c]

[a]*Natural Products Discovery Group, Department of Chemistry and Biochemistry, Stephenson Life Sciences Research Center, 101 Stephenson Parkway, University of Oklahoma, Norman, OK 73019 U.S.A.*

[b]*College of Dentistry, 975 NE 10th Street, The University of Oklahoma Health Sciences Center, Oklahoma City, OK 73014 U.S.A.*

[c]*Graduate Program in Ecology and Evolutionary Biology, University of Oklahoma, Norman, OK, USA 73019 U.S.A.*

*To whom correspondence should be addressed. Tel: +1 (405) 325-6969. E-mail: rhcichewicz@ou.edu.

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General Experimental Procedures. NMR data were obtained on a Varian VNMR spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C) with a triple resonance probe at 22 ± 0.5 °C. Electrospray-ionization mass spectrometry data were collected on an IonSpec (Varian, Inc.) 9.4 T FT-ICR instrument. ESI MS/MS analyses were performed on a LCT premier (Waters Corp.) time-of-flight instrument. Flash chromatography was performed on a Biotage Isolera One using a 100 g C_{18} column with a flow rate of 50 mL/min. HPLC separations were carried out on a Shimadzu system using a SCL-10A VP controller and Gemini 5µm C_{18} column (110Å, 250 x 21.2 mm) with a flow rate of 10 mL/min. All solvents were of ACS grade or better. Optical rotation measurement were performed on a Rudolph Research Autopol III automatic polarimeter; $[\alpha]_D$ values are given in $deg \cdot cm^2 \cdot g^{-1}$.

Preparation and extraction of bacterial culture. A culture of *Streptococcus mutans* UA159 was prepared by inoculating 15 L of brain-heart infusion (BHI) broth with 100 mL of a stationary phase *S. mutans* UA159 culture. The culture was incubated under microaerobic conditions at 37 °C for 36 h. The culture was extracted three times with equal volumes of ethyl acetate, which was then evaporated *in vacuo* to generate the *S. mutans* UA159 extract.

Mutanobactin A (1): white solid; $[\alpha]_D^{25}$ = -8.0 (*c* 0.001 in MeOH) ; λ_{max} (MeOH) 221 nm (ε/dm^3 mol^{-1} cm^{-1} 38 900); ^{1}H, ^{13}C, and ^{15}N NMR data, see Table S1; HRESIMS (FT-ICR) *m/z* $[M-H]^-$ 719.41713 (calcd. for $C_{36}H_{59}N_6O_7S$, 719.41714).

Table S1 NMR Spectroscopic Data (DMSO-d_6, 500 MHz for ^{1}H, 125 MHZ for ^{13}C) for mutanobactin A (**1**)

position	δ_C, mult.[a]	δ_H (*J* in Hz)	δ_N[b]
1	50.4, CH	4.43, ddd (3.7, 9.0, 11.0)	
2a	40.4, CH_2	1.44, m	
2b		1.81, ddd (3.9, 10.5, 13.8)	
3	24.2, CH	1.59, m	
4	20.9, CH_3	0.82, d (6.6)	
5	23.5, CH_3	0.92, d (6.7)	
6	170.5, C		
7	48.0, CH	4.52, quintet (6.8)	
8	17.7, CH_3	1.17, d (6.7)	
9	169.7, C		
10	61.0, CH	4.12, dd (3.7, 8.9)	
11a	29.6, CH_2	1.72, m	
11b		2.13, m	
12	24.5, CH_2	1.90, m	
13a	46.8, CH_2	3.43, m	
13b		3.65, ddd (4.5, 7.5, 9.8)	
14	171.6, C		
15	58.8, CH	3.57, dd (8.3, 10.0)	
16	26.2, CH	2.33, m	
17	20.4, CH_3	0.84, d (6.6)	
18	18.8, CH_3	0.77, d (6.8)	
19	168.8, C		
20	52.2, CH	4.87 ddd (2.6, 8.0, 9.0)	
21a	28.5, CH_2	2.23, dd (2.6, 16.0)	
21b		3.19, dd (9.0, 16.0)	
22	170.4, C		
23a	43.7, CH_2	2.79, m	
23b		3.28, m	
24	41.0, CH	3.25, m	
25	61.7, CH	3.87, d (9.8)	
26	167.7, C		
27	203.8, C		
28a	41.4, CH_2	2.33, m	
28b		2.44, dd (6.0, 16.6)	
29	23.1, CH_2	1.44, m	
30	28.7, CH_2	1.20, m	
31	22.1, CH_2	1.25, m	
32	28.8, CH_2	1.23, m	
33	22.1, CH_2	1.25, m	
34	31.3, CH_2	1.23, m	
35	28.9, CH_2	1.27, m	
36	14.0, CH_3	0.85, t (6.8)	
C1-NH		8.59, d (9.0)	120.0
C7-NH		7.77, d (6.5)	112.0
C10-NH			nd[c]
C15-NH		8.05, d (8.5)	107.5
C20-NH		7.23, d (8.0)	116.0
C23-NH		7.90, dd (5.3, 9.0)	105.5

[a]Determined by HSQC experiment at 500 MHz.
[b]Determined by HMBC experiment at 500 MHz.
[c] nd: not detected

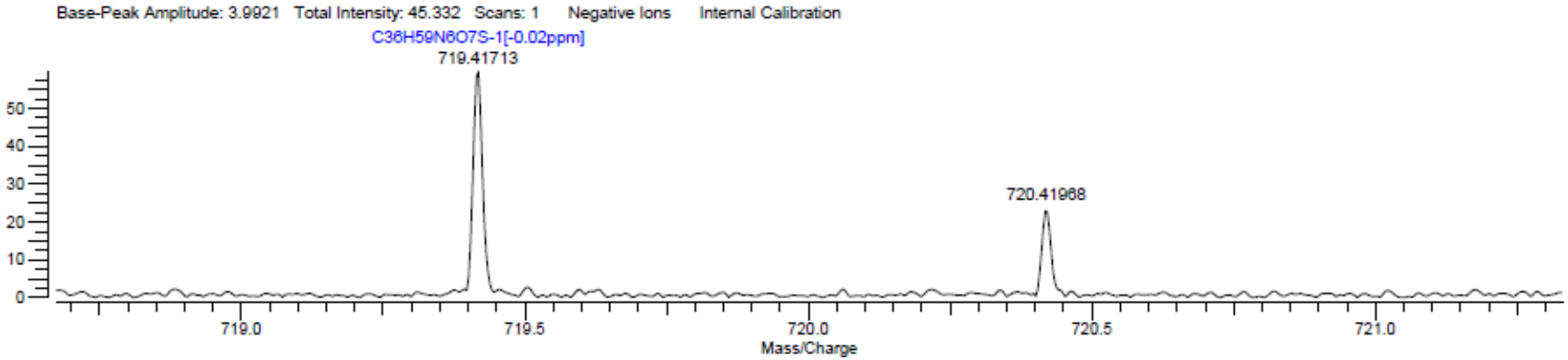

Fig. S1 HRESIMS (FT-ICR) data for mutanobactin A (**1**)

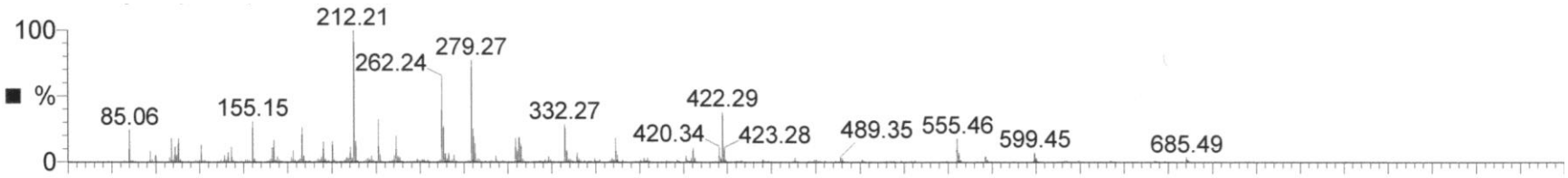

Fig. S2 ESI MS/MS data for mutanobactin A (**1**)

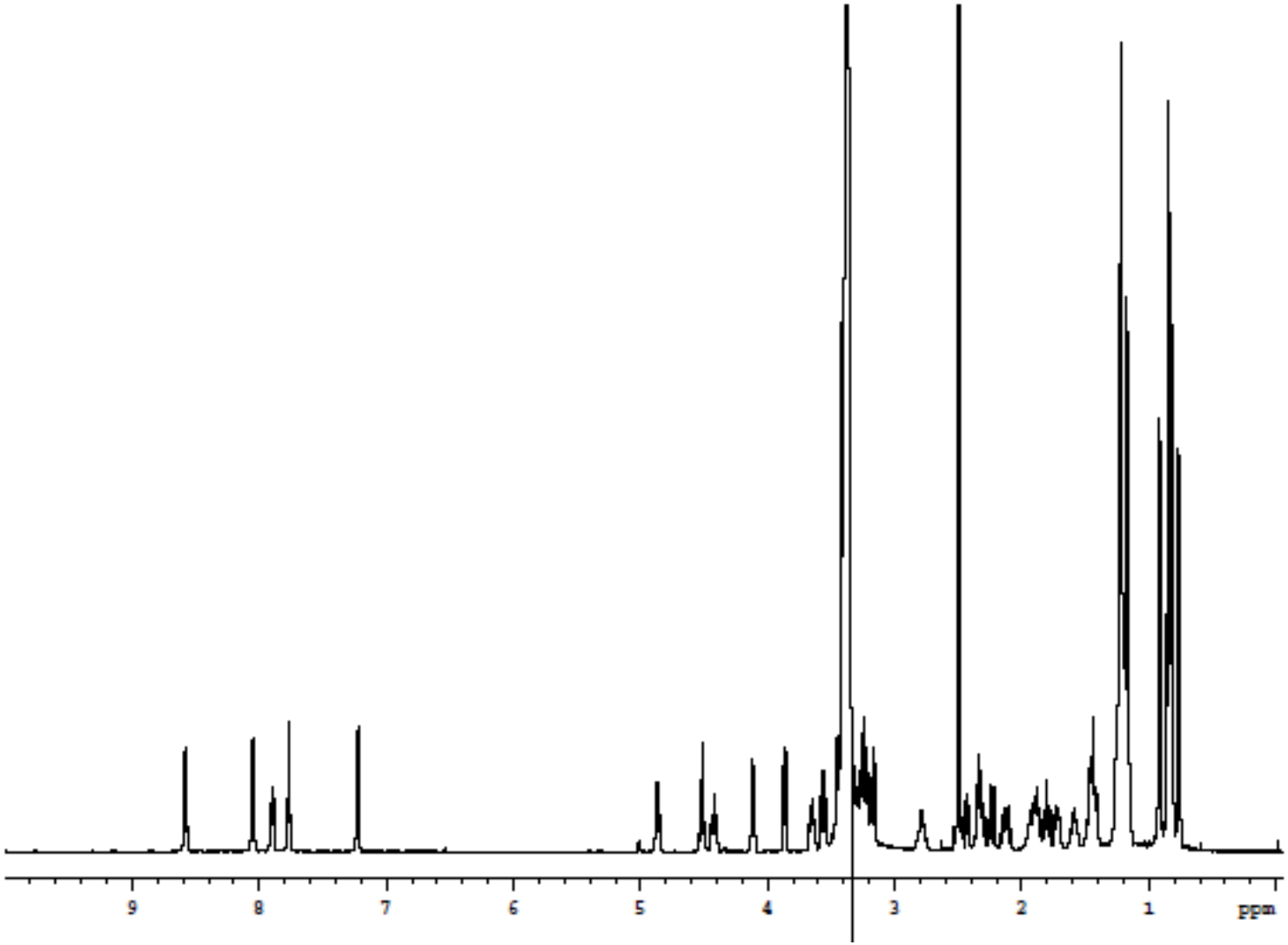

Fig. S3 ^{1}H NMR spectrum for mutanobactin A (**1**)

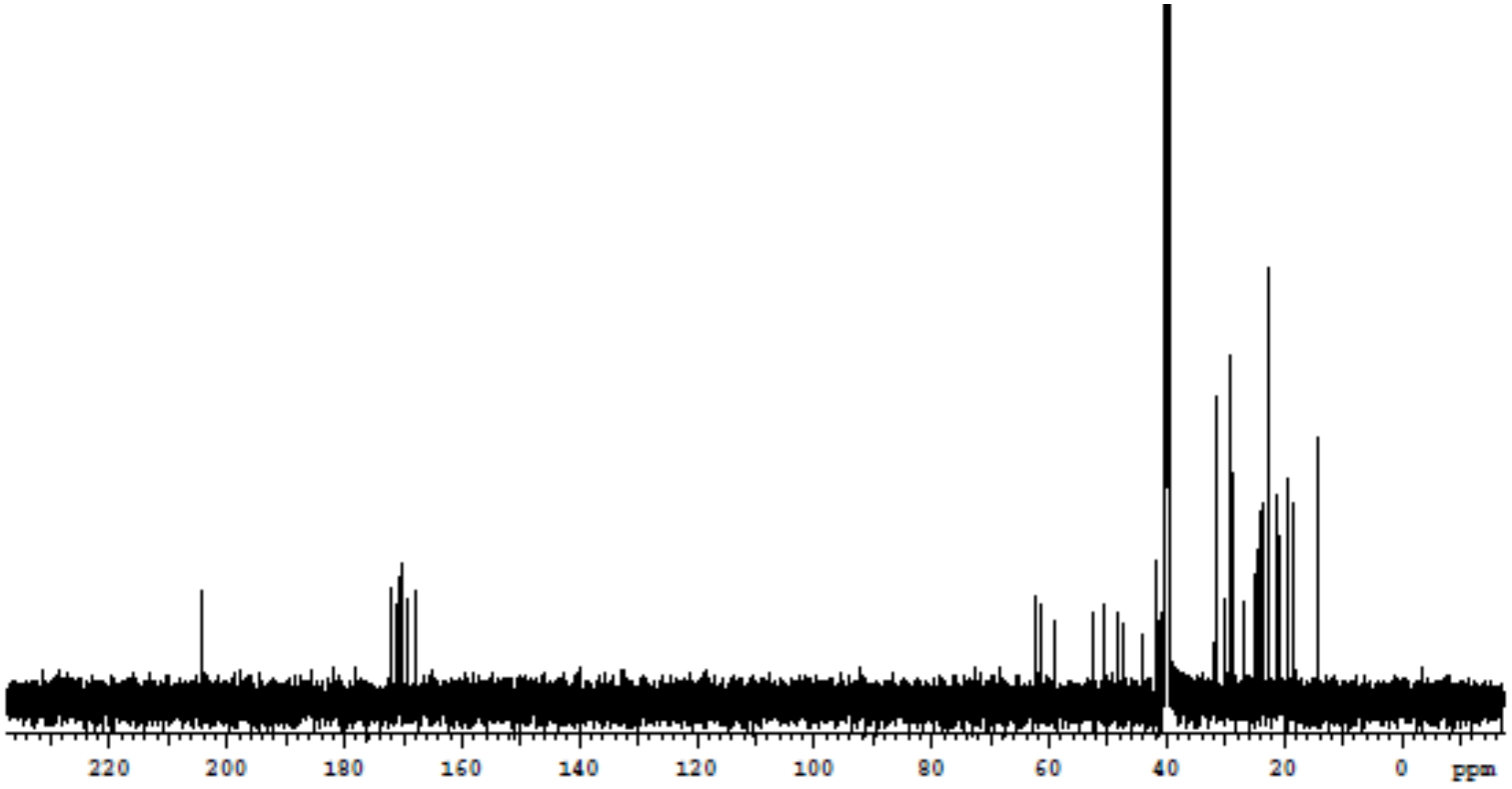

Fig. S4 ^{13}C NMR spectrum for mutanobactin A (**1**)

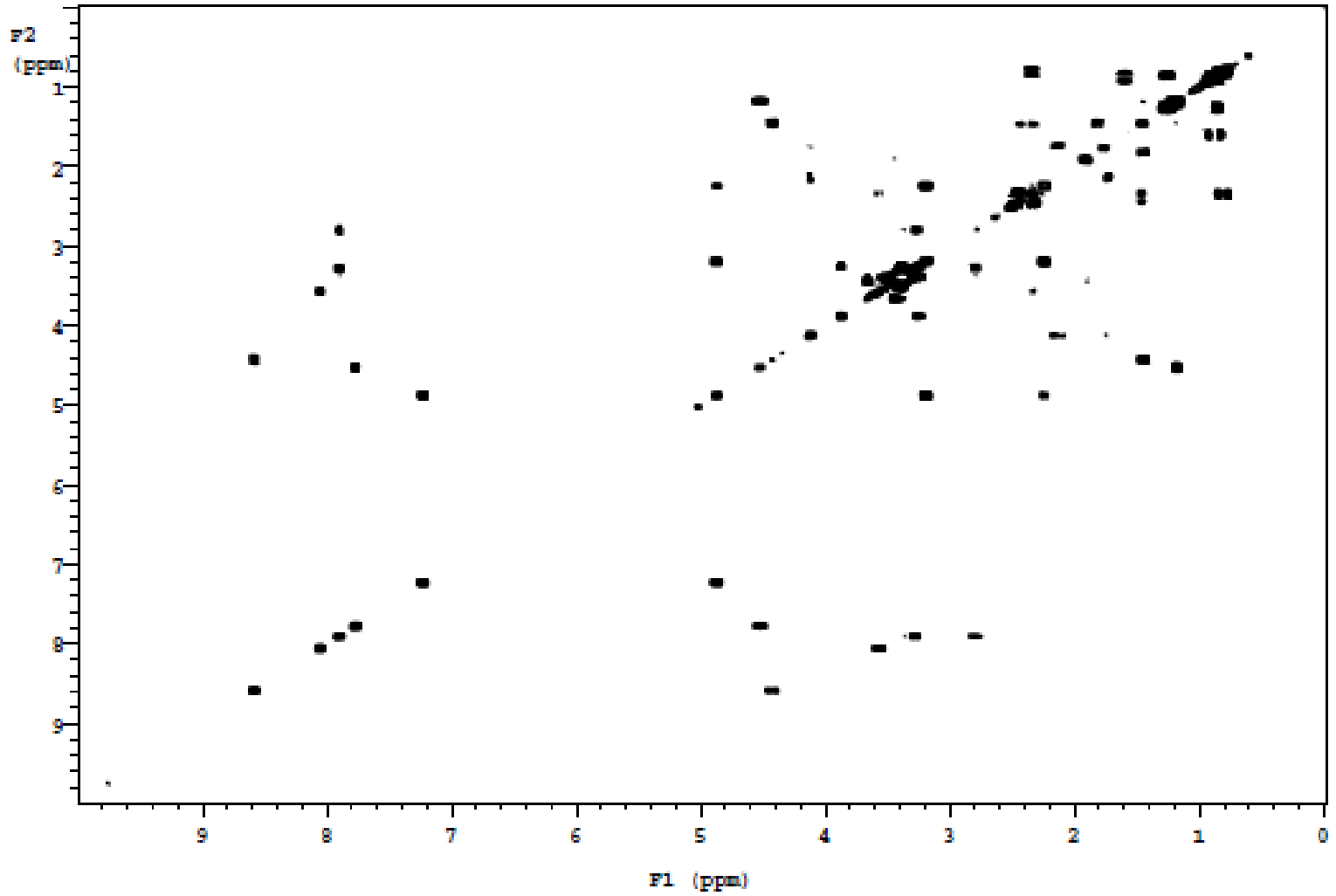

Fig. S5 ^{1}H–^{1}H COSY NMR spectrum for mutanobactin A (**1**)

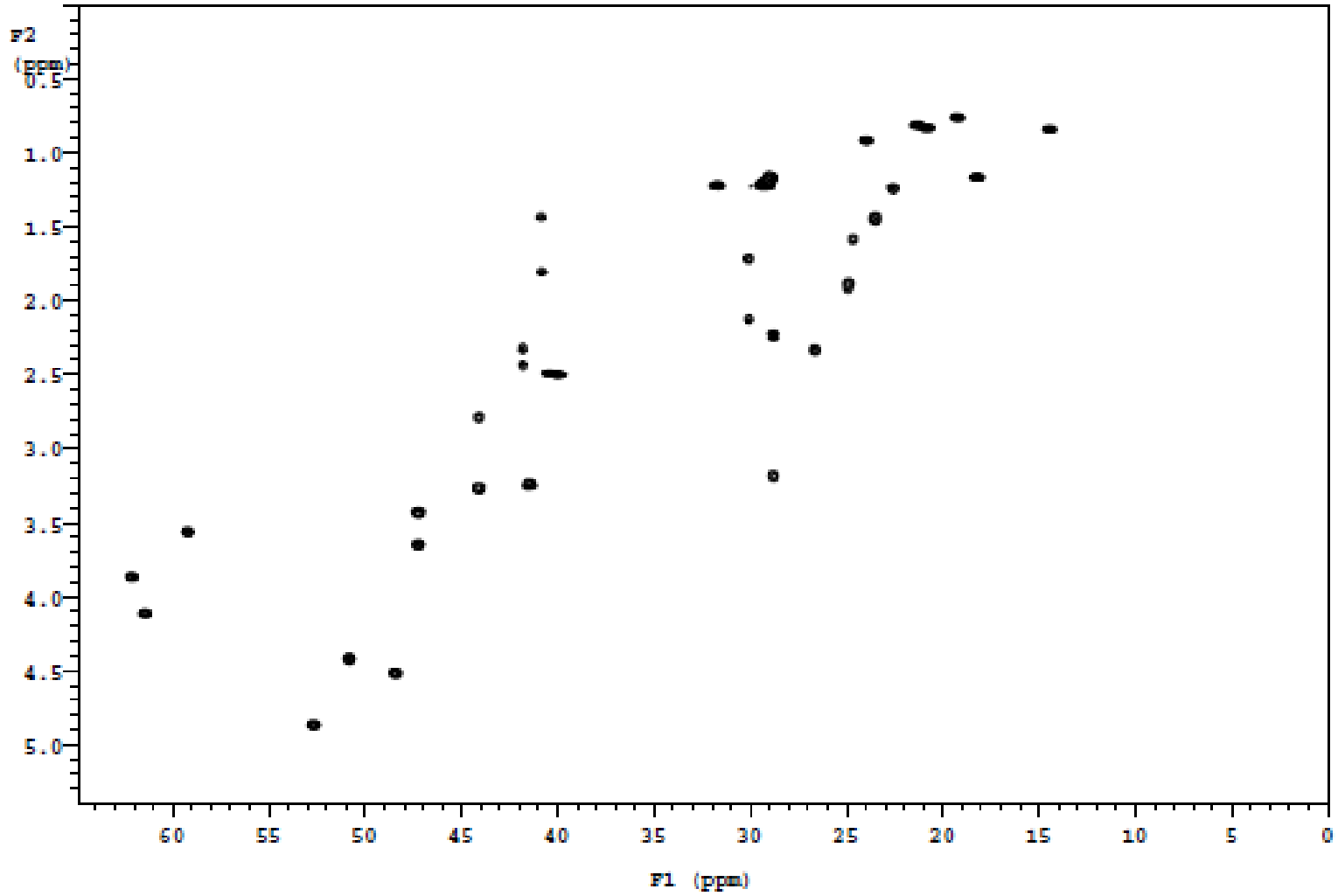

Fig. S6 ^{1}H–^{13}C HSQC NMR spectrum for mutanobactin A (**1**)

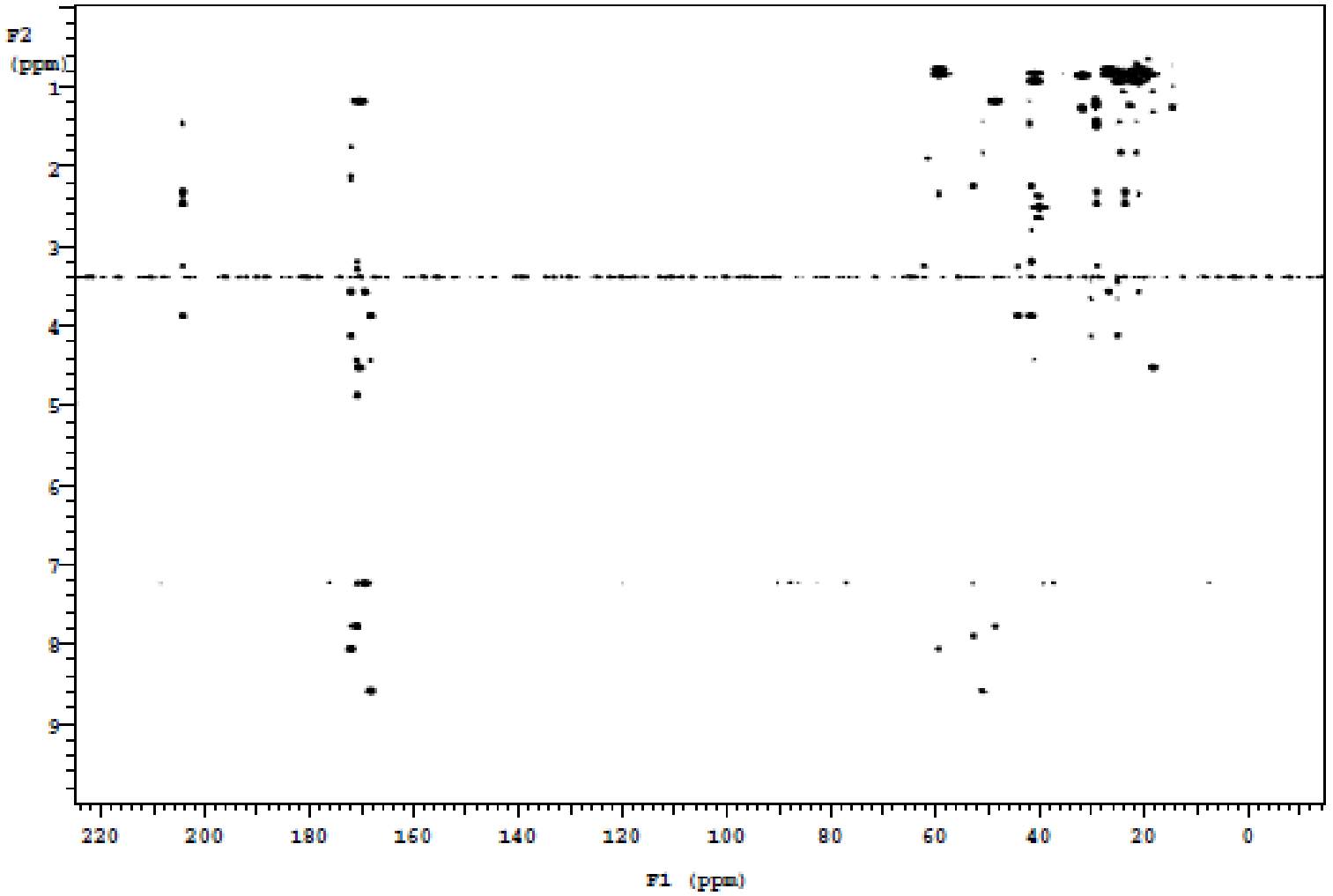

Fig. S7 ^{1}H–^{13}C HMBC NMR spectrum for mutanobactin A (**1**)

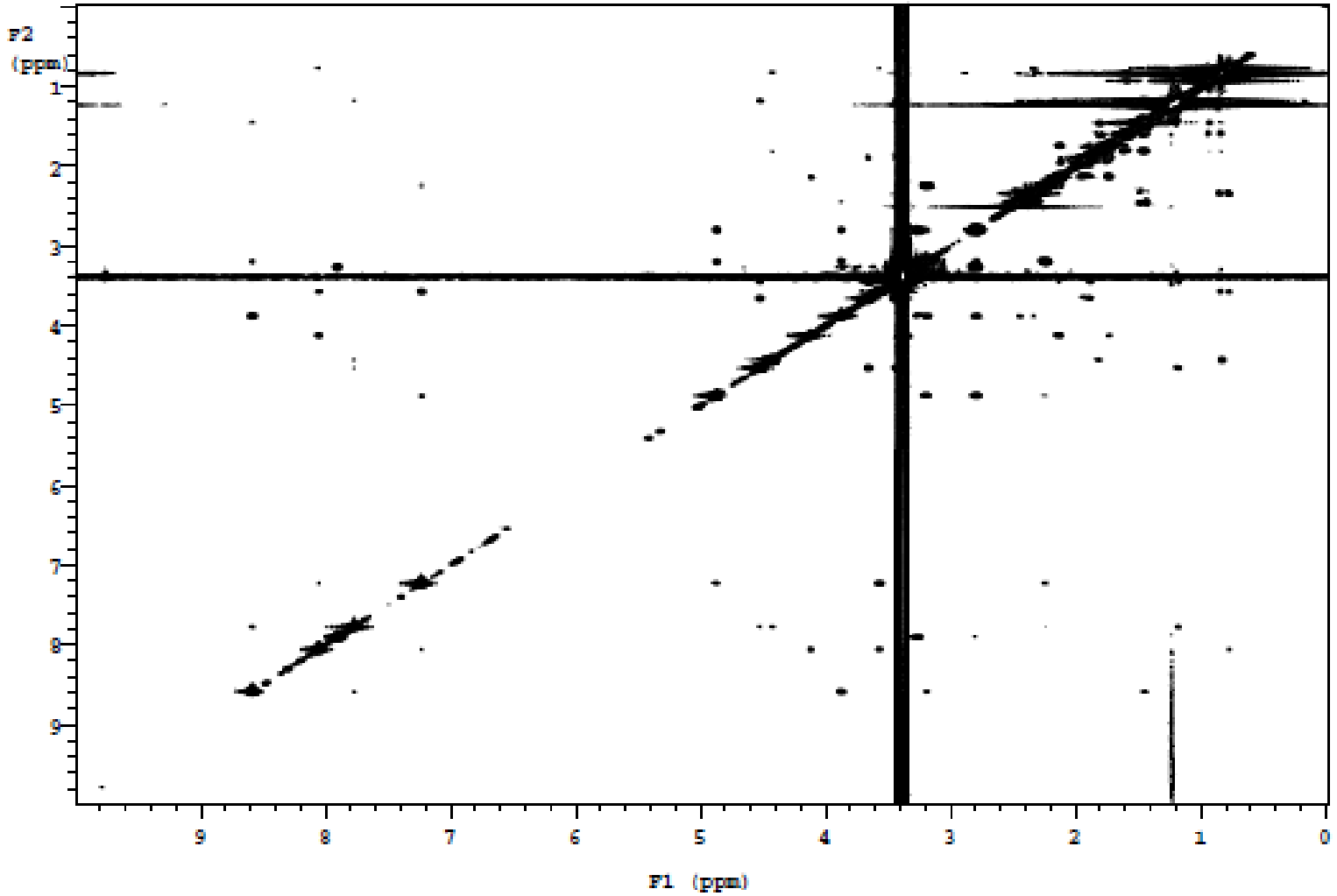

Fig. S8 ^{1}H–^{1}H NOESY NMR spectrum for mutanobactin A (**1**)

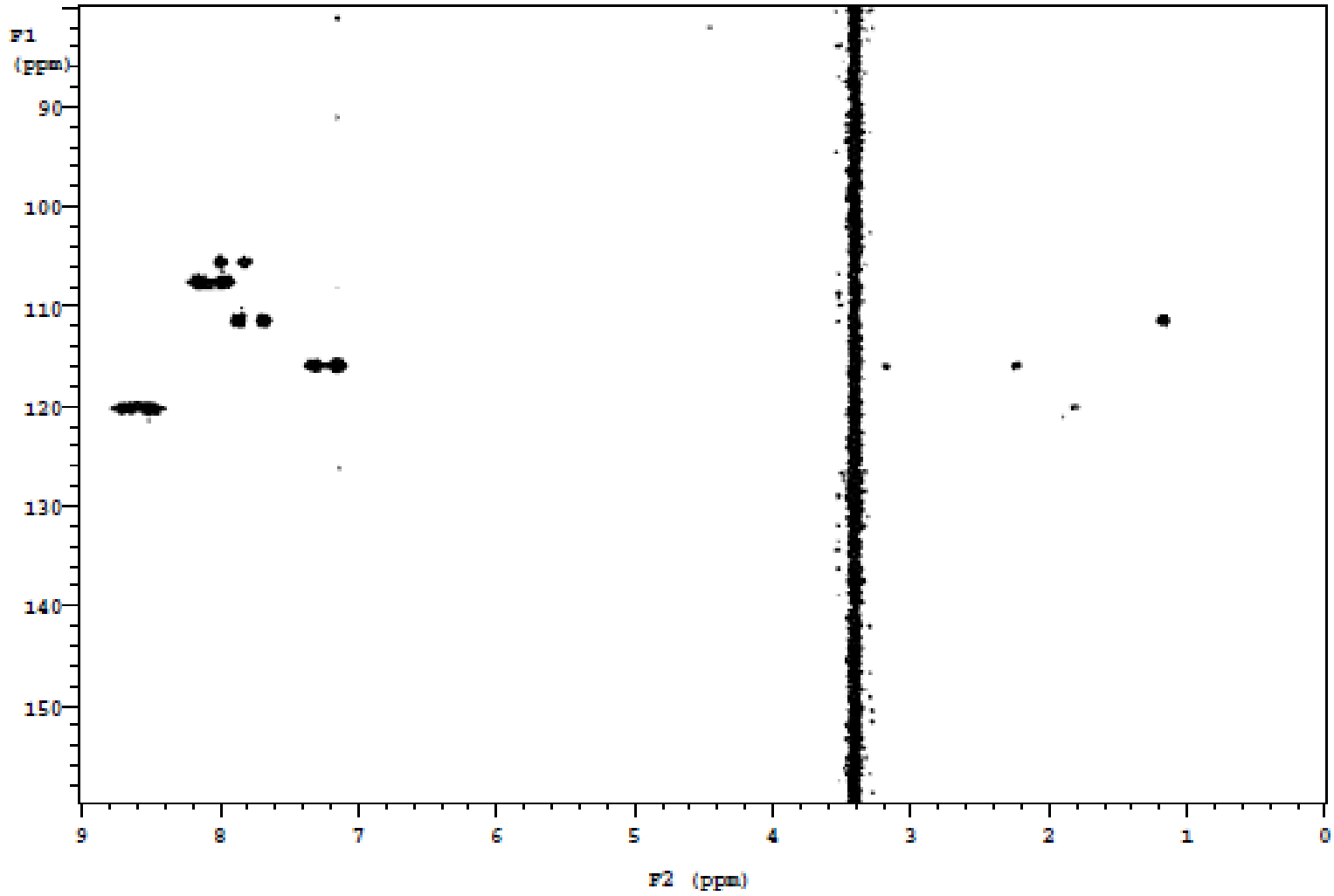

Fig. S9 ^{1}H–^{15}N HMBC NMR spectrum for mutanobactin A (**1**)

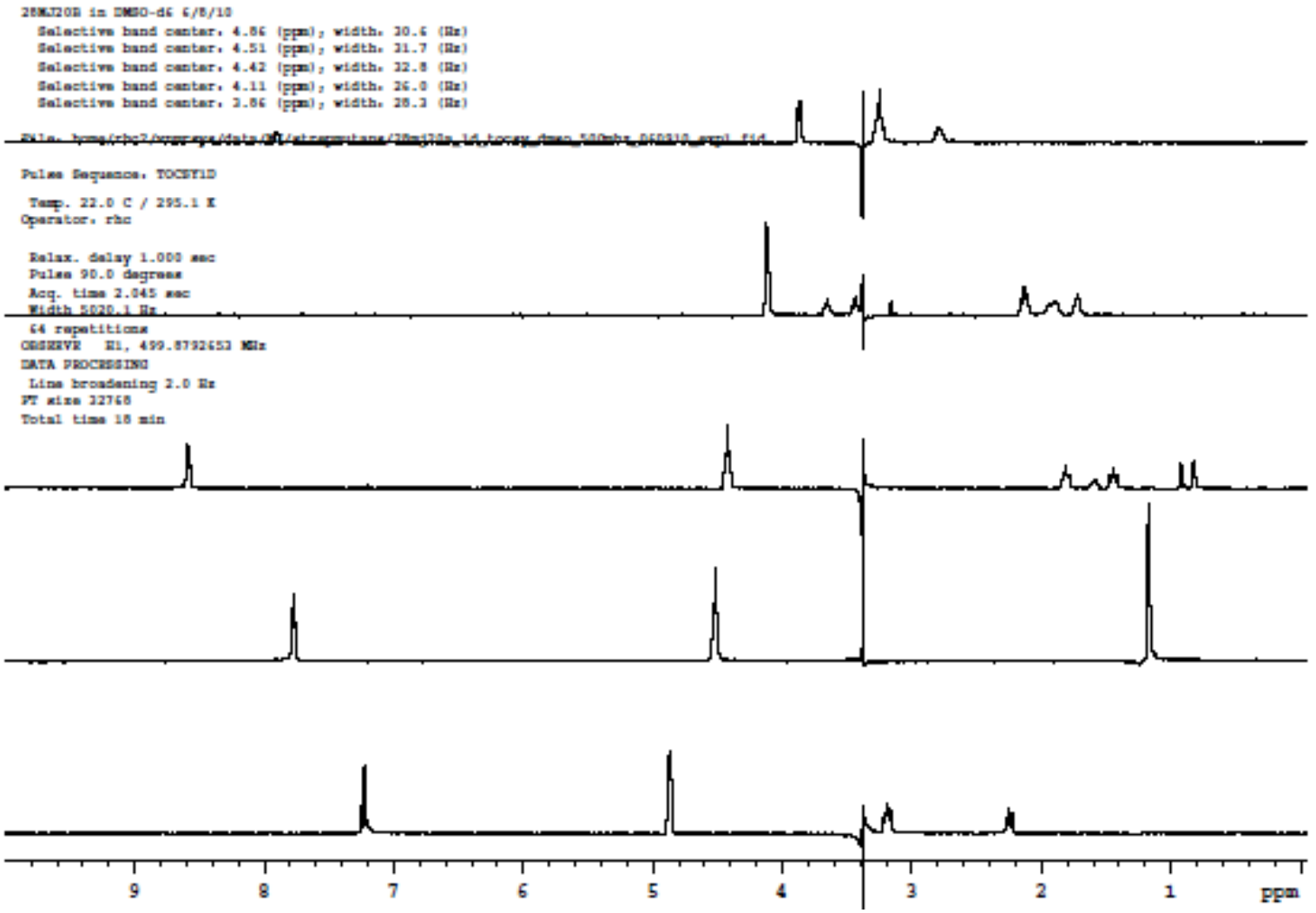

Fig. S10 1D ^{1}H–^{1}H TOCSY NMR spectra for mutanobactin A (**1**) (panel 1 of 3)

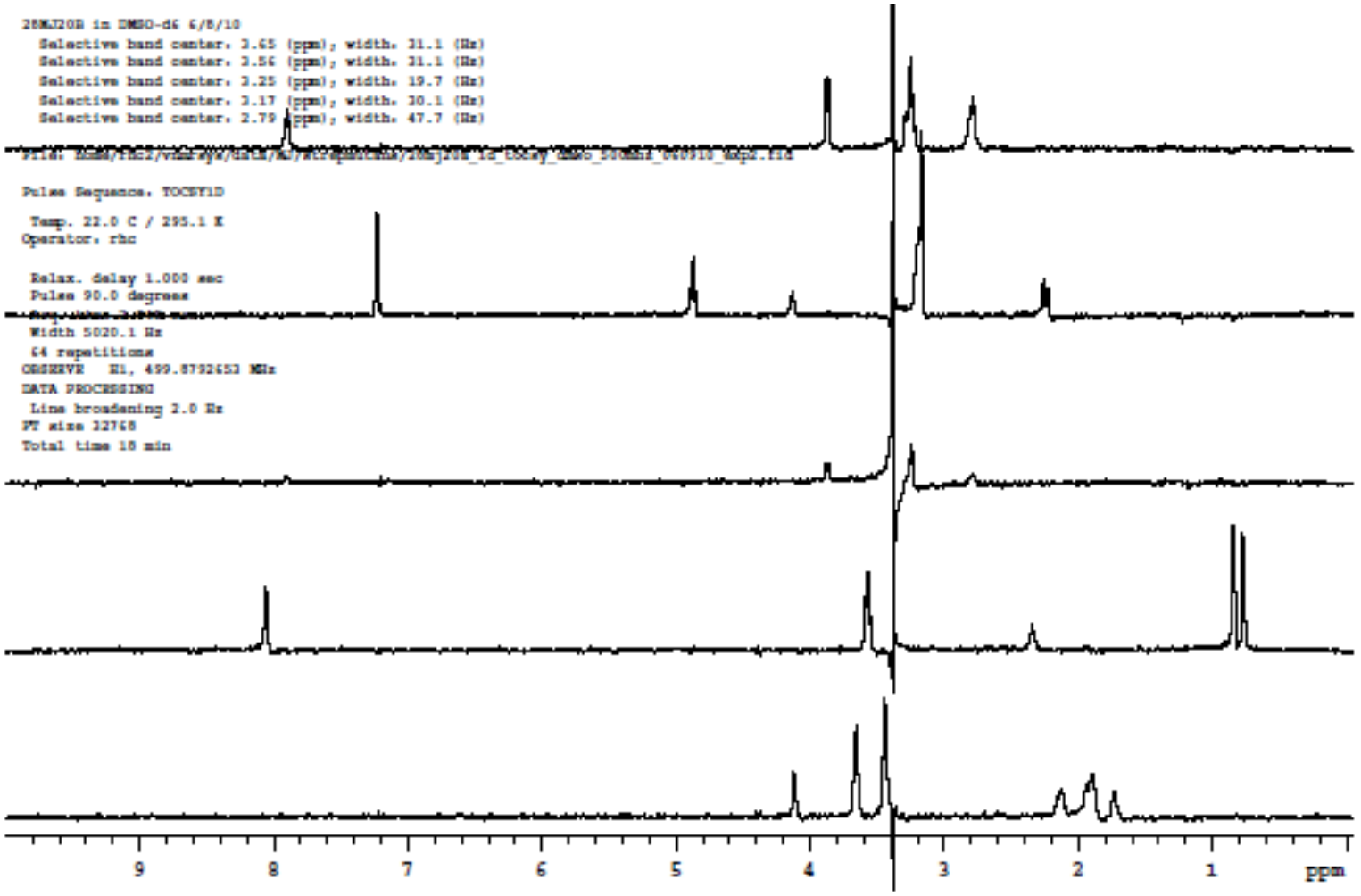

Fig. S10 1D ^{1}H–^{1}H TOCSY NMR spectra for mutanobactin A (**1**) (panel 2 of 3)

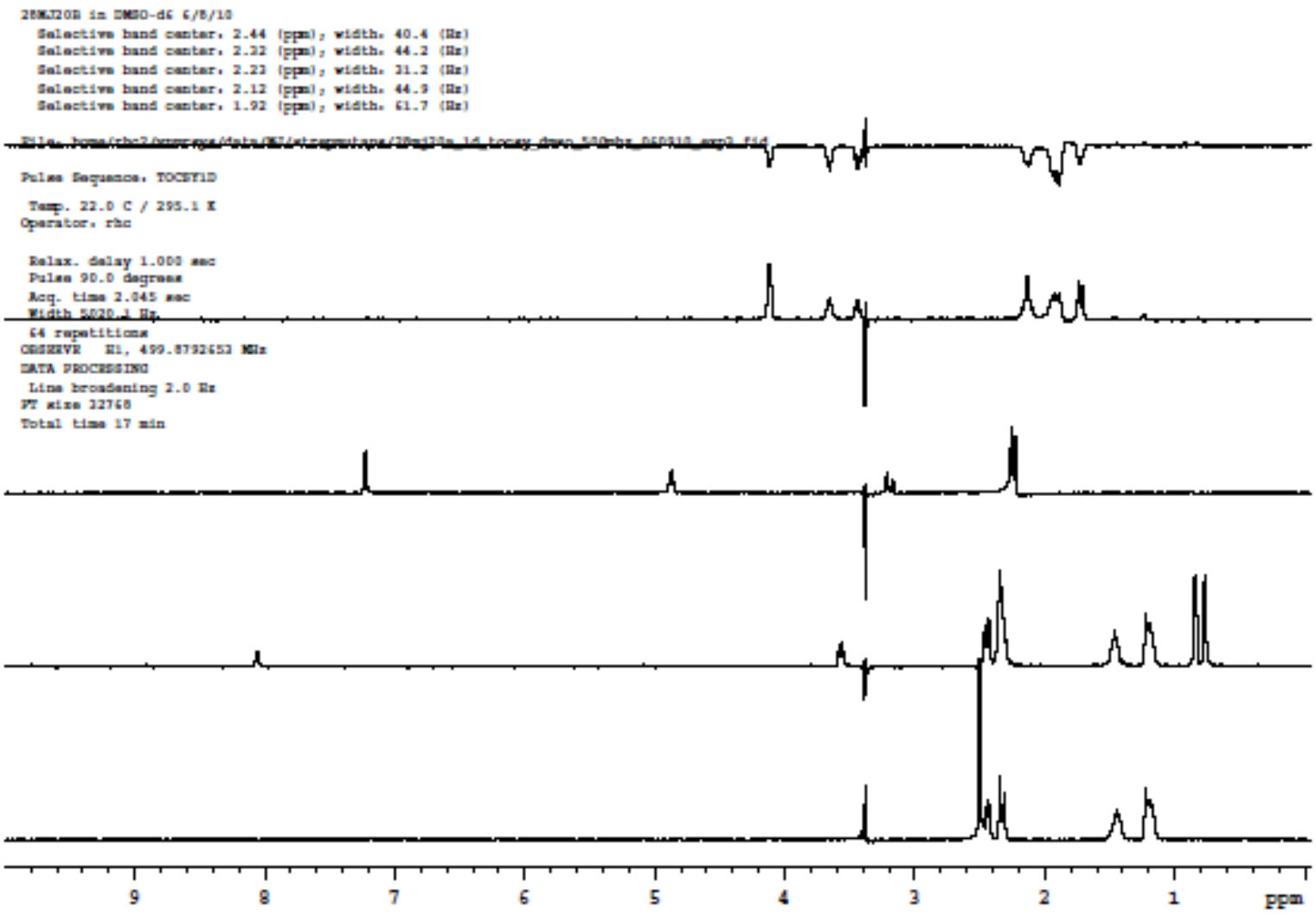

Fig. S10 1D ^{1}H–^{1}H TOCSY NMR spectra for mutanobactin A (**1**) (panel 3 of 3)