SUPPORTING INFORMATION:

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A Comparison of Methanobactins from *Methylosinus trichosporium* OB3b and *Methylocystis* strain SB2 Predicts Methanobactins are Synthesized from Diverse Peptide Precursors Modified to Create a Common Core for Binding and Reducing Copper Ions

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Figure S1: Mass spectrum for metal-free mb-SB2

Figure S2: The proposed structure for mb-SB2 based on the NMR analysis, an a summary of the correlations observed in 2D NMR experiments

Figure S3: The long-range ^{1}H-^{13}C correlations observed in an [^{1}H-^{13}C] HMBC spectrum for metal-free mb-SB2 after the hydrolysis and decarboxylation of its oxazolone rin.

Table S1: The ^{1}H, ^{13}C and ^{15}N resonance assignments for Cu(I)-mb-SB2

Table S2: The ^{1}H and ^{13}C resonance assignments for metal-free mb-SB2, before and after the hydrolysis and decarboxylation of its oxazolone ring.

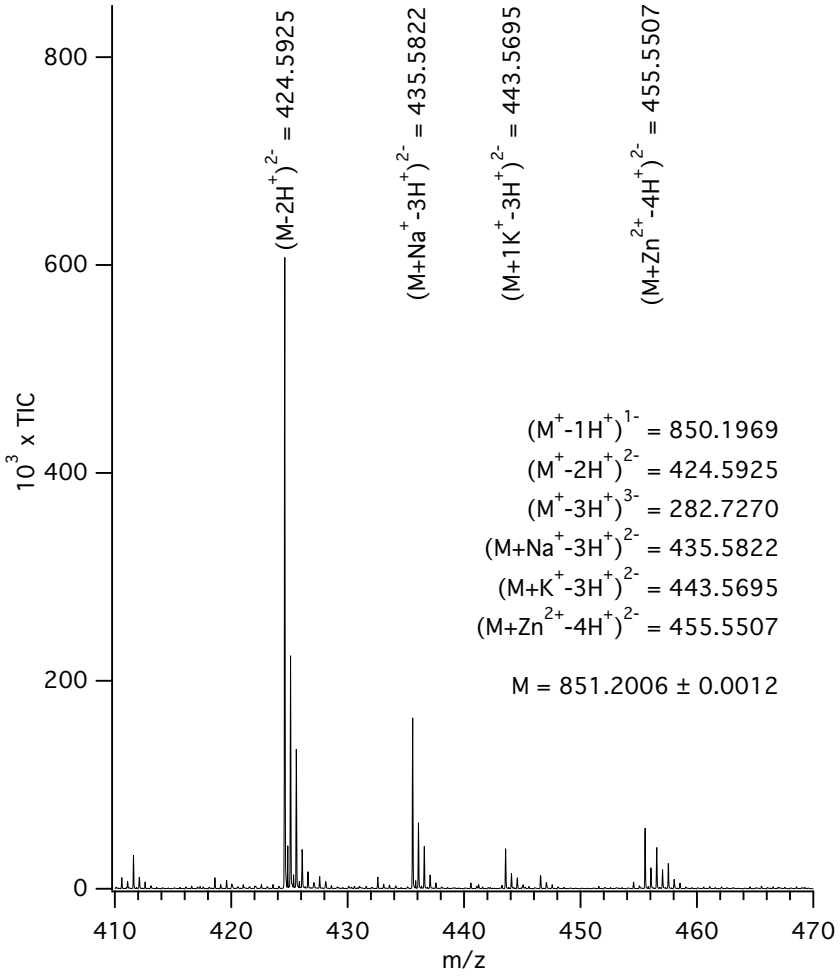

FIGURE S1: The mass spectrum of mb-SB2, focusing in on the m/z region containing -2 charged species. The m/z values used to calculate the neutral exact mass are shown and include the m/z values for the -1 and -3 charged formed (data not shown).

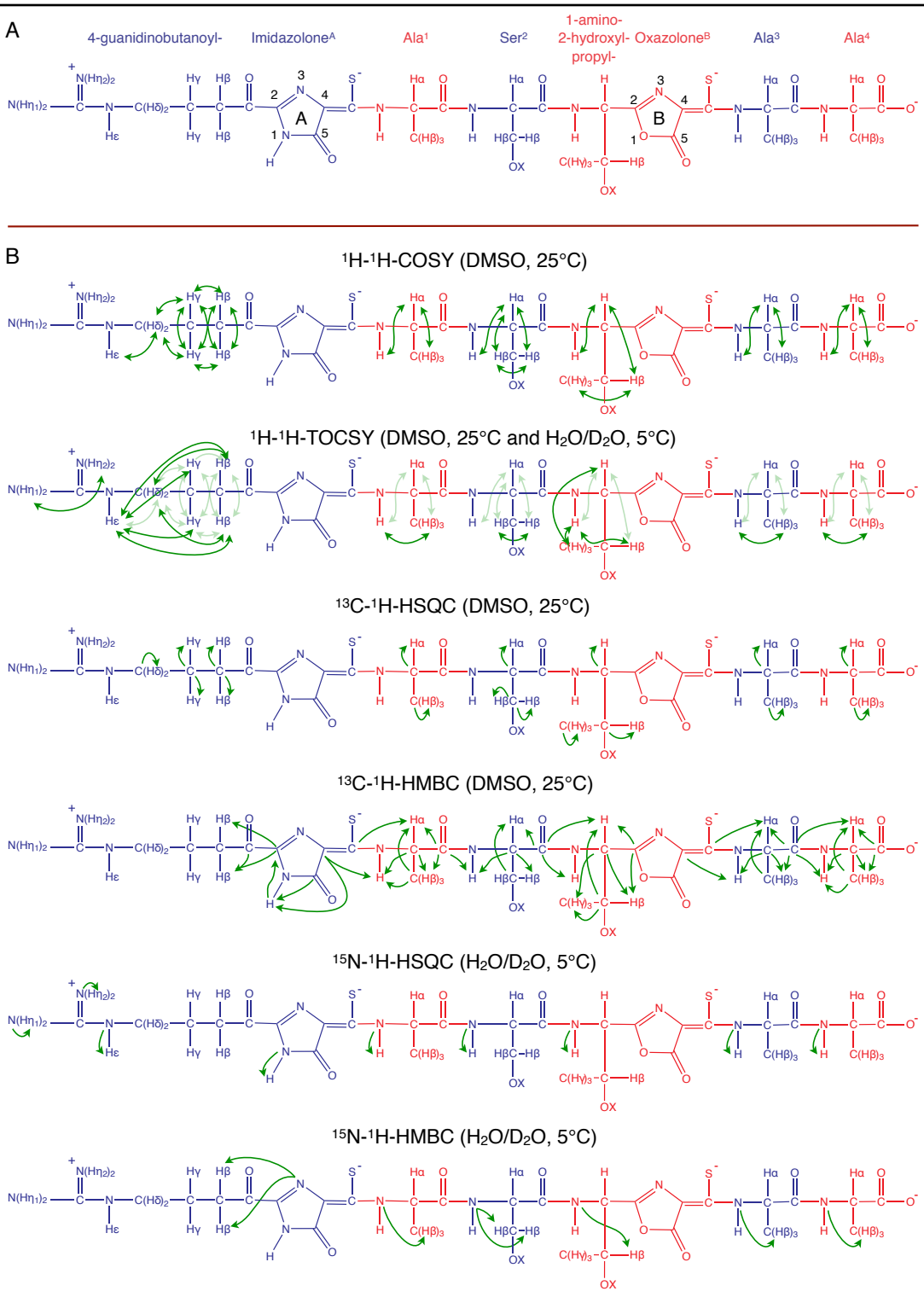

Figure S2: (A) The proposed structure for mb-SB2 based on the NMR analysis, and (B) a summary of the correlation observed in 2D NMR experiments, which were used to determine the proposed structure for mb-SB2 shown in (A) and in Figure 5.

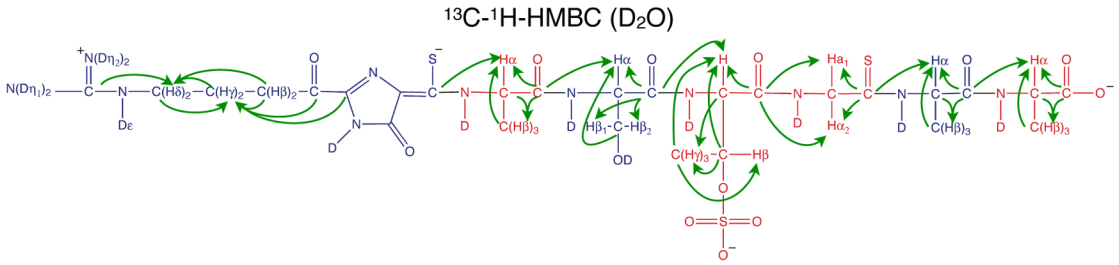

Figure S3. The long-range ^{1}H-^{13}C correlations observed in an ^{1}H-^{13}C-HMBC experiment that was run on the isolated product after hydrolysis and decarboxylation of the oxazolone B-ring in mb-SB2.

Table S1: ^{1}H, ^{13}C, and ^{15}N Resonance assignments for Cu^{+}-bound methanobactin from *Methylocystis* species SB2

		Resonances (ppm)			
		H_2O - 5°C	DMSO - 25°C	DMSO - 25°C	H_2O - 5°C
	Atom	^{1}H	^{1}H	^{13}C	^{15}N
4-Guanidino-butanoyl-	C^{α}			171.30	
	C^{β}			30.92	
	C^{γ}			27.88	
	C^{δ}			40.60	
	N^{ε}				84.00
	C^{ζ}			N/A	
	$N^{\eta 1}$				69.79
	$N^{\eta 2}$				70.91
	$H^{\beta 1}$	2.69	2.91		
	$H^{\beta 2}$	2.95	3.13		
	$H^{\gamma 1}$	1.65	1.80		
	$H^{\gamma 2}$	1.77	1.88		
	H^{δ}	3.15	3.24		
	H^{ε}	7.00	7.45		
	$H^{\eta 1}$	6.52	6.99		
	$H^{\eta 2}$	6.90	7.34		
Imidazolone A	N^{1}				174.04
	C^{2}			139.24	
	N^{3}				292.08
	C^{4}			107.10	
	C^{5}			160.07	
	C^{6}			188.04	
	H^{1}	11.26	11.34		
Ala^{1}	N				144.67
	C			172.25	
	C^{α}			56.40	
	C^{β}			17.38	
	H^{N}	11.70	12.21		
	H^{α}	4.59	4.62		
	H^{β}	1.65	1.69		
Ser^{2}	N				110.99
	C			170.18	
	C^{α}			54.13	
	C^{β}			62.20	
	H^{N}	8.03	7.96		
	H^{α}	4.73	4.65		
	$H^{\beta 1}$	3.73	3.69		

		Resonances (ppm)			
		H_2O - 5°C	DMSO - 25°C	DMSO - 25°C	H_2O - 5°C
	Atom	^{1}H	^{1}H	^{13}C	^{15}N
1-Amino-2-hydroxy-propyl-	N				119.59
	C^{α}			51.57	
	C^{β}			73.34	
	C^{γ}			17.98	
	H^{N}	7.40	7.33		
	H^{α}	4.90	4.78		
	H^{β}	3.81	4.04		
	H^{γ}	1.01	1.03		
Oxazolone B	C^{2}			146.93	
	N^{3}				232.44
	C^{4}			107.10	
	C^{5}			N/A	
	C^{6}			179.83	
Ala^{3}	N				128.85
	C			171.96	
	C^{α}			52.52	
	C^{β}			19.58	
	H^{N}	8.23	8.77		
	H^{α}	4.81	5.11		
	H^{β}	1.59	1.61		
Ala^{4}	N				129.96
	C			173.95	
	C^{α}			47.80	
	C^{β}			17.26	
	H^{N}	8.45	8.79		
	H^{α}	4.10	4.46		
	H^{β}	1.35	1.51		

Table S2: ^{1}H and ^{13}C Resonance assignments for metal-free methanobactin from *Methylocystis* species SB2 after hydrolysis of the Oxazolone B ring. Data were collected in either H_2O/D_2O or D_2O at 5°C.*

		Resonances (ppm)			
	Atom	^{1}H		^{13}C	
4-Guanidino-butanoyl-	C^{α}			180.85	
	C^{β}			27.94	(27.57)
	C^{γ}			25.43	(25.51)
	C^{δ}			40.37	(40.11)
	C^{ζ}			156.06	
	$H^{\beta 1}$	2.70	(2.60)		
	$H^{\beta 1}$	2.70	(2.77)		
	H^{γ}	1.91	(1.89)		
	H^{δ}	3.23	(3.22)		
	H^{ε}	7.36			
	$H^{\eta 1}$	6.37			
	$H^{\eta 2}$	6.91			
Imidazolone A	C^{2}			138.78	
	C^{6}			190.92	
	H^{1}	11.15			
Ala[1]	C			175.46	
	C^{α}			55.00	(55.36)
	C^{β}			17.07	(16.75)
	H^{N}	11.81			
	H^{α}	**4.90**	**(4.80)**		
	H^{β}	1.58	(1.58)		
Ser[2]	C			172.02	
	C^{α}			55.26	(55.37)
	C^{β}			60.50	(60.56)
	H^{N}	8.54			
	H^{α}	4.55	(4.54)		
	$H^{\beta 1}$	3.89	(3.91)		
	$H^{\beta 2}$	3.93	(3.91)		

		Resonances (ppm)			
	Atom	^{1}H		^{13}C	
Thr[B]	C			170.55	
	C^{α}			**57.82**	**(51.91)**
	C^{β}			74.72	(75.48)
	C^{γ}			16.99	(16.99)
	H^{N}	8.44			
	H^{α}	**4.55**	**(4.94)**		
	H^{β}	**4.89**	**(4.77)**		
	H^{γ}	1.39	(1.35)		
Gly[B]	C			**199.83**	
	C^{α}			**49.30**	
	H^{N}	**8.55**			
	$H^{\alpha 1}$	**4.23**			
	$H^{\alpha 2}$	**4.33**			
Ala[3]	C			172.20	
	C^{α}			**55.00**	**(52.98)**
	C^{β}			17.07	(17.40)
	H^{N}	9.54			
	H^{α}	**4.81**	**(4.92)**		
	H^{β}	1.49	(1.49)		
Ala[4]	C			179.69	
	C^{α}			50.78	(50.83)
	C^{β}			16.84	(17.09)
	H^{N}	8.20			
	H^{α}	4.10	(4.11)		
	H^{β}	1.32	(1.33)		

* The values in parentheses are the corresponding assignments for unhydrolyzed mb-SB2 in D_2O at 5°C. The values highlighted in bold type are are those values that differ more than 1.0 ppm for ^{13}C and 0.1 ppm for ^{1}H.