Pterulamides I-VI, New Linear Peptides from a Malaysian *Pterula* Species

Gerhard Lang,[†] Maya Mitova,[†] Anthony L. J. Cole,[‡] Laily Bin Din,[§] Sabaratnam Vikineswary,[⊥] Noorlidah Abdullah, [⊥] John W. Blunt,[†] Murray H. G. Munro*,[†]

Supporting Information

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* To whom correspondence should be addressed. Tel.: +64-3-3642434. Fax: +64-3-3642429. E-mail: murray.munro@canterbury.ac.nz.
† Department of Chemistry.
‡ School of Biological Sciences.
§ School of Chemical Sciences and Food Technology
⊥ Institute of Biological Sciences

Table S1: NMR data of pterulamide II (2; 500 MHz in $CDCl_3$):

Position	δ_C [a]	δ_H	COSY	HMBC	TOCSY	ROESY
MTP [b]						
CO	165.9					
α	111.1	6.05 *d* 14.6	β	β, CO	β	*Ala*-NMe, SMe
β	147.9	7.80 *d* 14.6	α	α, CO, SMe	α	SMe
S-Me	15.0	2.37 *s*		β		α, β
Ala						
CO	172.3					
α	49.9	5.55 *q* 6.7	β	CO	β	NMe, *Ile1*-NMe
β	14.8	1.28 *d* 6.7	α	α, CO	α	NMe, *Ile1*-NMe
N-Me	30.9	3.04 *s*		α, *MTP*-CO		α, β, *MTP*- α
Ile1						
CO	171.7					
α	57.4	5.21 *d* 10.7	β	β, βMe, CO	β, βMe, γ, γ', δ	*Val1*-NMe, *Val1*-α, NMe
β	33.0	2.11 *m*	α, γ, βMe		α, βMe, γ, γ', δ	NMe
β-Me	15.7	0.86	β	α, β, γ	α, β, γ, γ', δ	
γ	24.3	1.28 + 0.99	β, δ		α, β, βMe, δ	
δ	10.6	0.85	γ		α, β, βMe, γ, γ'	
N-Me	30.1	2.97 *s*		α, *Ala*-CO		α, β, *Ala*-α, *Ala*-β
Val1						
CO	170.7					
α	61.1	4.53 *br*	β	CO	β, γ, γ'	*Ile1*-α
β	26.2	2.30 *m*	α, γ, γ'		α, γ, γ'	NMe
γ	19.2	0.86	β	β, γ'	α, β, γ'	α, NMe
γ'	18.4	0.74 *d* 6.3	β	β, γ	α, β, γ	NMe
N-Me	31.7	3.09 *s*		*Ile1*-CO		β, γ, γ', *Ile1*-α
Val2						
CO	173.4					
α	54.3	4.63 *t* 8.3	β, NH	β, γ, γ', CO	β, γ, γ'	*Ile2*–NMe
β	30.9	2.01 *m*	α, γ+γ'		α, γ, γ'	
γ+γ'	18.49	0.86	β	α, β	α, β	
NH		7.25	α		α	
Ile2						
CO	170.5					
α	61.4	4.68 *d* 11.5	β	β, βMe, CO, *Val2*-CO	β, βMe, γ, γ', δ	
β	31.5	2.10 *m*	α,γ, βMe		α, βMe, γ, γ', δ	NMe, NHMe
β-Me	18.5	0.89 *m*	β	α, β, γ	α, β, γ, γ', δ	
γ	24.5	1.28 + 0.91	β, δ		α, β, βMe, δ	
δ	10.4	0.83	γ		α, β, βMe, γ, γ'	
N-Me	31.1	3.16 *s*		α, *Val2*-CO		β,. NHMe, *Val2*-α
CON*H*		6.82 *br*	CONH*Me*		CONH*Me*	
CONH*Me*	26.1	2.76 *d* 4.4	CON*H*	*Ile2*-CO	CON*H*	*Ile2*-β, *Ile2*–NMe

[a] ^{13}C shifts are from the HSQC-DEPT and HMBC spectra

[b] MTP = *(E)*-3-methylthiopropenoyl residue

Table S2: NMR data of pterulamide III (3; 500 MHz in $CDCl_3$):

Position	δ_C[a]	δ_H	COSY	HMBC	TOCSY	ROESY
Benzoyl						
CO	171.7					
1	135.7					
2,6	126.8	7.36 *m*	3, 4, 5	4	(3,5), 4	*Ala*-NMe
3,5	128.6	7.41 *m*	2, 4, 6	1, (2,6)	(2,6), 4	
4	129.8	7.41 *m*	2, 3, 5, 6	(2,6), (3,5)	(2,6), (3,5)	
Ala						
CO	172.1					
α	49.2	5.59 *q* 6.7	β		β	NMe, *Ile1*-NMe
β	14.4	1.38 *d* 6.7	α	α, CO	α	NMe
N-Me	33.1	2.96 *s*		α, *Bz*-CO		α, β, *Bz*-2,6
Ile1						
CO	171.7					
α	57.0	5.28 *d* 10.3	β	β, CO	β, βMe, γ, γ', δ	*Val1*-NMe, γ
β	32.9	2.19 *m*	α, γ, β-Me		α, βMe, γ, γ', δ	NMe
β-Me	15.7	0.87 *m*	β	α, β, γ	α, β, γ, γ', δ	
γ	24.1	1.38, 1.07 *m*	β, δ		α, β, βMe, δ	α
δ	10.6	0.91 *m*	γ		α, β, βMe, γ, γ'	
N-Me	30.2	3.10 *s*		α		β, *Ala*-α
Val1						
CO	170.5					
α	61.1	4.57 *br*	β	CO	β, γ, γ'	γ
β	26.2	2.30 *m*	α, γ, γ'		α, γ, γ'	NMe
γ	19.3	0.86 *m*	β	β	α, β, γ'	α, NMe
γ'	18.2	0.76 *d* 6.3	β	β, γ	α, β, γ	NMe
N-Me	31.0	3.10 *s*		*Ile1*-CO		β,γ, γ', *Ile1*-α
Val2						
CO	173.0					
α	53.8	4.67 *m*	β, NH	CO	β, γ, γ'	*Ile2*–NMe
β	31.1	1.99 *m*	α, γ, γ'		α, γ, γ'	
γ	24.5	0.86 *m*	β	α, β, γ'	α, β	
γ'	18.7	0.83 *m*		β, γ		
NH		7.05 *br*	α			
Ile2						
CO	170.2					
α	60.9	4.67 *m*	β	CO	β, βMe, γ, γ', δ	γ
β	31.1	2.10 *m*	α, γ, β-Me		α, βMe, γ, γ', δ	NMe
βMe	19.0	0.87 *m*	β	α, β, γ	α, β, γ, γ', δ	
γ	24.2	1.30, 0.99 *m*	β, δ		α, β, βMe, δ	α
δ	10.4	0.81 *m*	γ		α, β, βMe, γ, γ'	
NMe	30.9	3.13 *s*		α, *Val2*-CO		β, *Val2*-α
CON*H*		6.49 *br*	CONH*Me*		CONH*Me*	
CONH*Me*	25.8	2.76 *d* 4.4	CON*H*	*Ile2*-CO	CON*H*	

[a] ^{13}C shifts are from the HSQC-DEPT and HMBC spectra

Table S3: NMR data of pterulamide IV (4; 500 MHz in $CDCl_3$):

Position	δ_C[a]	δ_H	COSY	HMBC	TOCSY	ROESY
Cinnamoyl						
CO	166.8					
α	116.4	6.87 *d* 15.5	β	C-1	β	*Ala*-NMe, (2,6)
β	143.7	7.72 *d* 15.5	α	C-1	α	
C-1	137.7					
C-2,6	127.7	7.53 *m*	3, 4, 5		3, 4, 5	*cinnamoyl*-α
C-3,5	128.7	7.37 *m*	2, 4, 6	C-1	2, 4, 6	
C-4	129.7	7.37 *m*	2, 3, 5, 6		2, 3, 5, 6	
Ala						
CO	172.1					
α	49.1	5.67 *q* 7.1	β		β	*Ile1*-NMe
β	14.5	1.31 *d* 7.1	α		α	NMe
N-Me	30.4	3.11 *s*		α, *cinnamoyl*-CO		β, *cinnamoyl*-α
Ile1[b]						
CO	171.7					
α	56.9	5.25 *d* 11.1	β		β, βMe, γ, γ', δ	*Val1*-NMe
β	32.6	2.16 *m*	α, γ, β-Me		α, βMe, γ, γ', δ	NMe
β-Me	15.4	0.86 *m*	β	α, β, γ	α, β, γ, γ', δ	
γ	23.9	1.31 *m* + 1.02	β, δ		α, β, βMe, δ	NMe
δ	10.3	0.86	γ		α, β, βMe, γ, γ'	
N-Me	29.9	3.00 *s*		α, *Ala*-CO		β, γ, *Ala*-α
Val1[b]						
CO						
α	60.6	4.43 *br*	β		β, γ, γ'	
β	25.9	2.33 *m*	α, γ, γ'		α, γ, γ'	NMe
γ	19.3	0.87 *m*	β	β, γ'	α, β, γ'	
γ'	17.9	0.76 *d* 6.7	β	β, γ	α, β, γ	NMe
N-Me	30.5	3.08 *s*		*Ile1*-CO		β, γ', *Ile1*-α
Val2[b]						
CO	173.0					
α	53.4	4.67 *t* 8.5	β, NH		β, γ, γ'	*Ile2*–NMe
β	30.7	1.98 *m*	α, γ, γ'		α, γ, γ'	
γ	17.6	0.84	β	α, β	α, β	
γ'	15.4	0.84	β	α, β	α, β	
NH		6.70 *br*	α			
Ile2[b]						
CO	171.0					
α	60.7	4.60 *d* 11.1	β		β, βMe, γ, γ', δ	
β	31.1	2.12 *m*	α,γ, βMe		α, βMe, γ, γ', δ	NMe
β-Me	18.8	0.87 *m*	β	α, β, γ	α, β, γ, γ', δ	
γ	23.8	1.28 *m* + 0.94	β, δ		α, β, βMe, δ	
δ	10.1	0.81	γ		α, β, βMe, γ, γ'	
N-Me	30.4	3.10 *s*		α, *Val2*-CO		β, *Val2*-α
CON*H*[d]		6.22 *br*	CONH*Me*		NH*Me*	
CONH*Me*	25.5	2.76 *d* 4.8	CON*H*	*Ile2*-CO	N*H*	

[a] ^{13}C shifts from HSQC-DEPT and HMBC spectra

[b] similar amino acids are numbered consecutively from *N*- to *C*-terminal end

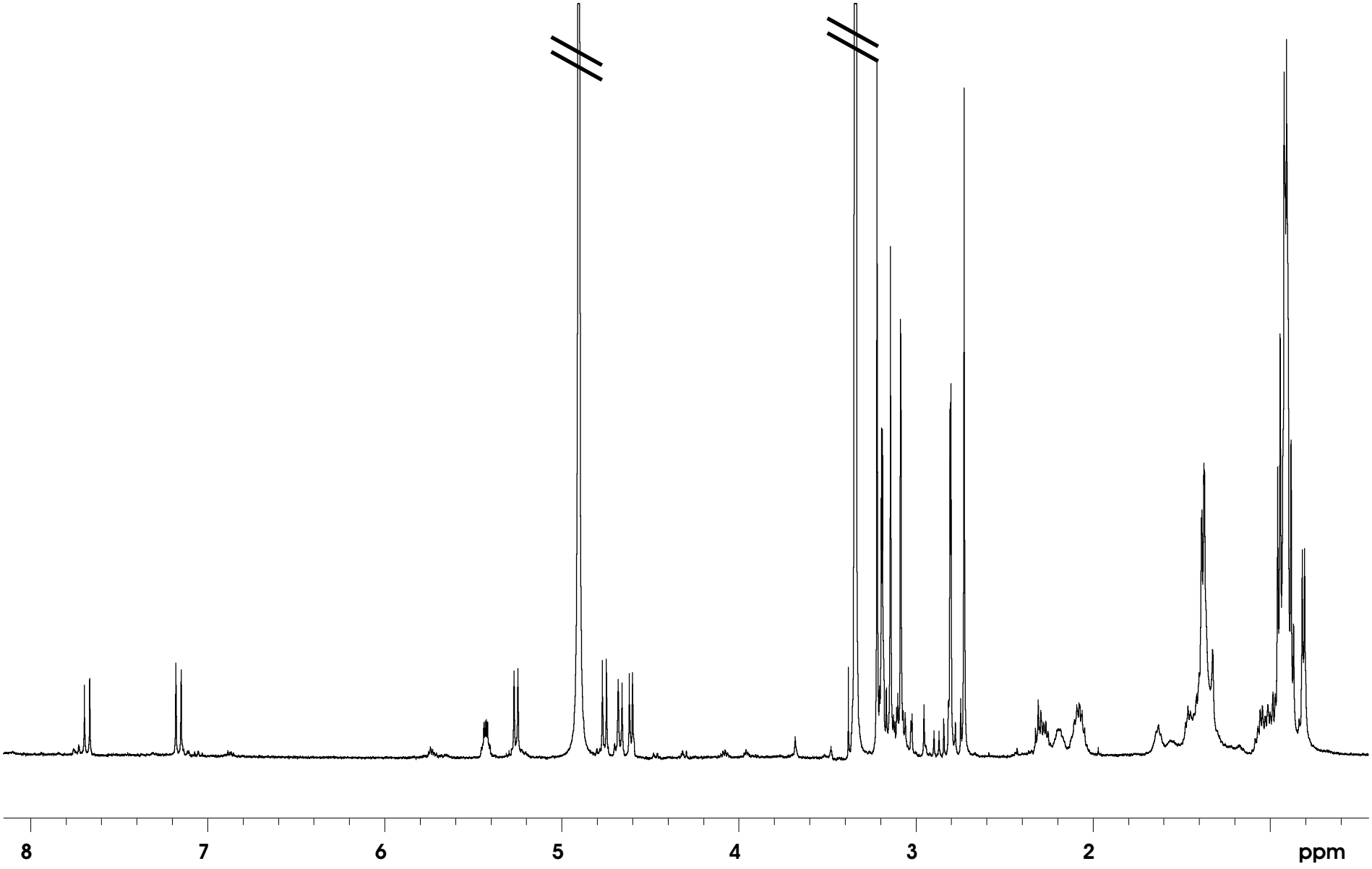
Table S4: NMR data of pterulamide VI (6; 500 MHz in $CDCl_3$):

Position	δ_C[a]	δ_H	COSY	HMBC	ROESY	TOCSY
Bz						
CO	172.0					
1	136.4					
2/6	126.6	7.29 *m*	3/5 o. 4	CO, 2/6, 4	*Val1*-NMe	
3/5	128.8	7.40	2/6	2/6, 3/5		
4	129.7	7.40	2/6	2/6, 3/5		
Val1[b]						
CO	170.6					
α	58.4	5.33 *d* 11.0	β	CO, β, γ, γ', NMe, *Bz*-CO	β, γ, γ'	β, γ, γ'
β	26.9	2.43	α, γ, γ'	α	α, γ, γ'	α, γ, γ'
γ	19.6	0.93	β	α, β, γ'	α, β	α, β
γ'	18.2	0.98 *d* 6.5	β	α, β, γ	α, β	α, β
N-Me	32.9	2.87 *s*		α, *Bz*-CO	*Bz*-2/6	
Val2[b]						
CO	171.0					
α	58.6	5.22 *d* 11.0	β	CO, β, γ, γ', NMe	*Val3*-NMe, β, γ, γ'	β, γ, γ'
β	27.3	2.42	α, γ, γ'		β, γ, γ'	β, γ, γ'
γ	19.9	0.90	β	α, β, γ'	α, γ, γ'	α, γ, γ'
γ'	17.9	0.84	β	α, β, γ	α, β	α, β
N-Me	30.6	3.11 *s*		α, *Val1*-CO		
Val 3[b]						
CO	169.5					
α	62.7	4.58	β	CO, β, γ, γ', NMe	*Val4*-NH, β, γ, γ'	β, γ, γ'
β	26.0	2.26	α, γ, γ'		α, γ, γ'	α, γ, γ'
γ	18.4	0.74 *d* 6.5	β	α, β, γ'	α, β	α, β
γ'	19.5	0.89	β	α, β, γ	α, β	α, β
N-Me	30.6	3.04 *s*		α, *Val2*-CO	*Val2*-α	
Val4[b]						
CO	172.4					
α	53.8	4.71 *t* 9.0	β, NH	CO, β, γ	β, γ, γ'	NH, β, γ, γ'
β	31.1	1.95 *m*	α, γ, γ'		α, γ, γ'	NH, α, γ, γ'
γ	17.8	0.82	β	α, β	α, β	NH, α, β
γ'	~18	0.85	β	α, β, γ	α, β	NH, α, β
NH		6.54 *d* 9.0	α	*Val3*-CO	*Val3*-α	α, β, γ, γ'
Ile						
CO	171.8					
α	56.5	5.28 *d* 11.0	β	CO, β, β-Me, NMe	β, β-Me	β, β-Me, γ
β	33.5	2.14 *m*	α, β-Me		α, γ	α, β-Me, γ
β-Me	15.3	0.87	β	α, β, γ	α	α, β
γ	24.1	0.94+1.25 *m*			β	
δ	10.7	0.82		β, γ		
N-Me	30.7	3.10 *s*		α, *Val4*-CO		
Val5[b]						
CO	171.4					
α	63.9	4.65	β	CO	β, γ, γ'	β, γ, γ'
β	26.9	2.30	α, γ, γ'		α, γ, γ'	α, γ, γ'
γ	18.9	0.79	β	α, β, γ'	α, β	α, β
γ'	19.5	1.05 *d* 6.0	β	α, β, γ	α, β	α, β
N-Me	33.1	3.10 *s*		α, *Ile*-CO		

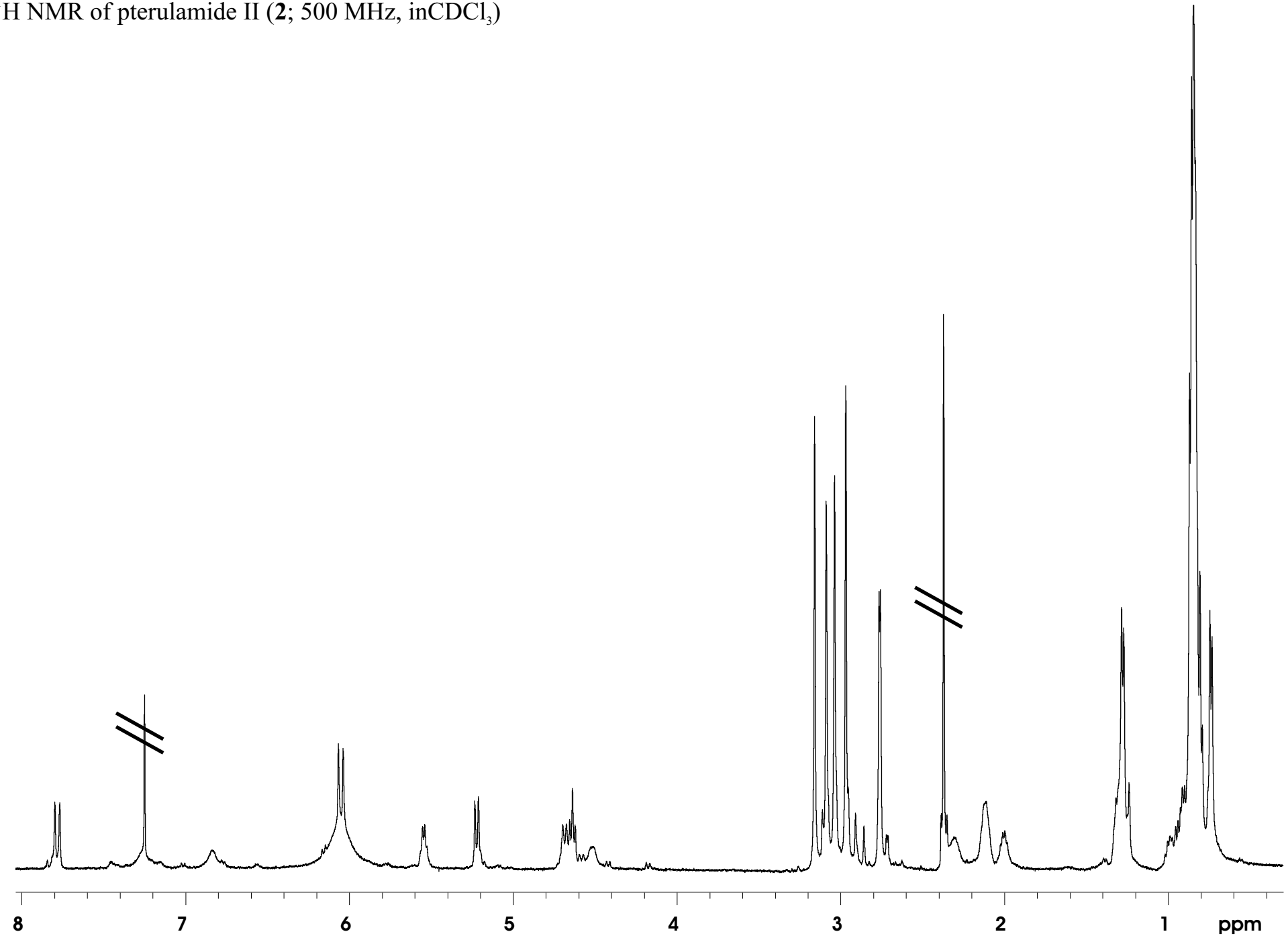
[a] ^{13}C shifts from HSQC-DEPT and HMBC spectra

[b] similar amino acids are numbered consecutively from *N*- to *C*-terminal end

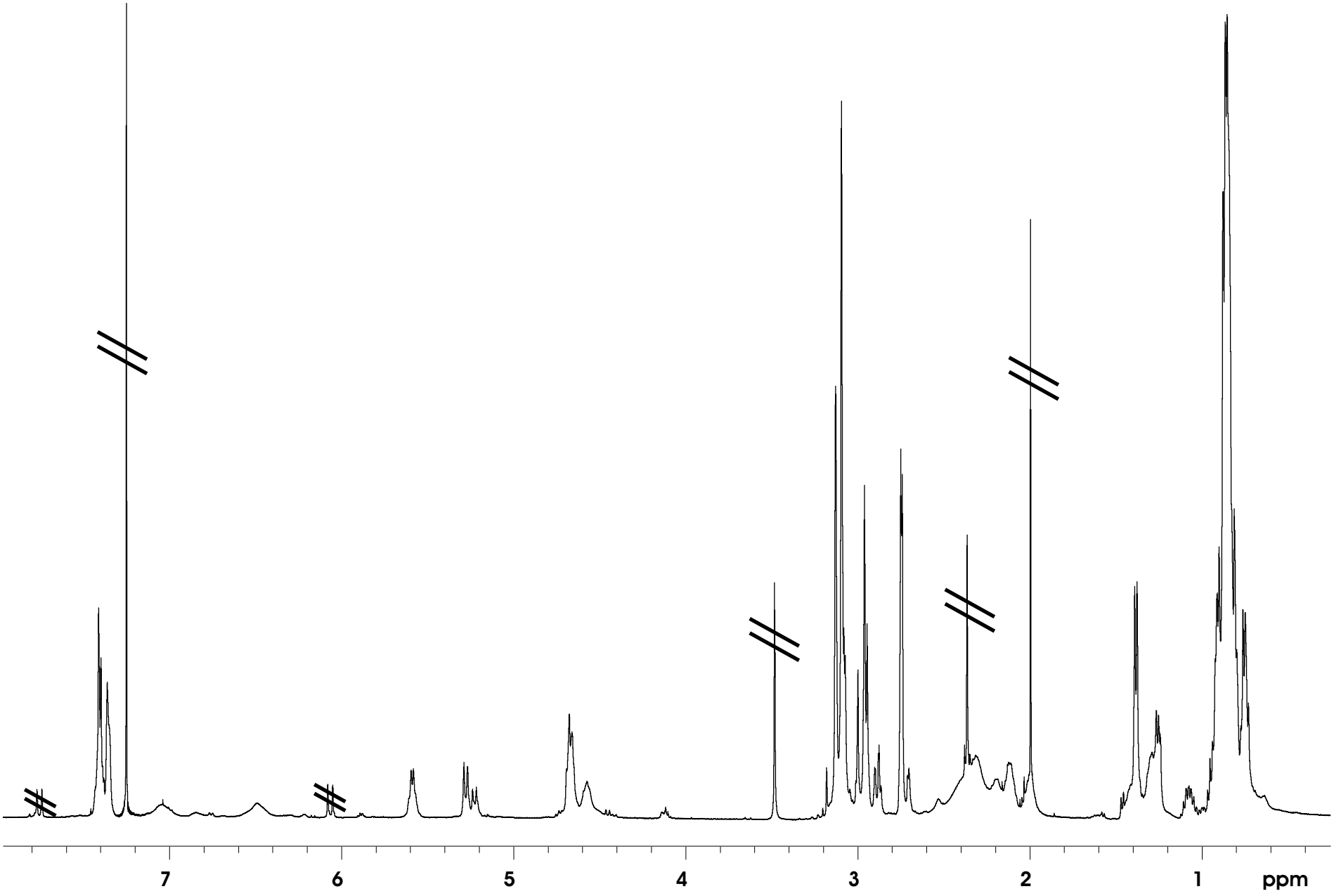
S5: ^{1}H NMR of pterulamide I (**1**; 500 MHz, in MeOH-d_4)



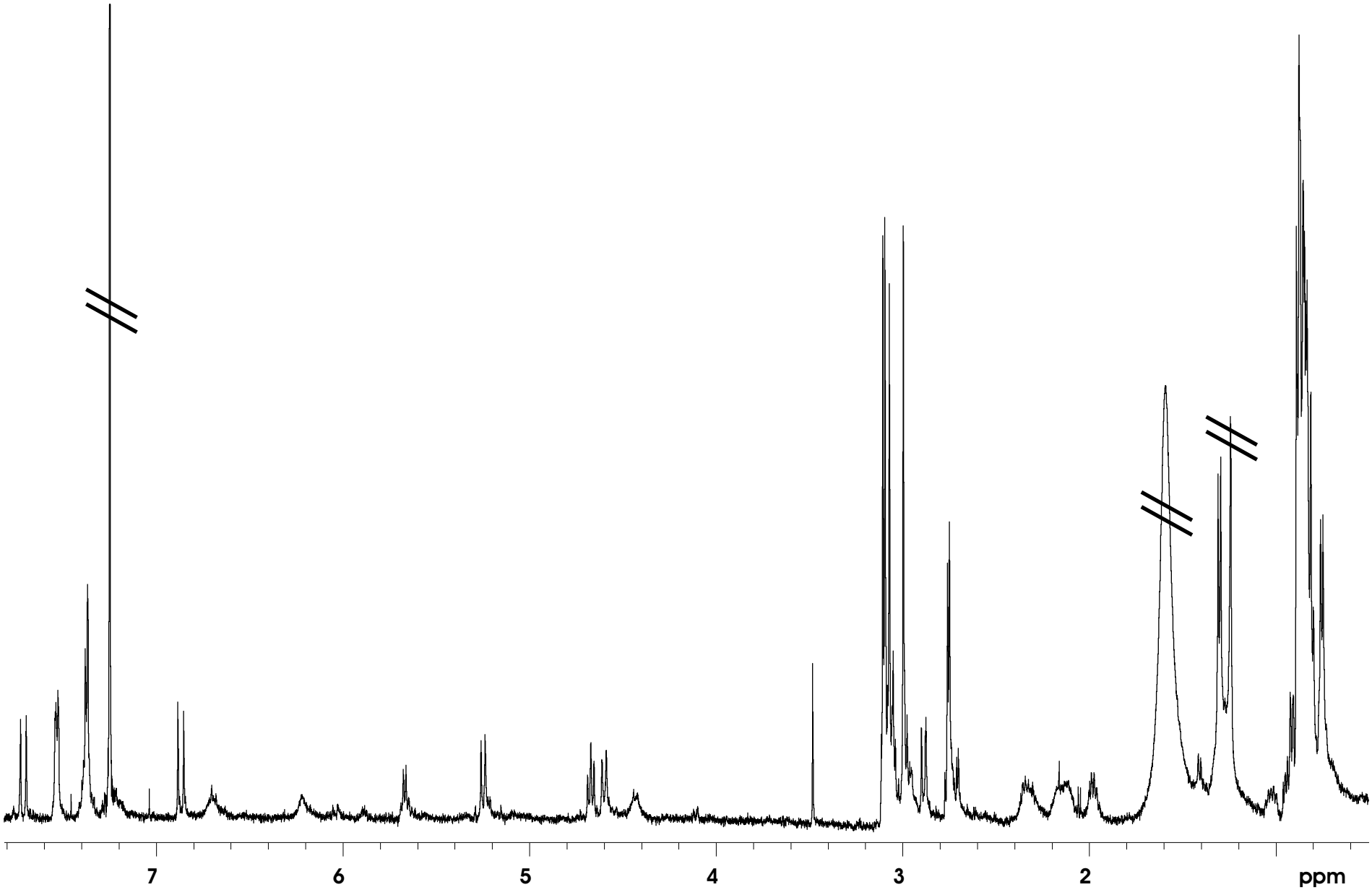
S6: ^{1}H NMR of pterulamide II (**2**; 500 MHz, in$CDCl_3$)



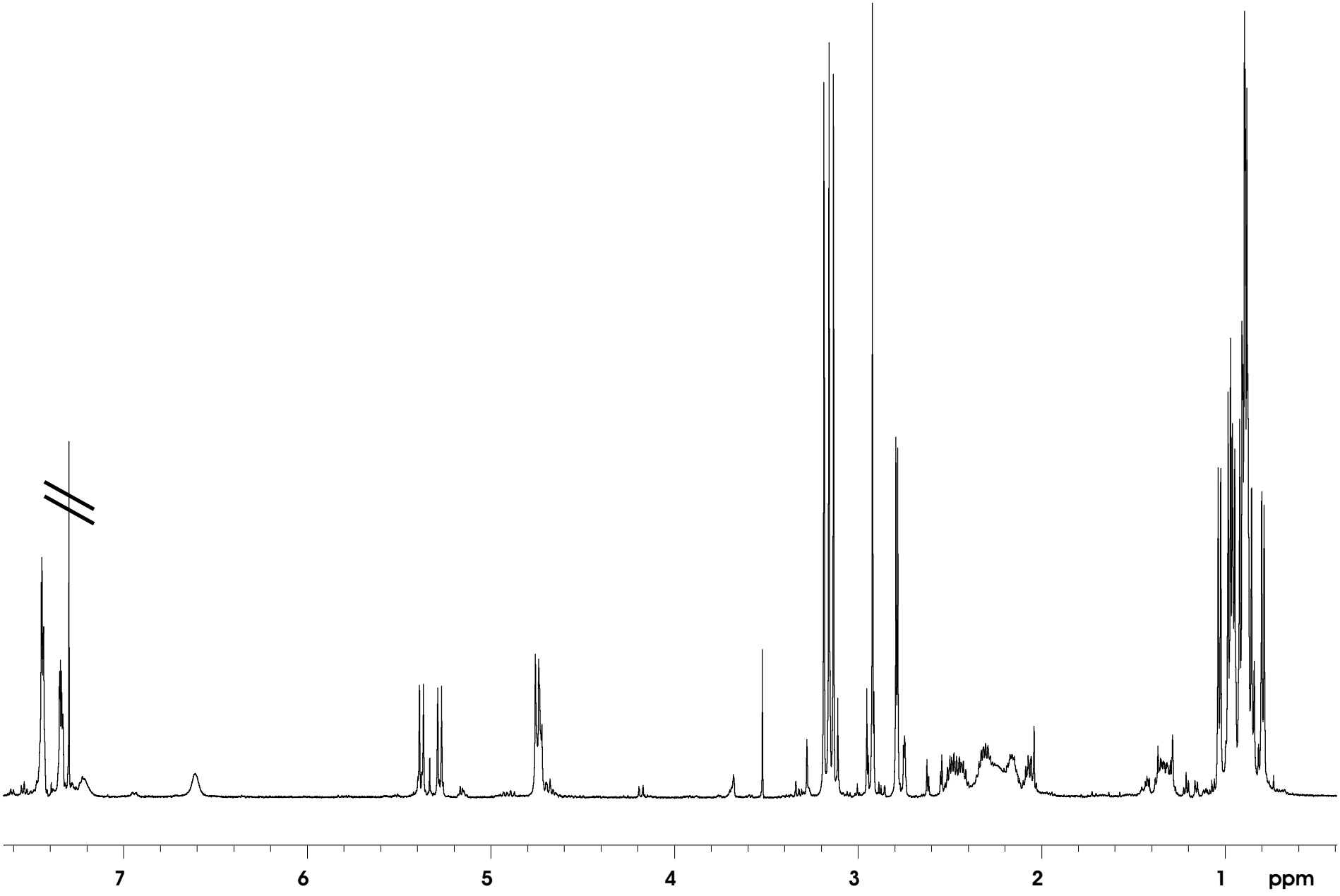
S7: ^{1}H NMR of pterulamide III (**3**; 500 MHz, in$CDCl_3$)



S8: ^{1}H NMR of pterulamide IV (**4**; 500 MHz, in$CDCl_3$)



S9: ^{1}H NMR of pterulamide V (**5**; 500 MHz, in$CDCl_3$)



S10: ^{1}H NMR of pterulamide VI (**6**; 500 MHz, in$CDCl_3$)