Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Prealamethicin F50 and related peptaibols from *Trichoderma arundinaceum*

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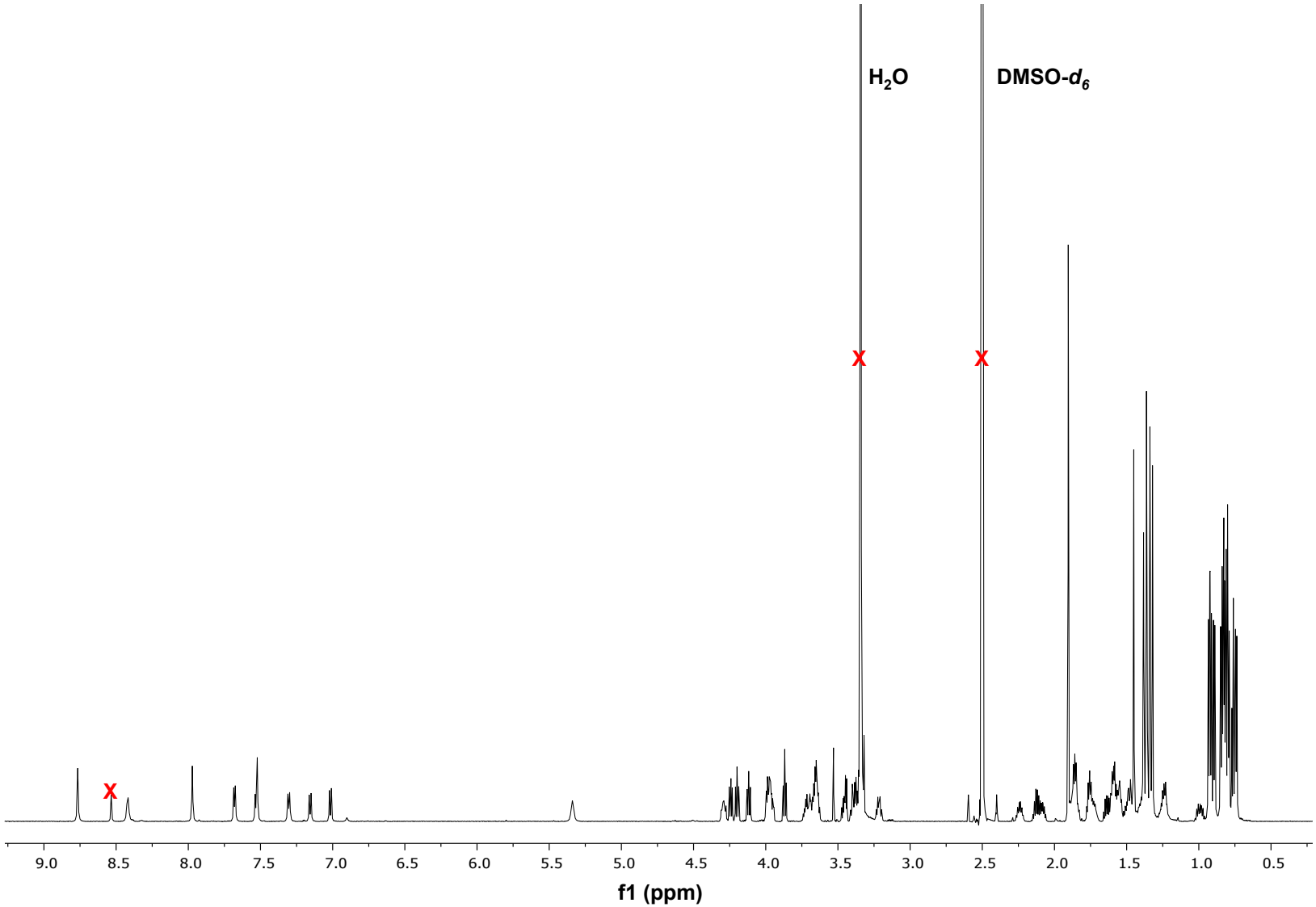

Figure S1. ^{1}H-NMR of compound **1** in DMSO-d_6 recorded at 700 MHz.

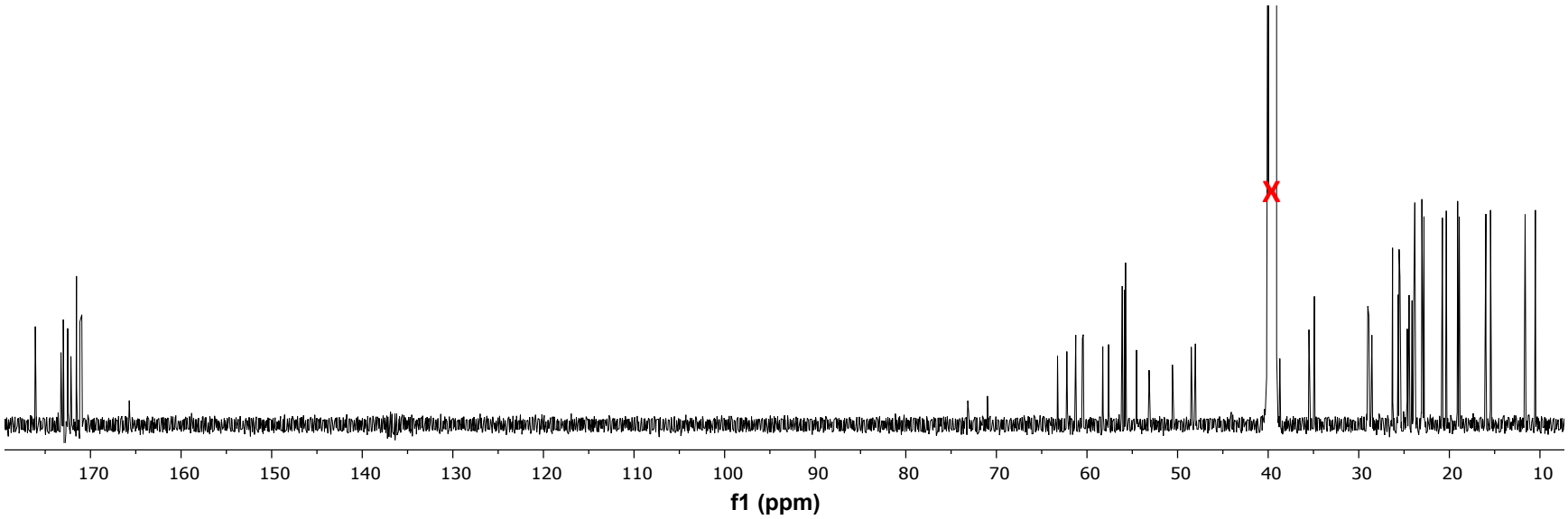

Figure S2. ^{13}C-NMR of compound **1** in DMSO-d_6 recorded at 125 MHz.

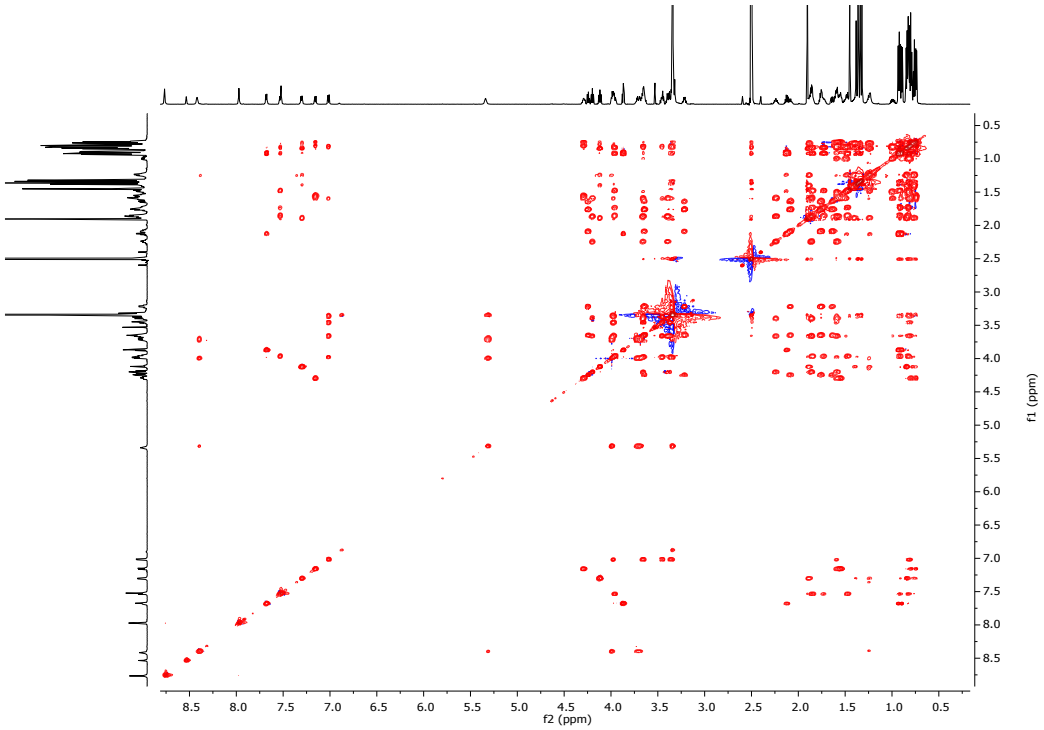

Figure S3. ^{1}H-^{1}H TOCSY spectrum of compound **1** in DMSO-d_6.

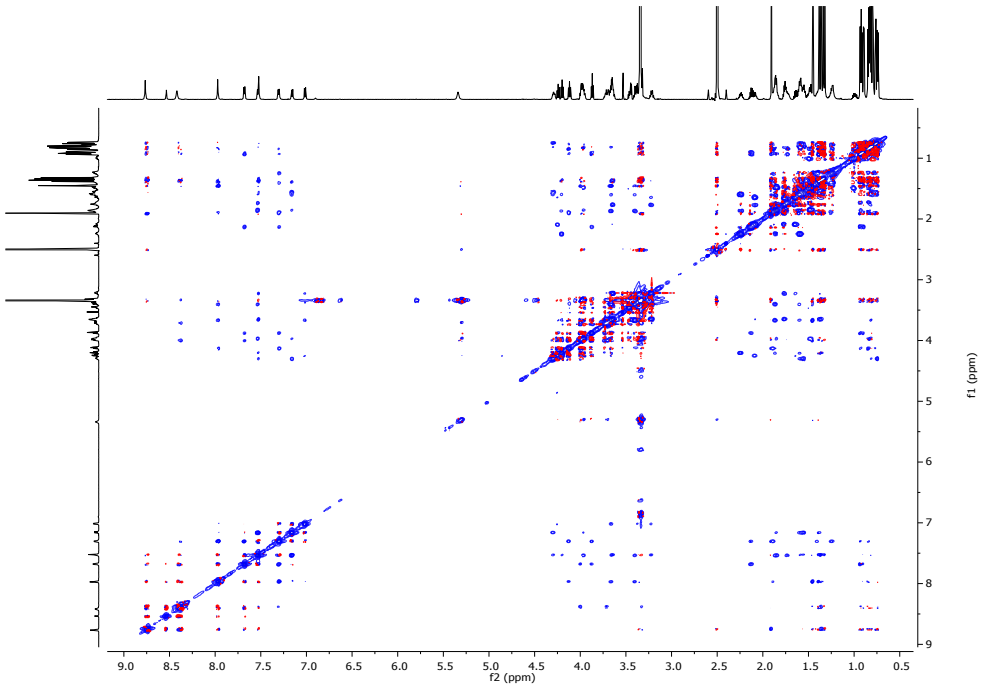

Figure S4. ^{1}H-^{1}H NOESY spectrum of compound **1** in DMSO-d_6.

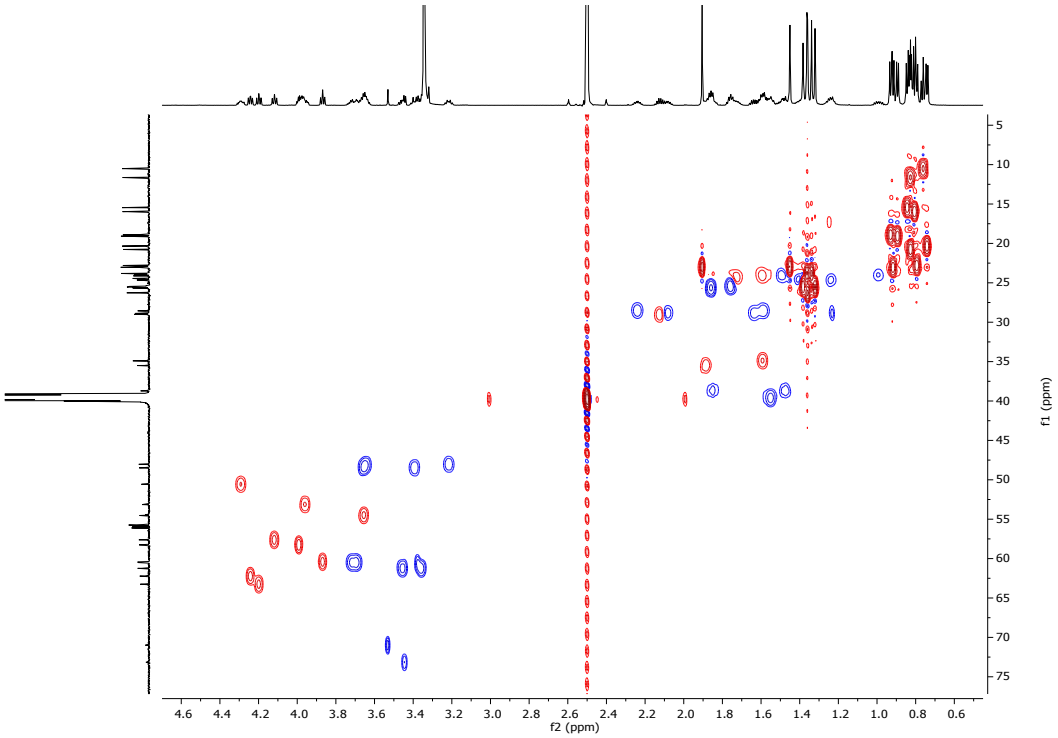

Figure S5. ^{1}H-^{13}C HSQC spectrum of compound **1** in DMSO-d_6.

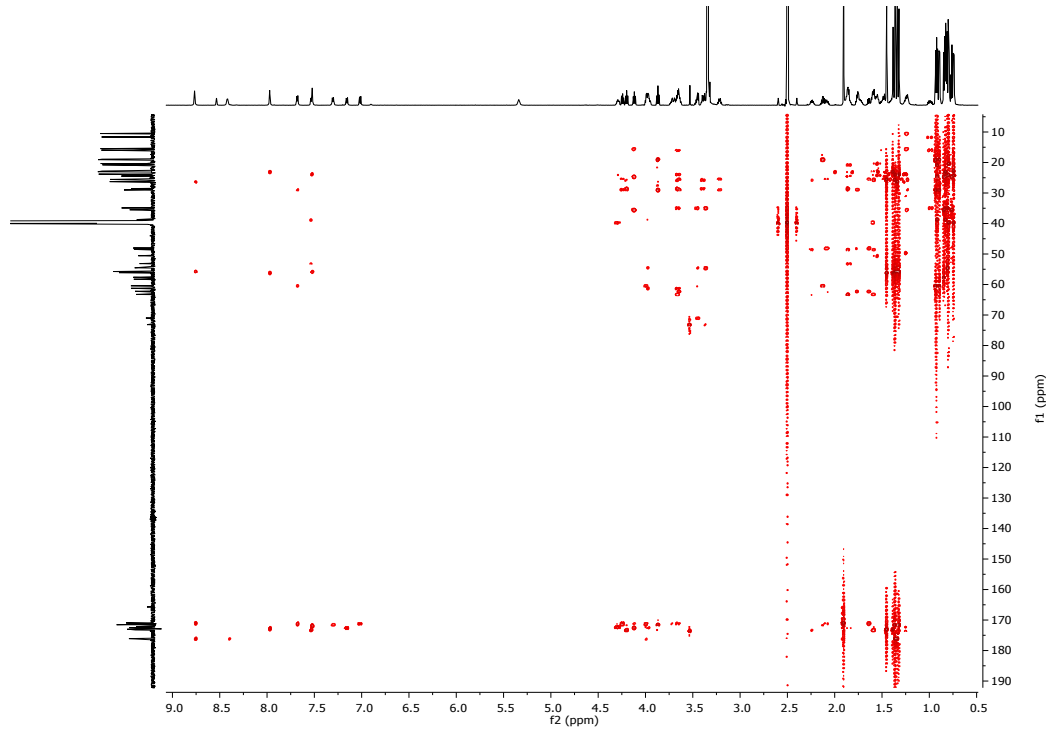

Figure S6. ^{1}H-^{13}C HMBC spectrum of compound **1** in DMSO-d_6.

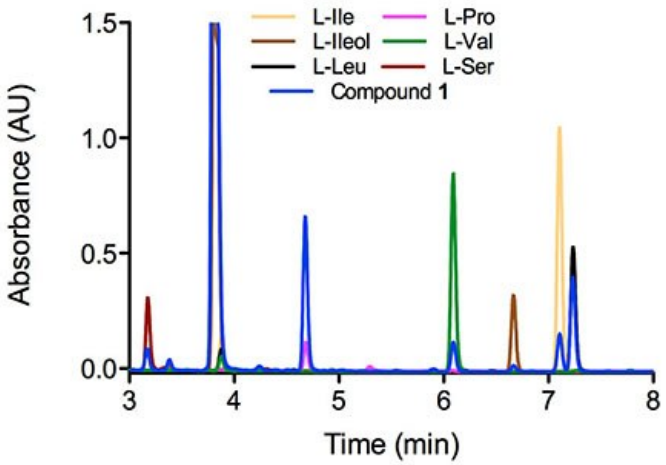

Figure S7. Marfey's analysis of compound **1**.

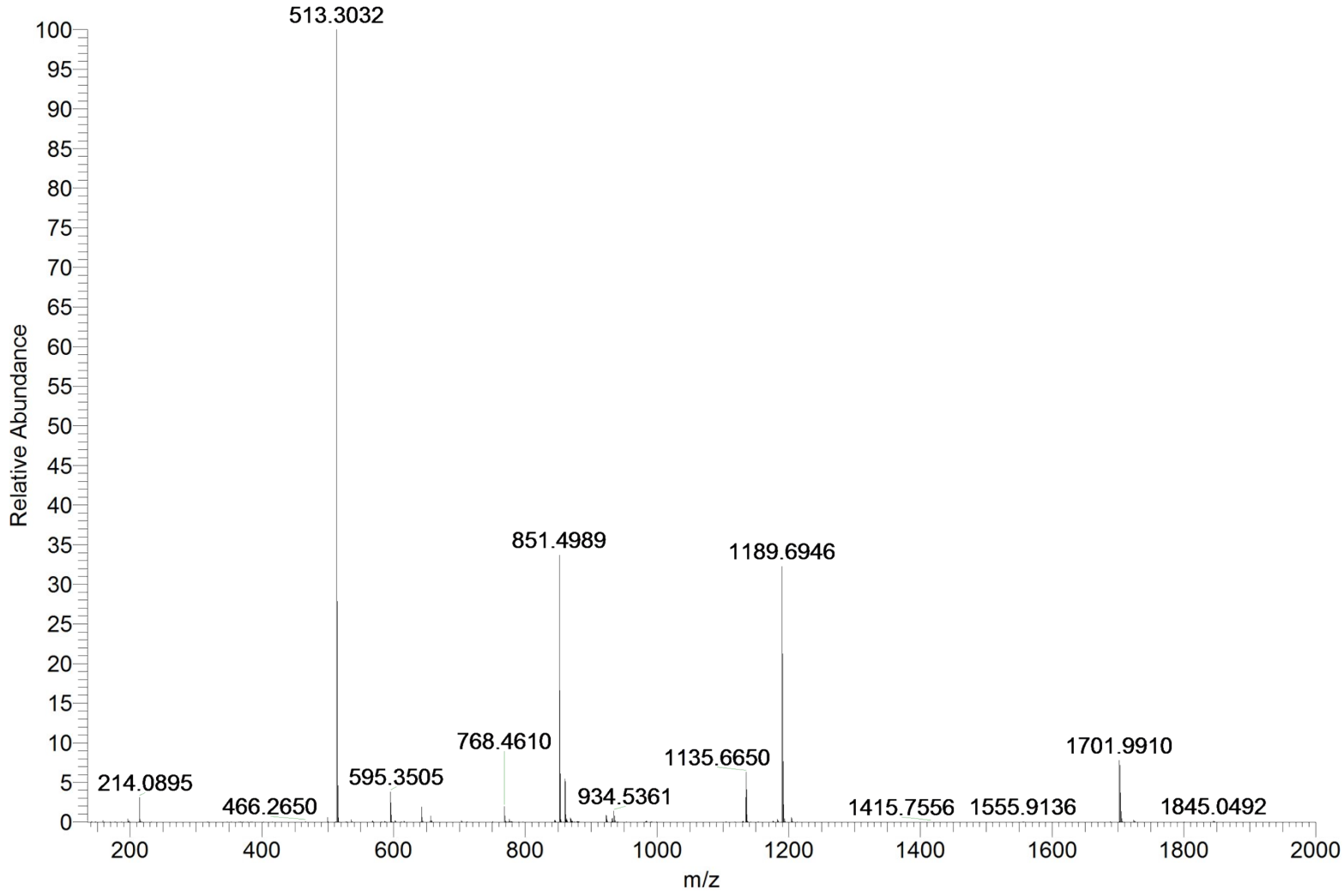

Figure S8. HRESIMS of compound **2** showing insource fragmentation.

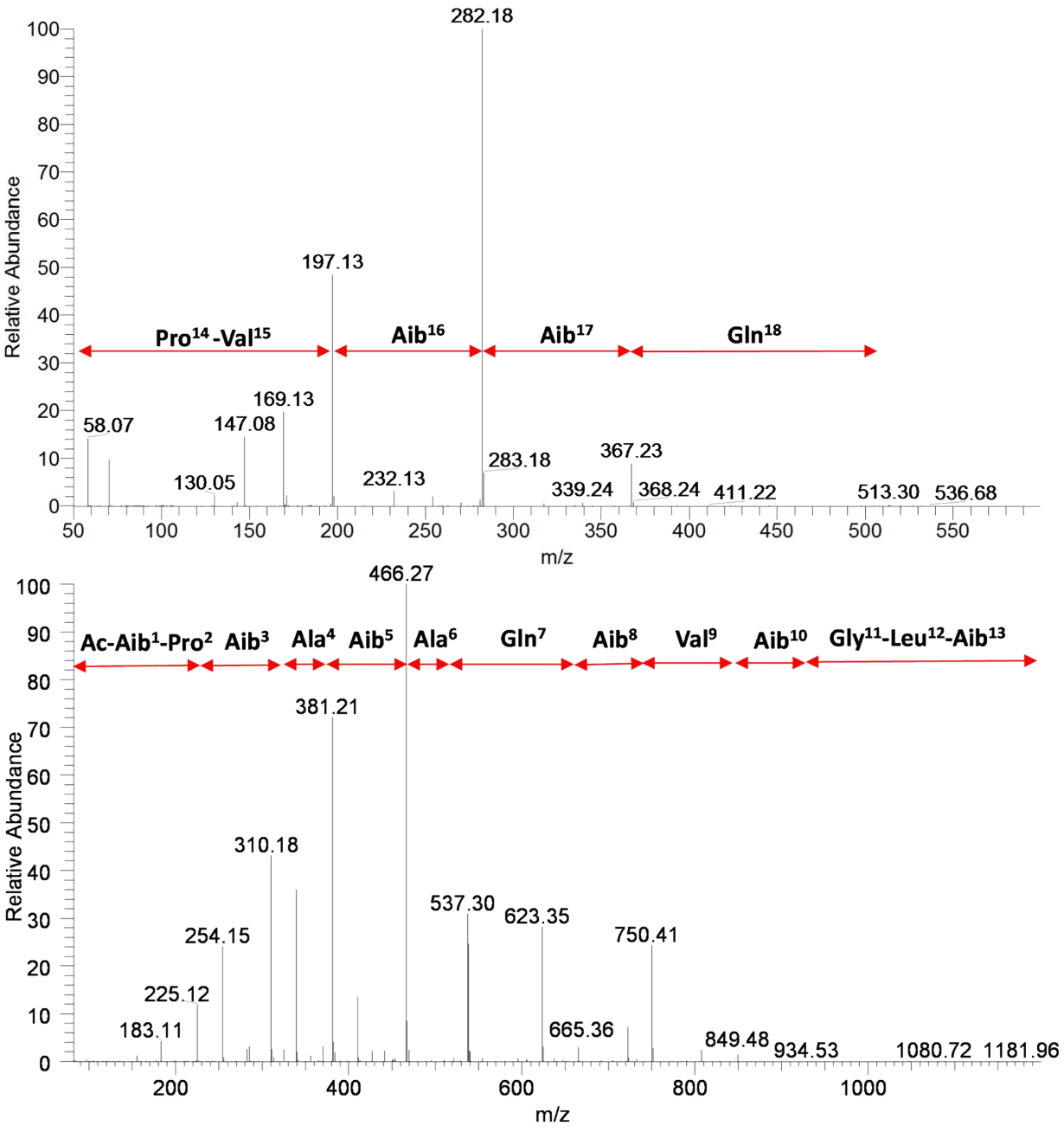

Figure S9. The sequential losses of amino acids for each in-source fragment at *m/z* 1189.69 (top) and *m/z* 513.30 (bottom) for compound **2**.

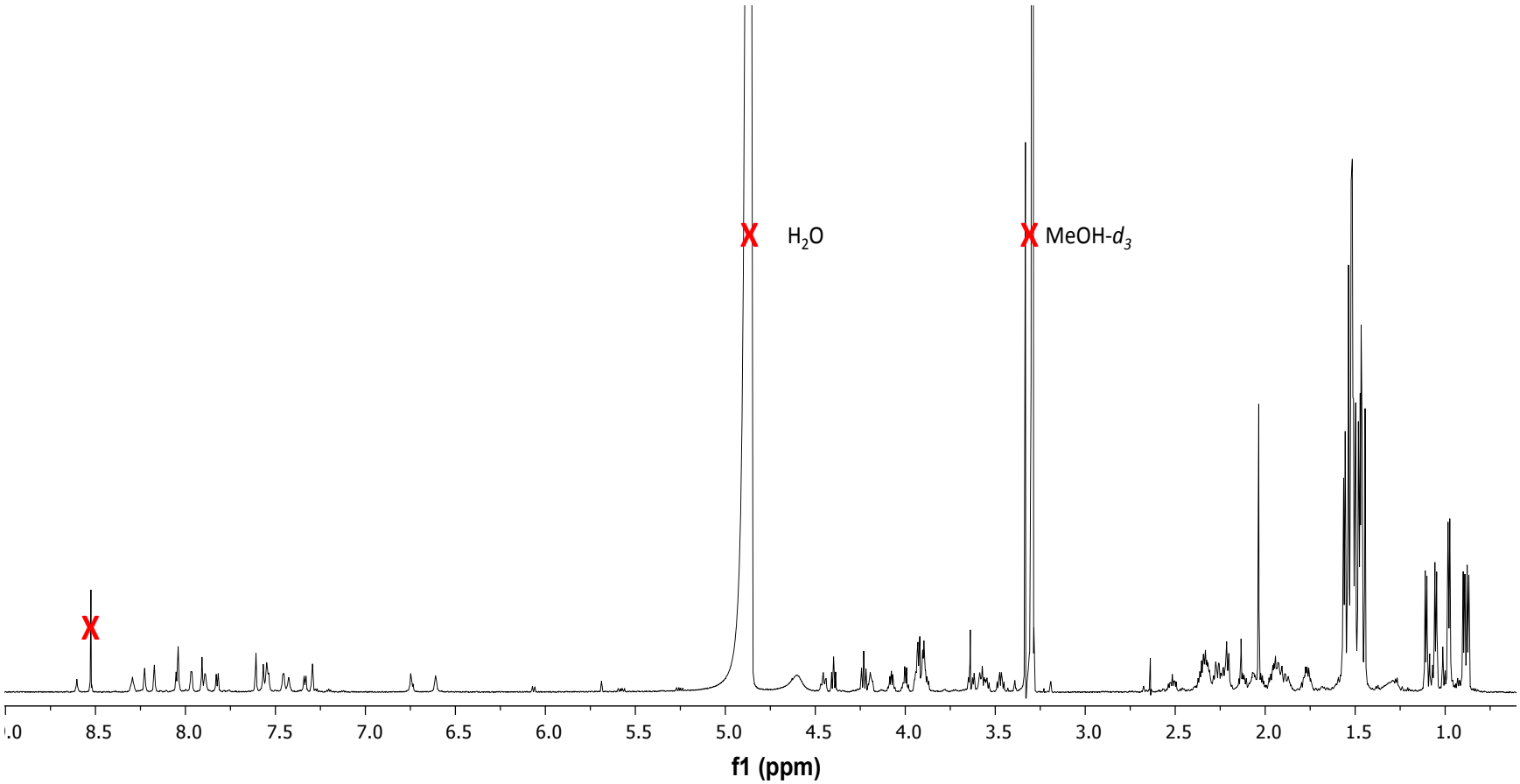

Figure S10. ^{1}H-NMR of compound **2** in MeOH-d_3 recorded at 700 MHz.

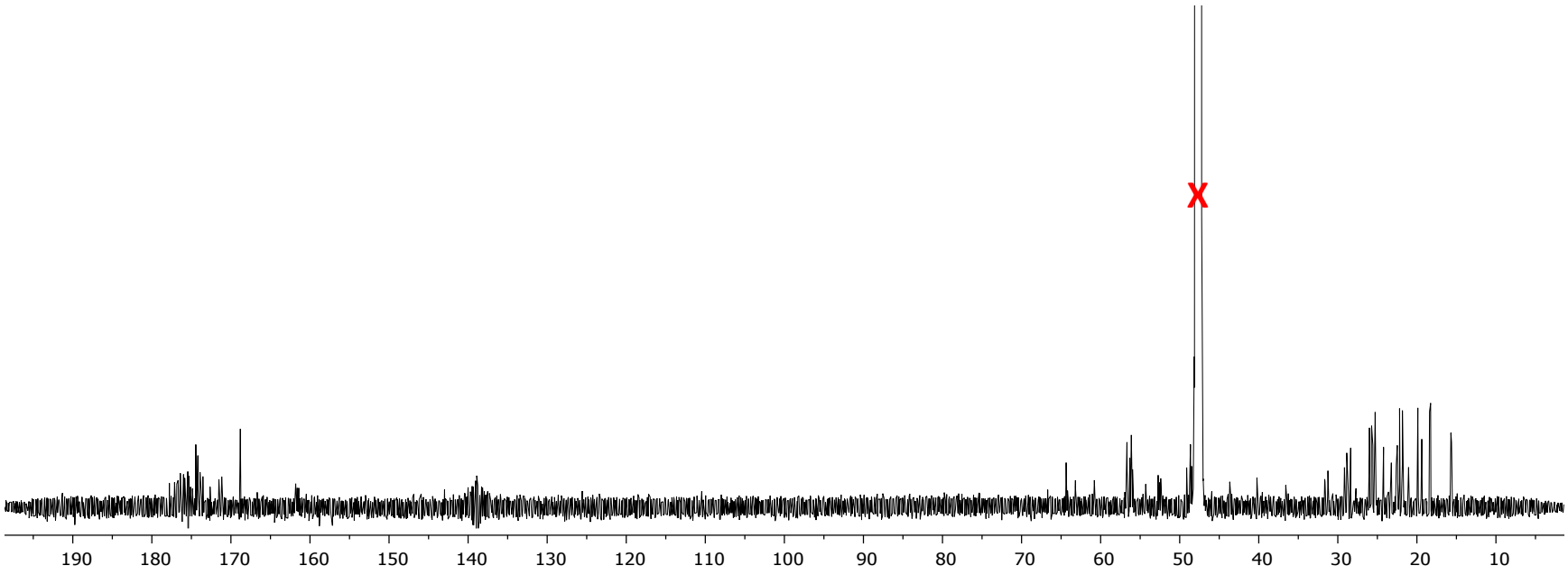

Figure S11. ^{13}C-NMR of compound **2** in MeOH-d_3 recorded at 125 MHz.

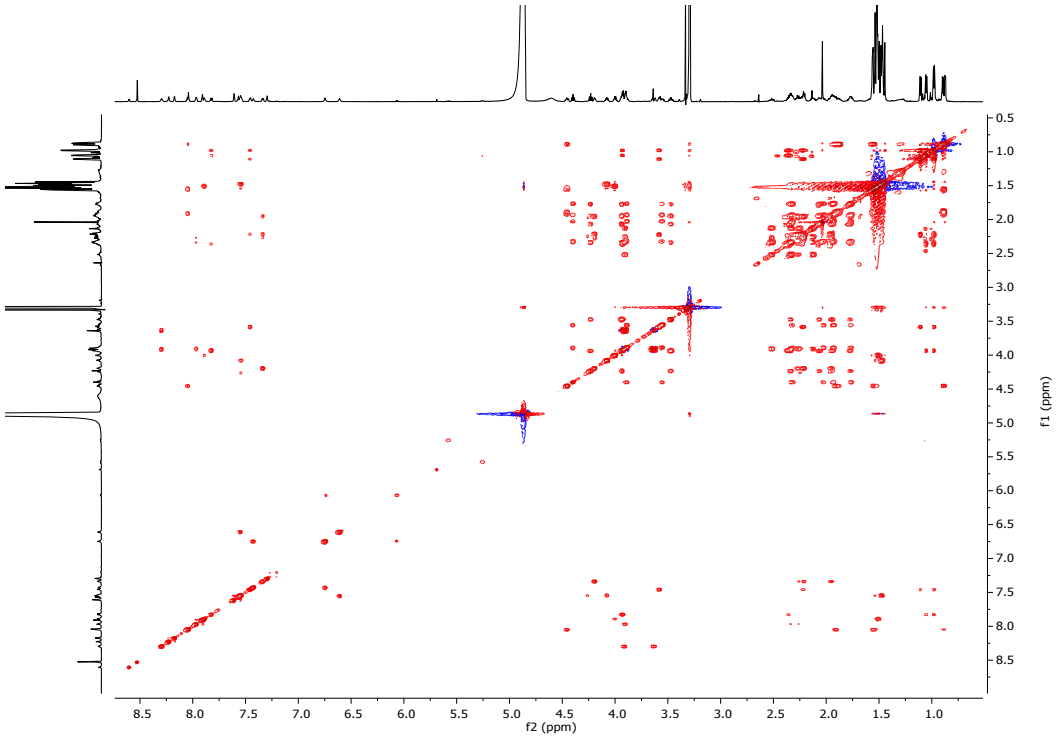

Figure S12. ^{1}H-^{1}H TOCSY spectrum of compound **2** in MeOH-d_3.

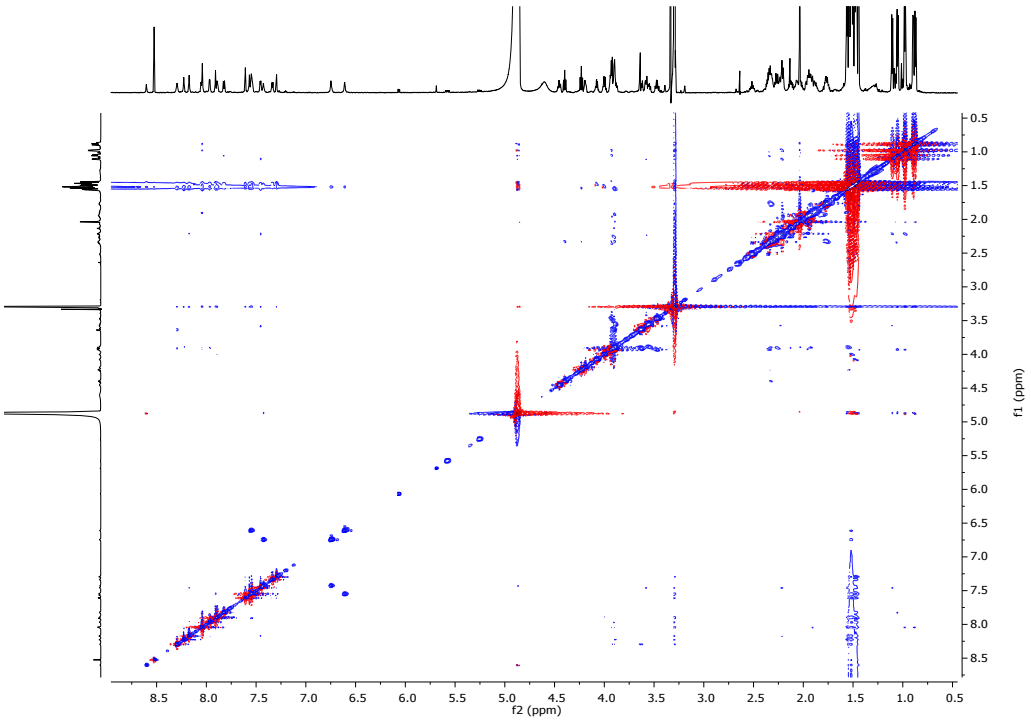

Figure S13. ^{1}H-^{1}H NOESY spectrum of compound **2** in MeOH-d_3.

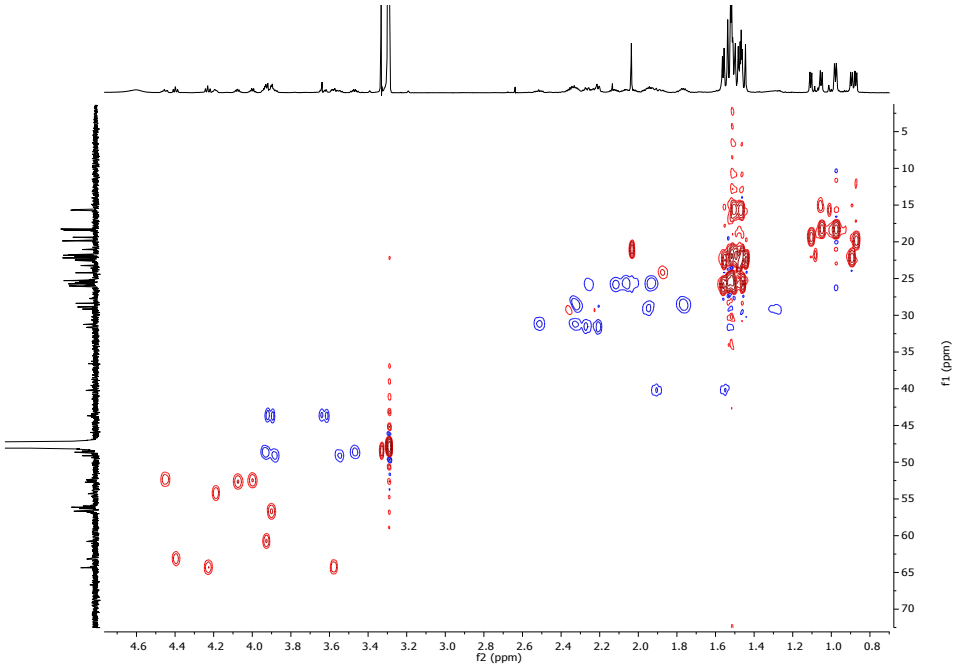

Figure S14. ^{1}H-^{13}C HSQC spectrum of compound **2** in MeOH-d_3.

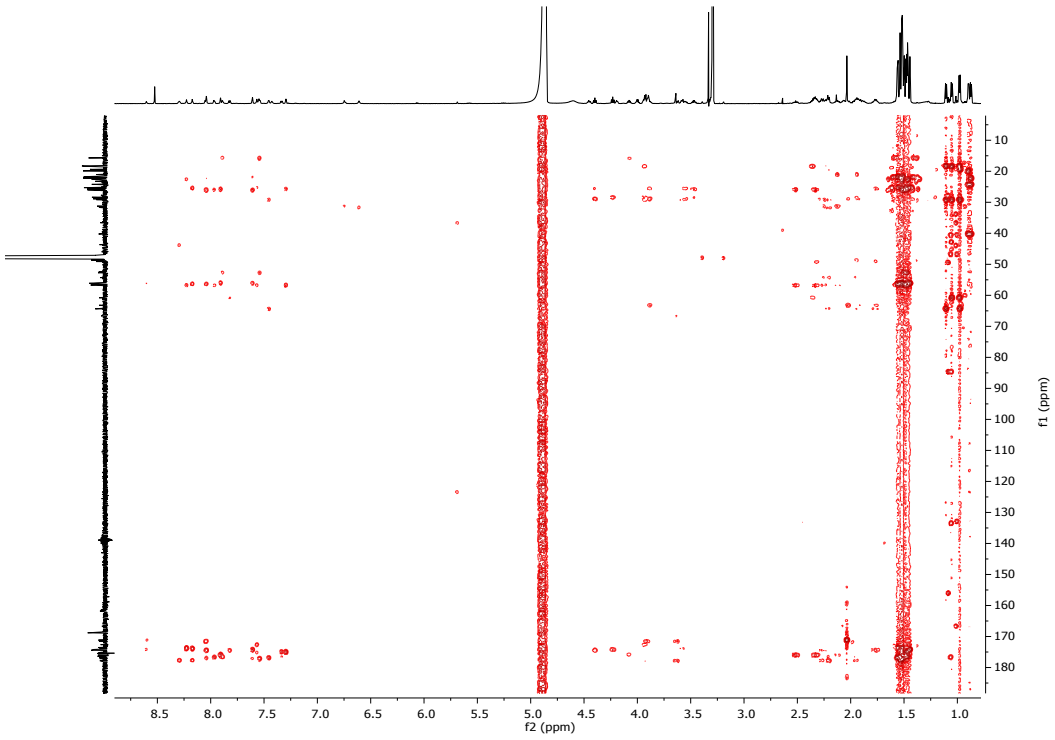

Figure S15. ^{1}H-^{13}C HMBC spectrum of compound **2** in MeOH-d_3.

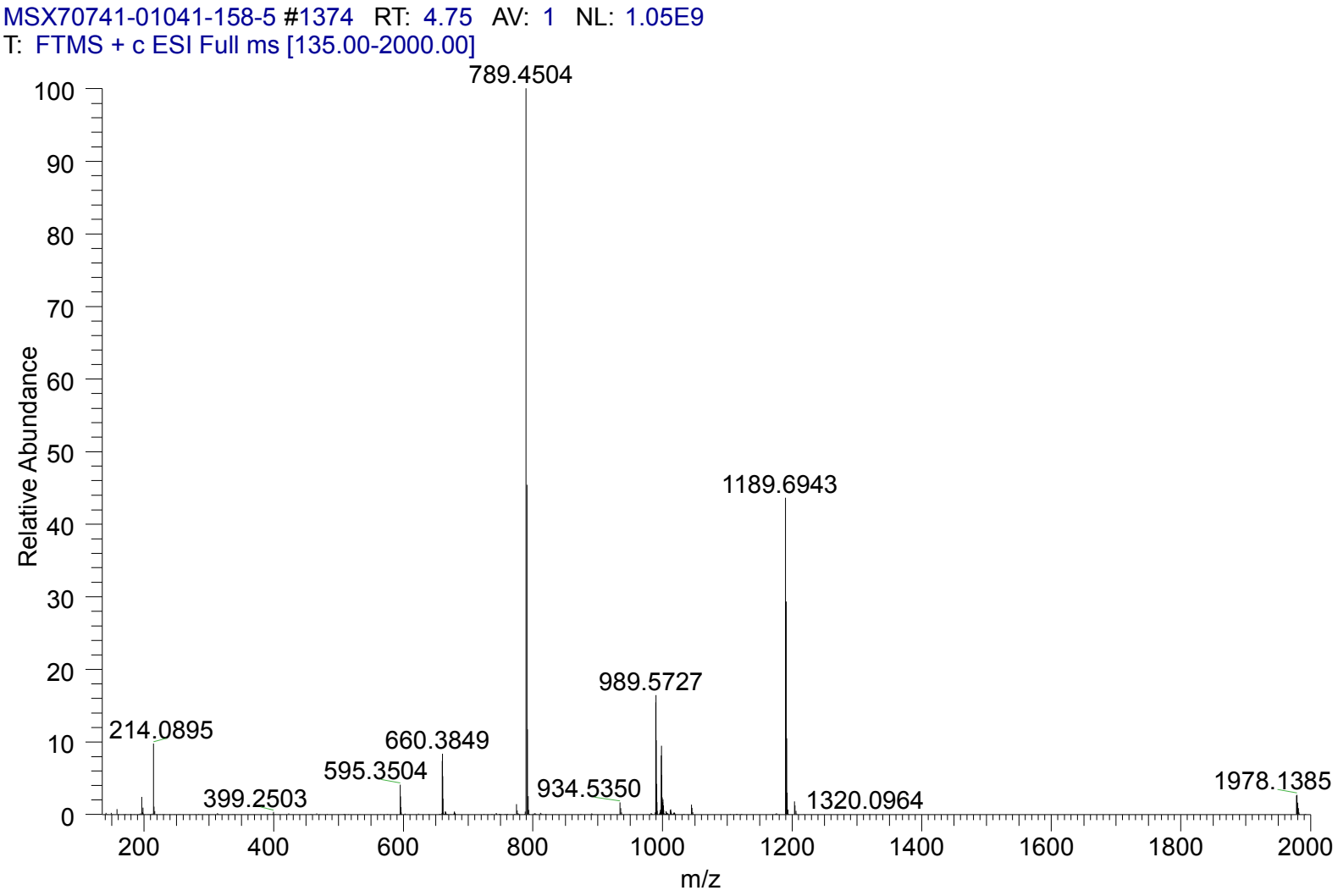

Figure S16. HRESIMS of compound **3** showing insource fragmentation.

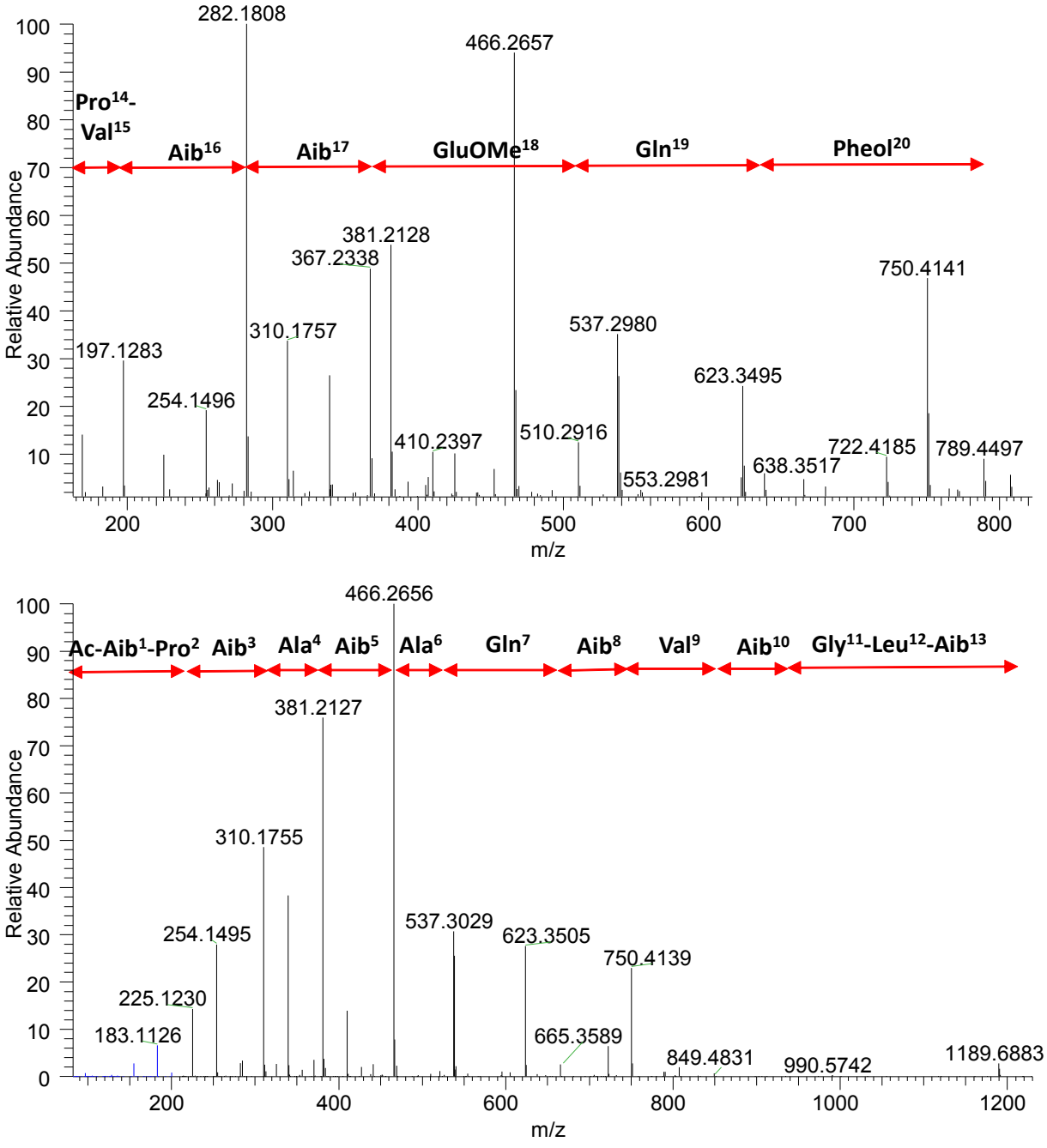

Figure S17. The sequential losses of amino acids for each in-source fragment at *m/z* 1189.69 (top) and *m/z* 789.45 (bottom) for compound **3**.

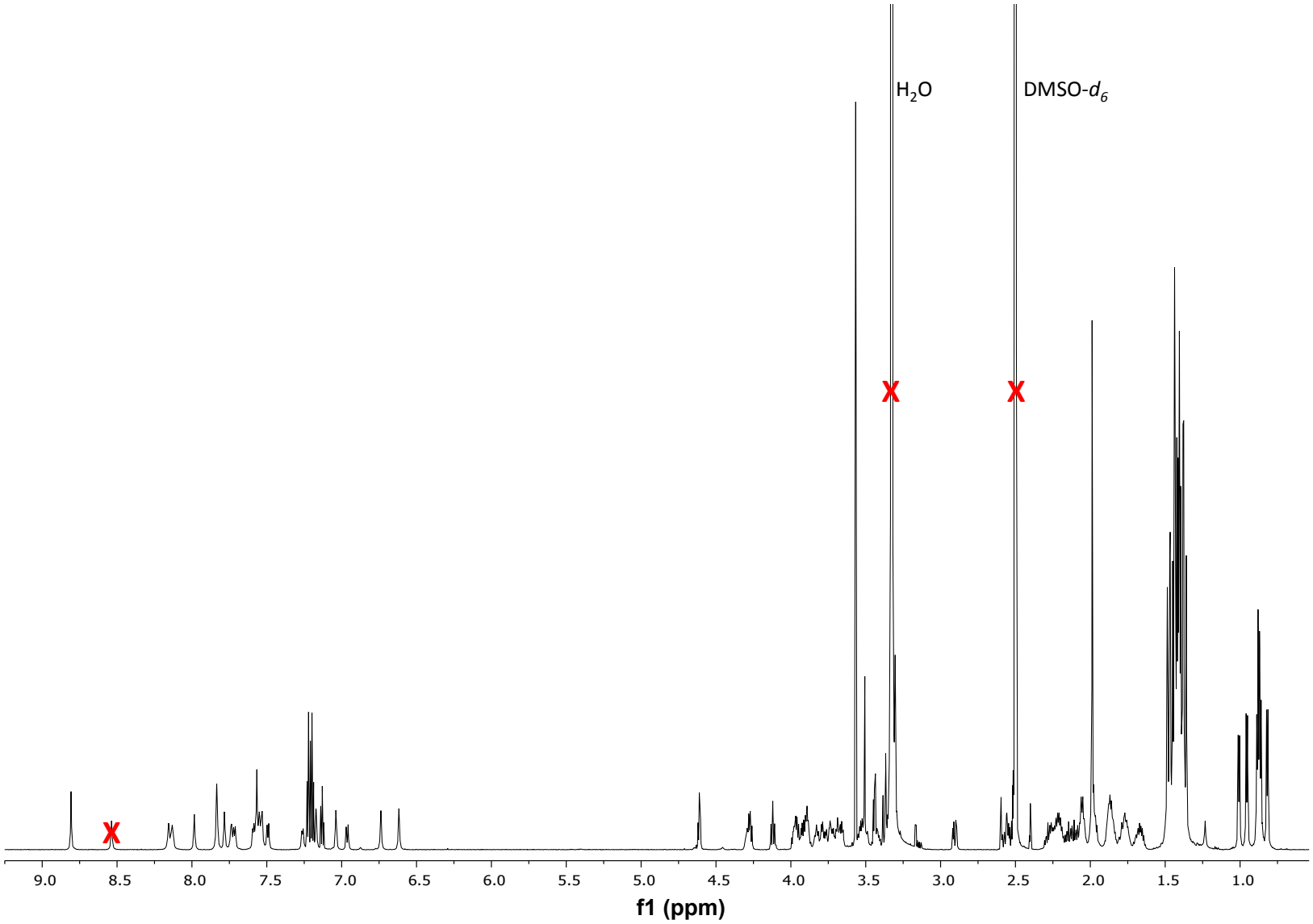

Figure S18. ^{1}H-NMR of compound **3** in DMSO-d_6 recorded at 700 MHz.

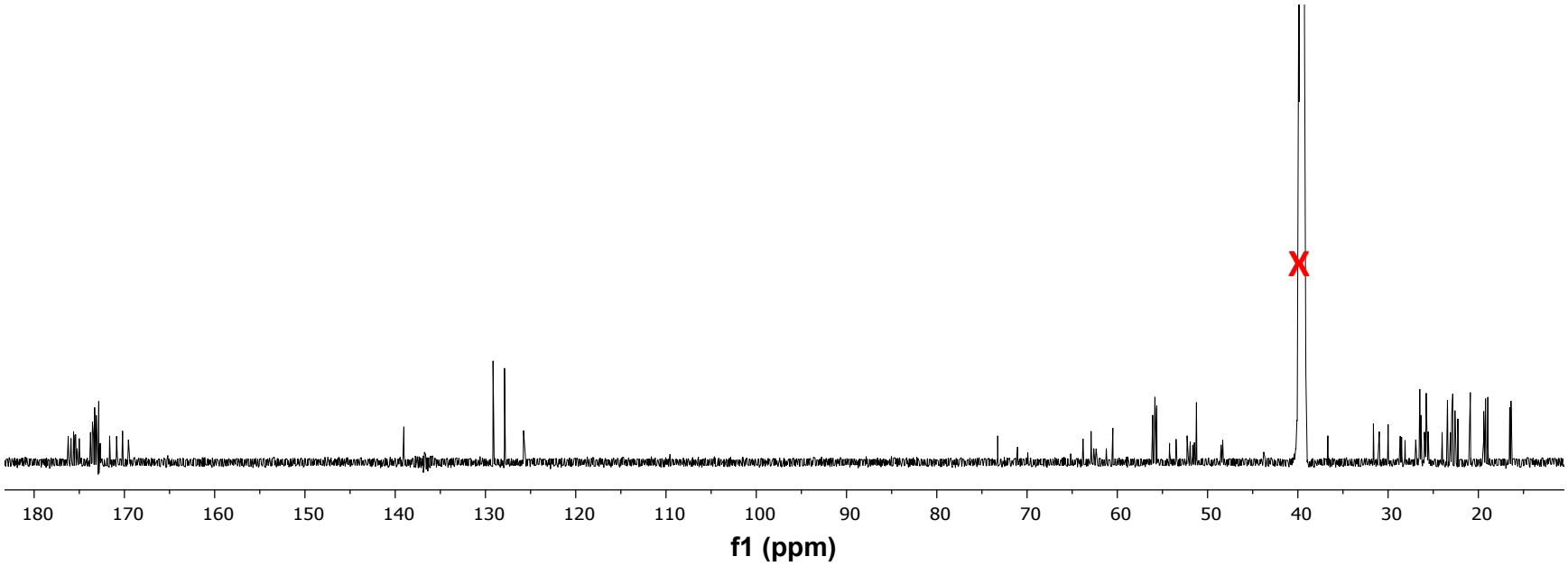

Figure S19. ^{13}C-NMR of compound **3** in DMSO-d_6 recorded at 125 MHz.

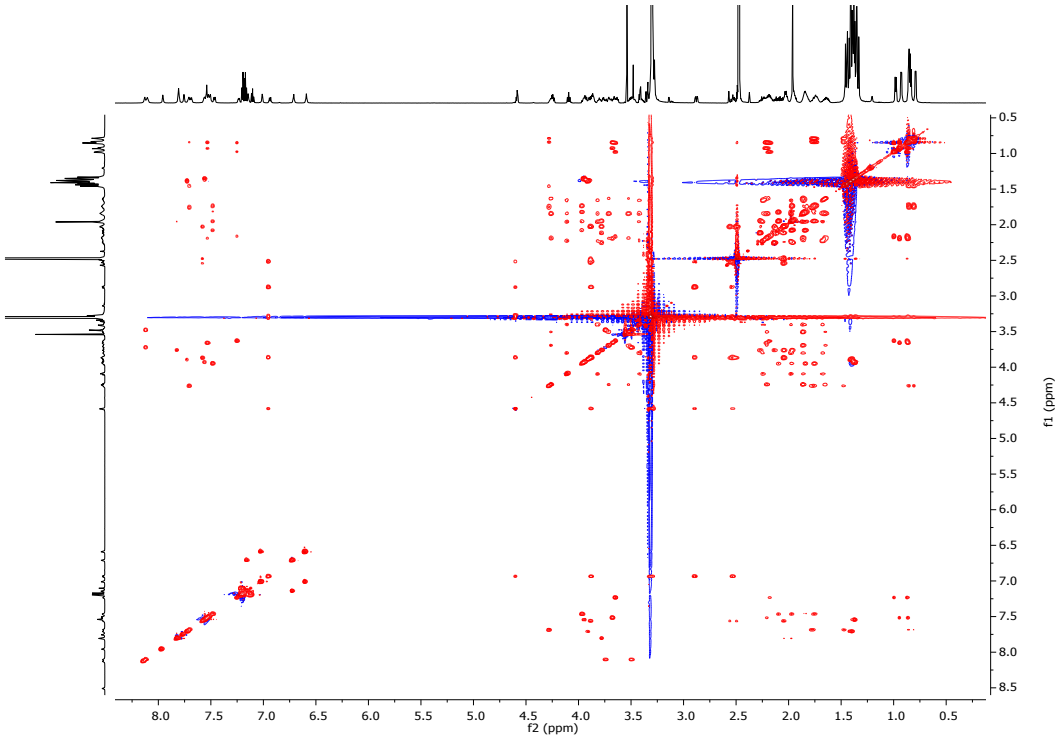

Figure S20. ^{1}H-^{1}H TOCSY spectrum of compound **3** in DMSO-d_6.

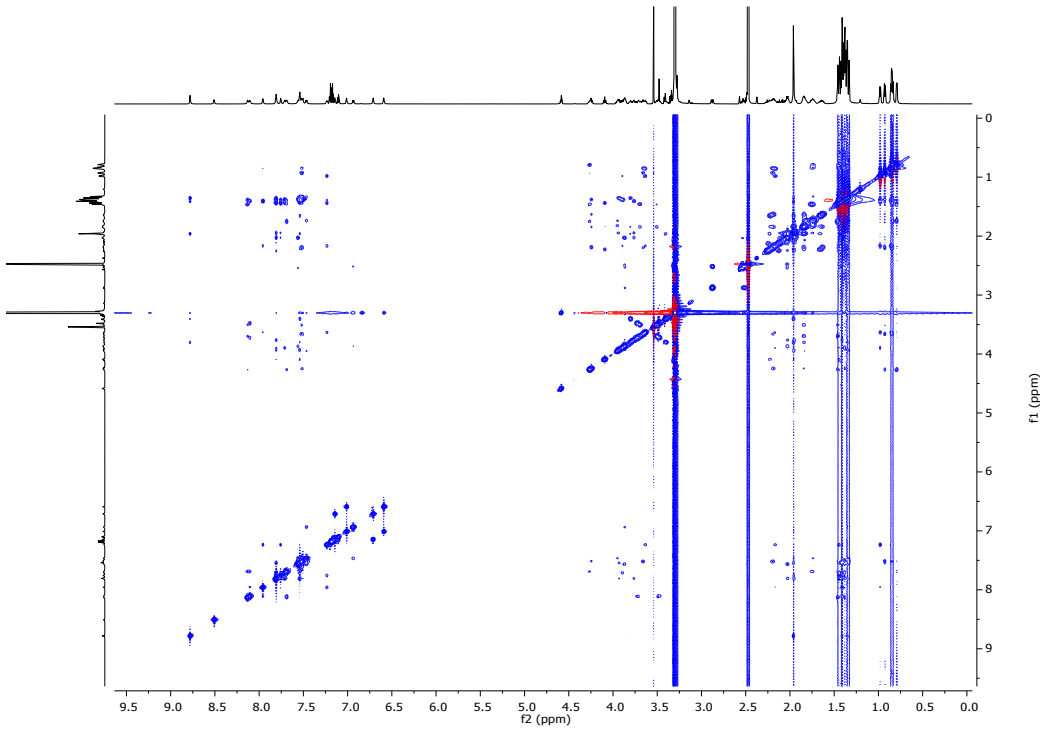

Figure S21. ^{1}H-^{1}H NOESY spectrum of compound **3** in DMSO-d_6.

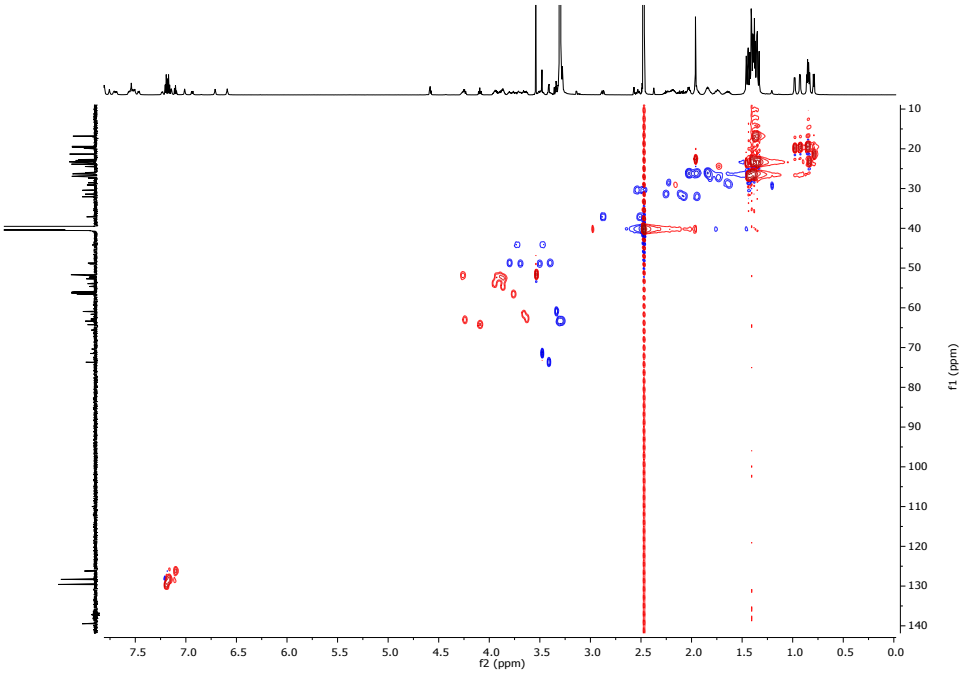

Figure S22. ^{1}H-^{13}C HSQC spectrum of compound **3** in DMSO-d_6.

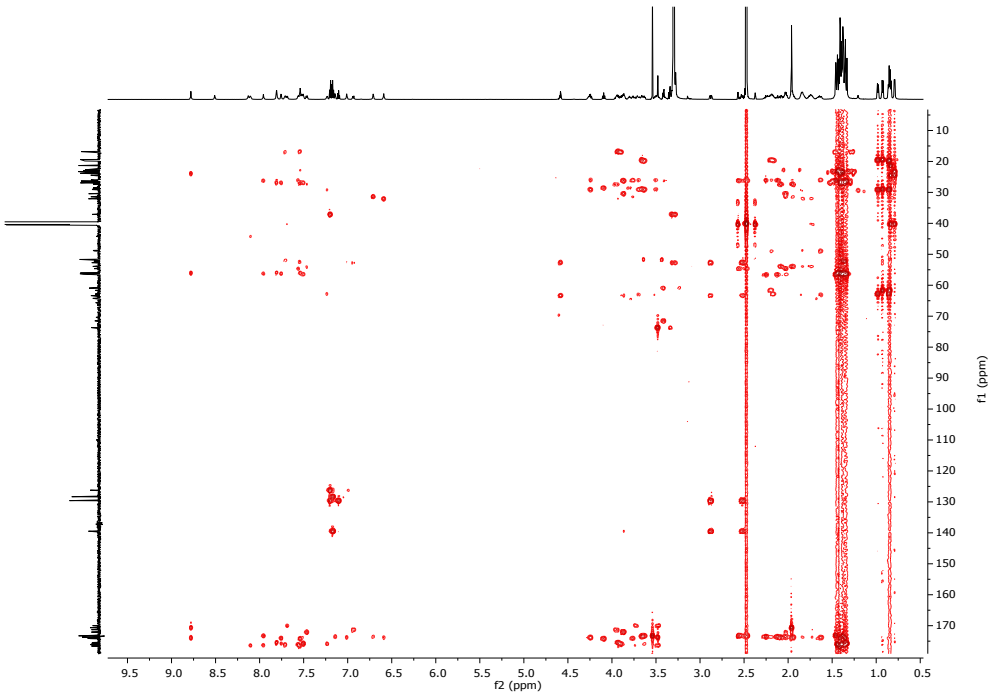

Figure S23. ^{1}H-^{13}C HMBC spectrum of compound **3** in DMSO-d_6.

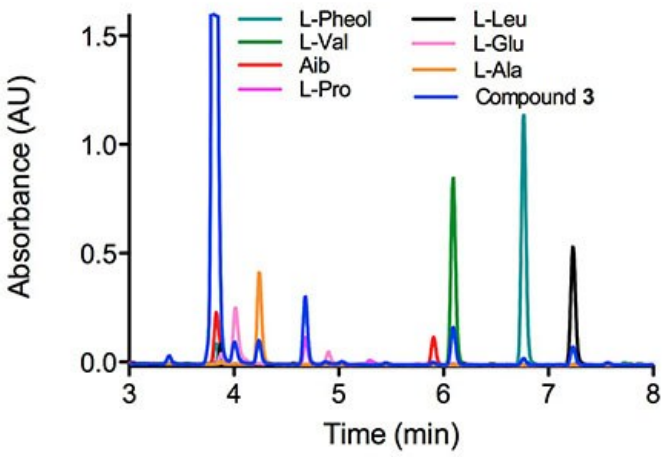

Figure S24. Marfey's analysis of compound **3**.

Table S1. NMR Spectroscopic data for compound **2**, **3** and **4** (700 and 175 MHz, ^{1}H and ^{13}C)

	2			**3**[a]			**4**		
position	δ_C	type	δ_H, mult. (*J* in Hz)	δ_C	type	δ_H, mult. (*J* in Hz)	δ_C	type	δ_H, mult. (*J* in Hz)
Ac									
C═O	172.5	C		170.2	C		172.5	C	
CH_3	22.4	CH_3	2.05, *s*	22..3	CH_3	1.99, *s*	22.5	CH_3	2.05, *s*
***Aib*[1]**									
C═O	175.5	C		173.5	C		175.5	C	
α	57.5	C		55.6	C		57.4	C	
β	23.8	CH_3	1.46, *s*	23.4	CH_3	1.38, *s*	23.8	CH_3	1.46, *s*
γ	26.9	CH_3	1.54, *s*	25.6	CH_3	1.43, *s*	26.6	CH_3	1.53, *s*
NH			8.62			8.81, *s*			8.63, *s*
***Pro*[2]**									
C═O	175.5	C		173.8	C		175.6	C	
α	65.7	CH	4.25, *t* (8.3)	63.8	CH	4.12, *t* (8.5)	65.7	CH	4.25, *t* (8.4)
β_1	29.7	CH_2	1.80, *m*	28.1	CH_2	1.67, *m*	29.7[a]	CH_2	1.80, *m*
β_2			2.36, *m*			2.26, *m*			2.34, *m*
γ_1	27.1	CH_2	1.96, *m*	25.8	CH_2	1.87, *m*	27.1	CH_2	1.96, *m*
γ_2			2.08, *m*			1.99, *m*			2.08, *m*
δ_1	50.0	CH_2	3.49, *td* (10.5, 6.2)	48.3	CH_2	3.43, *m*	50.0	CH_2	3.49, *td* (5.6, 9.8)
δ_2			3.95, *m*			3.83, *m*			3.95, *m*
***Aib*[3]**									
C═O	178.5	C		175.6	C		178.5	C	
α	57.4	C		55.7	C		57.4	C	
β	23.2	CH_3	1.54, *s*	22.7	CH_3	1.43, *s*	23.1	CH_3	1.54, *s*
γ	27.4	CH_3	1.55, *s*	26.5	CH_3	1.47, *s*	27.4	CH_3	1.56, *s*
NH			7.63, *s*			7.57, *s*			7.62, *s*
***Ala*[4]**									
C═O	177.4	C		175.7	C		177.2	C	
α	54.1	CH	4.02, *m*	52.0	CH	3.91, *m*	54.1	CH	4.09, *qd* (7.7, 5.6)
β	17.1	CH_3	1.49, *d* (7.7)	16.5	CH_3	1.41, *d*, (overlapped)	17.1	CH_3	1.49, *d* (7.7)
NH			7.56, *d* (5.8)			7.74, *d* (3.9)			7.55, *d* (5.6)
***Aib*[5]**									
C═O	177.8	C		176.2	C		177.8	C	
α	57.3	C		55.5	C		57.3	C	
β	23.1	CH_3	1.54, *s*	22.5	CH_3	1.44, *s*	23.1	CH_3	1.54, *s*
γ	27.1	CH_3	1.56, *s*	26.3	CH_3	1.45, *s*	27.1	CH_3	1.56, *s*
NH			7.92, *s*			7.83, *s*			7.94, *s*
***Ala*[6]**									
C═O	178.2	C		175.0	C		178.2	C	
α	54.1	CH	4.10, *m*	51.6	CH	3.96, *m*	54.1	CH	4.02, *m*
β	17.0	CH_3	1.53, *d* (overlapped)	16.4	CH_3	1.38, *d* (overlapped)	17.0	CH_3	1.53, *d* (overlapped)
NH			7.91, *brs*			7.57, *brs* (overlapped)			7.92, *brs*
***Gln*[7]**									
C═O	175.8	C		173.6	C		175.8		
α	58.0	CH	3.92, *m*	56.2	CH	3.79, *m*	58.1	CH	3.92, *m*
β_1	27.1	CH_2	2.14, *m*	25.9	CH_2	1.97, *m*	27.1	CH_2	2.14, *m*
β_2			2.27, *m*			2.06, *m*			2.27, *m*
γ_1	32.6	CH_2	2.35	31.0	CH_2	2.14, *m*	32.6	CH_2	2.34, *m*
γ_2			2.55, *ddd* (14.9, 9.8, 5.4)			2.28, *m*			2.54, *ddd* (15.4, 9.8, 5.4)
δ	177.3	C		173.1	C		177.3	C	
NH			7.98, *d* (4.8)			7.83, *brs*			7.99, *d* (4.9)
δ-NH_2			6.76, *brs*			6.74, *brs*			6.77, *brs*
			7.44, *brs*			7.17, *brs*			7.44, *brs*
***Aib*[8]**									
C═O	178.2	C		175.4	C		178.2	C	
α	57.6	C		55.8	C		57.6	C	
β	23.4	CH_3	1.51, *s*	22.8	CH_3	1.40, *s*	23.3	CH_3	1.52, *s*
γ	27.3	CH_3	1.55, *s*	26.5	CH_3	1.41, *s*	27.4	CH_3	1.55, *s*
NH			8.06, *s*			7.78, *s*			8.09, *s*
***Val*[9]**									
C═O	175.3	C		173.0	C		175.3	C	
α	65.7	CH	3.60, *m*	62.4	CH	3.66, *m*	65.7	CH	3.58, *m*
β	30.5	CH	2.23, *m*	28.7	CH	2.20, *m*	30.4	CH	2.25, *m*
γ	19.6	CH_3	1.00, *d* (6.8)	19.1	CH_3	0.88, *d* (6.5)	19.6	CH_3	1.00, *d* (7.0)
δ	20.7	CH_3	1.12, *d* (6.8)	19.4	CH_3	1.01, *d* (6.5)	20.9	CH_3	1.14, *d* (7.0)
NH			7.47, *d* (5.1)			7.26, d (6.1)			7.49, *d* (4.9)
***Aib*[10]**									
C═O	179.0	C		175.9	C		179.0	C	
α	57.7	C		55.8	C		57.6	C	
β	26.8	CH_3	1.54, *s*	22.8	CH_3	1.41, *s*	26.8	CH_3	1.54, *s*
γ	27.1	CH_3	1.56, *s*	25.7	CH_3	1.43, *s*	27.1	CH_3	1.56, *s*
NH			8.19, *s*			7.98, *s*			8.23, *s*
***Gly*[11]**									
C═O	172.9	C		169.6	C		173.0	C	
α_1	45.0	CH_2	3.66, *m*	43.8	CH_2	3.51, *m*	45.1	CH_2	3.66, *m*
α_2			3.93, *m*			3.74, *m*			3.93, *m*
NH			8.31, *brt* (6.2)			8.13, *brt* (5.2)			8.34, *brt* (6.3)

***Leu*[12]**									
C═O	175.8	C		173.3	C		175.8	C	
α	54.1	CH	4.47, *m*	51.5	CH	4.29, *m*	54.1	CH	4.47, *ddd* (10.5, 7.0, 3.5)
β_1	41.6	CH_2	1.59, *m* (overlapped)	40.1	CH_2	1.49, *m* (overlapped)	41.5	CH_2	1.59, *m* (overlapped)
β_2			1.96, *m*			1.79, *m*			1.96, *m*
γ	25.6	CH	1.91, *m*	24.0	CH	1.77, *m*	25.7	CH	1.91, *m*
δ	21.2	CH_3	0.89, *d* (6.5)	20.9	CH_3	0.82, *d* (6.4)	21.3	CH_3	0.92, *d* (6.3)
ε	23.6	CH_3	0.91, *d* (6.5)	22.8	CH_3	0.87, *d* (6.9)	23.4	CH_3	0.94, *d* (6.3)
NH			8.07, *d* (overlapped)			7.72, *d* (7.8)			8.11, *d* (7.7)
***Aib*[13]**									
C═O	174.9	C		172.9	C		174.9	C	
α	58.1	C		55.9	C		58.1	C	
β	23.8	CH_3	1.57, *s*	25.8	CH_3	1.40, *s*	23.7	CH_3	1.61, *s*
γ	26.8	CH_3	1.55, *s*	23.1	CH_3	1.49, *s*	26.7	CH_3	1.54, *s*
NH			8.24, *s*			8.16, *s*			8.41, *s*
***Pro*[14]**									
C═O	175.8	C		173.4	C		176.4	C	
α	64.6	CH	4.42, *t* (8.5)	62.6	CH	4.27, *dd* (7.5, 6.8)	64.7	CH	4.39, *dd* (9.1, 6.3)
β_1	29.7	CH_2	1.80, *m*	28.5	CH_2	1.66, *m*	30.0	CH_2	1.80, *m*
β_2			2.36, *m*			2.22, *m*			2.32, *m*
γ_1	27.0	CH_2	1.98, *m*	25.7	CH_2	1.88, *m*	26.9	CH_2	1.99, *m*
γ_2			2.08, *m*						2.08, *m*
δ_1	50.5	CH_2	3.58, *m*	48.5	CH_2	3.53, *m*	50.6	CH_2	3.75, *m*
δ_2			3.93, *m*			3.72, *m*			3.87, *dt* (11.2, 5.6)
***Val*[15]**									
C═O	174.1	C		173.1	C		175.3	C	
α	62.2	CH	3.96, *m*	61.2	CH	3.69, *m*	64.3	CH	3.74, *m*
β	32.6	CH	2.39, *m*	28.7	CH	2.22, *m*	30.5	CH	2.34, *m*
γ	19.6	CH_3	1.00, *d* (6.7)	18.9	CH_3	0.88, *d* (6.7)	19.5	CH_3	0.98, *d* (7.0)
δ	19.7	CH_3	1.08, *d* (6.8)	19.2	CH_3	0.96, *d* (6.7)	20.2	CH_3	1.07, *d* (7.0)
NH			7.84, *d* (8.0)			7.54, *d* (8.5)			7.64, *d* (8.4)
***Aib*[16]**									
C═O	175.5	C		175.5	C		177.6	C	
α	58.1	C		56.0	C		57.6	C	
β	23.4	CH_3	1.54, *s*	23.0	CH_3	1.36 *s*	23.4	CH_3	1.54, *s*
γ	27.1	CH_3	1.55, *s*	26.4	CH_3	1.40, *s*	27.4	CH_3	1.55, *s*
NH			7.58, *s*			7.53, *s*			7.60, *s*
***Aib*[17]**									
C═O	176.3	C		175.6	C		178.7	C	
α	58.1	C		56.0	C		57.7	C	
β	23.4	CH_3	1.48, *s*	23.1	CH_3	1.49, *s*	23.4	CH_3	1.53, *s*
γ	27.1	CH_3	1.50, *s*	26.5	CH_3	1.47, *s*	27.4	CH_3	1.55, *s*
NH			7.31, *s*			7.53, *s*			7.82, *s*
***Gln/Glu*[18]**									
C═O	177.8	C		171.6	C		175.5	C	
α	55.6	CH	4.21, *m*	54.2	CH	3.90, *m*	57.0	CH	4.02, *m*
β_1, β_2	27.1	CH_2	1.96, *m*	26.0	CH_2	2.06, *m*	28.0	CH_2	2.25, *m*
γ_1	33.0	CH_2	2.23, *m*	30.0	CH_2	2.50, *m* (overlapped)	33.2	CH_2	2.43, *dt* (16.1, 8.4)
γ_2			2.30, *m*			2.57, *m*			2.62, *ddd* (15.4, 9.1, 6.3)
δ	179.0	C		172.8	C		177.6	C	
NH			7.35, *d* (7.4)			7.59, *d* (6.0)			7.79, *d* (5.6)
δ-NH_2			6.63, *brs*			-			6.79, *brs*
			7.57, *brs*			-			7.44, *brs*
δ-OMe	-		-	51.2	CH_3	3.57, *s*	-		-
***Gln*[19]**									
C═O	-			170.9	C		174.0	C	
α	-		-	53.5	CH	3.97, *m*	55.7	CH	4.15, *m*
β	-		-	26.9	CH_2	1.76, *m*	28.0	CH_2	2.02, *m*
						1.85, *m*			
γ_1	-		-	31.6	CH_2	1.98, *m*	32.9	CH_2	2.20, *m*
γ_2			-			2.10, *m*			2.34, *m*
δ	-		-	173.3	C		177.3	C	
NH			-			7.49, *d* (7.9)			7.88, *d* (7.0)
δ-NH_2			-			6.62. *brs*			6.63, *brs*
			-			7.04, *brs*			7.34, *brs*
***Pheol*[20]**									
$\underline{CH_2}$–OH	-		-	62.9	CH_2	3.33, overlapped	64.9	CH_2	3.61, *brs*
α	-		-	52.3	CH	3.89, *m*	54.5	CH	4.15, *m*
β_1	-		-	36.7	CH_2	2.54, *dd* (overlapped)	38.0	CH_2	2.73, *dd* (14.0, 9.1)
β_2			-			2.91, *dd* (13.7, 4.7)			2.94, *dd* (14.0, 5.6)
γ	-		-	139.0	C		139.8	C	
δ	-		-	129.2	CH	7.23, *dd* (8.1, 1.2)	130.4	CH	7.28, *d* (7.7)
ε	-		-	127.9	CH	7.20, *t* (7.6))	129.1	CH	7.22, *t* (7.7)
ζ	-		-	125.8	CH	7.13, *tt* (6.6, 1.5)	127.1	CH	7.14, *t* (7.7)
NH			-			6.96, *d* (9.0)			7.32, *d* (9.1)
CH_2–$\underline{OH}$						4.61, *t* (5.9)			-

[a]Recorded in DMSO-d_6, the chemical shifts for methyl groups in Aib residues may be exchangeable.