

Electronic Supplementary Information

Marine Drugs

Denigrins H-L: Sulfated Derivatives of Denigrins D and E from a New Zealand *Dictyodendrilla* c.f. *dendyi* Marine Sponge

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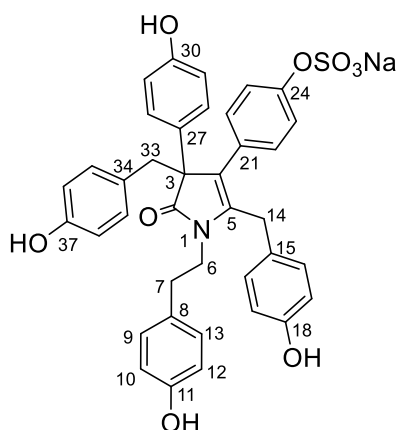
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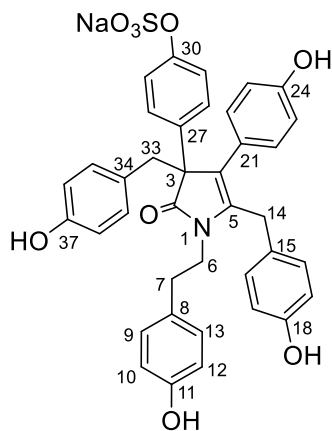
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Table S1. ^1H and ^{13}C NMR data of denigrin H (**1**)

No.	$\delta_{\text{C}}^{\text{a}}$	^1H δ_{H} , (mult, J in Hz) ^b	HMBC (^1H to ^{13}C)	COSY
2	183.6			
3	62.3			
4	124.8			
5	139.9			
6	44.4	3.41 (1H, m) 3.11 ^c (1H, m)	C-2	H-6, H-7 H-7
7	34.9	2.70 (1H, m) 2.19 (1H, m)	C-6, C-9/13 C-8, C-9/13	H-7
8	130.8			
9/13	130.9	6.712 ^d (2H, d, 8.5)	C-7, C-11	H-9/13
10/12	116.2	6.65 (2H, d, 8.5)	C-8	
11	157.1			
14	31.0	3.77 (1H, d, 17.0) 3.28 ^e (1H, m)	C-5, C-15, C-16/20 C-4, C-5, C-15, C-16/20	H-14
15	128.2			
16/20	130.1	6.34 (2H, d, 8.4)	C-14, C-18	
17/19	116.9	6.705 ^d (2H, d, 8.6)	C-15	H-16/20
18	157.3			
21	131.7			
22/26	130.0	6.79 (2H, d, 8.9)	C-4, C-24	
23/25	122.1	7.07 (2H, d, 8.9)	C-24, C-21	H-22/26
24	152.8			
27	132.0			
28/32	129.0	7.25 (2H, d, 8.8)	C-3, C-30	H-29/31
29/31	116.8	6.87 (2H, d, 8.8)	C-27	
30	158.1			
33	38.5	3.64 (1H, d, 12.9) 3.09 ^c (1H, d (12.7))	C-3, C-4, C-34, C-35/39 C-2, C-3, C-34, C-35/39	H-33
34	128.4			
35/39	132.5	6.72 (2H, d, 8.7)	C-33, C-37	H-36/38
36/38	115.8	6.64 (2H, d, 8.6)	C-34	
37	157.6			

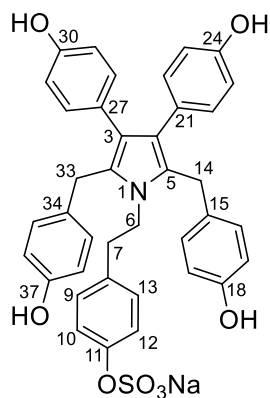
^a recorded at 150 MHz in CD_3OD , ^b recorded at 600 MHz in CD_3OD , ^c signal overlap, ^d values given to 3 decimal places to separate signals, ^e signal partially obscured

Table S2. ^1H and ^{13}C NMR data of denigrin I (**2**)

No.	$\delta_{\text{C}}^{\text{a}}$	^1H δ_{H} , (mult, J in Hz) ^b	HMBC (^1H to ^{13}C)	COSY
2	182.9			
3	62.4			
4	124.9			
5	138.7			
6	44.3	3.41 (1H, m) 3.08 ^c (1H, m)	C-2	H-6, H-7 H-7
7	34.9	2.69 (1H, m) 2.18 (1H, ddd)	C-9/13 C-6, C-9/13	H-7
8	130.6			
9/13	131.0	6.706 ^d (2H, d, 8.4)	C-7, C-11	H-9/13
10/12	116.2	6.65 (2H, d, 8.6)	C-8	
11	157.1			
14	31.1	3.79 (1H, d, 16.9) 3.29 ^e (1H, m)	C-5, C-15, C-16/20 C-4, C-5, C-15, C-16/20	H-14
15	128.40 ^{f, g}			
16/20	130.1	6.34 (2H, d, 8.3)	C-14, C-18	
17/19	116.8	6.714 ^d (2H, d, 8.4)	C-15	H-16/20
18	157.2			
21	126.1			
22/26	130.3	6.66 (2H, d, 8.9)	C-4, C-24	H-22/26
23/25	116.0	6.56 (2H, d, 8.7)	C-21, C-24	
24	157.63 ^g			
27	137.9			
28/32	128.8	7.42 (2H, d, 9.1)	C-3, C-30	H-29/31
29/31	122.8	7.39 (2H, d, 9.0)	C-27, C-30	
30	153.5			
33	38.6	3.68 (1H, d, 12.9) 3.09 ^c (1H, d, 12.7)	C-3, C-4, C-34, C-35/39 C-2, C-3, C-35/39, C-34	H-33
34	128.41 ^{f, g}			
35/39	132.6	6.68 (2H, d, 8.6)	C-33	H-36/38
36/38	115.7	6.63 (2H, d, 8.7)	C-34, C-37	
37	157.58 ^g			

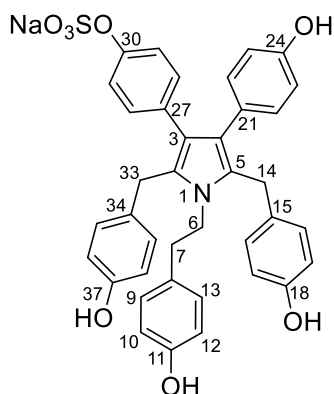
^a recorded at 150 MHz in CD_3OD , ^b recorded at 600 MHz in CD_3OD , ^c signal overlap, ^d values given to 3 decimal places to separate signals, ^e signal partially obscured, ^f assignment interchangeable, ^g values given to 2 decimal places to separate signals

Table S3. ^1H and ^{13}C NMR data of denigrin J (**3**)



No.	δ_{C} ^a	^1H δ_{H} , (mult, <i>J</i> in Hz) ^b	HMBC (^1H to ^{13}C)	COSY
2/5	128.3			
3/4	123.4			
6	47.1	3.59 (2H, m)	C-7, C-2/5	H-7
7	37.7	2.45 (2H, m)	C-6, C-9/13, C-8	
8	136.6			
9/13	130.6	6.78 (2H, d, 8.5)	C-7, C-11	
10/12	122.5	7.13 (2H, d 8.4)	C-8, C-11	H-9/13
11	152.6			
14/33	30.7	3.85 (4H, s)	C-3/4, C-2/5, C-16/20–35/39, C-15/34	
15/34	132.8			
16/20–35/39	130.0	6.93 (4H, d, 8.6)	C-14/33, C-18/37	H16/20-35/39
17/19–36/38	116.3	6.69 (4H, d, 8.5)	C-15/34, C-18/37	
18/37	156.7			
21/27	129.7			
22/26–28/32	132.5	6.92 (4H, d, 8.6)	C-3/5, C-24/30	H23/25-29/31
23/25–29/31	115.6	6.61 (4H, d, 8.7)	C-21/27, C-24/30	
24/30	156.1			

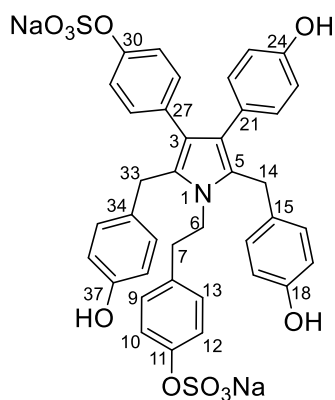
^a recorded at 150 MHz in CD_3OD , ^b recorded at 600 MHz in CD_3OD

Table S4. ¹H and ¹³C NMR data of denigrin K (**4**)

No.	δ_c^a	¹ H δ_H (mult, <i>J</i> in Hz) ^b	HMBC (¹ H to ¹³ C)	COSY
2	128.73 ^{c, d}			
3	122.9			
4	123.4			
5	128.68 ^{c, d}			
6	47.3	3.58 (2H, m)	C-2, C-7, C-5	H-7
7	37.6	2.45 (2H, m)	C-6, C-9/13	
8	130.94 ^c			
9/13	130.92 ^c	6.66 (2H, d, 9.0)	C-7, C-11	
10/12	116.1	6.63 (2H, d, 8.3)	C-8, C-11	
11	157.0			
14/33	30.57 30.63	3.80 (4H, s)	C-2, C-3, C-4, C-5, C-15, C-16/20, C-35/39, C-34	
15	132.7 ^e			
16/20	129.92 ^{c, f}	6.89 ^g (2H, d, 8.3)	C-14/33, C-18	H17/19
17/19	116.32 ^{c, h}	6.70 ⁱ (2H, d, 9.0)	C-15, C-18	
18	156.68 ^{c, j}			
21	129.4			
22/26	132.5	6.92 (2H, d 9.0)	C-4, C-24	H-23/25
23/25	115.7	6.62 (2H, d, 8.3)	C-21, C-24	
24	156.2			
27	135.2			
28/32	132.0	7.06 (2H, d, 8.6)	C-3, C-30	
29/31	121.9	7.12 (2H, d, 8.3)	C-27, C-30	H-28/32
30	151.6			
34	132.8 ^e			
35/39	129.87 ^{c, f}	6.91 ^g (2H, d, 8.3)	C-14/33, C-37	H-36/38
36/38	116.30 ^{c, h}	6.69 ⁱ (2H, d, 8.3)	C-14/33, C-34, C-37	
37	156.70 ^{c, j}			

^a recorded at 150 MHz in CD₃OD, ^b recorded at 600 MHz in CD₃OD, ^c values given to 2 decimal places to separate signals, ^{d-j} assignment may be interchanged

Table S5. ^1H and ^{13}C NMR data of denigrin L (**5**)



No.	$\delta_{\text{C}}^{\text{a}}$	^1H δ_{H} (mult, J in Hz) $^{\text{b}}$	HMBC (^1H to ^{13}C)	COSY
2	128.6 $^{\text{c}}$			
3	123.0			
4	123.5			
5	128.7 $^{\text{c}}$			
6	47.2	3.61 (2H, m)	C-2, C-5	H-7
7	37.6	2.45 (2H, m)	C-9/13, C-8	
8	136.5			
9/13	130.4	6.80 (2H, d, 8.6)	C-7, C-11	
10/12	122.5	7.14 $^{\text{d}}$ (2H, d, 8.6)	C-7, C-8	H-9/13
11	152.5			
14	30.7	3.94 (2H, s)	C-2, C-3, C-15	
15	132.7 $^{\text{e, f}}$			
16/20	130.00 $^{\text{g, h}}$	6.95 $^{\text{i}}$ (2H, d, 8.6)	C-18	C-17-19
17/19	116.41 $^{\text{g, j}}$	6.710 $^{\text{k, l}}$ (2H, d, 8.6)	C-15, C-18	
18	156.83 $^{\text{g, m}}$			
21	129.3			
22/26	132.6 $^{\text{e}}$	6.95 $^{\text{h}}$ (2H, d, 8.6)	C-4, C-24	C-23/25
23/25	115.8	6.63 (2H, d, 8.7)	C-21, C-24	
24	156.3			
27	135.1 $^{\text{f}}$			
28/32	132.0	7.09 (2H, d, 8.8)	C-3, C-30	
29/31	121.9	7.14 $^{\text{d}}$ (2H, d, 8.6)	C-30	H-28/32
30	151.7			
33	30.7	3.87 (2H, s)	C-4, C-5, C-34	
34	132.6 $^{\text{e, f}}$			
35/39	129.96 $^{\text{g, h}}$	6.95 $^{\text{i}}$ (2H, d, 8.6)	C-37	C-36/38
36/38	116.37 $^{\text{g, j}}$	6.708 $^{\text{k, l}}$ (2H, d, 8.6)	C-34, C37	
37	156.78 $^{\text{g, m}}$			

$^{\text{a}}$ recorded at 150 MHz in CD_3OD , $^{\text{b}}$ recorded at 600 MHz in CD_3OD , $^{\text{c-e, h-j, l-m}}$ assignment may be interchanged, $^{\text{f}}$ assigned based on denigrin J (**3**) and K (**4**), $^{\text{g}}$ values given to 2 decimal places to separate signals, $^{\text{k}}$ values given to 3 decimal places to separate signals

Figure S1a. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of denigrin H (**1**)

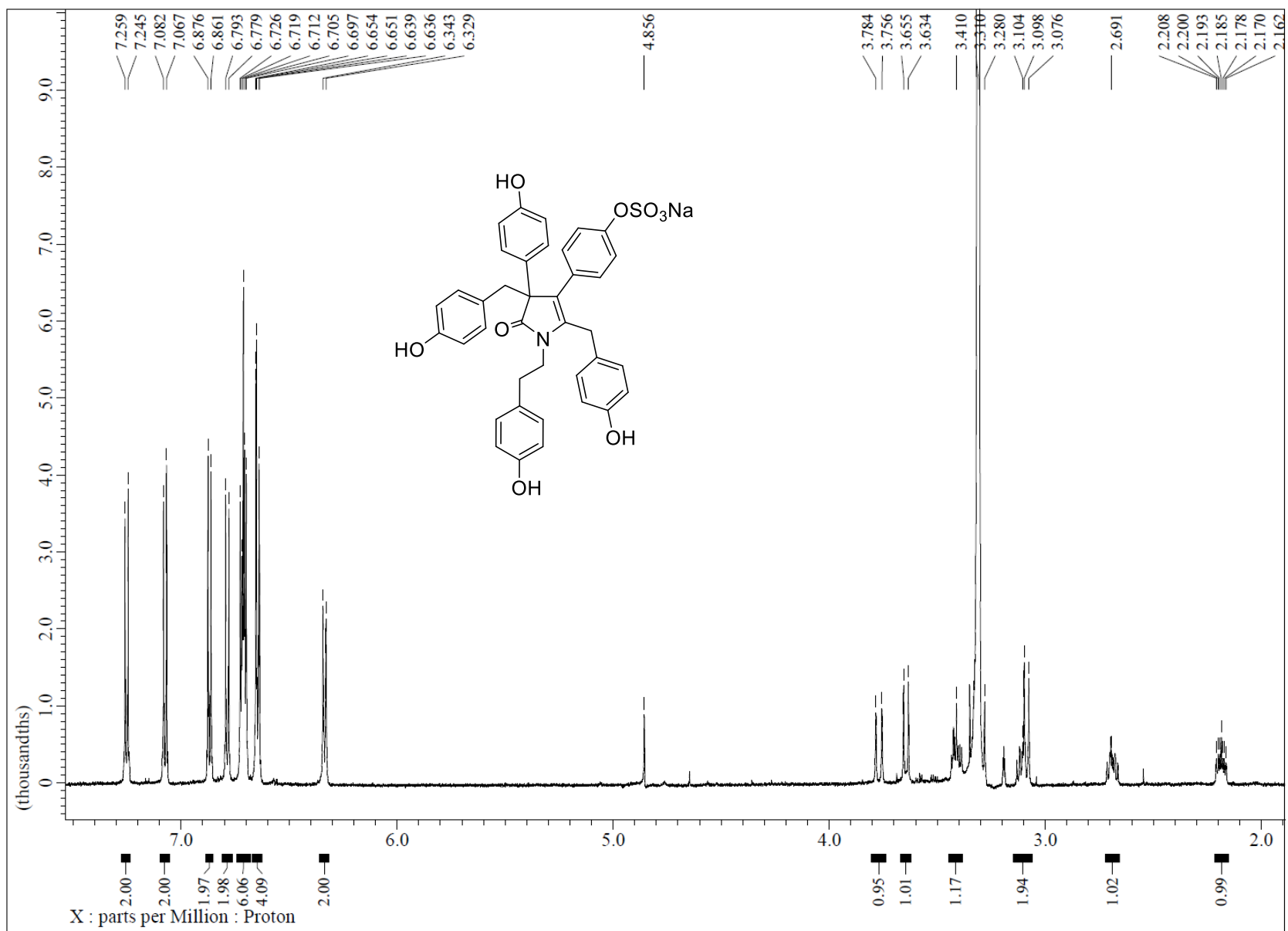


Figure S1b. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum of denigrin H (**1**)

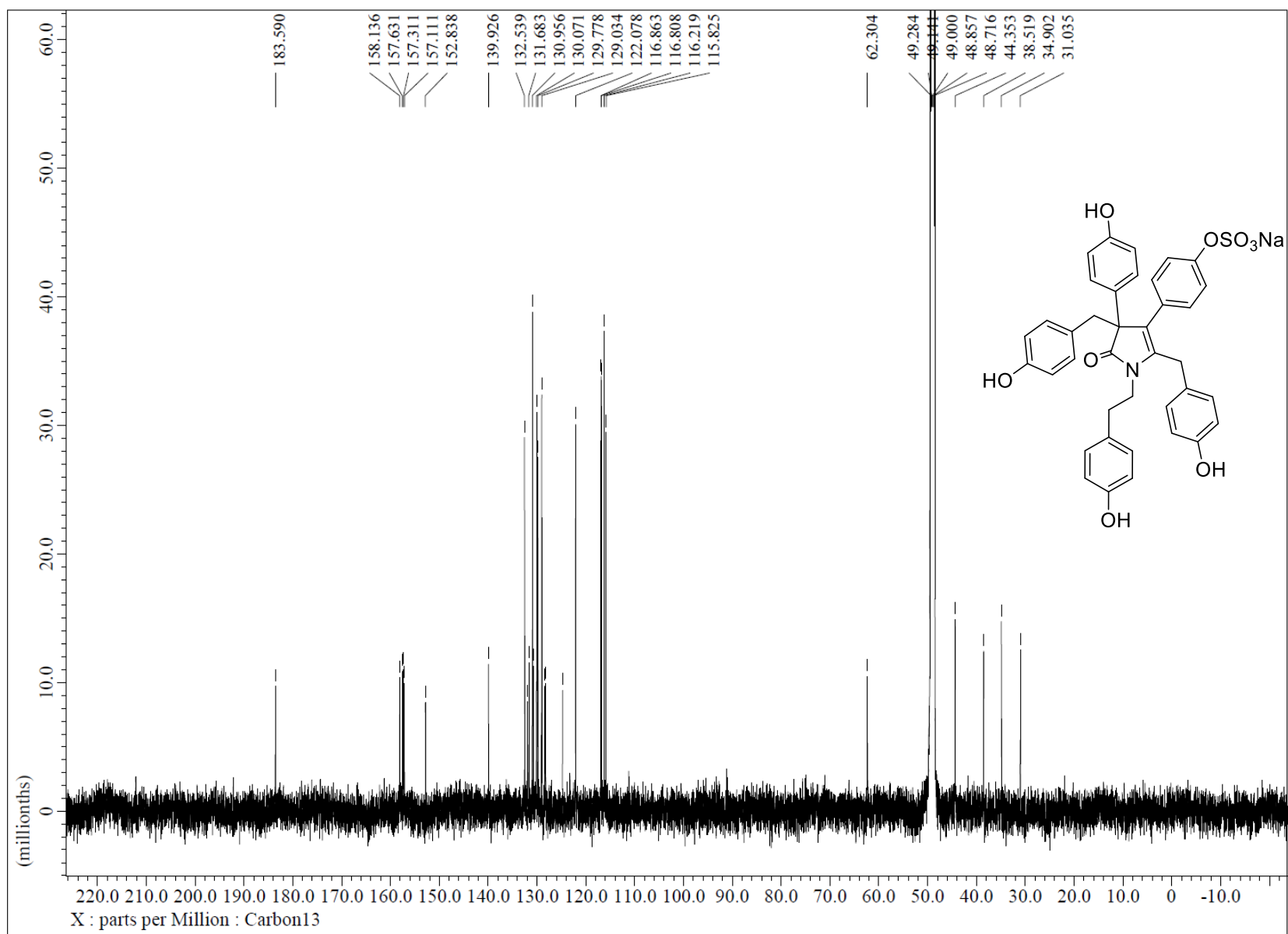


Figure S1c. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum expansion 1 of denigrin H (**1**)

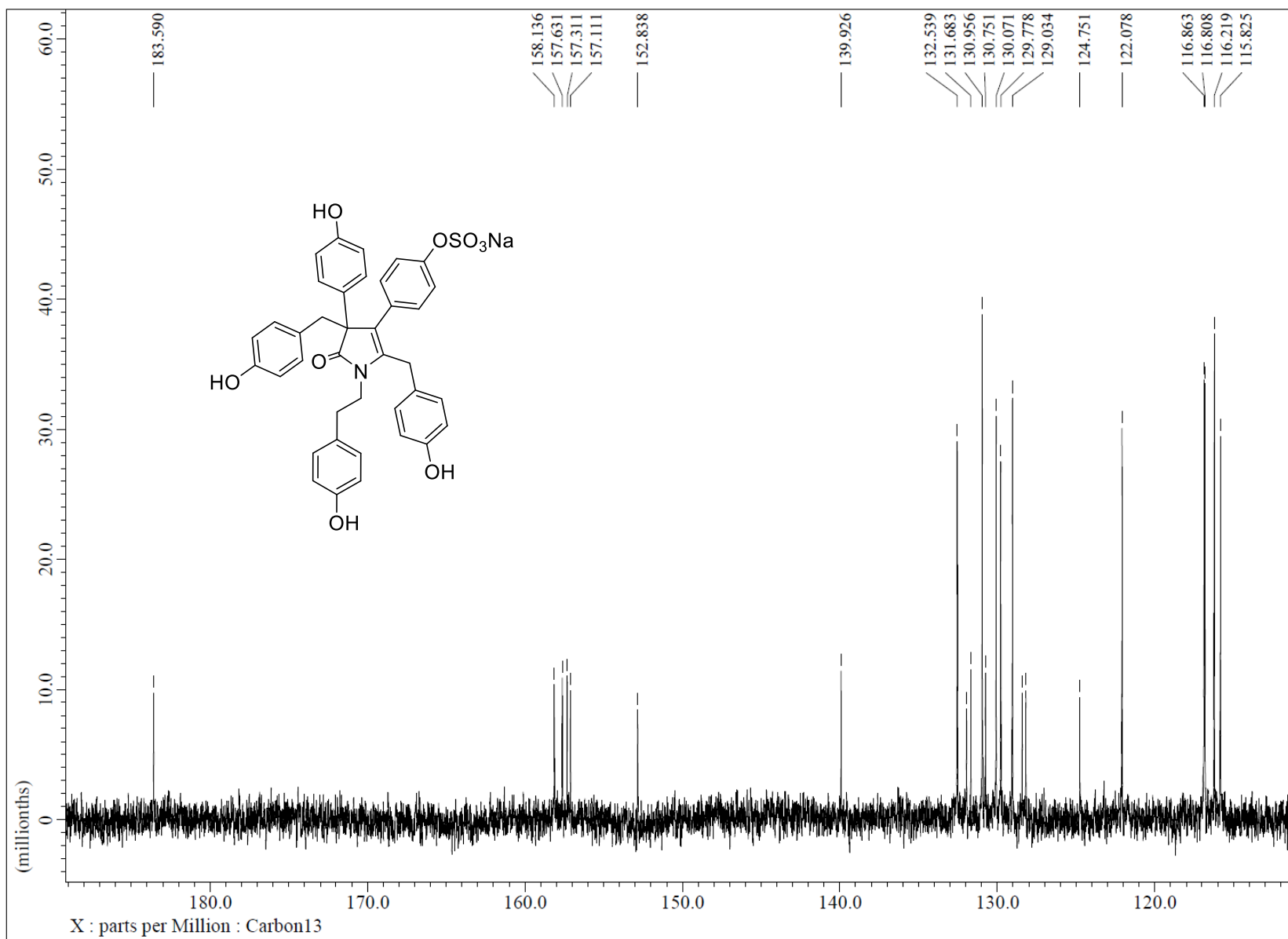


Figure S1d. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum expansion 2 of denigrin H (**1**)

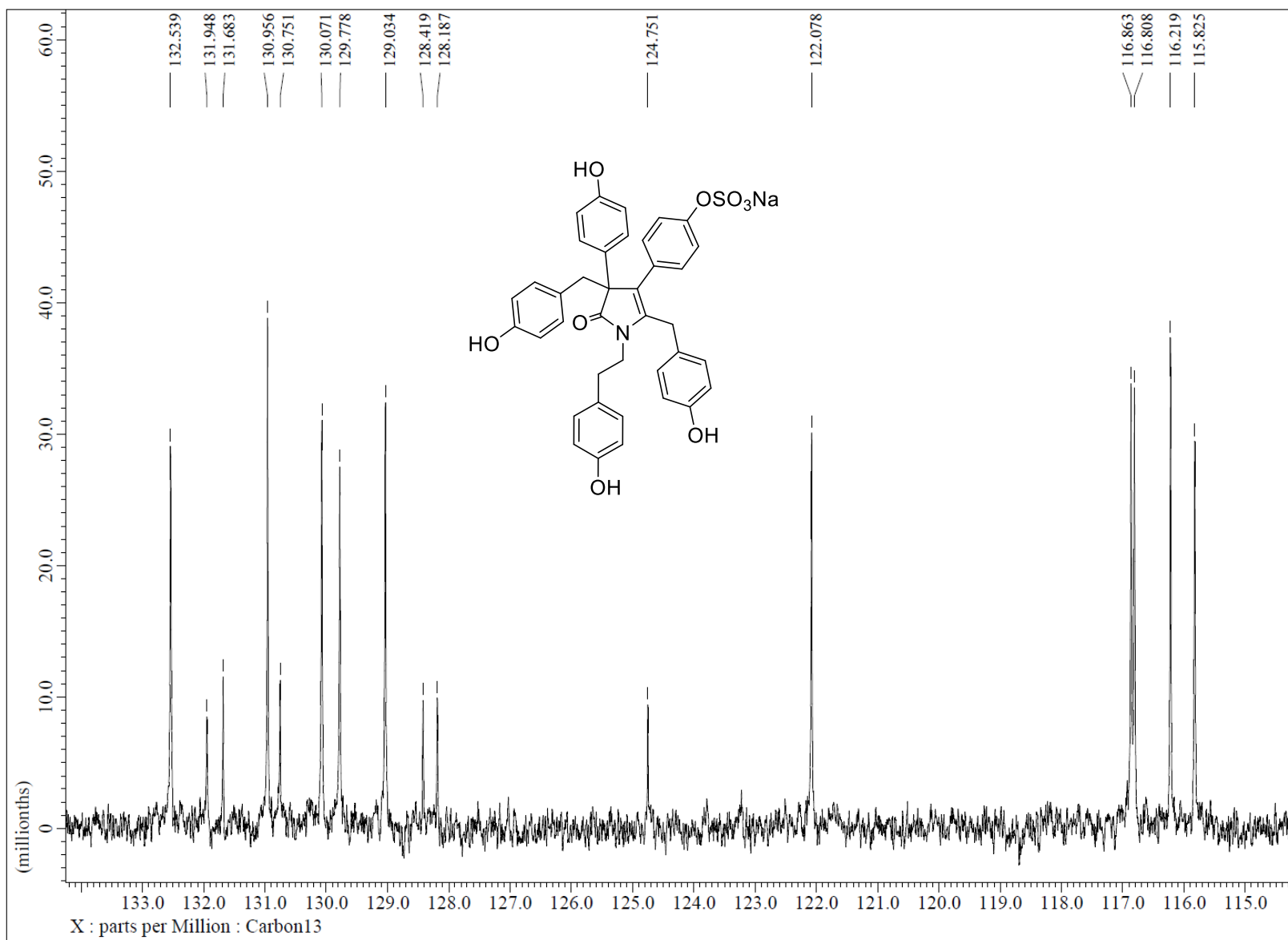


Figure S1e. COSY (methanol-*d*4) spectrum of denigrin H (**1**)

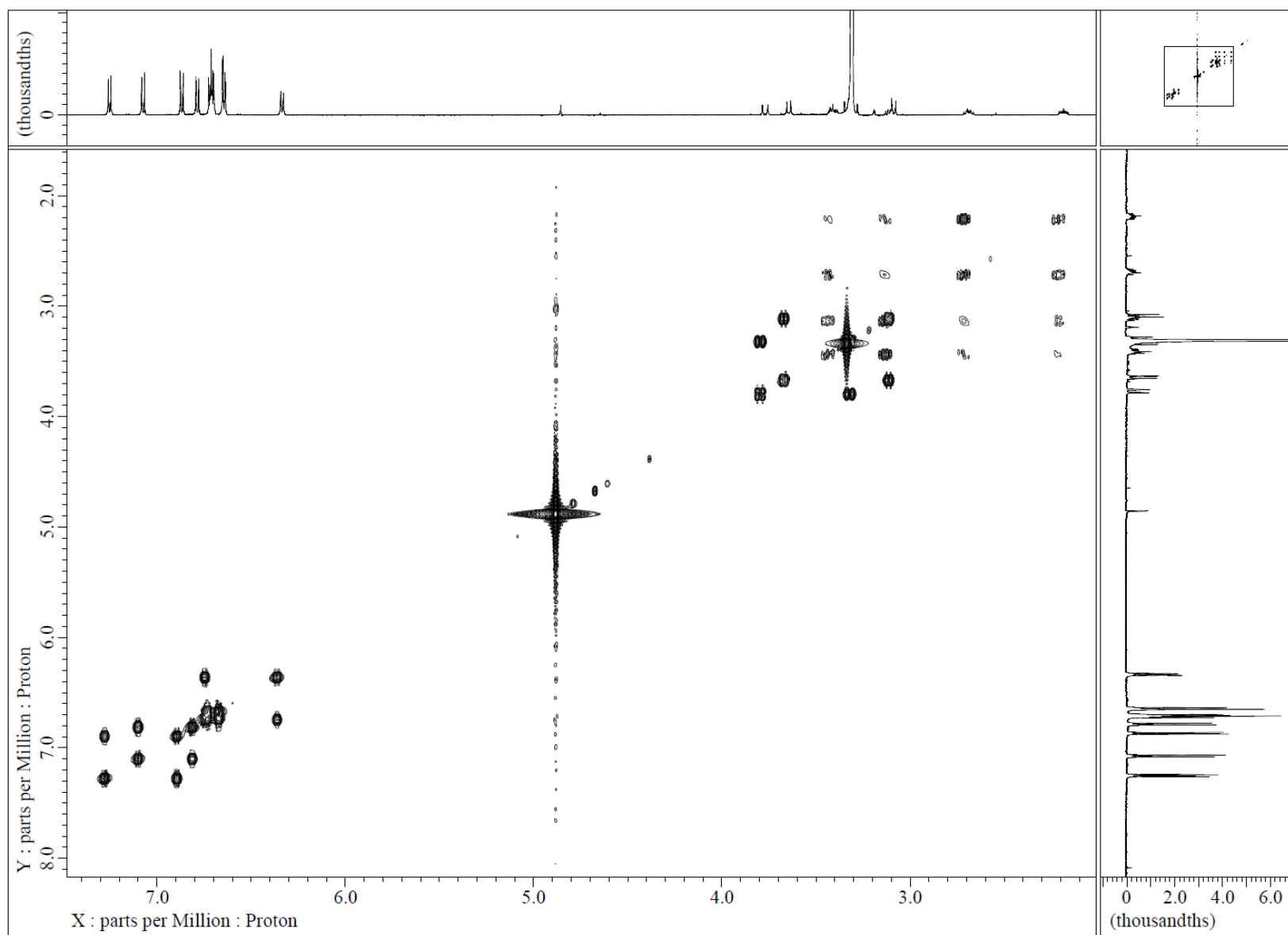


Figure S1f. COSY (methanol-*d*₄) spectrum of denigrin H (**1**)

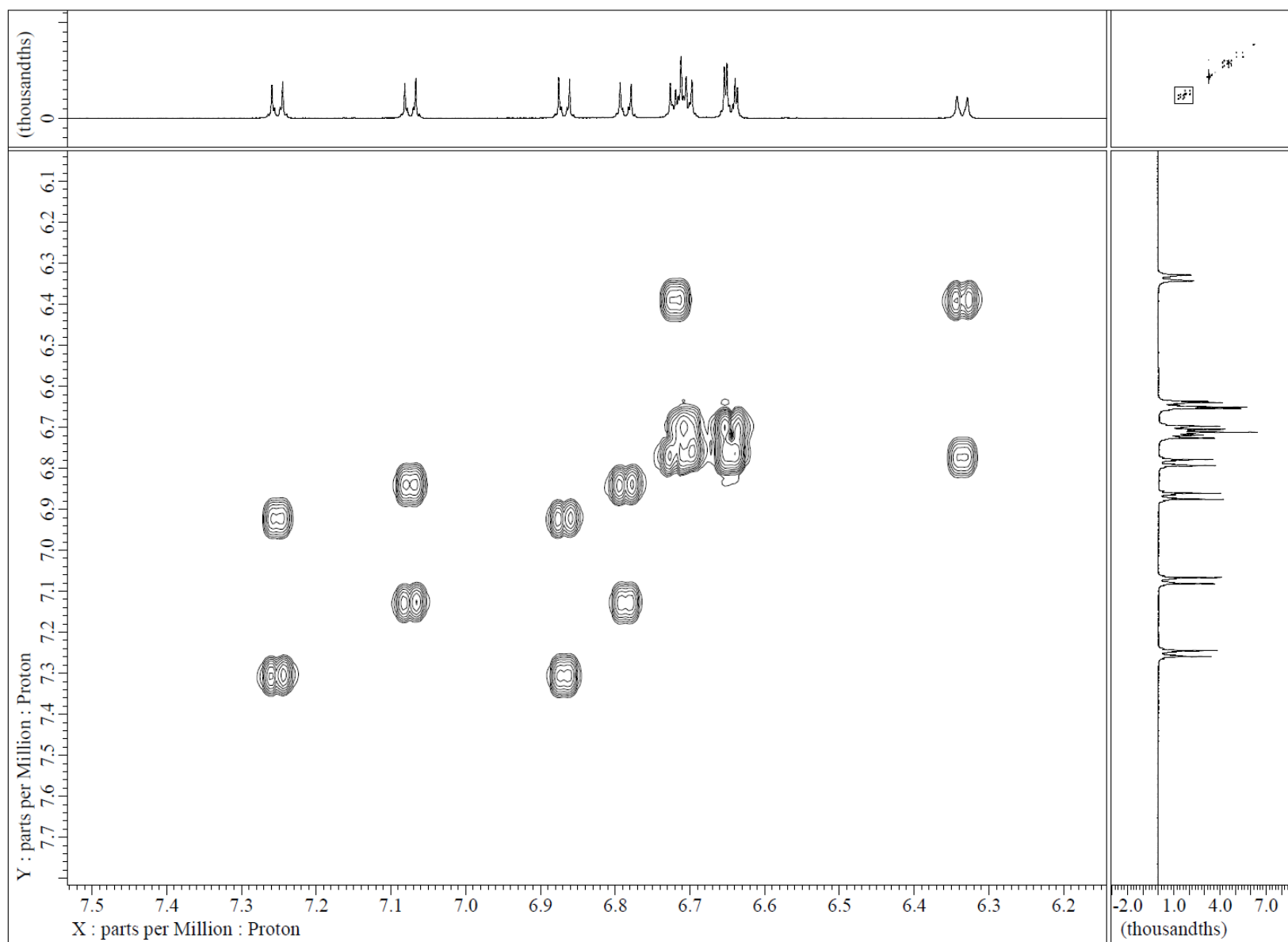


Figure S1g. gHSQC (methanol-*d*4) spectrum of denigrin H (**1**)

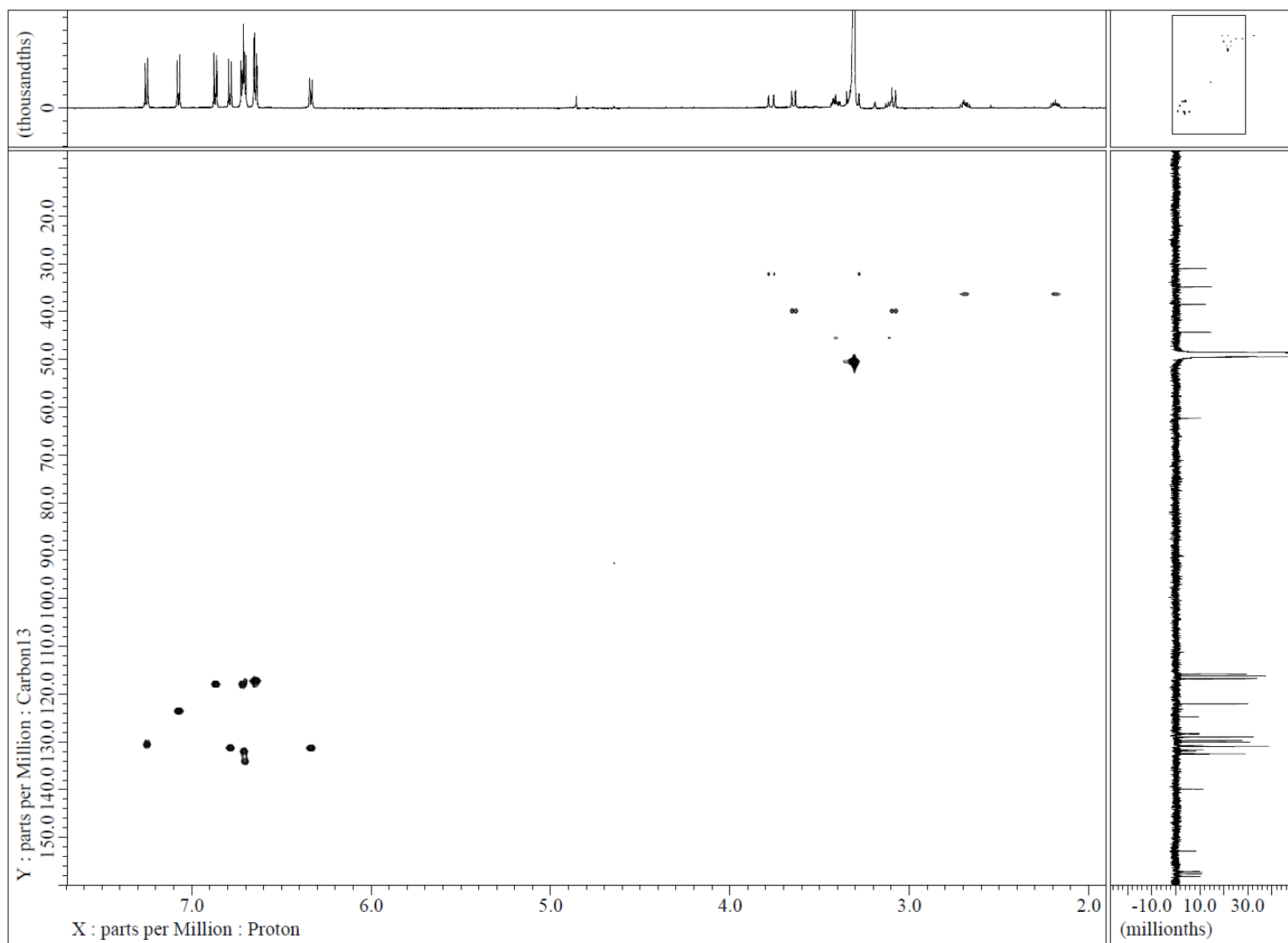


Figure S1h. gHMBC (methanol-*d*₄) spectrum of denigrin H (**1**)

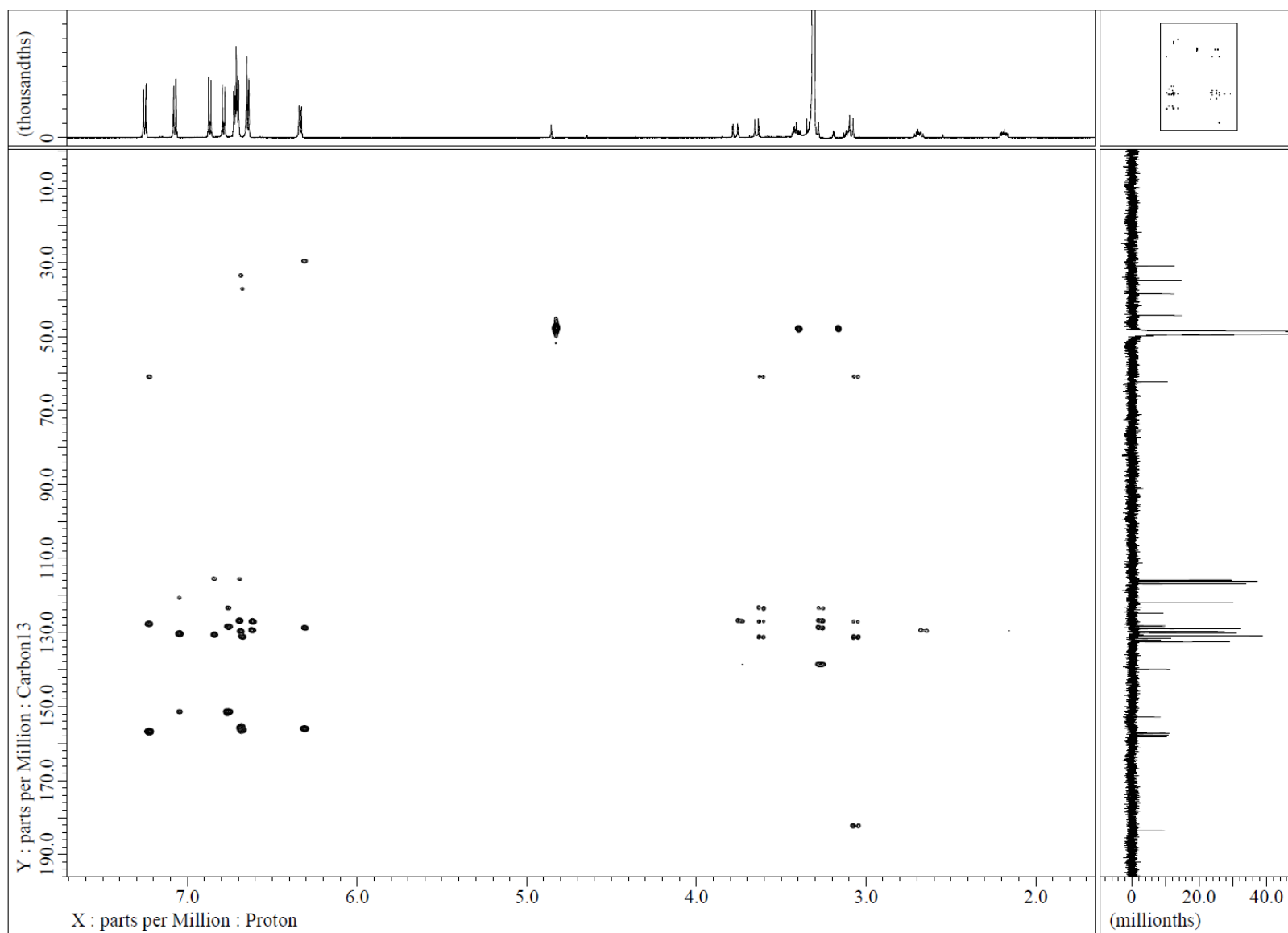


Figure S1i. gHMBC (methanol-*d*4) spectrum expansion of denigrin H (**1**)

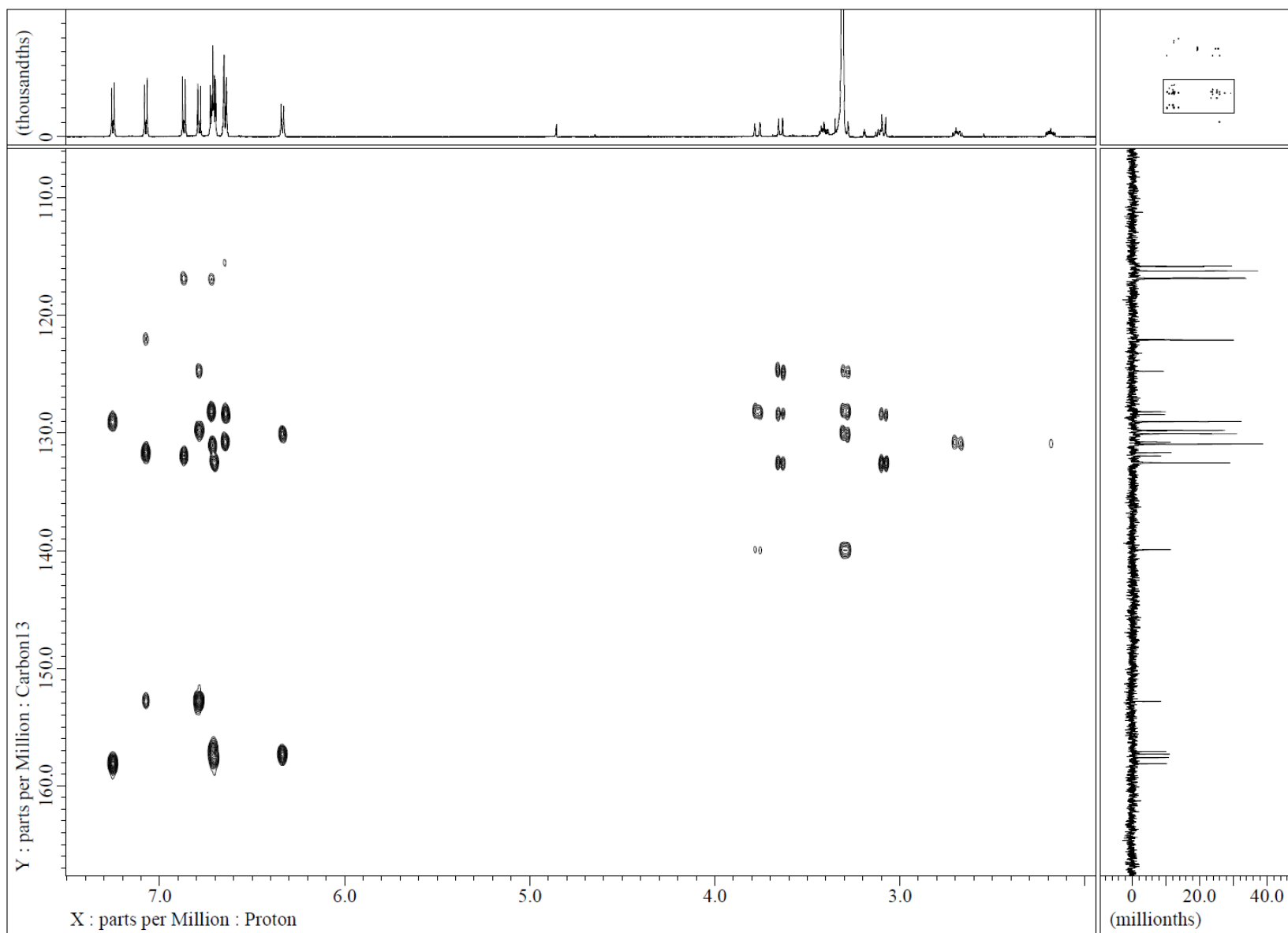


Figure S1j. HRESIMS spectrum of denigrin H (**1**) in negative ion mode

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Corrector Fill	46 V
n/a	n/a	Set Capillary Exit	-150.0 V	Set Pulsar Pull	800 V
Scan Begin	50 m/z	Set Hexapole RF	80.0 V	Set Pulsar Push	800 V
Scan End	1500 m/z	Set Skimmer 1	-50.0 V	Set Reflector	1700 V
		Set Hexapole 1	-25.0 V	Set Flight Tube	8600 V
				Set Detector TOF	2250 V

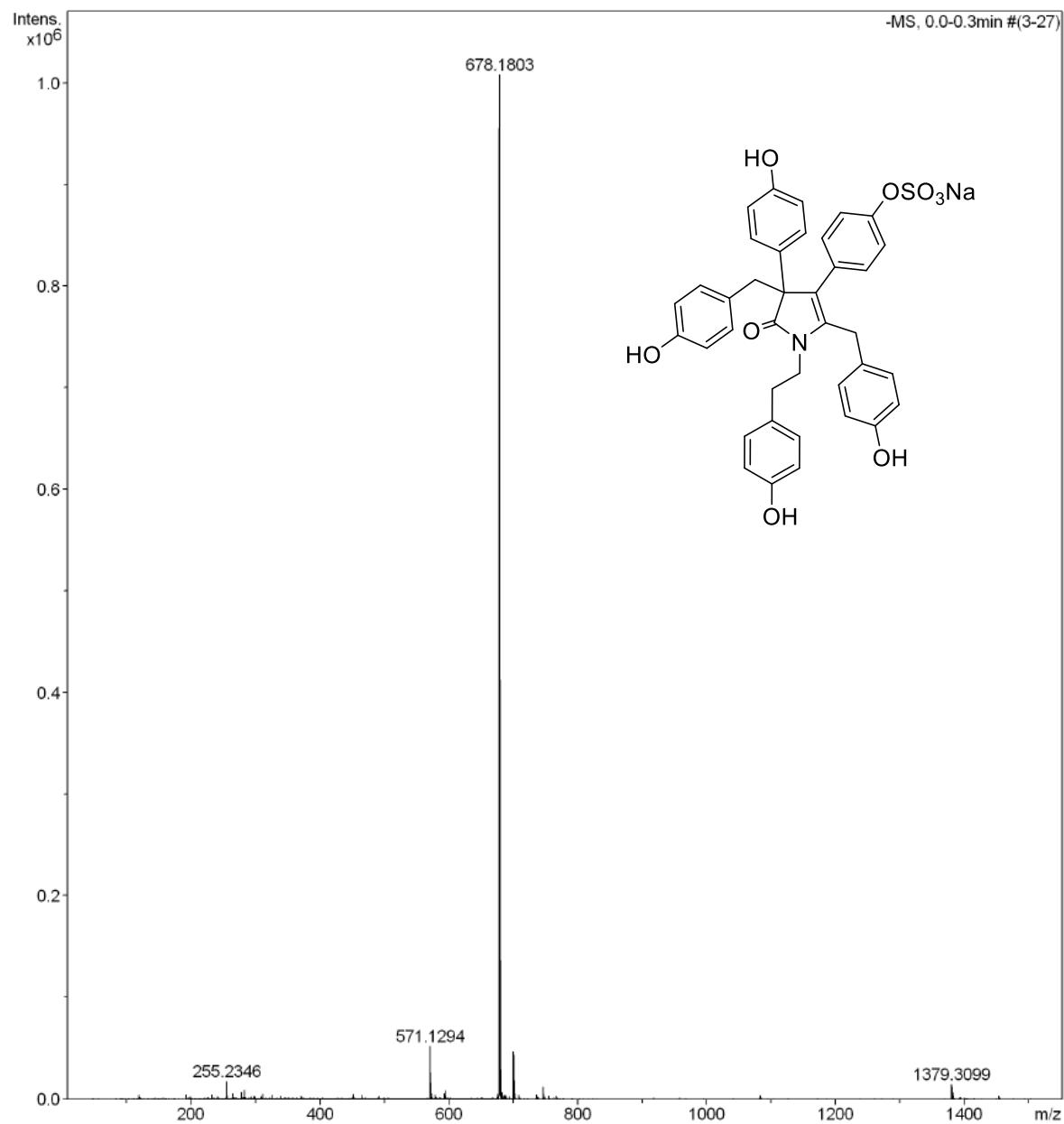


Figure S2a. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of denigrin I (**2**)

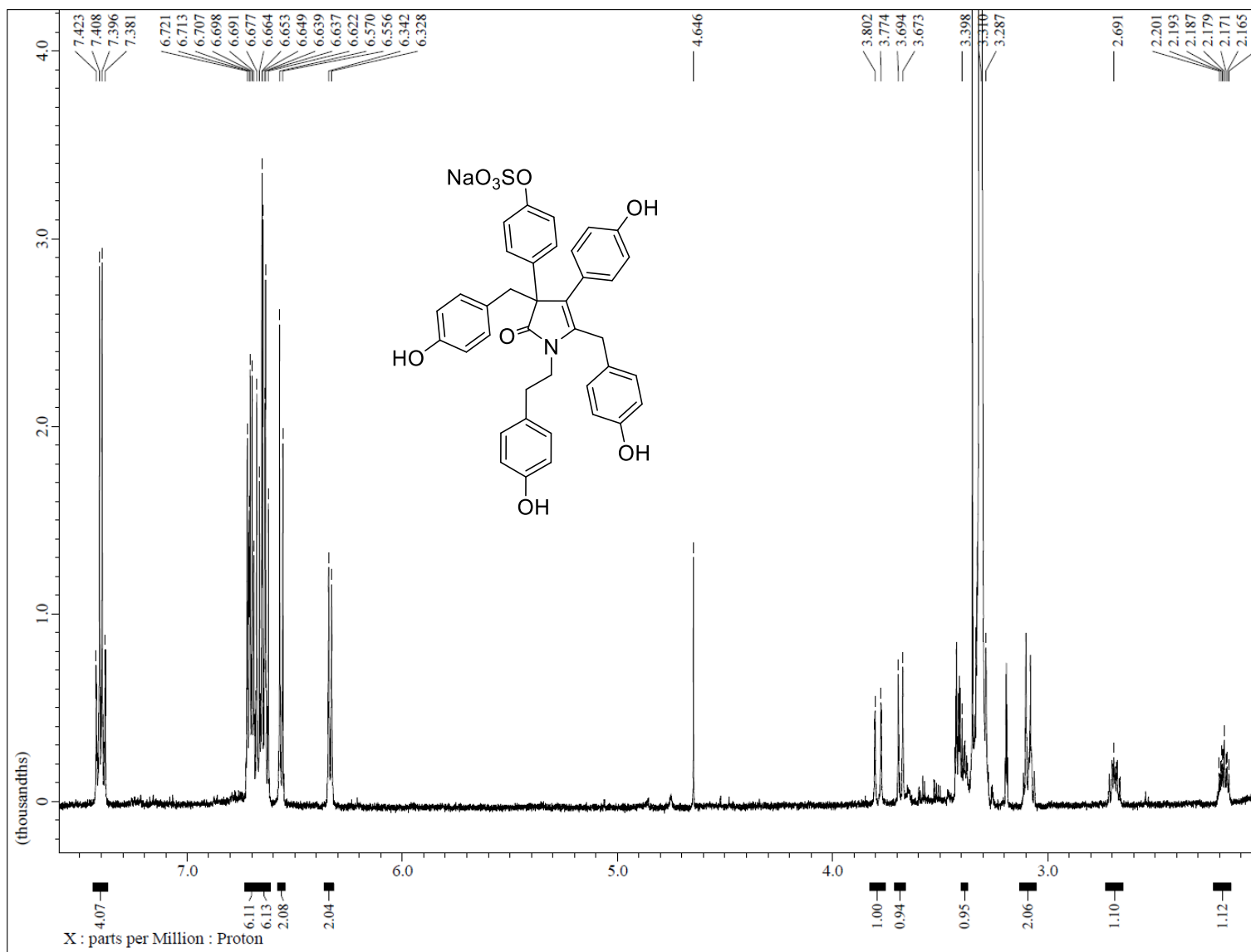


Figure S2b. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum of denigrin I (**2**)

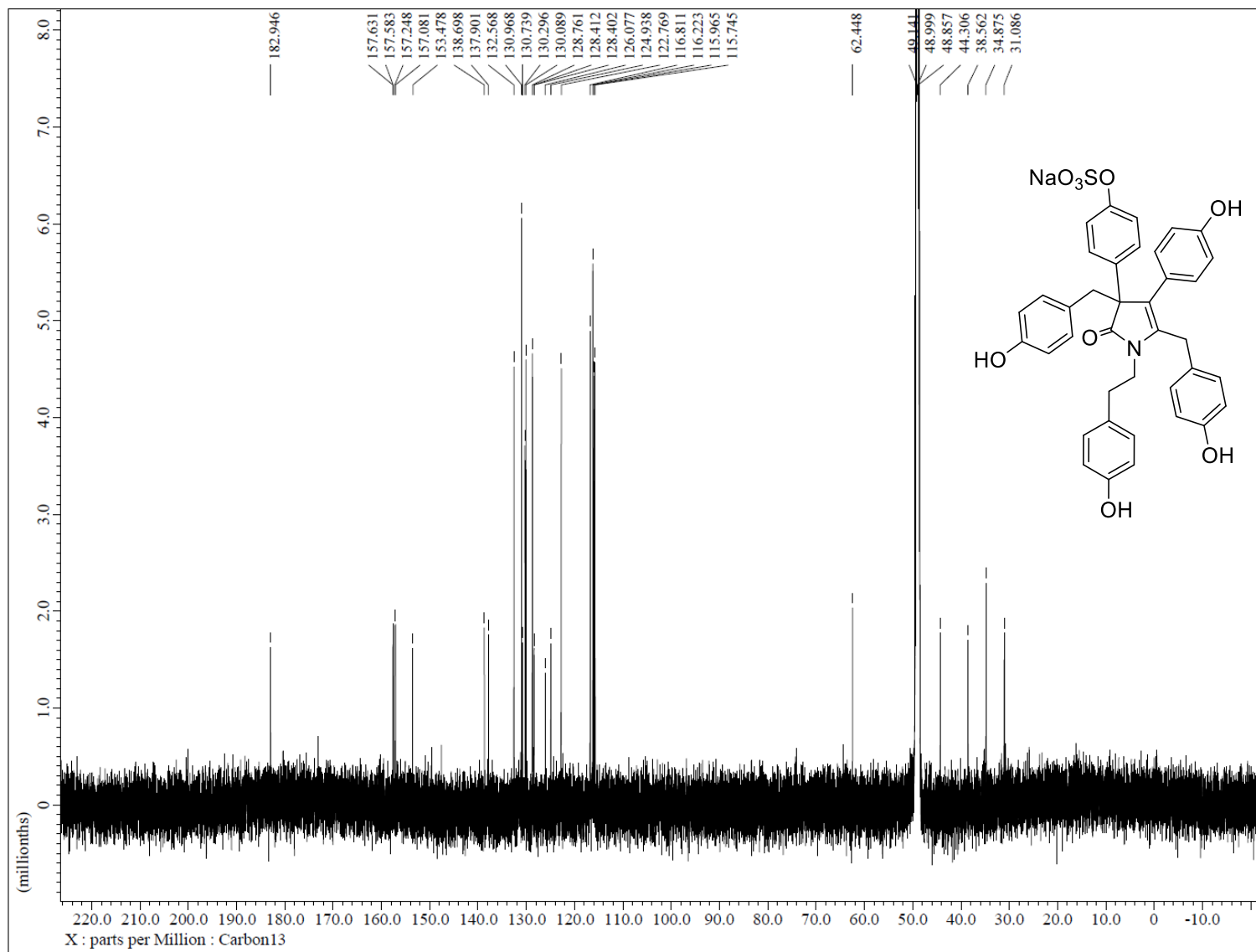


Figure S2c. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum expansion of denigrin I (**2**)

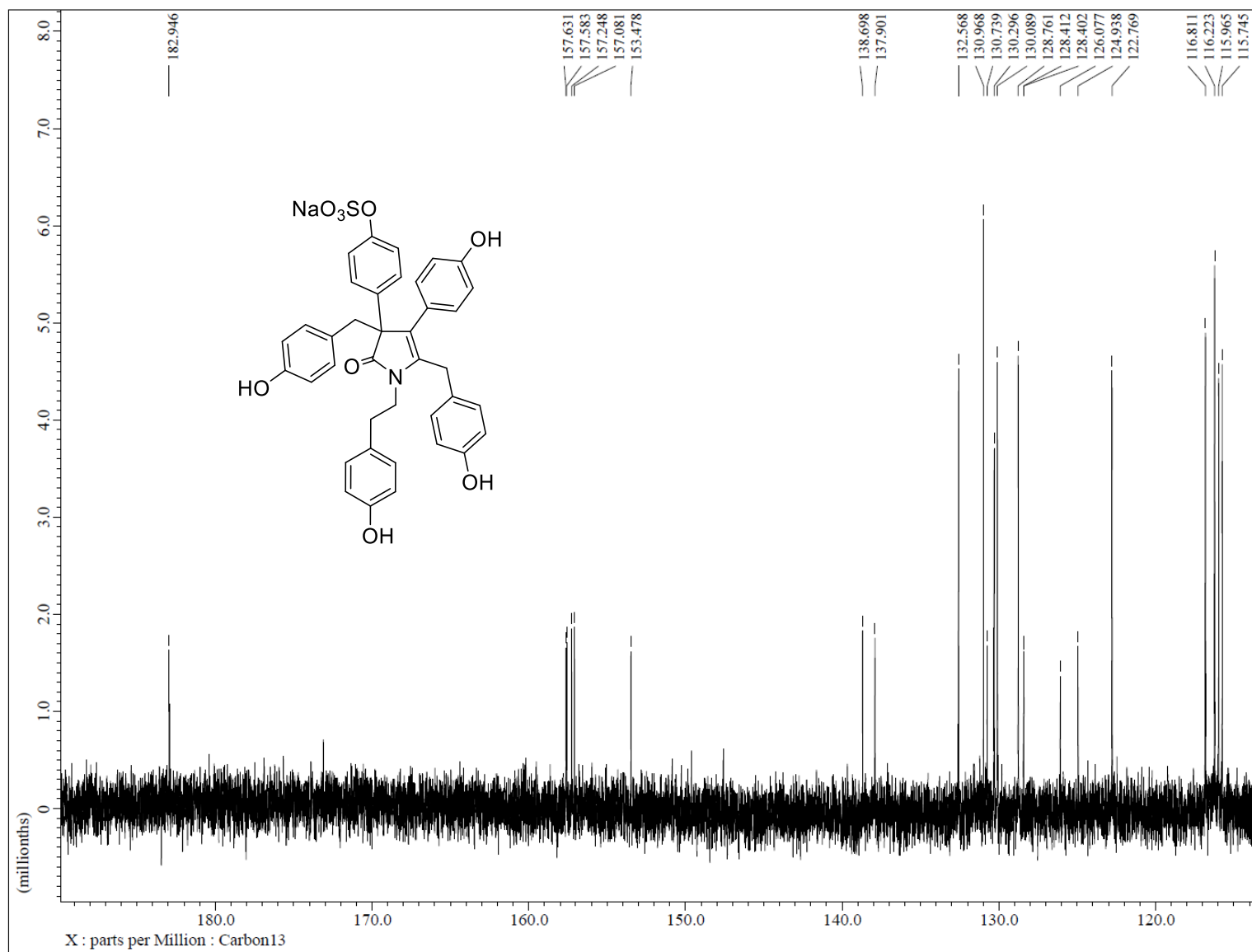


Figure S2d. COSY (methanol-*d*₄) spectrum of denigrin I (**2**)

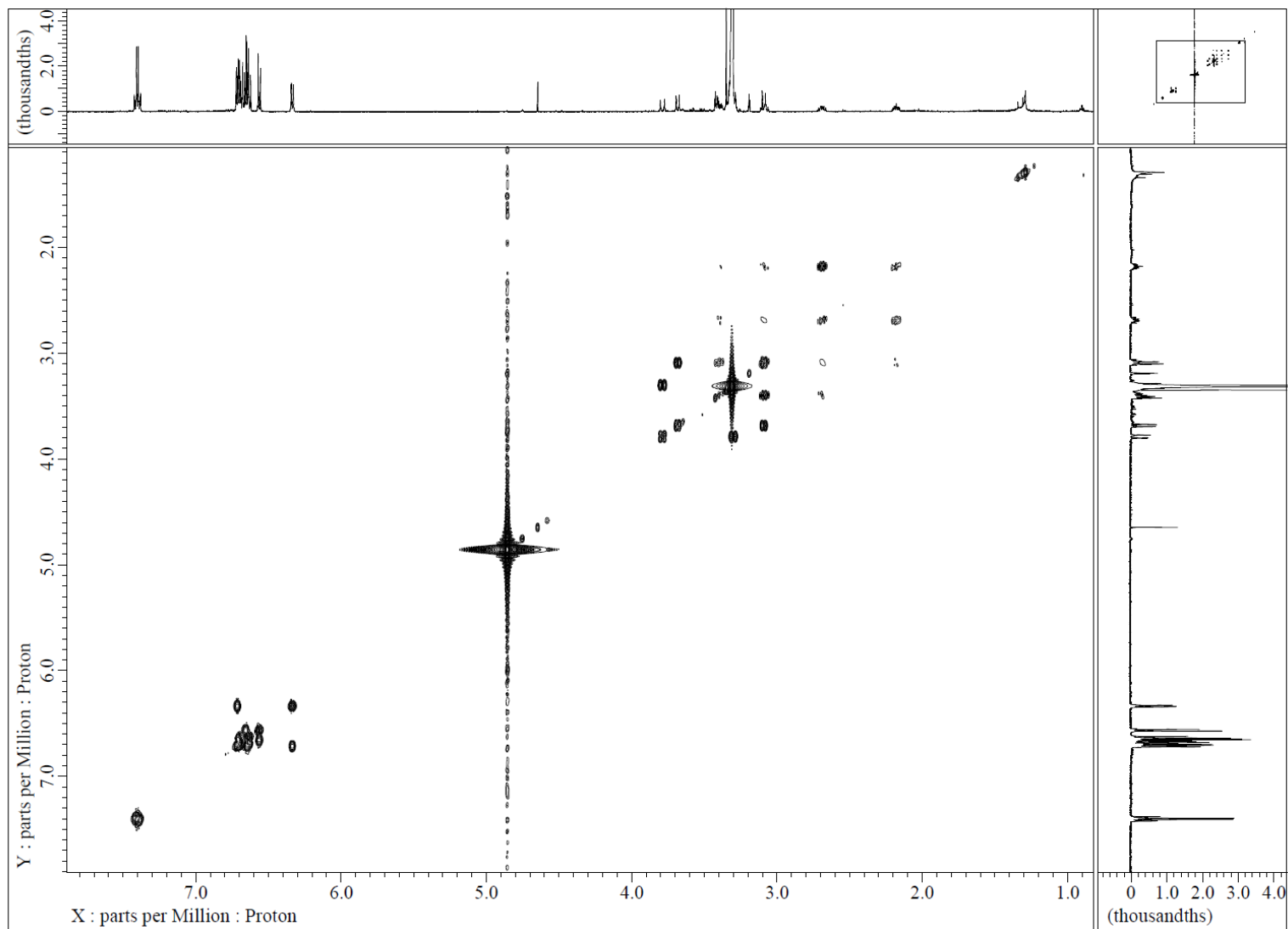


Figure S2e. gHSQC (methanol-d₄) spectrum of denigrin I (**2**)

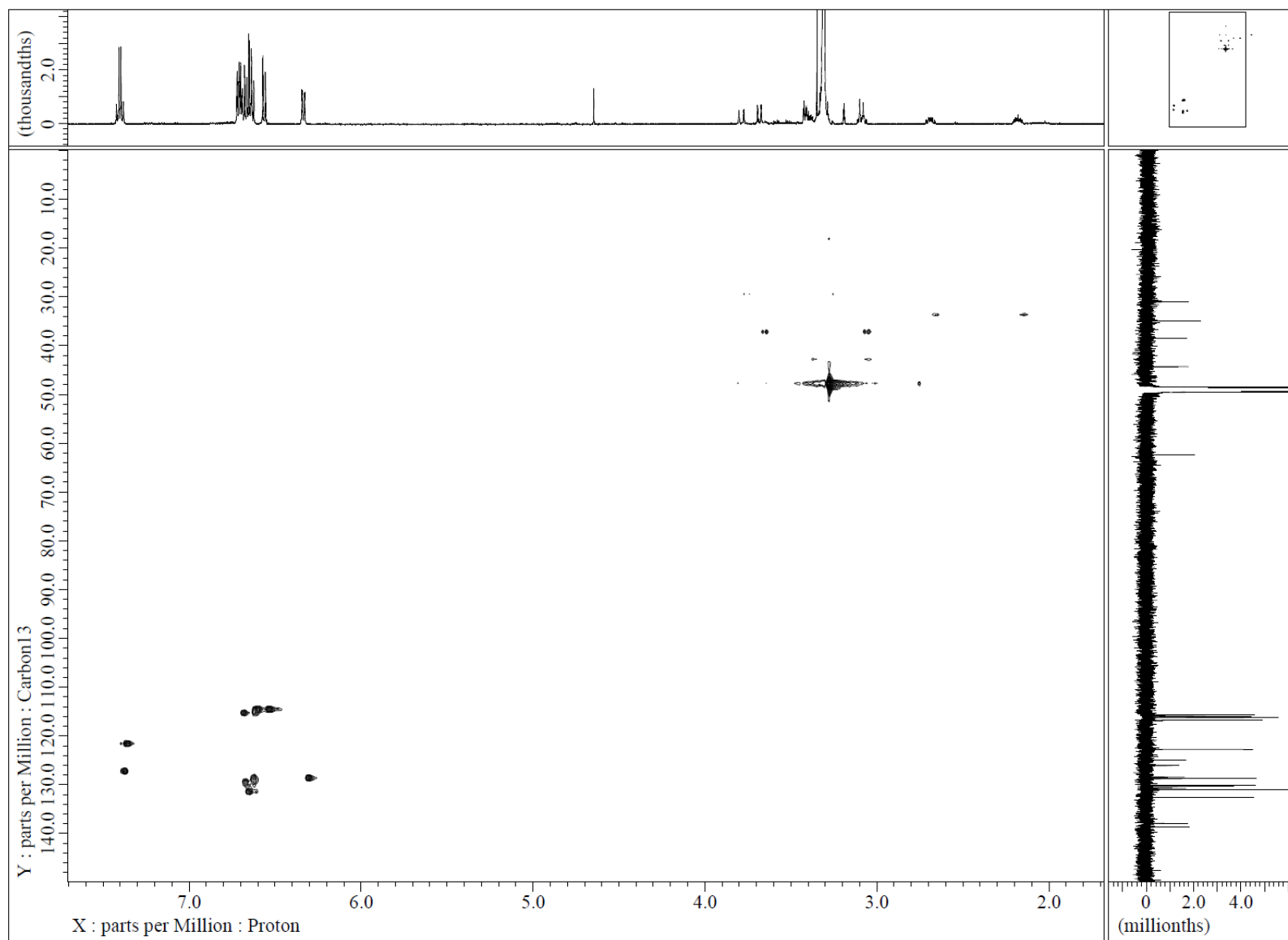


Figure S2f. gHMBC (methanol-*d*₄) spectrum of denigrin I (**2**)

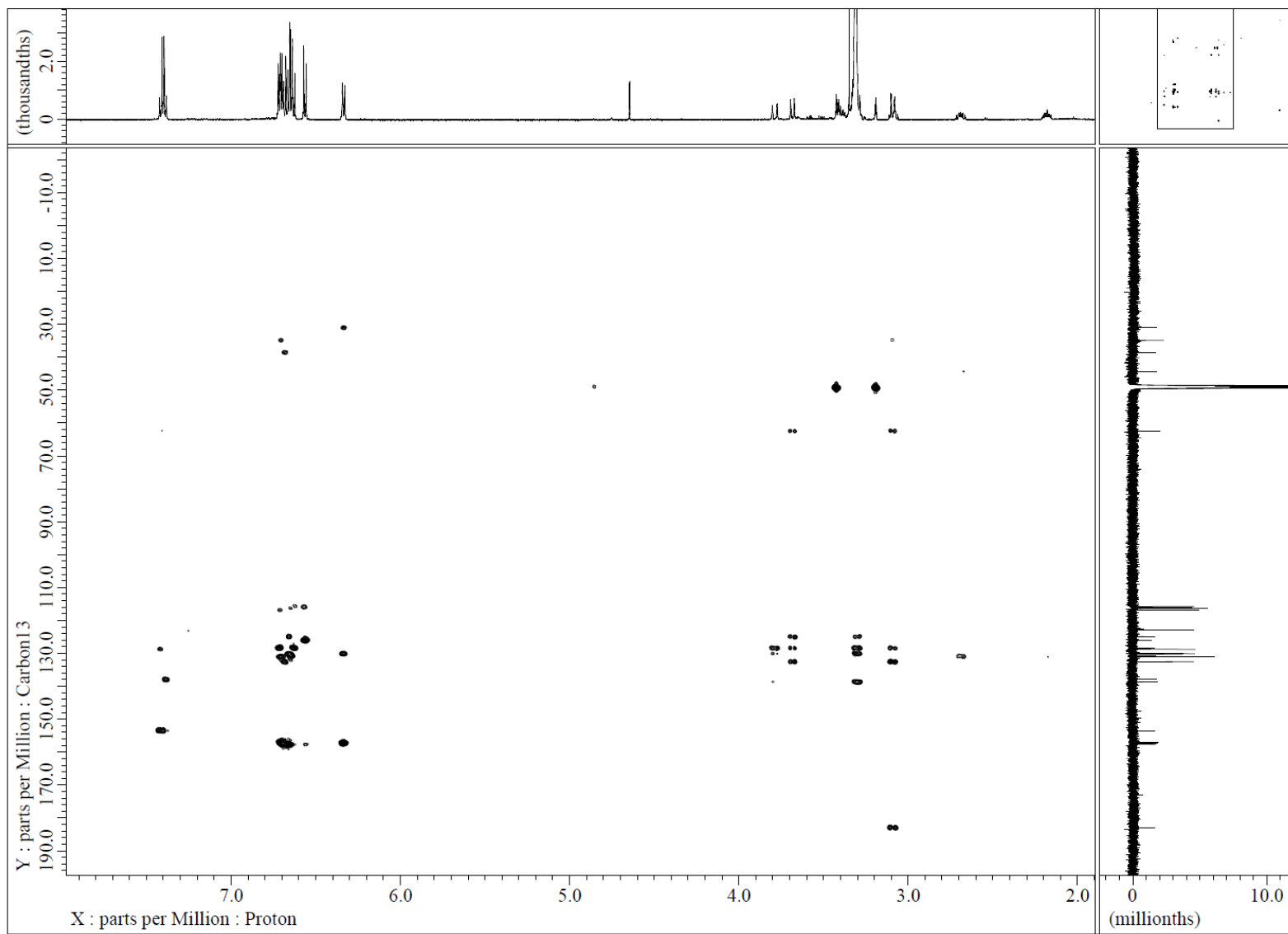


Figure S2g. gHMBC (methanol-*d*₄) spectrum expansion of denigrin I (**2**)

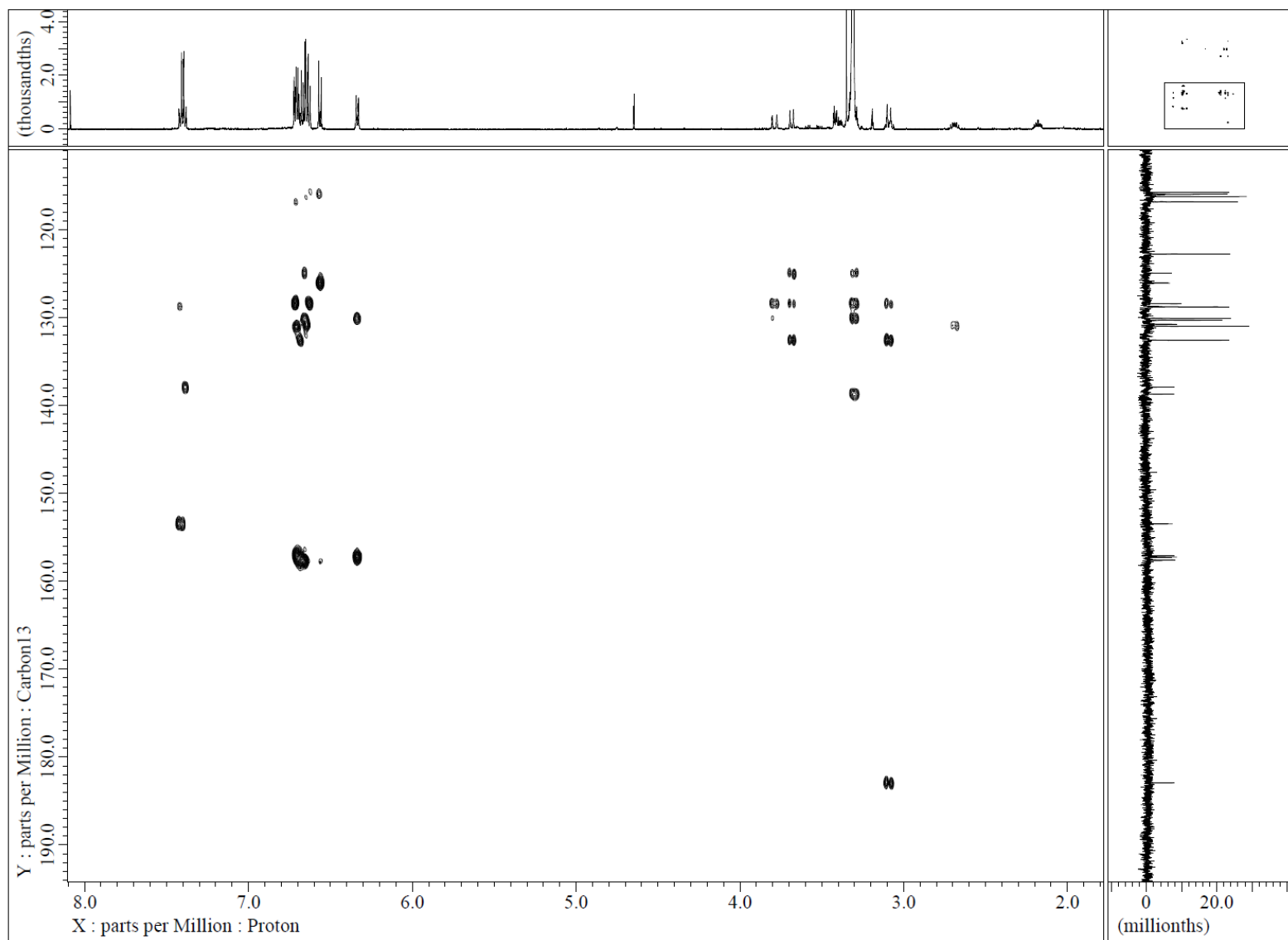


Figure S2h. HRESIMS spectrum of denigrin I (**2**) in negative ion mode

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Corrector Fill	46 V
n/a	n/a	Set Capillary Exit	-150.0 V	Set Pulsar Pull	800 V
Scan Begin	50 m/z	Set Hexapole RF	80.0 V	Set Pulsar Push	800 V
Scan End	1500 m/z	Set Skimmer 1	-50.0 V	Set Reflector	1700 V
		Set Hexapole 1	-25.0 V	Set Flight Tube	8600 V
				Set Detector TOF	2250 V

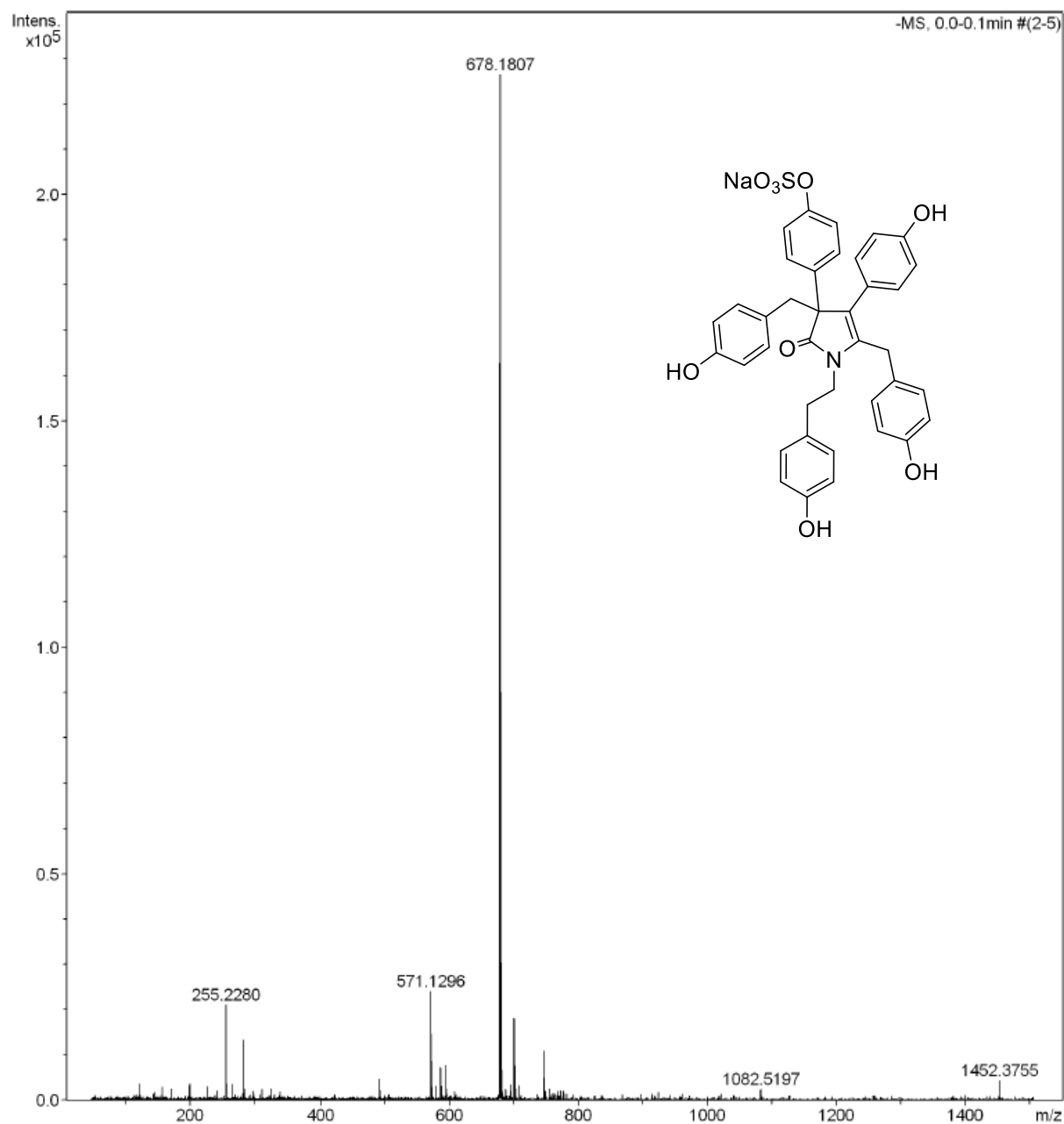


Figure S3a. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of denigrin J (**3**)

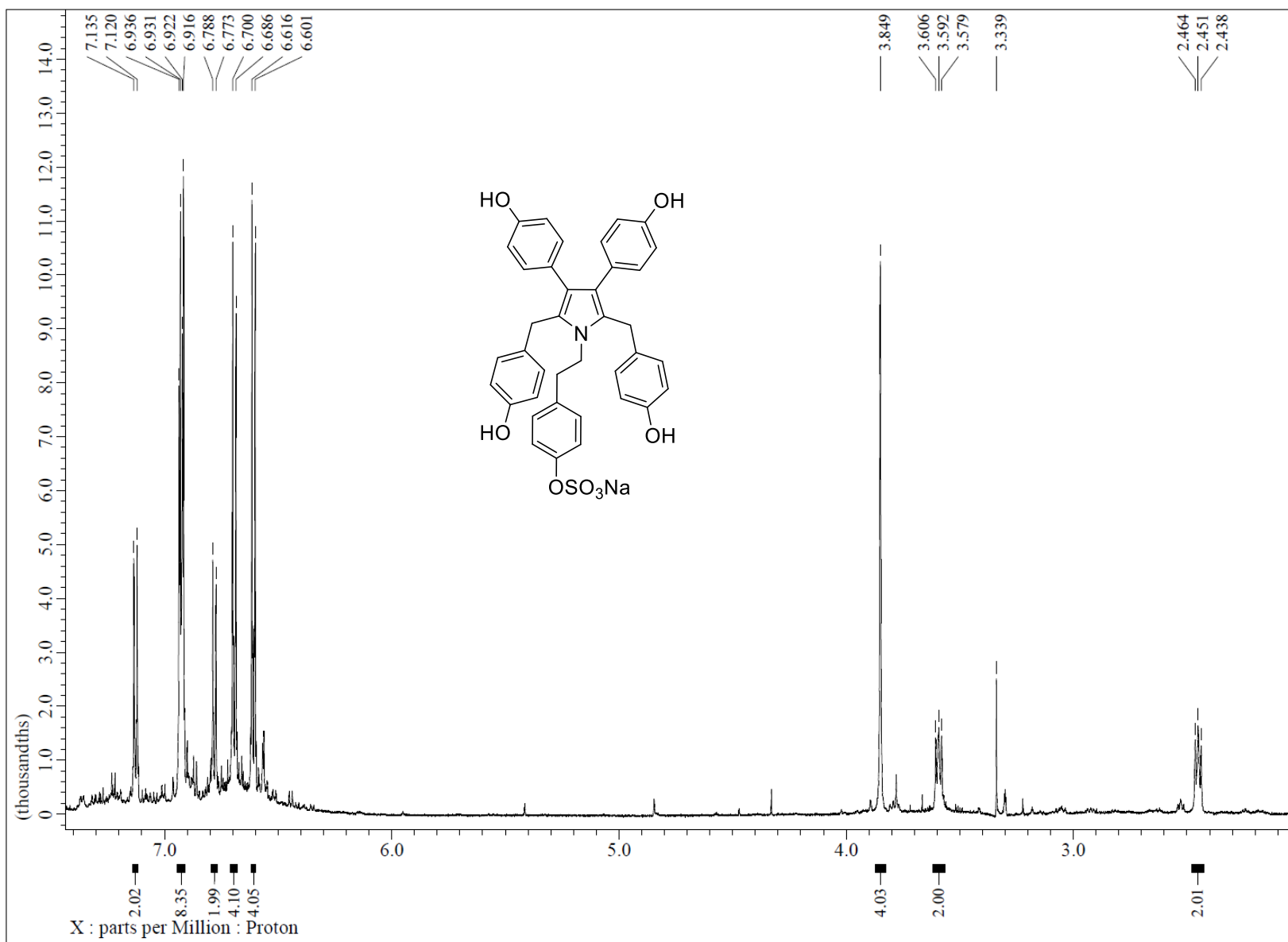


Figure S3b. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum of denigrin J (**3**)

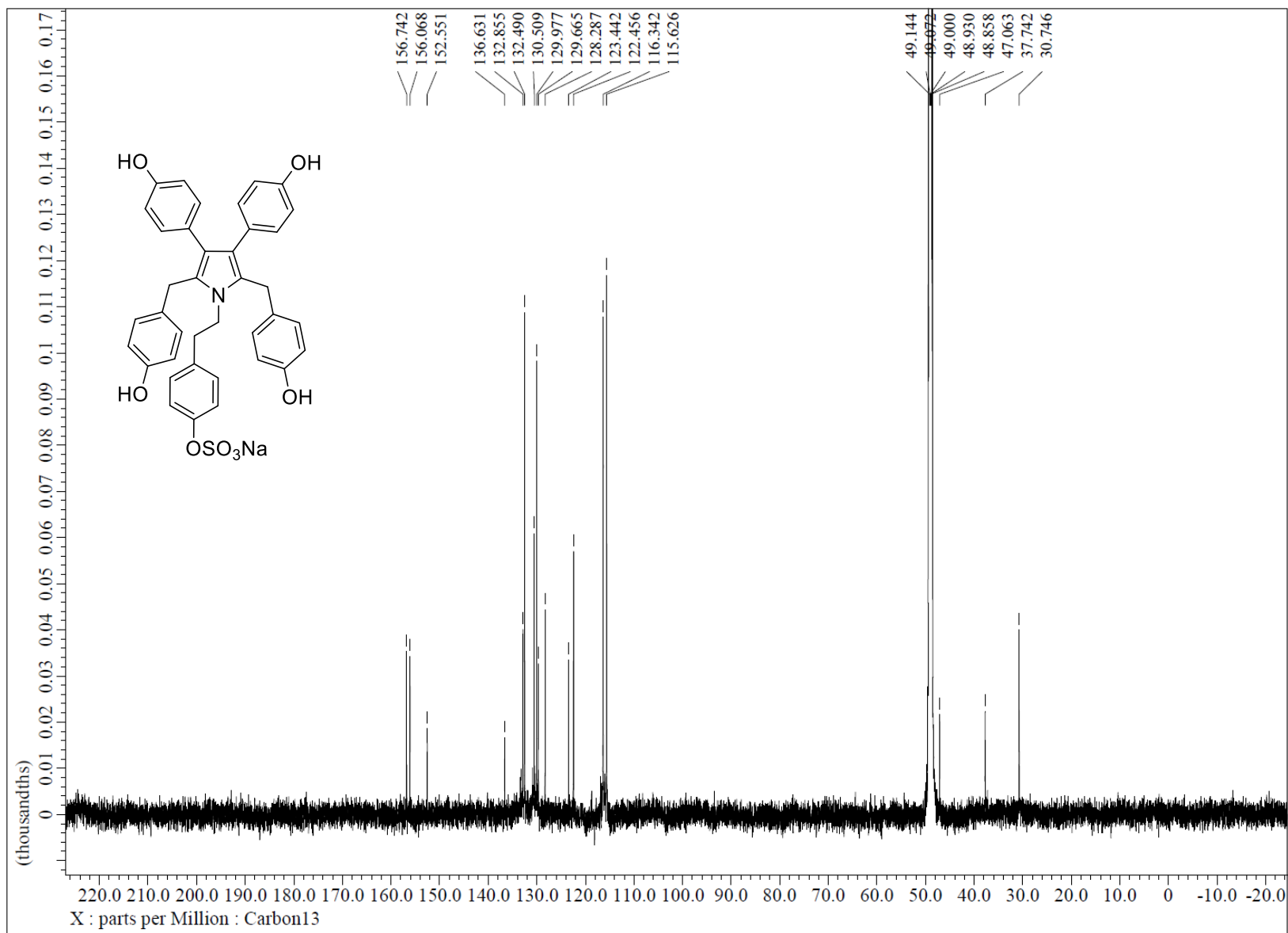


Figure S3c. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum expansion of denigrin J (**3**)

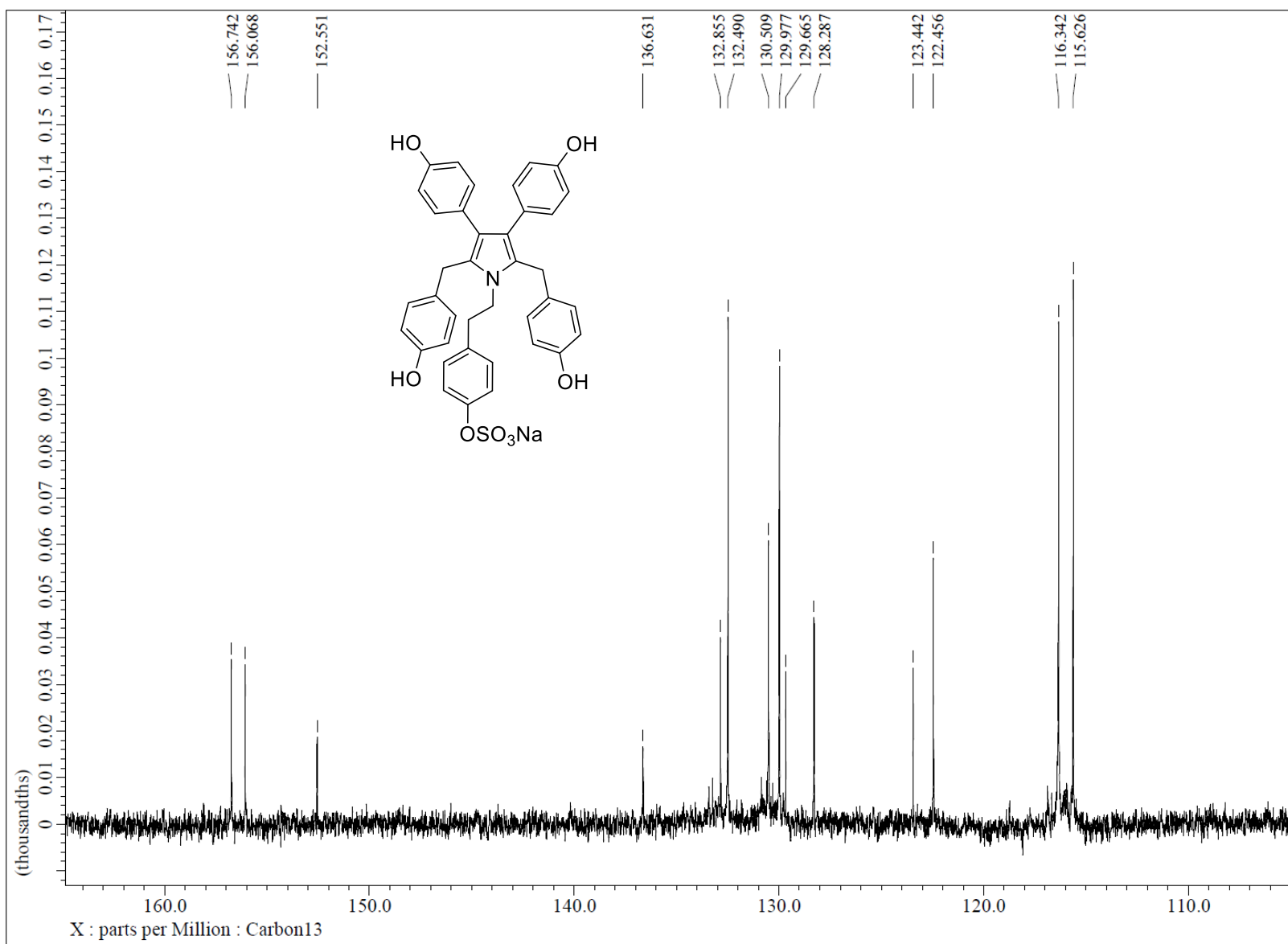


Figure S3d. COSY (methanol-*d*₄) spectrum of denigrin J (**3**)

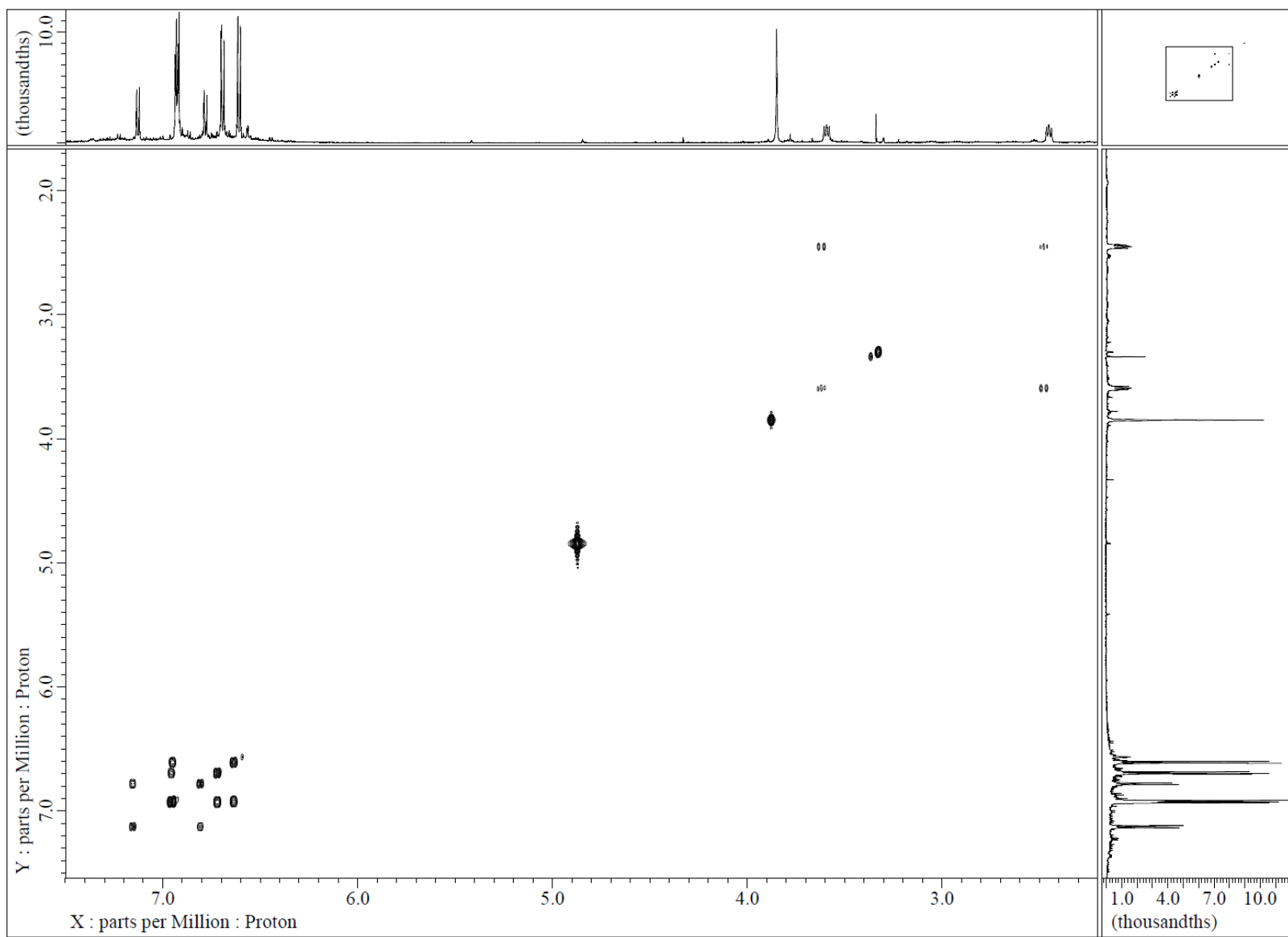


Figure S3e. gHSQC (methanol-*d*4) spectrum of denigrin J (**3**)

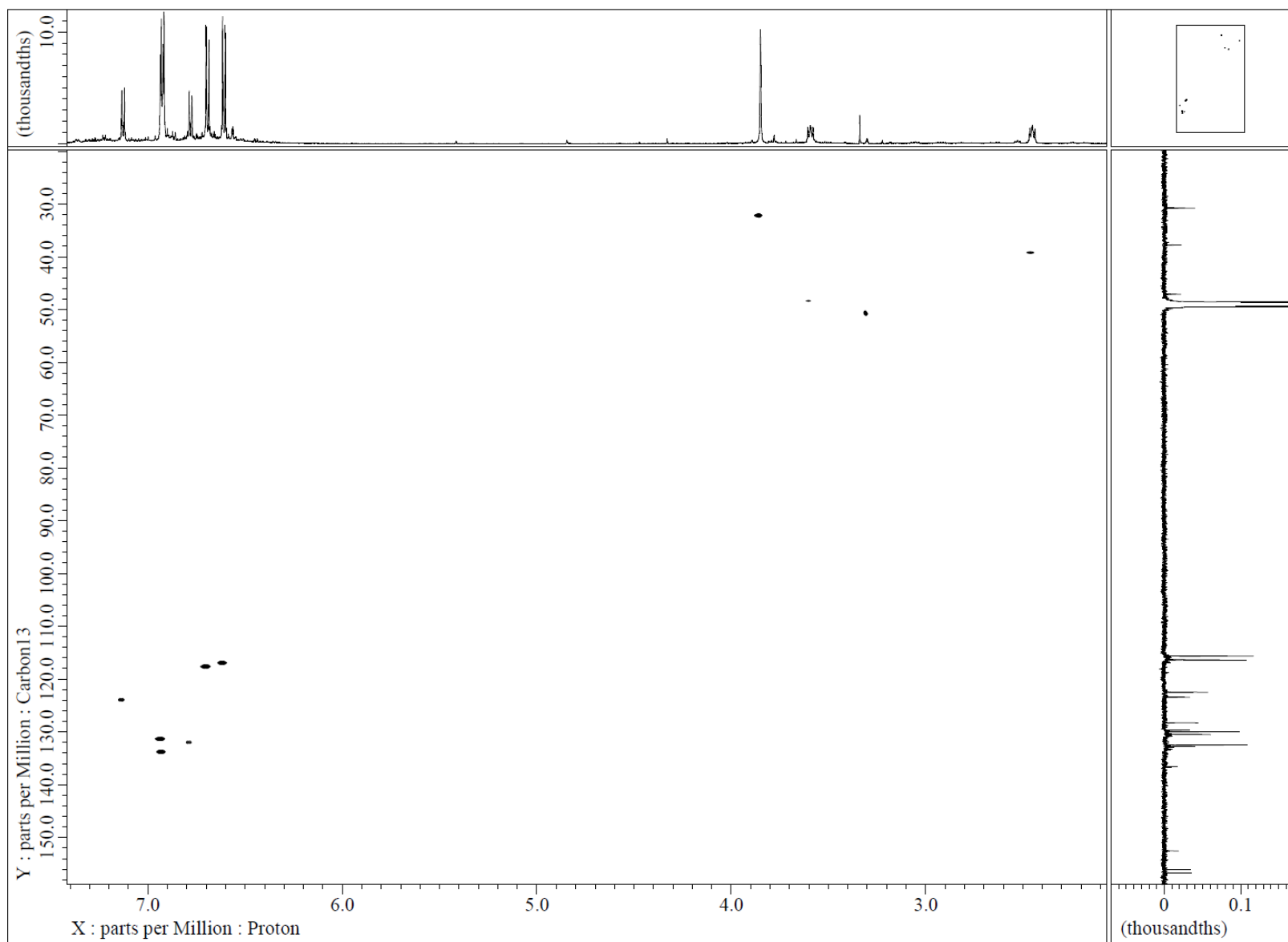


Figure S3f. gHMBC (methanol-*d*4) spectrum of denigrin J (**3**)

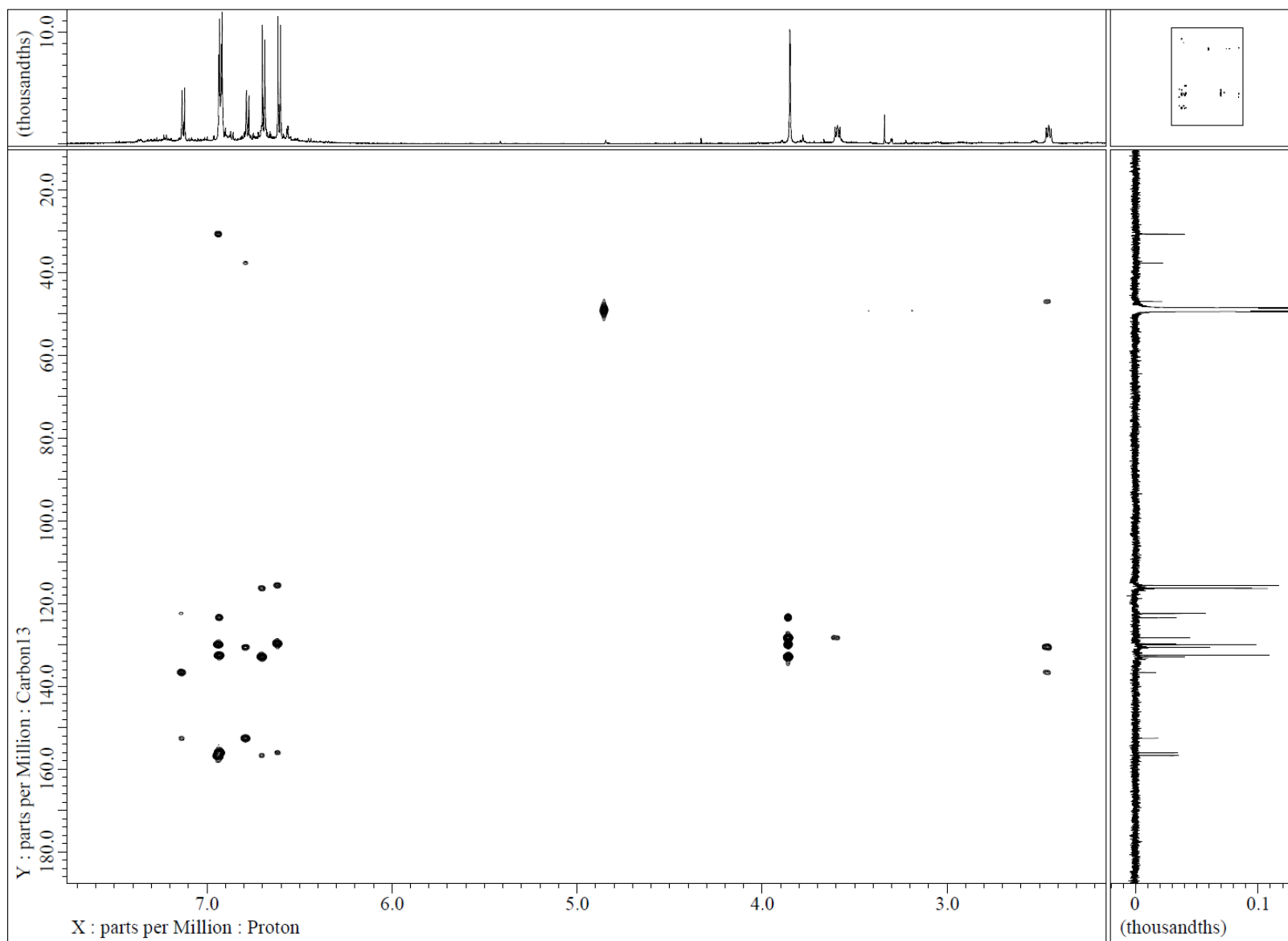


Figure S3g. gHMBC (methanol-*d*₄) spectrum expansion of denigrin J (**3**)

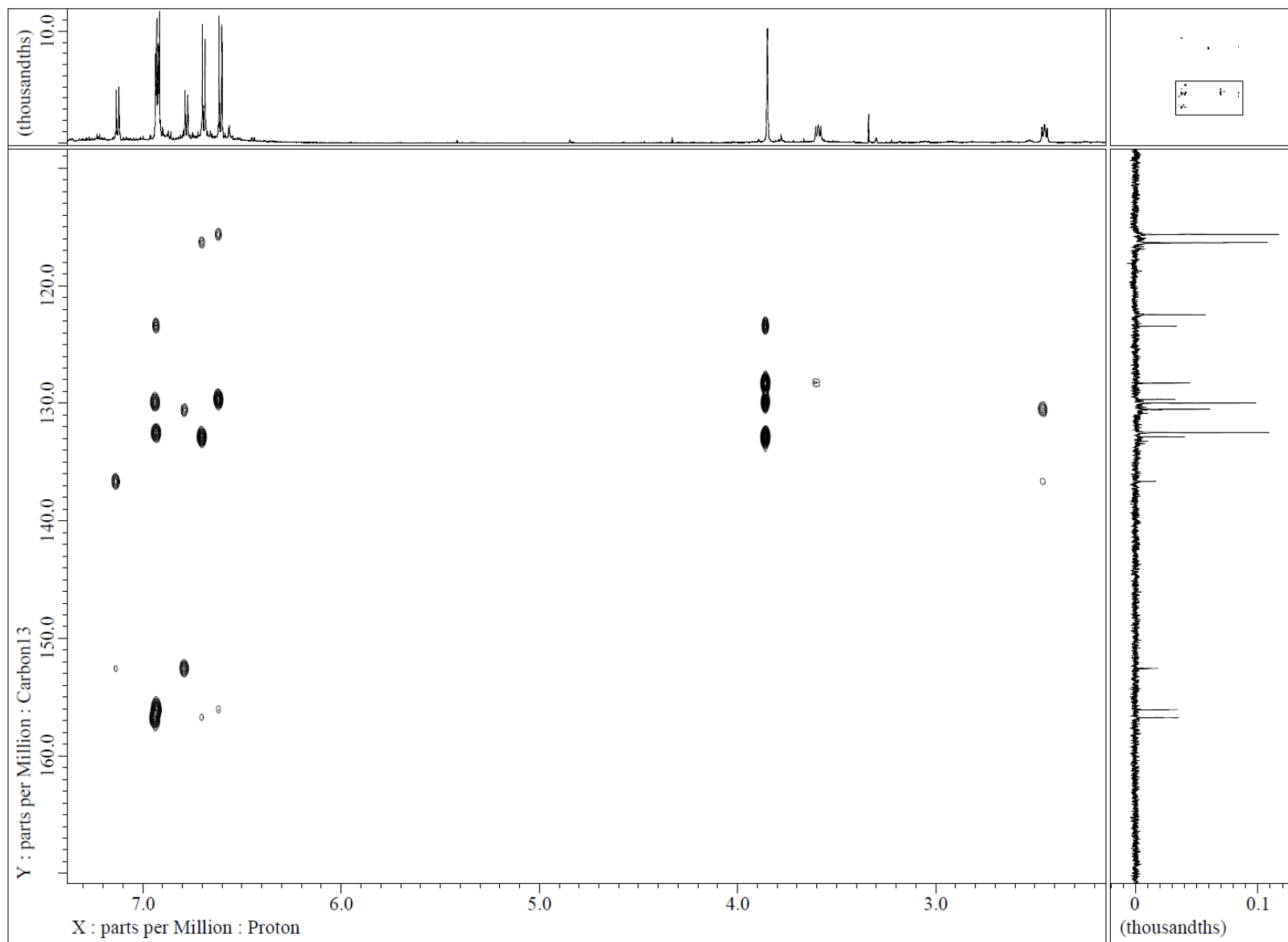


Figure S3h. HRESIMS spectrum of denigrin J (**3**) in negative ion mode

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Corrector Fill	46 V
n/a	n/a	Set Capillary Exit	-150.0 V	Set Pulsar Pull	800 V
Scan Begin	50 m/z	Set Hexapole RF	80.0 V	Set Pulsar Push	800 V
Scan End	1500 m/z	Set Skimmer 1	-50.0 V	Set Reflector	1700 V
		Set Hexapole 1	-25.0 V	Set Flight Tube	8600 V
				Set Detector TOF	2250 V

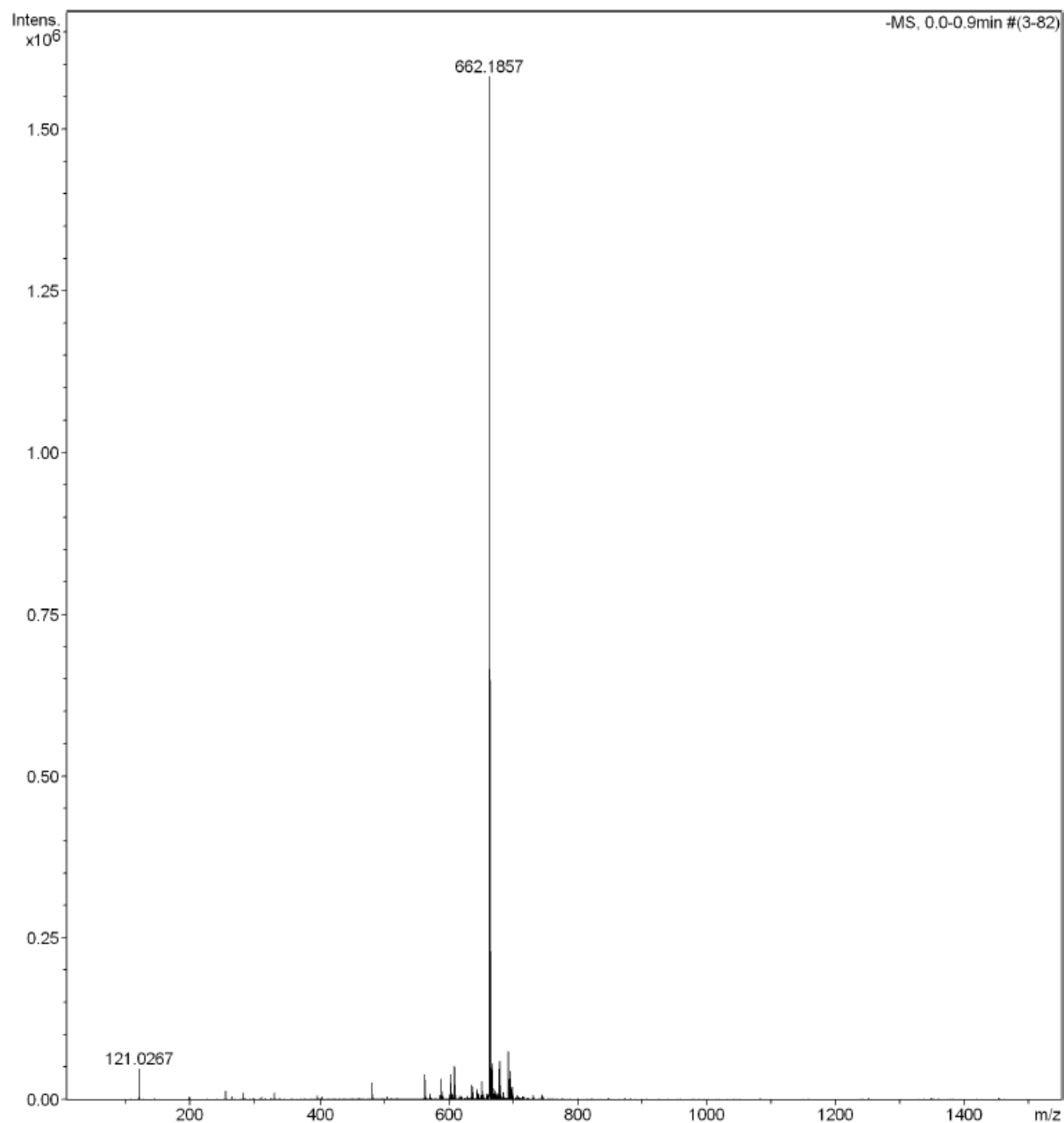


Figure S4a. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of denigrin K (**4**)

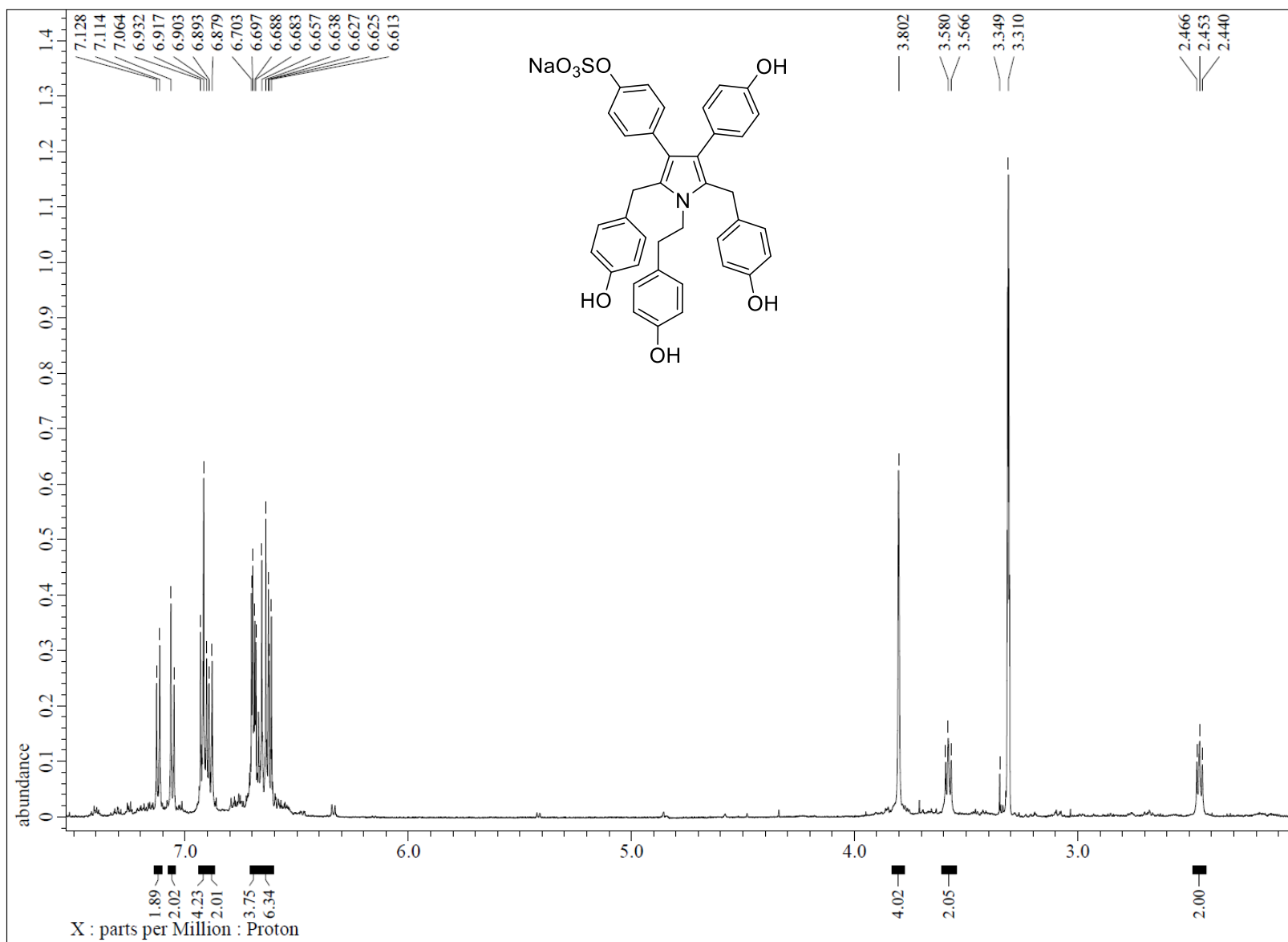


Figure S4b. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum of denigrin K (**4**)

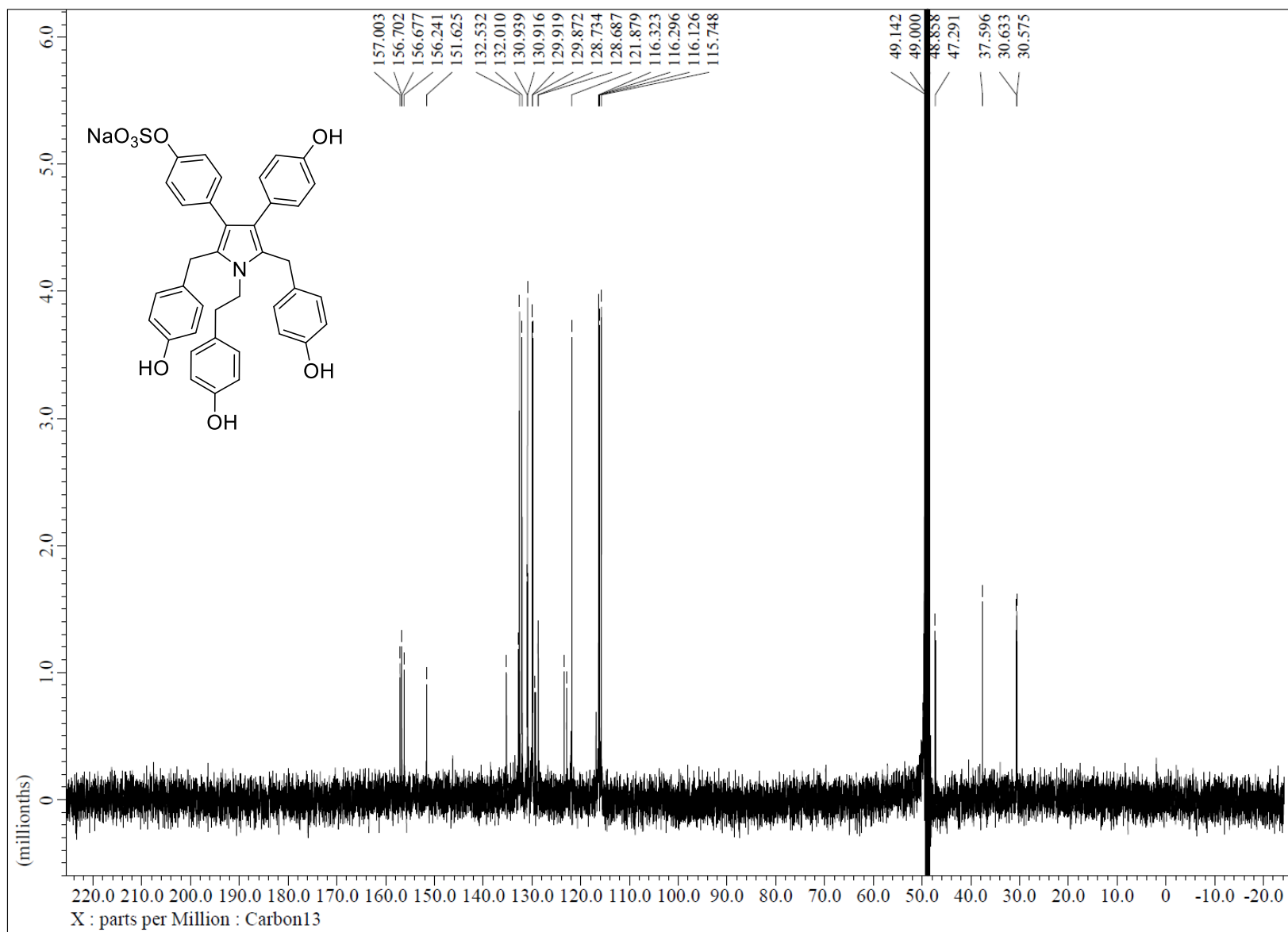


Figure S4c. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum expansion 1 of denigrin K (**4**)

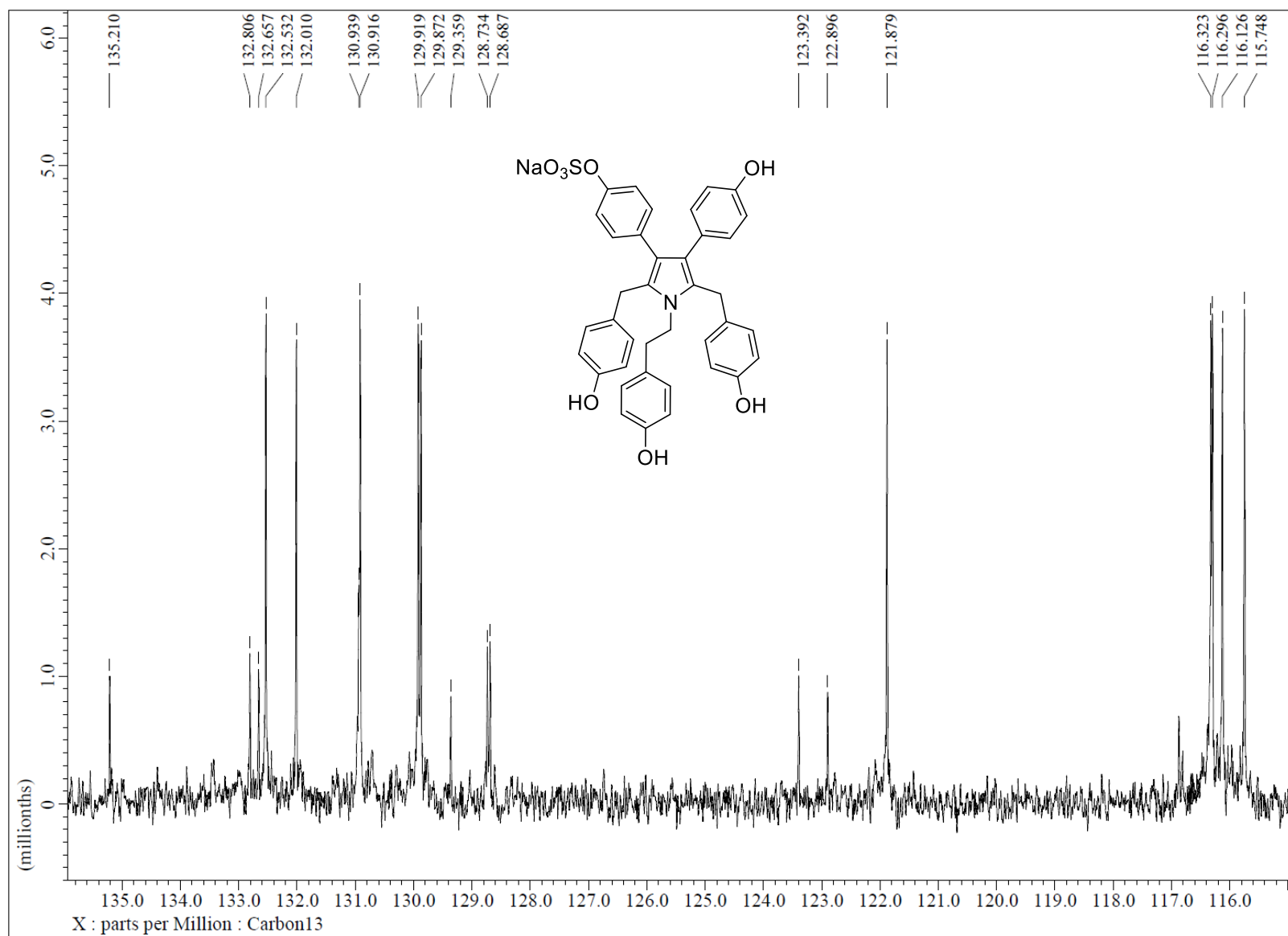


Figure S4d. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum expansion 2 of denigrin K (**4**)

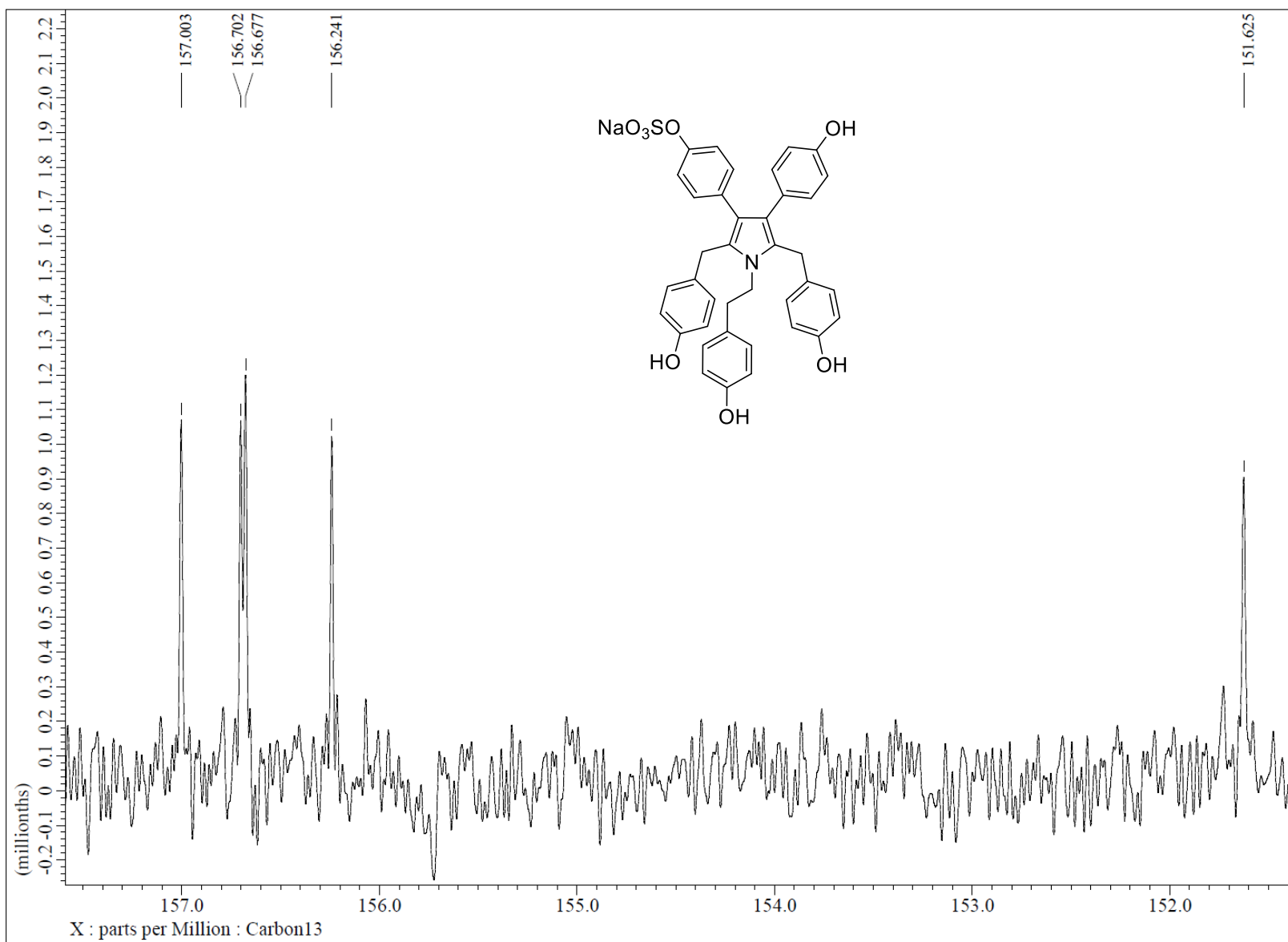


Figure S4e. COSY (methanol-*d*4) spectrum of denigrin K (**4**)

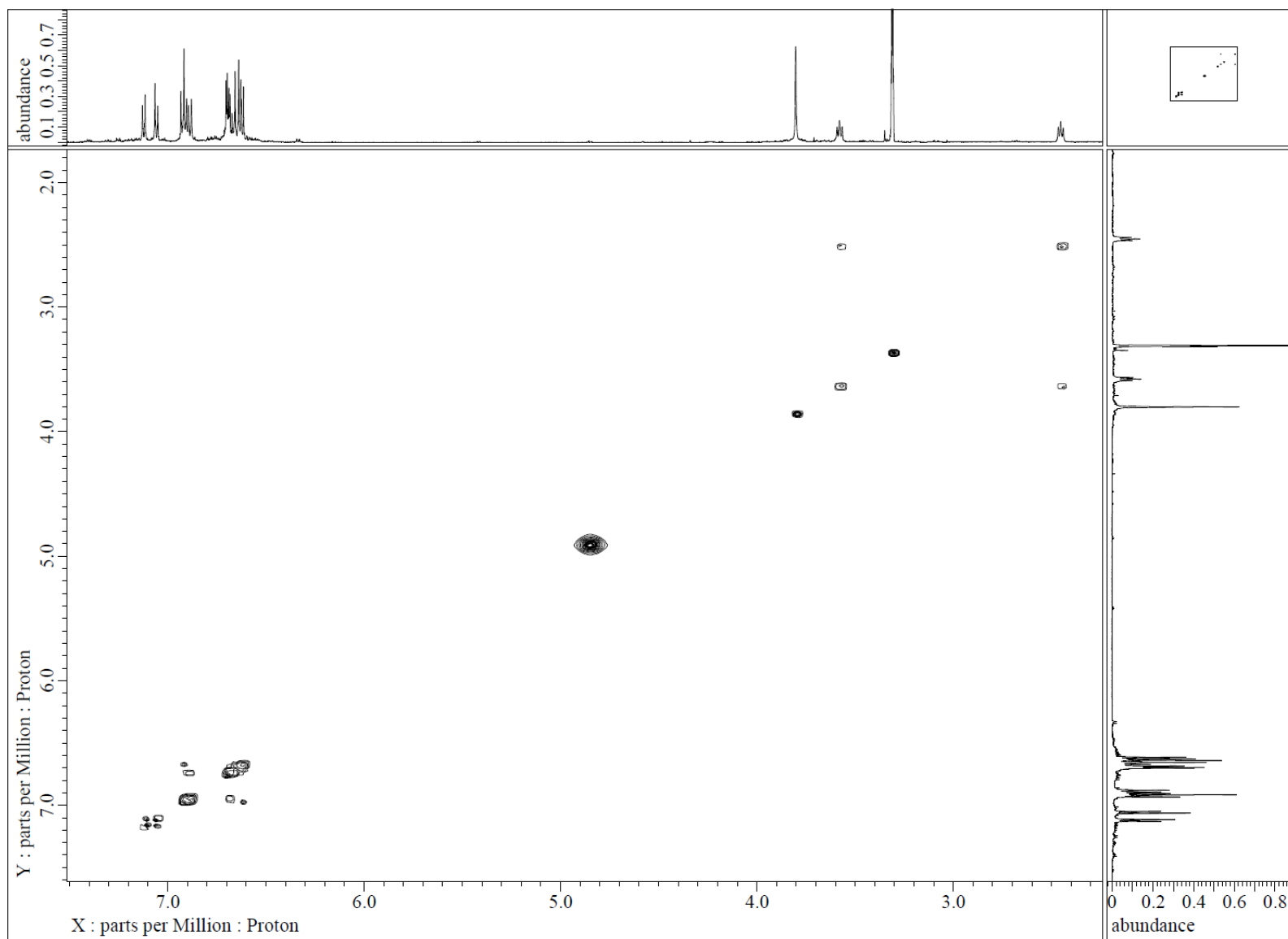


Figure S4f. gHSQC (methanol-*d*4) spectrum of denigrin K (**4**)

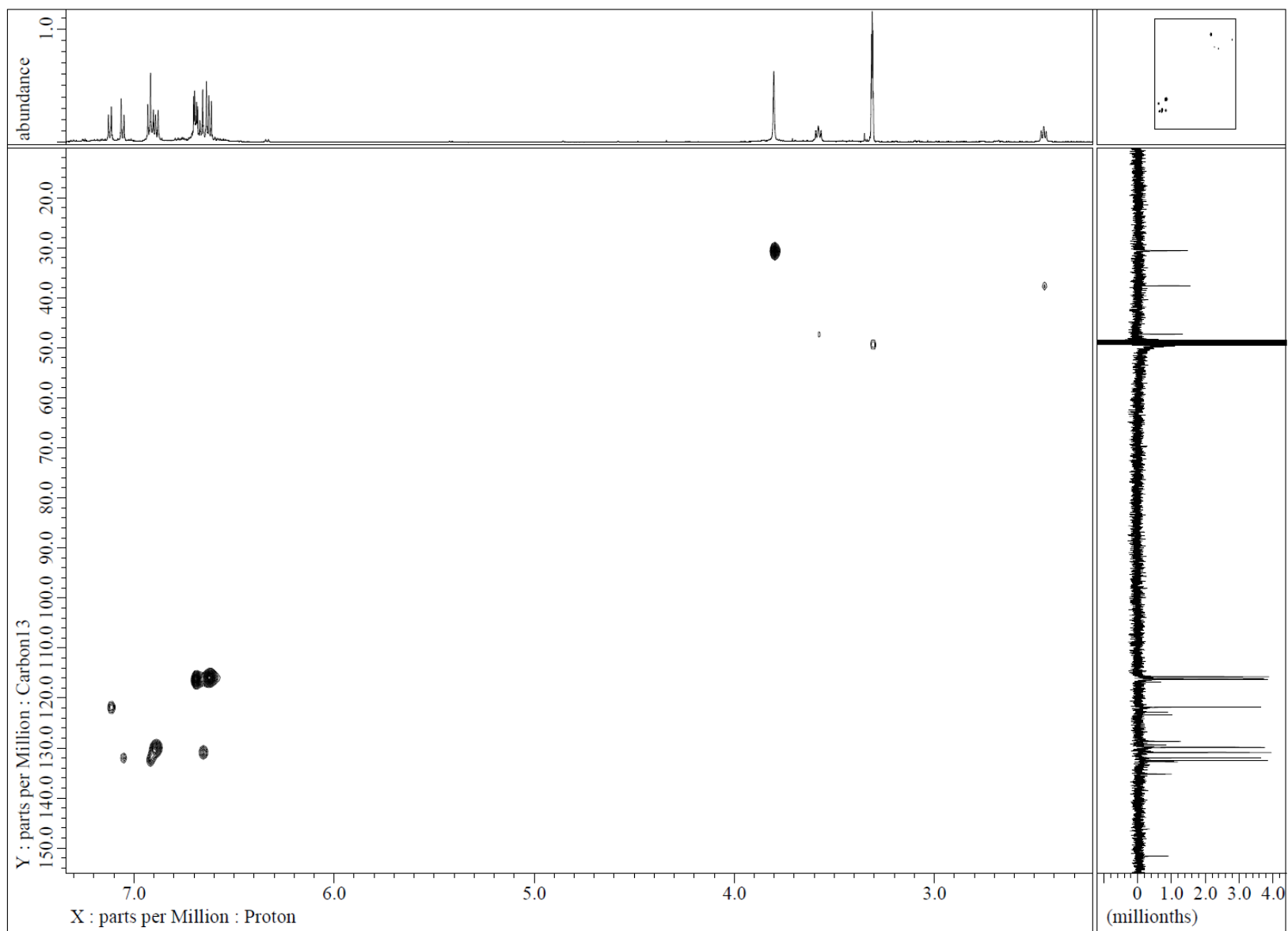


Figure S4g. gHMBC (methanol-*d*4) spectrum of denigrin K (**4**)

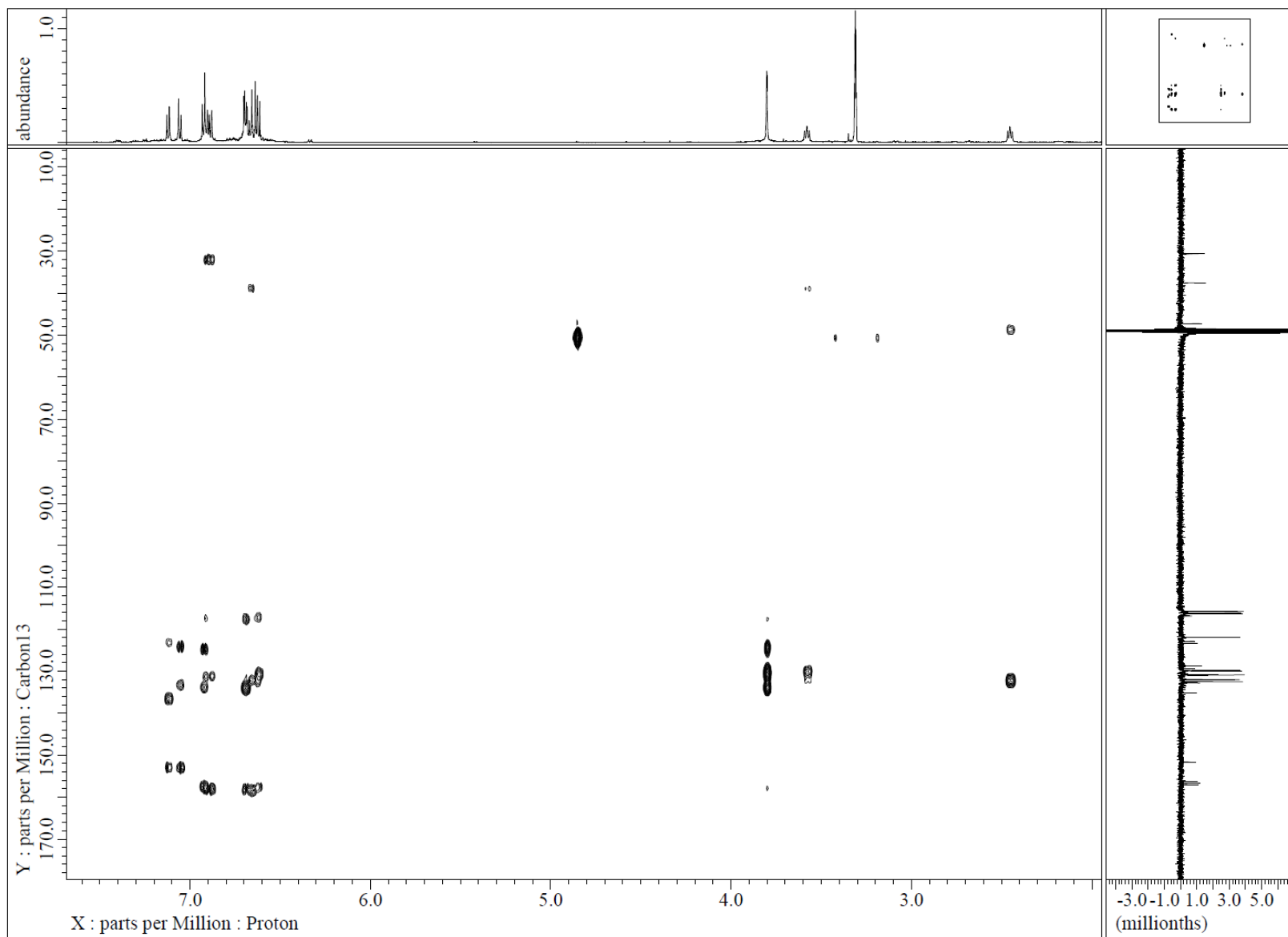


Figure S4h. gHMBC (methanol-*d*₄) spectrum expansion of denigrin K (**4**)

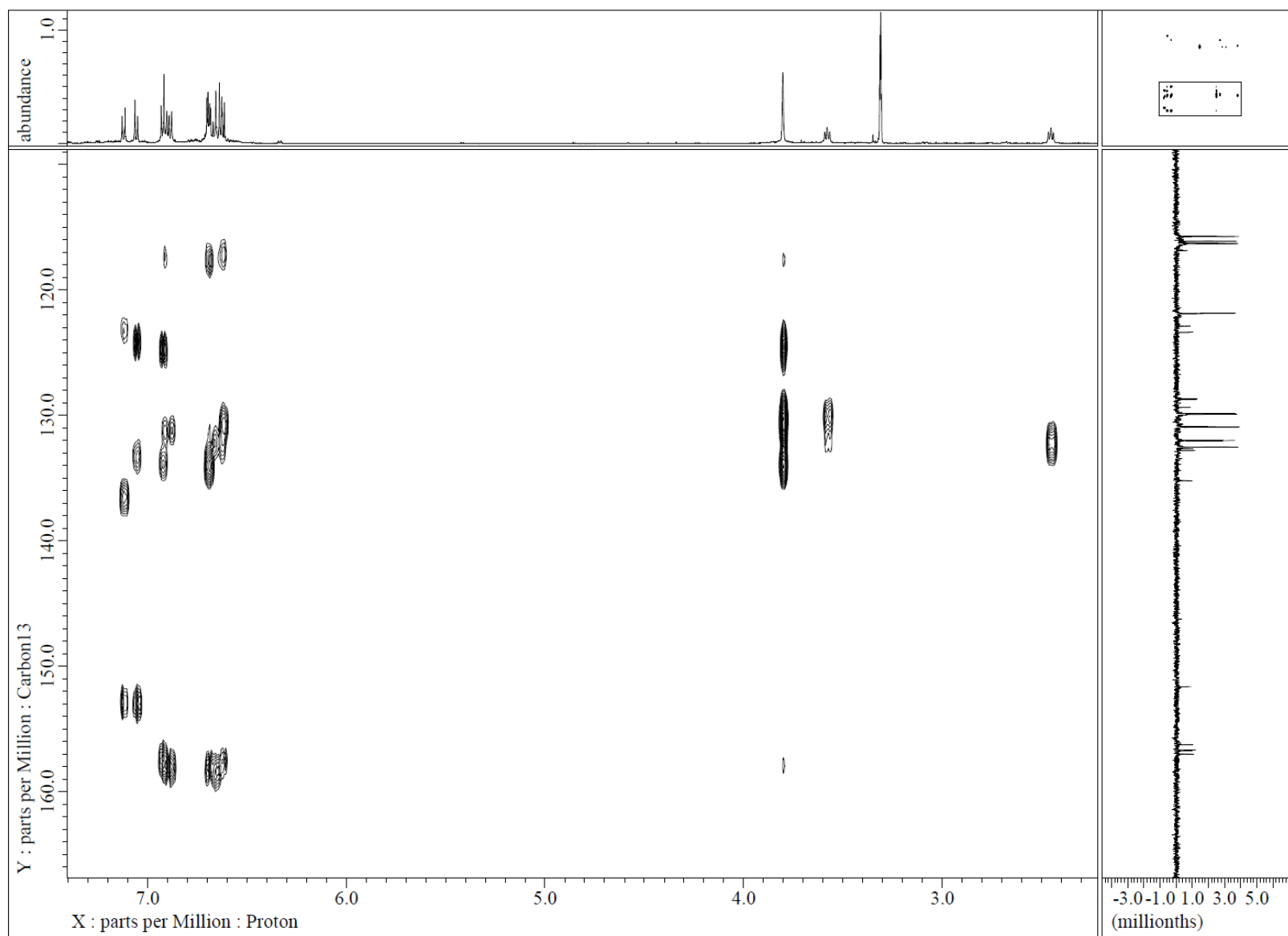


Figure S4i. HRESIMS spectrum of denigrin K (**4**) in negative ion mode

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Corrector Fill	46 V
n/a	n/a	Set Capillary Exit	-150.0 V	Set Pulsar Pull	800 V
Scan Begin	50 m/z	Set Hexapole RF	80.0 V	Set Pulsar Push	800 V
Scan End	1500 m/z	Set Skimmer 1	-50.0 V	Set Reflector	1700 V
		Set Hexapole 1	-25.0 V	Set Flight Tube	8600 V
				Set Detector TOF	2250 V

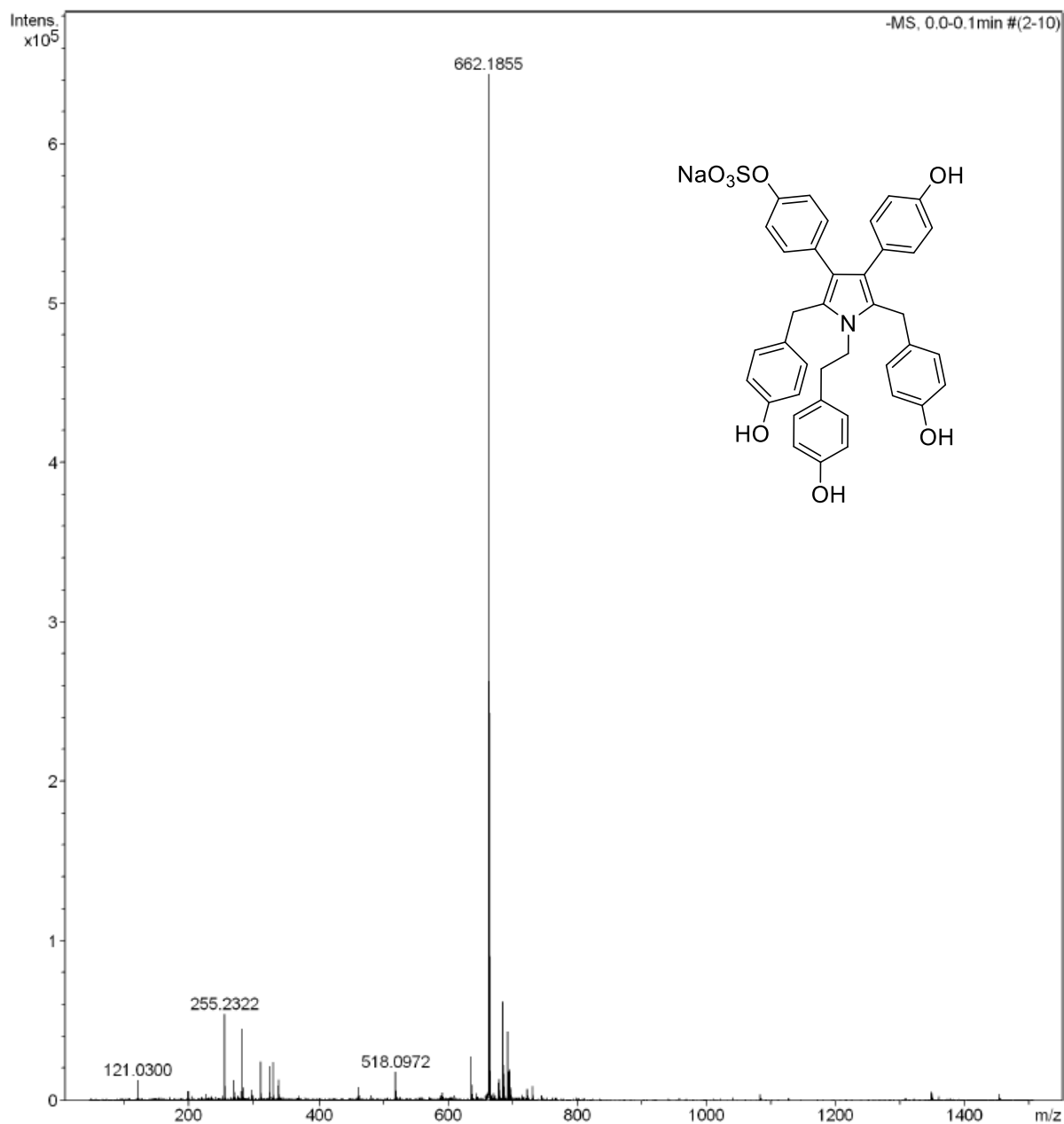


Figure S5a. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of denigrin L (5)

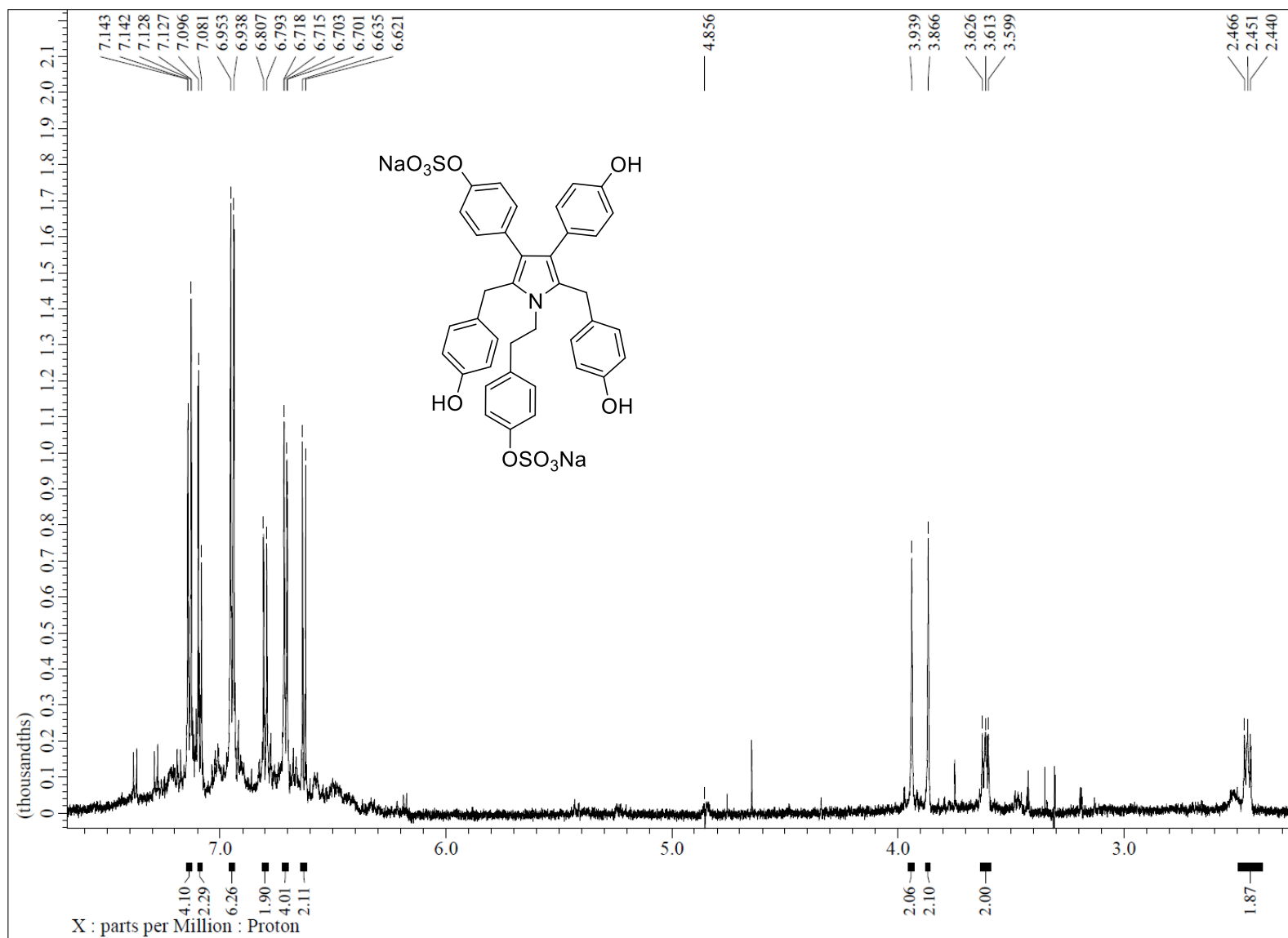


Figure S5b. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum of denigrin L (5)

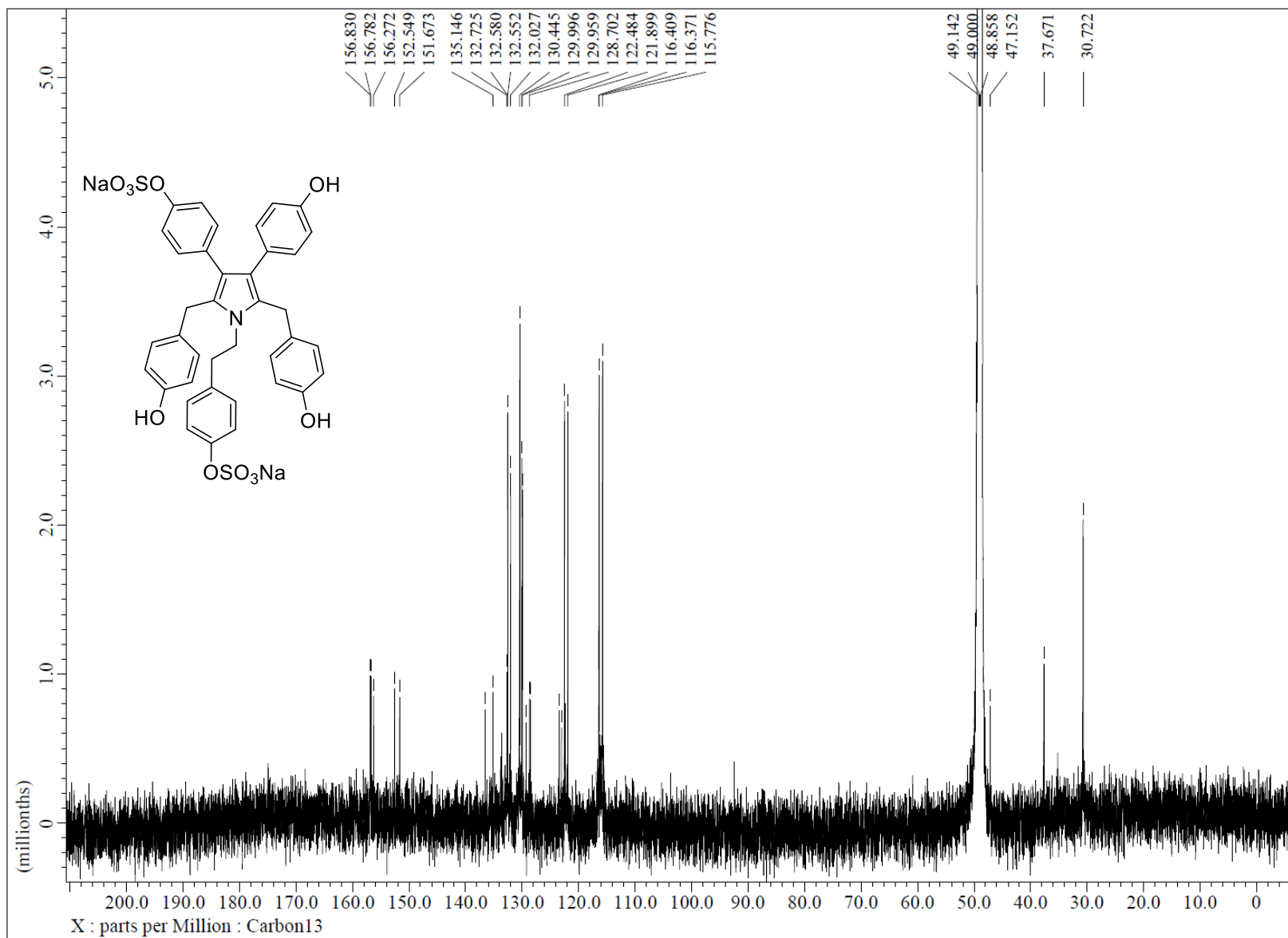


Figure S5c. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum expansion of denigrin L (**5**)

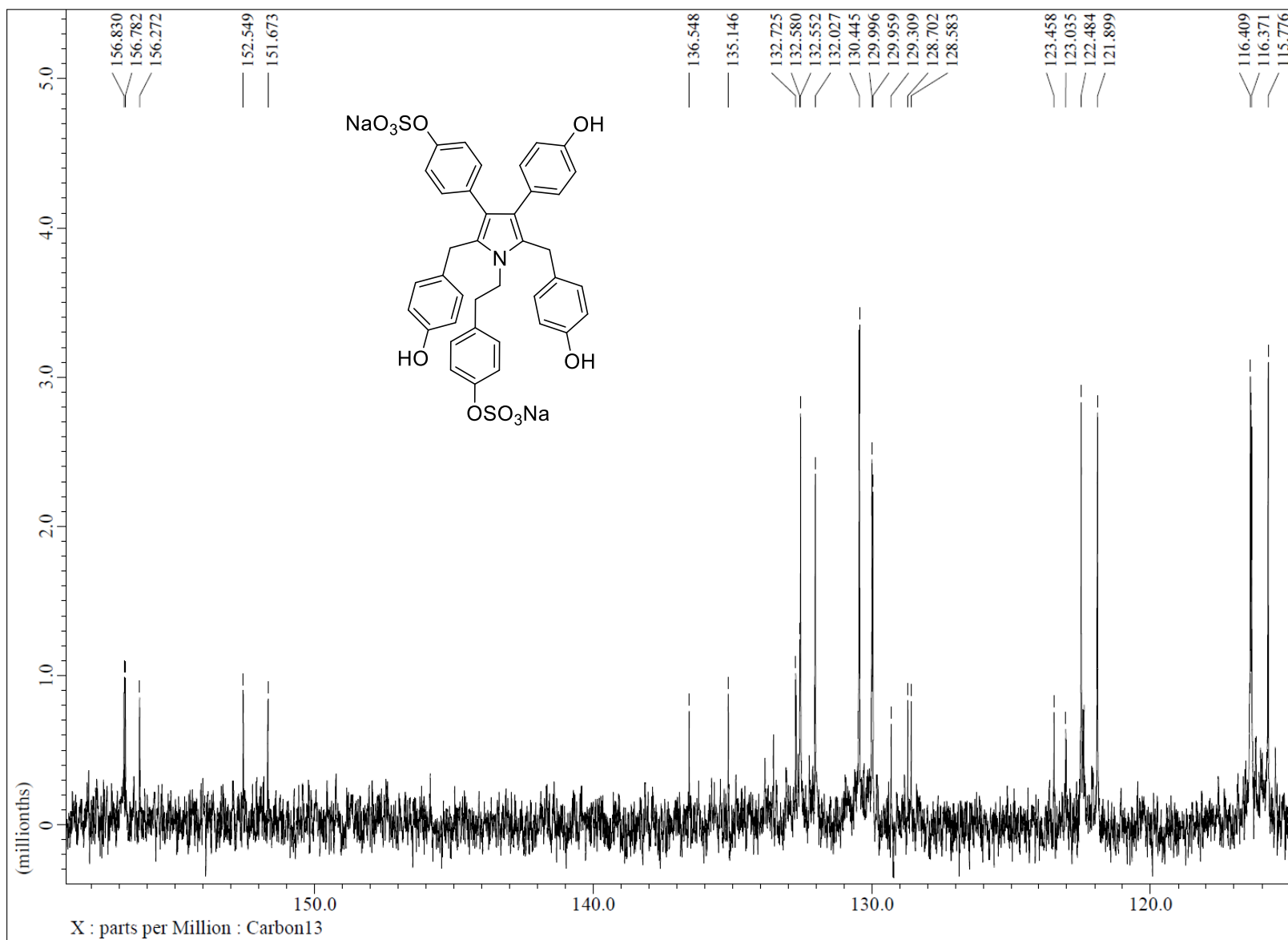


Figure S5d. COSY (methanol-*d*₄) spectrum of denigrin L (5)

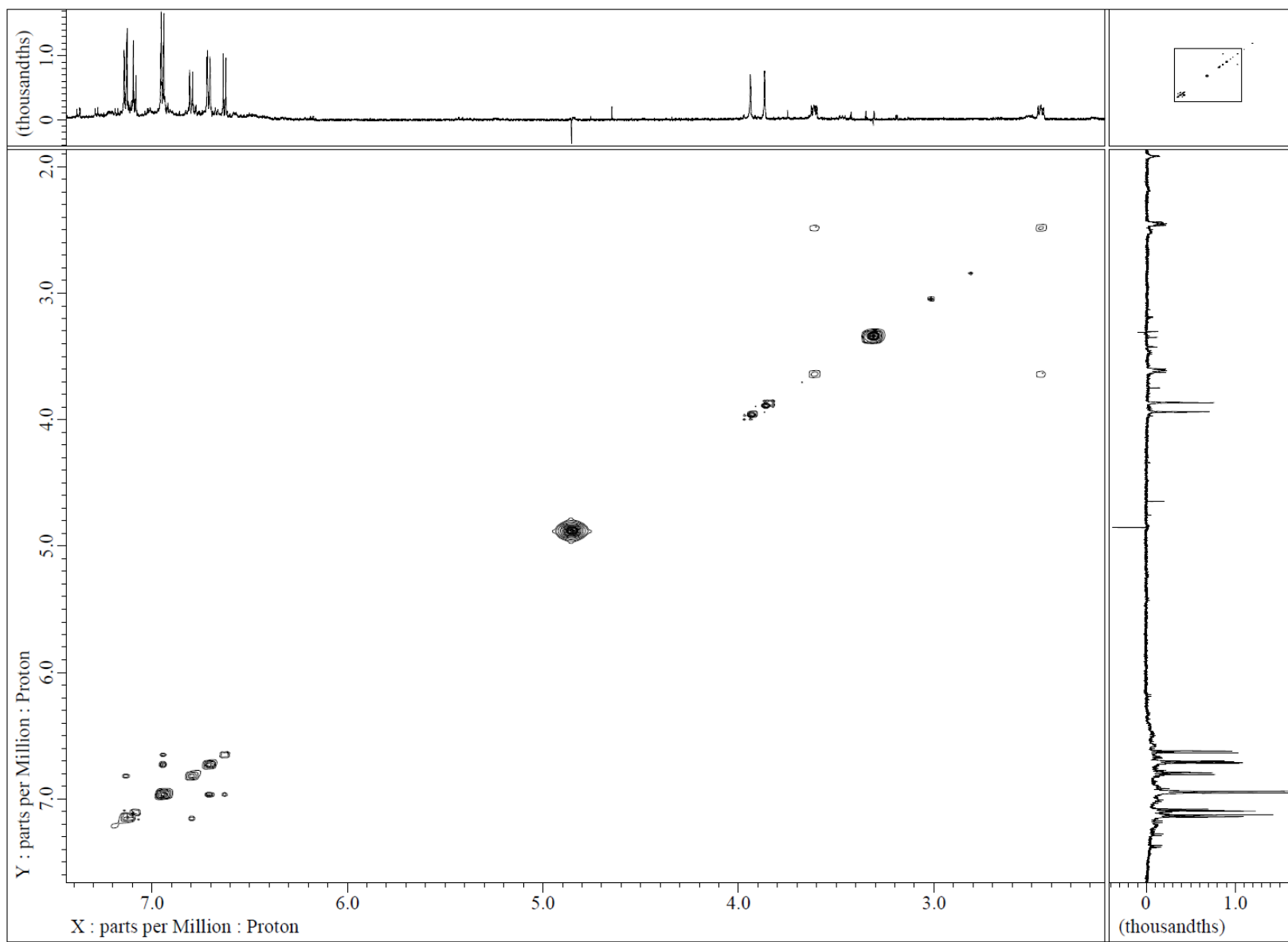


Figure S5e. gHSQC (methanol-*d*₄) spectrum of denigrin L (**5**)

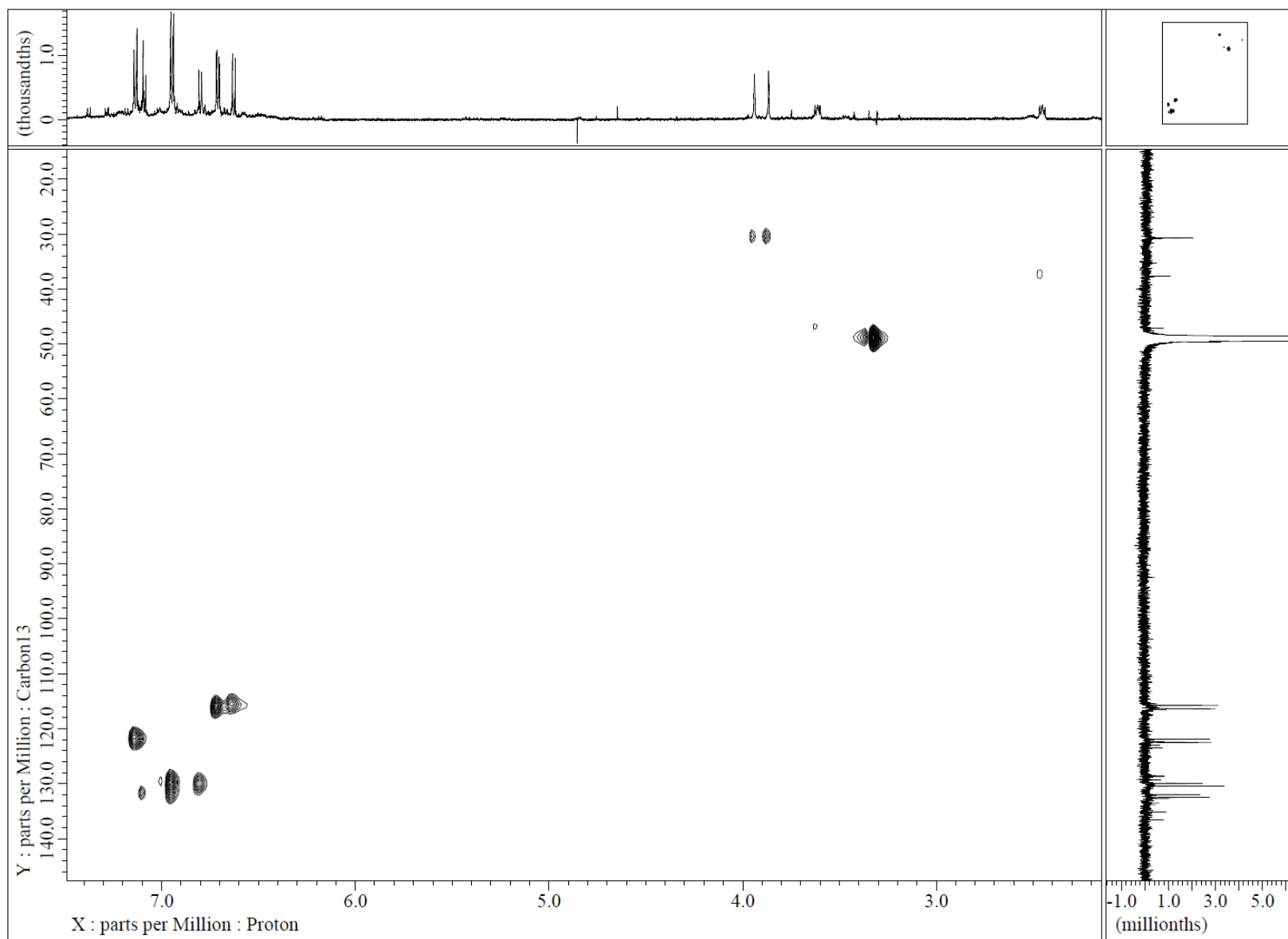


Figure S5f. gHMBC (methanol-*d*4) spectrum of denigrin L (**5**)

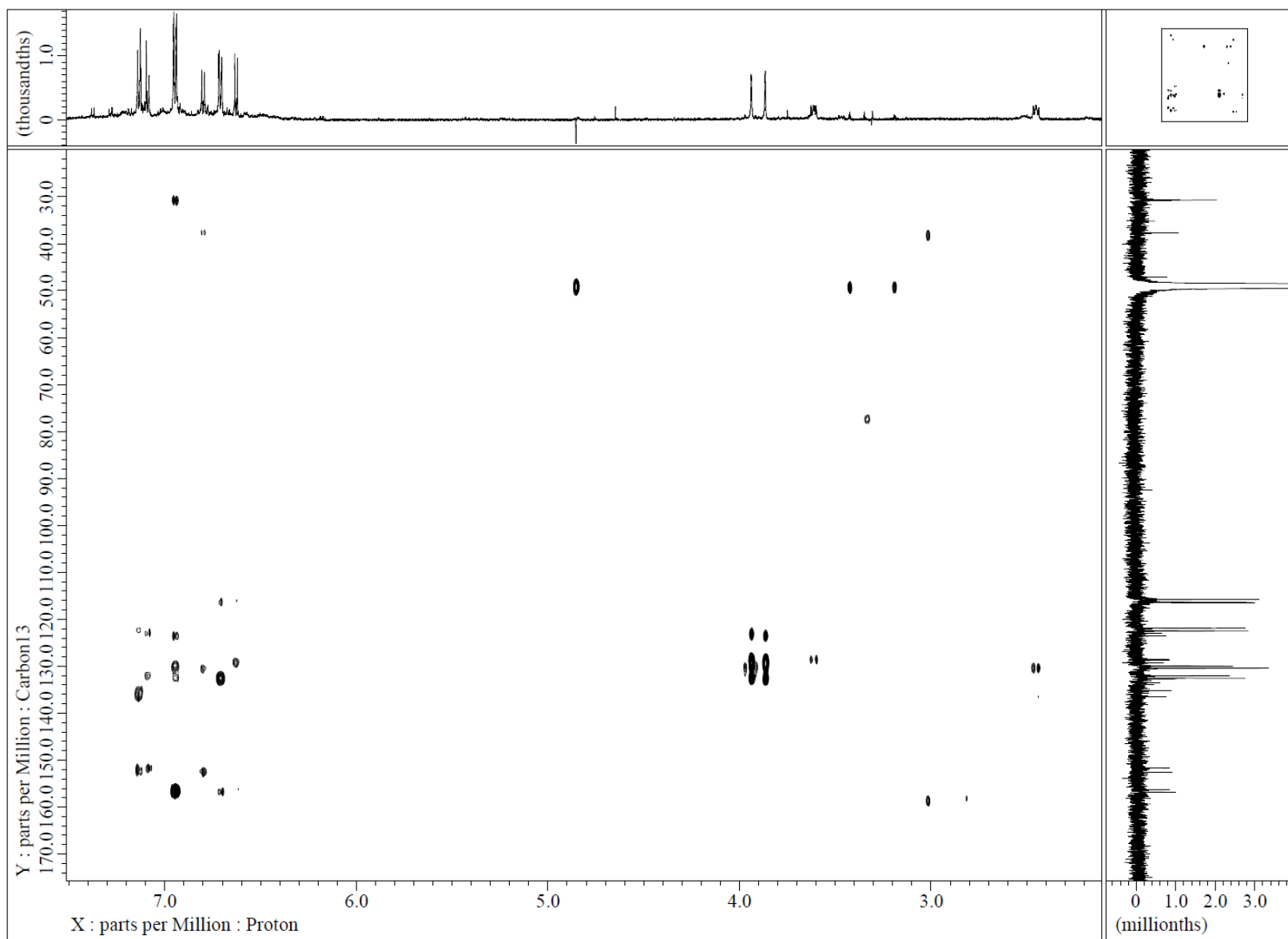


Figure S5g. gHMBC (methanol-*d*4) spectrum expansion of denigrin L (**5**)

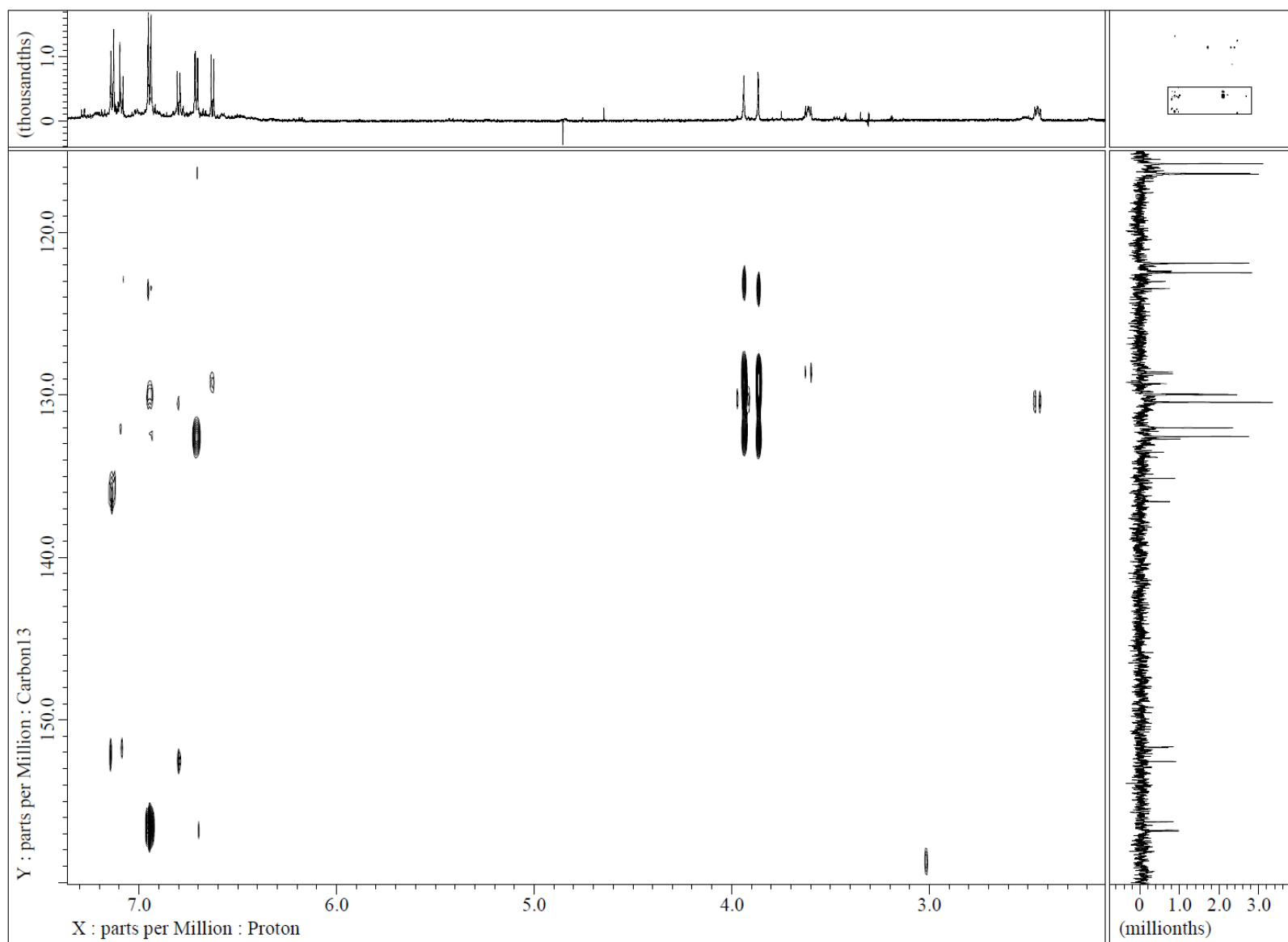


Figure S5h. HRESIMS spectrum of denigrin L (**5**) in negative ion mode

Acquisition Parameter

Source Type ESI
n/a n/a
Scan Begin 50 m/z
Scan End 1500 m/z

Ion Polarity Negative
Set Capillary Exit -150.0 V
Set Hexapole RF 80.0 V
Set Skimmer 1 -50.0 V
Set Hexapole 1 -25.0 V

Set Corrector Fill 46 V
Set Pulsar Pull 800 V
Set Pulsar Push 800 V
Set Reflector 1700 V
Set Flight Tube 8600 V
Set Detector TOF 2250 V

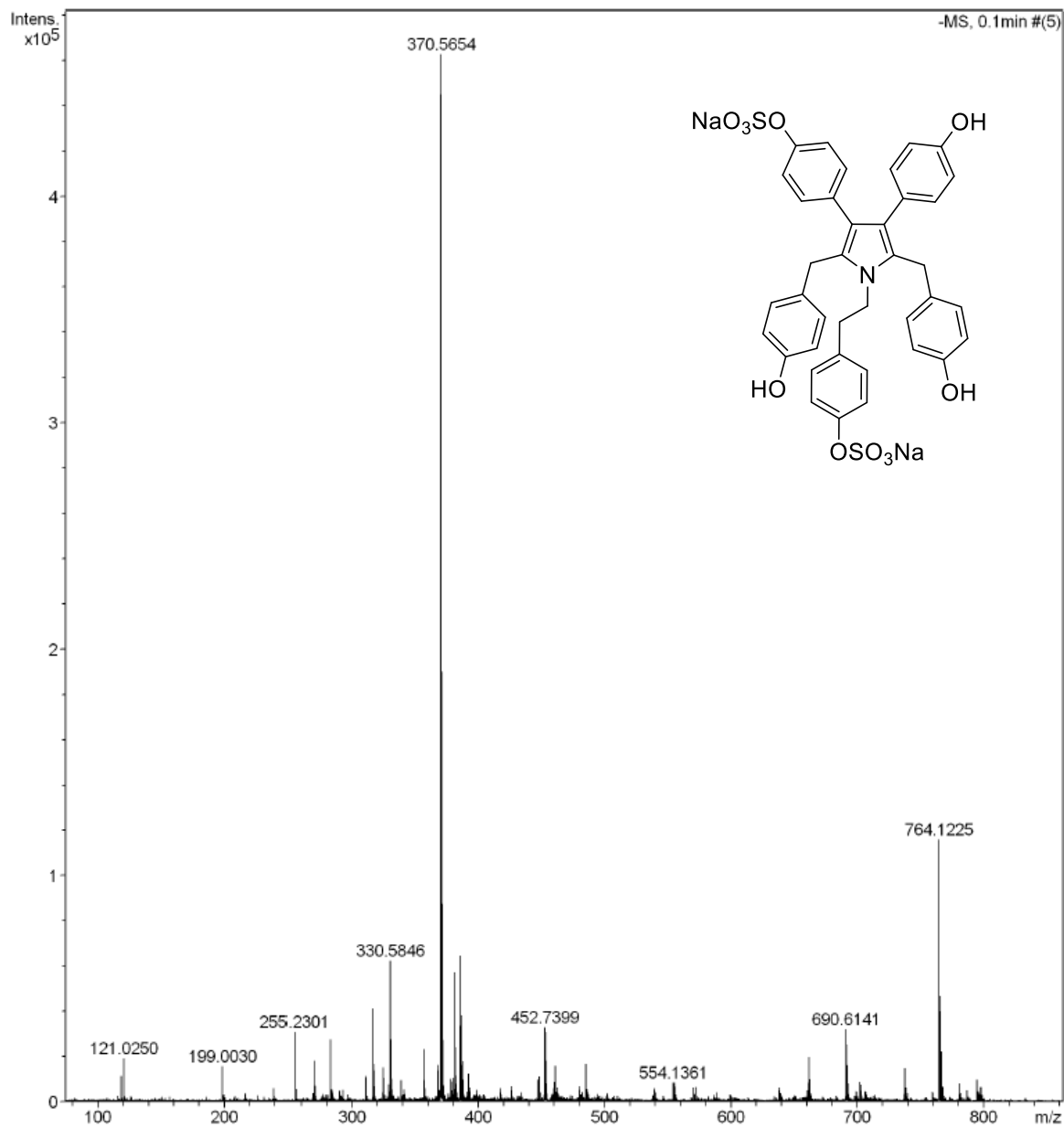


Figure S6a. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of denigrin E (**6**)

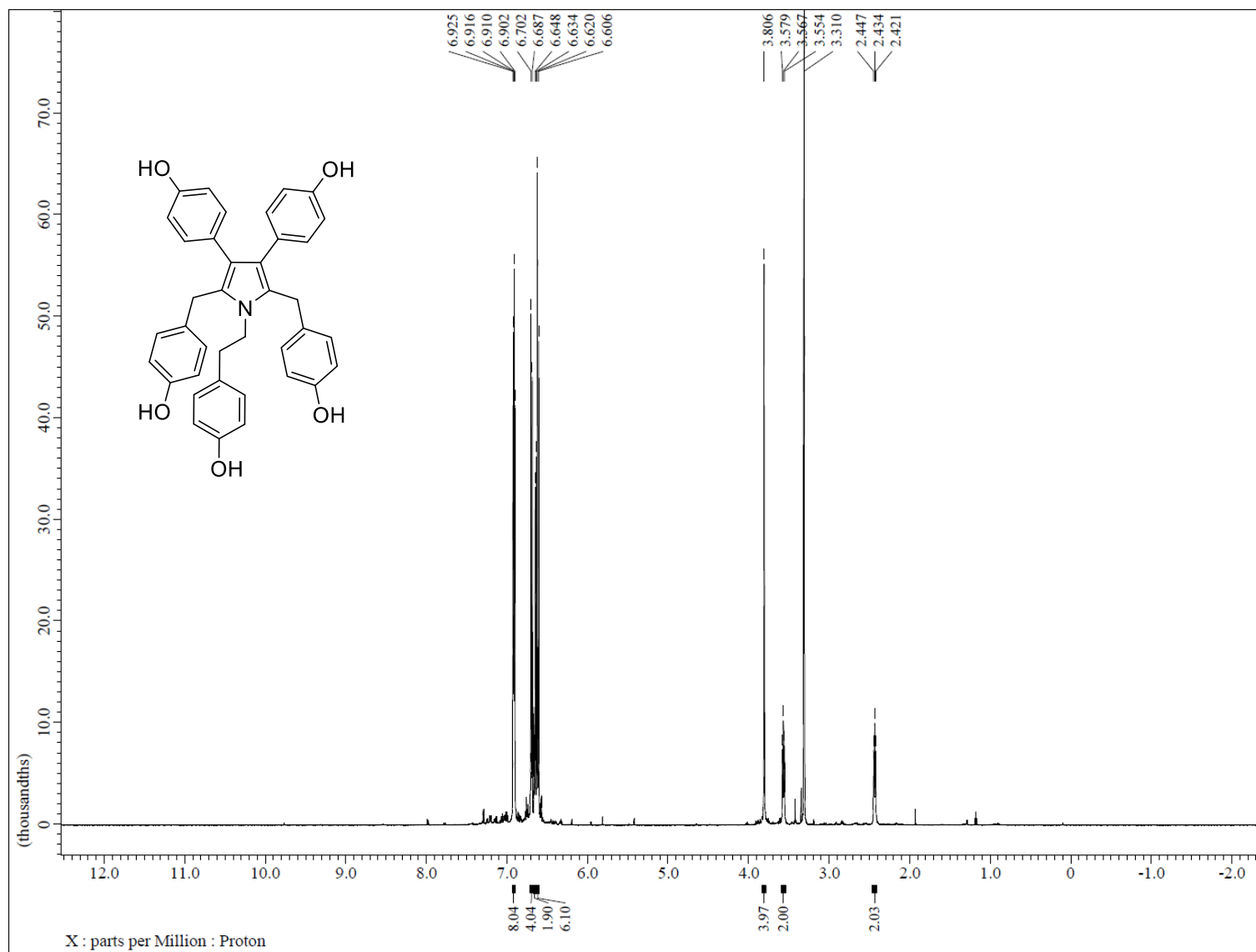


Figure S6b. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum of denigrin E (6)

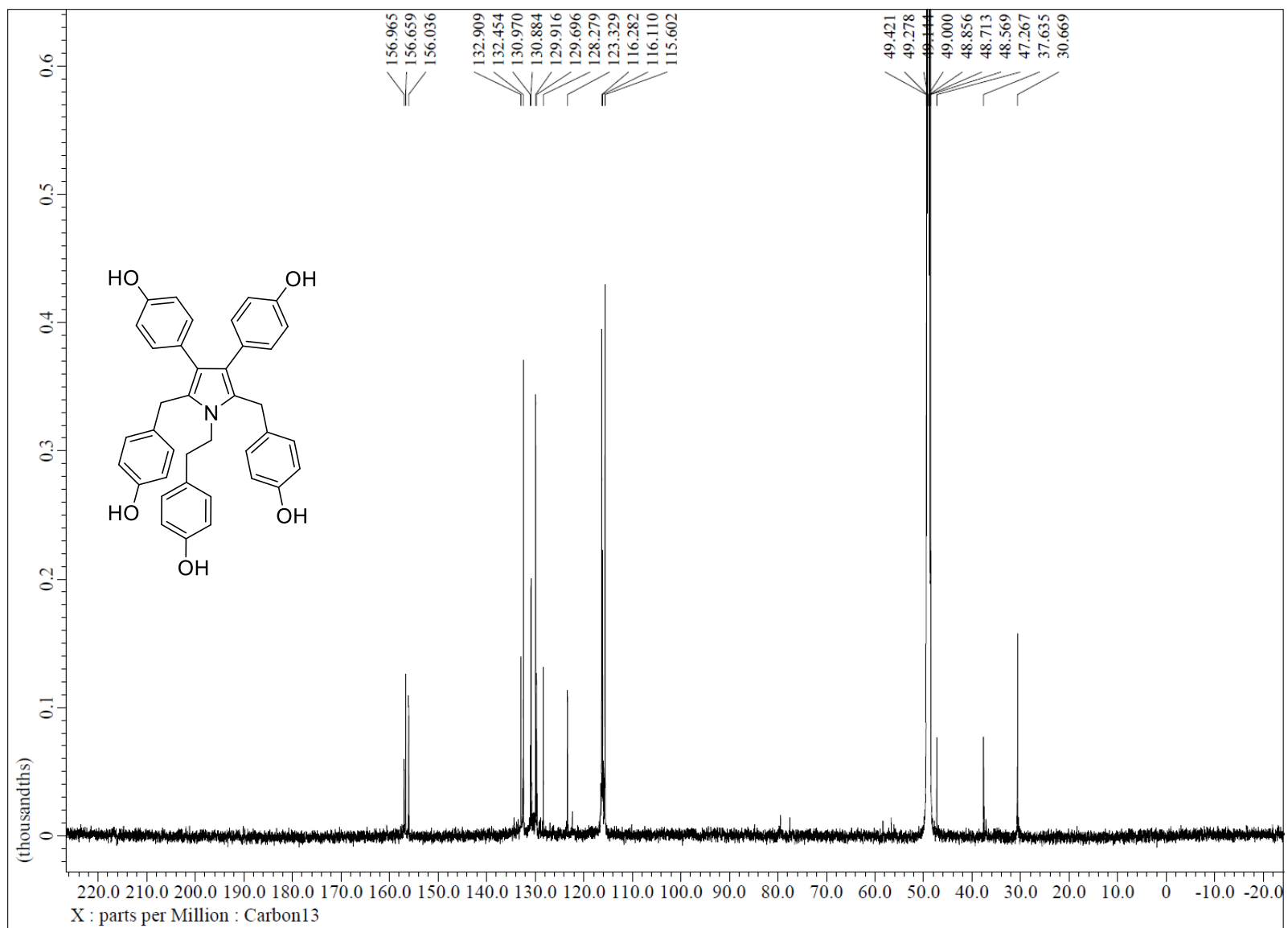


Figure S6c. ^{13}C NMR (methanol- d_4 , 150 MHz) spectrum expansion of denigrin E (**6**)

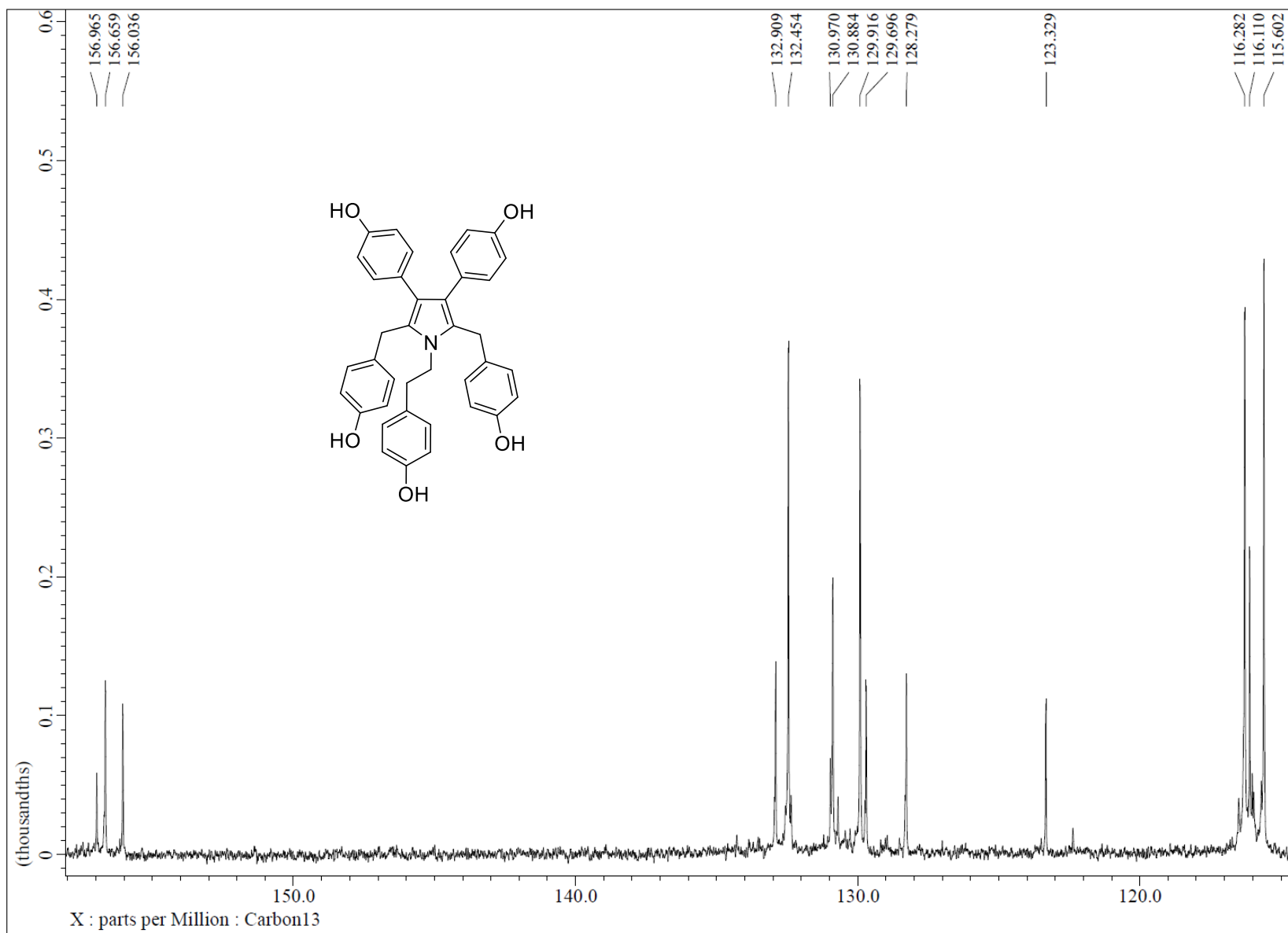


Figure S7. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of dictyodendrin C

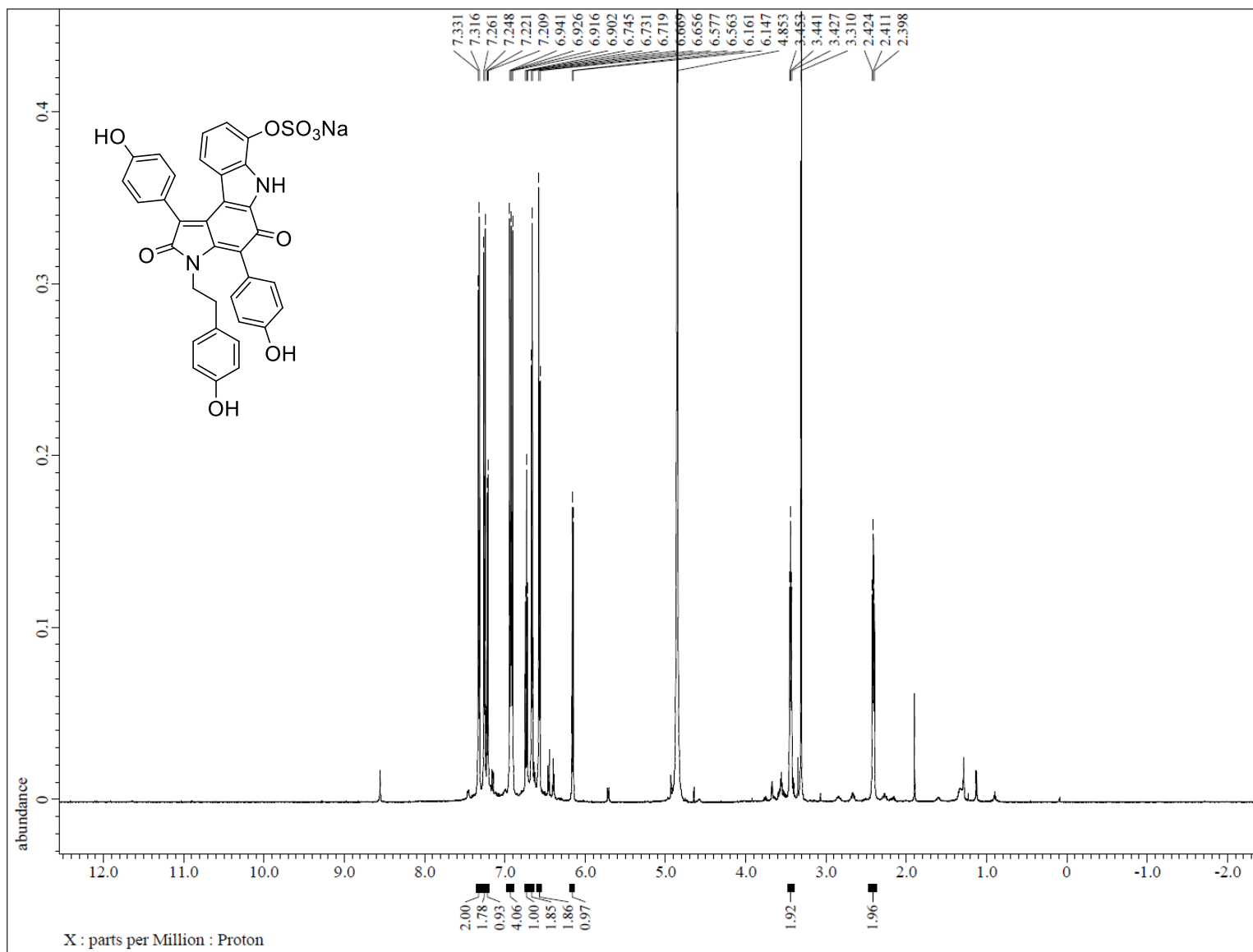


Figure S8. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of dictyodendrin D

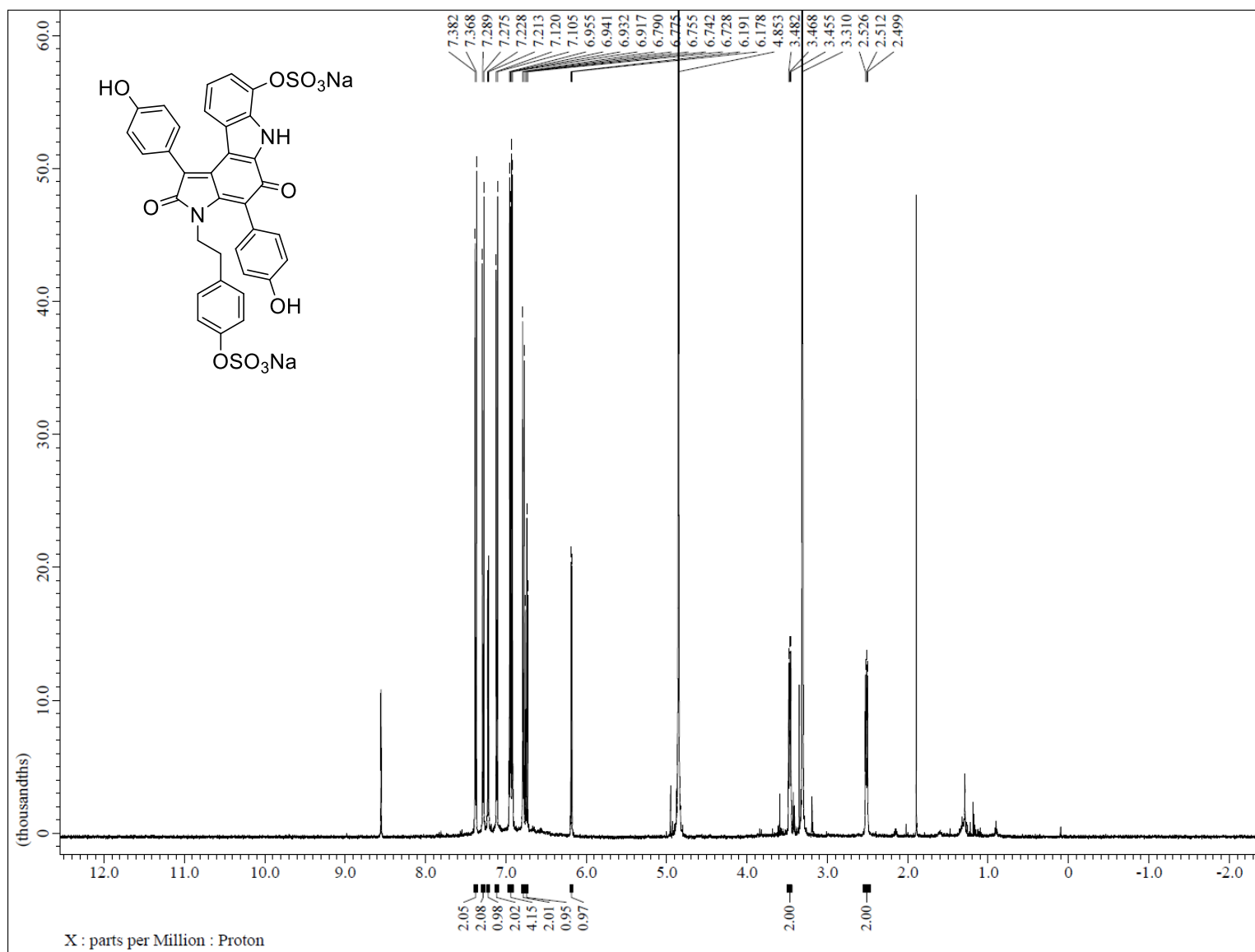


Figure S9. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of dictyodendrin F

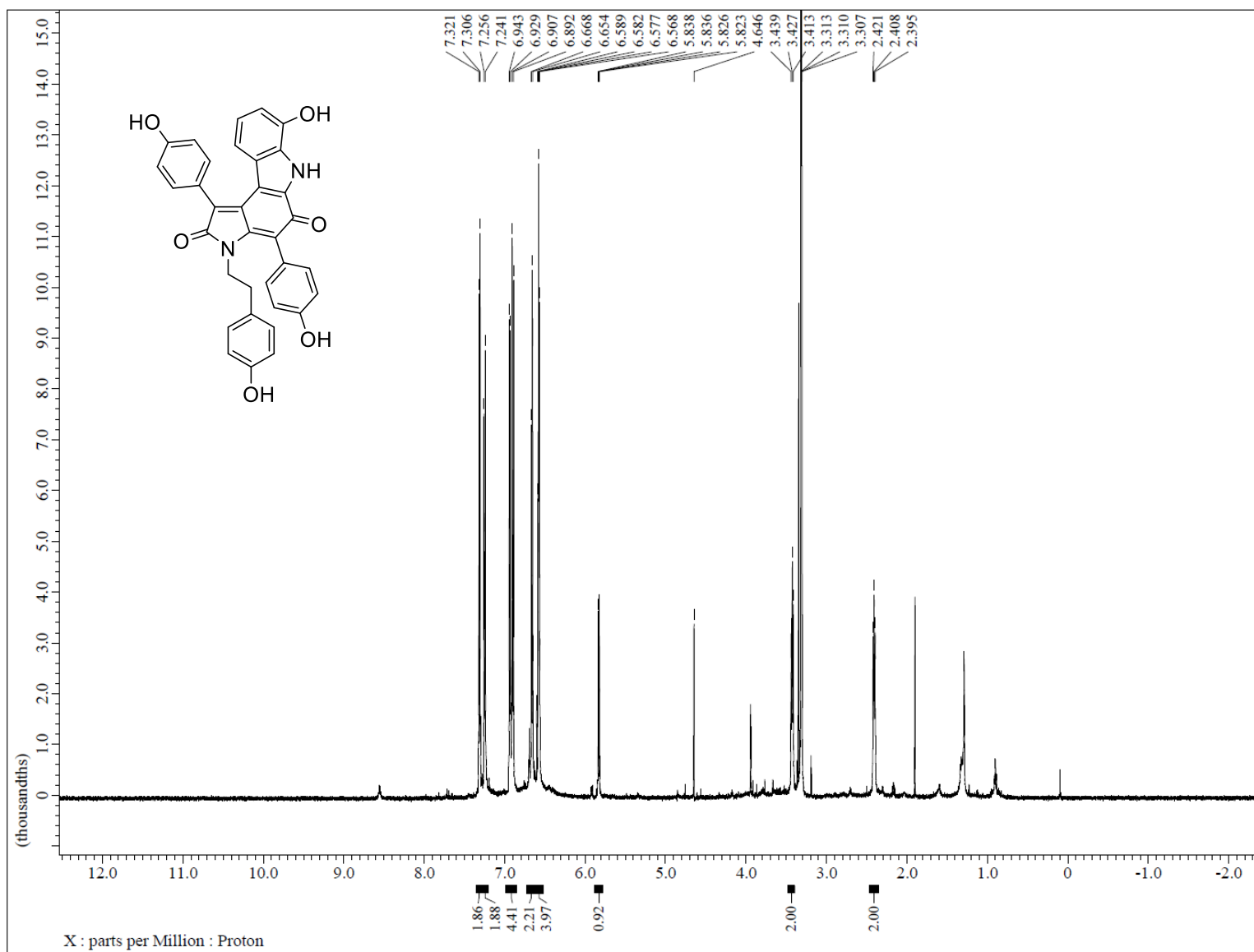


Figure S10. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of dactypyrrole A

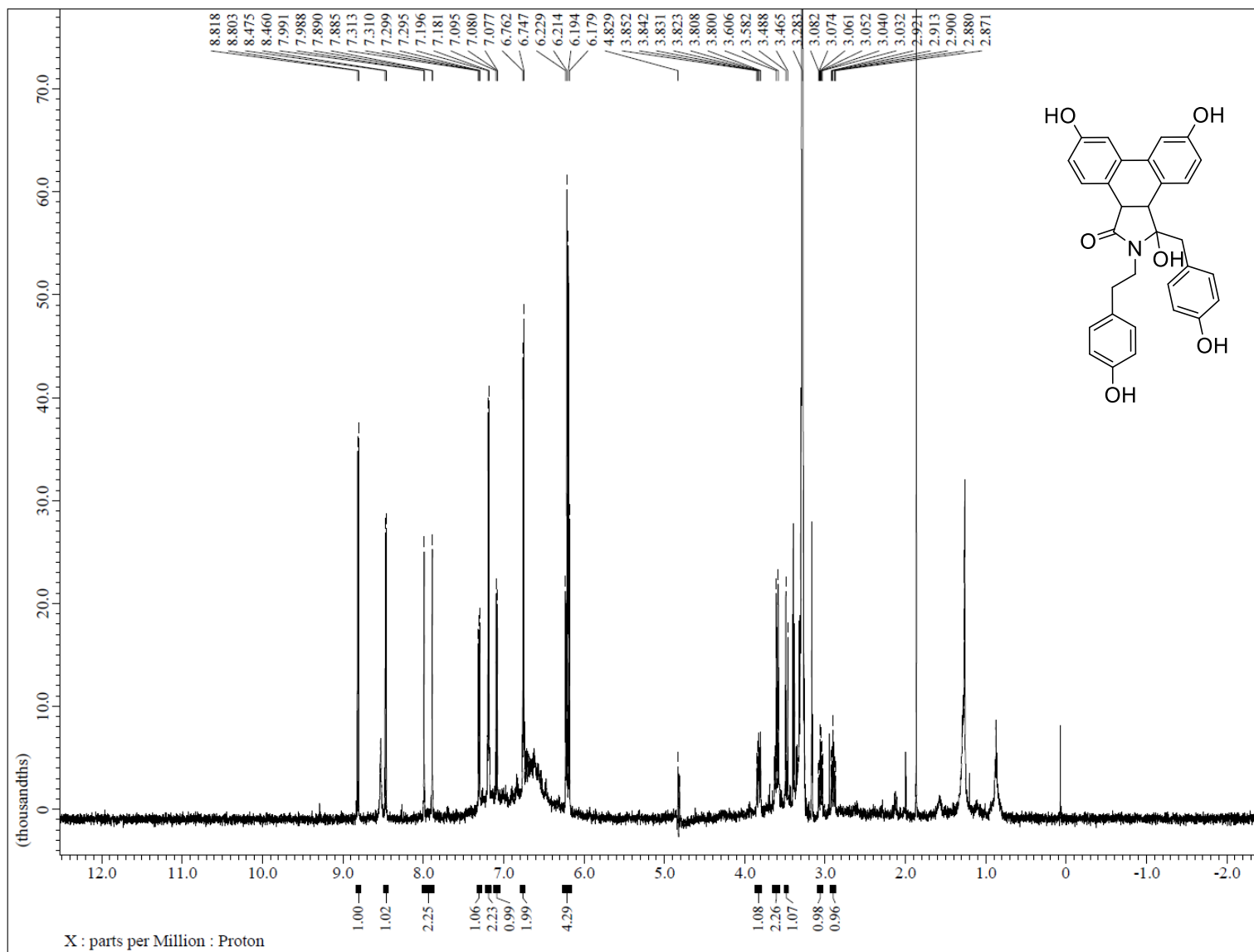


Figure S11. ^1H NMR (methanol- d_4 , 600 MHz) spectrum of lamellarin O1

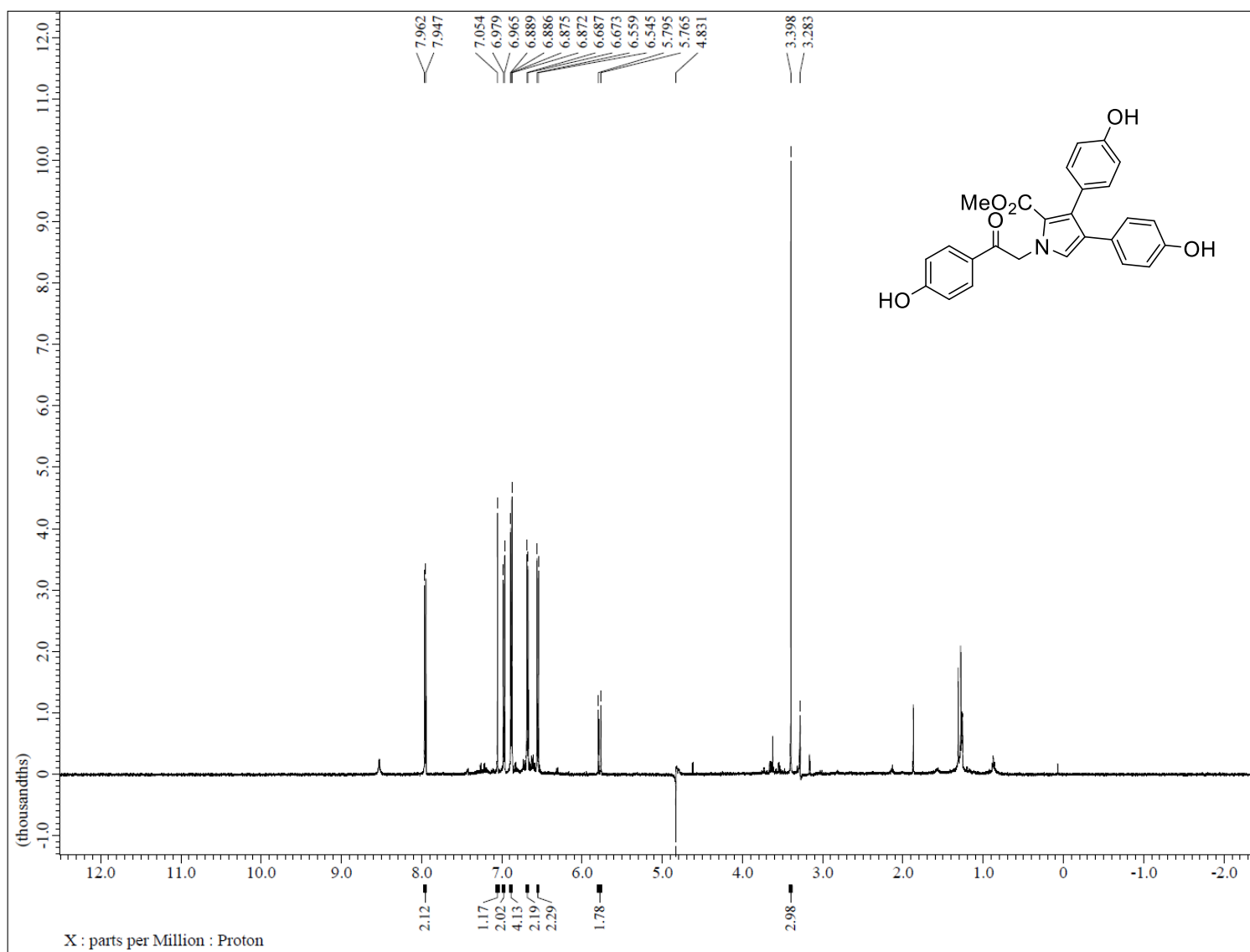


Table S6. Cytotoxicity assay - IC₅₀ values for compounds **1-6**, dictyodendrin C, D, and F, dactylpyrrole A and lamellarin O1

Compound	IC ₅₀ (μM)
1	> 100
2	78
3	> 100
4	> 100
5	> 100
6	> 100
Dictyodendrin C	> 100
Dictyodendrin D	60
Dictyodendrin F	48
Dactylpyrrole A	> 100
Lamellarin O1	> 100