

S1 Appendix

Analytical Data for the Chimaphilin Family of Metabolites

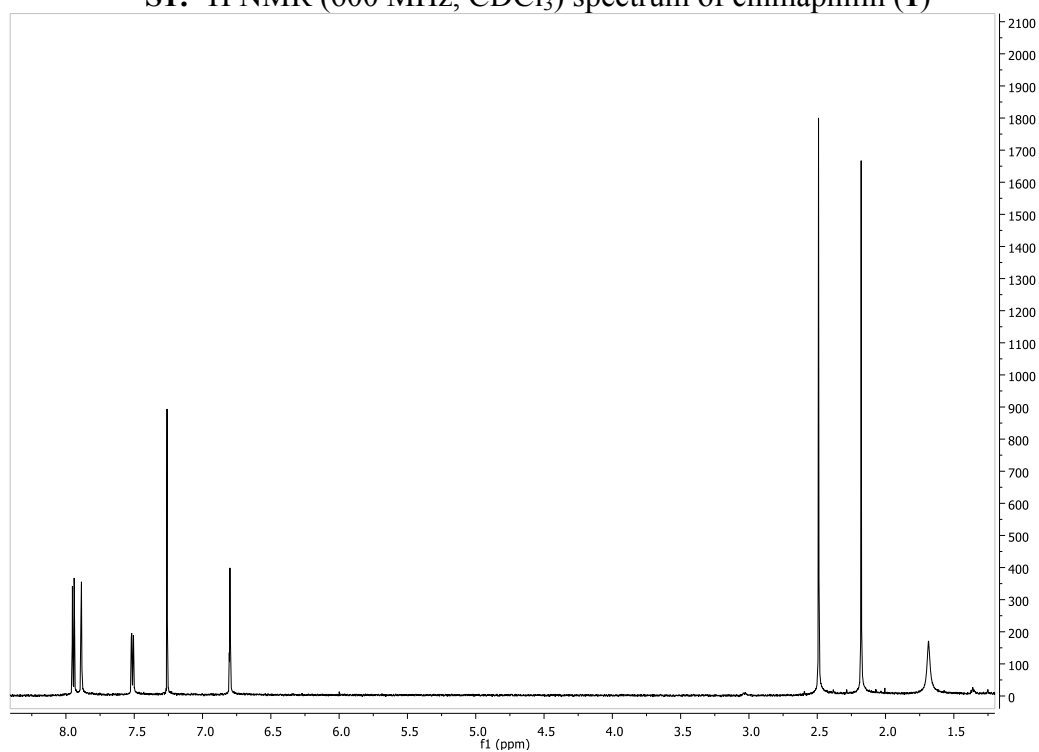
NMR Spectroscopic Data:

- Figure S1** ^1H NMR (600 MHz, CDCl_3) spectrum of chimaphilin (**1**)
Figure S2 ^{13}C NMR (150 MHz, CDCl_3) spectrum for chimaphilin (**1**)
Figure S3 ^1H NMR (600 MHz, CDCl_3) spectrum of 3-hydroxy-chimaphilin (**2**)
Figure S4 ^{13}C NMR (150 MHz, CDCl_3) spectrum for 3-hydroxy-chimaphilin (**2**)
Figure S5 ^1H NMR (600 MHz, CDCl_3) spectrum of 3-chloro-chimaphilin (**3**)
Figure S6 ^{13}C NMR (125 MHz, CDCl_3) spectrum for 3-chloro-chimaphilin (**3**)
Figure S7 gHSQC (^1H 500 MHz, CDCl_3) spectrum for 3-chloro-chimaphilin (**3**)
Figure S8 gCOSY (^1H 500 MHz, CDCl_3) spectrum for 3-chloro-chimaphilin (**3**)
Figure S9 gHMBC (^1H 500 MHz, CDCl_3) spectrum for 3-chloro-chimaphilin (**3**)
Table S1 ^1H and ^{13}C NMR data table for 3-chloro-chimaphilin (**3**) in CDCl_3
Table S2 ^1H and ^{13}C NMR assignments for chimaphilin (**1**), 3-hydroxy-chimaphilin (**2**), and 3-chloro-chimaphilin (**3**) in CDCl_3

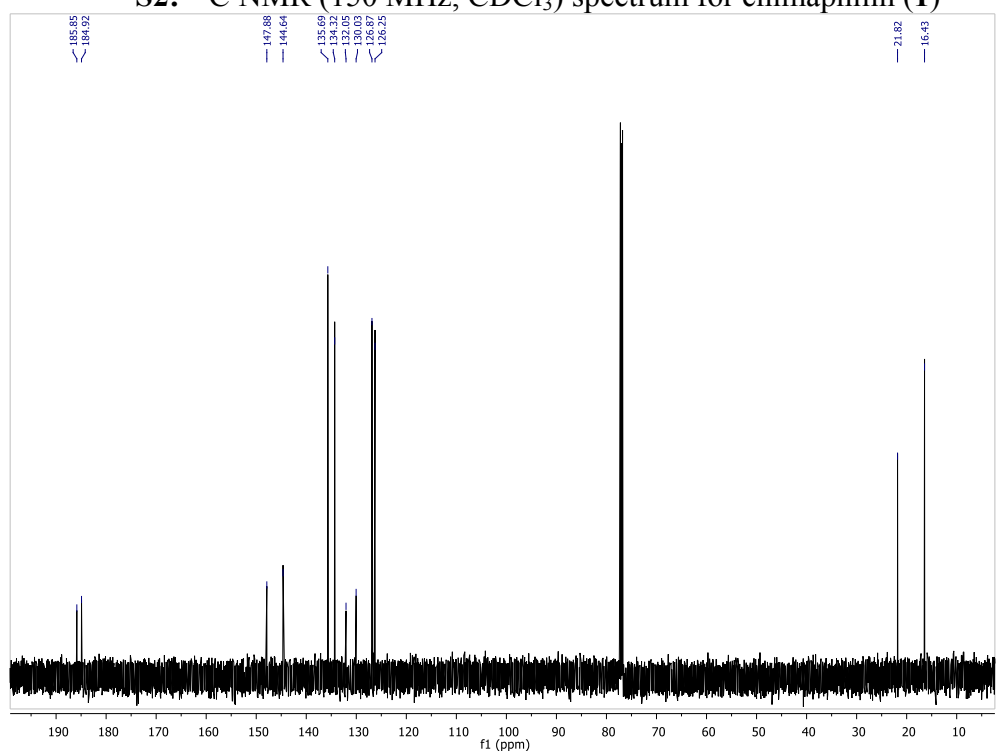
HRESIMS Data:

- Figure S10** HRESIMS spectrum for chimaphilin (**1**)
Figure S11 HRESIMS spectrum for 3-hydroxy-chimaphilin (**2**)
Figure S12 HRESIMS spectrum for 3-chloro-chimaphilin (**3**)

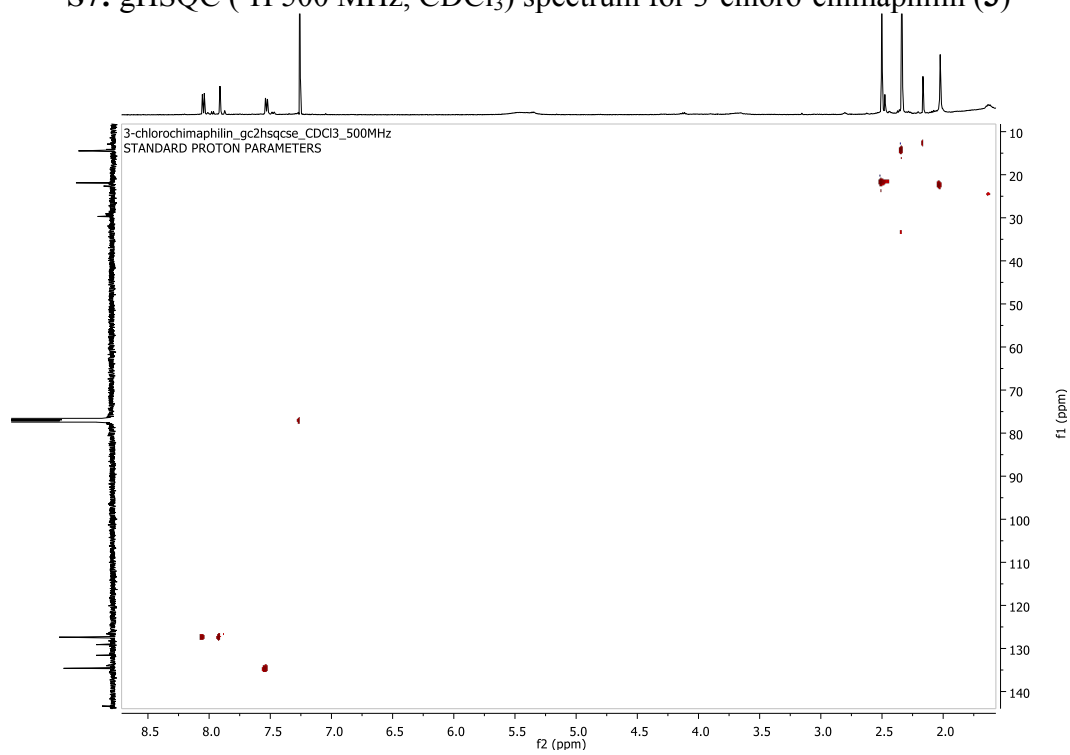
S1: ^1H NMR (600 MHz, CDCl_3) spectrum of chimaphilin (1)



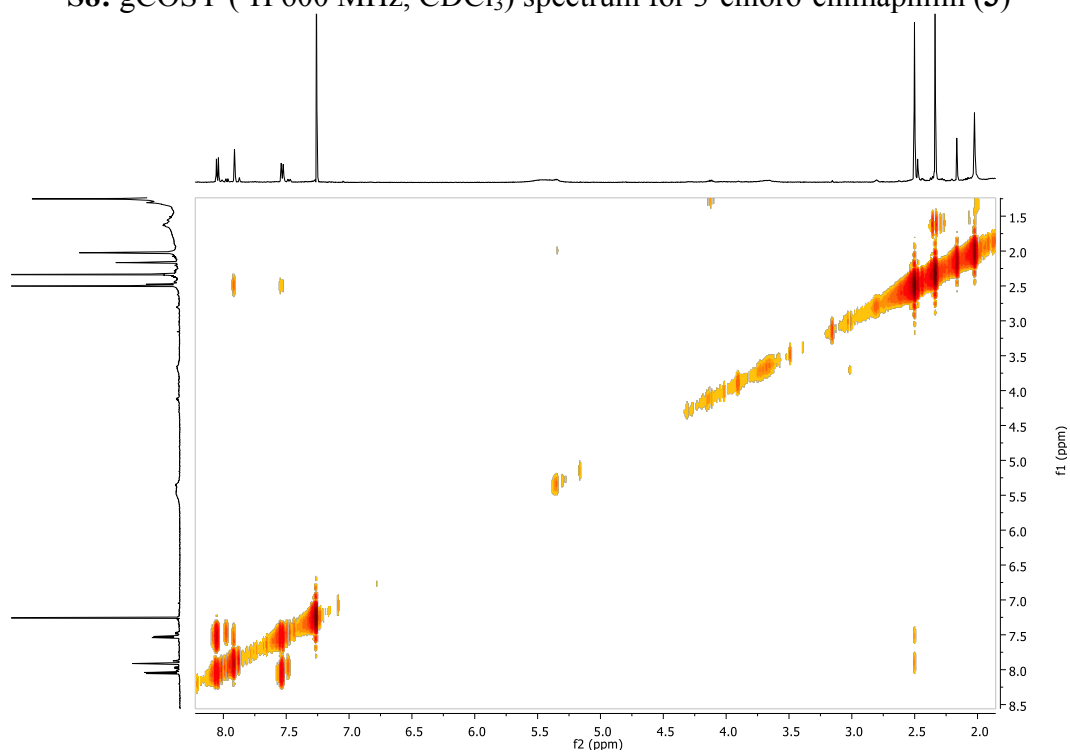
S2: ^{13}C NMR (150 MHz, CDCl_3) spectrum for chimaphilin (1)



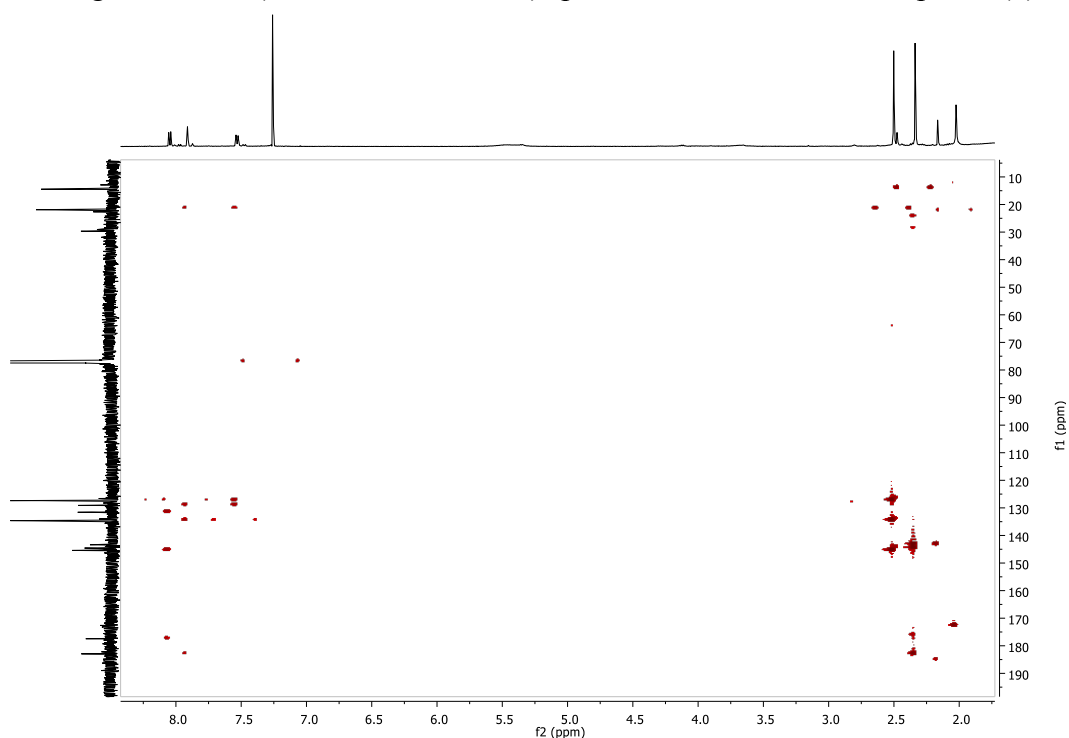
S7: gHSQC (^1H 500 MHz, CDCl_3) spectrum for 3-chloro-chimaphilin (**3**)



S8: gCOSY (^1H 600 MHz, CDCl_3) spectrum for 3-chloro-chimaphilin (**3**)



S9: gHMBCAD (^1H 500 MHz, CDCl_3) spectrum for 3-chloro-chimaphilin (**3**)



S1: ^1H and ^{13}C NMR data table for 3-chloro-chimaphilin (**3**) in CDCl_3

position	$\delta_{\text{C}}^{\text{b}}$	δ_{H} (J in Hz) ^a	HMBC ^a	COSY ^c
1	182.9			
2	143.4 ^d			
3	144.6 ^d			
4	177.4			
5	131.6			
6	127.4	8.05 (d; 7.8)	4, 5, 10	7
7	134.6	7.53 (d; 7.8)	6, 8, 8-Me	6, 8-Me, 9
8	129.1			
9	127.4	7.91 (s)	1, 7, 8, 8-Me	7, 8-Me
10	145.4			
2-Me	14.5	2.34 (s)	1, 2, 3, 4	
8-Me	21.9	2.50 (s)	7, 9, 10	7, 9

^a500 MHz for ^1H NMR, gHMBCAD, ^b125 MHz for ^{13}C NMR, ^c600 MHz for gCOSY

^dAmbiguous assignment

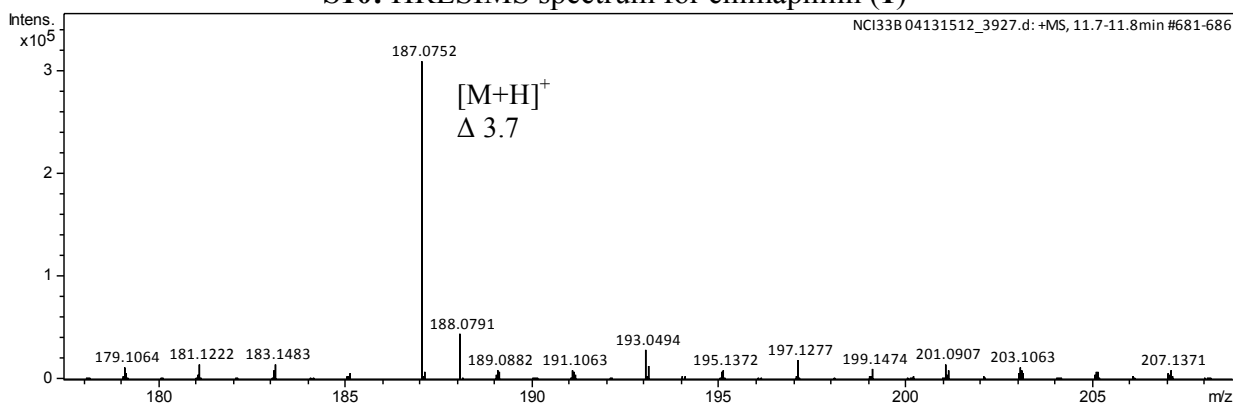
S2: ^1H and ^{13}C NMR assignments for chimaphilin (**1**), 3-chloro-chimaphilin (**2**), and 3-hydroxy-chimaphilin (**3**) in CDCl_3

Cmpd Position	Chimaphilin		3-chlorochimaphilin		3-hydroxychimaphilin	
	$\delta_{\text{C}}^{\text{c}}$	$\delta_{\text{H}}^{\text{a}}$	$\delta_{\text{C}}^{\text{d}}$	$\delta_{\text{H}}^{\text{b}}$	$\delta_{\text{C}}^{\text{c}}$	$\delta_{\text{H}}^{\text{a}}$
1	184.5		182.9		185.5	
2	148.2		143.4 ^d		145.2	
3	144.6	6.69 (s)	144.6 ^d		153.5	
4	185.9		177.4		181.5	
5	126.2		131.6		126.3	
6	135.7	7.82 (d; 7.8)	127.4	8.05 (d; 7.8)	132.8	7.97 (d; 7.7)
7	134.3	7.42 (d; 7.8)	134.6	7.53 (d; 7.8)	133.4	7.46 (d; 7.7)
8	126.8		129.1		127.2	
9	132.0	7.77 (s)	127.4	7.91 (s)	127.0	7.91 (s)
10	131.1		145.4		120.0	
2-Me	16.4	2.06 (s)	14.5	2.34 (s)	8.64	2.09 (s)
8-Me	21.8	2.38 (s)	21.9	2.50 (s)	22.06	2.49 (s)

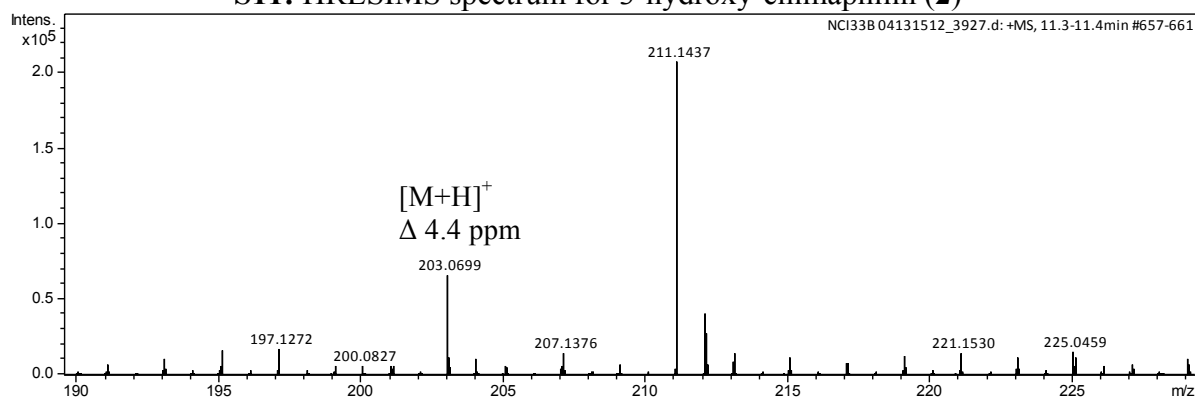
^a600 MHz, ^b150 MHz, ^c125 MHz

^dAmbiguous assignment

S10: HRESIMS spectrum for chimaphilin (**1**)



S11: HRESIMS spectrum for 3-hydroxy-chimaphilin (**2**)



S12: HRESIMS spectrum for 3-chloro-chimaphilin (3)

