

SUPPORTING INFORMATION

Expanding antibiotic chemical space around the nidulin pharmacophore

Mahmud T. Morshed,^a Daniel Vuong,^b Andrew Crombie,^b Alastair E. Lacey,^b
Peter Karuso,^a Ernest Lacey^{a,b} and Andrew M. Piggott^{a*}

^a Department of Molecular Sciences, Macquarie University, NSW 2109, Australia.

^b Microbial Screening Technologies, Smithfield, NSW 2164, Australia.

Table of Contents

Table S1. ¹ H (600 MHz) and ¹³ C (150 MHz) NMR data for 7-carboxyfolipastatin (1) in DMSO- <i>d</i> ₆	4
Table S2. ¹ H (600 MHz) and ¹³ C (150 MHz) NMR data for 4,7-dichlorounguinol (2) in DMSO- <i>d</i> ₆	5
Table S3. ¹ H (600 MHz) and ¹³ C (150 MHz) NMR data for 7-bromounguinol (3) in DMSO- <i>d</i> ₆	6
Table S4. ¹ H (600 MHz) and ¹³ C (150 MHz) NMR data for 2-chloro-7-bromounguinol (4) in DMSO- <i>d</i> ₆	7
Table S5. ¹ H (600 MHz) and ¹³ C (150 MHz) NMR data for 7-bromofolipastatin (5) in DMSO- <i>d</i> ₆	8
Table S6. ¹ H (600 MHz) and ¹³ C (150 MHz) NMR data for 5-bromoagonodepside B (6) in DMSO- <i>d</i> ₆	9
Table S7. ¹ H (600 MHz) and ¹³ C (150 MHz) NMR data for unguidepside A (7) in DMSO- <i>d</i> ₆	10
Table S8. ¹ H (600 MHz) and ¹³ C (150 MHz) NMR data for 3-bromounguidepside A (8) in DMSO- <i>d</i> ₆	11
Table S9. ¹ H (500 MHz) and ¹³ C (125 MHz) NMR data for decarboxyunguidepside A (9) in DMSO- <i>d</i> ₆	12
Table S10. ¹ H (500 MHz) and ¹³ C (125 MHz) NMR data for unguinolic acid (10) in DMSO- <i>d</i> ₆	13
Table S11. ¹ H (500 MHz) and ¹³ C (125 MHz) NMR data for decarboxyunguinolic acid (11) in DMSO- <i>d</i> ₆	14
Table S12. ¹ H (500 MHz) and ¹³ C (125 MHz) NMR data for 5-chlorounguinolic acid (12) in DMSO- <i>d</i> ₆	15
Table S13. Recipes for microbiological media	16
Figure S1. Fractionation scheme for <i>A. unguis</i> grown on YES Agar plates	17
Figure S2. Fractionation scheme for <i>A. unguis</i> grown in YES media supplemented with 0.5% NaCl	18
Figure S3. Fractionation scheme for <i>A. unguis</i> grown in YES media supplemented with 1% KBr	19
Figure S4. Fractionation scheme for <i>A. unguis</i> grown on leached barley	20
Figure S5. ¹ H NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 7-carboxyfolipastatin (1)	21
Figure S6. ¹³ C NMR spectrum (150 MHz, DMSO- <i>d</i> ₆) of 7-carboxyfolipastatin (1)	22
Figure S7. ¹ H- ¹³ C HSQC NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 7-carboxyfolipastatin (1)	23
Figure S8. ¹ H- ¹³ C HMBC NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 7-carboxyfolipastatin (1)	24
Figure S9. ¹ H- ¹ H COSY NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 7-carboxyfolipastatin (1)	25
Figure S10. ¹ H- ¹ H ROESY NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 7-carboxyfolipastatin (1)	26
Figure S11. ¹ H NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 4,7-dichlorounguinol (2)	27
Figure S12. ¹³ C NMR spectrum (150 MHz, DMSO- <i>d</i> ₆) of 4,7-dichlorounguinol (2)	28
Figure S13. ¹ H- ¹³ C HSQC NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 4,7-dichlorounguinol (2)	29
Figure S14. ¹ H- ¹³ C HMBC NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 4,7-dichlorounguinol (2)	30
Figure S15. ¹ H- ¹ H COSY NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 4,7-dichlorounguinol (2)	31
Figure S16. ¹ H- ¹ H ROESY NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of 4,7-dichlorounguinol (2)	32

* Corresponding author: Ph: +61-2-9850-8251; Fax: +61-2-9850-8313; Email: andrew.piggott@mq.edu.au

Figure S17. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguinol (3).....	33
Figure S18. ^{13}C NMR spectrum (150 MHz, $\text{DMSO}-d_6$) of 7-bromounguinol (3).....	34
Figure S19. $^1\text{H}-^{13}\text{C}$ HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguinol (3).....	35
Figure S20. $^1\text{H}-^{13}\text{C}$ HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguinol (3).....	36
Figure S21. $^1\text{H}-^1\text{H}$ COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguinol (3).....	37
Figure S22. $^1\text{H}-^1\text{H}$ ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguinol (3)	38
Figure S23. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguinol (4).....	39
Figure S24. ^{13}C NMR spectrum (150 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguinol (4).....	40
Figure S25. $^1\text{H}-^{13}\text{C}$ HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguinol (4).....	41
Figure S26. $^1\text{H}-^{13}\text{C}$ HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguinol (4).....	42
Figure S27. $^1\text{H}-^1\text{H}$ COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguinol (4).....	43
Figure S28. $^1\text{H}-^1\text{H}$ ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguinol (4).....	44
Figure S29. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)	45
Figure S30. ^{13}C NMR spectrum (150 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)	46
Figure S31. $^1\text{H}-^{13}\text{C}$ HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)	47
Figure S32. $^1\text{H}-^{13}\text{C}$ HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5).....	48
Figure S33. $^1\text{H}-^1\text{H}$ COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)	49
Figure S34. $^1\text{H}-^1\text{H}$ ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5).....	50
Figure S35. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (6)	51
Figure S36. ^{13}C NMR spectrum (150 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (6)	52
Figure S37. $^1\text{H}-^{13}\text{C}$ HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (6)	53
Figure S38. $^1\text{H}-^{13}\text{C}$ HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (6)	54
Figure S39. $^1\text{H}-^1\text{H}$ COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (6)	55
Figure S40. $^1\text{H}-^1\text{H}$ ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (6).....	56
Figure S41. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7).....	57
Figure S42. ^{13}C NMR spectrum (150 MHz, $\text{DMSO}-d_6$) of unguidepside A (7).....	58
Figure S43. $^1\text{H}-^{13}\text{C}$ HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7).....	59
Figure S44. $^1\text{H}-^{13}\text{C}$ HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7)	60
Figure S45. $^1\text{H}-^1\text{H}$ COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7).....	61
Figure S46. $^1\text{H}-^1\text{H}$ ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7)	62
Figure S47. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 3-bromounguidepside A (8).....	63
Figure S48. ^{13}C NMR spectrum (150 MHz, $\text{DMSO}-d_6$) of 3-bromounguidepside A (8).....	64
Figure S49. $^1\text{H}-^{13}\text{C}$ HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 3-bromounguidepside A (8).....	65
Figure S50. $^1\text{H}-^{13}\text{C}$ HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 3-bromounguidepside A (8).....	66
Figure S51. $^1\text{H}-^1\text{H}$ COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 3-bromounguidepside A (8).....	67
Figure S52. $^1\text{H}-^1\text{H}$ ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 3-bromounguidepside A (8)	68
Figure S53. ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (9).....	69
Figure S54. ^{13}C NMR spectrum (125 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (9).....	70
Figure S55. $^1\text{H}-^{13}\text{C}$ HSQC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (9).....	71
Figure S56. $^1\text{H}-^{13}\text{C}$ HMBC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (9).....	72
Figure S57. $^1\text{H}-^1\text{H}$ COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (9).....	73
Figure S58. $^1\text{H}-^1\text{H}$ ROESY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (9).....	74

Figure S59. ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of unguinolic acid (10).....	75
Figure S60. ^{13}C NMR spectrum (125 MHz, $\text{DMSO}-d_6$) of unguinolic acid (10).....	76
Figure S61. ^1H - ^{13}C HSQC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of unguinolic acid (10).....	77
Figure S62. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of unguinolic acid (10).....	78
Figure S63. ^1H - ^1H COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of unguinolic acid (10).....	79
Figure S64. ^1H - ^1H ROESY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of unguinolic acid (10).....	80
Figure S65. ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguinolic acid (11).....	81
Figure S66. ^{13}C NMR spectrum (125 MHz, $\text{DMSO}-d_6$) of decarboxyunguinolic acid (11).....	82
Figure S67. ^1H - ^{13}C HSQC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguinolic acid (11).....	83
Figure S68. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguinolic acid (11).....	84
Figure S69. ^1H - ^1H COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguinolic acid (11).....	85
Figure S70. ^1H - ^1H ROESY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguinolic acid (11).....	86
Figure S71. ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of 5-chlorounguinolic acid (12).....	87
Figure S72. ^{13}C NMR spectrum (125 MHz, $\text{DMSO}-d_6$) of 5-chlorounguinolic acid (12).....	88
Figure S73. ^1H - ^{13}C HSQC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of 5-chlorounguinolic acid (12).....	89
Figure S74. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of 5-chlorounguinolic acid (12).....	90
Figure S75. ^1H - ^1H COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of 5-chlorounguinolic acid (12).....	91
Figure S76. ^1H - ^1H ROESY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of 5-chlorounguinolic acid (12).....	92
Figure S77. UV-vis spectrum of 7-carboxyfolipastatin (1) in MeOH.....	93
Figure S78. UV-vis spectrum of 4,7-dichlorounguinol (2) in MeOH.....	93
Figure S79. UV-vis spectrum of 7-bromounguinol (3) in MeOH.....	94
Figure S80. UV-vis spectrum of 2-chloro-7-bromounguinol (4) in MeOH.....	94
Figure S81. UV-vis spectrum of 7-bromofolipastatin (5) in MeOH.....	95
Figure S82. UV-vis spectrum of 5-bromoagonodepside B (6) in MeOH.....	95
Figure S83. UV-vis spectrum of unguidepside A (7) in MeOH.....	96
Figure S84. UV-vis spectrum of 3-bromounguidepside A (8) in MeOH.....	96
Figure S85. UV-vis spectrum of decarboxyunguidepside A (9) in MeOH.....	97
Figure S86. UV-vis spectrum of unguinolic acid (10) in MeOH.....	97
Figure S87. UV-vis spectrum of decarboxyunguinolic acid (11) in MeOH.....	98
Figure S88. UV-vis spectrum of 5-chlorounguinolic acid (12) in MeOH.....	98
Figure S89. HR-ESI(+)-MS spectrum of 7-carboxyfolipastatin (1).....	99
Figure S90. HR-ESI(+)-MS spectrum of 4,7-dichlorounguinol (2).....	100
Figure S91. HR-ESI(+)-MS spectrum of 7-bromounguinol (3).....	101
Figure S92. HR-ESI(+)-MS spectrum of 2-chloro-7-bromounguinol (4).....	102
Figure S93. HR-ESI(+)-MS spectrum of 7-bromofolipastatin (5).....	103
Figure S94. HR-ESI(+)-MS spectrum of 5-bromoagonodepside B (6).....	104
Figure S95. HR-ESI(+)-MS spectrum of unguidepside A (7).....	105
Figure S96. HR-ESI(-)-MS spectrum of 3-bromounguidepside A (8).....	106
Figure S97. HR-ESI(-)-MS spectrum of decarboxyunguidepside A (9).....	107
Figure S98. HR-ESI(+)-MS spectrum of unguinolic acid (10).....	108
Figure S99. HR-ESI(-)-MS spectrum of decarboxyunguinolic acid (11).....	109
Figure S100. HR-ESI(-)-MS spectrum of 5-chlorounguinolic acid (12).....	110

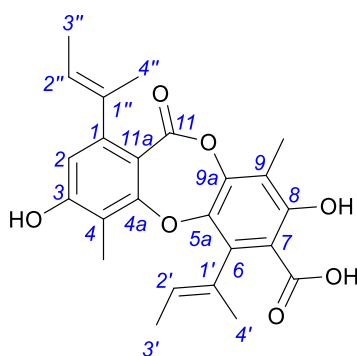
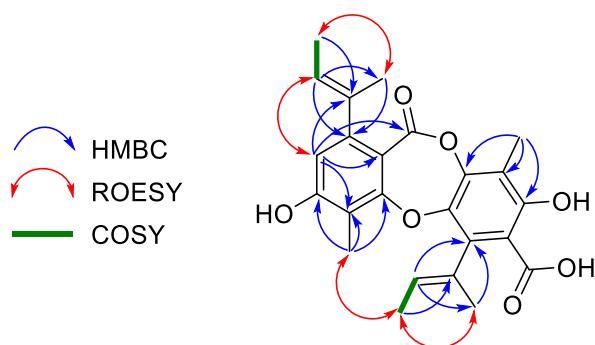


Table S1. ^1H (600 MHz) and ^{13}C (150 MHz) NMR data for 7-carboxyfolipastatin (**1**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		148.1			
2	6.55, s	111.4	3, 4, 11, 11a, 1''		2'', 4''
3		159.9			
4		113.2			
4a		162.0			
5a		139.5			
6		136.8			
7		114.6			
8		160.3			
9		114.0			
9a		143.8			
11		163.9			
11a		110.5			
1'		133.7			
2'	4.93, qq (6.7, 1.5)	119.6	6, 3', 4'	3'	
3'	1.65, dq (6.7, 1.0)	13.9	1', 2'	2'	4', 4-Me
4'	1.81, dq (1.5, 1.0)	18.8	6, 1', 2'		3', 4-Me
1''		135.9			
2''	5.34, qq (6.7, 1.6)	123.5	1, 3'', 4''	3''	2
3''	1.64, dq (6.7, 1.0)	14.1	1'', 2''	2''	4''
4''	1.78, dq (1.6, 1.0)	17.5	1, 1'', 2''		2, 3''
4-Me	2.06, s	8.5	3, 4, 4a		3', 4'
9-Me	2.03, s	9.0	8, 9, 9a		
3-OH	10.53, s				
8-OH	^a				
7-CO ₂ H	17.75, br s	169.7			

^a Not observed



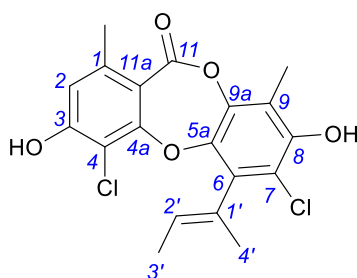
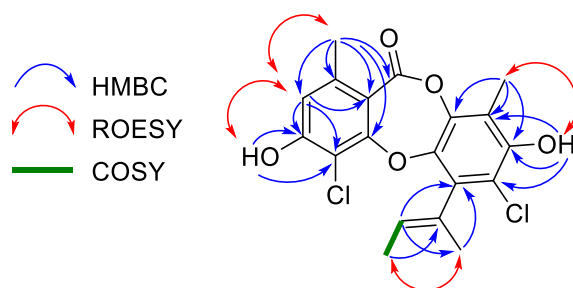


Table S2. ^1H (600 MHz) and ^{13}C (150 MHz) NMR data for 4,7-dichlorourouguinol (**2**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		142.7			
2	6.74, q (0.7)	115.6	3, 4, 11, 11a, 1-Me		1-Me, 3-OH
3		157.8			
4		108.7			
4a		158.8			
5a		141.46 ^a			
6		134.2			
7		116.6			
8		149.0			
9		117.1			
9a		141.48 ^a			
11		161.5			
11a		112.2			
1'		129.4			
2'	5.32, qq (6.8, 1.5)	126.8	6, 1', 3', 4'	3'	
3'	1.74, dq (6.8, 1.1)	13.9	1', 2'	2'	4
4'	1.86, dq (1.5, 1.1)	17.4	6, 1', 2'		4
1-Me	2.34, d (0.7)	20.8	1, 2, 11, 4a, 11a		2
9-Me	2.18, s	10.3	8, 9, 9a		8-OH
3-OH	11.38, s		2, 3, 4		2
8-OH	9.43, s		7, 8, 9		9-Me

^a Assignments interchangeable



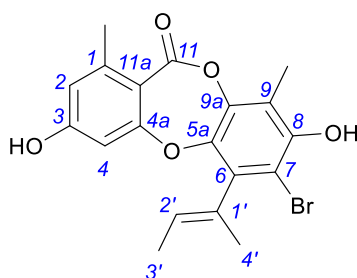
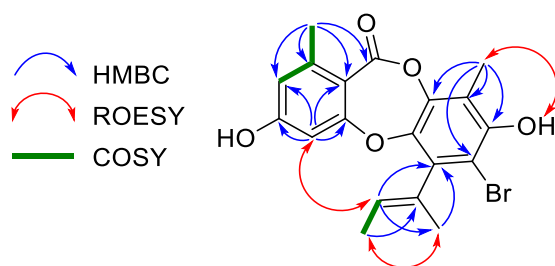


Table S3. ^1H (600 MHz) and ^{13}C (150 MHz) NMR data for 7-bromounguinol (**3**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		144.9			
2	6.56, dd (2.4, 0.8)	115.8	3, 4, 11a, 1-Me	4, 1-Me	1-Me
3		161.9 ^a			
4	6.31, d (2.4)	104.6	2, 3, 4a, 11, 11a	2	2', 3'
4a		161.8 ^a			
5a		141.0			
6		135.9			
7		108.0			
8		149.5			
9		116.9			
9a		142.2			
11		162.8			
11a		111.2			
1'		130.9			
2'	5.25, qq (6.8, 1.4)	125.8	6, 3', 4'	3'	4
3'	1.84, dq (6.8, 1.0)	13.4	1', 2'	2'	4, 4'
4'	1.86, dq (1.4, 1.0)	17.1	6, 1', 2'		3'
1-Me	2.33, s	20.7	1, 2, 11, 11a	2	2
9-Me	2.17, s	10.6	7, 8, 9, 9a		8-OH
3-OH	10.64, s				
8-OH	9.22, s				9-Me

^a Assignments interchangeable



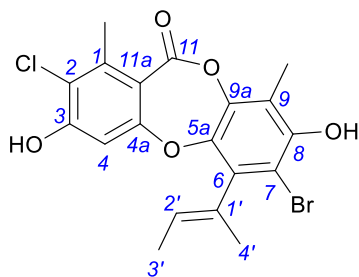
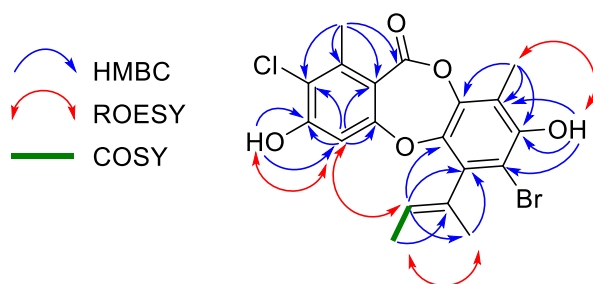


Table S4. ^1H (600 MHz) and ^{13}C (150 MHz) NMR data for 2-chloro-7-bromounguinol (**4**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		141.3			
2		113.0			
3		157.6			
4	6.58, s	105.1	2, 3, 4a, 11a		3', 4', 3-OH
4a		160.5			
5a		141.0			
6		135.9			
7		108.2			
8		149.7			
9		117.0			
9a		142.1			
11		161.7			
11a		119.2			
1'		130.7			
2'	5.25, qq (6.8, 1.1)	126.1	5a, 3', 4', 6	3'	
3'	1.85, dq (6.8, 1.1)	13.5	1', 2'	2'	4
4'	1.86, s	17.1	1', 2', 3', 6,		4
1-Me	2.38, s	18.2	1, 2, 11, 11a		
9-Me	2.17, s	10.5	8, 9, 9a		8-OH
3-OH	11.52, s		3, 4		4
8-OH	9.28, s		7, 8, 9		9-Me



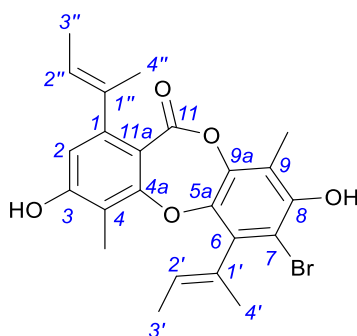
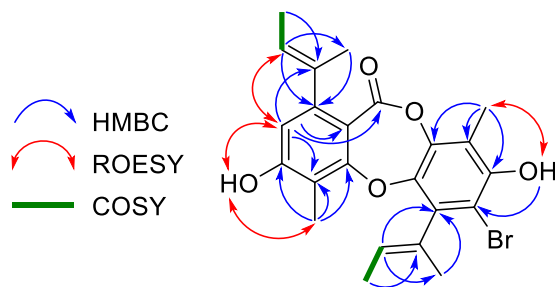


Table S5. ^1H (600 MHz) and ^{13}C (150 MHz) NMR data for 7-bromofolipastatin (**5**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		148.5			
2	6.56, s	111.9	3, 4, 11, 11a, 1''		2'', 4'' 3-OH
3		159.9 ^a			
4		113.2			
4a		161.2 ^a			
5a		142.5			
6		135.8			
7		108.5			
8		149.6			
9		116.8			
9a		142.3			
11		162.9			
11a		109.9			
1'		131.8			
2'	5.33, qq (6.8, 1.5)	126.6	6, 3', 4'	3'	
3'	1.76, dq (6.8, 1.1)	13.7	1', 2'	2'	4'
4'	1.83, dq (1.5, 1.1)	17.3	6, 1', 2'		3'
1''		135.6			
2''	5.35, qq (6.8, 1.4)	123.9	1, 3'', 4''	3''	2
3''	1.65, dq (6.8, 1.1)	14.0	1'', 2''	2''	4''
4''	1.78, dq (1.4, 1.1)	17.4	1, 1'', 2''		2, 3''
4-Me	2.05, s	8.5	3, 4, 4a		3-OH
9-Me	2.18, s	10.4	8, 9, 9a		8-OH
3-OH	10.53, s		2, 3, 4		4-Me
8-OH	9.28, s		7, 8, 9		9-Me

^a Assignments interchangeable



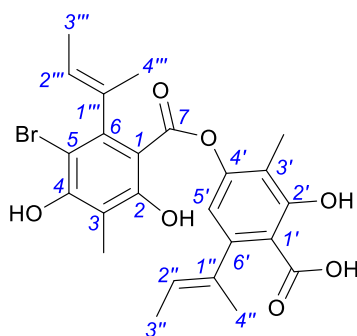
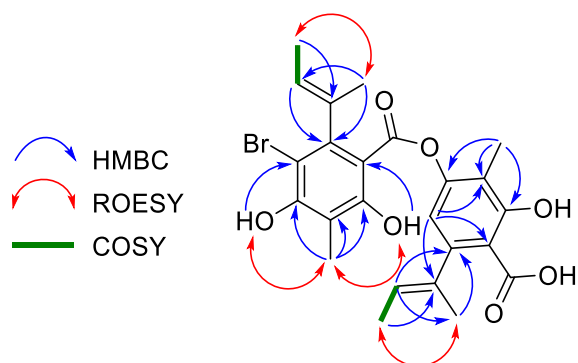


Table S6. ^1H (600 MHz) and ^{13}C (150 MHz) NMR data for 5-bromoagonodepside B (**6**) in $\text{DMSO}-d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		113.1			
2		154.5 ^a			
3		112.7			
4		154.2 ^a			
5		103.2			
6		142.5			
7		166.0			
1'		112.0			
2'		159.0			
3'		116.9			
4'		151.6			
5'	6.30, s	113.7	1', 3', 4', 1'', 1'-CO ₂ H		2'', 3'', 4''
6'		145.5			
1''		137.0			
2''	5.30, qq (6.5, 1.4)	121.5	6', 3'', 4''	3''	3''
3''	1.65, dq (6.5, 1.0)	13.7	6', 1'', 2'', 4''	2''	4''
4''	1.84, dq (1.4, 1.0)	18.2	6', 1'', 2''		5', 3''
1'''		136.0			
2'''	5.31, qq (6.5, 1.4)	123.9	6, 3''', 4'''	3'''	3'''
3'''	1.66, dq (6.5, 1.0)	13.4	6, 1''', 2''', 4'''	2'''	4'''
4'''	1.87, dq (1.4, 1.0)	17.2	6, 1''', 2'''		3'''
3-Me	2.12, s	10.0	2, 3, 4, 6		2-OH, 4-OH
3'-Me	1.99, s	9.0	2', 3', 4'		
2-OH	9.69, s		1, 2		3-Me
4-OH	9.42, s		3, 4, 5		3-Me
2'-OH	11.41, br s				
1'-CO ₂ H	13.62, br s	171.7			

^a Assignments interchangeable



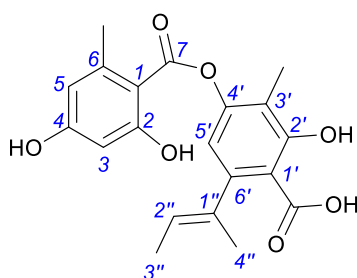
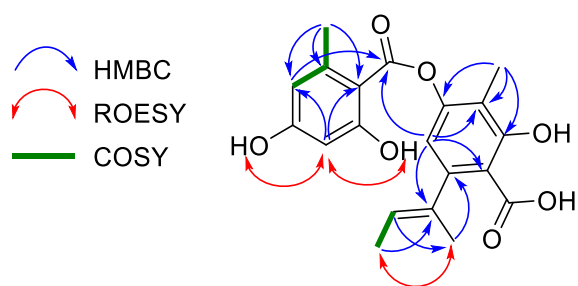


Table S7. ^1H (600 MHz) and ^{13}C (150 MHz) NMR data for unguidepside A (**7**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		108.3			
2		160.0			
3	6.22, d (2.4)	100.4	1, 2, 5		2-OH, 4-OH
4		161.1			
5	6.21, d (2.4)	109.8	3, 4, 7, 6-Me	6-Me	6-Me
6		140.3			
7		166.9			
1'		112.1			
2'		158.8			
3'		116.8			
4'		151.6			
5'	6.45, s	114.1	1', 3', 4', 1''		4''
6'		145.4			
1''		136.9			
2''	5.30, qq (6.7, 1.4)	121.5	6', 3'', 4''	3''	
3''	1.65, dq (6.7, 1.1)	13.7	1'', 2''	2''	4''
4''	1.85, dq (1.4, 1.1)	18.2	6', 1'', 2''		5', 3''
6-Me	2.34, s	21.3	1, 5, 6	5	5
3'-Me	2.01, s	9.2	2', 3', 4'		
2-OH	10.34, s		1, 2, 3		3
4-OH	9.99, s		3, 4, 5		3
2'-OH	11.39, br s				
1'-CO ₂ H	13.63, br s	171.8			



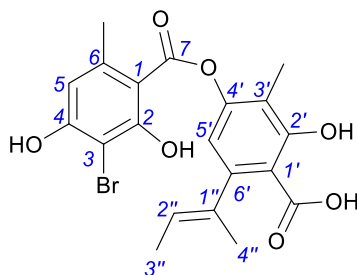
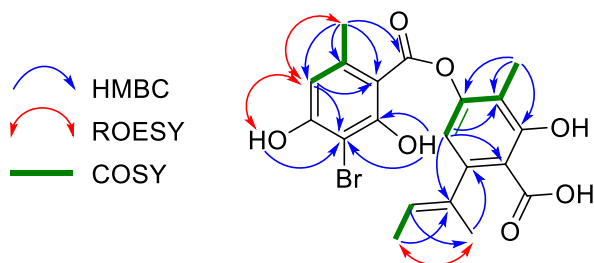


Table S8. ^1H (600 MHz) and ^{13}C (150 MHz) NMR data for 3-bromounguidepside A (**8**) in $\text{DMSO}-d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		106.9			
2		158.9			
3		96.1			
4		159.1			
5	6.50, s	110.9	1, 3, 4, 7, 6-Me	6-Me	6-Me, 4-OH
6		140.3			
7		167.8			
1'		112.8			
2'		158.5			
3'		116.6			
4'		151.0			
5'	6.57, s	114.0	1', 3', 4', 1''	3'-Me	4''
6'		145.4			
1''		136.7			
2''	5.32, qq (6.8, 1.4)	121.7	6', 3'', 4''	3''	
3''	1.65, dq (6.8, 1.0)	13.7	1'', 2''	2''	4''
4''	1.85, dq (1.4, 1.0)	18.1	6', 1'', 2''		5', 3''
6-Me	2.40, s	22.6	1, 5, 6, 7	5	5
3'-Me	1.99, s	9.3	2', 3', 4'	5'	
2-OH	11.16, s		1, 2, 3		
4-OH	11.13, s		3		5
2'-OH	11.31, br s				
1'-CO ₂ H	13.64, br s	171.6			



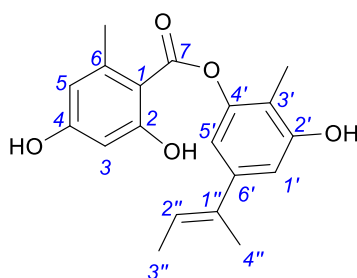
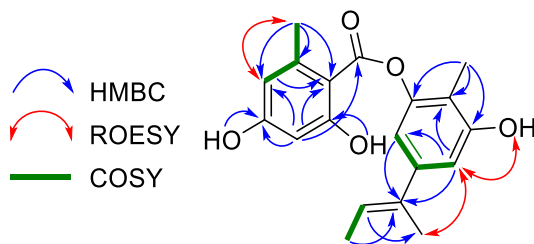


Table S9. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data for decarboxyunguidepside A (**9**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		107.9			
2		160.5			
3	6.21, d (2.4)	100.4	1, 4, 5, 7		
4		161.1			
5	6.22, d (2.4)	110.0	1, 3, 6-Me	6-Me	6-Me
6		140.5			
7		167.7			
1'	6.76, d (1.7)	109.2	2', 3', 5', 1''	5'	4'', 2'-OH
2'		156.1			
3'		115.2			
4'		149.8			
5'	6.60, d (1.7)	109.6	1', 3', 4', 1''	1'	2'', 4''
6'		141.5			
1''		134.1			
2''	5.81, qq (6.8, 1.2)	121.5	6', 4''	3''	5'
3''	1.73, dq (6.8, 1.0)	14.0	1'', 2''	2''	
4''	1.90, dq (1.2, 1.0)	15.0	6', 1'', 2''		1', 5'
6-Me	2.38, s	21.7	1, 5, 6	5	5
3'-Me	1.96, s	9.1	2', 3', 4'		
2-OH	10.48, s		1, 2, 3		
4-OH	10.01, s				
2'-OH	9.56, s		2', 3'		1'



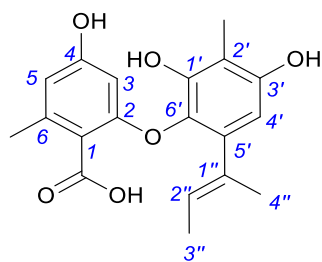
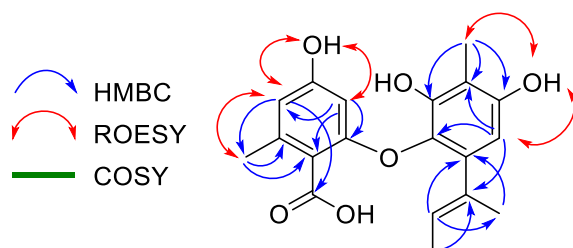


Table S10. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data for unguinolic acid (**10**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		115.3			
2		157.6			
3	5.76, d (2.3)	99.6	1, 2, 4, 5	5	4'', 4-OH
4		159.4			
5	6.22, d (2.3)	111.0	1, 3, 4, 1-CO ₂ H, 6-Me	3, 6-Me	6-Me, 4-OH
6		138.3			
1'		148.6			
2'		110.8			
3'		153.3			
4'	6.20, s	106.0	2', 3', 6', 1''		4'', 3'-OH
5'		136.4			
6'		132.1			
1''		133.7			
2''	5.48, qq (6.8, 1.3)	124.4	5', 3'', 4''	3''	
3''	1.56, dq (6.8, 1.0)	14.3	1'', 2''	2''	4''
4''	1.75, dq (1.3, 1.0)	17.0	5', 1'', 2''		4', 3''
6-Me	2.22, s	20.2	1, 5, 6	5	5
2'-Me	1.95, s	9.3	1', 2', 3'		3'-OH
4-OH	9.59, s		3, 4, 5		3, 5
1'-OH	8.50, br s				
3'-OH	9.12, s		2', 3', 4'		4', 2'-Me
1-CO ₂ H	12.76, br s	169.5			



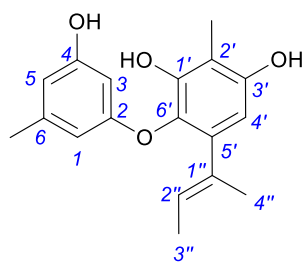
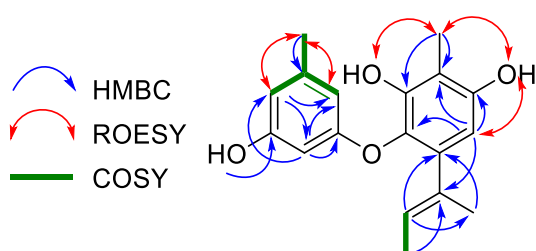


Table S11. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data for decarboxyunguinalic acid (**11**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1	6.00, br m	106.9	2, 3, 5, 6-Me	6-Me	6-Me
2		159.5			
3	5.85, dd (2.2)	99.4	1, 2, 4, 5		
4		157.8			
5	6.11, br m	108.9	1, 3, 4, 6-Me	6-Me	6-Me
6		138.7			
1'		148.3			
2'		110.5			
3'		152.3			
4'	6.15, s	105.7	2', 3', 6', 1''		2'', 4'', 3'-OH
5'		135.8			
6'		131.7			
1''		133.5			
2''	5.36, qq (6.8, 1.2)	123.2	5', 3'', 4''	3''	4'
3''	1.52, dq (6.8, 1.0)	13.7	1'', 2''	2''	
4''	1.72, dq (1.2, 1.0)	16.6	5', 1'', 2''		4'
6-Me	2.10, s	21.2	1, 5, 6	1, 5	1, 5
2'-Me	1.96, s	9.0	1', 2', 3'		1'-OH, 3'-OH
4-OH	9.09, s		3, 4, 5		
1'-OH	8.38, s		1', 2', 6'		2'-Me
3'-OH	9.01, s		2', 3', 4'		4', 2'-Me



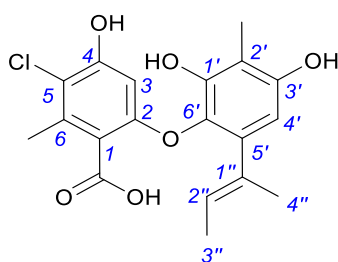


Table S12. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data for 5-chlorouruguinolic acid (**12**) in $\text{DMSO-}d_6$

Pos.	δ_{H} , mult (J in Hz)	δ_{C}	HMBC	COSY	ROESY
1		116.8			
2		154.2			
3	6.02, s	99.6	1, 2, 4, 5, 1-CO ₂ H		2'', 4'', 4-OH
4		154.3			
5		113.0			
6		134.2			
1'		148.0			
2'		110.6			
3'		152.9			
4'	6.20, s	105.7	2', 3', 6', 1''		2'', 4'', 3'-OH
5'		135.9			
6'		131.2			
1''		132.9			
2''	5.44, qq (6.7, 1.4)	124.0	5', 3'', 4''	3''	3, 4', 3''
3''	1.55, dq (6.7, 1.0)	13.8	1'', 2''	2''	2''
4''	1.74, dq (1.4, 1.0)	16.5	5', 1'', 2''		3, 4'
6-Me	2.27, s	17.3	1, 5, 6		
2'-Me	1.96, s	8.9	1', 2', 3'		3'-OH
4-OH	10.22, s		3, 4, 5		3
1'-OH	8.41, br s				
3'-OH	9.16, s		2', 3', 4'		4', 2'-Me
1-CO ₂ H	12.94, br s	168.1			

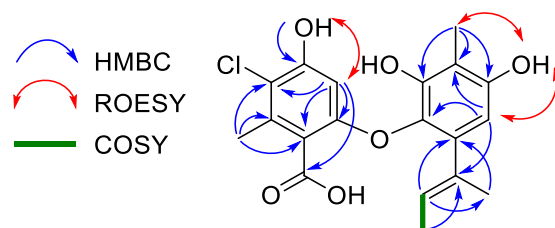


Table S13. Recipes for microbiological media

Glycerol casein agar (GCA)		*Trace element solution	
Ingredient	Quantity		
		CaCl ₂ .2H ₂ O	3 g
Glycerol	30 g	FeC ₆ O ₇ H ₅	1 g
Casein peptone (Amyl)	2 g	MnSO ₄	0.2 g
K ₂ HPO ₄	1 g	ZnCl ₂	0.1 g
NaCl	1gm	CuSO ₄ .5H ₂ O	0.025 g
MgSO ₄ .7H ₂ O	0.5 g	Na ₂ B ₄ O ₇ .10H ₂ O	0.02 g
Trace element solution*	5 mL	CoCl ₂	0.004
Deionised water	1000 mL	Na ₂ MoO ₄ .2H ₂ O	0.01
Bacteriological agar ^a (Amyl)	20 g	Deionised water	1000 mL
Autoclave	121 °C	Filter sterilise	

Yeast Extract agar		Malt extract agar	
Ingredient	Quantity	Ingredient	Quantity
Yeast Extract (Difco)	20 g	Bacteriological peptone (Difco)	3 g
Sucrose (Amyl)	150 g	Malt Extract (Amyl)	60 g
Bacteriological Agar ^a (Amyl)	20 g	Bacteriological glucose (Amyl)	60 g
Deionised water	1000 mL	Distilled water	1000 mL
Autoclave	121 °C	Adjust pH to 5.5	
		Bacteriological agar ^a (Amyl)	20 g
		Autoclave	121 °C

Czapeks Dox agar		Oatmeal agar	
Ingredient	Quantity	Ingredient	Quantity
Czapeks Dox Media (Oxoid)	45.4 g	Oatmeal	60 g
Deionised water	1000 mL	Agar ^a	12.5
Autoclave	121 °C	Distilled water	1000 mL
		Autoclave	121 °C

^a Omit agar for liquid media

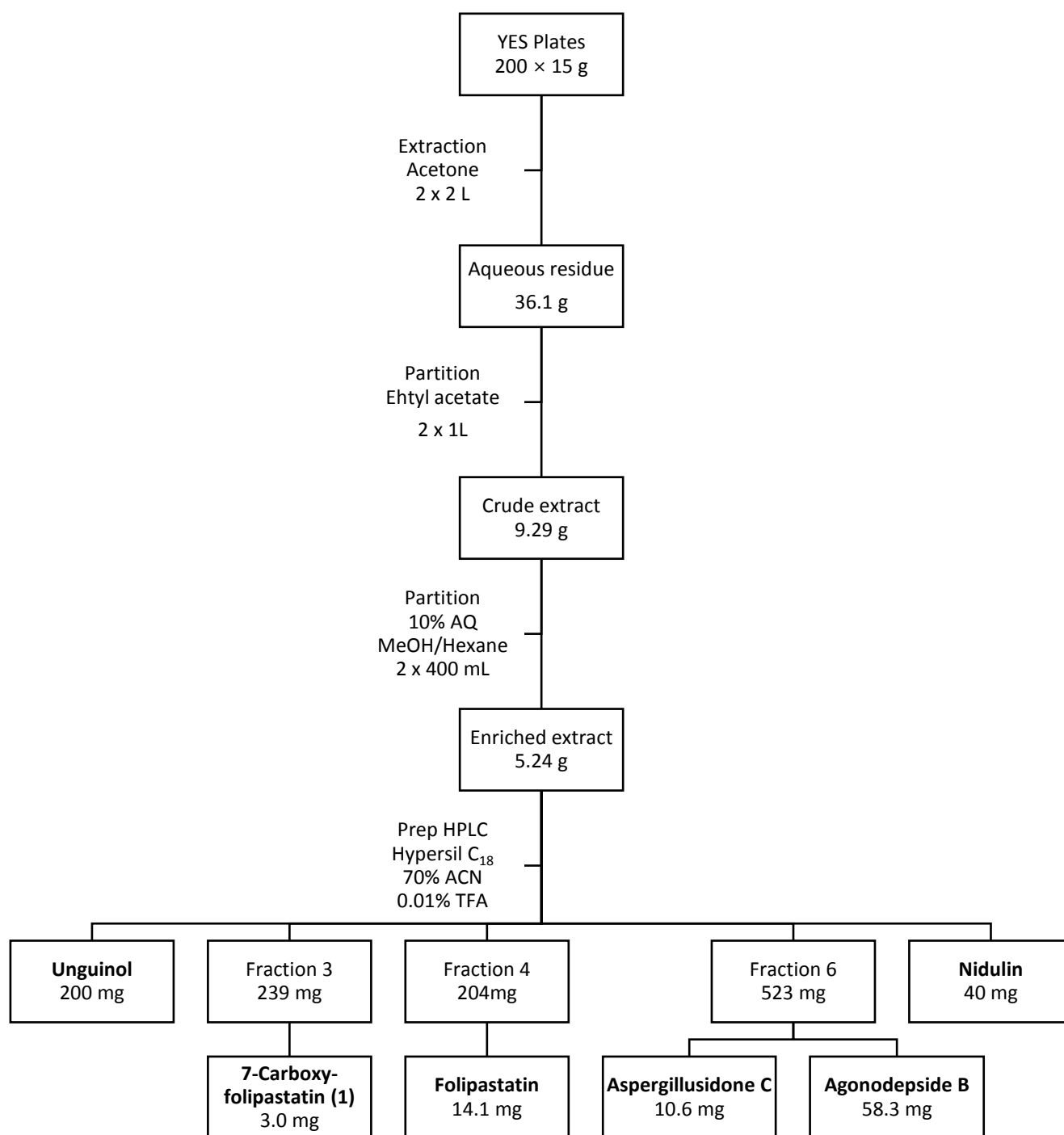


Figure S1. Fractionation scheme for *A. unguis* grown on YES Agar plates

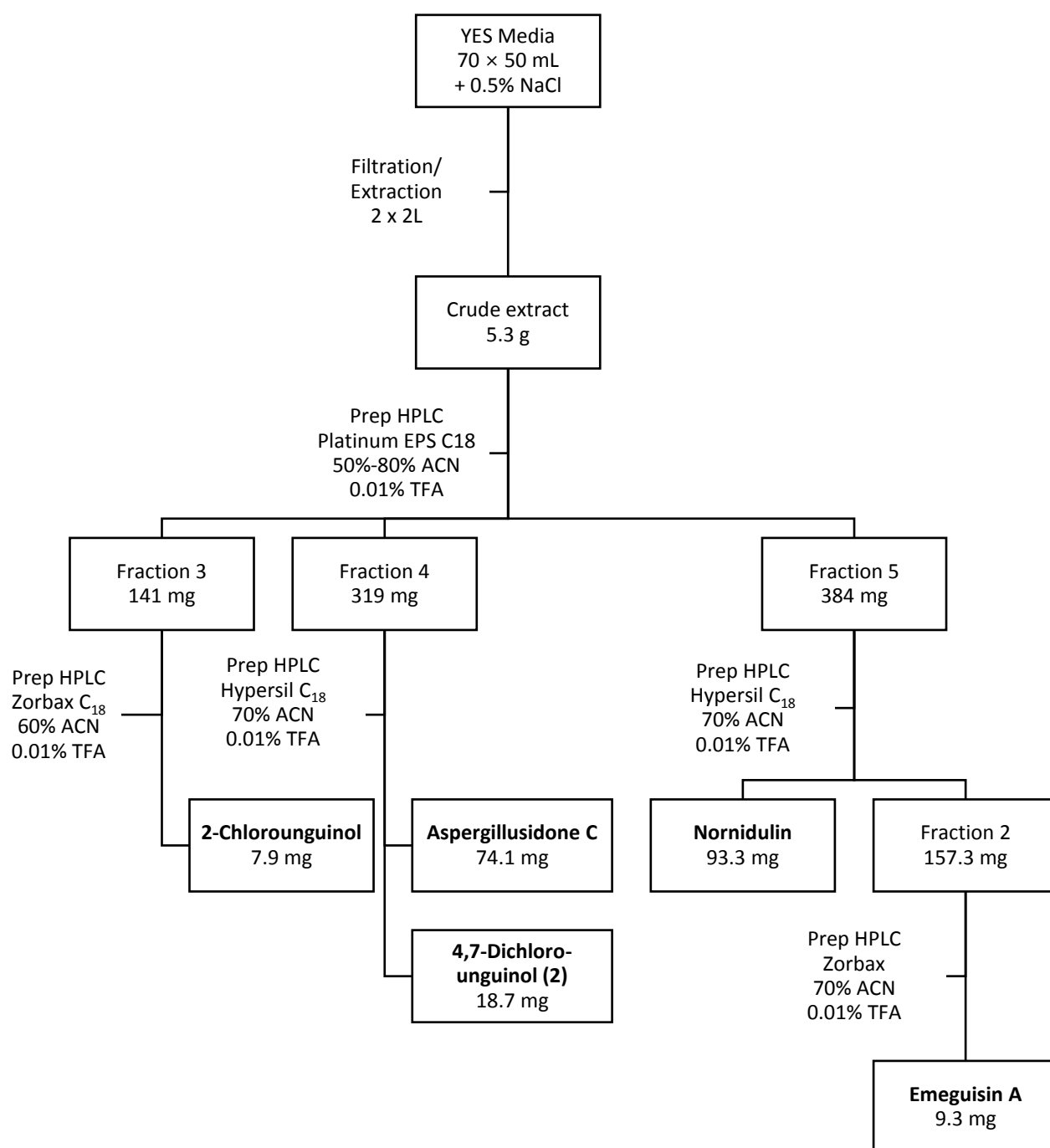


Figure S2. Fractionation scheme for *A. unguis* grown in YES media supplemented with 0.5% NaCl

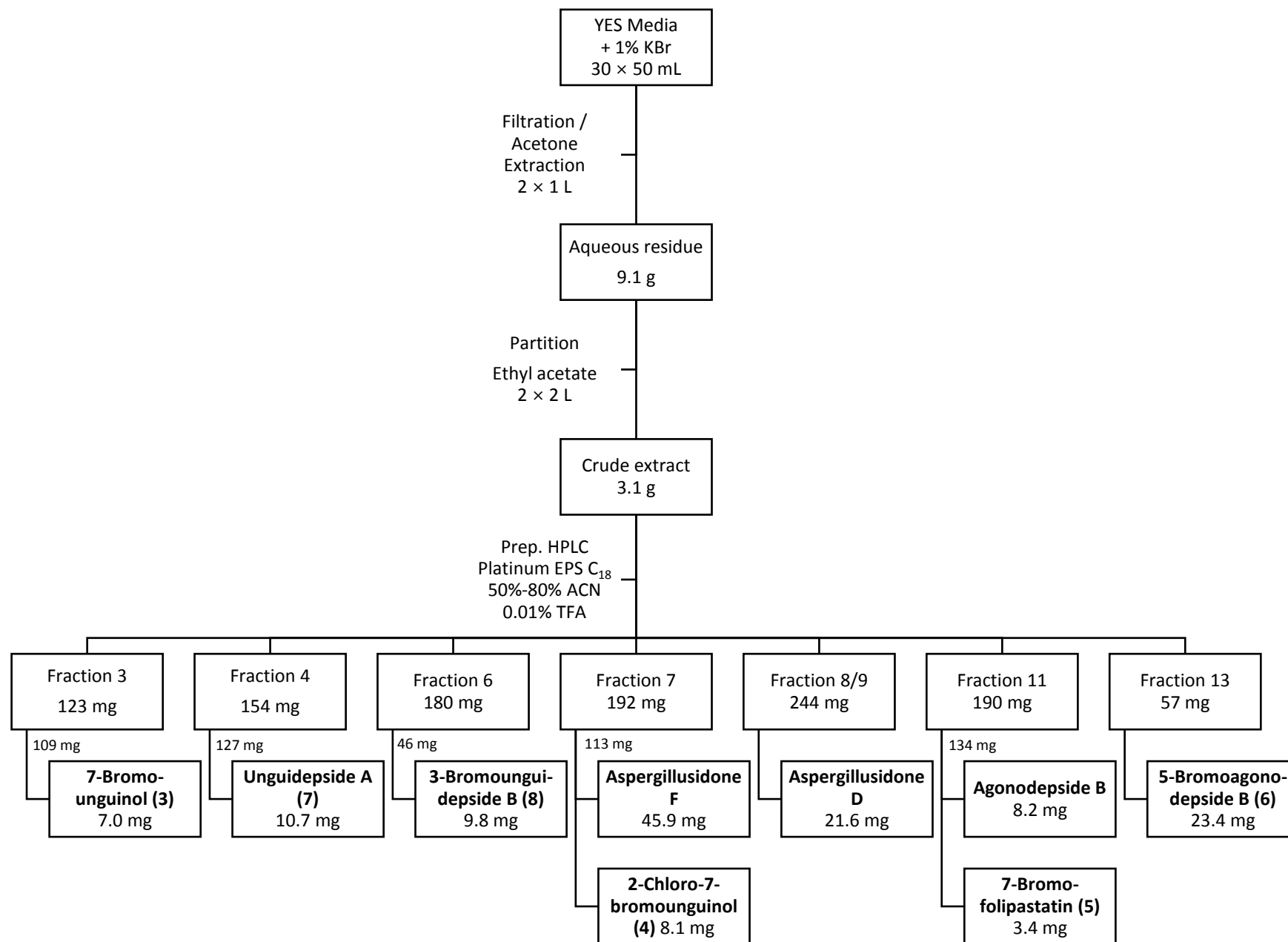


Figure S3. Fractionation scheme for *A. unguis* grown in YES media supplemented with 1% KBr

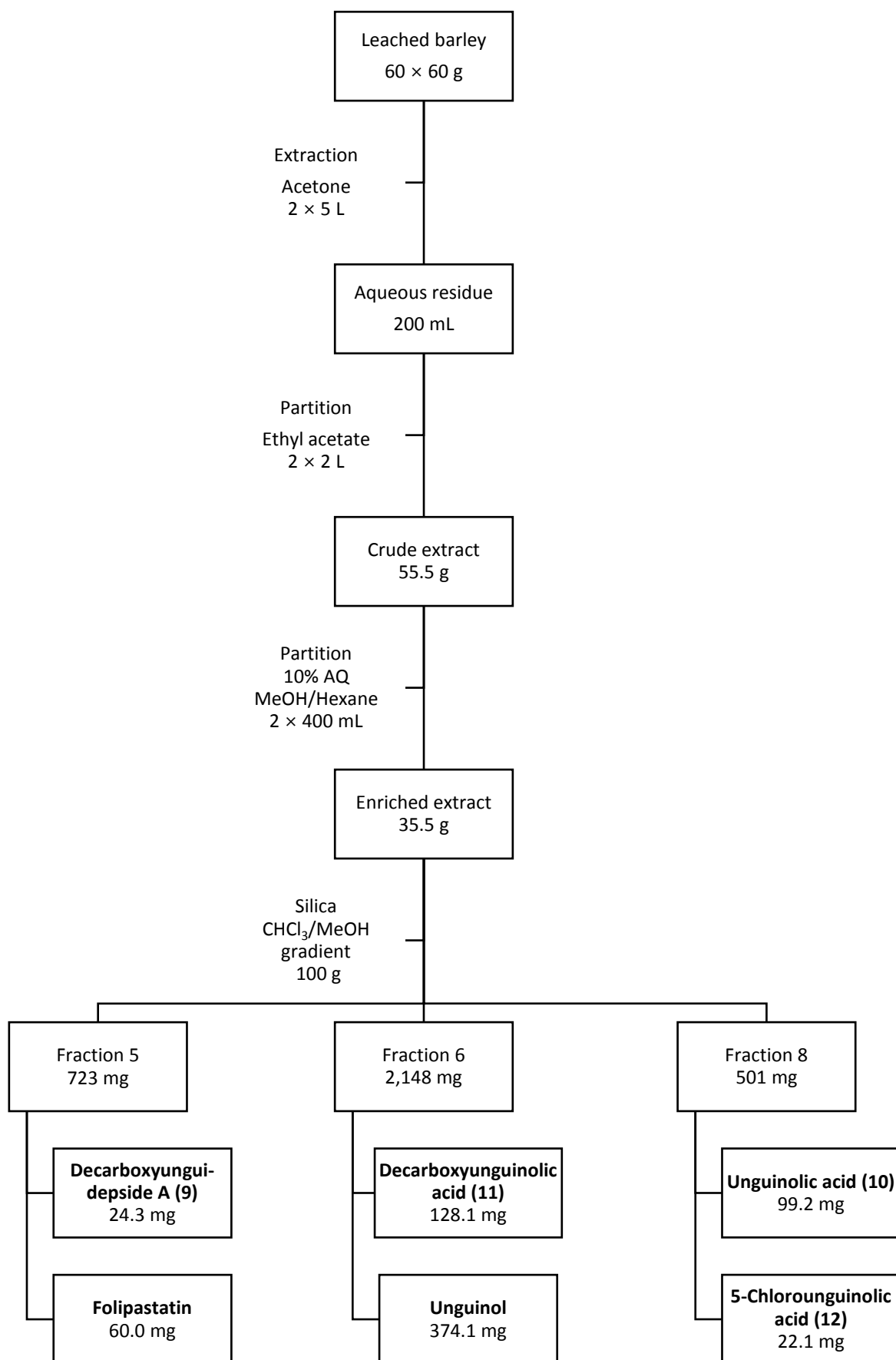


Figure S4. Fractionation scheme for *A. unguis* grown on leached barley

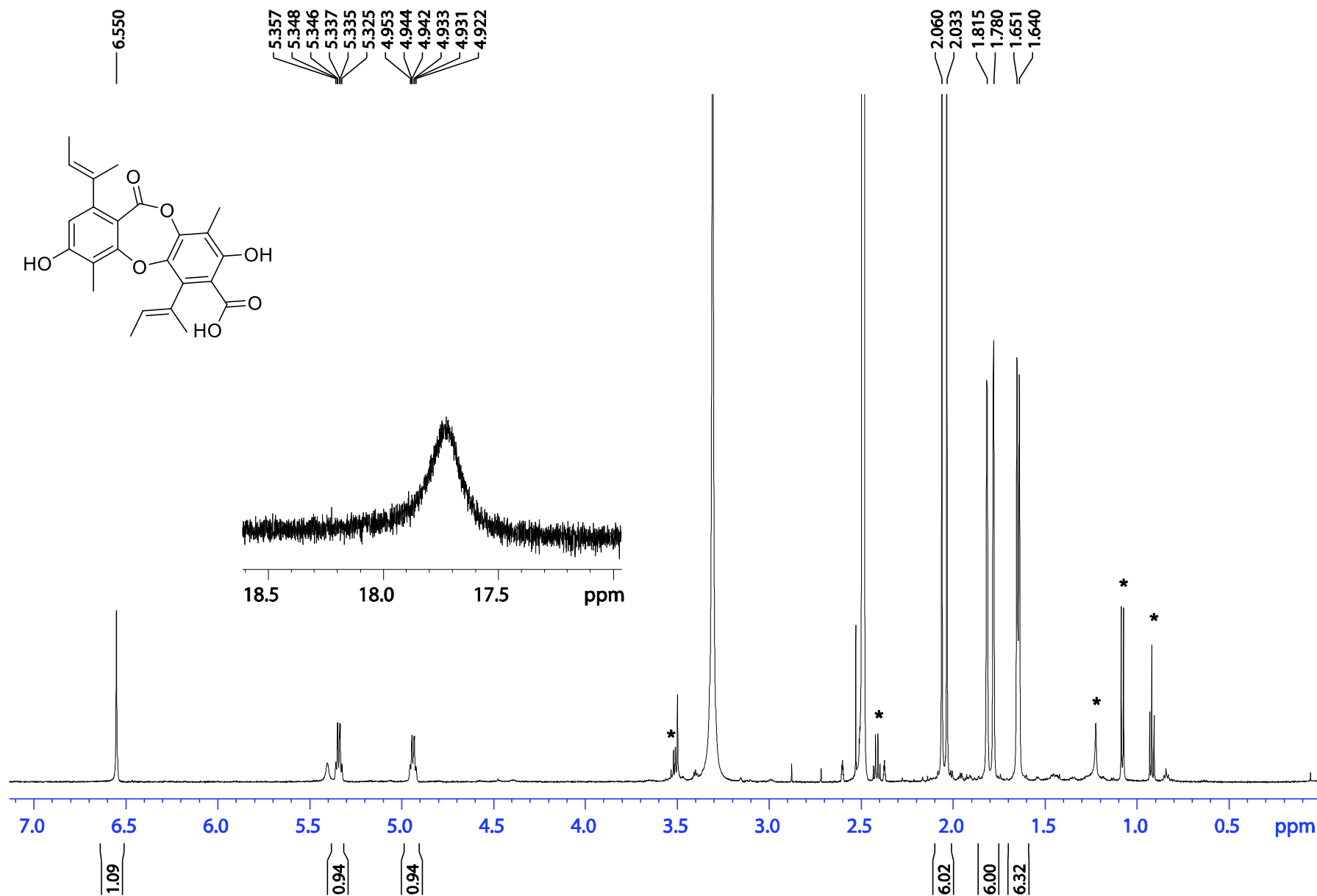


Figure S5. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of 7-carboxyfolipastatin (**1**). * = Minor unrelated impurity

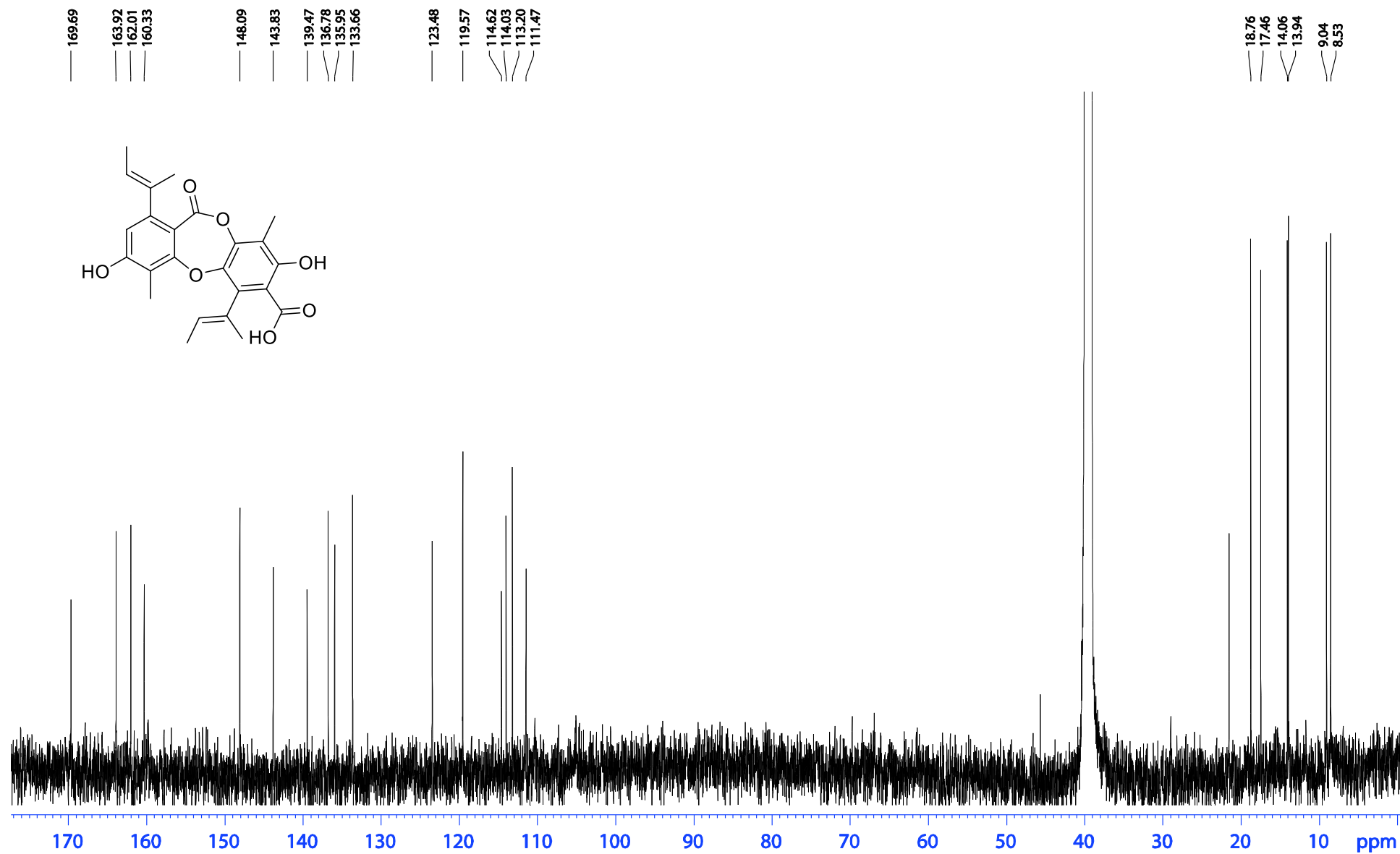


Figure S6. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of 7-carboxyfolipastatin (**1**)

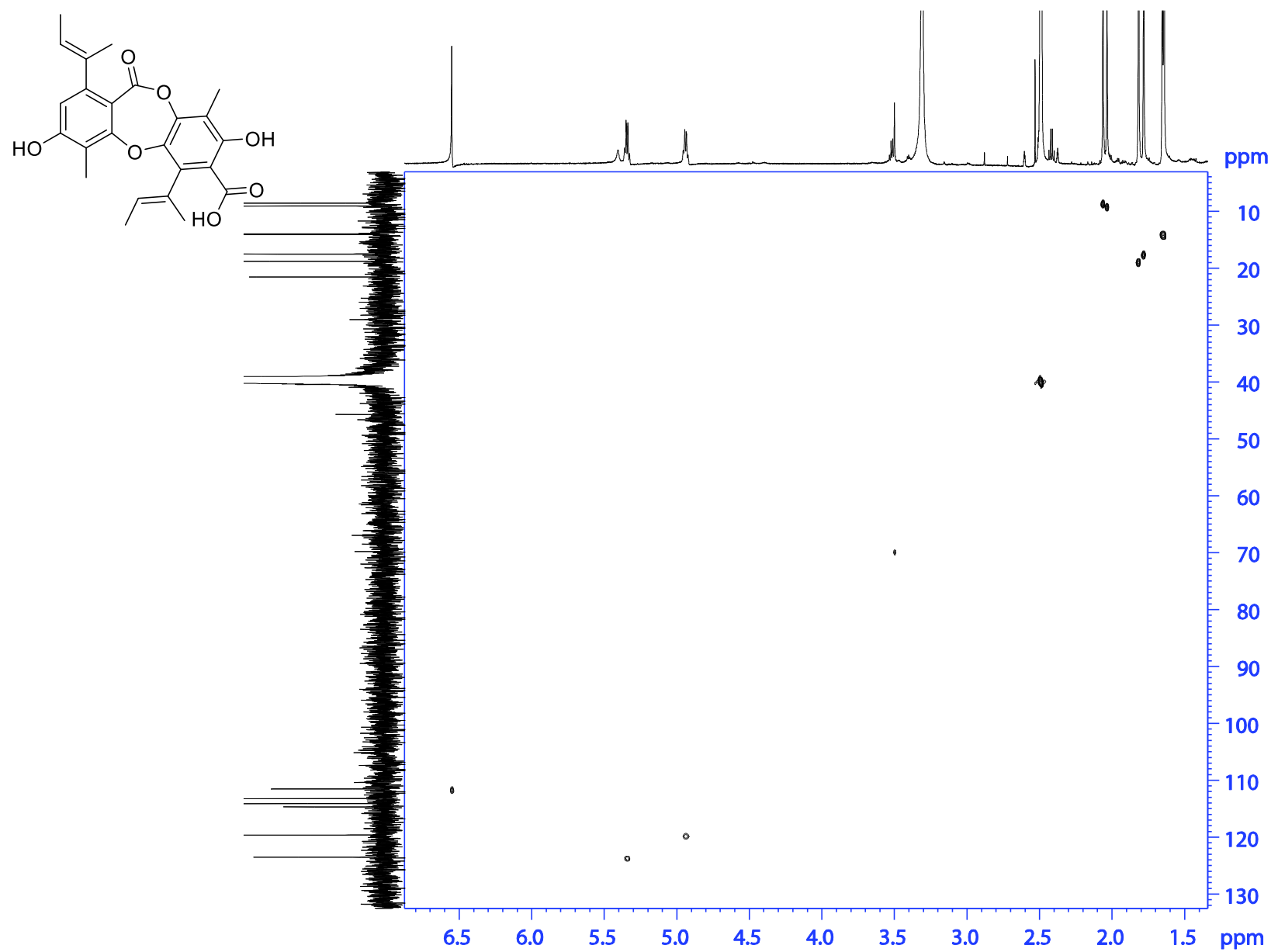


Figure S7. ^1H - ^{13}C HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-carboxyfolipastatin (1)

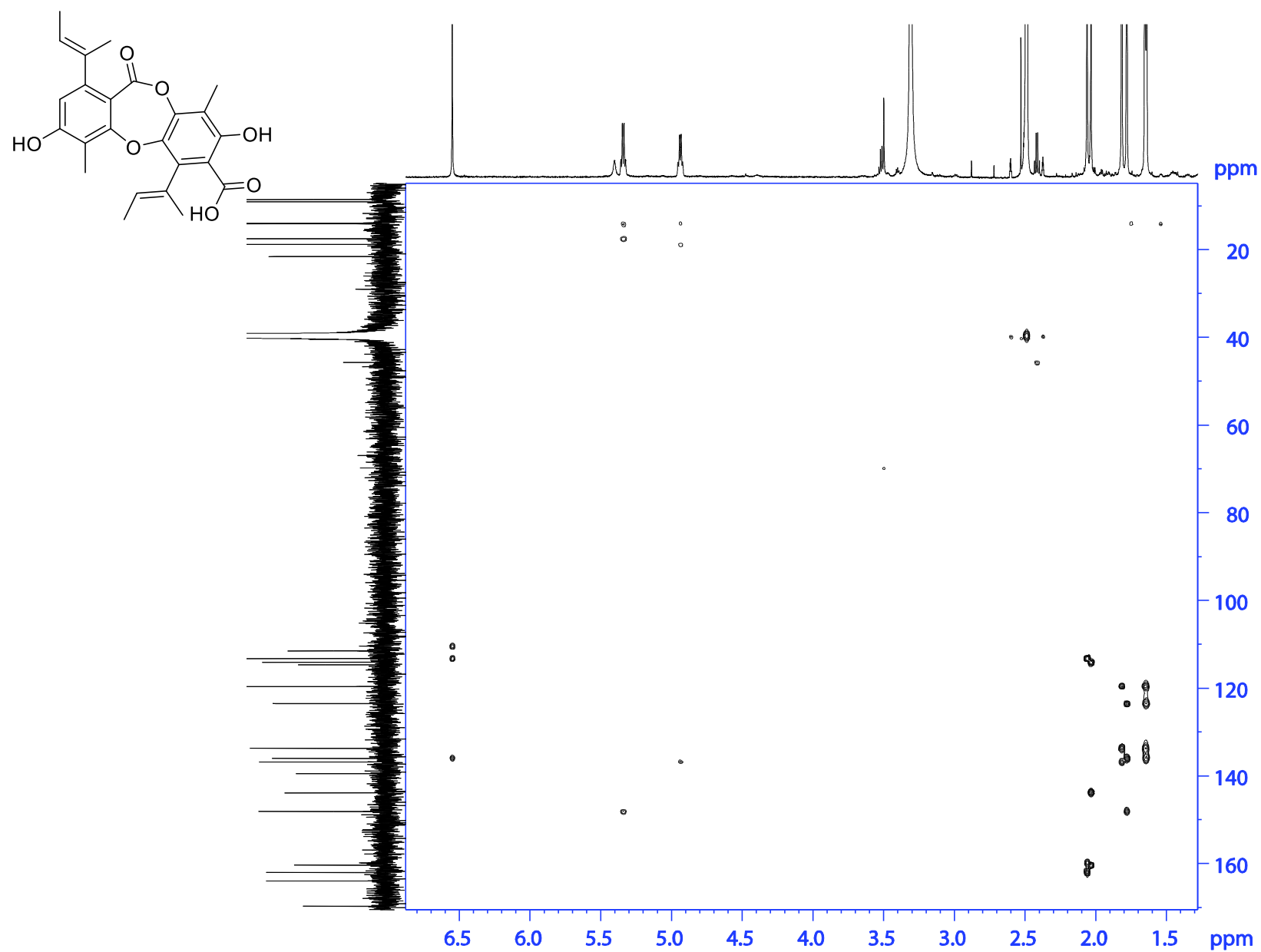


Figure S8. ^1H - ^{13}C HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-carboxyfolipastatin (1)

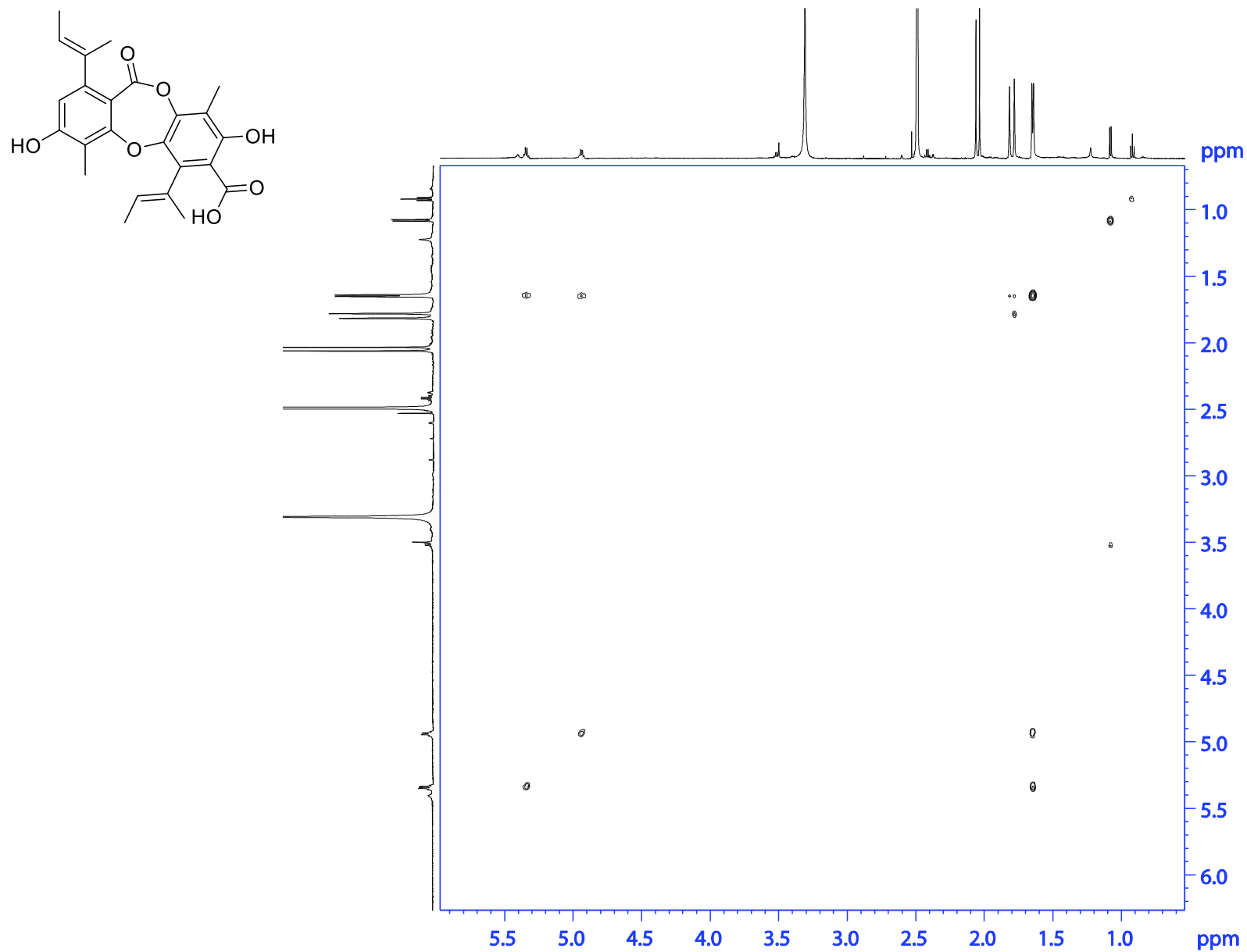


Figure S9. ¹H-¹H COSY NMR spectrum (600 MHz, DMSO-*d*₆) of 7-carboxyfolipastatin (**1**)

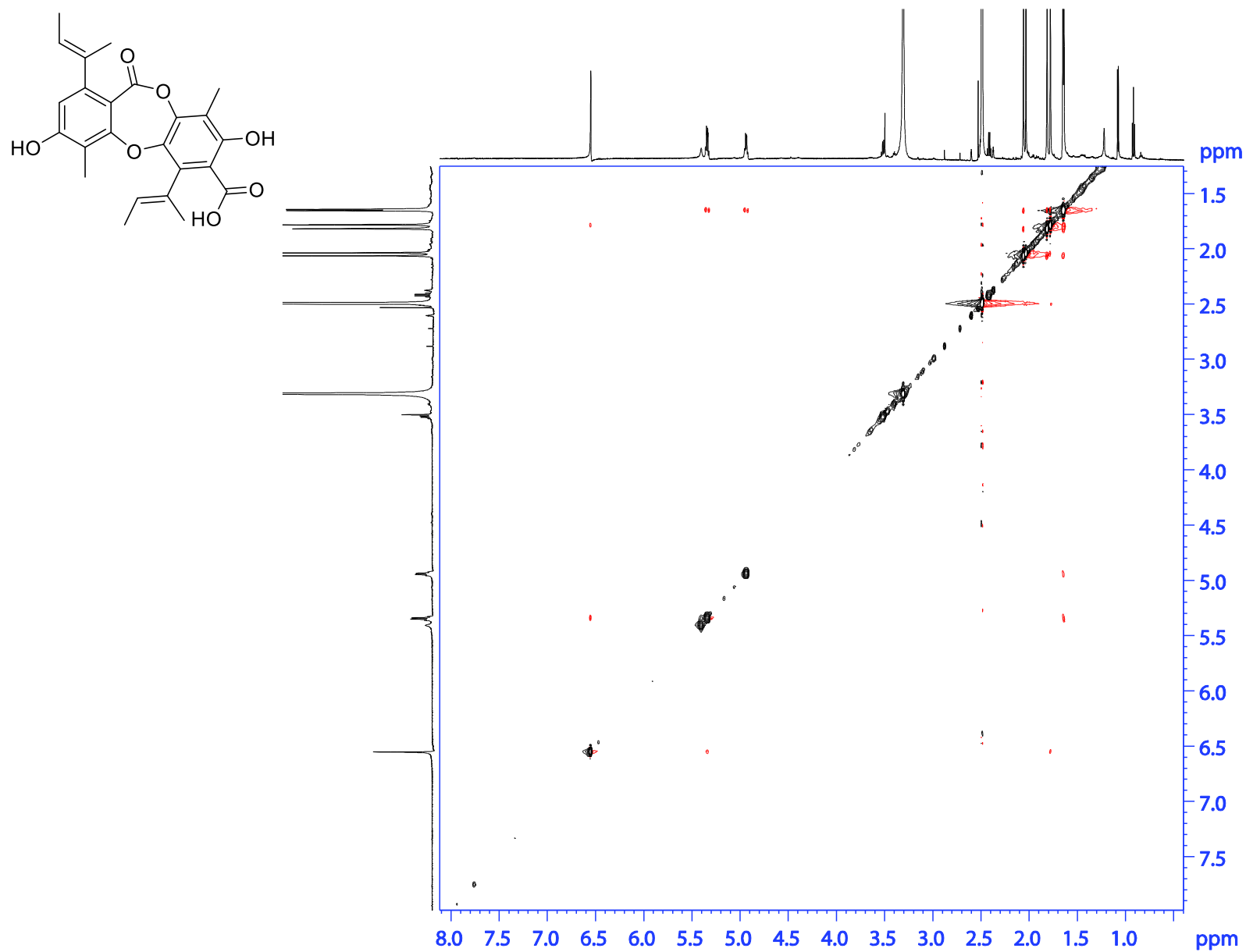


Figure S10. ^1H - ^1H ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-carboxyfolipastatin (**1**)

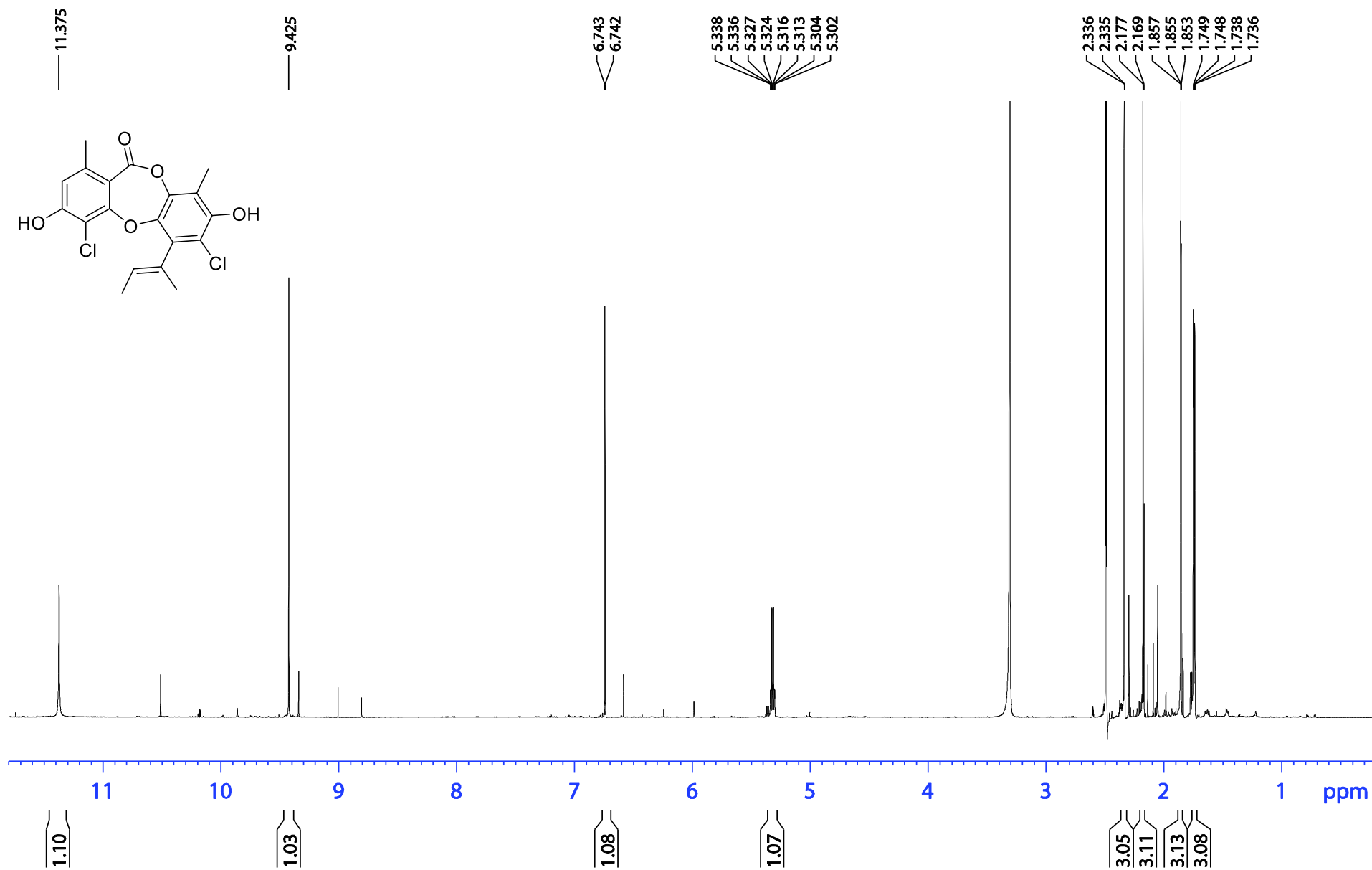


Figure S11. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of 4,7-dichlorounginol (2)

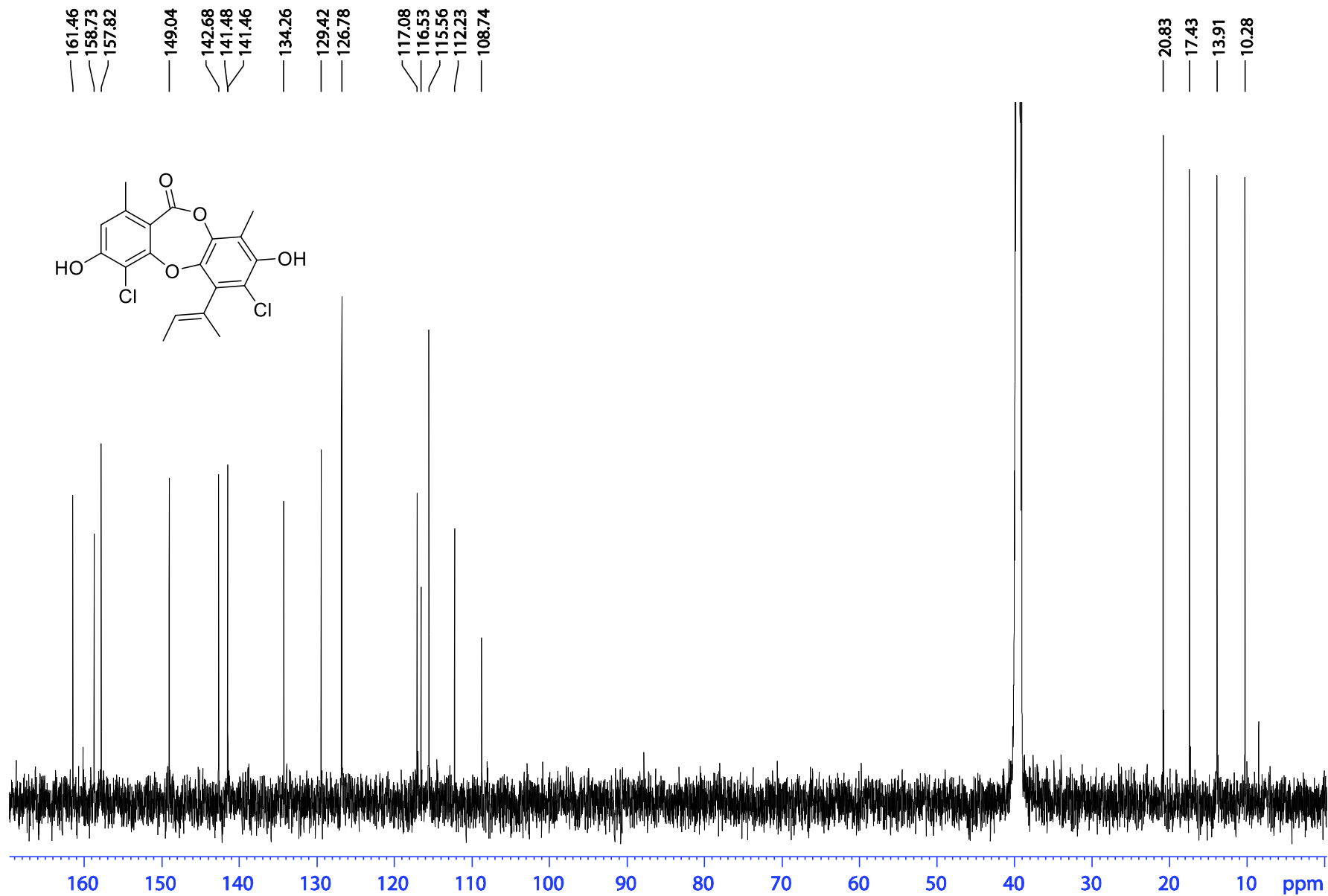


Figure S12. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of 4,7-dichlorounguinol (2)

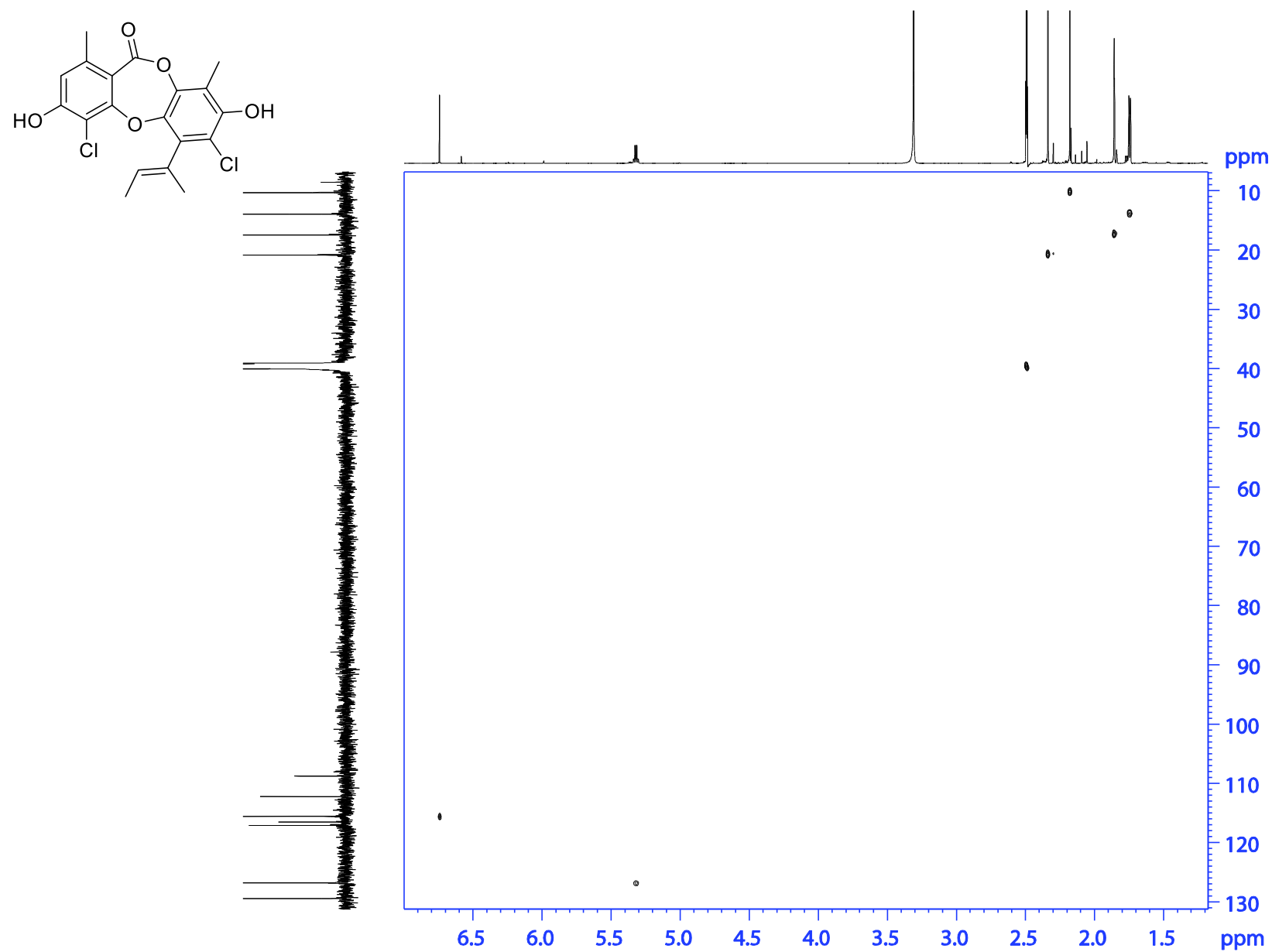


Figure S13. ¹H-¹³C HSQC NMR spectrum (600 MHz, DMSO-*d*₆) of 4,7-dichlorounguinol (2)

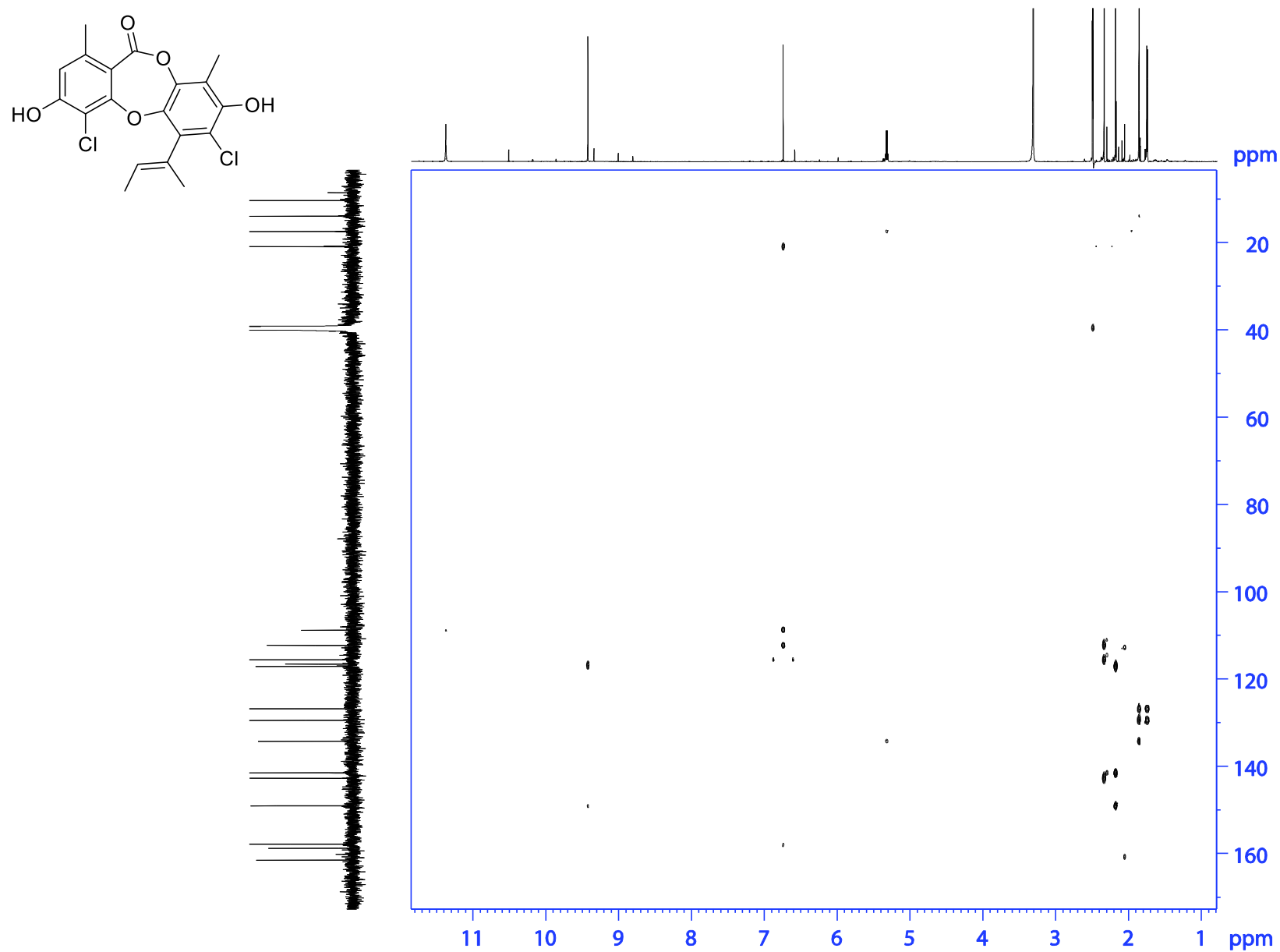


Figure S14. ^1H - ^{13}C HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 4,7-dichlorounguinol (2)

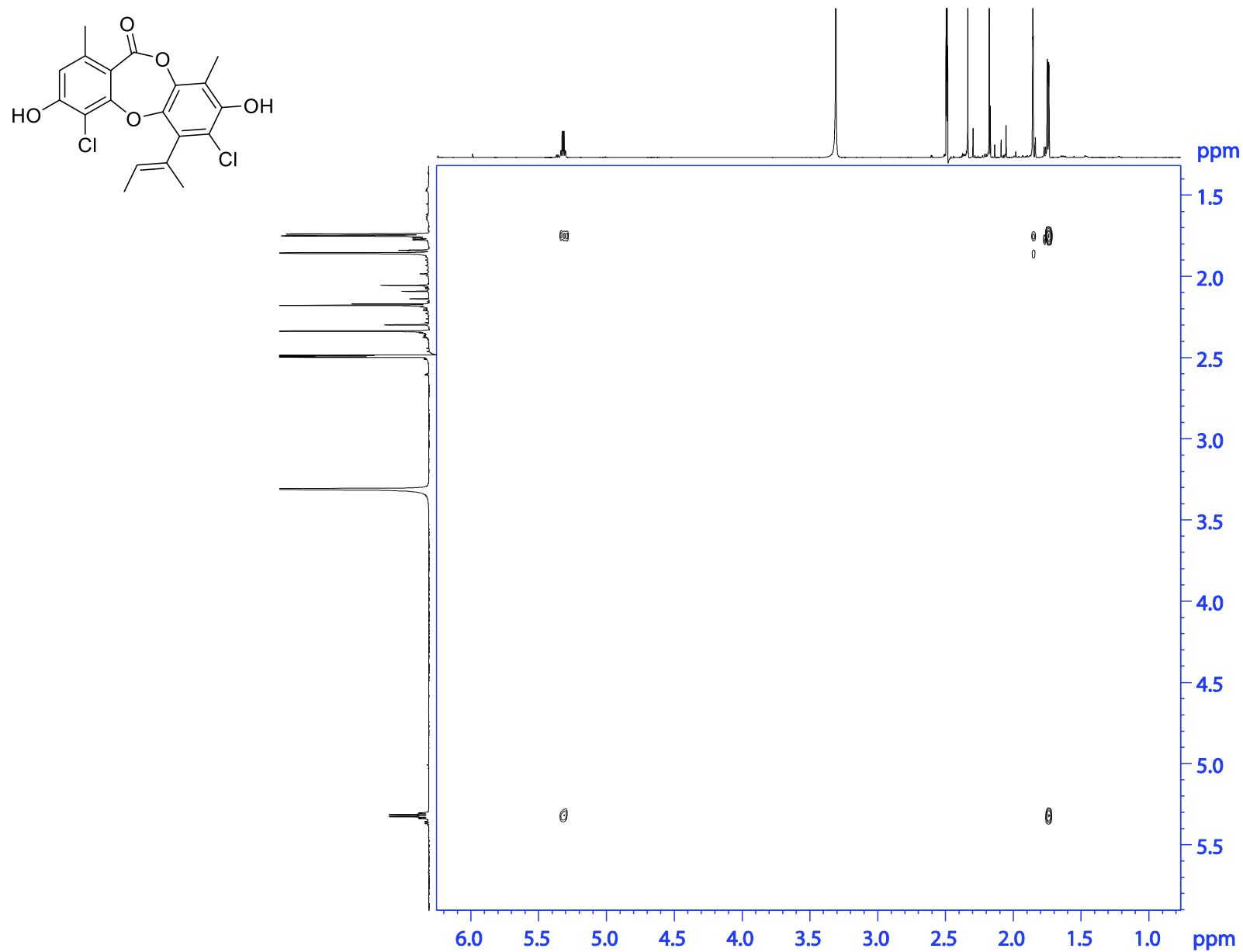


Figure S15. ^1H - ^1H COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 4,7-dichlorounguinol (2)

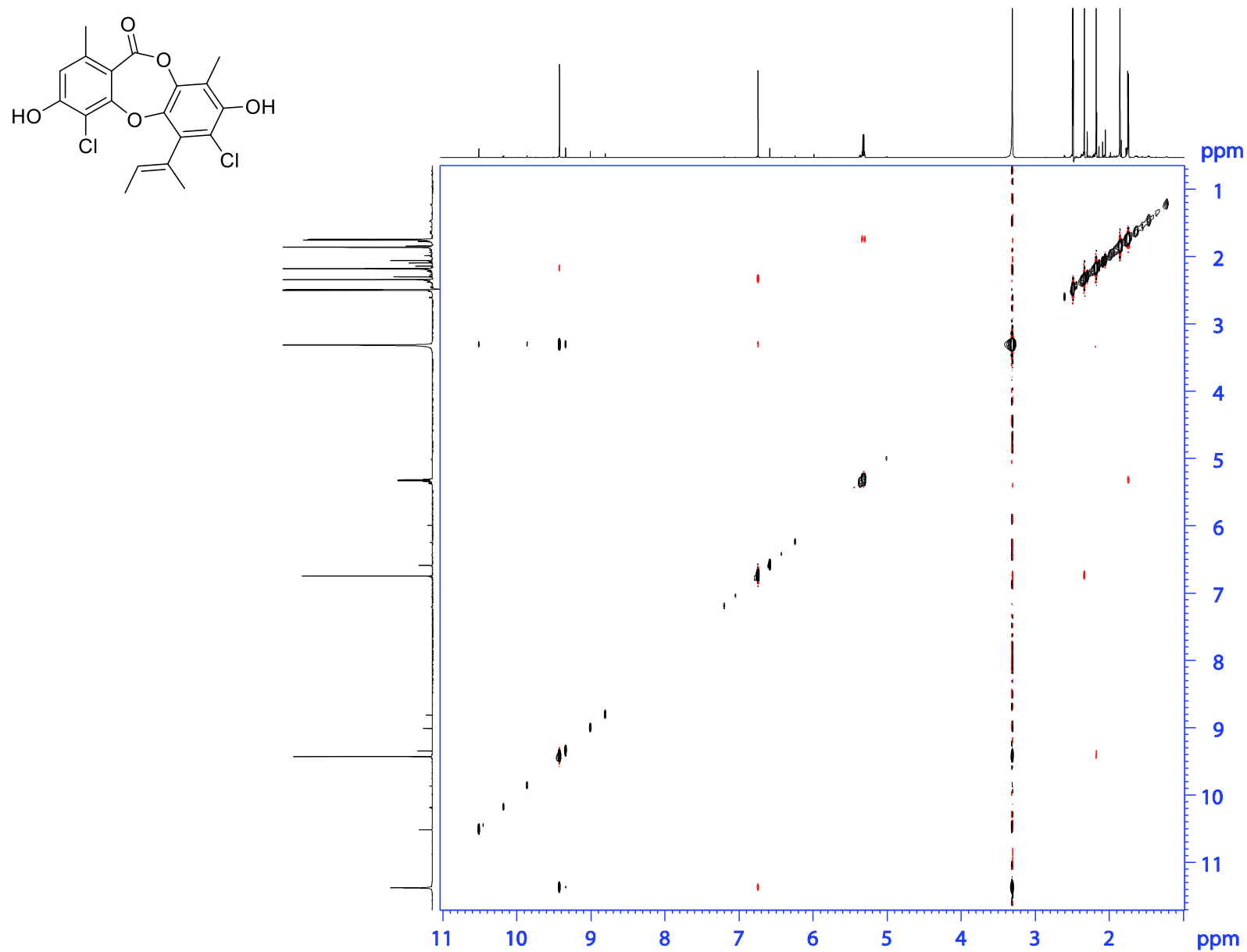


Figure S16. ^1H - ^1H ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 4,7-dichlorounginol (2)

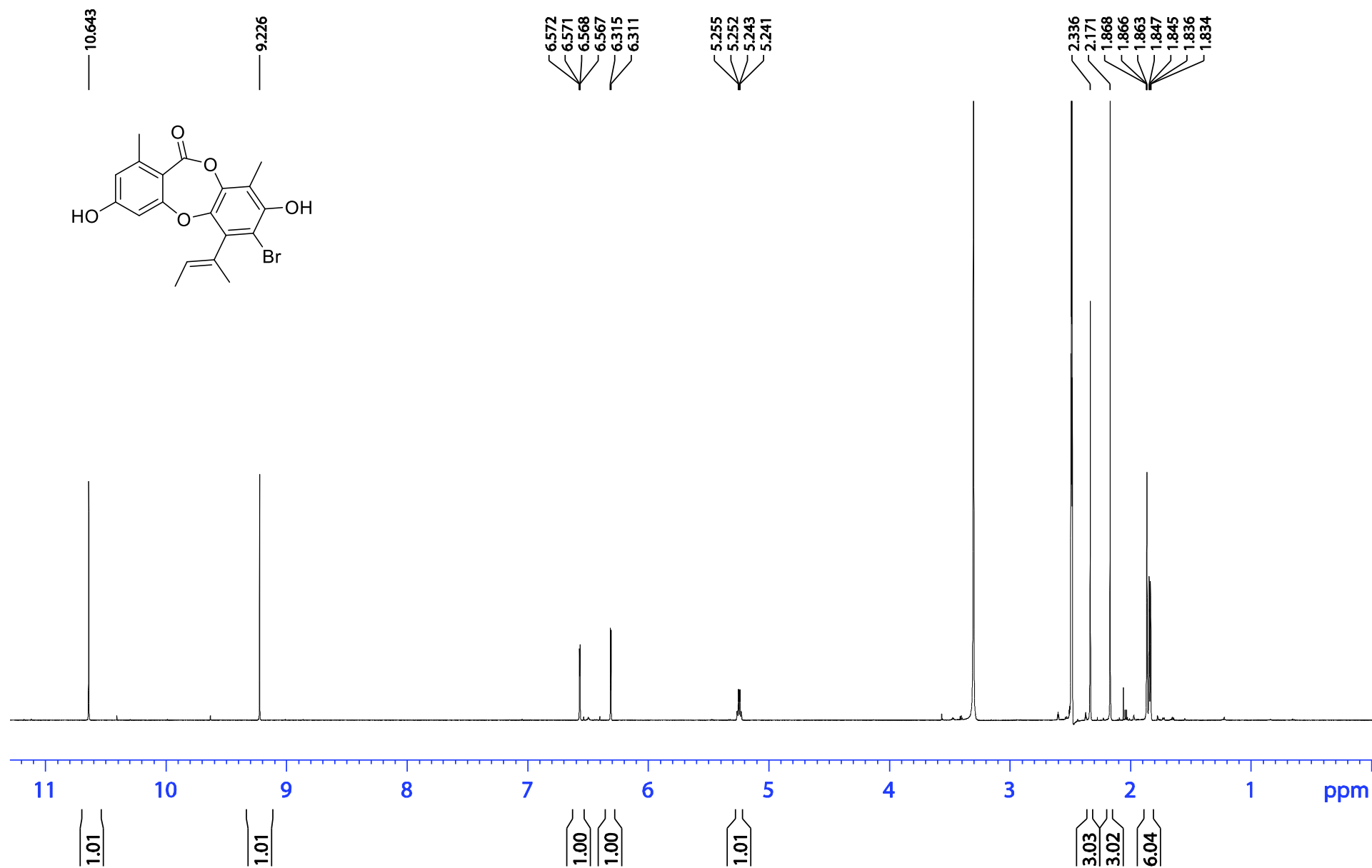


Figure S17. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of 7-bromounguiol (3)

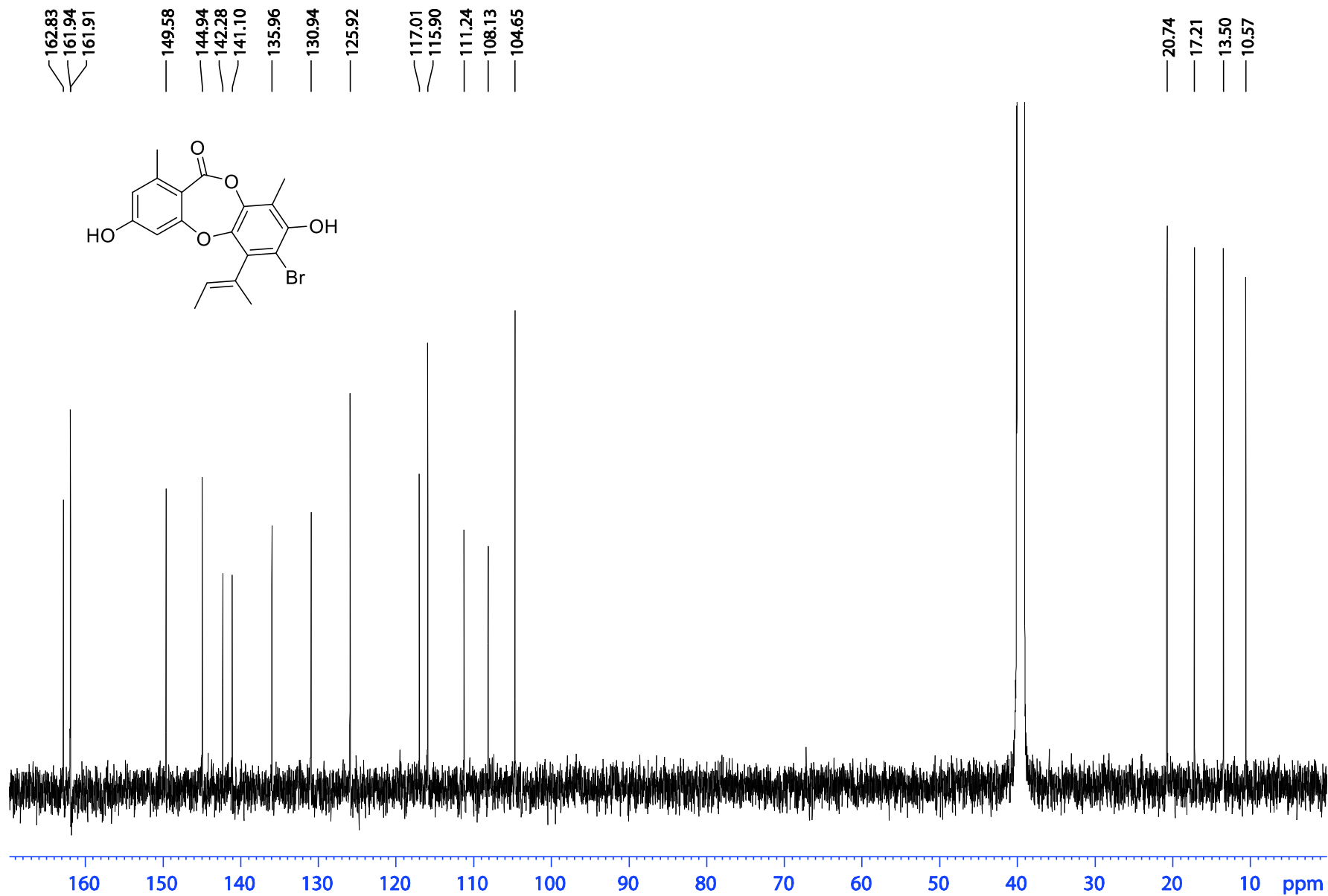


Figure S18. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of 7-bromounguinol (3)

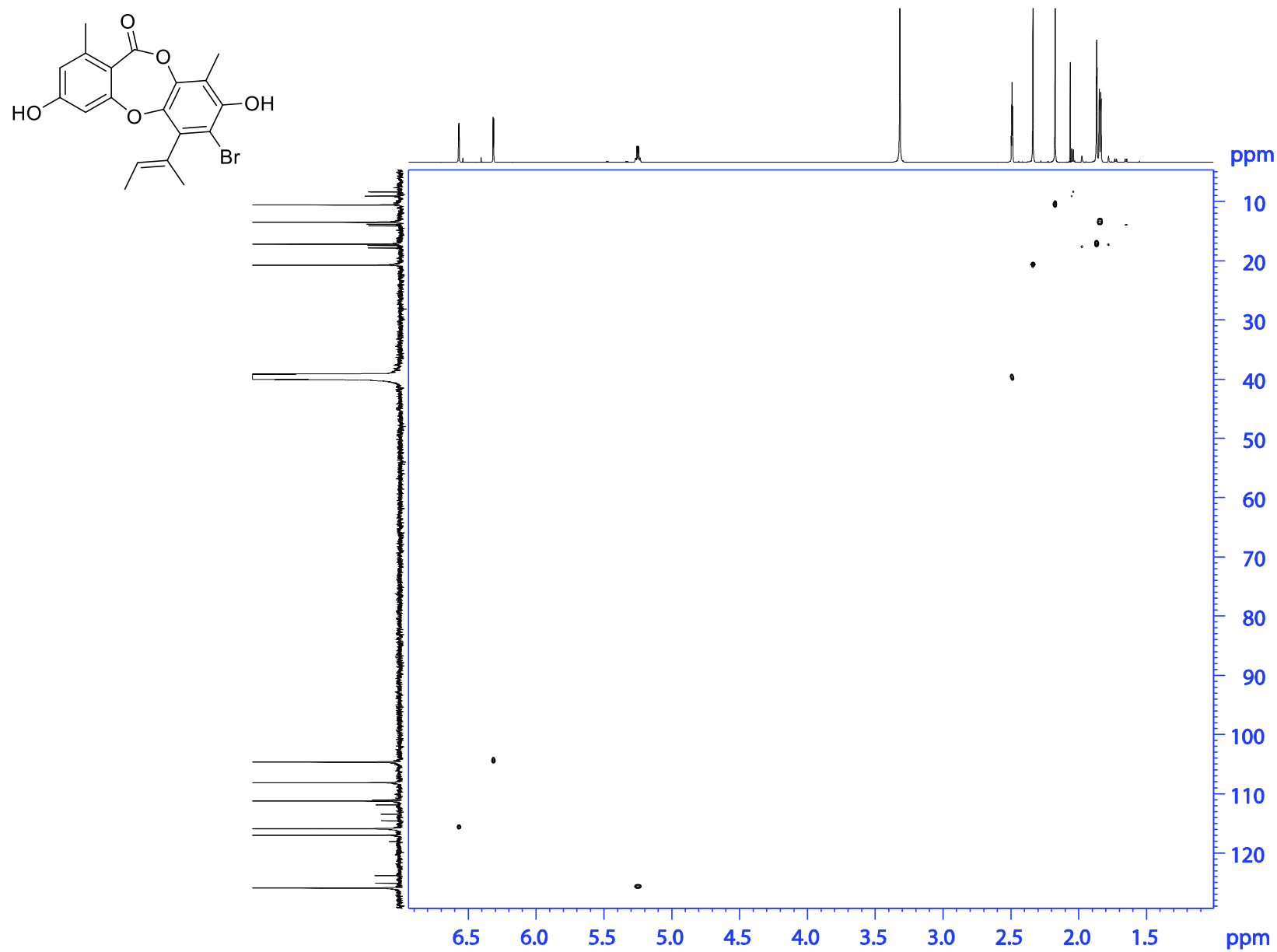


Figure S19. ^1H - ^{13}C HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguiol (3)

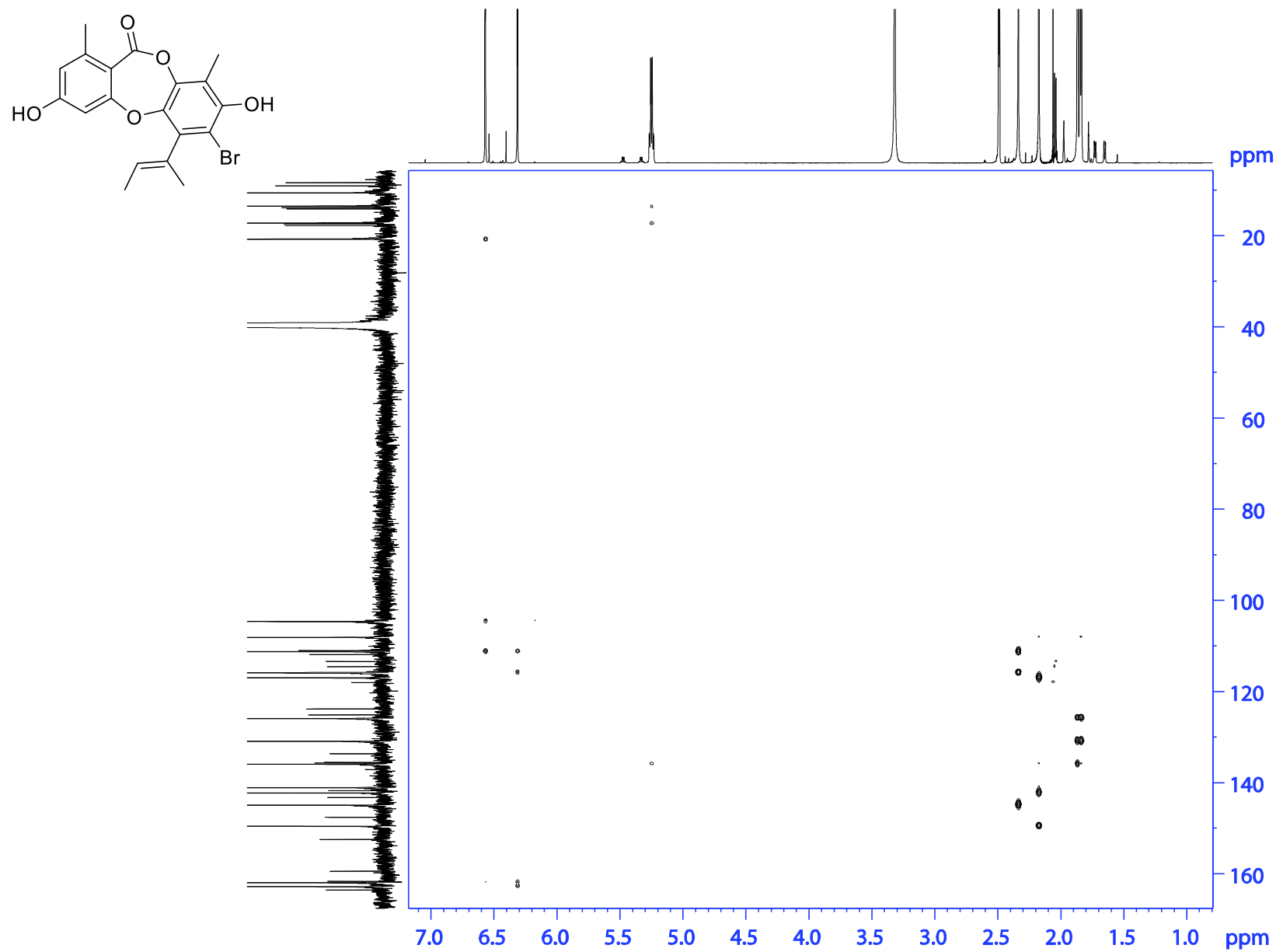


Figure S20. ^1H - ^{13}C HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguinol (3)

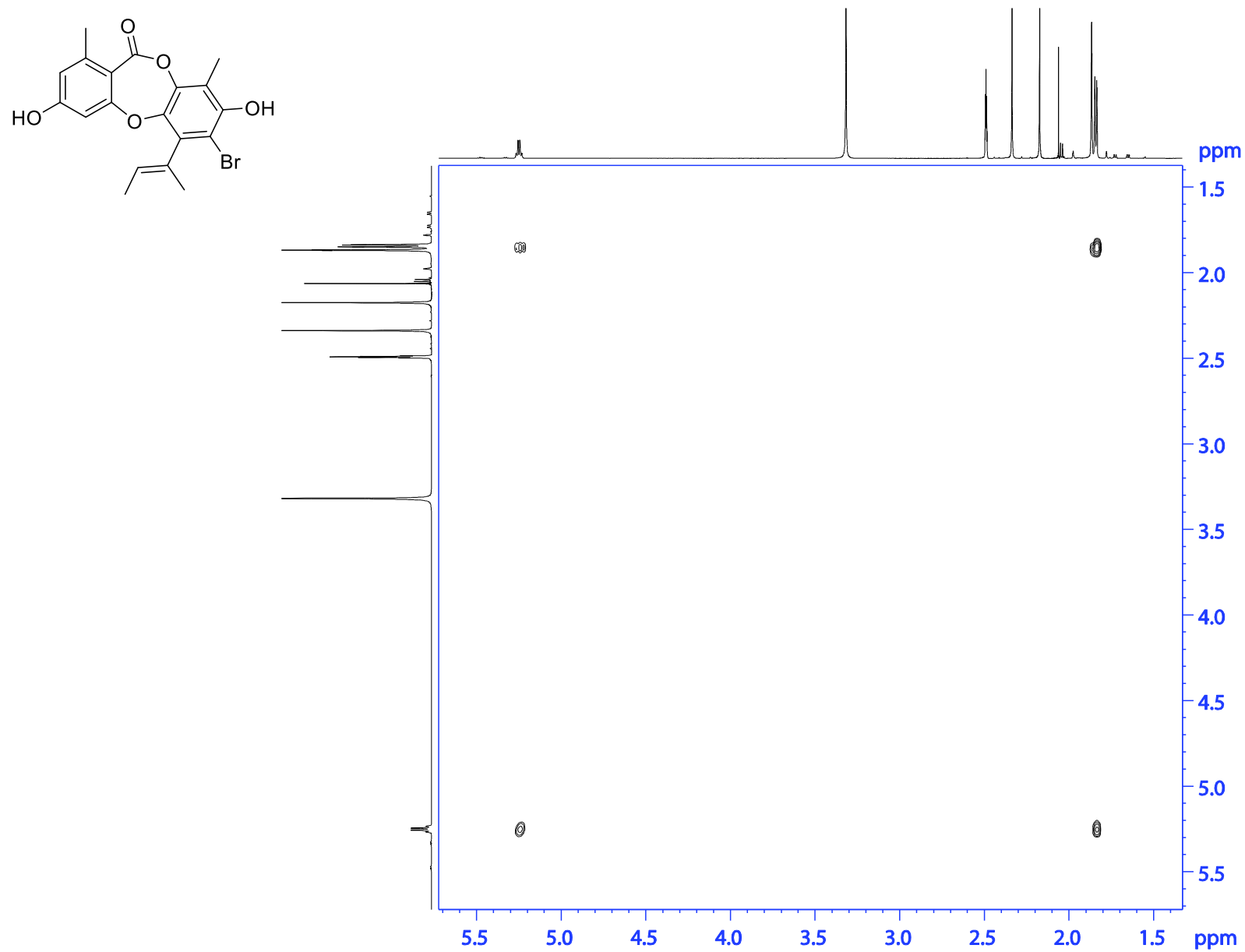


Figure S21. ^1H - ^1H COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguiol (3)

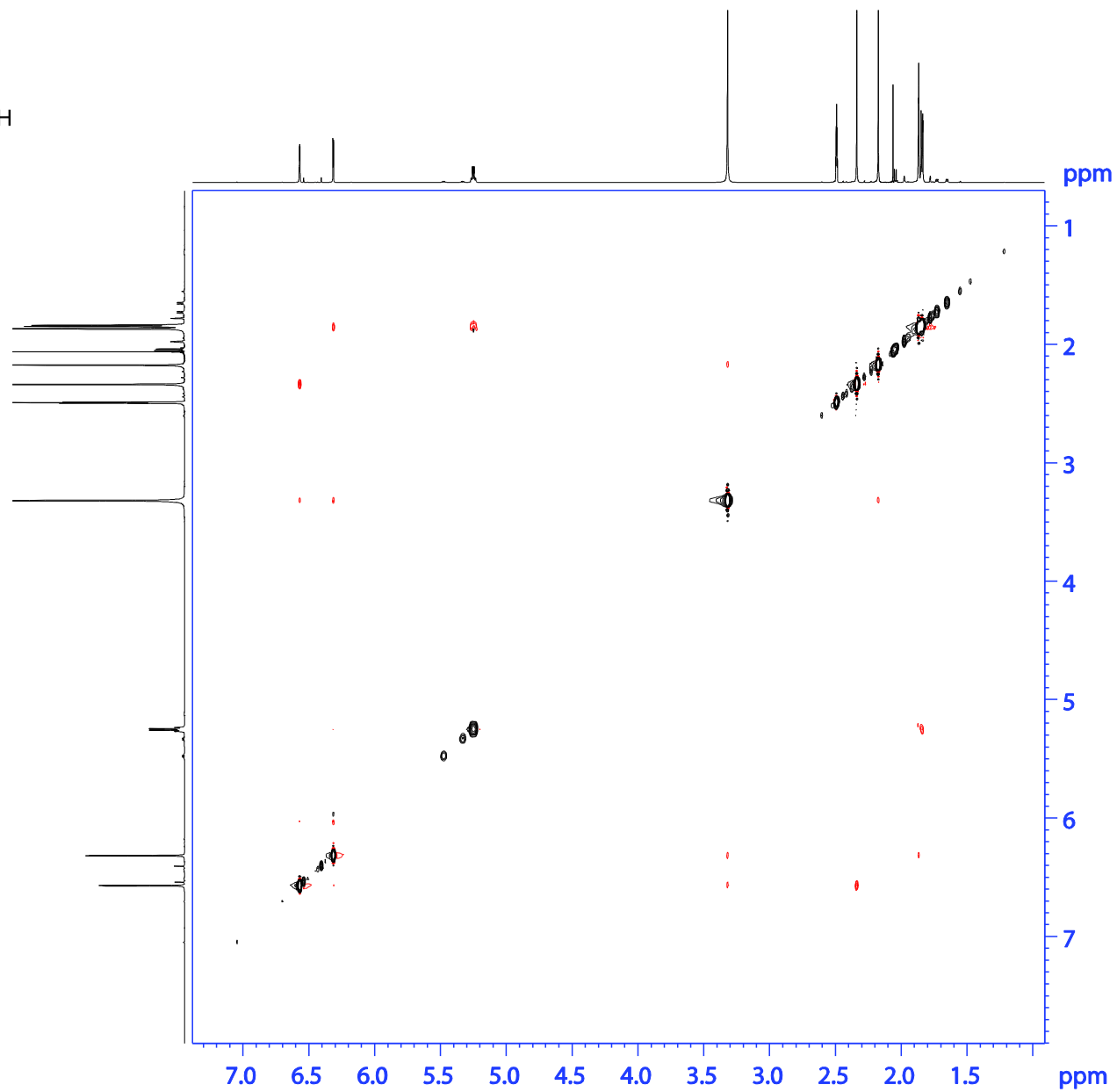
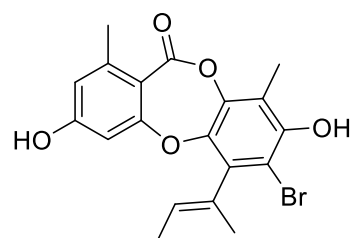


Figure S22. ^1H - ^1H ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromounguinol (**3**)

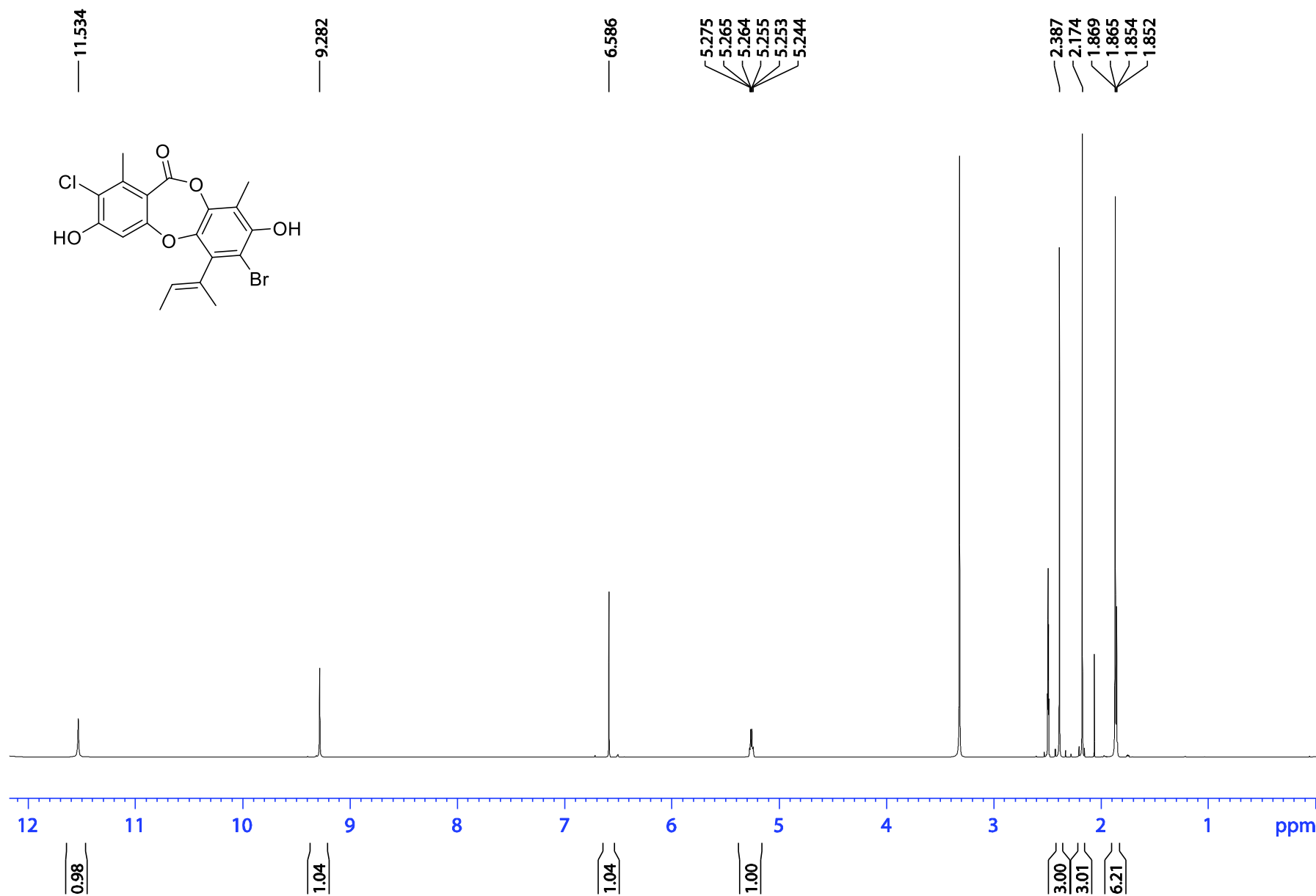


Figure S23. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of 2-chloro-7-bromounguiol (4)

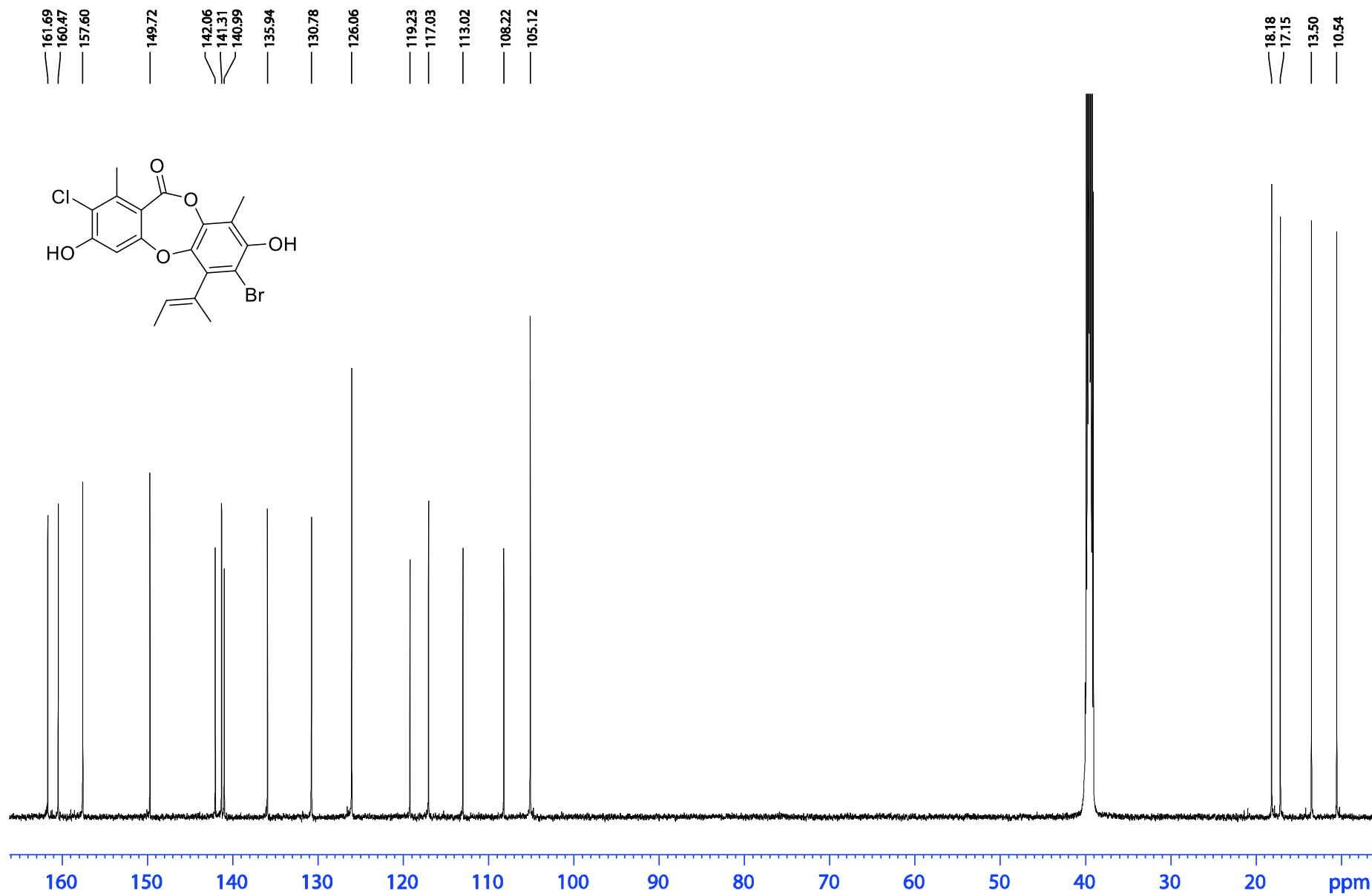


Figure S24. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of 2-chloro-7-bromounguinol (4)

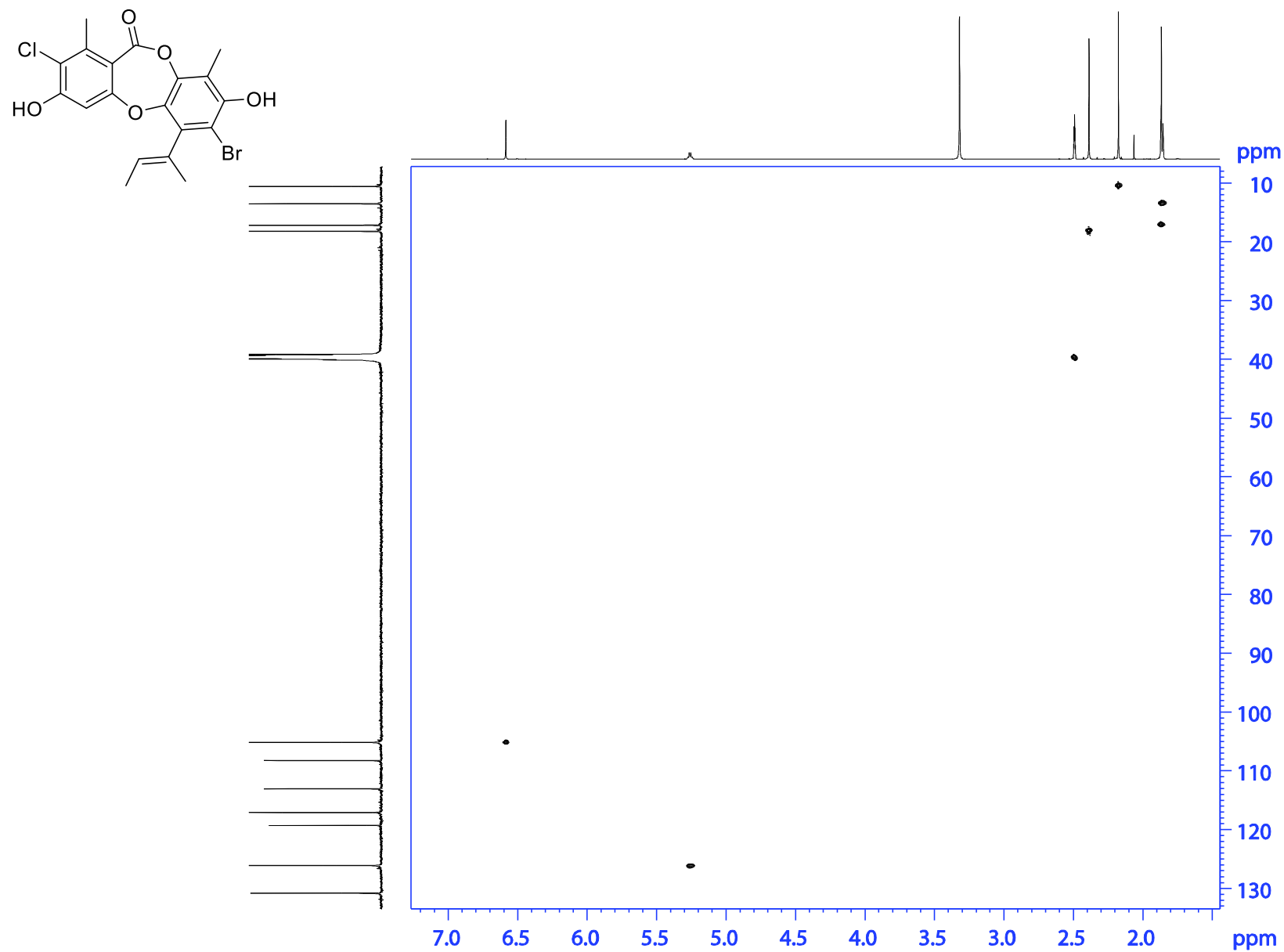


Figure S25. ¹H-¹³C HSQC NMR spectrum (600 MHz, DMSO-*d*₆) of 2-chloro-7-bromounguinol (**4**)

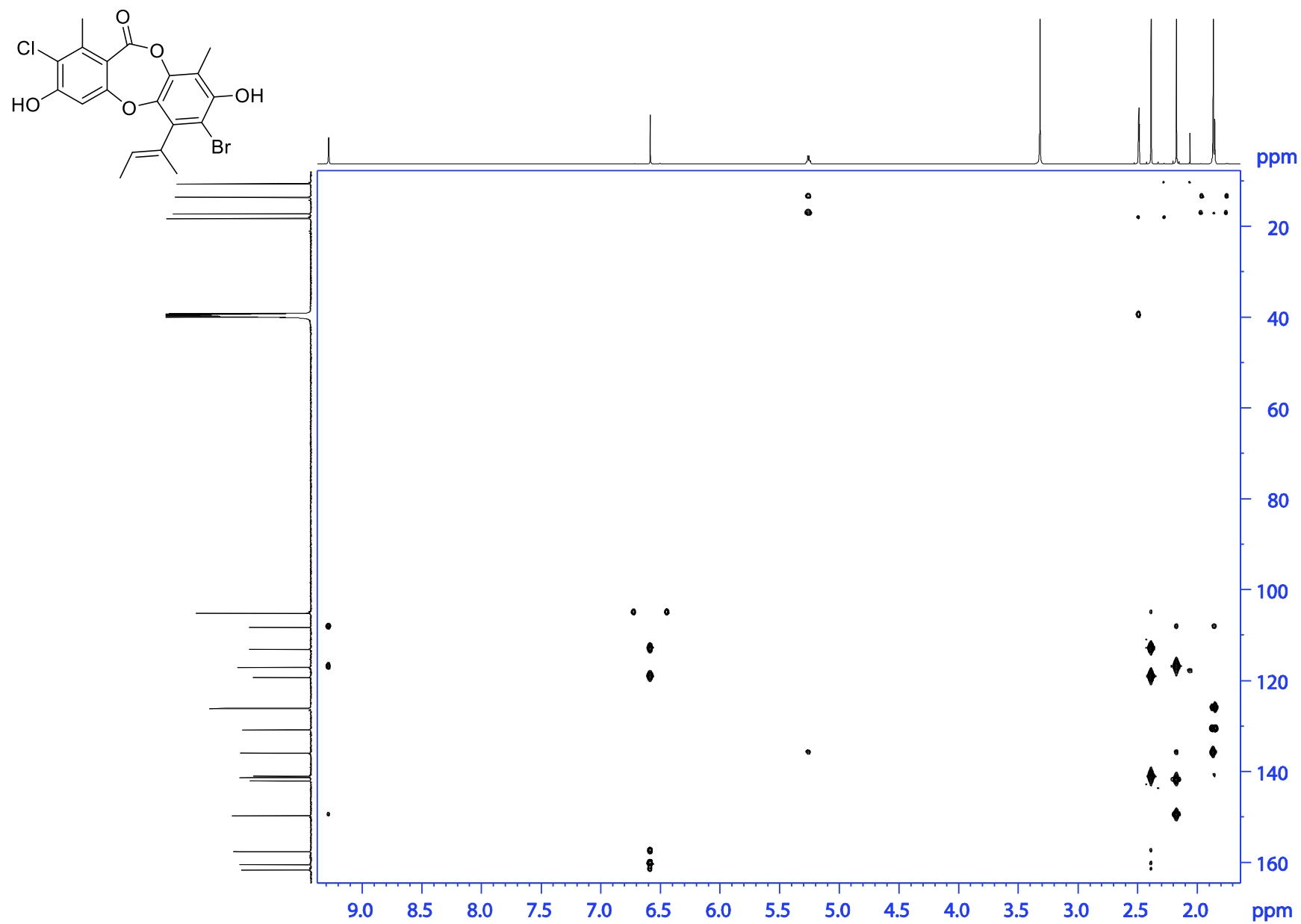


Figure S26. ^1H - ^{13}C HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguinol (**4**)

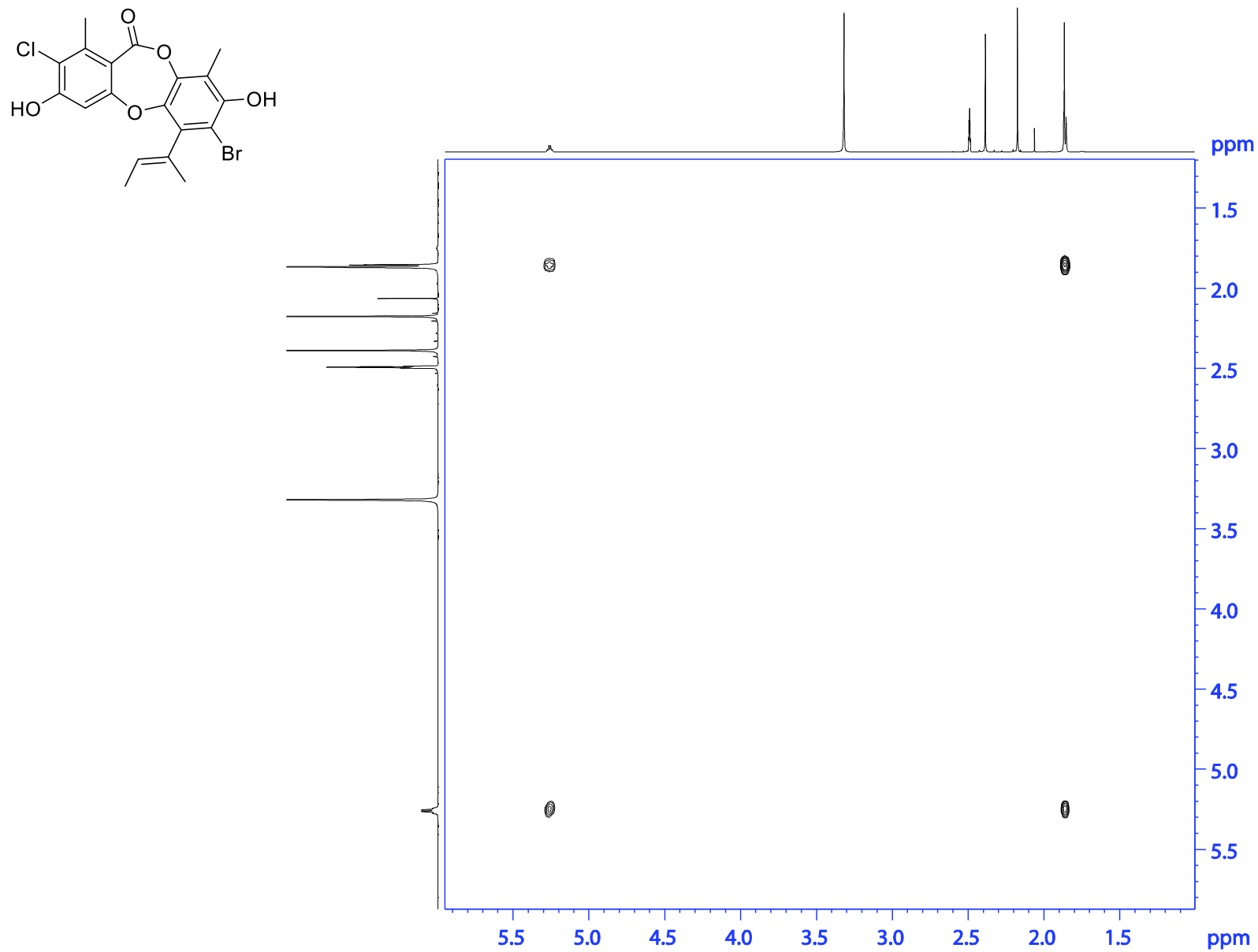


Figure S27. ^1H - ^1H COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguinol (4)

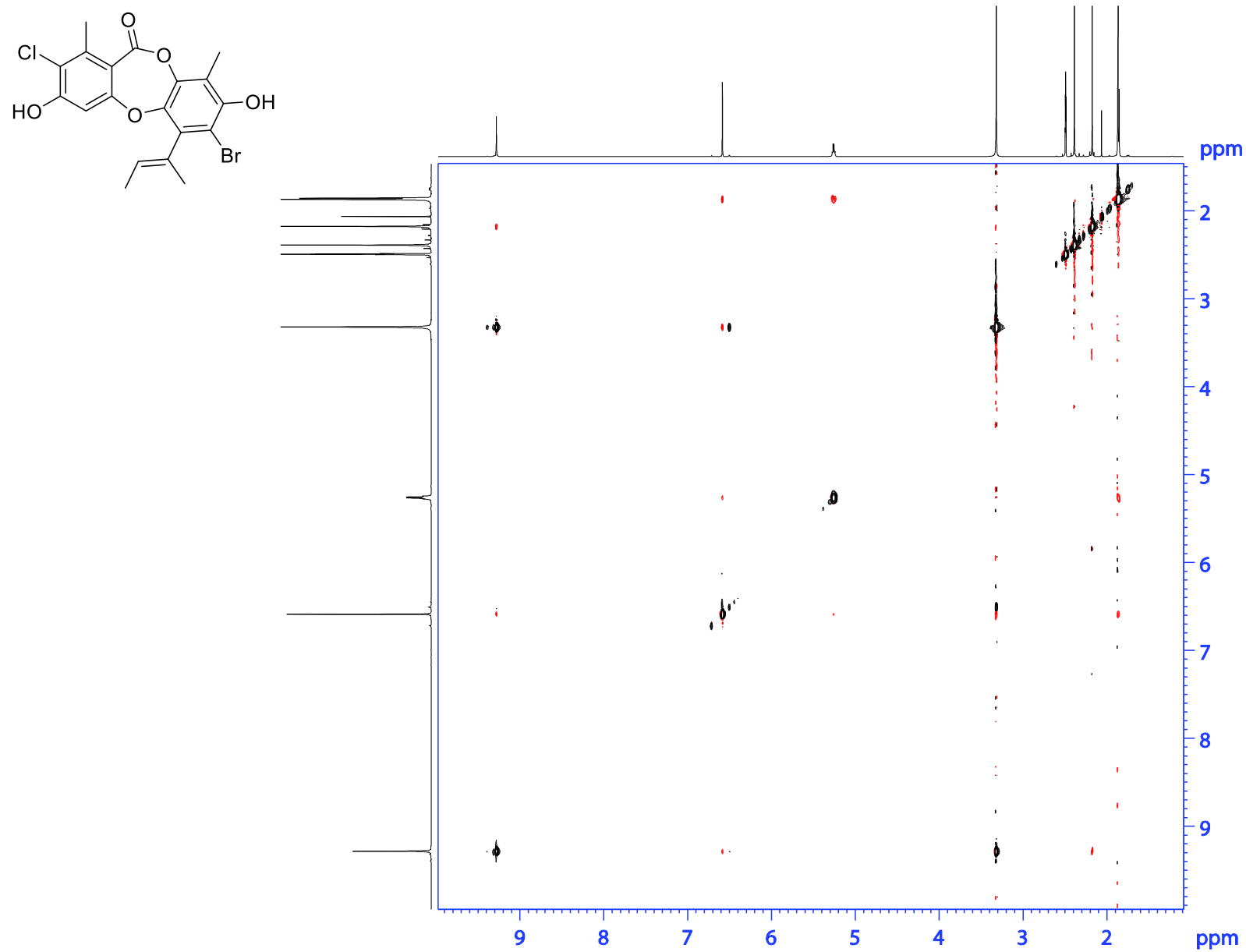


Figure S28. ^1H - ^1H ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 2-chloro-7-bromounguiol (4)

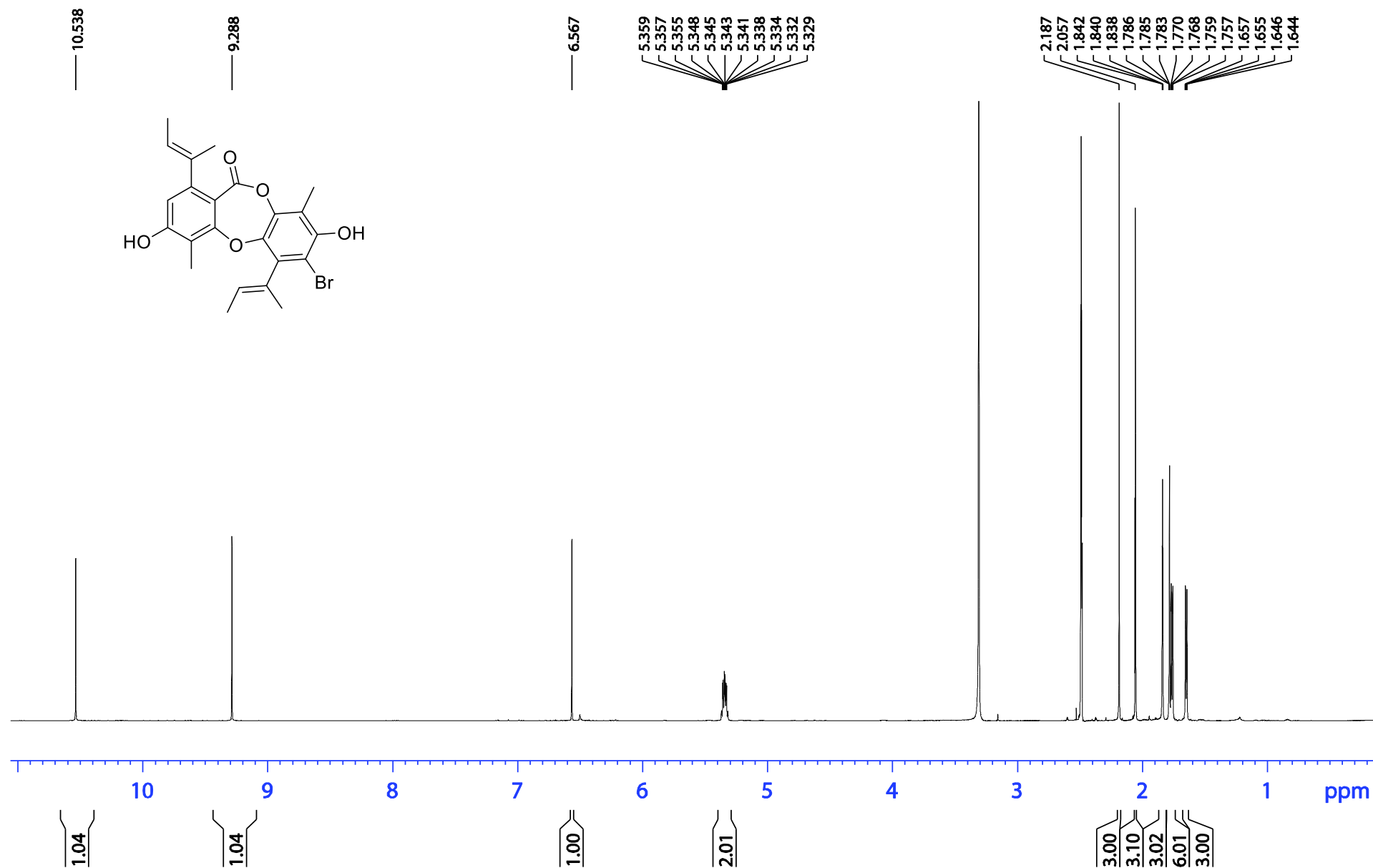


Figure S29. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)

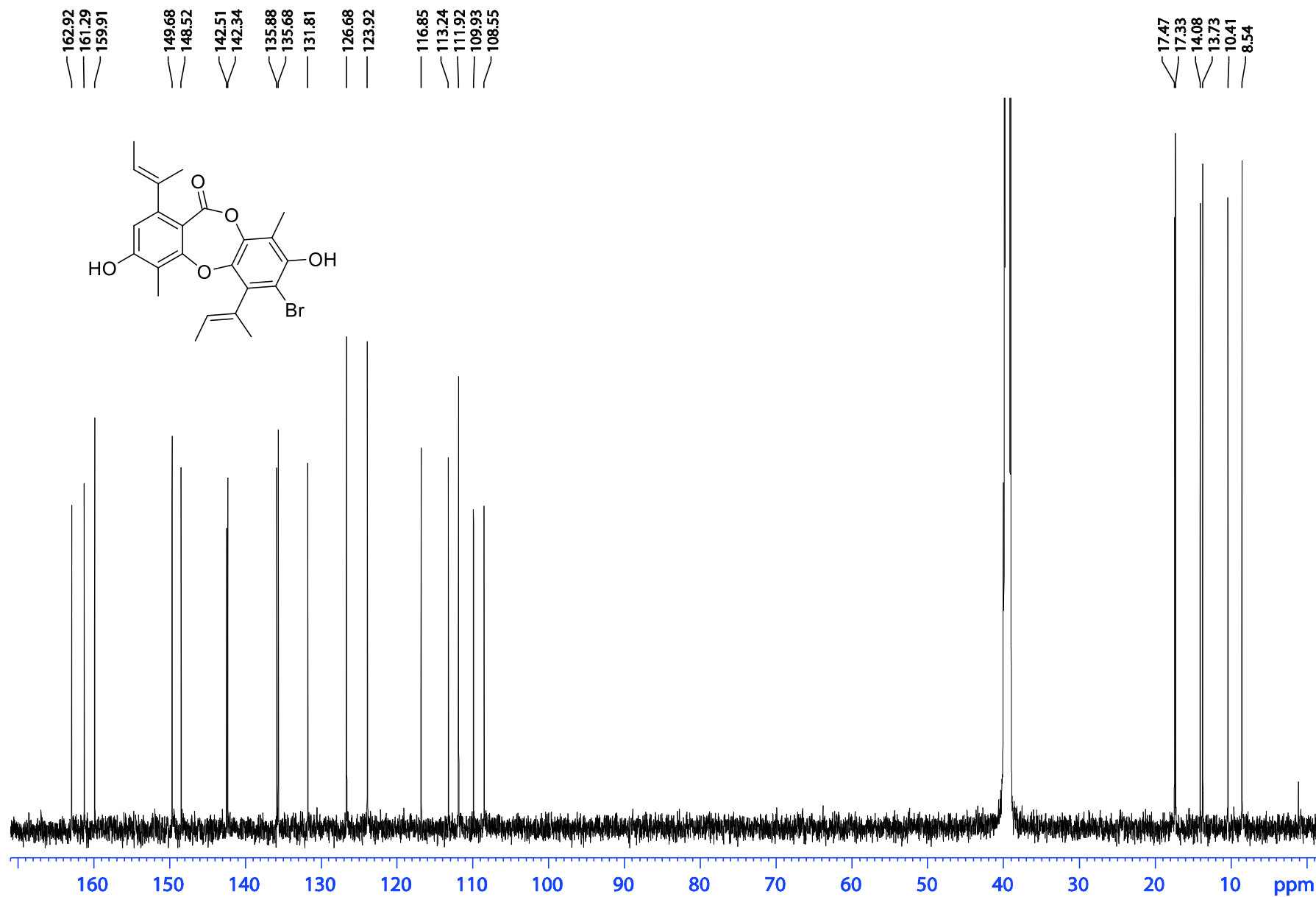


Figure S30. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of 7-bromofolipastatin (5)

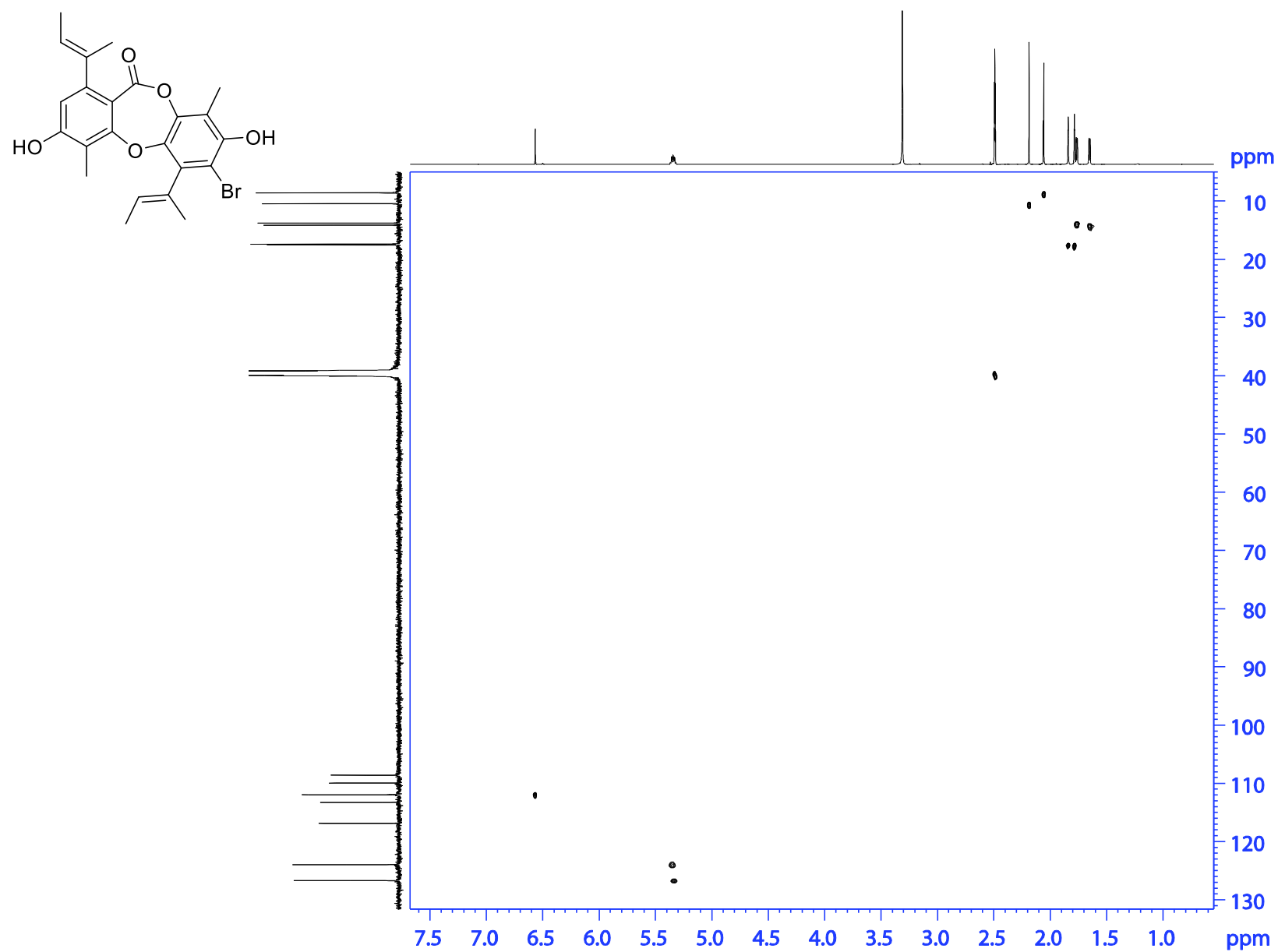


Figure S31. ^1H - ^{13}C HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)

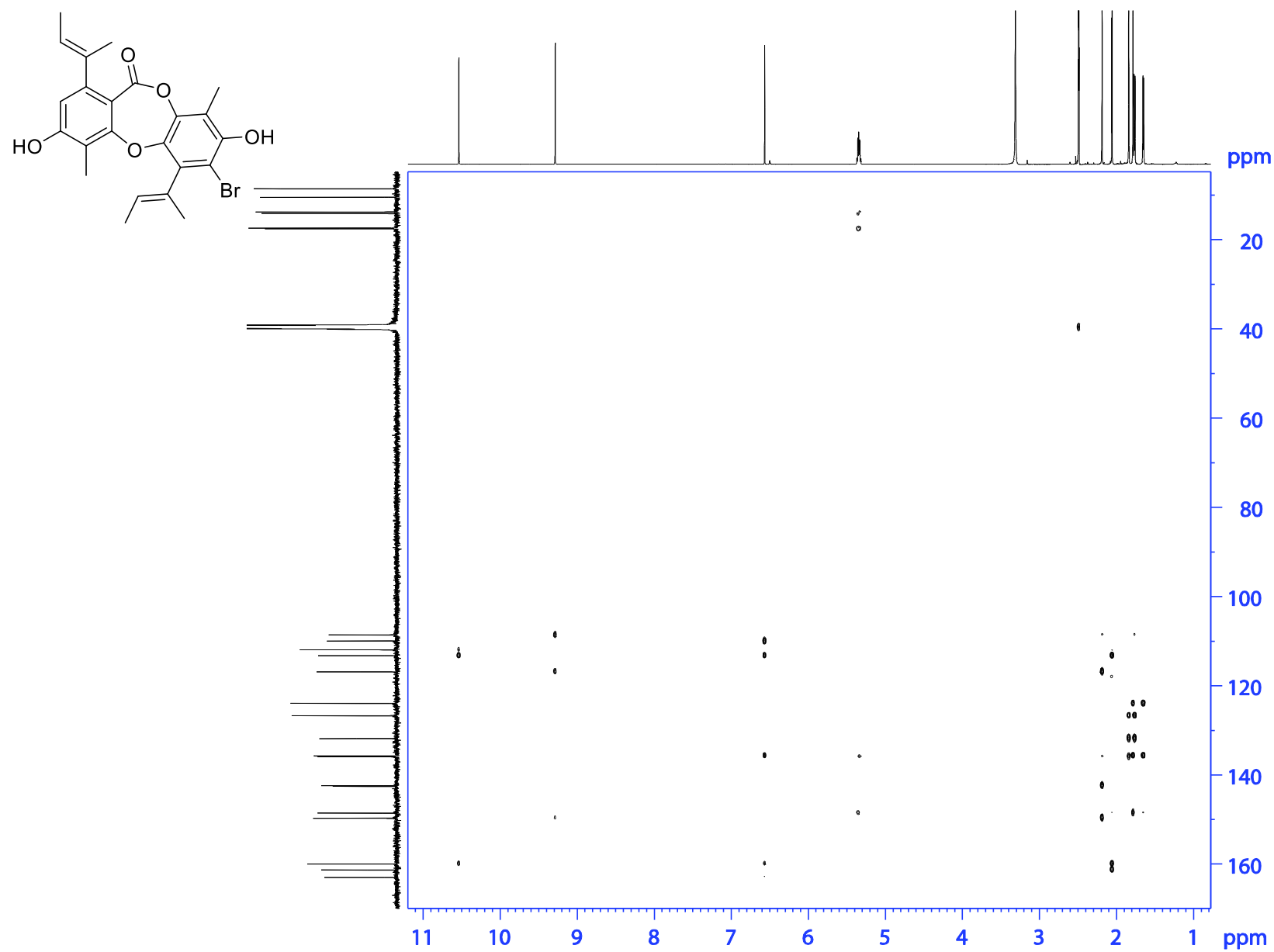


Figure S32. ^1H - ^{13}C HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)

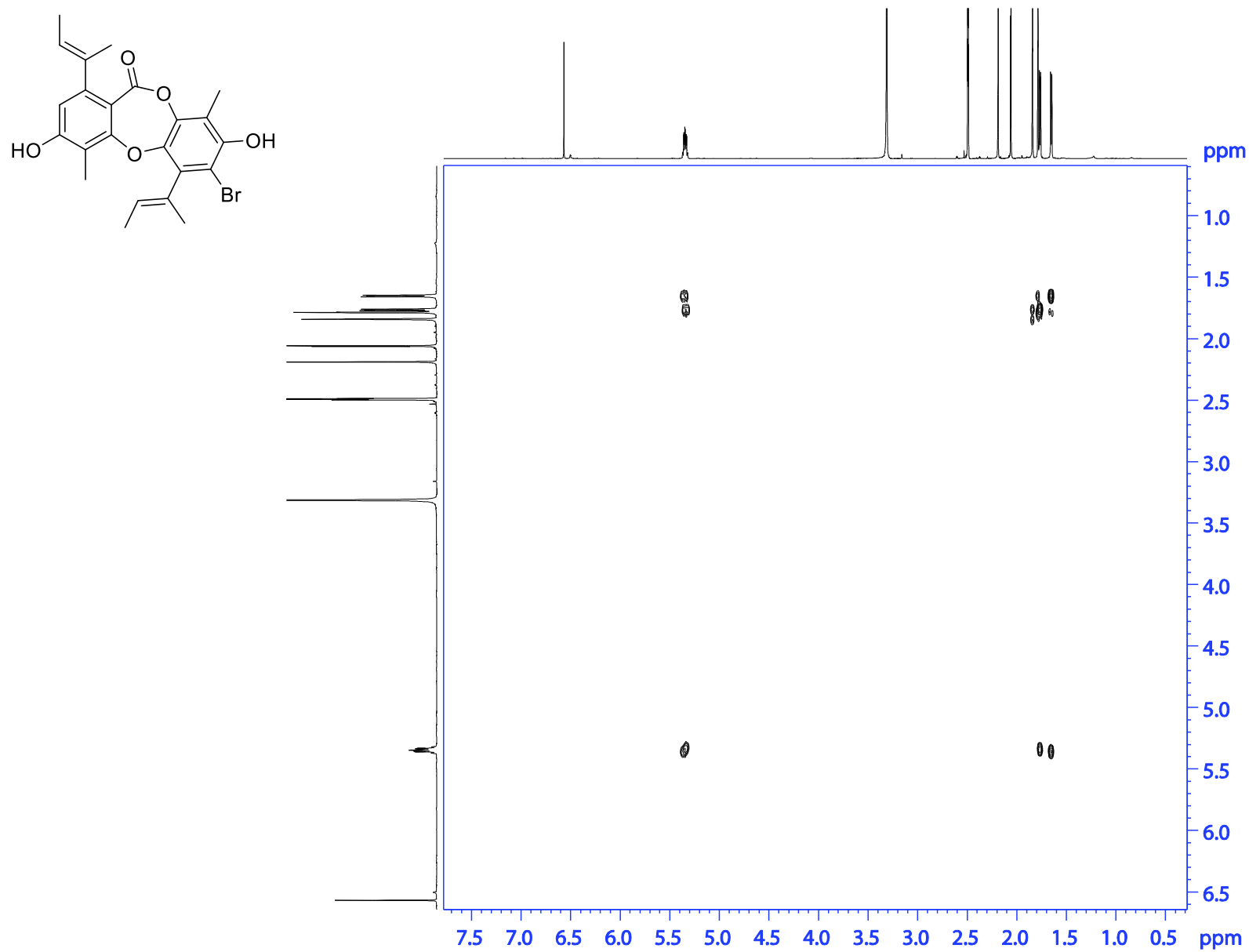


Figure S33. ^1H - ^1H COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)

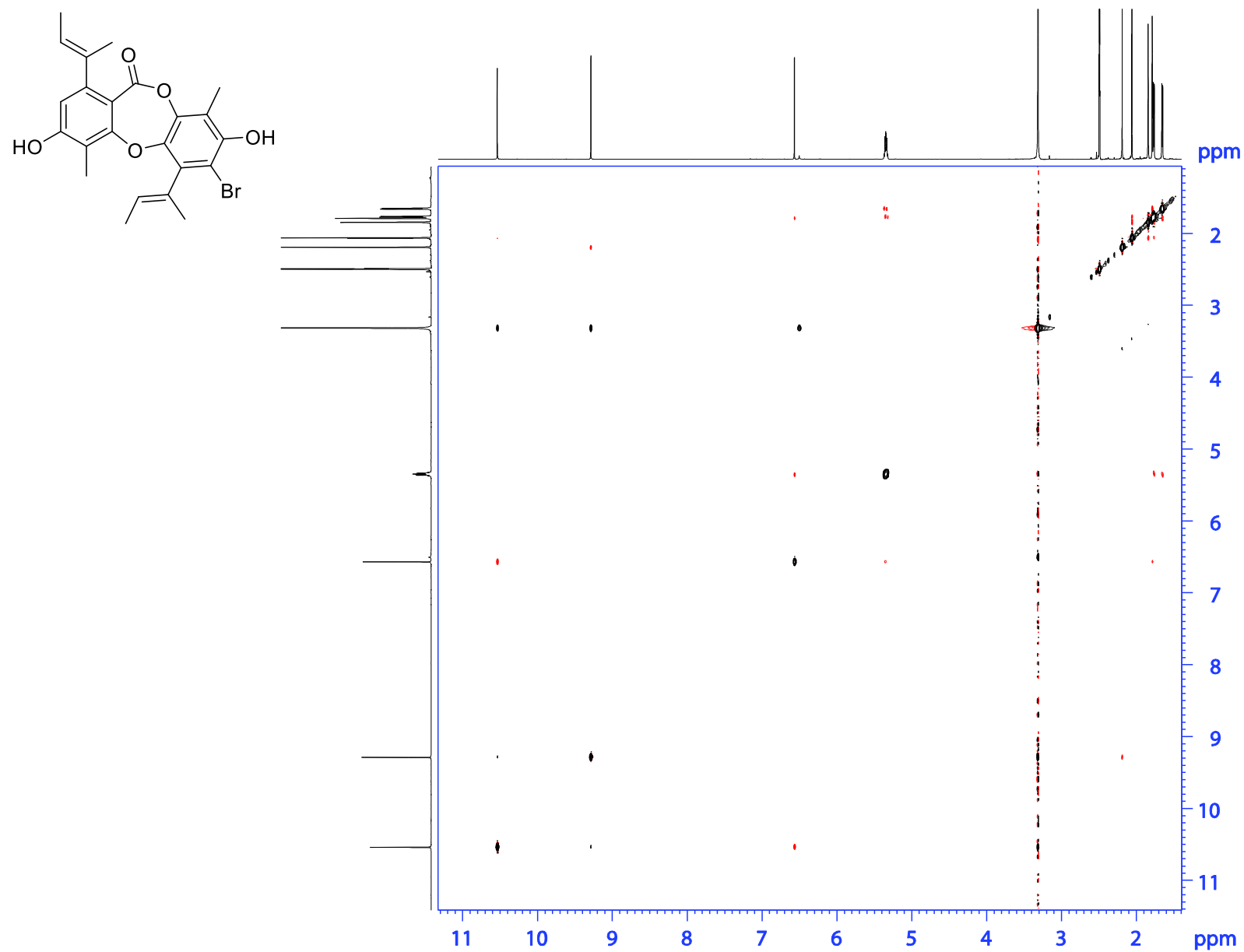


Figure S34. ^1H - ^1H ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 7-bromofolipastatin (5)

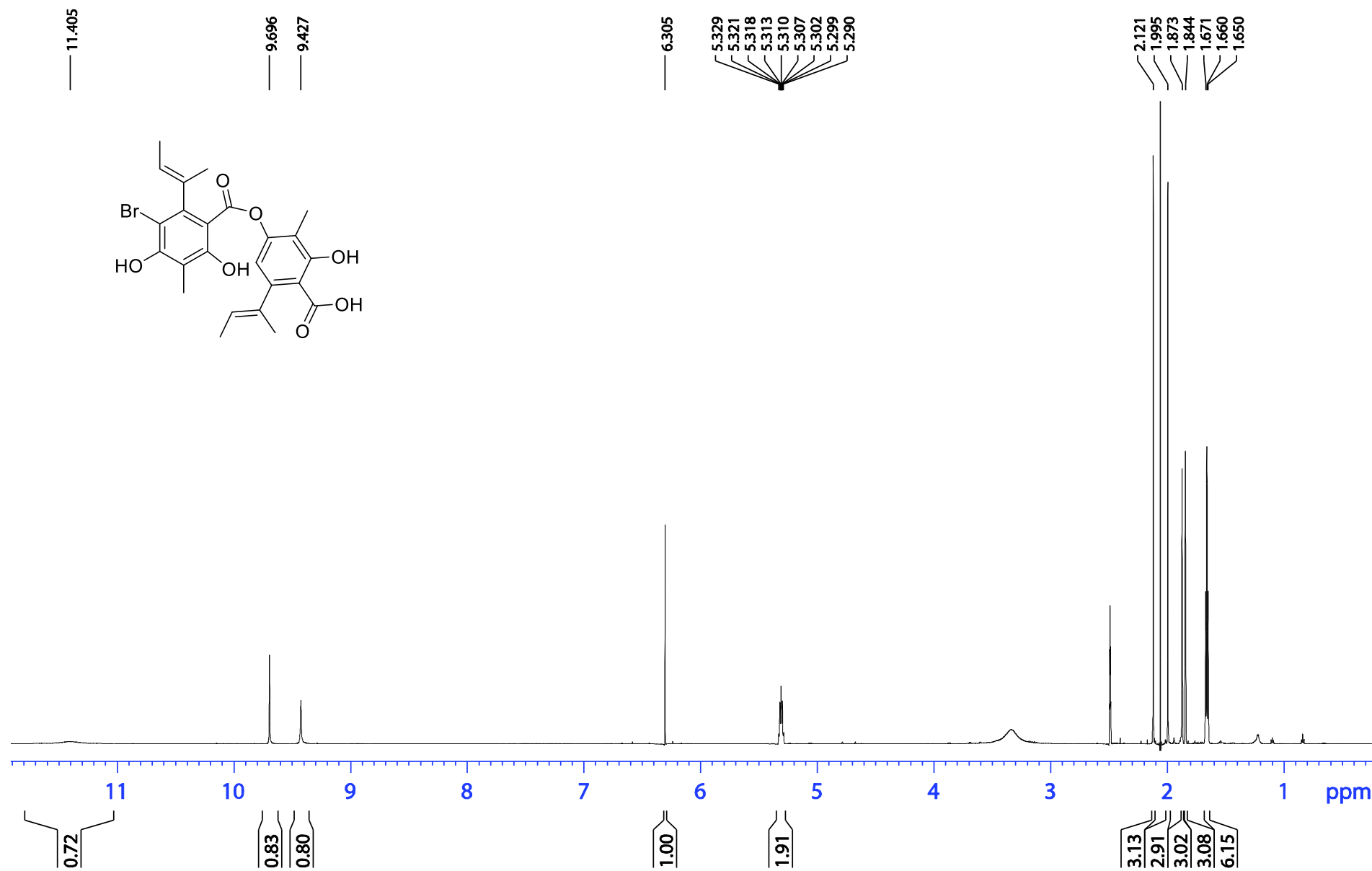


Figure S35. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of 5-bromoaggonodepside B (6)

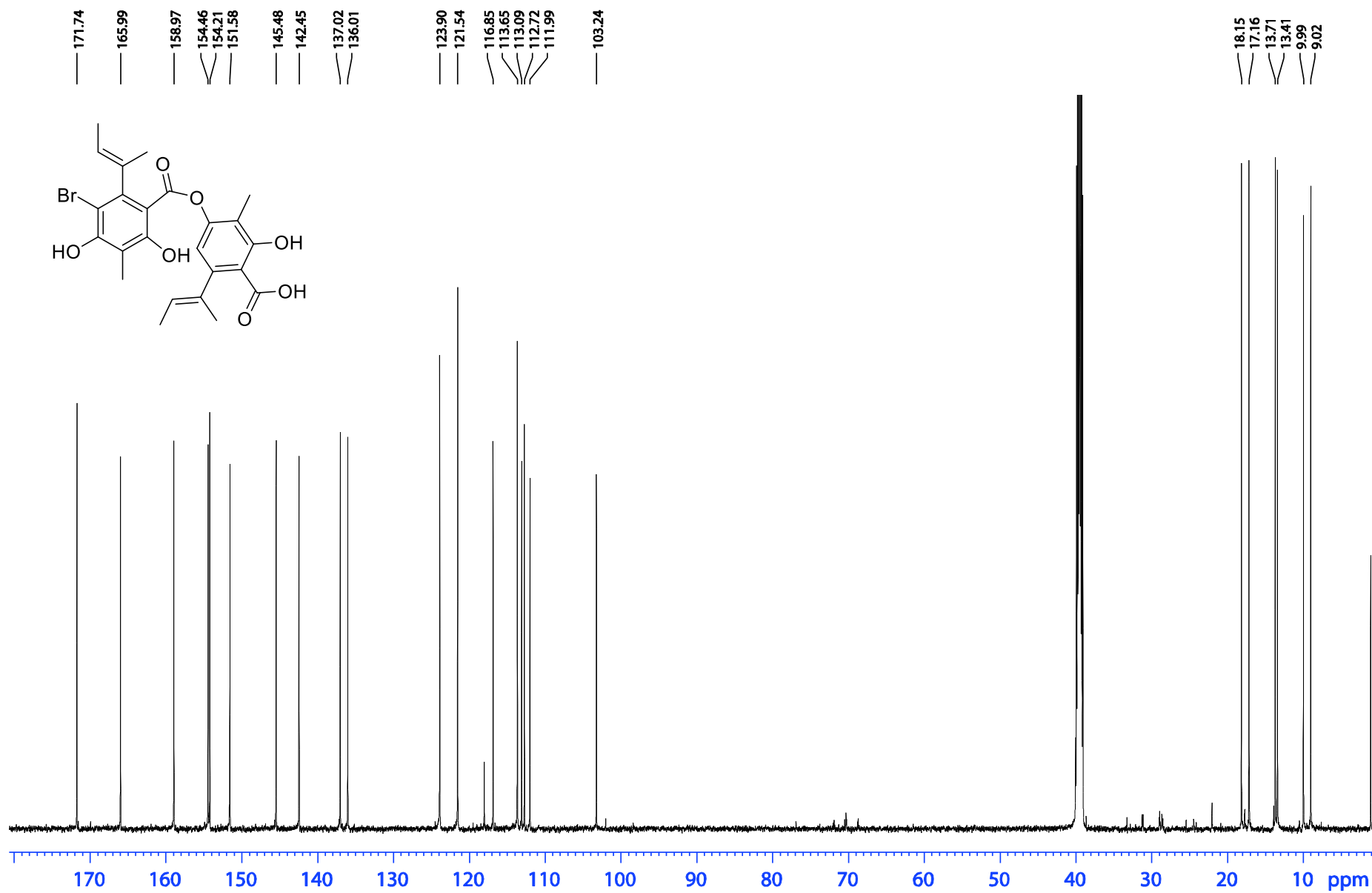


Figure S36. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of 5-bromoagonodepside B (6)

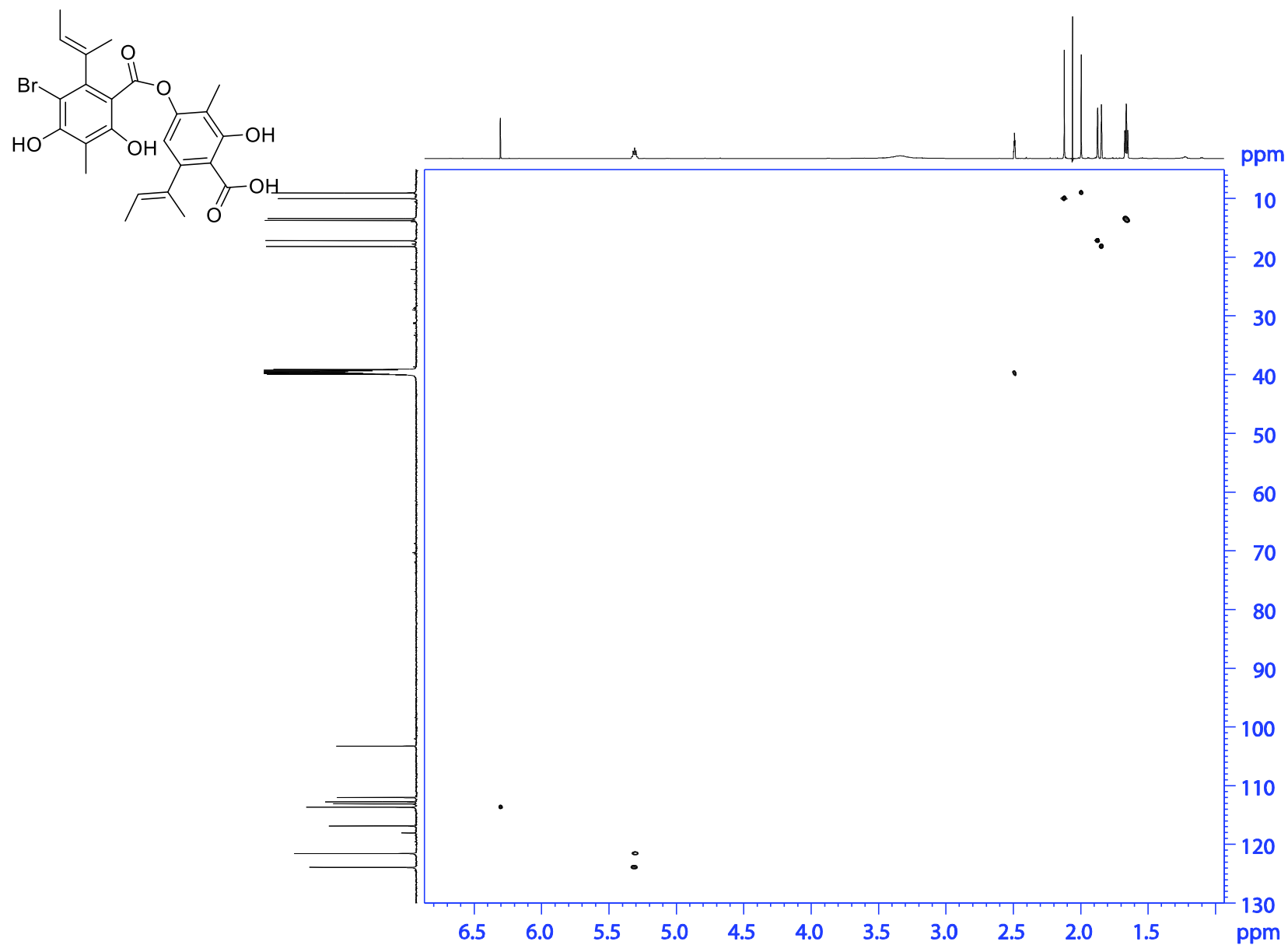


Figure S37. ^1H - ^{13}C HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagnonodepside B (**6**)

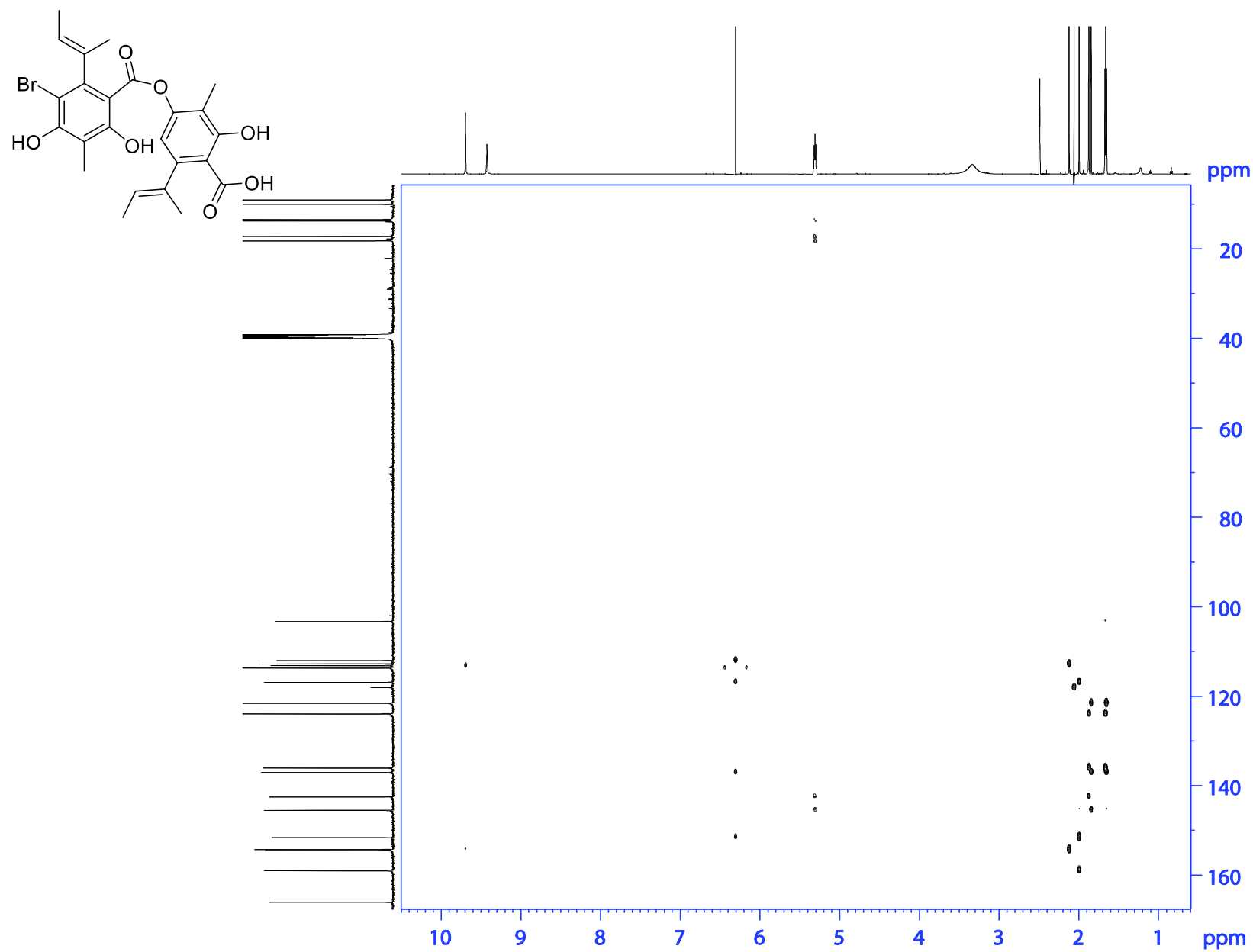


Figure S38. ^1H - ^{13}C HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (6)

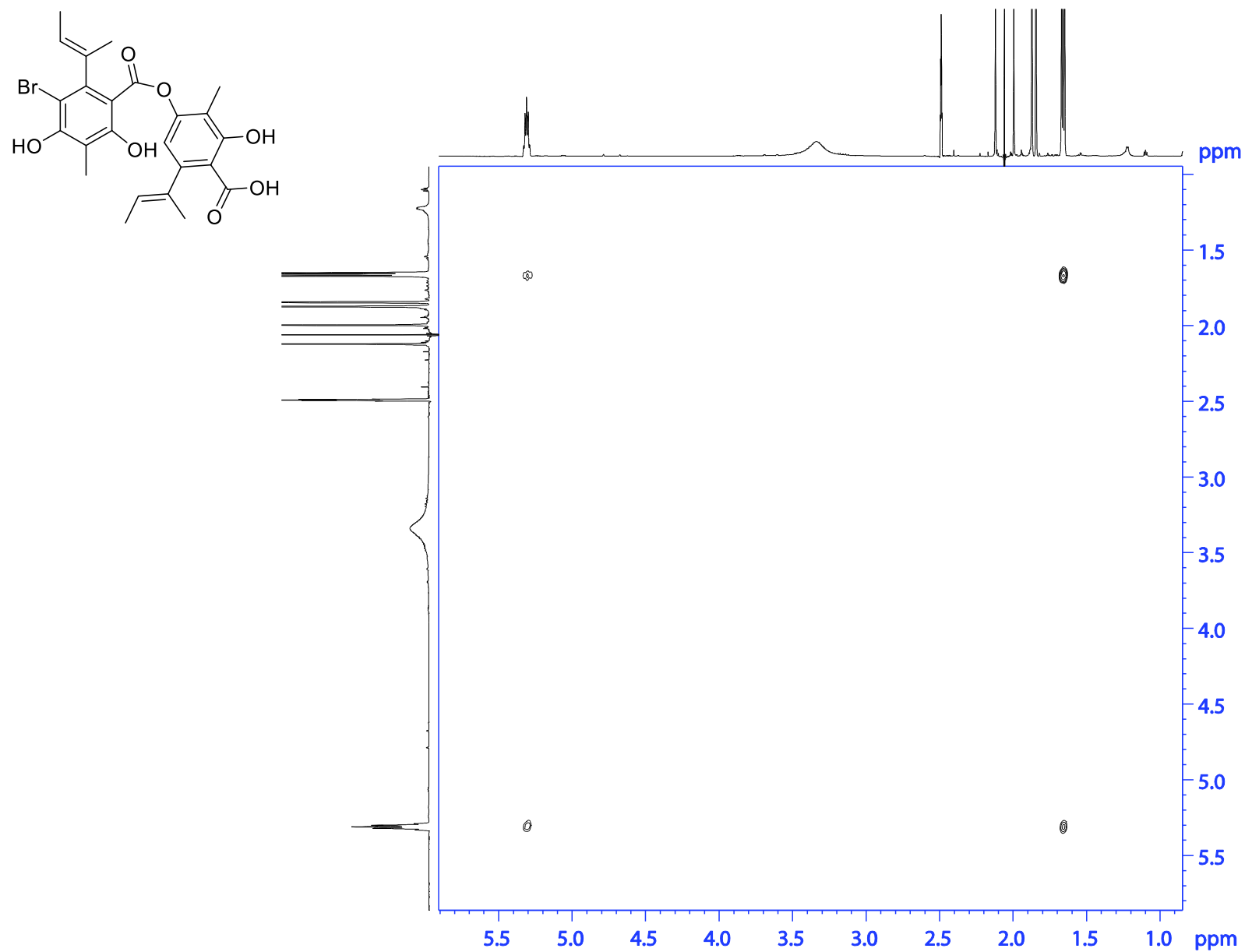


Figure S39. ^1H - ^1H COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (6)

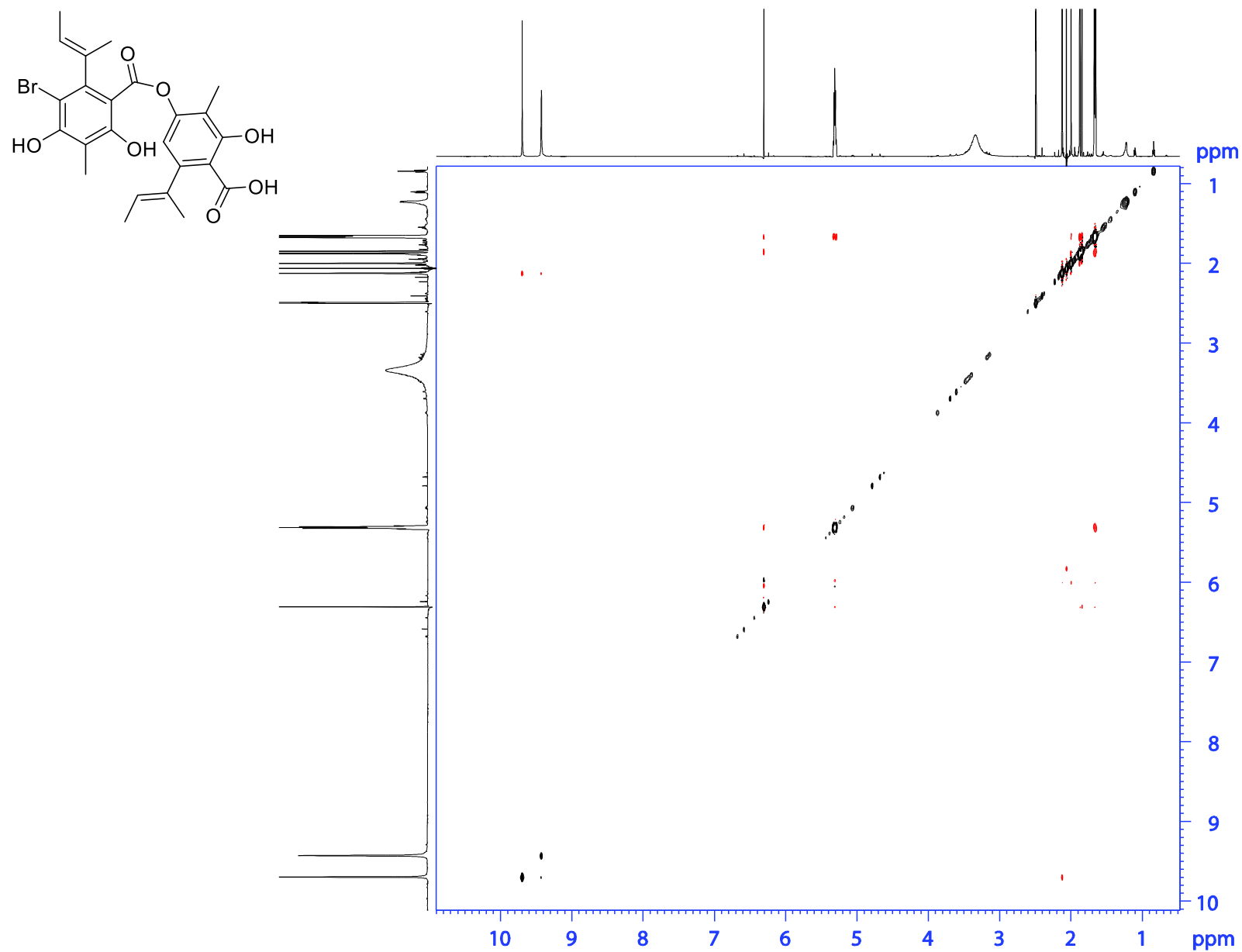


Figure S40. ^1H - ^1H ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5-bromoagonodepside B (**6**)

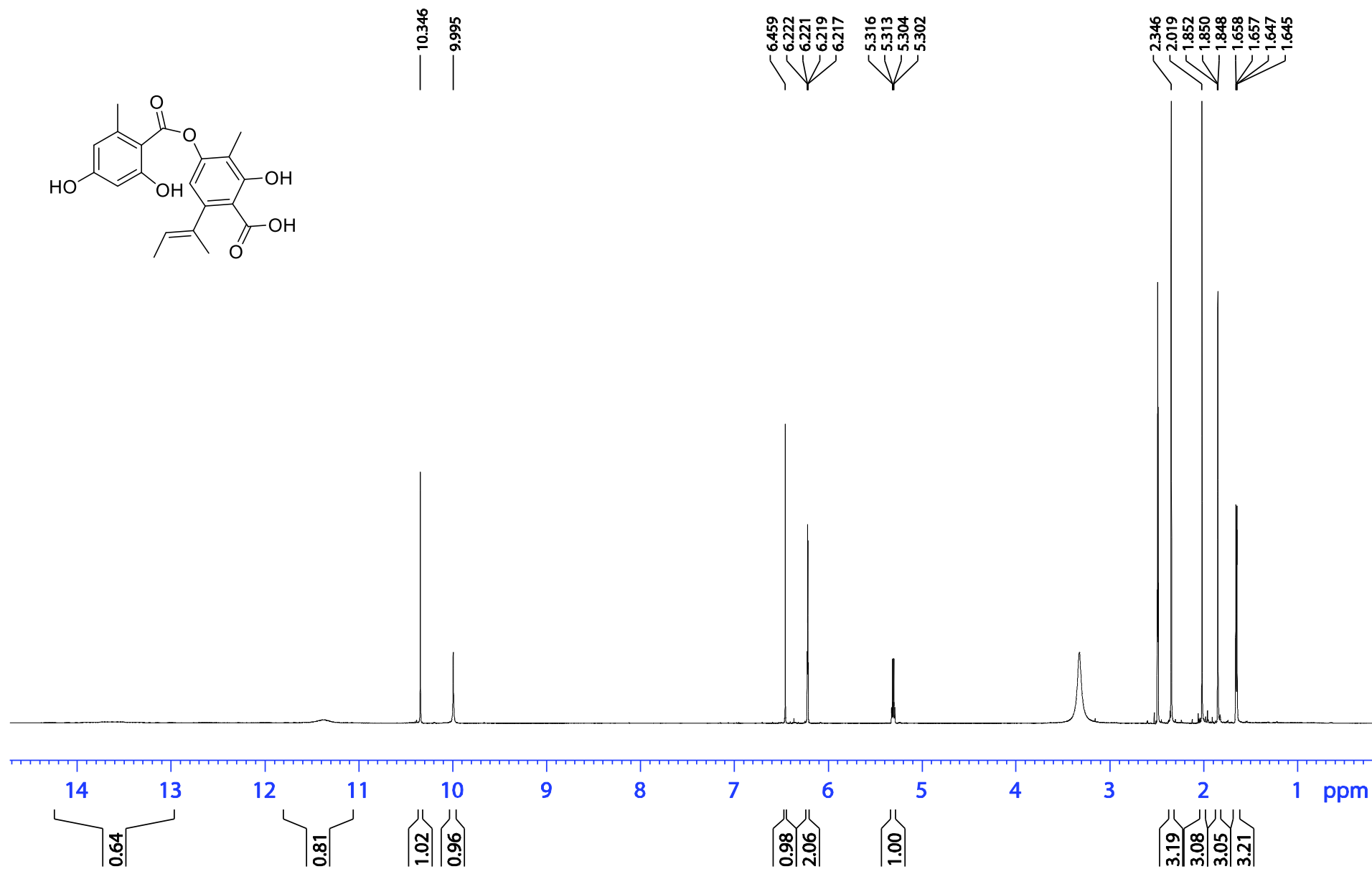


Figure S41. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of unguidepside A (7)

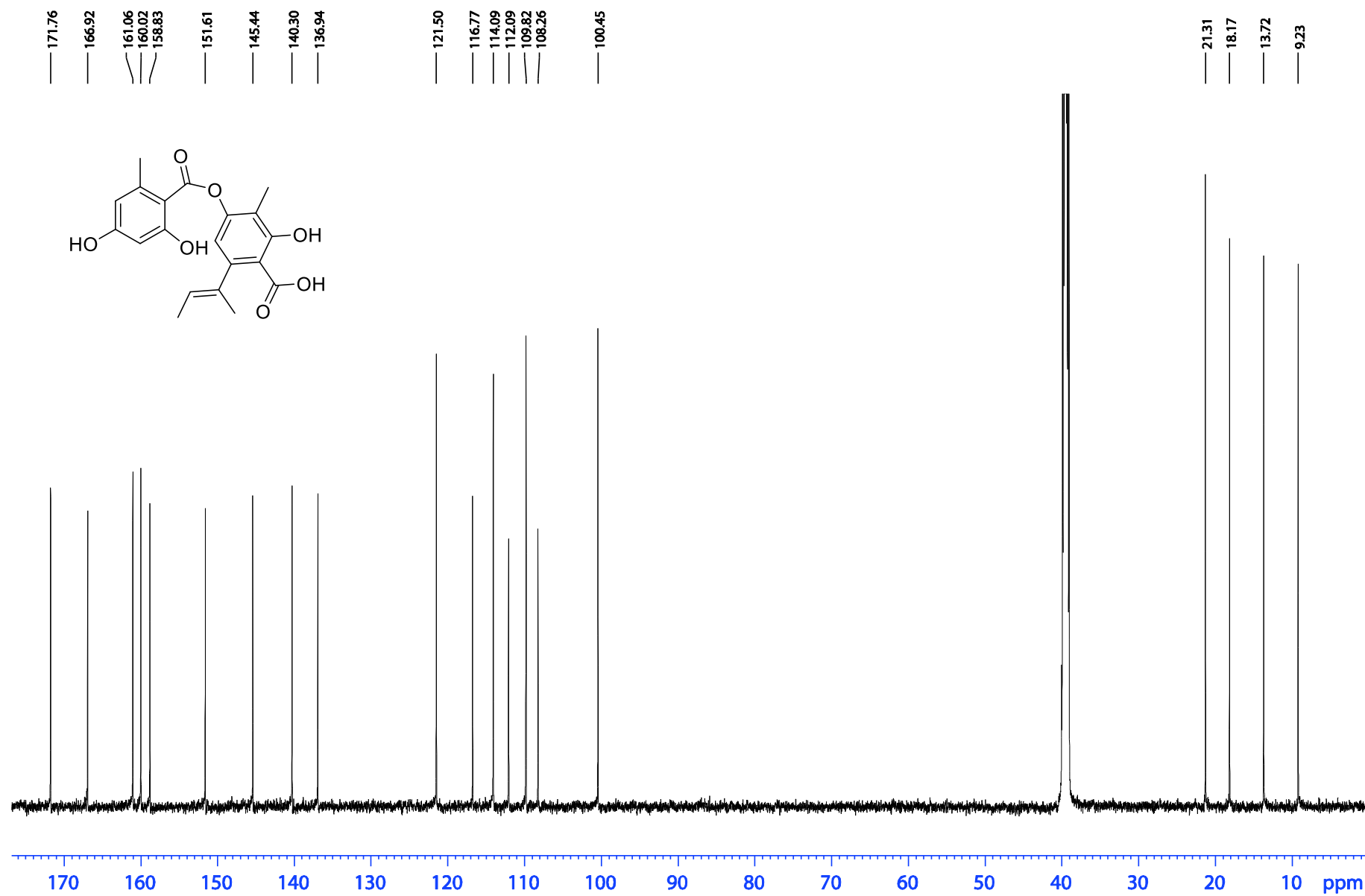


Figure S42. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of unguidepside A (7)

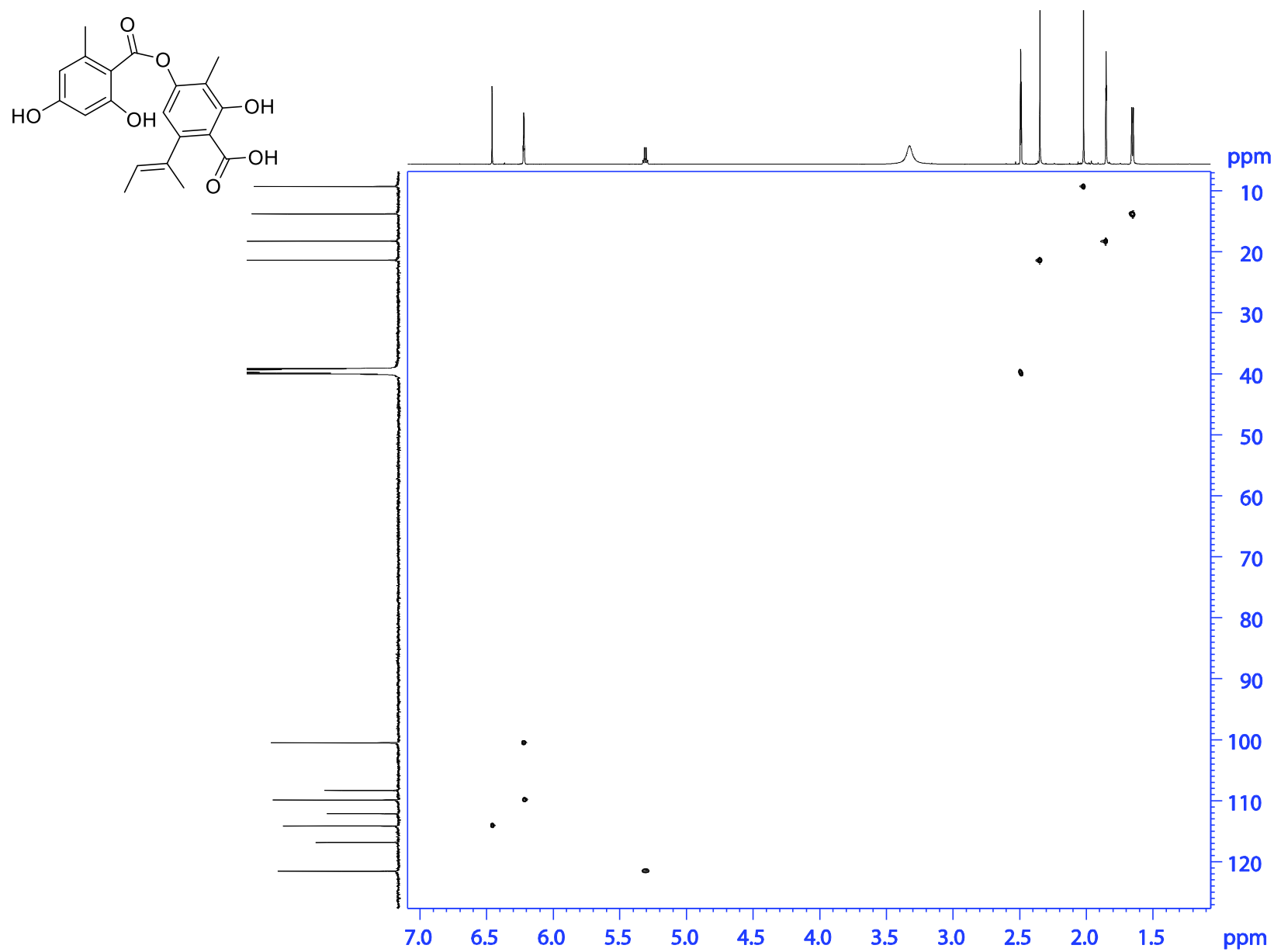


Figure S43. ^1H - ^{13}C HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7)

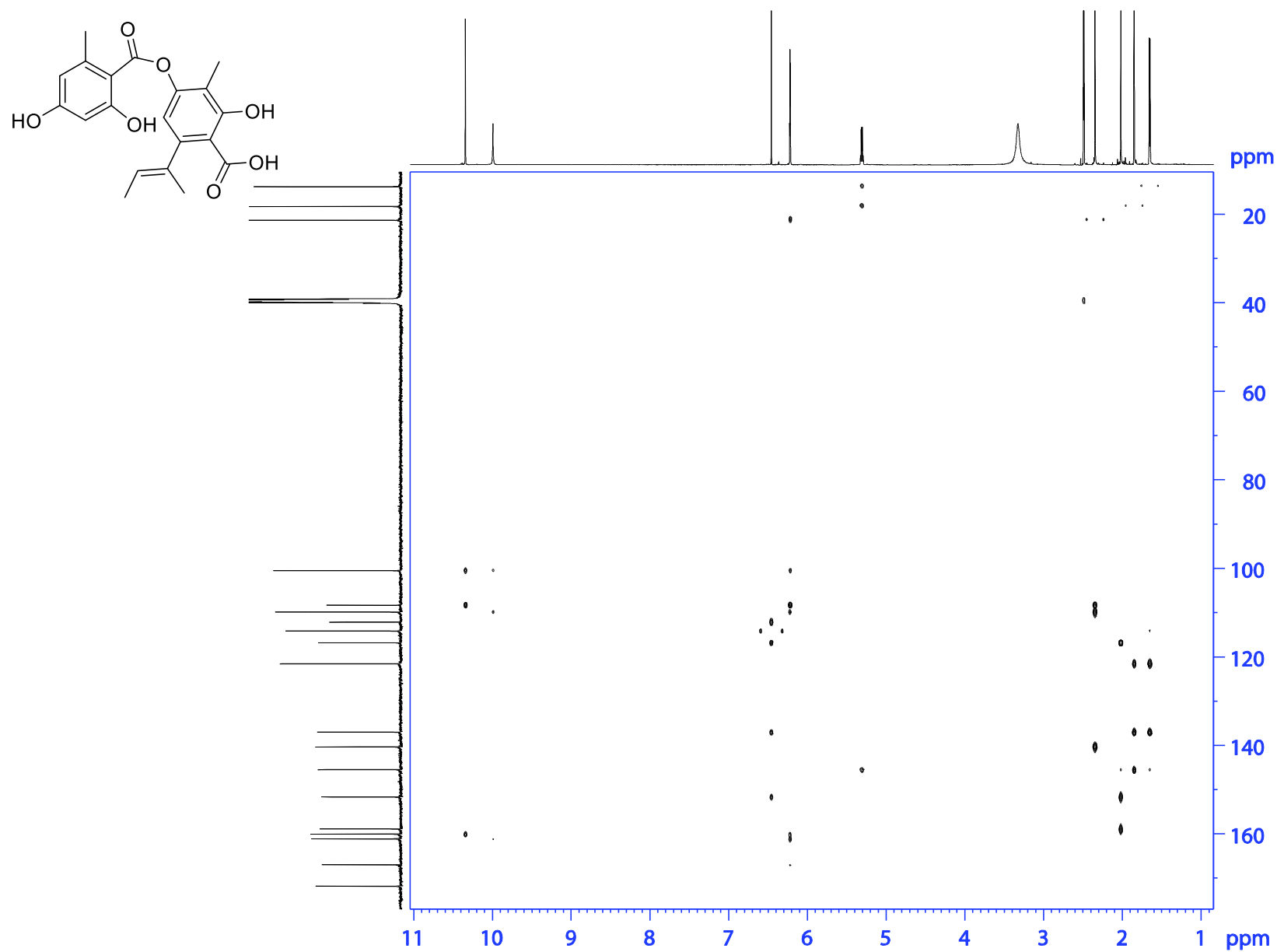


Figure S44. ^1H - ^{13}C HMBC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7)

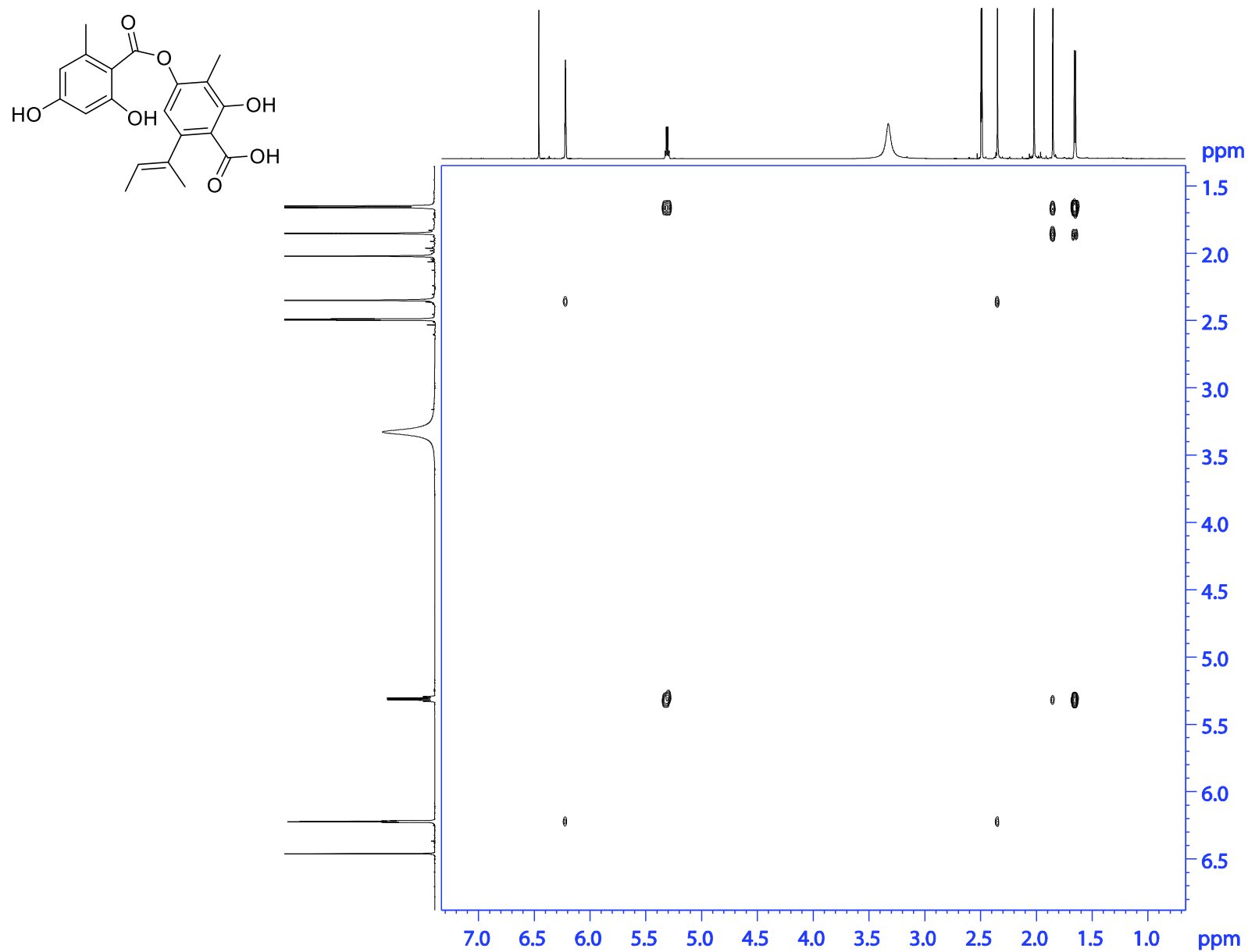


Figure S45. ^1H - ^1H COSY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7)

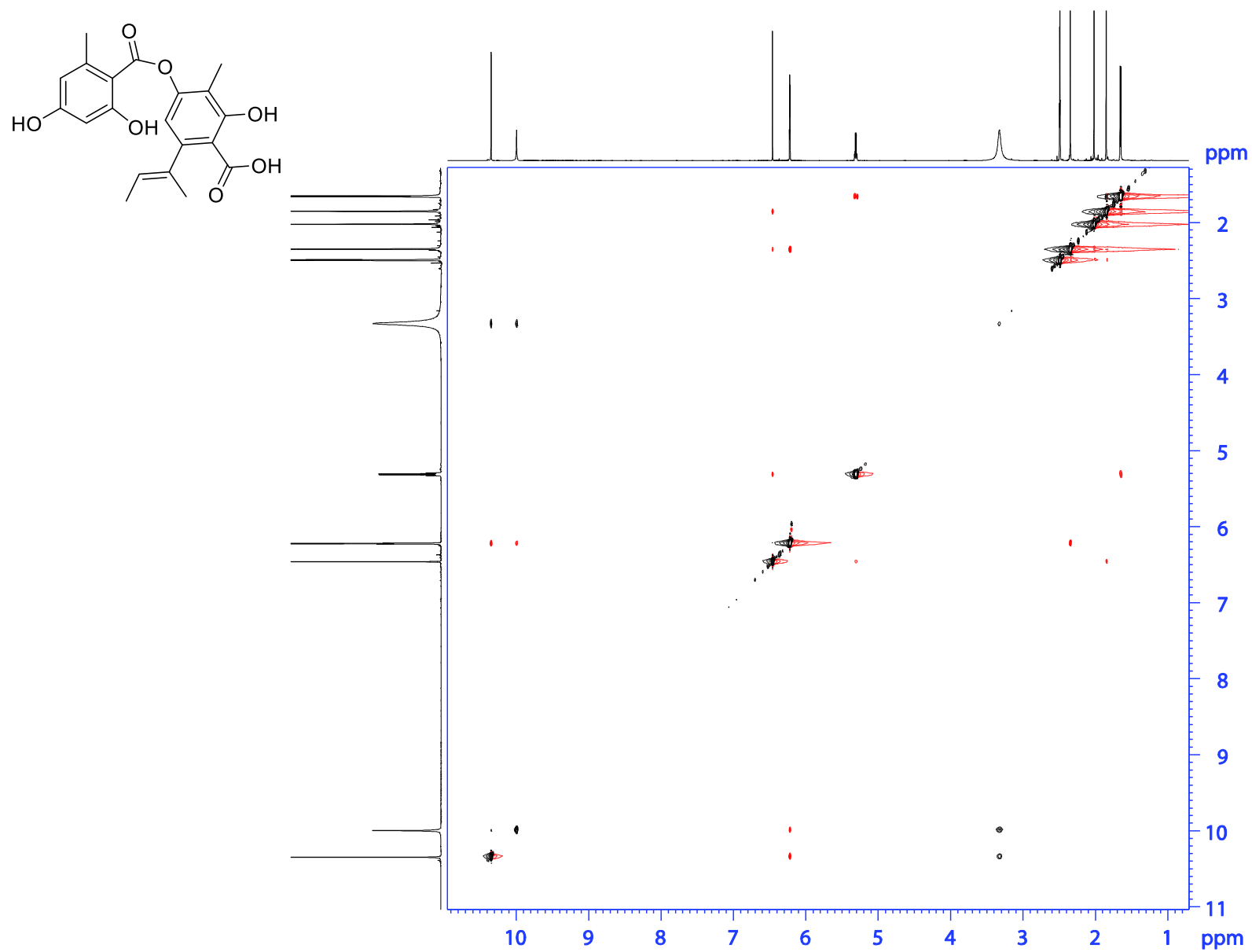


Figure S46. ^1H - ^1H ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of unguidepside A (7)

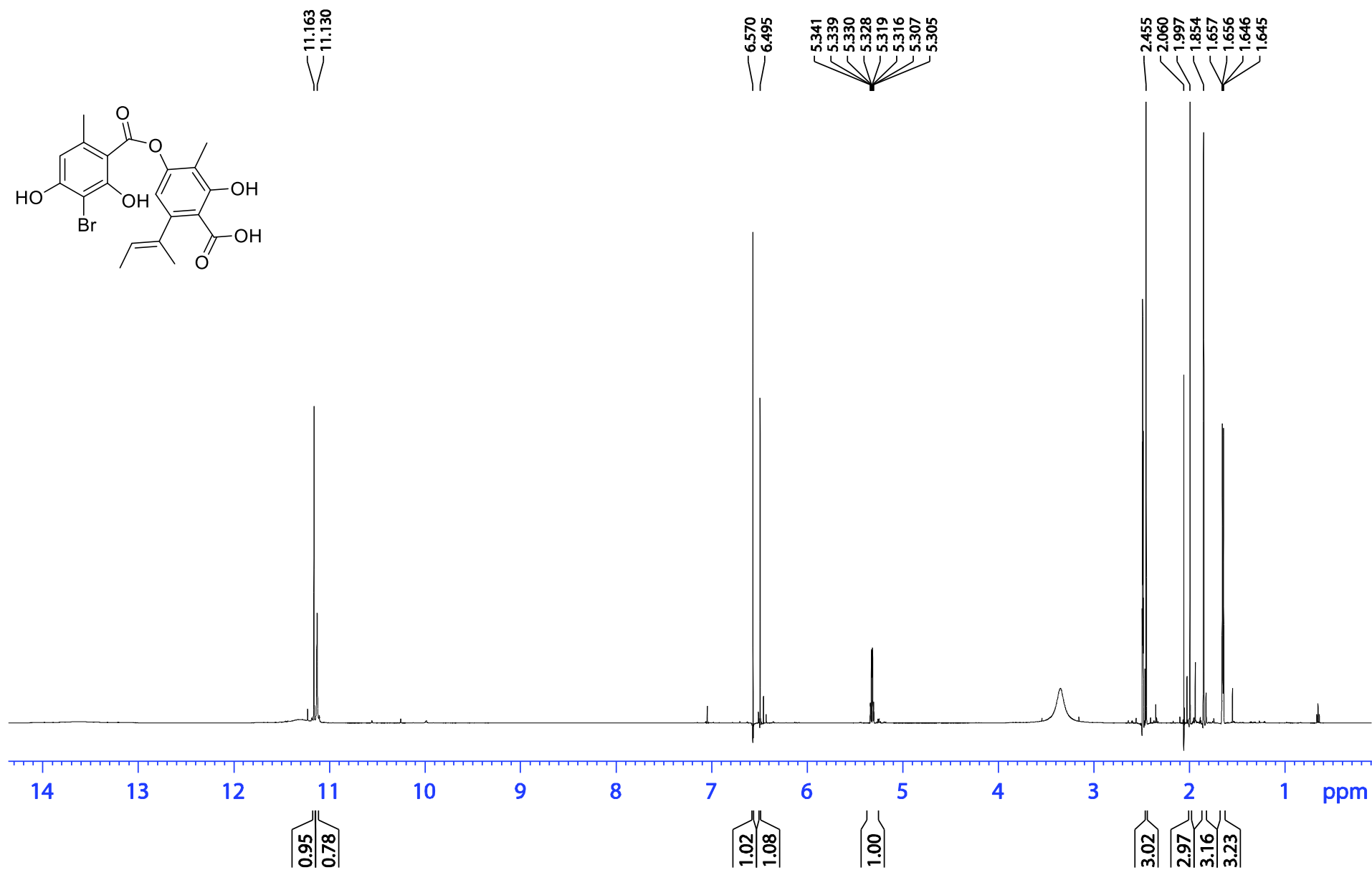


Figure S47. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of 3-bromounguidepside A (8)

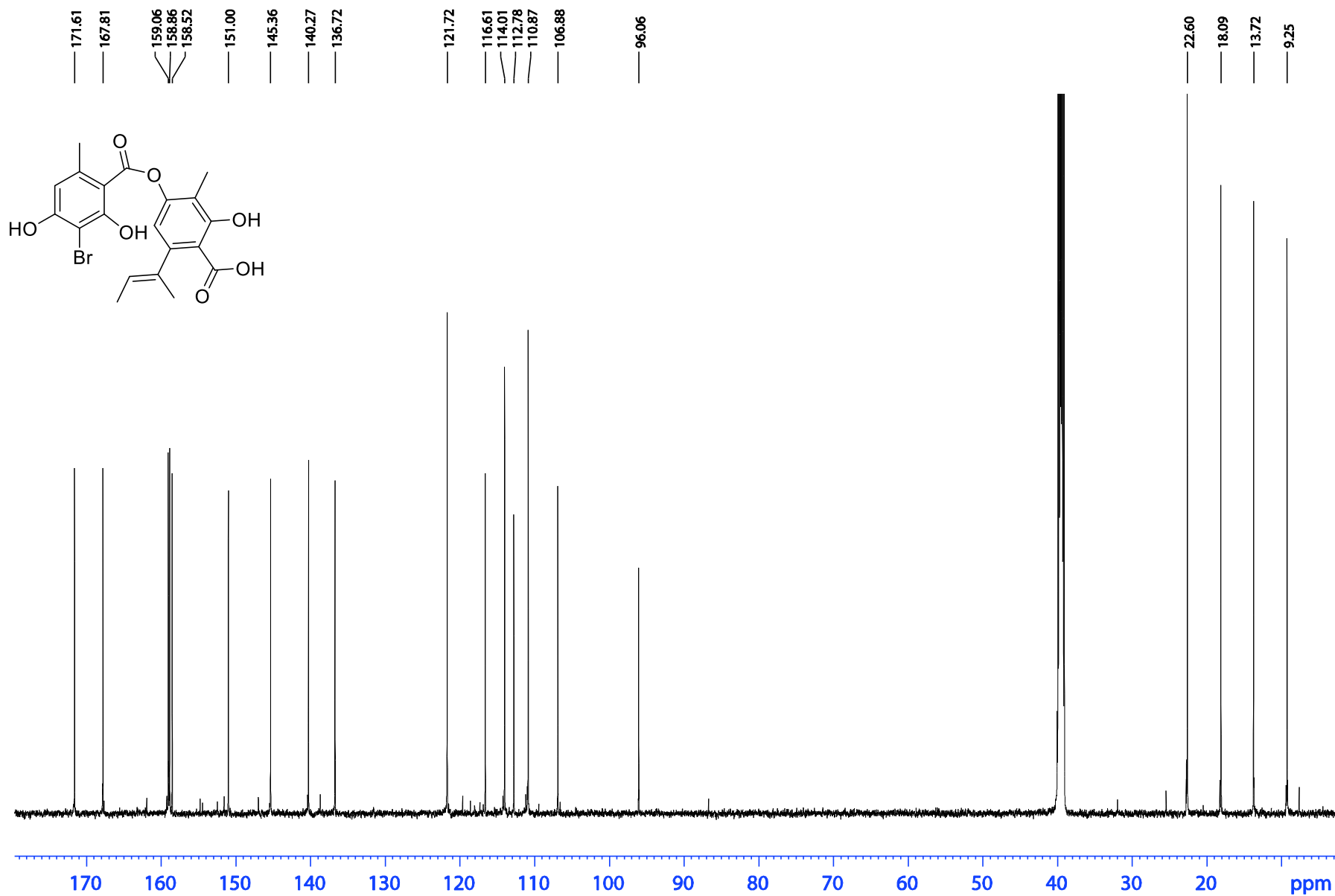


Figure S48. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of 3-bromounguidepside A (8)

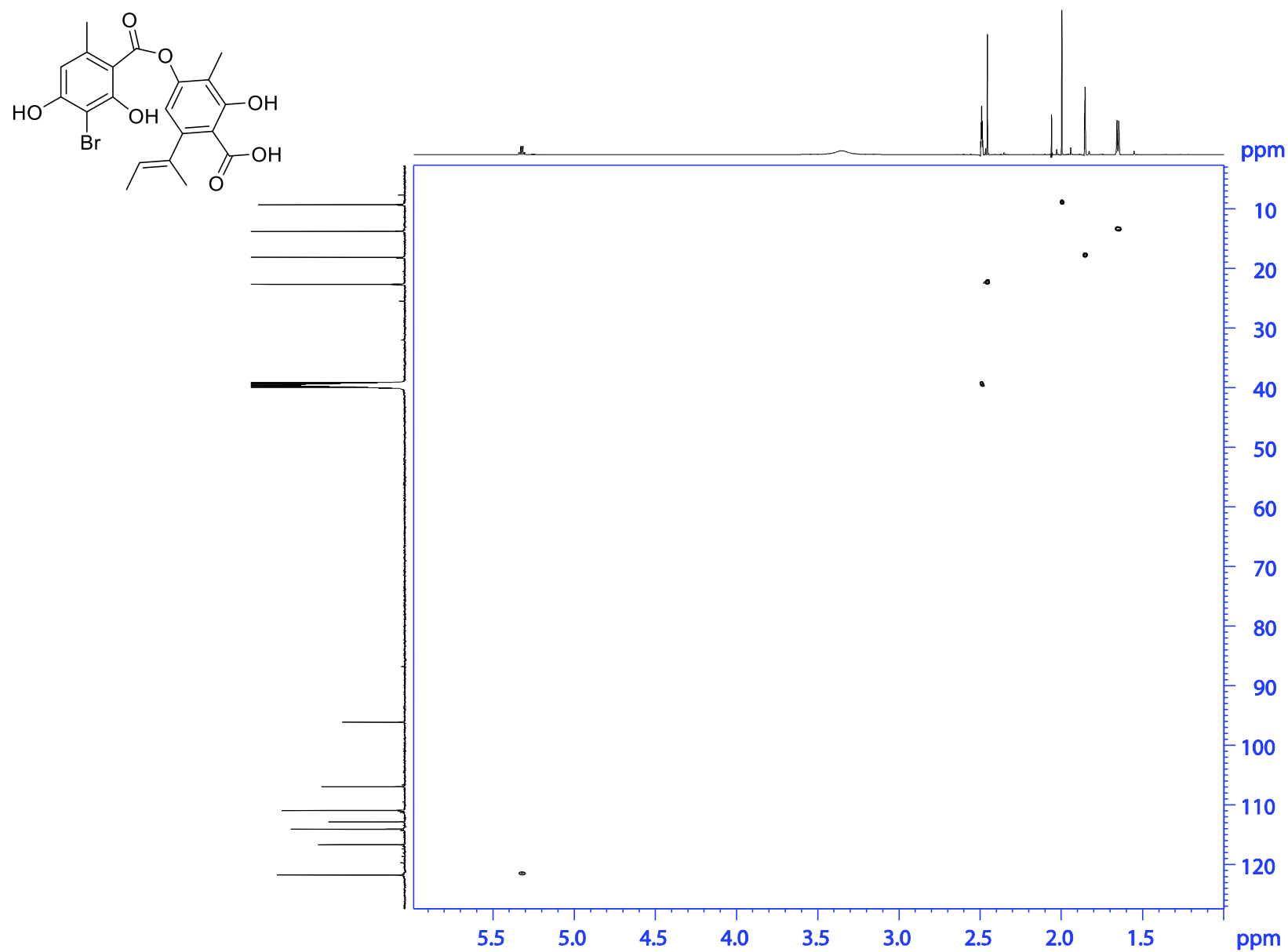


Figure S49. ^1H - ^{13}C HSQC NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 3-bromounguidepside A (**8**)

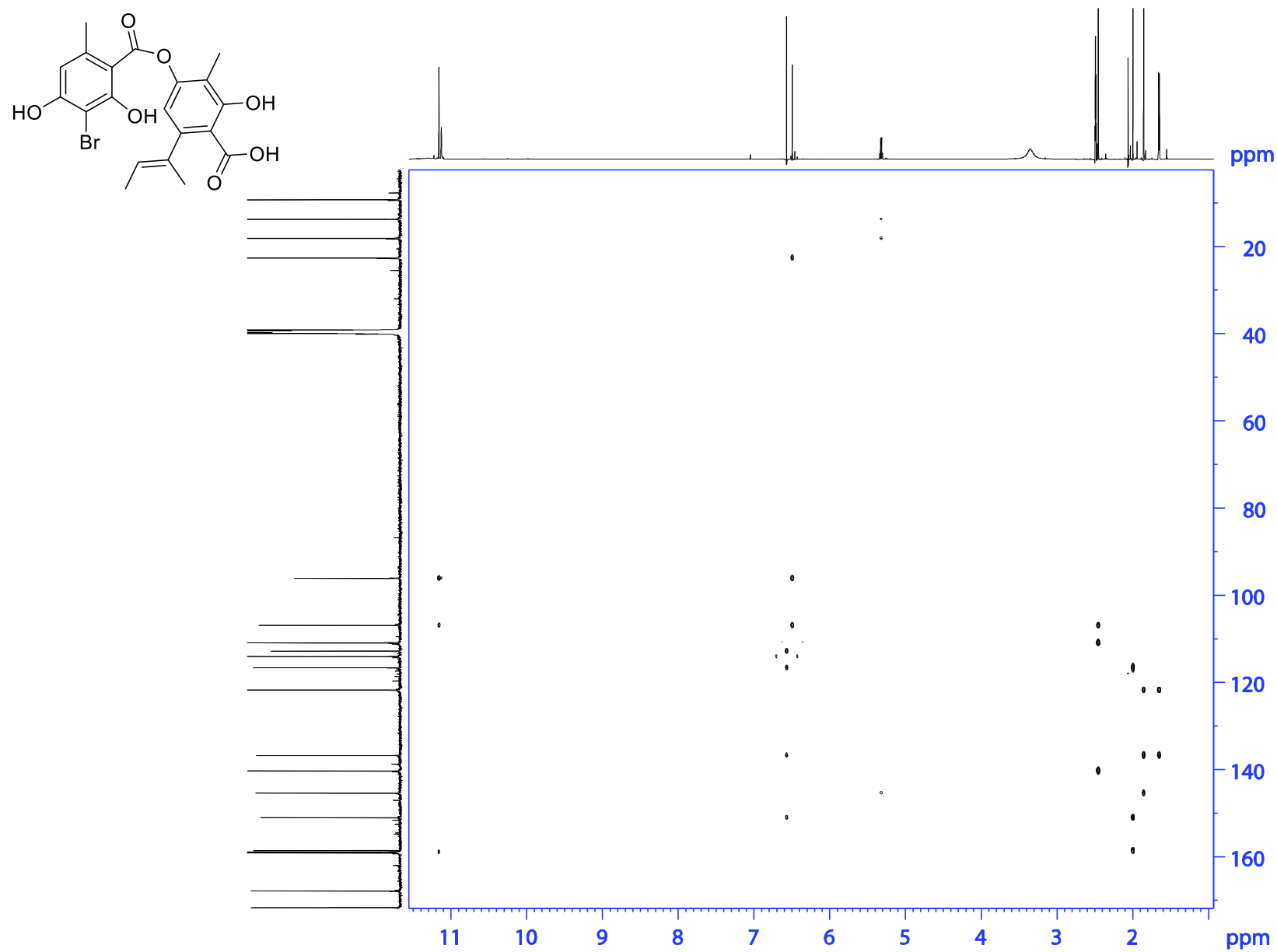


Figure S50. ^1H - ^{13}C HMBC NMR spectrum (600 MHz, $\text{DMSO-}d_6$) of 3-bromounguidepside A (8)

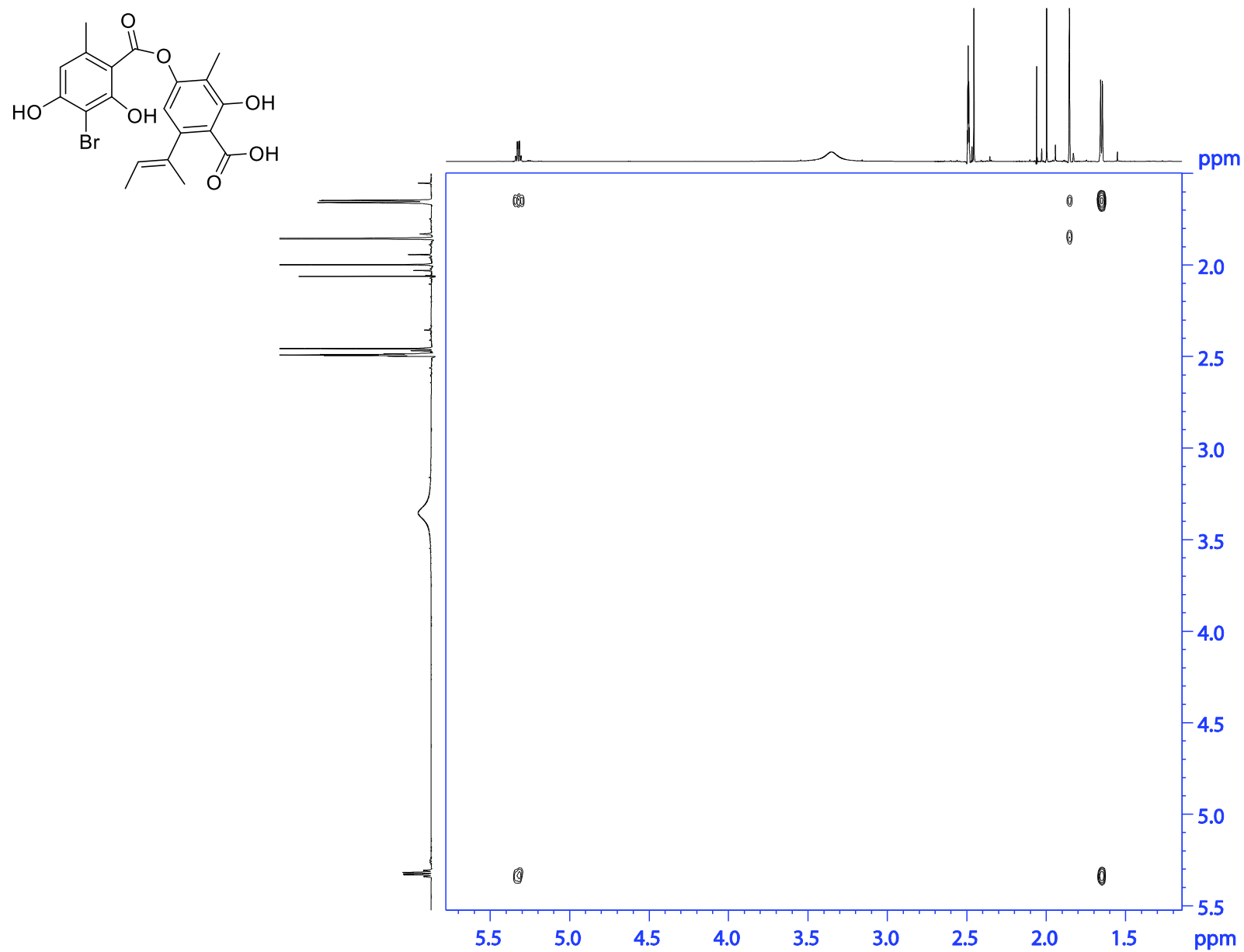


Figure S51. ^1H - ^1H COSY NMR spectrum (600 MHz, DMSO- d_6) of 3-bromounguidepside A (**8**)

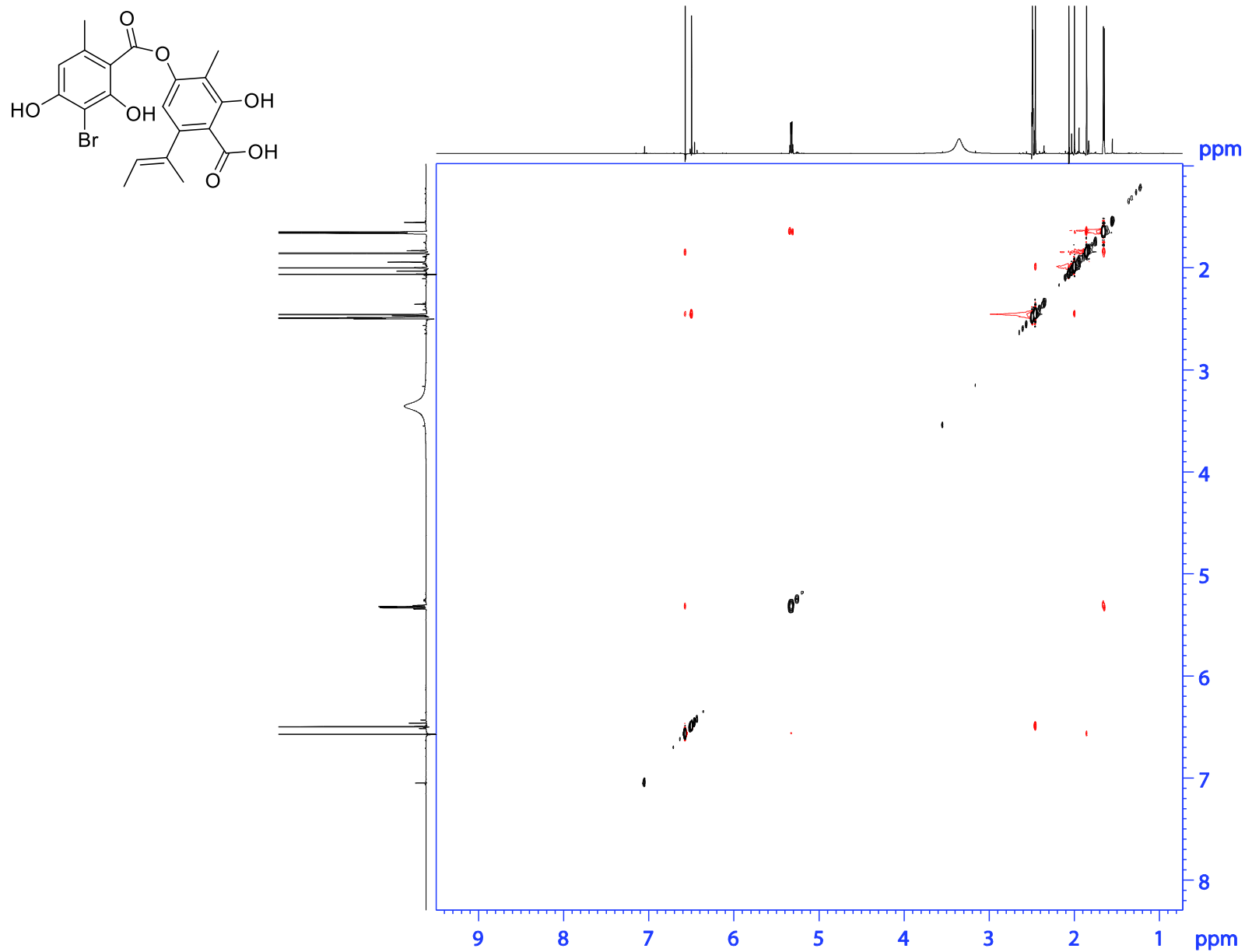


Figure S52. ^1H - ^1H ROESY NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 3-bromounguiside A (**8**)

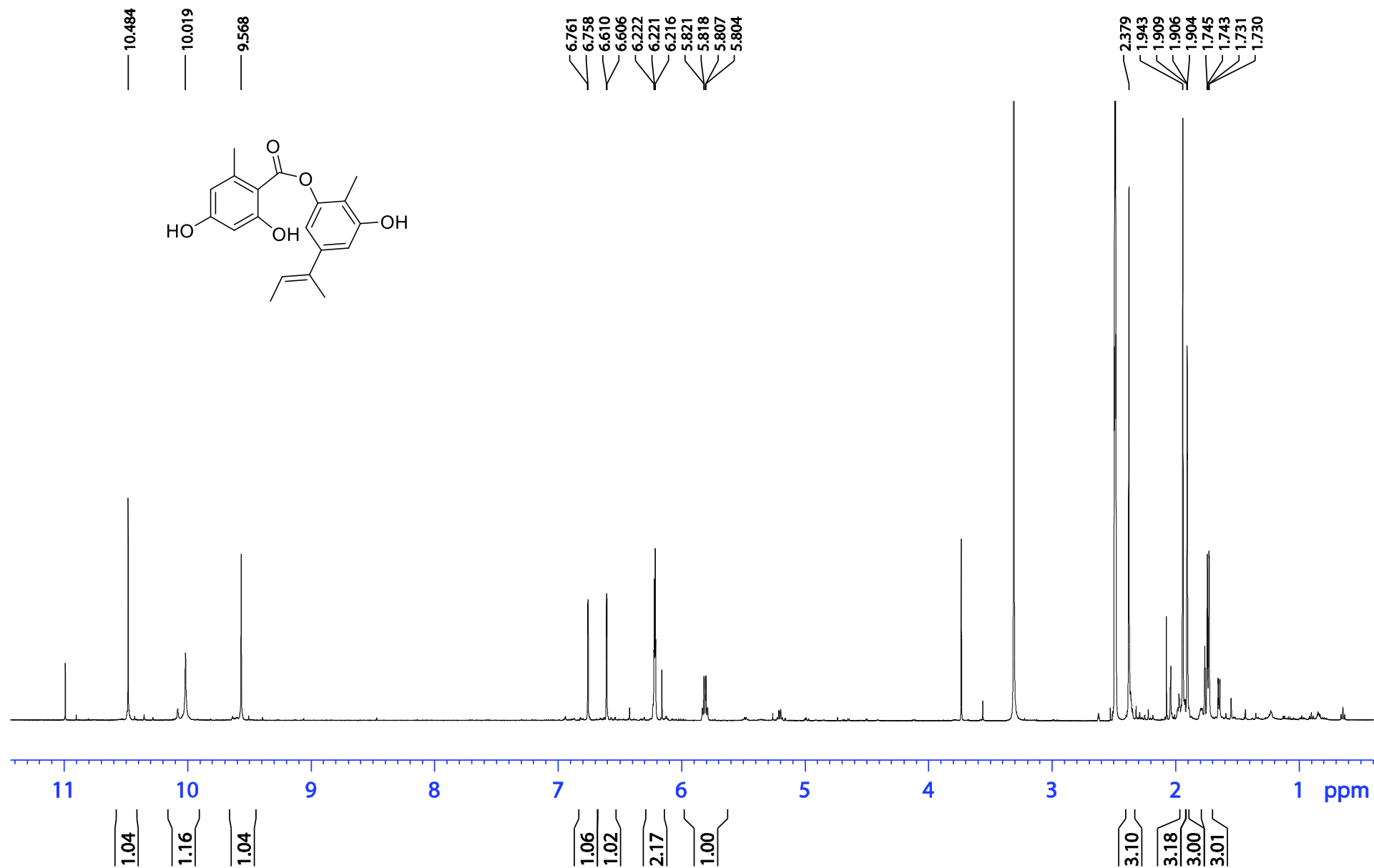


Figure S53. ¹H NMR spectrum (500 MHz, DMSO-*d*₆) of decarboxyunguidepside A (9)

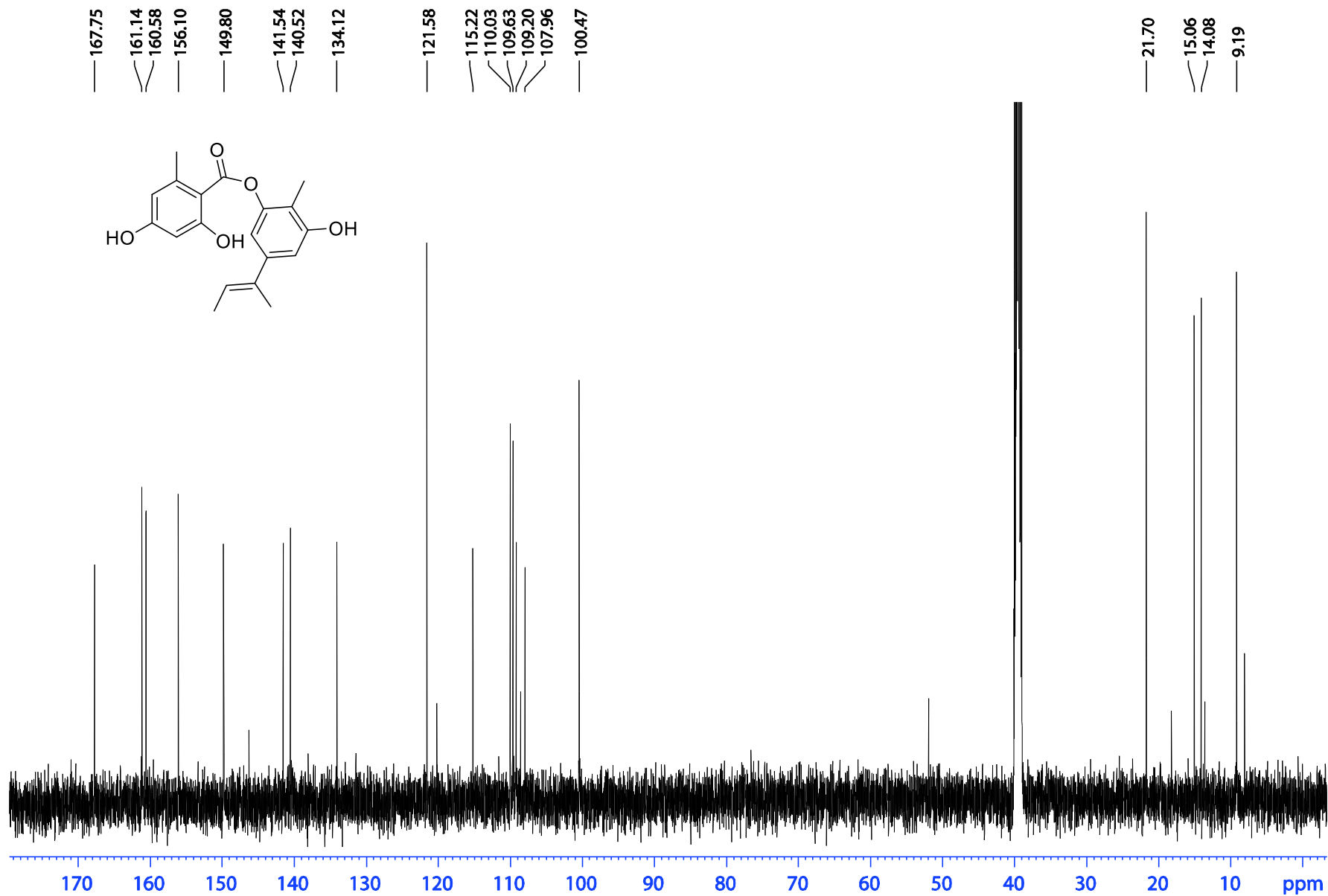


Figure S54. ¹³C NMR spectrum (125 MHz, DMSO-*d*₆) of decarboxyunguidepside A (9)

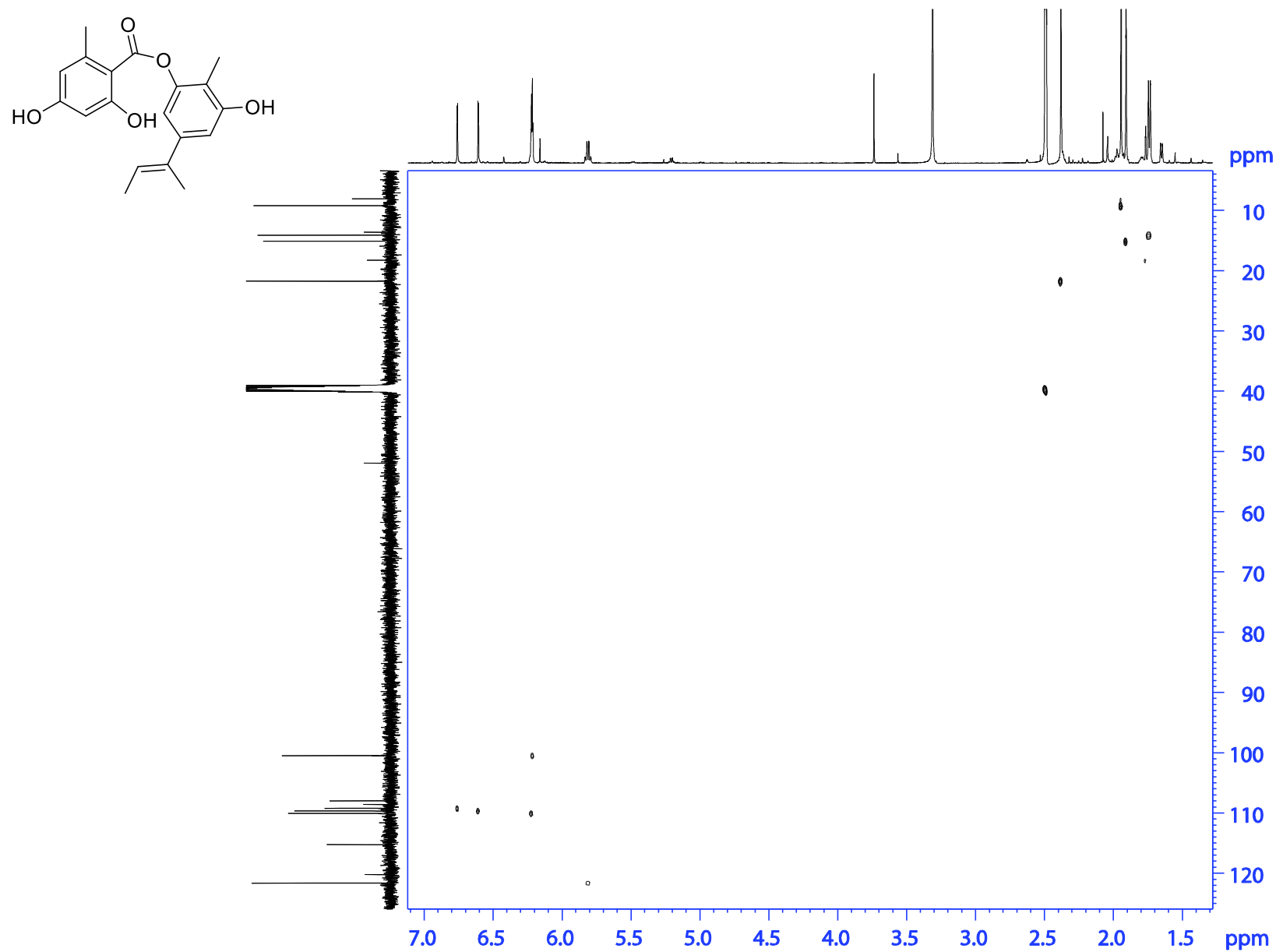


Figure S55. ^1H - ^{13}C HSQC NMR spectrum (500 MHz, DMSO- d_6) of decarboxyunguidepside A (9)

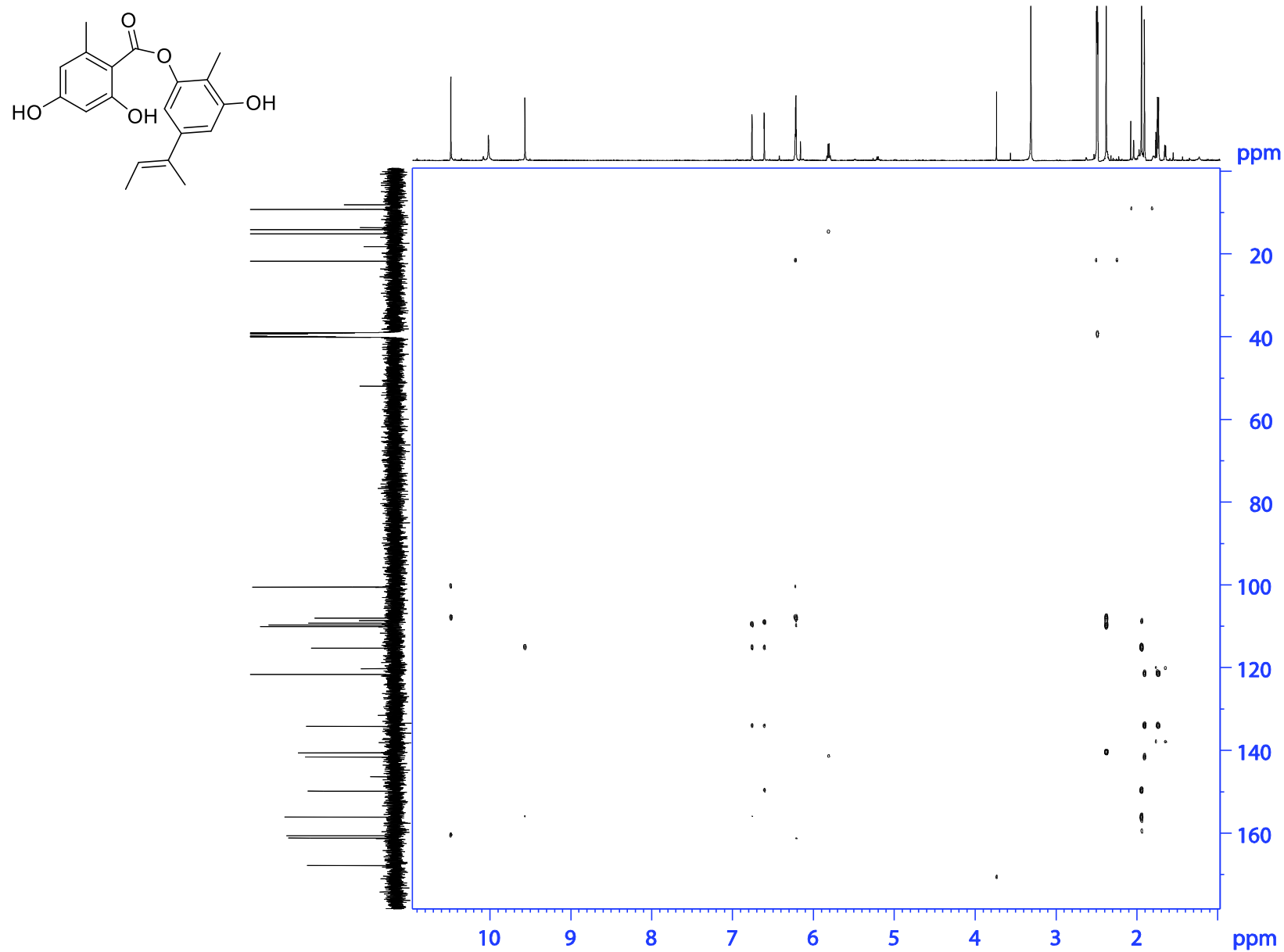


Figure S56. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (**9**)

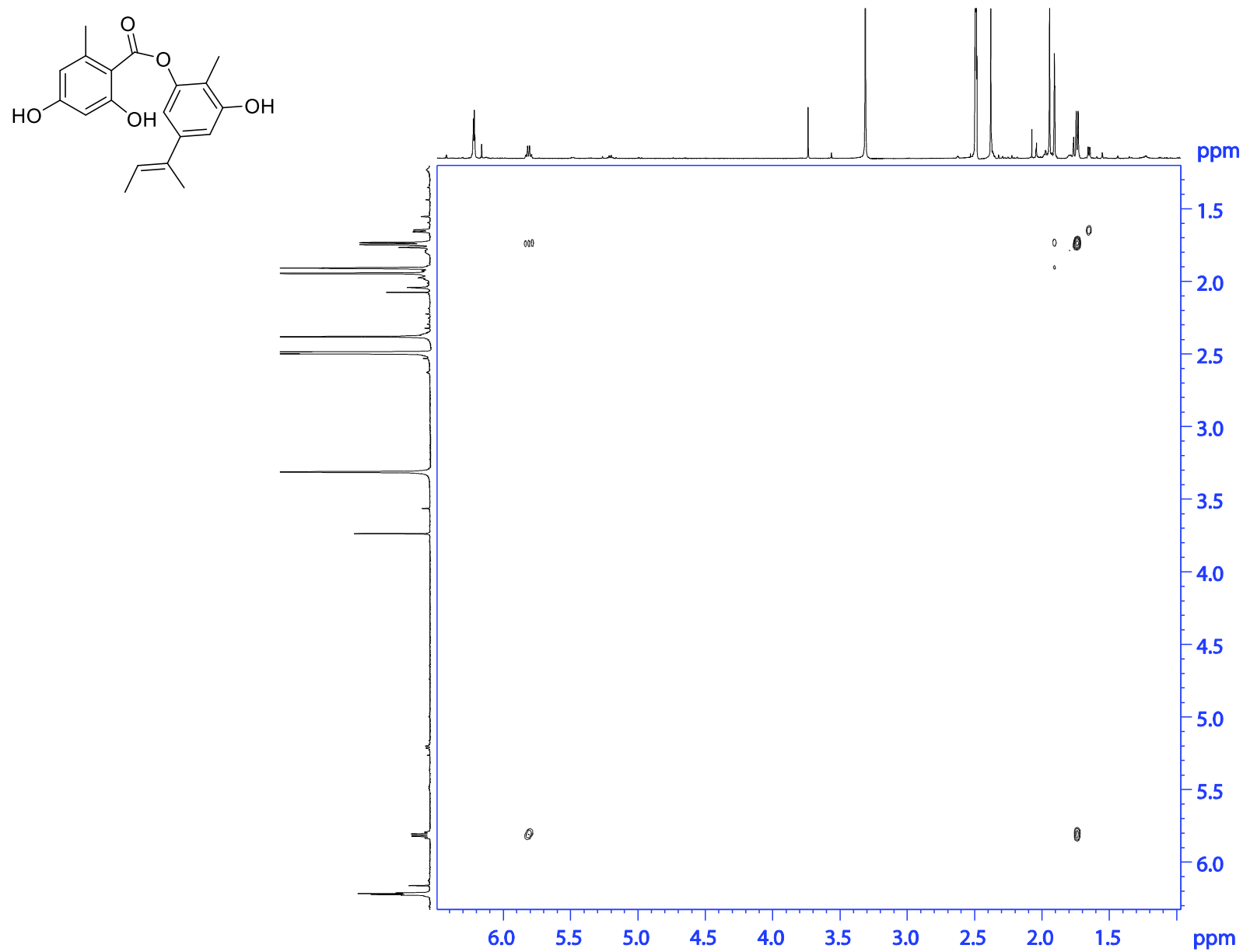


Figure S57. ^1H - ^1H COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (9)

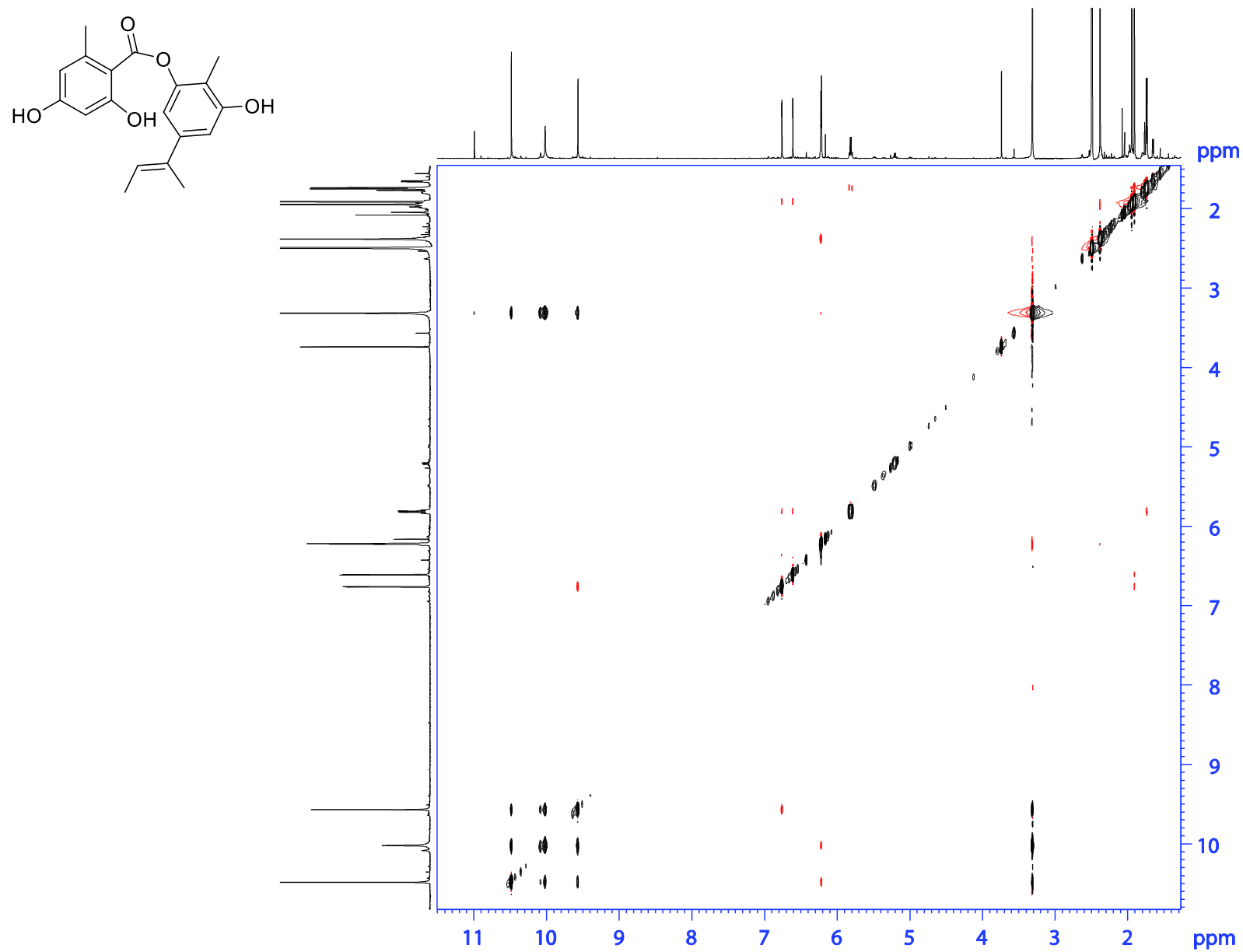


Figure S58. ^1H - ^1H ROESY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguidepside A (**9**)

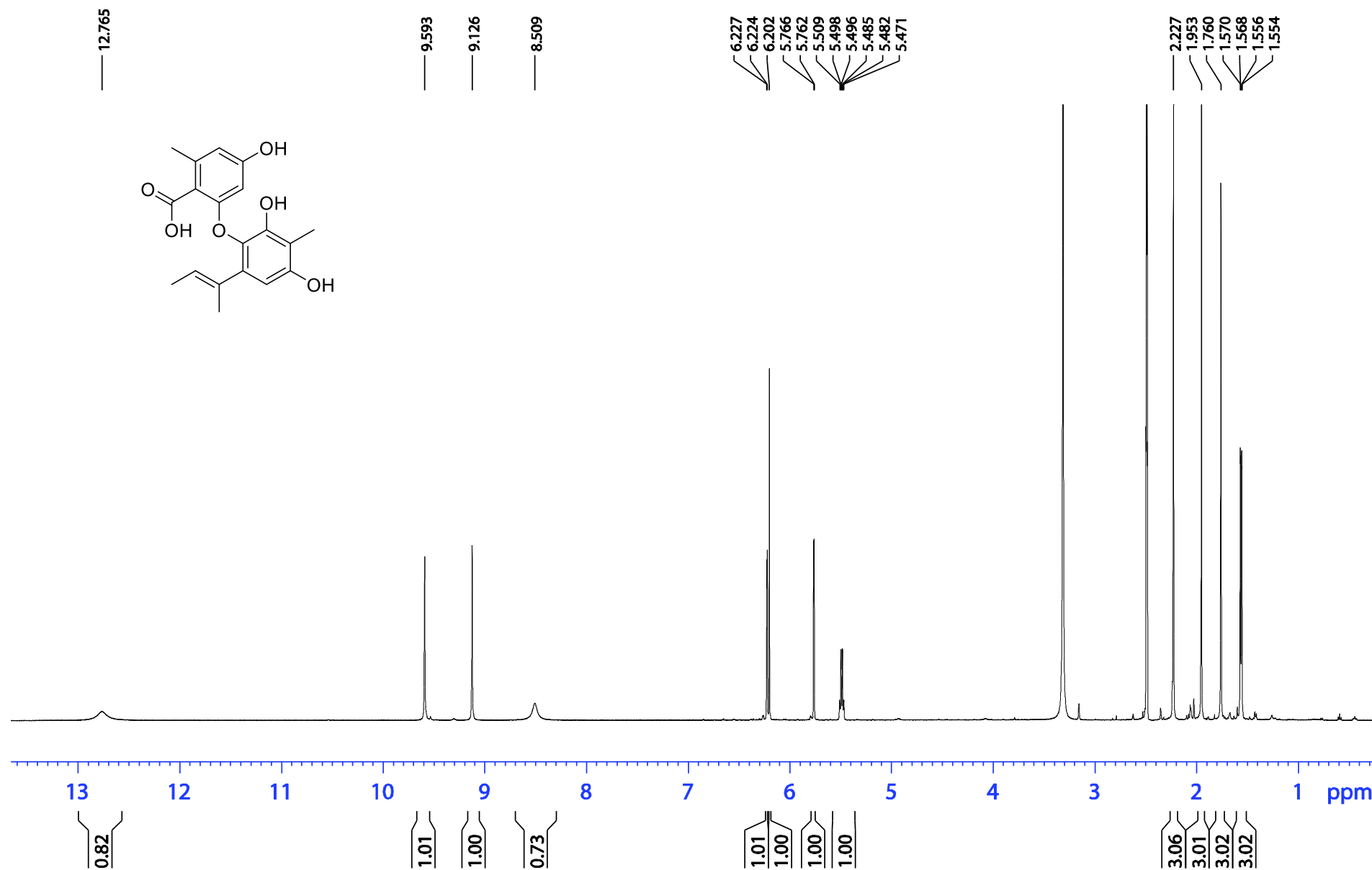


Figure S59. ¹H NMR spectrum (500 MHz, DMSO-*d*₆) of unguinolic acid (10)

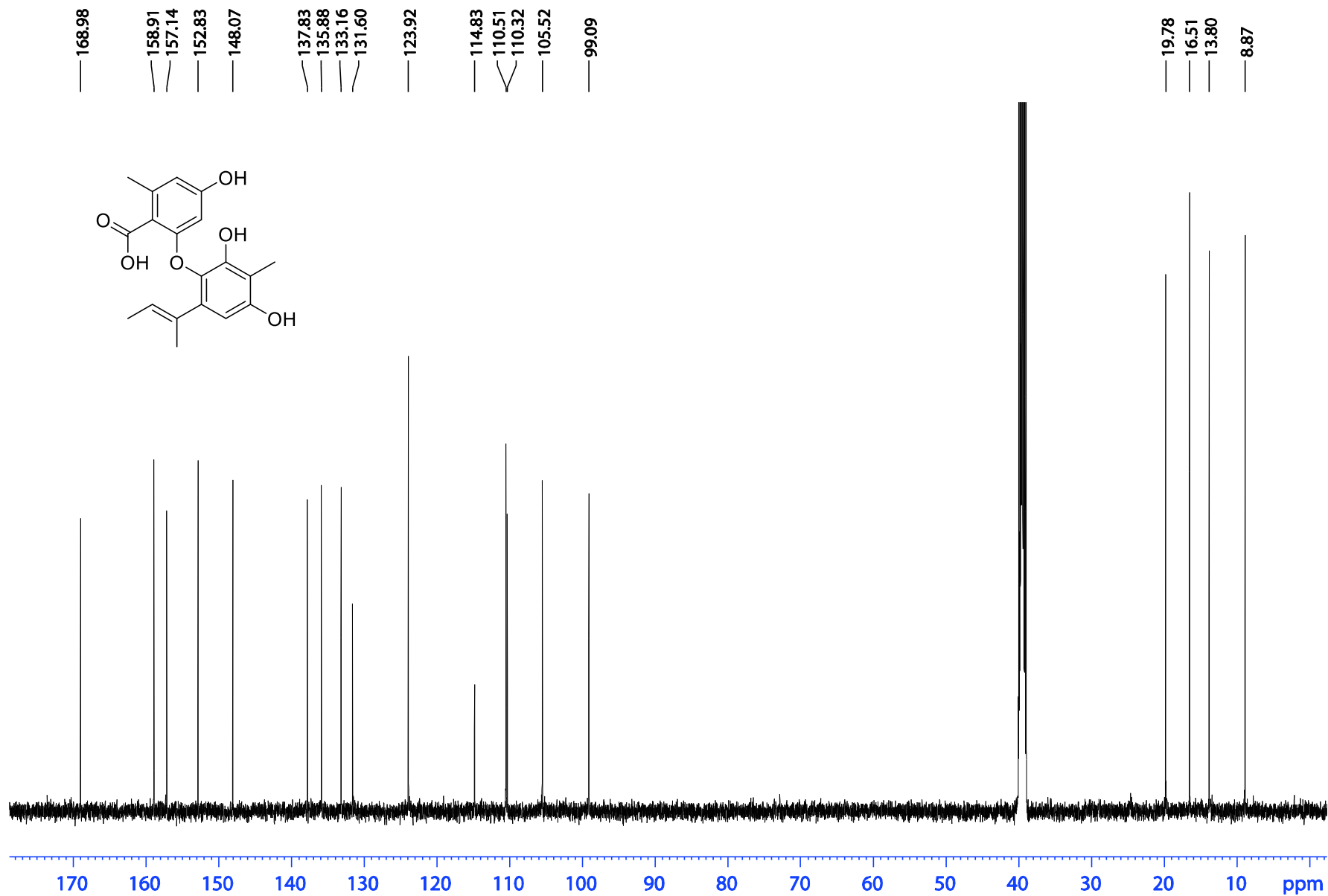


Figure S60. ¹³C NMR spectrum (125 MHz, DMSO-*d*₆) of unguinolic acid (10)

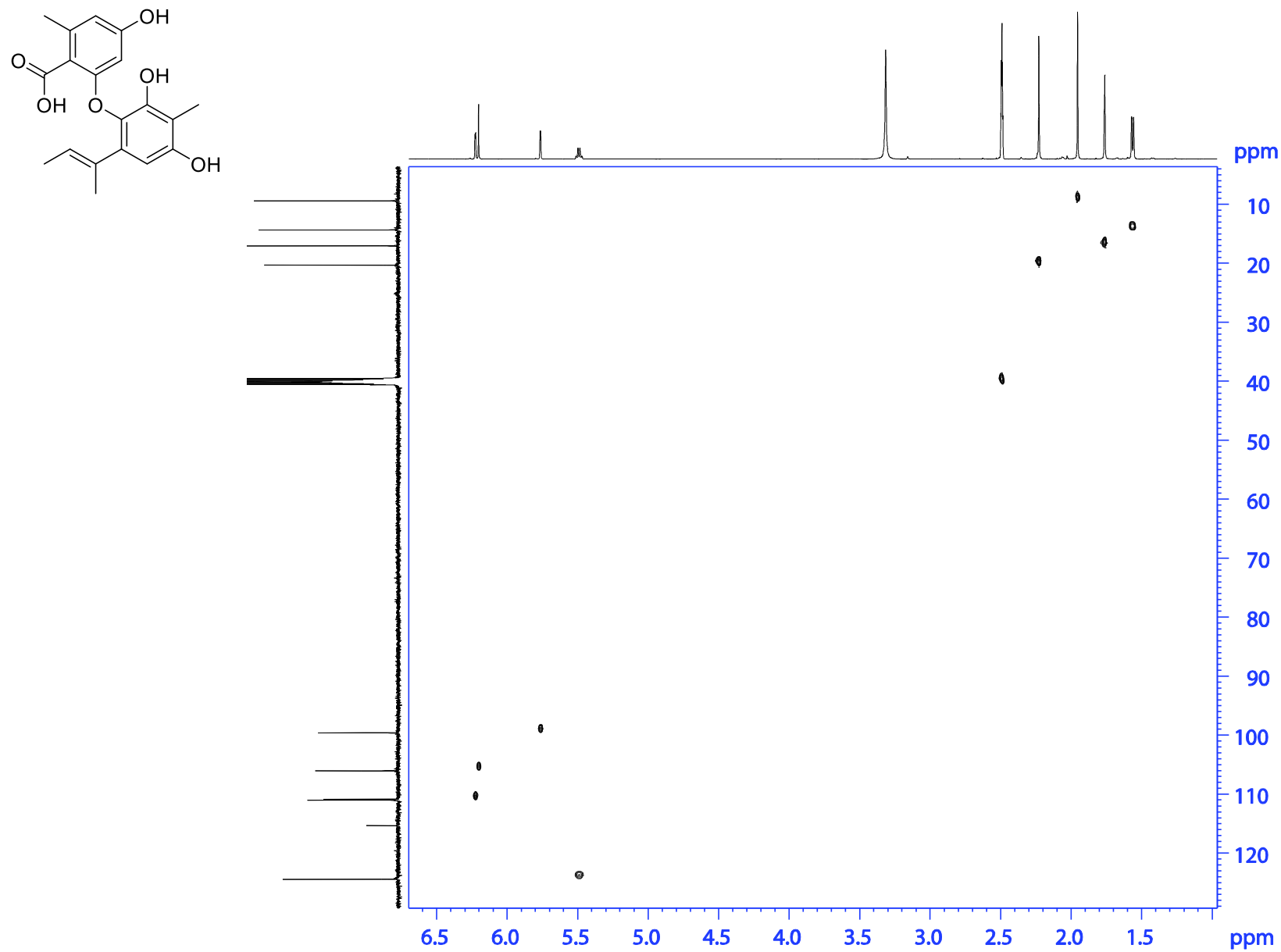


Figure S61. ¹H-¹³C HSQC NMR spectrum (500 MHz, DMSO-*d*₆) of unguinolic acid (10)

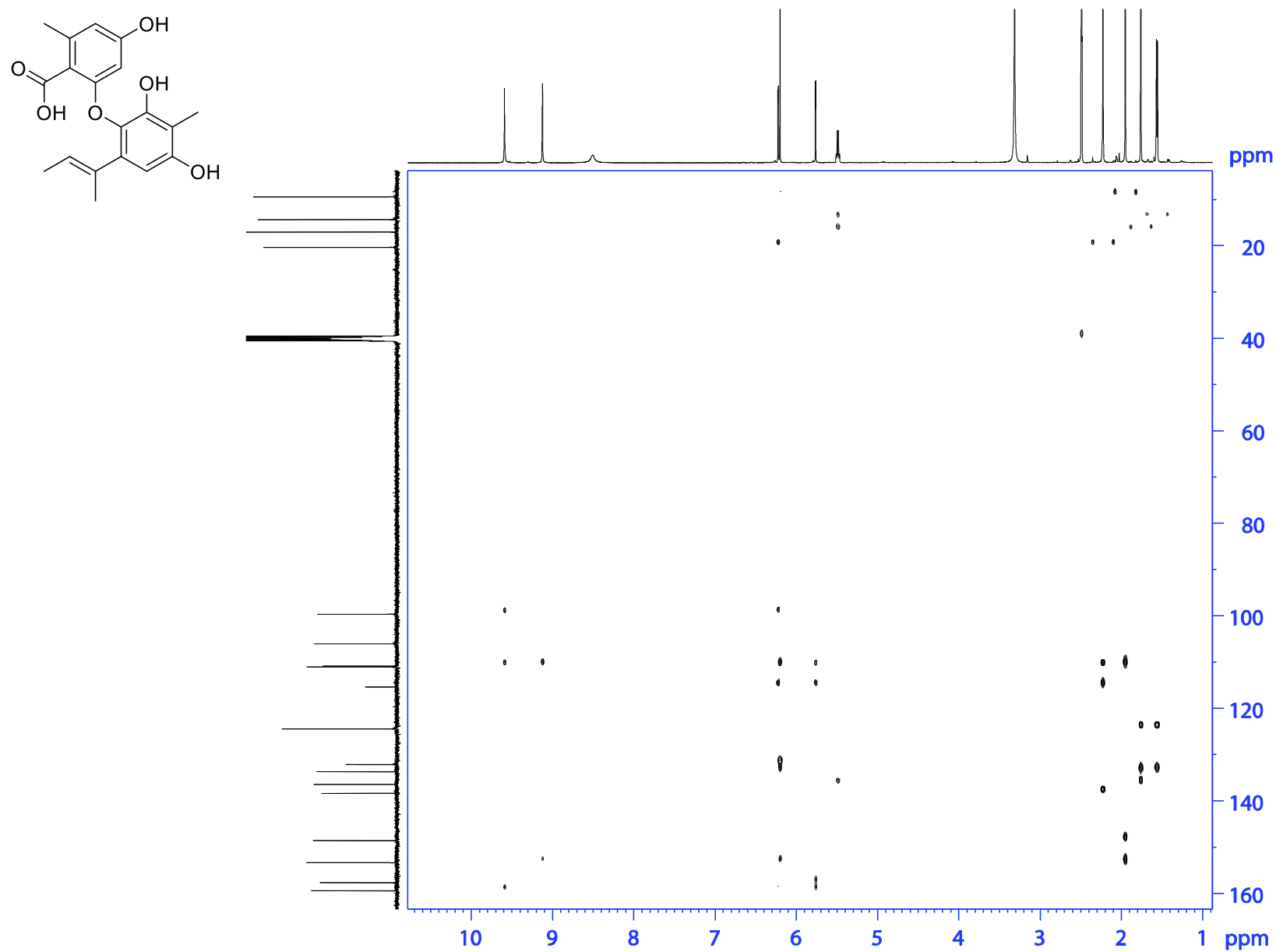


Figure S62. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of unguinolic acid (**10**)

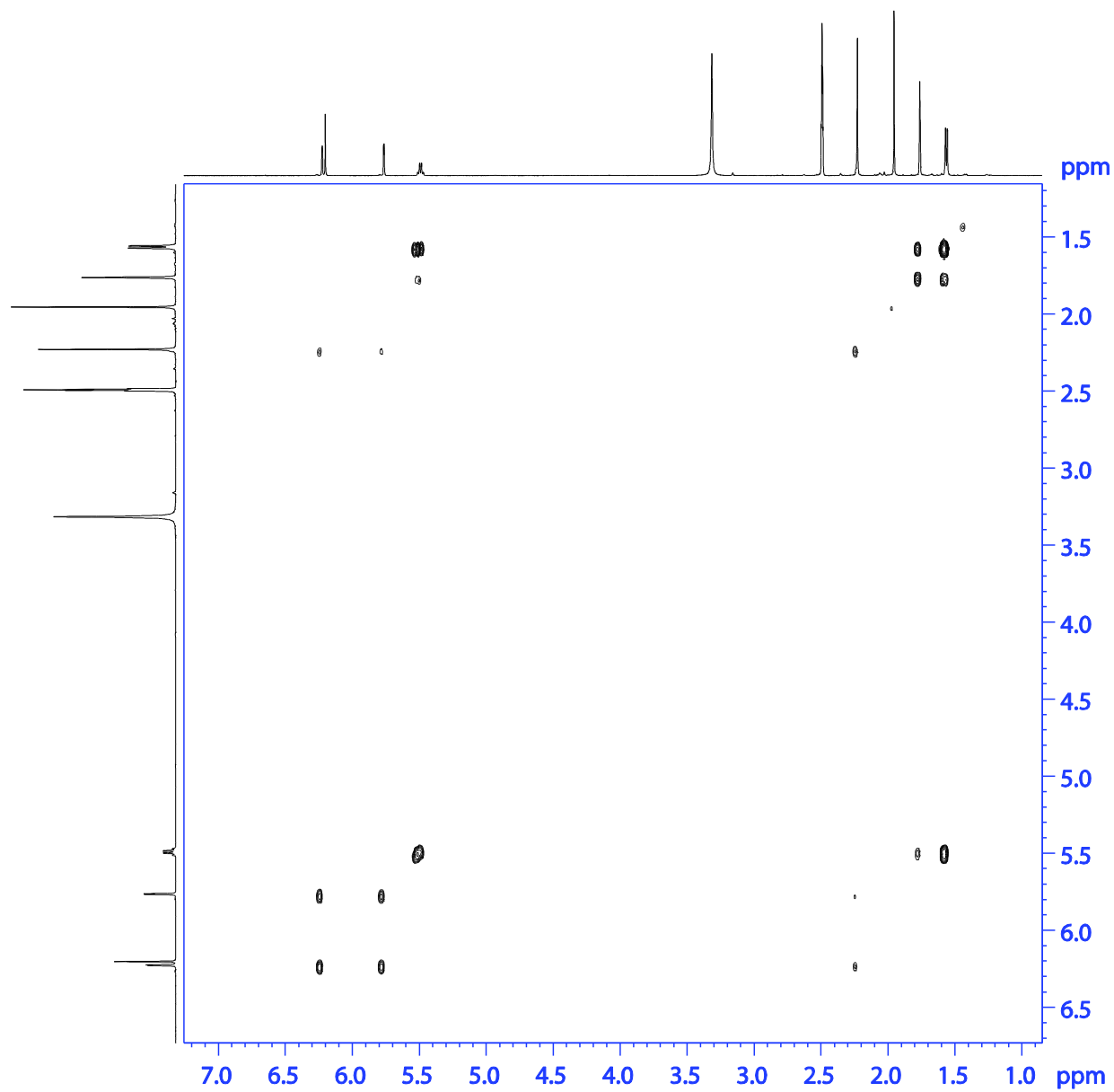
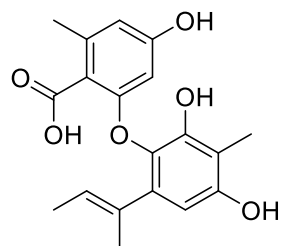


Figure S63. ^1H - ^1H COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of unguinolic acid (**10**)

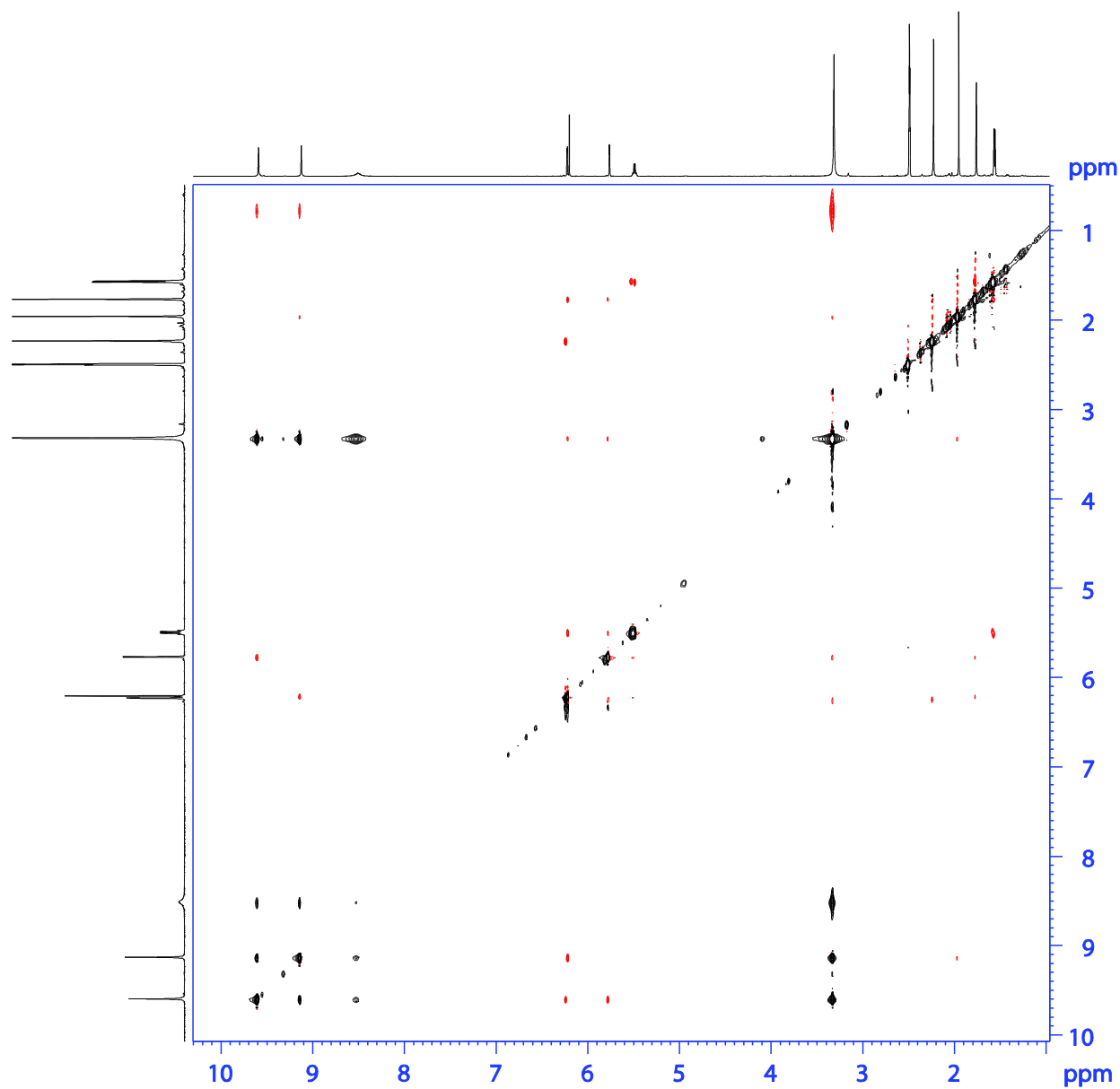
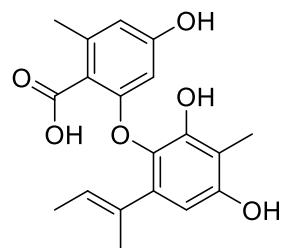


Figure S64. ^1H - ^1H ROESY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of unguinolic acid (**10**)

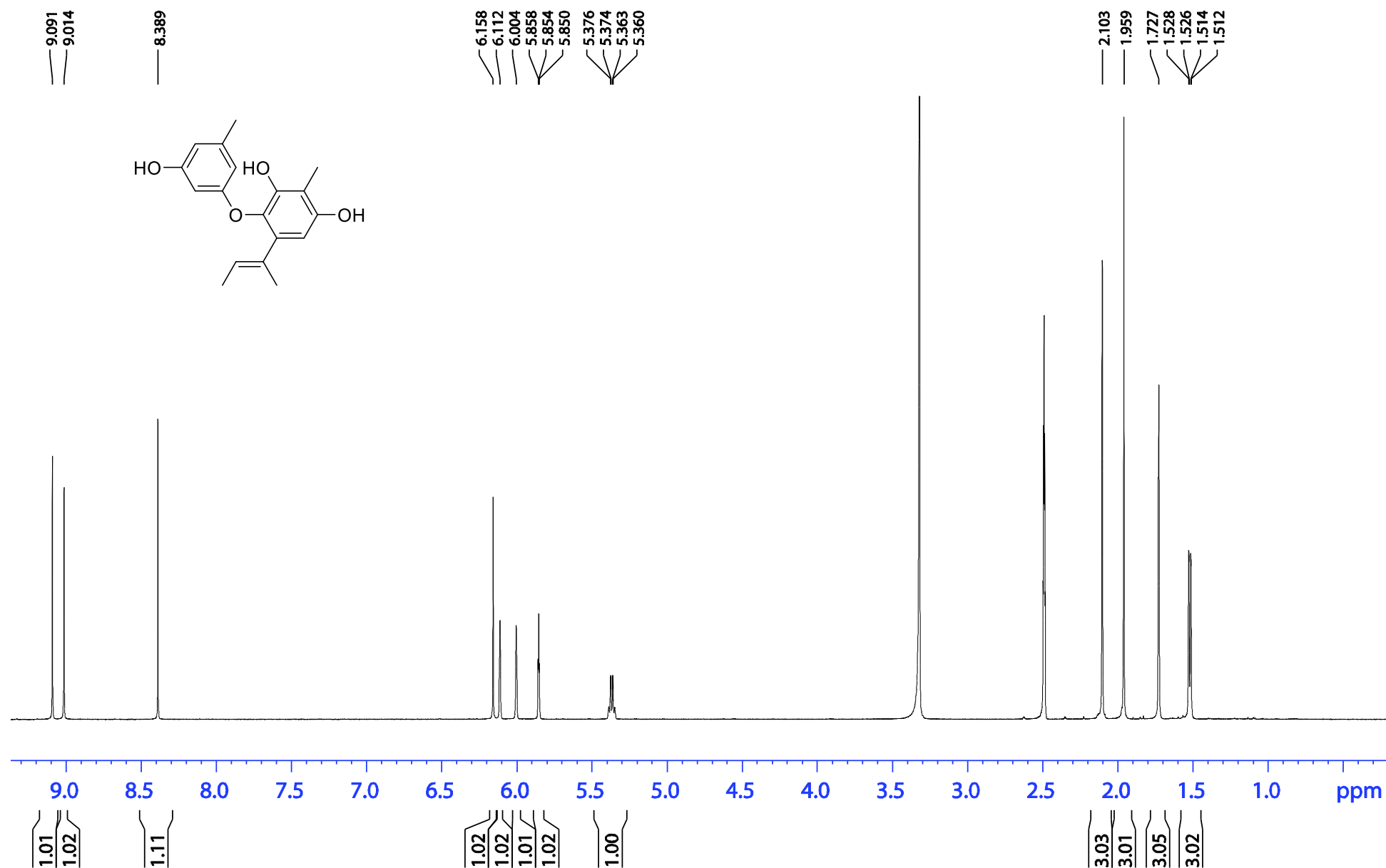


Figure S65. ¹H NMR spectrum (500 MHz, DMSO-*d*₆) of decarboxyunguinalic acid (11)

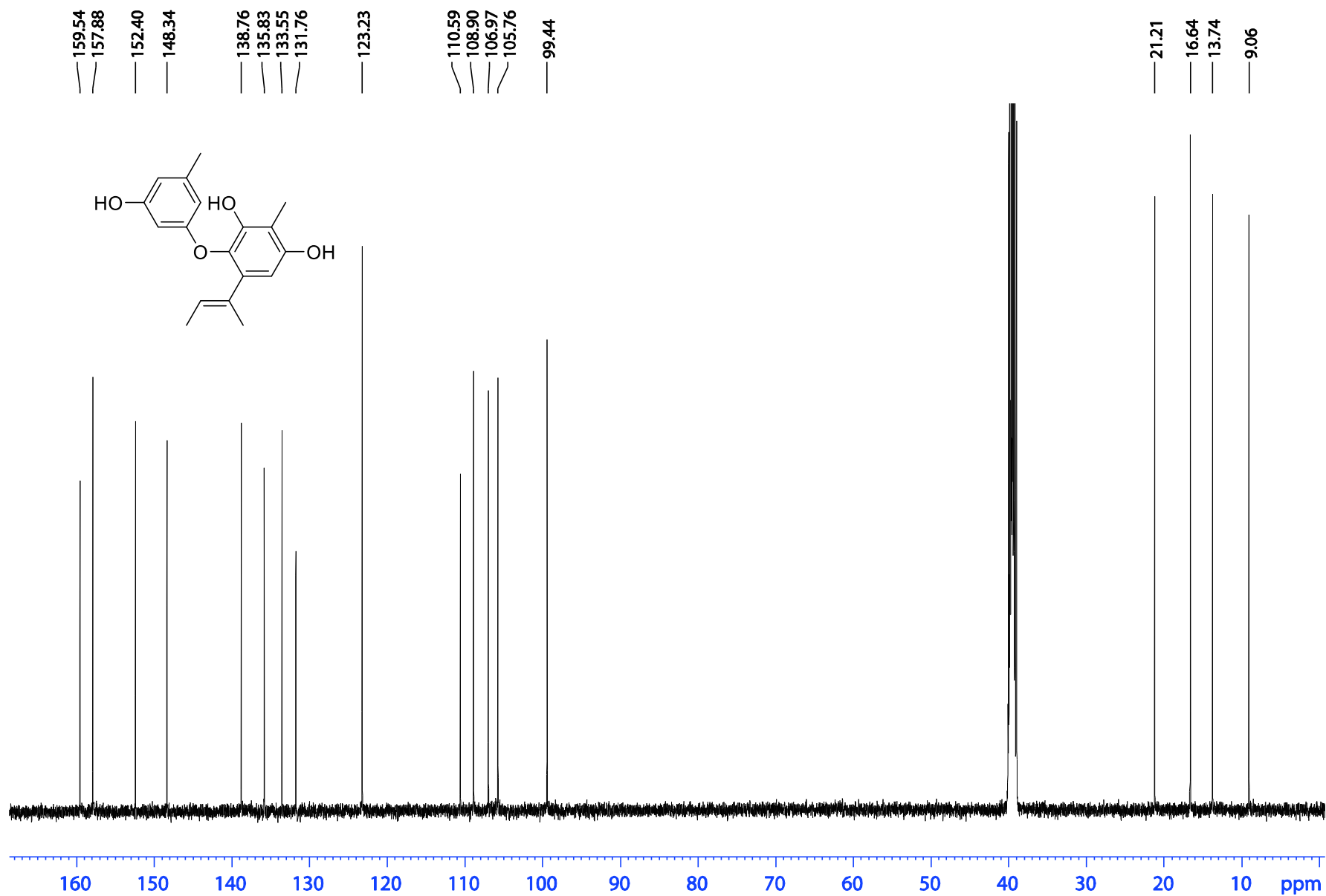


Figure S66. ¹³C NMR spectrum (125 MHz, DMSO-*d*₆) of decarboxyunguinoic acid (11)

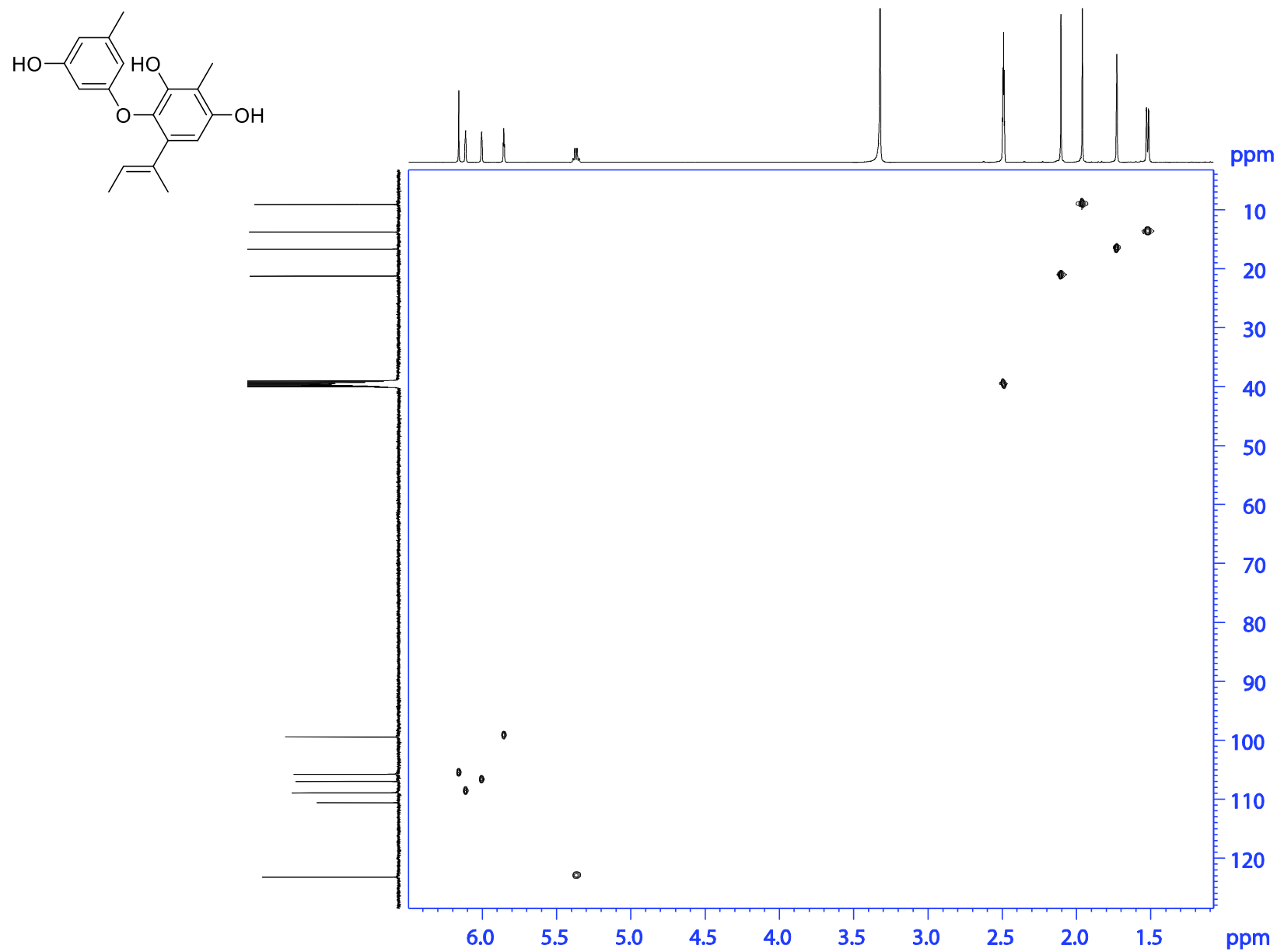


Figure S67. ^1H - ^{13}C HSQC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguinoic acid (11)

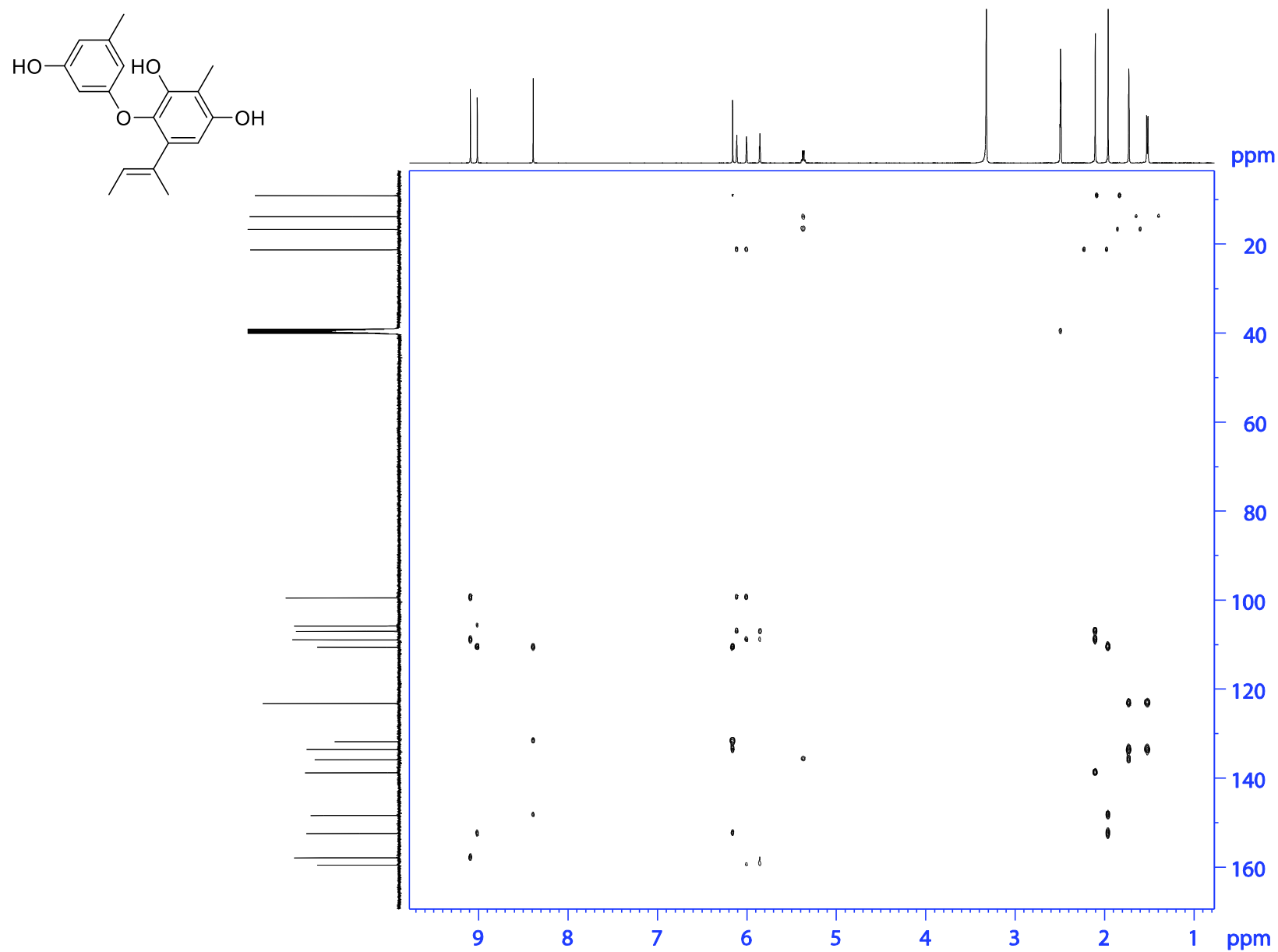


Figure S68. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguinic acid (11)

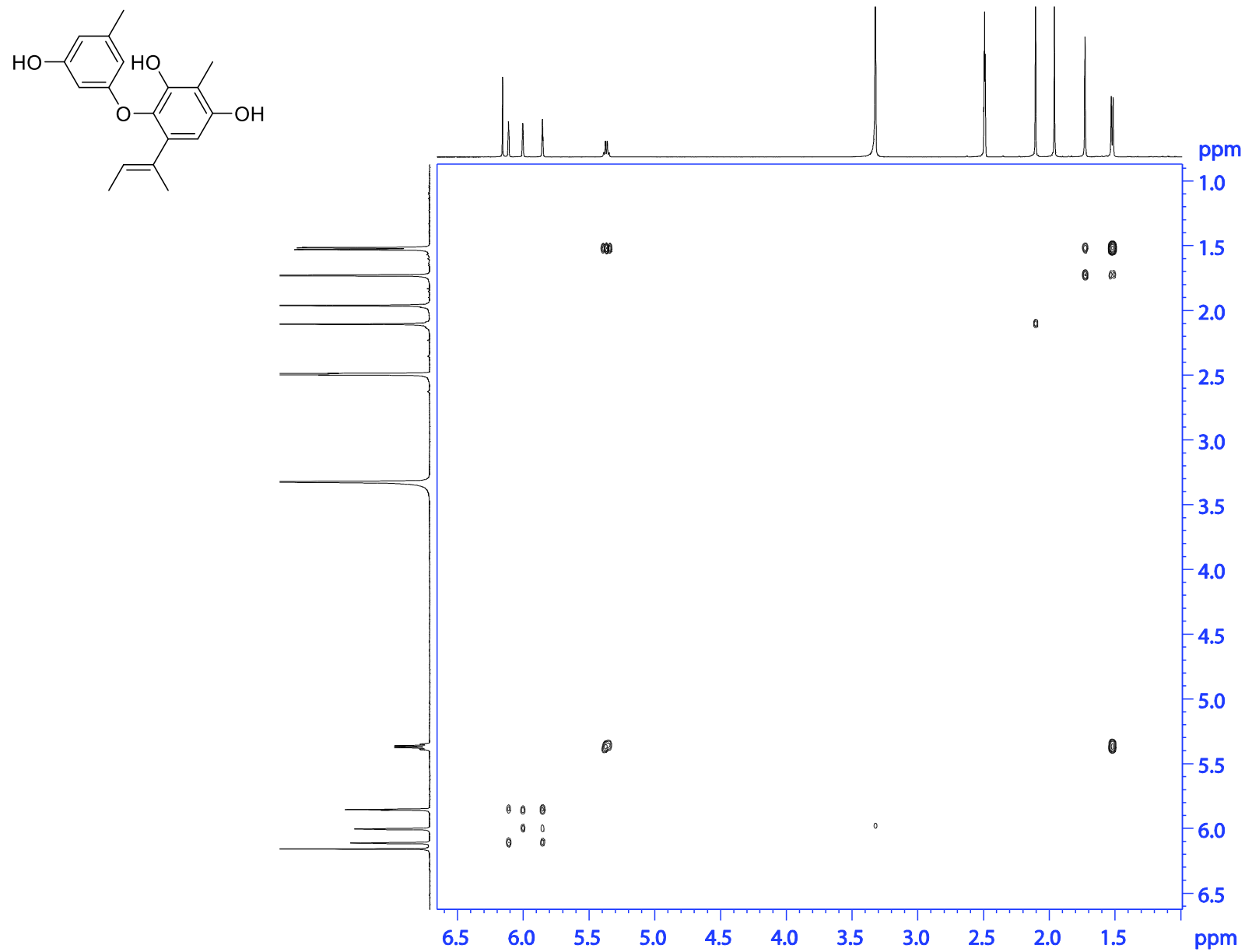


Figure S69. ^1H - ^1H COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of decarboxyunguinic acid (**11**)

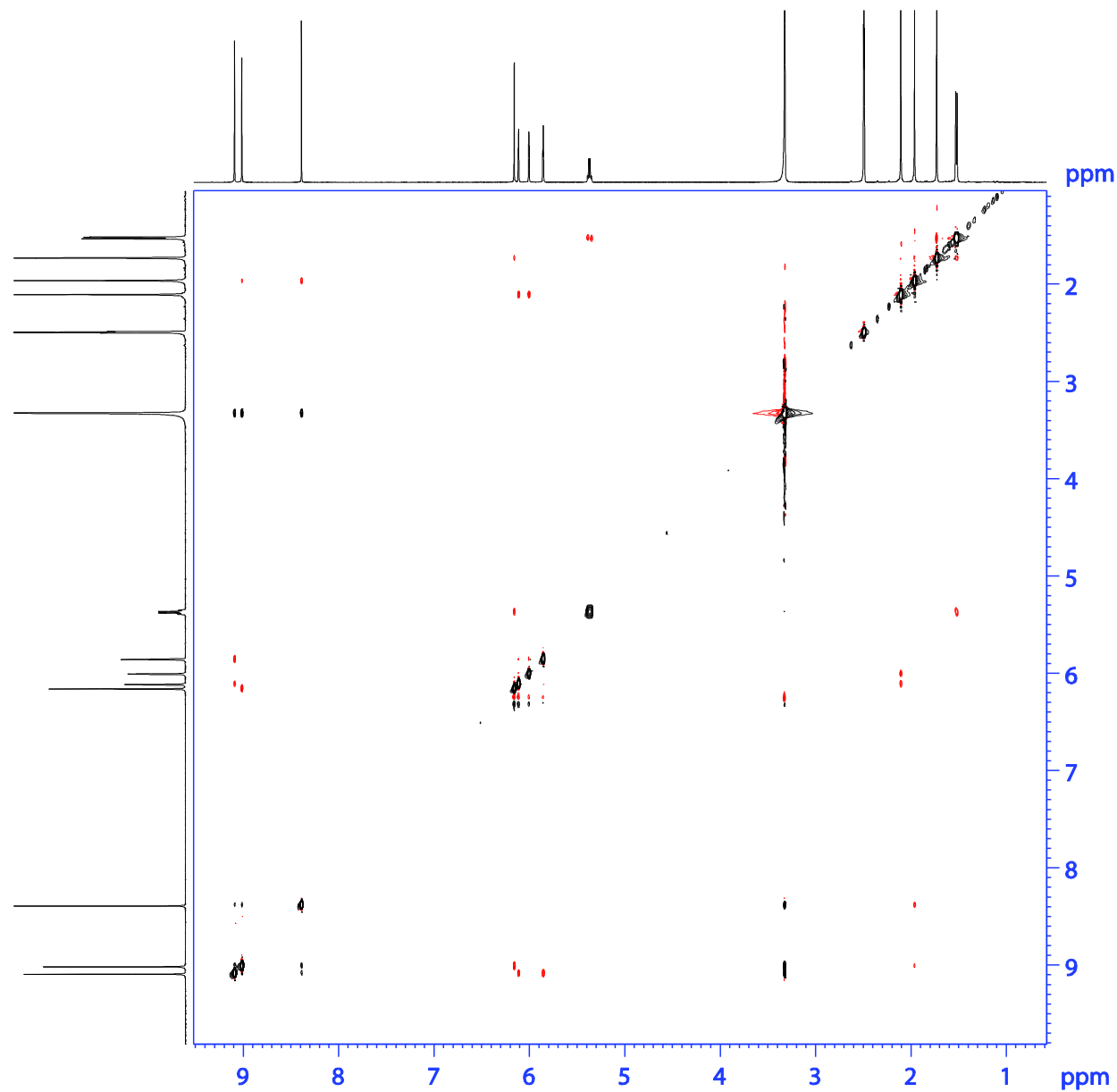
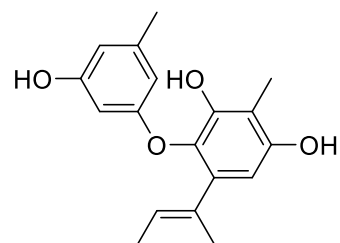


Figure S70. ^1H - ^1H ROESY NMR spectrum (500 MHz, $\text{DMSO-}d_6$) of decarboxyunguinic acid (**11**)

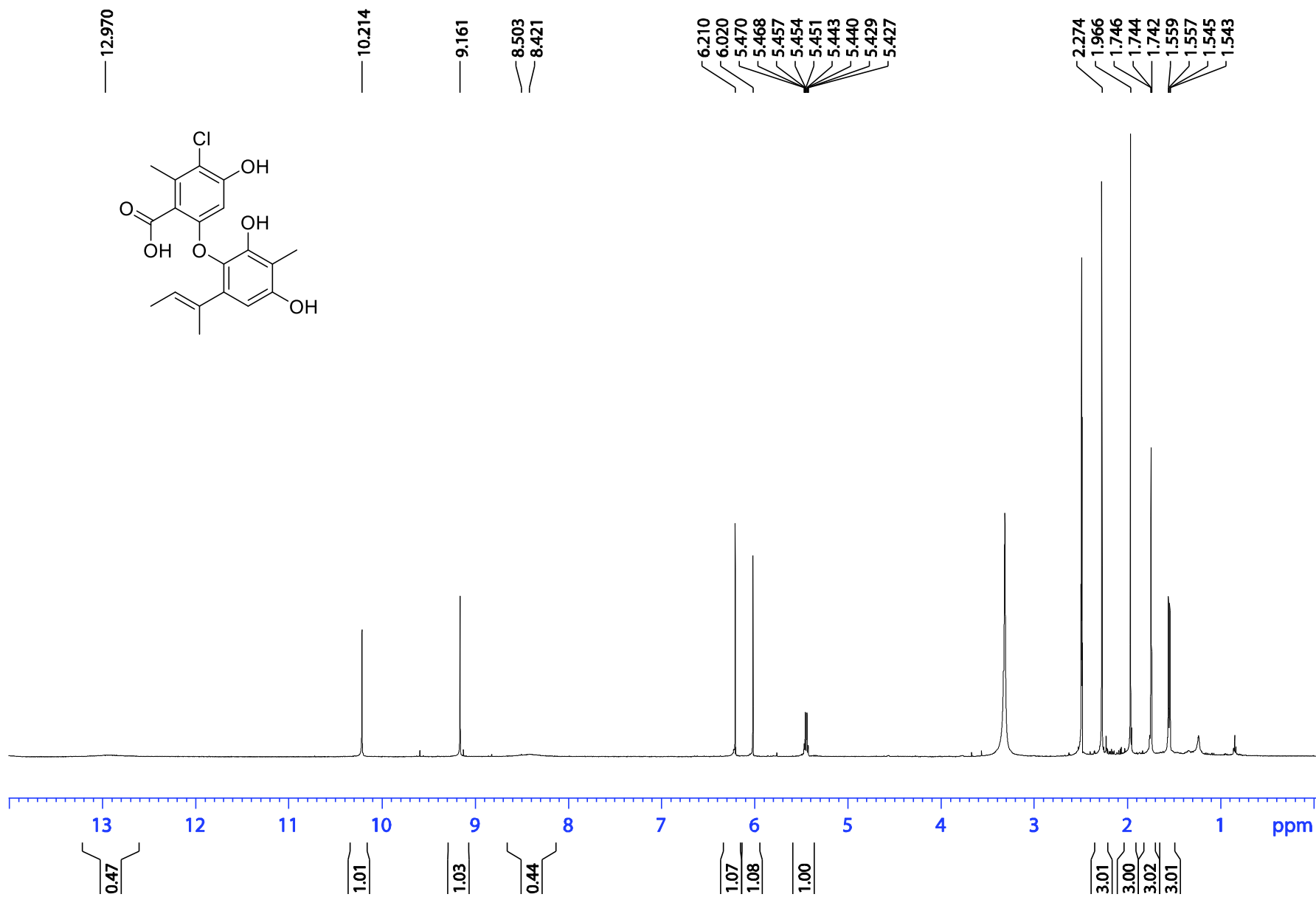


Figure S71. ¹H NMR spectrum (500 MHz, DMSO-*d*₆) of 5-chlorourguinollic acid (12)

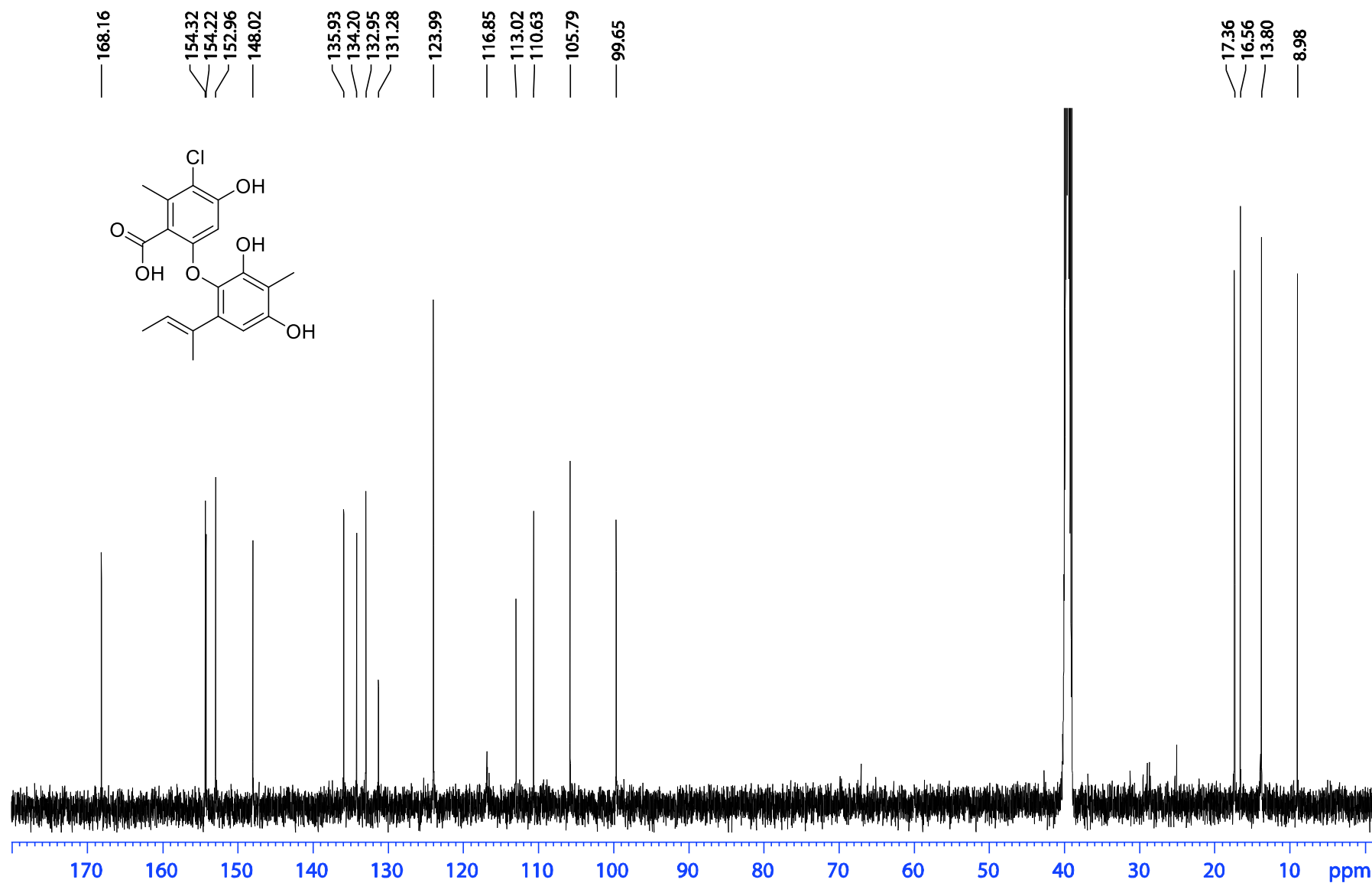


Figure S72. ¹³C NMR spectrum (125 MHz, DMSO-*d*₆) of 5-chlorourguinollic acid (12)

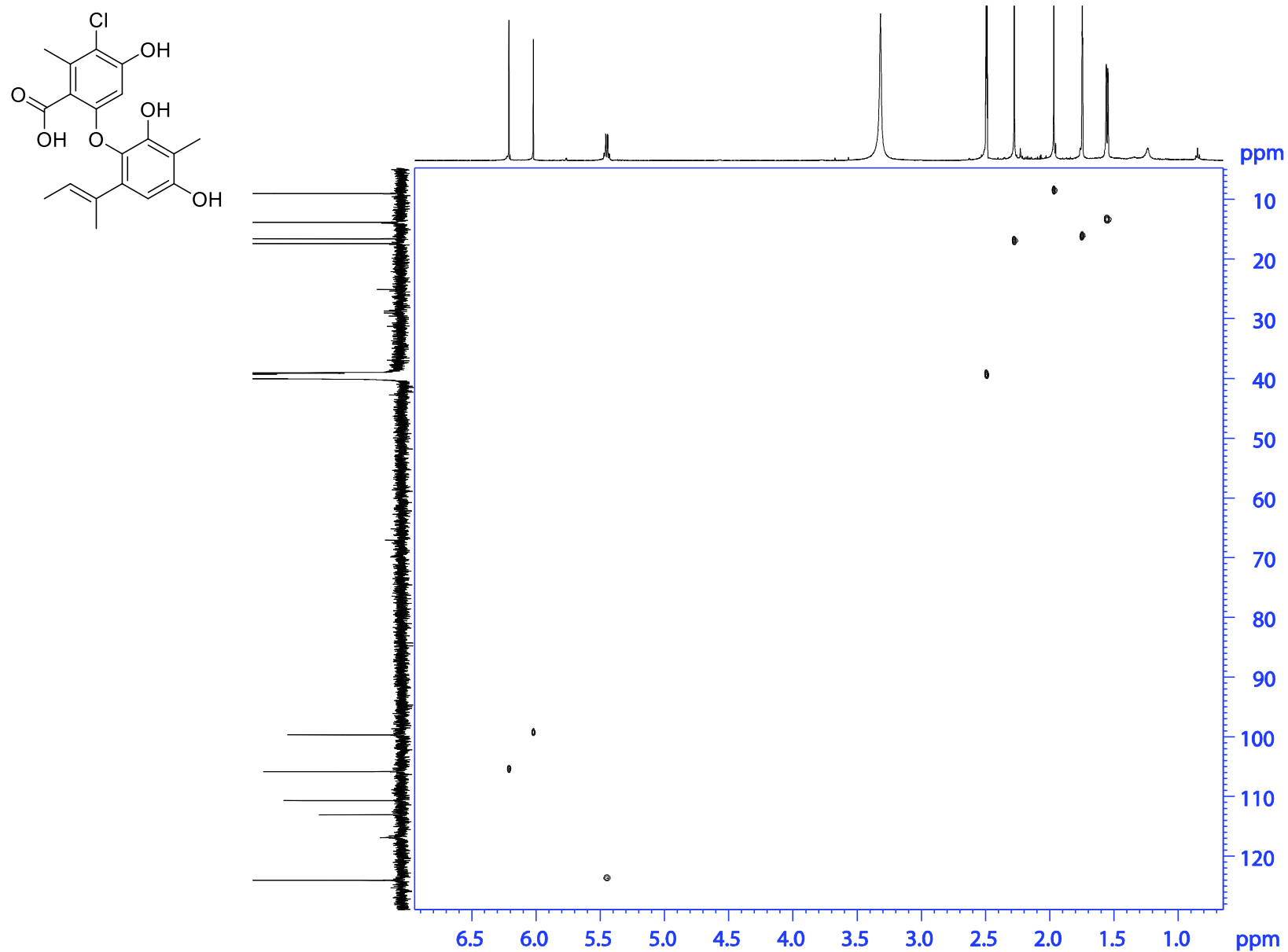


Figure S73. ¹H-¹³C HSQC NMR spectrum (500 MHz, DMSO-*d*₆) of 5-chlorounguinolic acid (12)

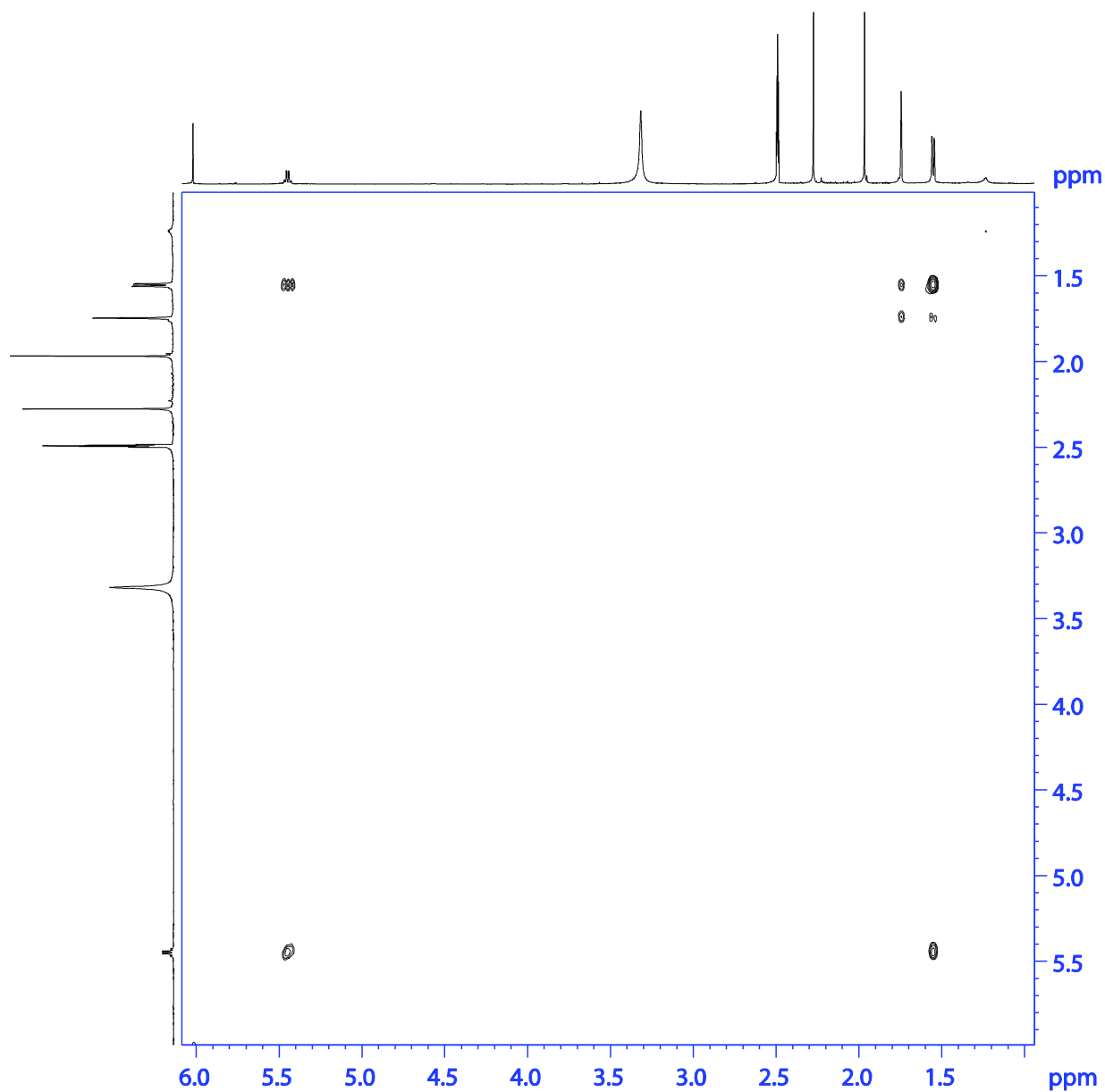
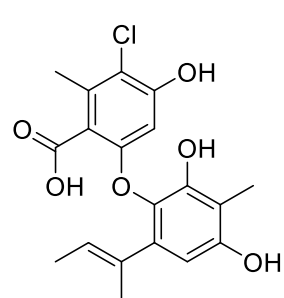


Figure S75. ^1H - ^1H COSY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of 5-chlorouruguinic acid (**12**)

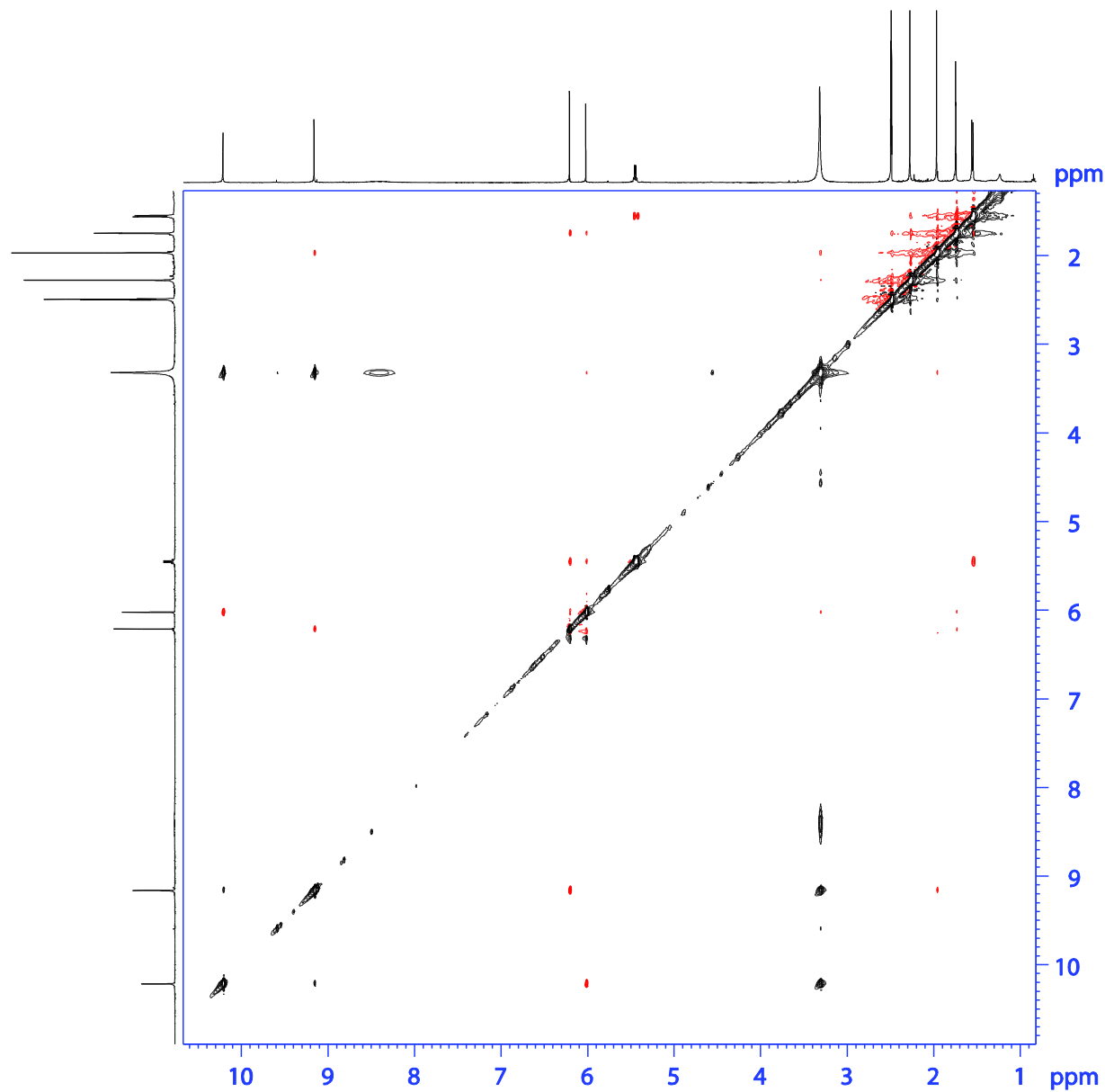
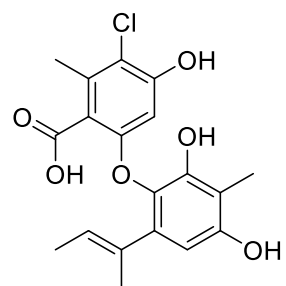


Figure S76. ^1H - ^1H ROESY NMR spectrum (500 MHz, $\text{DMSO}-d_6$) of 5-chlorourguinol-6-ol (**12**)

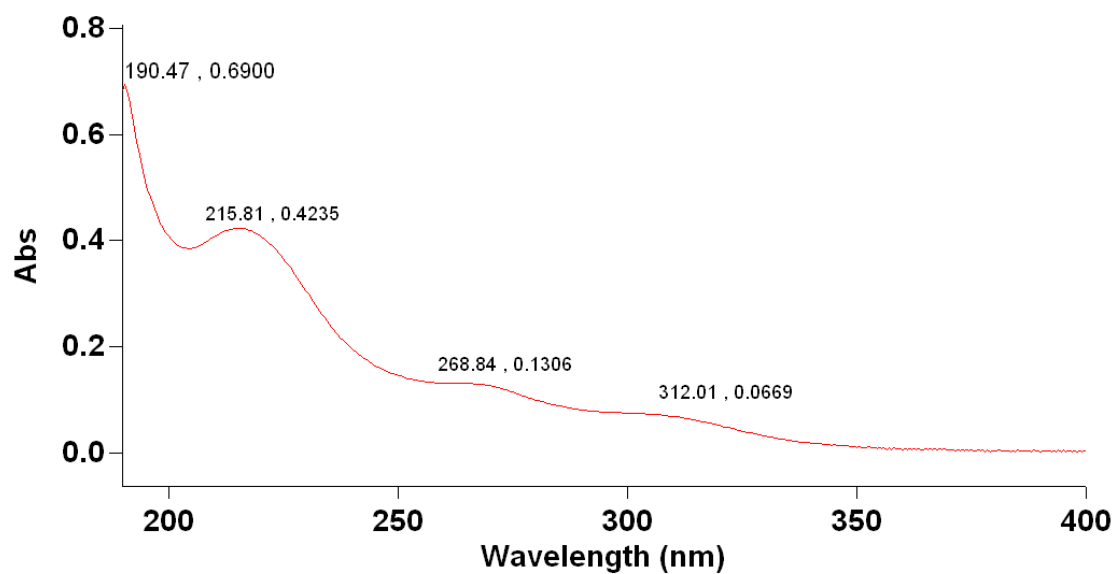


Figure S77. UV-vis spectrum of 7-carboxyfolipastatin (1) in MeOH

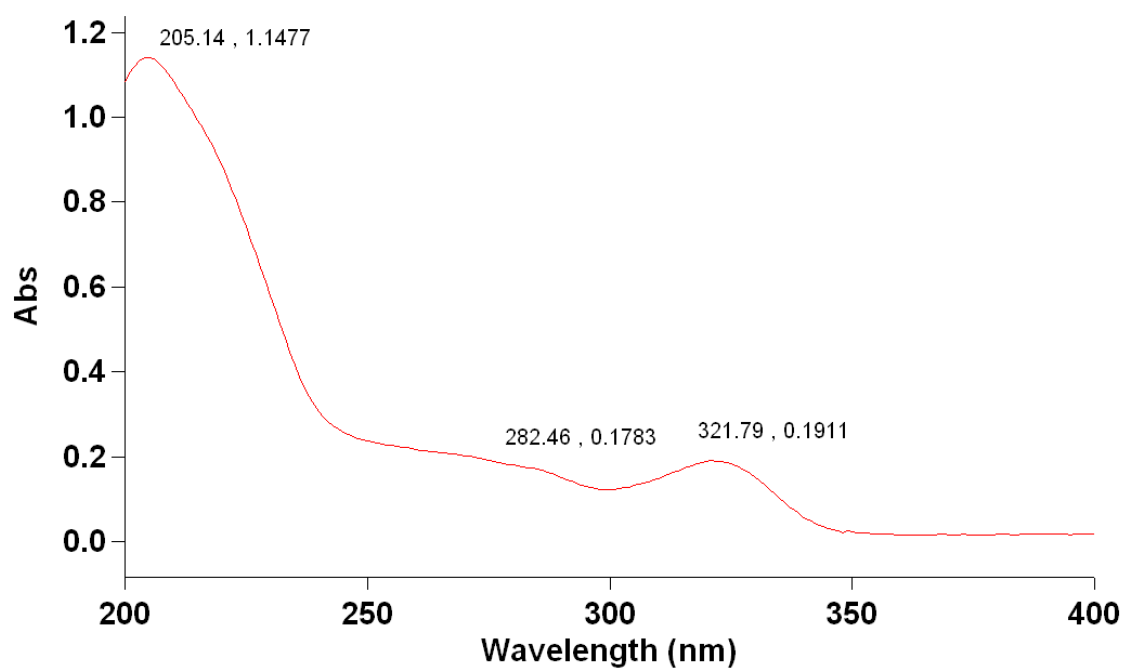


Figure S78. UV-vis spectrum of 4,7-dichlorounguinol (2) in MeOH

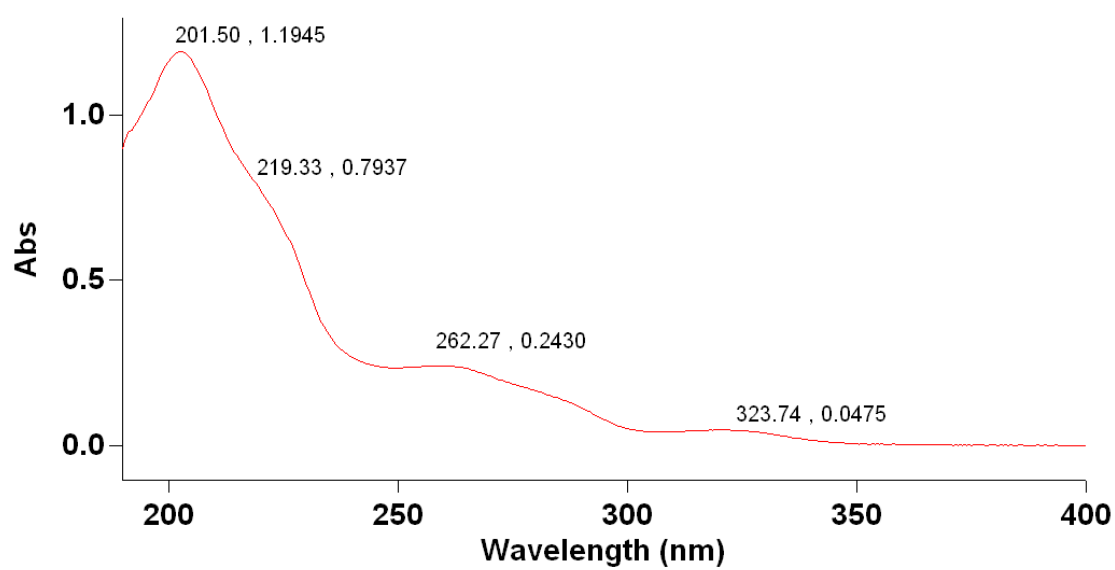


Figure S79. UV-vis spectrum of 7-bromounguinol (**3**) in MeOH

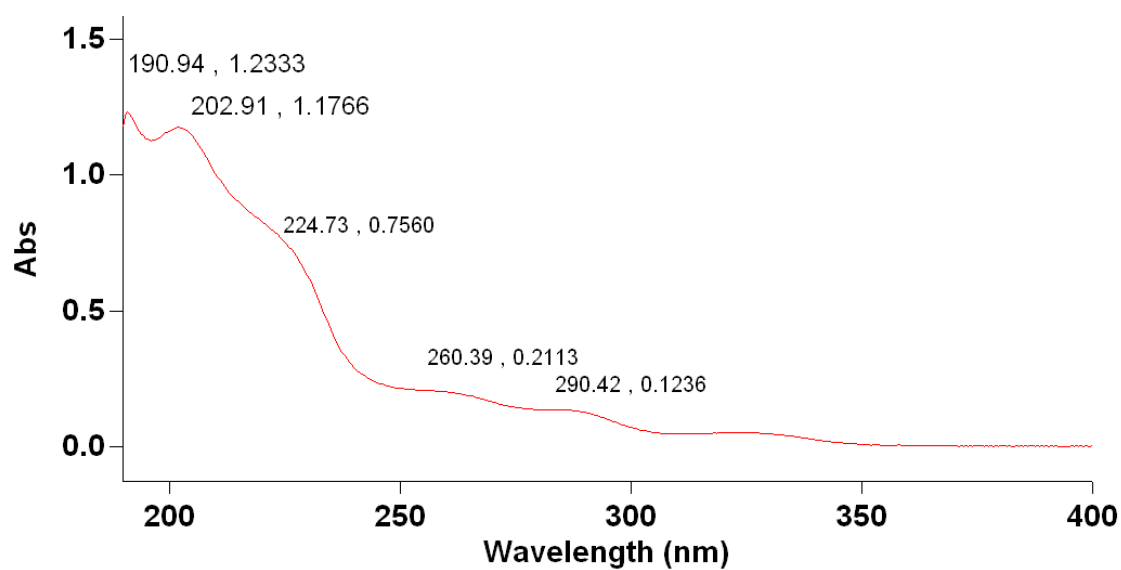


Figure S80. UV-vis spectrum of 2-chloro-7-bromounguinol (**4**) in MeOH

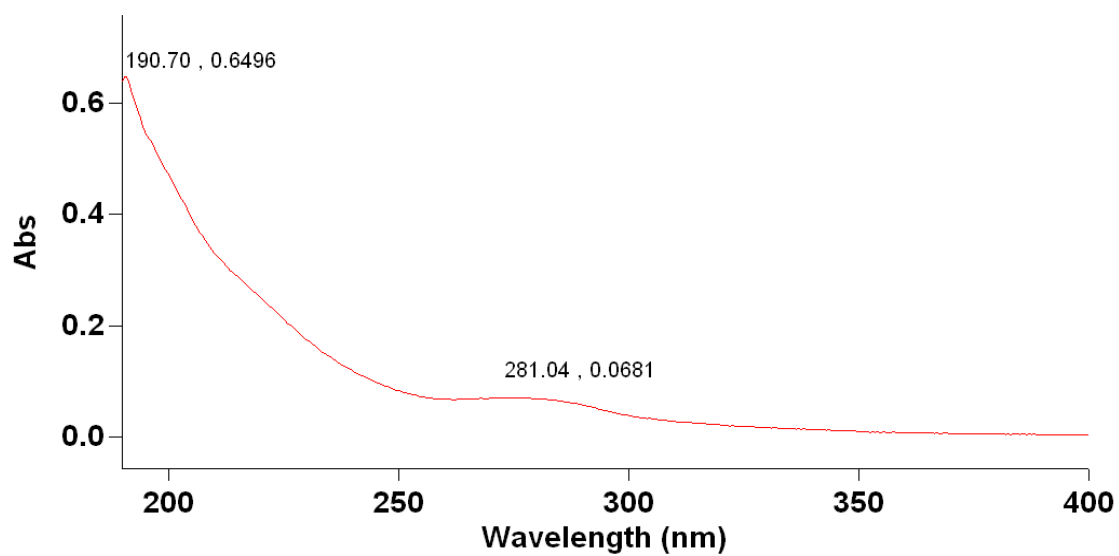


Figure S81. UV-vis spectrum of 7-bromofolipastatin (5) in MeOH

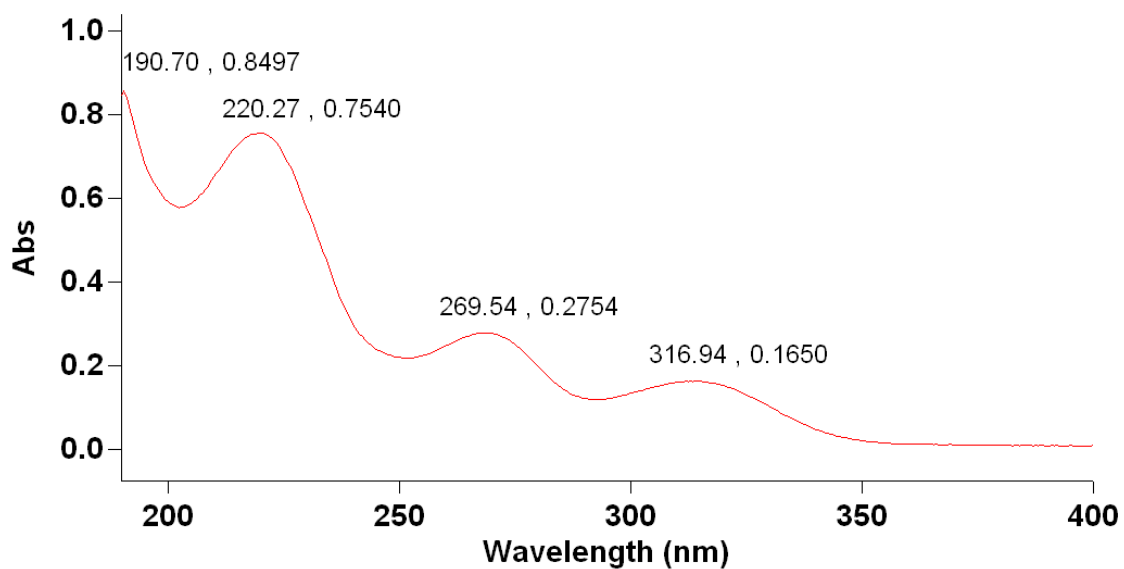


Figure S82. UV-vis spectrum of 5-bromoagonodepside B (6) in MeOH

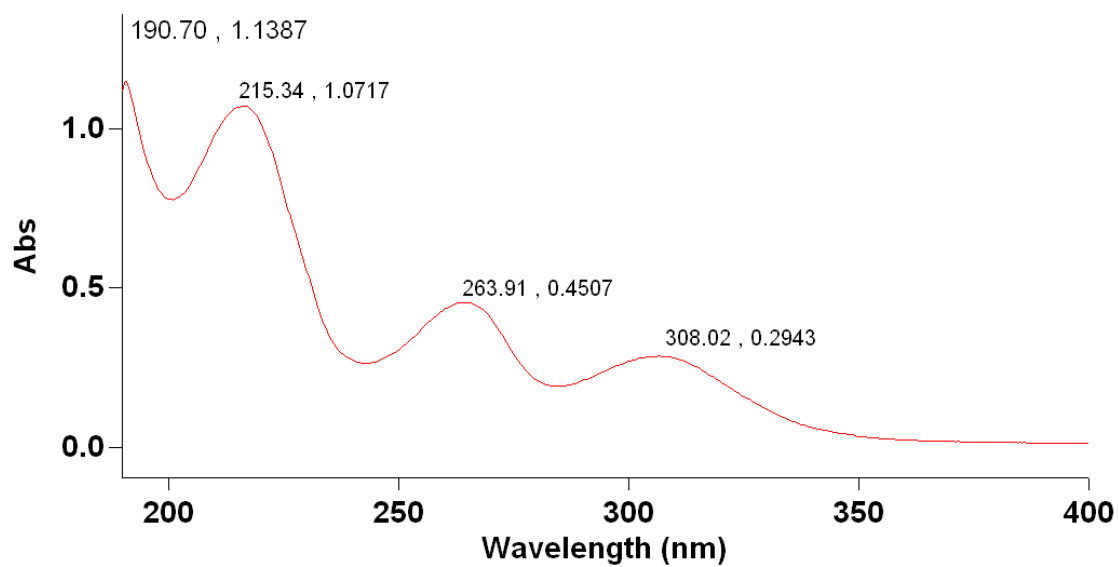


Figure S83. UV-vis spectrum of unguidepside A (7) in MeOH

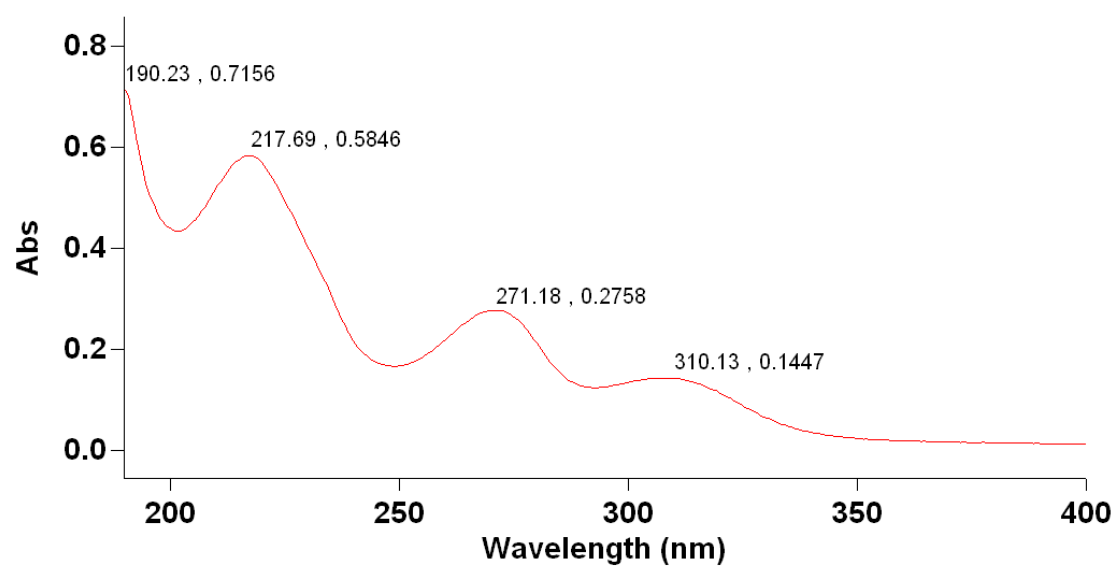


Figure S84. UV-vis spectrum of 3-bromounguidepside A (8) in MeOH

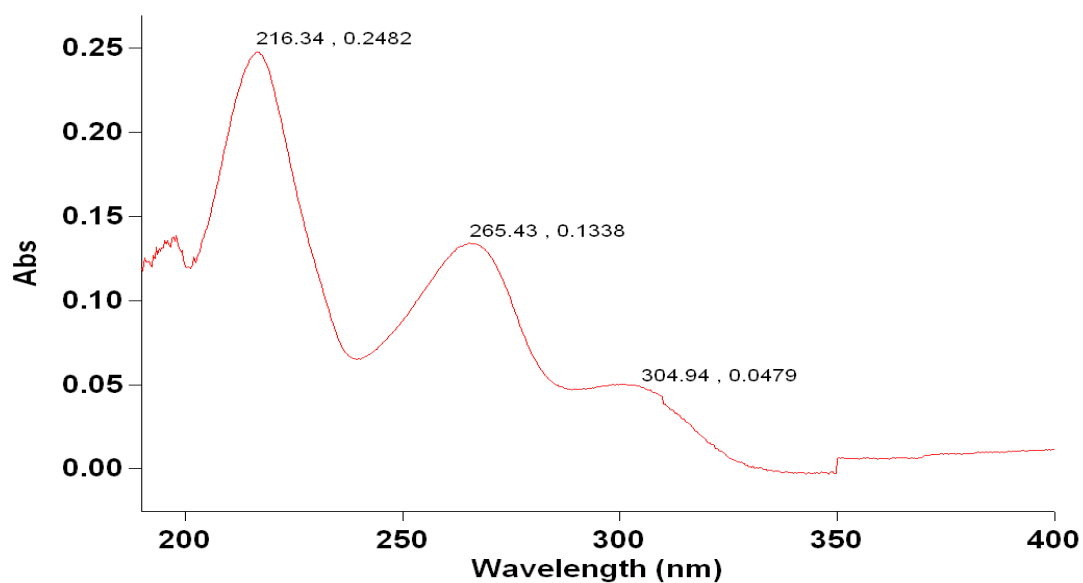


Figure S85. UV-vis spectrum of decarboxyunguidepside A (**9**) in MeOH

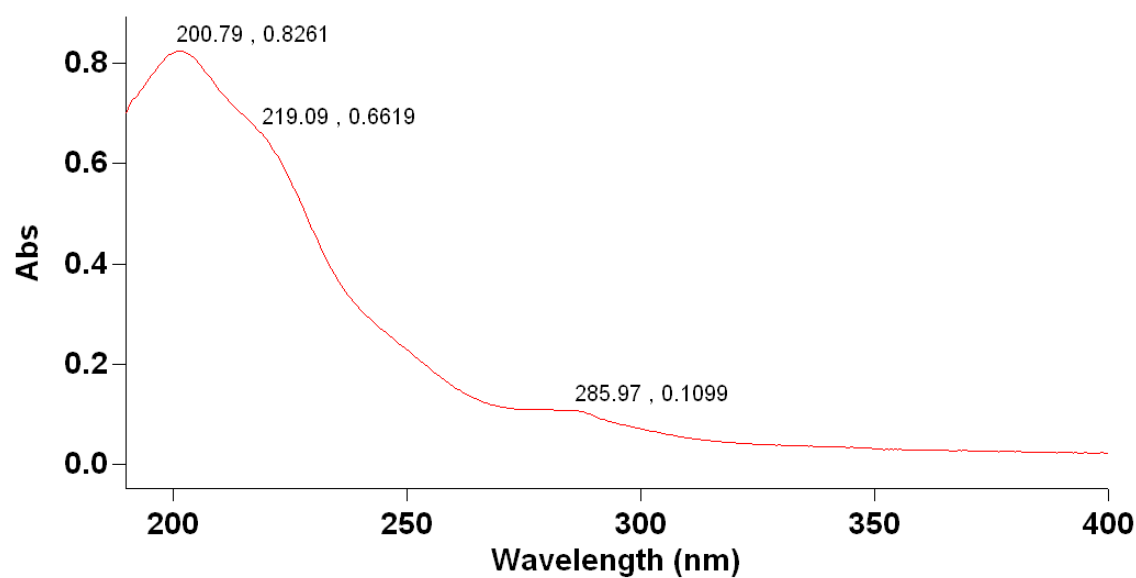


Figure S86. UV-vis spectrum of unguinolic acid (**10**) in MeOH

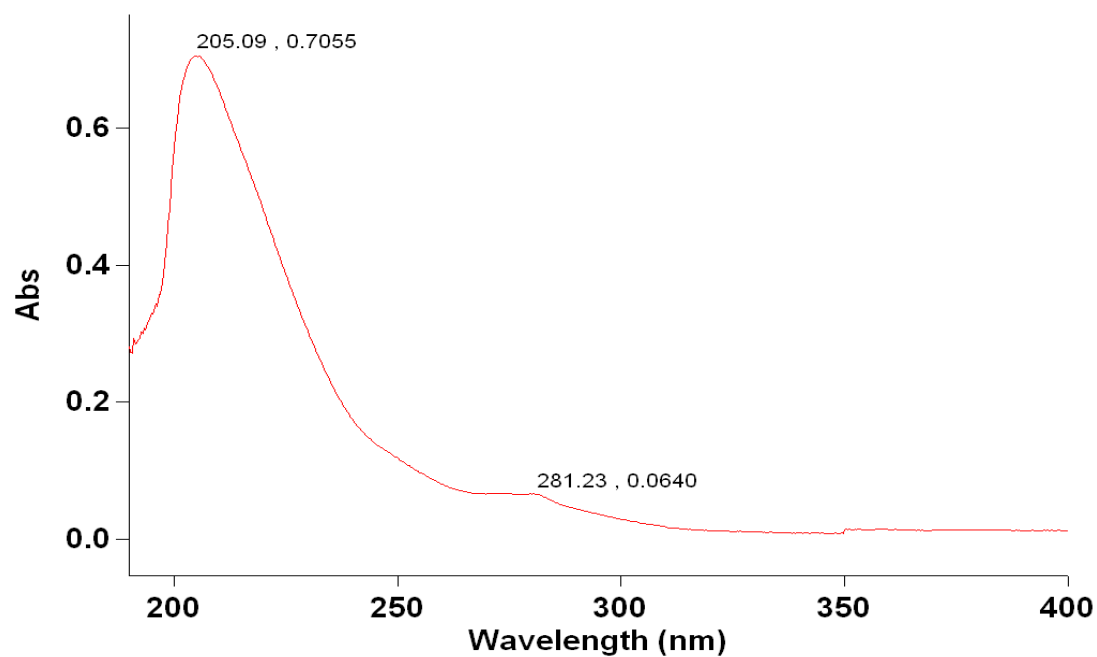


Figure S87. UV-vis spectrum of decarboxyunguinalic acid (11) in MeOH

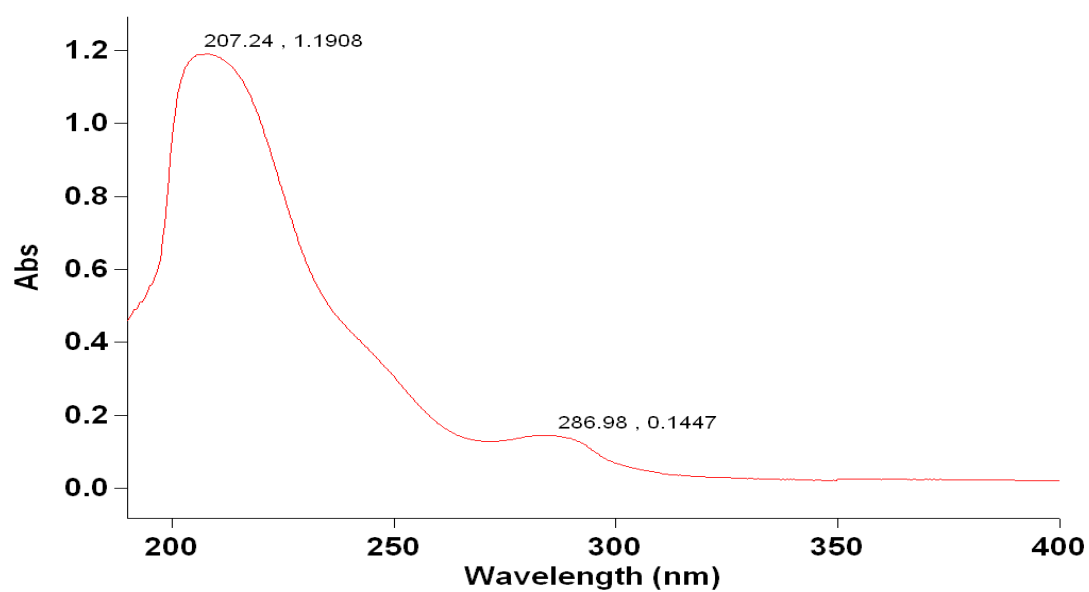


Figure S88. UV-vis spectrum of 5-chlorounguinalic acid (12) in MeOH

Polar_Peak_HRMS_POS #66-386 RT: 0.08-0.46 AV: 321 NL: 2.69E7
T: FTMS + p ESI Full ms [200.00-1000.00]

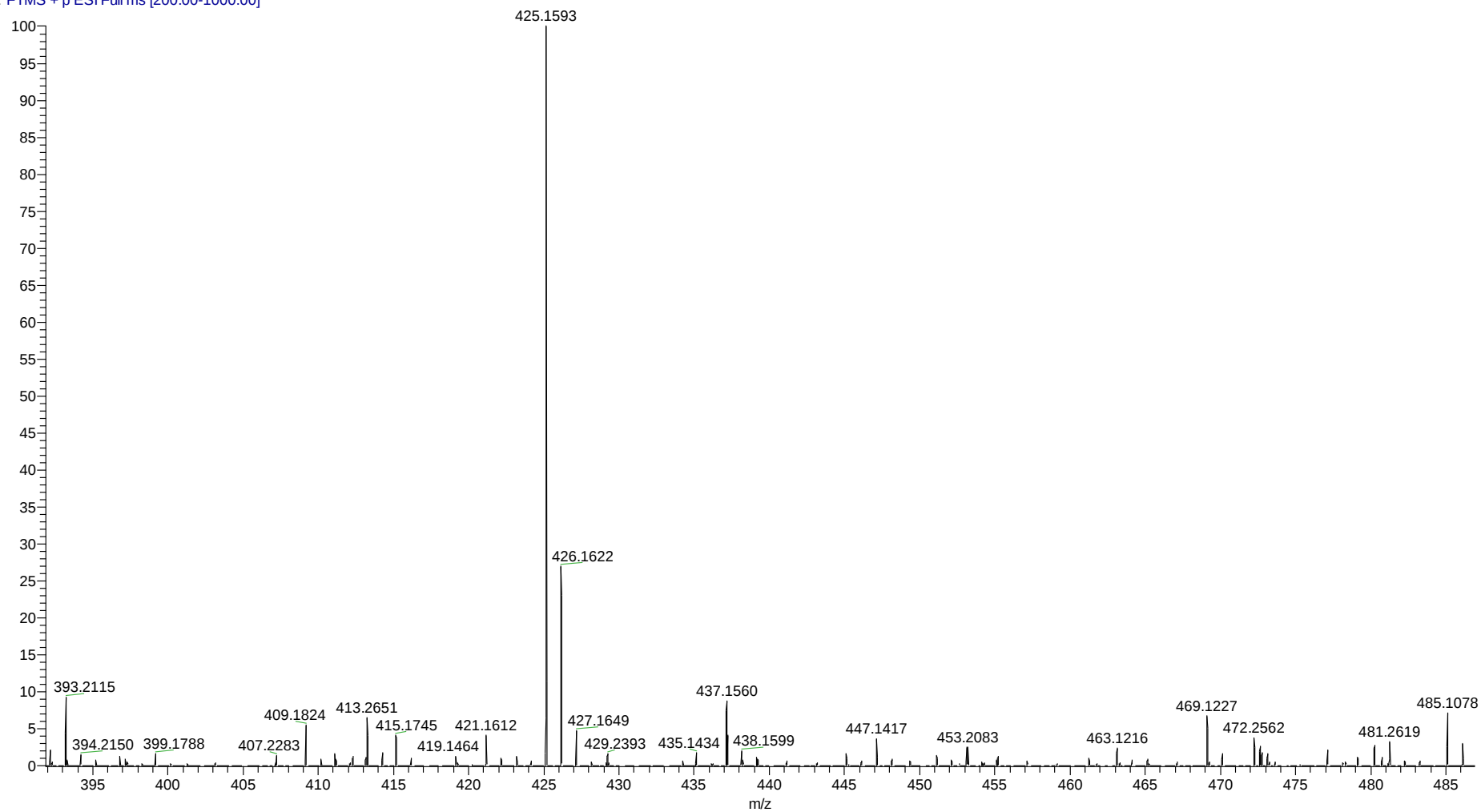


Figure S89. HR-ESI(+)-MS spectrum of 7-carboxyfolipastatin (**1**)

180221_AC12_100_10_Dichlorounguinol_Positive_4 #403-649 RT: 1.76-2.84 AV: 247 NL: 5.70E8
T: FTMS + p ESI Full ms [150.0000-2000.0000]

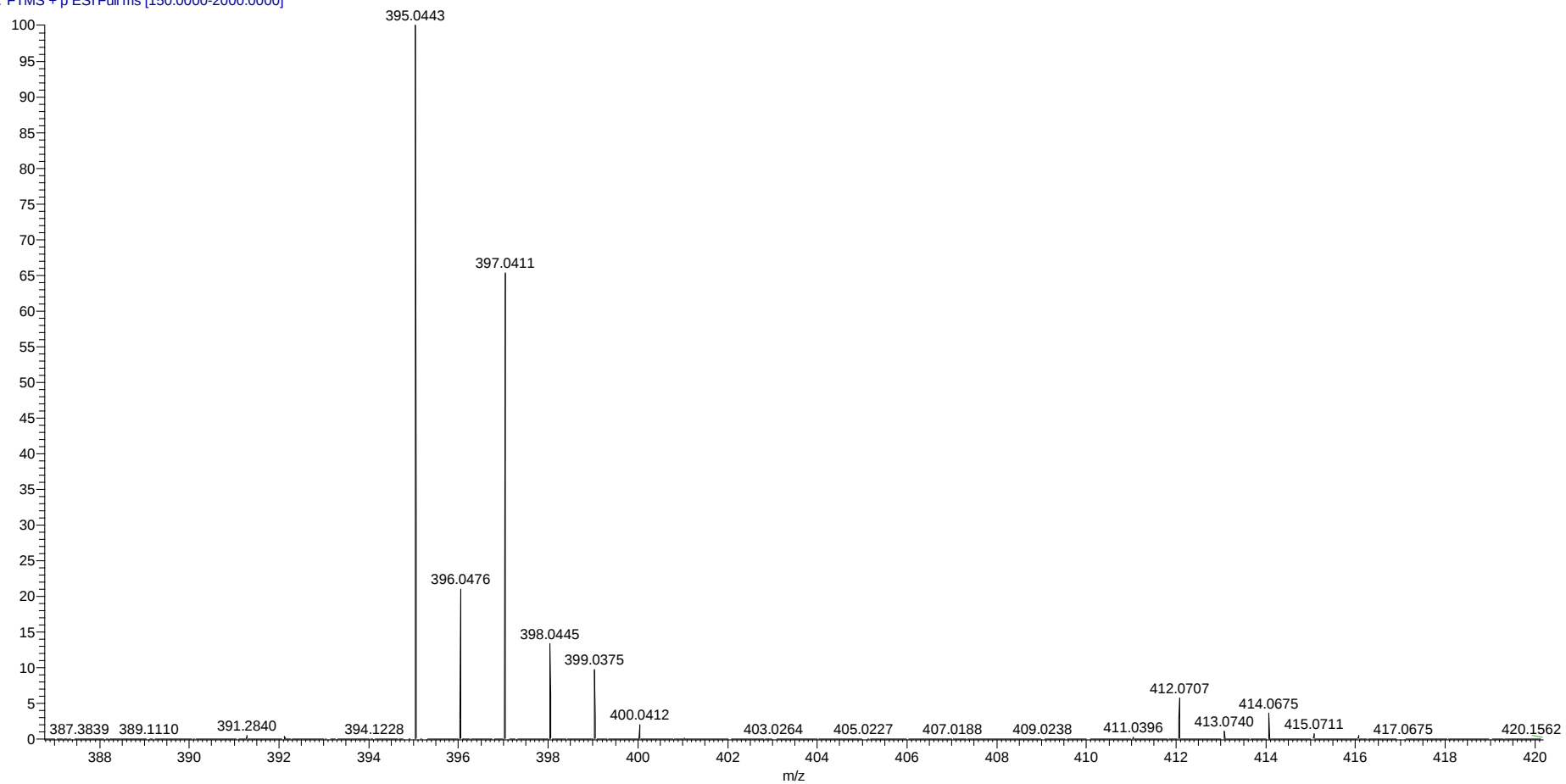


Figure S90. HR-ESI(+)-MS spectrum of 4,7-dichlorounguinol (2)

DBP_4_P4_POS #7-18 RT: 0.02-0.04 AV: 12 NL: 1.20E7
T: FTMS + p ESI Full ms [150.00-2100.00]

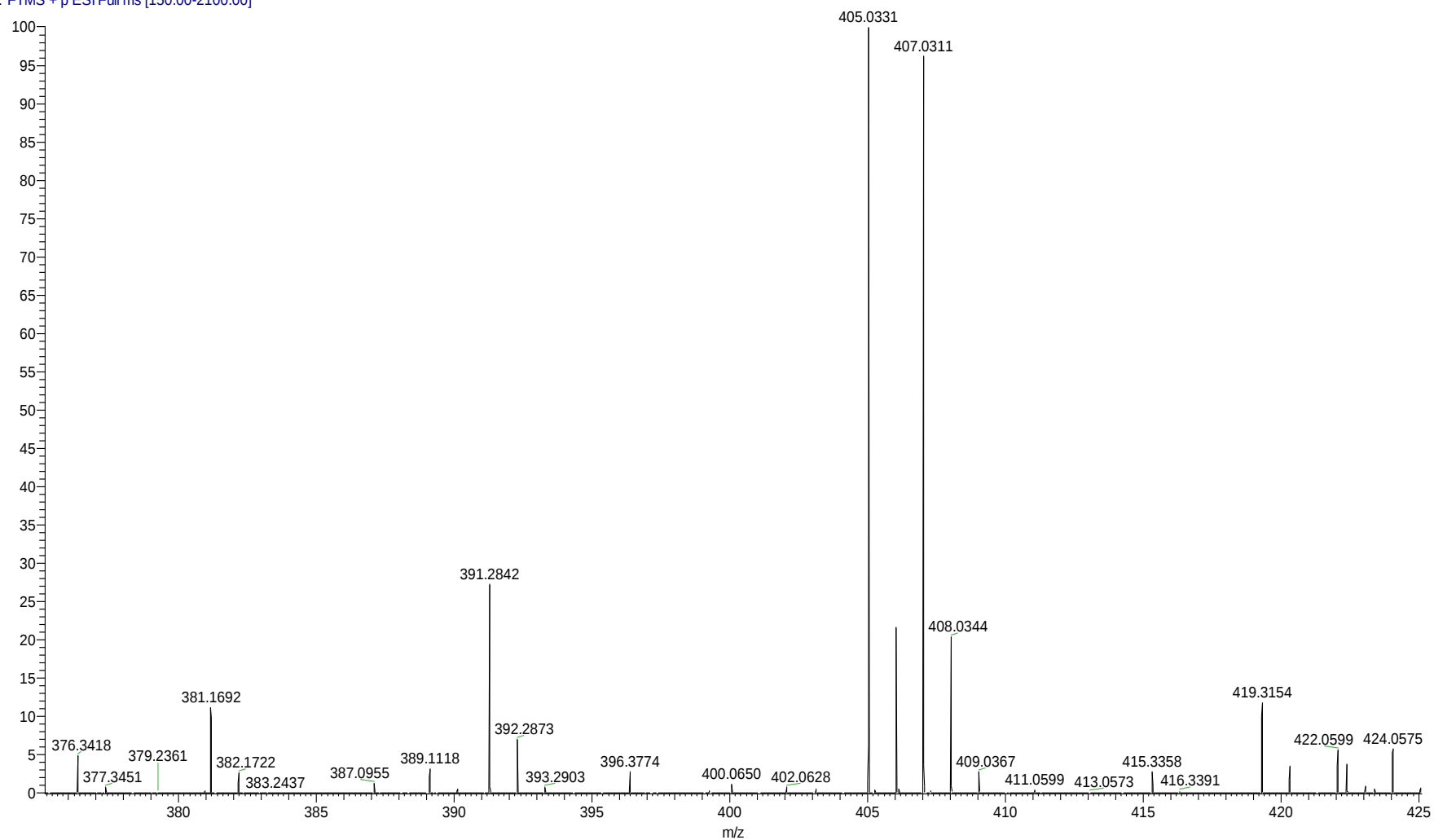


Figure S91. HR-ESI(+)-MS spectrum of 7-bromounguinol (3)

DBP_7_P2_HRMS_POS #54-344 RT: 0.06-0.41 AV: 291 NL: 7.88E6
T: FTMS + p ESI Full ms [200.00-1000.00]

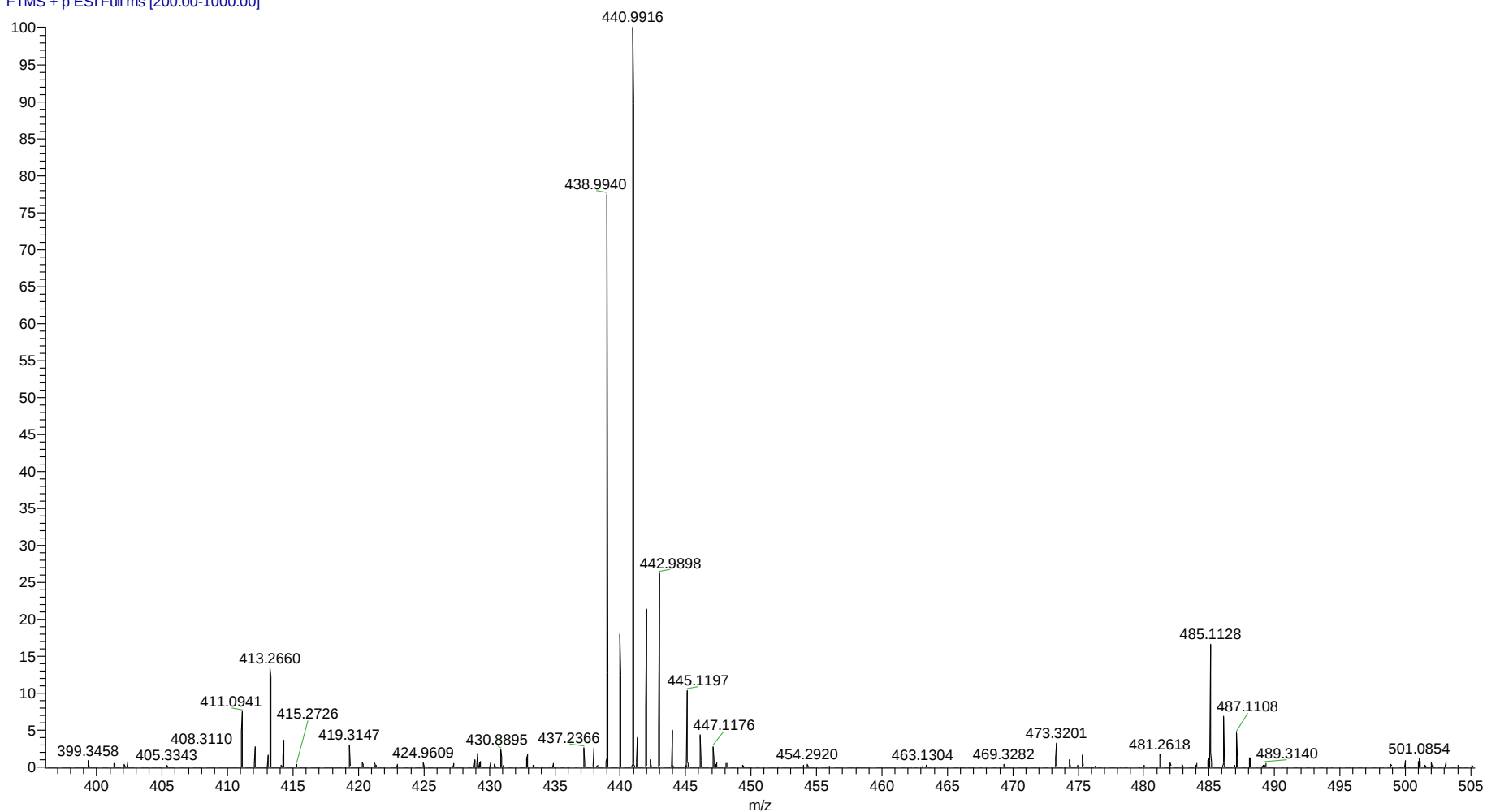


Figure S92. HR-ESI(+)-MS spectrum of 2-chloro-7-bromounginol (**4**)

DBP_11_P8_POS #15-48 RT: 0.03-0.11 AV: 34 NL: 5.31E7
T: FTMS + p ESI Full ms [150.00-2100.00]

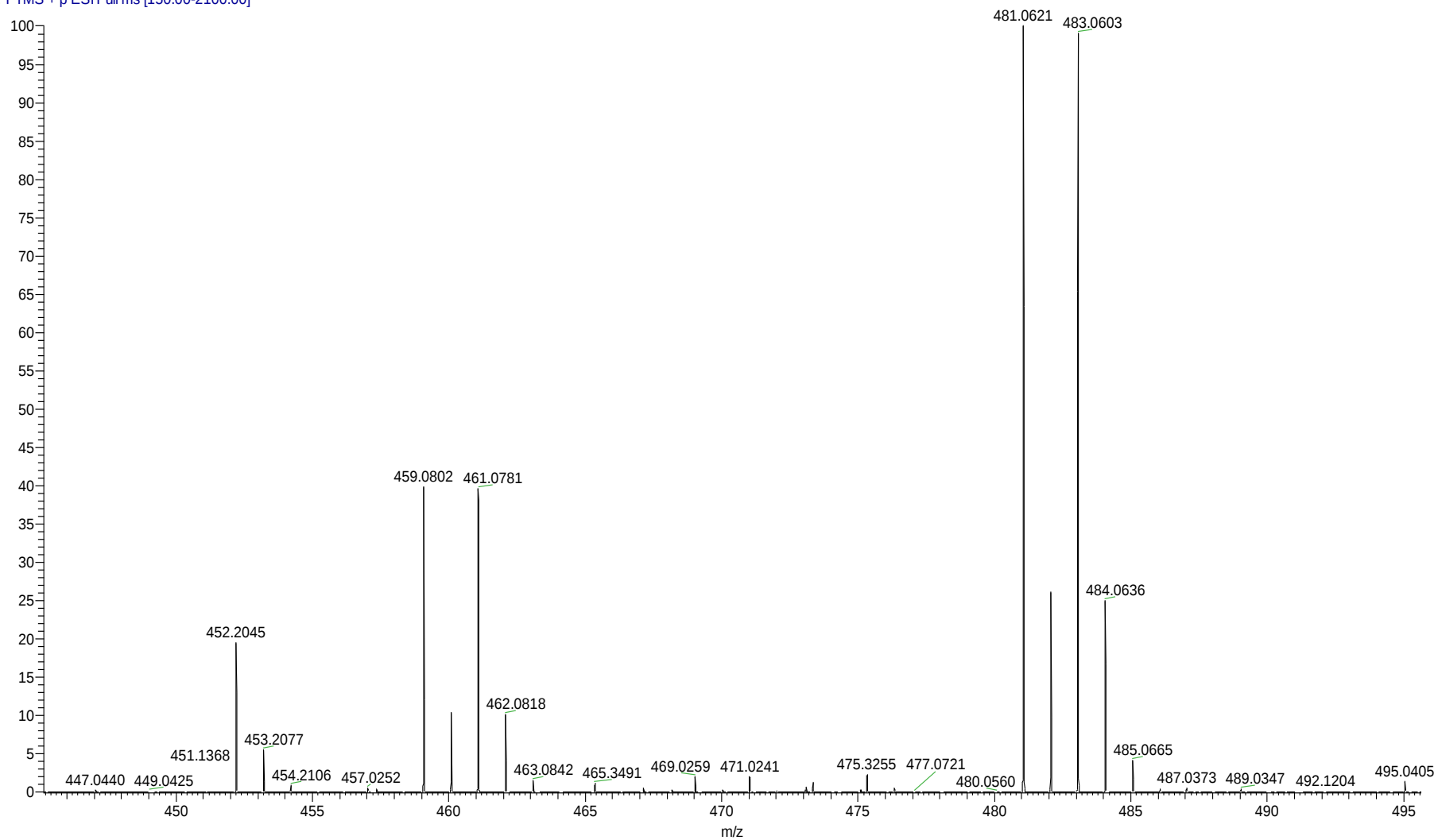


Figure S93. HR-ESI(+)-MS spectrum of 7-bromofolipastatin (5)

DBP_13_P1_HRMS_POS #70-294 RT: 0.08-0.35 AV: 225 NL: 3.04E6
T: FTMS + p ESI Full ms [200.00-1000.00]

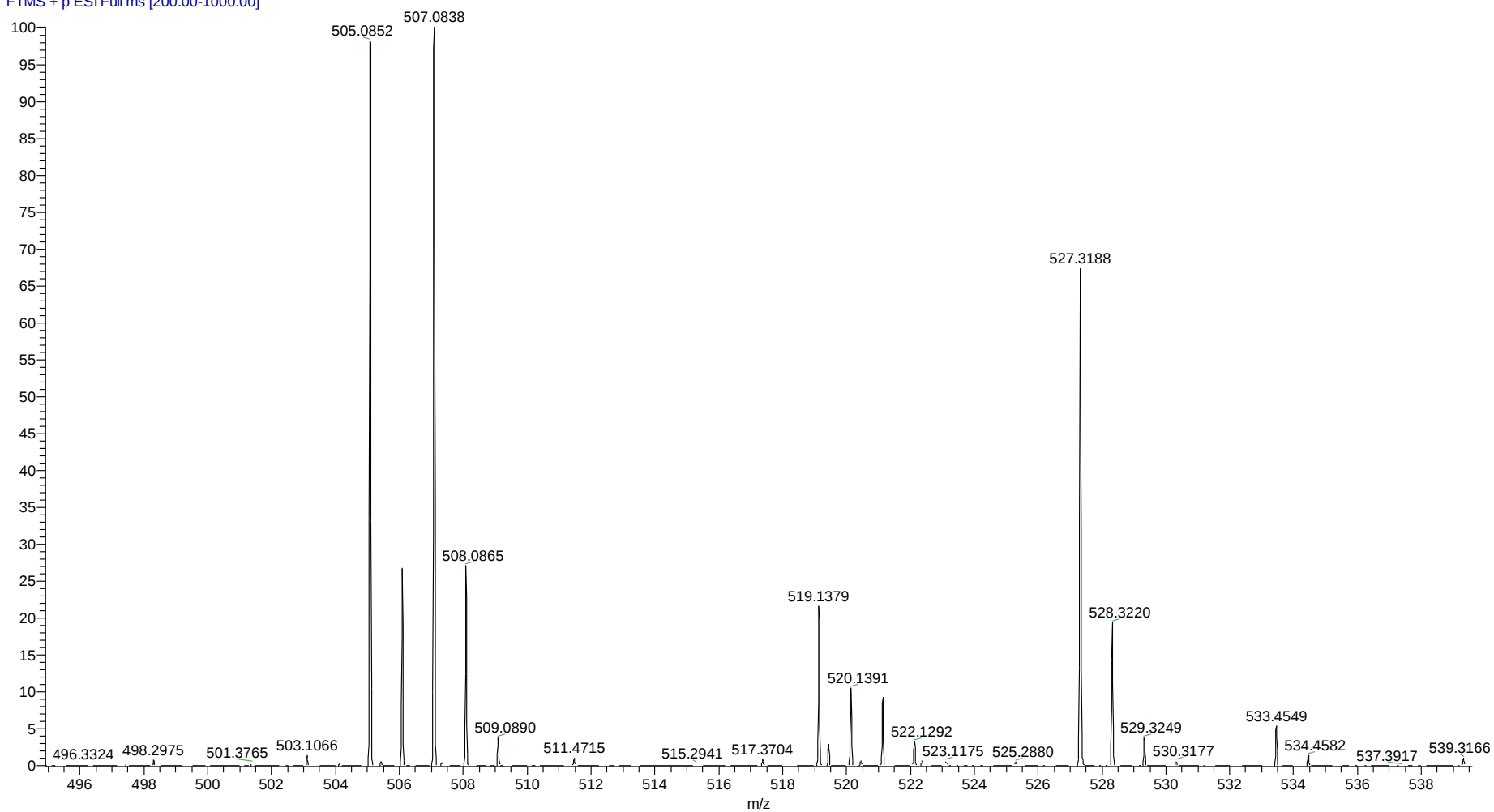


Figure S94. HR-ESI(+)-MS spectrum of 5-bromoagonodepside B (**6**)

DBP_4_P1_HRMS_POS #58-253 RT: 0.07-0.30 AV: 196 NL: 1.36E7
T: FTMS + p ESI Full ms [200.00-1000.00]

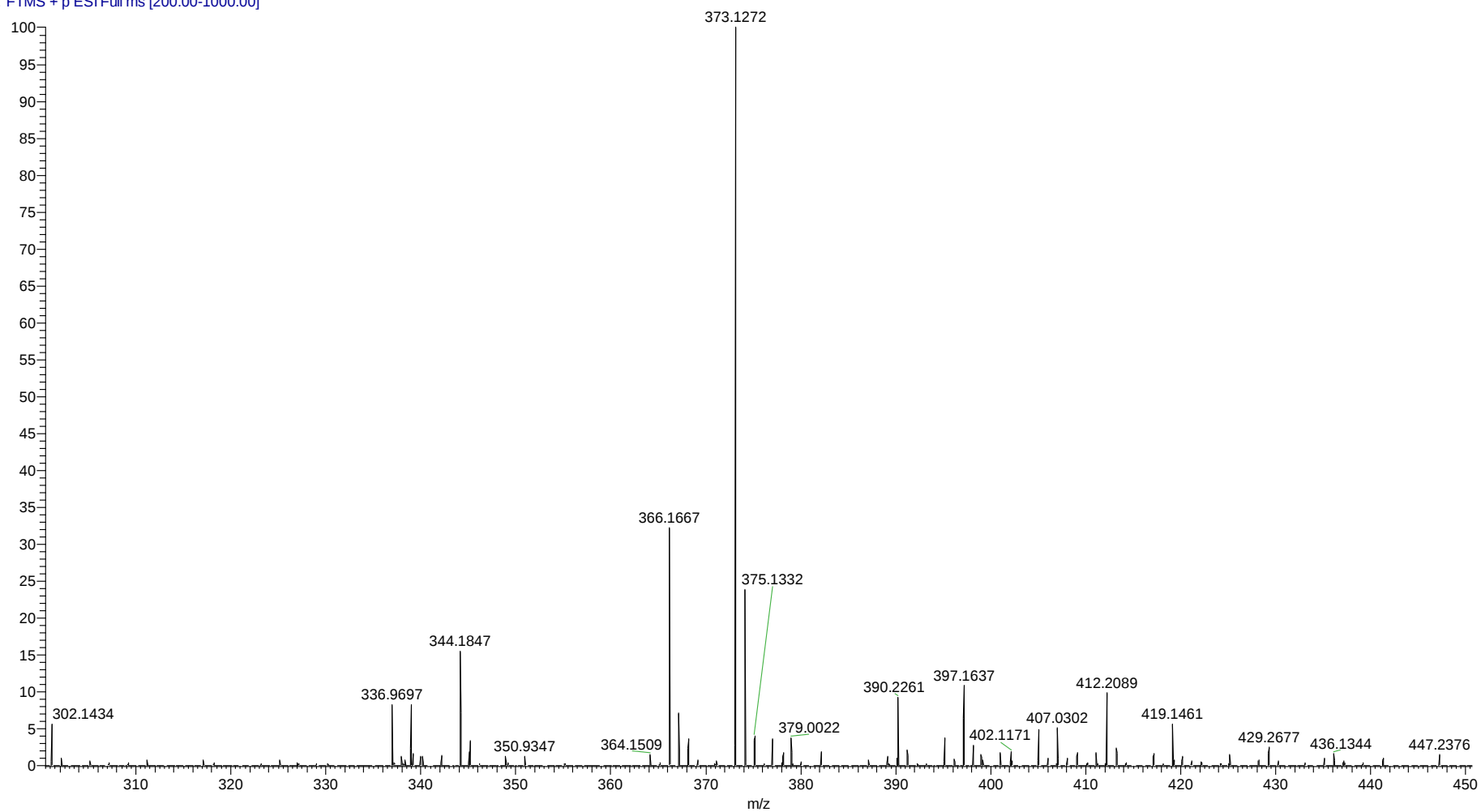


Figure S95. HR-ESI(+)-MS spectrum of unguidepside A (7)

DBP_6_P1_HRMS_NEG #60-379 RT: 0.07-0.45 AV: 320 NL: 5.80E8
T: FTMS - p ESI Full ms [200.00-1000.00]

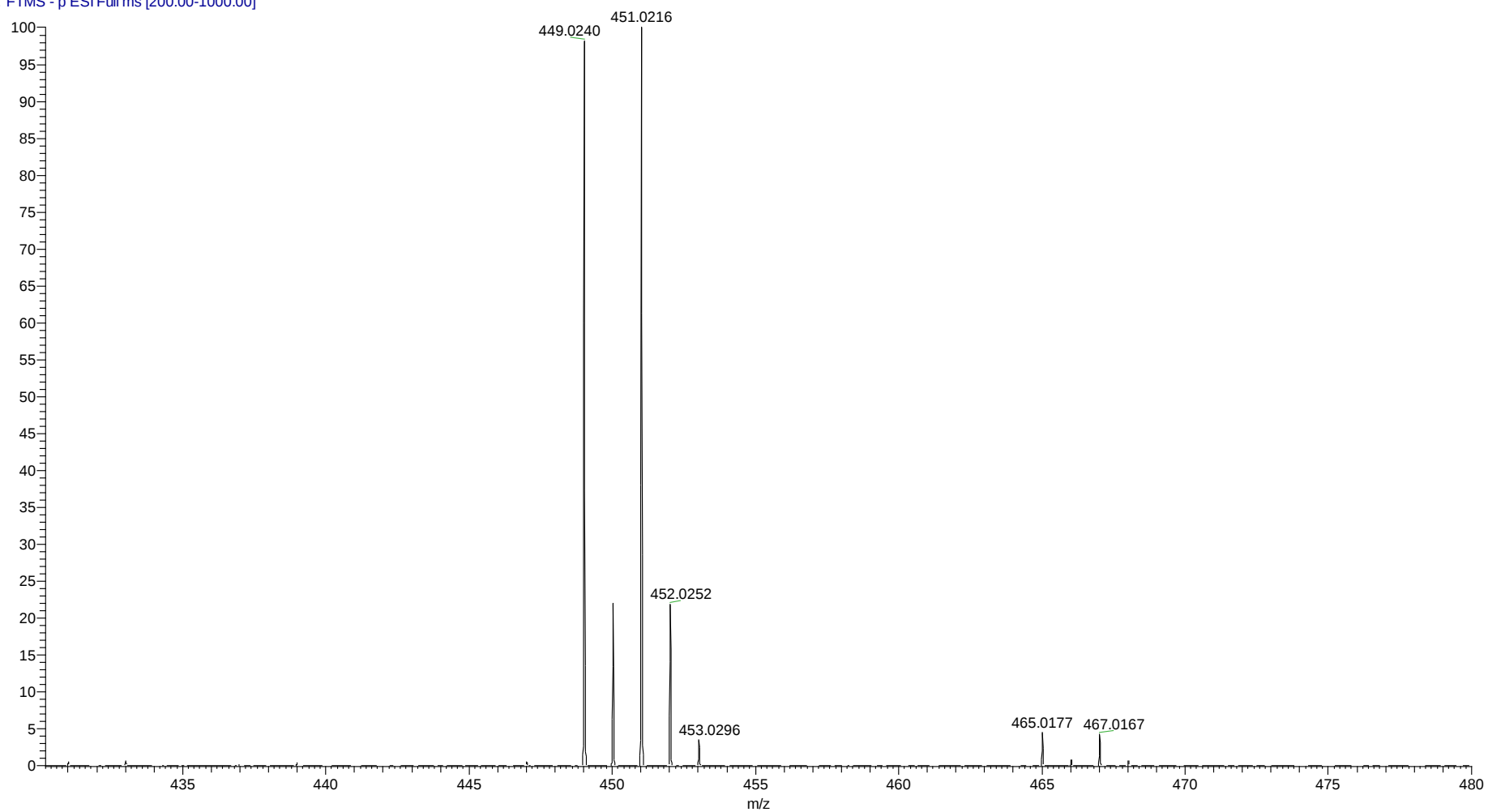


Figure S96. HR-ESI(-)-MS spectrum of 3-bromounguidepside A (**8**)

AC_14_134_6_Neg #34-47 RT: 0.40-0.53 AV: 14 NL: 4.39E7
T: FTMS - p ESI Full ms [150.0000-1800.0000]

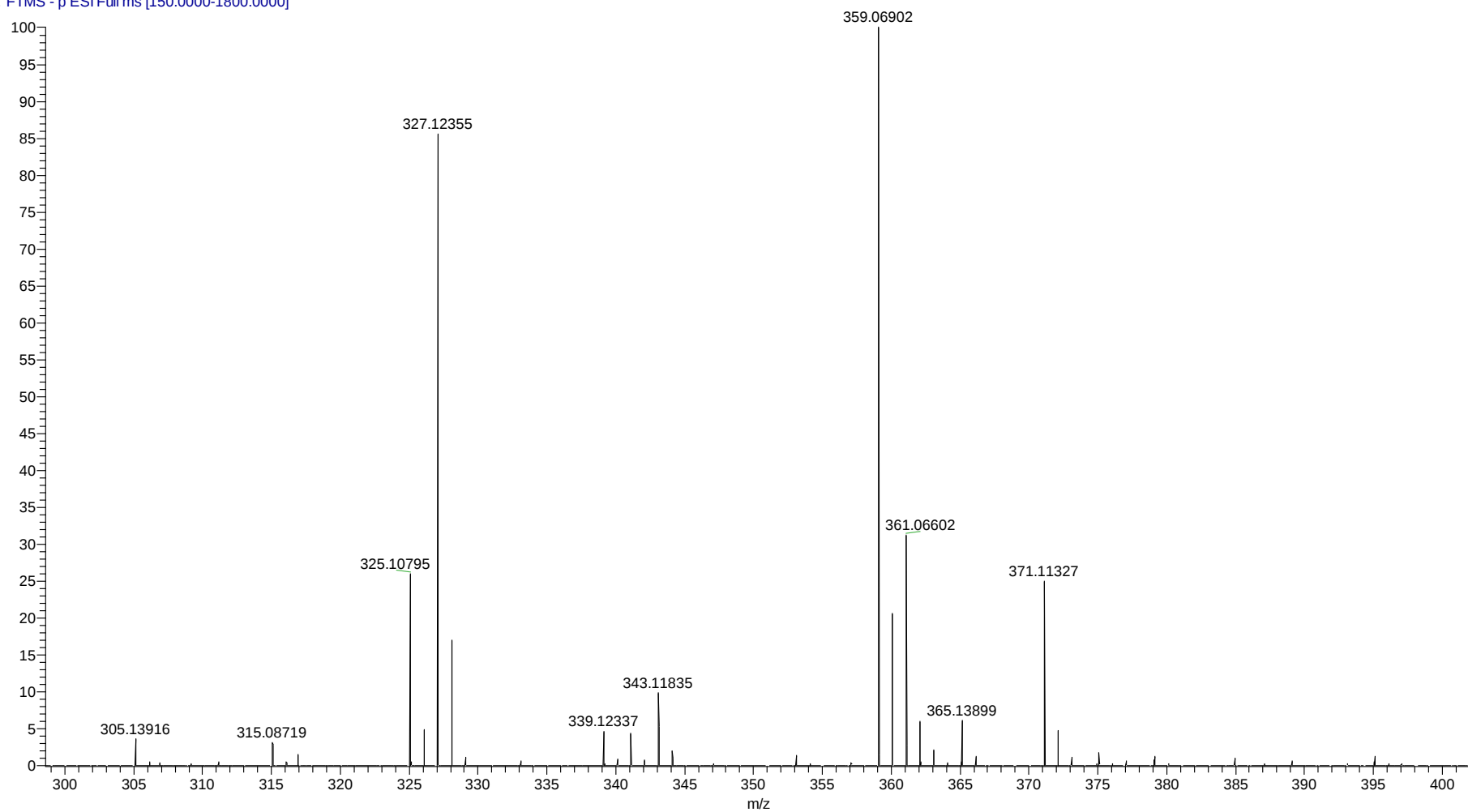


Figure S97. HR-ESI(-)-MS spectrum of decarboxyunguidepside A (9)

unguilonic_acid_HRMS_POS #60-365 RT: 0.07-0.43 AV: 306 NL: 1.34E8
T: FTMS + p ESI Full ms [200.00-1000.00]

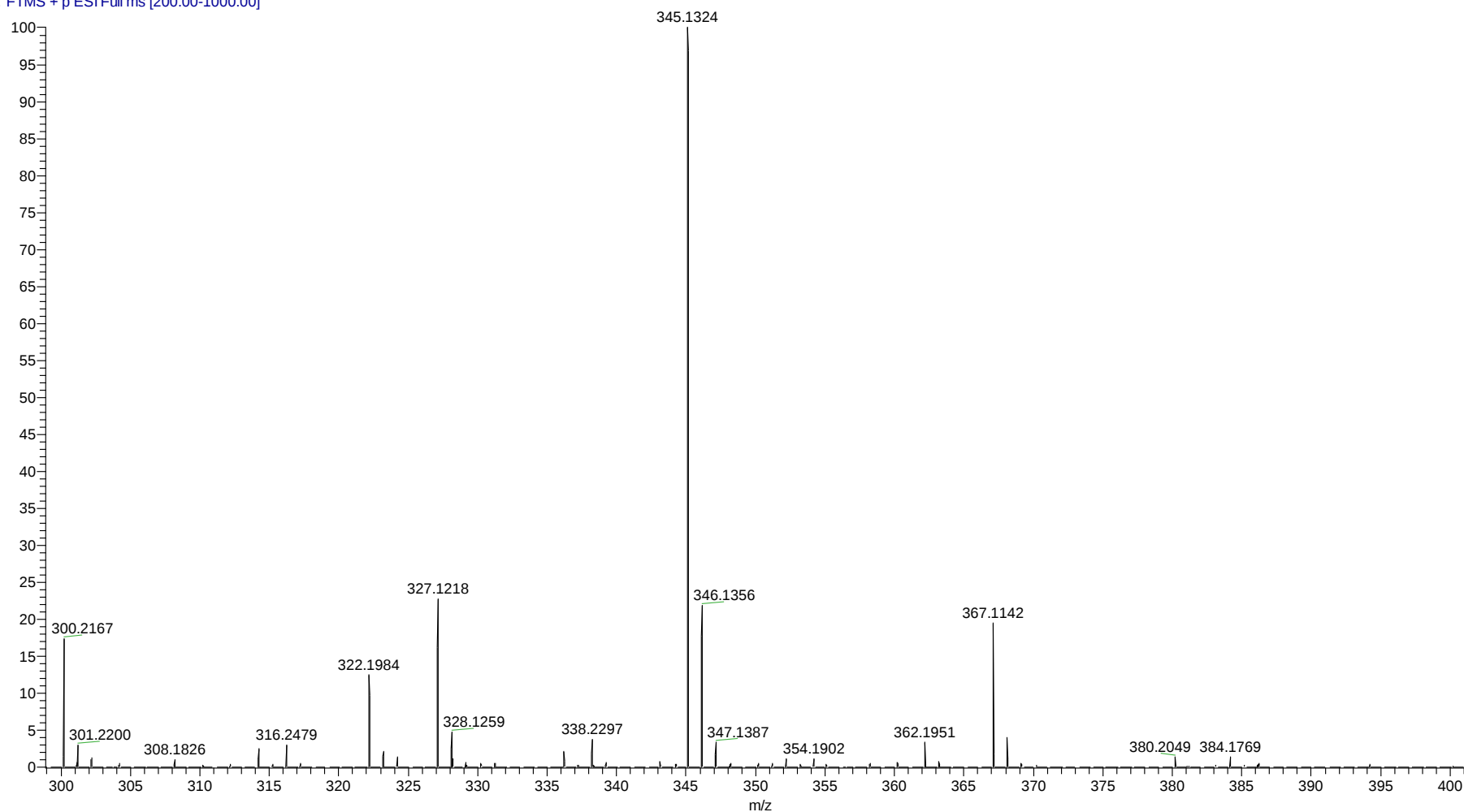


Figure S98. HR-ESI(+)-MS spectrum of unguinolic acid (**10**)

AC_14_126_4_Neg_D #41-55 RT: 0.50-0.63 AV: 15 NL: 5.89E8
T: FTMS - p ESI Full ms [150.0000-1800.0000]

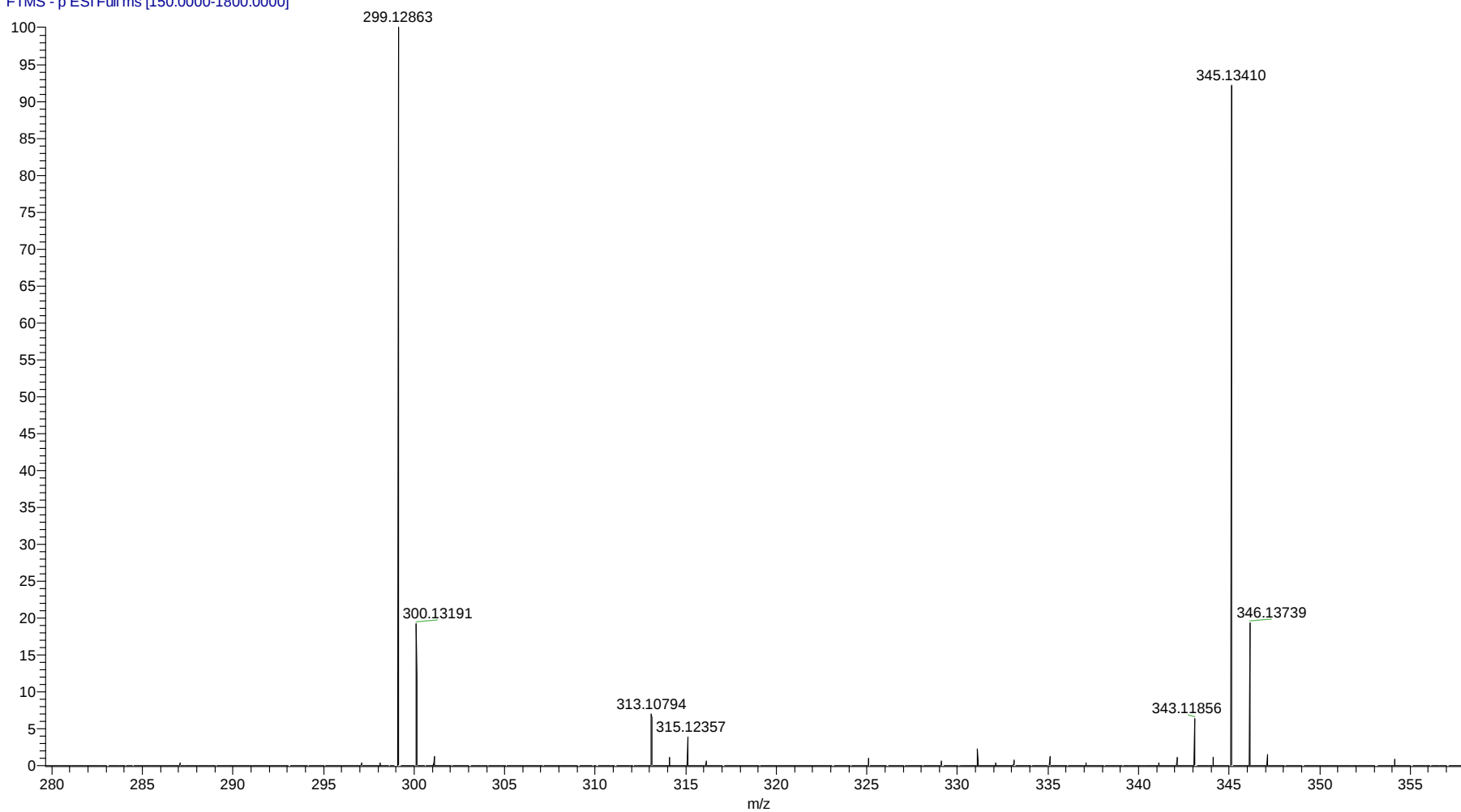


Figure S99. HR-ESI(-)-MS spectrum of decarboxyunguinic acid (**11**)

AC_14_129_4_Neg_D #41-51 RT: 0.50-0.59 AV: 11 NL: 3.01E8
T: FTMS - p ESI Full ms [150.0000-1800.0000]

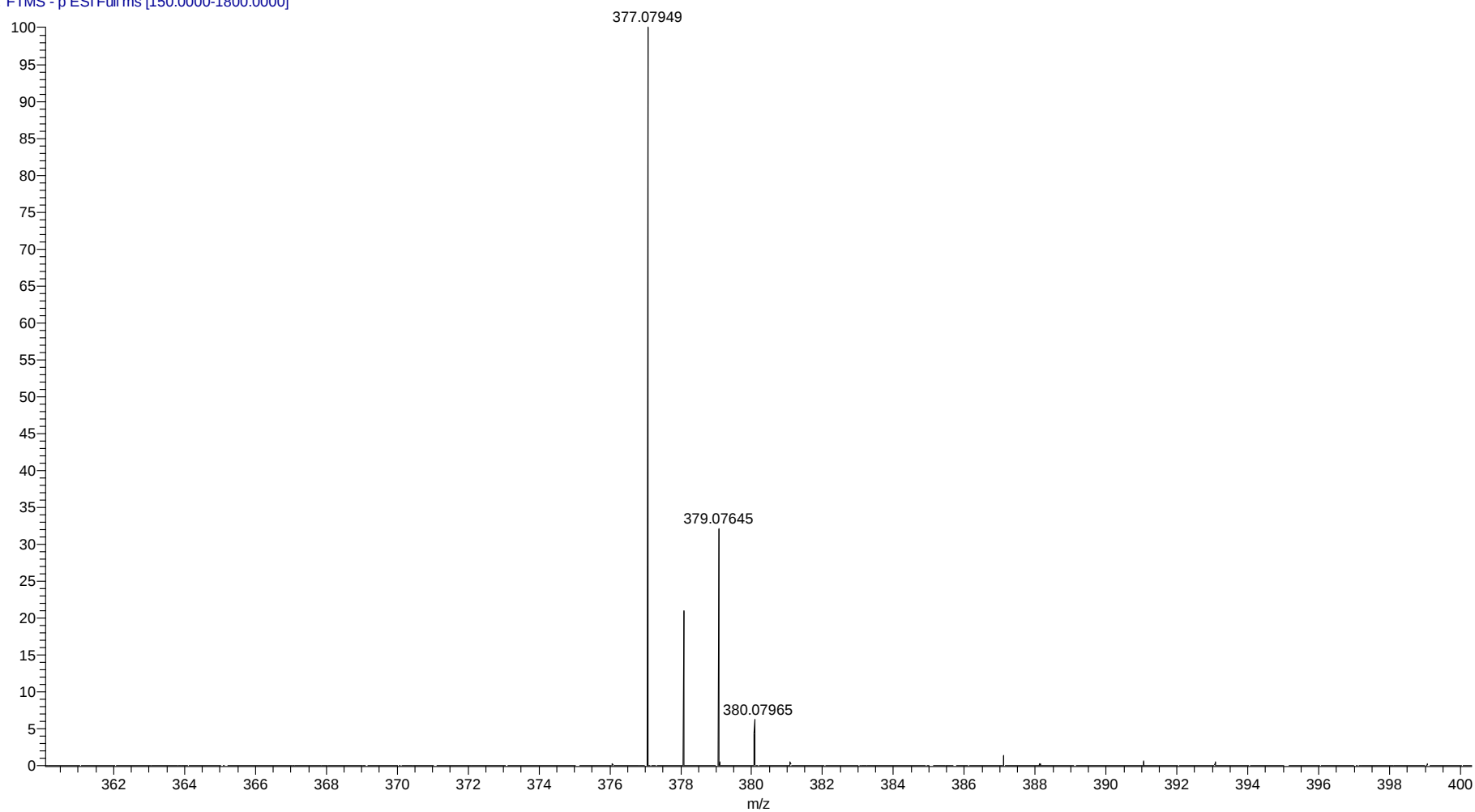


Figure S100. HR-ESI(-)-MS spectrum of 5-chlorounguinolic acid (**12**)