Supporting Information

The Absolute Configurations of Hyperilongenols A–C: Rare 12,13-*Seco*-Spirocyclic Polycyclic Polyprenylated Acylphloroglucinols with Enolizable *β*,*β*'-Tricarbonyl Systems from *Hypericum longistylum* Oliv.

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Figure S1. ^{1}H NMR (800 MHz) spectrum of compound **1** (Recorded in C_5D_5N, 343 K)

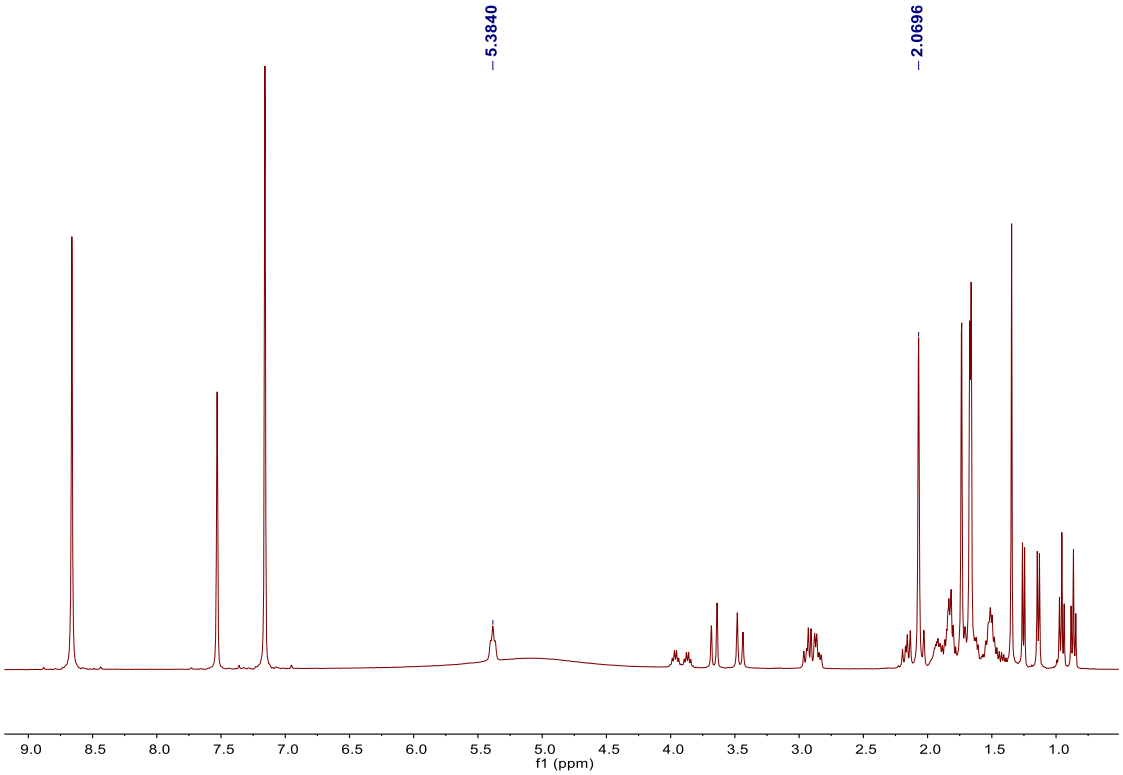

Figure S2. ^{1}H NMR (800 MHz) spectrum of compound **1** (Recorded in C_5D_5N, 313 K)

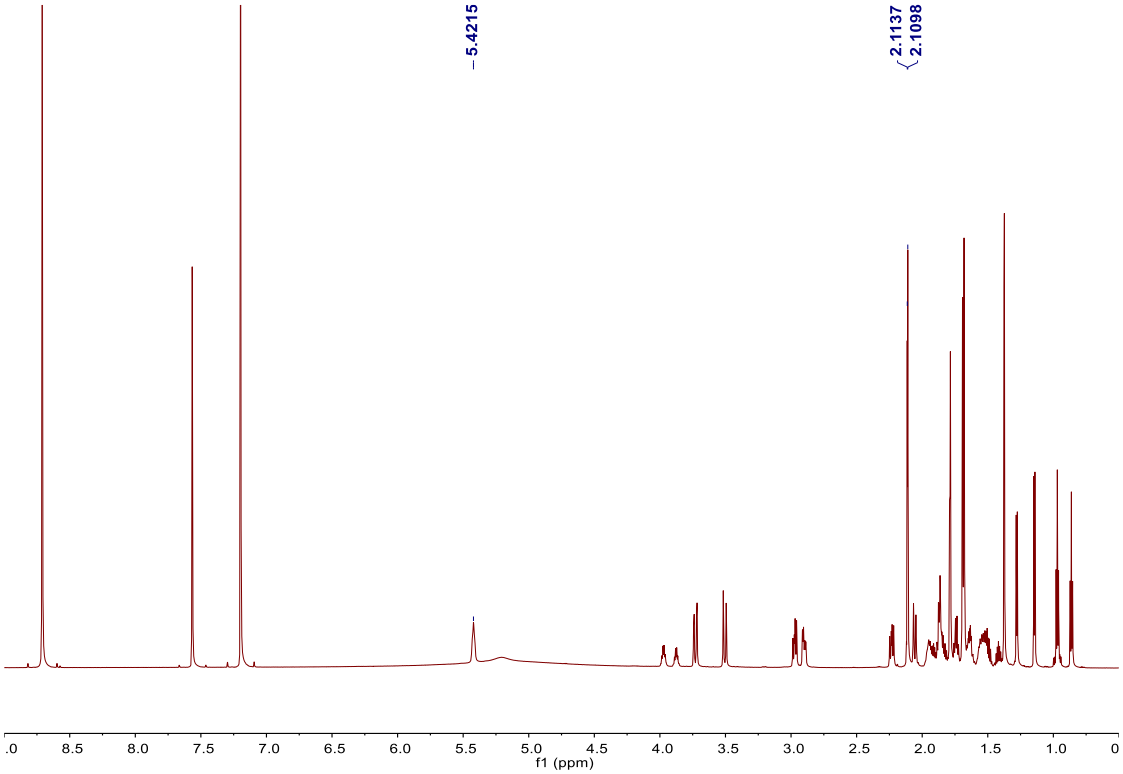

Figure S3. ^{1}H NMR (800 MHz) spectrum of compound **1** (Recorded in C_5D_5N, 298 K)

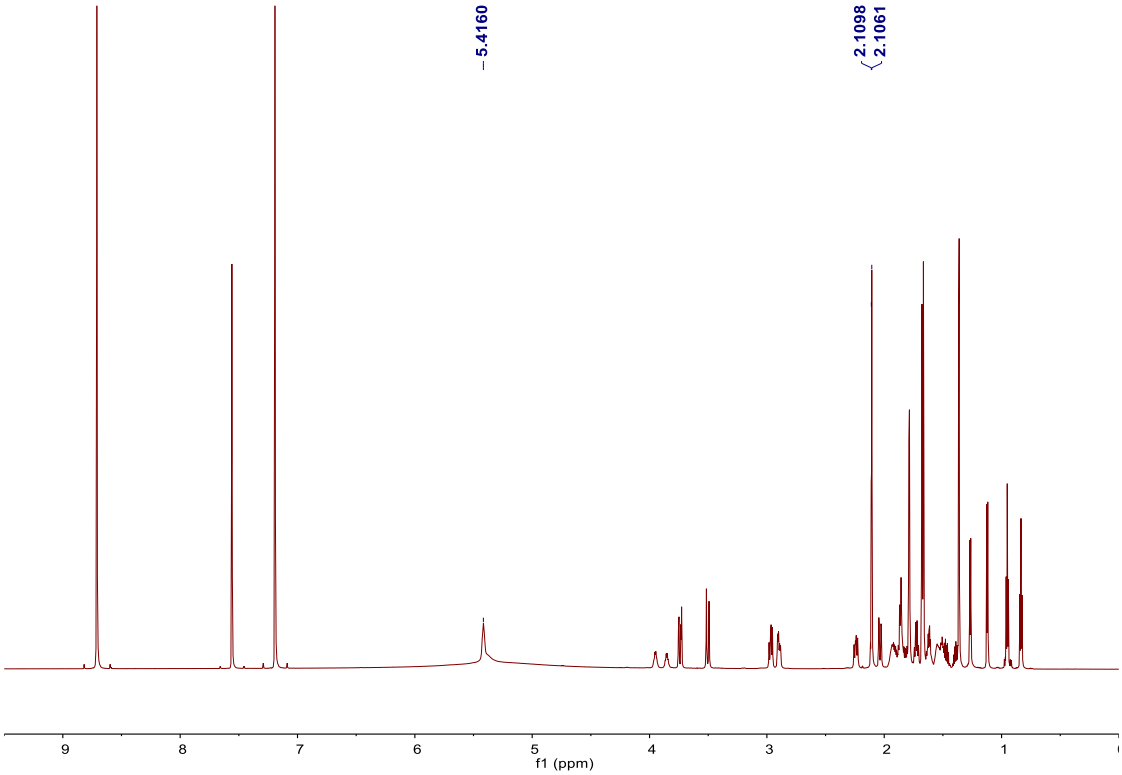

Figure S4. ^{1}H NMR (800 MHz) spectrum of compound **1** (Recorded in C_5D_5N, 280 K)

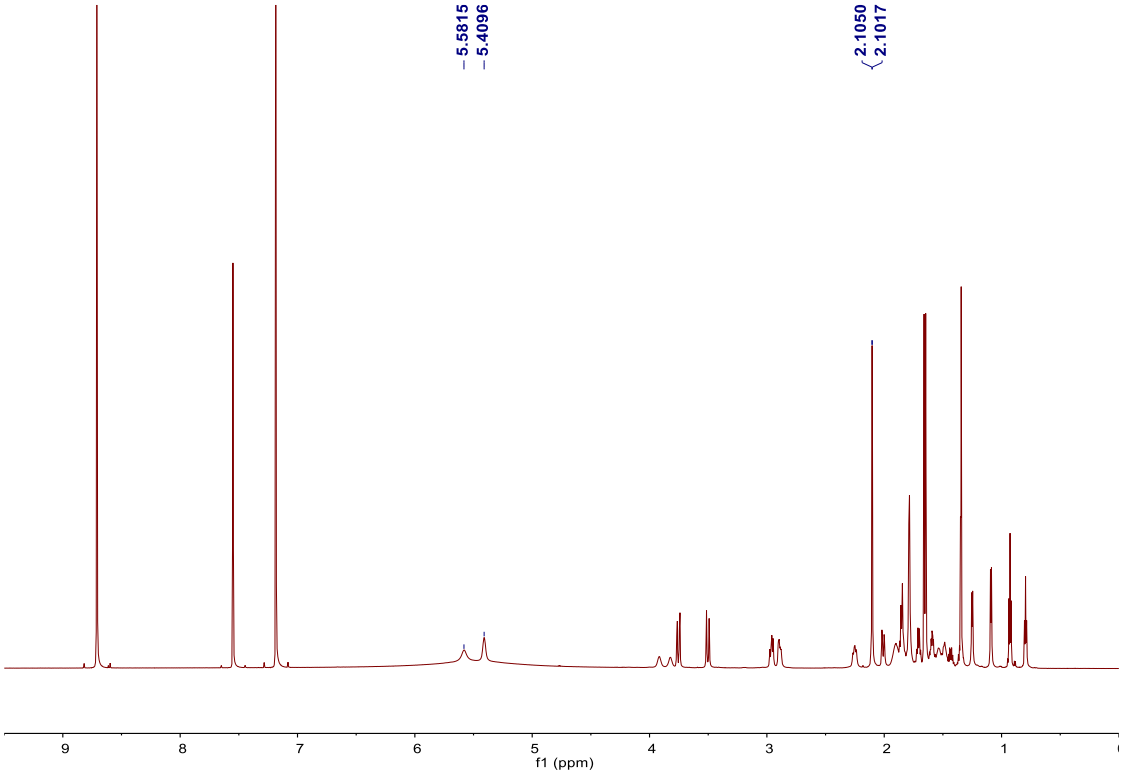

Figure S5. ^{1}H NMR (800 MHz) spectrum of compound **1** (Recorded in $CDCl_3$, 313 K)

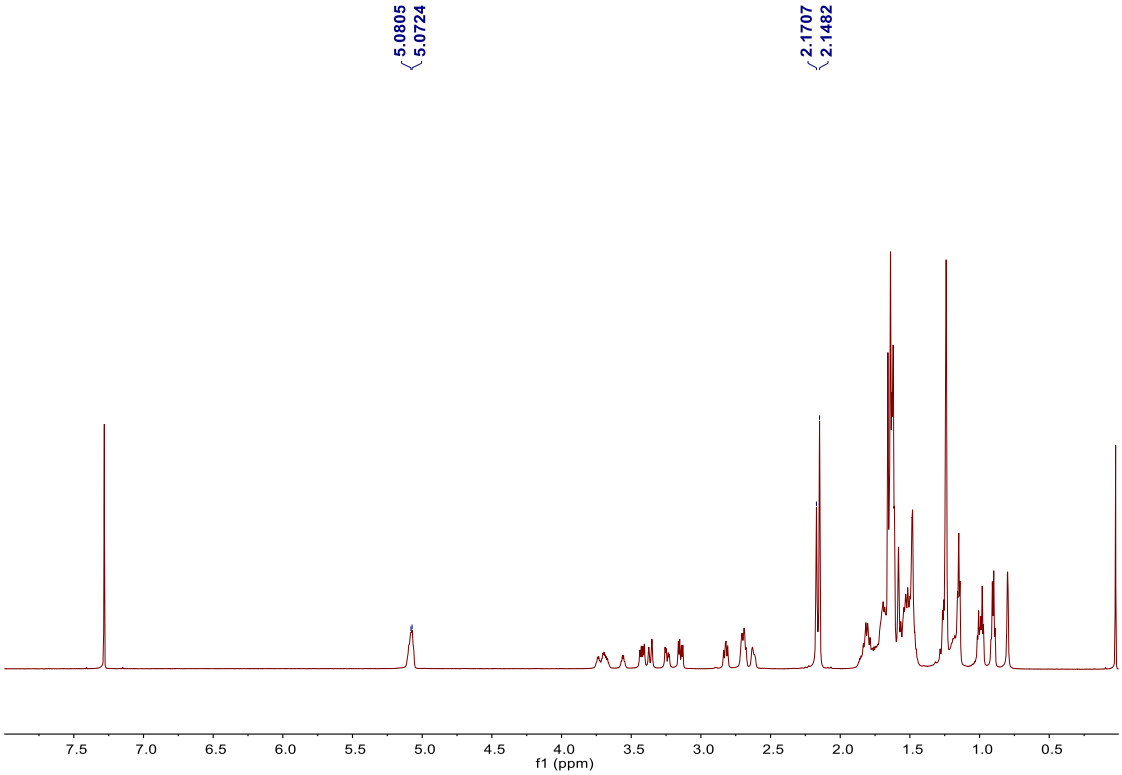

Figure S6. ^{1}H NMR (800 MHz) spectrum of compound **1** (Recorded in $CDCl_3$, 308 K)

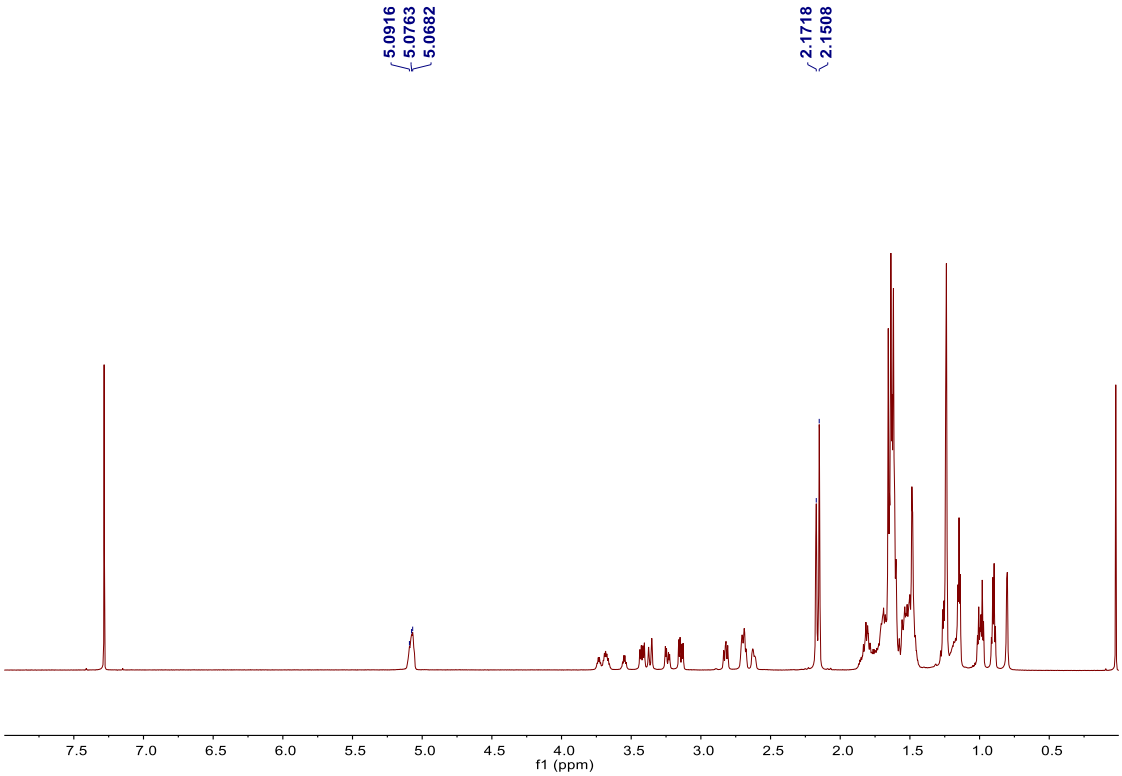

Figure S7. ^{1}H NMR (800 MHz) spectrum of compound **1** (Recorded in $CDCl_3$, 298 K)

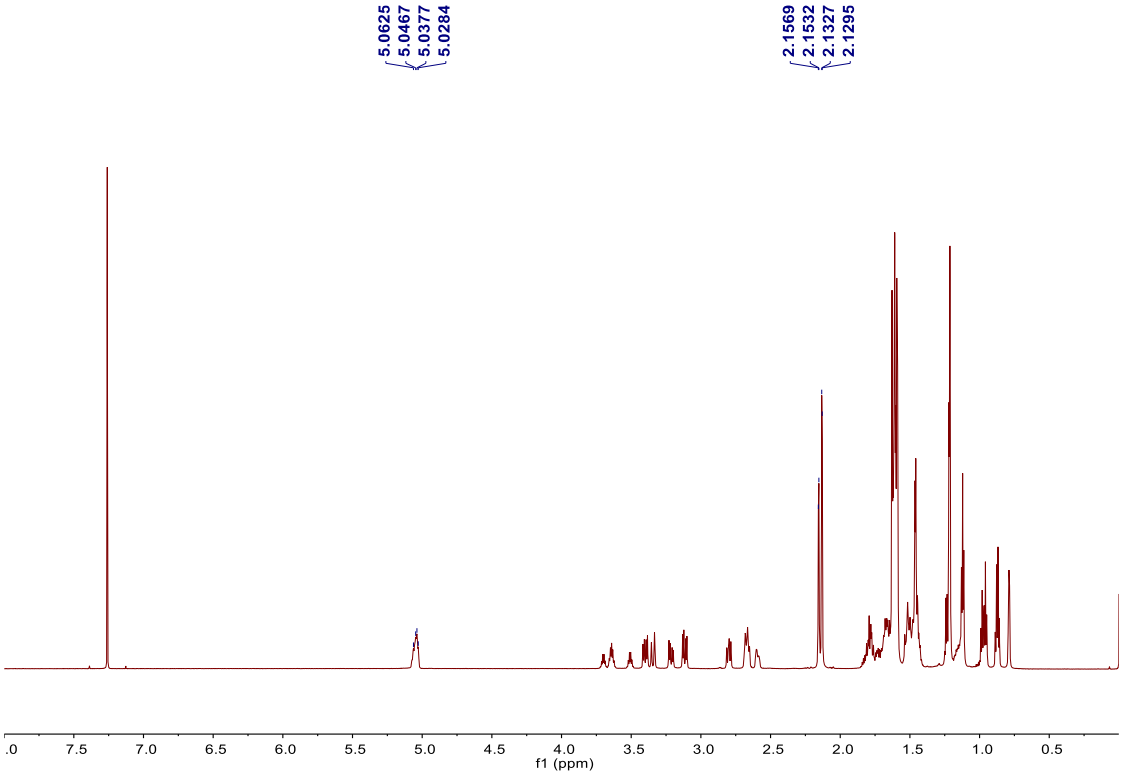

Figure S8. ^{1}H NMR (800 MHz) spectrum of compound **1** (Recorded in $CDCl_3$, 280 K)

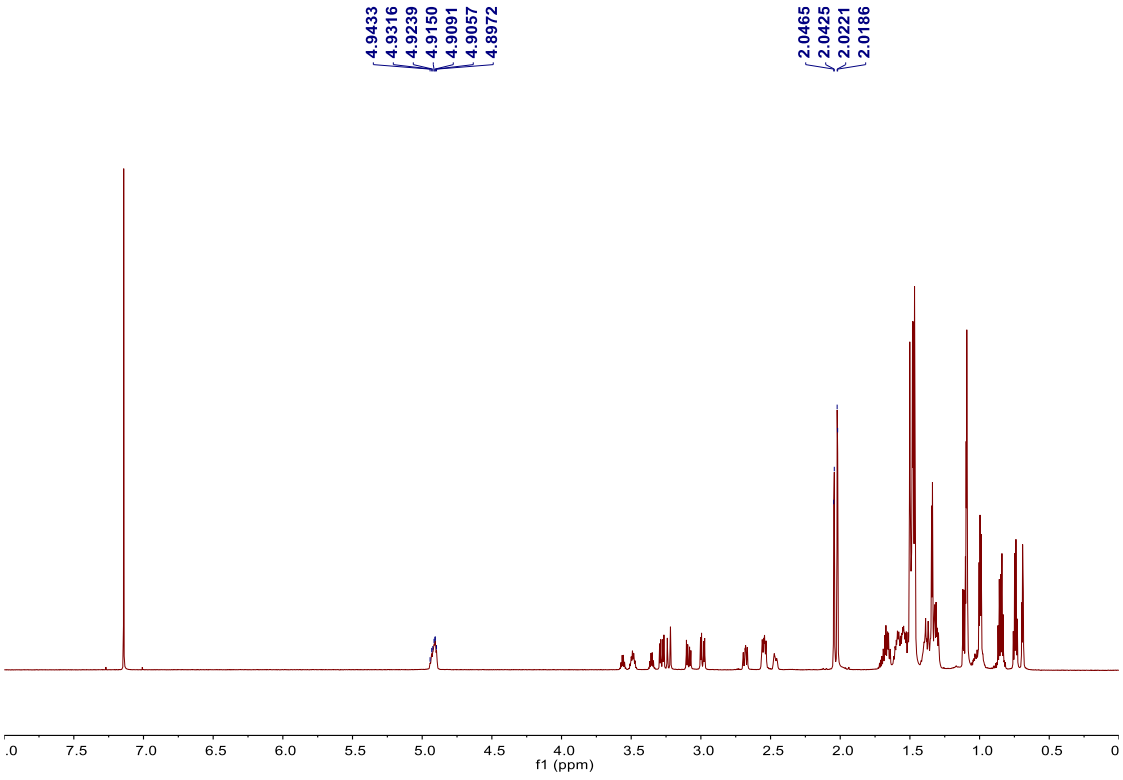

Figure S9. ^{1}H NMR (600 MHz) spectrum of compound **1** (Recorded in C_5D_5N, 298 K)

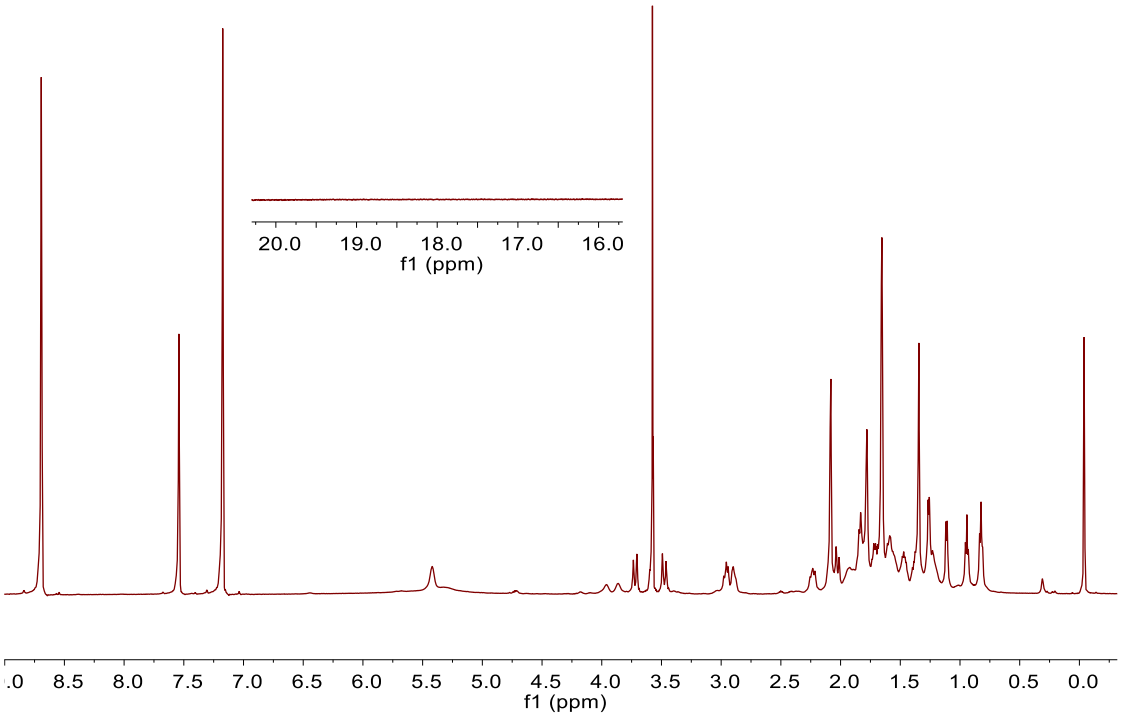

Figure S10. ^{1}H NMR (600 MHz) spectrum of compound **1** (Recorded in $CDCl_3$, 313 K)

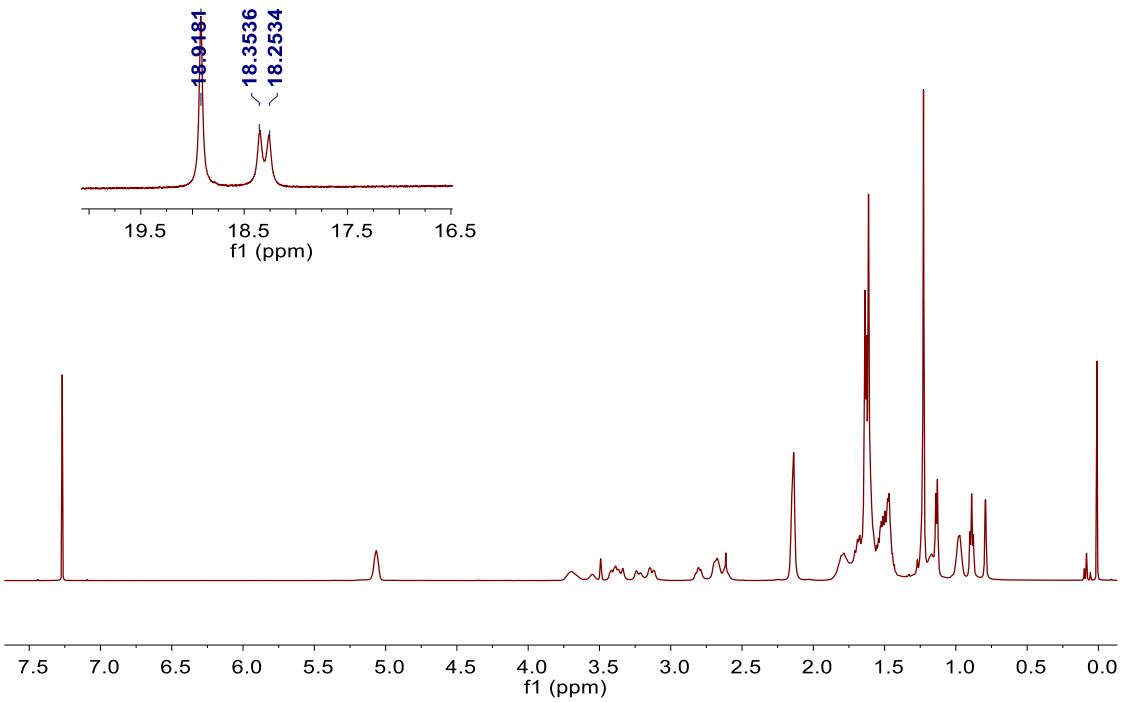

Figure S11. ^{1}H NMR (600 MHz) spectrum of compound **1** (Recorded in $CDCl_3$, 298 K)

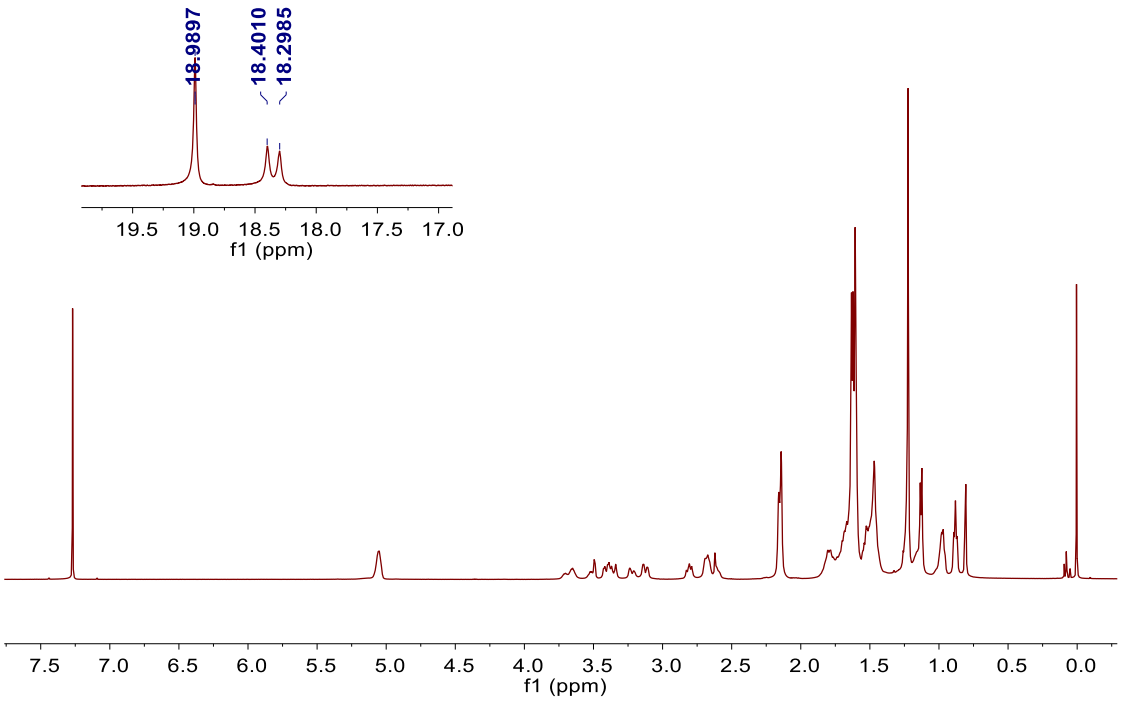

Figure S12. Key ^{1}H-^{1}H COSY (black bonds) and HMBC (arrows) correlations of compounds **2**–**3.**

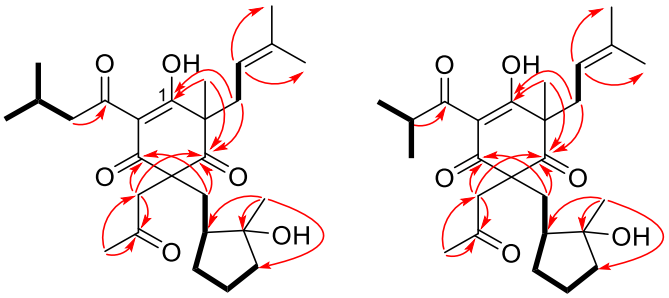

Figure S13. ^{1}H NMR (600 MHz) spectrum of compound **2** (Recorded in C_5D_5N, 298 K)

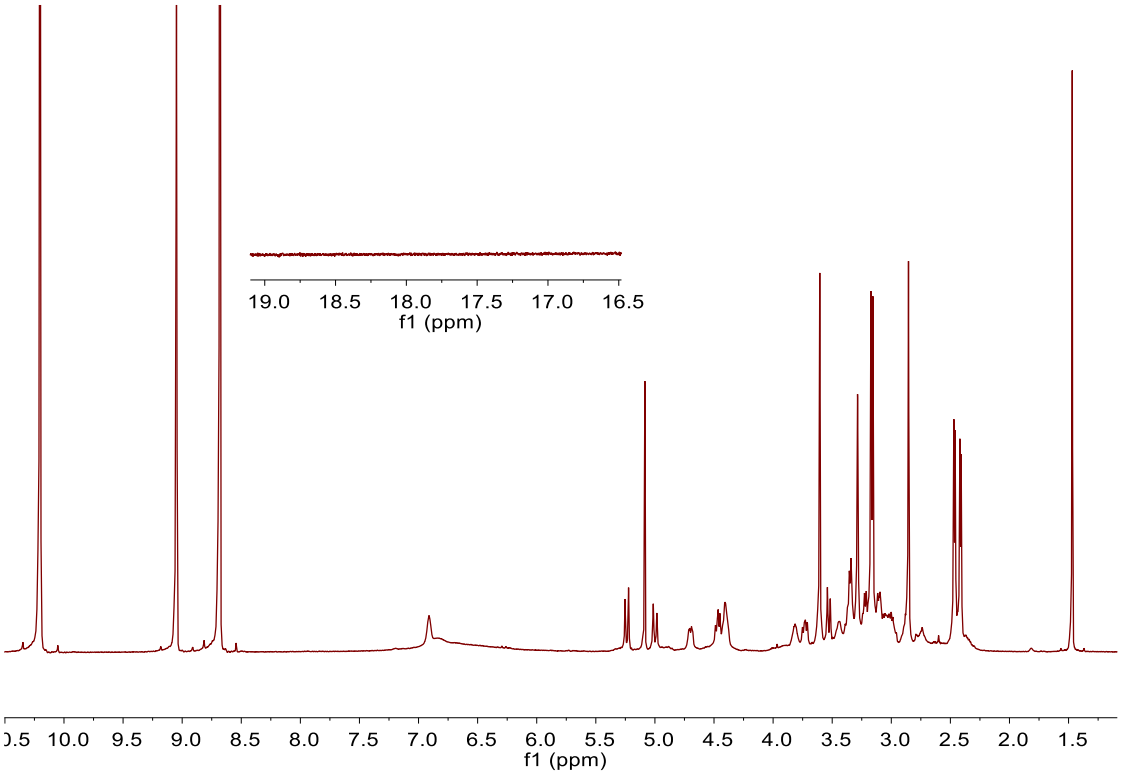

Figure S14. ^{1}H NMR (600 MHz) spectrum of compound **3** (Recorded in C_5D_5N, 298 K)

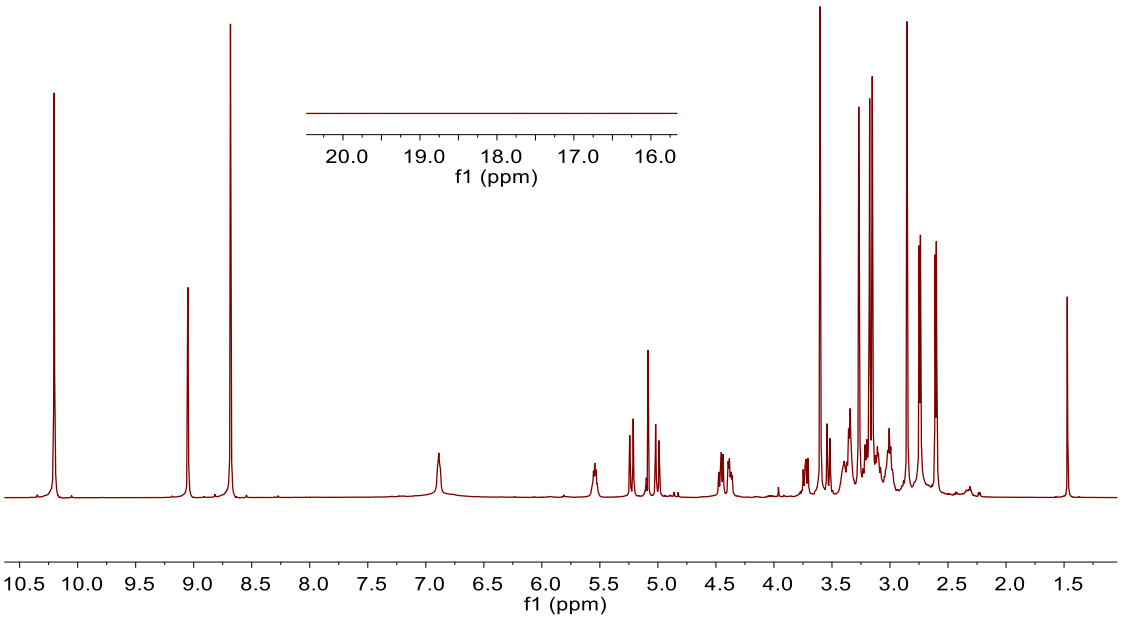

Figure S15. ^{1}H NMR (600 MHz) spectrum of compound **2** (Recorded in $CDCl_3$, 313 K)

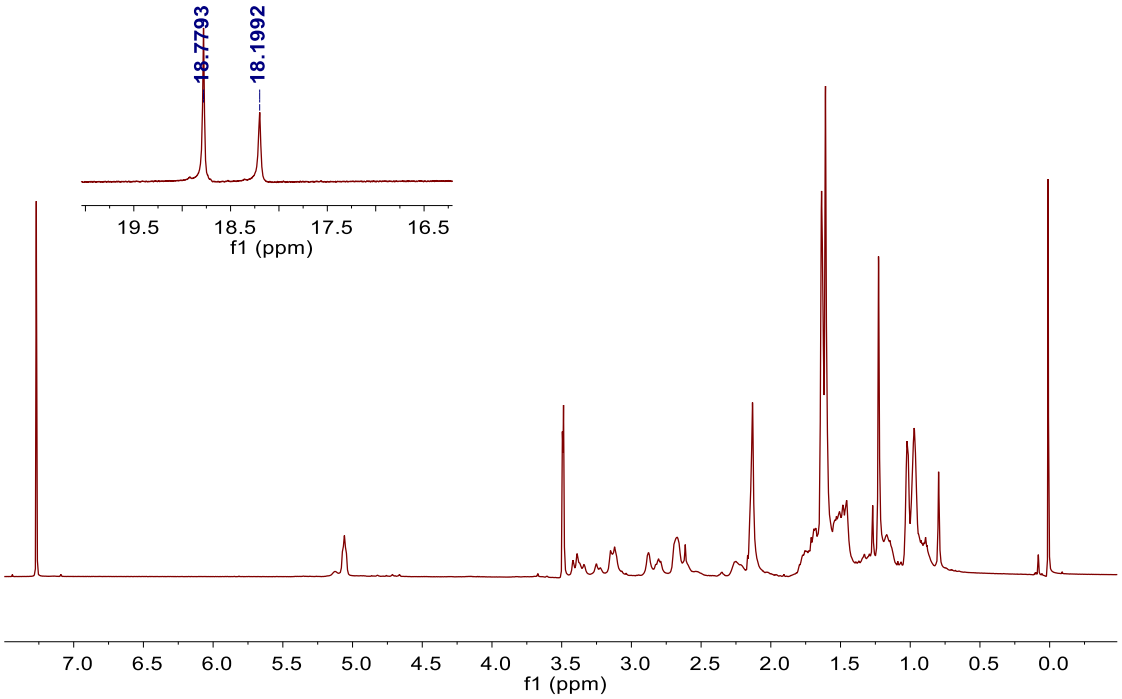

Figure S16. ^{1}H NMR (600 MHz) spectrum of compound **2** (Recorded in $CDCl_3$, 298 K)

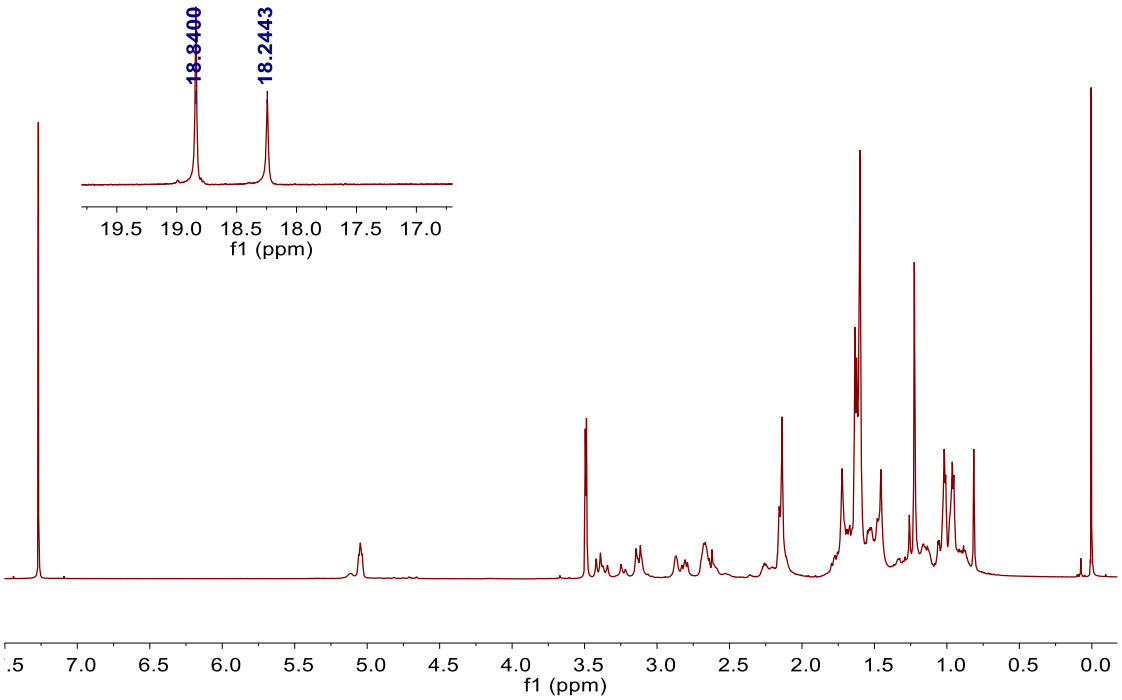

Figure S17. ^{1}H NMR (600 MHz) spectrum of compound **3** (Recorded in $CDCl_3$, 313 K)

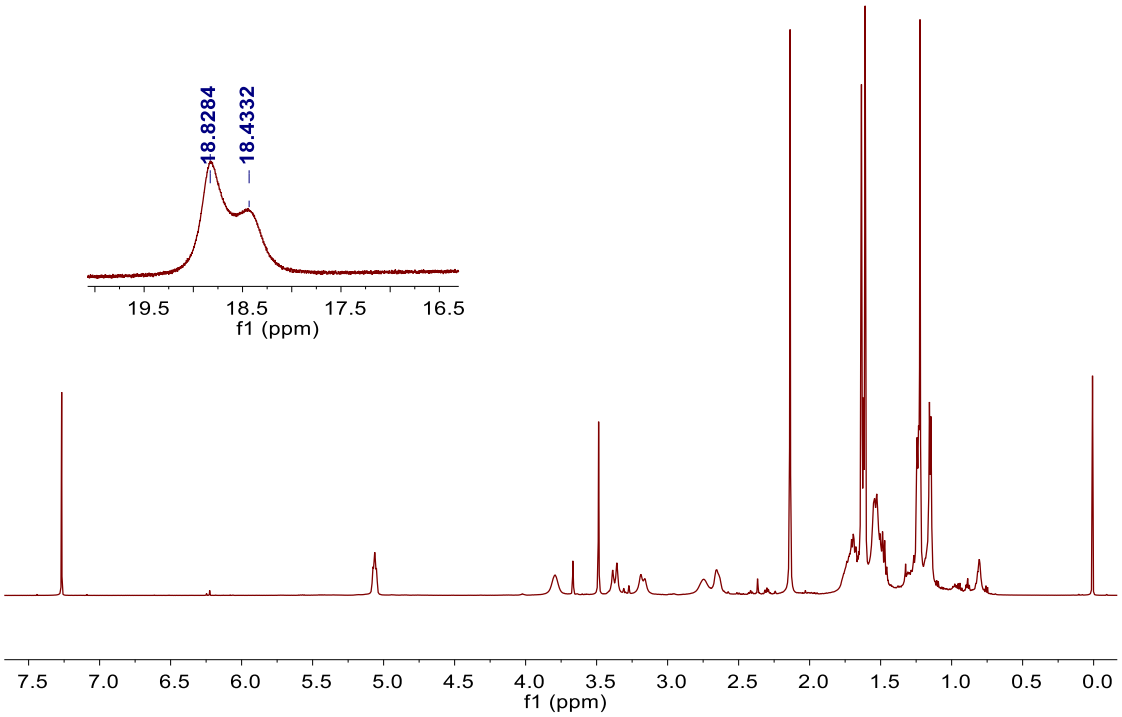

Figure S18. ^{1}H NMR (600 MHz) spectrum of compound **3** (Recorded in $CDCl_3$, 298 K)

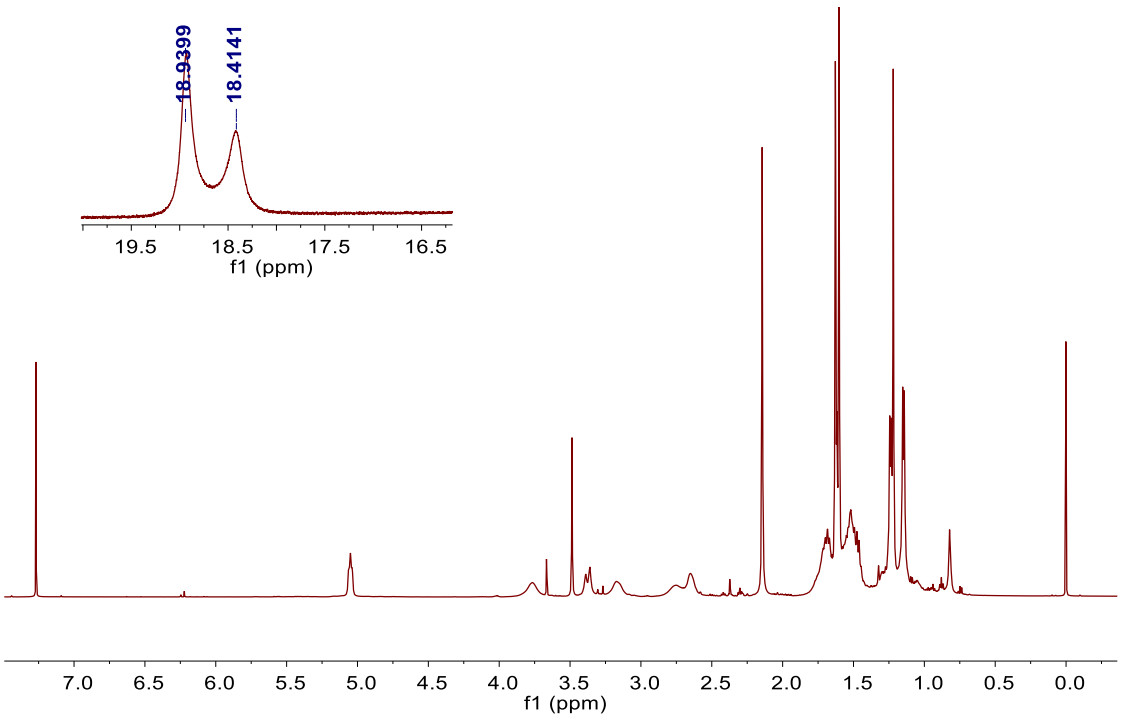

Figure S19. The mutual transformations of enol tautomers of compound **2.**

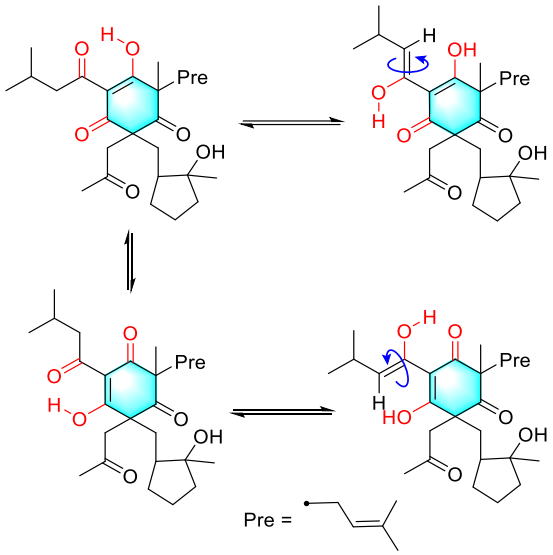

Figure S20. The mutual transformations of enol tautomers of compound **3.**

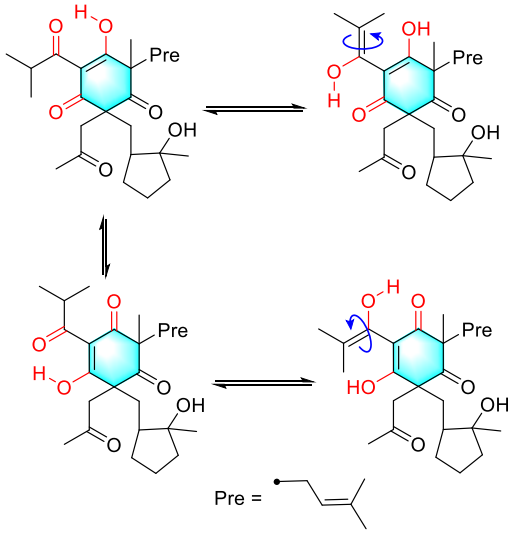

Figure S21. Experimental ECD spectra of **1**−**3**.

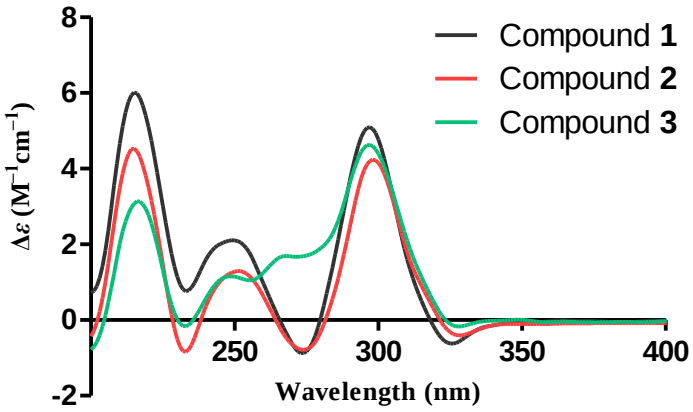

Figure S22. ^{1}H NMR (600 MHz) spectrum of compound **1** (Recorded in DMSO-d_6, 298 K)

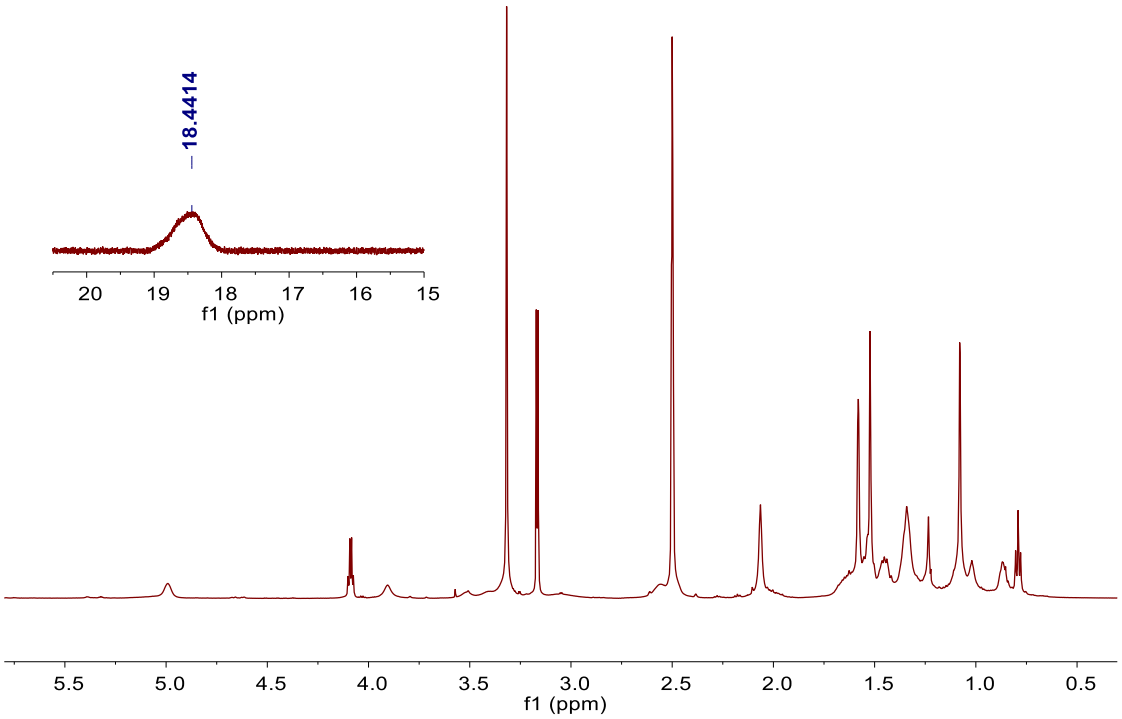

Figure S23. ^{1}H NMR (600 MHz) spectrum of compound **2** (Recorded in DMSO-d_6, 298 K)

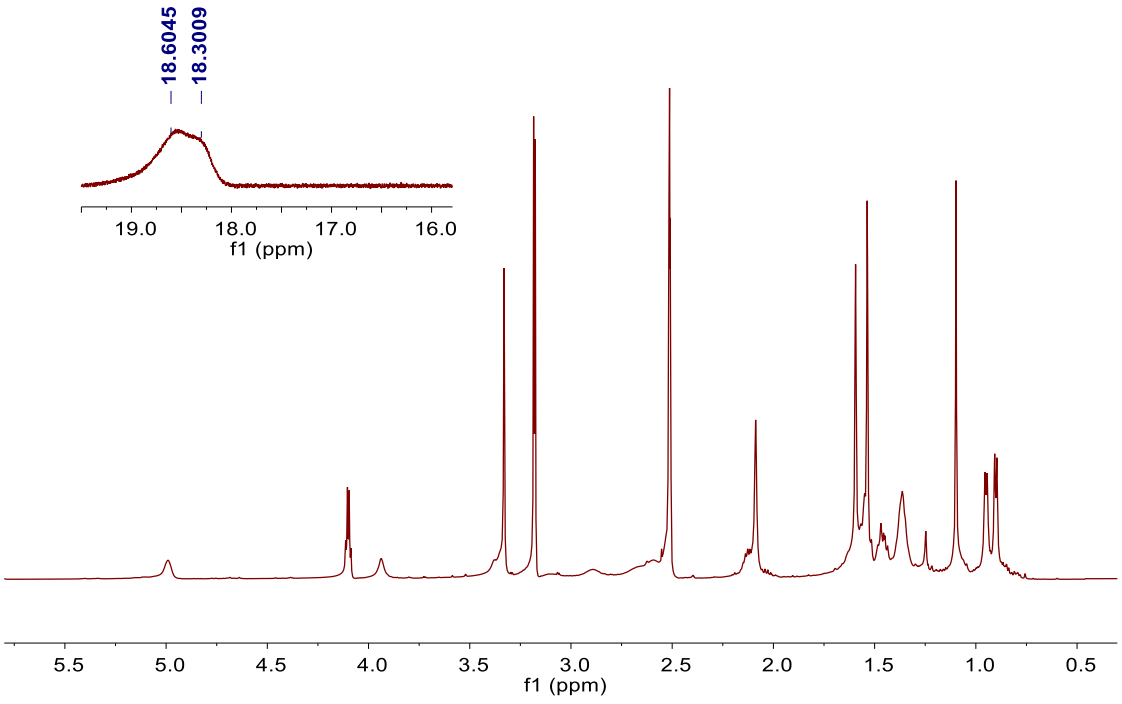

Figure S24. ^{1}H NMR (600 MHz) spectrum of compound **3** (Recorded in DMSO-d_6, 298 K)

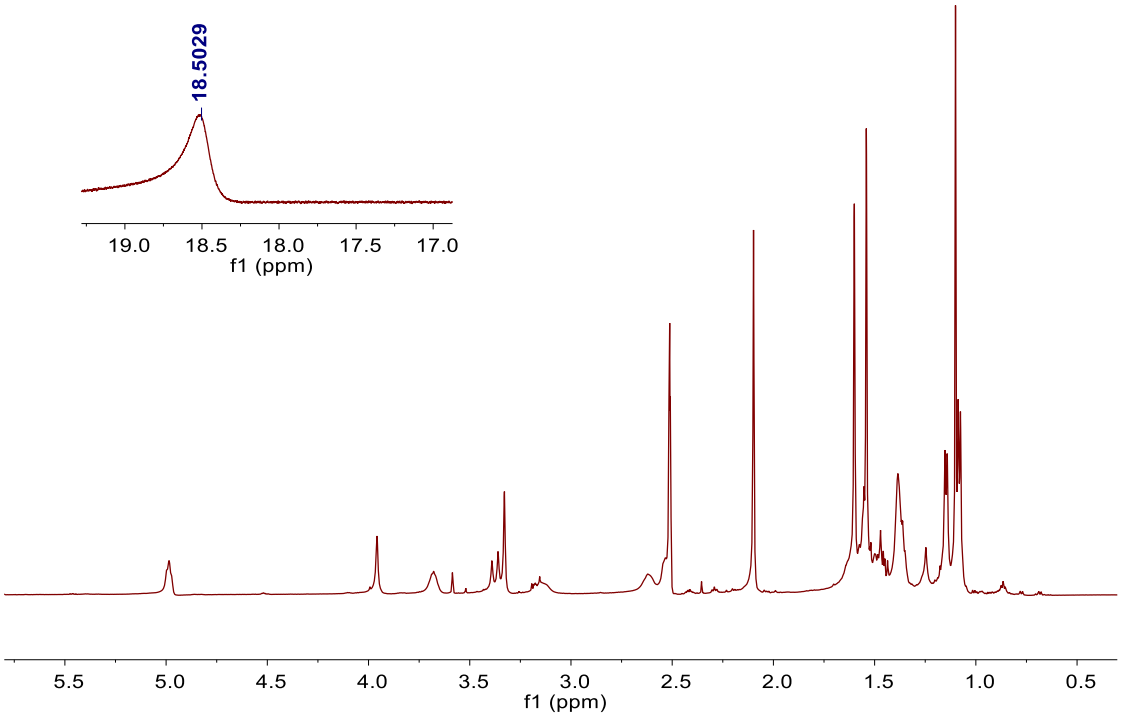

Table S1 PPAPs with enolizable *β*,*β*'-triC or *β*-diC systems

The PPAPs with enolizable *β*,*β*'-tricarbonyl (*β*,*β*'-triC) systems	
Numbers	Name
1–6	hyperascyrones A–F[1]
7–10	hyperbeanols A–D[2]
11	chipericumin E[3]
12–14	semsinones A–C[4]
15–20	oblongifolin L, N–Q, T–U [5]
21–24	oblongifolin AA, Z, V, L[6]
25–28	oblongifolin A–D[7]
29	Oblongifolin E[8]
30–31	guttiferone I–J[9]
32	garcicowin B[10]
33–34	6-epi-guttiferone J
35–36	guttiferone K–L[12]
37–38	guttiferone O–P[13]
39	guttiferone G[14]

40–44	guttiferone A–E[15]
45–47	guttiferone M
48–51	7-epi-garcinol
52	guttiferone Q[18]
53	cowanone[19]
54	garcimultiflorone K[20]
55–59	Garcimultiflorone D–F
60–63	garciesculentone B–E[22]
64	xanthochymol[23]
65	laxifloranone[24]
66–67	guttiferone H
68–69	guttiferone M–N[26]
70	guttiferone F[27]
71	camboginol[28]
72	garcimultiflorone H[29]
73	trijapin D[30]
74	garcinielliptone HF[31]
The PPAPs with enolizable *β*–dicarbonyl (*β*–diC) systems	
Numbers	Name
75	nemorosone[32]
76	Hydroxynemorosone[32]
77	chamone I[33]
78	chamone II[33]
79	garcinialiptone D[34]
80–81	hyperevolutin A–B[35]
82	hyperibine J[36]
83	Hyperfirin[36]
84	Secohyperforin[37]
85	Adsecohyperforin[37]
86	garcinielliptone F[38]

87	adhyperfirin[39]
88	adhyperforin[40]
89-90	prolifenone A–B[41]
91	enervosanone[42]

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Table S2 Antibacterial activities of compounds **1**−**3** with MIC_{50} Values ± SD (μM)

	Escherichia coli ATCC25922	*Pseudomonas aeruginosa* ATCC27853	Staphylococcus aureus subsp. Aureus ATCC29213	*Salmonella enterica subsp. enterica* ATCC14028
1	-[b]	-[b]	-[b]	-[b]
2	-[b]	-[b]	11.24 ± 0.04	-[b]
3	-[b]	-[b]	70.76 ± 1.92	-[b]
Penicillin[a]	-[b]	-[b]	0.533 ± 0.03	-[b]

[a]Penicillin was used as positive control.

[b]not detected (practical limit of detection).

Figure S25. ^{1}H NMR (400 MHz) spectrum of compound **1** (Recorded in C_5D_5N, 298 K).

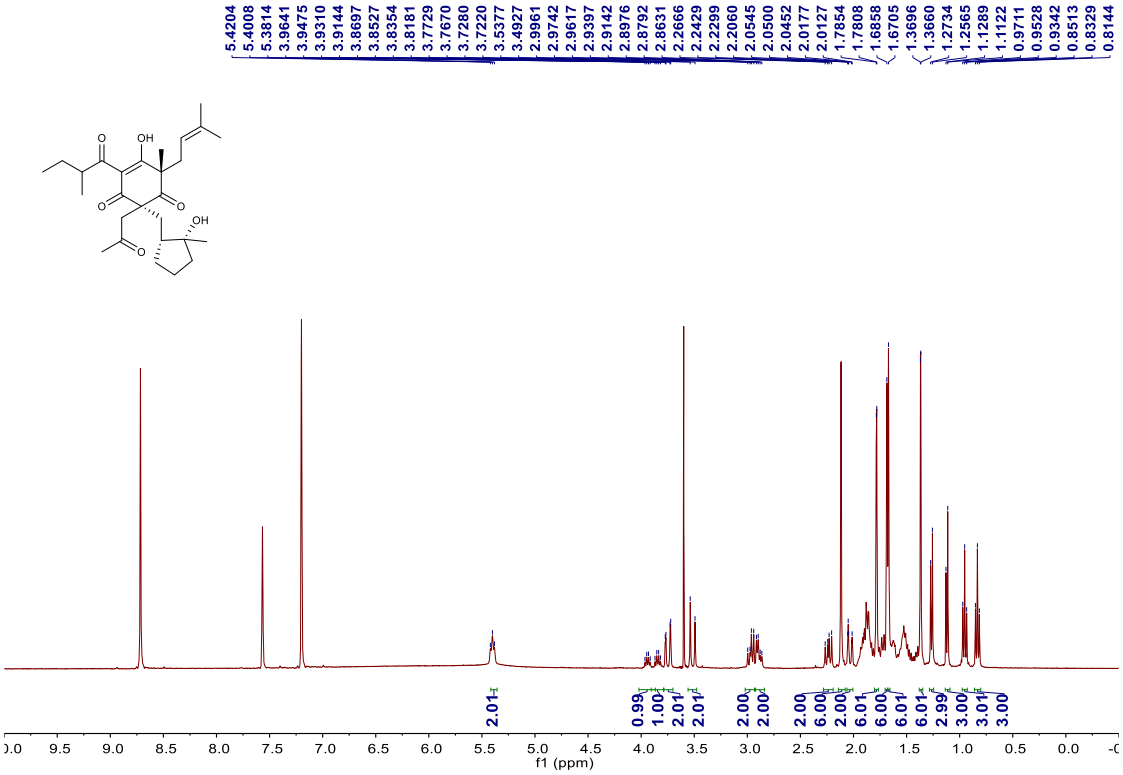


Figure S26. ^{13}C NMR (100 MHz) spectrum of compound **1** (Recorded in C_5D_5N, 298 K)

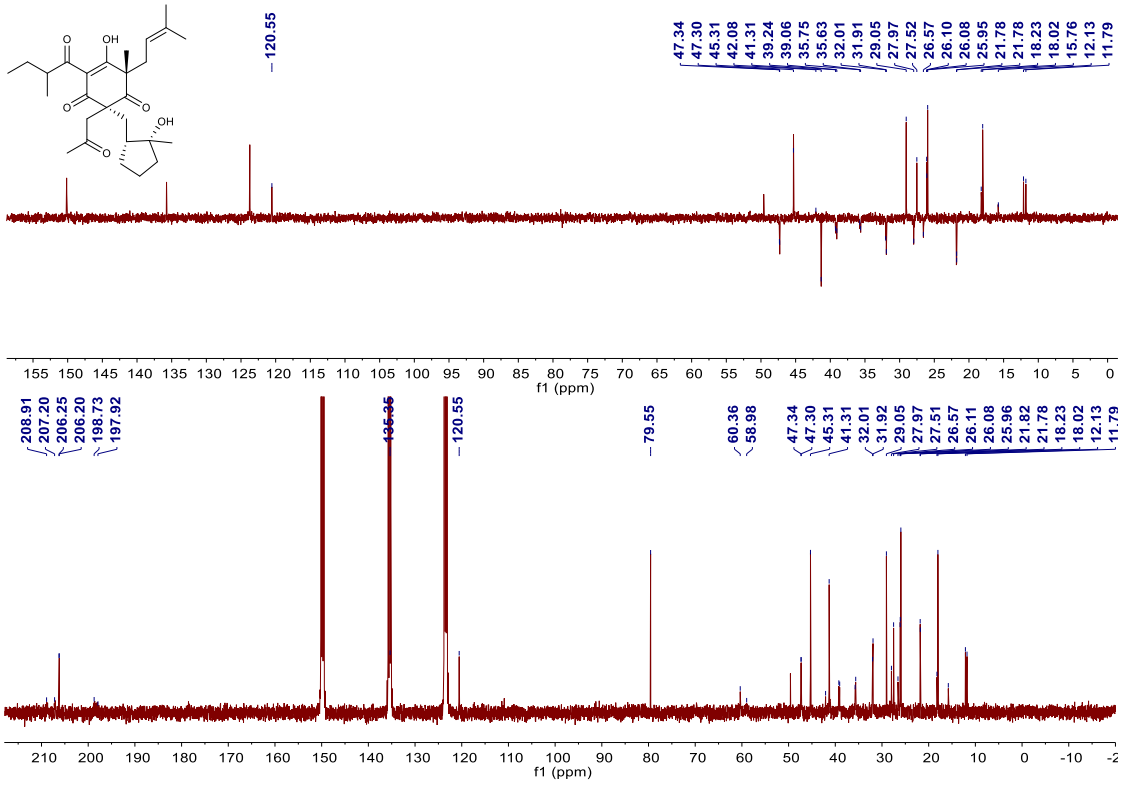


Figure S27. HSQC spectrum of compound **1** (Recorded in C_5D_5N, 298 K)

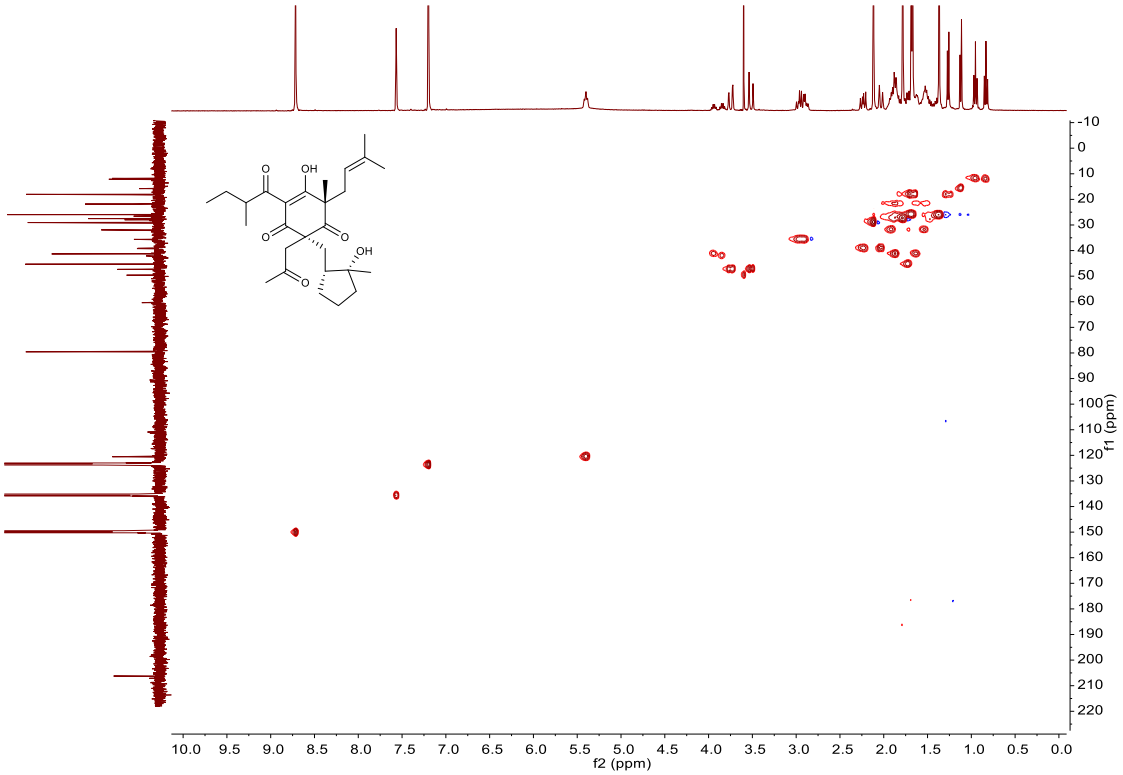


Figure S28. ^{1}H–^{1}H COSY spectrum of compound **1** (Recorded in C_5D_5N, 298 K)

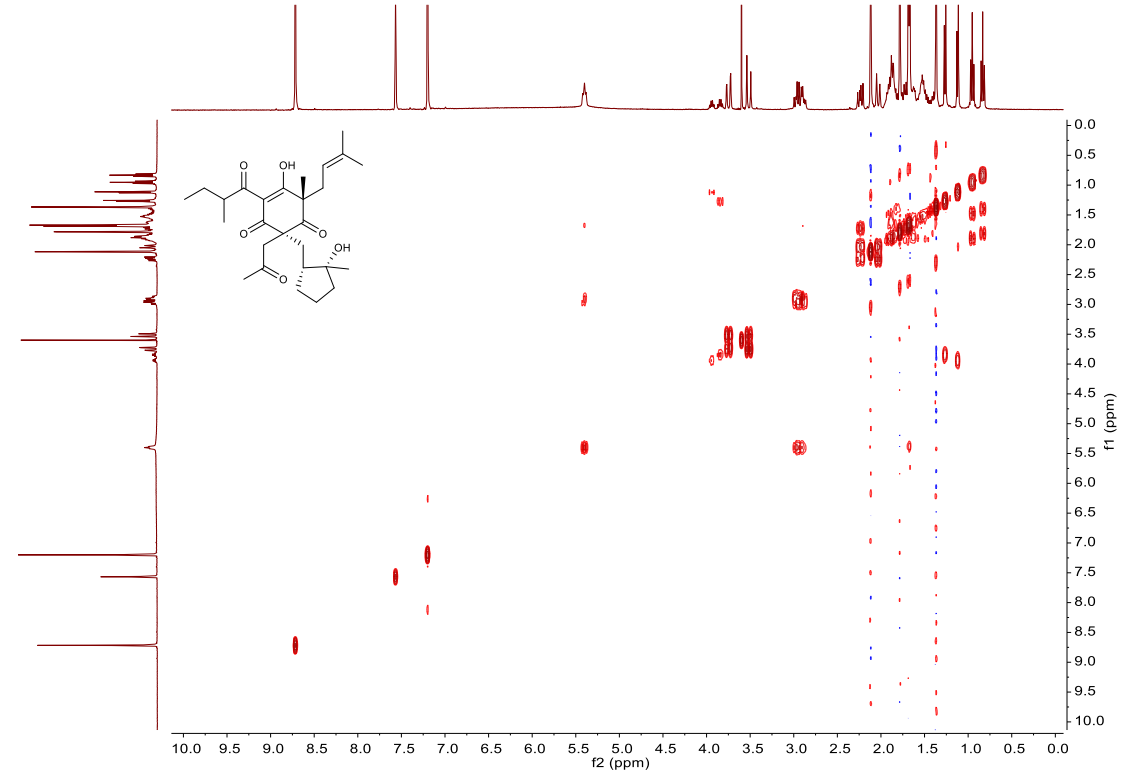


Figure S29. HMBC spectrum of compound **1** (Recorded in C_5D_5N, 298 K)

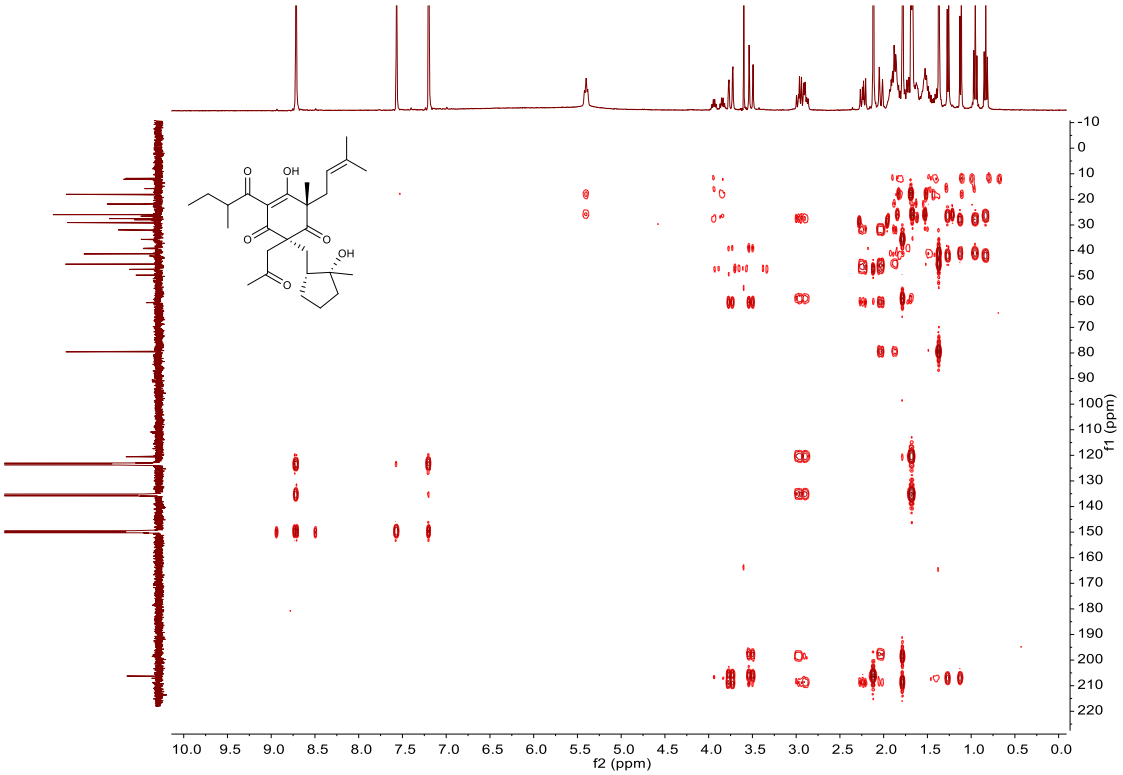


Figure S30. NOESY spectrum of compound **1** (Recorded in C_5D_5N, 298 K)

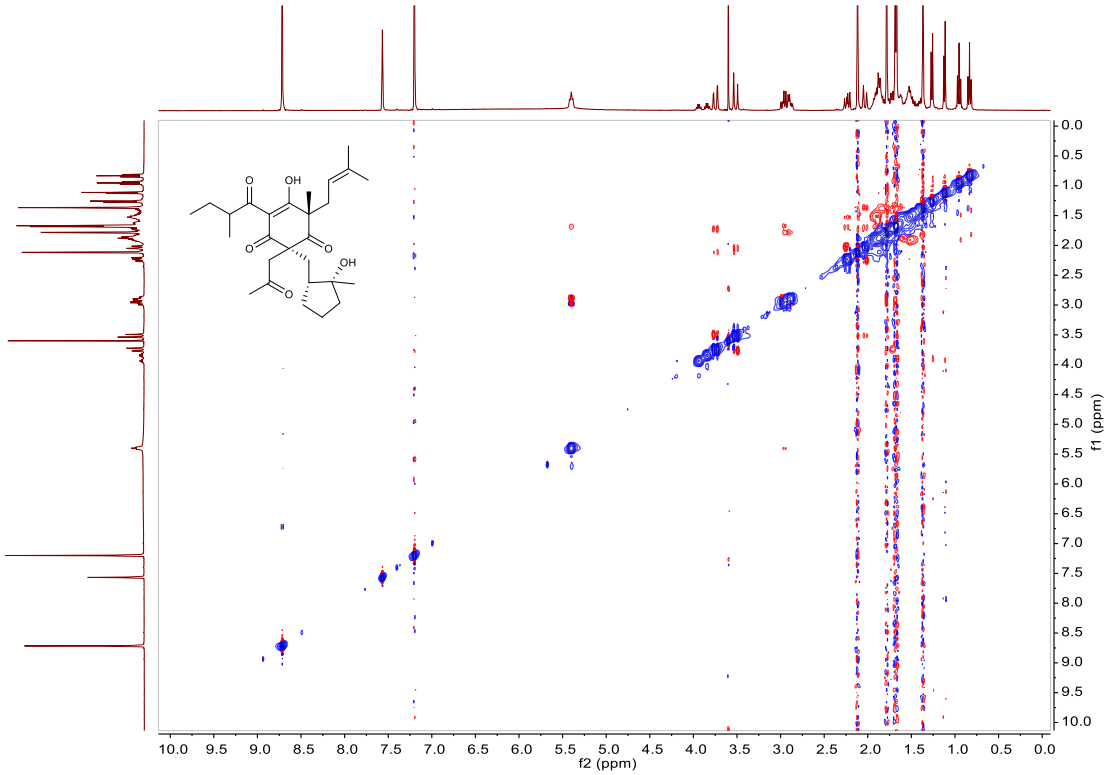


Figure S31. HRESIMS of compound **1.**

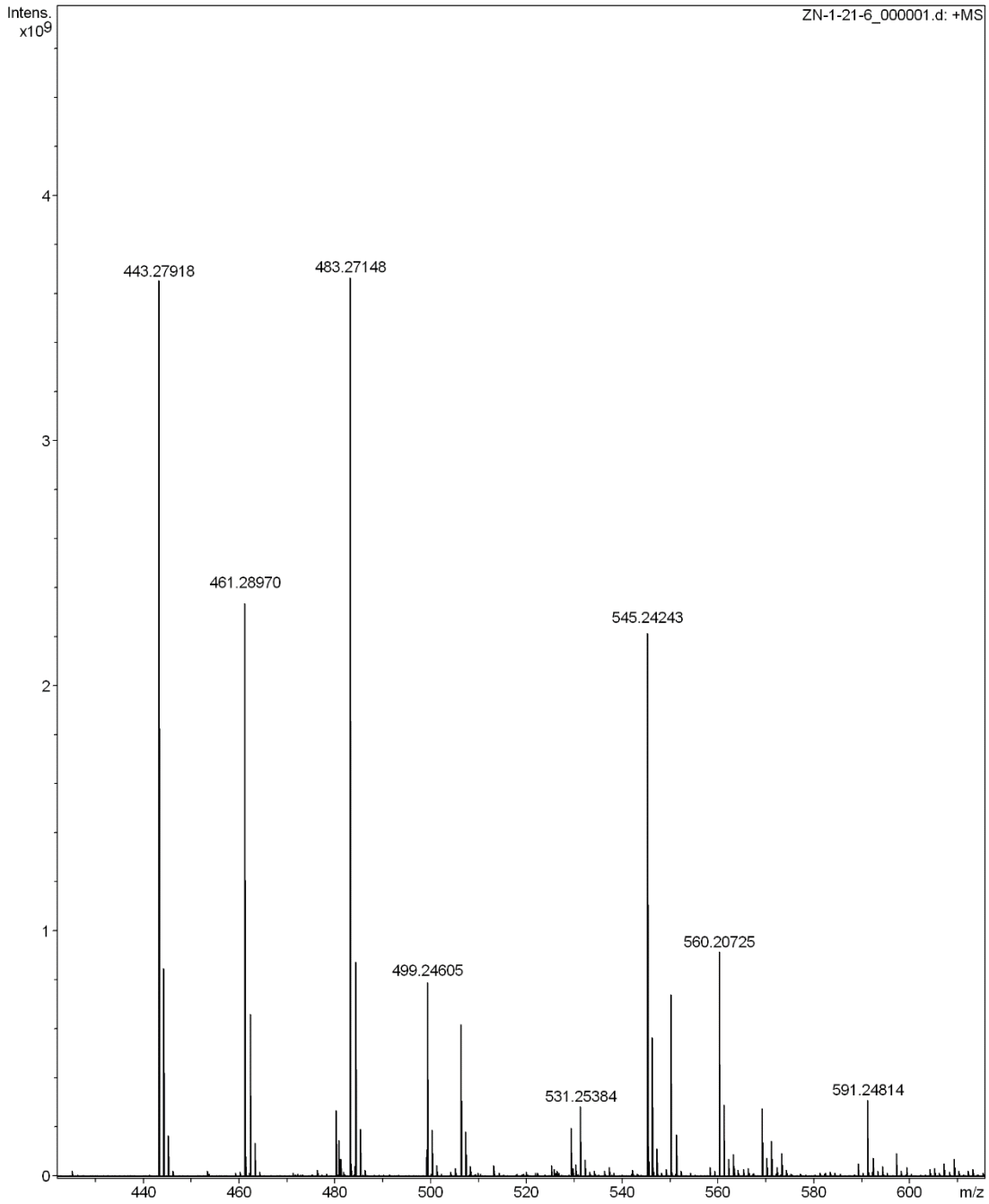


Figure S32. UV spectrum of compound **1**

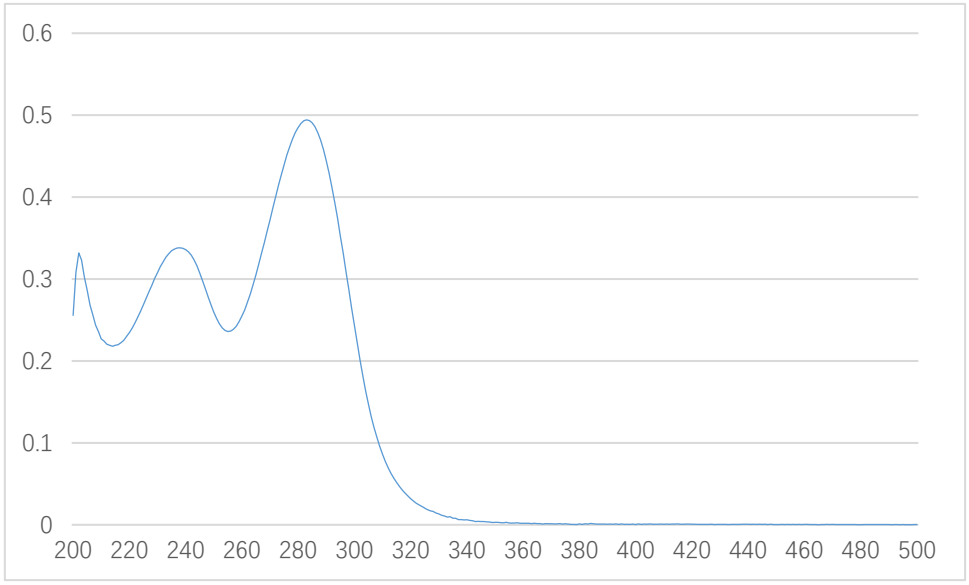


Figure S33. IR spectrum of compound **1**

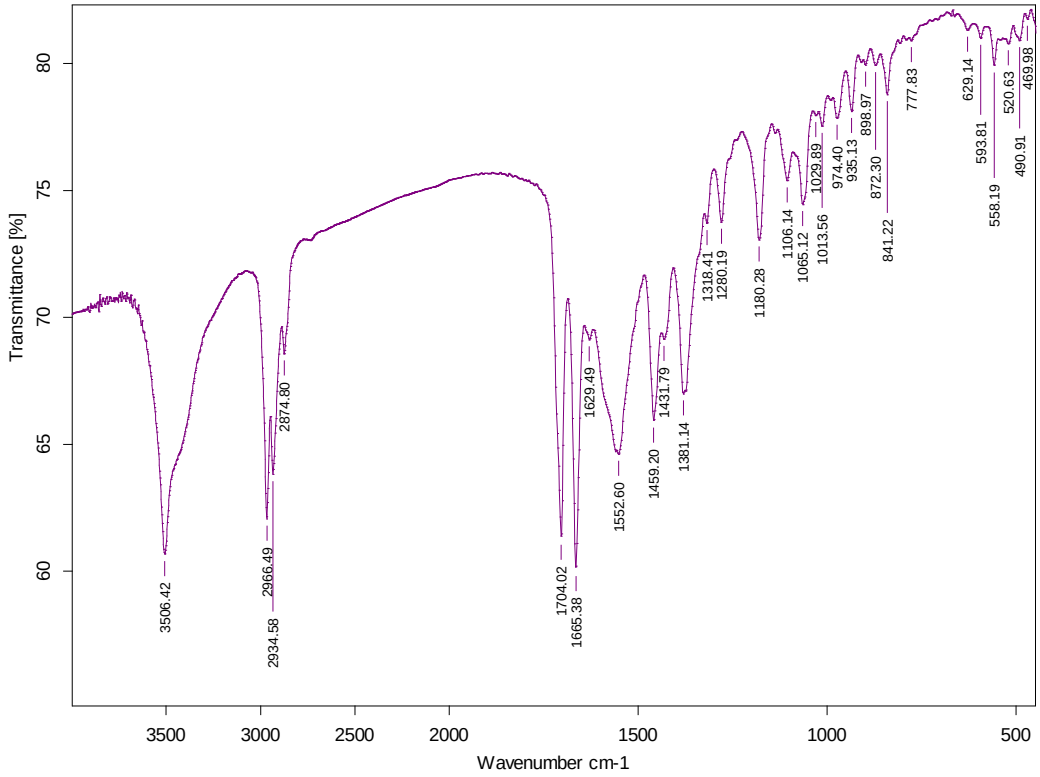


Figure S34. ^{1}H NMR (400 MHz) spectrum of compound **2** (Recorded in C_5D_5N, 298 K)

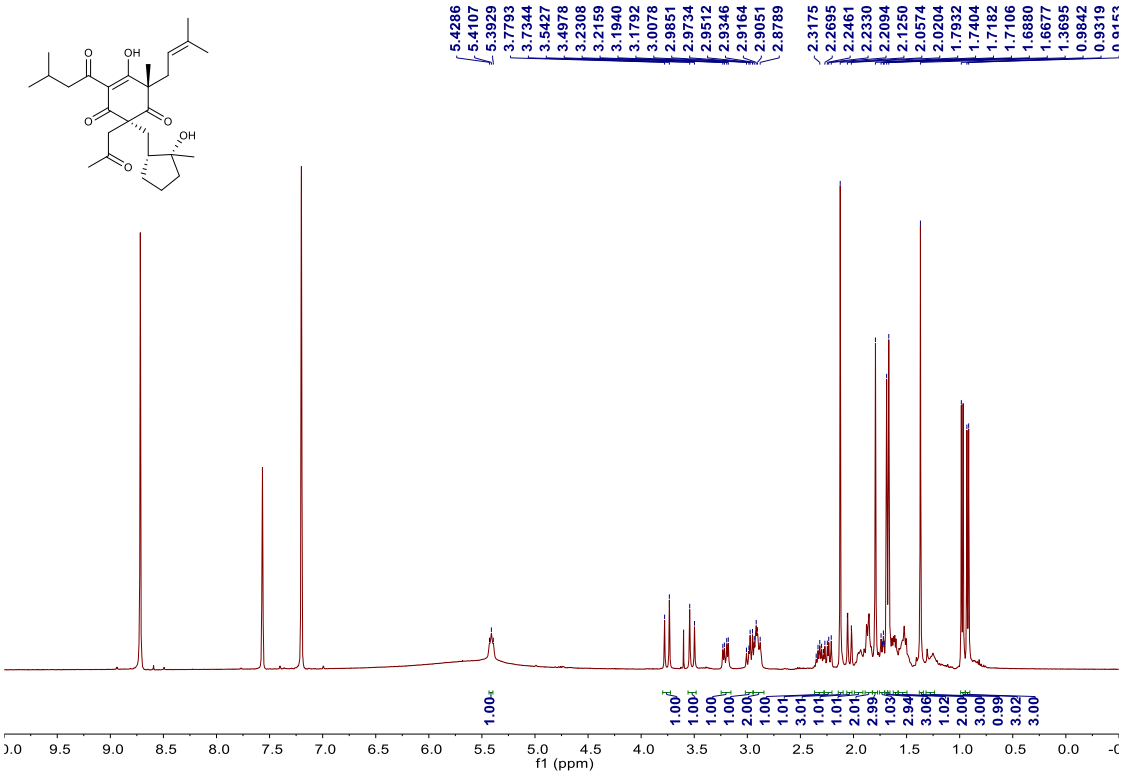


Figure S35. ^{13}C NMR (100 MHz) spectrum of compound **2** (Recorded in C_5D_5N, 298 K)

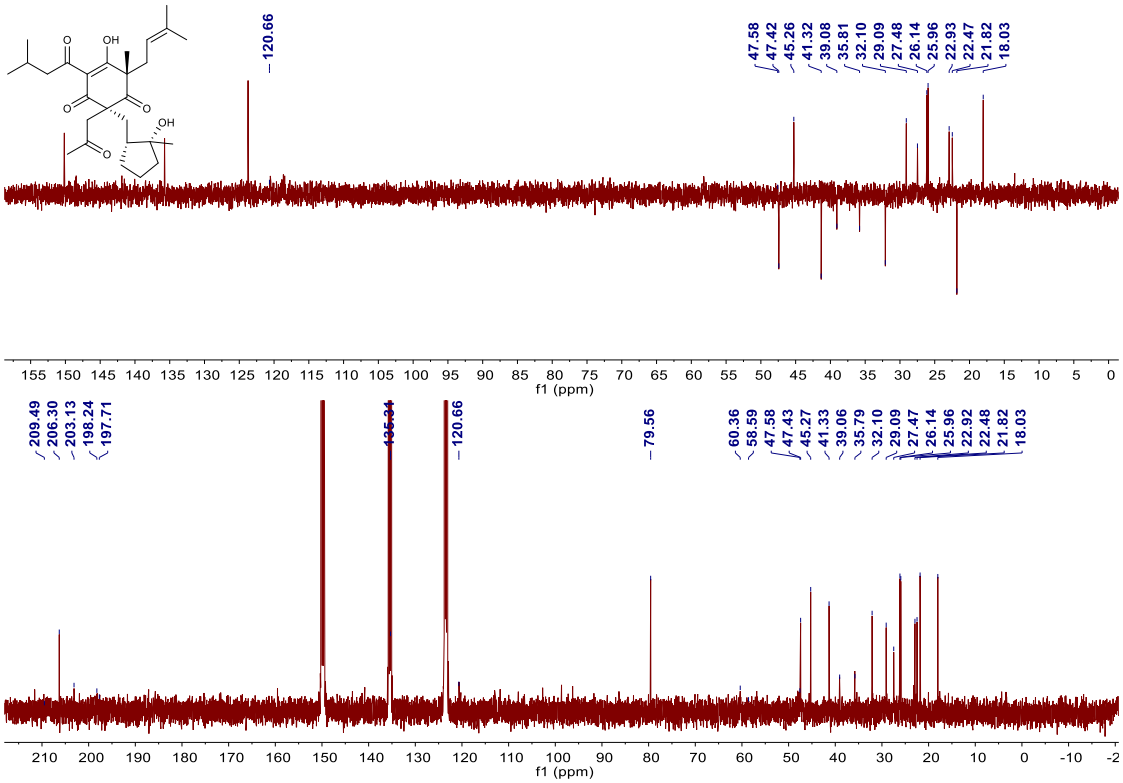


Figure S36. HSQC spectrum of compound **2** (Recorded in C_5D_5N, 298 K)

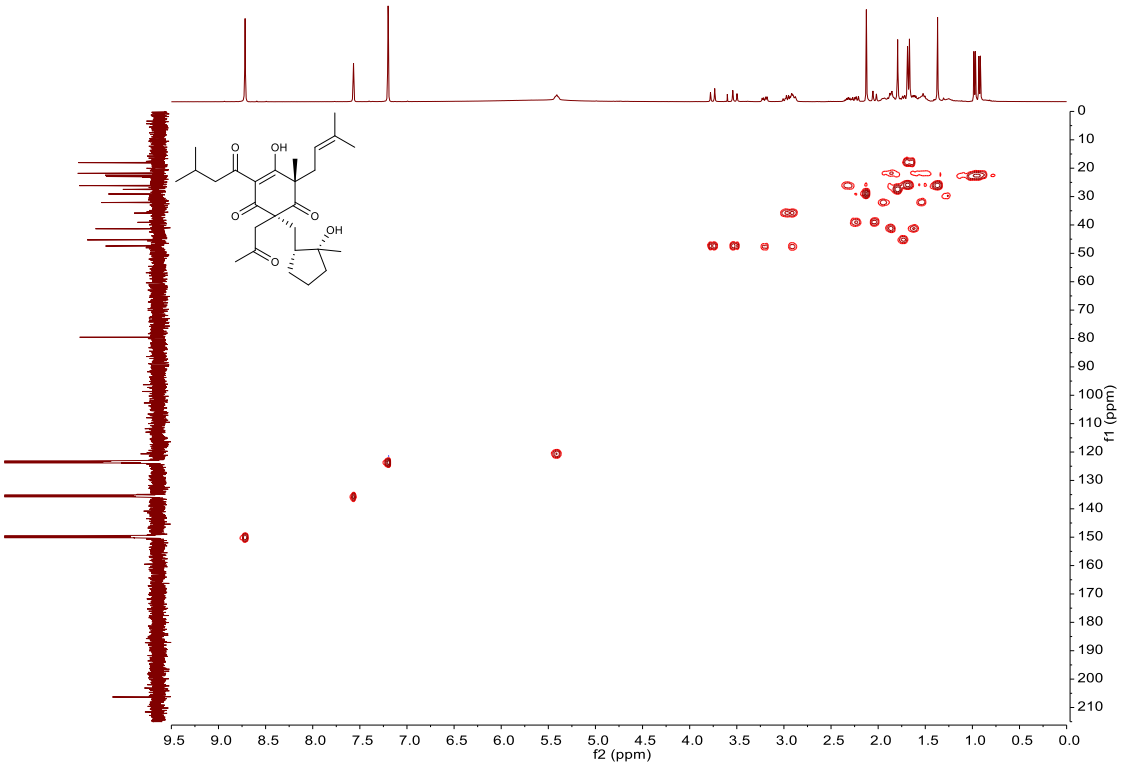


Figure S37. ^{1}H–^{1}H COSY spectrum of compound **2** (Recorded in C_5D_5N, 298 K)

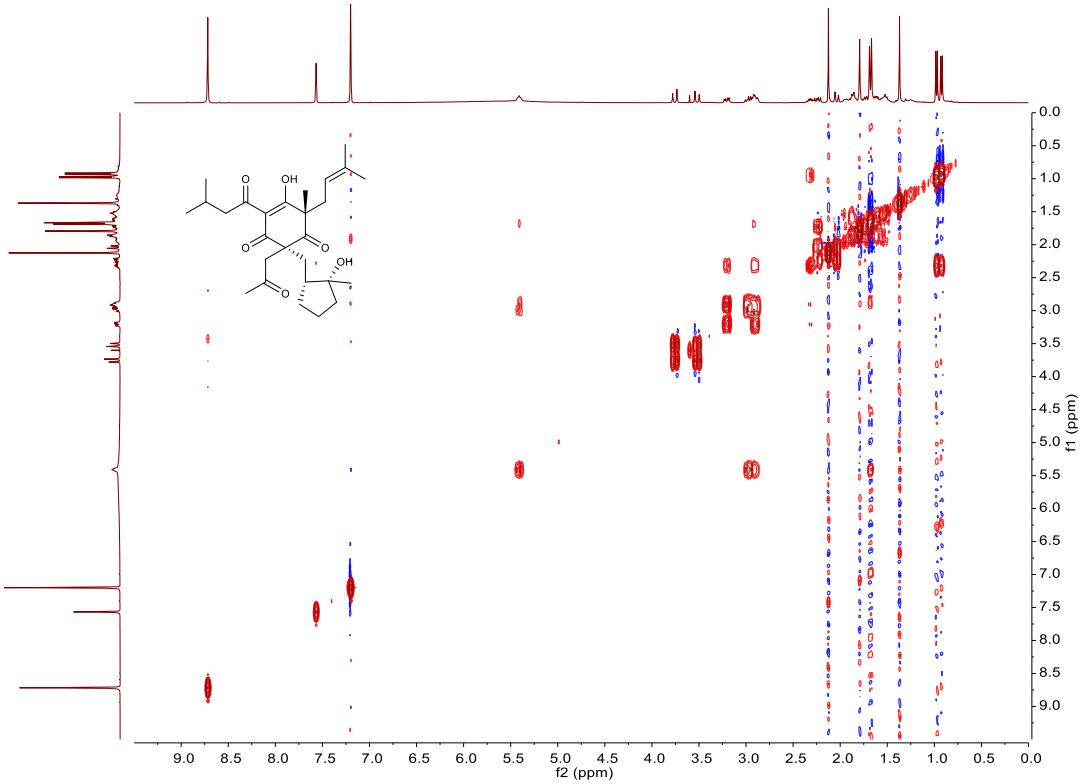


Figure S38. HMBC spectrum of compound **2** (Recorded in C_5D_5N, 298 K)

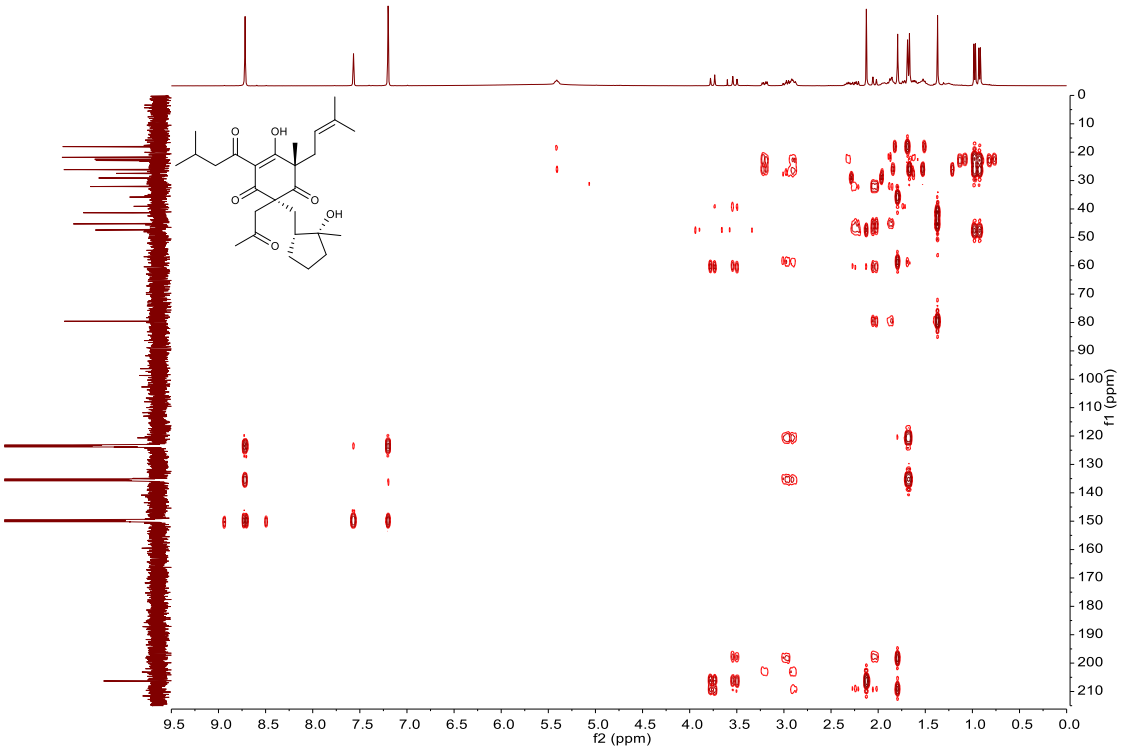


Figure S39. NOESY spectrum of compound **2** (Recorded in C_5D_5N, 298 K)

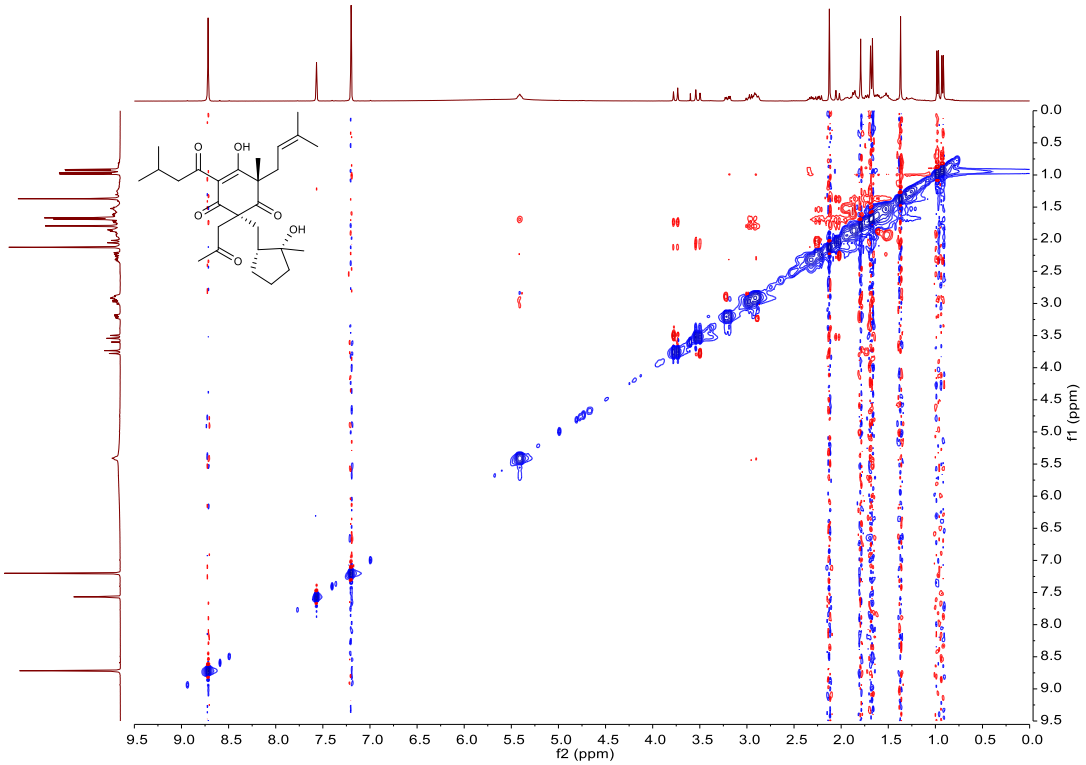


Figure S40. HRESIMS of compound **2.**

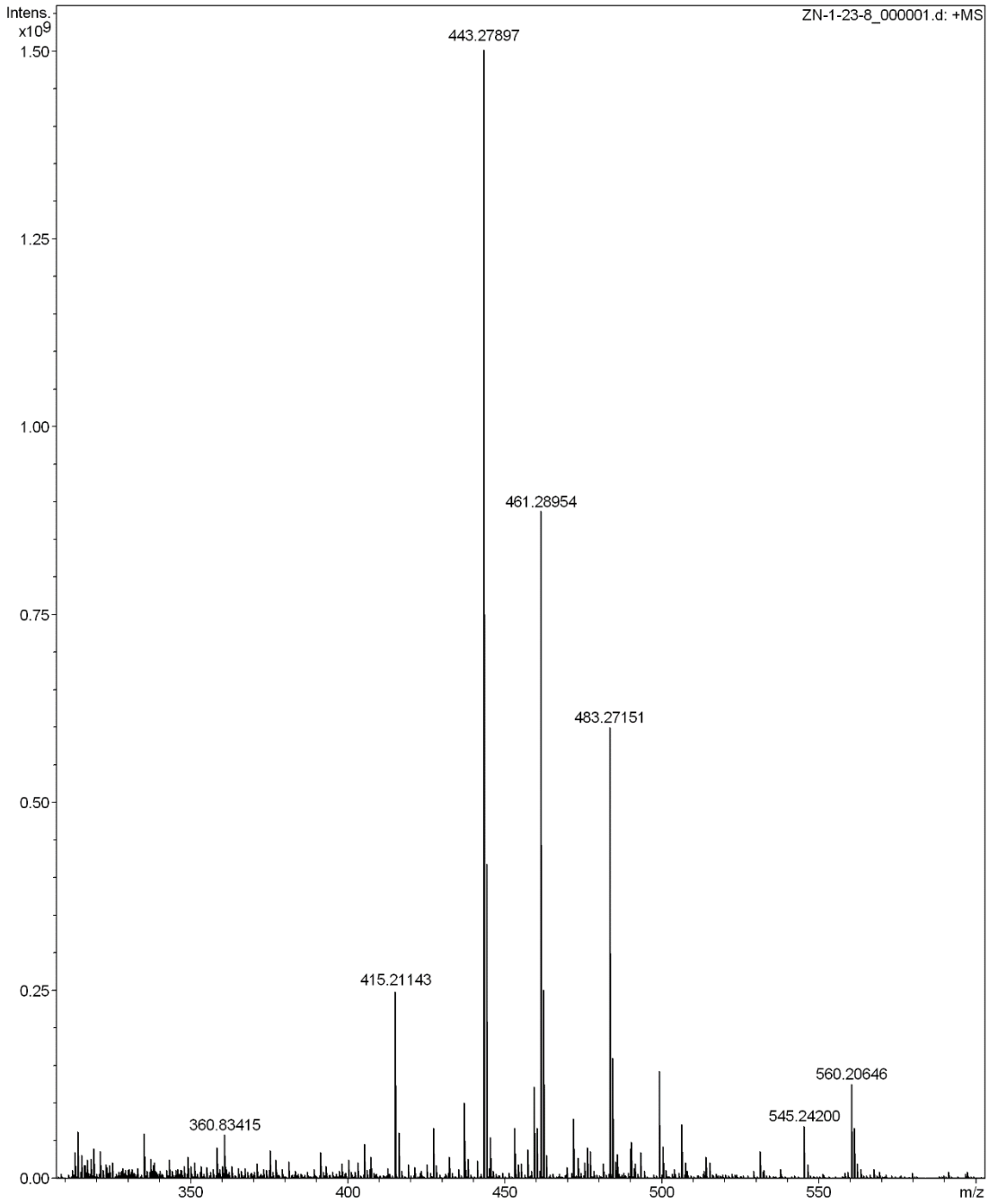


Figure S41. UV spectrum of compound **2**

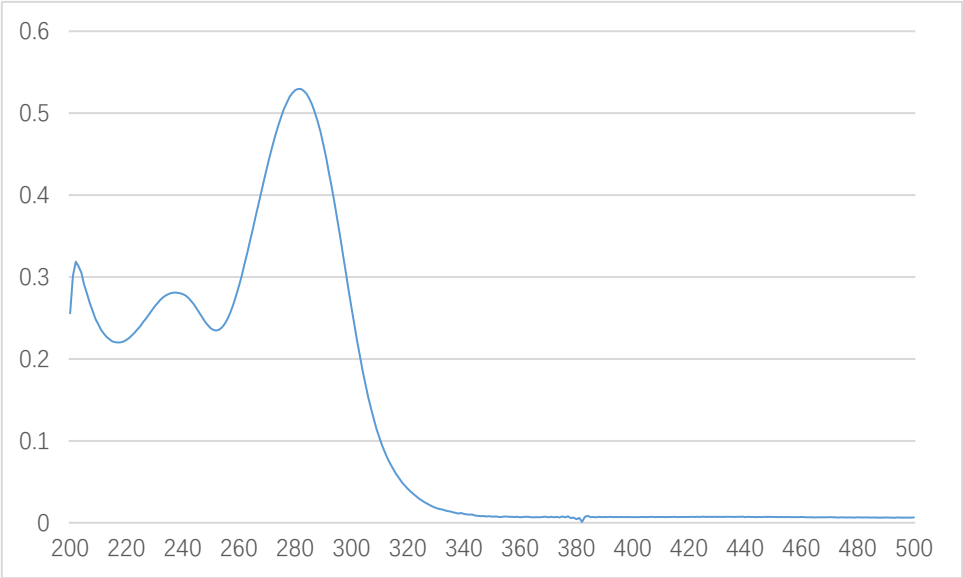


Figure S42. IR spectrum of compound **2**

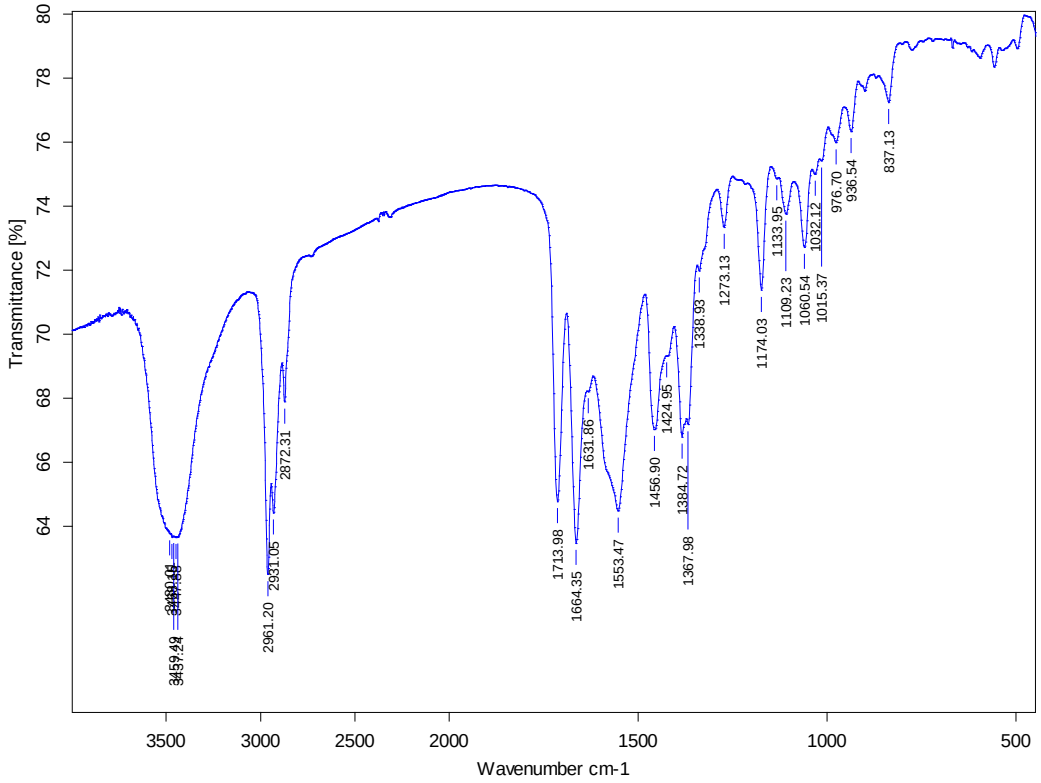


Figure S43. ^{1}H NMR (400 MHz) spectrum of compound **3** (Recorded in C_5D_5N, 298 K)

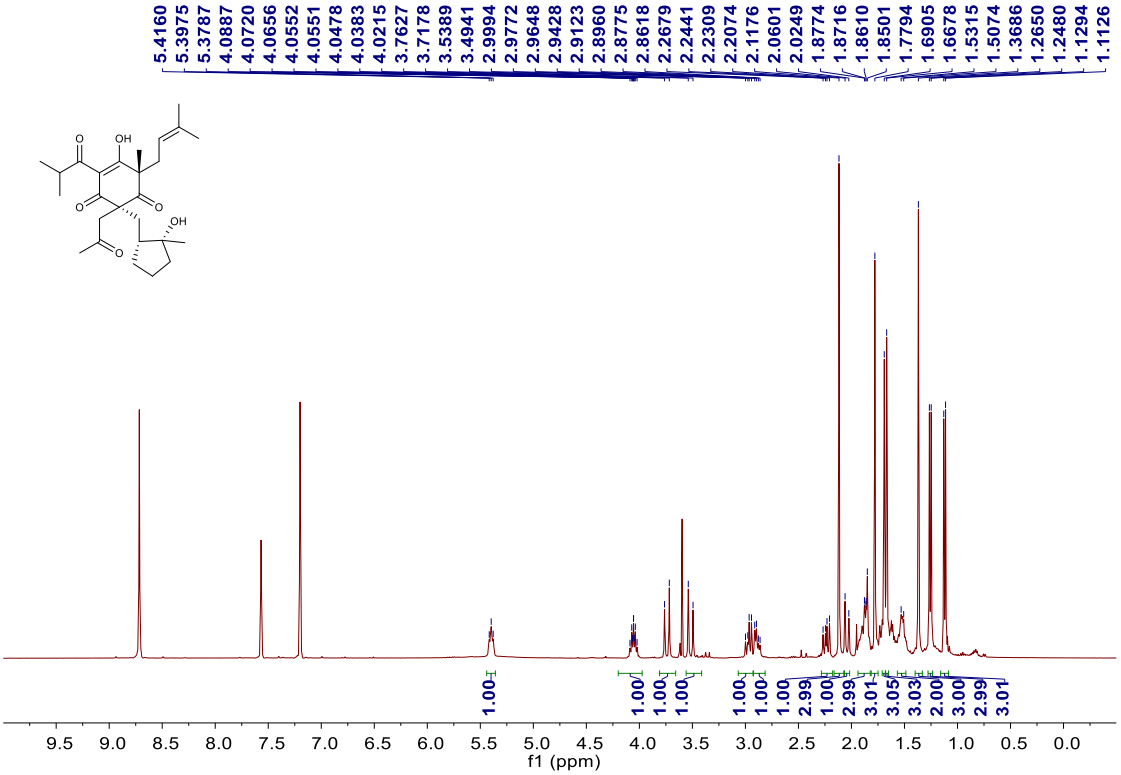


Figure S44. ^{13C} NMR (100 MHz) spectrum of compound **3** (Recorded in C_5D_5N, 298 K)

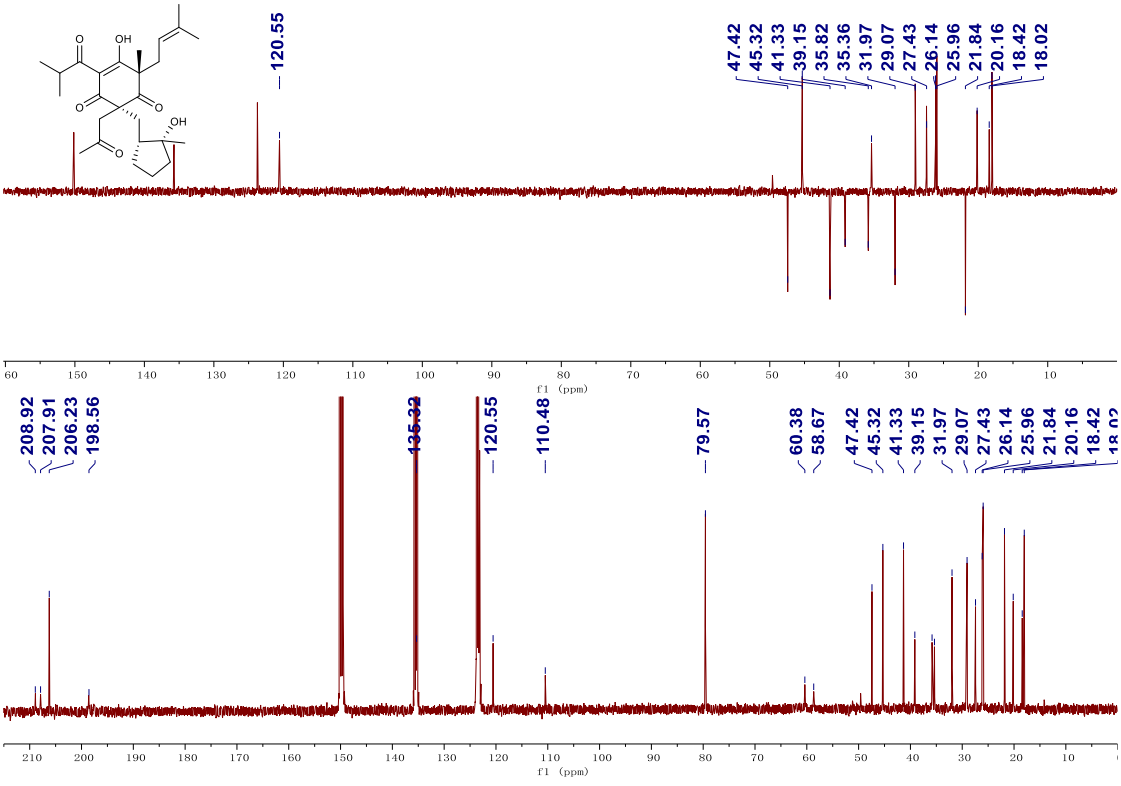


Figure S45. HSQC spectrum of compound **3** (Recorded in C_5D_5N, 298 K)

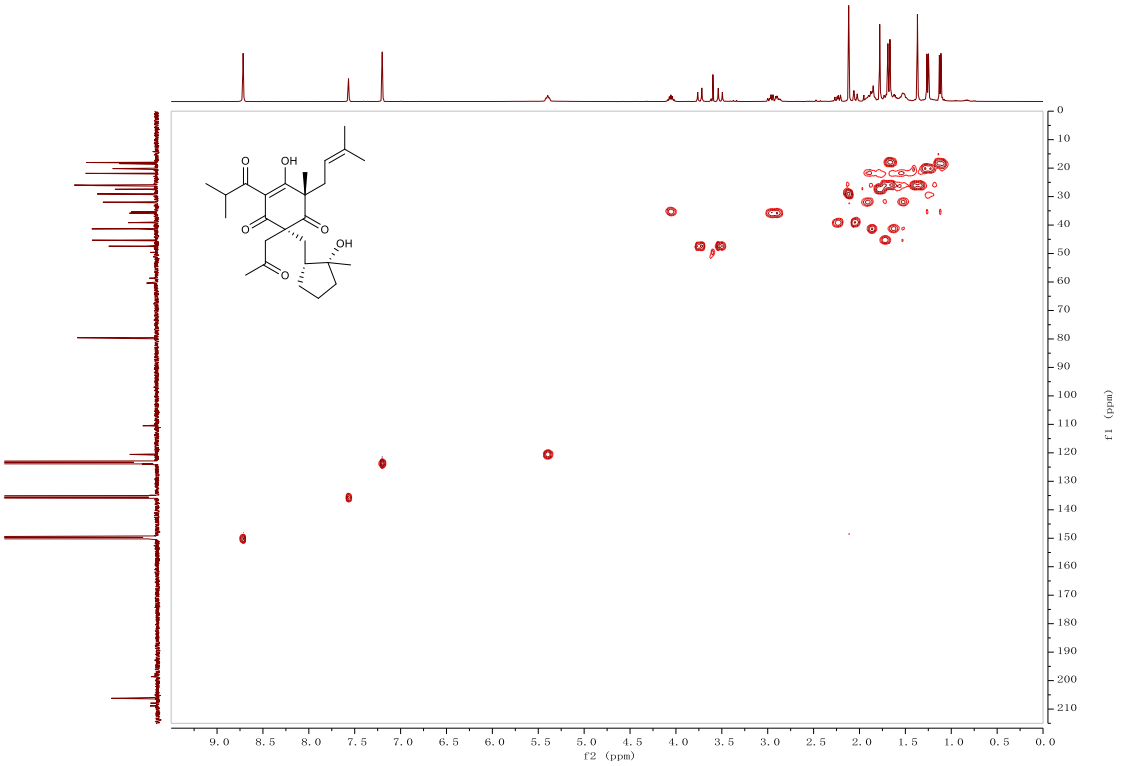


Figure S46. ^{1}H–^{1}H COSY spectrum of compound **3** (Recorded in C_5D_5N, 298 K)

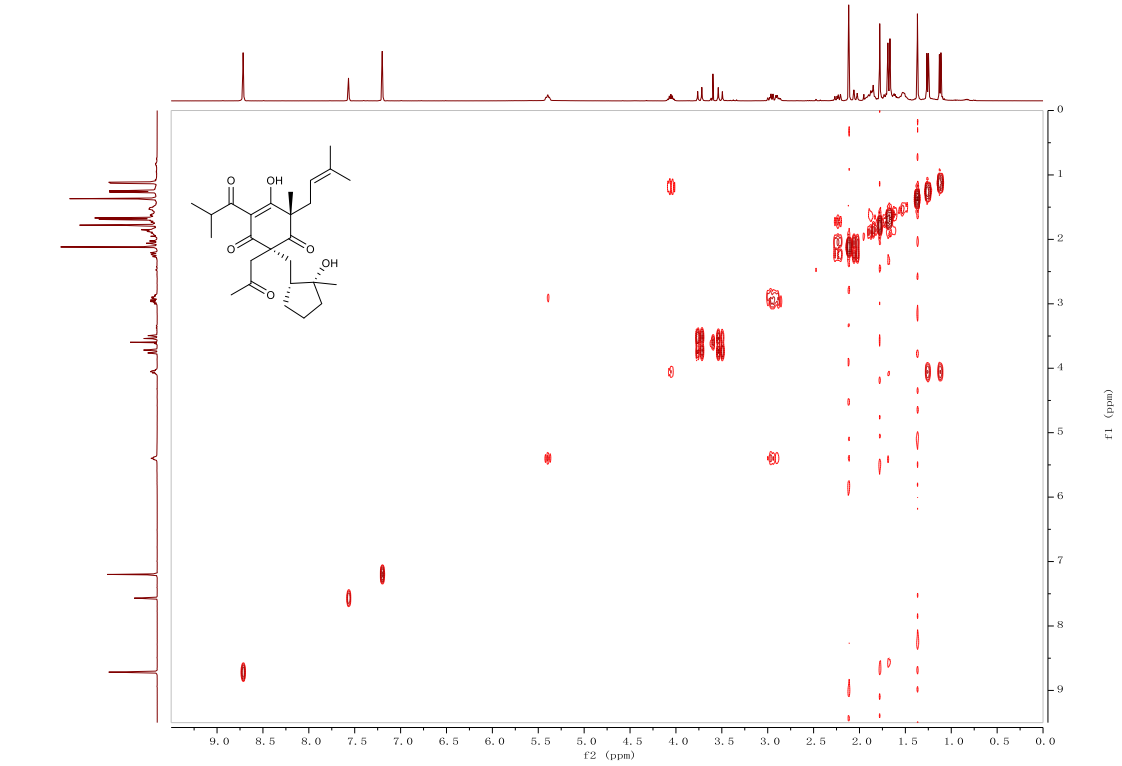


Figure S47. HMBC spectrum of compound **3** (Recorded in C_5D_5N, 298 K)

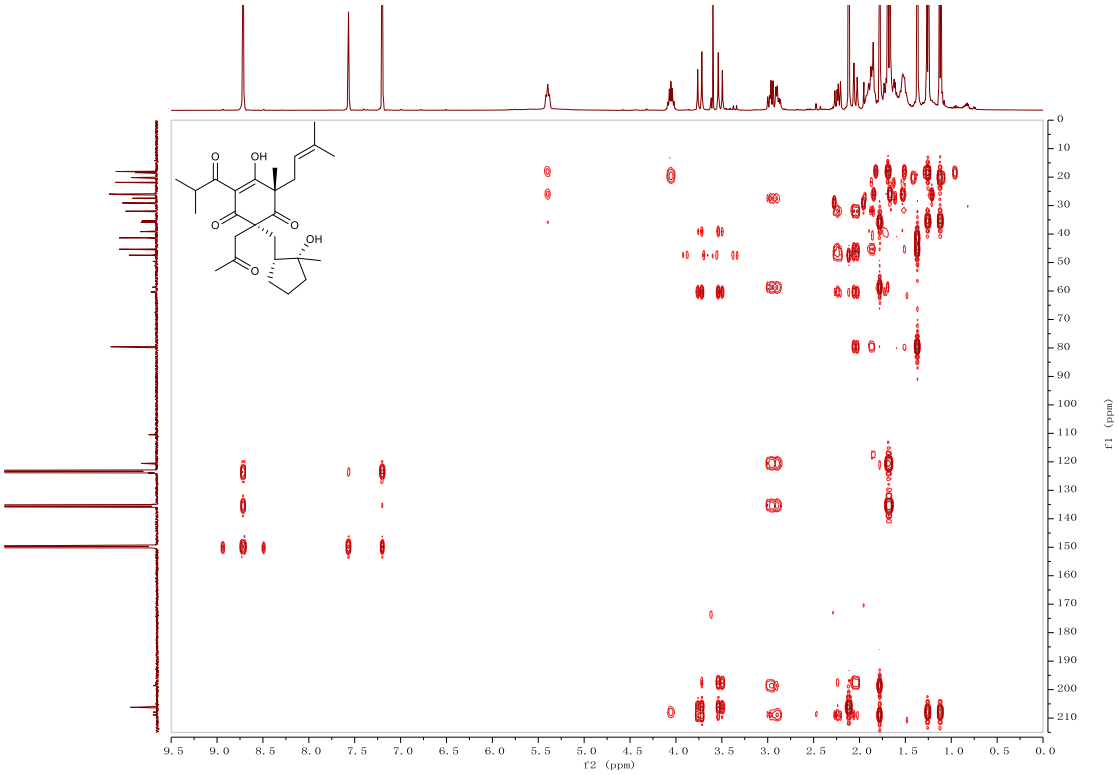


Figure S48. NOESY spectrum of compound **3** (Recorded in C_5D_5N, 298 K)

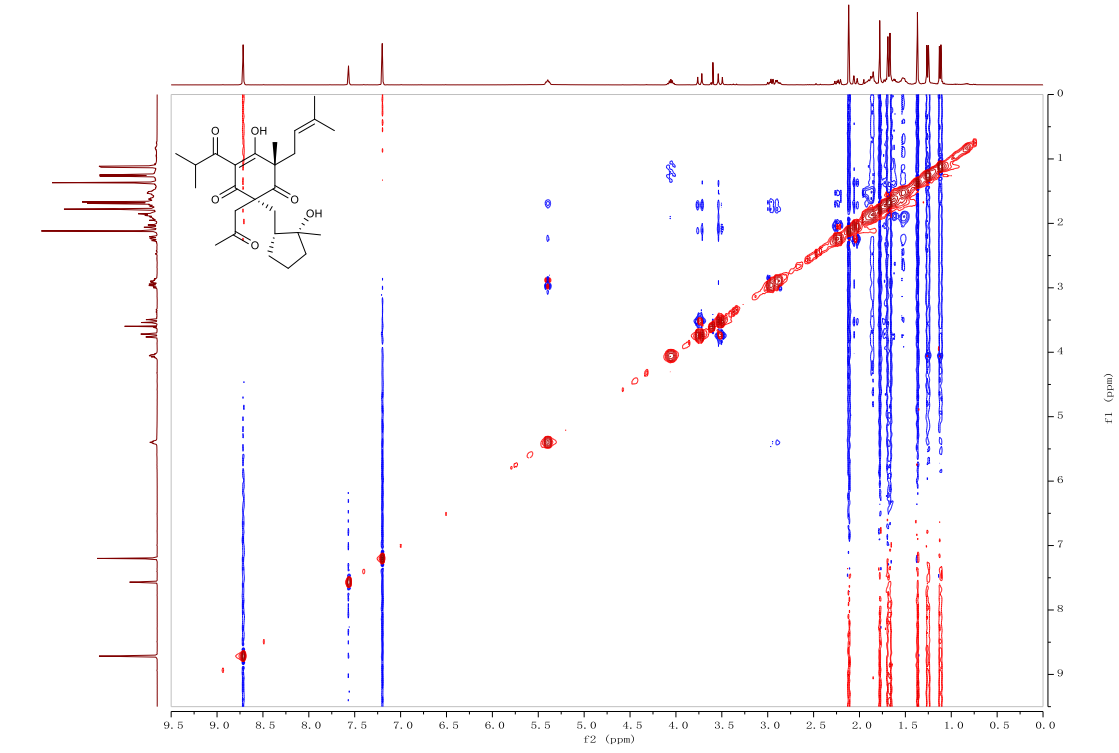


Figure S49. HRESIMS of compound **3.**

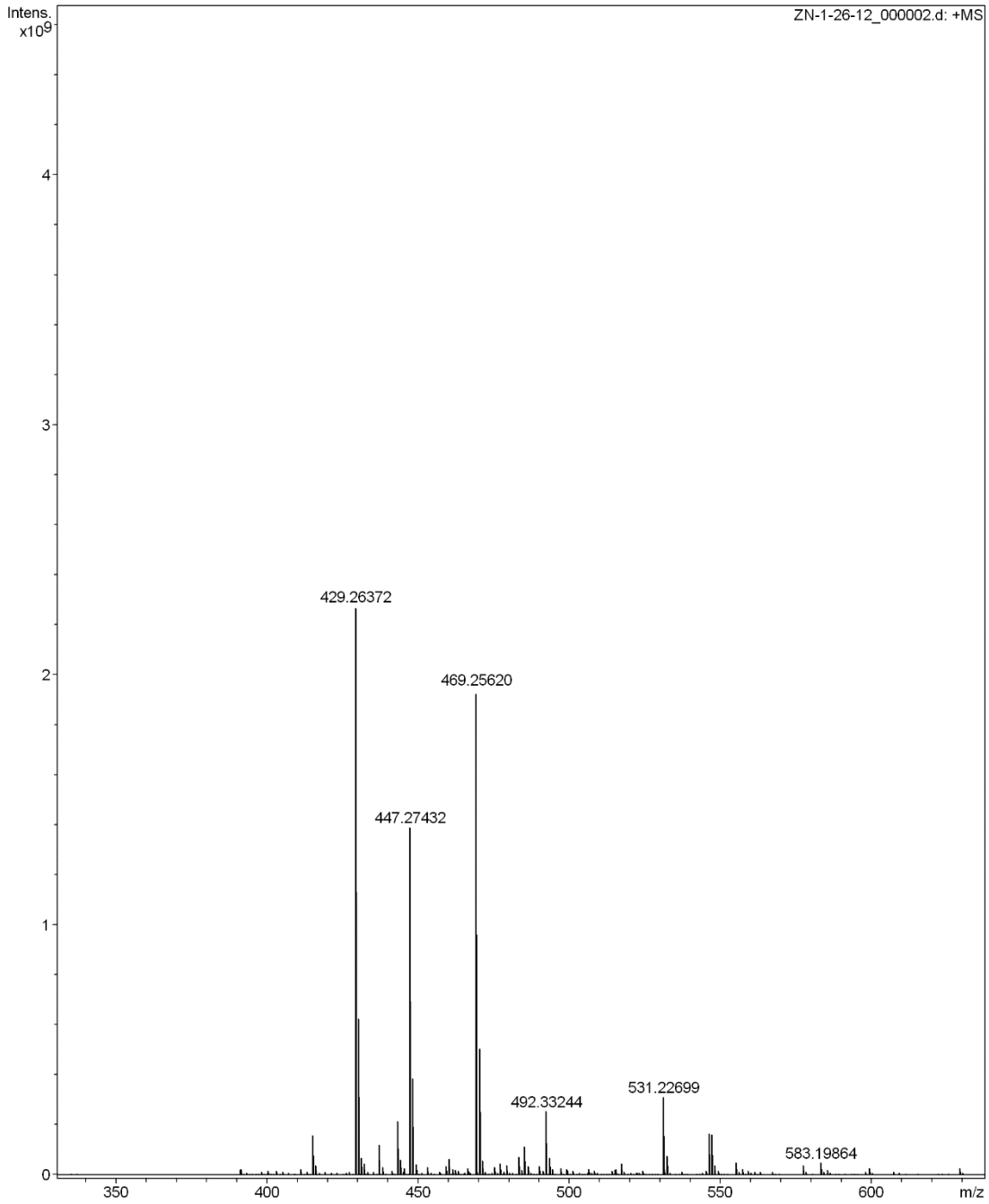


Figure S50. UV spectrum of compound **3**

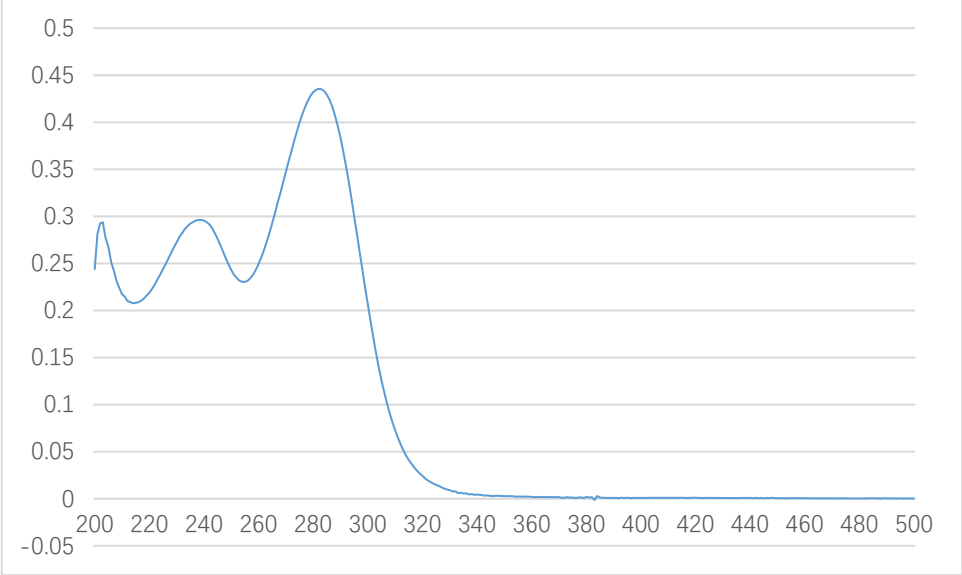


Figure S51. IR spectrum of compound **3**

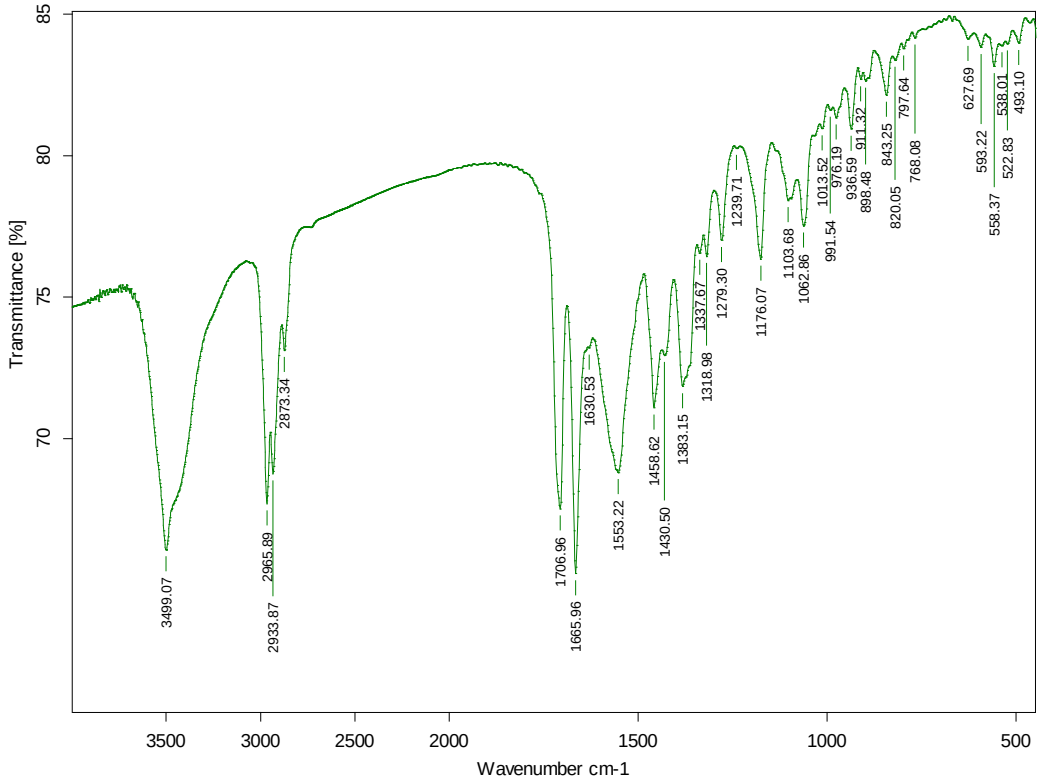


Figure S52. ^{1}H NMR (800 MHz) spectrum of compound **4** (Recorded in $CDCl_3$, 298 K)

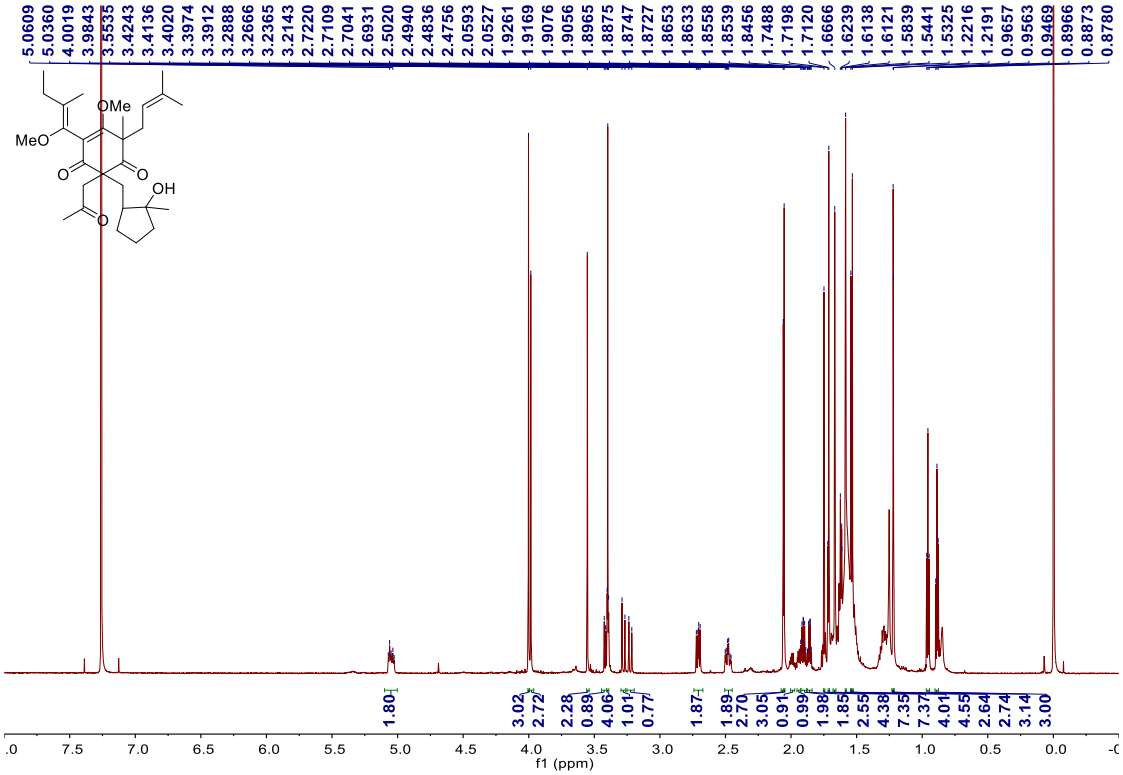


Figure S53. ^{13}C NMR (200 MHz) spectrum of compound **4** (Recorded in $CDCl_3$, 298 K)

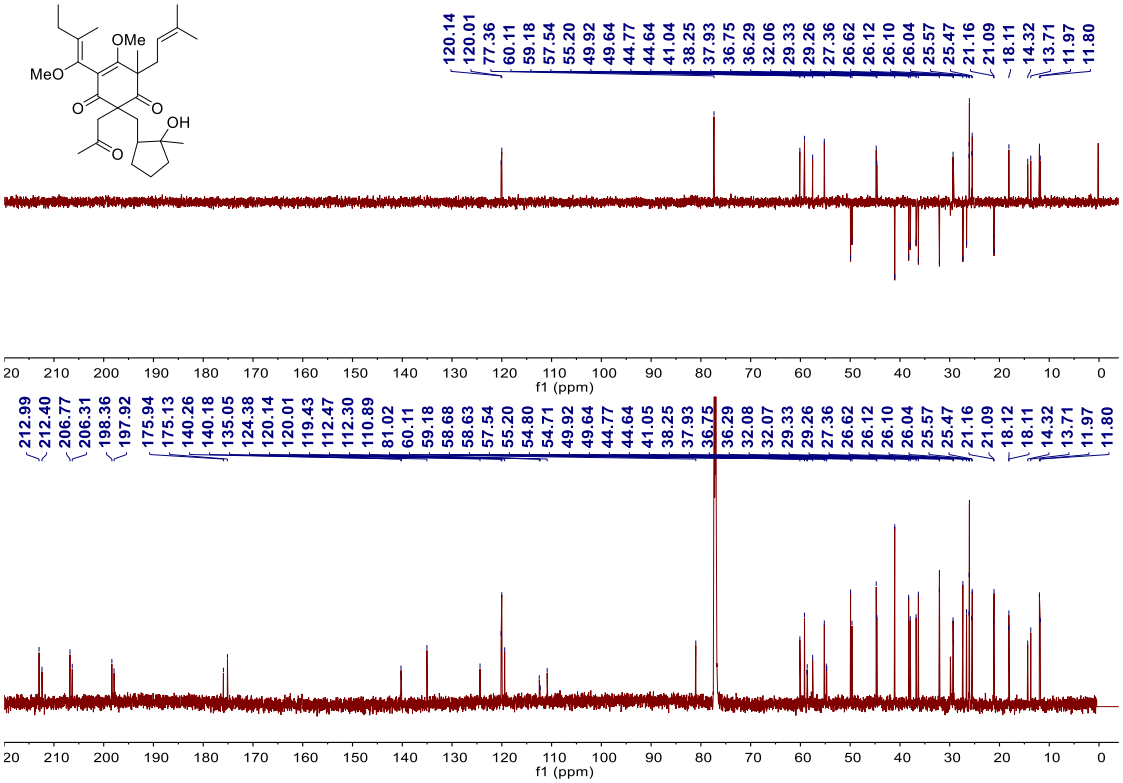


Figure S54. HSQC spectrum of compound **4** (Recorded in $CDCl_3$, 298 K)

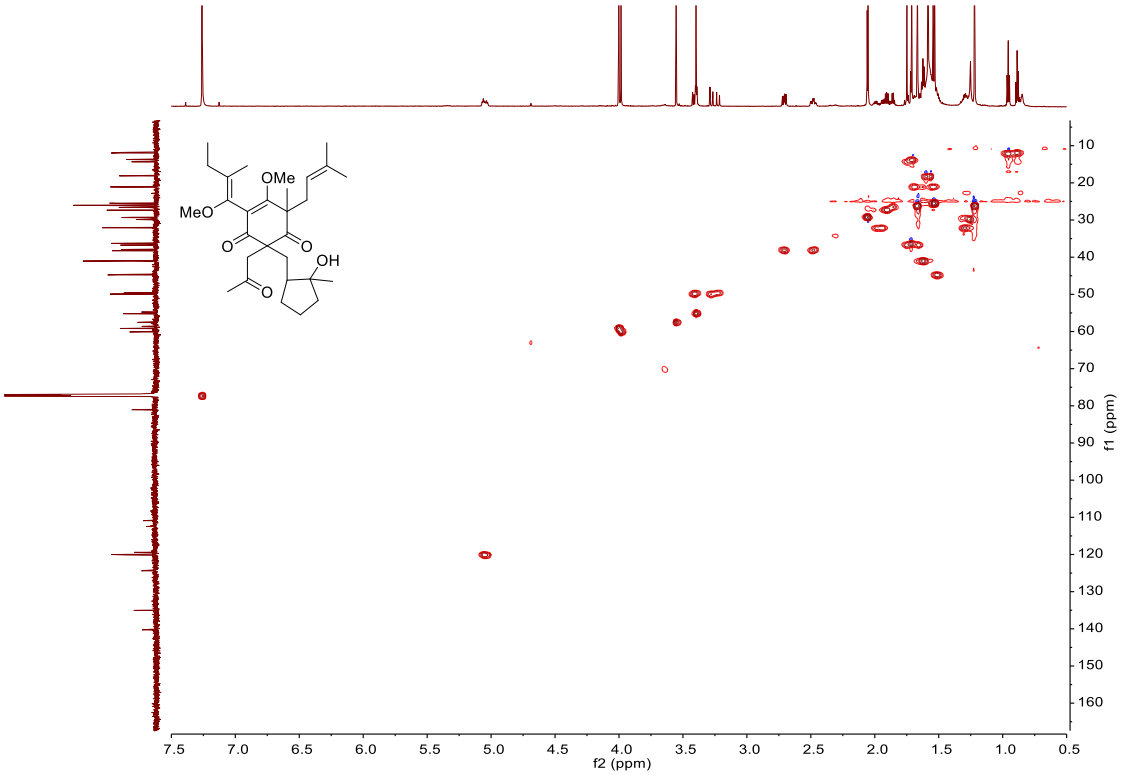


Figure S55. HMBC spectrum of compound **4** (Recorded in $CDCl_3$, 298 K)

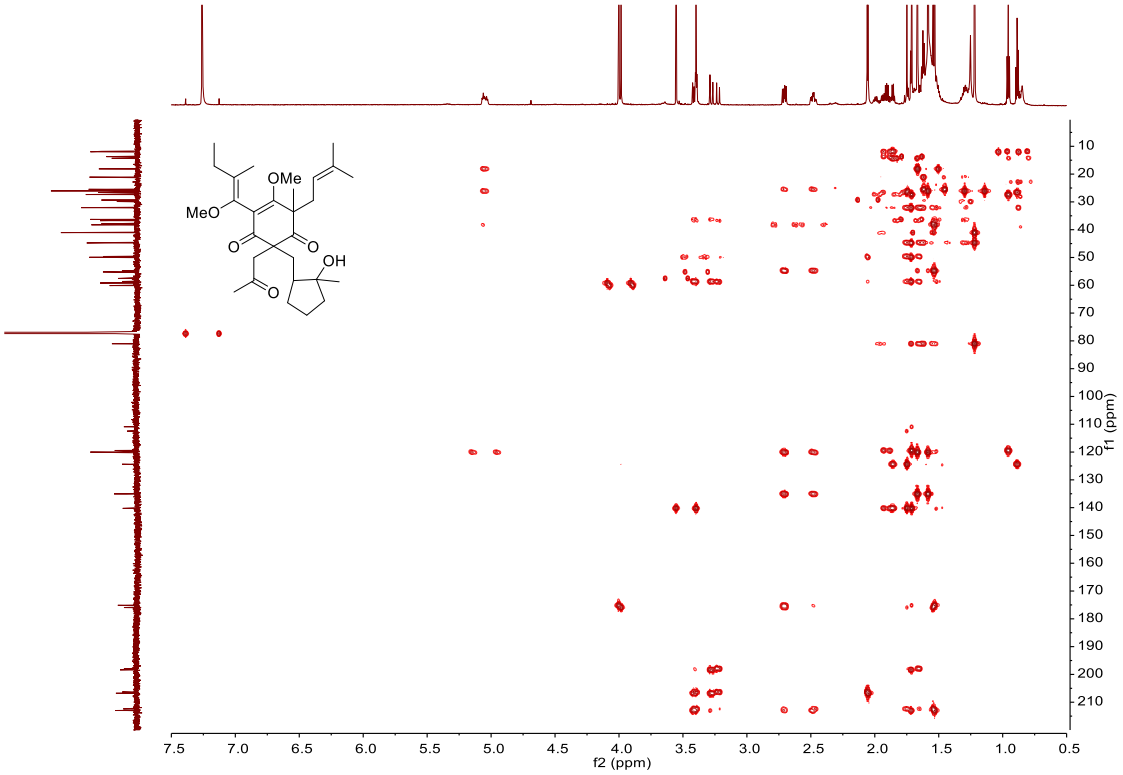
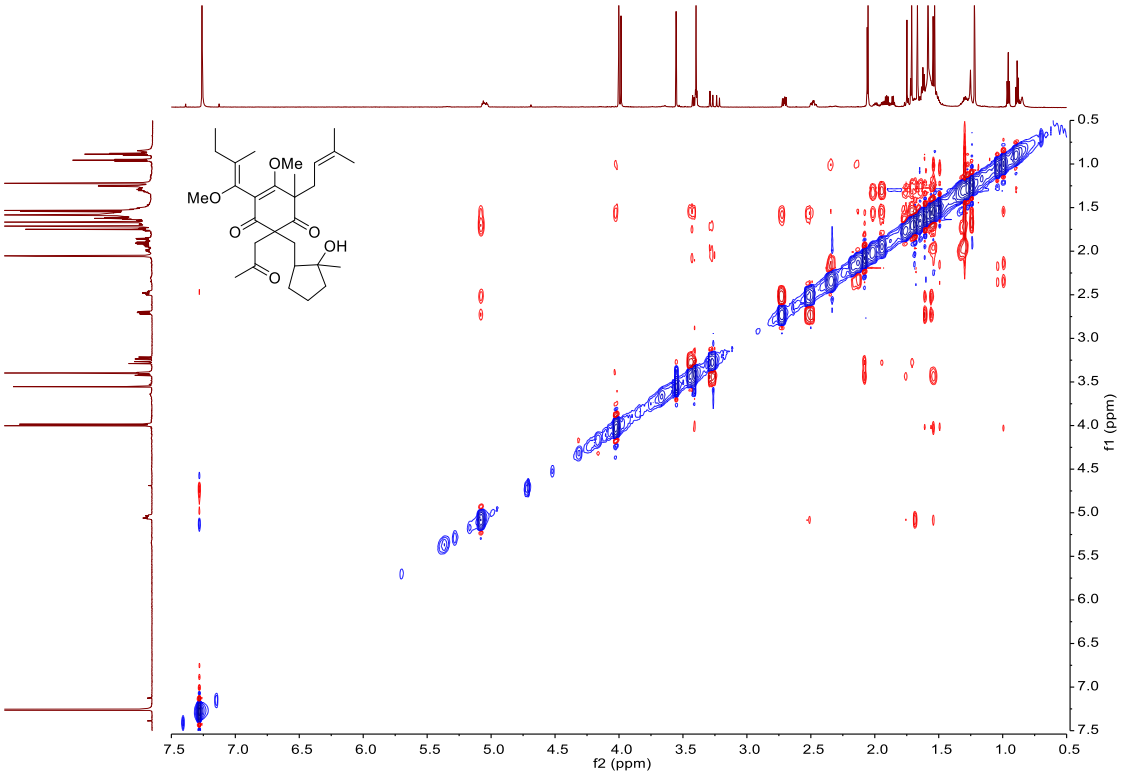


Figure S56. NOESY spectrum of compound **4** (Recorded in $CDCl_3$, 298 K)



Figures S57. HRESIMS of compound **4**

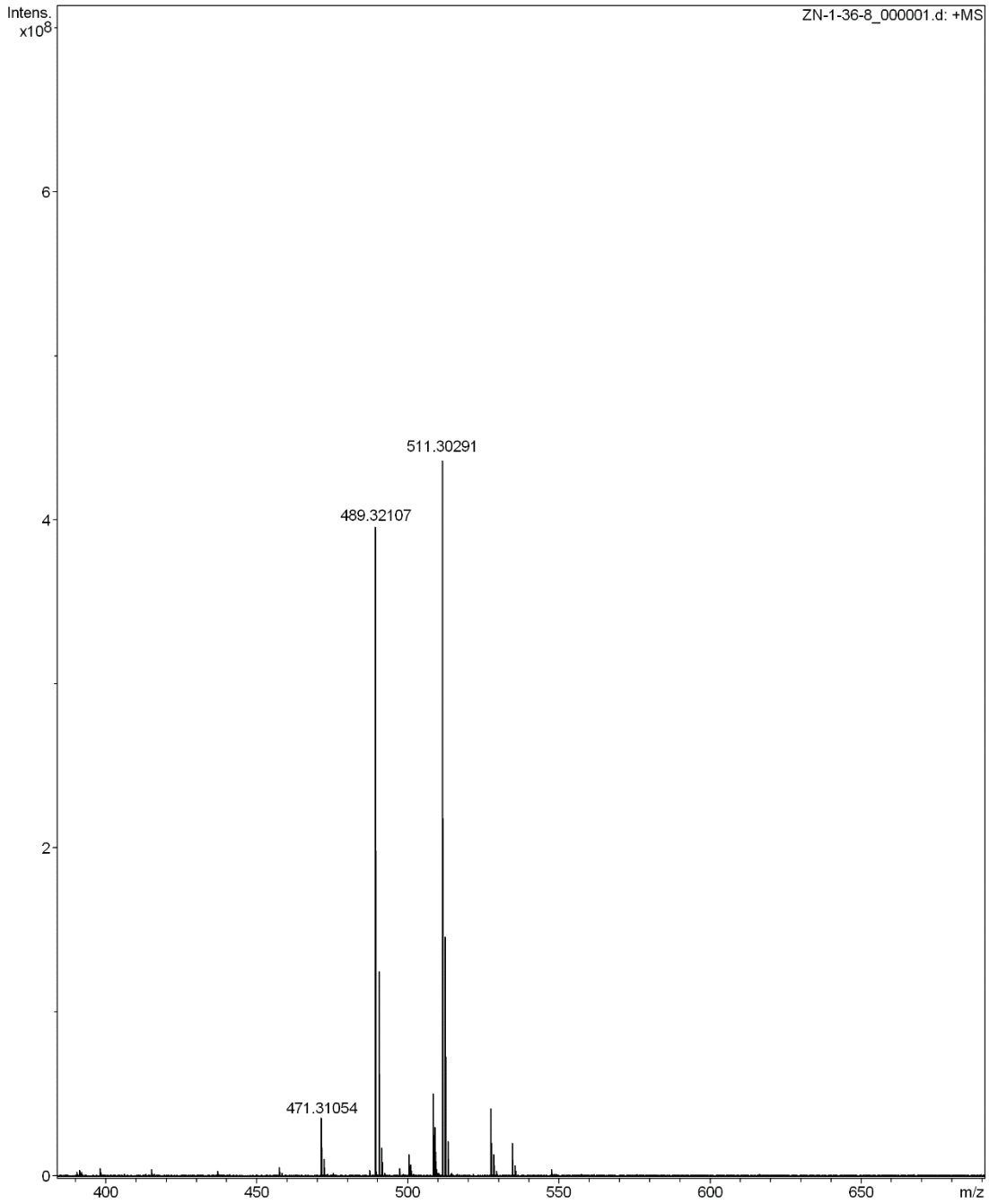


Figure S58. ^{1}H NMR (800 MHz) spectrum of compound **5** (Recorded in $CDCl_3$, 298 K)

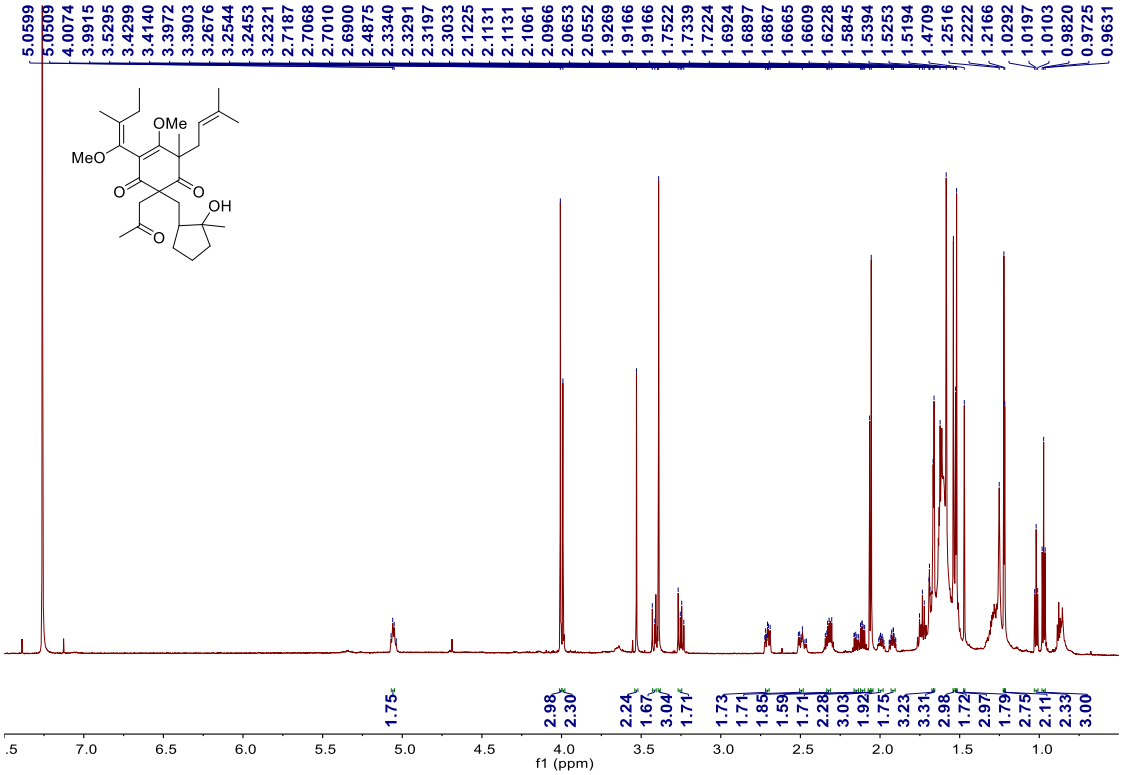


Figure S59. ^{13}C NMR (200 MHz) spectrum of compound **5** (Recorded in $CDCl_3$, 298 K)

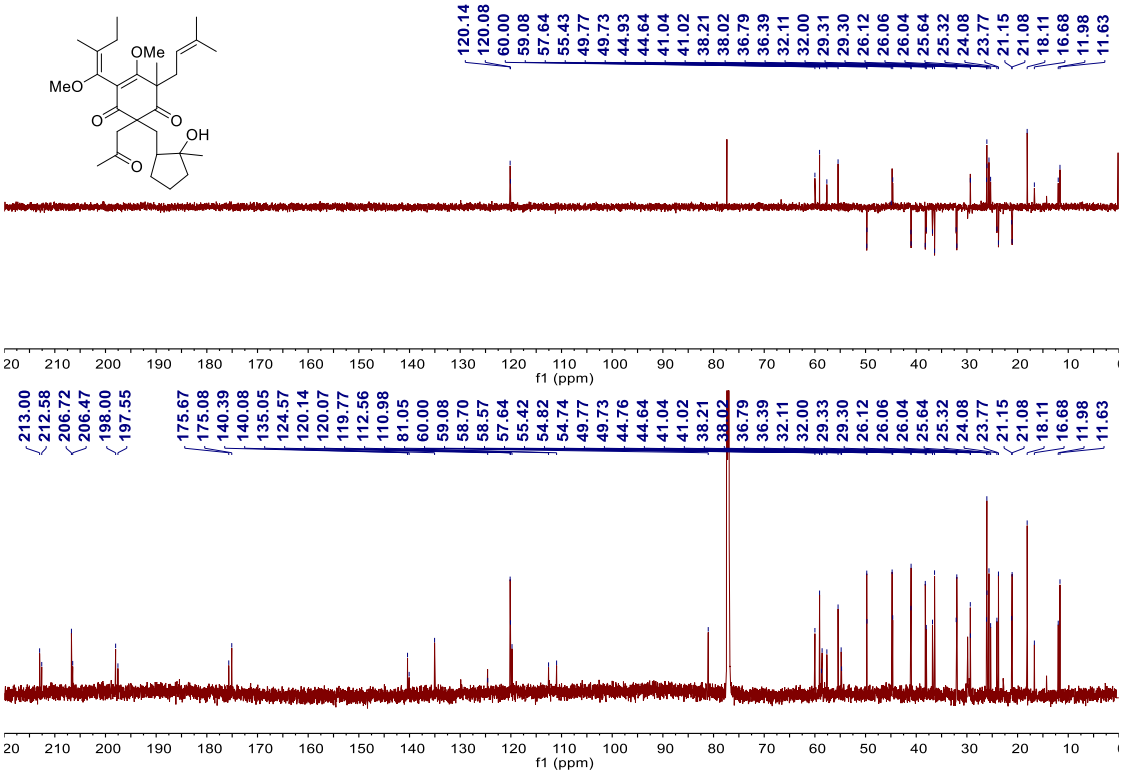


Figure S60. HSQC spectrum of compound **5** (Recorded in $CDCl_3$, 298 K)

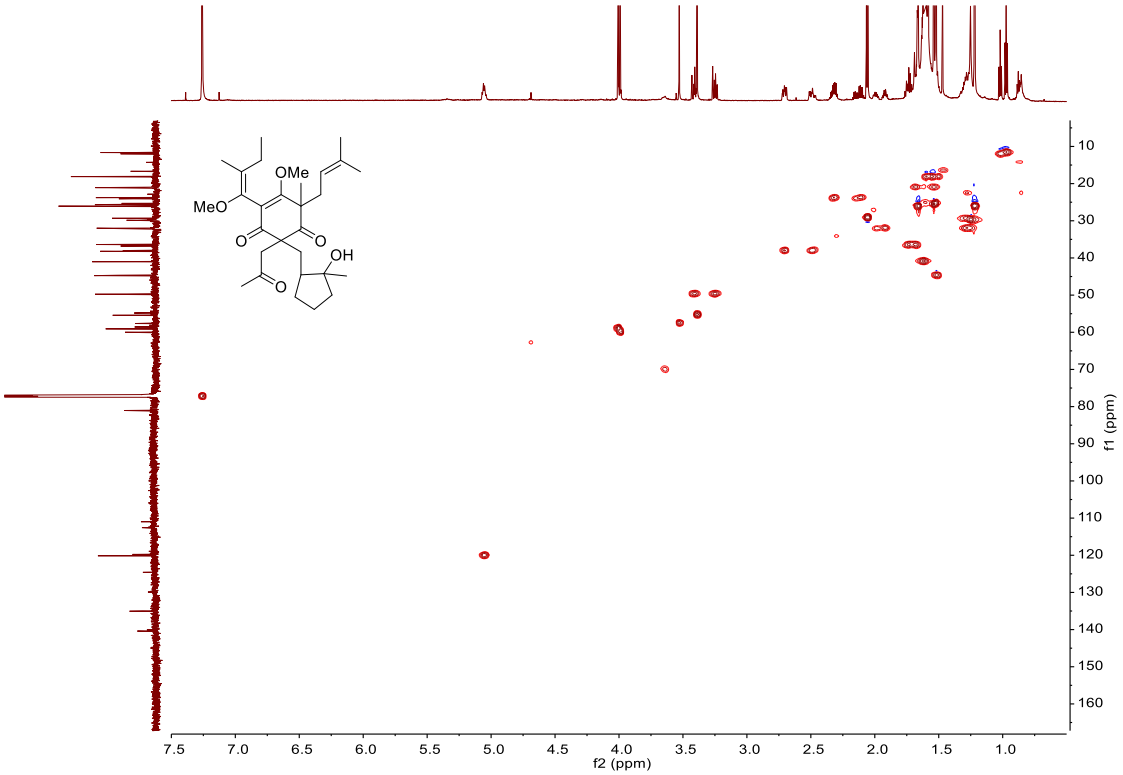


Figure S61. HMBC spectrum of compound **5** (Recorded in $CDCl_3$, 298 K)

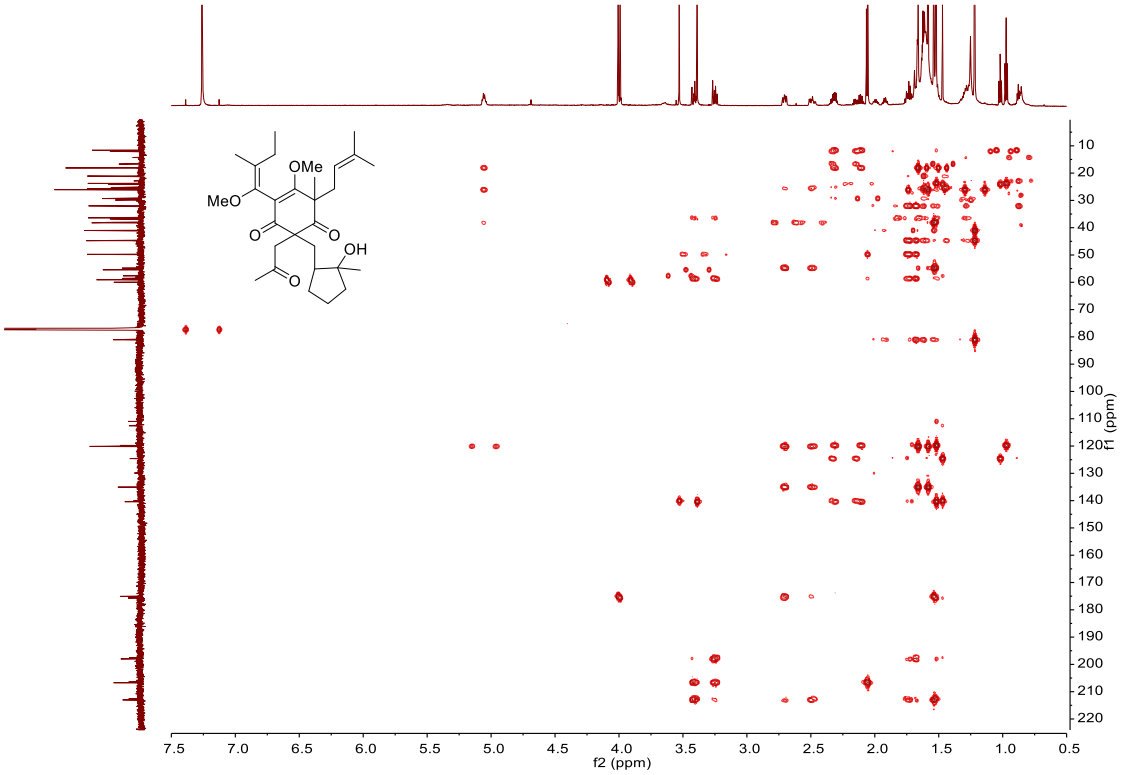


Figure S62. NOESY spectrum of compound **5** (Recorded in $CDCl_3$, 298 K)

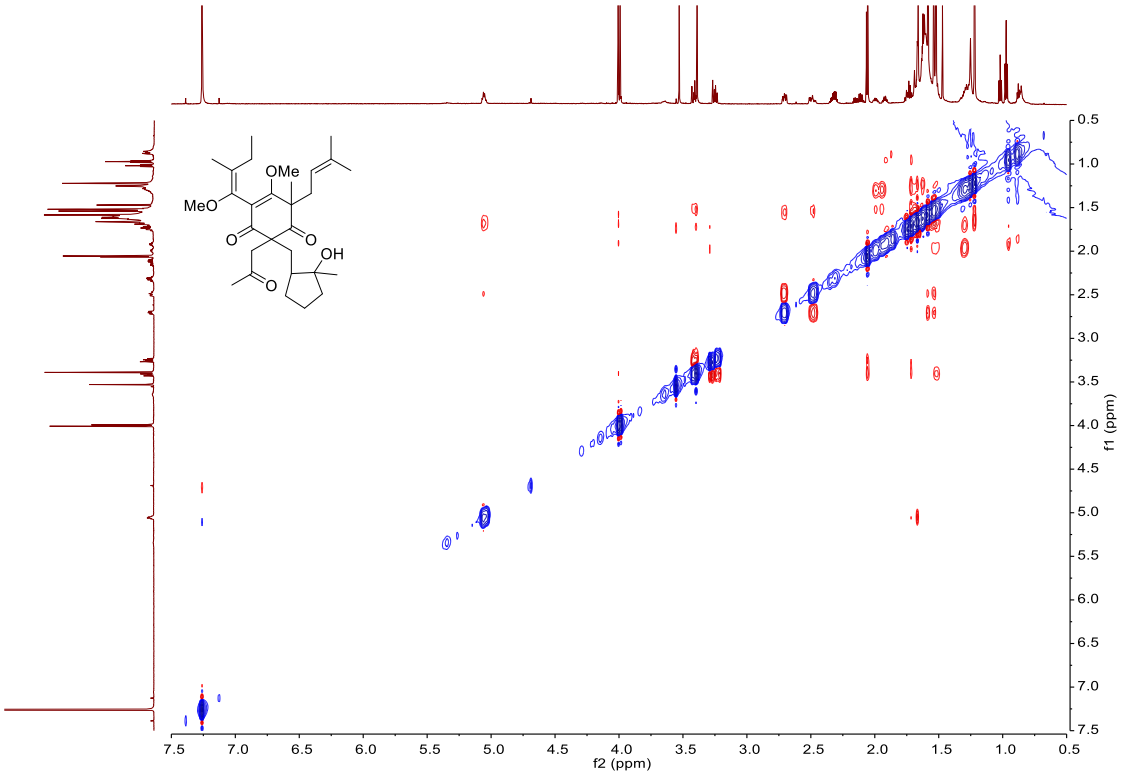


Figure S63. HRESIMS of compound **5**

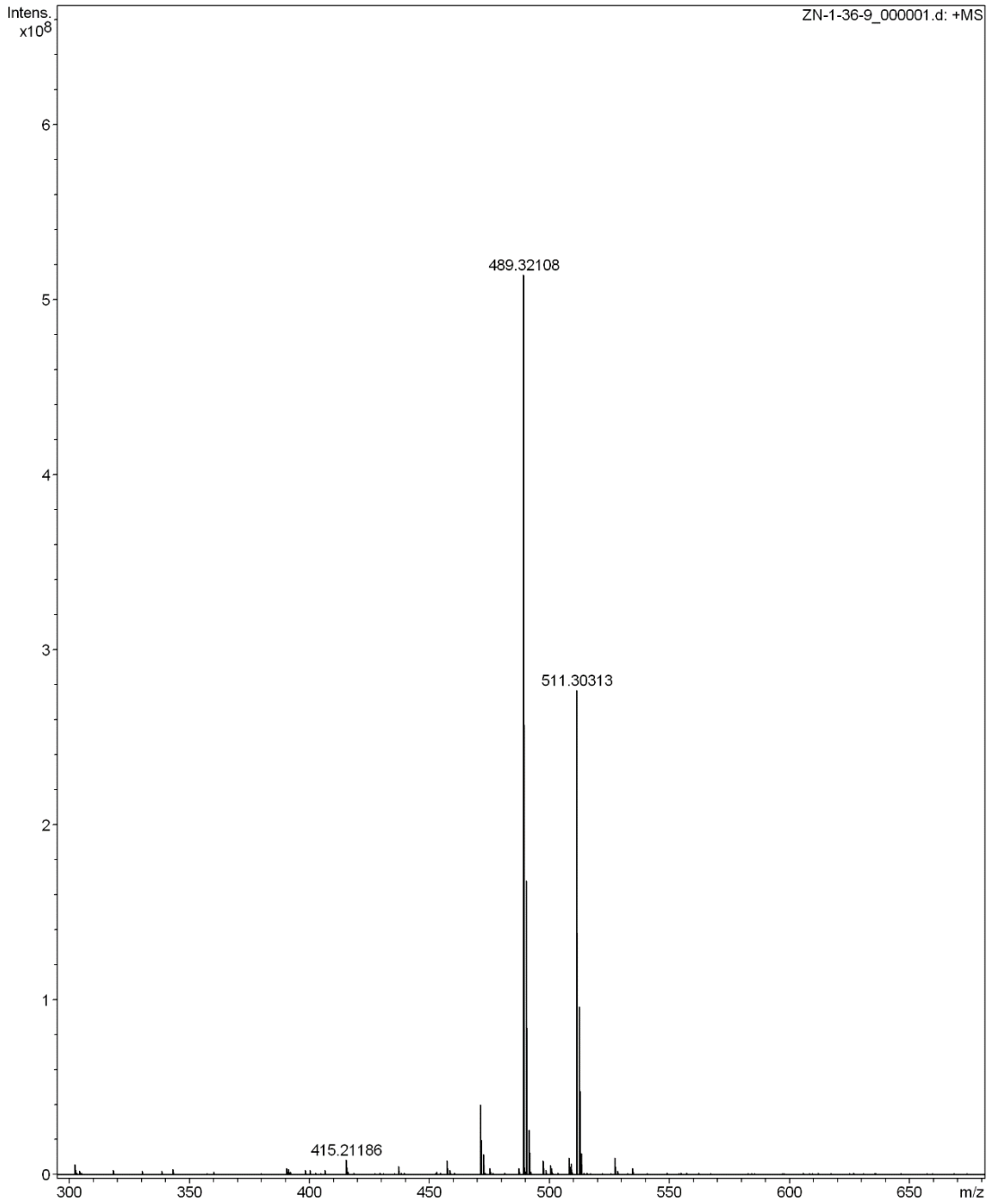


Figure S64. ^{1}H NMR (800 MHz) spectrum of compound **6** (Recorded in $CDCl_3$, 298 K)

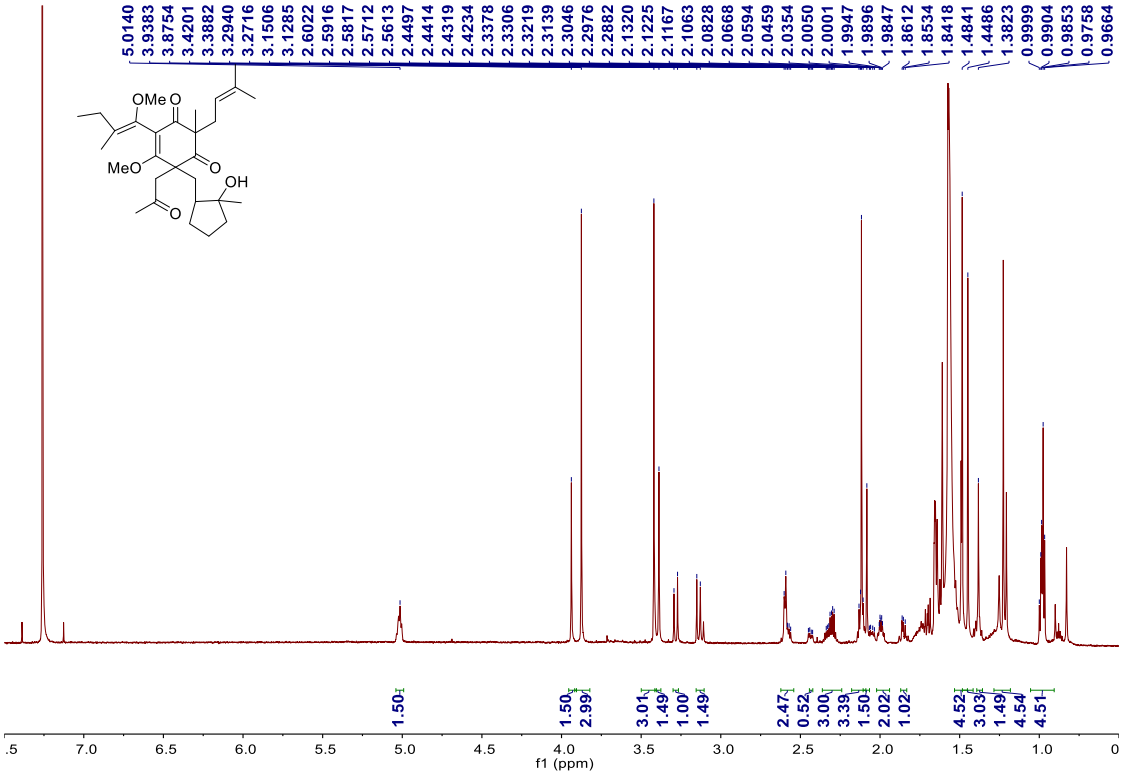


Figure S65. ^{13}C NMR (200 MHz) spectrum of compound **6** (Recorded in $CDCl_3$, 298 K)

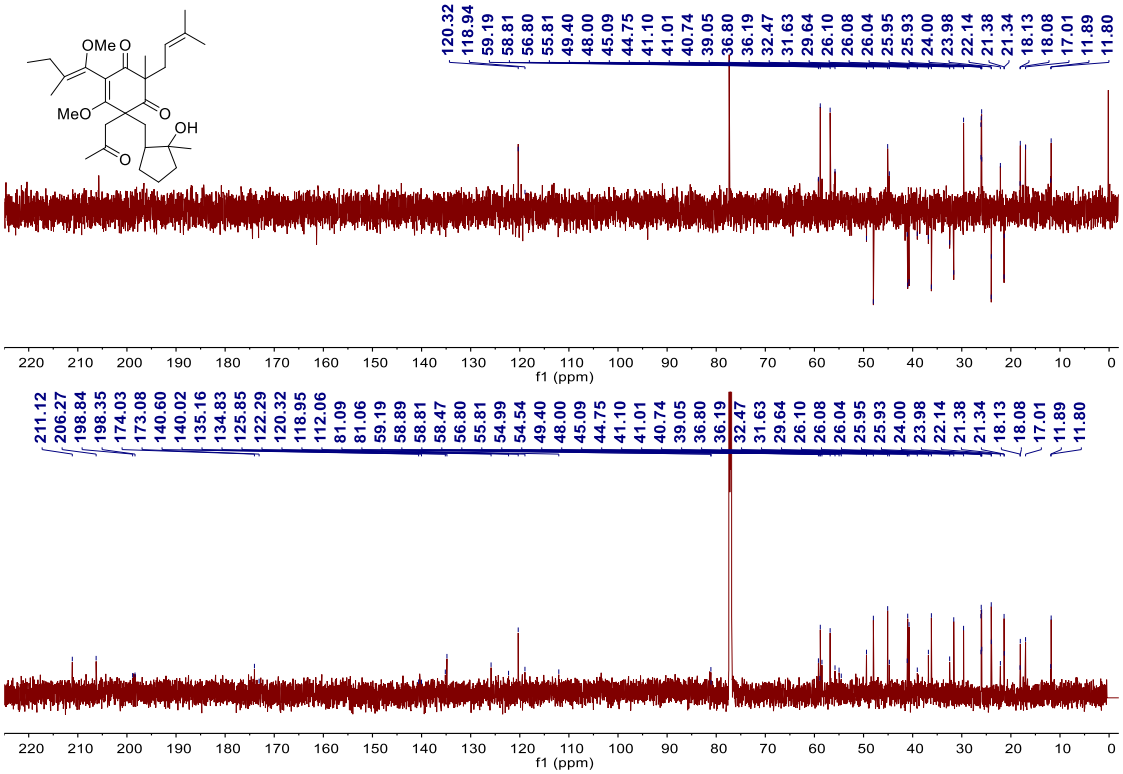


Figure S66. HSQC spectrum of compound **6** (Recorded in $CDCl_3$, 298 K)

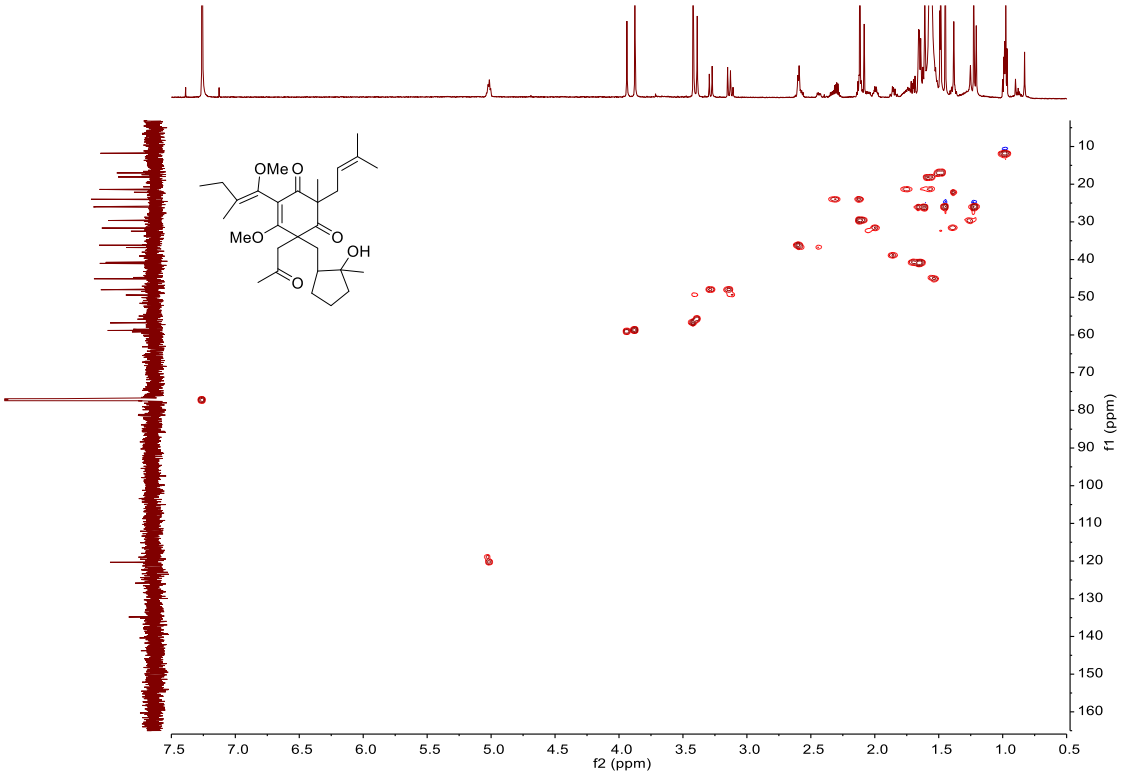


Figure S67. HMBC spectrum of compound **6** (Recorded in $CDCl_3$, 298 K)

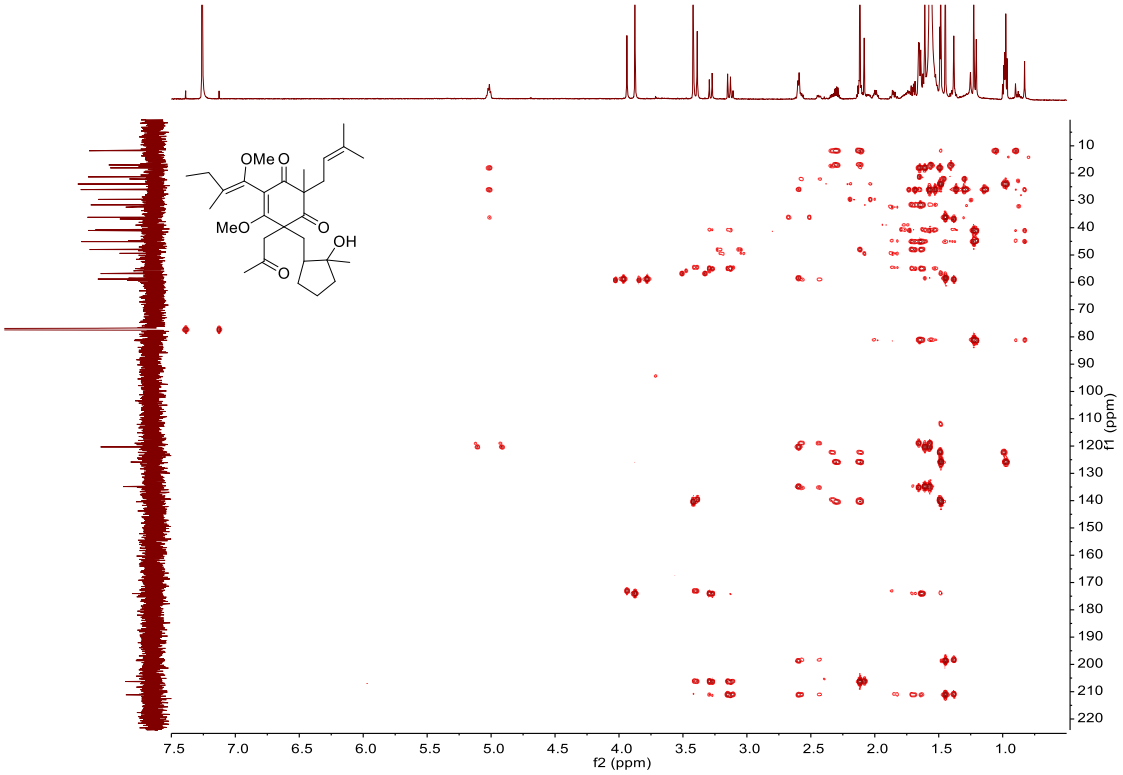


Figure S68. NOESY spectrum of compound **6** (Recorded in $CDCl_3$, 298 K)

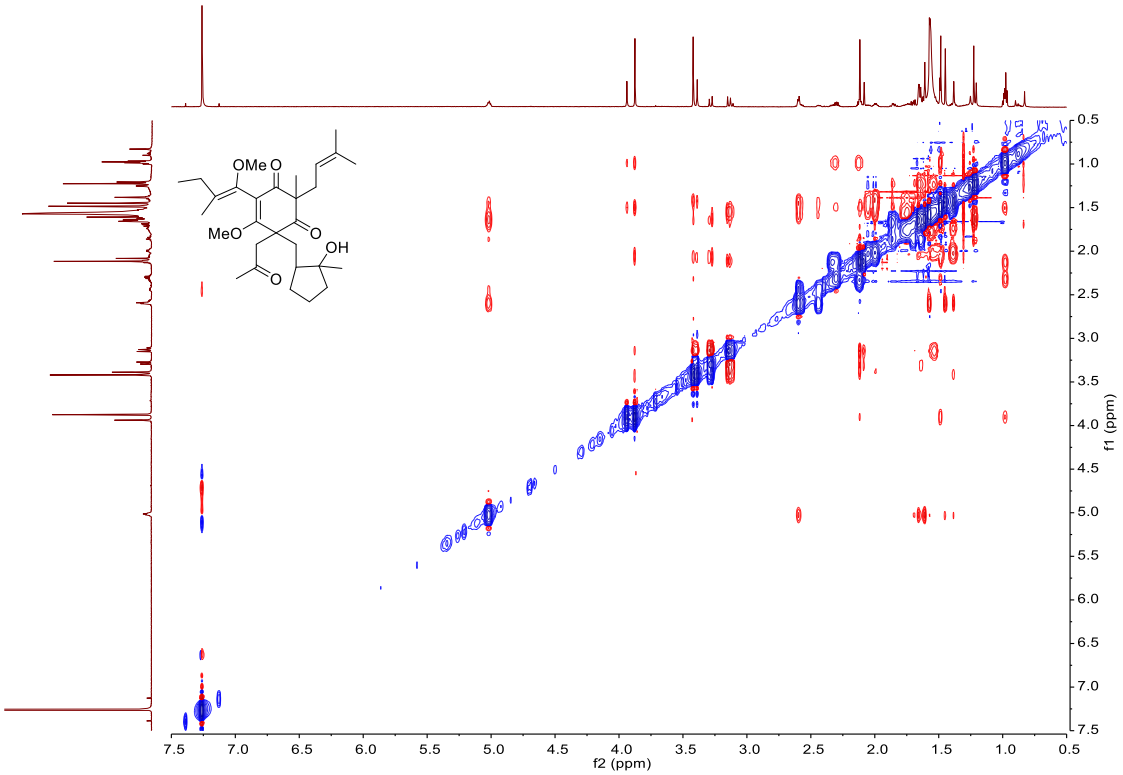


Figure S69. HRESIMS of compound **6**

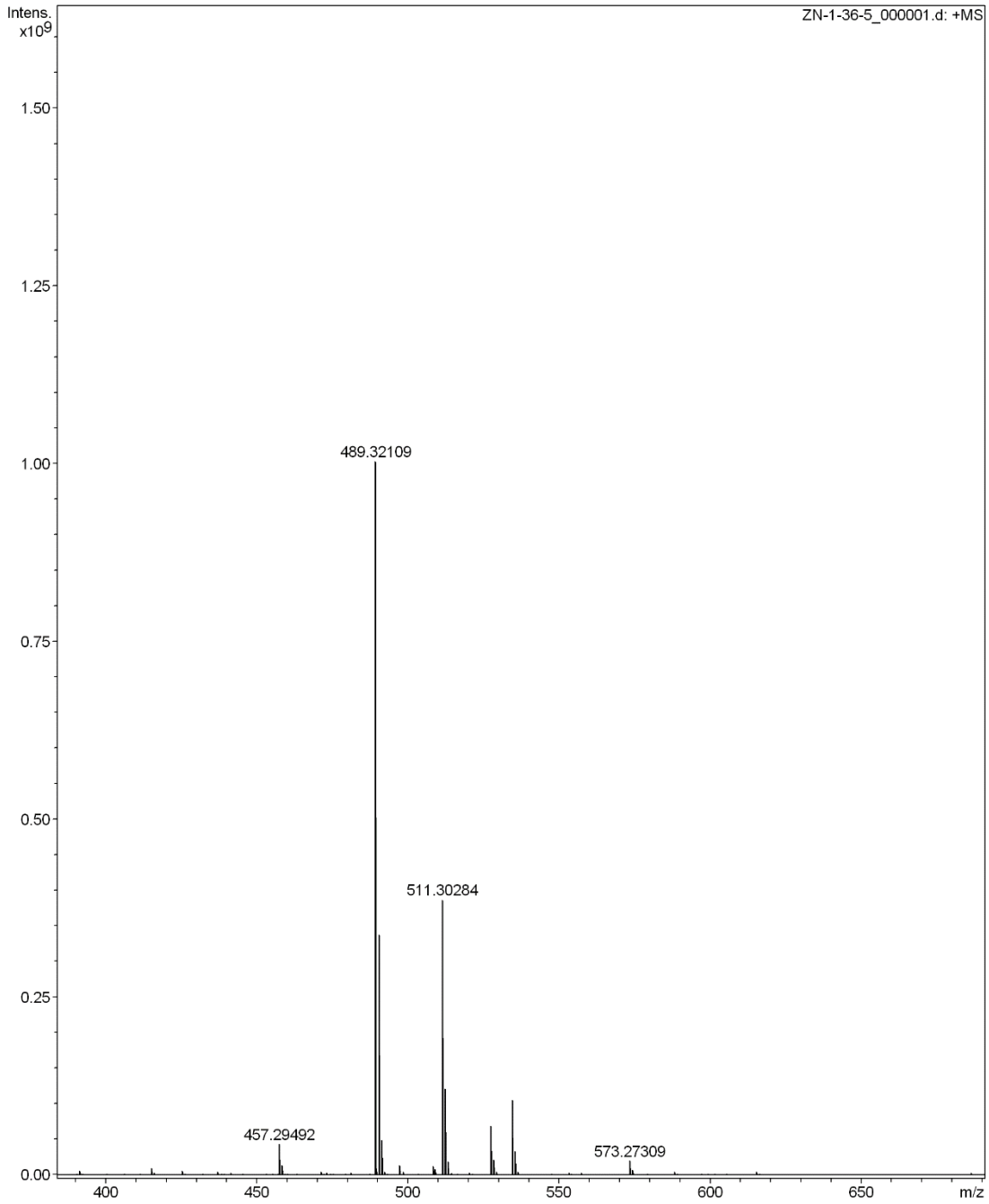


Figure S70. ^{1}H NMR (800 MHz) spectrum of compound **7** (Recorded in $CDCl_3$, 298 K)

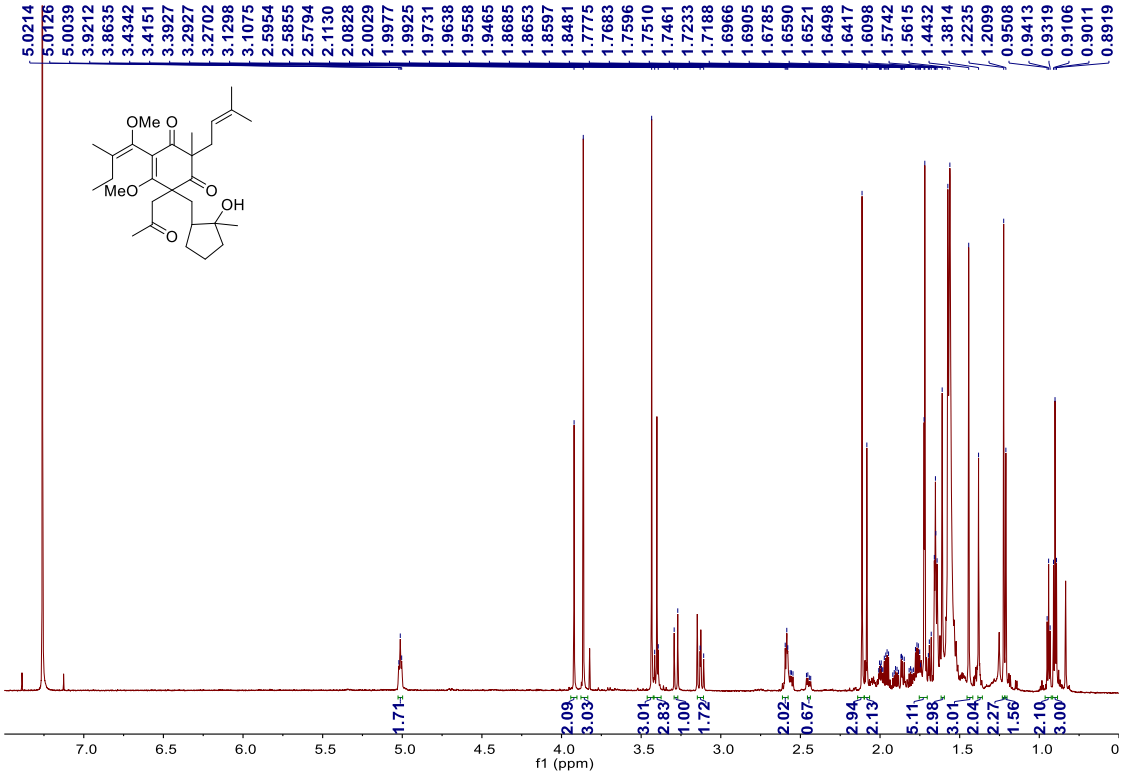


Figure S71. ^{13}C NMR (200 MHz) spectrum of compound **7** (Recorded in $CDCl_3$, 298 K)

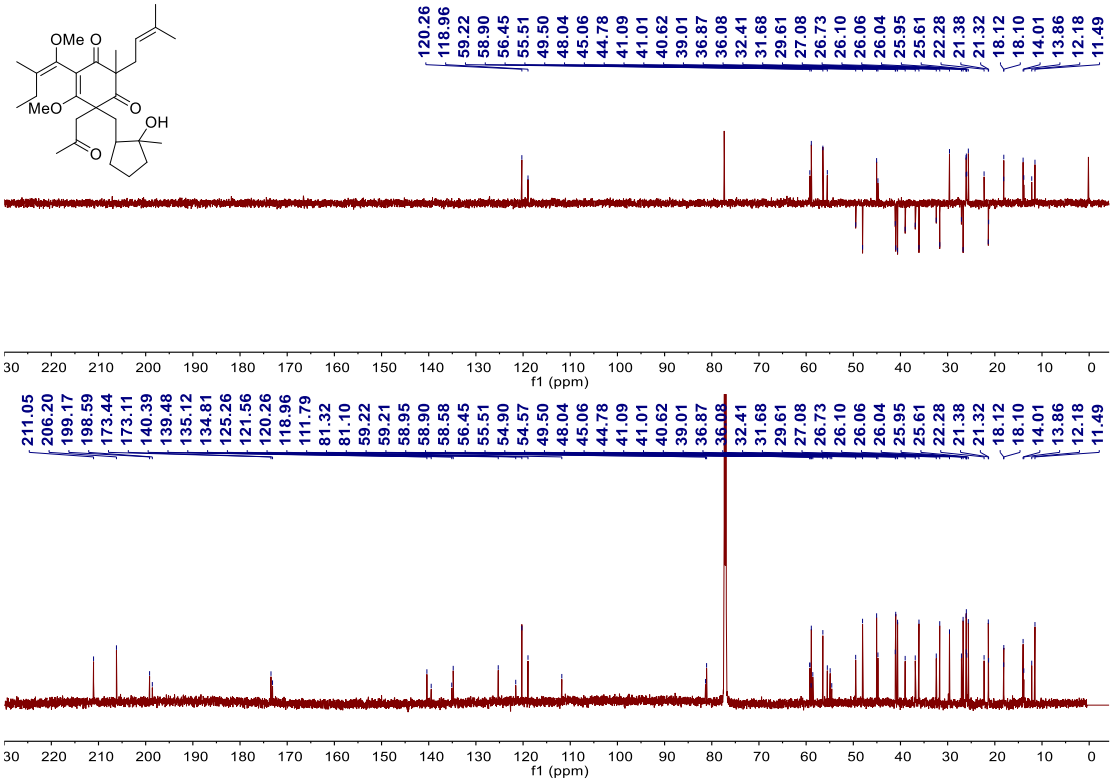


Figure S72. HSQC spectrum of compound **7** (Recorded in $CDCl_3$, 298 K)

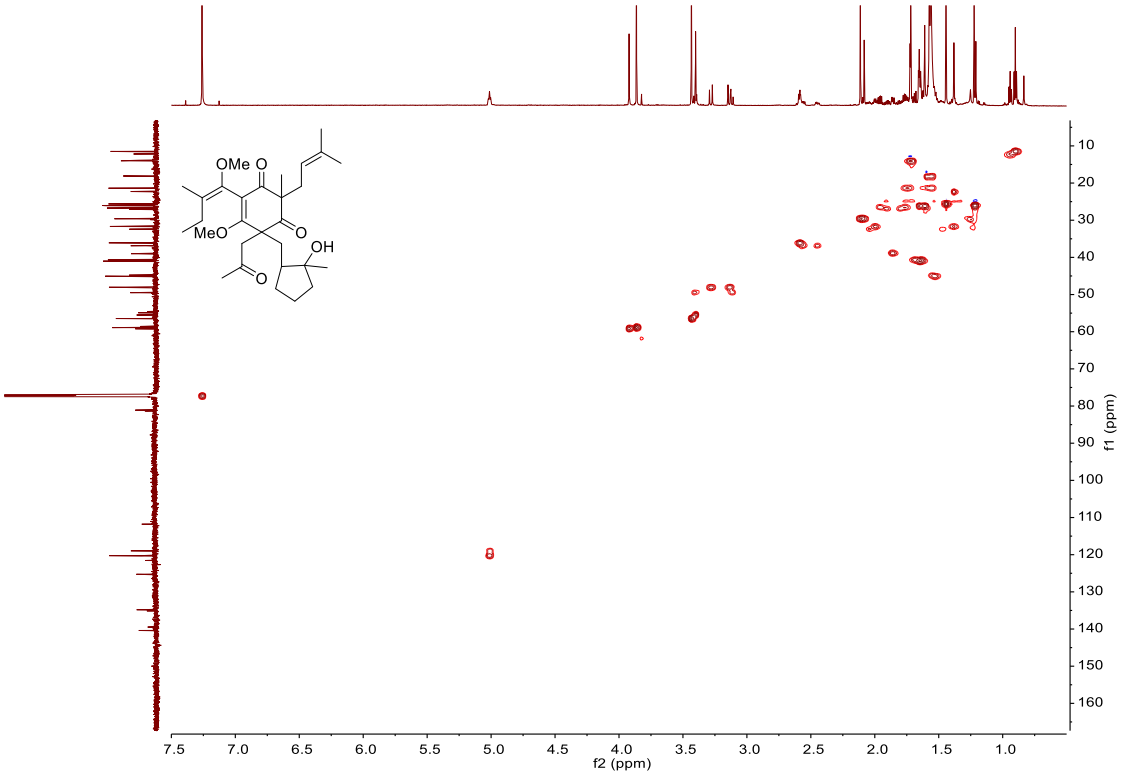


Figure S73. HMBC spectrum of compound **7** (Recorded in $CDCl_3$, 298 K)

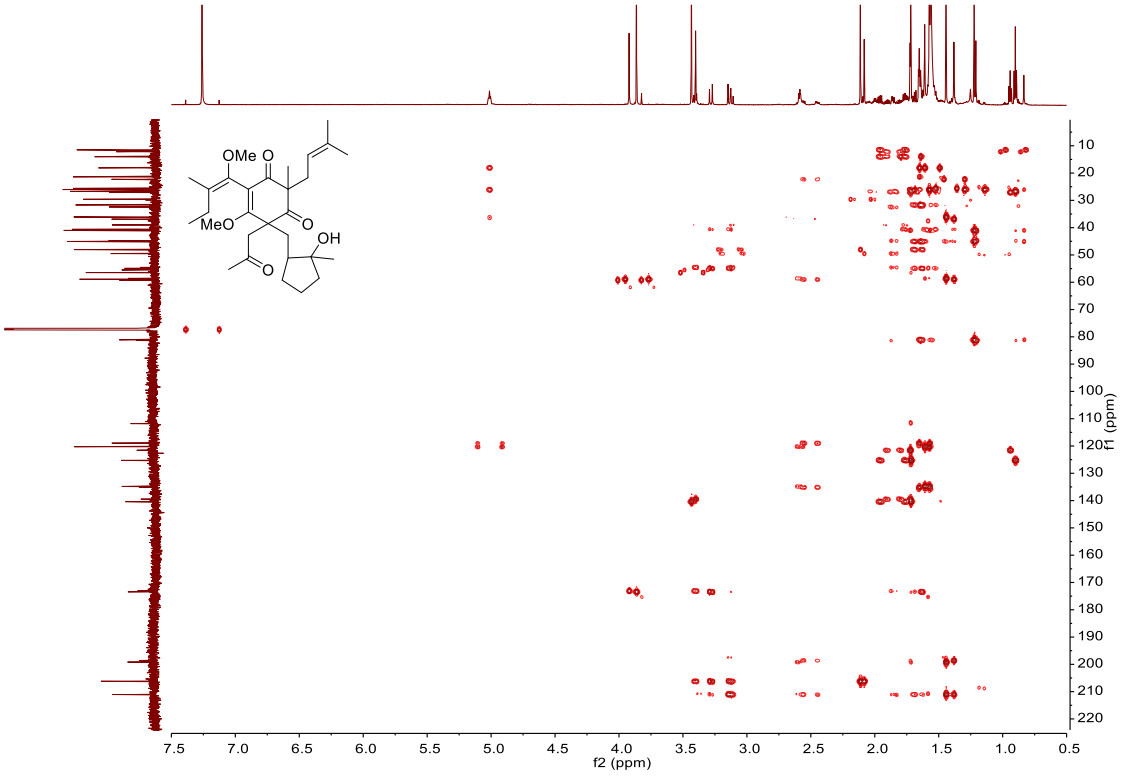


Figure S74. NOESY spectrum of compound **7** (Recorded in $CDCl_3$, 298 K)

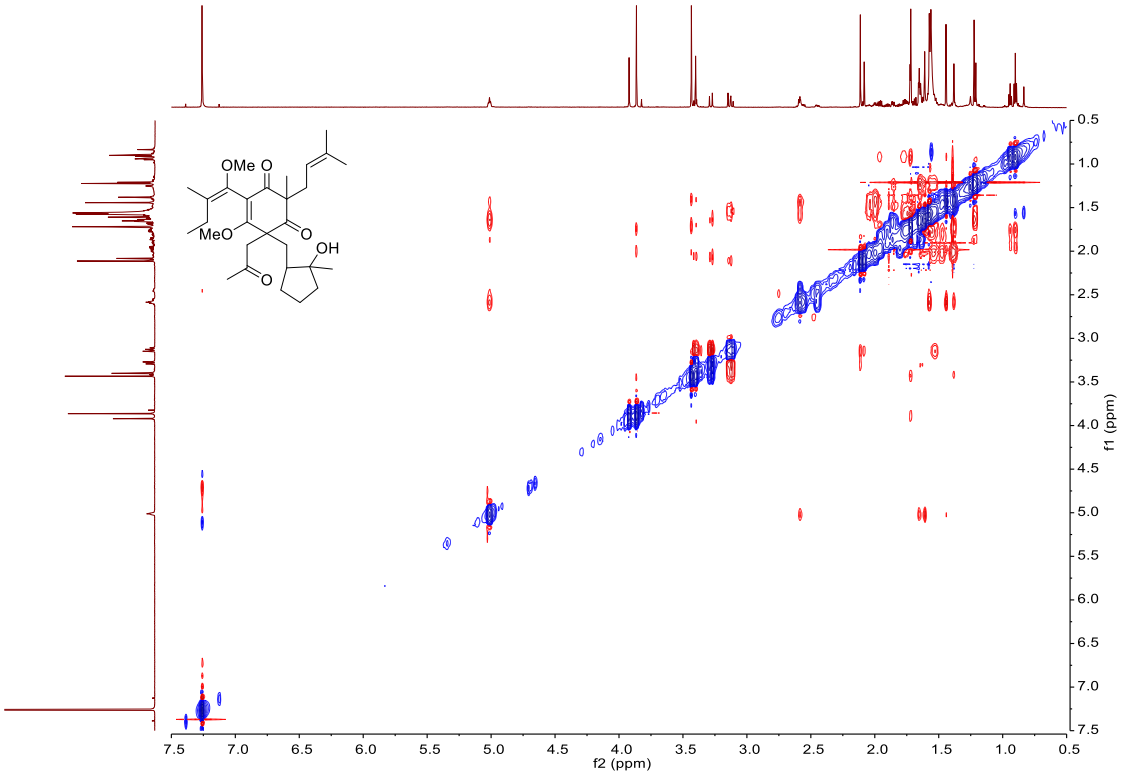


Figure S75. HRESIMS of compound **7**

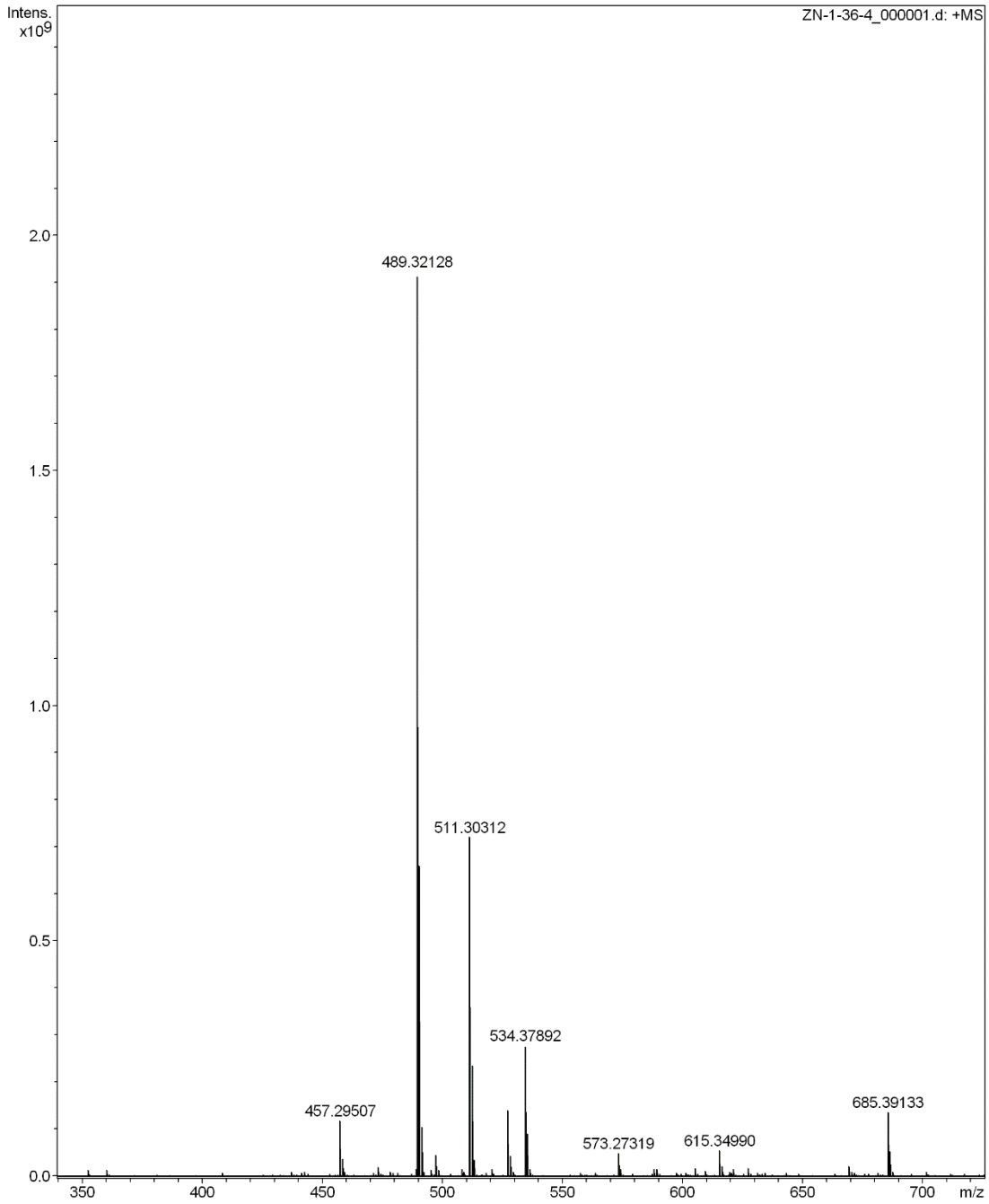


Figure S76. ^{1}H NMR (800 MHz) spectrum of compound **8** (Recorded in $CDCl_3$, 298 K)

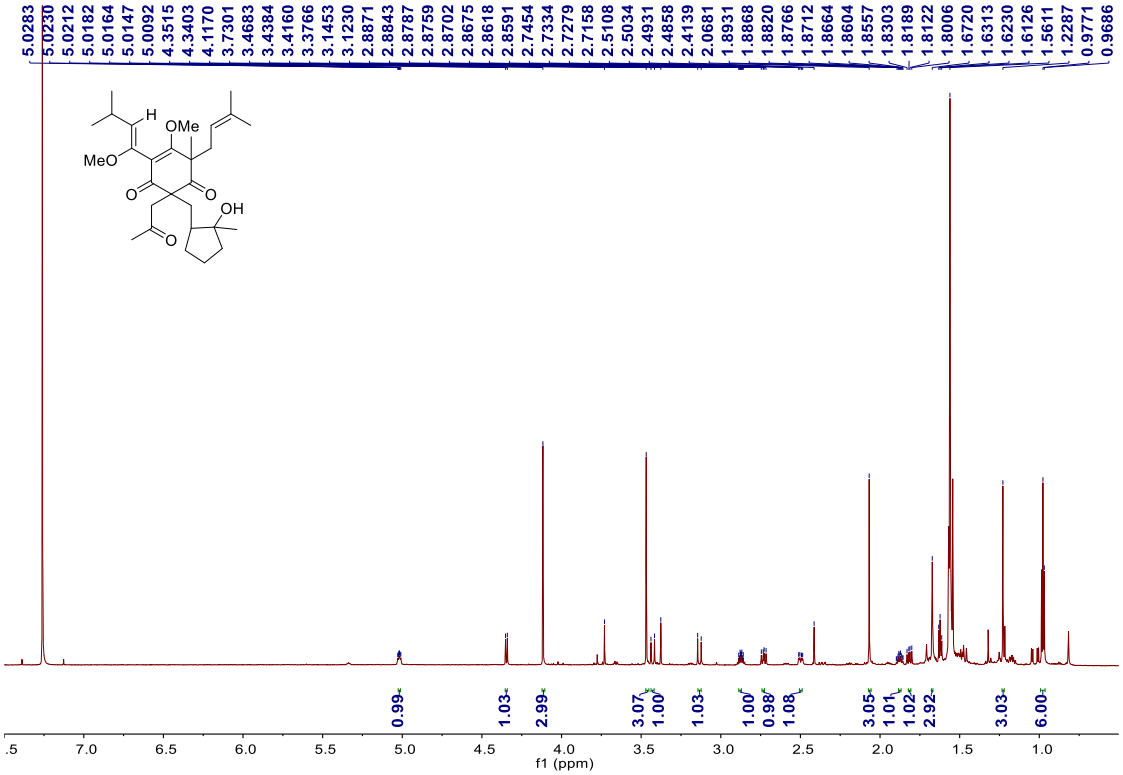


Figure S77. ^{13}C NMR (200 MHz) spectrum of compound **8** (Recorded in $CDCl_3$, 298 K)

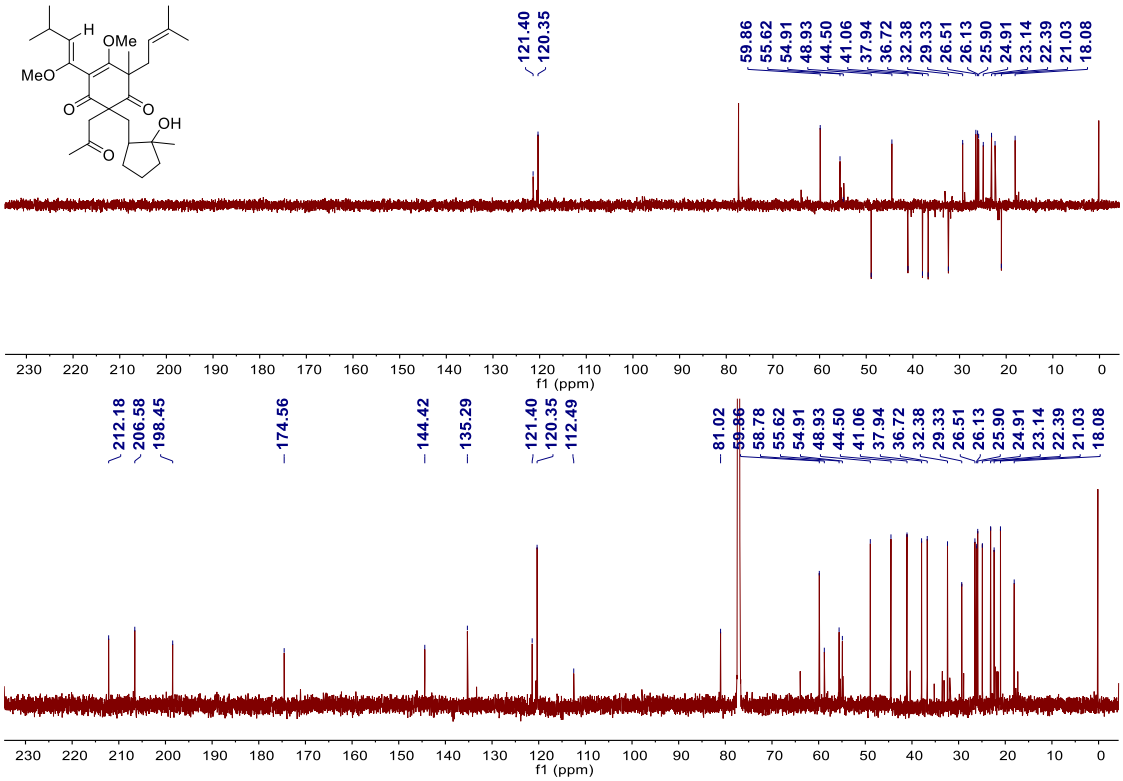


Figure S78. HSQC spectrum of compound **8** (Recorded in $CDCl_3$, 298 K)

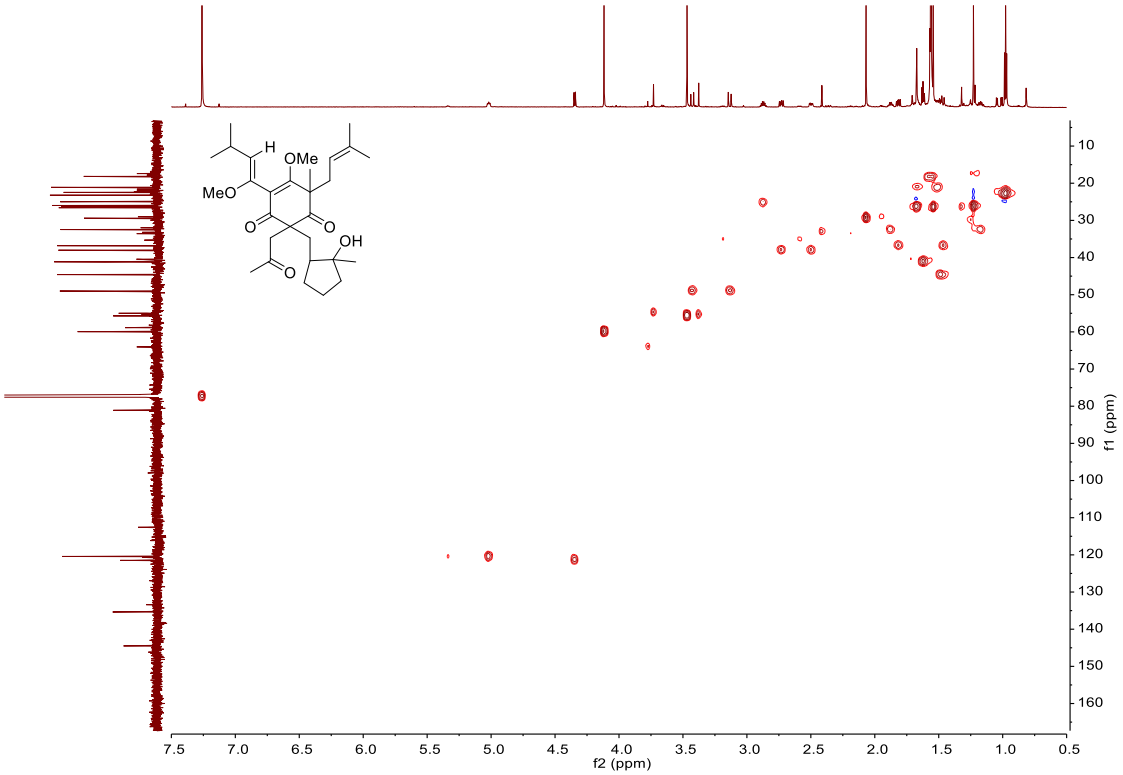


Figure S79. ^{1}H–^{1}H COSY spectrum of compound **8** (Recorded in $CDCl_3$, 298 K)

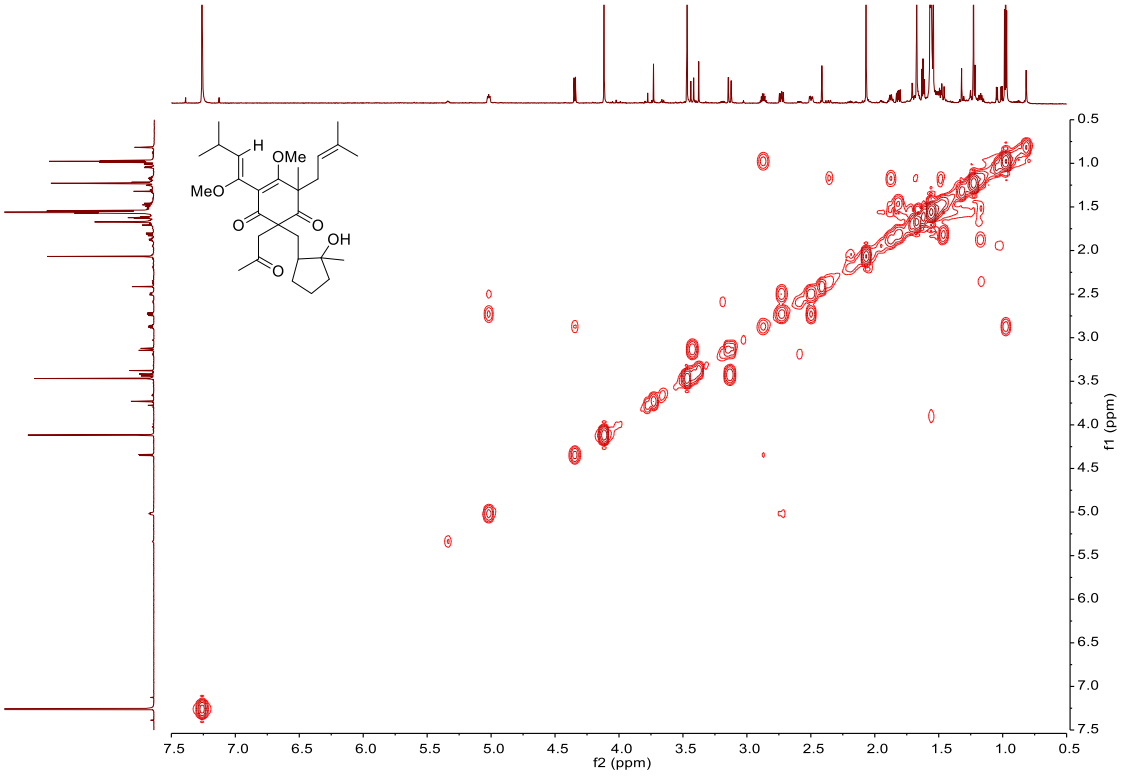


Figure S80. HMBC spectrum of compound **8** (Recorded in $CDCl_3$, 298 K)

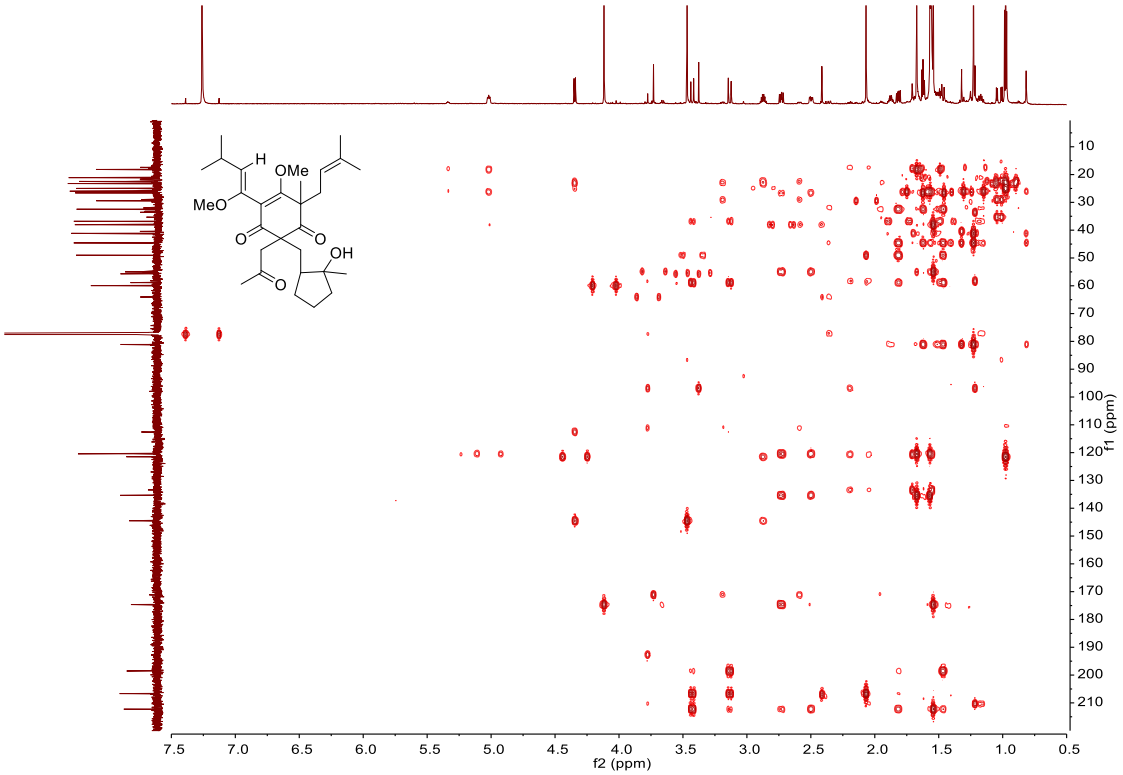


Figure S81. NOESY spectrum of compound **8** (Recorded in $CDCl_3$, 298 K)

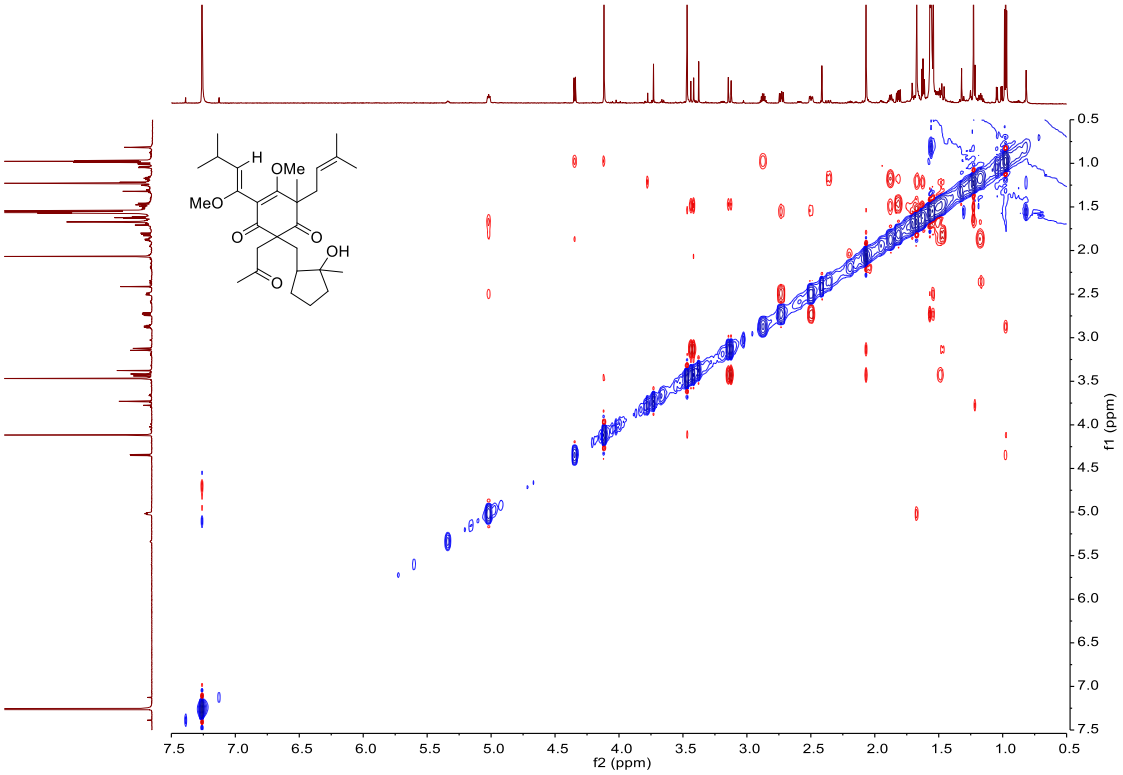


Figure S82. HRESIMS of compound **8**

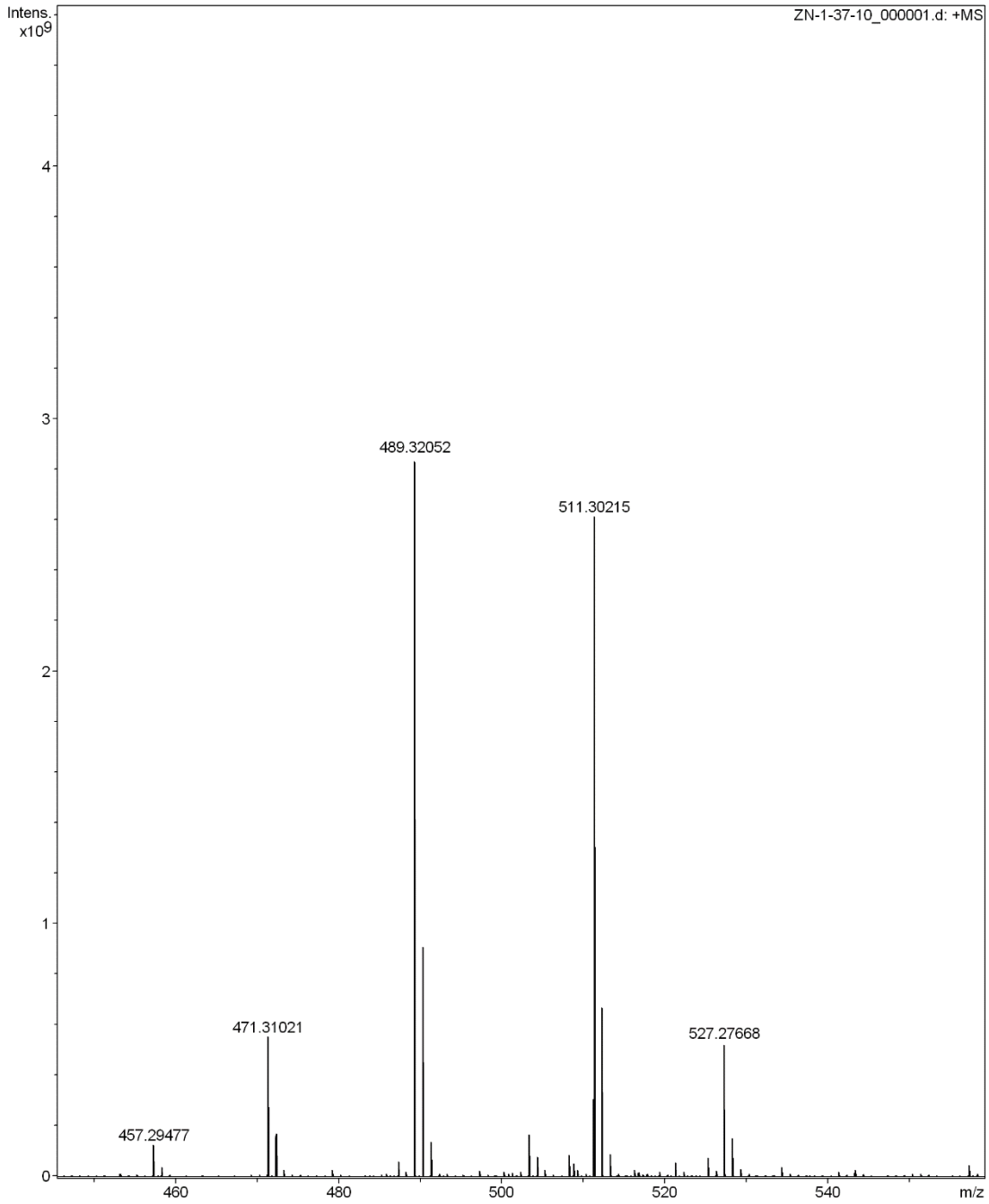


Figure S83. ^{1}H NMR (600 MHz) spectrum of compound **9** (Recorded in $CDCl_3$, 298 K)

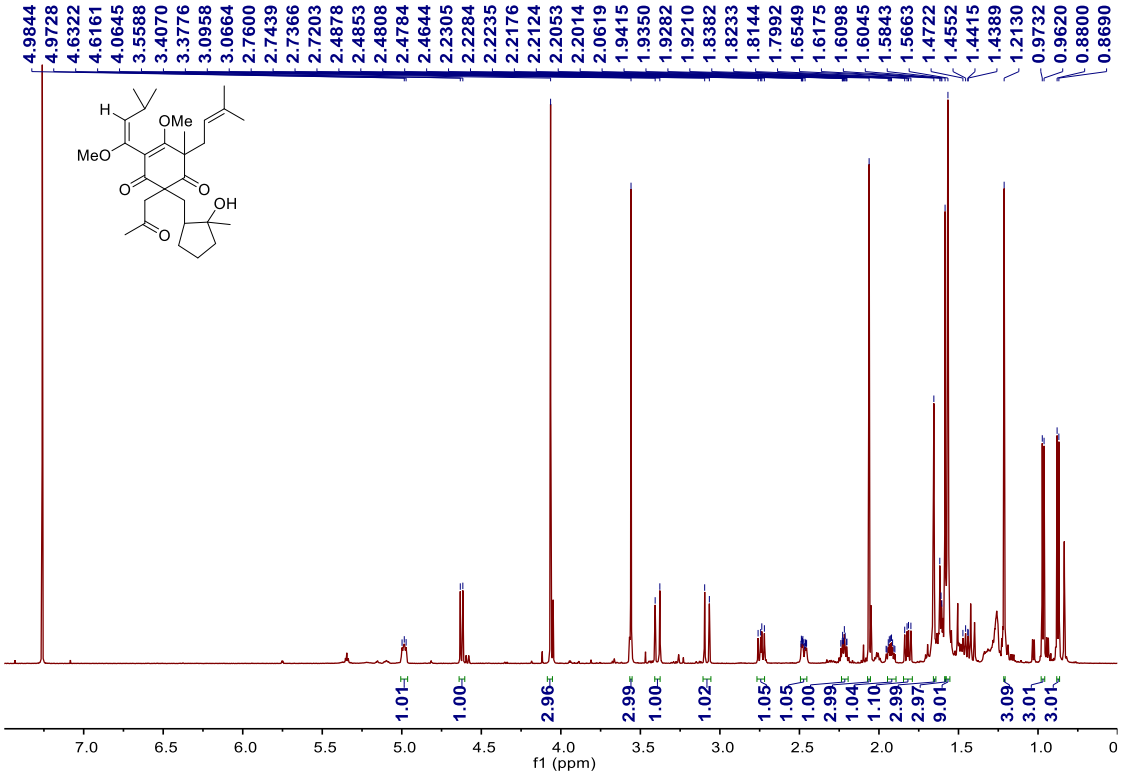


Figure S84. ^{13}C NMR (150 MHz) spectrum of compound **9** (Recorded in $CDCl_3$, 298 K)

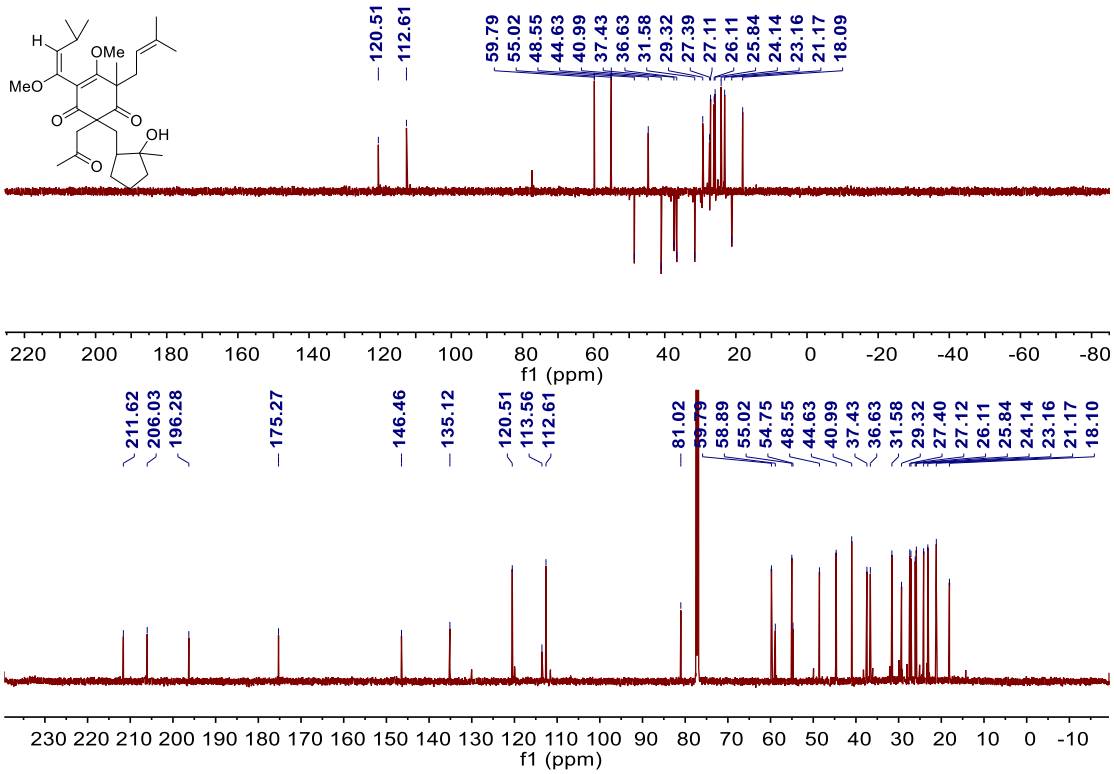


Figure S85. HSQC spectrum of compound **9** (Recorded in $CDCl_3$, 298 K)

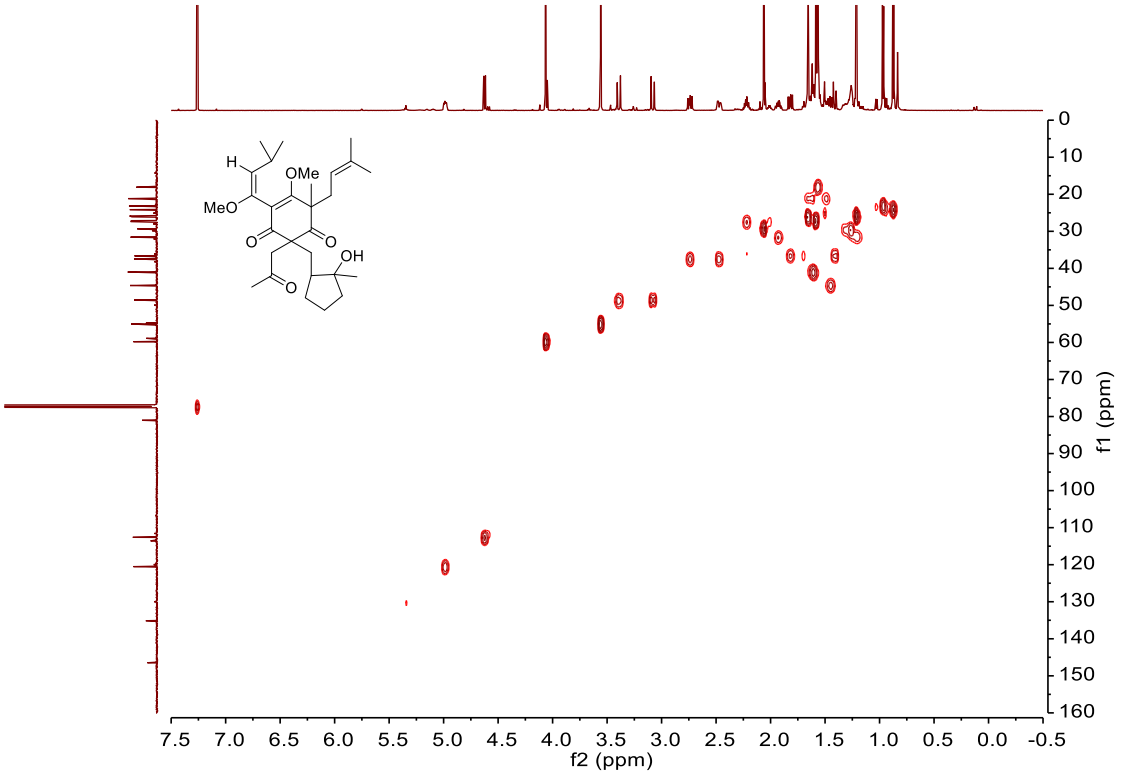


Figure S86. ^{1}H–^{1}H COSY spectrum of compound **9** (Recorded in $CDCl_3$, 298 K)

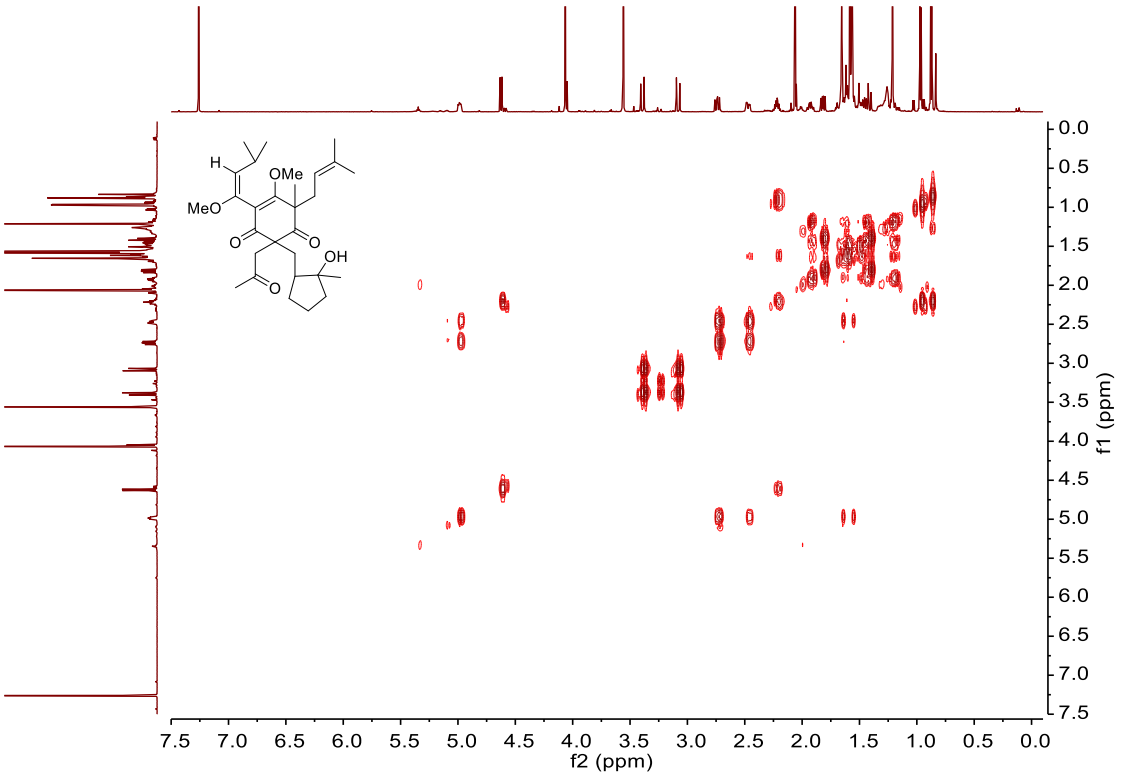


Figure S87. HMBC spectrum of compound **9** (Recorded in $CDCl_3$, 298 K)

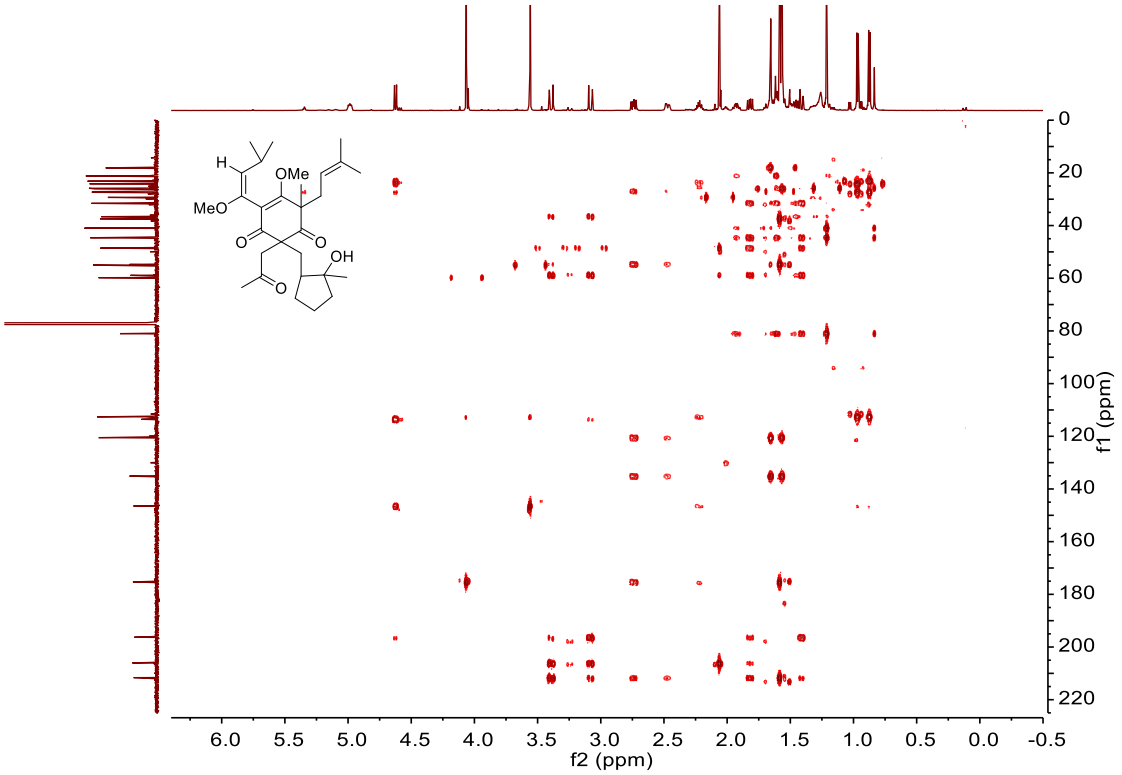


Figure S88. NOESY spectrum of compound **9** (Recorded in $CDCl_3$, 298 K)

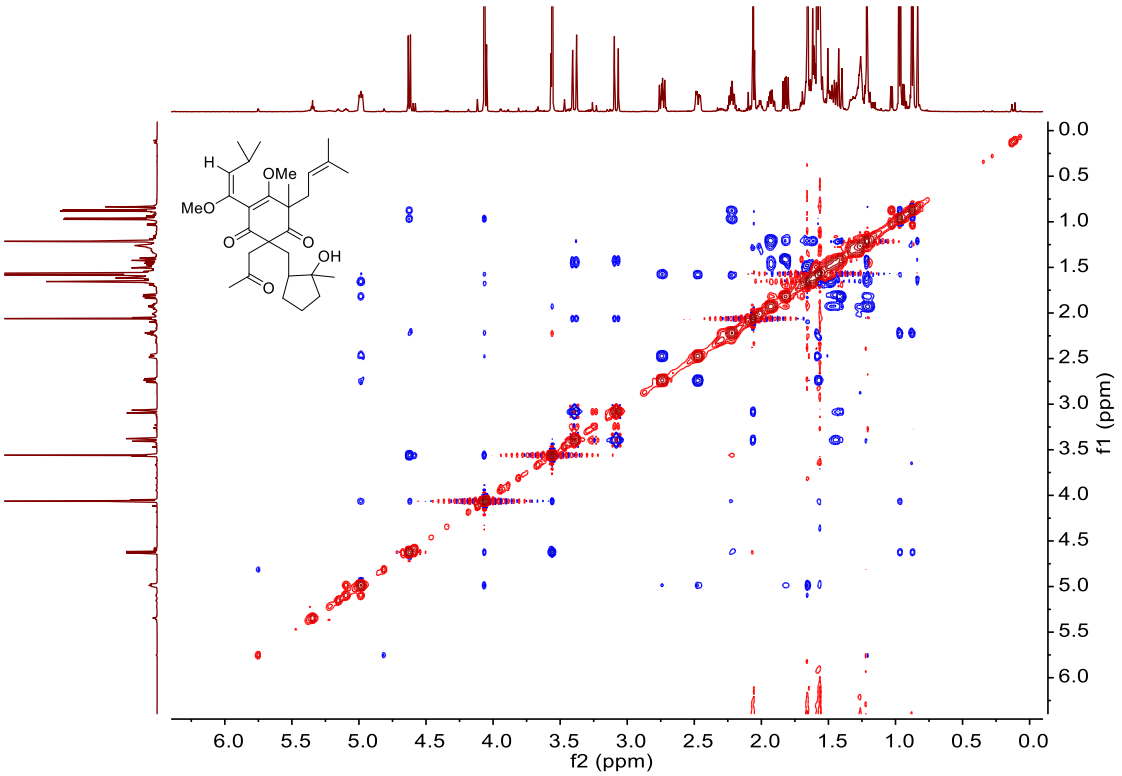


Figure S89. HRESIMS compound **9**

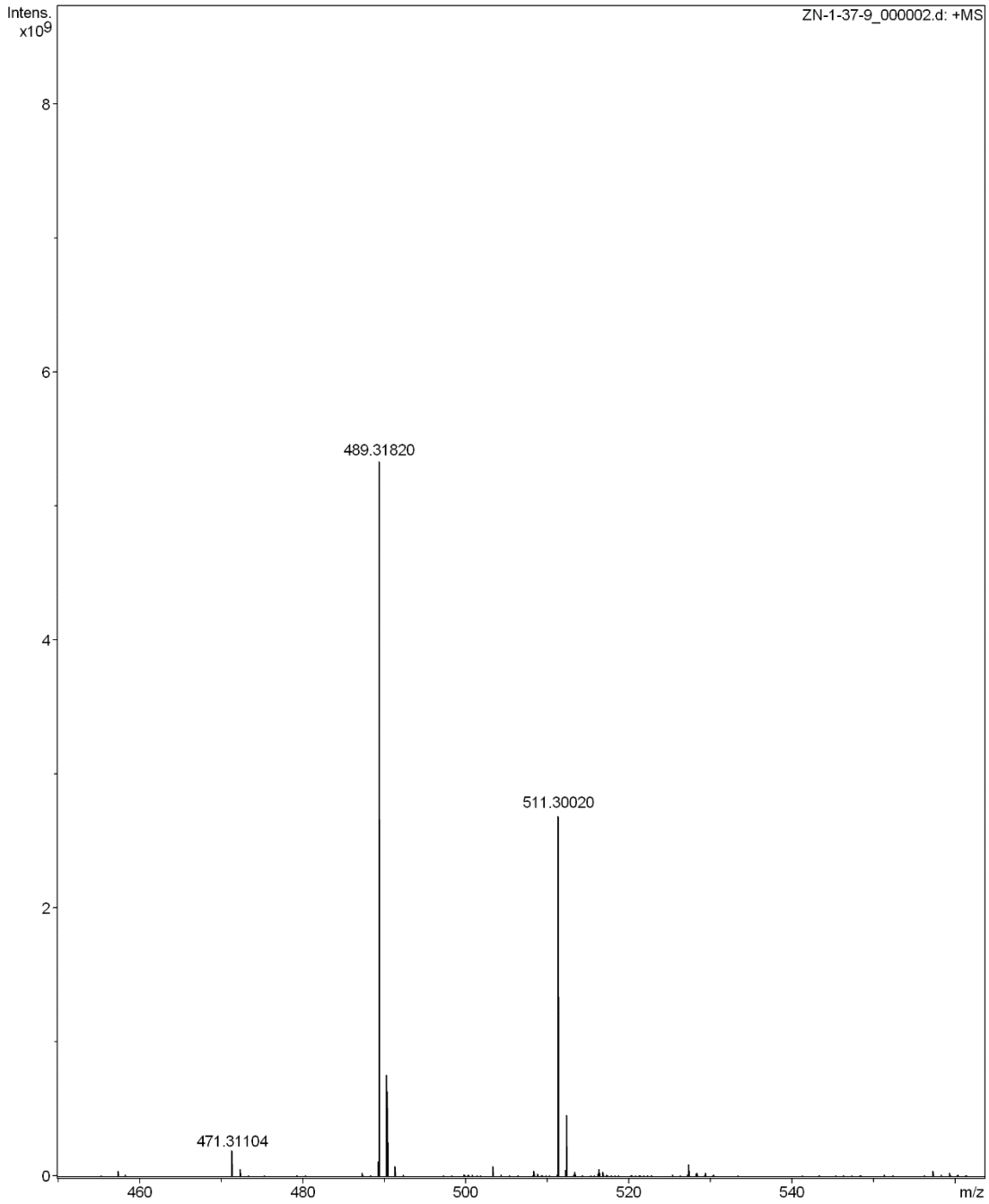


Figure S90. ^{1}H NMR (800 MHz) spectrum of compound **10** (Recorded in $CDCl_3$, 298 K)

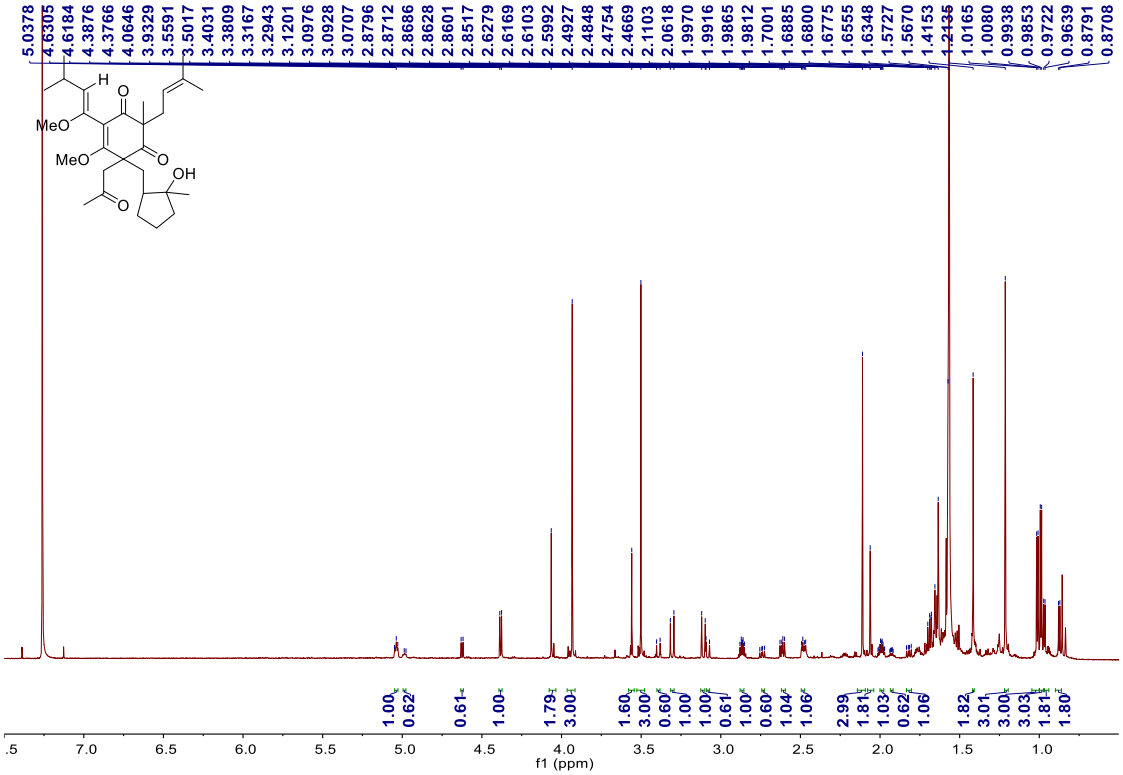


Figure S91. ^{13}C NMR (200 MHz) spectrum of compound **10** (Recorded in $CDCl_3$, 298 K)

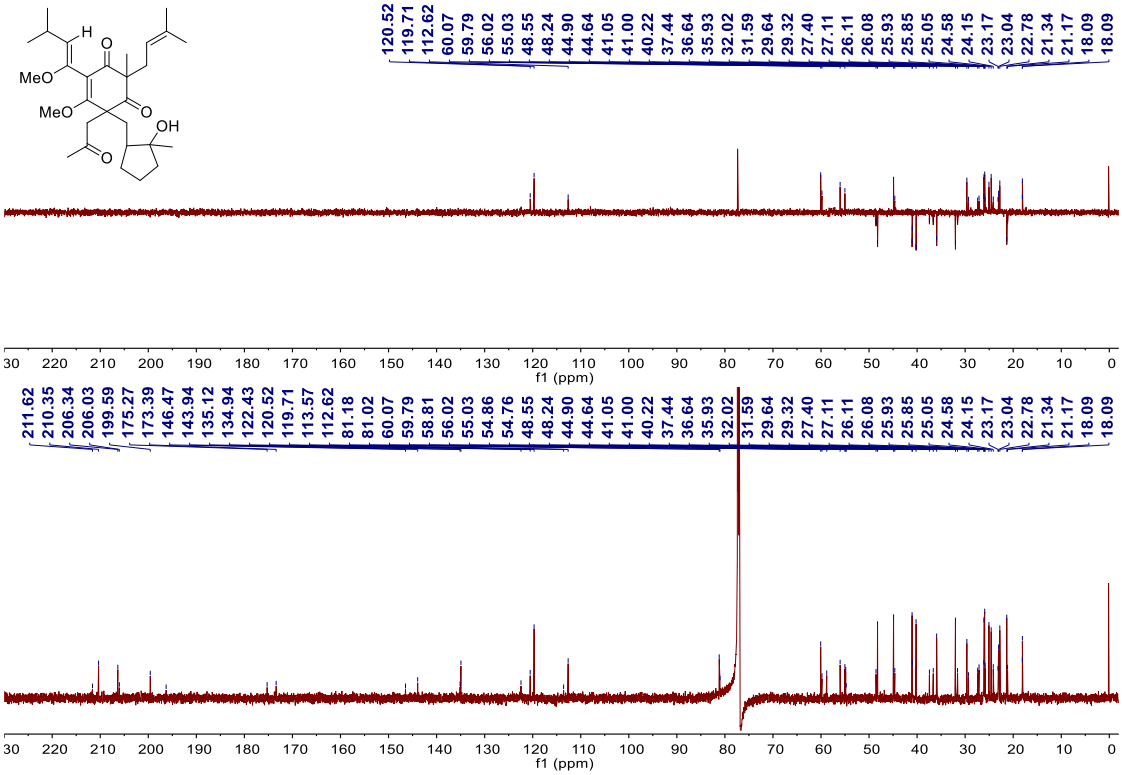


Figure S92. HSQC spectrum of compound **10** (Recorded in $CDCl_3$, 298 K)

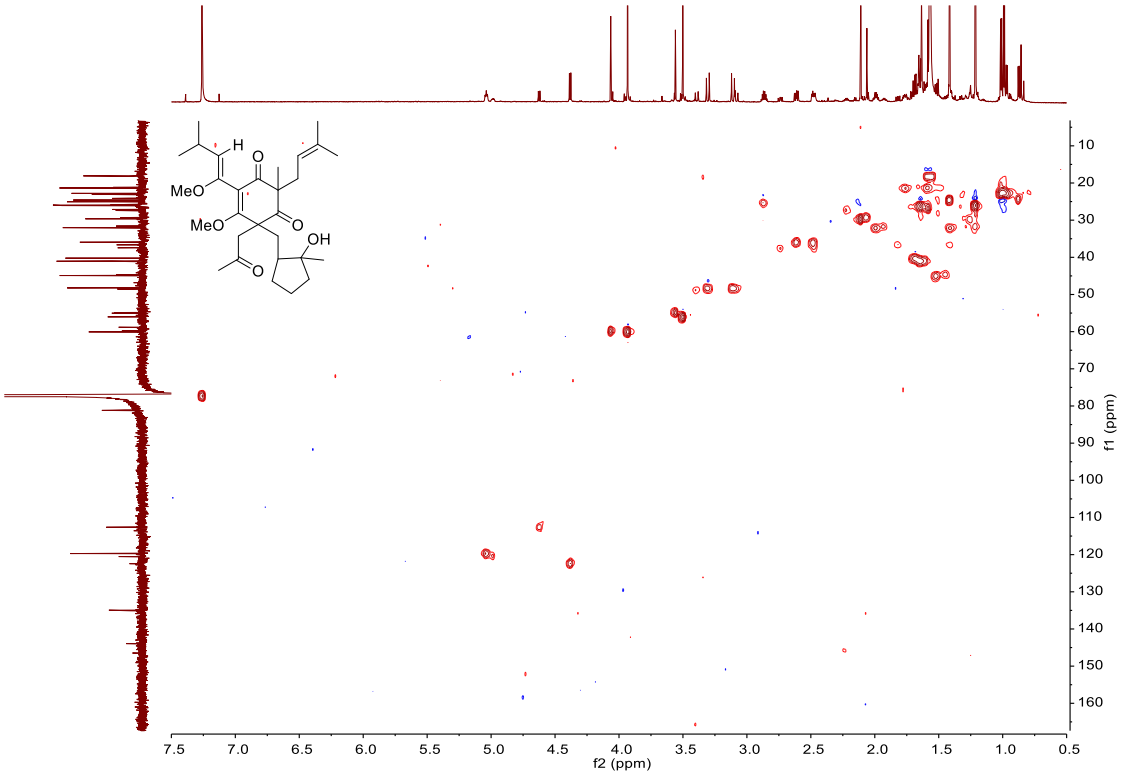


Figure S93. ^1H–^1H COSY spectrum of compound **10** (Recorded in $CDCl_3$, 298 K)

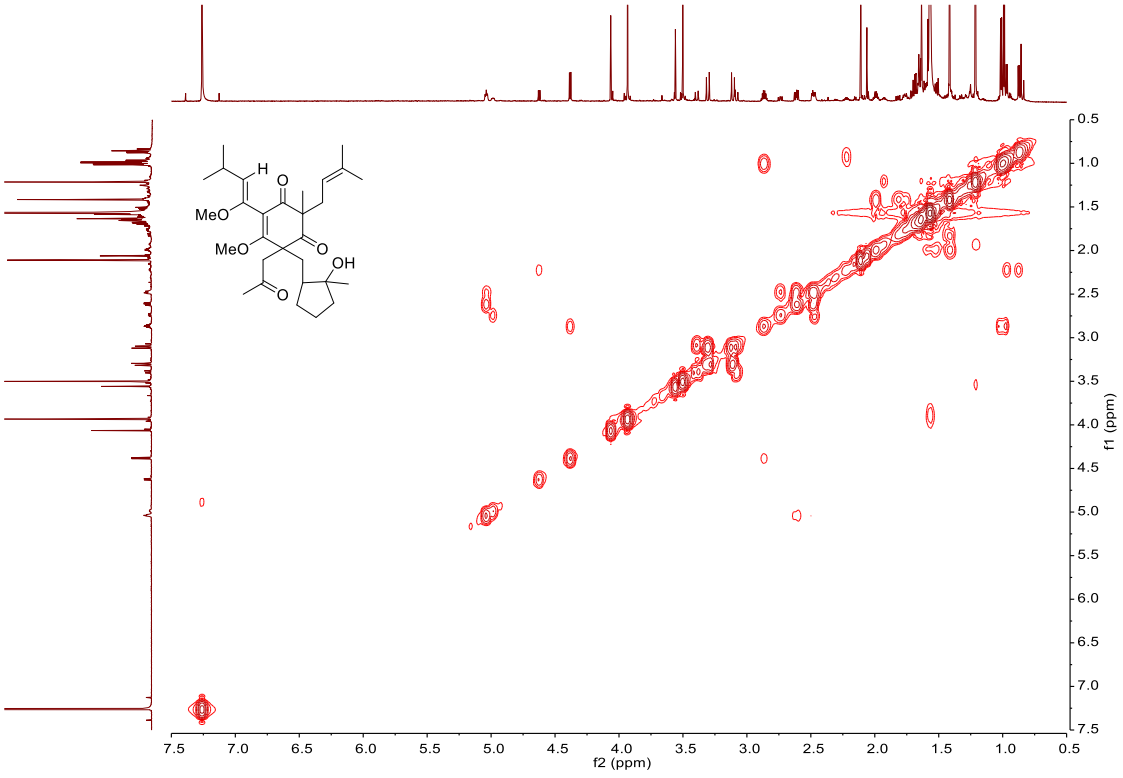


Figure S94. HMBC spectrum of compound **10** (Recorded in $CDCl_3$, 298 K)

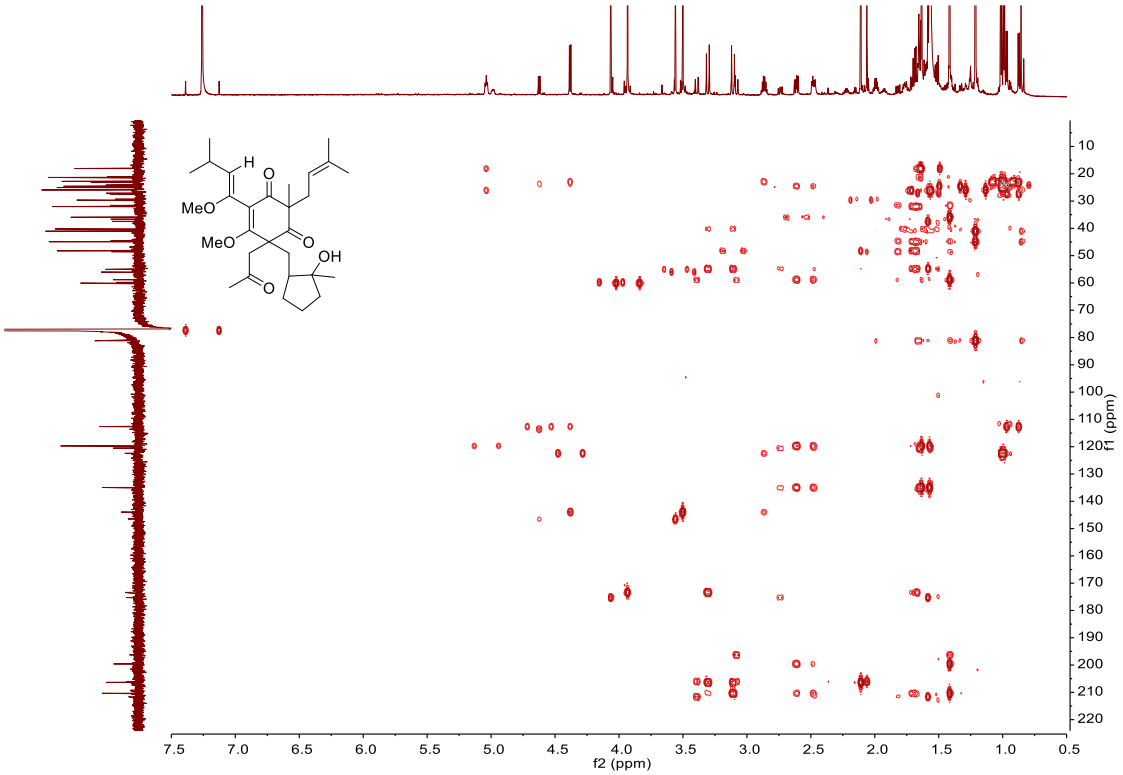


Figure S95. NOESY spectrum of compound **10** (Recorded in $CDCl_3$, 298 K)

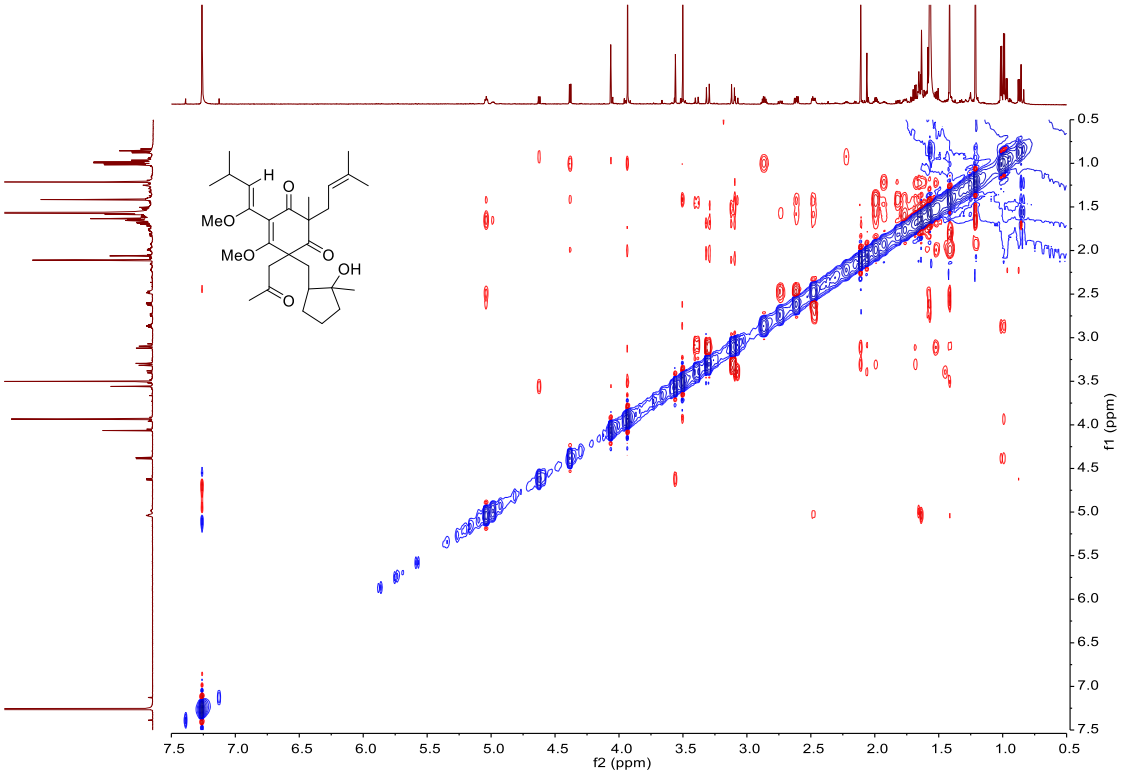


Figure S96. HRESIMS of compound **10**

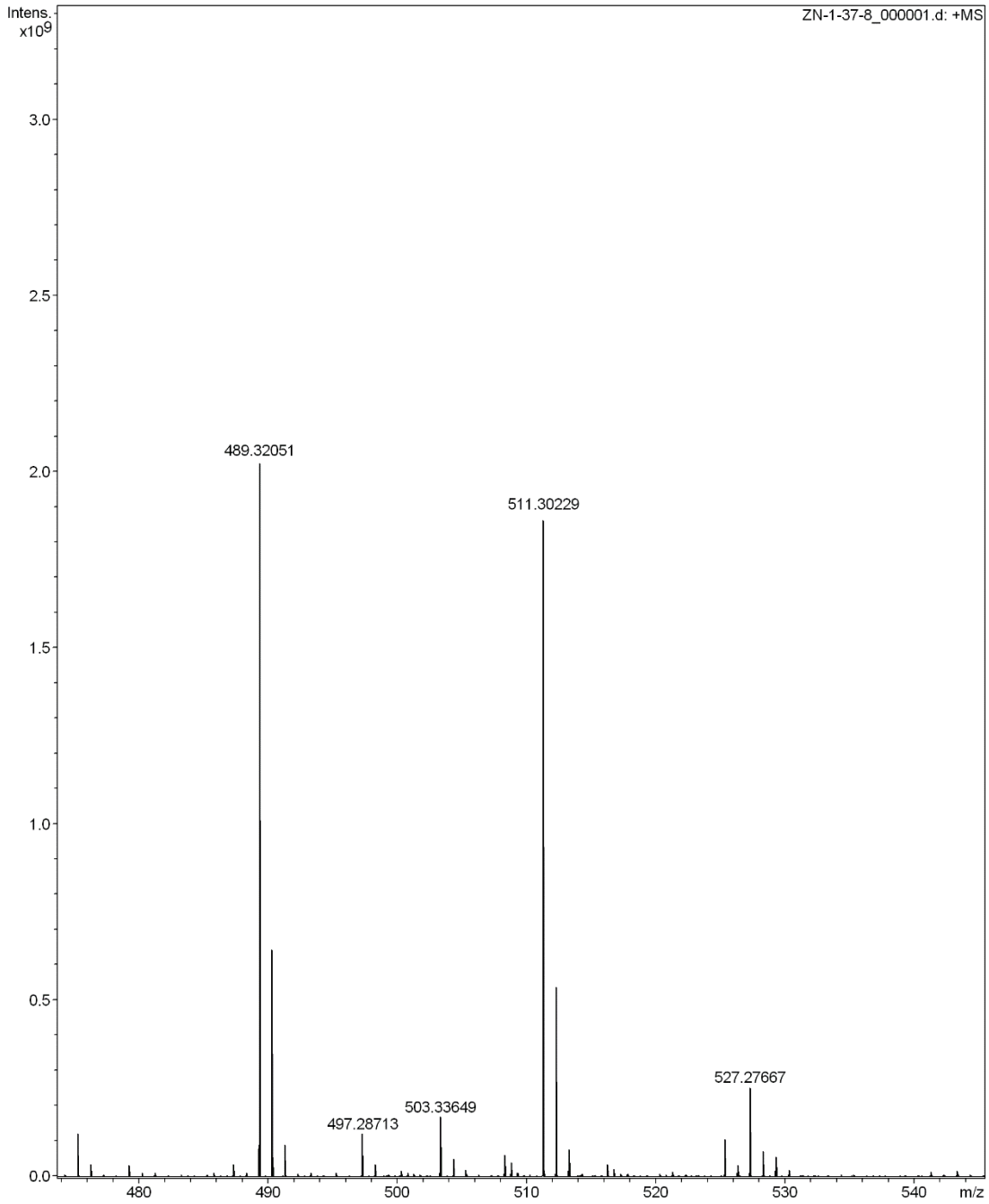


Figure S97. ^{1}H NMR (800 MHz) spectrum of compound **11** (Recorded in $CDCl_3$, 298 K)

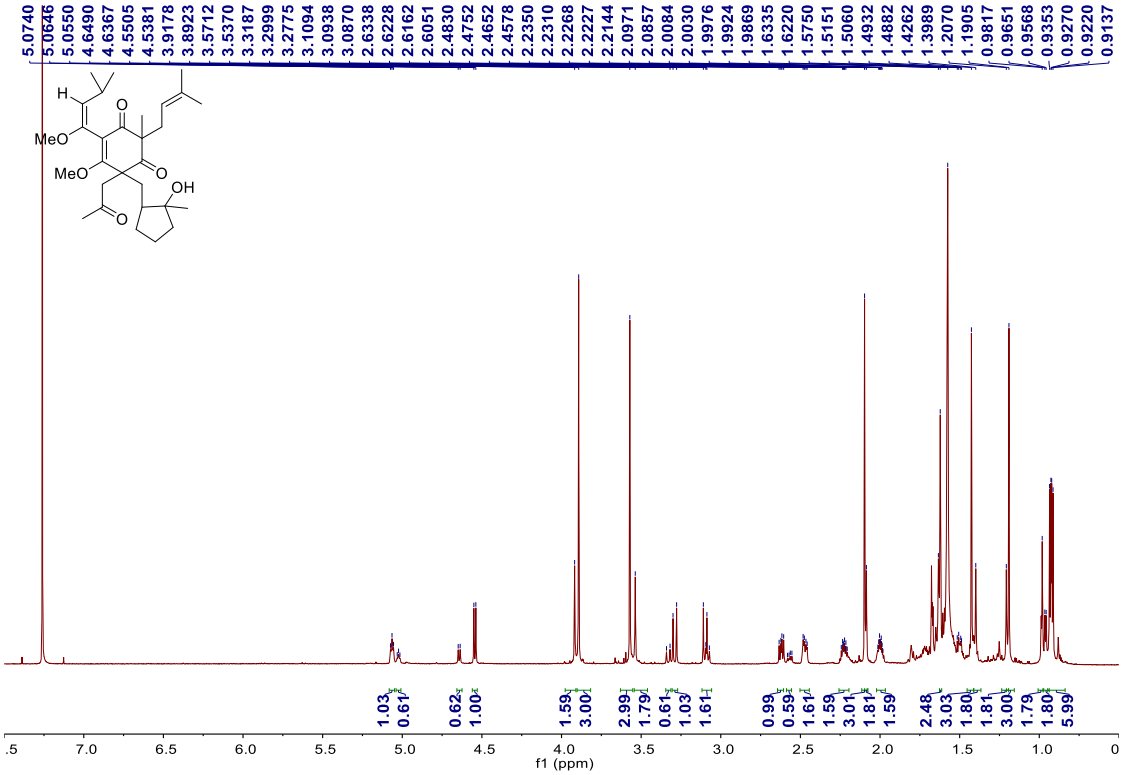


Figure S98. ^{13}C NMR (200 MHz) spectrum of compound **11** (Recorded in $CDCl_3$, 298 K)

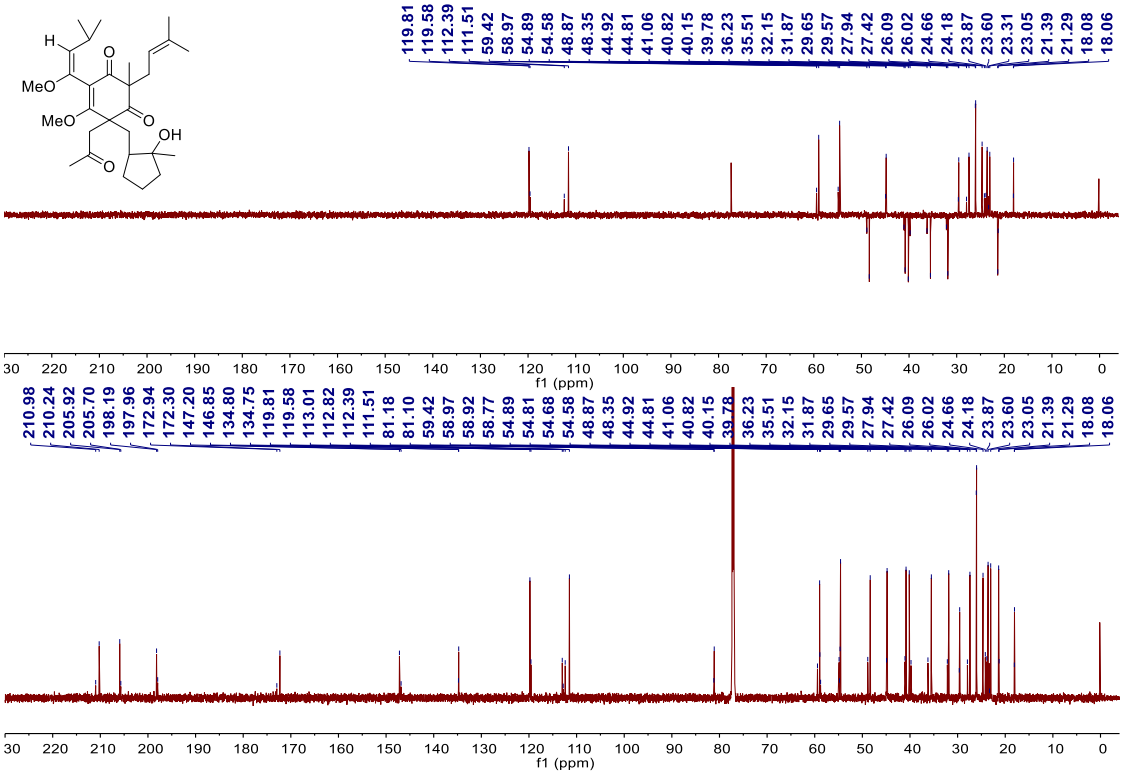


Figure S99. HSQC spectrum of compound **11** (Recorded in $CDCl_3$, 298 K)

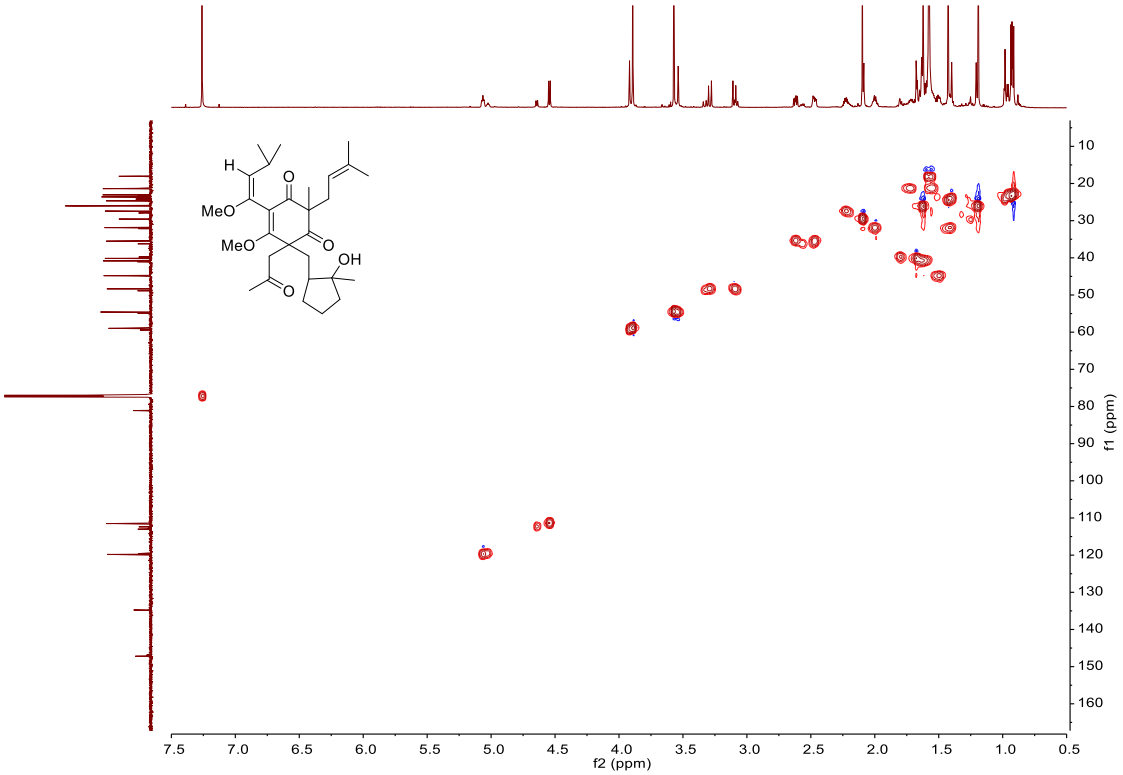


Figure S100. ^1H–^1H COSY spectrum of compound **11** (Recorded in $CDCl_3$, 298 K)

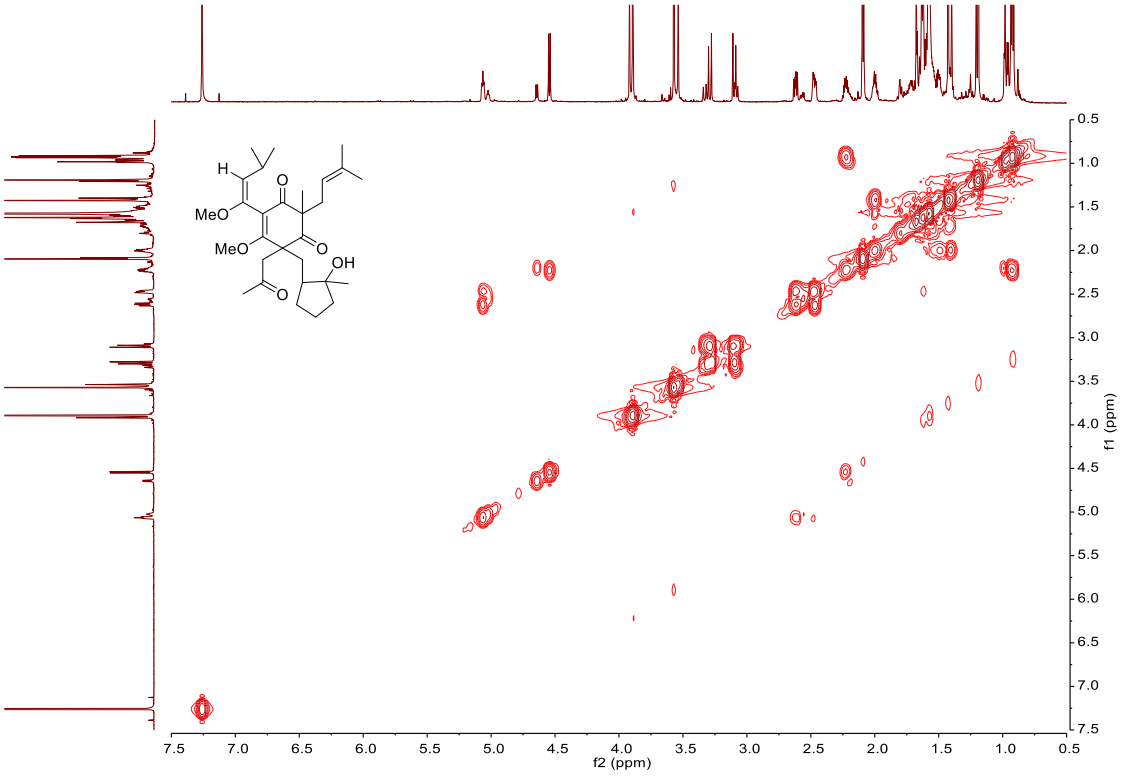


Figure S101. HMBC spectrum of compound **11** (Recorded in $CDCl_3$, 298 K)

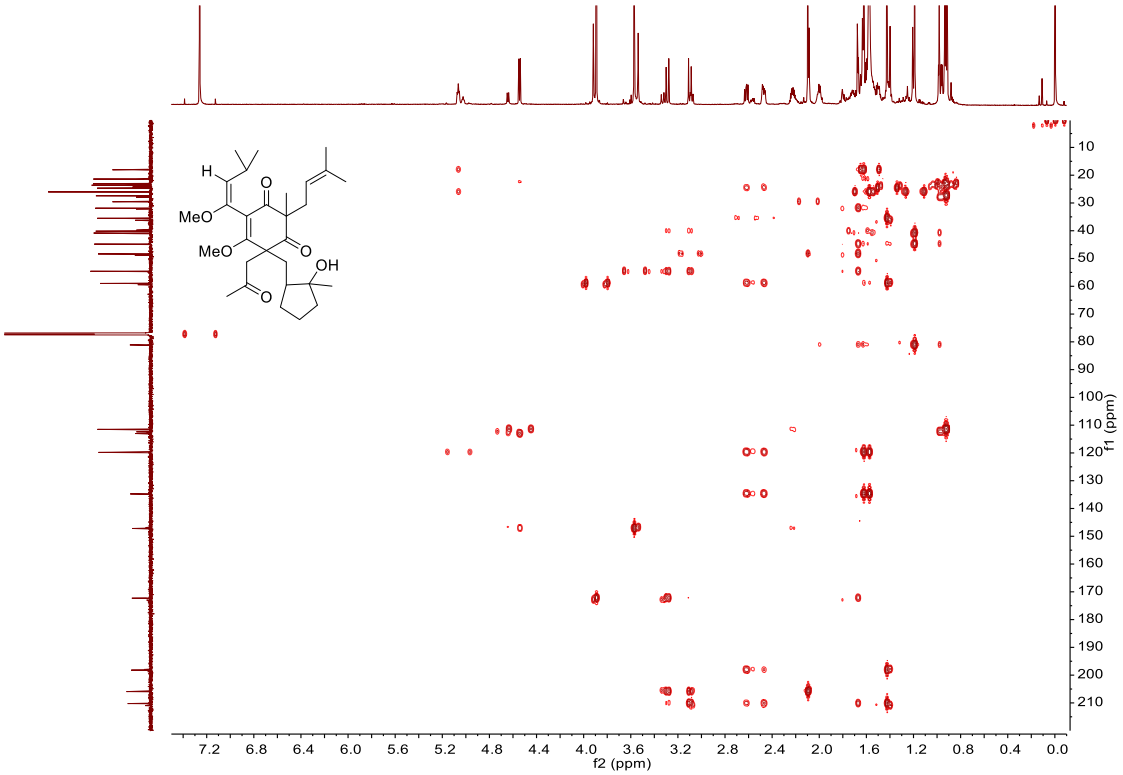


Figure S102. NOESY spectrum of compound **11** (Recorded in $CDCl_3$, 298 K)

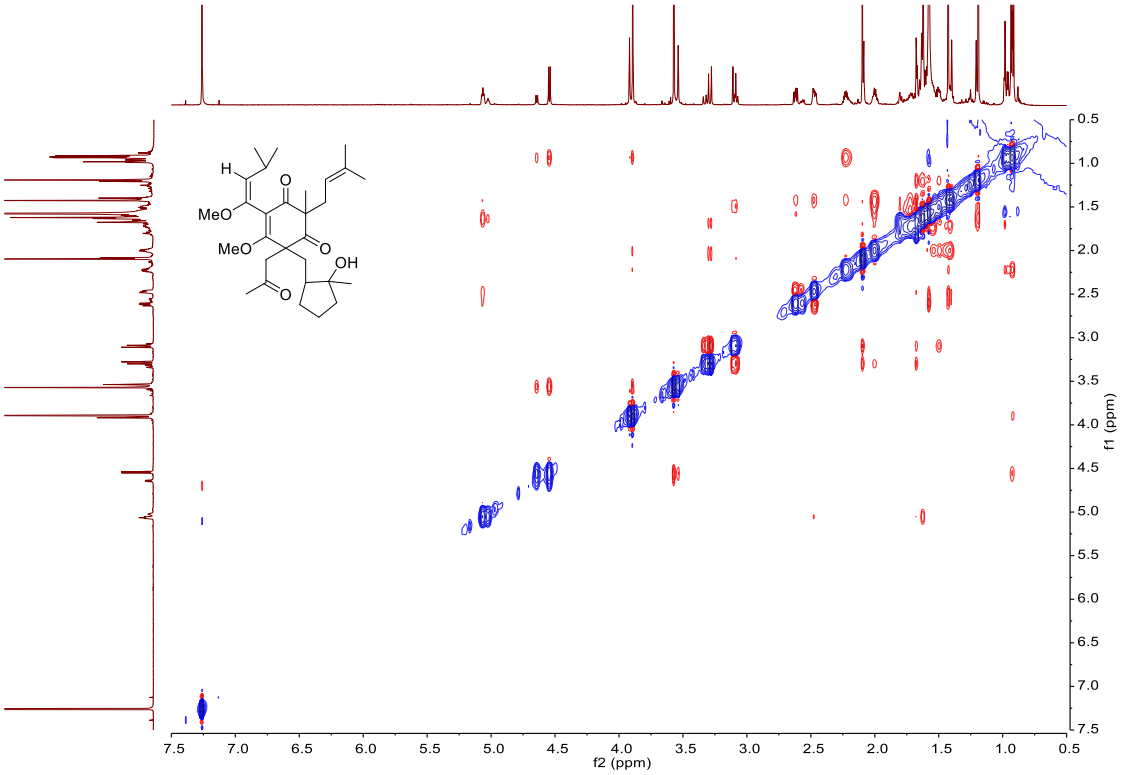


Figure S103. HRESIMS of compound **11**

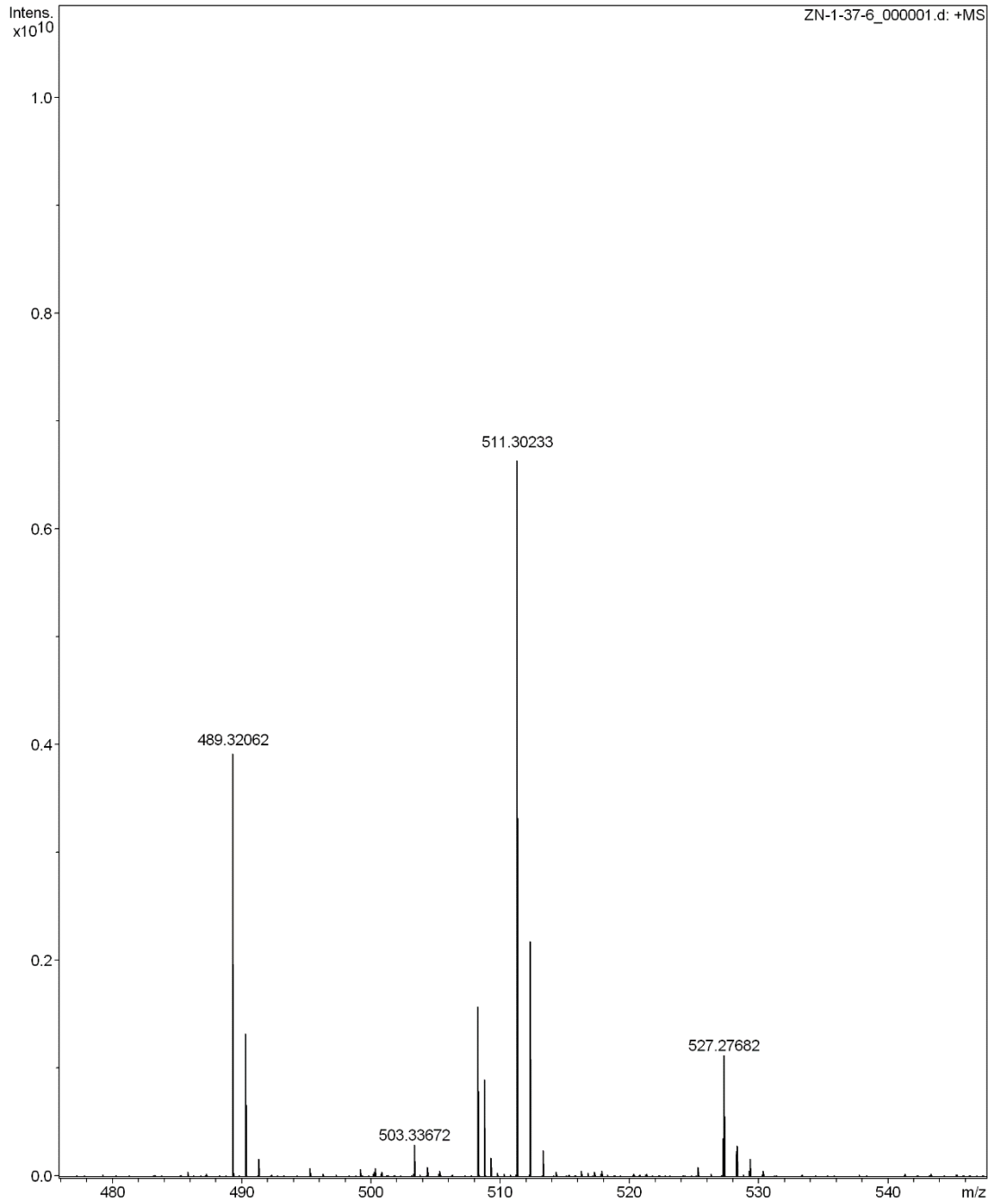


Figure S104. ^{1}H NMR (600 MHz) spectrum of compound **12** (Recorded in $CDCl_3$, 298 K)

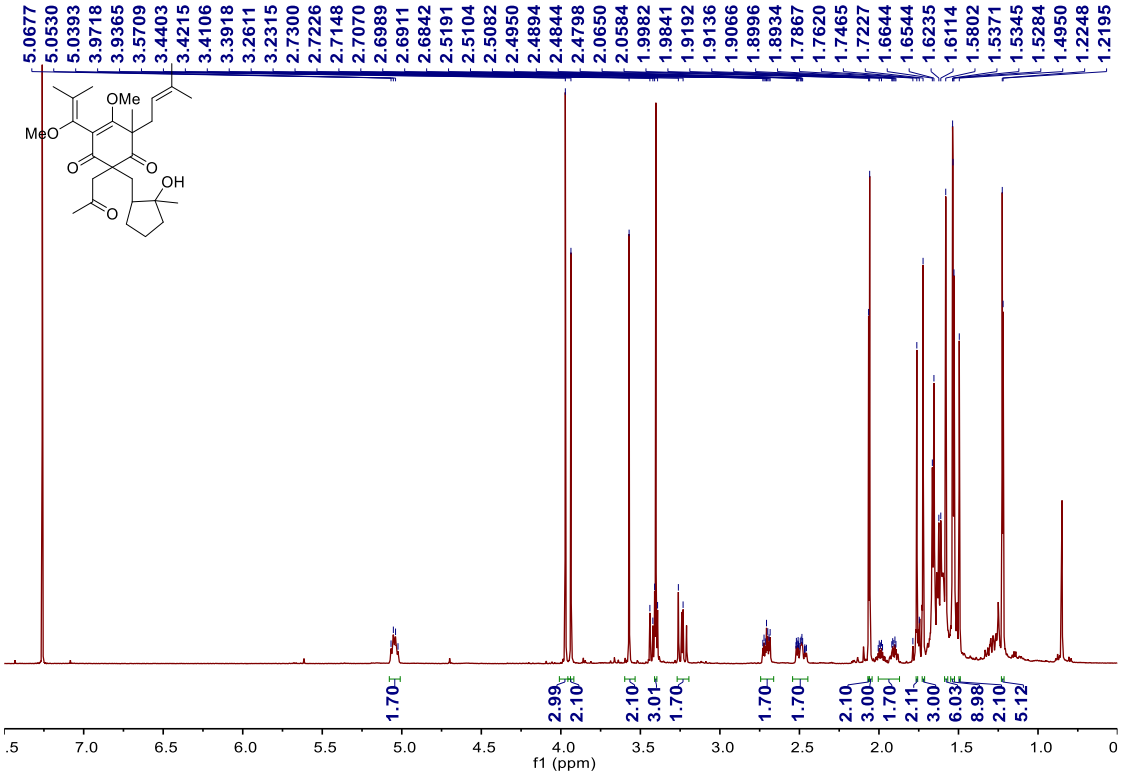


Figure S105. ^{13}C NMR (150 MHz) spectrum of compound **12** (Recorded in $CDCl_3$, 298 K)

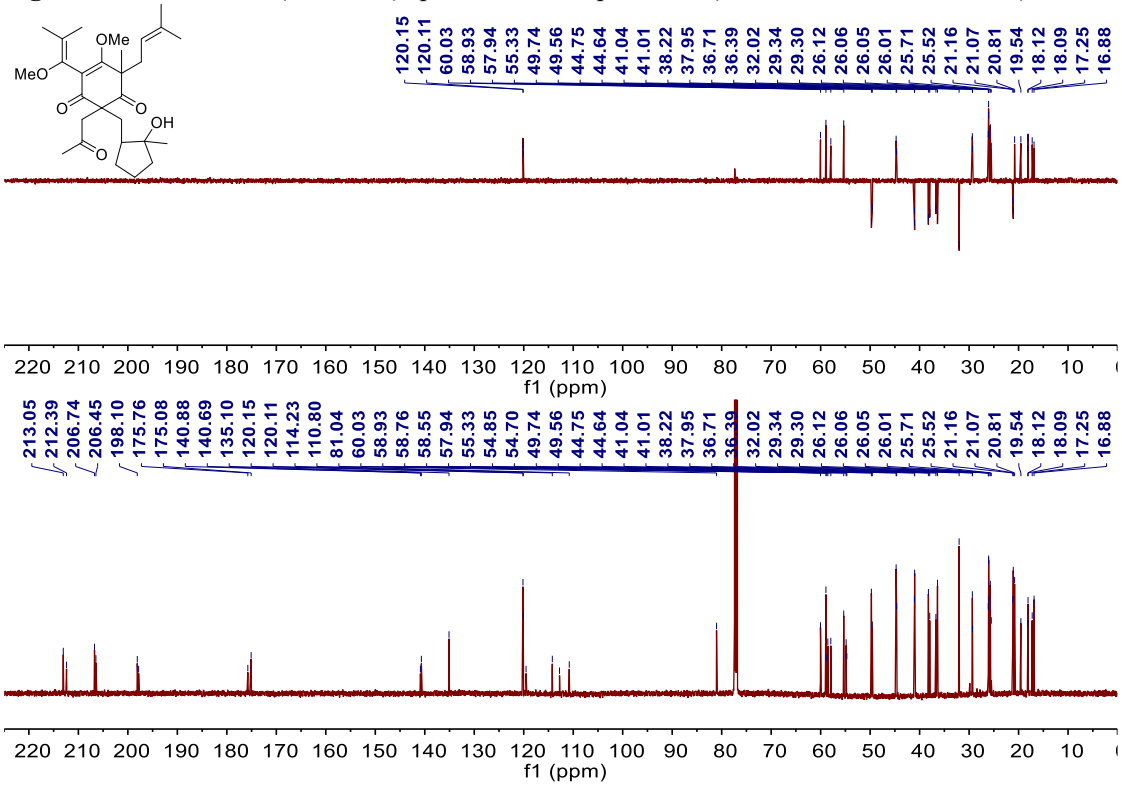


Figure S106. HSQC spectrum of compound **12** (Recorded in $CDCl_3$, 298 K)

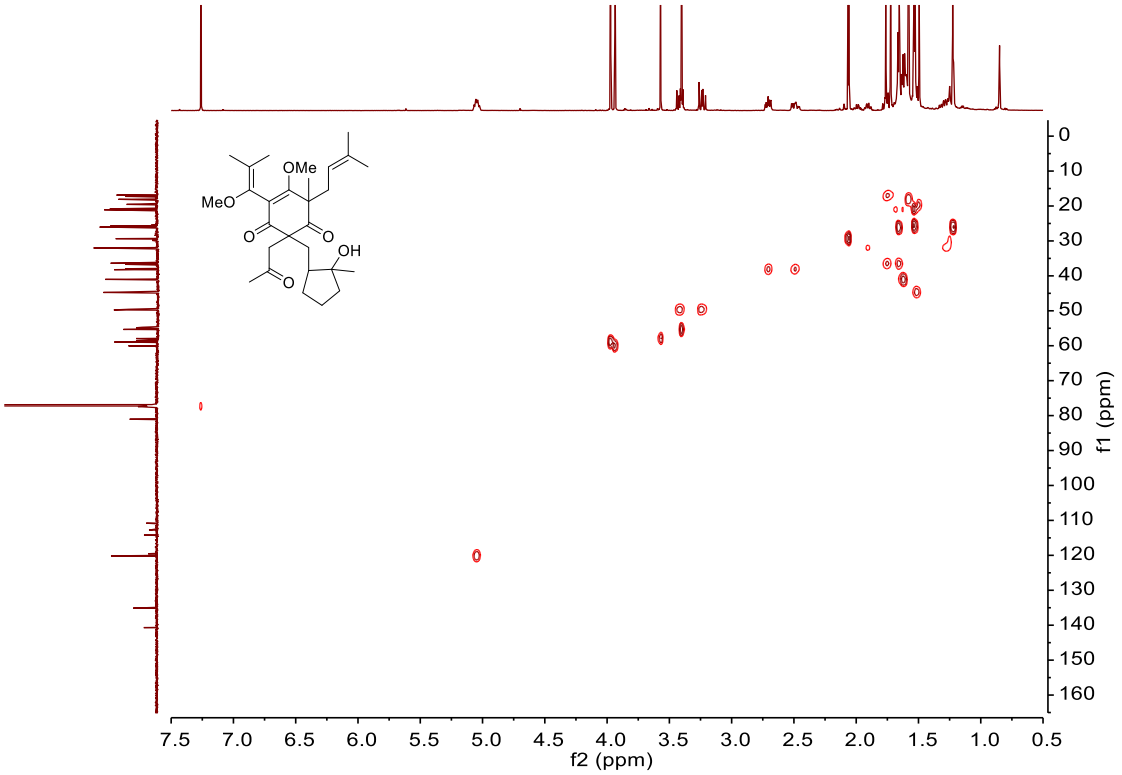


Figure S107. ^1H–^1H COSY spectrum of compound **12** (Recorded in $CDCl_3$, 298 K)

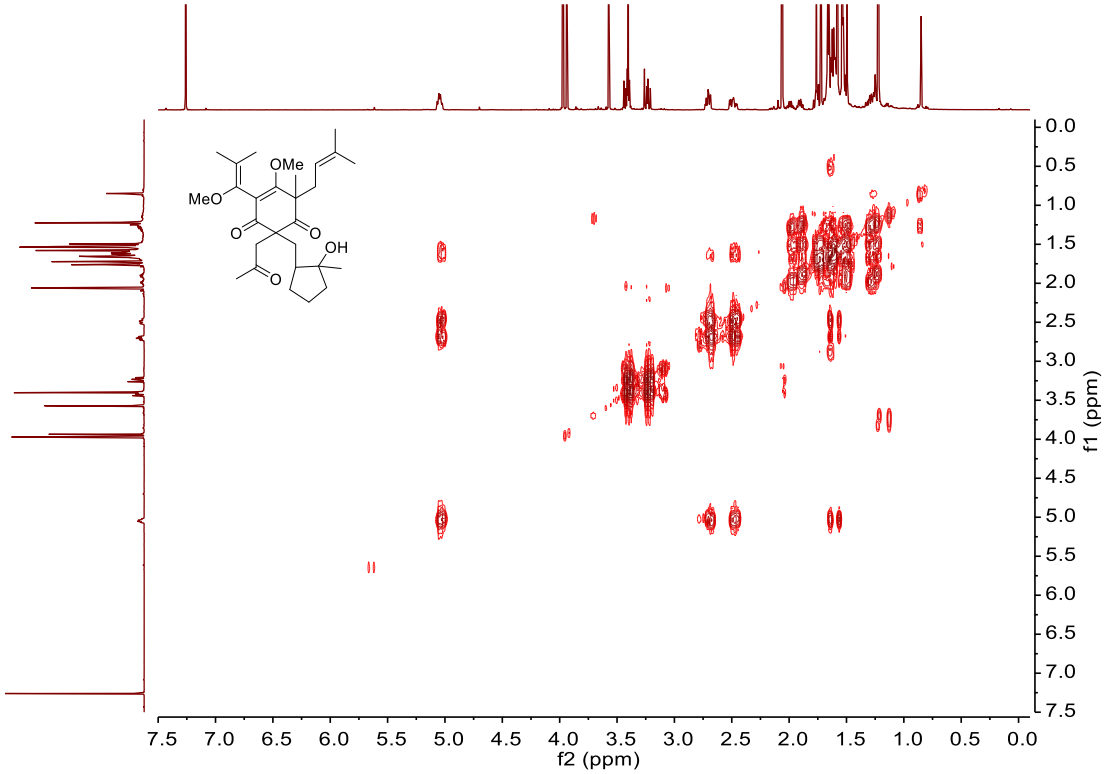


Figure S108. HMBC spectrum of compound **12** (Recorded in $CDCl_3$, 298 K)

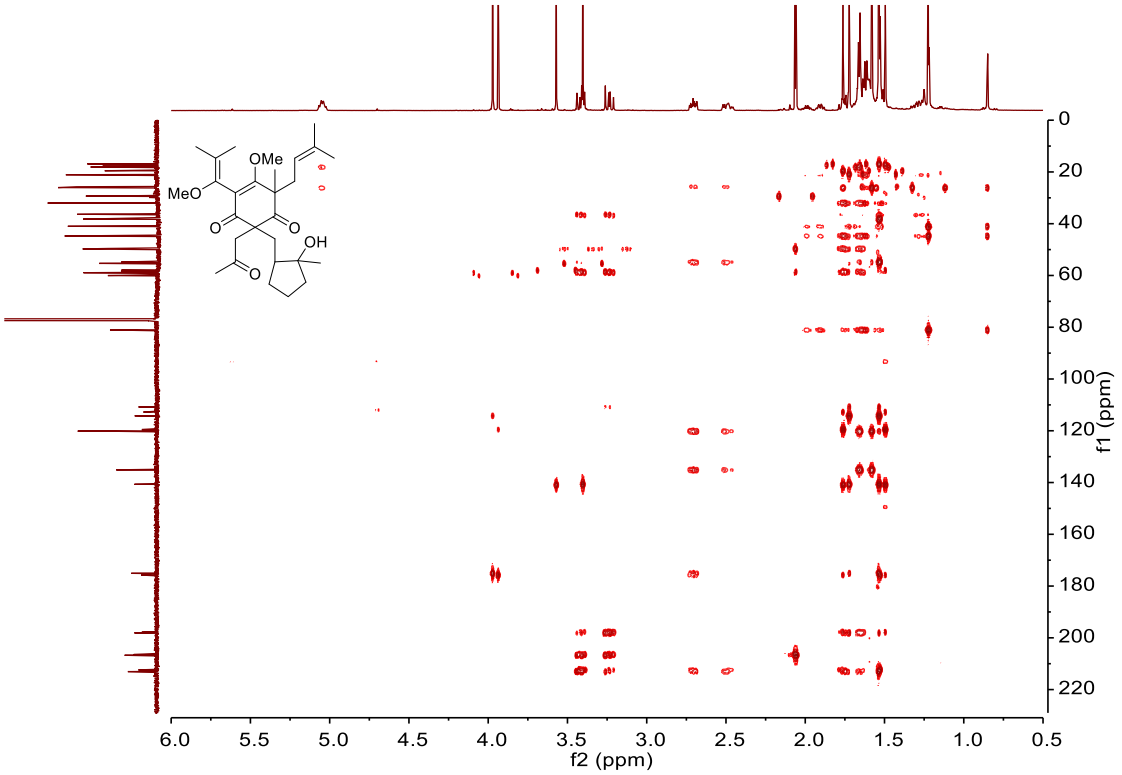


Figure S109. NOESY spectrum of compound **12** (Recorded in $CDCl_3$, 298 K)

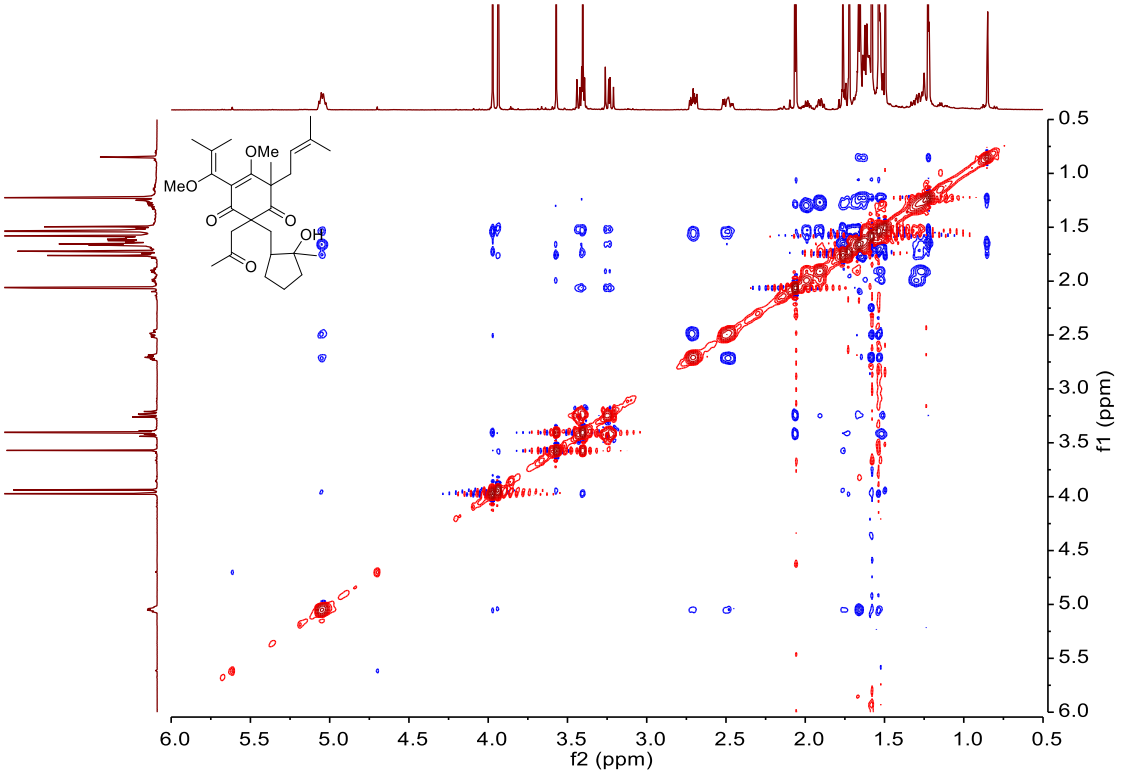


Figure S110. HRESIMS of compound **12**

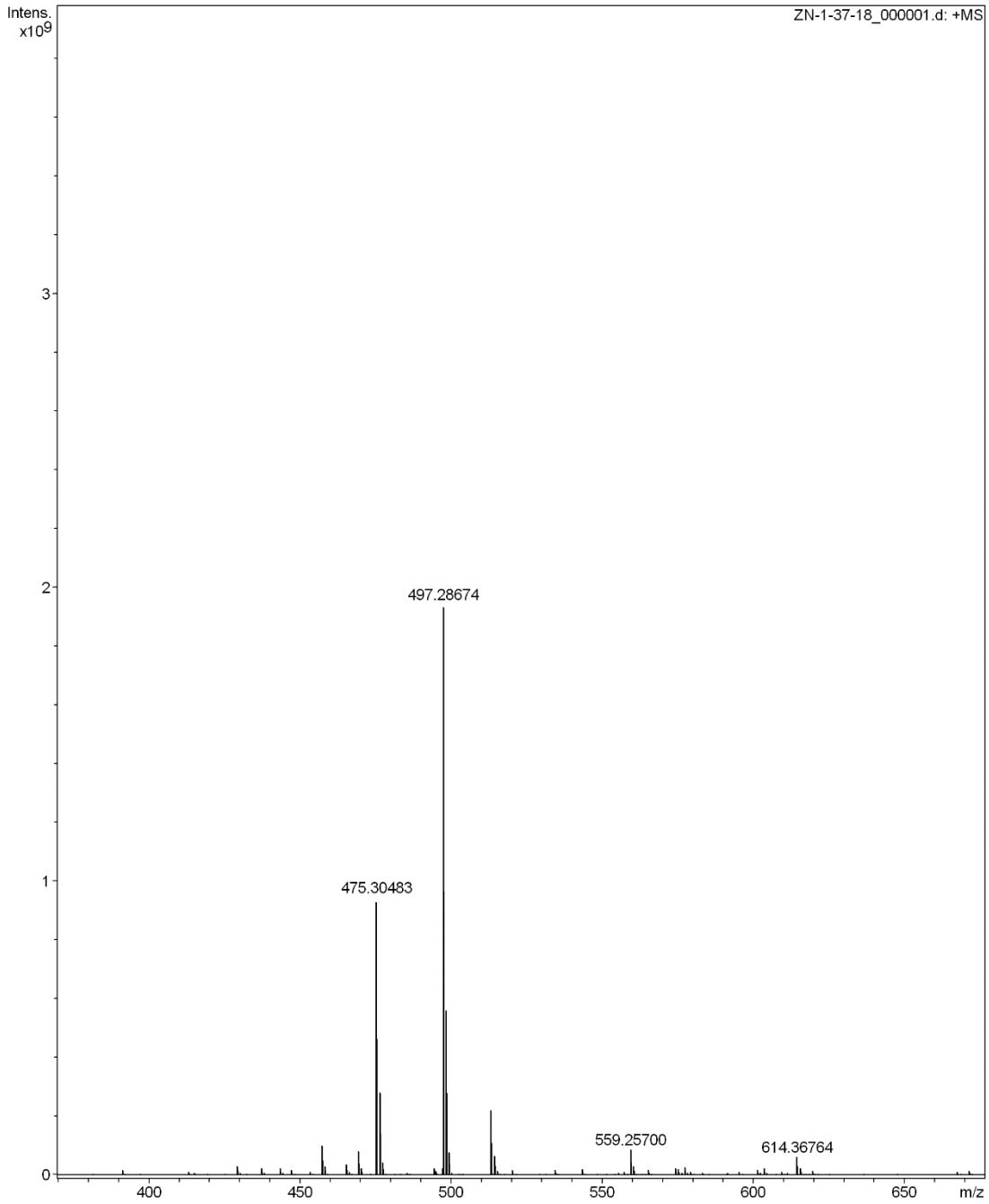


Figure S111. ^{1}H NMR (600 MHz) spectrum of compound **13** (Recorded in $CDCl_3$, 298 K)

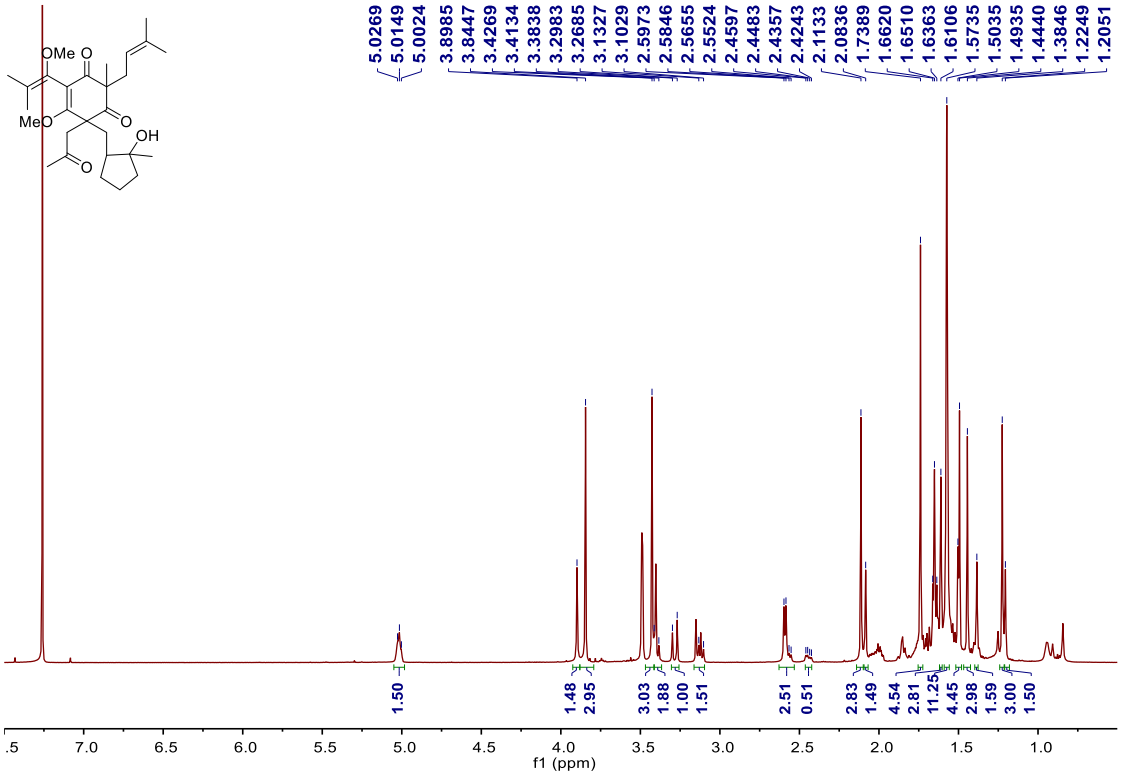


Figure S112. ^{13}C NMR (150 MHz) spectrum of compound **13** (Recorded in $CDCl_3$, 298 K)

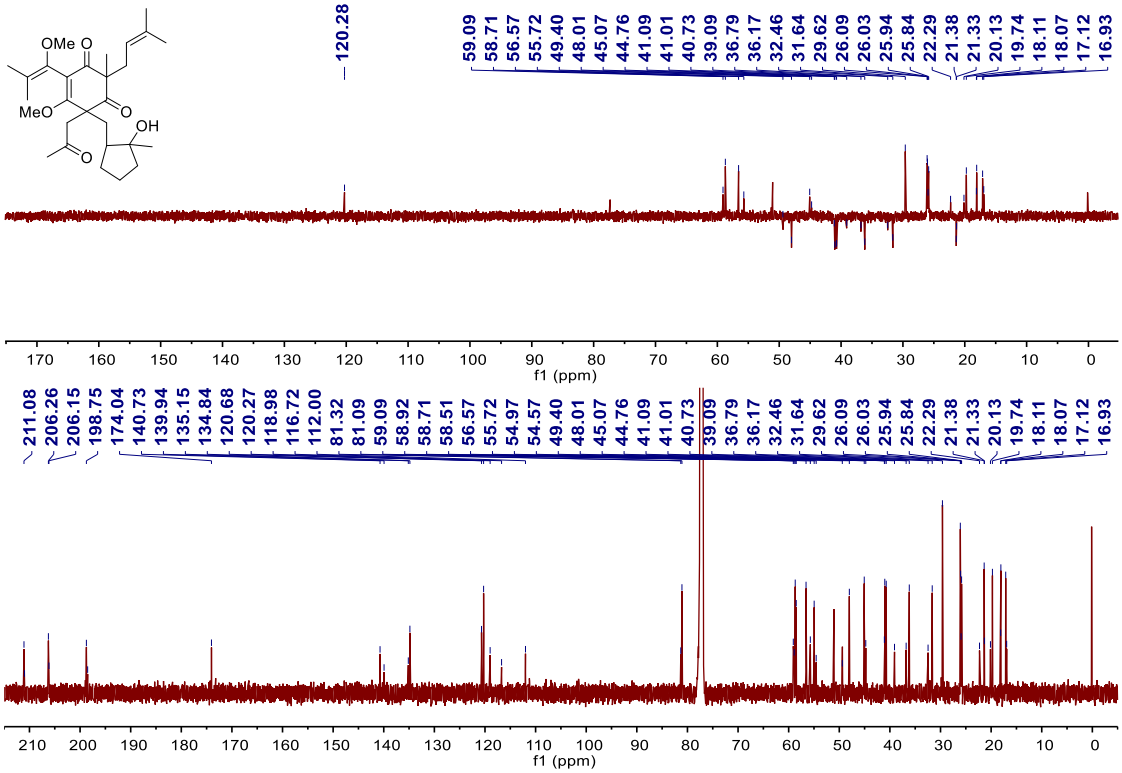


Figure S113. HSQC spectrum of compound **13** (Recorded in $CDCl_3$, 298 K)

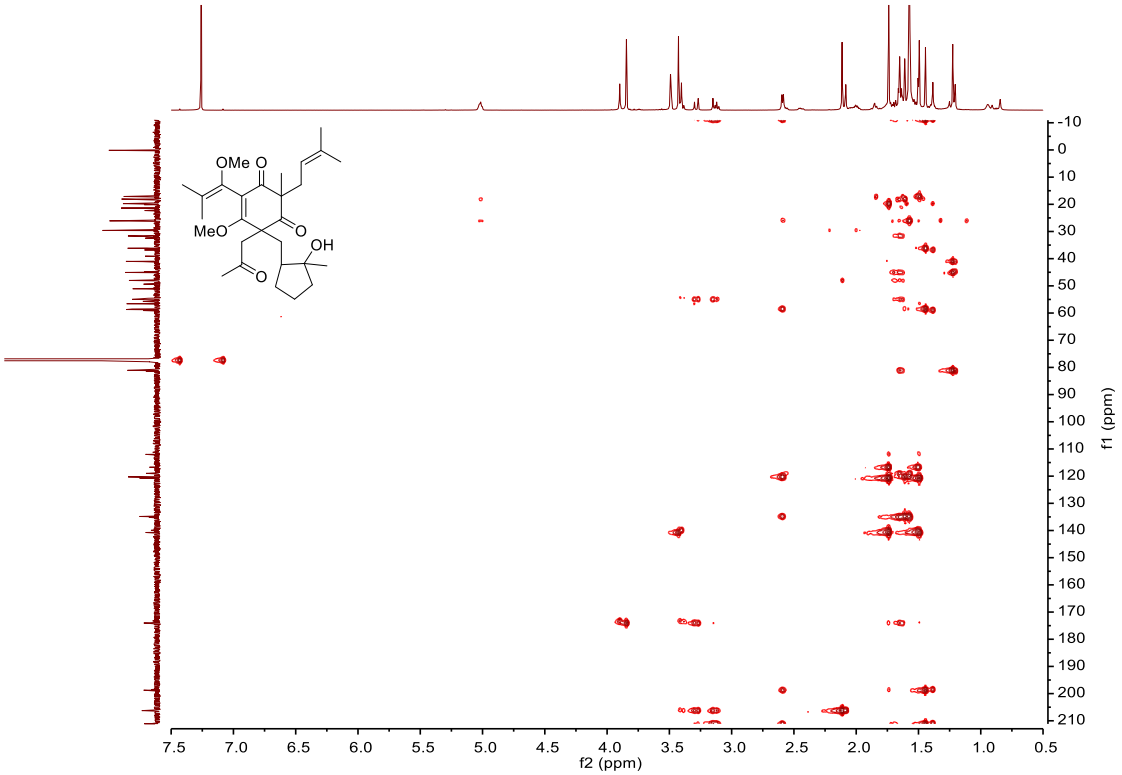


Figure S114. HMBC spectrum of compound **13** (Recorded in $CDCl_3$, 298 K)

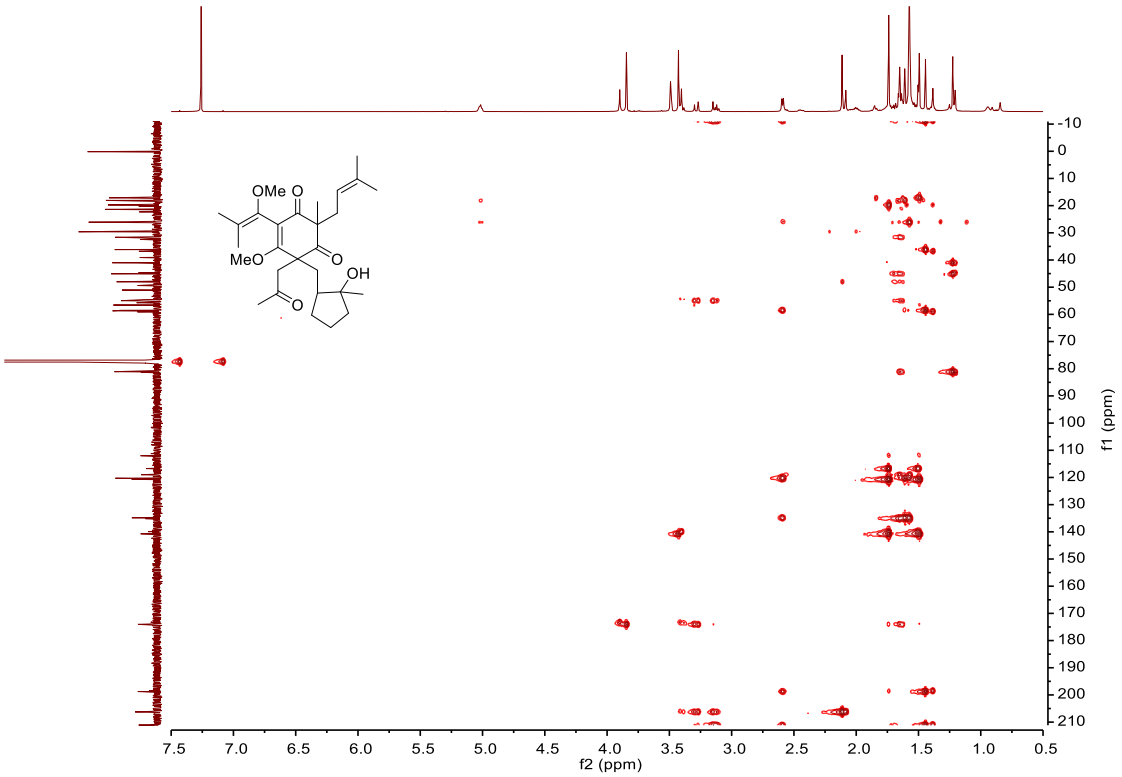


Figure S115. NOESY spectrum of compound **13** (Recorded in $CDCl_3$, 298 K)

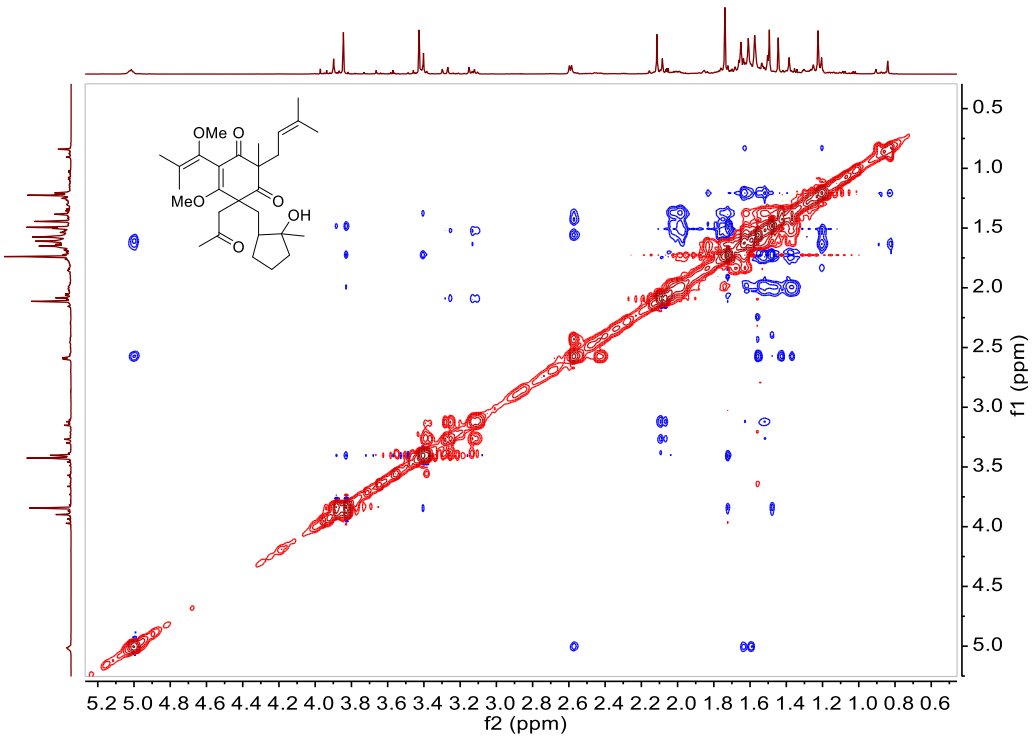


Figure S116. HRESIMS of compound **13**

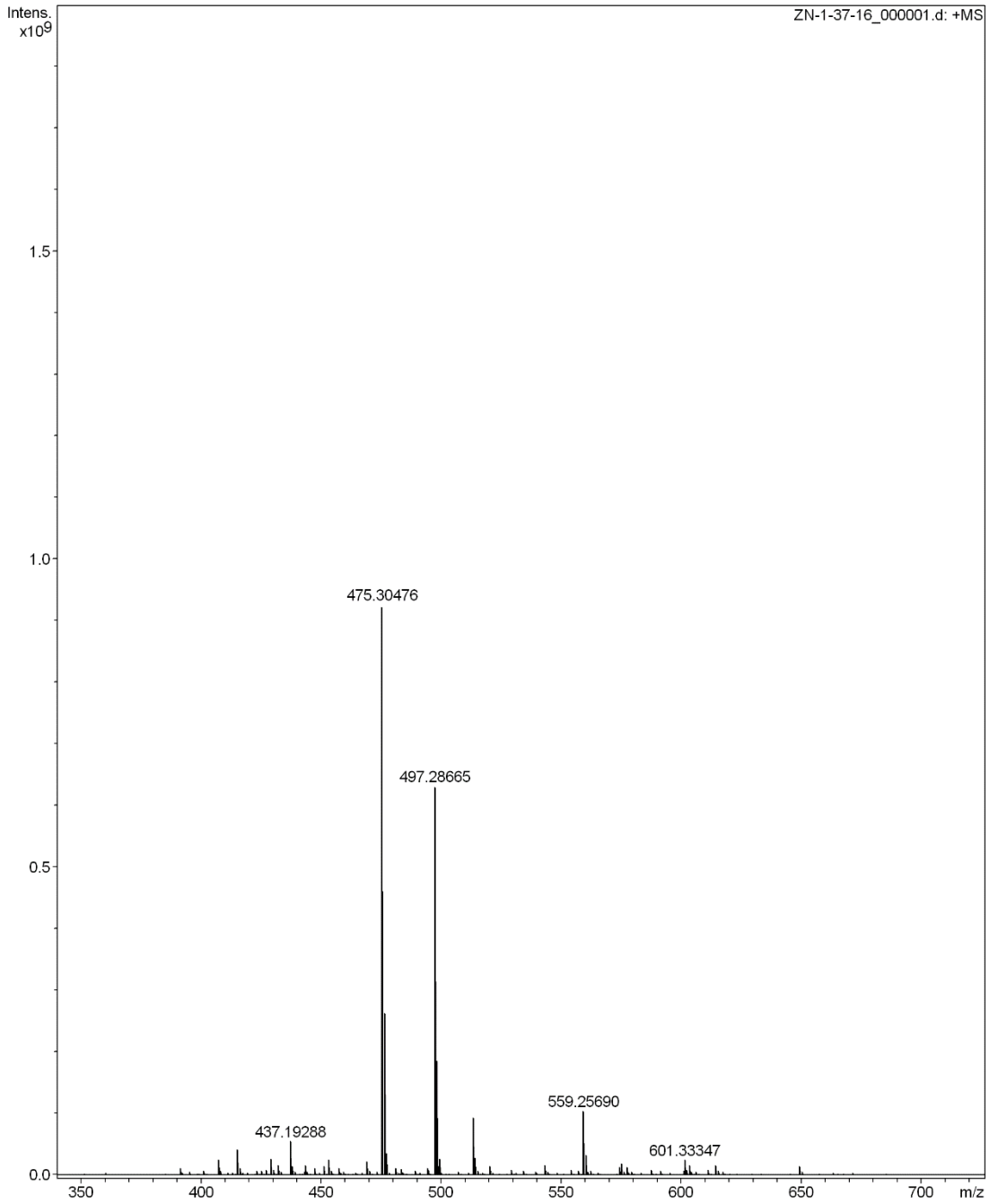


Figure S117. Experimental ECD spectra of **1**, **4**–**7**.

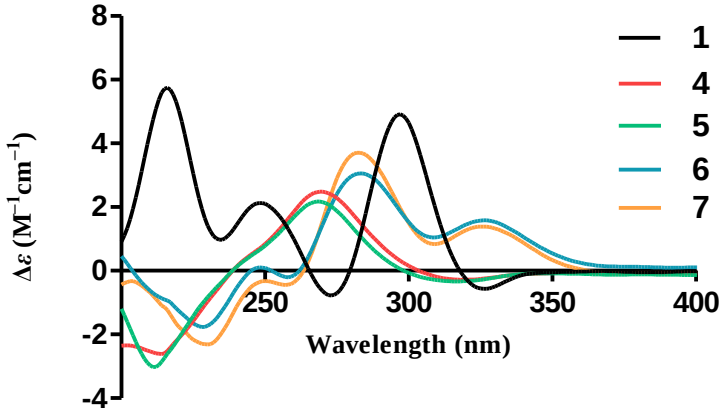


Figure S118. Experimental ECD spectra of **2**, **8**–**11**.

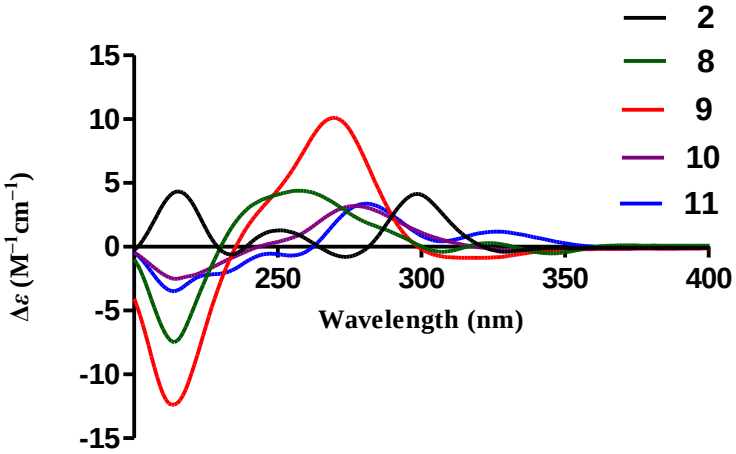


Figure S119. Experimental ECD spectra of **3**, **12**–**13**.