Supporting Information for

Enantiomeric pairs of meroterpenoids with 11/5/6 spiro-heterocyclic systems from *Hypericum kouytchense*

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Table S1. X-ray crystallographic data for (−)-hyperkouytin A (**1a**)[a].

Empirical formula	$C_{48}H_{64}O_5$	
Formula weight	720.99	
Temperature	173.01 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.7093(5) Å	α= 90 °.
	b = 18.6794(10) Å	β= 90 °.
	c = 23.1009(13) Å	γ = 90 °.
Volume	4189.7(4) $Å^3$	
Z	4	
Density (calculated)	1.143 Mg/m^3	
Absorption coefficient	0.361 mm^{-1}	
F(000)	1568	
Crystal size	0.1 x 0.06 x 0.05 mm^3	
Theta range for data collection	3.915 to 54.872 °.	
Index ranges	-8<=h<=11, -22<=k<=22, -28<=l<=28	
Reflections collected	41441	
Independent reflections	7901 [R(int) = 0.0327]	
Completeness to theta = 53.594 °	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.6456	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7901 / 0 / 488	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0814	
R indices (all data)	R1 = 0.0367, wR2 = 0.0837	
Absolute structure parameter	0.05(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.180 and -0.199 e.$Å^{-3}$	

[a]Crystals of **1a** were obtained from a mixed solvent (MeOH/H_2O, 5:1).

Table S2. X-ray crystallographic data for (+)-hyperkouytin B (**2b**)[a].

Empirical formula	$C_{43}H_{56}O_5$	
Formula weight	652.87	
Temperature	173.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.2293(5) Å	α= 90 °.
	b = 23.5572(14) Å	β= 90 °.
	c = 34.549(2) Å	γ = 90 °.
Volume	7511.5(8) $Å^3$	
Z	8	
Density (calculated)	1.155 Mg/m^3	
Absorption coefficient	0.372 mm^{-1}	
F(000)	2832	
Crystal size	0.1 x 0.06 x 0.05 mm^3	
Theta range for data collection	3.449 to 54.974 °.	
Index ranges	-11<=h<=5, -28<=k<=23, -41<=l<=42	
Reflections collected	47528	
Independent reflections	14111 [R(int) = 0.0514]	
Completeness to theta = 53.594 °	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5413	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14111 / 0 / 884	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.1128	
R indices (all data)	R1 = 0.0740, wR2 = 0.1309	
Absolute structure parameter	0.06(11)	
Extinction coefficient	0.00150(12)	
Largest diff. peak and hole	0.234 and -0.200 $e.Å^{-3}$	

[a]Crystals of **2b** were obtained from a mixed solvent ($MeOH/H_2O$, 5:1).

Table S3. X-ray crystallographic data for (+)-hyperkouytin D (**4b**)[a].

Empirical formula	$C_{48}H_{64}O_5$	
Formula weight	720.99	
Temperature	173.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.4449(13) Å	α= 90 °.
	b = 18.494(3) Å	β= 90 °.
	c = 24.612(4) Å	γ = 90 °.
Volume	4299.0(10) $Å^3$	
Z	4	
Density (calculated)	1.114 Mg/m^3	
Absorption coefficient	0.352 mm^{-1}	
F(000)	1568	
Crystal size	0.1 x 0.05 x 0.05 mm^3	
Theta range for data collection	4.362 to 54.950 °.	
Index ranges	-9<=h<=11, -22<=k<=22, -30<=l<=30	
Reflections collected	46312	
Independent reflections	8130 [R(int) = 0.0462]	
Completeness to theta = 53.594 °	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.6274	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8130 / 24 / 488	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0664, wR2 = 0.1927	
R indices (all data)	R1 = 0.0721, wR2 = 0.2024	
Absolute structure parameter	0.08(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.172 and -0.454 $e.Å^{-3}$	

[a]Crystals of **4b** were obtained from a mixed solvent ($MeOH/H_2O$, 5:1).

Table S4. X-ray crystallographic data for (+)-hyperkouytin E (**5b**)[a].

Empirical formula	$C_{48}H_{64}O_5$	
Formula weight	720.99	
Temperature	296 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 46.394(4) Å	α= 90 °.
	b = 9.7640(8) Å	β= 105.973(5) °.
	c = 19.7131(15) Å	γ = 90 °.
Volume	8585.0(12) $Å^3$	
Z	8	
Density (calculated)	1.116 Mg/m^3	
Absorption coefficient	0.353 mm^{-1}	
F(000)	3136	
Crystal size	0.1 x 0.02 x 0.01 mm^3	
Theta range for data collection	3.487 to 55.200 °.	
Index ranges	-56<=h<=55, -11<=k<=11, -24<=l<=24	
Reflections collected	54815	
Independent reflections	16239 [R(int) = 0.0685]	
Completeness to theta = 53.594 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4572	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16239 / 1 / 975	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0661, wR2 = 0.1679	
R indices (all data)	R1 = 0.1007, wR2 = 0.1958	
Absolute structure parameter	0.06(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.506 and -0.319 $e.Å^{-3}$	

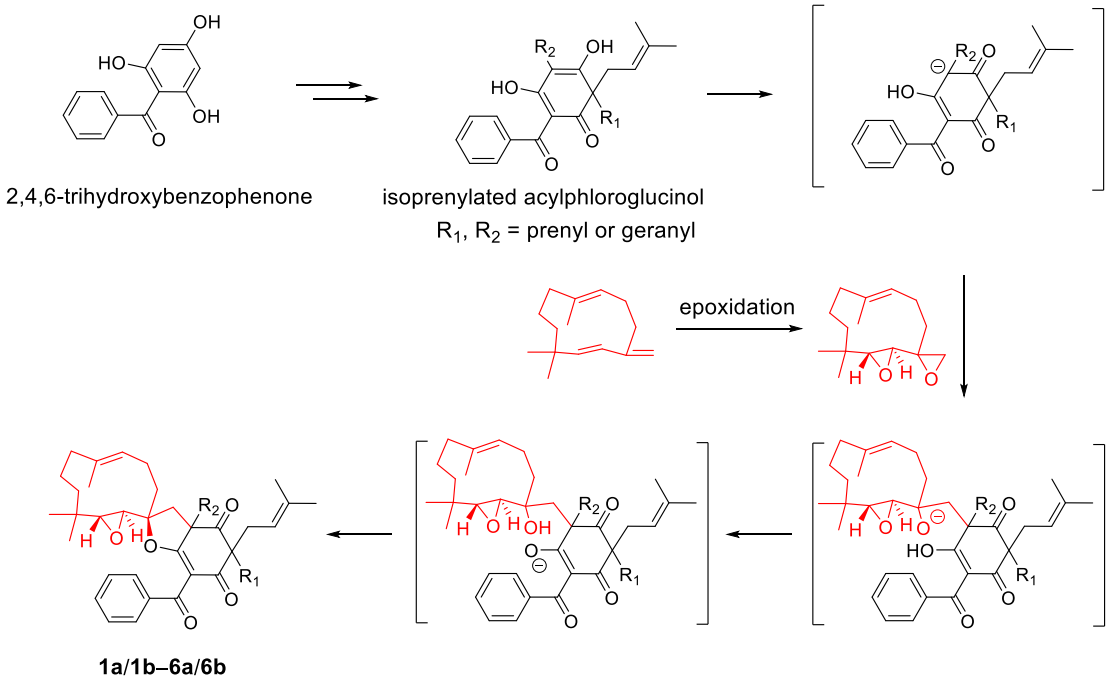
[a]Crystals of **5b** were obtained from a mixed solvent (MeOH/H_2O, 5:1).

Table S5. X-ray crystallographic data for (−)-hyperkouytin F (**6a**)[a].

Empirical formula	$C_{43}H_{56}O_5$	
Formula weight	652.87	
Temperature	296 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 13.7143(6) Å	α= 90 °.
	b = 9.7311(4) Å	β= 96.506(3) °.
	c = 14.4170(6) Å	γ = 90 °.
Volume	1911.63(14) $Å^3$	
Z	2	
Density (calculated)	1.134 Mg/m^3	
Absorption coefficient	0.362 mm^{-1}	
F(000)	708	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
Theta range for data collection	2.684 to 55.162 °.	
Index ranges	-15<=h<=16, -11<=k<=11, -17<=l<=17	
Reflections collected	28908	
Independent reflections	7217 [R(int) = 0.0556]	
Completeness to theta = 53.594 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5931	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7217 / 1 / 442	
Goodness-of-fit on F^2	1.177	
Final R indices [I>2sigma(I)]	R1 = 0.0742, wR2 = 0.1706	
R indices (all data)	R1 = 0.1331, wR2 = 0.2020	
Absolute structure parameter	0.03(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.228 and -0.232 e.$Å^{-3}$	

[a]Crystals of **6a** were obtained from a mixed solvent (MeOH/H_2O, 5:1).

Scheme S1. Hypothetical biosynthetic pathways for **1a/1b−6a/6b**.



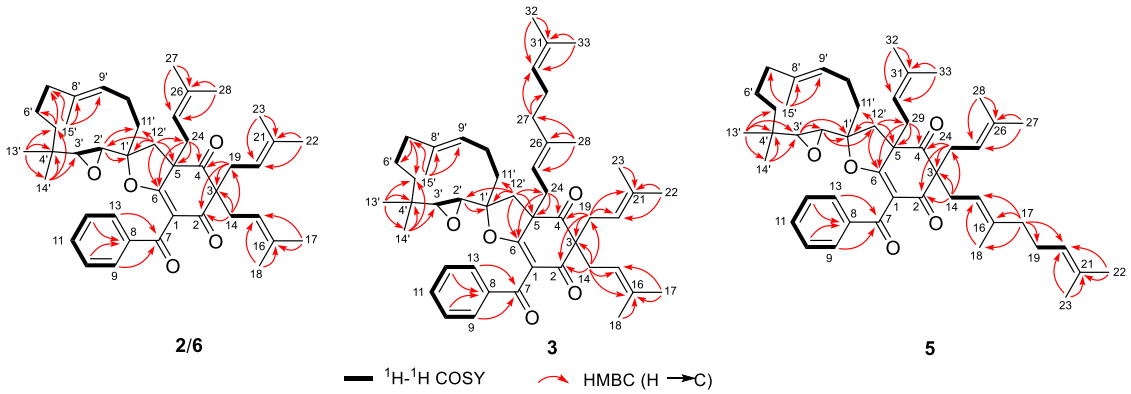


Fig. S1. Key ^{1}H-^{1}H COSY and HMBC correlations of **2**, **3**, **5**, and **6**.

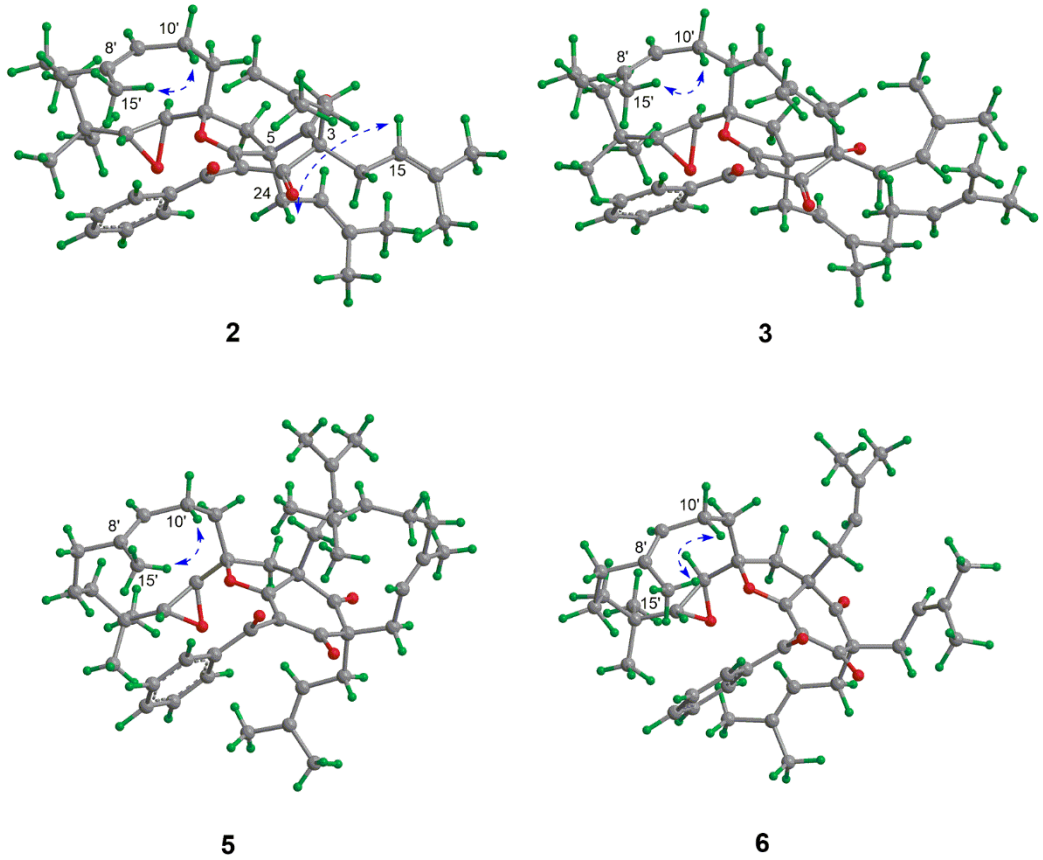
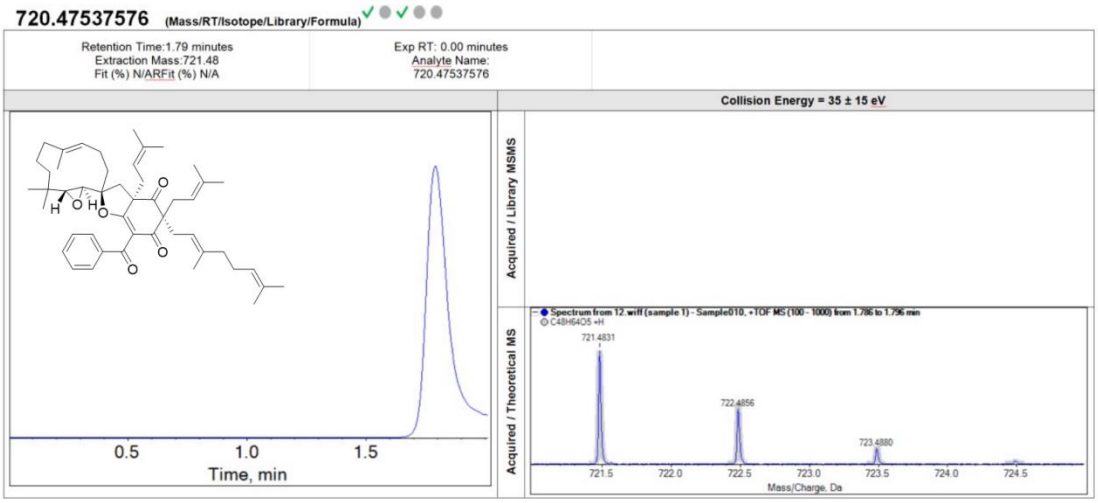


Fig. S2. Key NOESY correlations of **2**, **3**, **5**, and **6**.

Original Spectroscopic Data

Fig. S3. Positive HR-ESIMS spectrum of hyperkouytin A (**1**).



Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
720.47537576(GZ-34)	95%	C48H64O5	2093778	5	721.4827	721.4831	0.6	0.00	1.79	1.79	5.6%	N/A

Fig. S4. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin A (**1**).

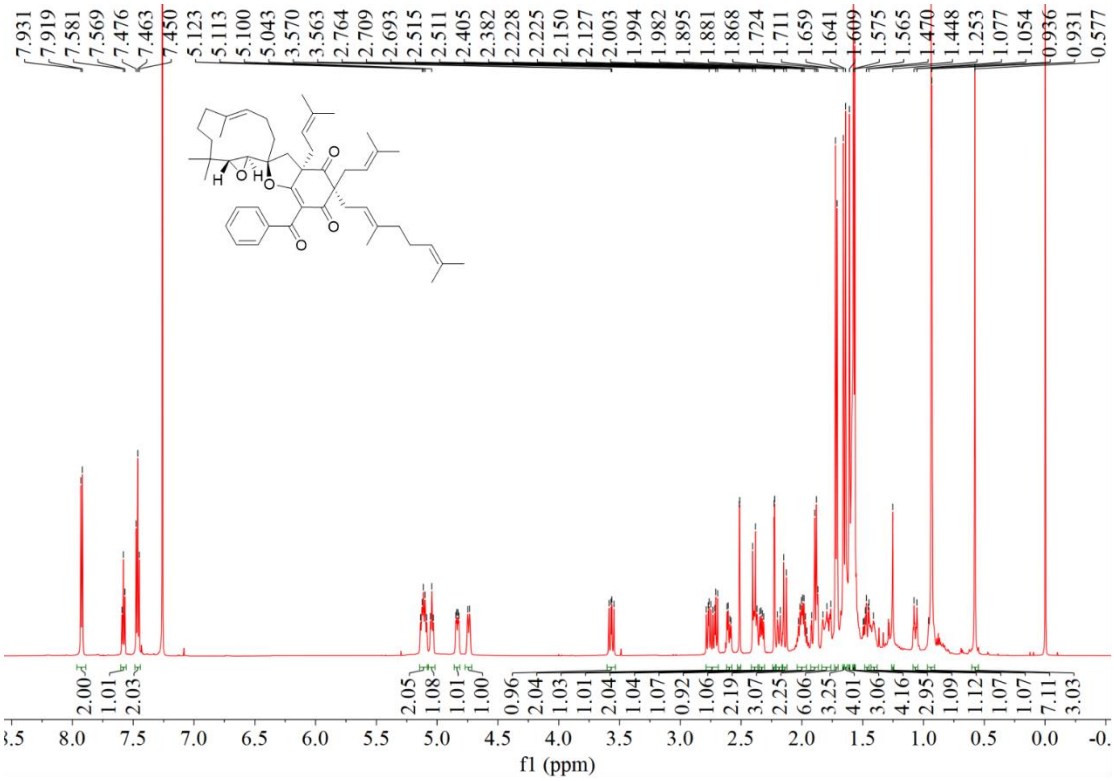


Fig. S5. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin A (**1**).

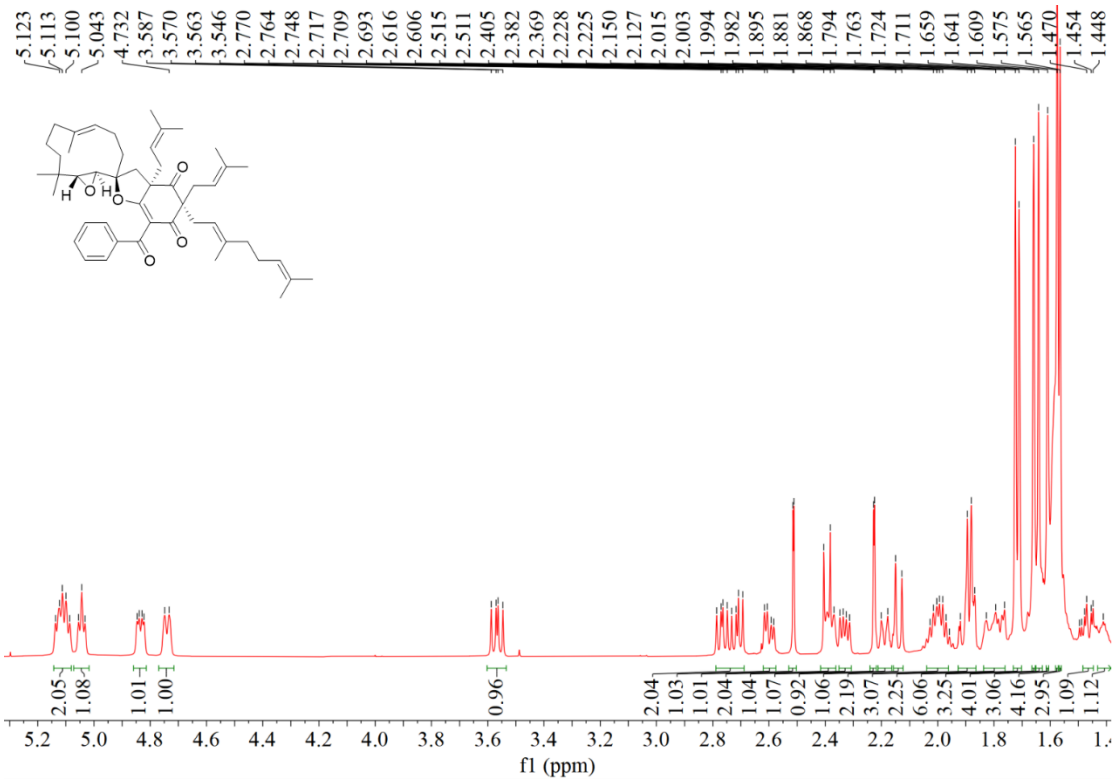


Fig. S6. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin A (**1**).

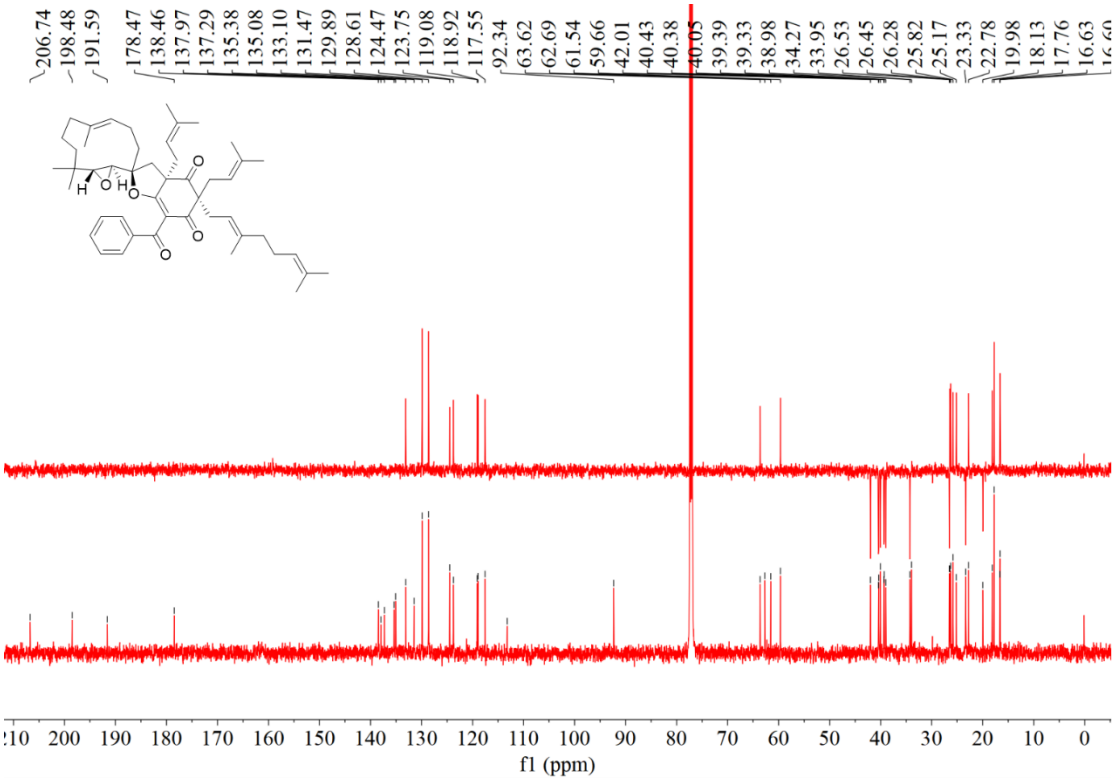


Fig. S7. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin A (**1**).

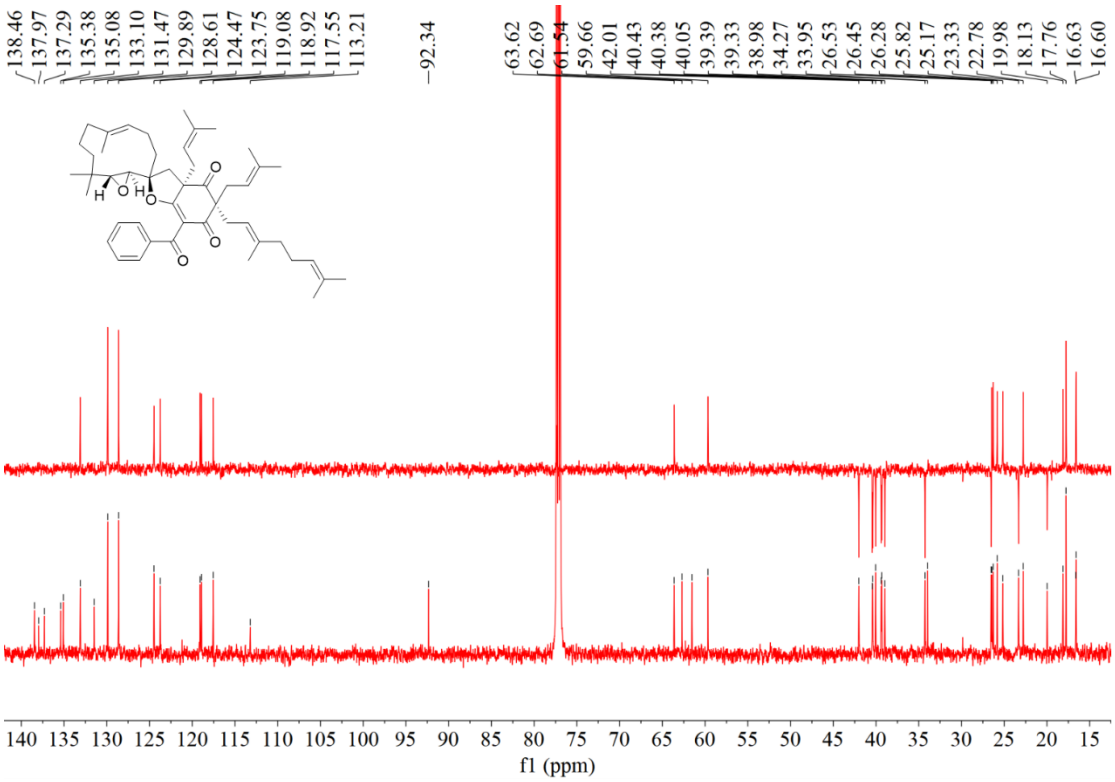


Fig. S8. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin A (**1**).

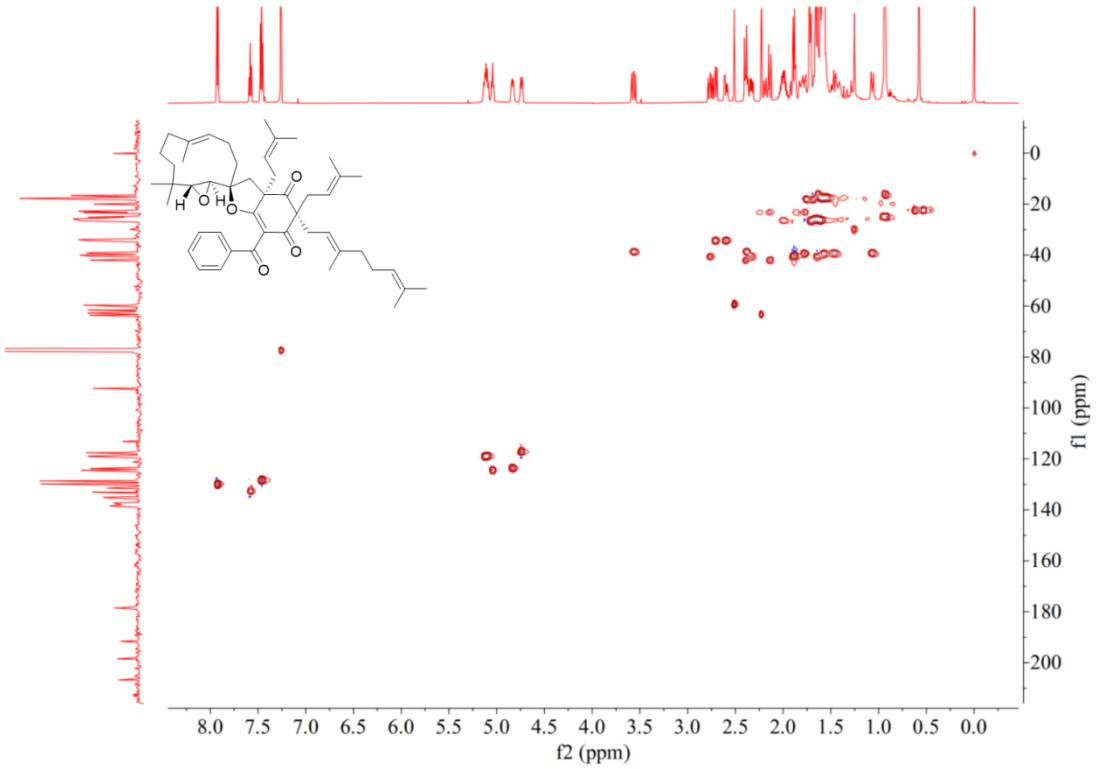


Fig. S9. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin A (**1**).

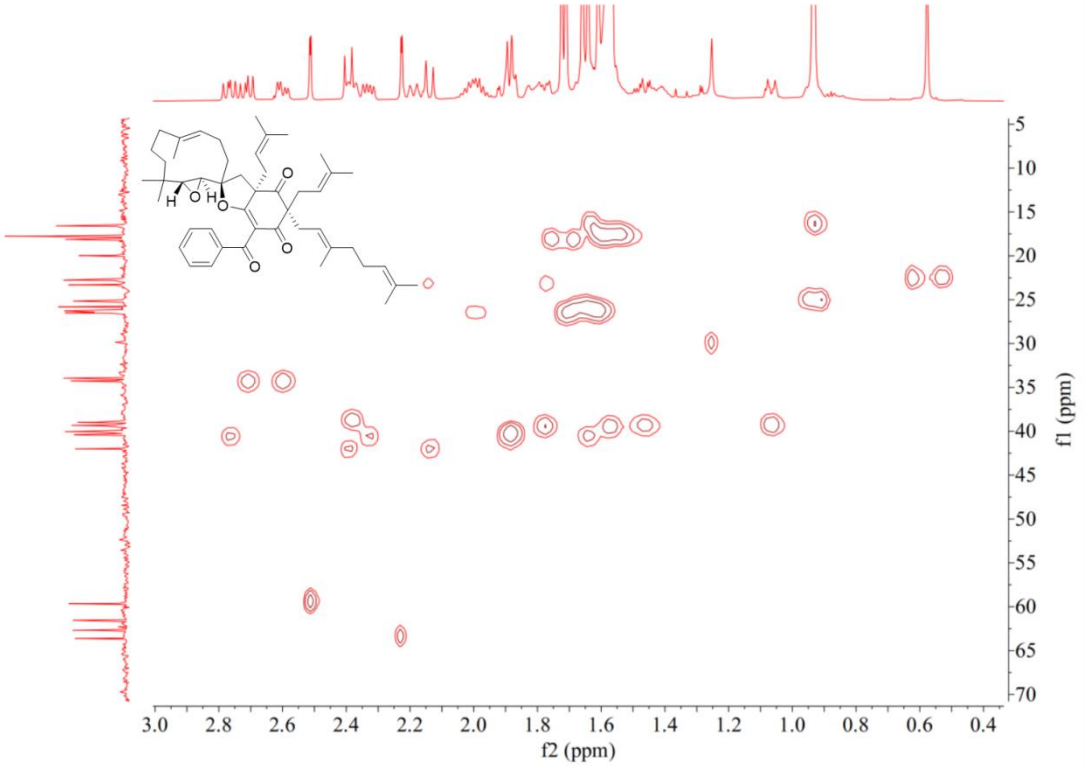


Fig. S10. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of hyperkouytin A (**1**).

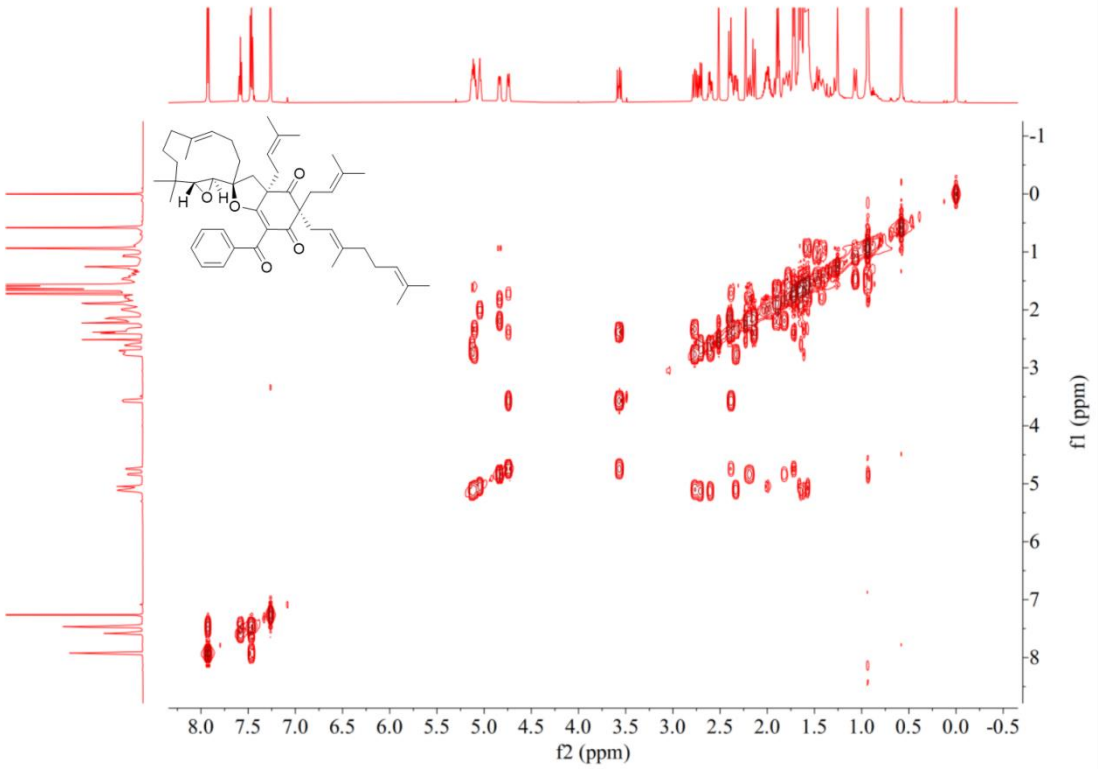


Fig. S11. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin A (**1**).

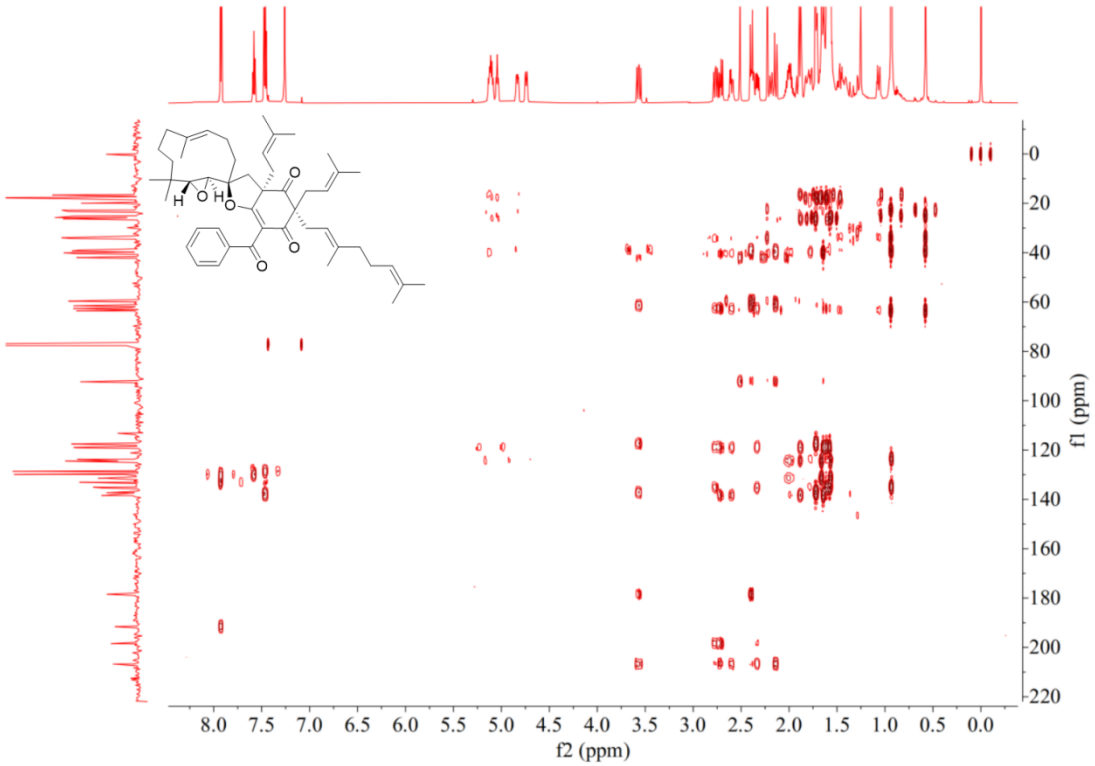


Fig. S12. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin A (**1**).

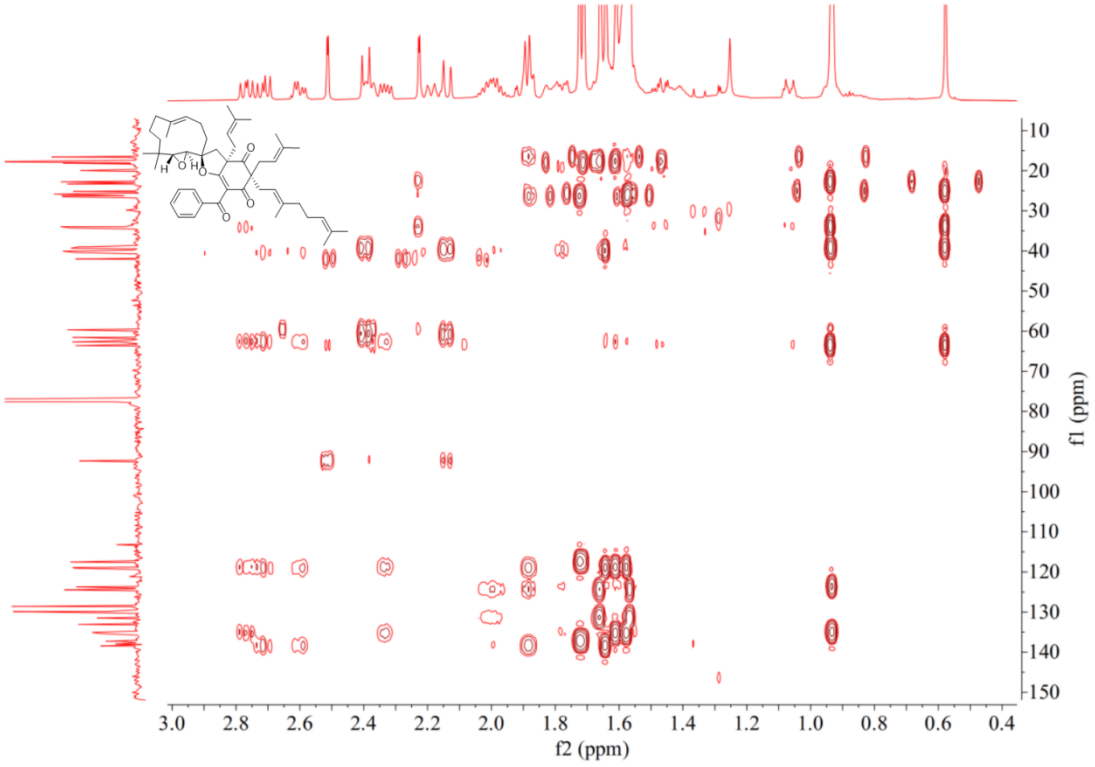


Fig. S13. NOESY (600 MHz, $CDCl_3$) spectrum of hyperkouytin A (**1**).

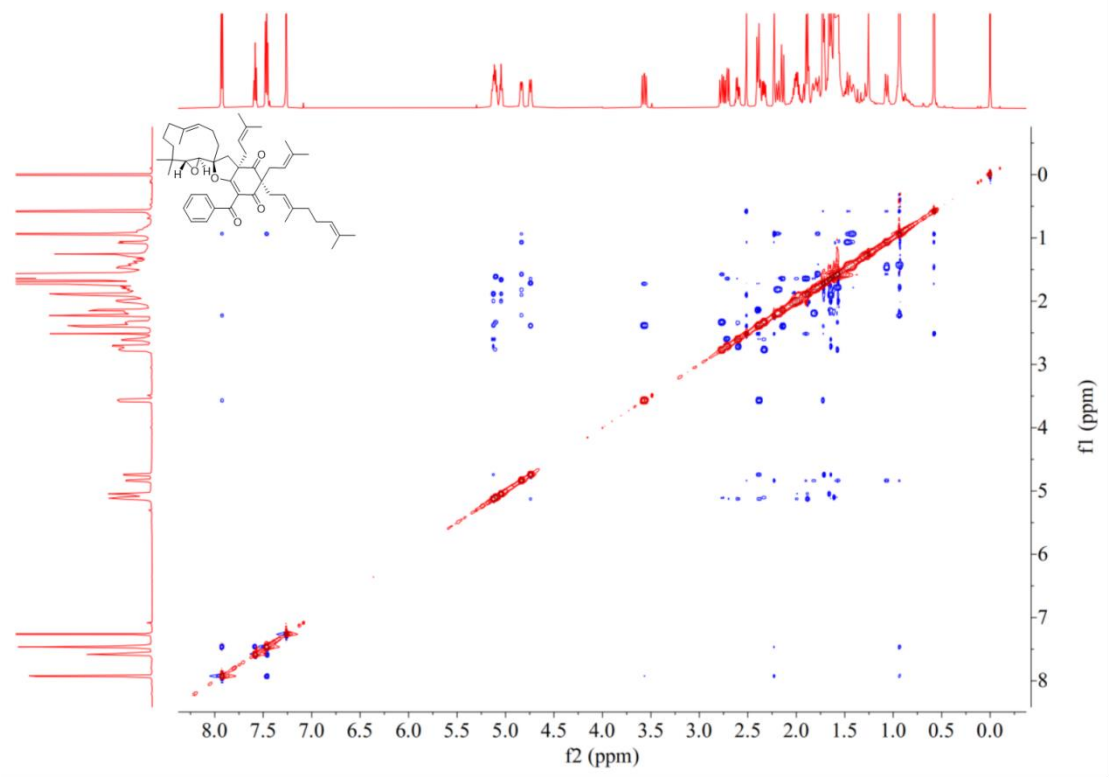


Fig. S14. IR spectrum of hyperkouytin A (**1**).

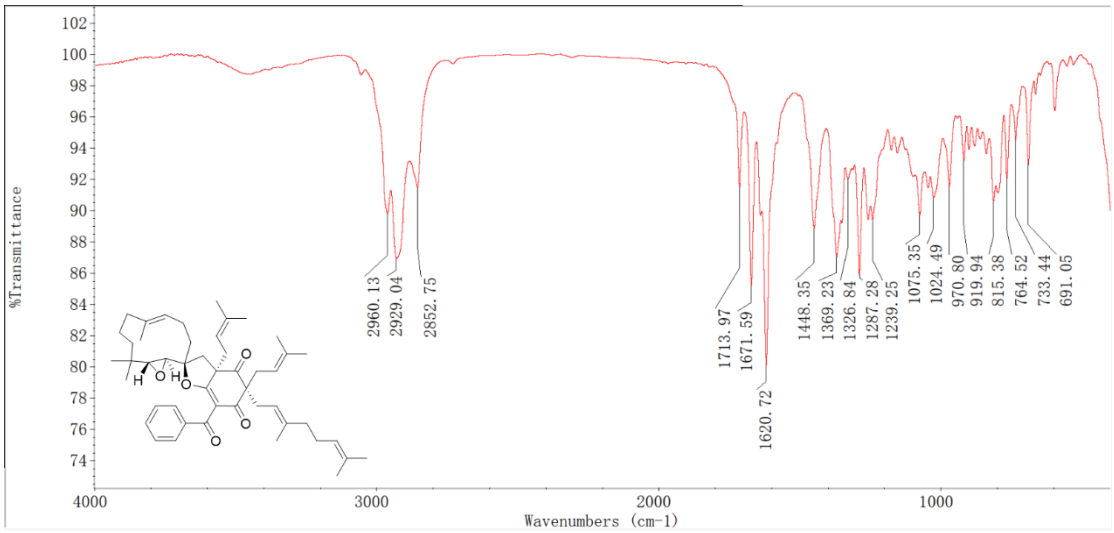


Fig. S15. UV spectrum of hyperkouytin A (**1**).

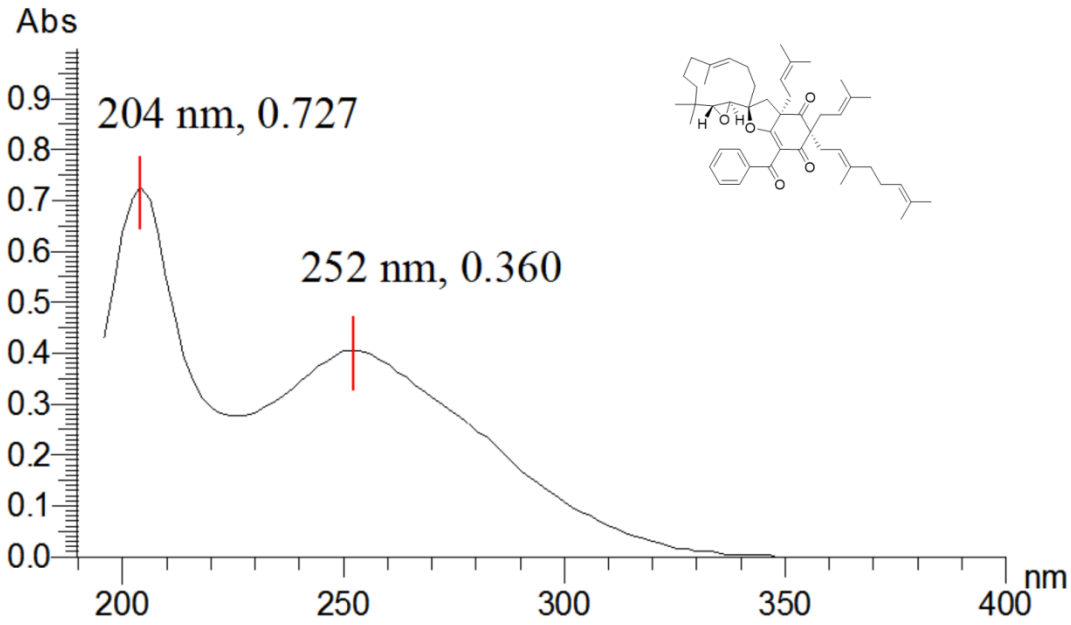
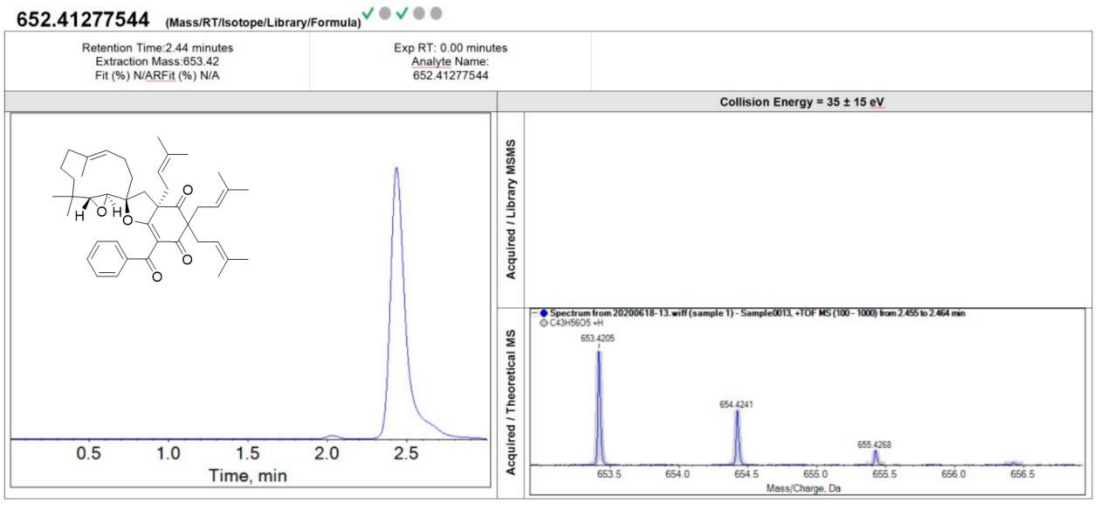


Fig. S16. Positive HR-ESIMS spectrum of hyperkouytin B (**2**).



Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
652.41277544	98%	C43H56O5	105720	5	653.4201	653.4205	0.7	0.00	2.44	2.44	0.5%	N/A

Fig. S17. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin B (**2**).

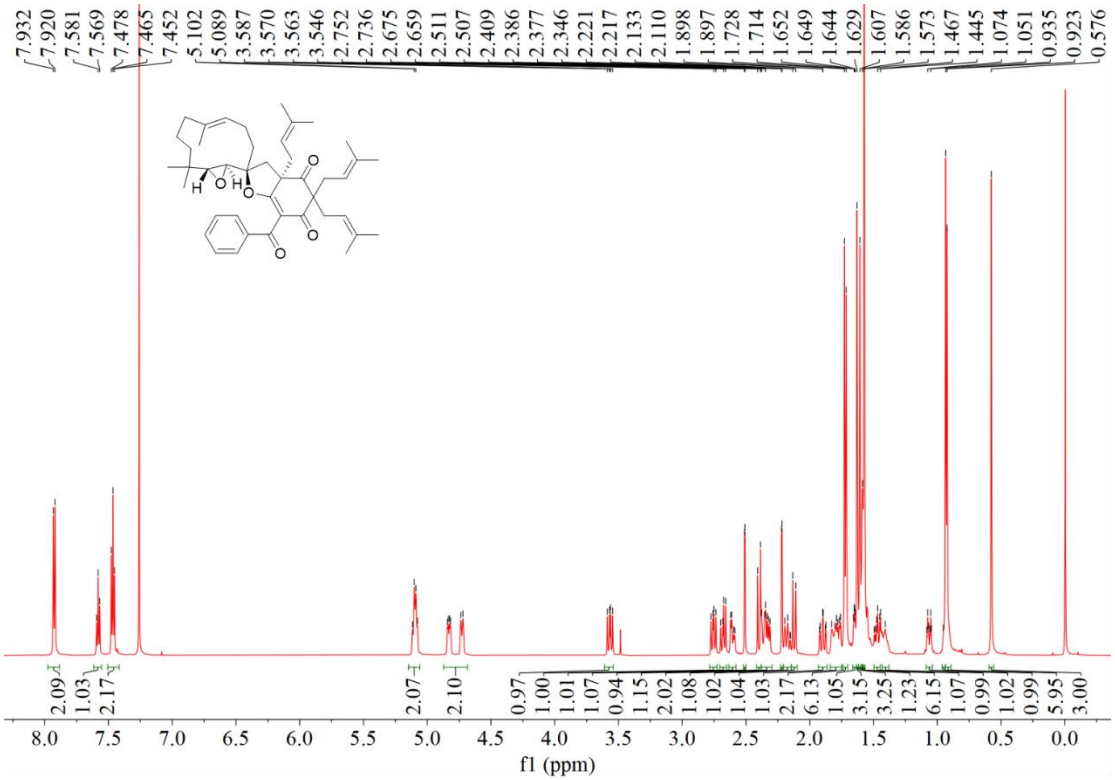


Fig. S18. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin B (**2**).

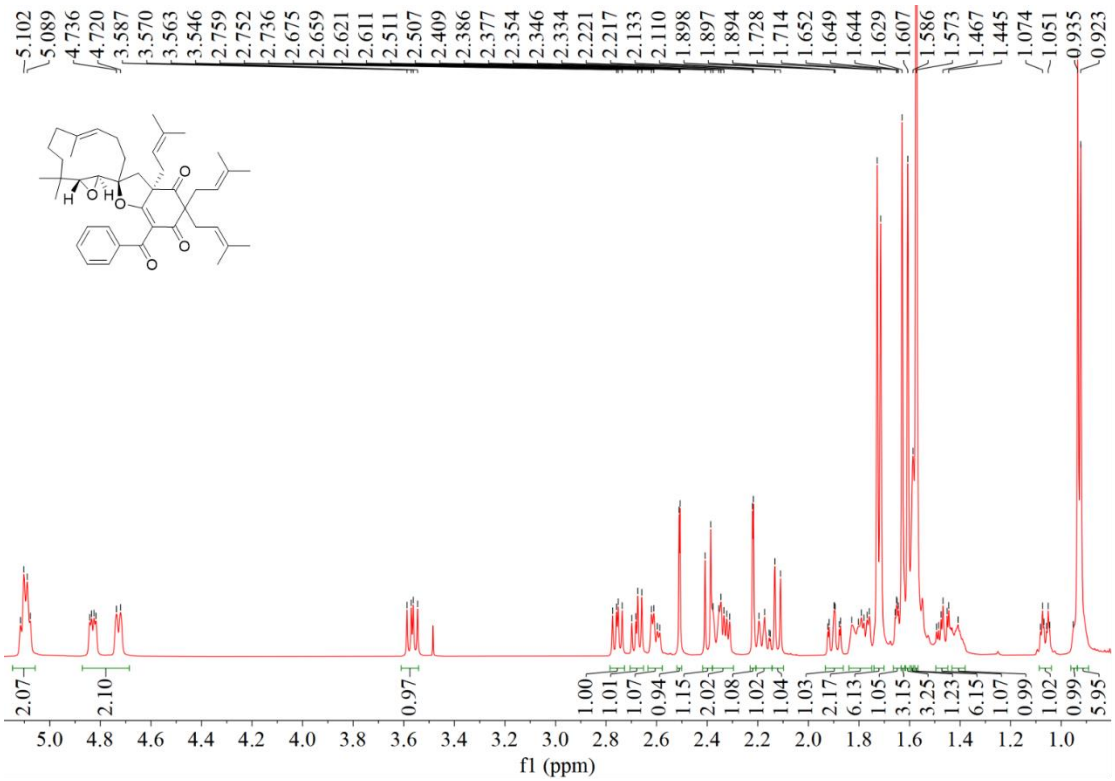


Fig. S19. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin B (**2**).

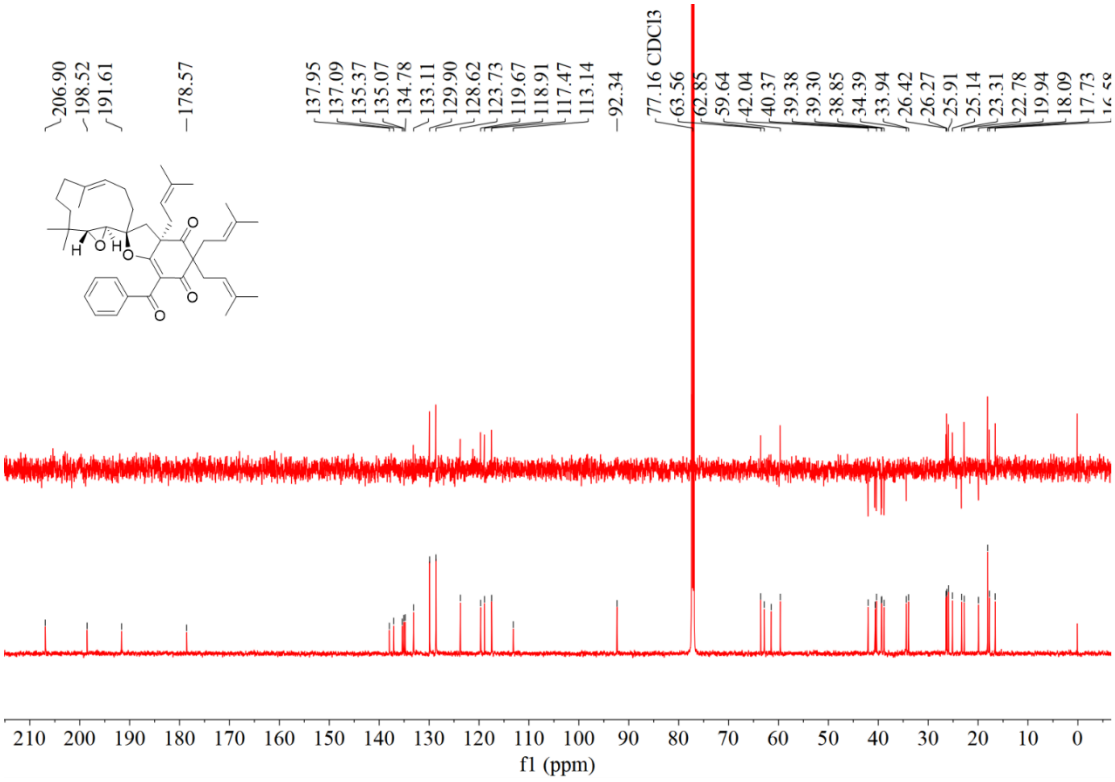


Fig. S20. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin B (**2**).

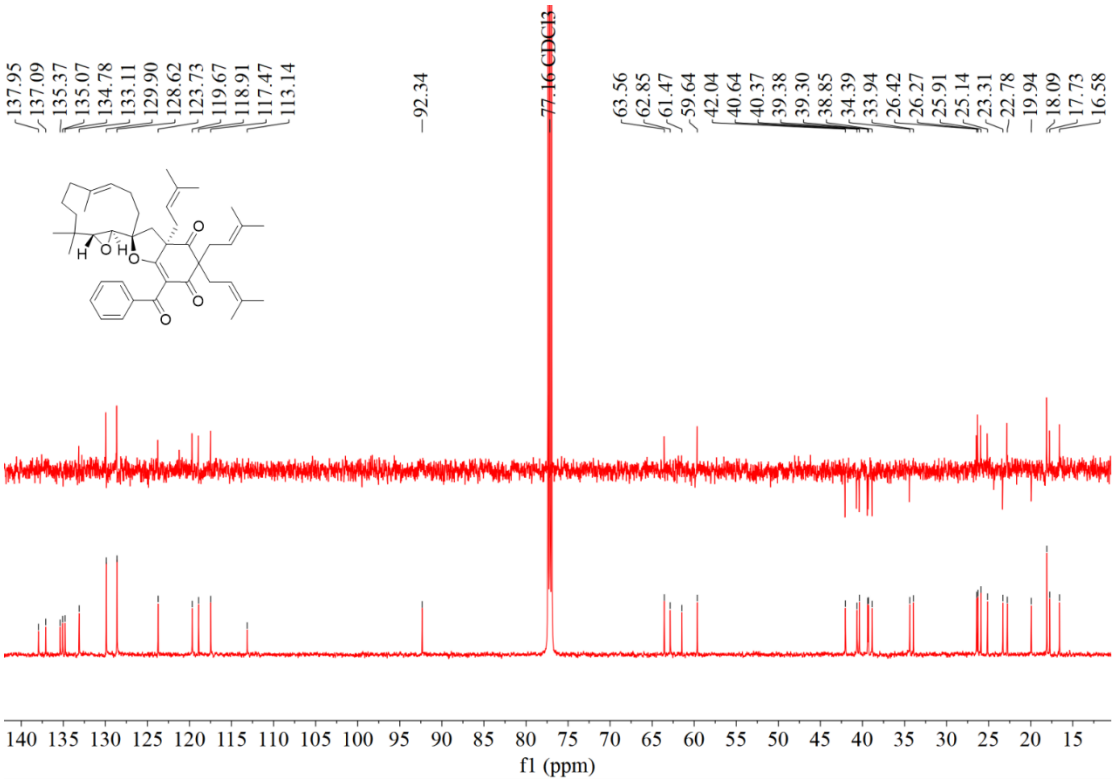


Fig. S21. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin B (**2**).

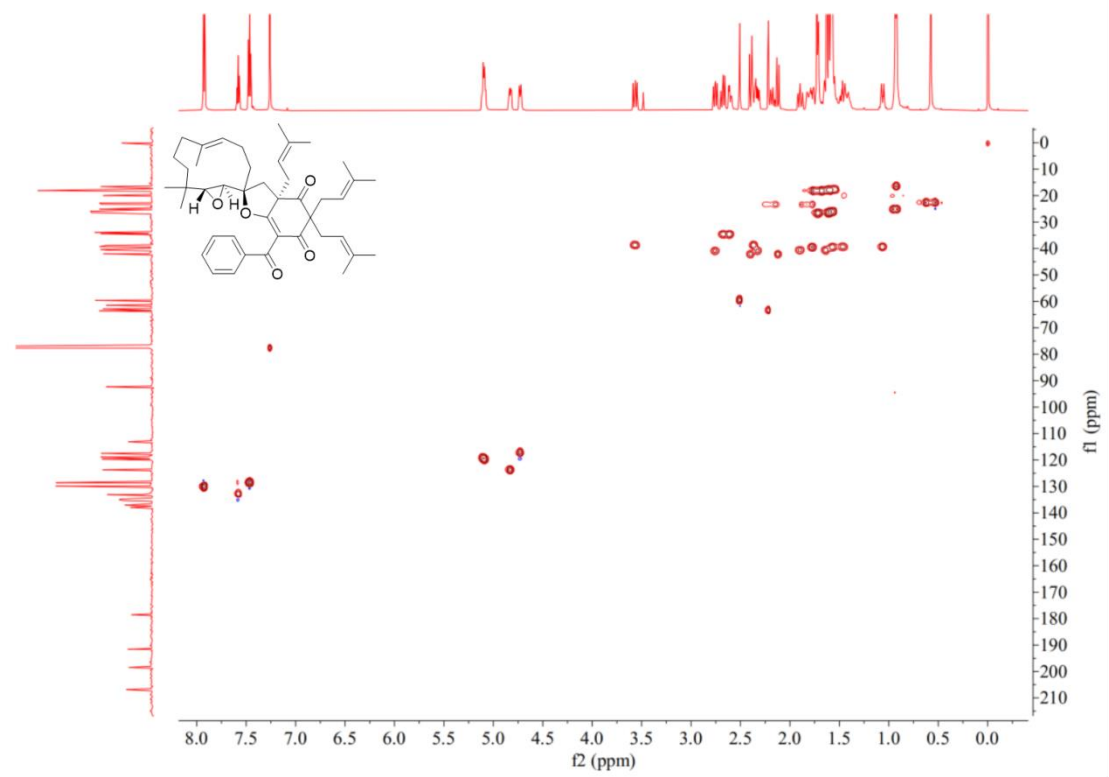


Fig. S22. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin B (**2**).

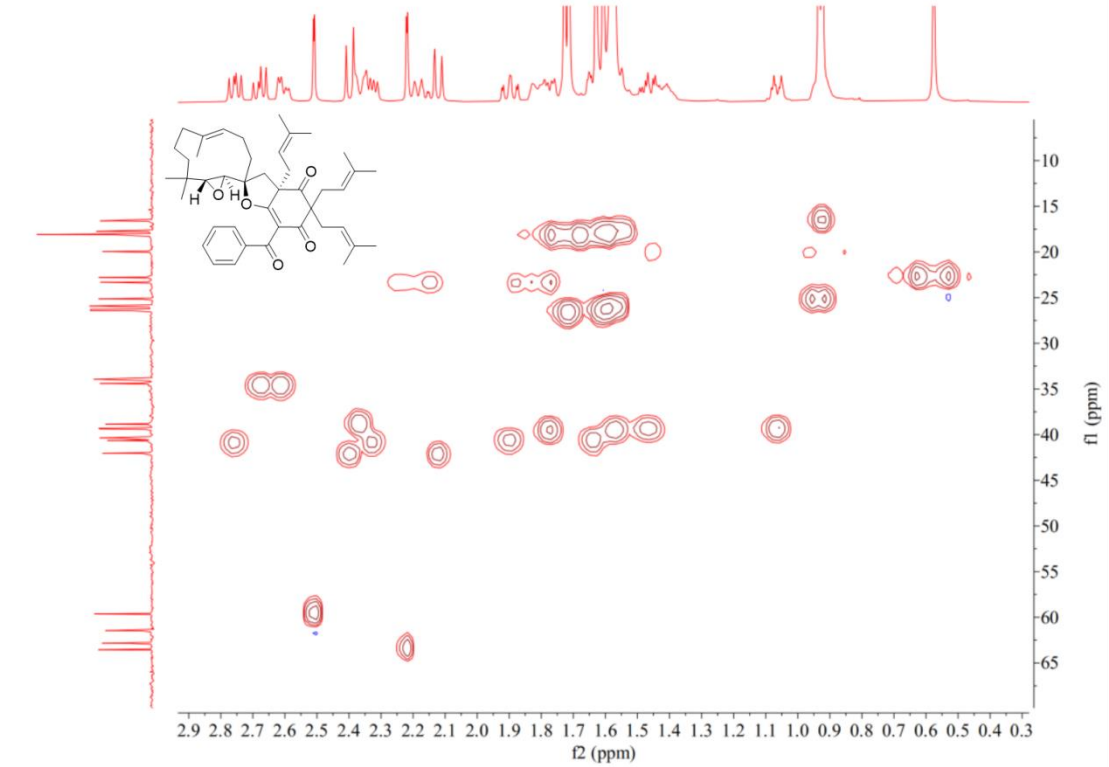


Fig. S23. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of hyperkouytin B (**2**).

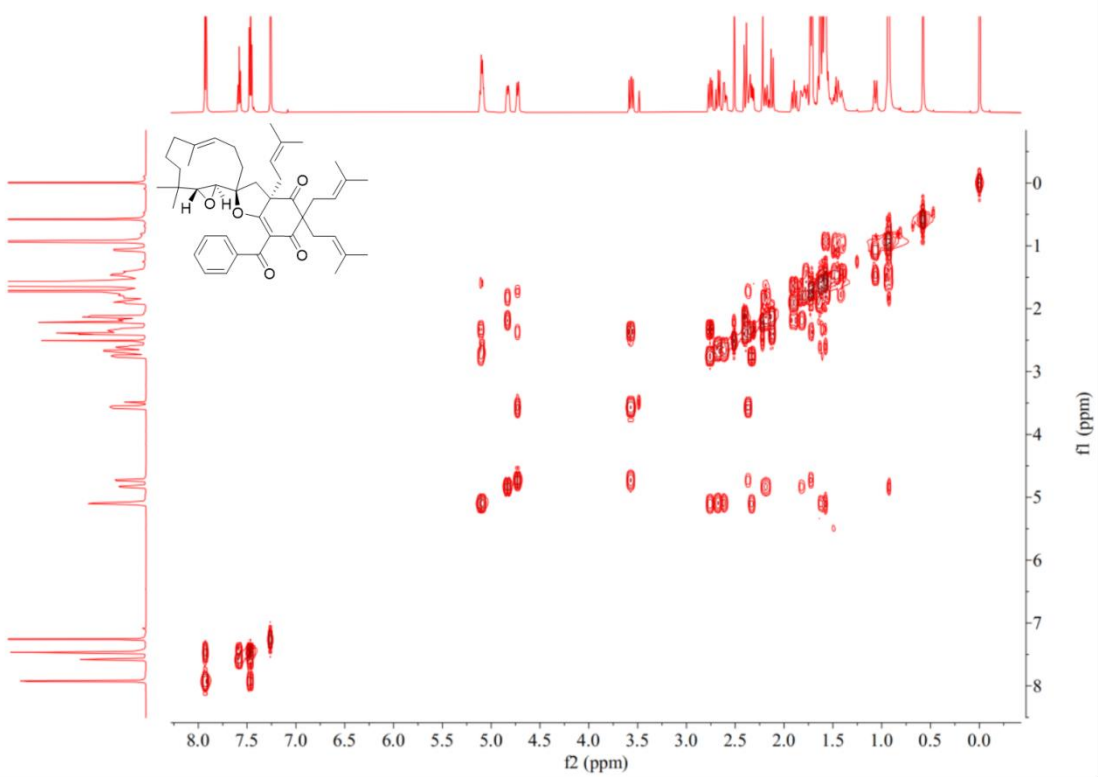


Fig. S24. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin B (**2**).

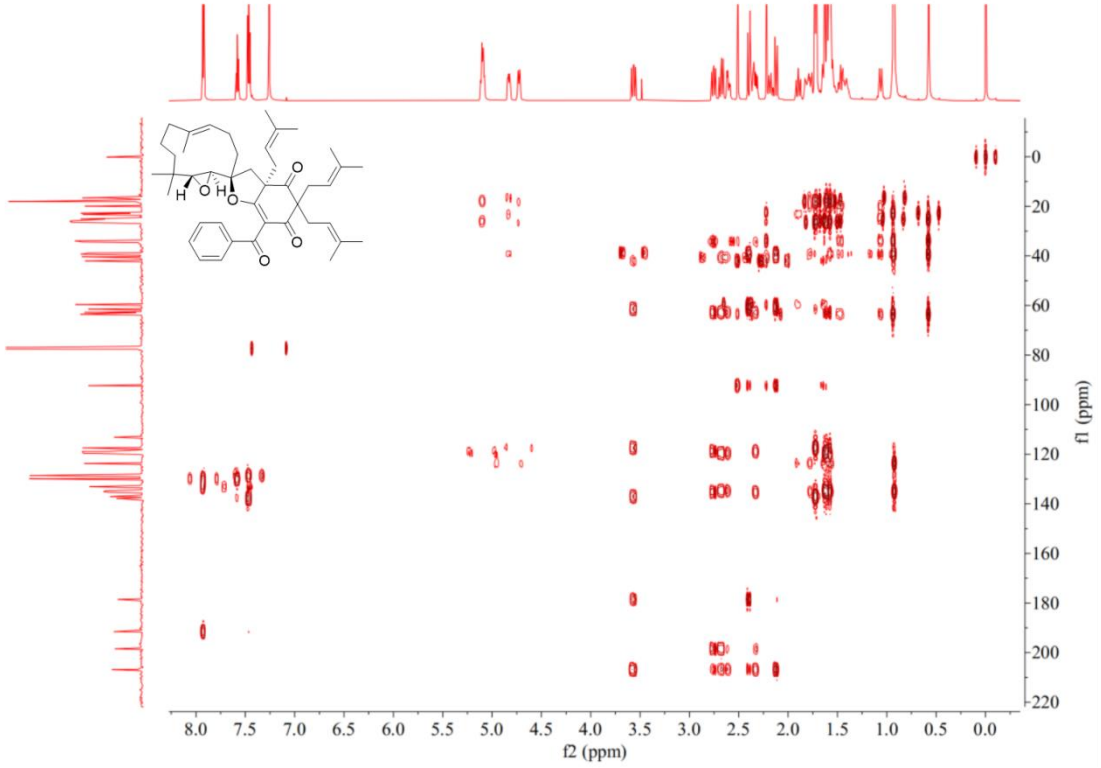


Fig. S25. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin B (**2**).

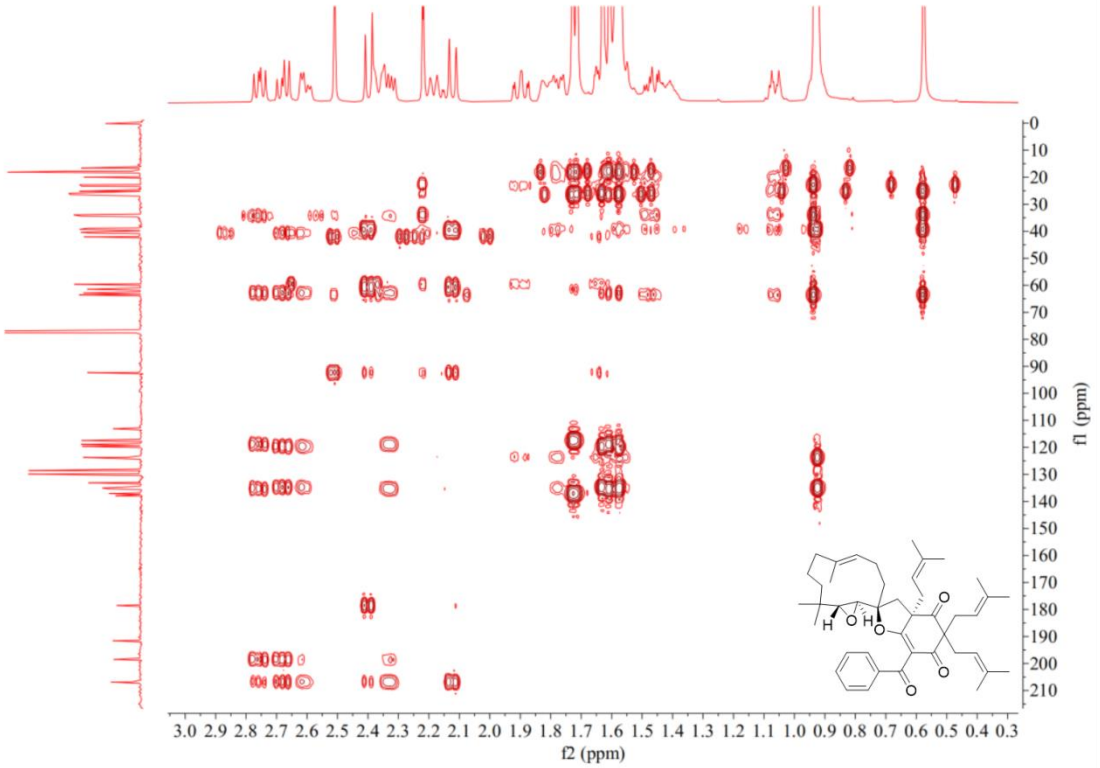


Fig. S26. NOESY (600 MHz, $CDCl_3$) spectrum of hyperkouytin B (**2**).

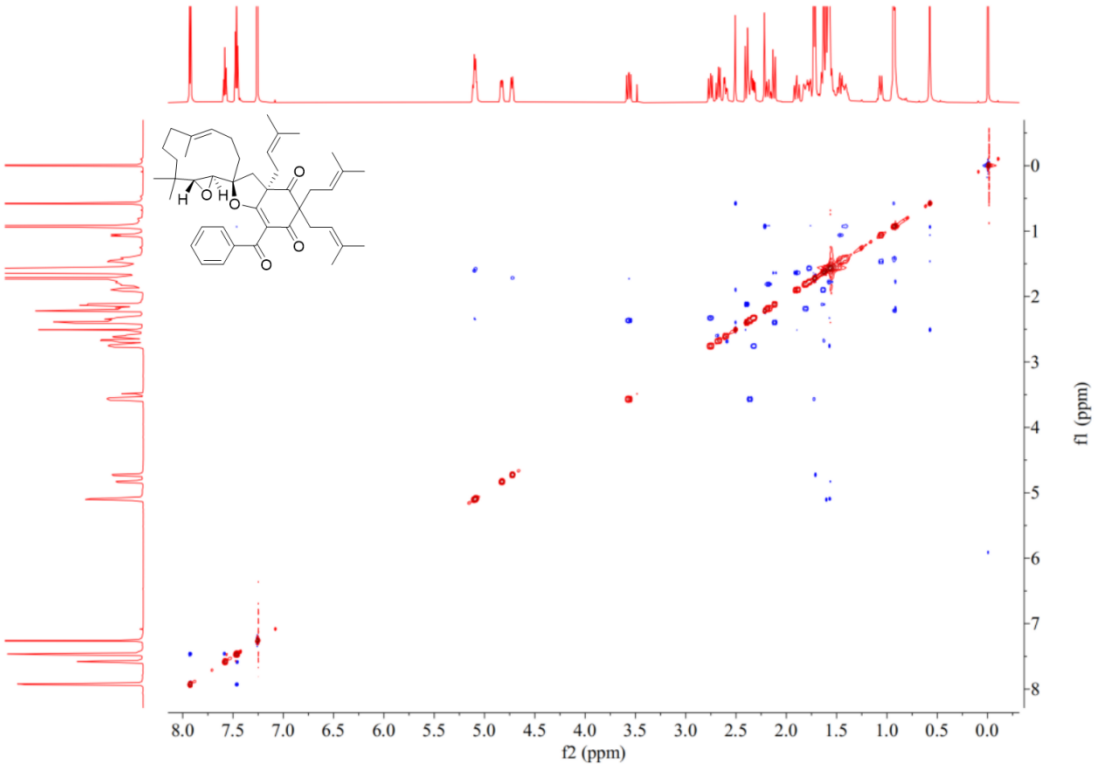


Fig. S27. IR spectrum of hyperkouytin B (**2**).

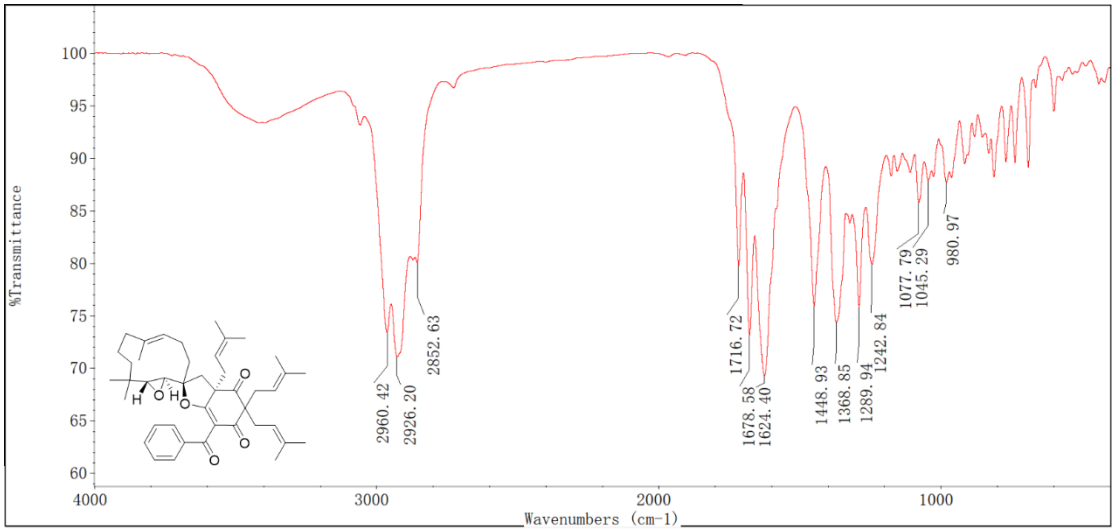


Fig. S28. UV spectrum of hyperkouytin B (**2**).

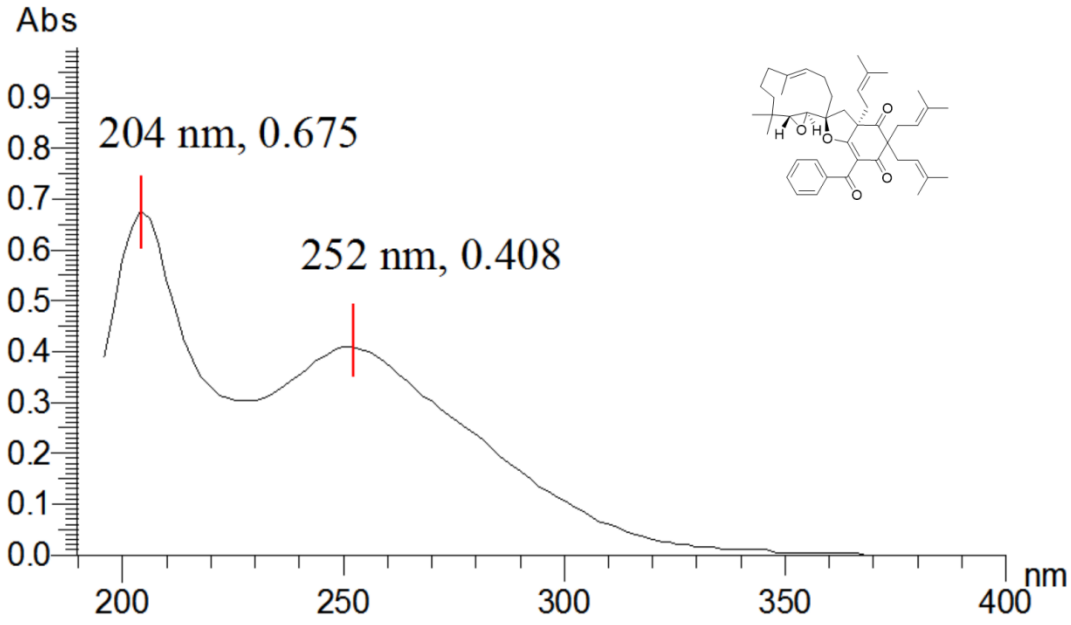
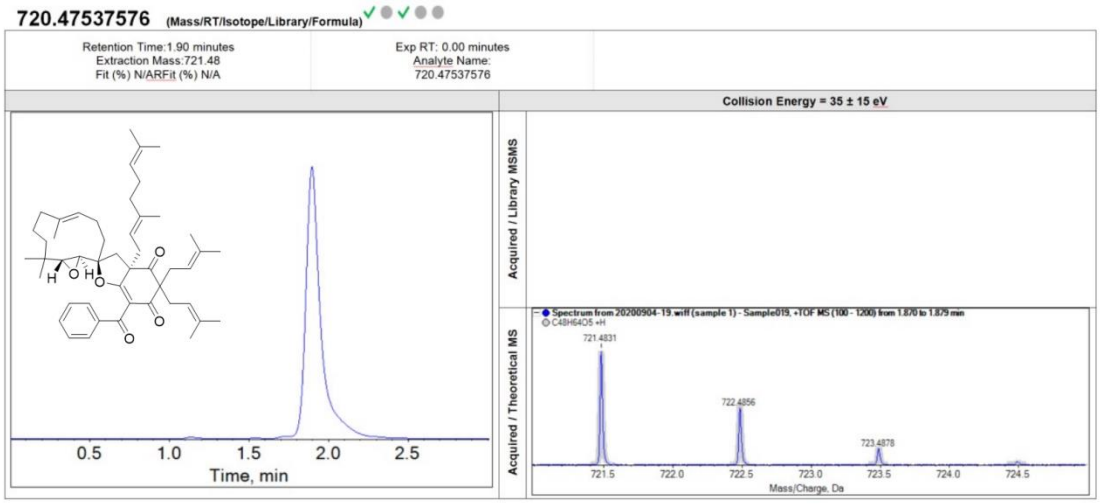


Fig. S29. Positive HR-ESIMS spectrum of hyperkouytin C (**3**).



Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
720.47537576(GZ-33)	96%	C48H64O5	1253500	5	721.4827	721.4831	0.6	0.00	1.90	1.90	4.3%	N/A

Fig. S30. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin C (**3**).

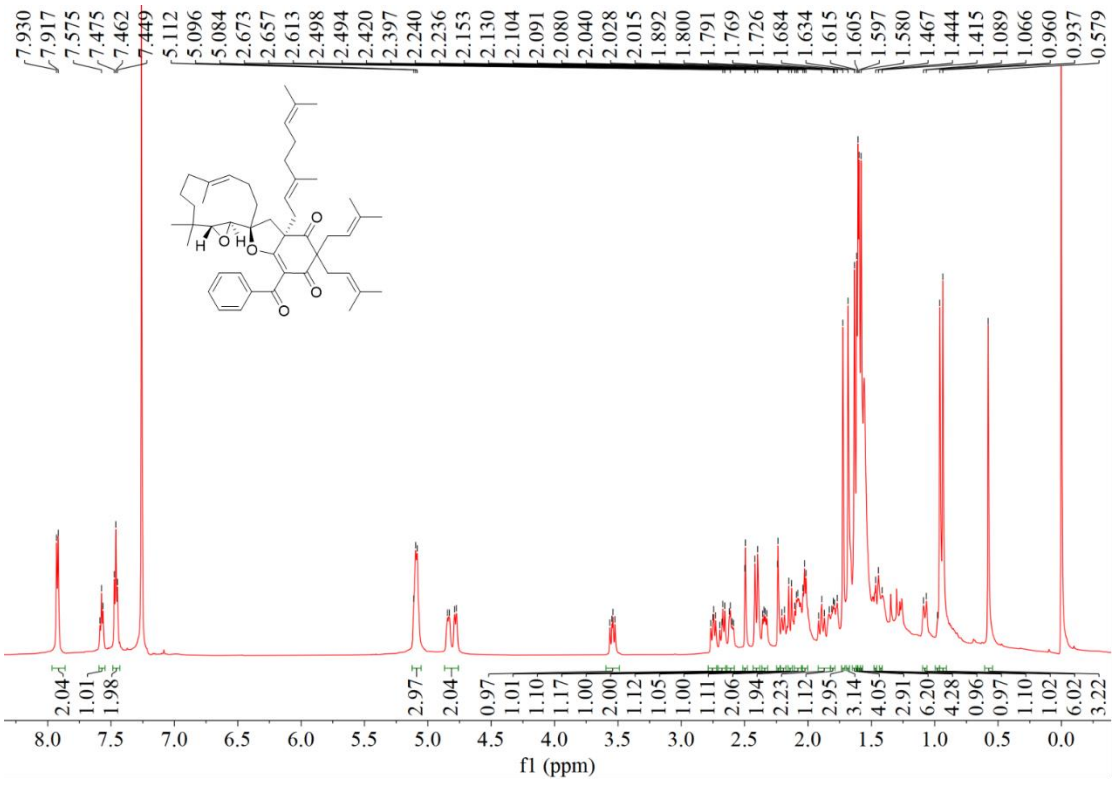


Fig. S31. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin C (**3**).

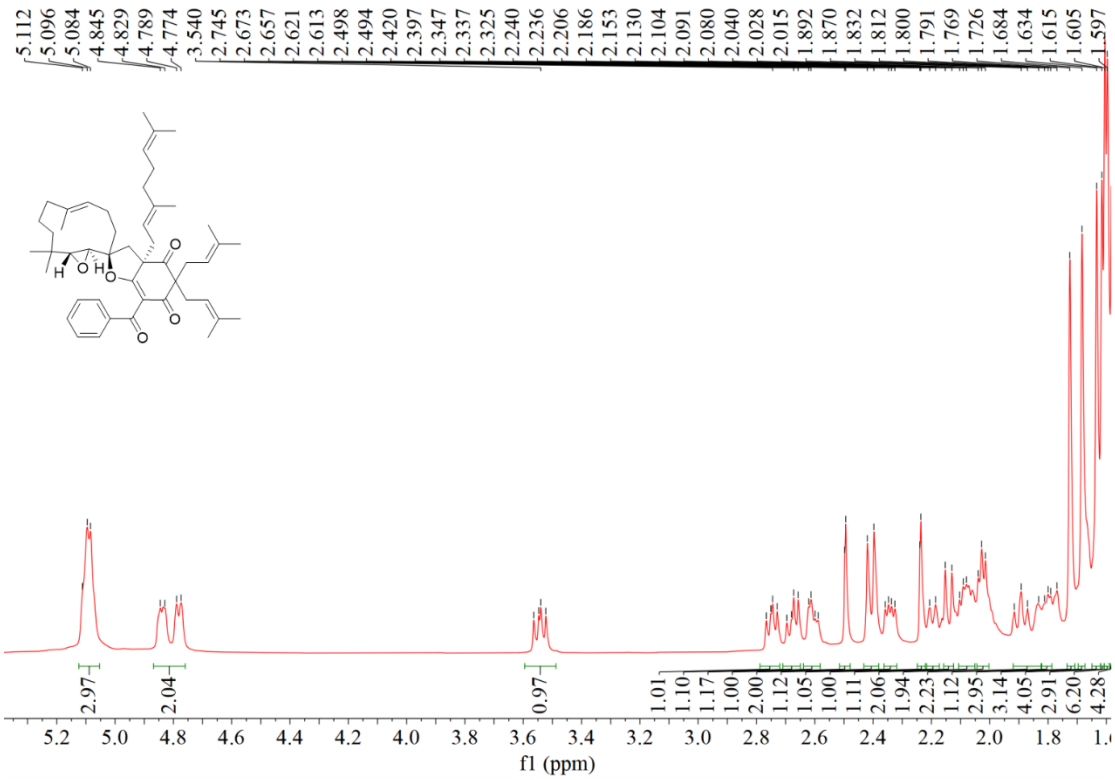


Fig. S32. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin C (**3**).

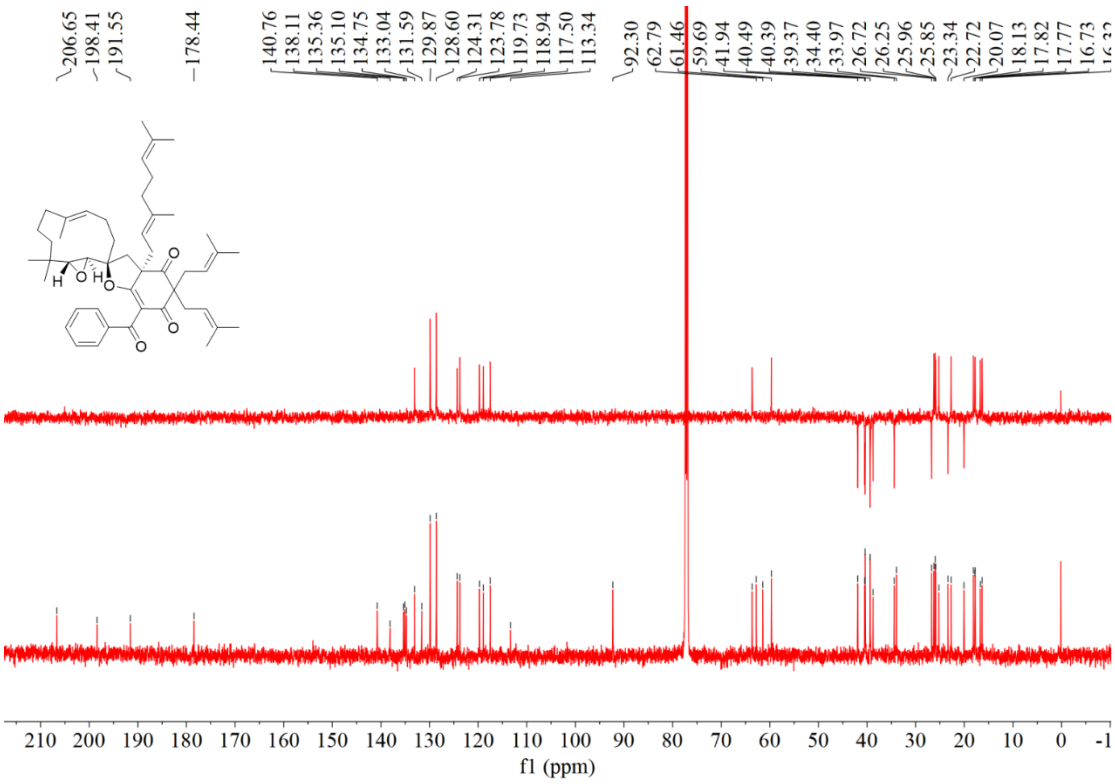


Fig. S33. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin C (**3**).

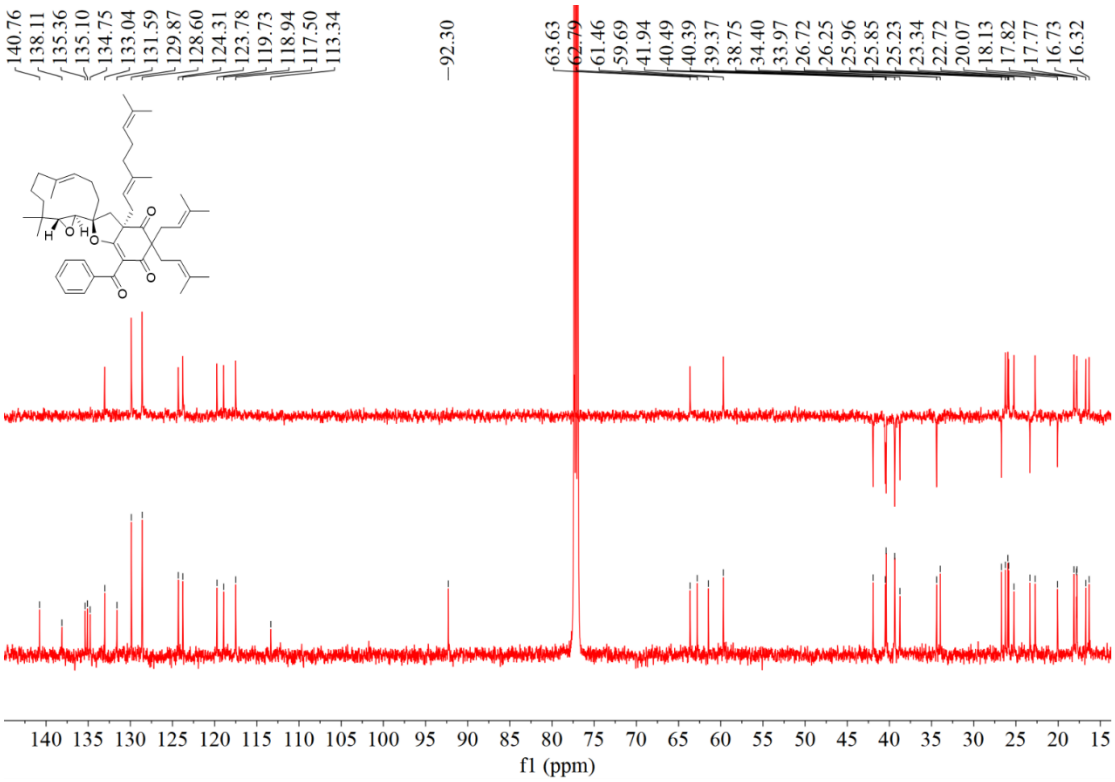


Fig. S34. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin C (**3**).

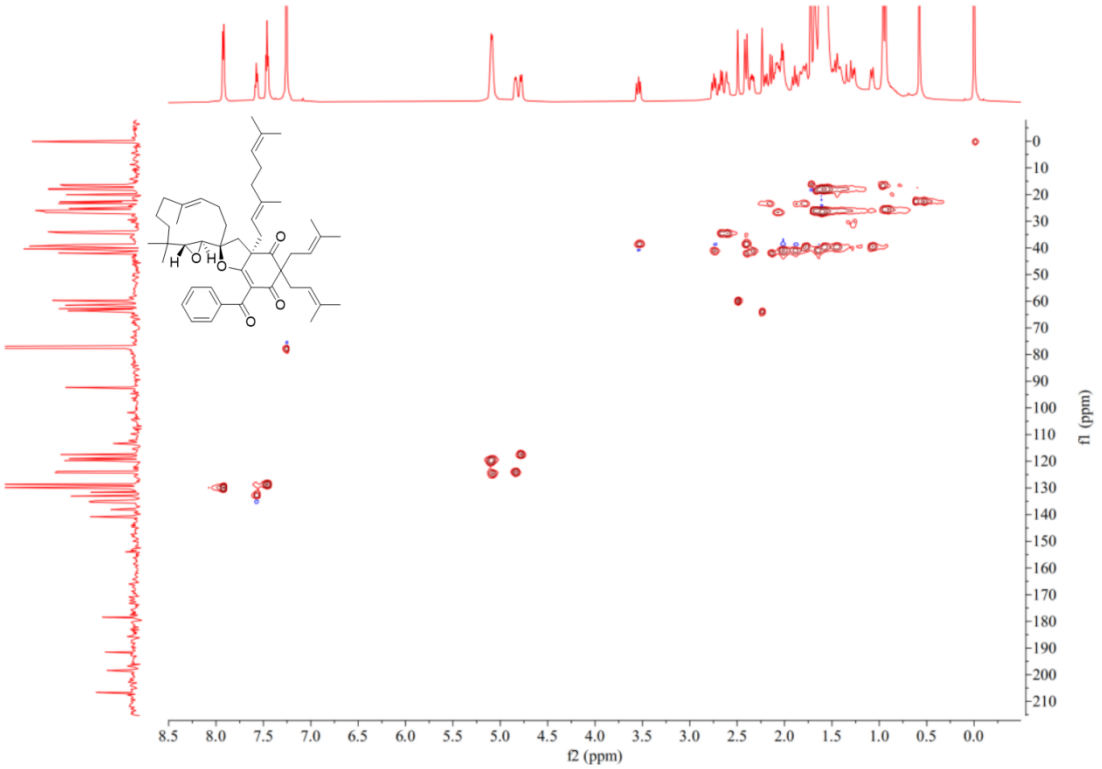


Fig. S35. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin C (**3**).

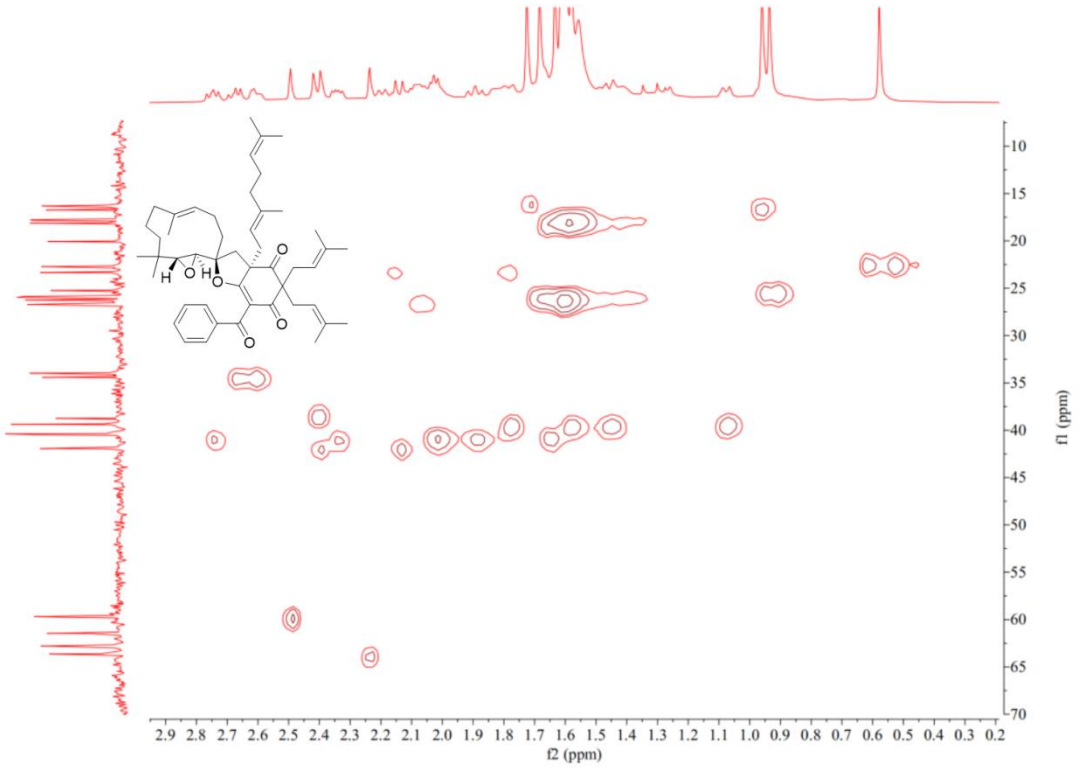


Fig. S36. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of hyperkouytin C (**3**).

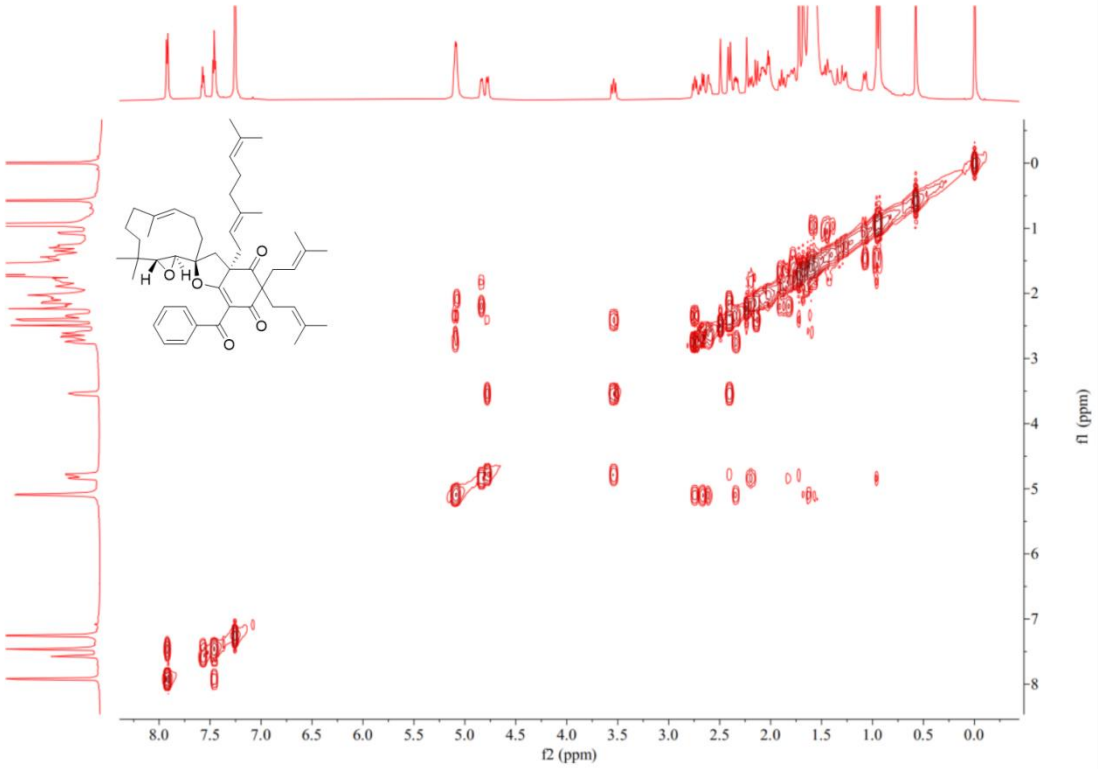


Fig. S37. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin C (**3**).

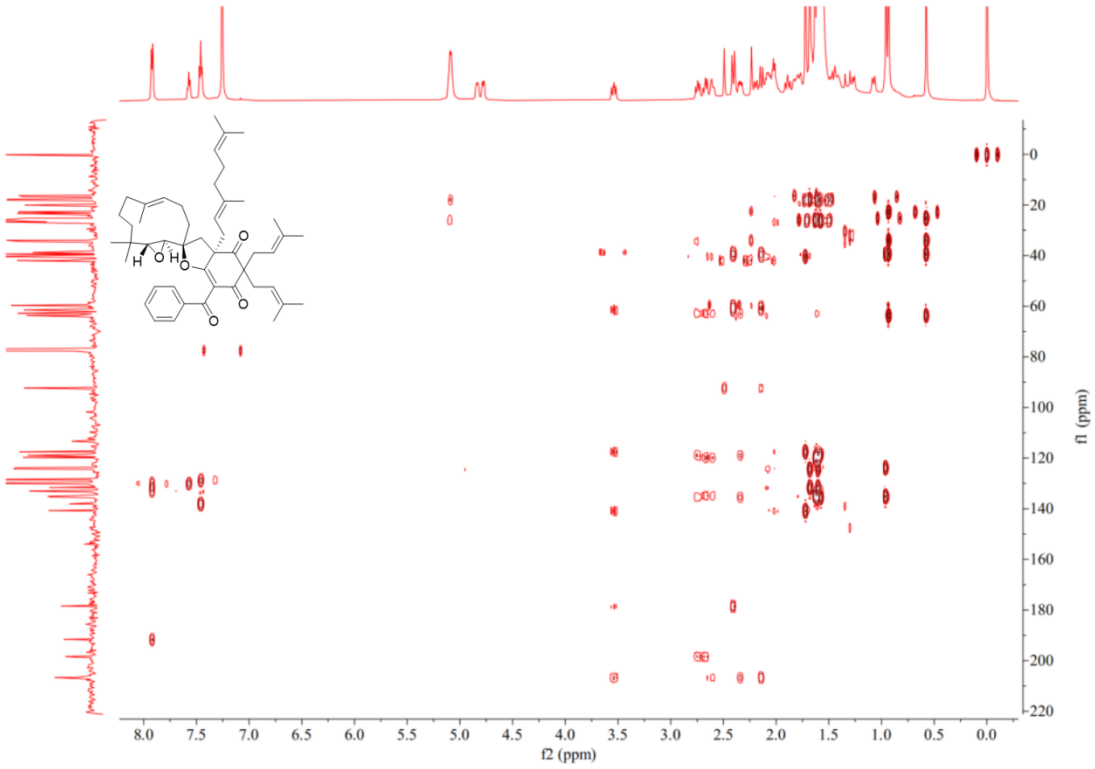


Fig. S38. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin C (**3**).

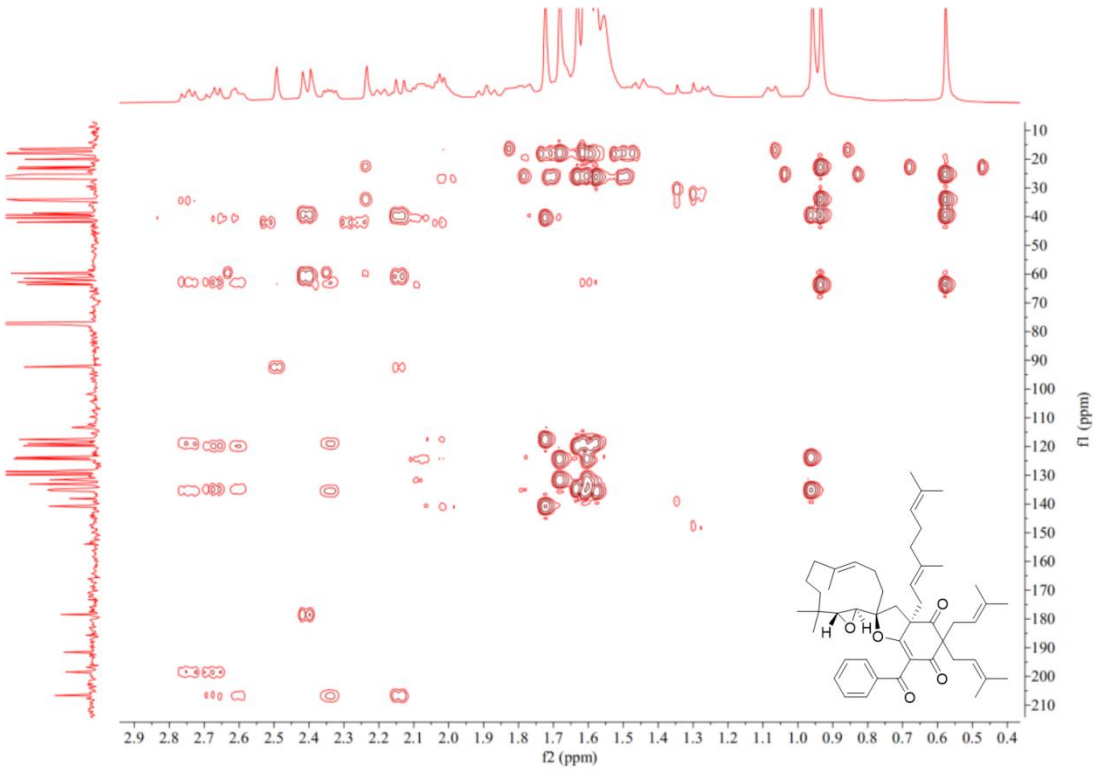


Fig. S39. NOESY (600 MHz, $CDCl_3$) spectrum of hyperkouytin C (**3**).

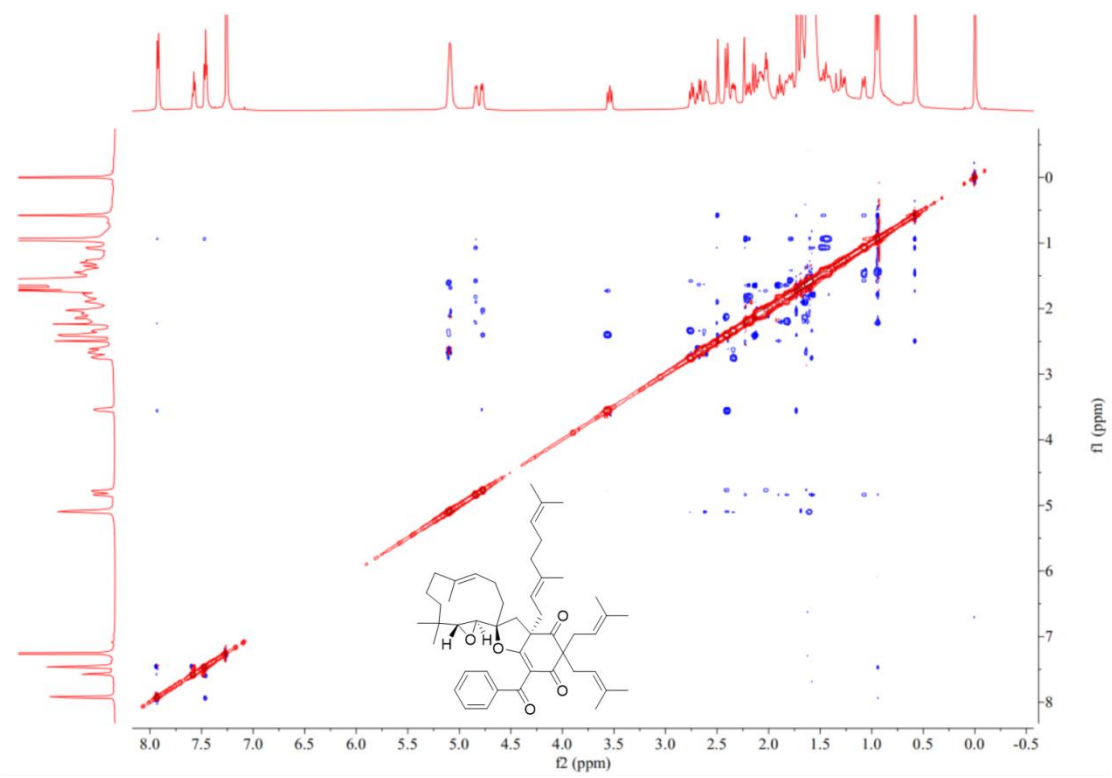


Fig. S40. IR spectrum of hyperkouytin C (**3**).

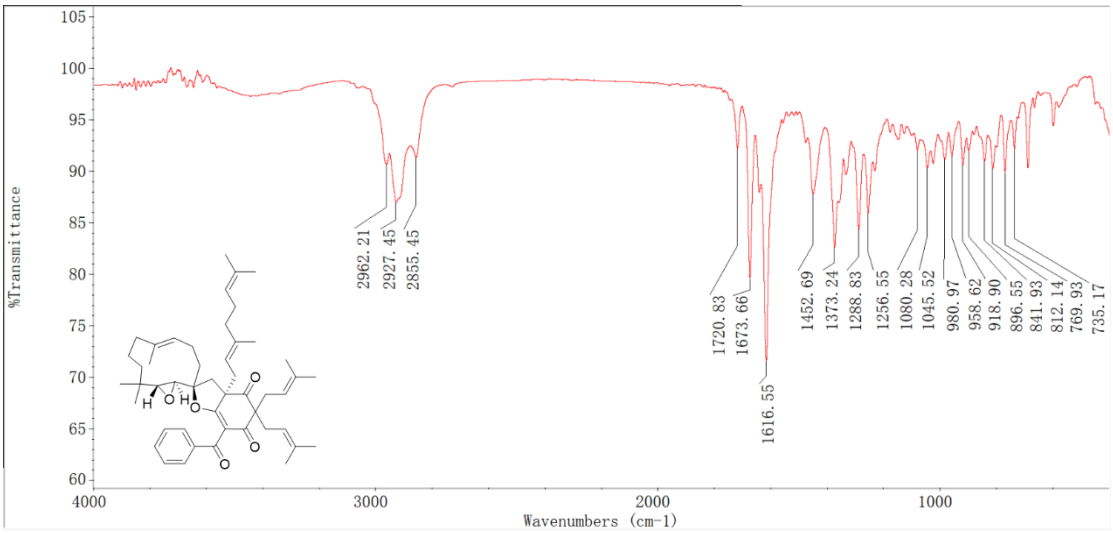


Fig. S41. UV spectrum of hyperkouytin C (**3**).

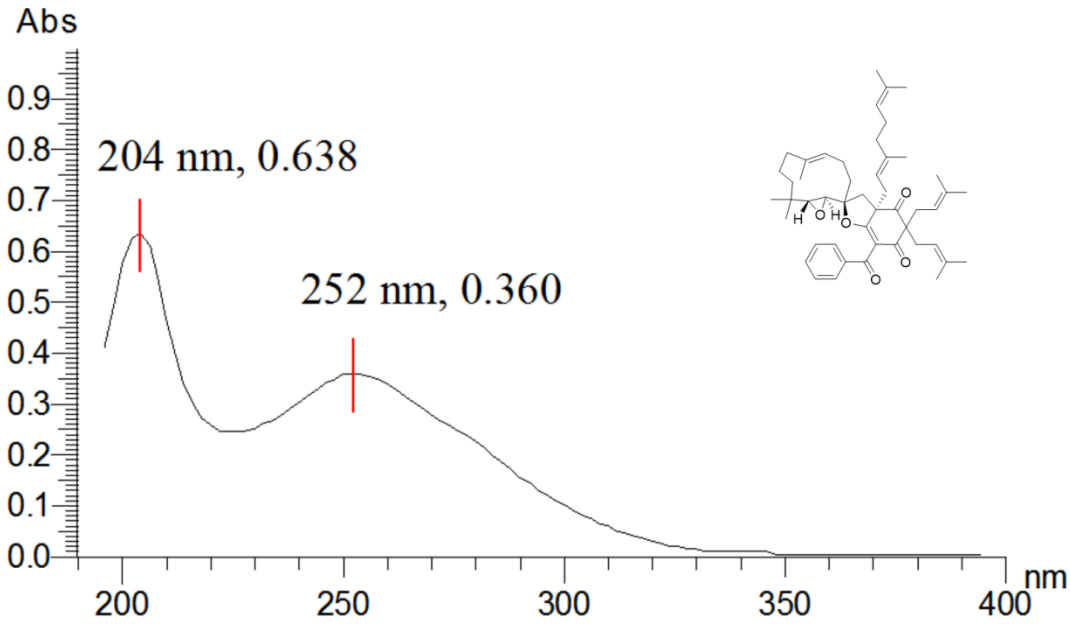
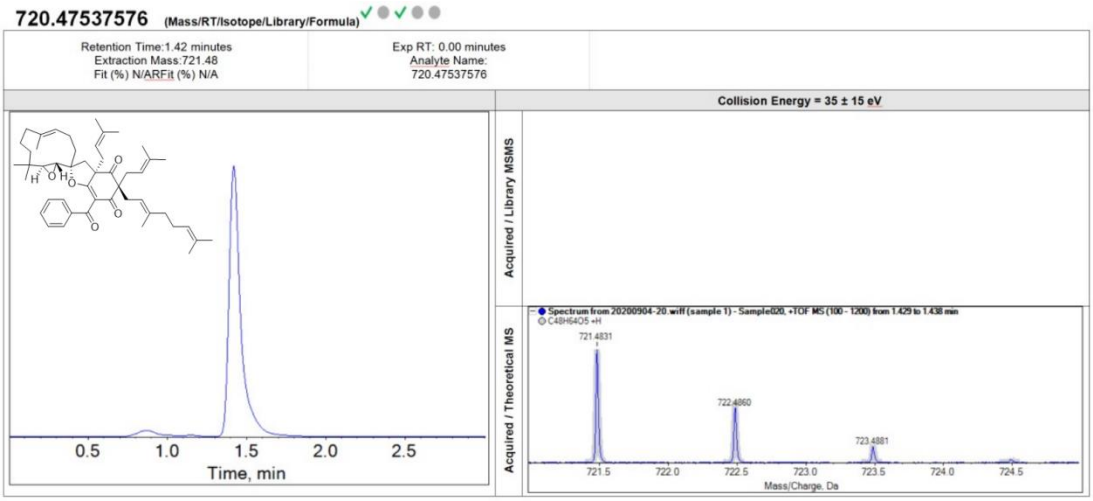


Fig. S42. Positive HR-ESIMS spectrum of hyperkouytin D (**4**).



Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
720.47537576(GZ-30)	94%	C48H64O5	511589	5	721.4827	721.4831	0.6	0.00	1.42	1.42	6.3%	N/A

Fig. S43. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin D (**4**).

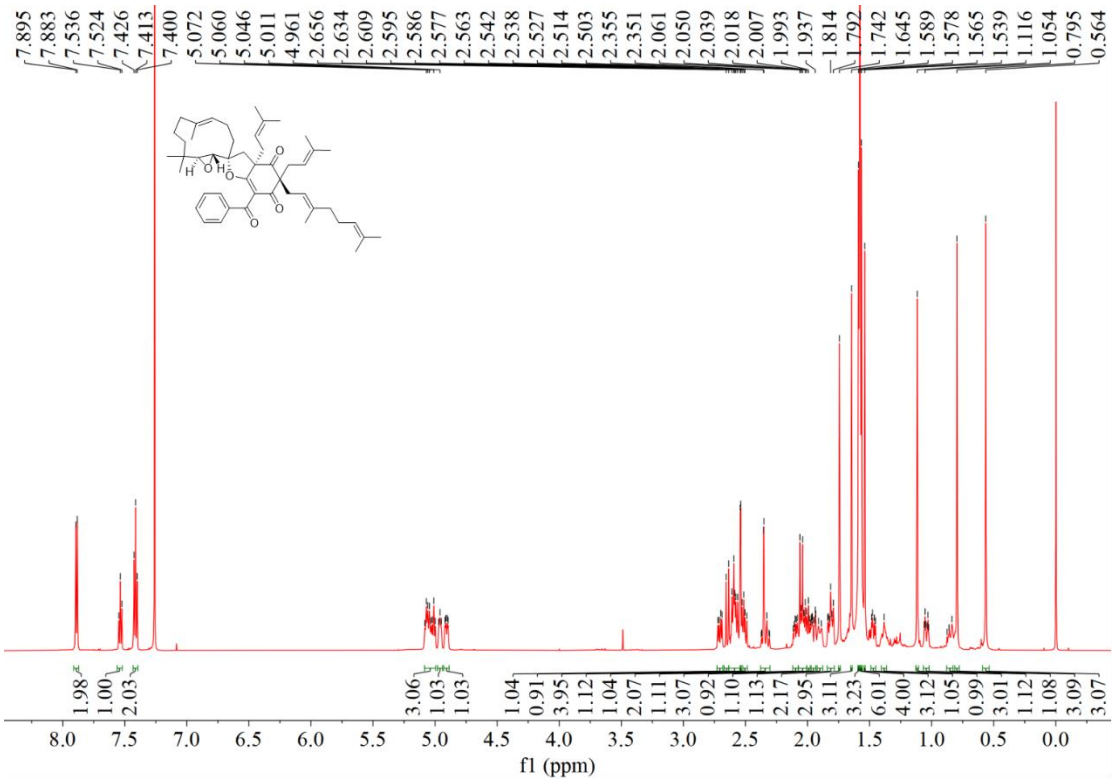


Fig. S44. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin D (**4**).

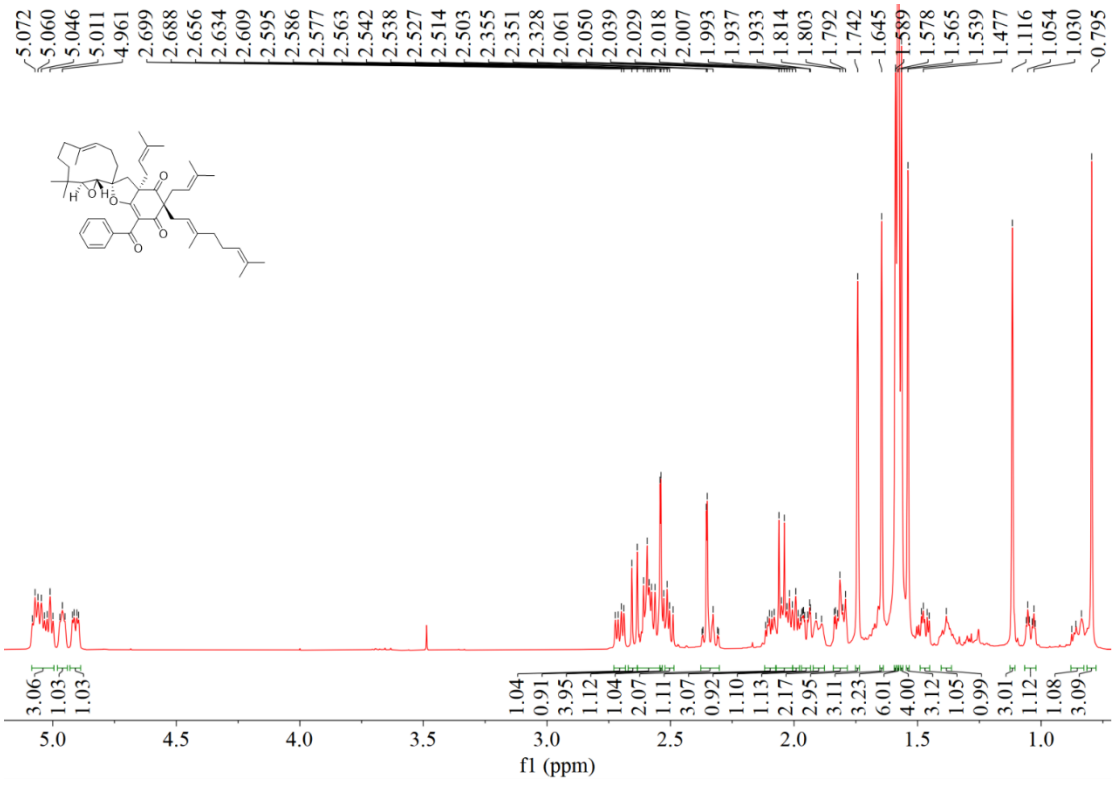


Fig. S45. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin D (**4**).

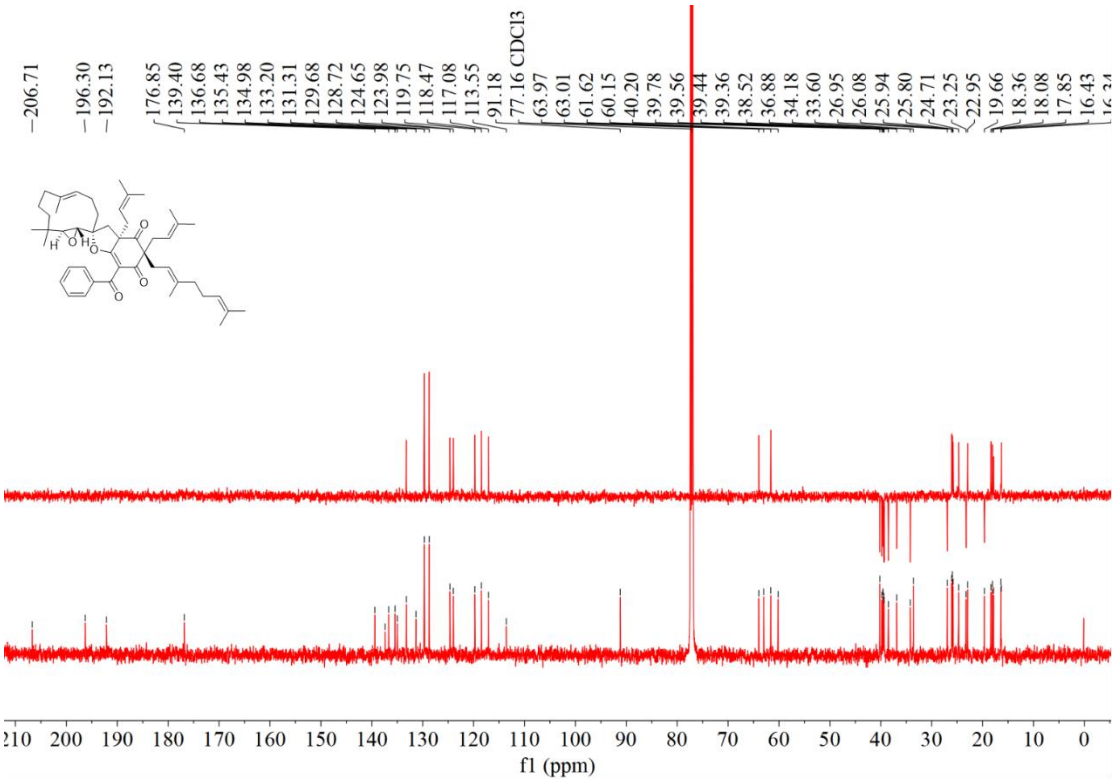


Fig. S46. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin D (**4**).

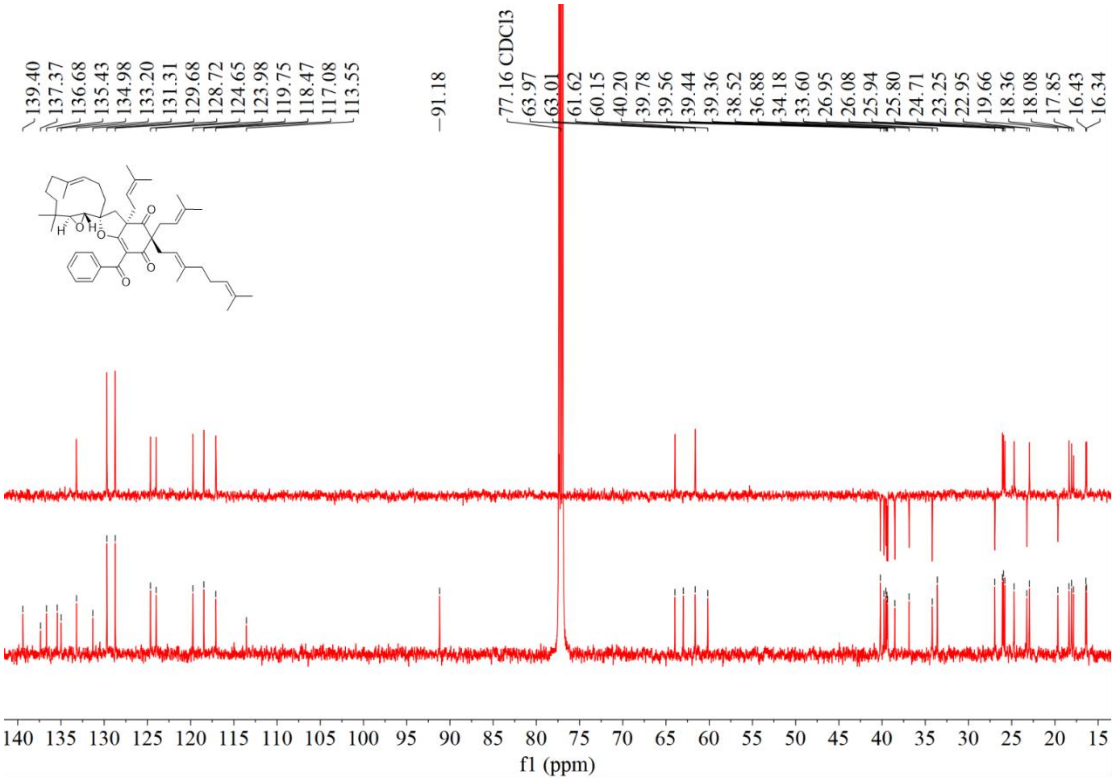


Fig. S47. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin D (**4**).

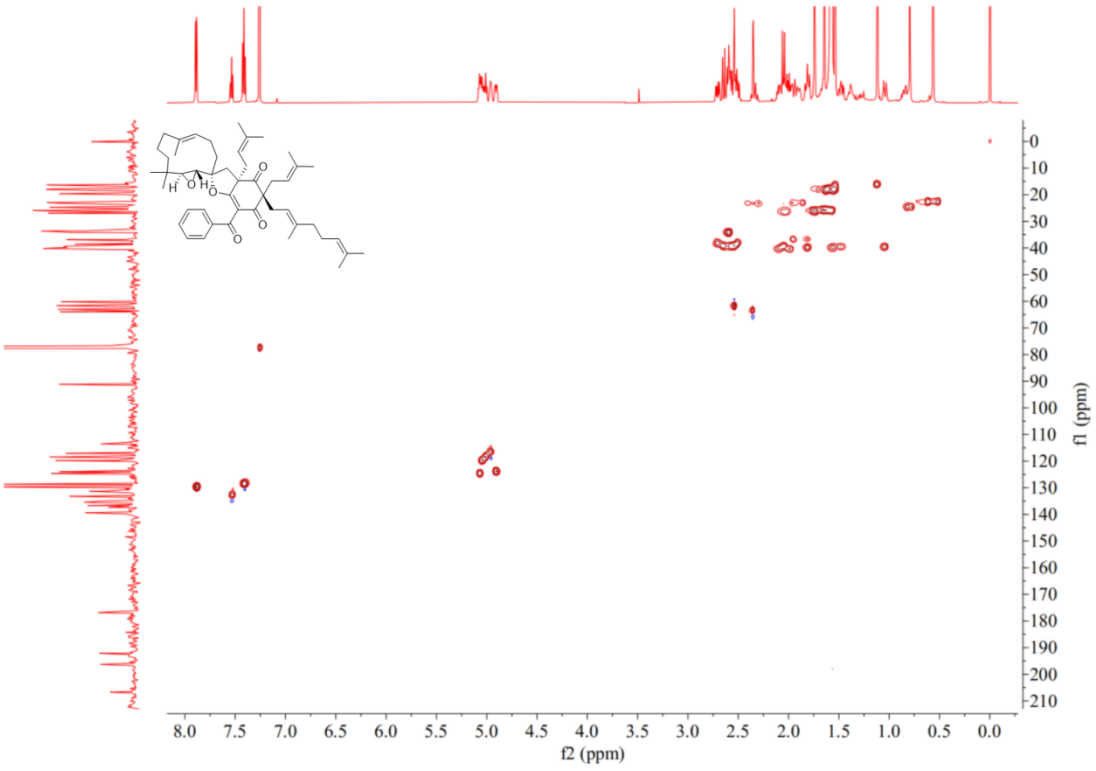


Fig. S48. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin D (**4**).

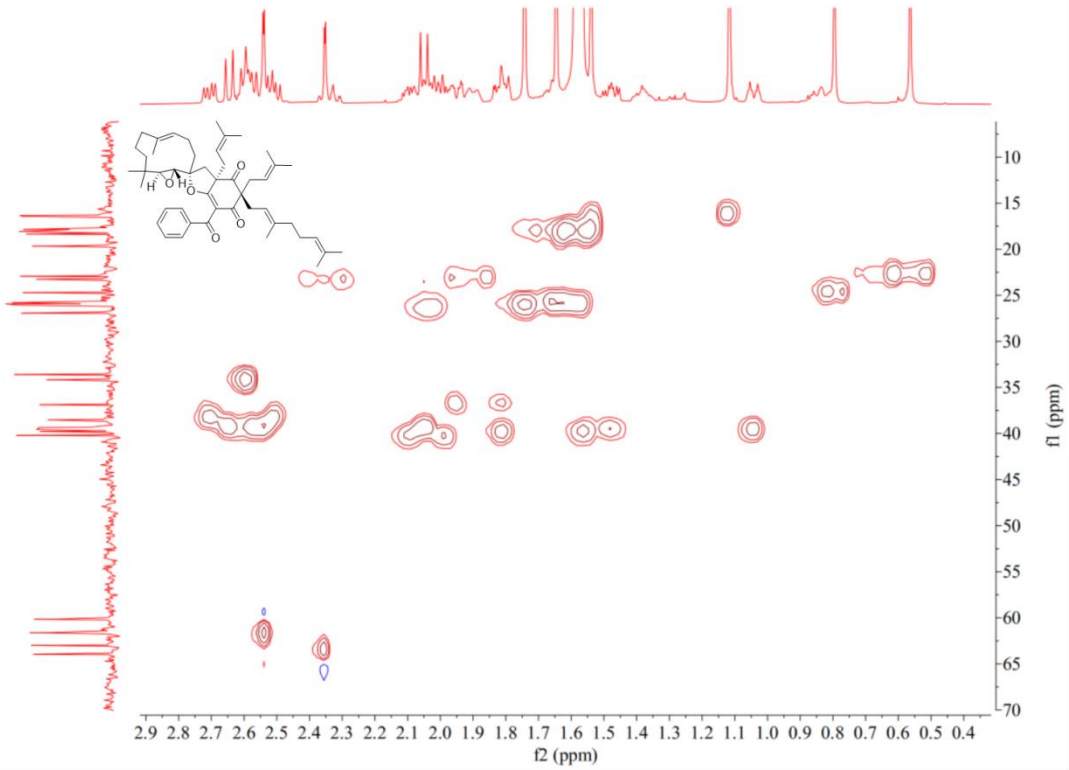


Fig. S49. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of hyperkouytin D (**4**).

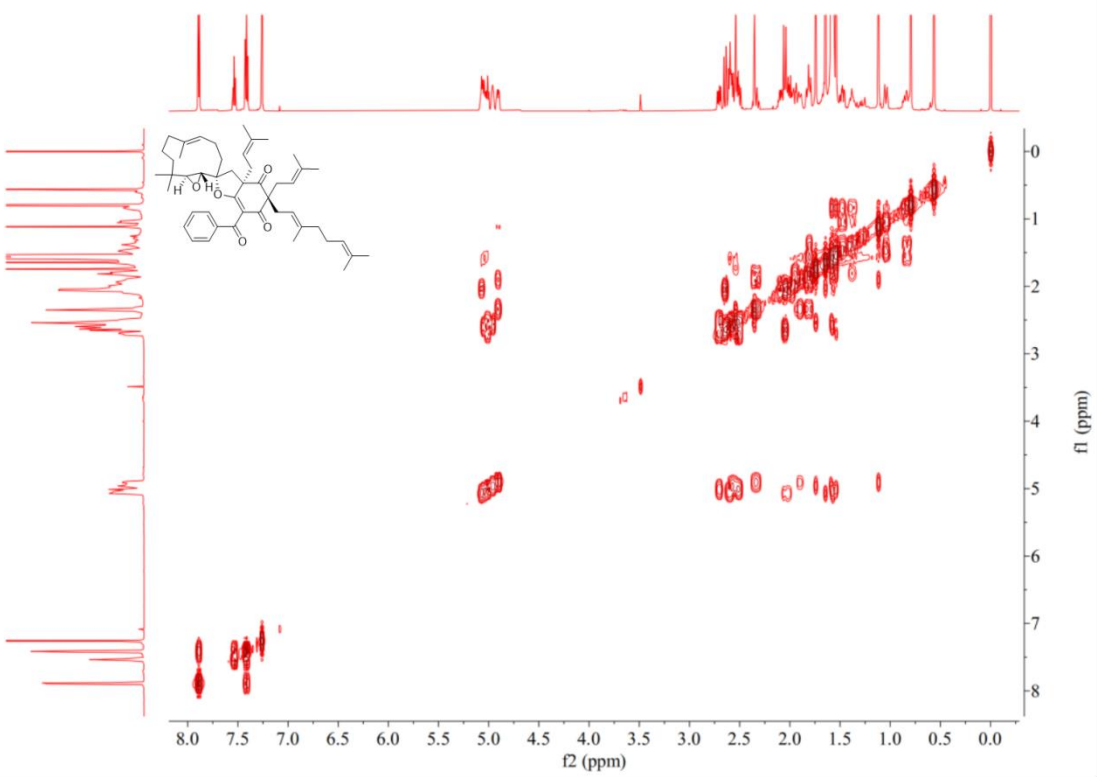


Fig. S50. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin D (**4**).

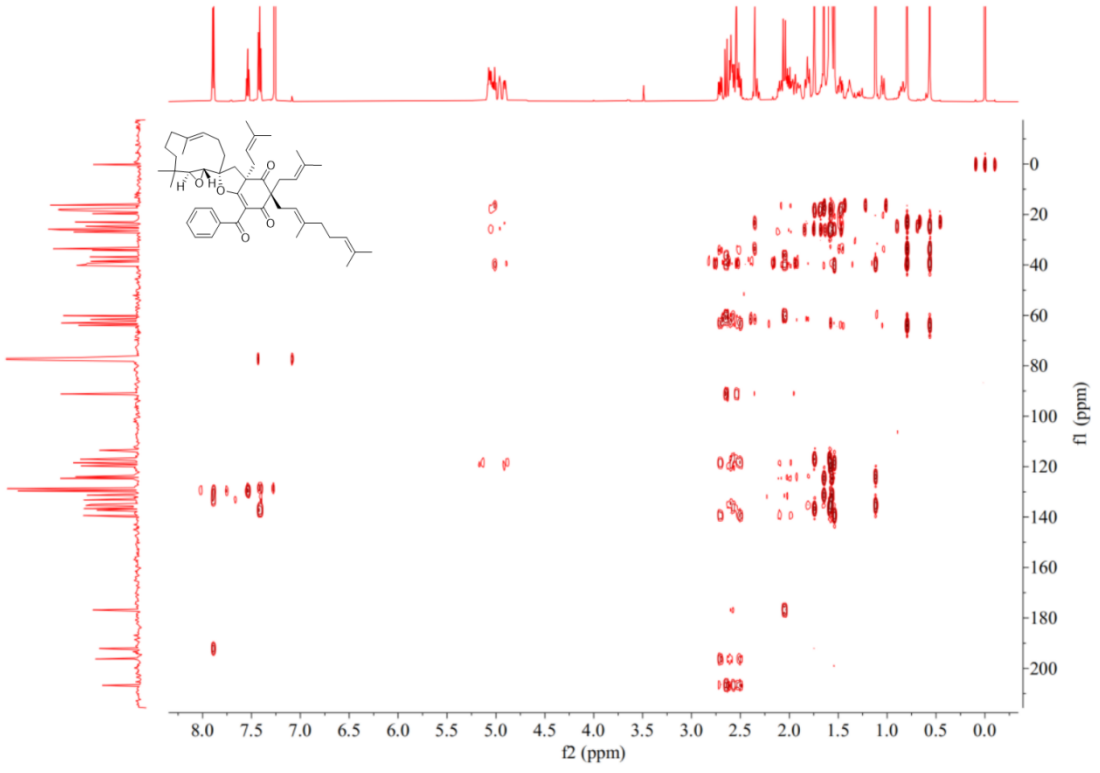


Fig. S51. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin D (**4**).

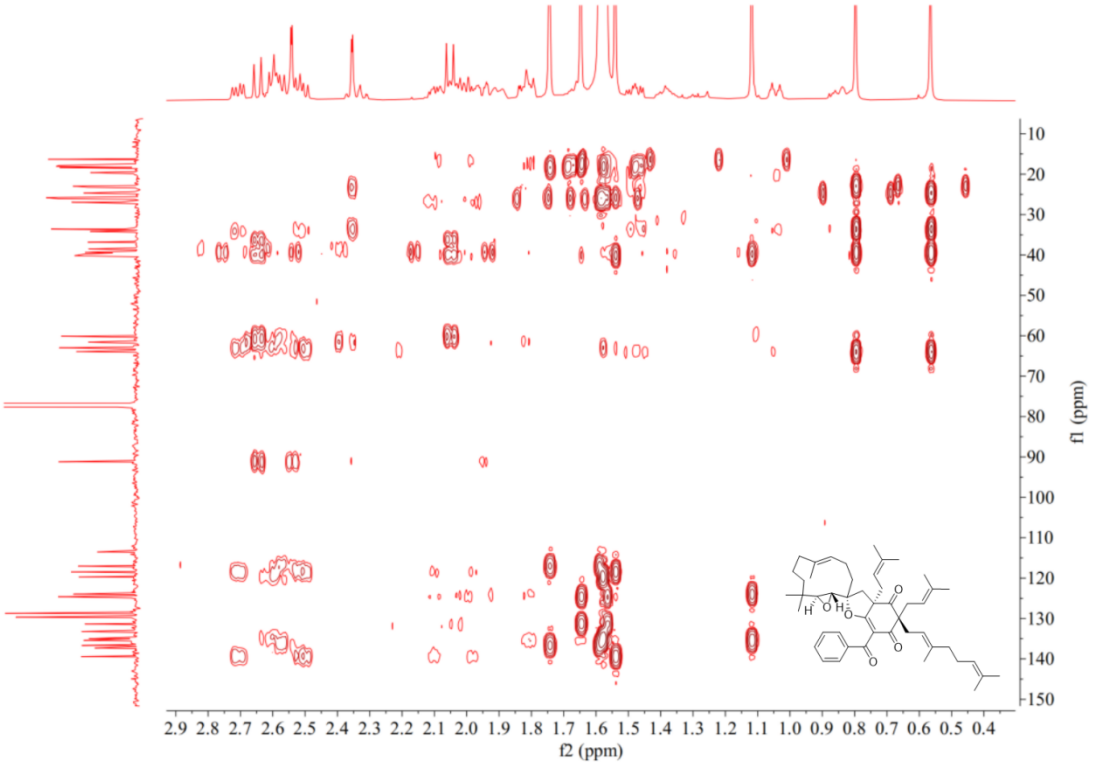


Fig. S52. NOESY (600 MHz, $CDCl_3$) spectrum of hyperkouytin D (**4**).

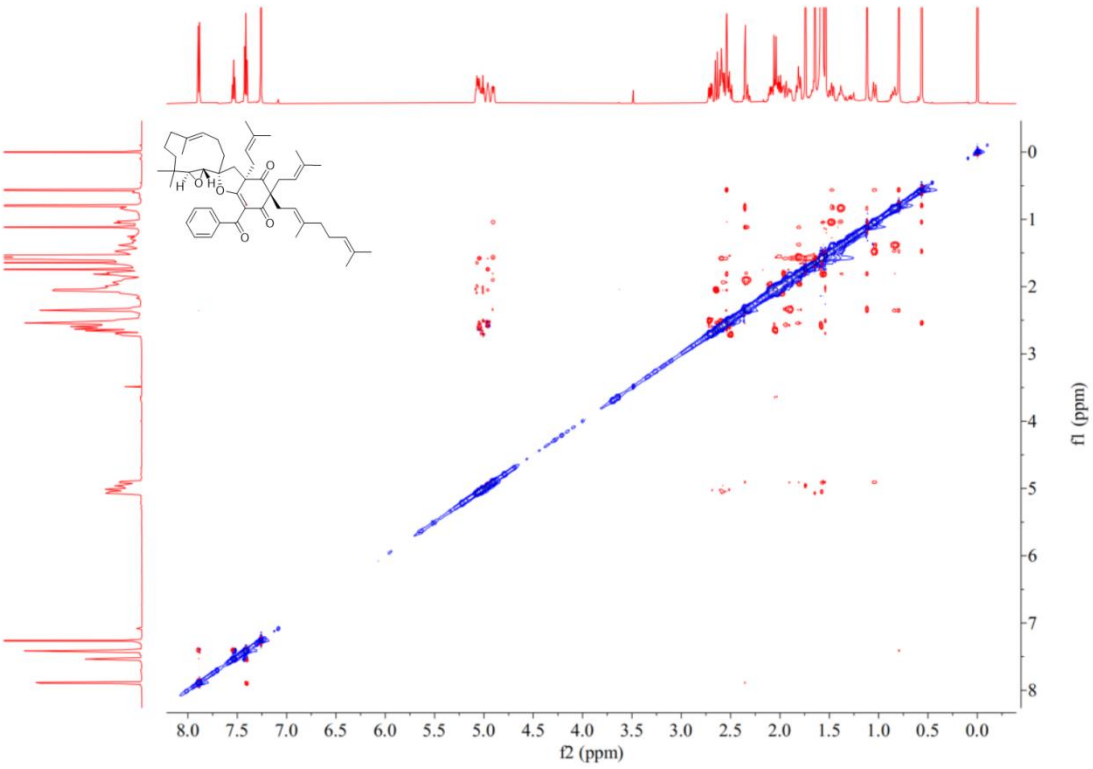


Fig. S53. IR spectrum of hyperkouytin D (**4**).

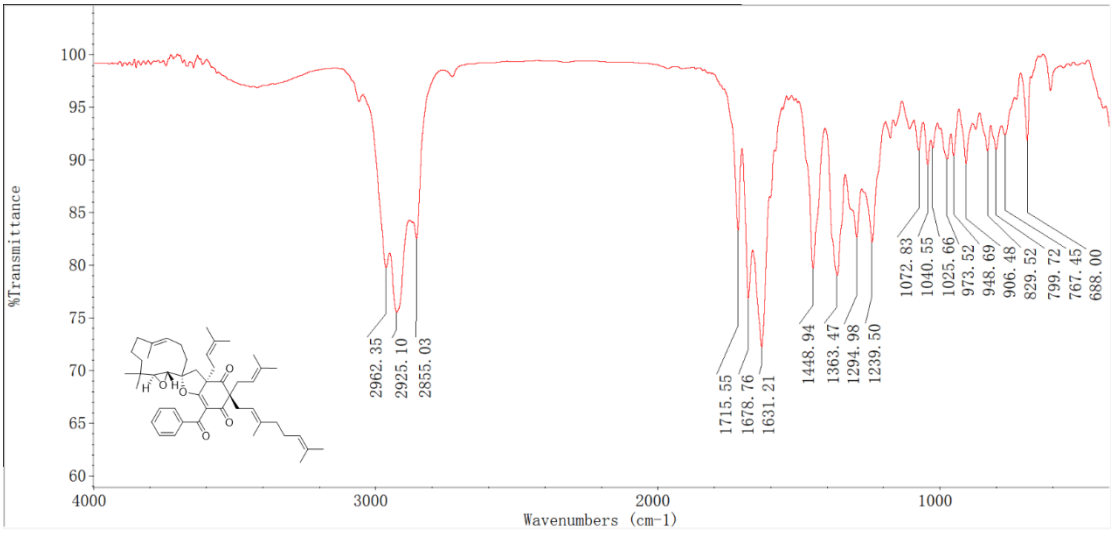


Fig. S54. UV spectrum of hyperkouytin D (**4**).

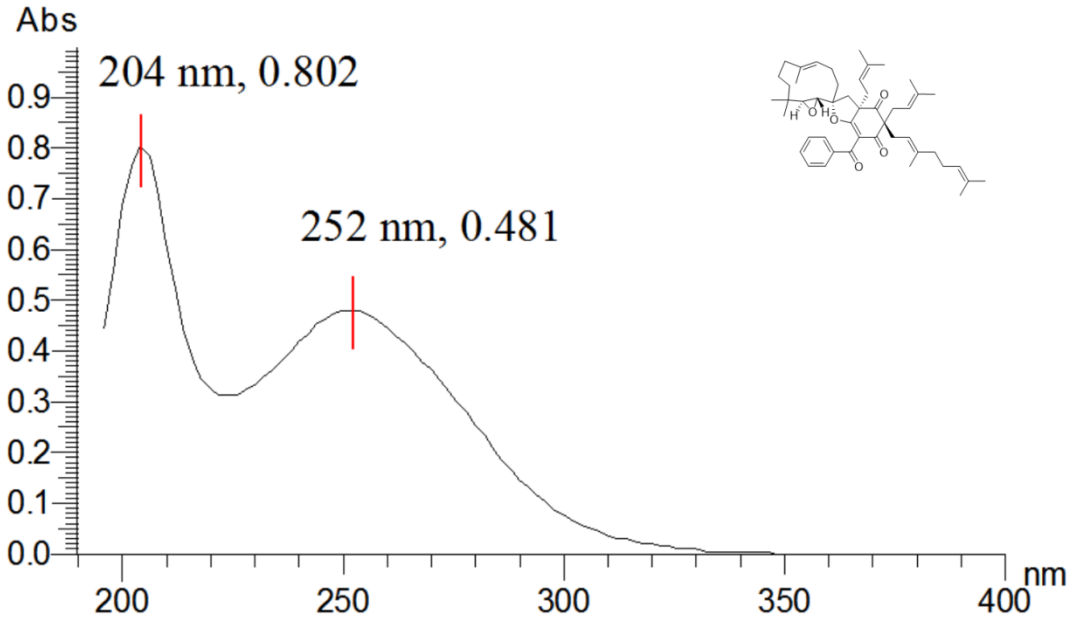
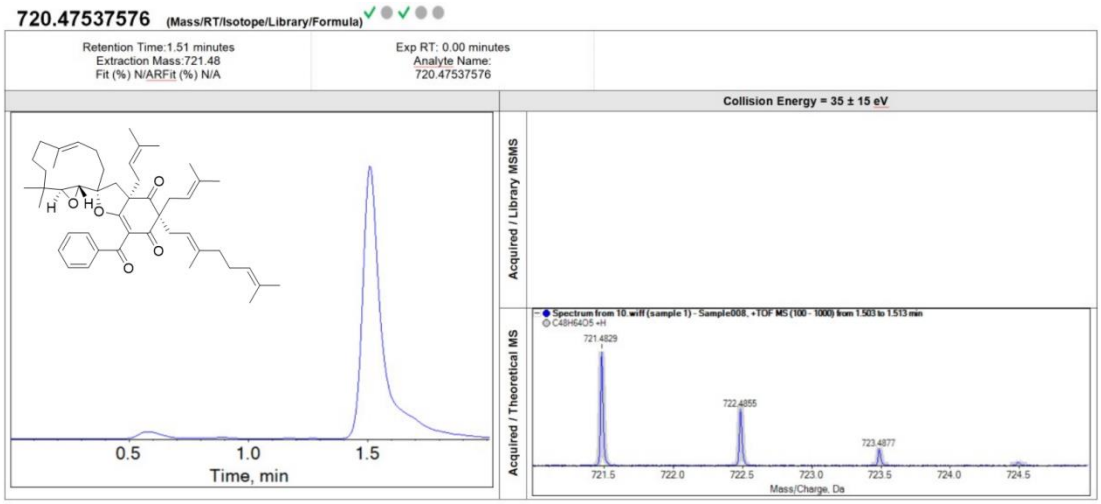


Fig. S55. Positive HR-ESIMS spectrum of hyperkouytin E (**5**).



Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
720.47537576(GZ-31)	96%	C48H64O5	955629	5	721.4827	721.4829	0.4	0.00	1.51	1.51	5.2%	N/A

Fig. S56. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin E (**5**).

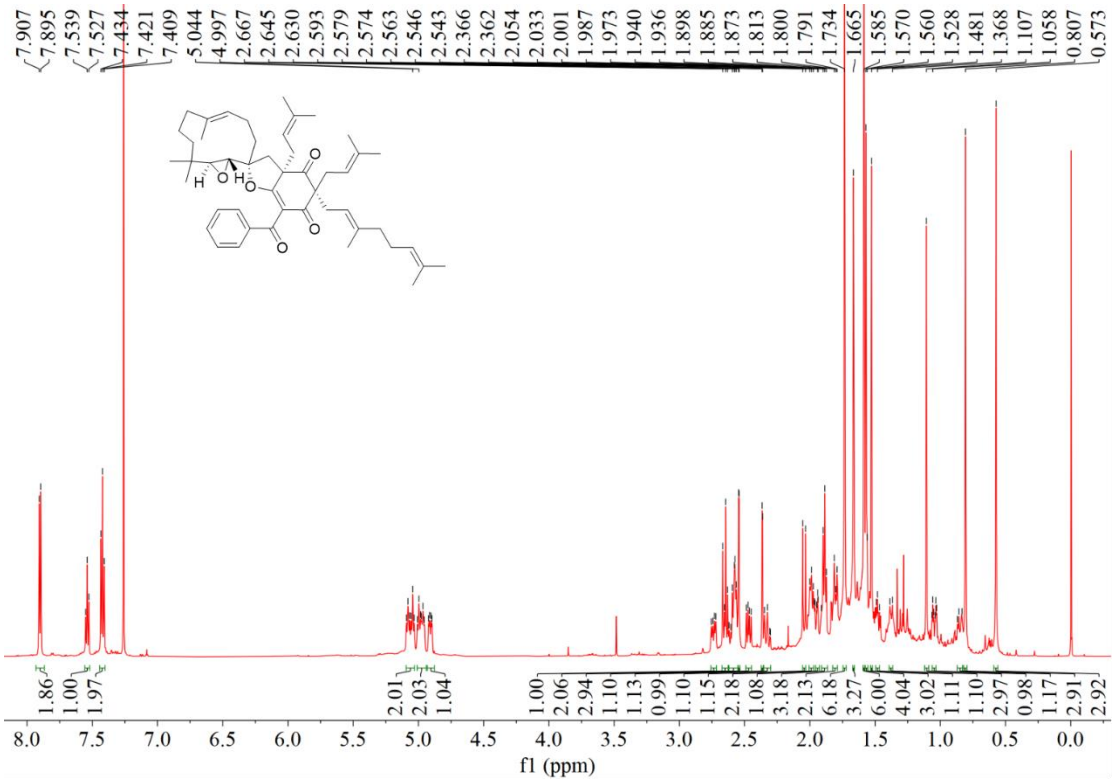


Fig. S57. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin E (**5**).

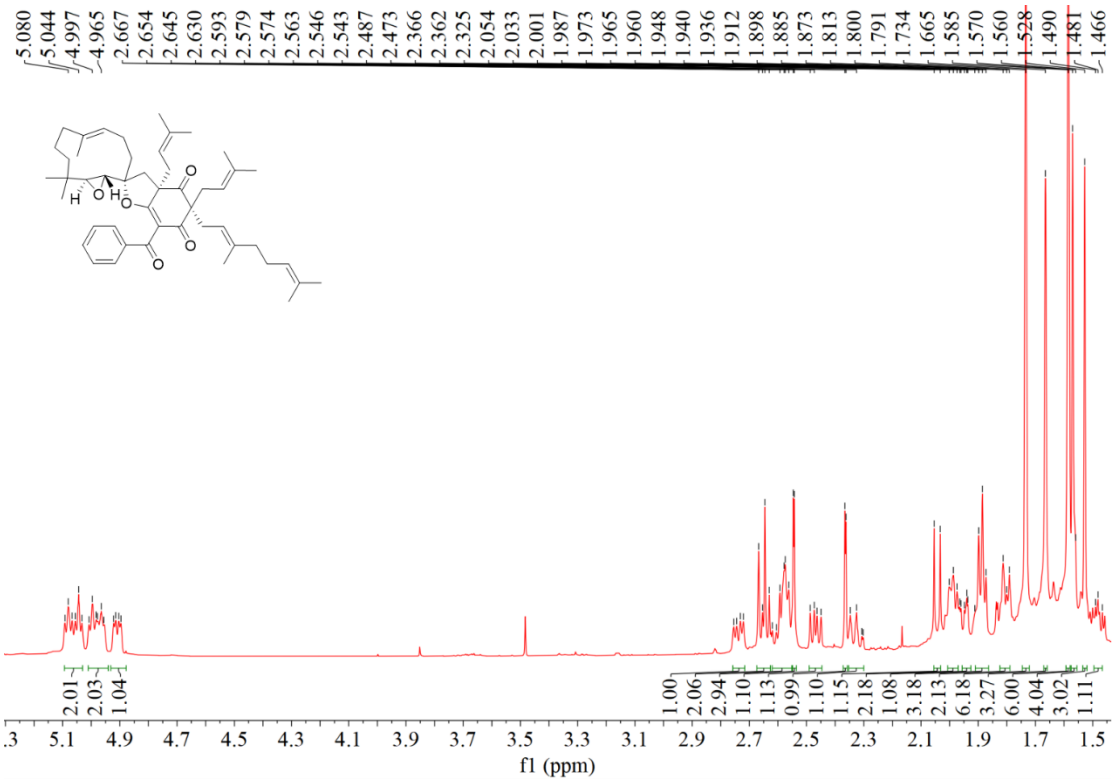


Fig. S58. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin E (**5**).

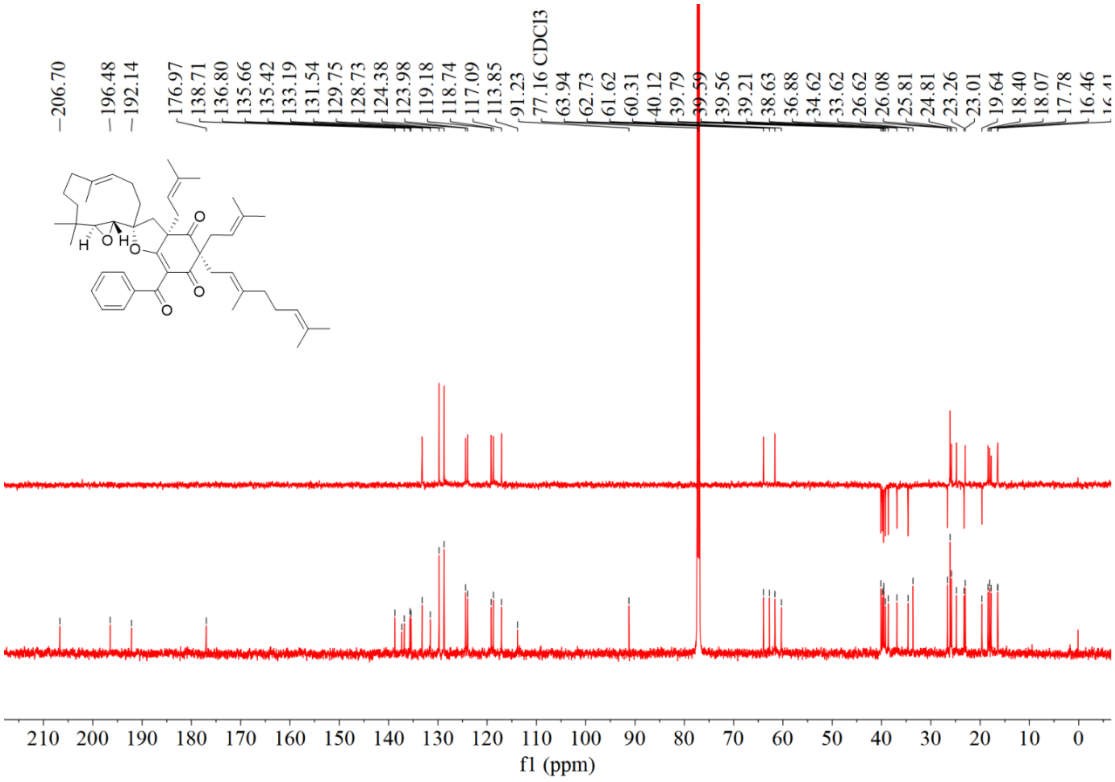


Fig. S59. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin E (**5**).

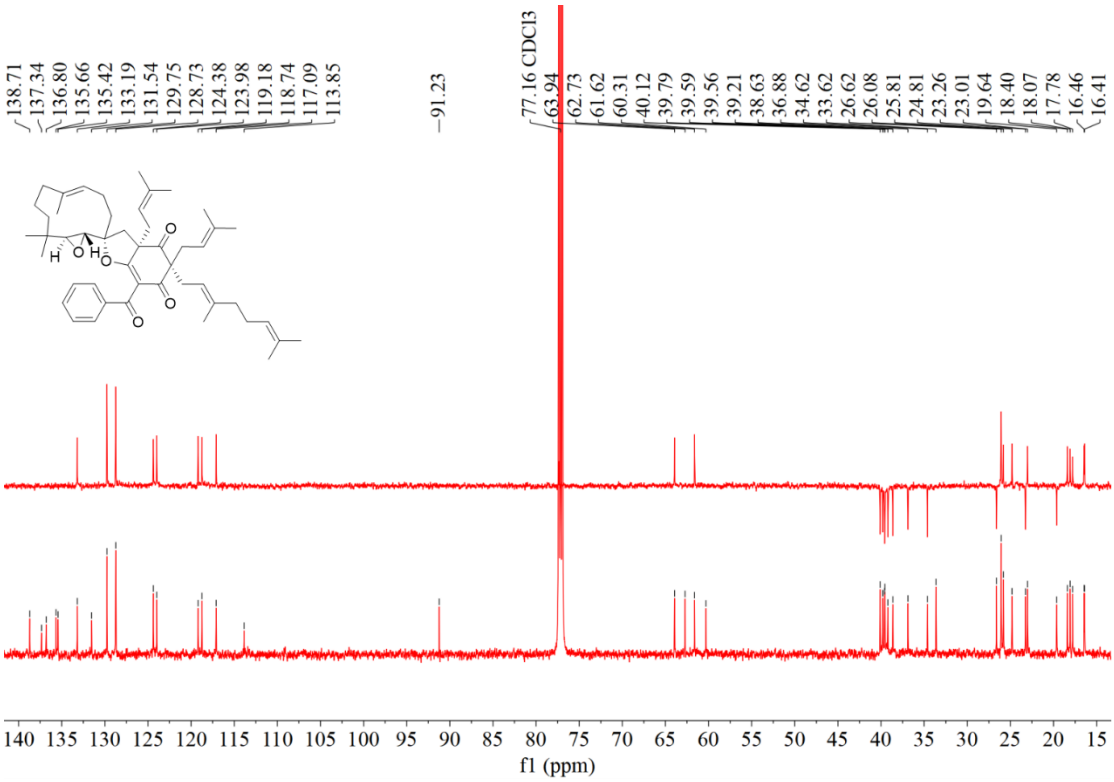


Fig. S60. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin E (**5**).

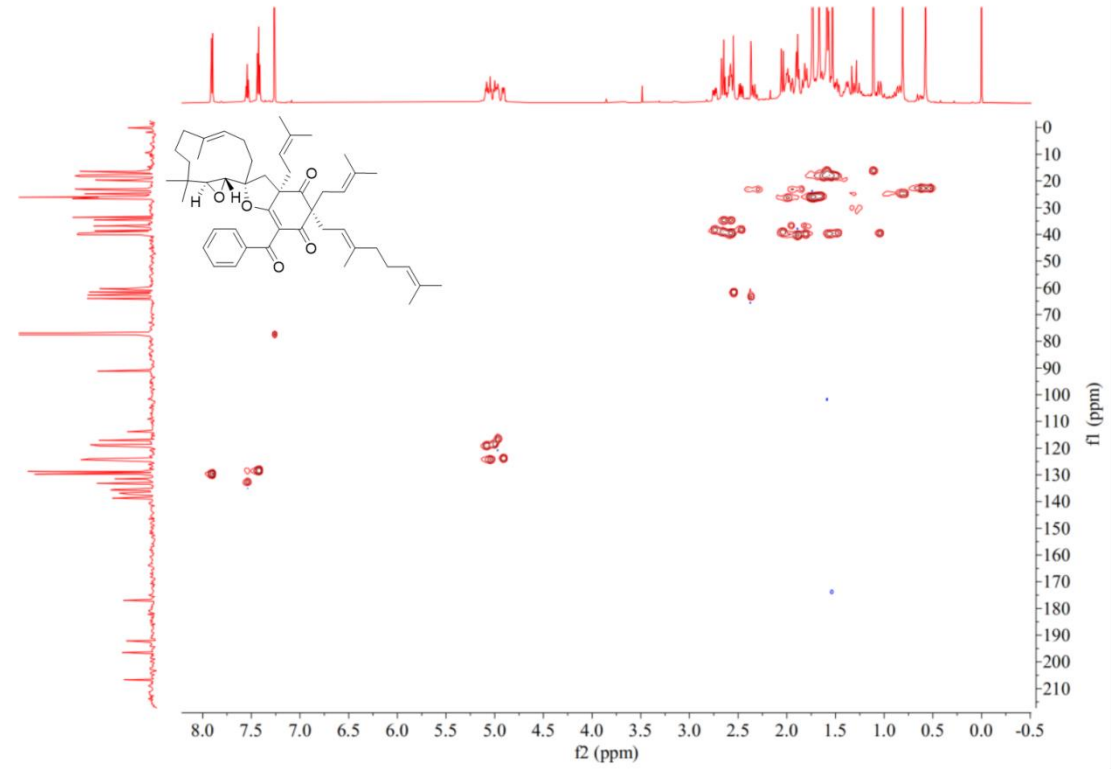


Fig. S61. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin E (**5**).

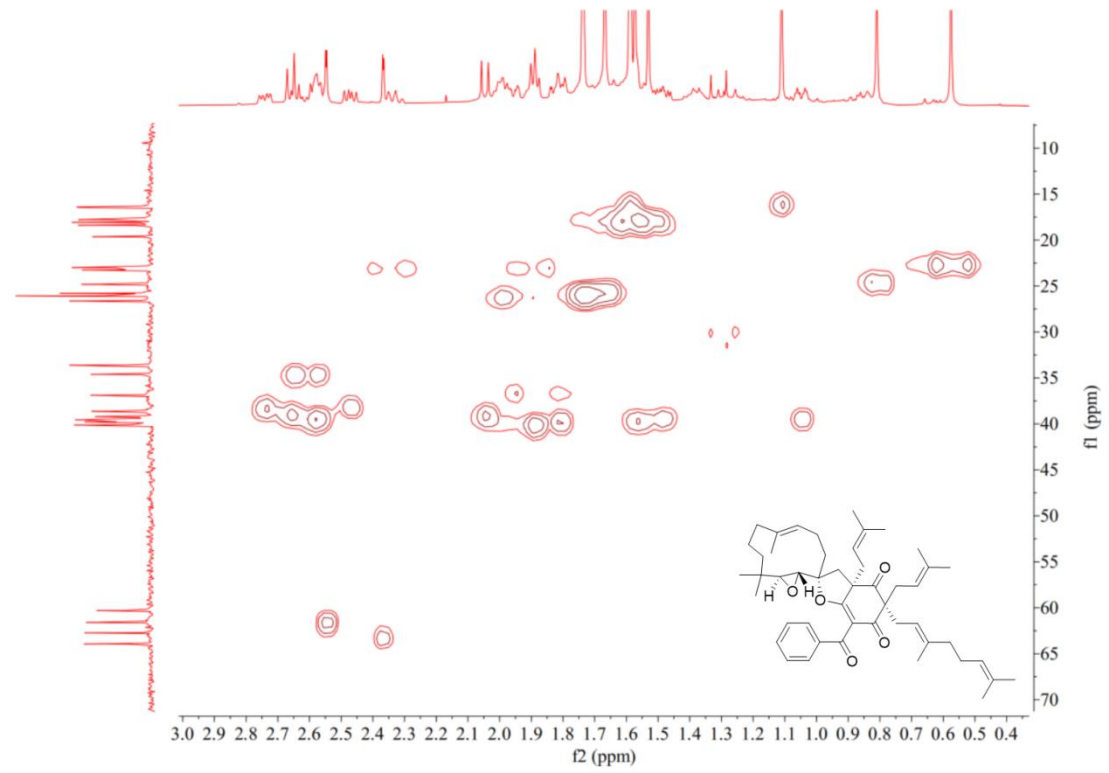


Fig. S62. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of hyperkouytin E (**5**).

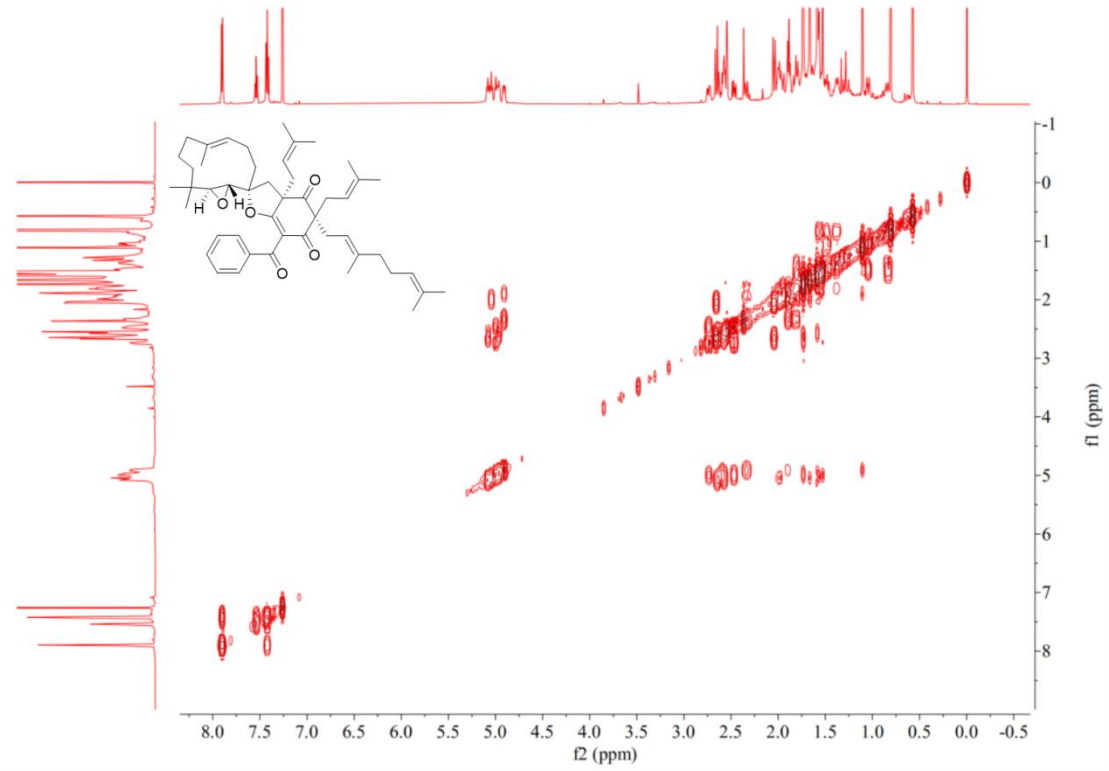


Fig. S63. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin E (**5**).

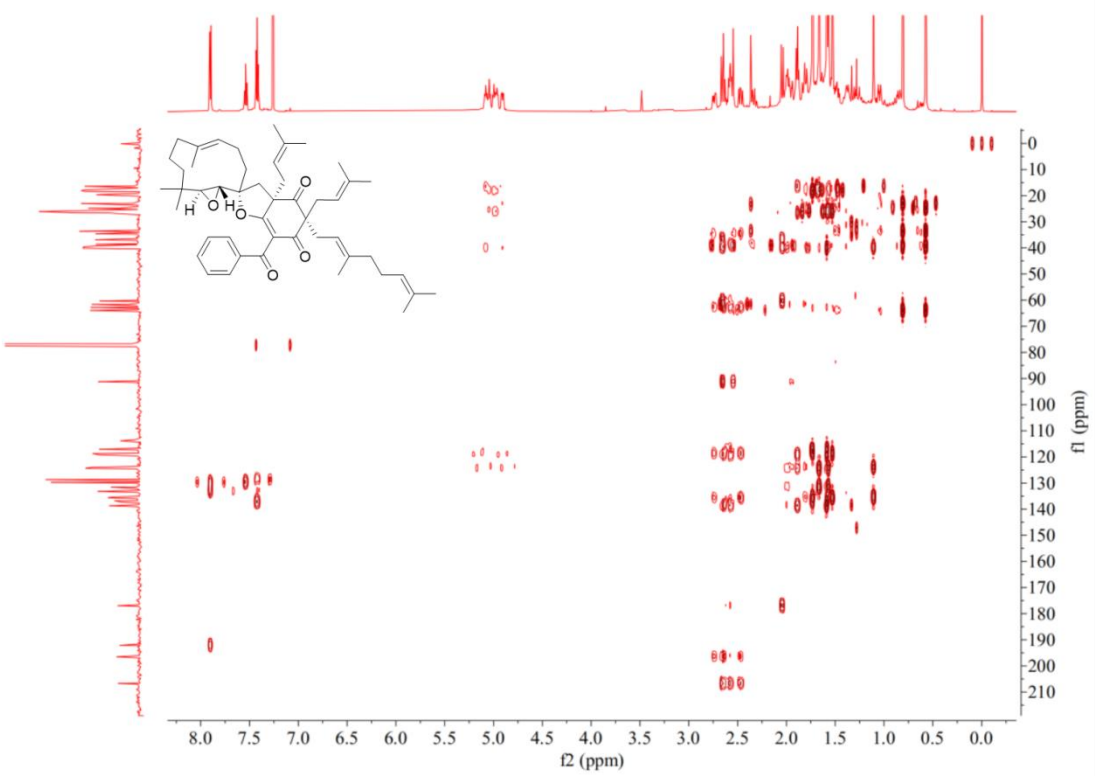


Fig. S64. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin E (**5**).

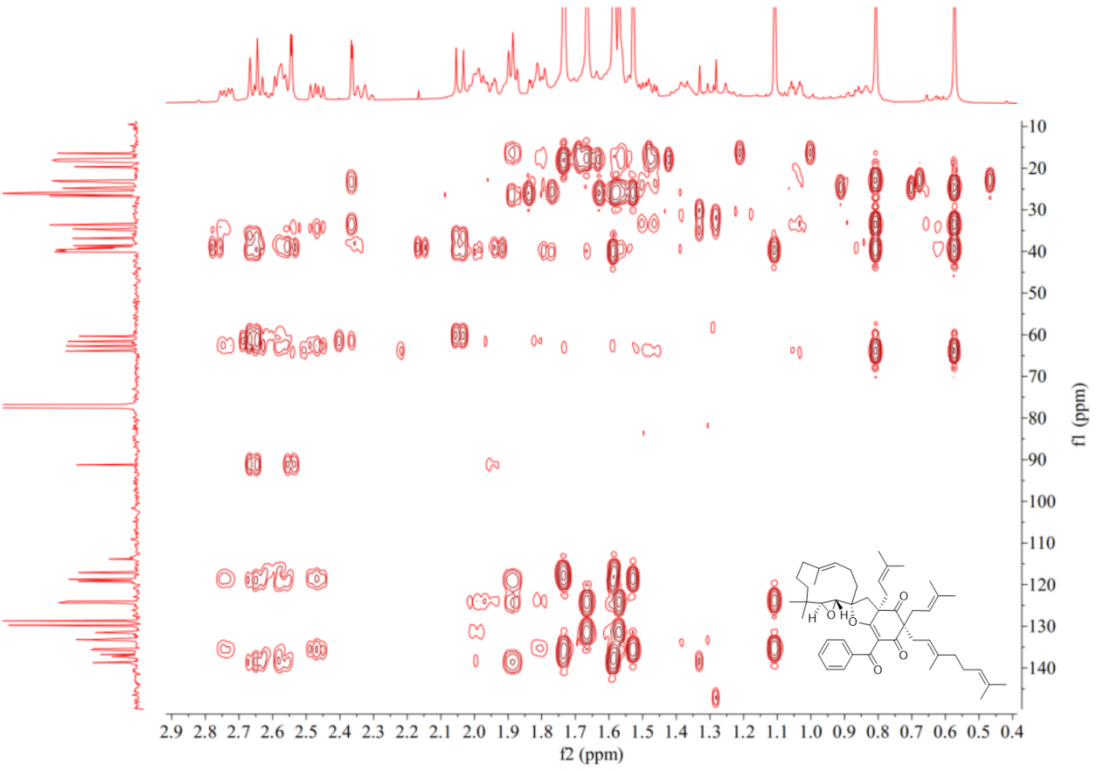


Fig. S65. NOESY (600 MHz, $CDCl_3$) spectrum of hyperkouytin E (**5**).

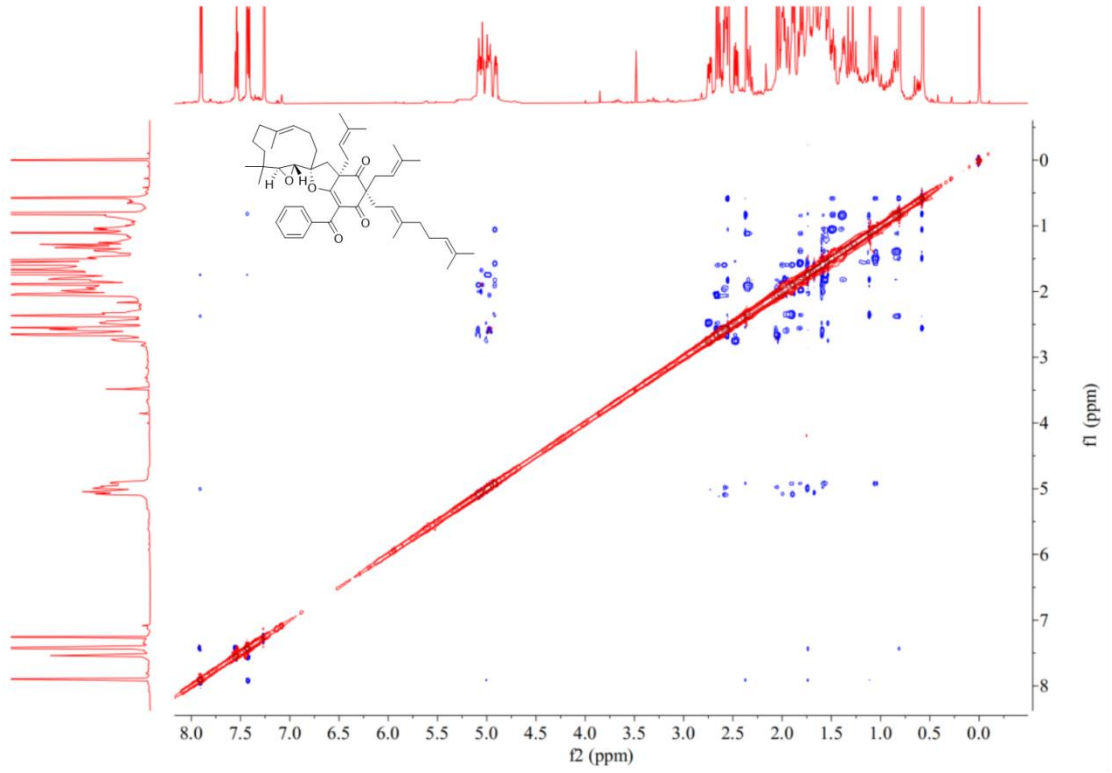


Fig. S66. IR spectrum of hyperkouytin E (**5**).

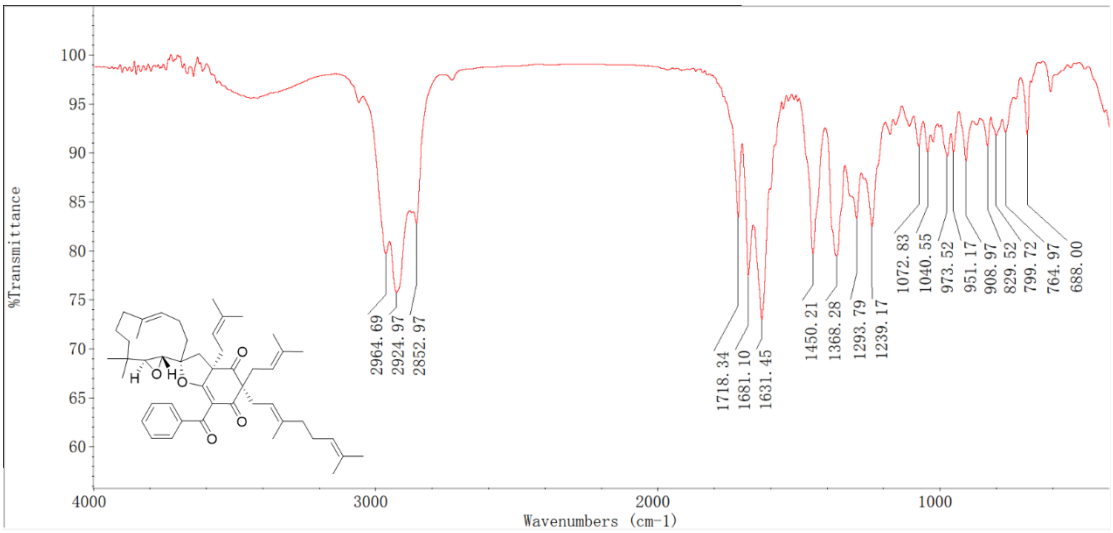


Fig. S67. UV spectrum of hyperkouytin E (**5**).

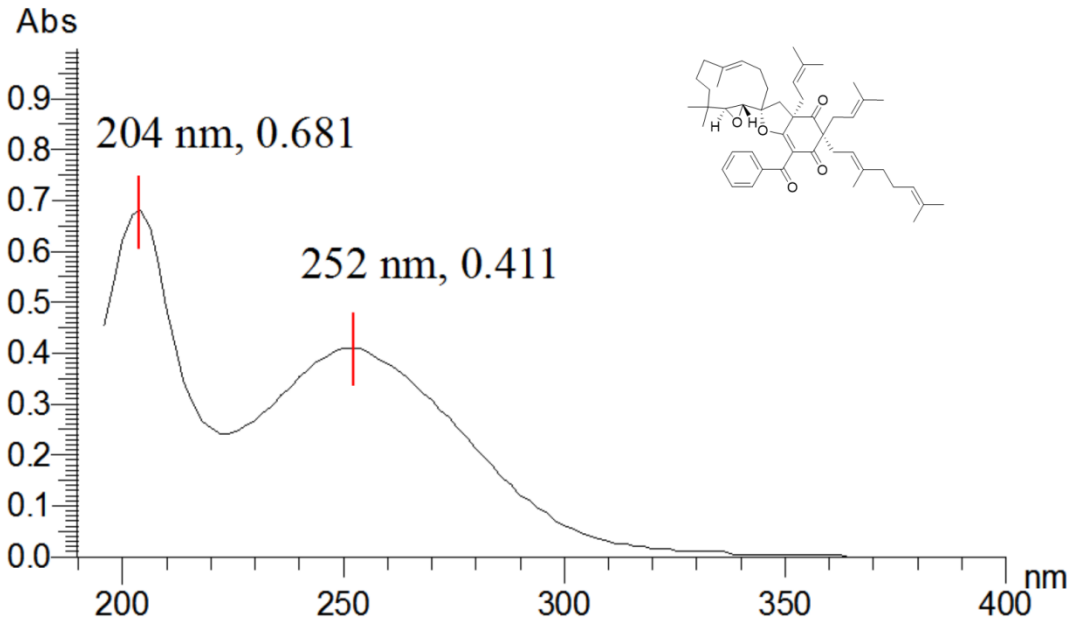
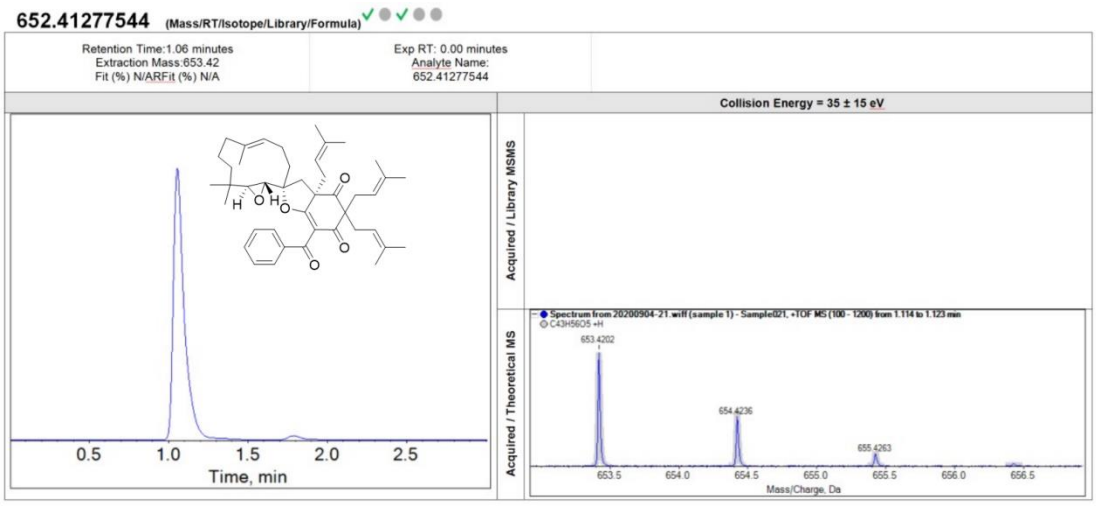


Fig. S68. Positive HR-ESIMS spectrum of hyperkouytin F (**6**).



Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
652.41277544(GZ-35)	97%	C43H56O5	4077764	5	653.4201	653.4202	0.2	0.00	1.06	1.06	5.0%	N/A

Fig. S69. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin F (**6**).

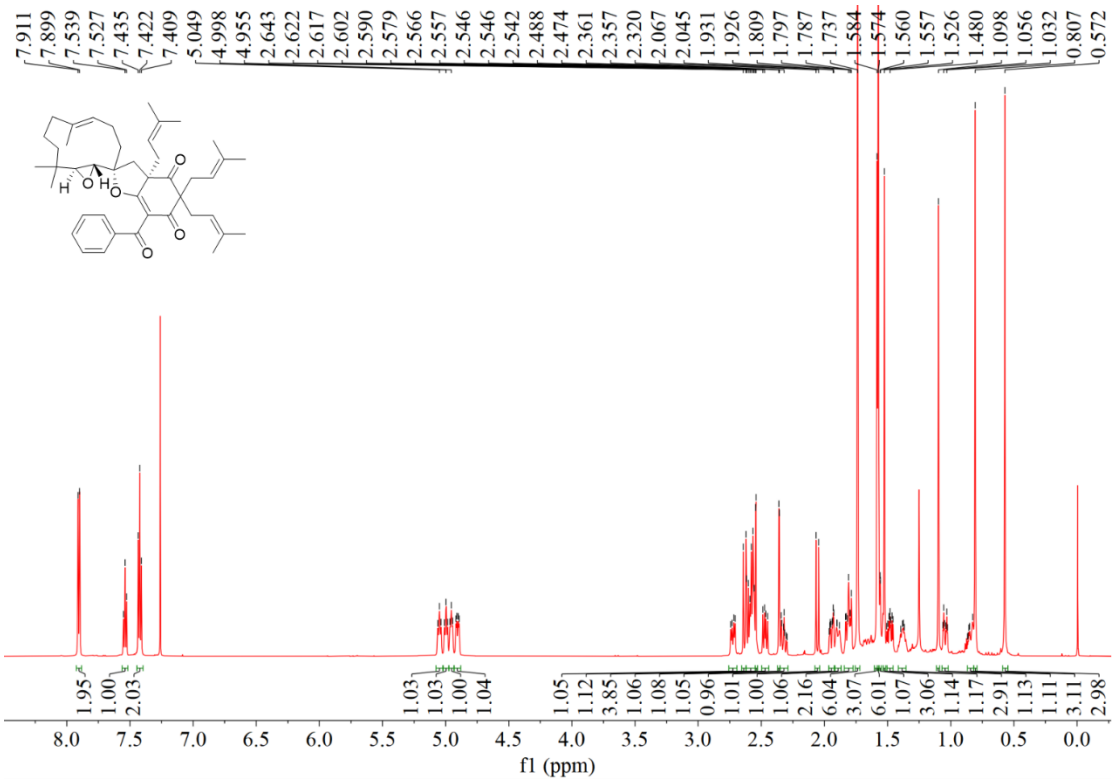


Fig. S70. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of hyperkouytin F (**6**).

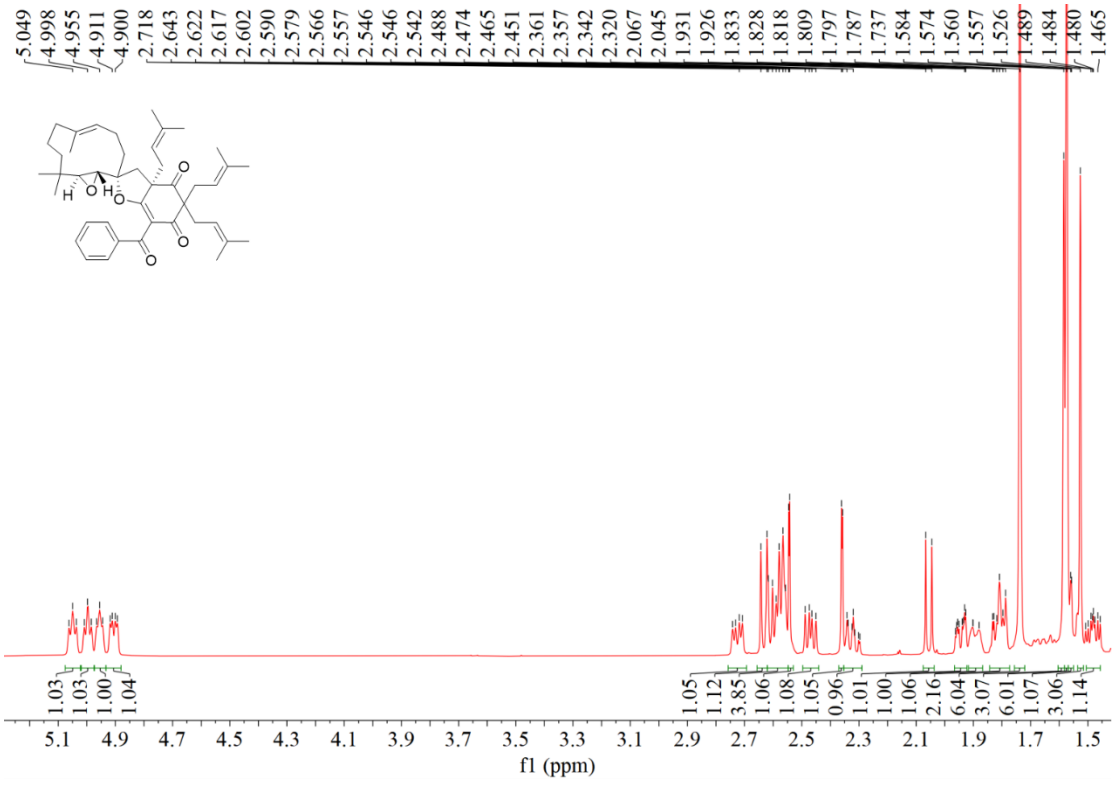


Fig. S71. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin F (**6**).

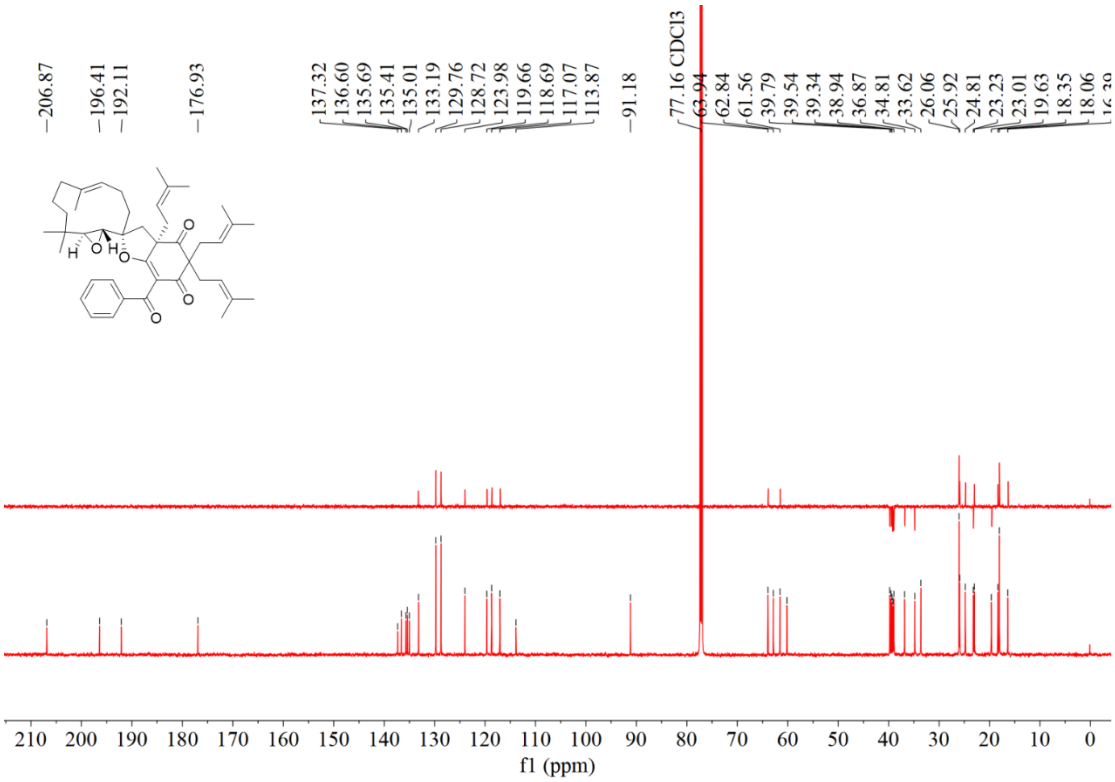


Fig. S72. ^{13}C NMR and DEPT (150 MHz, $CDCl_3$) spectra of hyperkouytin F (**6**).

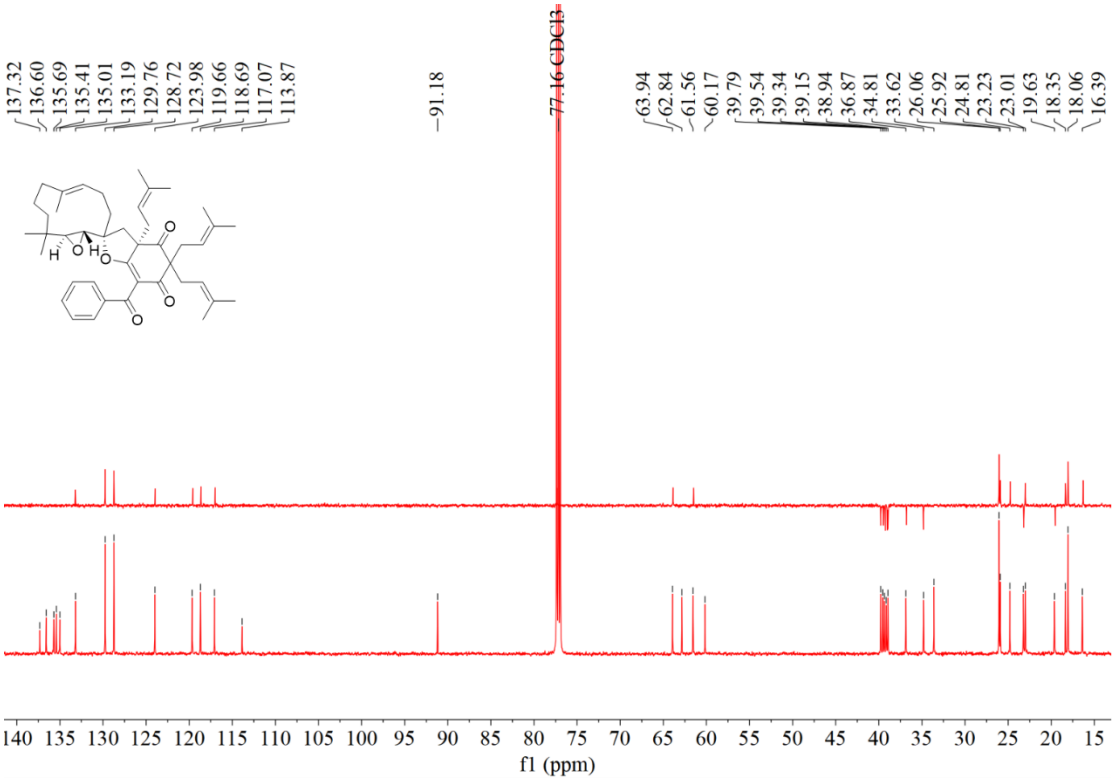


Fig. S73. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin F (**6**).

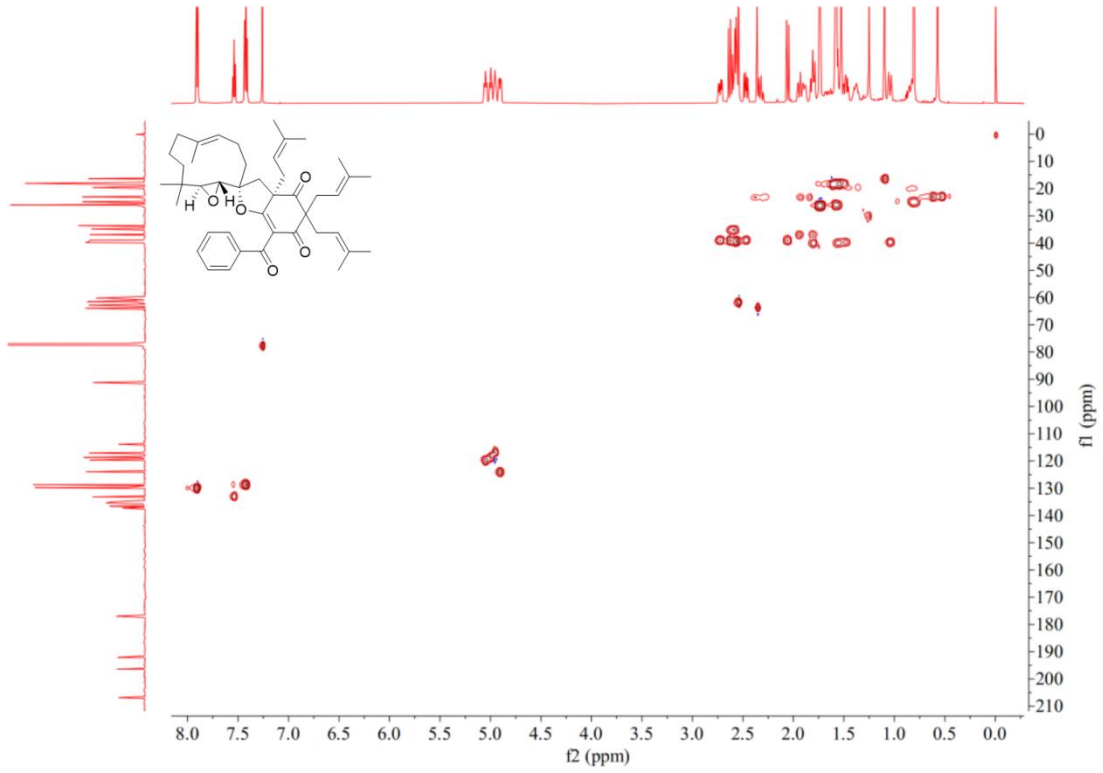


Fig. S74. HSQC (600 MHz, $CDCl_3$) spectrum of hyperkouytin F (**6**).

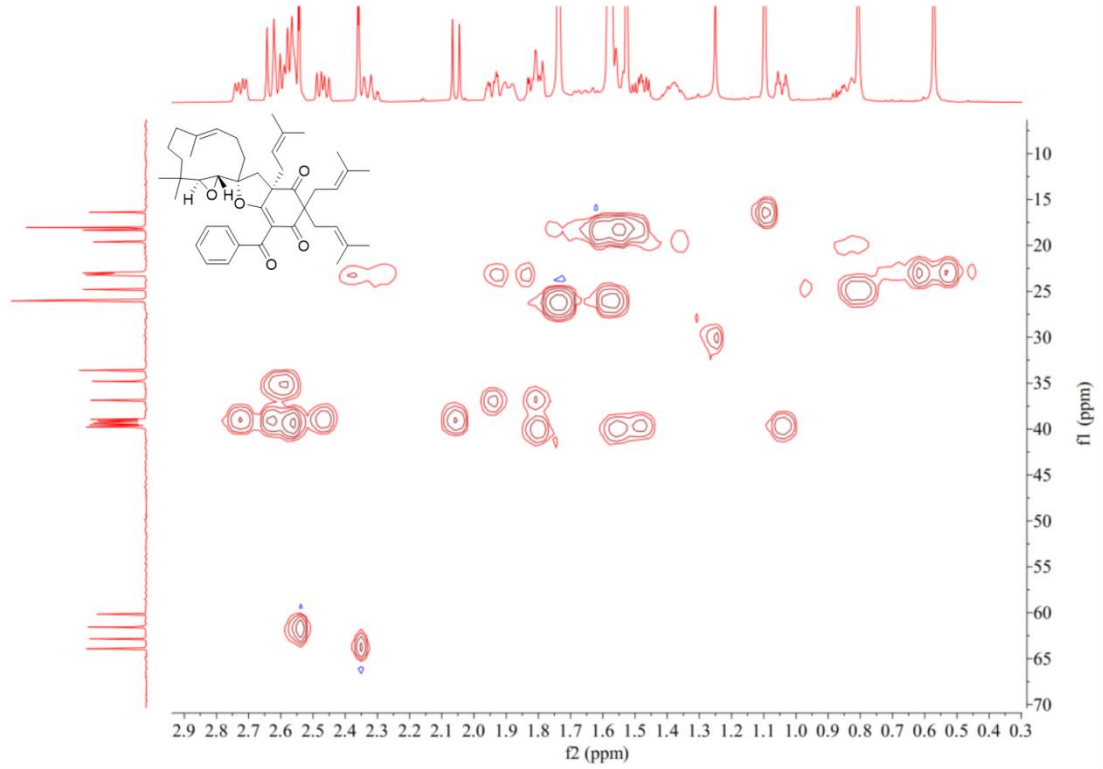


Fig. S75. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of hyperkouytin F (**6**).

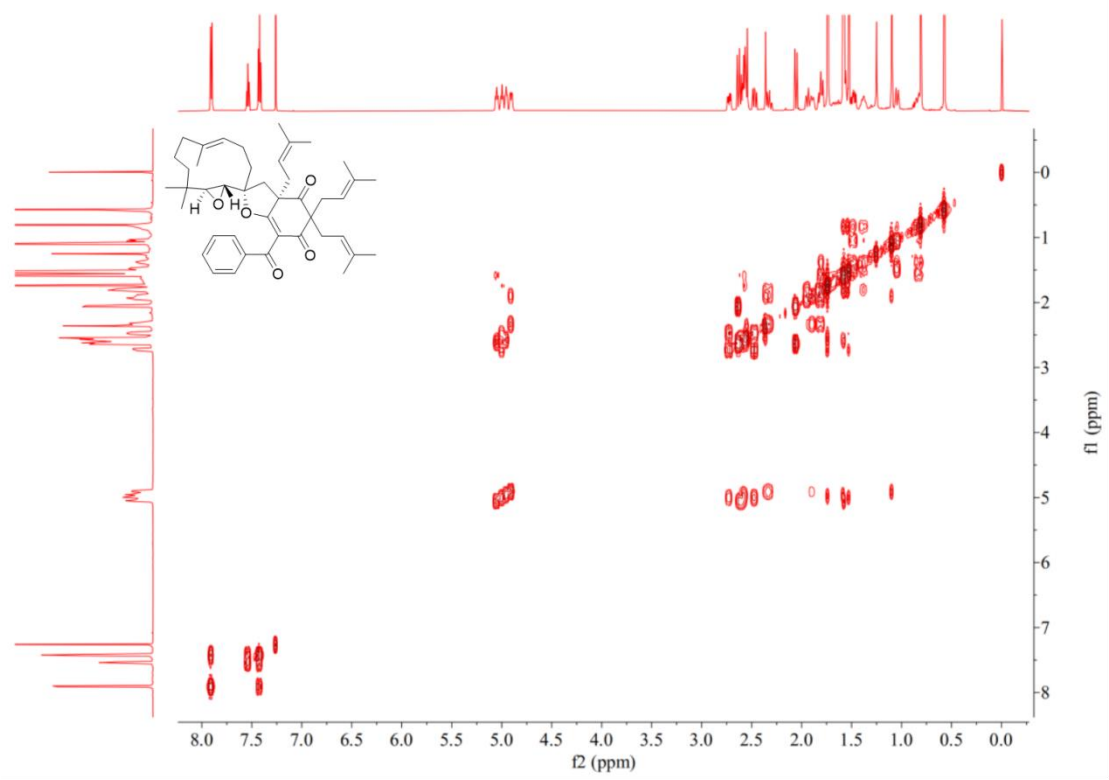


Fig. S76. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin F (**6**).

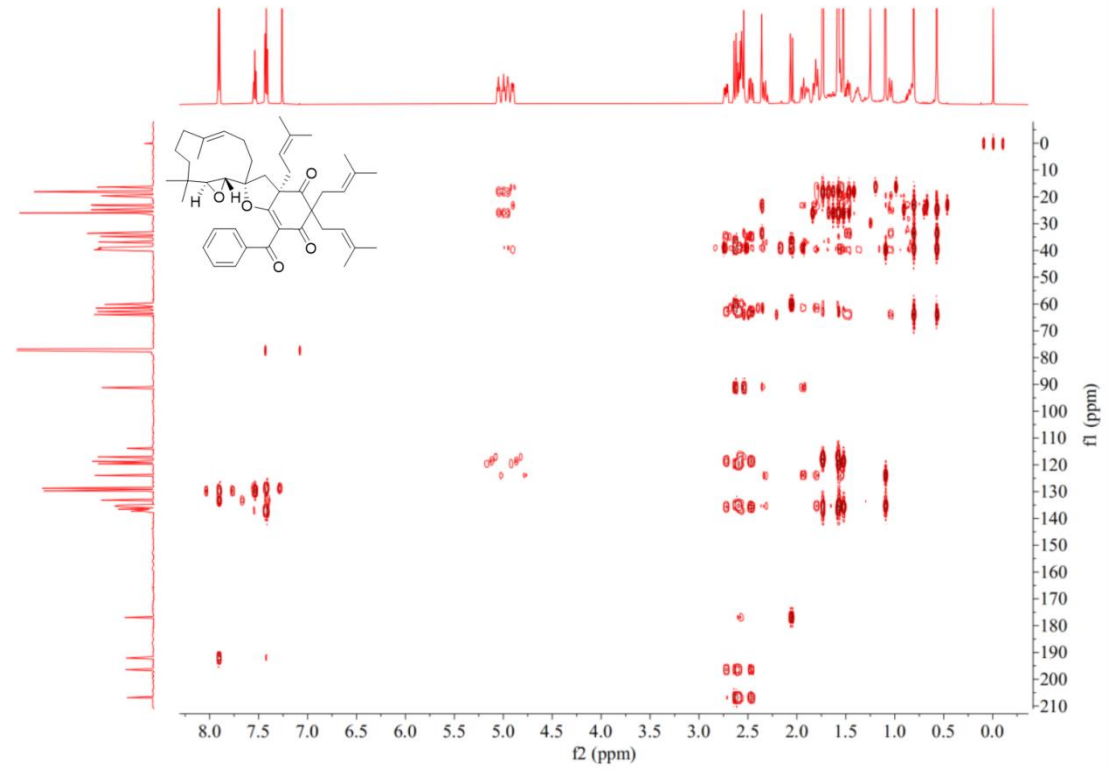


Fig. S77. HMBC (600 MHz, $CDCl_3$) spectrum of hyperkouytin F (**6**).

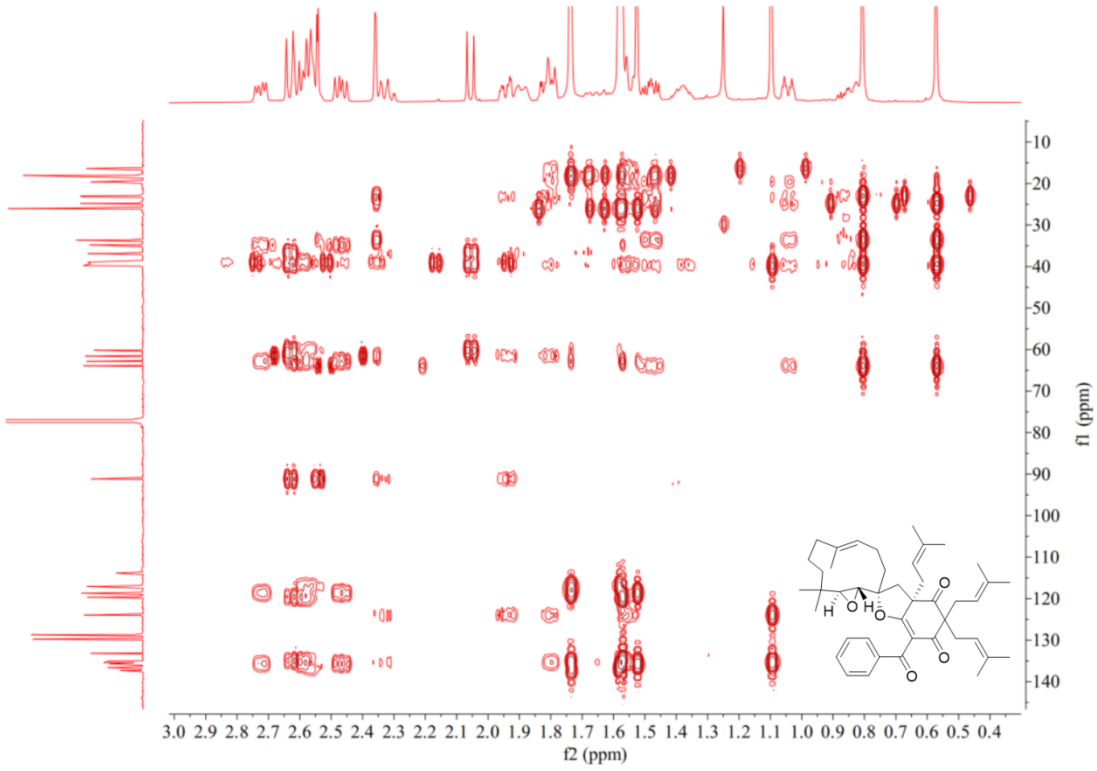


Fig. S78. NOESY (600 MHz, $CDCl_3$) spectrum of hyperkouytin F (**6**).

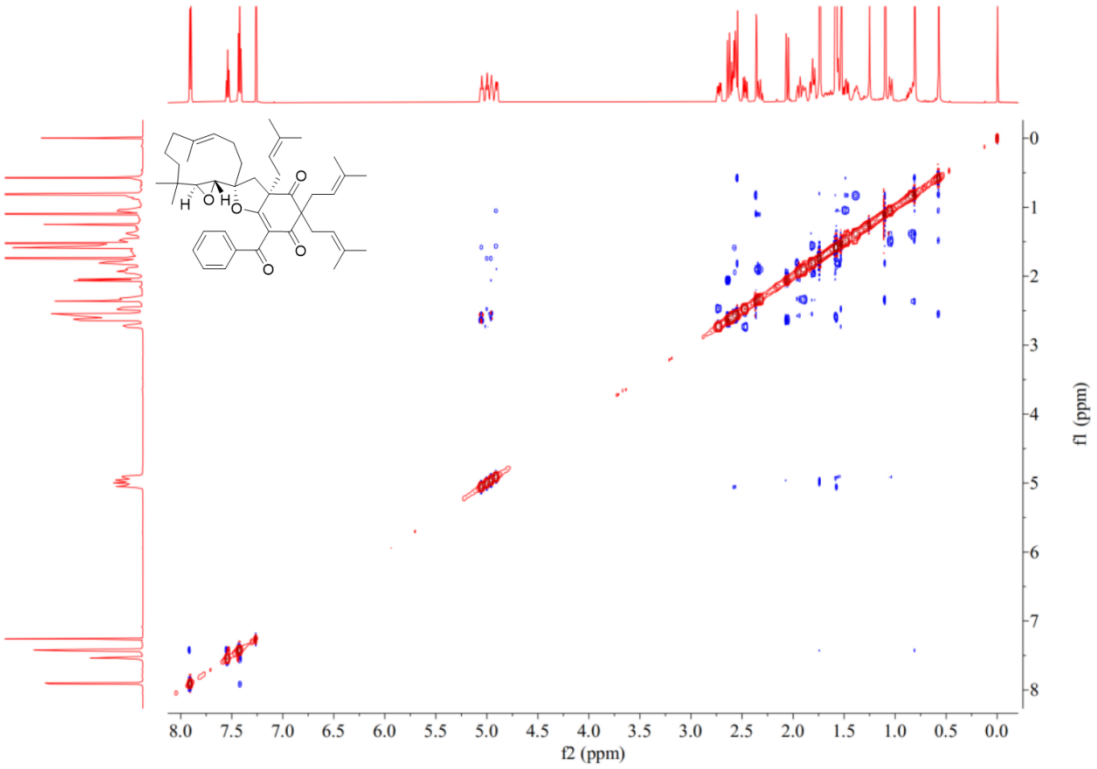


Fig. S79. IR spectrum of hyperkouytin F (**6**).

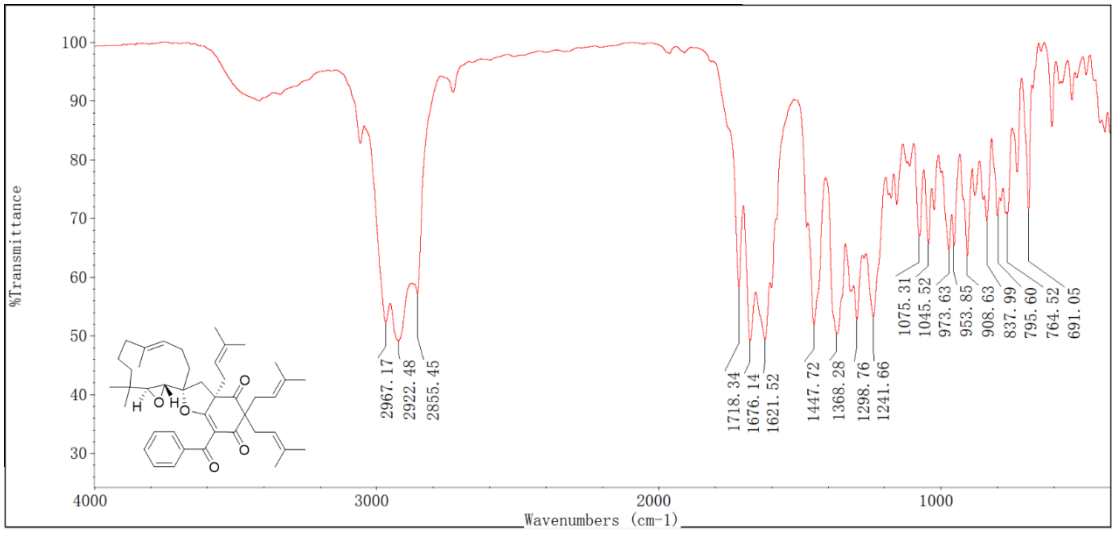


Fig. S80. UV spectrum of hyperkouytin F (**6**).