Supplementary material

NMR-guided isolation of anti-inflammatory carabranolides from the fruits of *Carpesium abrotanoides* L.

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Contents of Supplementary Information

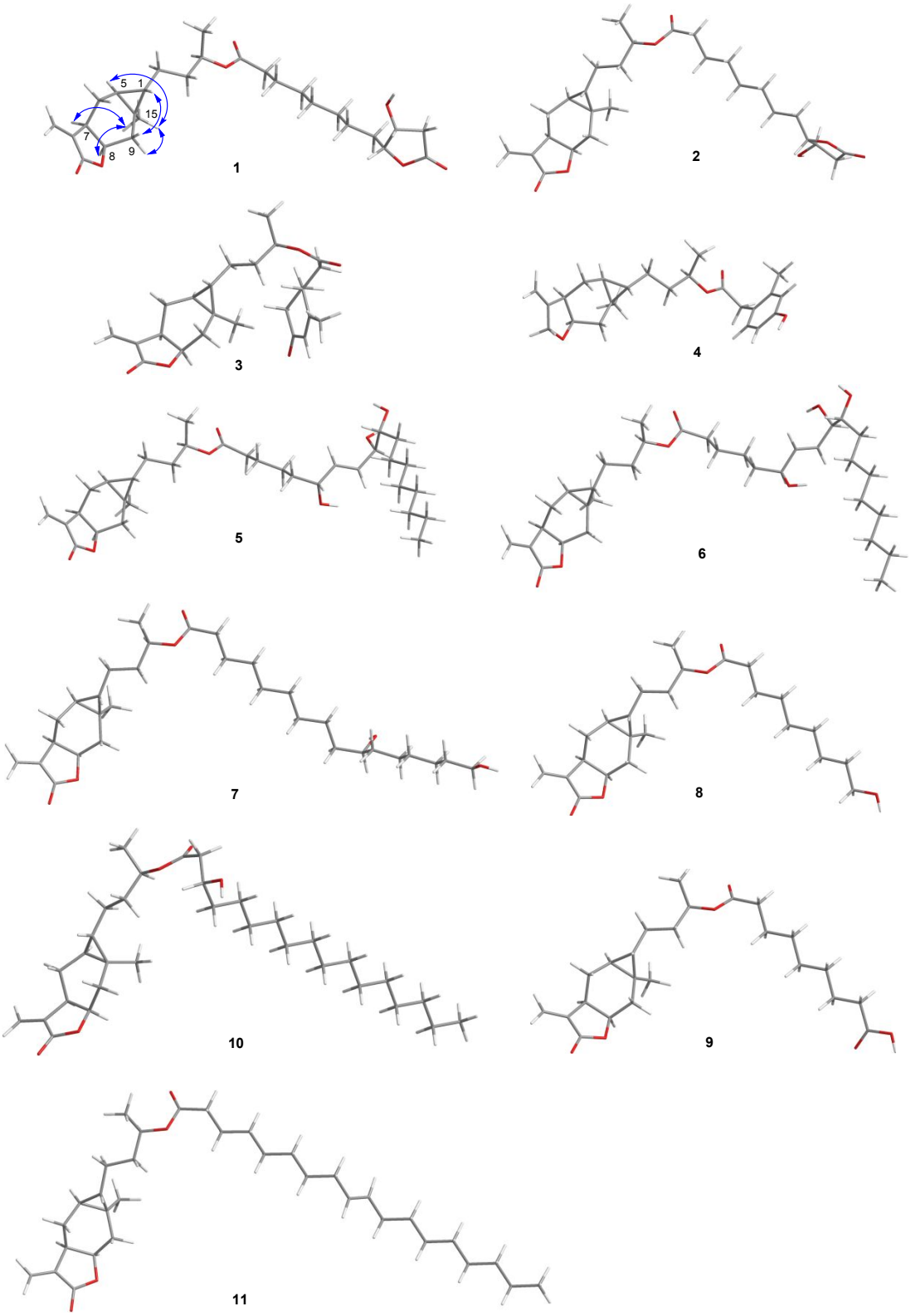


Figure S1.Key NOESY correlations of **1–11**.

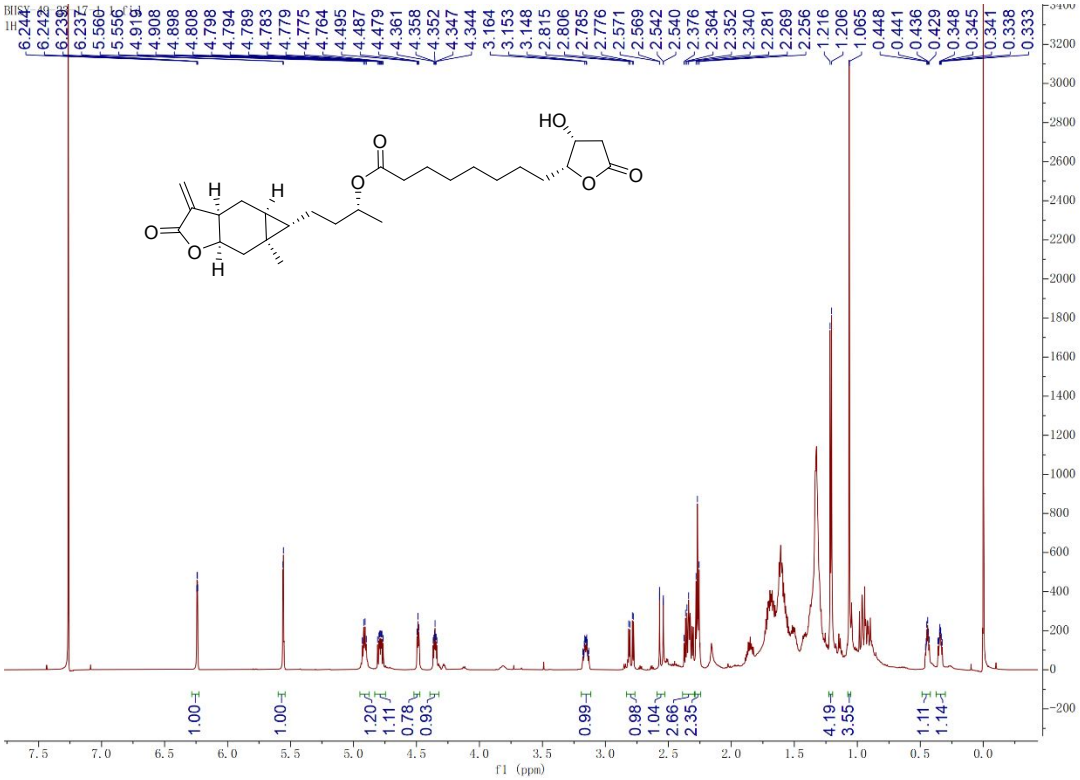


Figure S2. ^{1}H NMR spectrum (600 MHz) of carabrolate A (**1**) in $CDCl_3$

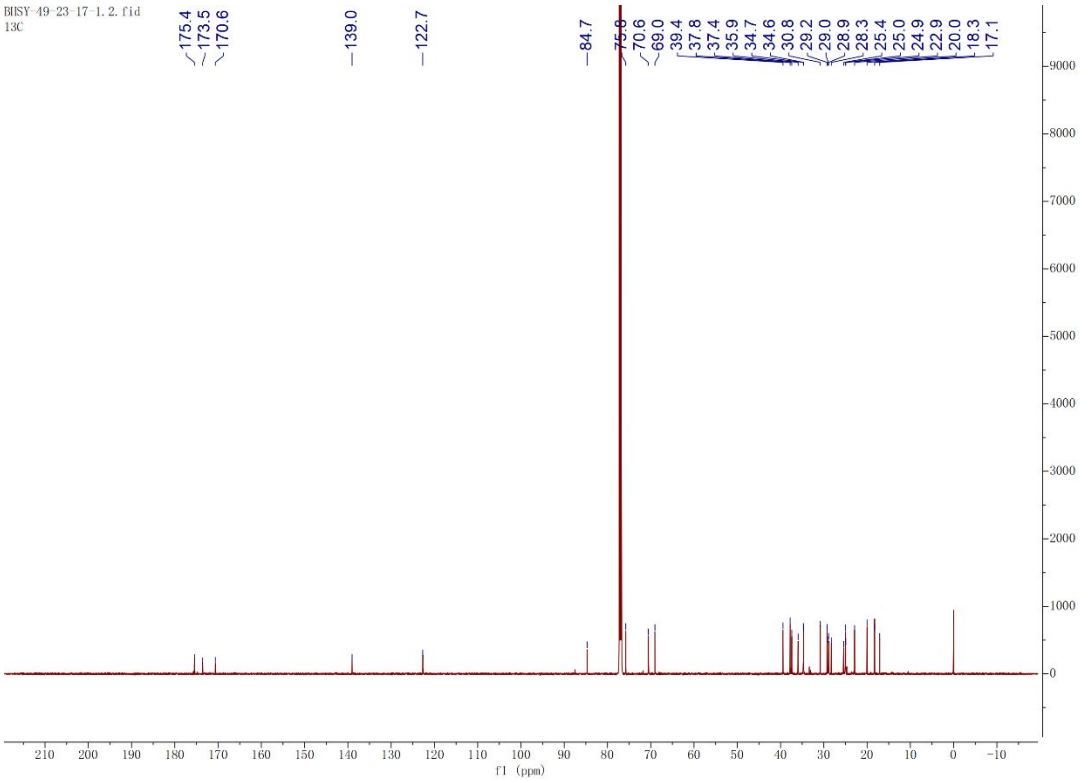


Figure S3. ^{13}C NMR spectrum (150 MHz) of carabrolate (**1**) in $CDCl_3$

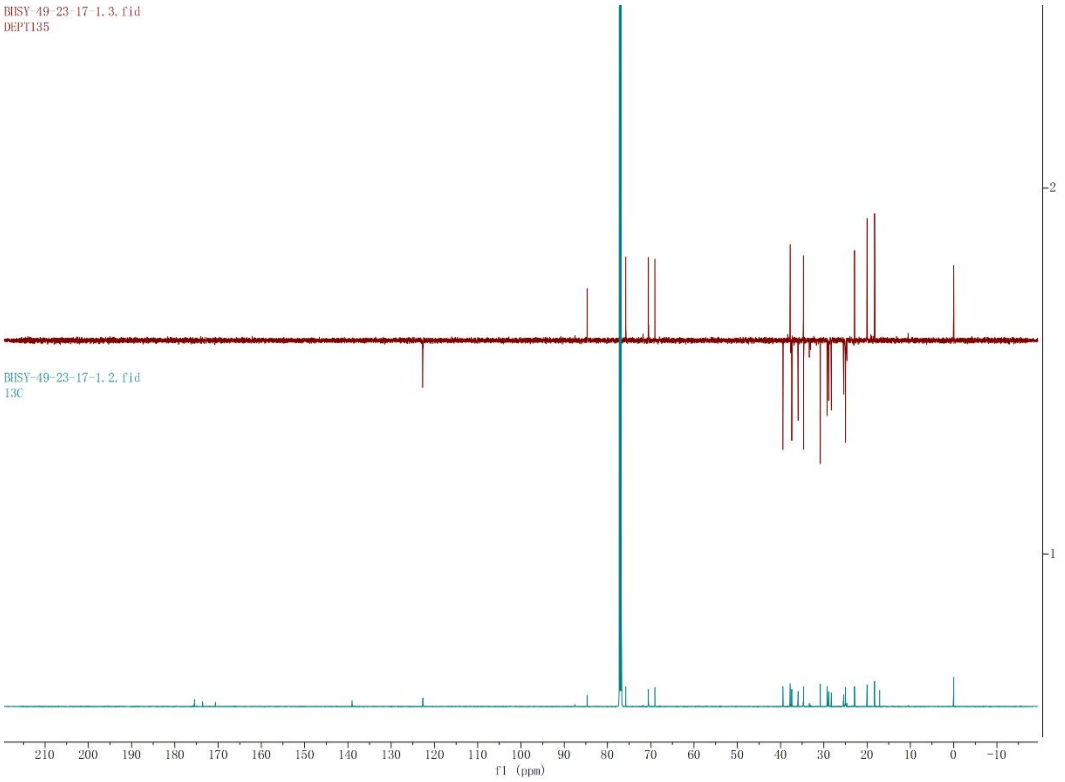


Figure S4. DEPT 135 spectrum (150 MHz) of carabrolate A (**1**) in $CDCl_3$

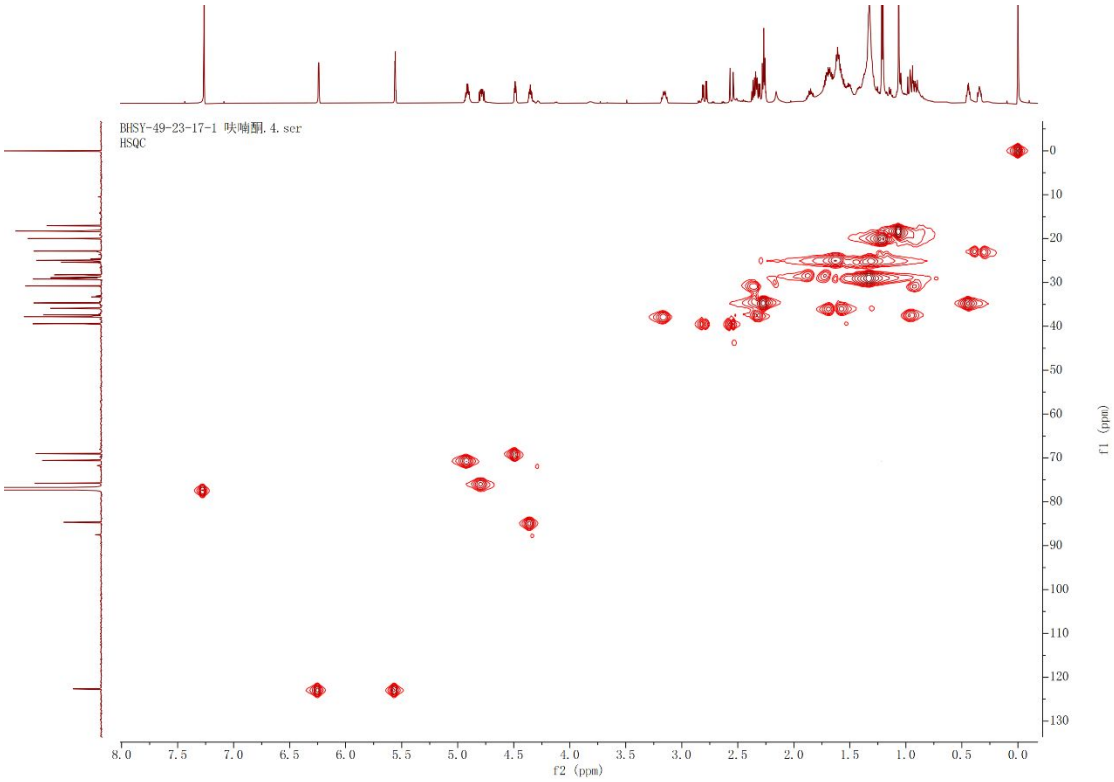


Figure S5. HSQC spectrum (600 MHz) of carabrolate A (**1**) in $CDCl_3$

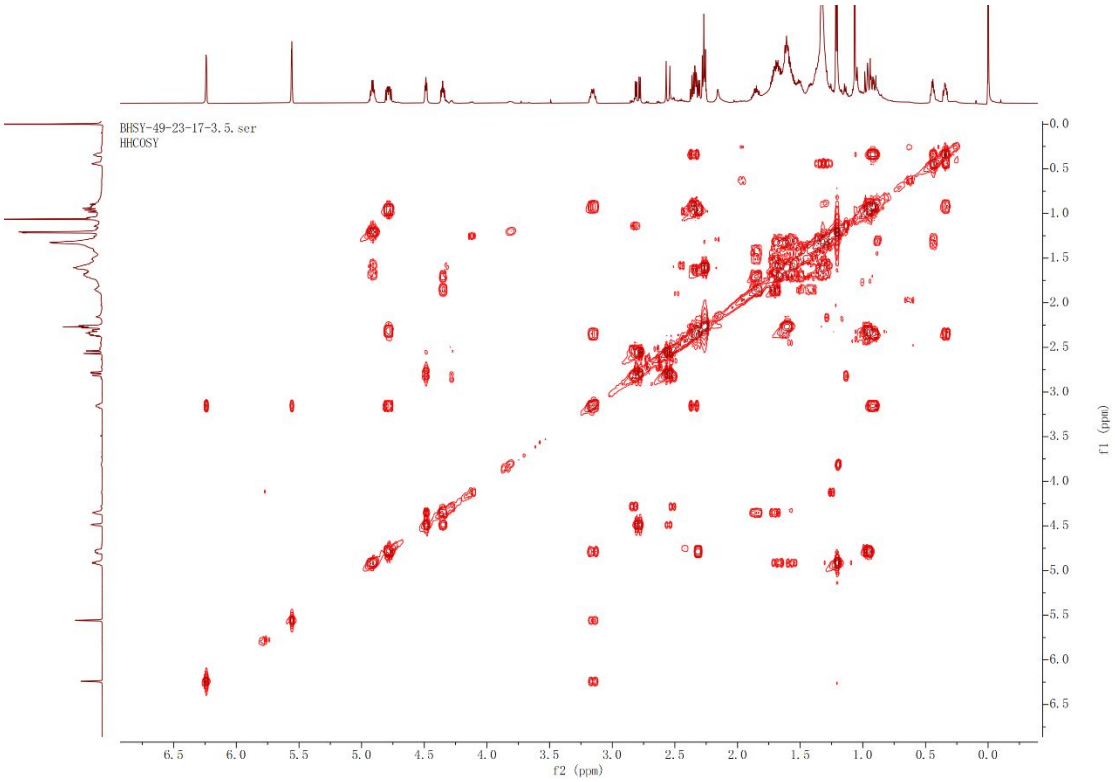


Figure S6. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate A (**1**) in $CDCl_3$

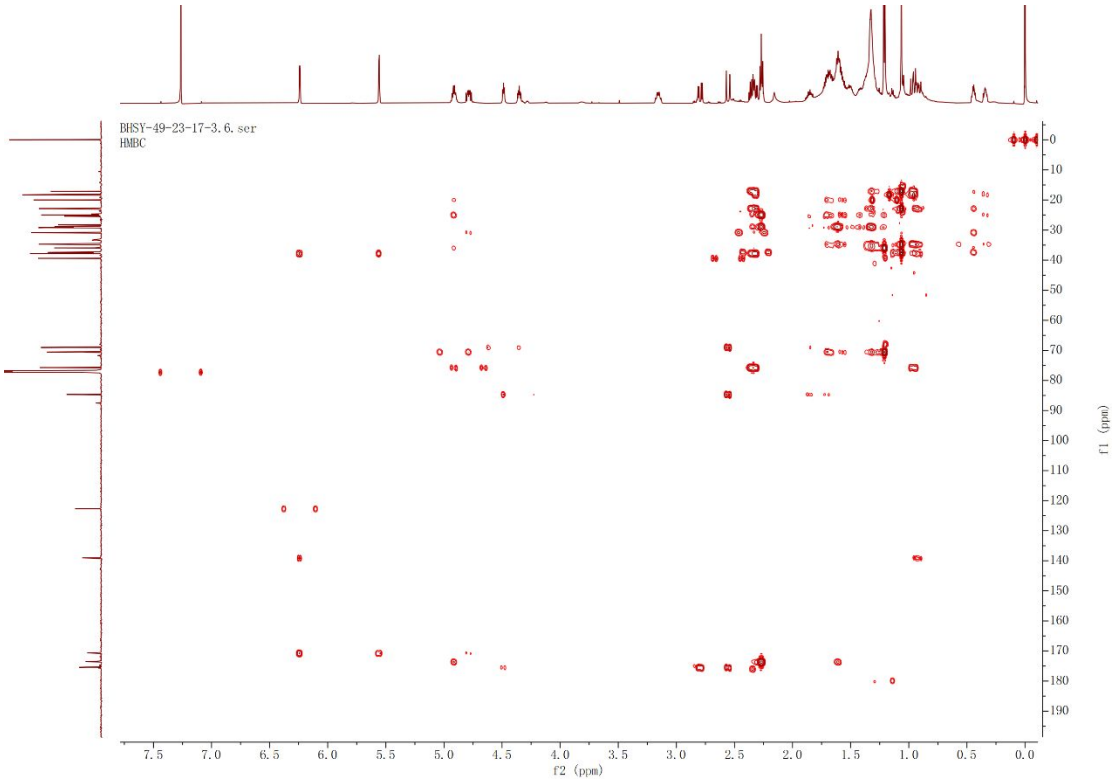


Figure S7. HMBC spectrum (600 MHz) of carabrolate A (**1**) in $CDCl_3$

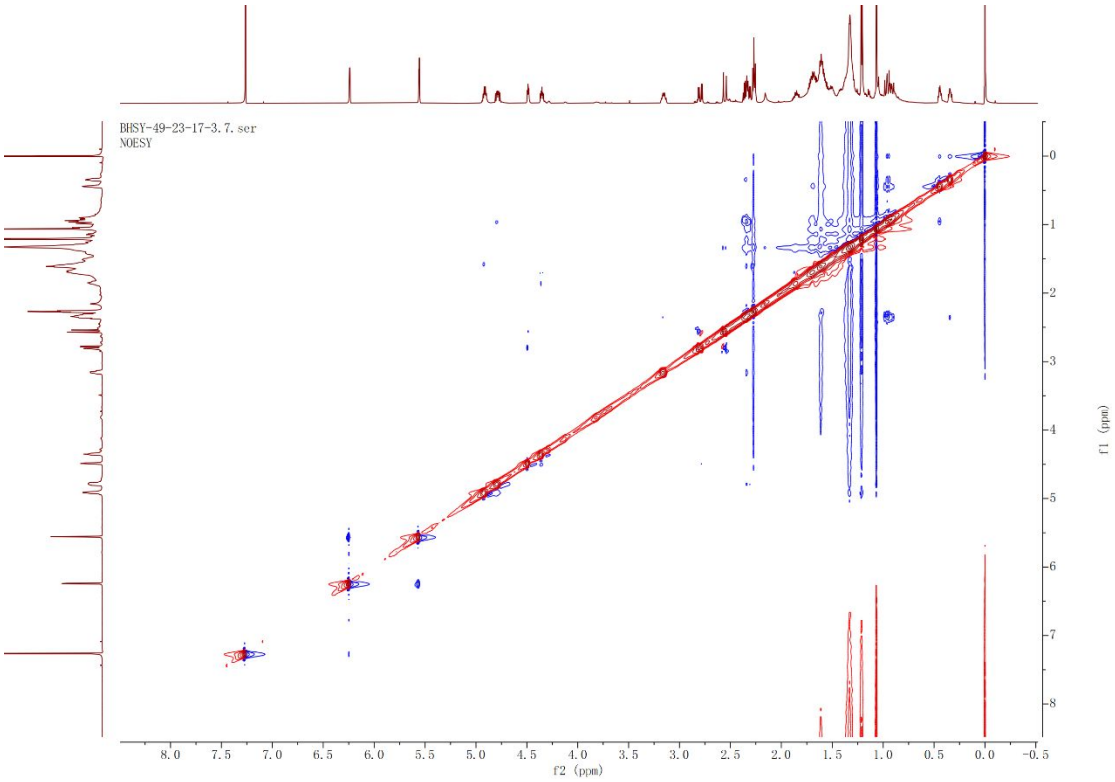


Figure S8. NOESY spectrum (600 MHz) of carabrolate A (**1**) in $CDCl_3$

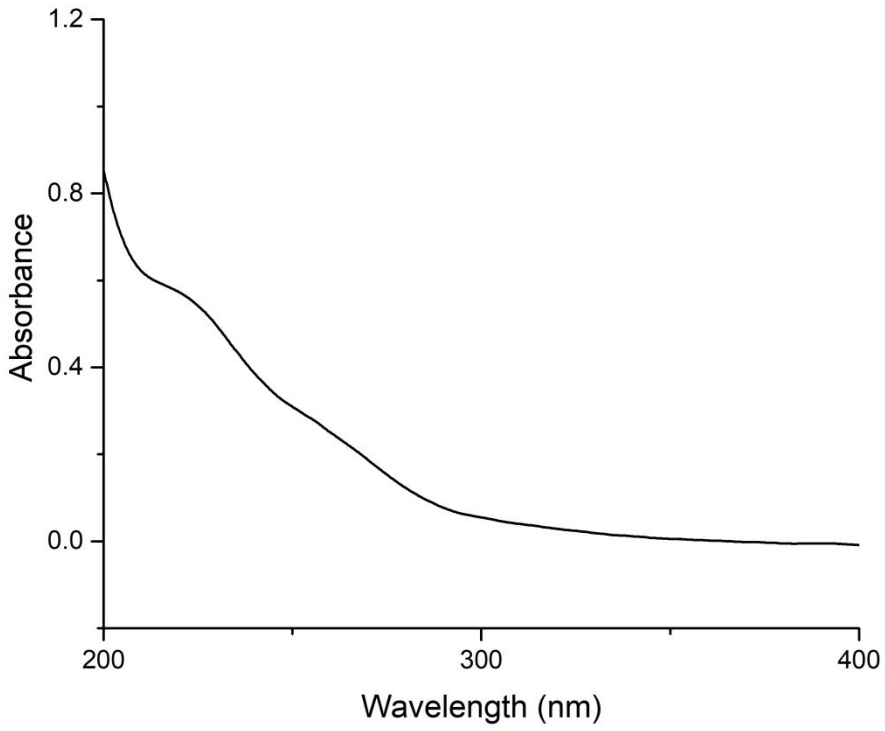


Figure S9. UV spectrum of carabrolate A (**1**) in MeOH

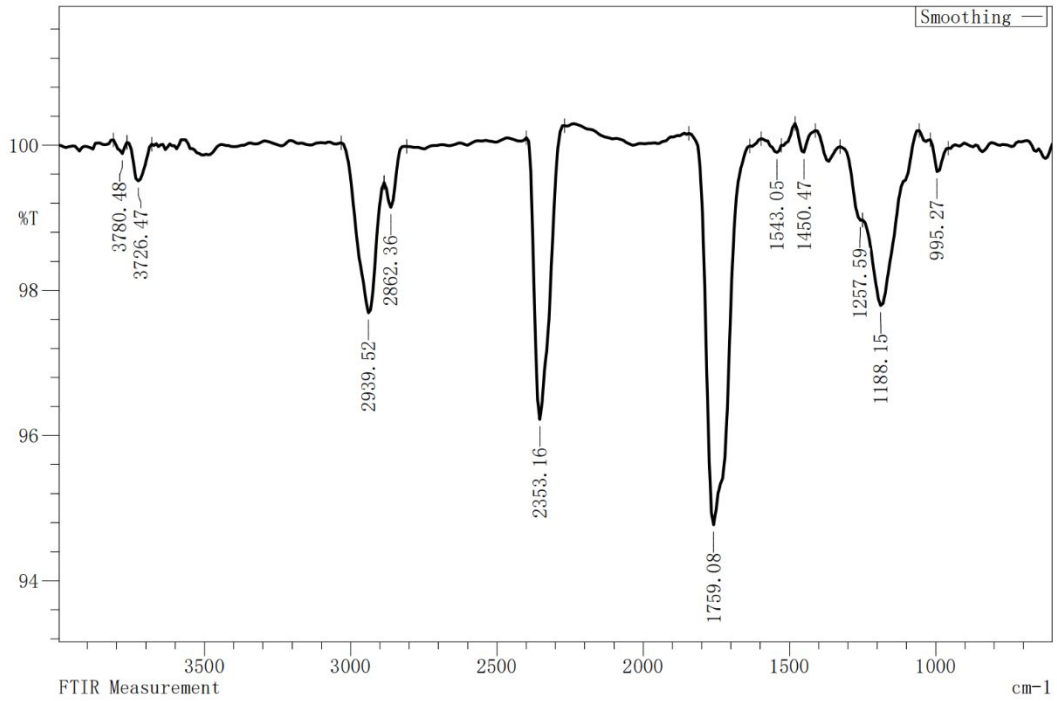
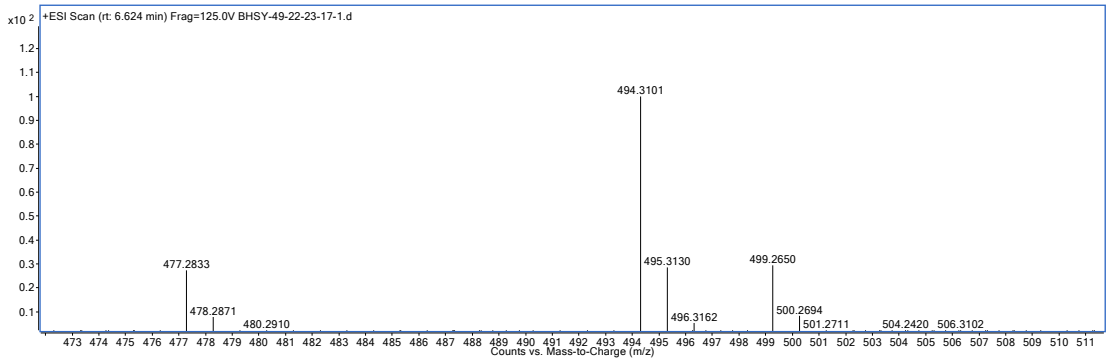


Figure S10. IR spectrum (film on KBr plate) of carabrolate A (**1**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{27}H_{40}O_7$	96.5	476.276	476.2774	477.2847	2.9	$C_{27}H_{41}O_7$	477.2833
$C_{27}H_{40}O_7$	97.62	476.2763	476.2774	494.3112	2.37	$C_{27}H_{44}NO_7$	494.3101

Figure S11. HRESIMS spectrum of carabrolate A (**1**)

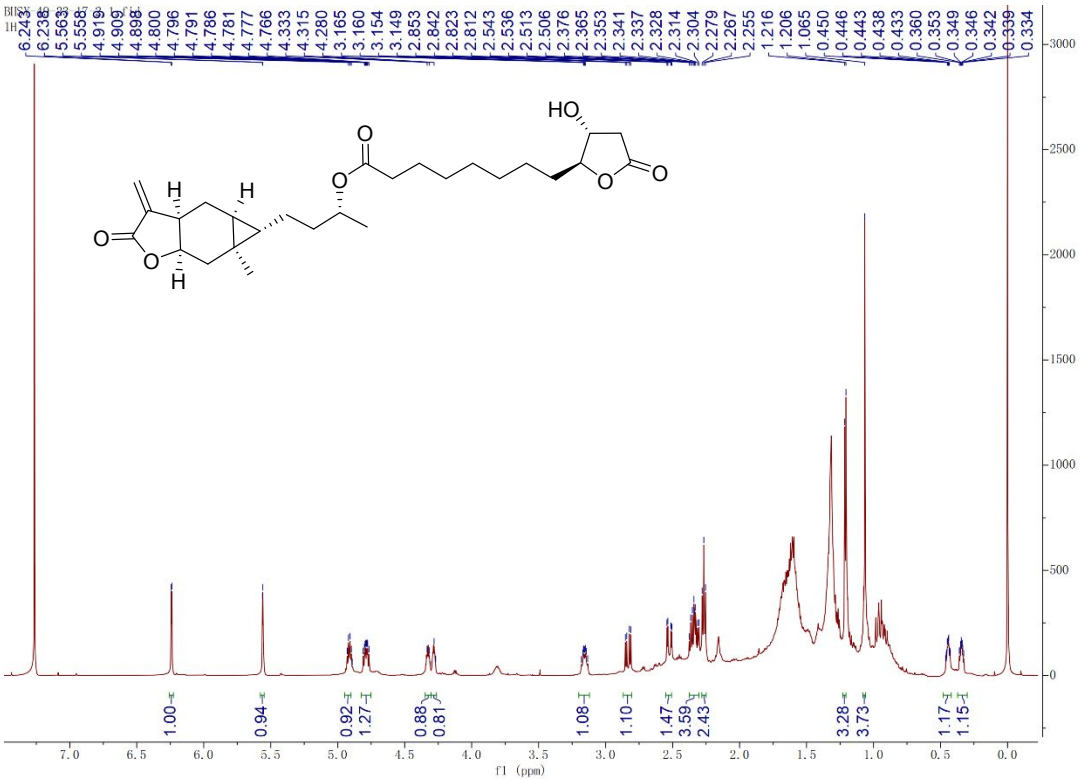


Figure S12. ^{1}H NMR spectrum (600 MHz) of carabrolate B (**2**) in $CDCl_3$

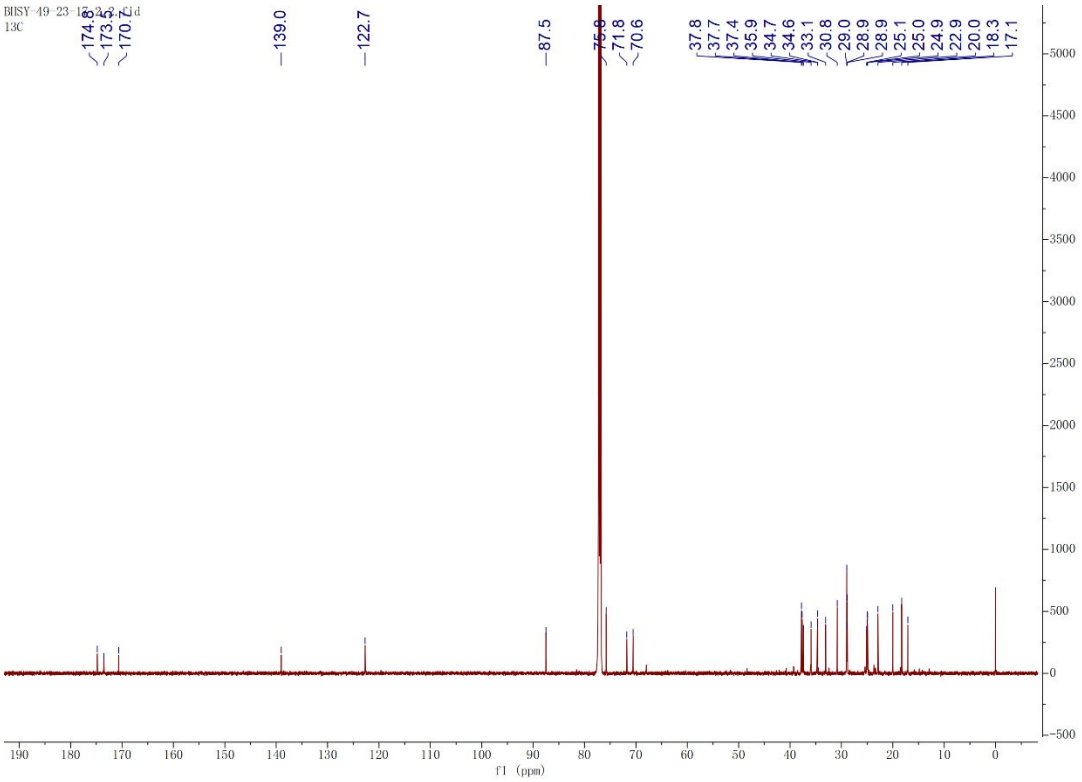


Figure S13. ^{13}C NMR spectrum (150 MHz) of carabrolate B (**2**) in $CDCl_3$

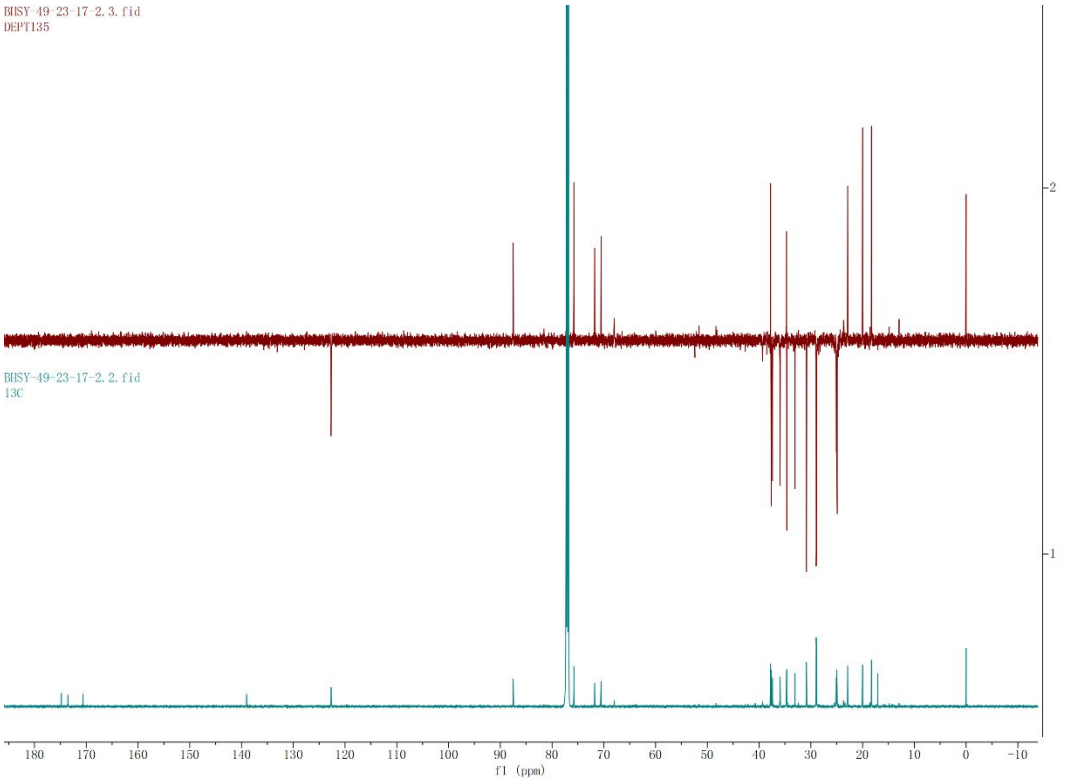


Figure S14. DEPT 135 spectrum (150 MHz) of carabrolate B (**2**) in $CDCl_3$

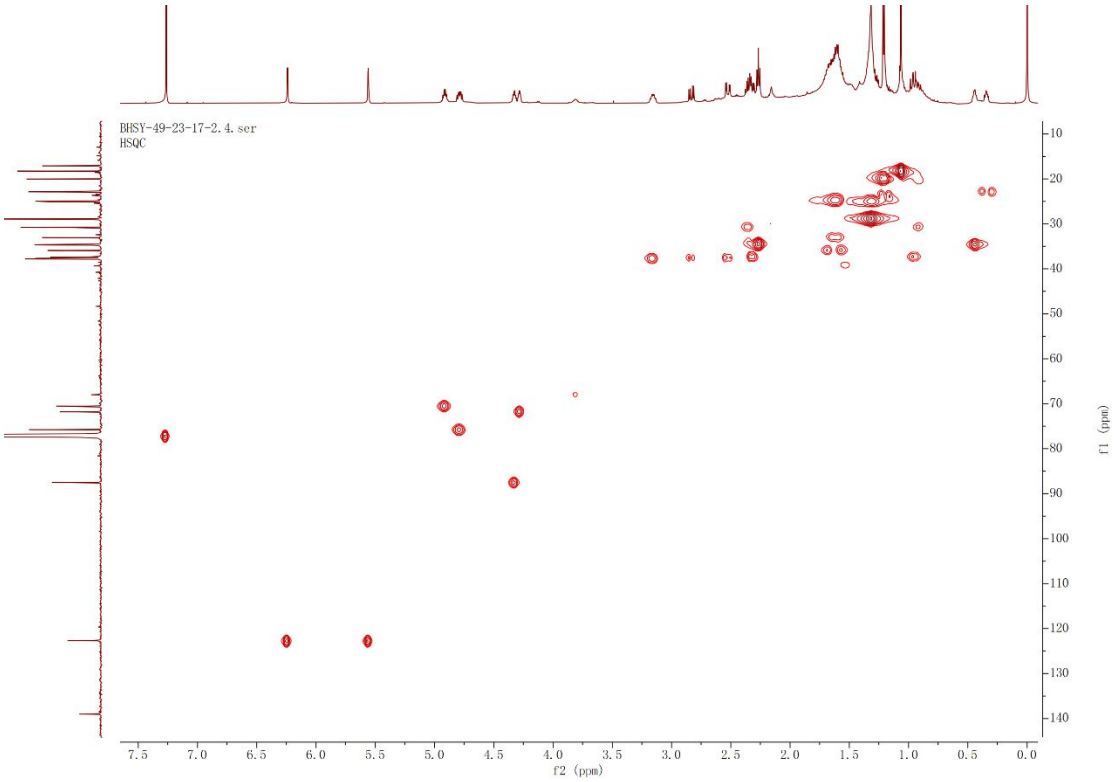


Figure S15. HSQC spectrum (600 MHz) of carabrolate B (**2**) in $CDCl_3$

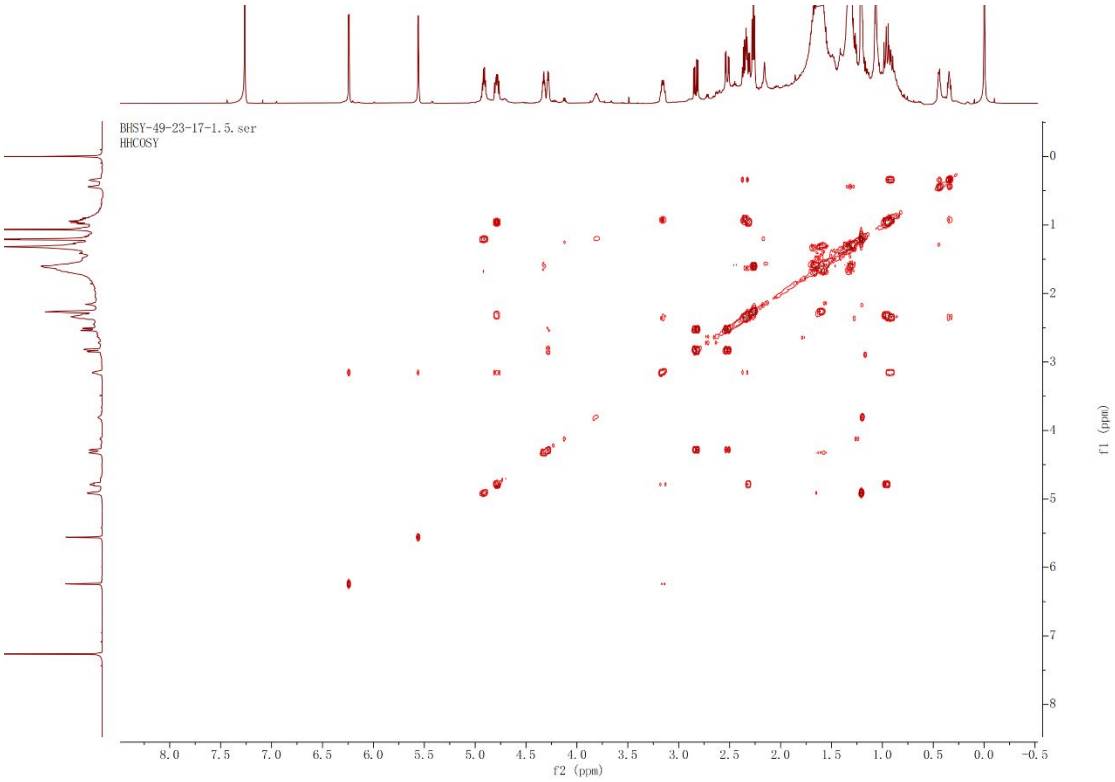


Figure S16. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate B (**2**) in $CDCl_3$

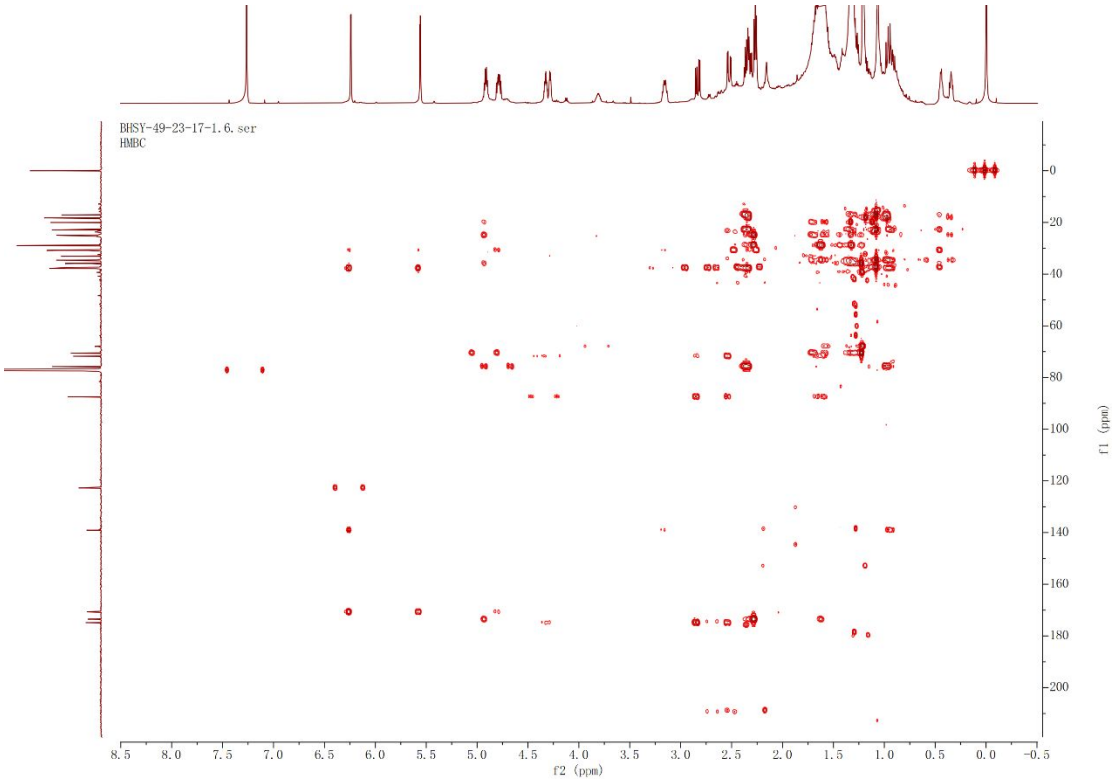


Figure S17. HMBC spectrum (600 MHz) of carabrolate B (**2**) in $CDCl_3$

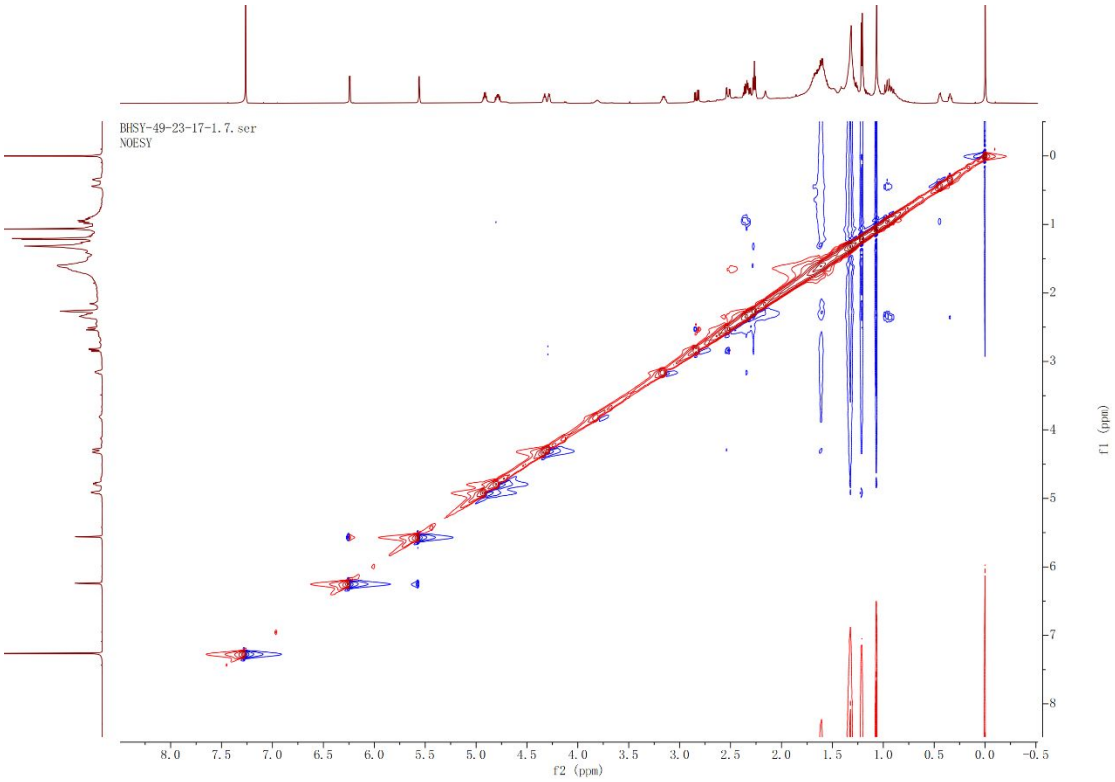


Figure S18. NOESY spectrum (600 MHz) of carabrolate B (**2**) in $CDCl_3$

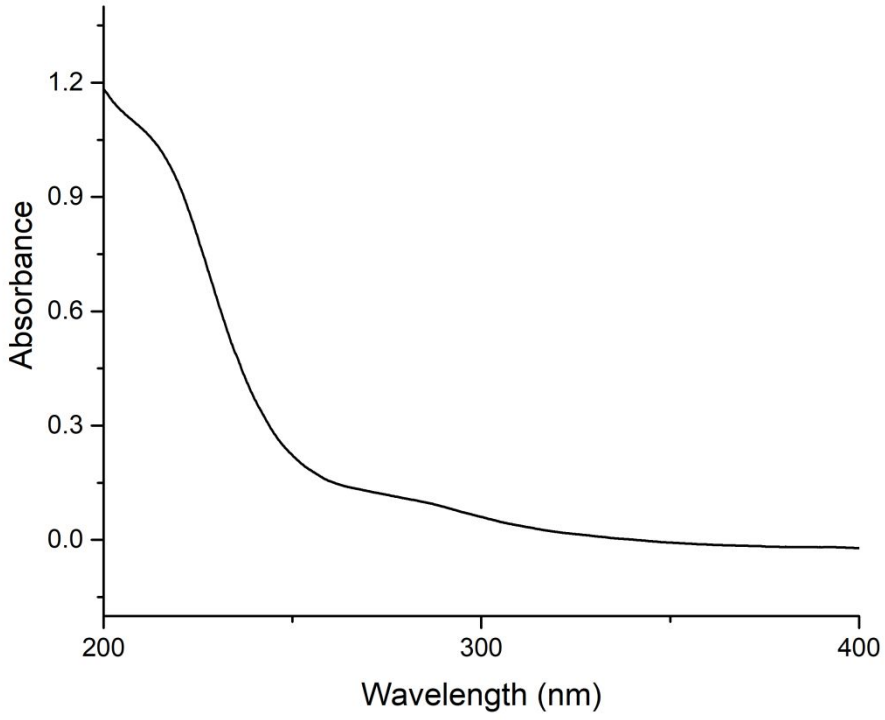


Figure S19. UV spectrum of carabrolate B (**2**) in MeOH

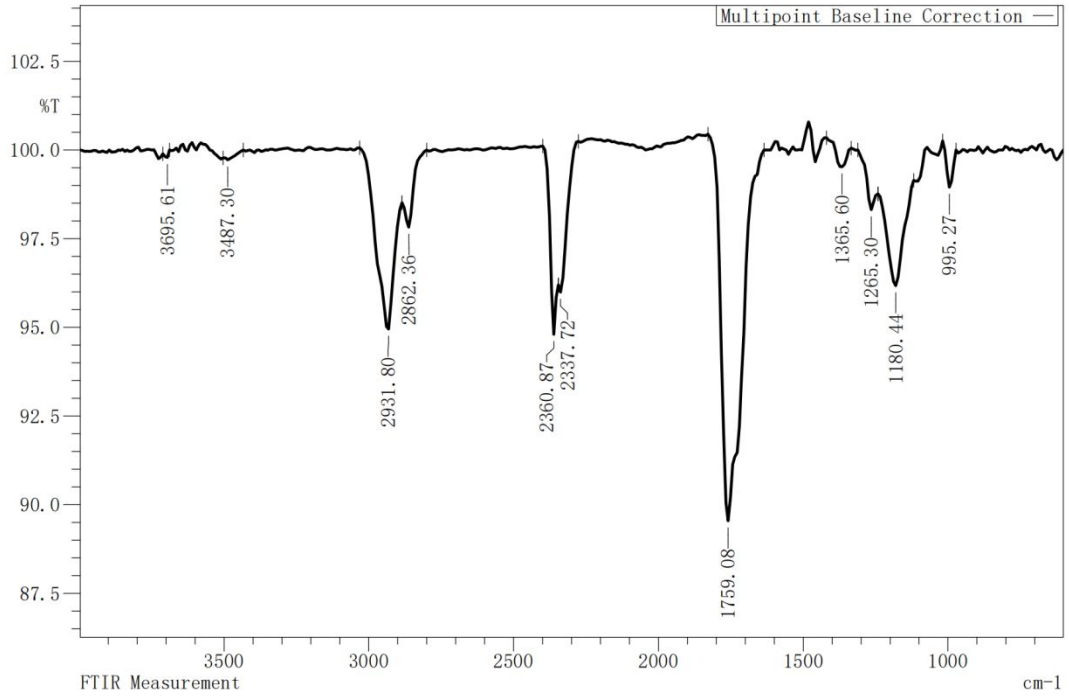
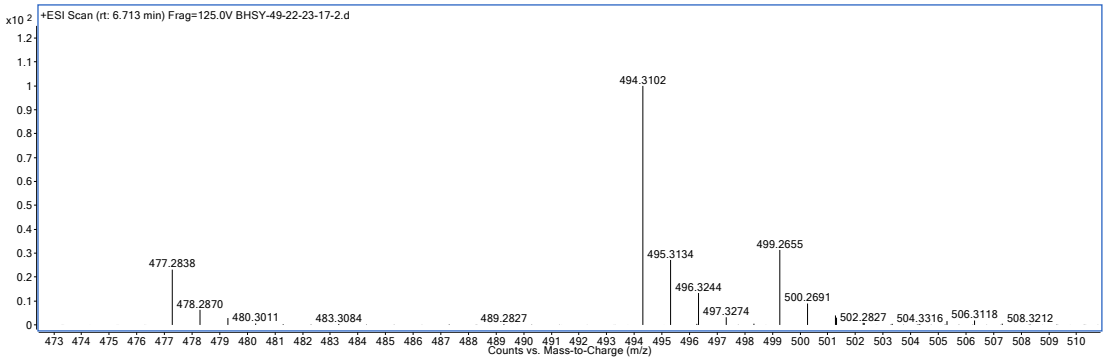


Figure S20. IR spectrum (film on KBr plate) of carabrolate B (**2**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{27}H_{40}O_7$	98.54	476.2765	476.2774	477.2847	1.85	$C_{27}H_{41}O_7$	477.2838
$C_{27}H_{40}O_7$	98.01	476.2764	476.2774	494.3112	2.16	$C_{27}H_{44}NO_7$	494.3102

Figure S21. HRESIMS spectrum of carabrolate B (**2**).

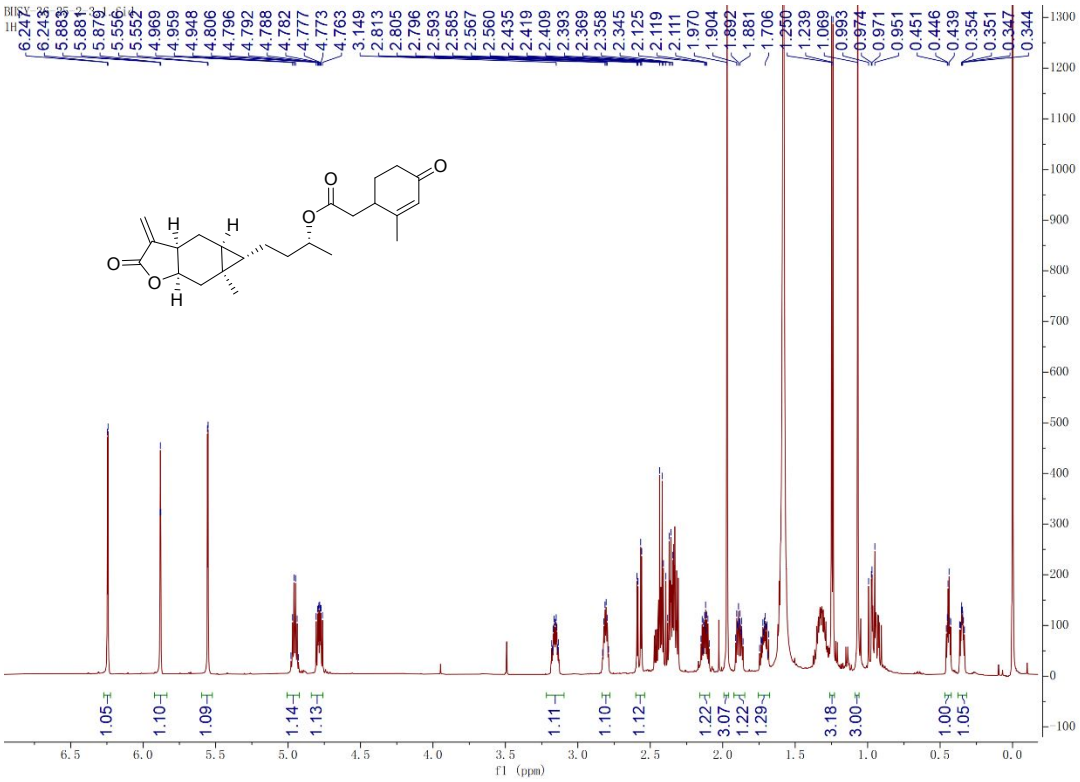


Figure S22. ^{1}H NMR spectrum (600 MHz) of carabrolate C (**3**) in $CDCl_3$

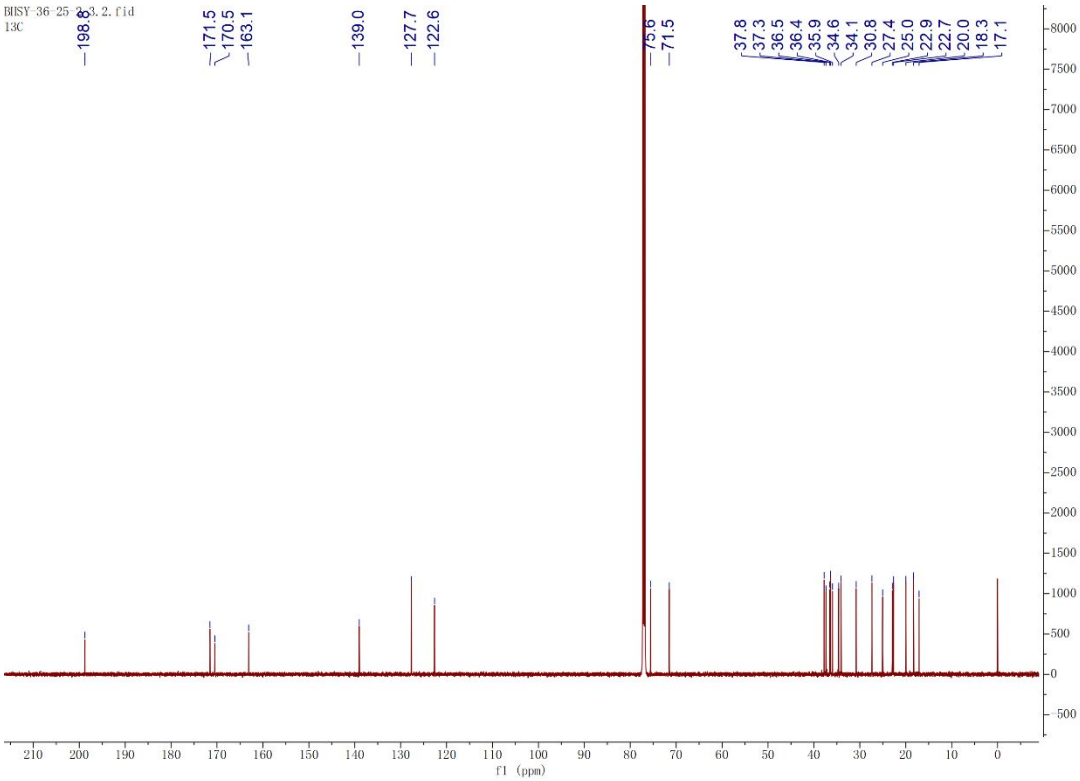


Figure S23. ^{13}C NMR spectrum (150 MHz) of carabrolate C (**3**) in $CDCl_3$

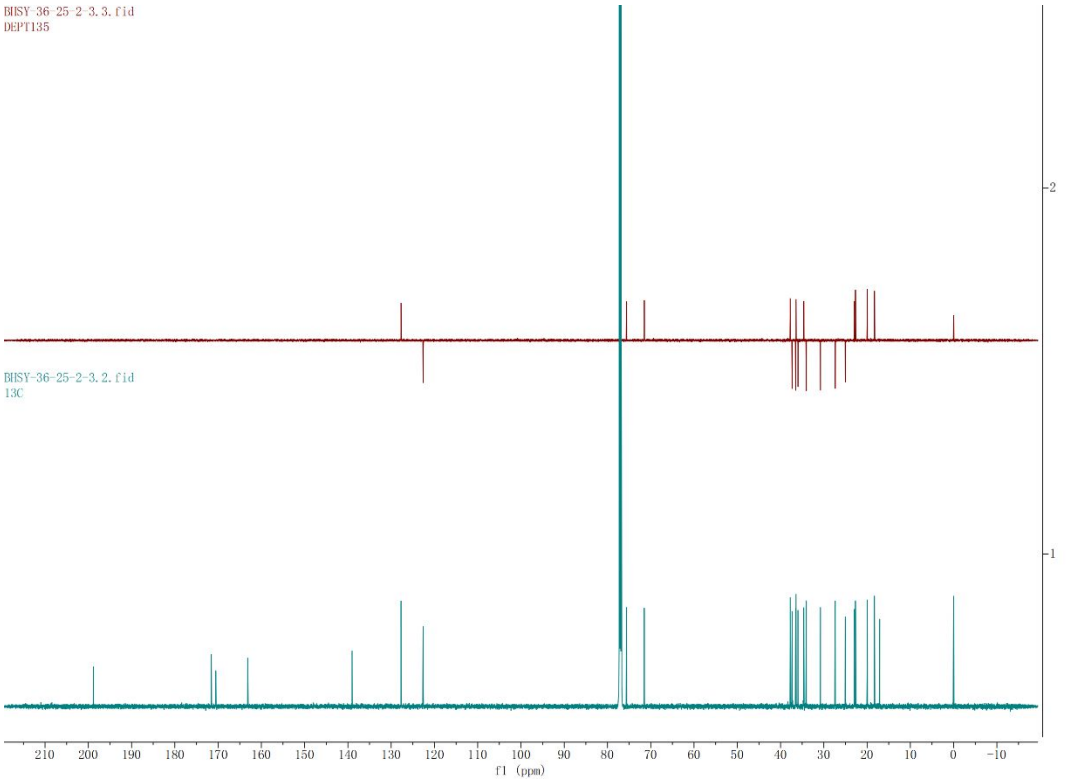


Figure S24. DEPT 135 spectrum (150 MHz) of carabrolate C (**3**) in $CDCl_3$

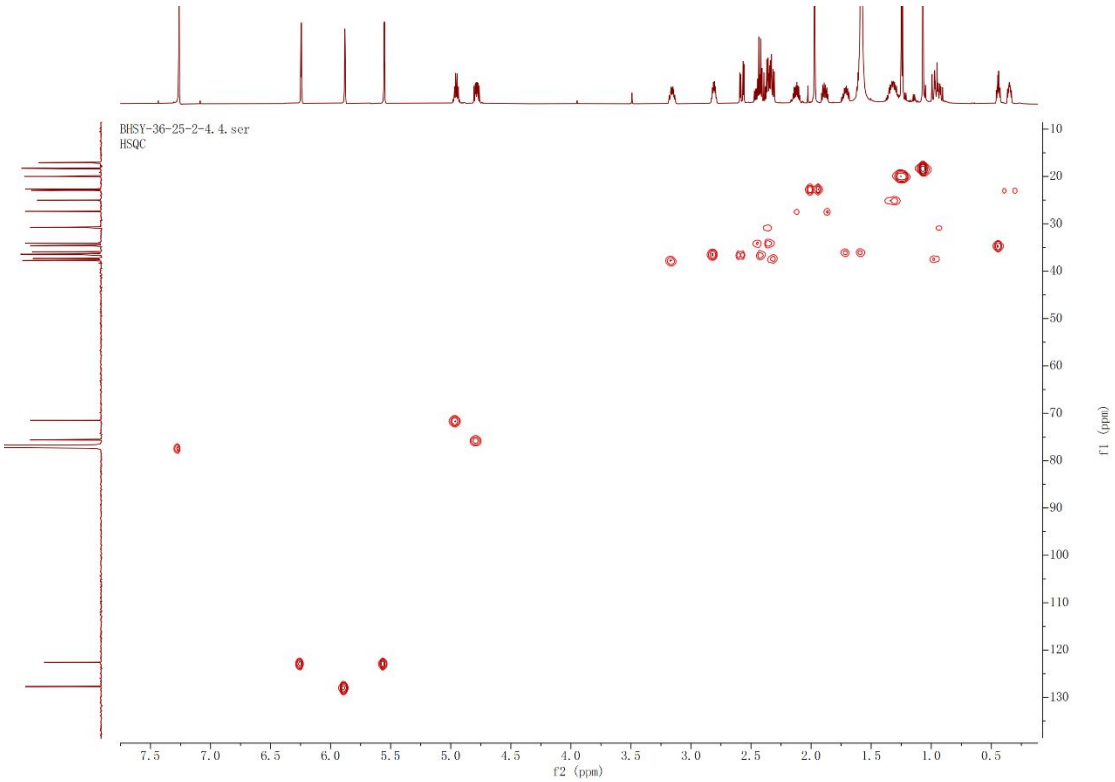


Figure S25. HSQC spectrum (600 MHz) of carabrolate C (**3**) in $CDCl_3$

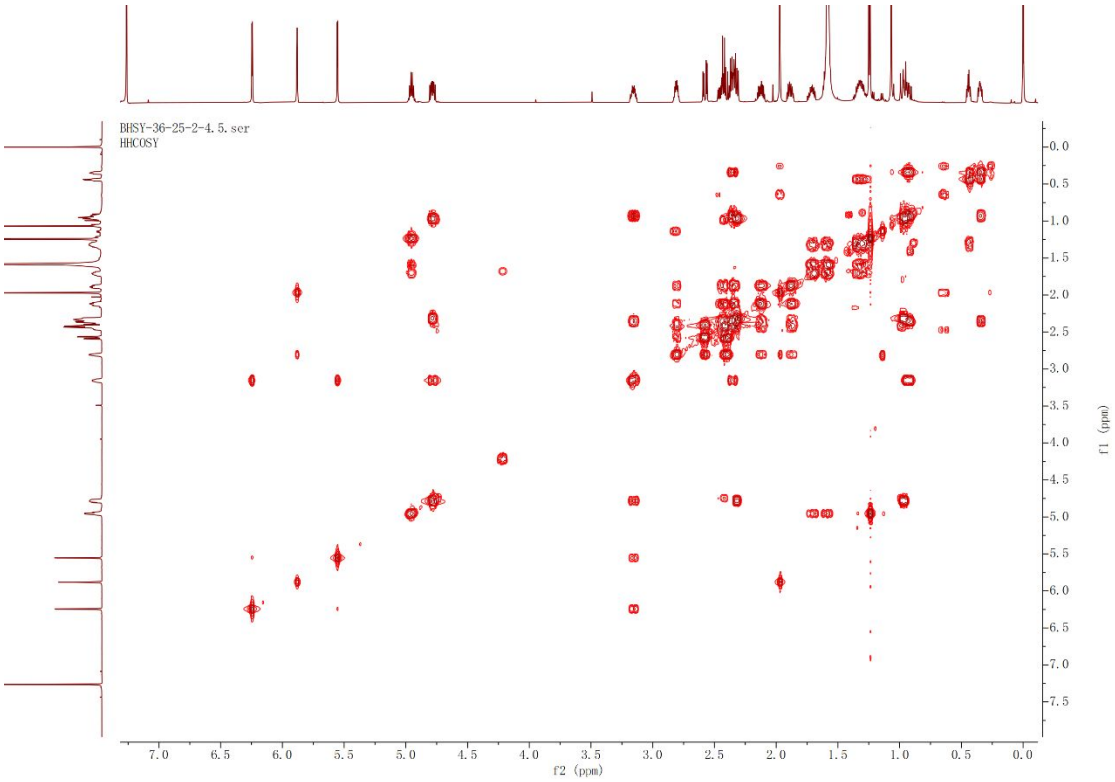


Figure S26. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate C (**3**) in $CDCl_3$

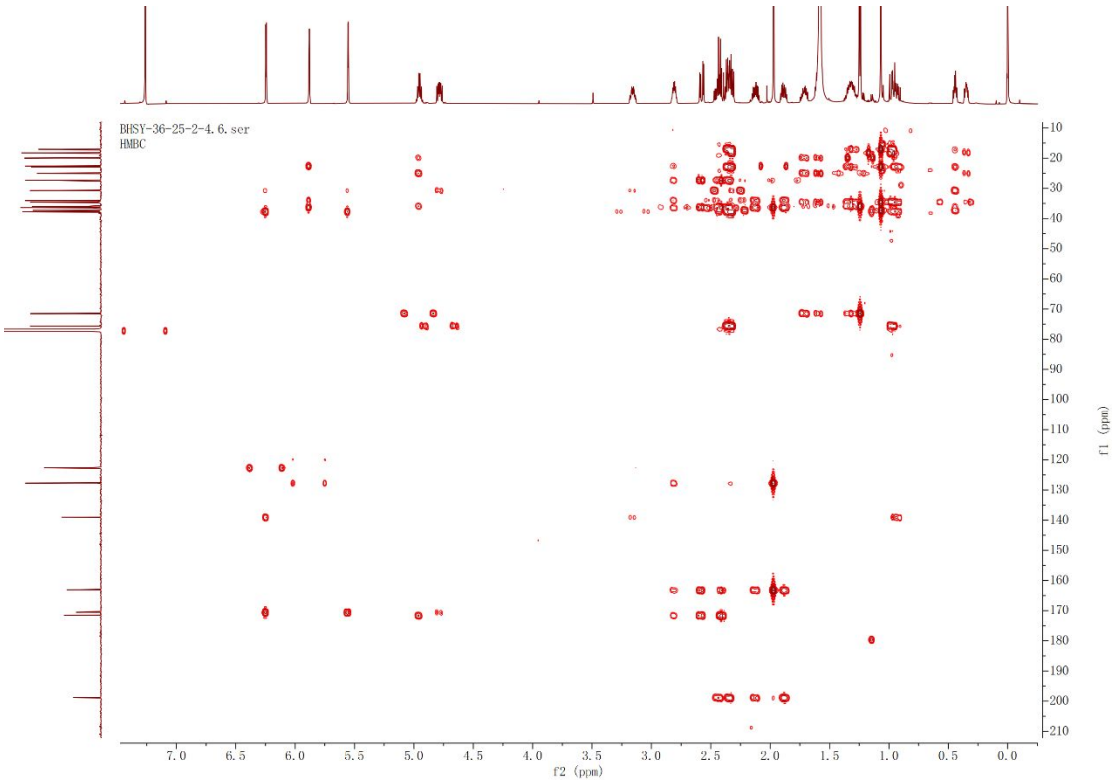


Figure S27. HMBC spectrum (600 MHz) of carabrolate C (**3**) in $CDCl_3$

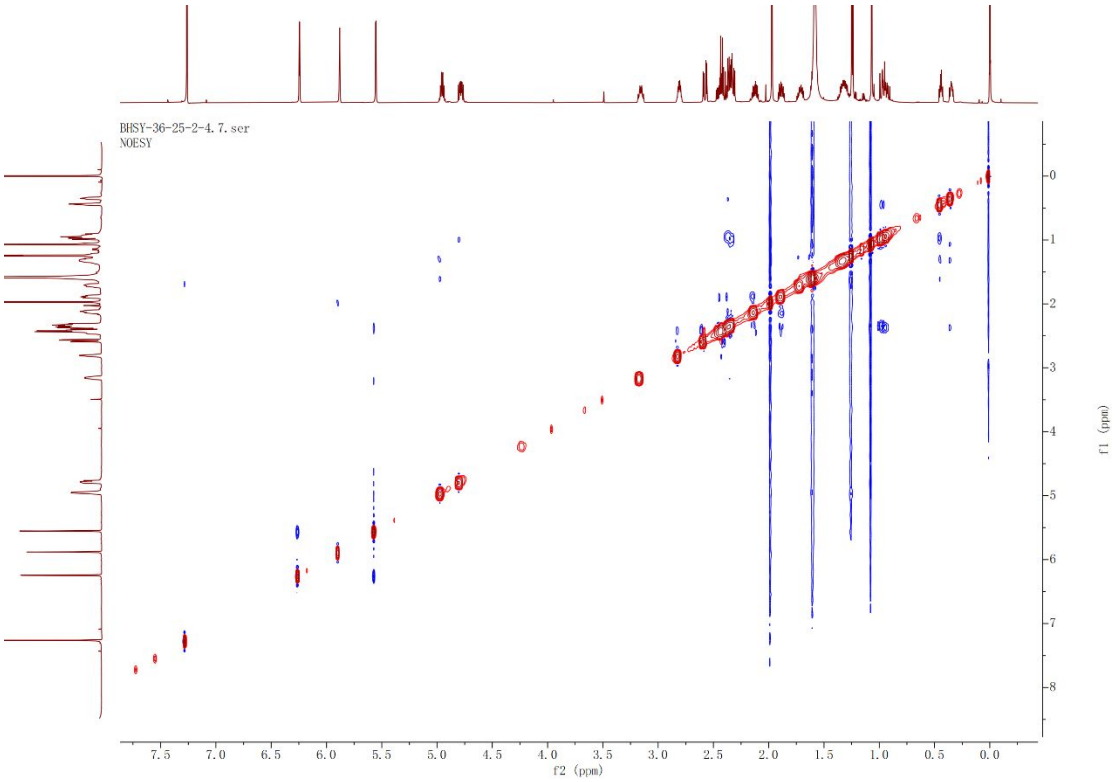


Figure S28. NOESY spectrum (600 MHz) of carabrolate C (**3**) in $CDCl_3$

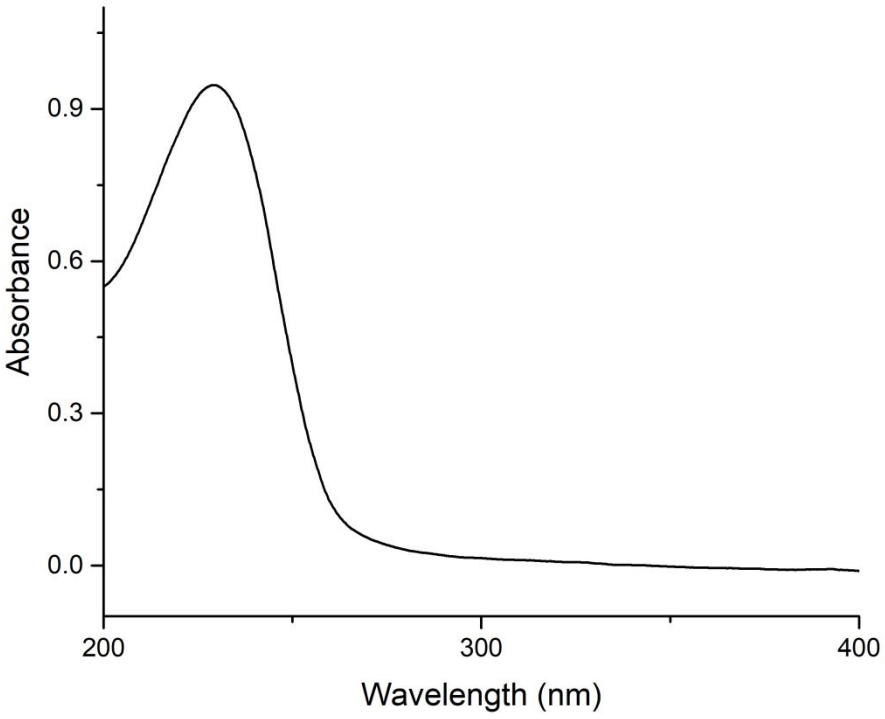


Figure S29. UV spectrum of carabrolate C (**3**) in MeOH

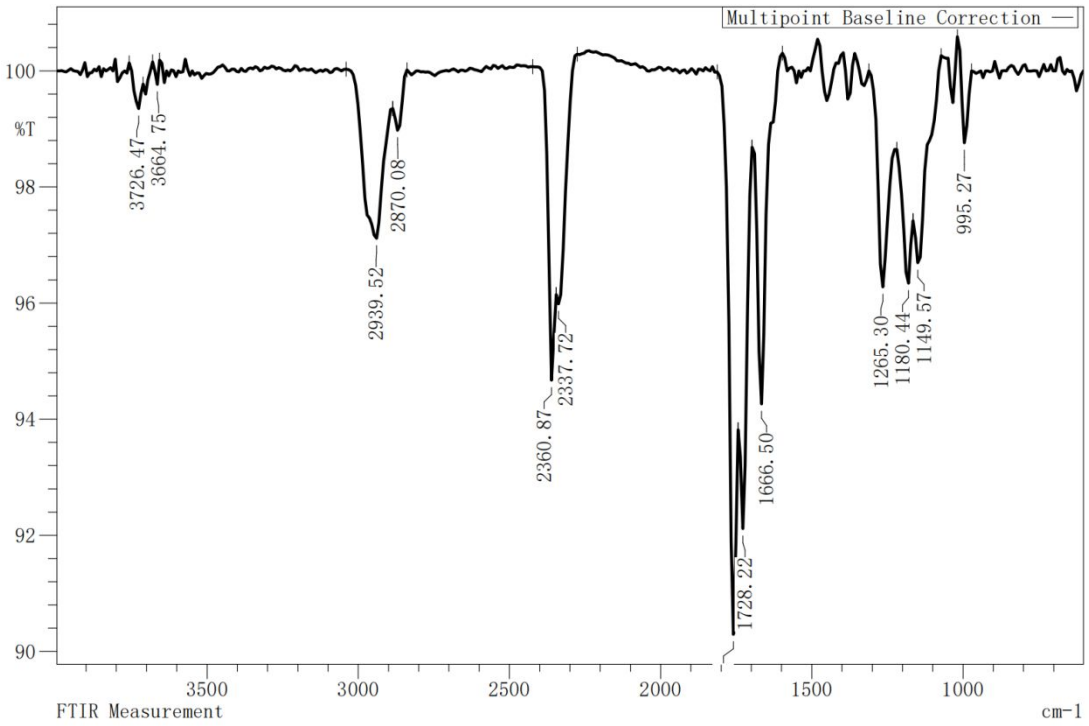
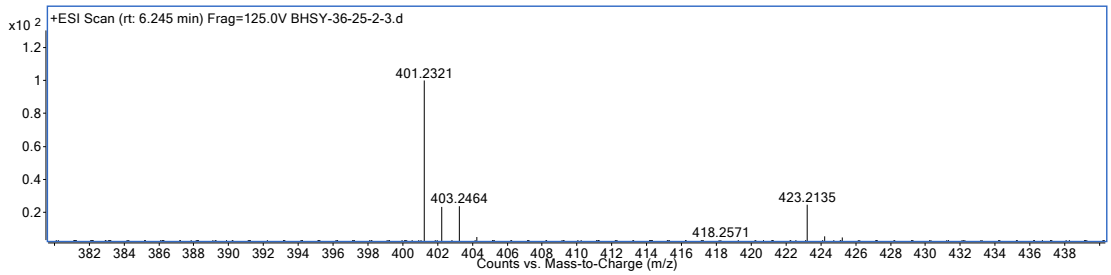


Figure S30. IR spectrum (film on KBr plate) of carabrolate C (**3**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{27}H_{40}O_7$	98.54	476.2765	476.2774	477.2847	1.85	$C_{27}H_{41}O_7$	477.2838
$C_{27}H_{40}O_7$	98.01	476.2764	476.2774	494.3112	2.16	$C_{27}H_{44}NO_7$	494.3102

Figure S31. HRESIMS spectrum of carabrolate C (**3**)

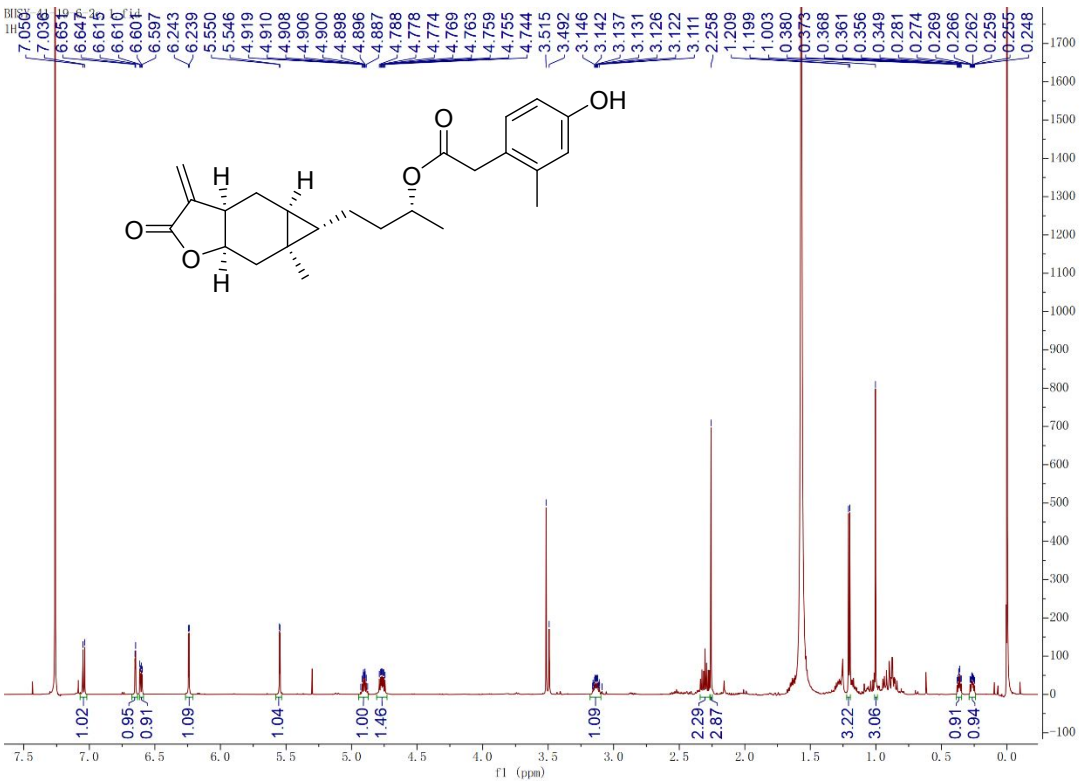


Figure S32. ^{1}H NMR spectrum (600 MHz) of carabrolate D (**4**) in $CDCl_3$

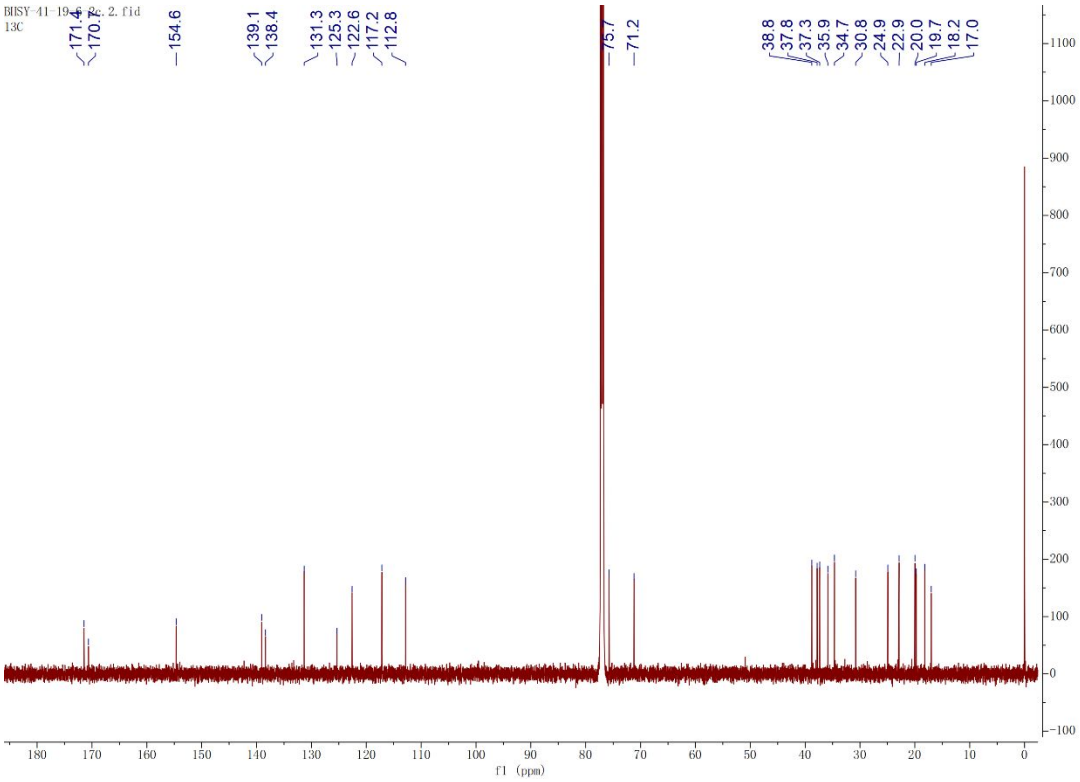


Figure S33. ^{13}C NMR spectrum (150 MHz) of carabrolate D (**4**) in $CDCl_3$

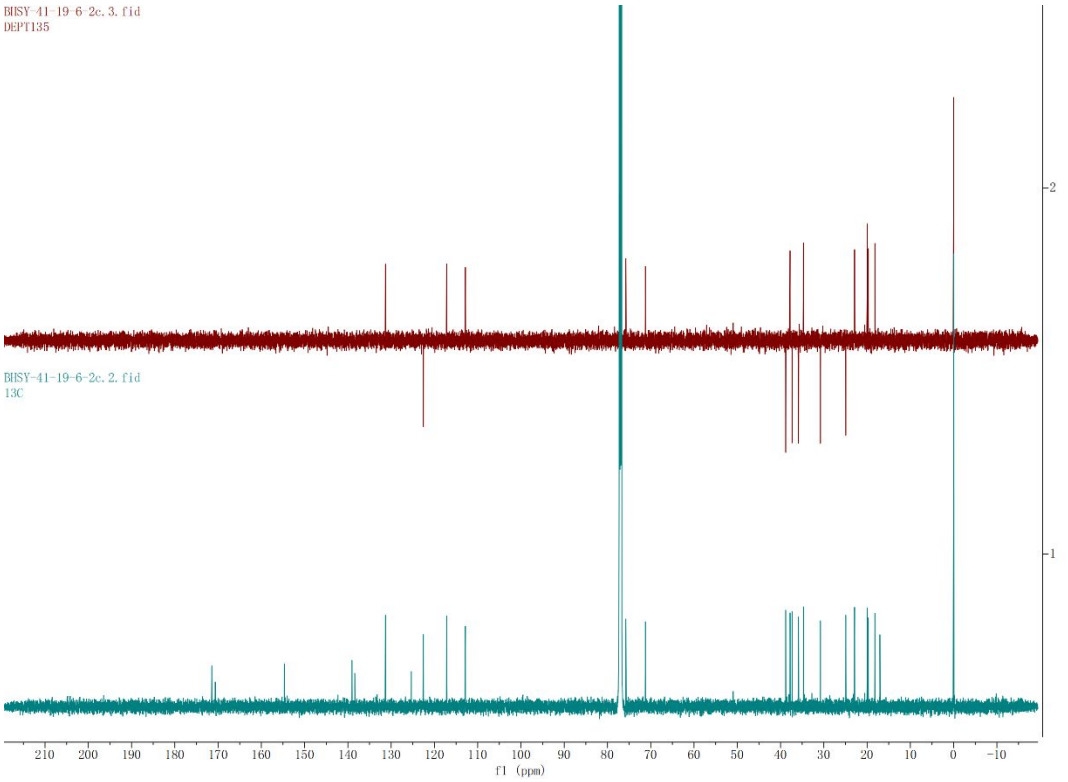


Figure S34. DEPT 135 spectrum (150 MHz) of carabrolate D (**4**) in $CDCl_3$

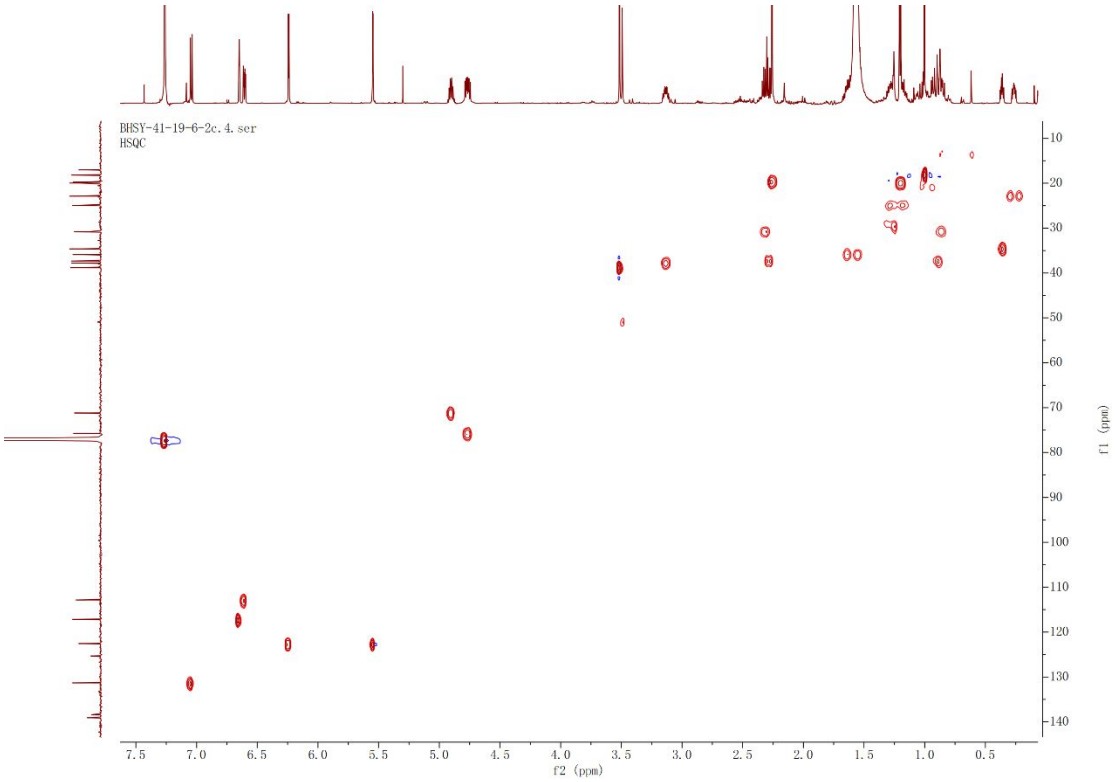


Figure S35. HSQC spectrum (600 MHz) of carabrolate D (**4**) in $CDCl_3$

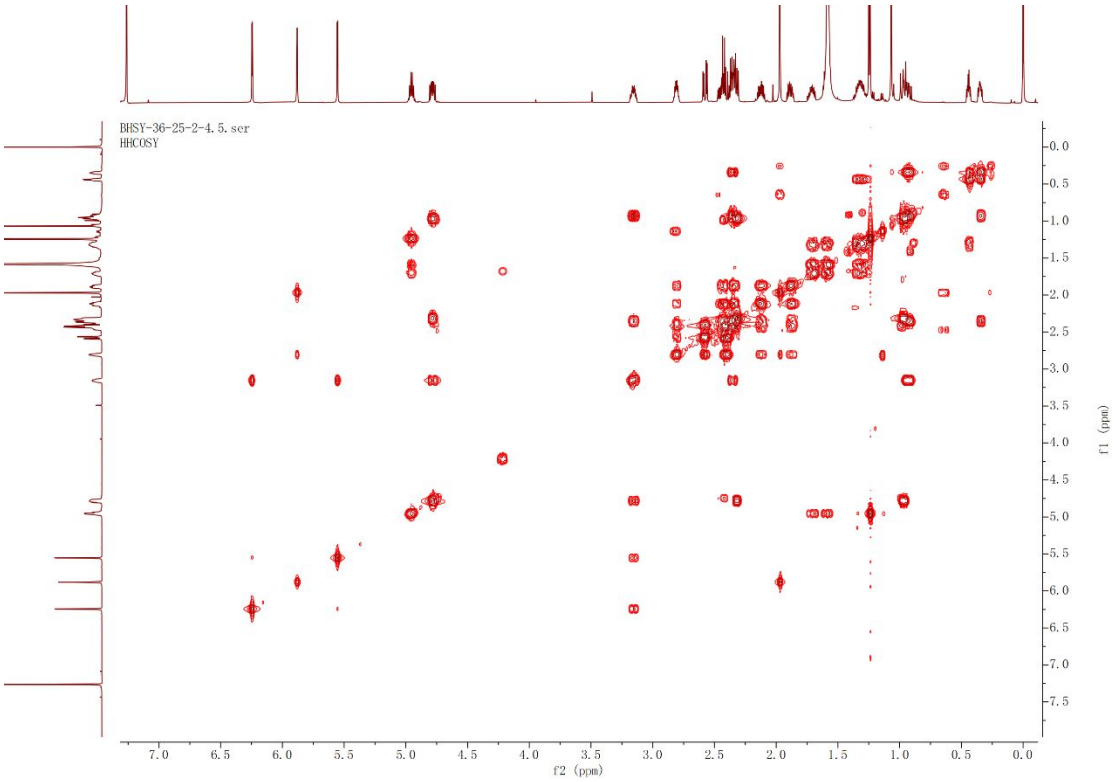


Figure S36. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate D (**4**) in $CDCl_3$

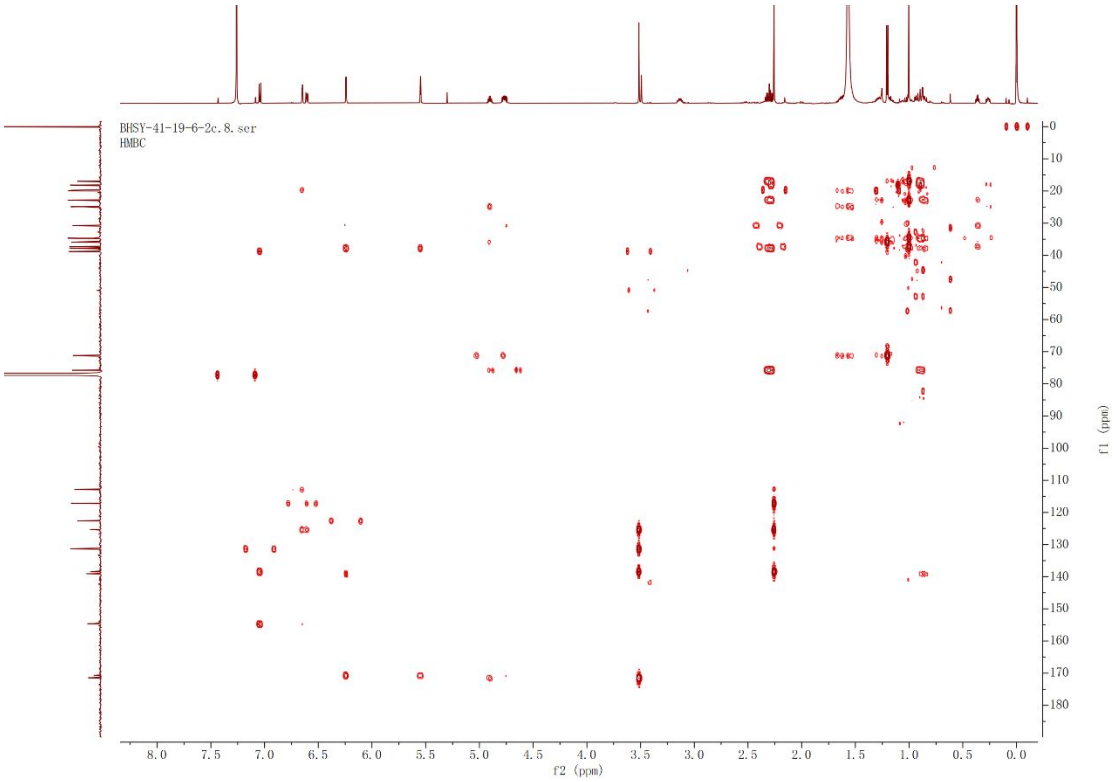


Figure S37. HMBC spectrum (600 MHz) of carabrolate D (**4**) in $CDCl_3$

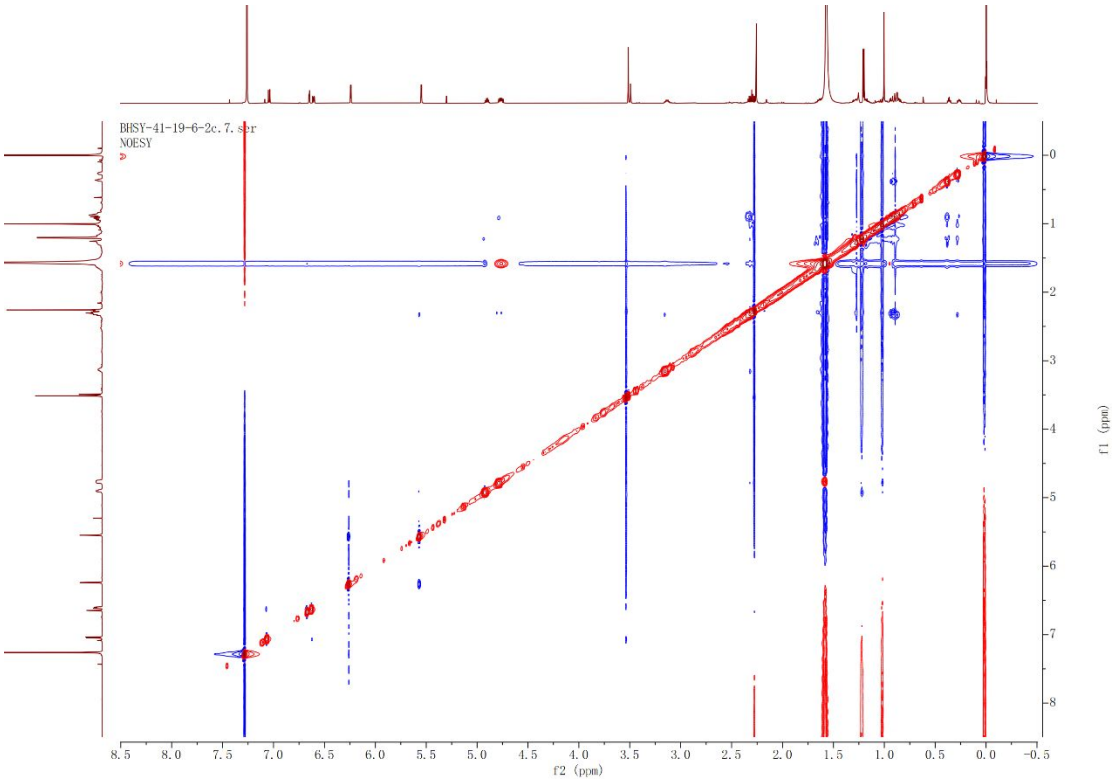


Figure S38. NOESY spectrum (600 MHz) of carabrolate D (**4**) in $CDCl_3$

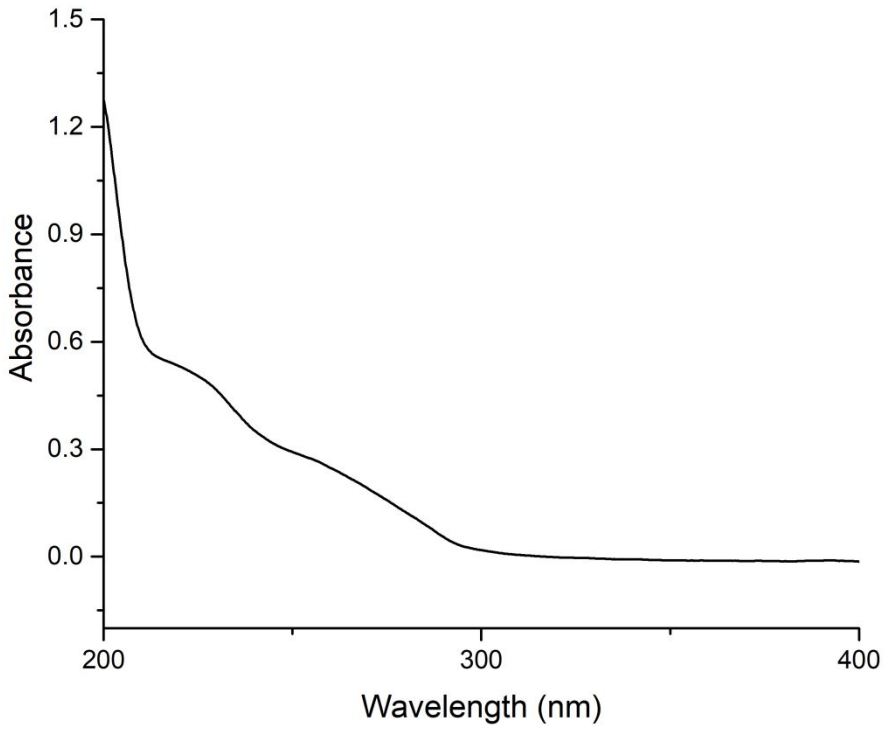


Figure S39. UV spectrum of carabrolate D (**4**) in MeOH

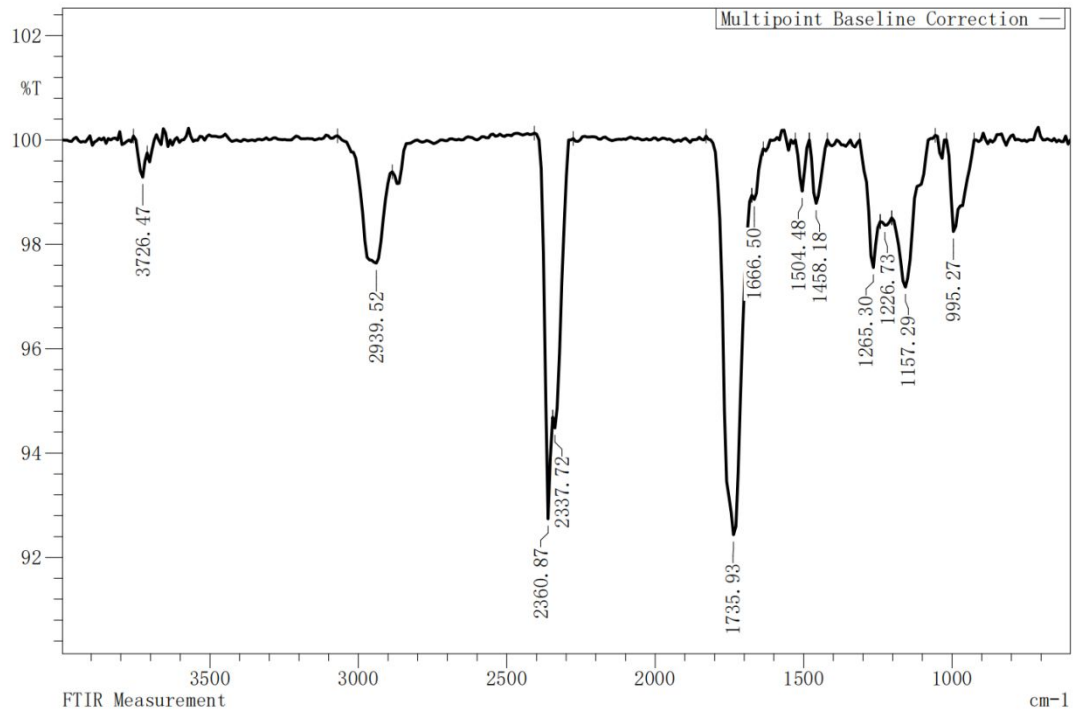
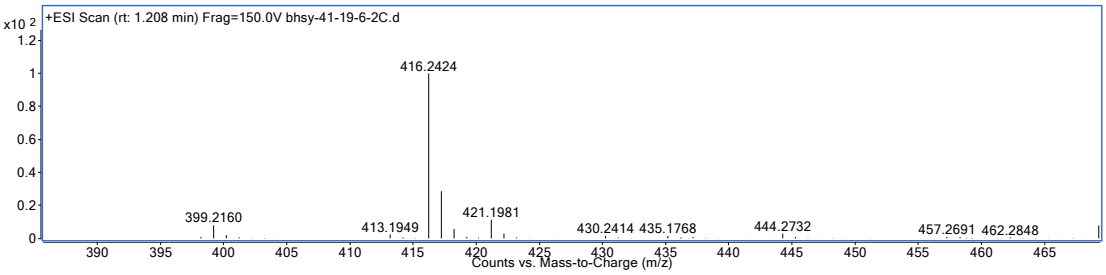


Figure S40. IR spectrum (film on KBr plate) of carabrolate D (**4**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{24}H_{30}O_5$	99.09	398.2087	398.2093	399.2166	1.51	$C_{24}H_{31}O_5$	399.216
$C_{24}H_{30}O_5$	98.59	398.2086	398.2093	416.2431	1.88	$C_{24}H_{34}NO_5$	416.2424

Figure S41. HRESIMS spectrum of carabrolate D (**4**)

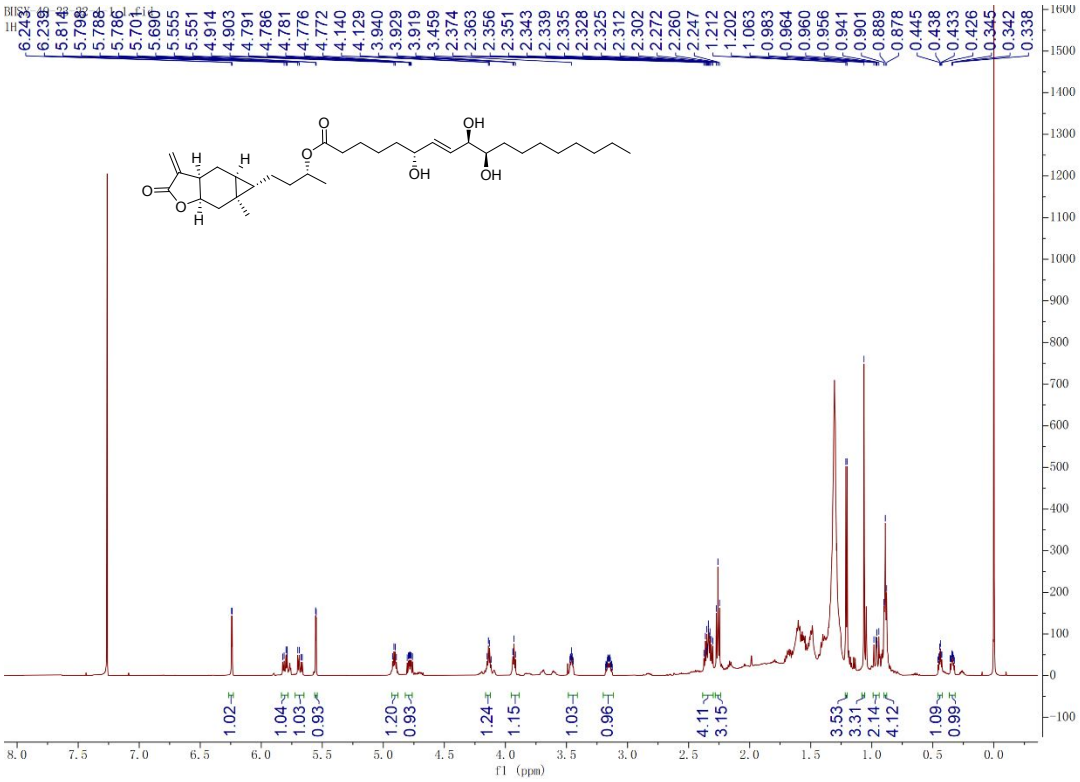


Figure S42. ^{1}H NMR spectrum (600 MHz) of carabrolate E (**5**) in $CDCl_3$

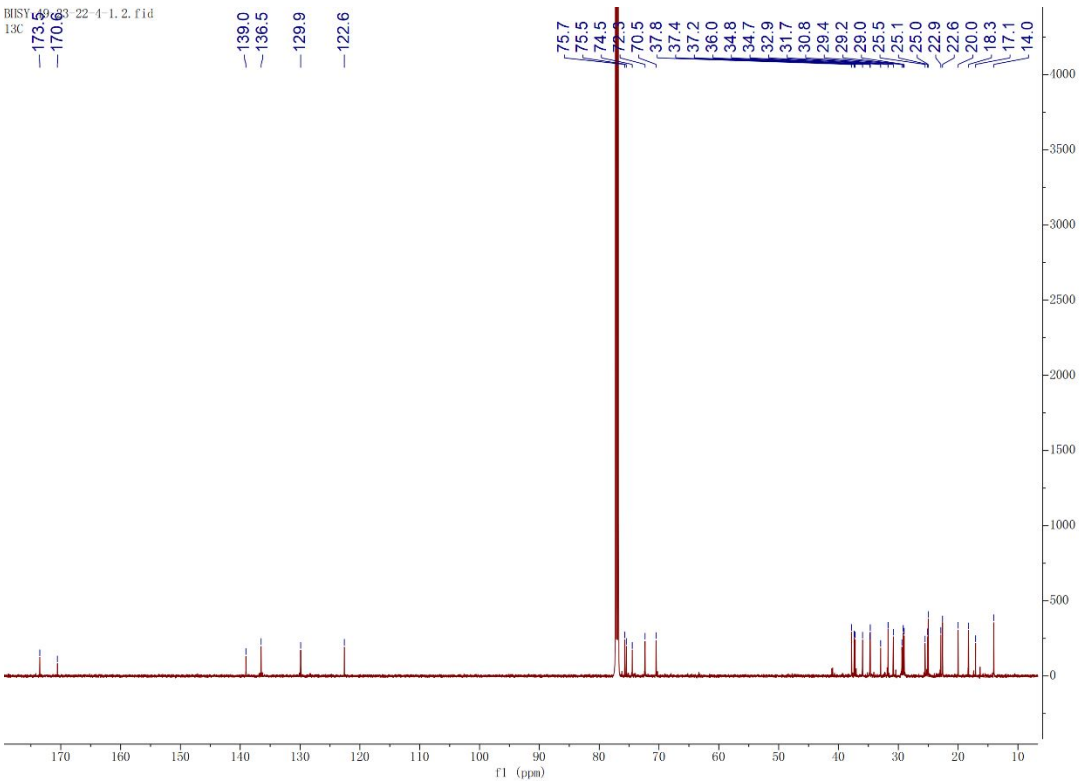


Figure S43. ^{13}C NMR spectrum (150 MHz) of carabrolate E (**5**) in $CDCl_3$

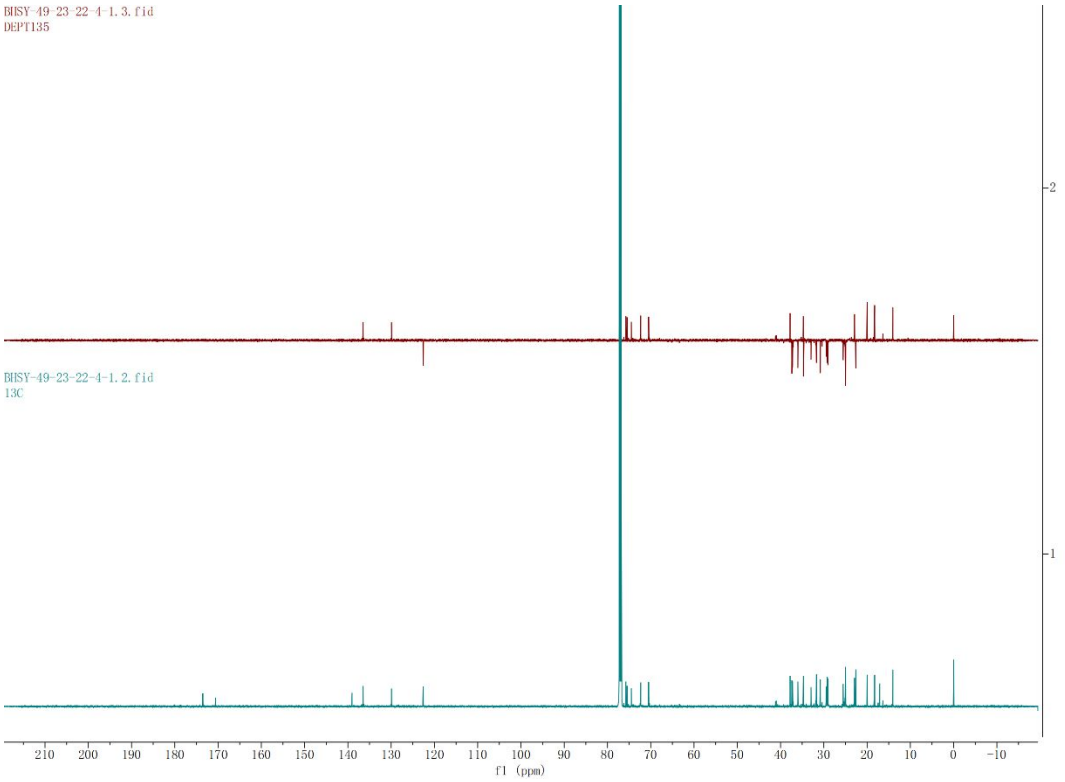


Figure S44. DEPT 135 spectrum (150 MHz) of carabrolate E (**5**) in $CDCl_3$

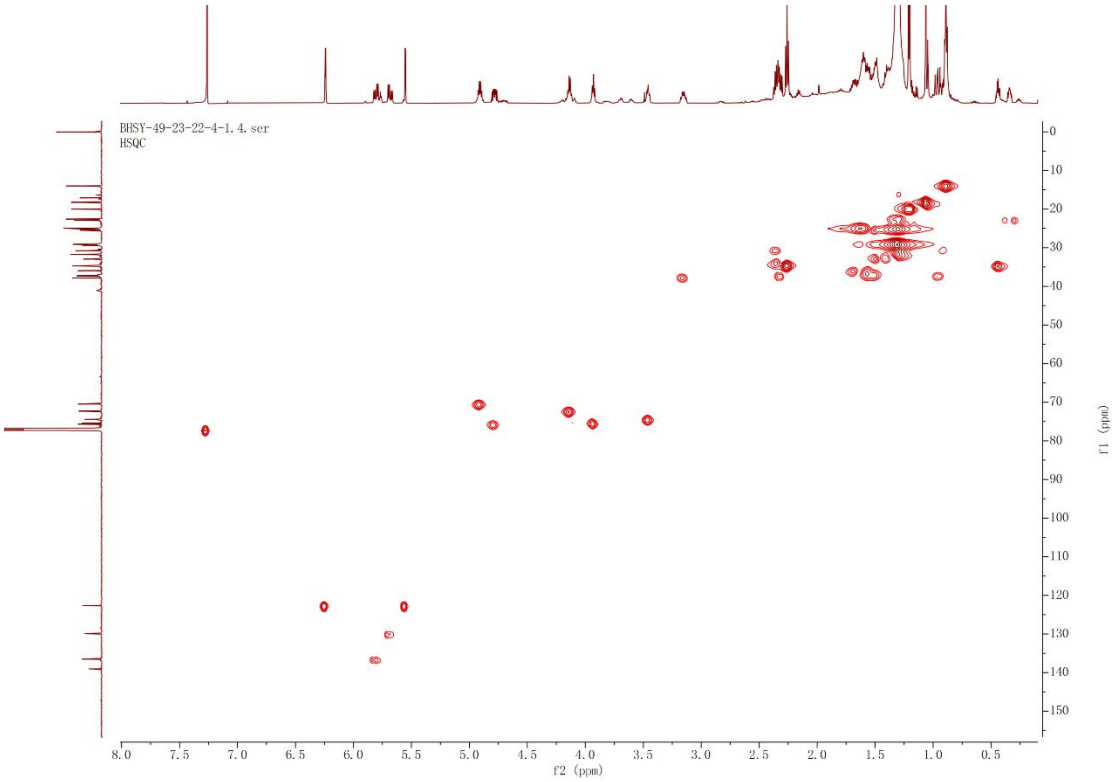


Figure S45. HSQC spectrum (600 MHz) of carabrolate E (**5**) in $CDCl_3$

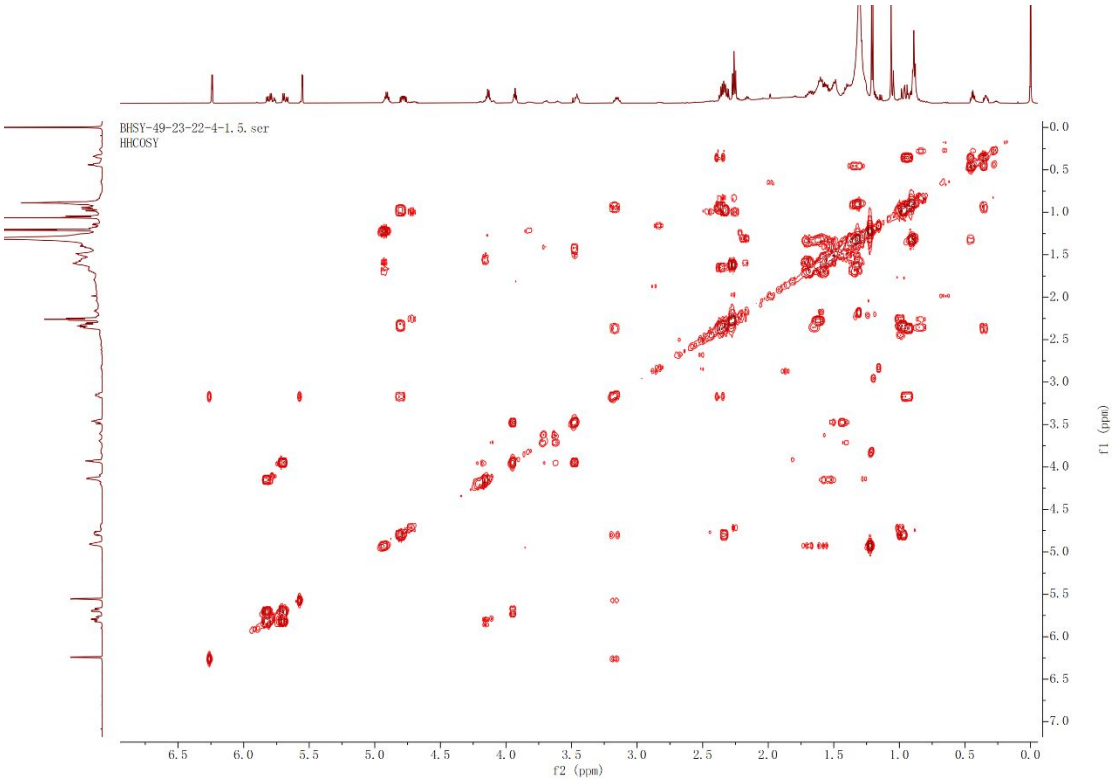


Figure S46. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate E (**5**) in $CDCl_3$

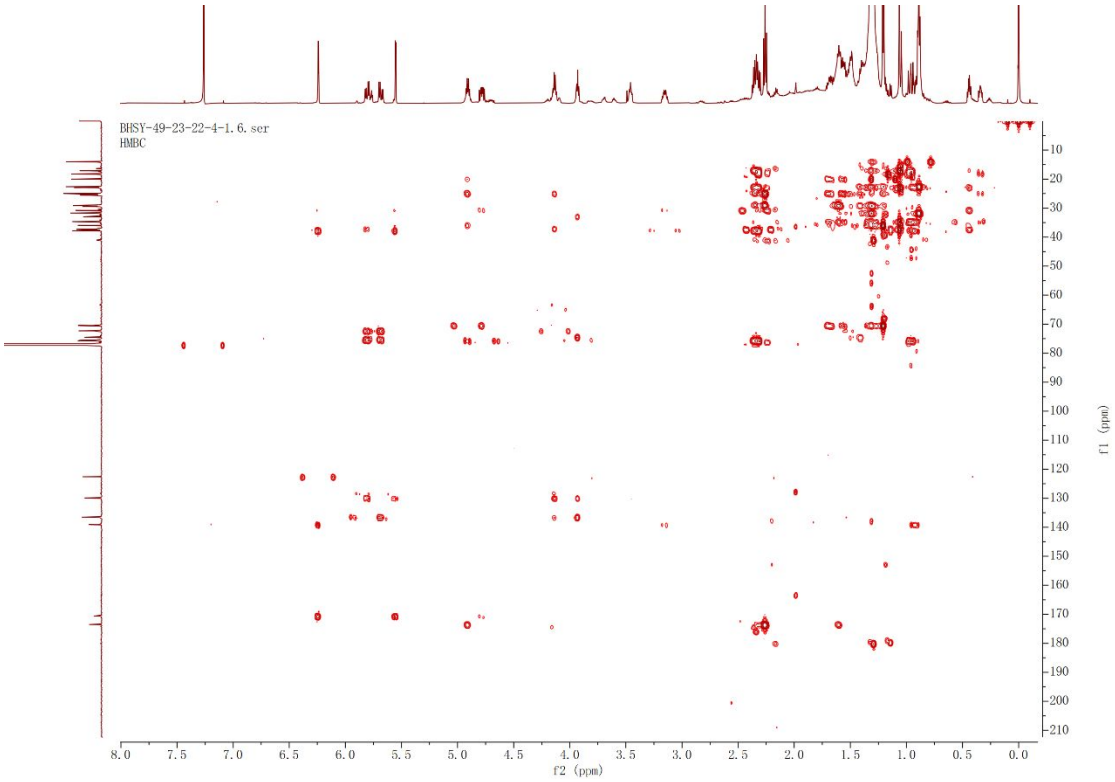


Figure S47. HMBC spectrum (600 MHz) of carabrolate E (**5**) in $CDCl_3$

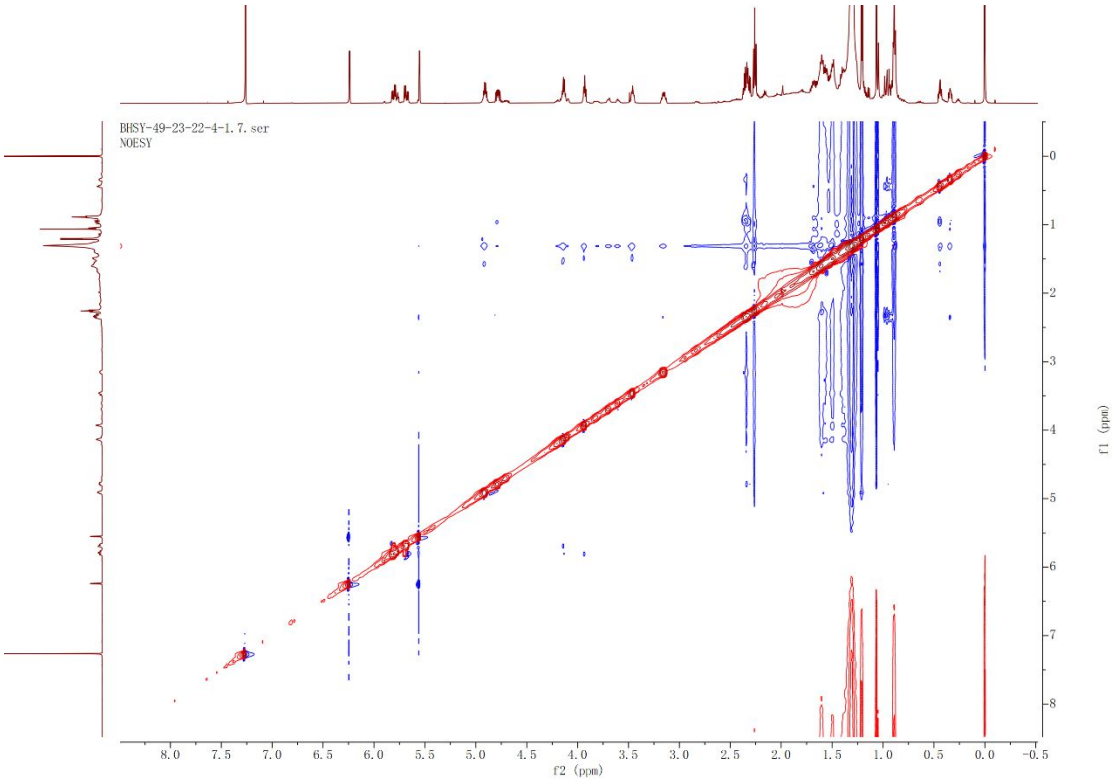


Figure S48. NOESY spectrum (600 MHz) of carabrolate E (**5**) in $CDCl_3$

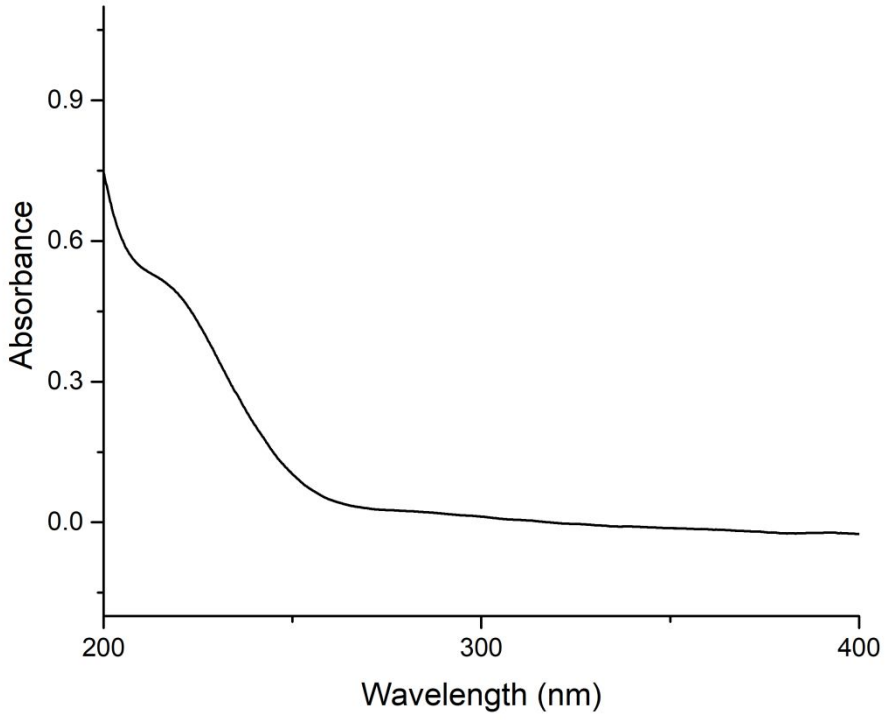


Figure S49. UV spectrum of carabrolate E (**5**) in MeOH

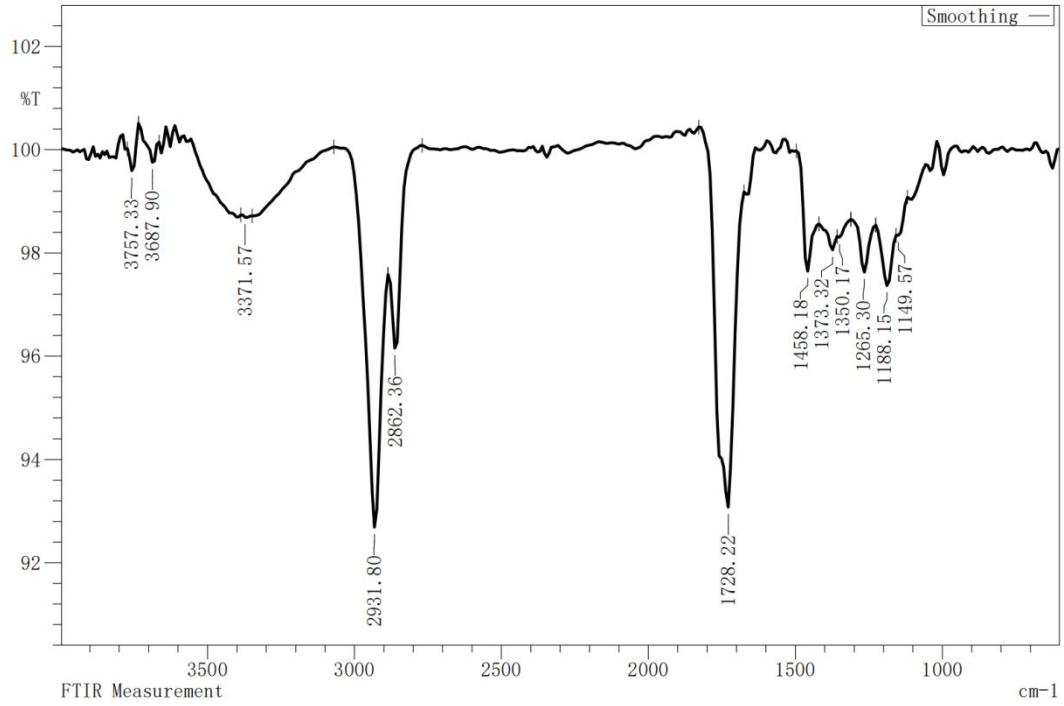
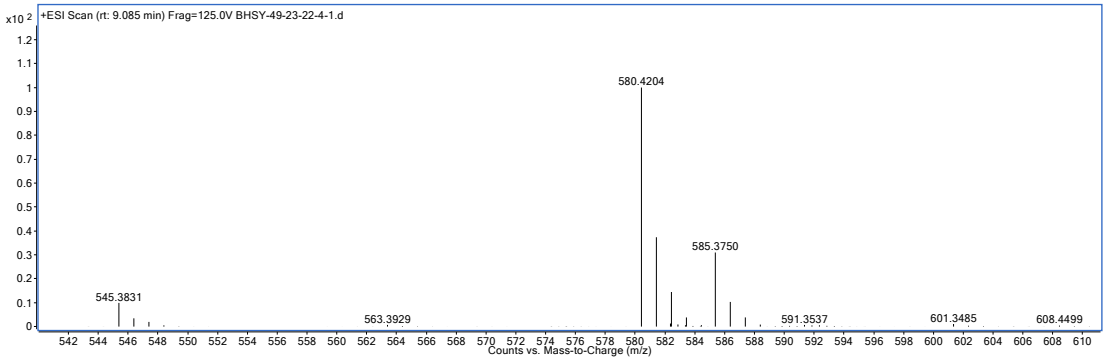


Figure S50. IR spectrum (film on KBr plate) of carabrolate E (**5**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{33}H_{54}O_7$	99.77	562.3866	562.387	580.4208	0.68	$C_{30}H_{58}NO_7$	580.4204
$C_{33}H_{54}O_7$	97.86	562.3858	562.387	585.3762	2.09	$C_{30}H_{54}NaO_7$	585.375

Figure S51. HRESIMS spectrum of carabrolate E (**5**)

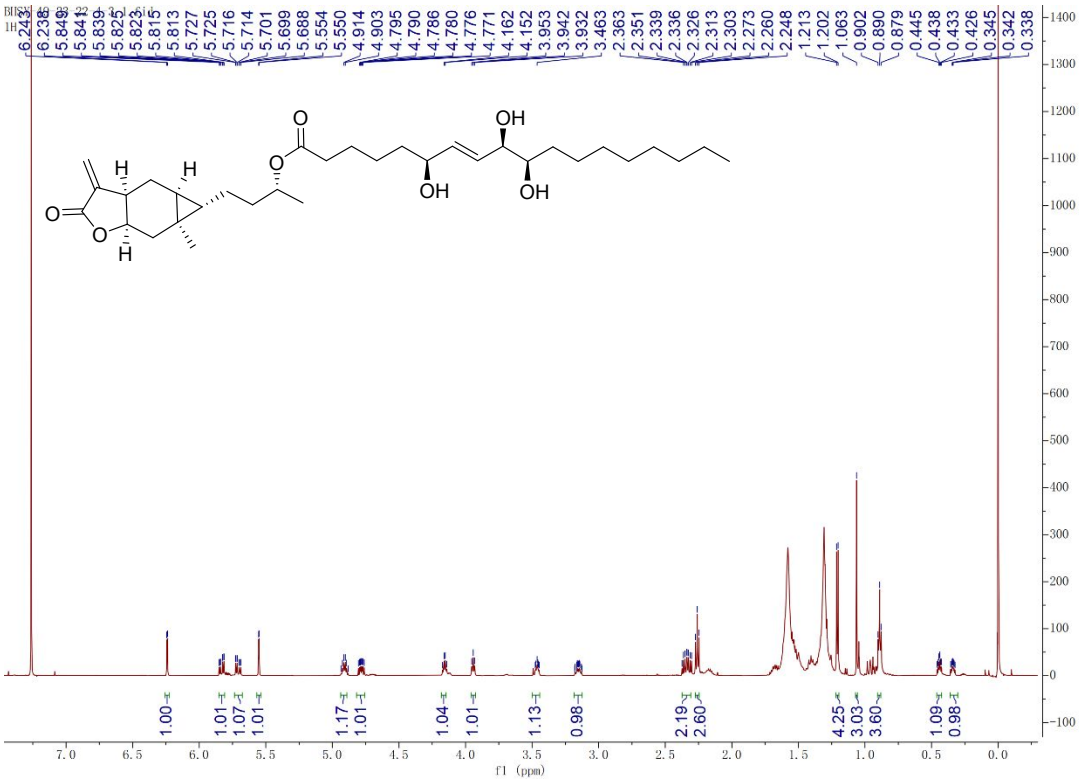


Figure S52. ^{1}H NMR spectrum (600 MHz) of carabrolate F (**6**) in $CDCl_3$

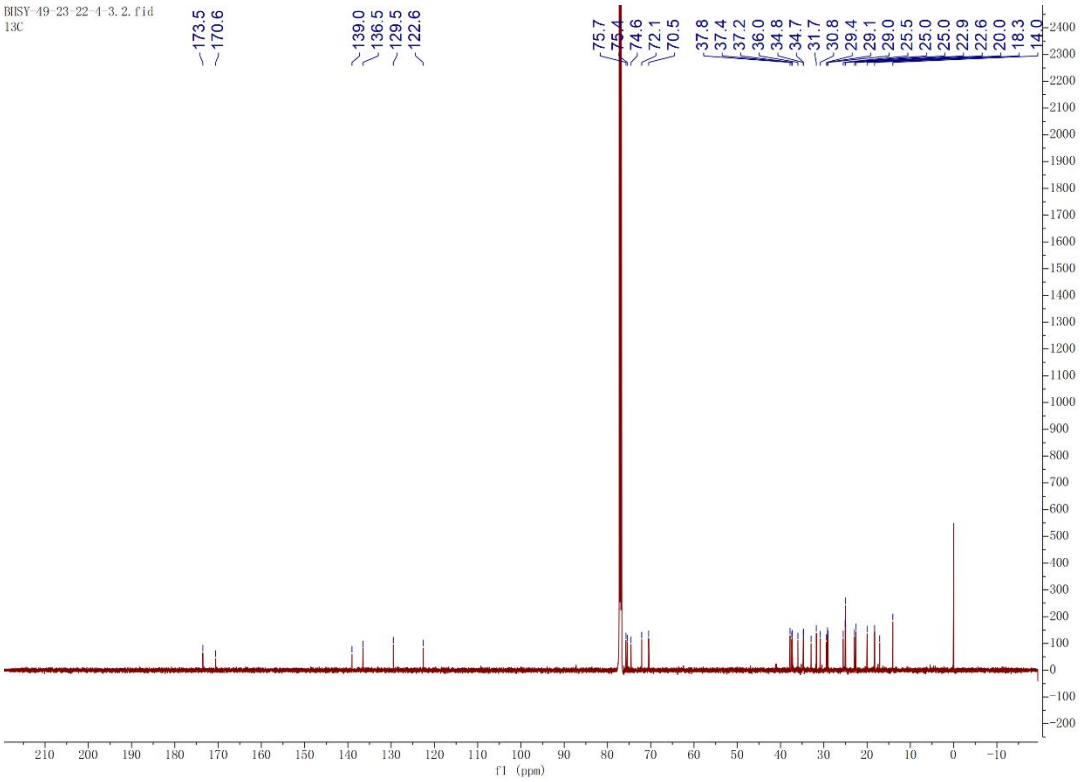


Figure S53. ^{13}C NMR spectrum (150 MHz) of carabrolate F (**6**) in $CDCl_3$

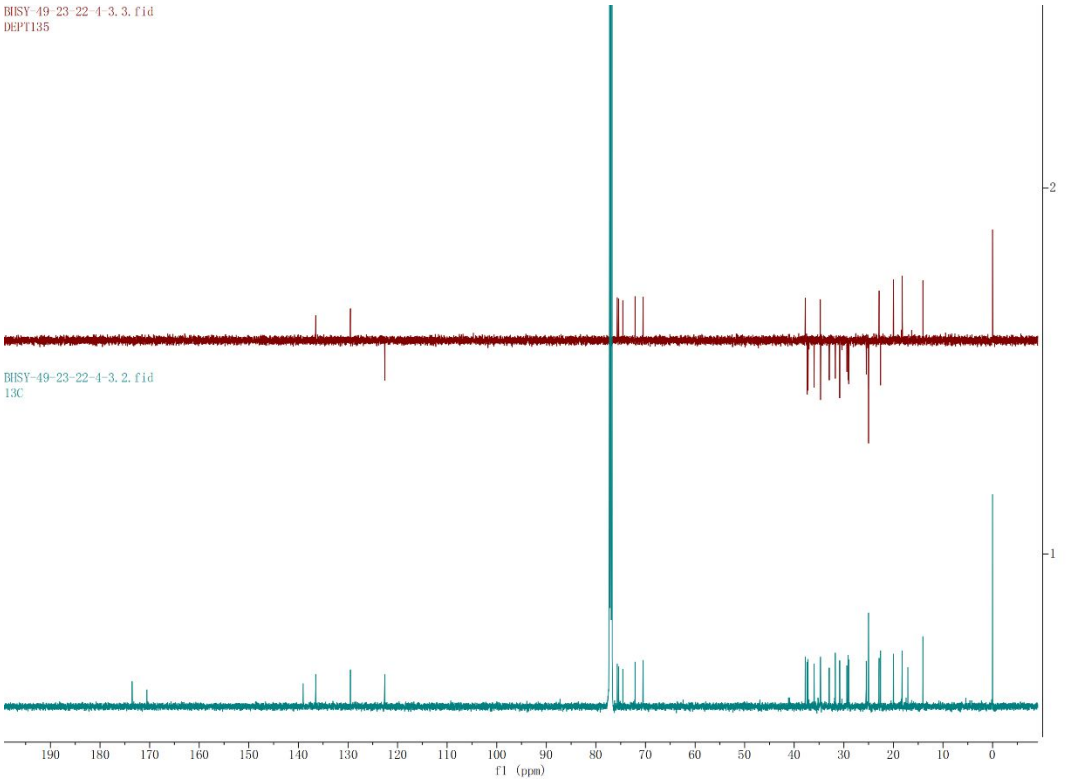


Figure S54. DEPT 135 spectrum (150 MHz) of carabrolate F (**6**) in $CDCl_3$

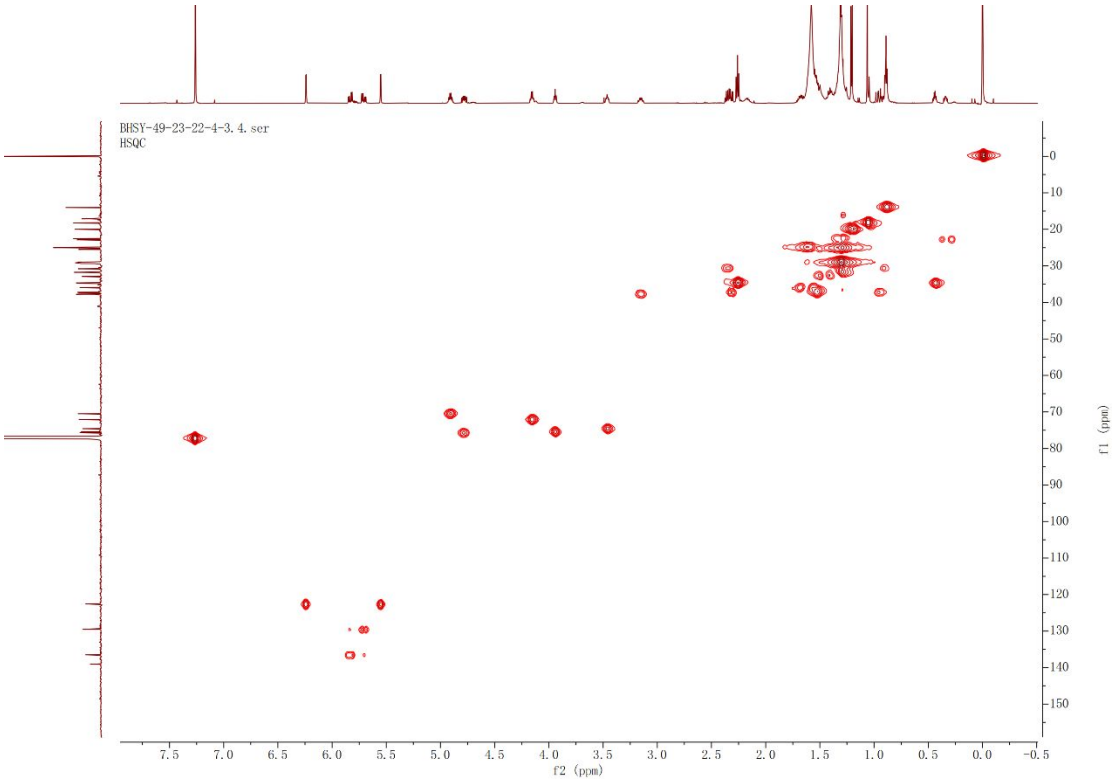


Figure S55. HSQC spectrum (600 MHz) of carabrolate F (**6**) in $CDCl_3$

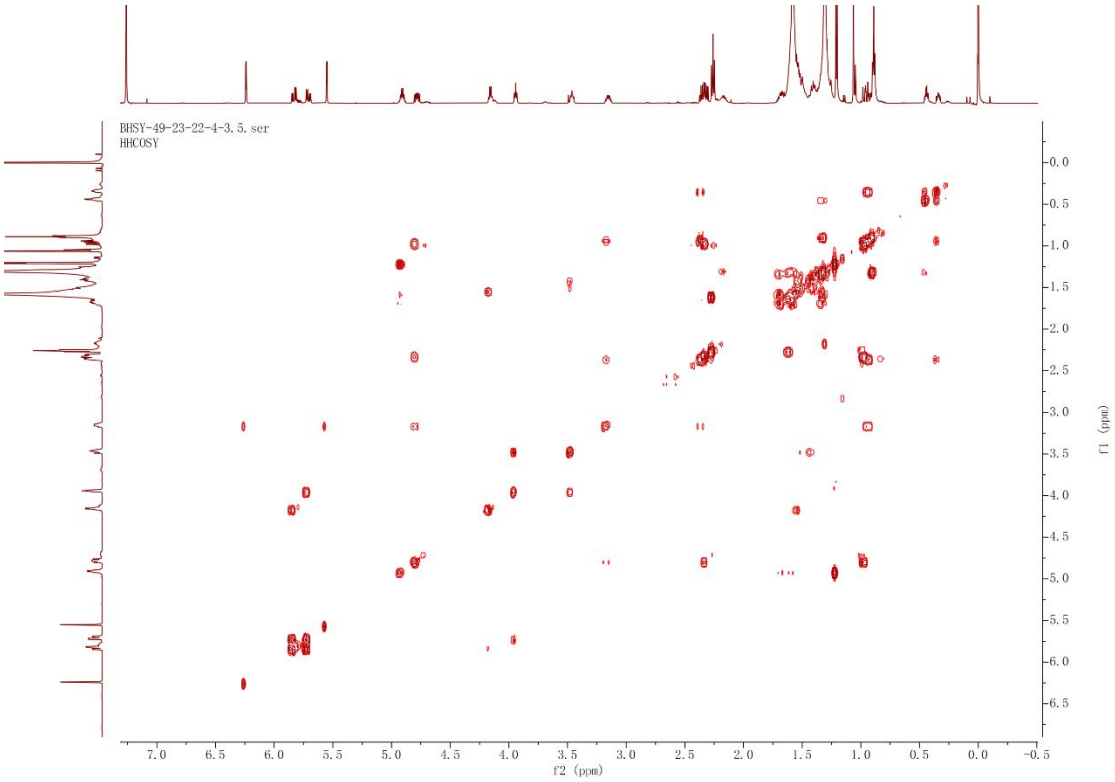


Figure S56. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate F (**6**) in $CDCl_3$

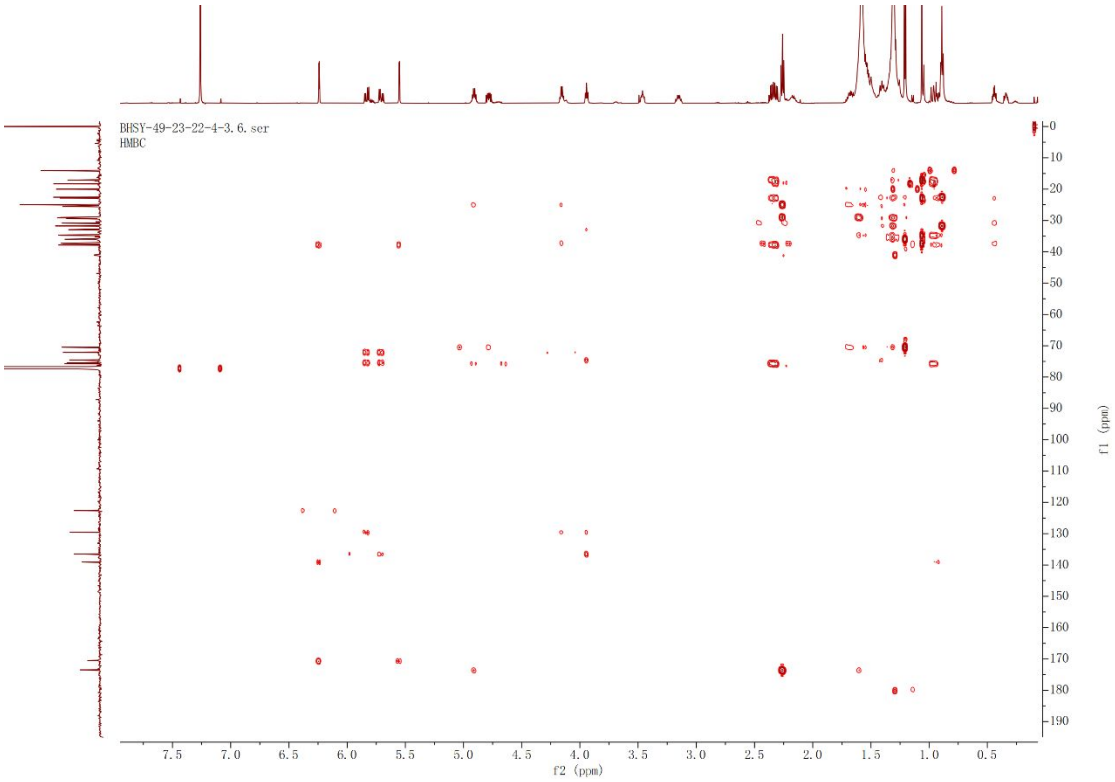


Figure S57. HMBC spectrum (600 MHz) of carabrolate F (**6**) in $CDCl_3$

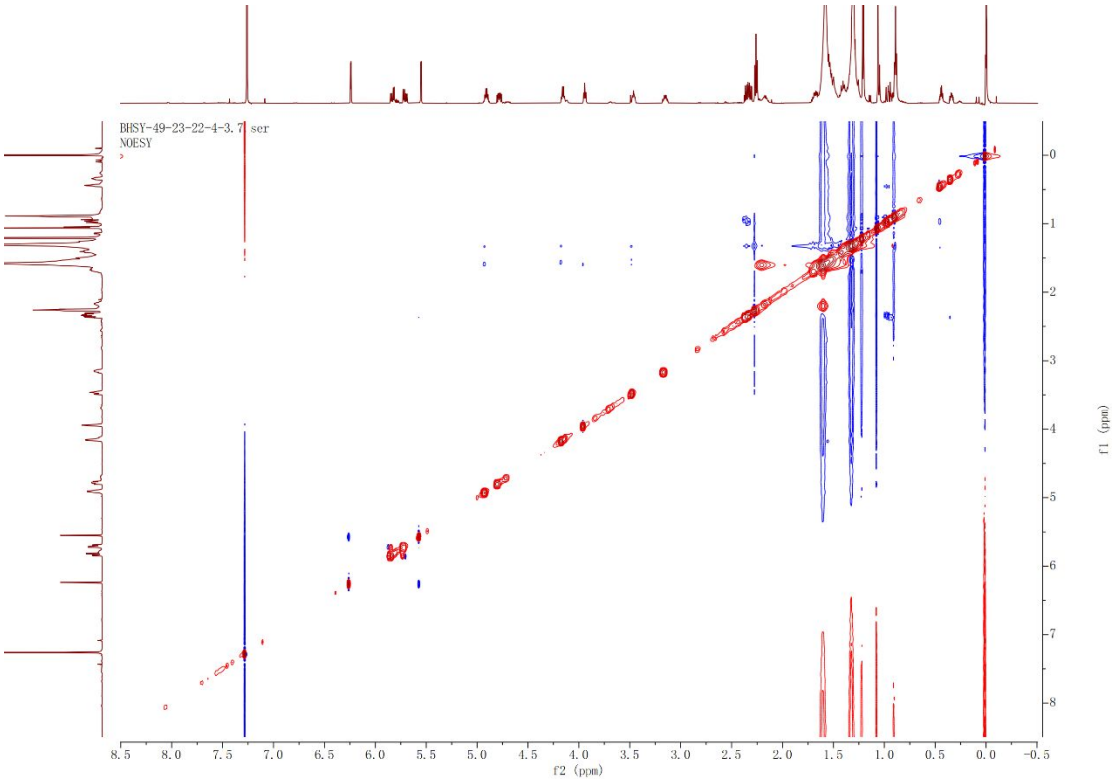


Figure S58. NOESY spectrum (600 MHz) of carabrolate F (**6**) in $CDCl_3$

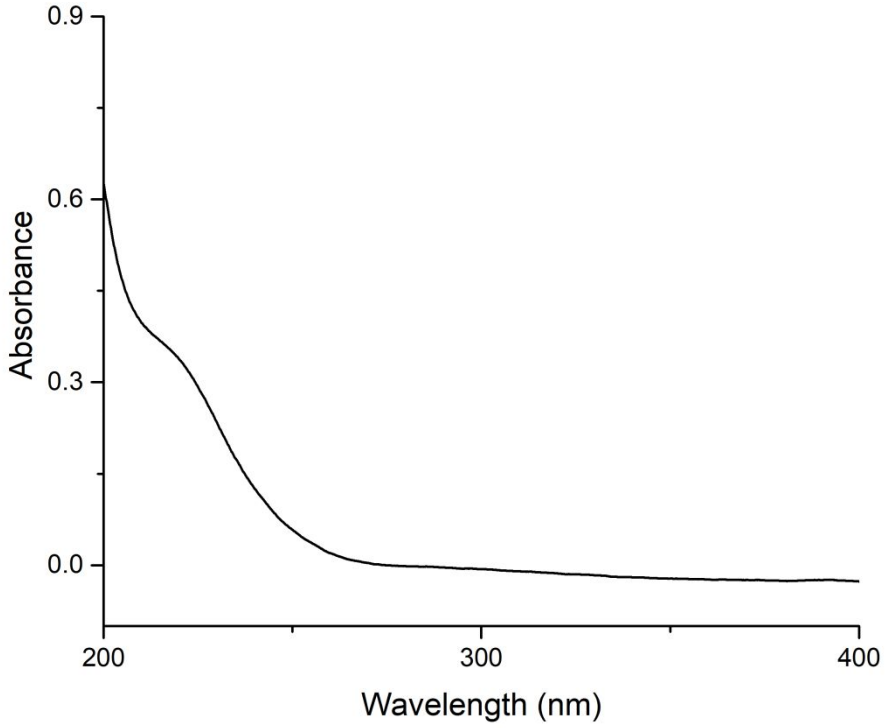


Figure S59. UV spectrum of carabrolate F (**6**) in MeOH

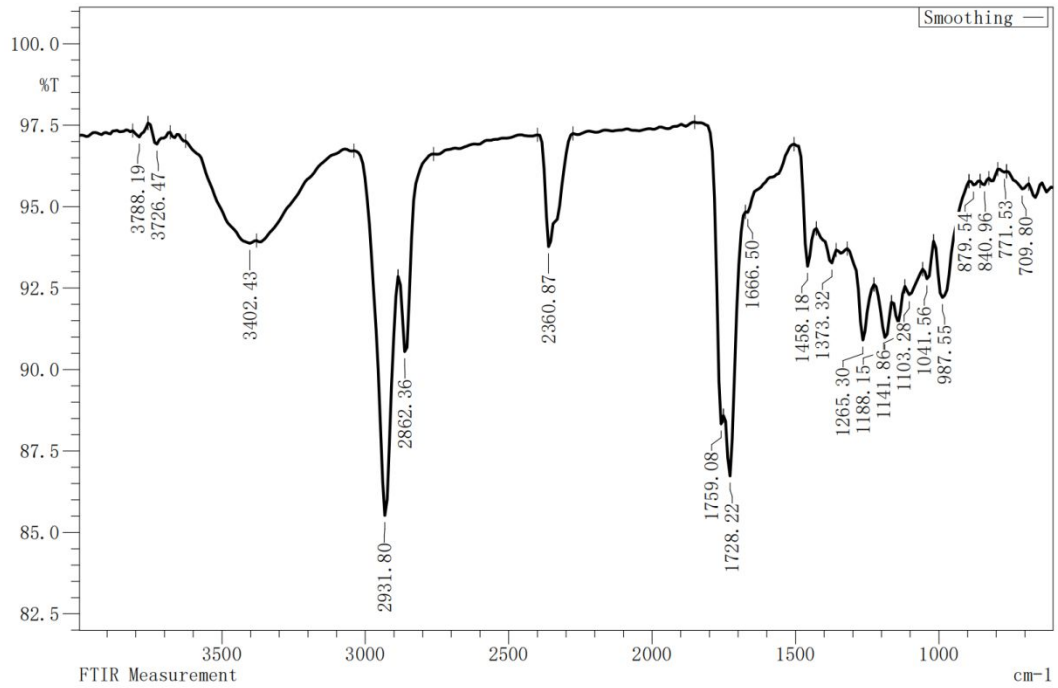
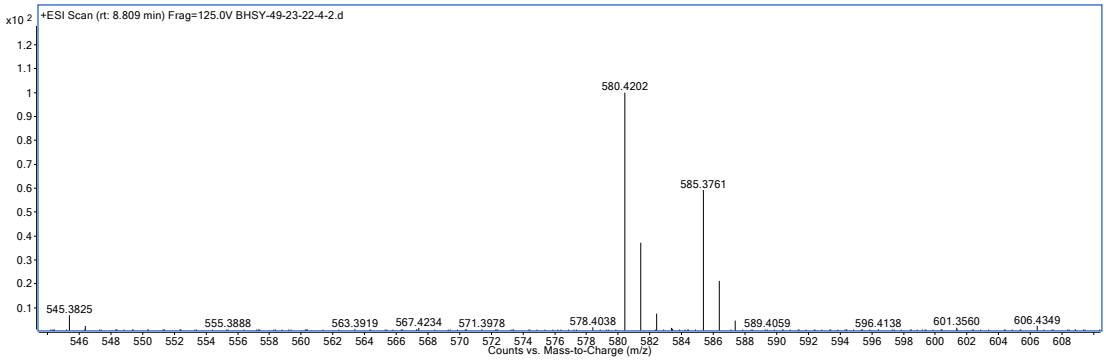
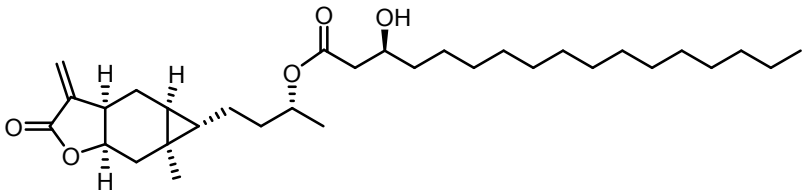


Figure S60. IR spectrum (film on KBr plate) of carabrolate F (**6**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{33}H_{54}O_7$	99.47	562.3864	562.387	580.4208	1.03	$C_{30}H_{58}NO_7$	580.4202
$C_{33}H_{54}O_7$	99.99	562.3869	562.387	585.3762	0.13	$C_{30}H_{54}NaO_7$	585.3761

Figure S61. HRESIMS spectrum of carabrolate F (**6**)



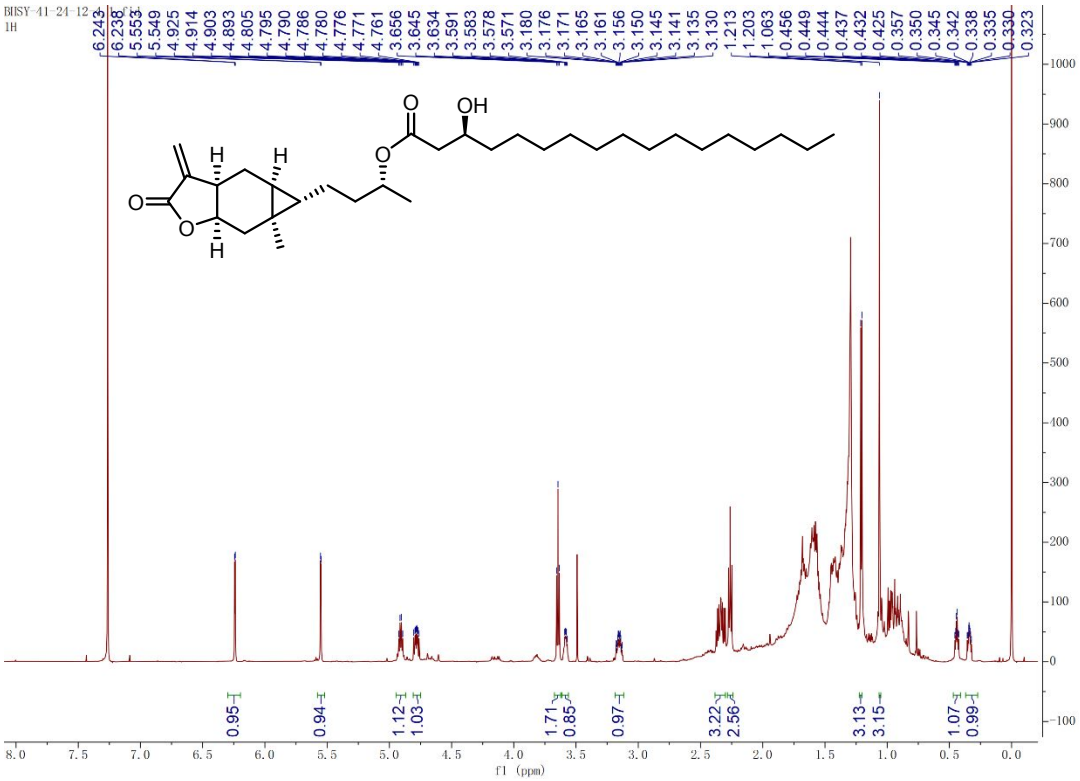


Figure S62. ^{1}H NMR spectrum (600 MHz) of carabrolate G (**7**) in $CDCl_3$

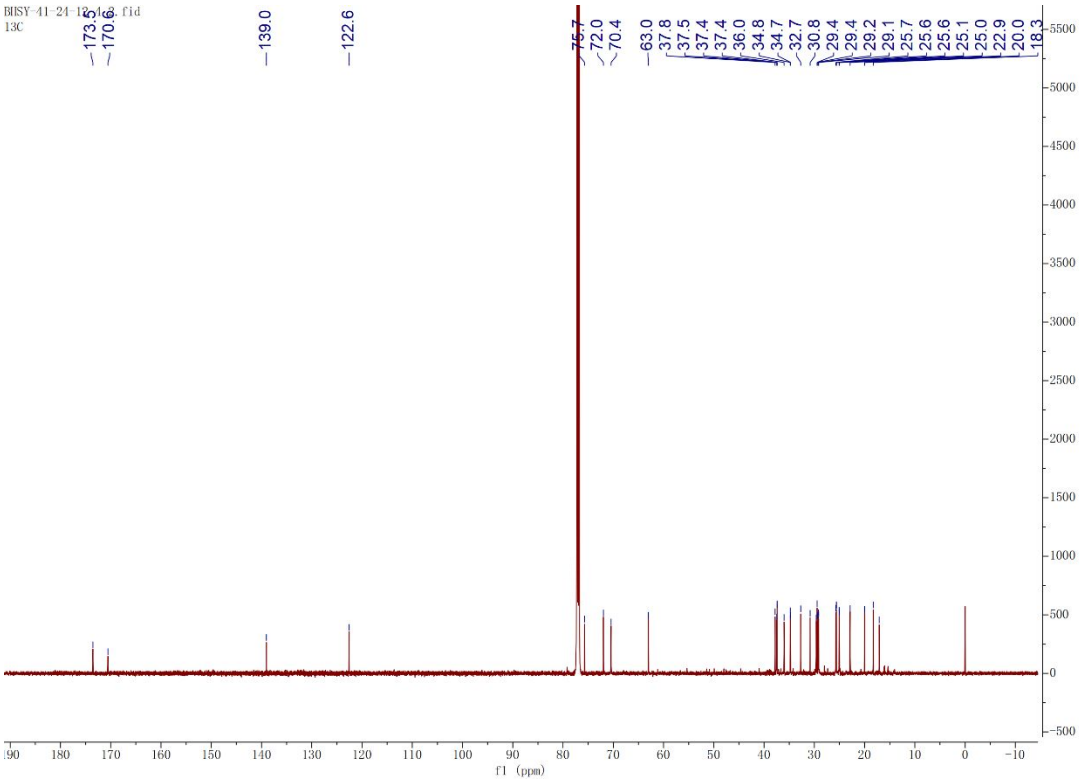


Figure S63. ^{13}C NMR spectrum (150 MHz) of carabrolate G (**7**) in $CDCl_3$

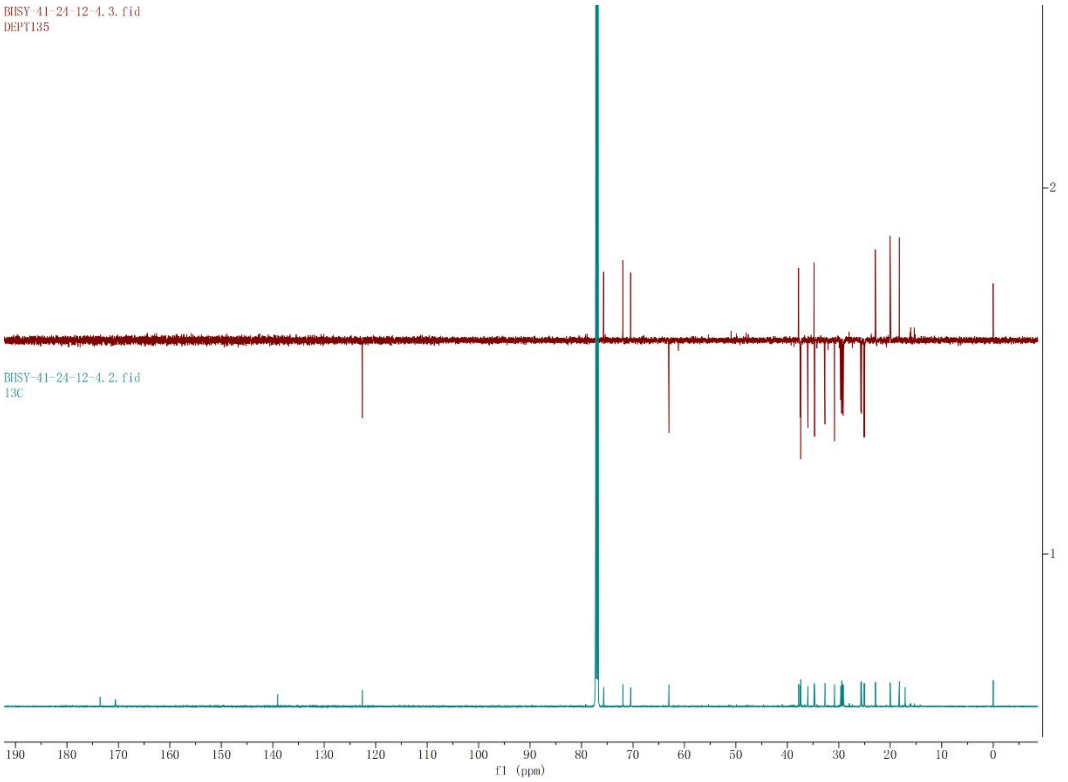


Figure S64. DEPT 135 spectrum (150 MHz) of carabrolate G (**7**) in $CDCl_3$

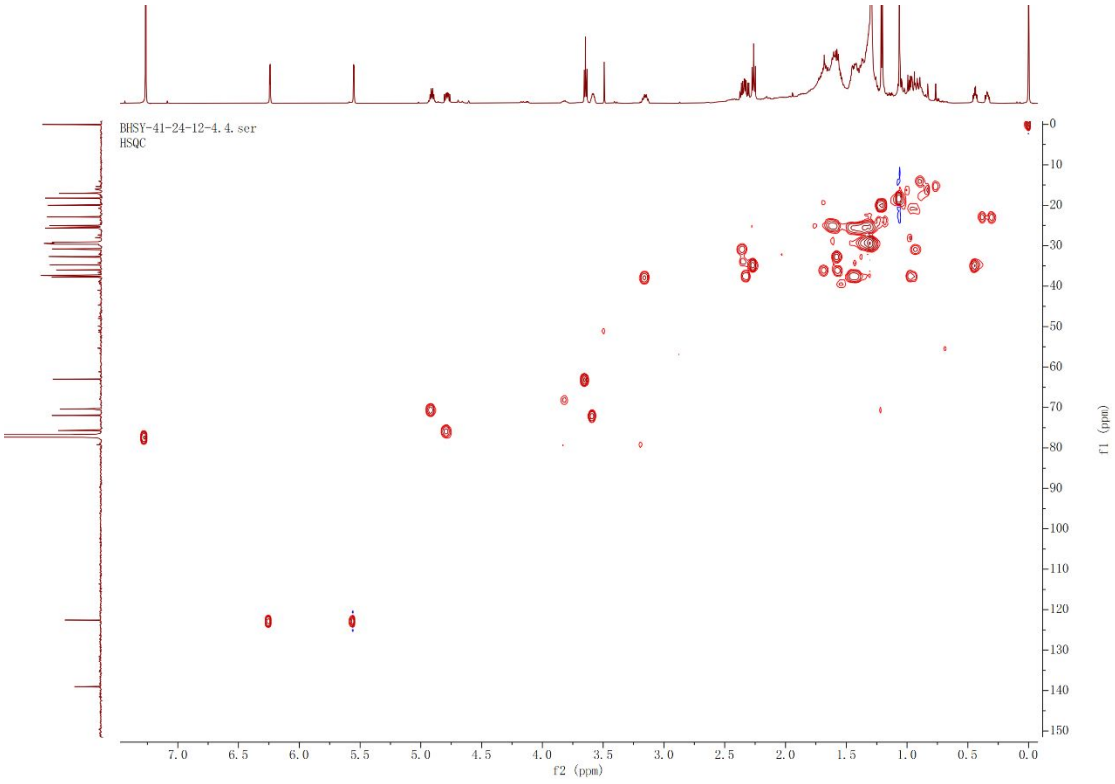


Figure S65. HSQC spectrum (600 MHz) of carabrolate G (**7**) in $CDCl_3$

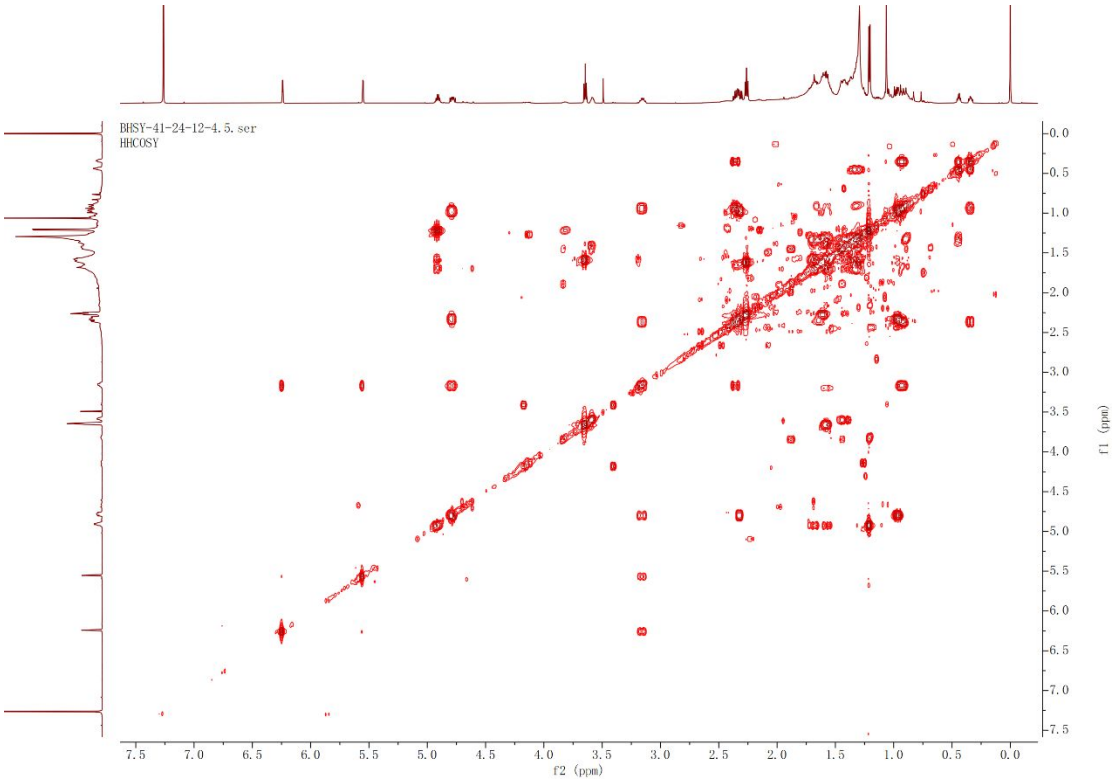


Figure S66. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate G (**7**) in $CDCl_3$

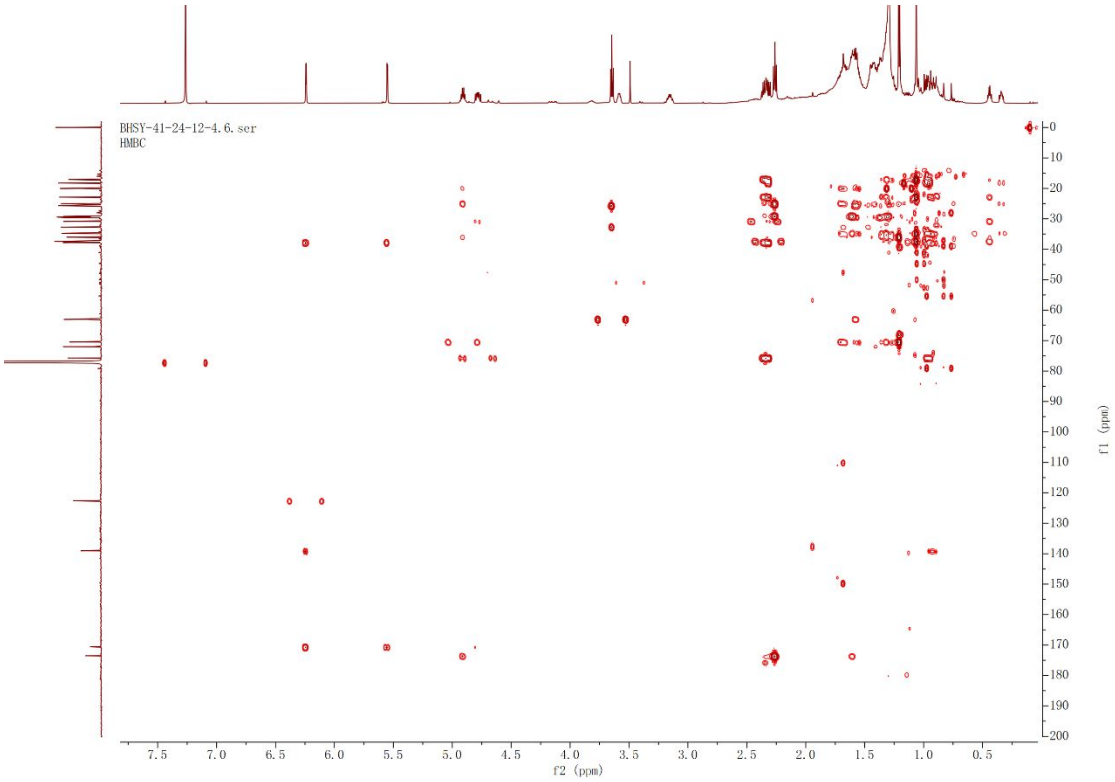


Figure S67. HMBC spectrum (600 MHz) of carabrolate G (**7**) in $CDCl_3$

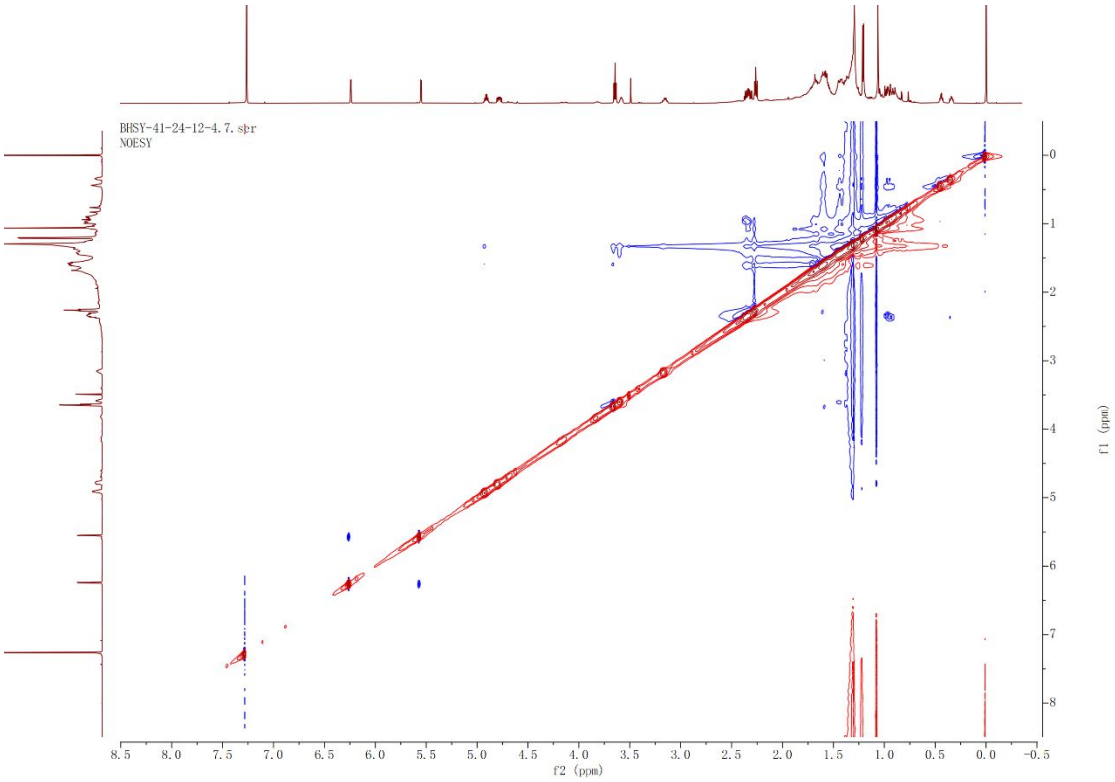


Figure S68. NOESY spectrum (600 MHz) of carabrolate G (**7**) in $CDCl_3$

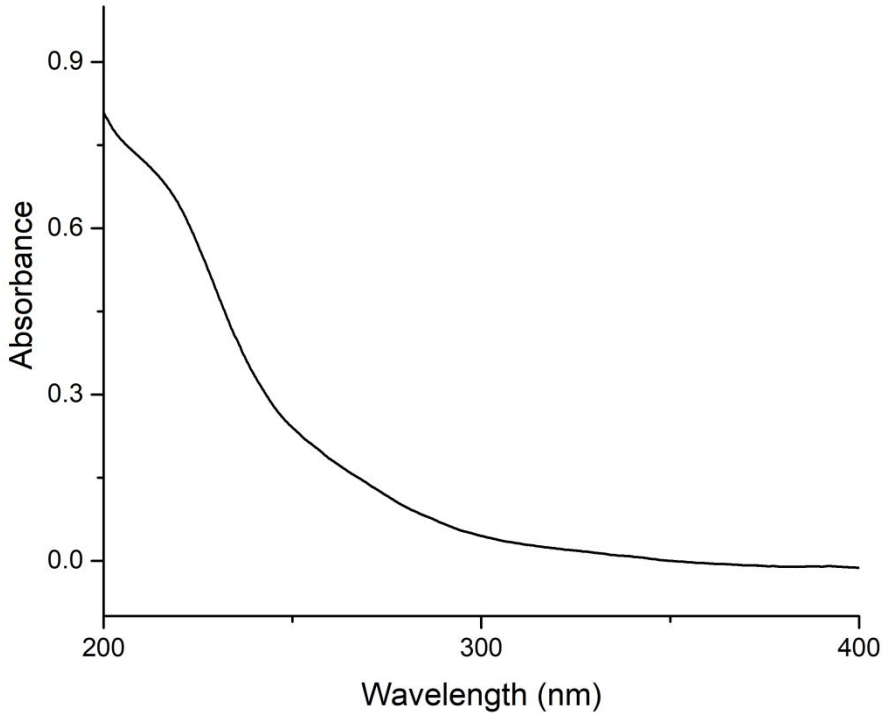


Figure S69. UV spectrum of carabrolate G (**7**) in MeOH

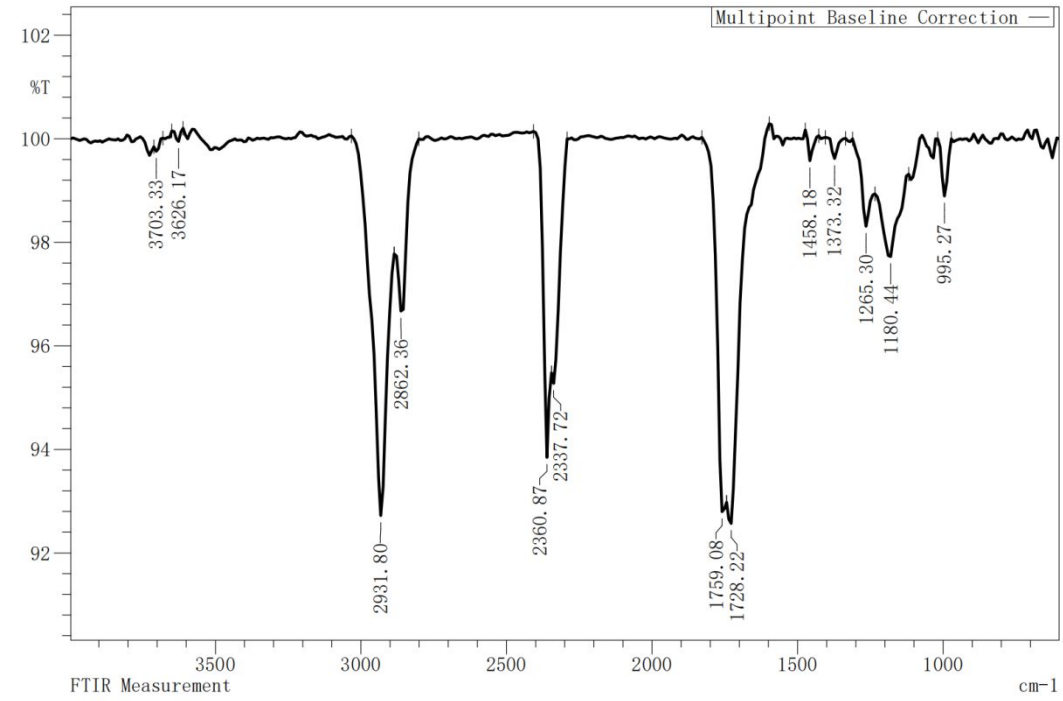
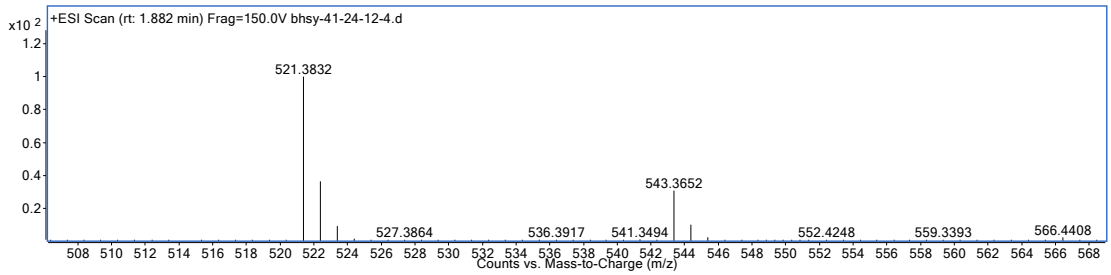


Figure S70. IR spectrum (film on KBr plate) of carabrolate G (**7**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{31}H_{52}O_6$	99.59	520.3759	520.3764	521.3837	0.9	$C_{31}H_{53}O_6$	521.383
$C_{31}H_{52}O_6$	99.68	520.376	520.3764	543.3656	0.79	$C_{31}H_{52}NaO_6$	543.3652

Figure S71. HRESIMS spectrum of carabrolate G (**7**)

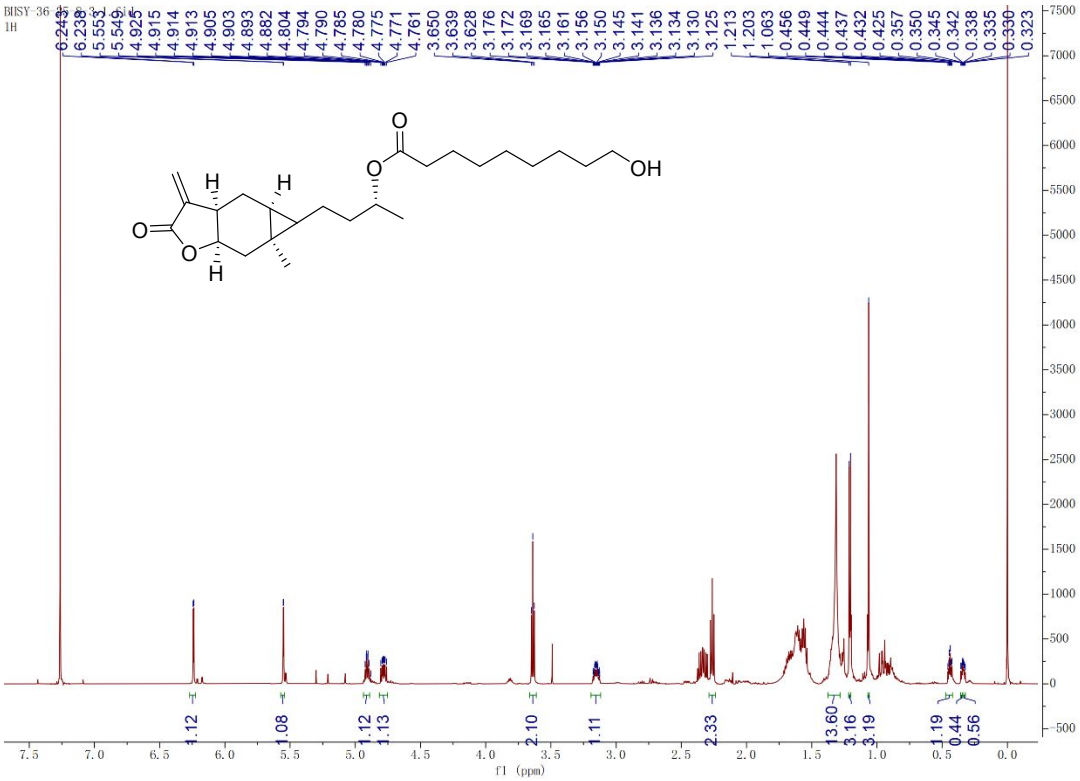


Figure S72. ^{1}H NMR spectrum (600 MHz) of carabrolate H (**8**) in $CDCl_3$

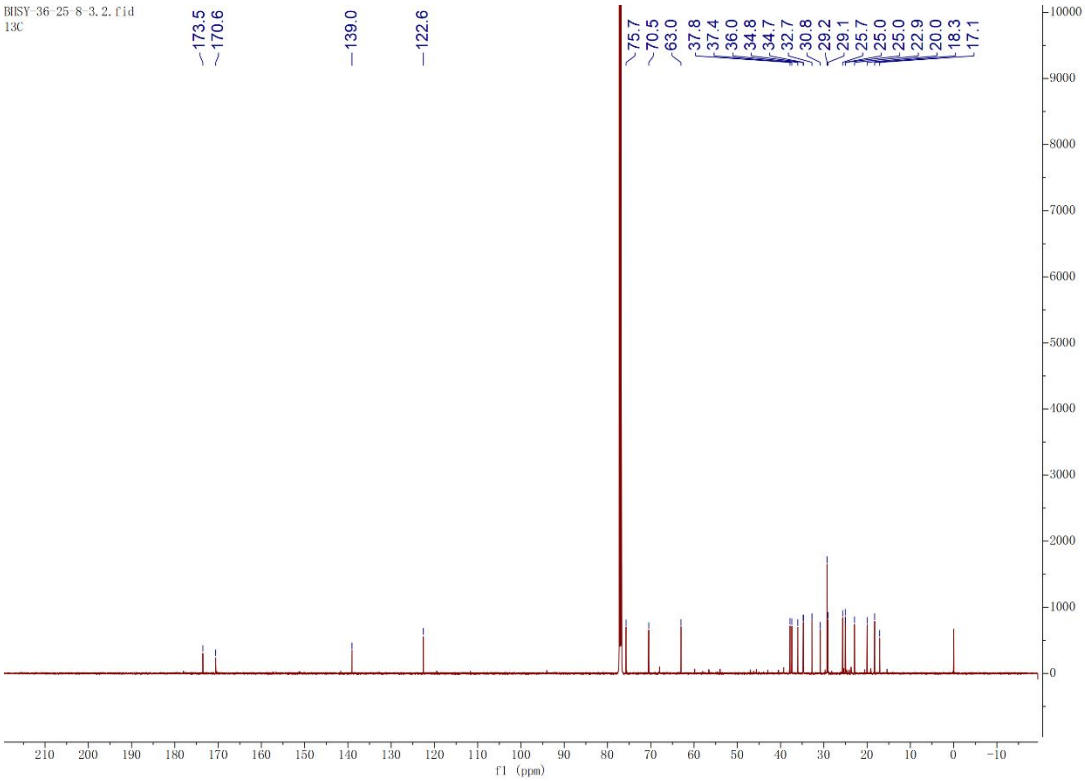


Figure S73. ^{13}C NMR spectrum (150 MHz) of carabrolate H (**8**) in $CDCl_3$

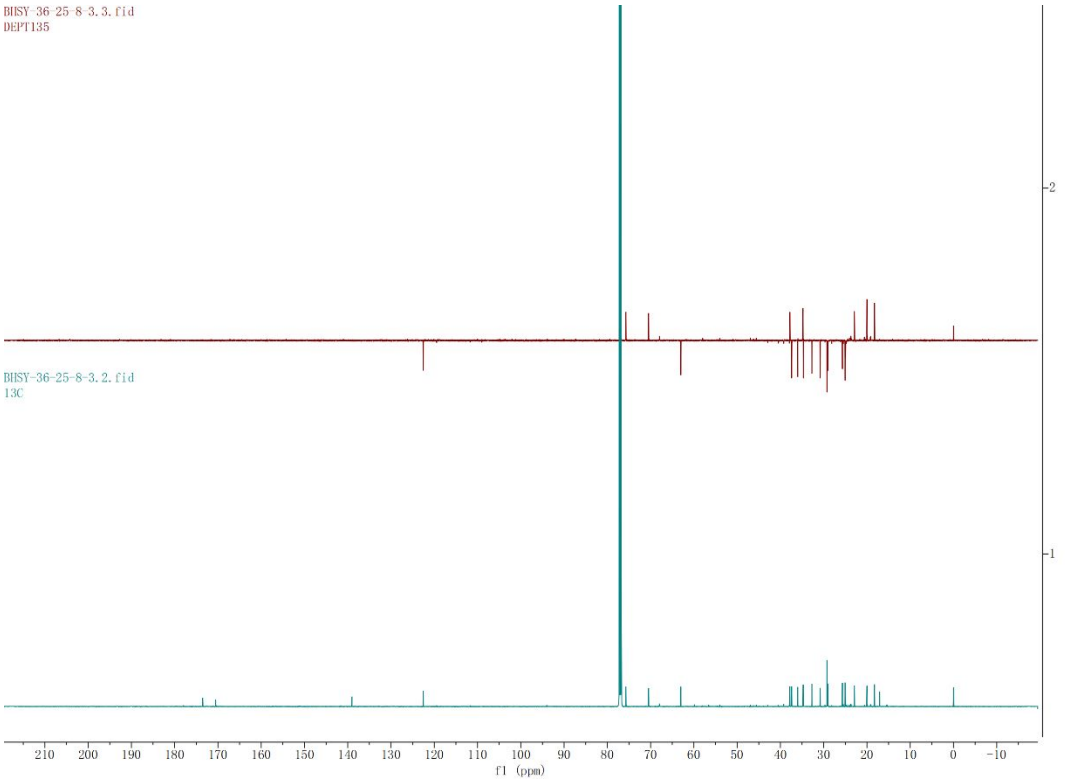


Figure S74. DEPT 135 spectrum (150 MHz) of carabrolate H (**8**) in $CDCl_3$

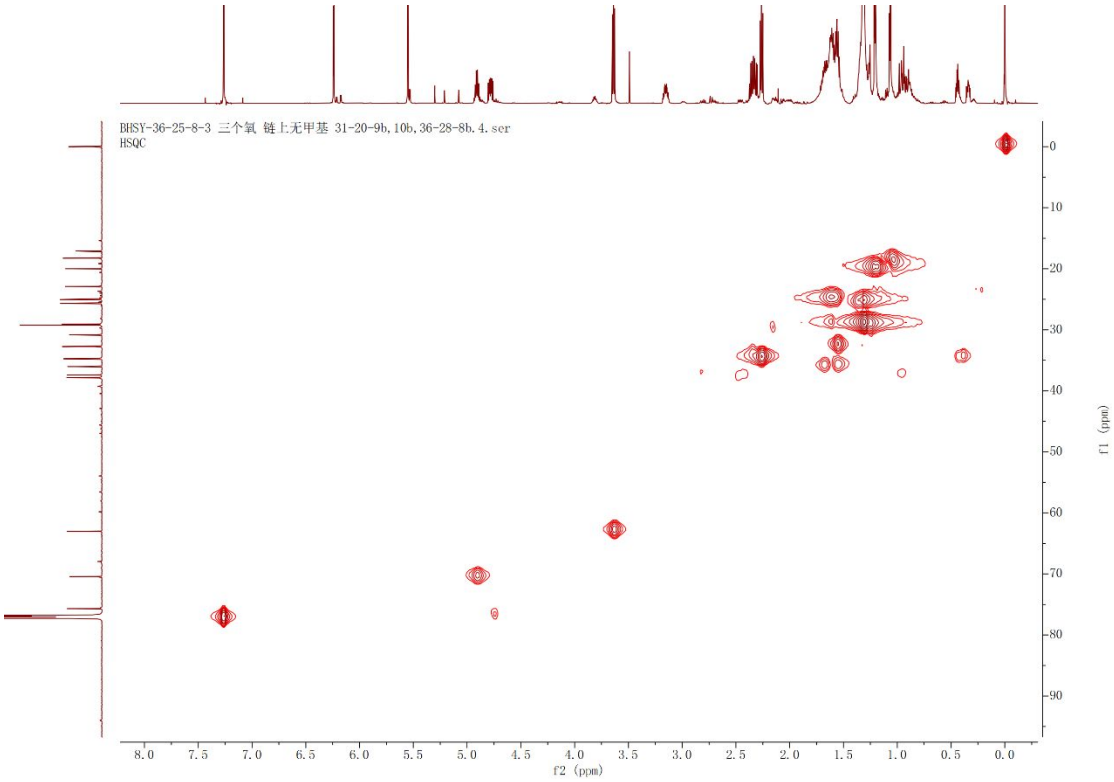


Figure S75. HSQC spectrum (600 MHz) of carabrolate H (**8**) in $CDCl_3$

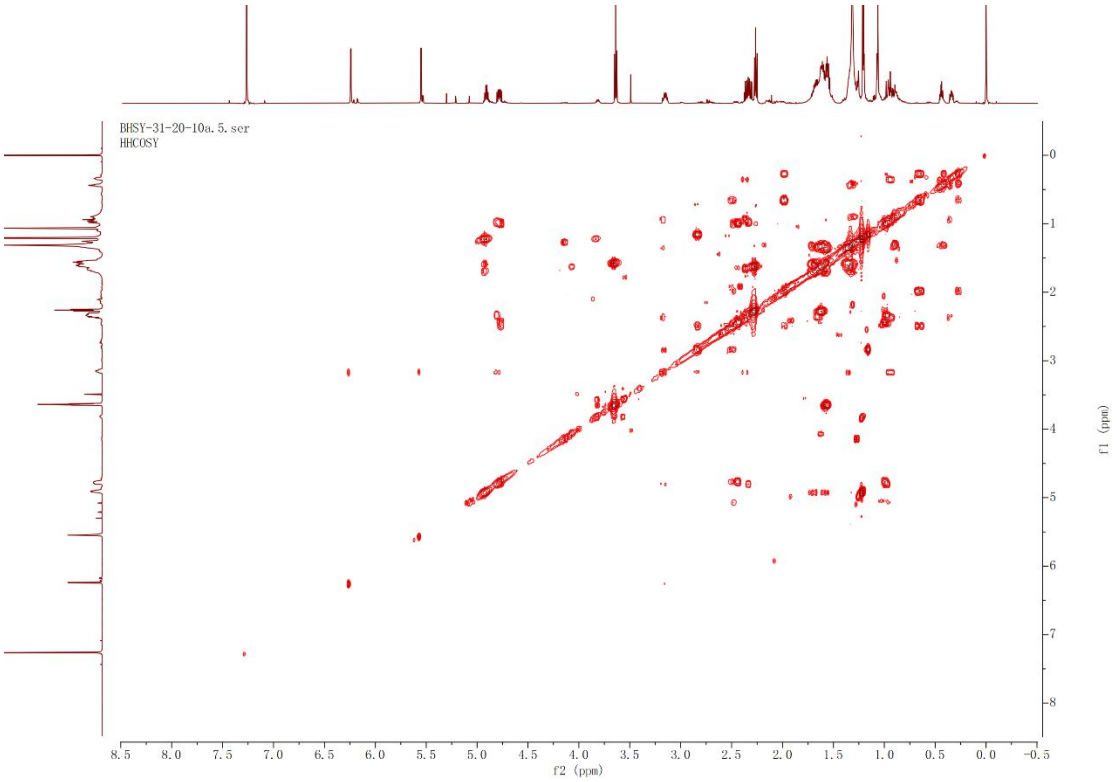


Figure S76. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate H (**8**) in $CDCl_3$

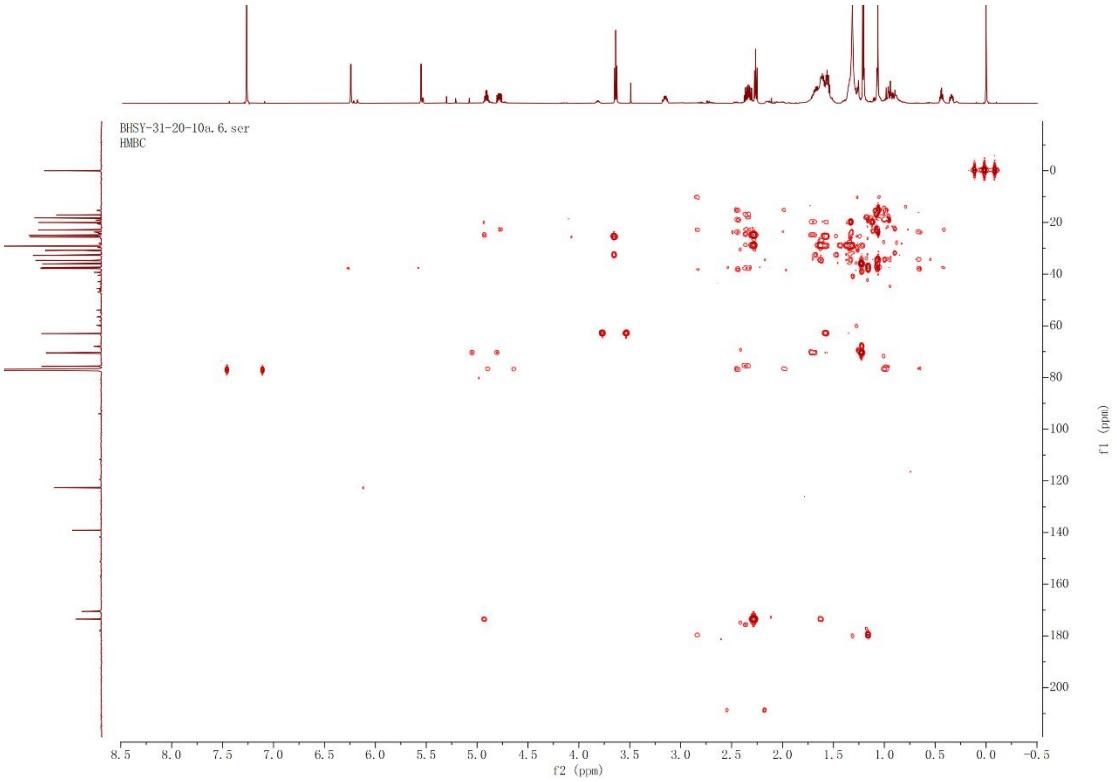


Figure S77. HMBC spectrum (600 MHz) of carabrolate H (**8**) in $CDCl_3$

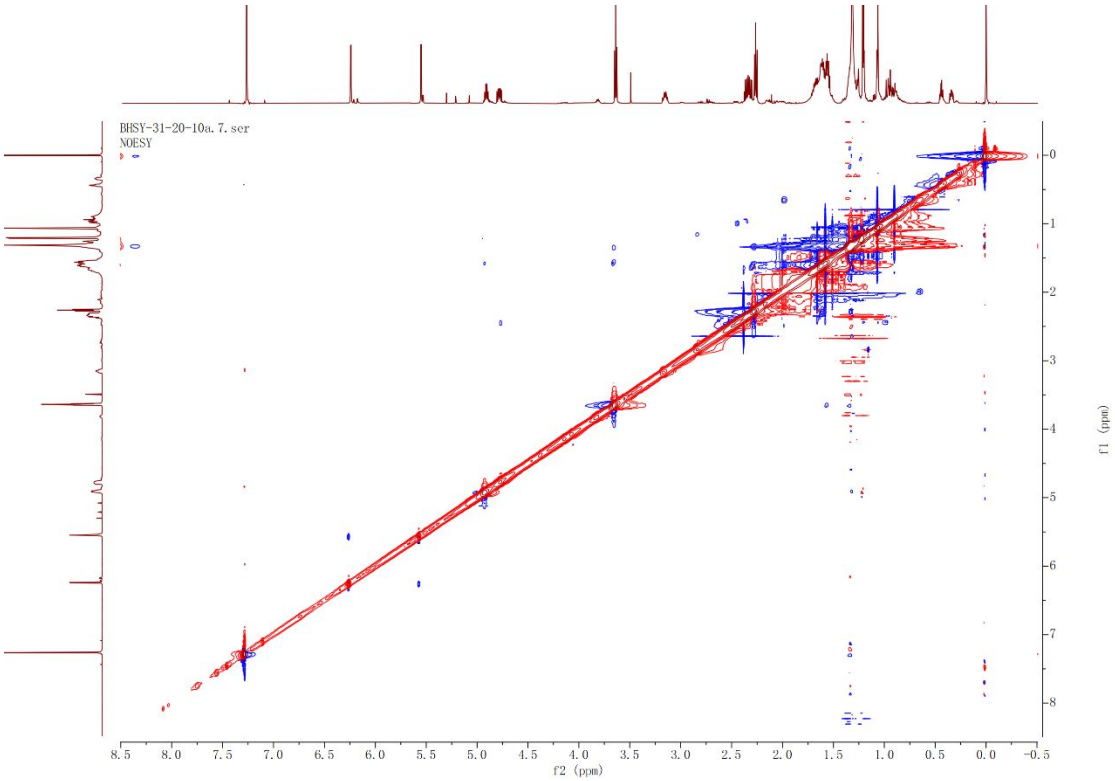


Figure S78. NOESY spectrum (600 MHz) of carabrolate H (**8**) in $CDCl_3$

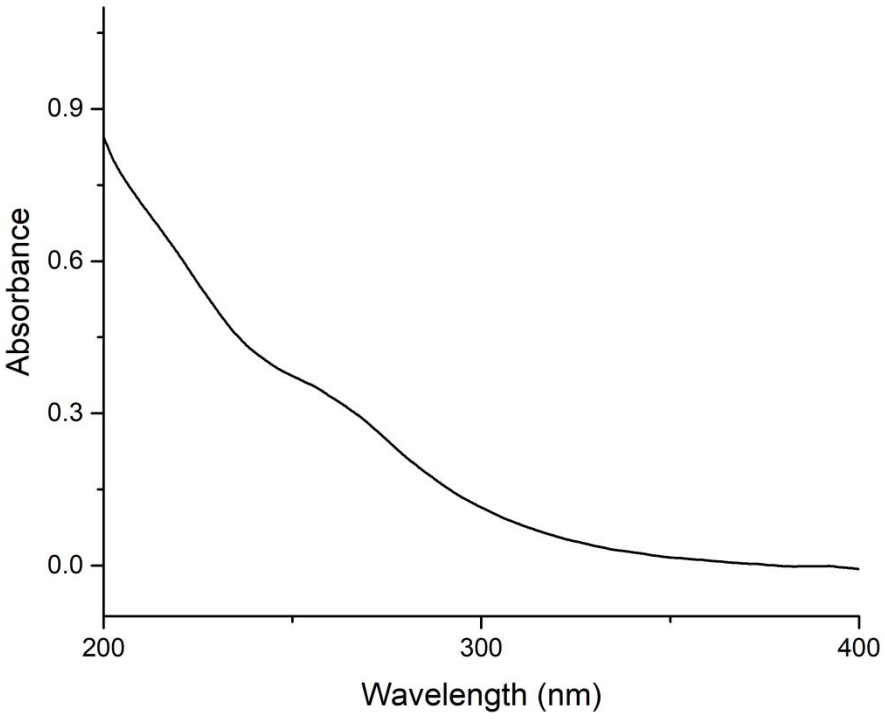


Figure S79. UV spectrum of carabrolate H (**8**) in MeOH

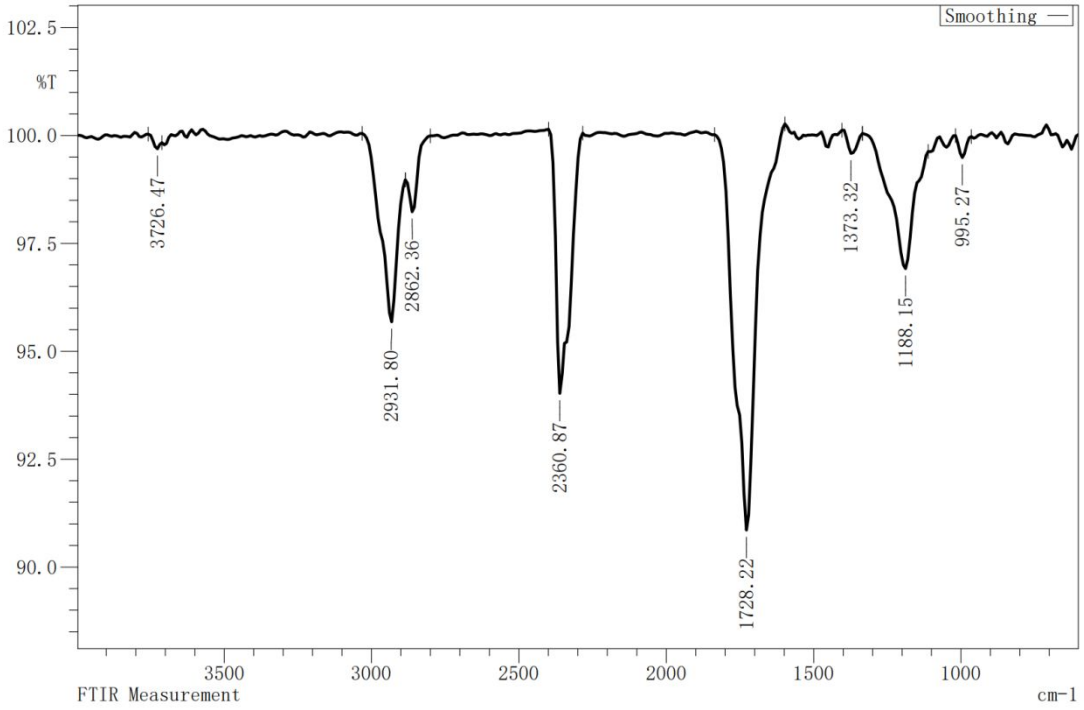
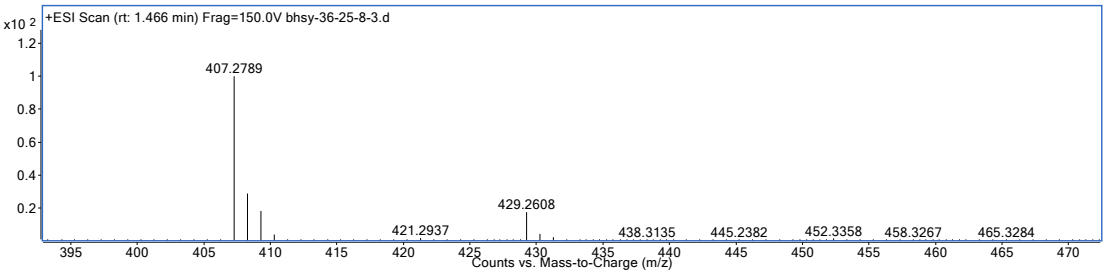


Figure S80. IR spectrum (film on KBr plate) of carabrolate H (**8**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{24}H_{38}O_5$	99.78	406.2716	406.2719	407.2792	0.74	$C_{24}H_{39}O_5$	407.2789
$C_{24}H_{38}O_5$	99.7	406.2716	406.2719	429.2611	0.85	$C_{24}H_{38}NaO_5$	429.2608

Figure S81. HRESIMS spectrum of carabrolate H (**8**)

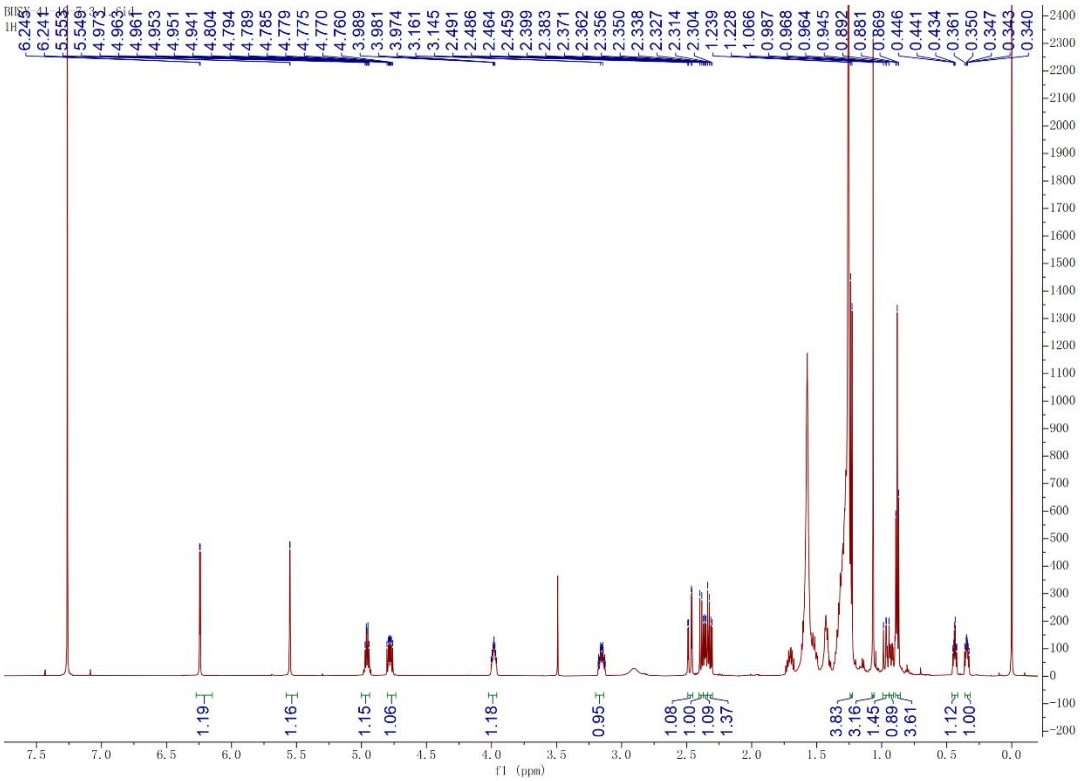


Figure S82. ^{1}H NMR spectrum (600 MHz) of carabrolate I (**9**) in $CDCl_3$

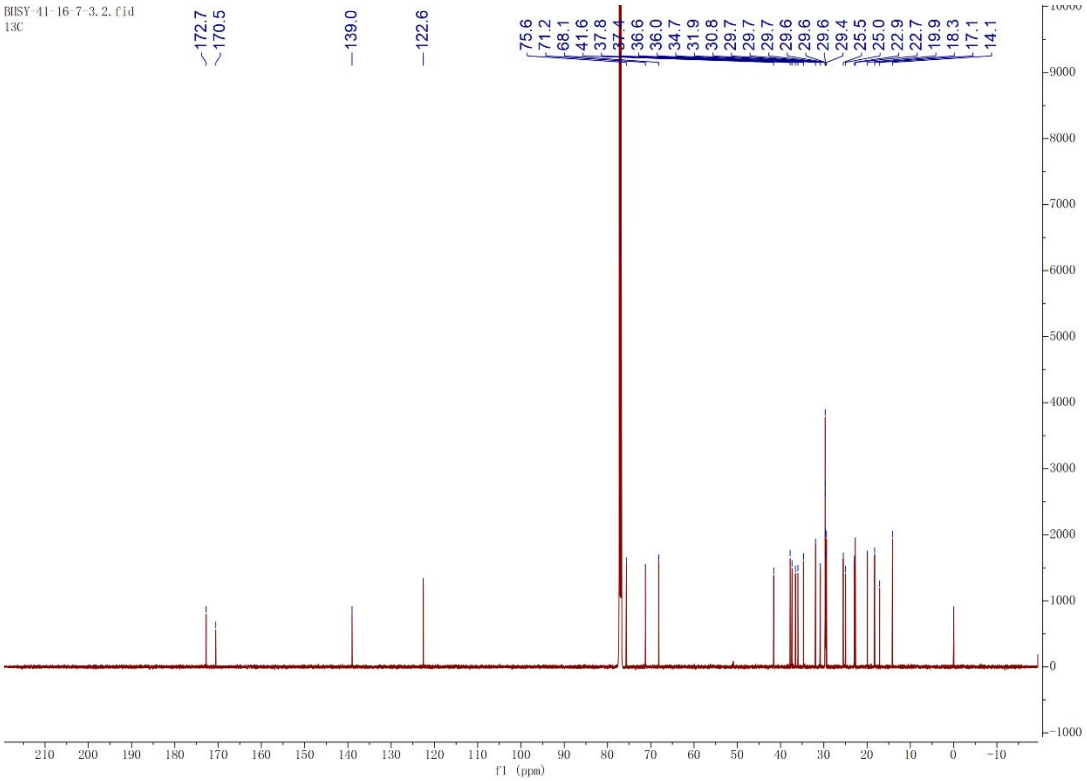


Figure S83. ^{13}C NMR spectrum (150 MHz) of carabrolate I (**9**) in $CDCl_3$

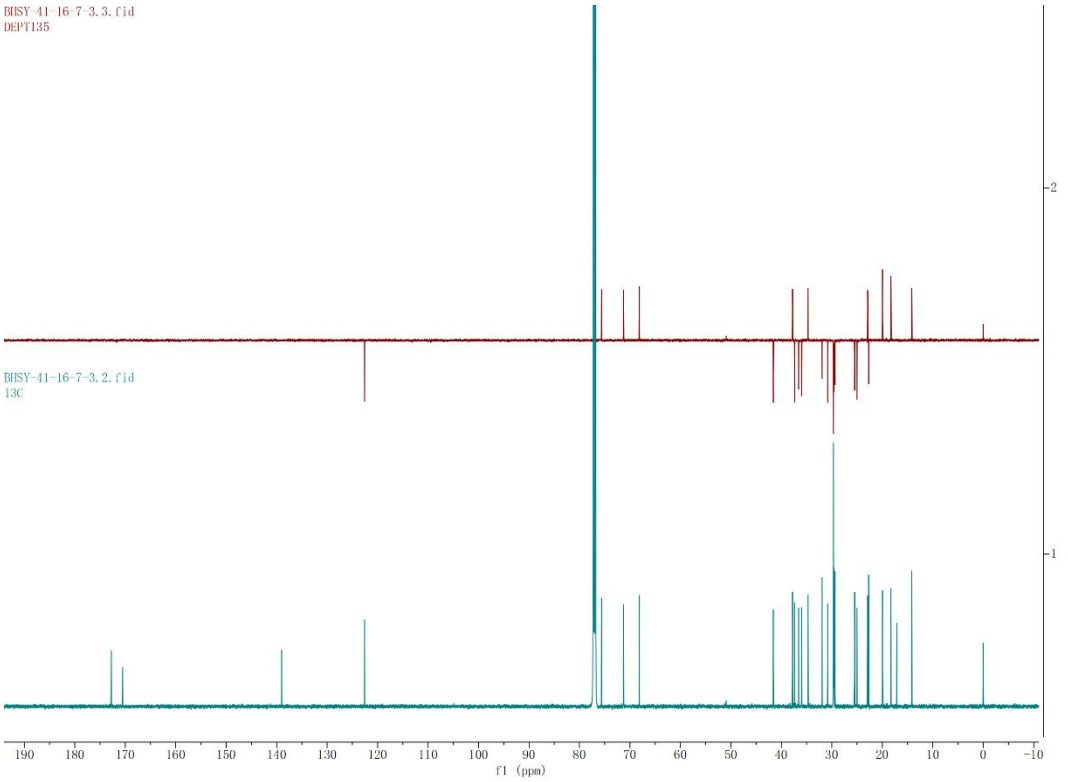


Figure S84. DEPT 135 spectrum (150 MHz) of carabrolate I (**9**) in $CDCl_3$

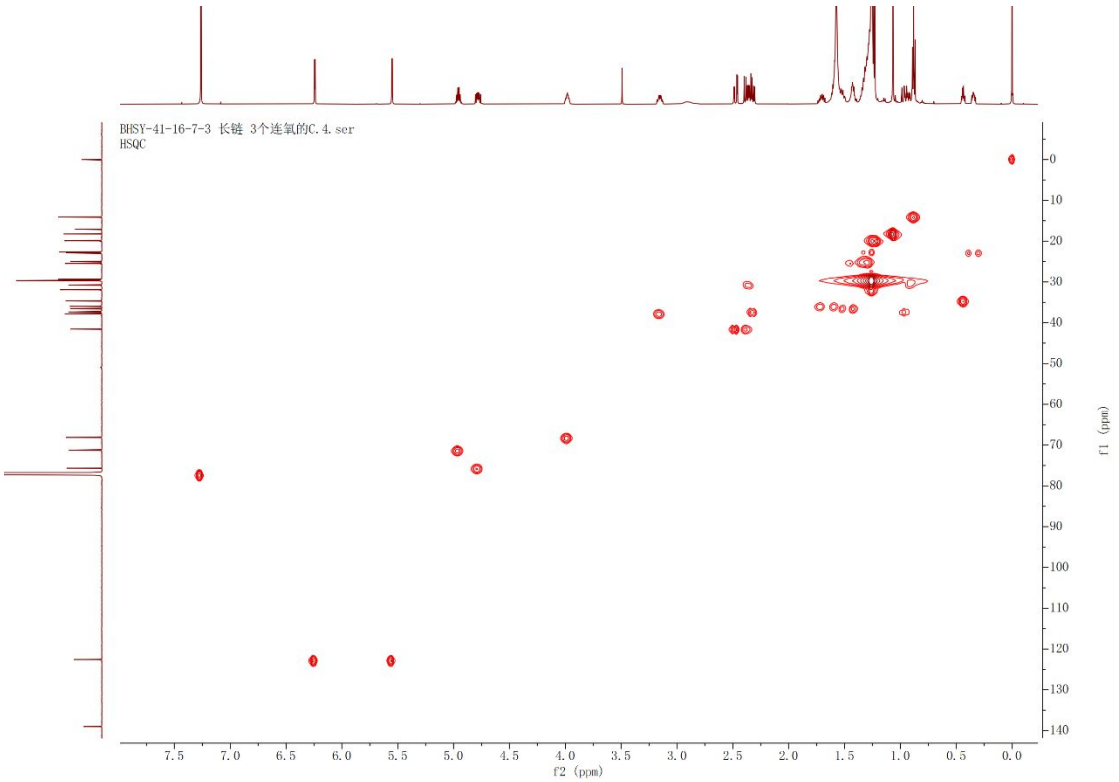


Figure S85. HSQC spectrum (600 MHz) of carabrolate I (**9**) in $CDCl_3$

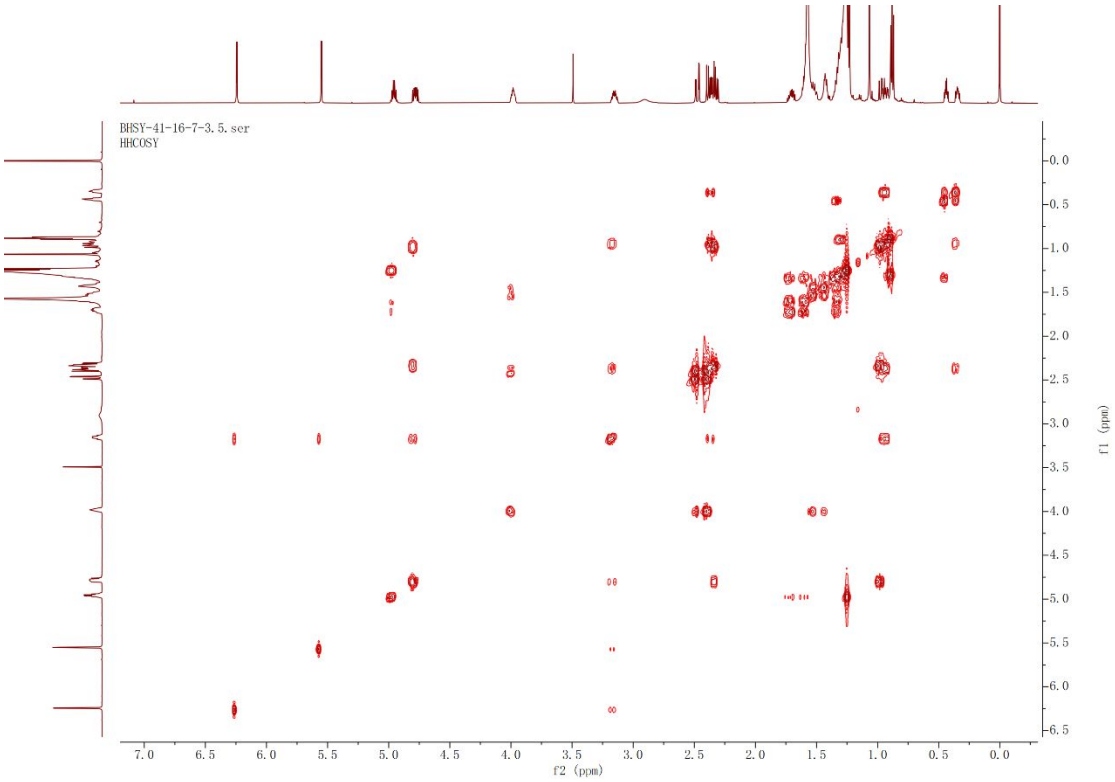


Figure S86. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate I (**9**) in $CDCl_3$

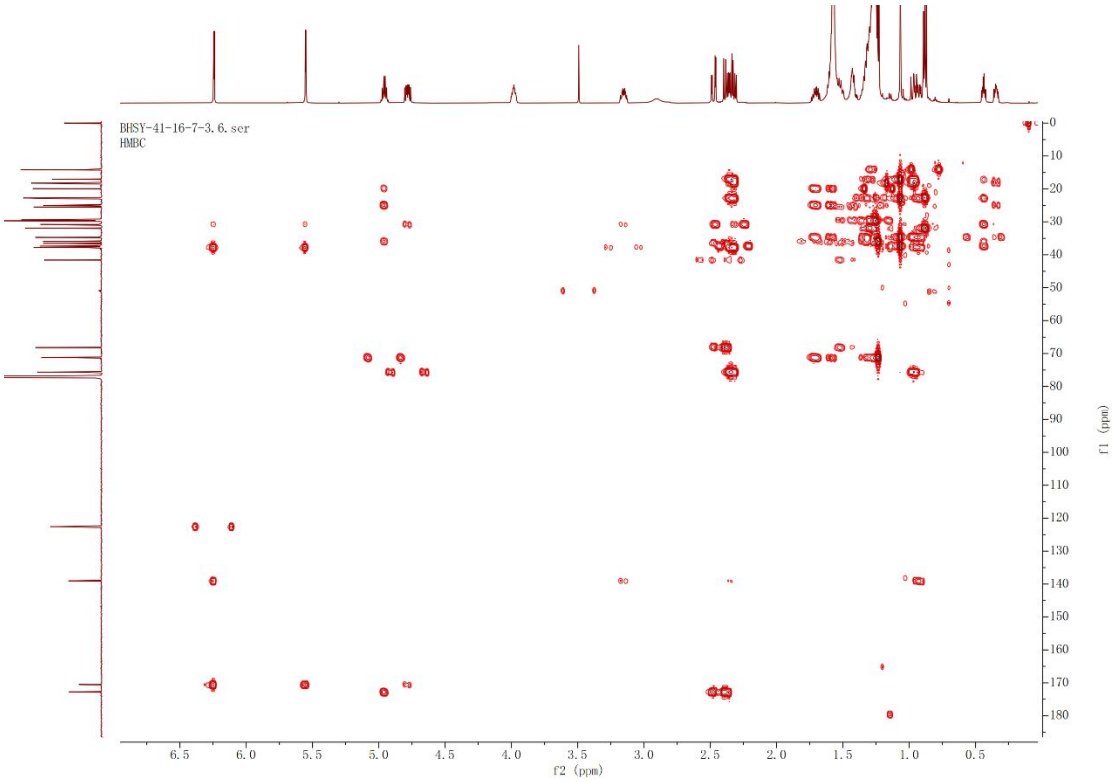


Figure S87. HMBC spectrum (600 MHz) ofcarabrolate I (**9**) in $CDCl_3$

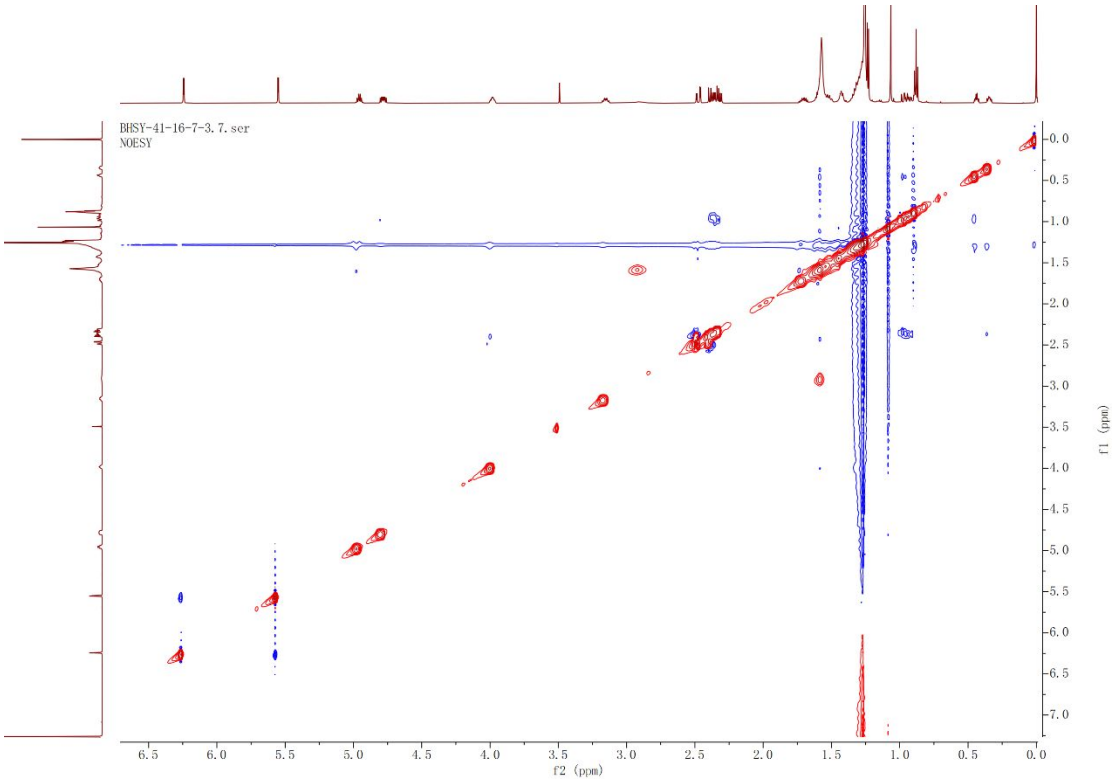


Figure S88. NOESY spectrum (600 MHz) of carabrolate I (**9**) in $CDCl_3$

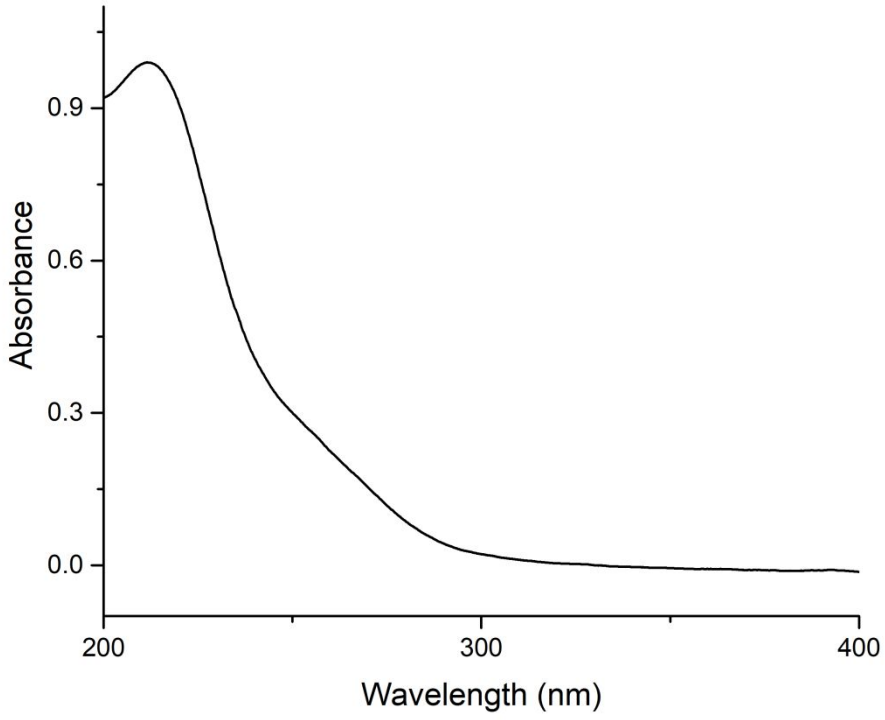


Figure S89. UV spectrum of carabrolate I (**9**) in MeOH

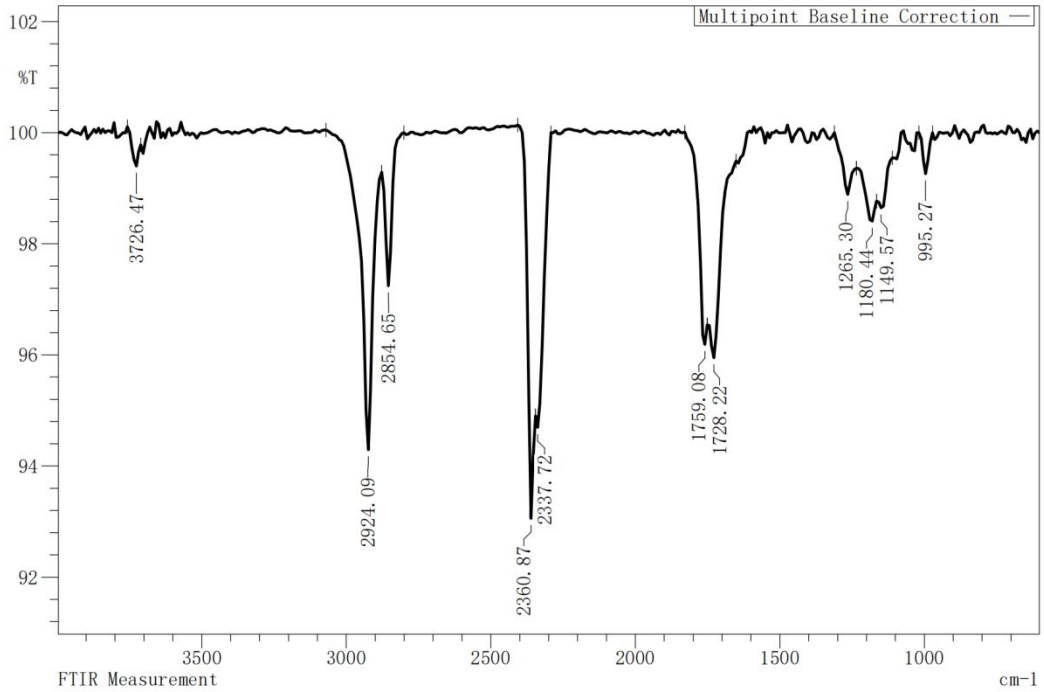
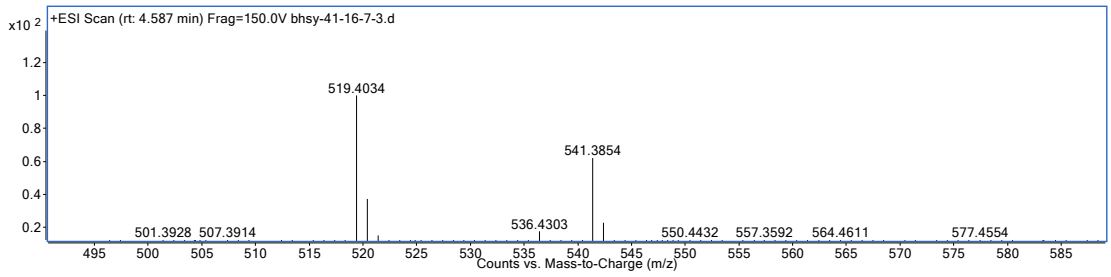


Figure S90. IR spectrum (film on KBr plate) of carabrolate I (**9**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{32}H_{54}O_5$	98.14	518.3961	518.3971	519.4044	1.93	$C_{32}H_{55}O_5$	519.4034
$C_{32}H_{54}O_5$	98.34	518.3962	518.3971	541.3863	1.82	$C_{32}H_{54}NaO_5$	541.3854

Figure S91. HRESIMS spectrum of carabrolate I (**9**)

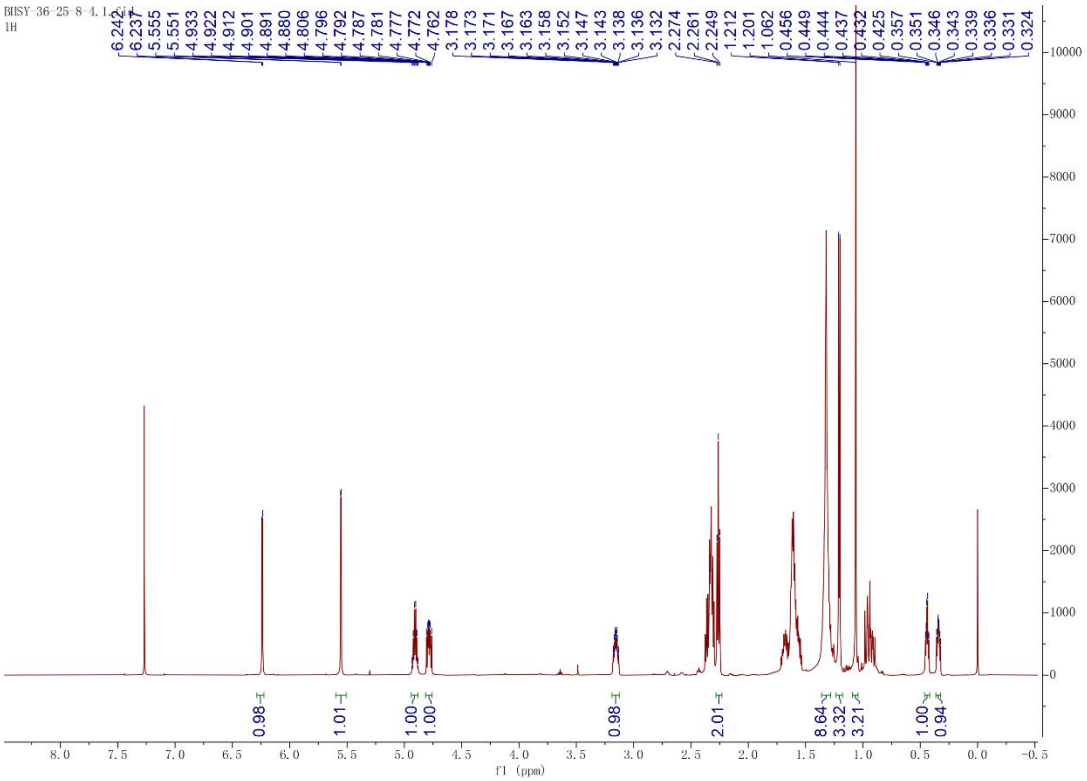


Figure S92. ^{1}H NMR spectrum (600 MHz) of carabrolate J (**10**) in $CDCl_3$

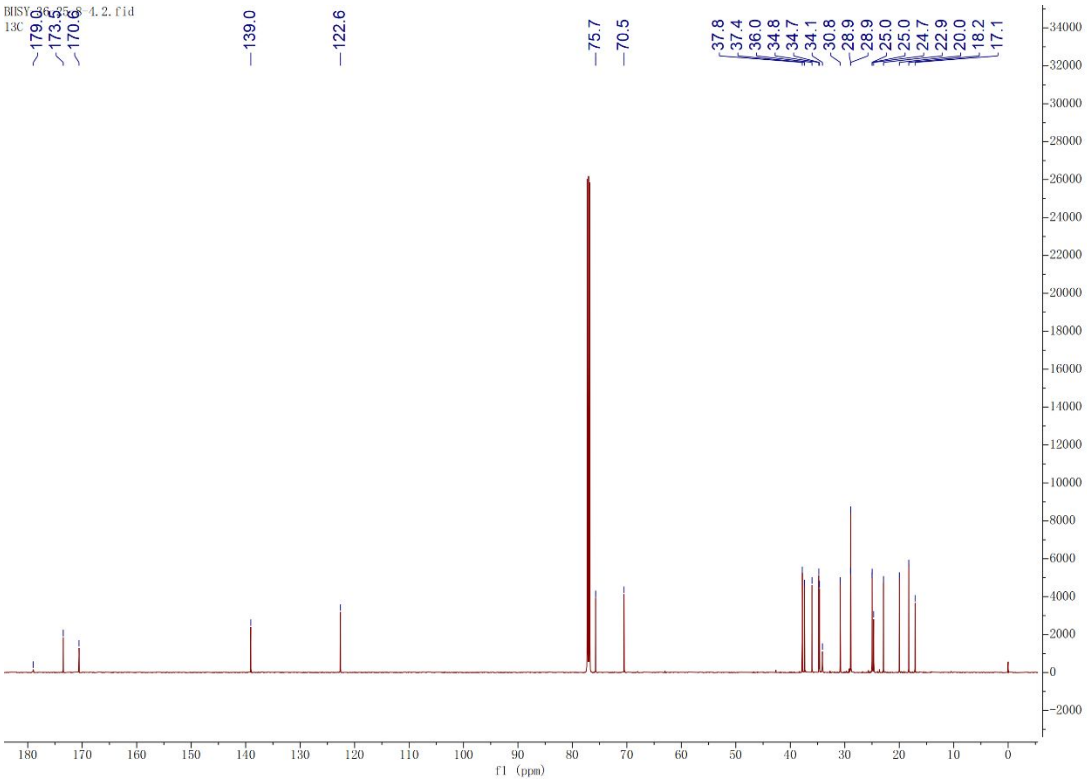


Figure S93. ^{13}C NMR spectrum (150 MHz) of carabrolate J (**10**) in $CDCl_3$

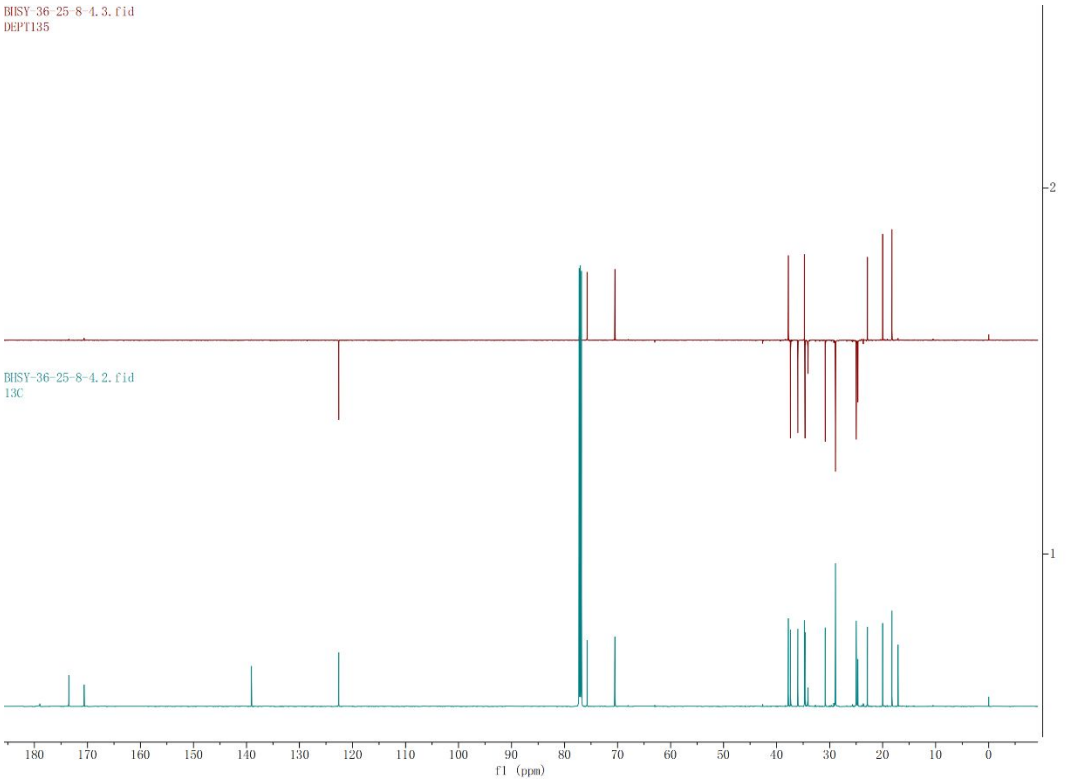


Figure S94. DEPT 135 spectrum (150 MHz) of carabrolate J (**10**) in $CDCl_3$

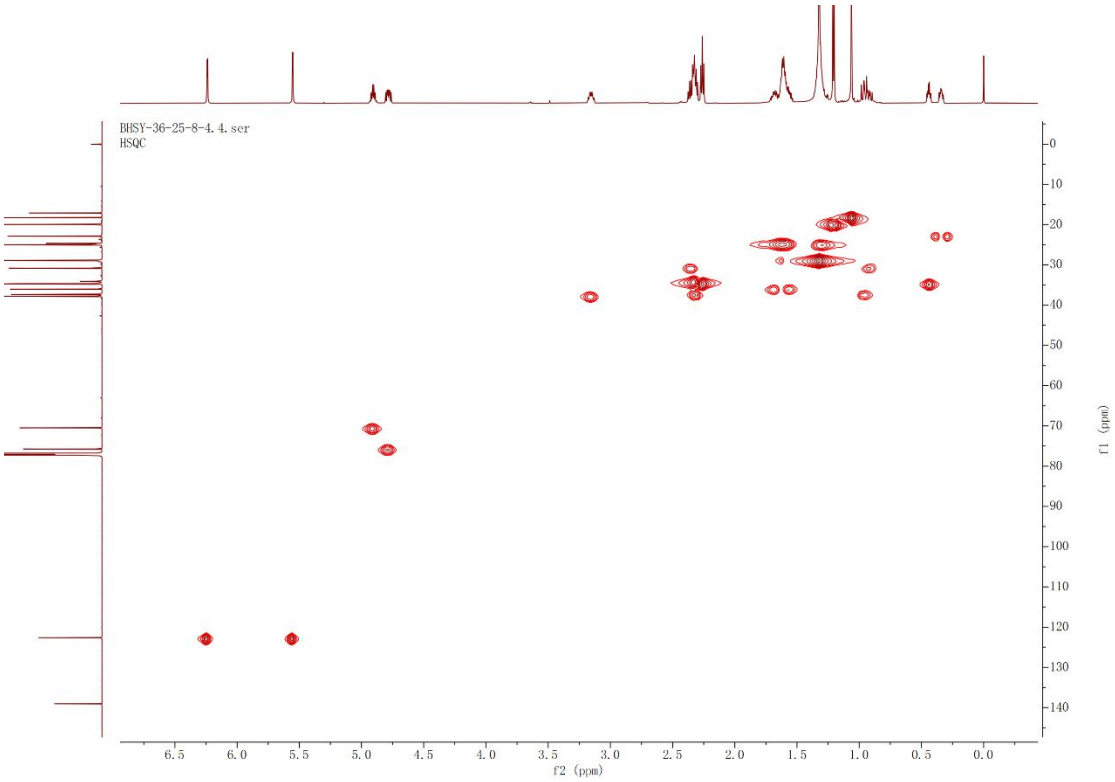


Figure S95. HSQC spectrum (600 MHz) of carabrolate J (**10**) in $CDCl_3$

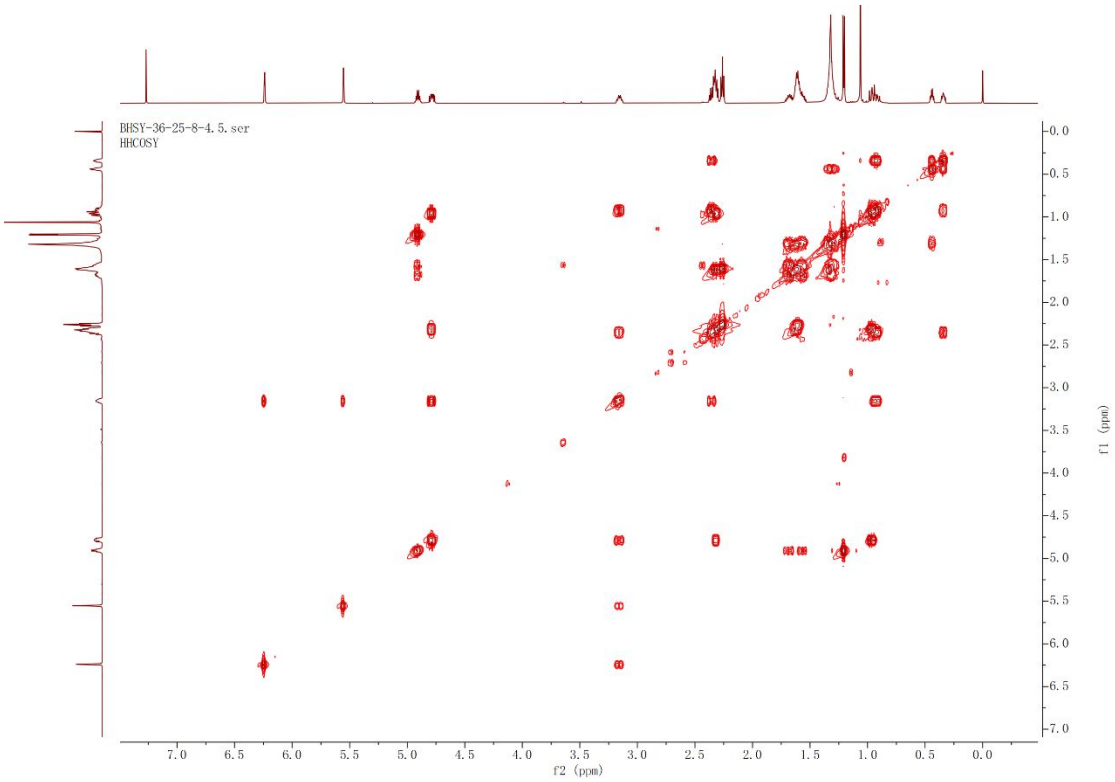


Figure S96. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate J (**10**) in $CDCl_3$

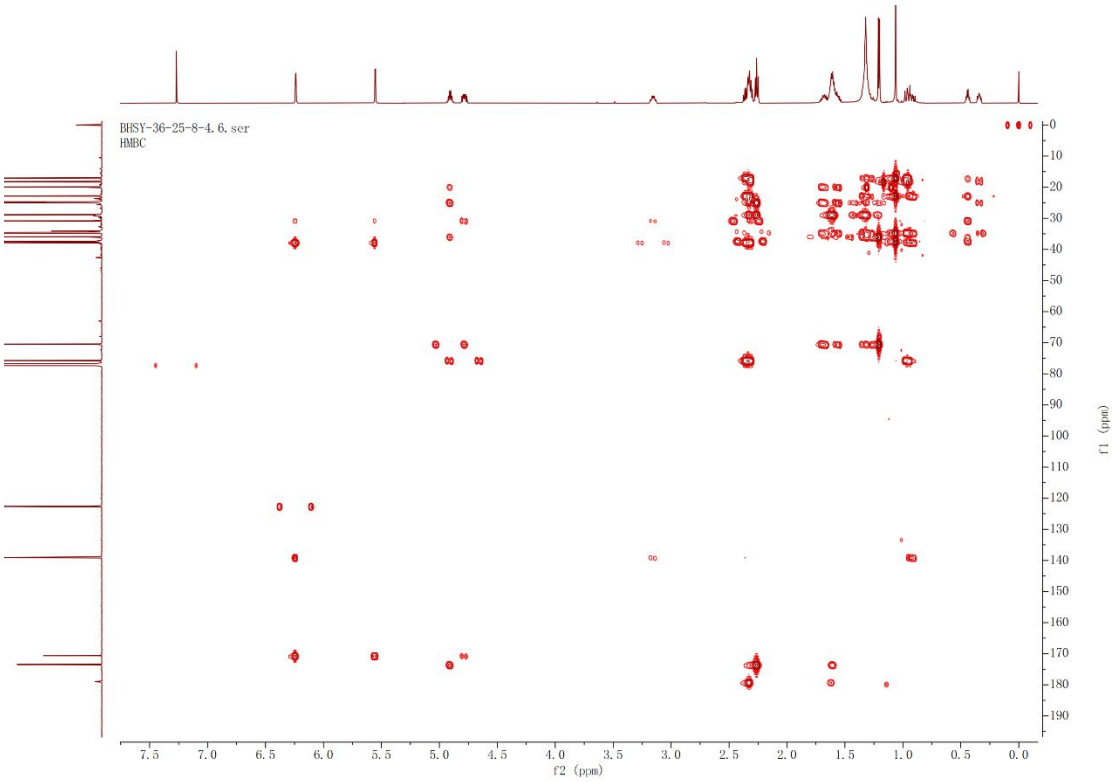


Figure S97. HMBC spectrum (600 MHz) of carabrolate J (**10**) in $CDCl_3$

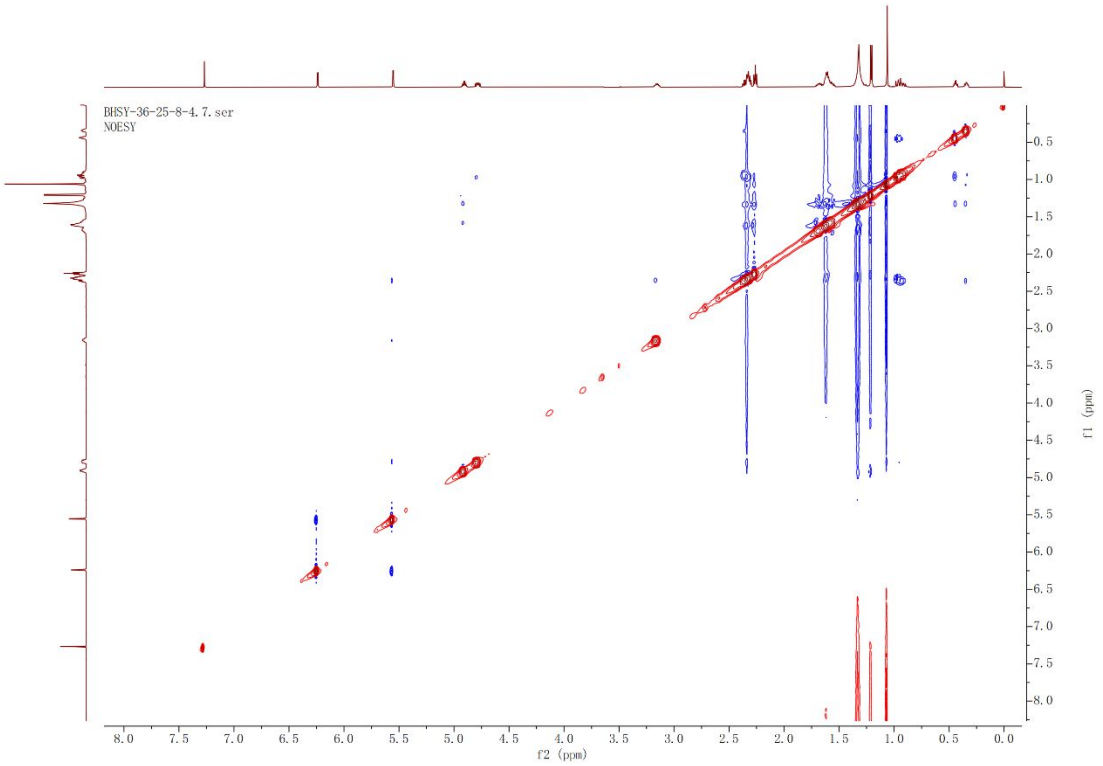


Figure S98. NOESY spectrum (600 MHz) of carabrolate J (**10**) in $CDCl_3$

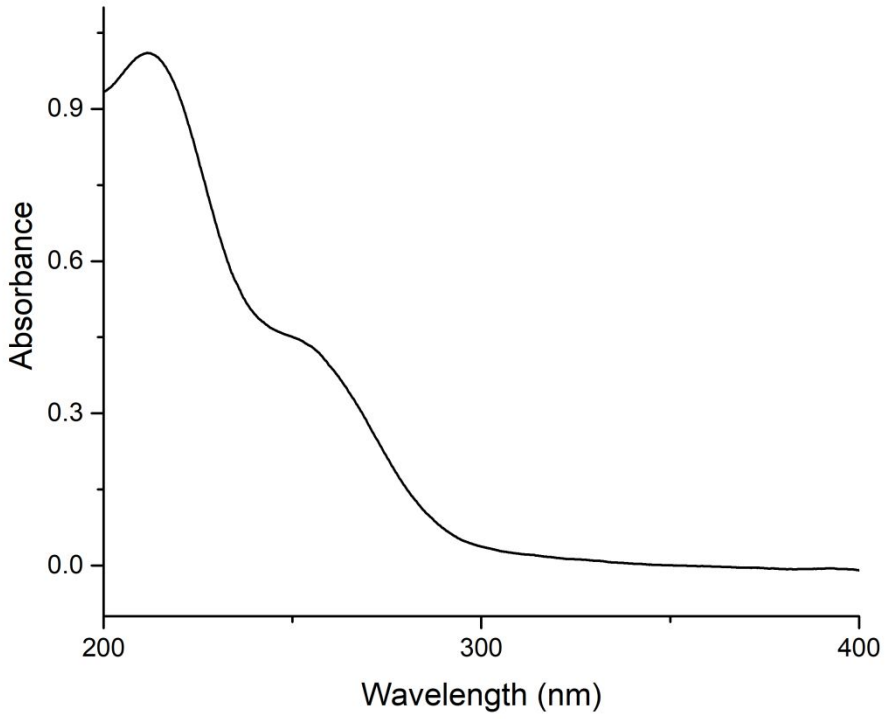


Figure S99. UV spectrum of carabrolate J (**10**) in MeOH

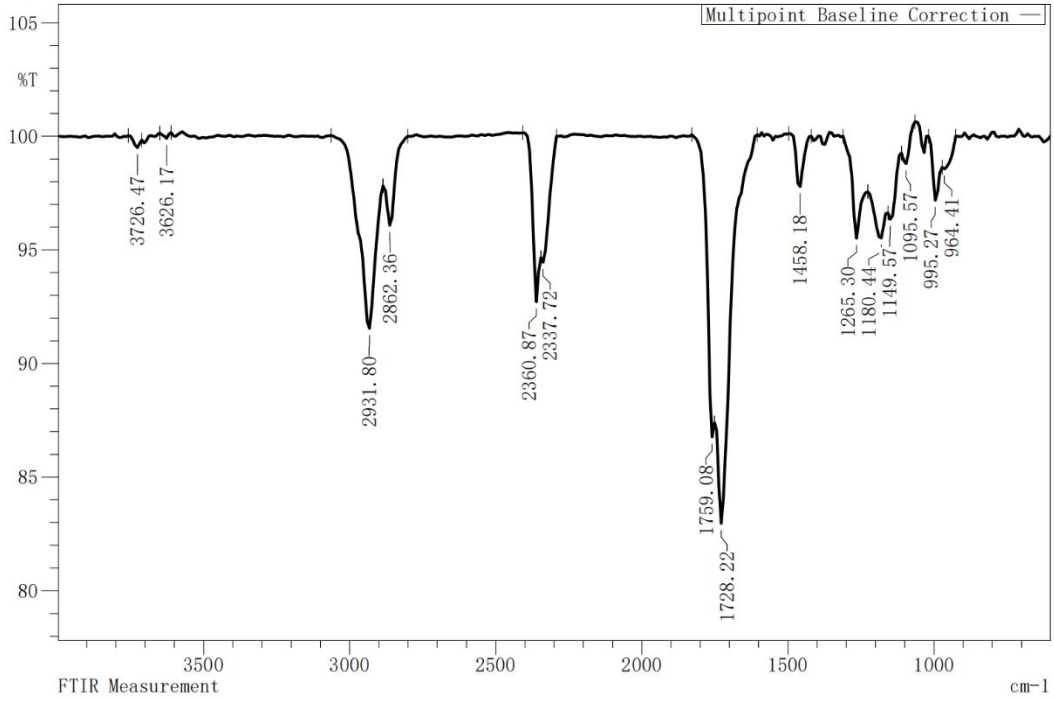
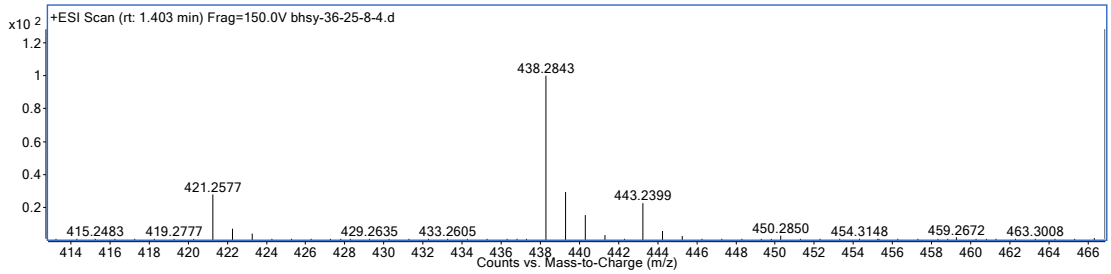


Figure S100. IR spectrum (film on KBr plate) of carabrolate J (**10**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{24}H_{36}O_6$	98.62	420.2504	420.2512	421.2585	1.82	$C_{24}H_{37}O_6$	421.2577
$C_{24}H_{36}O_6$	98.79	420.2505	420.2512	438.285	1.7	$C_{24}H_{40}NO_6$	438.2843

Figure S101. HRESIMS spectrum of carabrolate J (**10**)

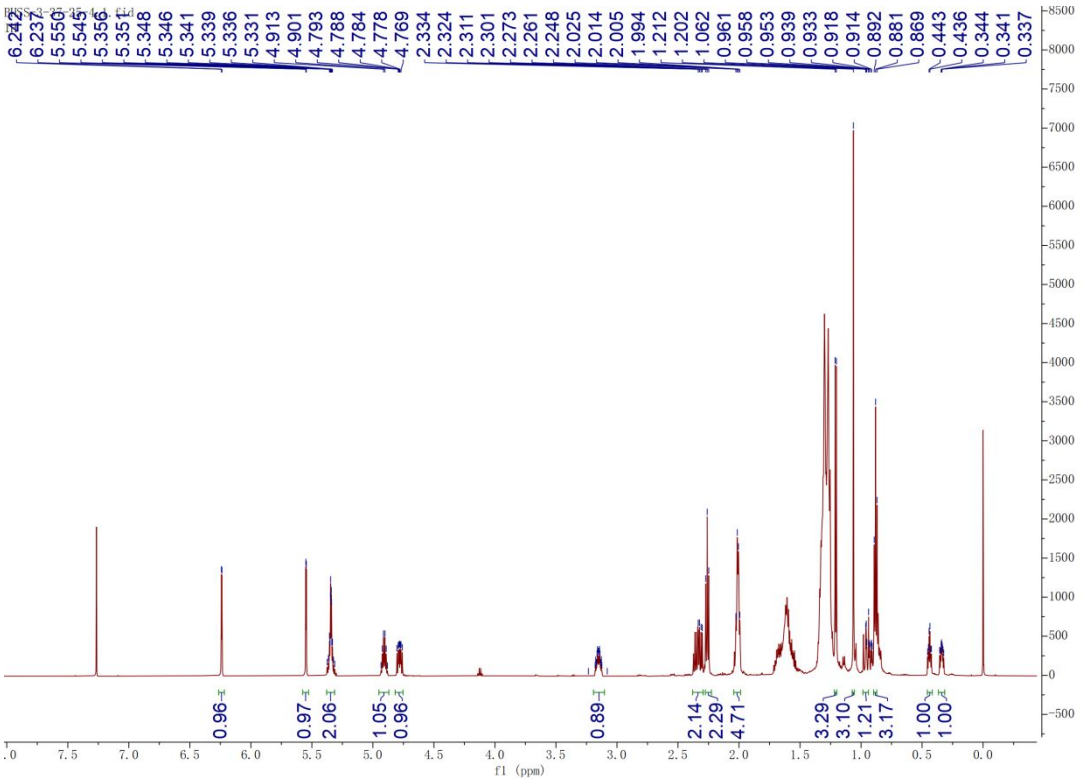


Figure S102. ^{1}H NMR spectrum (600 MHz) of carabrolate K (**11**) in $CDCl_3$

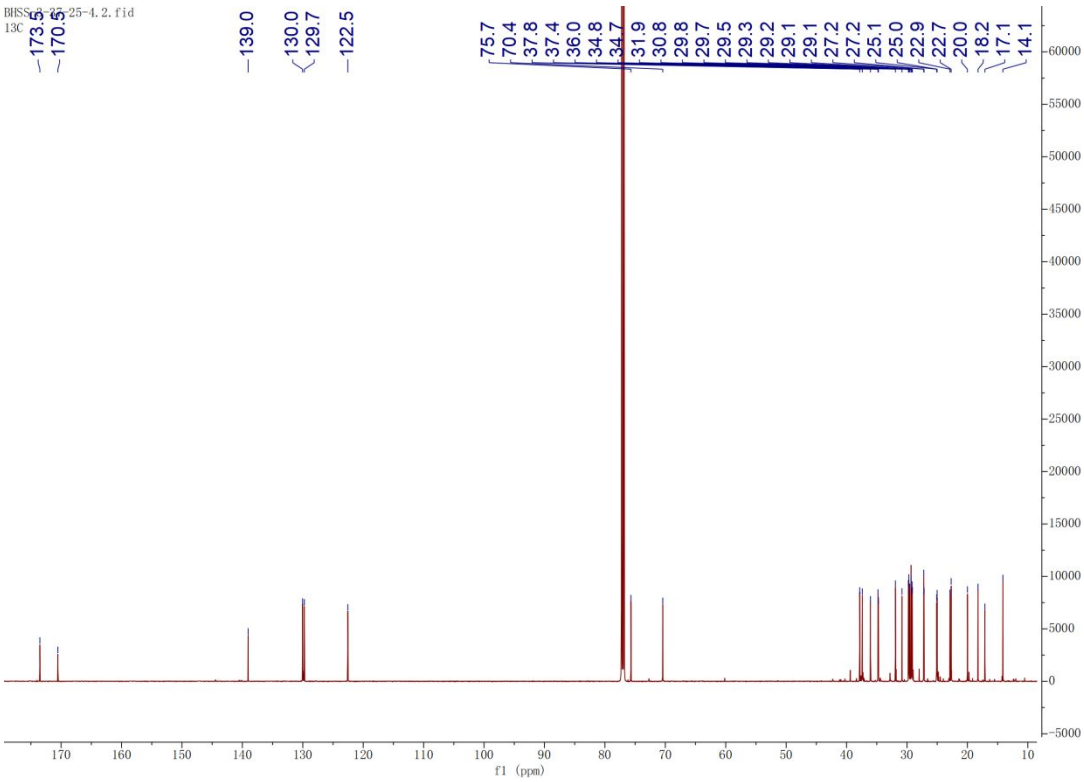


Figure S103. ^{13}C NMR spectrum (150 MHz) of carabrolate K (**11**) in $CDCl_3$

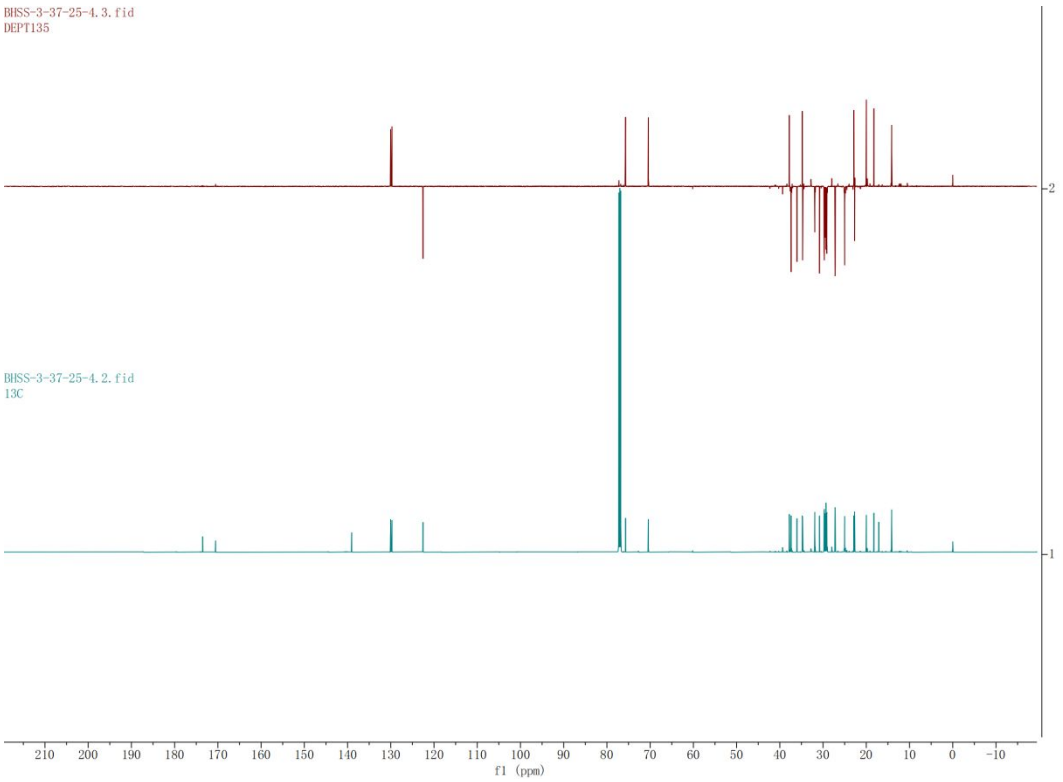


Figure S104. DEPT 135 spectrum (150 MHz) of carabrolate K (**11**) in $CDCl_3$

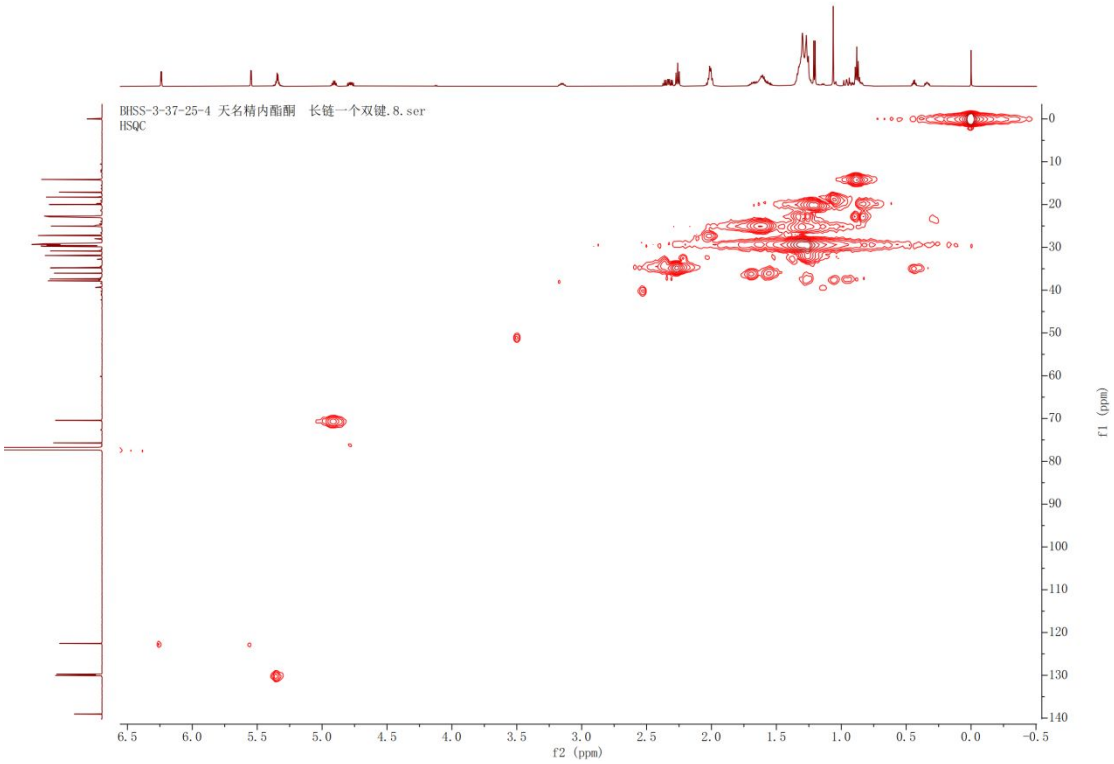


Figure S105. HSQC spectrum (600 MHz) of carabrolate K (**11**) in $CDCl_3$

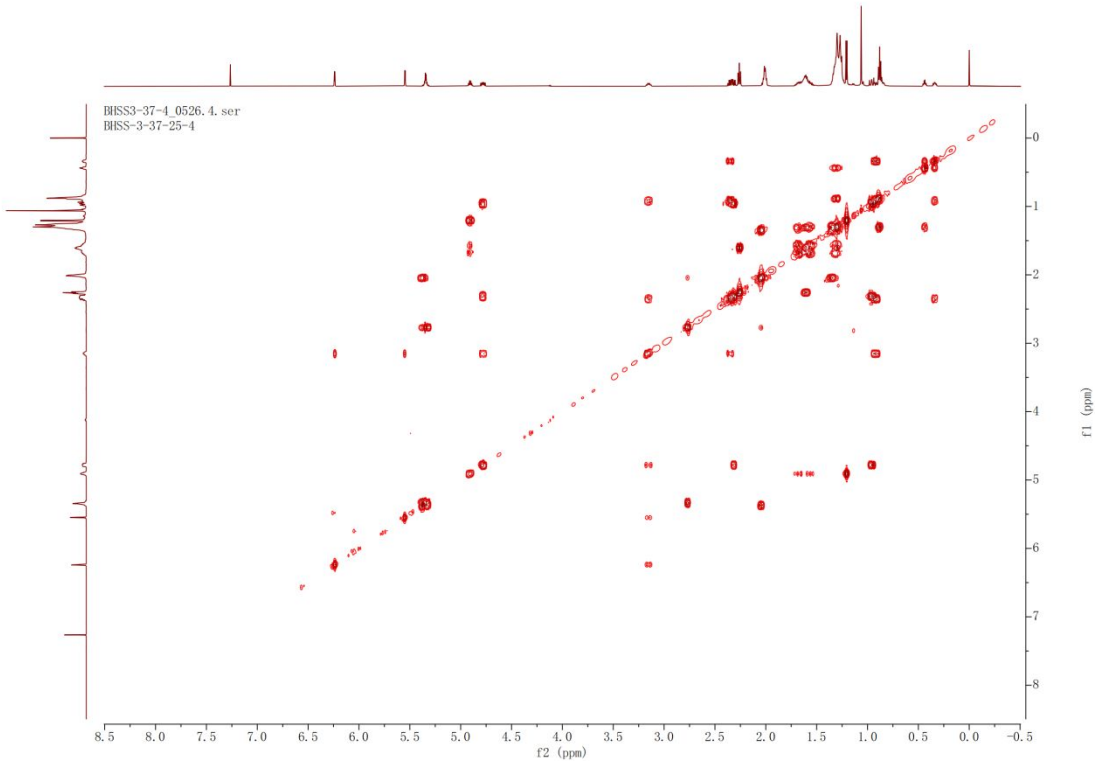


Figure S106. ^{1}H-^{1}H COSY spectrum (600 MHz) of carabrolate K (**11**) in $CDCl_3$

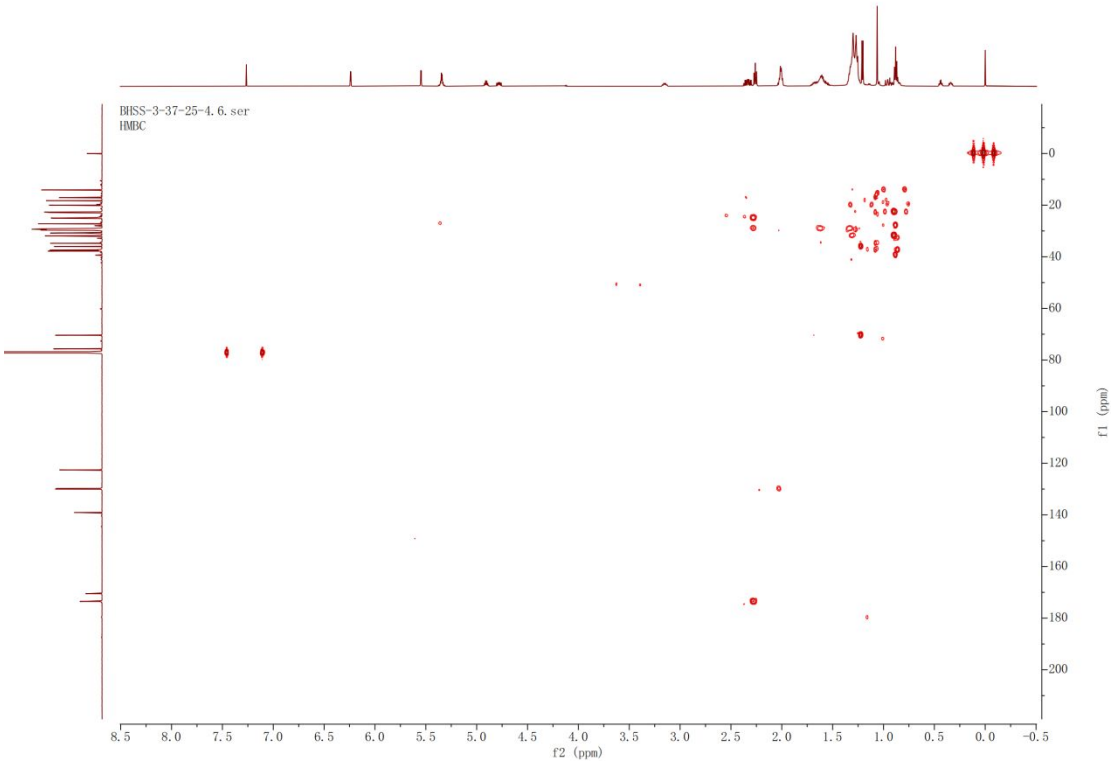


Figure S107. HMBC spectrum (600 MHz) of carabrolate K (**11**) in $CDCl_3$

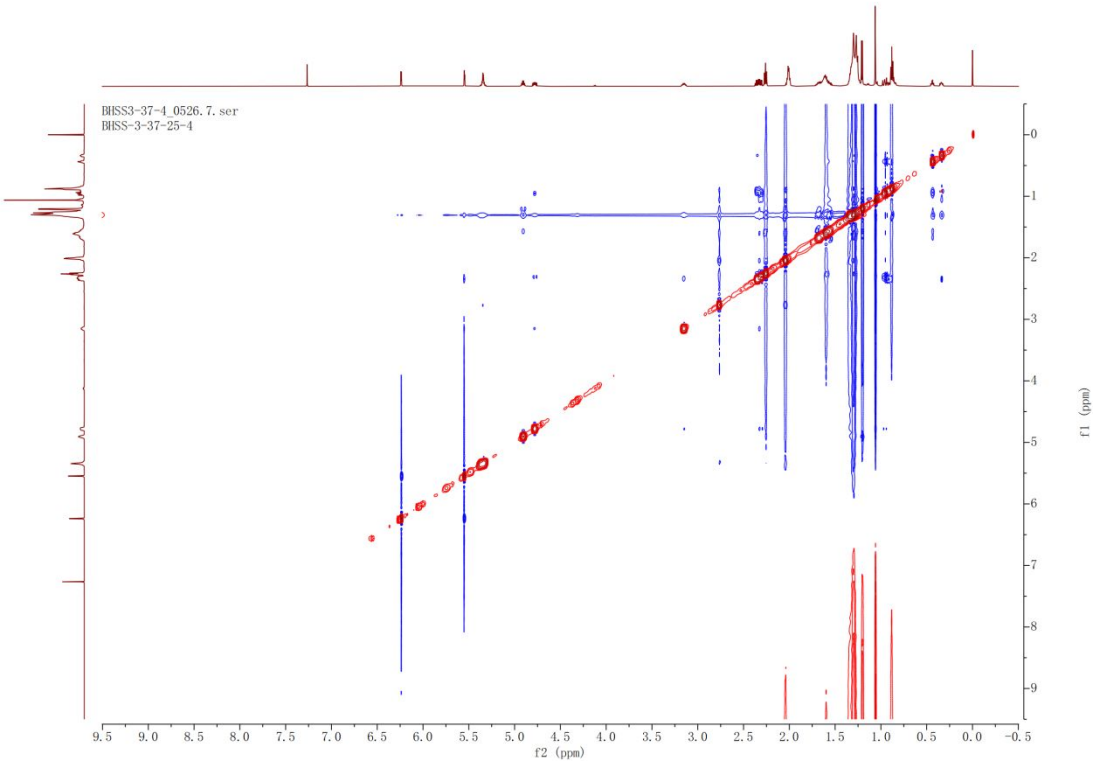


Figure S108. NOESY spectrum (600 MHz) of carabrolate K (**11**) in $CDCl_3$

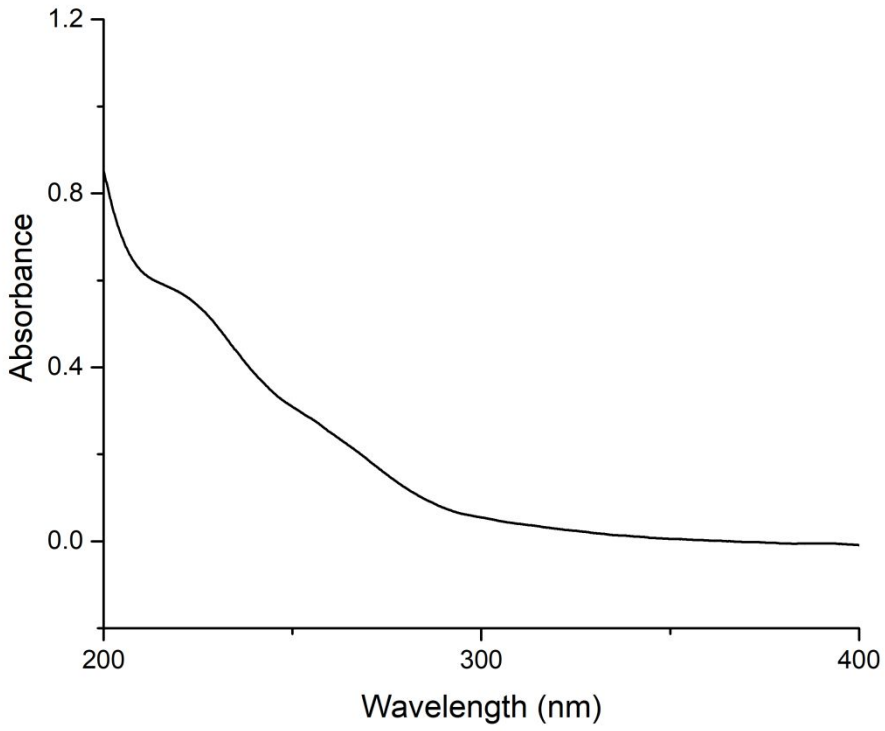


Figure S109. UV spectrum of carabrolate J (**10**) in MeOH

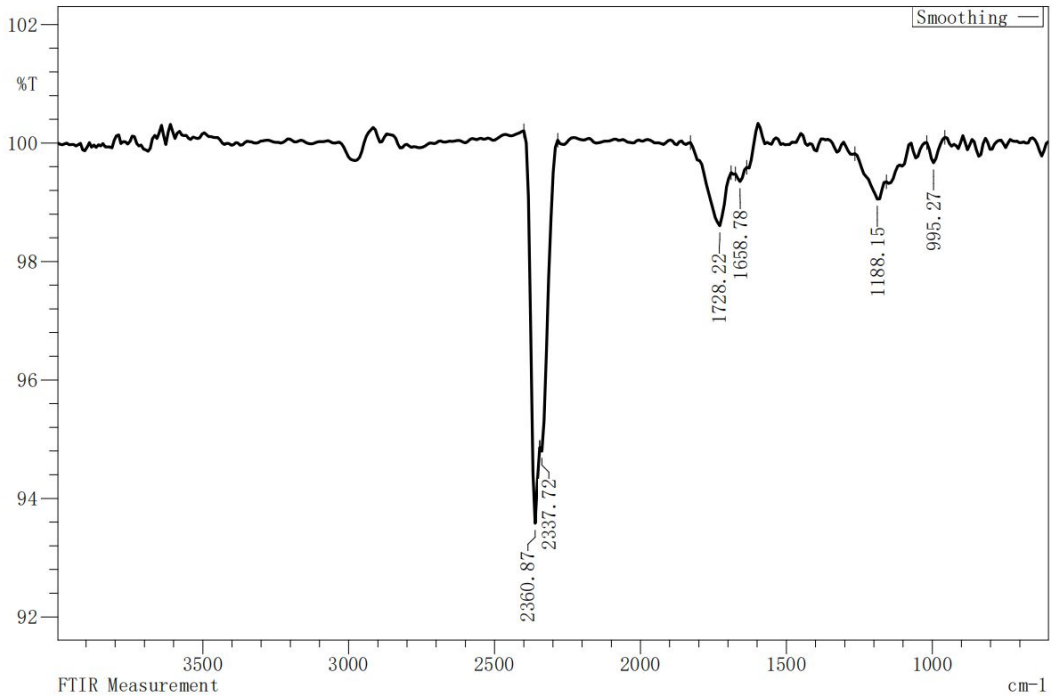
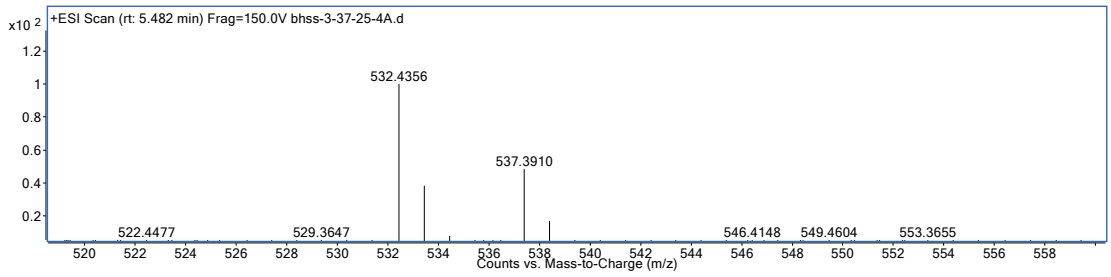
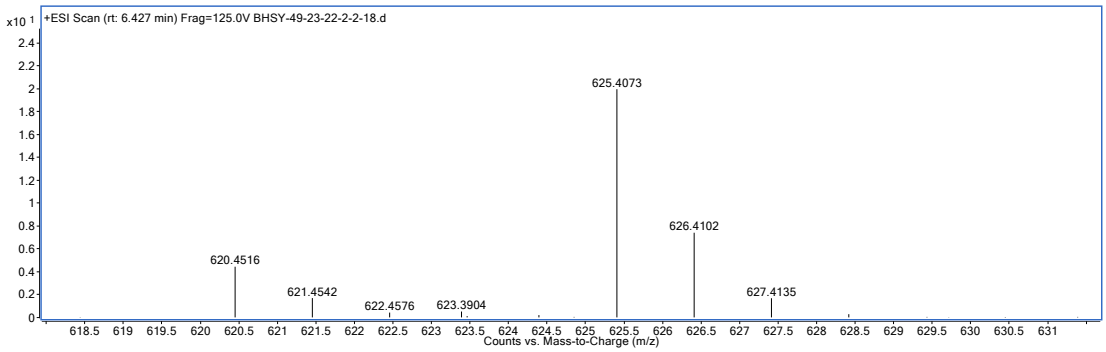


Figure S110. IR spectrum (film on KBr plate) of carabrolate K (**11**)



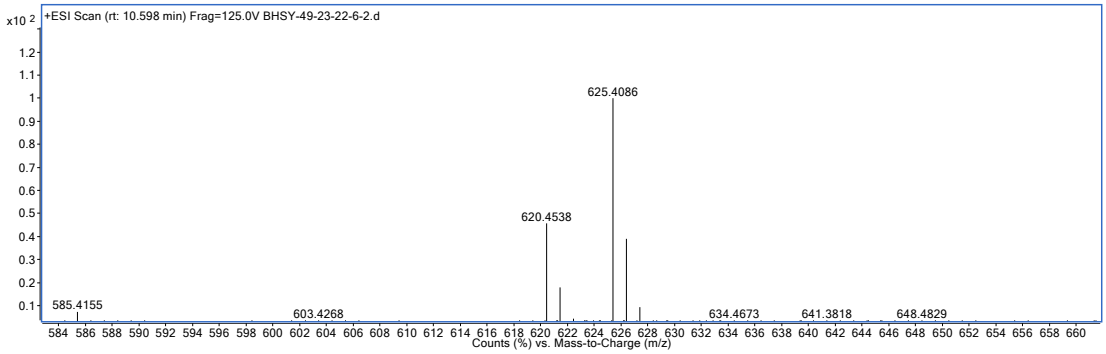
Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{33}H_{54}O_4$	99.64	514.4018	514.4022	532.436	0.85	$C_{33}H_{58}NO_4$	532.4356
$C_{33}H_{54}O_4$	99.65	514.4018	514.4022	537.3914	0.84	$C_{33}H_{54}NaO_4$	537.391

Figure S111. HRESIMS spectrum of carabrolate K (**11**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{36}H_{58}O_7$	99.87	602.4178	602.4183	620.4521	0.8	$C_{36}H_{62}NO_7$	620.4516
$C_{36}H_{58}O_7$	99.98	602.4181	602.4183	625.4075	0.29	$C_{36}H_{58}NaO_7$	625.4073

Figure S112. HRESIMS spectrum of the ketal of carabrolate E (**5**)



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	Ion Formula	m/z
$C_{36}H_{58}O_7$	97.7	602.4195	602.4183	603.4255	-2.11	$C_{36}H_{59}O_7$	603.4268
$C_{36}H_{58}O_7$	98.18	602.4194	602.4183	625.4075	-1.87	$C_{36}H_{58}NaO_7$	625.4086

Figure S113. HRESIMS spectrum of the ketal of carabrolate F (**6**)

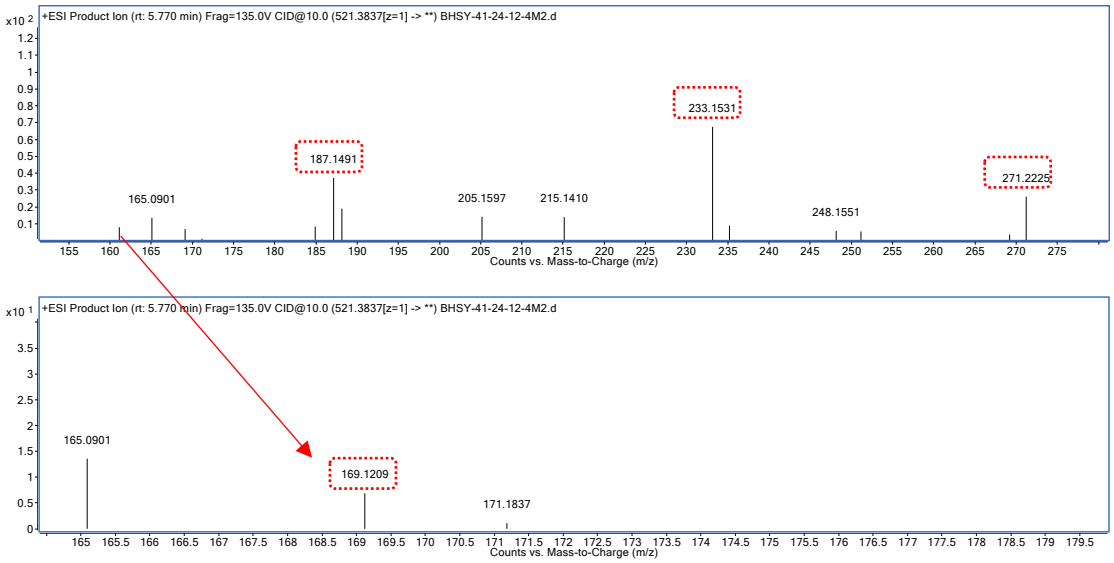


Figure S114. MS/MS spectrum (positive mode) of carabrolate G (**7**).

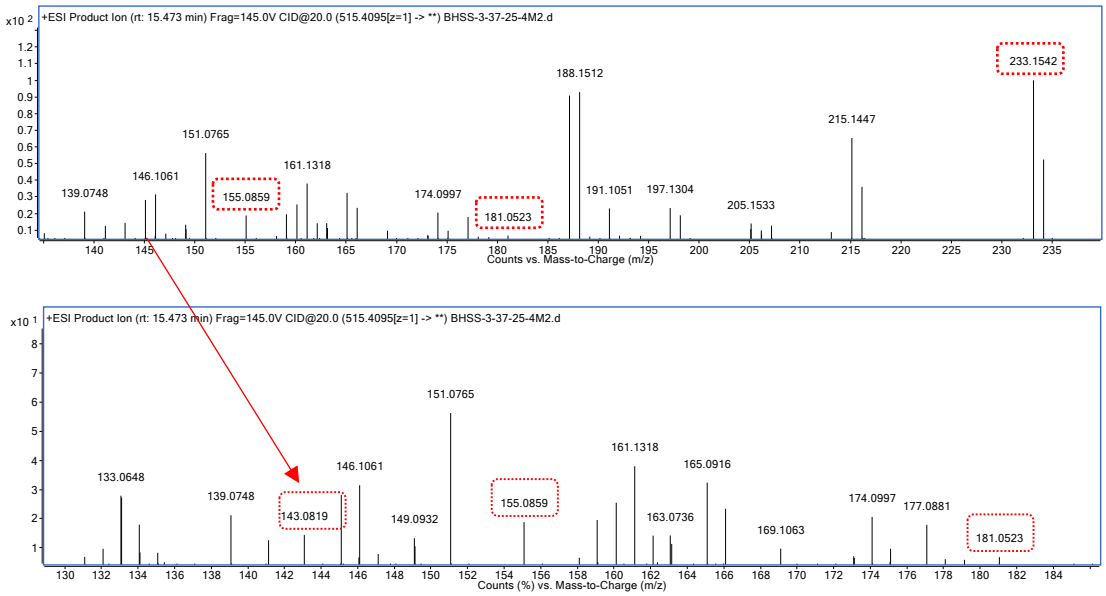


Figure S115. MS/MS spectrum (positive mode) of carabrolate K (**11**).

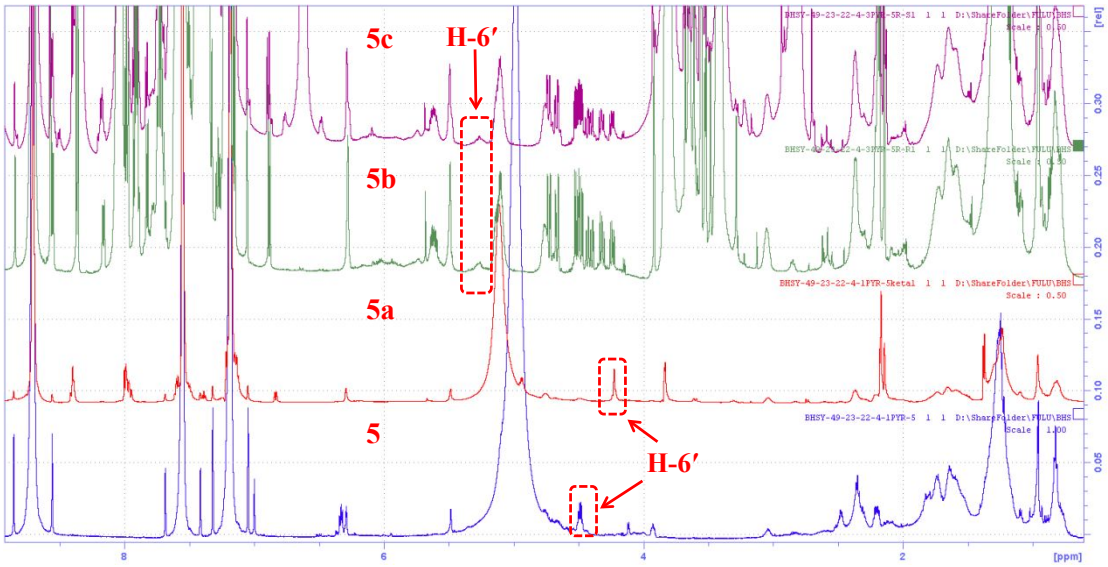


Figure S116. ^{1}H NMR spectra (600 MHz) of **5**, **5a**, **5b**, and **5c** in C_5D_5N. **5a:** the ketal of **5**; **5b**: (*S*)-MTPA esters of **5a**; **5b**: (*R*)-MTPA esters of **5a**.

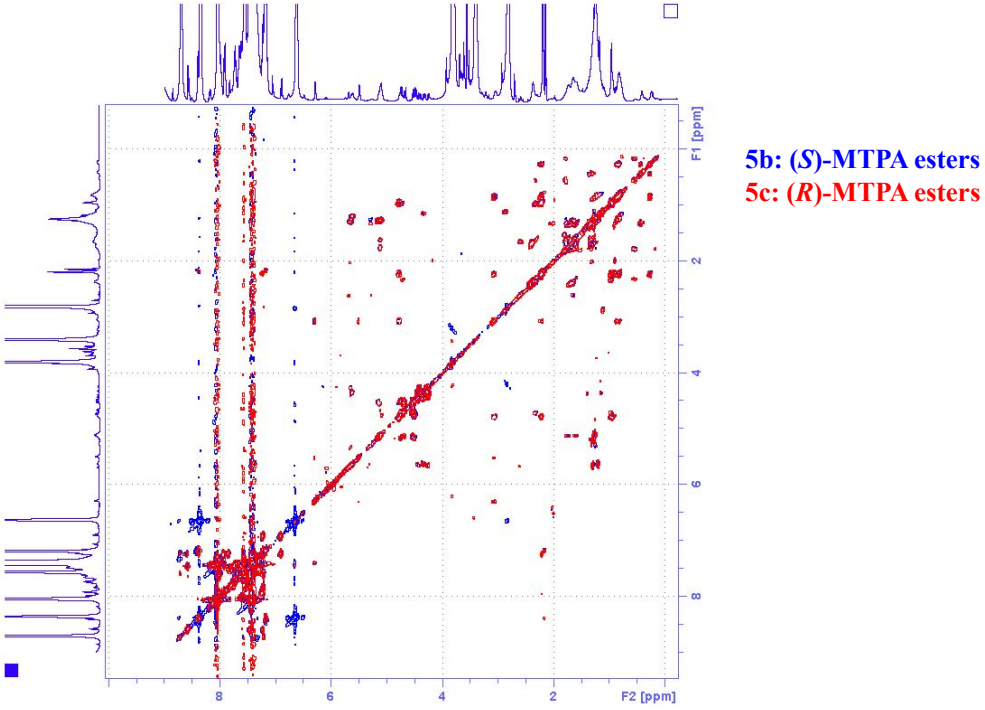
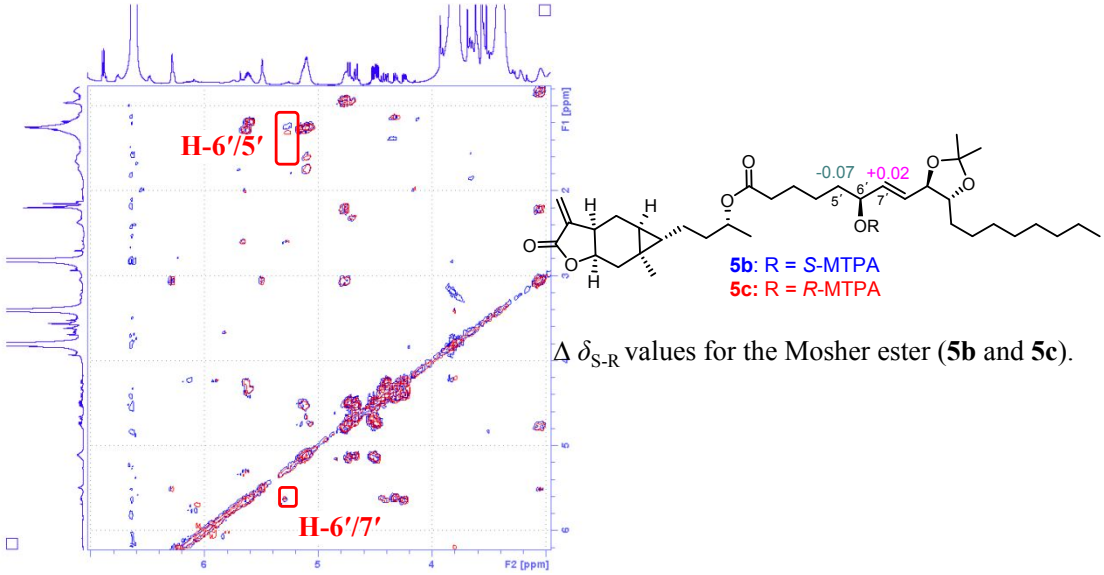


Figure S117. ^{1}H-^{1}H COSY spectra (600 MHz) of **5b** and **5c** in C_5D_5N.



$\Delta\ \delta_{S-R}$ values for the Mosher ester (**5b** and **5c**).

Figure S118. Enlarged ^{1}H-^{1}H COSY spectra (600 MHz) of **5b** and **5c** in C_5D_5N.

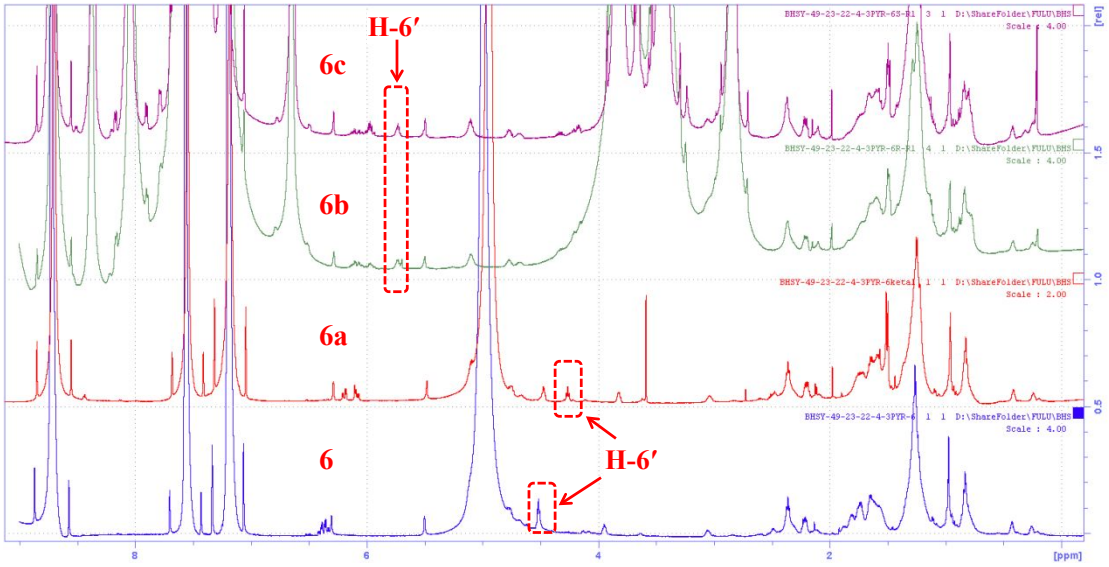


Figure S119. ^{1}H NMR spectra (600 MHz) of **6**, **6a**, **6b**, and **6c** in C_5D_5N. **6a**: the ketal of **6**; **6b**: (*S*)-MTPA esters of **6a**; **6b**: (*R*)-MTPA esters of **6a**.

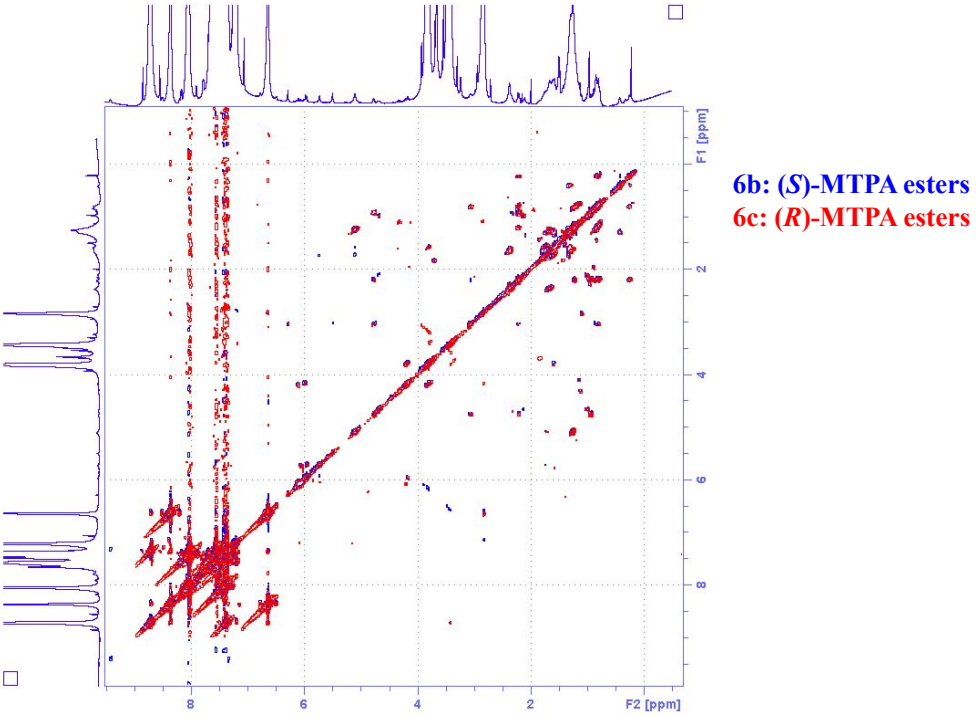
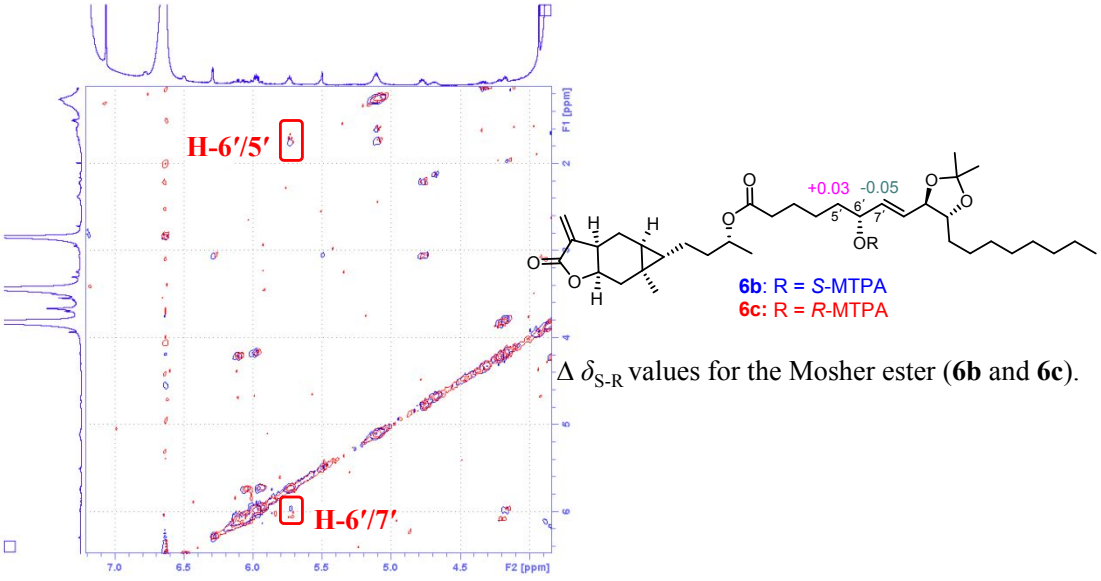


Figure S120. ^{1}H-^{1}H COSY spectra (600 MHz) of **6b** and **6c** in C_5D_5N.



$\Delta\,\delta_{S\text{-}R}$ values for the Mosher ester (**6b** and **6c**).

Figure S121. Enlarged ^{1}H-^{1}H COSY spectra (600 MHz) of **6b** and **6c** in C_5D_5N.

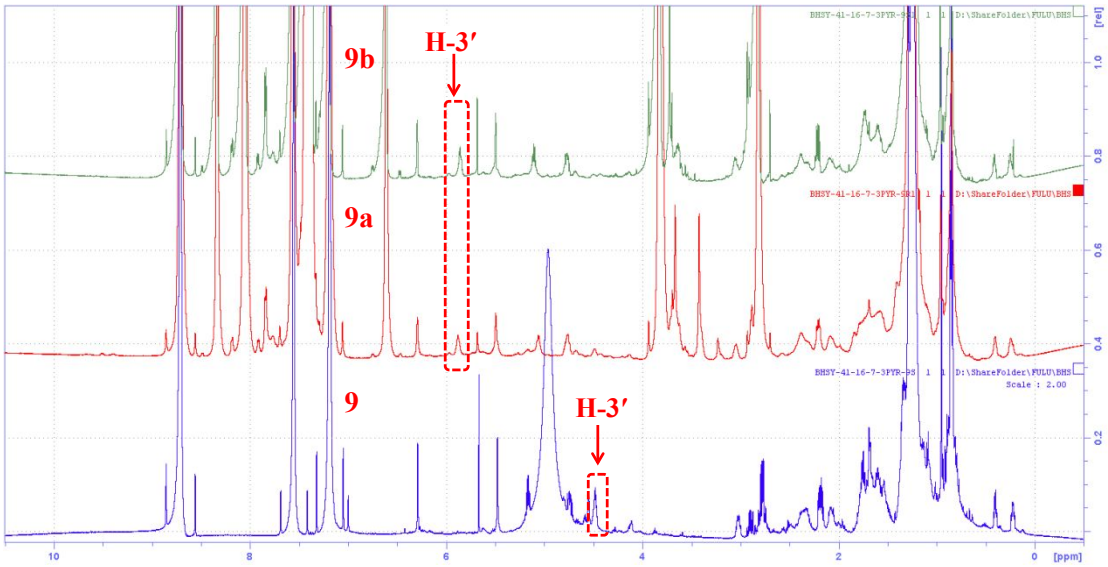


Figure S122. ^{1}H NMR spectra (600 MHz) of **9**, **9a**, and **9b** in C_5D_5N. **9a**: (*S*)-MTPA esters of **9**; **9b**: (*R*)-MTPA esters of **9**.

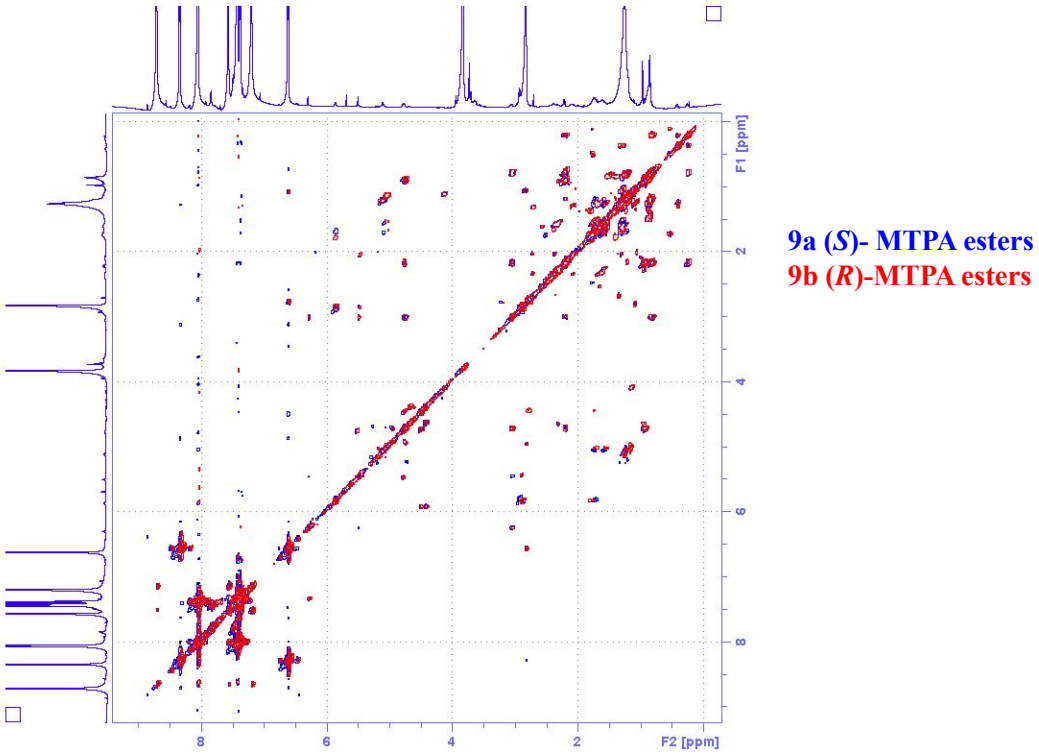


Figure S123. ^{1}H-^{1}H COSY spectra (600 MHz) of **9a** and **9b** in C_5D_5N.

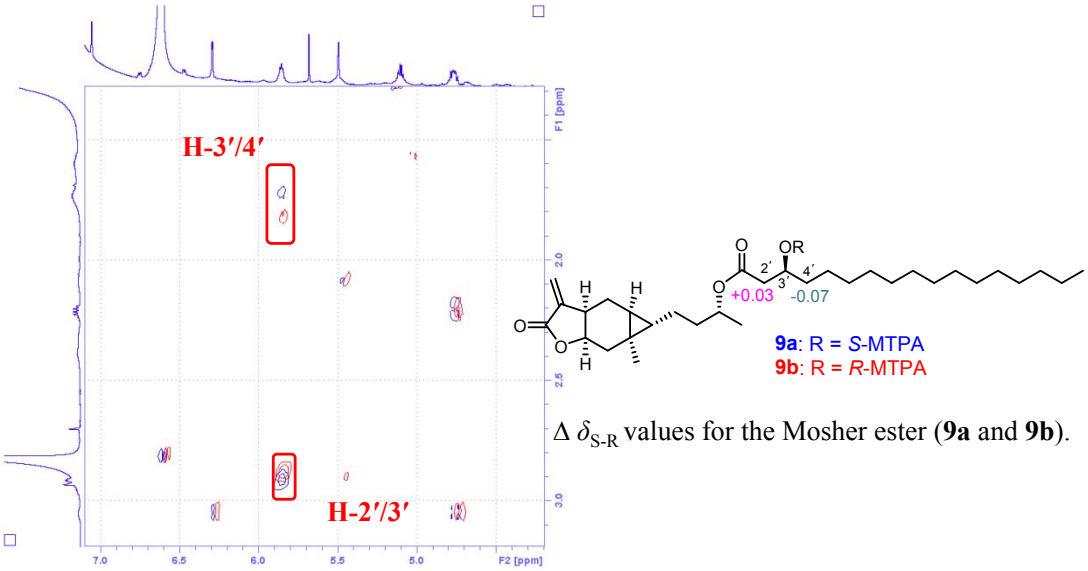


Figure S124. Enlarged ^{1}H-^{1}H COSY spectra (600 MHz) of **9a** and **9b** in C_5D_5N.