

Derivatives Semisynthesis, Structure Elucidation and Anti-*Mycobacterium marinum* Activity of a Series of Marine-Derived 14-Membered Resorcylic Acid Lactones with Interesting Ketal groups

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Table S1. Different ketone reagents used to generate compounds **10–37**.

No.	reagents	yield	No.	reagents	yield
10	3-Pentanone	93%	24	2,5-Hexanedione	35.2%
11	Pinacolone	79.4%	25	Acetylacetone	54.4%
12	Pinacolone	24.1%	26	Acetylacetone	36.3%
13	Cyclohexyl methyl ketone	69.7%	27	3-Pentanone	58.8%
14	Cyclohexyl methyl ketone	33.2%	28	4'-Chloroacetophenone	54.5%
15	Acetophenone	63.7%	29	2,5-Hexanedione	53.9%
16	Acetophenone	43.1%	30	2,5-Hexanedione	32.3%
17	4-Fluoroacetophenone	64.8%	31	Acetophenone	58.5%
18	4-Fluoroacetophenone	41.7%	32	Acetophenone	37.6%
19	2'-Chloroacetophenone	65.4%	33	2'-Chloroacetophenone	55.7%
20	2'-Chloroacetophenone	33.8%	34	2'-Chloroacetophenone	31.9%
21	4'-Chloroacetophenone	56.6%	35	Pinacolone	49.3%
22	4'-Chloroacetophenone	32.3%	36	Cyclohexyl methyl ketone	62.5%
23	2,5-Hexanedione	52.8%	37	Cyclohexyl methyl ketone	41.7%

^aAll reagents used in this study are commercial reagents.

Table S2. Key ^{13}C NMR data (δ) for diastereoisomers.^a

compound	4'	5'	6'
11	68.7, CH	82.9, CH	75.1, CH
12	69.7, CH	80.8, CH	75.9, CH
13	68.8, CH	82.1, CH	75.0, CH)
14	69.4, CH	80.9, CH	75.5, CH
15	69.1, CH	81.6, CH	76.5, CH
16	69.4, CH	82.9, CH	75.7, CH
17	69.0, CH	81.7, CH	76.5, CH
18	69.2, CH	82.9, CH	75.8, CH
19	69.0, CH	81.6, CH	76.3, CH
20	69.2, CH	82.9, CH	75.5, CH
21	69.0, CH	81.7, CH	76.5, CH
22	69.2, CH	82.9, CH	75.9, CH
23	68.8, CH	82.3, CH	75.4, CH
24	69.0, CH	81.9, CH	77.4, CH
25	68.6, CH	82.1, CH	75.5, CH
26	69.1, CH	82.1, CH	76.0, CH
29	68.2, CH	81.8, CH	75.6, CH
30	68.5, CH	81.4, CH	75.9, CH
31	68.4, CH	81.0, CH	76.6, CH
32	68.8, CH	82.4, CH	75.9, CH
33	68.3, CH	81.0, CH	76.4, CH
34	68.6, CH	82.4, CH	75.7, CH
36	68.2, CH	81.6, CH	75.2, CH
37	68.8, CH	80.4, CH	75.8, CH

^a Solvent: CDCl_3 .

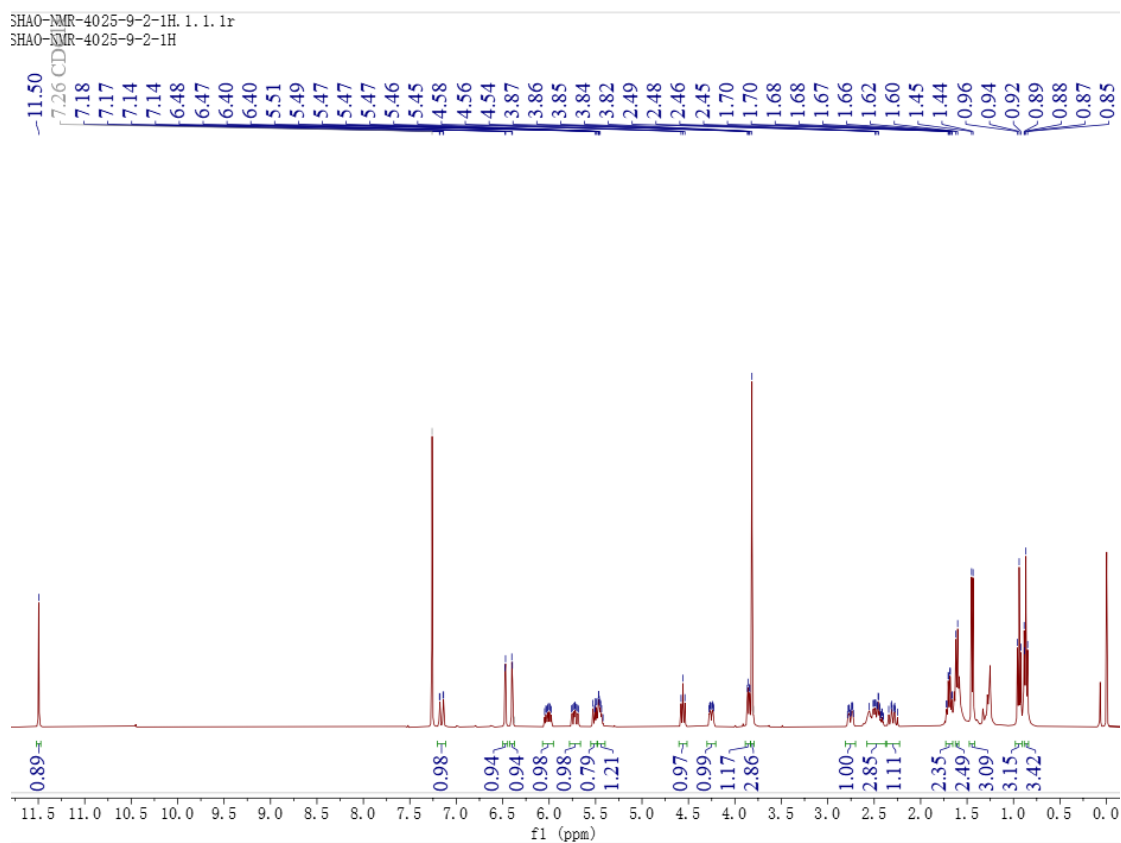


Figure S1. ^1H NMR (400 MHz, Chloroform-*d*) spectrum of compound **10**.

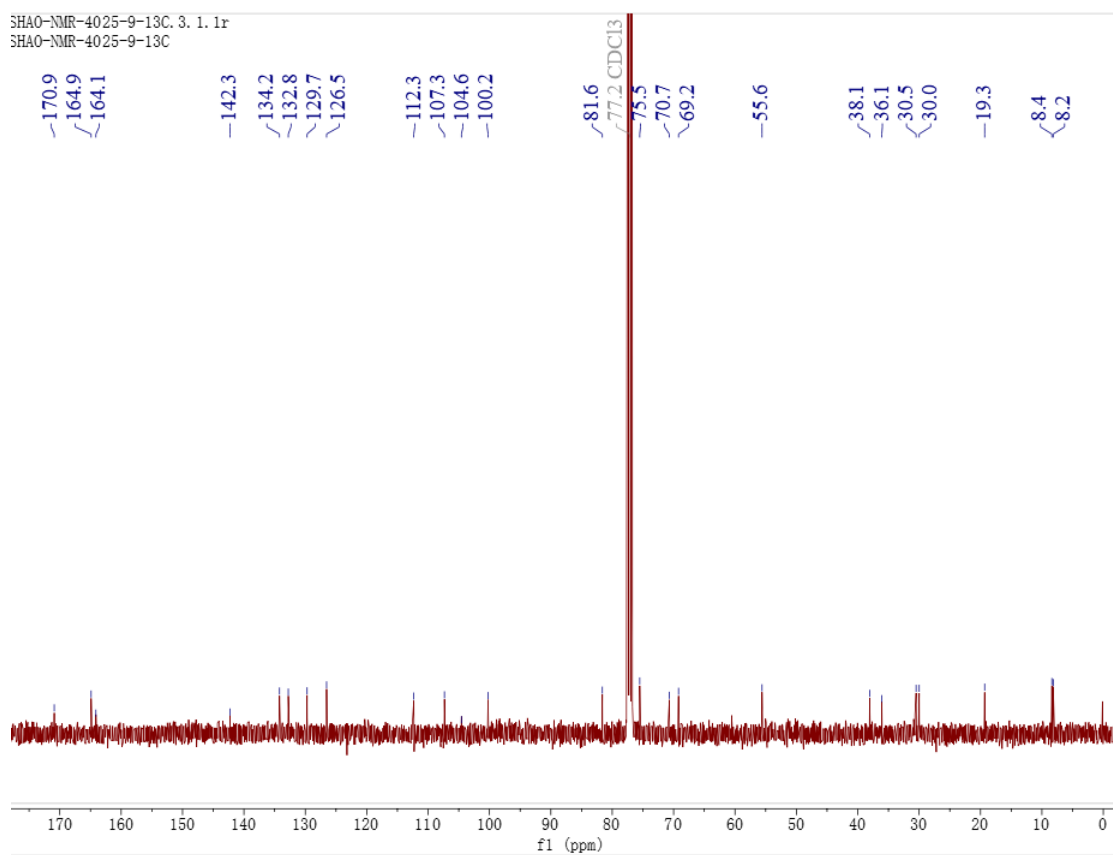


Figure S2. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **10**.

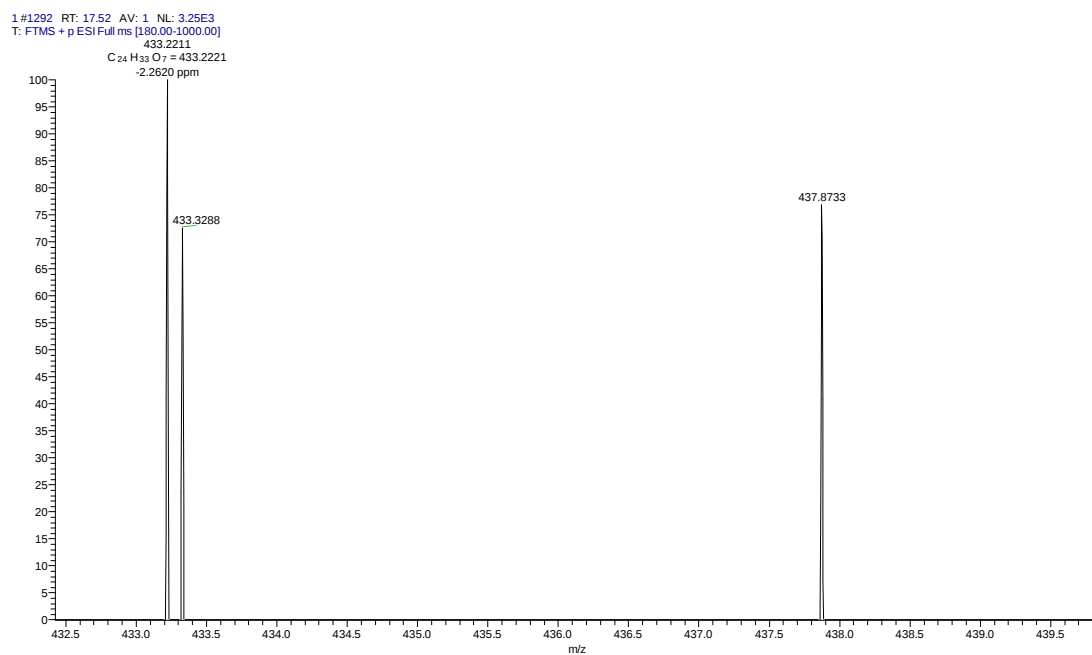


Figure S3. HR-ESI-MS spectrum of compound 10.

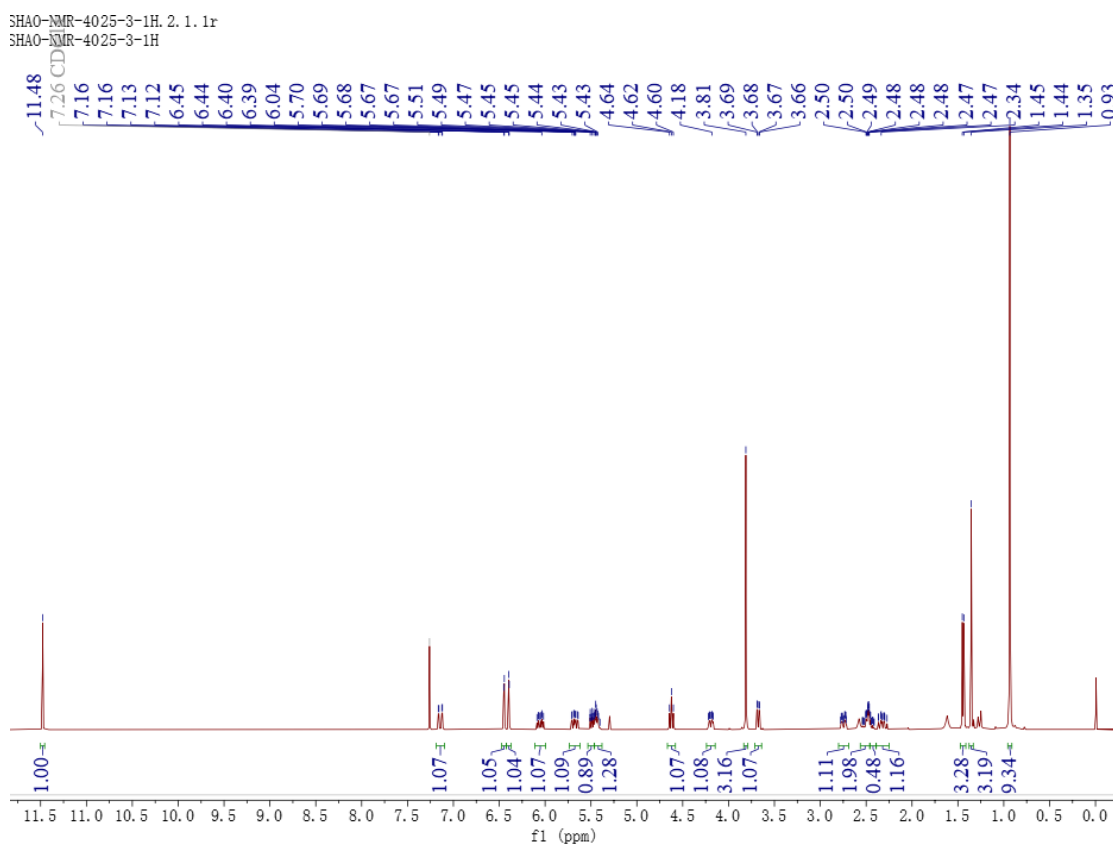


Figure S4. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 11.

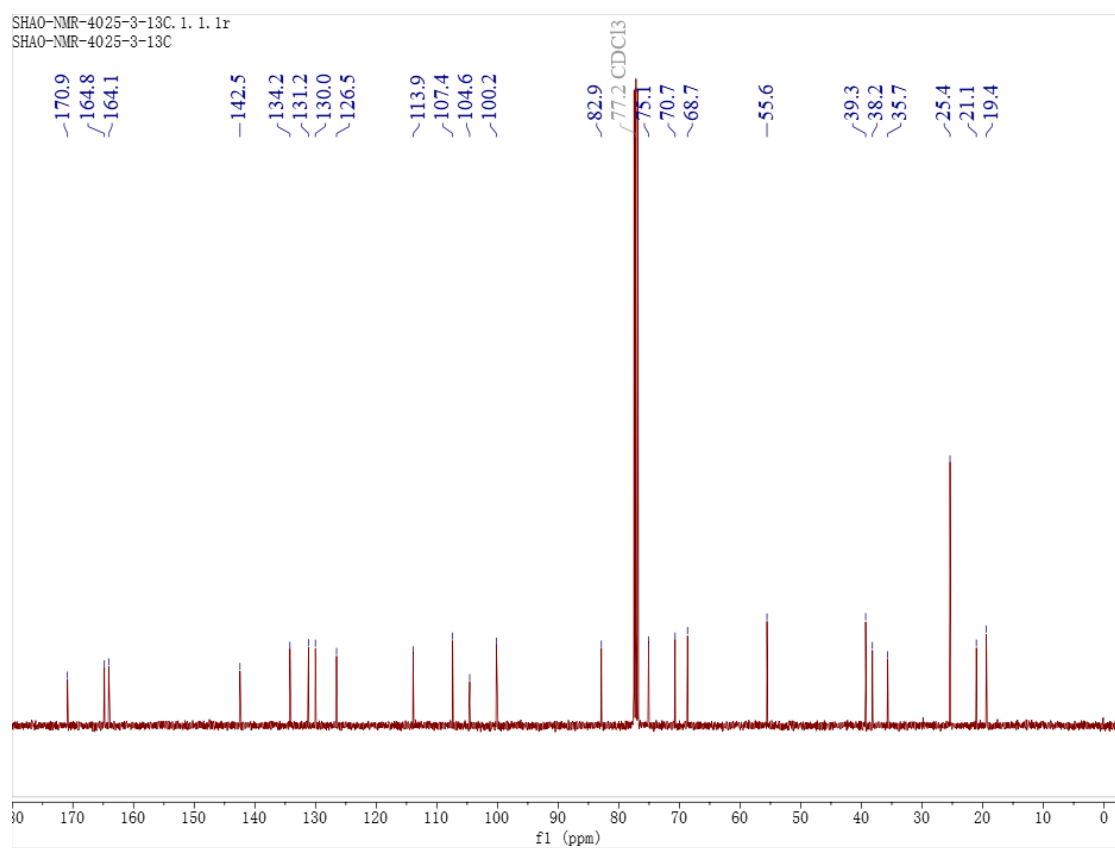


Figure S5. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound **11**.

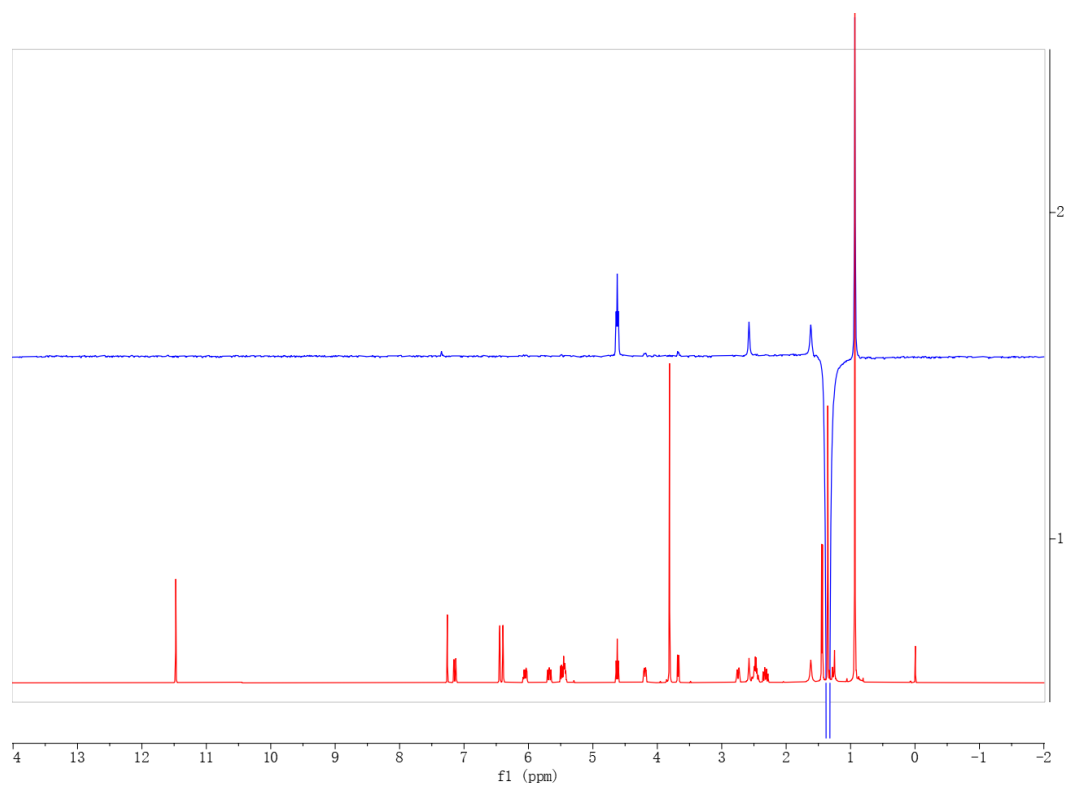


Figure S6. 1D NOE spectrum of compound **11**

1 #1376 RT: 18.64 AV: 1 NL: 1.14E4
T: FTMS + p ESI Full ms [180.00-1000.00]

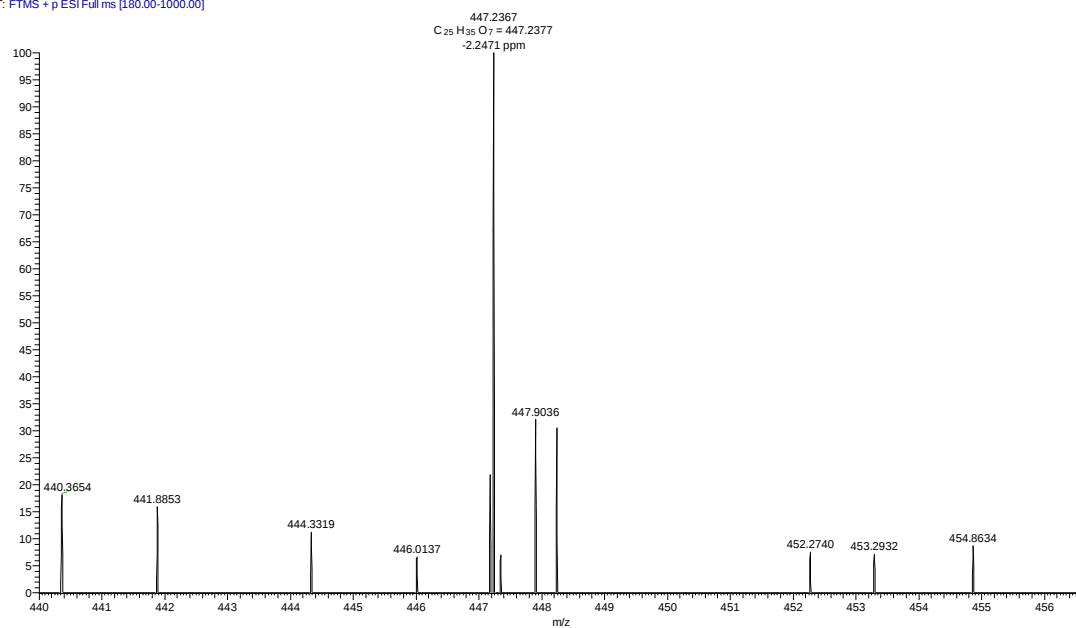


Figure S7. HR-ESI-MS spectrum of compound 11.

SHAO-NMR-4025-10-2-1H. 1. 1. 1r
SHAO-NMR-4025-10-2-1H

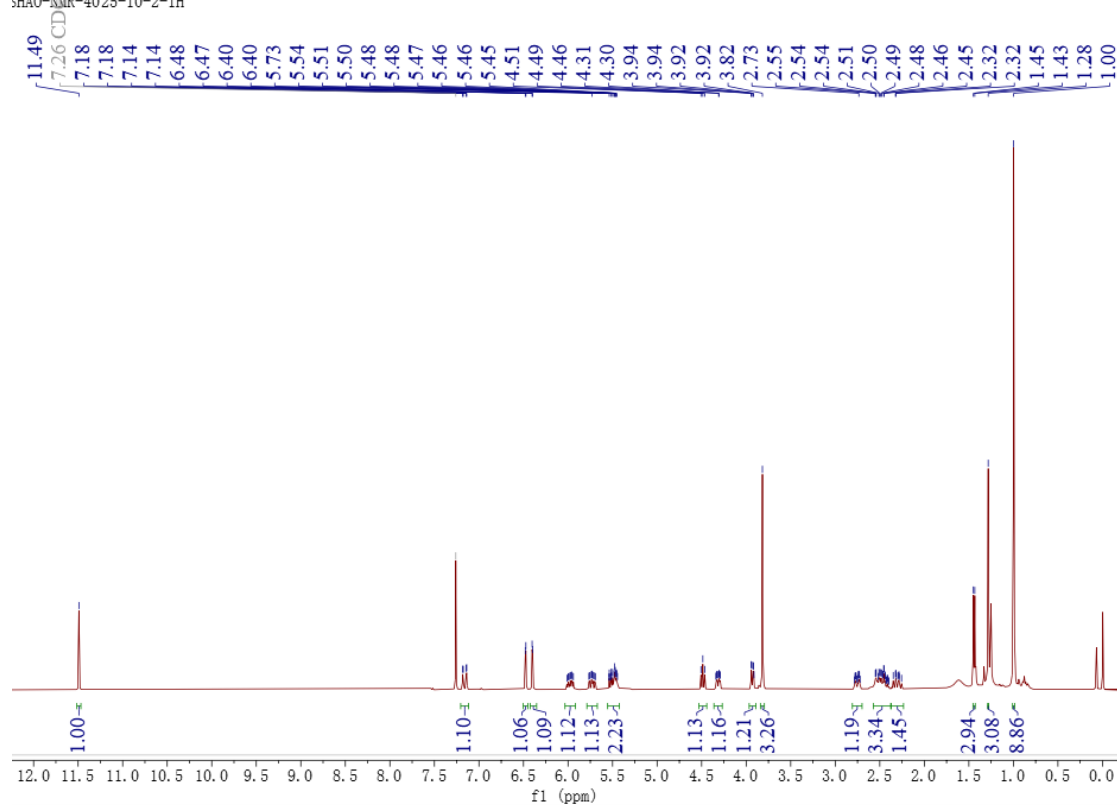


Figure S8. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 12.

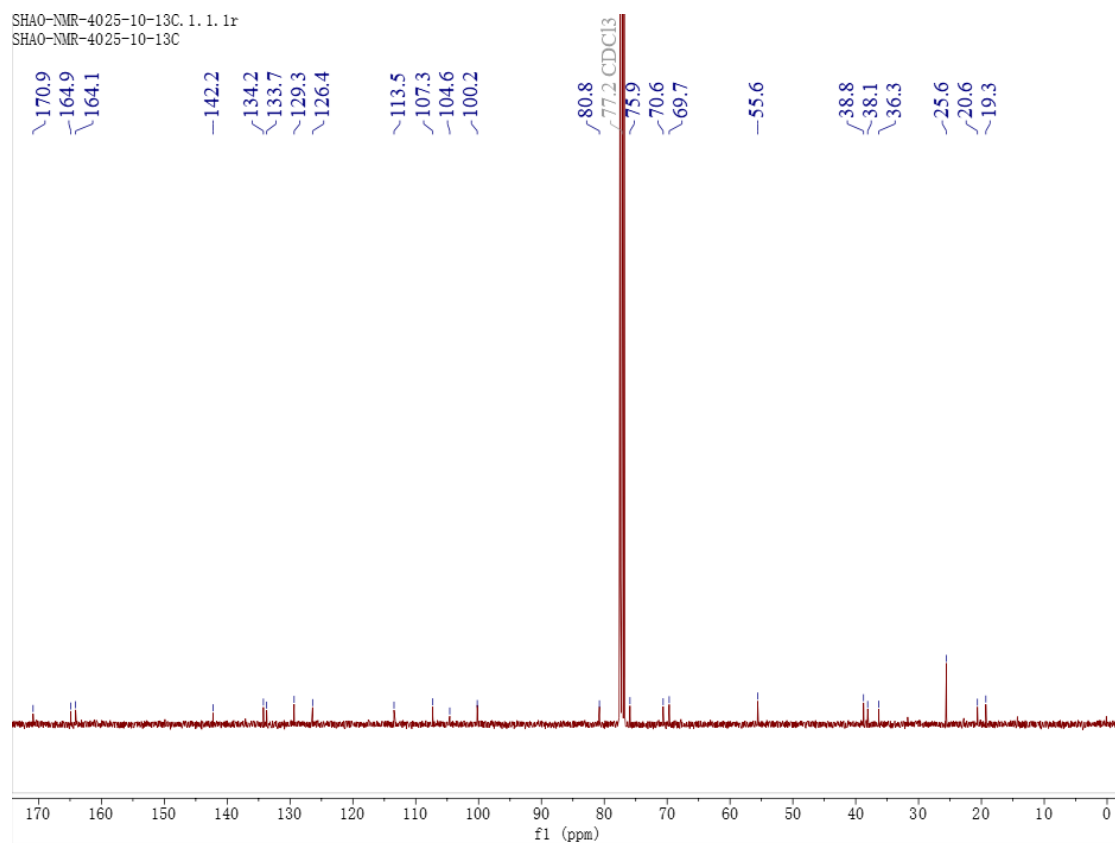


Figure S9. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **12**.

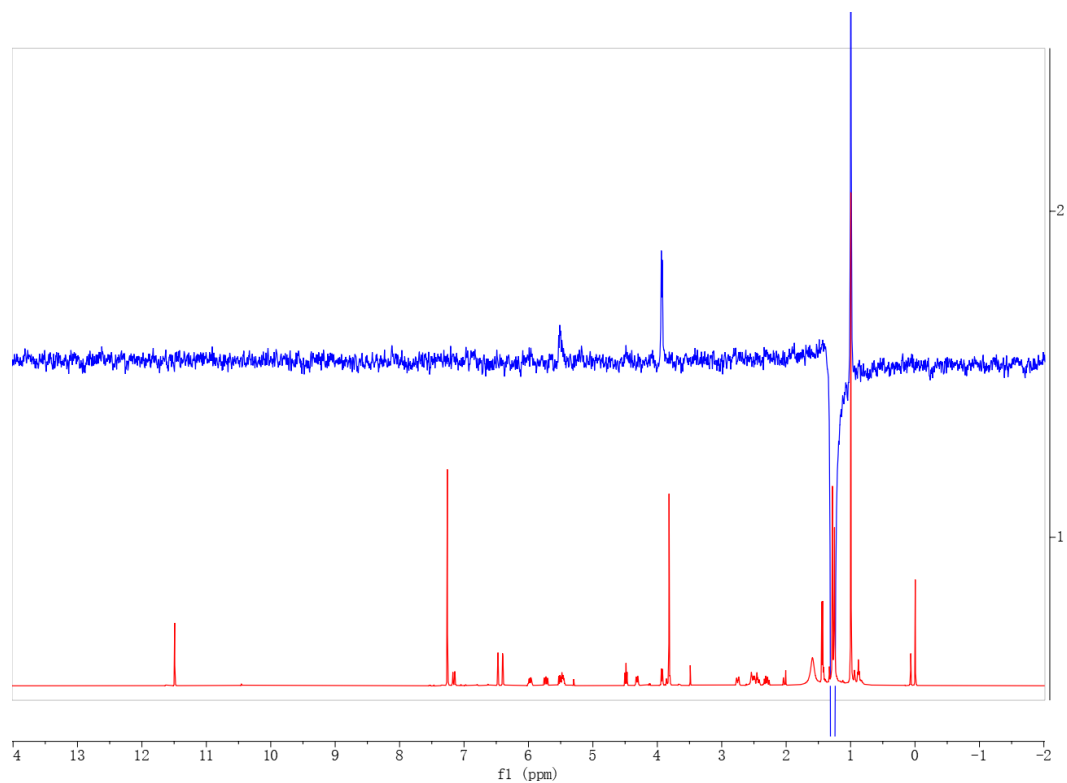


Figure S10. 1D NOE spectrum of compound **12**.

2 #1323 RT: 18.50 AV: 1 NL: 8.78E3
T: FTMS + p ESI Full ms [180.00-1000.00]

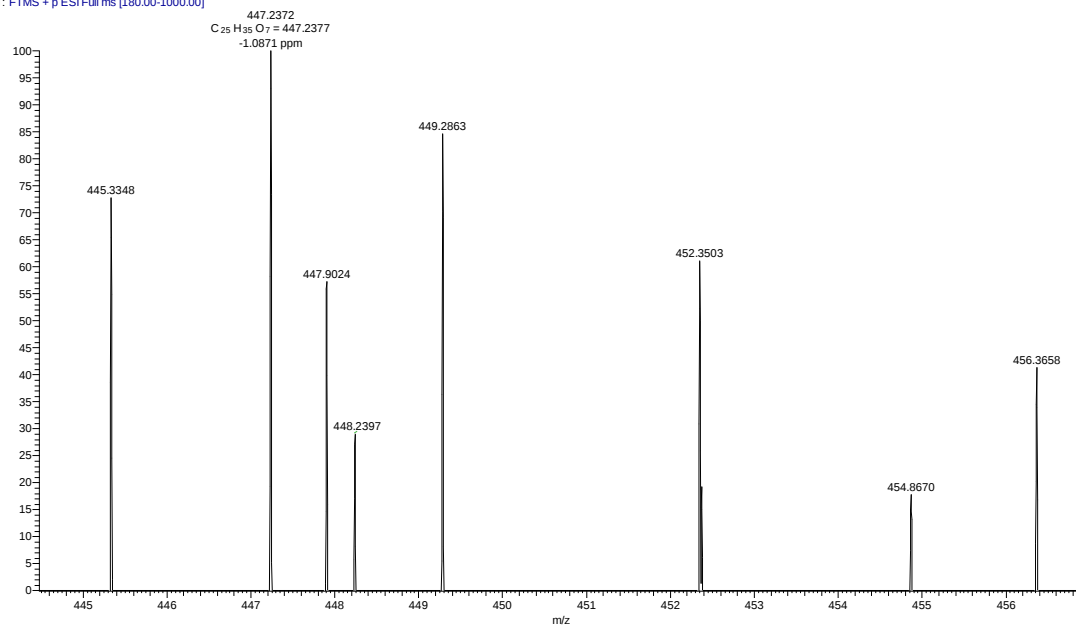


Figure S11. HR-ESI-MS spectrum of compound 12.

SHAO-NMR-4025-4-1H. 1. 1. 1r
SHAO-NMR-4025-4-1H

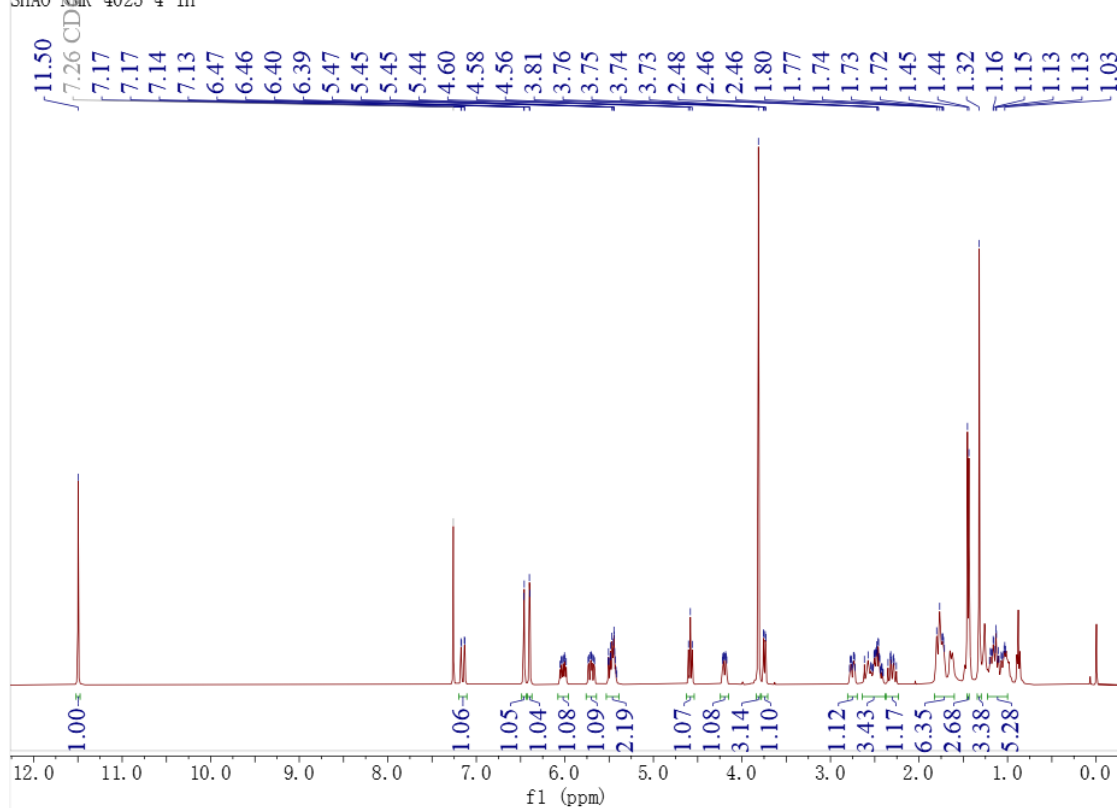


Figure S12. 1H NMR (400 MHz, Chloroform-*d*) spectrum of compound 13.

SHA0-NMR-4025-4-13C. 3. 1. 1r
SHA0-NMR-4025-4-13C

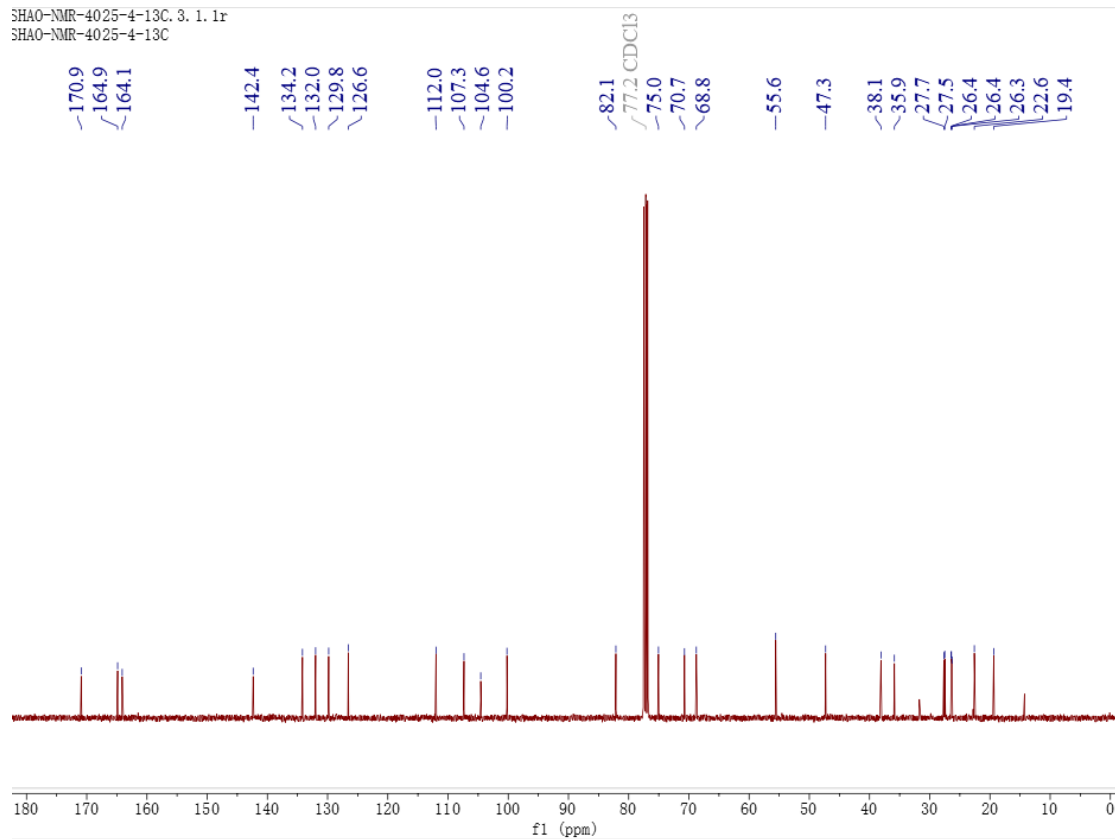


Figure S13. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound 13.

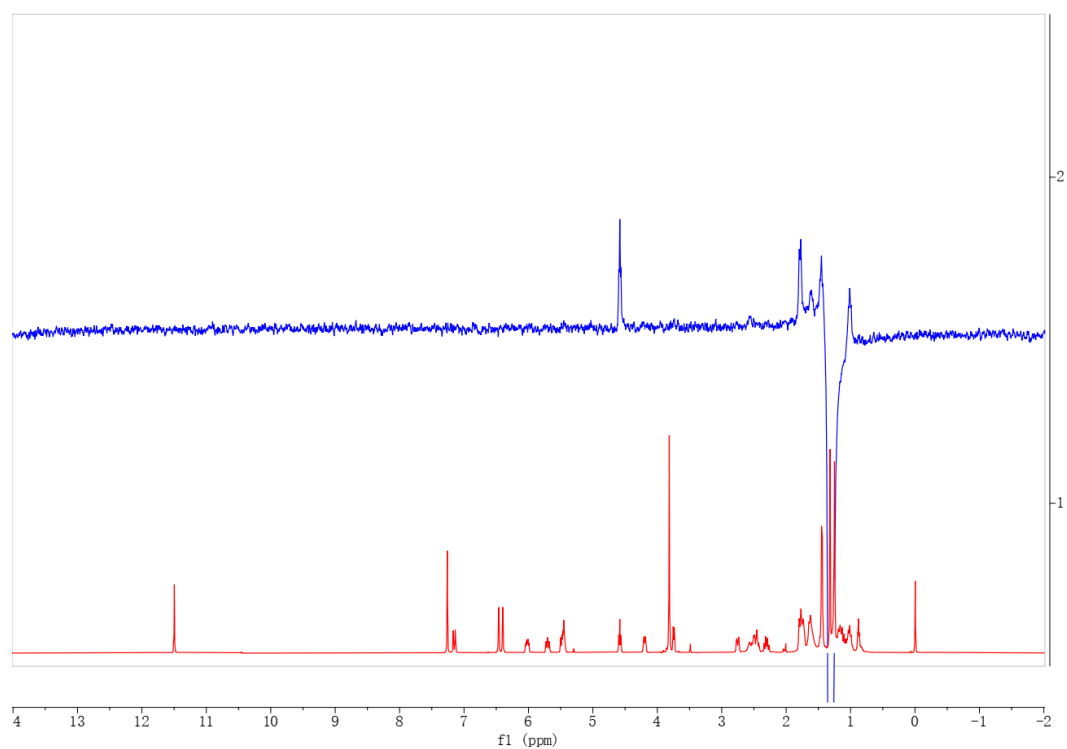


Figure S14. 1D NOE spectrum of compound 13

1 #1459 RT: 19.80 AV: 1 NL: 3.88E3
T: FTMS + p ESI Full ms [180.00-1000.00]

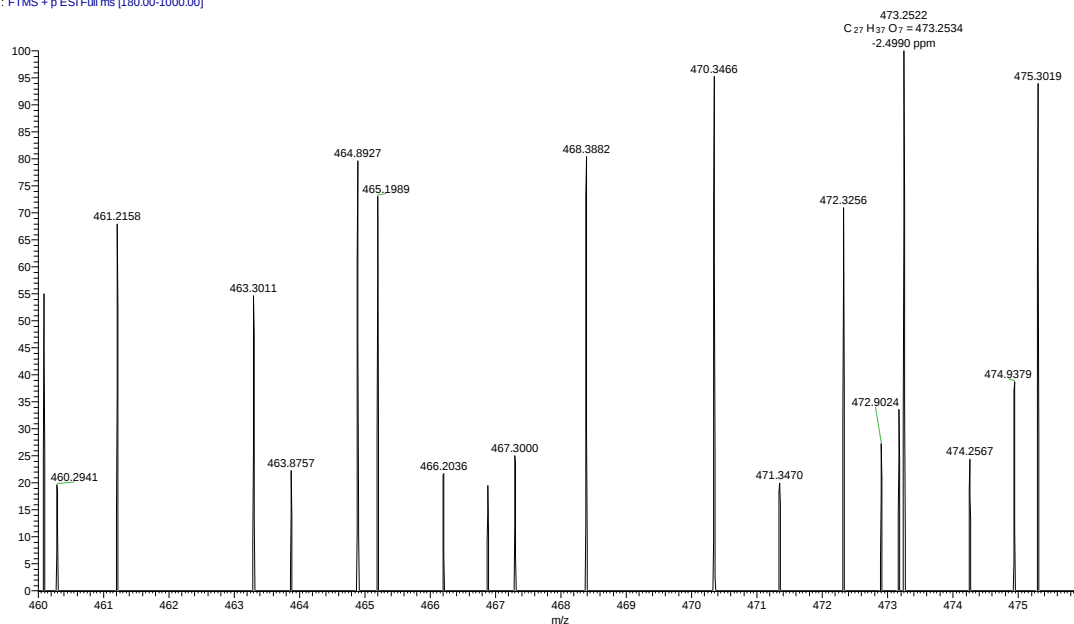


Figure S15. HR-ESI-MS spectrum of compound 13.

SHAO-NMR-4025-7-1H. 2. 1. 1r
SHAO-NMR-4025-7-1H

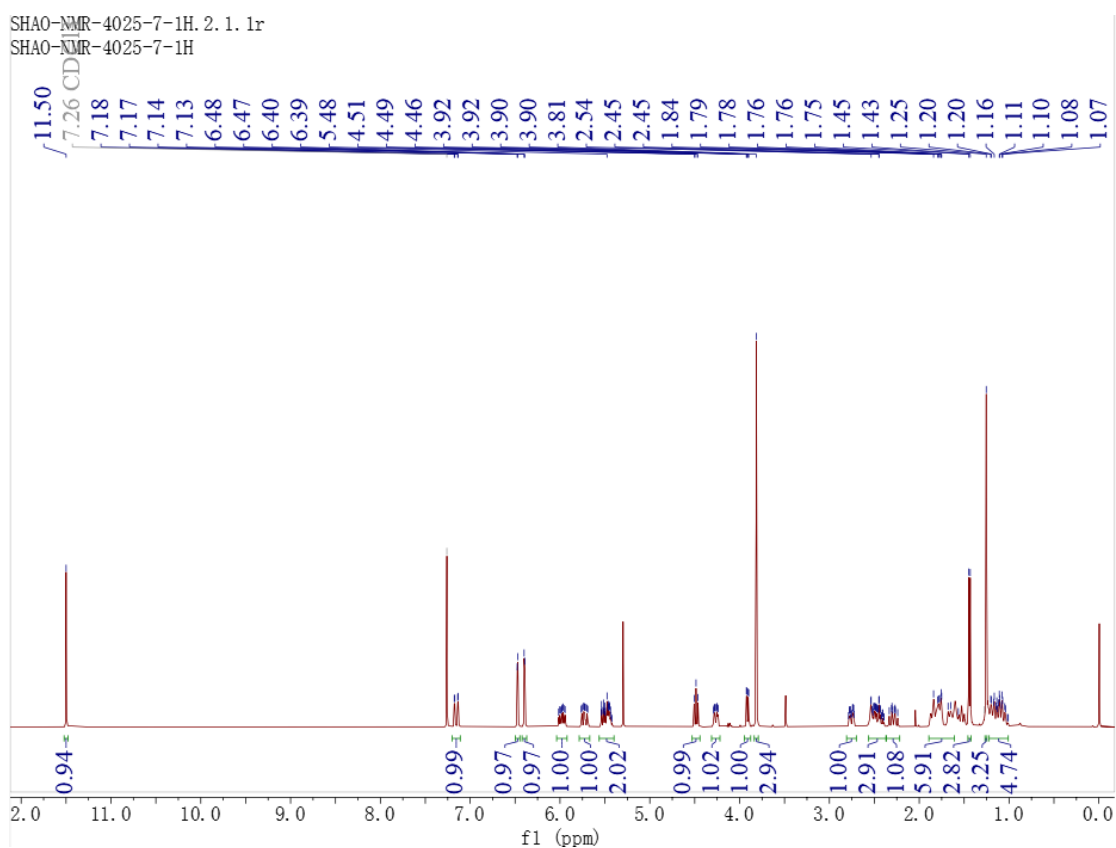


Figure S16. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 14.

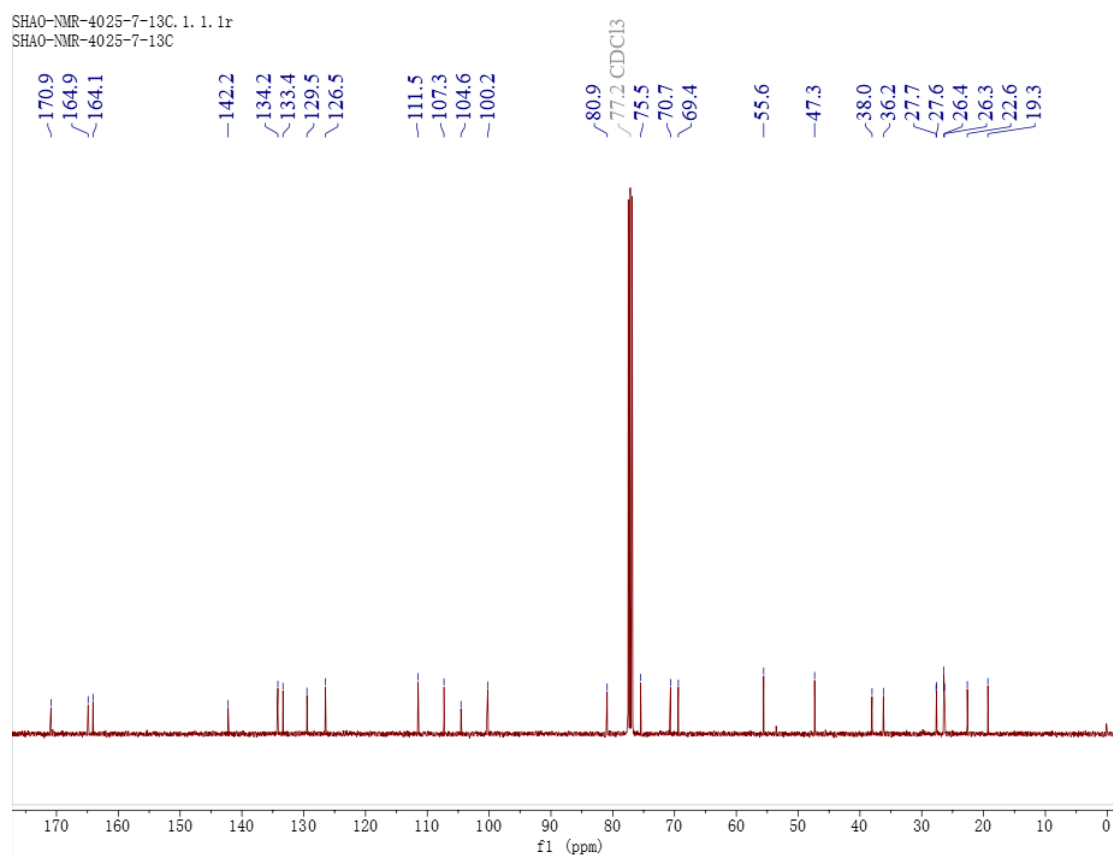


Figure S17. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound **14**.

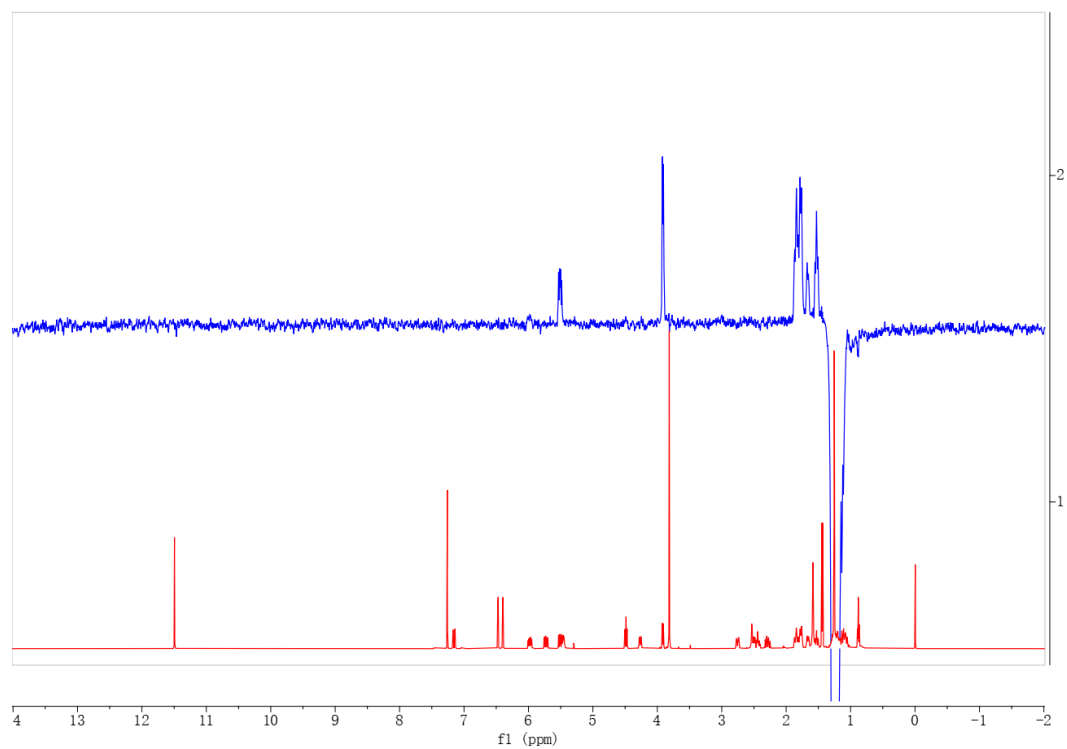


Figure S18. 1D NOE spectrum of compound **14**

Z #1412 RT: 19.58 AV: 1 NL: 5.59E3
T: FTMS + p ESI Full ms [180.00-1000.00]

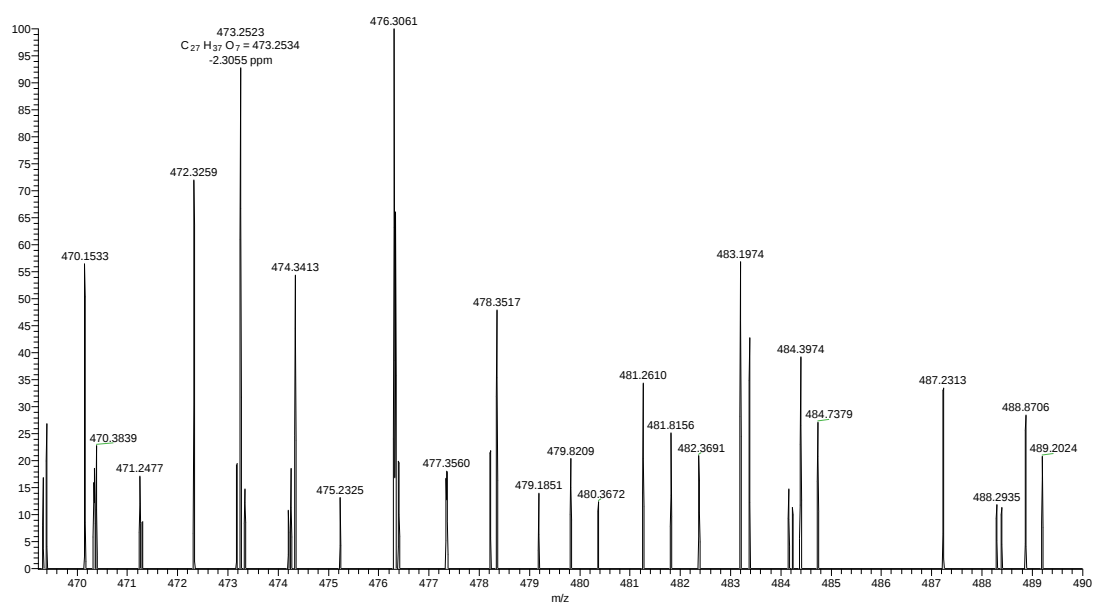


Figure S19. HR-ESI-MS spectrum of compound 14.

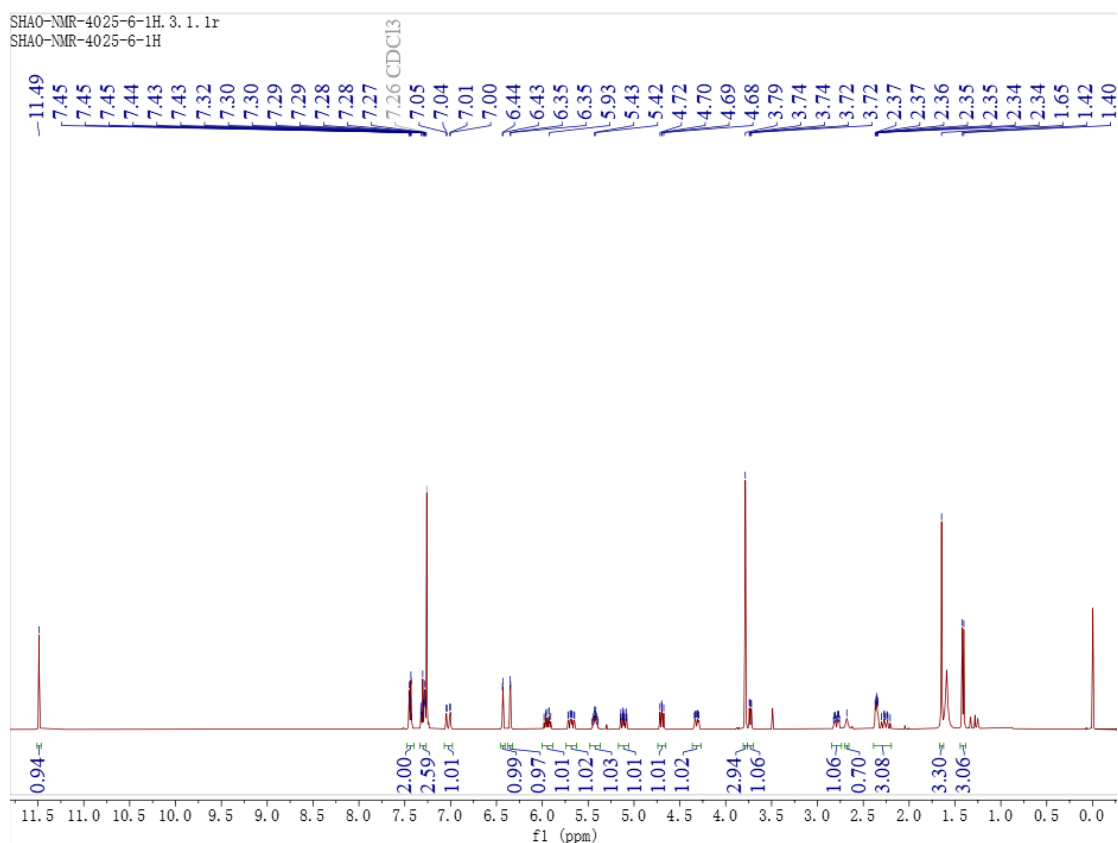


Figure S20. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 15.

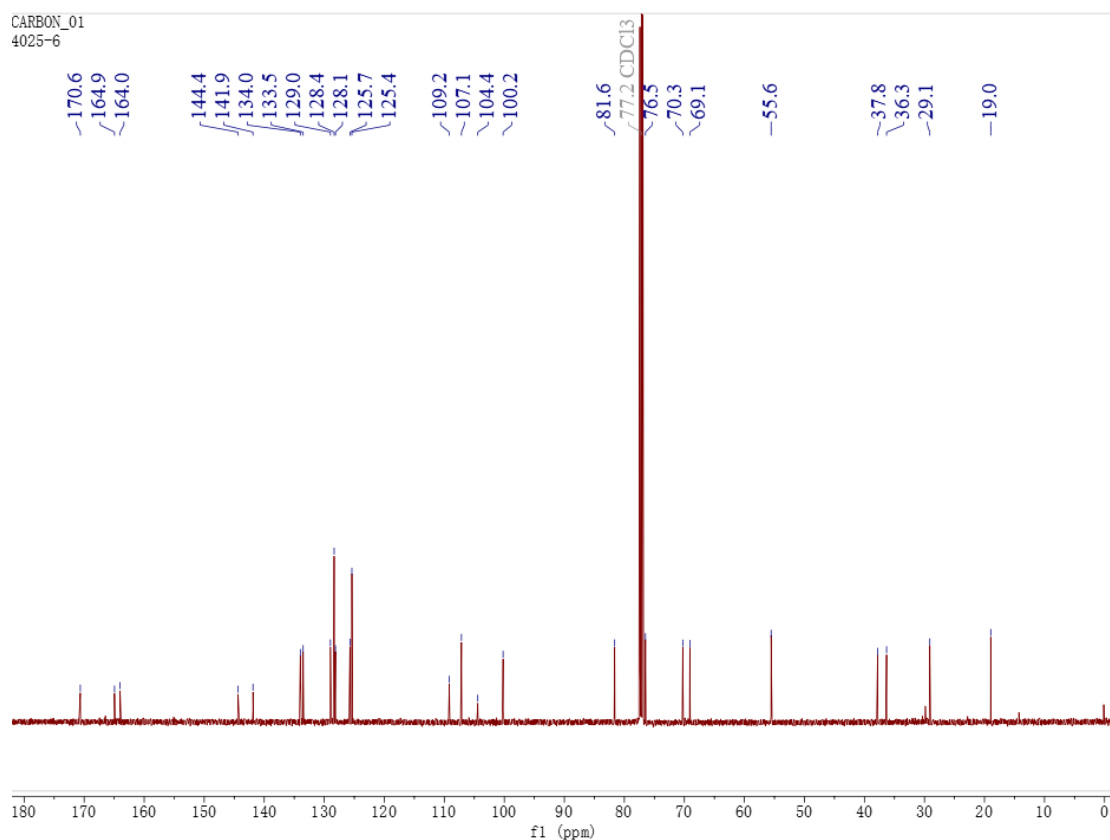


Figure S21. ^{13}C NMR (125MHz, Chloroform-*d*) spectrum of compound **15**.

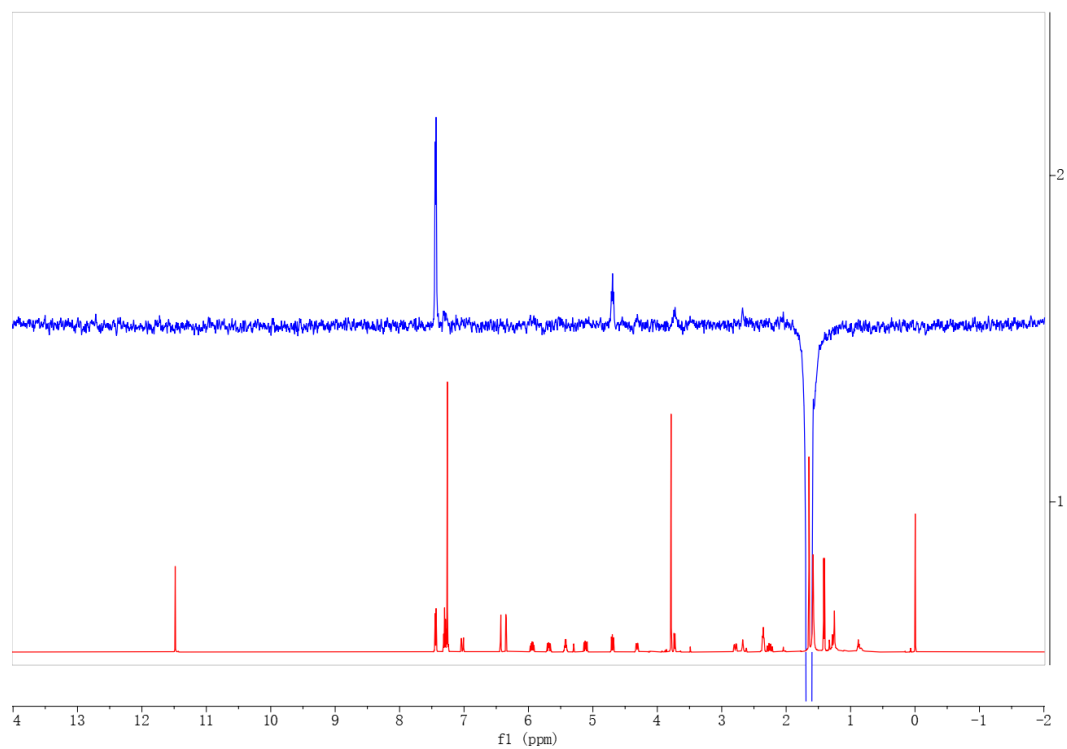


Figure S22. 1D NOE spectrum of compound **15**

3 #1511 RT: 17.89 AV: 1 NL: 3.74E5
T: FTMS + p ESI Full ms [180.00-1000.00]

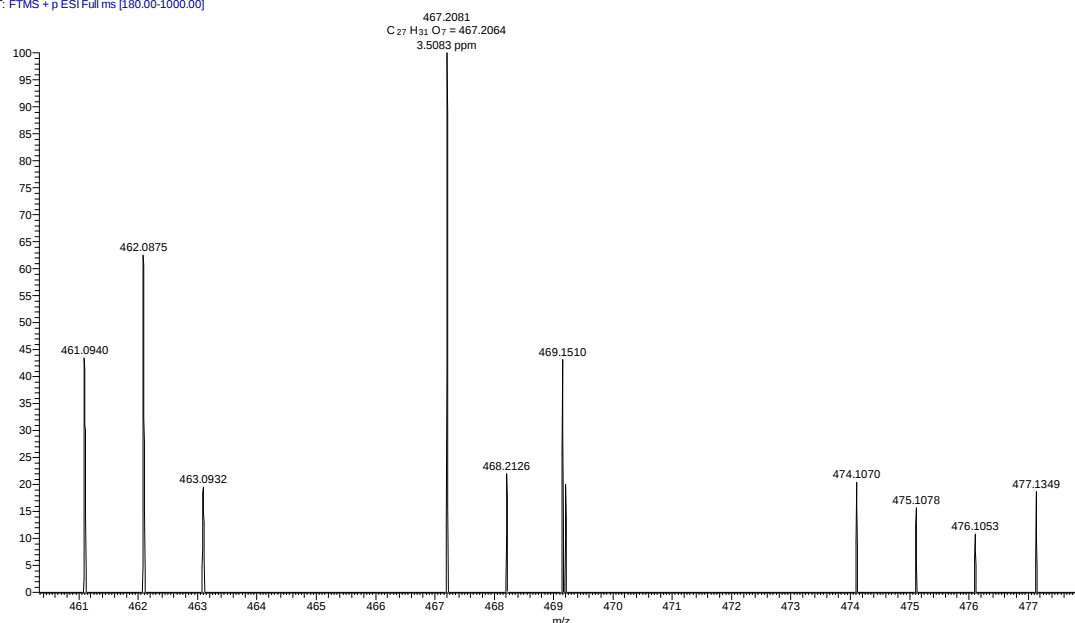


Figure S23. HR-ESI-MS spectrum of compound 15.

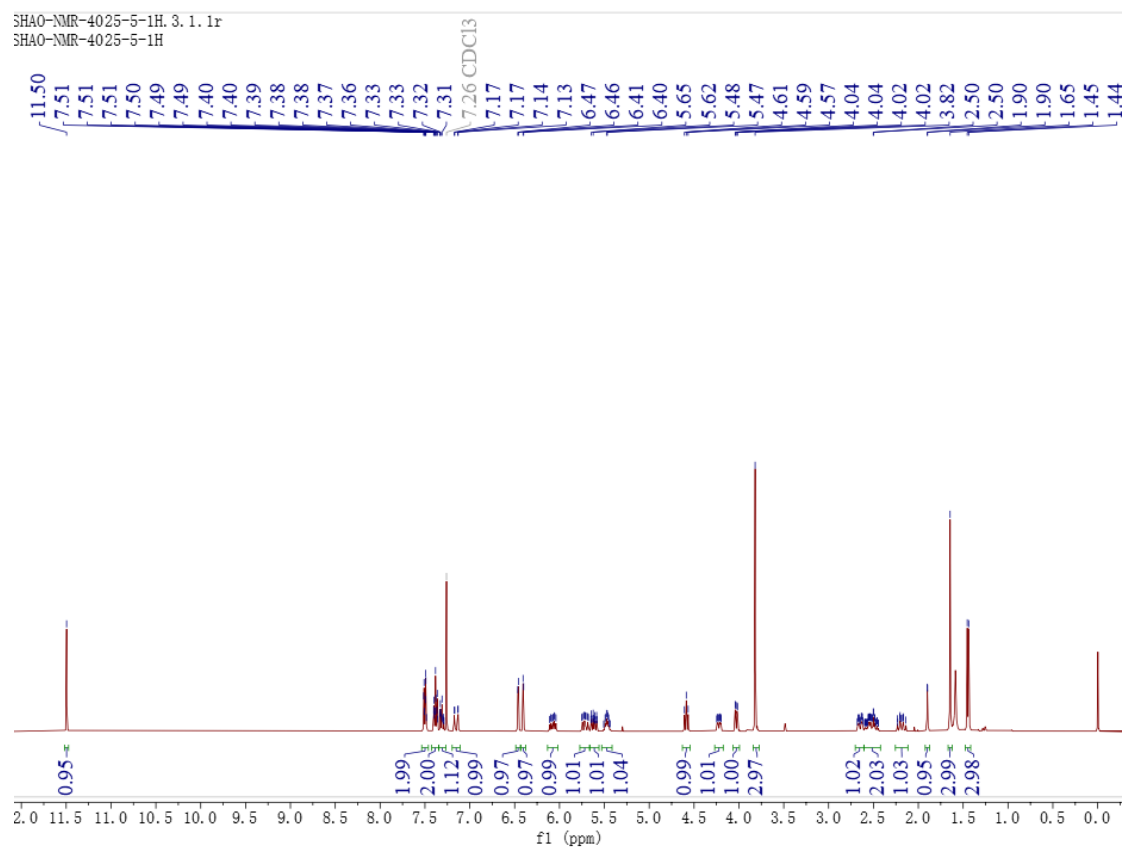


Figure S24. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 16.

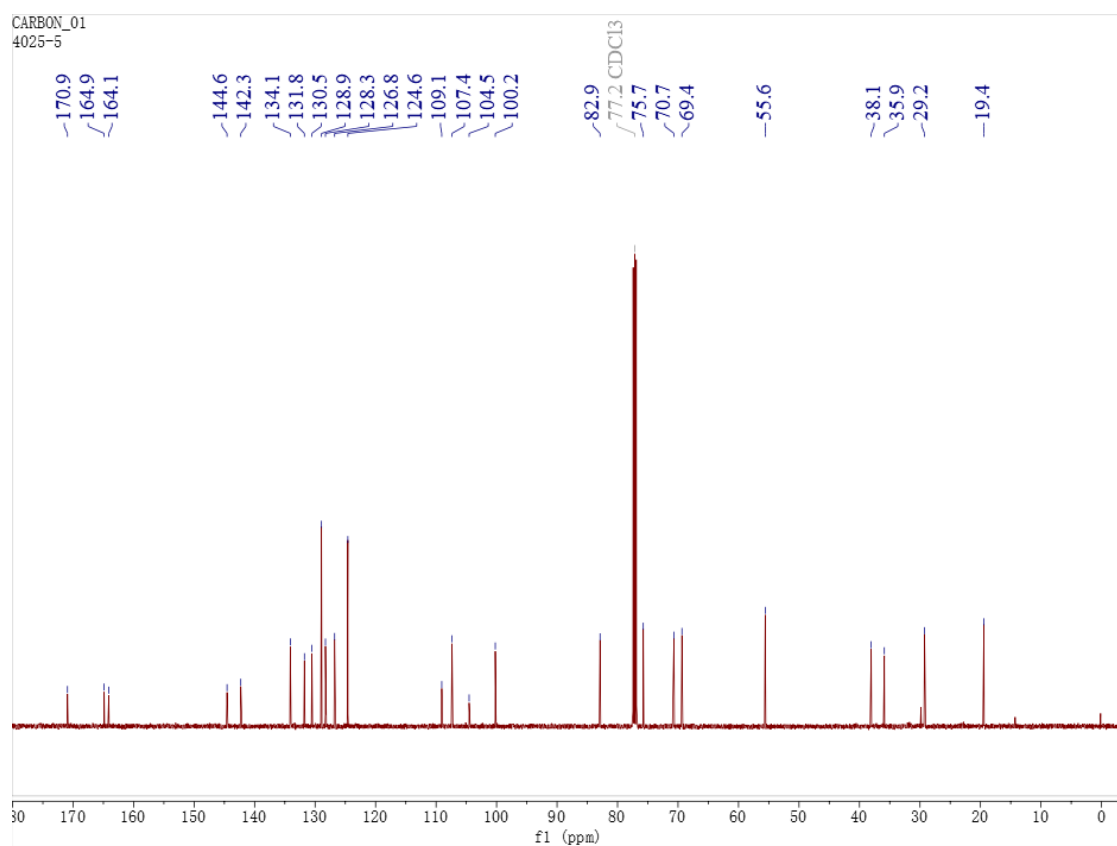


Figure S25. ¹³C NMR (125 MHz, Chloroform-*d*) spectrum of compound 16.

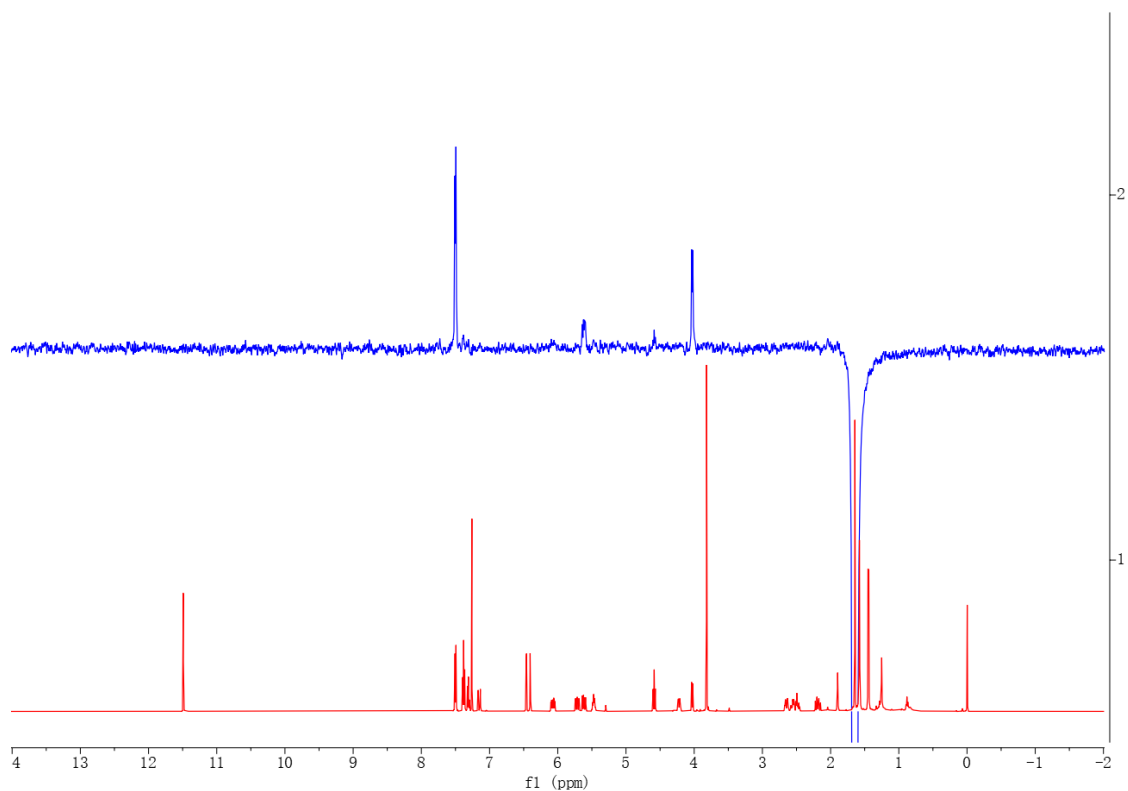


Figure S26. 1D NOE spectrum of compound 16

4 #1443 RT: 19.17 AV: 1 NL: 7.69E3
T: FTMS + p ESI Full ms [180.00-1000.00]

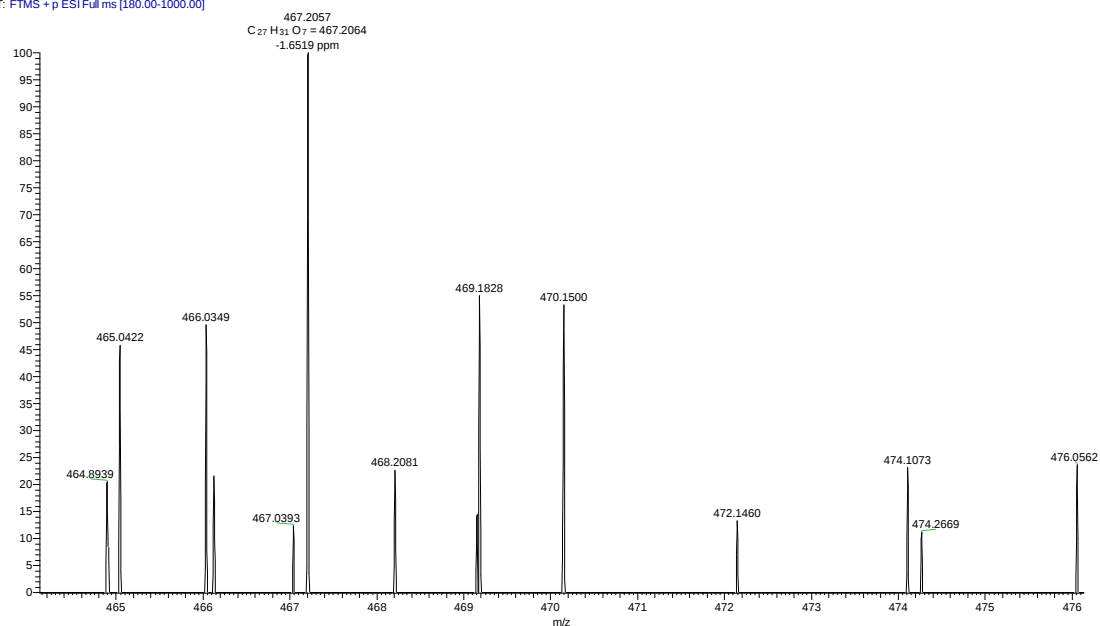


Figure S27. HR-ESI-MS spectrum of compound 16.

SHA0-NMR-4025-18-1H.r1. 1. 1r
SHA0-NMR-4025-18-1H

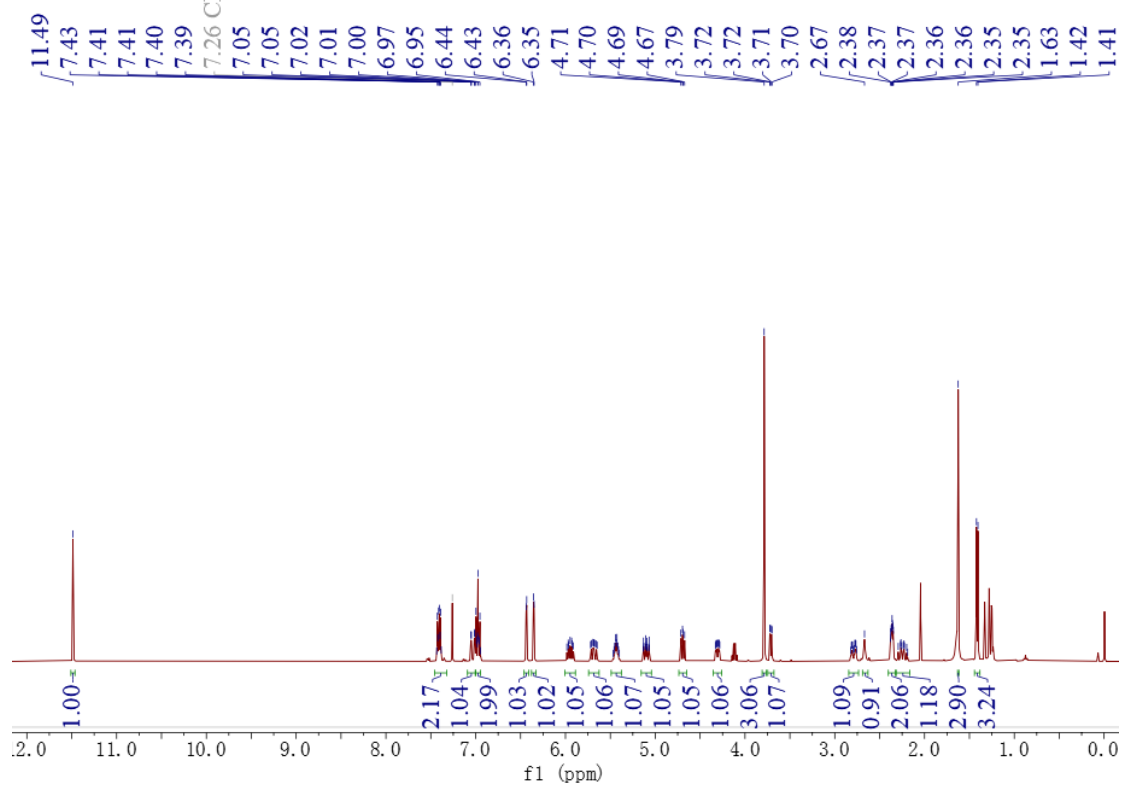


Figure S28. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 17.

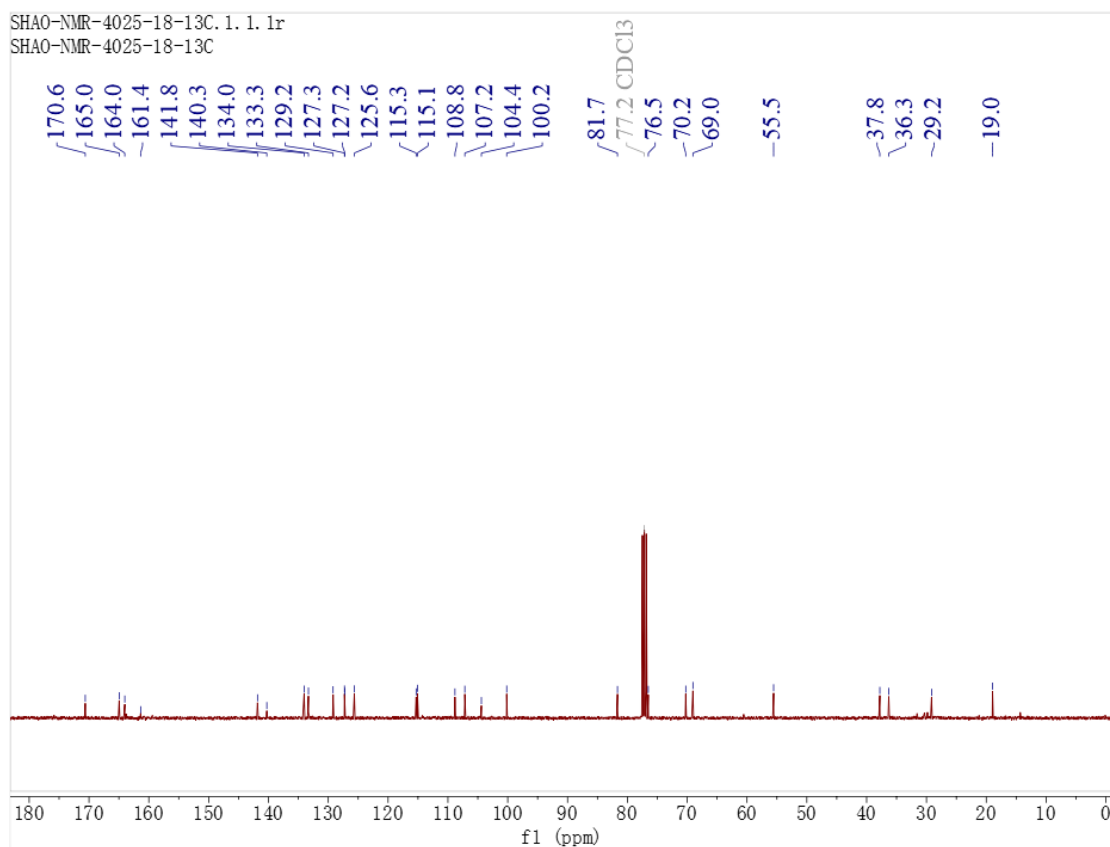


Figure S29. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound **17**.

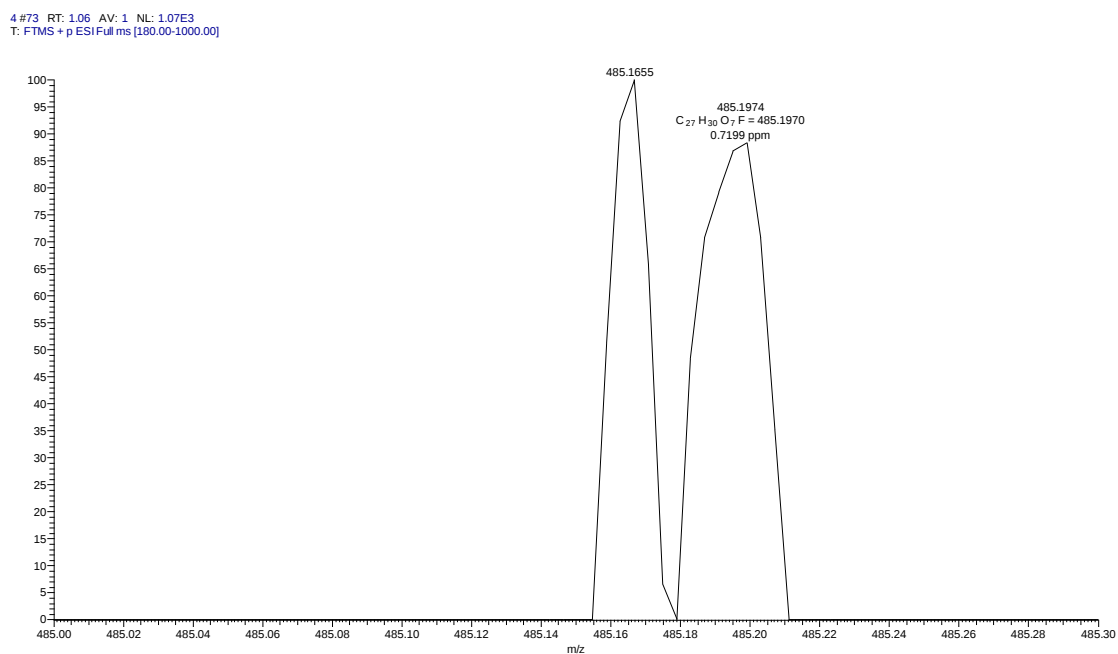


Figure S30. HR-ESI-MS spectrum of compound **17**.

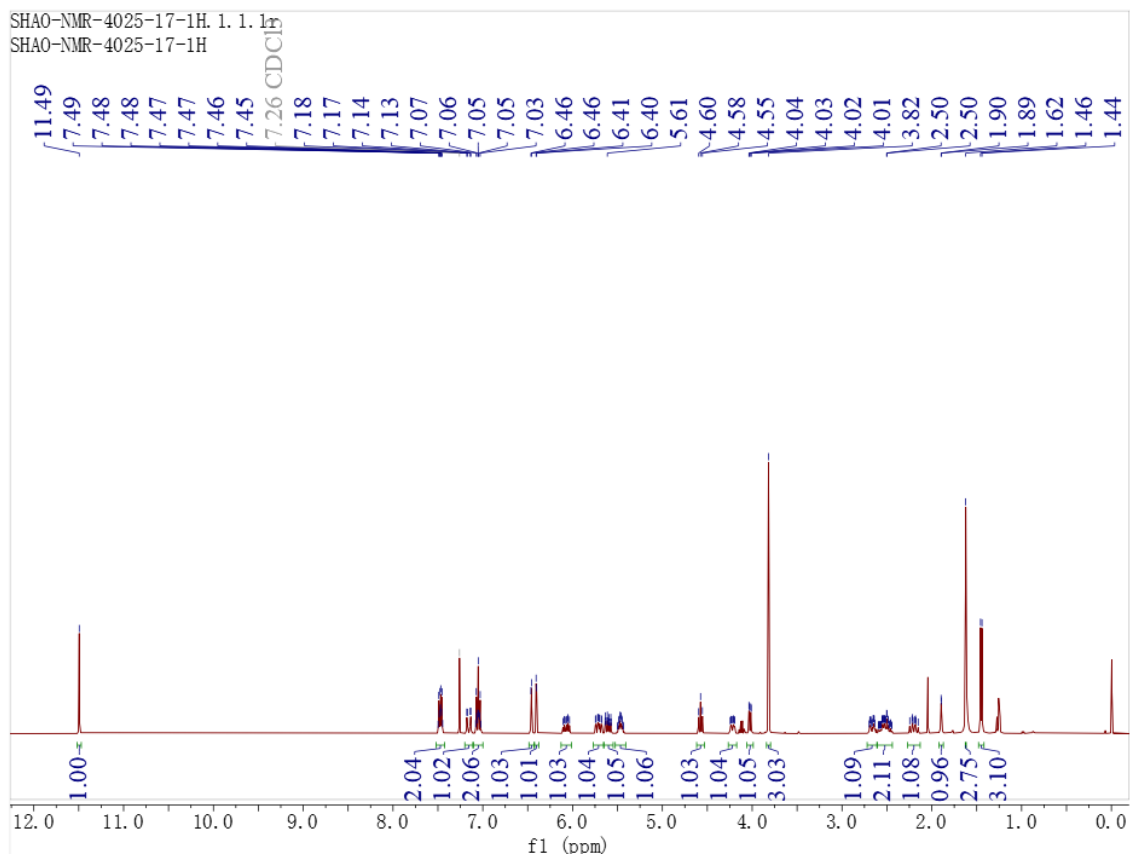


Figure S31. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 18.

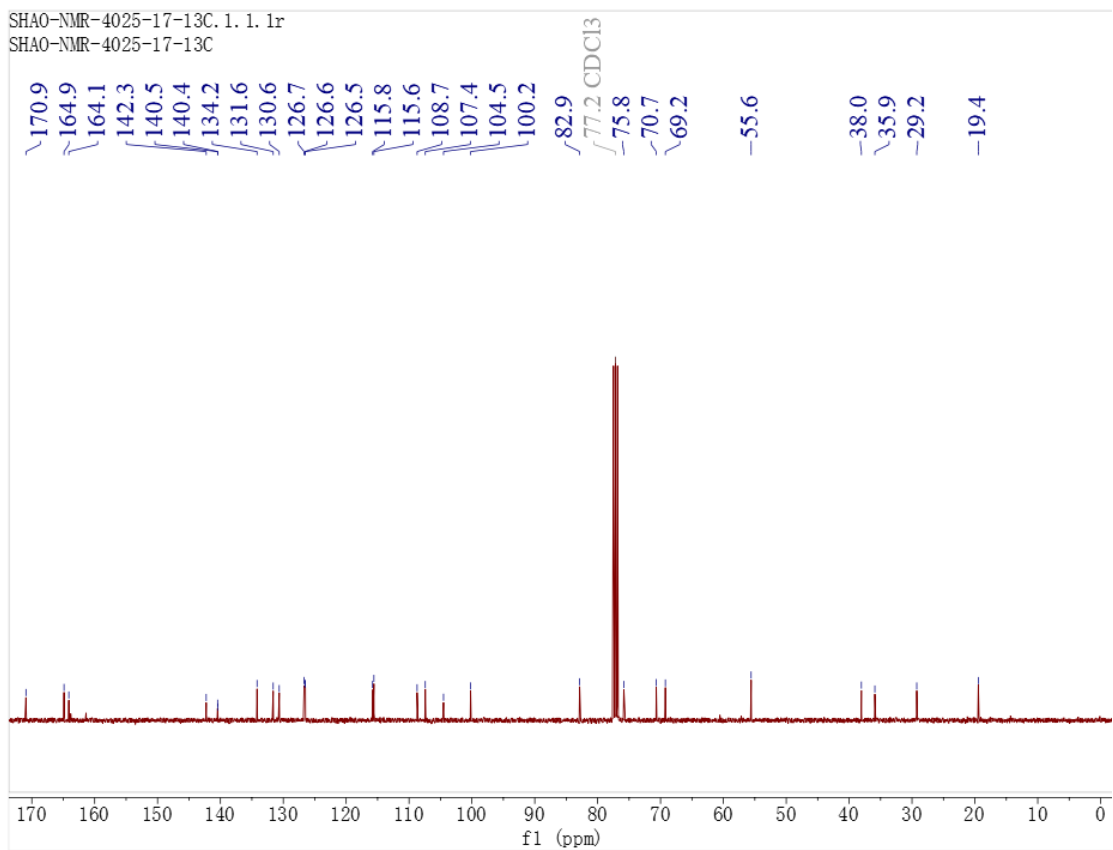


Figure S32. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound 18.

3 #355 RT: 5.30 AV: 1 NL: 6.61E2
T: FTMS + p ESI Full ms [180.00-1000.00]

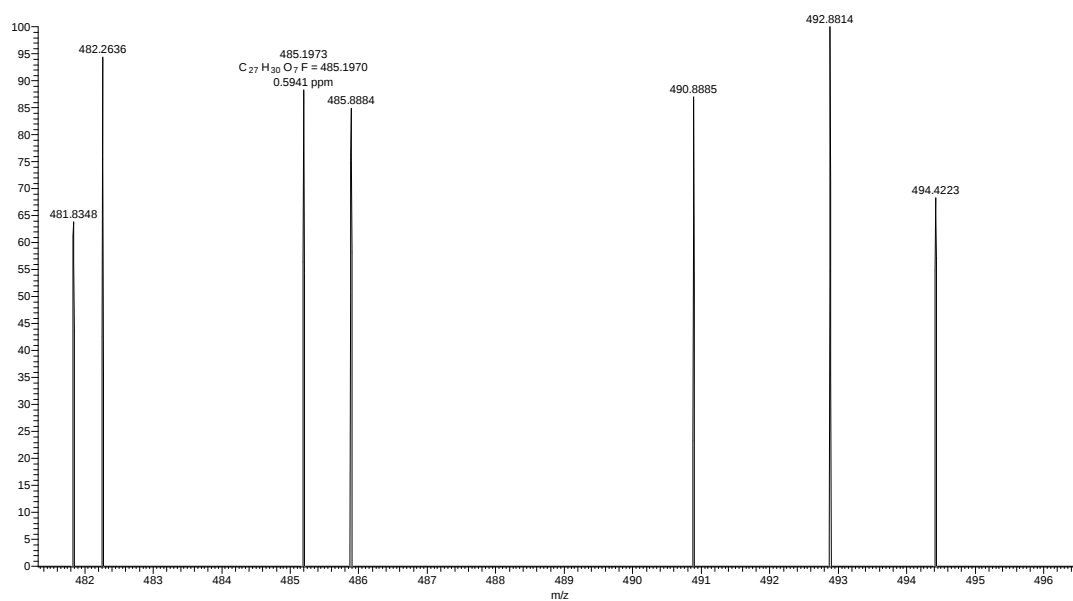


Figure S33. HR-ESI-MS spectrum of compound 18.

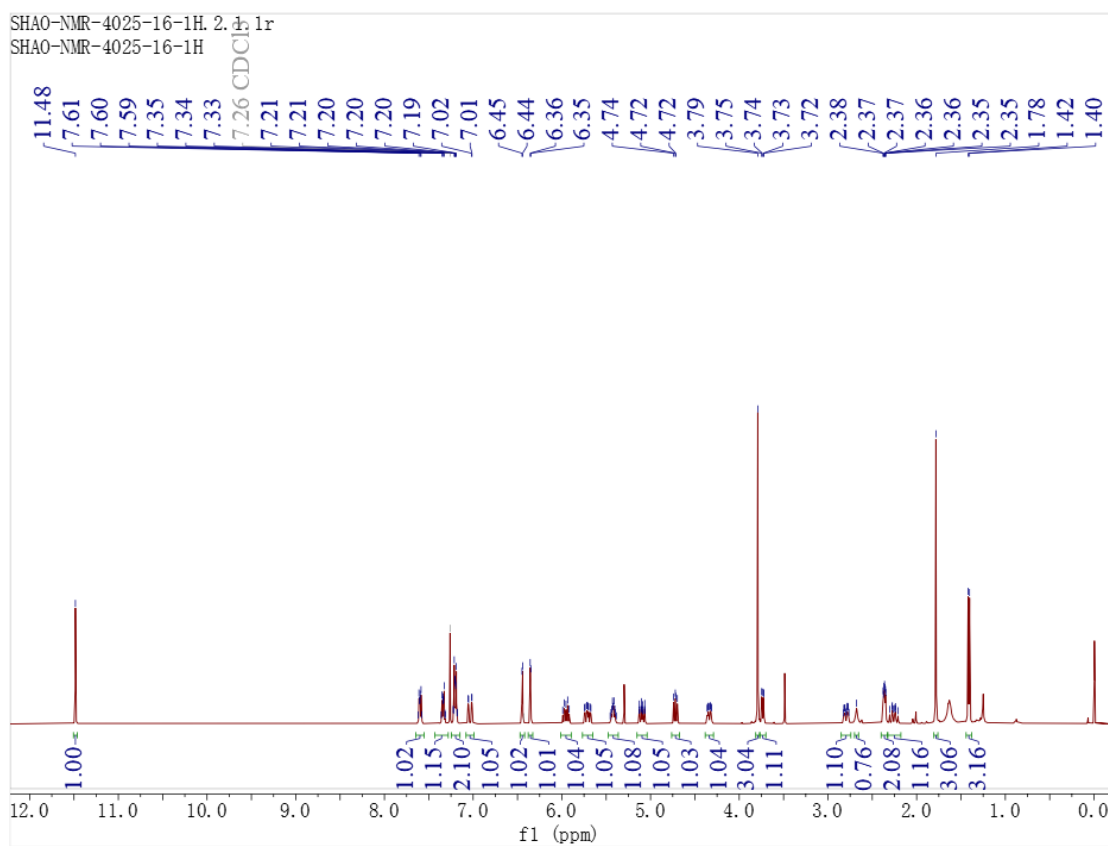


Figure S34. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 19.

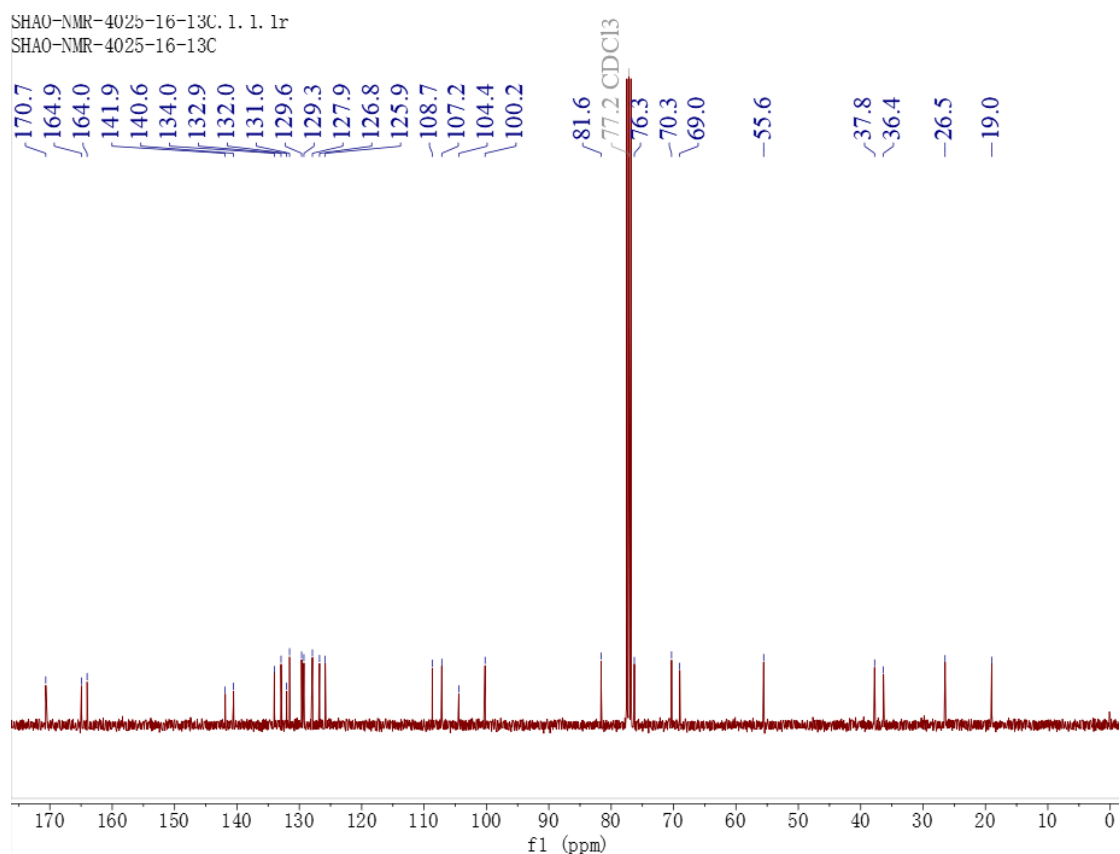


Figure S35. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **19**.

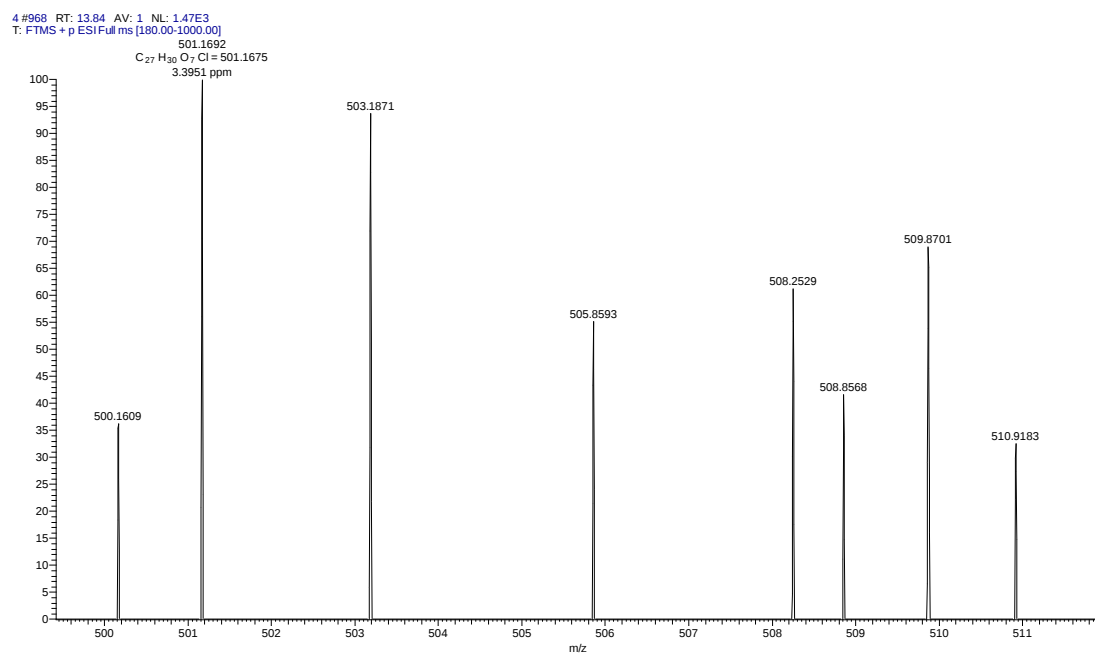


Figure S36. HR-ESI-MS spectrum of compound **19**.

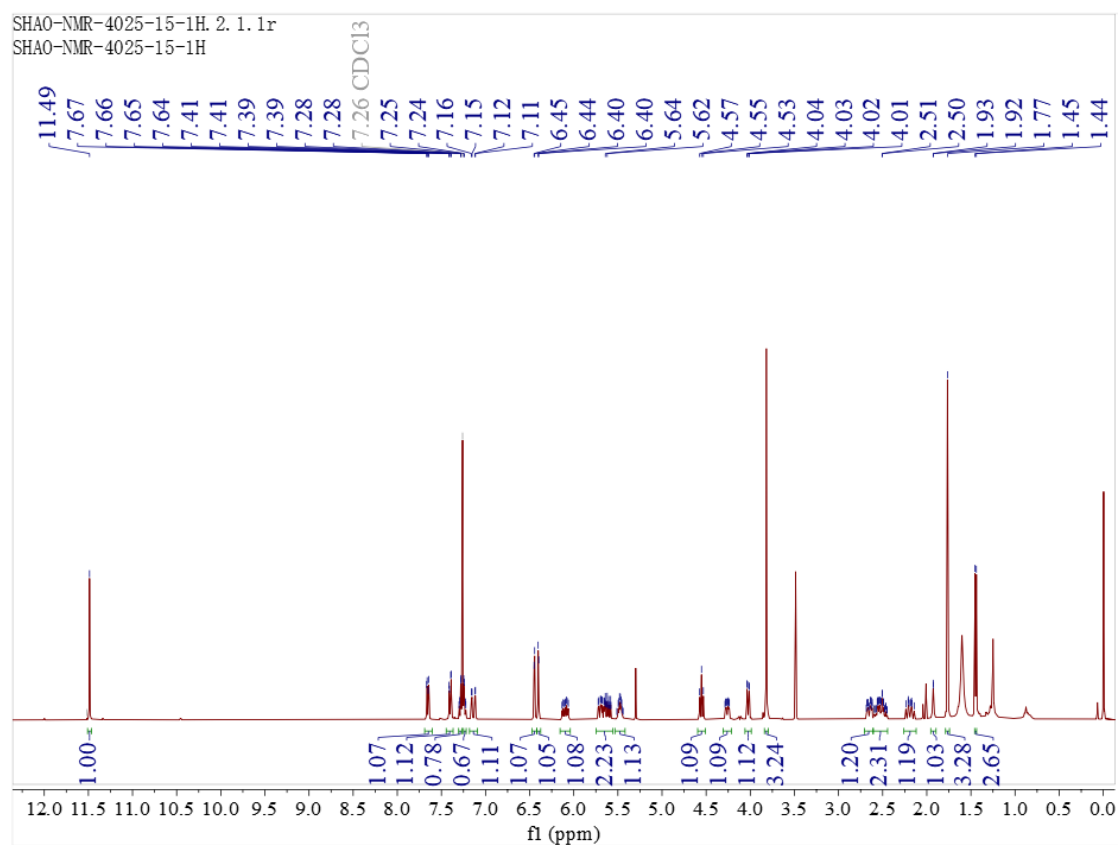


Figure S37. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 20.

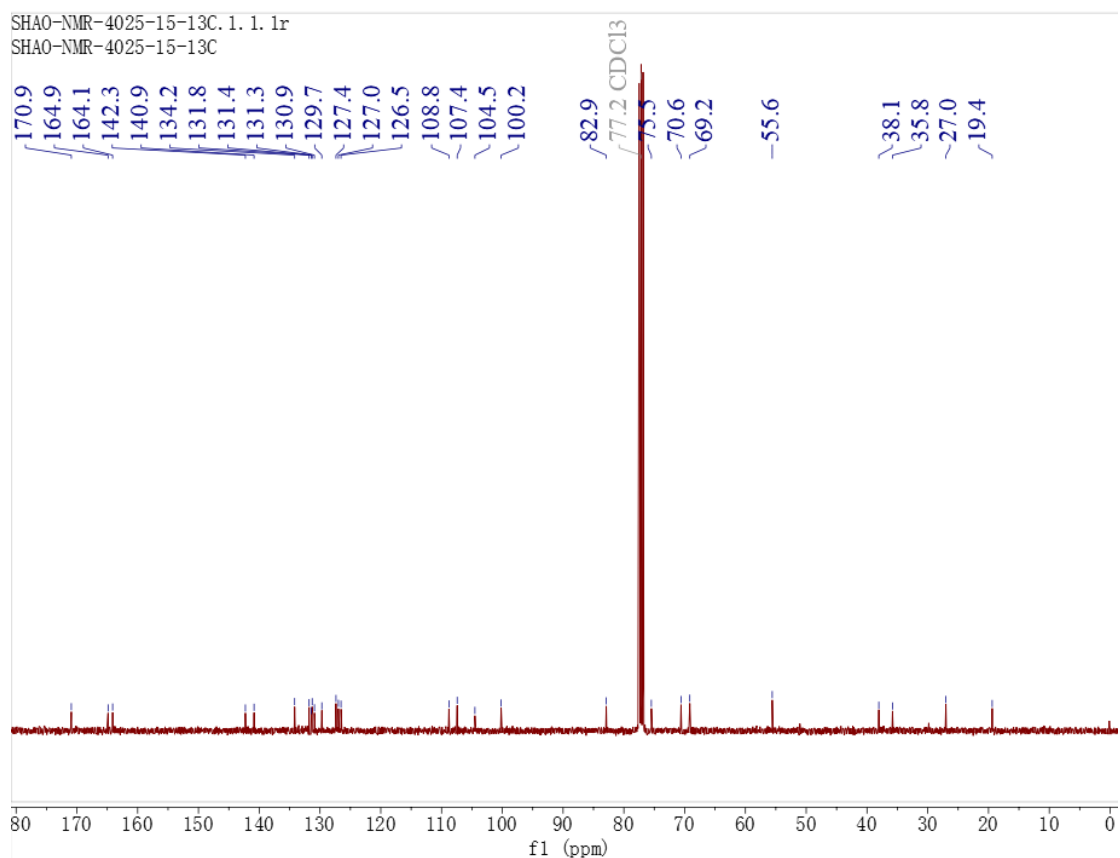


Figure S38. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound 20.

3 #479 RT: 7.15 AV: 1 NL: 8.33E2
T: FTMS + p ESI Full ms [180.00-1000.00]

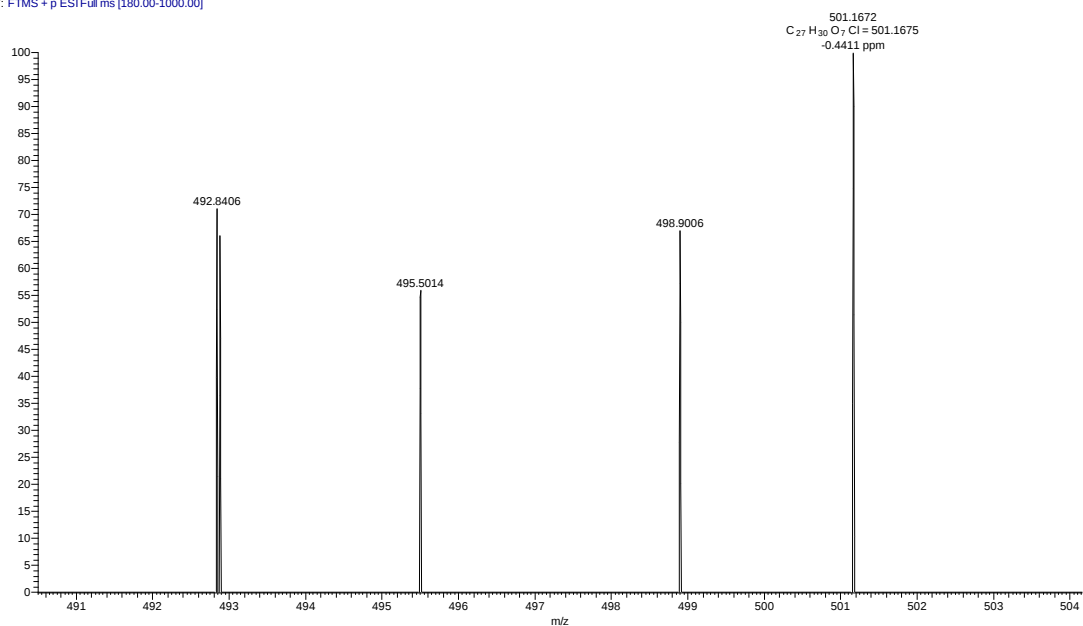


Figure S39. HR-ESI-MS spectrum of compound 20.

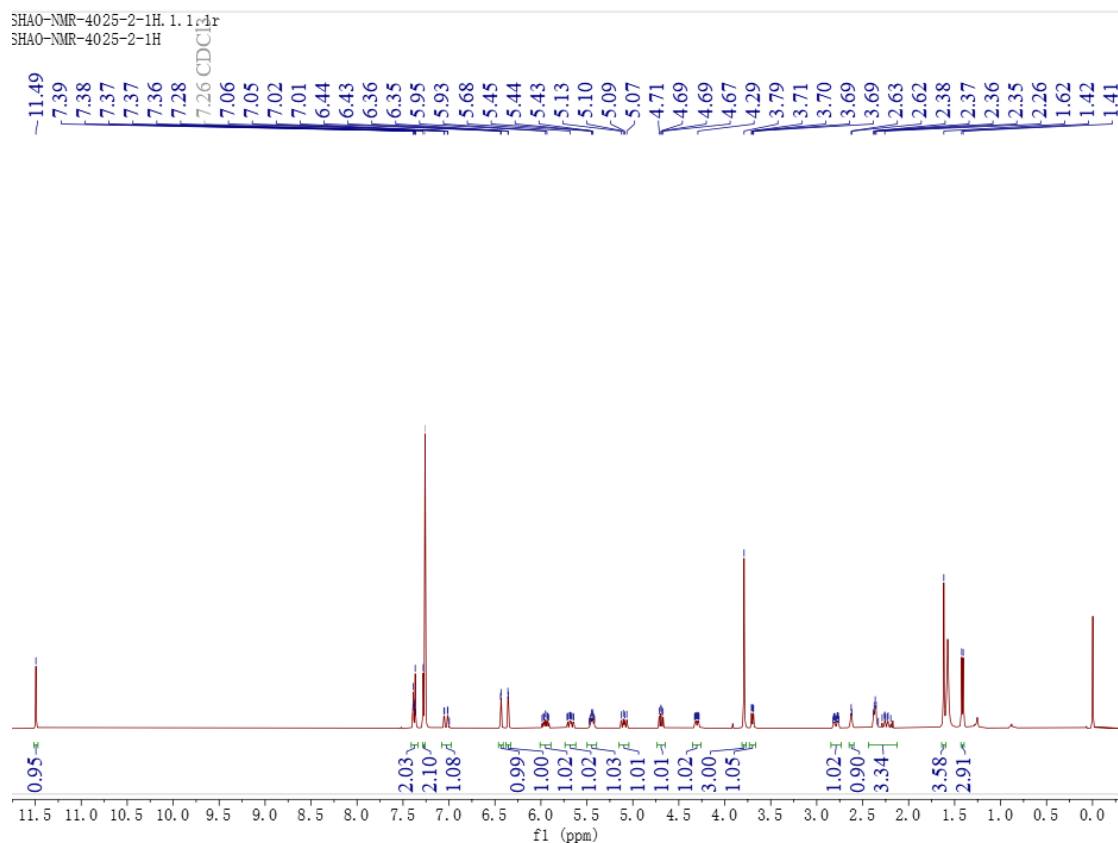


Figure S40. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 21

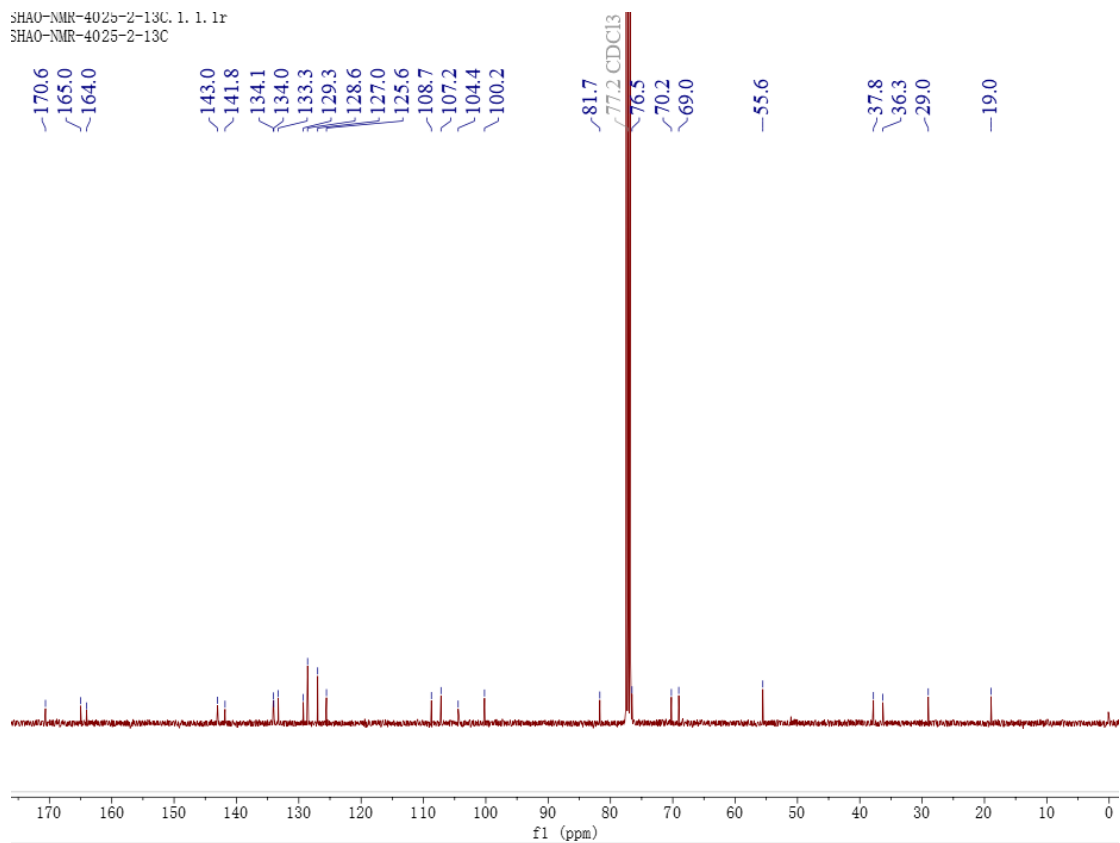


Figure S41. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **21**.

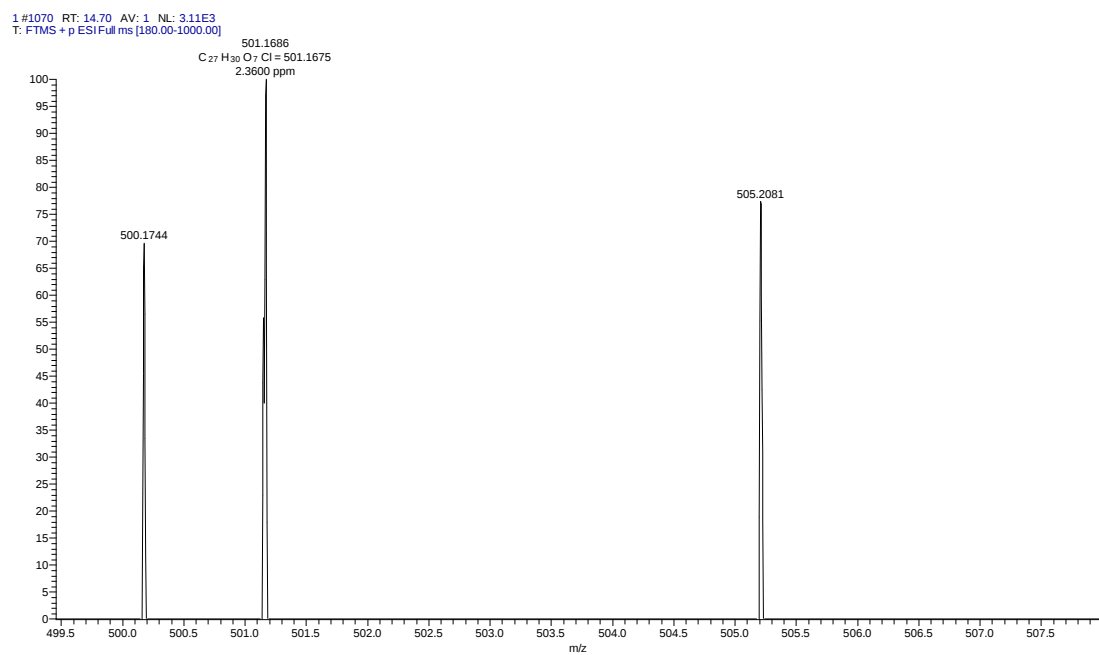


Figure S42. HR-ESI-MS spectrum of compound **21**.

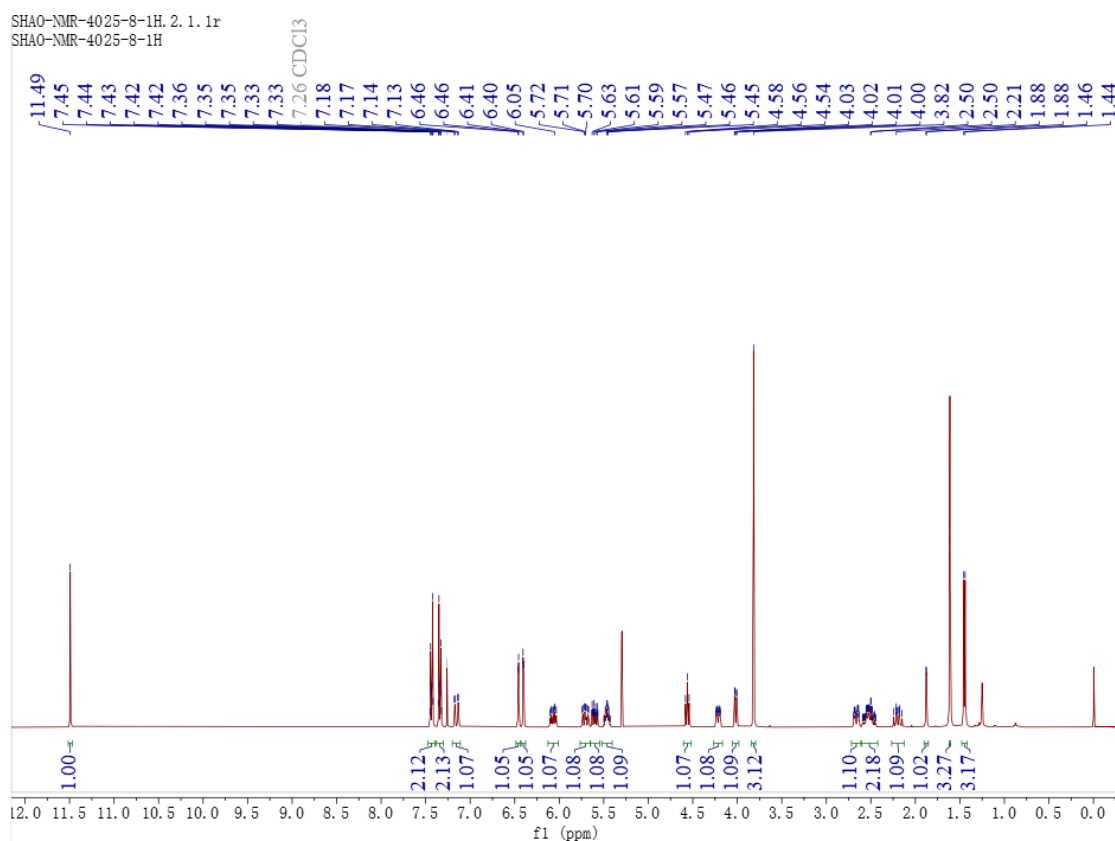


Figure S43. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 22.

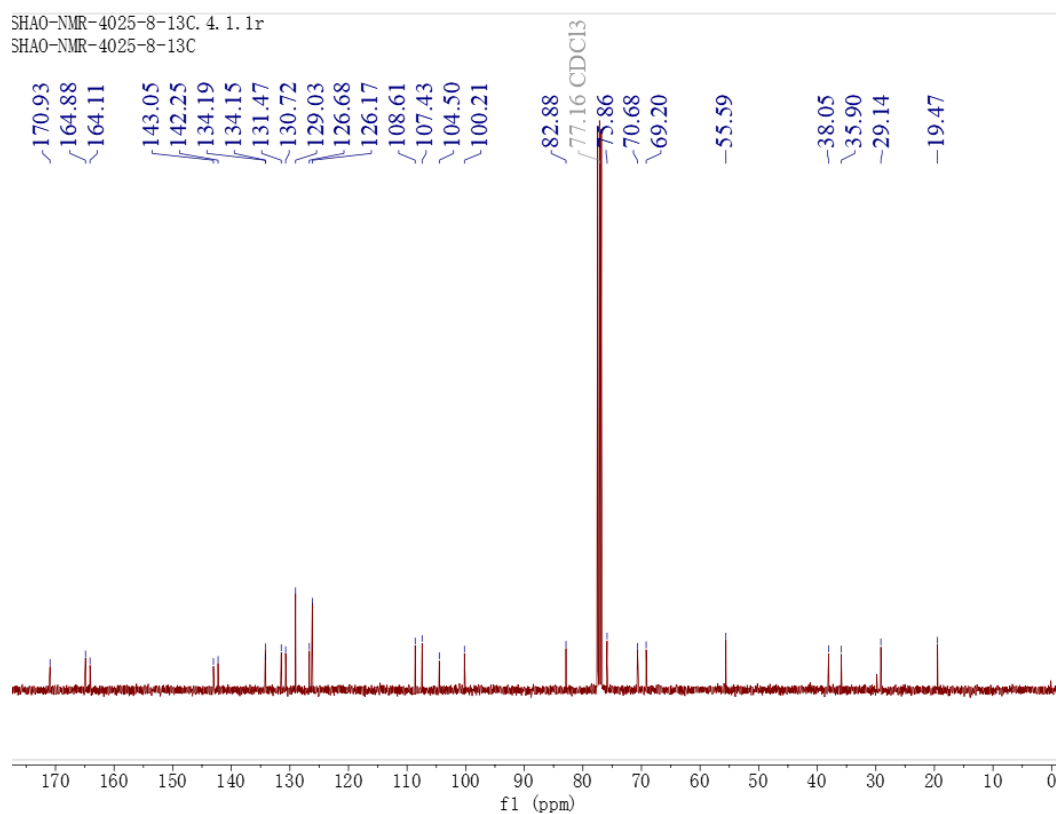


Figure S44. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound 22.

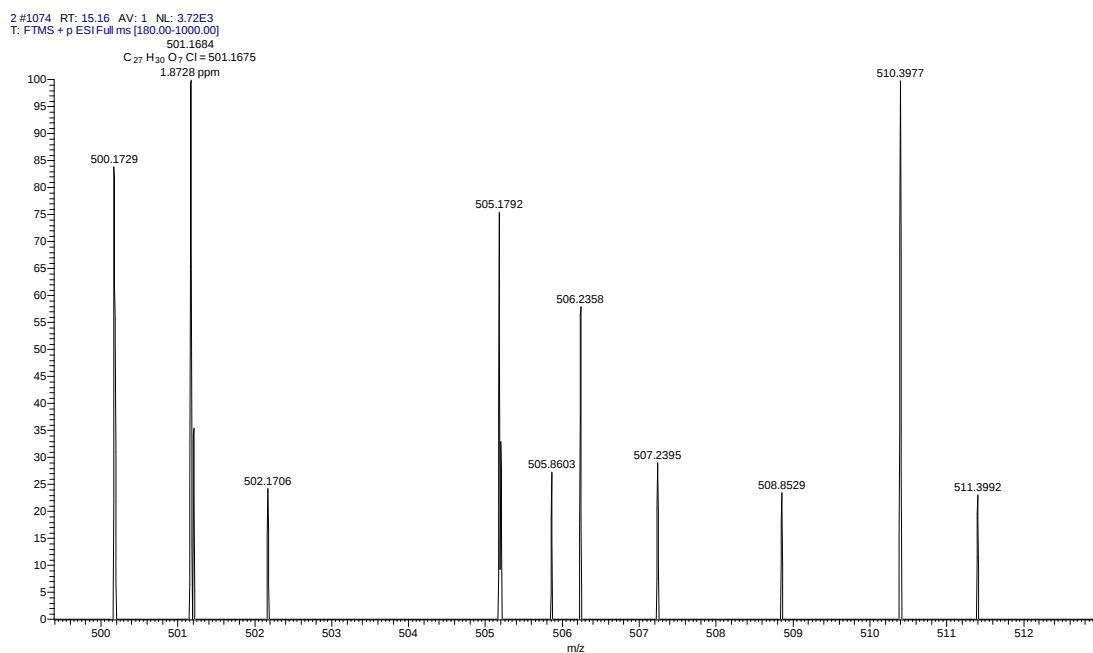


Figure S45. HR-ESI-MS spectrum of compound 22.

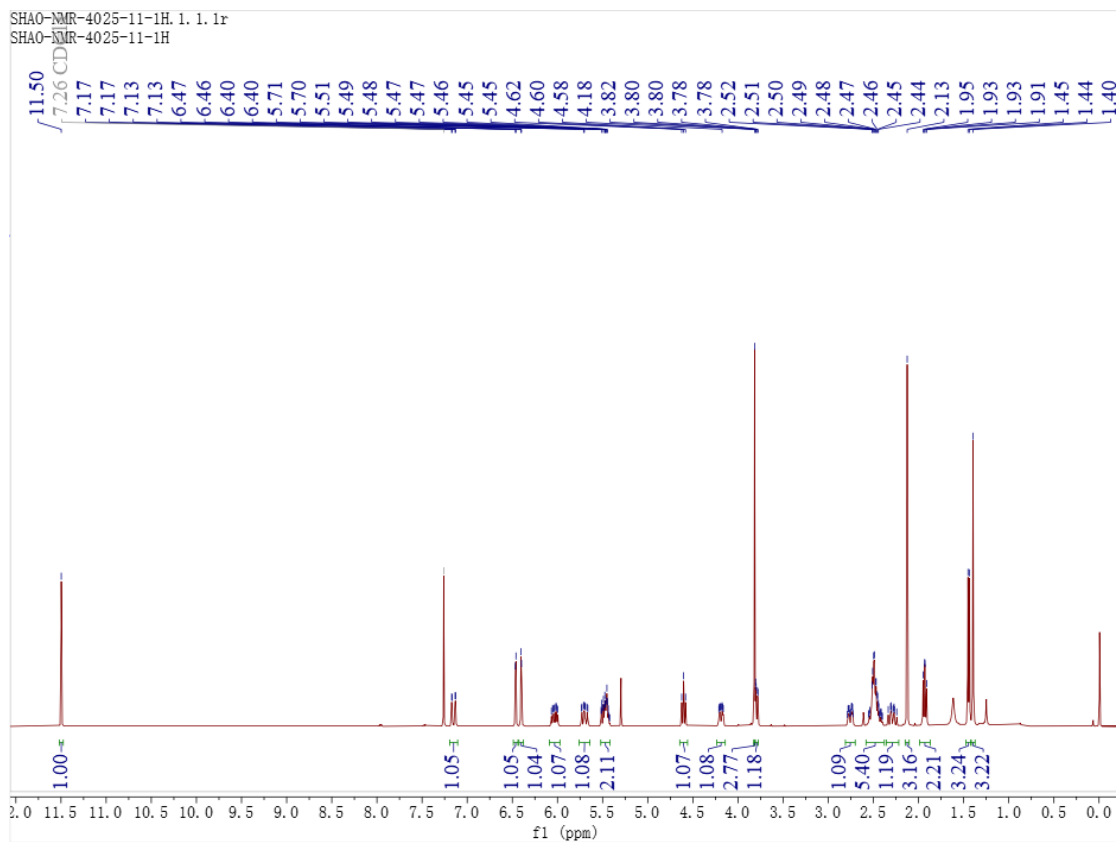


Figure S46. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 23.

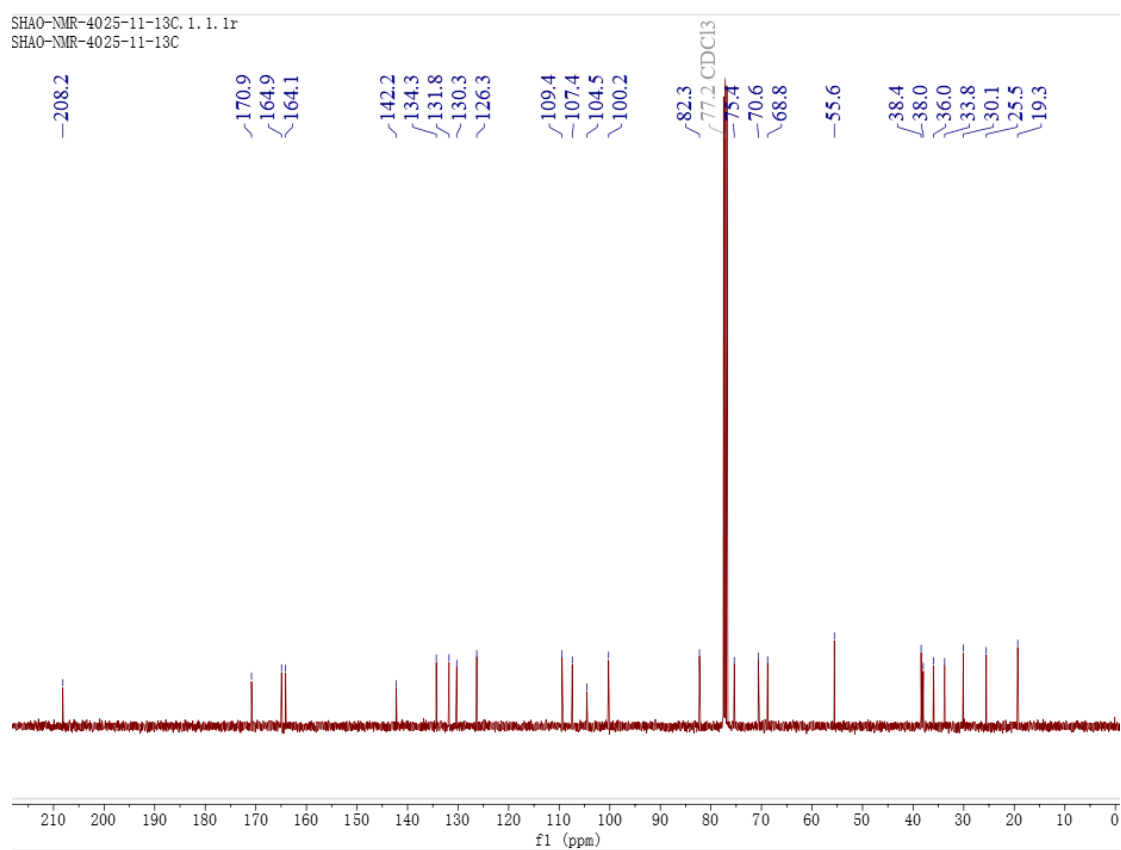


Figure S47. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **23**.

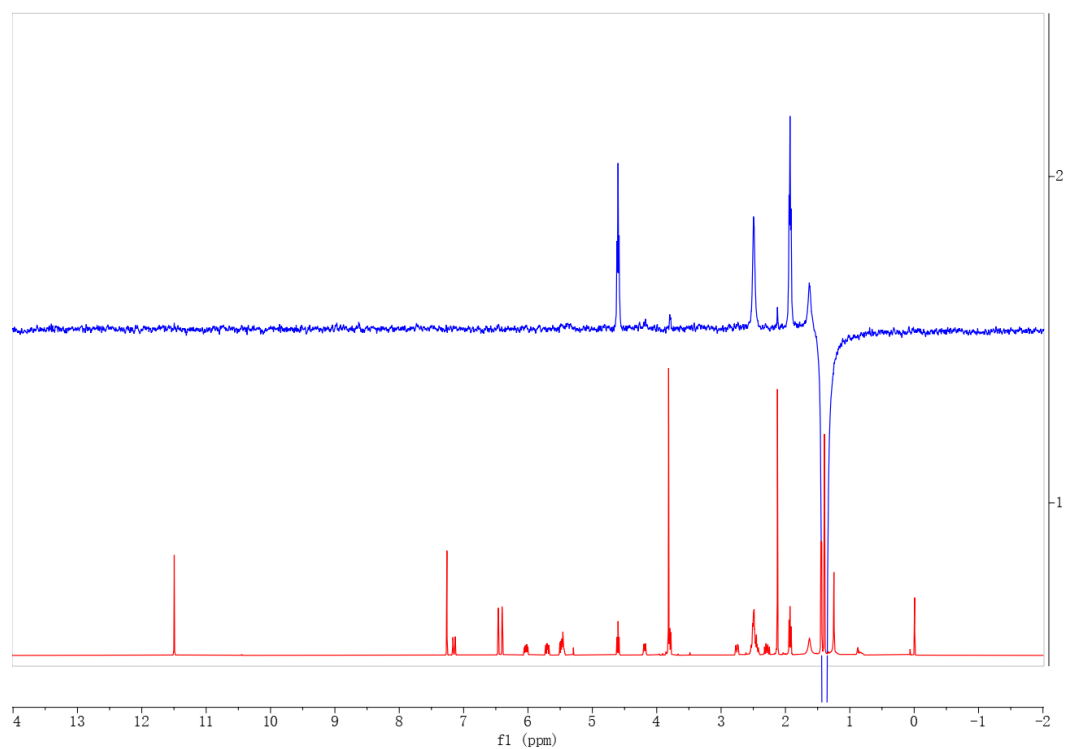


Figure S48. 1D NOE spectrum of compound **23**

1#1383 RT: 18.72 AV: 1 NL: 3.40E4
T: FTMS + p ESI Full ms [180.00-1000.00]

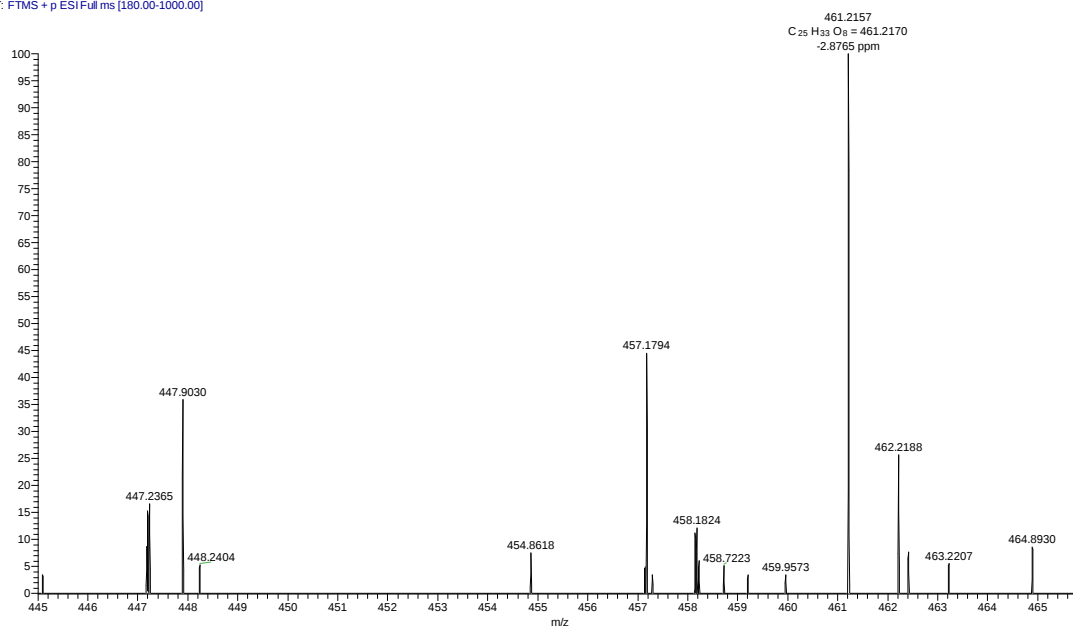


Figure S49. HR-ESI-MS spectrum of compound 23.

SHA0-NMR-4025-12-1H. 1. 1. 1r
SHA0-NMR-4025-12-1H

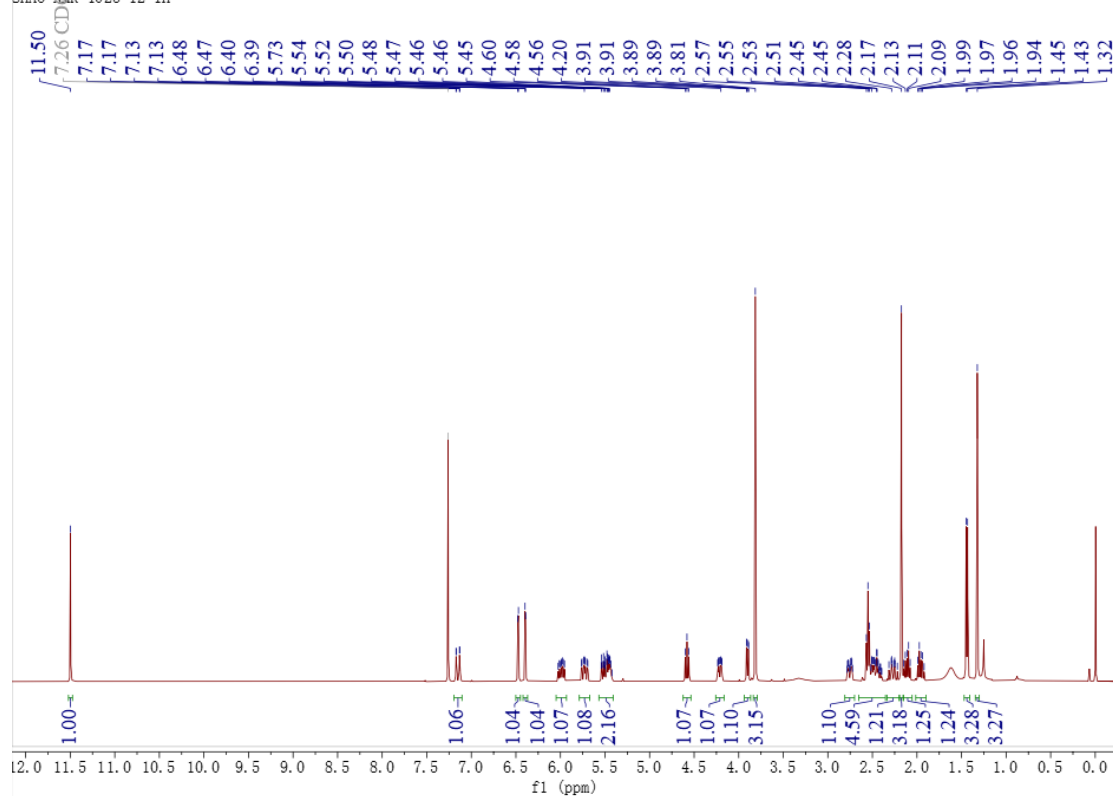


Figure S50. ¹H NMR (400 MHz, Chloroform-d) spectrum of compound 24.

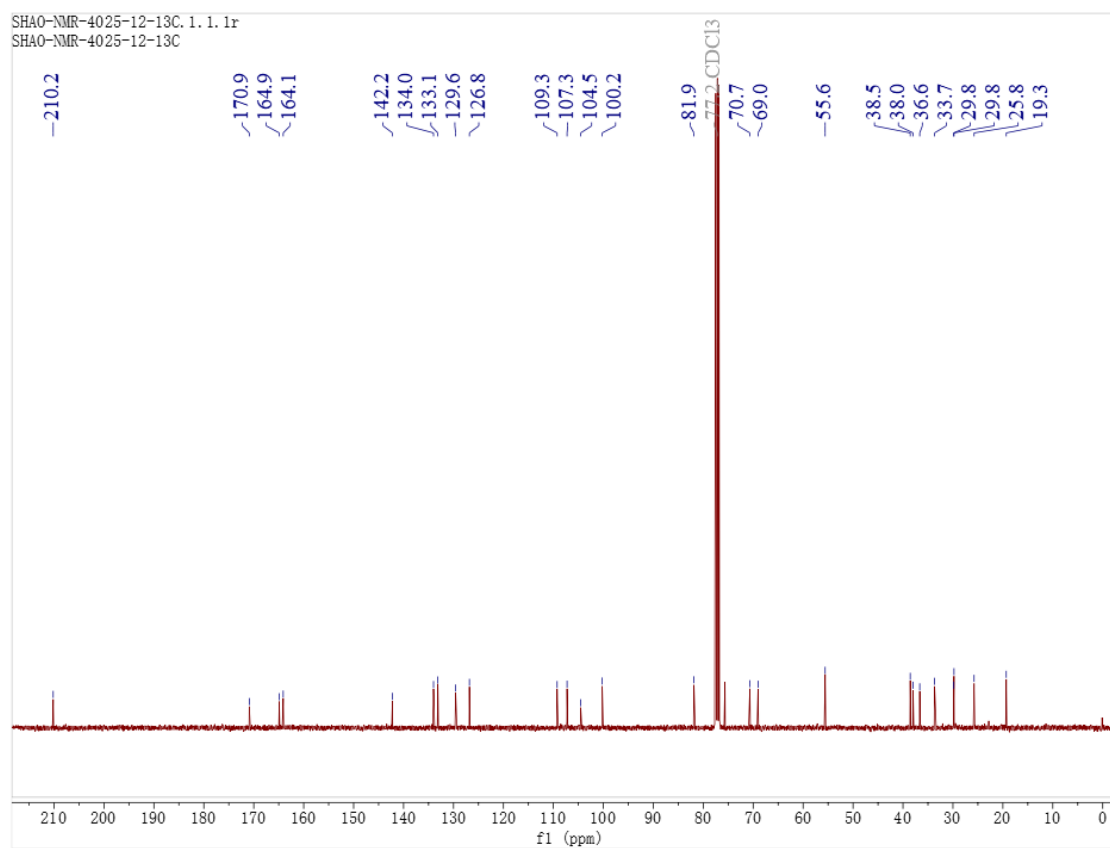


Figure S51. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **24**.

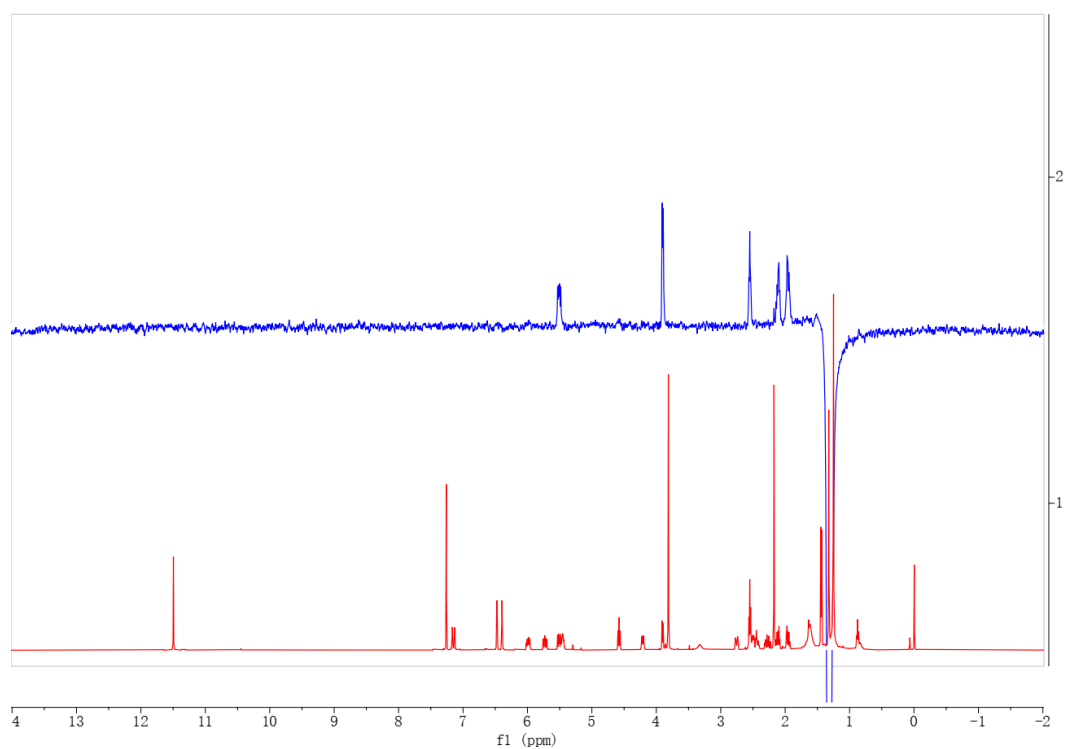


Figure S52. 1D NOE spectrum of compound **24**

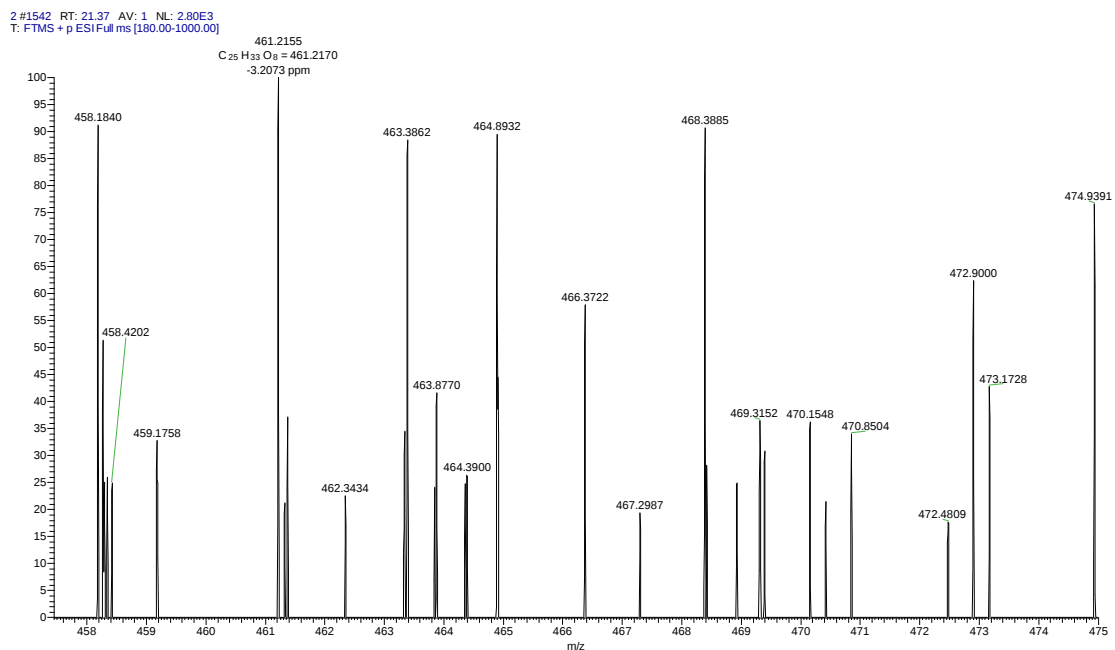


Figure S53. HR-ESI-MS spectrum of compound 24.

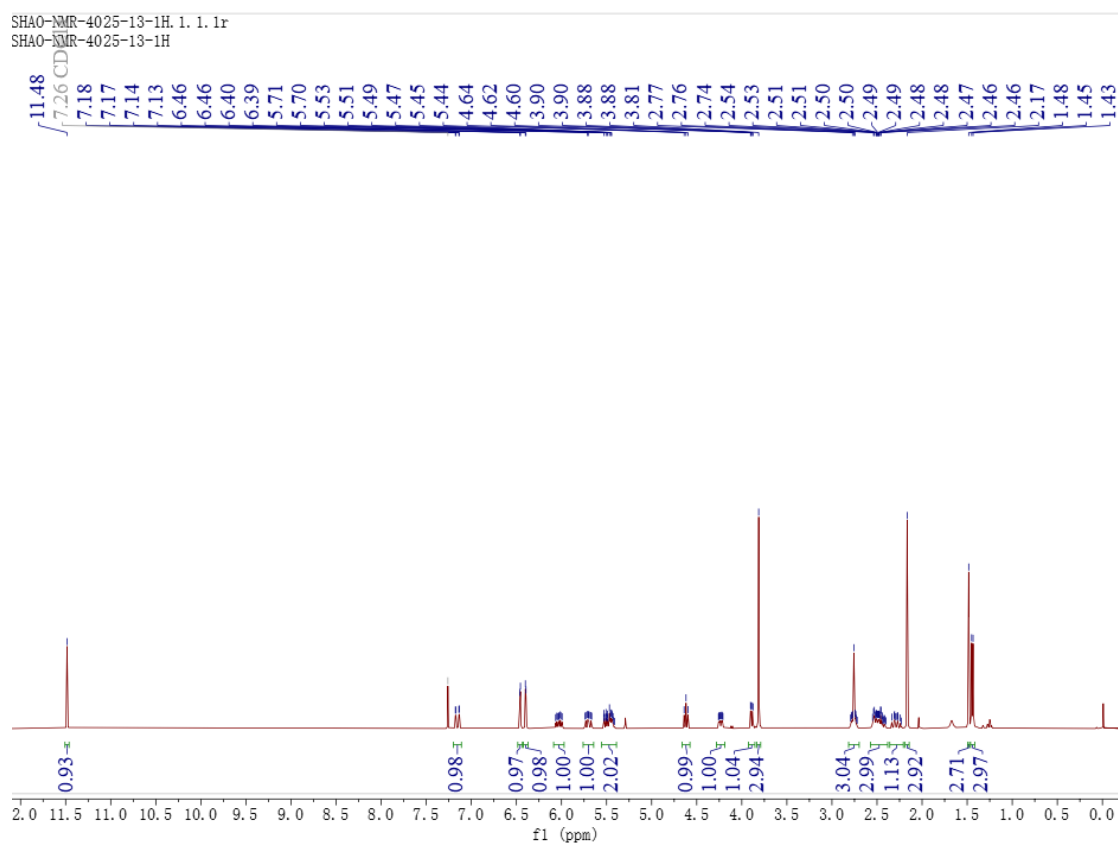


Figure S54. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 25.

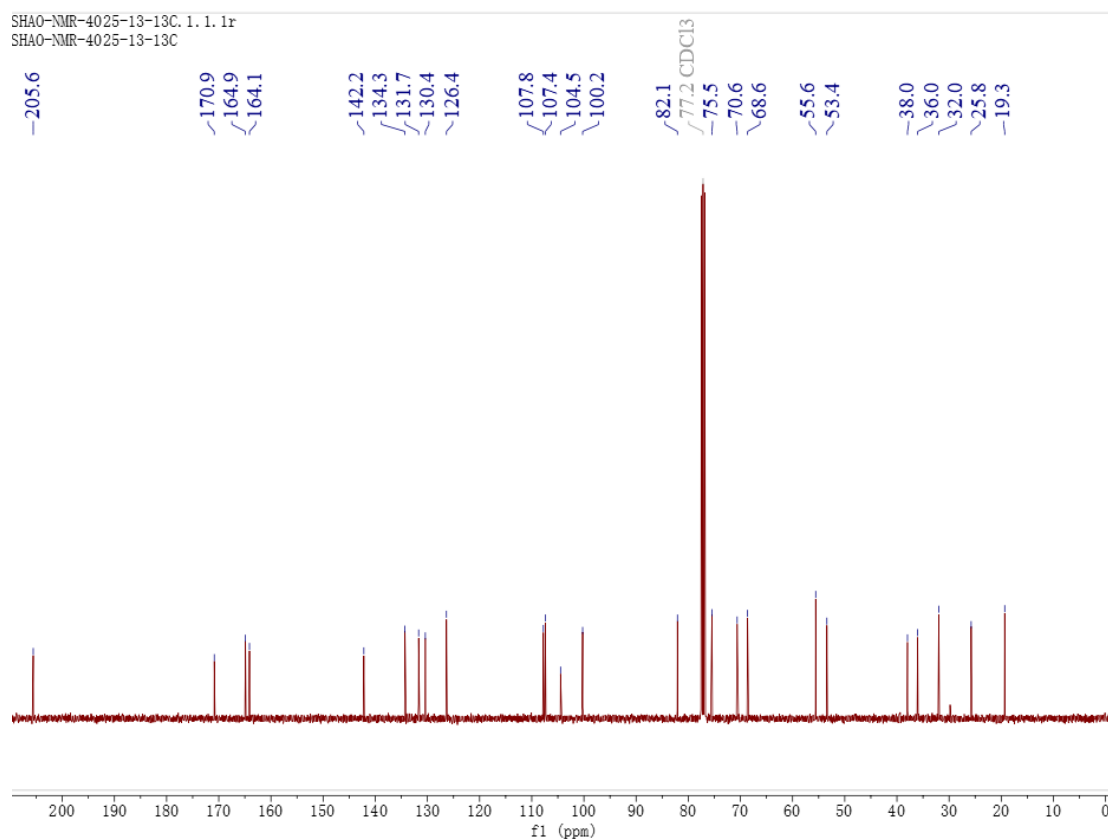


Figure S55. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **25**.

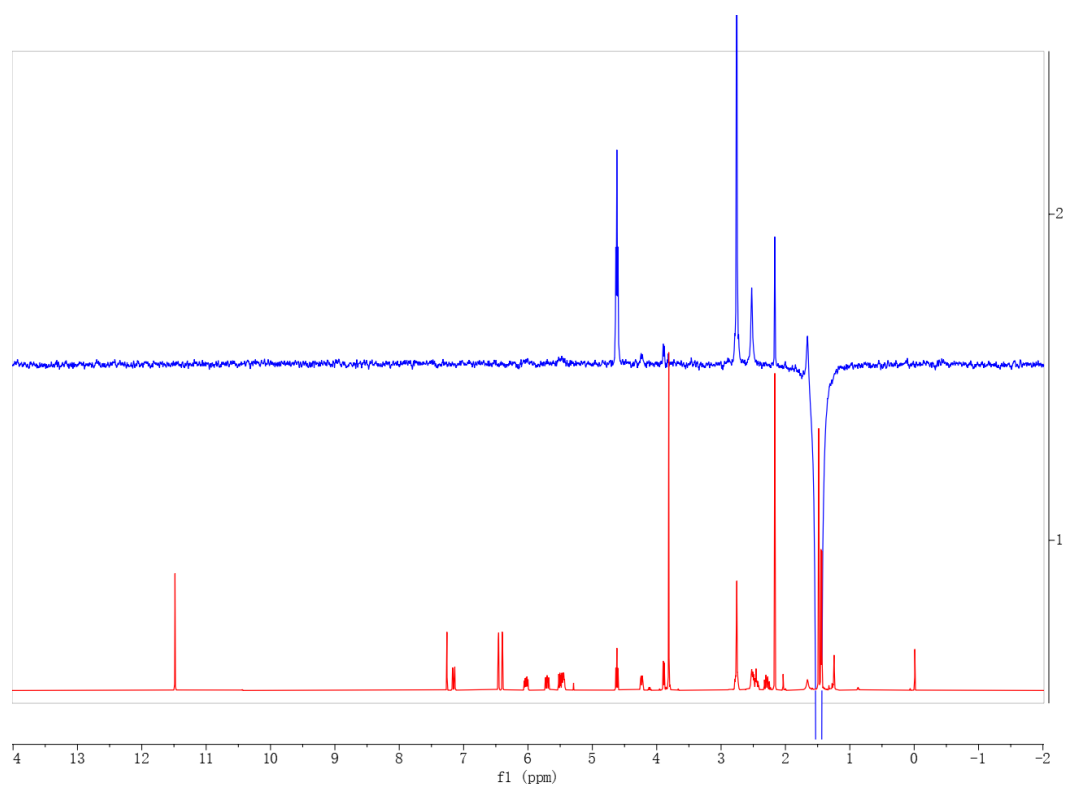


Figure S56. 1D NOE spectrum of compound **25**

3#1044 RT: 13.98 AV: 1 NL: 5.22E3
T: FTMS + p ESI Full ms [180.00-1000.00]

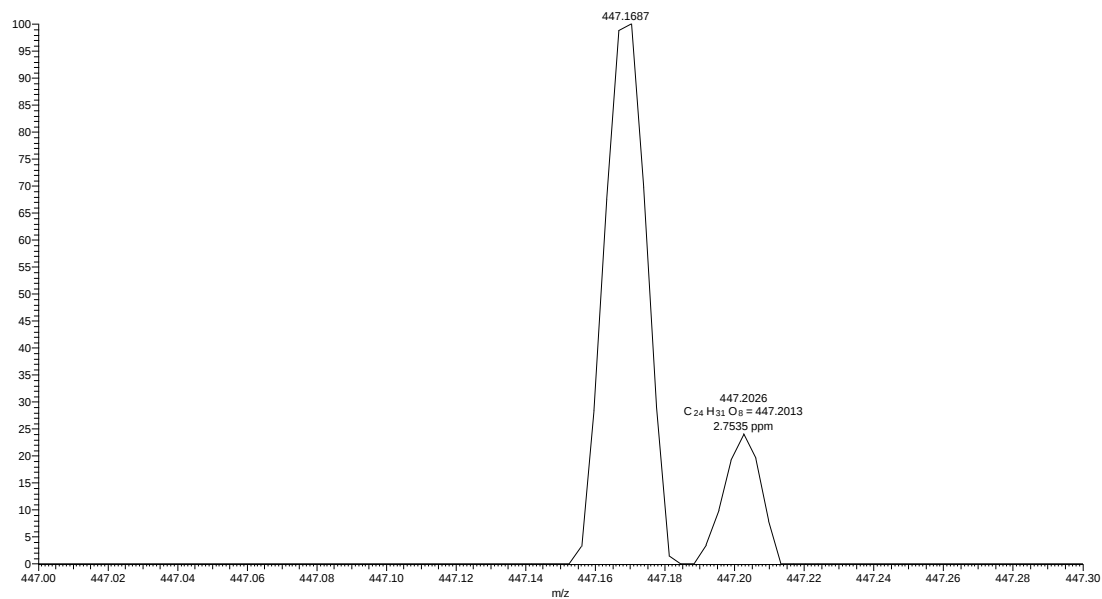


Figure S57. HR-ESI-MS spectrum of compound 25.

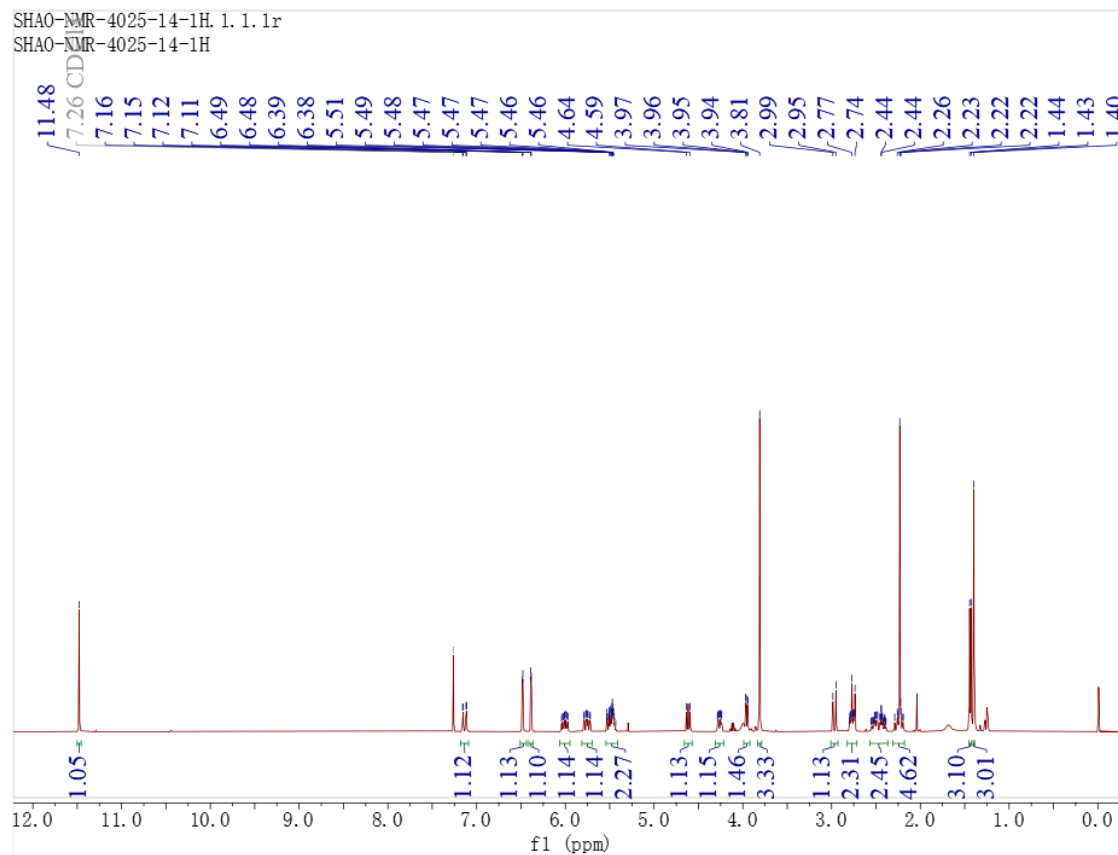


Figure S58. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 26.

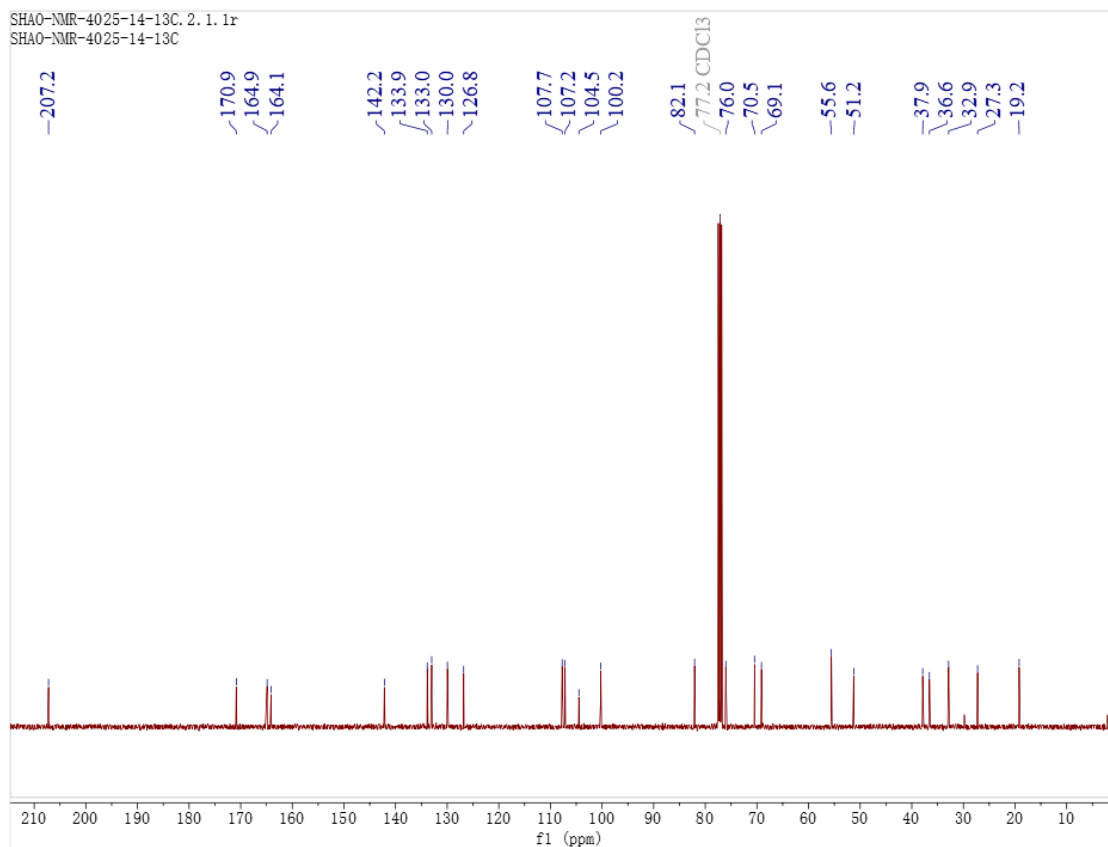


Figure S59. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **26**.

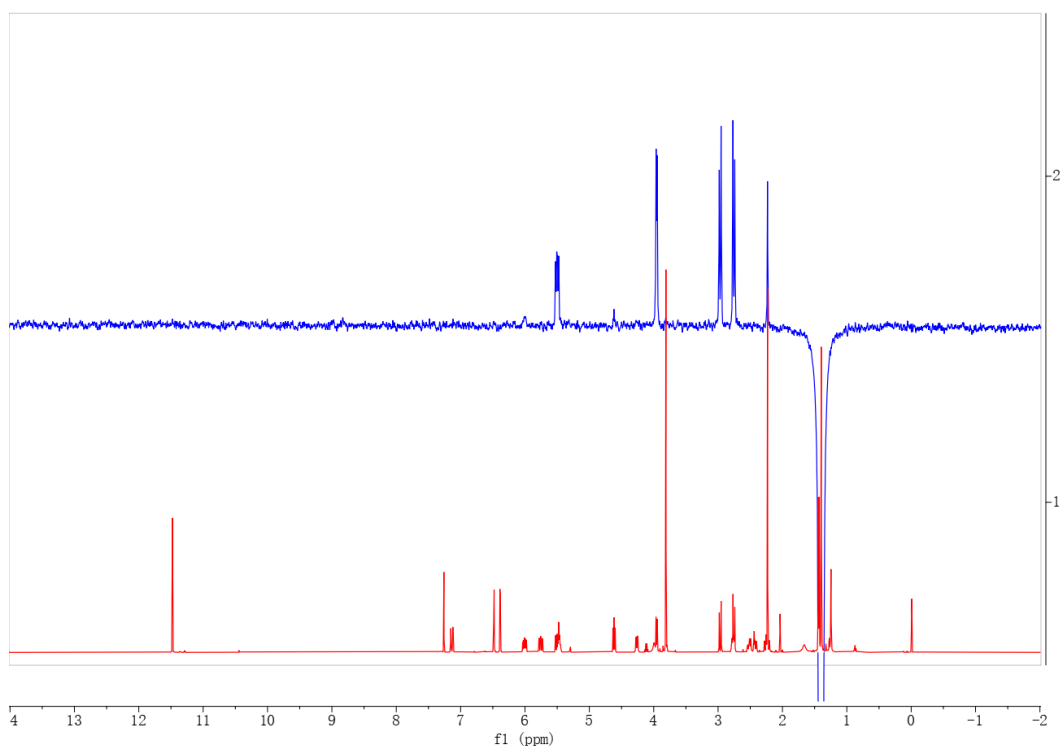


Figure S60. 1D NOE spectrum of compound **26**

4#1030 RT: 14.80 AV: 1 NL: 8.59E3
T: FTMS + p ESI Full ms [180.00-1000.00]

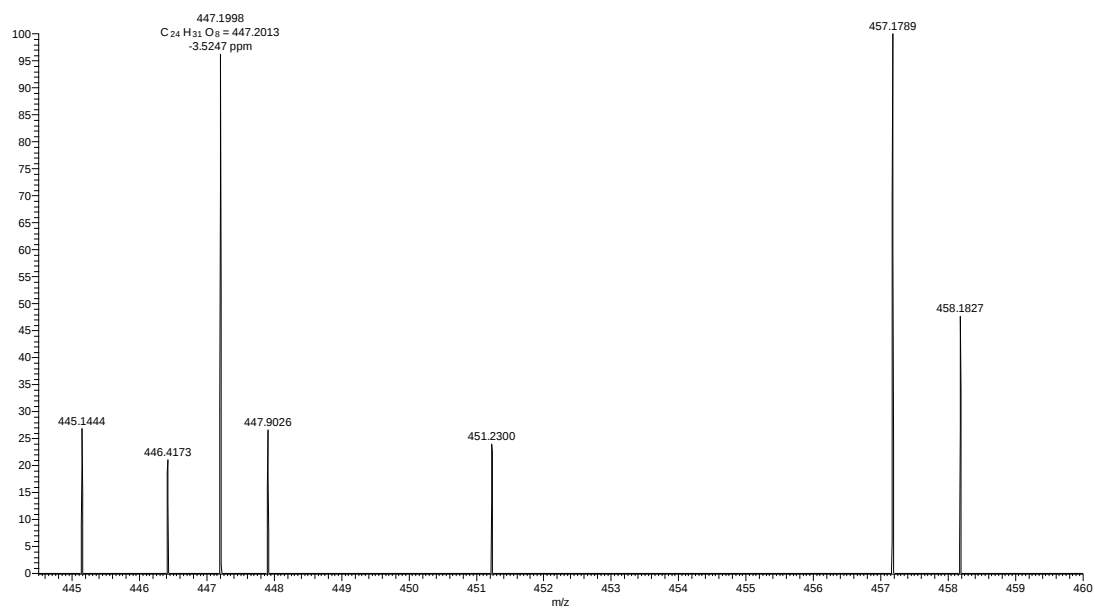


Figure S61. HR-ESI-MS spectrum of compound 26.

SHAO-NMR-4026-1-1H. 1. 1. 1r
SHAO-NMR-4026-1-1H

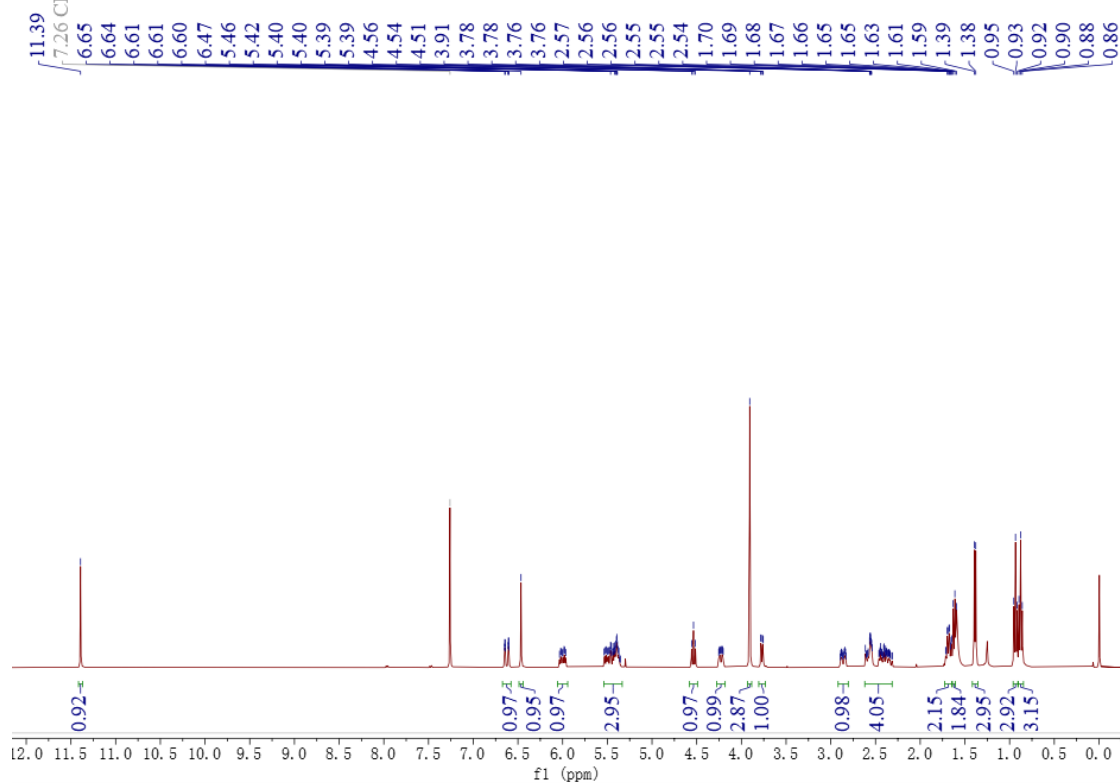


Figure S62. 1H NMR (400 MHz, Chloroform-*d*) spectrum of compound 27.

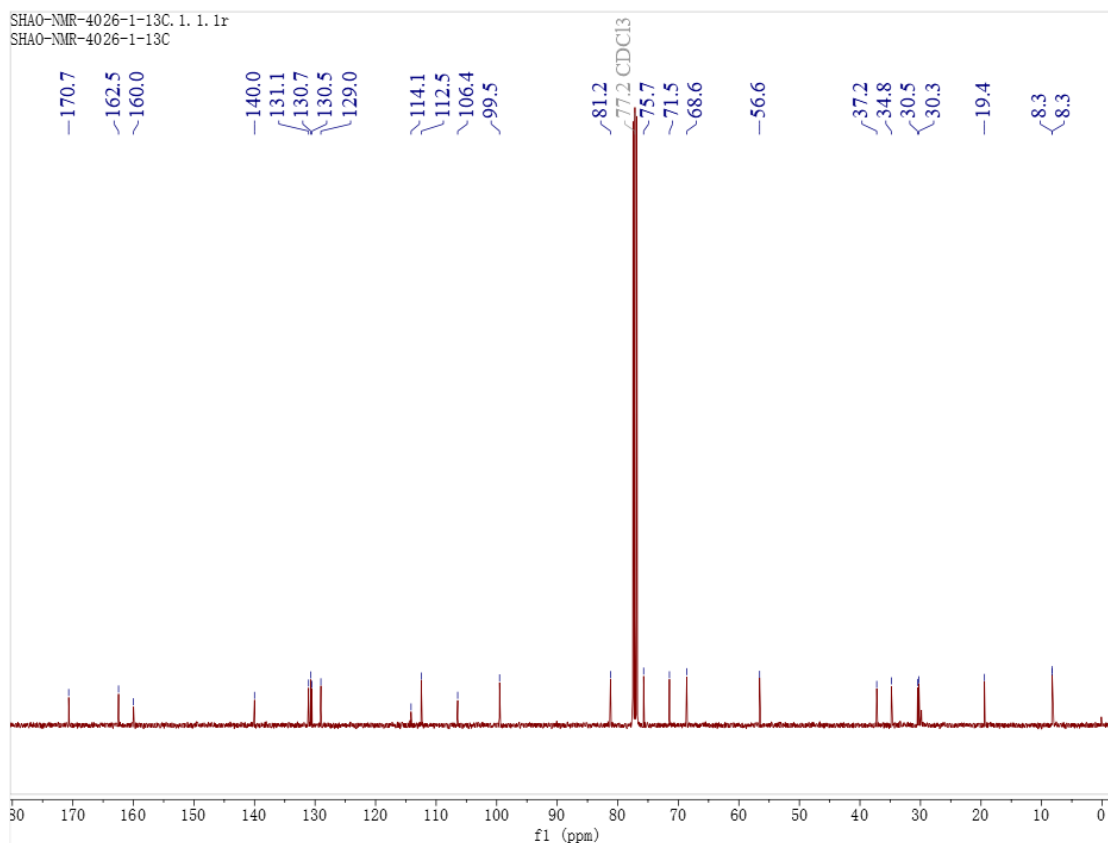


Figure S63. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound 27.

5 #1228 RT: 16.97 AV: 1 NL: 3.10E3
T: FTMS + p ESI Full ms [180.00-1000.00]

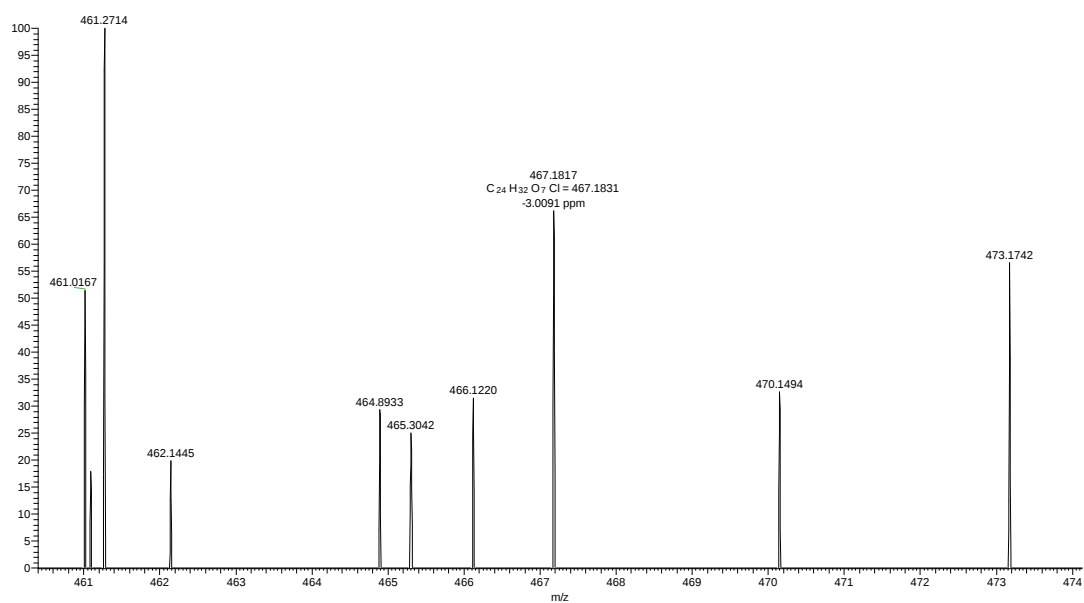


Figure S64. HR-ESI-MS spectrum of compound 27.

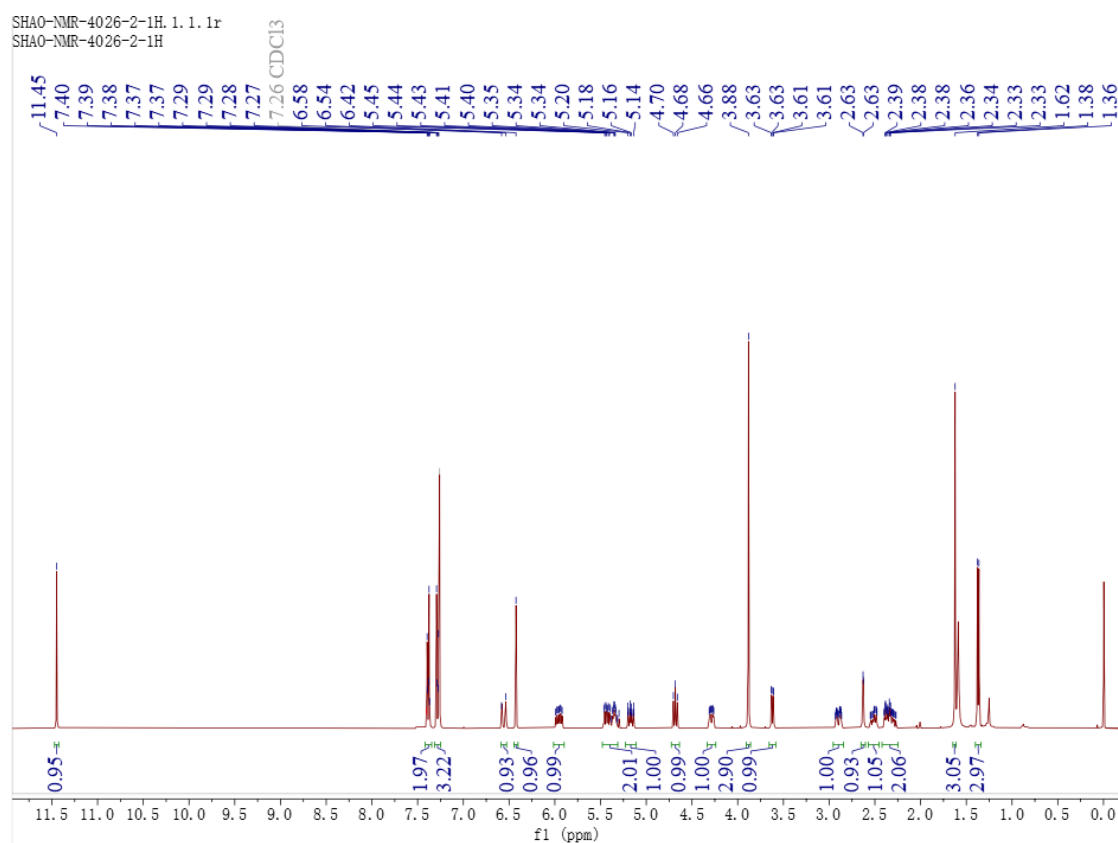


Figure S65. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 28.

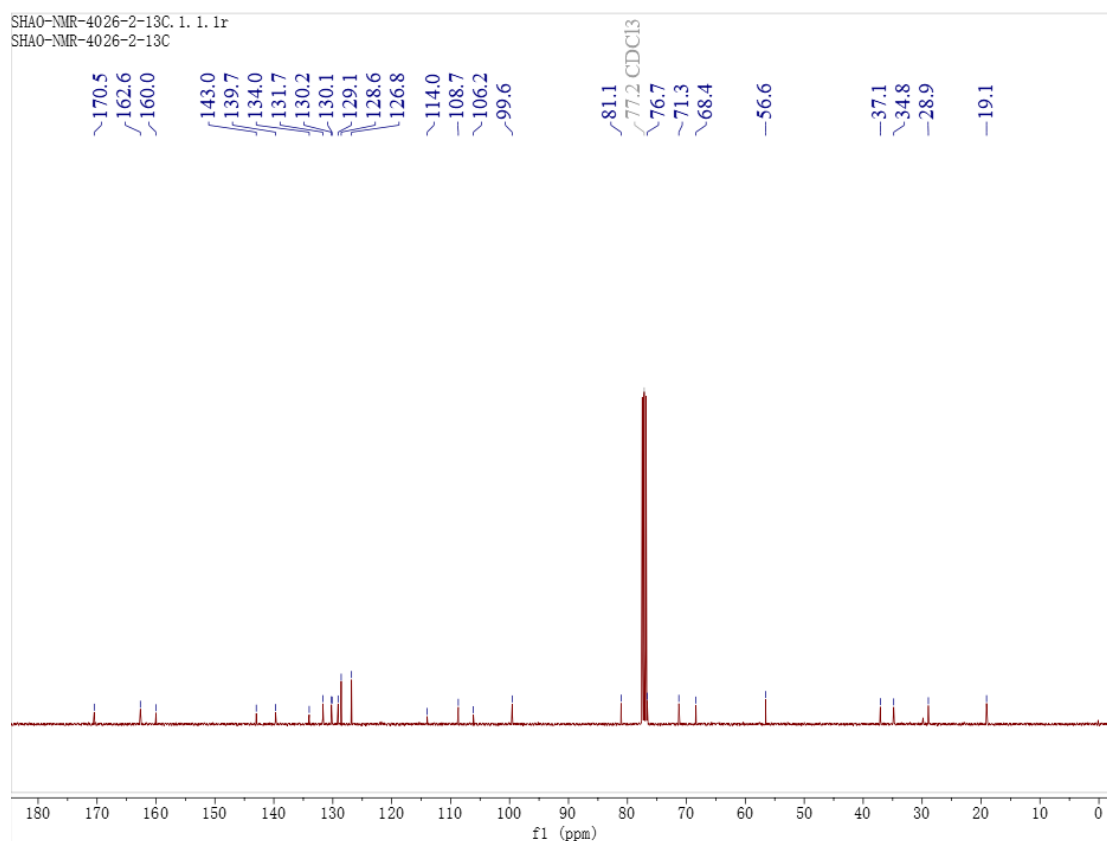


Figure S66. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound 28.

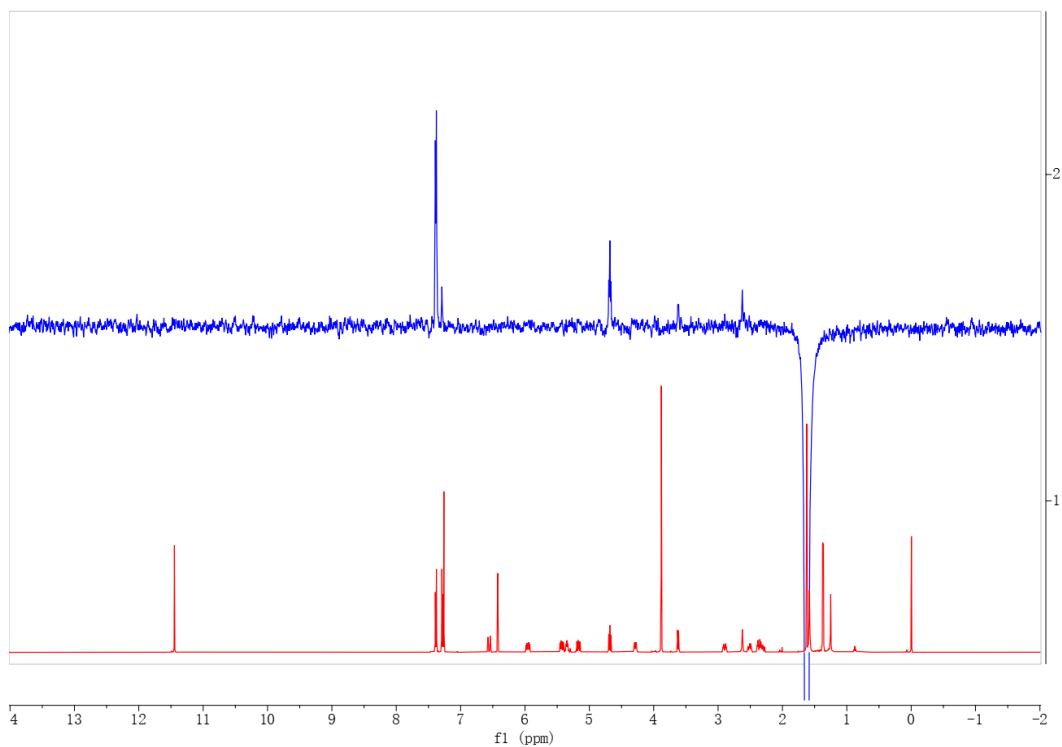


Figure S67. 1D NOE spectrum of compound 28

3 #1056 RT: 14.14 AV: 1 NL: 1.55E3
T: FTMS + p ESI Full ms [180.00-1000.00]

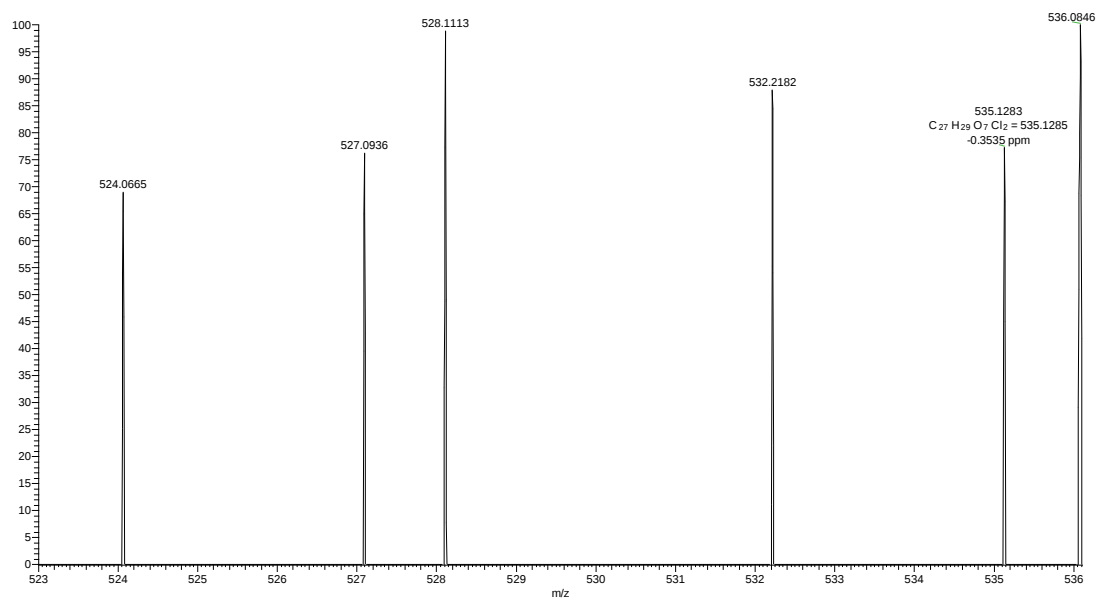


Figure S68. HR-ESI-MS spectrum of compound 28.

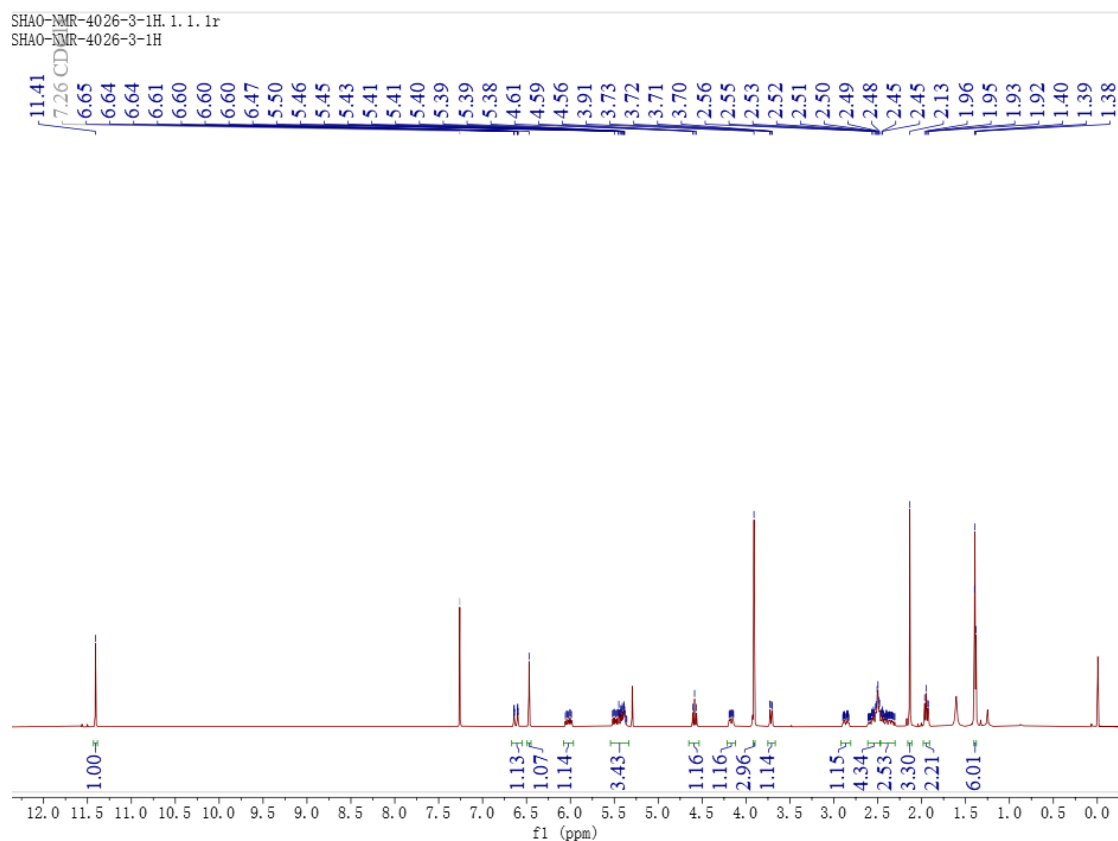


Figure S69. ^1H NMR (400 MHz, Chloroform-*d*) spectrum of compound **29**.

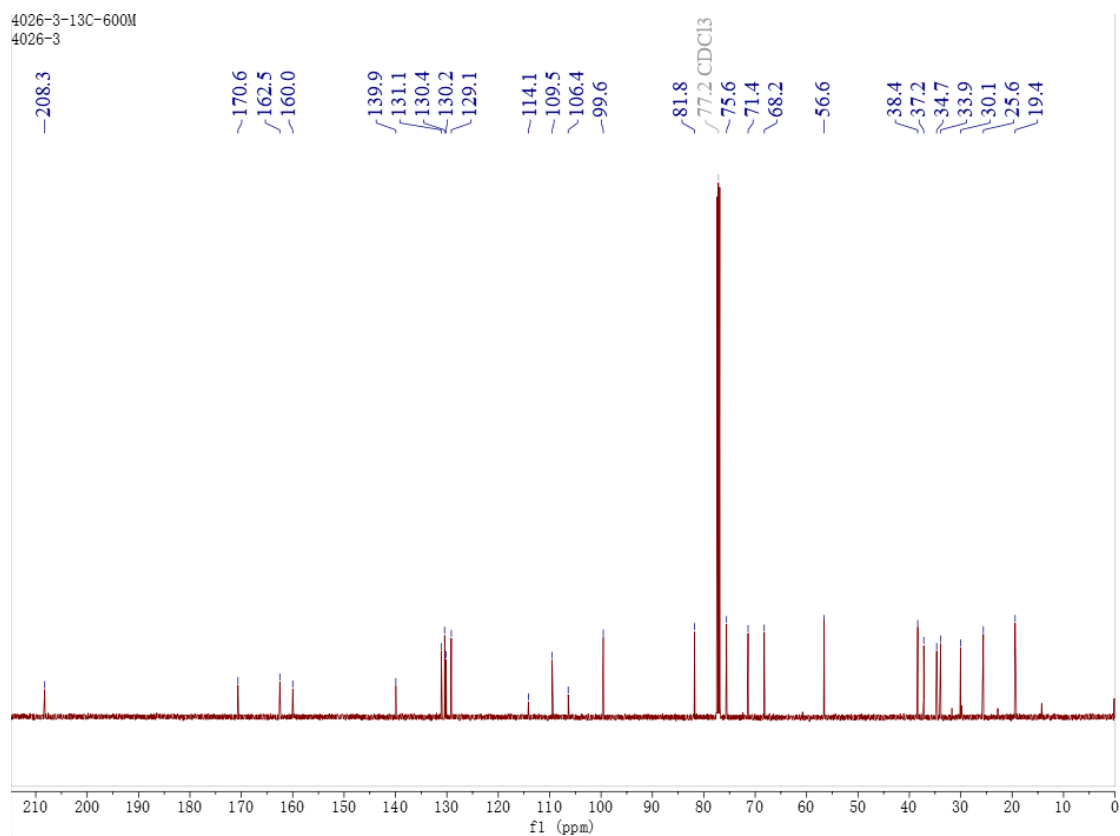


Figure S70. ^{13}C NMR (125 MHz, Chloroform-*d*) spectrum of compound **29**.

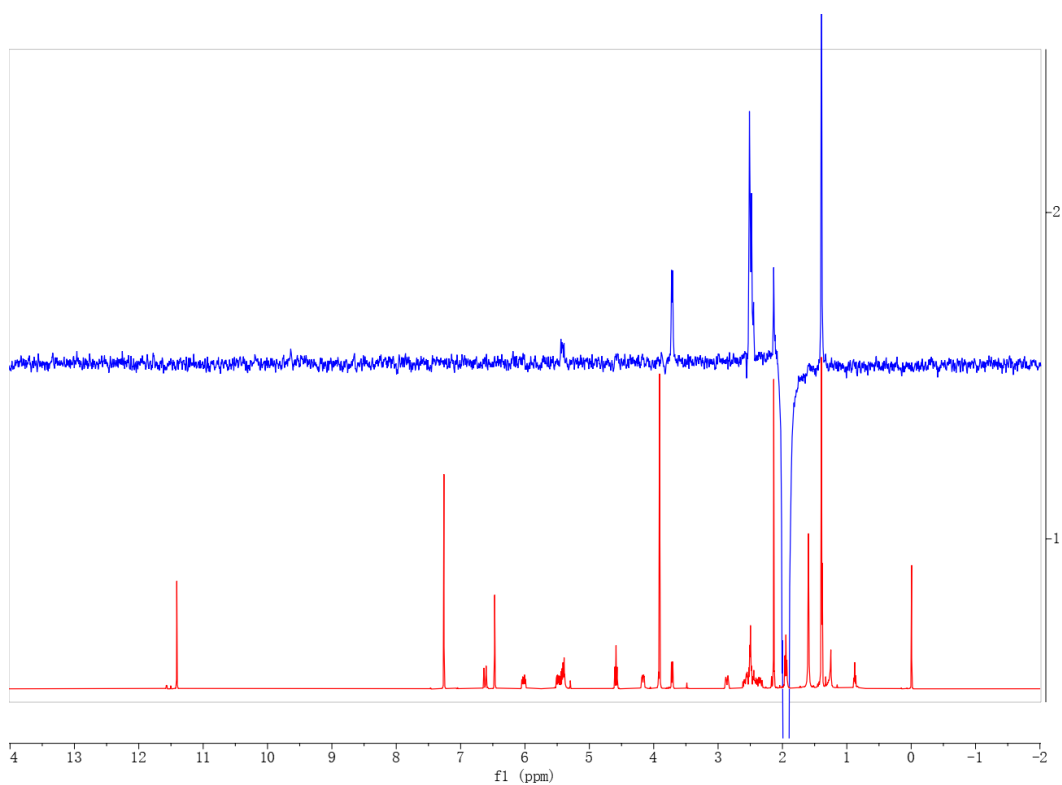


Figure S71. 1D NOE spectrum of compound **29**.

6 #1035 RT: 14.93 AV: 1 NL: 2.45E5
T: FTMS + p ESIFull.ms [180.00-1000.00]

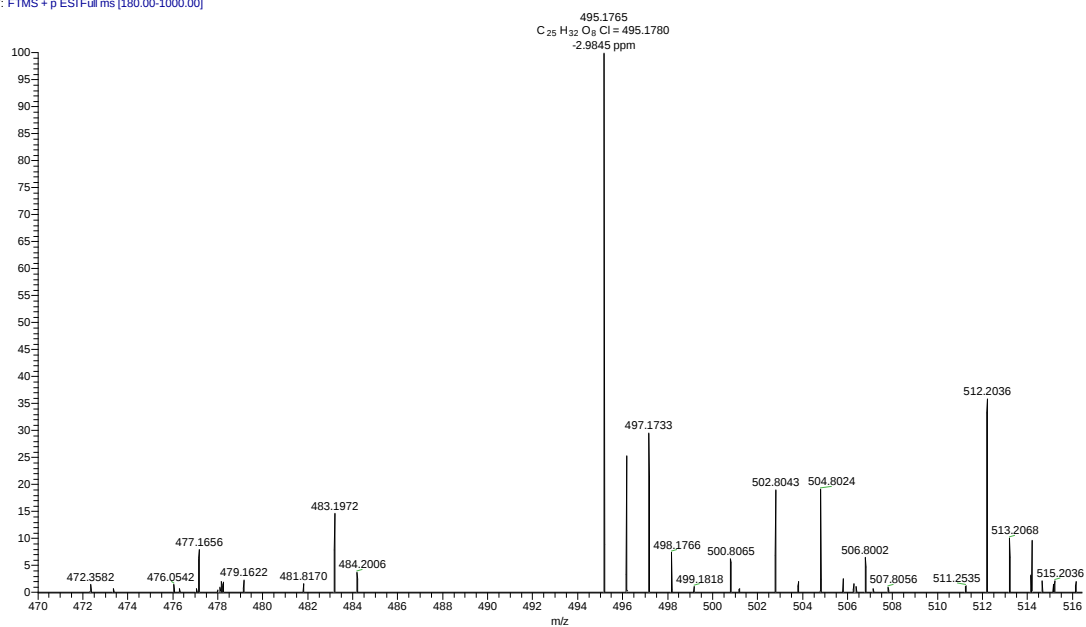


Figure S72. HR-ESI-MS spectrum of compound **29**.

SHAO-NMR-4026-4-1H. 1. 1. 1r
SHAO-NMR-4026-4-1H

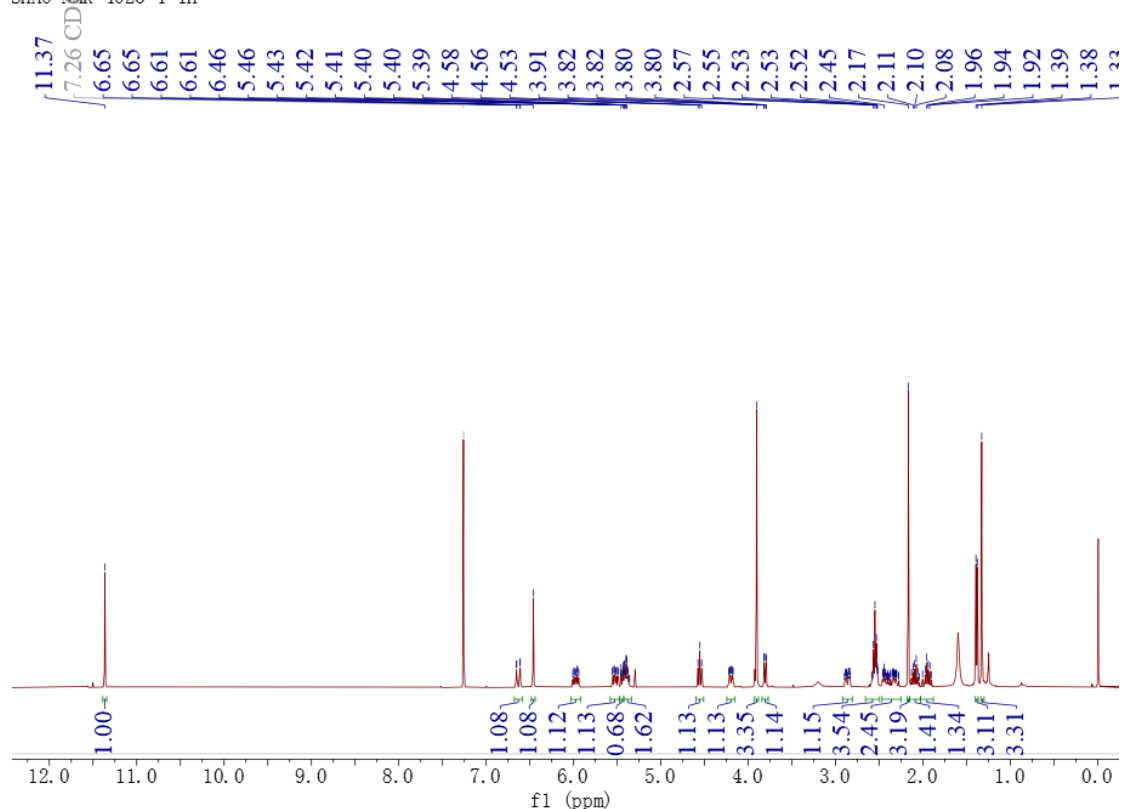


Figure S73. ^1H NMR (400 MHz, Chloroform- d) spectrum of compound 30.

SHAO-NMR-4026-4-13C. 1. 1. 1r
SHAO-NMR-4026-4-13C

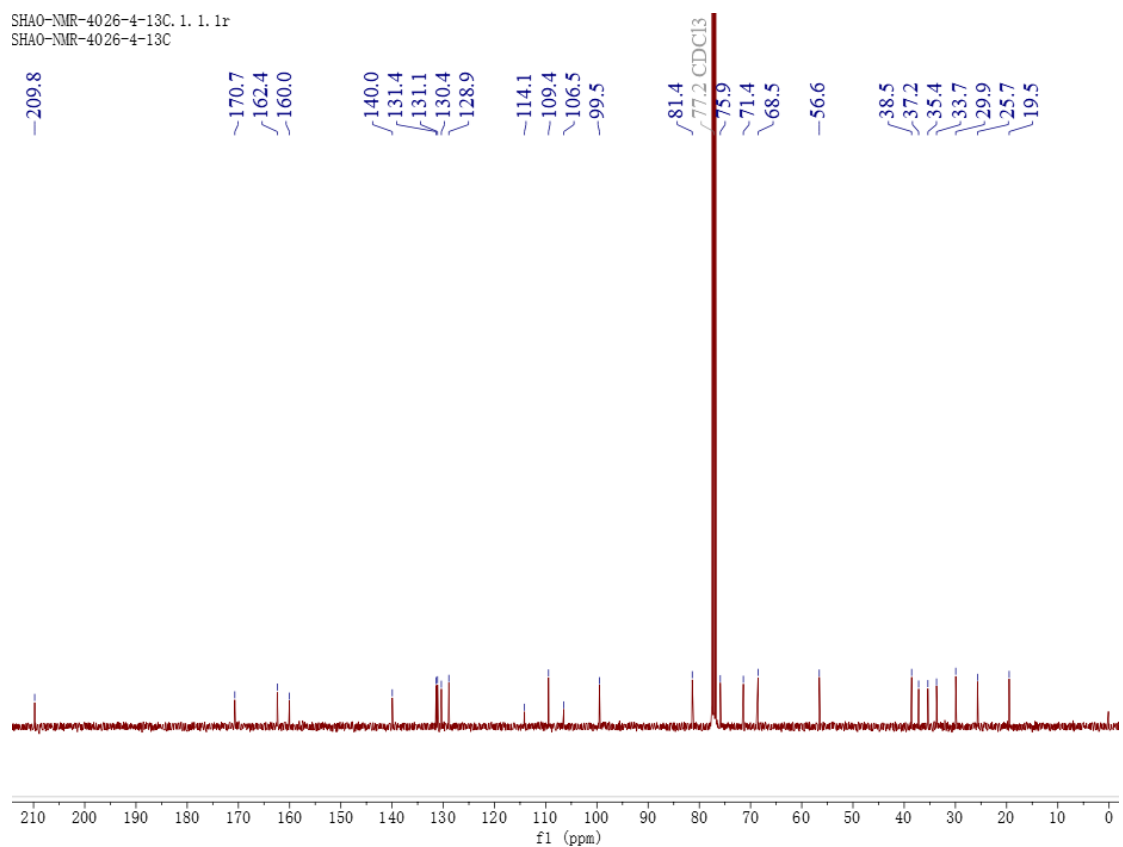


Figure S74. ^{13}C NMR (100 MHz, Chloroform- d) spectrum of compound 30.

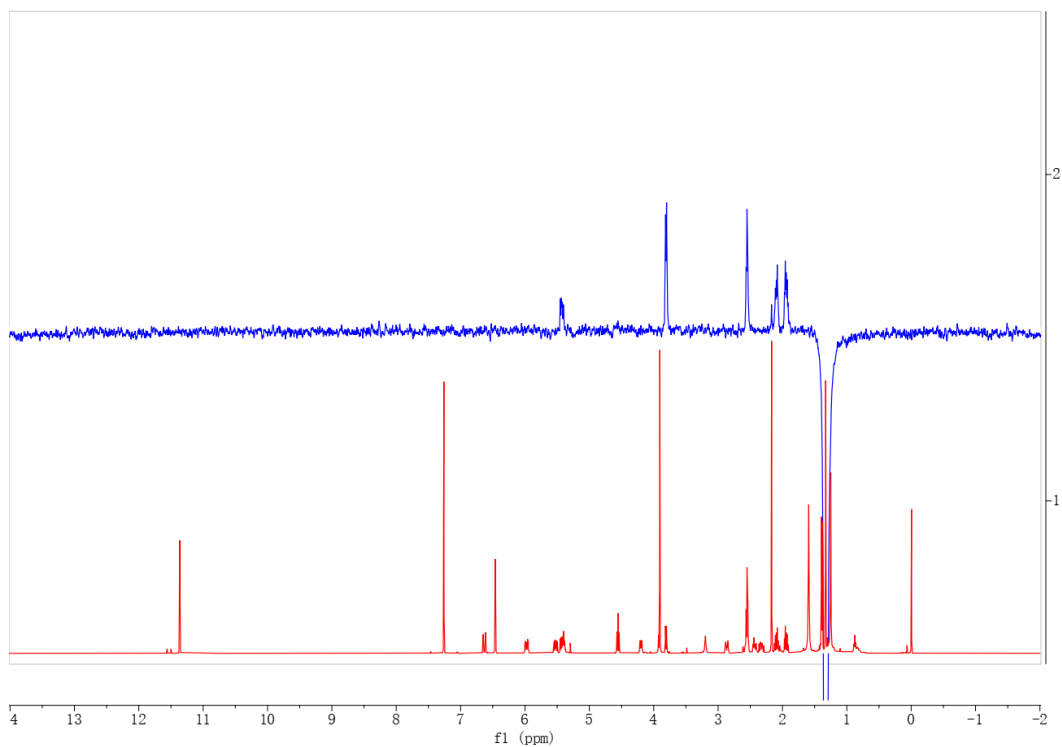


Figure S75. 1D NOE spectrum of compound **30**

5 #1073 RT: 15.20 AV: 1 NL: 2.05E4
T: FTMS + p ESIFull.ms [180.00-1000.00]

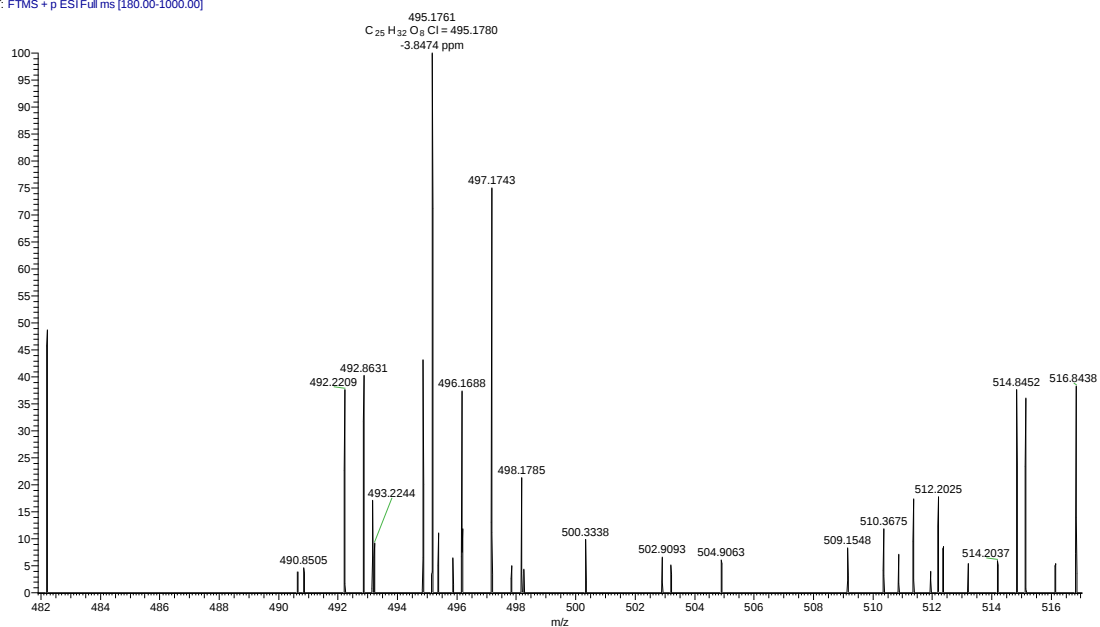


Figure S76. HR-ESI-MS spectrum of compound **30**.

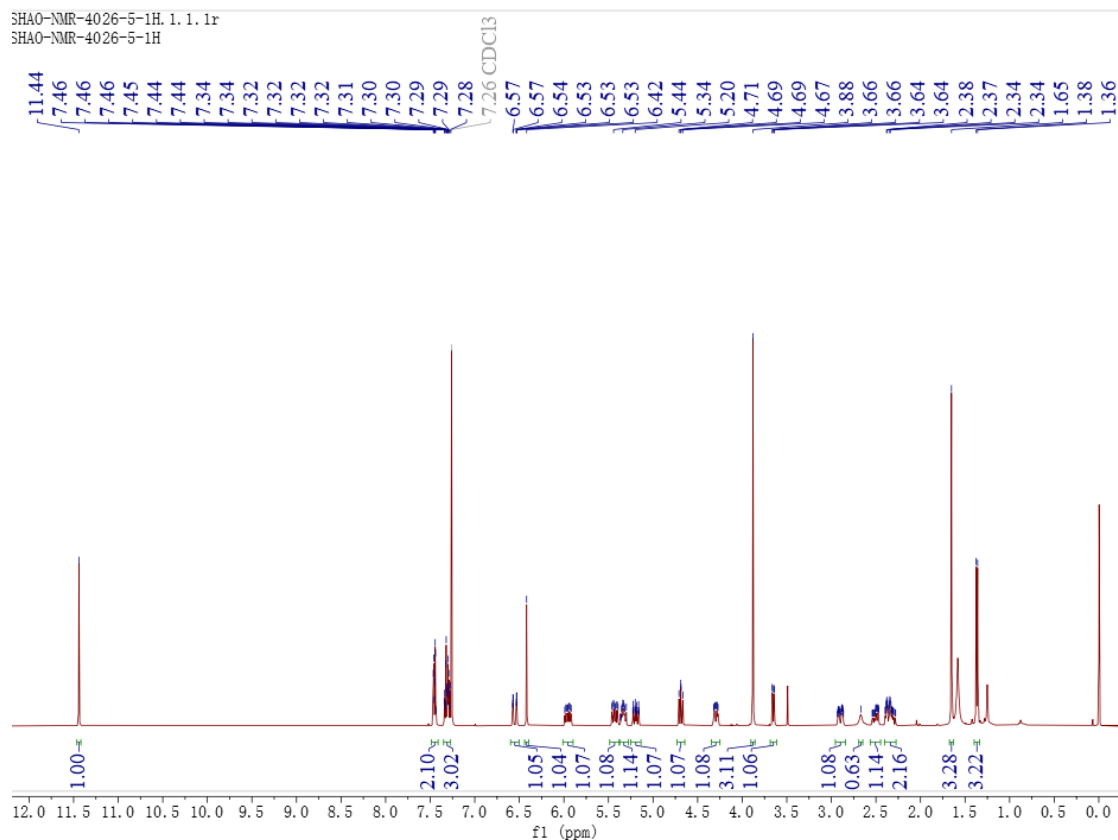


Figure S77. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound **31**.

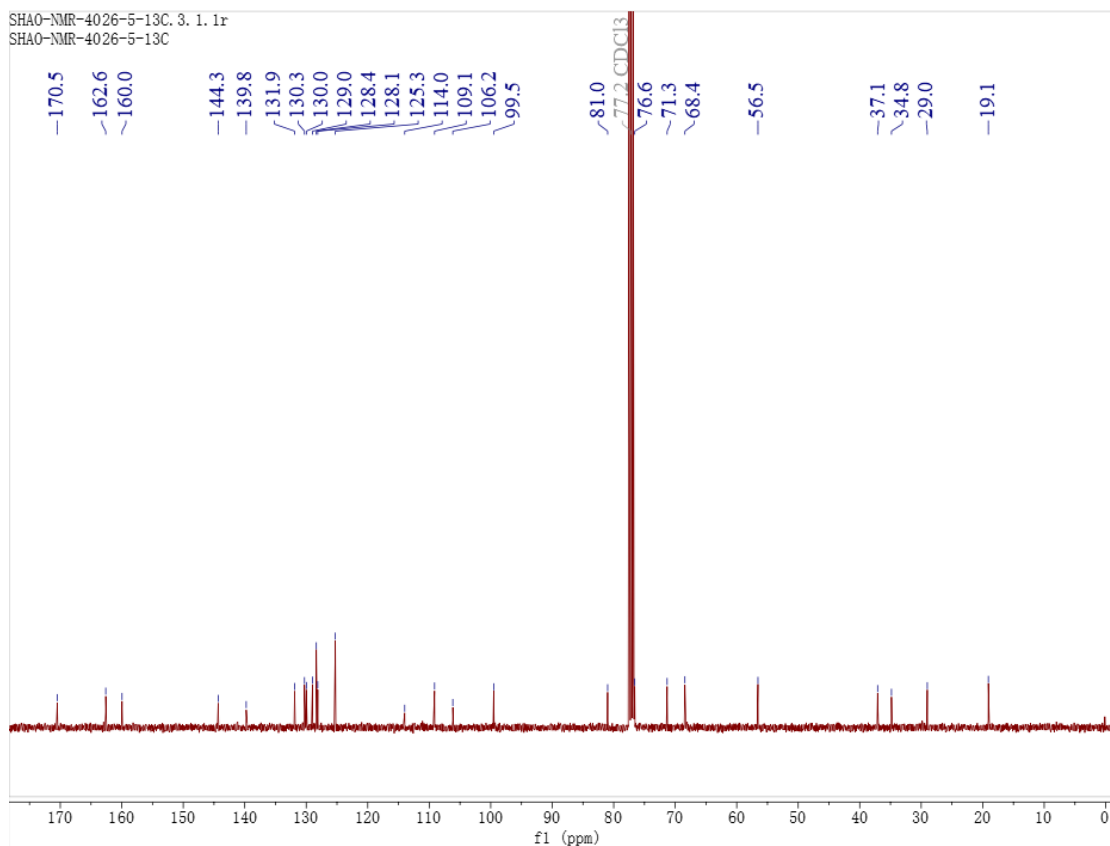


Figure S78. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound **31**.

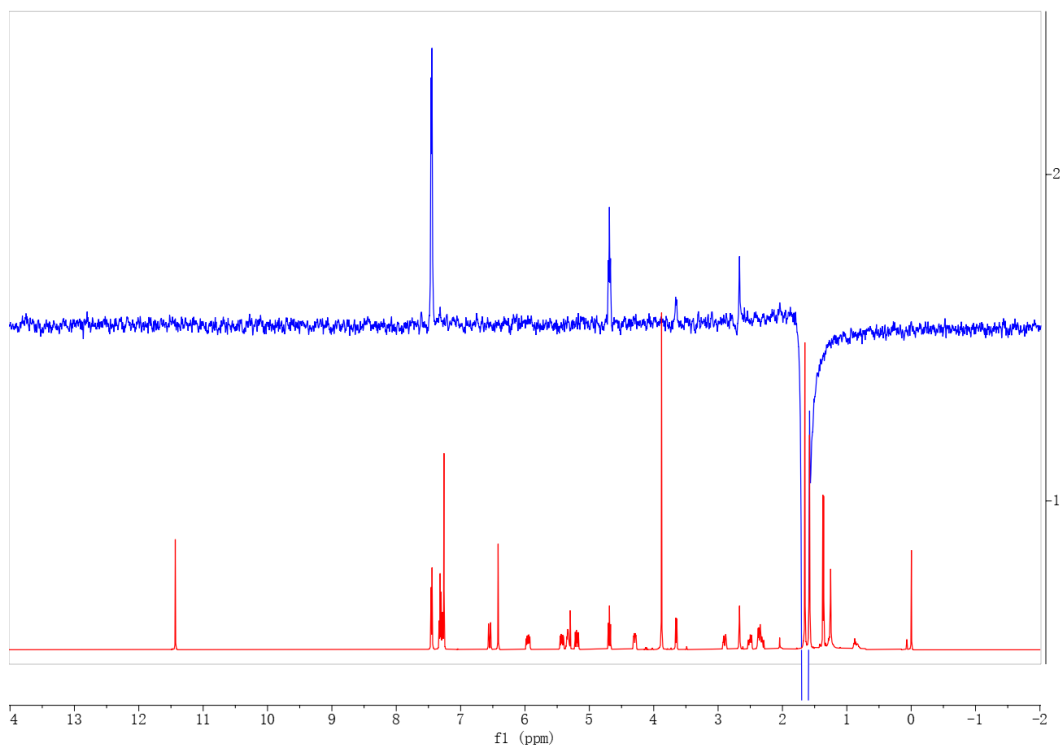


Figure S79. 1D NOE spectrum of compound **31**

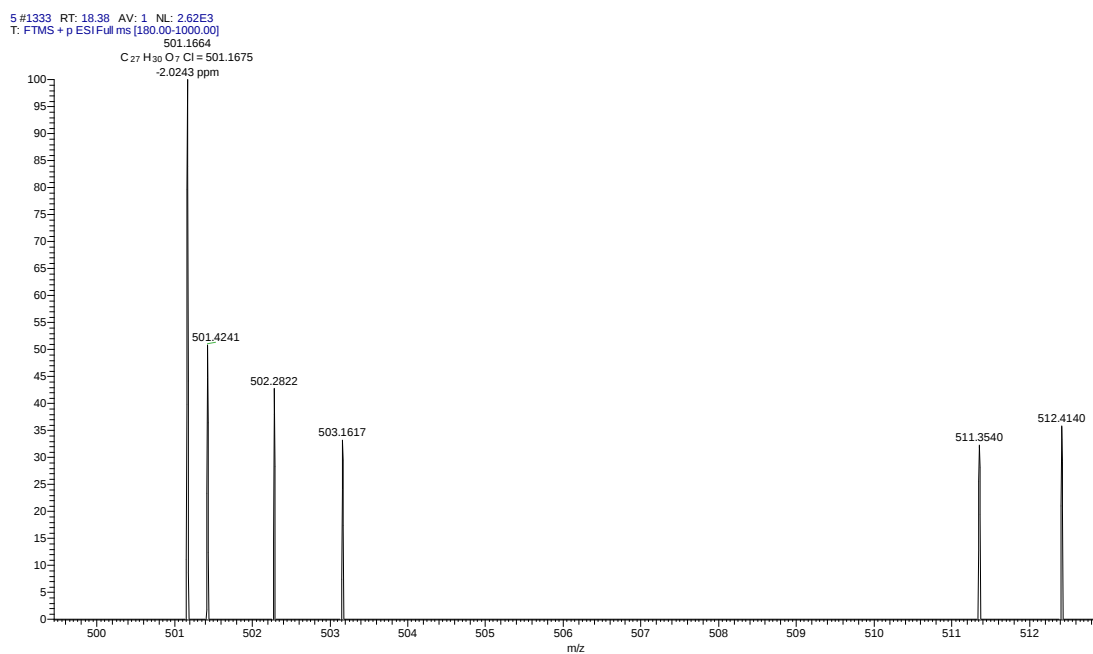


Figure S80. HR-ESI-MS spectrum of compound **31**.

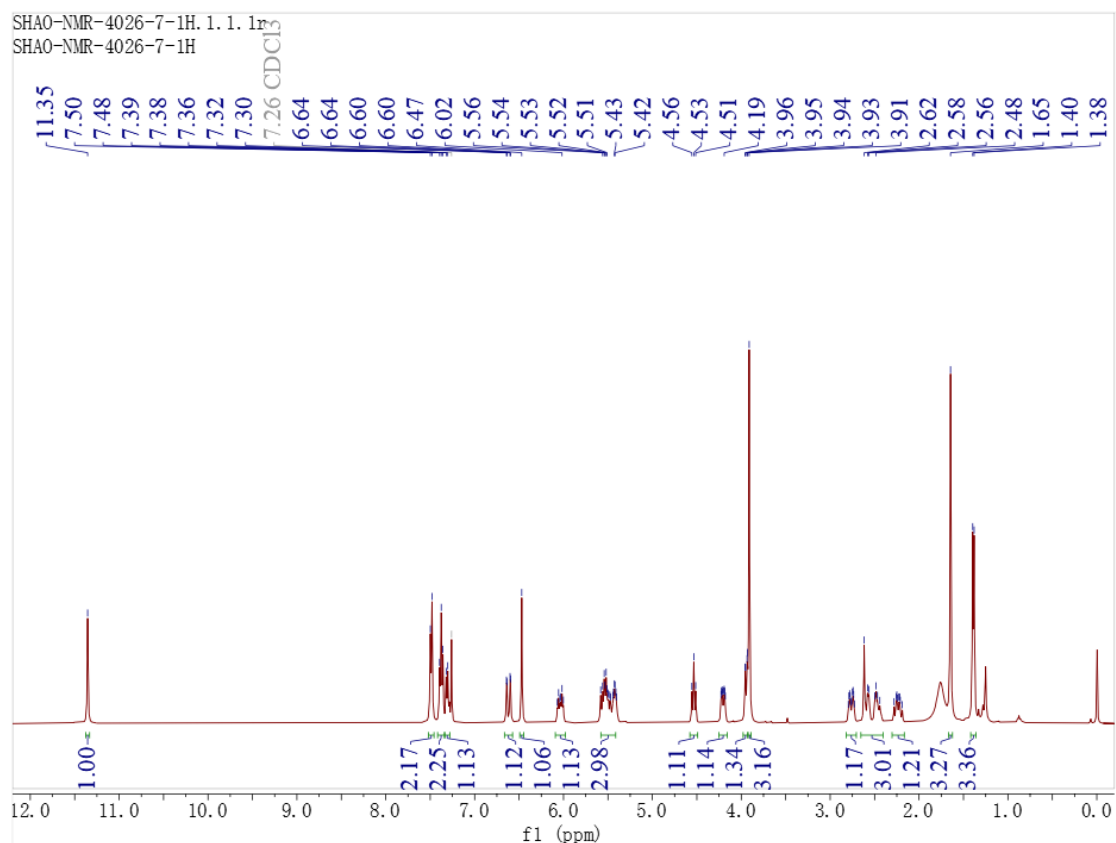


Figure S81. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound **32**.

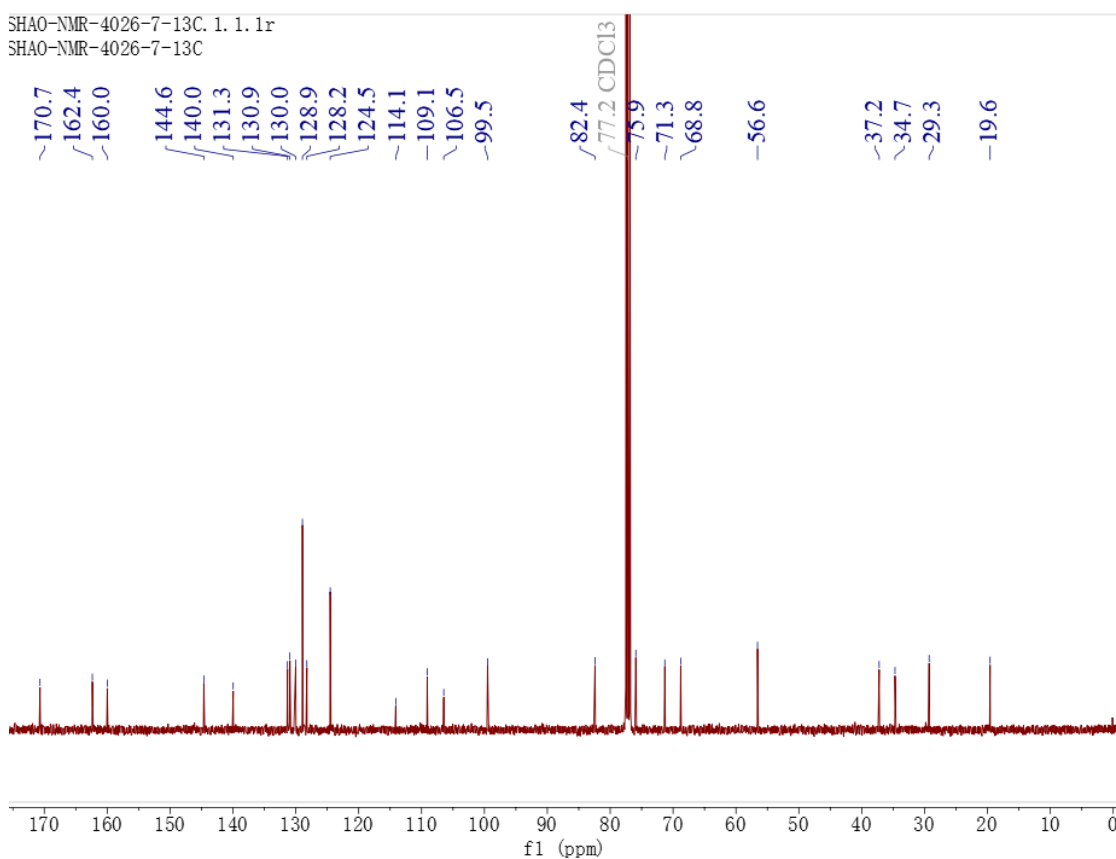


Figure S82. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound **32**.

6 #1299 RT: 18.31 AV: 1 NL: 4.44E3
T: FTMS + p ESI Full ms [180.00-1000.00]

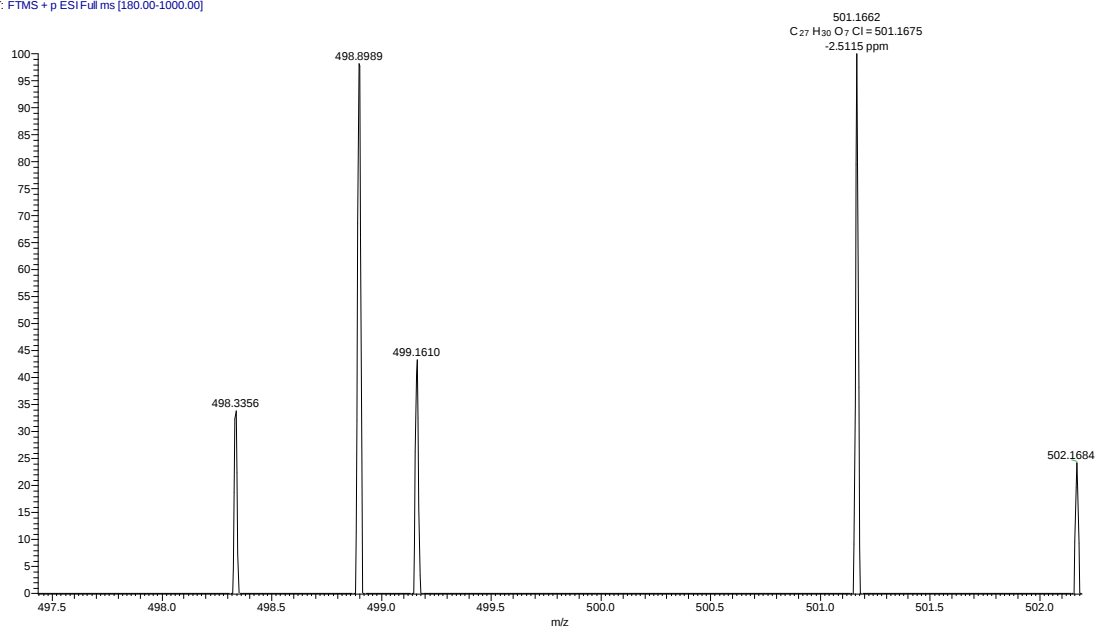


Figure S83. HR-ESI-MS spectrum of compound 32.

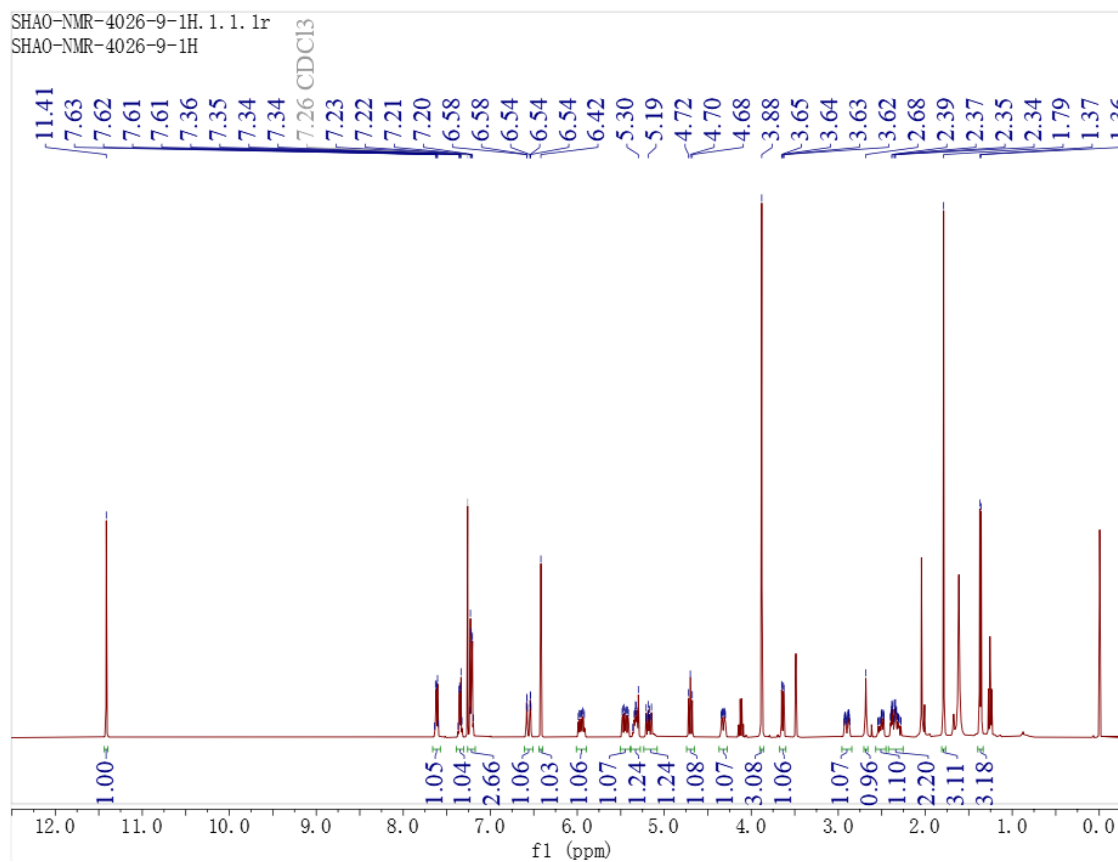


Figure S84. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 33.

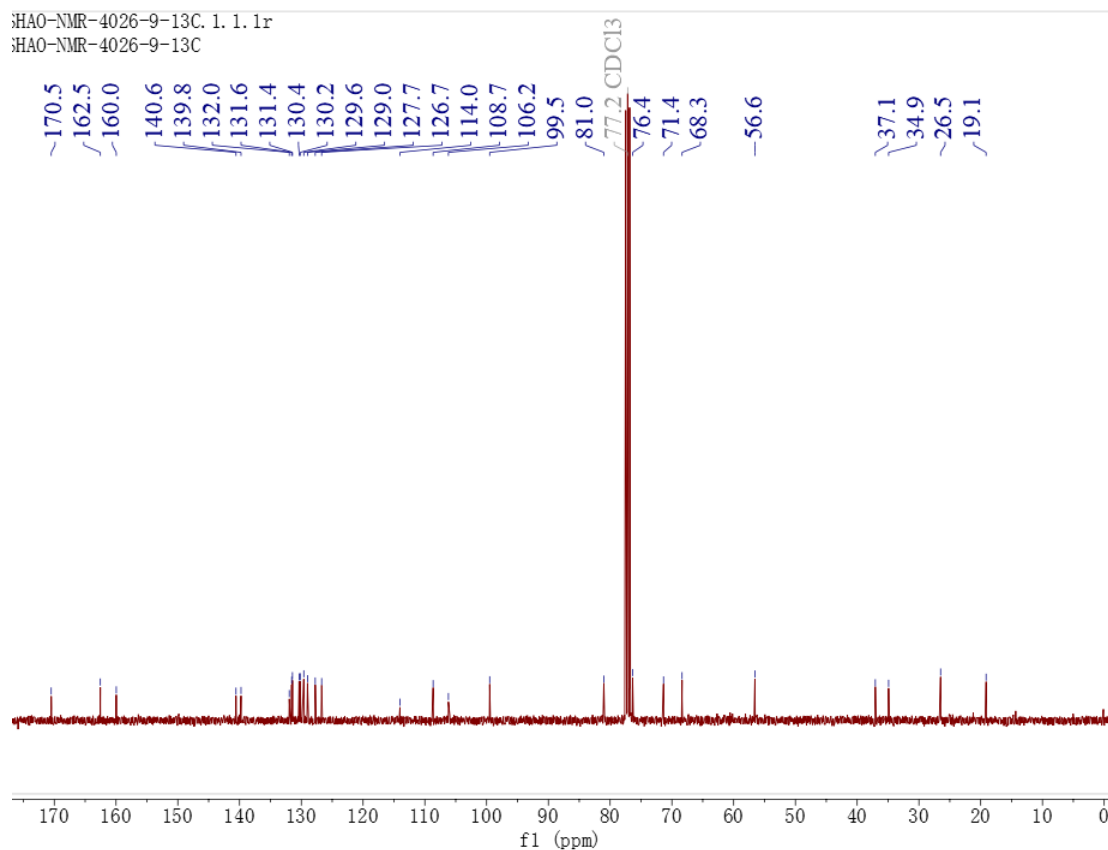


Figure S85. ^{13}C NMR (100 MHz, Chloroform- d) spectrum of compound **33**.

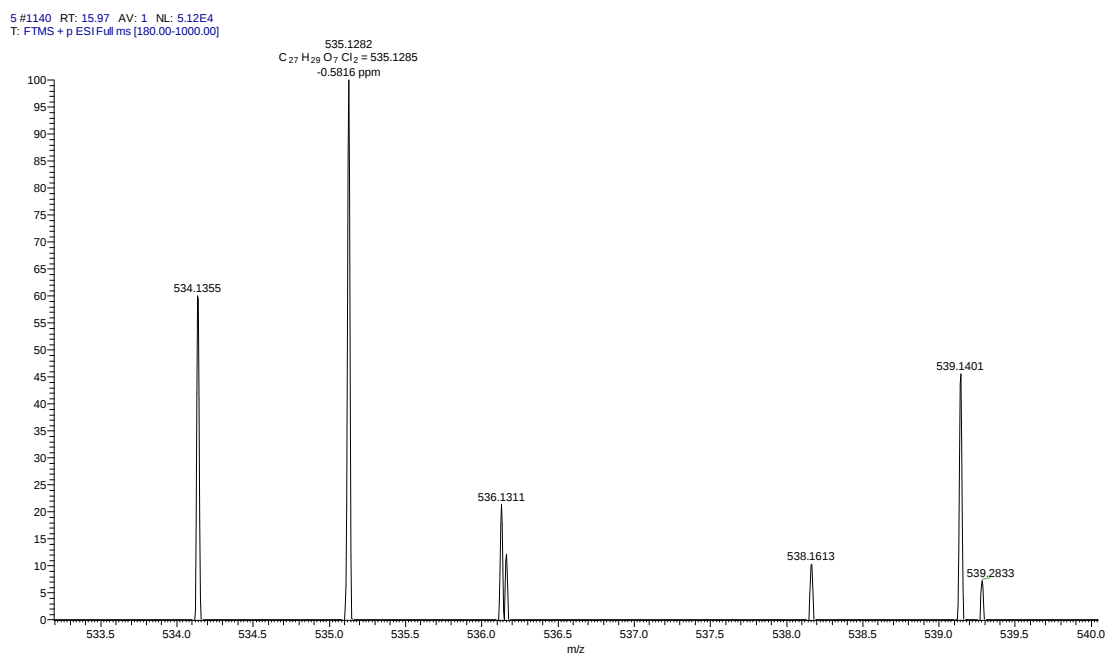


Figure S86. HR-ESI-MS spectrum of compound **33**.

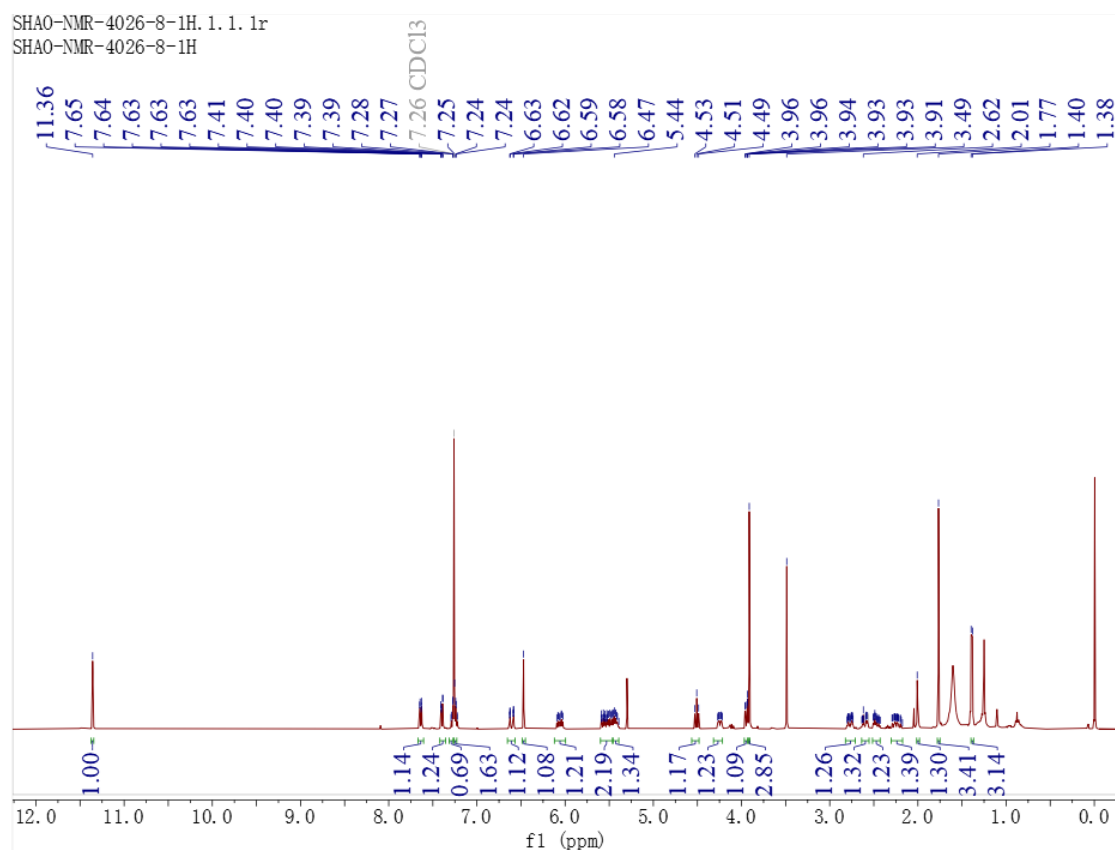


Figure S87. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound **34**.

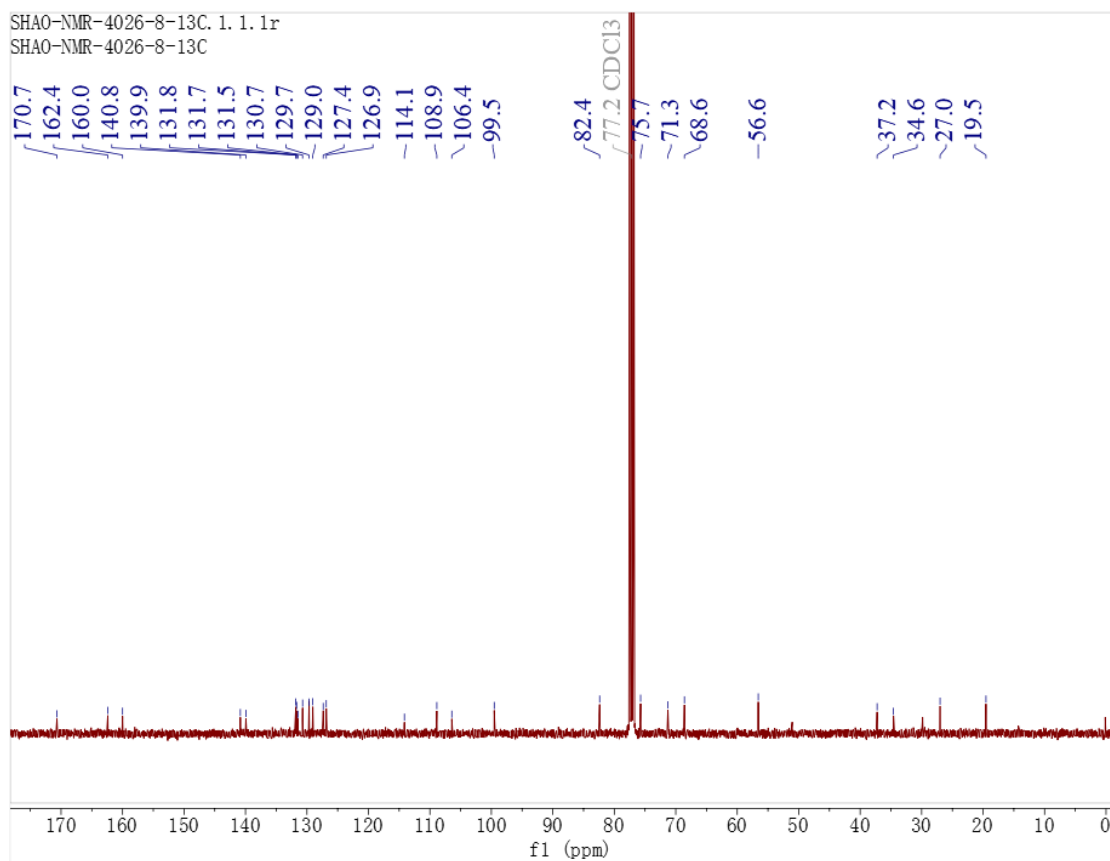


Figure S88. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound **34**.

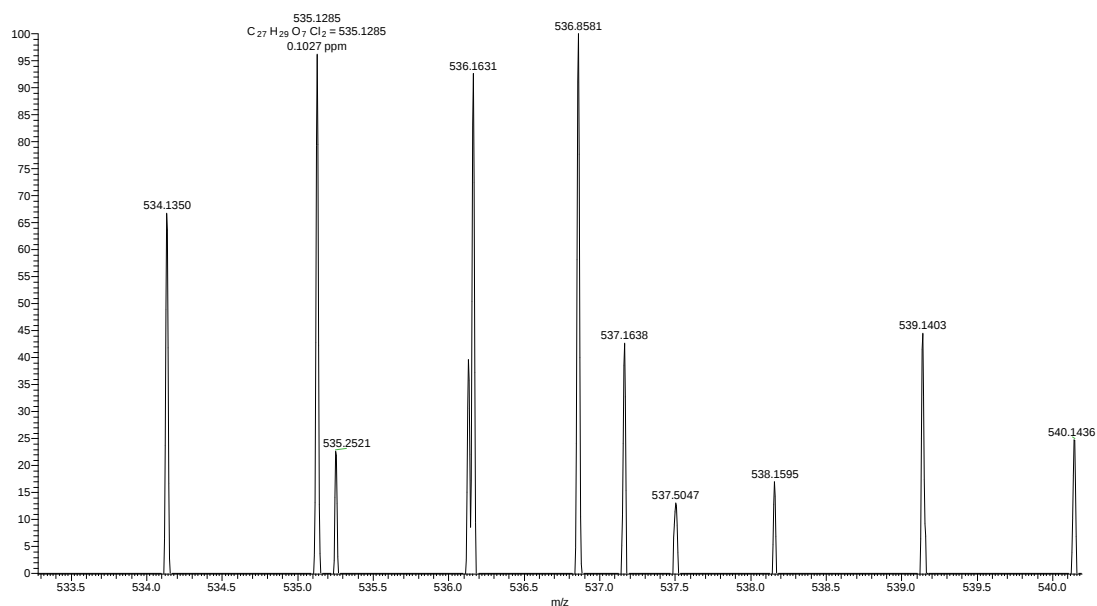


Figure S89. HR-ESI-MS spectrum of compound 34.

SHA0-NMR-4026-11-1H. 1. 1. 1r
SHA0-NMR-4026-11-1H

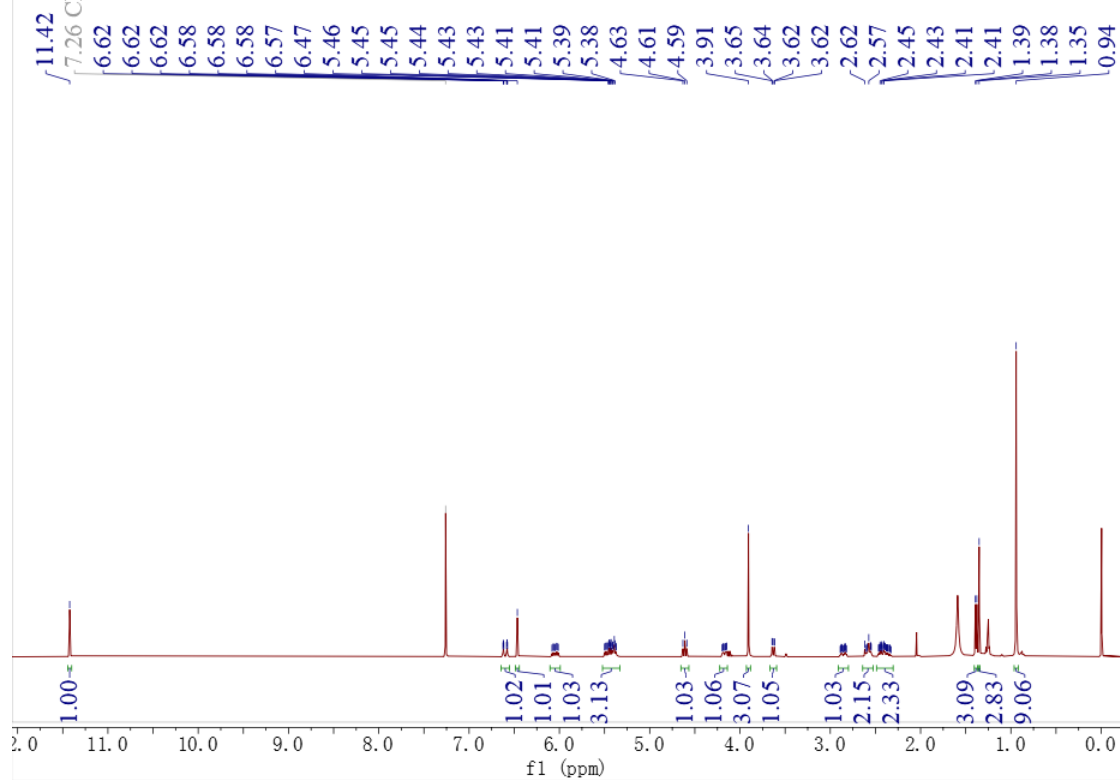


Figure S90. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 35.

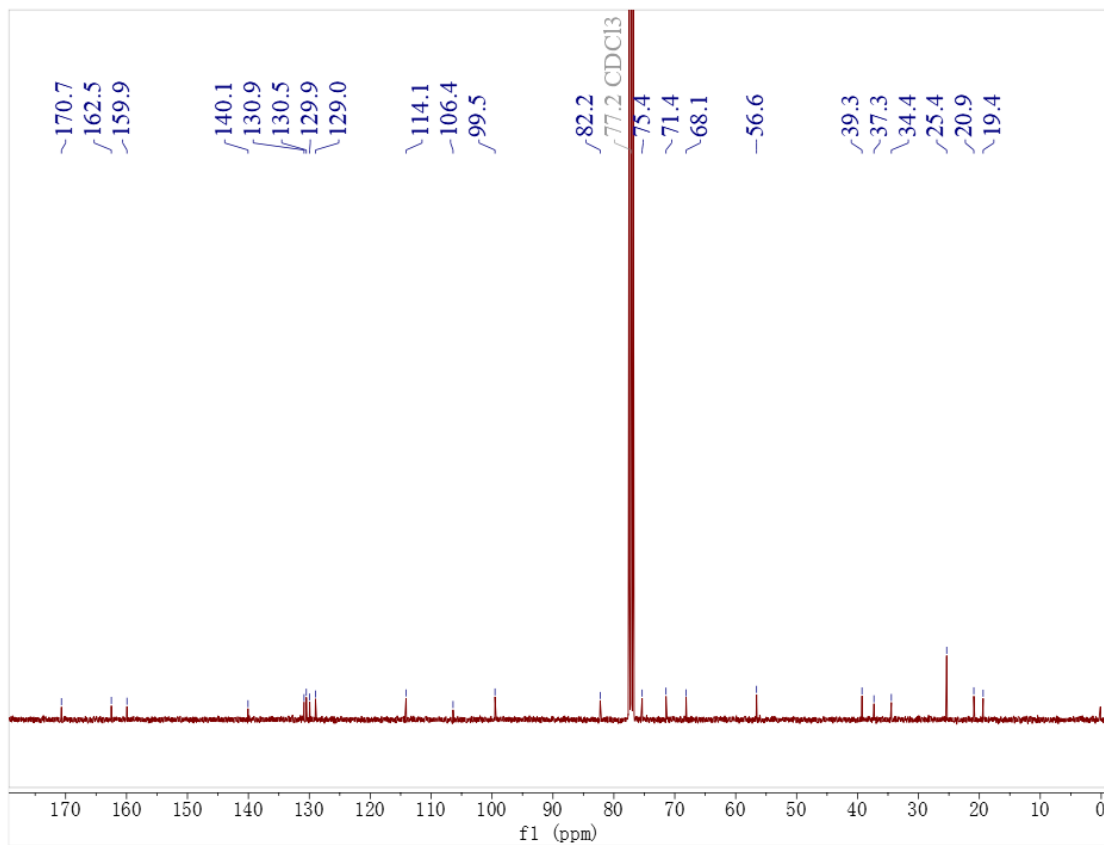


Figure S91. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound **35**.

5 #1416 RT: 19.46 AV: 1 NL: 2.57E3
T: FTMS + p ESI Full ms [180.00-1000.00]

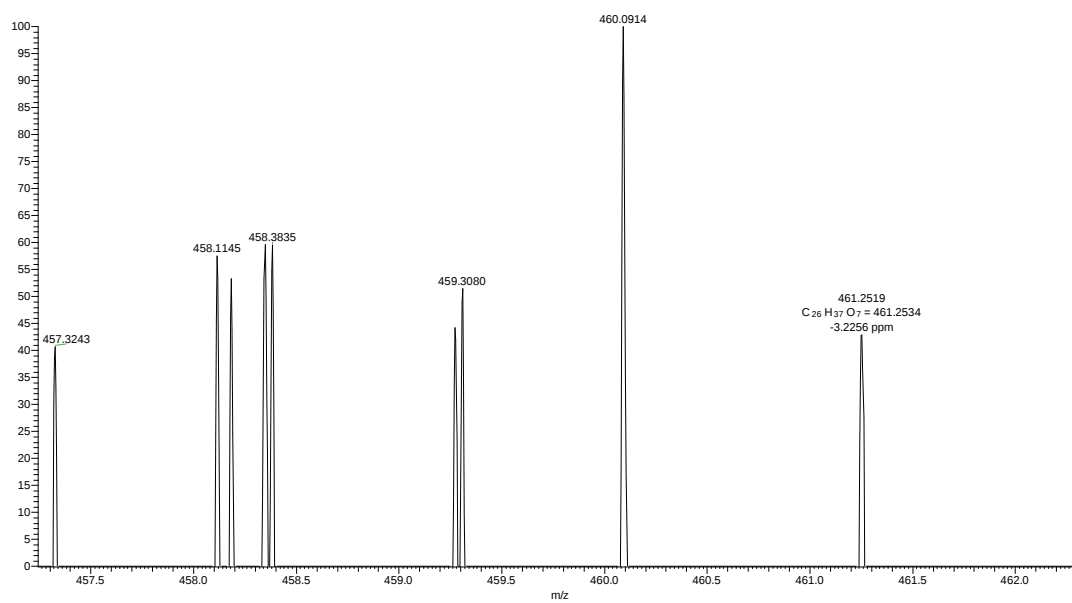


Figure S92. HR-ESI-MS spectrum of compound **35**.

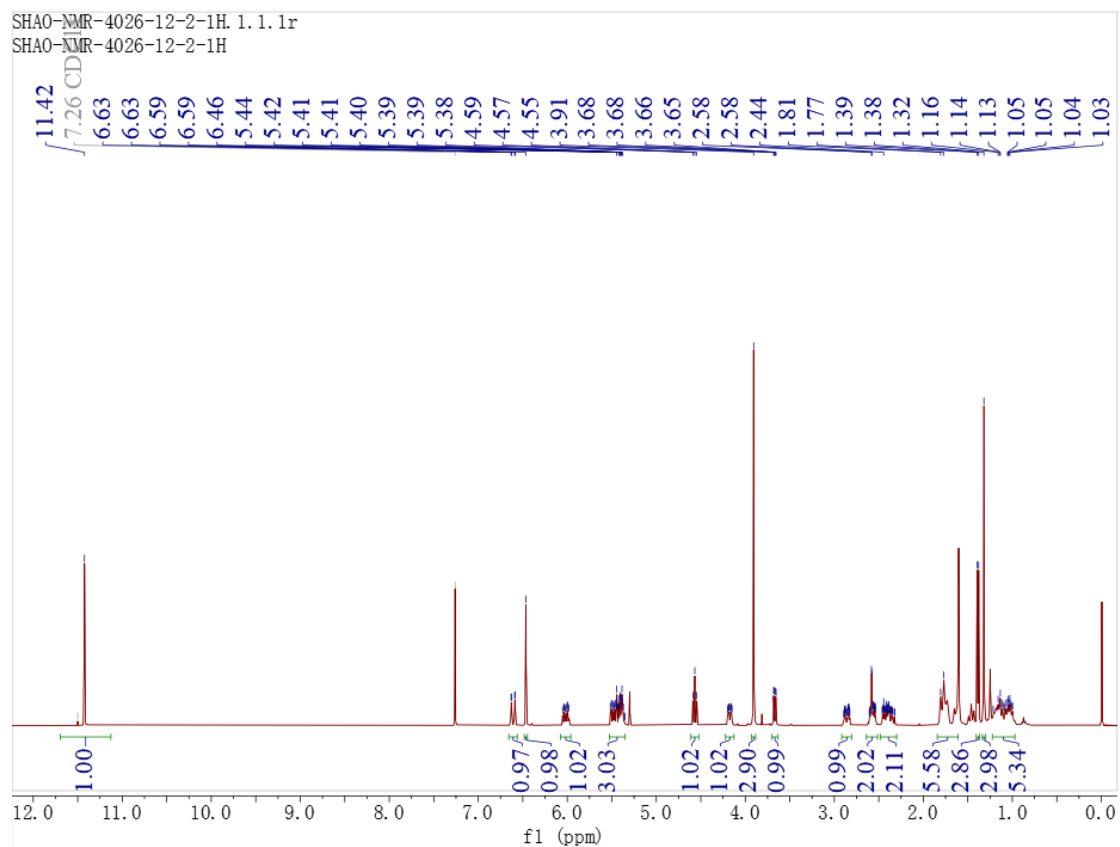


Figure S93. ^1H NMR (400 MHz, Chloroform-*d*) spectrum of compound **36**.

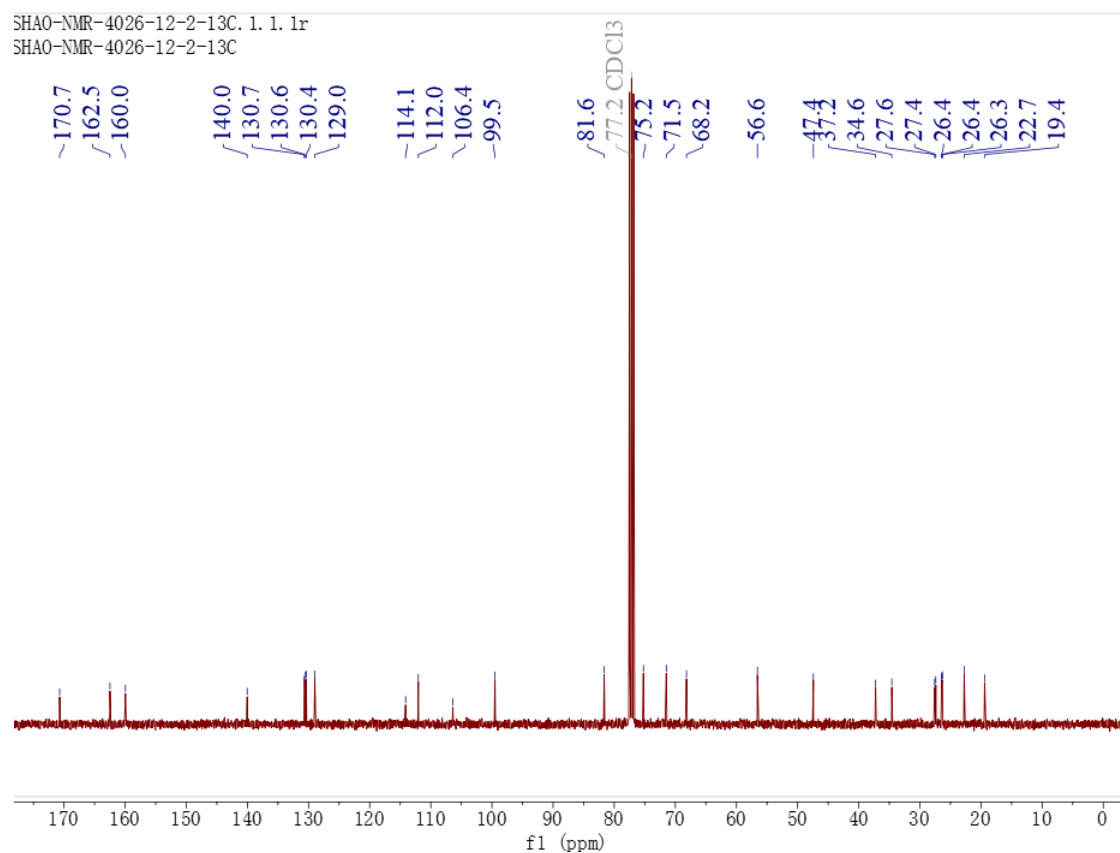


Figure S94. ^{13}C NMR (100 MHz, Chloroform-*d*) spectrum of compound **36**.

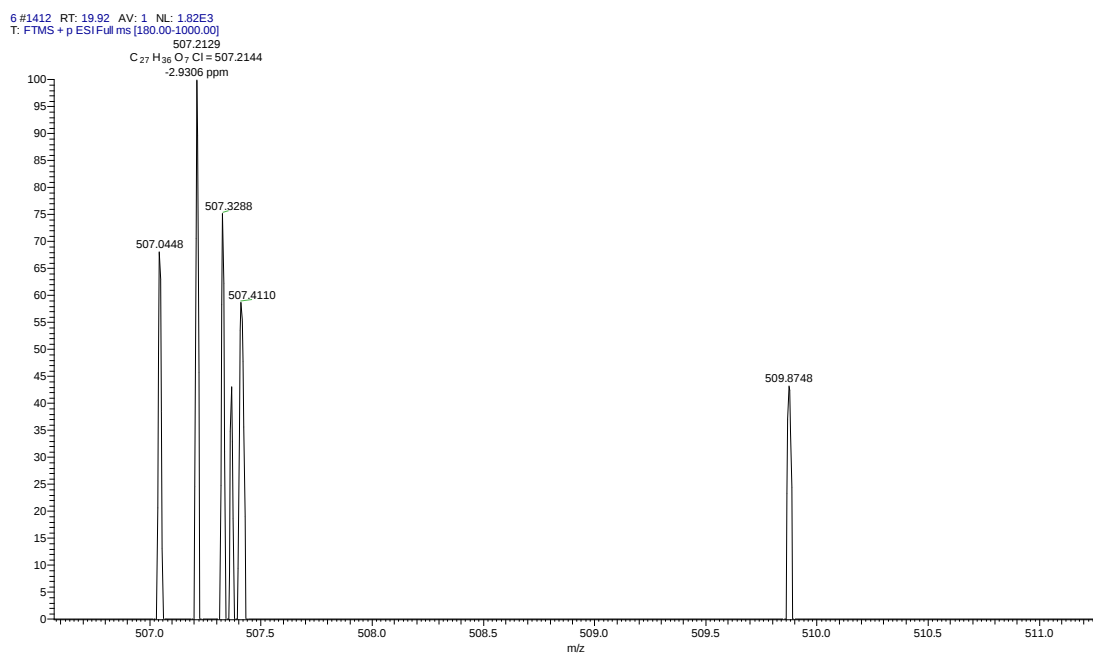


Figure S95. HR-ESI-MS spectrum of compound 36.

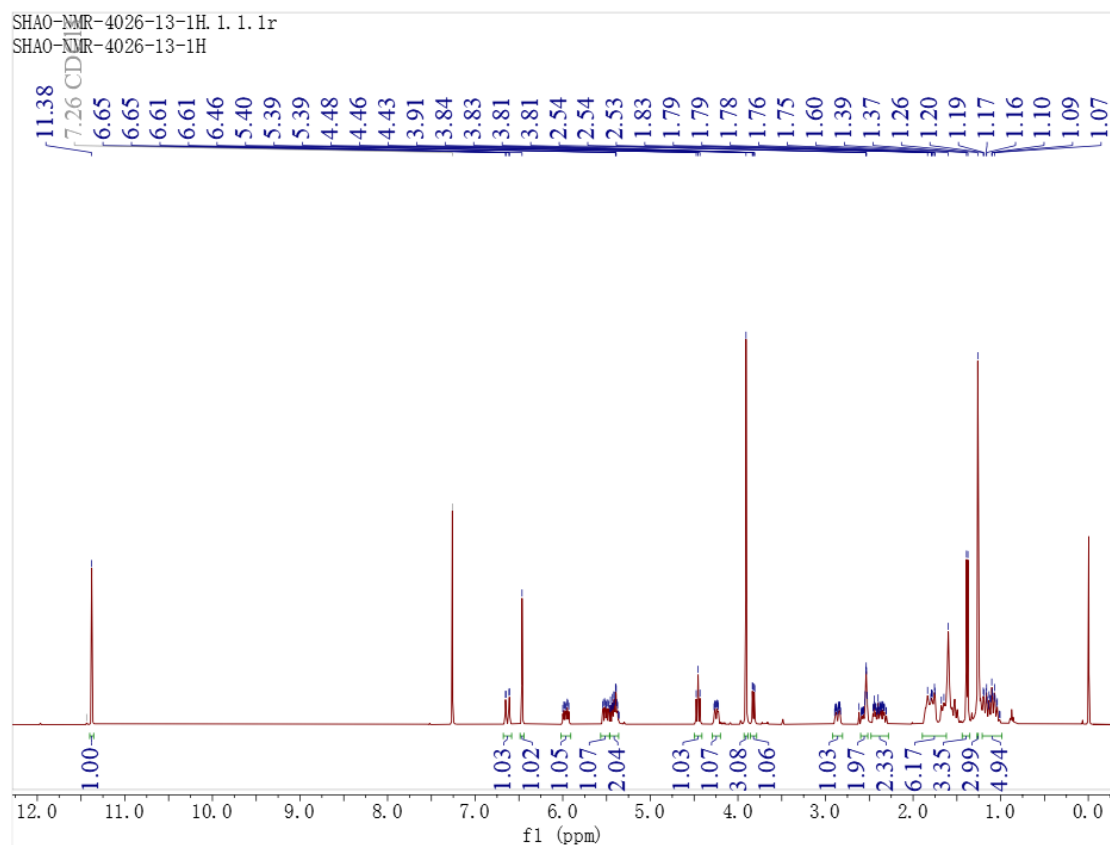


Figure S96. ¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound 37.

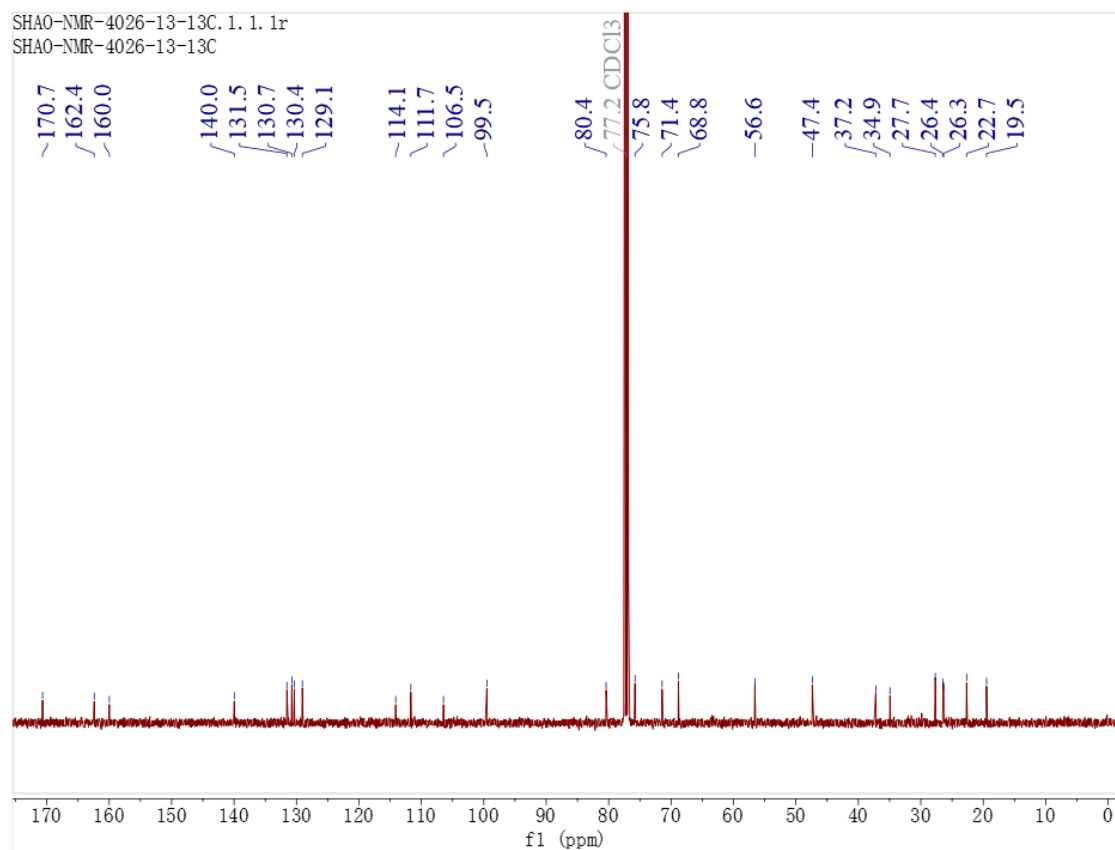


Figure S97. ¹³C NMR (100 MHz, Chloroform-*d*) spectrum of compound 37.

S #566 RT: 8.12 AV: 1 NL: 1.27E3
T: FTMS + p ESI Full ms [180.00-1000.00]

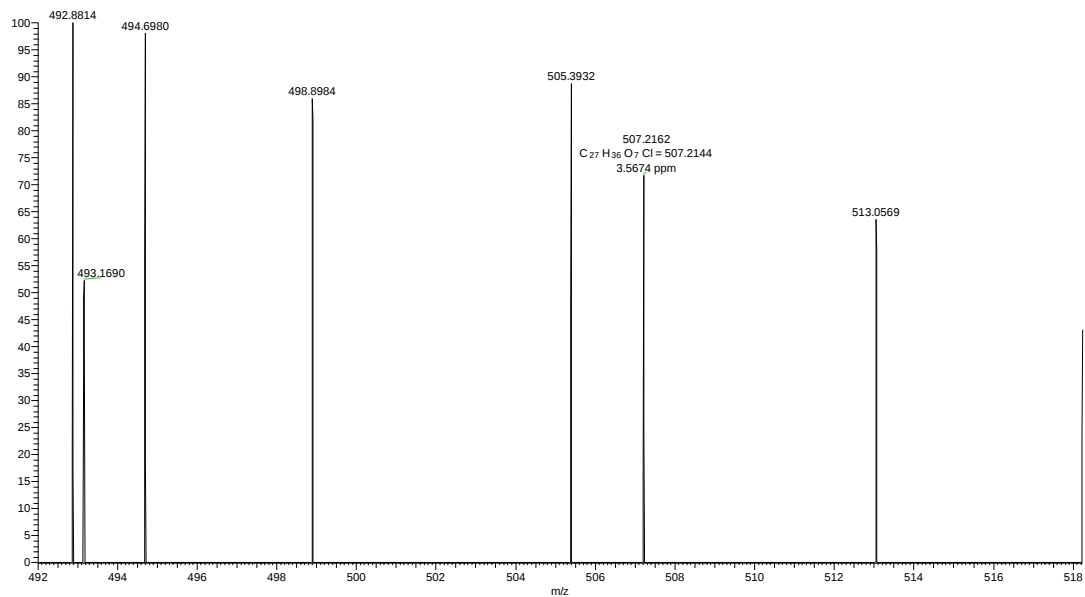


Figure S98. HR-ESI-MS spectrum of compound 37.