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Supporting Information

Malonylginsenosides with Potential Antidiabetic Activities from the Flower Buds of *Panax ginseng*

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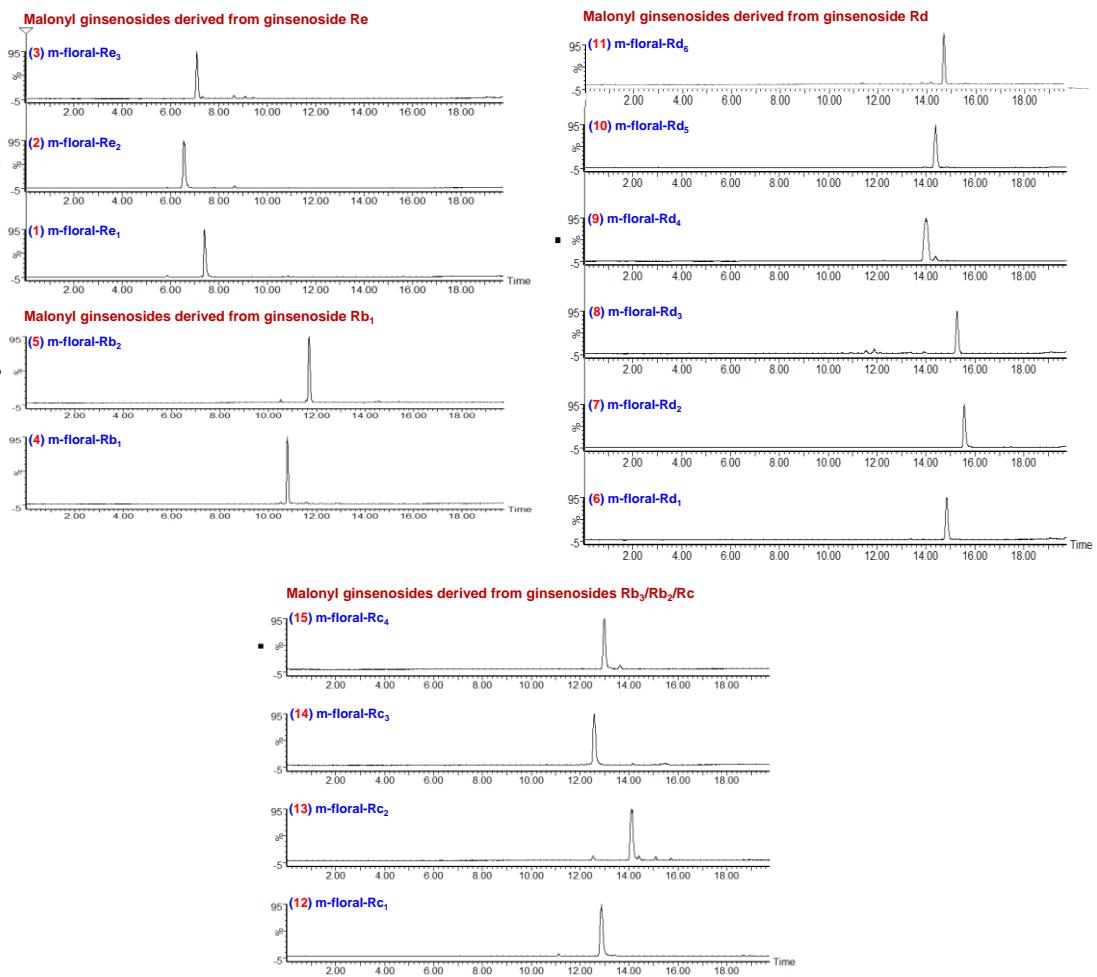


Figure S1. Purity determination of 15 new malonyl-ginsenosides isolated in this study by UHPLC/QTOF MS.

(1) m-floral-Re₁

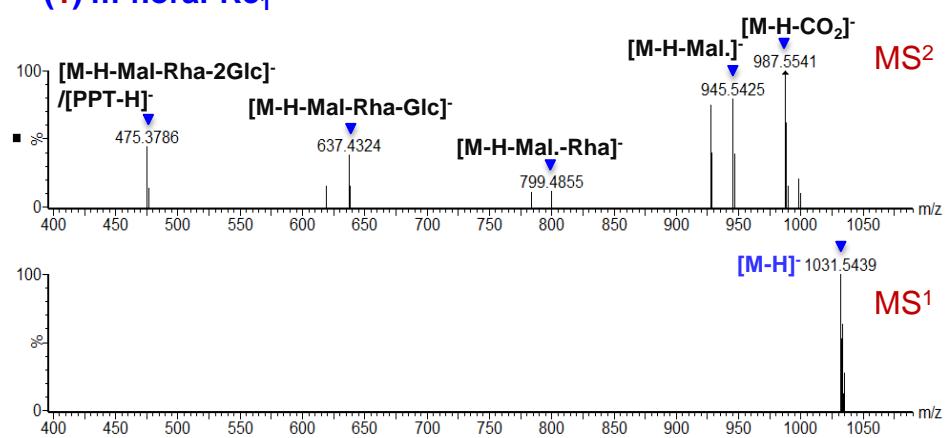


Figure S2. HRESIMS spectrum of compound **1**.

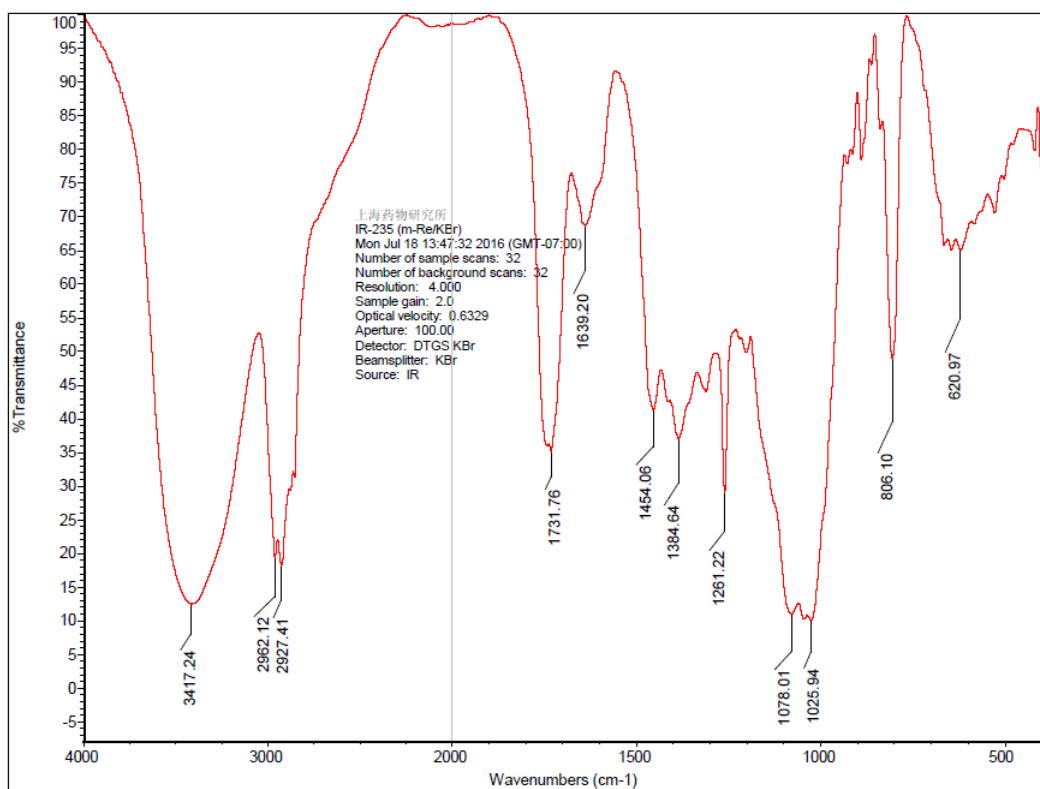


Figure S3. IR spectrum of compound **1**.

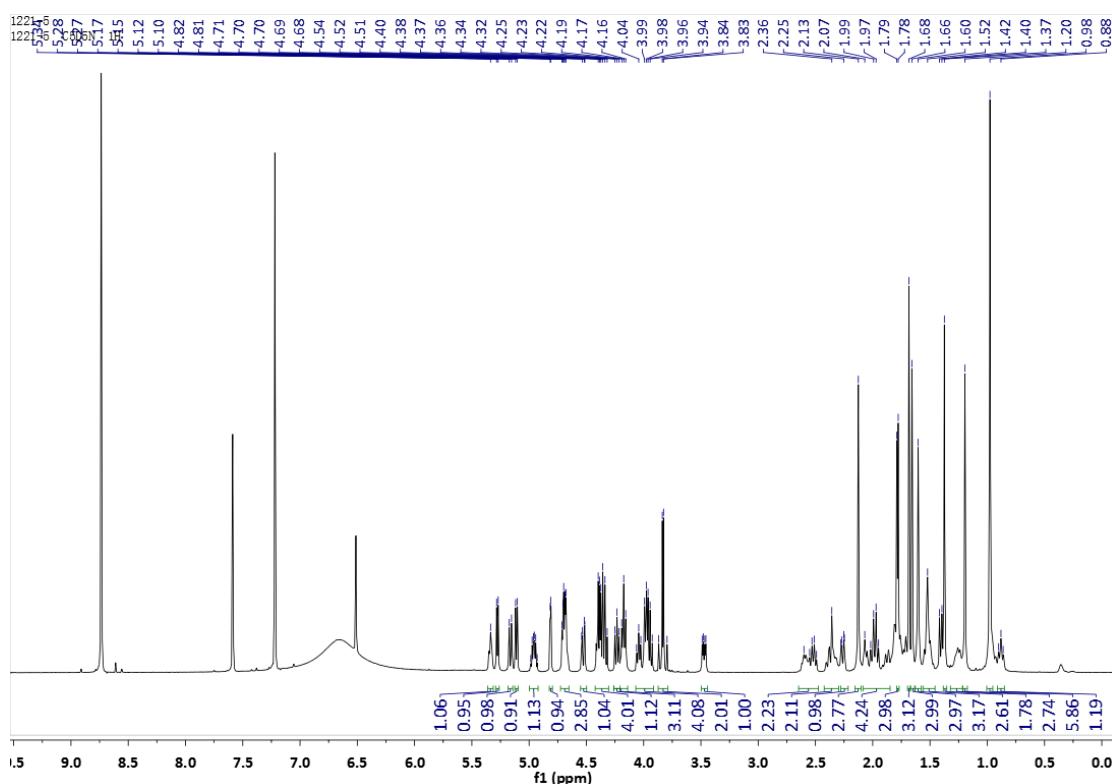


Figure S4. ^1H NMR spectrum of compound 1.

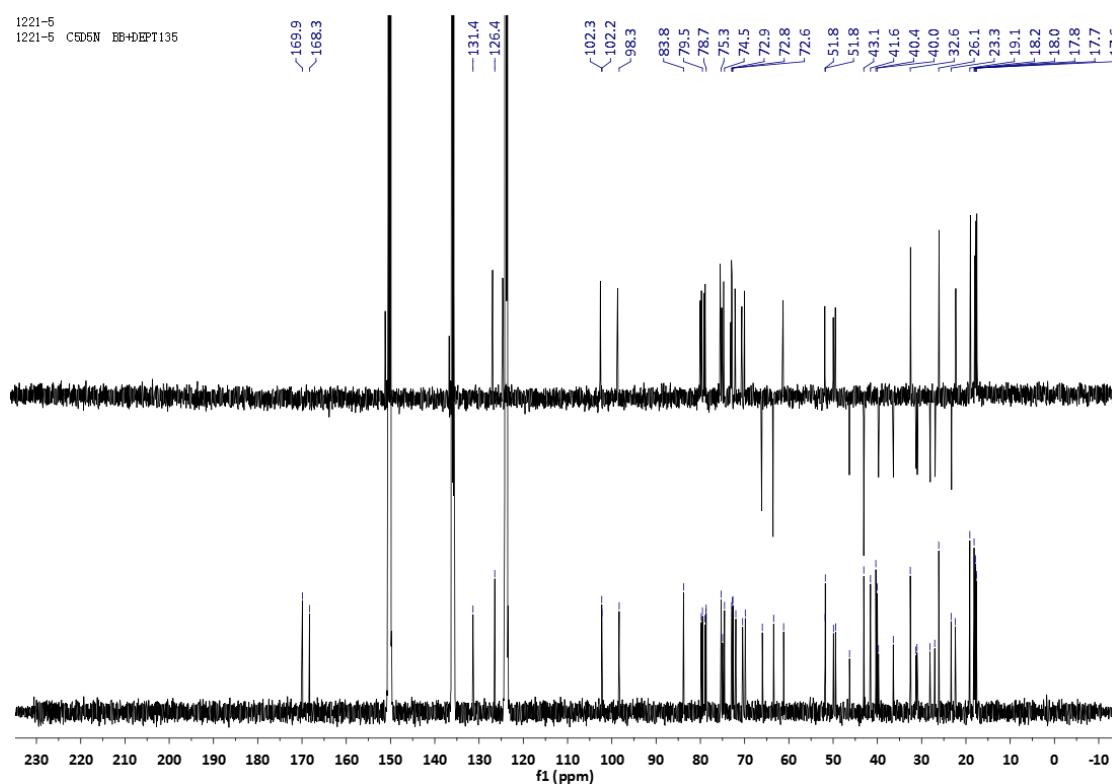


Figure S5. ^{13}C NMR and DEPT-135 spectra of compound 1.

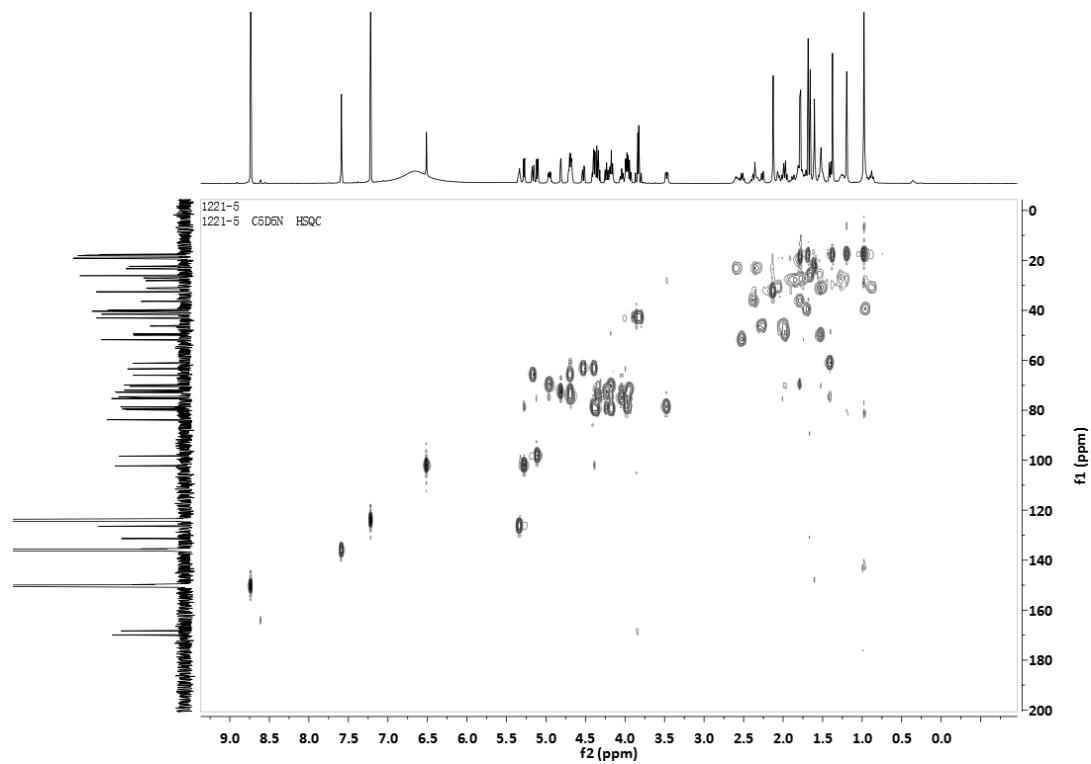


Figure S6. HSQC spectrum of compound 1.

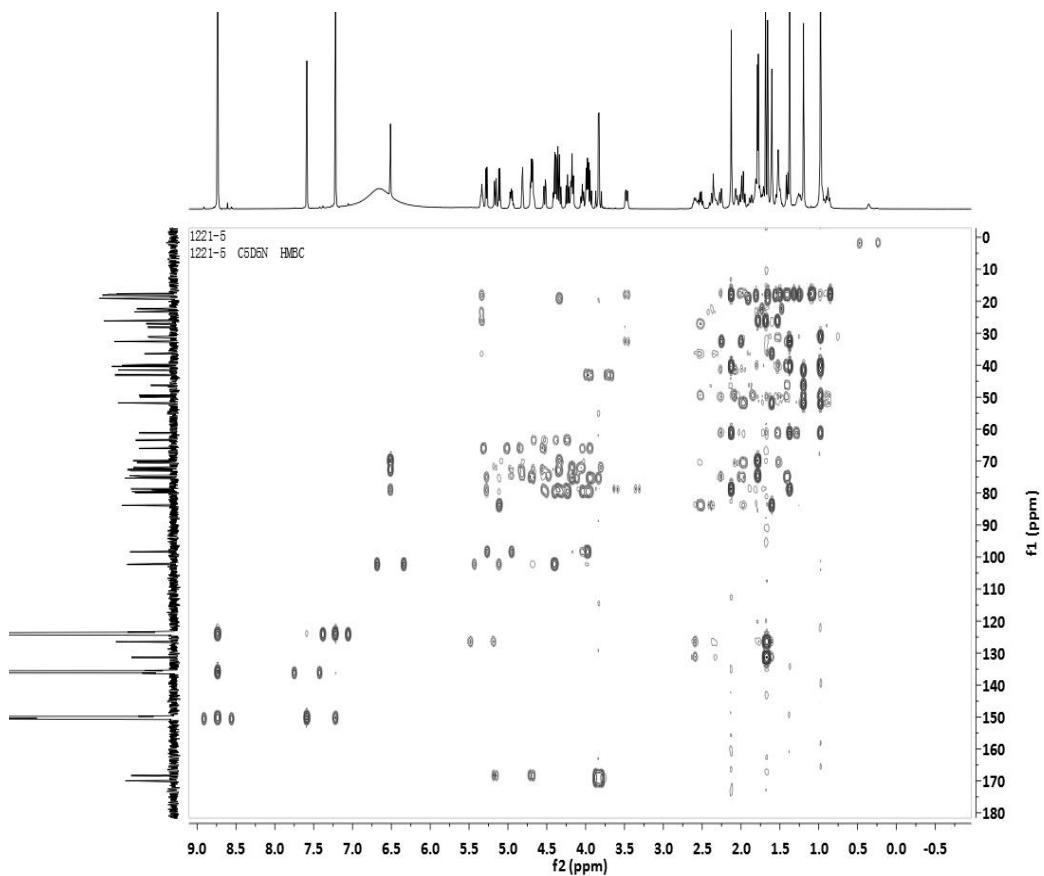


Figure S7. HMBC spectrum of compound 1.

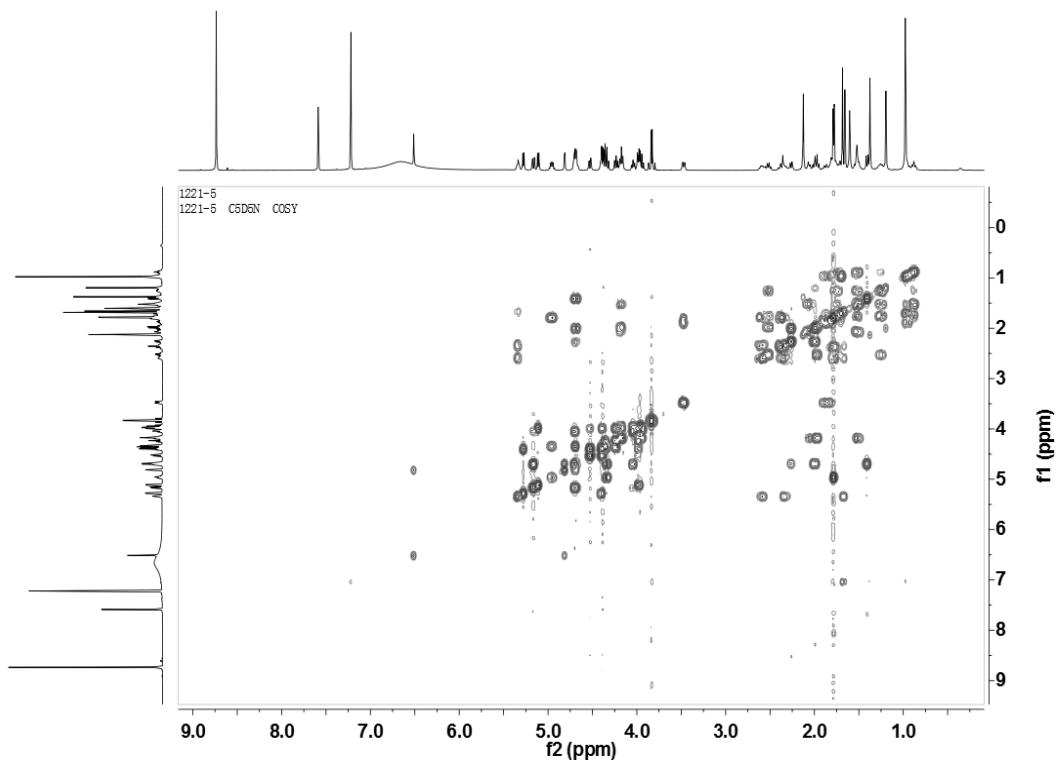


Figure S8. ^1H - ^1H COSY spectrum of compound **1**.

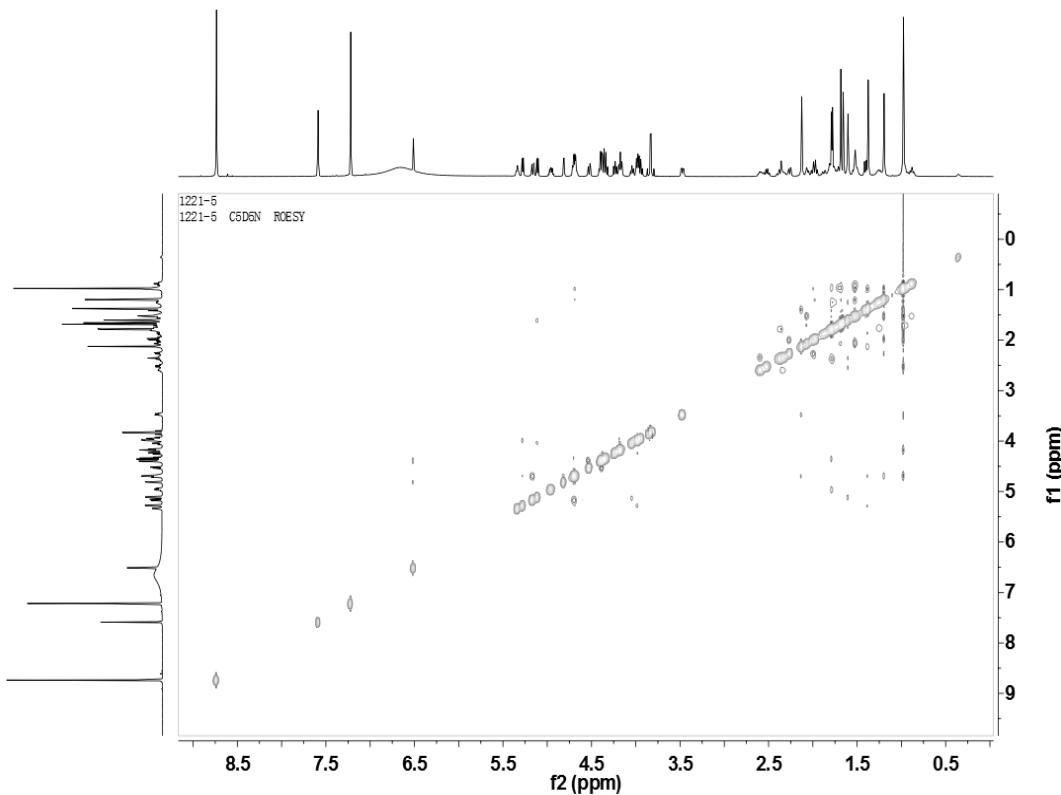


Figure S9. ROESY spectrum of compound **1**.

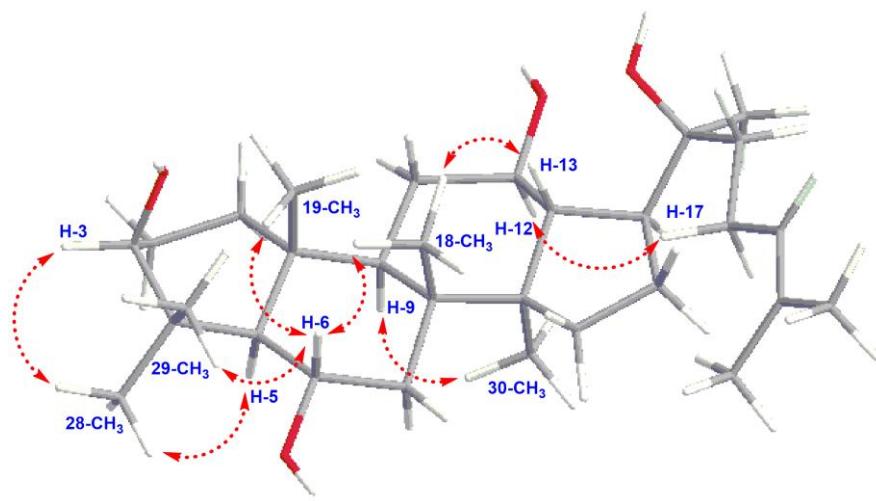


Figure S10. Key ROESY correlations of the sapogenin moiety of compound **1**.

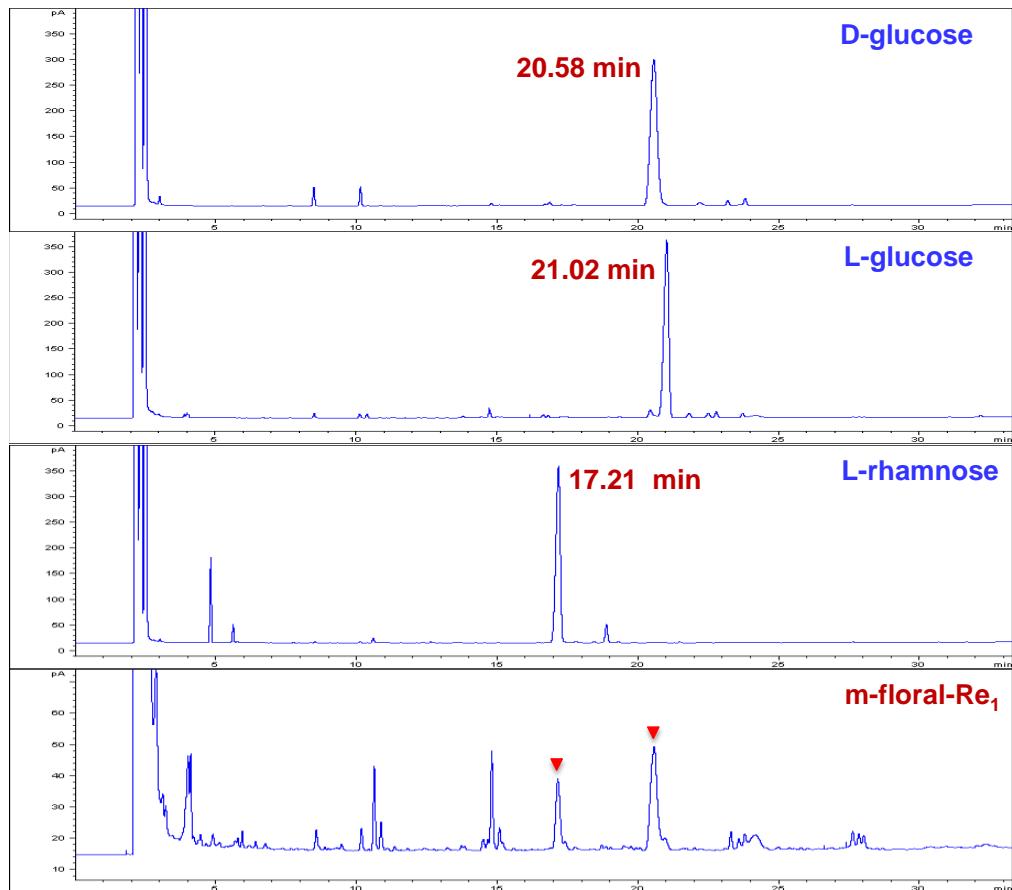


Figure S11. The GC chromatograms of compound **1** after acidic hydrolysis.

(2) m-floral-Re₂

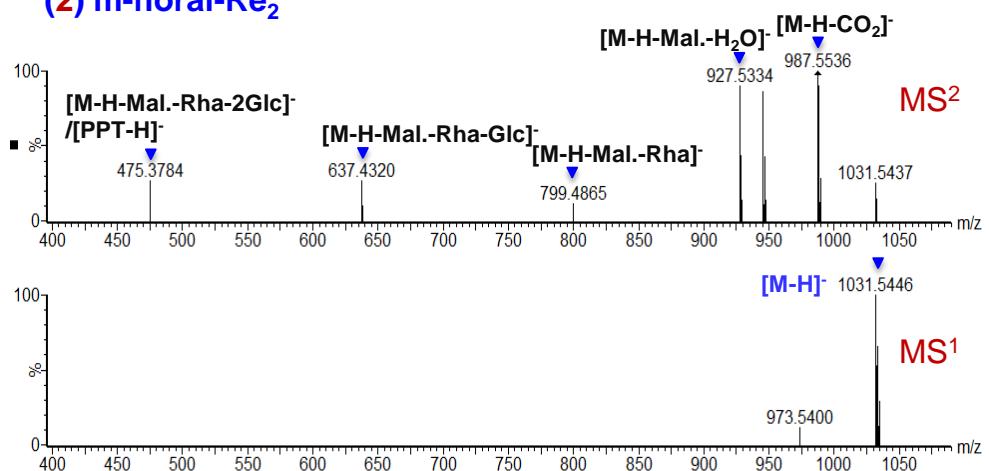


Figure S12. HRESIMS spectrum of compound 2.

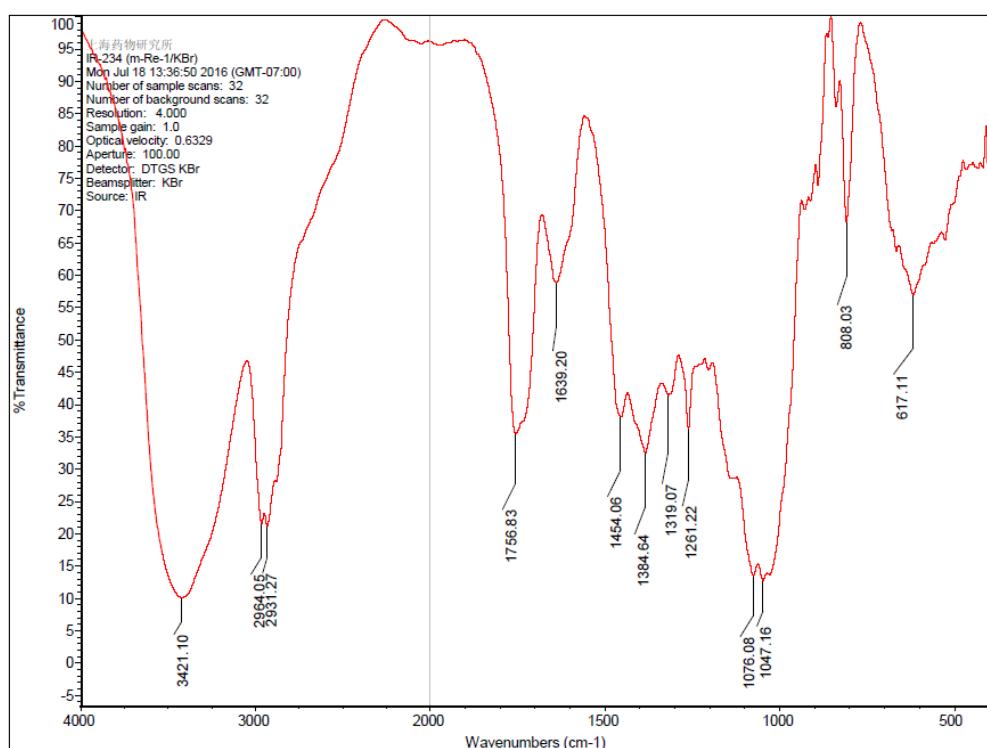


Figure S13. IR spectrum of compound 2.

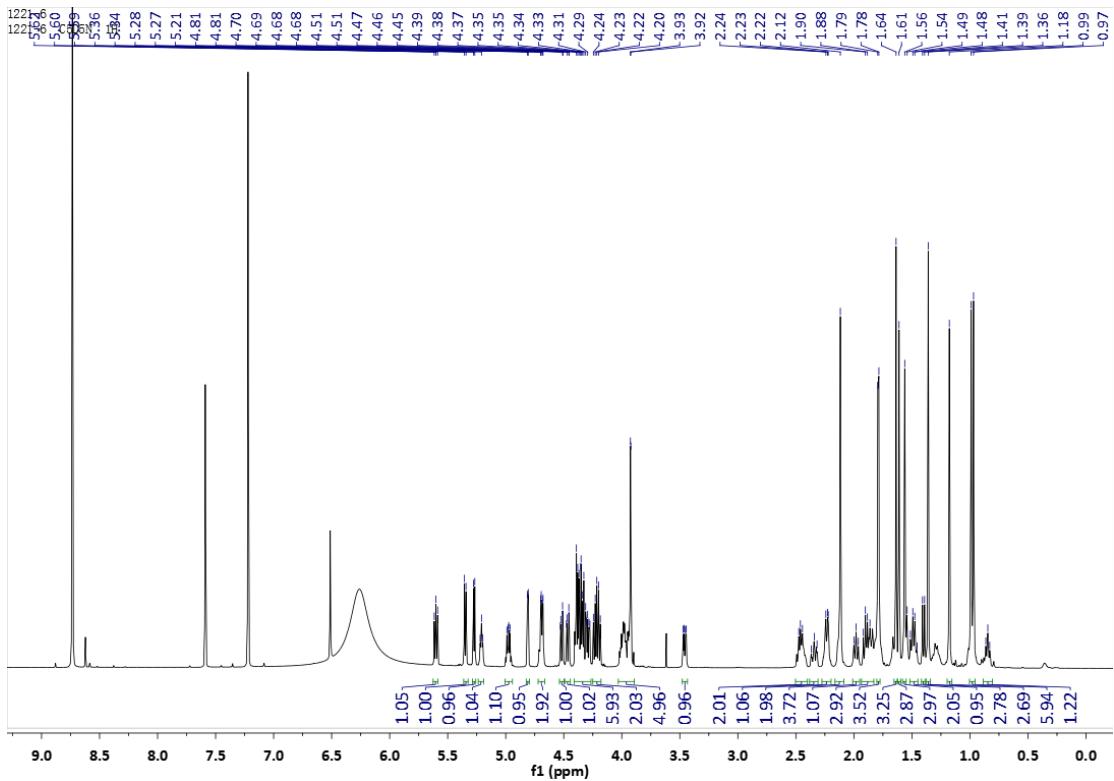


Figure S14. ^1H NMR spectrum of compound 2.

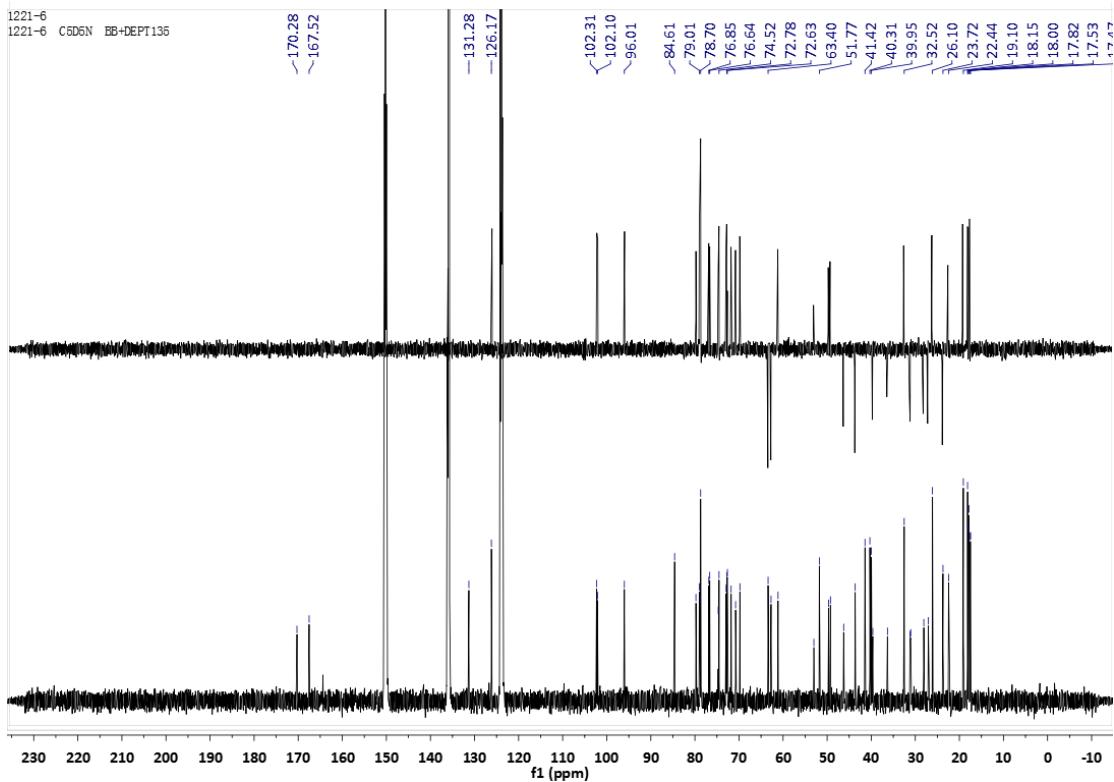


Figure S15. ^{13}C NMR and DEPT-135 spectra of compound 2.

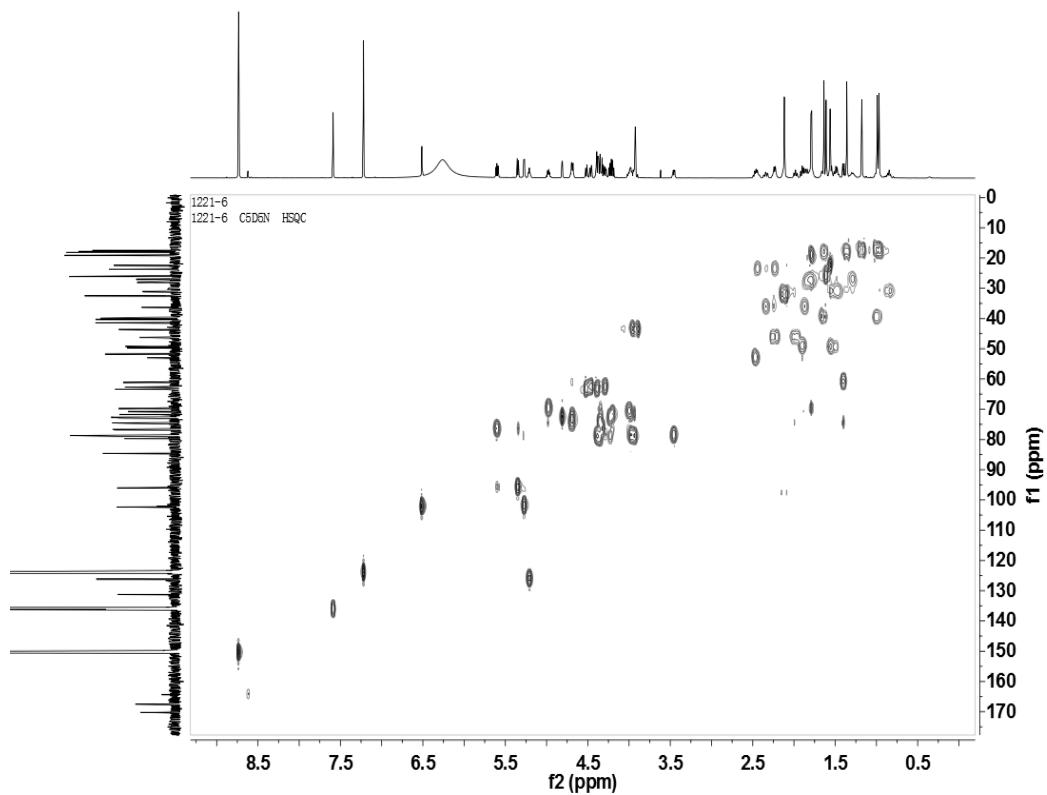


Figure S16. HSQC spectrum of compound 2.

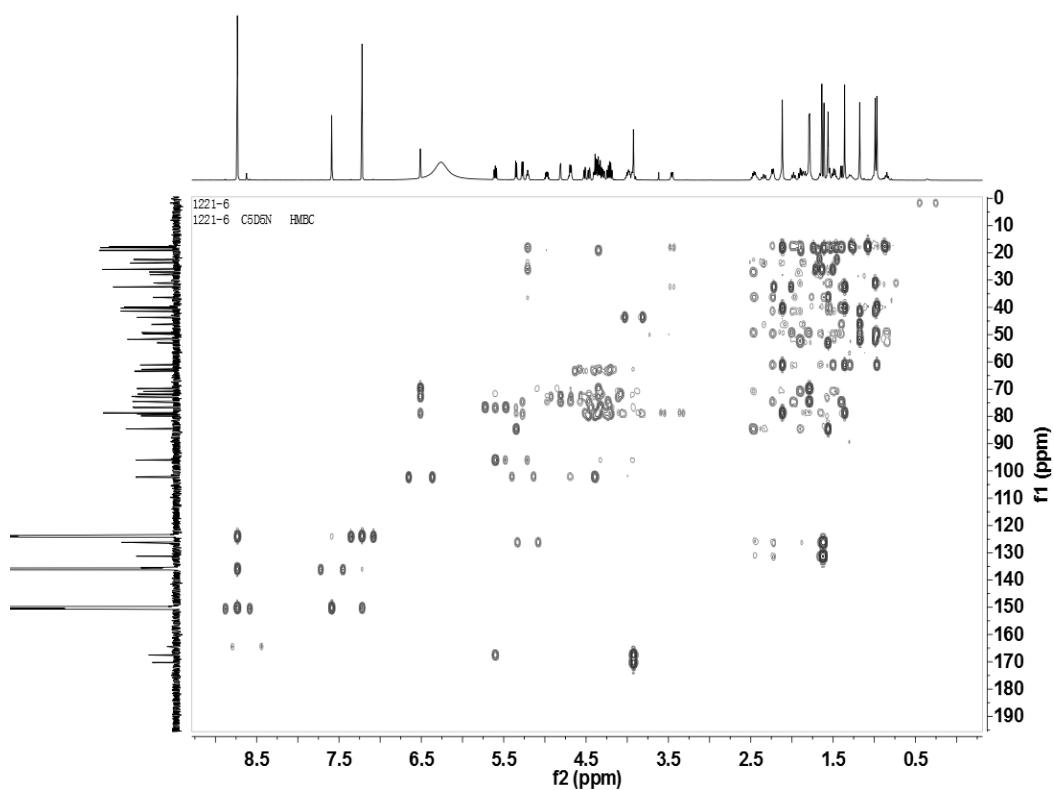


Figure S17. HMBC spectrum of compound 2.

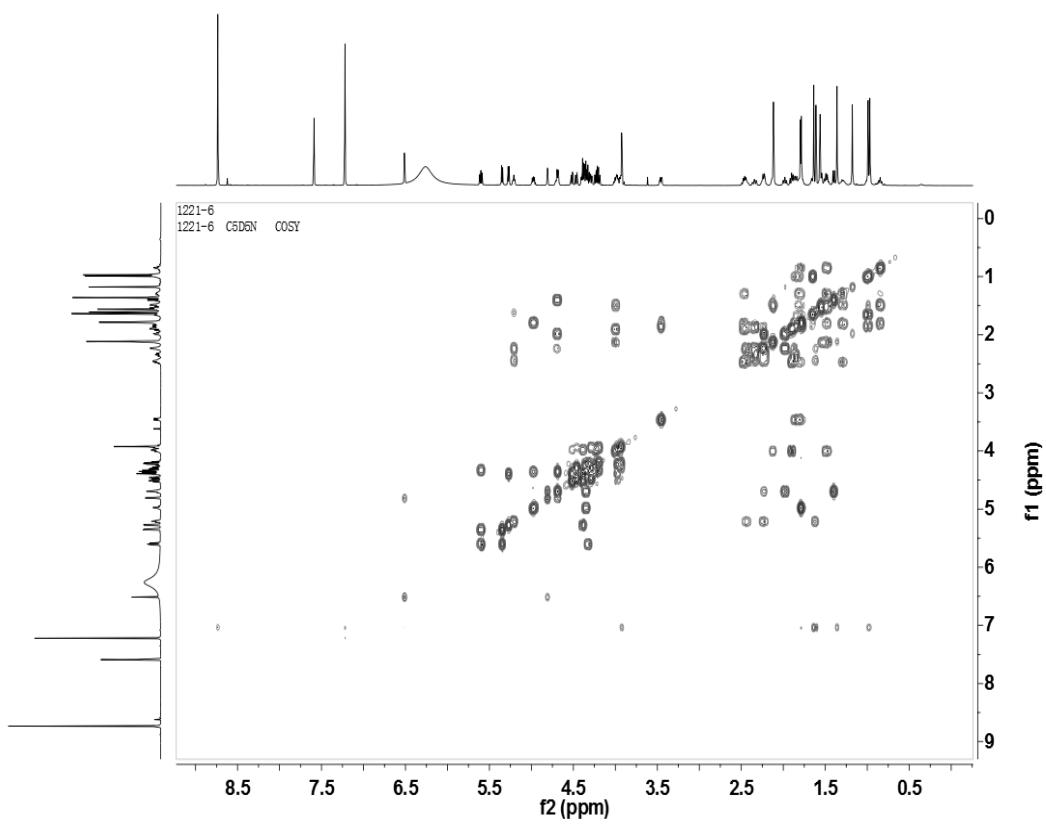


Figure S18. ^1H - ^1H COSY spectrum of compound 2.

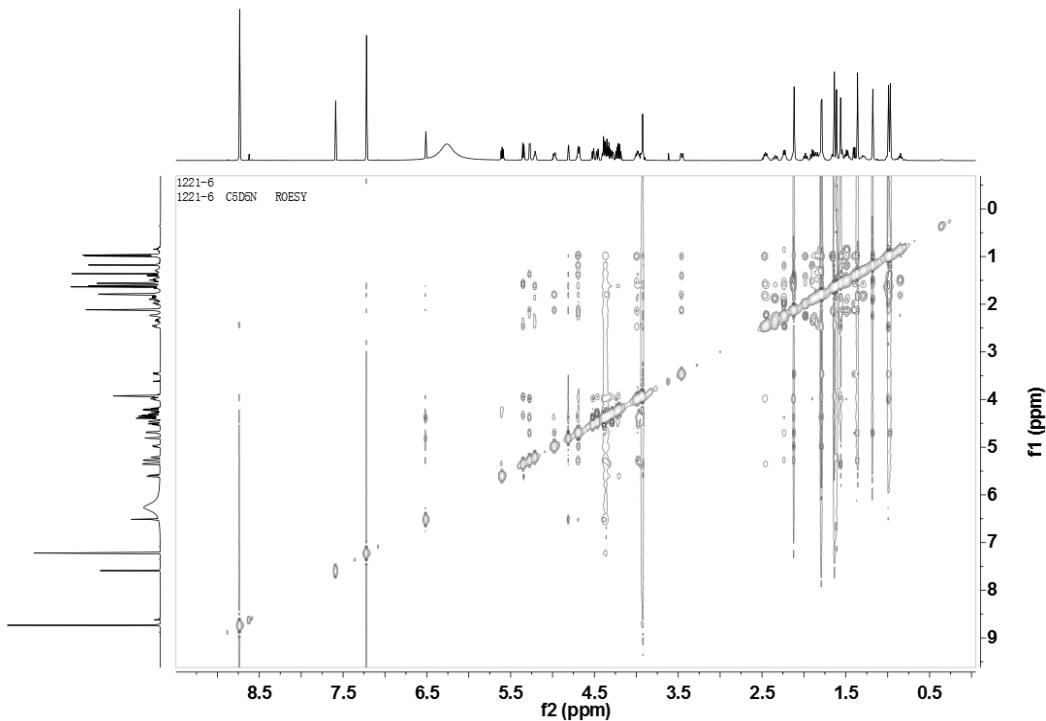


Figure S19. ROESY spectrum of compound 2.

(3) m-floral-Re₃

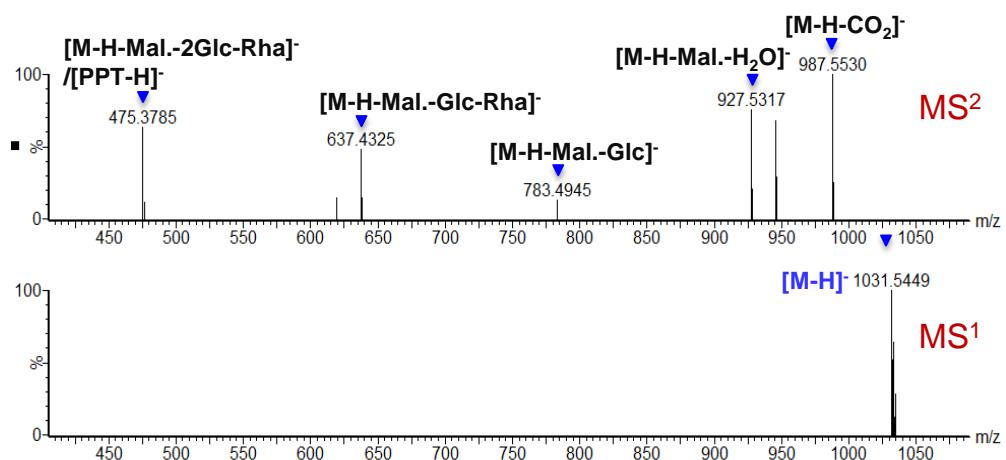


Figure S20. HRESIMS spectrum of compound 3.

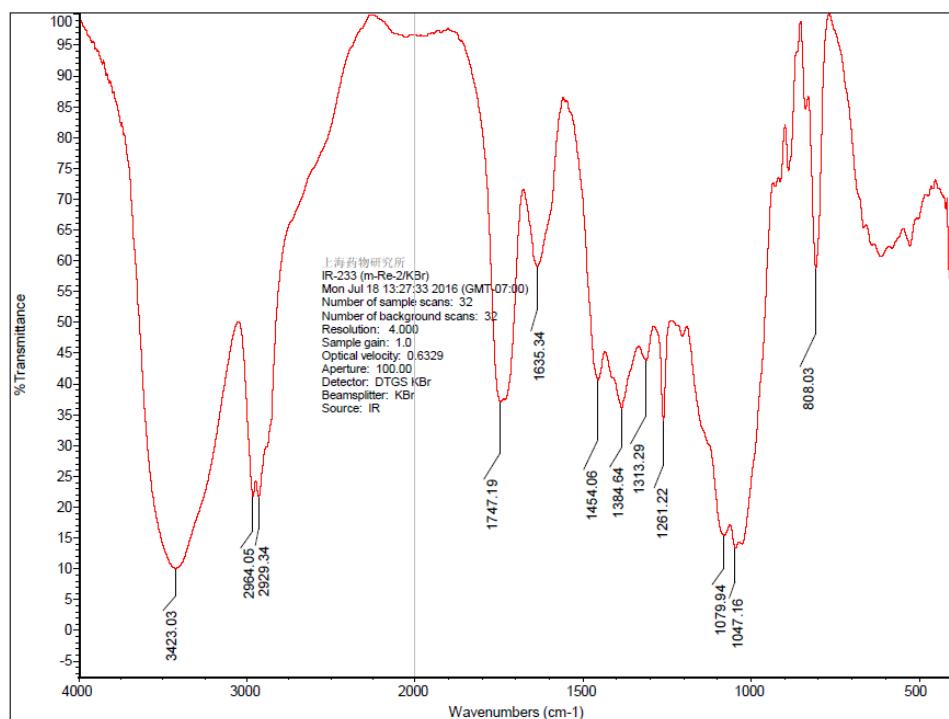


Figure S21. IR spectrum of compound 3.

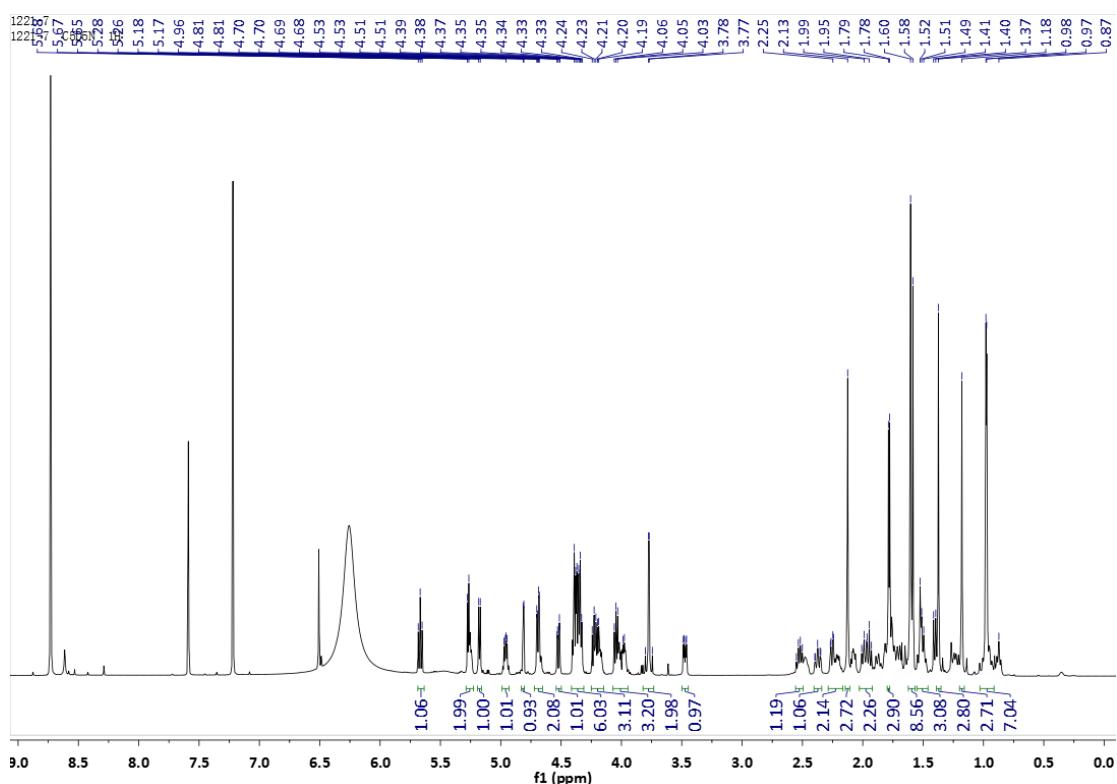


Figure S22. ^1H NMR spectrum of compound 3.

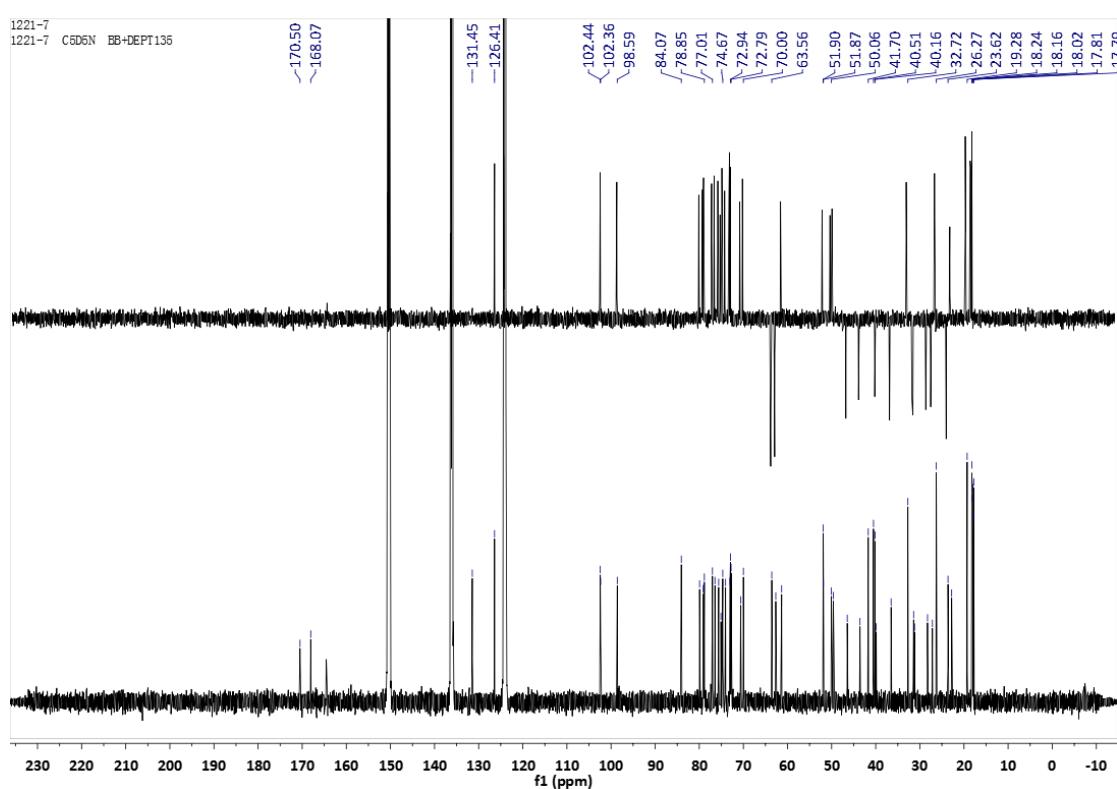


Figure S23. ^{13}C NMR and DEPT-135 spectra of compound 3.

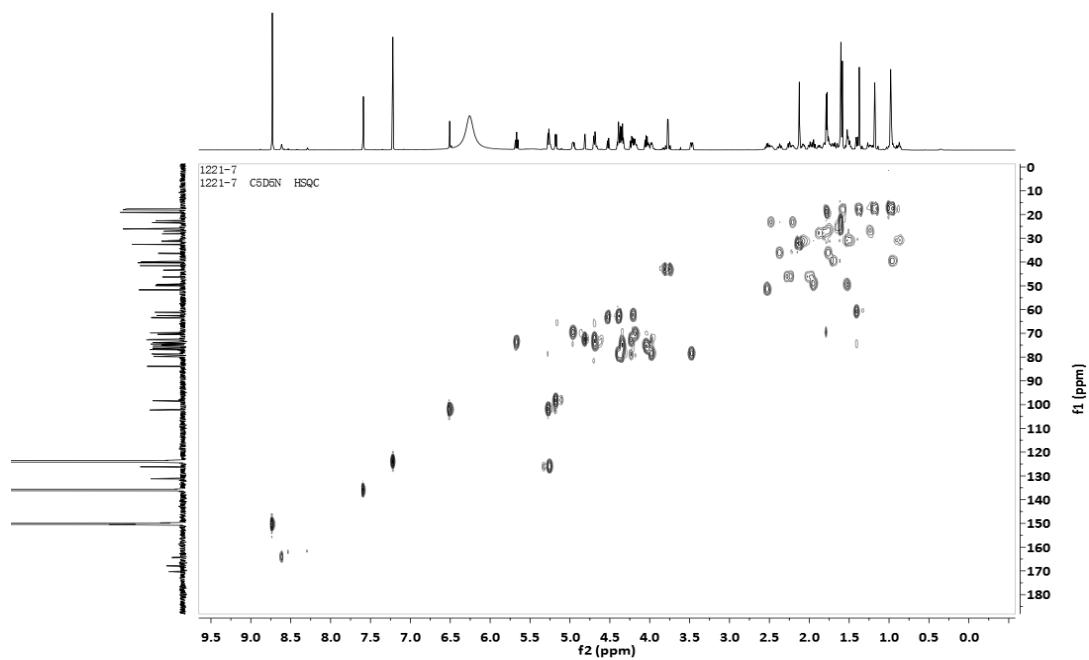


Figure S24. HSQC spectrum of compound 3.

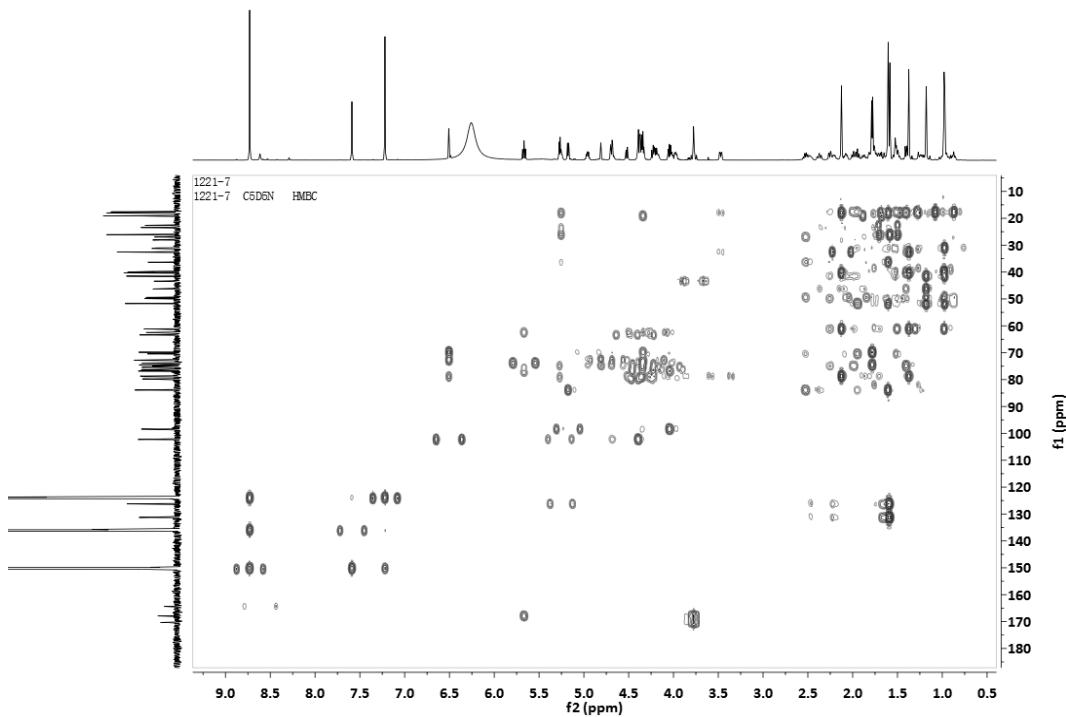


Figure S25. HMBC spectrum of compound 3.

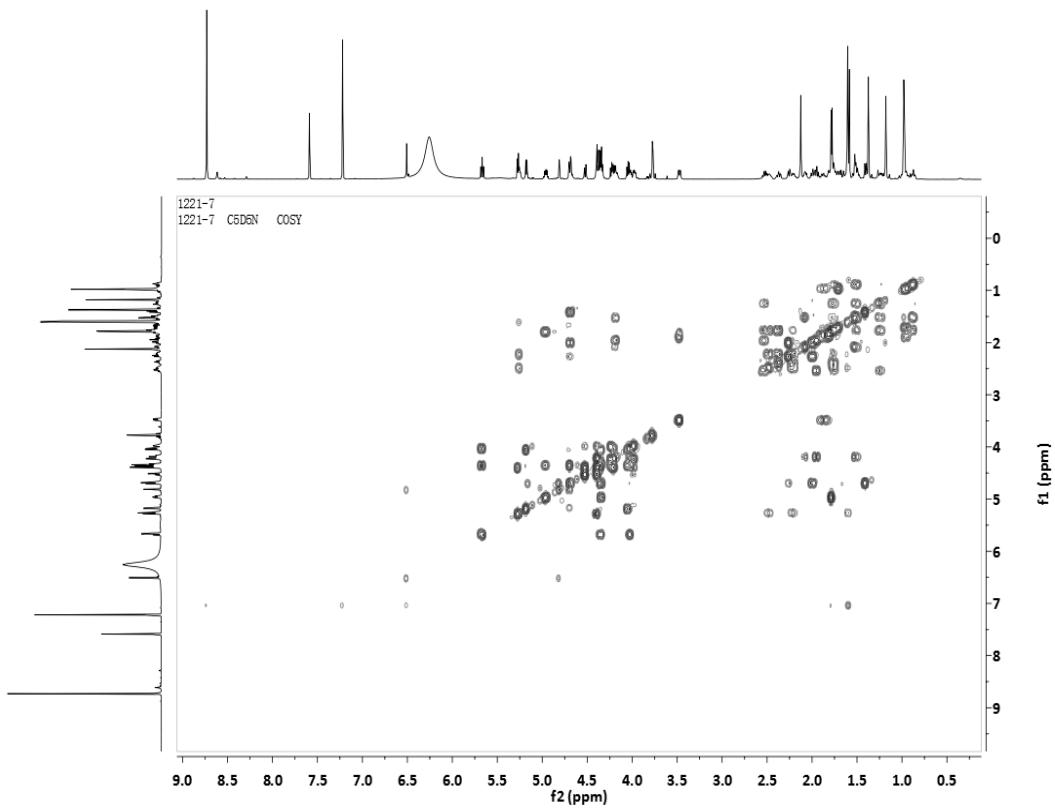


Figure S26. ^1H - ^1H COSY spectrum of compound 3.

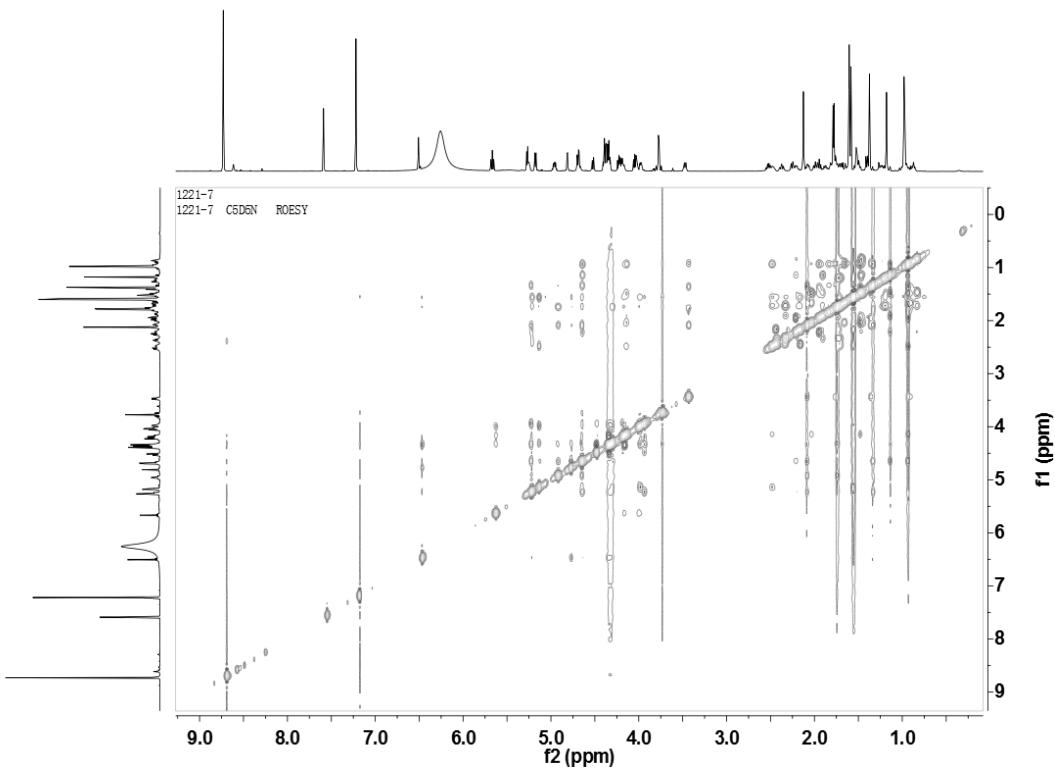


Figure S27. ROESY spectrum of compound 3.

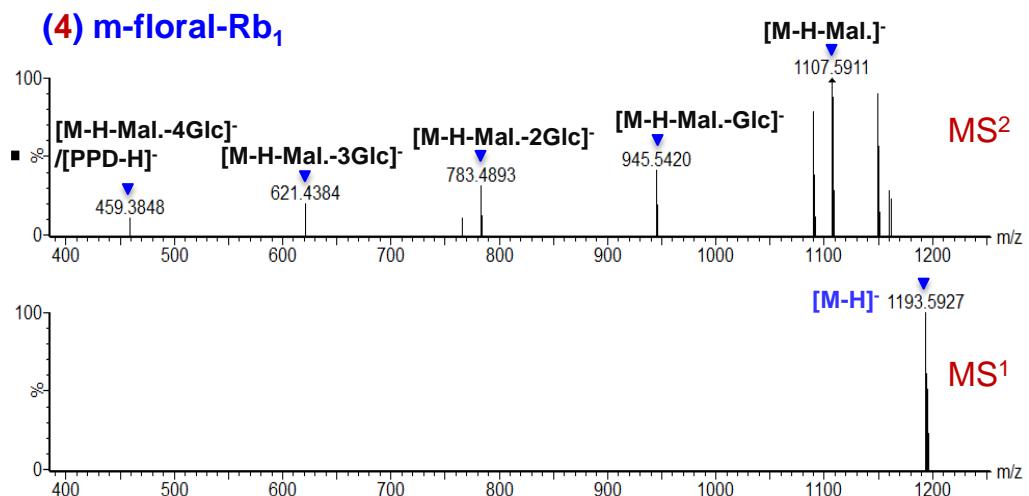


Figure S28. HRESIMS spectrum of compound 4.

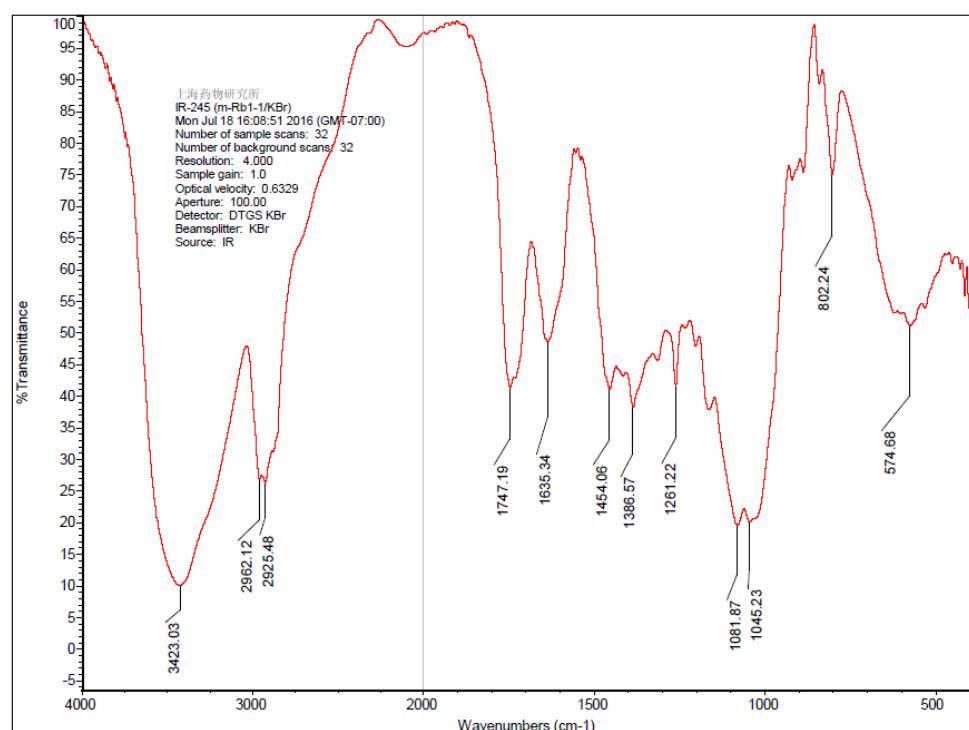


Figure S29. IR spectrum of compound 4.

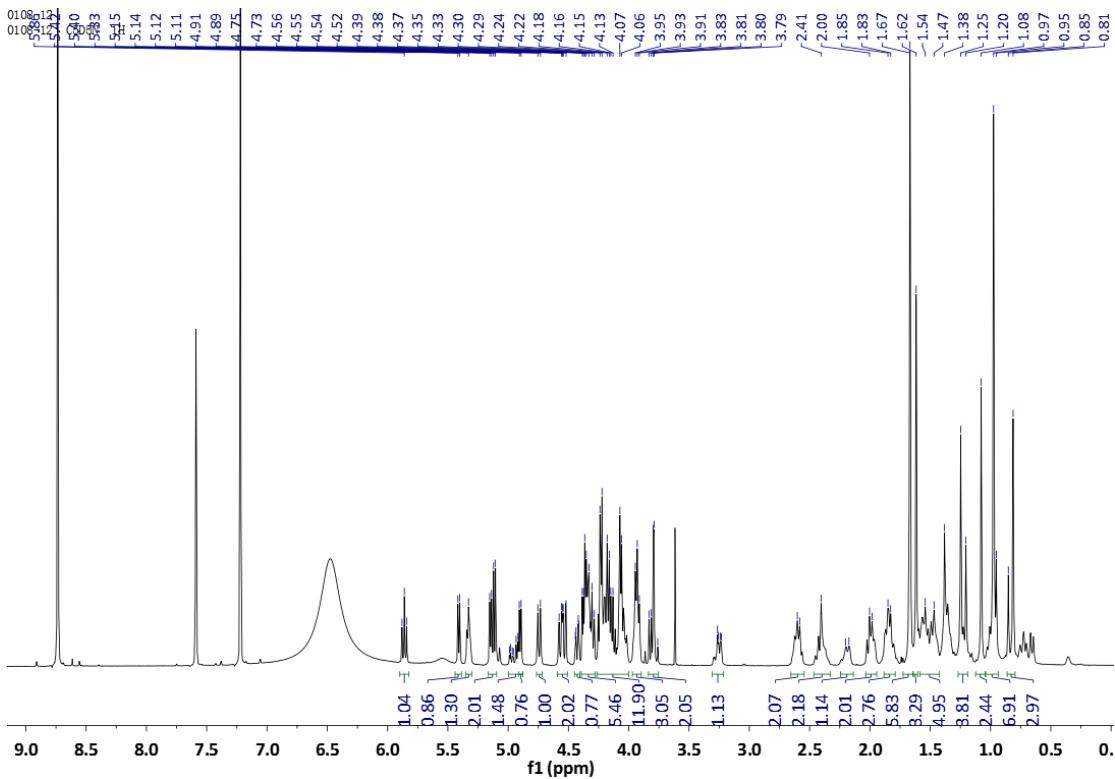


Figure S30. ^1H NMR spectrum of compound 4.

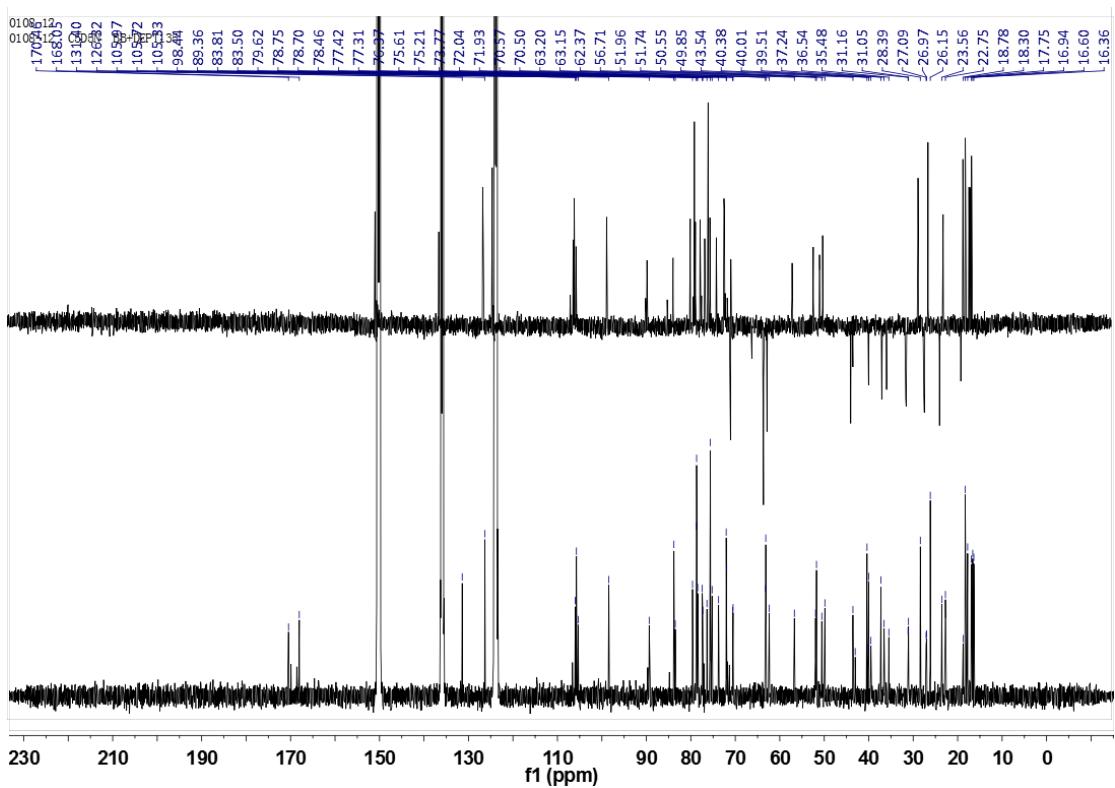


Figure S31. ^{13}C NMR and DEPT-135 spectrum of compound 4.

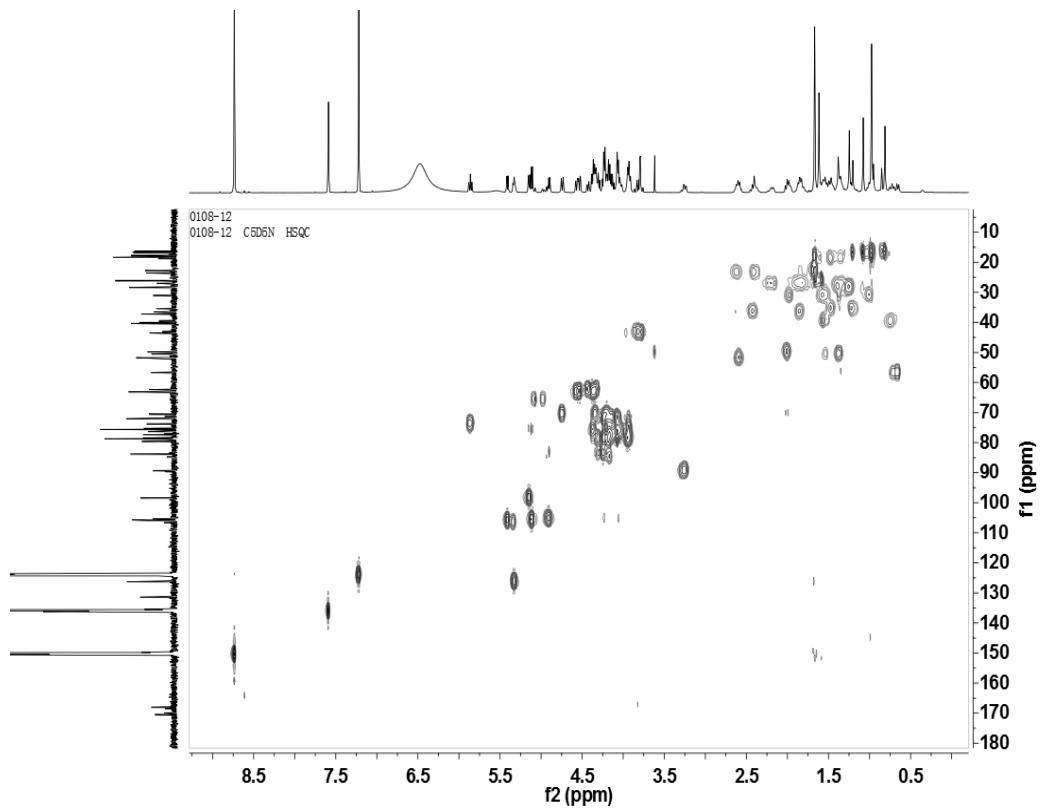


Figure S32. HSQC spectrum of compound 4.

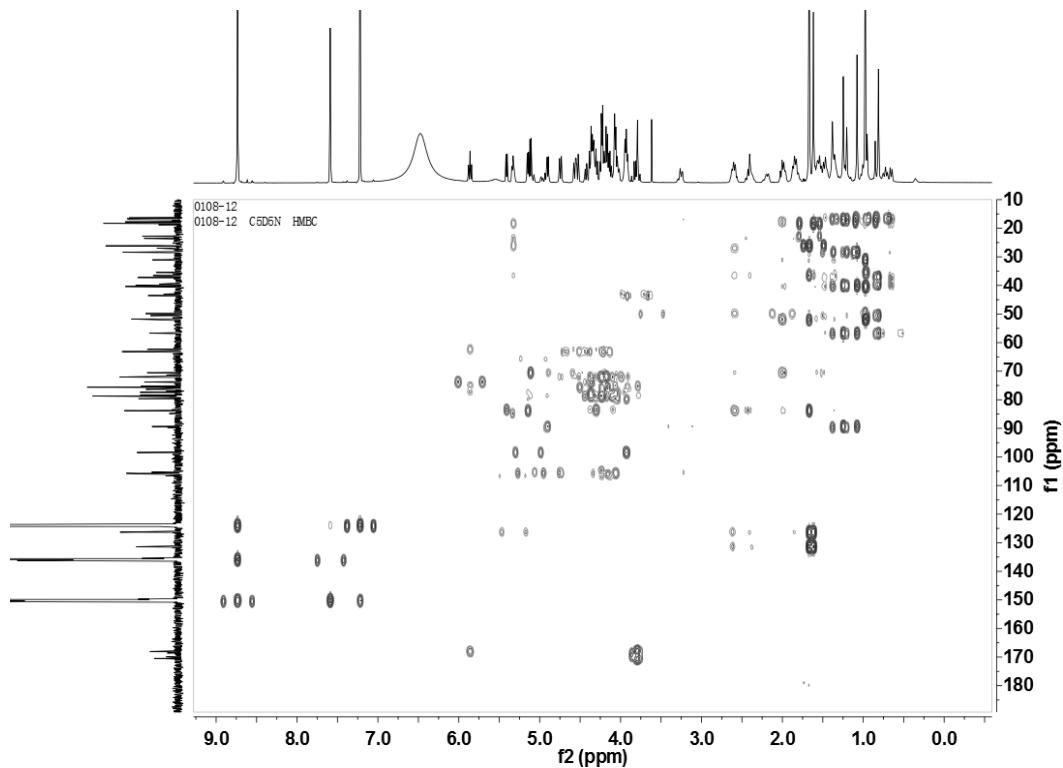


Figure S33. HMBC spectrum of compound 4.

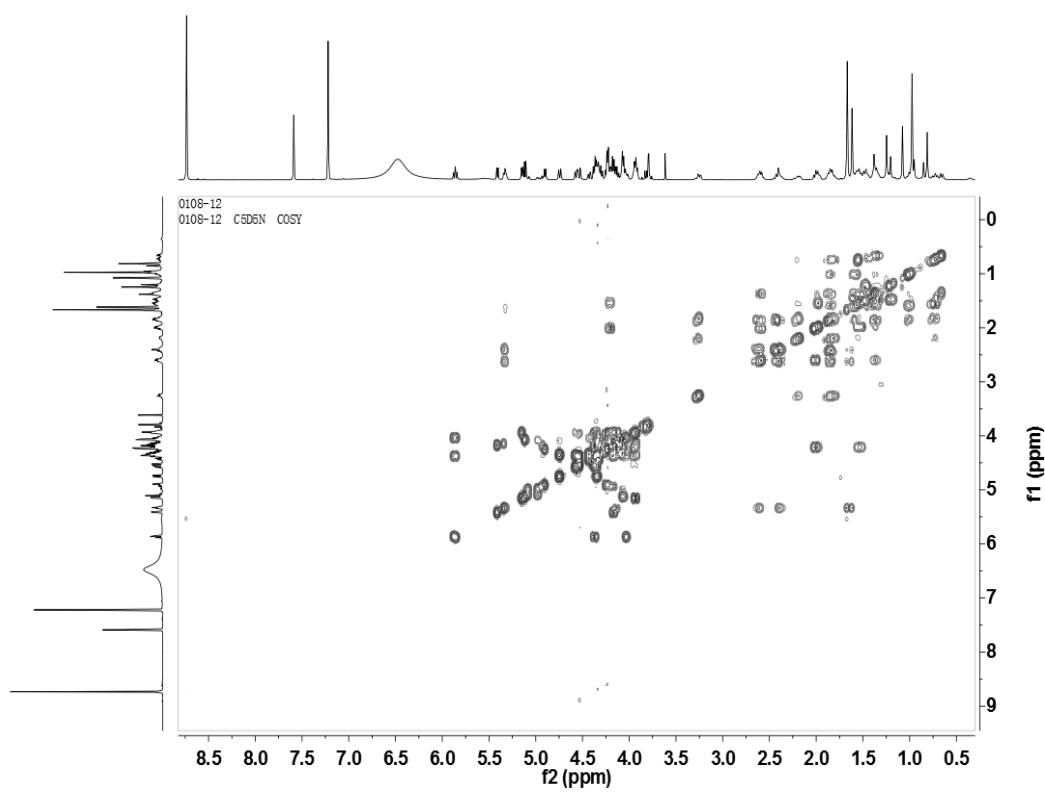


Figure S34. ^1H - ^1H COSY spectrum of compound 4.

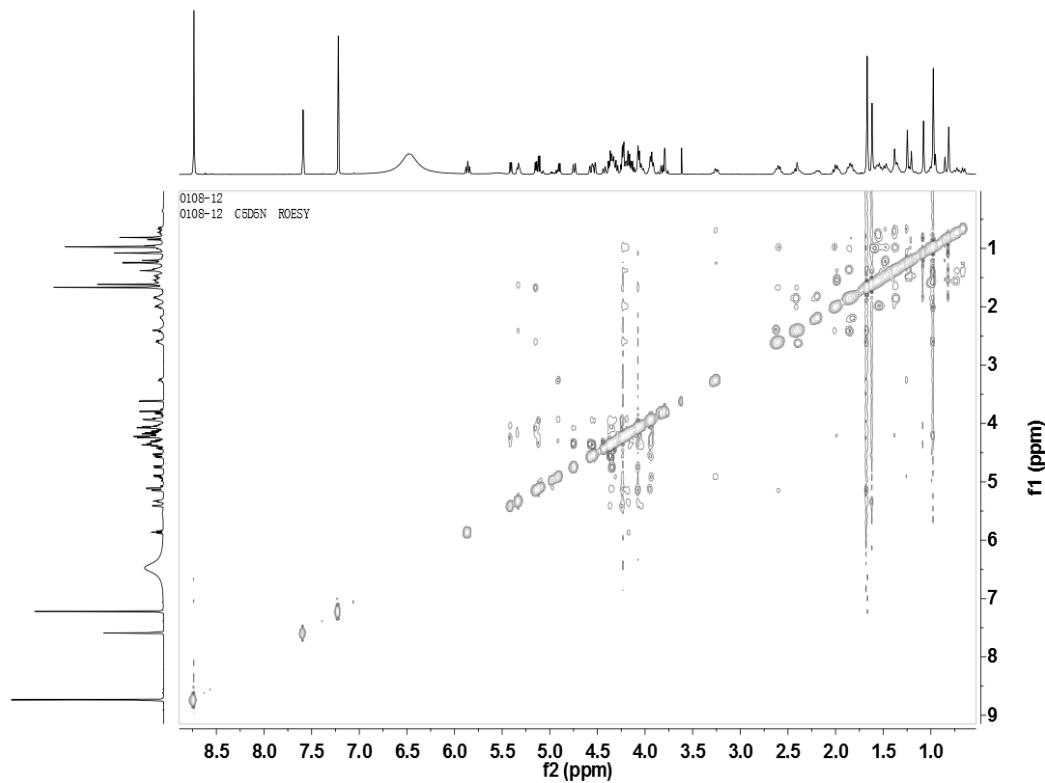


Figure S35. ROESY spectrum of compound 4.

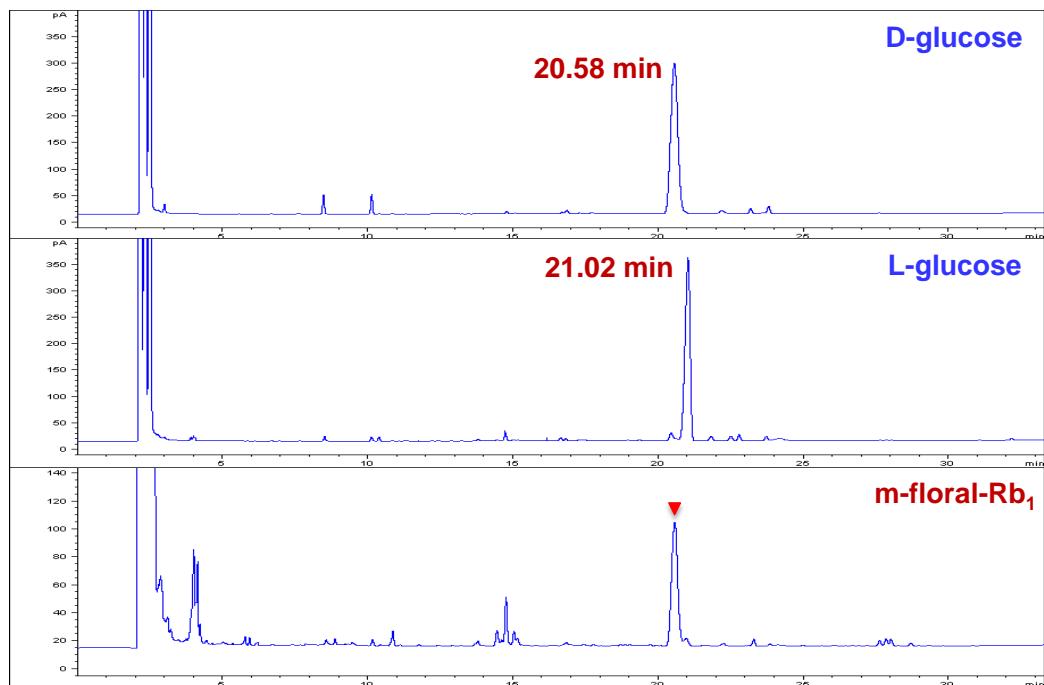


Figure S36. The GC chromatograms of compound 4 after acidic hydrolysis.

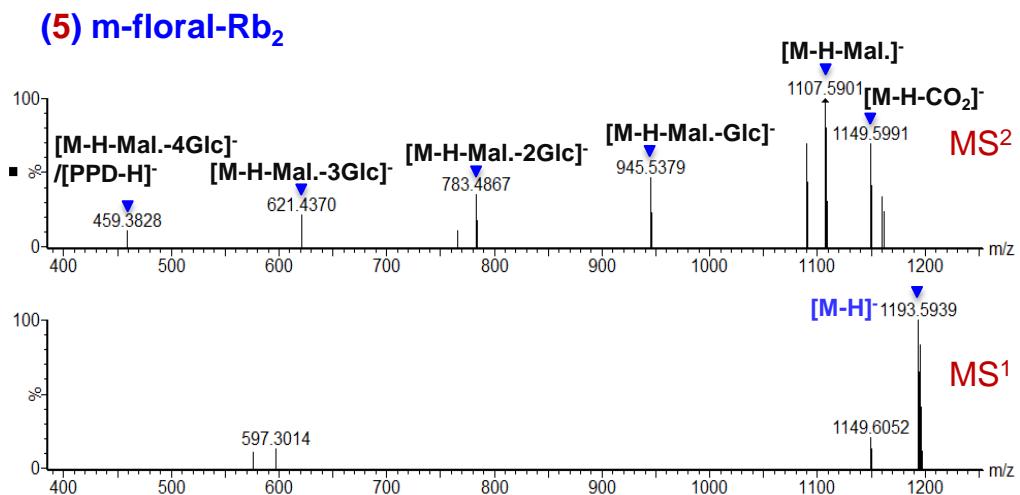


Figure S37. HRESIMS spectrum of compound 5.

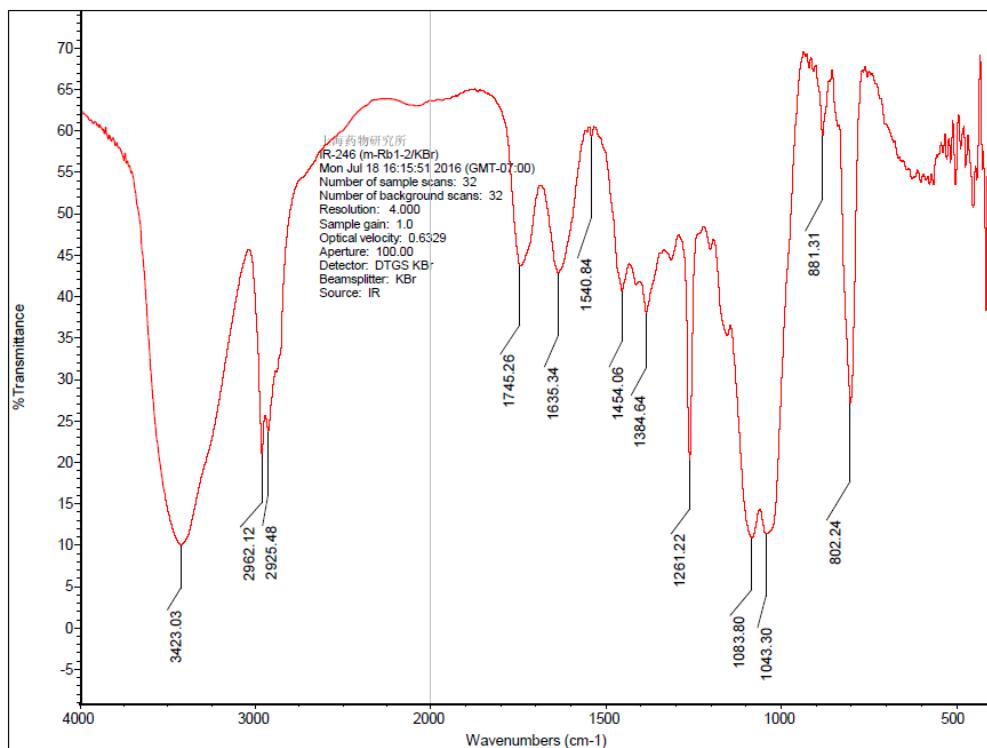


Figure S38. IR spectrum of compound **5**.

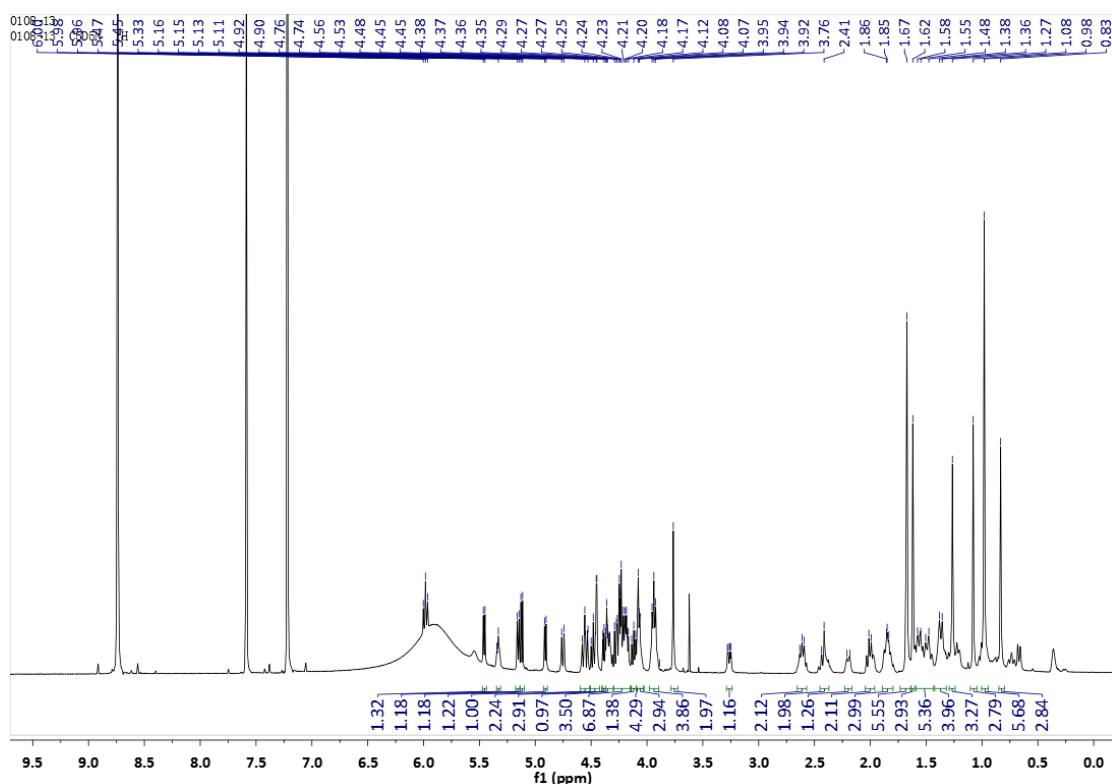


Figure S39. ^1H NMR spectrum of compound 5.

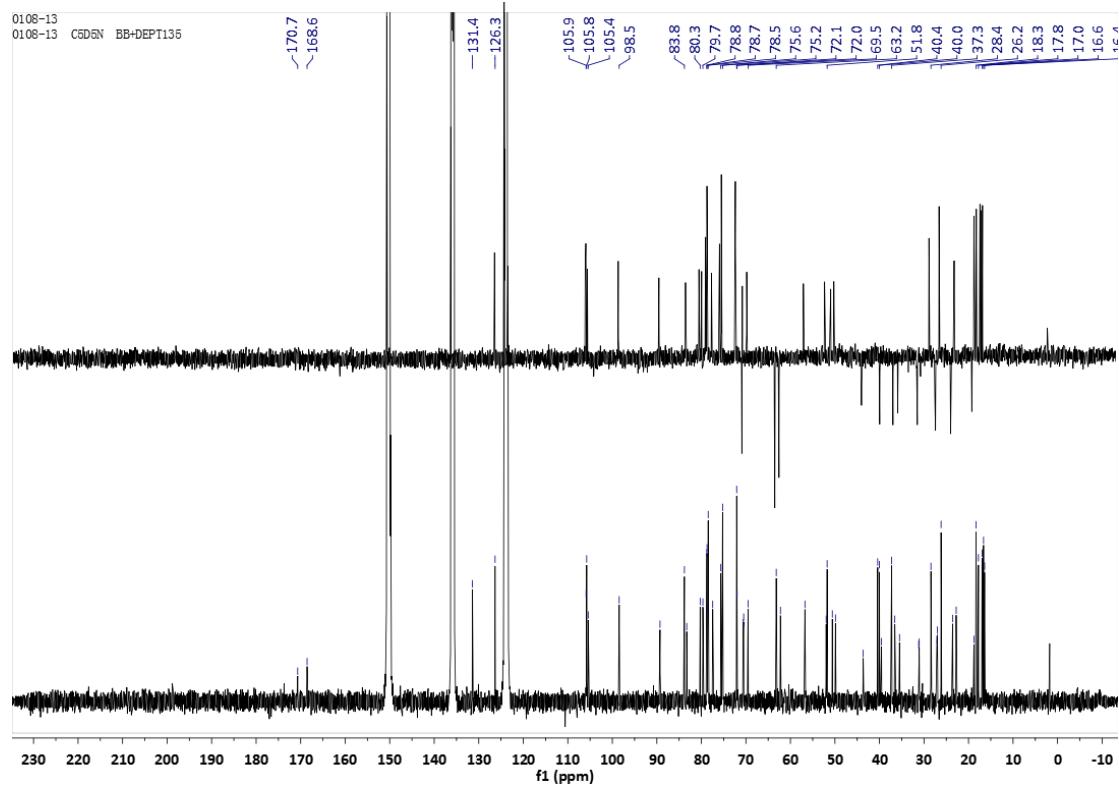


Figure S40. ^{13}C NMR and DEPT-135 spectra of compound 5.

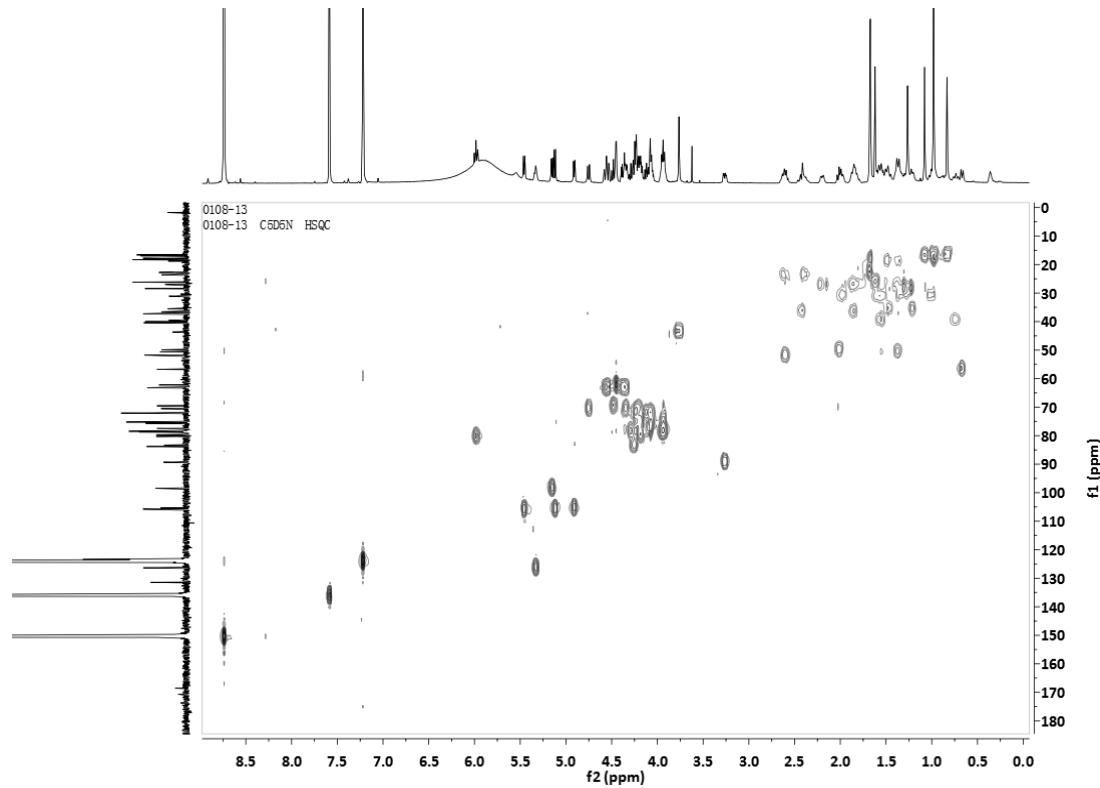


Figure S41. HSQC spectrum of compound 5.

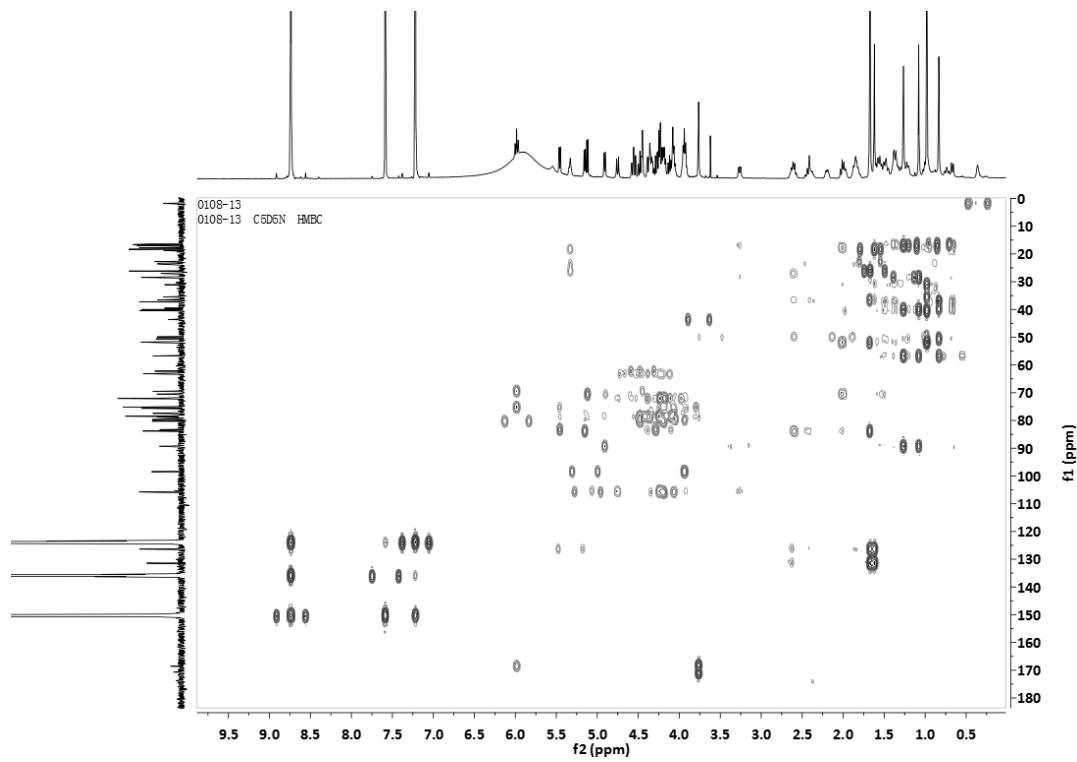


Figure S42. HMBC spectrum of compound 5.

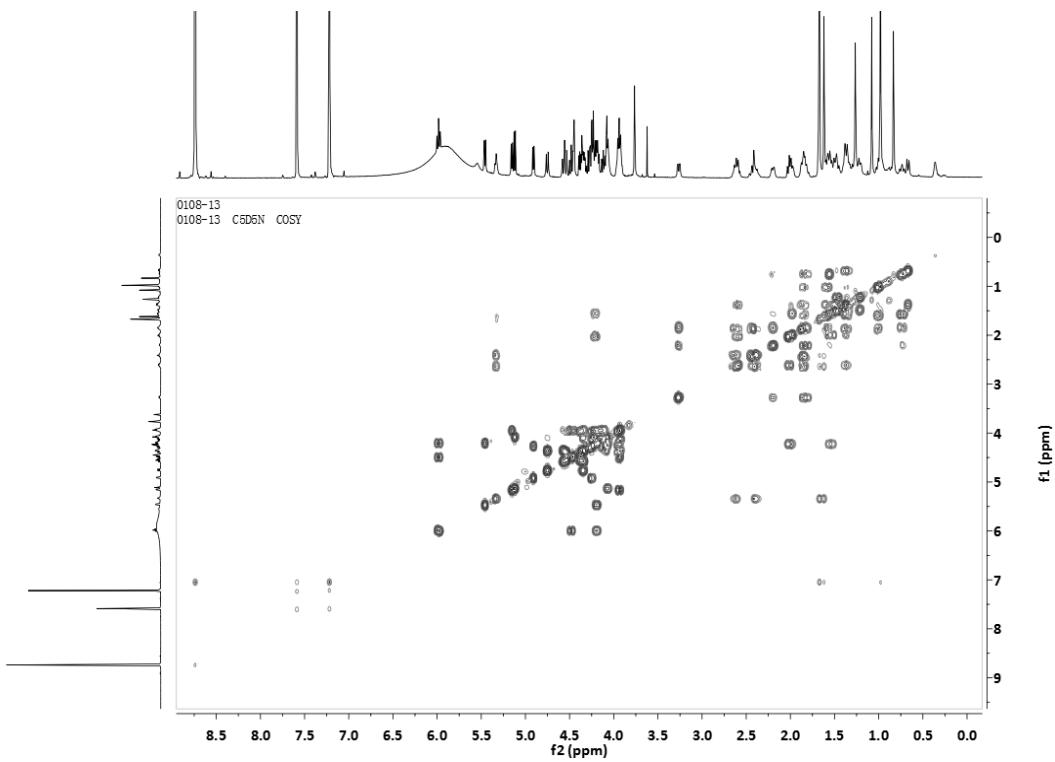


Figure S43. ^1H - ^1H COSY spectrum of compound 5.

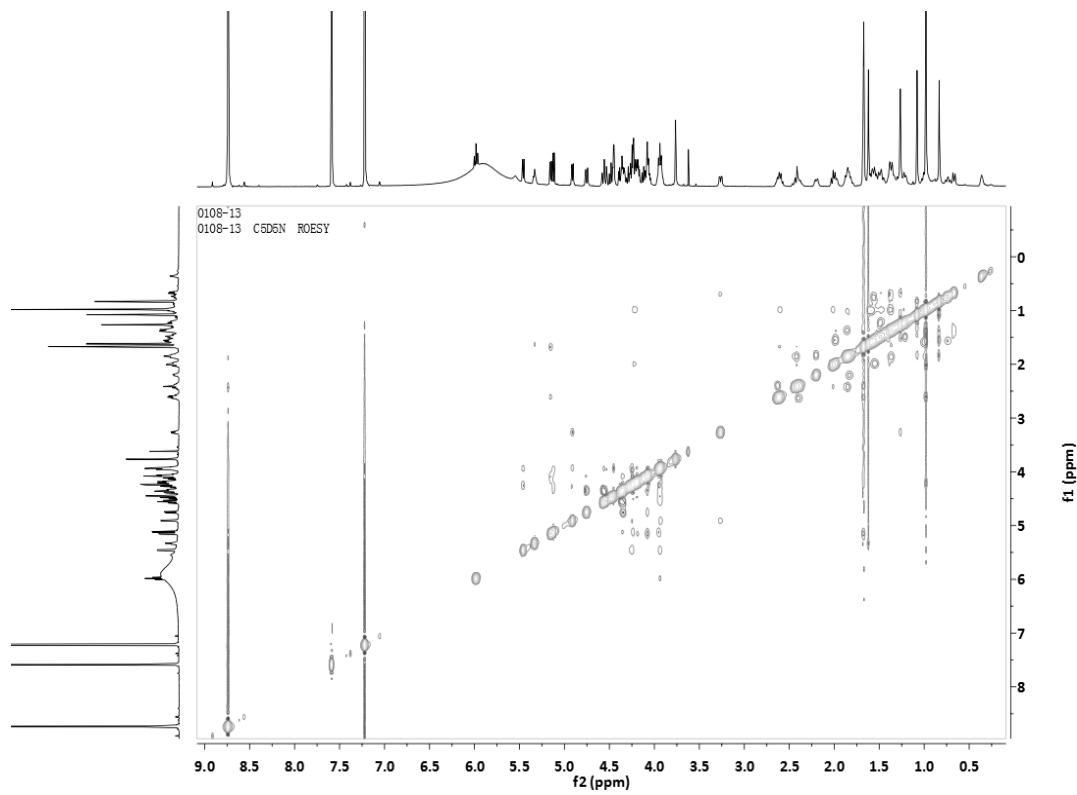


Figure S44. ROESY spectrum of compound 5.

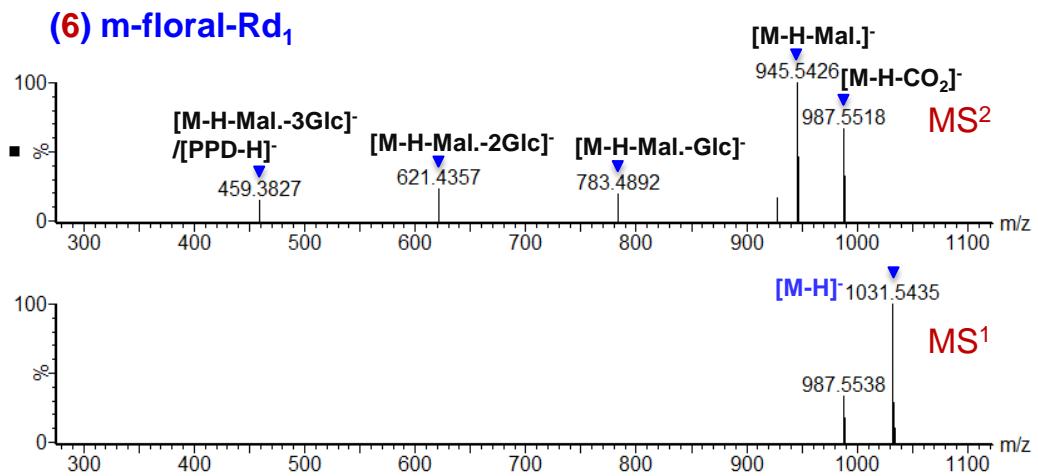


Figure S45. HRESIMS spectrum of compound 6.

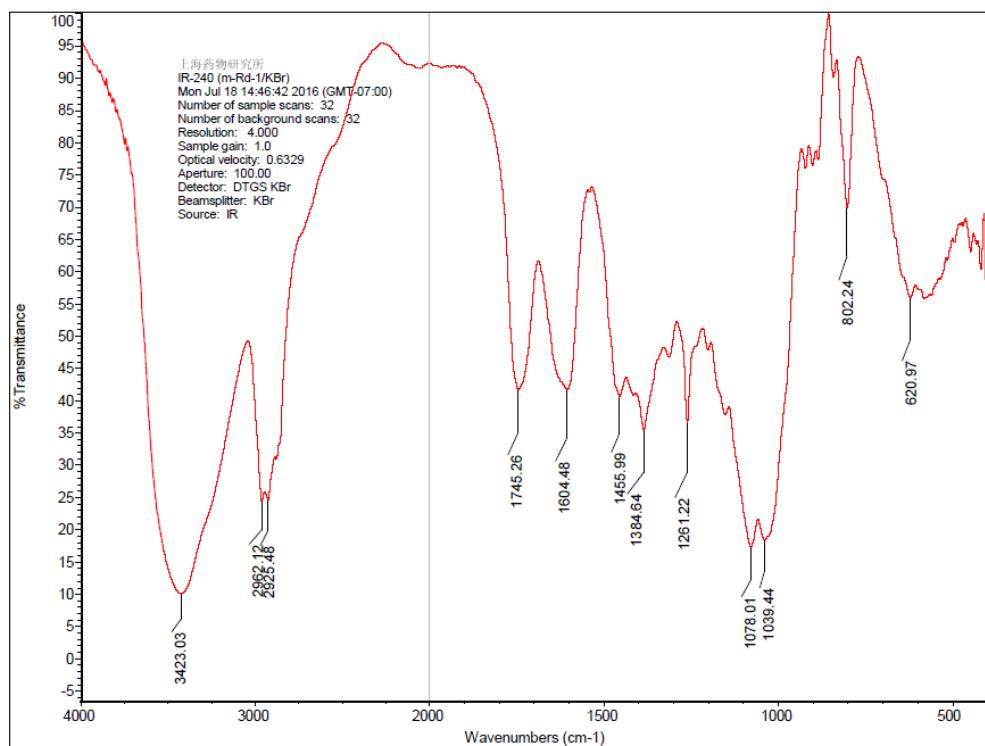


Figure S46. IR spectrum of compound **6**.

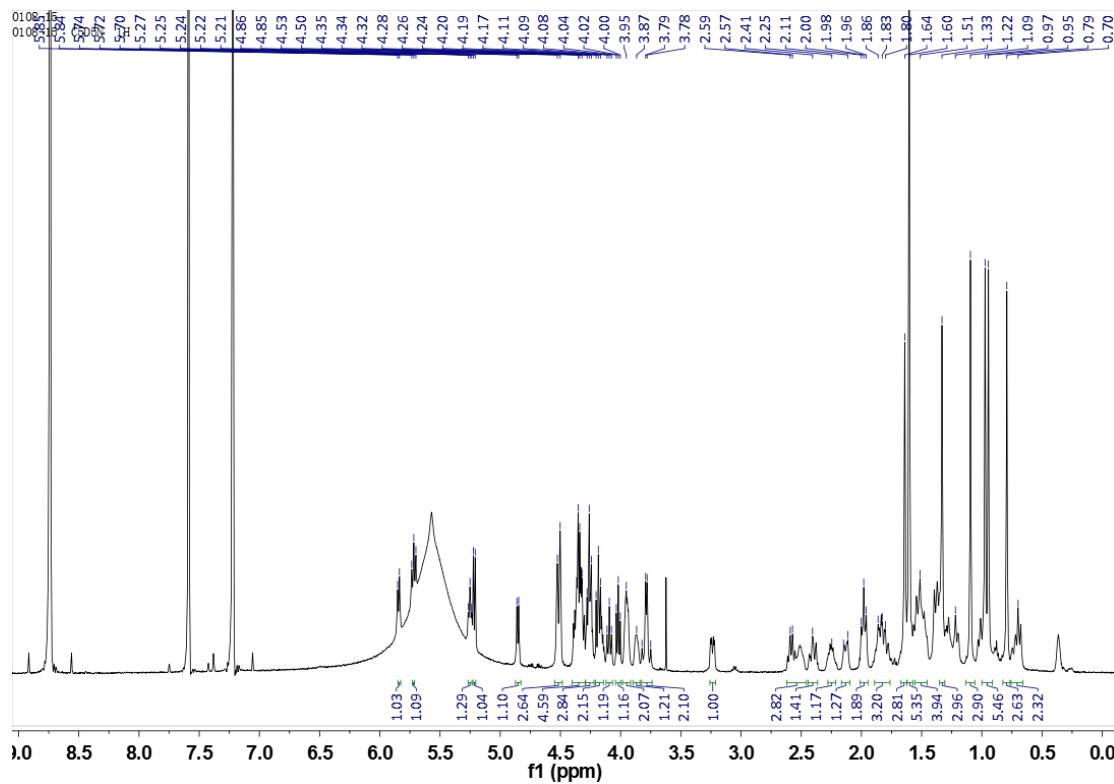


Figure S47. ^1H NMR spectrum of compound **6**.

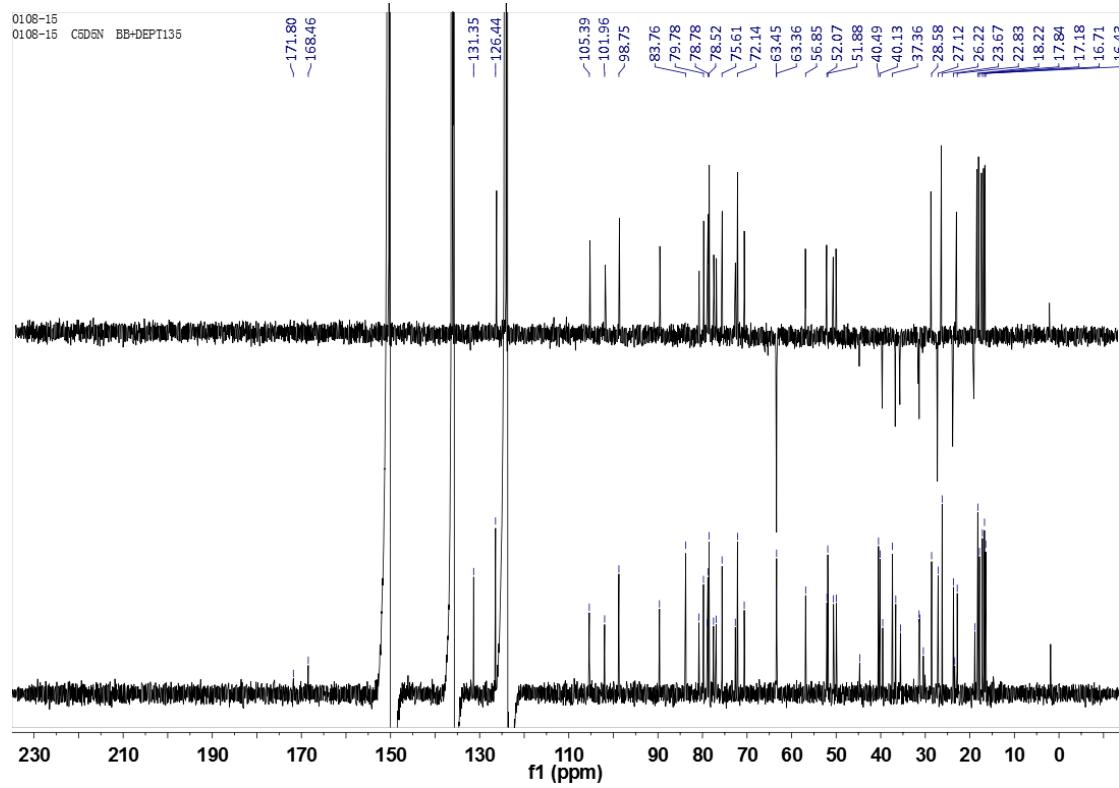


Figure S48. ^{13}C NMR spectrum of compound **6**.

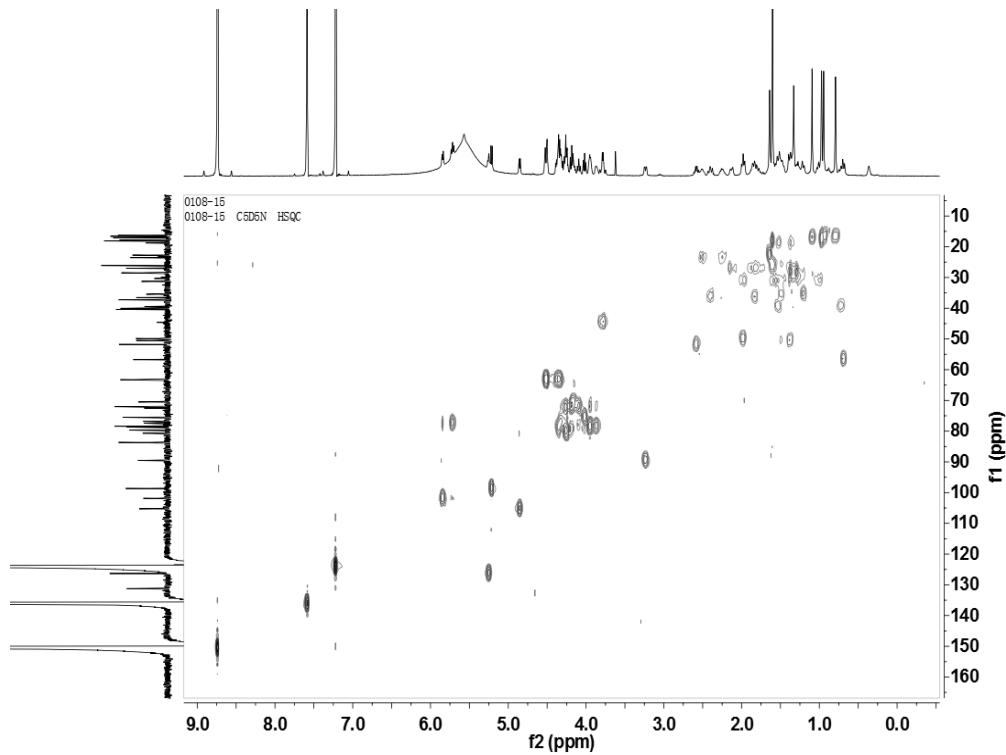


Figure S49. HSQC spectrum of compound **6**.

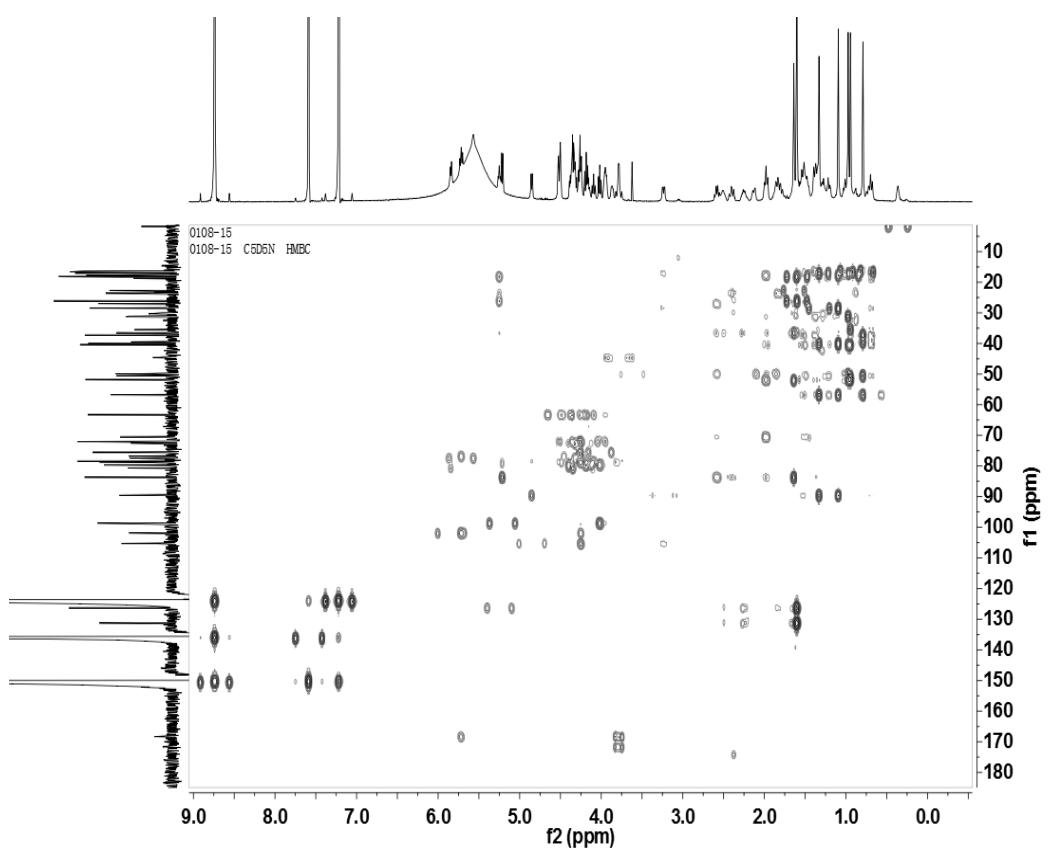


Figure S50. HMBC spectrum of compound **6**.

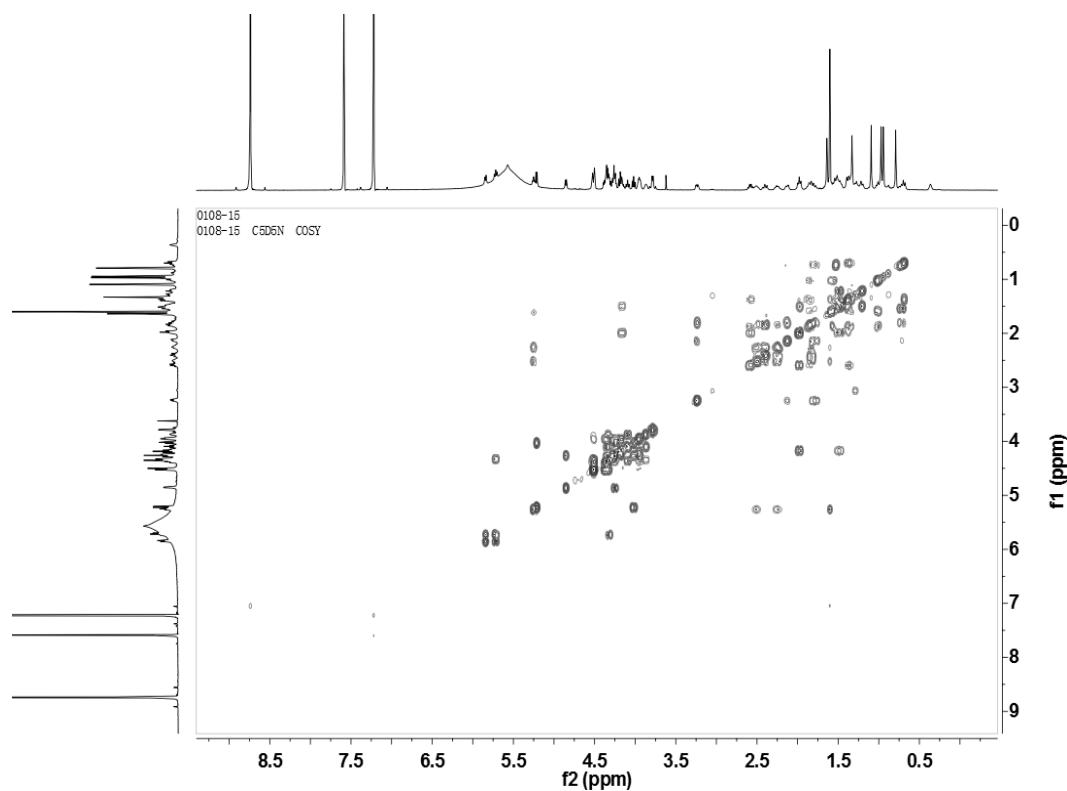


Figure S51. ^1H - ^1H COSY spectrum of compound **6**.

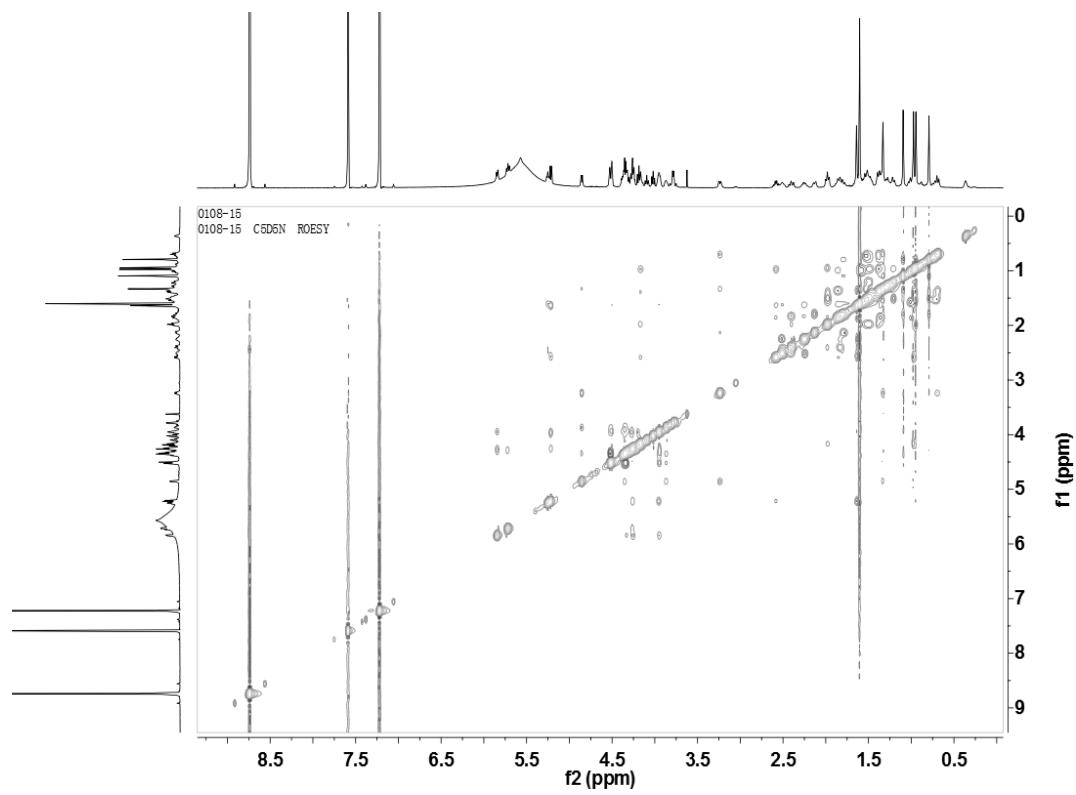


Figure S52. ROESY spectrum of compound 6.

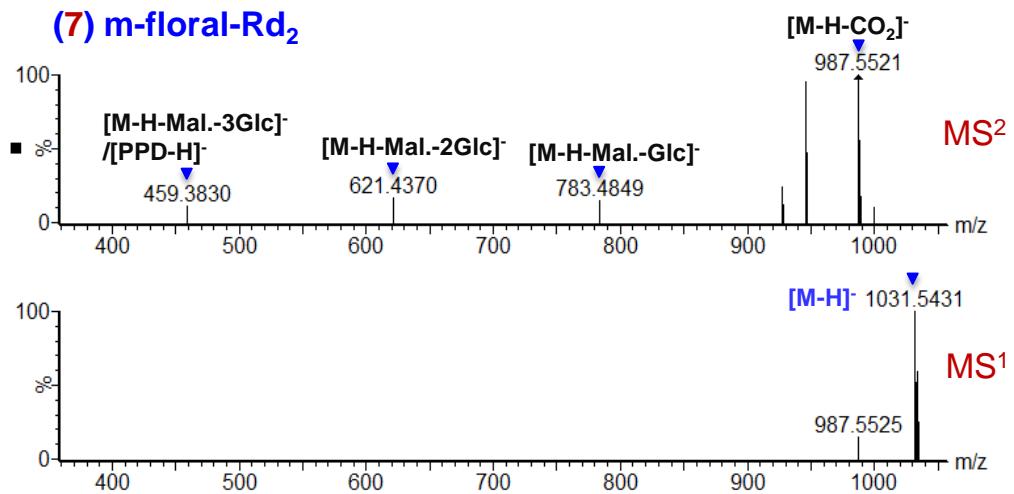


Figure S53. HRESIMS spectrum of compound 7.

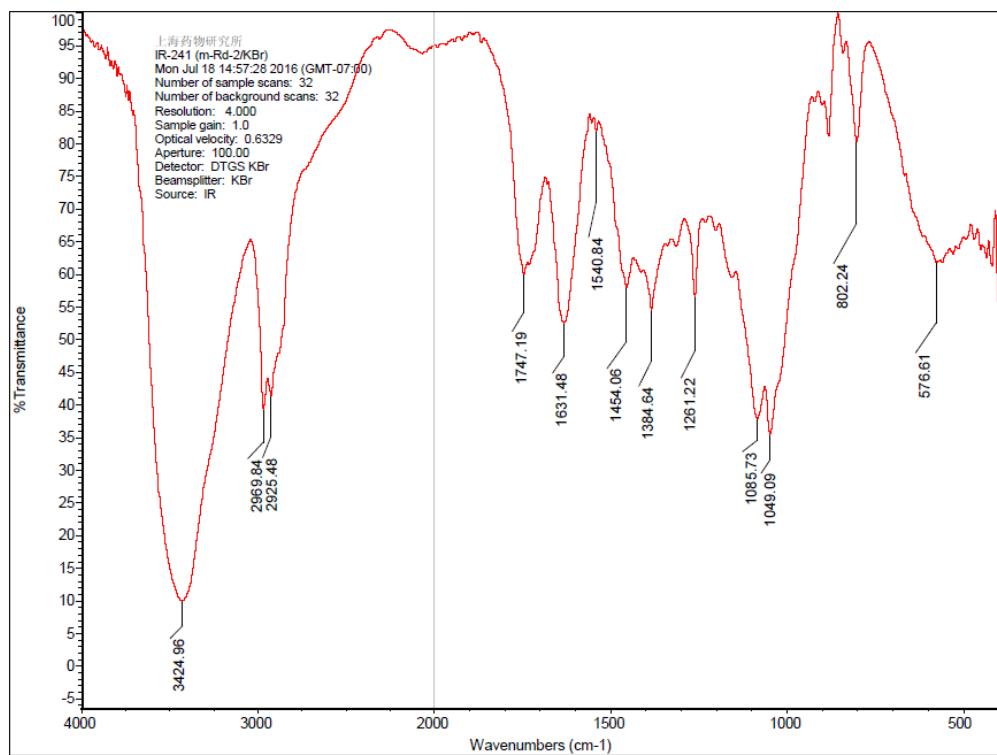


Figure 54. IR spectrum of compound 7.

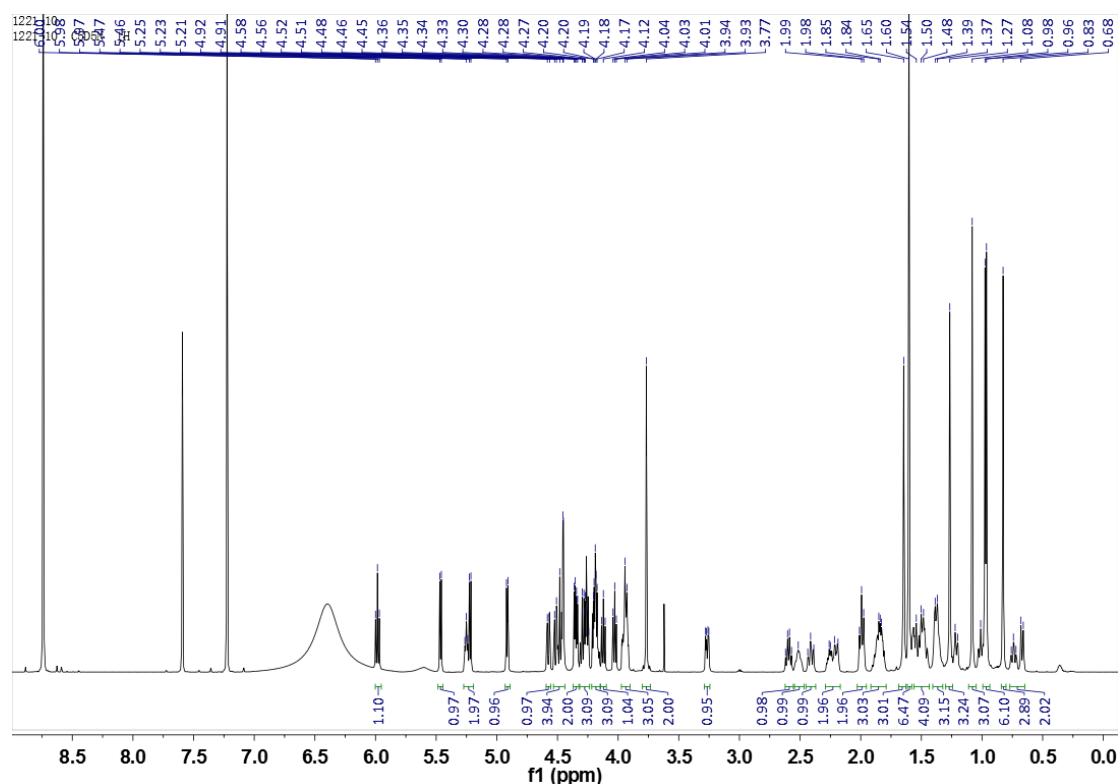


Figure S55. ¹H NMR spectrum of compound 7.

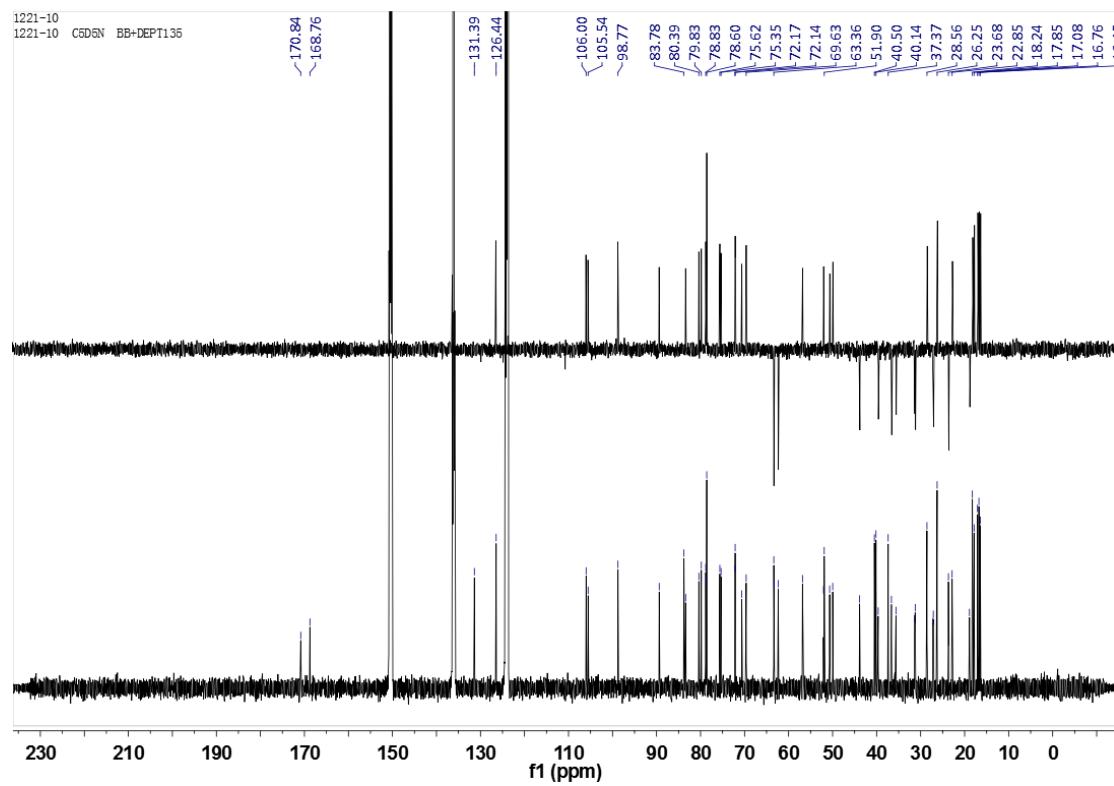


Figure S56. ^{13}C NMR and DEPT-135 spectra of compound 7.

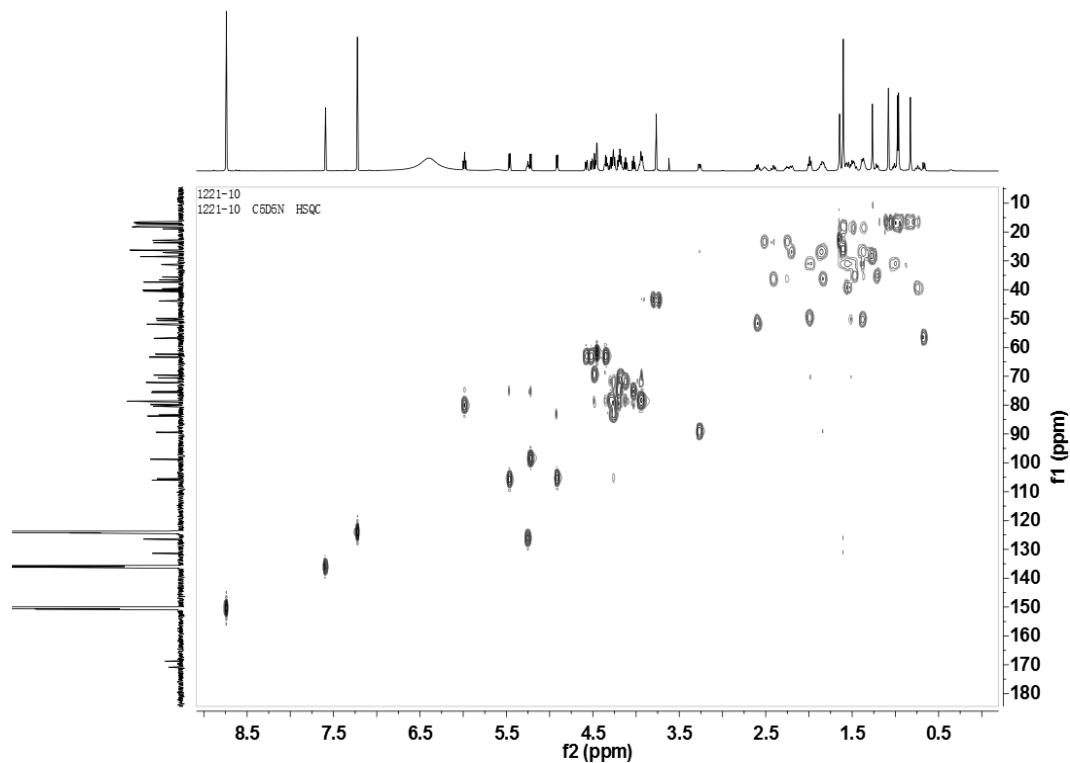


Figure S57. HSQC spectrum of compound 7.

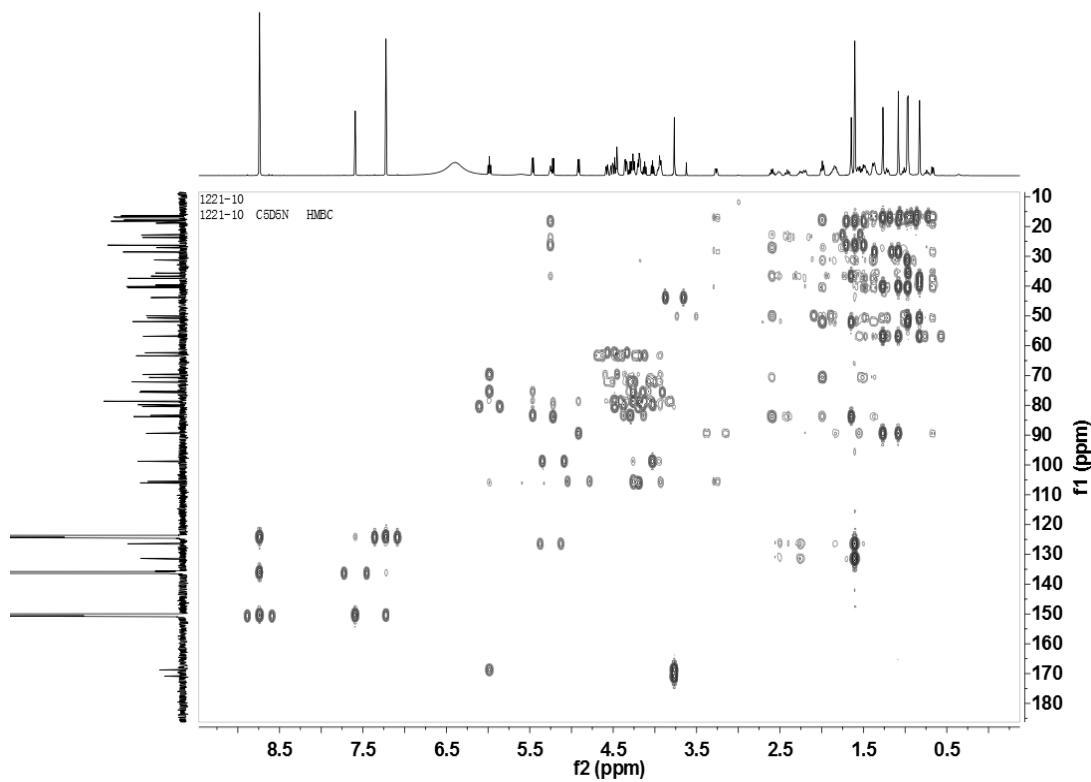


Figure S58. HMBC spectrum of compound 7.

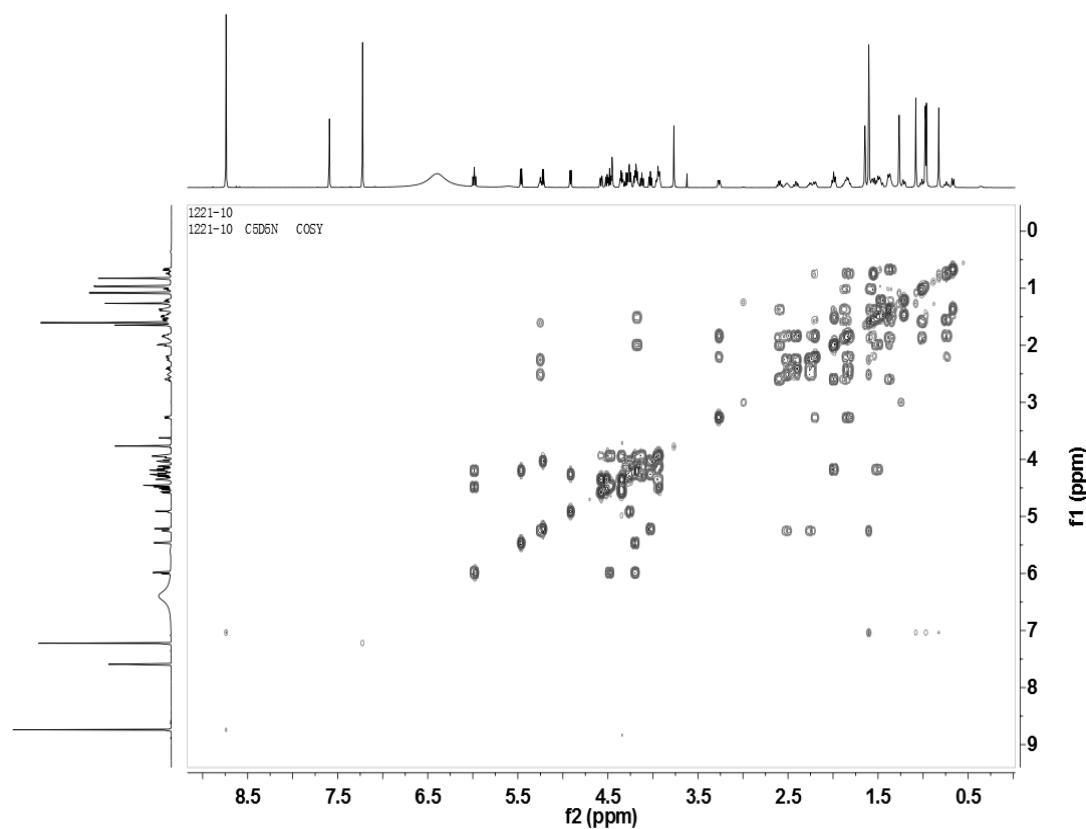


Figure S59. ^1H - ^1H COSY spectrum of compound 7.

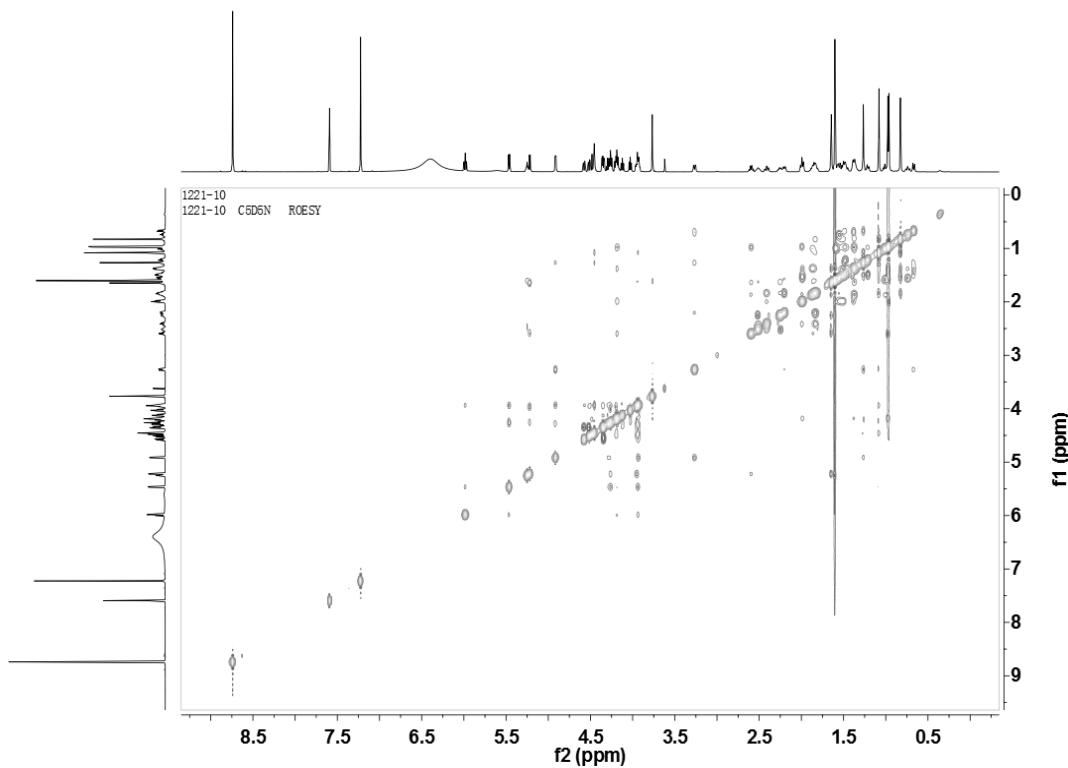


Figure S60. ROESY spectrum of compound 7.

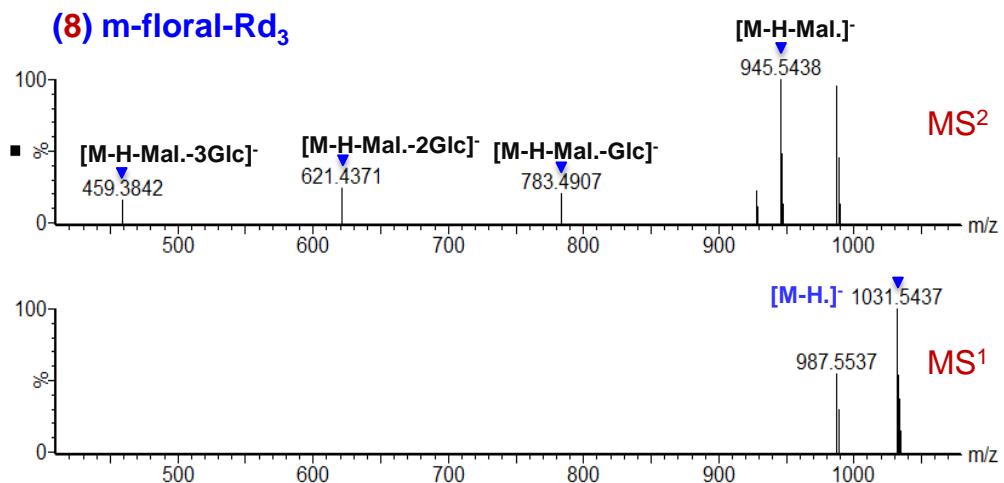


Figure S61. HRESIMS spectrum of compound 8.

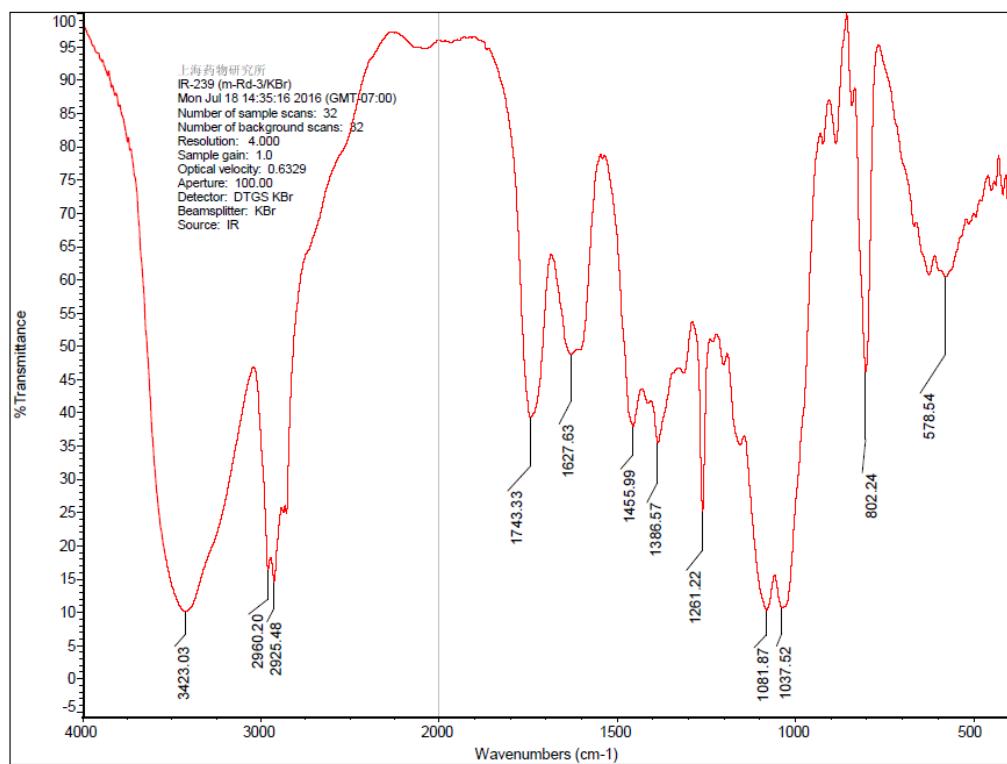


Figure S62. IR spectrum of compound **8**.

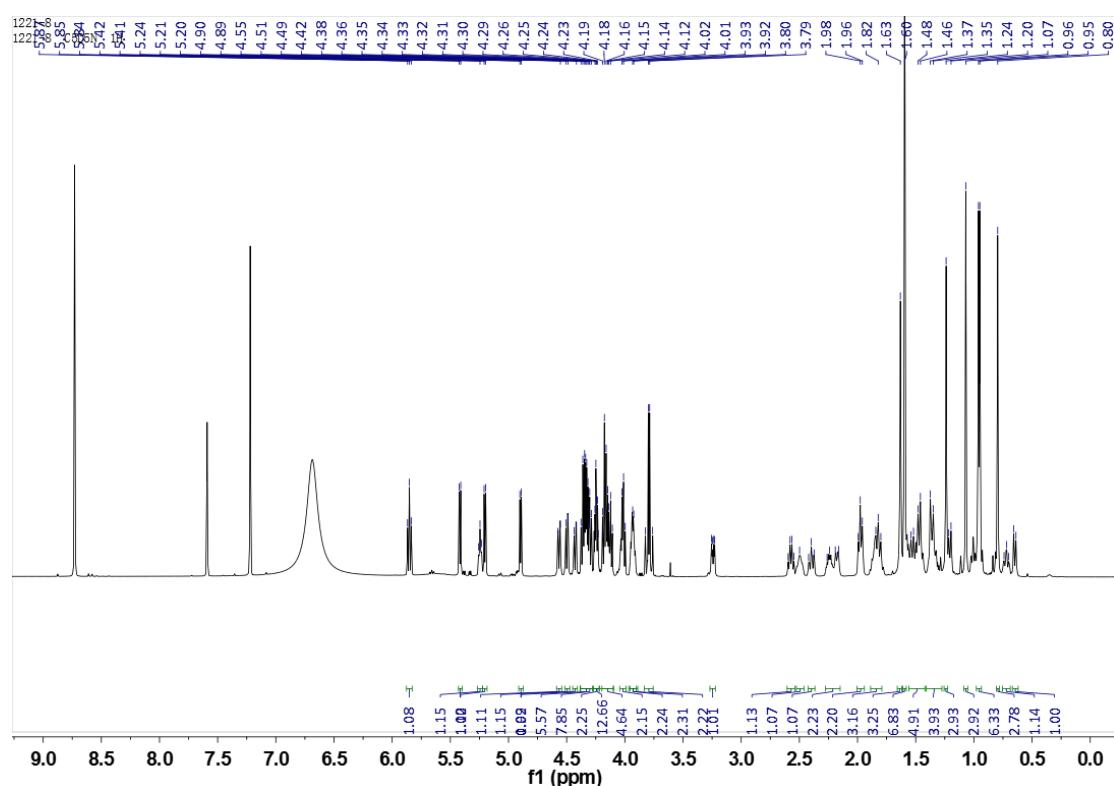


Figure S63. ^1H NMR spectrum of compound **8**.

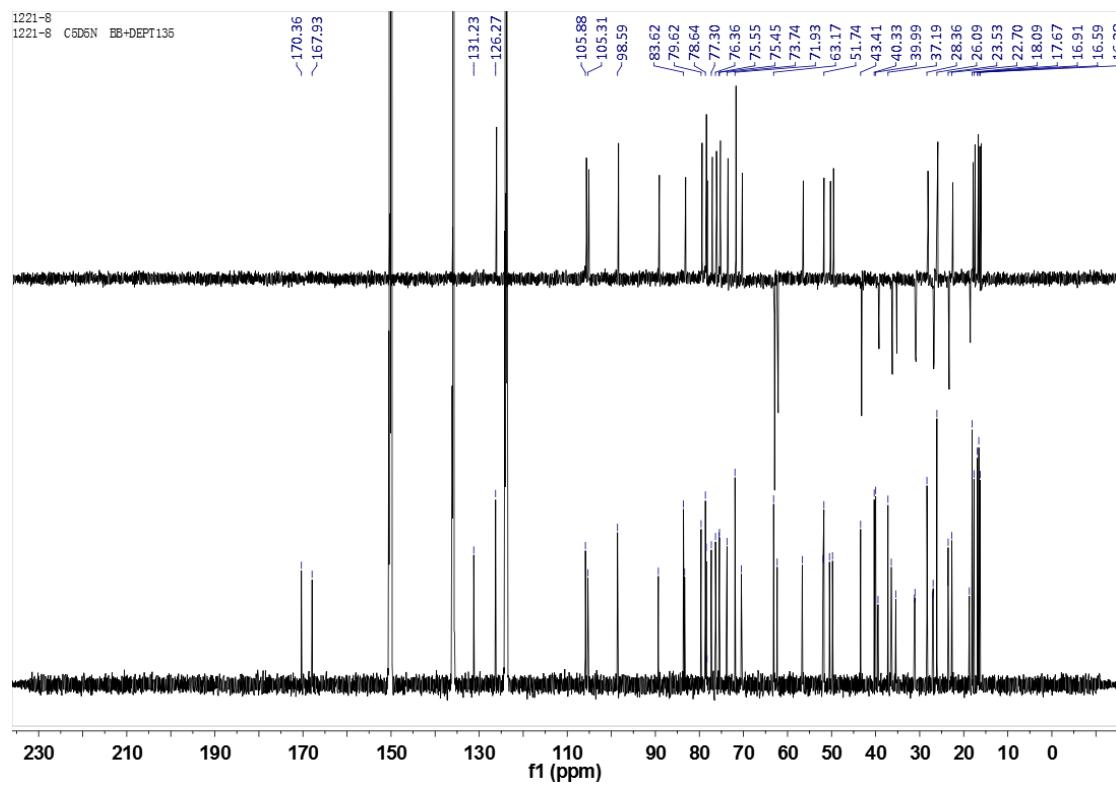


Figure S64. ^{13}C NMR and DEPT-135 spectra of compound **8**.

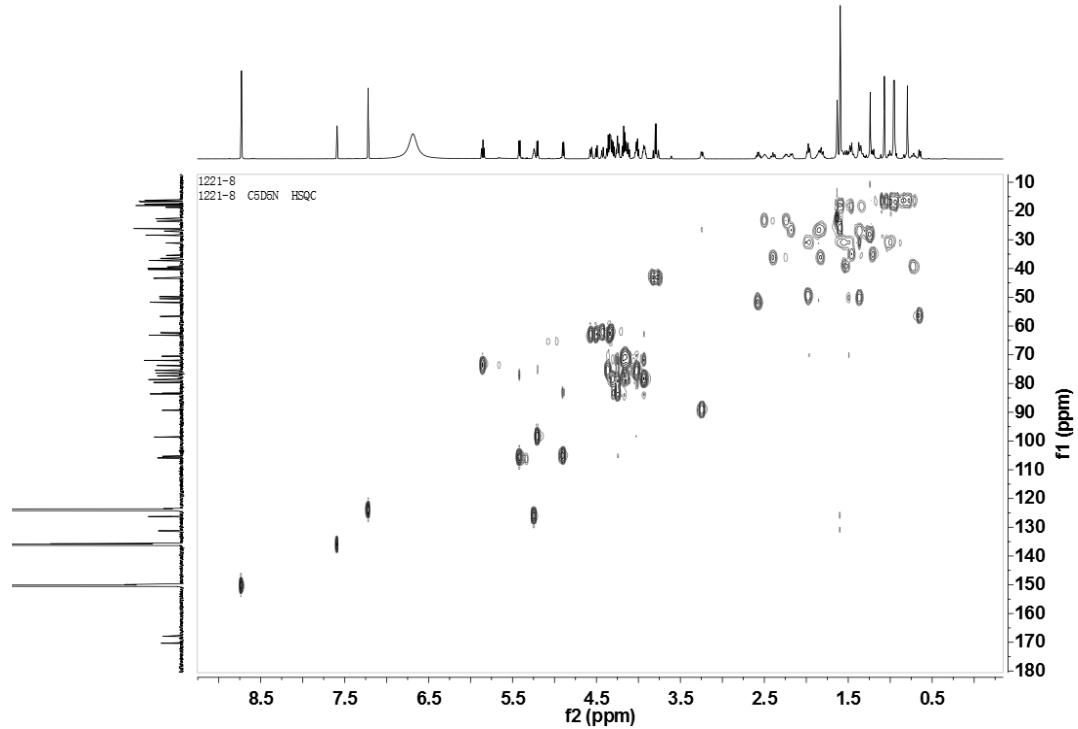


Figure S65. HSQC spectrum of compound **8**.

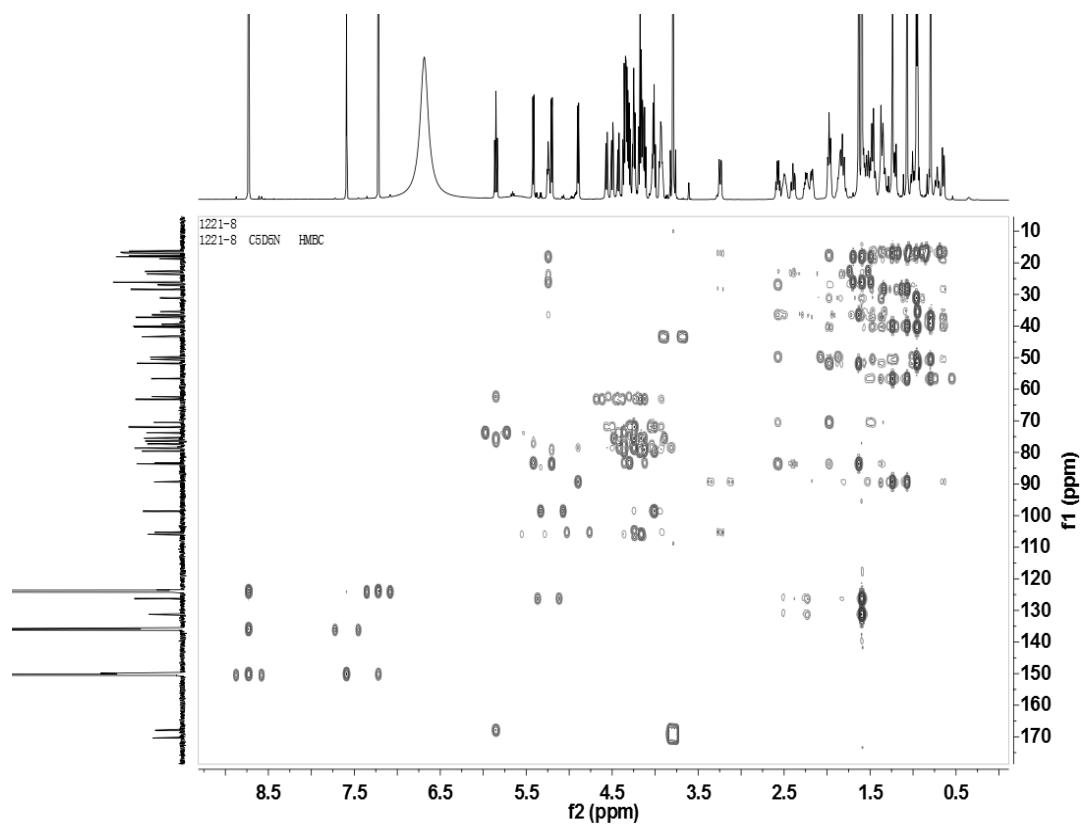


Figure S66. HMBC spectrum of compound **8**.

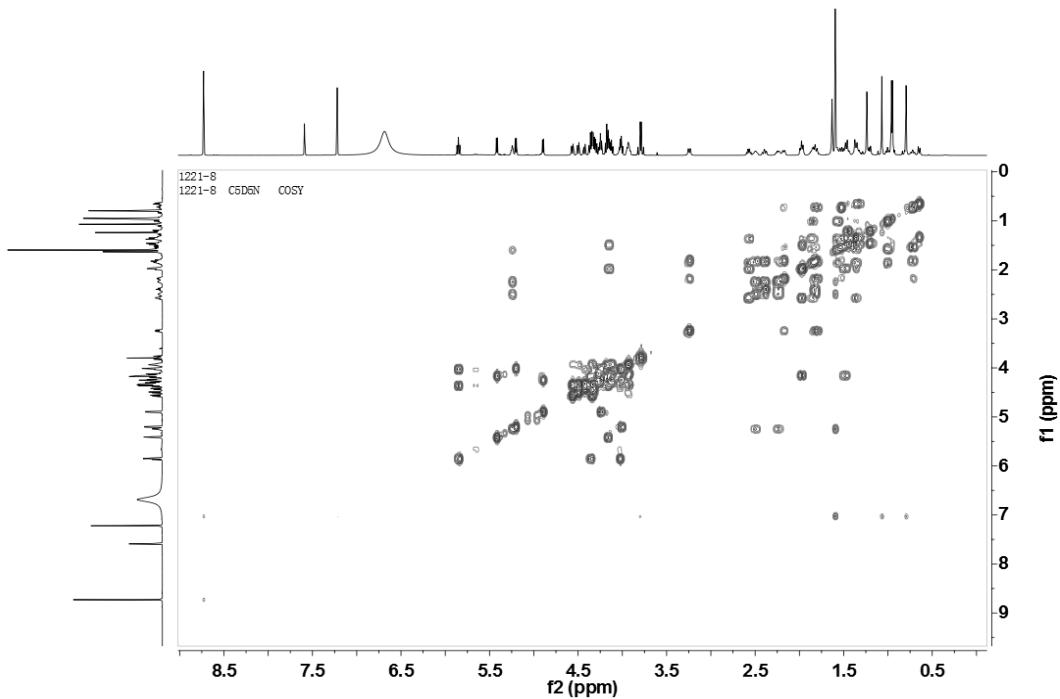


Figure S67. ^1H - ^1H COSY spectrum of compound **8**.

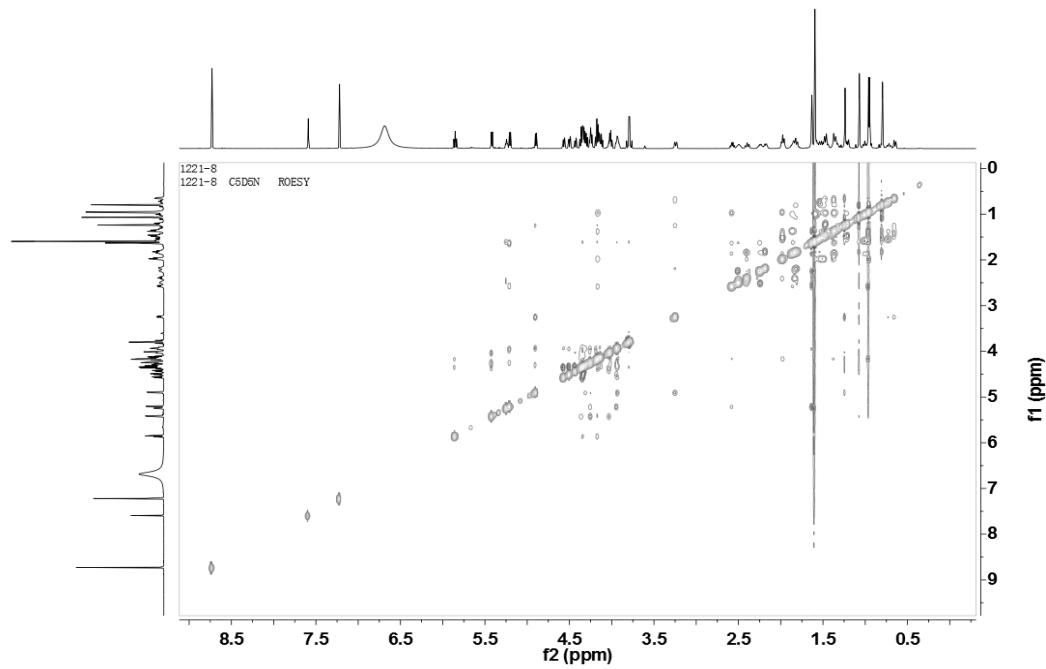


Figure S68. ROESY spectrum of compound **8**.

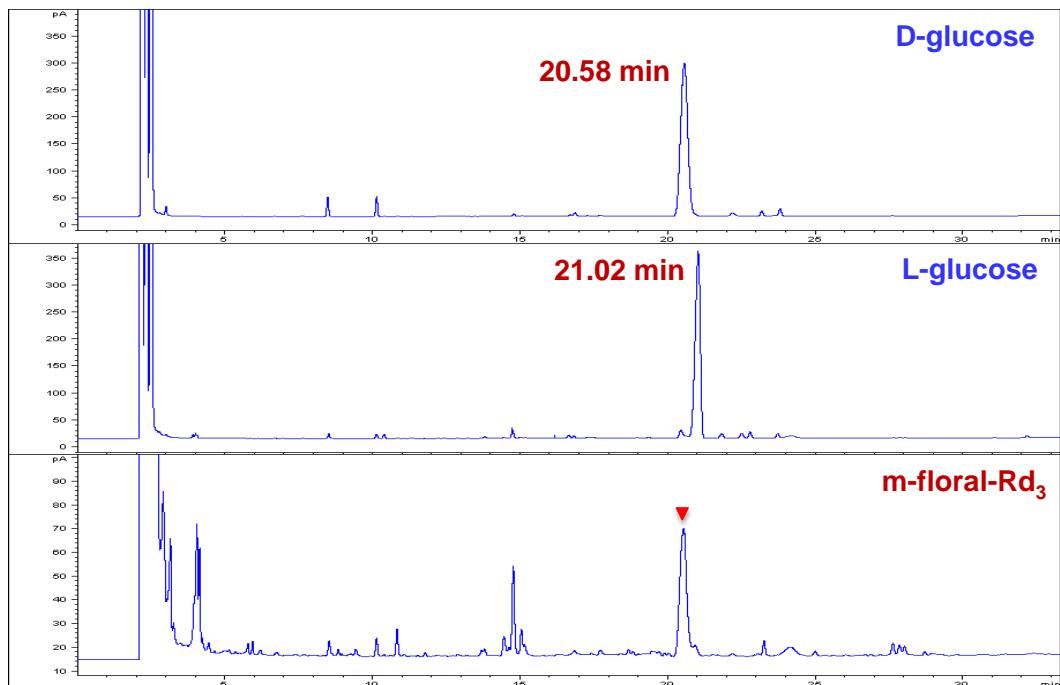


Figure S69. The GC chromatograms of compound **8** after acidic hydrolysis.

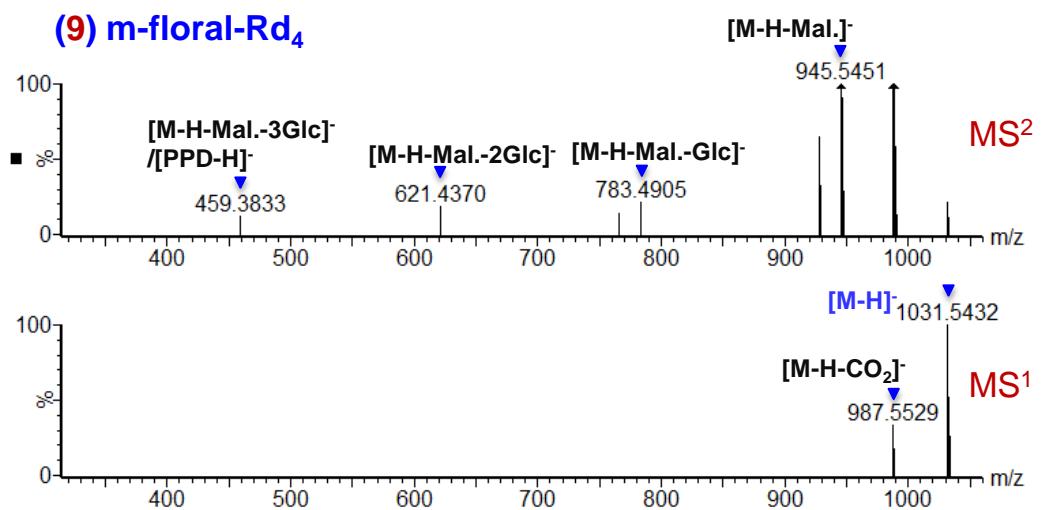


Figure S70. HRESIMS spectrum of compound 9.

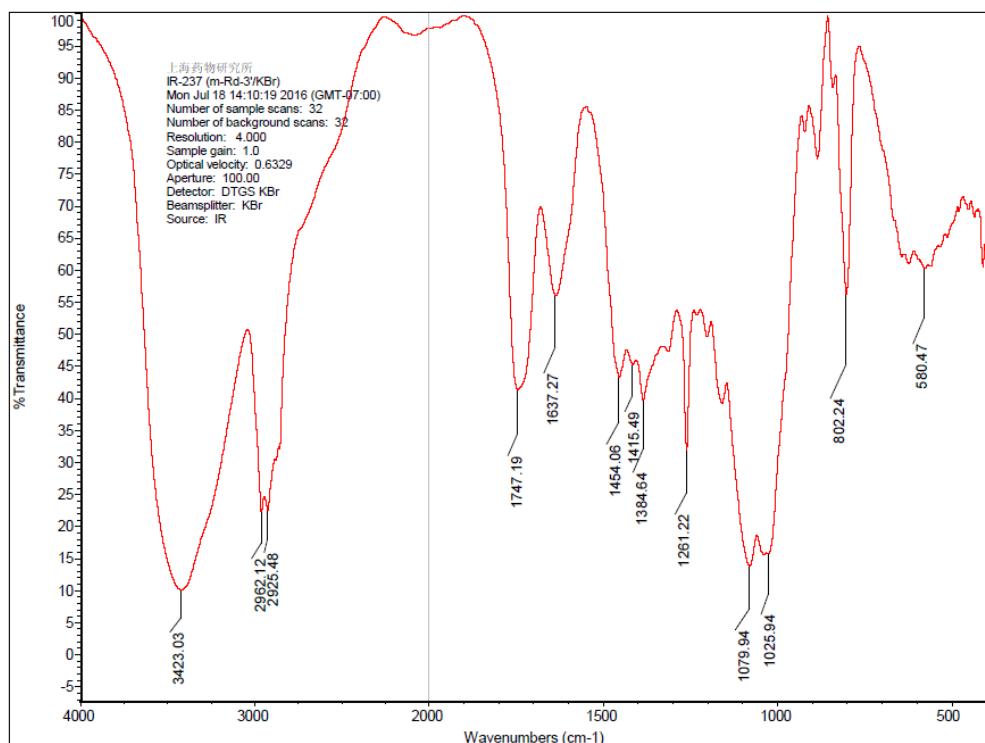


Figure S71. IR spectrum of compound 9.

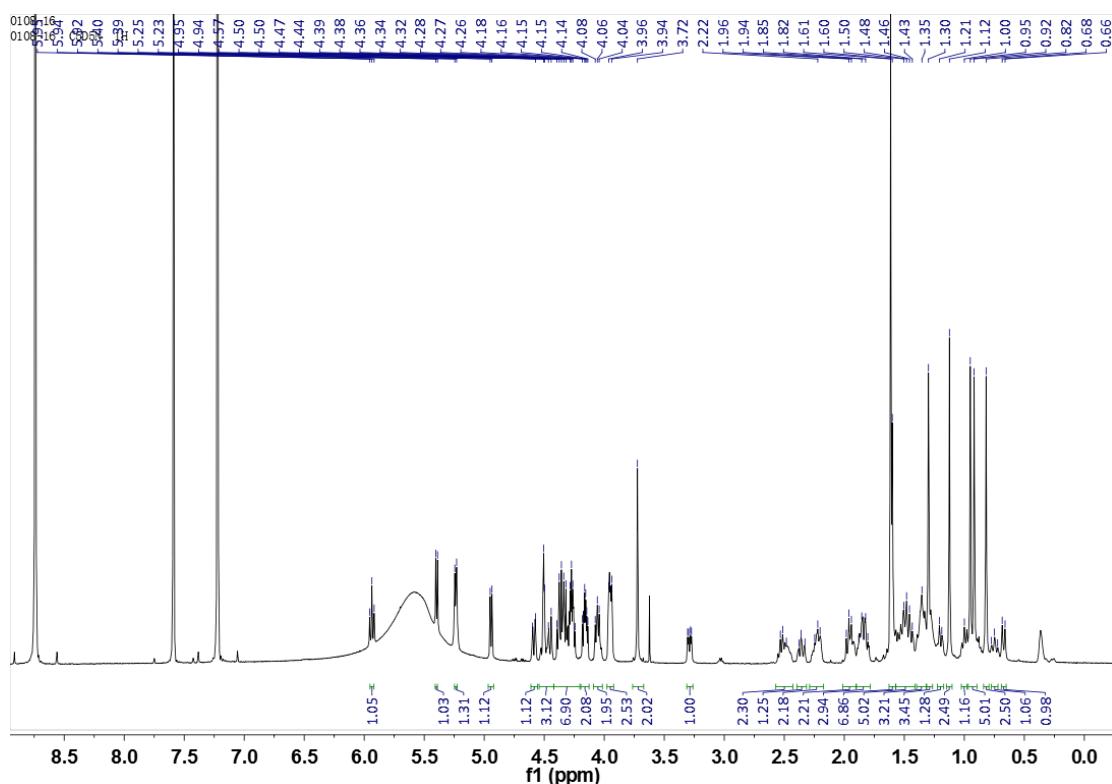


Figure S72. ^1H NMR spectrum of compound 9.

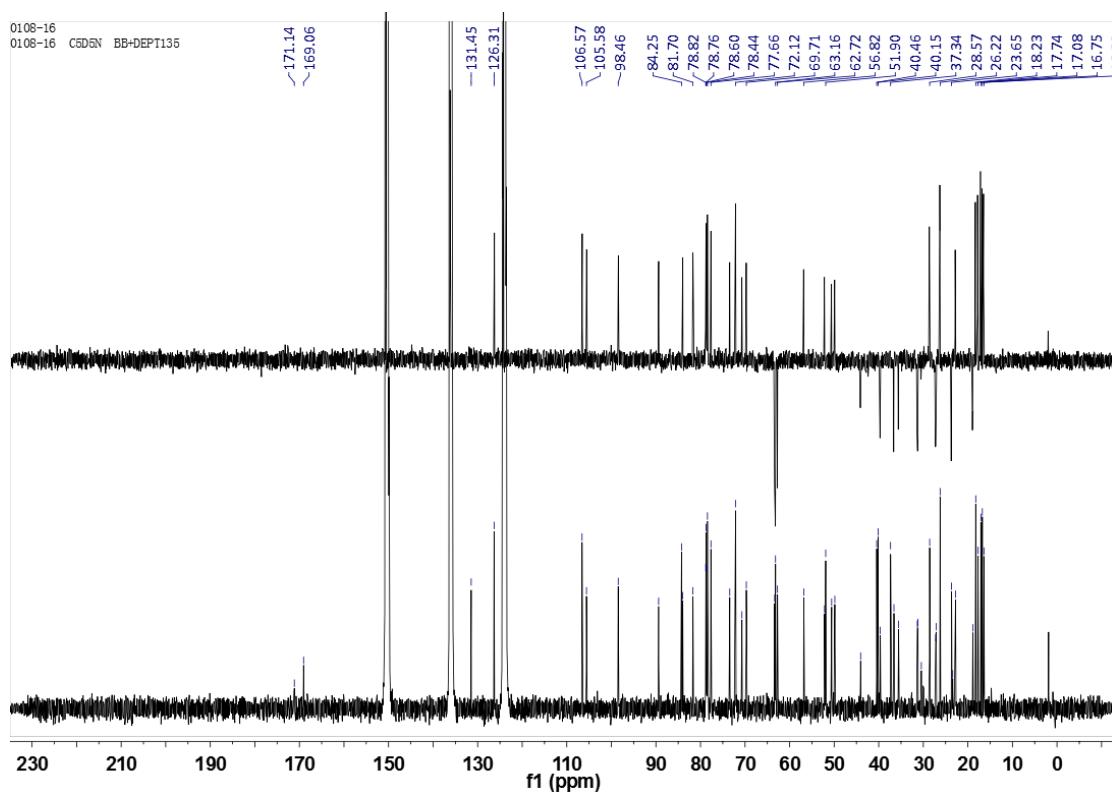


Figure S73. ^{13}C NMR and DEPT-135 spectra of compound 9.

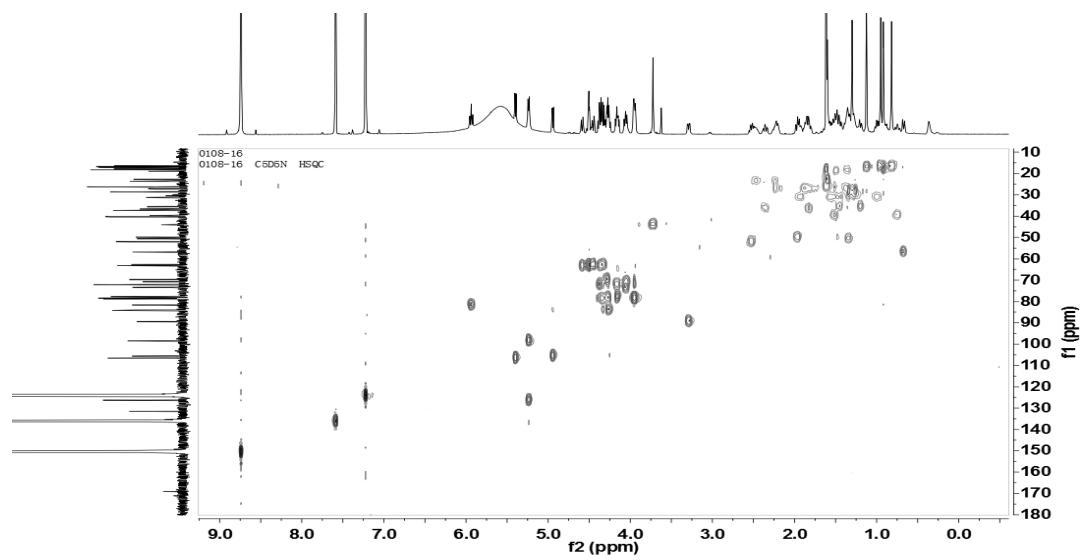


Figure S74. HSQC spectrum of compound 9.

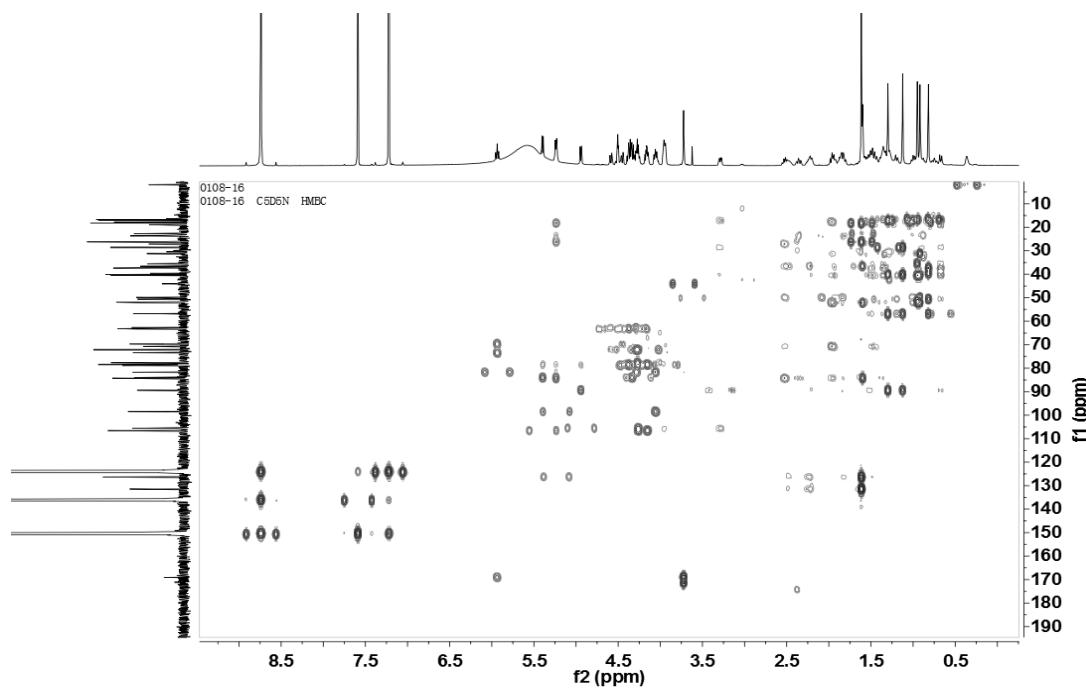


Figure S75. HMBC spectrum of compound 9.

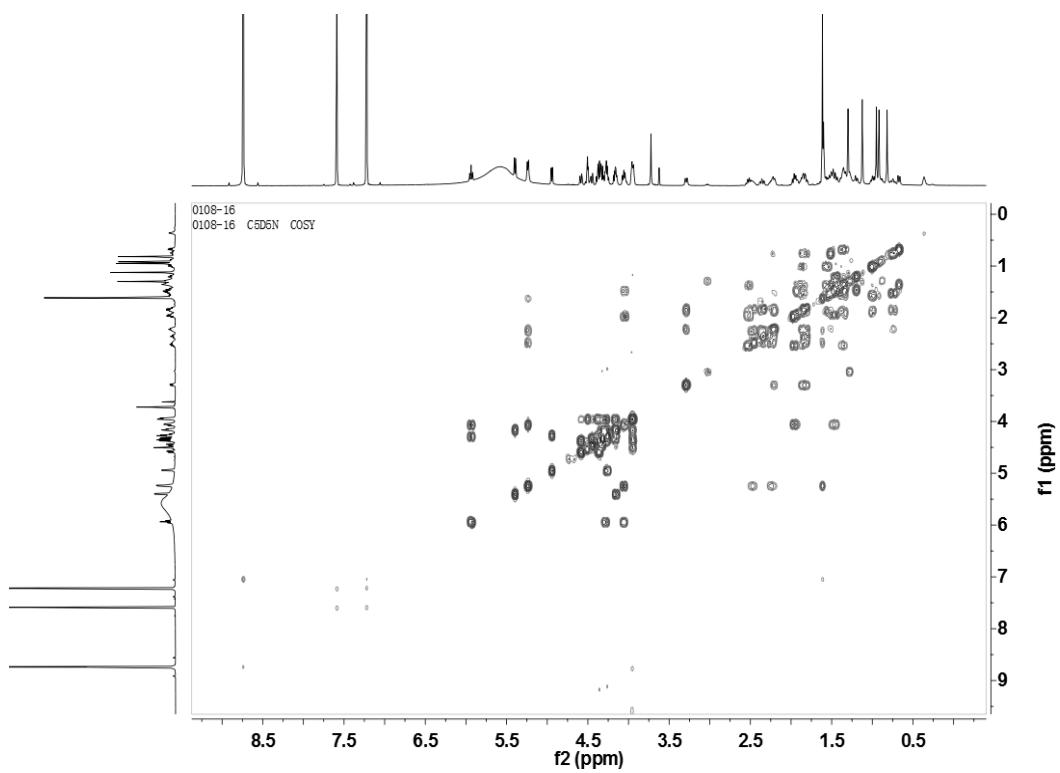


Figure S76. ^1H - ^1H COSY spectrum of compound **9**.

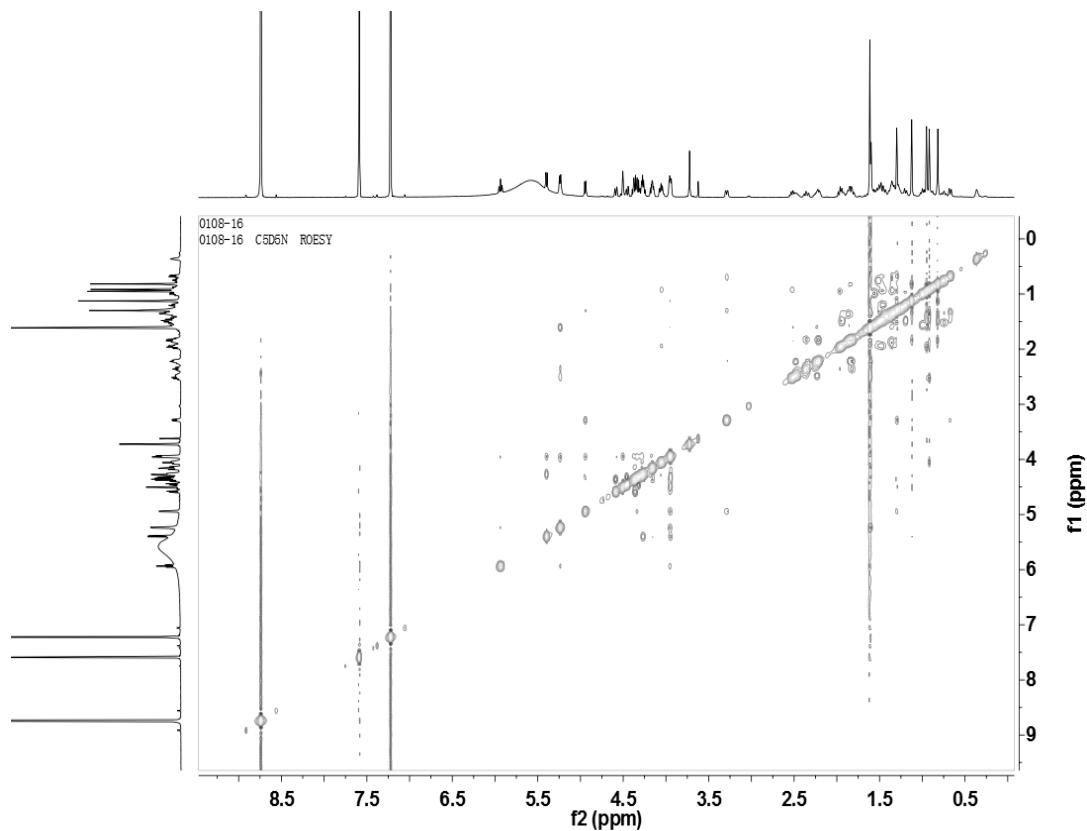


Figure S77. ROESY spectrum of compound **9**.

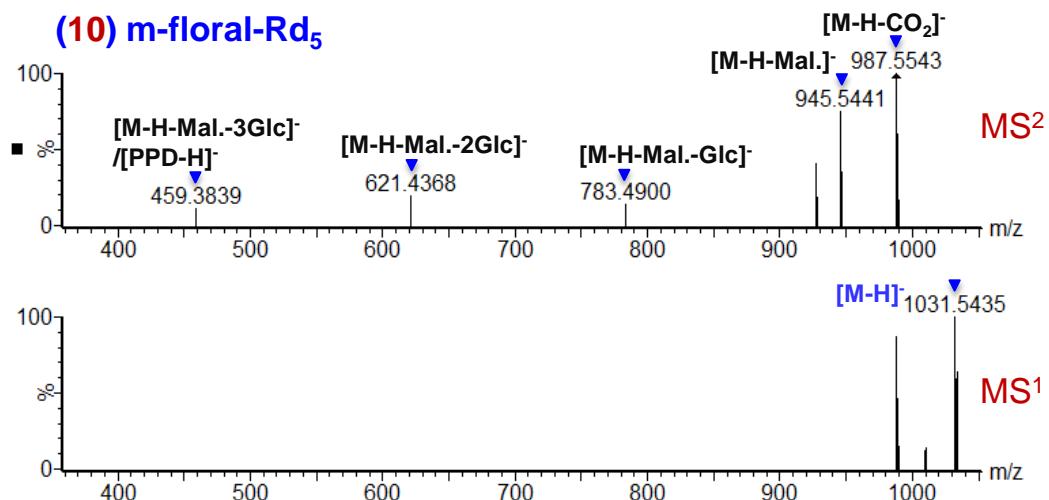


Figure S78. HRESIMS spectrum of compound **10**.

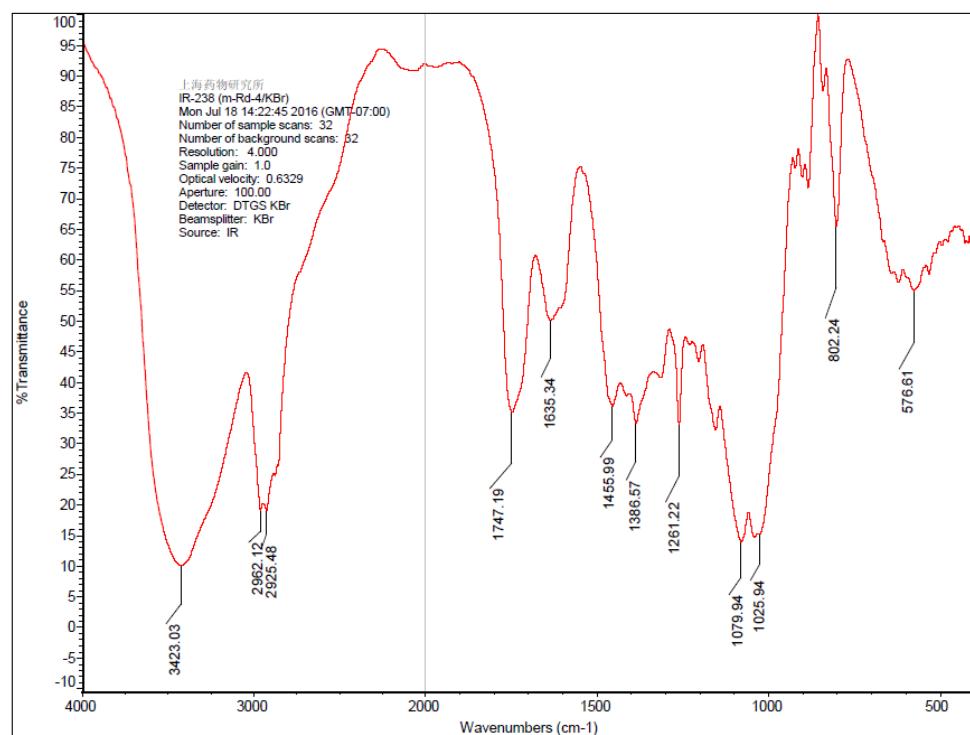


Figure S79. IR spectrum of compound **10**.

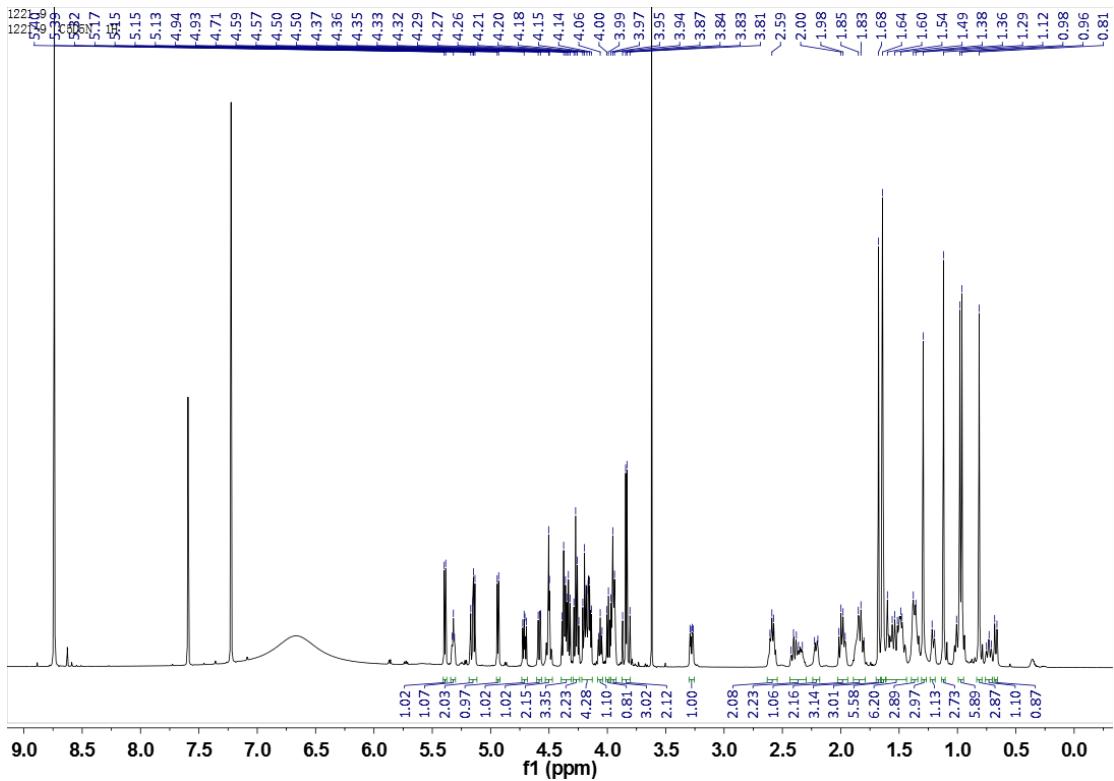


Figure S80. ^1H NMR spectrum of compound **10**.

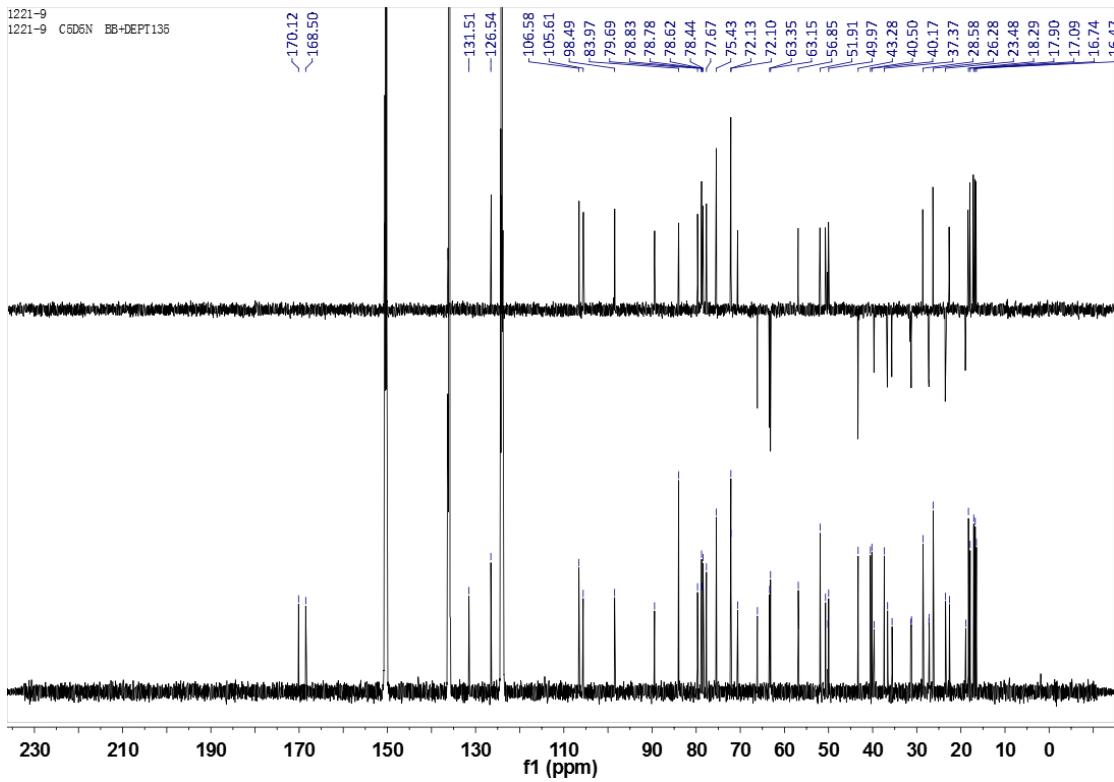


Figure S81. ^{13}C NMR and DEPT-135 spectra of compound **10**.

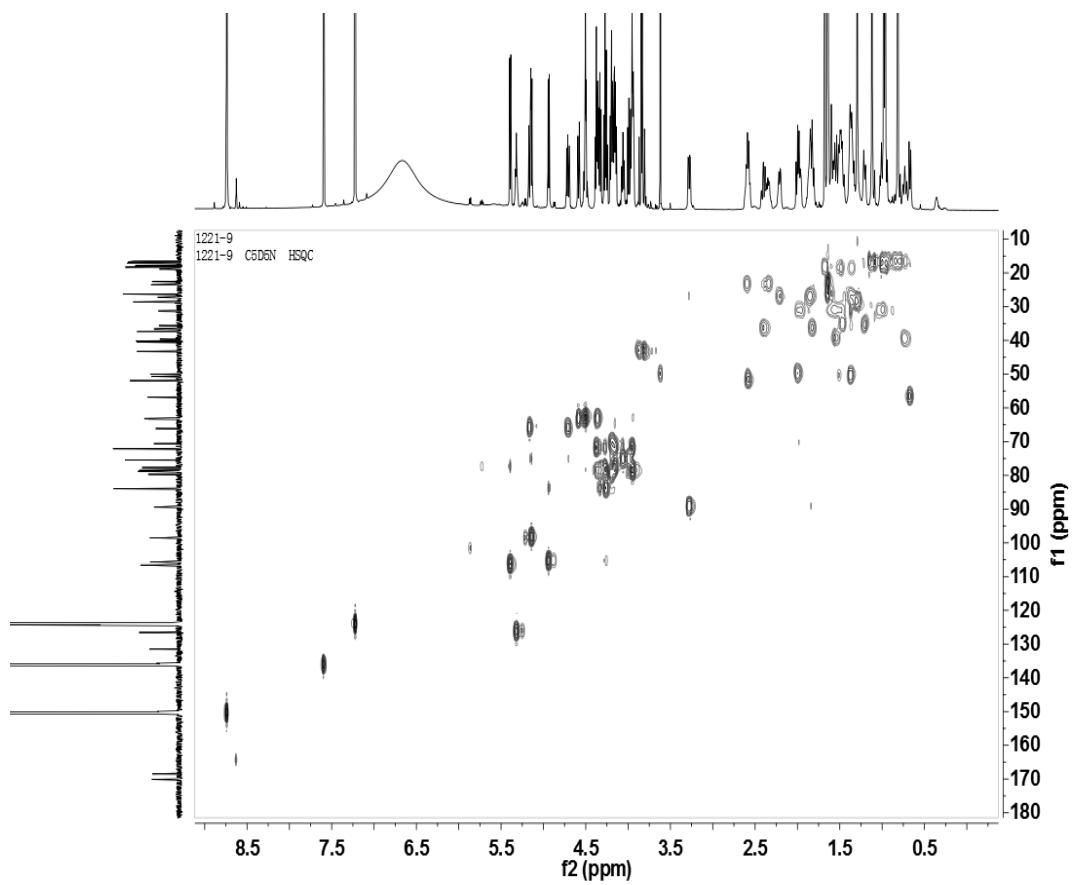


Figure S82. HSQC spectrum of compound **10**.

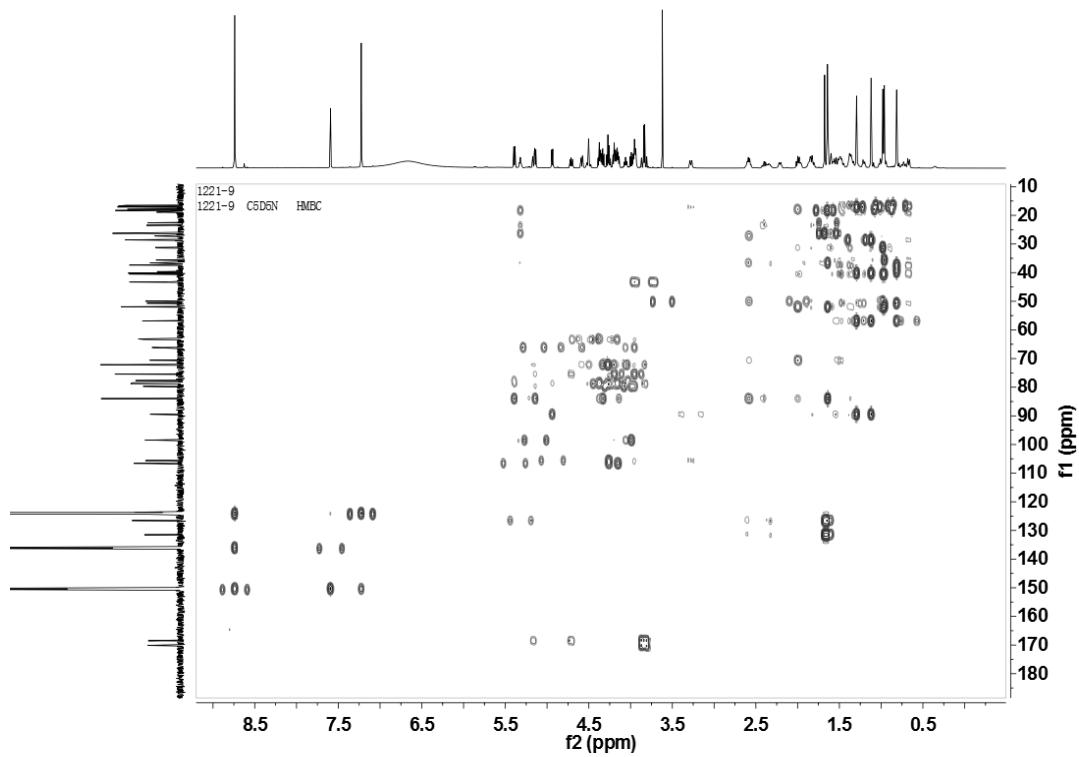


Figure S83. HMBC spectrum of compound **10**.

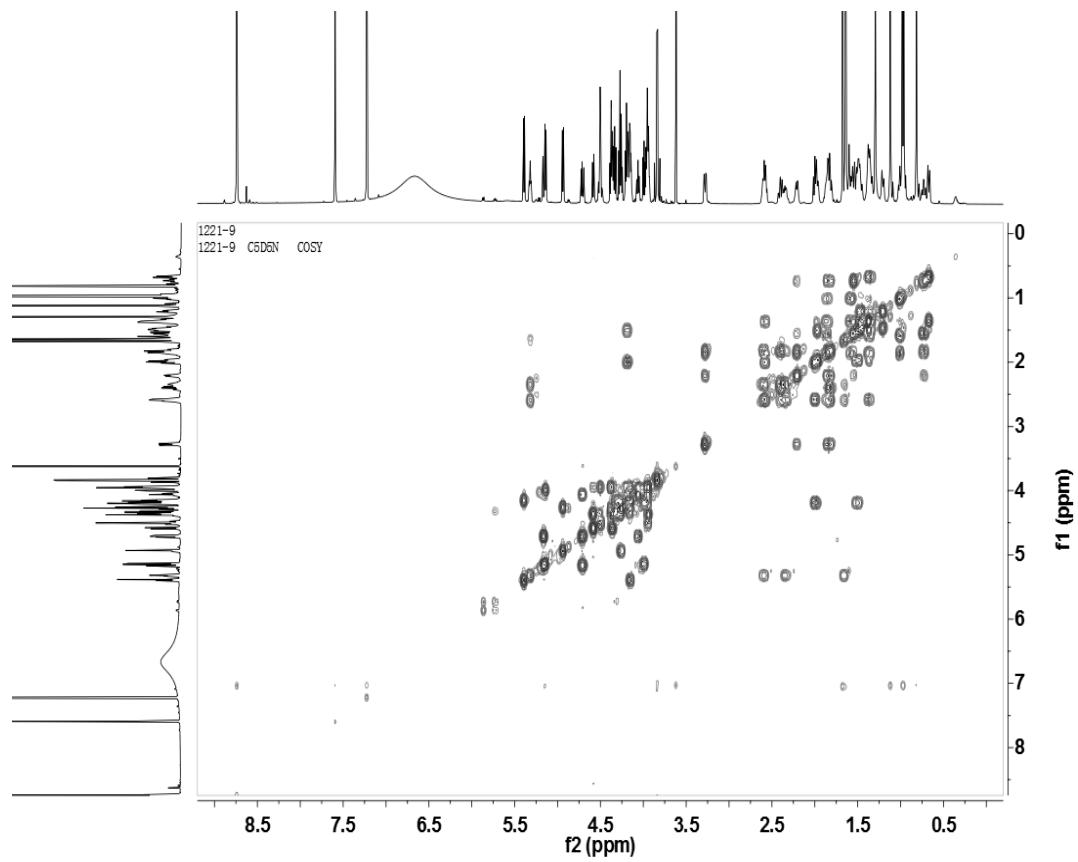


Figure S84. ^1H - ^1H COSY spectrum of compound **10**.

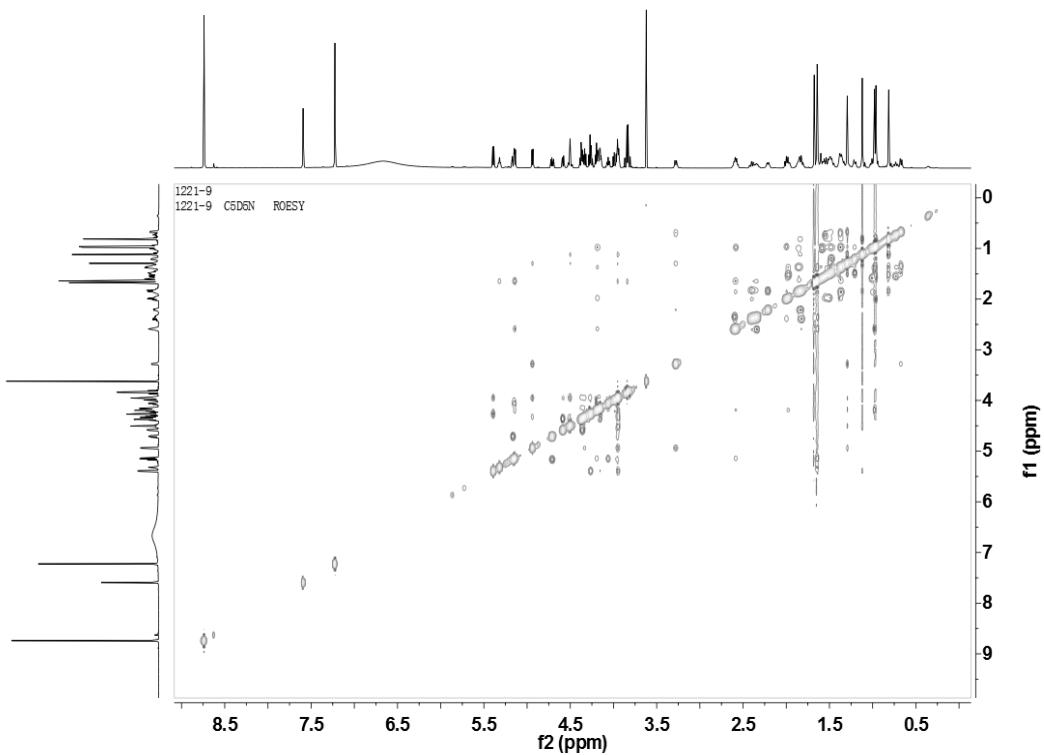


Figure S85. ROESY spectrum of compound **10**.

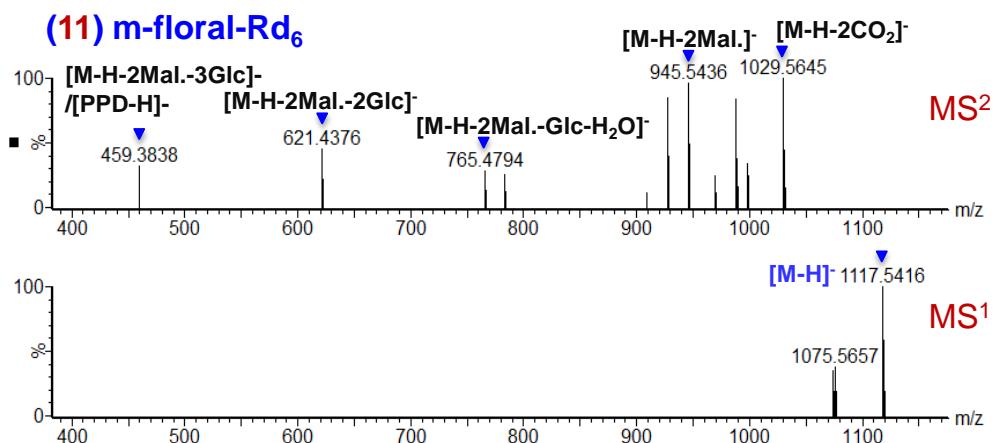


Figure S86. HRESIMS spectrum of compound **11**.

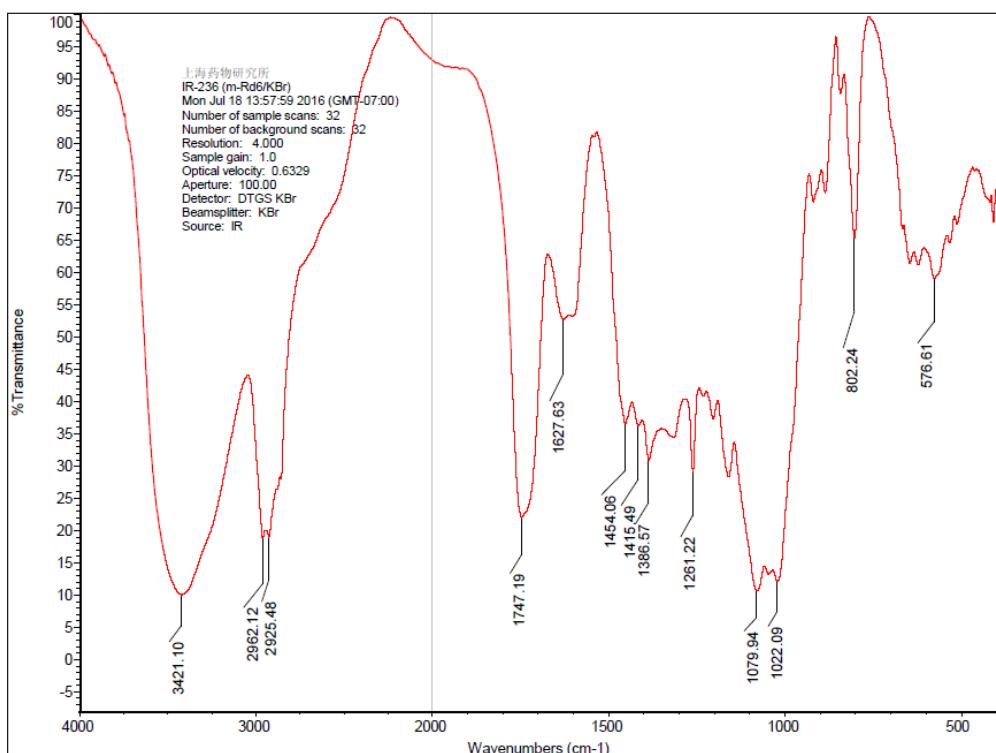


Figure S87. IR spectrum of compound **11**.

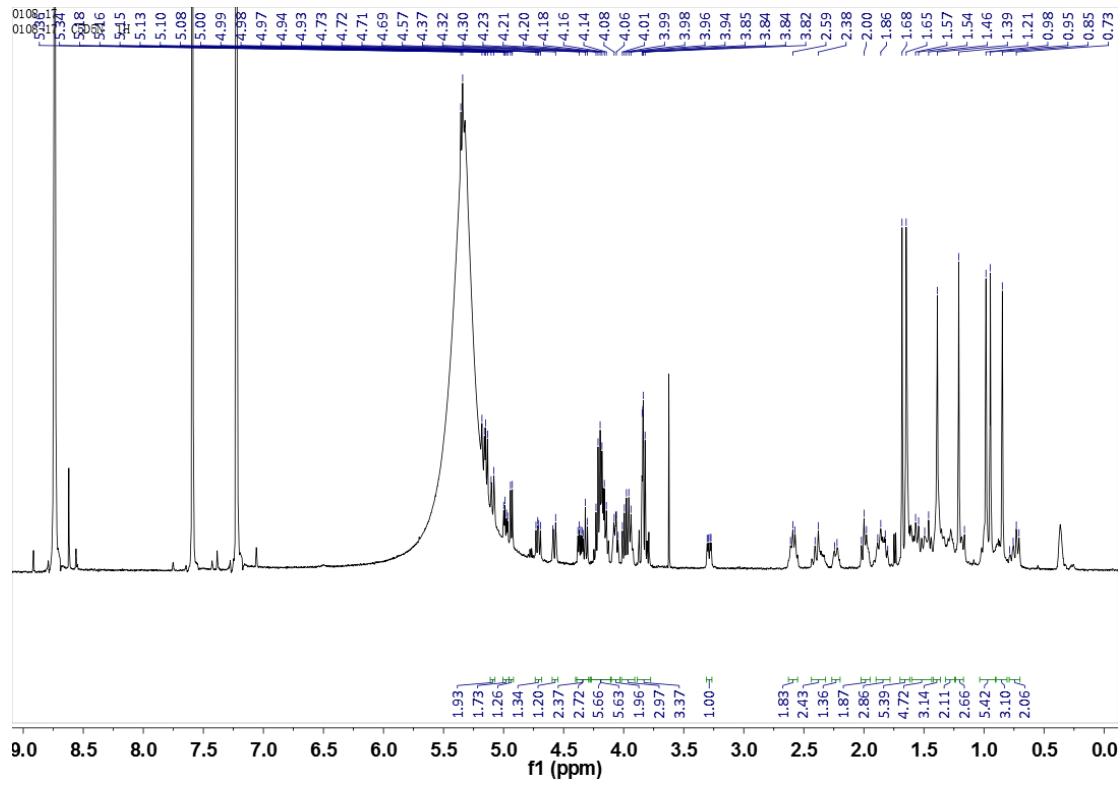
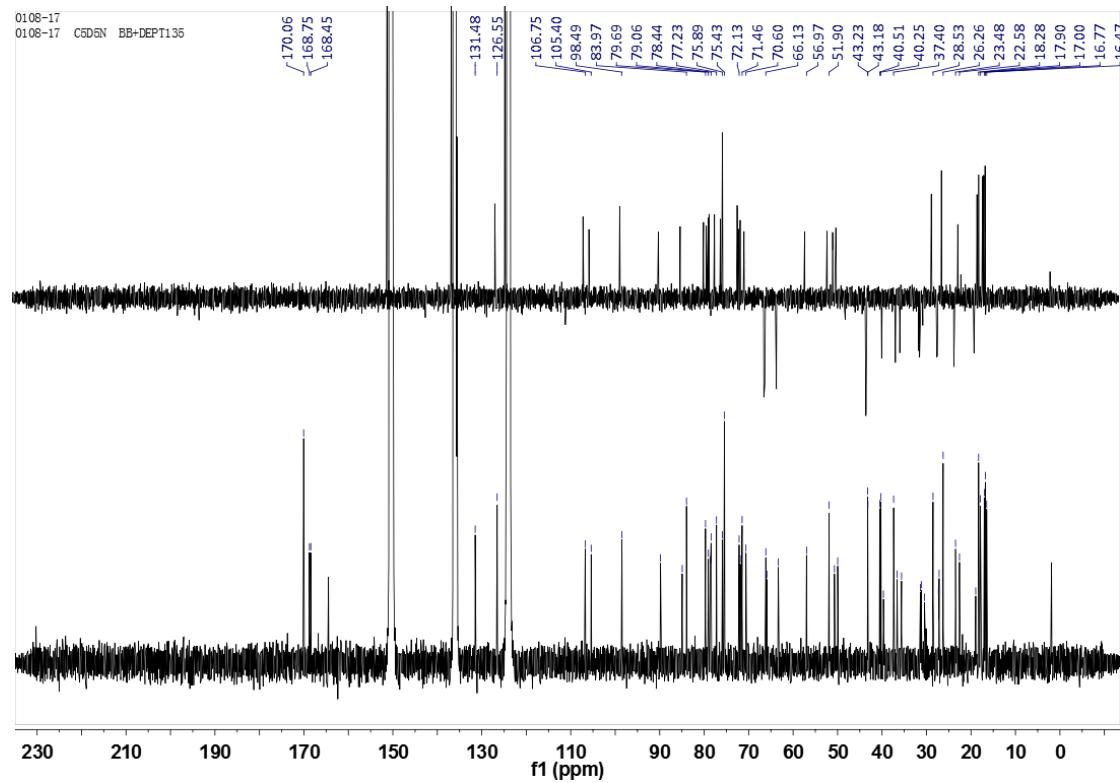


Figure S88. ^1H NMR spectrum of compound **11**.



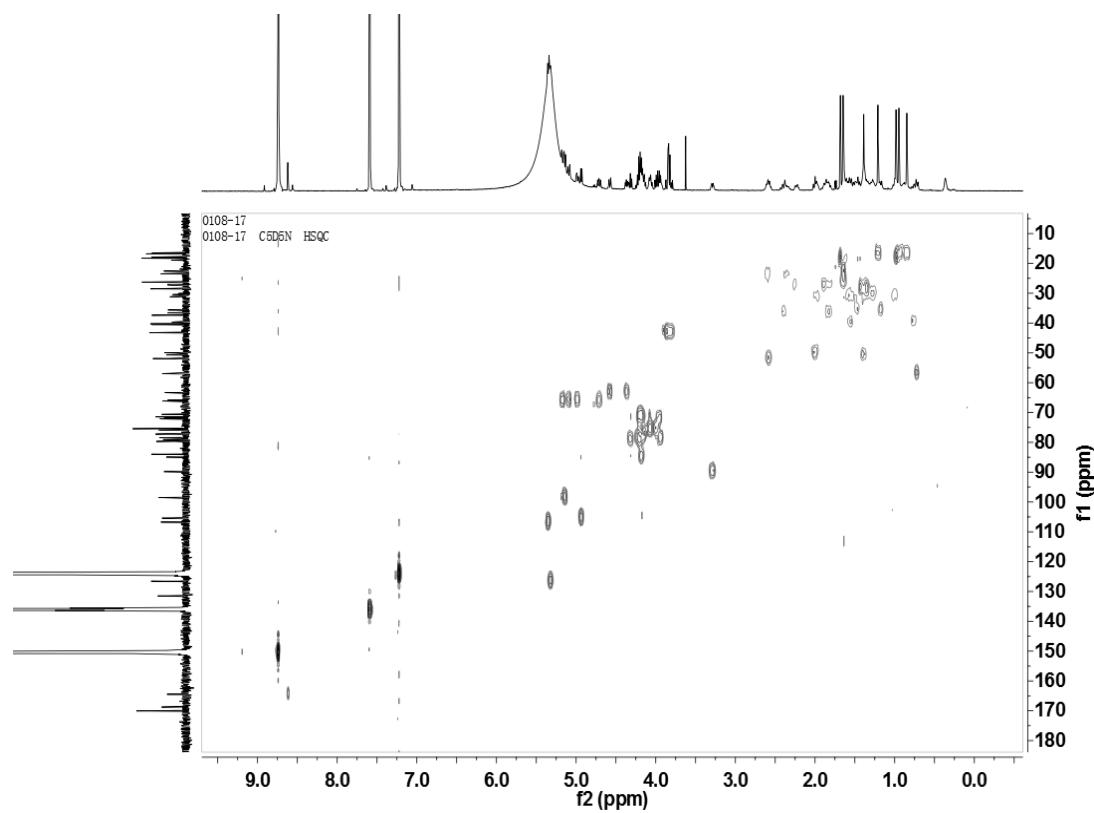


Figure S90. HSQC spectrum of compound 11.

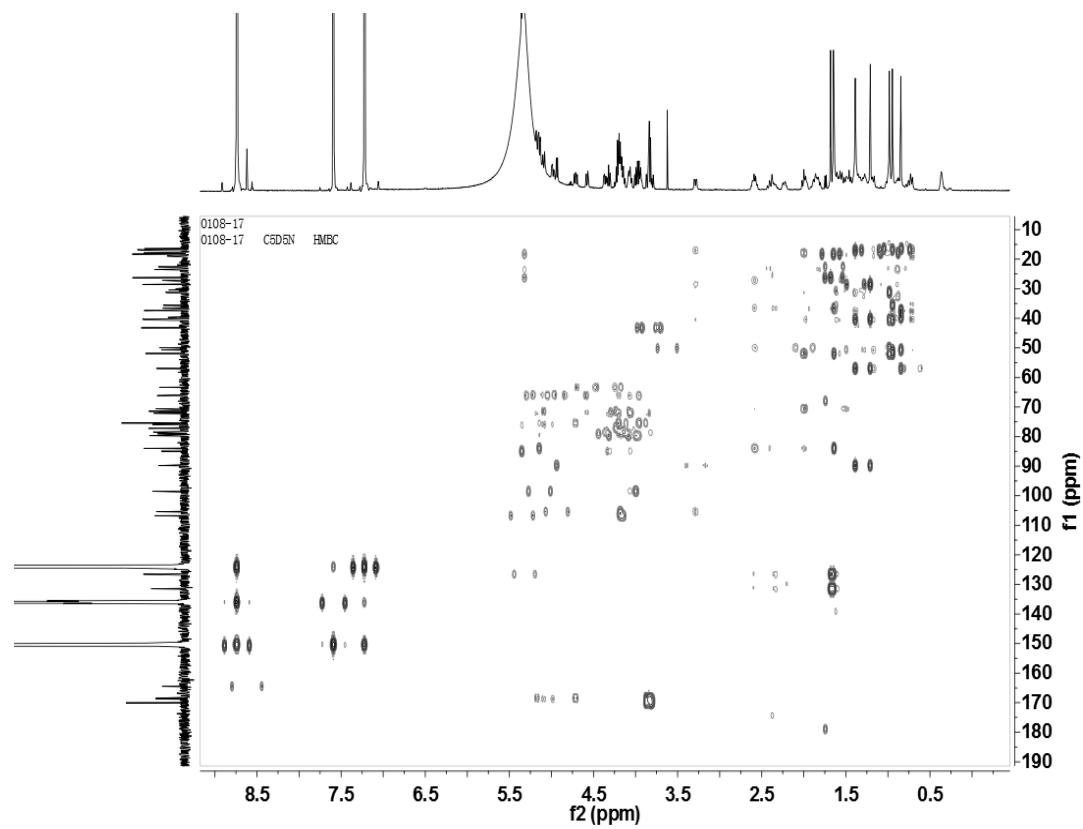


Figure S91. HMBC spectrum of compound 11.

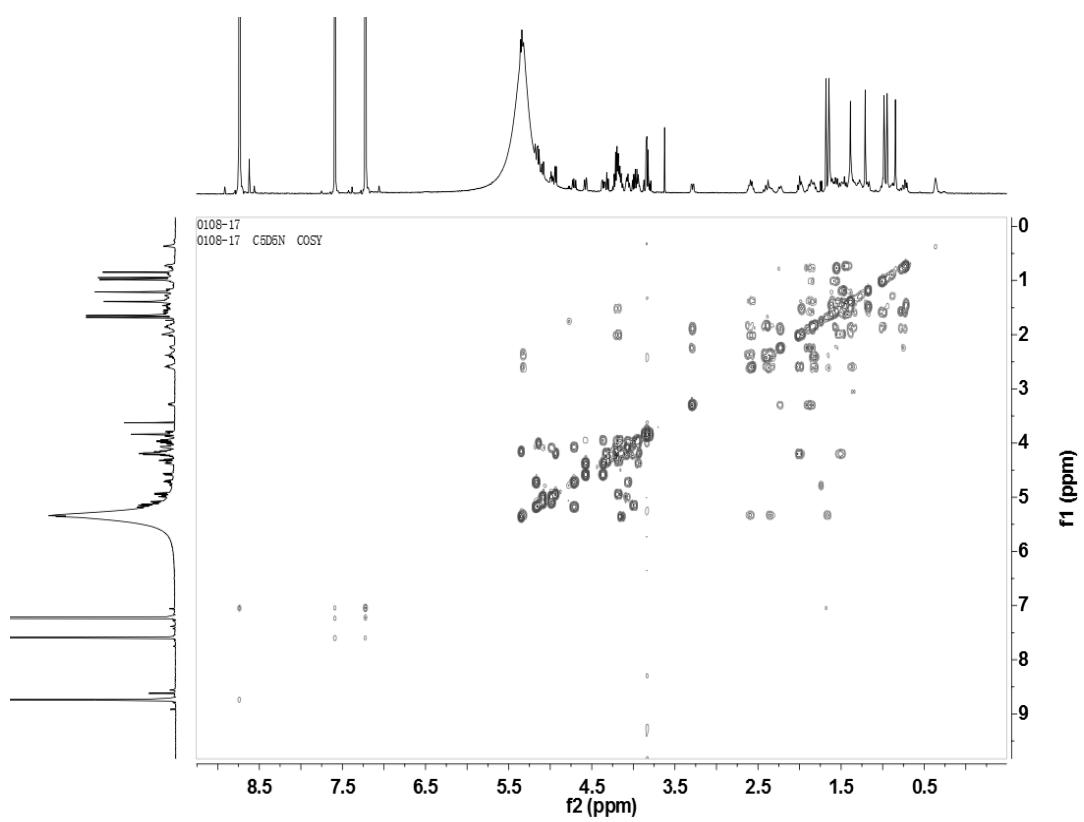


Figure S92. ^1H - ^1H COSY spectrum of compound 11.

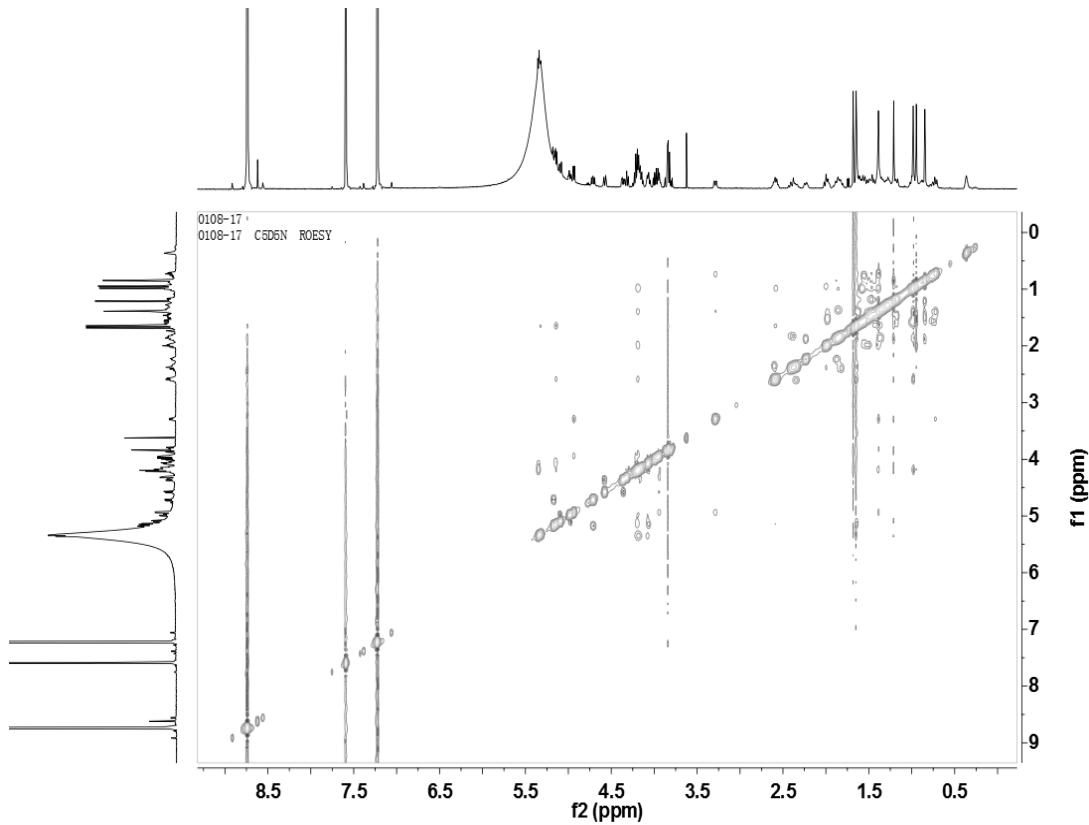


Figure S93. ROESY spectrum of compound 11.

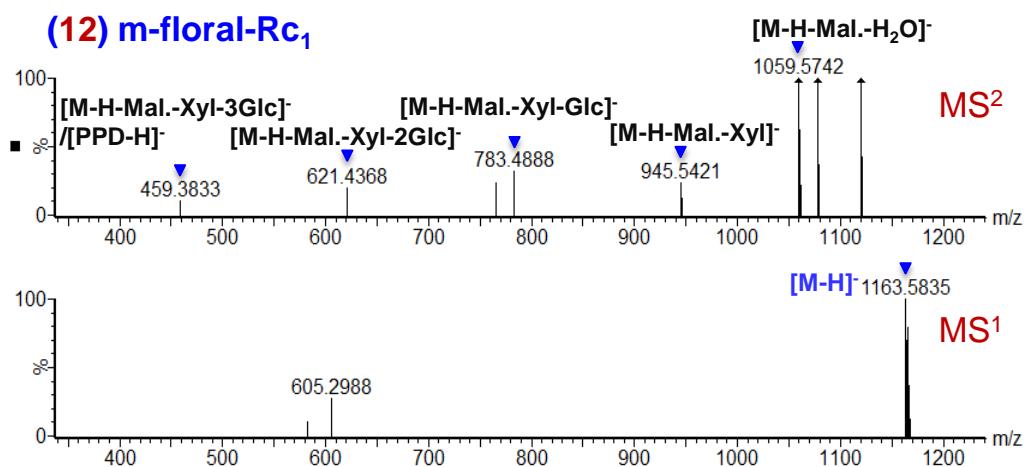


Figure S94. HRESIMS spectrum of compound 12.

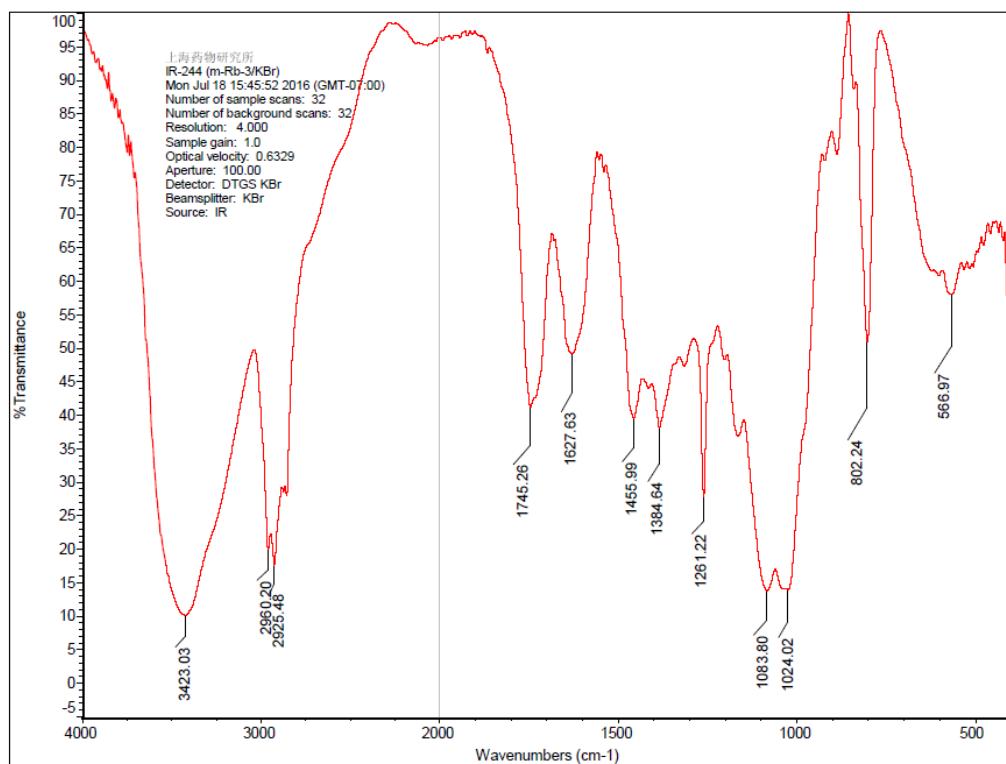


Figure S95. IR spectrum of compound 12.

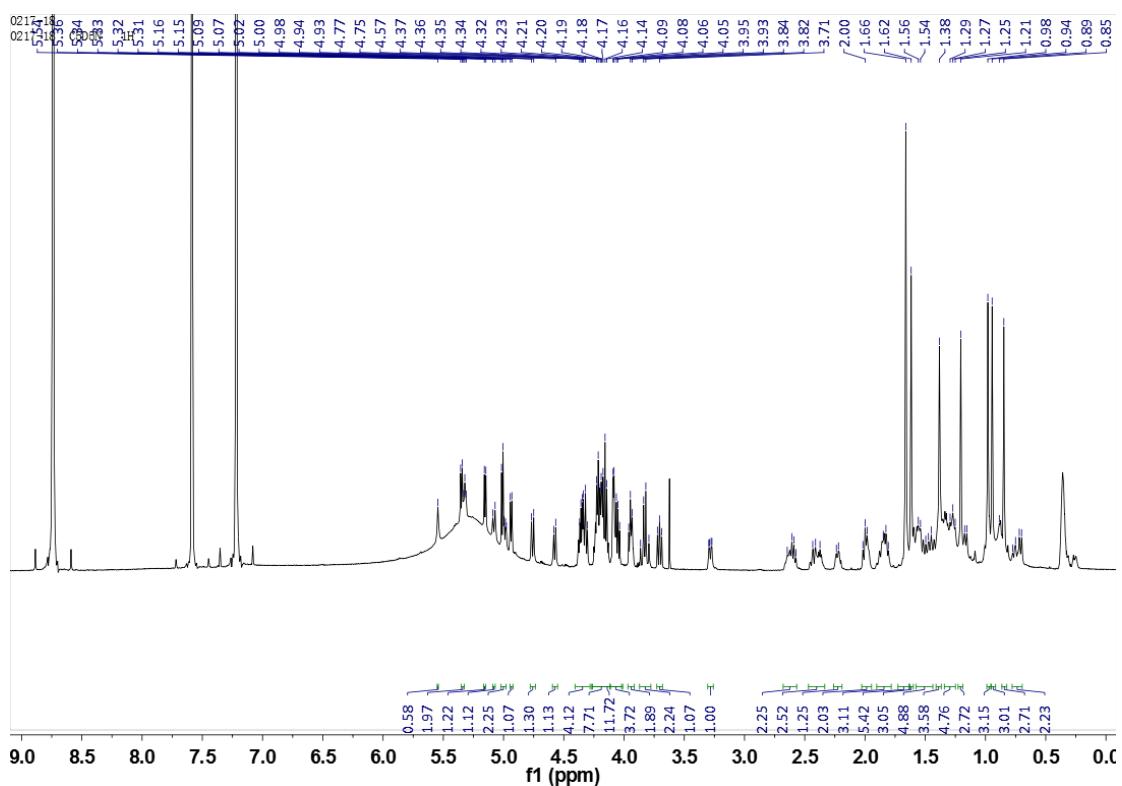


Figure S96. ^1H NMR spectrum of compound **12**.

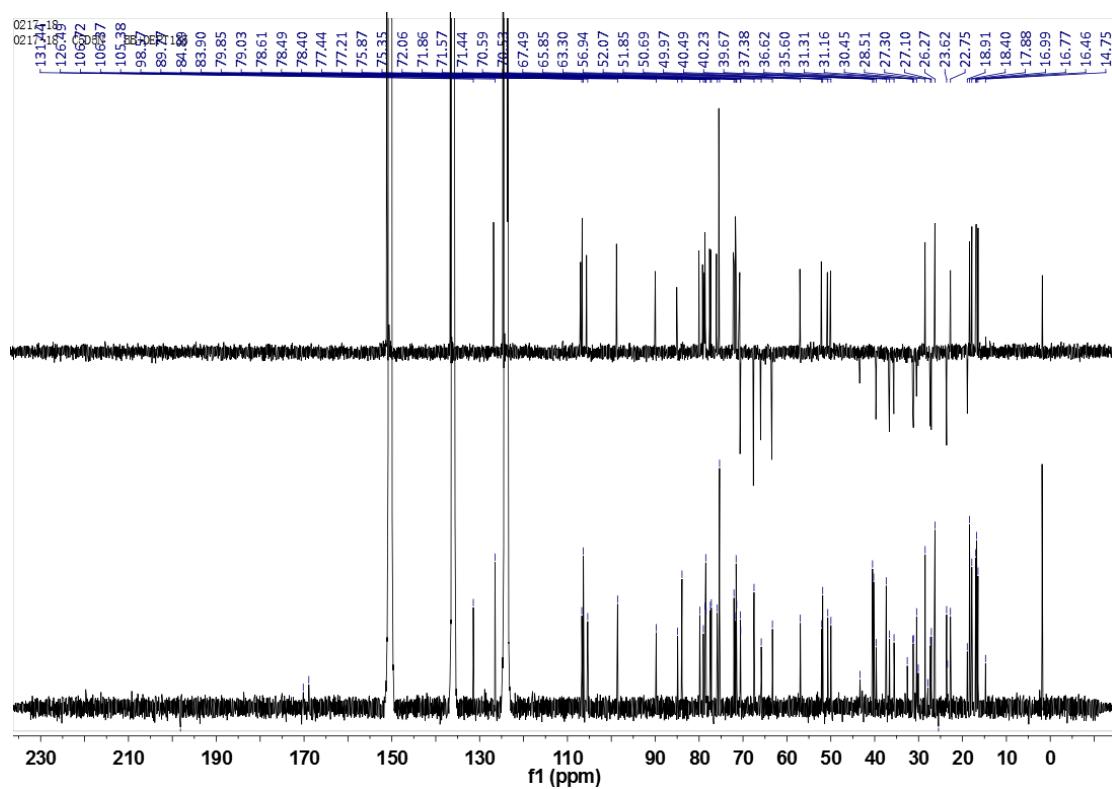


Figure S97. ^{13}C NMR and DEPT-135 spectrum of compound **12**.

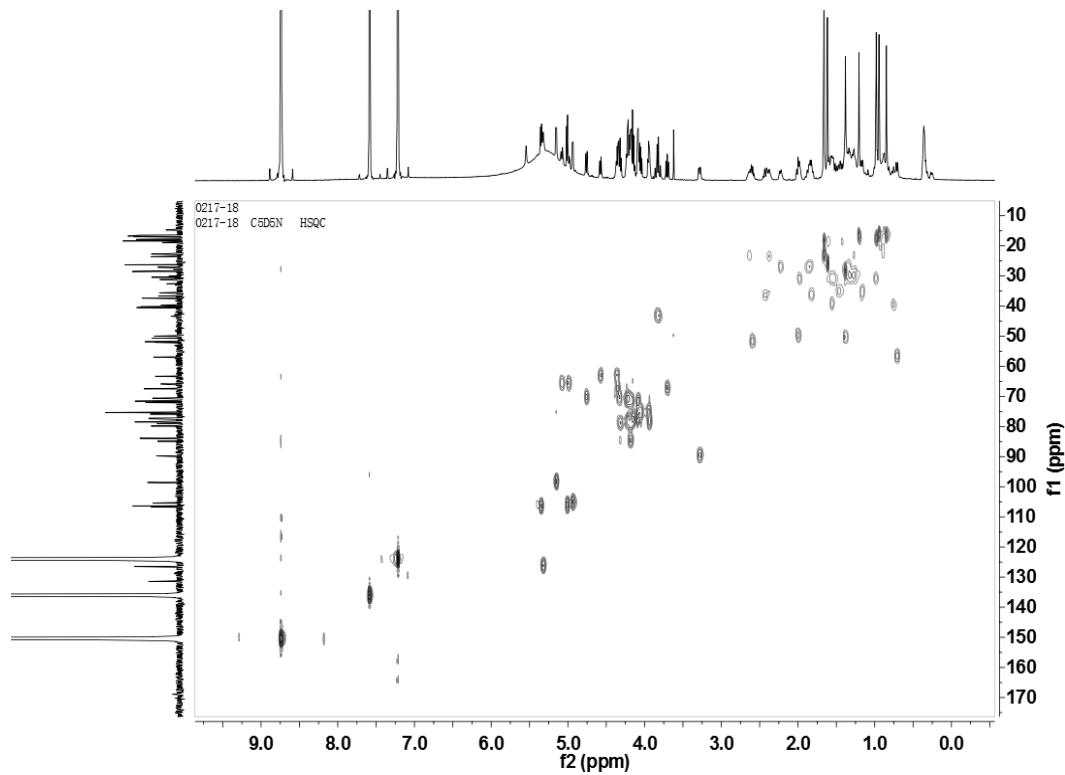


Figure S98. HSQC spectrum of compound **12**.

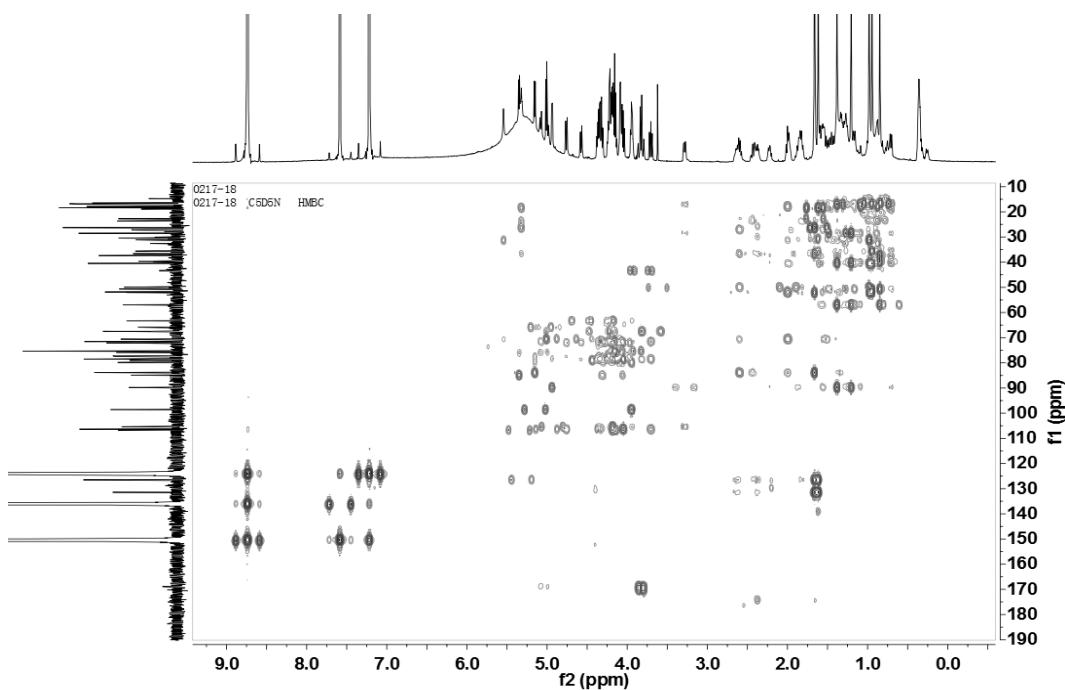


Figure S99. HMBC spectrum of compound **12**.

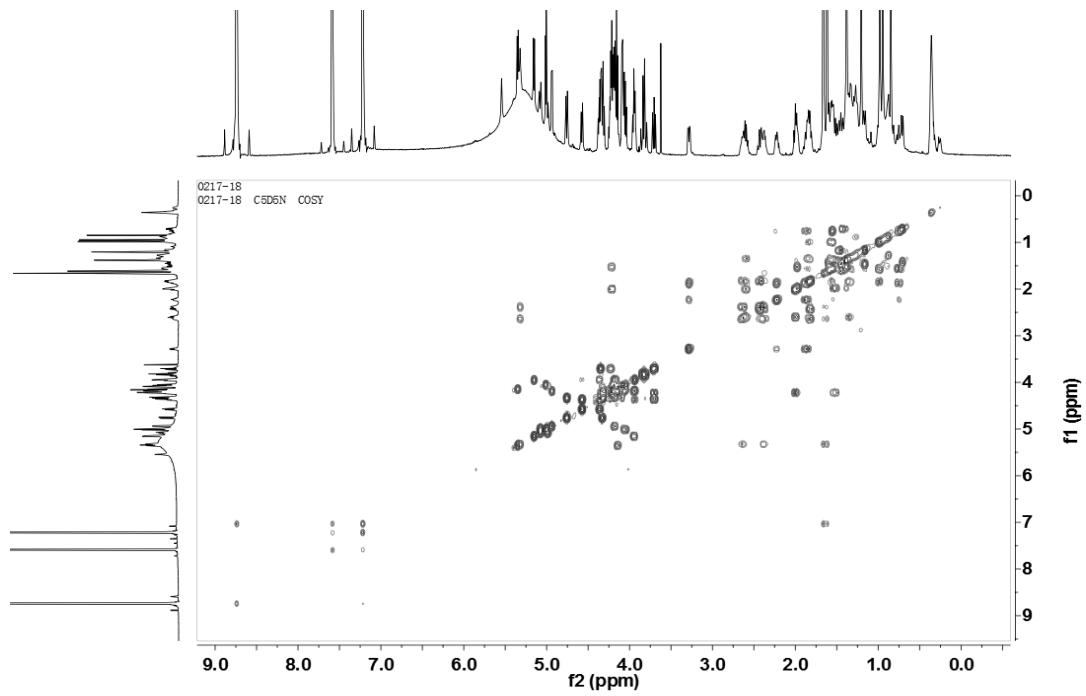


Figure S100. ^1H - ^1H COSY spectrum of compound **12**.

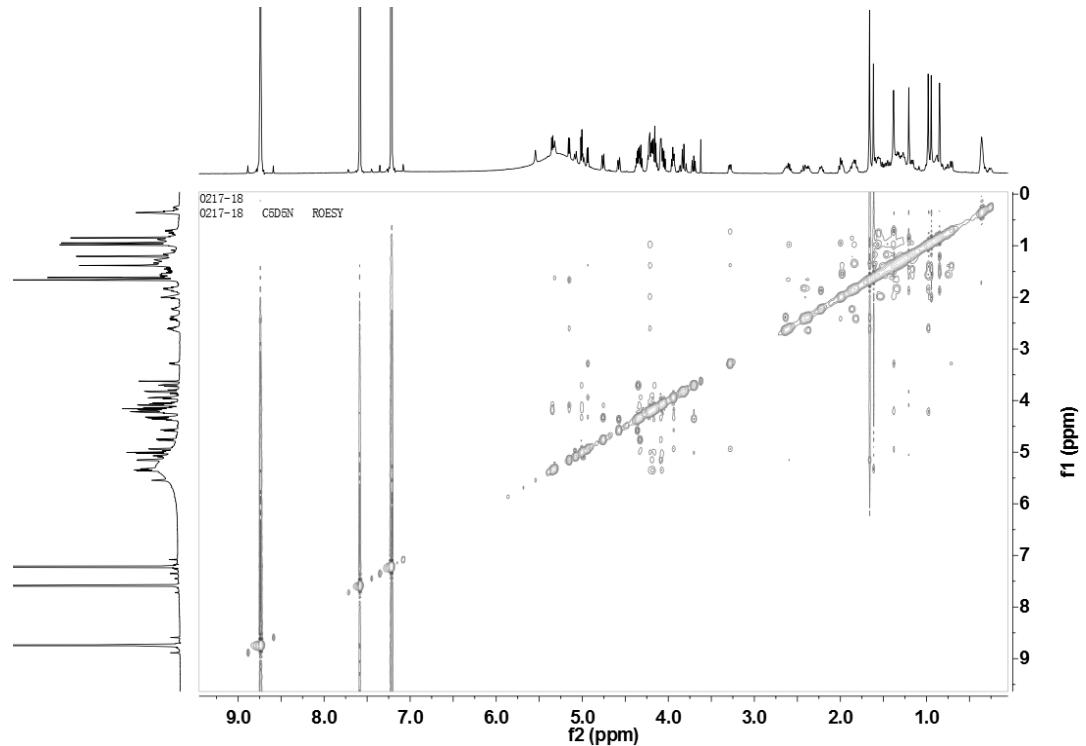


Figure S101. ROESY spectrum of compound **12**.

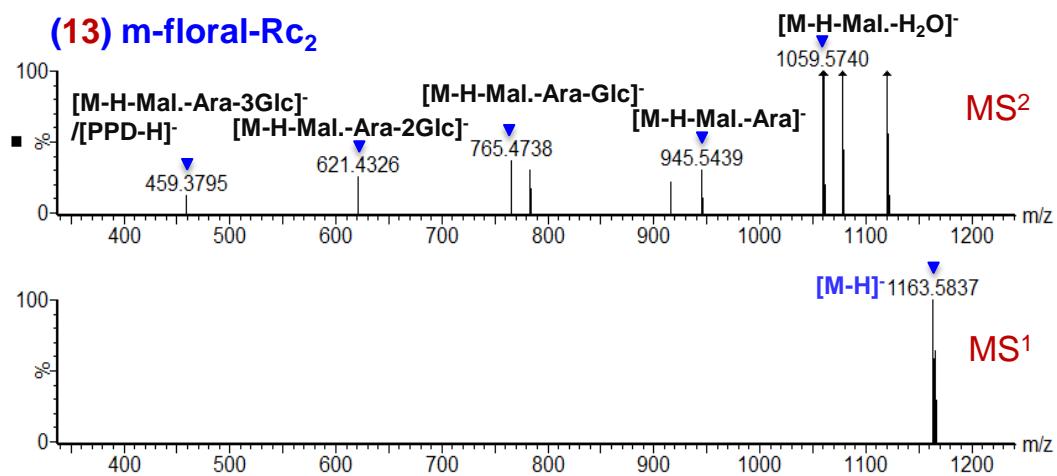


Figure S102. HRESIMS spectrum of compound 13.

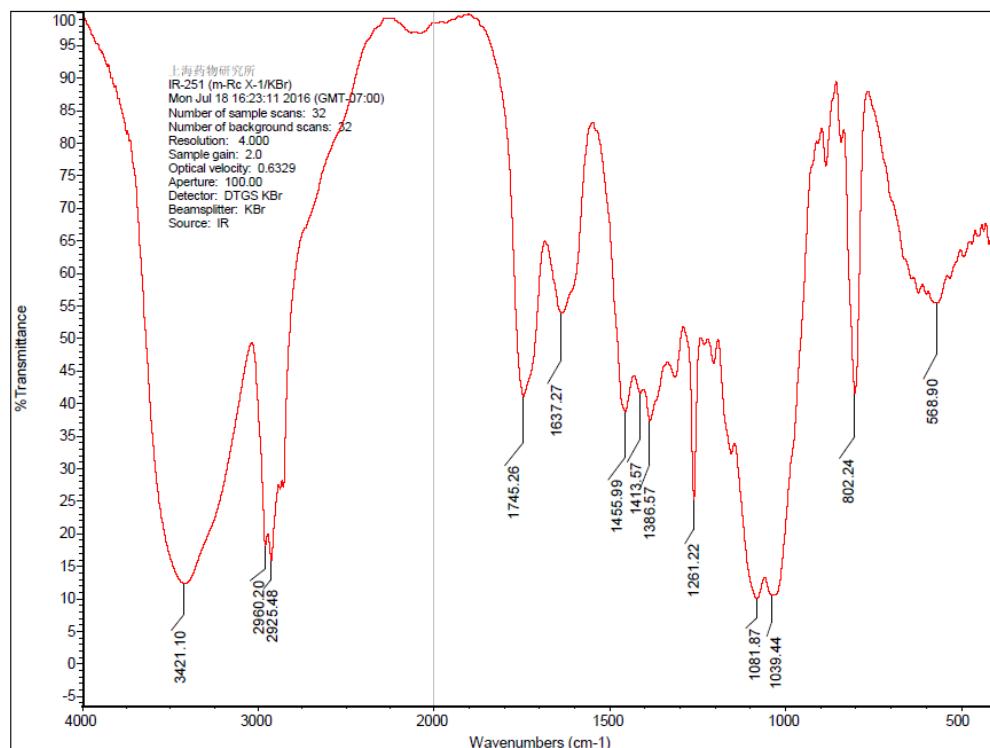


Figure S103. IR spectrum of compound 13.

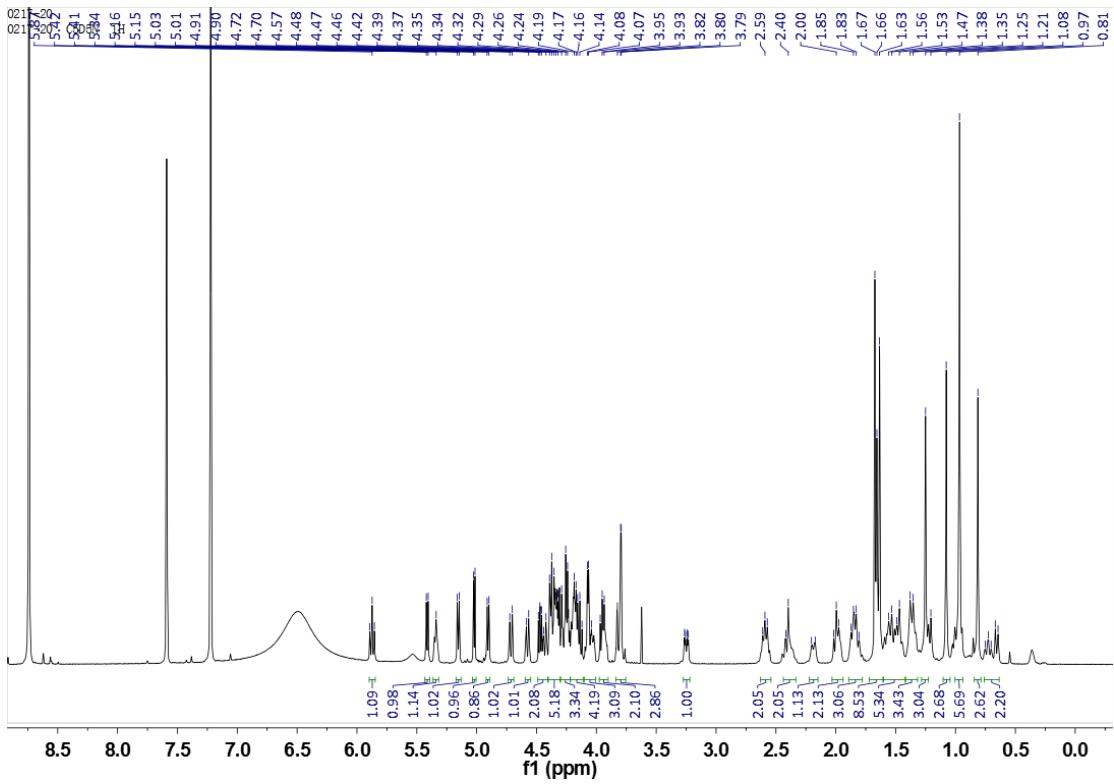


Figure S104. ^1H NMR spectrum of compound **13**.

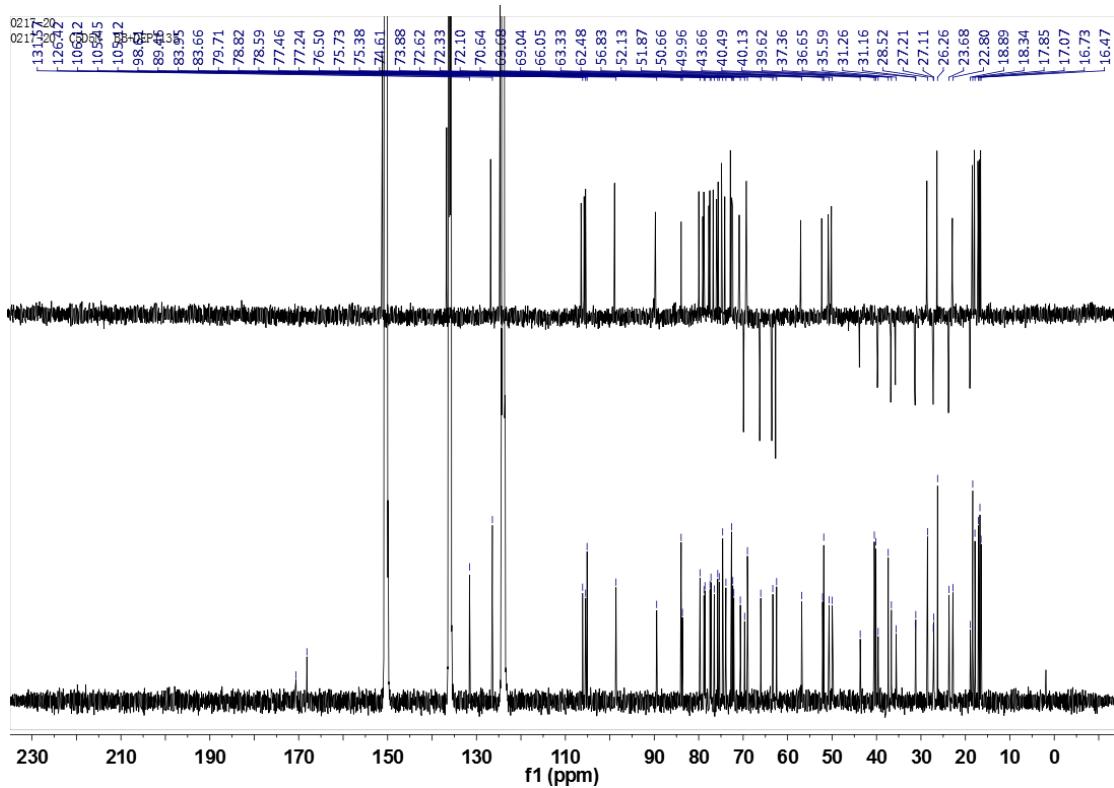


Figure S105. ^{13}C NMR and DEPT-135 spectra of compound **13**.

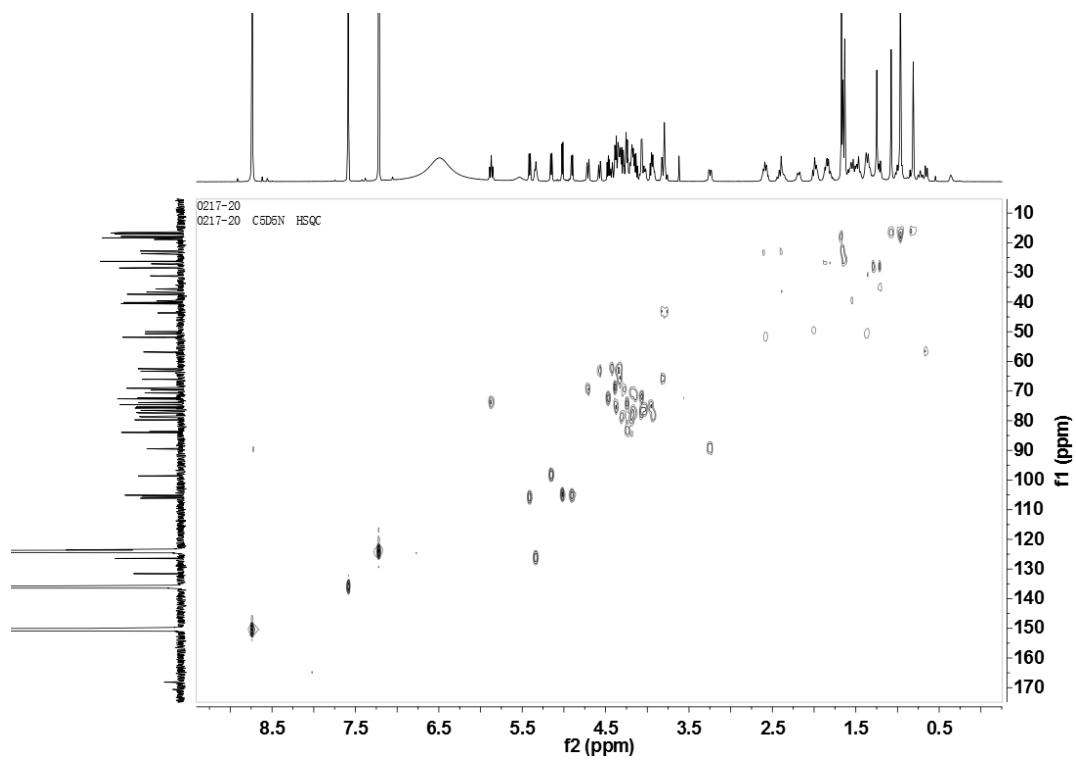


Figure S106. HSQC spectrum of compound 13.

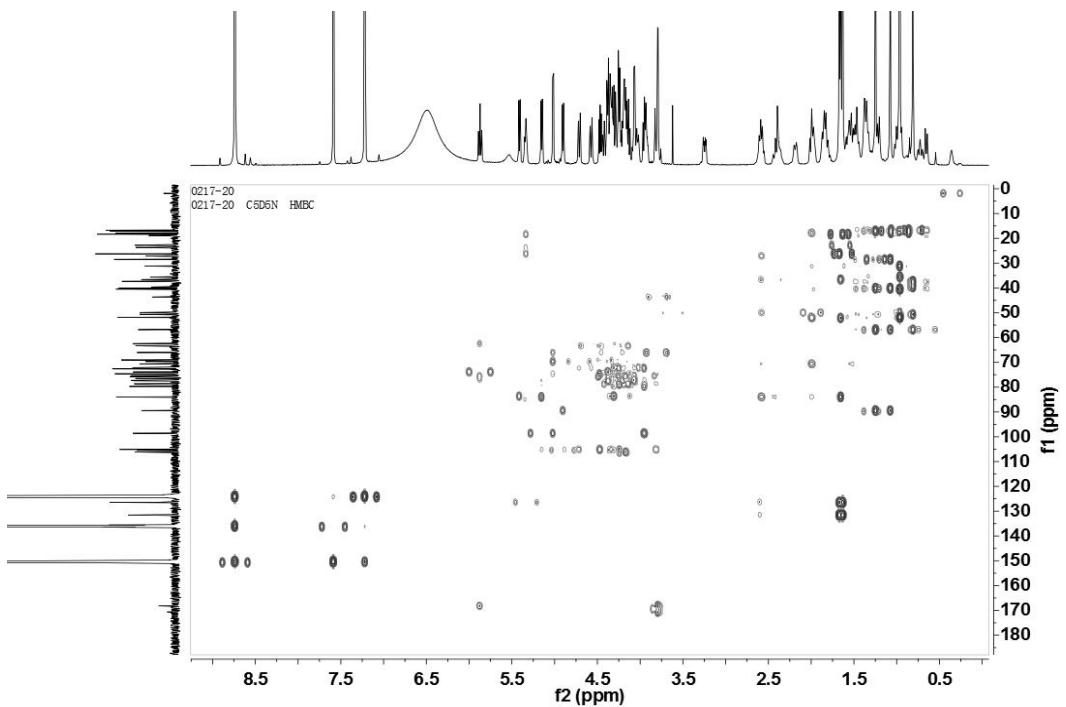


Figure S107. HMBC spectrum of compound 13.

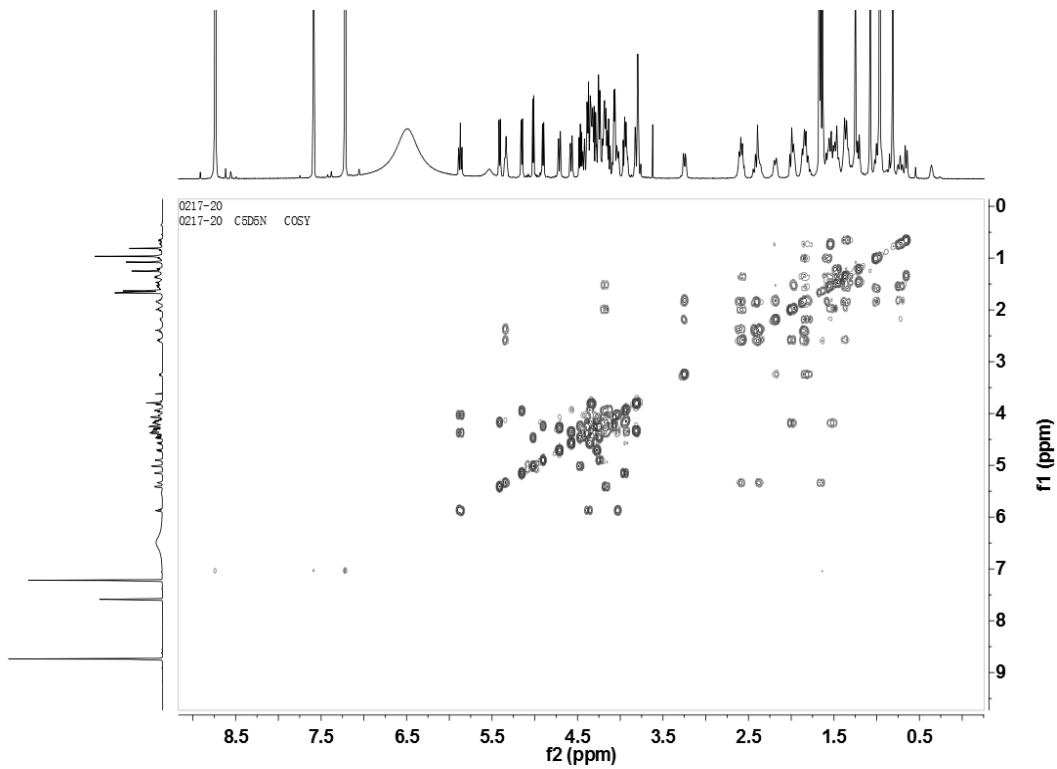


Figure S108. ^1H - ^1H COSY spectrum of compound **13**.

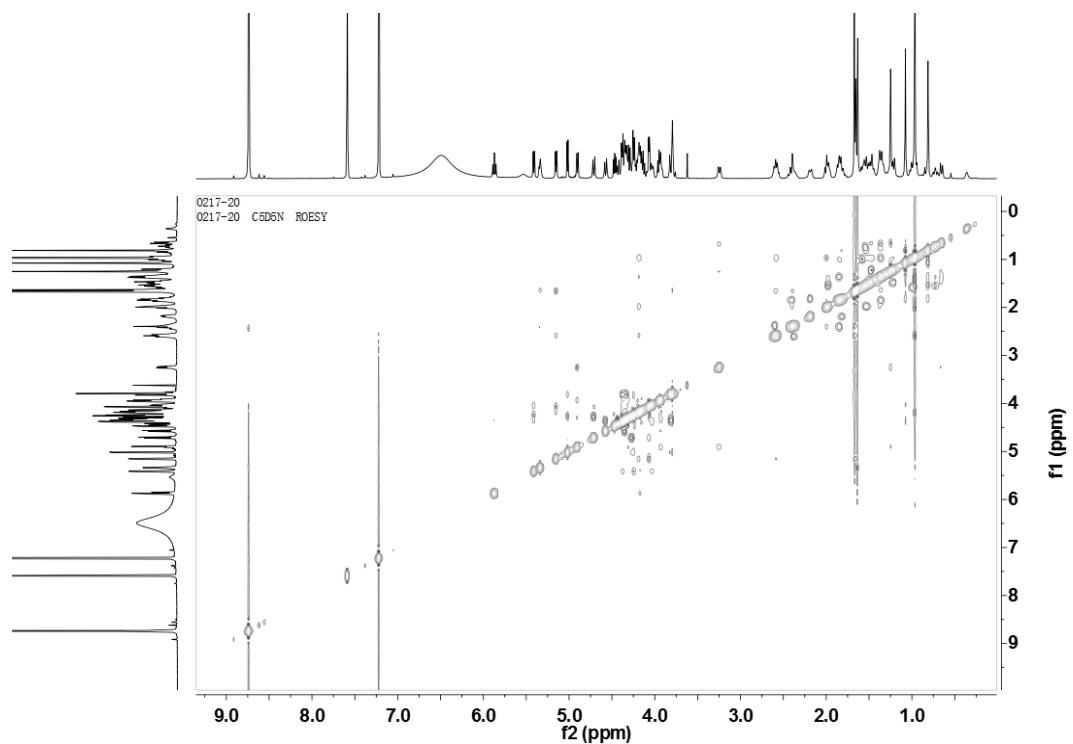


Figure S109. ROESY spectrum of compound **13**.

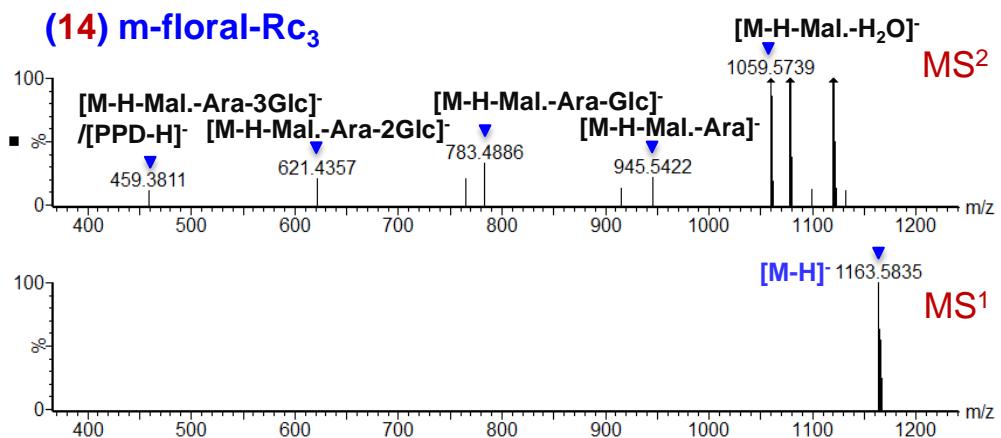


Figure S110. HRESIMS spectrum of compound 14.

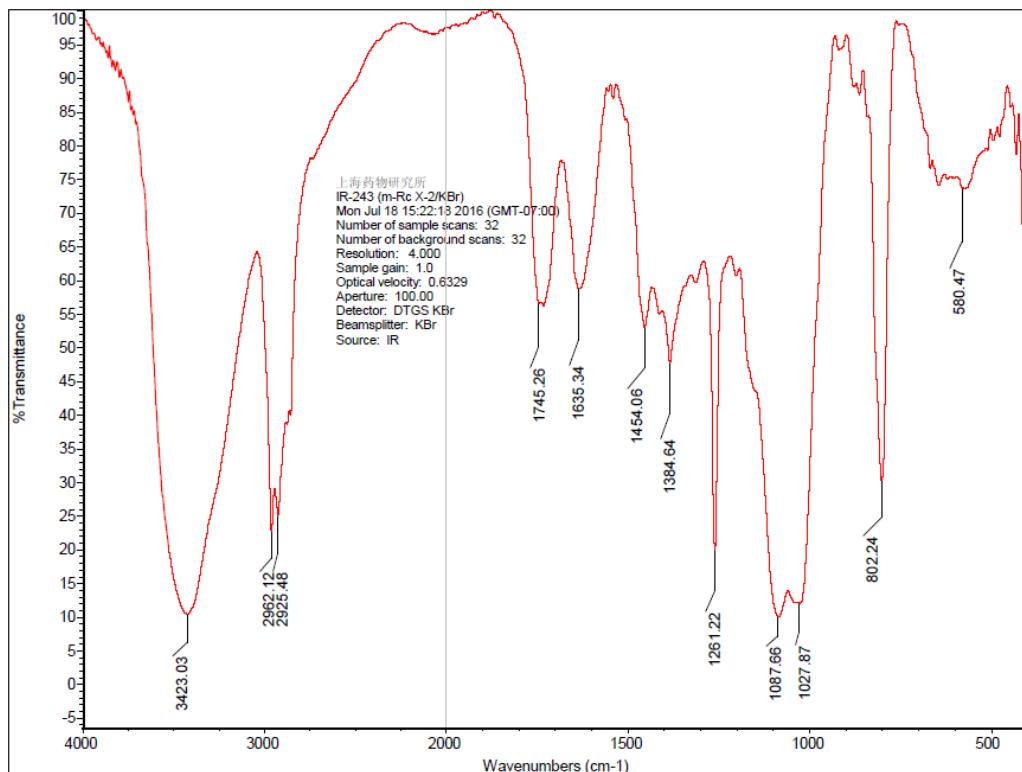


Figure S111. IR spectrum of compound 14.

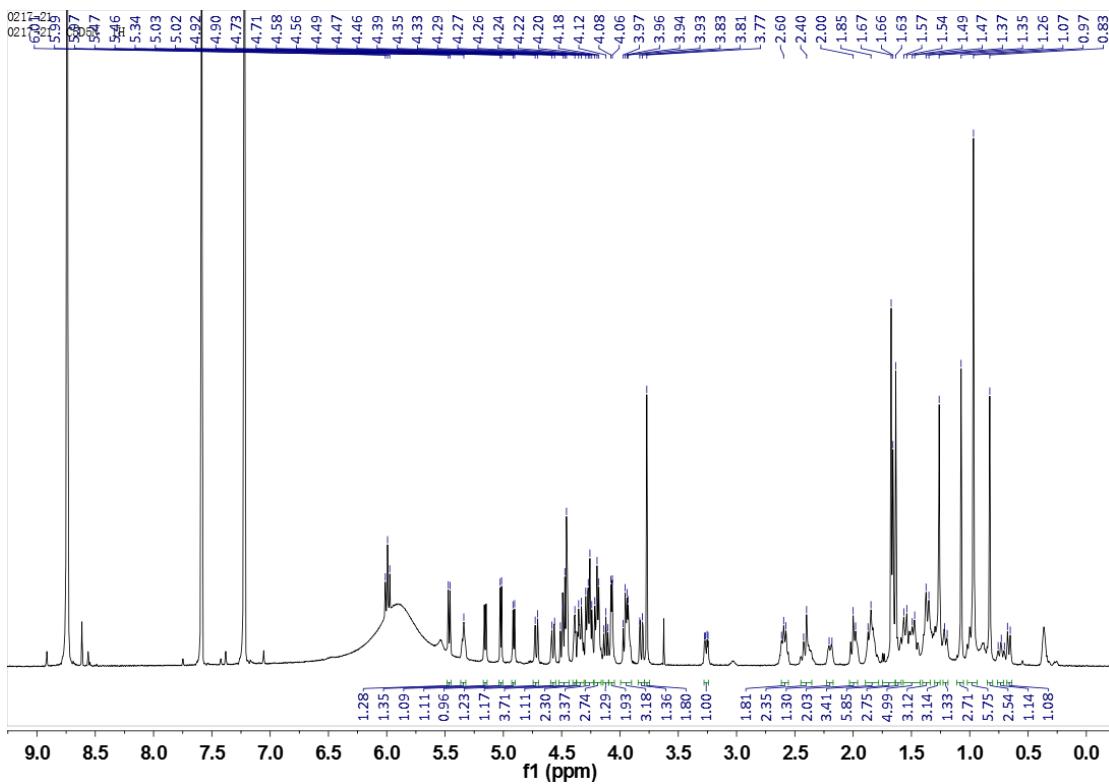


Figure S112. ^1H NMR spectrum of compound 14.

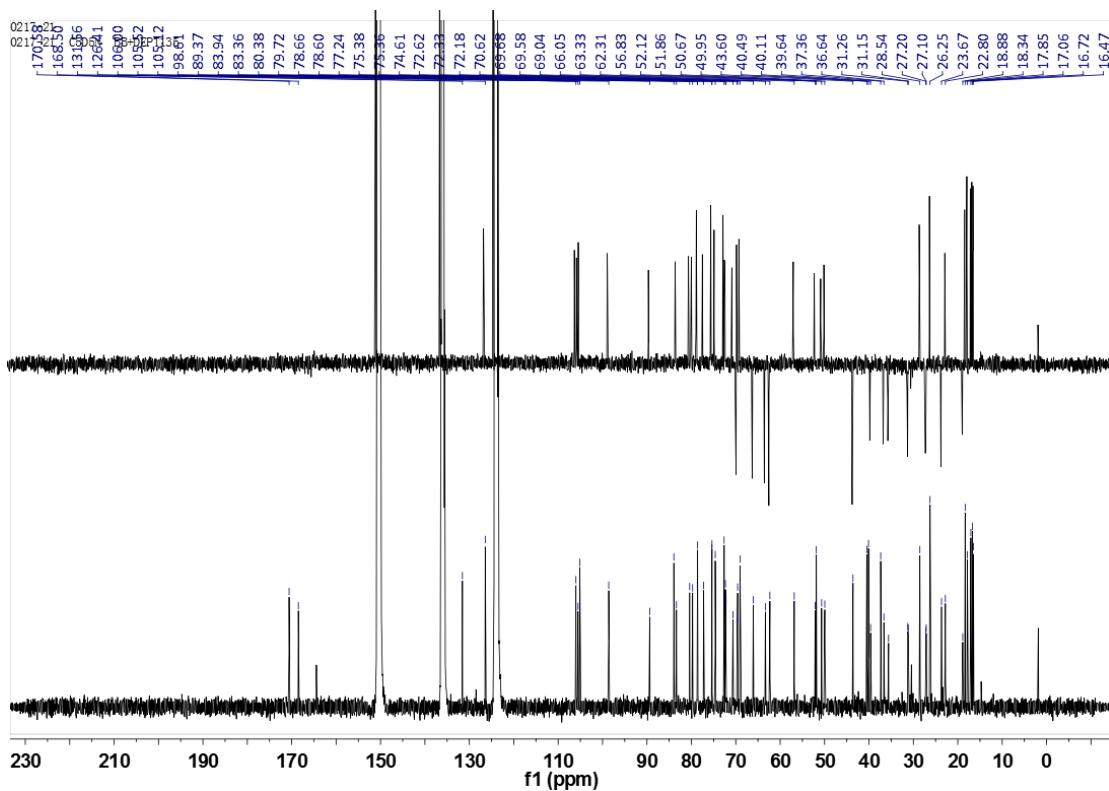


Figure S113. ^{13}C NMR and DEPT-135 spectra of compound **14**.

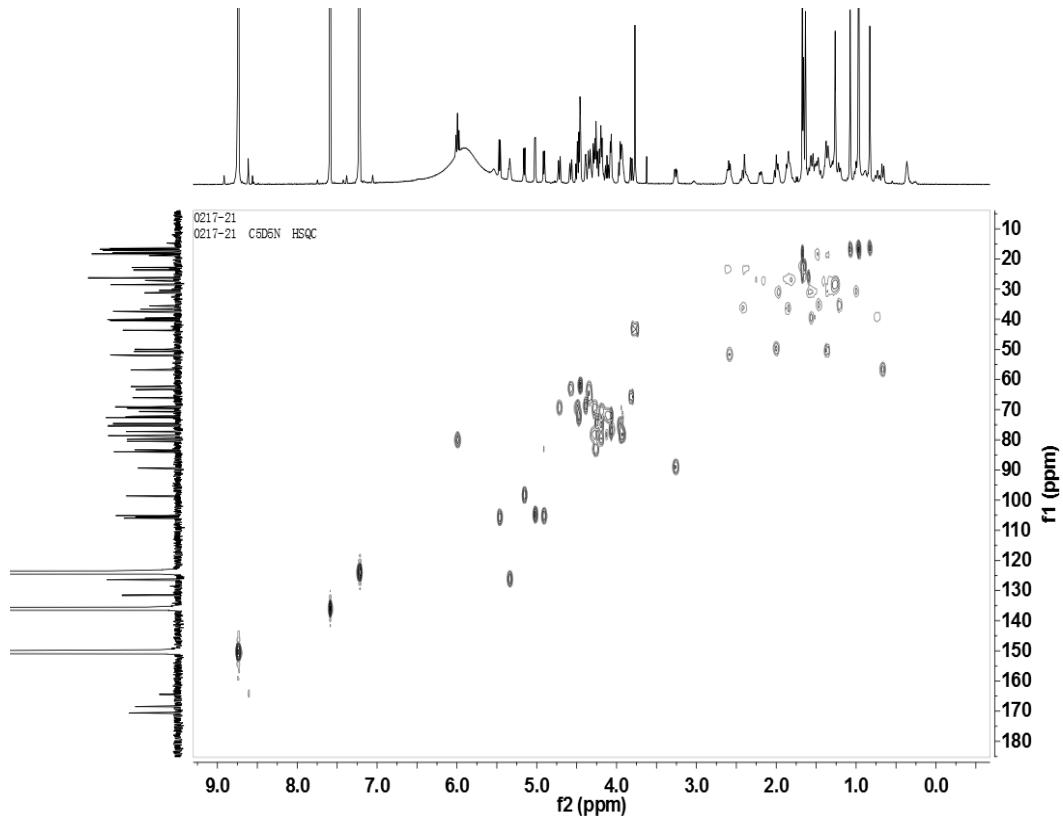


Figure S114. HSQC spectrum of compound **14**.

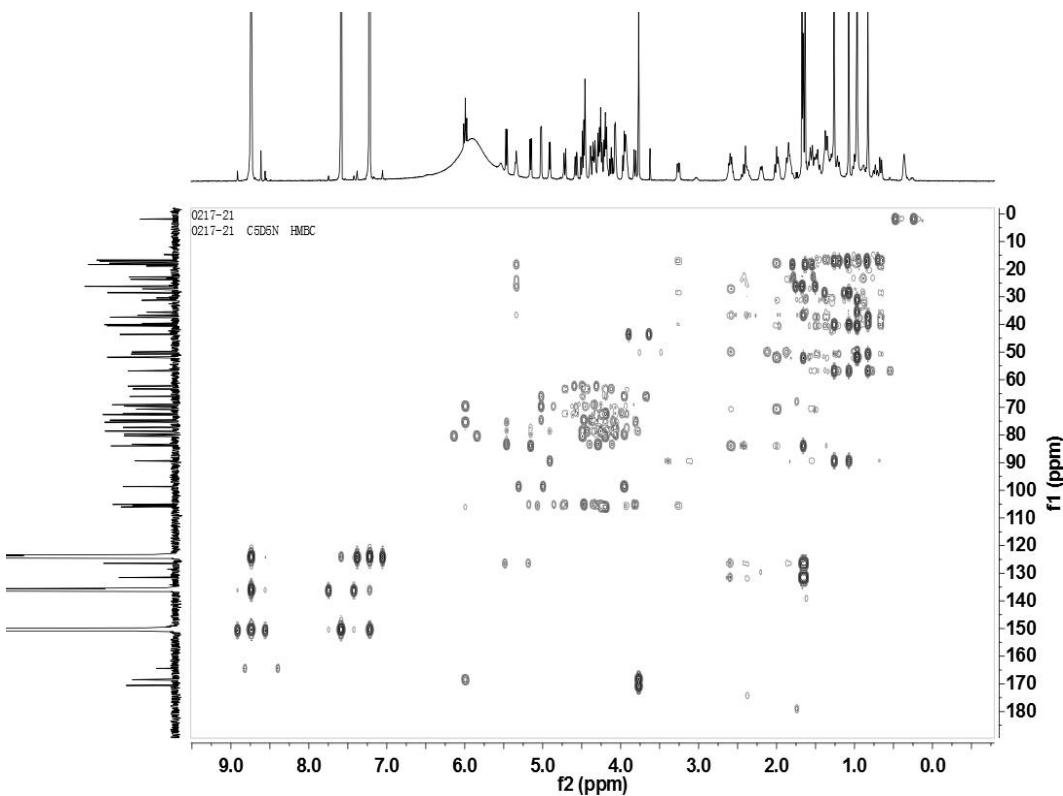


Figure S115. HMBC spectrum of compound **14**.

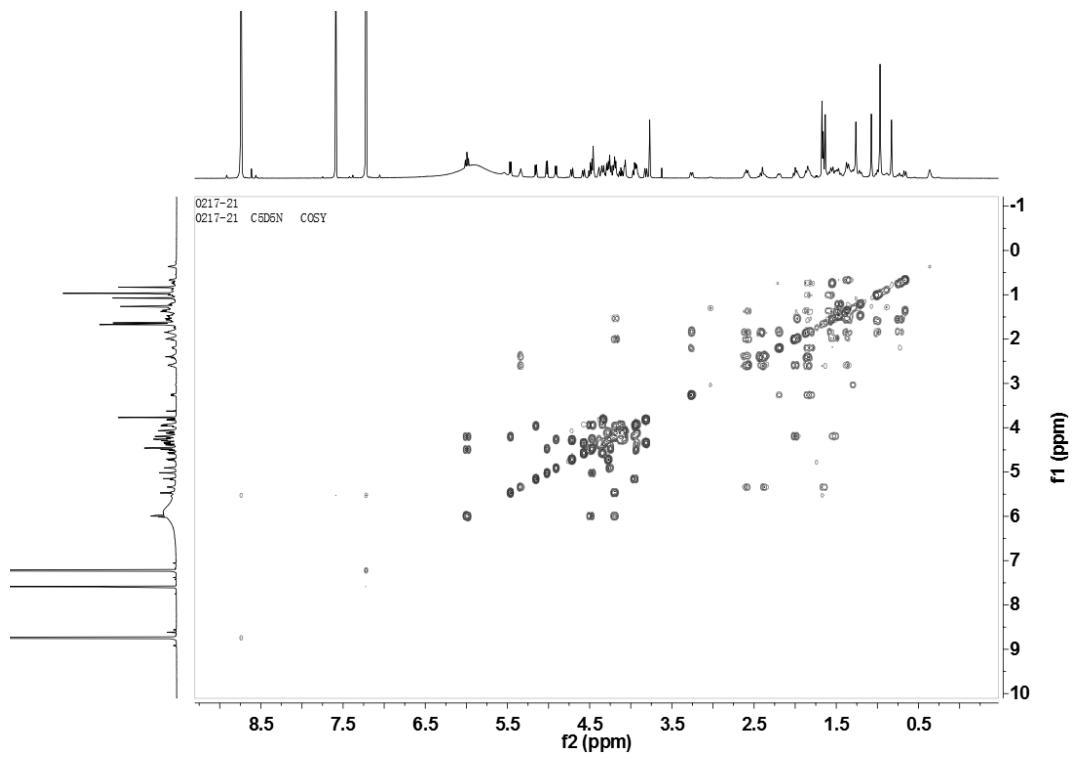


Figure S116. ^1H - ^1H COSY spectrum of compound **14**.

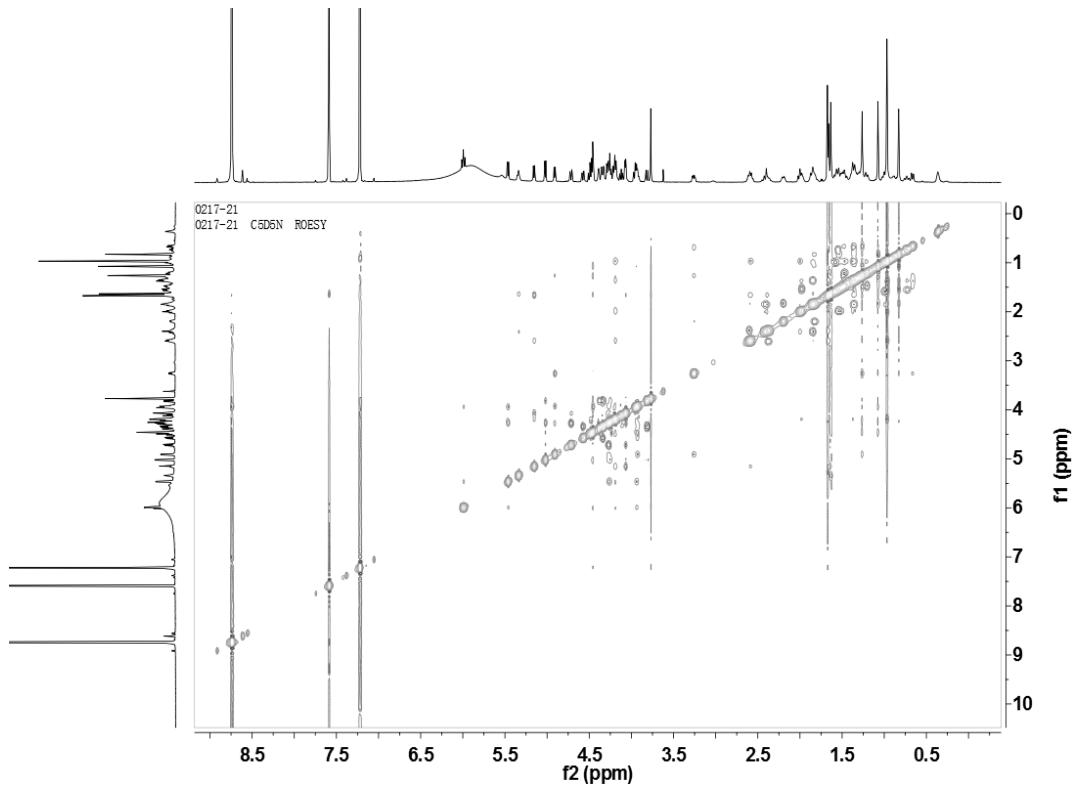


Figure S117. ROESY spectrum of compound **14**.

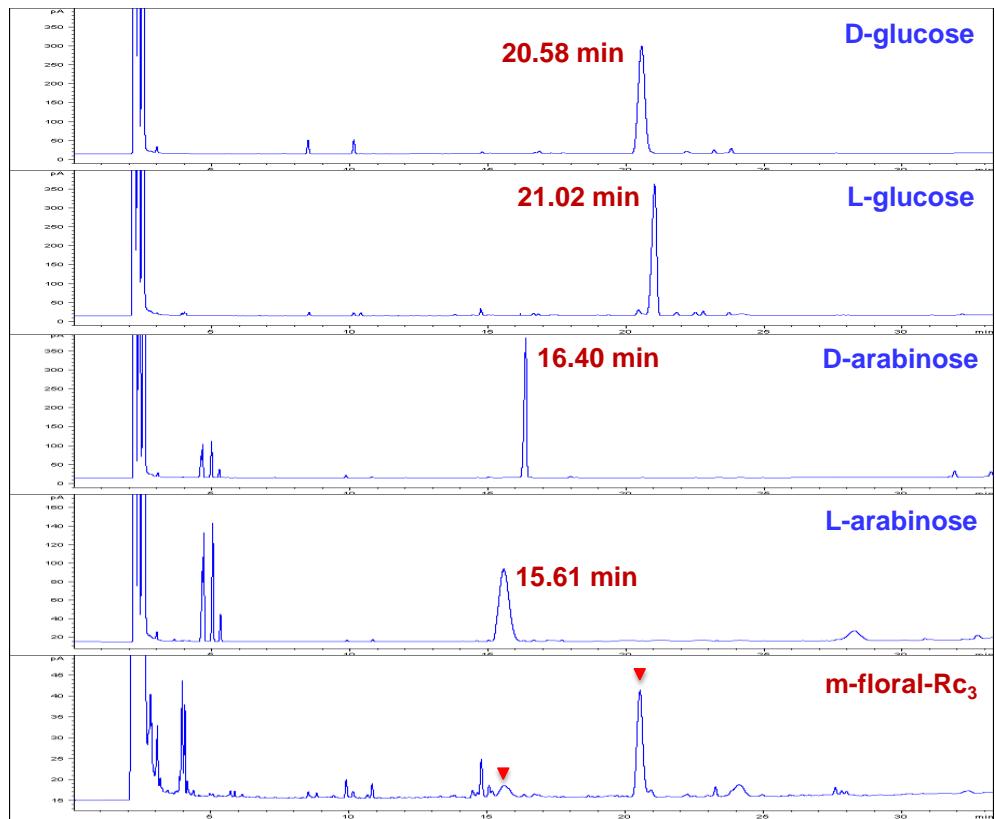


Figure S118. The GC chromatograms of compound **14** after acidic hydrolysis.

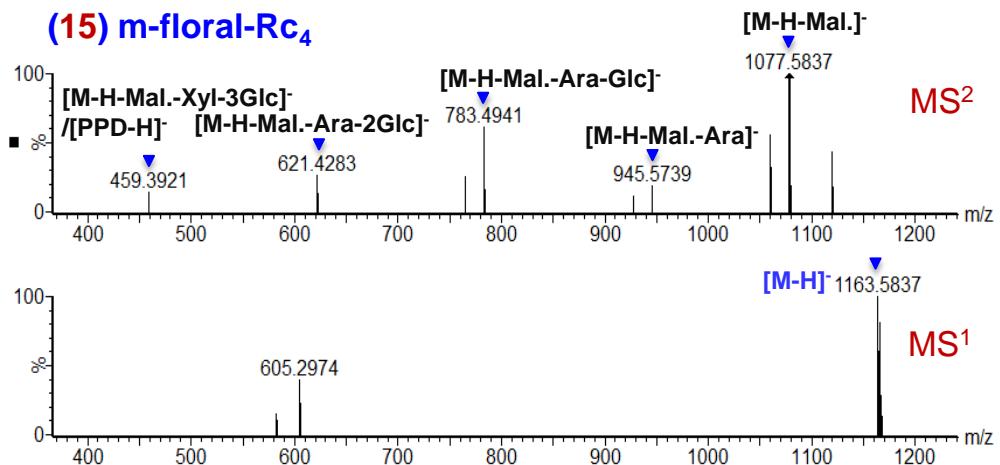


Figure S119. HRESIMS spectrum of compound **15**.

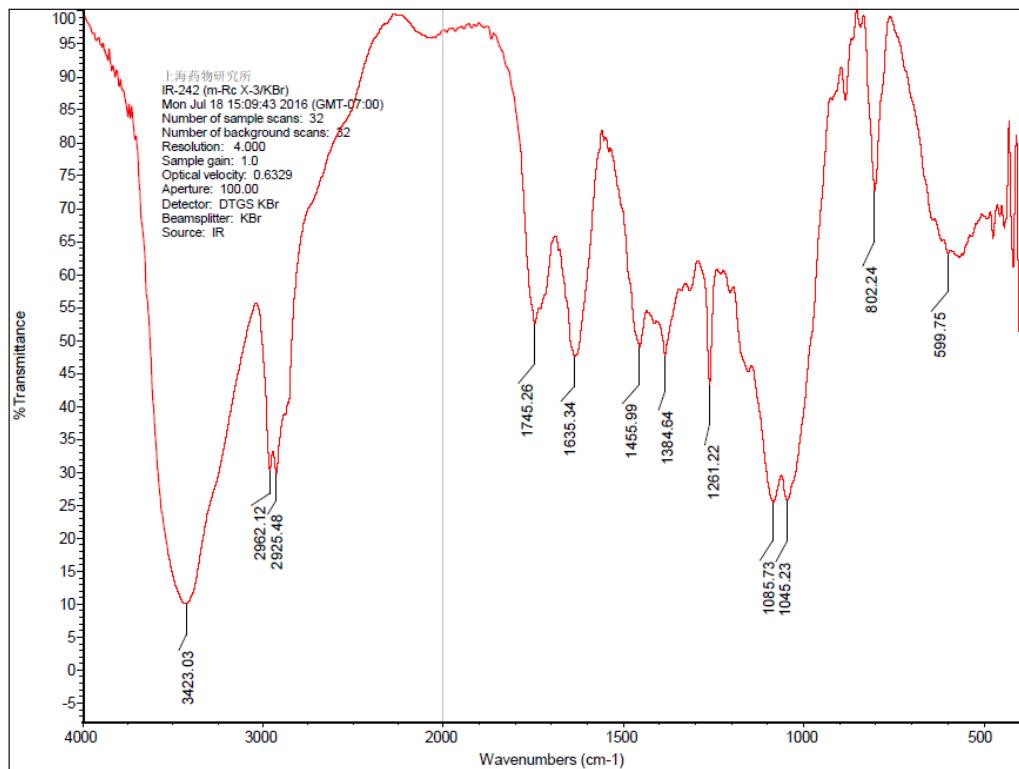


Figure S120. IR spectrum of compound **15**.

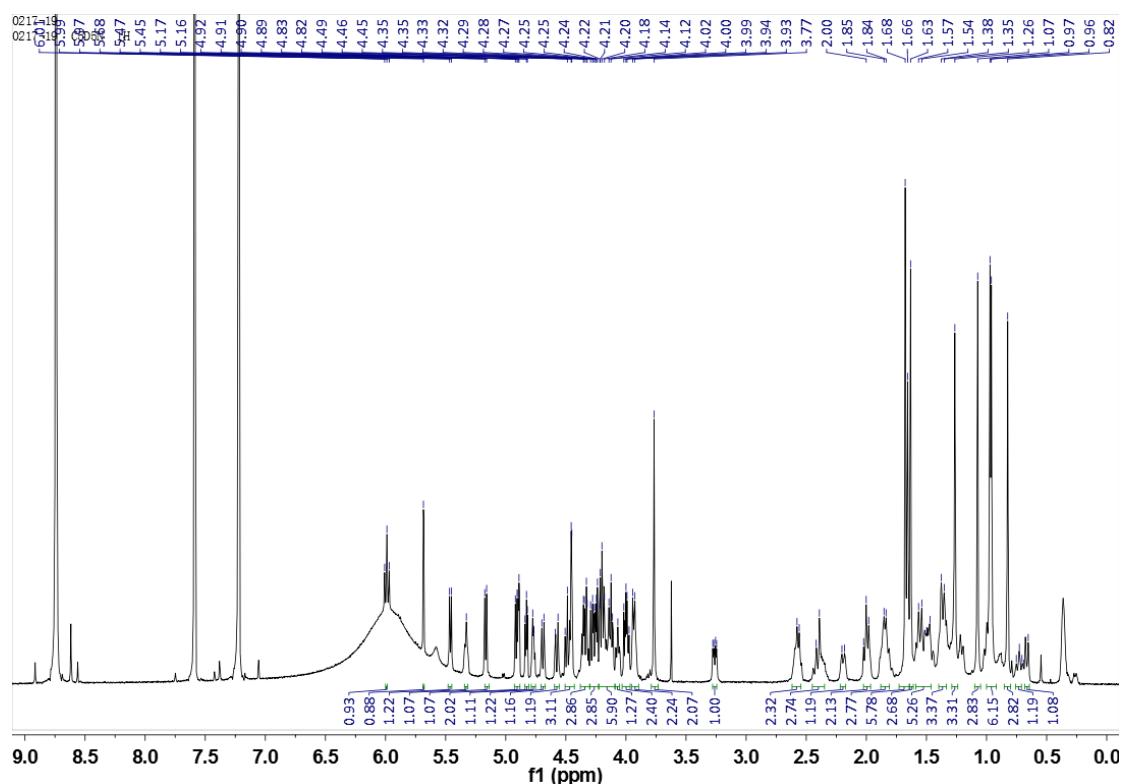


Figure S121. ^1H NMR spectrum of compound **15**.

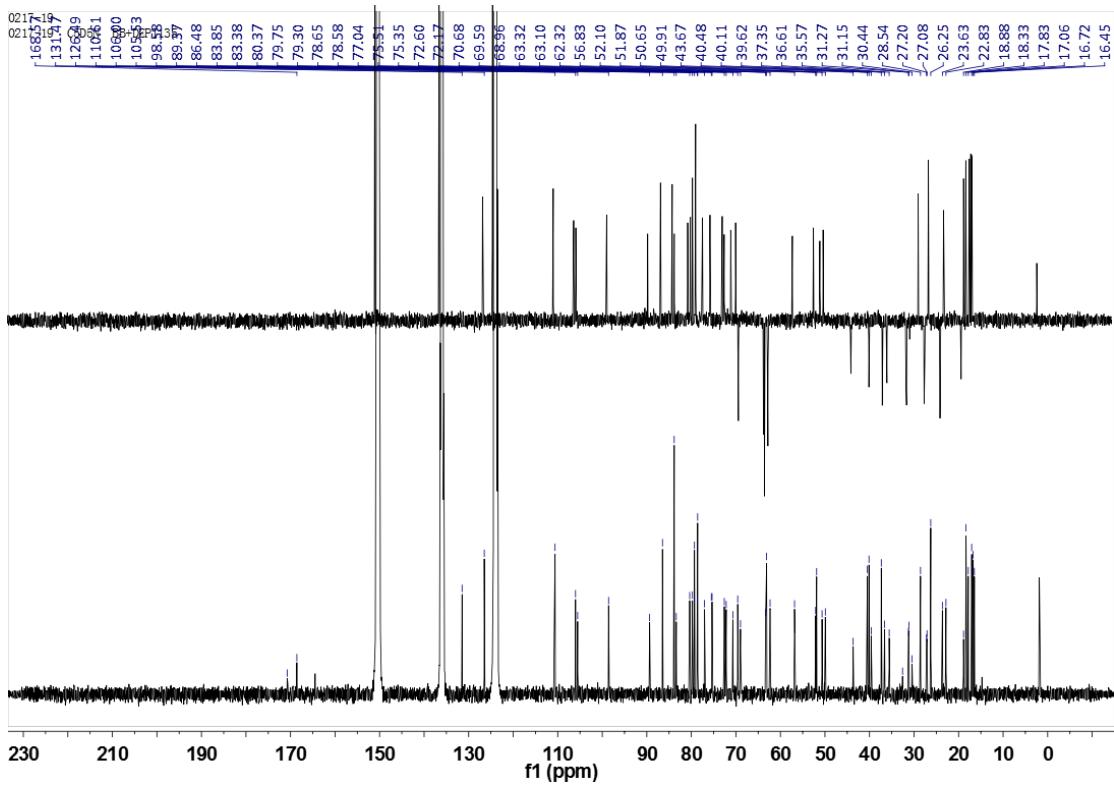


Figure S122. ^{13}C NMR and DEPT-135 spectra of compound **15**.

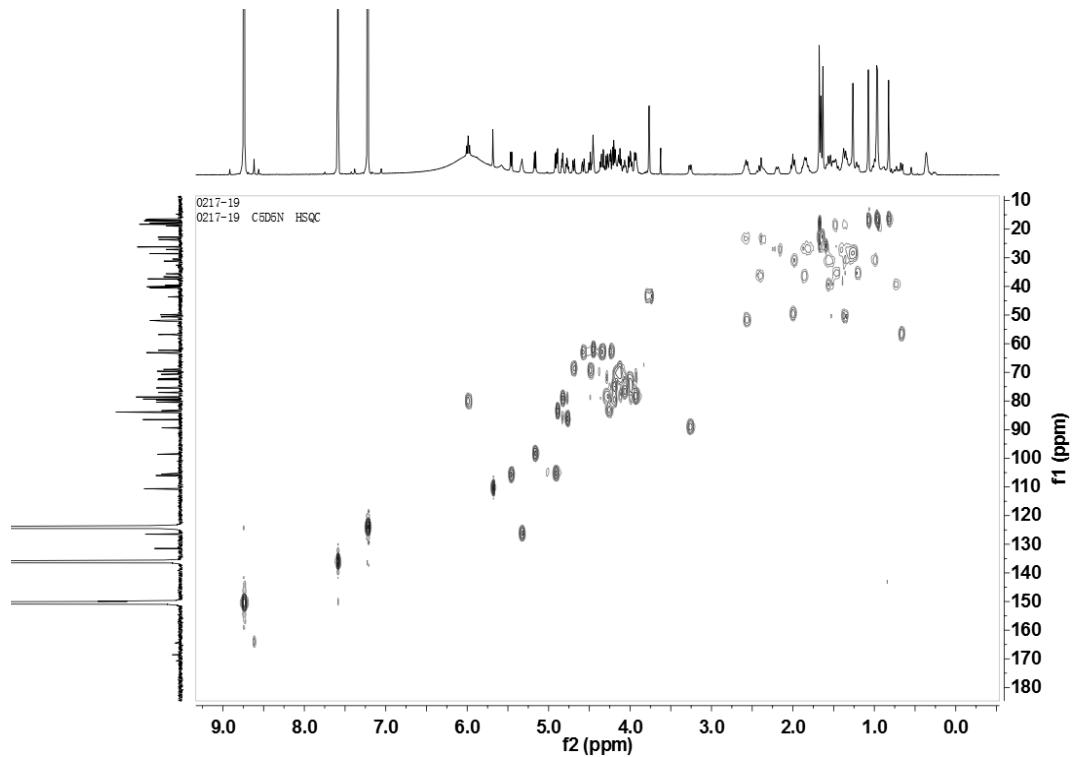


Figure S123. HSQC spectrum of compound **15**.

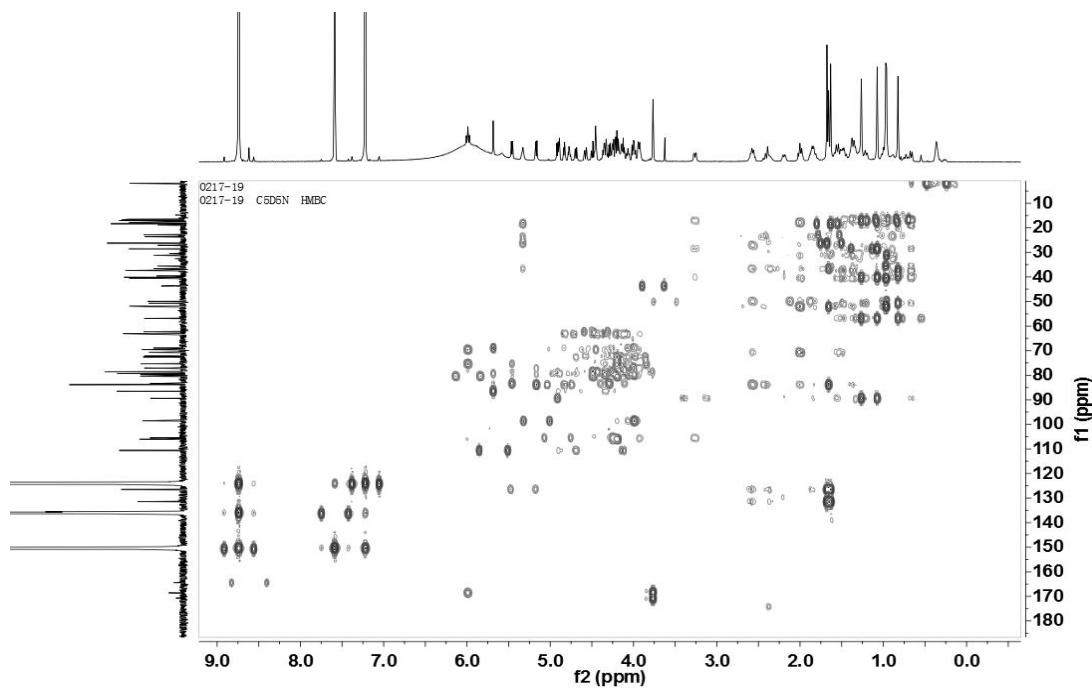


Figure S124. HMBC spectrum of compound **15**.

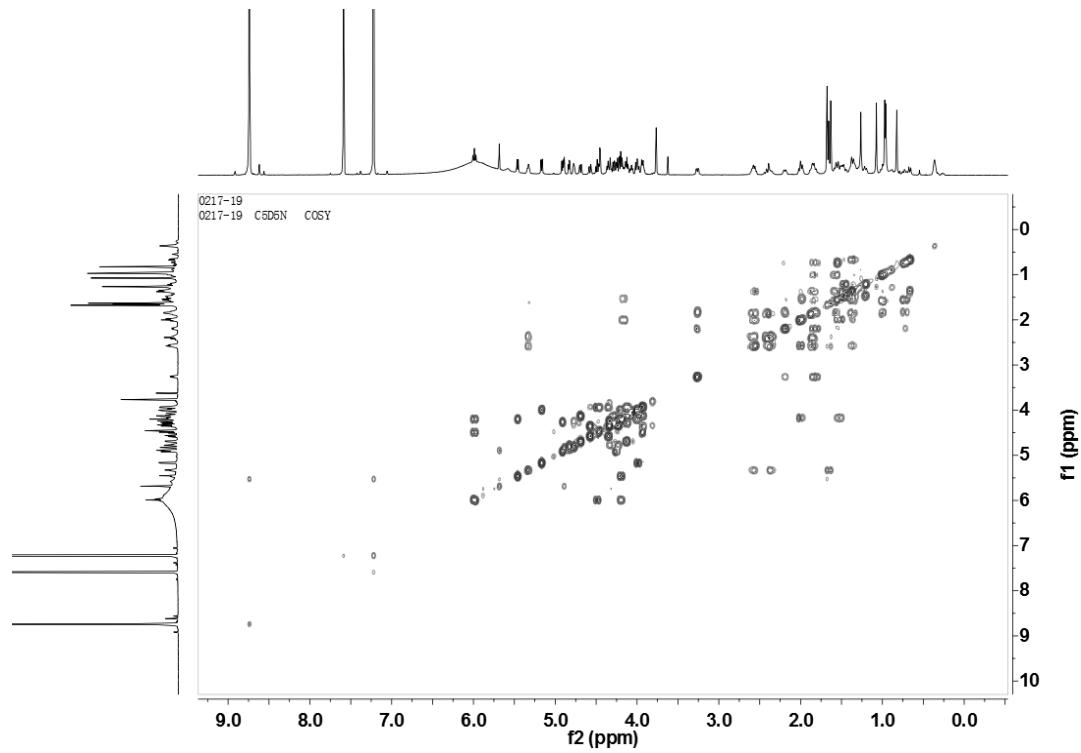


Figure S125. ^1H - ^1H COSY spectrum of compound **15**.

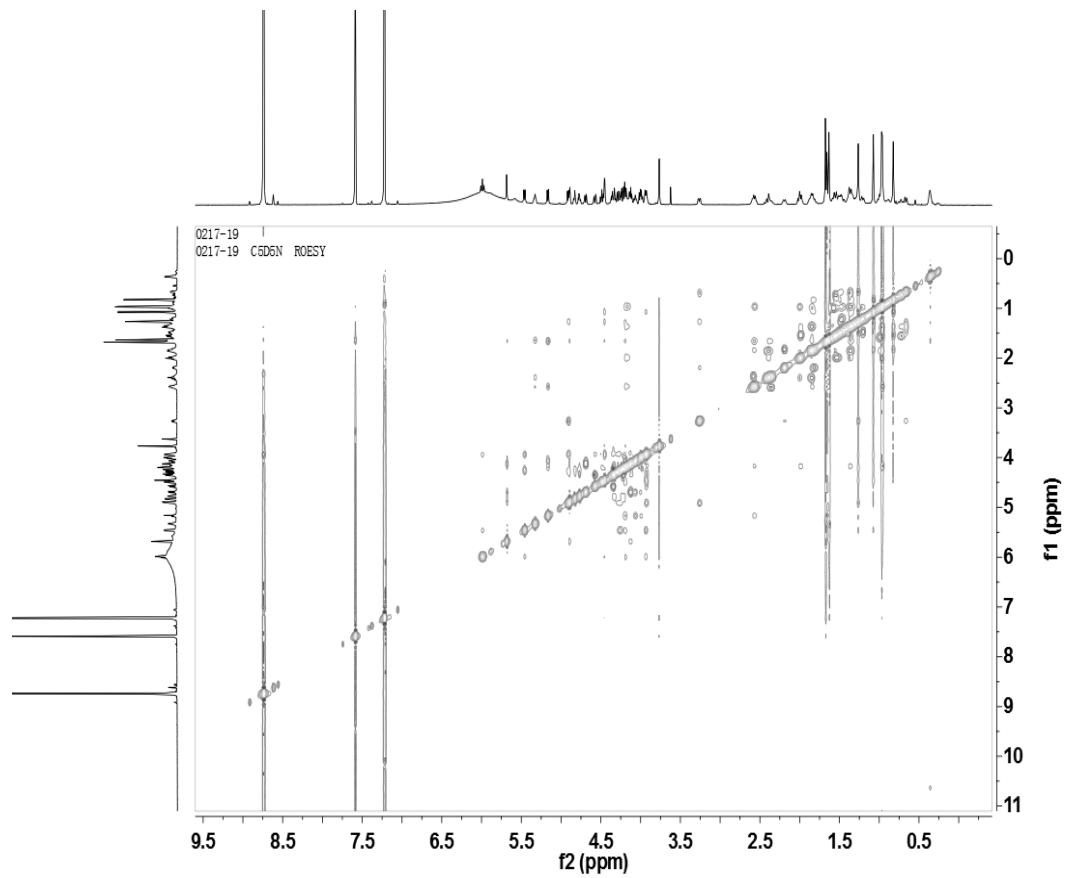


Figure S126. ROESY spectrum of compound **15**.

Table S1. NMR Spectroscopic Data (500 MHz, Pyridine-*d*5) for Malonylfloralginsenosides Rb₁ and Rb₂ (4 and 5).

position	m-floral-Rb ₁ (4)		m-floral-Rb ₂ (5)	
	δ_{C} , type	δ_{H} , mult (<i>J</i> in Hz)	δ_{C} , type	δ_{H} , mult (<i>J</i> in Hz)
1	39.5, CH ₂	1.57, m 0.75, m	39.5, CH ₂	1.55, m 0.75, m
2	27.0, CH ₂	2.16, m 1.83, m	27.0, CH ₂	2.20, m 1.85, m
3	89.4, CH	3.26, dd (11.5, 4.4)	89.2, CH	3.27, dd (11.7, 4.5)
4	40.0, C		40.0, C	
5	56.7, CH	0.67, m	56.7, CH	0.68, m
6	18.8, CH ₂	1.48, m 1.36, m	18.8, CH ₂	1.49, m 1.36, m
7	35.5, CH ₂	1.47, m 1.22, m	35.5, CH ₂	1.48, m 1.22, m
8	39.5, C		39.5, C	
9	50.3, CH	1.38, m	50.6, CH	1.37, m
10	37.2, C		37.3, C	
11	31.0, CH ₂	1.98, m 1.57, m	31.1, CH ₂	1.98, m 1.57, m
12	70.6, CH	4.20, m	70.6, CH	4.21, m
13	49.8, CH	1.98, m	49.9, CH	2.02, m
14	52.0, C		52.0, C	
15	31.2, CH ₂	1.57, m 1.01, m	31.2, CH ₂	1.57, m 1.00, m
16	27.1, CH ₂	1.83, m 1.34, m	27.1, CH ₂	1.86, m 1.37, m
17	51.7, CH	2.59, m	51.7, CH	2.60, m
18	16.4, CH ₃	0.97, s	16.4, CH ₃	0.98, s
19	16.6, CH ₃	0.81, s	16.6, CH ₃	0.83, s
20	83.8, C		83.8, C	
21	22.7, CH ₃	1.67, s	22.8, CH ₃	1.68, s
22	36.6, CH ₂	2.43, m 1.85, m	36.6, CH ₂	2.42, m 1.85, m
23	23.6, CH ₂	2.62, m 2.41, m	23.6, CH ₂	2.62, m 2.41, m
24	126.3, CH	5.33, m	126.3, CH	5.33, m
25	131.4, C		131.4, C	
26	26.1, CH ₃	1.62, s	26.2, CH ₃	1.62, s
27	18.3, CH ₃	1.67, s	18.3, CH ₃	1.67, s
28	28.4, CH ₃	1.25, s	28.4, CH ₃	1.23, s
29	16.9, CH ₃	1.08, s	16.9, CH ₃	1.08, s

30	17.7, CH ₃	0.97, s	17.8, CH ₃	0.98, s
3-Glc				
1'	105.3, CH	4.91, d (7.6)	105.4, CH	4.91, d (7.4)
2'	83.5, CH	4.25, m	83.3, CH	4.25, m
3'	78.5, CH	4.30, m	78.5, CH	4.31, m
4'	71.9, CH	4.14, m	72.1, CH	4.12, m
5'	78.7, CH	3.95, m	78.7, CH	3.94, m
6'	63.2, CH ₂	4.56, dd (12.0, 1.9) 4.37, m	63.2, CH ₂	4.56, m 4.36, m
2'-Glc				
1''	106.0, CH	5.41, d (7.6)	105.9, CH	5.46, d (7.6)
2''	77.5, CH	4.17, m	75.2, CH	4.21, m
3''	78.7, CH	4.23, m	80.2, CH	5.98, t (9.6)
4''	72.0, CH	4.35, m	69.5, CH	4.49, m
5''	78.7, CH	3.95, m	78.7, CH	3.95, m
6''	63.3, CH ₂	4.53, dd (12.0, 2.6) 4.35, m	63.2, CH ₂	4.53, m 4.38, t (5.3)
20-Glc				
1'''	98.4, CH	5.15, d (7.7)	98.5, CH	5.15, d (7.6)
2'''	75.6, CH	3.94, m	75.2, CH	3.95, m
3'''	79.6, CH	4.19, m	79.6, CH	4.19, m
4'''	72.0, CH	4.08, m	72.0, CH	4.09, m
5'''	77.3, CH	4.07, m	77.4, CH	4.10, m
6'''	70.5, CH ₂	4.75, d (10.9) 4.35, m	70.5, CH ₂	4.76, d (10.7) 4.34, m
6'''-Glc				
1''''	105.7, CH	5.12, d (7.7)	105.8, CH	5.12, d (7.7)
2''''	75.6, CH	4.07, m	75.6, CH	4.08, m
3''''	75.2, CH	4.37, m	78.5, CH	4.18, m
4''''	73.8, CH	5.86, t (9.7)	72.0, CH	4.25, m
5''''	76.4, CH	4.04,	78.7, CH	3.95, m
6''''	62.3, CH ₂	4.43, dd (12.0, 2.7) 4.34, m	62.2, CH ₂	4.48, t (9.4) 4.45, m
4''''-Mal.				
-O-CO	168.0, C		168.6, C	
CH ₂	43.5, CH ₂	3.79, m (2H)	43.6, CH ₂	3.76, m (2H)
COOH	170.5, C		170.7, C	

Table S2. NMR Spectroscopic Data (500 MHz, Pyridine-*d*5) for Malonylfloralginsenosides Rd₁–Rd₃ (**6–8**)

position	m-floral-Rd ₁ (6)		m-floral-Rd ₂ (7)		m-floral-Rd ₃ (8)	
	δ_c , type	δ_h , mult (J in Hz)	δ_c , type	δ_h , mult (J in Hz)	δ_c , type	δ_h , mult (J in Hz)
1	39.6, CH ₂	1.53, m 0.73, m	39.5, CH ₂	1.56, m 0.73, m	39.5, CH ₂	1.54, m 0.73, m
2	27.1, CH ₂	2.15, m 1.85, m	27.0, CH ₂	2.20, m 1.85, m	27.0, CH ₂	2.18, m 1.85, m
3	89.6, CH	3.24, dd (11.5, 4.4)	89.2, CH	3.27, dd (11.7, 4.4)	89.3, CH	3.25, dd (11.7, 4.5)
4	40.5, C		40.4, C		40.3, C	
5	56.8, CH	0.69, m	56.7, CH	0.67, m	56.7, CH	0.66, m
6	18.9, CH ₂	1.52, m 1.36, m	18.8, CH ₂	1.48, m 1.36, m	18.7, CH ₂	1.46, m 1.34, m
7	35.6, CH ₂	1.49, m 1.21, m	35.5, CH ₂	1.47, m 1.21, m	35.4, CH ₂	1.46, m 1.21, m
8	40.1, C		40.0, C		40.0, C	
9	50.6, CH	1.38, m	50.5, CH	1.38, m	50.5, CH	1.37, m
10	37.4, C		37.2, C		37.2, C	
11	31.4, CH ₂	1.97, m 1.55, m	31.2, CH ₂	1.97, m 1.55, m	31.2, CH ₂	1.96, m 1.55, m
12	70.6, CH	4.18, m	70.5, CH	4.18, m	70.5, CH	4.17, m
13	50.0, CH	1.99, m	49.8, CH	1.99, m	50.0, CH	1.98, m
14	51.9, C		51.8, C		51.7, C	
15	31.2, CH ₂	1.55, m 1.00, m	31.1, CH ₂	1.55, m 1.00, m	31.1, CH ₂	1.55, m 0.99, m
16	27.1, CH ₂	1.87, m 1.37, m	27.1, CH ₂	1.85, m 1.37, m	27.1, CH ₂	1.85, m 1.36, m
17	51.9, CH	2.59, m	51.9, CH	2.59, m	51.9, CH	2.58, dd (16.5, 8.5)
18	16.4, CH ₃	0.97, s	16.3, CH ₃	0.97, s	16.3, CH ₃	0.96, s
19	16.7, CH ₃	0.79, s	16.6, CH ₃	0.83, s	16.6, CH ₃	0.80, s
20	83.8, C		83.2, C		83.4, C	
21	22.8, CH ₃	1.64, s	22.7, CH ₃	1.65, s	22.7, CH ₃	1.63, s
22	36.6, CH ₂	2.40, m 1.83, m	36.5, CH ₂	2.41, m 1.83, m	36.4, CH ₂	2.40, m 1.83, m
23	23.7, CH ₂	2.50, m 2.25, m	23.5, CH ₂	2.51, m 2.25, m	23.5, CH ₂	2.50, m 2.24, m
24	126.4, CH	5.25, t (7.0)	126.3, CH	5.25, t (7.2)	126.3, CH	5.25, t (7.0)
25	131.3, C		131.2, C		131.2, C	
26	26.2, CH ₃	1.60, s	26.1, CH ₃	1.60, s	26.1, CH ₃	1.60, s
27	18.2, CH ₃	1.60, s	18.1, CH ₃	1.60, s	18.1, CH ₃	1.60, s

28	28.6, CH ₃	1.33, s	28.4, CH ₃	1.27, s	28.4, CH ₃	1.24, s
29	17.2, CH ₃	1.10, s	16.9, CH ₃	1.08, s	16.9, CH ₃	1.07, s
30	17.8, CH ₃	0.94, s	17.7, CH ₃	0.96, s	17.7, CH ₃	0.95, s
		3-Glc		3-Glc		3-Glc
1'	105.4, CH	4.85, d (7.5)	105.4, CH	4.91, d (7.4)	105.4, CH	4.90, d (7.6)
2'	80.8, CH	4.26, m	83.6, CH	4.26, m	83.6, CH	4.25, m
3'	78.5, CH	4.35, m	78.5, CH	4.29, m	78.3, CH	4.31, m
4'	72.1, CH	4.10, t (9.4)	72.0, CH	4.12, t (9.3)	72.0, CH	4.12, m
5'	78.5, CH	3.88, m	78.5, CH	3.93, m	78.6, CH	3.92, m
6'	63.5, CH ₂	4.51, m	63.2, CH ₂	4.57, dd (11.7, 2.2)	63.1, CH ₂	4.57, dd (11.8, 2.2)
		4.37, m		4.35, m		4.34, m
		2'-Glc		2'-Glc		2'-Glc
1''	102.0, CH	5.83, d (7.9)	105.8, CH	5.46, d (7.6)	105.9, CH	5.42, d (7.7)
2''	77.5, CH	5.73, t (8.8)	75.2, CH	4.20, m	77.3, CH	4.17, m
3''	76.9, CH	4.33, m	80.2, CH	5.98, t (9.5)	75.4, CH	4.37, m
4''	72.6, CH	4.26, m	69.5, CH	4.48, m	73.7, CH	5.86, t (9.6)
5''	78.7, CH	3.95, m	78.5, CH	3.94, m	76.4, CH	4.03, m
6''	63.4, CH ₂	4.51, m	63.2, CH ₂	4.52, dd (11.7, 2.5)	63.1, CH ₂	4.50, dd (11.7, 2.5)
		4.36, m		4.36, d (4.5)		4.36, m
		20-Glc		20-Glc		20-Glc
1'''	98.7, CH	5.21, d (7.7)	98.6, CH	5.22, d (7.7)	98.6, CH	5.21, d (7.7)
2'''	75.6, CH	4.03, t (8.2)	75.5, CH	4.03, t (8.3)	75.5, CH	4.02, m
3'''	79.8, CH	4.27, m	79.7, CH	4.26, m	79.5, CH	4.25, m
4'''	72.1, CH	4.09, m	72.0, CH	4.18, m	72.0, CH	4.18, m
5'''	78.9, CH	3.95, m	78.7, CH	3.93, m	78.6, CH	4.03, m
6'''	63.3, CH ₂	4.51, m	62.2, CH ₂	4.48, d (11.0)	62.3, CH ₂	4.42, dd (11.9, 2.8)
		4.36, m		4.45, m		4.33, m
		2"-Mal.		3"-Mal.		4"-Mal.
-O-CO	168.5, C		168.6, C		167.9, C	
CH2	44.7, CH ₂	3.79, dd (2H, 21.4, 15.2)	43.4, CH ₂	3.77, d (2H, 15.7)	43.4, CH ₂	3.79, dd (2H, 22.1, 15.4)
COOH	171.8, C		170.7, C		170.4, C	

Table S3. NMR Spectroscopic Data (500 MHz, Pyridine-*d*5) for Malonylfloralginsenosides Rd4–Rd6 (**9–11**)

position	m-floral-Rd4 (9)		m-floral-Rd5 (10)		m-floral-Rd6 (11)	
	δ_c , type	δ_h , mult (J in Hz)	δ_c , type	δ_h , mult (J in Hz)	δ_c , type	δ_h , mult (J in Hz)
1	39.6, CH ₂	1.51, m 0.76, m	39.5, CH ₂	1.56, m 0.73, m	39.7, CH ₂	1.55, m 0.73, m
2	27.0, CH ₂	2.23, m 1.86, m	27.0, CH ₂	2.20, m 1.85, m	27.2, CH ₂	2.26, m 1.88, m
3	89.4, CH	3.29, dd (11.7, 4.3)	89.3, CH	3.27, dd (11.9, 4.4)	89.8, CH	3.29, dd (11.6, 4.4)
4	40.5, C		40.3, C		40.5, C	
5	56.8, CH	0.68, m	56.7, CH	0.67, m	57.0, CH	0.72, m
6	18.9, CH ₂	1.50, m 1.36, m	18.7, CH ₂	1.48, m 1.36, m	18.9, CH ₂	1.46, m 1.42, m
7	35.5, CH ₂	1.45, m 1.20, m	35.4, CH ₂	1.47, m 1.20, m	35.6, CH ₂	1.46, m 1.17, m
8	40.1, C		40.0, C		40.2, C	
9	50.6, CH	1.34, m	50.5, CH	1.38, m	50.7, CH	1.39, m
10	37.3, C		37.2, C		37.4, C	
11	31.3, CH ₂	1.94, m 1.55, m	31.2, CH ₂	1.95, m 1.55, m	31.4, CH ₂	1.98, m 1.55, m
12	70.7, CH	4.05, m	70.5, CH	4.18, m	70.6, CH	4.19, m
13	49.8, CH	1.95, m	50.0, CH	2.00, m	50.0, CH	2.01, m
14	51.9, C		51.7, C		51.9, C	
15	31.2, CH ₂	1.55, m 1.00, m	31.1, CH ₂	1.56, m 0.99, m	31.2, CH ₂	1.56, m 1.00, m
16	27.1, CH ₂	1.87, m 1.37, m	27.1, CH ₂	1.85, m 1.36, m	27.3, CH ₂	1.88, m 1.42, m
17	51.9, CH	2.52, m	51.9, CH	2.58, m	51.9, CH	2.59, m
18	16.4, CH ₃	0.95, s	16.3, CH ₃	0.98, s	16.5, CH ₃	0.98, s
19	16.7, CH ₃	0.82, s	16.6, CH ₃	0.81, s	16.8, CH ₃	0.85, s
20	84.0, C		83.8, C		84.0, C	
21	22.8, CH ₃	1.60, s	22.5, CH ₃	1.64, s	22.6, CH ₃	1.64, s
22	36.6, CH ₂	2.36, m 1.83, m	36.5, CH ₂	2.40, m 1.82, m	36.6, CH ₂	2.39, m 1.82, m
23	23.7, CH ₂	2.46, m 2.24, m	23.3, CH ₂	2.59, m 2.34, m	23.5, CH ₂	2.60, m 2.36, m
24	126.3, CH	5.24, m	126.4, CH	5.32, t (7.1)	126.5, CH	5.32, m
25	131.4, C		131.4, C		131.5, C	
26	26.2, CH ₃	1.61, s	26.1, CH ₃	1.64, s	26.3, CH ₃	1.64, s
27	18.2, CH ₃	1.61, s	18.1, CH ₃	1.67, s	18.3, CH ₃	1.68, s
28	28.6, CH ₃	1.30, s	28.4, CH ₃	1.29, s	28.5, CH ₃	1.39, s

29	17.1, CH ₃	1.12, s	16.9, CH ₃	1.12, s	17.0, CH ₃	1.21, s
30	17.7, CH ₃	0.92, s	17.7, CH ₃	0.96, s	17.9, CH ₃	0.95, s
3-Glc						
1'	105.6, CH	4.94, d (7.6)	105.5, CH	4.94, d (7.5)	105.4, CH	4.94, d (7.6)
2'	84.2, CH	4.27, m	83.8, CH	4.26, m	84.9, CH	4.19, m
3'	78.8, CH	4.30, m	78.3, CH	4.33, m	78.6, CH	4.32, m
4'	72.1, CH	4.16, m	72.0, CH	4.16, m	71.9, CH	4.17, m
5'	78.8, CH	3.94, m	78.6, CH	3.95, m	78.5, CH	3.95, m
6'	63.4, CH ₂	4.59, dd (12.0, 1.9)	63.2, CH ₂	4.58, dd (11.8, 2.2)	63.2, CH ₂	4.58, dd (11.8, 2.0)
		4.36, m		4.37, m		4.36, m
2'-Glc						
1''	106.6, CH	5.40, d (7.6)	106.4, CH	5.39, d (7.6)	106.7, CH	5.35, d (7.6)
2''	77.7, CH	4.17, m	77.6, CH	4.15, m	77.2, CH	4.15, m
3''	78.6, CH	4.27, m	78.5, CH	4.27, m	79.1, CH	4.22, m
4''	72.1, CH	4.37, m	72.0, CH	4.37, m	71.5, CH	4.33, m
5''	78.8, CH	3.95, m	78.7, CH	3.95, m	75.9, CH	4.09, m
6''	63.2, CH ₂	4.51, m	63.0, CH ₂	4.52, m	65.9, CH ₂	5.10, dd (11.8, 1.6)
		4.36, m		4.36, m		4.99, dd (11.8, 5.0)
20-Glc						
1'''	98.5, CH	5.24, d (7.8)	98.3, CH	5.14, d (7.7)	98.5, CH	5.14, d (7.8)
2'''	73.4, CH	4.07, m	75.3, CH	3.99, m	75.4, CH	4.01, m
3'''	81.7, CH	5.95, t (9.2)	79.5, CH	4.20, m	79.7, CH	4.21, m
4'''	69.7, CH	4.29, m	72.0, CH	4.18, m	72.1, CH	4.18, m
5'''	78.4, CH	3.98, m	75.3, CH	4.06, m	75.9, CH	4.07, m
6'''	62.7, CH ₂	4.46, m	65.9, CH ₂	5.16, dd (11.6, 1.8)	66.1, CH ₂	5.17, dd (11.8, 1.9)
		4.33, m		4.71, dd (11.7, 7.6)		4.72, dd (11.6, 7.4)
3'''-Mal.						
-O-CO	169.1, C		168.4, C		168.4, C	
CH2	44.1, CH ₂	3.72, t (2H, 16.3)	43.4, CH ₂	3.84, dd (2H, 22.3, 15.5)	43.4, CH ₂	3.83, m (2H)
COOH	171.3, C		170.0, C		170.1, C	
6'''-Mal.						
-O-CO					168.7, C	
CH2					43.2, CH ₂	3.83, m (2H)
COOH					170.1, C	
6'''-Malonyl						

Table S4. NMR Spectroscopic Data (500 MHz, Pyridine-*d*5) for Malonylfloralginsenosides Rc₁-Rc₄ (**12-15**)

	m-floral-Rc ₁ (12)		m-floral-Rc ₂ (13)		m-floral-Rc ₃ (14)		m-floral-Rc ₄ (15)	
position	δ_c , type	δ_h , mult (J in Hz)	δ_c , type	δ_h , mult (J in Hz)	δ_c , type	δ_h , mult (J in Hz)	δ_c , type	δ_h , mult (J in Hz)
1	39.7, CH ₂	1.56, m	39.6, CH ₂	1.54, m	39.6, CH ₂	1.56, m	39.6, CH ₂	1.56, m
		0.75, m		0.73, m		0.73, m		0.73, m
2	27.3, CH ₂	2.22, m	27.2, CH ₂	2.21, m	27.2, CH ₂	2.20, m	27.2, CH ₂	2.19, m
		1.84, m		1.81, m		1.81, m		1.82, m
3	89.8, CH	3.27, dd (11.5, 4.2)	89.5, CH	3.24, dd (11.5, 4.2)	89.4, CH	3.26, dd (11.6, 4.3)	89.4, CH	3.26, dd (11.7, 4.3)
4	40.5, C		40.5, C		40.5, C		40.5, C	
5	56.9, CH	0.70, m	56.8, CH	0.65, m	56.8, CH	0.67, m	56.8, CH	0.66, m
6	18.9, CH ₂	1.47, m	18.9, CH ₂	1.47, m	18.9, CH ₂	1.47, m	18.9, CH ₂	1.48, m
		1.41, m		1.35, m		1.36, m		1.36, m
7	35.6, CH ₂	1.47, m	35.6, CH ₂	1.46, m	35.6, CH ₂	1.47, m	35.6, CH ₂	1.46, m
		1.16, m		1.21, m		1.22, m		1.21, m
8	40.2, C		40.1, C		40.1, C		40.1, C	
9	50.7, CH	1.39, m	50.7, CH	1.35, m	50.7, CH	1.37, m	50.6, CH	1.37, m
10	37.4, C		37.4, C		37.4, C		37.3, C	
11	31.2, CH ₂	1.98, m	31.2, CH ₂	1.99, m	31.1, CH ₂	1.97, m	31.1, CH ₂	1.98, m
		1.54, m		1.58, m		1.58, m		1.55, m
12	70.6, CH	4.21, m	70.6, CH	4.17, m	70.6, CH	4.19, m	70.7, CH	4.17, m
13	50.0, CH	2.00, m	50.0, CH	1.97, m	50.0, CH	2.00, m	49.9, CH	2.00, m
14	51.8, C		51.9, C		51.9, C		51.9, C	
15	31.3, CH ₂	1.54, m	31.3, CH ₂	1.58, m	31.3, CH ₂	1.58, m	31.3, CH ₂	1.58, m
		0.99, m		1.03, m		1.00, m		0.99, m
16	27.1, CH ₂	1.84, m	27.1, CH ₂	1.86, m	27.1, CH ₂	1.85, m	27.1, CH ₂	1.87, m
		1.34, m		1.38, m		1.40, m		1.40, m
17	52.1, CH	2.60, m	52.1, CH	2.58, m	52.1, CH	2.59, m	52.1, CH	2.57, m

18	16.5, CH ₃	0.94, s	16.5, CH ₃	0.96, s	16.5, CH ₃	0.97, s	16.4, CH ₃	0.97, s
19	16.8, CH ₃	0.85, s	16.7, CH ₃	0.82, s	16.7, CH ₃	0.83, s	16.7, CH ₃	0.82, s
20	83.9, C		83.9, C		83.9, C		83.9, C	
21	22.7, CH ₃	1.66, s	22.8, CH ₃	1.66, s	22.8, CH ₃	1.64, s	22.8, CH ₃	1.63, s
22	36.6, CH ₂	2.41, m	36.6, CH ₂	2.38, m	36.6, CH ₂	2.42, m	36.6, CH ₂	2.41, m
		1.82, m		1.86, m		1.85, m		1.85, m
23	23.6, CH ₂	2.64, m	23.7, CH ₂	2.59, m	23.7, CH ₂	2.60, m	23.6, CH ₂	2.57, m
		2.37, m		2.39, m		2.40, m		2.39, m
24	126.5, CH (7.0)	5.32, t	126.4, CH	5.34, m	126.4, CH	5.34, m	126.5, CH	5.32, m
25	131.4, C		131.6, C		131.6, C		131.5, C	
26	26.3, CH ₃	1.61, s	26.3, CH ₃	1.63, s	26.2, CH ₃	1.67, s	26.2, CH ₃	1.67, s
27	18.4, CH ₃	1.66, s	18.3, CH ₃	1.67, s	18.3, CH ₃	1.67, s	18.3, CH ₃	1.67, s
28	28.5, CH ₃	1.38, s	28.5, CH ₃	1.29, s	28.5, CH ₃	1.26, s	28.5, CH ₃	1.26, s
29	17.0, CH ₃	1.20, s	17.1, CH ₃	1.07, s	17.1, CH ₃	1.07, s	17.1, CH ₃	1.07, s
30	17.9, CH ₃	0.97, s	17.8, CH ₃	0.96, s	17.8, CH ₃	0.97, s	17.8, CH ₃	0.96, s
		3-Glc	3-Glc	3-Glc	3-Glc			
1'	105.4, CH (7.5)	4.93, d	105.4, CH (7.5)	4.90, d	105.5, CH	4.91, d (7.4)	105.5, CH	4.91, d (7.4)
2'	84.9, CH	4.19, m	83.7, CH	4.24, m	83.4, CH	4.26, m	83.4, CH	4.26, m
3'	78.6, CH	4.32, m	78.8, CH	4.31, m	78.8, CH	4.27, m	78.6, CH	4.27, m
4'	72.1, CH	4.17, m	72.3, CH	4.15, m	72.3, CH	4.12, t (9.2)	72.2, CH	4.12, t (9.2)
5'	78.5, CH	3.94, m	78.6, CH	3.93, m	78.7, CH	3.94, m	78.6, CH	3.93, m
6'	63.2, CH ₂ (12.1, 2.3)	4.57, dd	63.3, CH ₂	4.57, dd (11.9, 2.1)	63.3, CH ₂	4.57, dd (12.1, 2.1)	63.3, CH ₂	4.57, dd (11.8, 2.1)
		4.37, m		4.37, m		4.35, m		4.34, m
		2'-Glc	2'-Glc	2'-Glc	2'-Glc			
1''	106.7, CH (7.7)	5.35, d	106.1, CH (7.7)	5.41, d	106.0, CH	5.46, d (7.6)	106.0, CH	5.46, d (7.6)

2"	77.4, CH	4.15, m CH	77.5, CH	4.17, m CH	75.4, CH 80.4, CH (9.6)	4.20, m 5.99, t (9.6)	75.3, CH 80.4, CH	4.20, m 5.99, t (9.5)
3"	78.5, CH	4.22, m CH	75.7, CH	4.37, m CH	80.4, CH 69.6, CH (9.6)	5.99, t 4.49, m 69.6, CH	80.4, CH 69.6, CH	5.99, t (9.5) 4.49, t (9.4)
4"	71.9, CH	4.27, m CH	73.9, CH	5.87, t (9.6)	69.6, CH 4.46, m	4.49, m 62.3, CH ₂	69.6, CH 62.3, CH ₂	4.49, t (9.4) 4.45, m
5"	75.9, CH	4.06, m CH	76.5, CH	4.03, m CH	78.6, CH 4.33, m	3.94, m 4.33, m	78.6, CH 4.33, m	3.94, m
6"	65.8, CH ₂	5.07, d (11.2)	62.5, CH ₂	4.42, m 4.99, m	62.2, CH ₂ 4.33, m	4.46, m 4.33, m	62.3, CH ₂ 4.33, m	4.45, m
		20-Glc		20-Glc		20-Glc		20-Glc
1'''	98.6, CH	5.15, d (7.6)	98.6, CH	5.15, d (7.7)	98.6, CH 75.4, CH	5.15, d 3.96, m	98.6, CH 75.5, CH	5.16, d (7.8) 3.99, m
2'''	75.4, CH	3.95, m CH	75.4, CH	3.95, m CH	75.4, CH 79.7, CH	3.96, m 4.19, m	75.5, CH 79.7, CH	3.99, m 4.20, m
3'''	79.8, CH	4.19, m CH	79.7, CH	4.19, m CH	79.7, CH 72.1, CH	4.19, m 4.07, m	79.7, CH 72.6, CH	4.20, m 4.06, m
4'''	71.6, CH	4.08, m CH	72.1, CH	4.07, m CH	72.2, CH 69.7, CH ₂	4.07, m 4.27, m	72.6, CH 69.0, CH ₂	4.06, m 4.69, dd
5'''	77.2, CH	4.09, m CH	77.2, CH	4.04, m CH	77.2, CH 69.7, CH ₂	4.07, m 4.28, m	77.0, CH 4.13, m	4.06, m
		6'''-Xyl		6'''-Ara (<i>p</i>)		6'''-Ara (<i>p</i>)		6'''-Ara (<i>f</i>)
1'''	106.4, CH	5.01, d (7.4)	105.1, CH	5.02, d (6.0)	105.1, CH 72.6, CH	5.02, d 4.48, m	110.6, CH 83.9, CH	5.68, d (1.2) 4.90, m
2'''	75.3, CH	4.05, m CH	72.6, CH	4.47, dd (7.7, 6.2)	72.6, CH 74.6, CH	4.48, m 4.25, m	83.9, CH 79.3, CH	4.90, m 4.83, m
3'''	78.6, CH	4.20, m CH	74.6, CH	4.24, m CH	74.6, CH 69.0, CH	4.25, m 4.38, m	86.5, CH 86.5, CH	4.77, m
4'''	71.4, CH	4.23, m CH	69.0, CH	4.39, m CH	69.0, CH 66.0, CH ₂	4.38, m 4.33, m	86.5, CH 63.1, CH ₂	4.77, m 4.35, m
5'''	67.5, CH ₂	4.35, dd (11.1, 10.1)	66.0, CH ₂	4.33, m 3.70, m	66.0, CH ₂ 3.82, m	4.33, m 3.82, dd (11.8, 2.0)	63.1, CH ₂ 4.24, m	4.35, m
		6'''-Mal.		4'''-Mal.		3'''-Mal.		3'''-Mal.
-O-CO	169.4, C		168.2, C		168.5, C		168.6, C	
CH ₂	43.5,	3.82, dd	43.7,	3.79, dd	43.6, CH ₂	3.77, s (11.8, 2.0)	43.7, CH ₂	3.74, s (2H)

CH ₂	(2H, 26.4, 15.7)	CH ₂	(2H, 26.4, 15.7)	(2H)
COOH	174.2, C	170.6, C	170.6, C	170.7, C
