

# Supporting Information

## Lupane Triterpenes from Leave of *Acanthopanax gracilistylus*

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## Contents of Supporting Information

NO.	Contents	Pages
1	<b>Figure S1.</b> Photo of <i>Acanthopanax gracilistylus</i> W. W. Smith	1
2	<b>Figure S2.</b> <sup>1</sup> H NMR spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	2
3	<b>Figure S3.</b> Expand <sup>1</sup> H NMR spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	2
4	<b>Figure S4.</b> Expand <sup>1</sup> H NMR spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	3
5	<b>Figure S5.</b> <sup>13</sup> C NMR spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	3
6	<b>Figure S6.</b> Expand <sup>13</sup> C NMR spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	4
7	<b>Figure S7.</b> Expand <sup>13</sup> C NMR spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	4
8	<b>Figure S8.</b> Expand <sup>13</sup> C NMR spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	5
9	<b>Figure S9.</b> DEPT spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	5
10	<b>Figure S10.</b> Expand DEPT spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	6
11	<b>Figure S11.</b> HSQC spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	6
12	<b>Figure S12.</b> Expand HSQC spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	7
13	<b>Figure S13.</b> Expand HSQC spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	7
14	<b>Figure S14.</b> HMBC spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	8
15	<b>Figure S15.</b> Expand HMBC spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	8
16	<b>Figure S16.</b> Expand HMBC spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	9
17	<b>Figure S17.</b> <sup>1</sup> H- <sup>1</sup> H COSY spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	9
18	<b>Figure S18.</b> Expand <sup>1</sup> H- <sup>1</sup> H COSY spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	10
19	<b>Figure S19.</b> Expand <sup>1</sup> H- <sup>1</sup> H COSY spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	10
20	<b>Figure S20.</b> NOESY spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	11
21	<b>Figure S21.</b> Expand NOESY spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	11
22	<b>Figure S22.</b> Expand NOESY spectrum of acangraciligenin S in acetone- <i>d</i> <sub>6</sub>	12
23	<b>Figure S23.</b> ESIMS spectrum of acangraciligenin S	13
24	<b>Figure S24.</b> HRESIMS spectrum of acangraciligenin S	13
25	<b>Figure S25.</b> <sup>1</sup> H NMR spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	14
26	<b>Figure S26.</b> Expand <sup>1</sup> H NMR spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	14
27	<b>Figure S27.</b> Expand <sup>1</sup> H NMR spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	15
28	<b>Figure S28.</b> Expand <sup>1</sup> H NMR spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	15
29	<b>Figure S29.</b> <sup>13</sup> C NMR spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	16
30	<b>Figure S30.</b> Expand <sup>13</sup> C NMR spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	16
31	<b>Figure S31.</b> Expand <sup>13</sup> C NMR spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	17
32	<b>Figure S32.</b> HSQC spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	17
33	<b>Figure S33.</b> Expand HSQC spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	18
34	<b>Figure S34.</b> Expand HSQC spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	18
35	<b>Figure S35.</b> HMBC spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	19
36	<b>Figure S36.</b> Expand HMBC spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	19
37	<b>Figure S37.</b> Expand HMBC spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	20
38	<b>Figure S38.</b> Expand HMBC spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	20
39	<b>Figure S39.</b> <sup>1</sup> H- <sup>1</sup> H COSY spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	21
40	<b>Figure S40.</b> Expand <sup>1</sup> H- <sup>1</sup> H COSY spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	21
41	<b>Figure S41.</b> Expand <sup>1</sup> H- <sup>1</sup> H COSY spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	22
42	<b>Figure S42.</b> Expand <sup>1</sup> H- <sup>1</sup> H COSY spectrum of acangraciliside S in methanol- <i>d</i> <sub>4</sub>	22

43	<b>Figure S43.</b> NOESY spectrum of acangraciliside S in methanol- $d_4$	23
44	<b>Figure S44.</b> Expand NOESY spectrum of acangraciliside S in methanol- $d_4$	23
45	<b>Figure S45.</b> Expand NOESY spectrum of acangraciliside S in methanol- $d_4$	24
46	<b>Figure S46.</b> ESIMS spectrum of acangraciliside S	25
47	<b>Figure S47.</b> HRESIMS spectrum of acangraciliside S	25
48	<b>Figure S48.</b> $^1\text{H}$ NMR spectrum of <b>2a</b> in acetone- $d_6$	26
49	<b>Figure S49.</b> Expand $^1\text{H}$ NMR spectrum of <b>2a</b> in acetone- $d_6$	26
50	<b>Figure S50.</b> Expand $^1\text{H}$ NMR spectrum of <b>2a</b> in acetone- $d_6$	27
51	<b>Figure S51.</b> $^{13}\text{C}$ NMR spectrum of <b>2a</b> in acetone- $d_6$	27
52	<b>Figure S52.</b> Expand $^{13}\text{C}$ NMR spectrum of <b>2a</b> in acetone- $d_6$	28
53	<b>Figure S53.</b> Expand $^{13}\text{C}$ NMR spectrum of <b>2a</b> in acetone- $d_6$	28
54	<b>Figure S54.</b> Expand $^{13}\text{C}$ NMR spectrum of <b>2a</b> in acetone- $d_6$	29
55	<b>Figure S55.</b> DEPT spectrum of <b>2a</b> in acetone- $d_6$	29
56	<b>Figure S56.</b> Expand DEPT spectrum of <b>2a</b> in acetone- $d_6$	30
57	<b>Figure S57.</b> $^1\text{H}$ NMR spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	30
58	<b>Figure S58.</b> Expand $^1\text{H}$ NMR spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	31
59	<b>Figure S59.</b> Expand $^1\text{H}$ NMR spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	31
60	<b>Figure S60.</b> $^{13}\text{C}$ NMR spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	32
61	<b>Figure S61.</b> Expand $^{13}\text{C}$ NMR spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	32
62	<b>Figure S62.</b> Expand $^{13}\text{C}$ NMR spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	33
63	<b>Figure S63.</b> Expand $^{13}\text{C}$ NMR spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	33
64	<b>Figure S64.</b> DEPT spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	34
65	<b>Figure S65.</b> Expand DEPT spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	34
66	<b>Figure S66.</b> Expand DEPT spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	35
67	<b>Figure S67.</b> HSQC spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	35
68	<b>Figure S68.</b> Expand HSQC spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	36
69	<b>Figure S69.</b> Expand HSQC spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	36
70	<b>Figure S70.</b> HMBC spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	37
71	<b>Figure S71.</b> Expand HMBC spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	37
72	<b>Figure S72.</b> Expand HMBC spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	38
73	<b>Figure S73.</b> Expand HMBC spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	38
74	<b>Figure S74.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	39

75	<b>Figure S75.</b> Expand $^1\text{H}$ - $^1\text{H}$ COSY spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	39
76	<b>Figure S76.</b> Expand $^1\text{H}$ - $^1\text{H}$ COSY spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	40
77	<b>Figure S77.</b> NOESY spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	40
78	<b>Figure S78.</b> Expand NOESY spectrum of $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$	41
79	<b>Figure S79.</b> $^1\text{H}$ NMR spectrum of acankoreoside C in methanol- $d_4$	41
80	<b>Figure S80.</b> Expand $^1\text{H}$ NMR spectrum of acankoreoside C in methanol- $d_4$	42
81	<b>Figure S81.</b> Expand $^1\text{H}$ NMR spectrum of acankoreoside C in methanol- $d_4$	42
82	<b>Figure S82.</b> Expand $^1\text{H}$ NMR spectrum of acankoreoside C in methanol- $d_4$	43
83	<b>Figure S83.</b> $^{13}\text{C}$ NMR spectrum of acankoreoside C in methanol- $d_4$	43
84	<b>Figure S84.</b> Expand $^{13}\text{C}$ NMR spectrum of acankoreoside C in methanol- $d_4$	44
85	<b>Figure S85.</b> Expand $^{13}\text{C}$ NMR spectrum of acankoreoside C in methanol- $d_4$	44
86	<b>Table S1.</b> NMR spectral data of compound <b>1</b> in acetone- $d_6$	45
87	<b>Table S2.</b> NMR spectral data of compound <b>2</b> in methanol- $d_4$	45
88	<b>Table S3.</b> NMR spectral data of compounds <b>3-4</b>	46



**Figure S1.** Photo of *Acanthopanax gracilistylus* W. W. Smith (Changsha City, Hunan Prov., by Liu Xiang-qian)

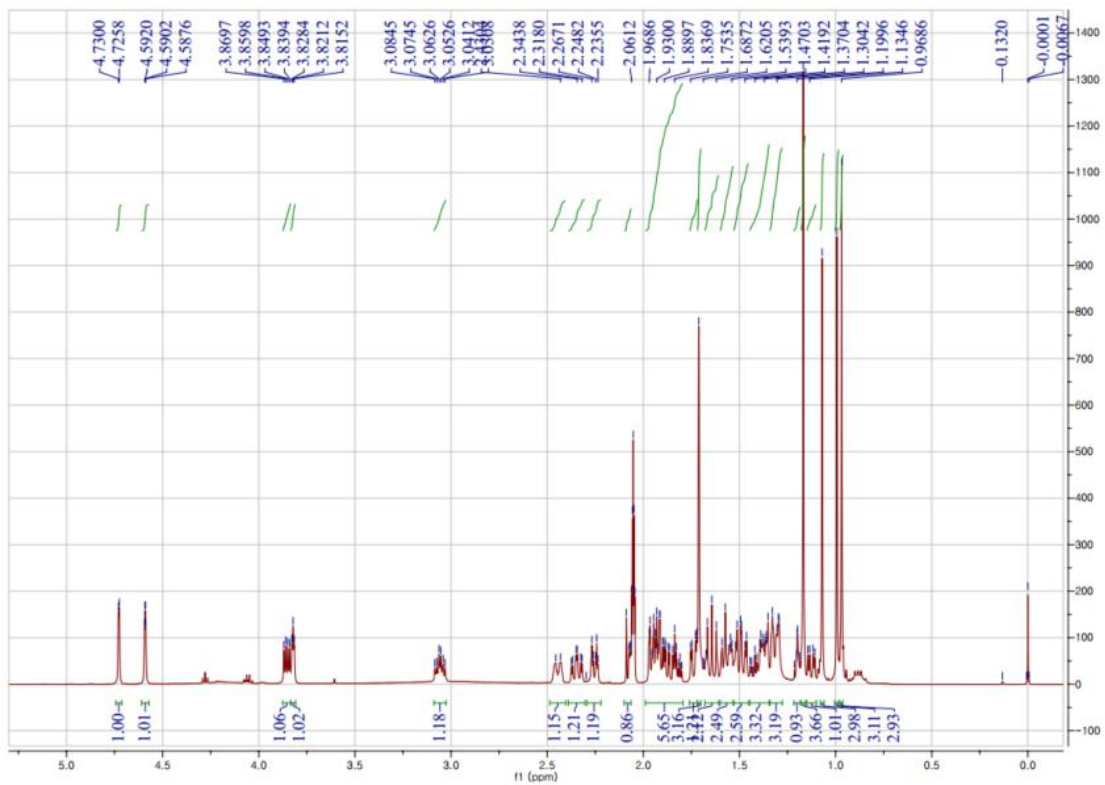


Figure S2.  $^1\text{H}$  NMR spectrum of acangraciligenin S in acetone- $d_6$

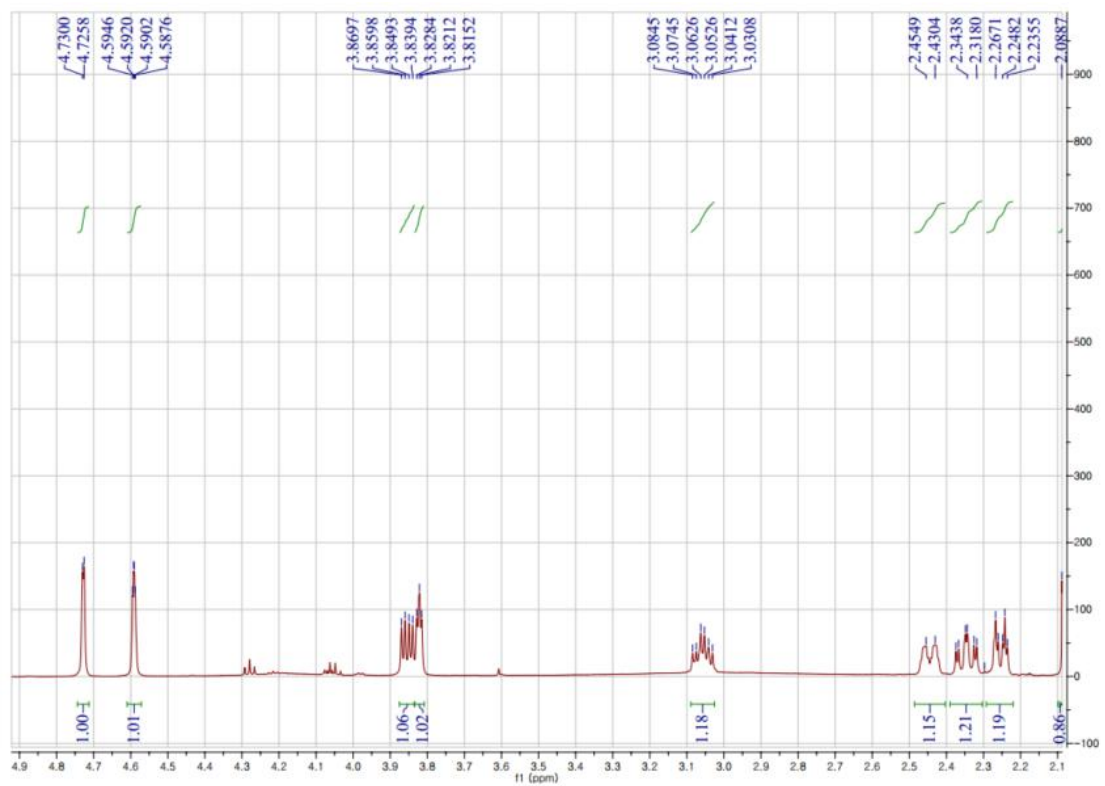


Figure S3. Expand  $^1\text{H}$  NMR spectrum of acangraciligenin S in acetone- $d_6$

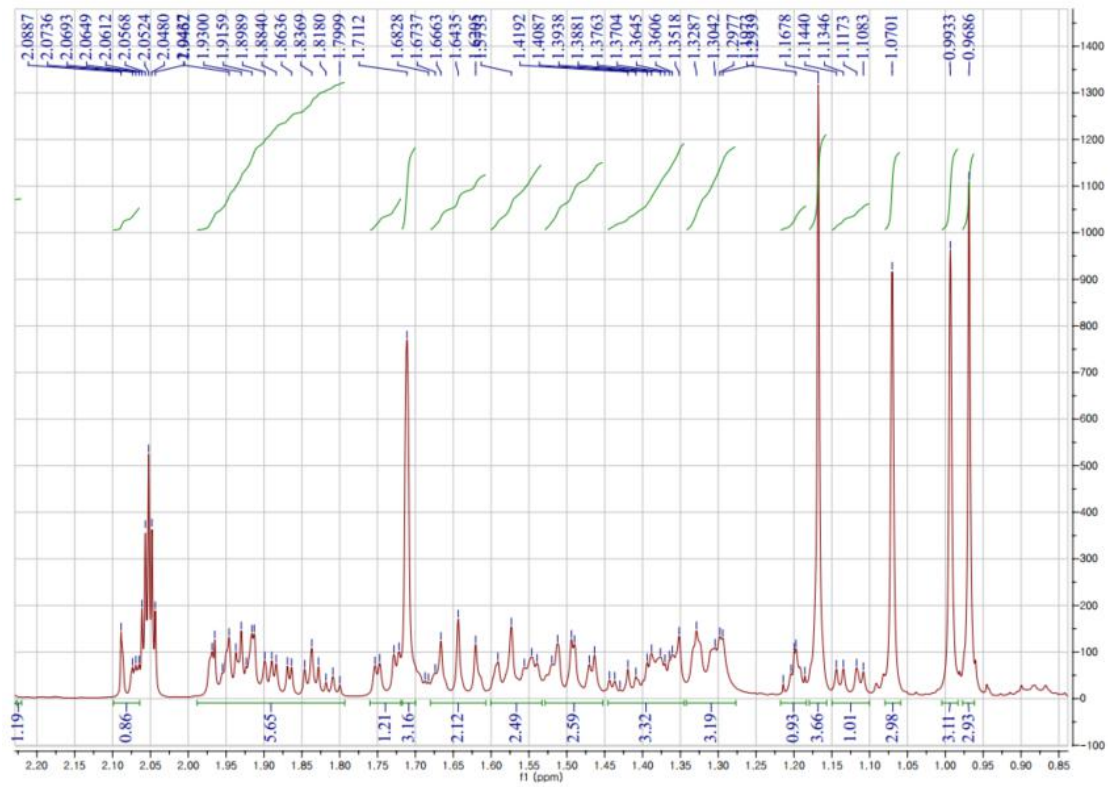


Figure S4. Expand  $^1\text{H}$  NMR spectrum of acangraciligenin S in acetone- $d_6$

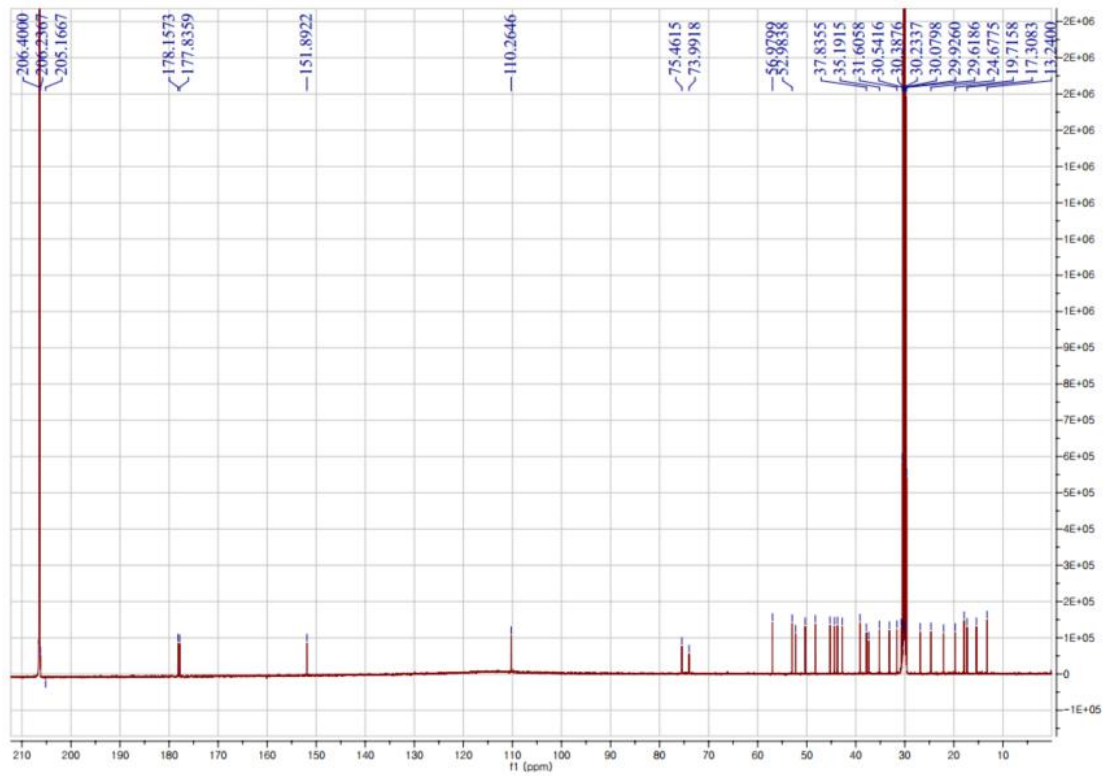


Figure S5.  $^{13}\text{C}$  NMR spectrum of acangraciligenin S in acetone- $d_6$



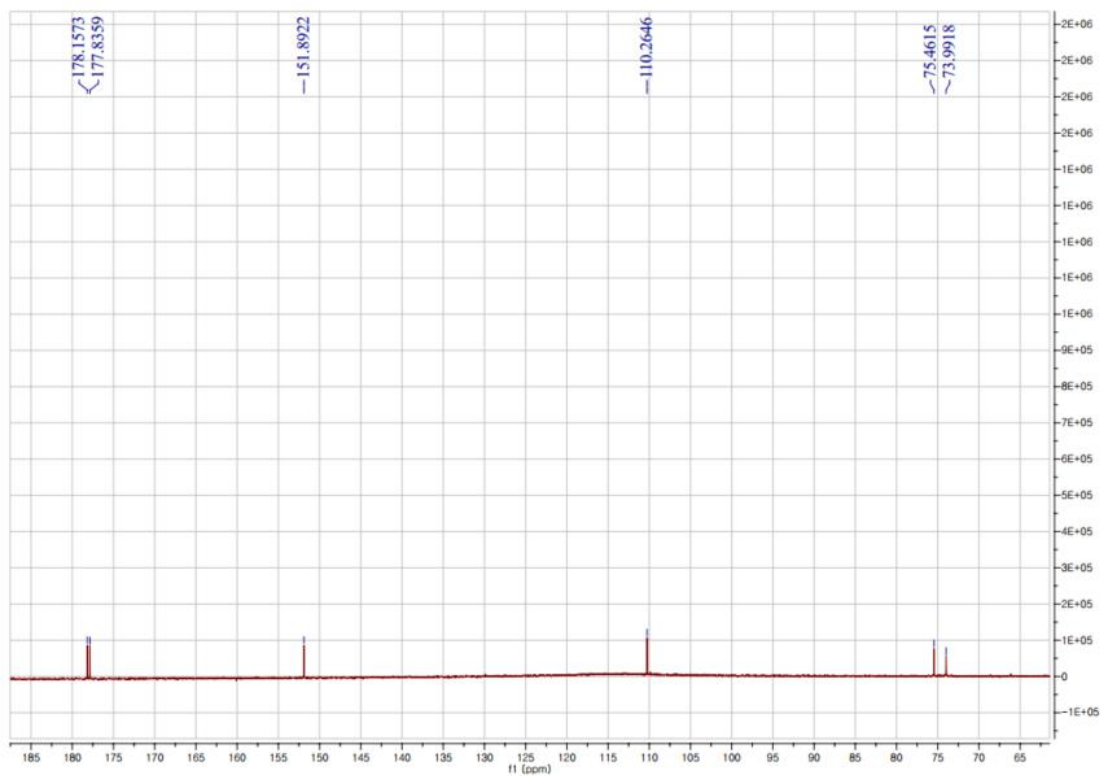


Figure S6. Expand  $^{13}\text{C}$  NMR spectrum of acangraciligenin S in acetone- $d_6$

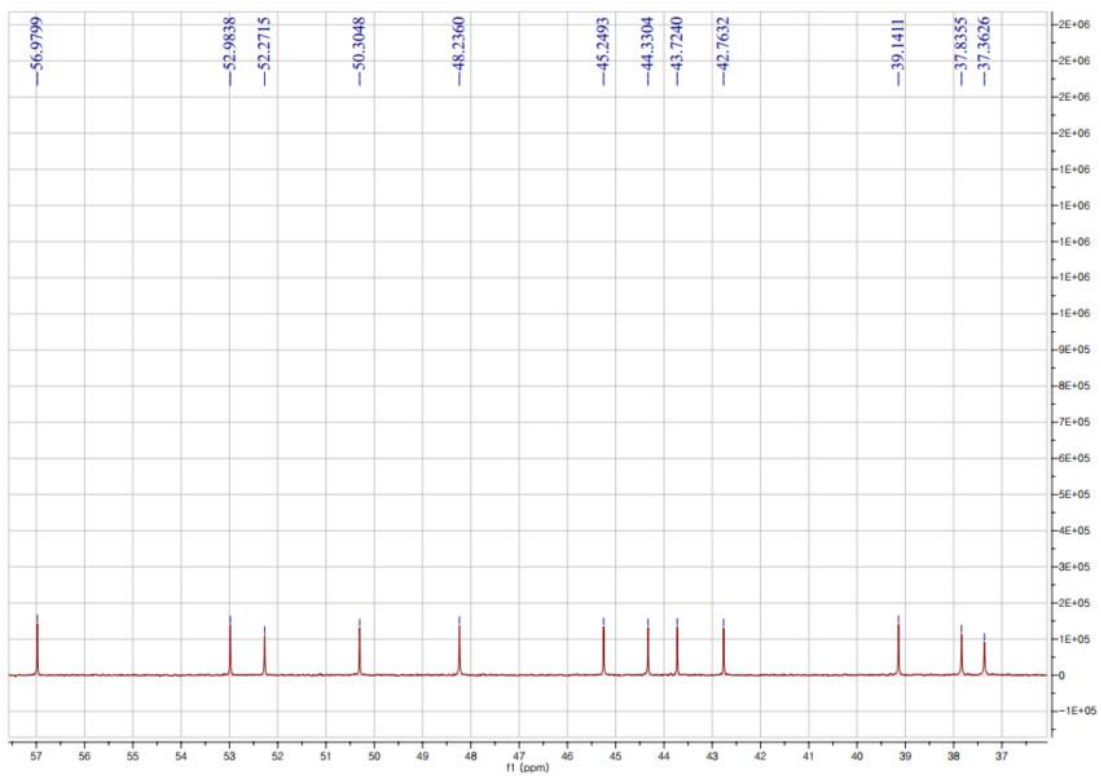


Figure S7. Expand  $^{13}\text{C}$  NMR spectrum of acangraciligenin S in acetone- $d_6$



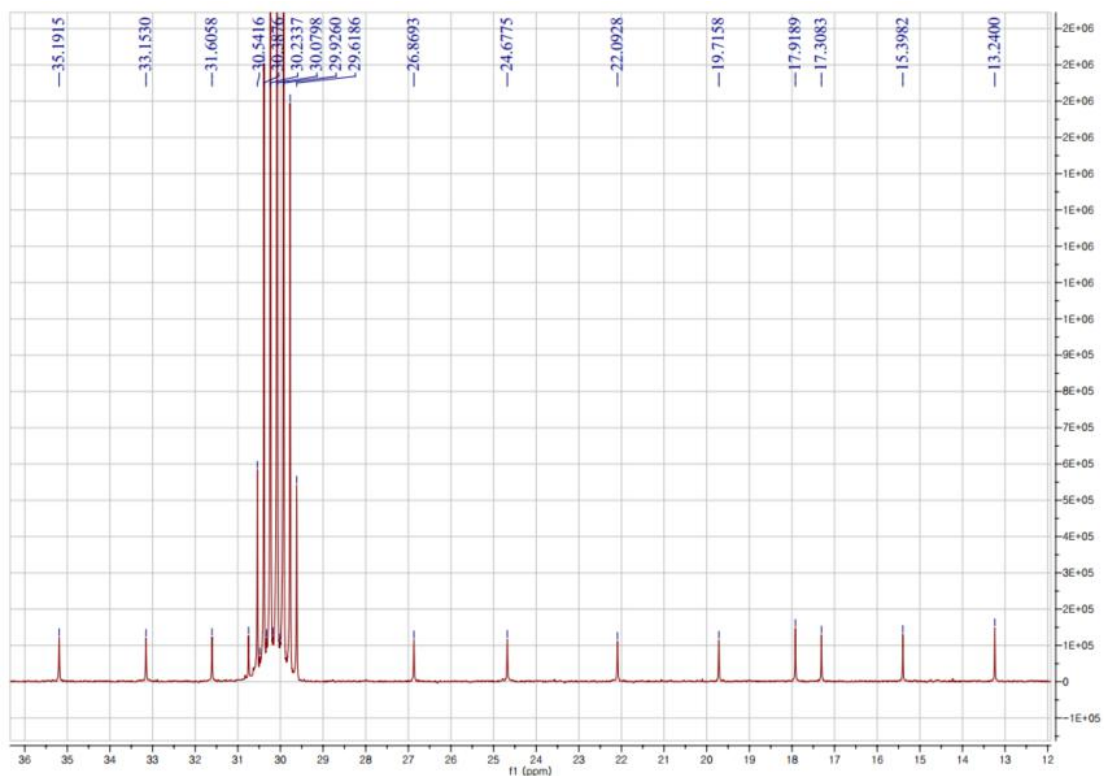


Figure S8. Expand <sup>13</sup>C NMR spectrum of acangraciligenin S in acetone-*d*<sub>6</sub>

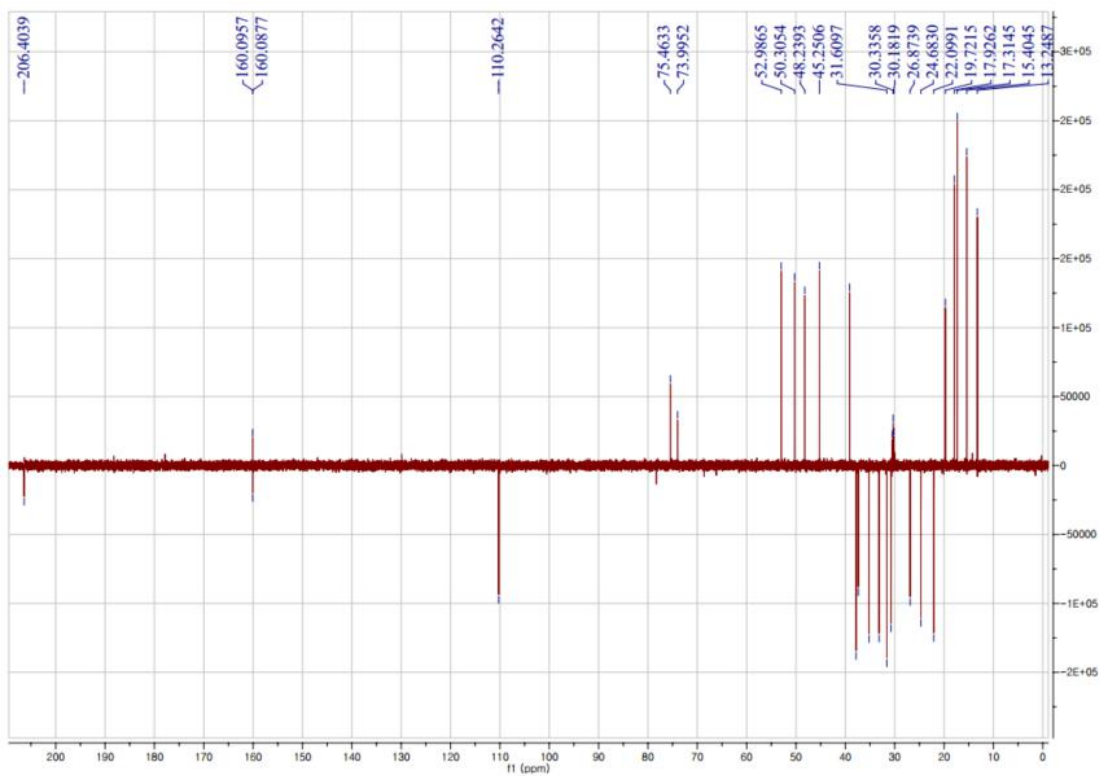


Figure S9. DEPT spectrum of acangraciligenin S in acetone-*d*<sub>6</sub>

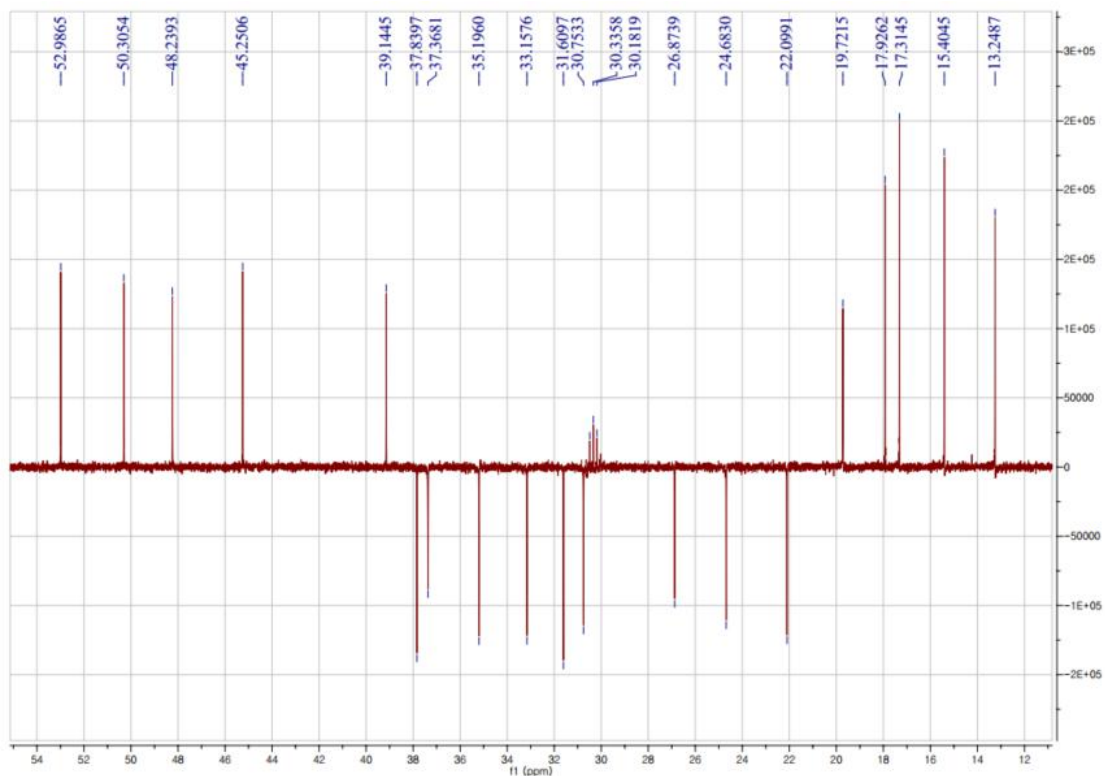


Figure S10. Expand DEPT spectrum of acangraciligenin S in acetone- $d_6$

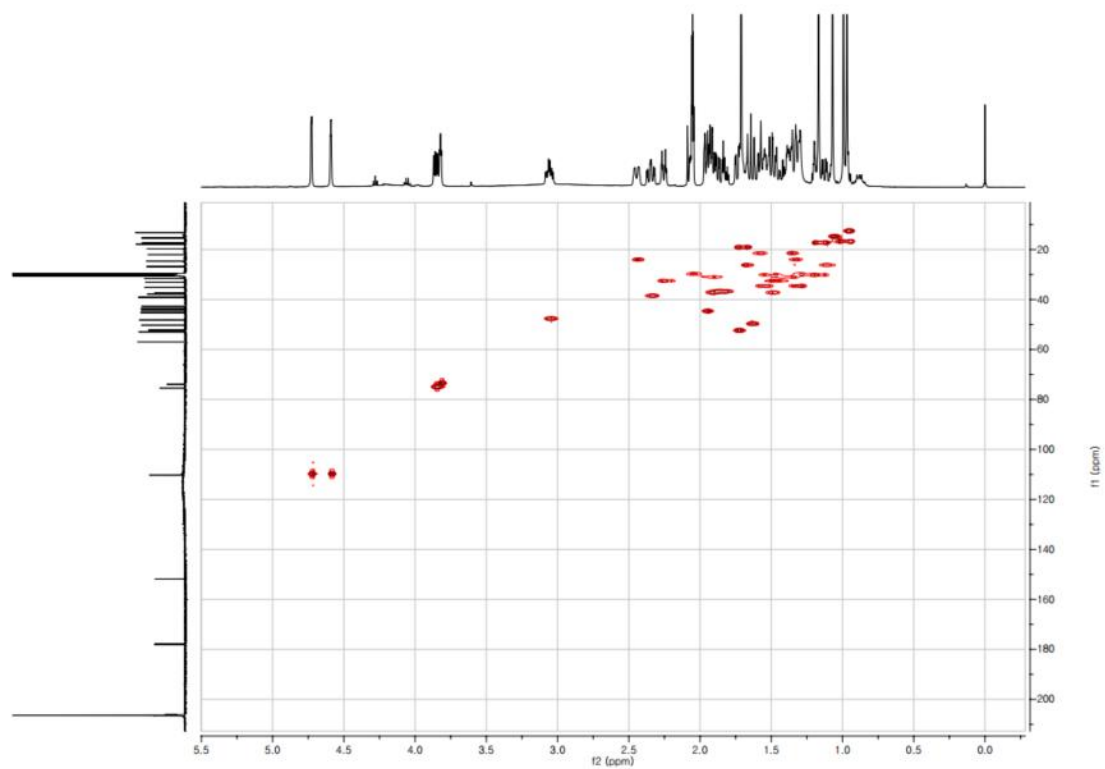


Figure S11. HSQC spectrum of acangraciligenin S in acetone- $d_6$

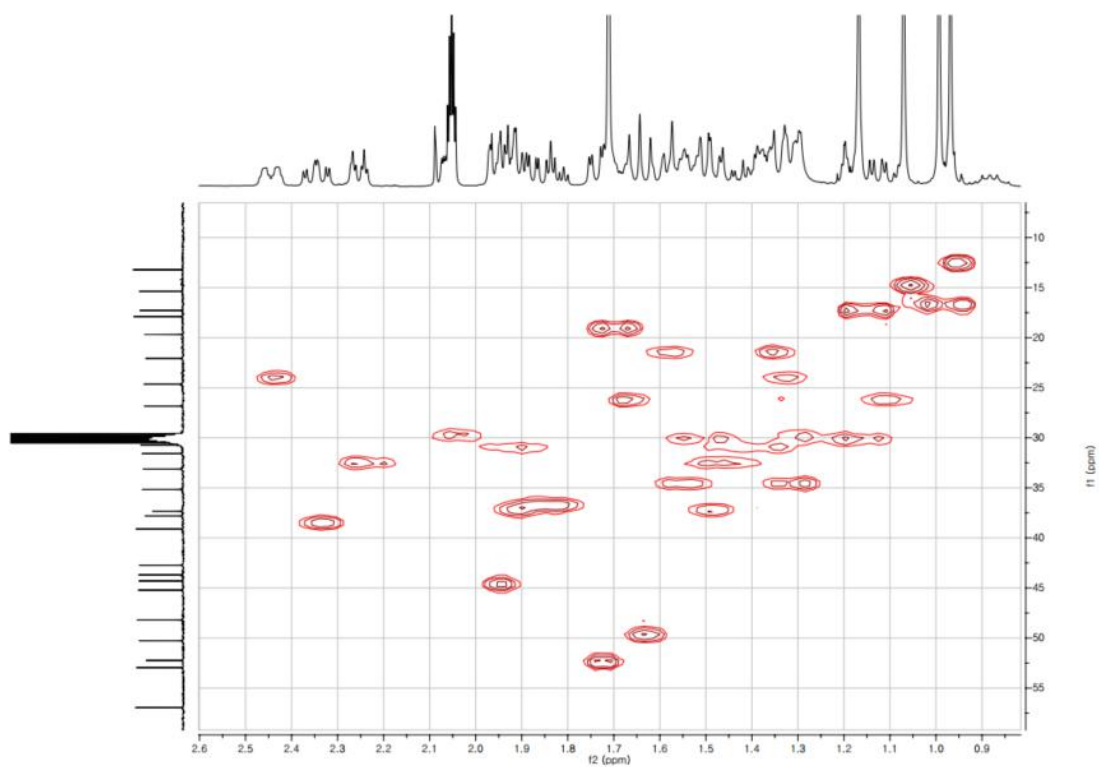


Figure S12. Expand HSQC spectrum of acangraciligenin S in acetone- $d_6$

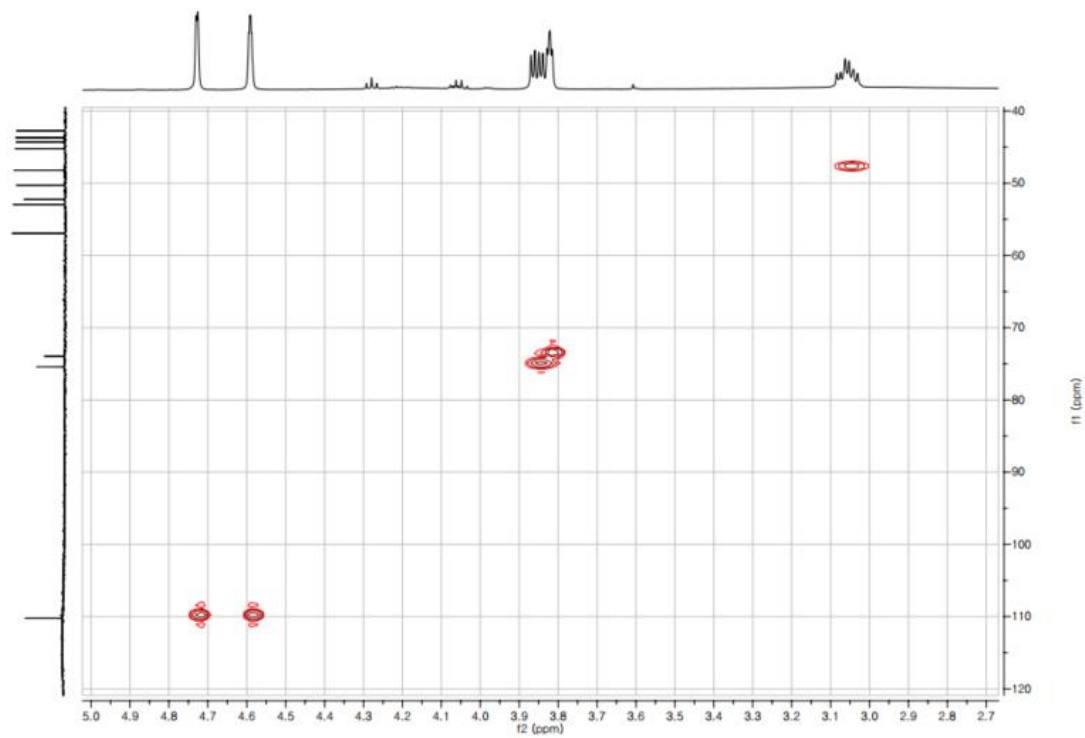


Figure S13. Expand HSQC spectrum of acangraciligenin S in acetone- $d_6$

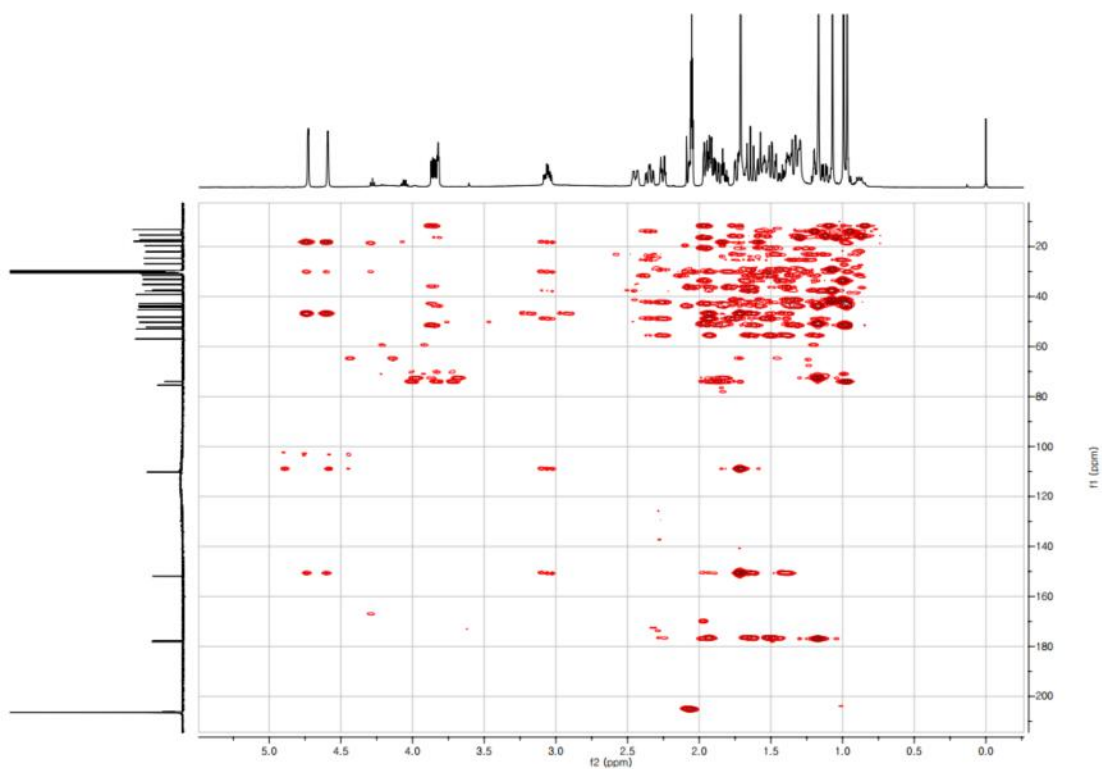


Figure S14. HMBC spectrum of acangraciligenin S in acetone- $d_6$

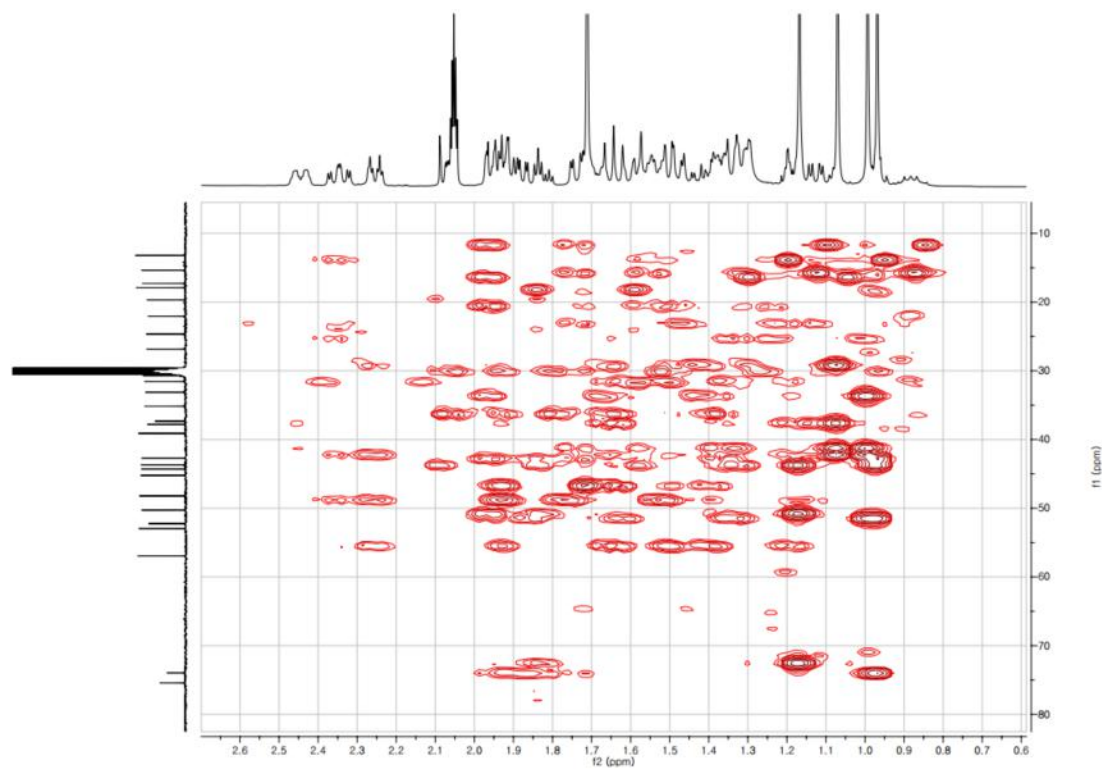


Figure S15. Expand HMBC spectrum of acangraciligenin S in acetone- $d_6$

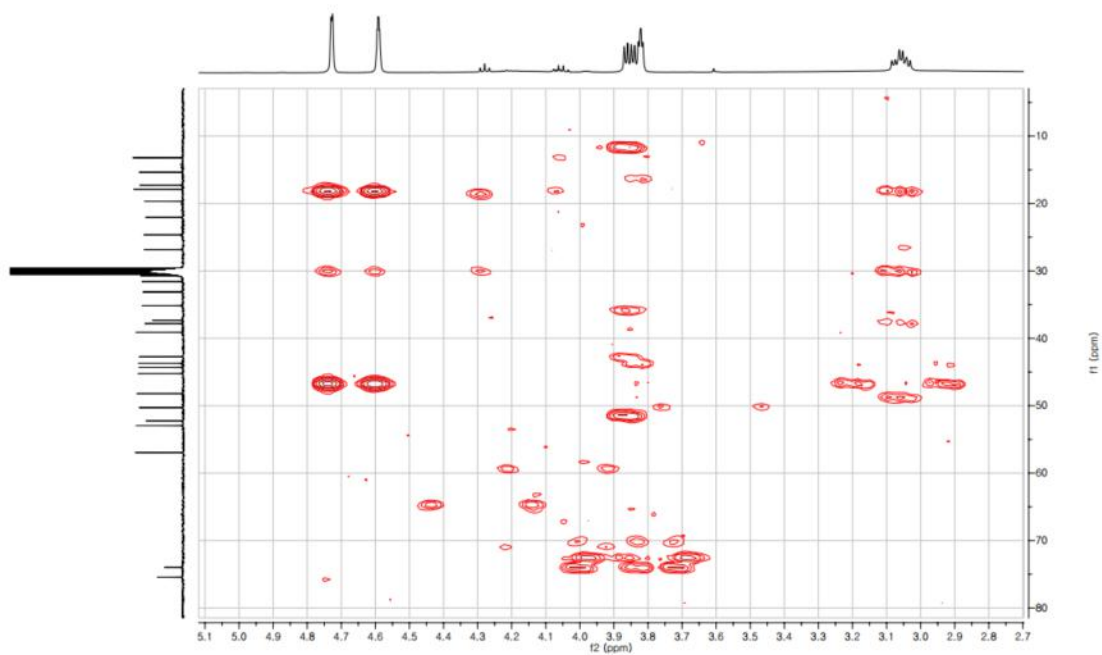


Figure S16. Expand HMBC spectrum of acangraciligenin S in acetone- $d_6$

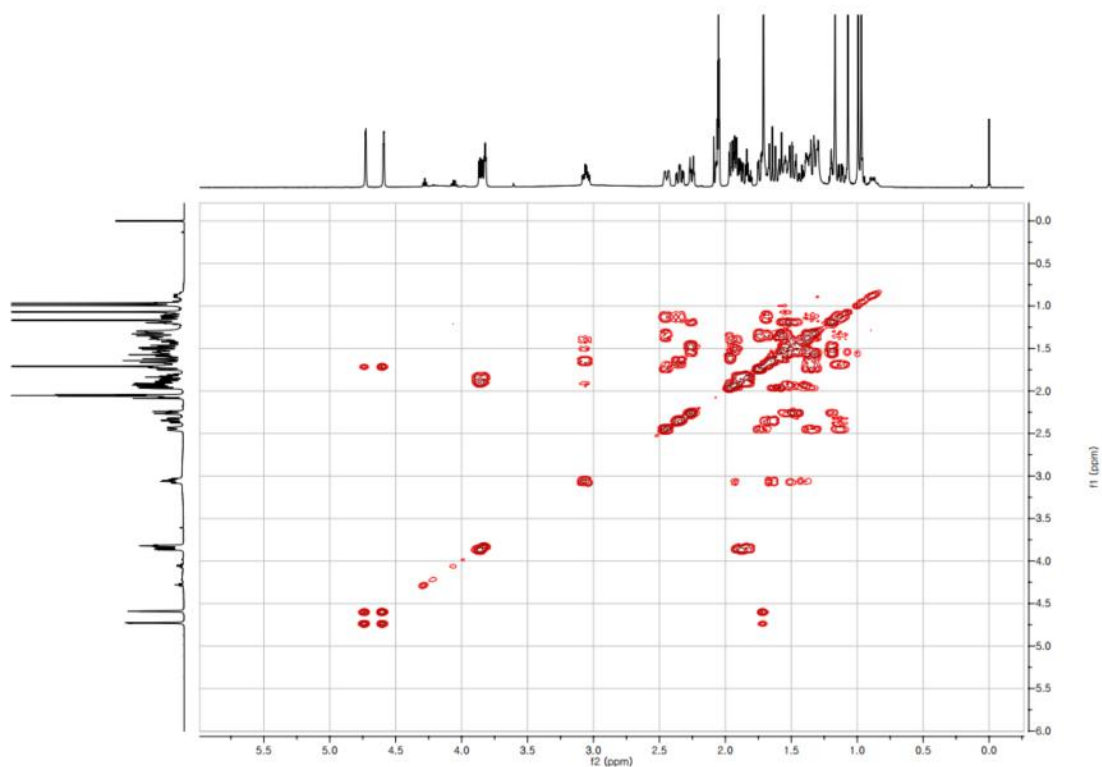


Figure S17.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of acangraciligenin S in acetone- $d_6$

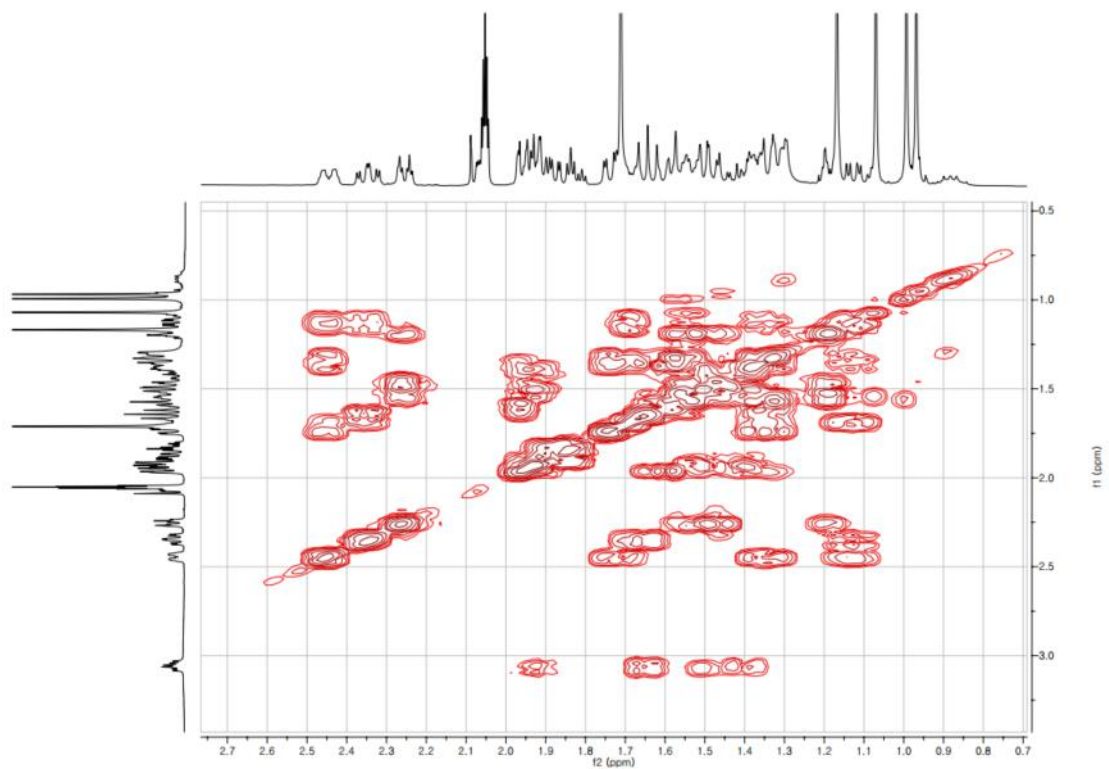


Figure S18. Expand  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of acangraciligenin S in acetone- $d_6$

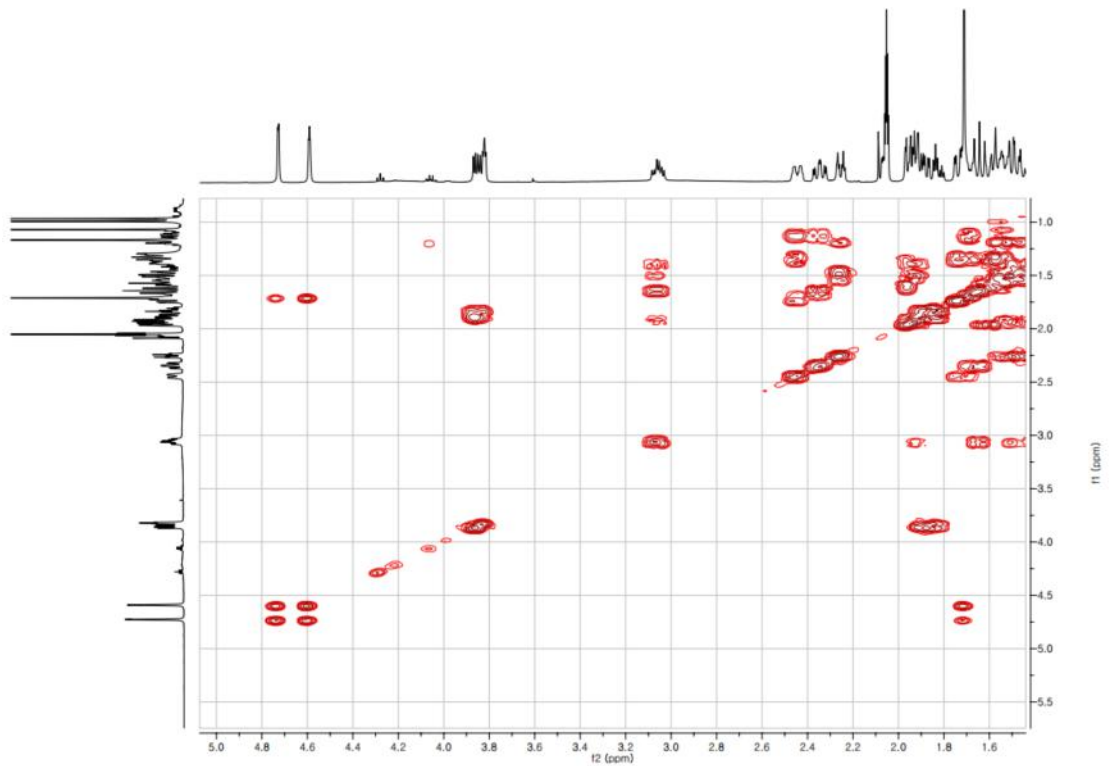


Figure S19. Expand  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of acangraciligenin S in acetone- $d_6$

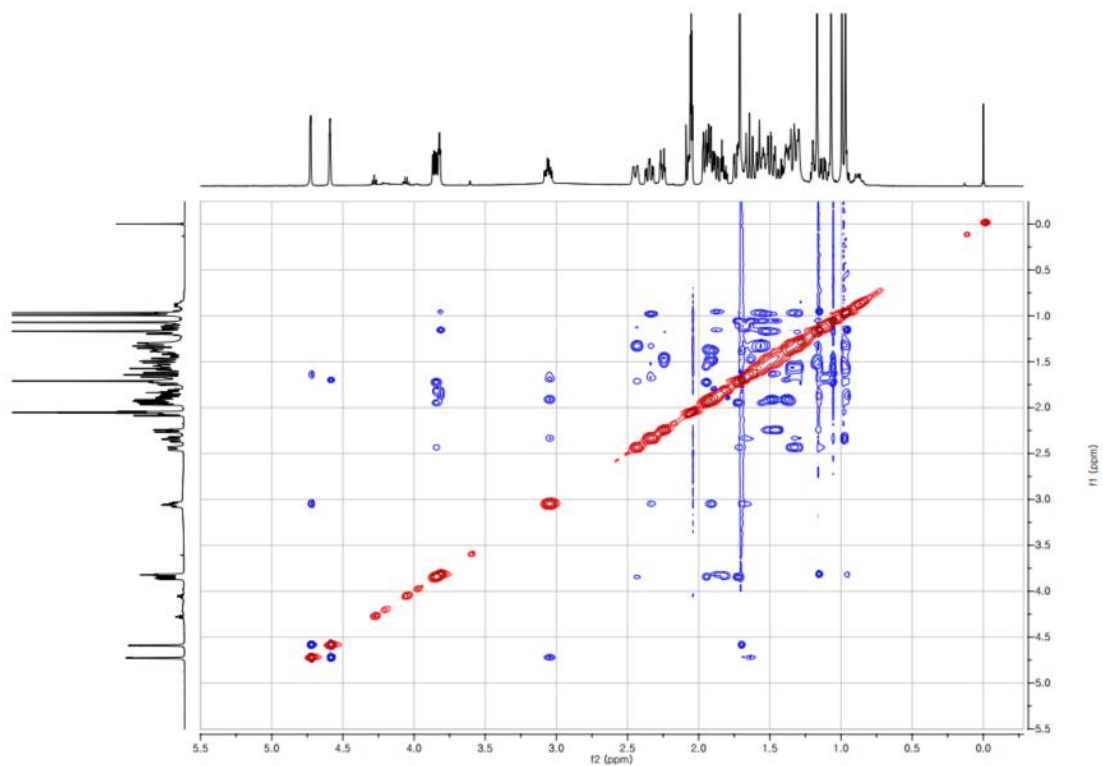


Figure S20. NOESY spectrum of acangraciligenin S in acetone- $d_6$

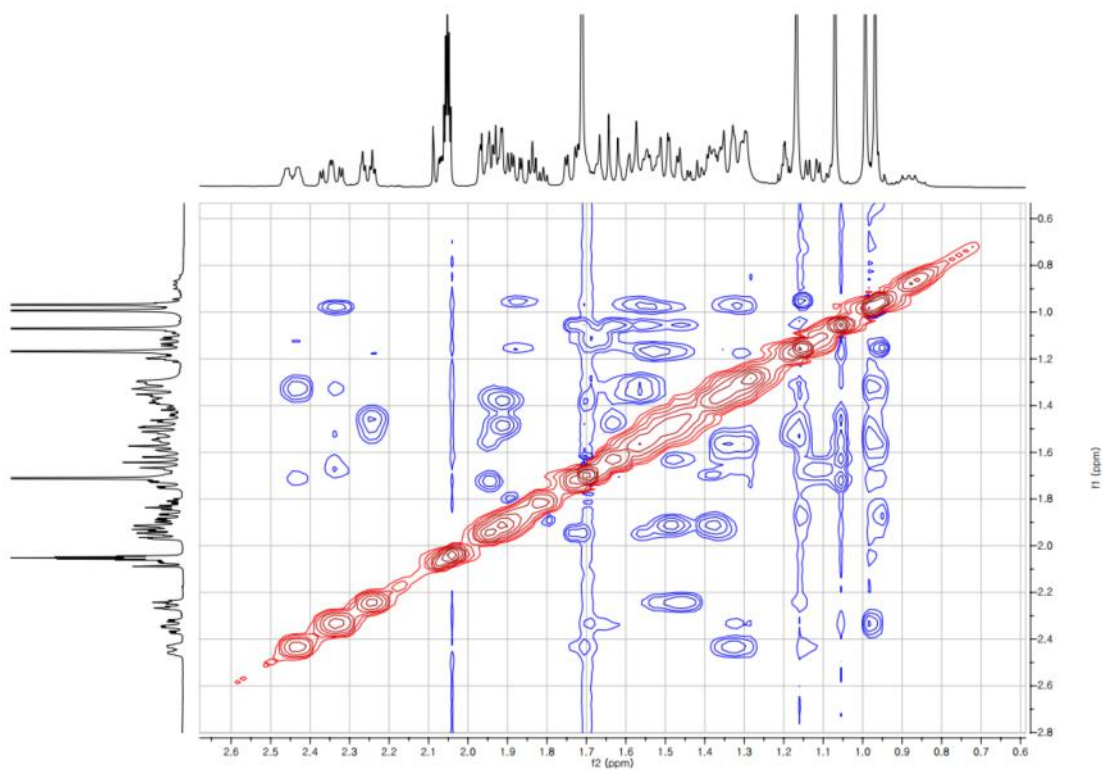


Figure S21. Expand NOESY spectrum of acangraciligenin S in acetone- $d_6$



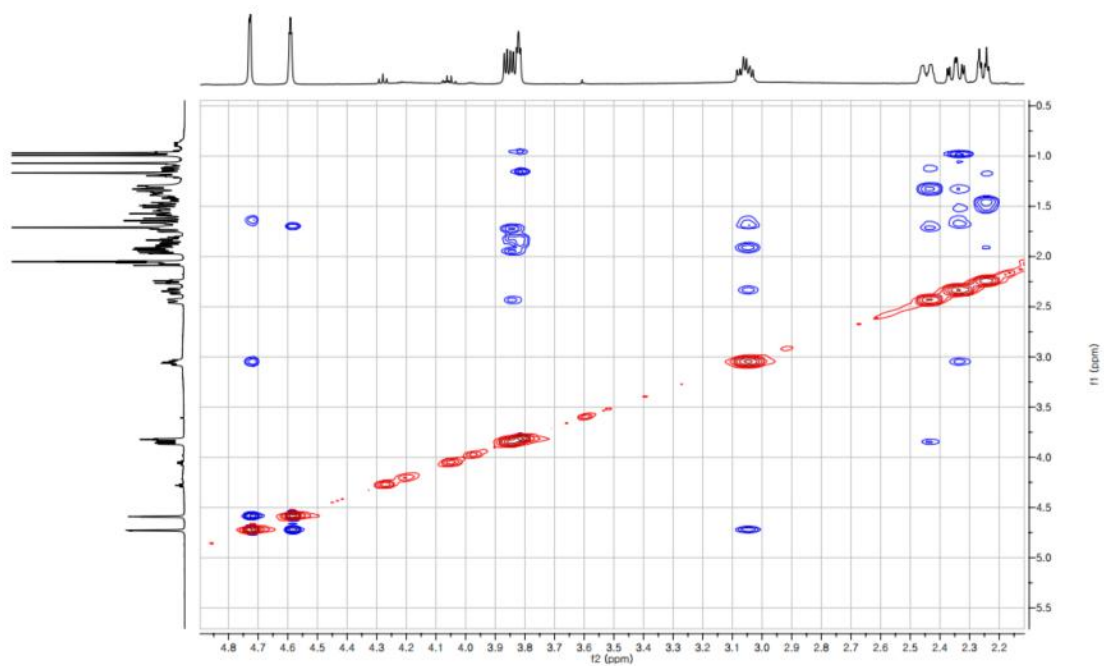


Figure S22. Expand NOESY spectrum of acangraciligenin S in acetone- $d_6$

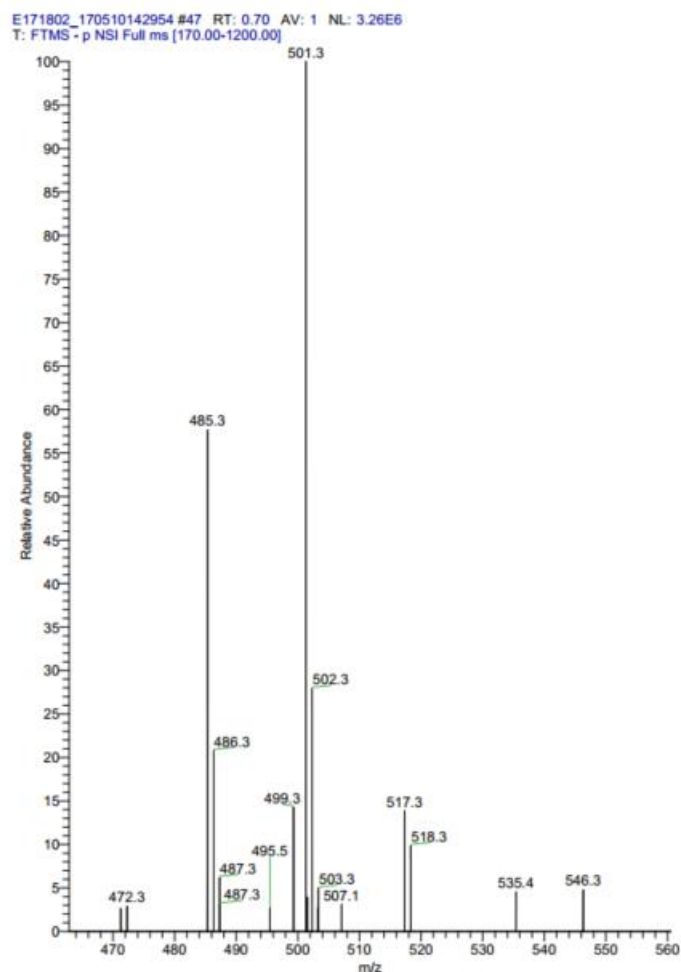


Figure S23. ESIMS spectrum of acangraciligenin S

National Center for Organic Mass Spectrometry in Shanghai  
Shanghai Institute of Organic Chemistry  
Chinese Academic of Sciences  
High Resolution MS DATA REPORT



Instrument: Thermo Fisher Scientific LTQ FTICR

Card Serial Number : E171801

Sample Serial Number: EA-1

Operator : ZHUFJ Date: 2017/05/11

Operation Mode: DART Negative

Elemental composition search on mass 501.32

m/z= 496.32-506.32

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
501.3221	501.3222	-0.20	8.5	C <sub>30</sub> H <sub>45</sub> O <sub>6</sub>
	501.3181	7.82	4.5	C <sub>25</sub> H <sub>45</sub> O <sub>8</sub> N <sub>2</sub>

Figure S24. HRESIMS spectrum of acangraciligenin S

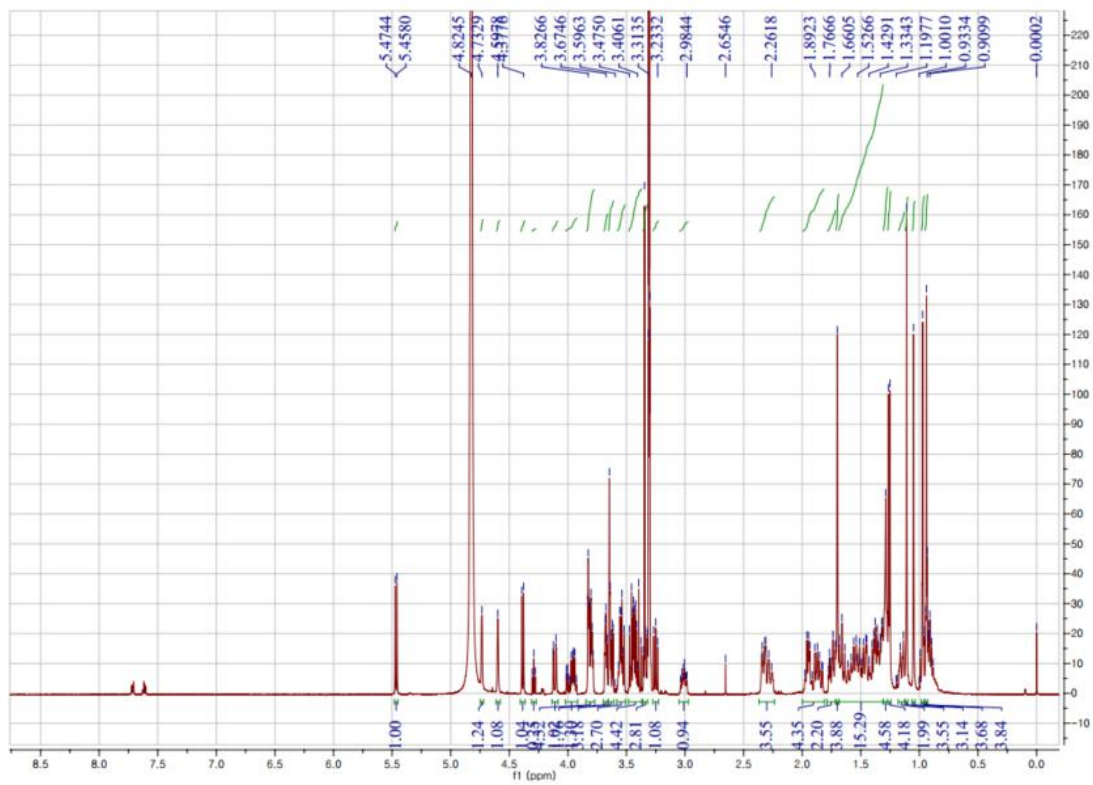


Figure S25.  $^1\text{H}$  NMR spectrum of acangraciliside S in methanol- $d_4$

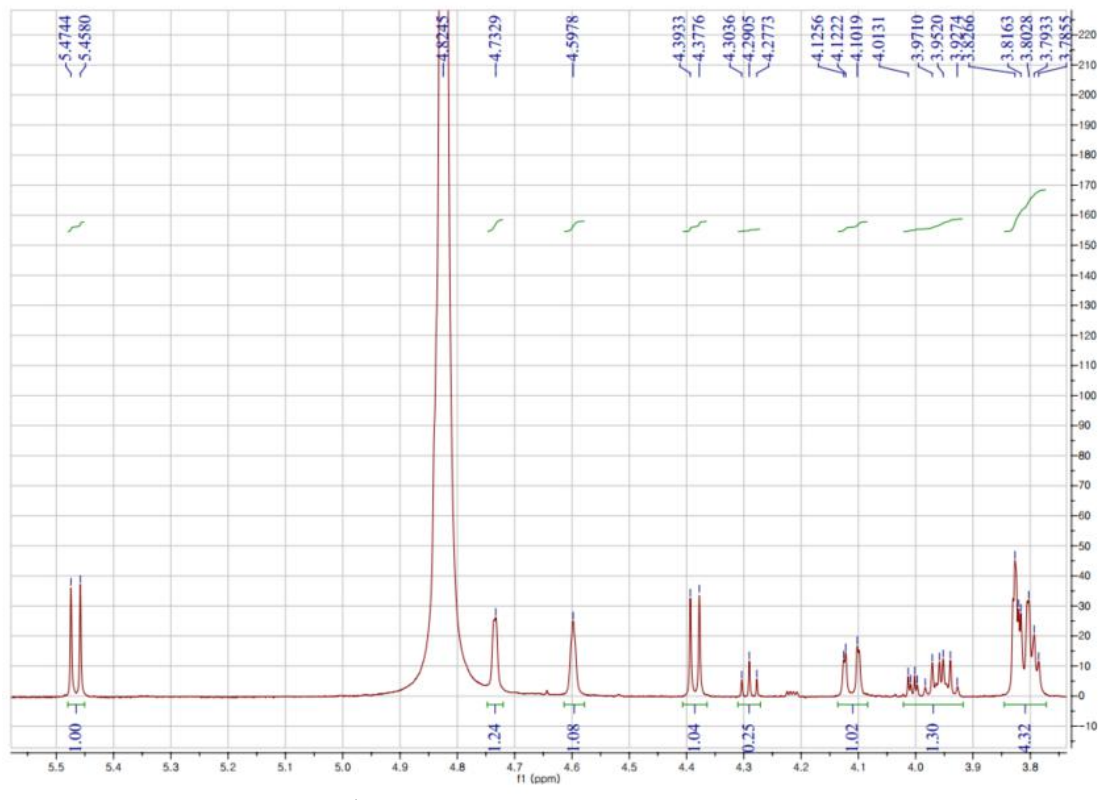


Figure S26. Expand  $^1\text{H}$  NMR spectrum of acangraciliside S in methanol- $d_4$

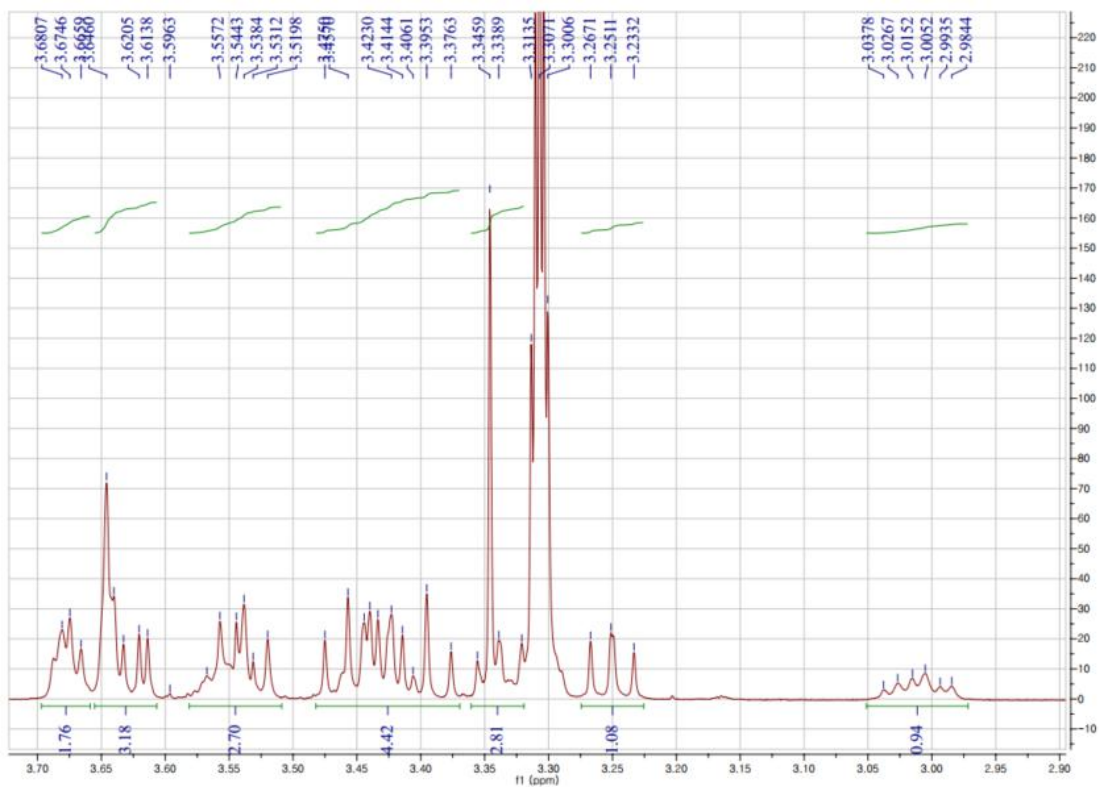


Figure S27. Expand  $^1\text{H}$  NMR spectrum of acangraciliside S in methanol- $d_4$

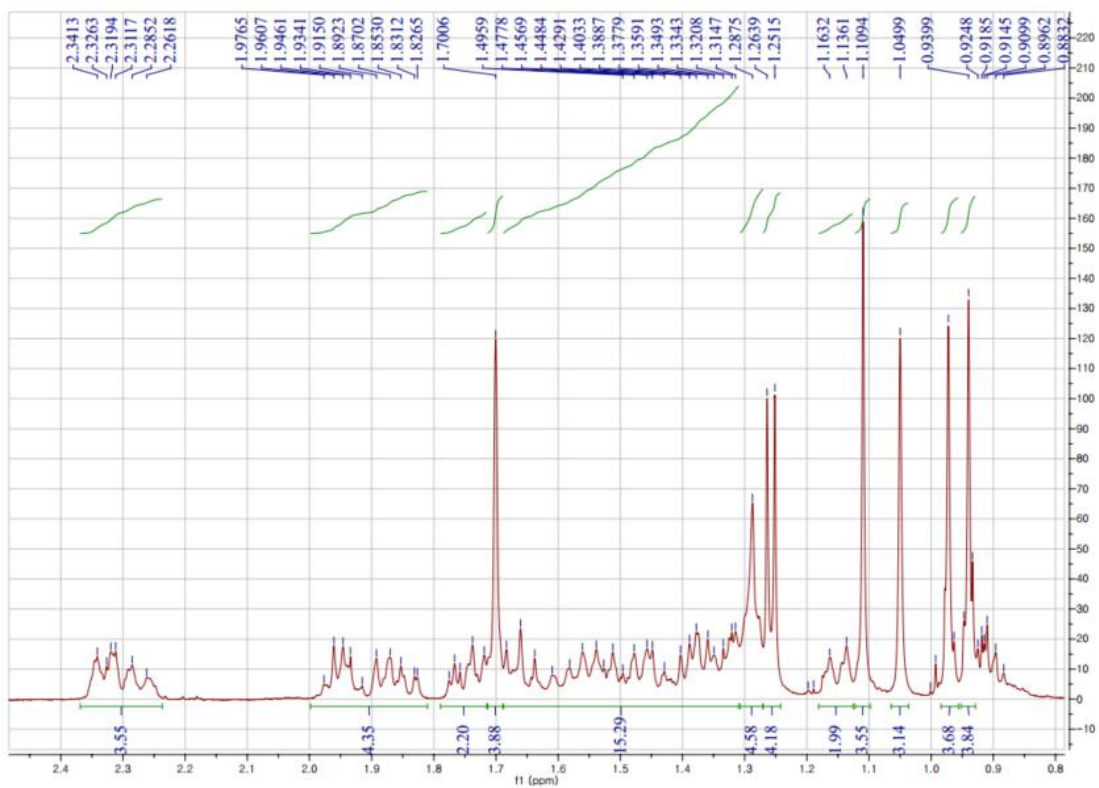


Figure S28. Expand  $^1\text{H}$  NMR spectrum of acangraciliside S in methanol- $d_4$

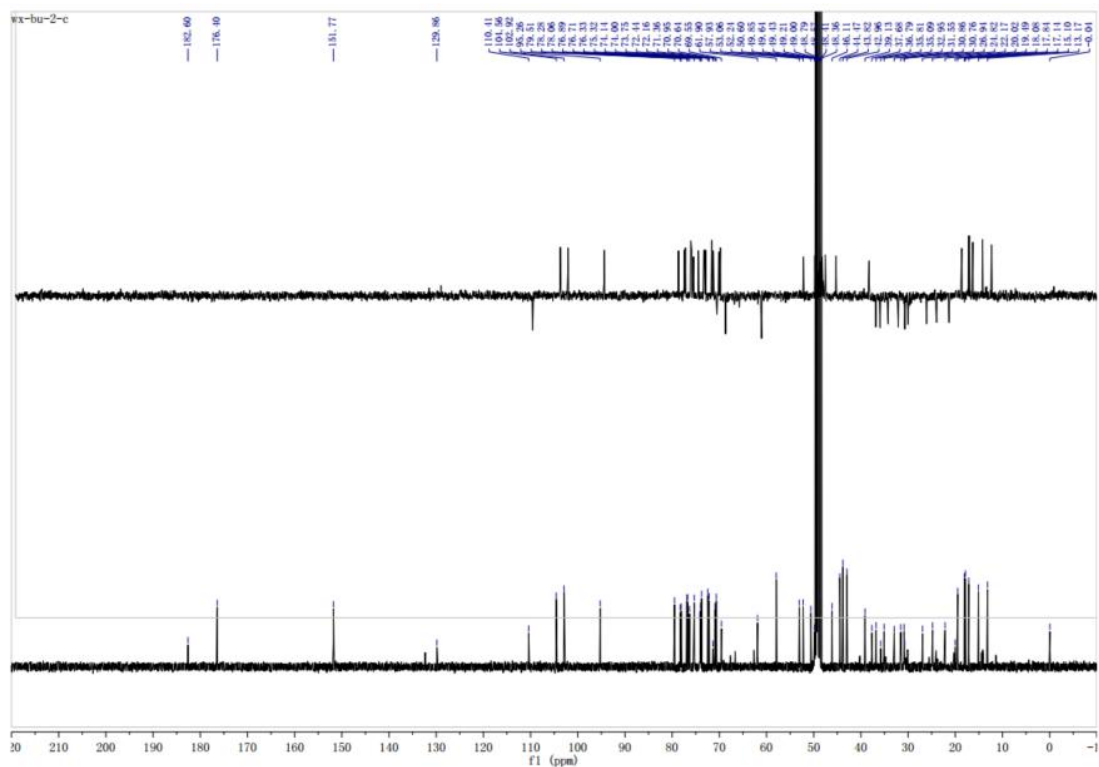


Figure S29.  $^{13}\text{C}$  NMR spectrum of acangraciliside S in methanol- $d_4$

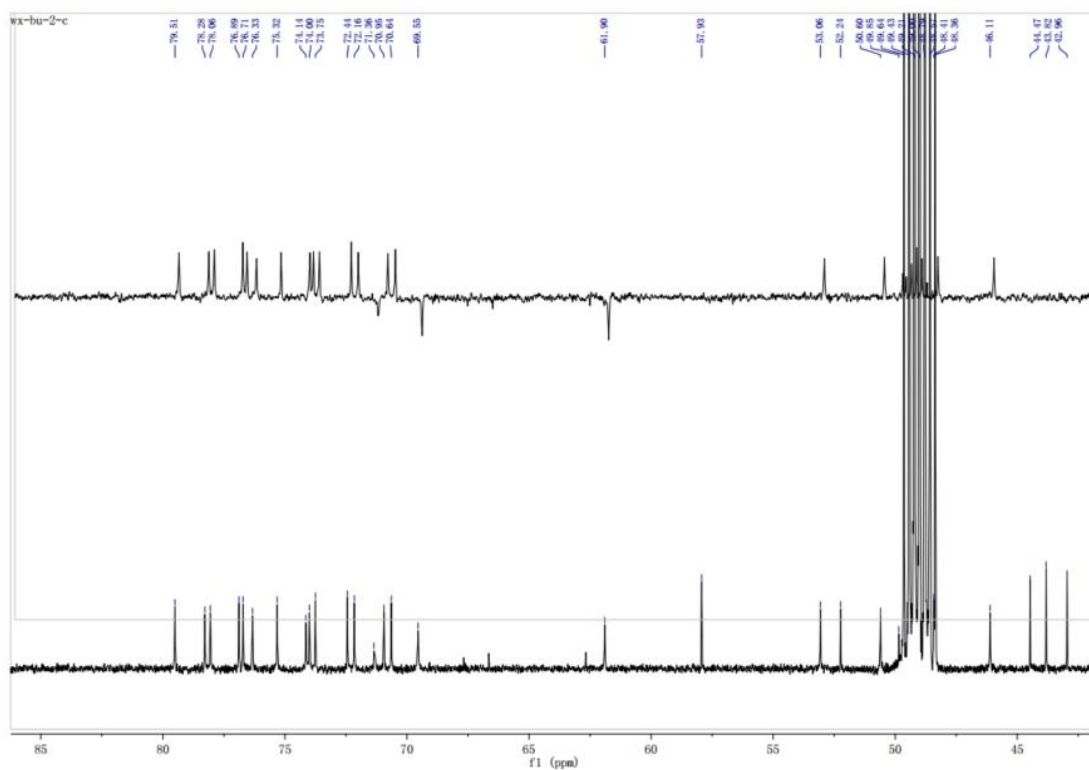


Figure S30. Expand  $^{13}\text{C}$  NMR spectrum of acangraciliside S in methanol- $d_4$

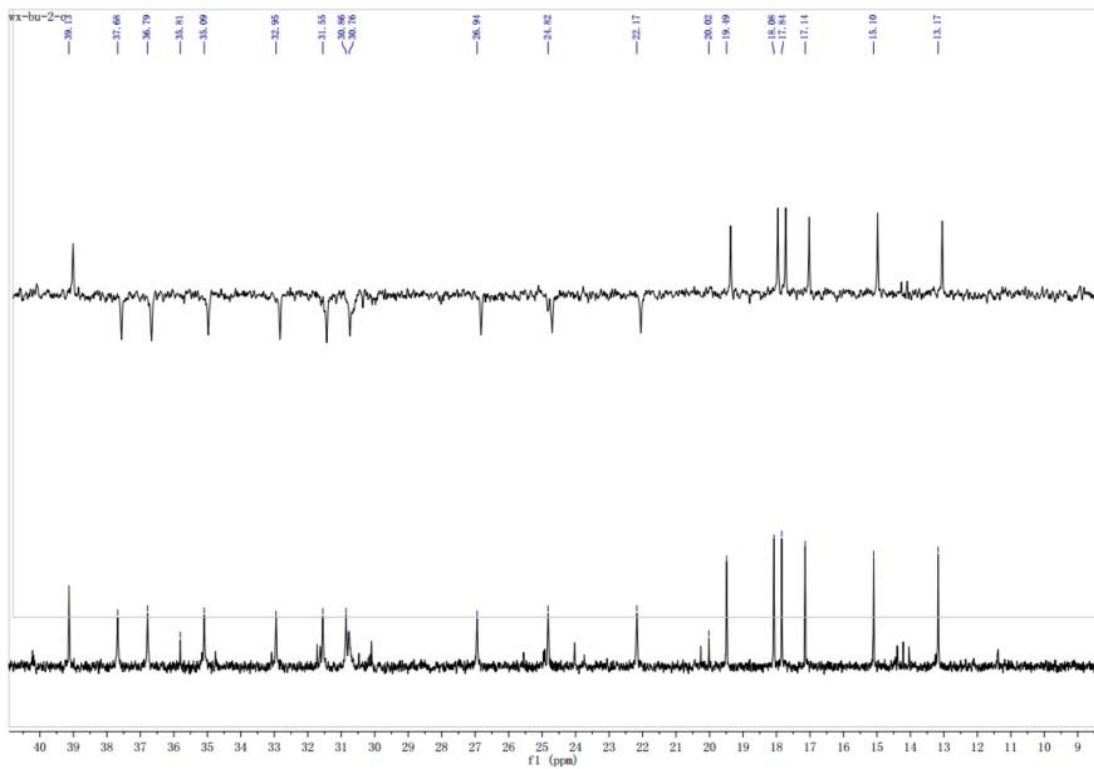


Figure S31. Expand  $^{13}\text{C}$  NMR spectrum of acangraciliside S in methanol- $d_4$

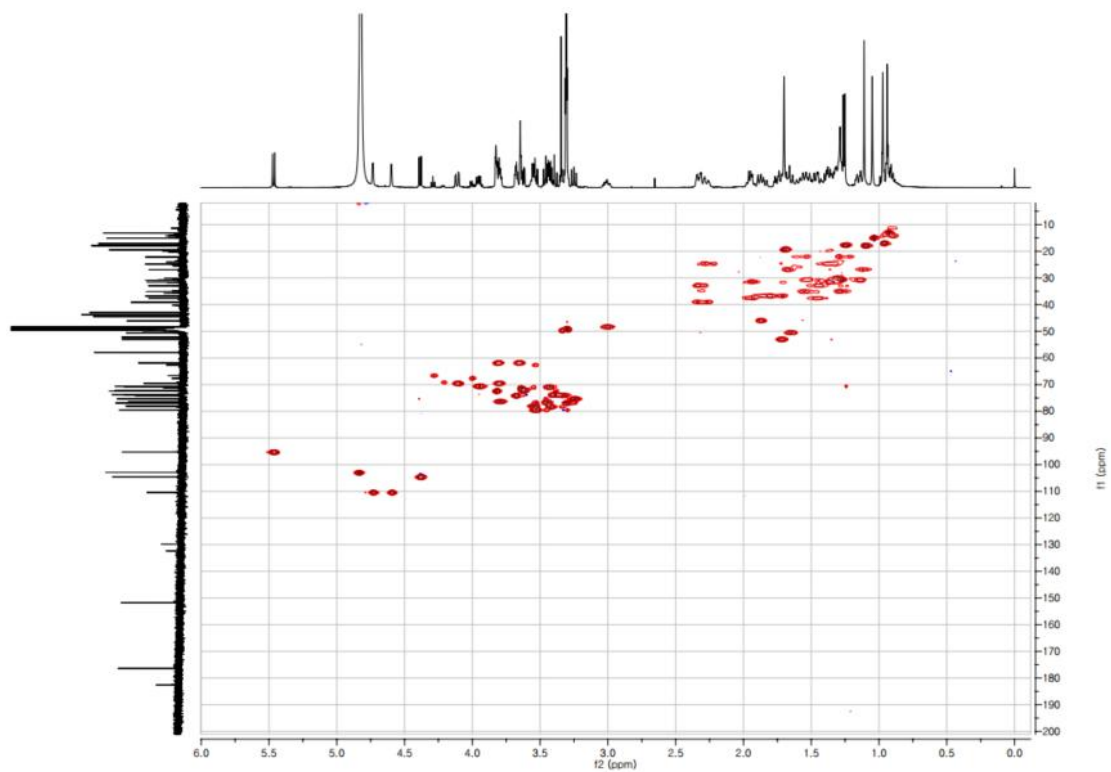


Figure S32. HSQC spectrum of acangraciliside S in methanol- $d_4$

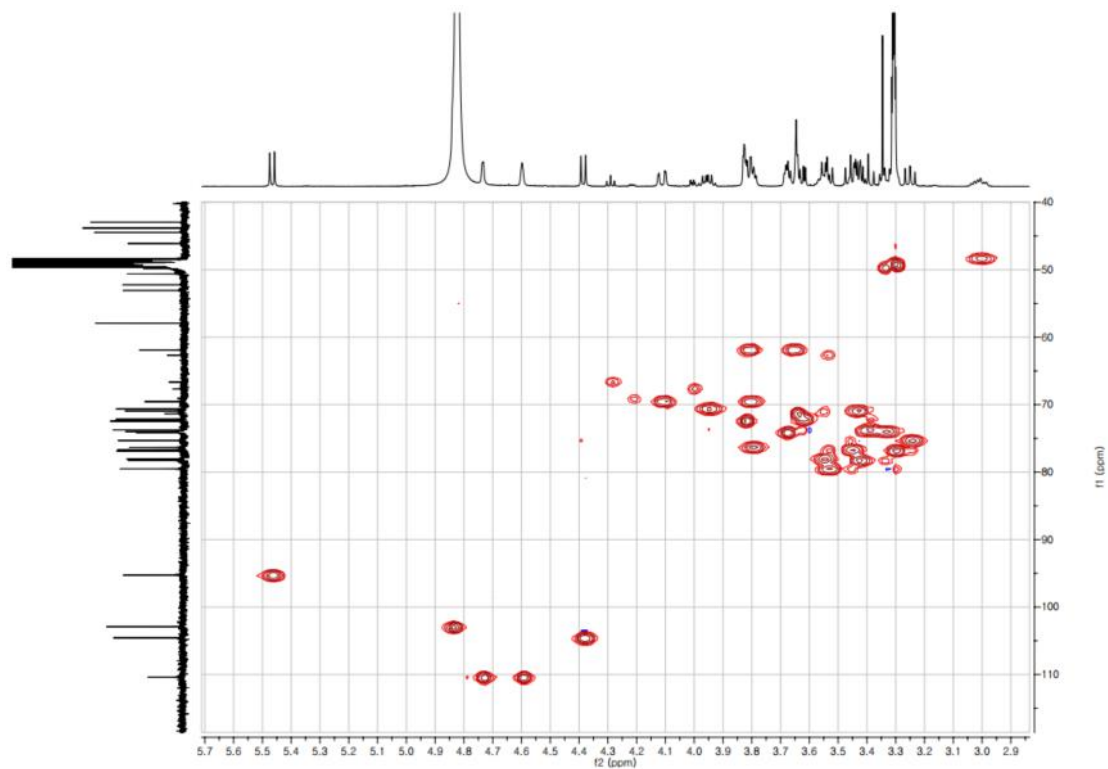


Figure S33. Expand HSQC spectrum of acangraciliside S in methanol- $d_4$

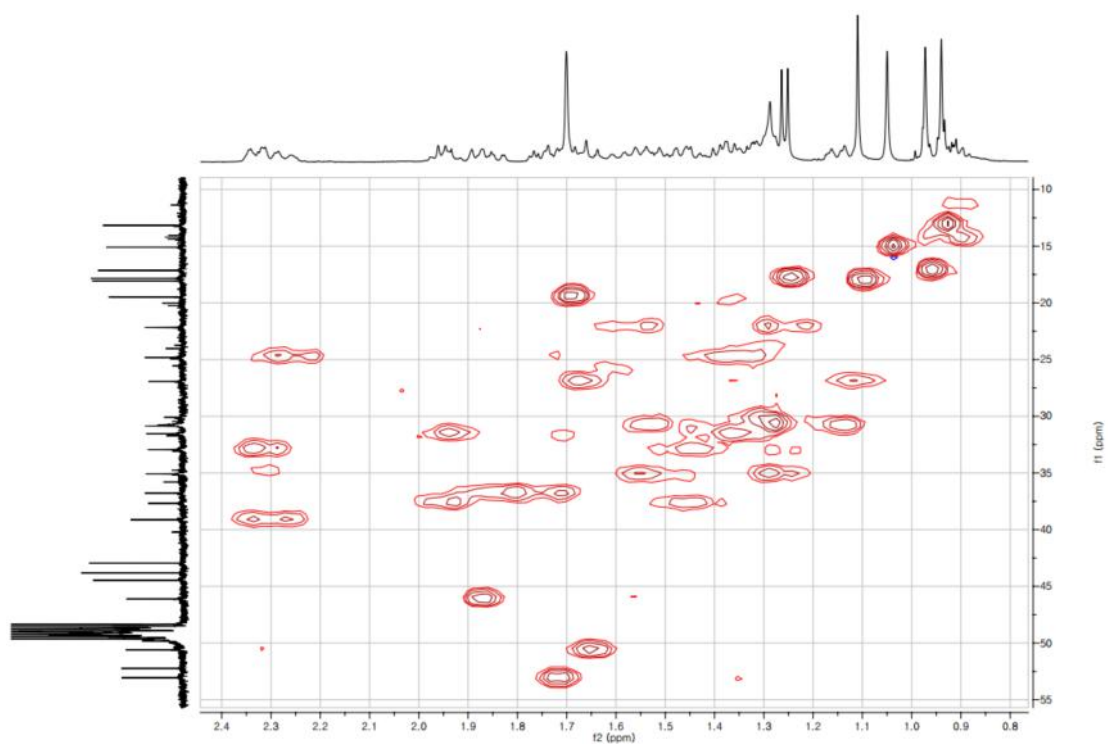


Figure S34. Expand HSQC spectrum of acangraciliside S in methanol- $d_4$



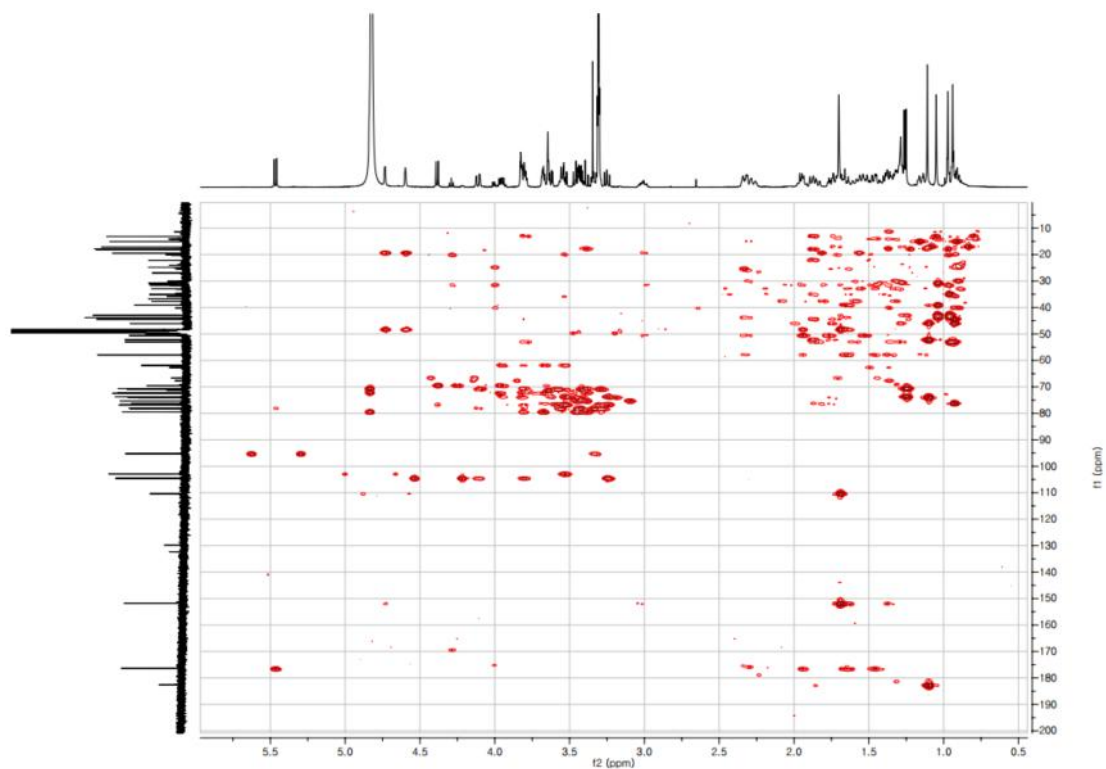


Figure S35. HMBC spectrum of acangraciliside S in methanol- $d_4$

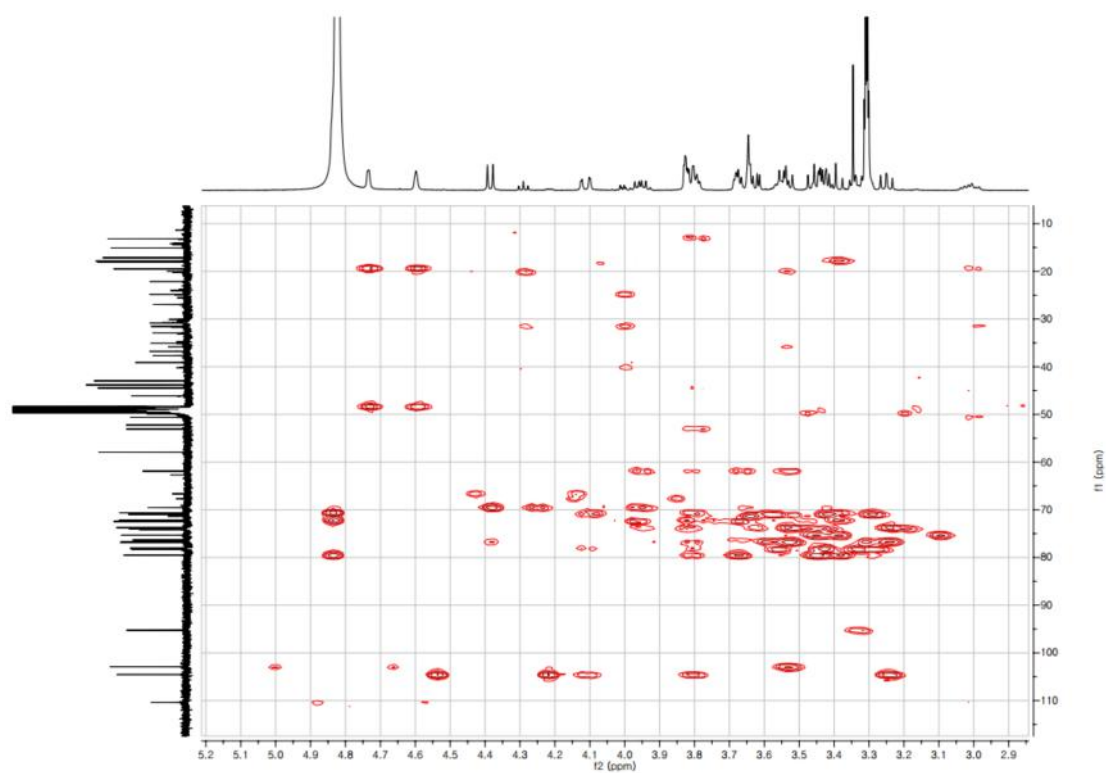


Figure S36. Expand HMBC spectrum of acangraciliside S in methanol- $d_4$

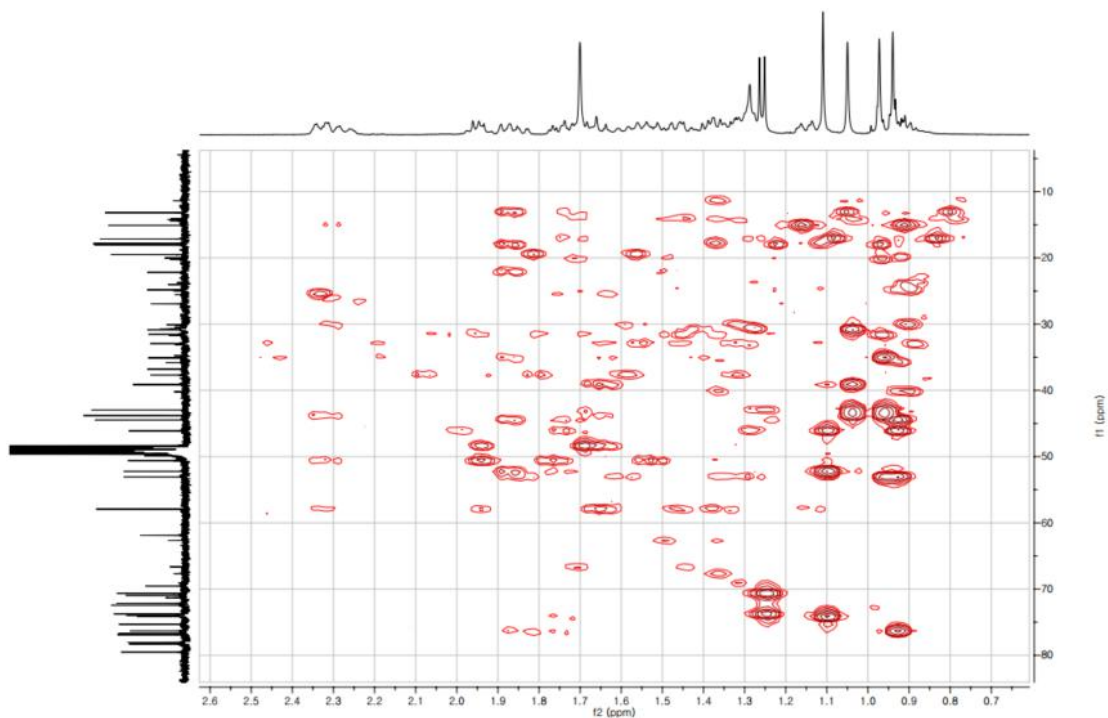


Figure S37. Expand HMBC spectrum of acangraciliside S in methanol- $d_4$

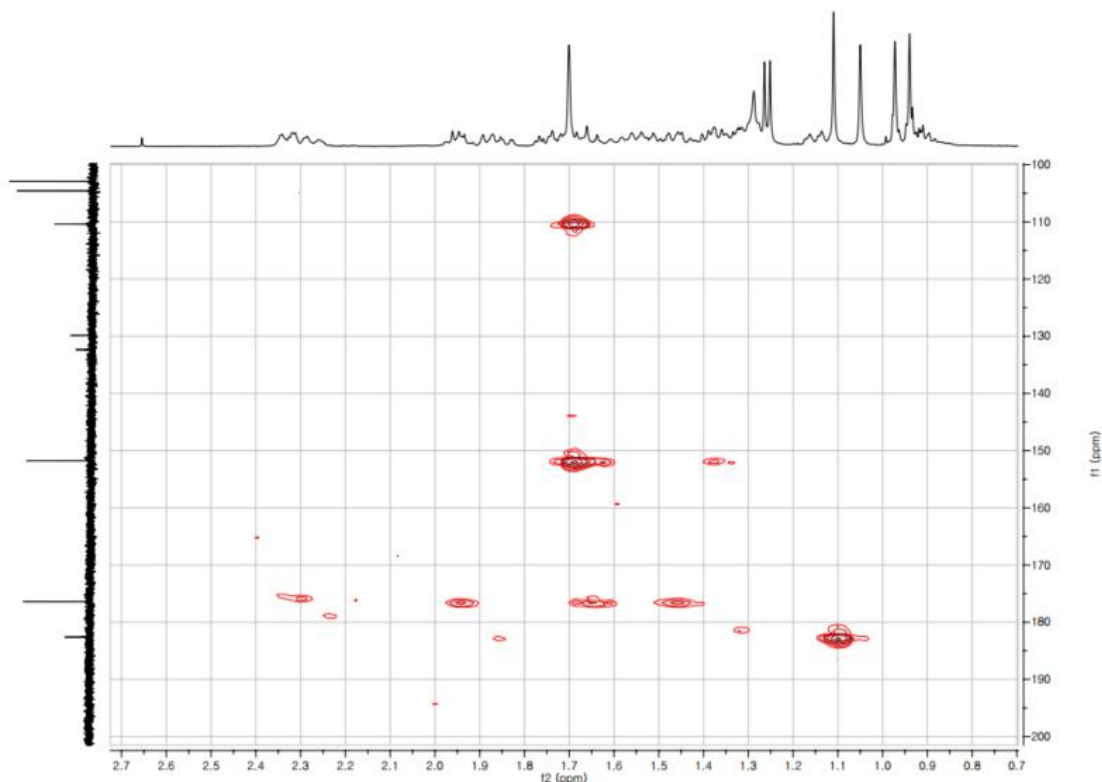


Figure S38. Expand HMBC spectrum of acangraciliside S in methanol- $d_4$

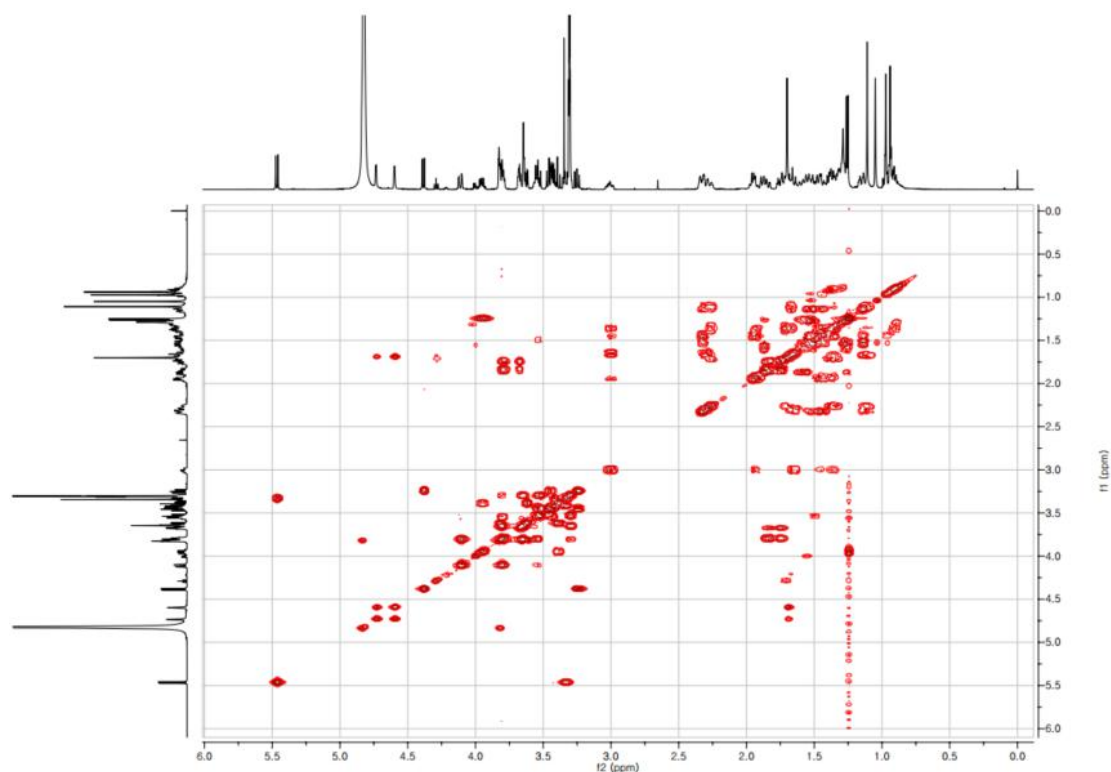


Figure S39.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of acangraciliside S in methanol- $d_4$

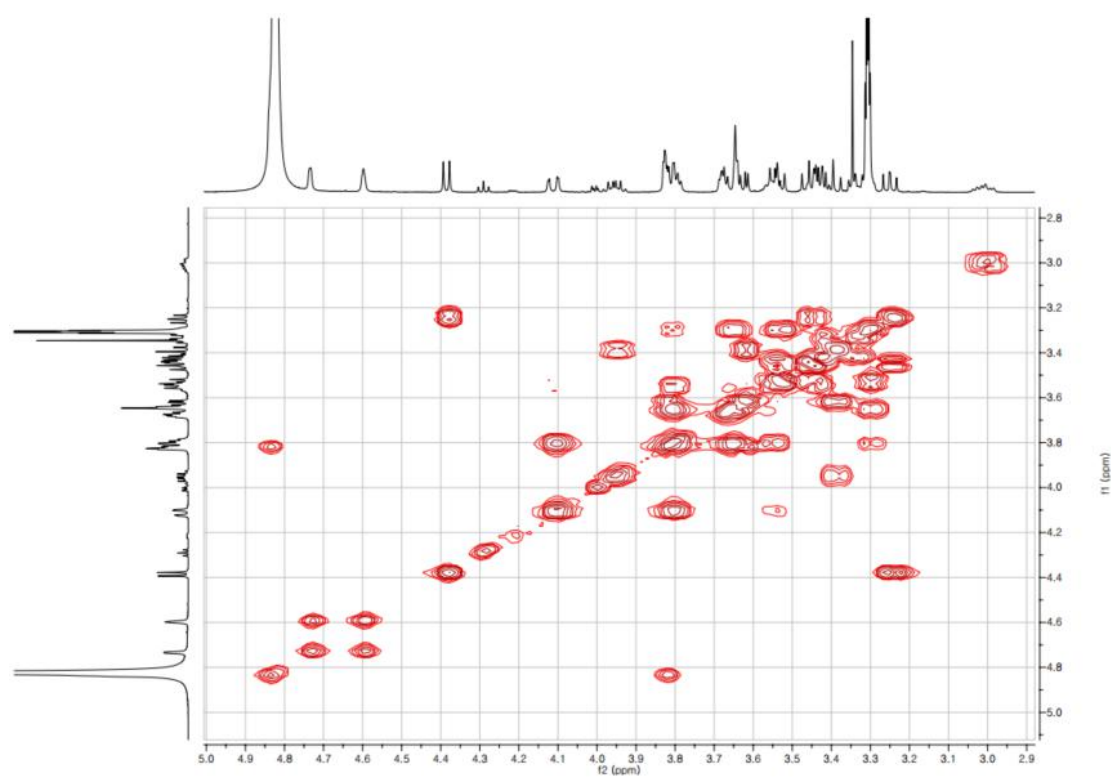


Figure S40. Expand  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of acangraciliside S in methanol- $d_4$

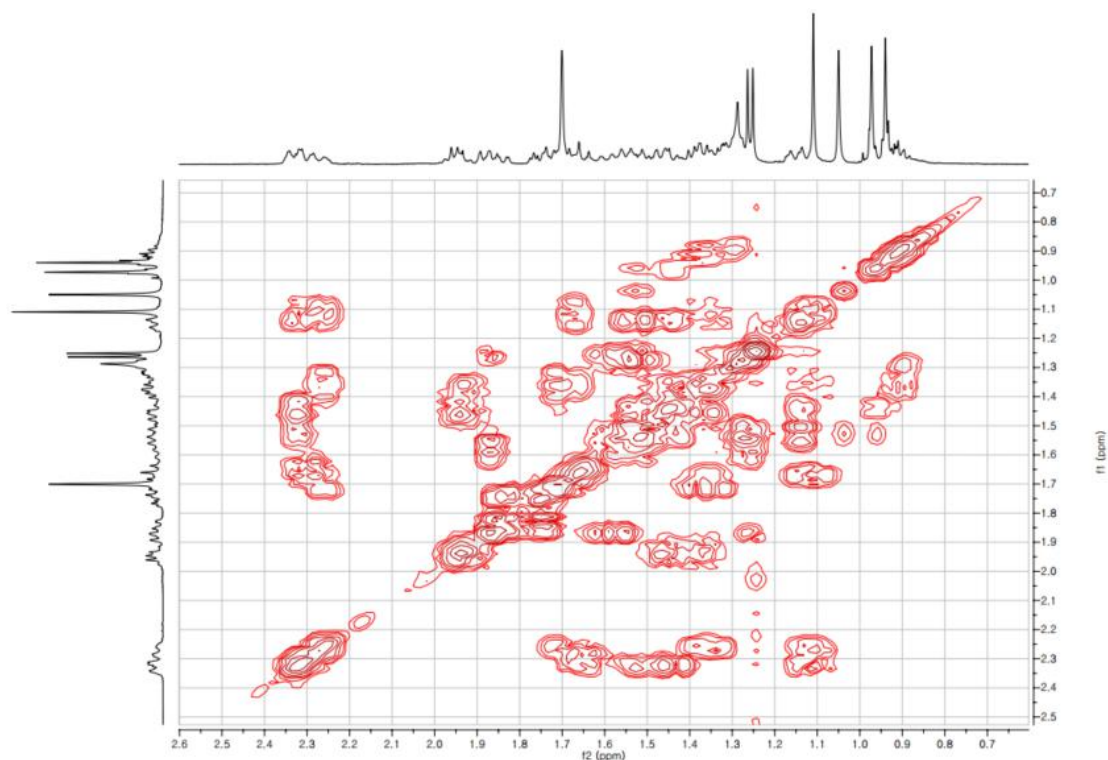


Figure S41. Expand  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of acangraciliside S in methanol- $d_4$

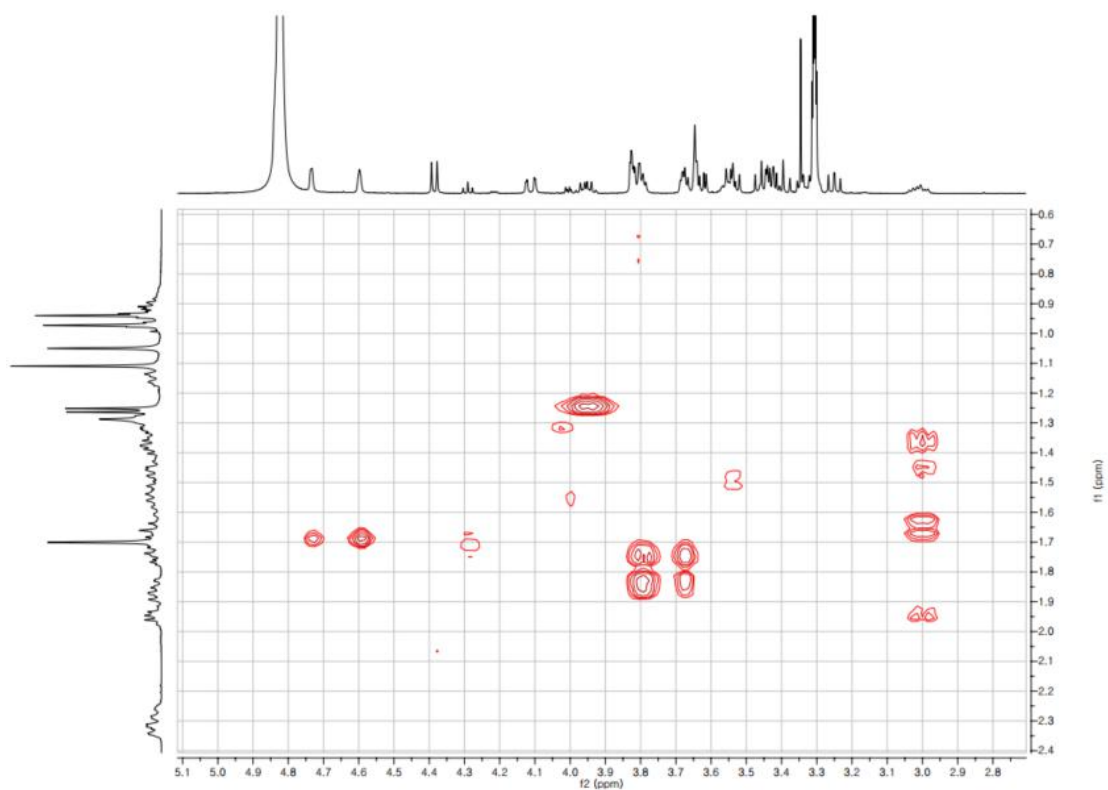


Figure S42. Expand  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of acangraciliside S in methanol- $d_4$

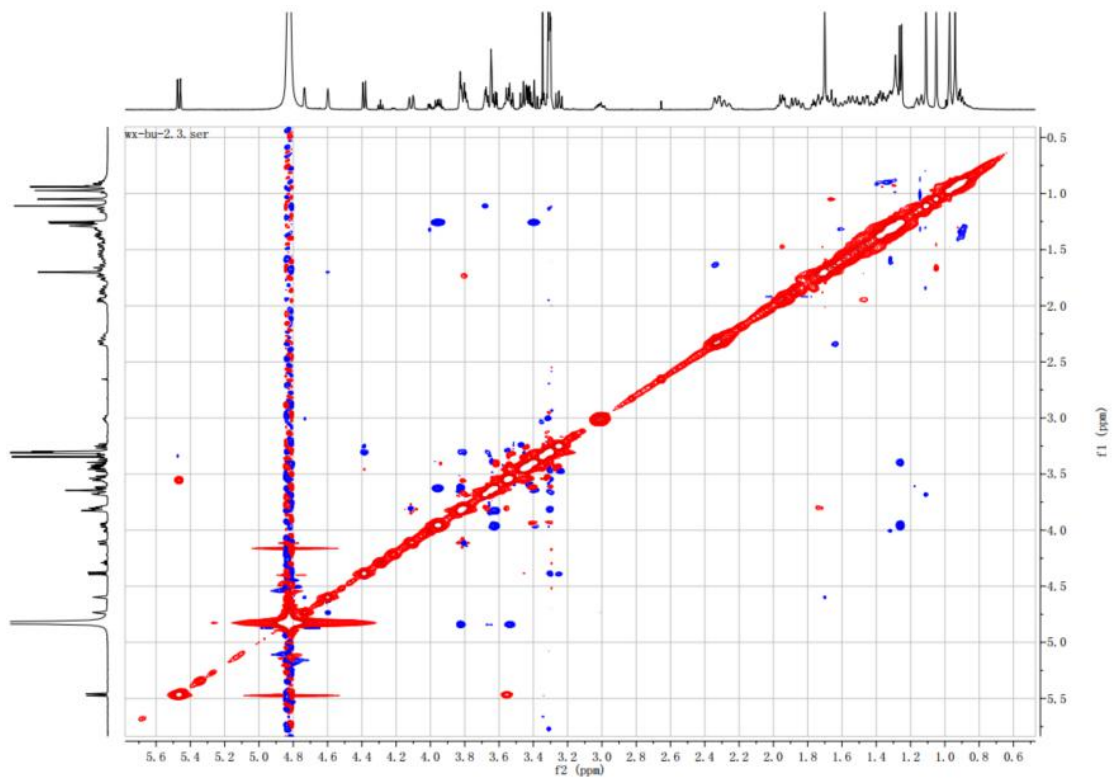


Figure S43. NOESY spectrum of acangraciliside S in methanol- $d_4$

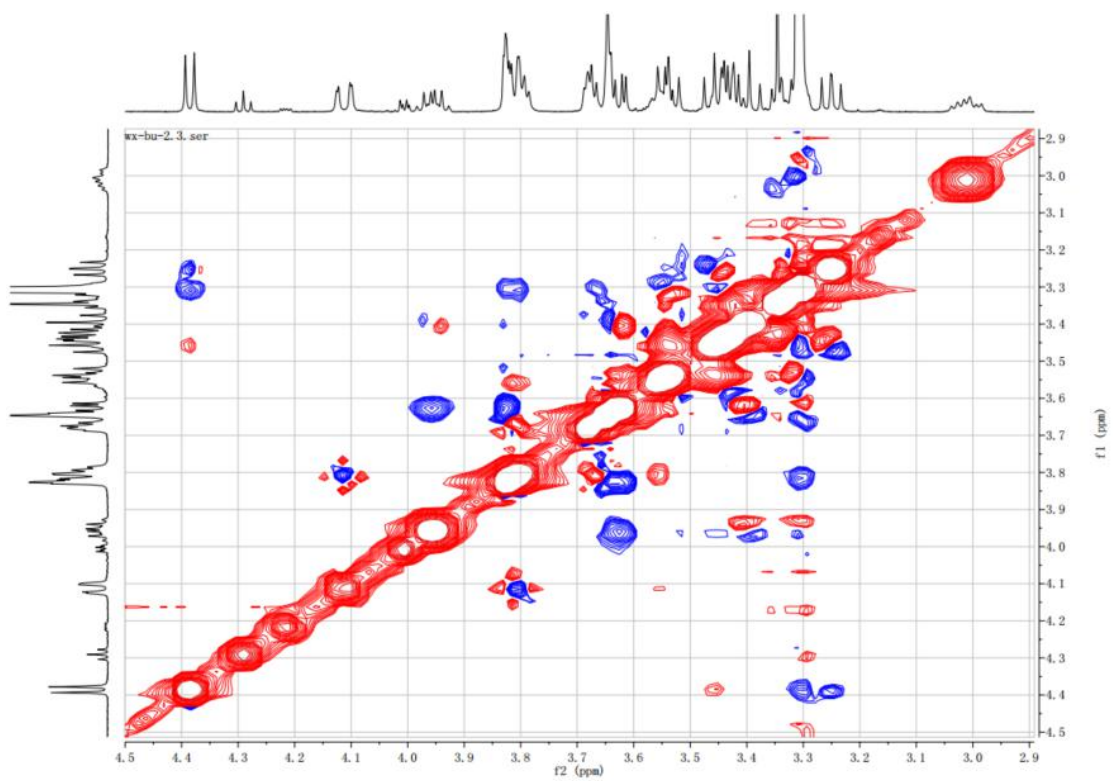
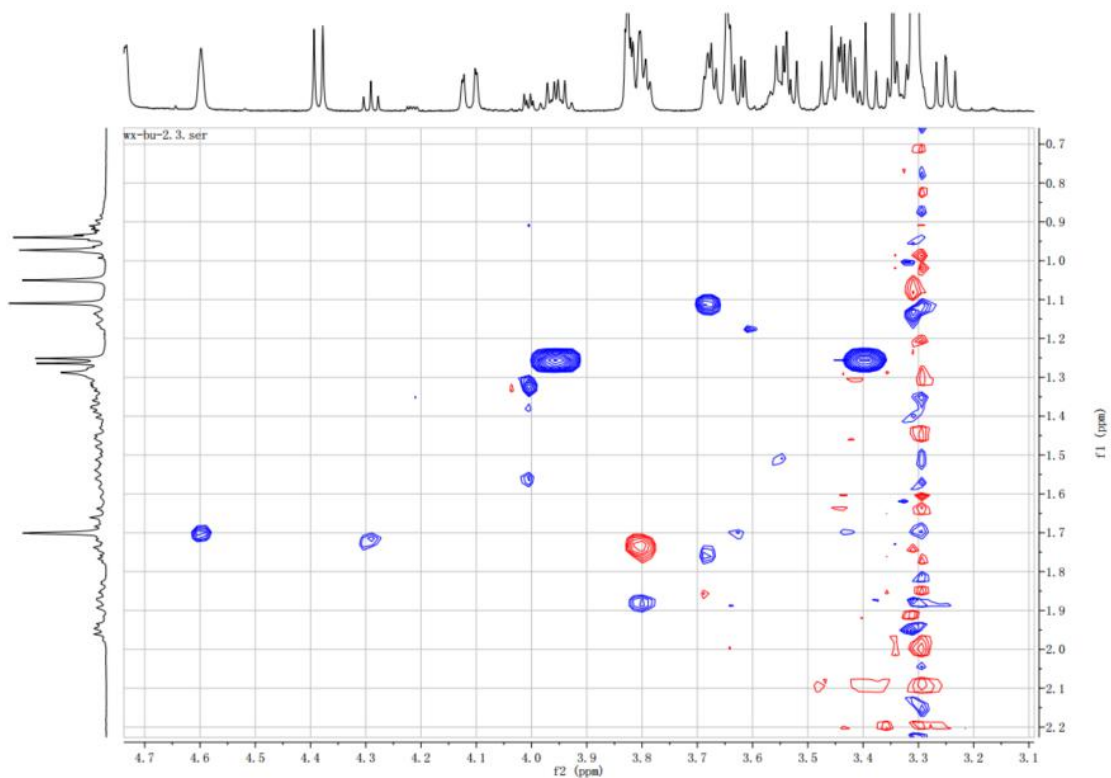


Figure S44. Expand NOESY spectrum of acangraciliside S in methanol- $d_4$



**Figure S45.** Expand NOESY spectrum of acangraciliside S in methanol- $d_4$



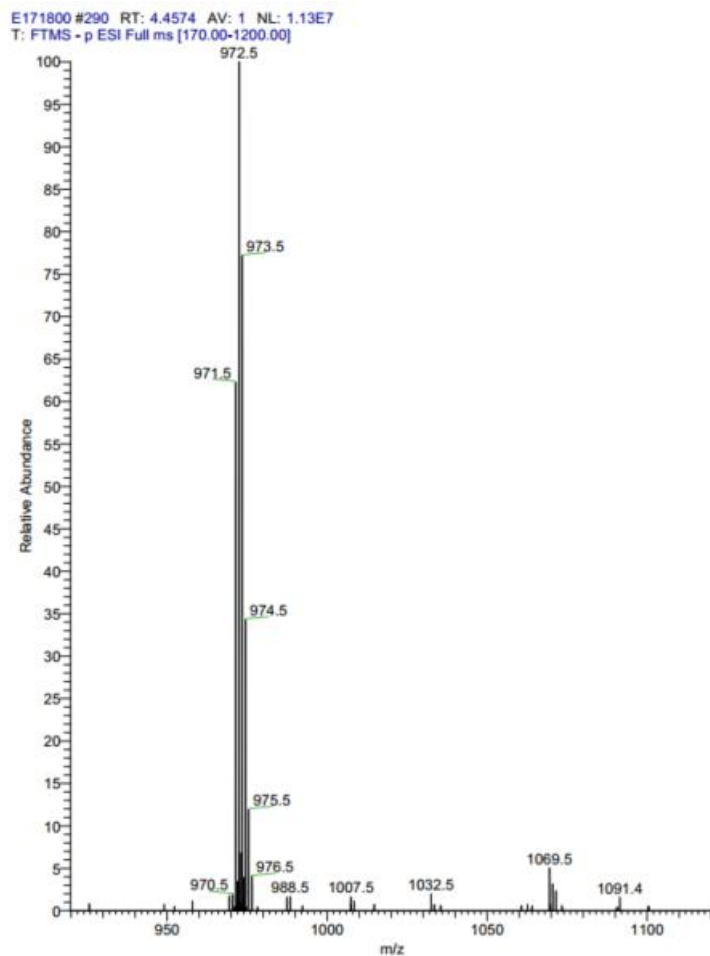


Figure S46. ESIMS spectrum of acangracilside S

National Center for Organic Mass Spectrometry in Shanghai  
Shanghai Institute of Organic Chemistry  
Chinese Academic of Sciences  
High Resolution MS DATA REPORT



Instrument: Thermo Fisher Scientific LTQ FTICR

Card Serial Number : E171800

Sample Serial Number: 1

Operator : ZHUFJ Date: 2017/05/09

Operation Mode: ESI Negative

Elemental composition search on mass 971.49

m/z= 966.49-976.49

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
971.4865	971.4857	0.84	11.5	C <sub>48</sub> H <sub>75</sub> O <sub>20</sub>
	971.4884	-1.92	16.0	C <sub>51</sub> H <sub>73</sub> O <sub>17</sub> N
	971.4911	-4.68	20.5	C <sub>54</sub> H <sub>71</sub> O <sub>14</sub> N <sub>2</sub>

Figure S47. HRESIMS spectrum of acangracilside S



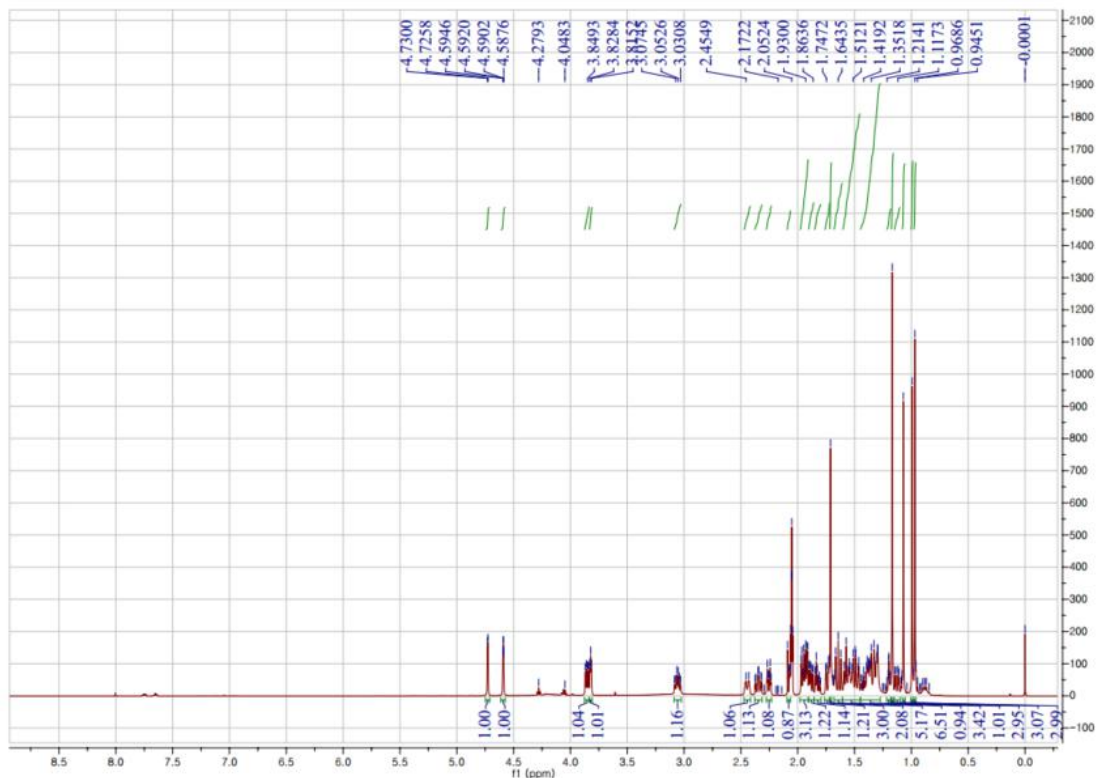


Figure S48.  $^1\text{H}$  NMR spectrum of **2a** in acetone- $d_6$

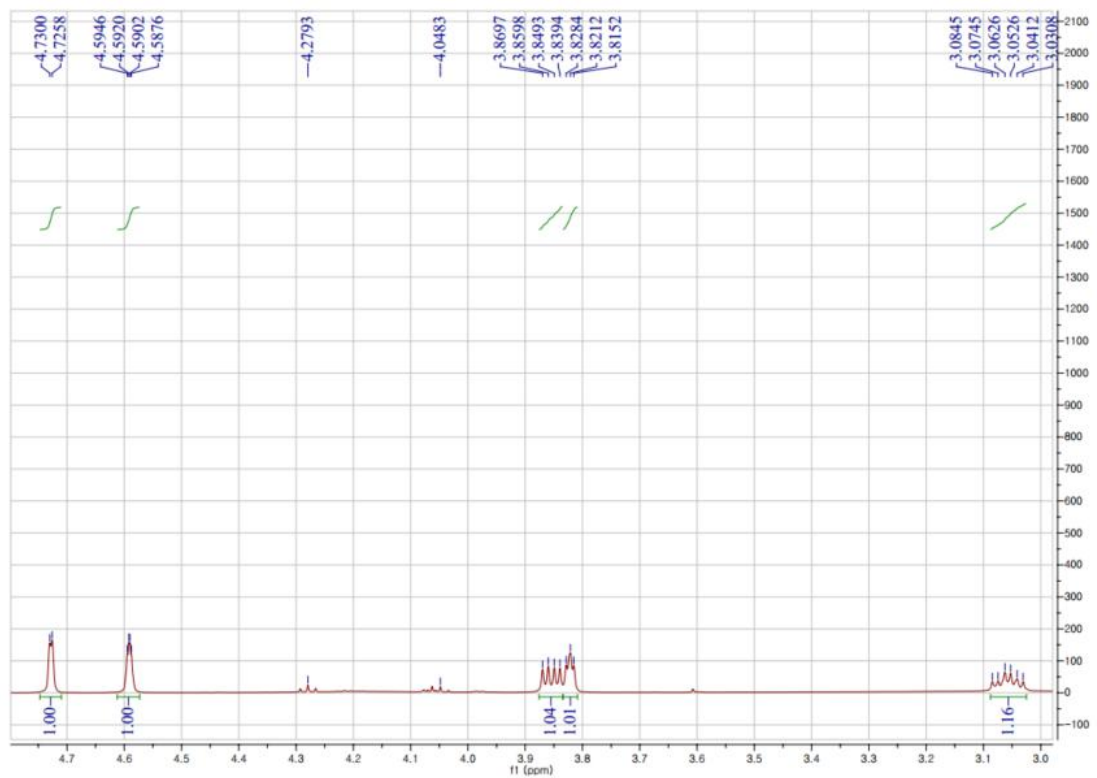


Figure S49. Expand  $^1\text{H}$  NMR spectrum of **2a** in acetone- $d_6$

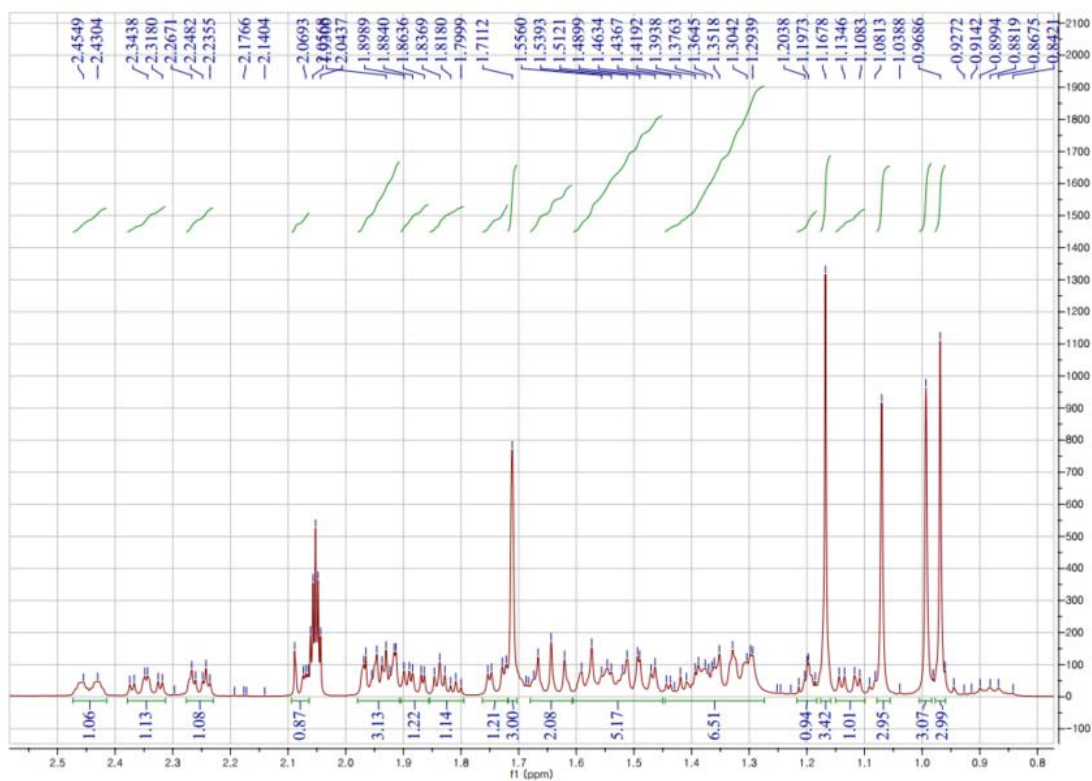


Figure S50. Expand  $^1\text{H}$  NMR spectrum of **2a** in acetone- $d_6$

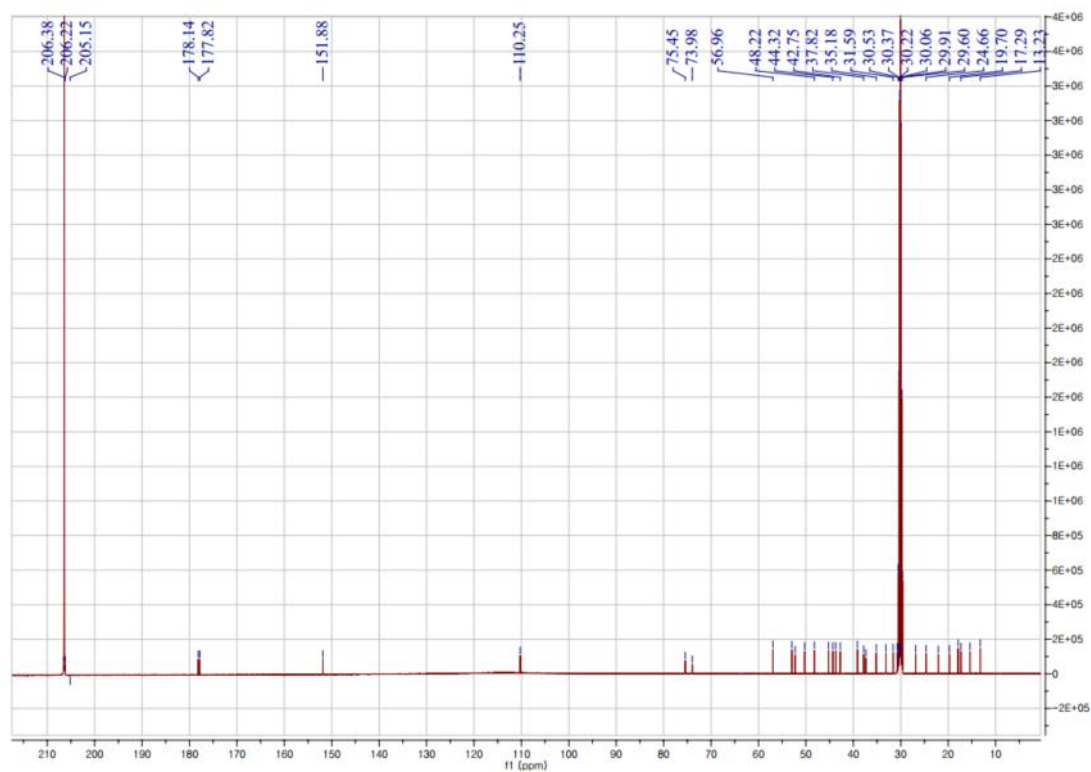


Figure S51.  $^{13}\text{C}$  NMR spectrum of **2a** in acetone- $d_6$

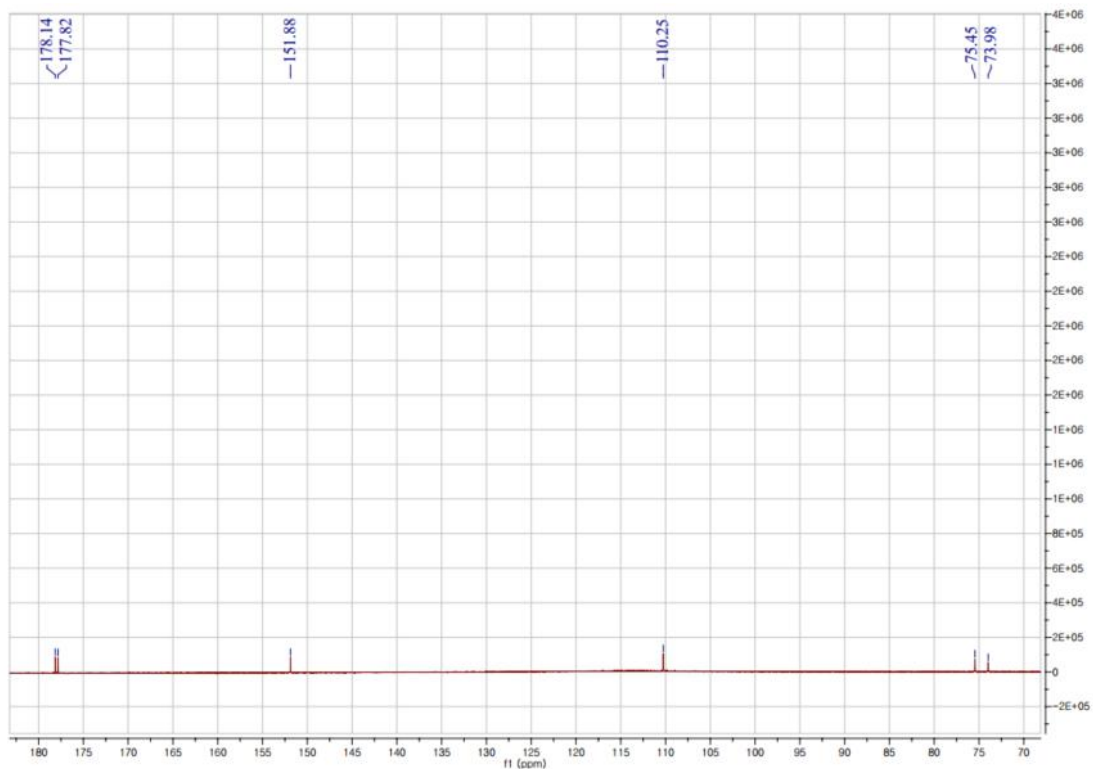


Figure S52. Expand  $^{13}\text{C}$  NMR spectrum of 2a in acetone- $d_6$

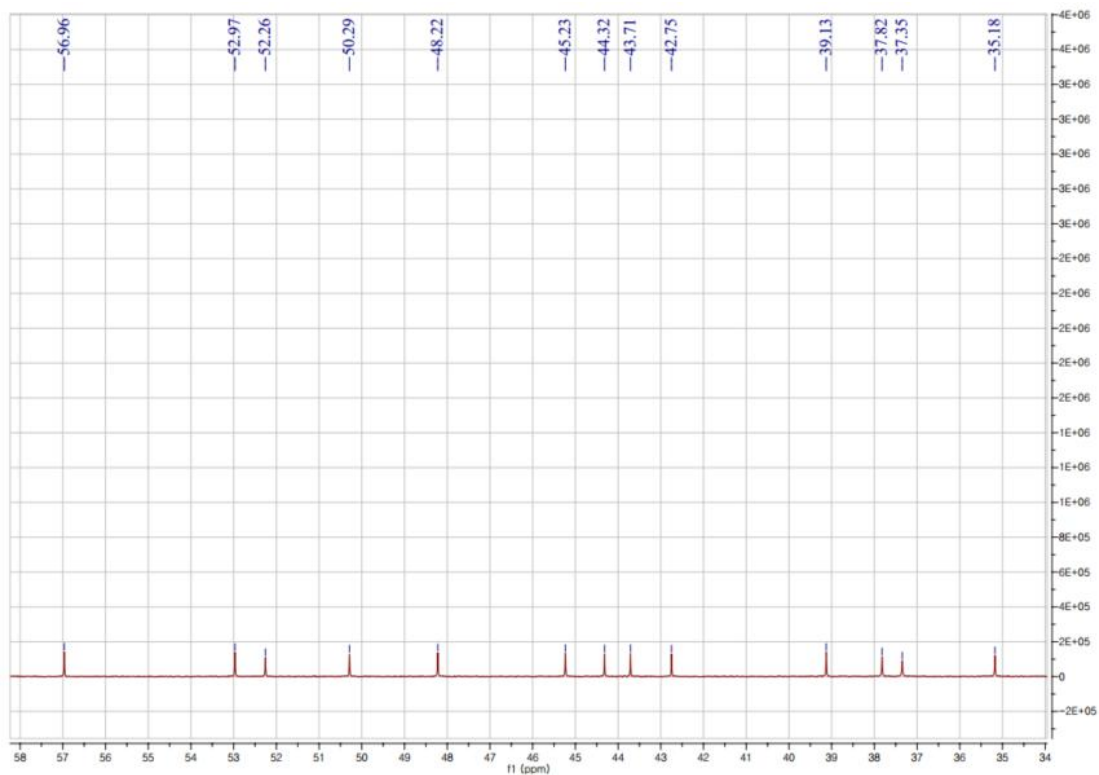


Figure S53. Expand  $^{13}\text{C}$  NMR spectrum of 2a in acetone- $d_6$

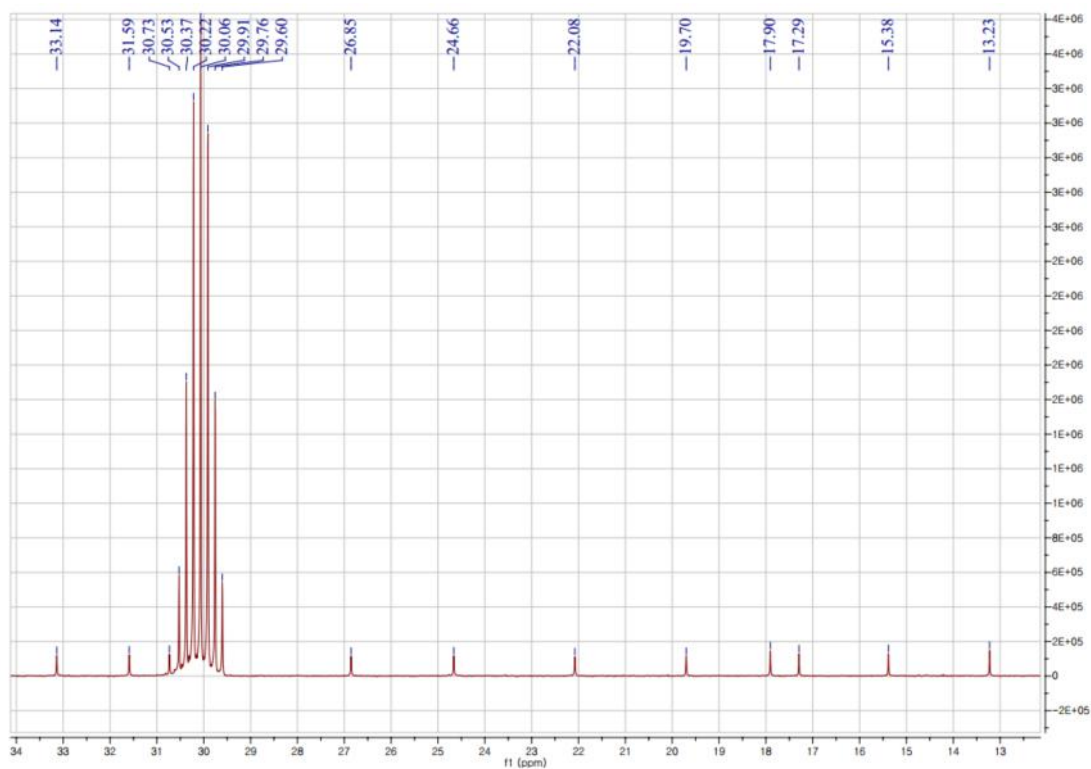


Figure S54. Expand  $^{13}\text{C}$  NMR spectrum of **2a** in acetone- $d_6$

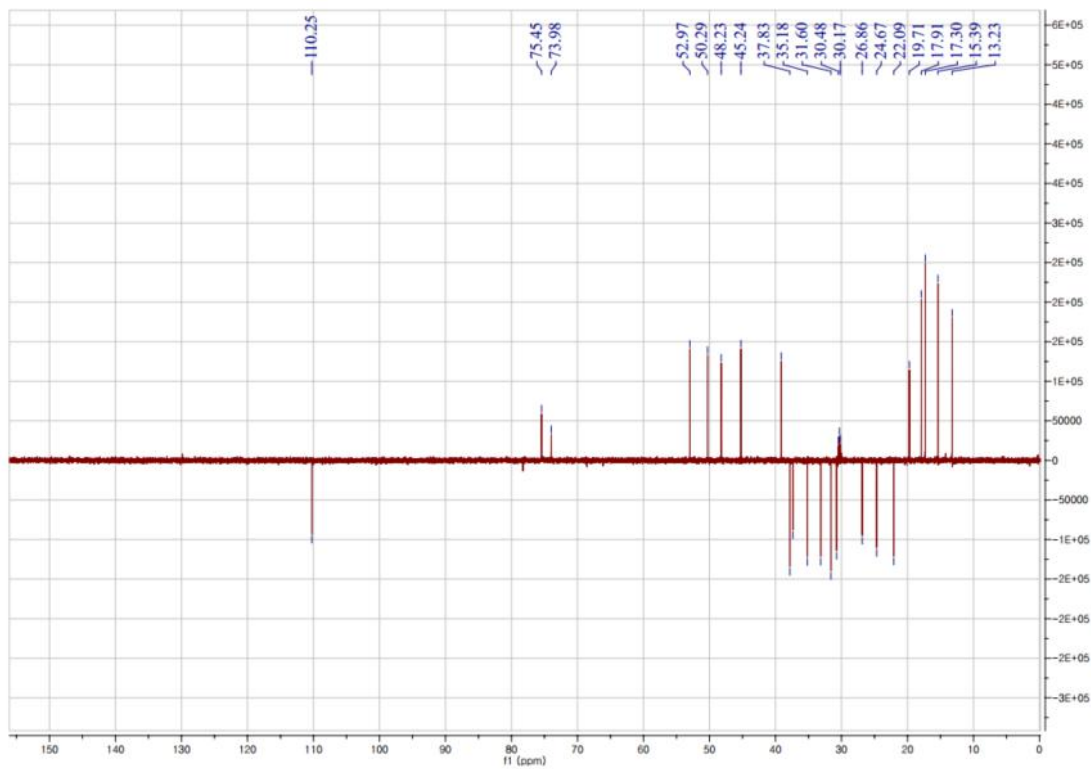


Figure S55. DEPT spectrum of **2a** in acetone- $d_6$

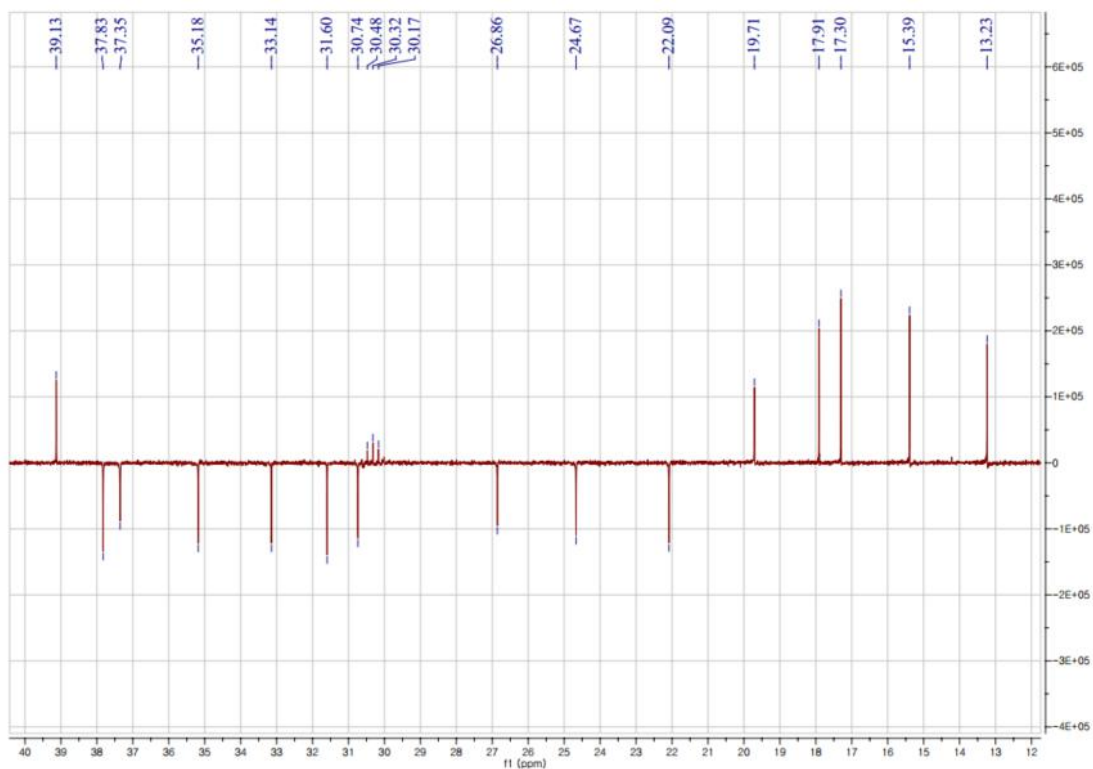


Figure S56. Expand DEPT spectrum of 2a in acetone-*d*<sub>6</sub>

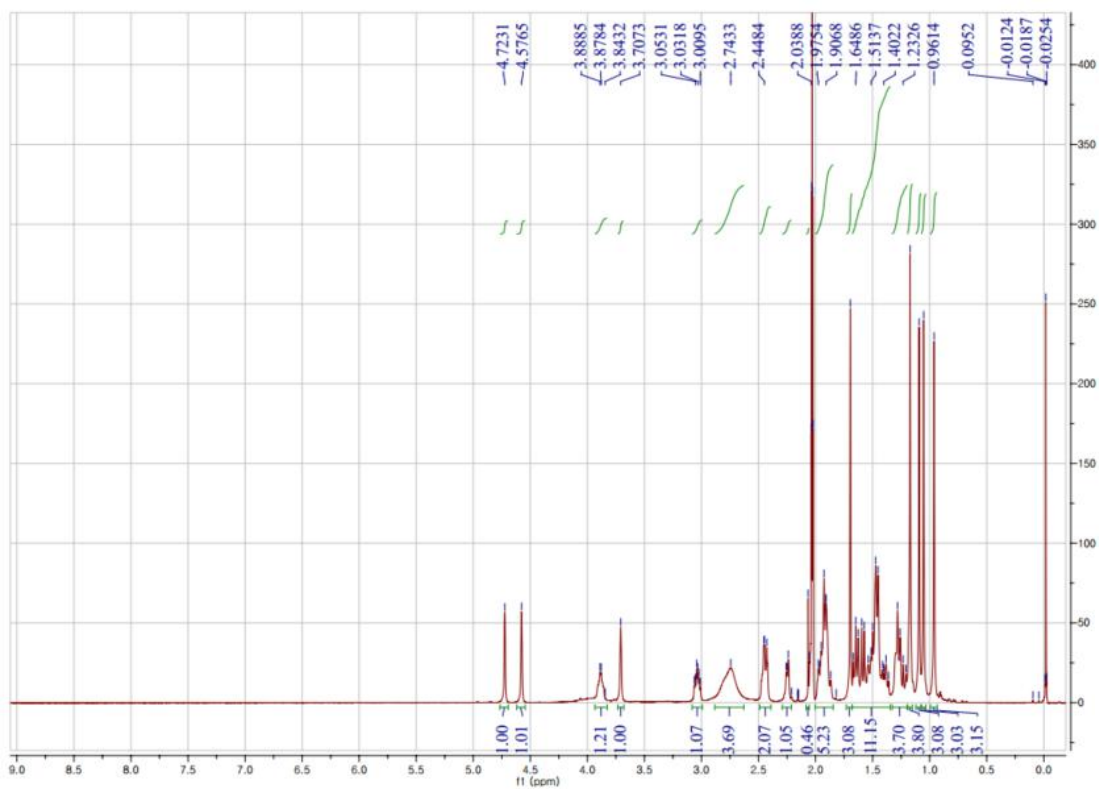


Figure S57. <sup>1</sup>H NMR spectrum of 3α,11α-dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone-*d*<sub>6</sub>

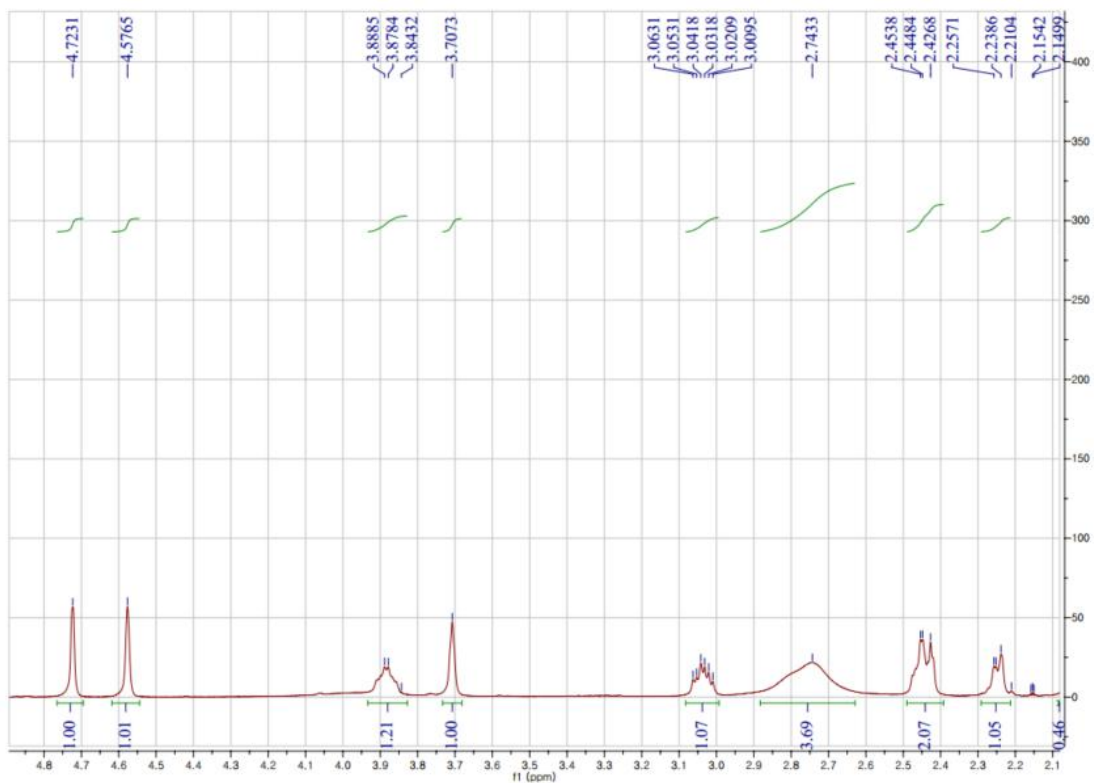


Figure S58. Expand  $^1\text{H}$  NMR spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

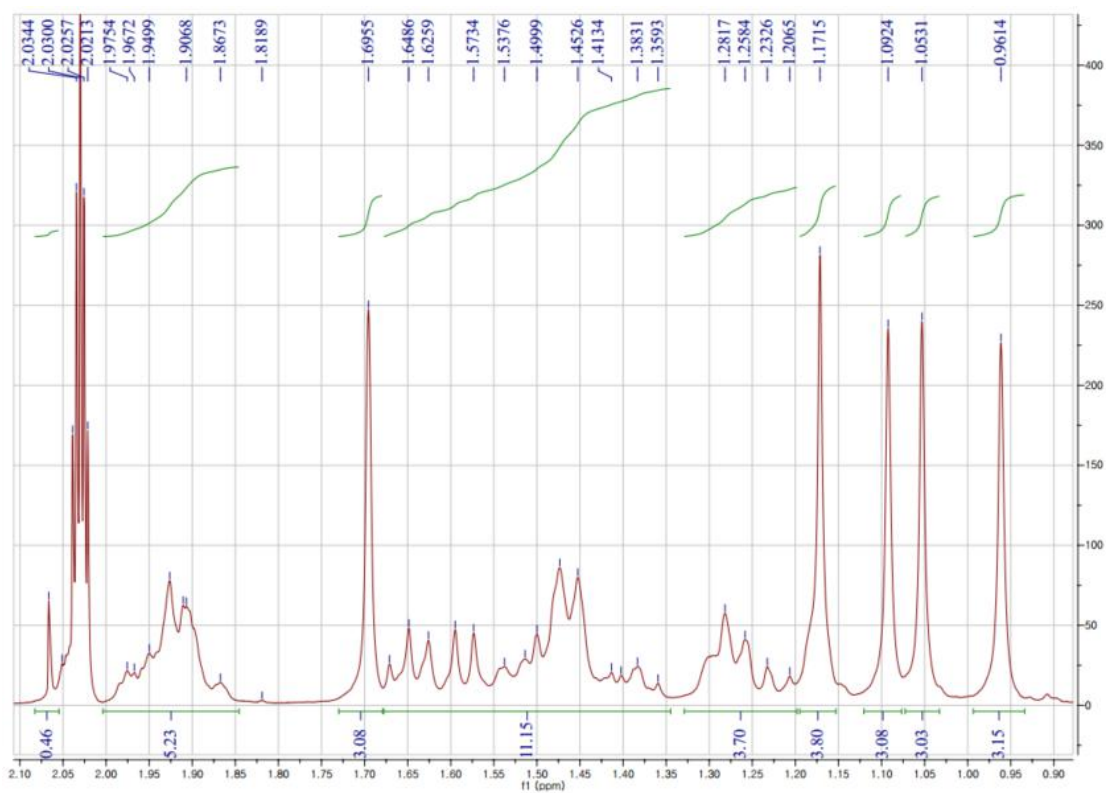


Figure S59. Expand  $^1\text{H}$  NMR spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$



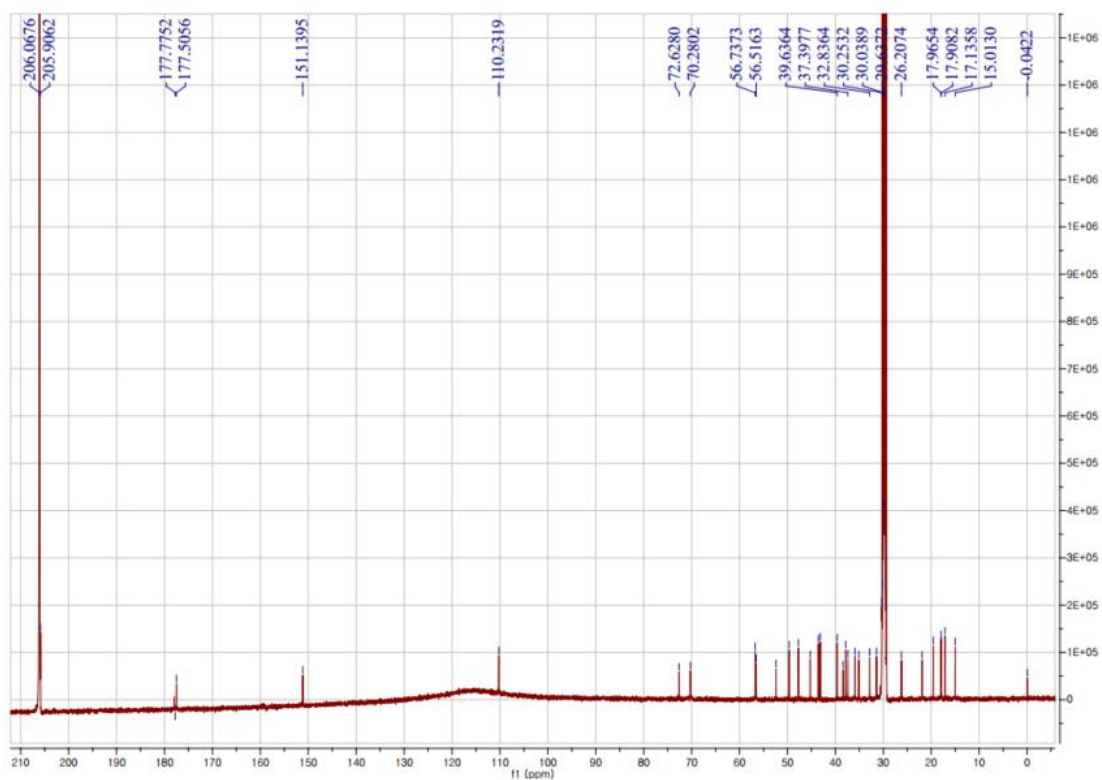


Figure S60.  $^{13}\text{C}$  NMR spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

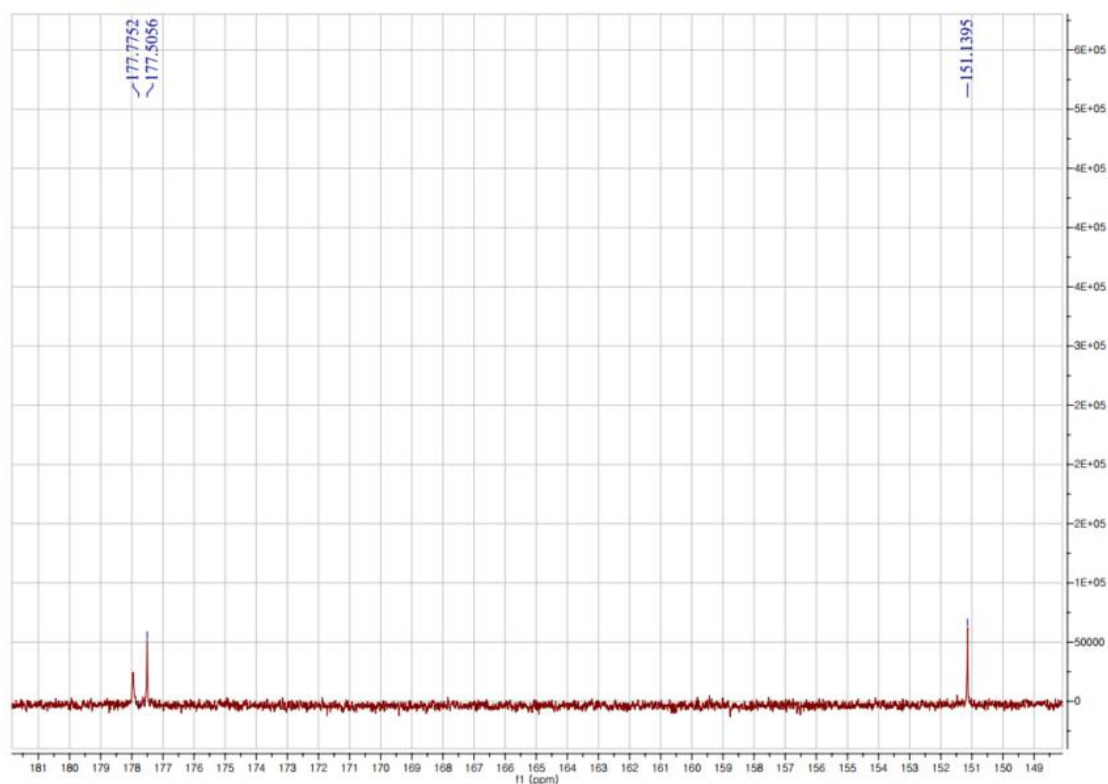


Figure S61. Expand  $^{13}\text{C}$  NMR spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$



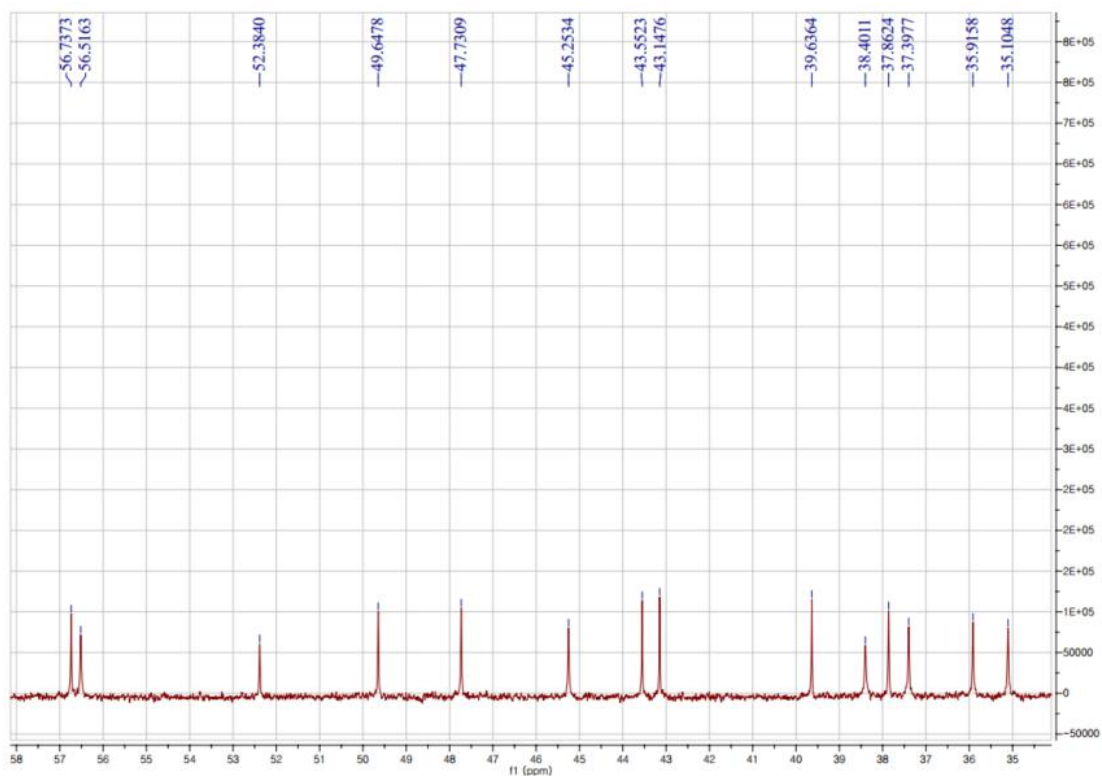


Figure S62. Expand  $^{13}\text{C}$  NMR spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

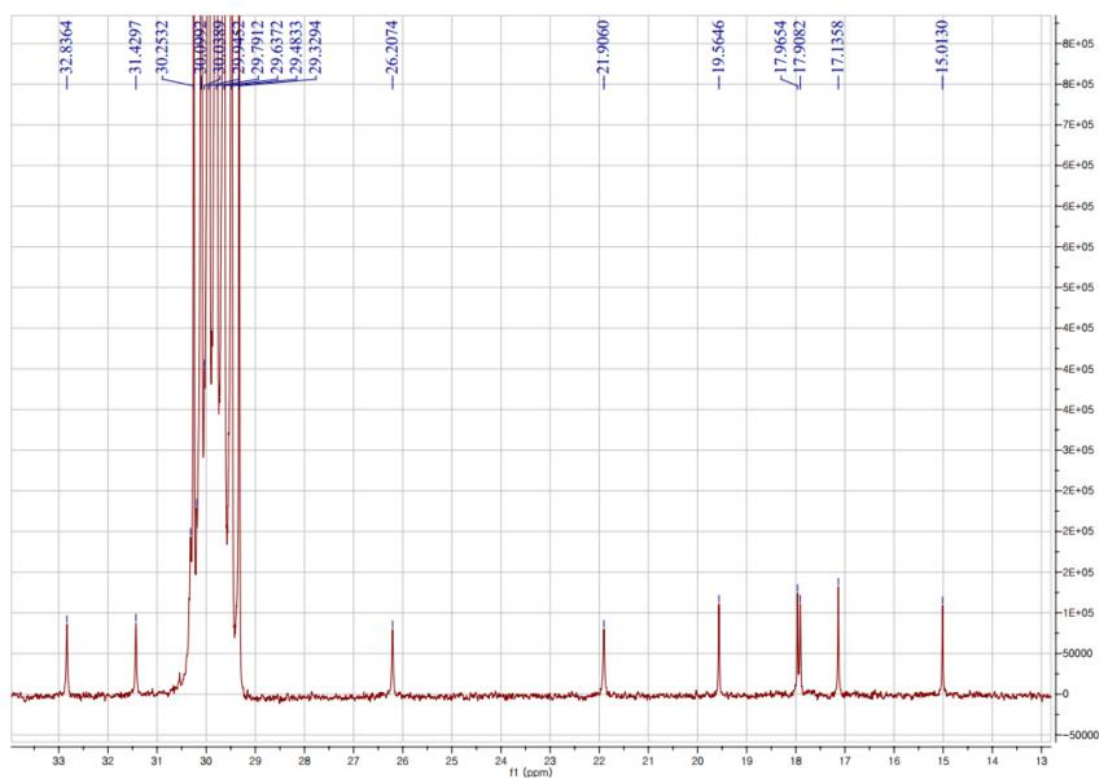


Figure S63. Expand  $^{13}\text{C}$  NMR spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

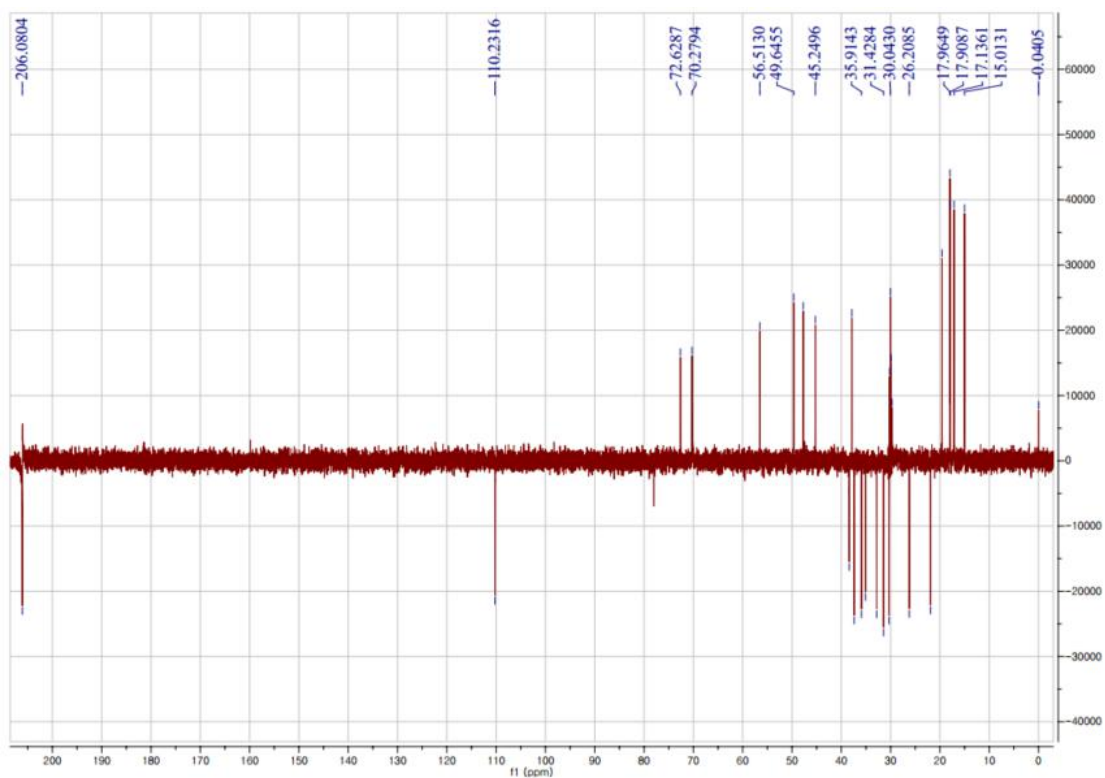


Figure S64. DEPT spectrum of 3α,11α-dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone-*d*<sub>6</sub>

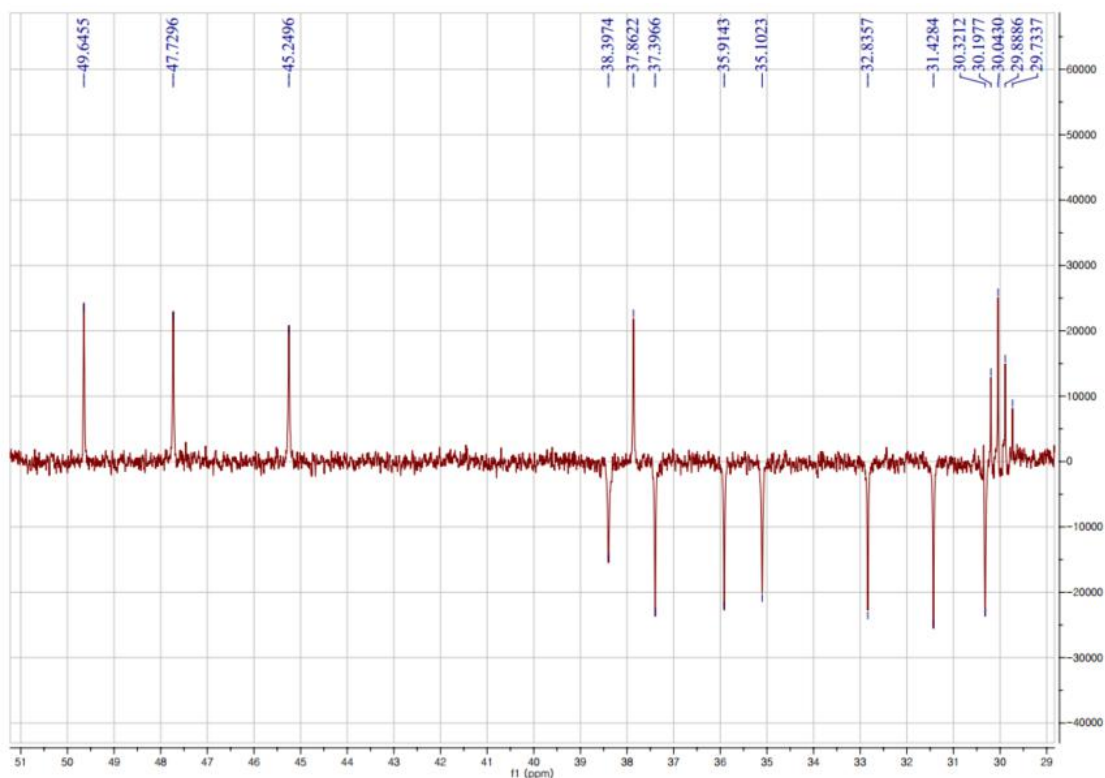


Figure S65. Expand DEPT spectrum of 3α,11α-dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone-*d*<sub>6</sub>

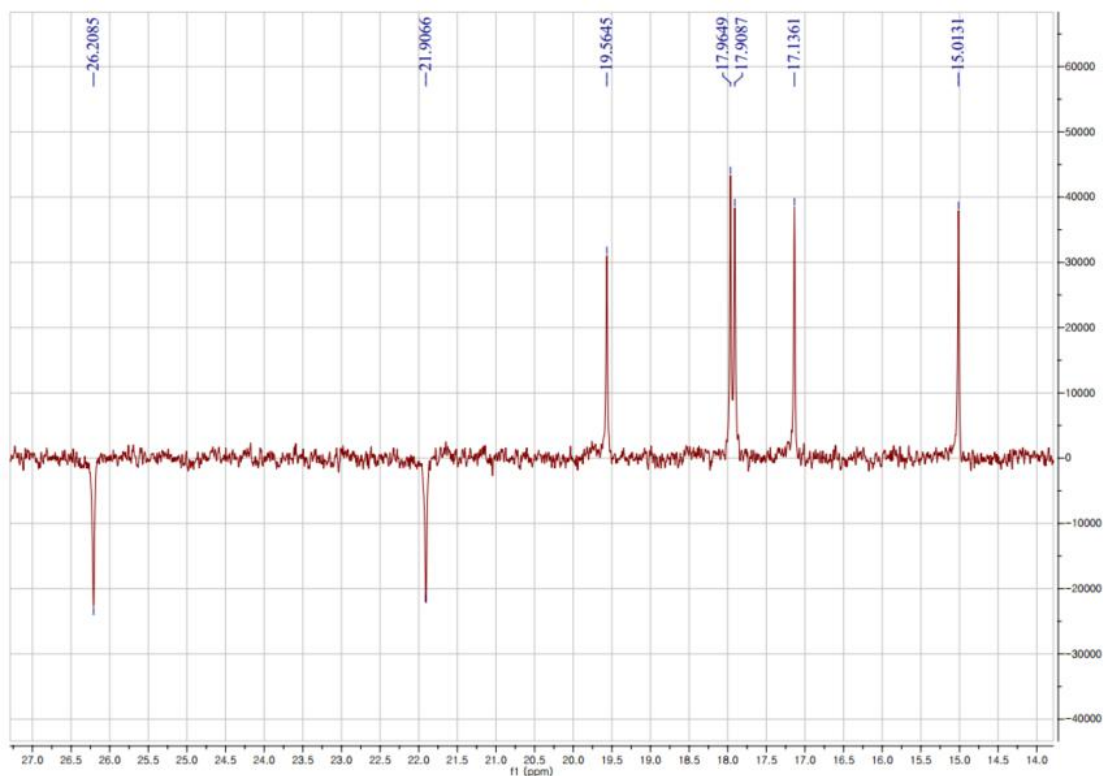


Figure S66. Expand DEPT spectrum of 3 $\alpha$ ,11 $\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

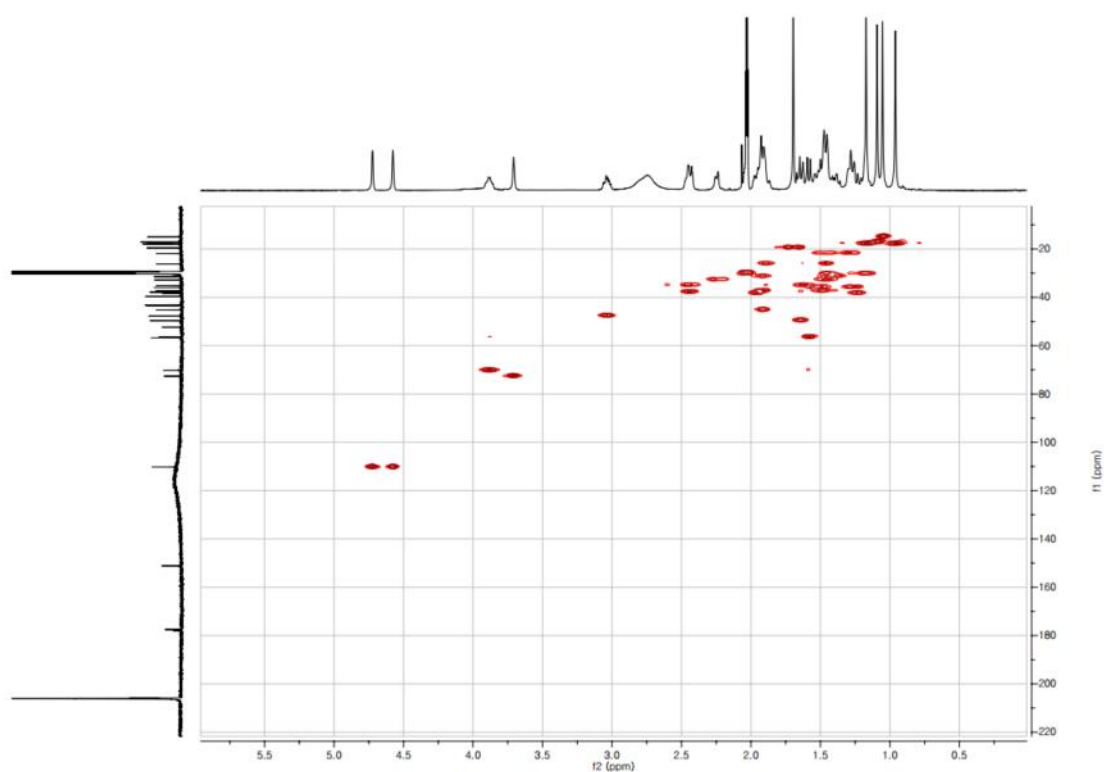


Figure S67. HSQC spectrum of 3 $\alpha$ ,11 $\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

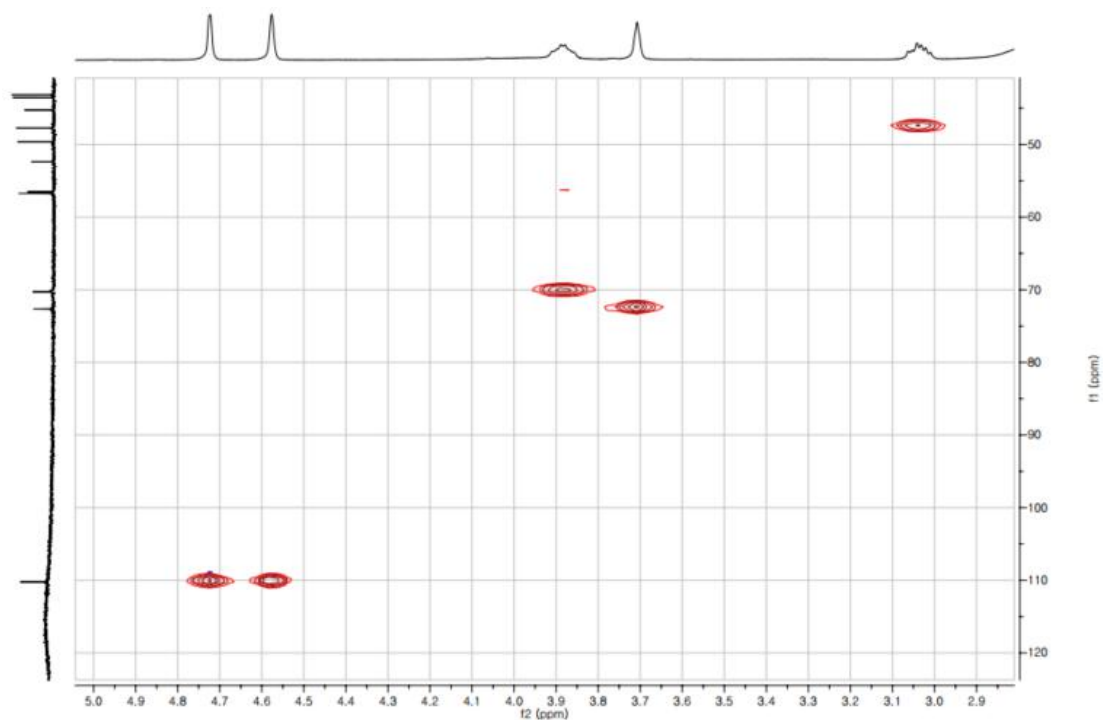


Figure S68. Expand HSQC spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

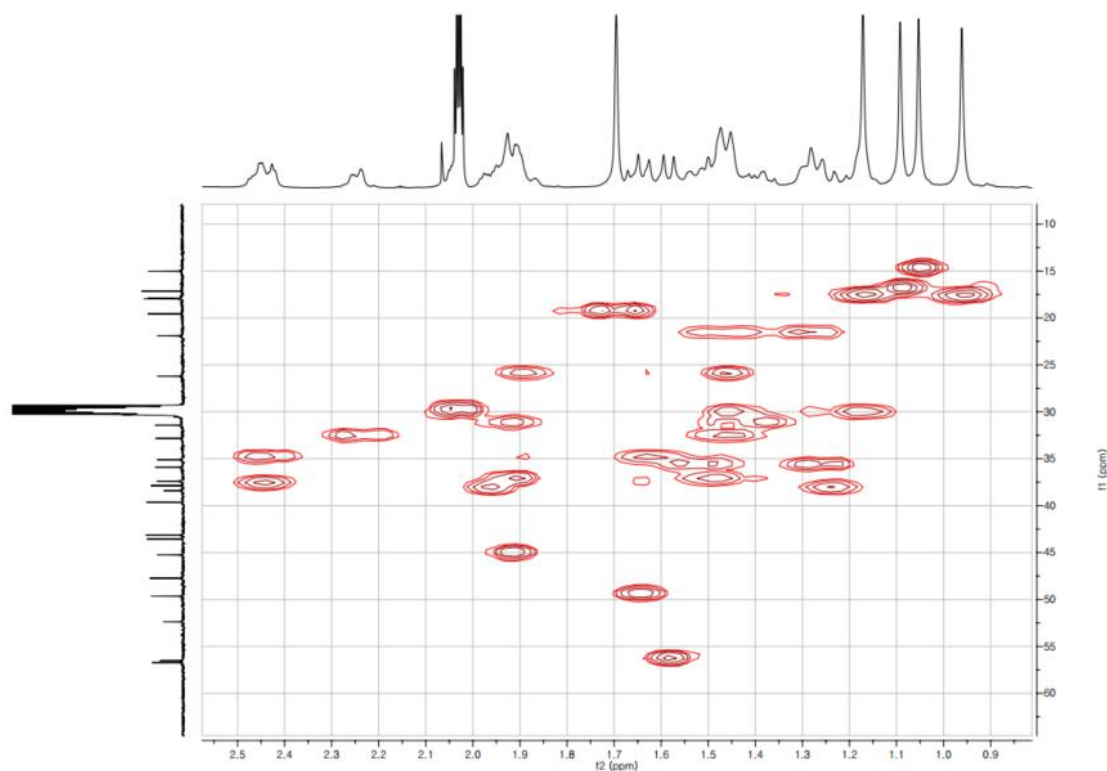


Figure S69. Expand HSQC spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

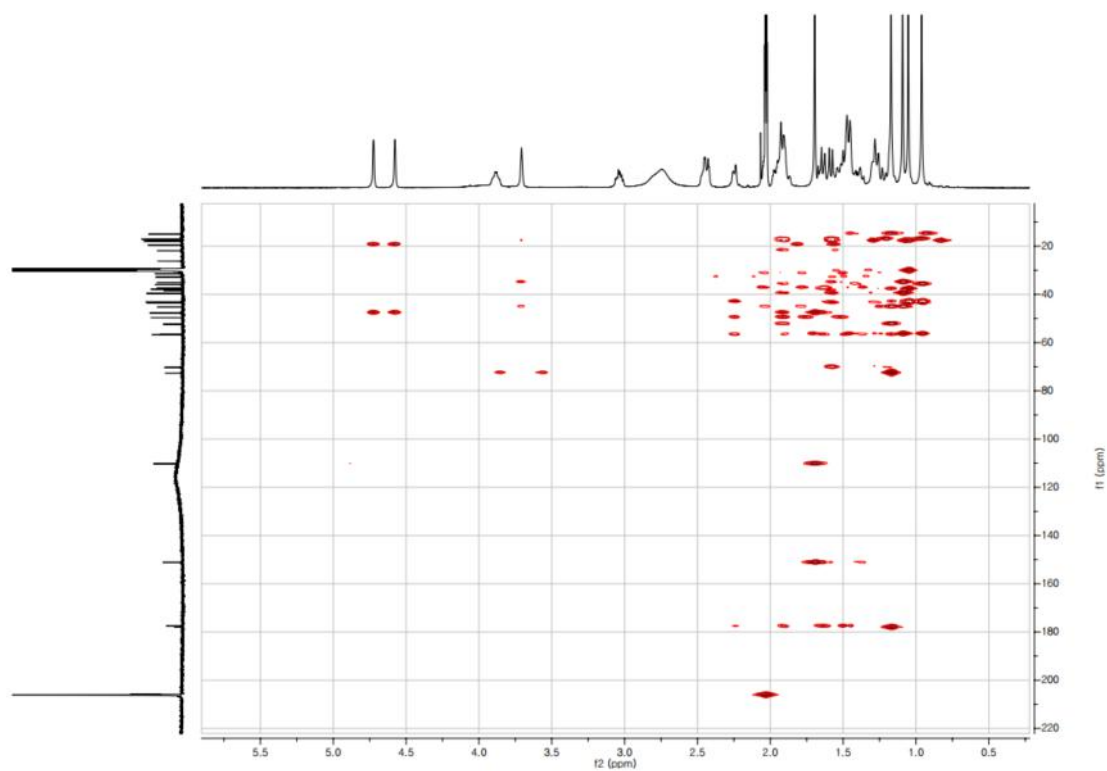


Figure S70. HMBC spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

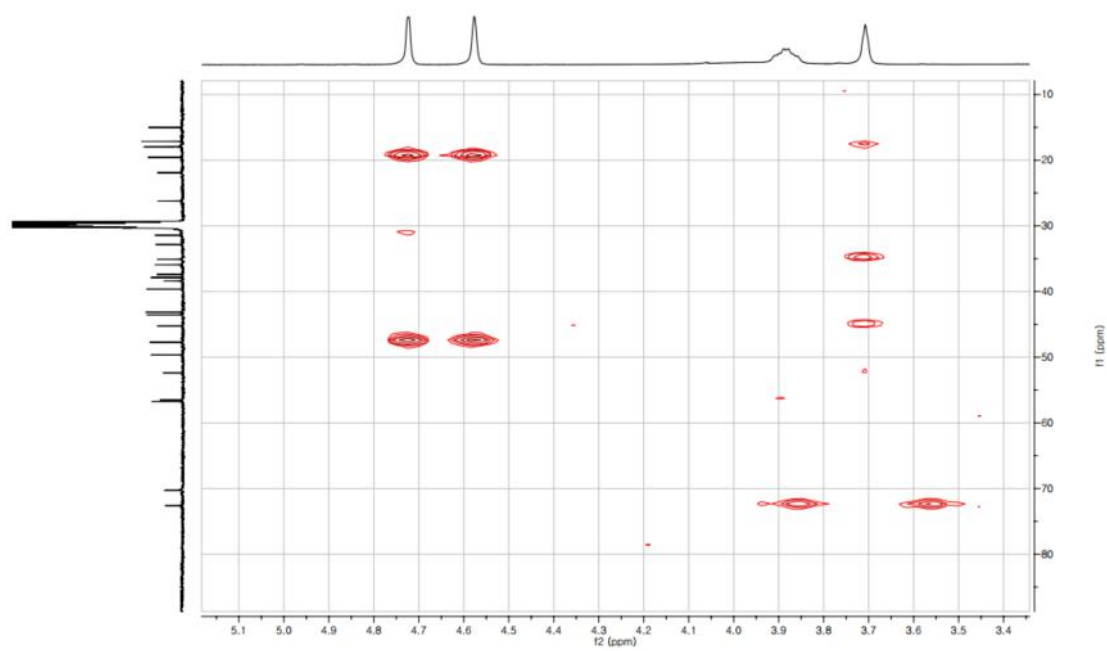


Figure S71. Expand HMBC spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

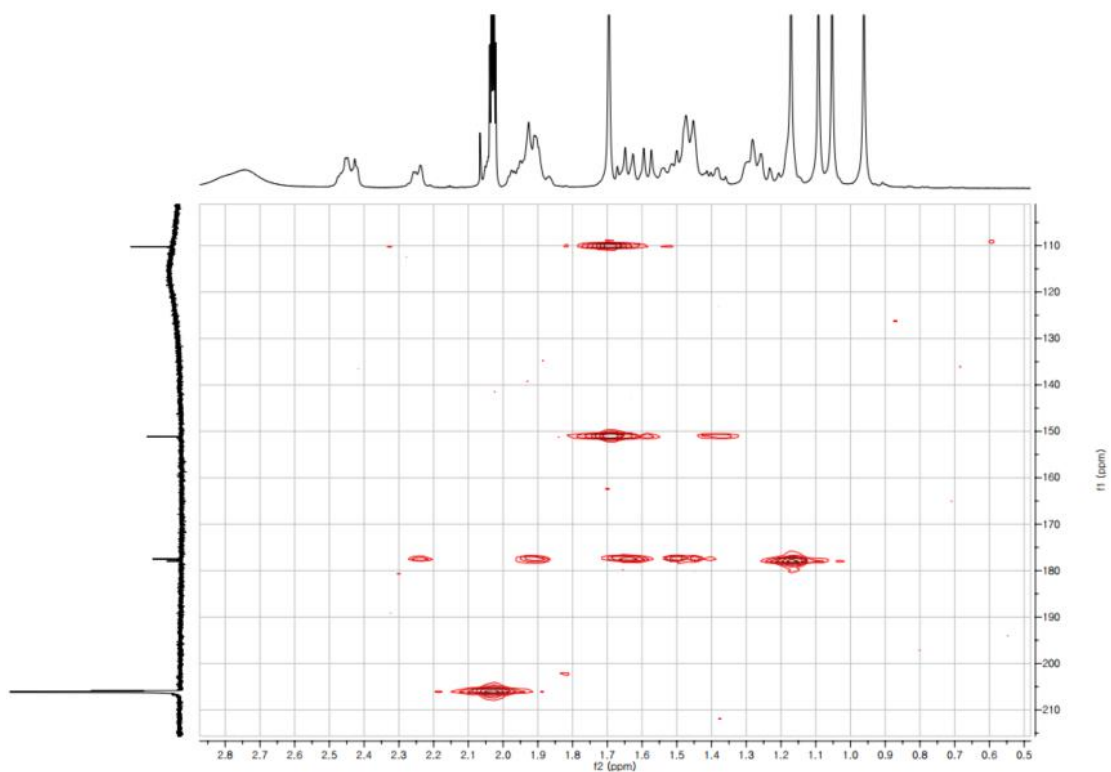


Figure S72. Expand HMBC spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

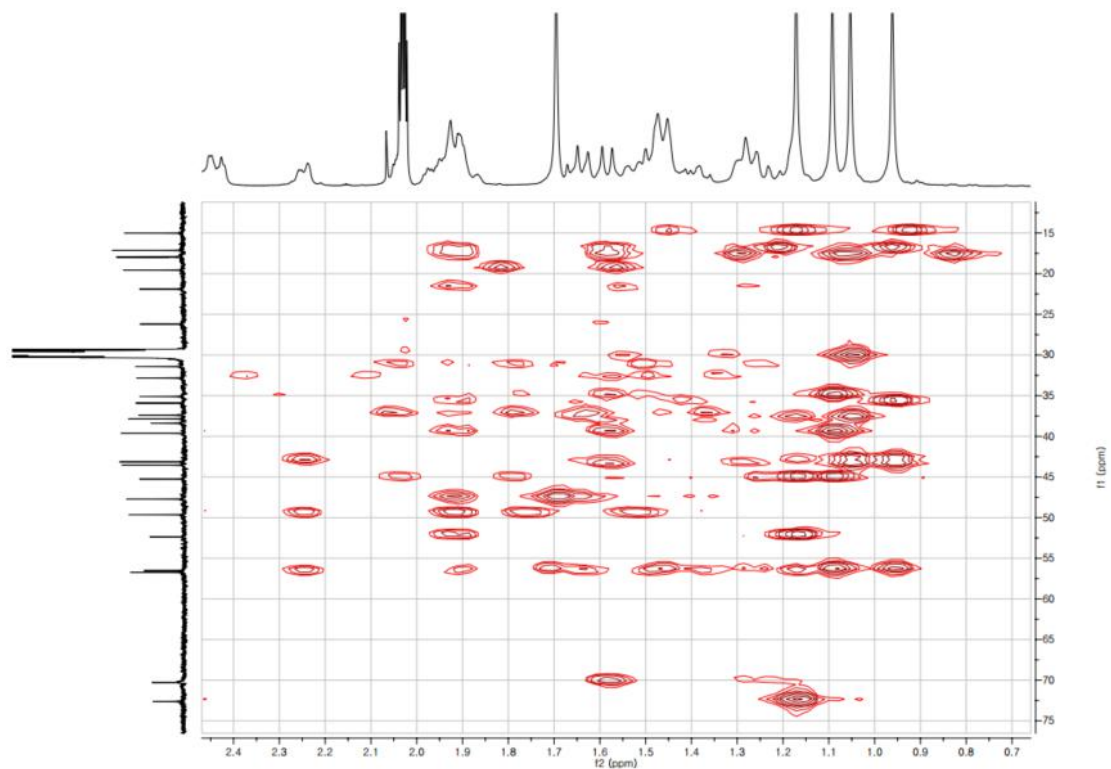
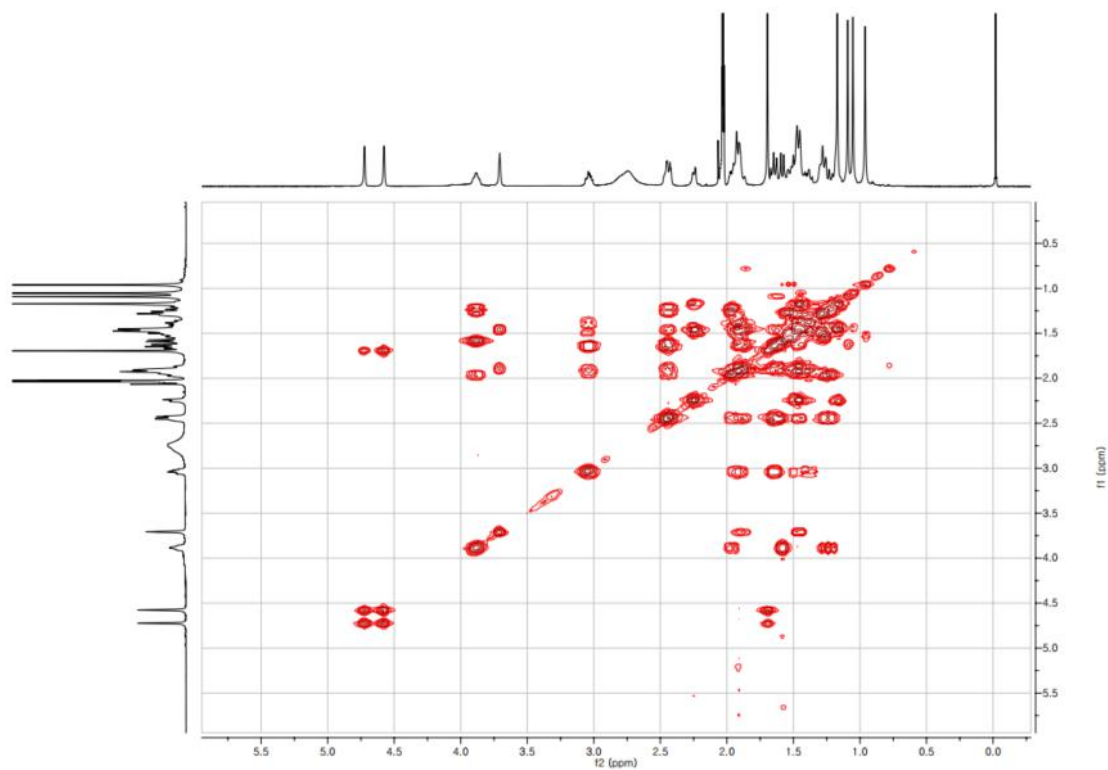
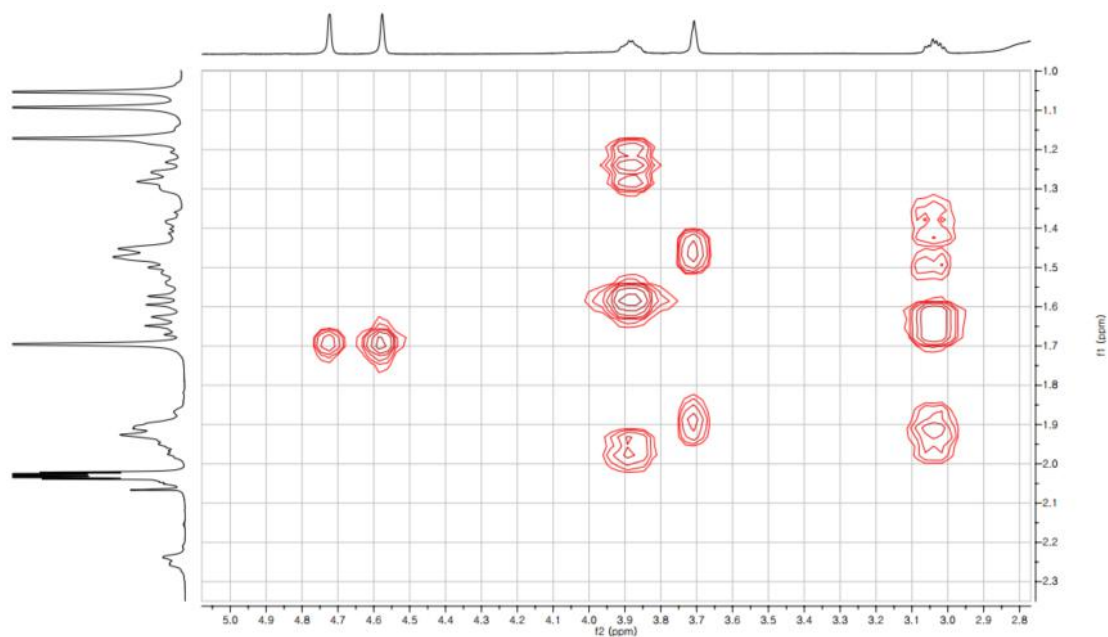


Figure S73. Expand HMBC spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

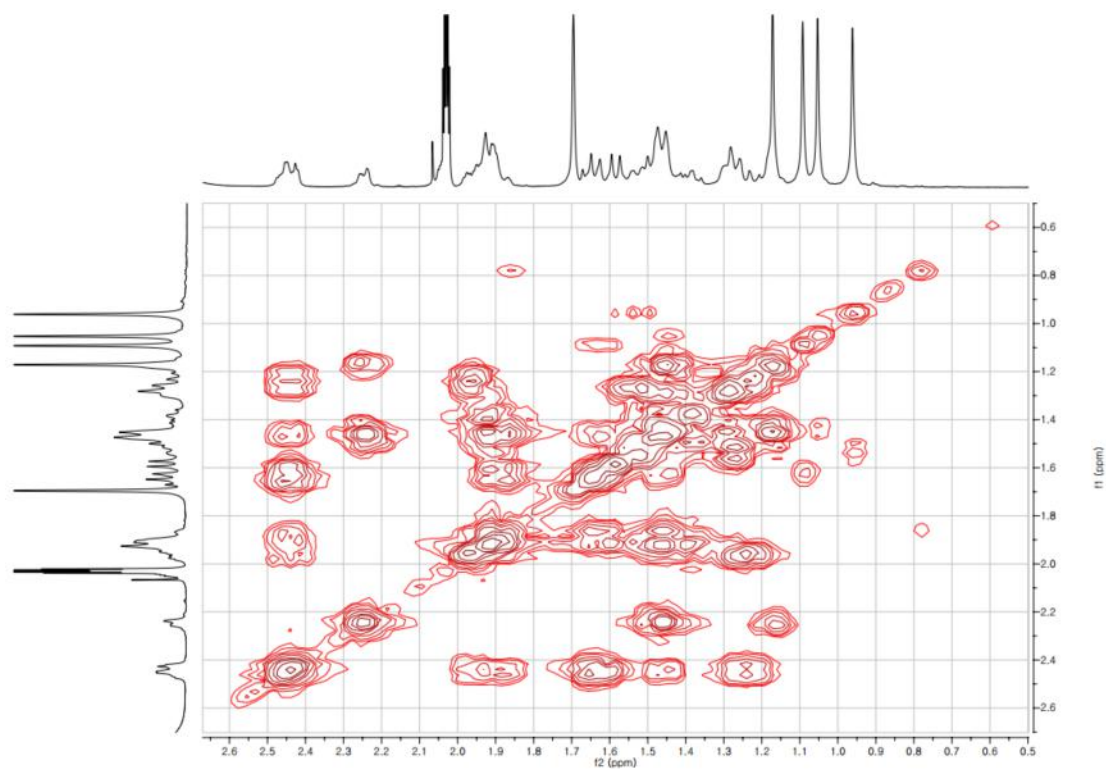


**Figure S74.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

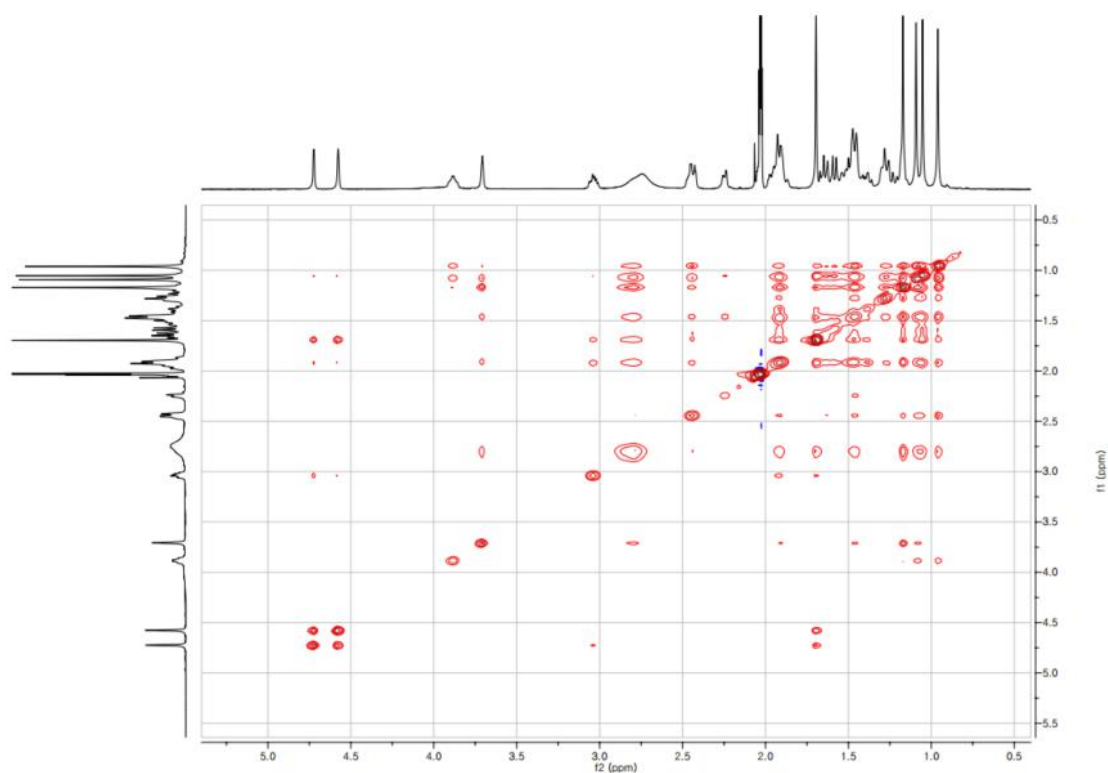


**Figure S75.** Expand  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$





**Figure S76.** Expand  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$



**Figure S77.** NOESY spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

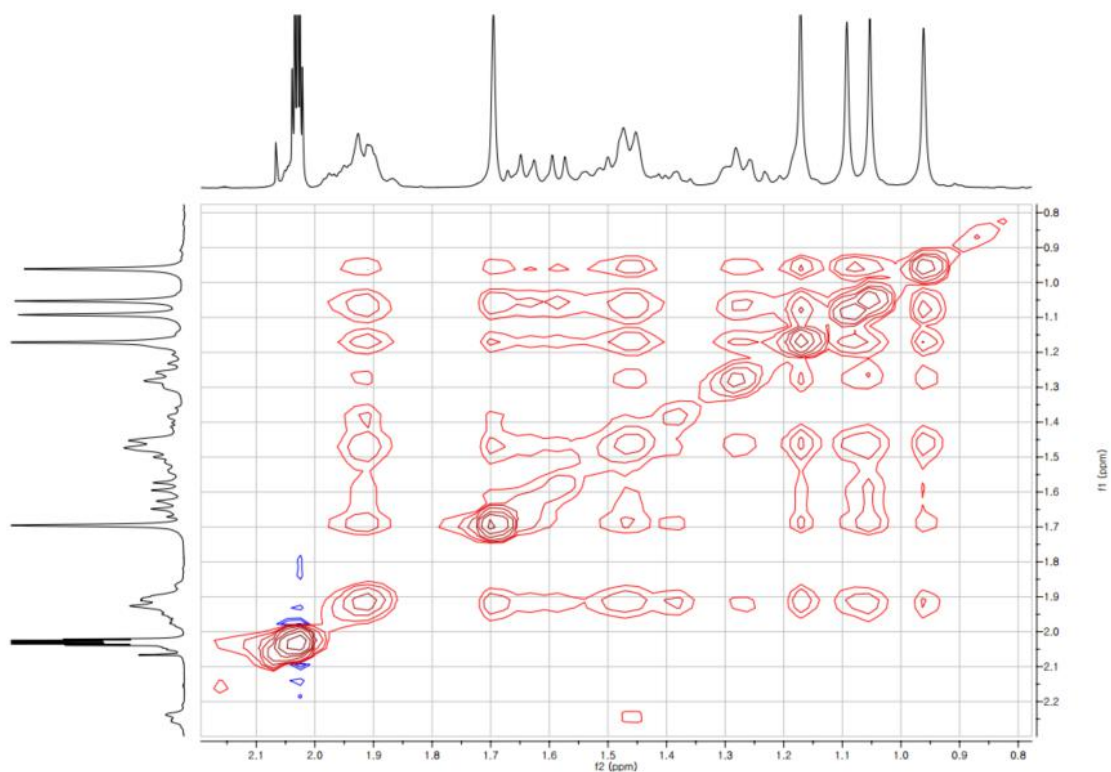


Figure S78. Expand NOESY spectrum of  $3\alpha,11\alpha$ -dihydroxy-lup-20(29)-en-23,28-dioic acid in acetone- $d_6$

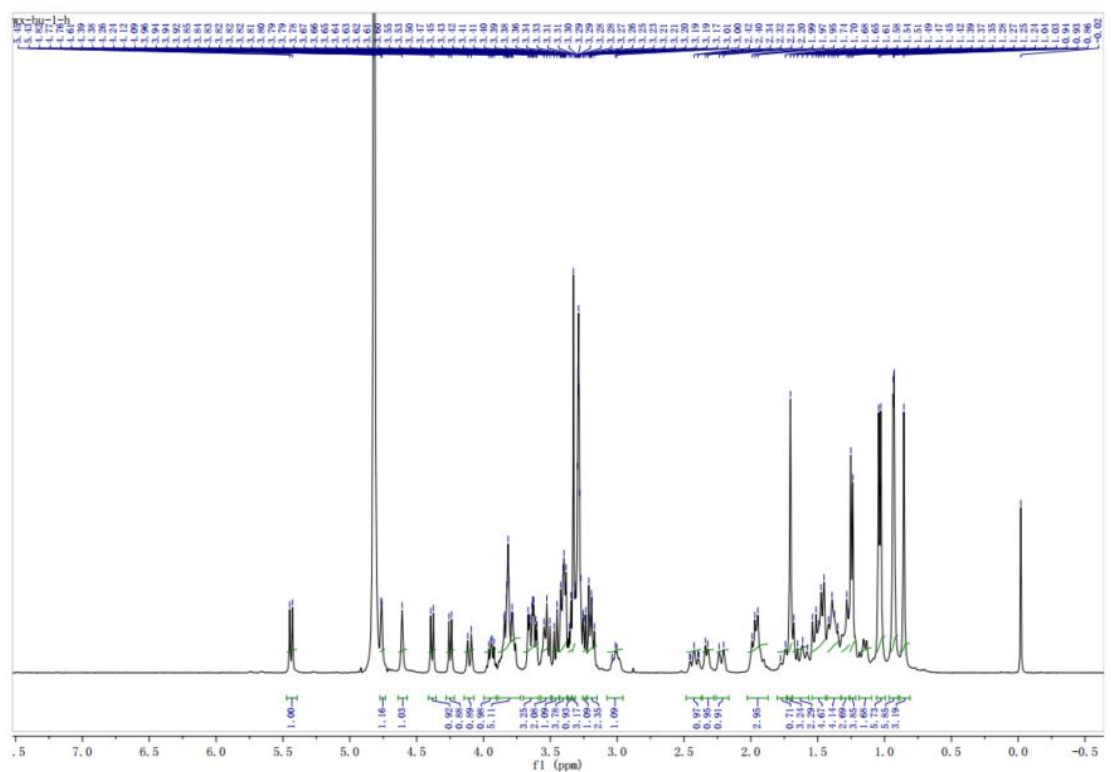


Figure S79.  $^1\text{H}$  NMR spectrum of acankoreoside C in methanol- $d_4$

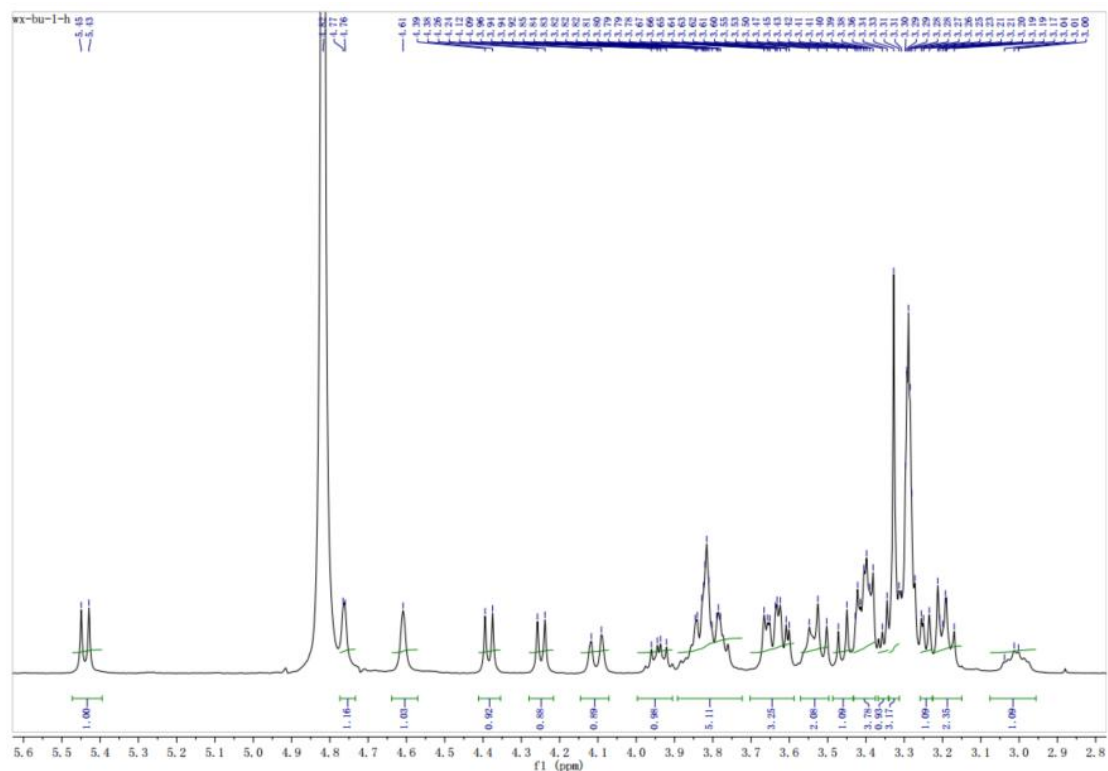


Figure S80. Expand  $^1\text{H}$  NMR spectrum of acankoreoside C in methanol- $d_4$

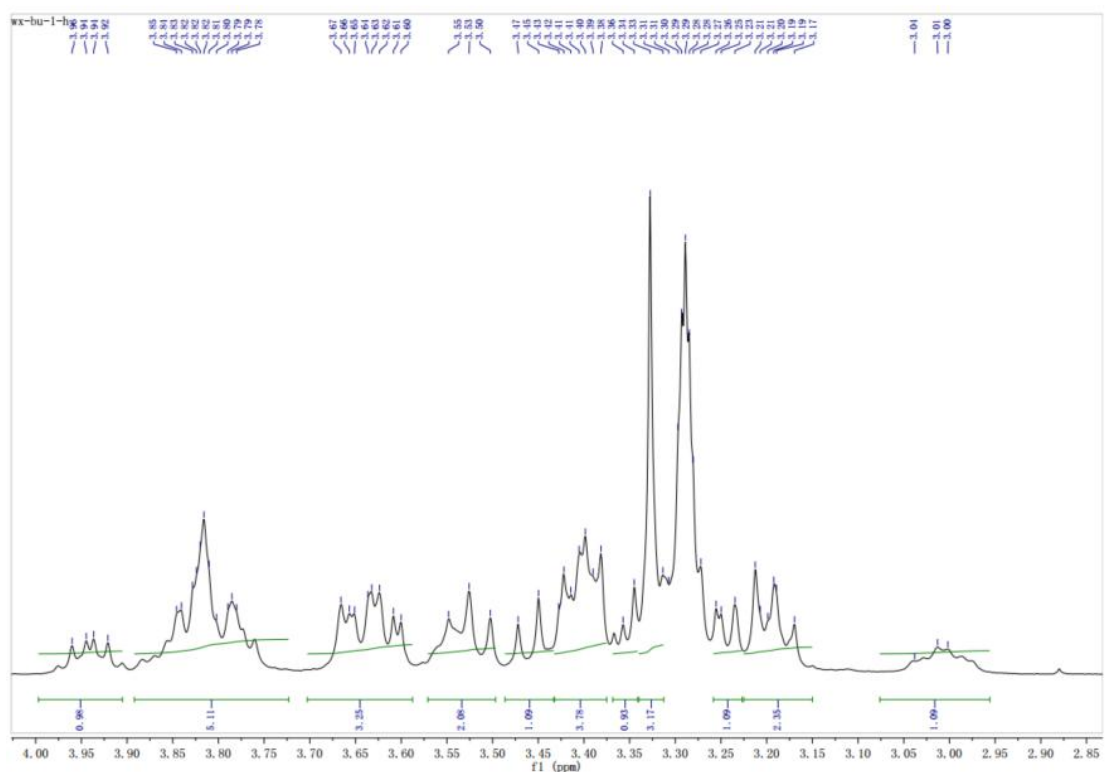


Figure S81. Expand  $^1\text{H}$  NMR spectrum of acankoreoside C in methanol- $d_4$

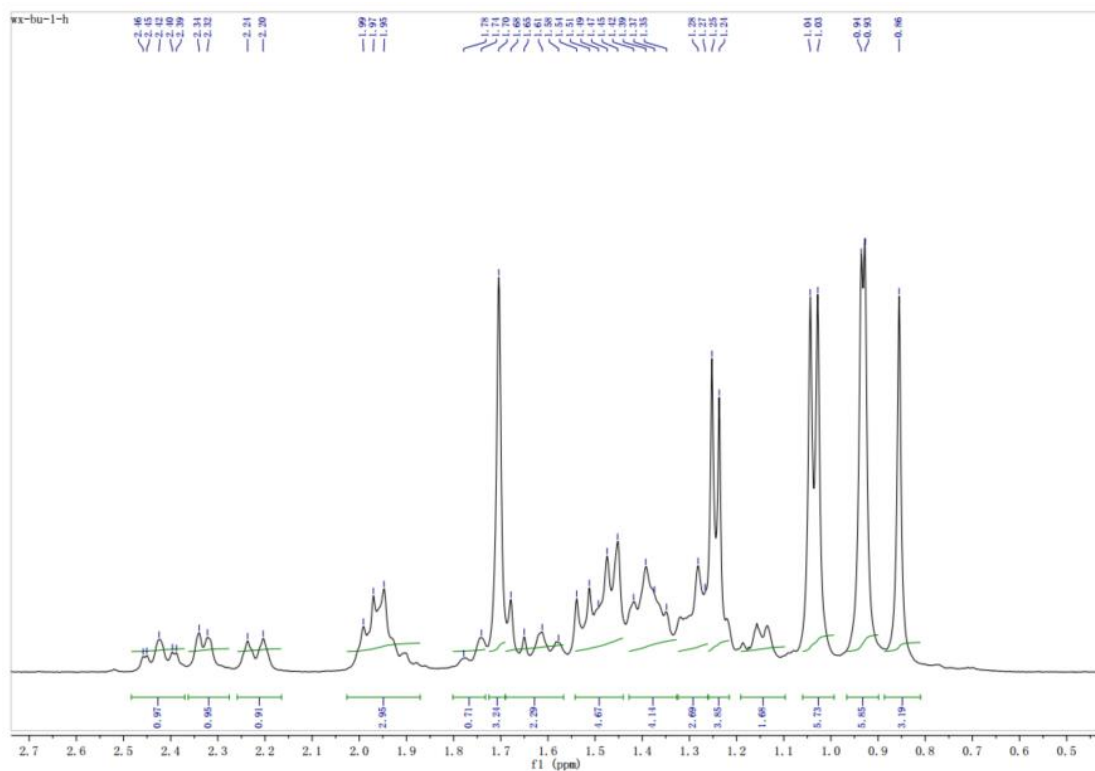


Figure S82. Expand  $^1\text{H}$  NMR spectrum of acankoreoside C in methanol- $d_4$

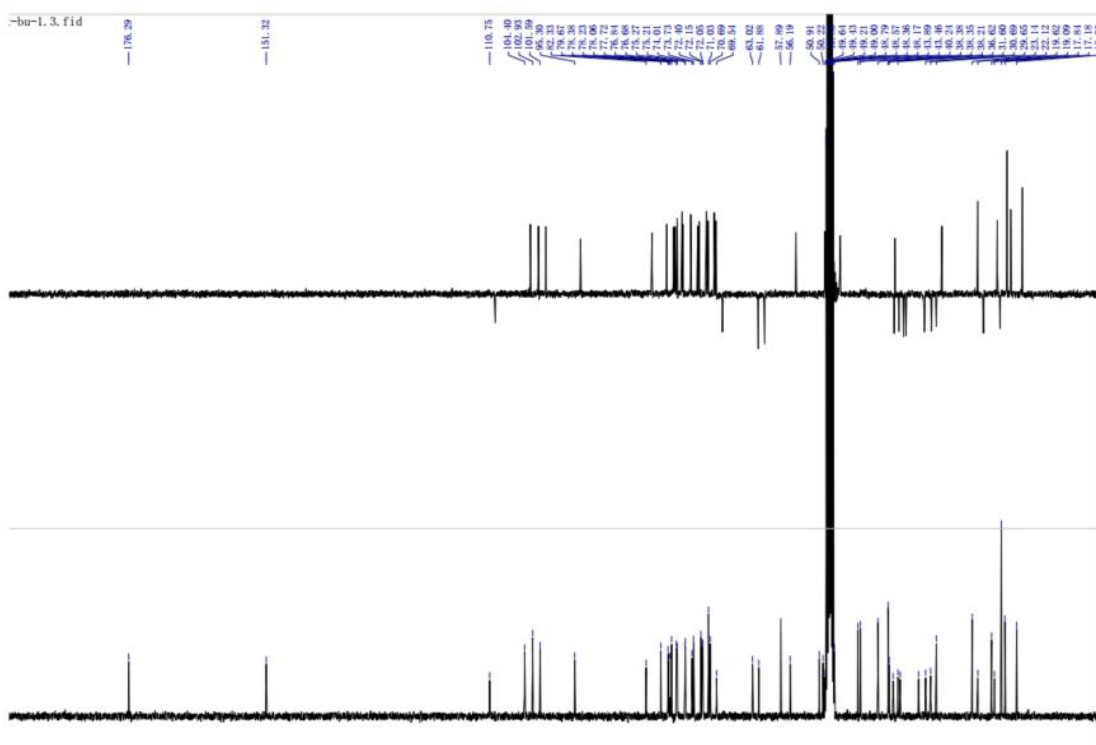
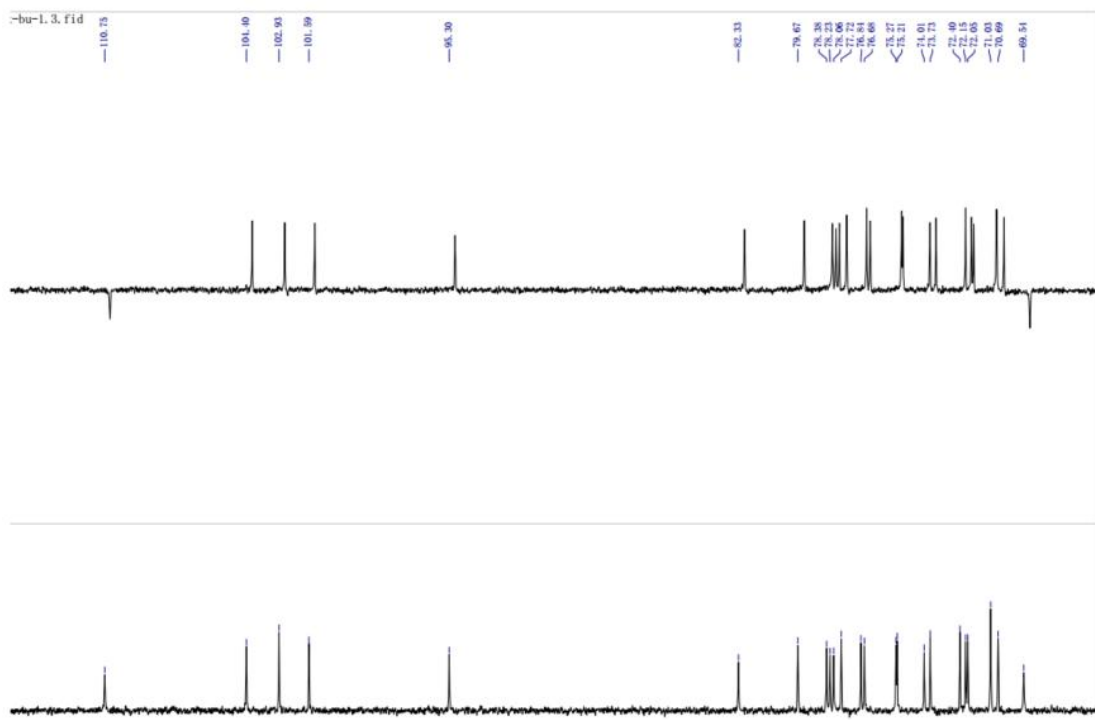


Figure S83.  $^{13}\text{C}$  NMR spectrum of acankoreoside C in methanol- $d_4$



**Table S1.** <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectral data of compound 1  
(acetone-*d*<sub>6</sub>, δ ppm)

Position	δ <sub>C</sub>	DEPT	δ <sub>H</sub> [mult. (J in Hz)]	HMBC correlations
C-1	75.46	CH	3.84 (1H, dd, 8.16, 3.96)	H-2, H-25
C-2	37.36	CH <sub>2</sub>	1.82 (1H, m); 1.87 (1H, m)	H-1
C-3	73.99	CH	3.82 (1H, t, 2.40)	H-2, H-24
C-4	52.27	C	-	H-2, H-5, H-24
C-5	45.25	CH	1.95 (1H, m)	H-3, H-6, H-7, H-24, H-25
C-6	22.09	CH <sub>2</sub>	1.35 (1H, m); 1.57 (1H, m)	H-5
C-7	35.19	CH <sub>2</sub>	1.31 (1H, m); 1.56 (1H, m)	H-5, H-26
C-8	42.76	C	-	H-6, H-9, H-11, H-26, H-27
C-9	52.98	CH	1.72 (1H, dd, 10.08, 2.68)	H-1, H-11, H-25, H-26
C-10	44.33	C	-	H-1, H-5, H-11, H-25
C-11	24.68	CH <sub>2</sub>	1.32 (1H, m); 2.43 (1H, brd, 9.80)	-
C-12	26.87	CH <sub>2</sub>	1.12 (1H, dd, 10.52, 3.76); 1.68 (1H, m)	-
C-13	39.14	CH	2.34 (1H, td, 10.32, 3.0)	H-12, H-18, H-27
C-14	43.72	C	-	H-13, H-16, H-26, H-27
C-15	30.75	CH <sub>2</sub>	1.20 (1H, m); 1.46 (1H, m)	H-16, H-27
C-16	33.15	CH <sub>2</sub>	1.48 (1H, m); 2.25 (1H, dt, 9.84, 2.8)	H-18
C-17	56.98	C	-	H-13, H-15, H-16, H-18, H-22
C-18	50.30	CH	1.64 (1H, m)	H-12, H-13, H-16, H-19, H-22
C-19	48.24	CH	3.05 (1H, td, 8.76, 4.0)	H-18, H-21, H-22, H-29, H-30
C-20	151.89	C	-	H-18, H-19, H-21, H-29, H-30
C-21	31.61	CH <sub>2</sub>	1.34 (1H, m); 1.90 (1H, m)	H-19, H-22
C-22	37.84	CH <sub>2</sub>	1.48 (1H, m); 1.92 (1H, m)	H-18, H-21
C-23	178.16	COOH	-	H-3, H-5, H-24
C-24	17.92	CH <sub>3</sub>	1.17 (3H, s)	H-5
C-25	13.24	CH <sub>3</sub>	0.97 (3H, s)	H-1, H-5, H-9
C-26	17.31	CH <sub>3</sub>	0.99 (3H, s)	H-7, H-9
C-27	15.40	CH <sub>3</sub>	1.07 (3H, s)	H-13, H-15
C-28	177.84	COOH	-	H-16, H-18, H-22
C-29	110.26	CH <sub>2</sub>	4.58 (1H, m); 4.72 (1H, d, 1.68)	H-19, H-30
C-30	19.72	CH <sub>3</sub>	1.71 (3H, s)	H-19, H-29

**Table S2.** <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectral data of compound 2 (methanol-*d*<sub>4</sub>, δ ppm)

Position	δ <sub>C</sub>	DEPT	δ <sub>H</sub> [mult. (J in Hz)]	HMBC correlations
Aglycone				
C-1	76.33	CH	3.80 (1H, m)	H-2, H-3, H-5, H-25
C-2	36.79	CH <sub>2</sub>	1.72 (1H, m); 1.80 (1H, m)	H-1
C-3	74.14	CH	3.67 (1H, m)	H-1, H-2, H-24
C-4	52.24	C	-	H-2, H-5, H-24
C-5	46.11	CH	1.87 (1H, m)	H-3, H-6, H-7, H-9, H-24, H-25
C-6	22.17	CH <sub>2</sub>	1.26 (1H, m); 1.58 (1H, m)	H-5, H-7
C-7	35.09	CH <sub>2</sub>	1.30 (1H, m); 1.55 (1H, m)	H-5, H-6, H-26
C-8	42.96	C	-	H-6, H-7, H-9, H-26, H-27
C-9	53.06	CH	1.72 (1H, m)	H-1/H-5/H-7/H-11/H-12/H-25/H-26
C-10	44.47	C	-	H-1, H-5, H-6, H-9, H-11, H-25
C-11	24.82	CH <sub>2</sub>	1.36 (1H, m); 2.28 (1H, m)	H-12
C-12	26.94	CH <sub>2</sub>	1.12 (1H, m); 1.68 (1H, m)	H-13
C-13	39.13	CH	2.27 (1H, m)	H-12, H-18, H-19, H-27
C-14	43.82	C	-	H-13, H-16, H-18, H-26, H-27
C-15	30.86	CH <sub>2</sub>	1.15 (1H, m); 1.54 (1H, m)	H-13, H-16, H-27
C-16	32.95	CH <sub>2</sub>	1.44 (1H, m); 2.33 (1H, m)	H-15, H-18, H-22
C-17	57.93	C	-	H-15, H-16, H-18, H-21, H-22

C-18	50.6	CH	1.65 (1H, m)	H-13, H-16, H-19, H-21, H-22
C-19	48.36	CH	3.0 (1H, m)	H-18, H-21, H-29, H-30
C-20	151.77	C	-	H-18, H-19, H-21, H-29, H-30
C-21	31.55	CH <sub>2</sub>	1.37 (1H, m); 1.94 (1H, m)	H-19, H-22
C-22	37.68	CH <sub>2</sub>	1.48 (1H, m); 1.94 (1H, m)	H-21
C-23	182.6	COOH	-	H-5, H-24
C-24	18.08	CH <sub>3</sub>	1.09 (3H, s)	H-5
C-25	13.17	CH <sub>3</sub>	0.95 (3H, s)	H-1, H-5, H-9
C-26	17.14	CH <sub>3</sub>	0.98 (3H, s)	H-7, H-9
C-27	15.1	CH <sub>3</sub>	1.03 (3H, s)	H-13, H-15
C-28	176.4	CO-S	-	H-16, H-18, H-22, glc-H-1
C-29	110.41	CH <sub>2</sub>	4.58 (1H, brs); 4.72 (1H, brs)	H-30
C-30	19.49	CH <sub>3</sub>	1.70 (3H, s)	H-19, H-29
C-28-O-inner glc				
1	95.26	CH	5.45 (1H, d, 6.56)	glcH-2
2	74.00	CH	3.33 (1H, m)	glcH-3
3	78.28	CH	3.42 (1H, m)	glcH-2, glcH-4, glcH-5
4	70.95	CH	3.43 (1H, m)	glcH-2, glcH-3, glcH-5, glcH-6
5	78.06	CH	3.54 (1H, m)	glcH-1, glcH-4, glcH-6
6	69.55	CH <sub>2</sub>	3.81 (1H, m); 4.11 (1H, dd, 9.48, 1.36)	glcH-1'
glc'(1→6)glc				
1'	104.56	CH	4.37 (1H, d, 6.28)	glcH-6, glcH-2'
2'	75.32	CH	3.23 (1H, m)	glcH-3', glcH-4'
3'	76.71	CH	3.45 (1H, m)	glcH-2', glcH-5'
4'	79.51	CH	3.53 (1H, m)	glcH-3', glcH-6', rha H-1''
5'	76.89	CH	3.30 (1H, m)	glcH-4', glcH-6'
6'	61.90	CH <sub>2</sub>	3.65 (1H, m); 3.80 (1H, m)	glcH-4'
rha(1→4)glc'				
1''	102.92	CH	4.84 (1H, overlapped)	glcH-4'
2''	72.44	CH	3.81 (1H, m)	rhaH-1'', rhaH-3'', rhaH-4''
3''	72.16	CH	3.62 (1H, m)	rhaH-1'', rhaH-2'', rhaH-4''
4''	73.75	CH	3.38 (1H, m)	rhaH-2'', rhaH-3'', rhaH-5'', rhaH-6''
5''	70.64	CH	3.95 (1H, m)	rhaH-1'', rhaH-4'', rhaH-6''
6''	17.84	CH <sub>3</sub>	1.25 (3H, d, 4.96)	rhaH-4''

**Table S3.** NMR spectral data of compounds **3-4**.

Position	<b>3</b> $\delta_c^{a,c}$	$\delta_H^{a,d}$ [mult. (J in Hz)]	<b>4</b> $\delta_c^{b,c}$	$\delta_H^{b,d}$ [mult. (J in Hz)]
Aglycone				
C-1	32.84	1.46 (1H, m); 2.24 (1H, m)	36.62	-
C-2	26.21	1.46 (1H, m); 1.90 (1H, m)	22.12	-
C-3	72.65	3.71 (1H, brs)	82.33	3.67 (1H, m)
C-4	52.39	-	38.35	-
C-5	45.26	1.92 (1H, m)	50.91	-
C-6	21.91	1.30 (1H, m); 1.48 (1H, m)	19.09	-
C-7	35.92	1.29 (1H, m); 1.55 (1H, m)	36.21	-
C-8	43.15	-	43.46	-
C-9	56.52	1.59 (1H, m)	56.19	1.72 (1H, m)
C-10	39.64	-	40.24	-
C-11	70.28	3.90 (1H, m)	70.69	3.85 (1H, m)
C-12	38.41	1.24 (1H, m); 1.96 (1H, m)	38.38	-
C-13	37.87	2.44 (1H, m)	38.21	2.79 (1H, m)
C-14	43.56	-	43.89	-
C-15	30.26	1.18 (1H, m); 1.46 (1H, m)	30.69	-



C-16	35.11	1.63 (1H, m); 2.45 (1H, m)	32.86	-
C-17	56.74	-	57.89	-
C-18	49.65	1.64 (1H, m)	50.22	1.65 (1H, m)
C-19	47.74	3.05 (1H, m)	48.17	3.01 (1H, m)
C-20	151.14	-	151.32	-
C-21	31.44	1.38 (1H, m); 1.91 (1H, m)	31.60	-
C-22	37.40	1.48 (1H, m); 1.92 (1H, m)	37.47	-
C-23	177.78	-	29.65	1.04 (3H, s)
C-24	17.92	1.17 (3H, s)	23.14	0.93 (3H, s)
C-25	17.97	0.96 (3H, s)	17.18	1.03 (3H, s)
C-26	17.14	1.09 (3H, s)	17.84	0.94 (3H, s)
C-27	15.02	1.05 (3H, s)	15.06	0.86 (3H, s)
C-28	177.51	-	176.29	-
C-29	110.26	4.58 (1H, brs); 4.72 (1H, brs)	110.75	4.61 (1H, brs); 4.76 (1H, brs)
C-30	19.57	1.70 (3H, s)	19.62	1.70 (3H, s)
C-28-O-inner glc				
1			95.30	5.45 (1H, d, 6.56)
2			74.01	3.32 (1H, m)
3			78.23	3.40 (1H, m)
4			71.03	3.41 (1H, m)
5			77.72	3.53 (1H, m)
6			69.54	3.81 (1H, m); 4.12 (1H, dd, 9.48, 1.36)
glc'(1→6)glc				
1'			104.4	4.39 (1H, d, 6.28)
2'			75.21	3.23 (1H, m)
3'			76.68	3.43 (1H, m)
4'			79.67	3.52 (1H, m)
5'			76.84	3.28 (1H, m)
6'			61.8	3.65 (1H, m); 3.80 (1H, m)
rha(1→4)glc'				
1''			102.93	4.84 (1H, overlapped)
2''			72.40	3.81 (1H, m)
3''			72.15	3.62 (1H, m)
4''			73.73	3.38 (1H, m)
5''			70.69	3.95 (1H, m)
6''			17.84	1.25 (3H, d, 4.96)
C-3-O-glc''				
1'''			101.59	4.26 (1H, d, 6.56)
2'''			75.27	3.32 (1H, m)
3'''			78.38	3.52 (1H, m)
4'''			72.05	3.84 (1H, m)
5'''			78.06	3.53 (1H, m)
6'''			63.02	3.62 (1H, m); 3.82 (1H, m)

Note: Assignments were done by HMQC, HMBC,  $^1\text{H}$ - $^1\text{H}$  COSY, and NOESY experiments; Glc: D-glucopyranosyl; Rha: L-rhamnopyranosyl; <sup>a</sup> Measured in  $\text{CD}_3\text{COCD}_3$ ; <sup>b</sup> Measured in  $\text{CD}_3\text{OD}$ ; <sup>c</sup> 100 MHz; <sup>d</sup> 400 MHz