

SUPPLEMENTARY MATERIAL

Three new resin glycosides compounds from *Argyrea acuta* and their α -glucosidase inhibitory activity

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Abstract

Three new phenolic compounds, acutacoside C (1), acutacoside D (2), and acutacoside E (3) were isolated from the aerial part of *Argyrea acuta*. The oligosaccharide chain was composed with two glucoses and three rhamnoses, and the aglycone was (11S)-hydroxyhexadecanoic acid (jalapinolic acid). The core of the three compounds was operculinic acid B, which was rare in resin glycosides. Their structures were established by a combination of spectroscopic and chemical methods. Compounds 1–3 have been evaluated for inhibitory activity against α -glucosidase, which all showed weak inhibitory activities.

Keywords: *Argyrea acuta*, resin glycosides, structural identification, α -glucosidase

Table S1. NMR Data for Compounds **1-3** in pyridine-*d*₅.

Position	1		2		3	
	¹³ C	¹ H	¹³ C	¹ H	¹³ C	¹ H
Glu-1	104.2	5.03 d (7.5)	104.4	5.12 d (8.0)	104.	4.93 d (6.5)
2	81.7	3.93 *	82.0	3.89 *	82.0	3.93 *
3	76.3	4.29*	76.6	4.19*	76.6	4.20*
4	71.6	4.24*	71.8	4.14*	71.8	4.14*
5	77.8	3.97 *	78.0	3.87 *	78.0	3.87 *
6	62.6	4.42 * 4.59 *	62.8	4.31 * 4.47 *	62.8	4.33 * 4.49 *
Rha-1	98.3	5.71 br s	98.6	5.61 br s	98.5	5.62 br s
2	73.3	6.15 br s	73.5	6.06 br s	73.5	6.05 br s
3	69.1	5.18 dd (9.5, 3.5)	69.5	5.07 dd (9.0, 3.5)	69.3	5.08 dd (9.5, 3.5)
4	81.7	4.31 dd (9.5, 9.5)	81.0	4.21 dd (9.0, 9.0)	82.0	4.21 dd (9.5, 9.5)
5	68.8	4.49*	69.0	4.37*	69.1	4.39*
6	18.9	1.72 d (6.0)	19.2	1.62 d (6.0)	19.1	1.62 d (6.0)
Rha'-1	100.0	5.99 br s	99.7	6.34 br s	100.	5.87 br s
2	72.8	6.44 br s	72.7	6.32 br s	73.0	6.36 br s
3	79.7	4.93 dd (9.0, 3.0)	80.0	4.84 dd (9.5, 3.5)	79.9	4.83 dd (8.5, 3.0)
4	78.2	4.26 dd (9.0, 9.0)	78.3	4.17 dd (9.5, 9.5)	78.4	4.16 dd (8.5, 8.5)
5	68.3	4.62*	68.4	4.44 *	68.5	4.50*
6	18.8	1.76 d (5.5)	19.1	1.69 d (6.5)	19.0	1.67 d (5.5)
Rha''-1	103.2	6.41 br s	99.8	5.96 br s	103.	6.31 br s
2	69.7	5.38 br s	74.1	6.29 br s	69.9	5.29 br s
3	73.1	6.11 dd (3.0, 10.0)	68.2	4.79 dd (3.5, 10.0)	73.3	6.02 dd (3.0, 10.0)
4	71.5	6.19 t (10.0)	74.7	5.82 t (10.0)	71.7	6.11 t (10.0)
5	67.9	4.56 *	68.2	4.49 dd (10.0, 6.5)	68.2	4.44 *
6	17.7	1.55 d (6.0)	18.0	1.54 d (6.5)	17.9	1.45 d (6.5)
Glu'-1	105.3	5.24 d (7.2)	105.0	4.92 d (7.5)	105.	5.14 d (7.5)
2	75.0	4.08 *	75.0	3.89 *	75.2	3.94 *
3	78.7	4.19*	78.4	4.19*	79.0	4.07*
4	71.3	4.05*	71.4	4.14*	71.5	3.97*
5	77.9	3.92 *	78.3	3.82 *	78.1	3.82 *
6	62.7	4.54 * 4.21 *	63.0	4.40 * 4.10 *	63.0	4.44 * 4.11 *
Ag-1	173.0		173.4		173.	
2	34.0	2.46 m, 2.39 m	34.3	2.47 m, 2.33 m	34.3	2.37 m, 2.30 m
11	82.5	4.00 *	82.8	3.99 *	82.7	3.90 *
16	14.1	0.83 t (7.5)	14.3	0.86 t (7.0)	14.3	0.83 t (7.5)
Cna-1	166.2		167.0		166.	
2	118.3	6.70 d (16.0)	118.7	6.37 d (16.0)	118.	6.60 d (16.0)
3	145.3	7.97 d (16.0)	145.2	7.66 d (16.0)	145.	7.87 d (16.0)
1'	134.6		134.6		134.	
2' and 6'	128.3	7.56 m	128.5	7.26 m	128.	7.46 m
3' and 5'	129.0	7.45 m	129.0	7.17 m	129.	7.35 m
4'	130.5	7.45 m	130.5	7.17 m	130.	7.35 m
Mba-1	175.8		176.4		176.	
2	41.3	2.59 m	41.2	2.53 m	41.6	2.49 m

2-CH ₃	16.7	1.25 d (7.0)	17.0	1.22 d (7.0)	17.0	1.15 d (7.0)
4	11.6	0.95 t (7.0)	11.7	0.92 t (7.0)	11.8	0.87 t (7.0)
Deca-1	173.4					
2	34.2	2.43 m				
12	14.1	0.93 t (5.5)				
Dodeca-1			173.9		173.	
2			34.4	2.37 m	34.4	2.35 m
12			14.3	0.86 t (7.0)	14.3	0.83 t (7.5)

Chemical shifts (δ) are in ppm relative to TMS. The spin coupling (J) is given in parentheses (Hz). Chemical shifts marked with an asterisk (*) indicate overlapped signals. Spin-coupled patterns are designated as follows: br s = broad singlet, d = doublet, t = triplet, m = multiplet. Abbreviations: Glc = glucose; Rha = rhamnose; Ag = 11- hydroxyhexadecanoyl; Mba = 2*S*-methylbutanoyl; Cna = *trans*-cinnamoyl; Deca = *n*-decanoyl; Dodeca = *n*-dodecanoyl.

Table S2 α -Glucosidase inhibition of compounds **1–3** and acarbose

Compound	α -Glucosidase Inhibition Constant	
	(IC ₅₀) [μ M]	
1	188.6 \pm 5.2	
2	157.8 \pm 4.6	
3	174.4 \pm 3.9	
acarbose	388.0 \pm 8.5	

^a IC₅₀ is defined as the concentration that resulted in a 50% α -glucosidase inhibition and the results are means \pm standard deviation of three independent replicates; ^b Positive control substance.

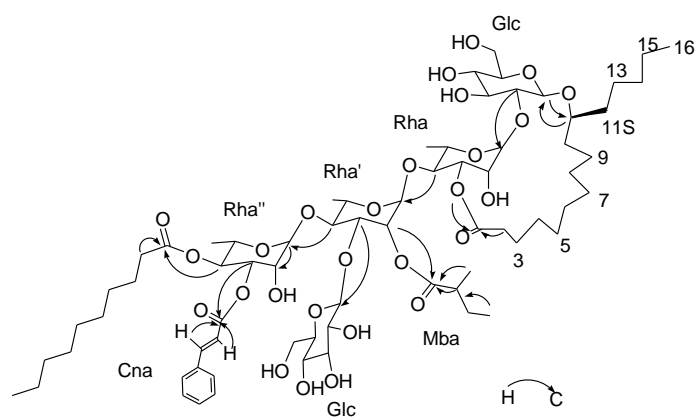


Figure S1. Key HMBCs from H to C for Acutacoside C (**1**)

The identification procedures of organic acids, sugars, and aglycone:

Compounds **1–3** (7 mg each) in 5% KOH (3 mL) were refluxed at 90 °C for 2 h, respectively. The reaction mixture was acidified to pH 4.0 with 2 mol/L HCl and extracted with hexane (3 mL × 2) and *n*-BuOH (3 mL × 2). The organic layer was washed with H₂O, dried over anhydrous Na₂SO₄, then methylated following. The hexane extract, was combined with 0.1 mL 0.5 M CH₃ONa solution, then shaken for 5 min at room temperature, before adding 5 µL CH₃COOH and 1 g anhydrous CaCl₂ powder, heating for 1 h, followed by centrifugation for 2–3 min at 2000–3000 rpm.min⁻¹. The supernatant was analyzed by GC-MS on a TRACE GC ULTRA DSQ II instrument under the following conditions: 30 m × 0.25 mm × 0.25 µm, TG-5MS (Thermo) column; He, 0.8 mL/min; 40 °C, 3min; 50–310 °C, Δ10 °C/min, 70 eV. 2-Methylbutyric acid methyl ester (*t_R* 4.39 min) *m/z* [M+H]⁺ 117 (5), 101 (23), 88 (96), 57 (100), 41 (55), 29 (45), 27 (19), and *trans*-cinnamic acid methyl ester (*t_R* 13.29 min) *m/z* [M]⁺ *m/z*162 (40), 131 (100), 103 (66), 77 (32), from **1–3** was identified. *n*-decanoic acid methyl ester (*t_R* 12.37 min): *m/z* 172 [M]⁺ (4), 155 (5), 143 (30), 129 (5), 87 (59), 74 (100), 55 (18) from **1** was identified. *n*-dodecanoyl acid methyl ester (*t_R*15.17 min) *m/z* [M]⁺ 200 (1), 172 (1), 168 (10), 157 (15), 143(18), 129 (7), 87 (64), 74 (100), 55 (25), 43 (20), 41 (18) from **2-3** was identified. The 2-methylbutanoic acid as proved to be *S* configuration by comparing the specific rotation with that of authentic 2*S*-methylbutanoic acid (Yin, Y.Q., Wang, J.S., Luo, J.G., Kong, L.Y., 2009). Acidic hydrolysis of operculinic acid B liberated the aglycone, 11-hydroxyhexadecanoic acid, which was identified *S*-configuration (Yin, Y.Q., *et al.*, 2008) and the monosaccharides mixture was derivatized and detected with GC-MS by comparison with those of authentic samples to improve as D-fucose, L-rhamnose and D-glucose (Luo, J.G., Ma, L., Kong, L.Y., 2008).

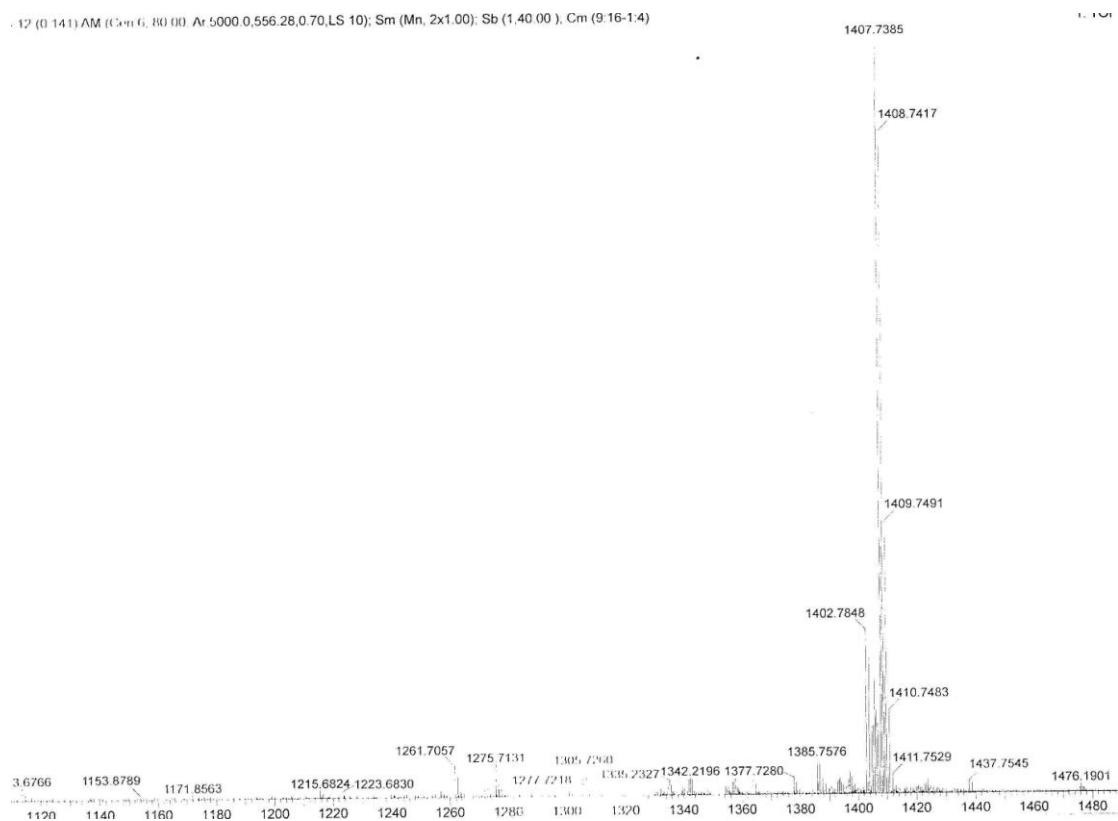


Figure S2. The HR-TOF-MS spectrum of compound **1**

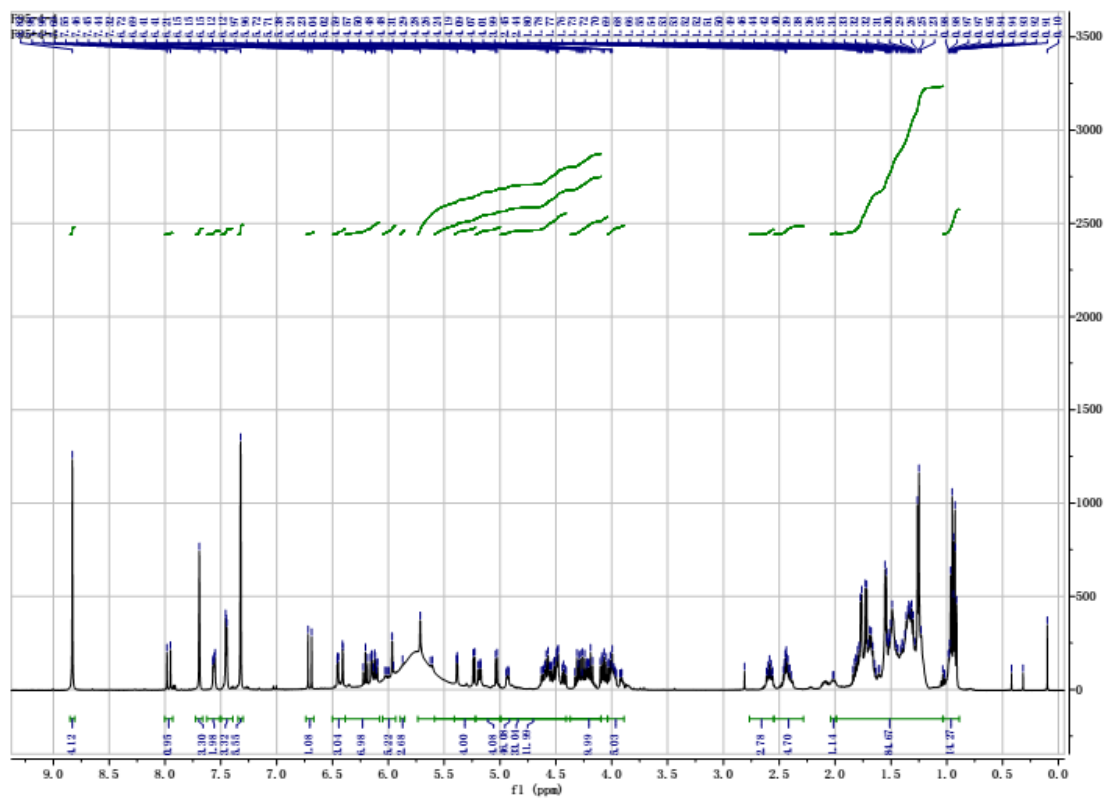


Figure S3. The ^1H -NMR spectrum of compound **1**

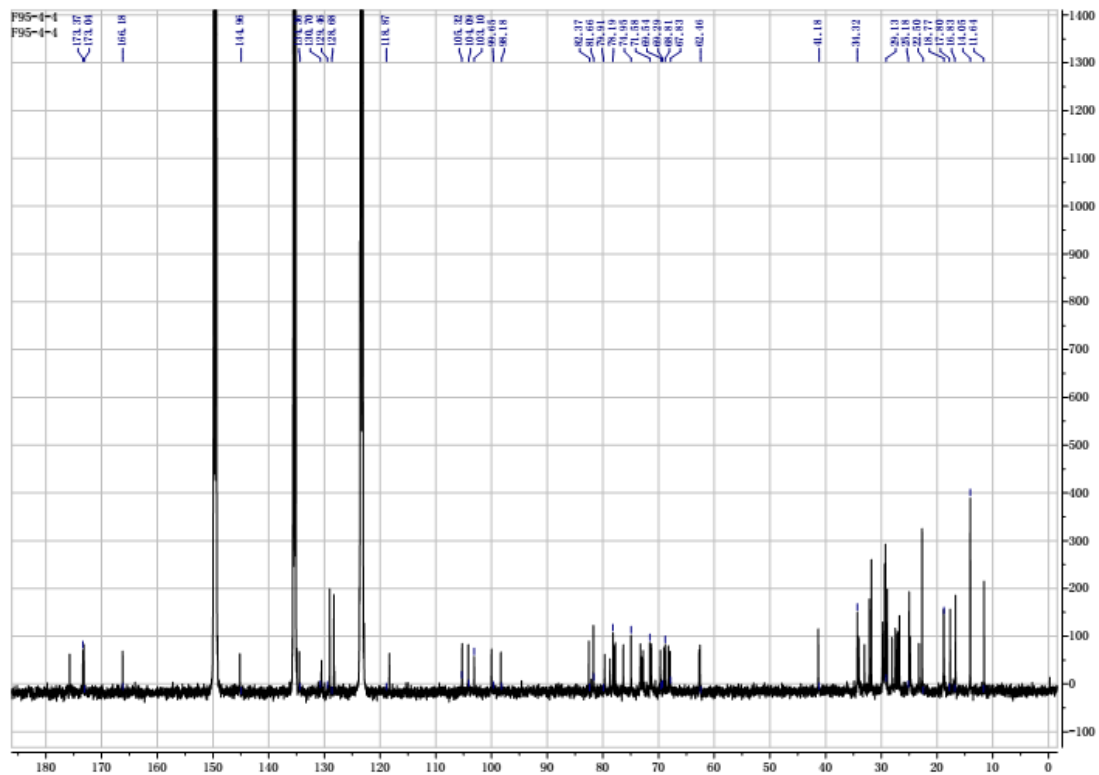


Figure S4. The ^{13}C -NMR spectrum of compound **1**

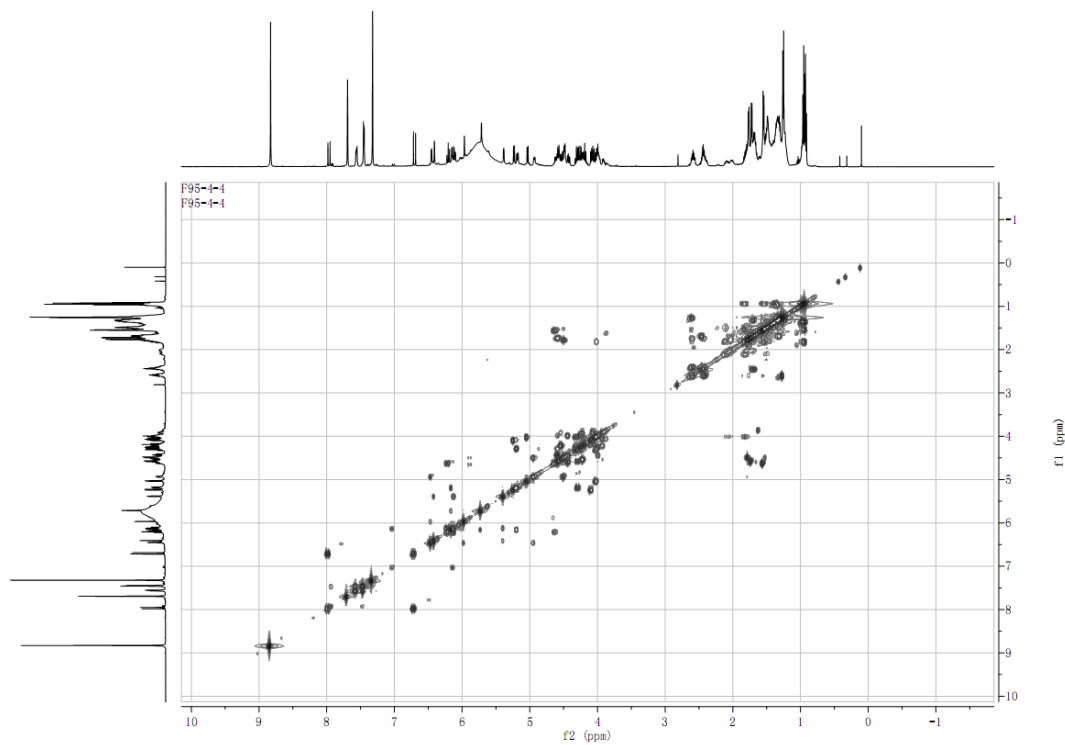


Figure S5. The TOCSY spectrum of compound **1**

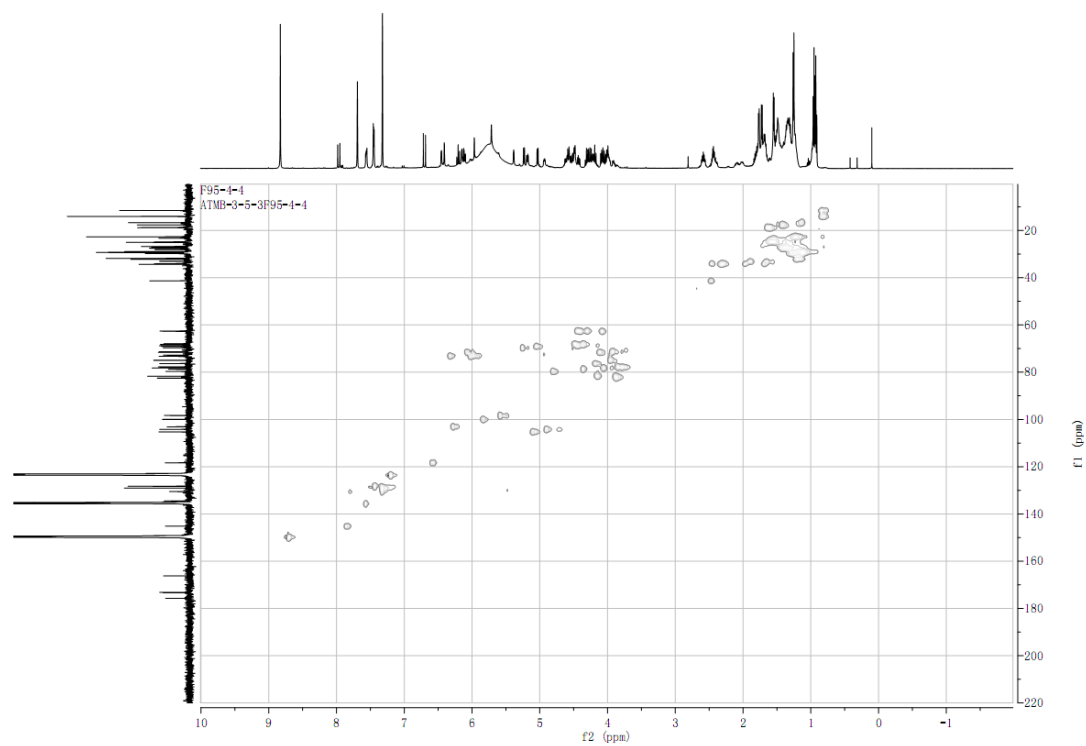


Figure S6. The HSQC spectrum of compound **1**

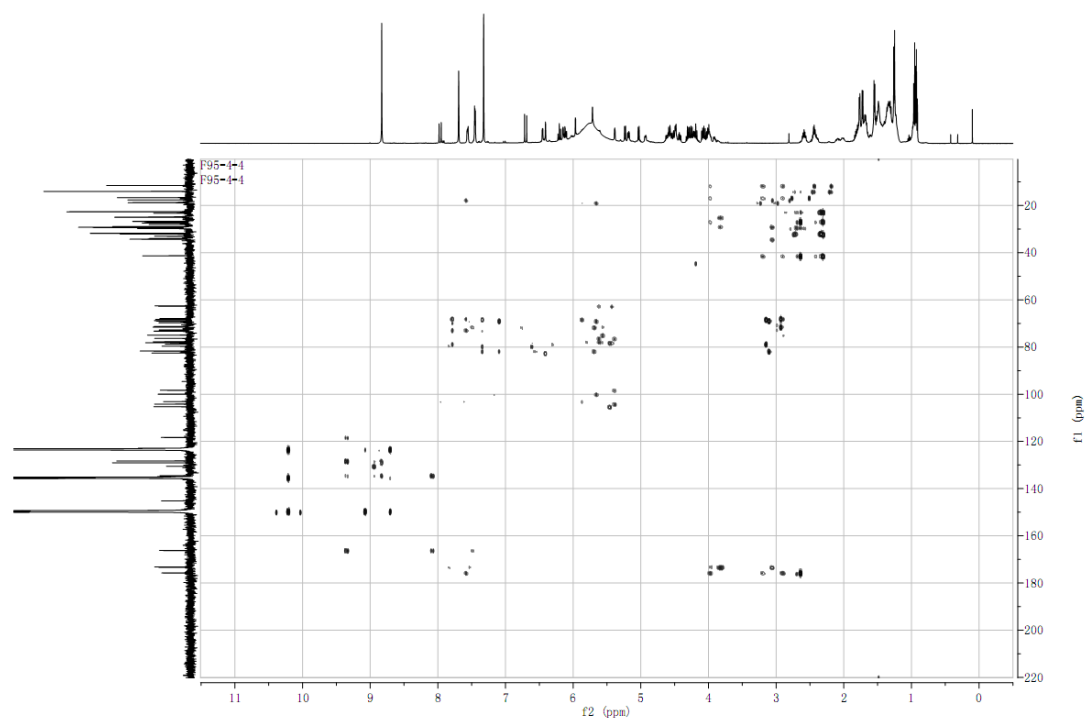


Figure S7. The HMBC spectrum of compound **1**

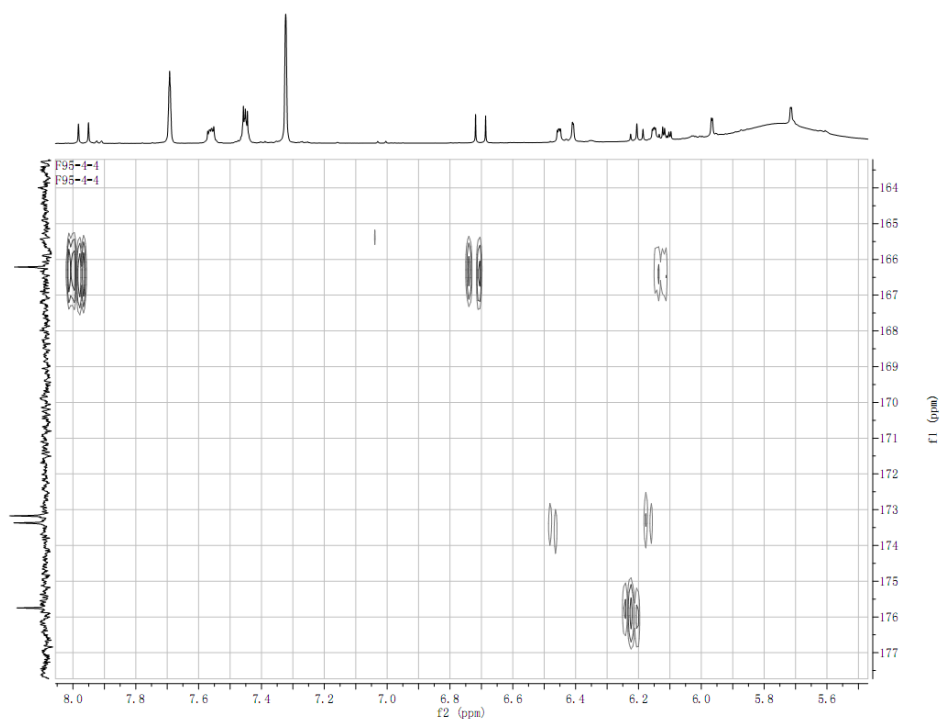


Figure S8. The enlarged HMBC spectrum of compound **1**

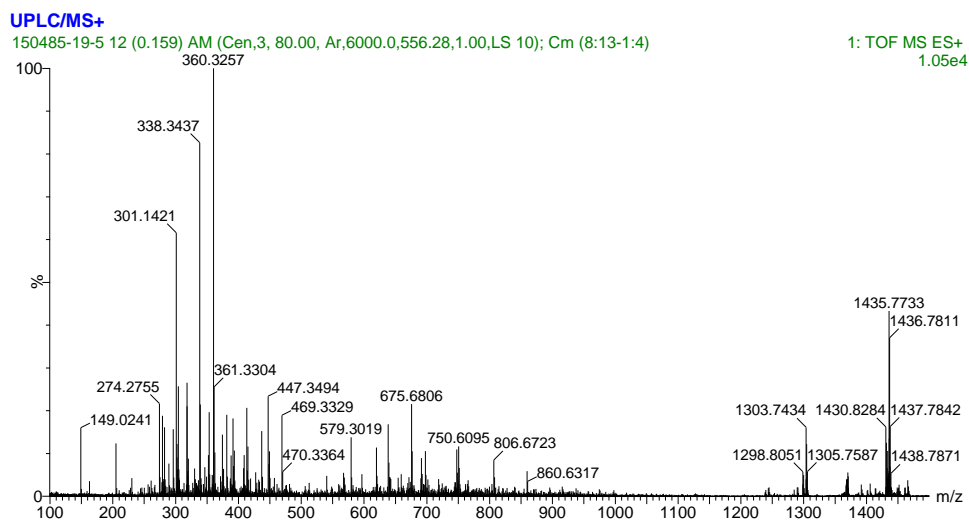


Figure S9. The HR-TOF-MS spectrum of compound **2**

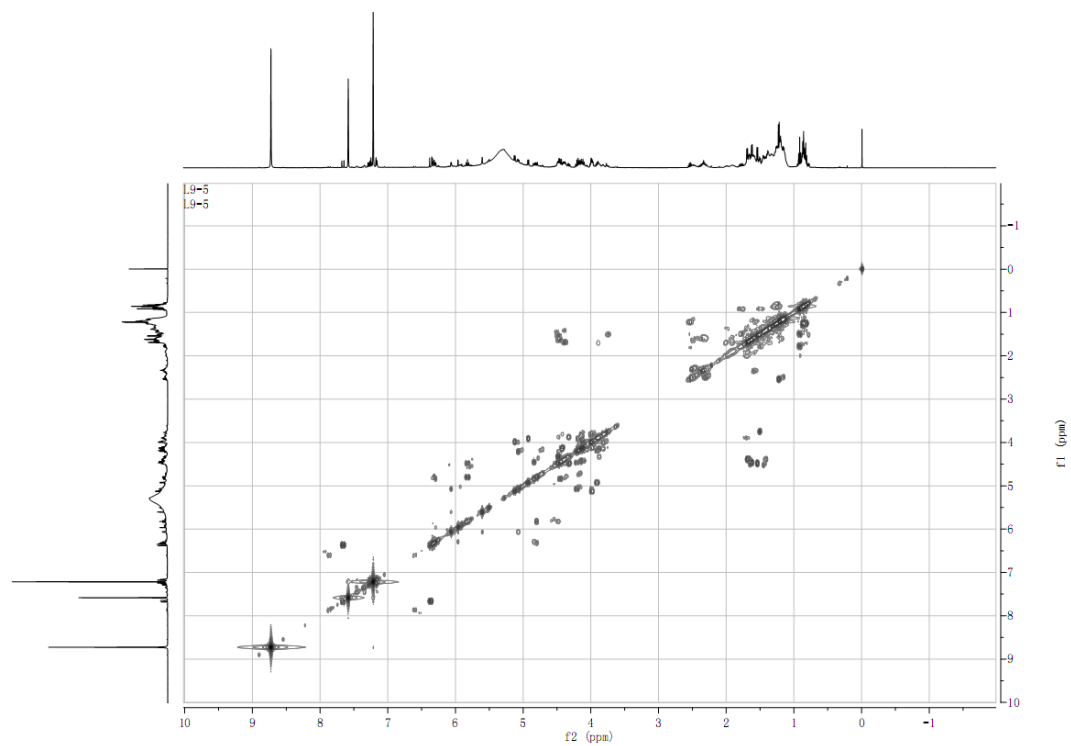


Figure S12. The TOCSY spectrum of compound **2**

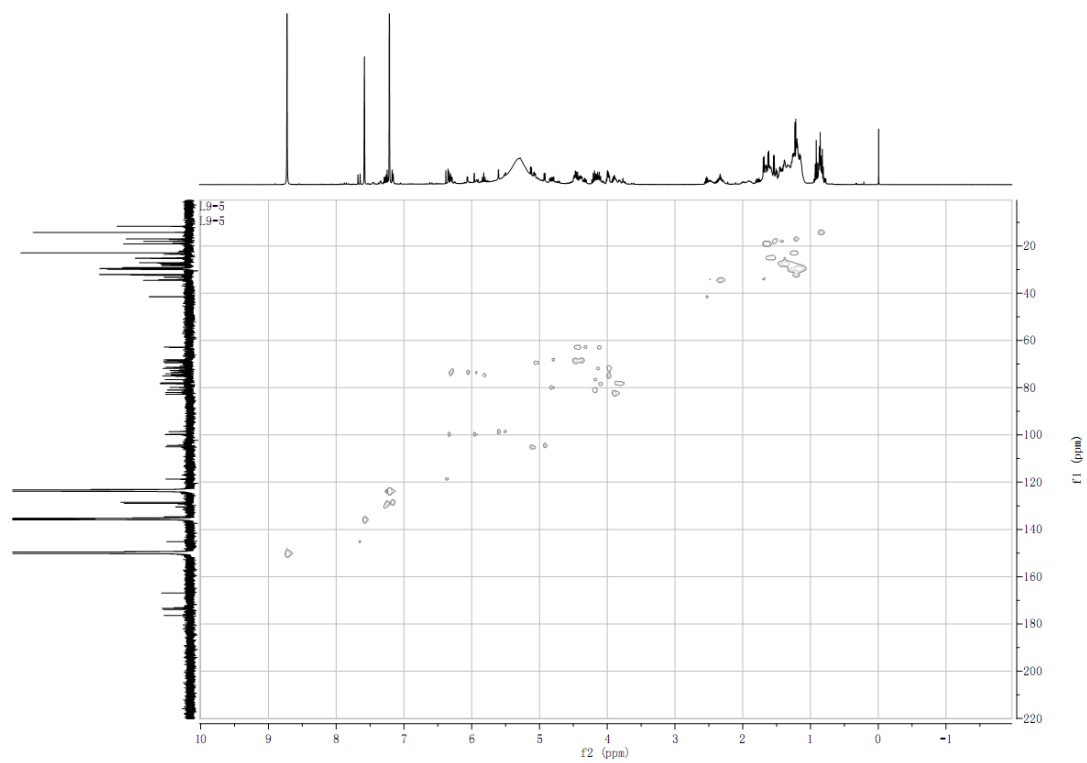


Figure S13. The HSQC spectrum of compound **2**

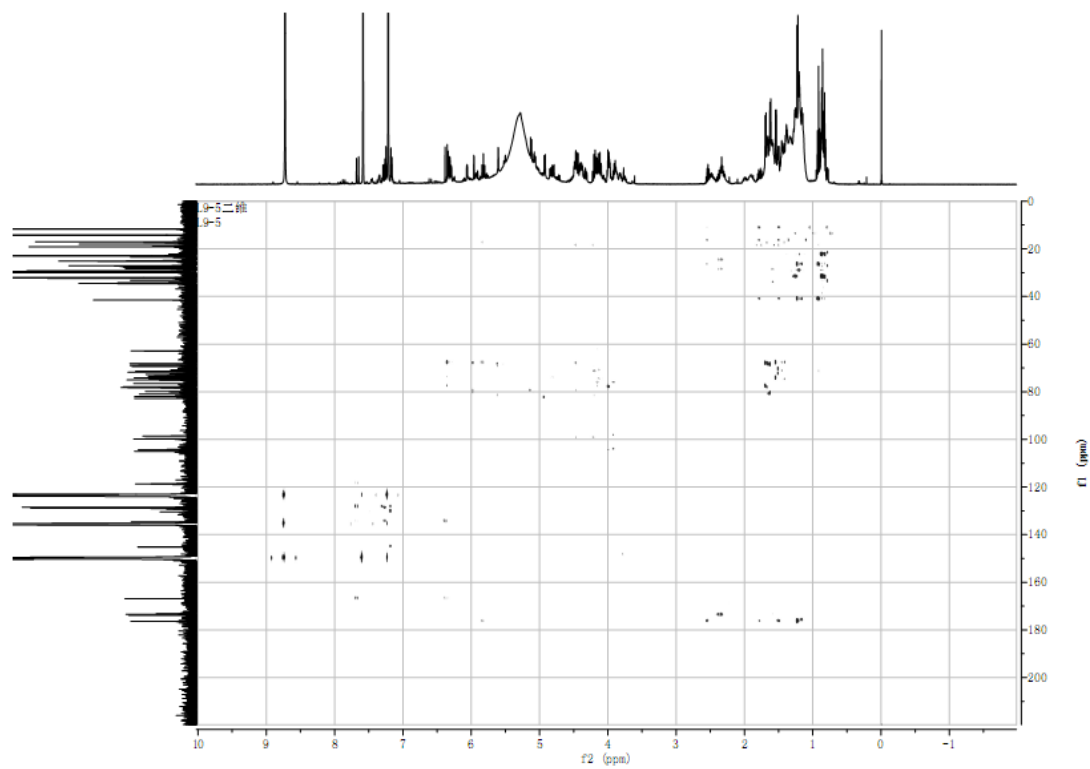


Figure S14. The HMBC spectrum of compound 2

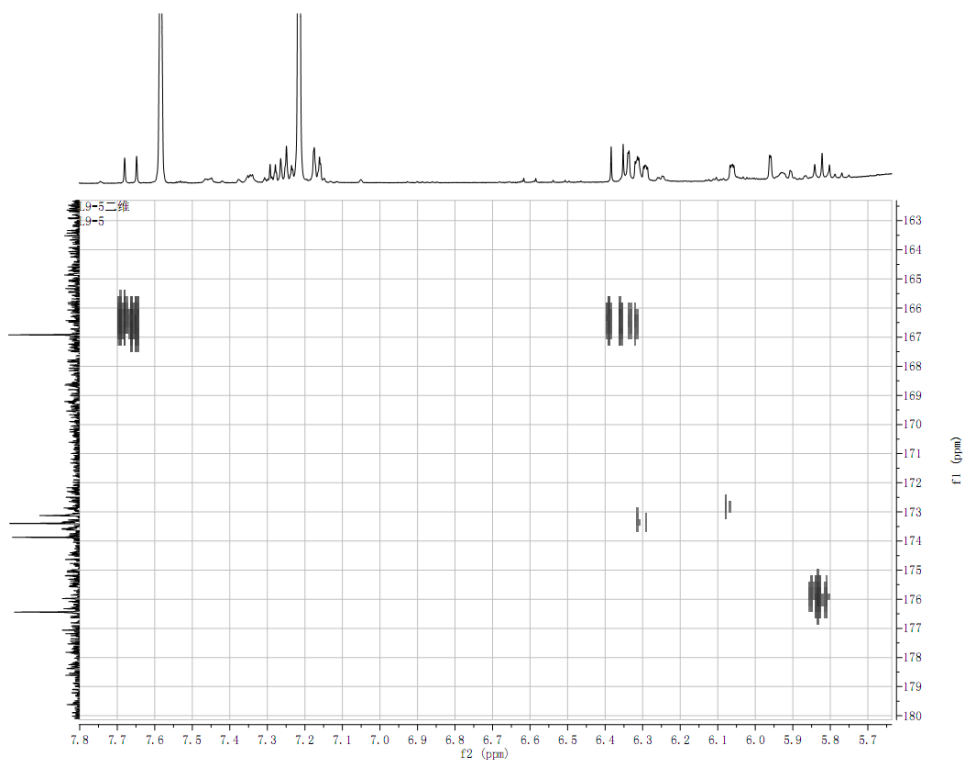


Figure S15. The enlarged HMBC spectrum of compound 2

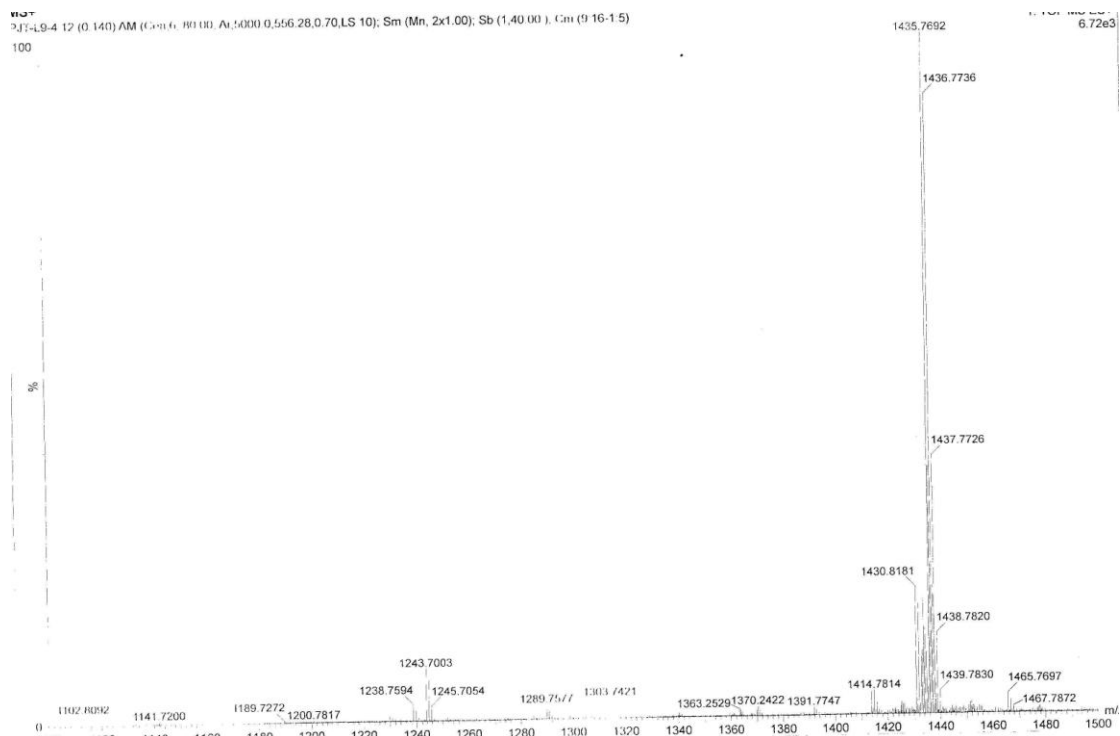


Figure S16. The HR-TOF-MS spectrum of compound **3**

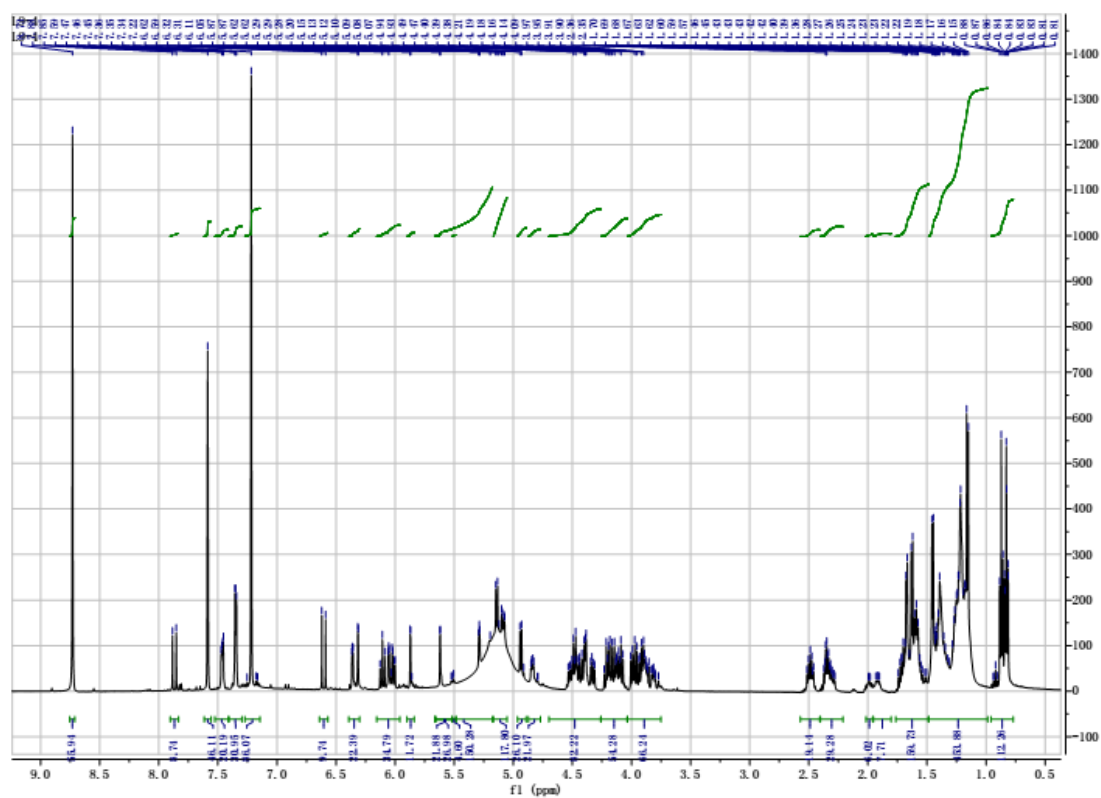


Figure S17. The $^1\text{H-NMR}$ spectrum of compound **3**

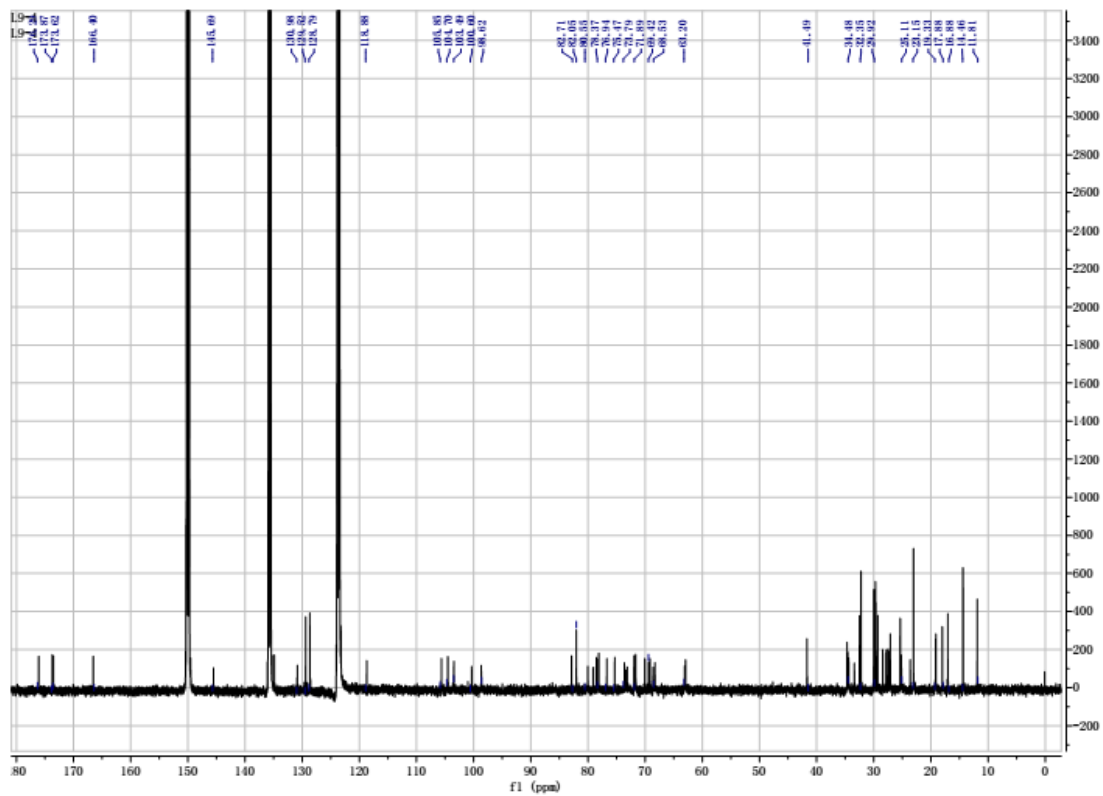


Figure S18. The ^{13}C -NMR spectrum of compound **3**

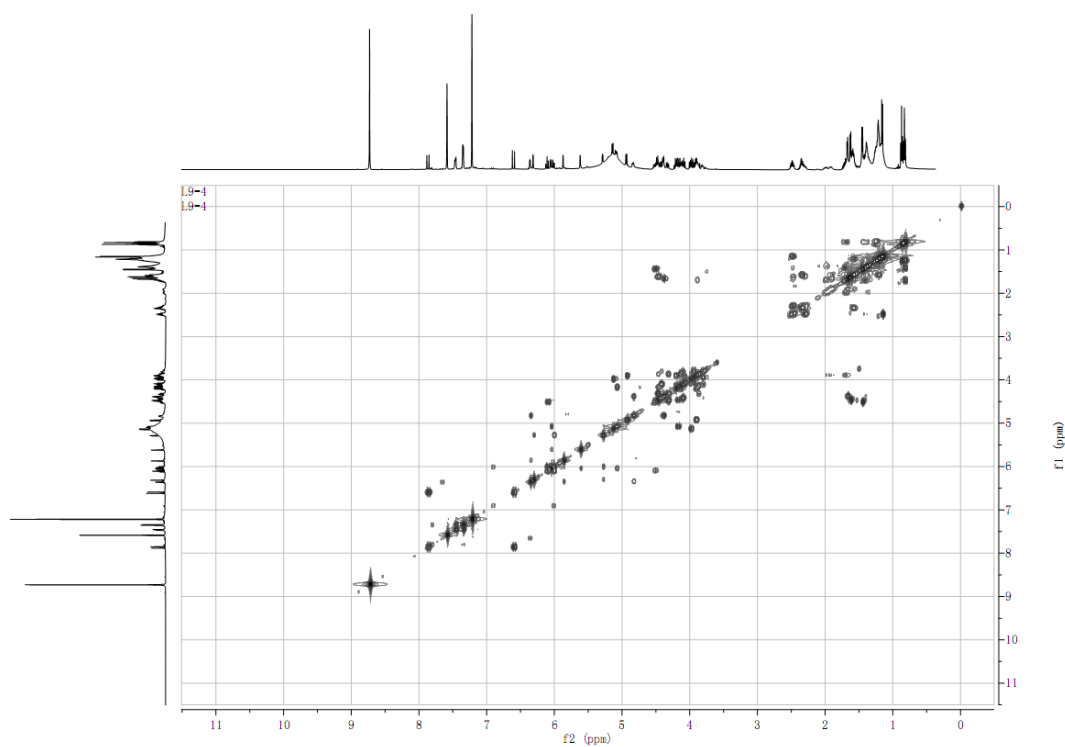


Figure S19. The TOCSY spectrum of compound **3**

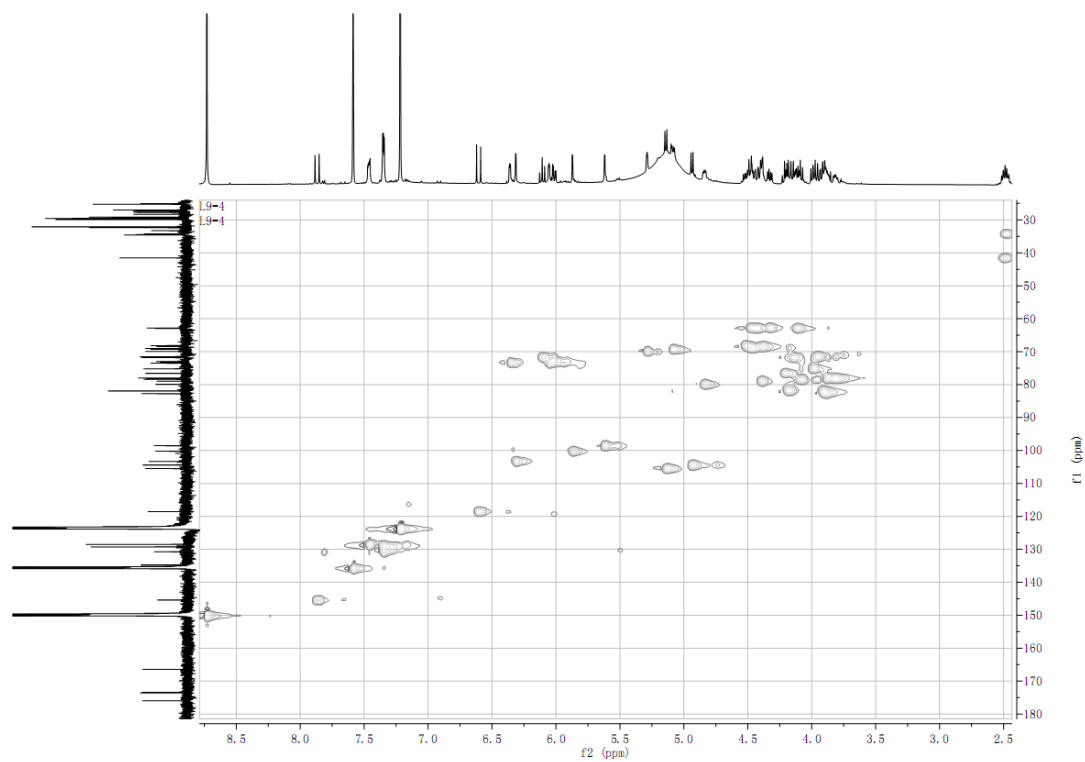


Figure S20. The HSQC spectrum of compound **3**

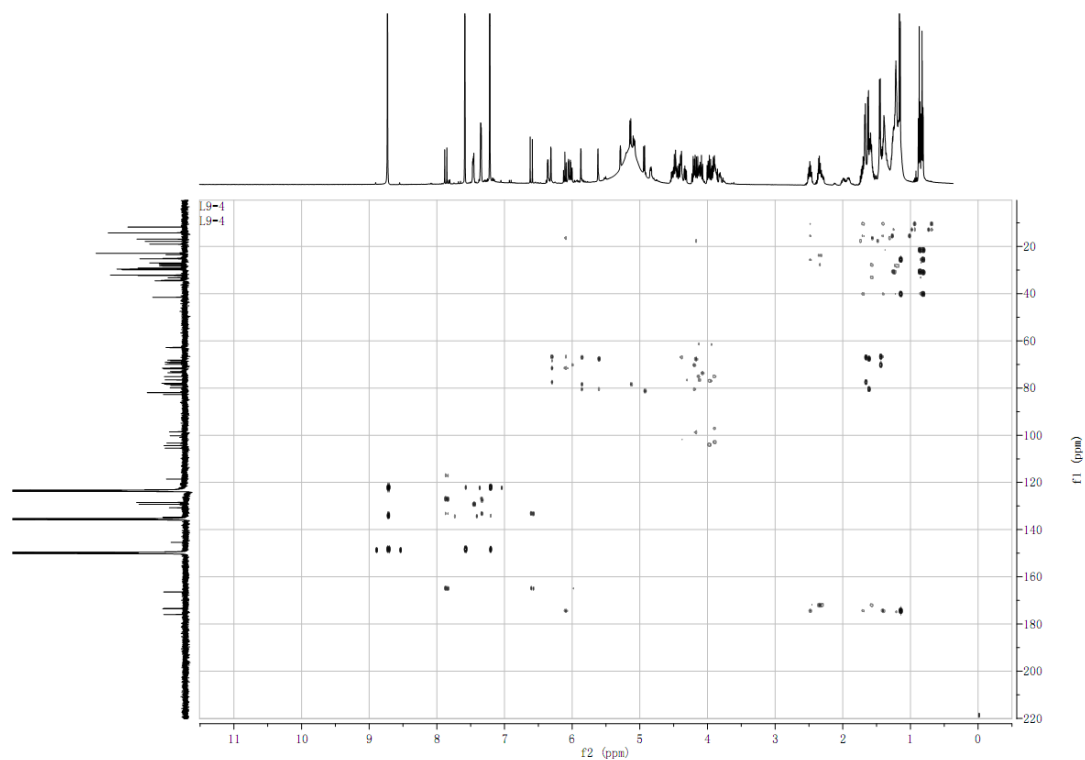


Figure S21. The HMBC spectrum of compound **3**

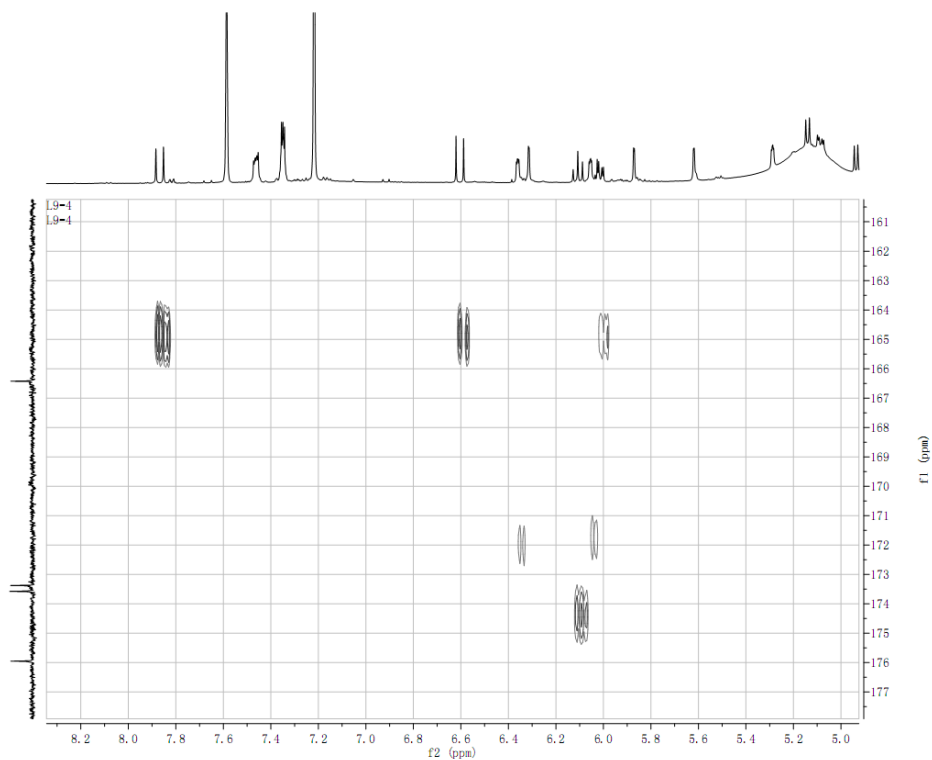
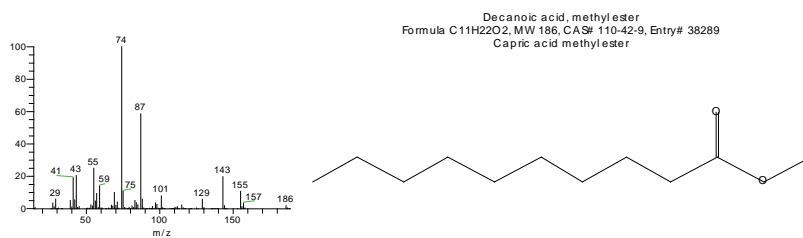
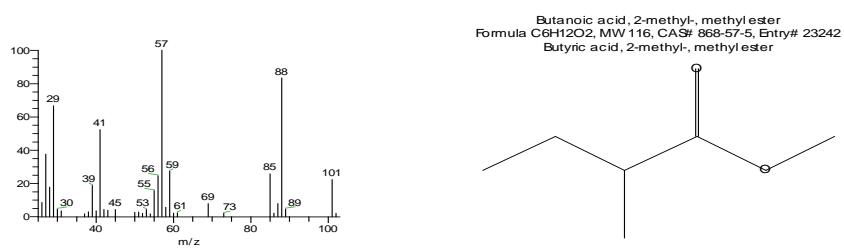


Figure S22. The enlarged HMBC spectrum of compound **3**



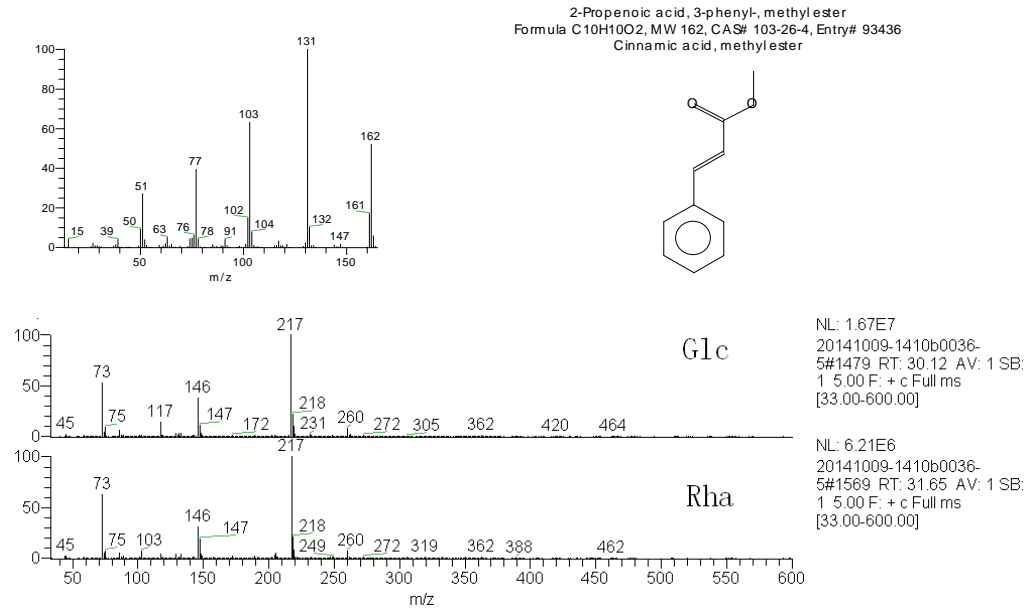


Fig S23. The GC-MS spectral of organic acid and sugar