Two new triterpenoid saponins from *Bupleurum marginatum* Wall. ex DC.

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Abstract

Two new triterpenoid saponins (**1** and **2**), together with two known saponins (**3** and **4**) were isolated from *Bupleurum marginatum* Wall. ex DC.. Their structures were elucidated by the comprehensive spectroscopic analysis. Compounds **1** and **2** represented the rare example of an oleanane-type triterpenoid with two sugar moieties at C-3 and C-28. The cytotoxic activity of four compounds was evaluated against normal heptocell BRL-3A *in vitro*.

Keywords

Bupleurum marginatum Wall. ex DC.; medicinal plant; triterpenoid saponins; cytotoxicity

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Table S1. ^{1}H NMR Data for compounds 1 and 2

No.	Comp.1	Comp.2	No.	Comp.1	Comp.2
1	1.90 m, 1.06 m	1.91 m, 1.03 m		**Glucose**	**Glucose**
				(1→C3 of agly)	**(1→C3 of agly)**
2	1.98 m, 1.76 m	1.97 m, 1.87 m	**1**	4.38 d, *J* = 7.9 Hz	4.54 d, *J* = 7.7 Hz
3	3.22 m	3.44 m	**2**	3.26 m	3.26 m
4			**3**	3.47 m	3.57 m
5	0.88 m	3.33 m	**4**	3.61 m	3.67 m
6	1.65m, 1.48 m	1.59 m, 1.45 m	**5**	3.43 m	3.58 m
7	2.48 m, 1.86 m	2.55 m, 1.96 m	**6**	4.13 m, 3.79 m	3.84 m
8				**Rhamnose**	**Rhamnose**
				(1→C4 of Glc)	**(1→C3 of Glc)**
9	2.01 m	2.07 m	**1**	4.92 d, *J* = 7.7 Hz	4.60 d, *J* = 7.7 Hz
10			**2**	3.89 m	3.87 m
11	5.62 d, *J* = 10.5 Hz	5.61 d, *J* = 11 Hz	**3**	3.65 m	3.30 m
12	6.45 d, *J* = 10.5 Hz	6.50 d, *J* = 11 Hz	**4**	3.25 m	3.56
13			**5**	3.96 m	3.40 m
14			**6**	1.29 d, *J* = 6.2 Hz	1.29 d, *J* = 6.4 Hz
15	1.98 m, 1.44 m	1.95 m, 1.45 m		**Glucose'**	**Xylose**
				(1→C6 of Glc)	**(1→C4 of Glc)**
16	4.21 m	4.06 m	**1**	4.34 d, *J* = 7.8 Hz	4.45 d, *J* = 7.8 Hz
17			**2**	3.26 m	3.69 m
18			**3**	3.37 m	3.30 m
19	1.42 m	1.51 m, 1.38 m	**4**	3.29 m	3.50 m
20			**5**	3.53 m	3.90 m
21	1.99 m, 1.77 m	1.77 m, 1.33 m	**6**	3.70 m	
22	1.76 m, 1.20 m	2.04 m, 1.66 m		**Glucose"**	**Glucose'**
				(1→C28)	**(1→C28)**
23	1.08 s	3.70 m	**1**	4.20 d, *J* =7.8 Hz	4.27 d, *J* =7.8 Hz
24	0.87 s	0.72 s	**2**	3.20 m	3.24 m
25	0.94 s	0.97 s	**3**	3.36 m	3.37 m
26	0.76 s	0.75 s	**4**	3.28 m	3.26 m
27	1.26 s	1.27 s	**5**	3.33 m	3.30 m
28	4.17 m, 3.23 m	3.72 m, 3.25 m	**6**	3.89 m	3.89 m
29	0.85 s	0.92 s			
30	3.30 m, 3.28 m	3.99 m, 3.29 m			

Table S2. ^{13}C NMR Data for compounds 1 and 2

No.	Comp.1	Comp.2	No.	Comp.1	Comp.2
1	38.0	37.7		**Glucose**	**Glucose**
				(1→C3 of agly)	**(1→C3 of agly)**
2	25.6	24.5	**1**	105.2	106.2
3	89.5	84.4	**2**	76.6	74.6
4	41.0	42.6	**3**	75.6	85.7
5	55.2	46.9	**4**	78.9	81.9
6	18.0	17.6	**5**	72.3	76.2
7	32.4	32.7	**6**	68.0	60.7
8	40.6	41.1		**Rhamnose**	**Rhamnose**
				(1→C4 of Glc)	**(1→C3 of Glc)**
9	53.5	53.5	**1**	101.6	103.3
10	38.9	36.4	**2**	71.0	69.3
11	126.0	125.5	**3**	70.7	70.2
12	125.3	125.4	**4**	73.5	76.0
13	136.5	136.2	**5**	69.3	70.7
14	36.1	36.0	**6**	16.5	15.5
15	30.6	30.6		**Glucose'**	**Xylose**
				(1→C6 of Glc)	**(1→C4 of Glc)**
16	67.7	67.8	**1**	103.5	103.6
17	43.5	44.3	**2**	74.3	70.3
18	130.2	130.7	**3**	76.8	70.2
19	32.0	31.5	**4**	76.7	69.3
20	37.0	40.5	**5**	73.8	63.8
21	28.6	29.1	**6**	61.5	
22	23.2	22.5		**Glucose"**	**Glucose'**
				(1→C28)	**(1→C28)**
23	26.8	63.8	**1**	103.4	103.4
24	15.1	11.4	**2**	73.9	73.9
25	17.3	17.7	**3**	76.7	76.8
26	16.2	16.2	**4**	70.3	74.6
27	20.7	20.7	**5**	70.1	76.6
28	71.6	80.3	**6**	61.2	61.4
29	19.4	19.7			
30	72.2	65.6			

Figure S1. The key HMBC (red arrows) and ^{1}H-^{1}H COSY (blue bold lines) correlations of compound 1

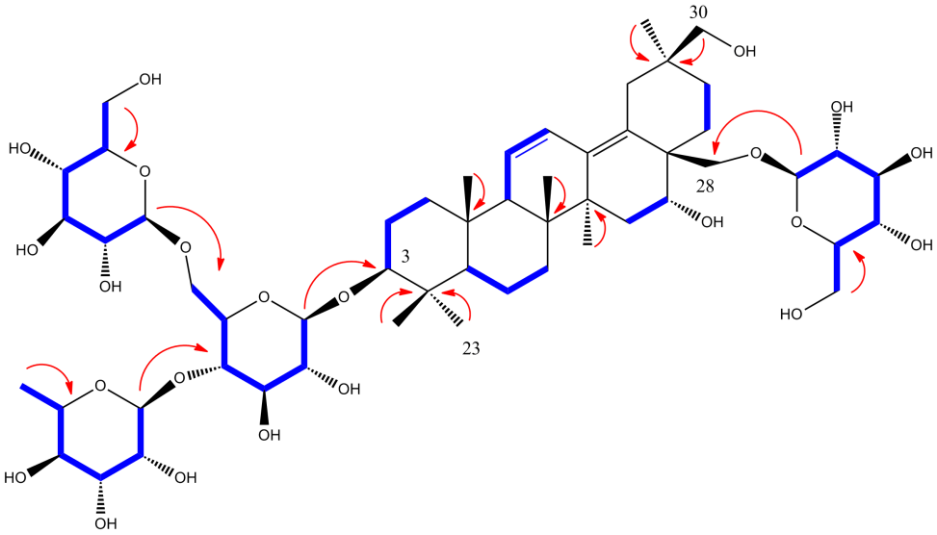


Figure S2. The key HMBC (red arrows) and ^{1}H-^{1}H COSY (blue bold lines) correlations of compound 2

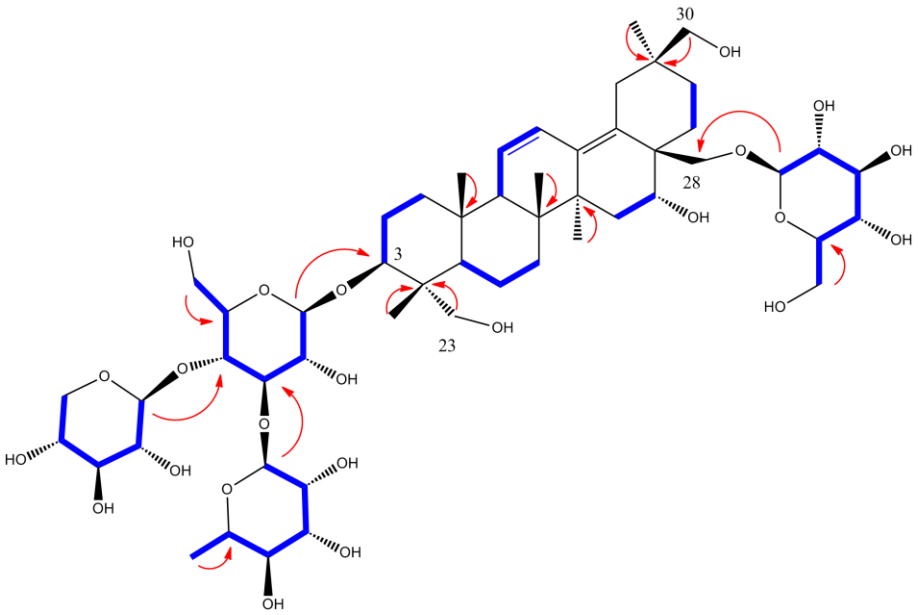


Figure S3. ^{1}H NMR (700 MHz, Methanol-D4) spectrum of compound 1

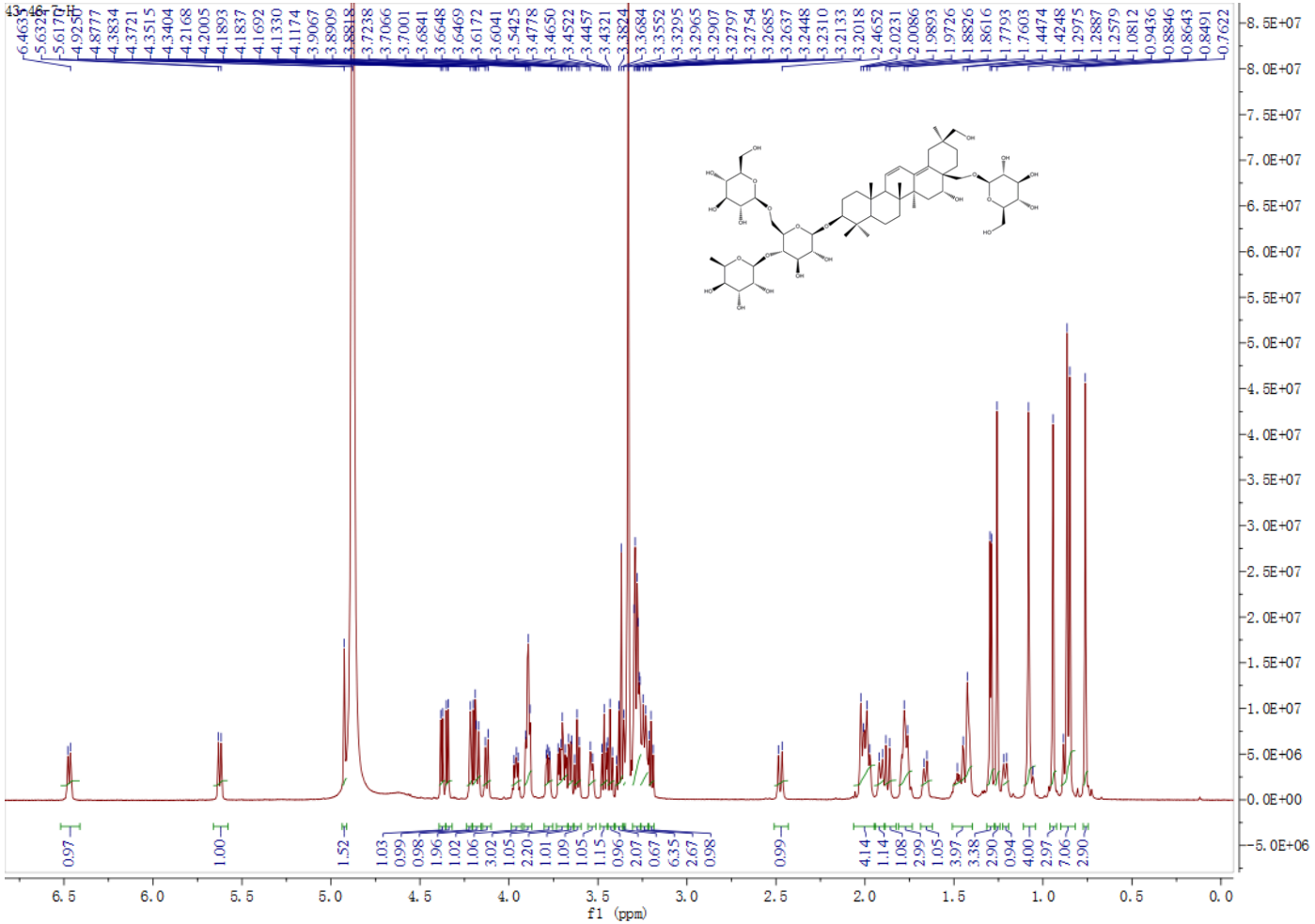


Figure S4. ^{13}C NMR (176 MHz, Methanol-D4) spectrum of compound 1

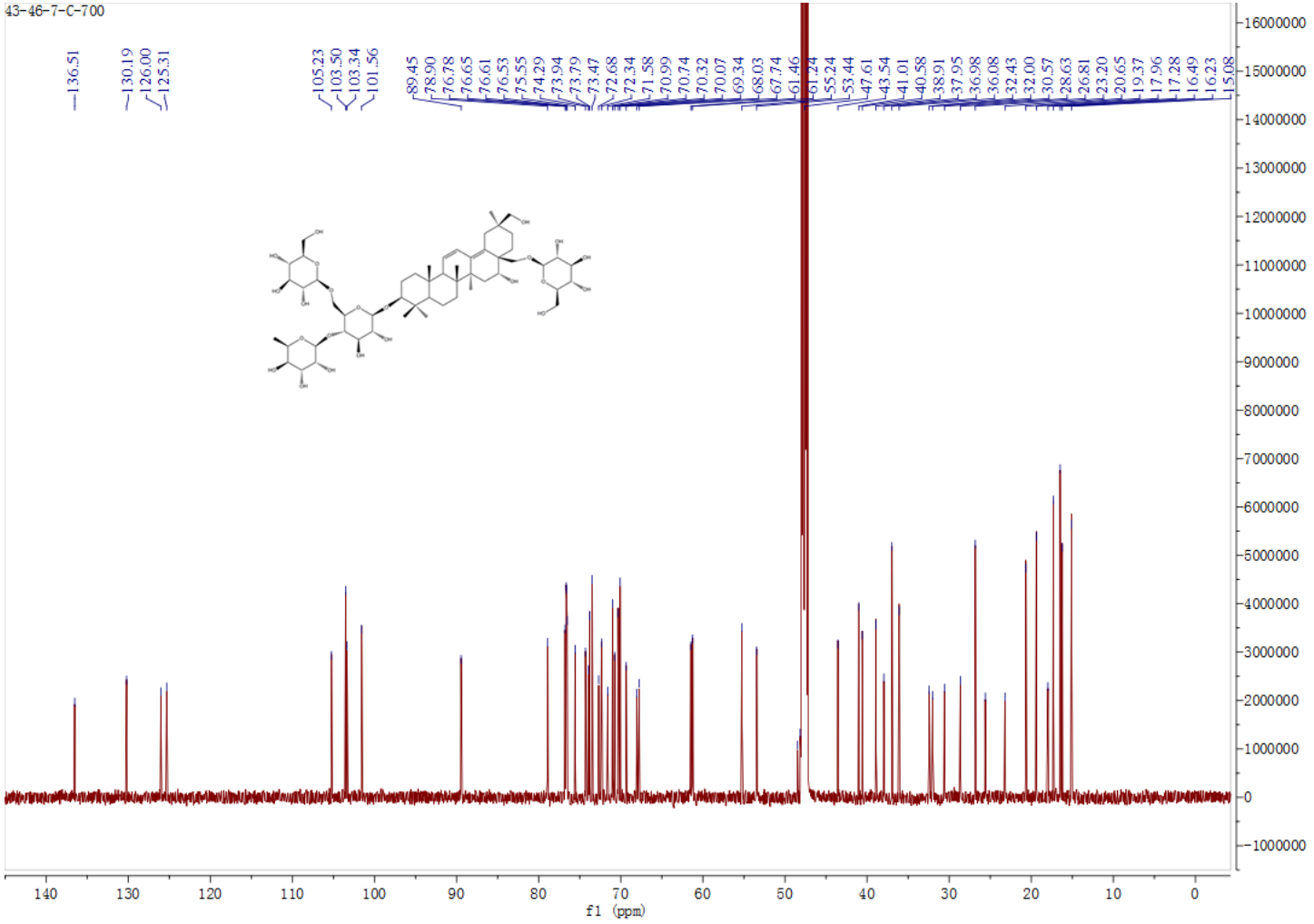


Figure S5. DEPT 135 (176 MHz, Methanol-D4) spectrum of compound 1

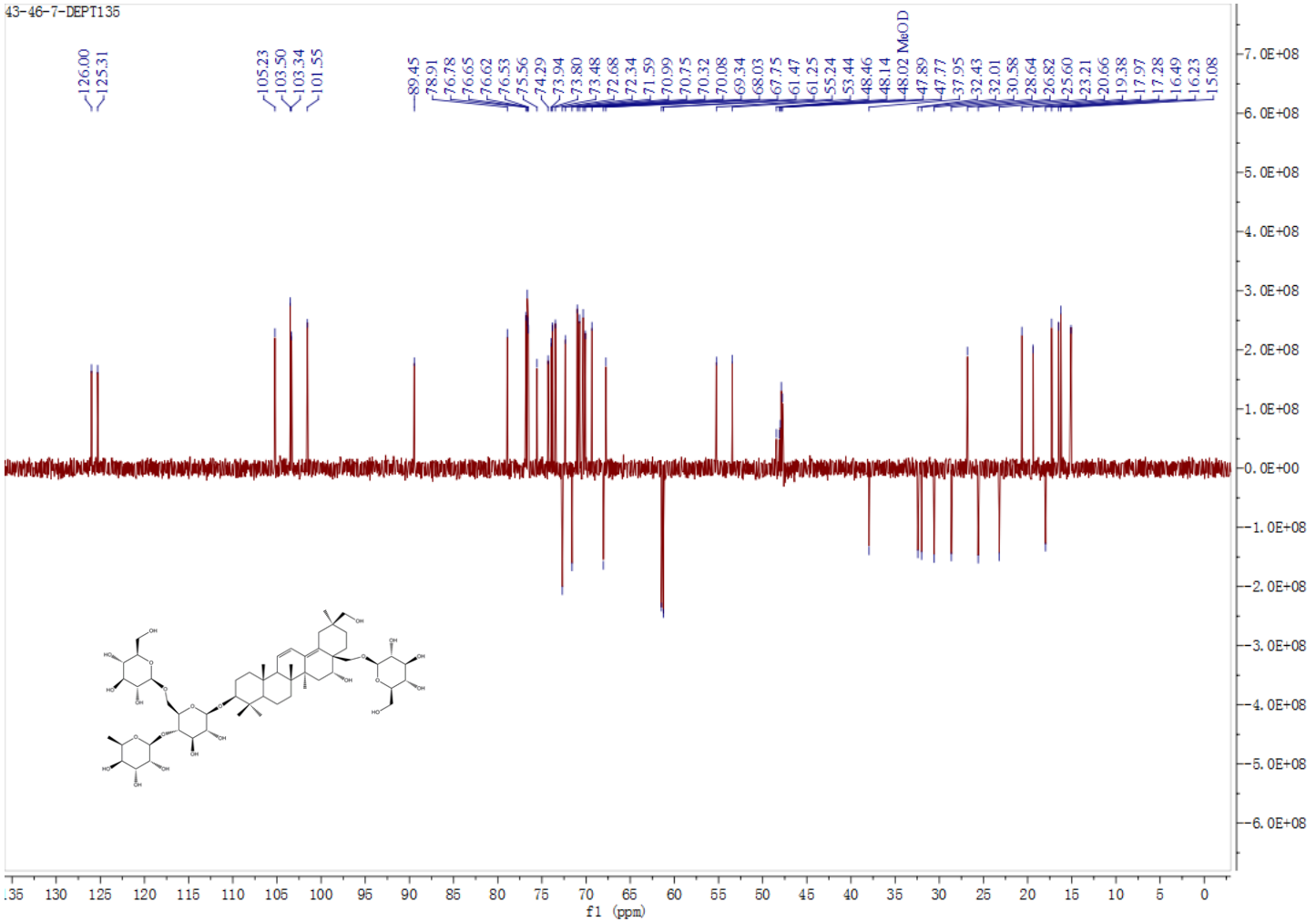


Figure S6. HSQC (700 MHz, Methanol-D4) spectrum of compound 1

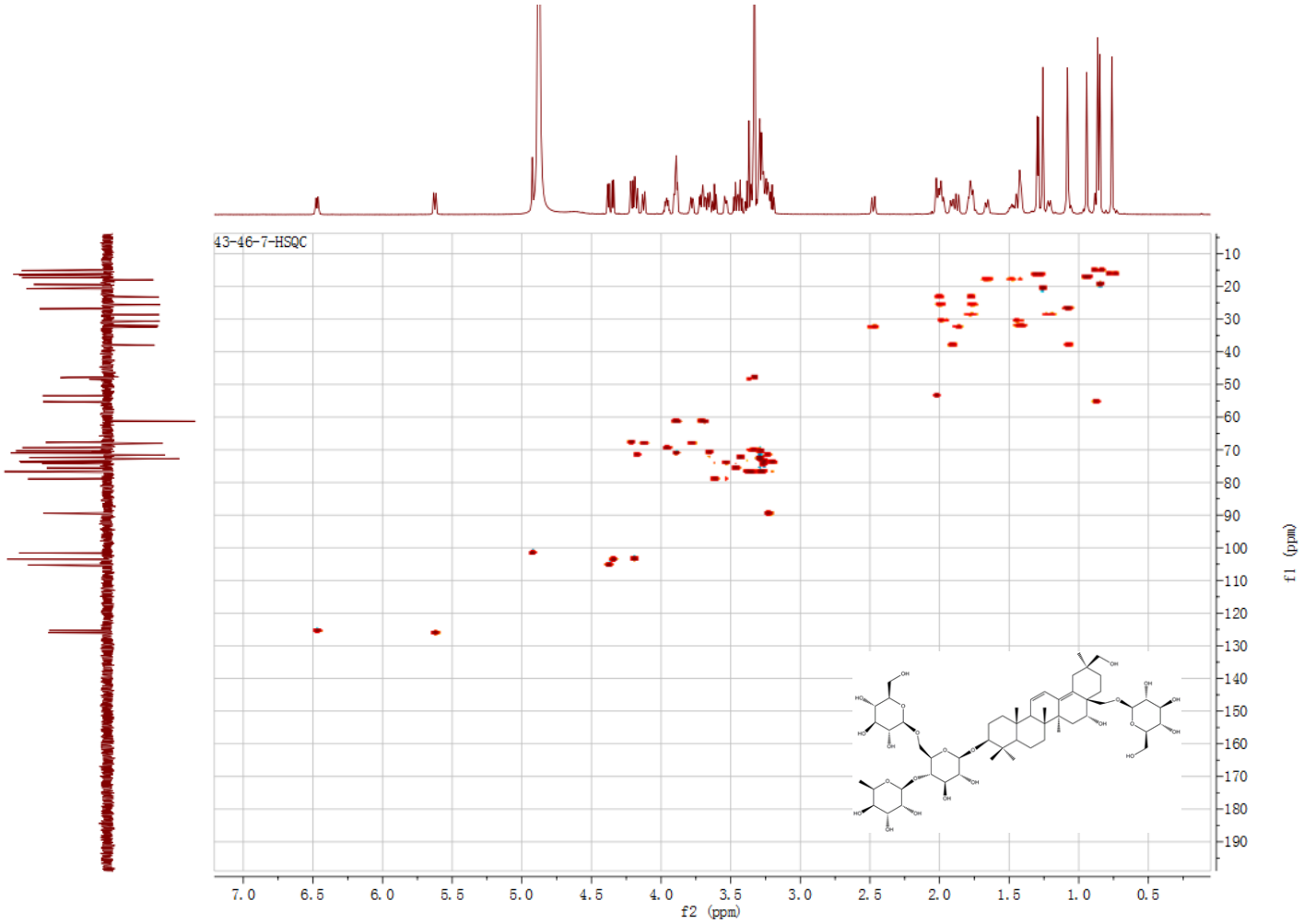


Figure S7. HMBC (700 MHz, Methanol-D4) spectrum of compound 1

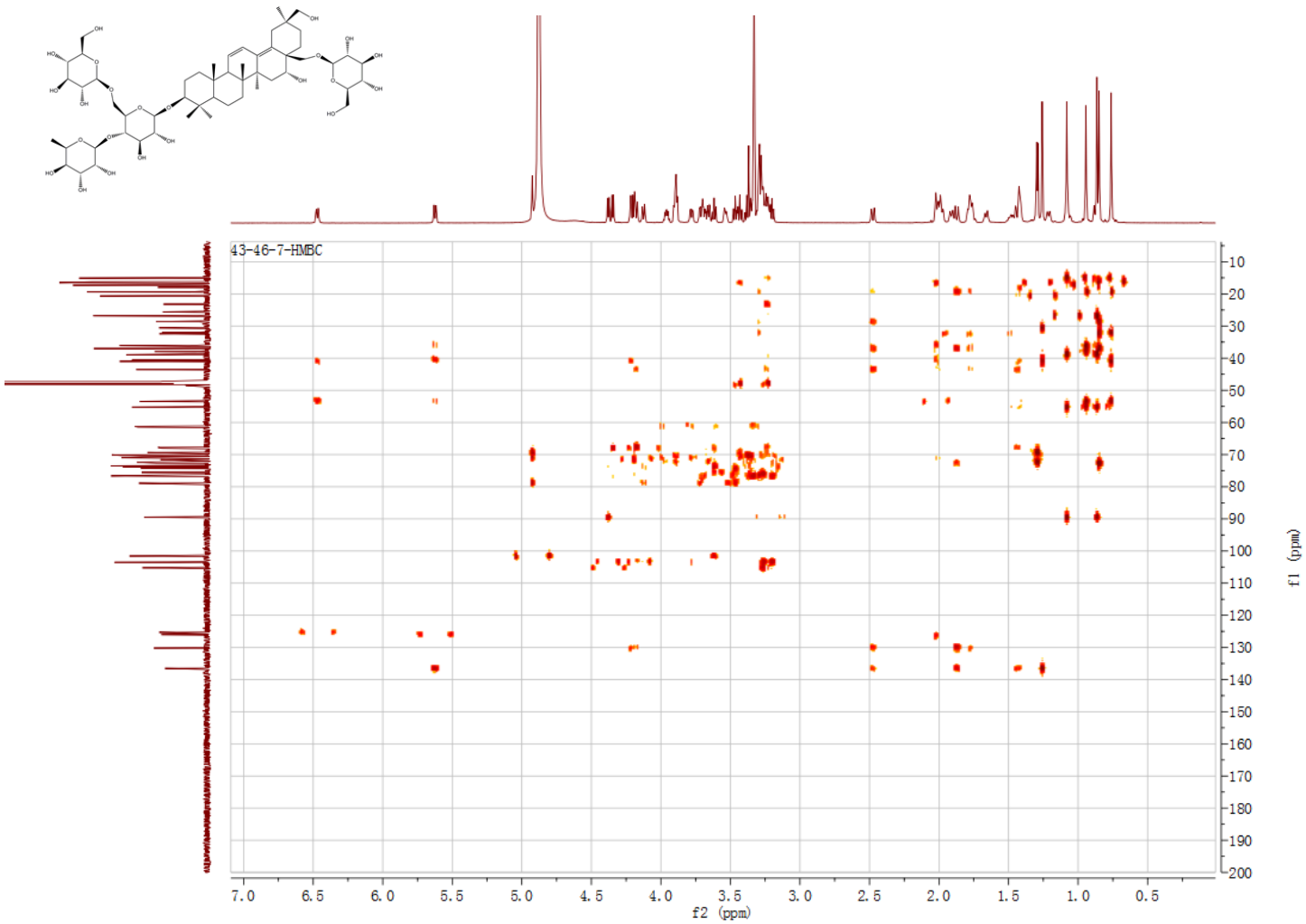


Figure S8. ^{1}H-^{1}H COSY (700 MHz, Methanol-D4) spectrum of compound 1

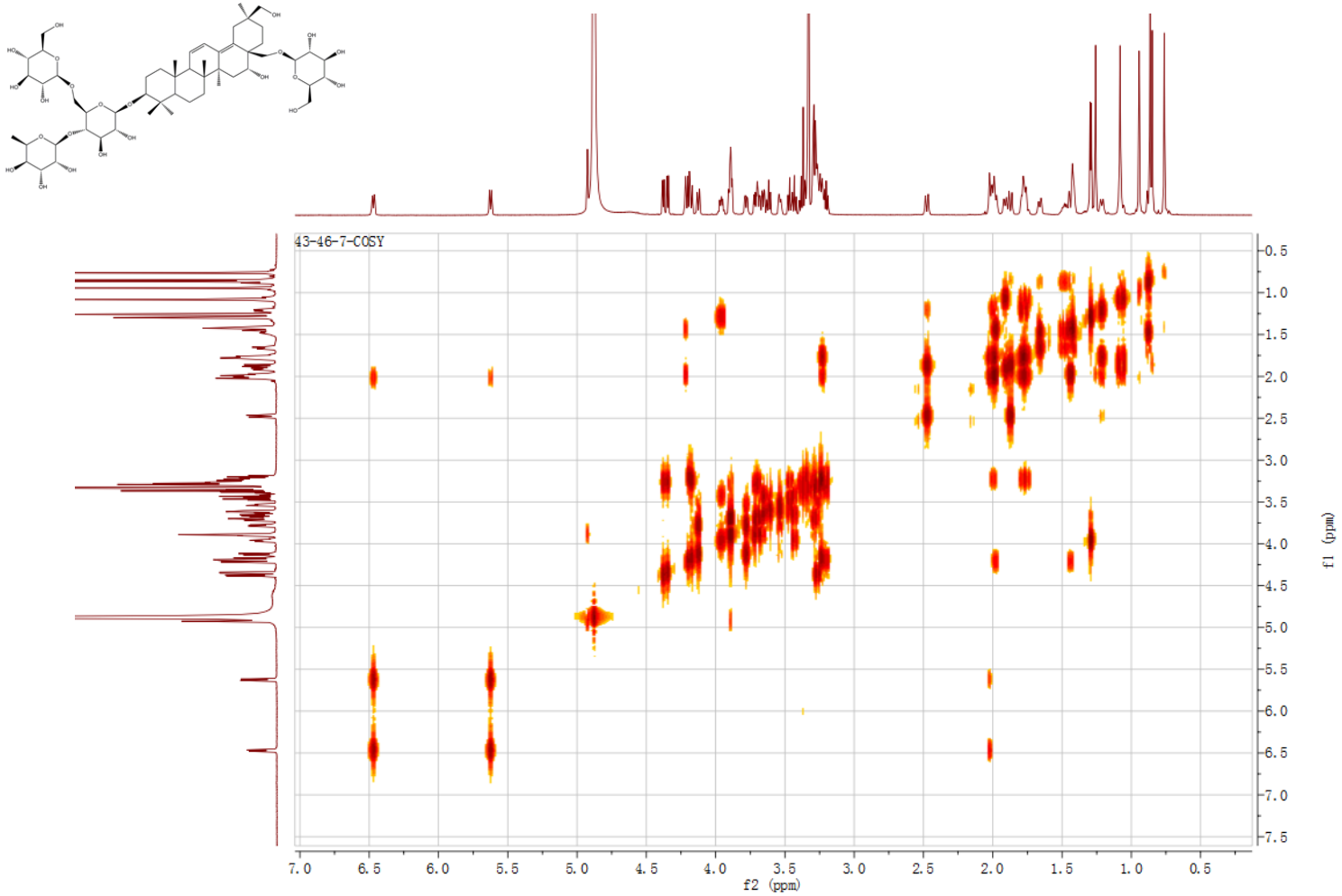
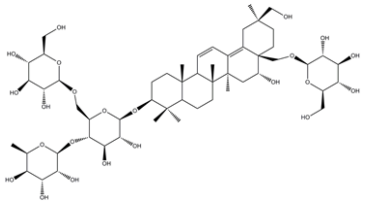


Figure S9. HR-ESI-MS of compound 1



Mass Spectrum SmartFormula Report

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Comment			

Acquisition Parameter

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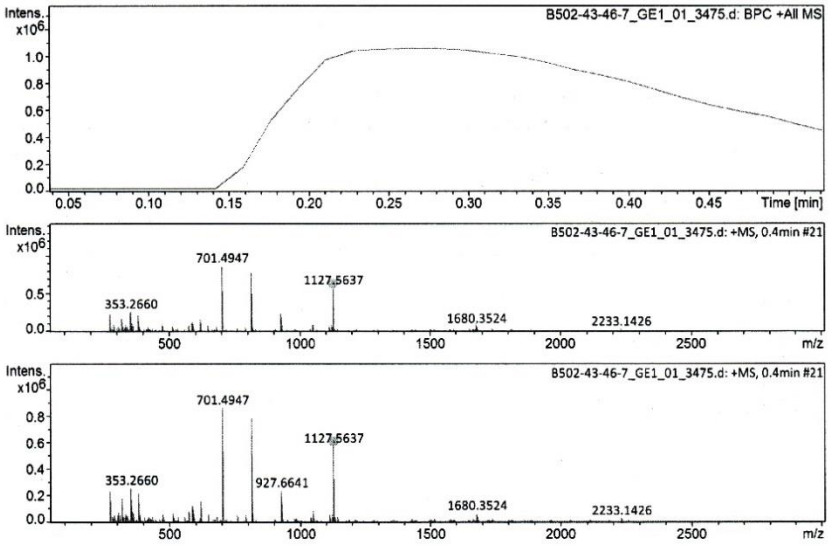
		Set Corona	0 nA	Set APCI Heater	0 °C



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B502-43-46-7_GE1_01_3475.d

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Figure S10. ^{1}H NMR (700 MHz, Methanol-D4) spectrum of compound 2

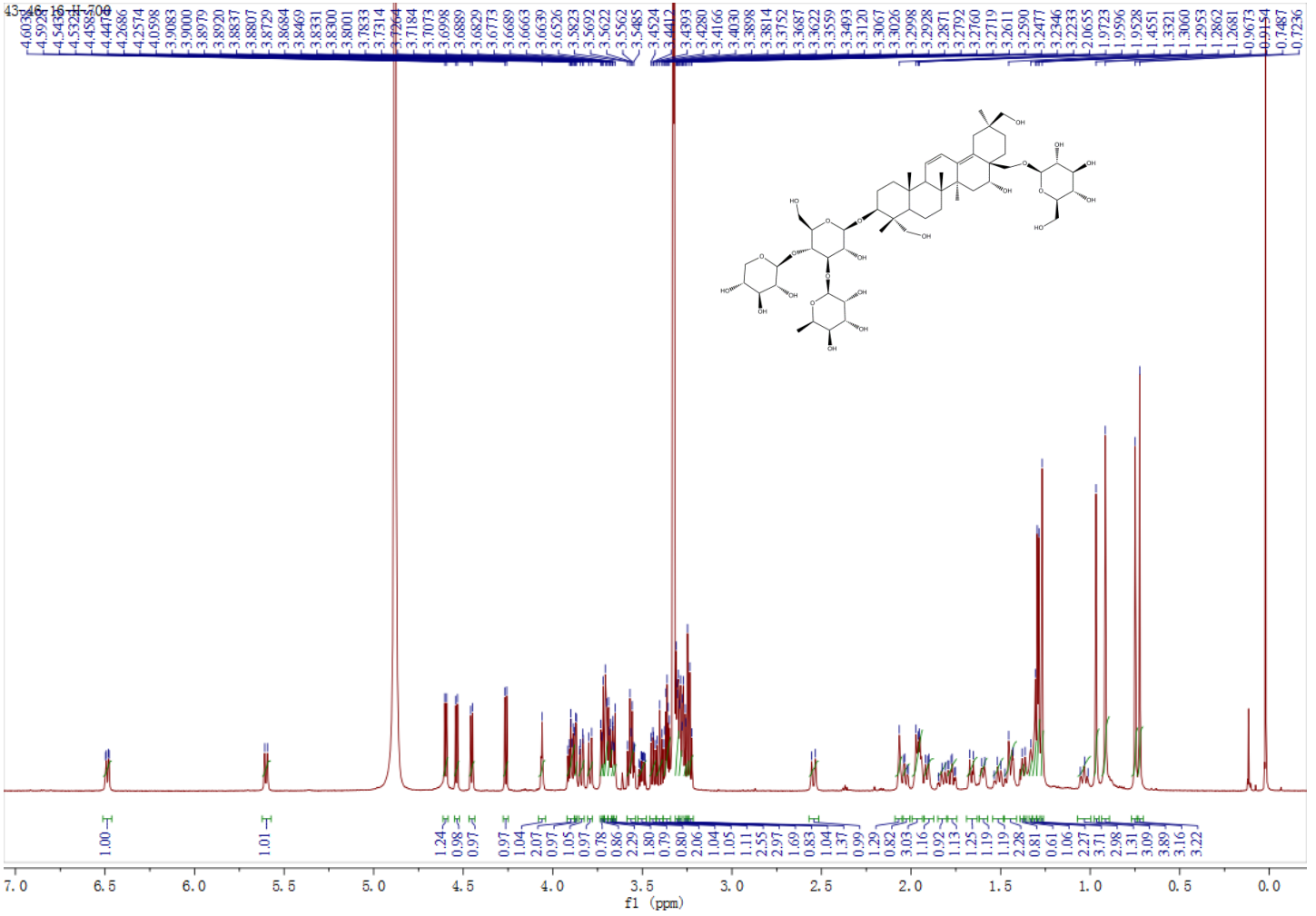


Figure S11. ^{13}C NMR (176 MHz, Methanol-D4) spectrum of compound 2

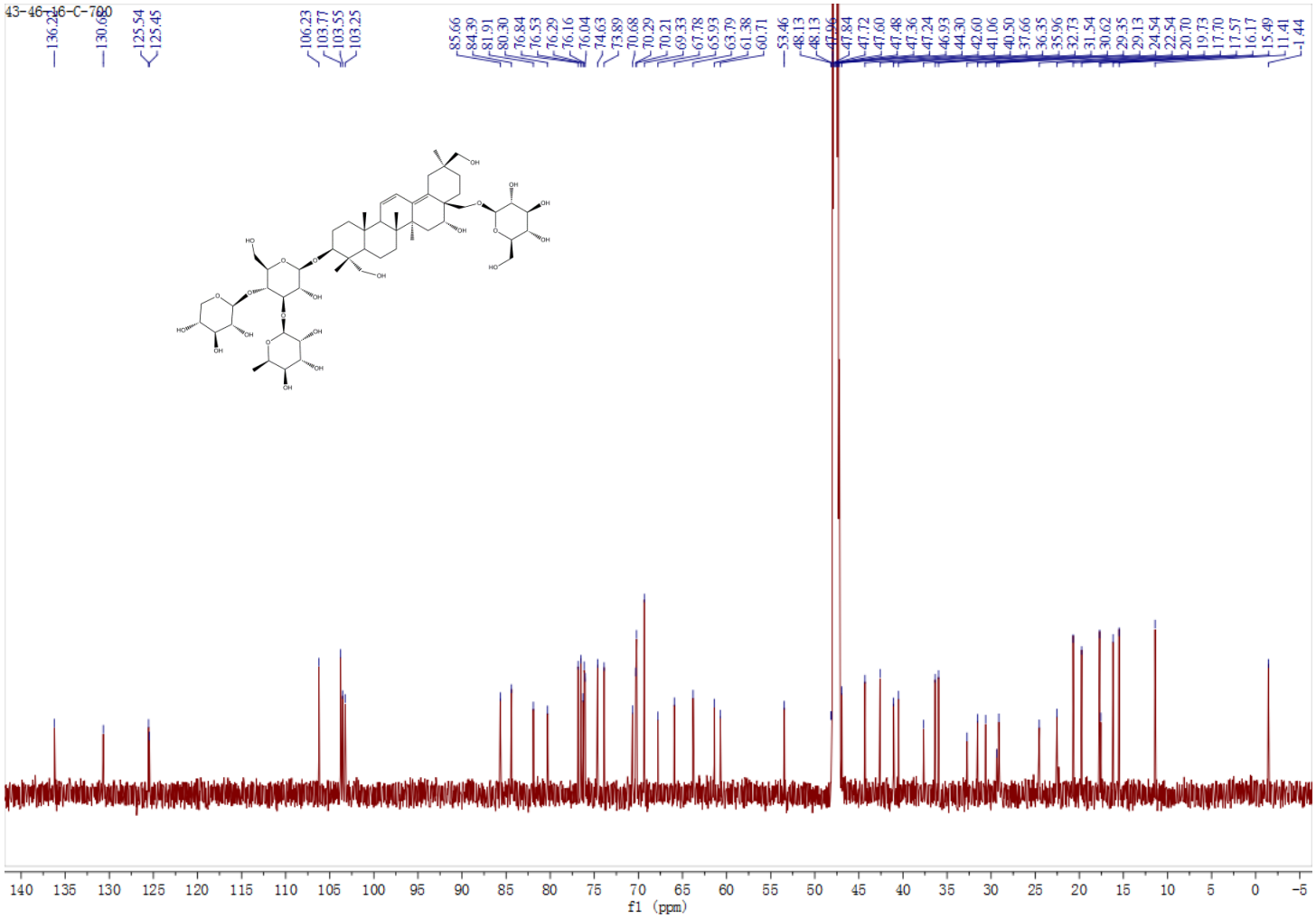


Figure S12. DEPT 135 (176 MHz, Methanol-D4) spectrum of compound 2

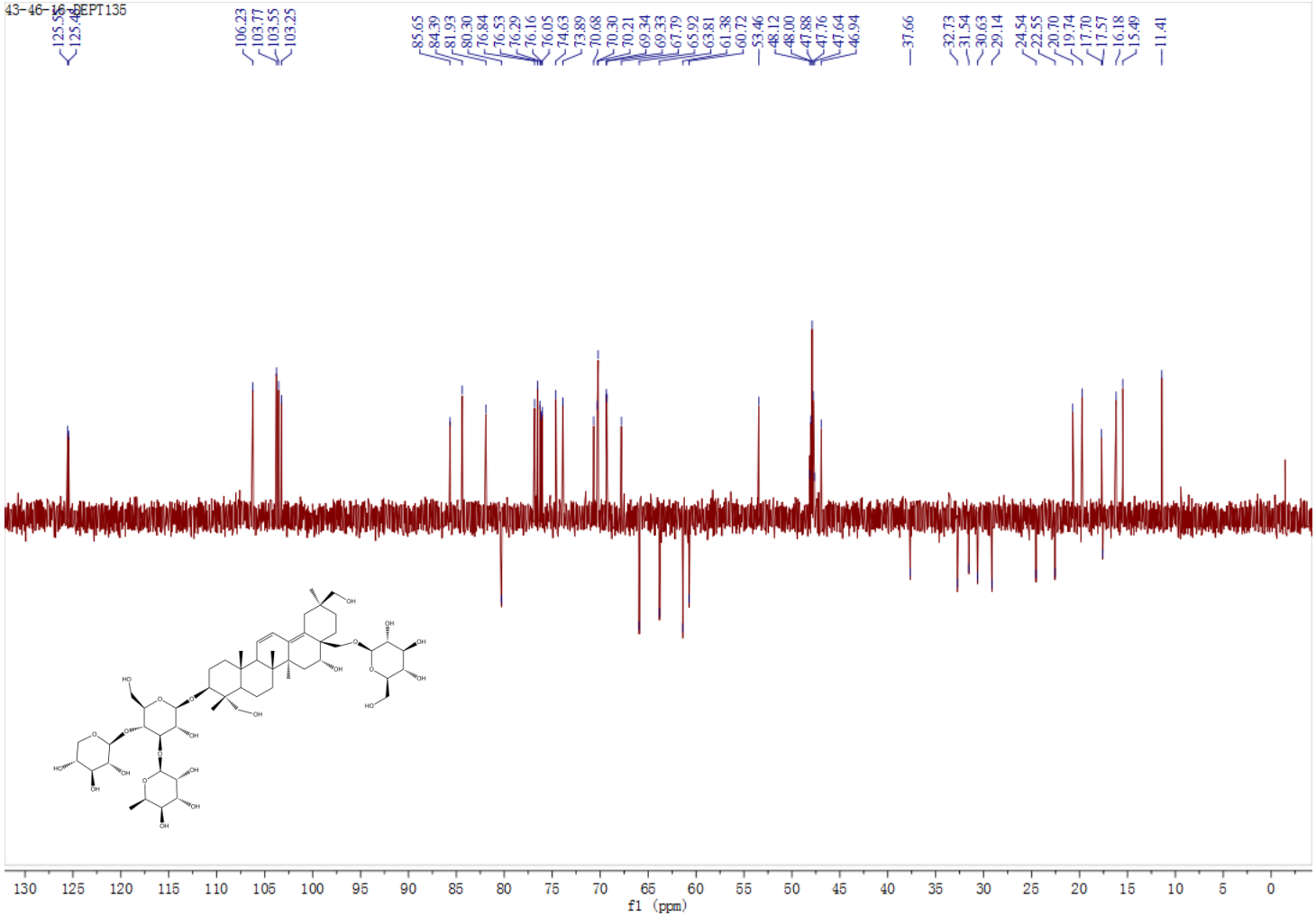


Figure S13. HSQC (700 MHz, Methanol-D4) spectrum of compound 2

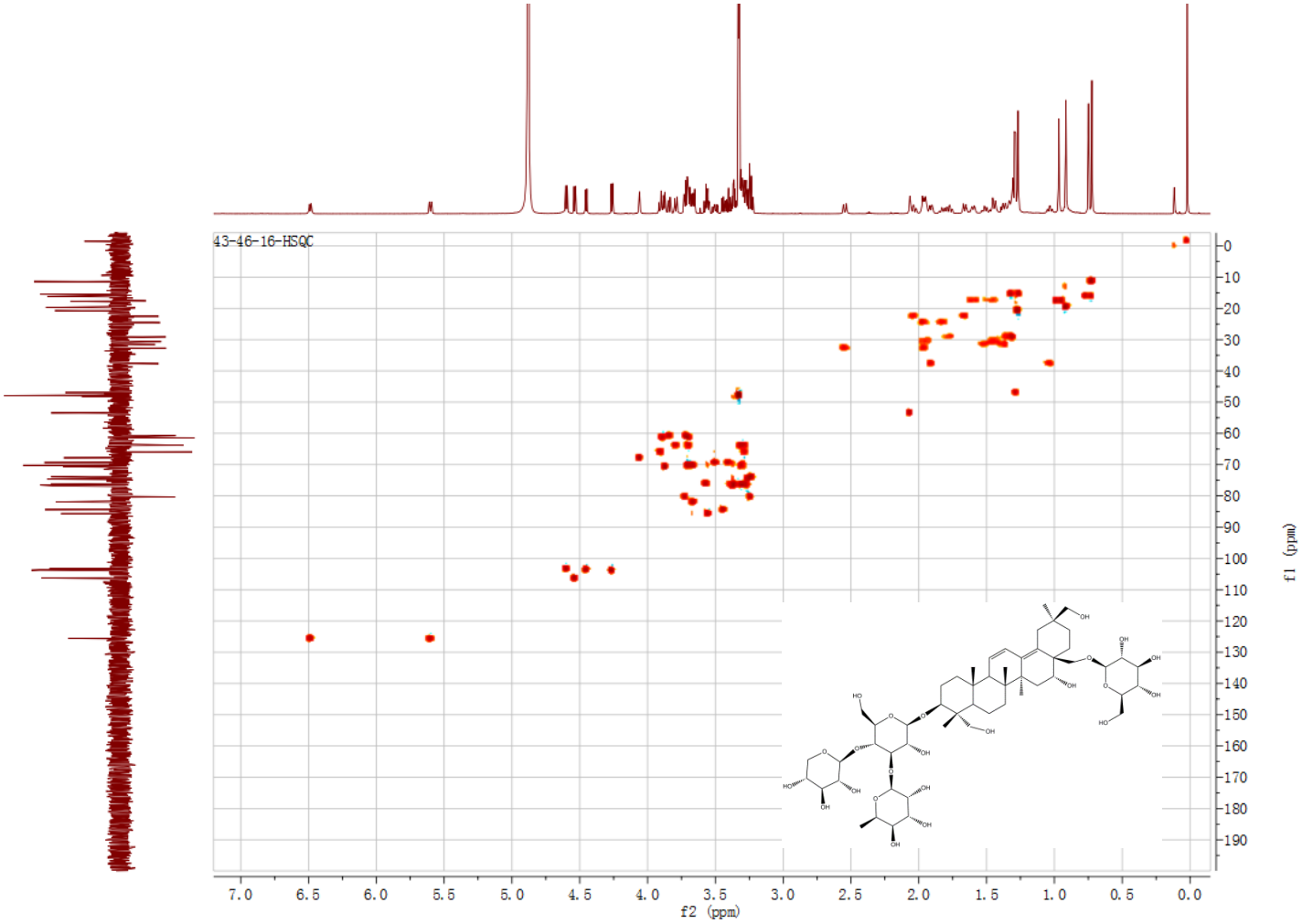


Figure S14. HMBC (700 MHz, Methanol-D4) spectrum of compound 2

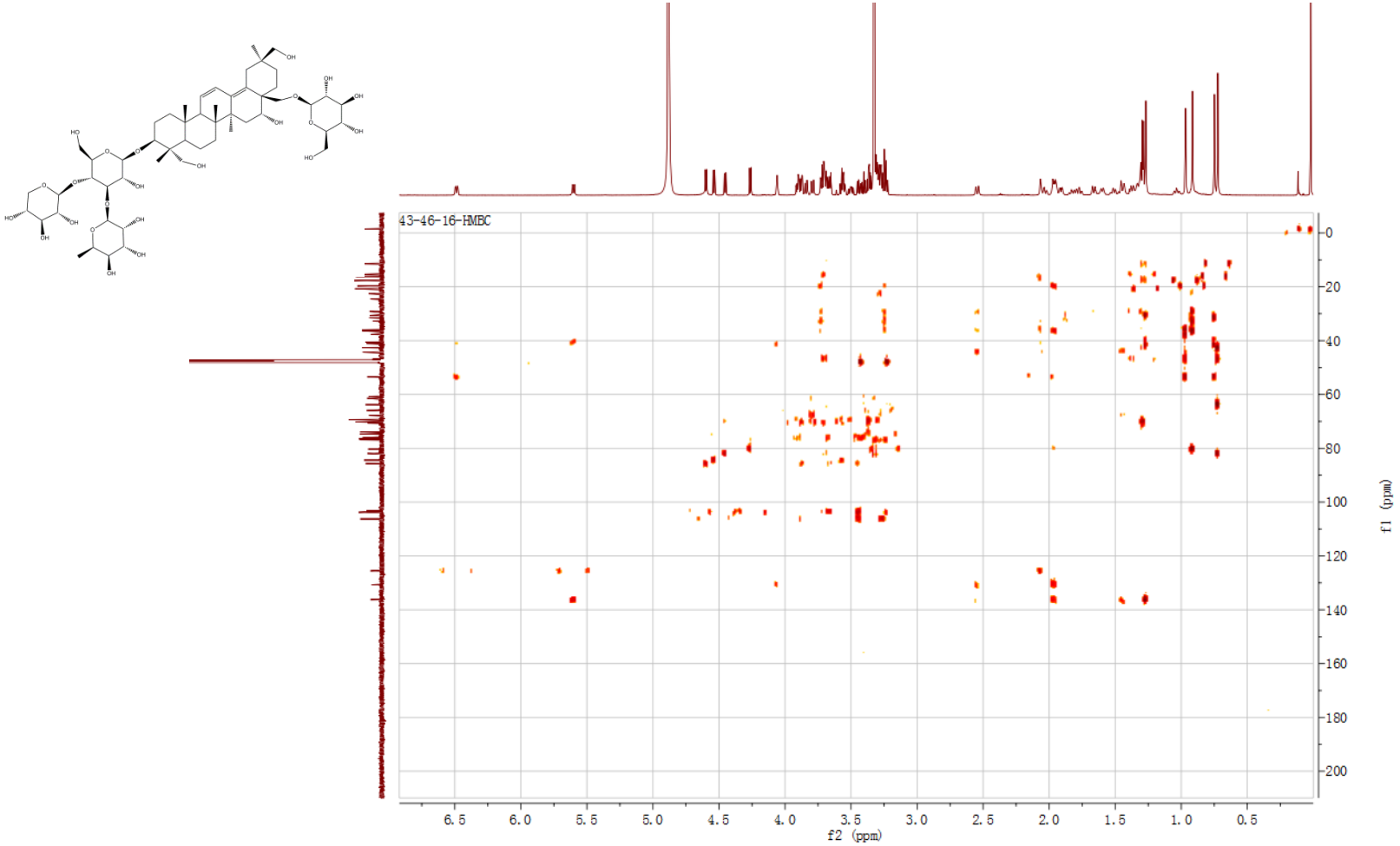


Figure S15. ^{1}H-^{1}H COSY (700 MHz, Methanol-D4) spectrum of compound 2

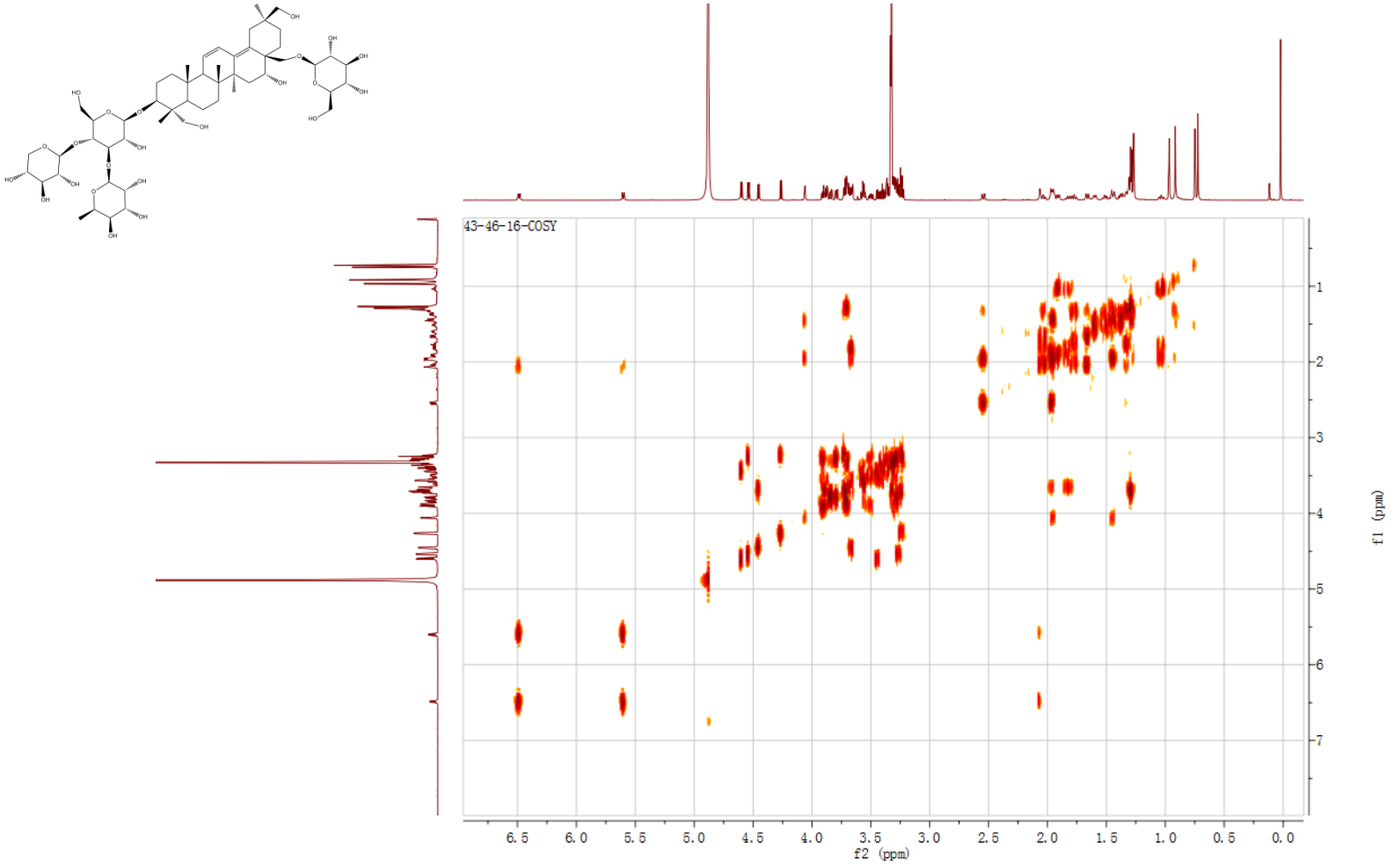
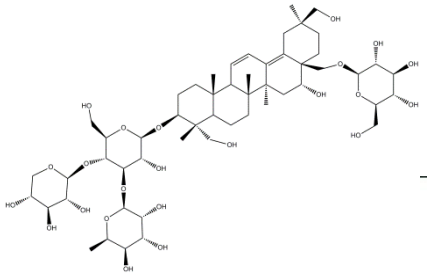


Figure S16. HR-ESI-MS of compound 2



Mass Spectrum SmartFormula Report

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Sample Name	B502-43-46-16	Instrument	compact 8255754.20156
Comment			

Acquisition Parameter

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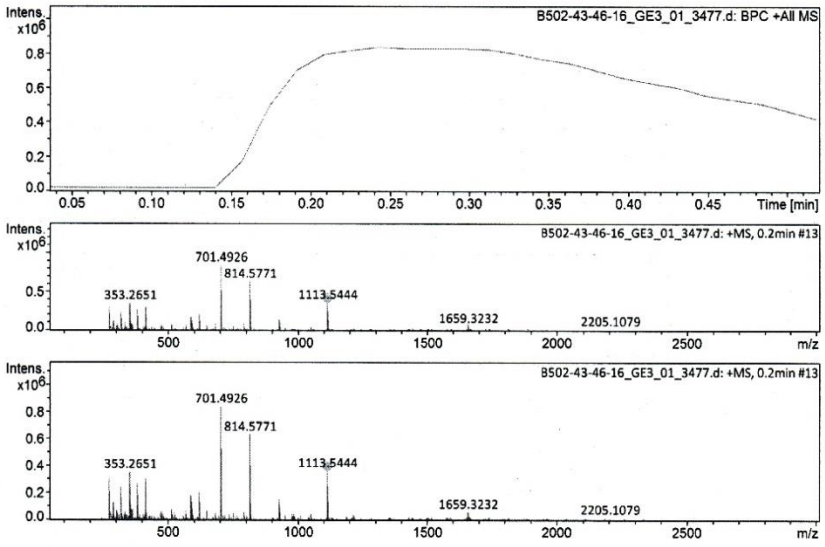
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
1113.5444	1	C53H86NaO23	1113.5452	0.7	42.2	1	100.00	11.0	even	ok	M+Na

Figure S17. ^{1}H NMR (700 MHz, Methanol-D4) spectrum of compound 3

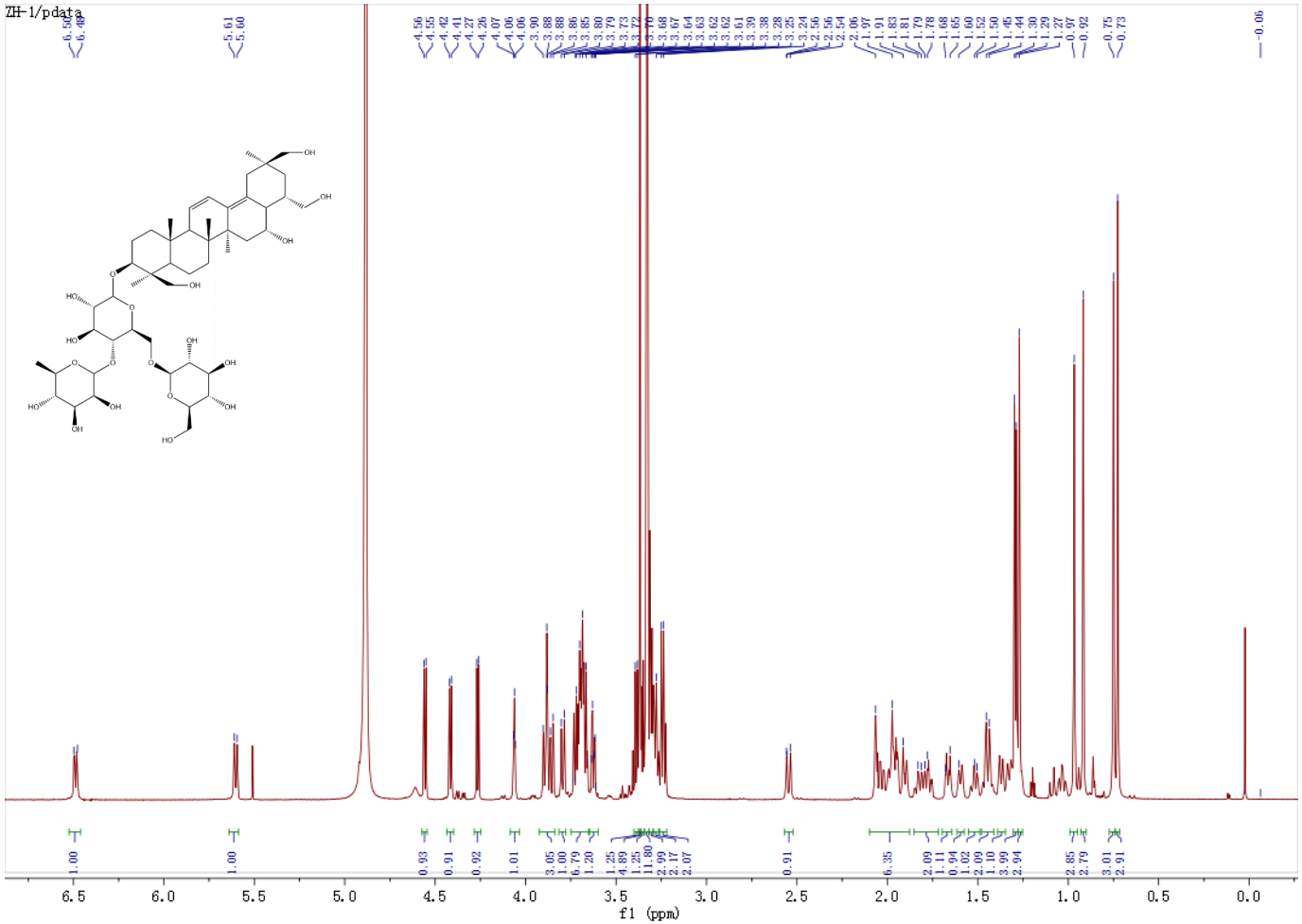


Figure S18. ^{13}C NMR (176 MHz, Methanol-D4) spectrum of compound 3

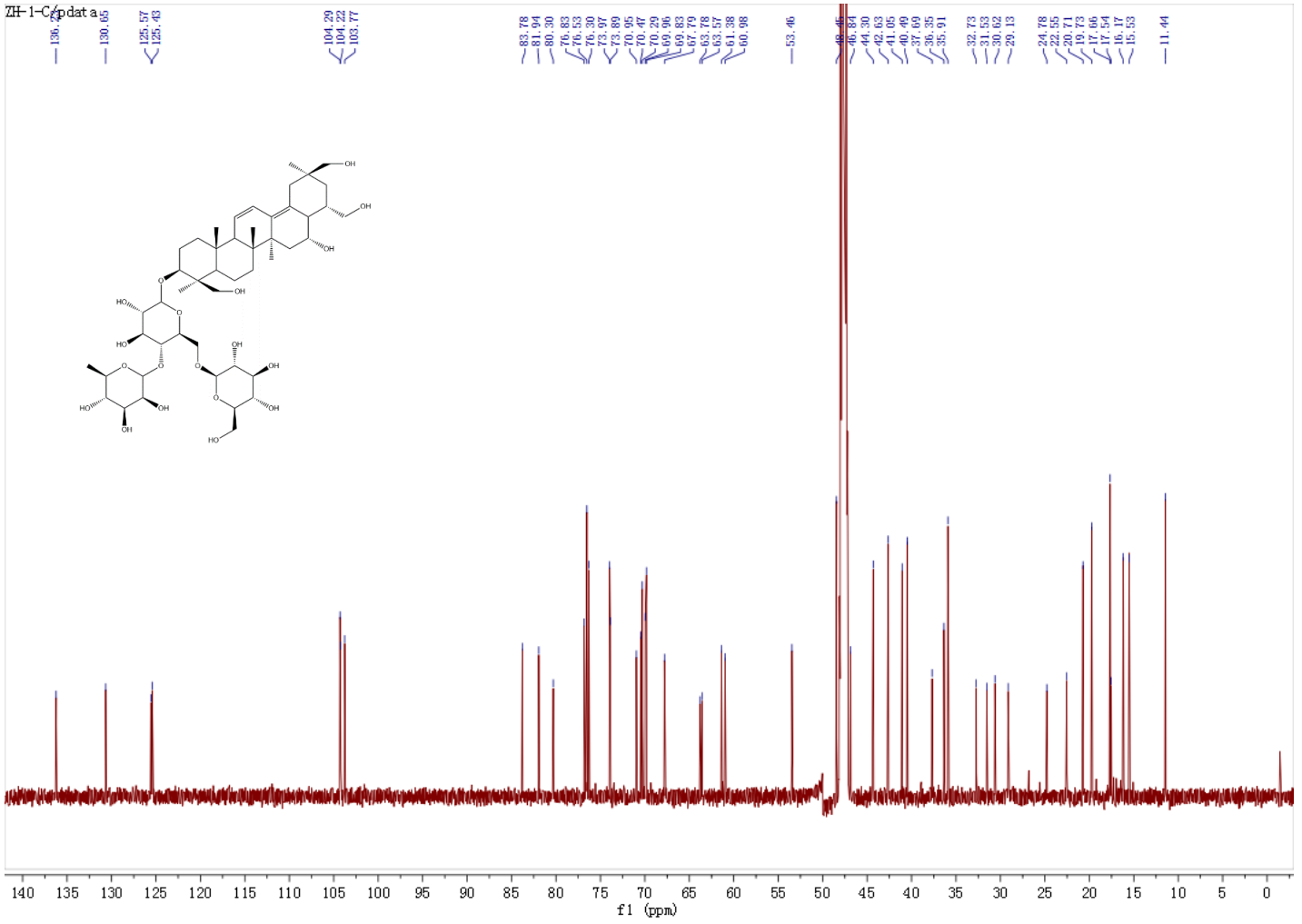


Figure S19. HR-ESI-MS of compound 3

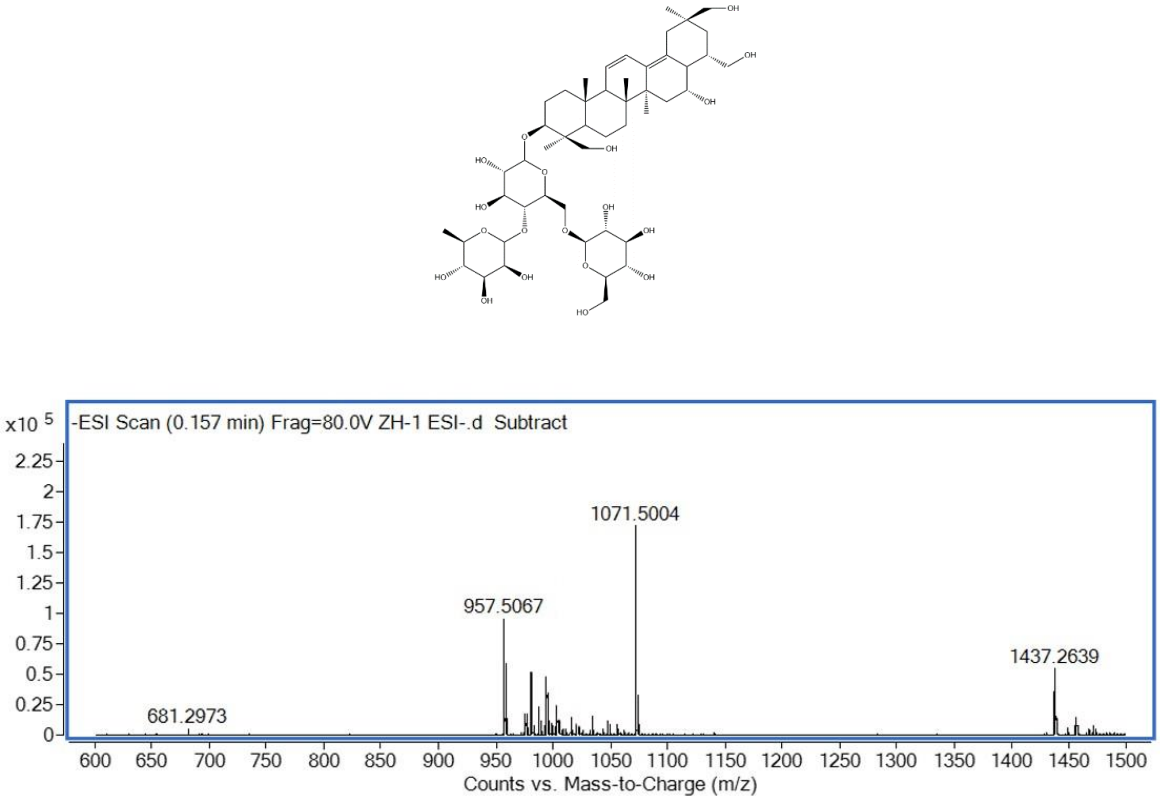


Figure S20. ^{1}H NMR (700 MHz, Methanol-D4) of compound 4

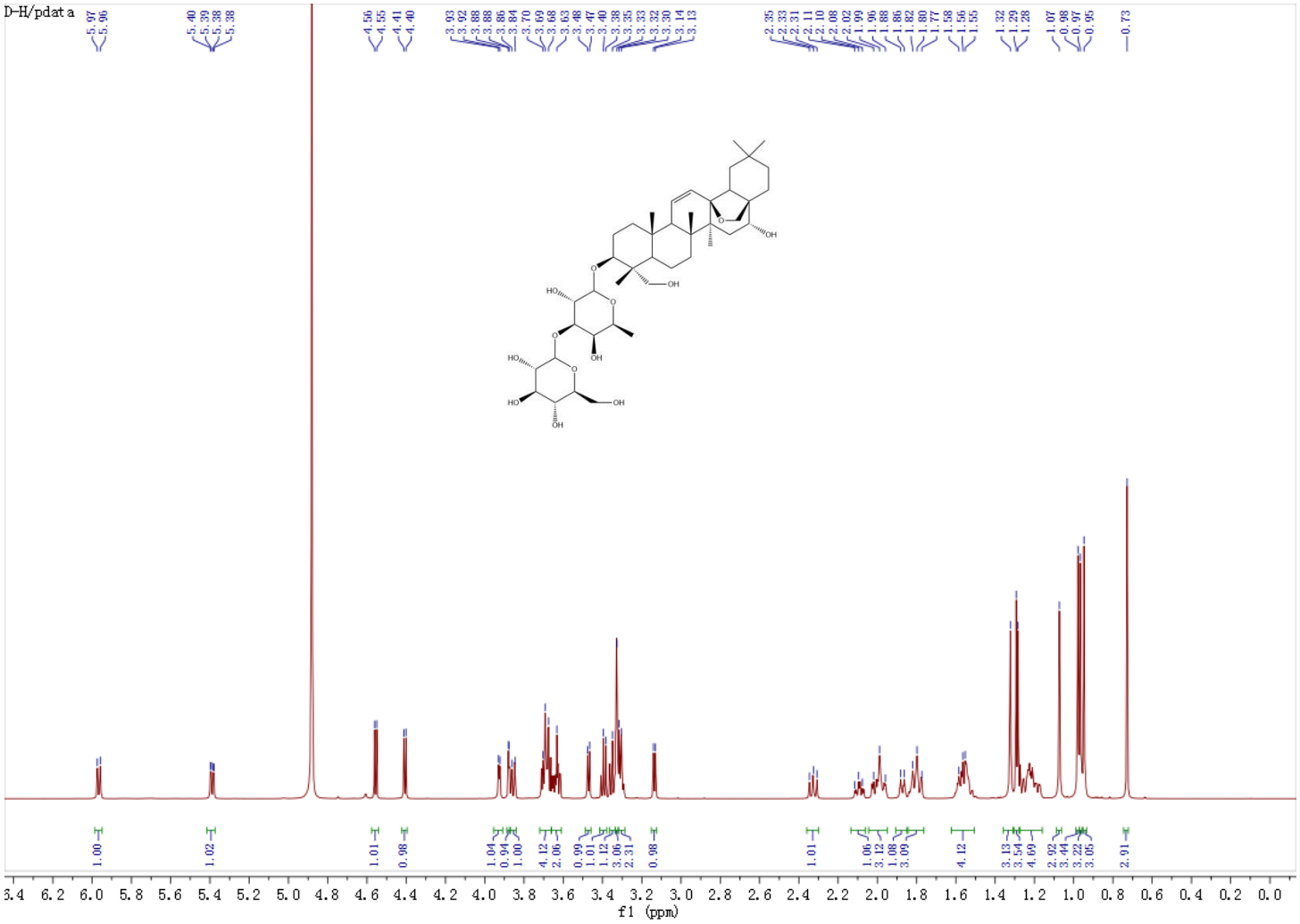


Figure S21. ^{13}C NMR (176 MHz, Methanol-D4) spectrum of compound 4

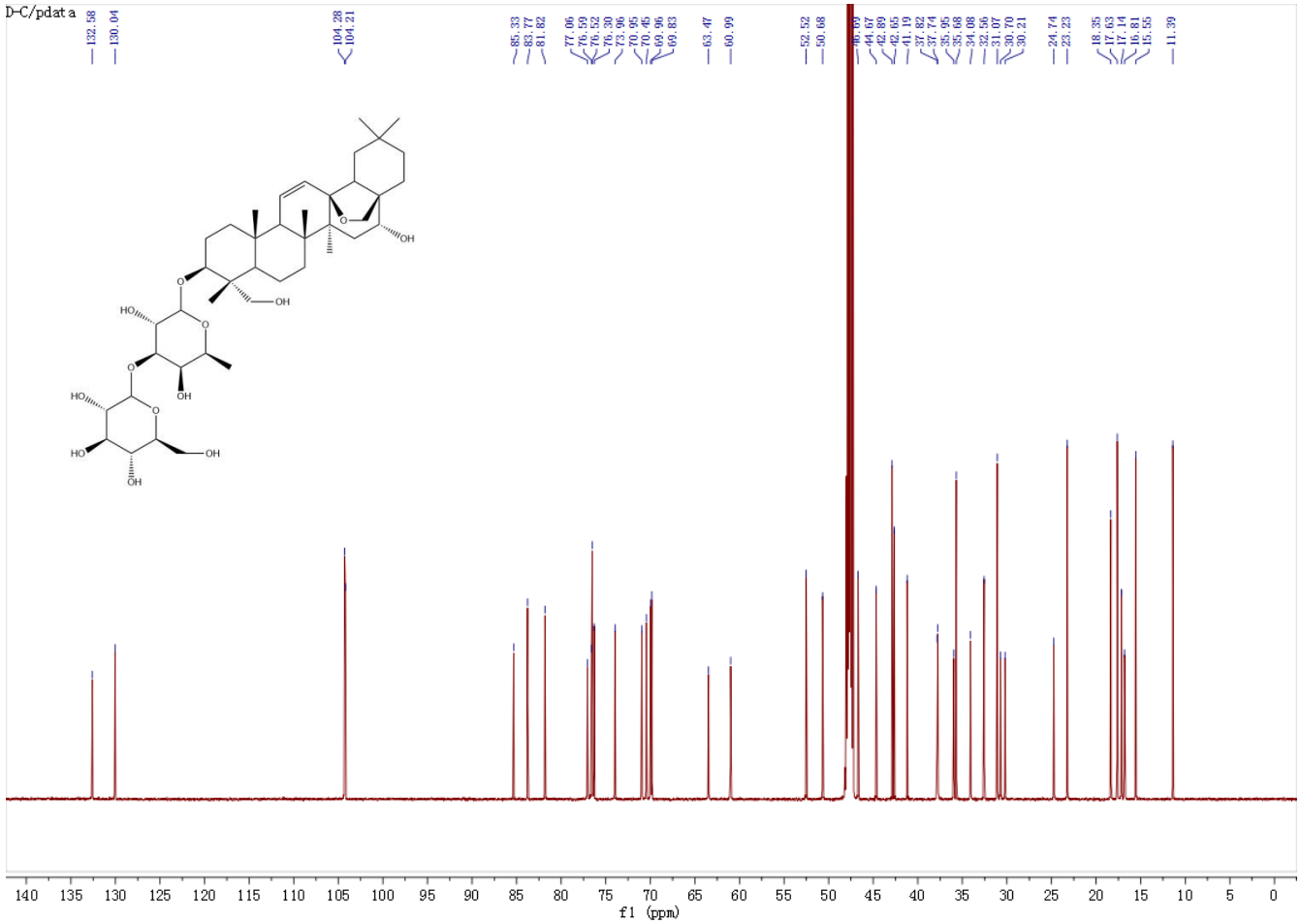


Figure S22. HR-ESI-MS of compound 4