Supporting Information for

Fortunoids A−C, Three Sesquiterpenoid Dimers with Different Carbon Skeletons from *Chloranthus fortunei*

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Figure S27. ROESY spectrum of fortunoid C (**3**) in CD_3OD

Figure S28. (+)-ESIMS spectrum of fortunoid C (**3**)

Figure S29. (–)-ESIMS spectrum of fortunoid C (**3**)

Figure S30. (+)-HRESIMS spectrum of fortunoid C (**3**)

Figure S31. IR spectrum of fortunoid C (**3**)

S1. Experimental Section

General Experimental Procedures. Optical rotations were determined on an Autopol VI polarimeter. UV data were obtained using a Shimadzu UV-2550 spectrophotometer. IR spectra were acquired on a Thermo IS5 spectrometer with KBr disks. NMR spectra were obtained on a Bruker AM-500 NMR spectrometer. ESIMS and HRESIMS were obtained on a Bruker Daltonics Esquire 3000 plus and a Waters-Micromass Q-TQF Ultima Global mass spectrometer, respectively. Semipreparative HPLC was performed on a Waters 1525 binary pump system with a Waters 2489 detector (210 nm) using a YMC-Pack ODS-A (250×10 mm, *S*-5 μm). Silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd.), C_{18} reversed-phase (RP-18) silica gel (20–45 μM, Fuji Silysia Chemical Ltd.), CHP20P MCI gel (75–150 μM, Mitsubishi Chemical Corporation), D101-macroporous absorption resin (Shanghai Hualing Resin Co., Ltd.), and Sephadex LH-20 gel (Amersham Biosciences) were used for column chromatography (CC). Precoated silica gel GF_{254} plates (Qingdao Haiyang Chemical Co., Ltd.) were used for TLC monitors. All solvents used for CC were of analytical grade (Shanghai Chemical Reagents Co., Ltd.), and solvents used for HPLC were of HPLC grade (J & K Scientific Ltd.).

Plant Material. Twigs of *C. fortunei* were collected in June 2013 in Guilin city, Guangxi Province, China, and were authenticated by Professor Shao-Qing Tang of Guangxi Normal University. A voucher specimen has been deposited in Shanghai Institute of Materia Medica, Chinese Academy of Sciences (accession no: CHF-2011-1Y).

Extraction and Isolation. Dried powder of *C. fortunei* (5 kg) was extracted with 95% EtOH at room temperature to give a crude extract (520 g), which was then partitioned between EtOAc and H_2O. The EtOAc soluble fraction (230 g) was subjected to CC (D101-macroporous absorption resin) eluted with 30%, 50%, 80% and 95% MeOH in H_2O to give four fractions 1−4, respectively. Fraction 2 (120 g) was separated by an MCI gel column (MeOH/H_2O, 4:6 to 9:1) to afford three fractions A−C. Fraction A (15 g) was chromatographed over a silica gel column and eluted with petroleum ether-acetone (from 50:1 to 1:5) in gradient to afford seven subfractions A1−A7. Fraction A7

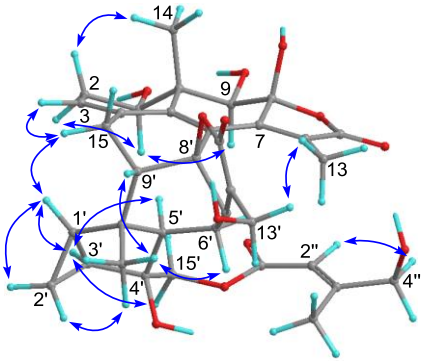
(6.1 g) was further separated on a column of reversed phase C_{18} silica gel (30−80% MeOH in H_2O) to yield three major components A7a−A7c, each of them were purified by silica gel CC ($CHCl_3$-MeOH, 500:1 to 50:1) and then semipreparative HPLC (35% CH_3CN in H_2O, 3 mL/min) to yield compounds **1** (3.4 mg), **2** (5.1 mg), and **3** (6.5 mg), respectively.

Fortunoid A (1): white, amorphous powder; $[\alpha]^{25}_D$ +1 (*c* 0.1, MeOH); UV(MeOH) λ_{max} (log ε) 219 (4.42) nm; CD (MeOH) λ ($\Delta\varepsilon$) 221 (–46.5), 256 (+21.7) nm; IR (KBr) ν_{max} 3432, 2930, 2847, 1754, 1639, 1444, 1380, 1290, 1223, 1152, 1075, 1005, 800.5 cm^{-1}; ^1H and ^{13}C NMR (CD_3OD) see Table S1; (+)-ESIMS *m/z* 669.4 $[M + H]^+$, 1359.5 $[2\ M + Na]^+$; (+)-HRESIMS *m/z* 691.2360 $[M + Na]^+$ (calcd for $C_{35}H_{40}O_{13}Na$, 691.2367).

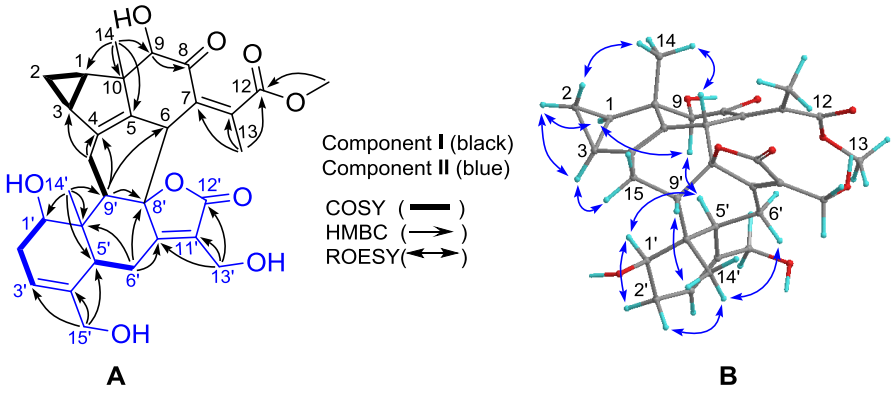
Fortunoid B (2): white, amorphous powder; $[\alpha]^{25}_D$ +194 (*c* 0.1, MeOH); UV(MeOH) λ_{max} (log ε) 221 (4.46) nm; CD (MeOH) λ ($\Delta\varepsilon$) 217 (–37.1), 253 (+7.3) nm; IR (KBr) ν_{max} 3438, 2920, 2853, 1754, 1652, 1441, 1382, 1261, 1219, 1149, 1079, 1037, 1008, 790 cm^{-1}; ^1H and ^{13}C NMR (CD_3OD) see Table S1; (+)-ESIMS *m/z* 635.4 $[M - H_2O + H]^+$, 1327.4 $[2\ M + Na]^+$; (+)-HRESIMS *m/z* 675.2407 $[M + Na]^+$ (calcd for $C_{35}H_{40}O_{12}Na$, 675.2417).

Fortunoid C (3): colorless gum; $[\alpha]^{25}_D$ –64 (*c* 0.2, MeOH); UV(MeOH) λ_{max} (log ε) 220 (4.19) nm; CD (MeOH) λ ($\Delta\varepsilon$) 210 (–7.1), 253 (+3.0) nm; IR (KBr) ν_{max} 3439, 2927, 2853, 1735, 1697, 1674, 1626, 2442, 1373, 1277, 1082, 1043, 986, 803 cm^{-1}; ^1H and ^{13}C NMR (CD_3OD) see Table S1; (+)-ESIMS *m/z* 553.2 $[M + H]^+$, 1127.5 $[2\ M + Na]^+$; (+)-HRESIMS *m/z* 575.2250 $[M + Na]^+$ (calcd for $C_{31}H_{36}O_9Na$, 575.2257).

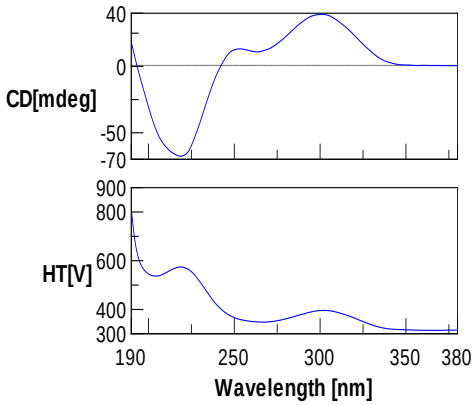
S2. Selected ROESY correlations of 2.

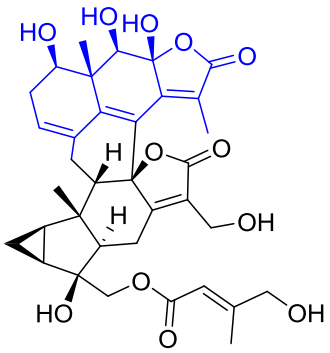


S3. (A) Selected HMBC, $^{1}H–^{1}H$ COSY and (B) ROESY correlations of 3.

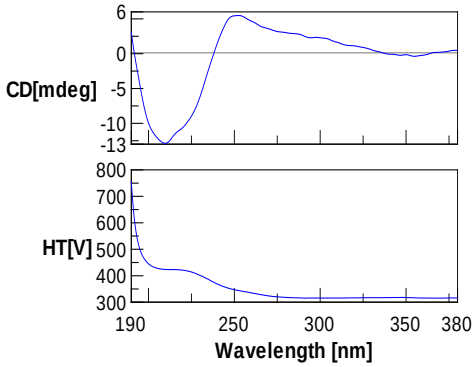


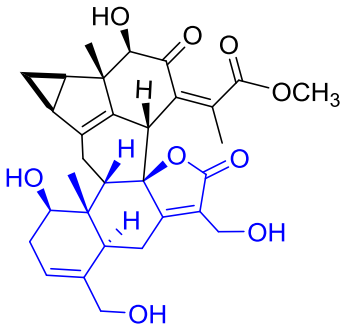
S4. CD spectra of fortunoid B (2) and fortunoid C (3) in CD_3OD.





fortunoid B (**2**)





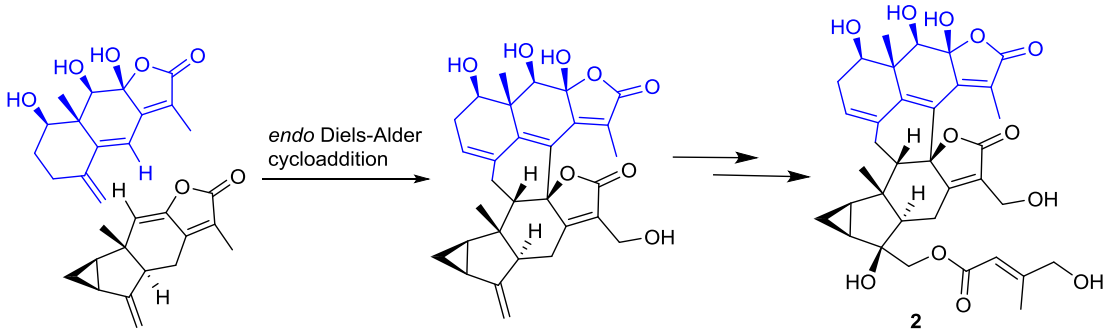
fortunoid C (**3**)

Table S1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR Data of **1**−**3** in CD_3OD

	1		**2**		**3**	
no.	δ_H (multi, *J* in Hz)	δ_C	δ_H (multi, *J* in Hz)	δ_C	δ_H (multi, *J* in Hz)	δ_C
1	1.58, td (8.8, 5.2)	33.4	4.09, dd (9.6, 4.3)	70.9	1.98,[b] m	27.1
2α	0.82, td (9.2, 6.1)	10.4	2.62, dt (19.0, 5.6)	34.4	0.98, m	16.4
2β	0.14, q (5.8)		2.33, m		0.36, m	
3	1.20, td (8.8, 5.9)	23.3	5.90, m	131.2	1.96,[b] m	25.7
4		88.5		130.8		144.3
5		208.1		151.1		133.6
6		75.5		120.9	3.98, d (3.8)	42.4
7		150.8		151.7		134.3
8		104.7		106.9		202.5
9	4.05, s	80.5	4.36, s	70.2	3.90, s	80.5
10		51.0		47.8		52.1
11		135.1		125.2		146.7
12		174.2		174.8		173.2
13	2.15, s	14.7	1.79, s	12.3	1.87, s	20.0
14	1.13, s	17.8	1.04, s	15.0	1.02, s	16.4
15α	2.26, m	42.3	2.96, dd (14.3, 2.4)	32.3	3.51, dd (16.1, 1.7)	24.5
15β			2.71,[a] dd		2.37,[c] m	
1′	1.33, m	30.0	1.90, m	26.3	3.74,[d] m	70.8
2′α	0.65, m	12.0	0.64, m	12.3	2.36,[c] m	33.4
2′β	1.26, m		1.21, m		2.04,[b] m	
3′	1.67	30.2	1.51, td (3.5, 8.3)	29.8	5.60, m	122.4
4′		79.3		78.3		137.9
5′	3.36, dd (12.2, 8.5)	52.9	2.74,[a] m	57.7	2.31,[c] m	41.7
6'α	2.96, dd (17.5, 8.5)	26.6	2.48, m	22.5	2.55, dd (18.4, 6.8)	26.4
6′β	2.87, dd (17.5, 12.2)		2.78, m		2.75, dd (18.4, 13.3)	
7′		170.2		172.8		170.6
8′		102.0		87.8		94.4
9′	3.21, dd (9.3, 5.8)	52.7	1.84, m	56.0		55.3
10′		44.6		45.6		42.8
11′		134.6		128.0		127.0
12′		173.2		175.2		174.4
13′	4.24, d (13.2)	54.4	4.29, d (13.1)	54.4	4.29, d (13.5)	54.4
	4.14, d (13.2)		4.24, d (13.1)		4.26, d (13.5)	
14′	0.76, s	20.6	0.92, s	26.6	0.79, s	17.0
15′	4.33, d (11.2)	71.7	4.01, s	71.2	3.82, m	63.9
	4.29, d (11.2)					
1″		168.4		168.5		
2″	6.10, m	113.8	6.07, d (1.5)	113.8		
3″		160.7		160.6		
4″	4.09, s	67.1	4.08, s	67.1		
5″	2.11, s	15.9	2.08, s	15.8		
12-OMe					3.76,[d] s	53.1

[a-d]Overlapping signals.

Scheme S1. Hypothetical Biosynthetic Pathway of **2.**



Scheme S2. Hypothetical Biosynthetic Pathway of **3.**

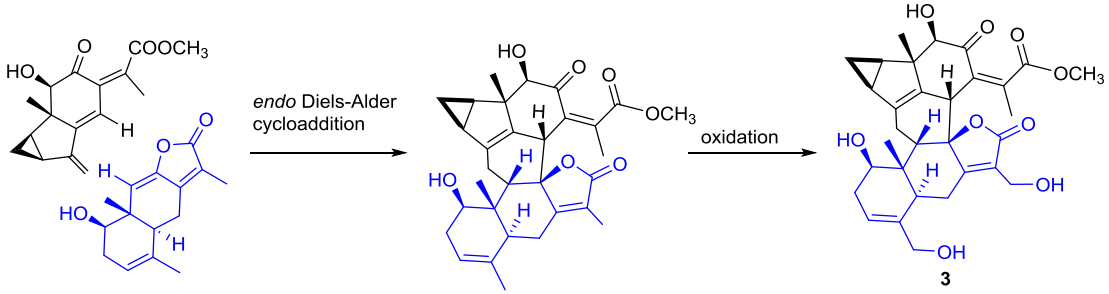


Figure S1. ^{1}H NMR spectrum of fortunoid A (**1**) in CD_3OD

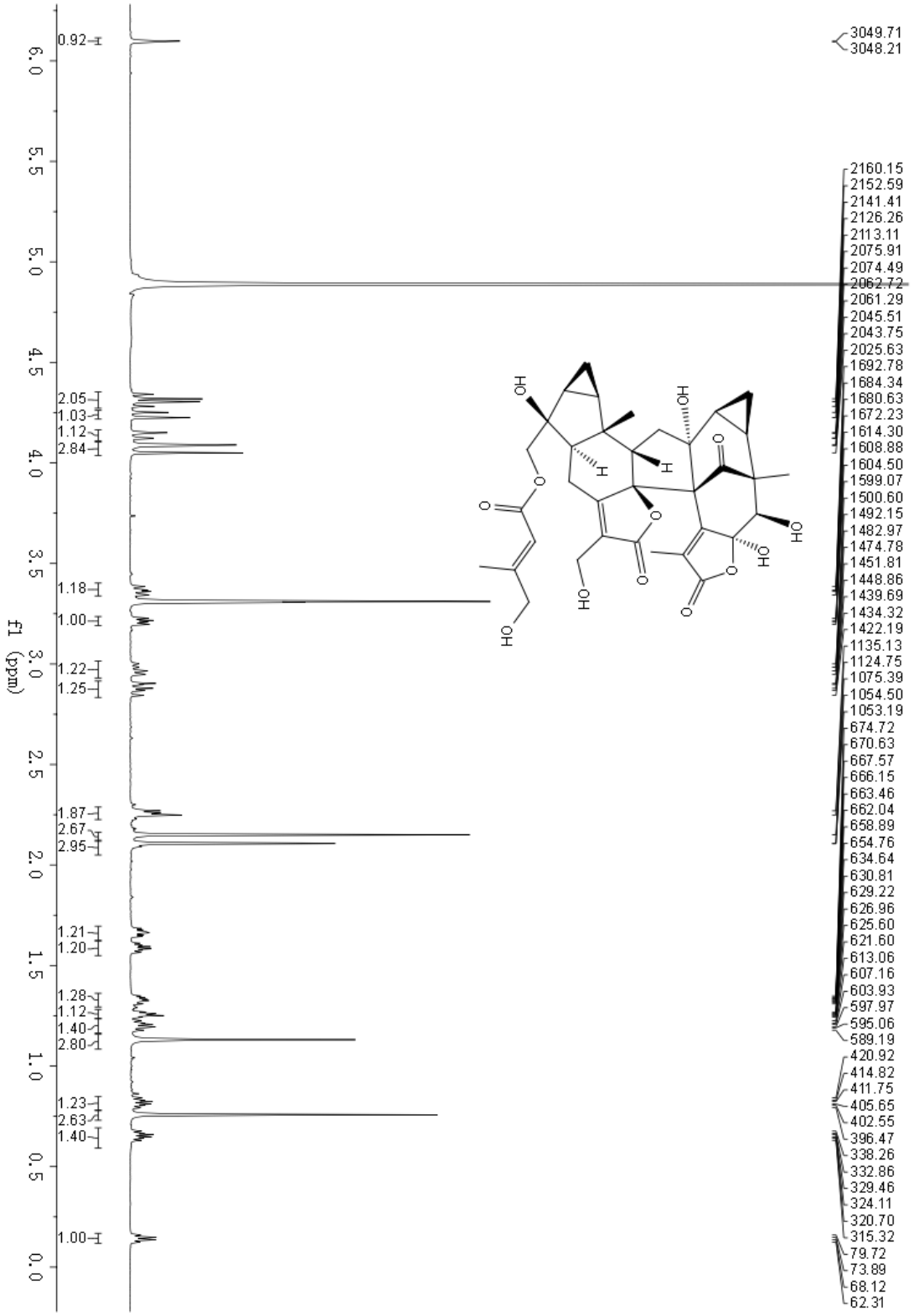


Figure S2. ^{13}C NMR spectrum of fortunoid A (**1**) in CD_3OD

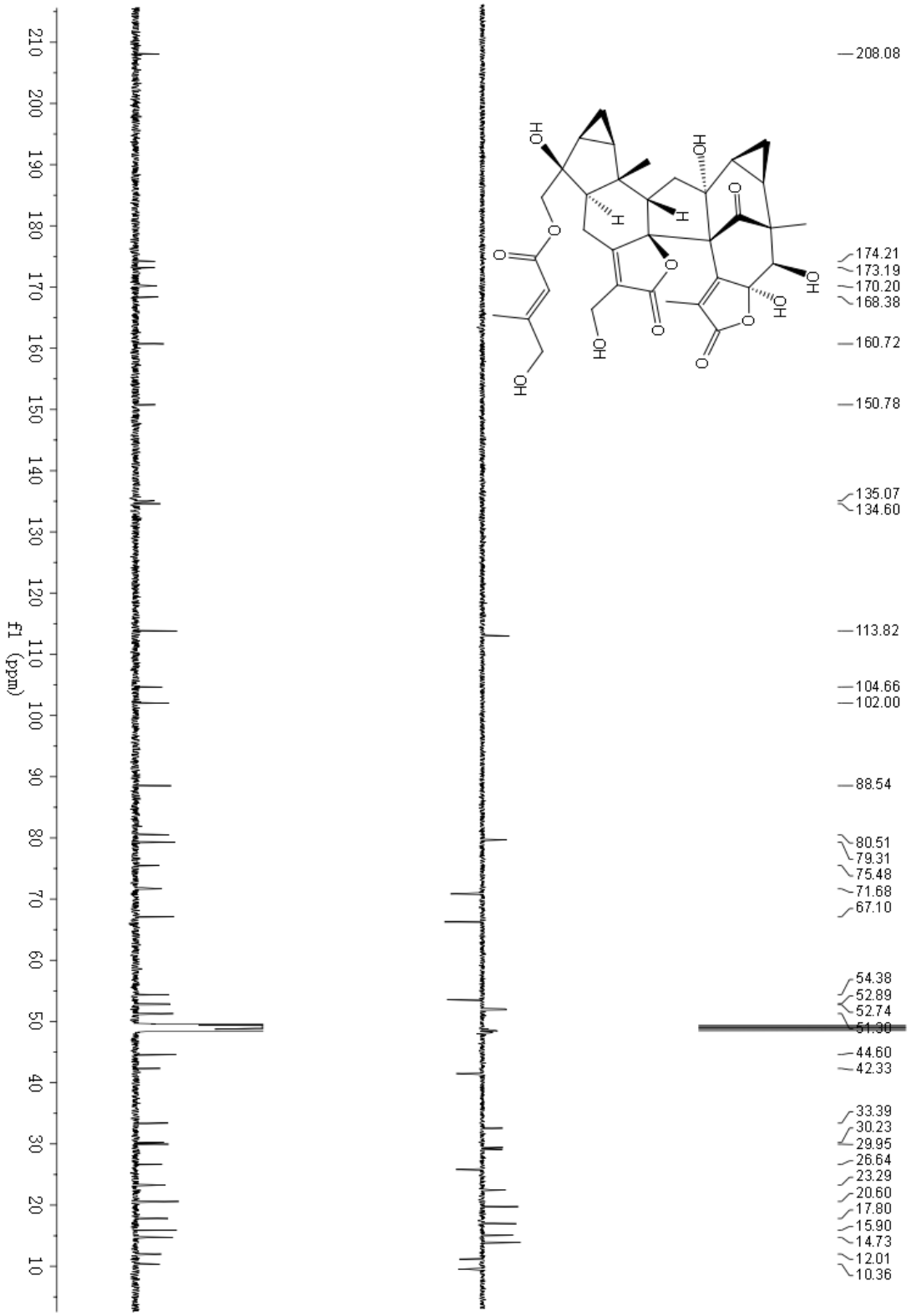


Figure S3. $^{1}H–^{1}H$ COSY spectrum of fortunoid A (**1**) in CD_3OD

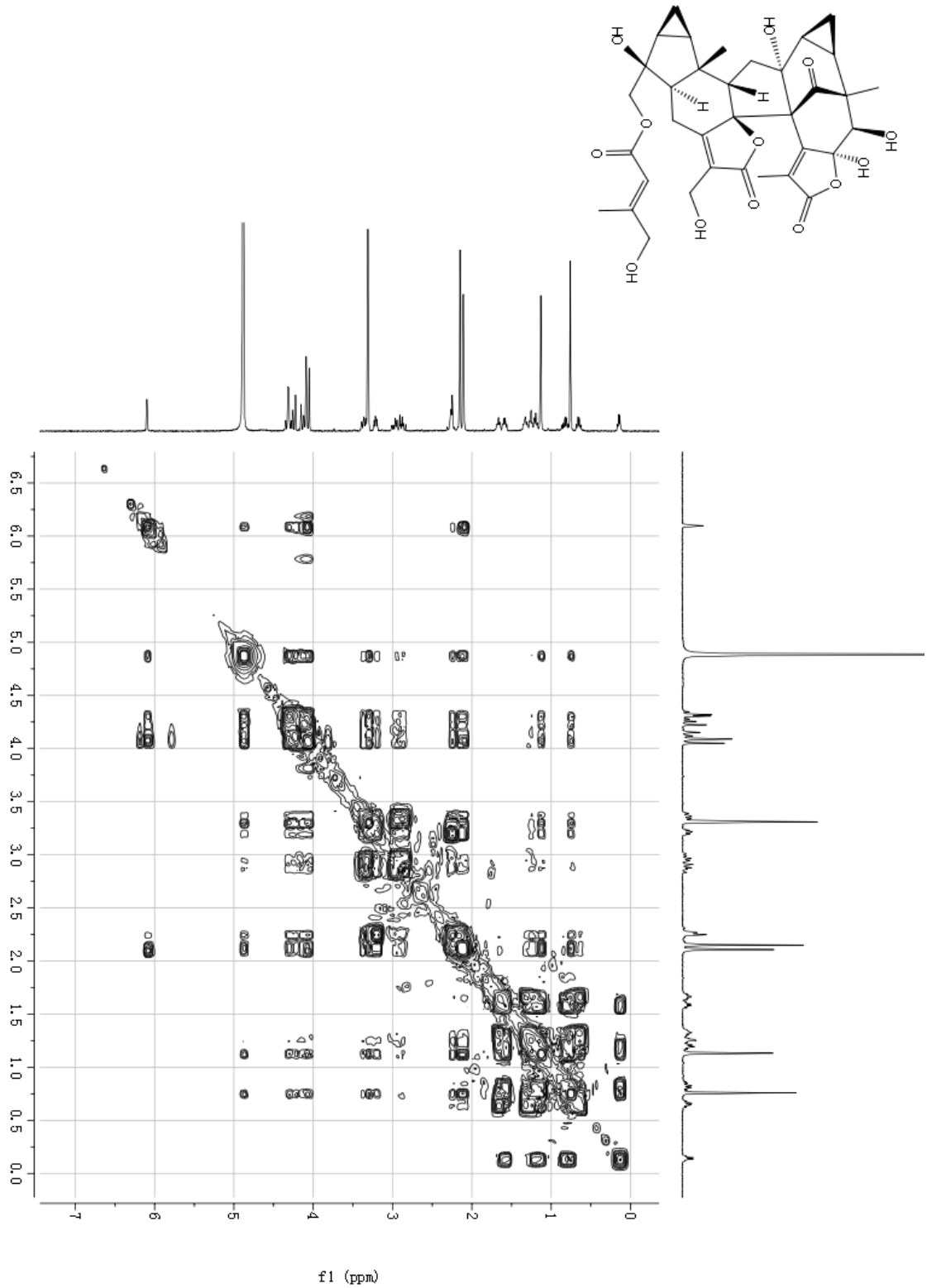


Figure S4. HSQC spectrum of fortunoid A (**1**) in CD_3OD

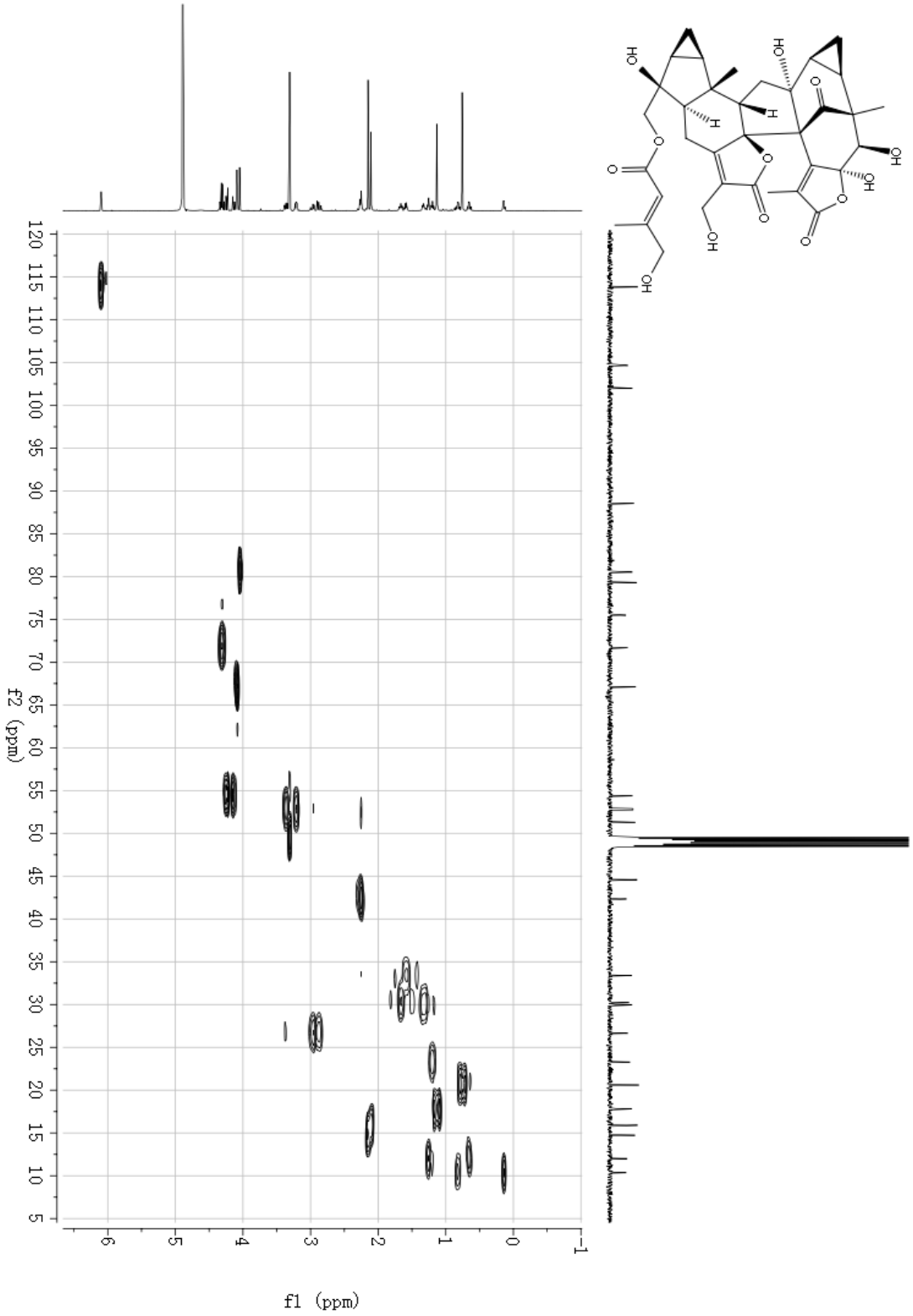


Figure S5. HMBC spectrum of fortunoid A (**1**) in CD_3OD

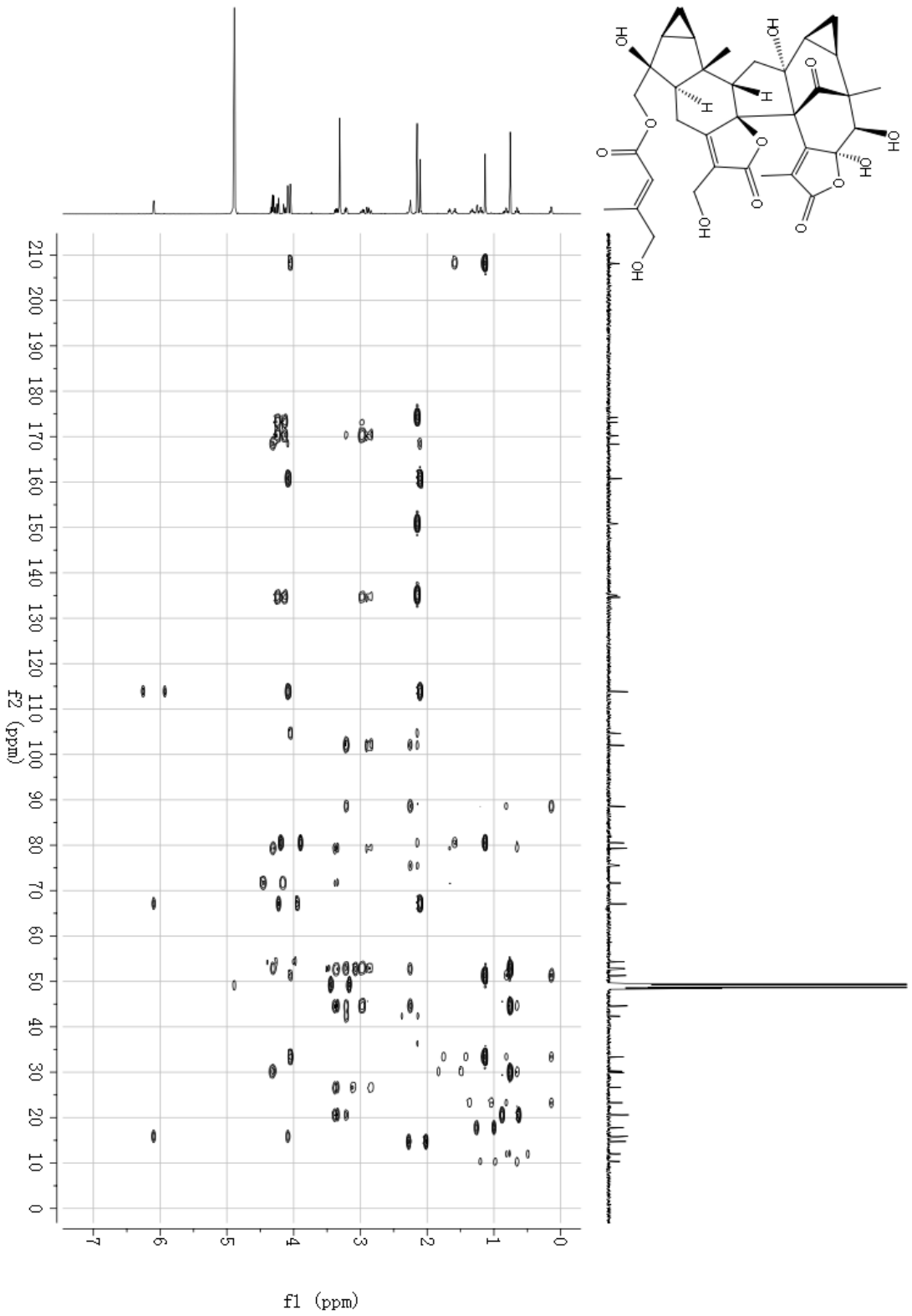


Figure S6. ROESY spectrum of fortunoid A (**1**) in CD_3OD

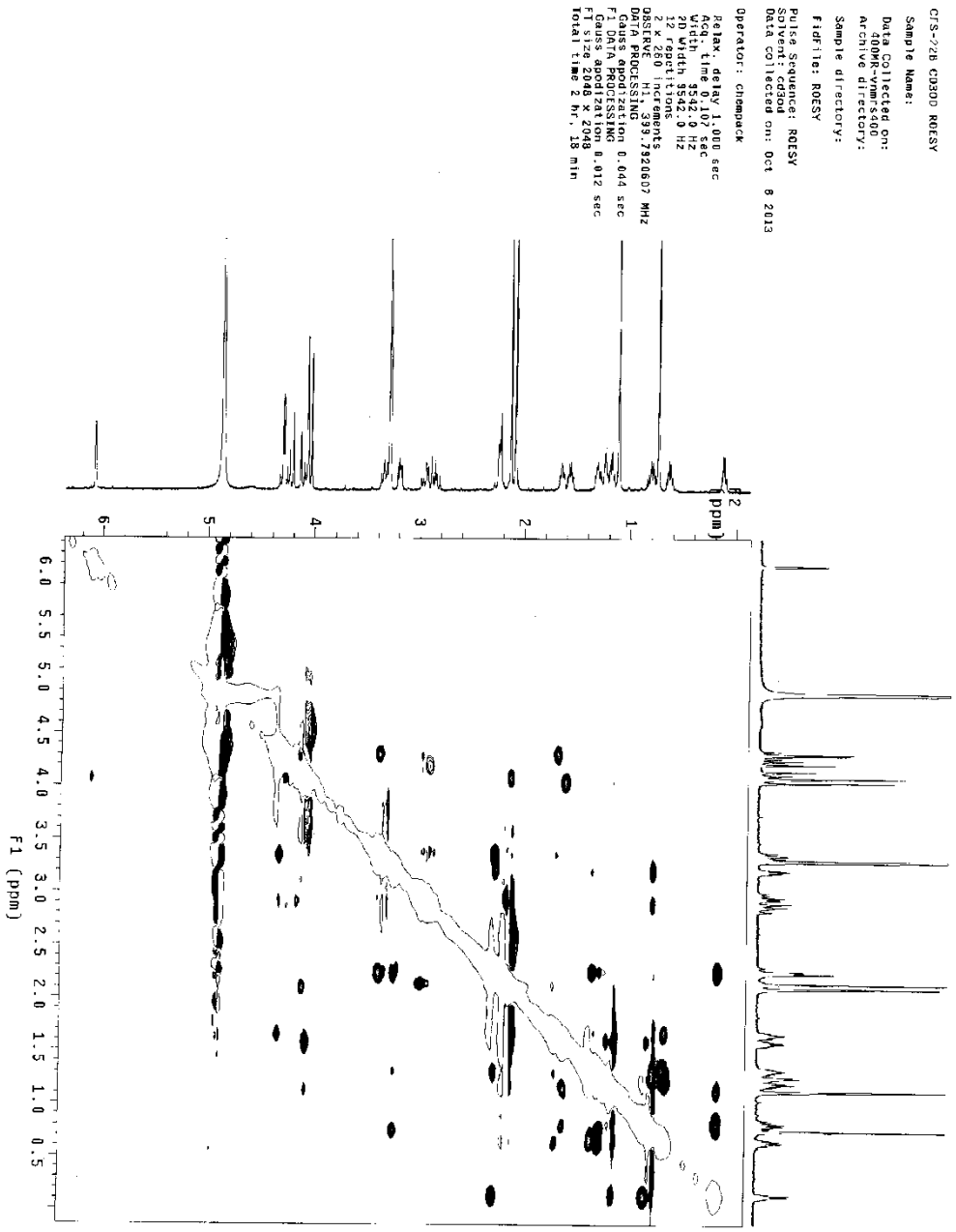


Figure S7. (+)-ESIMS spectrum of fortunoid A (**1**)

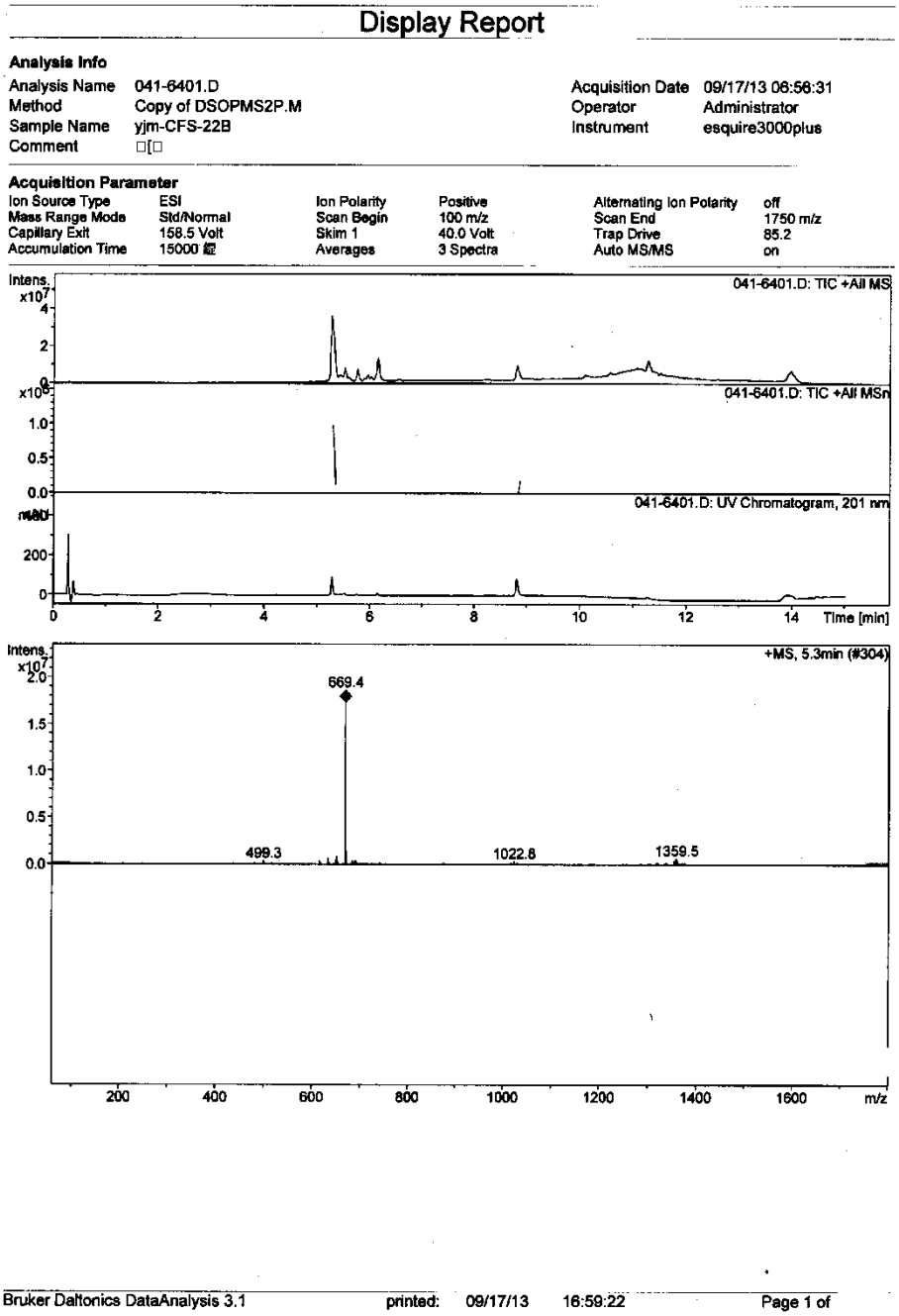


Figure S8. (−)-ESIMS spectrum of fortunoid A (**1**)

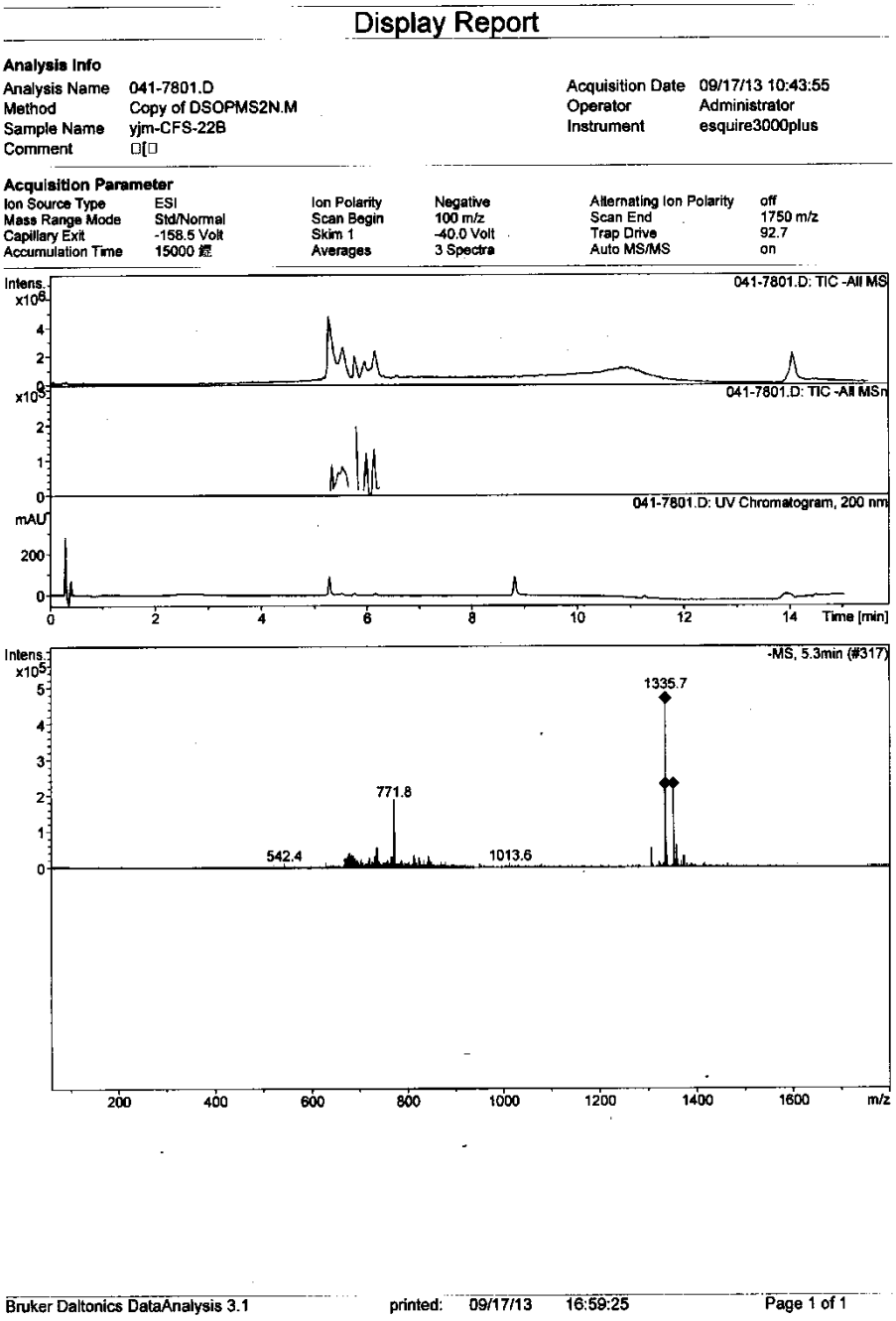


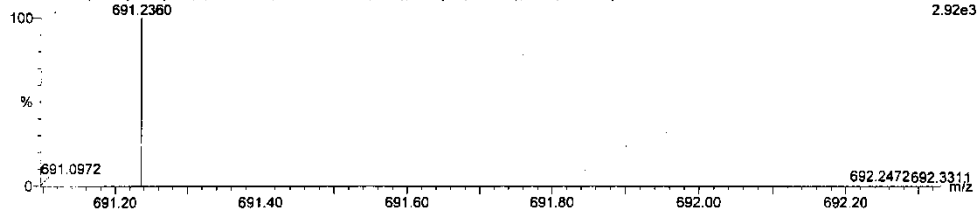
Figure S9. (+)-HRESIMS spectrum of fortunoid A (**1**)

Elemental Composition Report **Page 1**

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)

SIMM-Mass Spec Q-Tof Ultima 13-Nov-201311:00:46
CFS-22B
131023 260 (4.899) AM (Cen,5, 80.00, Ht,9000.0,702.86,0.70); Sm (Mn, 2x0.00); Cm (240:261) TOF MS ES+
2.92e3



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Maximum:	100.00		200.0	10.0	50.0					
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula			
691.2360	100.00	691.2367	-0.7	-1.0	15.5	1	C35	H40	O13	Na

Figure S10. IR spectrum of fortunoid A (**1**)

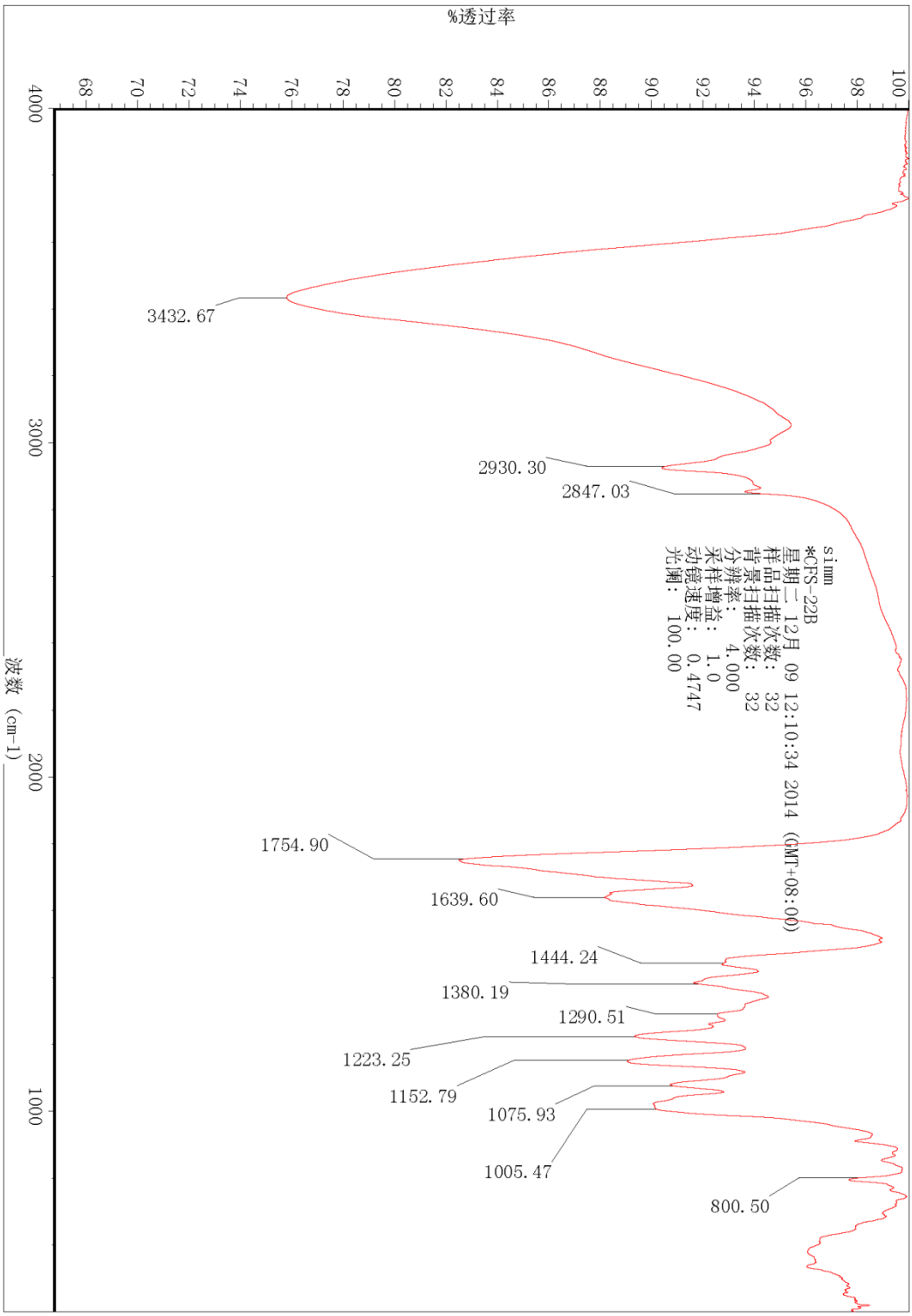


Figure S11. ^{1}H NMR spectrum of fortunoid B (**2**) in CD_3OD

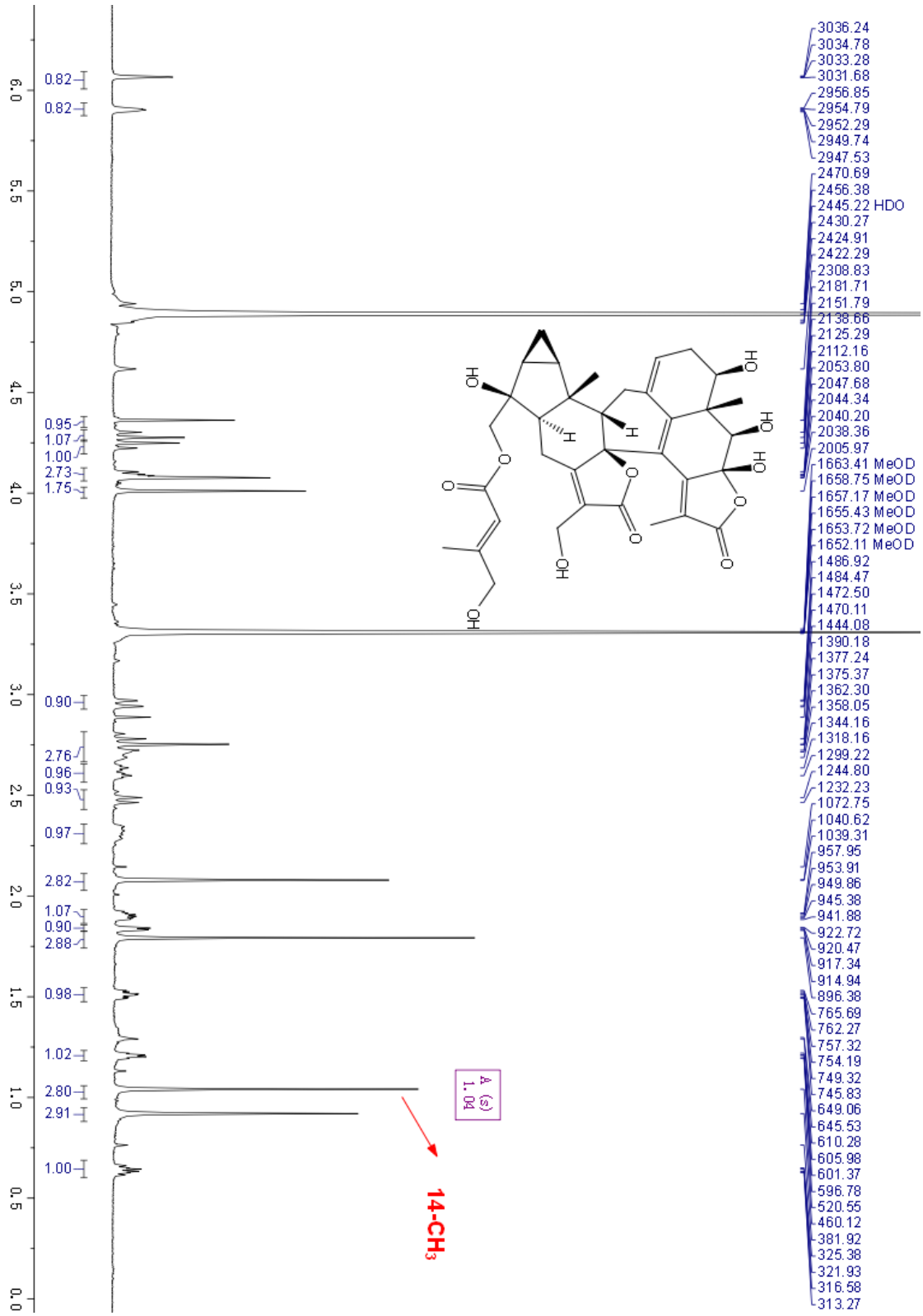


Figure S12. ^{1}H NMR spectrum of fortunoid B (**2**) in $CDCl_3$

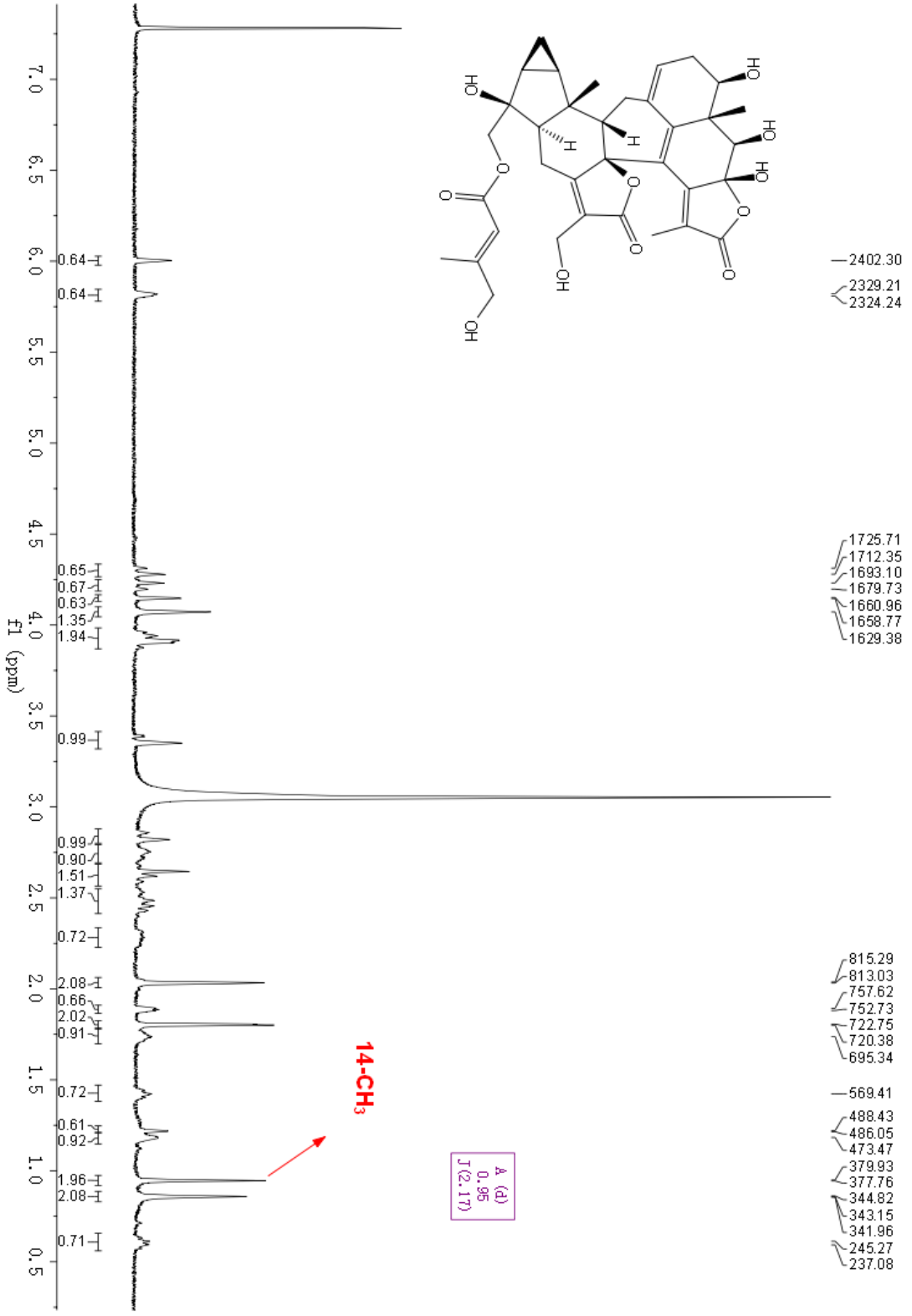


Figure S13. ^{1}H NMR spectrum of fortunoid B (**2**) in C_5D_5N

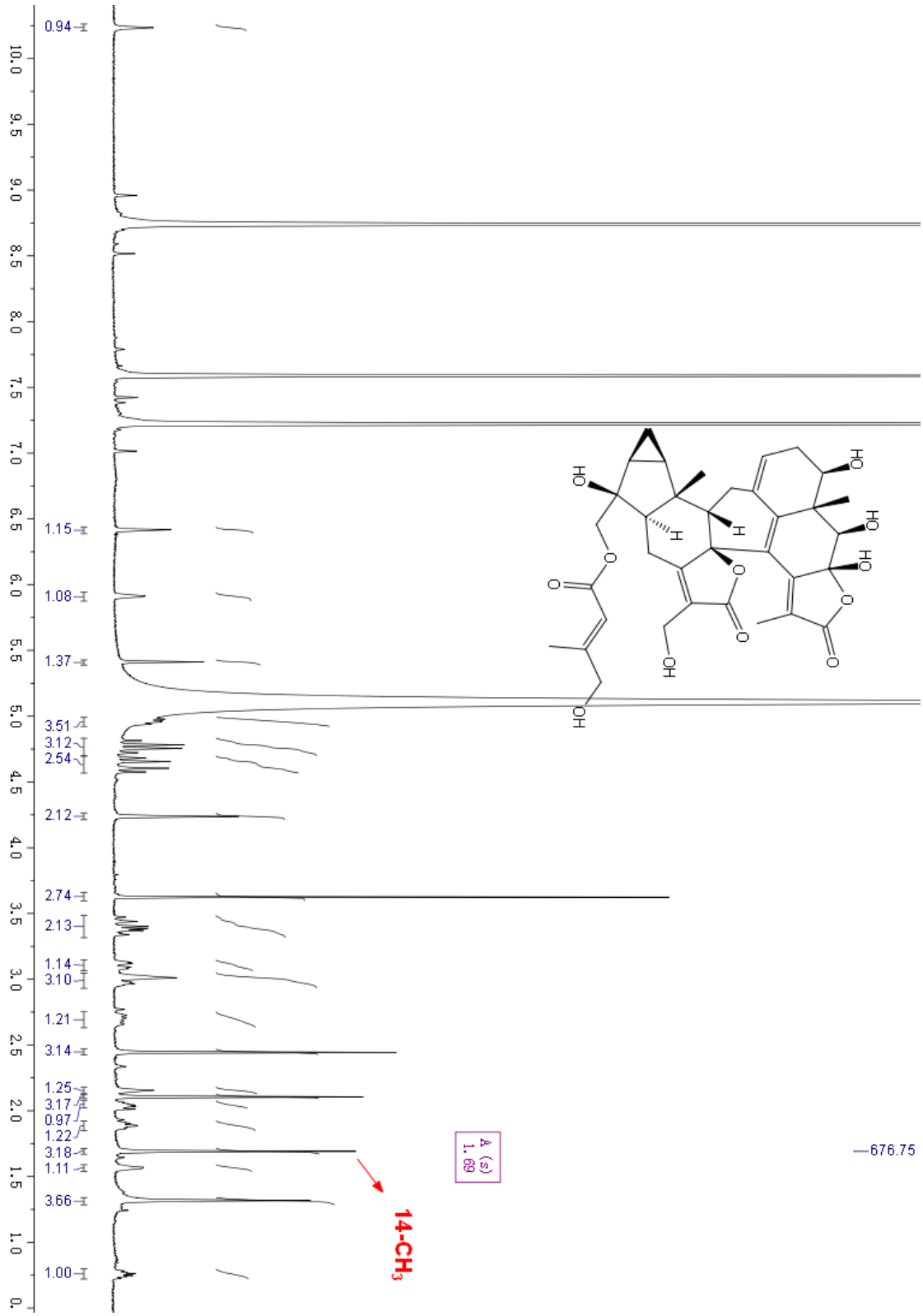


Figure S14. ^{13}C NMR spectrum of fortunoid B (**2**) in CD_3OD

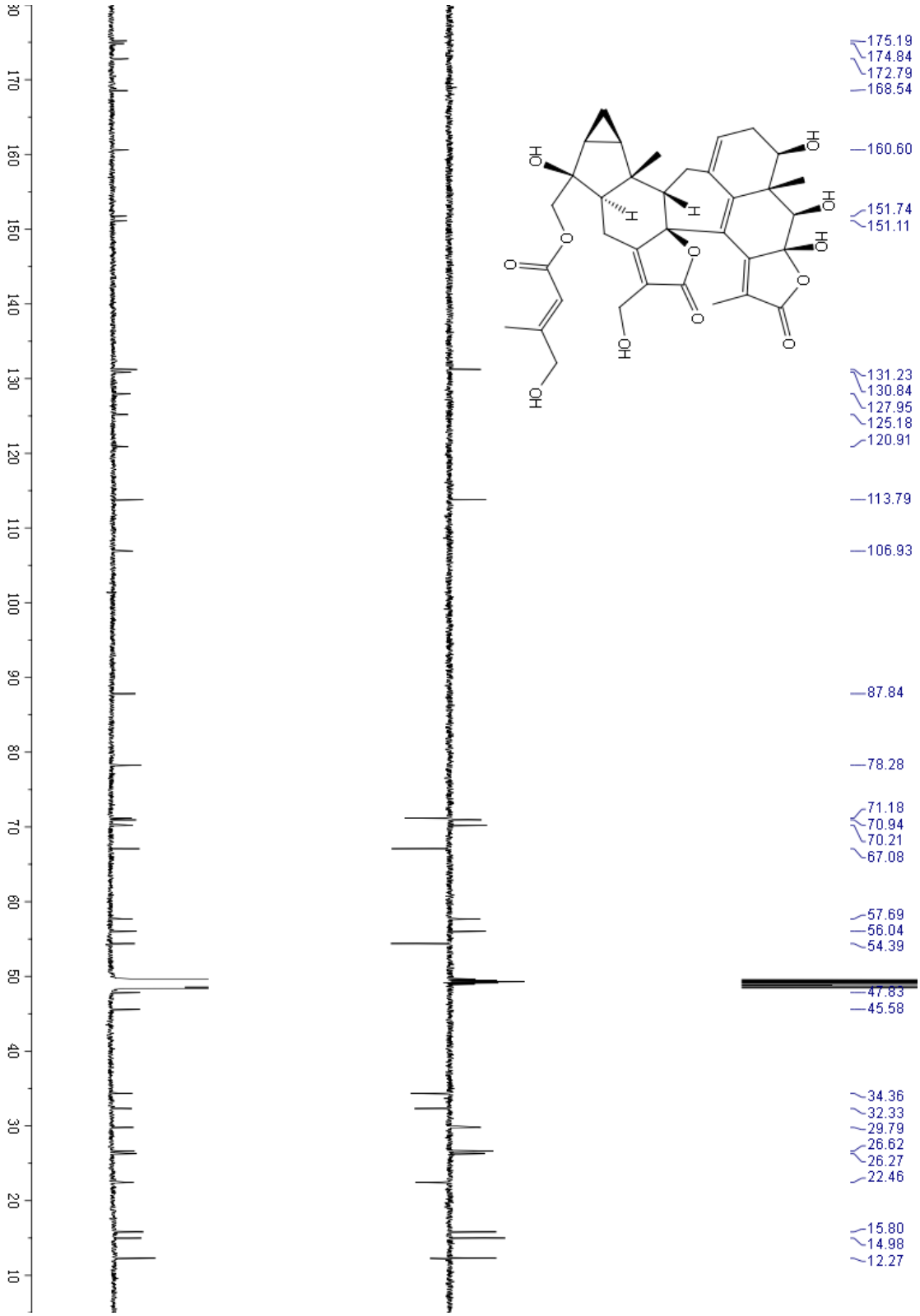


Figure S15. HSQC spectrum of fortunoid B (**2**) in CD_3OD

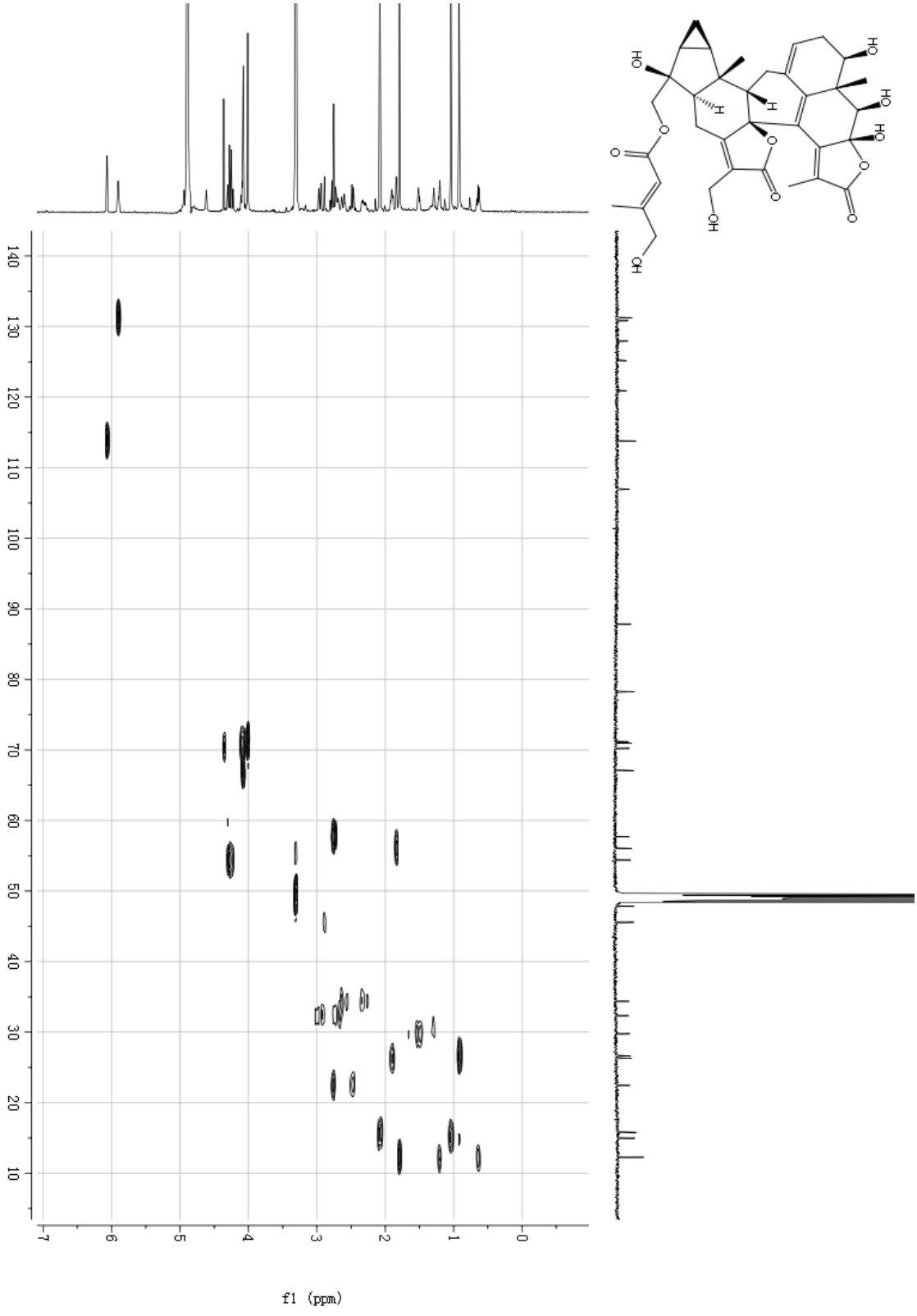


Figure S16. HMBC spectrum of fortunoid B (**2**) in CD_3OD

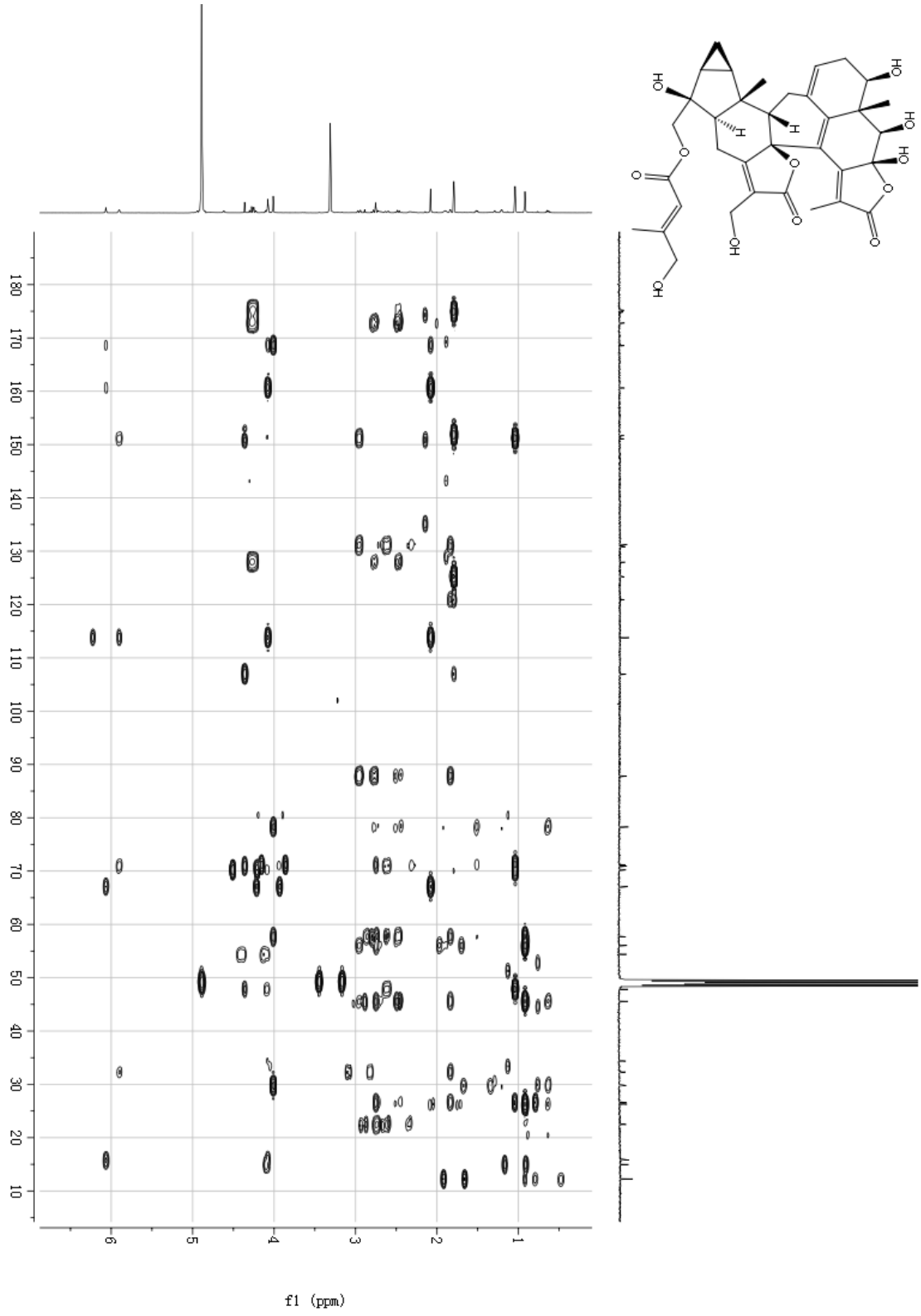


Figure S17. ROESY spectrum of fortunoid B (**2**) in CD_3OD

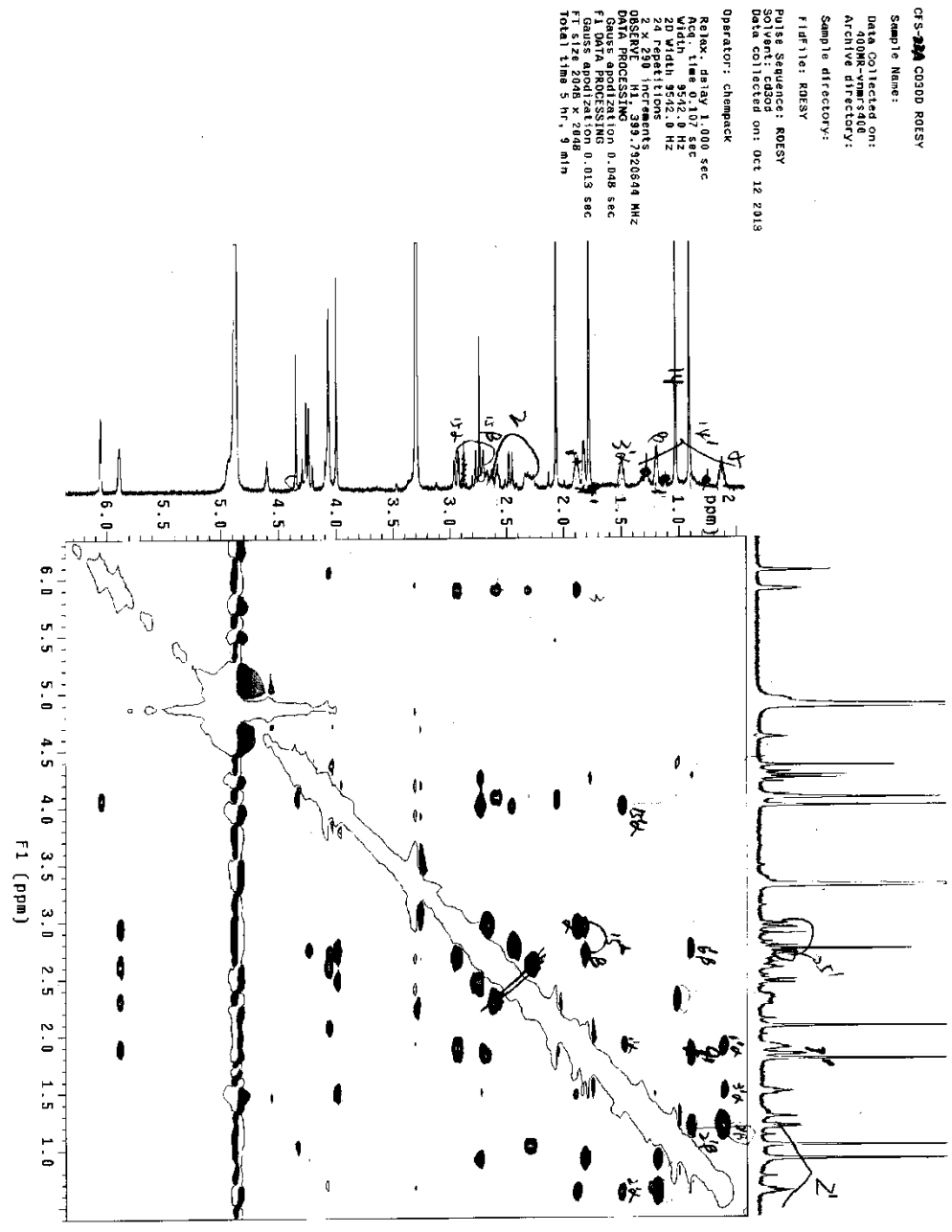


Figure S18. (+)-ESIMS spectrum of fortunoid B (**2**)

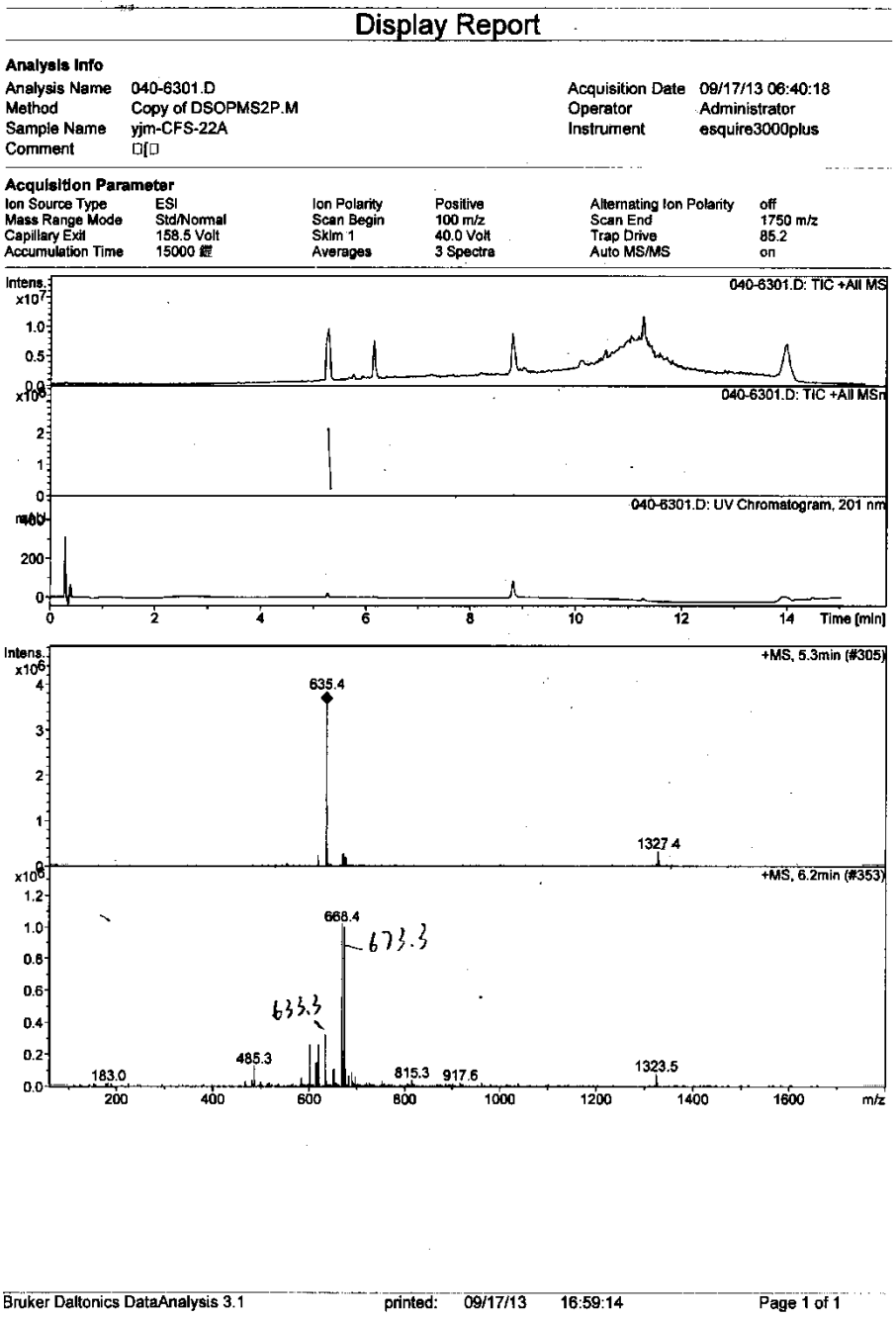


Figure S19. (−)-ESIMS spectrum of fortunoid B (**2**)

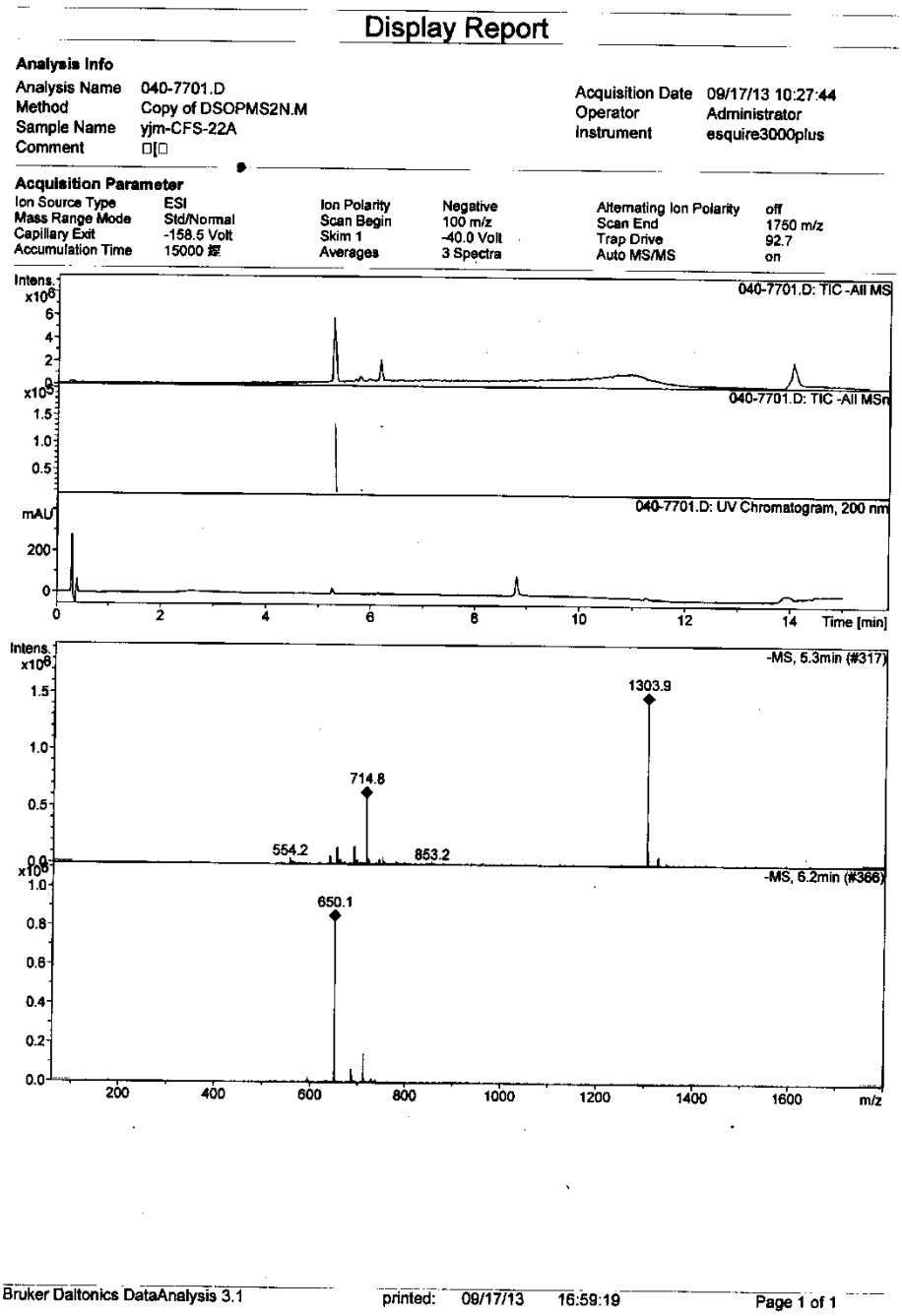


Figure S20. (+)-HRESIMS spectrum of fortunoid B (**2**)

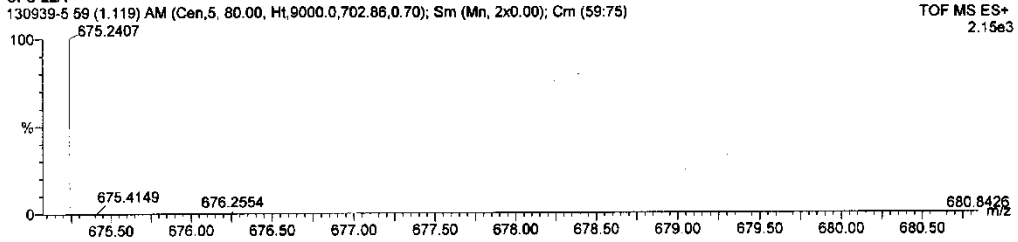
5

Elemental Composition Report **Page 1**

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)

SIMM-Mass Spec Q-Tof Ultima 28-Oct-201310:17:08
CFS-22A
130939-5 59 (1.119) AM (Cen,5, 80.00, Ht,9000.0,702.86,0.70); Sm (Mn, 2x0.00); Cm (59:75) TOF MS ES+
2.15e3



Minimum:	50.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
675.2407	100.00	675.2417	-1.0	-1.6	15.5	1	C35 H40 O12 Na

Figure S21. IR spectrum of fortunoid B (**2**)

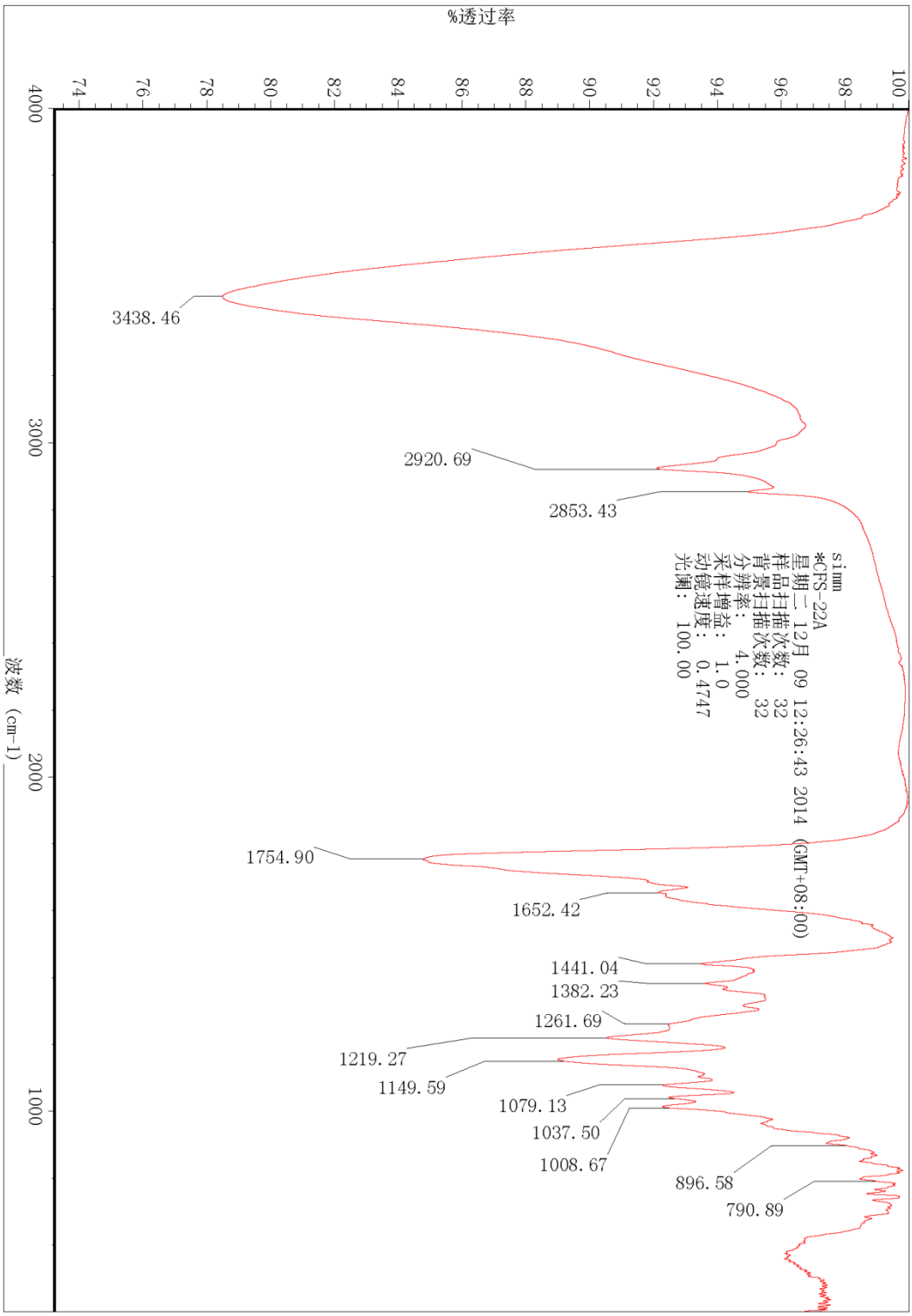


Figure S22. ^{1}H NMR spectrum of fortunoid C (**3**) in CD_3OD

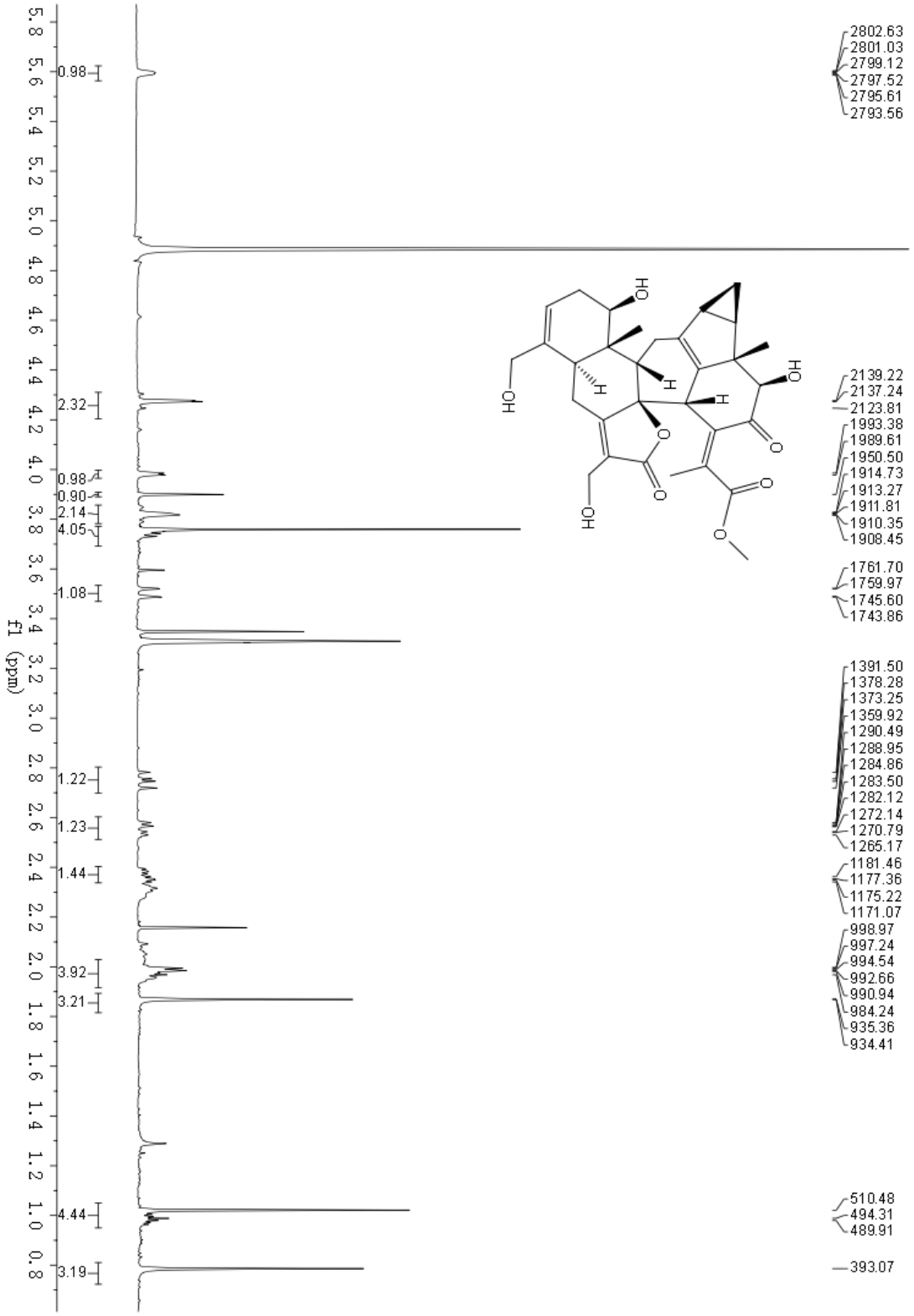


Figure S23. ^{13}C NMR spectrum of fortunoid C (**3**) in CD_3OD

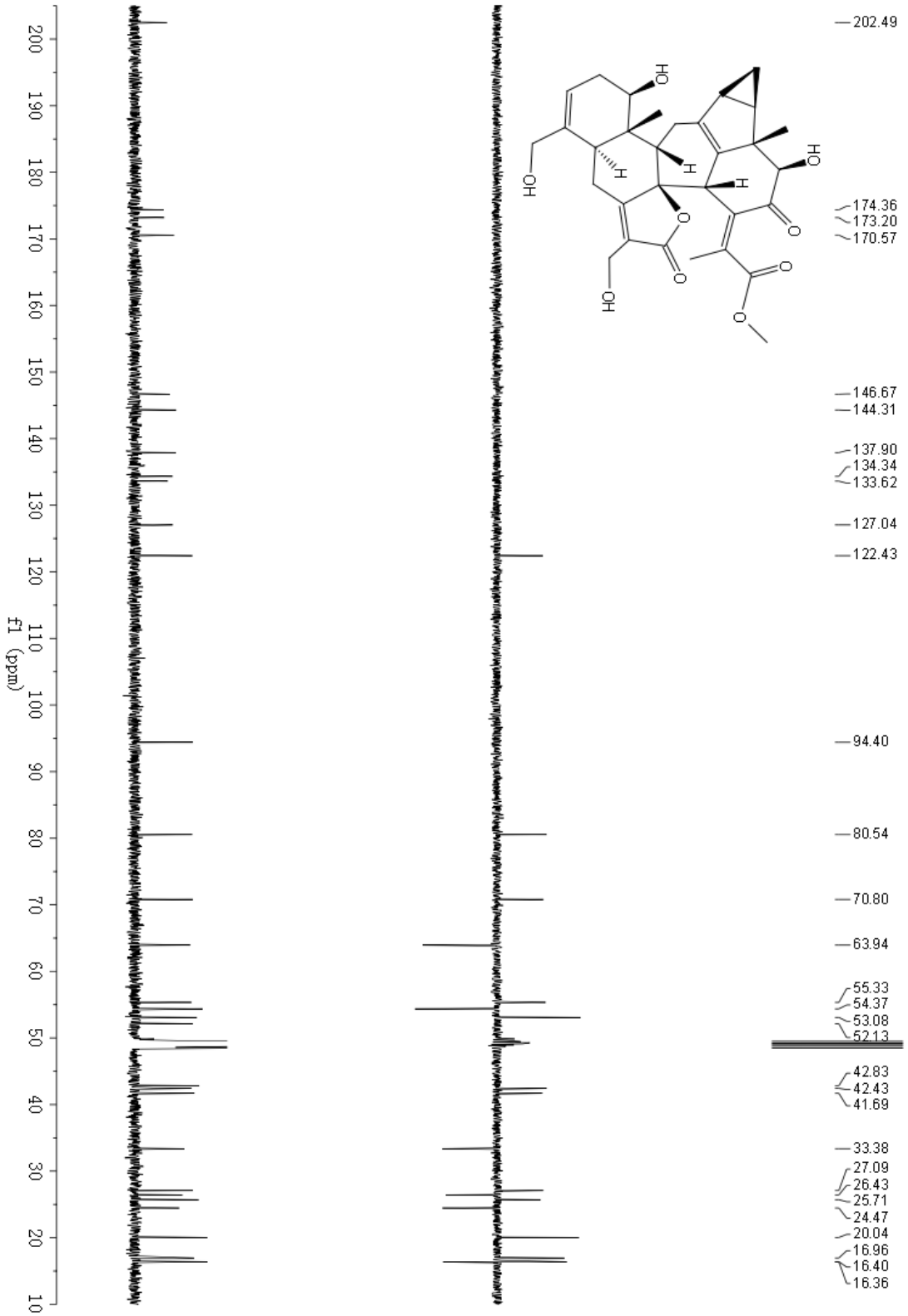


Figure S24. $^{1}H–^{1}H$ COSY spectrum of fortunoid C (**3**) in CD_3OD

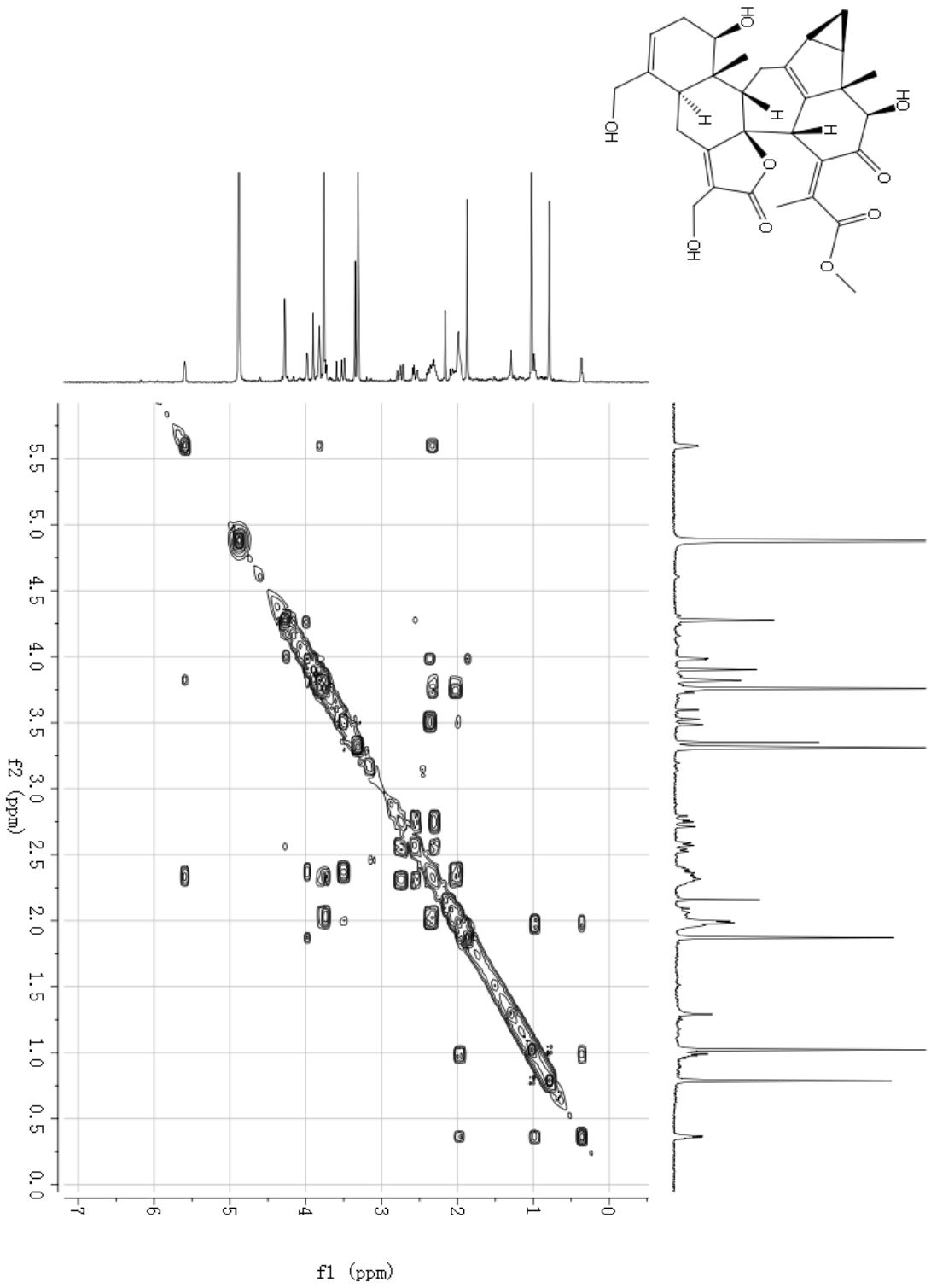


Figure S25. HSQC spectrum of fortunoid C (**3**) in CD_3OD

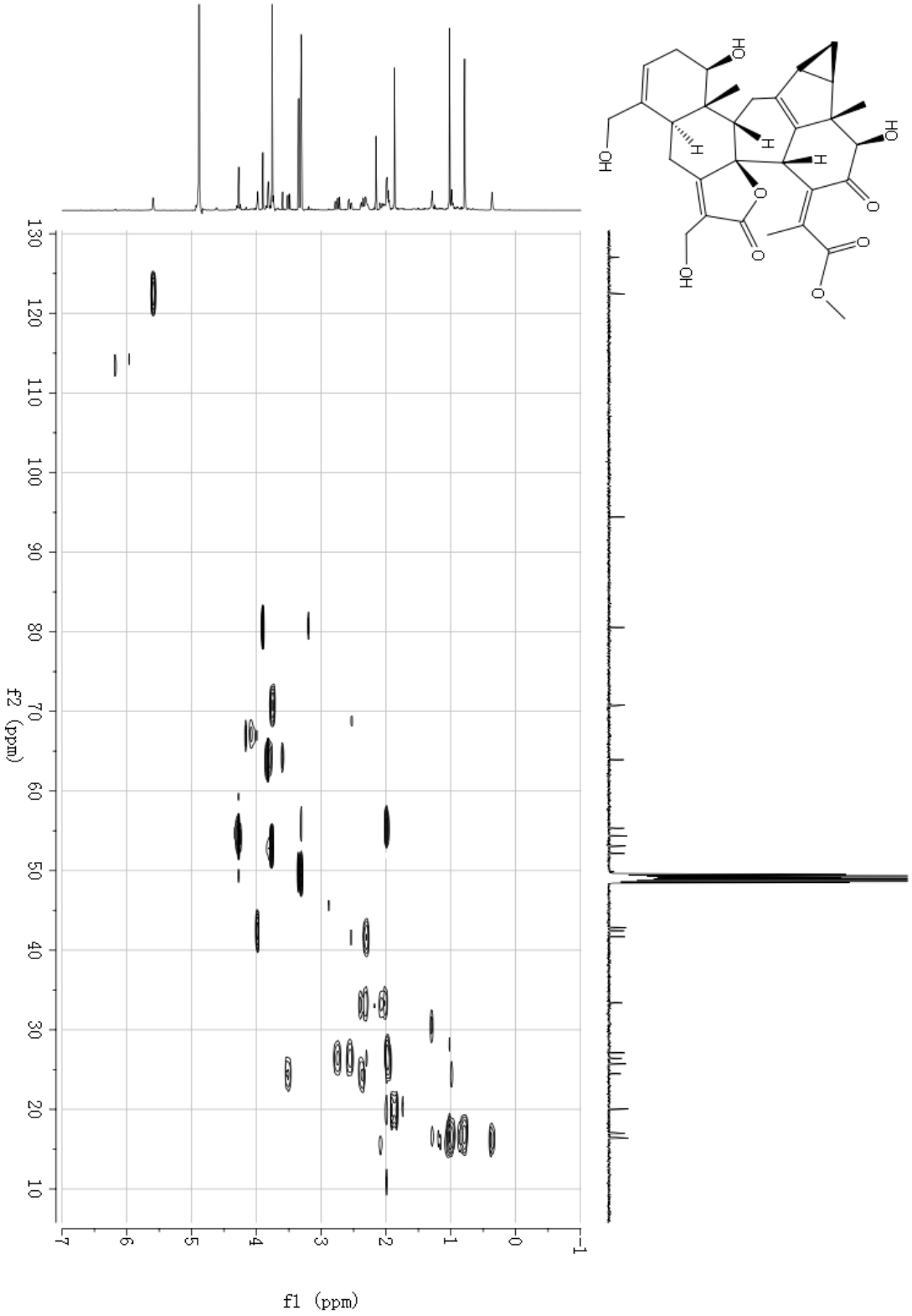


Figure S26. HMBC spectrum of fortunoid C (**3**) in CD_3OD

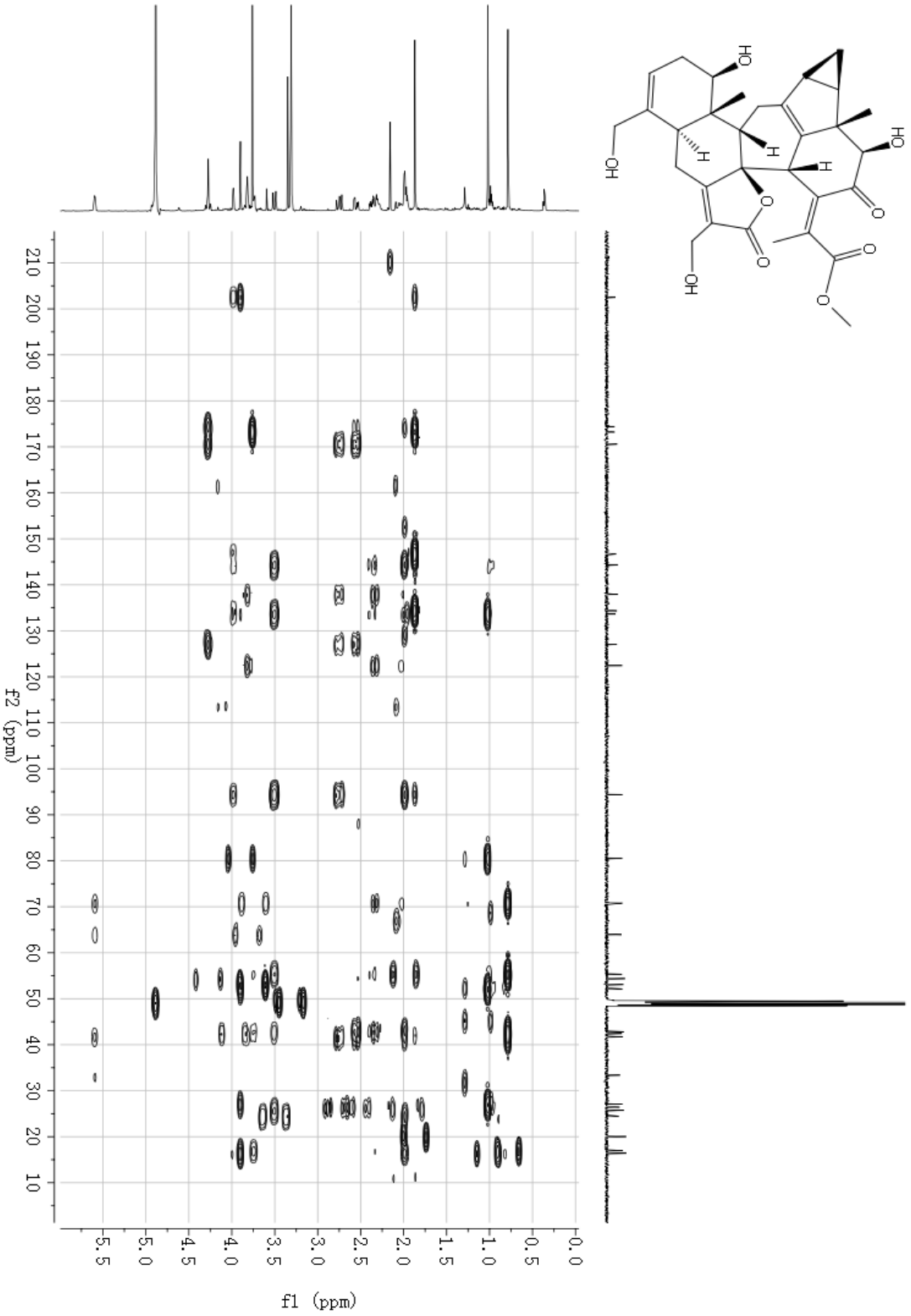


Figure S27. ROESY spectrum of fortunoid C (**3**) in CD_3OD

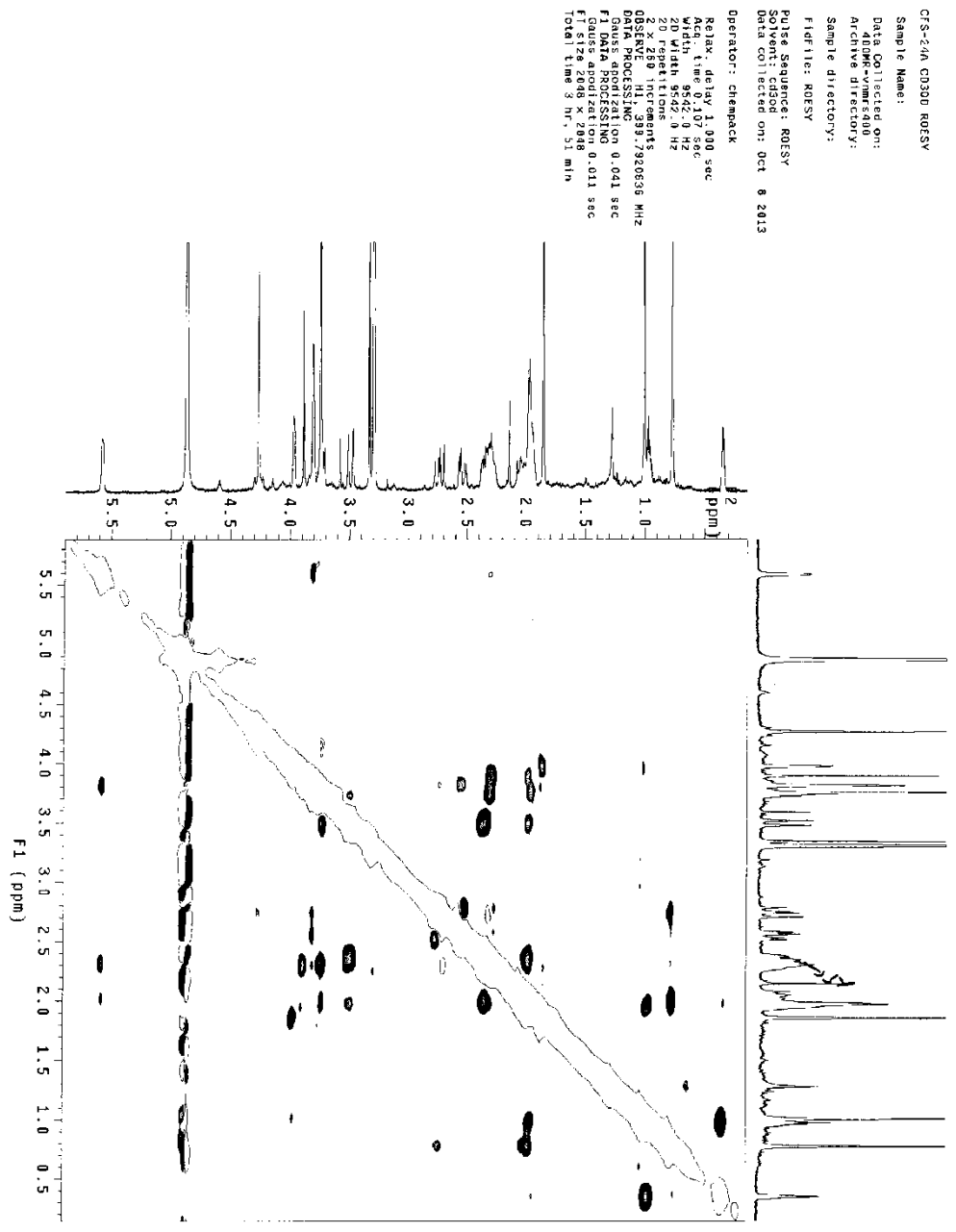


Figure S28. (+)-ESIMS spectrum of fortunoid C (**3**)

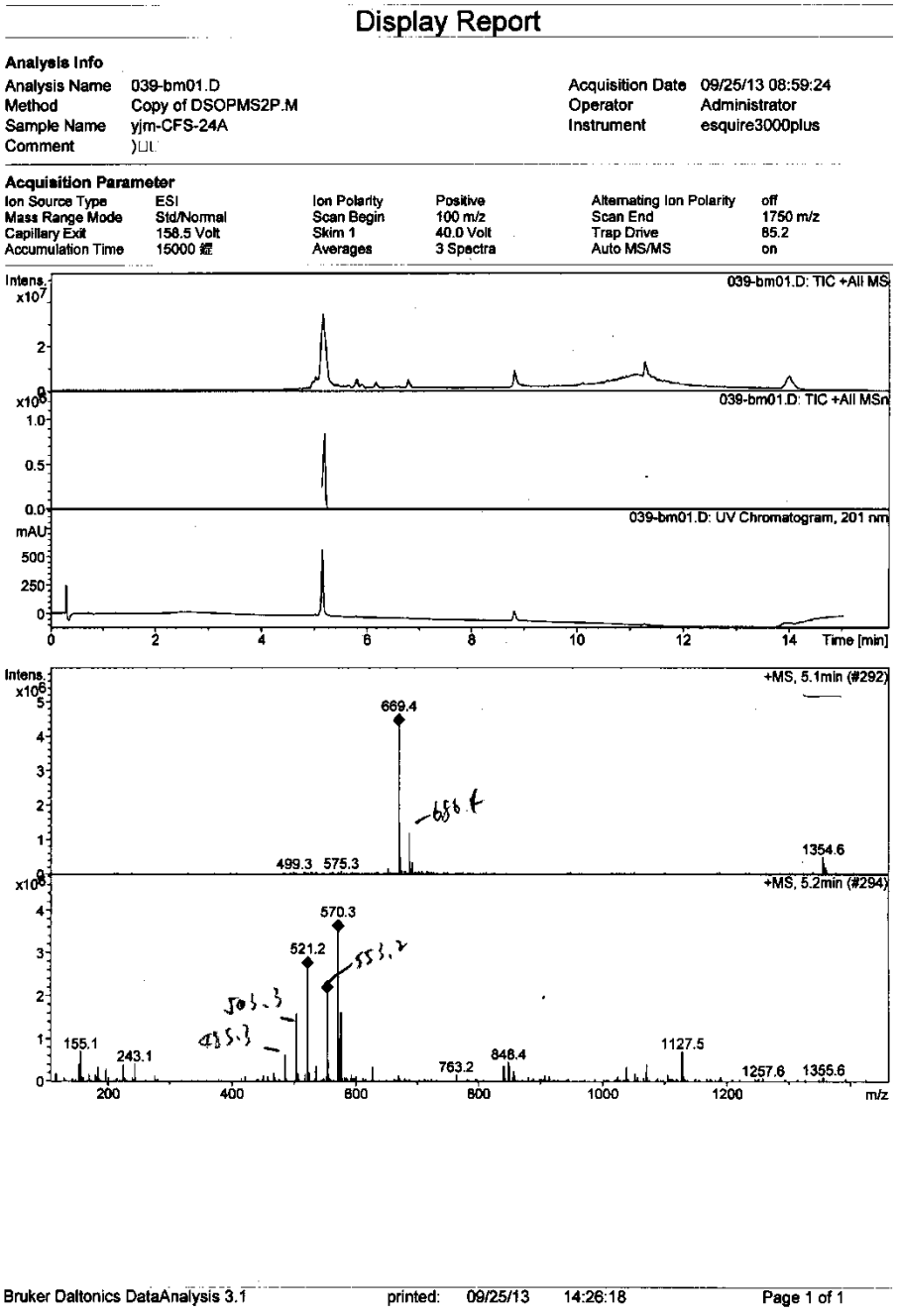


Figure S29. (−)-ESIMS spectrum of fortunoid C (**3**)

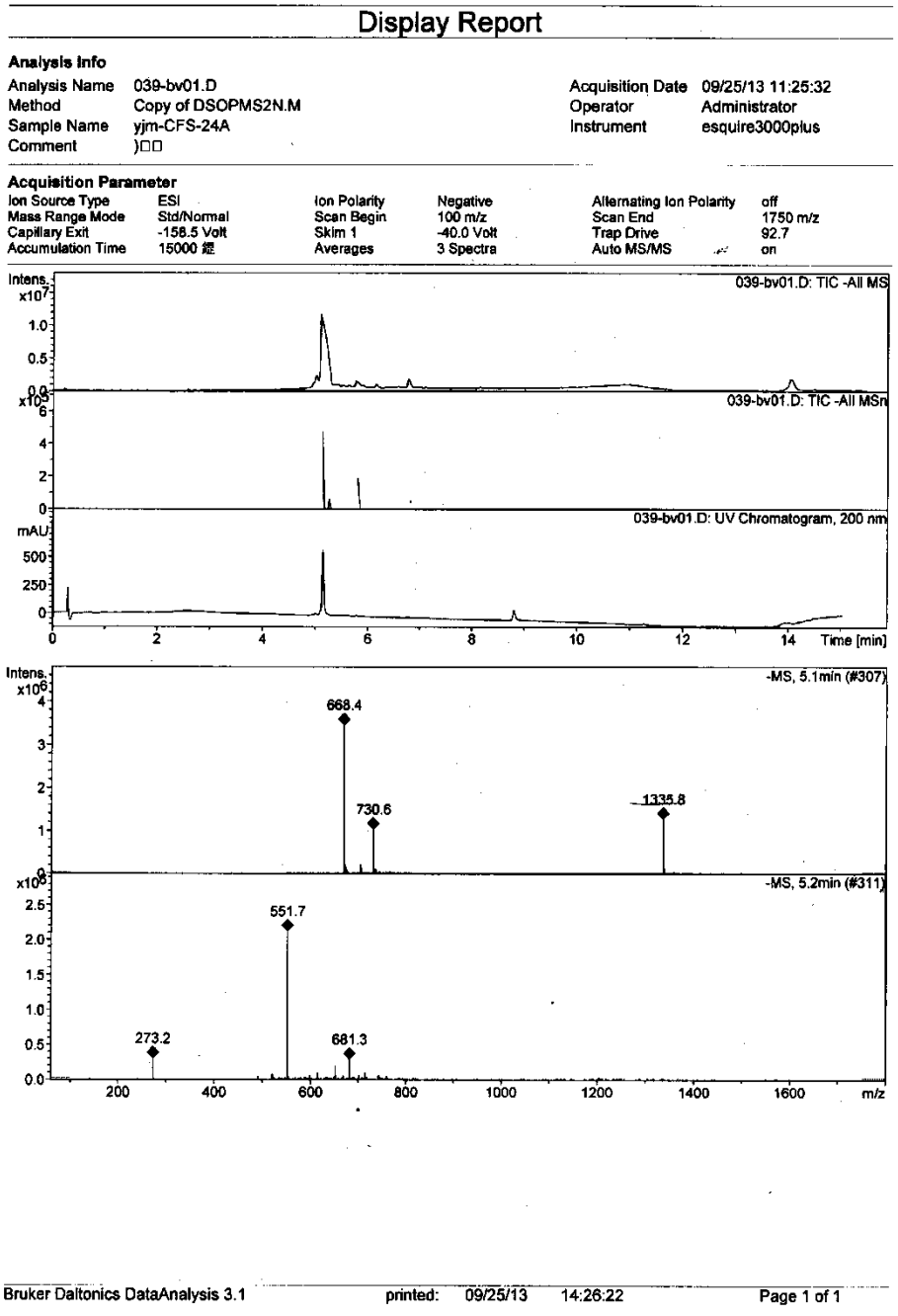


Figure S30. (+)-HRESIMS spectrum of fortunoid C (**3**)

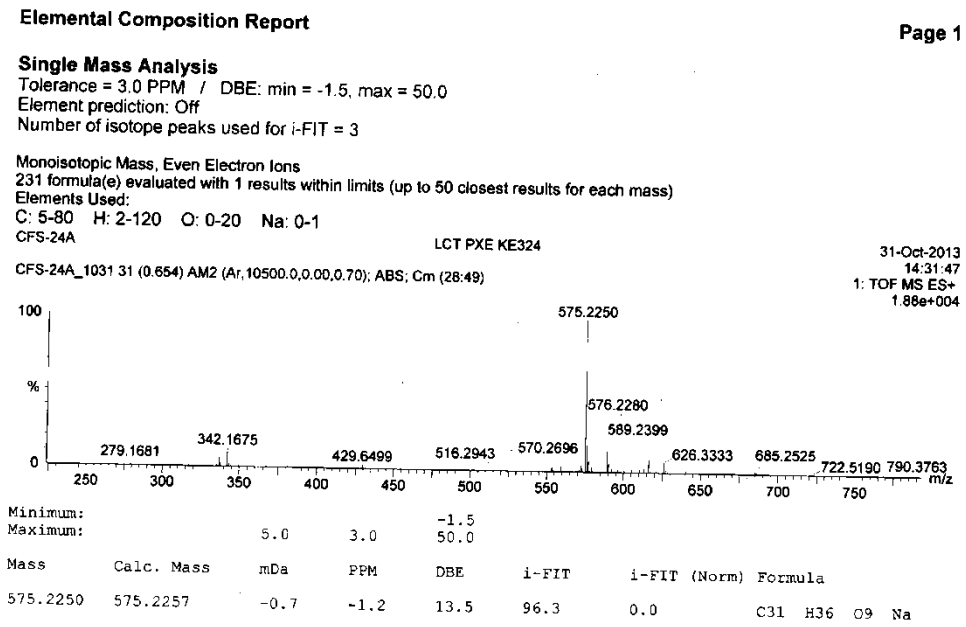


Figure S31. IR spectrum of fortunoid C (**3**)