Supporting Information

Trigochinins A–C: Three New Daphnane-type Diterpenoids from *Trigonostemon chinensis*

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For compound 3

S1. ^{1}H NMR Data of compounds 1–3 (in $CDCl_3$)

Table 1. ^{1}H NMR Data of Compounds **1**–**3** (in $CDCl_3$)[a]

no.	**1**	**2**	**3**
1	1.14 (m)	1.29 (m)	1.42 (m)
	1.94 (m)	2.01 (m)	2.16 (m)
2	2.20 (m)	2.45 (m)	2.43 (m)
3	4.18 (t, 10.2)	5.22 (d, 10.4)	5.12 (d, 10.1)
5	6.30 (s)	6.29 (s)	6.15 (s)
7	5.70 (d, 4.3)	5.70 (d, 4.3)	5.73 (d, 5.6)
8	2.29, (dd, 4.3, 1.4)	2.96 (dd, 4.3, 1.4)	2.74 (dd, 5.6, 0.9)
10	2.14 (m)	2.20 (m)	2.24 (dd, 13.4, 5.4)
11	2.23 (m)	2.23 (m)	1.82 (m)
12	6.37 (dd , 4.2, 1.4)	6.37 (dd, 4.3, 1.4)	4.16 (brs)
14	6.09 (brs)	6.10 (brs)	4.57 (brs)
16	5.49 (s)	5.49 (s)	5.24 (s)
	5.44 (s)	5.43 (s)	4.97 (s)
17	1.95 (s)	1.96 (s)	1.86 (s)
18	1.17 (d, 6.9)	1.18 (d, 6.8)	1.45 (d, 6.6)
19	0.95 (d, 7.2)	0.85 (d, 7.1)	0.84 (d, 7.1)
20	1.33 (s)	1.39 (s)	1.43 (s)
3′	8.12 (dd, 8.4, 1.5)	7.97 (dd, 8.3, 1.3)	7.79 (m)
4′	7.45 (m)	7.45 (m)	7.41 (m)
5′	7.90 (m)	7.59 (m)	7.38, m
6′	7.45 (m)	7.45 (m)	7.41 (m)
7′	8.12 (dd, 8.4, 1.5)	7.97 (dd, 8.3, 1.3)	7.79 (m)
3″	7.89 (dd, 8.3, 1.4)	7.89 (dd, 8.2, 1.3)	8.00 (dd, 8.4, 1.4)
4″	7.40 (m)	7.41 (m)	7.46 (m)
5″	7.88 (m)	7.54 (m)	7.59 (m)
6″	7.40 (m)	7.41 (m)	7.46 (m)
7″	7.89(dd, 8.3, 1.4)	7.89 (dd, 8.2, 1.3)	8.00 (dd, 8.4, 1.4)
HO-3	2.79 (d, 10.2)		
HO-9	3.61 (s)	3.52 (s)	
HO-13			3.81 (brs)
3-OAc		2.04 (s)	1.98 (s)*
5-OAc			
7-OAc	2.15 (s)	2.14 (s)	1.97 (s)*
12-OAc	1.94 (s)	1.94 (s)	
14-OAc	2.14 (s)	2.13 (s)	

[a] Data were recorded at 400 MHz, chemical shifts are in ppm, and the coupling constants *J* are in Hz (in parentheses); *it may be exchangeable in the same vertical column.

S2. ^{13}C NMR Data of compounds 1–3 (in $CDCl_3$)

Table 2. ^{13}C NMR Data of Compounds **1**–**3** (in $CDCl_3$)[a].

no.	**1**	**2**	**3**	no.	**1**	**2**	**3**
1	34.9	34.5	32.7	1′	165.9	165.8	108.8
2	32.8	31.0	30.4	2′	130.0	129.9	138.1
3	72.1	73.8	74.0	3′	129.9	129.5	125.3
4	92.8	91.0	90.7	4′	128.5	128.5	128.0
5	73.6	73.8	73.7	5′	130.0	133.4	129.5
6	84.8	83.9	83.4	6′	128.5	128.5	128.0
7	78.9	79.3	77.0	7′	129.9	129.5	125.3
8	39.3	39.2	39.1	1″	164.0	164.0	165.5
9	76.7	76.8	77.0	2″	129.6	129.5	129.6
10	49.6	49.6	48.1	3″	129.5	129.5	129.5
11	40.3	40.3	35.0	4″	128.5	128.5	128.5
12	72.7	72.6	79.6	5″	133.2	133.2	133.3
13	81.9	81.8	69.4	6″	128.5	128.5	128.5
14	75.3	75.2	76.2	7″	129.5	133.2	129.5
15	139.3	139.2	141.7	3-OAc		170.3	170.3
						20.6	20.6*
16	119.7	119.7	115.9	7-OAc	170.1	170.1,	171.6
					21.3	21.3	21.3*
17	20.1	20.1	18.2	12-OAc	169.3	169.3	
					20.8	20.8	
18	11.5	11.6	14.6	14-OAc	169.0	169.0	
					21.5	21.5	
19	15.5	15.8	15.9				
20	19.7	19.8	19.1				

[a] Data were recorded at 100 MHz, chemical shifts (δ) are in ppm; the full assignments were achieved by 2D NMR spectra; *it may be exchangeable in the same vertical column.

S3. Selected HMBC and ROESY correlations of compounds 2 and 3

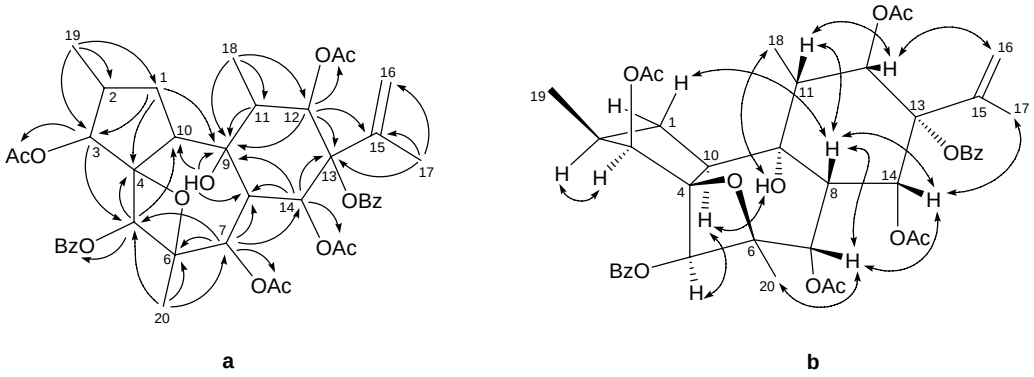


Figure 1. (a) Selected HMBC (H→C), and (b) ROESY (H↔H) correlations of **2**.

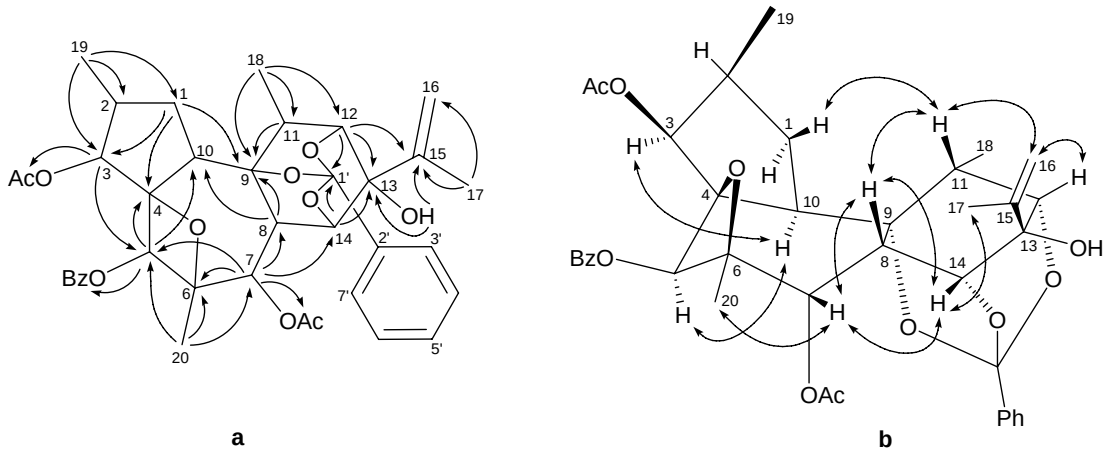


Figure 2. (a) Selected HMBC (H→C), and (b) ROESY (H↔H) correlations of **3**.

S4. Experimental Section

General Experimental Procedures

Melting points (not corrected) were determined using a SGW® X-4 apparatus (Shanghai Precision & Scientific Instrument Co., Ltd., China). Optical rotations were determined on a Perkin-Elmer 341 polarimeter, and CD spectra were obtained on a Jasco 810 spectrometer. UV spectra were recorded on a Shimadzu UV-2550 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 577 spectrometer with KBr disks. NMR spectra were acquired on a Bruker AM-400 spectrometer. The delays for the HMBC and the mixing times for the NOESY spectra, were 1 s and 220 ms, respectively. EIMS and HREIMS (70 eV) were carried out on a Finnigan MAT 95 mass spectrometer. ESIMS and HRESIMS were obtained on an Esquire 3000plus (Bruker Daltonics) and a Waters-Micromass Q-TOF Ultima Global electrospray mass spectrometer, respectively. Silica gel (200-300 mesh) (Qingdao Haiyang Chemical Co. Ltd.), C18 reverse-phased silica gel (150-200 mesh, Merck), MCI gel (CHP20P, 75-150 μM, Mitsubishi Chemical Industries Ltd.), and Sephadex LH-20 gel (Amersham Biosciences) were used for column chromatography. All solvents used for chromatography were of analytical grade (Shanghai Chemical Plant, Shanghai, People's Republic of China).

Plant Material

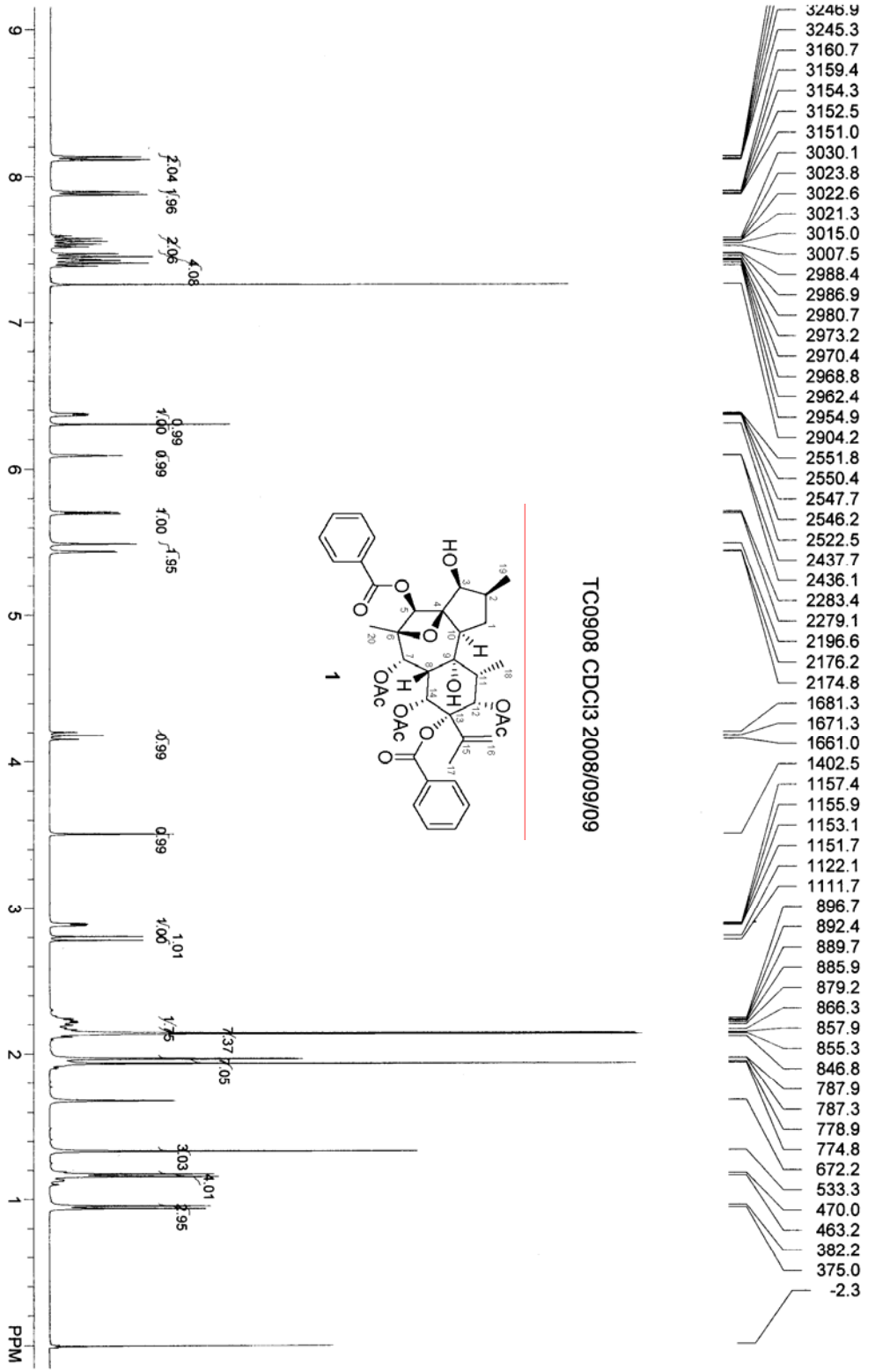
The plant material of *T. chinensis* was collected from Xishuangbanna, People's Republic of China, and was authenticated by Professor You-Kai Xu of Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences. A voucher specimen (accession number TCh-2005-2Y) has been deposited in the Shanghai Institute of Materia Medica.

Crystal Structure Analysis of trigochinin A (1)

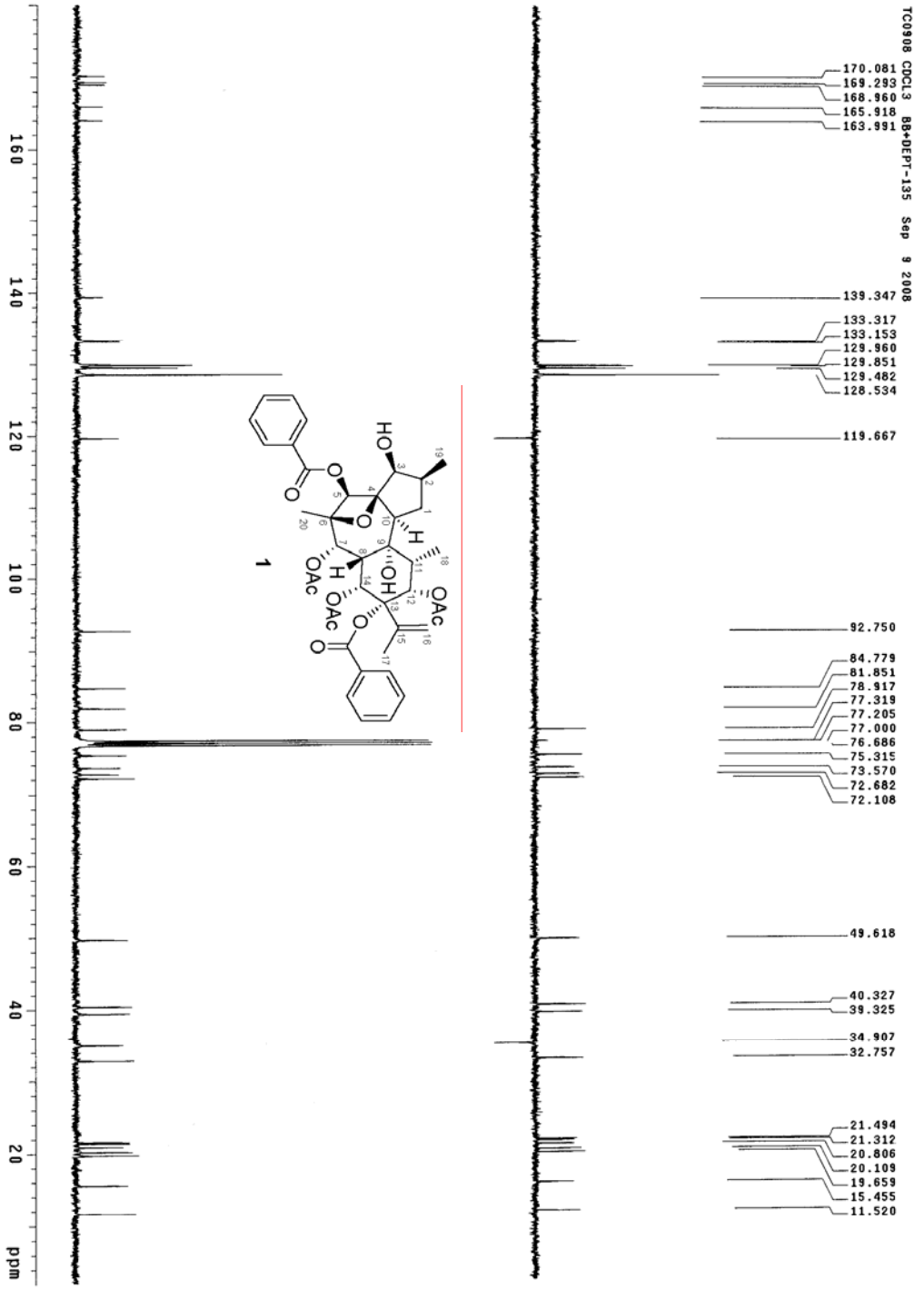
Crystal data were obtained on a Bruker SMART CCD detector employing graphite

monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K and operating in the ϕ-ω scan mode. The structure was solved by direct methods SHELXS-97 (G. M. Sheldrick, *SHELXS-97*: *Program for Crystal Structure Resolution*; University of Göttingen: Göttingen, Germany, 1997.) and refined with full-matrix least-squares calculations on F^2 using SHELXL-97 (G. M. Sheldrick, *SHELXL-97*: *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.). Crystallographic data for trigochinin A (**1**) have been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC-729840). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK. [fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk].

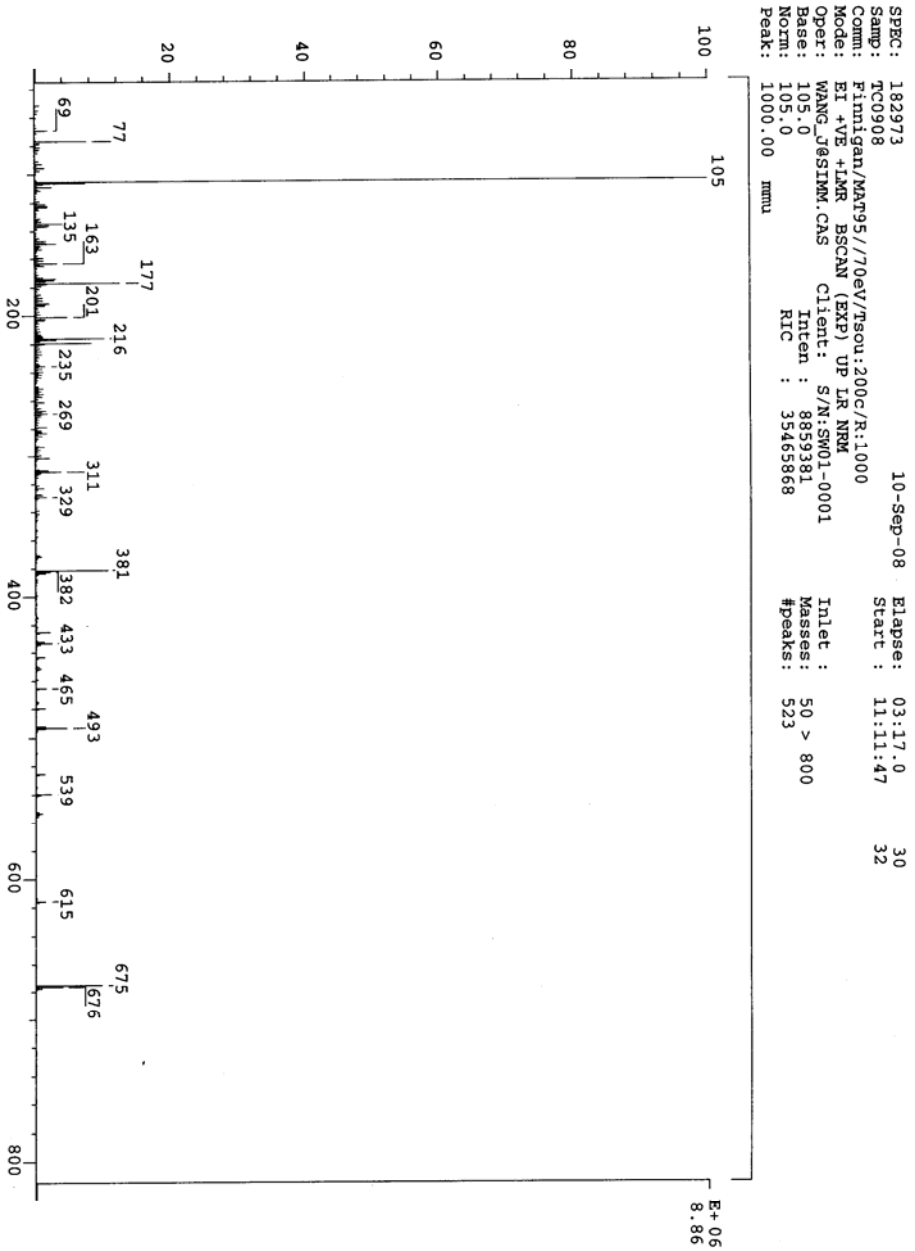
S5. ^{1}H NMR spectrum of trigochinin A (1)



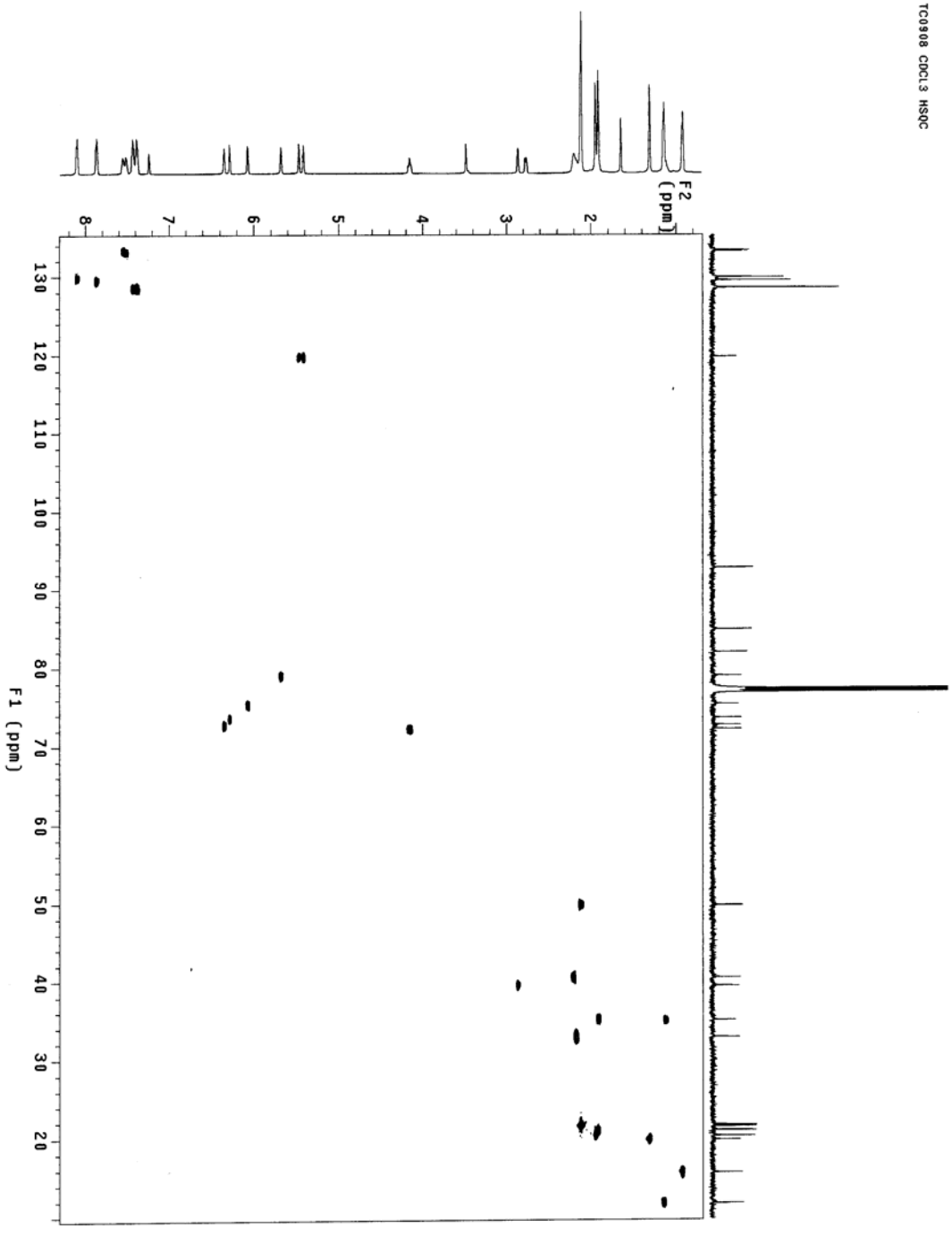
S6. ^{13}C NMR spectrum of trigochinin A (1)



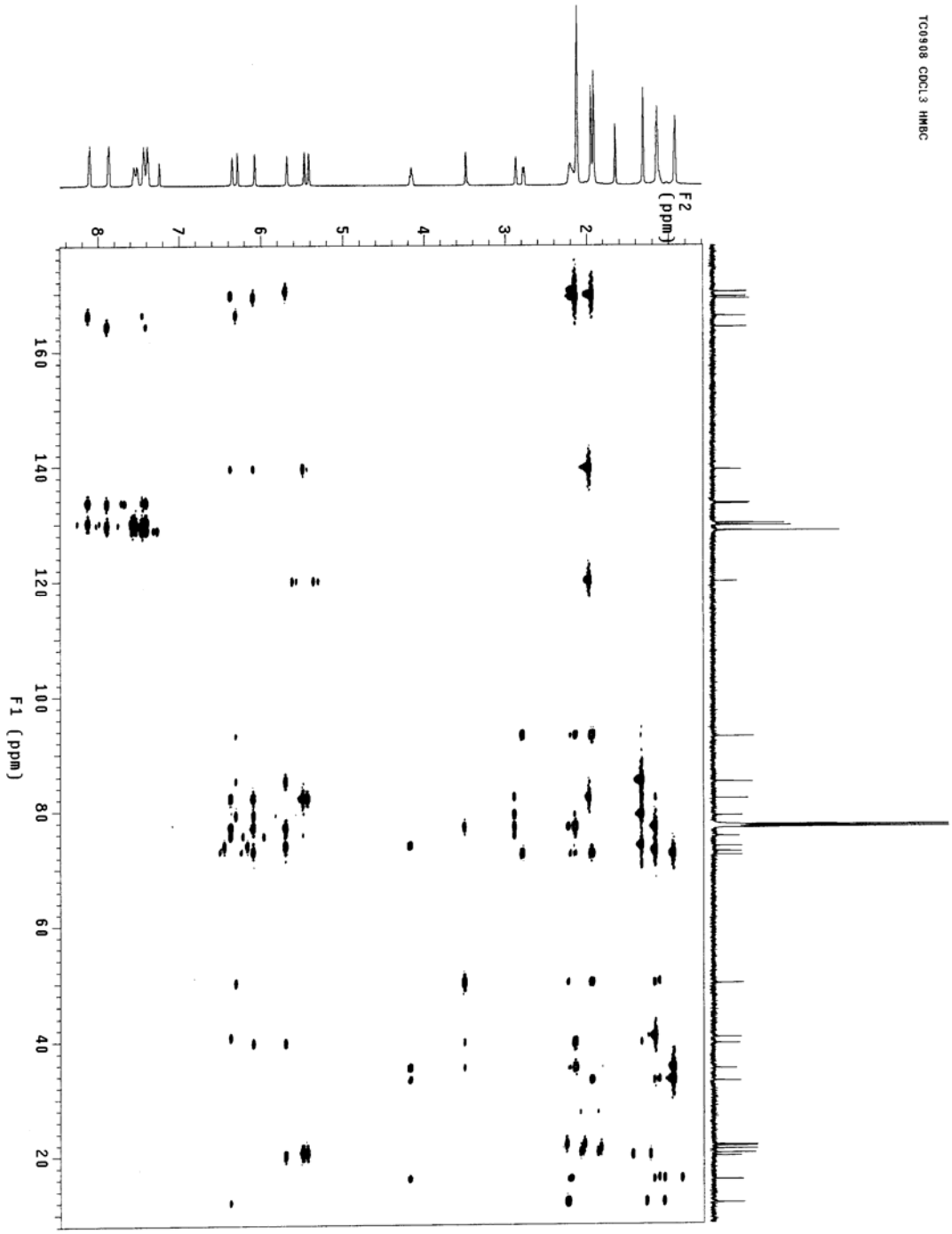
S7. EIMS of trigochinin A (1)



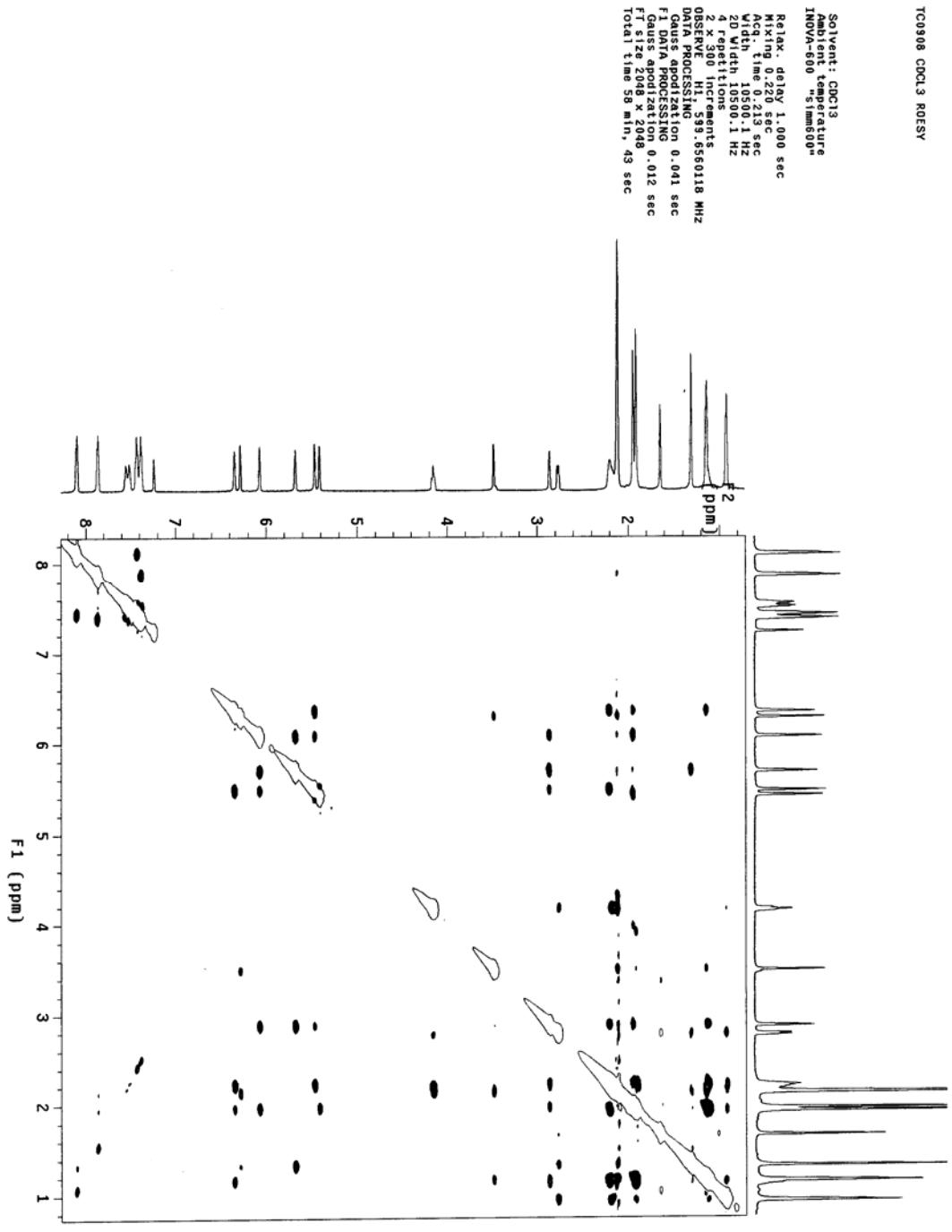
S8. HSQC spectrum of trigochinin A (1)



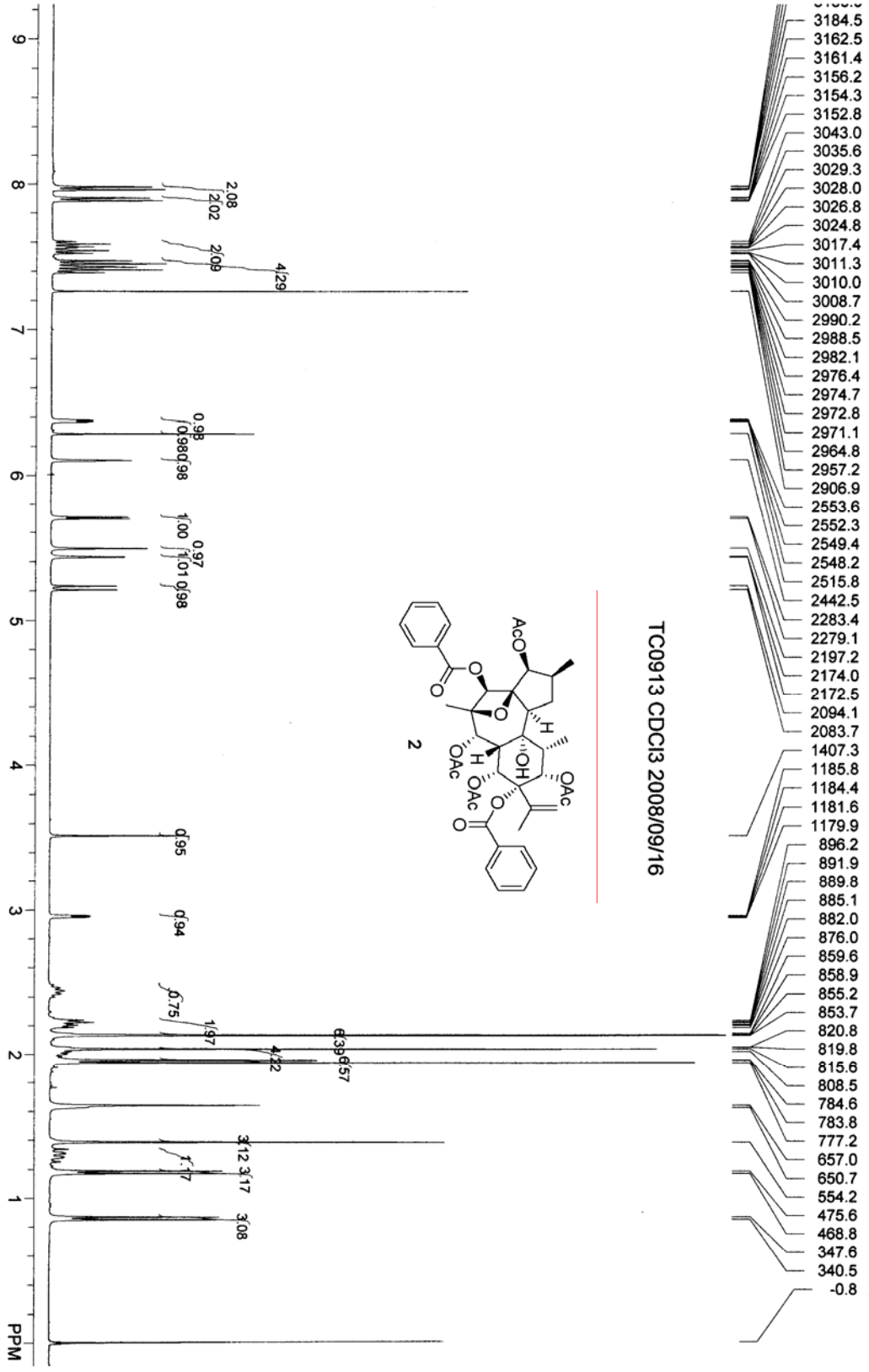
S9. HMBC Spectrum of trigochinin A (1)



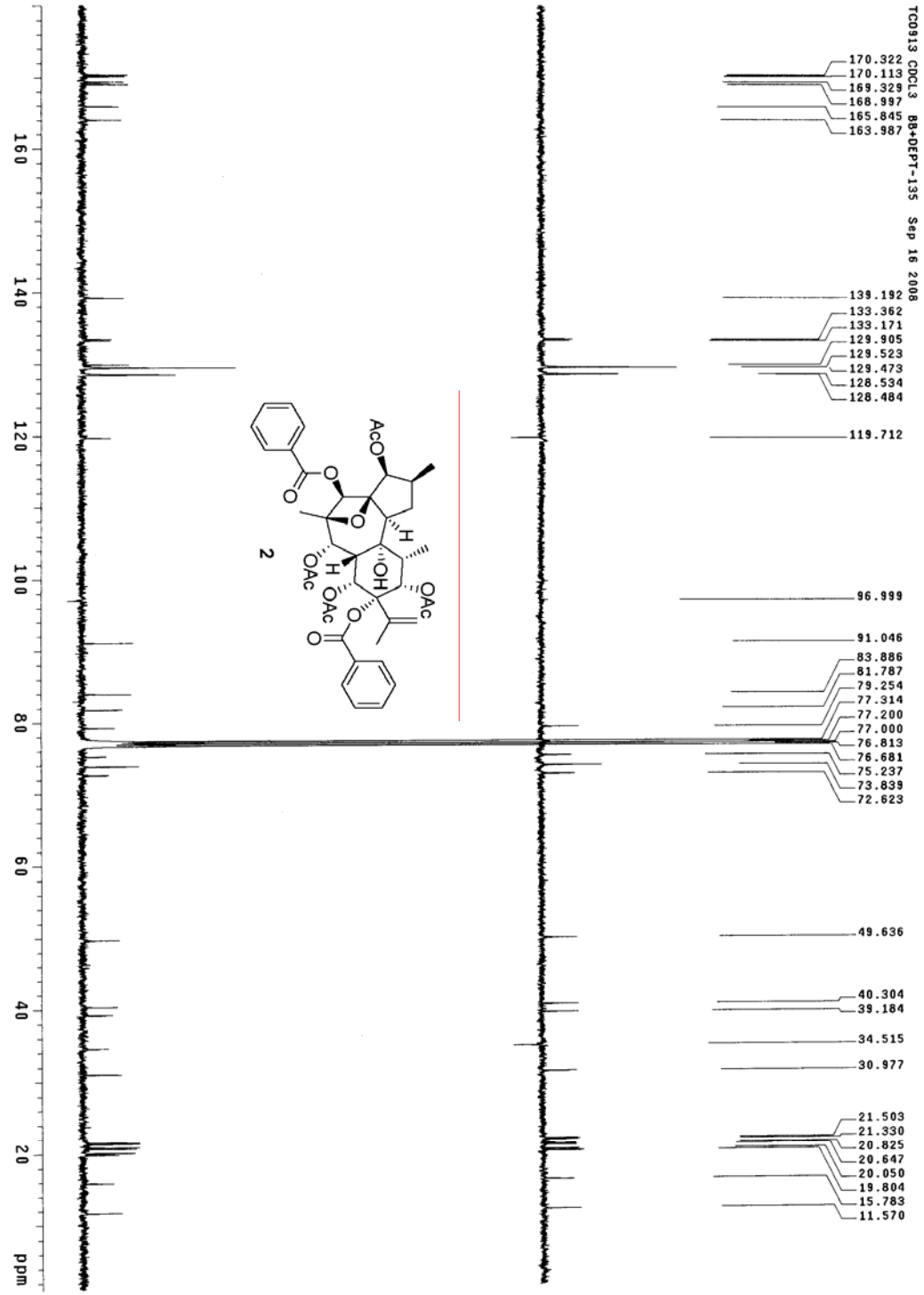
S10. ROESY spectrum of trigochinin A (1)



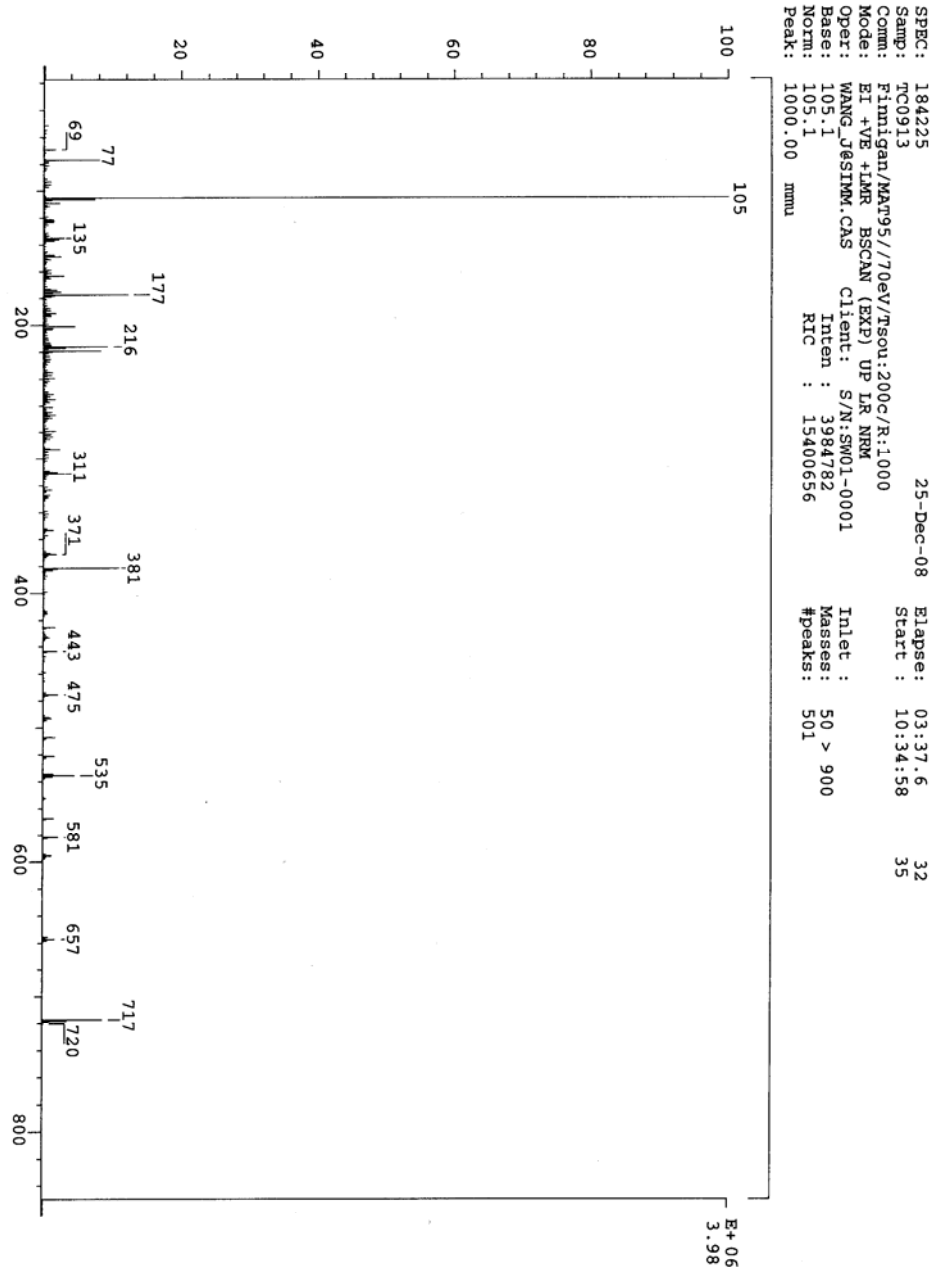
S11. ^{1}H NMR spectrum of trigochinin B (2)



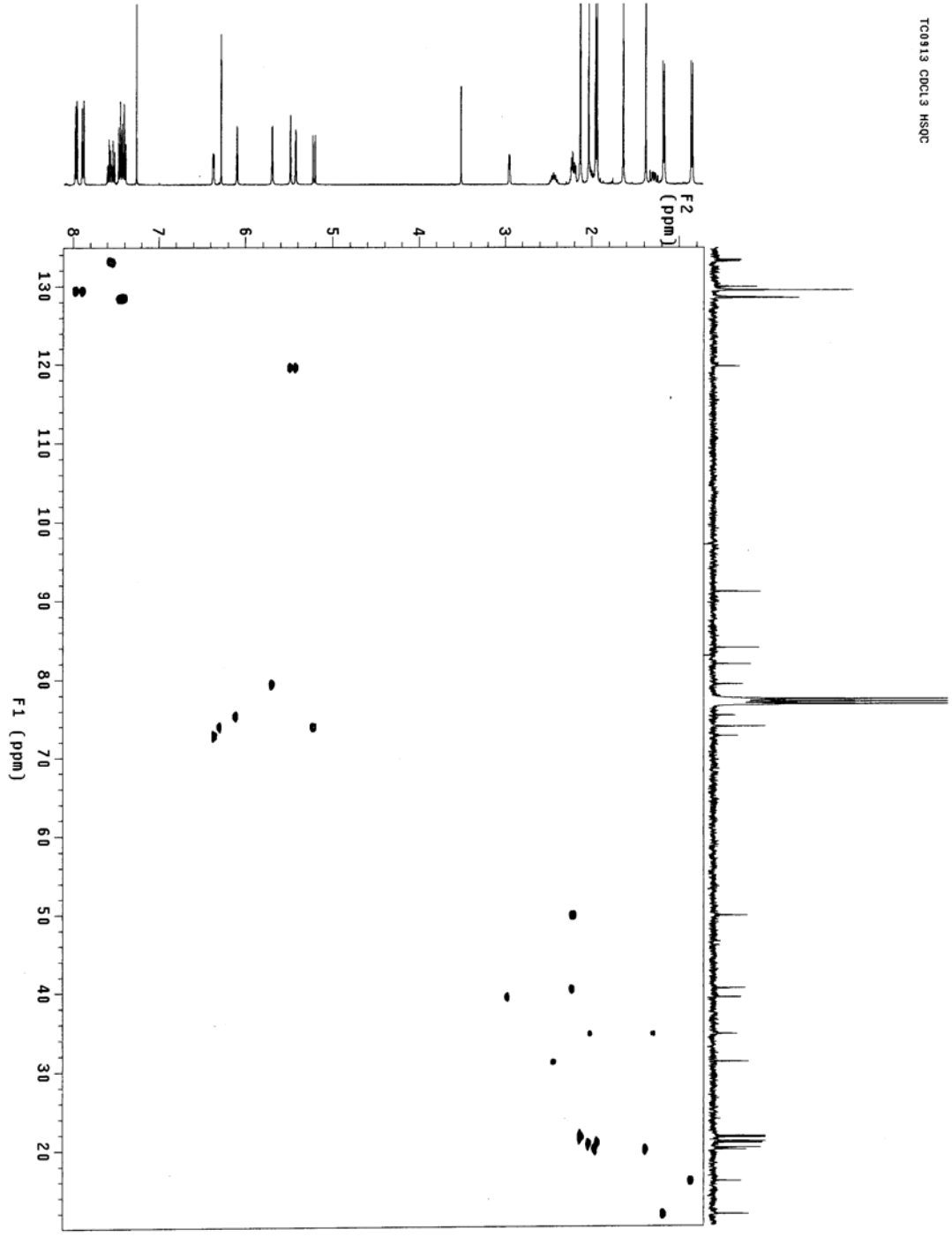
S12. ^{13}C NMR spectrum of trigochinin B (2)



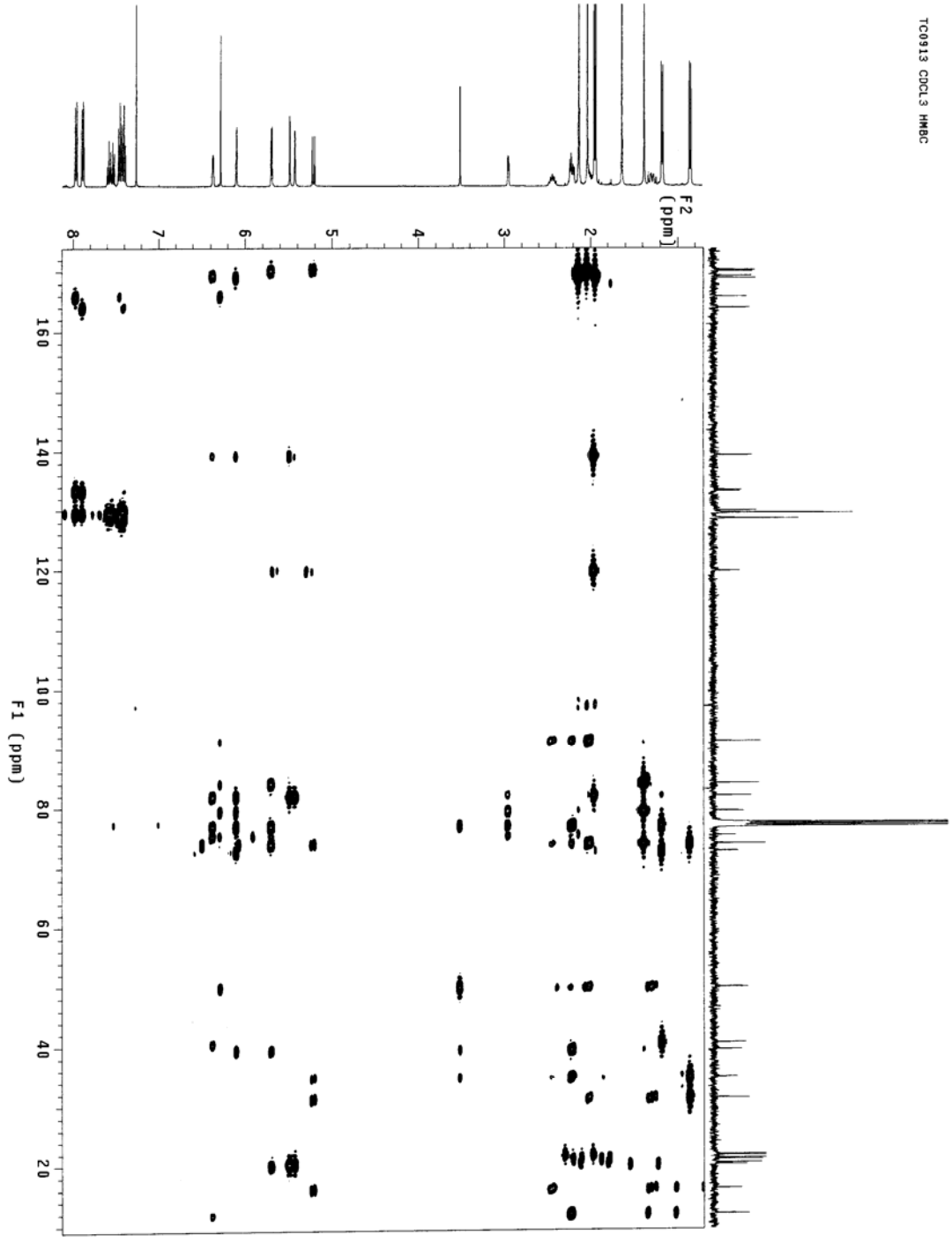
S13.EIMS of trigochinin B (2)



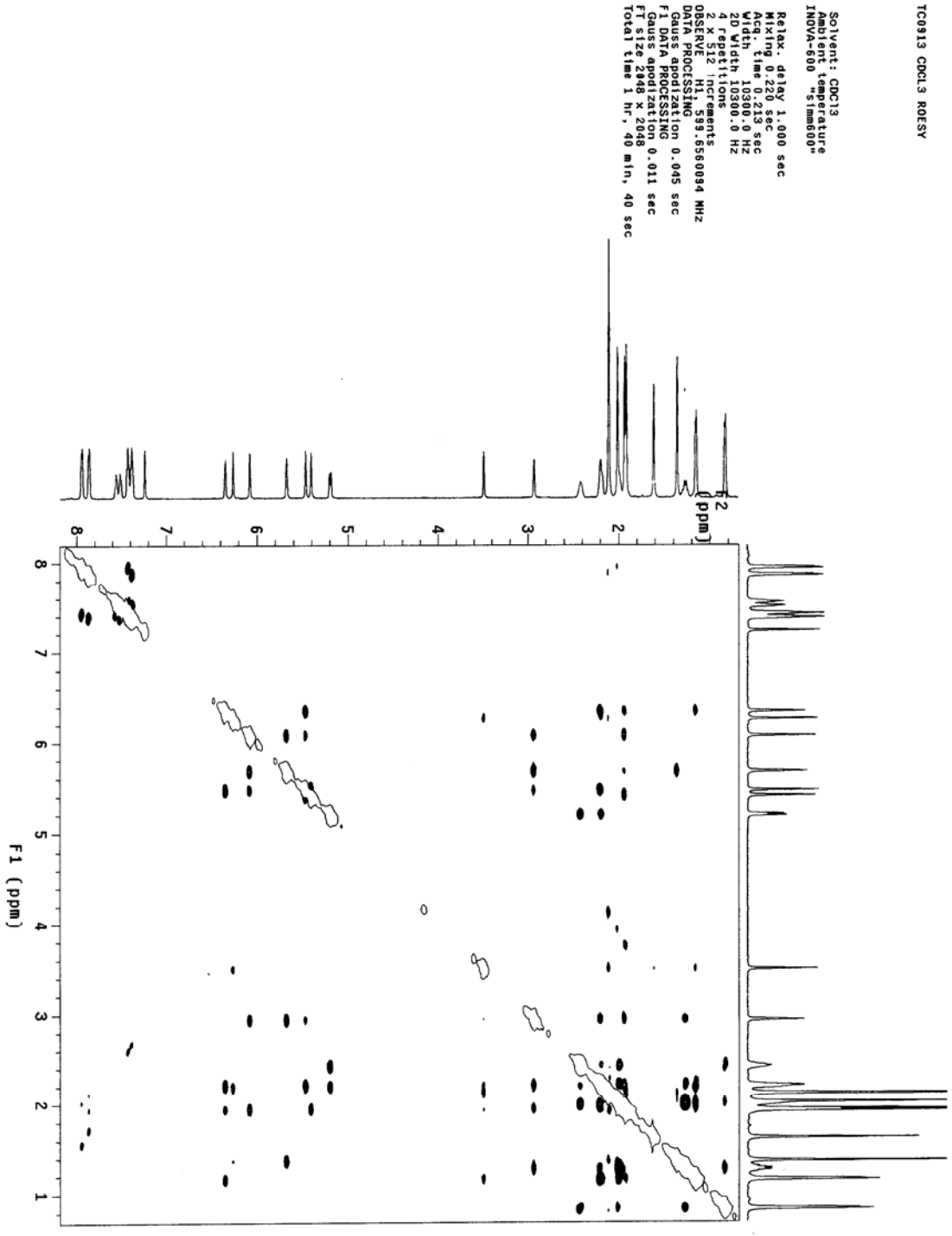
S14. HSQC spectrum of trigochinin B (2)



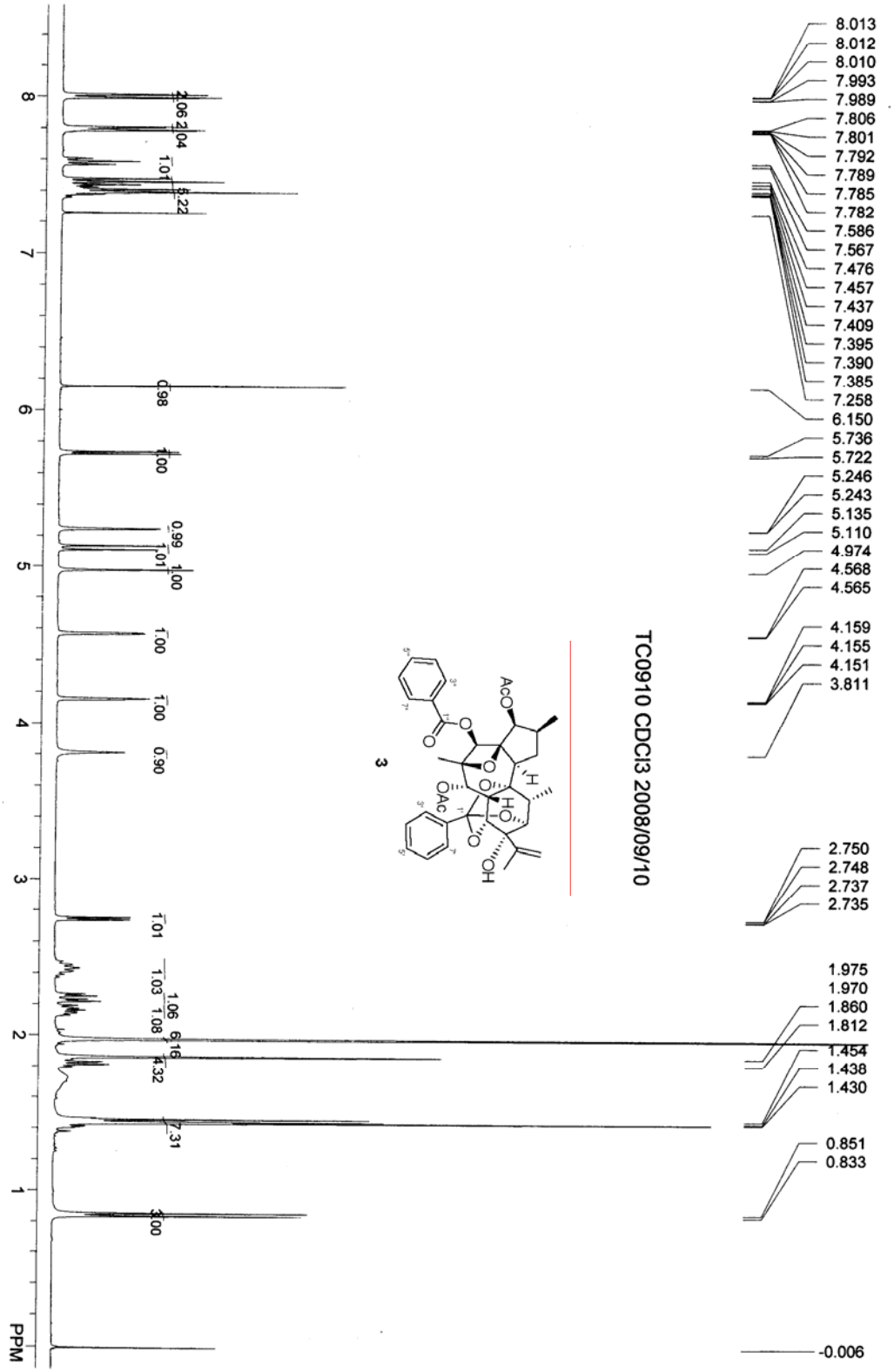
S15. HMBC spectrum of trigochinin B (2)



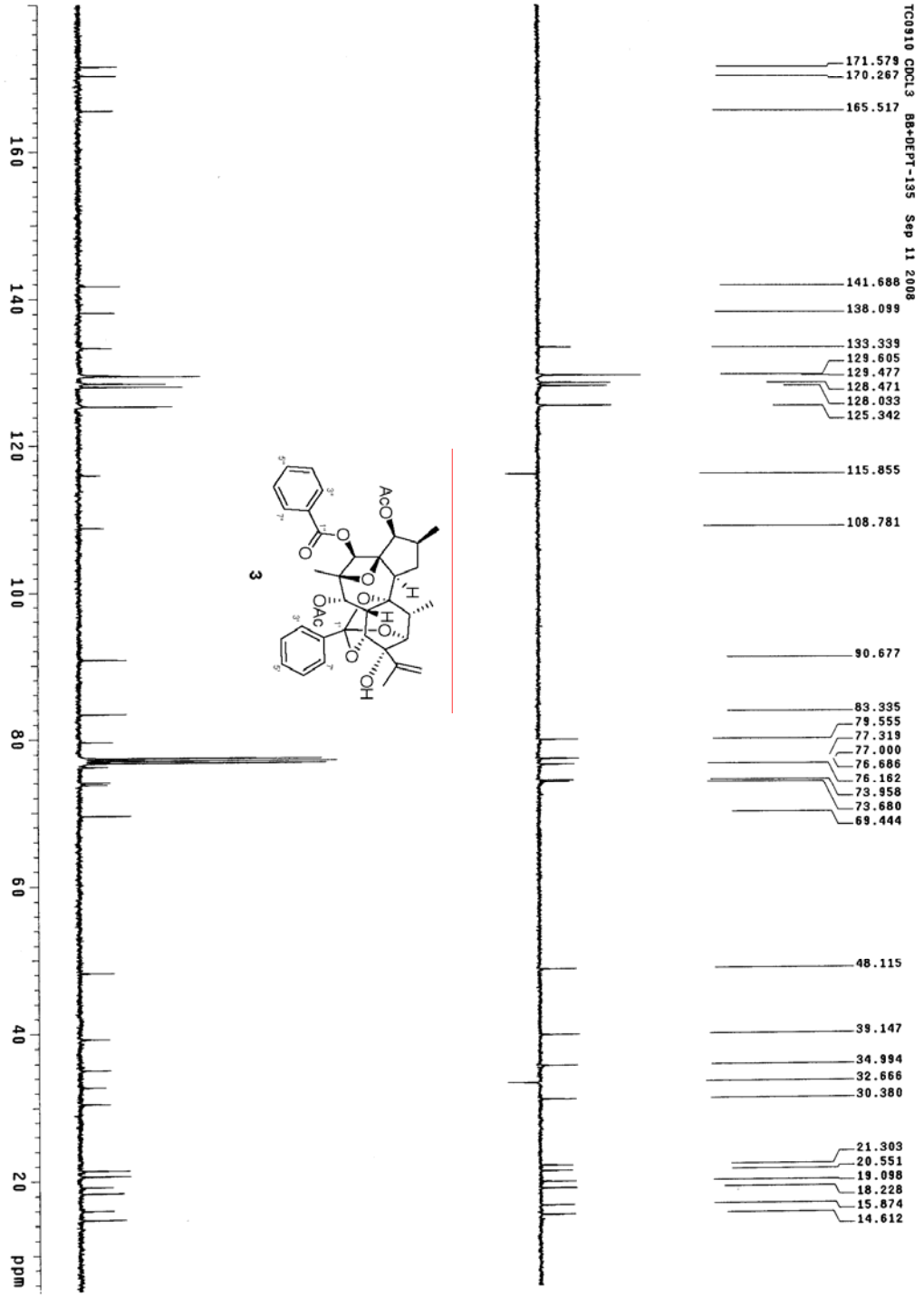
S16. ROESY spectrum of trigochinin B (2)



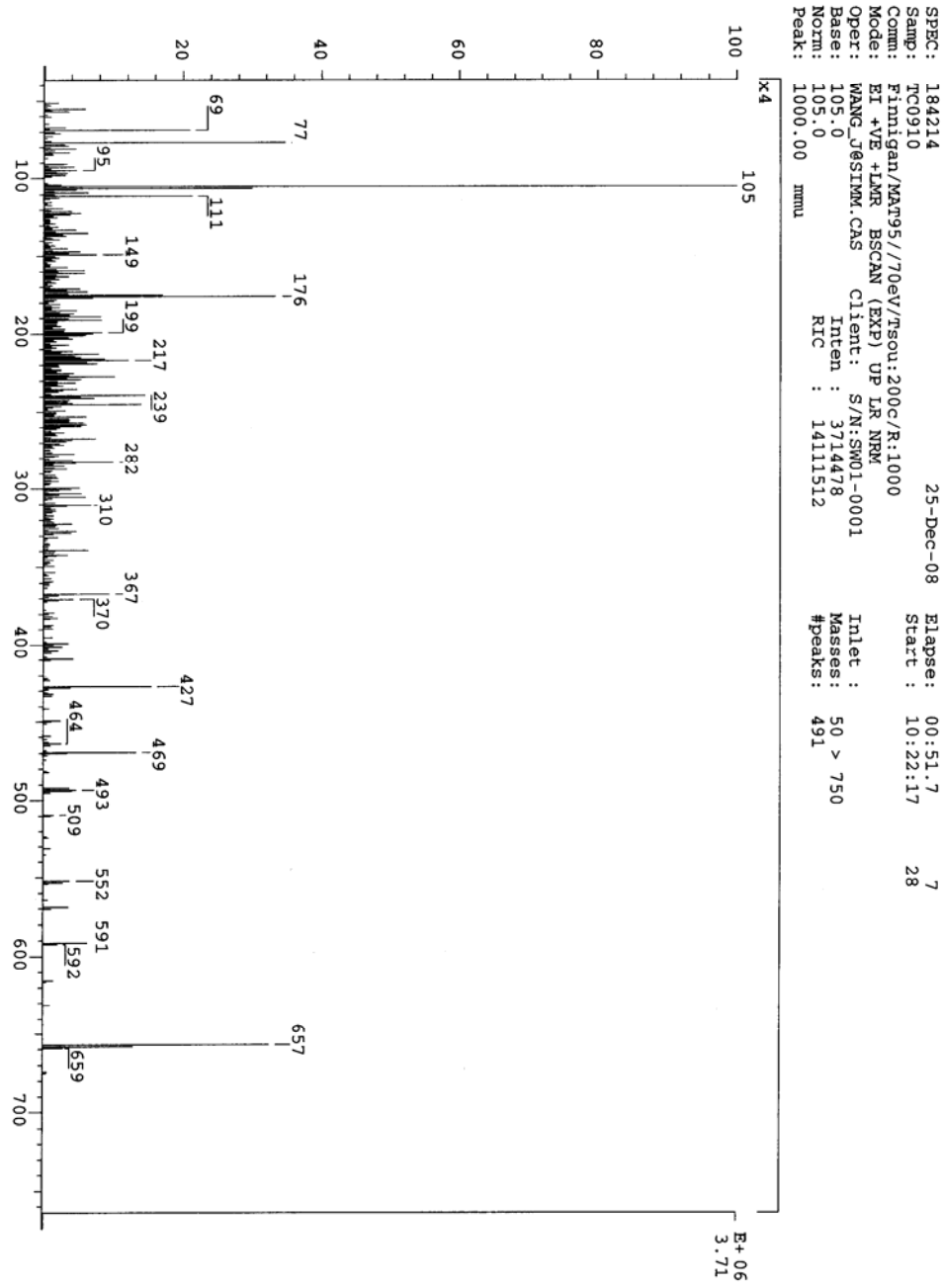
S17. ^{1}H NMR spectrum of trigochinin C (3)



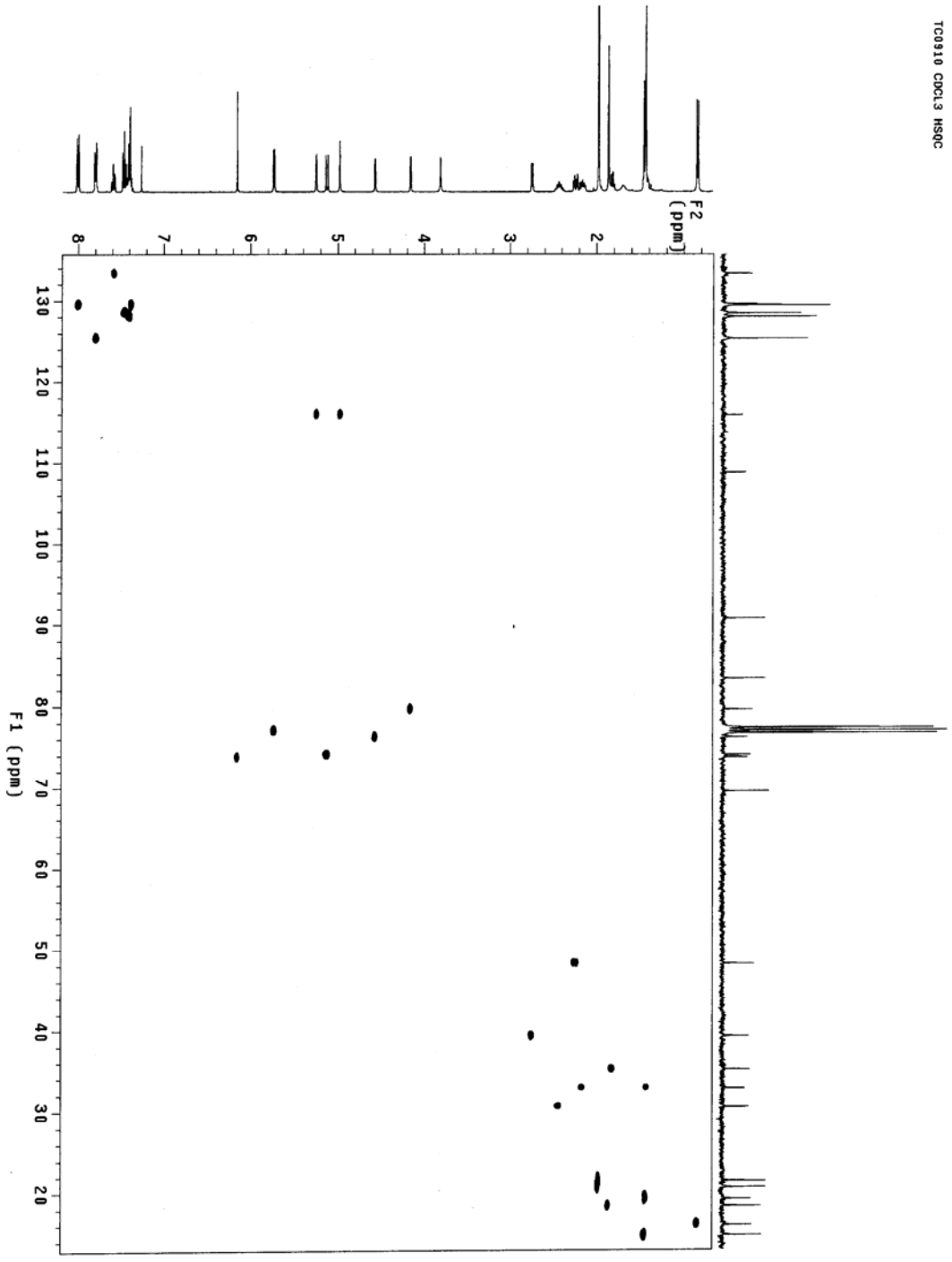
S18. ^{13}C NMR spectrum of trigochinin C (3)



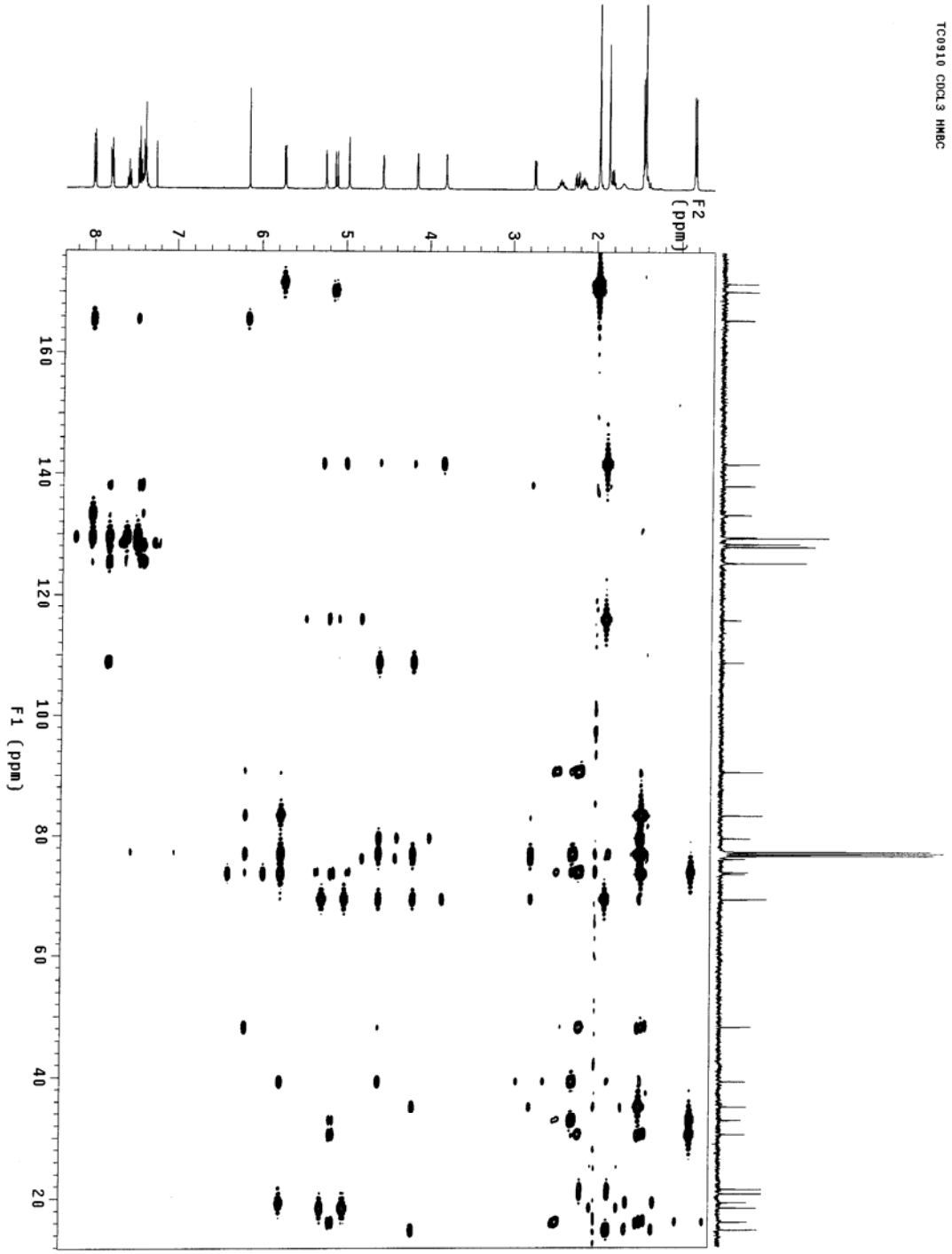
S19. EIMS of trigochinin C (3)



S20. HSQC spectrum of trigochinin C (3)



S21. HMBC spectrum of trigochinin C (3)



S22. ROESY spectrum of trigochinin C (3)