Support Information

Three New Triterpenoids Containing Four-Membered Ring from the Fruiting Body of *Ganoderma sinense*

Cui-Fang Wang[†‡], Jie-Qing Liu[†], Yu-Xin Yan[†‡], Jian-Chao Chen[†‡], Yang Lu[§], Yong-Hui Guo[§], and Ming-Hua Qiu*[,†]

[†]State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Science, Kunming 650204, P. R. China

[‡]Graduate school of Chinese Academy of Sciences, Beijing 100049, P. R. China

[§]Institute of Materia Medica, Chinese Academy of Medical Sciences, Beijing 100050, P.R. China

*Corresponding author. Phone: +86-871-5223257. Fax: +86-871-5223255. E-mail: mhchiu@mail.kib.ac.cn

Contents

Experimental Section

General Instruments. Melting points were determined on X-4 apparatus and uncorrected. Optical rotations were obtained on JASCO P-1020 digital polarimeter. IR spectra were recorded on a BRUKER TENSOR27 spectrometer. UV spectra were taken on Shimadzu 2401PC spectrophotometer. FAB-MS was determined on a VG Auto Spec-3000 mass spectrometer. Regular 1D-NMR spectra were measured on a Bruker AV-400 MHz instrument with TMS as internal standard. 2D-NMR spectra were measured on DRX-500 MHz spectrometer, and chemical shifts (δ) were reported using Pyridine-d_5 as the solvent.

Plant Material. The fruiting body of *G. sinense* was collected from Nanhua country of Yunnan province, China, in November 2008 and identified by Prof. Liu Peigui. (Kunming Institute of Botany, CAS). A voucher sample (No. 08112806) was deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The powder of fruiting body of G. sinense (50 kg) was extracted with MeOH by refluxing (80 °C, 80 L × 3, 4 h each time) and concentrated in vacuo to give a crude extract (5 kg), which was partitioned between H2O and EtOAc. The EtOAc fraction (1.5 kg) was repeatedly chromatographed on silica gel, C-18 reverse silica gel and sephadex LH-20 (MeOH) to yield methyl ganosinensate A (1, 12 mg), mixed 1a and 2 (31 mg). Further purification with HPLC (Agilent 110 HPLC system, Germany; Beckman C-18, 10 mm × 25 cm, 5 μm, U.S.A., CH3CN/H2O 40:60) led to the isolation of ganosinensic acid B (2, 13 mg) and ganosinensic acid A (1a, 8 mg).

Figure S1. ^{1}H NMR spectrum (500 MHz) of methyl ganosinensate A (1) in C_5D_5N

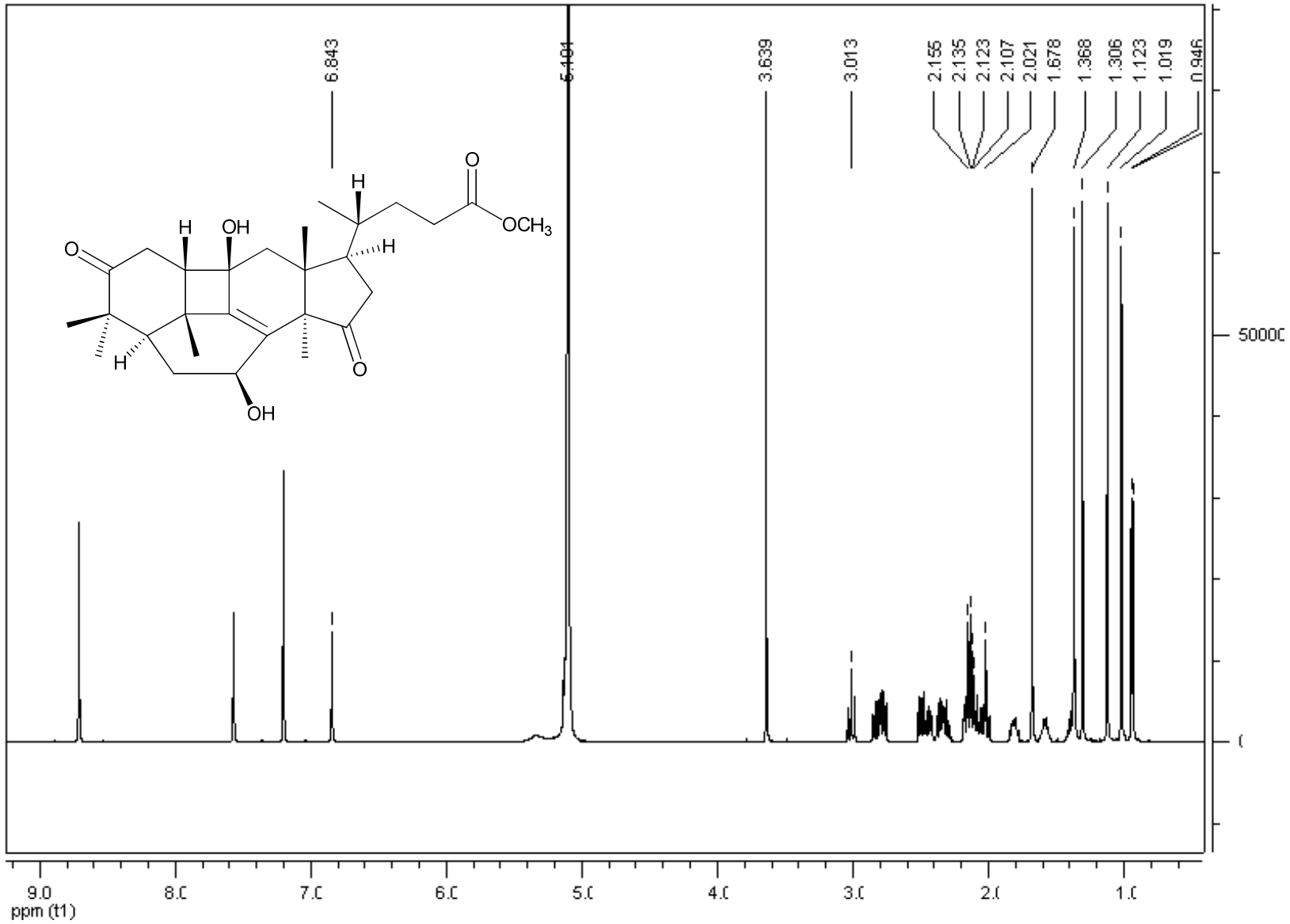


Figure S2. ^{13}C NMR spectrum( ) of methyl ganosinensate A (1) in C_5D_5N

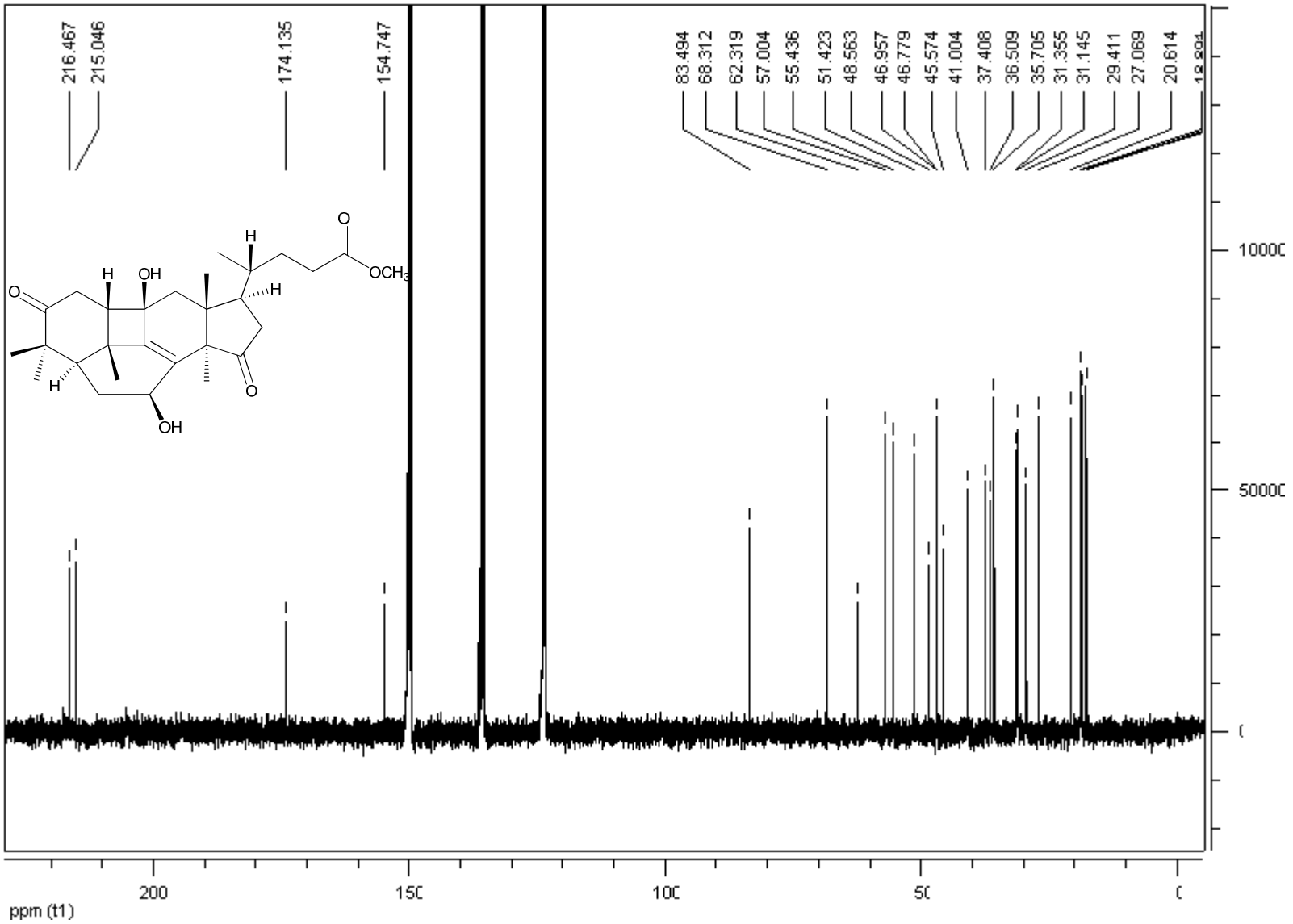


Figure S3. HSQC spectrum of methyl ganosinensate A (1)

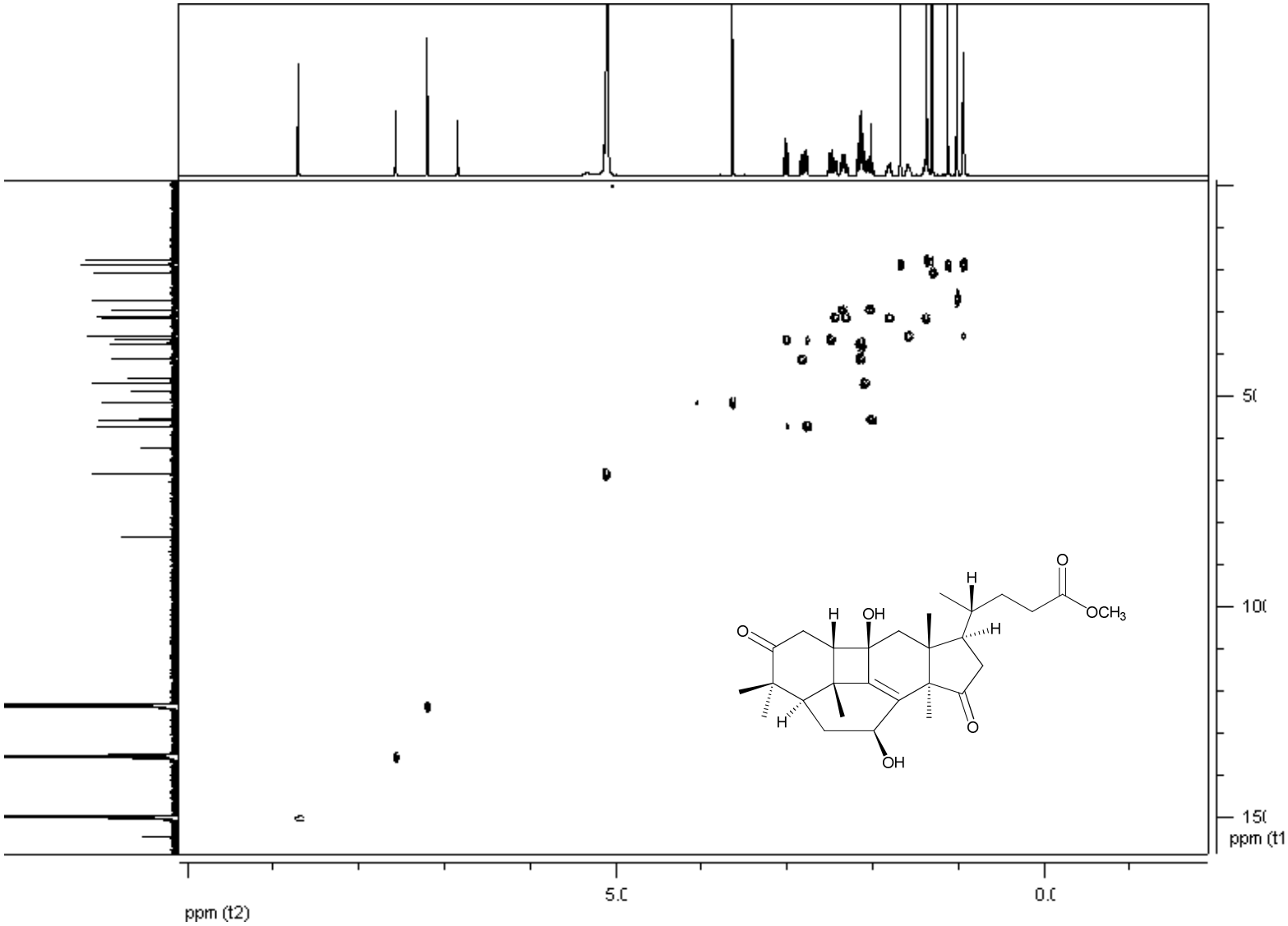


Figure S4. HMBC spectrum of methyl ganosinensate A (1)

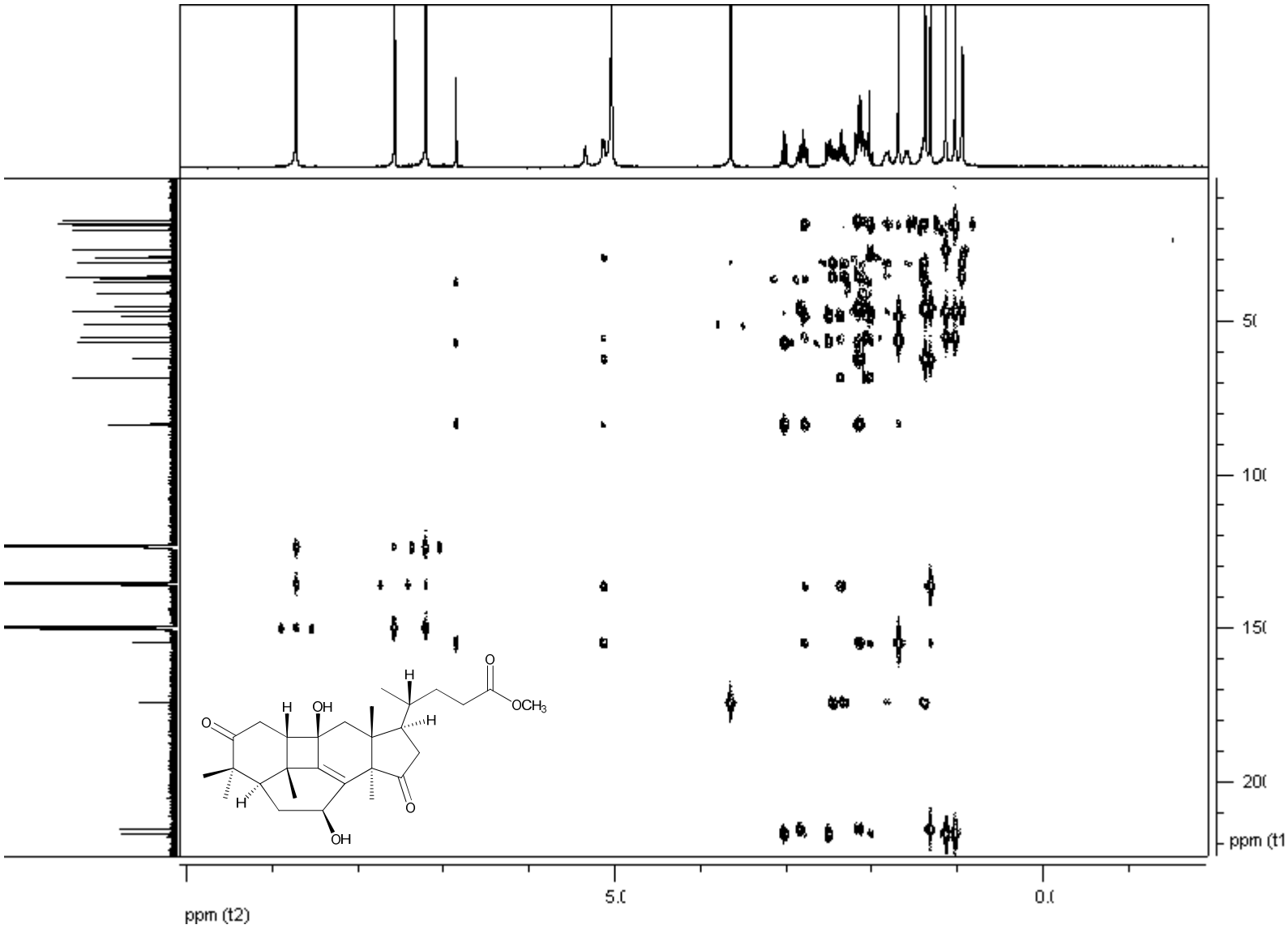


Figure S5. COSY spectrum of methyl ganosinensate A (1)

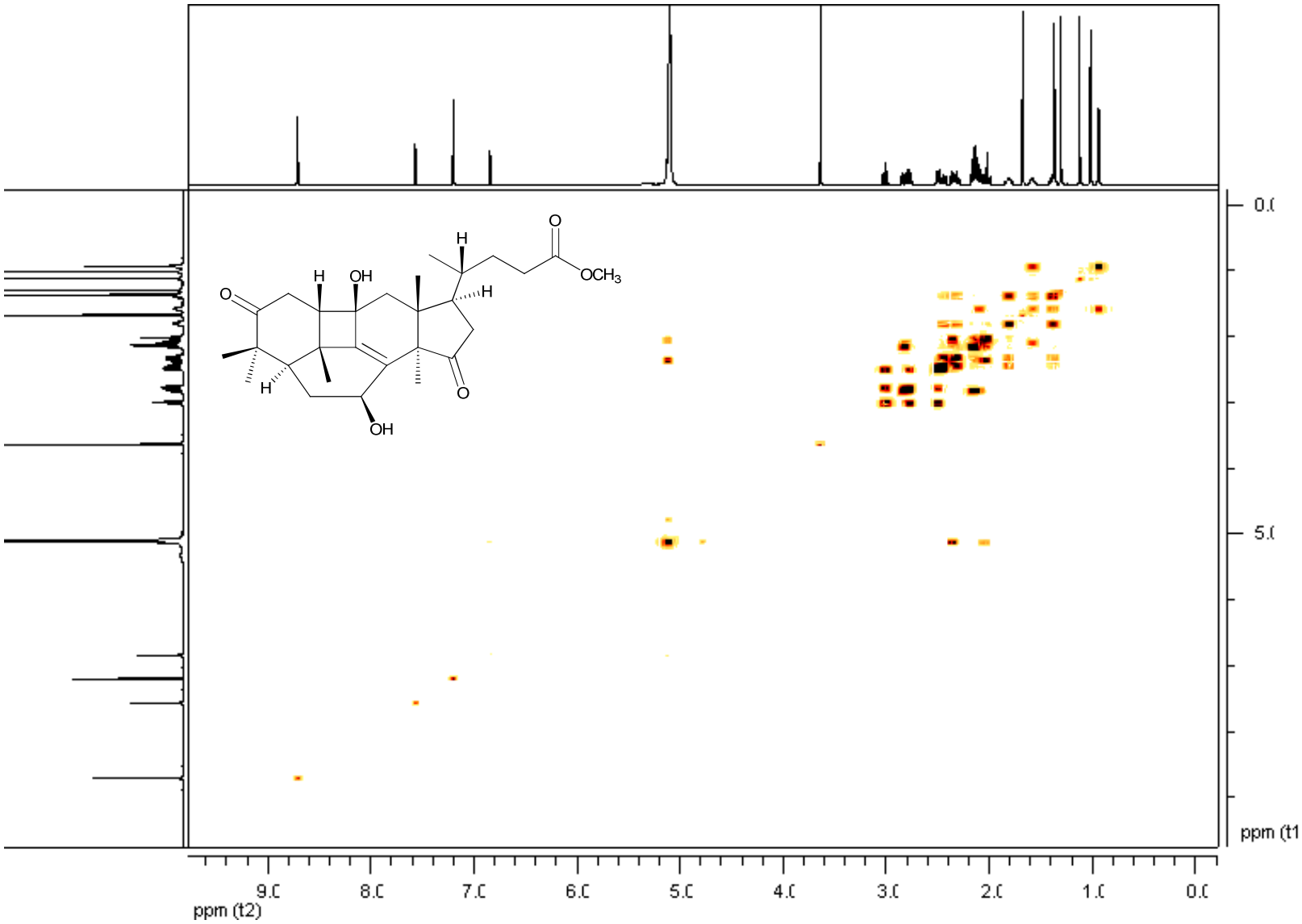


Figure S6. **ROESY spectrum of methyl ganosinensate A (1)**

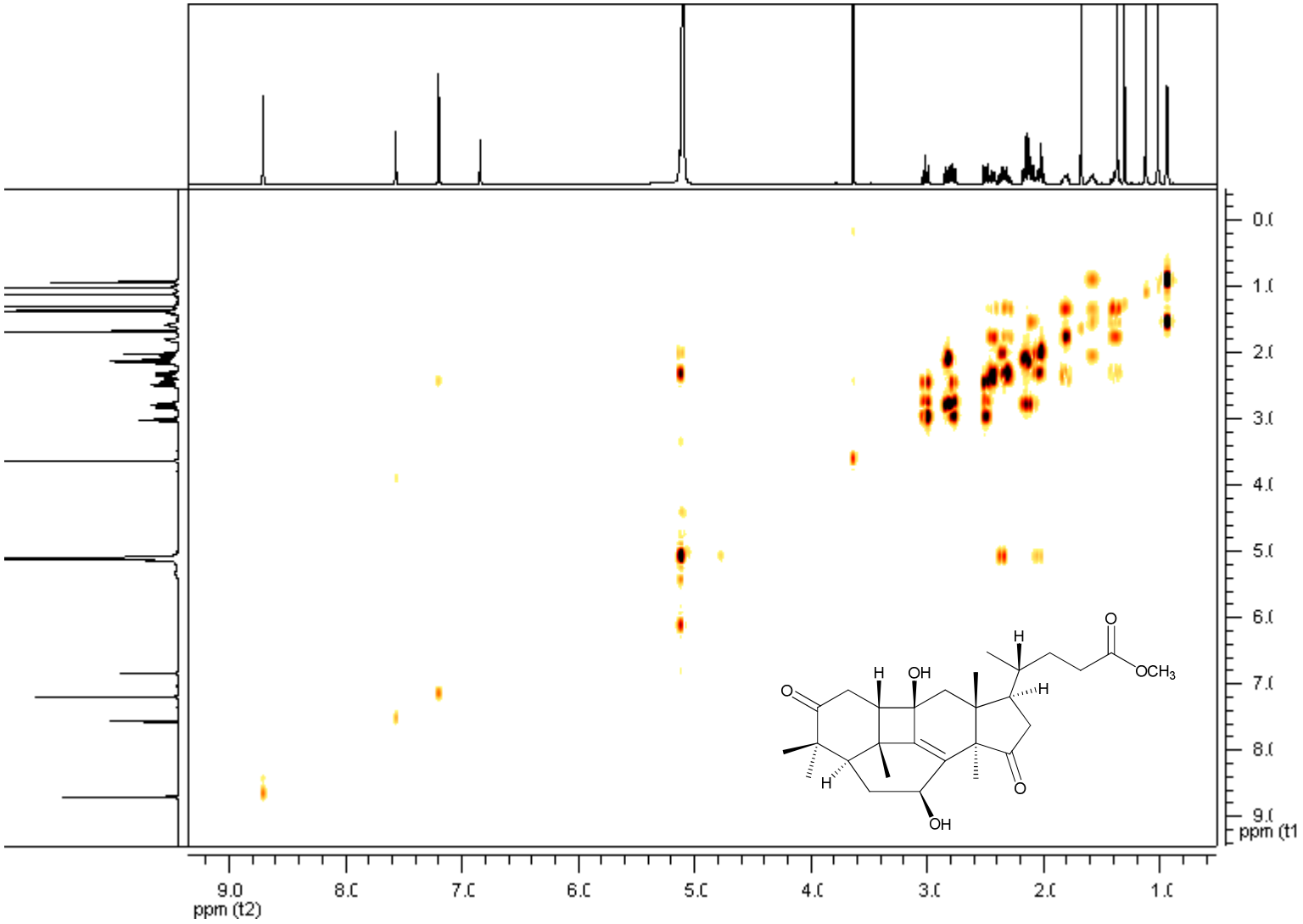


Figure S7. ^{1}H NMR spectrum (500 MHz) of ganosinensic acid B (2) in C_5D_5N

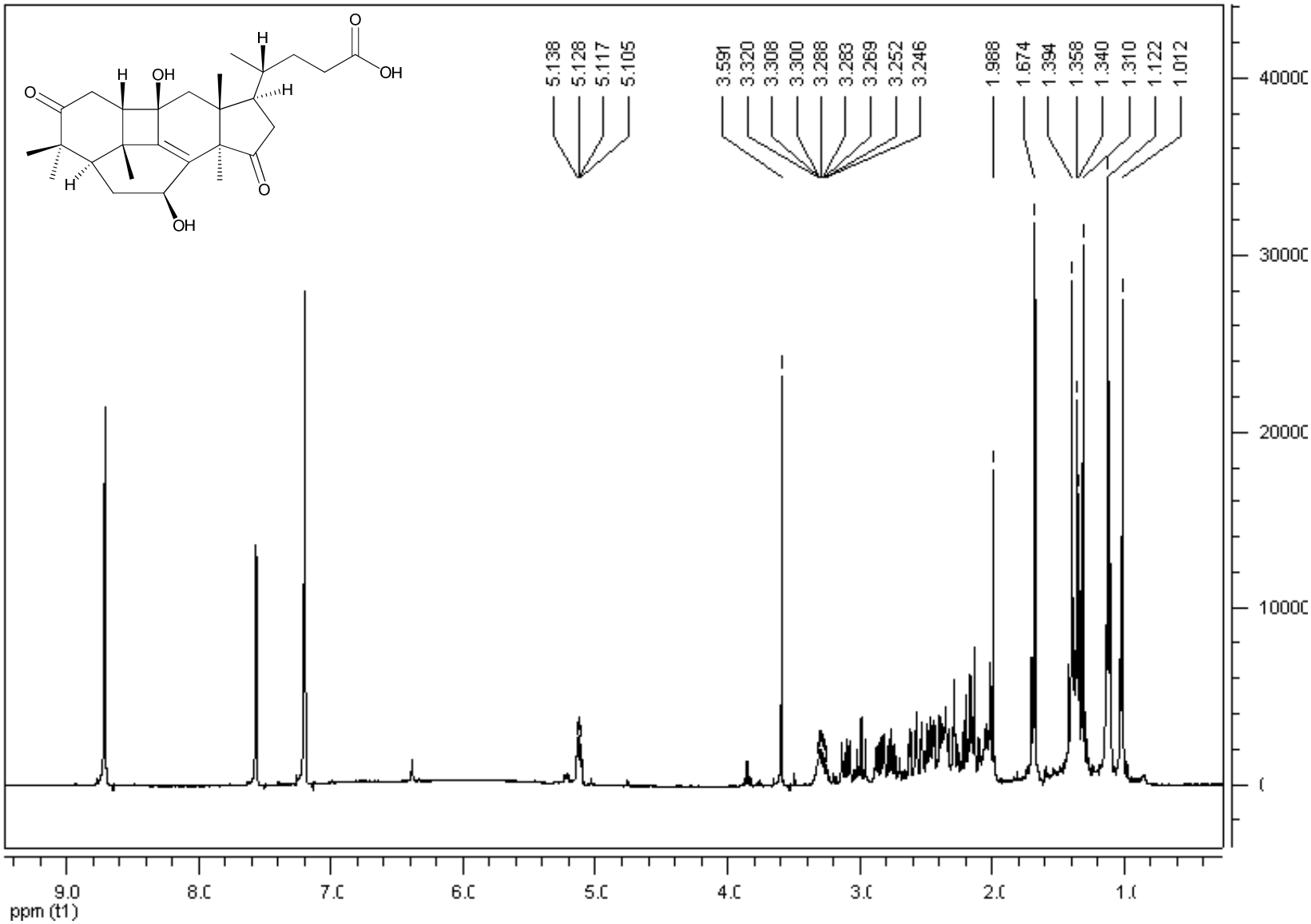


Figure S8. ^{13}**C NMR spectrum of ganosinensic acid B (2) in C_5D_5N**

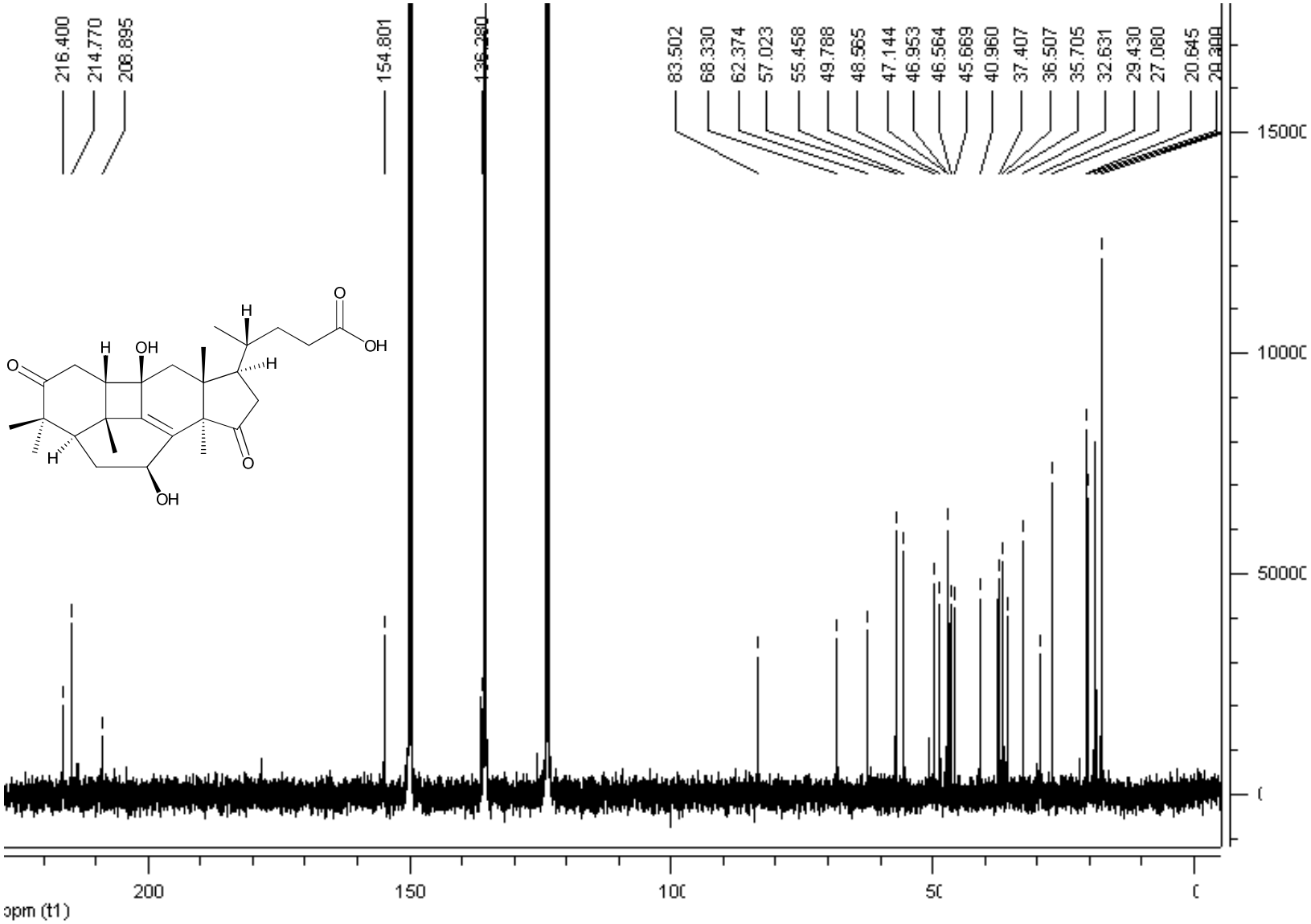


Figure S9. HSQC spectrum of ganosinensic acid B (2)

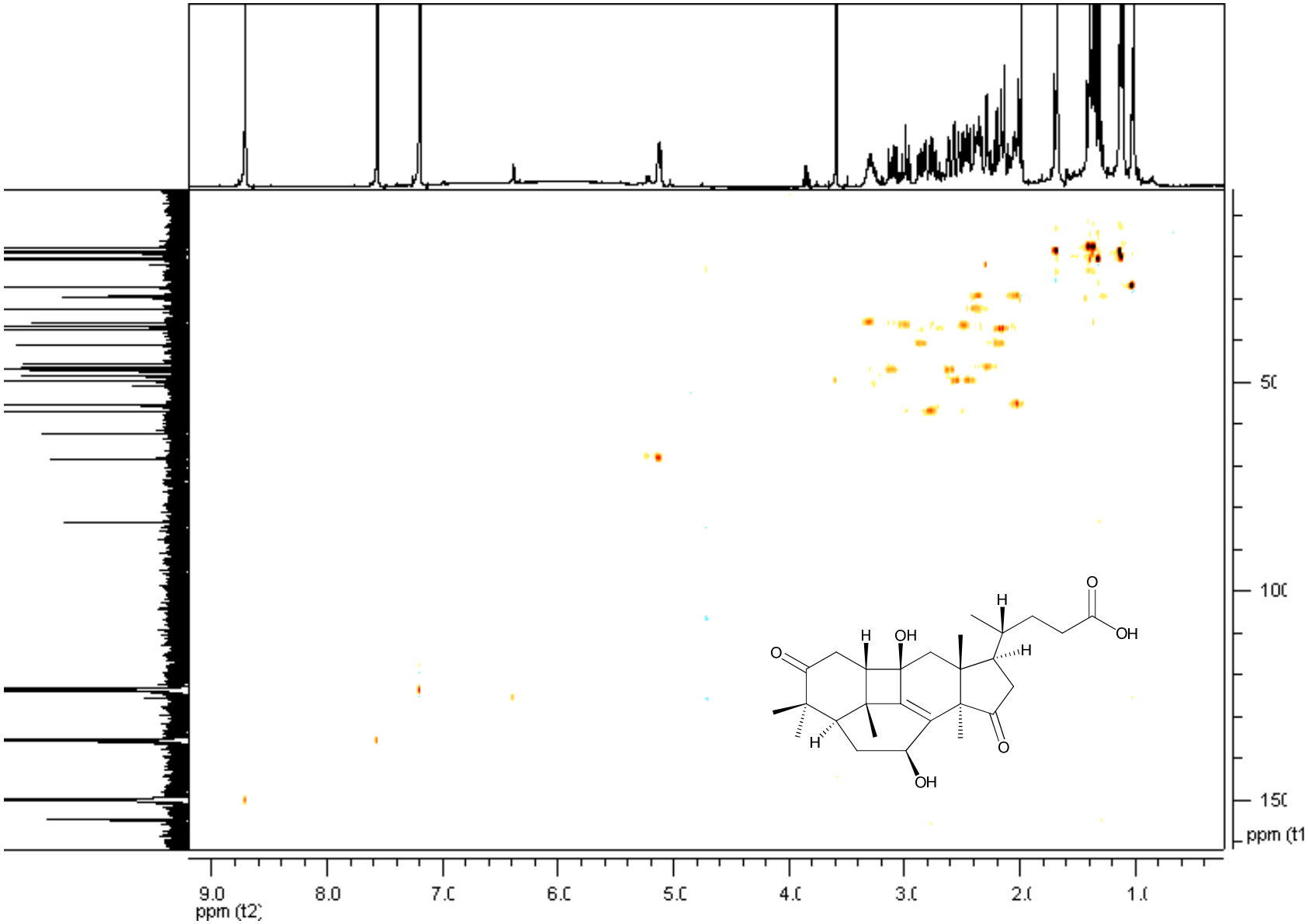


Figure S10. HMBC spectrum of ganosinensic acid B (2)

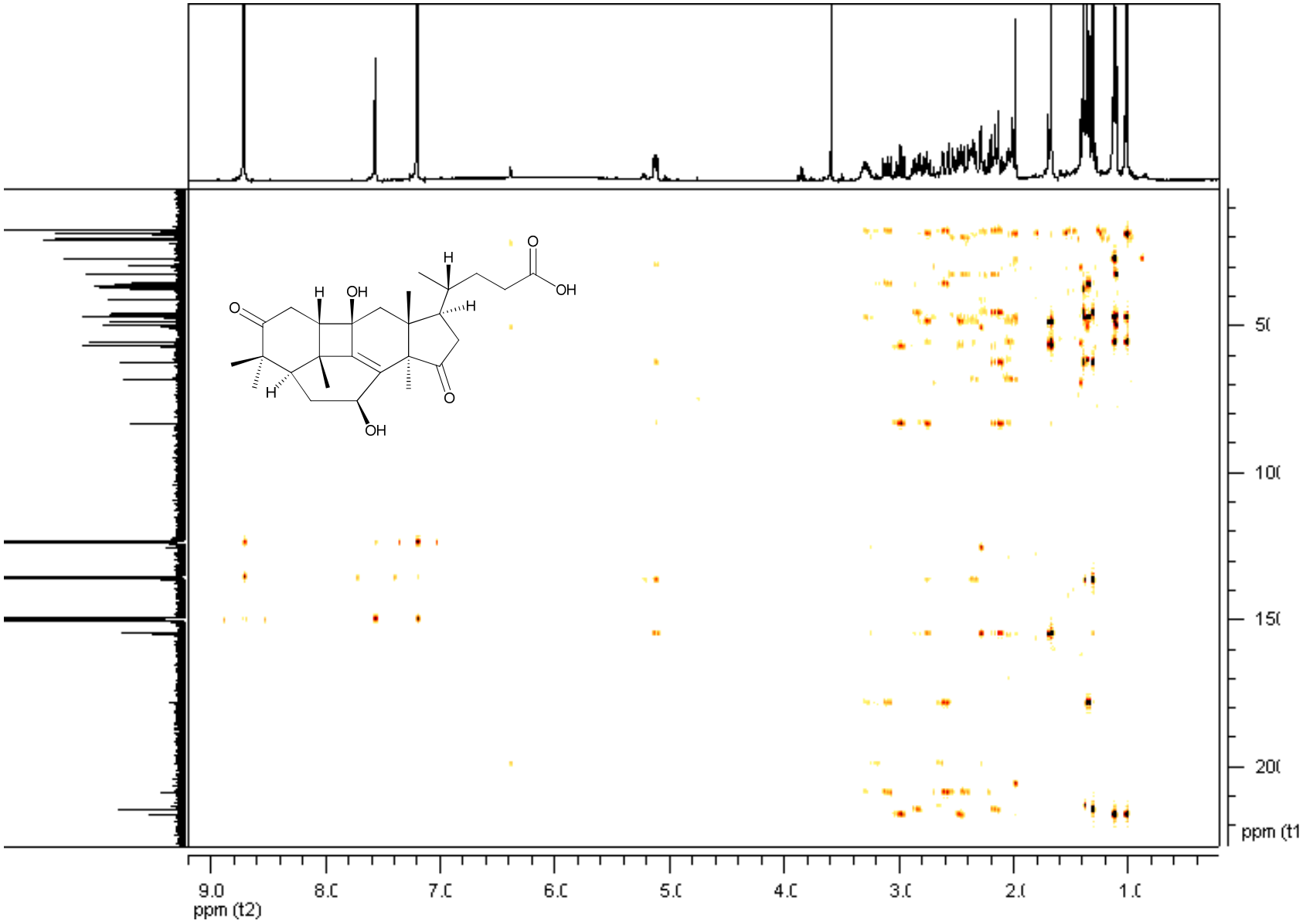


Figure S11. ^{1}H-^{1}H COSY spectrum of ganosinensic acid B (2)

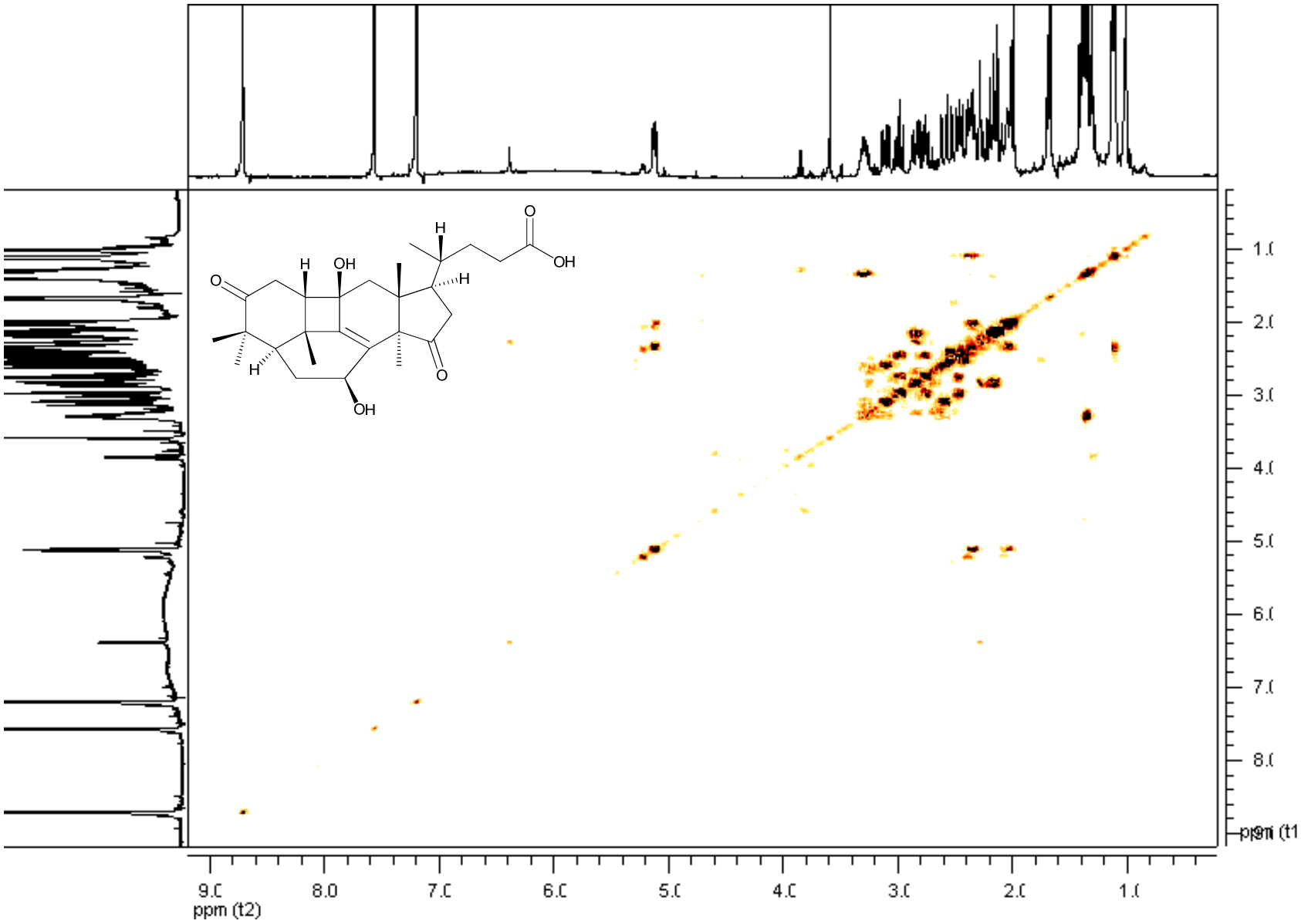


Figure S12. ROESY spectrum of ganosinensic acid B (2)

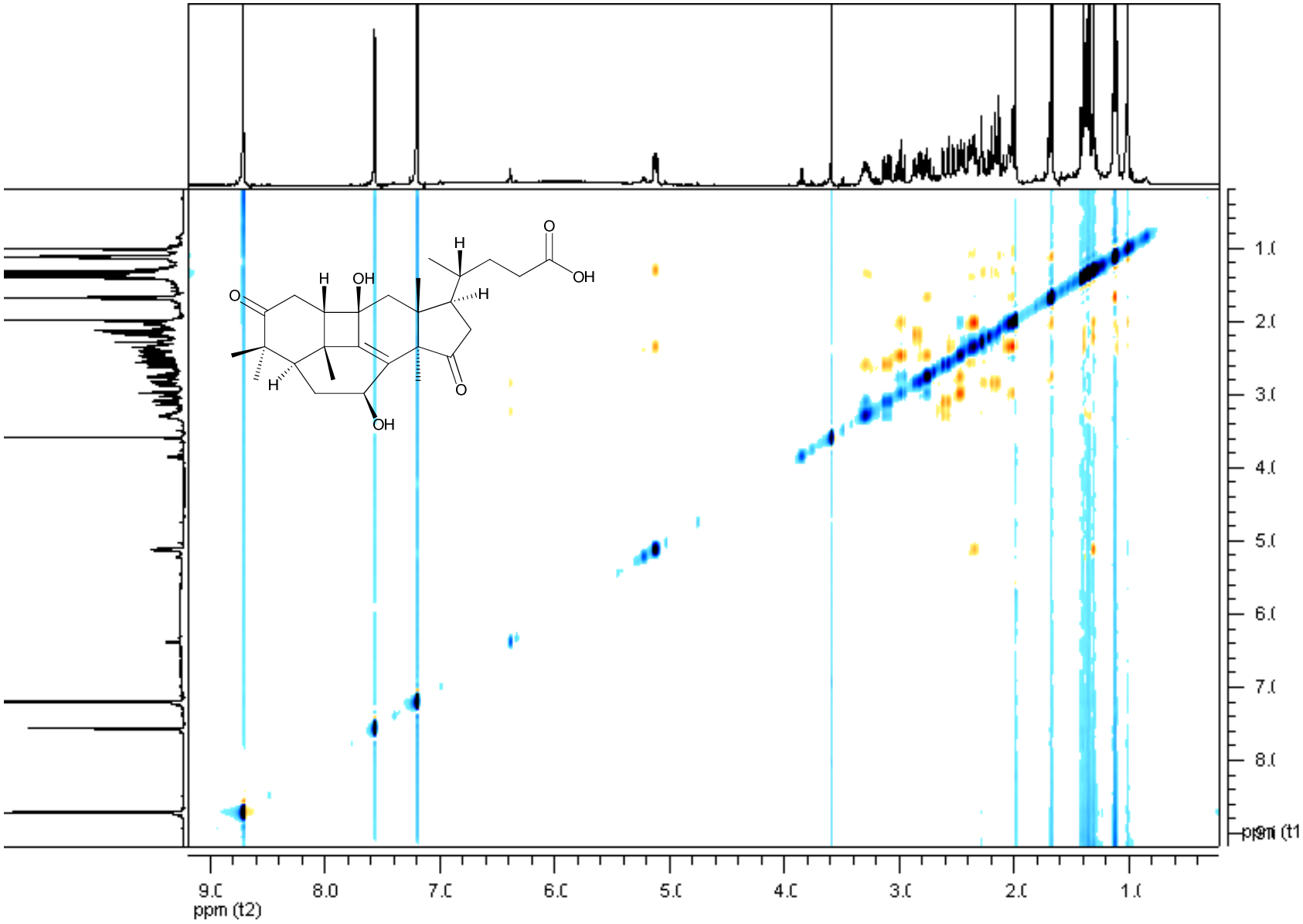


Figure S13. ^{1}H NMR spectrum (500 MHz) of ganosinensic acid A (1a) in C_5D_5N

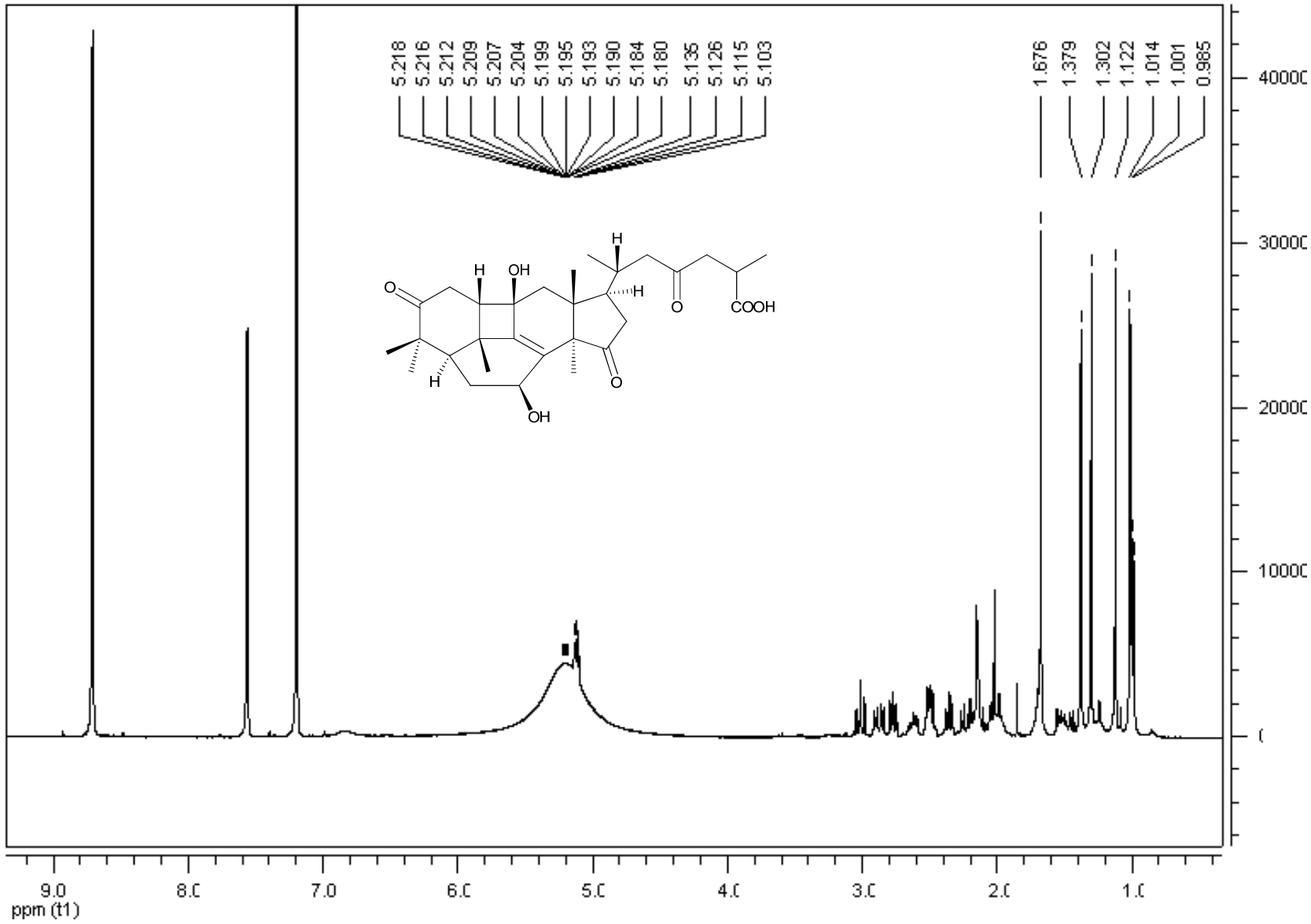


Figure S14. ^{13}**C NMR spectrum of ganosinensic acid A (1a) in C_5D_5N**

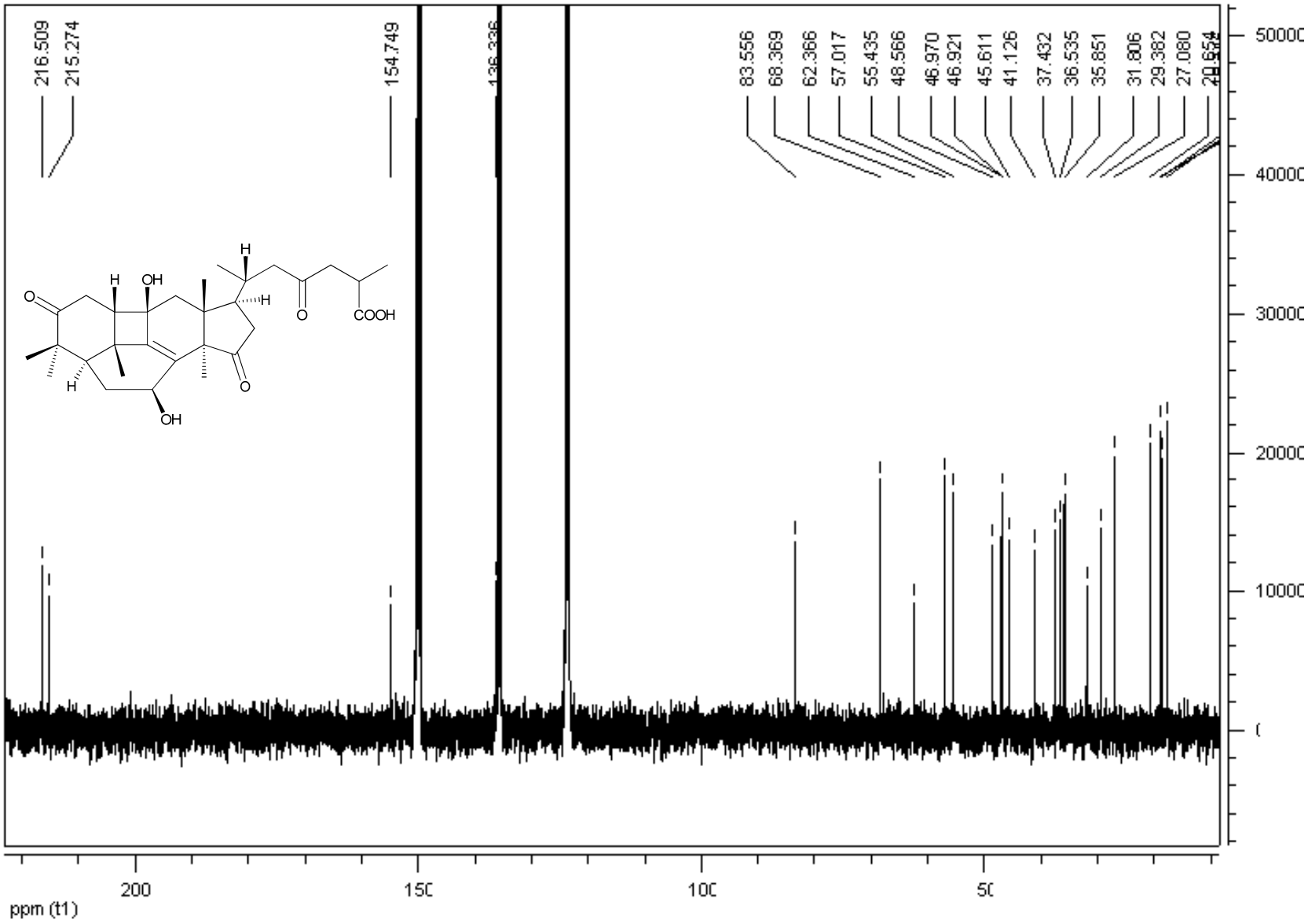


Figure S15. HSQC spectrum of ganosinensic acid A (1a)

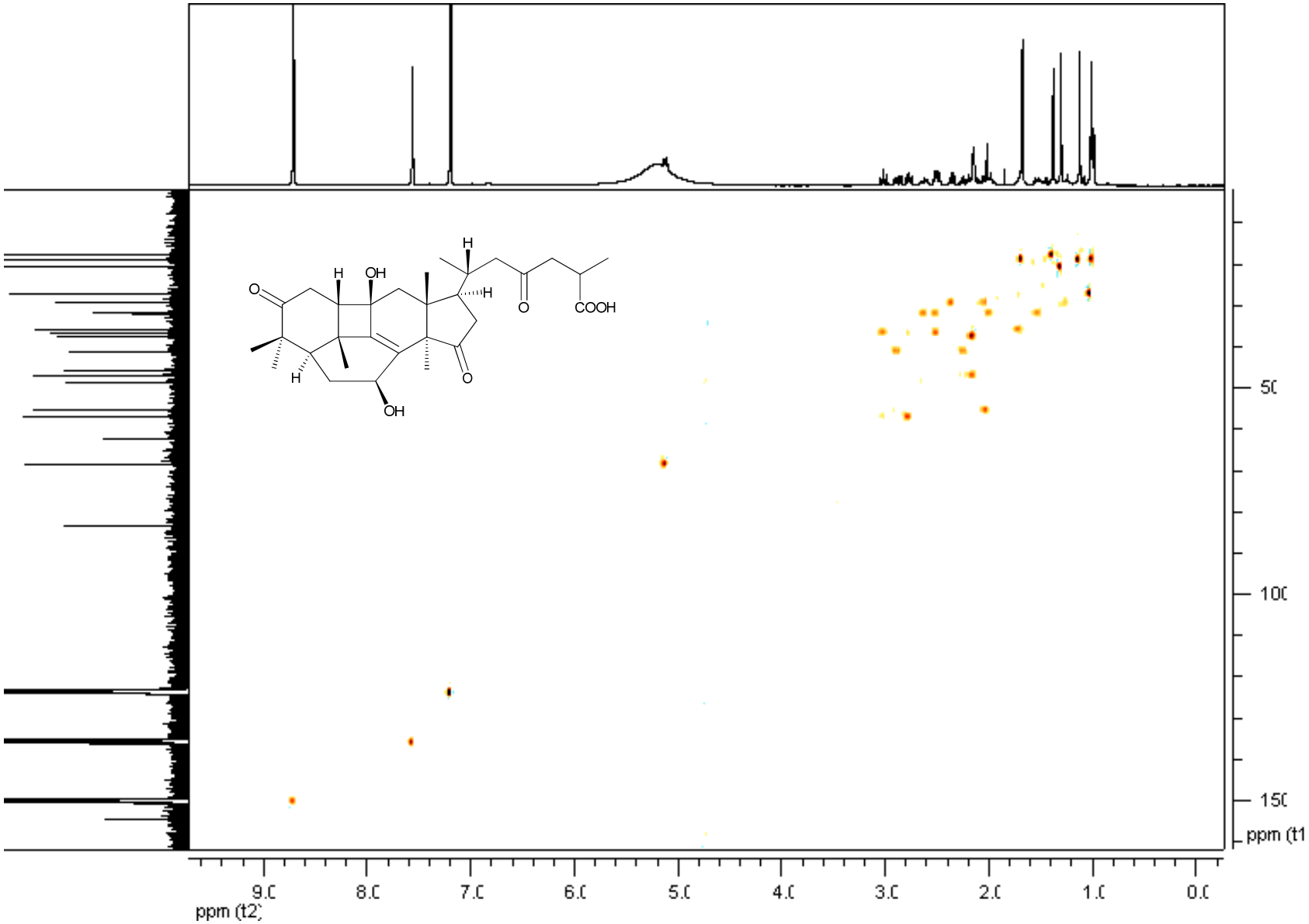


Figure S16. HMBC spectrum of ganosinensic acid A (1a)

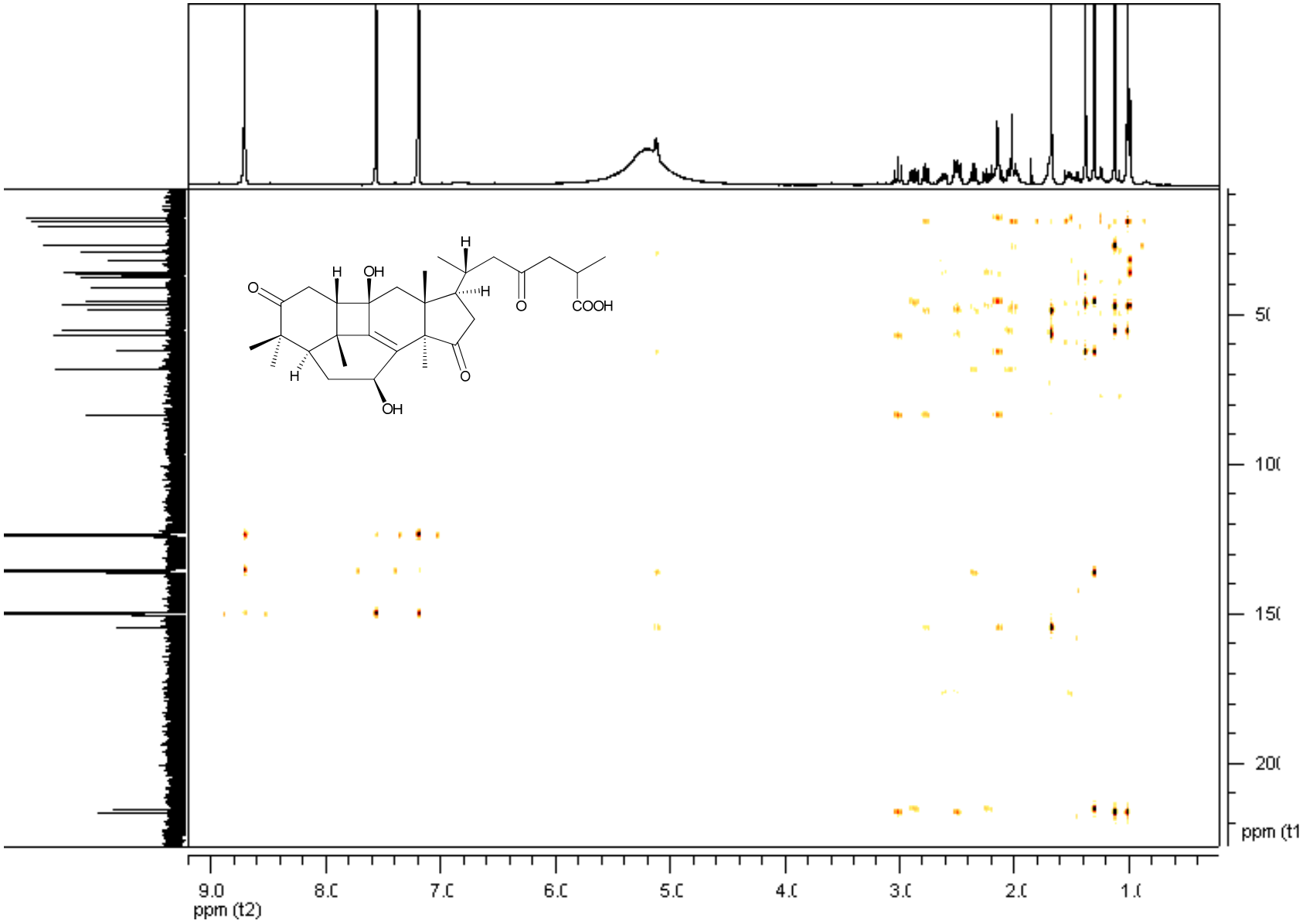


Figure S17. ^{1}H-^{1}H COSY spectrum of ganosinensic acid A (1a)

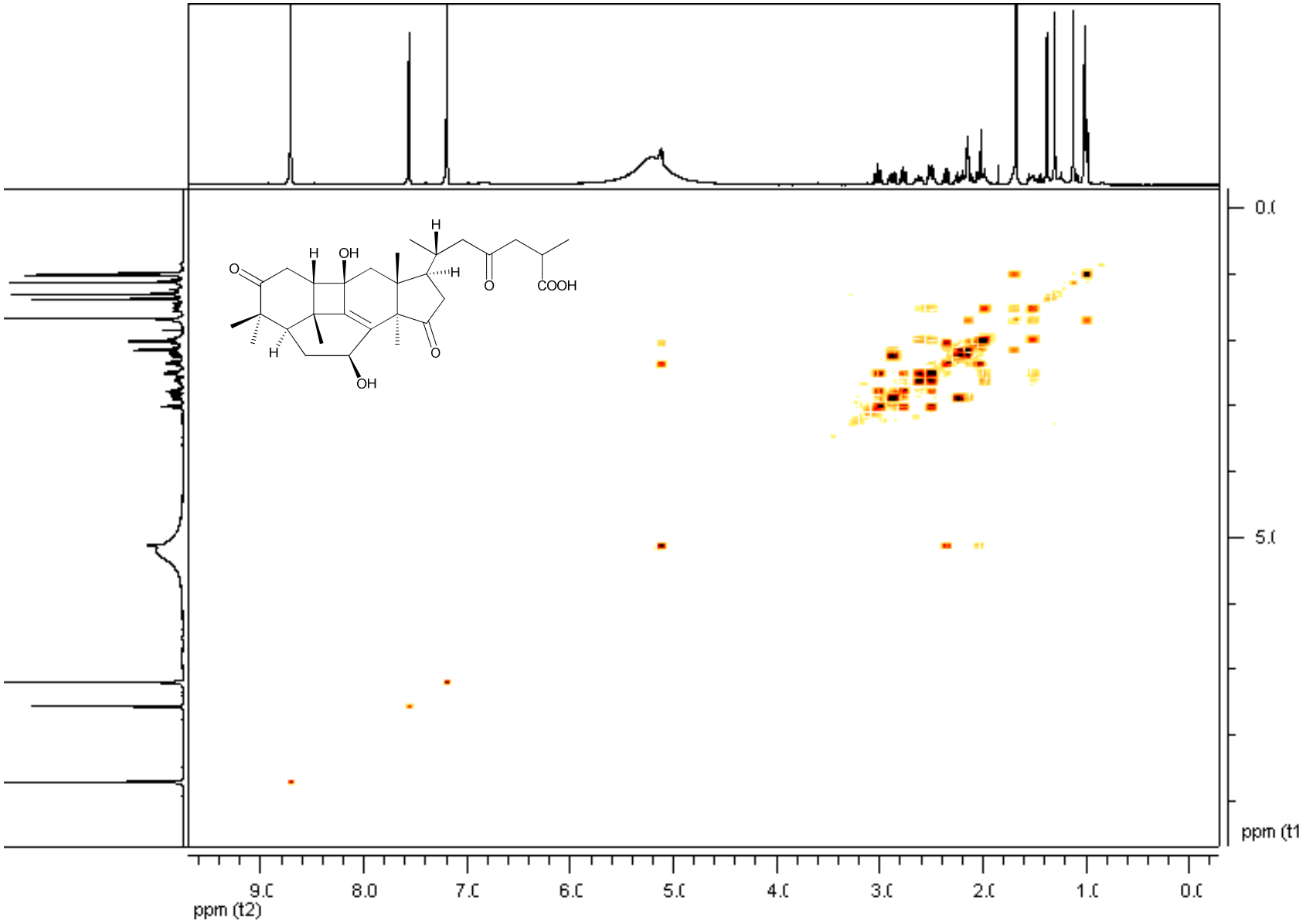
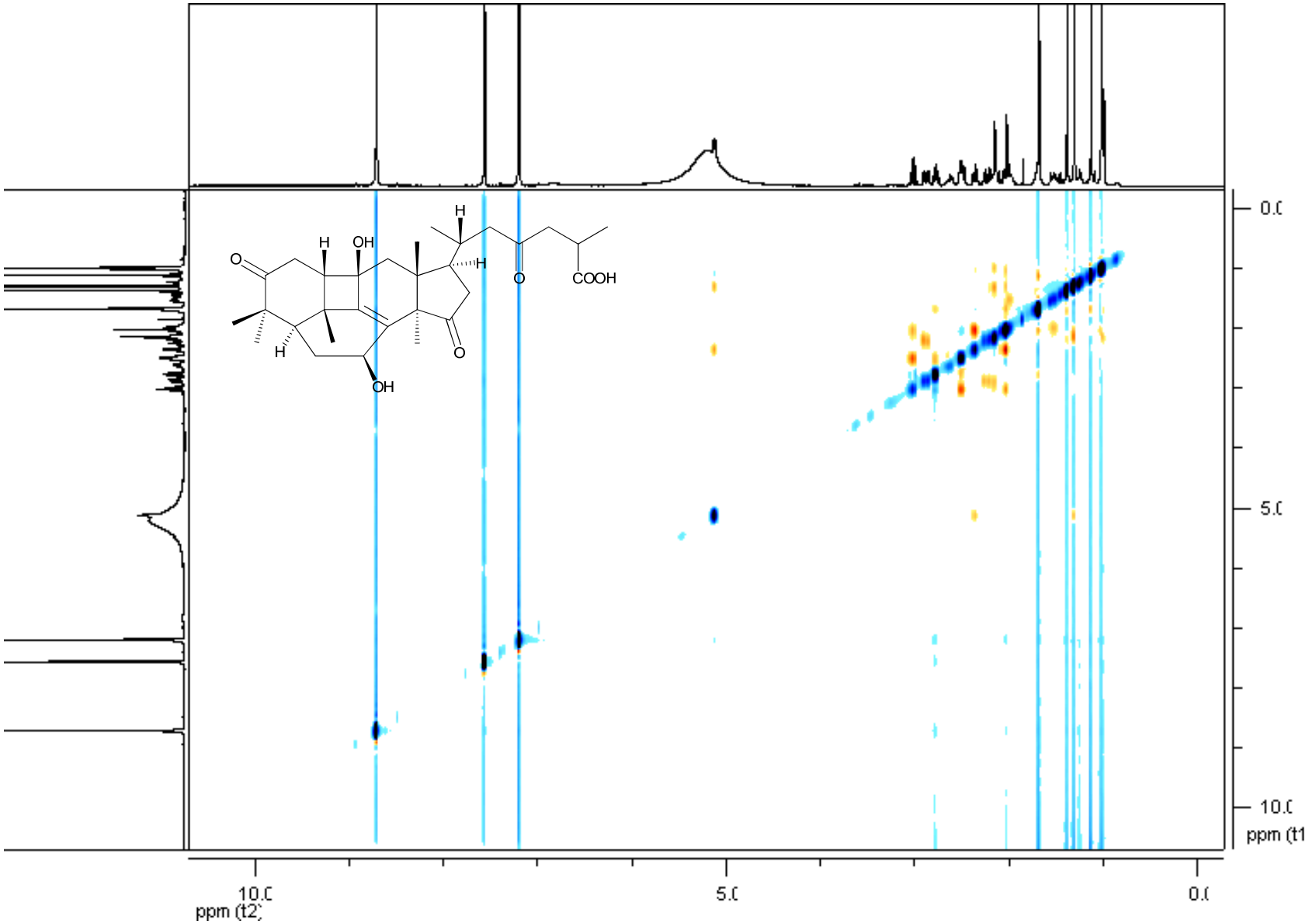


Figure S18. ROESY spectrum of ganosinensic acid A (1a)



X-ray Crystallographic Analysis of Methyl Ganosinensate A (1).

Crystallographic data for 1: $C_{28}H_{40}O_6$, M = 472.60, orthorhombic, space group P212121, α = 7.6814 (1) Å, b = 12.1284 (1) Å, c = 27.7022 (3) Å, V = 2580.82 (5) Å3, Z = 4, d = 1.216 g/cm3, crystal dimensions 0.10 × 0.10 × 0.20 mm was used for measurements on a MAC DIP-2030K diffractometer with a graphite monochromator (ω-2θ scans, 2θmax = 134.52°), Mo Kα radiation. The total number of independent reflections measured was 3692, of which 3439 were observed (|F |2 ≥ 2σ|F |2). Final indices: R1 = 0.0406, wR2 = 0.1111 (w = 1/σ|F |2), S = 1.035. The crystal structure of 1 was solved by direct method SHELXS-97 (Sheldrich, G. M. University of Gottingen: Gottingen, Germany, 1997) and the full-matrix least-squares calculations. Crystallographic data for the structure of 1 have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CCDC 755772). Copies of these data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk)

Table 1. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (A^2 x 10^3)

	x	y	z	U(eq)
O(1)	5700 (4)	-3022(2)	2022(1)	90(1)
O(2)	11831(2)	780(2)	943(1)	87(1)
O(3)	7198(2)	1605(2)	2381(1)	79(1)
O(4)	9813(3)	2674(2)	465(1)	85(1)
O(5)	3446(6)	6581(2)	-11(1)	92(1)
O(6)	3372(3)	7831(2)	553(1)	88(1)
C(1)	6647(3)	-261(2)	2078(1)	64(1)
C(2)	5463(3)	-1102(2)	1836(1)	72(1)
C(3)	6356(4)	-2228(2)	1831(1)	75(1)
C(4)	8116(3)	-2346(2)	1576(1)	66(1)
C(5)	8714(3)	-1161(2)	1470(1)	56(1)
C(6)	10384(3)	-880(2)	1201(1)	65(1)
C(7)	10166(3)	266(2)	972(1)	58(1)

C(8)	8840(2)	990(2)	1230(1)	52(1)
C(9)	8413(3)	738(2)	1683(1)	54(1)
C(10)	8578(3)	-386(2)	1905(1)	60(1)
C(11)	6752(3)	1028(2)	1948(1)	58(1)
C(12)	5454(3)	1685(2)	1642(1)	54(1)
C(13)	6477(3)	2470(2)	1307(1)	51(1)
C(14)	7644(3)	1752(2)	960(1)	50(1)
C(15)	8347(3)	2630(2)	633(1)	62(1)
C(16)	6923(3)	3463(2)	557(1)	64(1)
C(17)	5464(3)	3193(2)	929(1)	55(1)
C(18)	9363(5)	-3064(3)	1870(1)	92(1)
C(19)	7758(4)	-2945(2)	1096(1)	80(1)
C(20)	9913(4)	-532(3)	2313(1)	89(1)
C(21)	7654(3)	3251(2)	1603(1)	65(1)
C(22)	6523(3)	1014(2)	617(1)	55(1)
C(23)	4486(3)	4220(2)	1104(1)	61(1)
C(24)	3813(5)	4864(2)	674(1)	91(1)
C(25)	3112(4)	6007(2)	797(1)	88(1)
C(26)	3314(4)	6804(2)	399(1)	74(1)
C(27)	3508(5)	8691(2)	205(1)	96(1)
C(28)	3031(4)	3961(3)	1459(1)	84(1)
H(2A)	11732	1386	815	91
H(3A)	6320	1696	2545	99
H(1A)	6590	-352	2429	77
H(2B)	5213	-872	1508	86
H(2C)	4371	-1151	2010	86
H(5A)	7805	-885	1253	67
H(6A)	10607	-1425	952	78
H(6B)	11361	-877	1423	78
H(7A)	9750	157	641	69
H(12A)	4688	2107	1850	65
H(12B)	4747	1186	1451	65
H(16A)	6475	3414	231	77
H(16B)	7363	4203	610	77
H(17A)	4617	2713	767	66
H(18A)	9611	-2710	2172	94

H(18B)	10426	-3164	1693	94
H(18C)	8836	-3769	1928	94
H(19A)	7386	-3686	1161	90
H(19B)	8803	-2960	906	90
H(19C)	6863	-2562	922	90
H(20A)	11057	-602	2177	94
H(20B)	9638	-1184	2494	94
H(20C)	9876	98	2522	94
H(21A)	6946	3690	1815	97
H(21B)	8288	3725	1389	97
H(21C)	8458	2823	1791	97
H(22A)	7277	590	412	82
H(22B)	5789	1474	421	82
H(22C)	5815	525	806	82
H(23A)	5330	4690	1272	73
H(24A)	2894	4442	521	99
H(24B)	4750	4943	441	99
H(25A)	1887	5946	878	95
H(25B)	3718	6284	1079	95
H(27A)	3537	9390	367	93
H(27B)	2522	8665	-7	93
H(27C)	4557	8597	21	93
H(28A)	2471	4634	1555	96
H(28B)	3508	3602	1738	96
H(28C)	2196	3485	1307	96

Table 2. Bond lengths [A] and angles [deg] for A.

O(1)-C(3)	1.210(3)	C(1)-C(2)	1.523(4)
O(2)-C(7)	1.425(3)	C(1)-C(10)	1.566(3)
O(3)-H(3A)	0.8200	C(1)-C(11)	1.606(4)
O(4)-C(15)	1.220(3)	C(1)-H(1A)	0.9800
O(5)-C(26)	1.170(3)	C(2)-C(3)	1.528(4)
O(6)-C(26)	1.317(3)	C(2)-H(2B)	0.9700
O(6)-C(27)	1.424(4)	C(2)-H(2C)	0.9700
C(3)-C(4)	1.532(4)	C(19)-H(19B)	0.9600
C(4)-C(18)	1.528(4)	C(19)-H(19C)	0.9600
C(4)-C(5)	1.537(3)	C(20)-H(20A)	0.9600
C(4)-C(19)	1.539(4)	C(20)-H(20B)	0.9600
C(5)-C(6)	1.522(3)	C(20)-H(20C)	0.9600
C(5)-C(10)	1.532(3)	C(21)-H(21B)	0.9600
C(5)-H(5A)	0.9800	C(21)-H(21C)	0.9600
C(6)-C(7)	1.537(3)	C(22)-H(22A)	0.9600
C(6)-H(6A)	0.9700	C(22)-H(22B)	0.9600
C(6)-H(6B)	0.9700	C(22)-H(22C)	0.9600
C(7)-C(8)	1.523(3)	C(23)-C(24)	1.516(3)
C(7)-H(7A)	0.9800	C(23)-C(28)	1.521(3)
C(8)-C(9)	1.332(3)	C(23)-H(23A)	0.9800
C(8)-C(14)	1.502(3)	C(24)-C(25)	1.526(4)
C(9)-C(10)	1.501(3)	C(24)-H(24A)	0.9700
C(9)-C(11)	1.513(3)	C(24)-H(24B)	0.9700
C(10)-C(20)	1.537(3)	C(25)-C(26)	1.475(4)
C(11)-C(12)	1.532(3)	C(25)-H(25A)	0.9700
C(12)-C(13)	1.545(3)	C(25)-H(25B)	0.9700
C(12)-H(12A)	0.9700	C(27)-H(27A)	0.9600
C(12)-H(12B)	0.9700	C(27)-H(27B)	0.9600
C(13)-C(21)	1.546(3)	C(27)-H(27C)	0.9600
C(13)-C(17)	1.571(3)	C(28)-H(28A)	0.9600
C(13)-C(14)	1.575(3)	C(28)-H(28B)	0.9600
C(14)-C(15)	1.499(3)	C(28)-H(28C)	0.9600
C(14)-C(22)	1.564(3)		

C(15)-C(16)	1.504(4)	C(7)-O(2)-H(2A)	109.5
C(16)-C(17)	1.556(3)	C(11)-O(3)-H(3A)	109.5
C(16)-H(16A)	0.9700	C(26)-O(6)-C(27)	118.4(2)
C(16)-H(16B)	0.9700	C(2)-C(1)-C(10)	111.4(2)
C(17)-C(23)	1.534(3)	C(2)-C(1)-C(11)	125.7(2)
C(17)-H(17A)	0.9800	C(10)-C(1)-C(11)	88.7(2)
C(18)-H(18A)	0.9600	C(2)-C(1)-H(1A)	109.6
C(18)-H(18B)	0.9600	C(10)-C(1)-H(1A)	109.6
C(18)-H(18C)	0.9600	C(11)-C(1)-H(1A)	109.6
C(19)-H(19A)	0.9600	C(1)-C(2)-C(3)	109.6(2)
C(1)-C(2)-H(2B)	109.8	C(3)-C(2)-H(2B)	109.8
C(1)-C(2)-H(2C)	109.8	C(3)-C(2)-H(2C)	109.8
H(2B)-C(2)-H(2C)	108.2	O(1)-C(3)-C(2)	121.4(2)
O(1)-C(3)-C(4)	119.6(3)	C(2)-C(3)-C(4)	118.9(2)
C(18)-C(4)-C(3)	111.2(2)	C(18)-C(4)-C(5)	116.5(2)
C(3)-C(4)-C(5)	105.3(2)	C(18)-C(4)-C(19)	107.6(2)
C(3)-C(4)-C(19)	106.5(2)	C(5)-C(4)-C(19)	109.2(2)
C(6)-C(5)-C(10)	107.8(2)	C(6)-C(5)-C(4)	123.7(2)
C(10)-C(5)-C(4)	113.8(2)	C(6)-C(5)-H(5A)	102.9
C(10)-C(5)-H(5A)	102.9	C(4)-C(5)-H(5A)	102.9
C(5)-C(6)-C(7)	108.3(2)	C(5)-C(6)-H(6A)	110.0
C(7)-C(6)-H(6A)	110.0	C(5)-C(6)-H(6B)	110.0
C(7)-C(6)-H(6B)	110.0	H(6A)-C(6)-H(6B)	108.4
O(2)-C(7)-C(8)	112.0(3)	O(2)-C(7)-C(6)	108.7(2)
C(8)-C(7)-C(6)	113.6(2)	O(2)-C(7)-H(7A)	107.4
C(8)-C(7)-H(7A)	107.4	C(6)-C(7)-H(7A)	107.4
C(9)-C(8)-C(14)	117.3(2)	C(9)-C(8)-C(7)	118.3(2)
C(14)-C(8)-C(7)	122.0(2)	C(8)-C(9)-C(10)	125.0(2)
C(8)-C(9)-C(11)	127.6(2)	C(10)-C(9)-C(11)	94.8(2)
C(9)-C(10)-C(5)	104.0(3)	C(9)-C(10)-C(20)	117.5(2)
C(5)-C(10)-C(20)	117.5(3)	C(9)-C(10)-C(1)	87.6(2)
C(5)-C(10)-C(1)	111.4(2)	C(20)-C(10)-C(1)	114.7(2)
O(3)-C(11)-C(9)	108.6(2)	O(3)-C(11)-C(12)	111.4(2)
C(9)-C(11)-C(12)	113.7(2)	O(3)-C(11)-C(1)	107.4(2)
C(9)-C(11)-C(1)	85.7(2)	C(12)-C(11)-C(1)	126.8(2)

C(11)-C(12)-C(13)	108.8(2)	C(11)-C(12)-H(12A)	109.9
C(13)-C(12)-H(12A)	109.9	C(11)-C(12)-H(12B)	109.9
C(13)-C(12)-H(12B)	109.9	H(12A)-C(12)-H(12B)	108.3
C(12)-C(13)-C(21)	110.8(2)	C(12)-C(13)-C(17)	119.5(2)
C(21)-C(13)-C(17)	107.6(2)	C(12)-C(13)-C(14)	108.4(2)
C(21)-C(13)-C(14)	109.3(2)	C(17)-C(13)-C(14)	100.6(2)
C(15)-C(14)-C(8)	121.1(2)	C(15)-C(14)-C(22)	103.8(2)
C(8)-C(14)-C(22)	106.7(2)	C(15)-C(14)-C(13)	100.4(2)
C(8)-C(14)-C(13)	112.6(2)	C(22)-C(14)-C(13)	112.0(2)
O(4)-C(15)-C(14)	126.5(2)	O(4)-C(15)-C(16)	126.0(2)
C(14)-C(15)-C(16)	107.5(2)	C(15)-C(16)-C(17)	106.9(2)
C(15)-C(16)-H(16A)	110.4	C(17)-C(16)-H(16A)	110.4
C(15)-C(16)-H(16B)	110.4	C(17)-C(16)-H(16B)	110.4
H(16A)-C(16)-H(16B)	108.6	C(23)-C(17)-C(16)	113.0(2)
C(23)-C(17)-C(13)	119.0(2)	C(16)-C(17)-C(13)	101.6(2)
C(23)-C(17)-H(17A)	107.6	C(16)-C(17)-H(17A)	107.6
C(13)-C(17)-H(17A)	107.6	C(4)-C(18)-H(18A)	109.5
C(4)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
C(4)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	C(4)-C(19)-H(19A)	109.5
C(4)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
C(4)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(10)-C(20)-H(20A)	109.5
C(10)-C(20)-H(20B)	109.5	H(20A)-C(20)-H(20B)	109.5
C(10)-C(20)-H(20C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5	C(13)-C(21)-H(21A)	109.5
C(13)-C(21)-H(21B)	109.5	H(21A)-C(21)-H(21B)	109.5
C(13)-C(21)-H(21C)	109.5	H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5	C(14)-C(22)-H(22A)	109.5
C(14)-C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5
C(14)-C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5	C(24)-C(23)-C(28)	111.3(2)
C(24)-C(23)-C(17)	109.6(2)	C(28)-C(23)-C(17)	113.4(2)
C(24)-C(23)-H(23A)	107.4	C(28)-C(23)-H(23A)	107.4
C(17)-C(23)-H(23A)	107.4	C(23)-C(24)-C(25)	114.4(2)

C(23)-C(24)-H(24A)	108.7	C(25)-C(24)-H(24A)	108.7
C(23)-C(24)-H(24B)	108.7	C(25)-C(24)-H(24B)	108.7
H(24A)-C(24)-H(24B)	107.6	C(26)-C(25)-C(24)	113.0(2)
C(26)-C(25)-H(25A)	109.0	C(24)-C(25)-H(25A)	109.0
C(26)-C(25)-H(25B)	109.0	C(24)-C(25)-H(25B)	109.0
H(25A)-C(25)-H(25B)	107.8	O(5)-C(26)-O(6)	122.0(3)
O(5)-C(26)-C(25)	125.6(3)	O(6)-C(26)-C(25)	112.3(2)
O(6)-C(27)-H(27A)	109.5	O(6)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5	O(6)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5	H(27B)-C(27)-H(27C)	109.5
C(23)-C(28)-H(28A)	109.5	C(23)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5	C(23)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5	H(28B)-C(28)-H(28C)	109.5

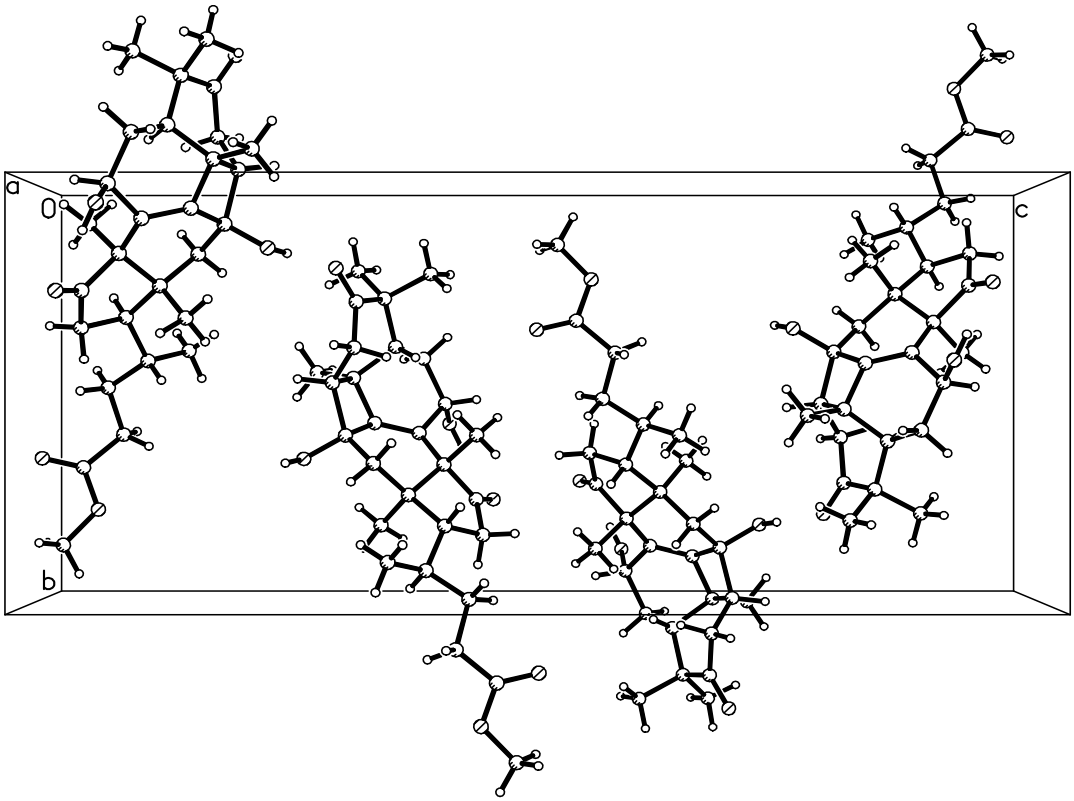


Figure 1 The crystal packing of methyl ganosinensate A

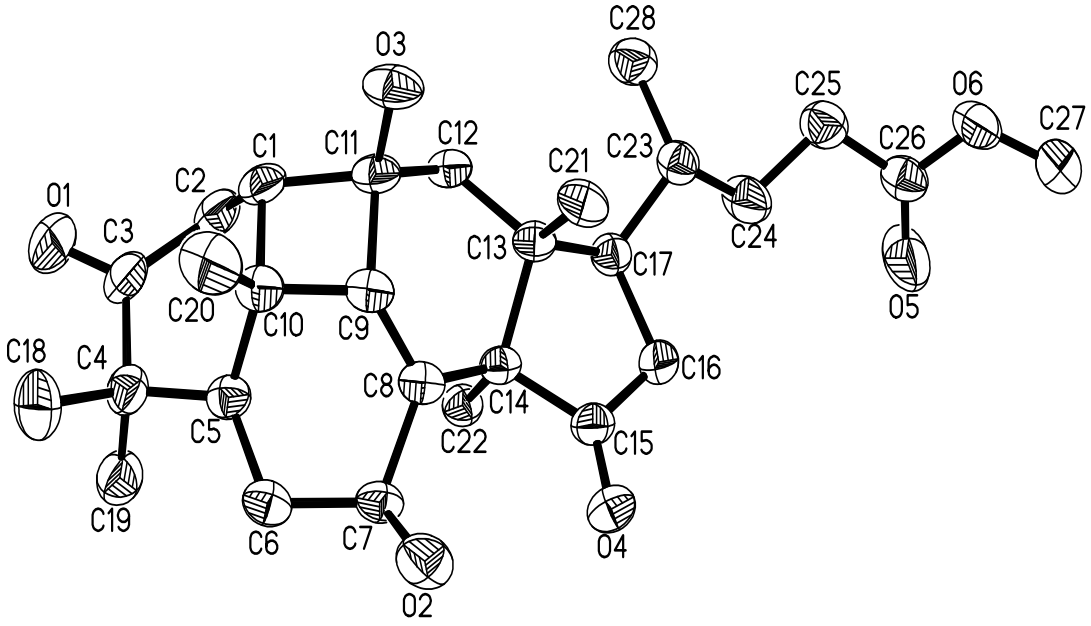


Figure 2. Single-crystal X-ray structure of methyl ganosinensate A