Supporting Information

Oceanalin A, a Hybrid α,ω-Bifunctionalized Sphingoid-Tetrahydroisoquinoline β-Glycoside from the Marine Sponge *Oceanapia* sp.

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S2 – S3 General procedure, isolation and oxidative degradation of **1**, characterization of **3**-**6**. Table S1: temperature dependent ^{1}H NMR (d_5-pyridine) of peracetate **4**.

S4 Table S2: ^{1}H NMR of **1a**, **3**-**6** (500 MHz).

S5 ^{1}H NMR spectrum (600 MHz, CD_3OD) of oceanalin A (**1**)

S6 ^{13}C NMR spectrum (125 MHz, CD_3OD) of oceanalin A (**1**)

S7 DEPT (125 MHz, CD_3OD) of oceanalin A **(1)**

S8 ^{1}H-^{1}H COSY Spectrum (500 MHz, CD_3OD) of oceanalin A **(1)**

S9 HSQC spectrum (600 MHz) of oceanalin A (**1**)

S10 HMBC spectrum (600 MHz, J = 10 Hz) of oceanalin A (**1**)

General Rotations ($[\alpha]_D$) were measured using a Perkin-Elmer 343 polarimeter. The circular dichroism (CD) spectrum were recorded on a Jasco J-500A spectropolarimeter in quartz cells of 1 cm path-length with the following parameters: λ range, 200-300 nm; band width 1 nm; scan speed 0.3 nm.sec^{-1}. The NMR spectra were recorded on a Bruker DPX-400, DRX-500, and DRX-600 spectrometers at 400, 500, 600 for ^{1}H, and 100, 125 and 150 MHz, for ^{13}C, respectively, with $(CH_3)_4Si$ as an internal standard. MALDI-TOF mass spectra were obtained on a Bruker Biflex III laser desorption mass-spectrometer coupled with delayed extraction using N_2 laser (λ 337 nm) on 2,5-dihydroxybenzoic acid (DHB) and α-cyano-4-hydroxy-cinnamic acid (CCA) as matrix. ESIMS mass spectra were obtained on a Surveyor MSQ Thermo Finnigan mass-spectrometer, coupled to an Agilent 1100 series HPLC, or by direct infusion in MeOH containing HCOOH (0.1%). FABMS and EIMS mass spectra were obtained on a AMD-604S mass-spectrometer (AMD-Intectra, Germany). FAB mass spectra were provided by the University of California, Riverside mass spectrometry facility.

Low pressure column liquid chromatography was performed using Si gel L (40/100 μm, Chemapol, Praha, Czech Republic). Silica gel plates (4.5 × 6.0 cm, 5-17 μ, Sorbfil, Russia) were used for thin layer chromatography. Preparative HPLC for isolation and separation of sphingolipids was carried out using a Rainin Binary HPLC system (Dynamax C_{18} column 10 × 250 mm, 5 μm, 3 mL/min) in 80:20:0.1 MeOH-H_2O-TFA with refractive index detection (Waters R401). Preparative HPLC separation of ozonolysis products was performed YMC Pack-ODS-A column (10 × 250 mm, 5 μm, 0.8 mL/min) in 80:20 ethanol-H_2O using an Agilent Series 1100 Instrument equipped with differential refractometer RID-DE14901810.

Animal Material.

A sponge specimen, *Oceanapia* sp. (order Haplosclerida, family Phloeodictyidae) was collected in November 1990 at a depth 48 meter by dredging near Scott reef, north western Australia (16° 33'6 S; 121° 07'1 E) during a scientific cruise aboard RV "Akademik Oparin".

A voucher specimen is kept under registration number PIBOC # O12-200 in the marine invertabrate collection of Pacific Institute of Bioorganic Chemistry (Vladivostok, Russia).

Oceanalin A (1). The sponge *Oceanapia* sp. was exhaustively extracted with MeOH and the *n*-BuOH-soluble fraction purified by Sephadex LH-20 (MeOH elution). The ninhydrin-positive fraction was separated repeatedly by reversed phase HPLC (Dynamax C_{18} 10 × 250 mm, 5 μm, 3 mL/min) in 80:20:0.1 MeOH-H_2O-TFA) to give **1** as a colorless glass (0.003% of dry weight). Oceanalin A (**1**), 4.0 mg. Colorless

solid; $[\alpha]_D$ –5.7° (*c* 0.14 EtOH), UV (MeOH), λ_{max} 238 nm (ε 7600), 288 (7850). ^{1}H and ^{13}C NMR see Table 1. ESIMS *m/z* $[M+Na]^+$ 737 (100 %), $[M+H_2]^{2+}$ 369 (30%). HRMS FAB *m/z* 737.5286 $[M+H]^+$ Calcd, $C_{41}H_{73}N_2O_9$ 737.5311. ^{1}H, ^{13}C NMR, see Table 1.

Octaacetyl Oceanalin A (1a). A sample of **1** (1.5 mg) was dissolved in pyridine (0.5 mL) and acetic anhydride (0.5 mL) and allowed to stand at 25°C for 18 h. Removal of the volatile material gave a residue (2.0 mg) of **1a,** MALDI MS *m/z* $[M+Na]^+$ 1095, $[\alpha]_D$ 0° (*c* 0.15 $CHCl_3$). ^{1}H NMR, see Table S2.

Hydrolysis of Oceanalin A (1). A solution of **1** (1.2 mg) in 6M HCl (1 mL) was heated at 100 °C for 2.5 h. The mixture was cooled and treated with ion-exchange resin Dowex (HCO_3^- form). The aqueous solution was separated and concentrated to afford D-galactose (0.4 mg).

Ozonolysis-Reduction of 1a. Ozone was bubbled through a solution of **1a** (2.0 mg) in MeOH at a temperature of –20 °C to –30 °C over 4 h. The solution was cooled and treated with an excess of $NaBH_4$ (5 mg). The mixture was left at room temperature overnight and quenched with acetic acid (to pH=7). The mixture was evaporated and treated with Ac_2O/pyridine (1:1, 0.5 mL) at room temperature, overnight. After removal of the volatiles, the residue was separated by chromatography (silica gel), using ethyl acetate as eluent, to afford a mixture of products **3**-**6** (1.0 mg). Separation of the mixture by preparative HPLC (C_{18}, 80:20 EtOH:H_2O) afforded the pure compounds **3**-**6**.

Peracetate 3. 0.7 mg, colorless solid, *m/z* 710 $[M+Na^+]$, $[\alpha]_D$ +1° (*c* 0.07 EtOH), ^{1}H NMR see Table S2.

Peracetate 4. 0.7 mg, colorless solid, *m/z* 528 $[M+Na^+]$, $[\alpha]_D$ 0° (*c* 0.07 EtOH), ^{1}H NMR see Table S2.

Peracetate 5. 0.2 mg, colorless solid, *m/z* 754 $[M+Na^+]$, $[\alpha]_D$ +1° (*c* 0.02 EtOH), ^{1}H NMR see Table S2.

Peracetate 6. 0.2 mg, colorless solid, *m/z* 484 $[M+Na^+]$, $[\alpha]_D$ ° (*c* 0.02 EtOH), ^{1}H NMR see Table S2.

Table S1. Variable temperature ^{1}H NMR Data for compound **4** (pyridine-d_5, 500 MHz)[a]

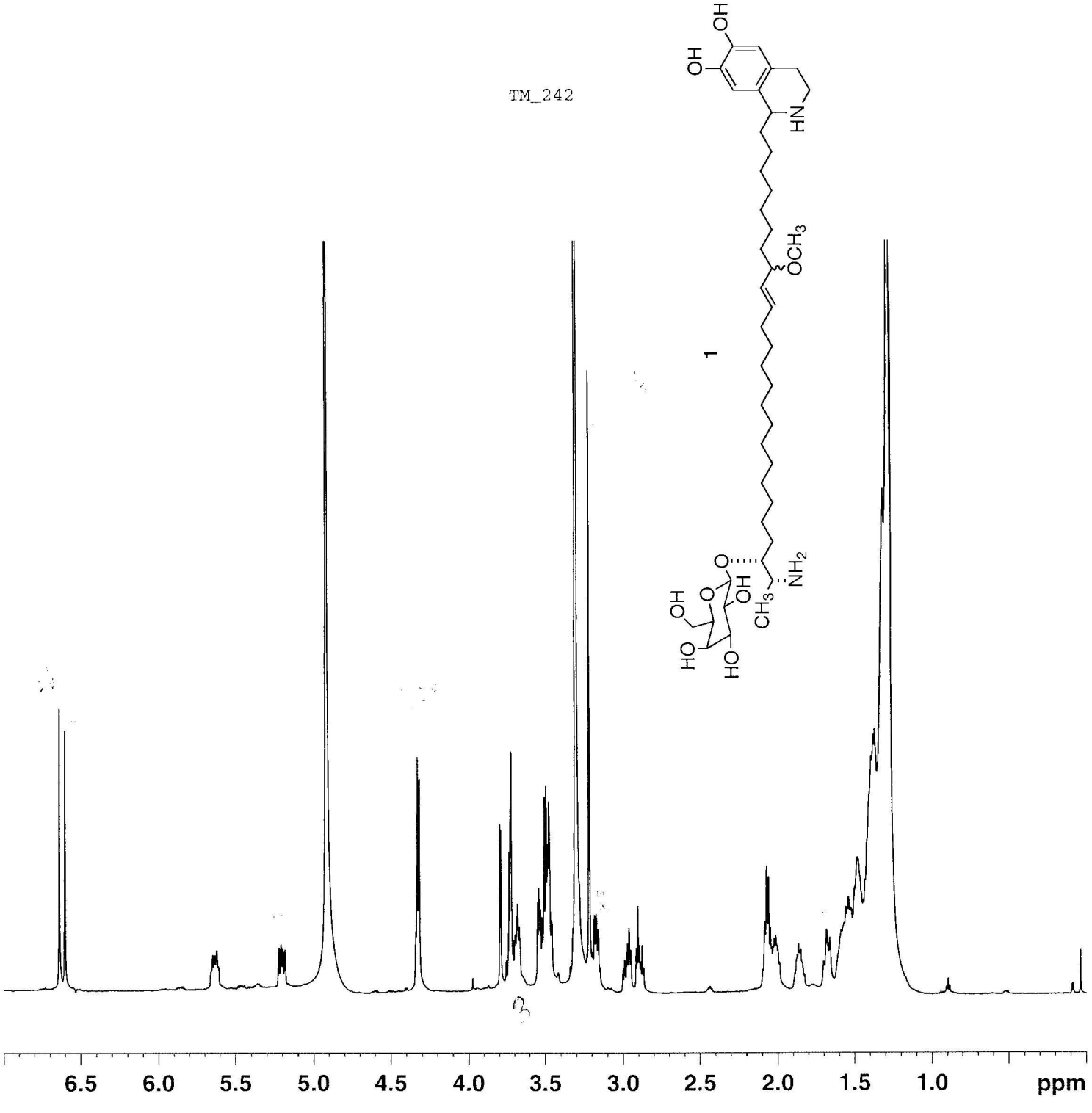
T /°C	δ OAc						δ OMe	
	C33a	C33b	C32	C27a	C27b	C17	C18a	C18b
27	2.320	2.305	2.315	2.204	2.193	2.053	3.403	3.394
40	2.292	2.282	2.290	2.188	2.171	2.036	3.395	3.382
60	2.263	2.263	2.256	2.166	2.146	2.016	3.374	3.374
80	2.238	2.238	2.232	2.129	2.129	1.996	3.365	3.365
100	2.222	2.222	2.217	2.113	2.113	1.981	3.357	3.357
110	2.210	2.210	2.204	2.107	2.107	1.976	3.355	3.355

[*a*]. For clarity, the numbering of **3**-**6** conforms to that of **1**. Designations 'a' and 'b' are arbitrary assignments of doubled AcO and OMe signals.

Table S2. ^{1}H NMR data for octa-acetyloceanalin A (**1a**) and degradation products **3**-**6**.[a]

#	1a	3	4	5	6
1	1.167 (d, 6.8)	1.165 (d, 6.8)	-	1.165 (d, 6.8)	-
2	4.09 (m)	4.09 (m)	-	4.09 (m)	-
3	3.49 (dt, 3.0, 6.5)	3.49 (dt, 2.7, 6.3)	-	3.49 (td, 6.2, 2.7)	-
6-13	1.25 (bs)	1.25 (bs)	-	1.25 (bs)	-
16	5.58 (m)	4.05 (t, 6.7)		3.35 (m)	
17	5.22 (dd, 8.3, 15.5)	-	4.16 (dt, 11.6, 3.7); 4.01 (ddd, 2.4, 6.0, 11.6)	4.02 (dd, 6.0. 11.6) 4.17 (dd, 3.3, 11.6)	
18	3.43 (m)	-	3.40 (m)	-	4.05 (m, 2H)
20-24	1.25 (s)	-	1.25 (bs)	-	1.25 (bs)
26	5.58 (m) 4.68 (m)	-	5.58 (dd, 5.5, 9.7) 4.69 (m)	-	5.58 (dd, 5.7, 9.5) 4.69 (m)
2-NHAc	5.84 (d, 8.3)	5.81 (d, 8.4)		5.84 (d, 8.3)	
28a	3.78 (ddd, 4.0, 5.4, 13.6)	-	3.78 (dt, 13.5, 5.1)	-	3.78 (m)
28b	3.52 (m)	-	3.52 (m)	-	3.50 (m)
29a	2.65-3.05 (m)	-	2.65-3.05 (m)	-	
29b	2.65-3.05 (m)	-	2.65-3.05 (m)	-	
31	6.93 (s)	-	6.93 (s)	-	6.93 (s)
34	6.94 (s)	-	6.95 (s)	-	6.95 (s)
OCH_3	3.230 (s)[b]; 3.233 (s)[b]	-	3.399 (s),[b] 3.404 (s)[b]	3.40 (s)	
1'	4.48 (d, 8.0)	4.48 (d, 7.9)	-	4.48 (d, 7.9)	-
2'	5.16 (dd, 8.0, 10,6)	5.16 (dd, 7.9, 10.6)	-	5.16 (dd, 7.9, 10.6)	-
3'	5.04 (dd, 3.3, 10.6)	5.04 (dd, 3.5, 10.6)	-	5.04 (dd, 3.3, 10.6)	-
4'	5.39 (dd, 0.8, 3.3)	5.39 (dd, 0.8, 3.5)	-	5.39 (dd, 0.8, 3.3)	-
5'	3.91 (dt, 0.8, 6.6)	3.91 (td, 6.7, 0.9)	-	3.90 (td, 6.6, 0.8)	-
6'	4.10 (dd, 6.6, 11.3) 4.19 (dd, 6.6, 11.3)	4.10 (dd, 6.7, 11.4) 4.19 (dd, 6.7, 11.4)	-	4.10 (dd, 6.6, 11.1) 4.19 (dd, 6.6, 11.1)	-
16-OAc		2.04 (s)			
17-OAc				2.08 (s)	
18-OAc					2.04 (s)
4xOAc	1.97 (s)	1.97 (s);	-	1.97 (s)	-
	2.00 (s)	1.99 (s);	-	1.99 (s)	-
	2.04 (s)	2.04 (s);	-	2.04 (s)	-
	2.05 (s)	2.05 (s)	-	2.05 (s)	-
32-OAc	2.28 (s)		2.28 (s)		2.28 (s)
33-OAc	2.27 (s)[b]; 2.29 (s)[b]		2.27 (s)[b]; 2.29 (s)[b]		2.27 (s)[b], 2.29 (s)[b]
27-NHAc	2.15 (s)[b]; 2.16 (s)[b]		2.15 (s)[b]; 2.16 (s)[b]		2.15 (s)[b], 2.16 (s)[b]

a, $CDCl_3$, 500 MHz, δ_H (mult, *J* Hz). For clarity, the numbering of **3**-**6** conforms to that of **1**; *b*, doubled signals.



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13C NMR (CD3OD, 125 MHz),
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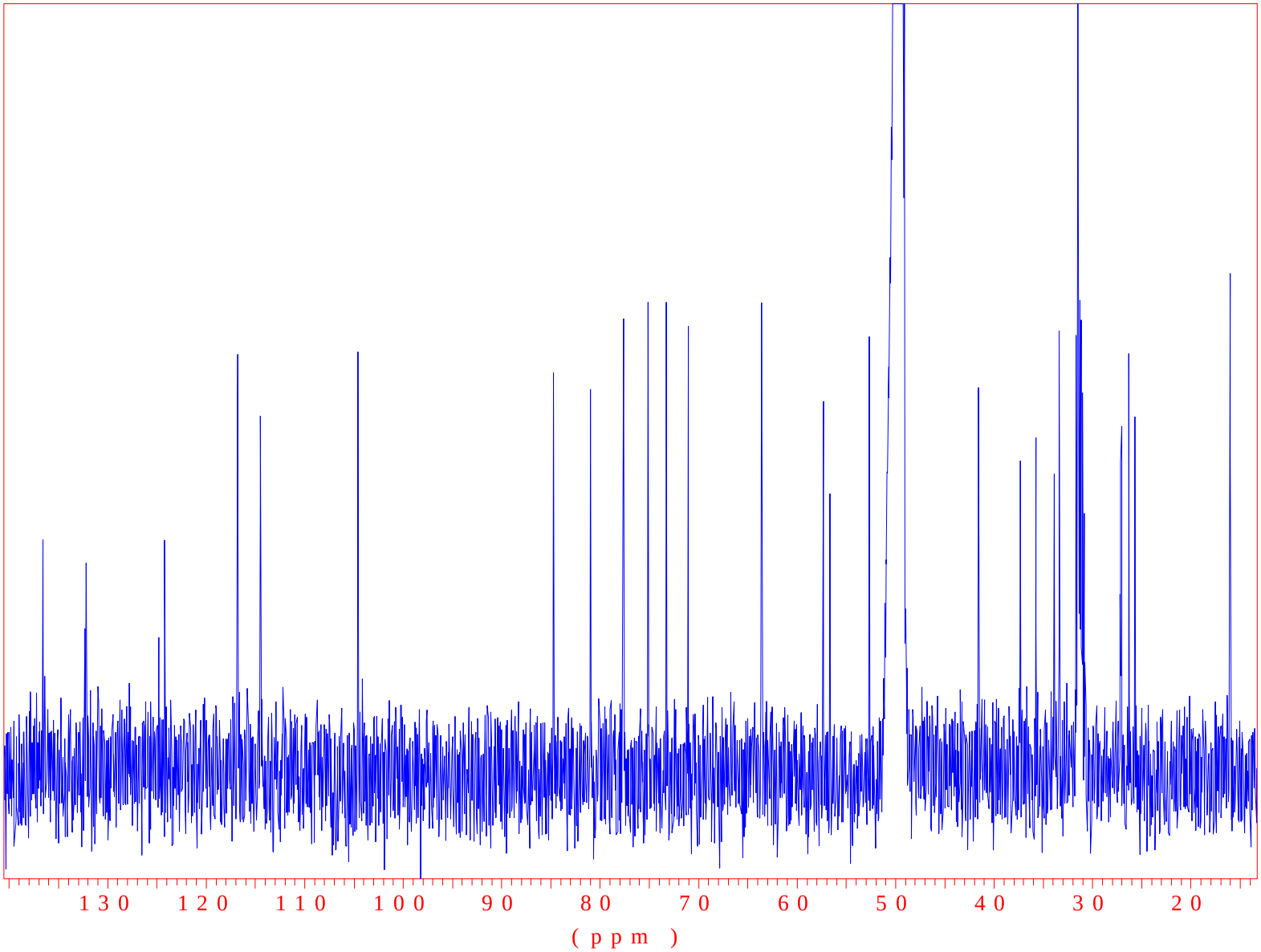

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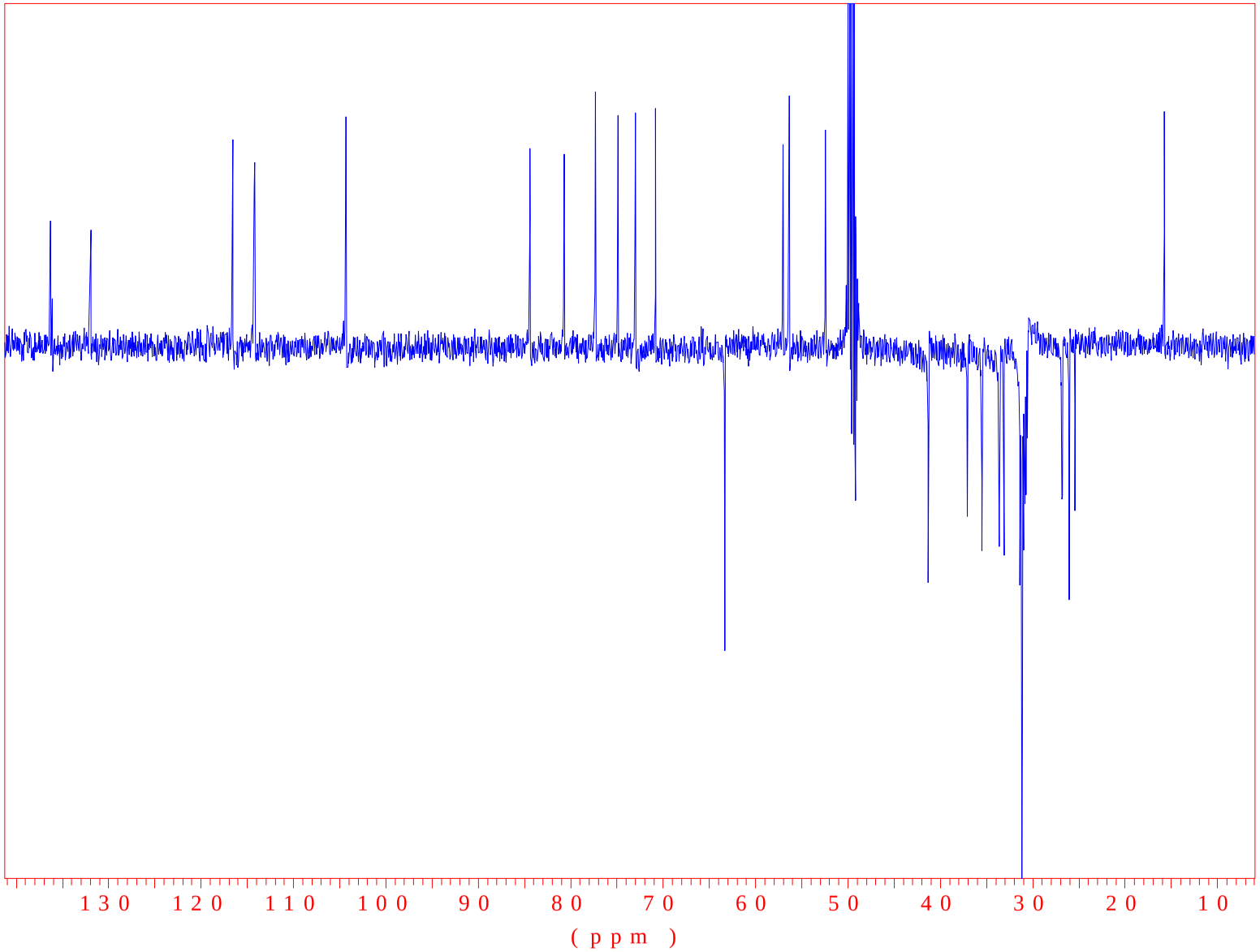

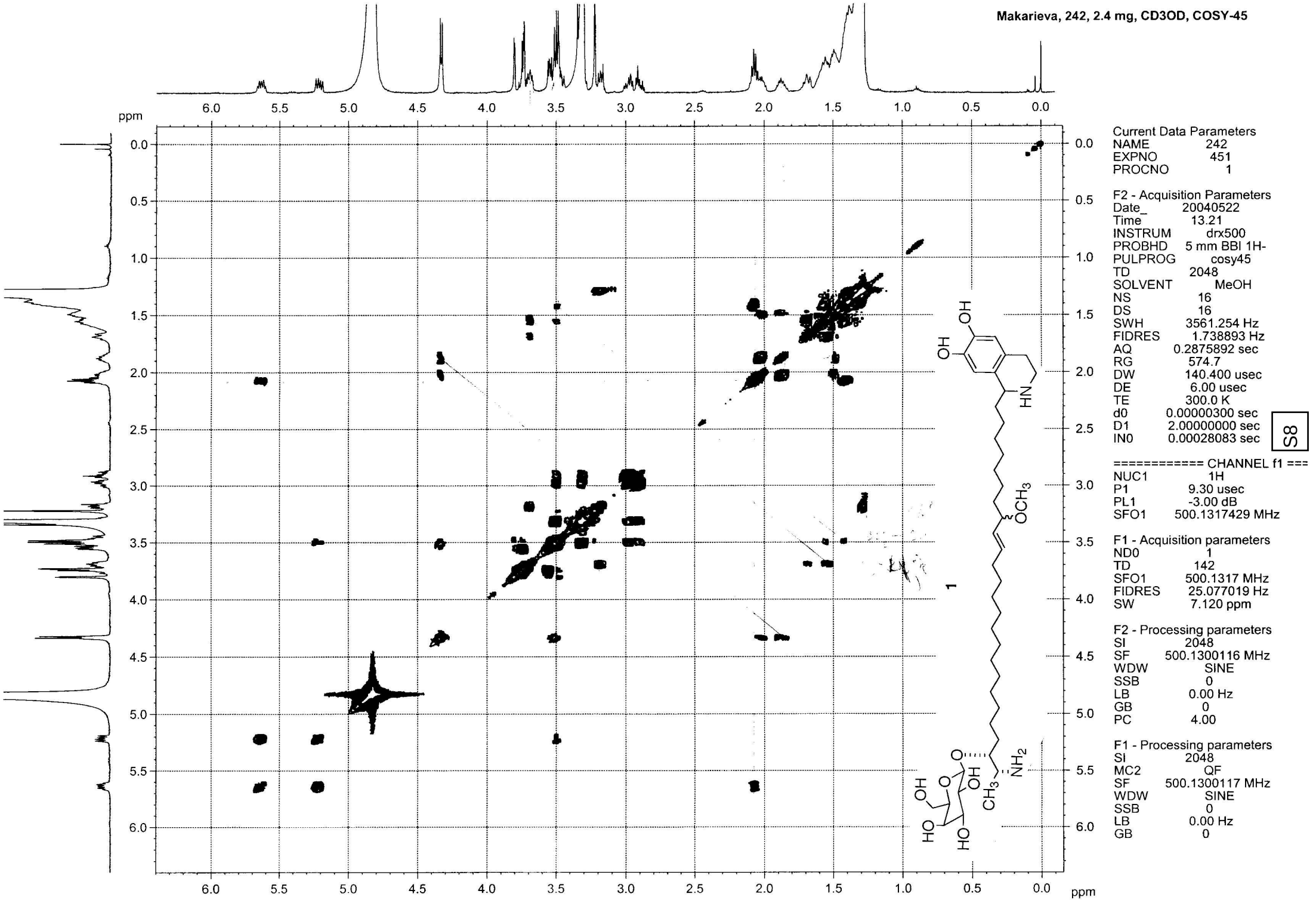
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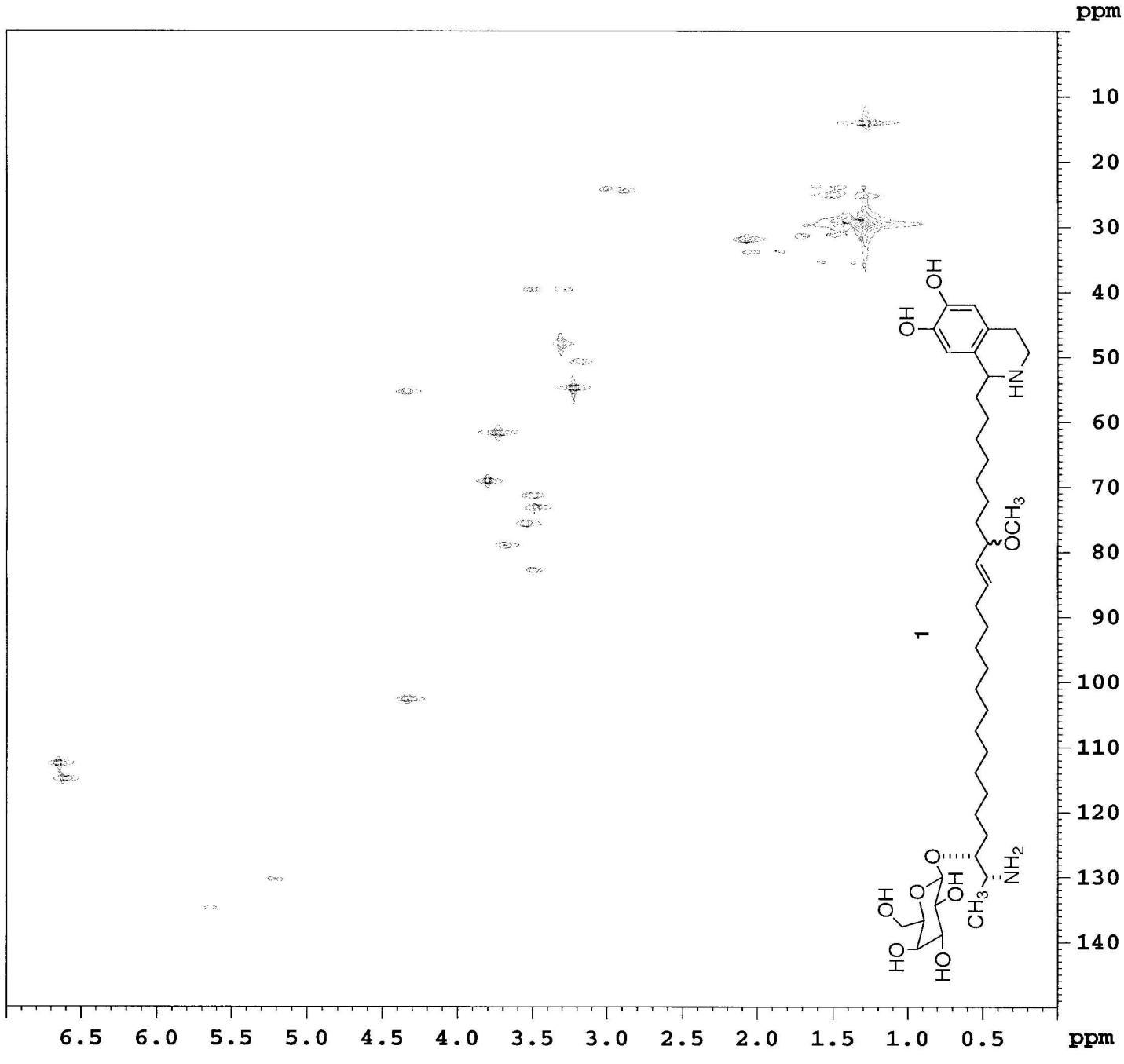

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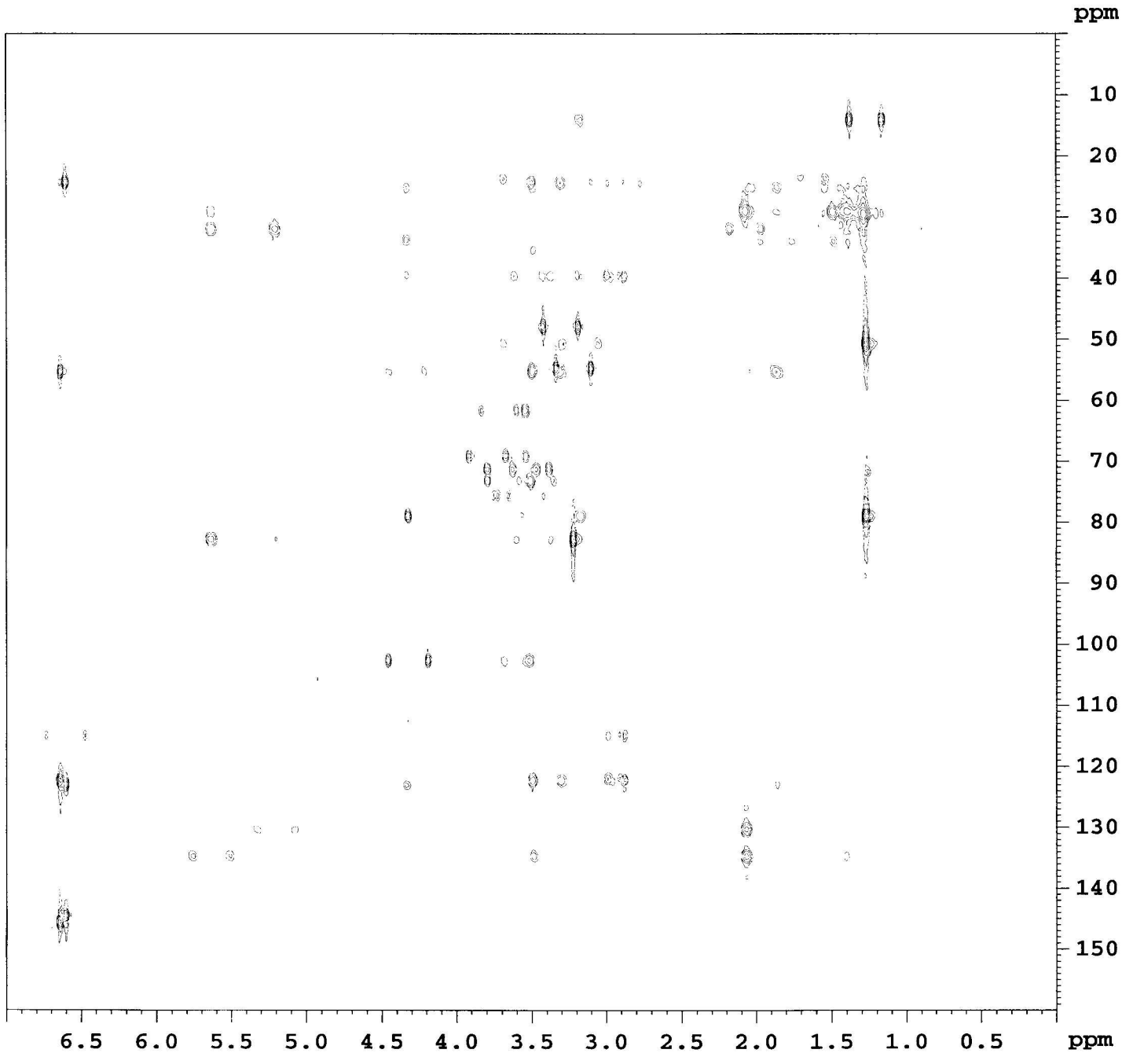

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