

SUPPORTING INFORMATION

Walsucochins A and B with an Unprecedented Skeleton Isolated from *Walsura cochinchinensis*

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- S20. ROESY spectrum (600 MHz) of Walsuchochin B (2) in CDCl_3 .
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- S22. Key ROESY correlations (in Figure) of Walsuchochin B (2).

S1. Experimental Section.

General Experimental Procedures.

Optical rotations were measured on a Perkin-Elmer 341 polarimeter. UV spectra were obtained on a Shimadzu UV-2550 Spectrophotometer. IR spectra were made on a Perkin-Elmer 577 spectrometer with KBr discs. 1D and 2 D NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer (except for the ^1H – ^1H COSY and ROESY spectra were performed on a Varian Unity-Inova 600 spectrometer) with TMS as internal standard. EIMS and HREIMS were measured on a Finnigan MAT 95 mass spectrometer. All the solvents used were of analytical grade (Shanghai Chemical Plant, Shanghai, People's Republic of China). Silica gel (200–300 mesh), silica gel H60 (Qingdao Haiyang Chemical Co. Ltd. Qingdao, People's Republic of China), Sephadex LH-20 (Amersham Biosciences), and MCI gel (CHP20P, 75–150 μm , Mitsubishi Chemical Industries Ltd.) were used for column chromatography. Pre-coated silica gel GF₂₅₄ plates (Qingdao Haiyang Chemical Co. Ltd. Qingdao, People's Republic of China) were used for TLC.

Plant Material.

The twigs and leaves of *Walsura cochinchinensis* were collected in August of 2005 from Hainan province, P. R. China, and were identified by Prof. S.-M. Huang, Department of Biology, Hainan University of China. A voucher specimen has been deposited in Shanghai Institute of Materia Medica, SIBS, Chinese Academy of Sciences, P. R. China. (accession number: WALC-2005-1Y).

Extraction and Isolation.

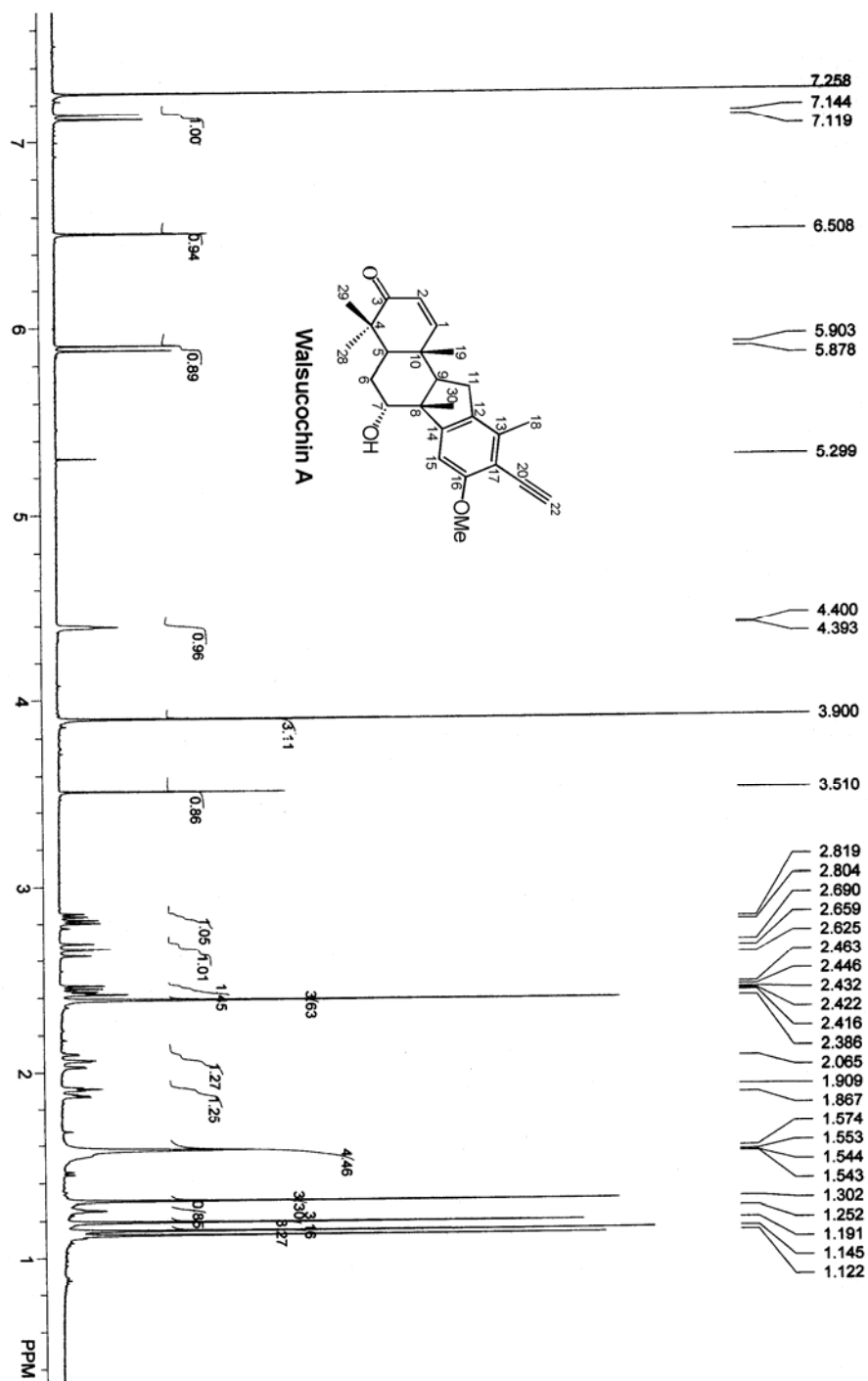
The air-dried powder of the plant material (2.5 kg) was percolated with 95% EtOH at room temperature to give 120 g of crude extract, which was then partitioned between EtOAc and water to obtain the EtOAc soluble fraction (50 g). The EtOAc soluble fraction was separated by column chromatography over silica gel eluted with petroleum ether/Me₂CO (20:1→0: 1) to give six fractions 1-6. Fraction 5 (5 g) was

chromatographed on a MCI-gel column (MeOH/H₂O, 5:5 to 9:1) to obtain four subfractions 5a–5d. Fraction 5b (1.2 g) was extensively separated over the columns of silica gel and Sephadex LH-20 to give a mixture of two major compounds, which was finally purified by semi-preparative HPLC (Waters 515 HPLC pump and Waters 2487 dual λ absorption detector, YMC-Pack ODS-A column, 250 \times 10 mm, CH₃CN/H₂O 80:20 as the mobile phase) to yield compounds **1** (10 mg) and **2** (6 mg).

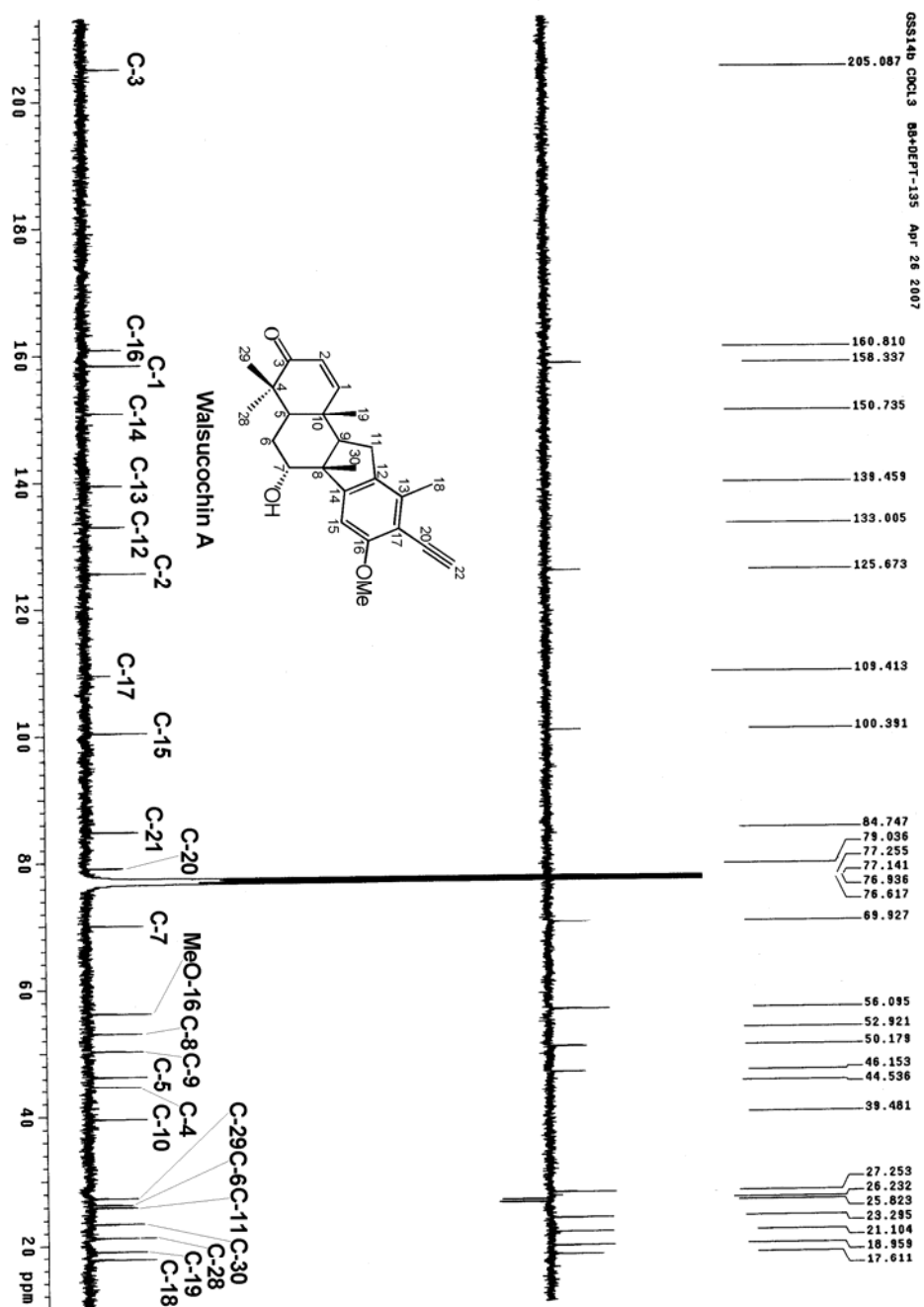
Walsucochin A (1): colorless powder; $[\alpha]_{\text{D}}^{20}$ 19 ($c = 0.200$, MeOH); UV (MeOH) λ_{max} (log ϵ) 215 (4.2), 248 (3.9), 258 (3.8), 297 (3.4), 307 (3.4) nm; CD (MeOH) λ_{max} 230 ($\Delta\epsilon +8.61$), 211 ($\Delta\epsilon -7.37$) nm; IR (KBr) ν_{max} 3437, 3320, 2098, 1664, 1603, 1580, 1464, and 829 cm⁻¹; for ¹H and ¹³C NMR data, see table 1; EI MS (70 eV): m/z 378 [M]⁺(100), 251 (24), 197 (14), 115 (6), 93 (7), 77 (8), 58 (18), 51 (6); HR EIMS m/z calcd for C₂₅H₃₀O₃, 378.2195; found, 378.2195 [M]⁺.

Walsucochin B (2): colorless powder; $[\alpha]_{\text{D}}^{20}$ -45 ($c = 0.100$, MeOH); UV (MeOH) λ_{max} (log ϵ) 258 (4.0), 250 (3.9) nm; CD (MeOH) λ_{max} 218 ($\Delta\epsilon -3.22$) nm; IR (KBr) ν_{max} 3433, 3320, 2098, 1709, 1603, 1580, 1462, and 1097 cm⁻¹; for ¹H and ¹³C NMR data, see table 1; EI MS m/z (70eV) 380 [M]⁺(100), 251 (20), 211 (30), 198 (20), 183 (16), 152 (5), 121 (10), 91 (5), 51 (3); HR EIMS m/z calcd for C₂₅H₃₂O₃, 380.2351; found, 380.2349 [M]⁺.

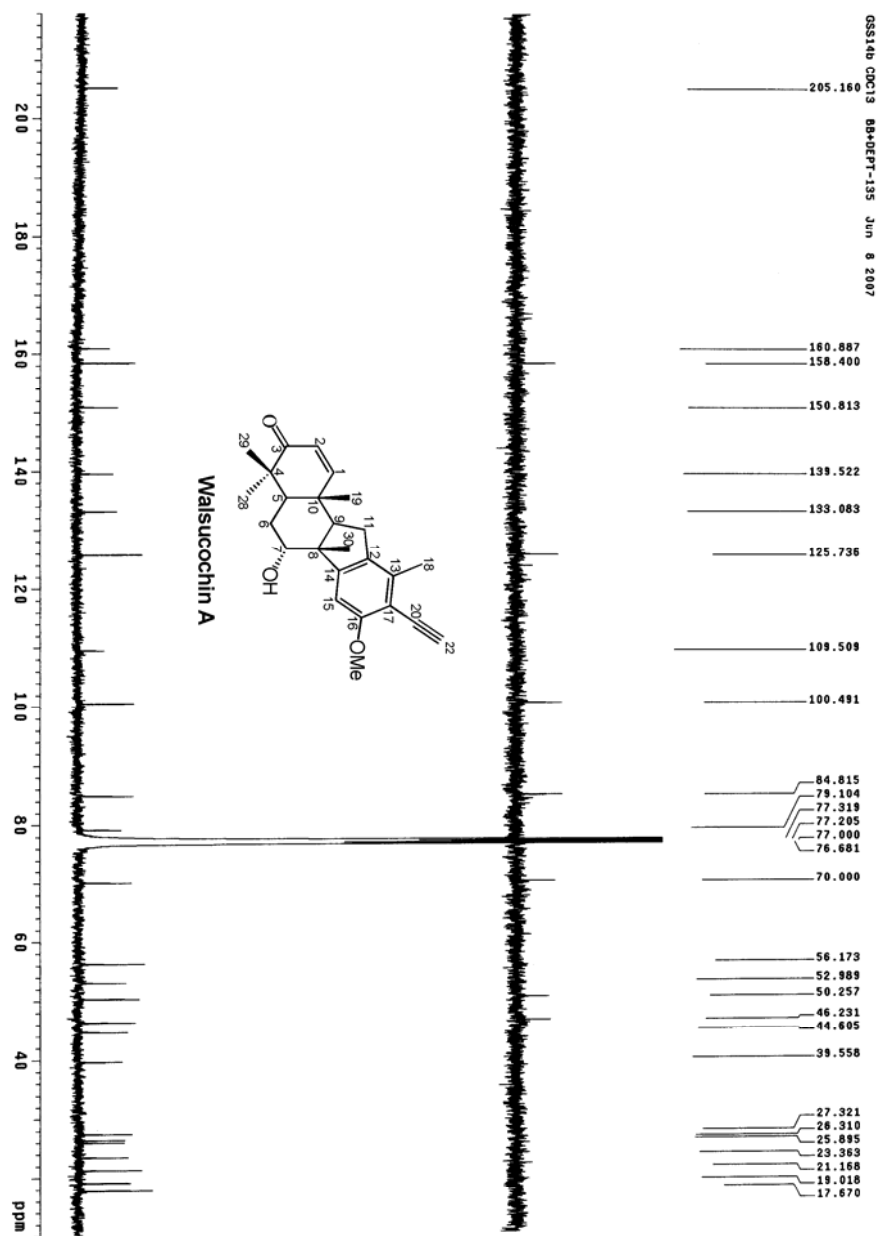
S2. ^1H NMR spectrum (400 MHz) of Walsucochin A (1) in CDCl_3 .



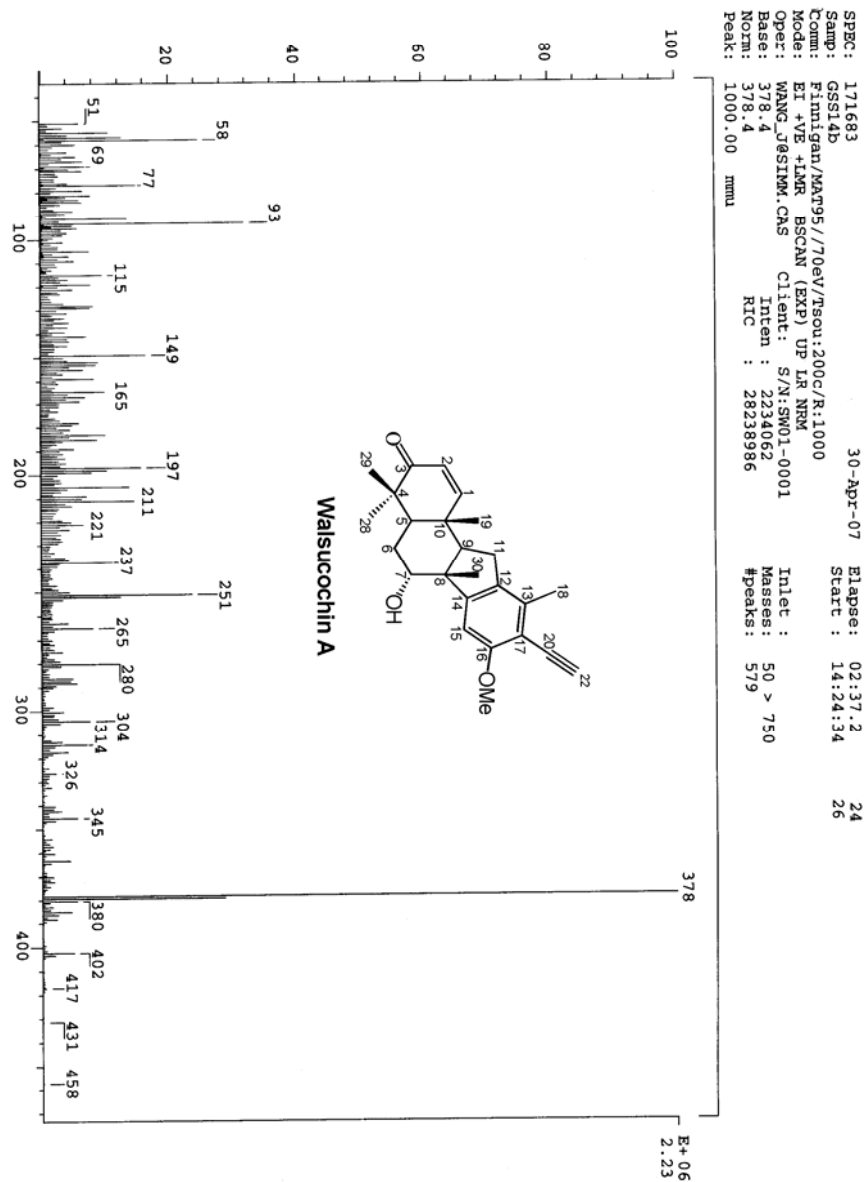
S3. ^{13}C NMR spectrum (100 MHz) of Walsucochin A (1) in CDCl_3 ($^1J_{\text{CH}}=140$ Hz).



S4. ^{13}C NMR spectrum (100 MHz) of Walsucochin A (1) in CDCl_3 ($^1J_{\text{CH}}=250$ Hz).



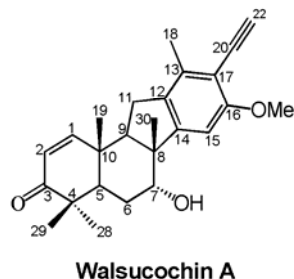
S5. EIMS spectrum of Walsucochin A (1).



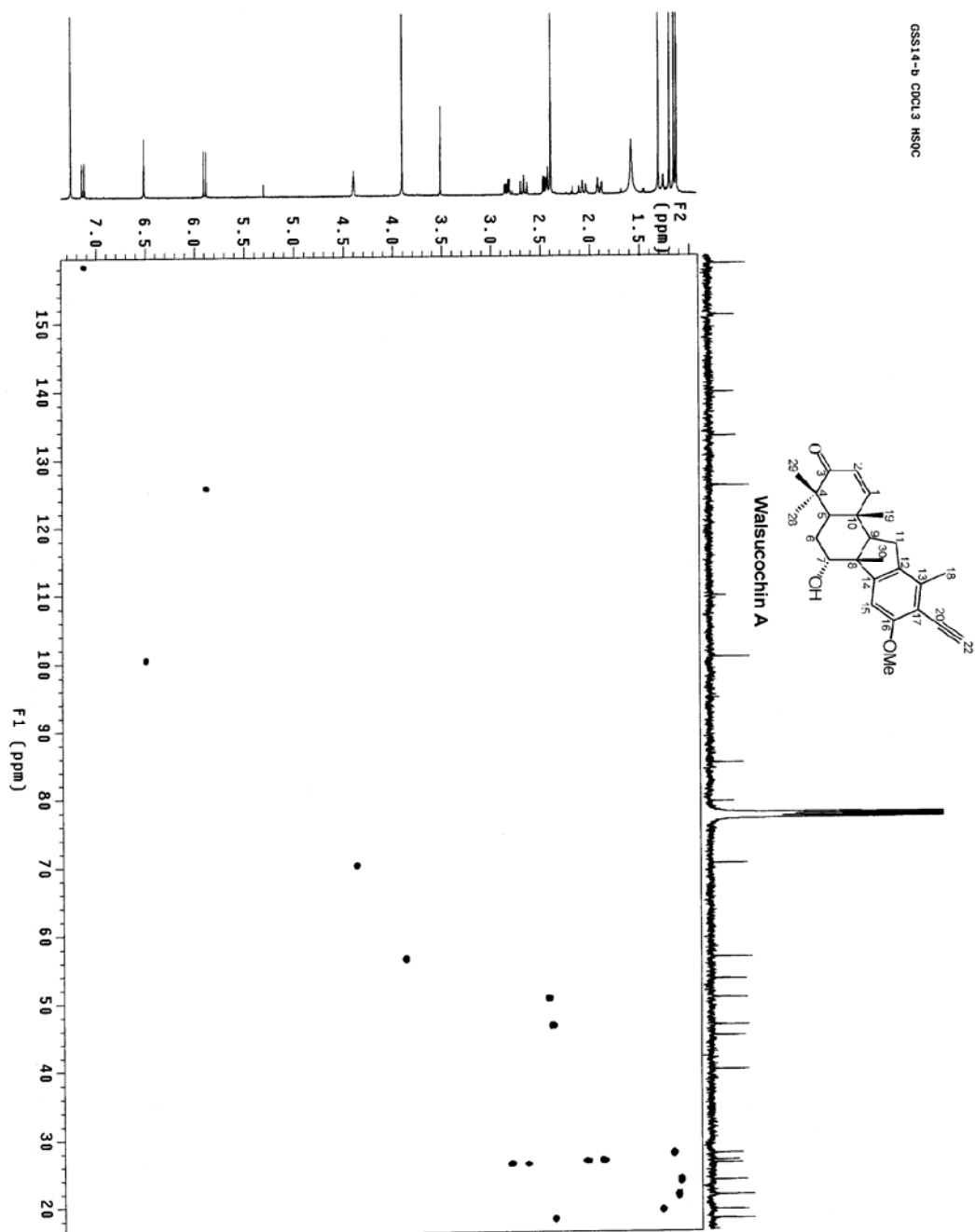
S6. HREIMS spectrum of Walsucochin A (1).

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 : (509) C30.H100.03
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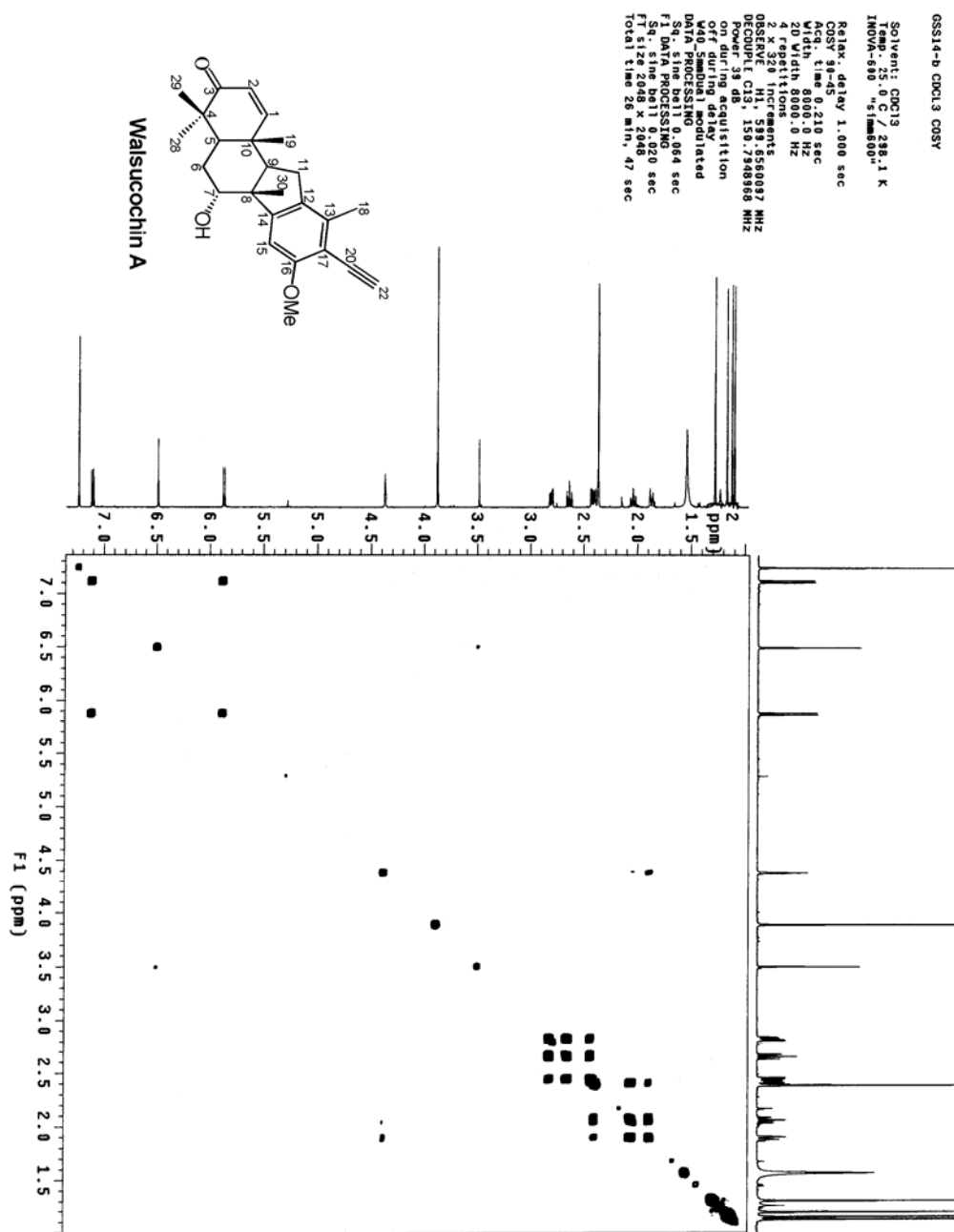
Mass	Intensity	%RA	%RIC	Delta	R+D	Composition
55.05284 *	24710	6.11	0.17	1.9	1.5	C4.H7
58.06296 *	72640	17.97	0.50			
67.05173 *	15337	3.79	0.11			
69.07104 *	13846	3.43	0.10	-0.6	1.5	C5.H9
77.03963 *	33231	8.22	0.23	-0.5	4.5	C6.H5
79.05618 *	16970	4.20	0.12	-1.4	3.5	C6.H7
81.07028 *	13136	3.25	0.09	0.1	2.5	C6.H9
84.08101 *	13420	3.32	0.09			
91.05403 *	24284	6.01	0.17	0.8	4.5	C7.H7
93.05871 *	27266	6.75	0.19			
93.07130 *	14272	3.53	0.10	-0.9	3.5	C7.H9
105.0739 *	12355	3.06	0.09			
115.0570 *	23006	5.69	0.16	-2.2	6.5	C9.H7
128.0625 *	17183	4.25	0.12	0.1	7.0	C10.H8
129.0701 *	20237	5.01	0.14	0.3	6.5	C10.H9
141.0710 *	23645	5.85	0.16	-0.5	7.5	C11.H9
152.0603 *	22722	5.62	0.16	2.3	9.0	C12.H8
153.0719 *	22225	5.50	0.15	-1.4	8.5	C12.H9
154.0761 *	14059	3.48	0.10	2.2	8.0	C12.H10
155.0861 *	19100	4.73	0.13	0.0	7.5	C12.H11
159.0801 *	24142	5.97	0.17	0.9	6.5	C11.H11.O
165.0704 *	28402	7.03	0.20	0.0	9.5	C13.H9
167.0831 *	15692	3.88	0.11			
178.0794 *	14556	3.60	0.10	-1.2	10.0	C14.H10
183.0812 *	31953	7.91	0.22	-0.3	8.5	C13.H11.O
185.0964 *	28118	6.96	0.19	0.3	7.5	C13.H13.O
193.1033 *	12568	3.11	0.09	-1.6	9.5	C15.H13
197.0957 *	55314	13.69	0.38	0.9	8.5	C14.H13.O
198.1012 *	32024	7.92	0.22			
199.1105 *	24071	5.96	0.17	1.8	7.5	C14.H15.O
205.0998 *	12426	3.07	0.09	1.9	10.5	C16.H13
209.0961 *	19953	4.94	0.14	0.5	9.5	C15.H13.O
210.1028 *	12355	3.06	0.09	1.7	9.0	C15.H14.O
211.1109 *	31527	7.80	0.22	1.3	8.5	C15.H15.O
221.0948 *	17609	4.36	0.12	1.8	10.5	C16.H13.O
223.1116 *	13207	3.27	0.09	0.7	9.5	C16.H15.O
236.1173 *	18603	4.60	0.13	2.8	10.0	C17.H16.O
237.1257 *	39763	9.84	0.28	2.2	9.5	C17.H17.O
241.1114 *	17680	4.37	0.12			
251.1454 *	96498	23.88	0.67	-1.8	9.5	C18.H19.O
252.1502 *	45728	11.31	0.32	1.3	9.0	C18.H20.O
265.1223 *	25846	6.39	0.18	0.5	10.5	C18.H17.O2
280.1461 *	39195	9.70	0.27	0.2	10.0	C19.H20.O2
314.2069 *	17112	4.23	0.12			
317.1925 *	14485	3.58	0.10	-1.9	11.5	C23.H25.O
345.1863 *	20166	4.99	0.14	-0.8	12.5	C24.H25.O2
363.1985 *	15408	3.81	0.11	-2.5	11.5	C24.H27.O3
378.2195 *	404172	100.00	2.80	0.0	11.0	C25.H30.O3
379.2225 *	103599	25.63	0.72			
380.2278 *	20663	5.11	0.14			
385.2643 *	18816	4.66	0.13			



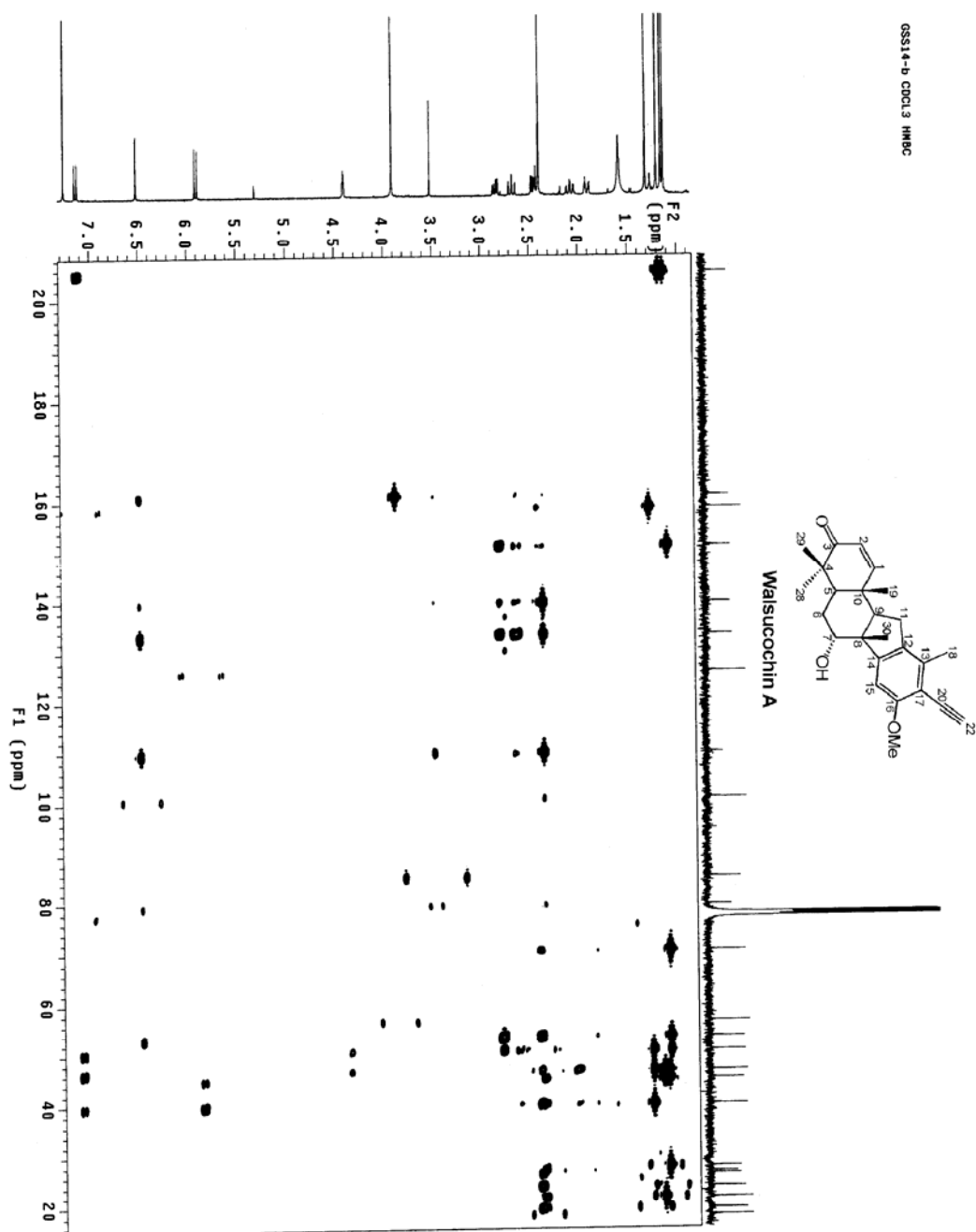
S7. HSQC spectrum (400 MHz) of Walsucochin A (1) in CDCl₃.



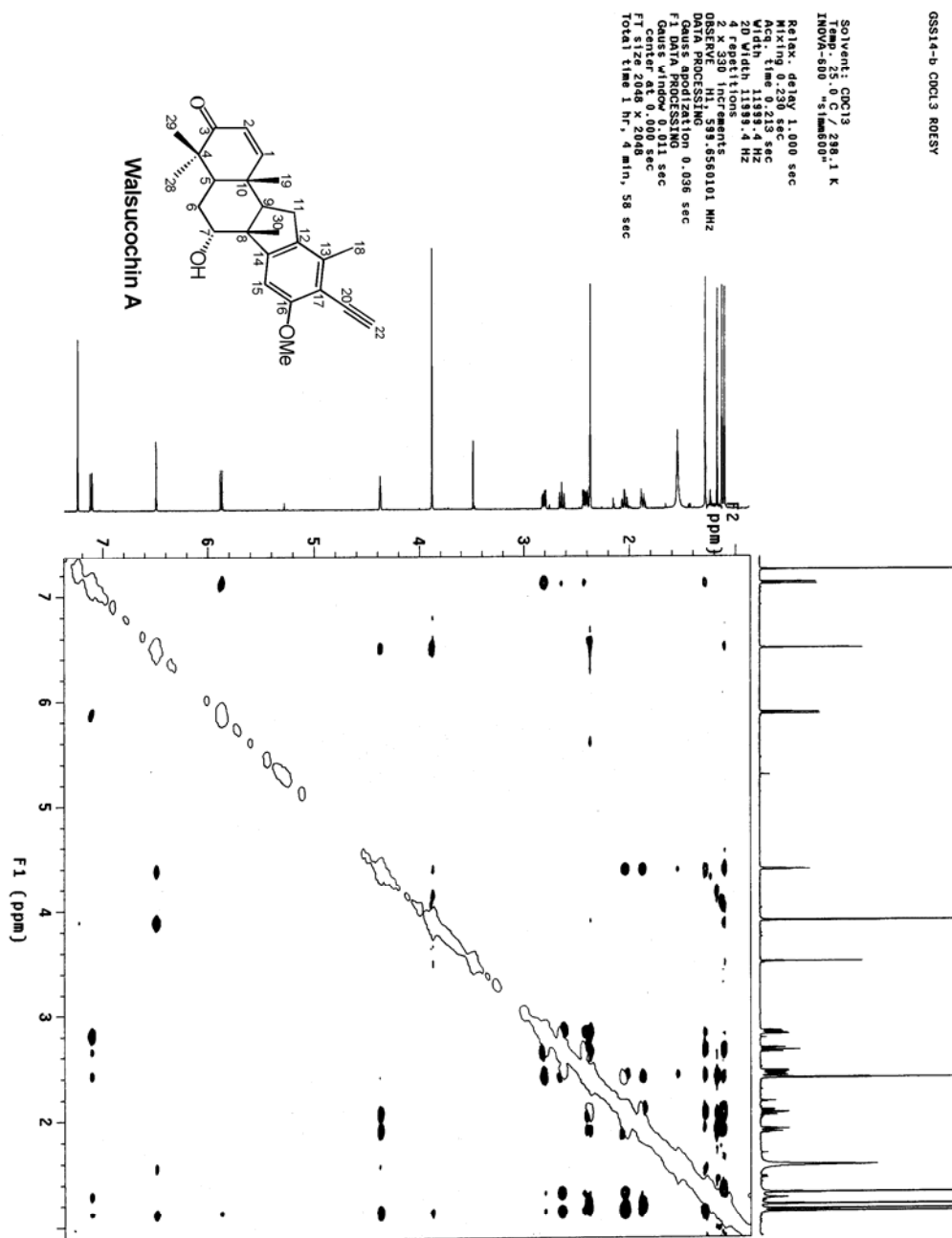
S8. ^1H - ^1H COSY spectrum (600 MHz) of Walsucochin A (1) in CDCl_3 .



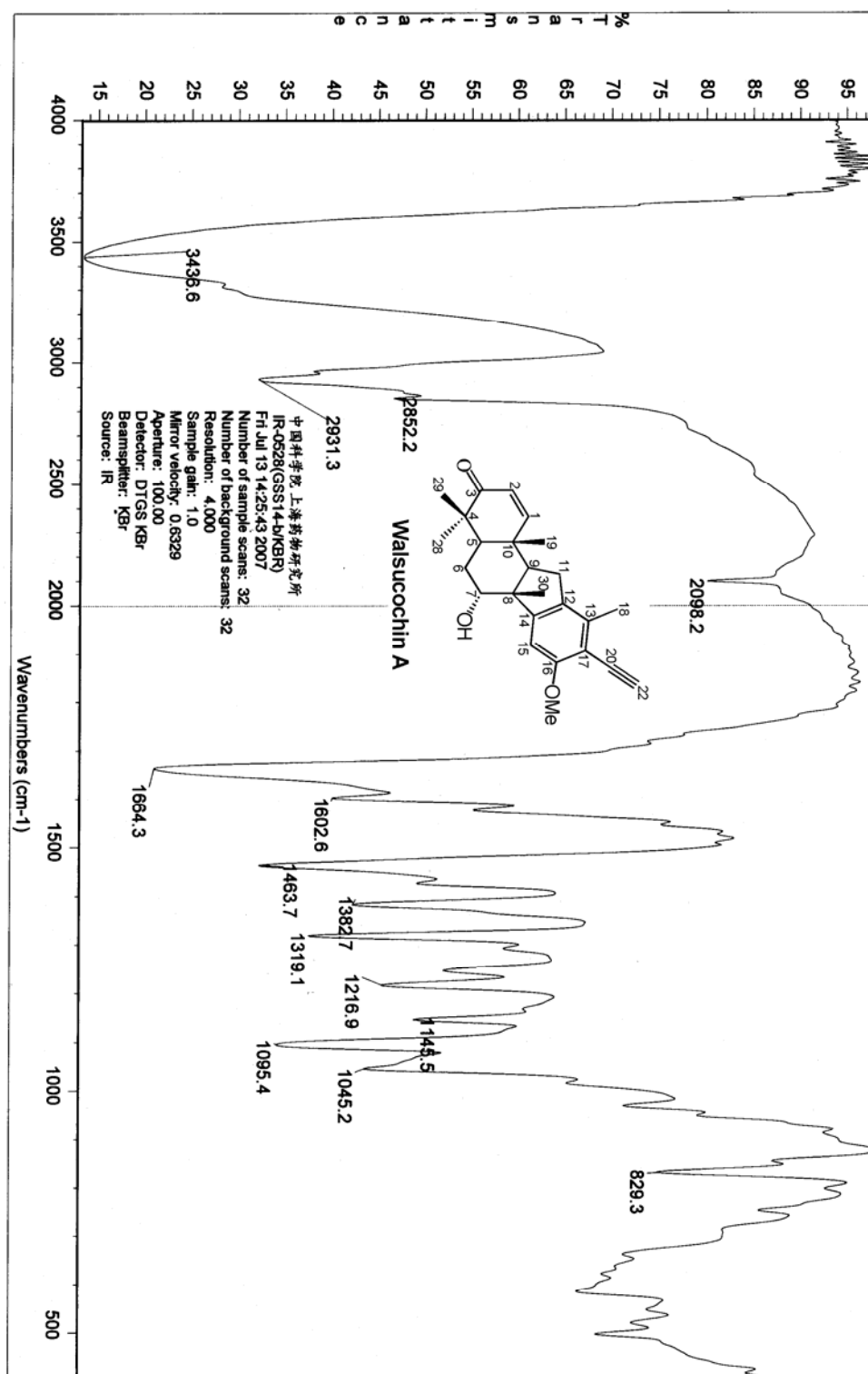
S9. HMBC spectrum (400 MHz) of Walsucochin A (1) in CDCl₃.



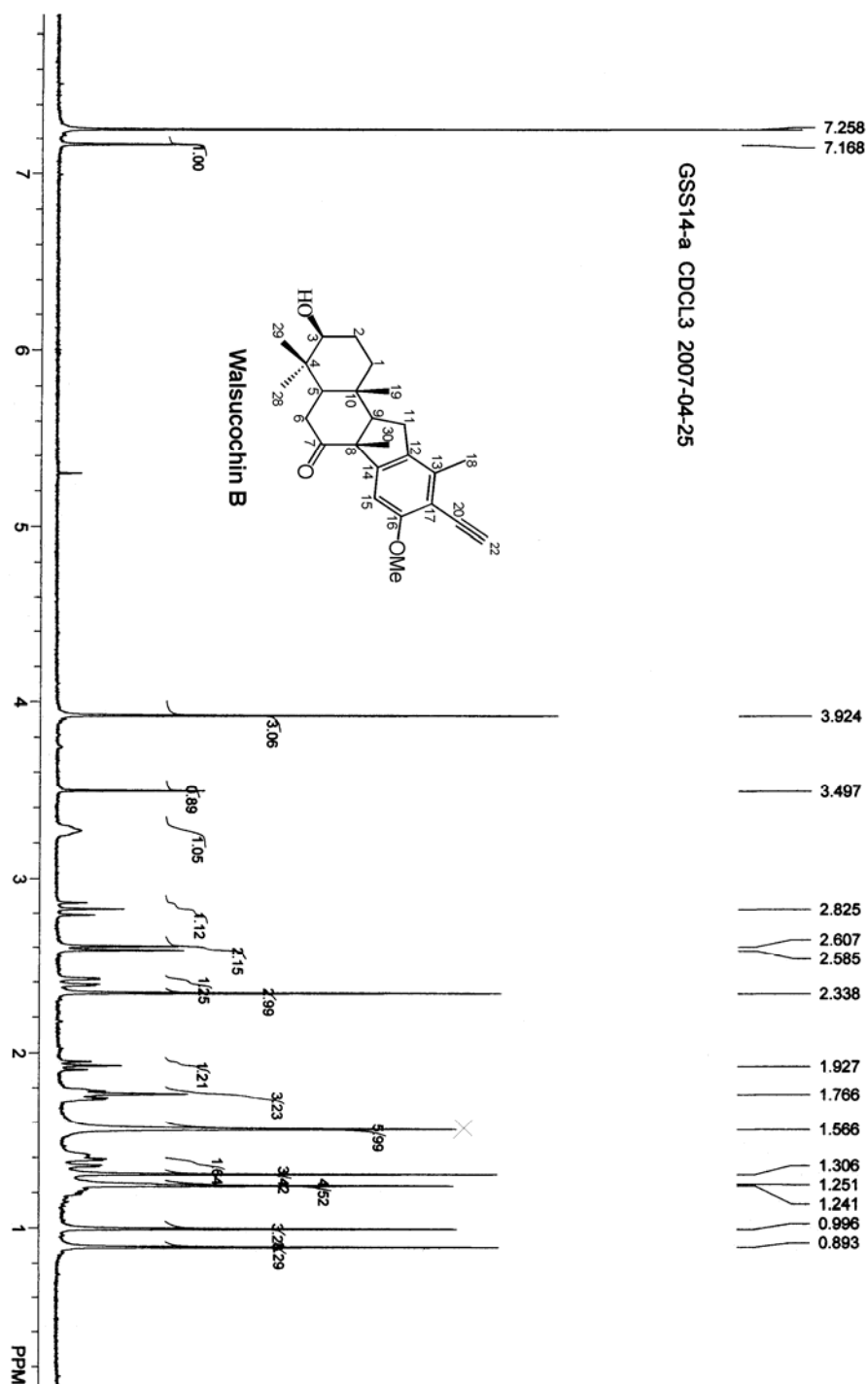
S10. ROESY spectrum (600 MHz) of Walsucochin A (1) in CDCl₃.



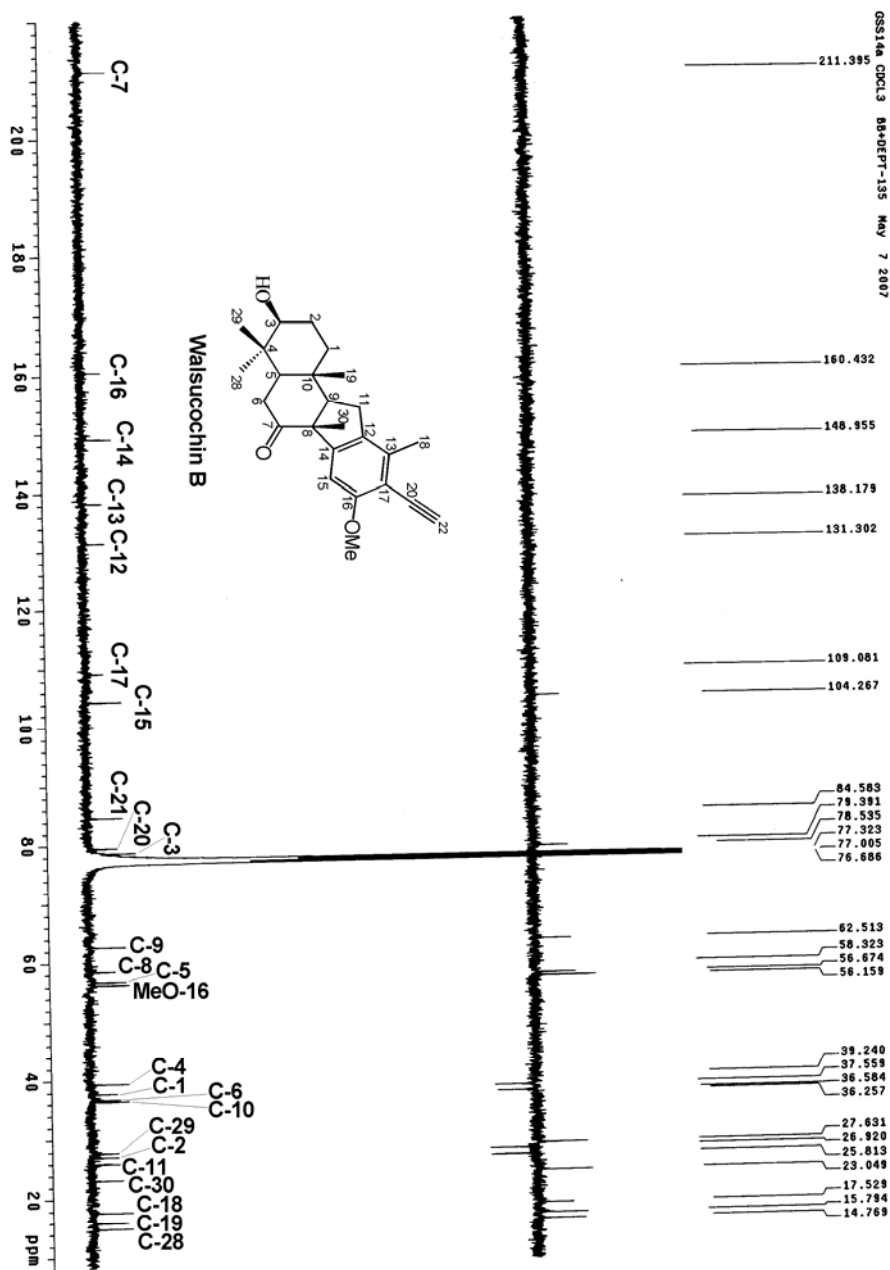
S11. IR (KBr disc) spectrum of Walsucochin A (1).



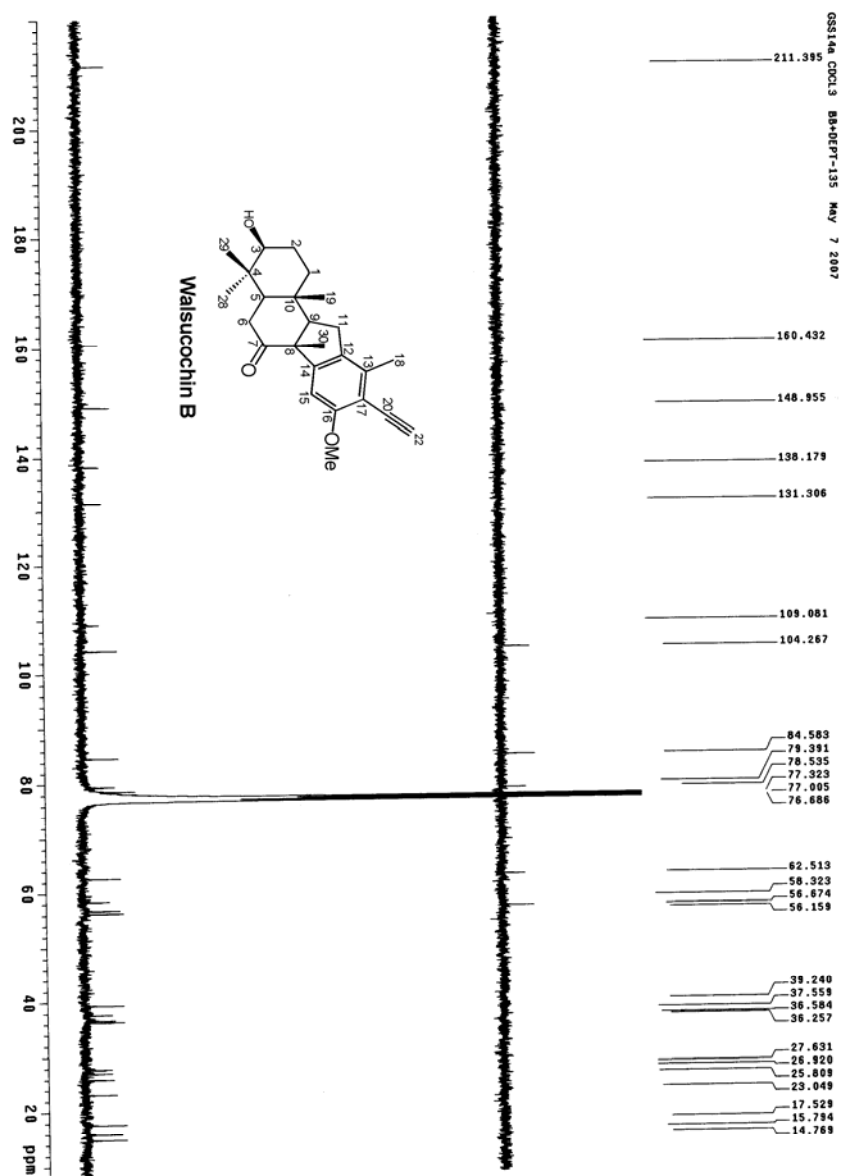
S12. ^1H NMR spectrum (400 MHz) of Walsucochin B (2) in CDCl_3 .



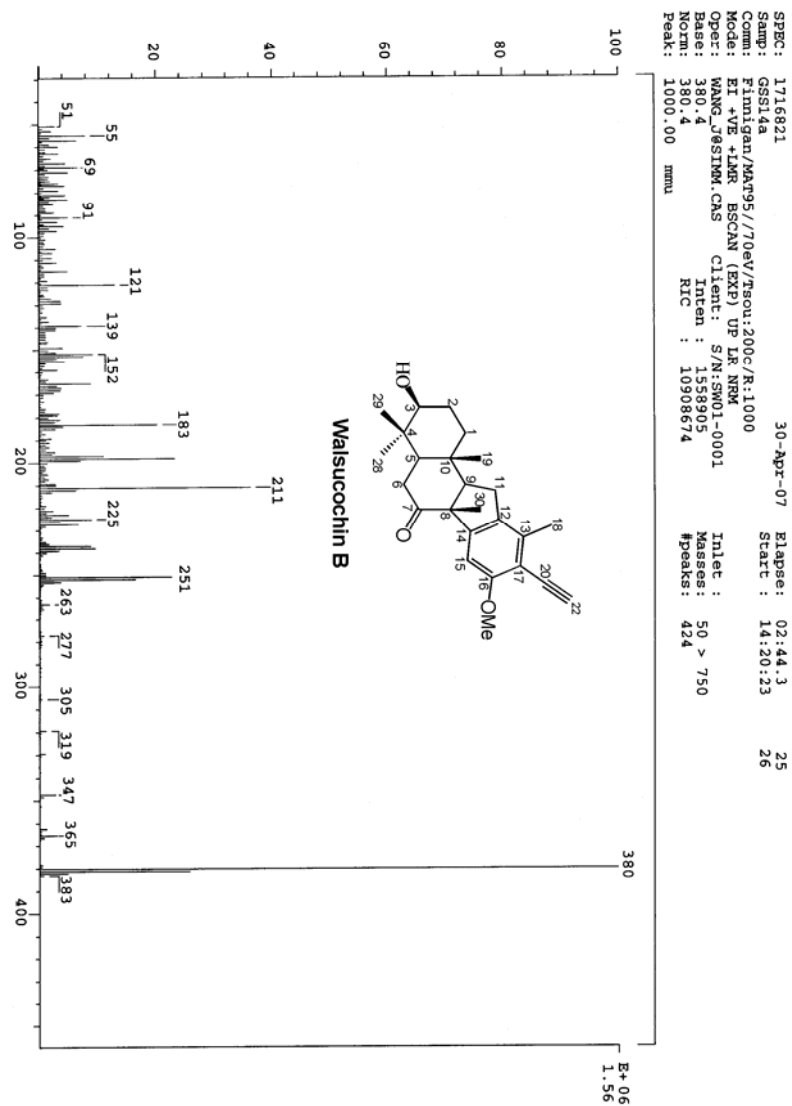
S13. ^{13}C NMR spectrum (100 MHz) of Walsucochin B (2) in CDCl_3 ($^1J_{\text{CH}} = 140 \text{ Hz}$).



S14. ^{13}C NMR spectrum (100 MHz) of Walsucochin B (2) in CDCl_3 . ($^1J_{\text{CH}} = 250 \text{ Hz}$).



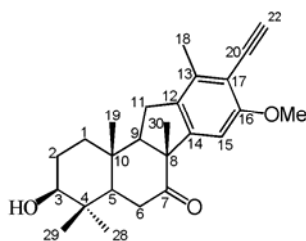
S15. EIMS spectrum of Walsucochin B (2).



S16. HREIMS spectrum of Walsucochin B (2).

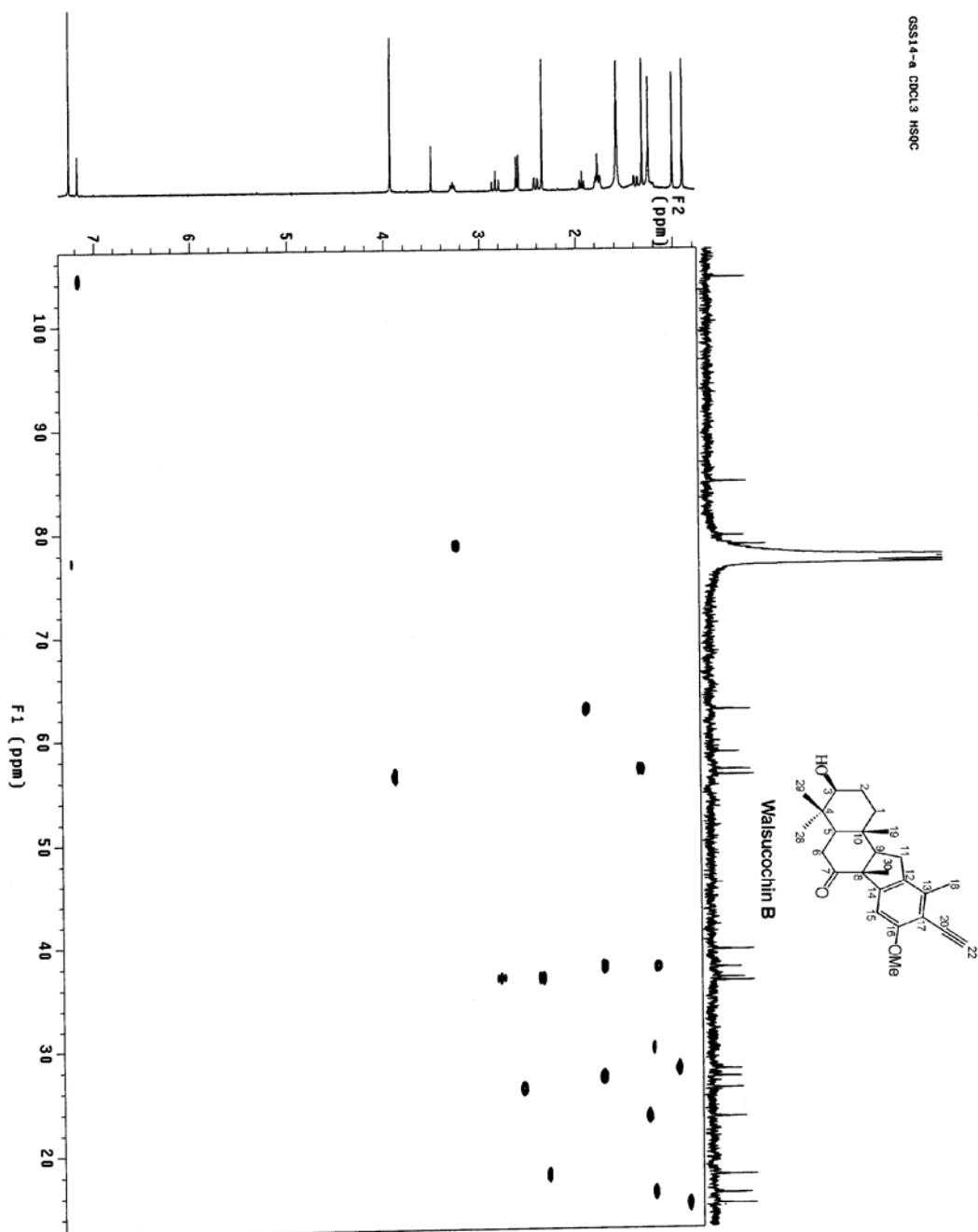
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 Mode: EI +VE +LMR BSCAN (EXP) UP HR NRM
 Oper: WANG_J@SIMM.CAS Client: S/N:SW01-0001 Inlet :
 Limt: (0)
 : (509) C30.H100.O3
 Peak: 1000.00 mmu R+D: -2.0 > 60.0
 Data: CMASS : converted

Mass	Intensity	%RA	%RIC	Delta	R+D	Composition
55.04182	*	53042	8.57	0.36		
57.05849	*	26698	4.31	0.18		
60.01032	*	38982	6.30	0.26		
67.05276	*	22793	3.68	0.15	2.0 2.5	C5.H7
69.07052	*	32947	5.32	0.22	-0.1 1.5	C5.H9
73.02896	*	23929	3.87	0.16	0.0 1.5	C3.H5.O2
81.07038	*	23432	3.79	0.16	0.0 2.5	C6.H9
83.08567	*	20805	3.36	0.14	0.4 1.5	C6.H11
88.05203	*	57515	9.30	0.39	0.4 1.0	C4.H8.O2
95.08569	*	18674	3.02	0.13	0.4 2.5	C7.H11
101.0594	*	36000	5.82	0.24	0.8 1.5	C5.H9.O2
121.1027	*	61066	9.87	0.41	-1.0 3.5	C9.H13
152.0628	*	32379	5.23	0.22	-0.2 9.0	C12.H8
153.0682	*	22438	3.63	0.15	2.3 8.5	C12.H9
165.0685	*	27834	4.50	0.19	1.9 9.5	C13.H9
183.0795	*	101540	16.41	0.69	1.5 8.5	C13.H11.O
184.0855	*	19242	3.11	0.13		
197.0980	*	49846	8.06	0.34	-1.3 8.5	C14.H13.O
198.1040	*	121706	19.67	0.83	0.5 8.0	C14.H14.O
199.1104	*	41042	6.63	0.28	1.9 7.5	C14.H15.O
211.0752	*	182630	29.52	1.24	0.7 9.5	C14.H11.O2
211.1098	*	19597	3.17	0.13	2.5 8.5	C15.H15.O
212.0776	*	25562	4.13	0.17		
223.1116	*	22651	3.66	0.15	0.7 9.5	C16.H15.O
225.1298	*	37420	6.05	0.25	-1.8 8.5	C16.H17.O
227.1067	*	28828	4.66	0.20	0.5 8.5	C15.H15.O2
237.1282	*	39692	6.41	0.27	-0.3 9.5	C17.H17.O
238.1357	*	54178	8.76	0.37	0.1 9.0	C17.H18.O
251.1448	*	125185	20.23	0.85	-1.2 9.5	C18.H19.O
252.1520	*	87480	14.14	0.59	-0.6 9.0	C18.H20.O
380.2349	*	618756	100.00	4.20	0.2 10.0	C25.H32.O3
381.2393	*	177943	28.76	1.21		
382.2403	*	29112	4.70	0.20		

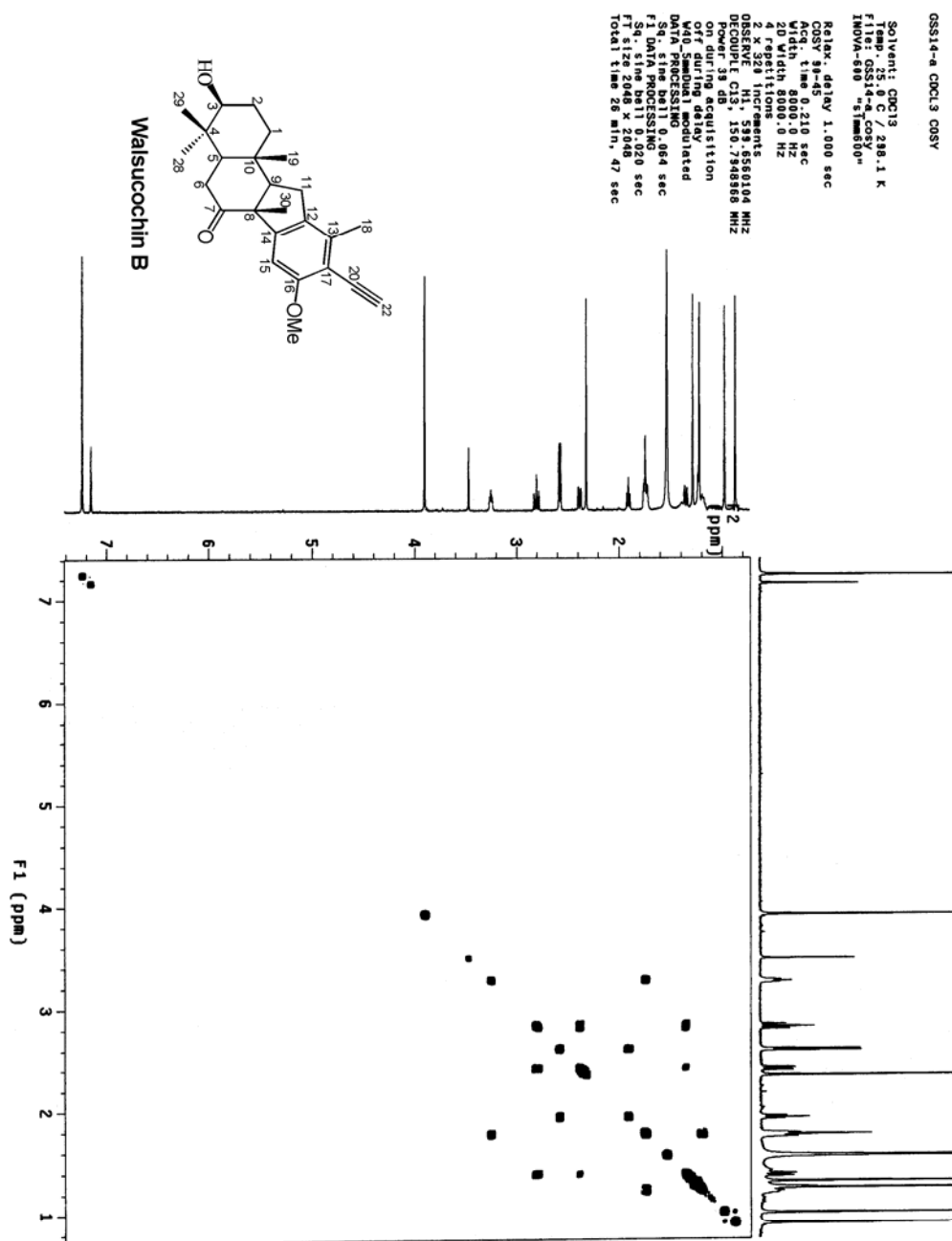


Walsucochin B

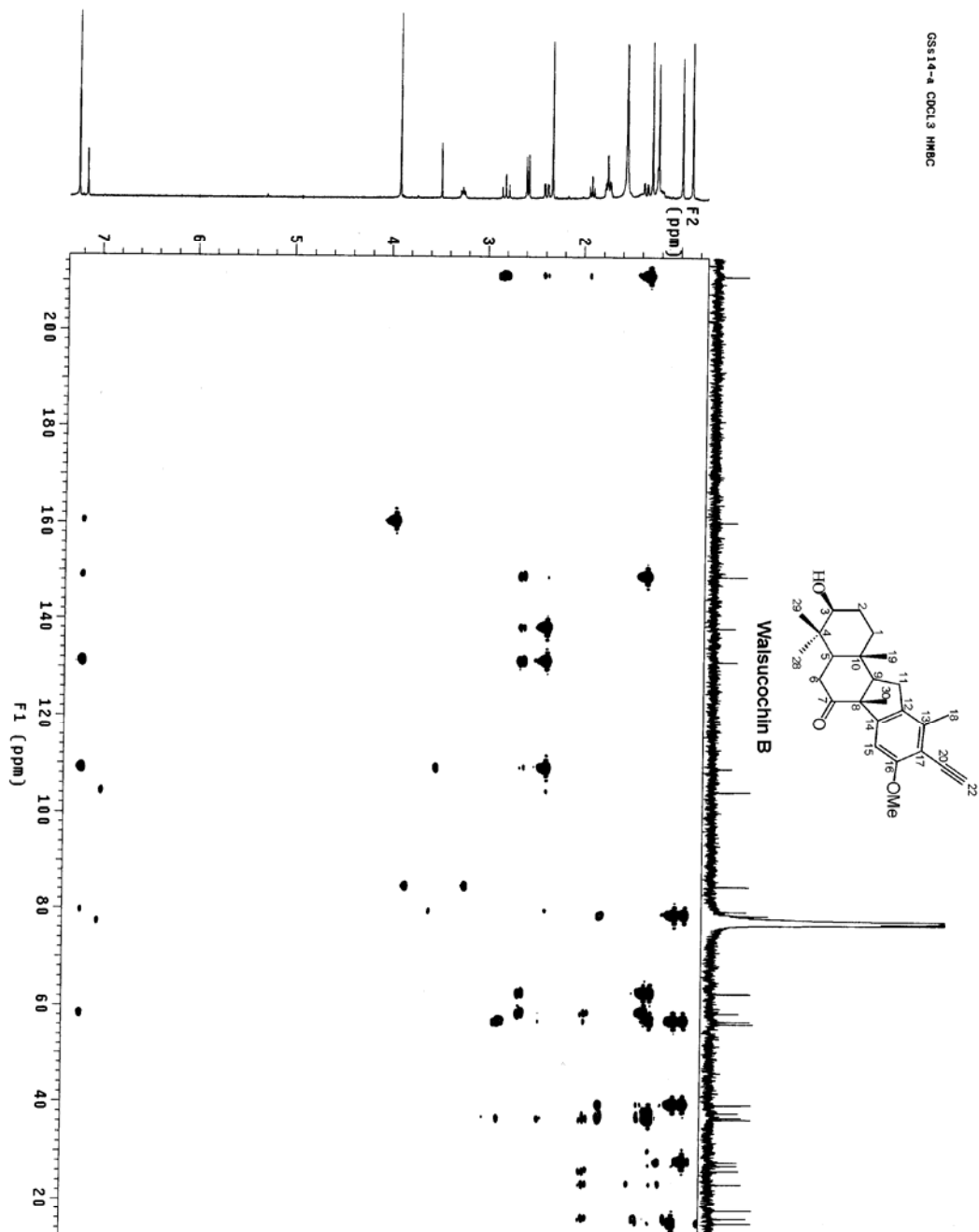
S17. HSQC spectrum (400 MHz) of Walsucochin B (2) in CDCl₃.



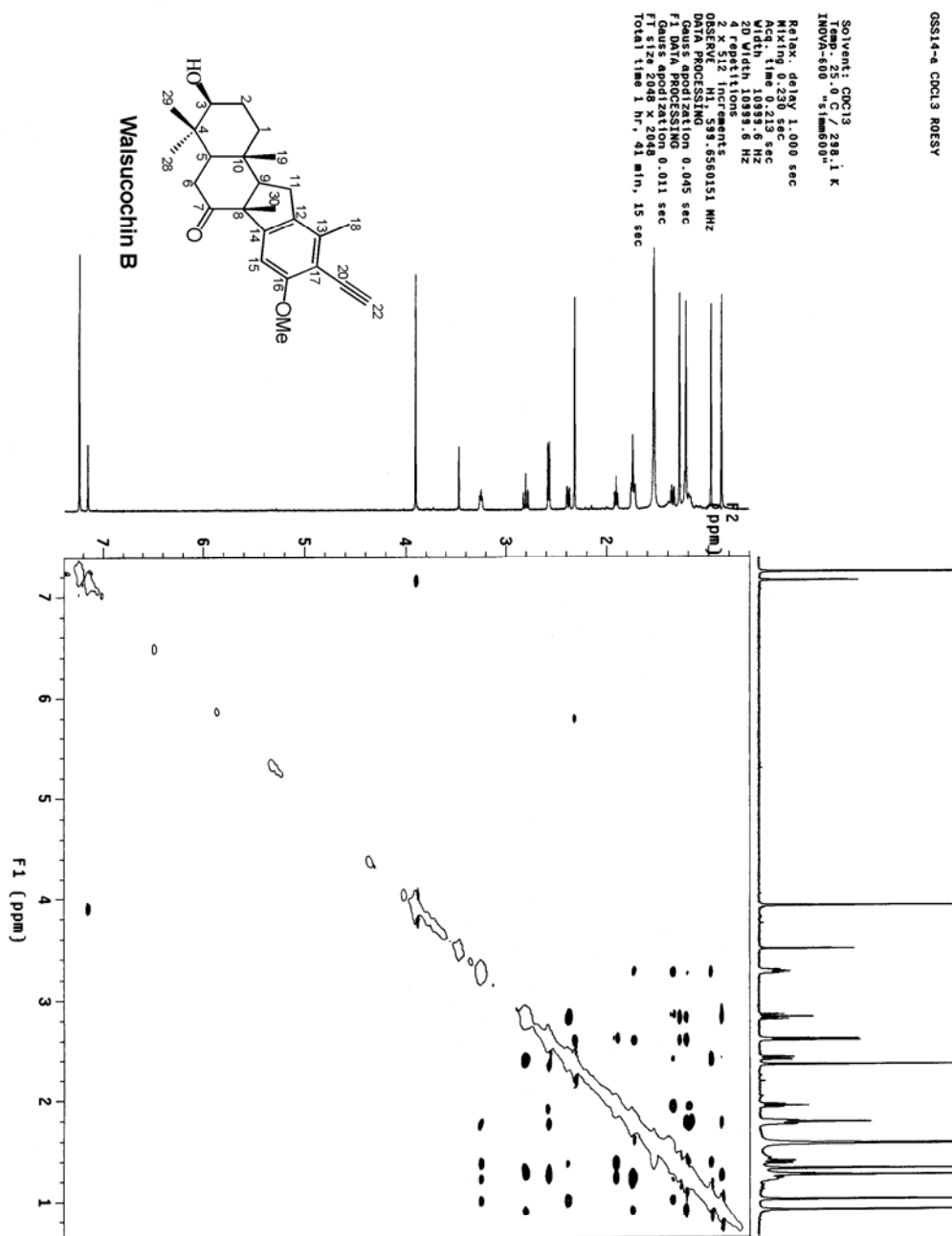
S18. ^1H - ^1H COSY spectrum (400 MHz) of Walsucochin B (2) in CDCl_3 .



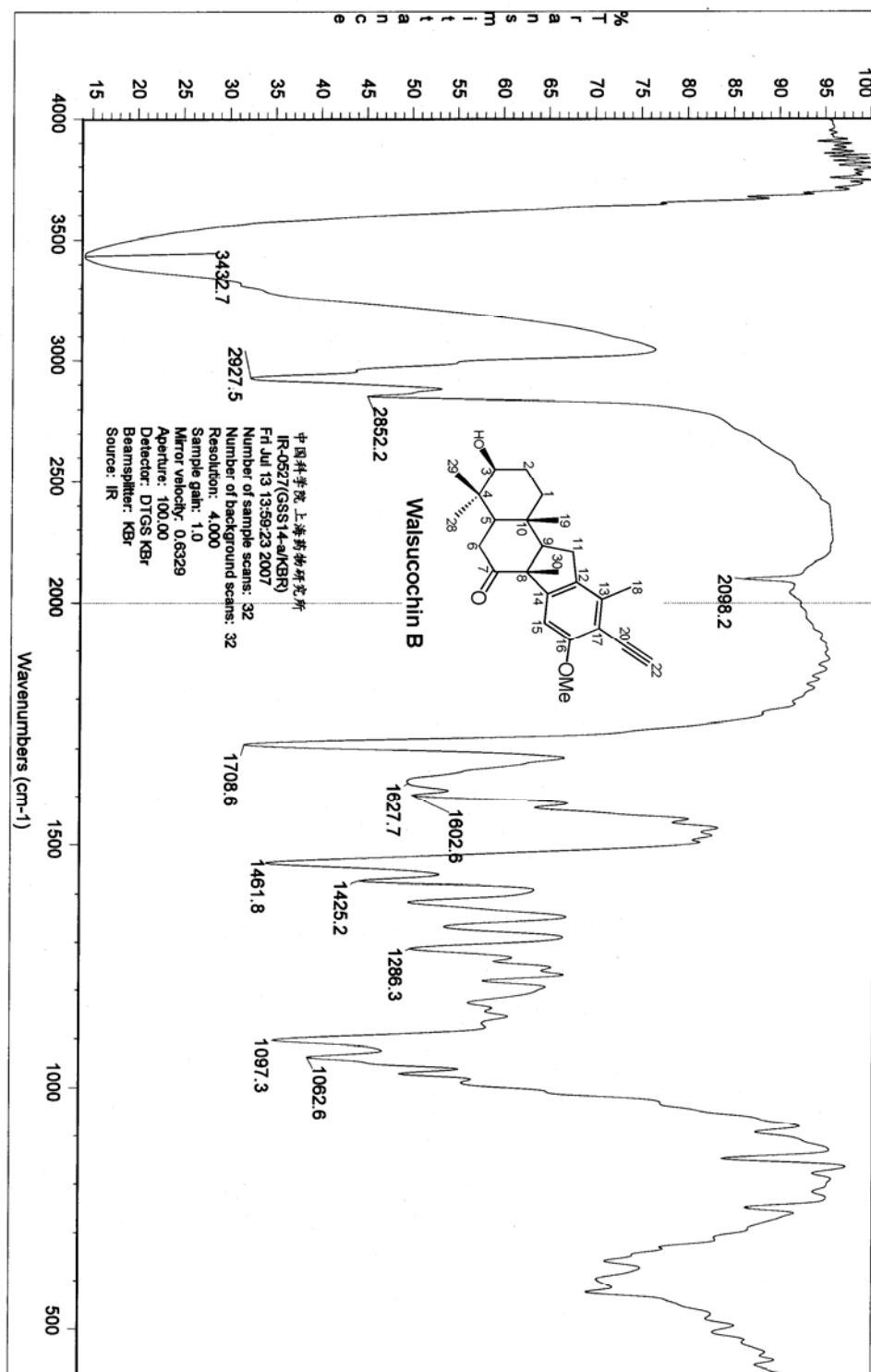
S19. HMBC spectrum (400 MHz) of Walsucochin B (2) in CDCl₃.



S20. ROESY spectrum (600 MHz) of Walsucochin B (2) in CDCl₃.



S21. IR (KBr disc) spectrum of Walsucochin B (2).



S22. Key ROESY correlations (in Figure) of Walsuchoin B (2).

