Supplementary Material (ESI) for Chemical Communications

Structure and Anti-HIV Activity of Micrandilactones B and C, New Nortriterpenoids Possessing a Unique Skeleton from *Schisandra micrantha*

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Supporting Information

Experimental Section

General Procedures. Melting points were recorded on XRC-1 micro melting point apparatus and are uncorrected. Optical rotations were measured in Horiba SEPA-300 polarimeter. UV spectra were measured using a Shimadzu UV-2401PC spectrophotometer. IR spectra were obtained on a Bio-Rad Win infrared spectrophotometer. 1D and 2D NMR experiments were performed on Bruker AM-400 and DRX-500 instruments. EI (70 eV) mass spectra were obtained on a VG Auto Spec-3000 spectrometer. Column chromatography was performed on silica gel (200-300 mesh, Qingdao Marine Chemical Inc., Qingdao, PR China) or on silica gel H (10-40 μm, Qingdao Marine Chemical Inc.). Fractions were monitored by TLC and spots were visualized by heating silica gel plates (200 ºC) sprayed with 10% H_2SO_4 in EtOH. HPLC separations were performed on a HP 1100 apparatus equipped with an RI detector and Zorbax SB-C-18 (Agilent, 9.4 mm×25 cm) column.

Plant Material. The leaves and stems of *S. micrantha* were collected in Dali, Yunnan, PR China, in November 2001. A voucher specimen (No. KIB 01-11-05) was deposited in the state key laboratory of Phytochemistry, Kunming Institute of Botany, and was identified by Prof. Su G. Wu.

Extraction and Isolation. The air-dried and powdered leaves and stems of *S. micrantha* (6.8 Kg) were extracted with 70% aqueous Me_2CO (24 L × 3) at room temperature and the extract was partitioned successively with petroleum ether (3 L) and EtOAc (5 L). The EtOAc extract (170 g) was subjected to column chromatography (CC) over silica gel eluting with a $CHCl_3$-Me_2CO (1:0–0:1, 180 L) gradient system to give fractions 1-5. Fr. 3 (15 g) was chromatographed on MCI-gel CHP 20P (50–90%

MeOH-H_2O, 5 L) to afforded three main fractions: 3a–c. Fr. 3a (9 g) was subjected to CC on silica gel, eluting with petroleum ether-EtOAc (3:1), $CHCl_3$-acetone (50:1), respectively, and was further purified by using RP-HPLC with 55% MeOH-H_2O (flow rate 3.0 mL/min) to afford **1** (11 mg). Fr. 3b (4 g) was repeatedly chromatographed over silica gel, using petroleum ether-acetone (9:1), and $CHCl_3$-MeOH (100:1), to give **2** (34 mg).

Physical Data

Micrandilactone B (1): Colorless prisms from MeOH; m.p. 179–180 ºC; $[\alpha]_D^{25.3}$ +7.81 (*c* 0.06, MeOH); UV (MeOH) λ_{max}: log ε 210.8 (4.07) nm; IR (KBr) ν_{max} 3440 (br), 2973, 2929, 1755, 1651, 1634, 1239, 1198, 1079 cm^{-1}; ^1H and ^{13}C NMR, data see Table 1; EIMS: *m/z* 516 (1) $[M]^+$, 498 (20), 480 (6), 420 (7), 403 (12), 354 (19), 303 (20), 272 (15), 257 (38), 176 (59), 137 (40), 97 (100); HRESIMS: calcd. for $C_{29}H_{40}O_8Na$ 539.2620; found 539.2634.

Micrandilatone C (2): Colorless flakes from MeOH; m.p. 172–173ºC; $[\alpha]_D^{22.9}$ +30.99 (*c* 0.24, MeOH); UV (MeOH) λ_{max}: log ε 203 (3.87), 276 (3.65) nm; IR (KBr): ν_{max} 3443 (br), 2927, 1772, 1717, 1700, 1634, 1623, 1456, 1376, 1065 cm^{-1}; ^1H and ^{13}C NMR, data see Table 1; EIMS: *m/z* 498 (1) $[M]^+$, 483 (8), 438 (8), 421 (6), 400 (8), 322 (10), 305 (40), 289 (20), 263 (10), 245 (70), 97 (65), 83 (40), 69 (100); ESIMS: *m/z* 557 (100) $[M+Na]^+$; HRESIMS calcd for $C_{29}H_{42}O_9$ 557.2726 $[M+Na]^+$, found 557.2739.

X-ray Crystallographic Analysis of micrandilactone B (1). $C_{29}H_{40}O_8$, M = 516.63, monoclinic, space group $P2_12_12_1$, a = 6.501(1), b = 12.672(1), c = 32.201(1) Å, V = 2652.7(2) $Å^3$, Z = 4, D_{calc} = 1.294 g cm^{-3}, crystal dimentions 0.10 × 0.20 × 0.40 mm. The total number of independent reflections measured was 3420, of which 2659 were observed ($|F|^2 \geq 8\sigma |F|^2$). The final indices were R_f = 0.069, R_w = 0.071 ($w = 1/\sigma|F|^2$).

X-ray data of micrandilactone C (2). Dimension: 0.10 × 0.30 × 0.50 mm. $(C_{29}H_{42}O_9)_2$, M = 534.65, triclinic, space group, *P1*, a = 7.878(1), b = 10.483(1), c = 18.484(1) Å, α = 84.67(1), β = 80.14(1), Y = 89.66(1)°, V = 1497.4(3) $Å^3$, Z = 1, d = 1.331 g cm^{-3}. The total number of independent reflections measured was 4589, of

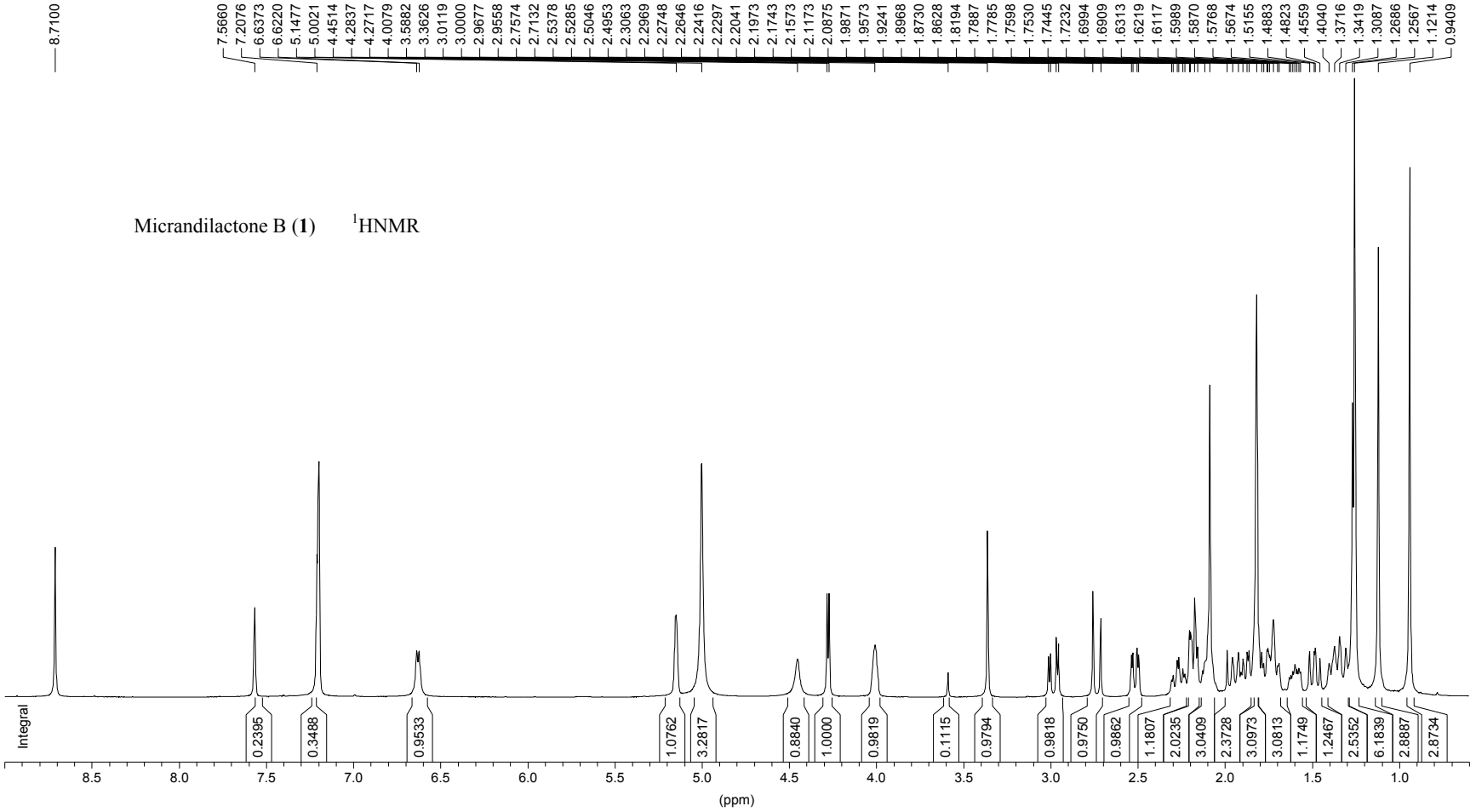
which 3735 were observed ($|F|^2 \geq 3\sigma|F|^2$). $R_f = 0.053$, $R_w = 0.051$ ($w = 1/\sigma|F|^2$).

All measurements of both crystal structures were made on a MAC DIP-2030K diffractometer with graphite-monochromated Mo Kα radiation. The data were collected by using the ω-2θ scan technique to a maximum 2θ value of 50.0º. The crystal structures were solved by direct the method SHELX-86 (Sheldrick, G. M. University of Gottingen, Federal Republic of Germany, **1985**), expanded using difference Fourier techniques, refined by the program and method NOMCSDP (Lu, Y., Wu, B. M. *Chin. Chem. Lett.* **1992**, *3*, 637–640), and full-matrix least-squares calculations. The non-hydrogen atoms were fined anisotropically and hydrogen atoms were included at their calculated positions. Crystallagraphic data for **1** and **2** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CCDC 236725, 257495). Copies of this data can be obtained, free of charge, on application to the CCDC via www.ccdc.com.ac.uk/conts/retrieving.html (or 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Anti-HIV-1 activity, cytotoxicity, selective index by **1** and **2**[a].

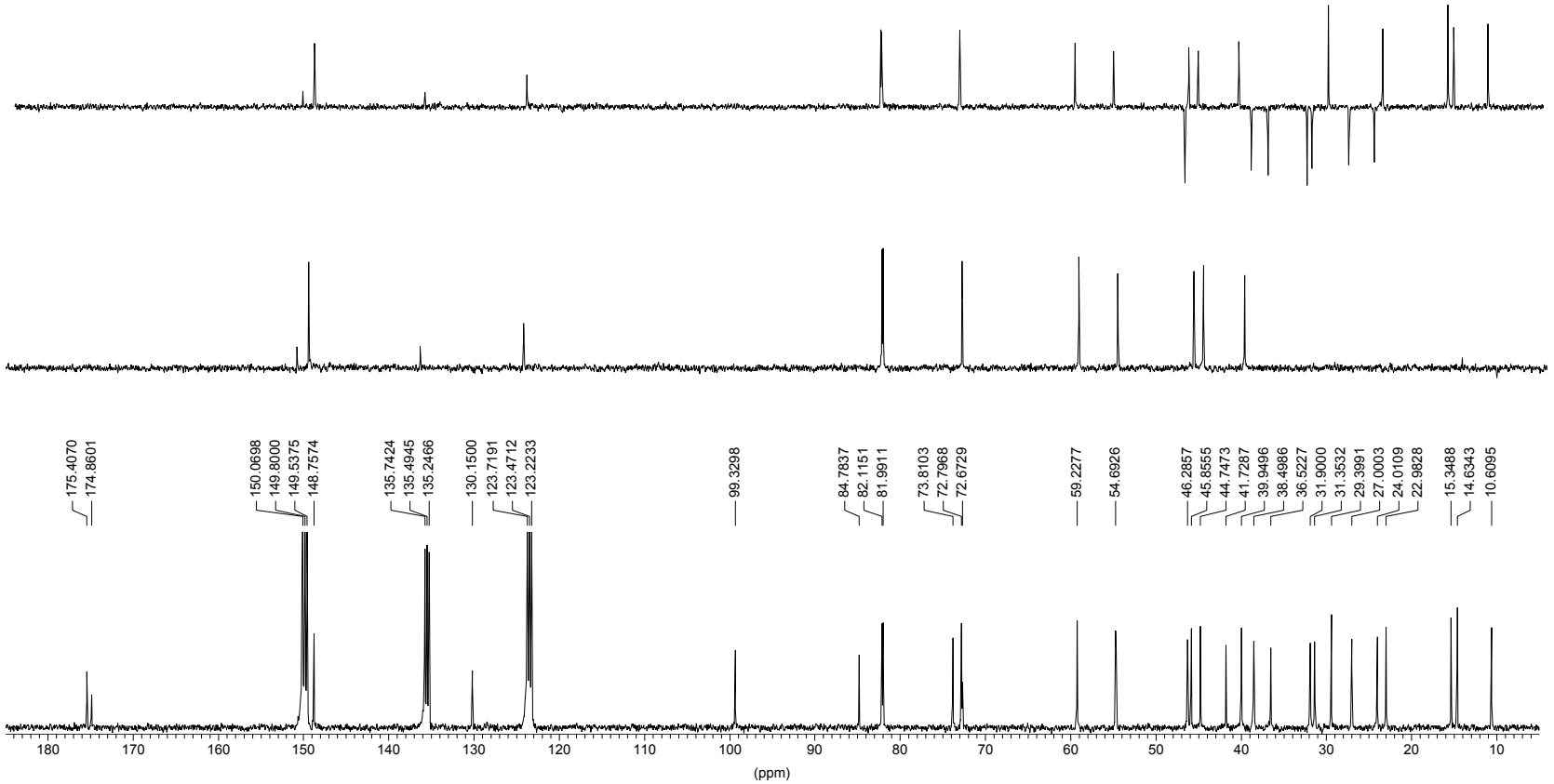
Compd	Cytotoxity	Syncytium		MTT protection[e]		
	CC_{50} (μg/mL)[b]	EC_{50} (μg/mL)[c]	SI[d]	CC_{50} (μg/mL)	EC_{50} (μg/mL)	SI
1	□200	42.66	□4.69			
2	□200	7.71	□25.94	□200	0.47	□425.5

[a] Data are expressed as means of three dependent measurements.
[b] Concentration required to reduce C8166 cells viability by 50%.
[c] Concentration required to reduce HIV-1_{IIIB} induced syncytium formation by 50% on C8166 cells.
[d] Selectivity index: ratio CC_{50}/ EC_{50}.
[e] Protective activities on HIV-1_{IIIB} infected MT-4 host cells from dying.

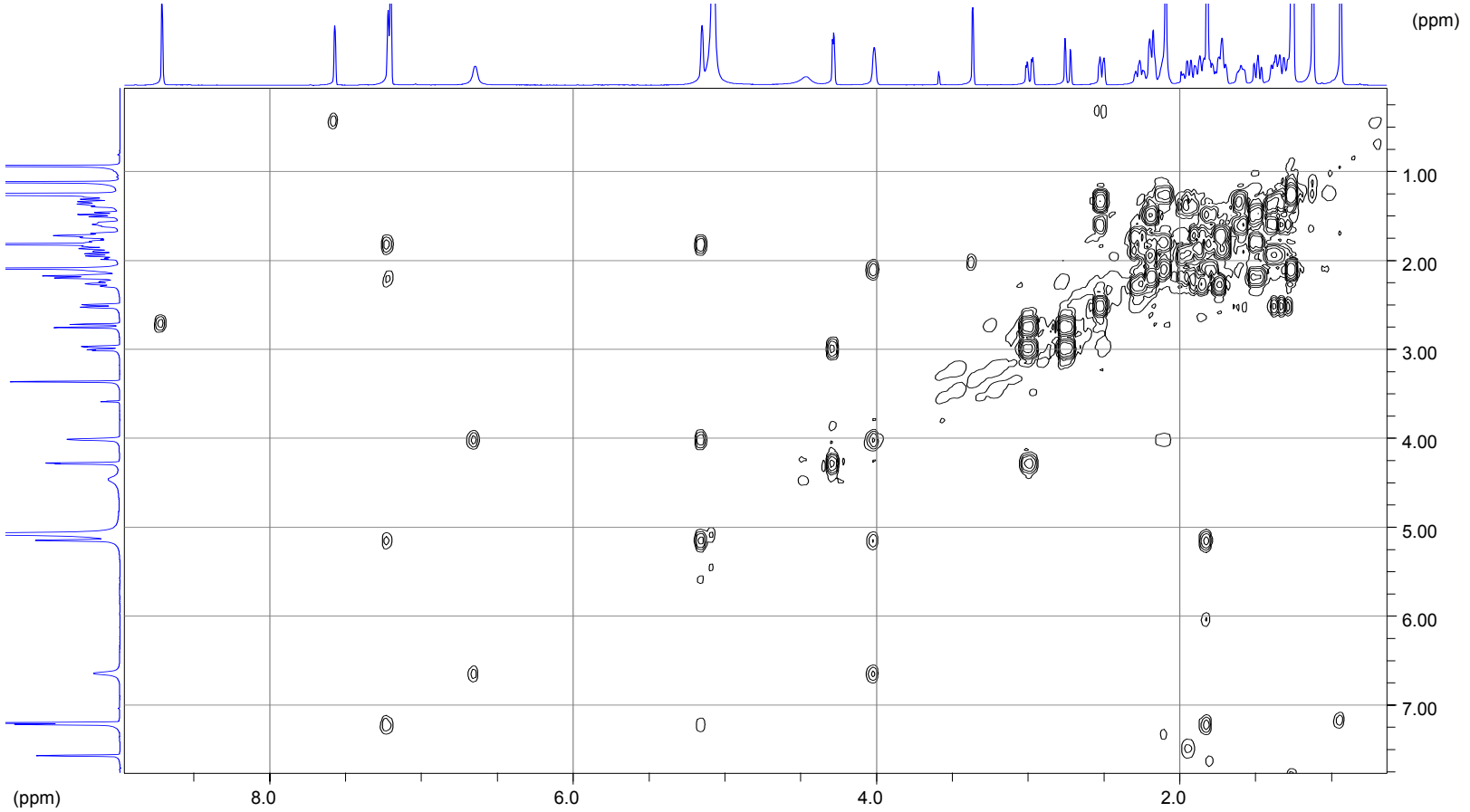


Micrandilactone B (**1**) ^{1}HNMR

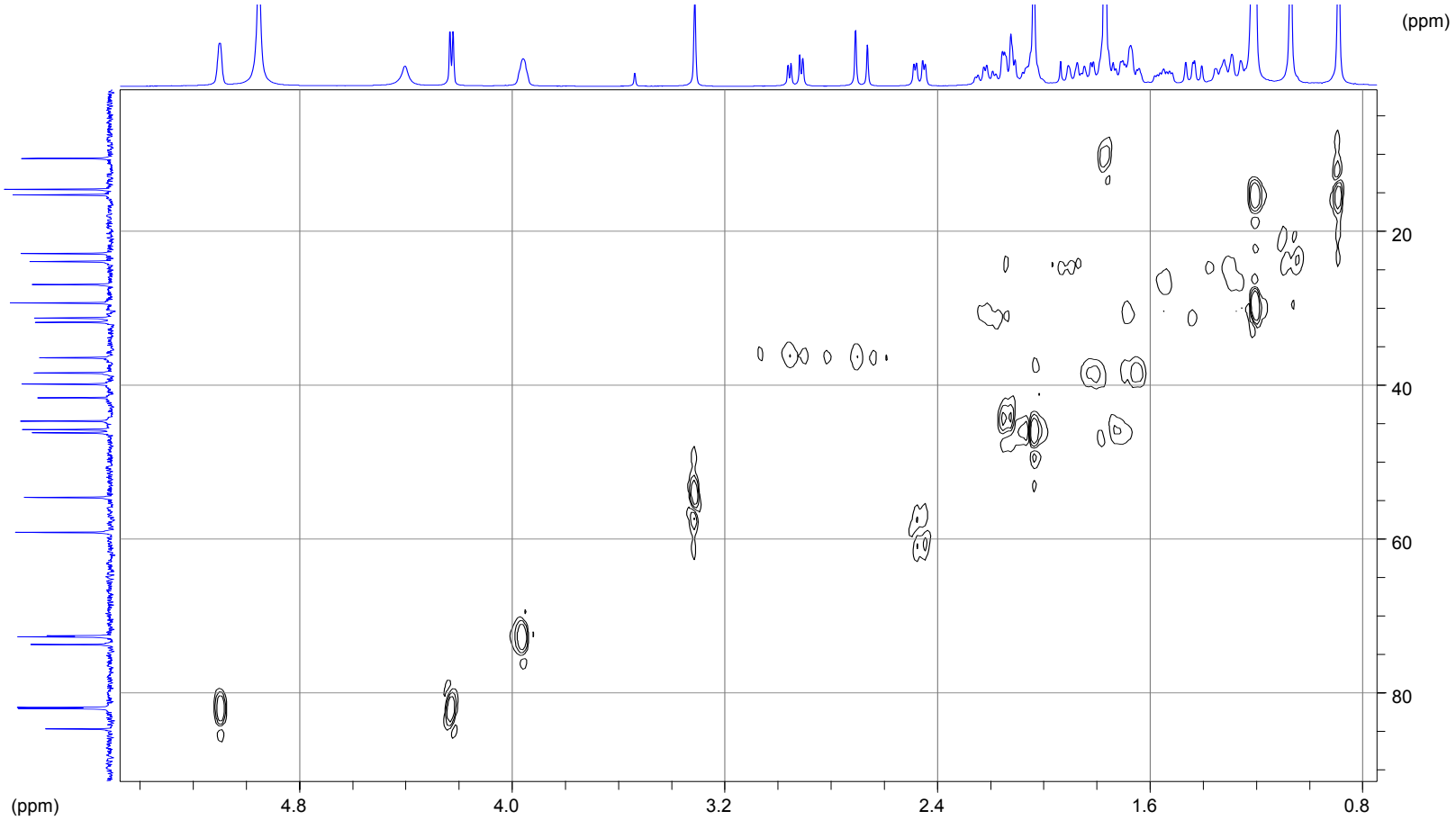
Micrandilactone B (**1**) ^{13}CNMR

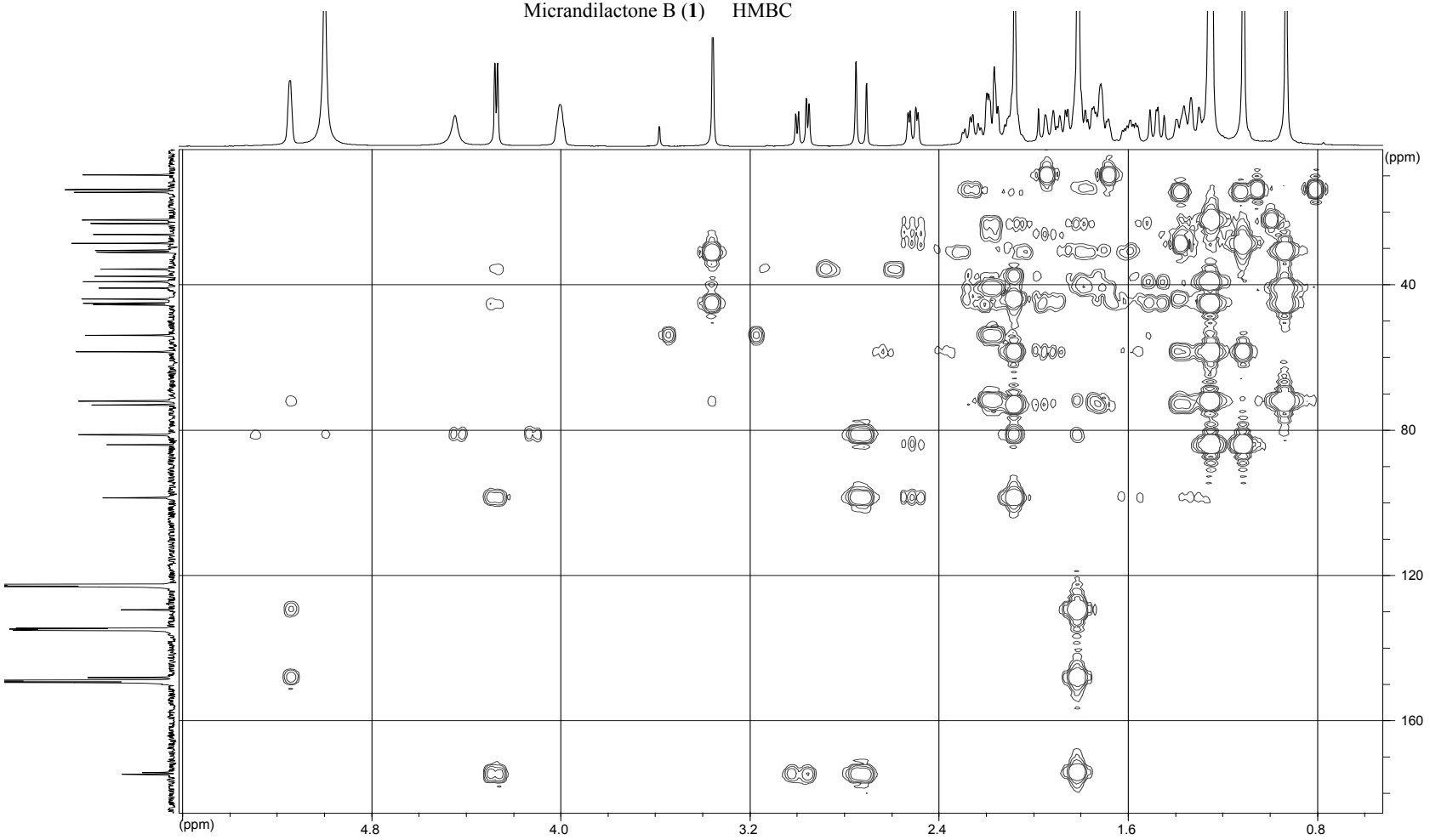


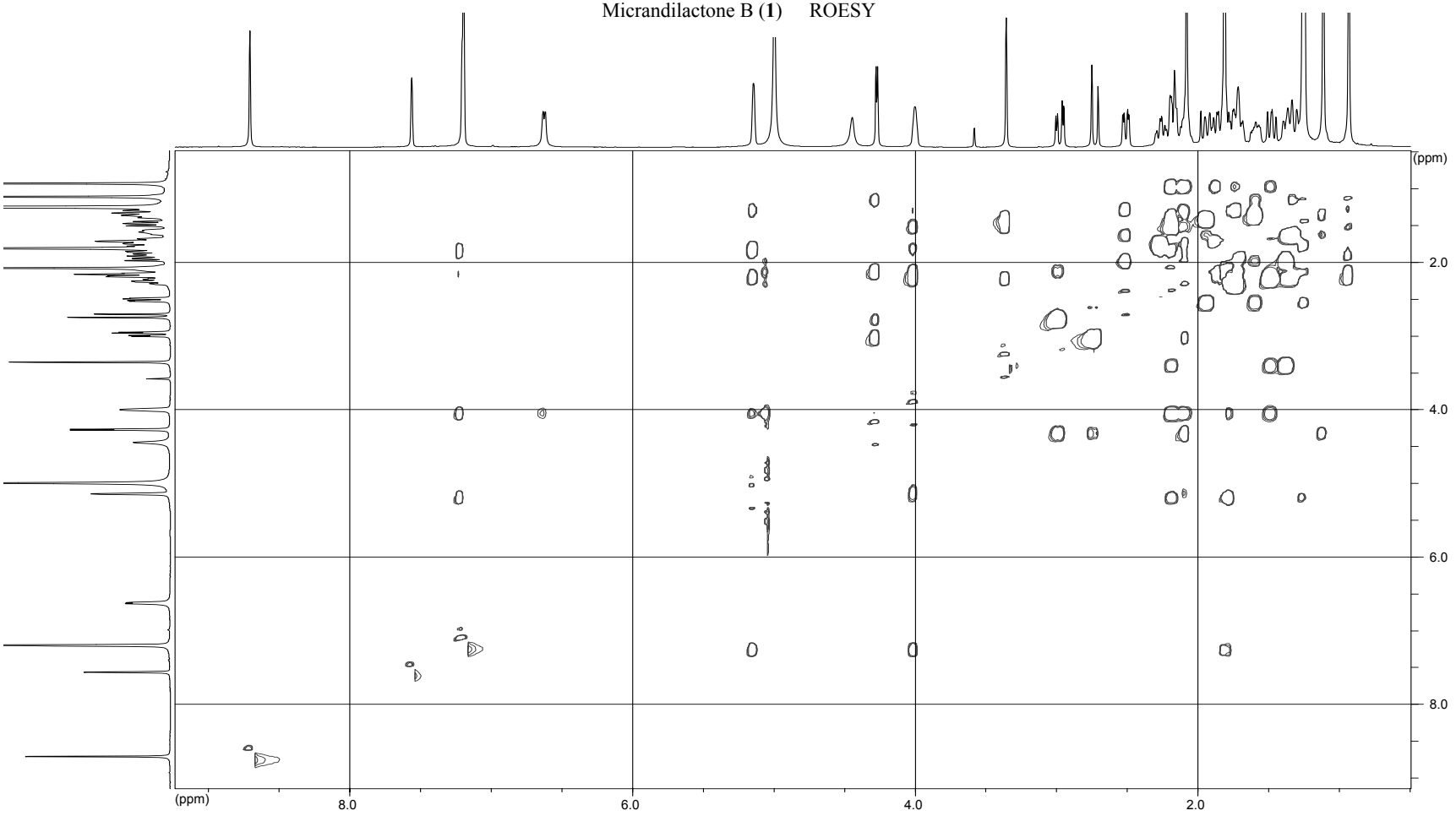
Micrandilactone B (**1**) ^{1}H-^{1}H COSY

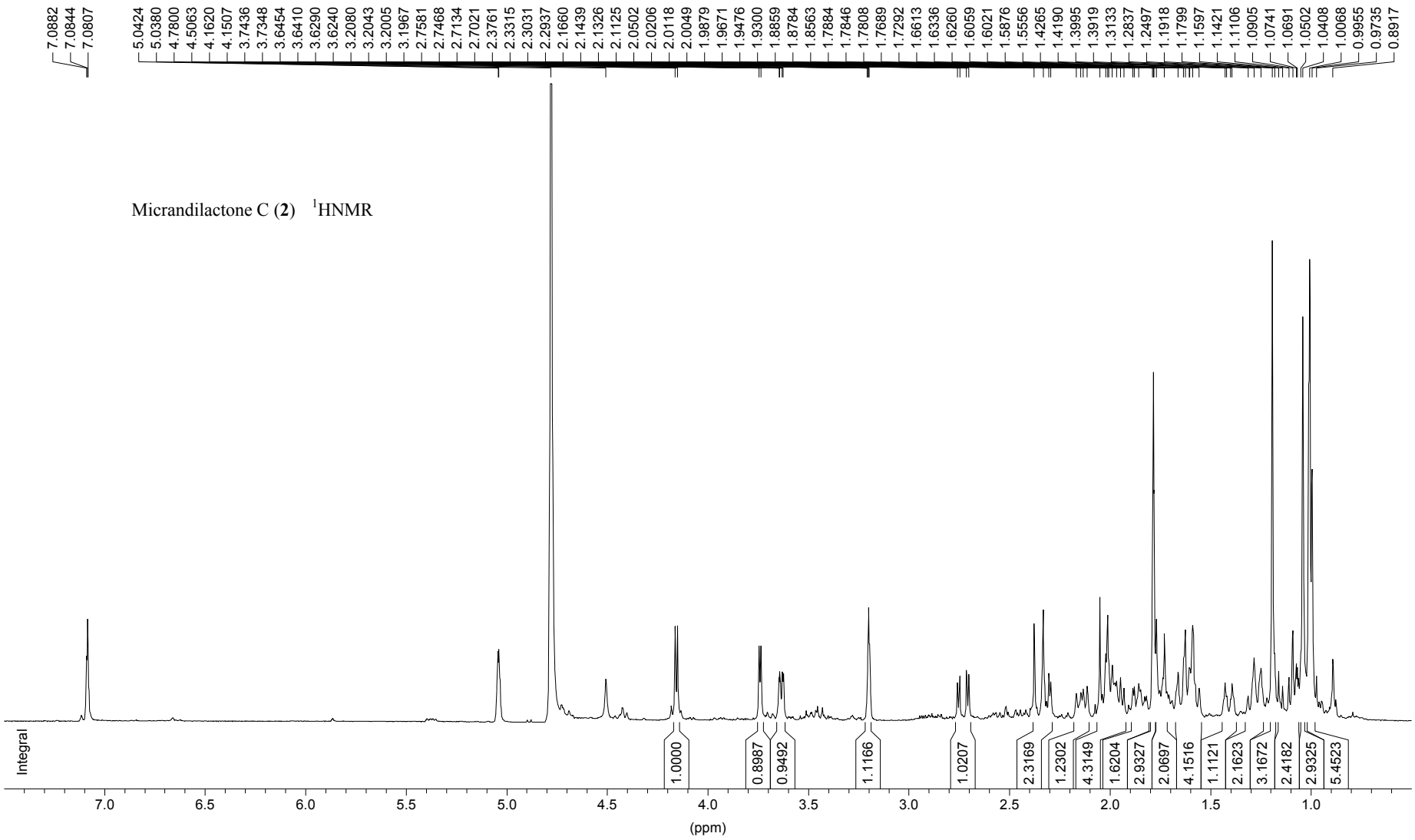


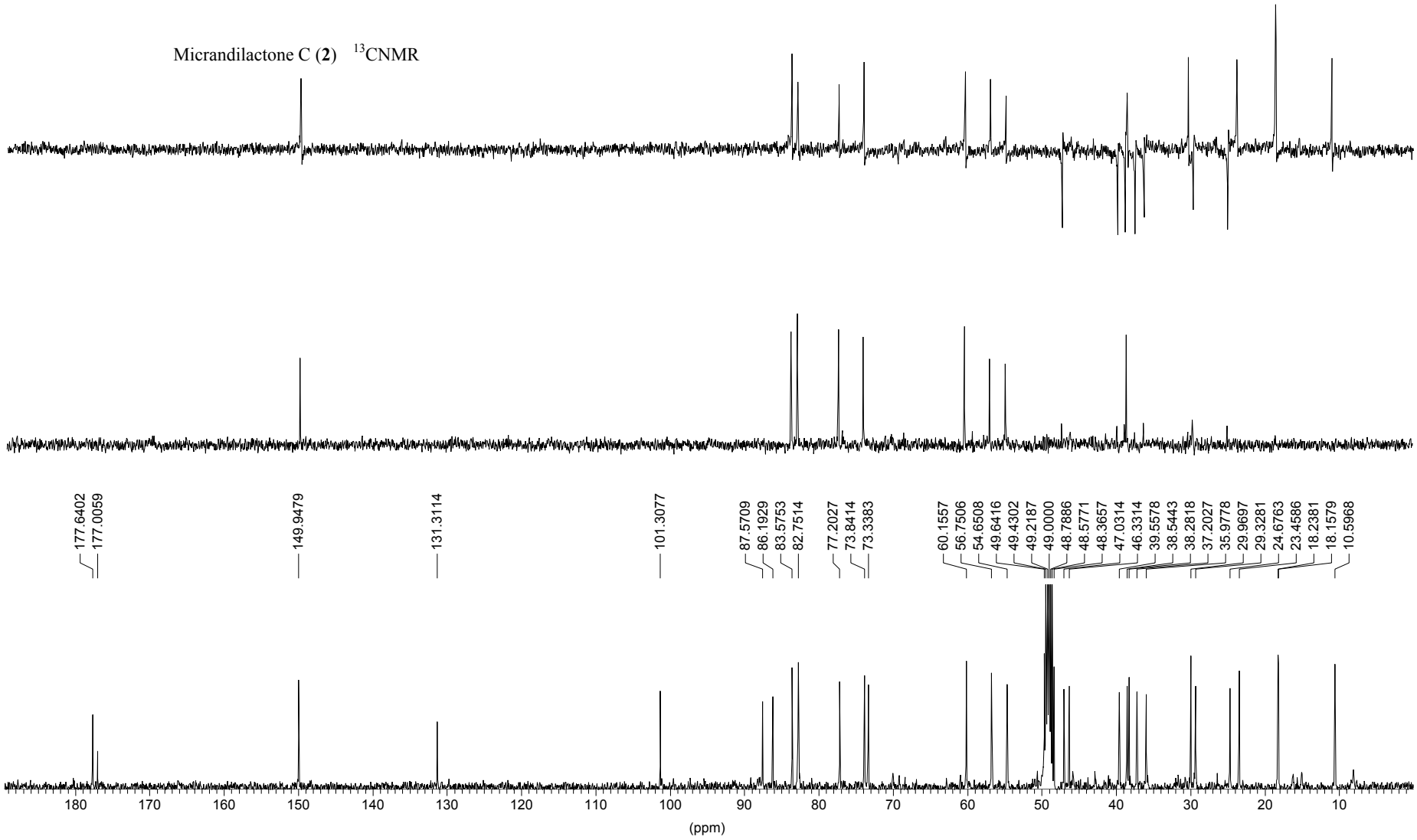
Micrandilactone B (**1**) HMQC

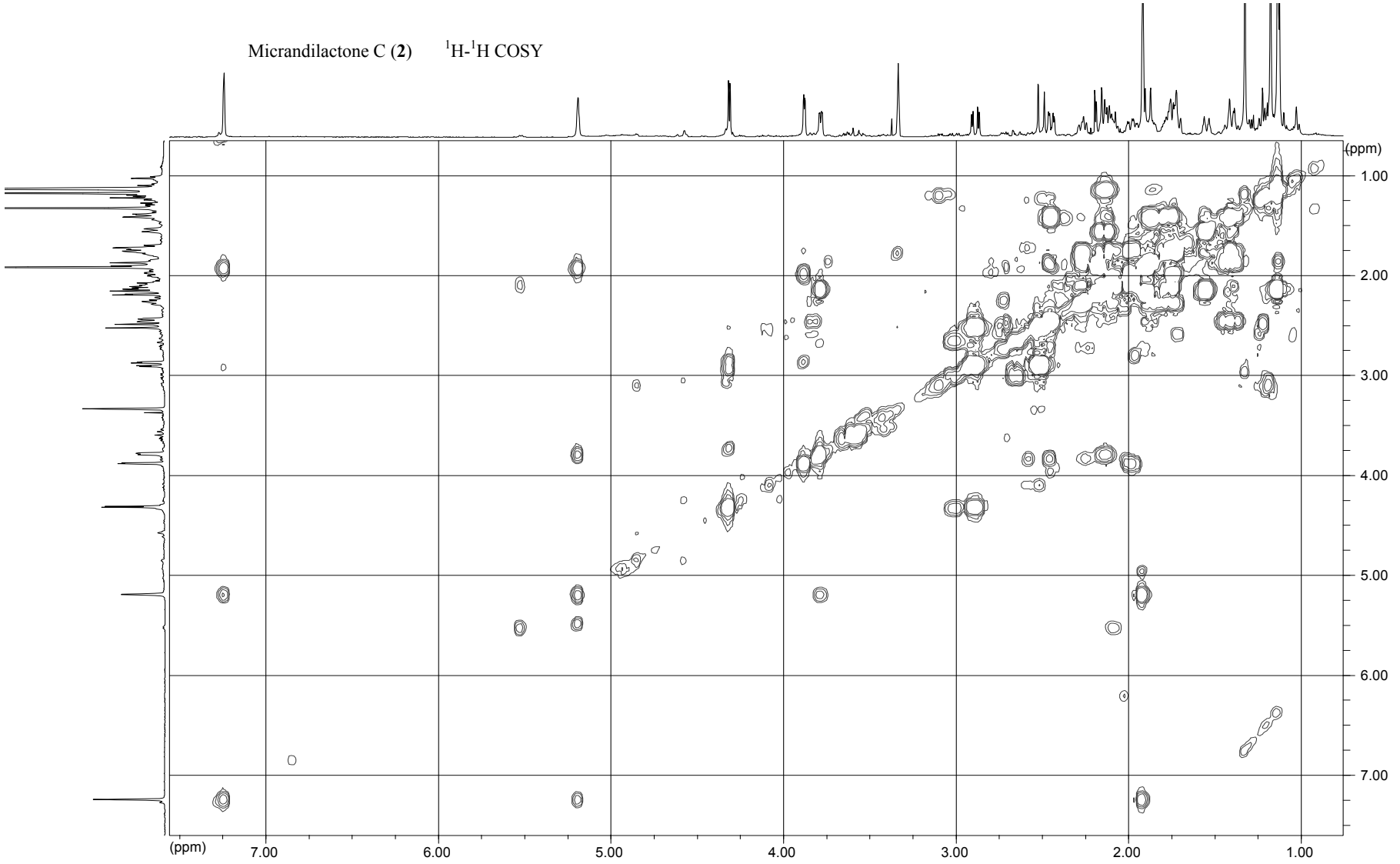


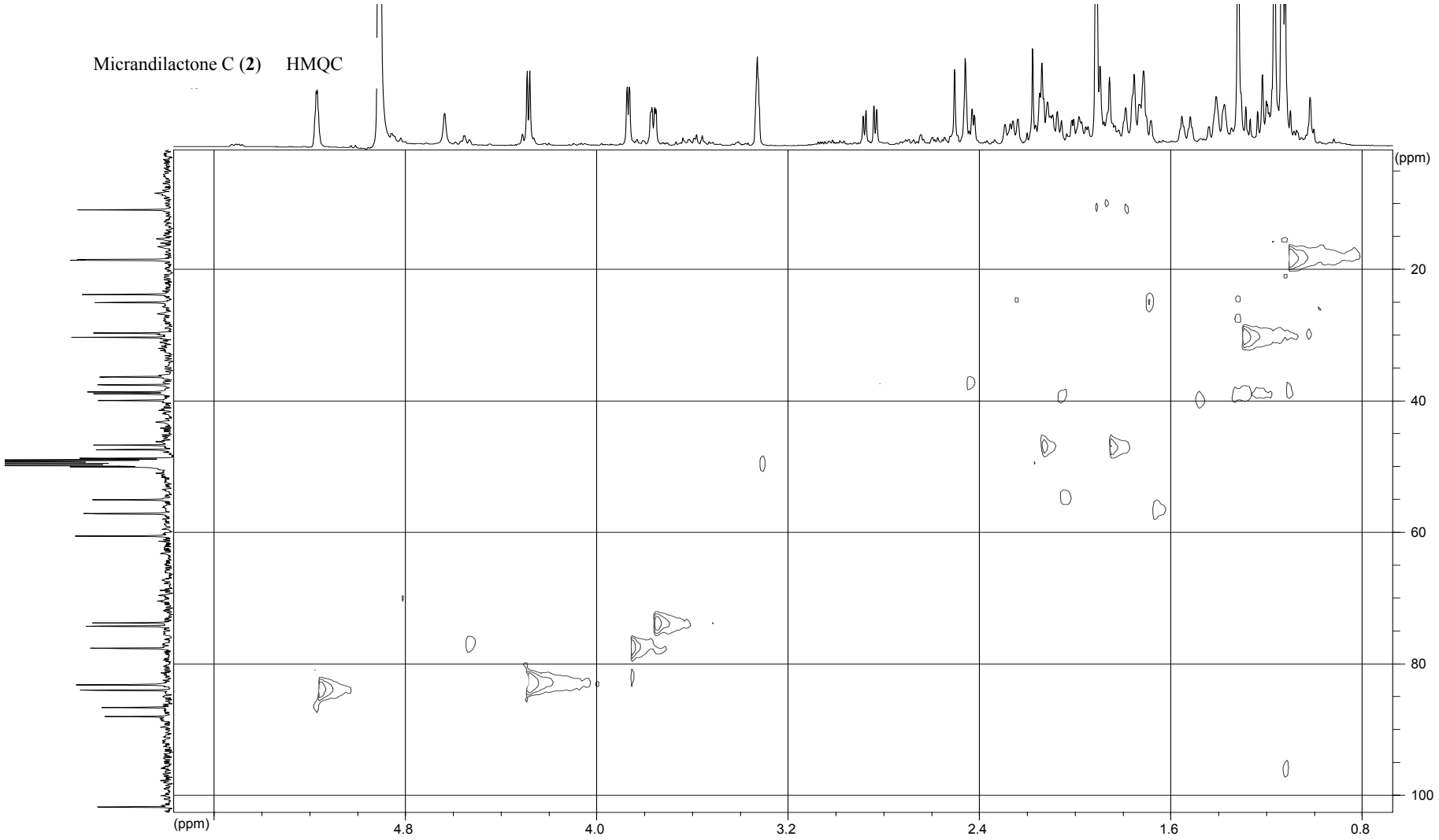


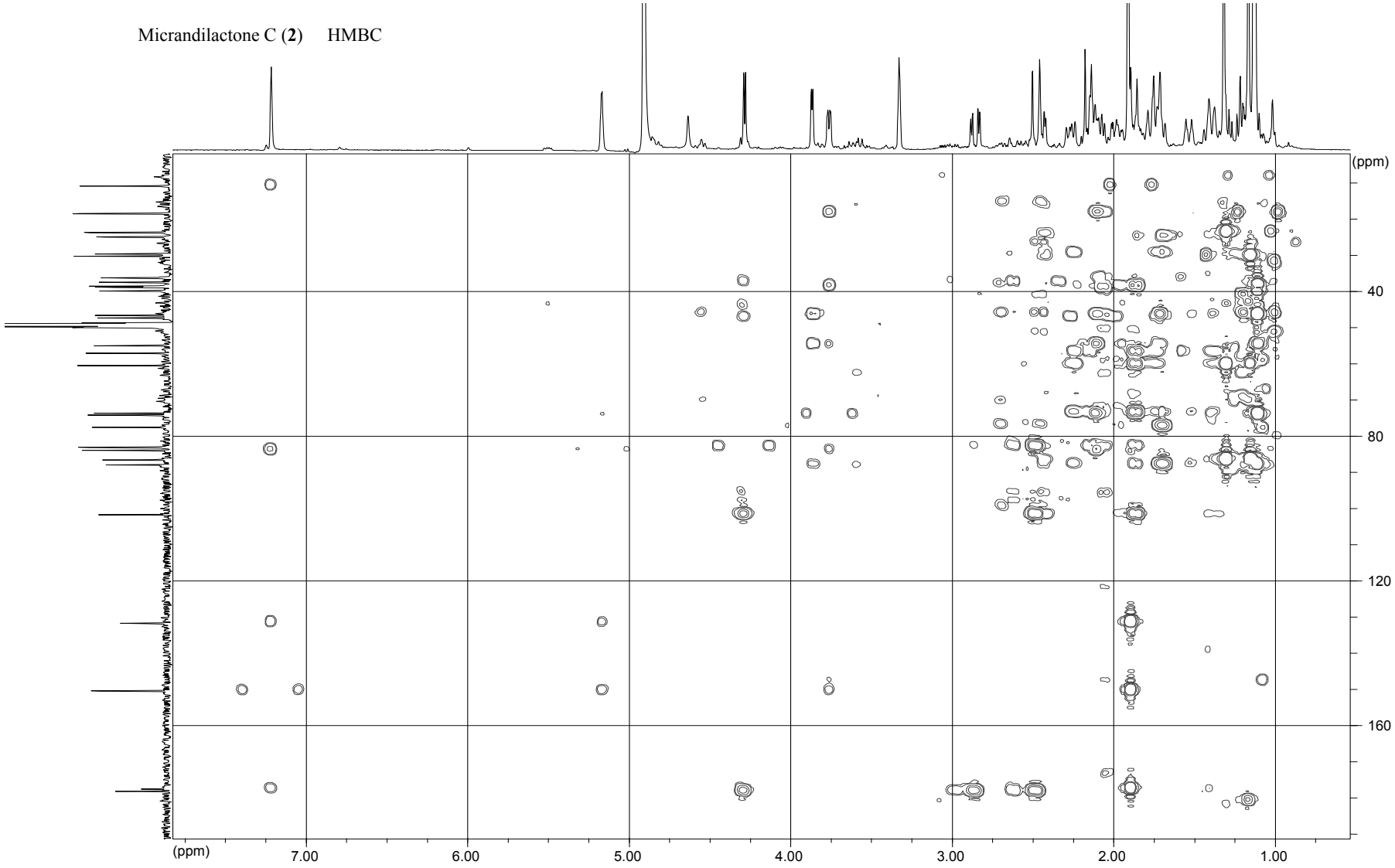












Micrandilactone C (**2**) REOSY