Synthesis and Biological Evaluation of (±)-Dinemasone C and Analogues

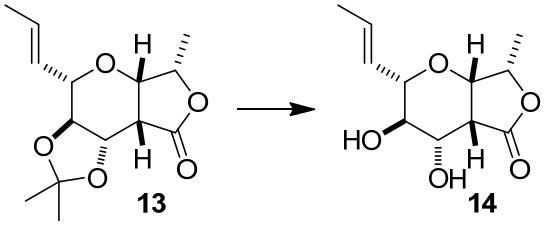
Amie M. Stewart,[†] Kathrin Meier,[‡] Barbara Schulz,[‡] Michael Steinert,[‡] and Barry B. Snider*[†]

[†]Department of Chemistry MS 015, Brandeis University, Waltham, Massachusetts 02454-9110

[‡] Institute of Microbiology, University of Braunschweig,

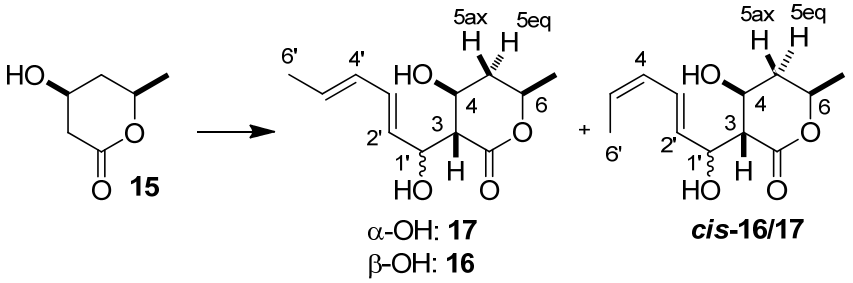
Spielmannstr. 7, 38106 Braunschweig, Germany

General Procedure. Reactions were conducted in flame- or oven-dried glassware under a nitrogen atmosphere and were stirred magnetically. The phrase "concentrated" refers to removal of solvents by means of a rotary evaporator attached to a diaphragm pump (15-60 Torr) followed by removal of residual solvents at < 1 Torr with a vacuum pump. Flash chromatography was performed on silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed using silica gel 60 F-254 pre-coated glass plates (0.25 mm). TLC Plates were analyzed by short wave UV illumination, or by dipping in vanillin stain (27 g of vanillin in 380 mL of EtOH, 50 mL of water and 20 mL of concentrated sulfuric acid) and heating on a hot plate or by spray with permanganate spray (5 g of $KMnO_4$ in 495 mL of water). THF was dried and purified by distillation from sodium/benzophenone. DIPEA and benzene were distilled from CaH_2. ^1H and ^{13}C NMR spectra were obtained on a 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane as internal standard unless otherwise indicated. Chemical shifts are reported in δ (ppm downfield from tetramethylsilane). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and br (broad). COSY spectra were recorded for all compounds and used to assign ^1H NMR spectra. IR spectra were acquired on an FT-IR spectrometer and are reported in wave numbers (cm^{-1}). High resolution mass spectra were obtained using the following ionization techniques: chemical ionization (CI), electron impact (EI), electrospray ionization analyzed by quadrupole time of flight (QTOF).



(2*S*,3*R*,4*S*,4a*R*,7*S*,7a*S*)-*rel*-Hexahydro-3,4-dihydroxy-7-methyl-2-(1*E*)-1-propen-1-yl-5*H*-furo[3,4-*b*]pyran-5-one (*nor*-Dinemasone B, 14). A solution of acetonide (**13**)[5b] (14 mg, 0.052 mmol) in 4:1 AcOH/H_2O (2.5 mL) was stirred at 25 °C for 3 h and concentrated with heating. Flash chromatography of the residue on silica gel (3% MeOH in CH_2Cl_2) yielded 10 mg

(84%) of *nor*-dinemasone B (**14**) as a white solid: mp 161-163 ˚C; ^{1}H NMR 5.85 (dq, 1, *J* = 15.6, 6.8), 5.53 (ddd, *J* = 15.6, 6.8, 1.8), 4.57 (dq, 1, *J* = 2.8, 6.8), 4.25 (d, 1 *J* = 10.4, OH), 4.20 (dd, 1, *J* = 3.4, 2.8), 3.88 (ddd, 1, *J* = 10.4, 9.2, 6.8), 3.55 (dd, 1, *J* = 9.2, 6.8), 3.29 (dd, 1, *J* = 9.2, 9.2), 3.15 (dd, 1, *J* = 6.8, 3.4), 2.54 (br s, 1, OH), 1.77 (dd, 3, *J* = 6.8, 1.8), 1.47 (d, 3, *J* = 6.8); ^{13}C NMR 176.8, 130.9, 127.0, 79.7, 78.7, 75.4, 73.7, 71.6, 46.3, 18.0, 13.4; IR (neat) 3297, 2909, 1753, 1638, 1092, 1053, 952; HRMS (QTOF ESI^{+}) calcd for $C_{11}H_{16}O_5Na$ (MNa^{+}) 251.0895, found 251.0899.

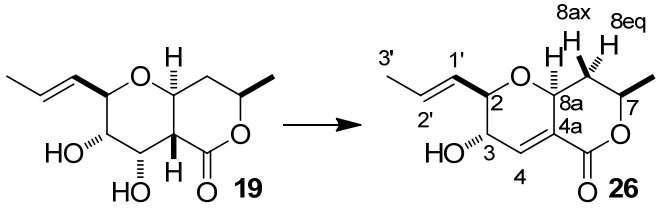


(3*S*,4*S*,6*R*)-*rel*-Tetrahydro-4-hydroxy-6-methyl-3-[(1*R*,2*E*,4*E*)-1-hydroxy-2,4-hexadien-1-yl]-2*H*-pyran-2-one (17) and (3*S*,4*S*,6*R*)-*rel*-Tetrahydro-4-hydroxy-6-methyl-3-[(1*S*,2*E*,4*E*)-1-hydroxy-2,4-hexadien-1-yl]-2*H*-pyran-2-one (16). Lithium diisopropylamide was prepared from diisopropylamine (2.4 mL, 17.3 mmol) and *n*-BuLi (13.3 mL, 1.3 M in hexanes, 17.3 mmol) in THF (30 mL) at 0 ºC. The solution was cooled to -78 ºC. A solution of **15** (898 mg, 6.90 mmol) in THF (10 mL) was added over 5 min. The mixture was stirred for 45 min and treated with a 4:1 mixture of (2*E*,4*E*)- and (2*E*,4*Z*)-2,4-hexadienal (0.92 mL, 8.34 mmol). The mixture was stirred for 3 h at -78 ºC and treated with 10% aqueous HCl solution (40 mL). After separation of the layers, the aqueous layer was extracted with ether (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Flash chromatography of the residue on silica gel (2:1 hexanes/EtOAc) yielded 694 mg (44%) of a 2:1 mixture of **17** and **16**, plus trace amounts of the 2*E*,4*Z* isomers (***cis*-16/17**). Flash chromatography of a different batch on silica gel (4:1 hexanes/EtOAc) yielded 536 mg (34%) of a 4:3 mixture **17** and **16** followed by 158 mg (10%) of pure **17** as a colorless gum.

Data for **17**: ^{1}H NMR 6.36 (dd, 1, *J* = 15.2, 10.8, H-3'), 6.06 (ddq, 1, *J* = 14.8, 10.8, 1.6, H-4'), 5.77 (dq, 1, *J* = 14.8, 6.8, H-5'), 5.69 (dd, 1, *J* = 15.2, 6.4, H-2'), 4.85-4.80 (m, 1, H-1'), 4.37 (ddq, 1, *J* = 12.0, 2.2, 6.4, H-6), 4.15-4.08 (m, 1, H-4), 3.04 (d, 1, *J* = 7.2, OH), 2.68 (dd, 1, *J* = 9.2, 3.4, H-3), 2.19 (ddd, 1, *J* = 12.0, 4.4, 2.2, H-5eq), 2.07 (d, 1, *J* = 4.0, OH), 1.77 (d, 3, *J* = 6.8, H-6'), 1.68 (ddd, 1, *J* = 12.0, 12.0, 12.0, H-5ax), 1.40 (d, 3, *J* = 6.4, H-6-Me); ^{13}C NMR 172.8, 132.6, 131.3, 130.2, 129.1, 73.7, 71.0, 64.7, 55.6, 39.1, 21.4, 18.1; IR (neat) 3410, 2979, 2932, 1707, 1390, 1257, 1087, 991; HRMS (QTOF ESI$^+$) calcd for $C_{12}H_{18}O_4Na$ (MNa^+) 249.1103, found 249.1102.

Partial data for **16** were determined from the mixture: ^{1}H NMR 5.11-5.07 (m, 1, H-1'), 4.25-4.18 (m, 1, H-4), 3.44 (d, 1, *J* = 1.2, OH), 2.85 (dd, 1, *J* = 9.2, 5.2, H-3), 2.55 (d, 1, *J* = 3.4, OH), 1.67 (ddd, 1, *J* = 12.0, 12.0, 12.0, H-5ax), 1.39 (d, 3, *J* = 6.4, H-6-Me). Other peaks overlapped with the major isomer **17**.

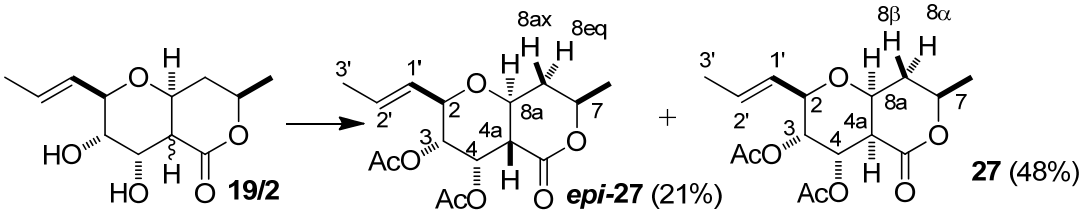
Partial data for ***cis*-16/17** were determined from the mixture: 6.71 (dd, 1, *J* = 15.6, 10.8).



(2*R*,3*S*,7*R*,8a*S*)-*rel*-3,7,8,8a-Tetrahydro-3-hydroxy-7-methyl-2-(1*E*)-1-propen-1-yl-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one (26). Pyridine (0.54 mL, 6.7 mmol) and acetic anhydride (0.32 mL, 3.4 mmol) were added to a solution of diol **19** (33 mg, 0.13 mmol) and DMAP (8 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). The solution was stirred for 18 h at 25 °C under nitrogen, diluted with CH_2Cl_2 (8 mL), and washed with 2 M HCl (1 × 10 mL). After separation of the layers, the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried over $MgSO_4$, and concentrated to give crude **25**.

Crude **25** was dissolved in MeOH (15 mL) and K_2CO_3 (590 mg, 4.2 mmol) was added. The mixture was stirred for 24 h at 25 °C, treated with 2 M HCl (10 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Flash

chromatography of the residue on MeOH-deactivated silica gel (3:1 hexanes/EtOAc) yielded 15 mg (49%) of **26** as a colorless gum: ^{1}H NMR 7.06 (br s, 1, $w_{1/2}$ = 8, H-4), 5.96 (dq, 1, *J* = 15.6, 6.4, H-2'), 5.56 (dd, 1, *J* = 15.6, 7.2, H-1'), 4.50 (ddq, 1, *J* = 12.4, 2.3, 6.0, H-7), 4.44 (br d, *J* = 12.4, H-8a), 4.21-4.16 (m, 1, H-3), 3.81 (dd, 1, *J* = 7.6, 7.2, H-2), 2.26 (br d, 1, *J* = 12.4, H-8eq), 1.90 (d, 1, *J* = 6.0, OH), 1.79 (d, 3, *J* = 6.4, H-3'-Me), 1.70 (ddd, 1, *J* = 12.4, 12.4, 12.4, H-8ax), 1.44 (d, 3, *J* = 6.0, H-7-Me); ^{13}C NMR 163.5, 139.5, 132.2, 130.4, 127.7, 79.7, 73.2, 71.2, 67.8, 37.1, 21.8, 18.1; IR (neat) 3414, 2980, 2935, 2858, 1714, 1652, 1247, 1109, 1048; MS (70 eV): *m*/*z* (%) = 154 (45), 139 (2), 125 (10), 113 (15), 112 (100); HRMS (QTOF ESI$^+$) calcd for $C_{12}H_{16}O_4Na$ (MNa^+) 247.0946, found 247.0948.



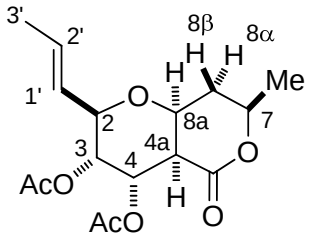
(2*R*,3*R*,4*S*,4a*R*,7*R*,8a*S*)-*rel*-3,4-bis(Acetyl)hexahydro-7-methyl-2-(1*E*)-1-propen-1-yl-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one (27). Acetic anhydride (8.9 μL, 0.094 mmol) and TMSOTf (1.0 μL, 0.0055 mmol) were added to a solution of a 2:1 mixture of **2** and **19** (7.6 mg, 0.031 mmol) in CH_2Cl_2 (0.5 mL) and the solution was stirred at 25 °C under nitrogen for 2 h. The reaction was treated with MeOH (0.1 mL), diluted with CH_2Cl_2 (5 mL), washed with water (5 mL), dried over $MgSO_4$ and concentrated. Flash chromatography of the residue on MeOH-deactivated silica gel (20% EtOAc in toluene) yielded 2.1 mg (21%) of ***epi*-27** followed by 4.9 mg (48%) of **27** as a colorless gum.

Data for ***epi*-27**: ^{1}H NMR 5.97 (dd, 1, *J* = 2.6, 2.3, H-4), 5.85 (dq, 1, *J* = 15.2, 6.4, H-2'), 5.37 (ddq, *J* = 15.2, 6.0, 2.0, H-1'), 4.74 (dd, 1, *J* = 10.0, 2.6, H-3), 4.52-4.44 (m, 1, H-7), 4.11-4.03 (m, 2, H-8a and H-2), 2.48 (dd, 1, *J* = 11.2, 2.3, H-4a), 2.33 (ddd, 1, *J* = 12.8, 3.5, 3.5, H-8eq), 2.09 (s, 3), 1.98 (s, 3), 1.78-1.68 (m, 1, H-8ax), 1.72 (dd, 3, *J* = 6.4, 2.0, H-3'-Me), 1.44 (d, 3, *J* = 6.0, H-7-Me).

Data for **27**: 5.81 (dd, 1, *J* = 3.5, 3.0, H-4), 5.80 (dq, 1, *J* = 15.2, 6.8, H-2'), 5.36 (ddq, *J* = 15.2, 8.2, 1.5, H-1'), 5.09 (dd, 1, *J* = 9.8, 3.0, H-3), 4.43 (ddd, *J* = 9.0, 3.5, 3.3, H-8a), 4.32-4.24 (m, 1, H-7), 4.06 (dd, *J* = 9.8, 8.2, H-2), 2.86 (dd, 1, *J* = 3.5, 3.5, H-4a), 2.42 (ddd, 1, *J* = 15.2, 9.0, 3.5, H-8α), 2.15 (s, 3), 1.98 (s, 3), 1.73 (ddd, 1, *J* = 15.2, 12.0. 3.3, H-8β), 1.69 (dd, 3, *J* = 6.8, 1.5, H-3'-Me), 1.39 (d, 3, *J* = 6.0, H-7-Me); ^{13}C NMR 169.6, 169.2, 169.1, 131.8, 127.3, 76.0, 72.2, 67.8, 67.7, 66.9, 44.5, 36.7, 21.0, 20.7, 20.5, 17.9; IR (neat) 1750, 1373, 1244, 1222, 1056; MS (70 eV): *m*/*z* (%) = 283 (5), 267 (3), 223 (85), 154 (100), 113 (90), 112 (95); HRMS (QTOF ESI$^+$) calcd for $C_{16}H_{22}O_7Na$ (MNa^+) 349.1263, found 349.1271; HRMS (QTOF MS ESI$^+$) calcd for $C_{16}H_{23}O_7$ (MH^+) 327.1444, found 327.1438. The ^{1}H and ^{13}C spectral data are identical to those reported by Krohn[1] as tabulated in Table S1 on page S9.

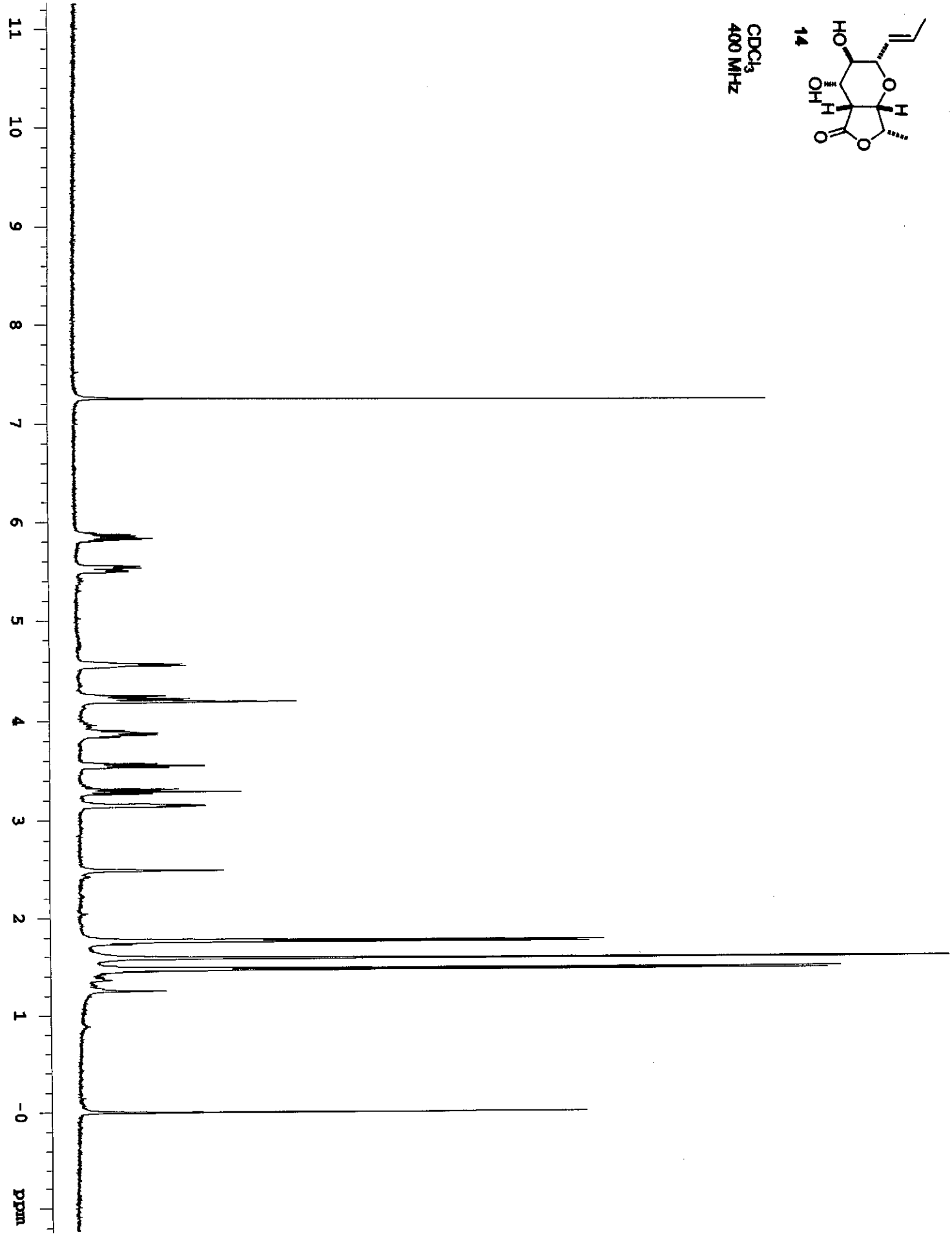
Tests for Biological Activity. For the agar diffusion assay,[14] the compounds were dissolved in acetone at a concentration of 1, 2 or 4 μg/μL. Fifty μL of the solution was transferred by pipette onto a sterile filter disc (0.05, 0.1 or 0.2 mg/filter disc), which was placed onto an appropriate agar growth medium for the respective test organisms (for *Escherichia coli*, *Bacillus megaterium*, *Microbotryum violaceum*, and *Chlorella fusca* see Schulz et al.,[14] and on YEB medium (10 g of *N*-(2-acetamido)-2-aminoethanesulfonic acid, 10 g of yeast extract, 0.4 g of cysteine, and 0.25 g of ferric pyrophosphate in 1000 mL of distilled water) for *Legionella pneumophila* Corby), and subsequently sprayed with a suspension of the respective test organism. The radii of the zones of inhibition in mm are reported in Table 1 and 2 for compounds **14**, **17**, **19**, **2**, and **26**, in Table 1 for the control substances penicillin, tetracycline, nystatin, actidione, and acetone, and in Table 2 for the control substance kanamycin.

Table S1. Comparison of the Spectral Data of Natural and Synthetic Dinemasone C Diacetate (**27**)



	Natural Dinemasone C Diacetate (**27**)			Synthetic Dinemasone C Diacetate (**27**)		
Atom #	^{13}C	^{1}H		^{13}C	^{1}H	
2	76.0	4.08	(dd, $J_{2,3}$ = 10.0, $J_{2,1'}$ = 7.7)	76.0	4.06	(dd, $J_{2,3}$ = 9.8, $J_{2,1'}$ = 8.2)
3	67.8	5.11	(dd, $J_{3,2}$ = 10.0, $J_{3,4}$ = 3.3)	67.7	5.09	(dd, $J_{3,2}$ = 9.8, $J_{3,4}$ = 3.0)
3-OAc	20.7	1.99	(s)	20.7	1.98	(s)
	169.2	—		169.2	—	
4	67.0	5.83	(dd, $J_{4,3}$ = $J_{4,4a}$ = 3.3)	66.9	5.81	(dd, $J_{4,4a}$ = 3.5, $J_{4,3}$ = 3.0)
4-OAc	20.9	2.14	(s)	21.0	2.15	(s)
	169.6	—		169.6	—	
4a	44.6	2.88	(dd, $J_{4a,4}$ = $J_{4a.8a}$ = 3.3)	44.5	2.86	(dd, $J_{4a,4}$ = 3.5, $J_{4a.8a}$ = 3.5)
5	169.0	—		169.1	—	
7	72.2	4.32	(m)	72.2	4.32-4.24 (m)	
7-Me	20.5	1.41	(d, $J_{7,7}$ = 6.2)	20.5	1.39	(d, $J_{7\text{-Me},7}$ = 6.0)
8α	36.7	2.44	(ddd, J_{gem} = 15.3, $J_{8,8a}$ = 9.3, $J_{8,7}$ = 3.6)	36.7	2.42	(ddd, $J_{8\alpha,8\beta}$ = 15.2, $J_{8\alpha,8a}$ = 9.0, $J_{8\alpha,7}$ = 3.5)
8β	—	1.75	(ddd, J_{gem} = 15.3, $J_{8,7}$ = 12.0, $J_{8,8a}$ = 3.3)	—	1.73	(ddd, $J_{8\beta,8\alpha}$ = 15.2, $J_{8\beta,7}$ = 12.0, $J_{8\beta,8a}$ = 3.3)
8a	67.9	4.44	(ddd, $J_{8a,8}$ = 9.3, $J_{8a,8}$ = $J_{8a,4a}$ 3.3)	67.8	4.43	(ddd, $J_{8a,8\alpha}$ = 9.0, $J_{8a,8\beta}$ = 3.3, $J_{8a,4a}$ = 3.5)
1'	127.4	5.38	(ddq, $J_{1',2'}$ = 15.3, $J_{1',2}$ =7.7, $J_{1',3'}$ = 1.7)	127.3	5.36	(ddq, $J_{1',2'}$ = 15.2, $J_{1',2}$ = 8.2, $J_{1',3'}$ = 1.5)
2'	131.5	5.79	(overlapped with H-4)	131.8	5.80	(dq, 1, $J_{2',1'}$ = 15.2, $J_{2',3'}$ = 6.8)
3' (Me)	17.9	1.70	(dd, $J_{3',2'}$ = 6.5, $J_{3',1'}$ = 1.7)	17.9	1.69	(dd, $J_{3',2'}$ = 6.8, $J_{3',1'}$ = 1.5)

^{1}H and ^{13}C NMR assignments were taken from reference 1.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H
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H
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10
9
8
7
6
5
4
3
2
1
0
ppm

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4	8012.897	79.710	56.9
5	7909.897	78.685	83.0
6	7772.564	77.319	161.1
7	7740.519	77.000	166.7
8	7708.475	76.681	163.1
9	7581.823	75.421	86.6
10	7413.208	73.744	91.4
11	7201.105	71.634	93.9
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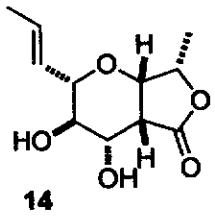
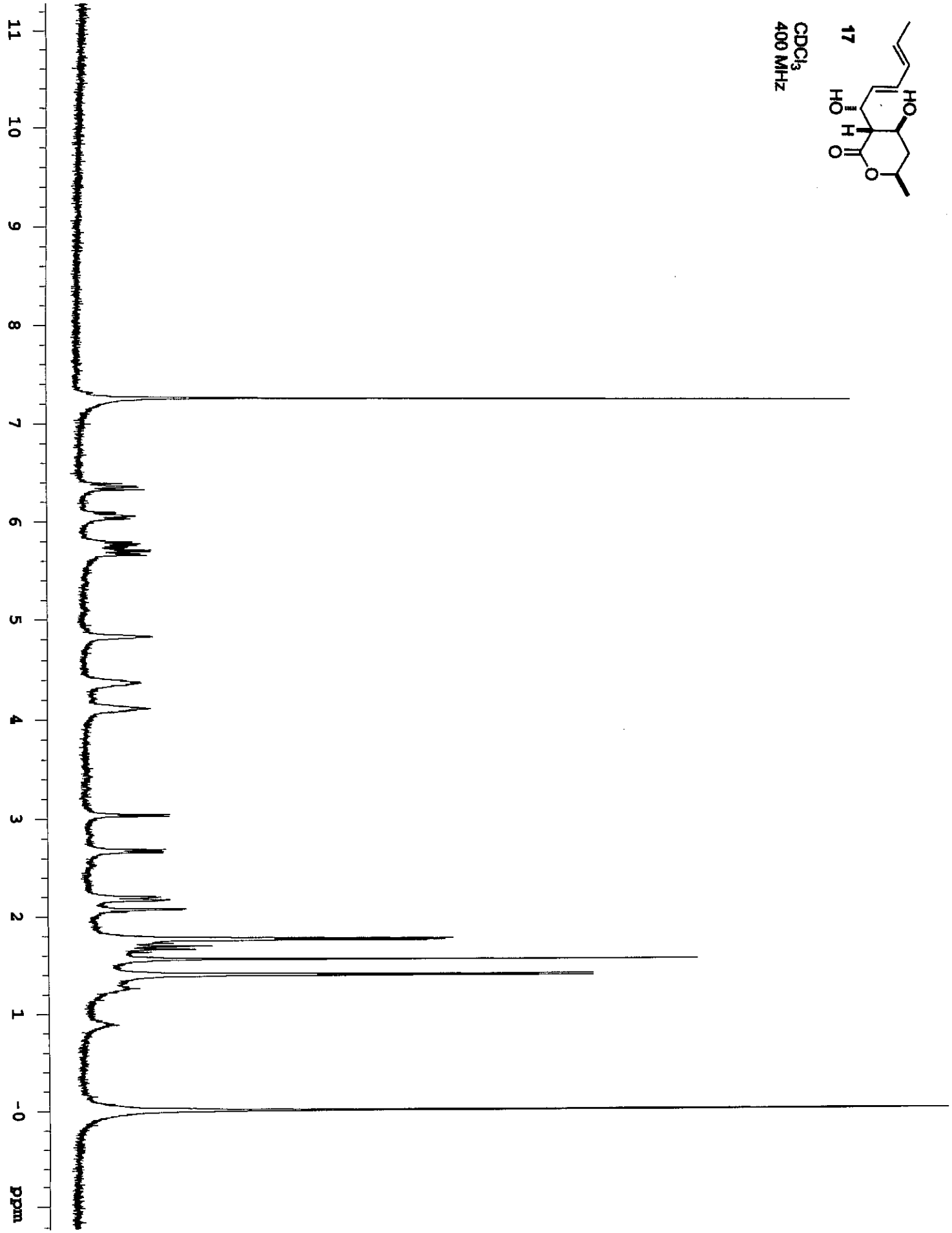


14

$CDCl_3$
100 MHz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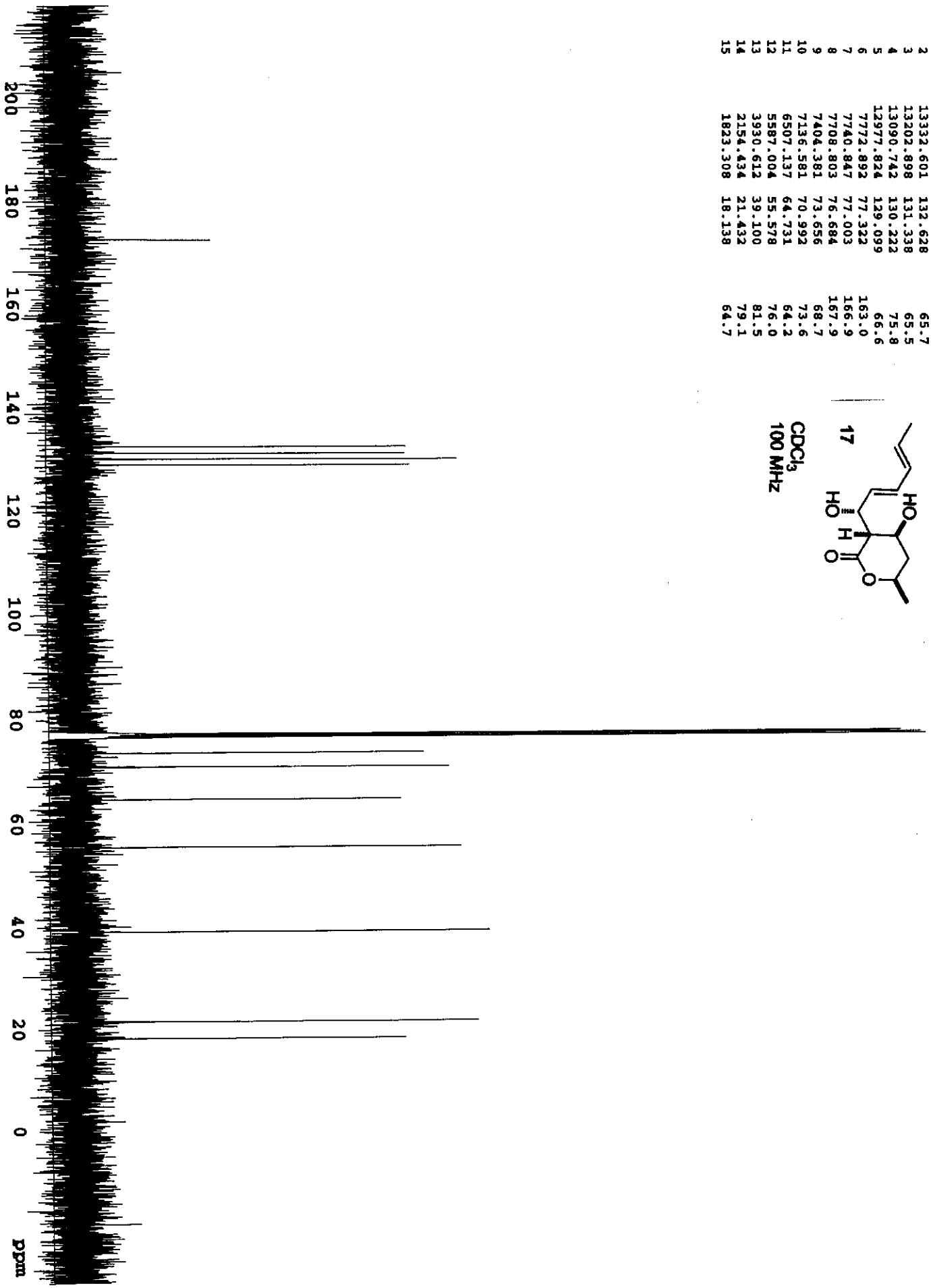
ppm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5 12977.824 129.099 66.6
6 7772.892 77.322 163.0
7 7740.847 77.003 166.9
8 7708.803 76.684 167.9
9 7404.381 73.656 68.7
10 7136.581 70.992 73.6
11 6507.137 64.731 64.2
12 5587.004 55.578 76.0
13 3930.612 39.100 81.5
14 2154.434 21.432 79.1
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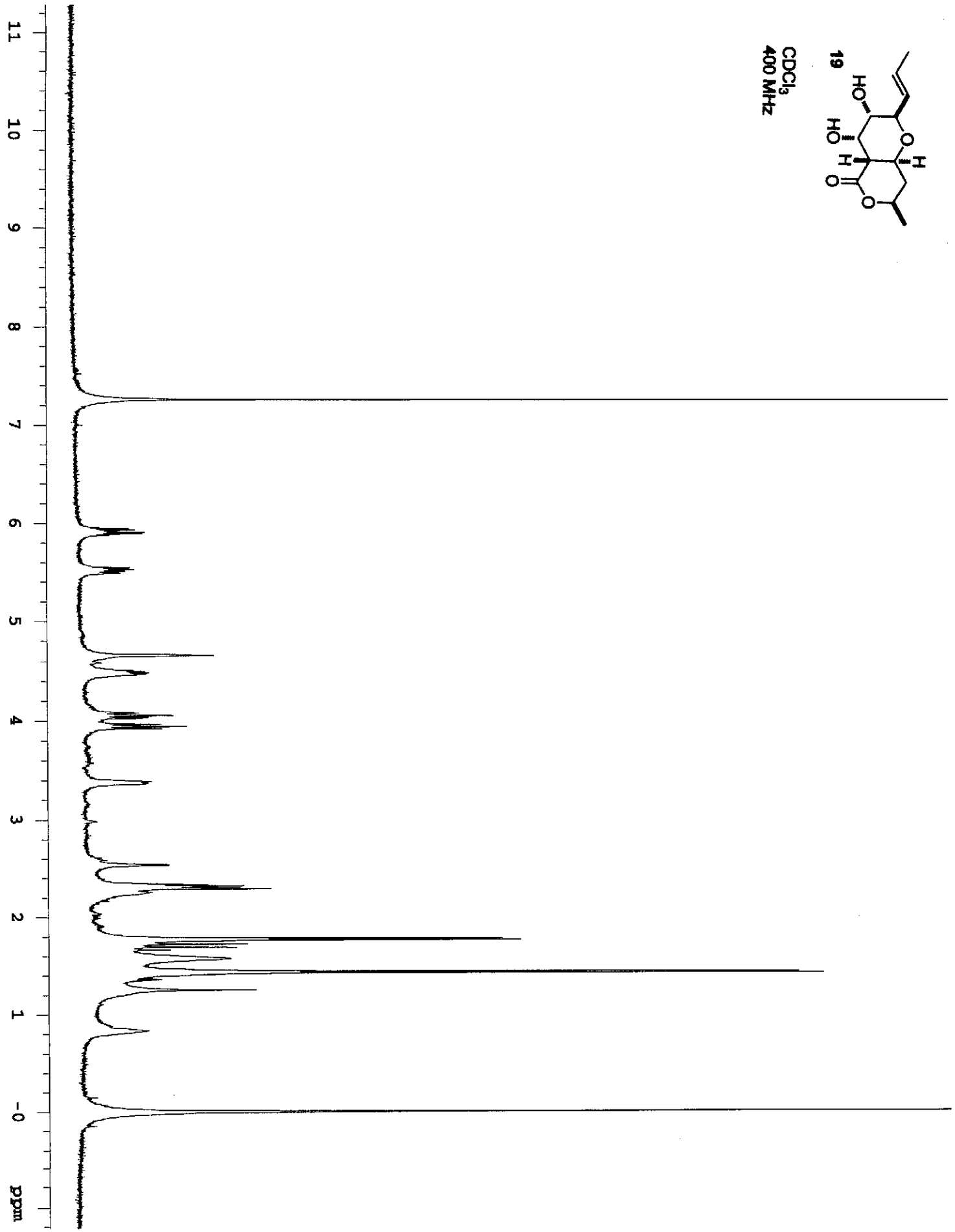
ppm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HO
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9
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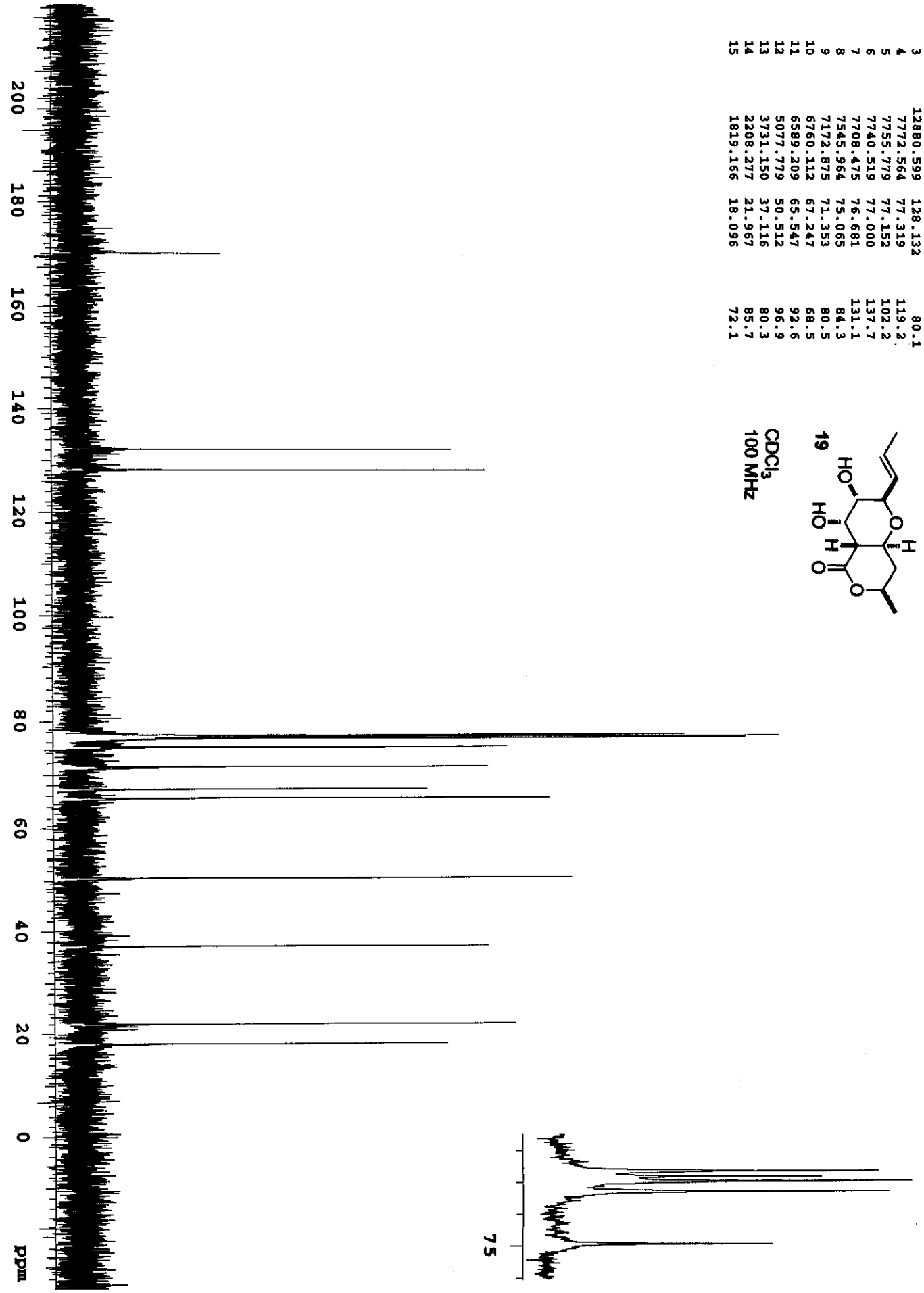
-0
ppm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7 7708.475 76.681 131.1
8 7545.964 75.065 84.3
9 7172.875 71.353 80.5
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180
160
140
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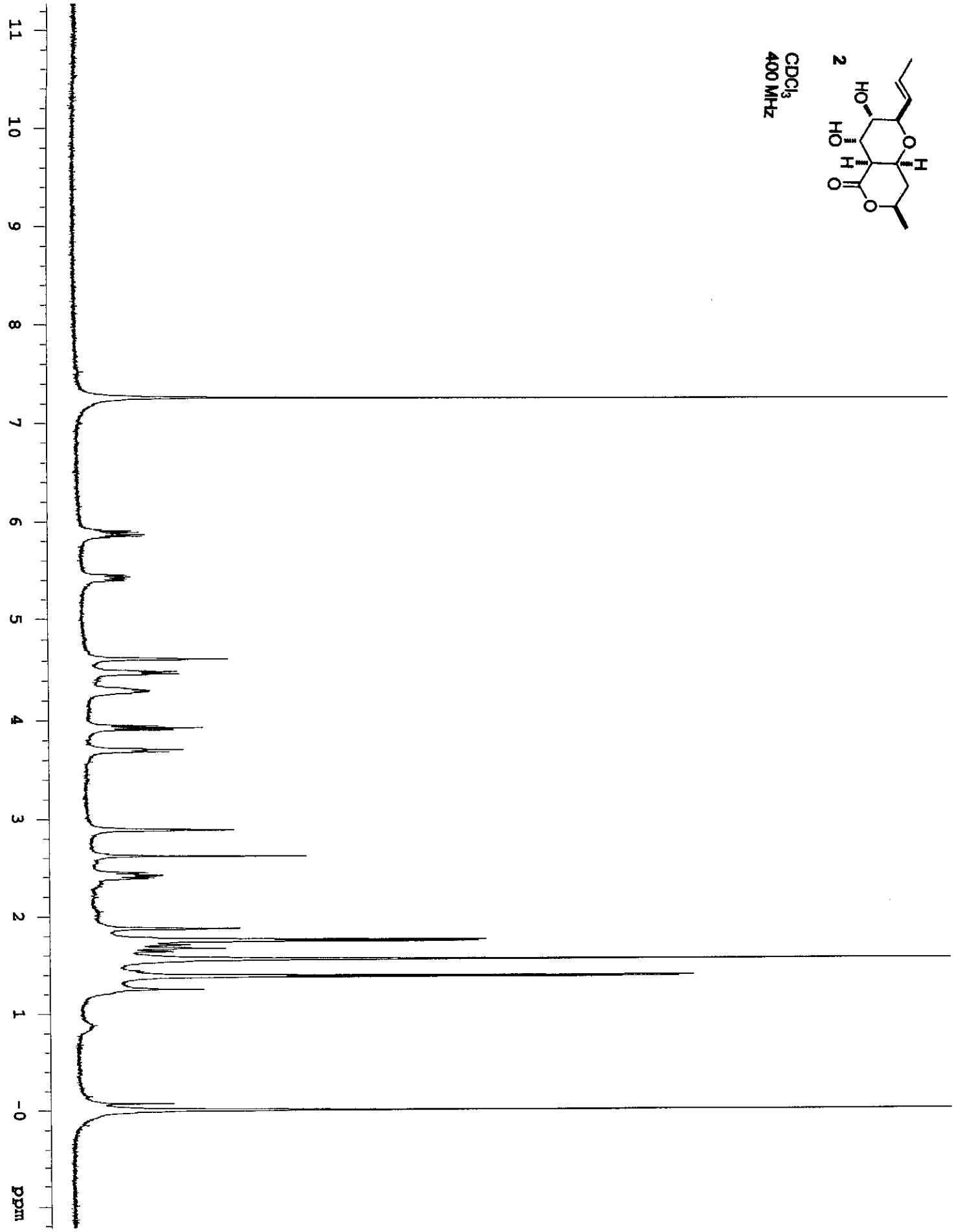
100
80
60
40
20
0
ppm
75

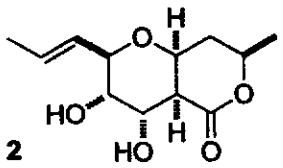

CDCl3
400 MHz
2
HO
HO
H
O
O
O
H
11
10
9
8
7
6
5
4
3
2
1
-0
ppm

ar-9-122-4

Pulse Sequence: gCOSY

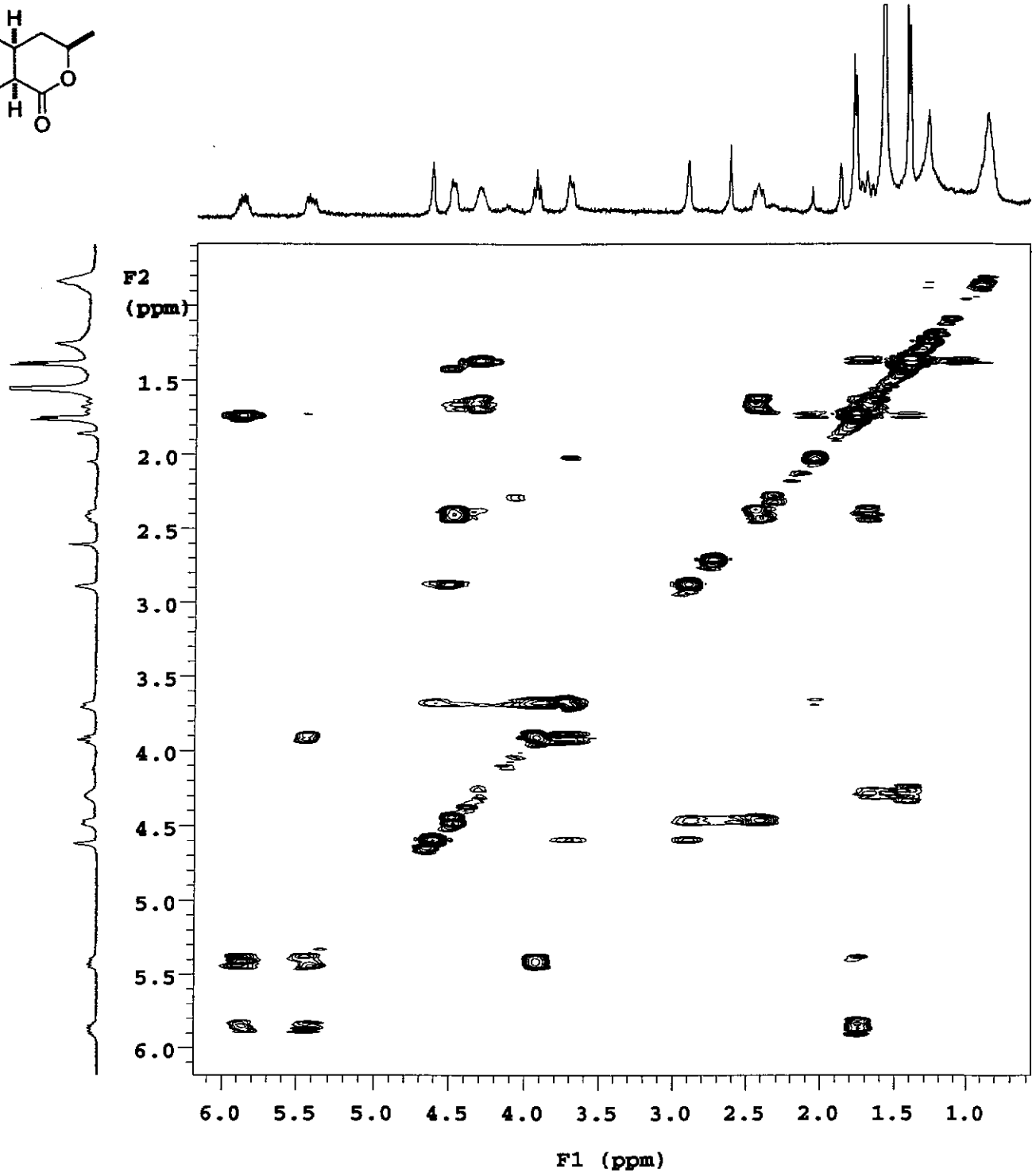
Solvent: CDCl3
Ambient temperature
File: ar-9-122-4-cosy
INOVA-400 "cosy"

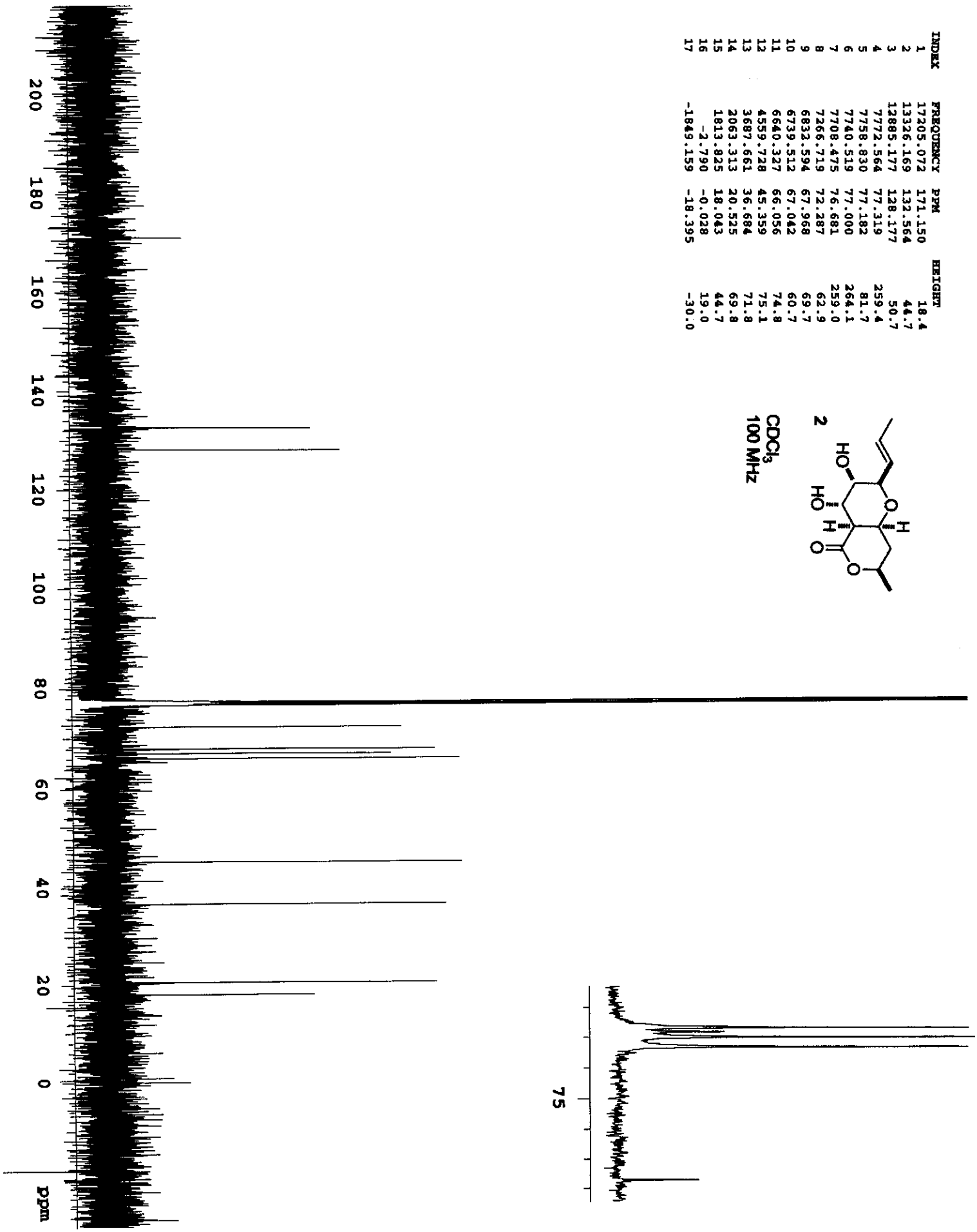
Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
Single scan
256 increments
OBSERVE H1, 399.7858130 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 0 min, -1 sec

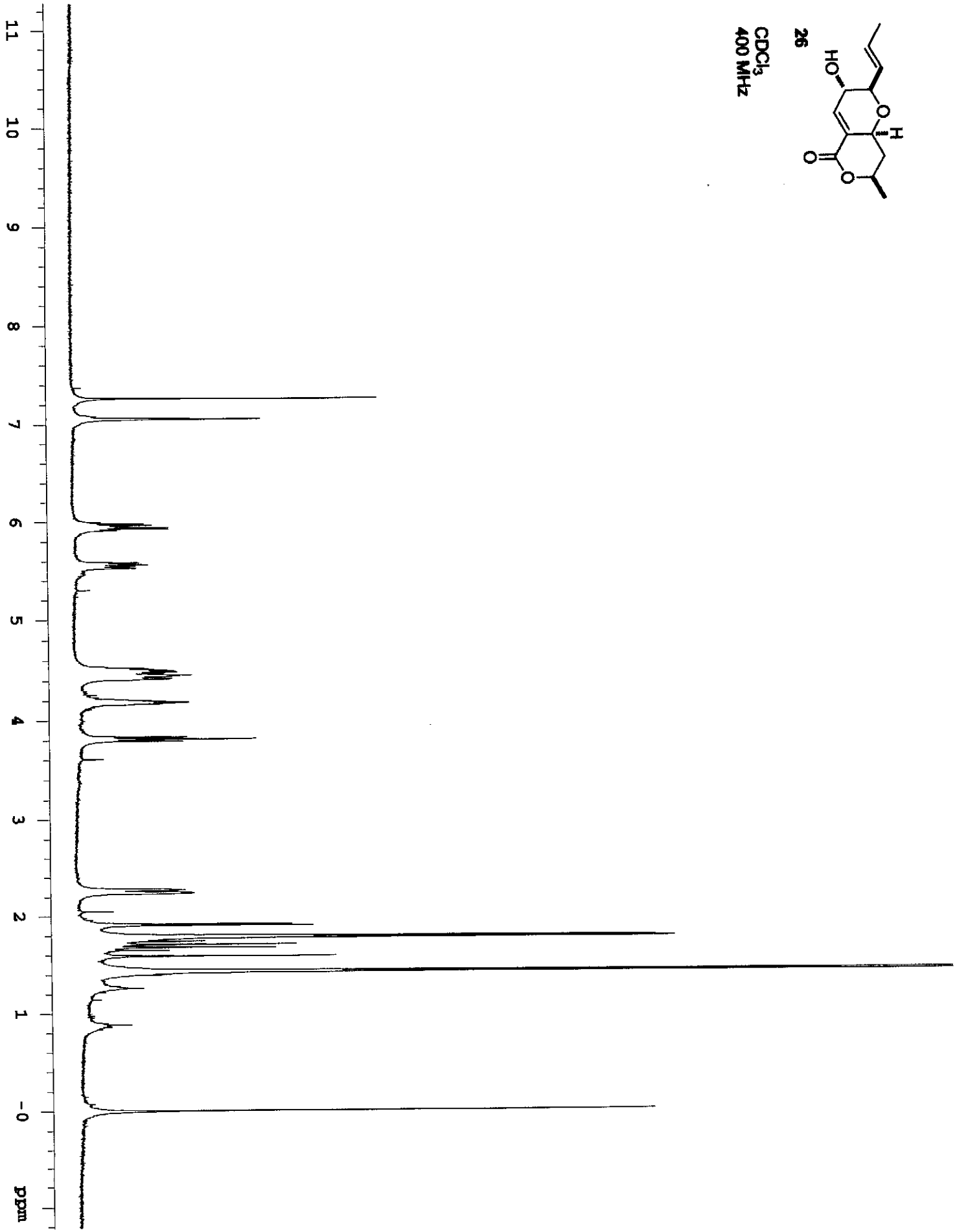


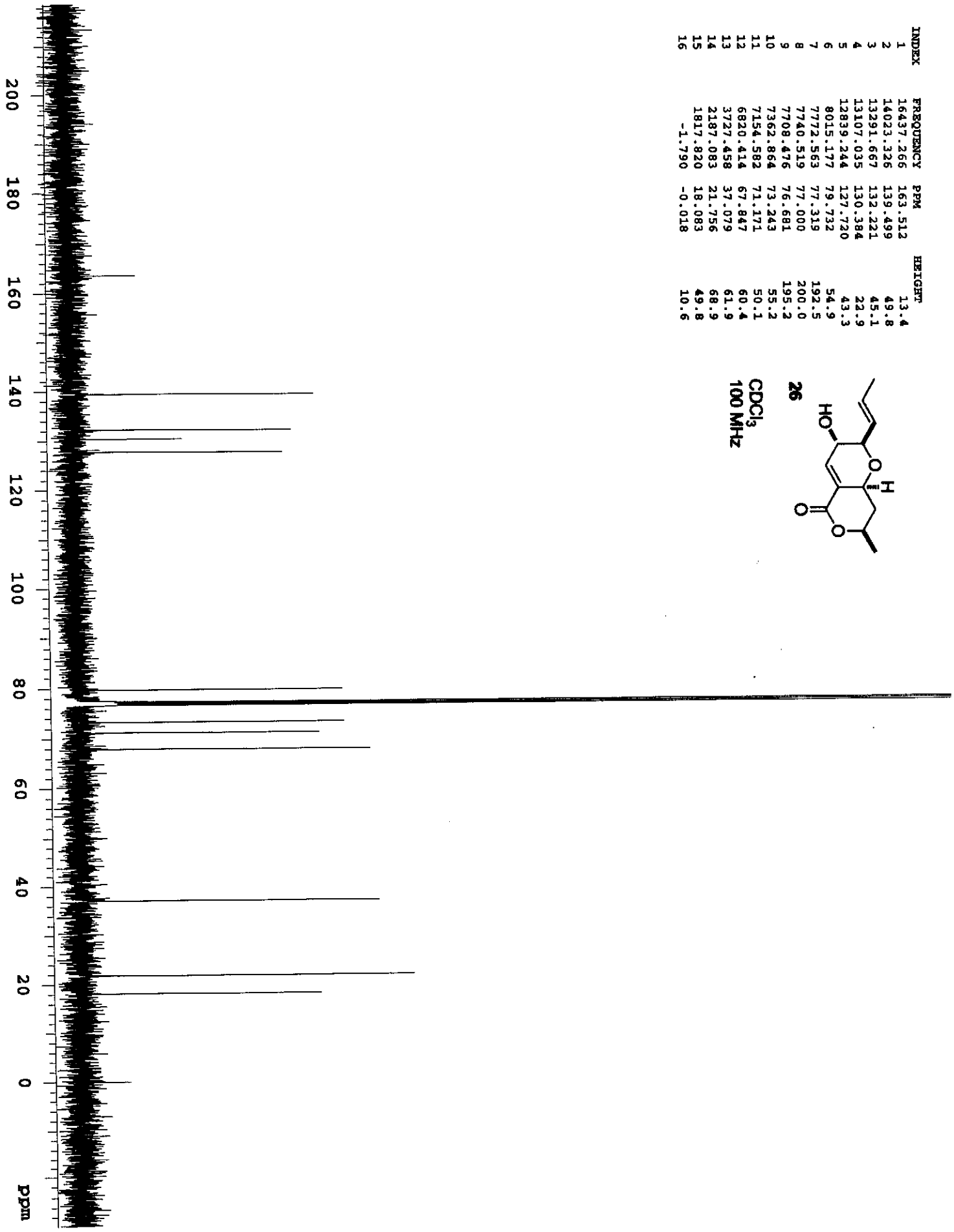
2

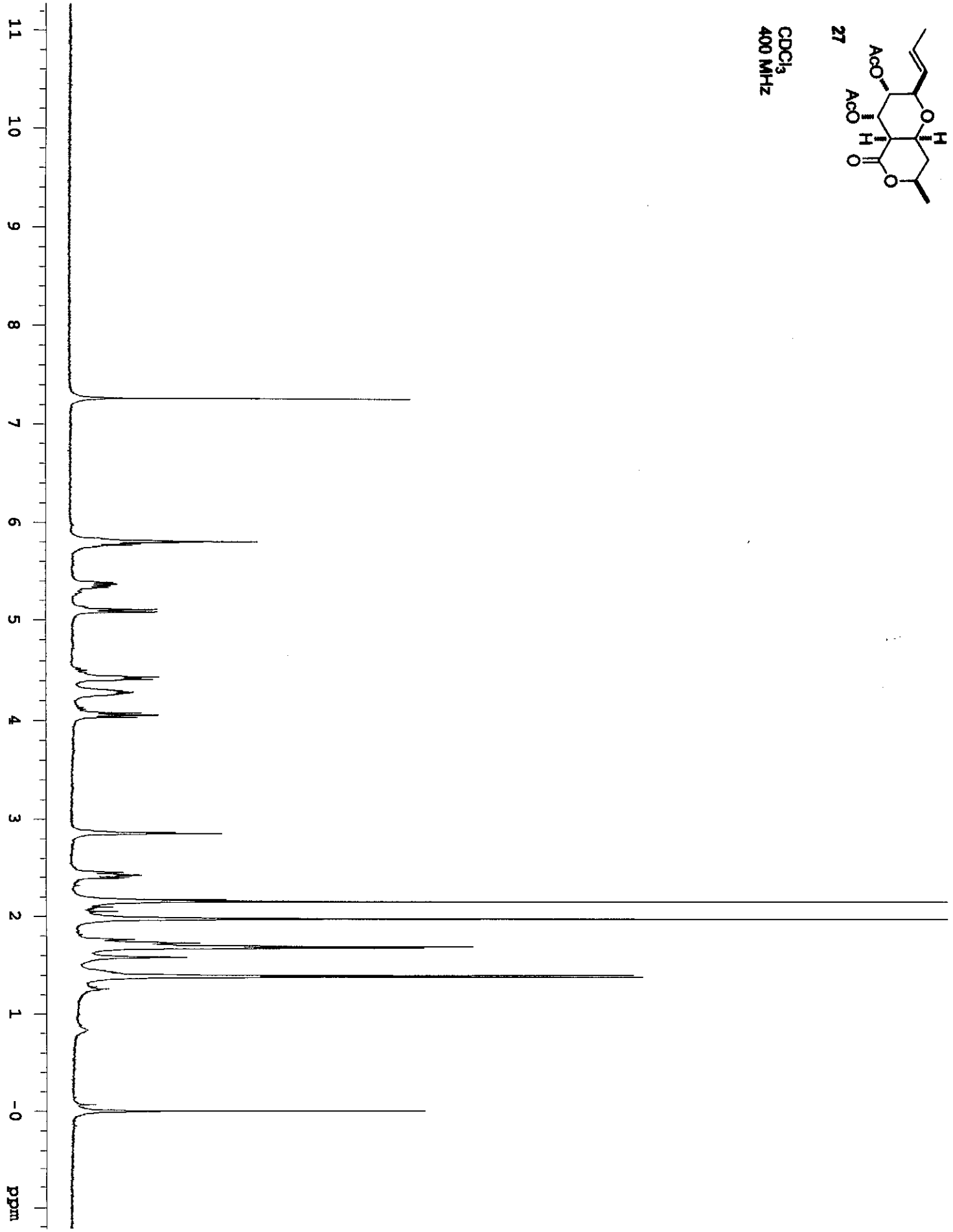
$CDCl_3$
400 MHz

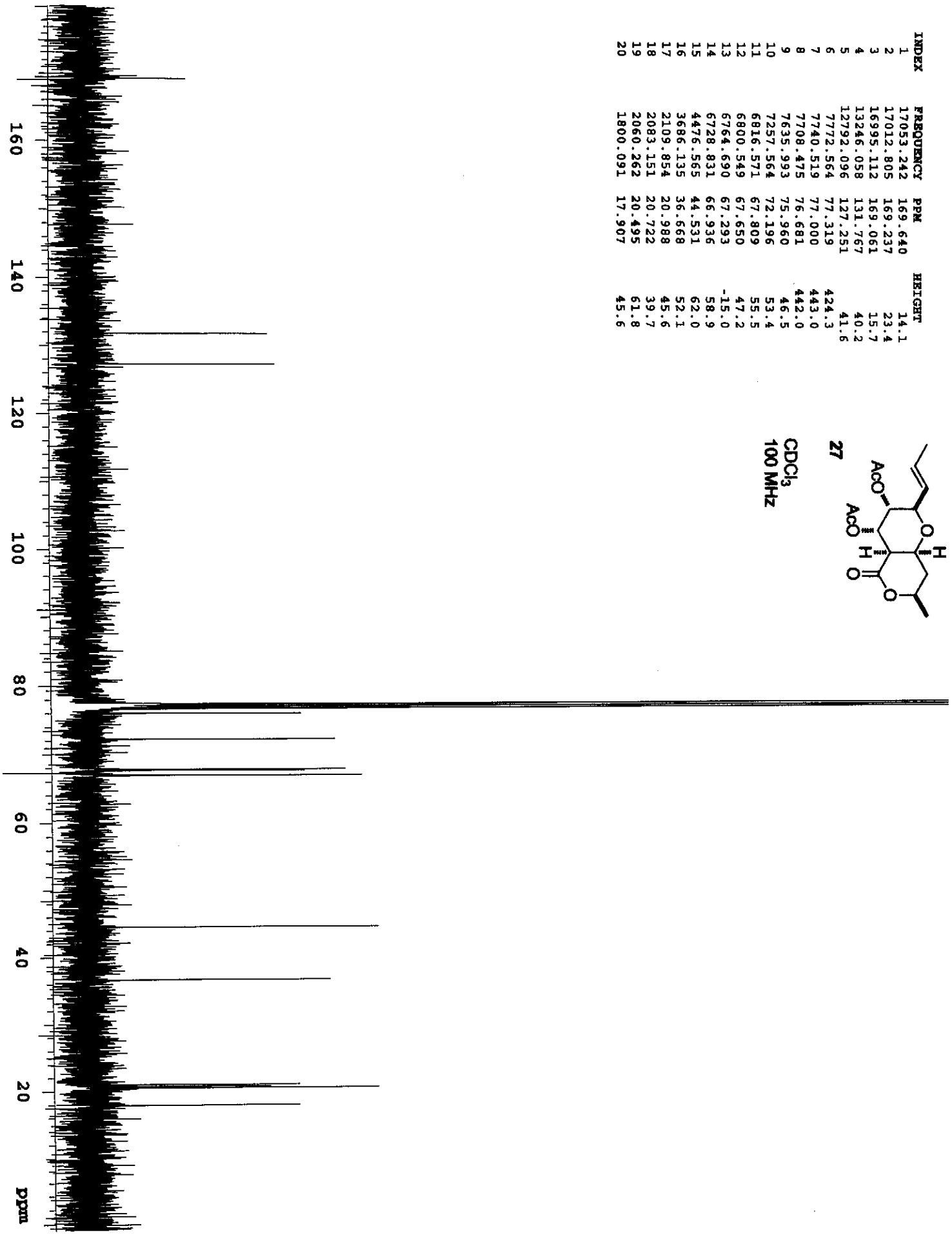



INDEX FREQUENCY PPM HEIGHT
1 17205.072 171.150 18.4
2 13326.169 132.564 44.7
3 12885.177 128.177 50.7
4 7772.564 77.319 259.4
5 7758.830 77.182 81.7
6 7740.519 77.000 264.1
7 7708.475 76.681 259.0
8 7266.719 72.287 62.9
9 6832.594 67.968 69.7
10 6739.512 67.042 60.7
11 6640.327 66.056 74.8
12 4559.728 45.359 75.1
13 3687.661 36.684 71.8
14 2063.313 20.525 69.8
15 1813.825 18.043 44.7
16 -2.790 -0.028 19.0
17 -1849.159 -18.395 -30.0
CDCl3
100 MHz
2
HO
HO
H
O
O
O
H
200
180
160
140
120
100
80
60
40
20
0
ppm
75


26
CDCl3
400 MHz
HO
O
H
O
O
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


INDEX FREQUENCY PPM HEIGHT
1 16437.266 163.512 13.4
2 14023.326 139.499 49.8
3 13291.667 132.221 45.1
4 13107.035 130.384 22.9
5 12839.244 127.720 43.3
6 8015.177 79.732 54.9
7 7772.563 77.319 192.5
8 7740.519 77.000 200.0
9 7708.476 76.681 195.2
10 7362.864 73.243 55.2
11 7154.582 71.171 50.1
12 6820.414 67.847 60.4
13 3727.458 37.079 61.9
14 2187.083 21.756 68.9
15 1817.820 18.083 49.8
16 -1.790 -0.018 10.6
26
CDCl3
100 MHz
HO
O
H
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm


CDCl3
400 MHz
27
AcO
AcO
H
H
O
O
O
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


INDEX FREQUENCY PPM HEIGHT
1 17053.242 169.640 14.1
2 17012.805 169.237 23.4
3 16995.112 169.061 15.7
4 13246.058 131.767 40.2
5 12792.096 127.251 41.6
6 7772.564 77.319 424.3
7 7740.519 77.000 443.0
8 7708.475 76.681 442.0
9 7635.993 75.960 46.5
10 7257.564 72.196 53.4
11 6816.571 67.809 55.5
12 6800.549 67.650 47.2
13 6764.690 67.293 -15.0
14 6728.831 66.936 58.9
15 4476.565 44.531 62.0
16 3686.135 36.668 52.1
17 2109.854 20.988 45.6
18 2083.151 20.722 39.7
19 2060.262 20.495 61.8
20 1800.091 17.907 45.6
AcO
AcO
H
O
O
O
H
27
CDCl3
100 MHz
160
140
120
100
80
60
40
20
ppm