Efficient Synthesis of the Tetracyclic Aminoquinone Moiety of Marmycin A

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Supporting Information

General Experimental Methods. 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. THF and ether were dried and purified by distillation from sodium/benzophenone. Pyridine, Et_3N, benzene, toluene, MeOH, and CH_2Cl_2 were distilled from CaH_2. ^1H and ^{13}C NMR spectra were obtained on a 400 MHz spectrometer in $CDCl_3$ unless otherwise indicated with tetramethylsilane as internal standard. 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). IR spectra were acquired on an FT-IR spectrometer and are reported in wave numbers (cm^{-1}). High resolution mass spectra were obtained using electron impact (EI).

5-Nitro-1,4-naphthoquinone (4) was prepared by the literature procedure.[5] Naphthoquinone (2 g, 12.65 mmol, purified by sublimation) was dissolved in 25 mL of well stirred concd sulfuric acid cooled in an ice bath. This solution was stirred for 2 min and a solution of sodium nitrate (7 g, 82.35 mmol) in 8 ml of concd sulfuric acid was added in two portions over one min. The ice bath was removed and the solution was allowed to warm to RT over 30 min and then stirred for an additional thirty min. The flask was then placed directly in a 40 °C oil bath and stirred for 20 min giving a homogenous yellow solution. The solution was cooled to RT and poured over 1 min into a 500 ml beaker containing a stir bar and half filled with ice. The yellow precipitate that formed as the mixture stirred was filtered off and washed with water (200 mL). The solid

was filtered through silica gel eluting with CH_2Cl_2. The resulting yellow solid was recrystallized from benzene giving 1.918 g (74.7%) of **4** as yellow needles: mp 168–169 °C (lit.[5] 167–168 °C); ^{1}HNMR 8.30 (d, 1, J = 7.9), 7.91 (dd, 1, J = 7.9, 7.9), 7.75 (d, 1, J = 7.9), 7.07 (d, 1, J = 10.4), 7.03 (d, 1, J = 10.4); ^{13}C NMR 182.5, 181.2, 148.2, 139.0, 138.1, 134.7, 132.6, 128.9, 127.5, 122.8. The spectral data are identical to those previously reported.[17]

1,2,3,4-Tetrahydro-3-methyl-8-nitrobenz[*a*]anthracene-7,12-dione (17). An approximately 1.5:1 mixture of 5-methyl-1-vinylcyclohex-1-ene (**5**) and 3-Methyl-1-vinylcyclohex-1-ene (**13**) was prepared as described by Motoyoshiya without experimental details.[6] 3-Methylcyclohexanone (3.365 g, 30 mmol in 10 mL of THF) was added over 30 min to a stirred solution of vinylmagnesium bromide (0.7 M in THF, 55.7 mL, 39 mmol) cooled in an ice bath under N_2. The ice bath was removed and the solution was allowed to warm to RT over 30 min. The flask was then placed directly in a 60 °C oil bath and stirred for 1 hr. The solution was cooled to RT and quenched by slow addition of saturated aqueous NH_4Cl (30 mL). The organic phase was separated and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated to give 4.52 g (107.5%) of a crude mixture of tertiary alcohols.[18]

The entire crude mixture of alcohols was taken up in 45 mL of THF and 0.5 mL of concd H_2SO_4 was added. The resulting solution was stirred for 72 h at 50 °C. The THF was removed at 100 torr and the residue was dissolved in 20 mL of pentane and the resulting solution was washed with water (3 × 3 ml) and dried (Na_2SO_4). The crude dienes were filtered through silica gel (pentane) and concentrated at 100 torr to give 2.57 g (70% from 3-methylcyclohexanone) of a 1.5:1 mixture of **5** and **13**.

Partial data for **5** determined from the mixture are identical to those of **5** determined from a similar mixture prepared by coupling of tributylvinylstannane with a mixture of cyclohexenyl triflates, except that all the literature peaks are 0.04 to 0.05 ppm

downfield:[6b] ^{1}H NMR 6.37 (dd, 1, J = 17.6, 10.4), 5.74 (br s, 1), 5.07 (d, 1, J = 17.6), 4.89 (d, 1, J = 10.4); 1.01 (d, 3, J = 6) .

Partial data for **13** determined from the mixture are identical to those of **13** determined from a similar mixture prepared by coupling of tributylvinylstannane with a mixture of cyclohexenyl triflates, except that all the literature peaks are 0.04 to 0.05 ppm downfield: [6b] ^{1}H NMR 6.34 (dd, 1, J = 17.6, 10.4), 5.60 (br s, 1), 5.07 (d, 1, J = 17.6), 4.91 (d, 1, J = 10.4); 0.995 (d, 3, J = 6).

A solution of nitroquinone **4** (1.16 g, 5.69 mmol) and 1.39 g (approx 11.4 mmol, 2 equiv) of the above 1.5:1 mixture of dienes **5** and **13** in EtOH (3 mL) was stirred for 12 h at RT and then heated in a 40 °C oil bath for 2 h. The Diels-Alder adduct precipitated as it formed as a white solid. The solution was concentrated to remove excess diene and EtOH giving 2.25 g (121%) of a complex mixture of at least three stereoisomers of 1,2,3,4,6,6a,12a,12b-octahydro-3-methyl-8-nitrobenz[*a*]anthracene-7,12-dione (**14**) and some 1,2,3,4,6,6a,12a,12b-octahydro-1-methyl-8-nitrobenz[*a*]anthracene-7,12-dione (**15**): ^{1}H NMR 0.90 (d, 0.4 × 3, J = 4.9), 0.82 (d, 0.3 × 3, J = 4.9), 0.75 (d, 0.3 × 3, J = 5.5).

The crude Diels-Alder adducts **14** and **15** (2.25 g) were dissolved in benzene (4 mL) and hexane (36 mL) was added. This solution was transferred to a 125-mL resealable tube containing 2.25 g of basic alumina (activity grade 1). The tube was purged with O_2, sealed, heated in a 110 °C oil bath for 2 h, and cooled. This process was repeated at which time all the **14** and **15** had been oxidized. The solution was filtered and the alumina was washed with $CHCl_3$. The combined filtrates were concentrated to give 1.40 g of a 9:1 mixture of **17** and 1,2,3,4-tetrahydro-1-methyl-8-nitrobenz[*a*]anthracene-7,12-dione (**18**) as a reddish orange solid. Recrystallization from $CHCl_3$ (25 mL) gave 1.15 g (63% from **4**) of pure **17**: mp 233-234 °C; ^{1}H NMR 8.44 (d, 1, J = 7.9), 8.07 (d, 1, J = 7.9), 7.87 (dd, 1, J = 7.9, 7.9), 7.71 (d, 1, J = 7.9), 7.50 (d, 1, J = 7.9), 3.55 (ddd, 1, J = 18, 5.5, 3.5), 3.25 (ddd, 1, J = 18, 12, 7), 2.98 (dd, 1, J = 17.0, 3.7), 2.56 (dd, 1, J =

17.0, 11.0), 2.08-2.01 (m, 1), 1.97-1.85 (m, 1), 1.39 (dddd, 1, J = 13, 12, 11, 5.5), 1.11 (d, 3, J = 6.7); ^{13}C 183.1, 180.3, 148.5, 146.6, 141.5, 135.9, 135.4, 134.3, 132.8, 130.1, 129.7, 126.8, 125.4, 124.1, 39.6, 39.2, 29.1, 27.7, 21.5; IR 3094, 1672, 1593, 1563, 1543, 1457, 1373, 1322, 1303, 1284, 1265; HRMS (EI) calcd for $C_{19}H_{15}NO_4$ (M^+) 321.1001, found 321.1002.

Partial data for **18** were determined from the mother liquor after recrystallization of **17**: ^{1}H NMR 4.38 (m, 1), 1.26 (d, 3, J = 6.7).

A similar sequence using 4 rather than 2 equiv of diene mixture gave a 15:1 mixture of **17** and **18**.

3-Methyl-8-nitrobenz[*a*]anthracene-7,12-dione (19). A solution of **17** (40 mg, 0.125 mmol) and DDQ (282 mg, 1.25 mmol, 10 equiv) in 2 mL of benzene was heated at 140 °C for 20 min in a microwave reactor. Flash chromatography on silica gel eluting with benzene (DDQ byproducts were retained on the column) afforded 28 mg (71%) of **19** as a yellow solid that was very slightly soluble in $CDCl_3$ and less soluble in CD_3OD, acetone-d_6, benzene-d_6, and DMSO-d_6 so that a ^{13}C NMR spectrum could not be obtained: mp 301-302 °C; ^{1}H NMR 9.52 (d, 1, J = 9.2), 8.52 (d, 1, J = 7.9), 8.27 (d, 1, J = 8.5), 8.16 (d, 1, J = 8.5), 7.92 (dd, 1, J = 7.9, 7.3), 7.75 (d, 1, J = 7.3), 7.73 (br s, 1), 7.64 (br d, 1, J = 9.2), 2.58 (s, 3); IR 1672, 1655 (sh), 1592, 1540, 1378, 1322, 1302, 821, 695; HRMS (EI) calcd for $C_{19}H_{11}NO_4$ (M^+) 317.0688, found 317.0688. Larger quantities of **19** were prepared by running 10 oxidations and combining the material prior to flash chromatography, which gave 267 mg (68%) of **19**.

8-Amino-3-methylbenz[*a*]anthracene-7,12-dione (3). Nitroquinone **19** (28 mg, 0.088 mmol) was suspended in water (3 mL). Na_2S (211 mg, 0.88 mmol) was added and the suspension was heated at 95 °C for 2 h and cooled. The red solid was filtered off and washed with water (20 mL). The solid was taken up in $CHCl_3$, which was dried (Na_2SO_4) and concentrated to give 23 mg (91%) of pure **3** as a red solid: mp 188-189 °C (lit.[4] 175-178 °C); ^{1}H NMR 9.56 (d, 1, J = 8.8), 8.35 (d, 1, J = 8.5), 8.08 (d, 1, J = 8.5),

7.66 (br s, 1,), 7.62 (d, 1, *J* = 7.3), 7.56 (d, 1, *J* = 8.8), 7.47 (dd, 1, *J* = 7.3, 8.5), 6.93 (d, 1, *J* = 8.5), 7.0-6.6 (br, 2, NH_2) 2.54 (s, 3); ^{13}C NMR 186.6, 185.6, 150.2, 138.6, 136.5, 136.1, 134.8, 134.6, 134.3, 132.0, 128.9, 128.5, 128.3, 127.6, 122.5, 122.2, 117.2, 112.9, 21.6; IR 3431, 3313, 1630, 1606, 1547, 1464, 1387, 1293, 1271, 1256, 812; HRMS (EI) calcd for $C_{19}H_{13}NO_2$ (M^+) 287.0946, found 287.0947. The ^{1}H and ^{13}C NMR spectra are identical to those reported.[4]

8-Amino-1,2,3,4-tetrahydro-3-methylbenz[*a*]anthracene-7,12-dione (16). Nitroquinone **17** (50 mg, 0.156 mmol) was suspended in water (5 mL). Na_2S (374 mg, 1.56 mmol) was added and the suspension was heated at 95 °C for 2 h and cooled. The reddish orange solid was filtered off and washed with water (20 mL). The solid was taken up in $CHCl_3$, which was dried (Na_2SO_4) and concentrated to give 45.4 mg (98%) of pure aminoquinone **16** as a reddish orange solid: mp 153-155 °C; ^{1}H NMR 8.09 (d, 1, *J* = 7.9), 7.51 (d, 1, *J* = 7.3), 7.41 (dd, 1, *J* = 8.5, 7.3), 7.40 (d, 1, *J* = 7.9), 6.89 (d, 1, *J* = 8.5), 6.8-6.6 (br, 2, NH_2) 3.54 (ddd, 1, *J* = 18, 5.5, 3.5), 3.22 (ddd, 1, *J* = 18, 12, 7), 2.92 (dd, 1, *J* = 17.0, 3.7), 2.50 (dd, 1, *J* = 17.0, 11.0), 2.05-1.93 (m, 1), 1.93-1.76 (m, 1), 1.34 (dddd, 1, *J* = 13, 12, 11, 5.5), 1.08 (d, 3, *J* = 6.7); ^{13}C NMR 185.9, 185.5, 150.2, 144.3, 140.4, 136.2, 134.5, 134.4, 134.3, 130.9, 124.5, 121.7, 116.9, 113.2, 39.5, 31.4, 29.2, 27.8, 21.6; IR 3439, 3323, 1630, 1606, 1543, 1460, 1375, 1283, 1263, 1171; HRMS (EI) calcd for $C_{19}H_{17}NO_2$ (M^+) 291.1259, found 291.1260.

In(OTf)$_3$-Catalyzed Condensation of Aminoquinone 3 with L-Rhamnal Acetate (2b). A solution of aminoquinone **3** (50 mg, 0.17 mmol), L-rhamnal acetate (**2b**) (54.6 mg, 0.255 mmol), In(OTf)$_3$ (9.6 mg, 0.017 mmol) in dry CH_2Cl_2 (8 mL) was stirred at 45 °C under N_2 for 12 h. The reaction mixture was cooled and diluted with water (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue (5:1 pentane/EtOAc) afforded **20** (20 mg, 27%) followed

by **21** (10.5 mg, 14%). The spectral data of **20** and **21** are identical to those reported by Yao and Zhang.[4]

References

17. (a) Cameron, D. W.; Feutrill, G. I.; Patti, A. F. *Aust. J. Chem.* **1979**, 32, 575-584. (b) Ishii, H.; Hanoaka, T. Asaka, T.; Harada, Y.; Ikeda, N. *Tetrahedron* **1976**, 32, 2693-2698.

18. Marcou, A.; Normant, H. *Bull. Soc. Chim. Fr.* **1965**, 3491-3494.

X-Ray Data Collection, Solution, and Refinement for Aminoquinone 3. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 30 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of three phi and one omega scan sets, with 0.5° steps in phi or omega; completeness was 99.2%. A total of 1916 frames were collected. Final cell constants were obtained from the xyz centroids of 5610 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, it first appeared that the crystals were orthorhombic, space group *Pmmn* or the noncentrosymmetric equivalents. No solution could be obtained in an orthorhombic space group. The data were therefore re-integrated in the monoclinic system, allowing a near 90-degree beta angle to vary. The final beta value was 90.060(5)º; space group $P2_1/n$ was chosen initially. Again, no solution could be obtained. The structure was first solved using SIR-92[2] in space group *Pn*; refinement would not proceed below $R = 36\%$. At this point ROTAX analysis[3] revealed a twin law -1 0 0.002 / 0 -1 0 / 0 0 1. Refinement using this twin law led to significant improvement ($R = 12\%$). It was clear at this stage that the correct space group was indeed $P2_1/n$, and the *Pn* structure was transformed to the correct space group. The structure refined to $R = 10\%$. Next, disorder *of a* $CHCl_3$ solvate molecule was examined. Difficulty in modeling the disorder was encountered; this appeared to arise from less-than-full occupancy of the solvate. The

chloroform occupancy refined to *ca.* 0.75, with *R* now at 8.2%. One of the Cl atoms had a very high anisotropic displacement parameter, and was split into two atoms. The final disorder/occupancy model led to a value of 0.758(5) for the solvate occupancy (atoms C(20), H(201), Cl(1) and Cl(3), with disordered Cl atoms Cl(20) and Cl(21) at occupancies each fixed to one-half of 0.758. Refinement (full-matrix-least squares) was performed using the Oxford University *Crystals for Windows* program.[4] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were first regularized with the use of restraints and subsequently allowed to ride on the corresponding carbon or nitrogen atoms. The scale factors for the two twin components were constrained to sum to 1.0; the value of the major twin component scale was 0.541(2). Upon reduction of the $CHCl_3$ occupancy to a value < 1.0, CheckCIF (PLATON) reports that the unit cell should be halved in the *c* direction and the space group revised. This is an artifact, which arises from the fact that the $CHCl_3$ is ignored in the ADDSYM calculation. Inspection of the full crystallographic data set shows an abundance of high-intensity data *hkl, l* = 2*n*+1. The final least-squares refinement converged to $R_1 = 0.0781$ ($I > 2\sigma(I)$, 5808 data) and $wR_2 = 0.1993$ (F^2, 6986 data, 434 parameters).

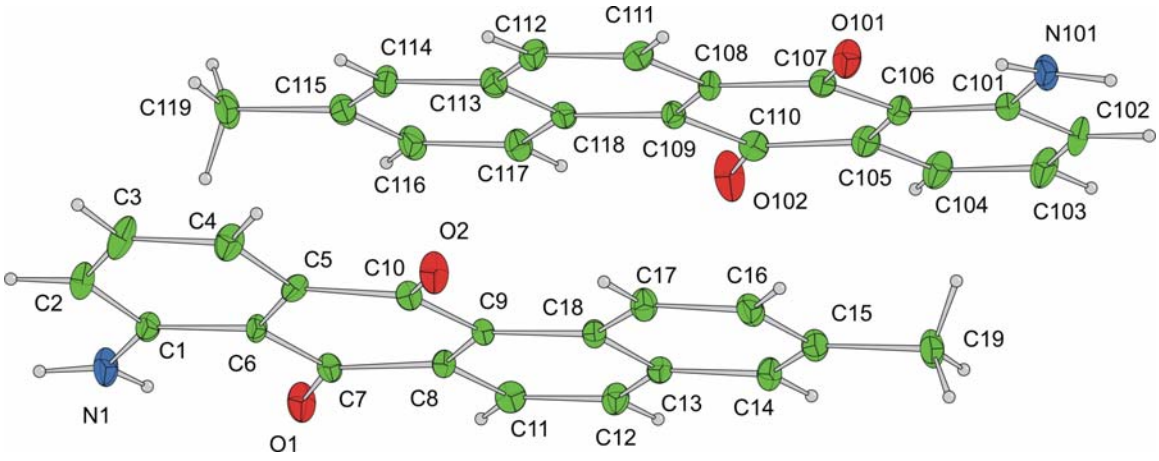
The crystal structure consists of eight amine molecules and 3.032 (4 × 0.758) chloroform molecules in the unit cell. The asymmetric unit of **3** contains 0.758 chloroform and two amine molecules. The two molecules, while symmetry-independent, are structurally identical within experimental error. The two independent molecules, labeled to show the corresponding atoms (*n*; 100 + *n*) are shown below.

1. Apex2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.

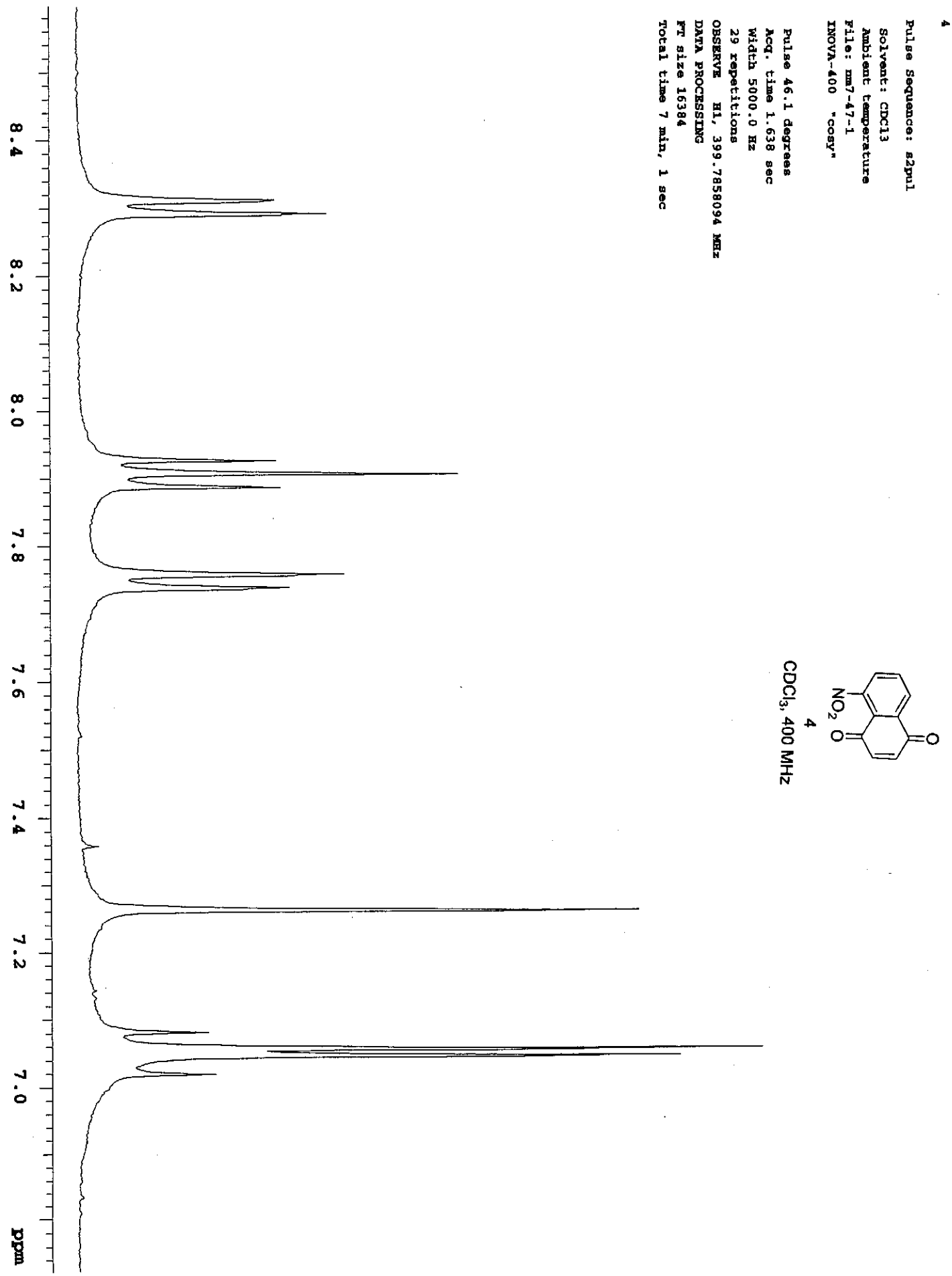
2. Altomare, A; Cascarano, G; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst*. **1994**, *27*, 435.

3. Cooper, R. I.; Gould, R. O.; Parsons, S.; Watkin, D. J. *J. Appl. Cryst.* **2002**, *35*, 168-174.

4. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487.



Two independent molecules of **3**, labeled to show the corresponding atoms (*n*; 100 + *n*)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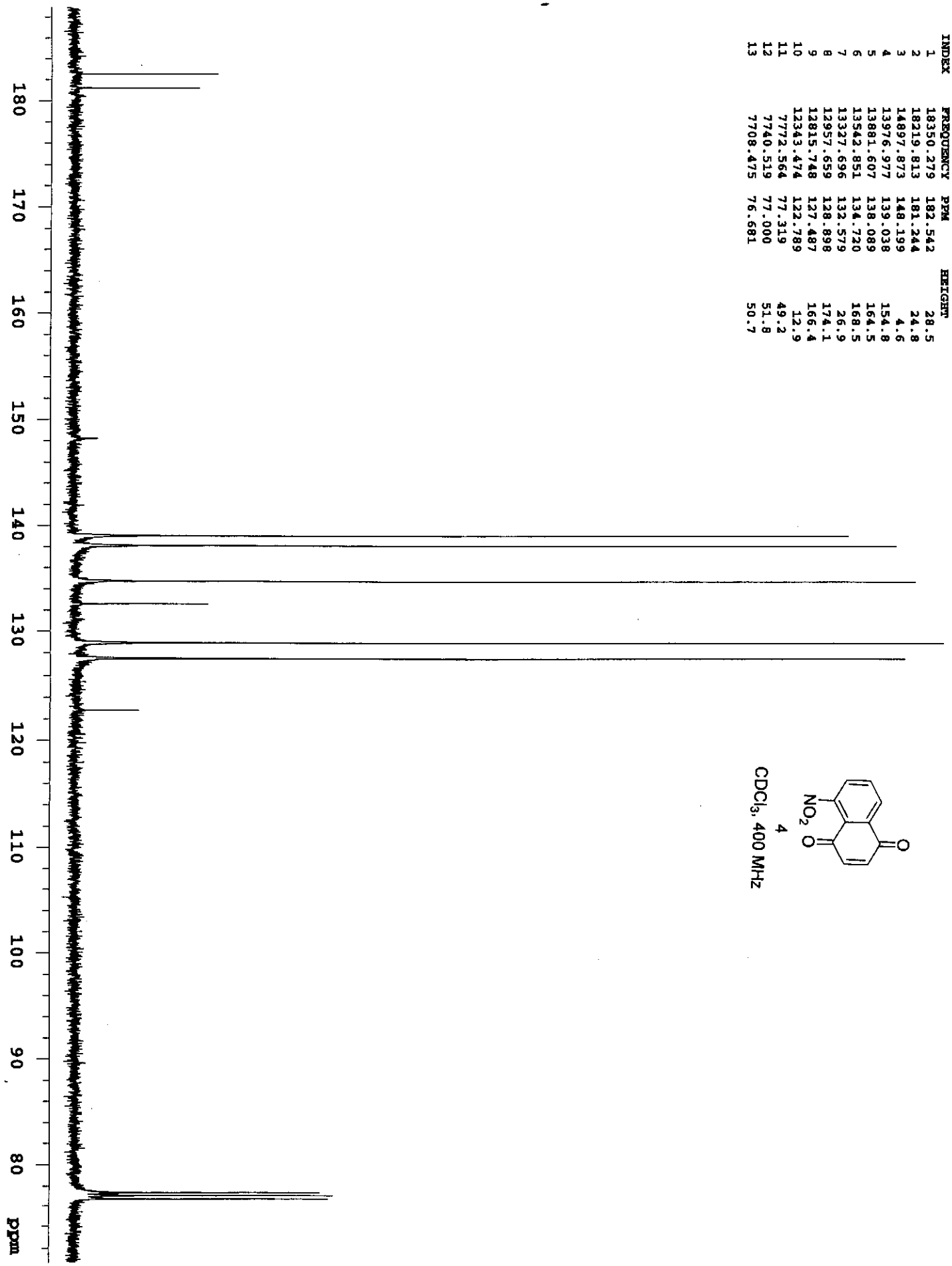
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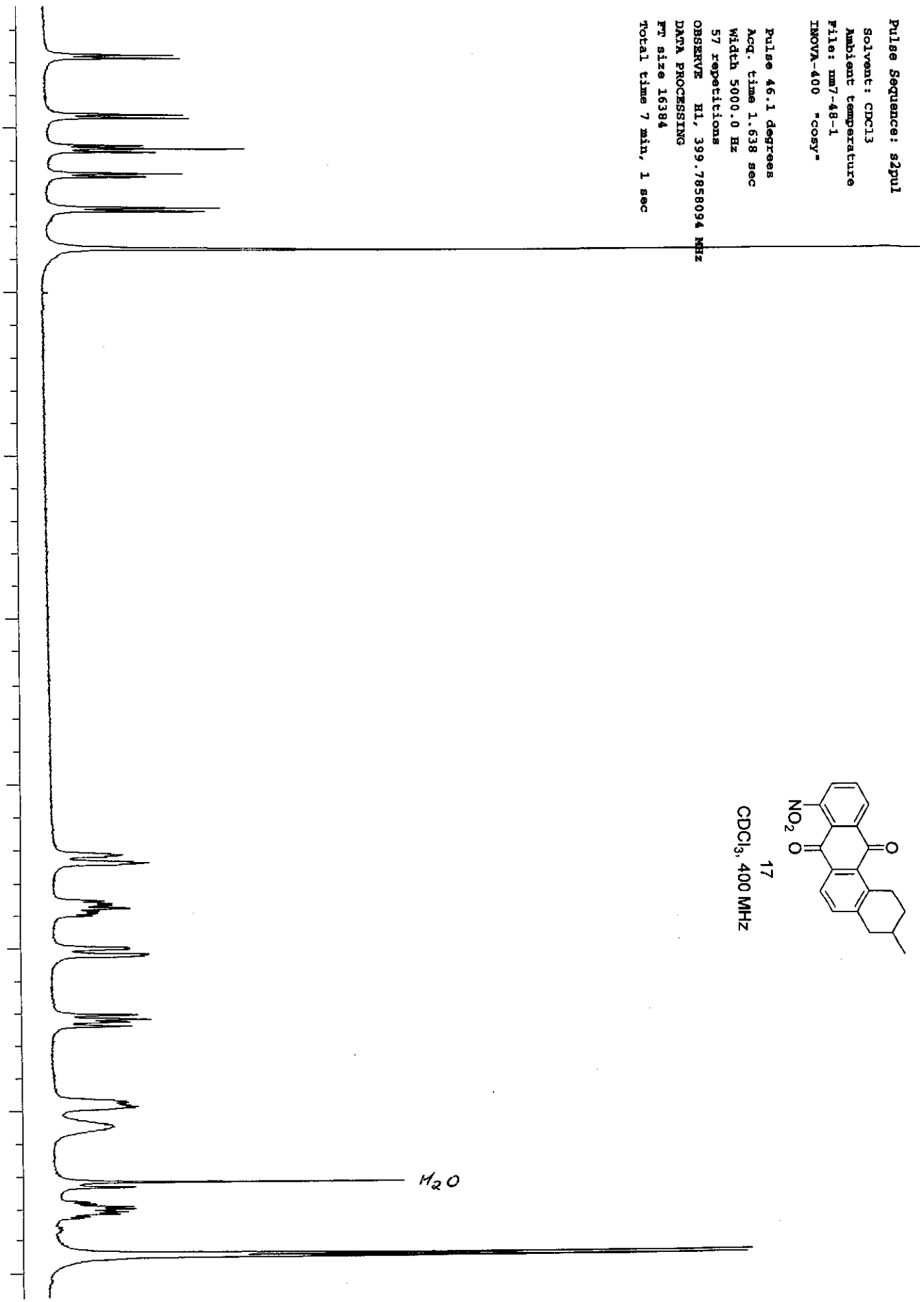
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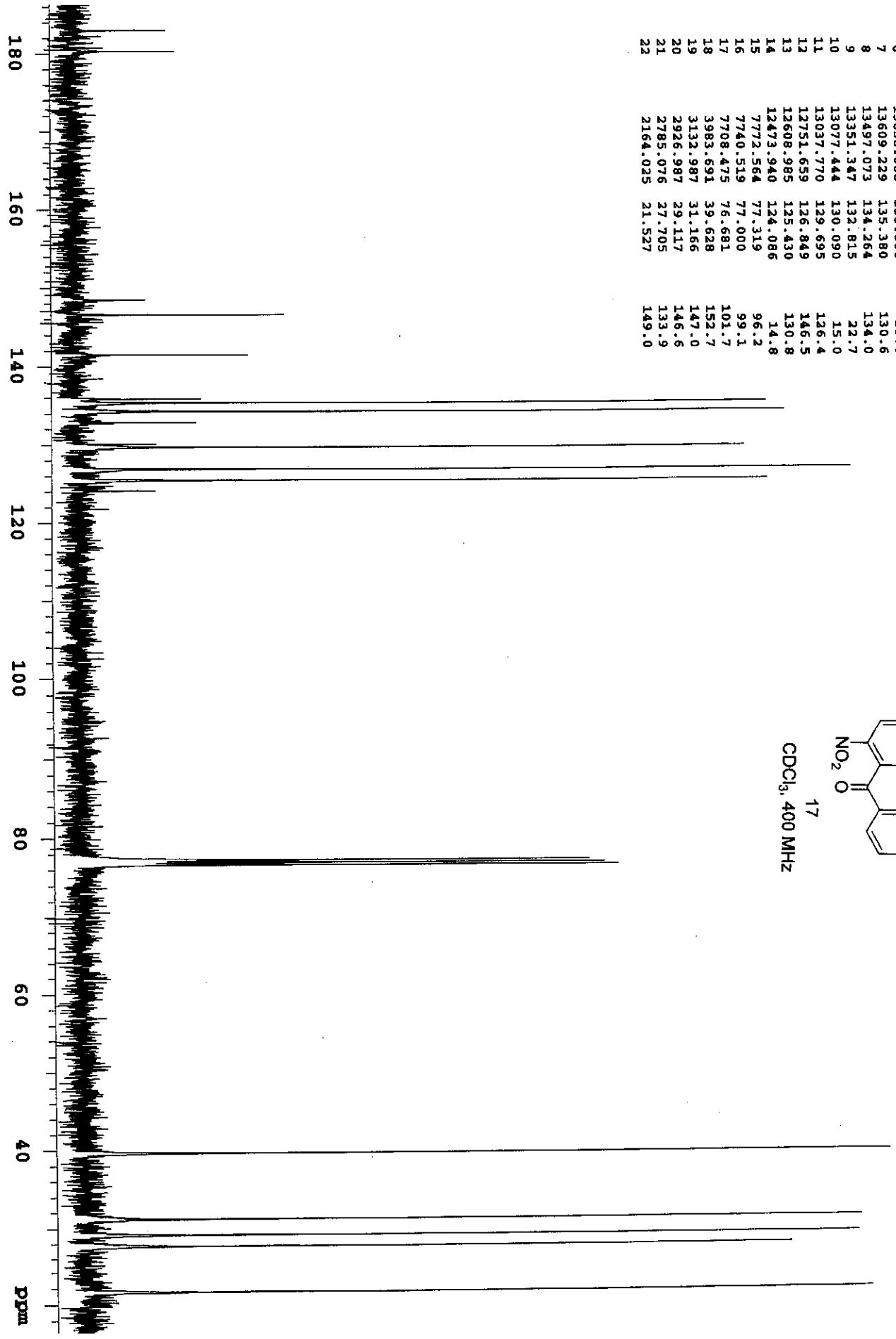
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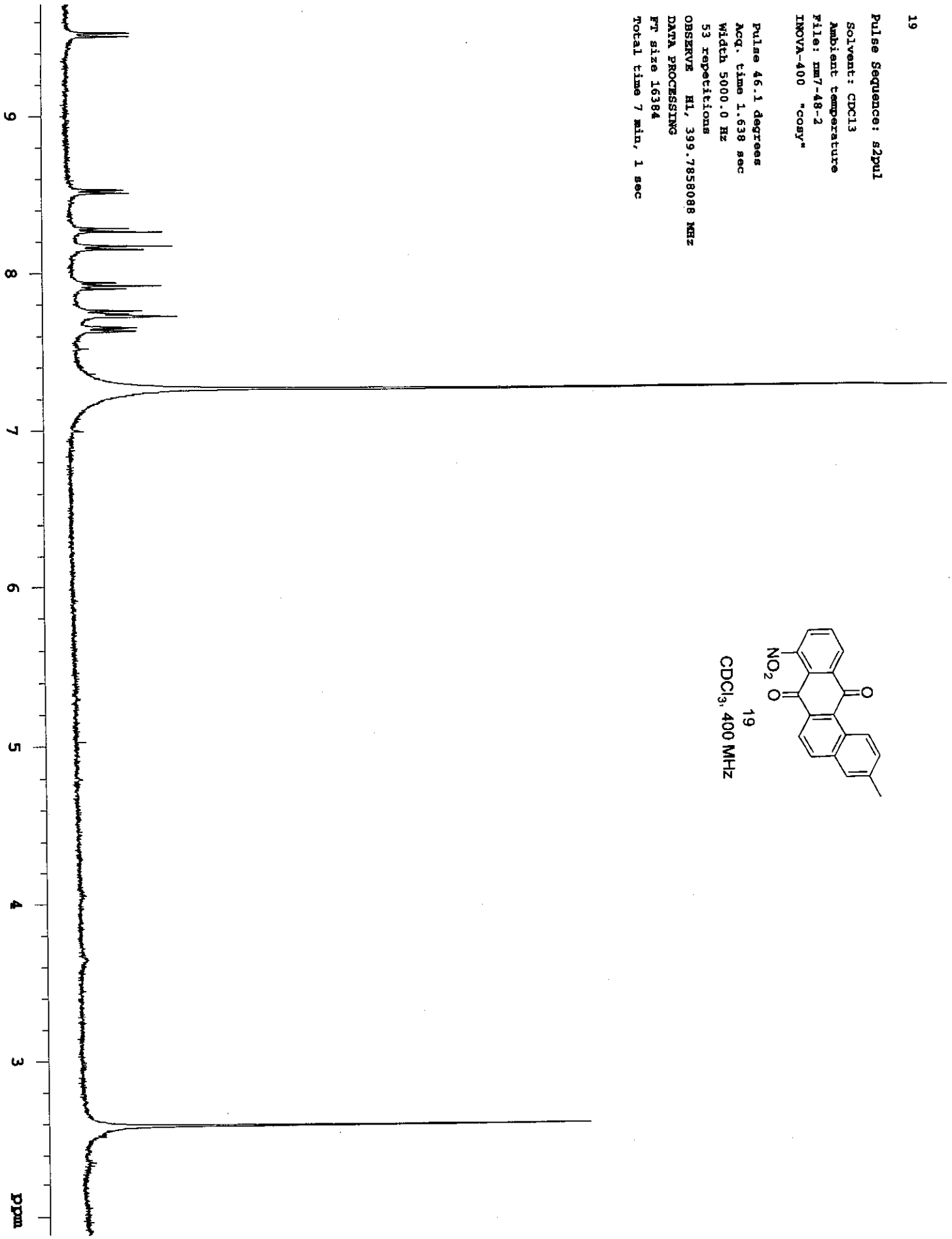
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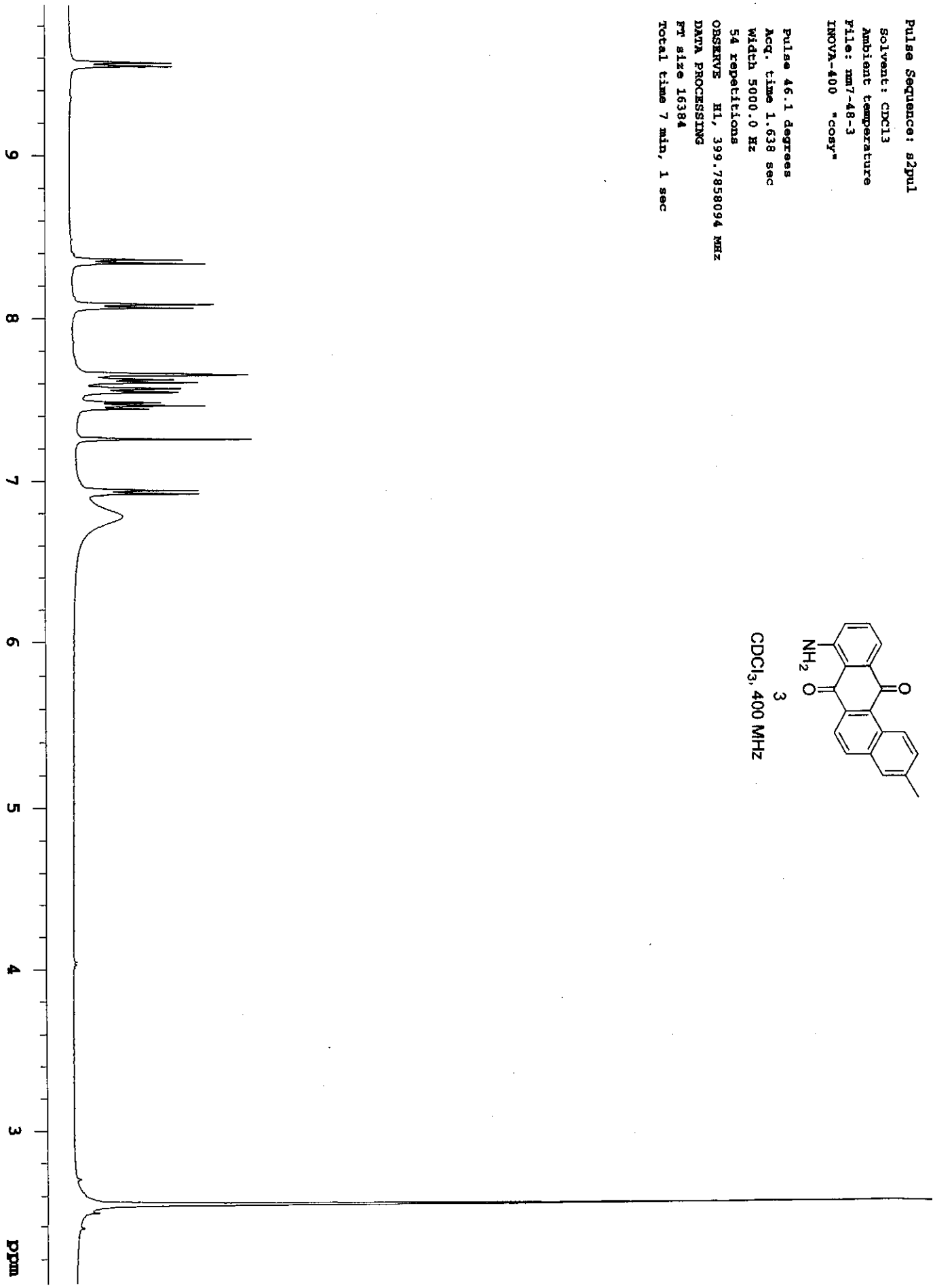
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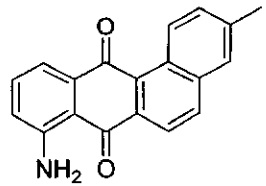
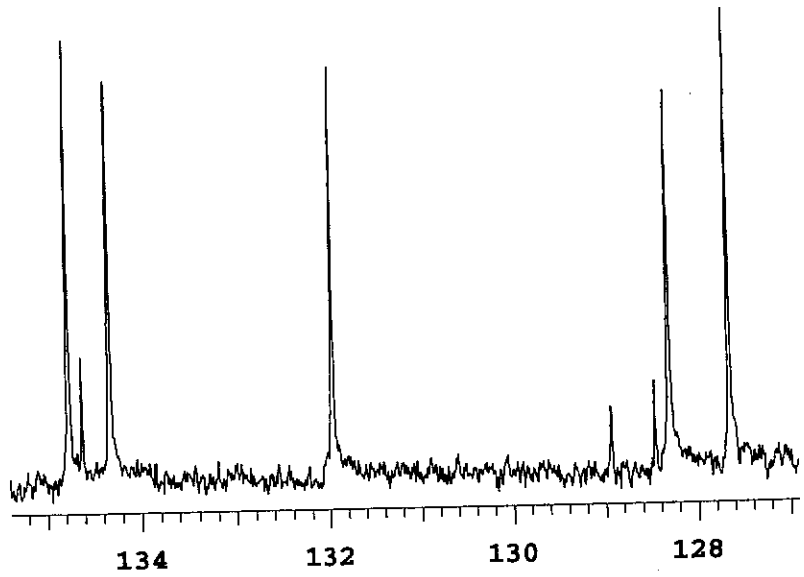
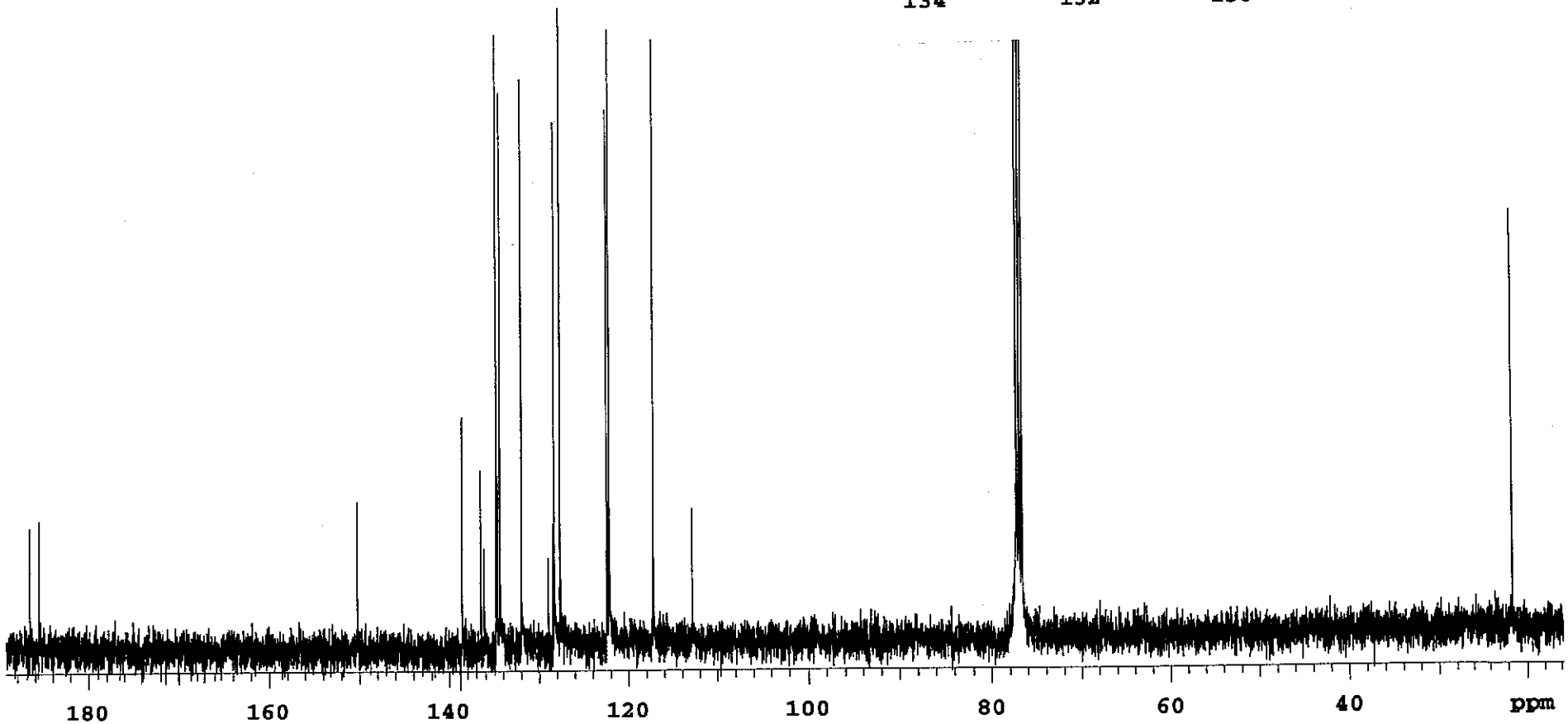


3

$CDCl_3$, 400 MHz



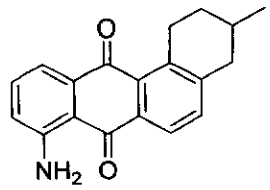


16

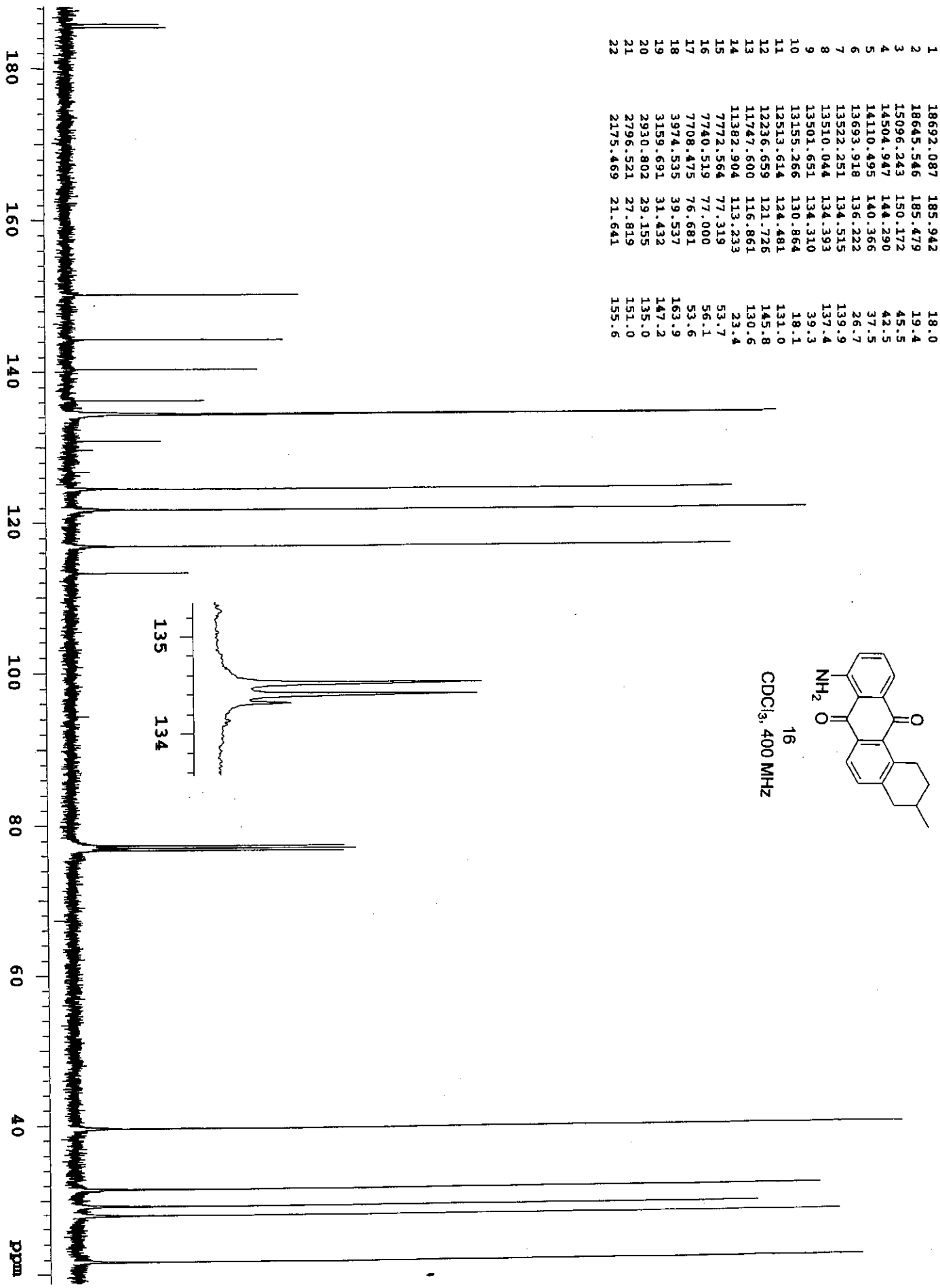
Pulse Sequence: s2pul

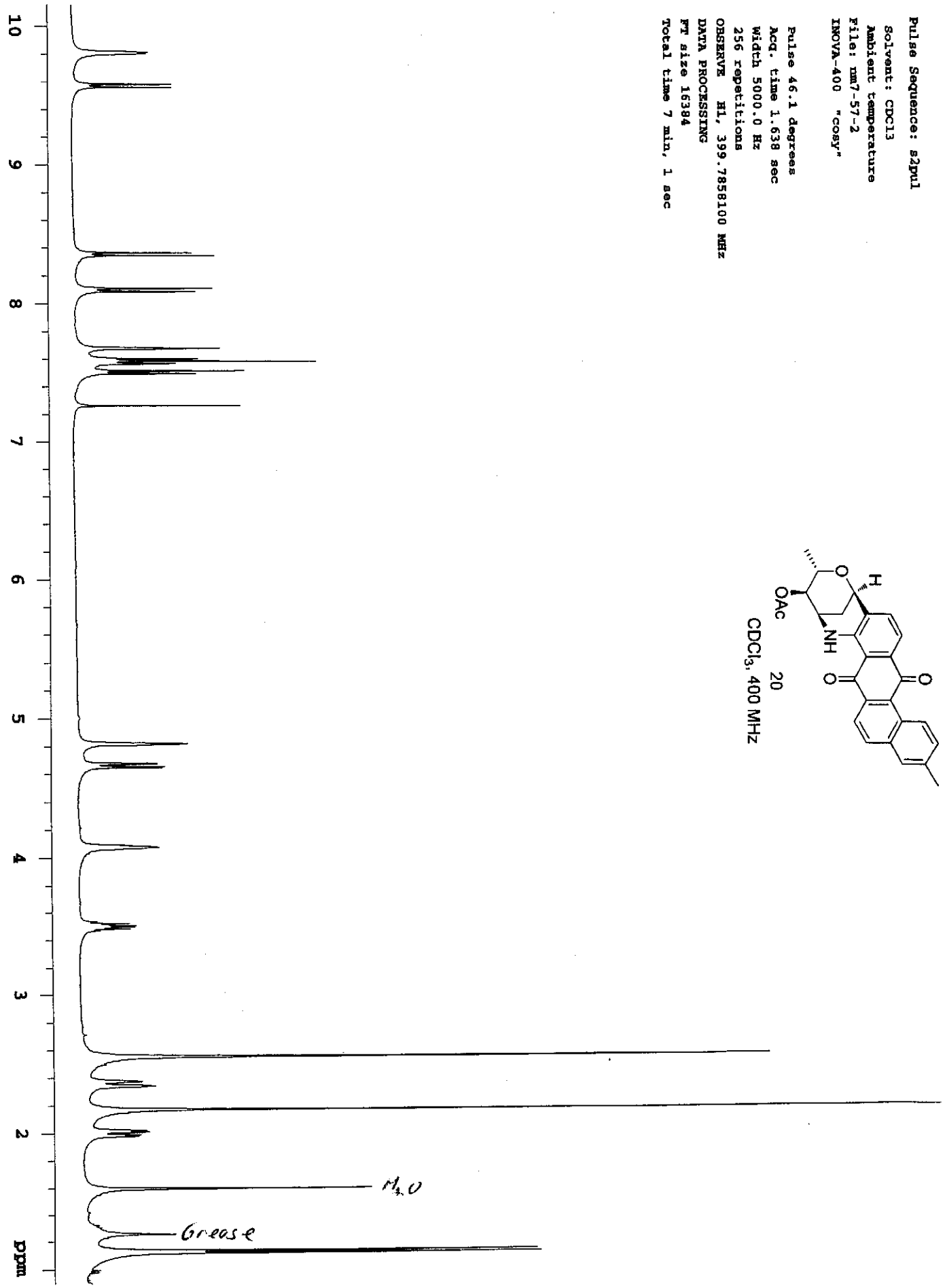
Solvent: CDCl3
Ambient temperature
File: nm7-57-1
INOVA-400 "cosy"

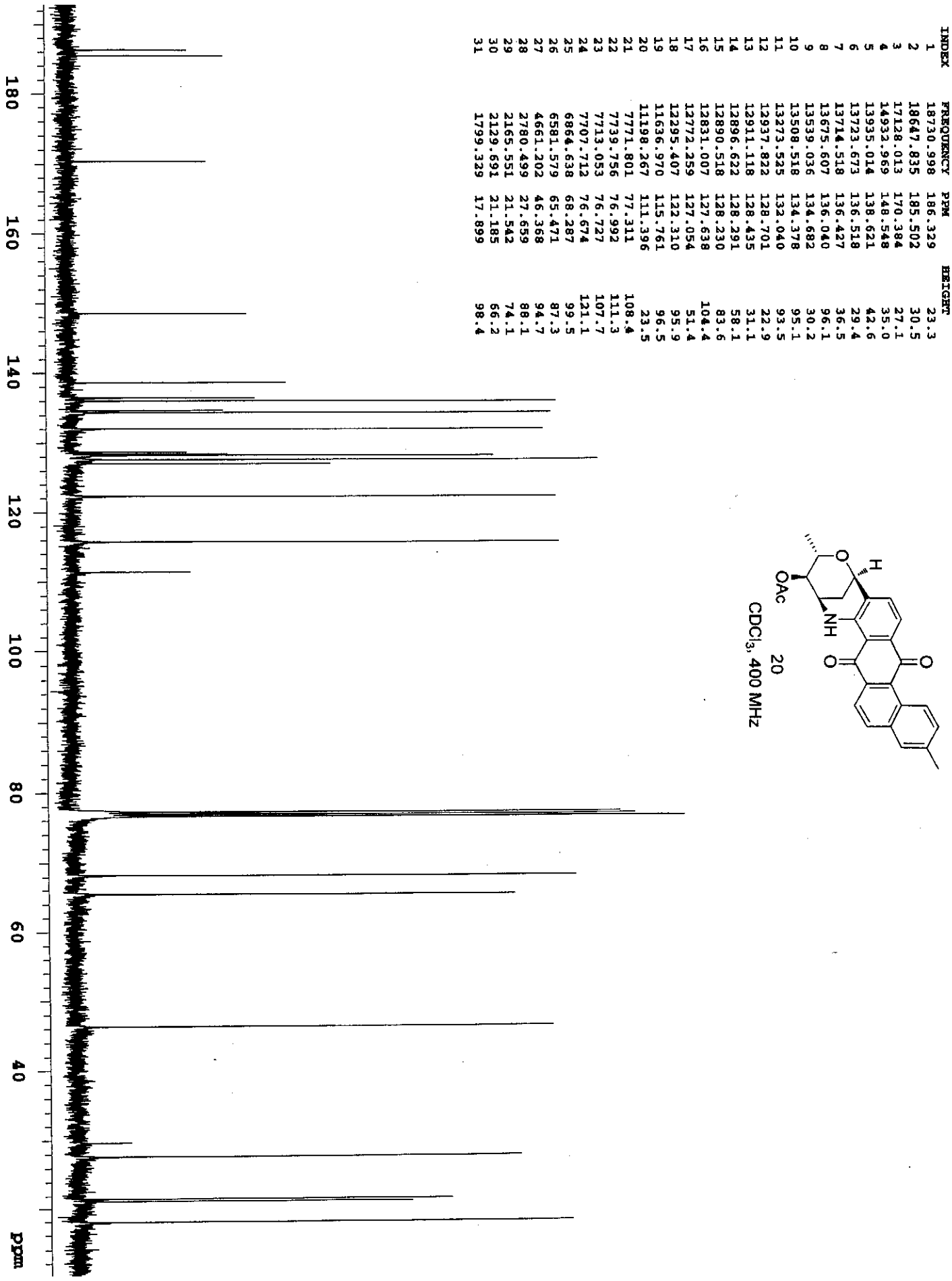
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
256 repetitions
OBSERVE H1, 399.7858088 MHz
DATA PROCESSING
FT size 16384
Total time 7 min, 1 sec

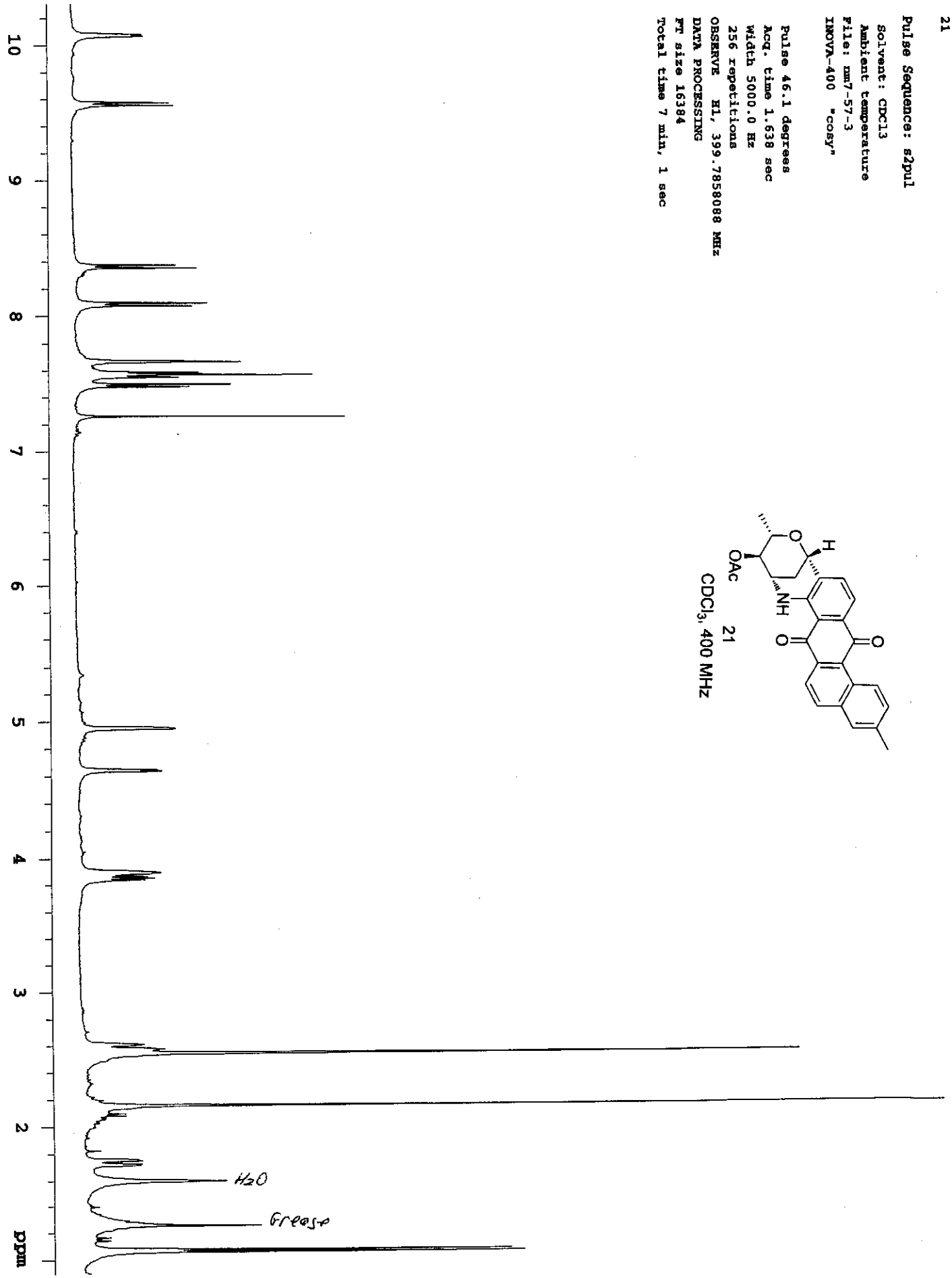


16
$CDCl_3$, 400 MHz


INDEX FREQUENCY PPM HEIGHT
1 18692.087 185.942 18.0
2 18645.546 185.479 19.4
3 15096.243 150.172 45.5
4 14504.947 144.290 42.5
5 14110.495 140.366 37.5
6 13693.918 136.222 26.7
7 13522.251 134.515 139.9
8 13510.044 134.393 137.4
9 13501.651 134.310 39.3
10 13155.266 130.864 18.1
11 12513.614 124.481 131.0
12 12236.659 121.726 145.8
13 11747.600 116.861 130.6
14 11382.904 113.233 23.4
15 7772.564 77.319 53.7
16 7740.519 77.000 56.1
17 7708.475 76.681 53.6
18 3974.535 39.537 163.9
19 3159.691 31.432 147.2
20 2930.802 29.155 135.0
21 2796.521 27.819 151.0
22 2175.469 21.641 155.6
NH2
O
O
16
CDCl3, 400 MHz
135
134
180
160
140
120
100
80
60
40
ppm


20
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: nm7-57-2
INOVA-400 "cosy"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
256 repetitions
OBSERVE H1, 399.7858100 MHz
DATA PROCESSING
FT size 16384
Total time 7 min, 1 sec
OAc
NH
O
H
20
CDCl3, 400 MHz
10
9
8
7
6
5
4
3
2
ppm
H2O
Grease


INDEX FREQUENCY PPM HEIGHT
1 18730.998 186.329 23.3
2 18647.835 185.502 30.5
3 17128.013 170.384 27.1
4 14932.969 148.548 35.0
5 13935.014 138.621 42.6
6 13723.673 136.518 29.4
7 13714.518 136.427 36.5
8 13675.607 136.040 96.1
9 13539.036 134.682 30.2
10 13508.518 134.378 95.1
11 13273.525 132.040 93.5
12 12937.822 128.701 22.9
13 12911.118 128.435 31.1
14 12896.622 128.291 58.1
15 12890.518 128.230 83.6
16 12831.007 127.638 104.4
17 12772.259 127.054 51.4
18 12295.407 122.310 95.9
19 11636.970 115.761 96.5
20 11198.267 111.396 23.5
21 7771.801 77.311 108.4
22 7739.756 76.992 111.3
23 7713.053 76.727 107.7
24 7707.712 76.674 121.1
25 6864.638 68.287 99.5
26 6581.579 65.471 87.3
27 4661.202 46.368 94.7
28 2780.499 27.659 88.1
29 2165.551 21.542 74.1
30 2129.691 21.185 66.2
31 1799.329 17.899 98.4
OAc
NH
O
H
O
O
O
20
CDCl3, 400 MHz
180
160
140
120
100
80
60
40
ppm


21
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: nm7-57-3
INOVA-400 "cosy"
Pulse 46.1 degrees
Acq. time 1.638 sec
Width 5000.0 Hz
256 repetitions
OBSERVE H1, 399.7858088 MHz
DATA PROCESSING
FT size 16384
Total time 7 min, 1 sec
H
O
NH
OAc
O
O
21
CDCl3, 400 MHz
10
9
8
7
6
5
4
3
2
ppm
H2O
Grease