10-17-00

Supporting Information

^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100.6 MHz) were recorded on a Bruker AM 400 spectrometer using the indicated solvents. ^{1}H NMR spectra (500 MHz) were recorded on a Bruker DRX 500 spectrometer. ^{13}C NMR spectra (67.5 MHz) were recorded on a Bruker AM 270 spectrometer. NMR chemical shifts are expressed in ppm upfield, relative to the internal solvent peak. High resolution mass spectra were recorded on a Finnigan MAT 95 SQ and IR spectra on a Nicolet FT-IR 750 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Melting points were determined on a *Leica* Galen III heater table microscope. Elemental analyses were recorded on a Elementar Vario El Fa. Analytik Jena. Analytical thin-layer chromatography was performed using silica gel 60 F254 precoated plates Merck, 0.25 mm thickness with a fluorescent indicator. Flash column chromatography was performed on Merck silica gel 60 (0.040-0.063 mm) using the indicated solvent. Chemicals were purchased from Aldrich or Merck and used without further purification. Metathesis reaction was performed in a Braun MB 150B-G glove box under a nitrogen atmosphere. Solvents were distilled under a nitrogen atmosphere from sodium-benzophenone (THF) or CaH_2 (CH_2Cl_2, DMF).

_N_-But-3-enyl-_N_-((1_R_,4_S_)-4-hydroxy-cyclopent-2-enyl)-2-nitro-benzenesulfonamide (5a)

To an ice-cooled solution of _N_-nosylbutenylamine (6.3 g, 0.025 mol) in DMF (100 mL) was added NaH (1.5 g as a 60% dispersion in oil, 0.037 mol). The mixture was stirred for 10 min at 0°C and 20 min at RT . A mixture of $Pd(OAc)_2$ (240 mg, 1.1 mmol), PPh_3 (1.68 g, 6.4 mmol) and **4** (3.0 g, 0.021 mol) in dry DMF (50 mL) was added in four portions. After 15 h the mixture was concentrated in vacuum, diluted with MTBE (75 mL), washed with a sat. NH_4Cl-solution (50 mL), dried ($MgSO_4$) and concentrated again. The resulting oil was chromatographed on silica gel (1:1 hexane/MTBE) to give **5a** as a colorless oil (5.9 g, 83%). $[\alpha]_D^{25}$ - 21.3° (c=1.165, $CHCl_3$).

IR ν 3542 (w), 3411 (m), 3077 (w), 2978 (m), 2945 (m), 1543 (s), 1373 (s), 1345 (s), 1161 (s), 777 (m) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (m, 1H); 7.70 (m, 2H); 7.62 (m, 1H); 6.00 (ddd, J = 6/3/3 Hz, 1H); 5.80 (m, 1H); 5.70 (m, 1H); 5.02 (m, 2H); 4.88 (m, 1H); 4.70 (m, 1H); 3.36 (ddd, J = 15/10/6 Hz, 1H); 3.18 (ddd, J = 15/10/6 Hz, 1H); 2.64 (ddd, J = 14/8/8 Hz, 1H); 2.34 (m, 2H); 1.75 (bs, 1H, OH), 1.50 (ddd, J = 14/5/5 Hz, 1H).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.9, 137.5, 134.4, 133.6, 133.3, 132.7, 131.6, 130.5, 124.0, 116.9, 74.1, 62.2, 43.7, 38.2, 35.4.

MS (EI) *m/z* (rel. intens.) 321 ($[M - OH]^+$, 4), 297 (64), 215 (100), 186 (100), 83 (88), 55 (72); HRMS calcd for $C_{15}H_{17}O_4N_2S$ $(M - OH)^+$ 321.0909; found 321.0911.

Anal. Calcd for $C_{15}H_{18}O_5N_2S$ C, 53.23; H, 5.32; N, 8.28; found C, 53.03; H, 5.63; N, 8.62.

_N_-But-3-enyl-_N_-[(1_R_,4_S_)-4-(*tert*-butyl-dimethyl-silanyloxy)-cyclopent-2-enyl]-2-nitro-benzenesulfonamide (5b).

To a solution of **5a** (5.9 g, 0.017 mol) and *tert*-butyldimethylsilyl chloride (2.88 g, 0.019 mol) in DMF (75 mL) was added imidazole (1.86 g, 0.027 mol). The mixture was stirred for 15 h at RT, concentrated in vacuum, diluted with MTBE (50 mL), washed with a saturated NH_4Cl-solution (25

mL), dried ($MgSO_4$) and concentrated again. The resulting oil was chromatographed on silica gel (4:1 hexane/MTBE) to give **5b** as a colorless solid (7.73 g, 98%). $[\alpha]_D^{25}$ - 31.8° (c=1.325, $CHCl_3$).

IR ν 3101 (w), 3067 (w), 2952 (w), 2928 (m), 1542 (s), 1372 (m), 1163 (m), 776 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (m, 1H); 7.68 (m, 2H); 7.60 (m, 1H); 5.92 (m, 1H); 5.76 (m, 1H); 5.68 (m, 1H); 5.02 (m, 2H); 4.88 (m, 1H); 4.64 (m, 1H); 3.28 (m, 2H); 2.54 (ddd, J = 15/9/8 Hz, 1H); 2.32 (m, 2H); 1.46 (ddd, J = 15/4/4 Hz, 1H); 0.96 (s, 9H); 0.06 (s, 3H); 0.04 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.8, 137.7, 134.4, 133.5, 133.0, 131.7, 131.5, 130.4, 123.8, 116.5, 74.4, 61.9, 43.1, 38.5, 35.3, 25.5, 17.7, -5.0.

MS (EI) *m/z* (relat. intens.) 437 ($[M- CH_3]^+$, 4), 395 (96), 197 (100), 73 (80);
HRMS calcd for $C_{20}H_{29}O_5N_2SSi$ $(M- CH_3)^+$ 437.1566; found 437.1566.

Anal. Calcd for $C_{21}H_{32}O_5N_2SSi$ C, 55.76; H, 7.07; N, 6.19; found C, 55.80; H, 7.08; N, 6.16.

(*R*)-6-[(*S*)-2-(*tert*-Butyl-dimethyl-silanyloxy)-but-3-enyl]-1-(2-nitro-benzenesulfonyl)-1,2,3,6-tetra-hydro-pyridine (3).

5b (3.5 g, 7.75 mmol) was dissolved in dry CH_2Cl_2 (75 mL, 0.1M) and C_2H_4 (75 mL) was bubbled slowly through the solution. **[Ru]** (65 mg, 0.08 mmol) was added and the mixture was stirred for 24 h at RT in a glovebox. The solvent was removed under vacuum and the residue was chromatographed on silica gel (4:1 hexane/MTBE) to give **3** as a colorless oil (3.3 g, 95%). $[\alpha]_D^{25}$ - 177.2° (c=0.815, $CHCl_3$).

IR ν 3092 (w), 3038 (w), 2954 (m), 2929 (m), 1546 (s), 1372 (m), 1359 (m), 1163 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 7/2 Hz, 1H); 7.63 (m, 3H); 5.78 (m, 3H); 5.18 (d, J = 17 Hz, 1H); 5.06 (d, J = 11 Hz, 1H); 4.46 (m, 1H); 4.20 (m, 1H); 3.98 (dd, J = 14/6 Hz, 1H); 3.23 (ddd, J = 14/12/4 Hz, 1H); 2.16 (m, 1H); 1.93 (ddd, J = 18/5/5 Hz, 1H); 1.86-1.70 (m, 2H); 0.92 (s, 9H); 0.06 (s, 3H); 0.02 (s, 3H).

^{13}C NMR (67.5 MHz, $CDCl_3$) δ 147.9, 140.6, 134.2, 133.3, 131.5, 130.5, 127.6, 124.8, 124.0, 114.8, 70.9, 50.9, 43.4, 38.7, 24.1, 25.8, 18.1, -3.6, -5.2.

MS (EI) *m/z* (relat. intens.) 437 ($[M- CH_3]^+$, 1), 395 (100), 267 (28), 186 (32), 75 (52);
HRMS calcd for $C_{20}H_{29}O_5N_2SSi$ $(M- CH_3)^+$ 437.1566; found 437.1567.

Anal. Calcd for $C_{21}H_{32}O_5N_2SSi$ C, 55.76; H, 7.07; N, 6.19; found C, 55.43; H, 7.05, N, 6.29.

(*R*)-6-[(*S*)-2-(*tert*-Butyl-dimethyl-silanyloxy)-but-3-enyl]-1-(benzyloxycarbonyl)-1,2,3,6-tetrahydro-pyridine (6).

To a solution of **3** (560 mg, 1.25 mmol) in DMF (20 mL) was added K_2CO_3 (345 mg, 2.5 mmol) and PhSH (137 mg, 1.37 mmol). The mixture was stirred for 4 h and heated to 45°C for a further 3 h. The solution was allowed to cool to RT and benzylchloroformiate (320 mg, 1.87 mmol) was added. After stirring overnight the mixture was diluted with MTBE (20 mL), washed with saturated NH_4Cl-solution (2*25 mL), dried ($MgSO_4$) and concentrated in vacuum. The resulting oil was

chromatographed on silica gel (4:1 hexane/MTBE) to give **6** as a colorless oil (642 mg, 82%) $[\alpha]_D^{25}$ -120.6 (c=0.35, $CHCl_3$).

IR ν 3034 (w), 2928 (m), 1701 (s), 1423 (m), 1250 (s), 1102 (m), 836 (m), 776 (m), 697 (w) cm^{-1}.

^1H NMR (400 MHz, DMSO, 80°C) δ 7.36 (m, 5H); 5.88 (ddd, J = 17/10/5 Hz, 1H); 5.80 (m, 2H); 5.18 (d, J = 17 Hz, 1H); 5.13 (s, 2H); 5.02 (d, J = 10 Hz, 1H); 4.50 (m, 1H); 4.26 (m, 1H); 4.06 (dd, J = 13/6 Hz, 1H); 2.96 (ddd, J = 13/11/4 Hz, 1H); 2.16 (m, 1H); 2.00 (d, J = 17 Hz, 1H); 1.80 (m, 1H); 1.74 (m, 1H); 0.90 (s, 9H); 0.02 (s, 3H); 0.04 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 70°C) δ 155.3, 141.0, 136.7, 128.5, 128.3, 127.7, 125.3, 124.6, 114.2, 71.1, 67.0, 49.0, 42.6, 36.9, 25.8, 24.8, 18.1, - 4.2, -5.0.

MS (EI) *m/z* (relat. intens.) 401 (M^+, 1), 344 (56), 172 (20), 91 (100);
HRMS calcd for $C_{23}H_{35}O_3NSi$ (M^+) 401.2386; found 401.2385.

Anal. Calcd for $C_{23}H_{35}O_3NSi$ C, 68.82; H, 8.73; N, 3.49; found C, 68.44; H, 8.62; N, 3.76.

(2*R*,3*R*,4*S*)-2-[(*S*)-2-(tert-Butyl-dimethyl-silanyloxy)-3,4-dihydroxy-butyl]-1-(benzyloxy carbonyl)-3,4-dihydroxy-piperidine (7).

To an ice cooled solution of **6** (450 mg, 1.12 mmol) in acetone/water 2:1 (25 mL) was added OsO_4 (14 mg, 0.05 mmol). After 10 min *N*-methylmorpholinoxide (360 mg, 2.65 mmol) was added to the brown solution in two portions. The mixture was allowed to warm up to RT and stirred overnight. Ethylacetate (25 mL) and brine (15 mL) was added to the solution and the aqueous layer was extracted three times with ethylacetate (15 mL). The combined organic layers was dried ($MgSO_4$) and concentrated in vacuum to give a dark brown oil of **7**.

IR ν 3410 (s), 2929 (s), 2857 (m), 1673 (s), 1430 (m), 1253 (m), 1083 (s), 837 (m), 776 (m), 697 (w) cm^{-1}.

^1H NMR (400 MHz, CD_3OD, 60°C, main diastereomer) δ 7.40 (m, 5H); 5.22 (s, 2H); 4.74 (ddd, J = 6/6/2 Hz, 1H); 4.20 (dd, J = 14/7 Hz, 1H); 3.88 (m, 3H); 3.76 (m, 2H); 3.60 (m, 1H); 3.12 (ddd, J = 14/13/3 Hz, 1H); 1.97 (m, 1H); 1.92 (dd, J = 7/6 Hz, 2H); 1.68 (m, 1H); 0.96 (s, 9H); 0.16 (s, 3H); 0.15 (s, 3H).

^{13}C NMR (100.6 MHz, CD_3OD, 60°C, main diastereomer) δ 157.9, 138.2, 129.4, 128.9, 128.8, 75.8, 72.4, 71.8, 68.3, 67.6, 64.3, 56.4, 39.4, 33.4 , 28.6, 26.4, 18.8, -4.2, -4.3.

MS (EI) *m/z* (relat. intens.) 412 ($[M- C_4H_9]^+$, 36), 368 (80), 206 (68), 91 (100), 73 (68);
HRMS calcd for $C_{19}H_{30}O_7NSi$ ($M- C_4H_9$)$^+$ 412.1719; found 412.1799.

***N*-(Benzyloxycarbonyl)-(3a*R*,4*R*,7a*S*)-4-{(*S*)-2-(*tert*-Butyl-dimethyl-silanyloxy)-3-hydroxy-4-[(4-methoxy-phenyl)-diphenyl-methoxy]-butyl}-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5-*c*]pyridine (8).**

The crude product **7** (~ 800mg), pyridine (670 mg, 8.5 mmol) and dimethyl-aminopyridine (47 mg, 0.43 mmol) were dissolved in CH_2Cl_2 (30 mL). 4-methoxytritylchloride (630mg, 2.0 mmol) was added in 10 portions slowly over 48 h under TLC-control. After complete conversion of **7**, the mixture was diluted with CH_2Cl_2 (30 mL), washed with a concentrated $CuSO_4$-solution (15 mL),

dried ($MgSO_4$) and concentrated in vacuum. The crude product (1.4 g) was dissolved in dimethoxypropane (30 mL) and pyridinium *p*-toluolsulfinate (20 mg) was added. The mixture was powerfully stirred for 78 h, then diluted with MTBE (10 mL) and filtered off. The solvent was removed under vacuum and the residue was chromatographed on silica gel (2:1 hexane/MTBE) to give **8** as a colorless oil (790 mg, 90% over 3 steps).

IR ν 3462 (w), 2952 (s), 2932 (s), 2893 (m), 2856 (m), 1699 (s), 1414 (m), 1251 (s), 1067 (s), 835 (m), 775 (m), 698 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, 70°C) δ 7.30 (m, 17H); 6.80 (m, 2H); 5.18 (m, 2H); 4.54 (m, 1H); 4.31 (m, 2H); 4.00- 3.60 (m, 4H); 3.80 (s, 3H); 3.22 (m, 2H); 1.86 (m, 2H); 1.62 (m, 2H); 1.4 (2s, 6H); 0.88 (3s, 9H); 0.00 (2s, 3H); -0.08 (2s, 3H).

^{13}C NMR (67.5 MHz, $CDCl_3$, RT) δ 158.6, 158.4, 147.1, 144.4, 139.2, 130.4, 129.1, 128.3, 127.9, 126.7, 113.1, 107.9, 81.6, 75.0, 70.4, 69.4, 66.9, 66.8, 66.3, 55.1, 51.8, 36.4, 36.2, 26.9, 26.8, 26.3, 25.7, 17.9, -2.1, -1.9.

MS (EI) *m/z* (relat. intens.) 725 ([M- C_4H_9]$^+$, 2), 312 (32); 273 (100), 91 (36);
HRMS calcd for $C_{42}H_{51}O_8NSi$ (M- C_4H_9)$^+$ 725.3383; found 725.3385.

_N_-(Benzyloxycarbonyl)-(3a*R*,4*R*,7a*S*)-4-[(*S*)-2-(*tert*-Butyl-dimethyl-silanyloxy)-3-oxo-propyl]-2,2-dimethyl-tetrahydro-[1,3] dioxolo [4,5-*c*]pyridine (9).

8 (100 mg, 0.13 mmol) was dissolved in Et_2O/formic acid 1:1 (10 mL) and stirred for 1 h. After complete removing of the 4-methoxytritylgroup, monitored by TLC, the mixture was cooled to 0°C and sodium periodate (42 mg, 0.2 mmol) was added. The mixture was stirred for 2 h, diluted with Et_2O (50 mL), washed with saturated $NaHCO_3$-solution (2*10 mL), dried ($MgSO_4$) and concentrated in vacuum. The residue was chromatographed on silica gel (hexane/MTBE 2:1) to give **9** as colorless oil (37mg, 61%). $[\alpha]_D^{25}$ + 14.3° (c=1.55, $CHCl_3$).

IR ν 3033 (w), 2930 (s), 2857 (m), 1736 (s), 1698 (s), 1413 (s), 1259 (s), 1212 (s), 1060 (s), 838 (s), 779 (m), 697 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$, 70°C) δ 9.58 (s, 1H); 7.36 (m, 5H); 5.17 (s, 2H); 4.60 (ddd, J = 8/6/2 Hz, 1H); 4.35 (m, 1H); 4.25 (dd, J = 6/1 Hz, 1H); 4.13 (m, 1H); 3.65 (m, 1H); 3.20 (m, 1H); 2.00 (ddd, J = 14/8/5 Hz, 1H); 1.86 (m, 3H); 1.45 (s, 3H); 1.33 (s, 3H); 0.95 (s, 9H); 0.12 (s, 3H); 0.10 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 70°C) δ 155.3, 136.8, 128.4, 127.8, 108.1, 77.2, 77.1, 74.8, 67.0, 48.8, 36.3, 26.8, 26.3, 25.6, 24.7, 18.1, -4.7, -5.0.

MS (EI) *m/z* (relat. intens.) 462 ([M-CH_3]$^+$, 20), 420 (56), 290 (76), 246 (100), 91 (100);
HRMS calcd for $C_{24}H_{36}O_6NSi$ (M- CH_3)$^+$ 462.2311; found 462.2315.

Anal. Calcd for, $C_{25}H_{39}O_6NSi*H_2O$ C, 60.60; H, 8.28; N, 2.82; found C, 60.89; H, 7.95; N, 3.17.

(3a*S*,7*S*,8a*R*,8b*R*)-7-(*tert*-Butyl-dimethyl-silanyloxy)-2,2-dimethyl-octahydro-1,3-dioxa-5a-aza-*as*-indacene (10).

To a solution of **9** (30 mg, 0.063 mmol) in dry methanol (5 mL) was added Pd/C (15 mg, 10% Pd on C). The mixture was exposed to 1 atm of hydrogen and stirred overnight. The solution was filtered of and concentrated in vacuum to give **10** as a light yellow oil (19 mg, 93%). $[\alpha]_D^{25}$ - 78.1° (c=0.6, $CHCl_3$).

IR ν 2929 (s), 2857 (m), 1379 (m), 1249 (s), 1215 (s), 1109 (s), 1064 (s), 837 (s), 776 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 4.38 (ddd, J = 12/4/2 Hz, 1H); 4.24 (ddd, J = 5.5/4/2 Hz, 1H); 3.75 (dd, J = 8/4 Hz, 1H); 3.30 (dd, J = 8/6 Hz, 1H); 2.76 (dd, J = 12/6 Hz, 1H); 2.28 (m, 2H); 2.14 (m, 2H); 2.00 (m, 2H); 1.80 (m, 1H); 1.50 (s, 3H); 1.32 (s, 3H); 0.88 (s, 9H); 0.04 (s, 3H); 0.02 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ 108.5, 79.2, 72.4, 71.1, 63.7, 63.6, 47.4, 40.6, 28.4, 26.4, 27.2, 25.9, 18.1, -4.8.

MS (EI) *m/z* (relat. intens.) 327 (M^+, 92), 312 (100), 270 (96), 212 (100), 111 (68), 82 (100);
HRMS calcd for $C_{17}H_{33}O_3NSi$ 327.2229; found 327.2229.

(2*S*,7*S*,8*R*,8a*R*)-Octahydro-indolizine-2,7,8-triol (1).

10 (20 mg, 0.66 mmol) was dissolved in acetic acid (80%) and the solution was heated to reflux for 2 h. The deep red solution was concentrated under vacuum and the residue was chromatographed on silica gel (MeOH) to give **1** as a colorless oil (5.6 mg, 53%). $[\alpha]_D^{25}$ + 35.7° (c= 1.35, $CHCl_3$).

IR ν 3340 (s), 2926 (s), 2825 (m), 1573 (m), 1406 (m), 1045 (s), 870 (w), 728 (w) cm^{-1}.

^1H NMR (500 MHz, CD_3OD) δ 4.35 (m, 1H); 3.92 (m, 1H); 3.40 (dd, J = 10/7 Hz, 1H); 3.25 (dd, J = 10/3 Hz, 1H); 2.68 (m, 2H); 2.45 (ddd, J = 12/12/3 Hz, 1H); 2.17 (dd, J = 10/5 Hz, 1H); 1.92 (ddd, J = 12/6/2 Hz, 1H); 1.85-1.70 (m, 3H).

^{13}C NMR (100.6 MHz, CD_3OD) δ 73.9, 67.9, 67.4, 62.5, 60.7, 45.4, 39.1, 30.8.

MS (EI) *m/z* (relat. intens.) 173 (M^+, 40), 156 (100), 69 (80);
HRMS calcd for $C_8H_{15}O_3N$ 173.1051; found 173.1054.

NOE (500 MHz, MeOD): 3.92 ppm (C^7-H) with 3.25 ppm (C^8-H) 5%.

(*R*)-6-[(*S*)-2-(hydroxy)-but-3-enyl]-1-(2-nitro-benzenesulfonyl)-1,2,3,6-tetrahydro-pyridine (11).

To a solution of **3** (1.0g, 2.2 mmol) in THF (20 mL) was added 1 M tetrabutylammoniumfluoride in THF (2.4 mL, 2.42 mmol). The mixture was stirred for 1 h, concentrated in vacuum and the resulting oil was chromatographed on silica gel (hexane/MTBE 1:1) to achieve **11** as a colorless oil (718 mg, 96%). $[\alpha]_D^{25}$ - 228.6° (c =0.625, $CHCl_3$).

IR ν 3540 (m), 3418 (m), 3093 (w), 2939 (m), 1543 (s), 1373 (s), 1162 (s), 1127 (m), 938 (m), 746 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 7/2 Hz, 1H); 7.70 (m, 2H); 7.65 (dd, J = 9/3 Hz, 1H); 5.90 (m, 2H); 5.76 (m, 1H); 5.28 (d, J = 17 Hz, 1H); 5.12 (d, J = 11 Hz, 1H); 4.58 (m, 1H); 4.16 (m, 1H); 3.98 (dd, J = 15/6 Hz, 1H); 3.28 (ddd, J = 15/12/4 Hz, 1H); 2.12 (m, 1H); 1.98-1.80 (m, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.6, 140.2, 133.6, 133.5, 131.7, 130.1, 126.9, 125.0, 123.8, 114.7, 69.8, 51.3, 41.8, 38.5, 23.5.

MS (EI) *m/z* (relat. intens.) 267 ([M- C_4H_7O]$^+$, 100), 186 (60), 80 (16);
HRMS calcd for $C_{11}H_{11}O_4N_2S$ 267.0439; found 267.0442.

Anal. Calcd for $C_{15}H_{18}O_5N_2S$ C, 53.25; H, 5.32; N, 8.28; found C, 53.13; H, 5.31; N, 8.29.

(*R*)-6-[1,2,3(*S*)-(trihydroxy)-butyl]-1-(2-nitro-benzenesulfonyl)-1,2,3,6-tetrahydro-pyridine (12).

To an ice cooled solution of **11** (100 mg, 0.3 mmol) in acetone/water 2:1 (12 mL) was added OsO_4 (7 mg, 0.03 mmol). After 10 min *N*-methylmorpholinoxide (44 mg, 0.33 mmol) was added to the brown solution in one portion. The mixture was allowed to warm up to RT and stirred overnight. Ethylacetate (10 mL) and brine (5 mL) were added to the solution and the aqueous layer was extracted three times with ethylacetate (15 mL). The combined organic layers were dried ($MgSO_4$), concentrated in vacuum and the resulting oil was chromatographed on silica gel (ethylacetate) to give **12** as a colorless oil (66 mg, 60%).

IR ν 3383 (s), 3096 (w), 2928 (m), 1543 (s), 1373 (m), 1162 (s), 746 (m) cm^{-1}.

^1H NMR (400 MHz, CD_3OD) δ 8.06 (dd, J = 7/2 Hz, 1H); 7.74 (m, 3H); 5.88 (m, 1H); 5.74 (dd, J = 10/5 Hz, 1H); 4.68 (bs, 1H); 3.94 (dd, J = 14.5/6 Hz, 1H); 3.70 (dd, J = 11/3.5 Hz, 1H); 3.64 (ddd, J = 10/6.5/3.5 Hz, 1H); 3.56 (dd, J = 11/6.5 Hz, 1H); 3.42 (m, 1H); 3.28 (ddd, J = 15/12/4 Hz, 1H); 2.08 (ddd, J = 14/10/3 Hz, 1H; m, 1H); 1.94 (ddd, J = 18/4/4 Hz, 1H); 1.74 (ddd, J = 14/10/6 Hz, 1H).

^{13}C NMR (100.6 MHz, CD_3OD) δ 149.7, 135.3, 133.4, 128.3, 135.4, 131.7, 126.8, 125.6, 76.9, 70.7, 64.8, 53.1, 40.1, 40.0, 25.4.

MS (EI) *m/z* (relat. intens.) 355 ([M-OH]$^+$, 1), 267 (100), 186 (100), 80 (26);
HRMS calcd for $C_{15}H_{19}O_6N_2S$ 355.0963; found 355.0963.

Anal. Calcd for $C_{15}H_{20}O_7N_2S$ C, 48.38; H, 5.37; N, 7.52; found C, 48.57; H, 5.50; N, 7.12.

(*R*)-6-[1,2,3(*S*)-(trihydroxy)-butyl]-1,2,3,6-tetrahydro-pyridine (13).

To a solution of **12** (900 mg, 2.42 mmol) in DMF (30 mL) was added K_2CO_3 (660 mg, 4.84 mmol) and PhSH (292 mg, 2.66 mmol). The mixture was stirred for 12 h and heated to 45°C for a further 2 h. The mixture was diluted with MTBE and extracted twice with 1 M aqueous hydrochloric acid (2*25 mL). The combined aqueous layers was washed with MTBE (3*15 mL), neutralized and concentrated in vacuum. The residue was chromatographed on silica gel (MeOH) to give **13** as a colorless oil (407 mg, 90%).

IR ν 3368 (s), 2960 (m), 2769 (s), 2446 (m), 1466 (m), 1209 (m), 1021 (m) cm^{-1}.

^1H NMR (400 MHz, CD_3OD) δ 5.98 (m, 1H); 5.76 (dd, J = 10 Hz, 1H); 4.04 (m, 1H); 3.84 (ddd, J = 9/6/2.5 Hz, 1H); 3.68 (dd, J = 11/4.5 Hz, 1H); 3.60 (ddd, J = 11/5 Hz, 1H); 3.52 (m, 1H); 3.40 (ddd, J = 13/5/5 Hz, 1H); 3.24 (ddd, J = 13/8/6 Hz, 1H); 2.38 (m, 2H); 2.04 (ddd, J = 15/5/2.5 Hz, 1H); 1.84 (ddd, J = 15/10/8 Hz, 1H).

^{13}C NMR (100.6 MHz, CD_3OD) δ 127.1, 126.1, 76.3, 71.4 , 64.3, 53.7, 40.9, 36.9, 22.8.

MS (EI) *m/z* (relat. intens.) (product acetylized) 355 (M^+ ,1), 312 (32), 124 (100), 82 (100);
HRMS calcd for $C_{17}H_{25}O_7N$ 355.1631; found 355.1635.

(2*S*,3*R*,9a*R*)-1,3,4,6,7,9a-Hexahydro-2*H*-quinolizine-2,3-diol (14).

To an ice-cooled solution of **13** (300 mg, 1.6 mmol) in dry pyridine was added PPh_3 (420 mg, 1.6 mmol) and then azodicarboxyclic acid diethylester (280 mg, 1.6 mmol) slowly via a syringe. The mixture was stirred for 18 h, concentrated in vacuum and the residue was chromatographed on silica gel (ethylacetate/MeOH 2:1) to afford **14** as a colorless solid (143 mg, 53%). $[\alpha]_D^{25}$ + 40.0° (c=0.864, Methanol).

IR ν 3334 (s), 2916 (s), 2832 (m), 1128 (m), 1068 (s), 1049 (s), 788 (m), 667 (m) cm^{-1}.

^1H NMR (400 MHz, CD_3OD) δ 5.74 (m, 1H); 5.44 (m, 1H); 3.99 (m, 1H); 3.77 (ddd, J = 11/5/3 Hz, 1H); 3.01 (d, J = 13 Hz, 1H); 2.86 (dd, J = 11/6 Hz, 1H); 2.71 (dd, J = 11/5 Hz, 1H); 2.52 (m, 2H); 2.38 (m, 1H); 2.05 (m, 1H); 1.83 (ddd, J = 14/3/3 Hz, 1H); 1.50 (ddd, J = 14/12/3 Hz, 1H).

^{13}C NMR (100.6 MHz, CD_3OD) δ 127.7, 125.3, 67.6, 67.0, 54.9, 53.9, 51.2, 36.2, 24.7.

MS (EI) *m/z* (relat. intens.) 169 (M+, 100), 124 (24), 81 (60);
HRMS calcd for $C_9H_{15}O_2N$ 169.1102; found 169.1107.

NOE (500 MHz, MeOD): 3.99 ppm (C^2-H) with 3.77 ppm (C^3-H) 4%; 3.99 ppm (C^2-H) with 1.50 ppm (C^1-Ha) 2.5%; 3.01 ppm (C^{9a}-H) with 1.83 ppm (C^1-Hb) 2%.

(1*R*,2*S*,7*R*,8*S*,9a*R*)-Octahydro-quinolizine-1,2,7,8-tetraol (2).

To an ice cooled solution of **14** (20 mg, 0.12 mmol) in acetone/water 2:1 (3 mL) was added OsO_4.(1 mg, 0.004 mmol). After 10 min *N*-methylmorpholinoxide (17 mg, 0.12 mmol) was added to the brown solution. The mixture was allowed to warm up to RT and stirred overnight. Ethylacetate (5 mL) and brine (5 mL) were added to the solution and the aqueous layer was extracted five times with ethylacetate (20 mL). The combined organic layers were dried ($MgSO_4$), concentrated in vacuum and the resulting oil was chromatographed on silica gel (MeOH) to give **2** as a colorless oil (19 mg, 81%). $[\alpha]_D^{25}$ + 58.1° (c= 1.19, methanol).

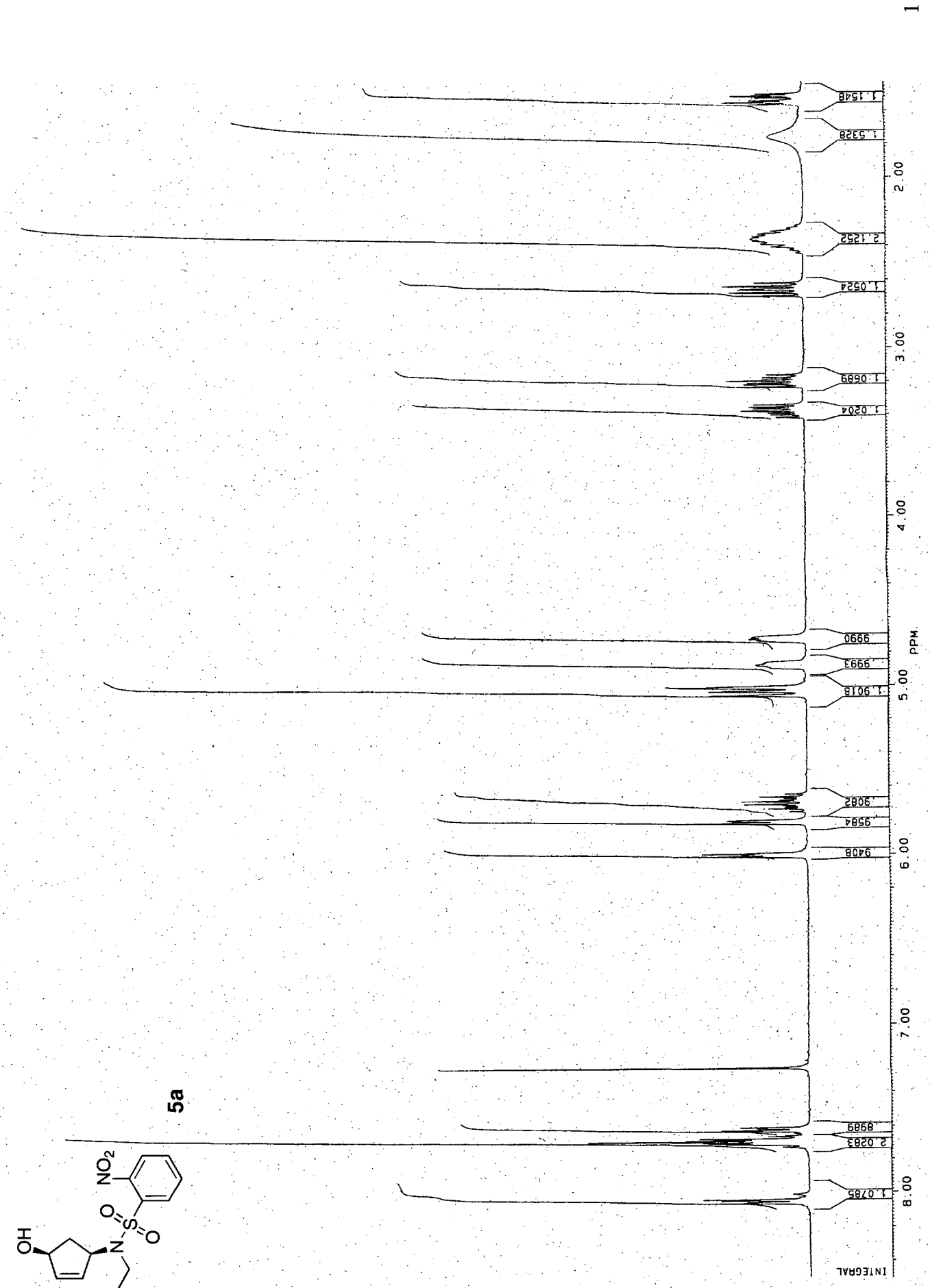
IR ν 3342 (s), 2920 (s), 1069 (s), 994 (m) cm^{-1}.

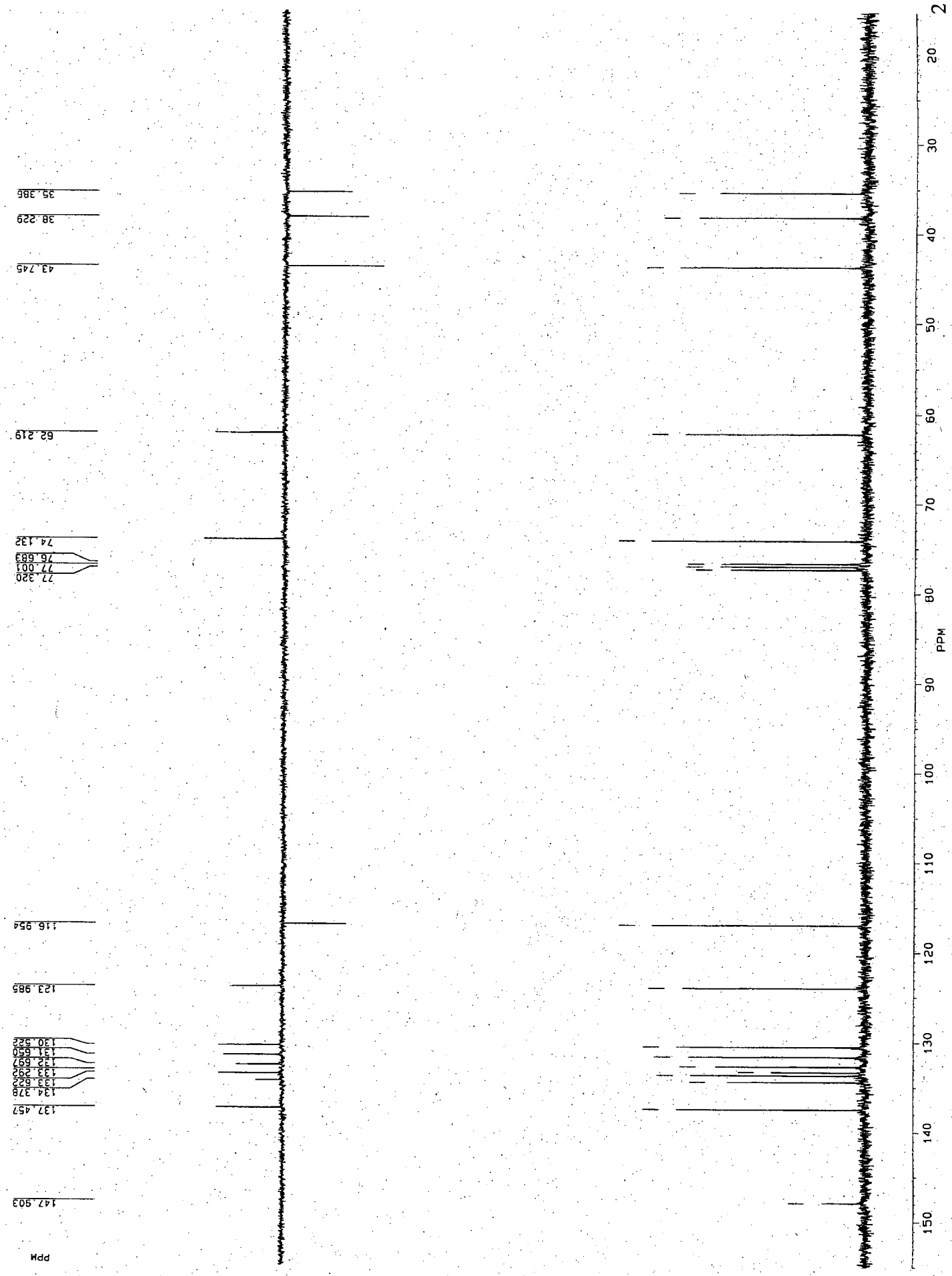
^{1}H NMR (500 MHz, CD_3OD) δ 3.95 (m, 1H); 3.90 (m, 1H); 3.65 (ddd, J = 11/4.5/3 Hz, 1H); 3.12 (dd, J = 10/3 Hz, 1H); 2.60 (dd, J = 11/4.5 Hz, 1H); 2.53 (m, 2H); 2.47 (m, 1H); 2.42 (dd, J = 11/11 Hz, 1H); 2.26 (ddd, J = 14/3/3 Hz, 1H); 1.77 (m, 2H); 1.28 (ddd, J = 13/11/2 Hz, 1 H).

^{13}C NMR (100.6 MHz, CD_3OD) δ 73.3, 68.2, 67.3, 66.9, 54.7, 53.9, 48.6, 34.1, 30.0.

MS (EI) *m/z* (relat. intens.) 203 (M+, 40), 186 (100), 129 (60), 56 (60);
HRMS calcd for $C_9H_{17}O_4N$ 203.1157; found 203.1155.

NOE (500 MHz, MeOD): 3.95 ppm (C^8-H) with 3.65 ppm (C^7-H) 4%; 3.90 ppm (C^2-H) with 3.12 ppm (C^1-H) 4%.

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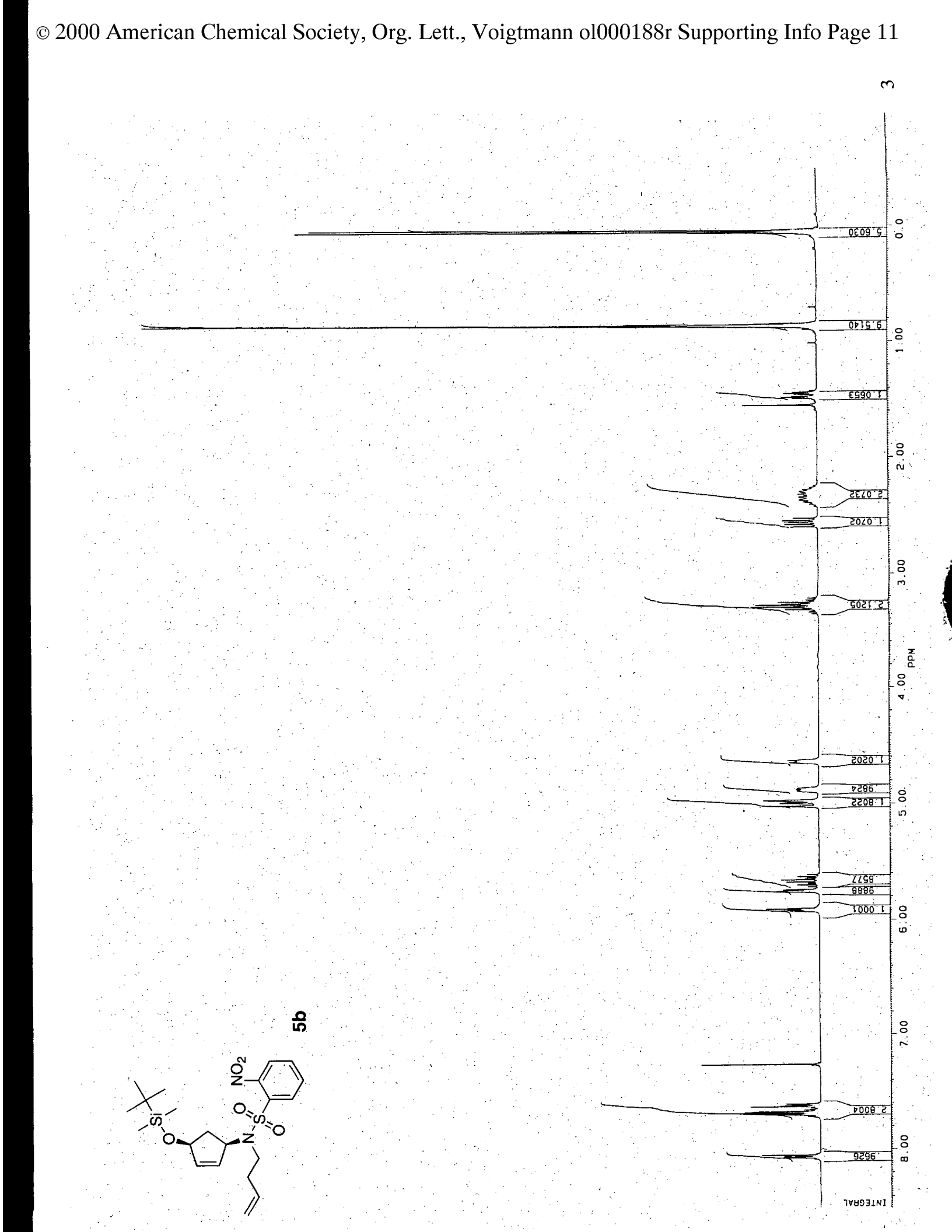
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5b

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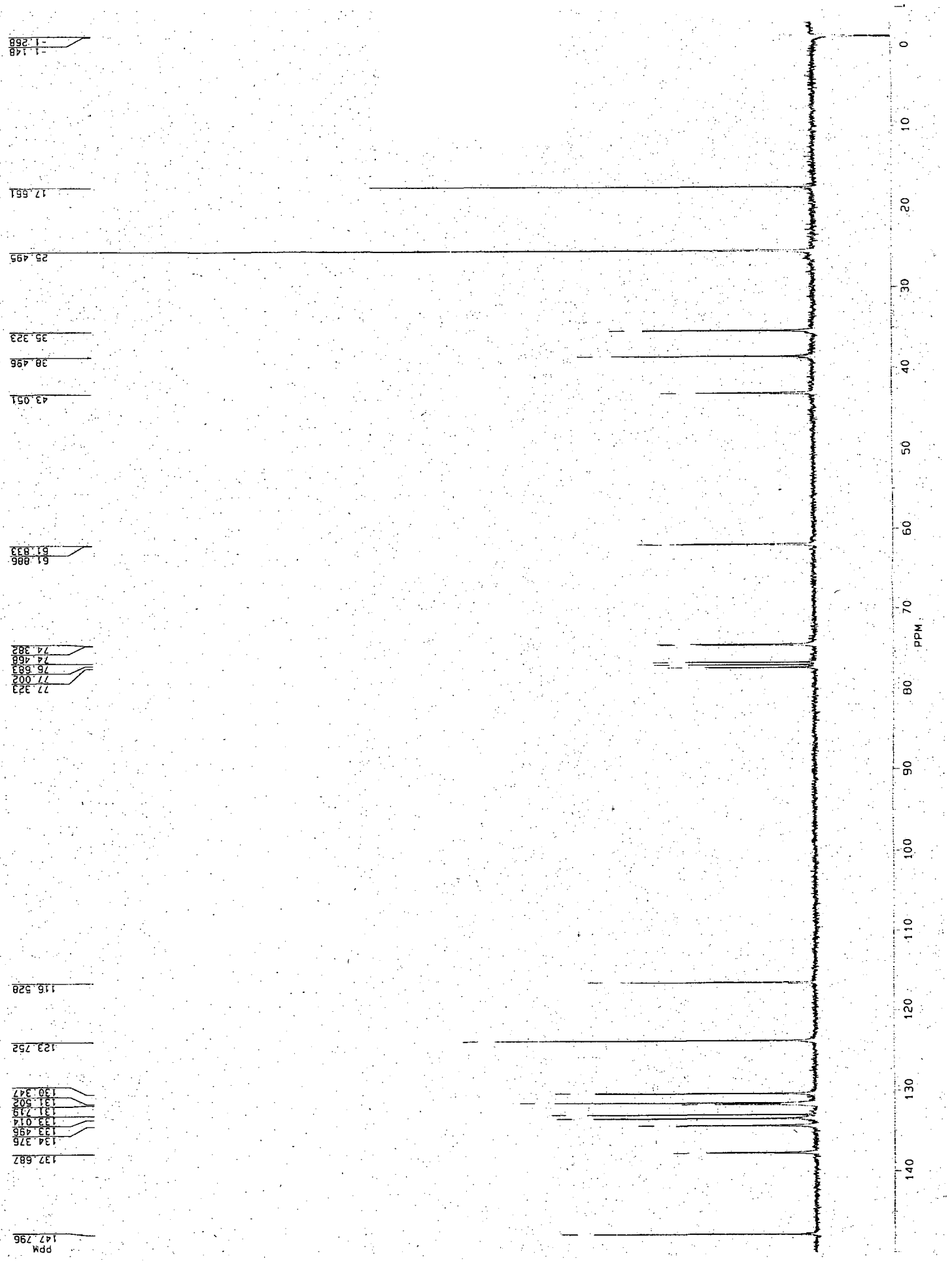
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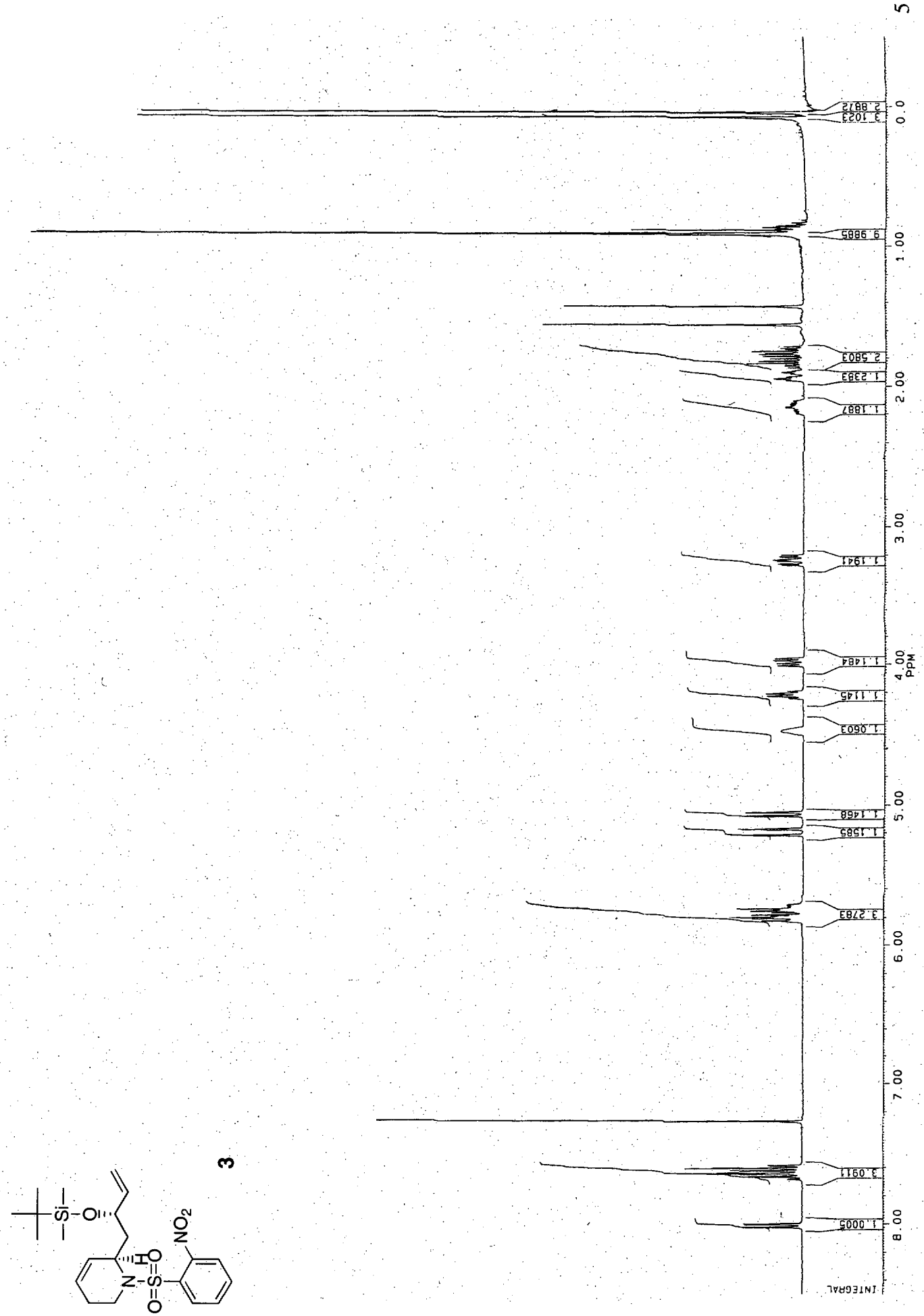

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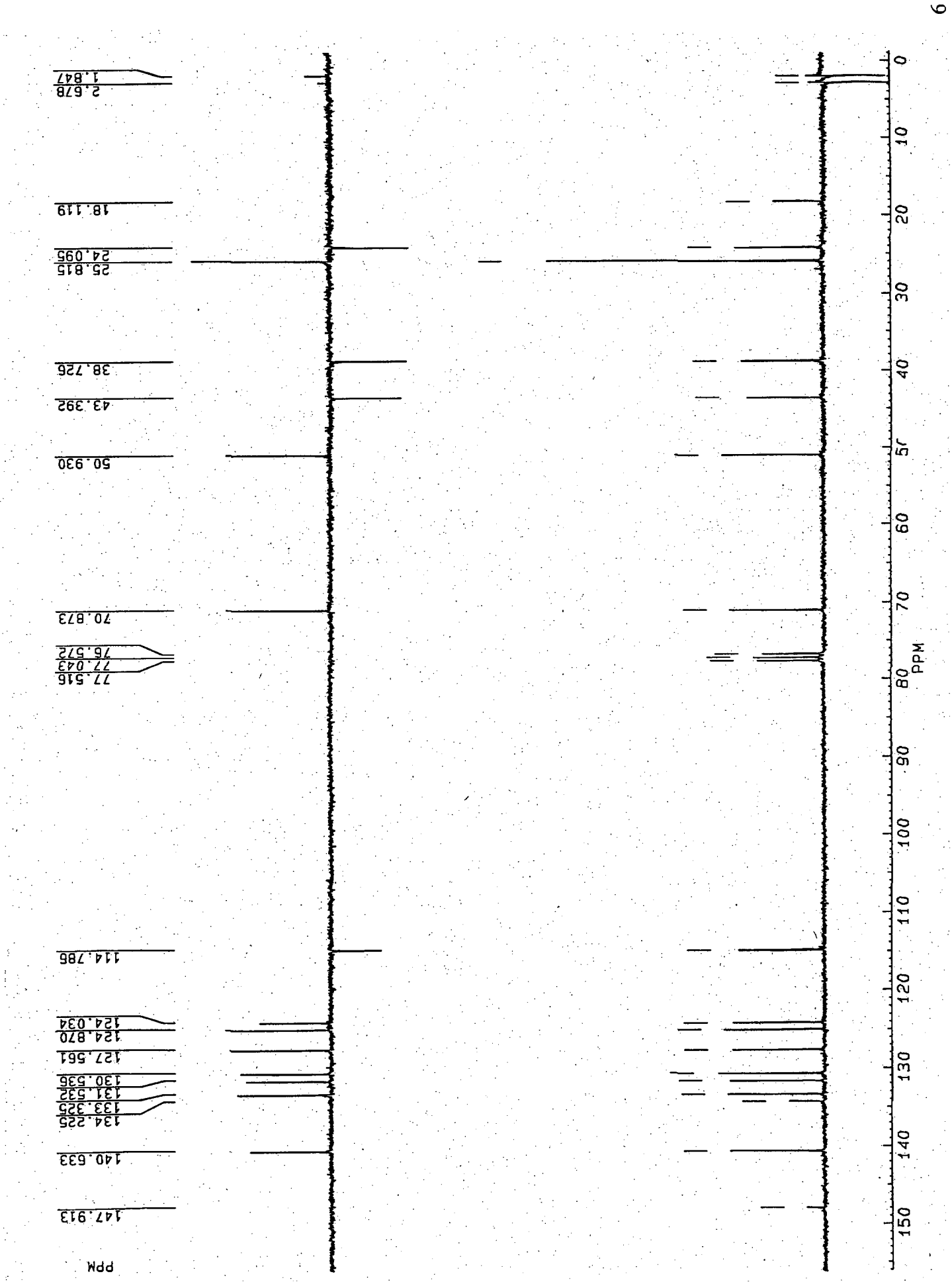

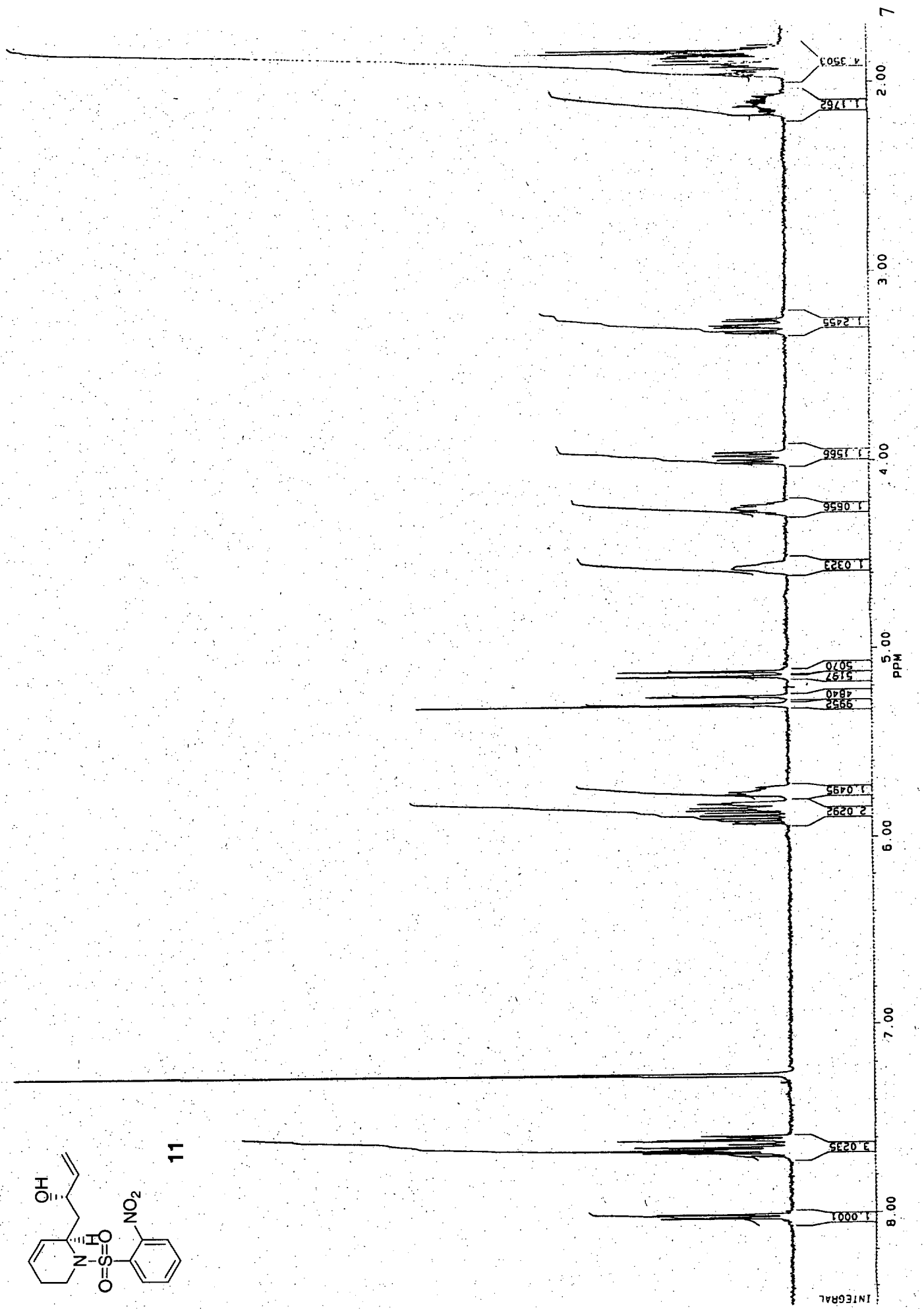
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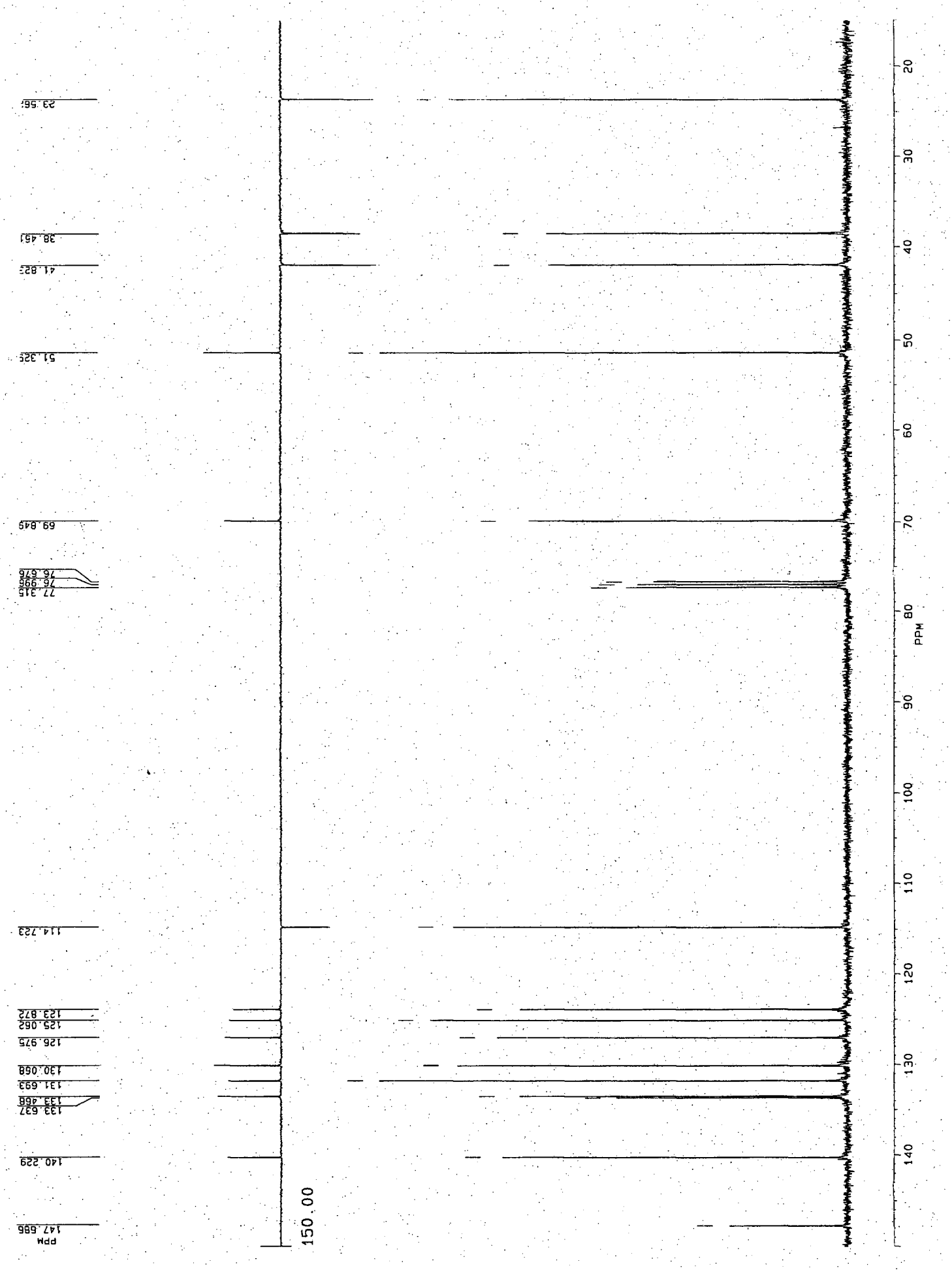
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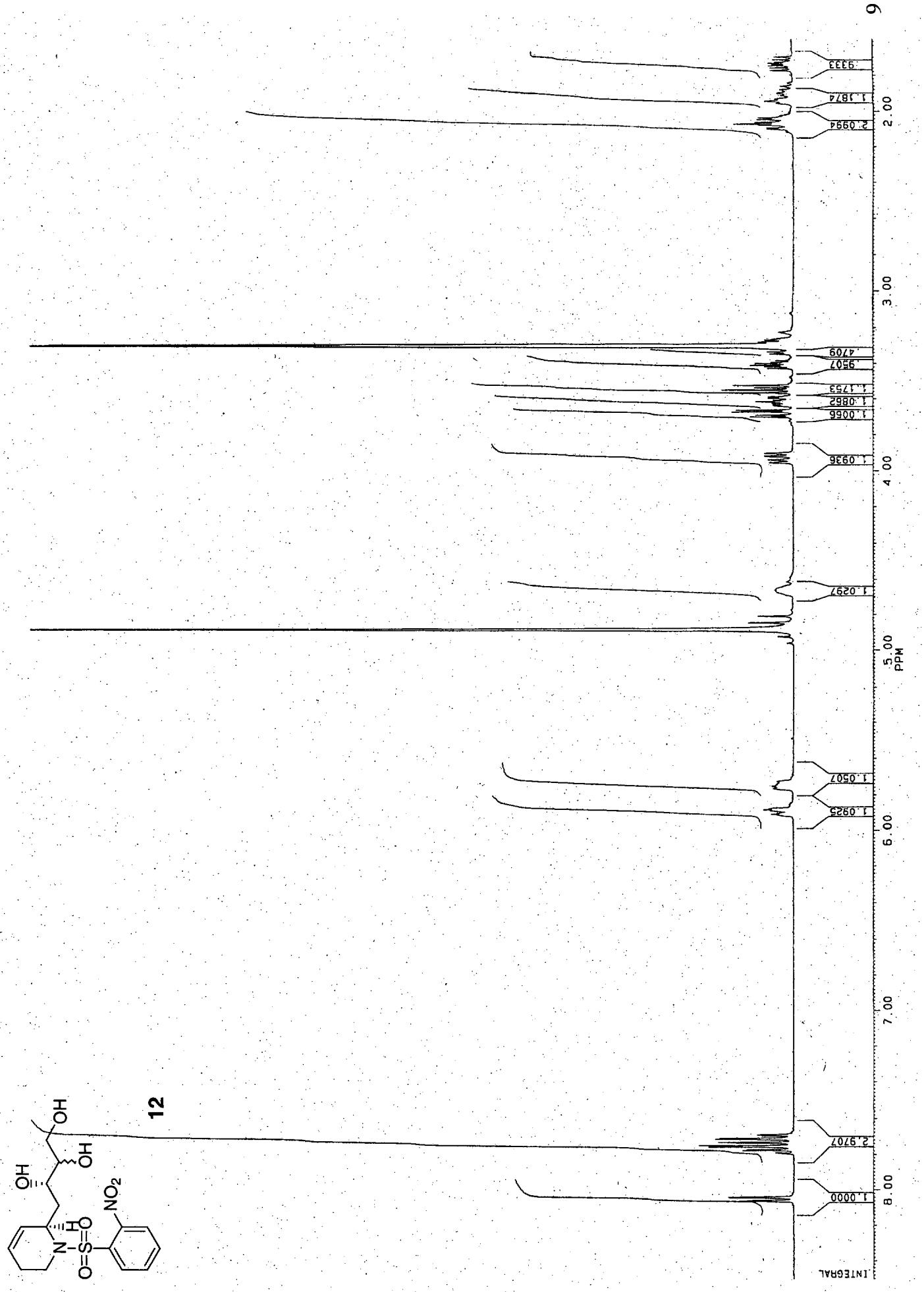
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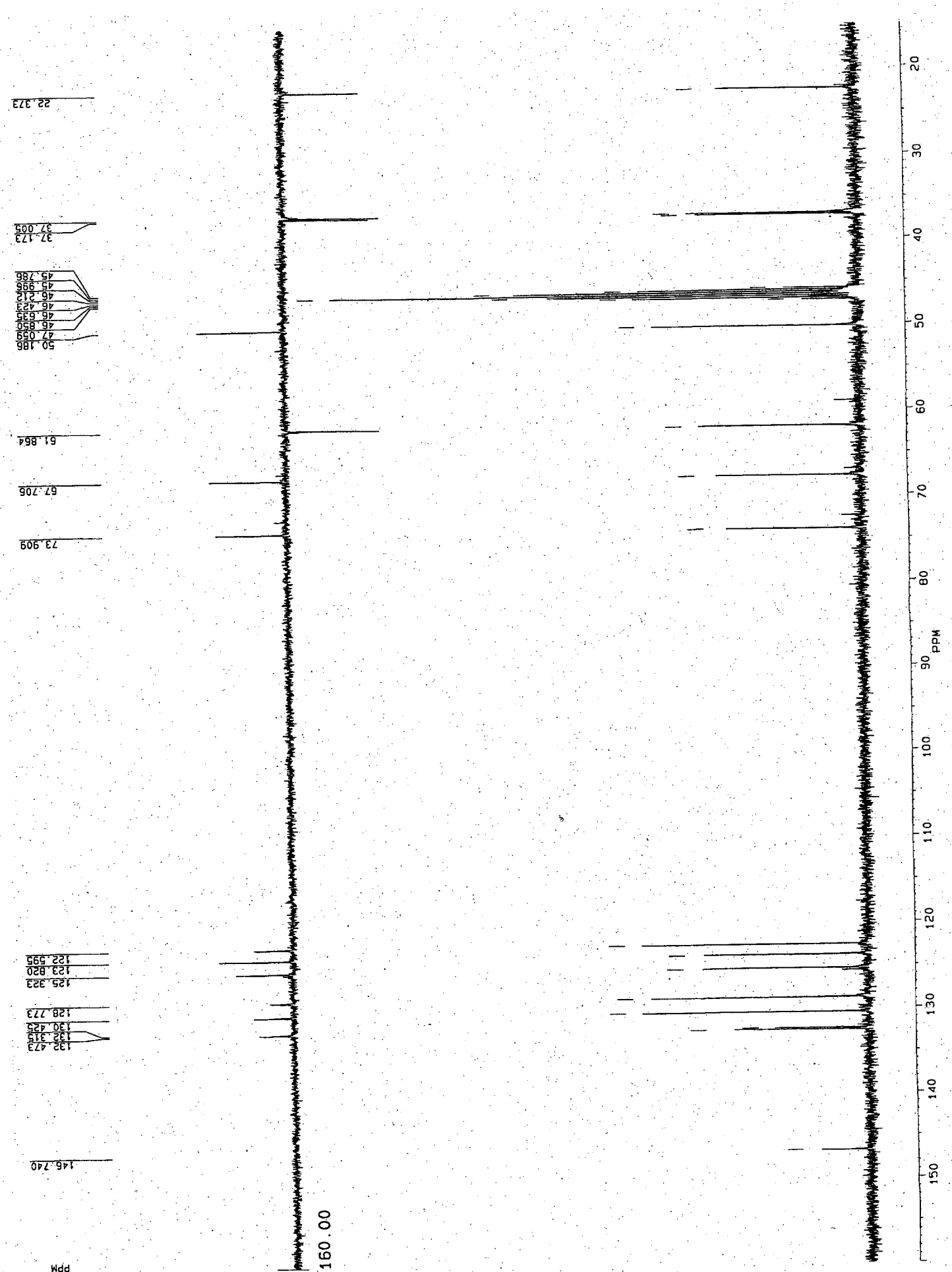
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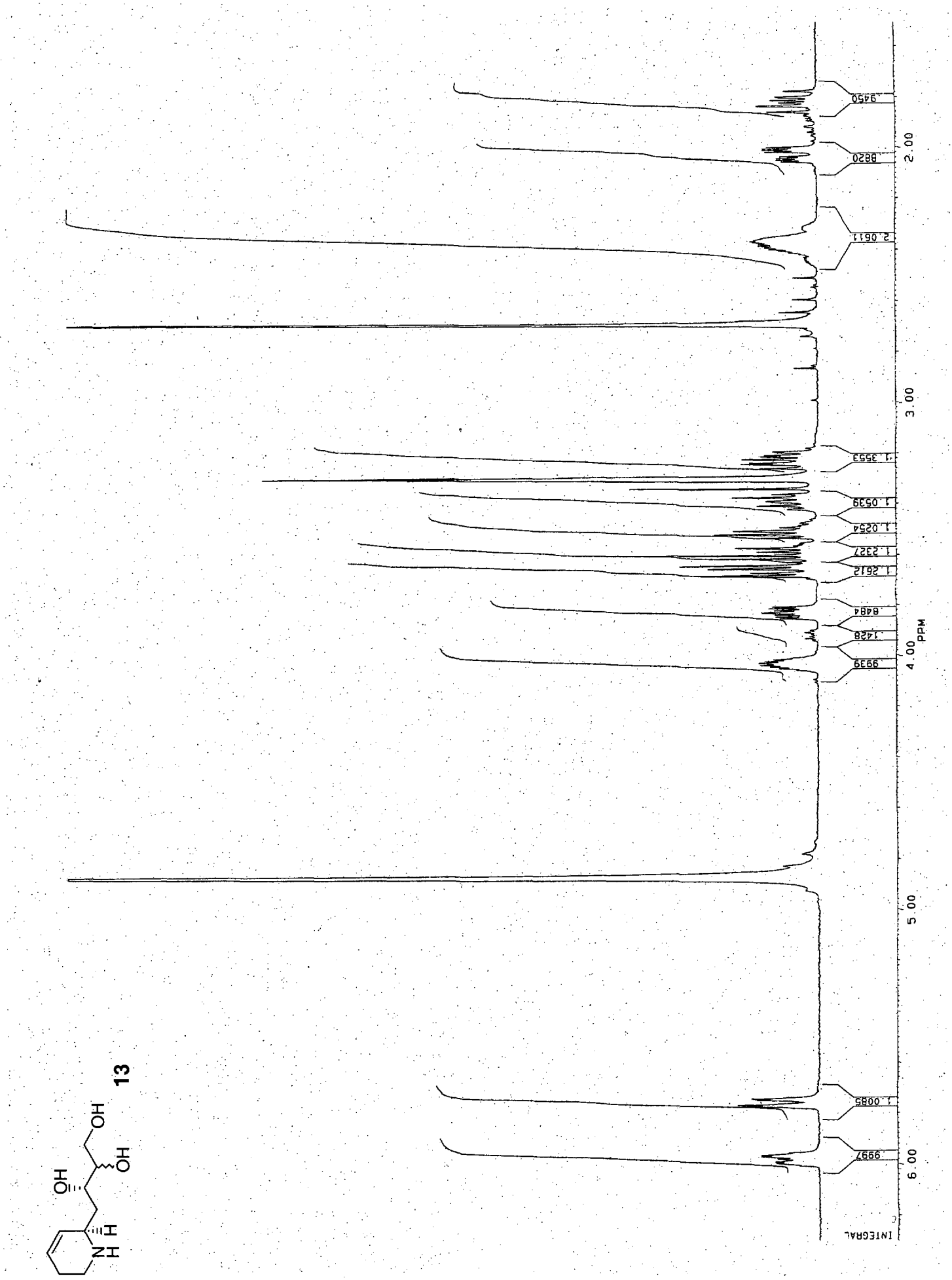
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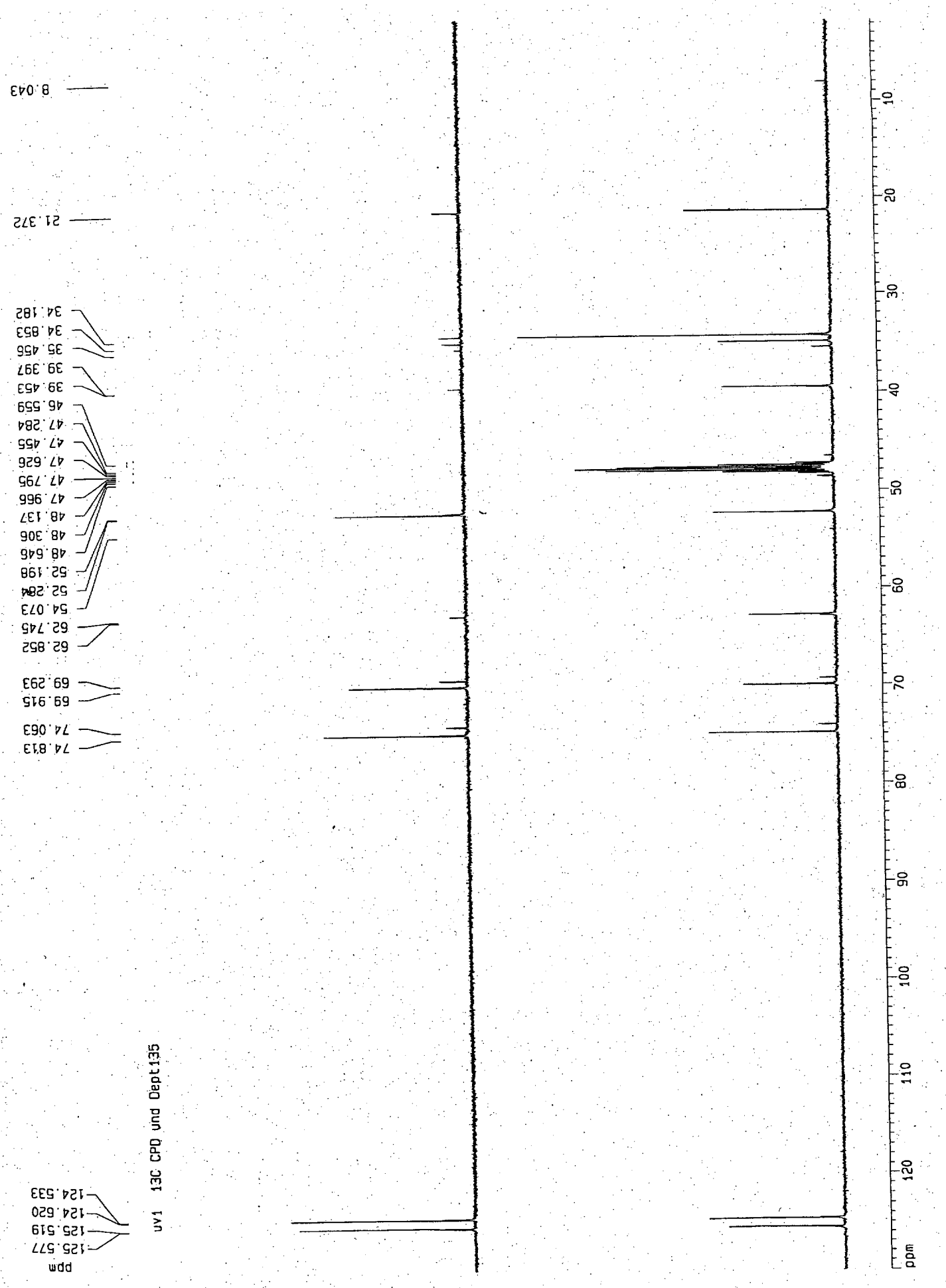
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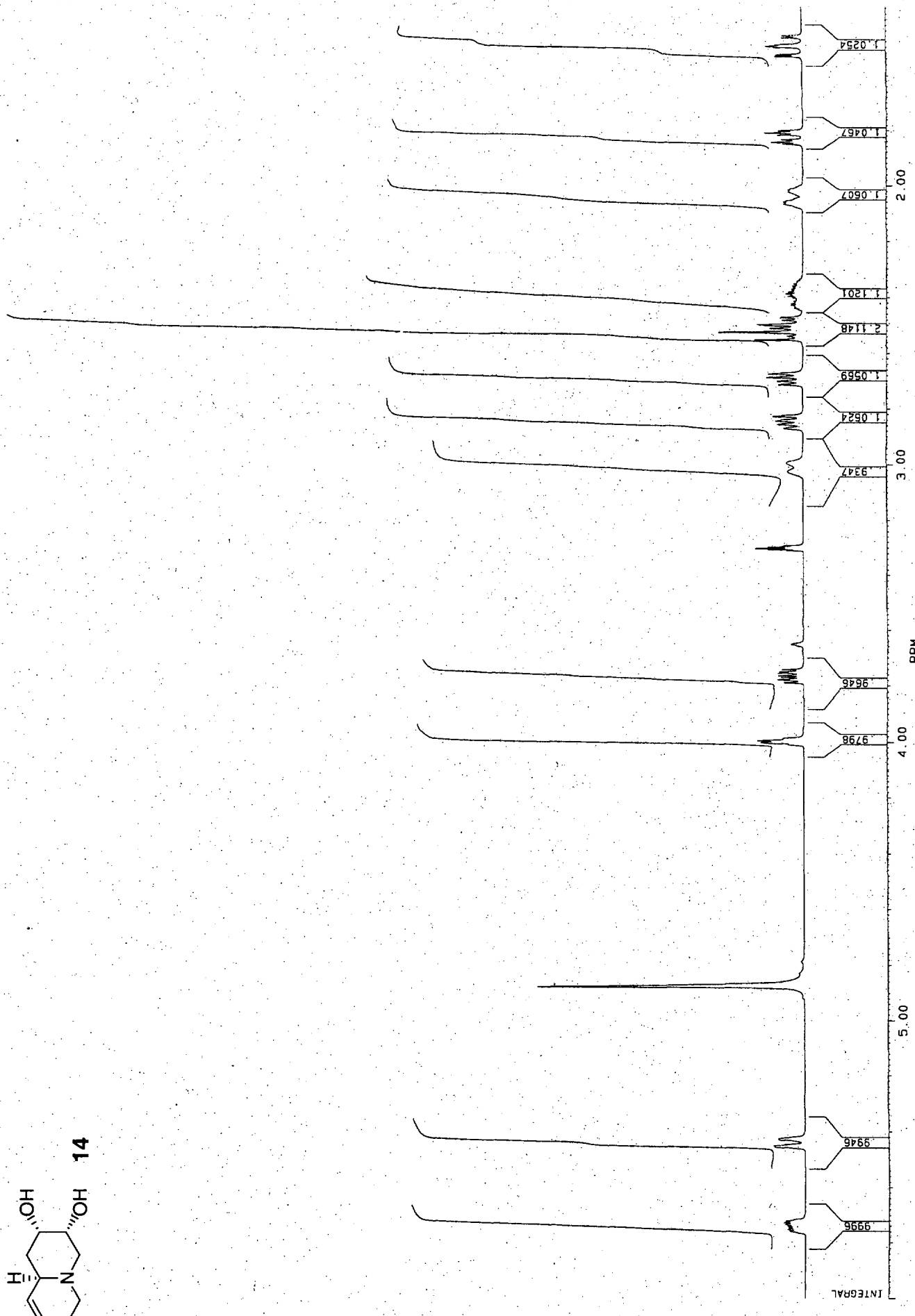
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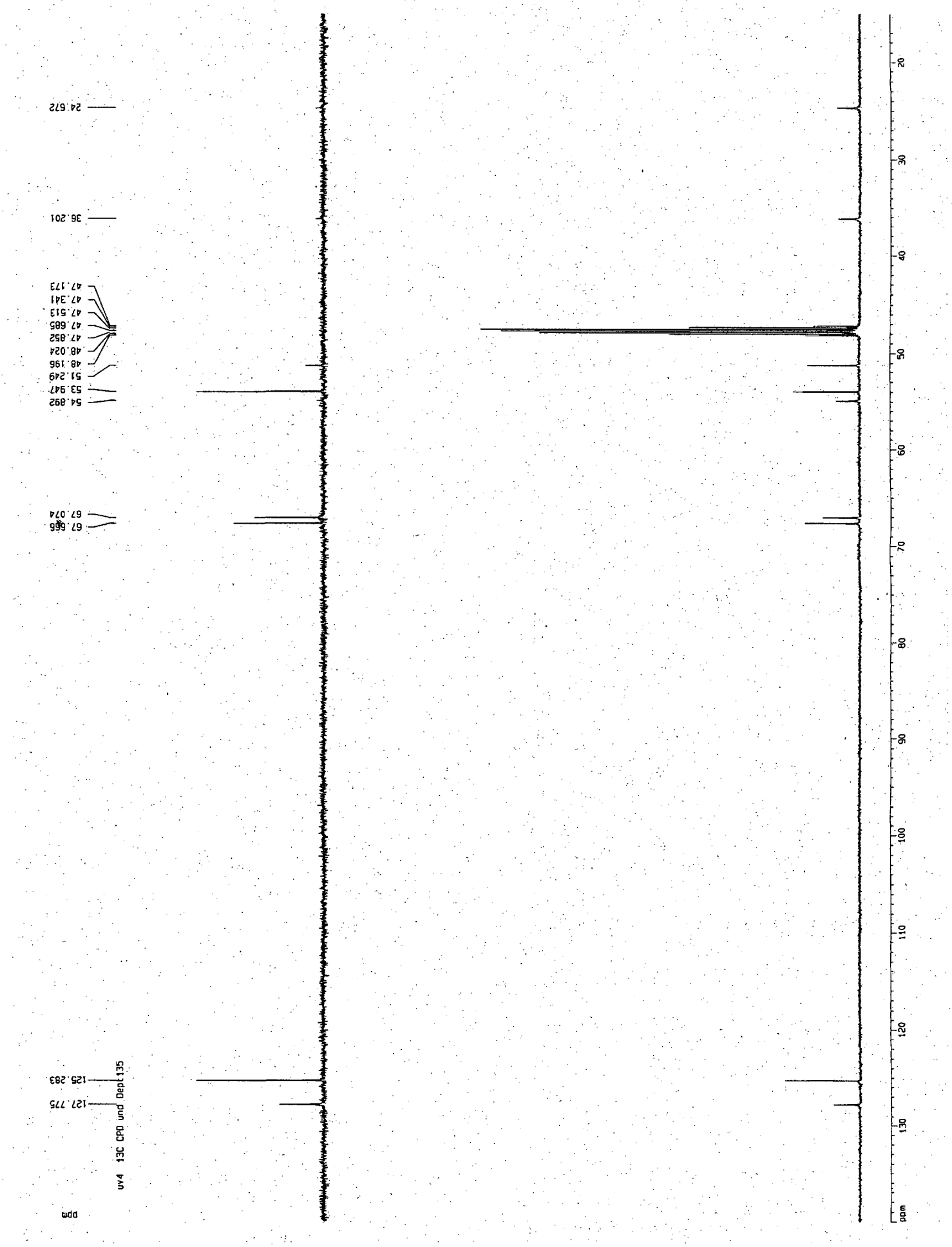
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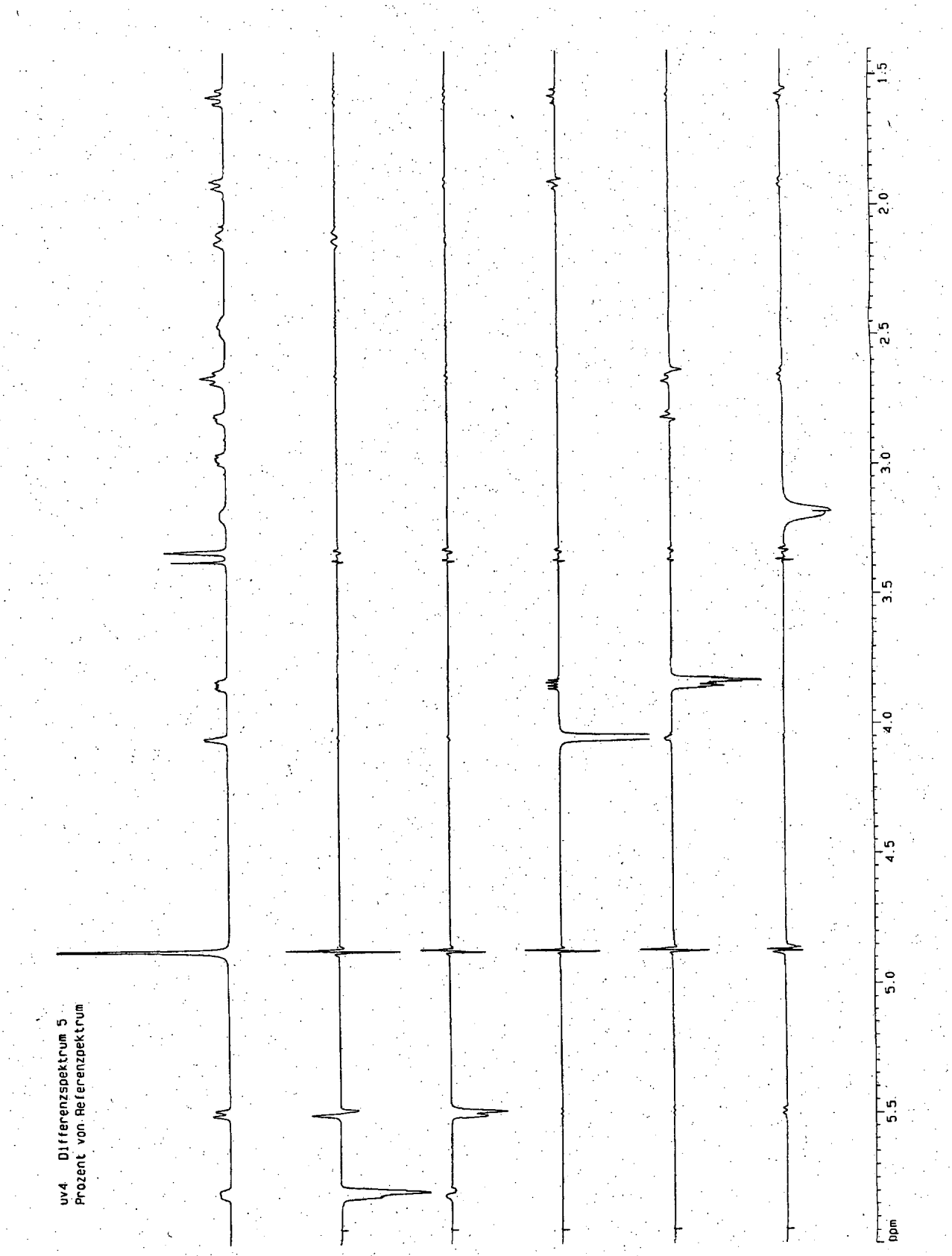

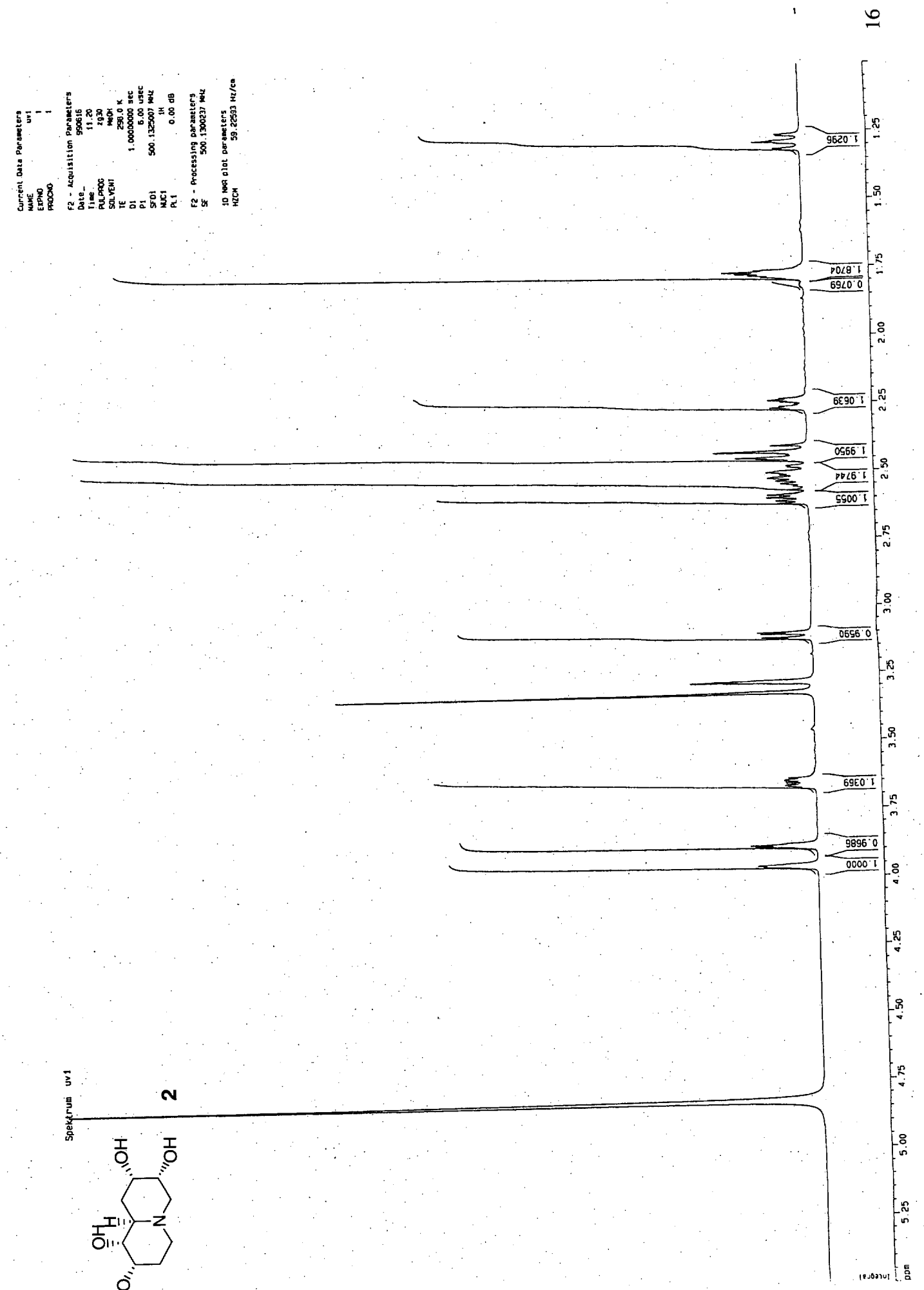

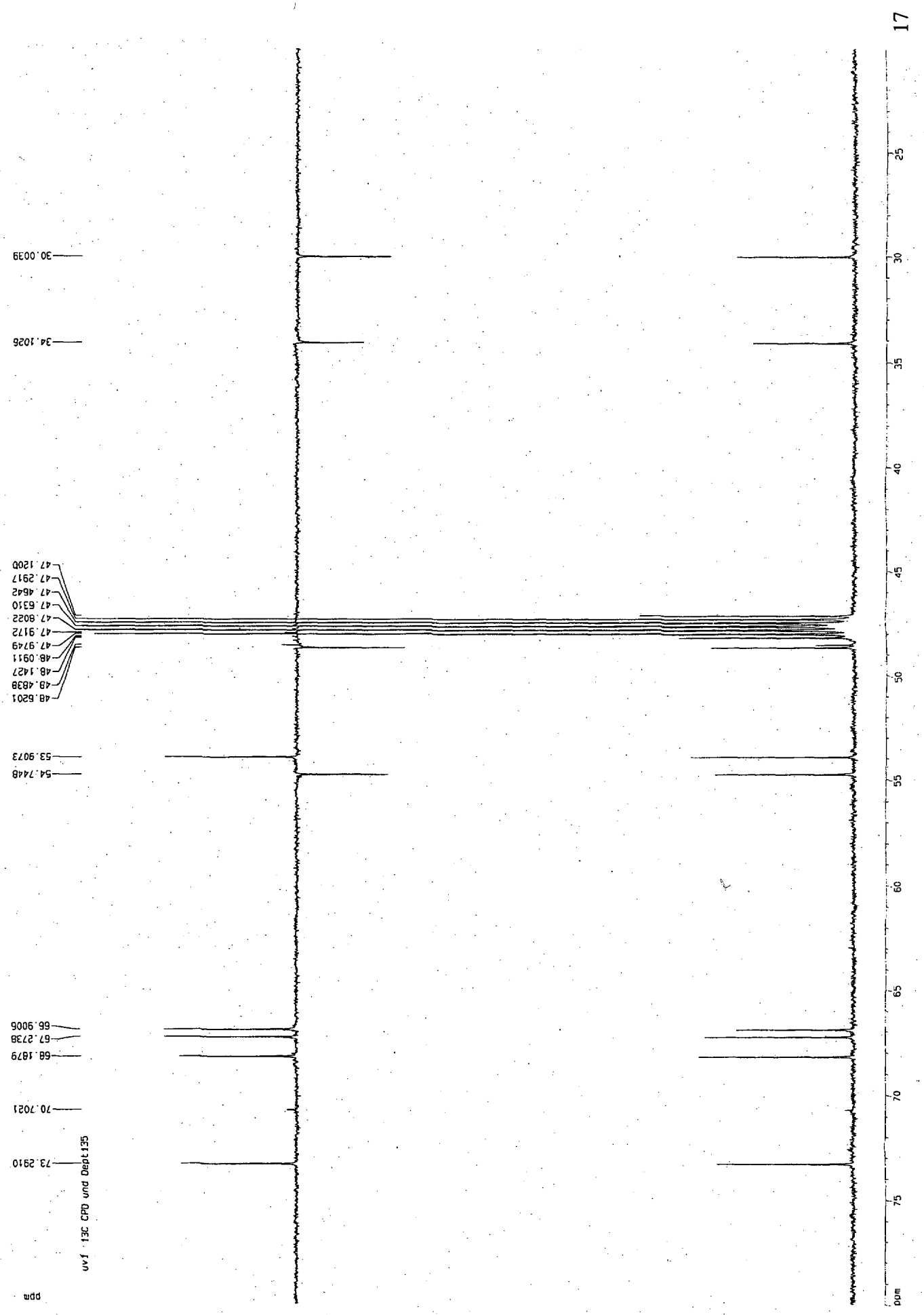


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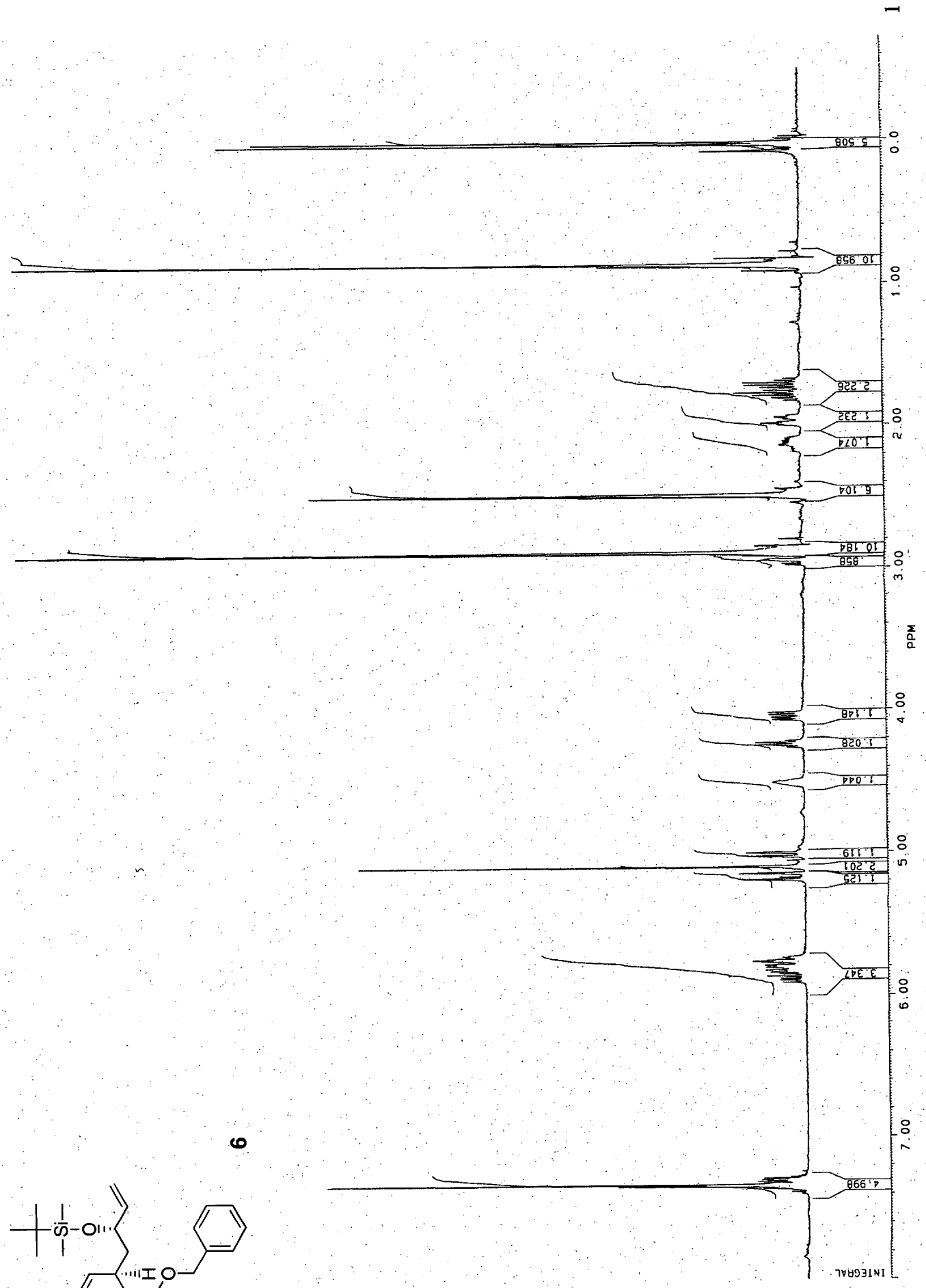
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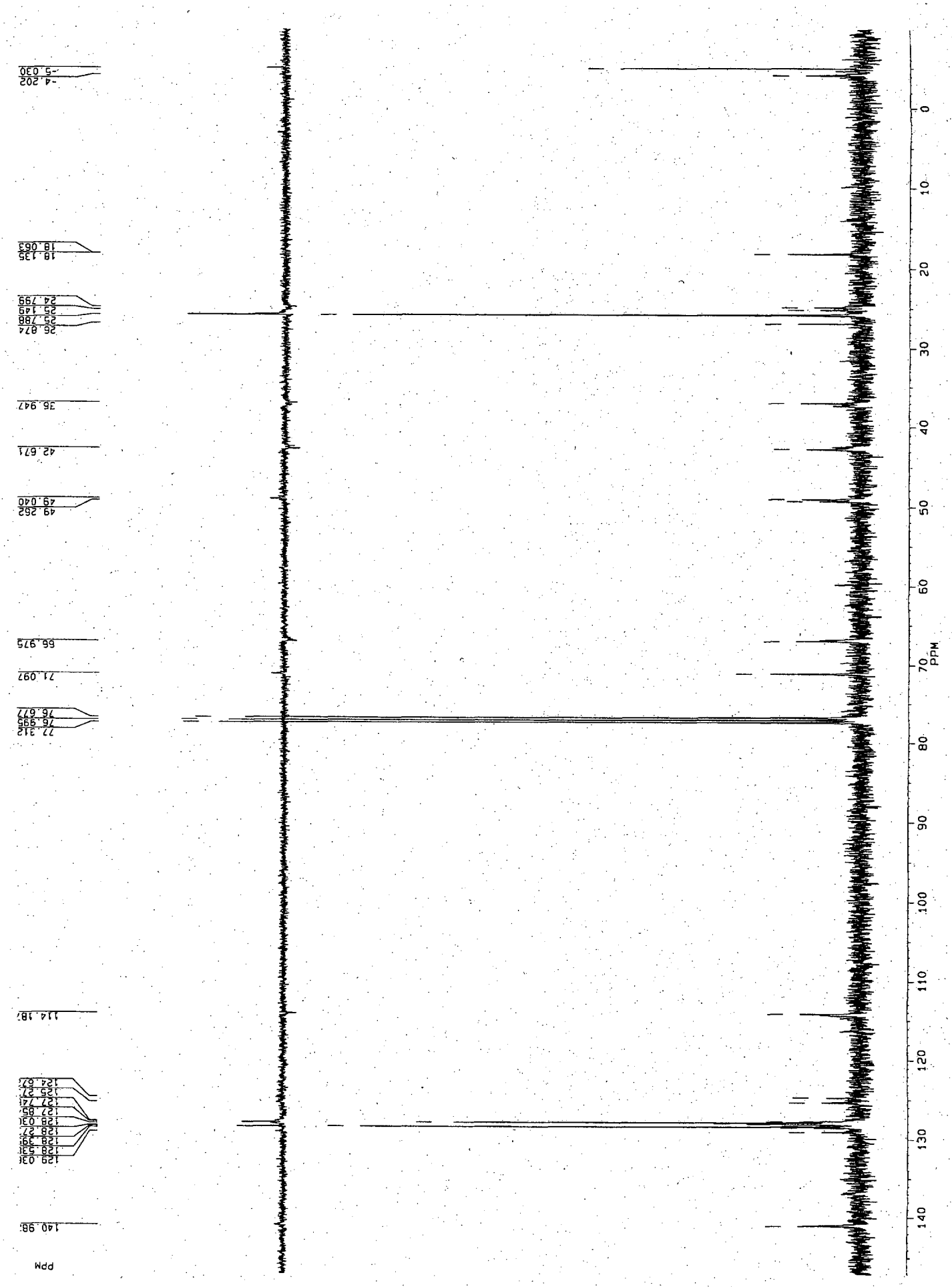
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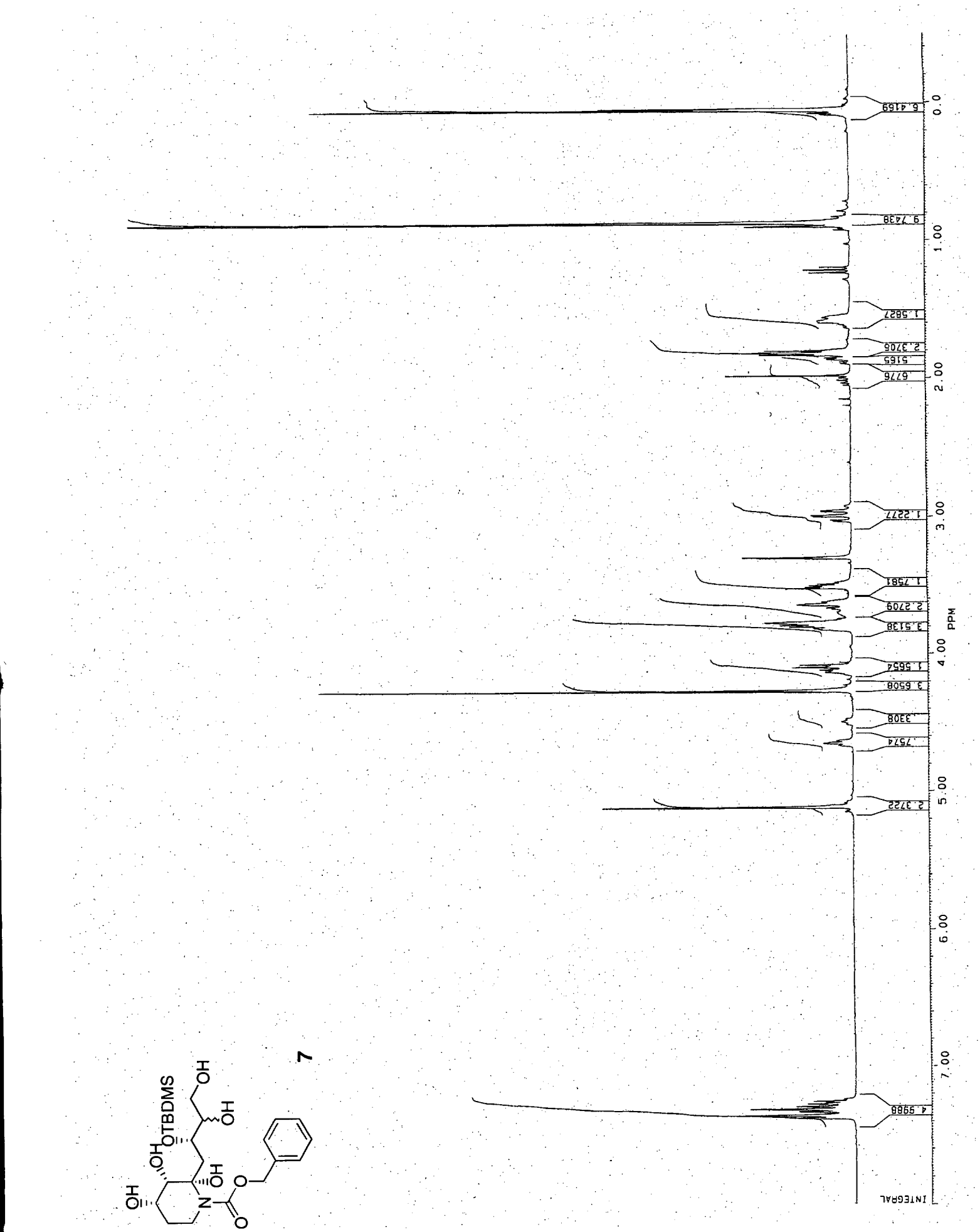
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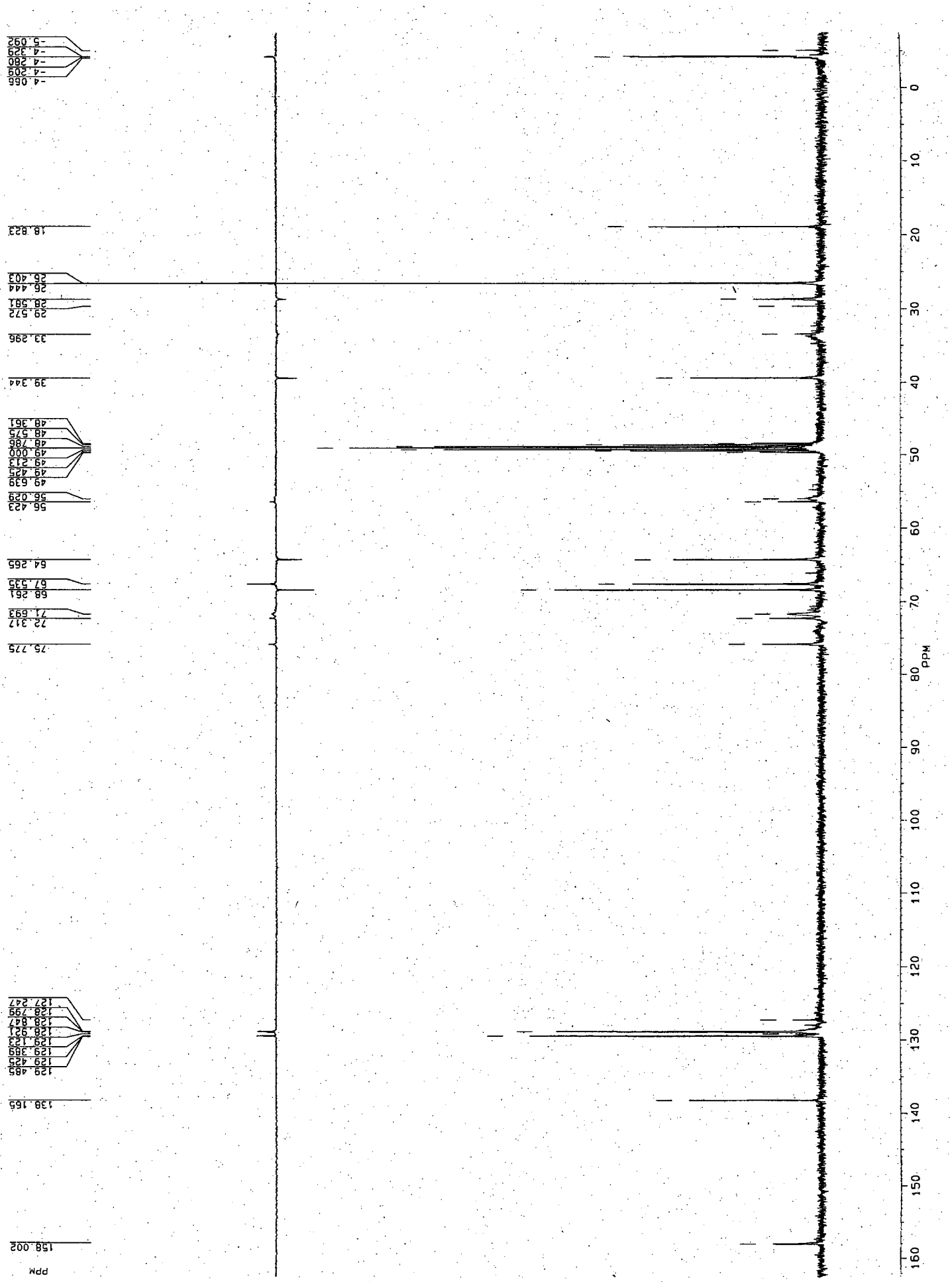

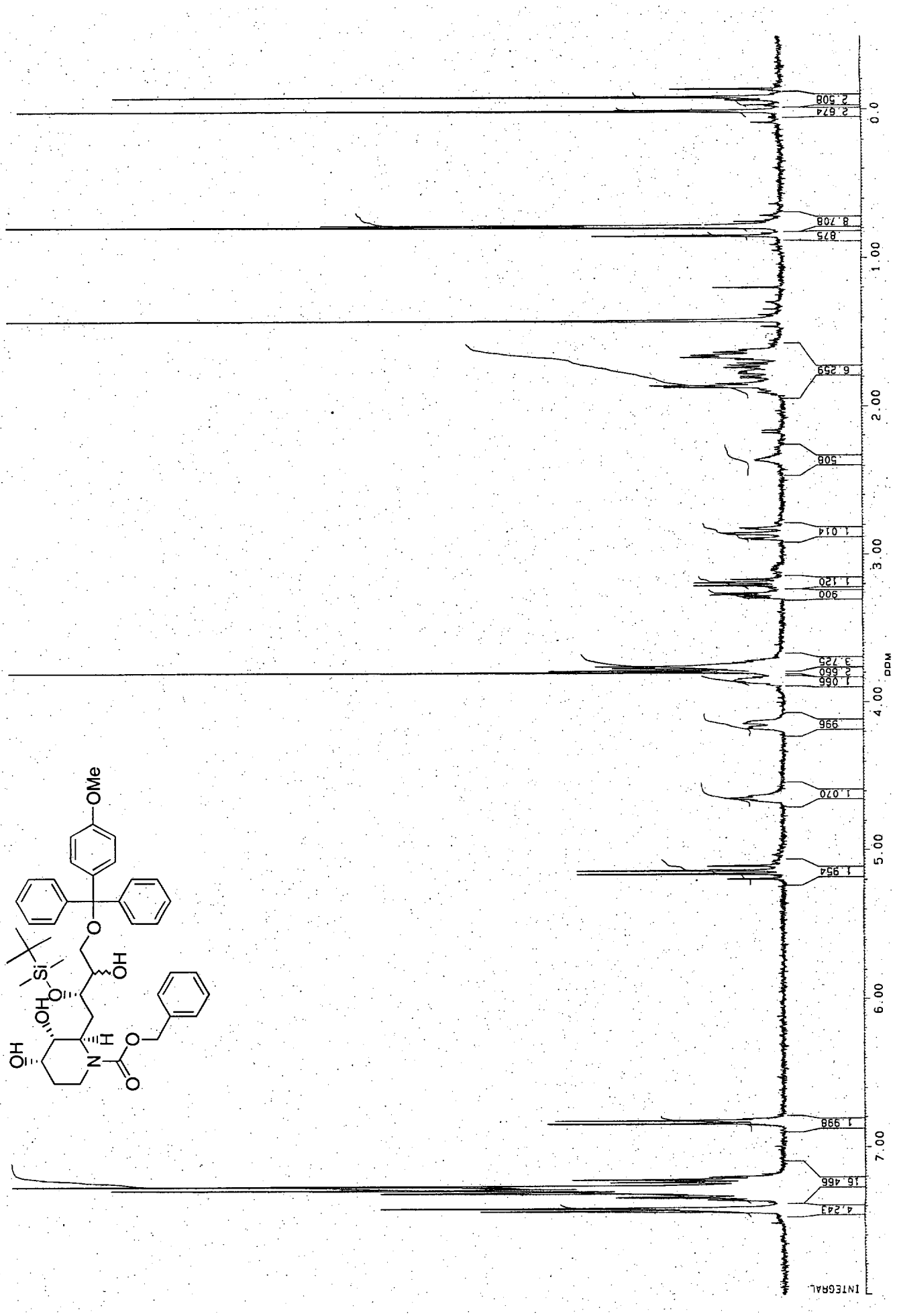
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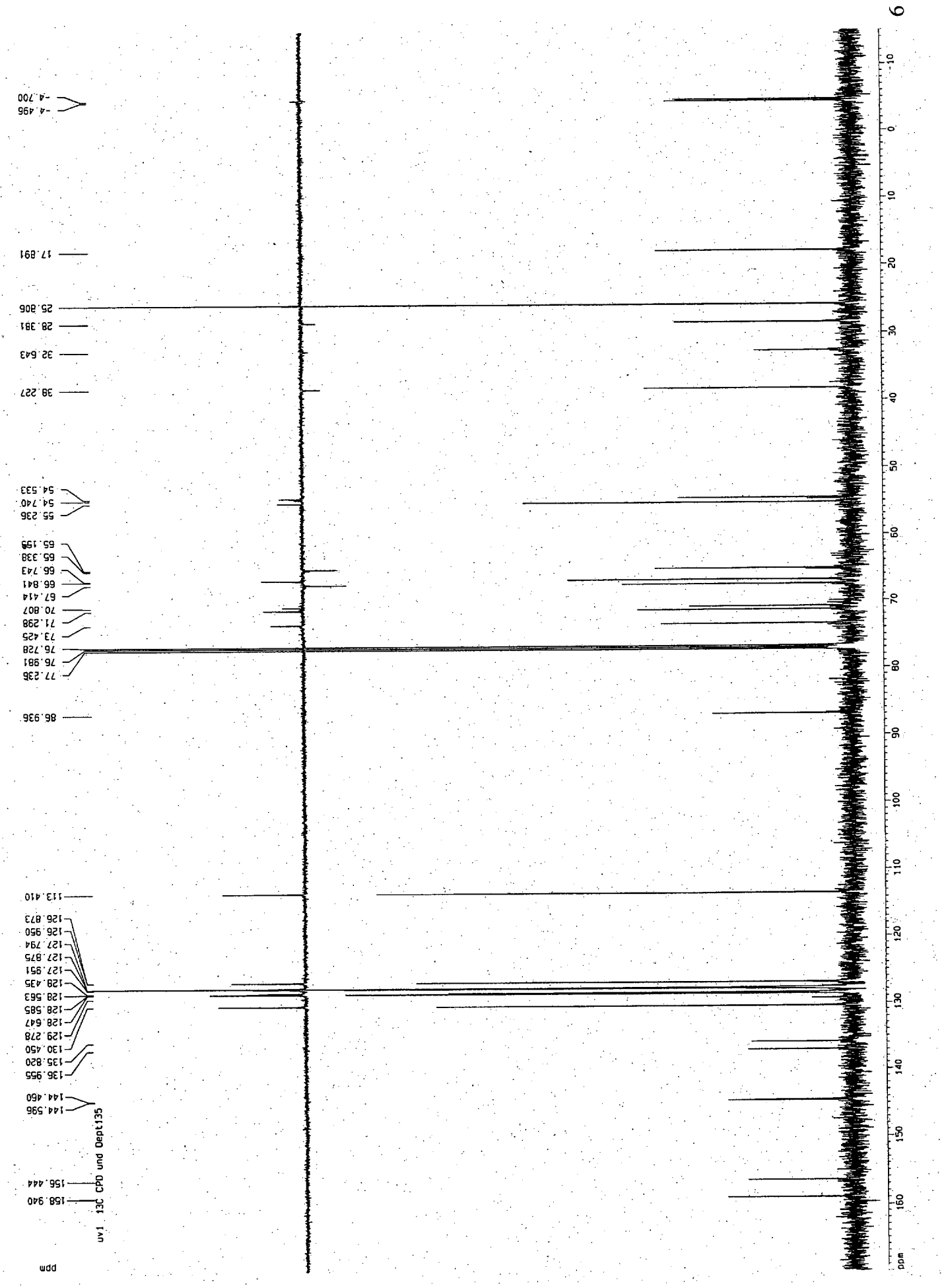

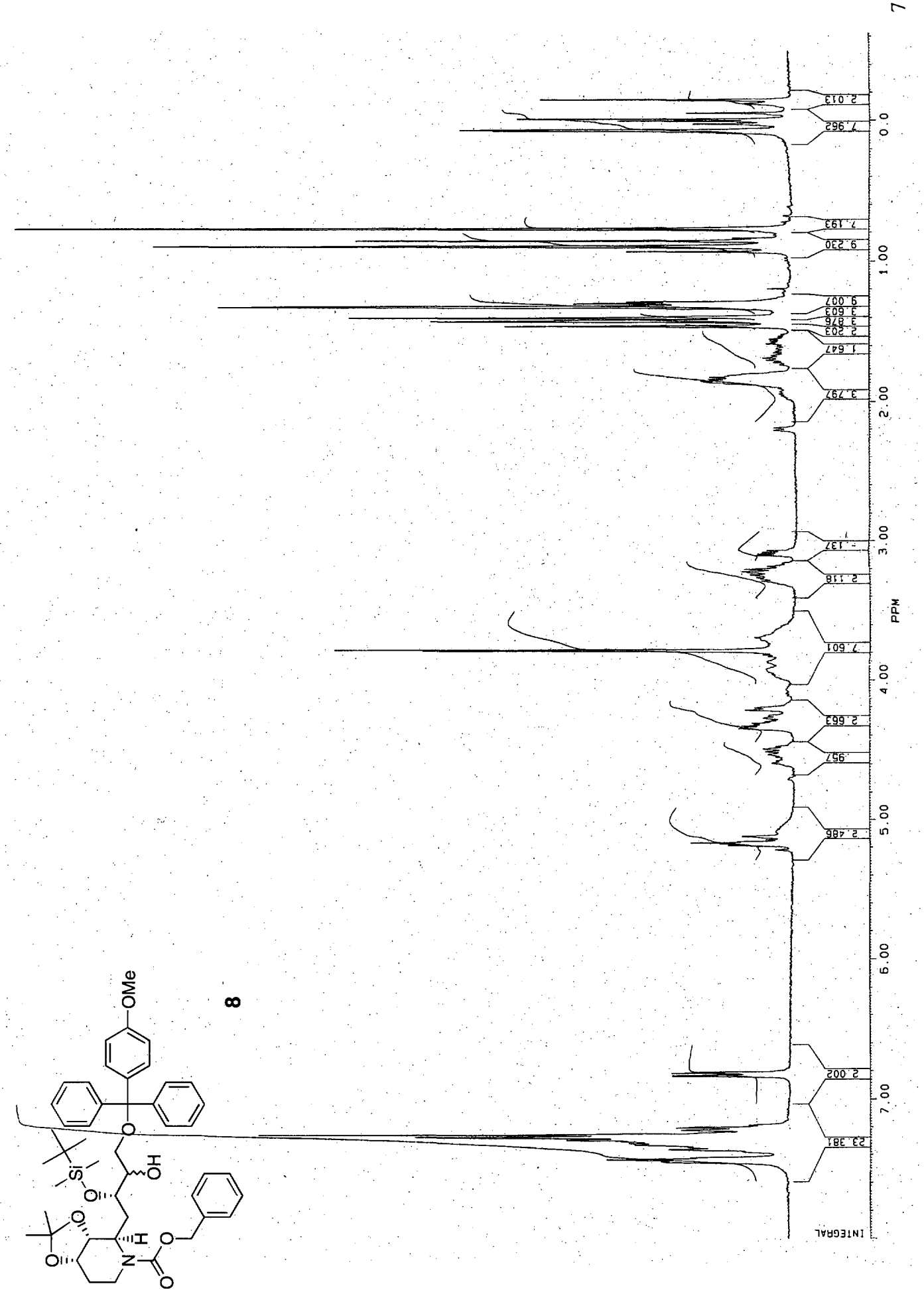

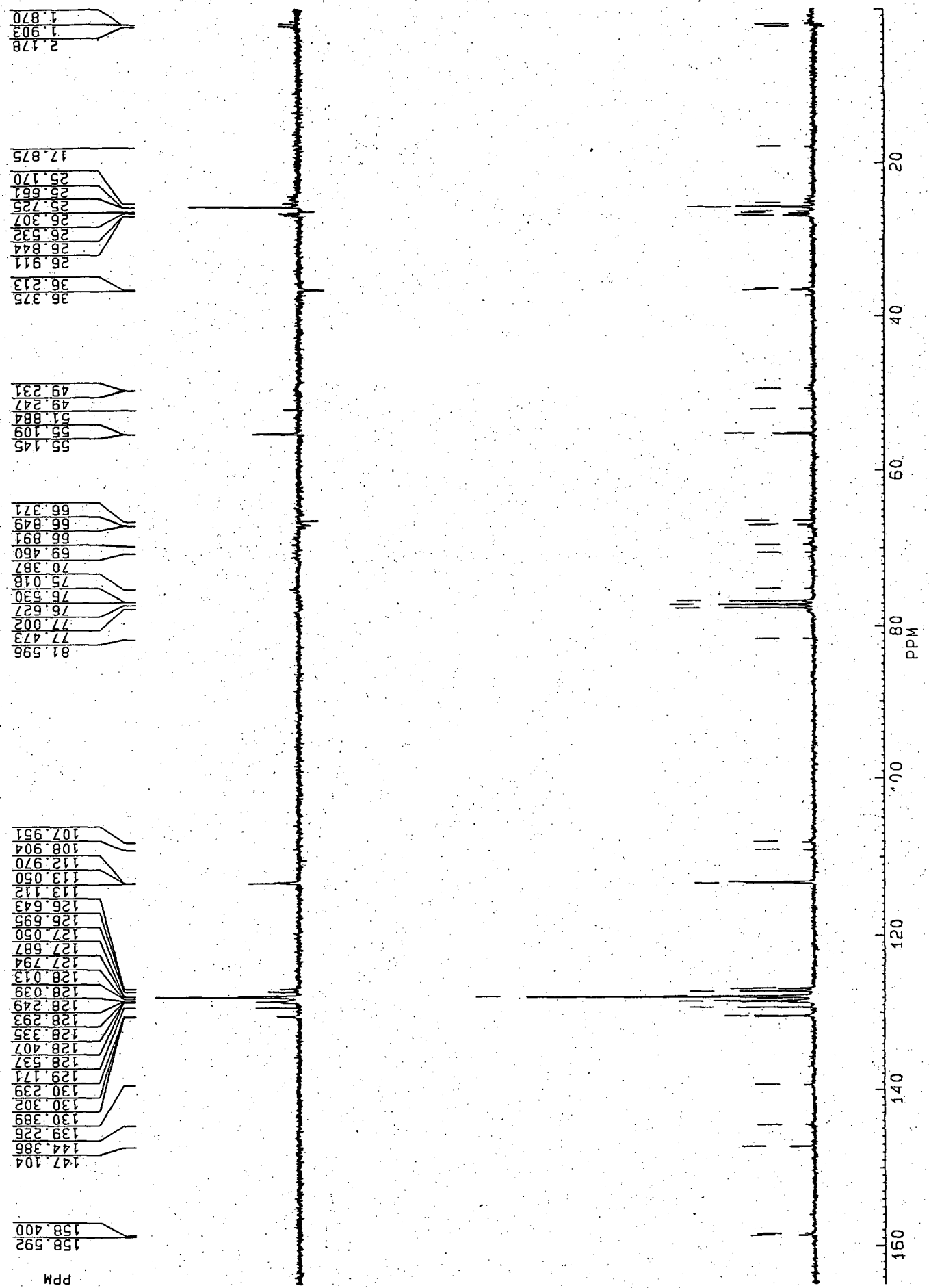

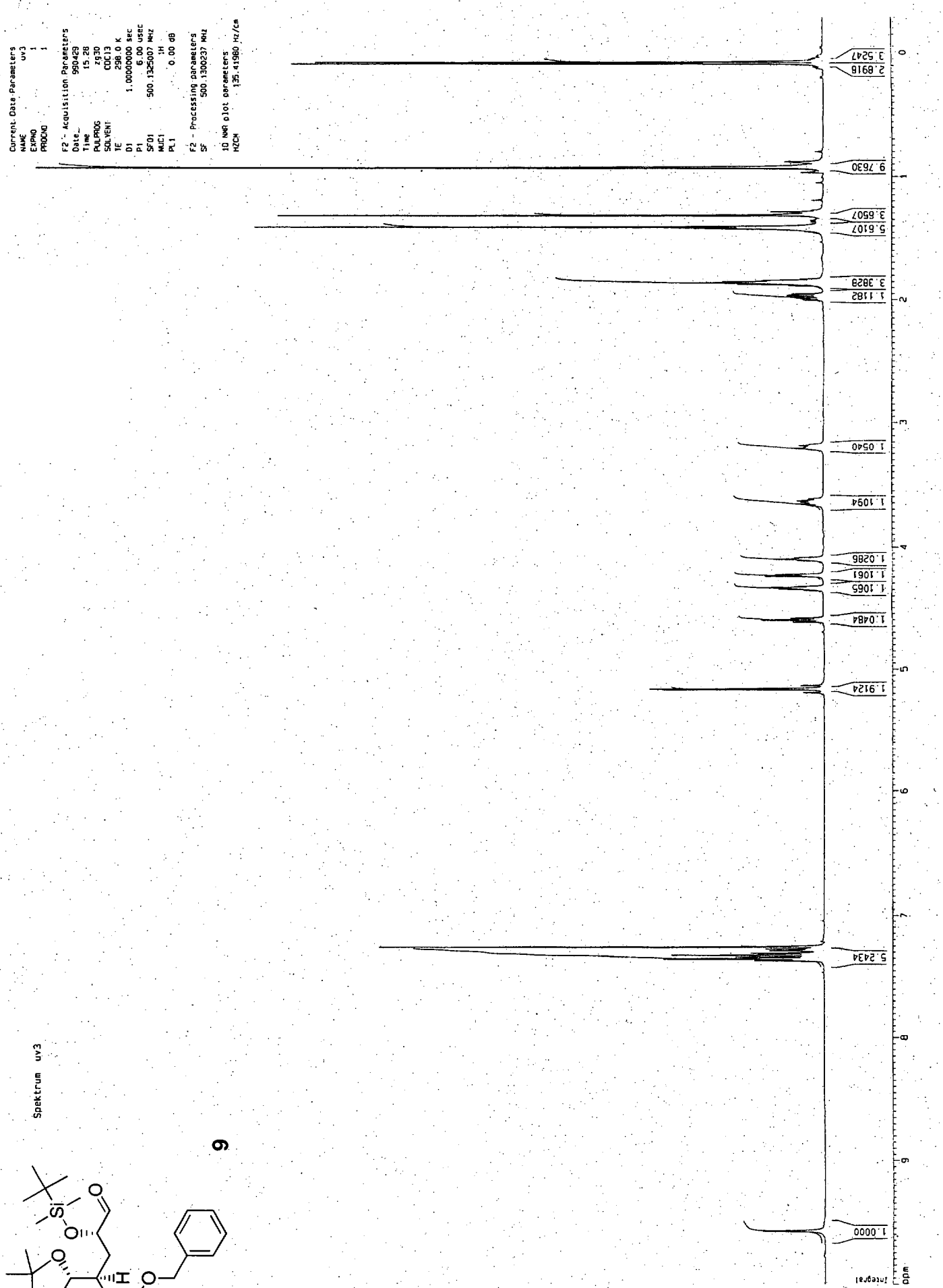

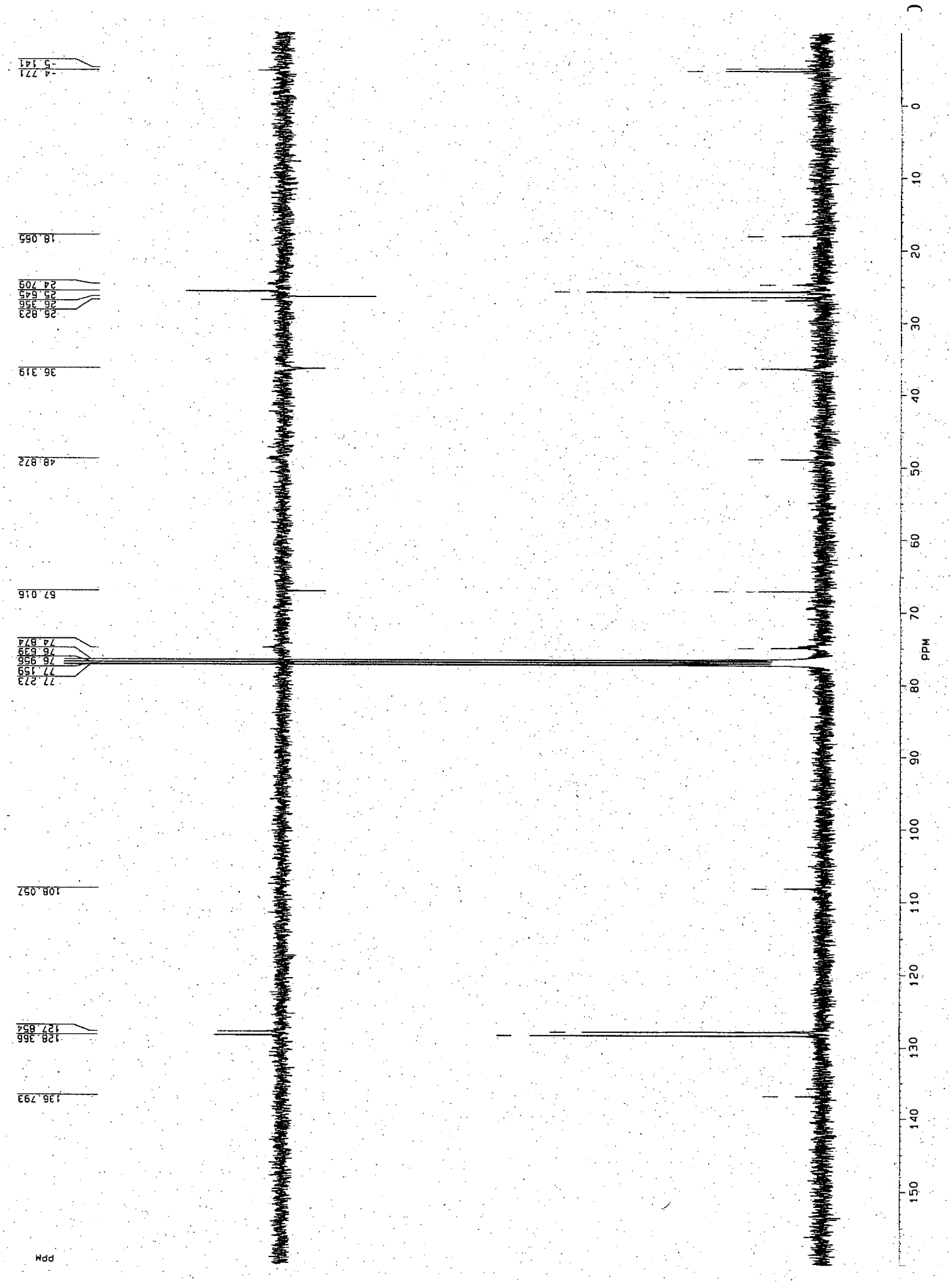
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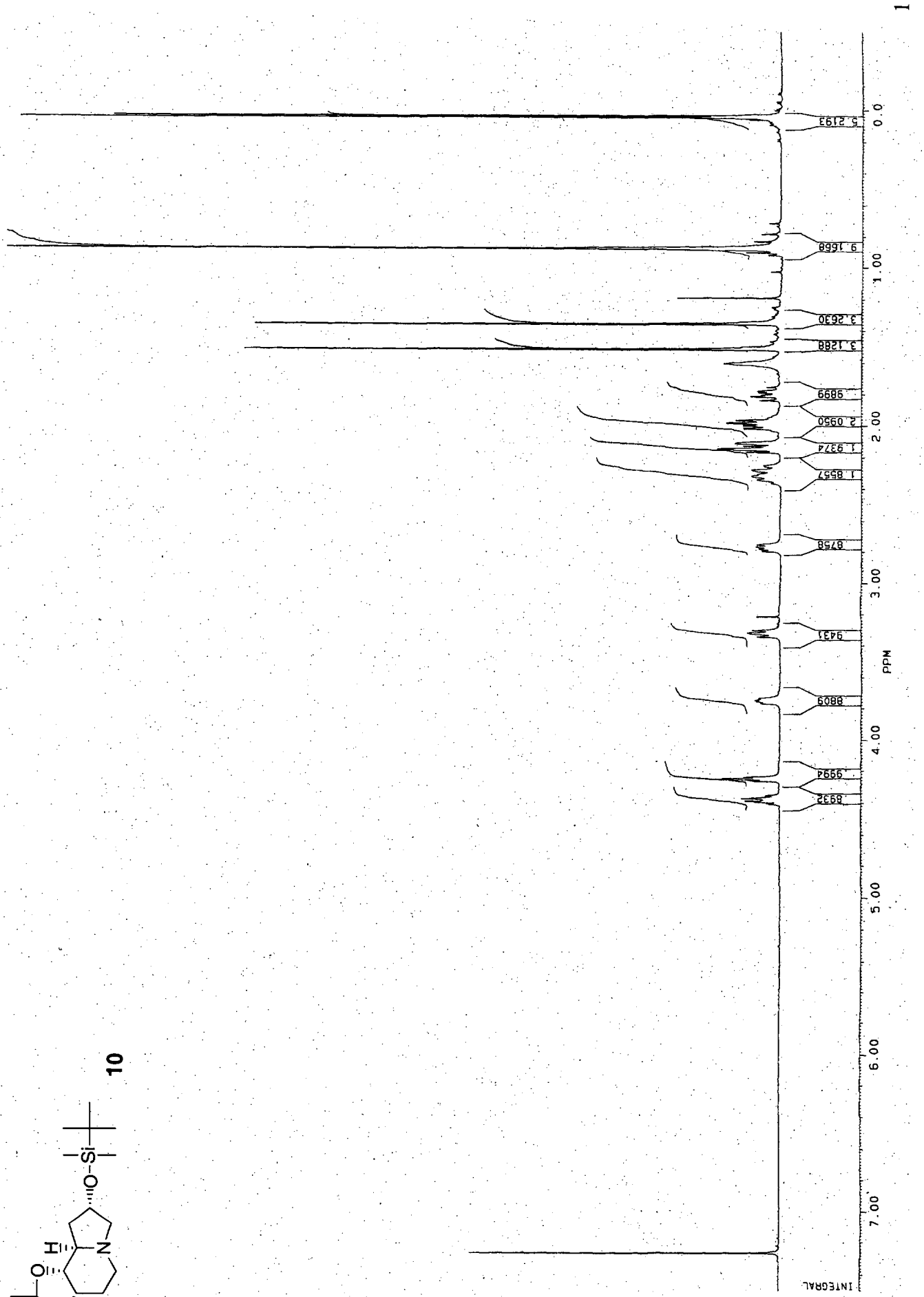

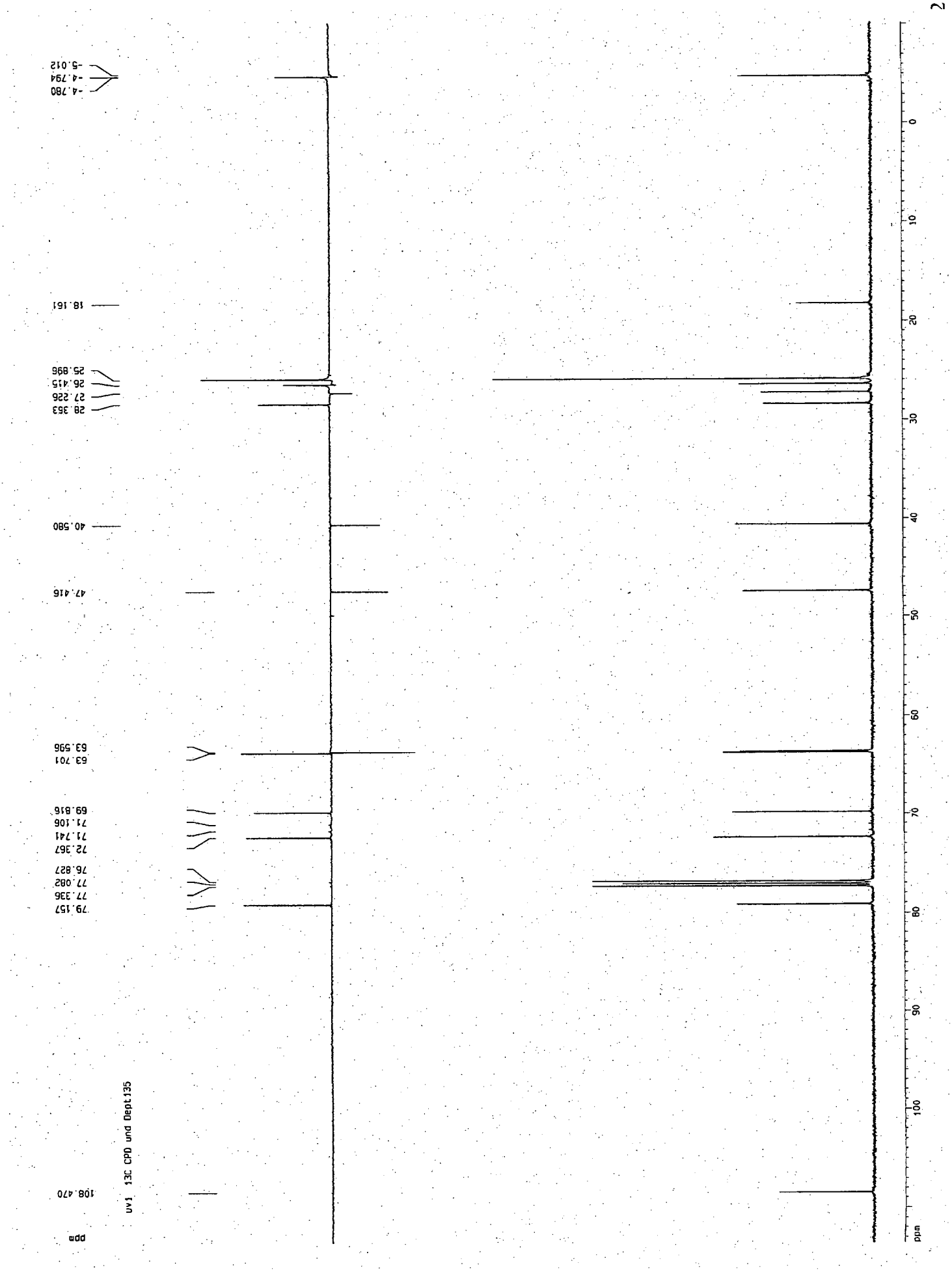
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30
40
50
60
70
80
90
100
ppm