SUPPORTING INFORMATION

Synthesis of Naturally-Occurring Pyridine Alkaloids Via Palladium-Catalyzed Coupling/Migration Chemistry

Yao Wang, Xiaoyang Dong, and Richard C. Larock*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

larock@iastate.edu

10-Iodo-1-decene (19). Triphenylphosphine (25.15 g, 96.0 mmol) and imidazole (8.70 g, 128 mmol) were dissolved in 200 ml of 3:1 Et_2O/CH_3CN at room temperature. To the resulting mixture was added 24.4 g (96.0 mmol) of iodine at 0-5 °C. After the addition was complete, the mixture was stirred at this temperature for an additional 20 min. To this mixture was added dropwise 11.1 g (64.0 mmol) of 9-decen-1-ol (90% purity) over 15 min. The reaction mixture was warmed to room temperature and left for 1 h. After work-up, the product was purified on a silica gel column and obtained in 88% yield: ^{1}H NMR ($CDCl_3$) δ 1.29-1.38 (br m, 10 H), 1.82 (quintet, J = 7.2, Hz, 2 H), 2.03 (q, J = 7.2 Hz, 2 H), 3.19 (t, J = 7.2 Hz, 2 H), 4.93 (ddt, J = 10.2, 1.8 Hz, 0.9 Hz, 1 H), 4.99 (ddt, J = 17.1, 1.8, 1.5 Hz, 1 H), 5.81 (ddt, J = 17.1, 10.2, 6.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 7.3, 28.6, 28.9, 29.1, 29.3, 30.6, 33.6, 33.8, 114.2, 139.1; IR (neat) 3074, 2925, 2852, 1640, 1462, 909 cm^{-1}; HRMS for $C_{10}H_{19}I$: calcd 266.0532, found 266.0530.

1,12-Tridecadiene (20). To 4.39 g (16.5 mmol) of 10-iodo-1-decene and 0.42 g (2.2 mmol) of CuI (used without purification) in anhydrous THF (40 ml) was added 22 ml (1.0 N, 22 mmol) of allylmagnesium bromide under N_2 at -78 °C. After the addition was

complete, the reaction mixture was allowed to warm to 0 °C and maintained at this temperature for 2 h and then further warmed to room temperature overnight. After filtration, the filtrate was diluted with saturated NaCl solution and extracted with ether. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to remove the solvent. The residue was distillated at 76-80 °C/2 mm Hg to give 1.78 g (60%) of **20**: ^{1}H NMR ($CDCl_3$) δ 1.27-1.37 (br m, 14 H), 2.03 (dt, *J* = 7.5, 6.9 Hz, 4 H), 4.92 (ddt, *J* = 10.2, 1.8, 0.9 Hz, 2 H), 4.99 (ddt, *J* = 17.1, 1.8, 1.5 Hz, 2 H), 5.81 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.0, 29.2, 29.5, 29.6, 33.9, 114.1, 139.3; IR (neat) 3076, 2924, 2853, 1641, 1464, 1439, 909 cm^{-1}; HRMS for $C_{13}H_{24}$: calcd 180.1878, found 180.1880.

2-Methyl-1,11-dodecadiene (33). To 1.07 g (44 mmol) of Mg metal turnings in 40 ml of anhydrous THF was added 4.89 g (40 mmol) of 2-bromopropene in 10 ml of THF at room temperature under N_2. After the addition was complete, the reaction mixture was refluxed for 8 h. The resulting Grignard solution was transferred by syringe to a suspension of 10-iodo-1-decene (5.6 g, 21 mmol) and CuI (used without purification, 0.40 g, 2.1 mmol) in 30 ml of anhydrous THF at -78 °C and stirred for 10 min. The mixture was allowed to warm to 0 °C and maintained at this temperature for 2 h and then kept at room temperature overnight. After filtration, the filtrate was poured into 150 ml of saturated NH_4Cl solution and extracted with hexane. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified on a silica gel column to

give 2.79 g (97%) of **33**: ^{1}H NMR ($CDCl_3$) δ 1.28 (br s, 8 H), 1.39 (m, 4 H), 1.70 (s, 3 H), 2.01 (m, 4 H), 4.65 (s, 1 H), 4.68 (s, 1 H), 4.92 (d, J = 10.2 Hz, 1 H), 4.98 (d, J = 17.1 Hz, 1 H), 5.81 (ddt, J = 17.1, 10.2, 6.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.5, 27.7, 29.1, 29.3, 29.4, 29.6, 33.9, 37.9, 109.6, 114.1, 139.3, 146.3 (one peak missing due to overlap); IR (neat) 3075, 2969, 2924, 2853, 1642, 1456, 909 cm^{-1}; HRMS for $C_{13}H_{24}$: calcd 180.1878, found 180.1878.

***N*-Benzyl tosylamide.** To 10.7 g (0.1 mol) of benzylamine in 32 ml of pyridine was gradually added 19.2 g (0.1 mol) of tosyl chloride at 0-5 °C. After the addition was complete, the resulting mixture was allowed to warm to room temperature and maintained at that temperature for 2 h, then raised to 70 °C for 4 h. After cooling to room temperature, the mixture was diluted with ethyl ether (500 ml), washed with 10% HCl solution and dried over anhydrous Na_2SO_4. After removal of the solvent, *N*-benzyl tosylamide was formed as crystals in 87% yield (22.7 g): mp 113-114 °C; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 2.12 (d, J = 6.0 Hz, 2 H), 4.74 (t, J = 6.0 Hz, 1 H), 7.17-7.28 (m, 5 H), 7.30 (d, J = 7.8 Hz, 2 H), 7.75 (d, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.6, 47.3, 127.2, 127.9, 128.7, 129.7, 136.3, 136.9, 143.5 (one peak missing due to overlap); IR ($CDCl_3$) 3361, 3284, 3033, 2925, 2872, 1599, 1456, 1330, 1162 cm^{-1}; HRMS for $C_{14}H_{14}NO_2S$ (M^+ – H): calcd 260.0745, found 260.0744.

Compounds 14a and 14b. Compounds **14a** and **14b** were obtained as an inseparable 86:14 mixture of isomers in 66% combined yield from the coupling of 3-iodopyridine, 2.5

equivs of 1,13-tetradecadiene and 2 equivs of benzylmethylamine in the presence of 1.0 equiv. of LiCl at 100 °C for 24 h: ^{1}H NMR ($CDCl_3$) δ 1.25-1.30 (br m, 14 H), 1.36 (quintet, J = 7.0 Hz, 2 H), 1.60 (quintet, J = 7.5 Hz, 2 H), 2.02 (q, J = 7.0 Hz, 2 H), 2.17 (s, 3 H), 2.59 (t, J = 7.5 Hz, 2 H), 2.69 (sextet, J = 7.5 Hz, 1 H, PyCH in **14b**), 2.96 (d, J = 6.5 Hz, 2 H), 3.03 (d, J = 6 Hz, 2 H, CH_2N in **14b**), 3.47 (s, 2 H), 5.52 (dt, J = 15.5, 6.5 Hz, 1 H), 5.58 (dt, J = 15.5, 6.5 Hz, 1 H), 7.19 (dd, J = 7.5, 4.5 Hz, 1 H), 7.24 (m, 1 H), 7.30 (m, 4 H), 7.47 (dt, J = 7.5, 1.5 Hz, 1 H), 8.42 (dd, J = 4.5, 1.5 Hz, 1 H), 8.44 (d, J = 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.2, 29.4, 29.5, 29.6, 29.6, 29.7, 29.8, 31.2, 32.5, 33.1, 42.0, 59.8, 61.6, 123.2, 126.9, 127.0, 128.2, 129.2, 134.4, 135.8, 138.0, 139.1, 147.2, 150.0 (one peak missing due to overlap); IR (neat) 3082, 3058, 3026, 2924, 1682, 1454, 1128, 1024 cm^{-1}; HRMS for $C_{27}H_{39}N_2$ ($M^+ - H$): calcd 391.3113, found 391.3107.

Compound 23a. Compound **23a** was obtained in 58% yield from the coupling of 3-iodopyridine, 2.5 equivs of 1,13-tetradecadiene and 2 equivs of *N*-benzyl tosylamide using the procedure above at 100 °C for 24 h: ^{1}H NMR ($CDCl_3$) δ 1.20-1.30 (br m, 16 H), 1.60 (quintet, J = 7.2 Hz, 2 H), 1.86 (m, 2 H), 2.43 (s, 3 H), 2.59 (t, J = 7.5 Hz, 2 H), 3.69 (d, J = 6.9 Hz, 2 H), 4.32 (s, 2 H), 5.06 (dt, J = 15.3, 6.9 Hz, 1 H), 5.37 (dt, J = 15.3, 6.9 Hz, 1 H), 7.19 (dd, J = 7.8, 4.8 Hz, 1 H), 7.23-7.35 (m, 5 H), 7.48 (d, J = 7.8 Hz, 1 H), 7.73 (d, J = 8.1 Hz, 2 H), 8.43 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.5, 28.9, 29.0, 29.1, 29.4, 29.6, 31.1, 32.1, 33.0, 48.9, 50.0, 123.3, 127.2, 127.5, 128.3, 128.4 129.6, 135.8, 136.2, 136.4, 137.6, 138.0, 143.1, 147.2, 150.0 (four peaks missing due to overlap); IR (neat) 3084, 3029, 2926,

2853, 1598, 1455, 1340, 1159 cm^{-1}; HRMS for $C_{33}H_{43}N_2O_2S$ ($M^+ - H$): calcd 531.3045, found 531.3050.

Compound 26. Compound **26** was obtained in 77% yield from the detosylation of compound **23a** using procedure B: ^1H NMR ($CDCl_3$) δ 1.20-1.30 (br m, 16 H), 1.60 (quintet, J = 7.2 Hz, 2 H), 2.02 (q, J = 6.6 Hz, 2 H), 2.58 (t, J = 7.5 Hz, 2 H), 3.26 (d, J = 5.7 Hz, 2 H), 3.83 (s, 2 H), 4.74 (br s, 1 H), 5.55 (dt, J = 15.3, 6.0 Hz, 1 H), 5.65 (dt, J = 15.3, 6.0 Hz, 1 H), 7.19 (dd, J = 7.8, 4.8 Hz, 1 H), 7.26-7.38 (m, 5 H), 7.48 (d, J = 7.8 Hz, 1 H), 8.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.2, 29.5, 29.6, 31.1, 32.4, 33.0, 49.9, 51.8, 123.2, 125.2, 127.6, 128.5, 128.8, 135.6, 135.8, 137.2, 138.0, 147.0, 149.8 (five peaks missing due to overlap); IR (neat) 3293 (N-H), 3084, 3028, 2922, 2850, 1681, 1455, 1360, 1112 cm^{-1}; HRMS for $C_{26}H_{37}N_2$($M^+ - H$): calcd 377.2957, found 377.2953.

Compounds 18a and 18b. Compounds **18a** and **18b** were obtained as an inseparable 86:14 mixture of isomers in 76% combined yield from the hydrogenation and debenzylation of compounds **14a** and **14b** using the above procedure: ^1H NMR ($CDCl_3$) δ 1.16 (d, J = 6.3 Hz, 3 H, CH_3 in **18b**), 1.22-1.30 (br m, 20 H), 1.60 (m, 2 H, CH_2CN), 1.70 (m, 2 H), 2.57 (s, 3 H), 2.60 (t, J = 7.5 Hz, 2 H), 2.82 (t, J = 7.5 Hz, 2 H), 6.00-6.23 (br m, 1 H), 7.20 (dd, J = 7.8, 5.1 Hz, 1 H), 7.48 (d, J = 7.8 Hz, 1 H), 8.42 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.1, 26.8, 29.1, 29.2, 29.5, 29.6, 30.1, 31.2, 32.7, 33.1, 37.5, 49.3, 123.3, 135.9, 138.1, 147.3, 150.1 (three peaks missing due to overlap); IR (neat) 3388 (N-H), 2925,

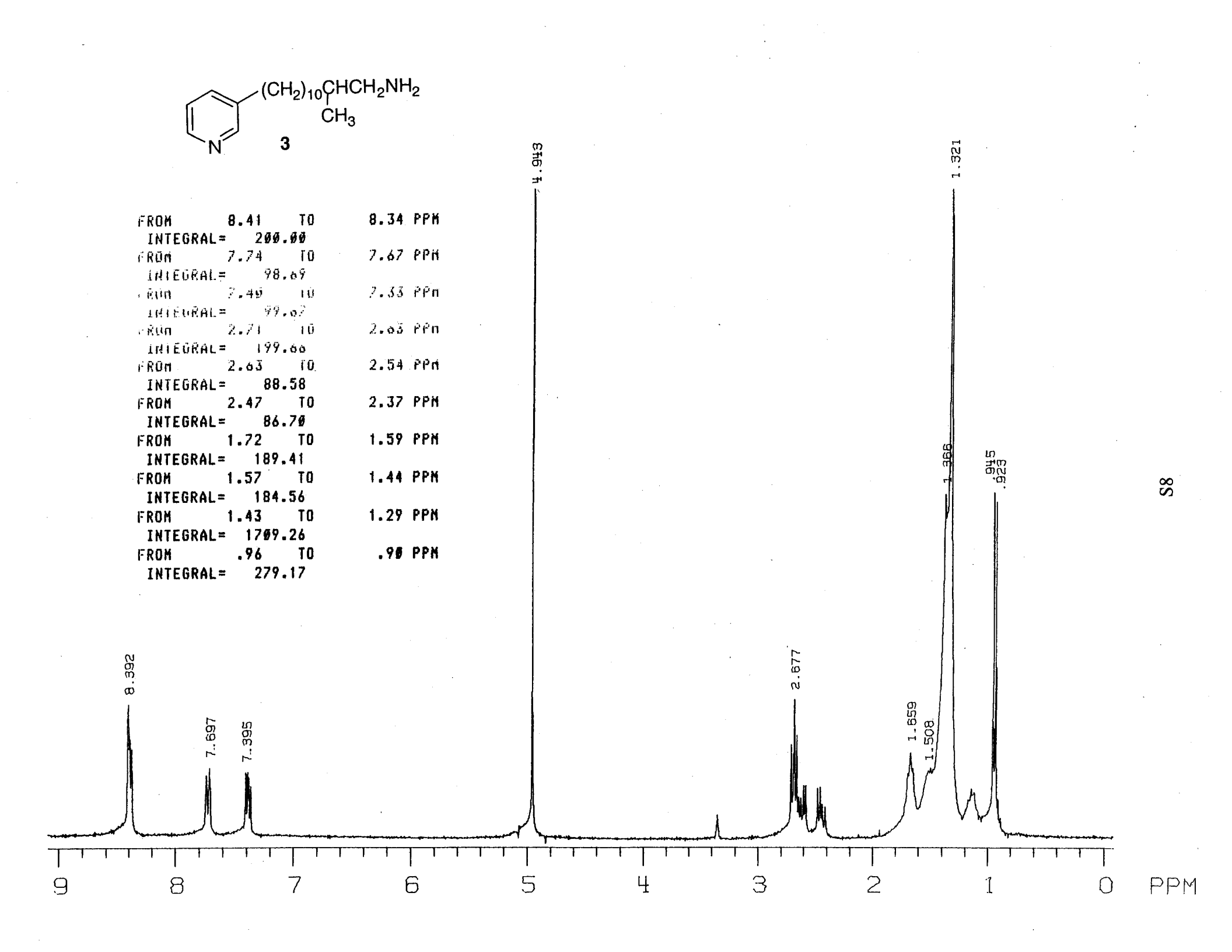
2853, 1592, 1465, 1362, 1047 cm^{-1}; HRMS for $C_{20}H_{35}N_2(M^+ - H)$: calcd 303.2879, found 303.2796.

Compound 27. Compound **27** was obtained in 67% yield from the hydrogenation and debenzylation of compound **26** using the above procedure: ^1H NMR (CD_3OD) δ 1.26-1.33 (br m, 20 H), 1.48 (m, 2 H), 1.62 (m, 2 H), 2.64 (t, *J* = 7.5 Hz, 2 H), 2.67 (t, *J* = 6.3 Hz, 2 H), 7.34 (dd, *J* = 7.8, 4.8 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 8.34 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.9, 29.2, 29.5, 29.7, 29.9, 31.2, 33.1, 33.3, 41.9, 123.2, 135.8, 138.0, 147.2, 150.0 (five peaks missing due to overlap); IR (neat) 3350 (N-H), 3264 (N-H) , 3028, 2927, 2854, 1576, 1464, 1026 cm^{-1}; HRMS for $C_{19}H_{34}N_2$: calcd 290.2722, found 290.2720.

Compounds 17a and 17b. To 33.4 mg of a mixture of compounds **14a** and **14b** (86:14) in 2 ml of 95% EtOH was added 5 mg of 5% Pd/C. The resulting mixture was stirred and flushed with H_2 (1 atm) at room temperature for 4 h. After filtration and removal of the solvent, compounds **17a** and **17b** were obtained in 61% combined yield: ^1H NMR ($CDCl_3$) δ 1.17 (d, *J* = 6.6 Hz, 3 H, $PyCCH_3$ in **17b**), 1.22-1.30 (br m, 20 H), 1.05 (m, 2 H), 1.61 (quintet, J = 7.5 Hz, 2 H), 2.18 (s, 3 H), 2.35 (t, *J* = 7.5 Hz, 2 H), 2.60 (t, *J* = 7.5 Hz, 2 H), 3.48 (s, 2 H), 7.19 (dd, *J* = 7.8, 4.8 Hz, 1 H), 7.23-7.31 (m, 5 H), 7.48 (d, *J* = 7.8 Hz, 1 H), 8.43 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.5, 29.2, 29.4, 29.5, 29.7, 29.9, 31.2, 33.1, 42.2, 57.6, 62.3, 123.2, 126.9, 128.2, 129.1, 135.8, 138.0, 139.2, 147.2, 150.0 (five peaks missing due to overlap); IR (neat) 3082, 3026, 2924, 2852, 1576, 1454, 1363, 1027 cm^{-1}; HRMS for $C_{27}H_{41}N_2$ $(M^+ - H)$: calcd 393.3269, found 393.3274.

Ethyl 2-methyl-11-dodecenoate (39). Ethyl propionate (1.72 ml, 15 mmol) was added to a 1 M THF solution containing 1 equiv of LDA at -78 °C. The ester enolate was allowed to form over a period of 40 min. 10-Iodo-decene (4.0 g, 15 mol) dissolved in 3 ml of HMPA was added at -78 °C. After stirring for 3 h at -78 °C, the mixture was treated with aq NH_4Cl, extracted over ether and dried with $MgSO_4$. The product was purified on a silica gel column and obtained in 59% yield: ^{1}H NMR ($CDCl_3$) δ 1.11 (d, J = 6.9 Hz, 3 H), 1.12-1.35 (m, 17 H), 2.10 (q, J = 6.9 Hz, 2 H), 2.40 (quintet, J = 6.9 Hz, 1 H), 4.11 (q, J = 7.2 Hz, 2 H), 4.93 (ddt, J = 10.2, 1.8 Hz, 0.9 Hz, 1 H), 4.99 (ddt, J = 17.1, 1.8, 1.5 Hz, 1 H), 5.81 (ddt, J = 17.1, 10.2, 6.6 Hz, 1 H).

2-Methyl-11-dodecen-1-ol (40). A suspension of $LiAlH_4$ (60.8 mg, 1.6 mmol) in 5 ml of dry ethyl ether was added to ethyl 2-methyl-11-dodecenoate in 1 ml of ethyl ether dropwise at a rate so as to produce a gentle reflux. The solution was stirred at room temperature for 3 h. Ten ml of water was added cautiously. To the mixture was then added 10% H_2SO_4 until the pH equaled 7. The mixture was extracted with ether and dried over Na_2SO_4. The product was purified on a silica gel column and obtained in 86% yield: ^{1}H NMR ($CDCl_3$) δ 0.91 (d, J = 6.9 Hz, 3 H), 1.28-1.64 (m, 14 H), 2.04 (q, J = 7.2 Hz, 2 H), 3.46 (m, 2 H), 4.94 (ddt, J = 10.2, 1.8, 0.9 Hz, 1 H),), 4.99 (ddt, J = 17.1, 1.8, 1.5 Hz, 1 H), 5.81 (ddt, J = 17.1, 10.2, 6.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.6, 27.0, 29.0, 29.2, 29.5. 29.6, 30.0, 33.2, 33.9, 35.8, 68.4, 114.1, 139.3; IR: 3412, 3100, 2893, 2887, 845 cm^{-1}.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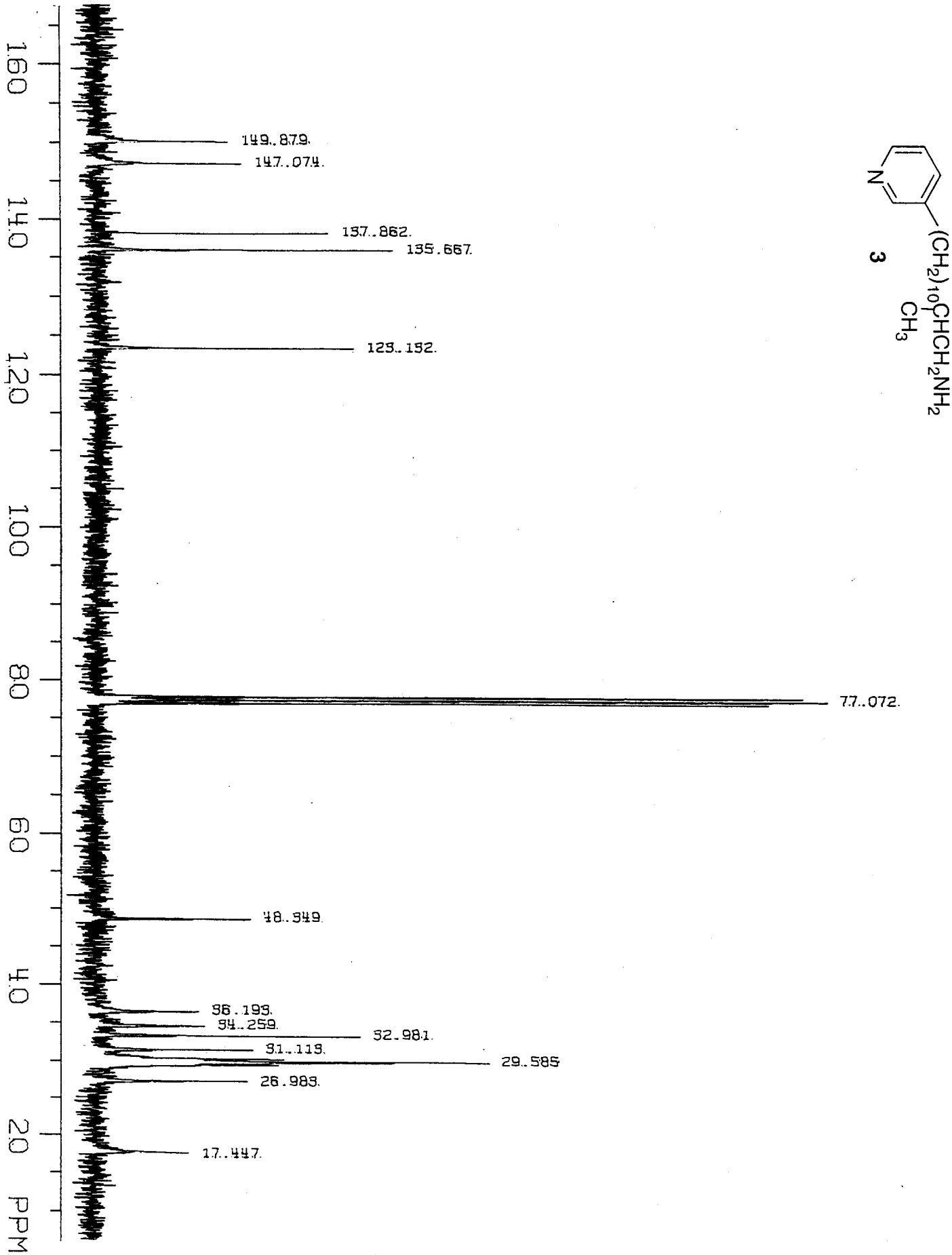
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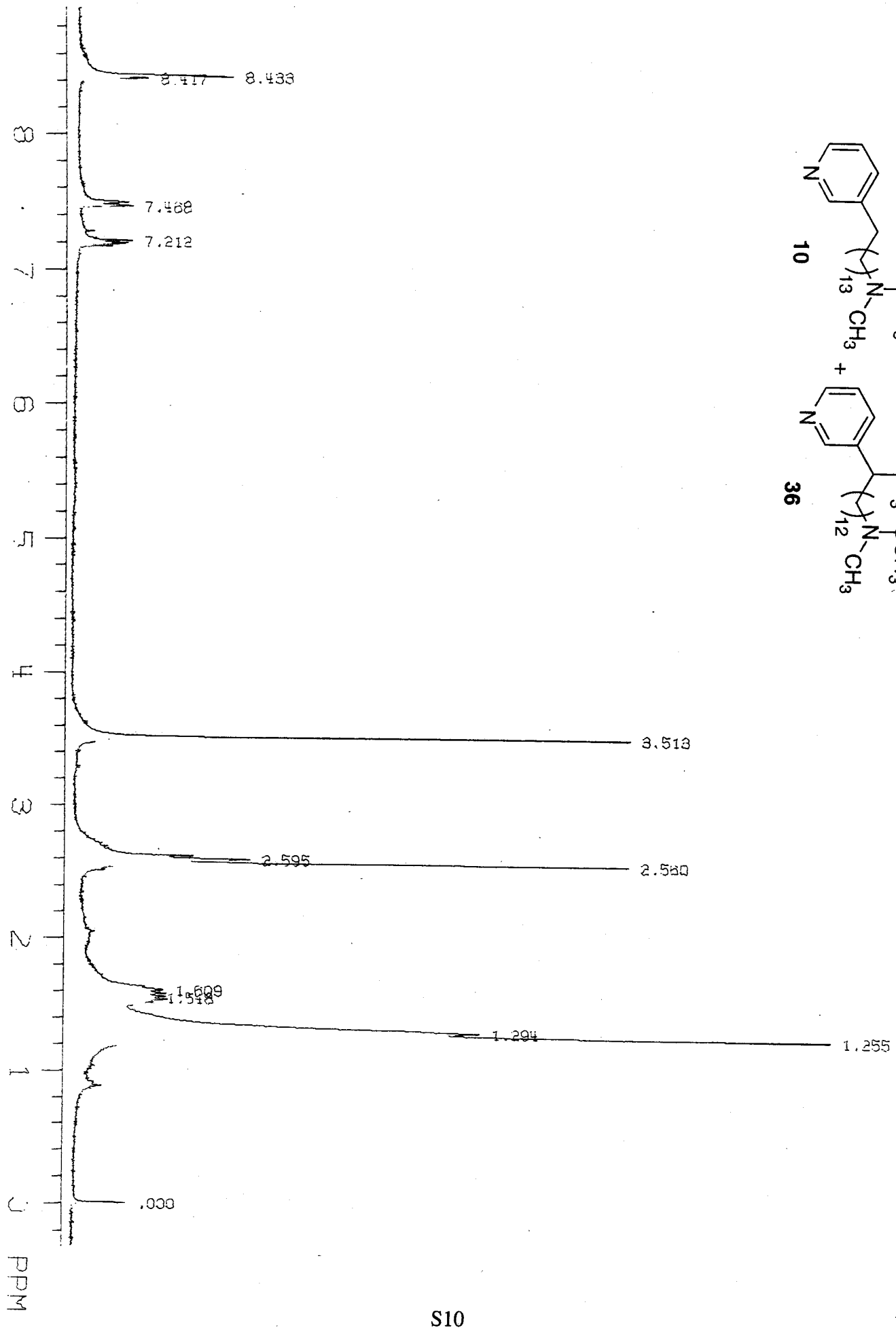
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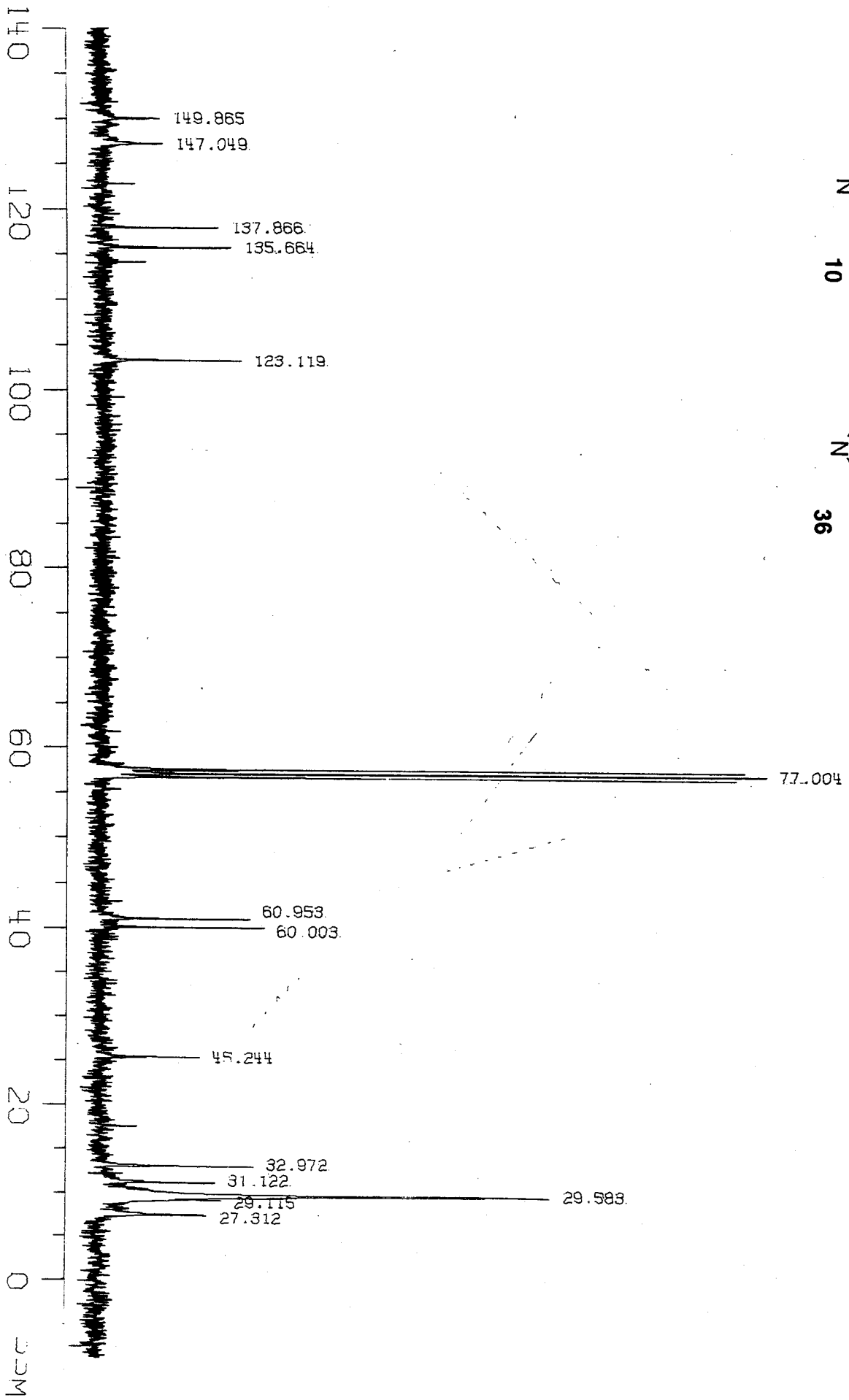
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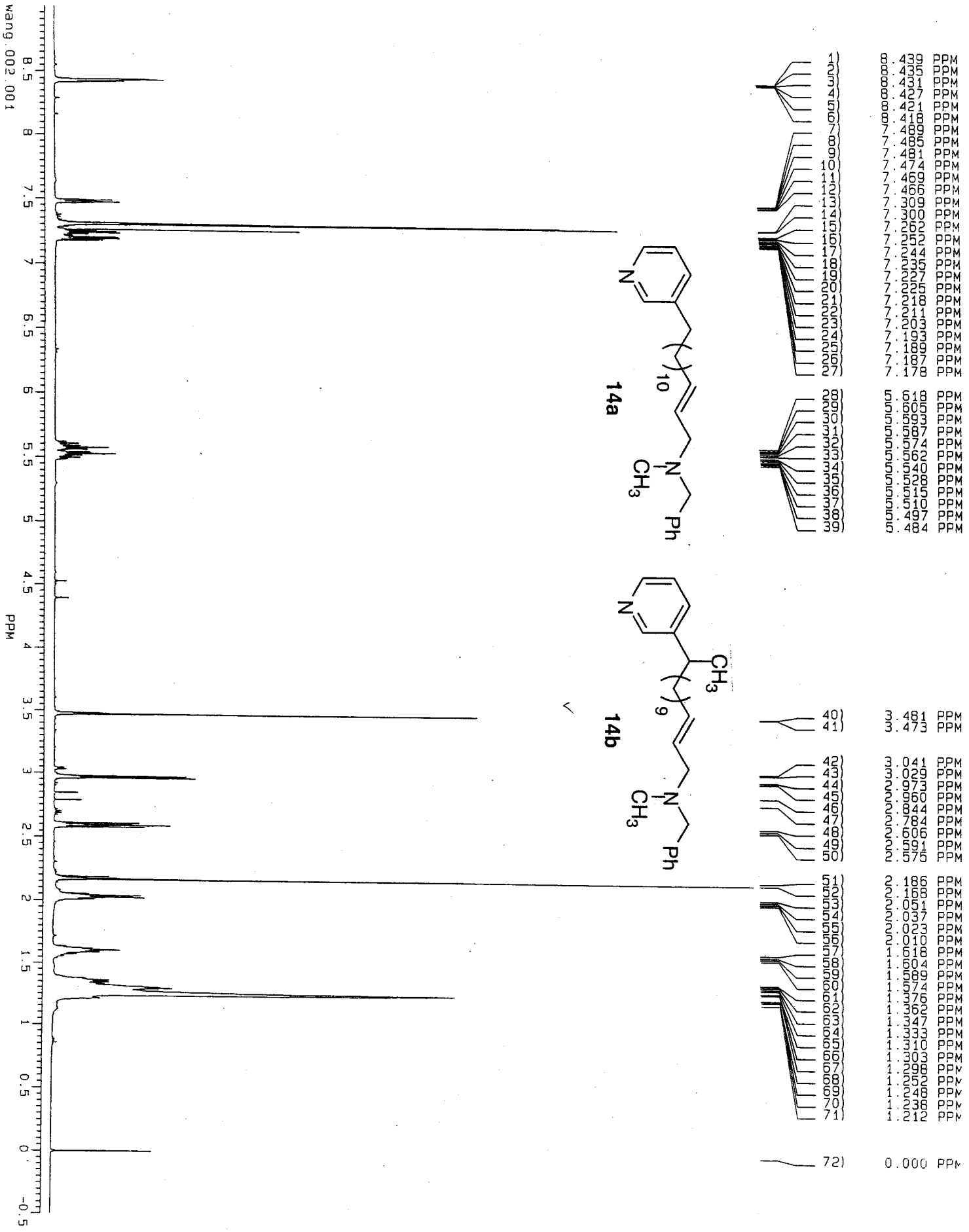
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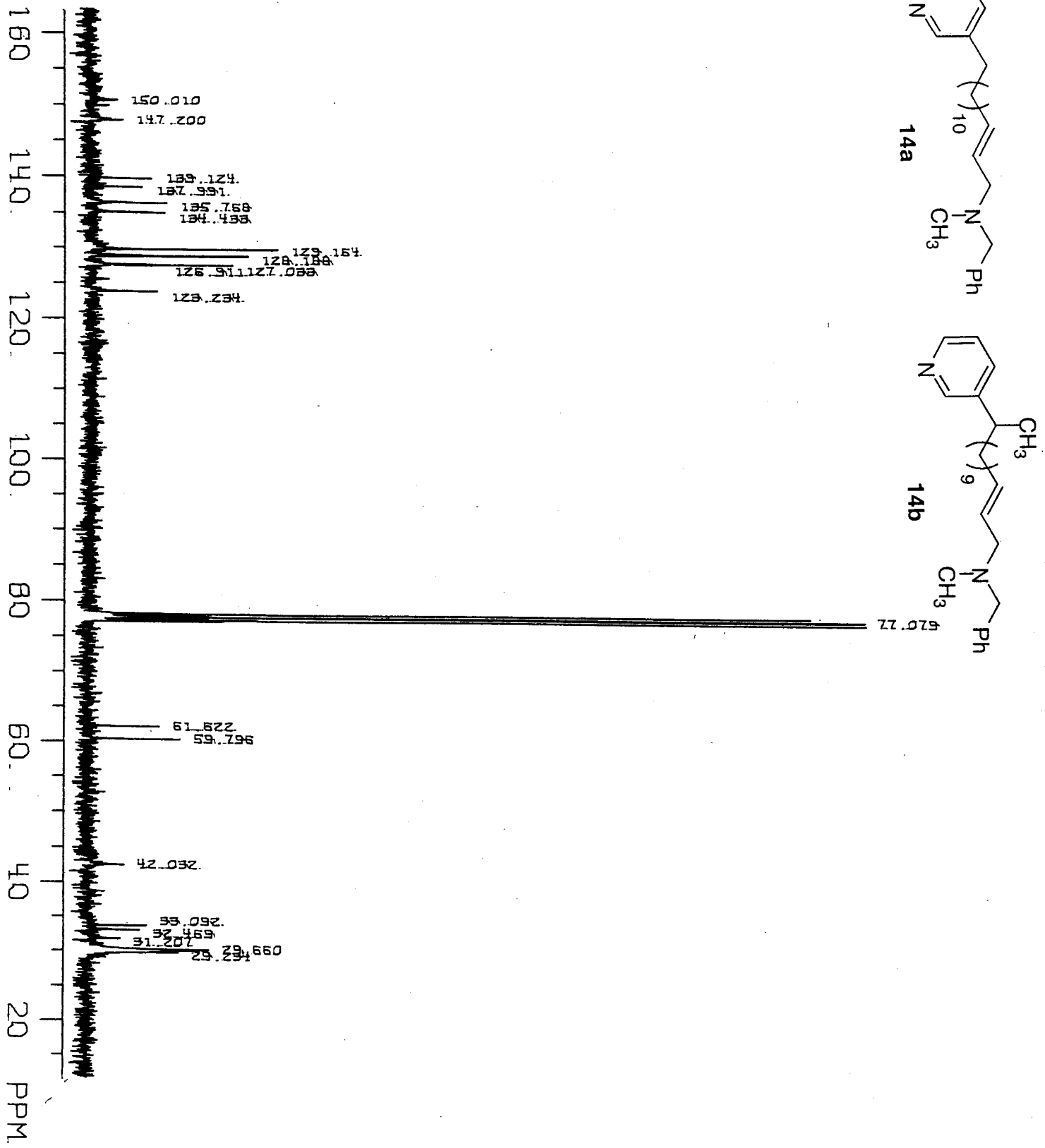
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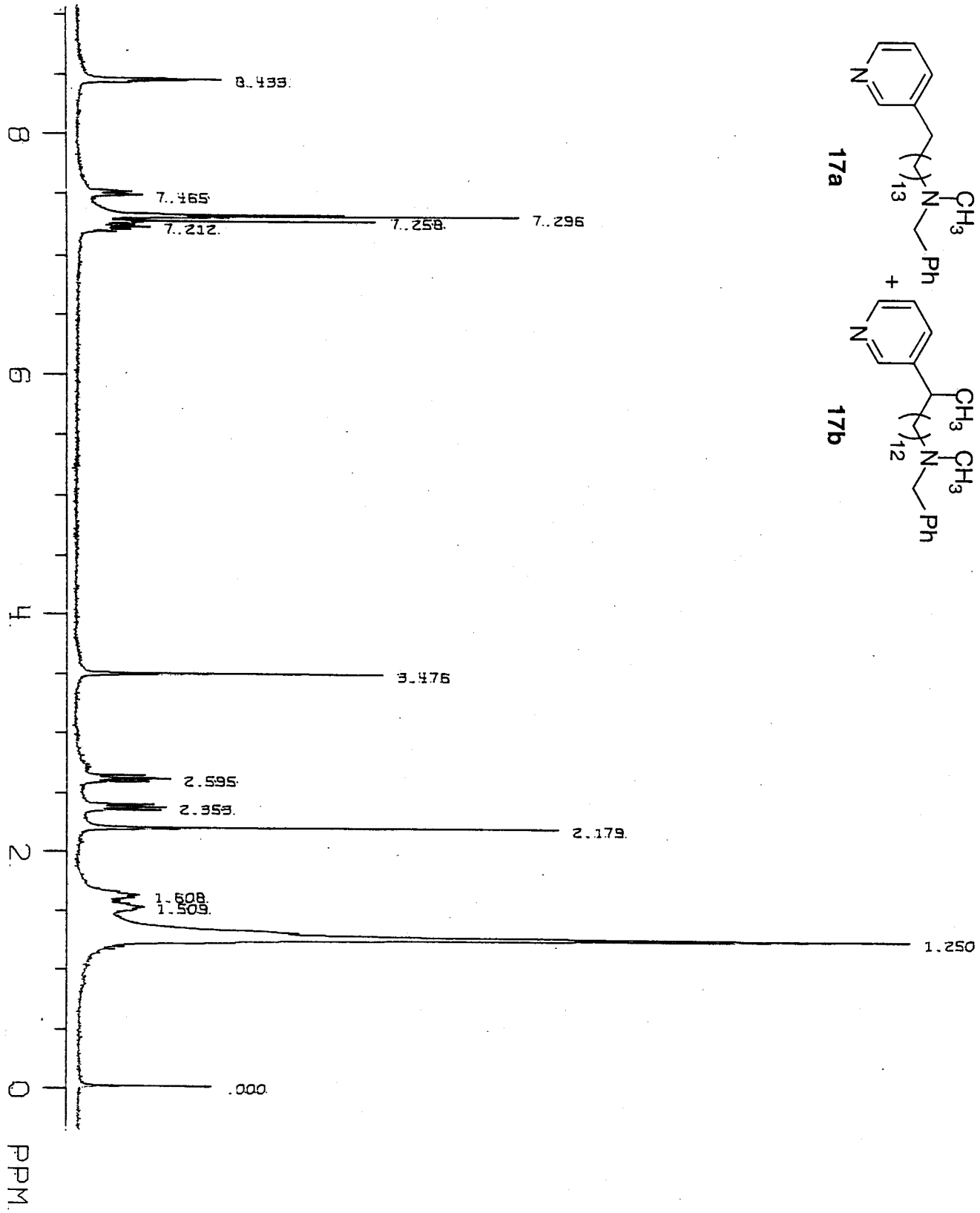
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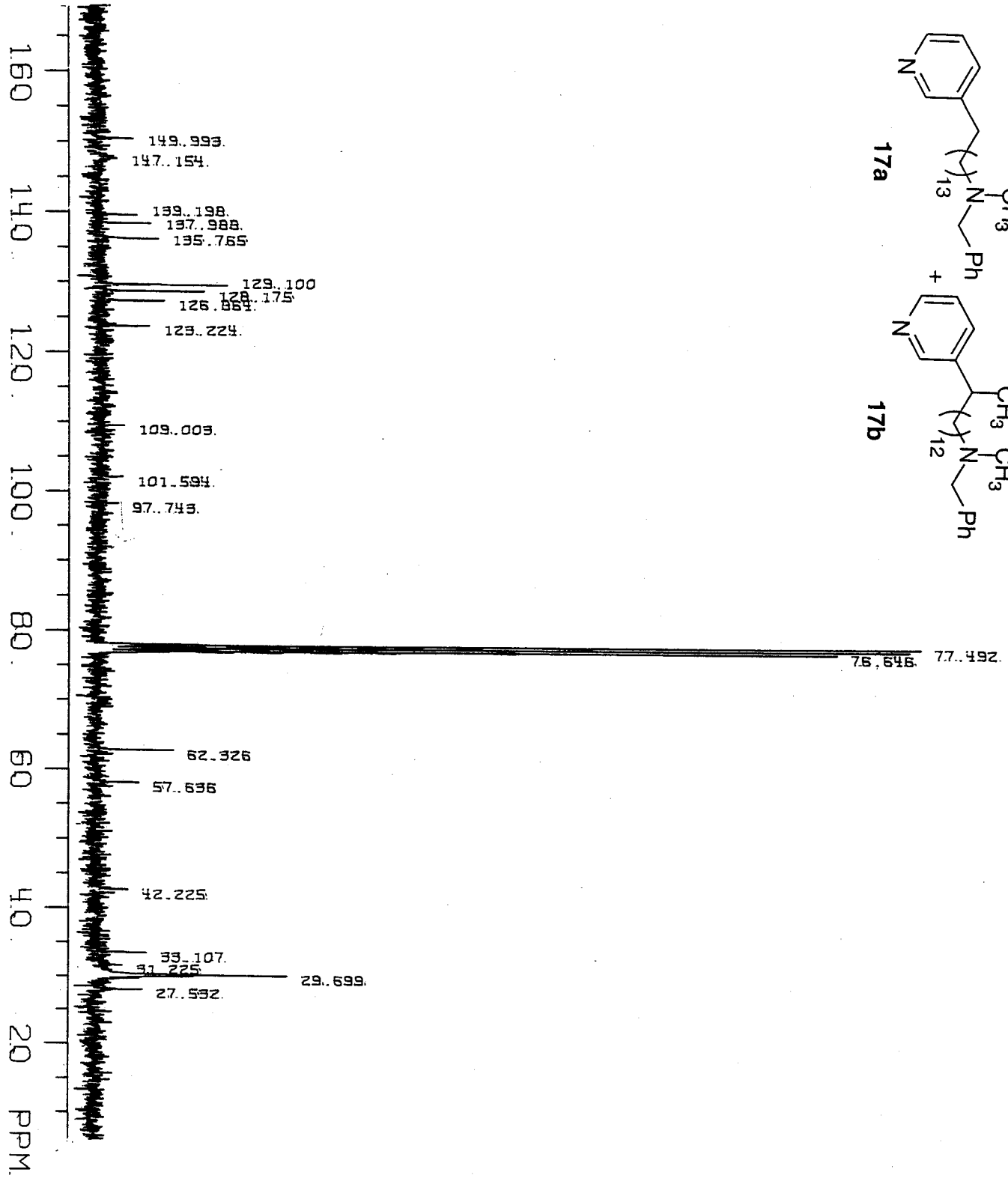
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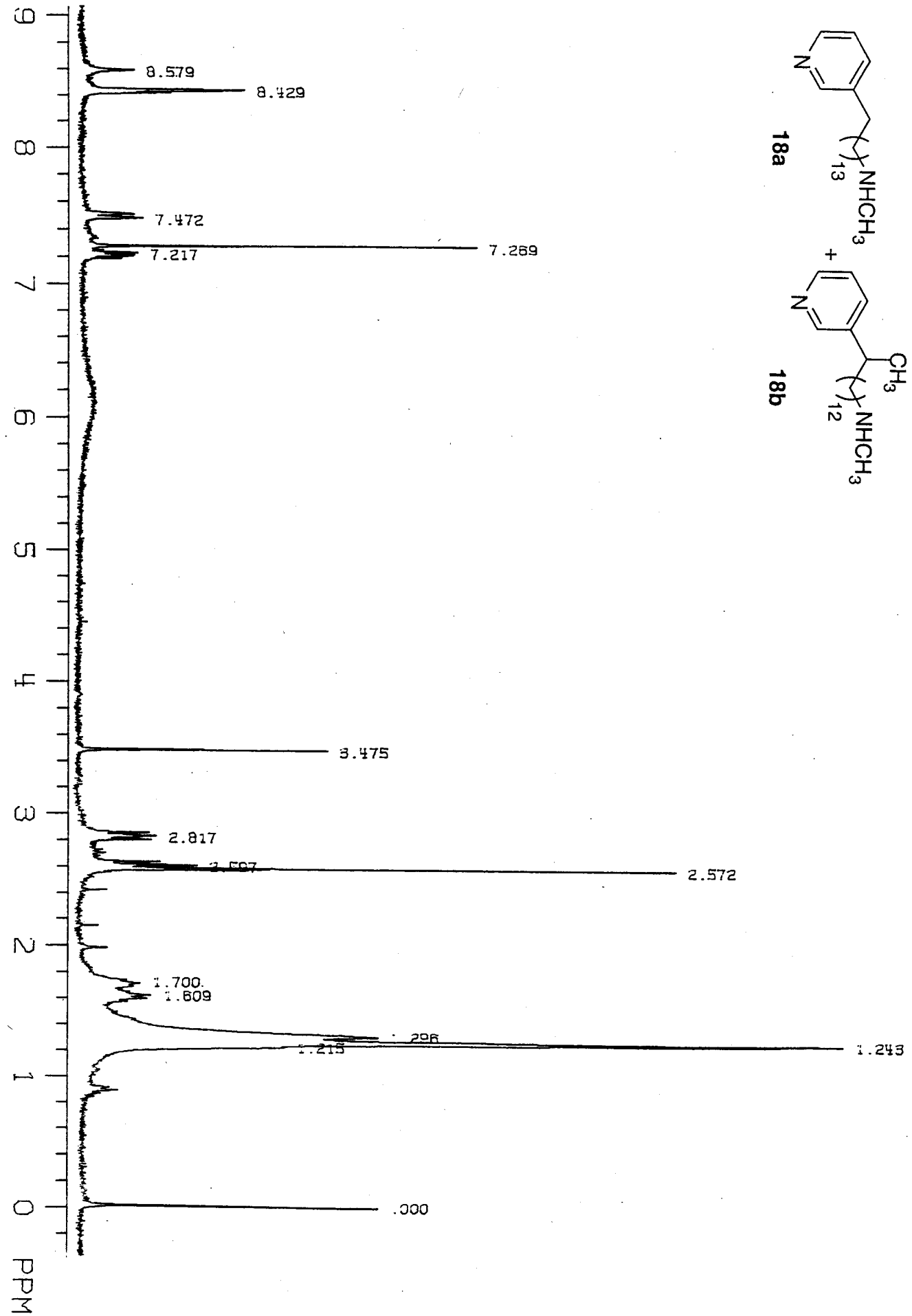
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7.269
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18b
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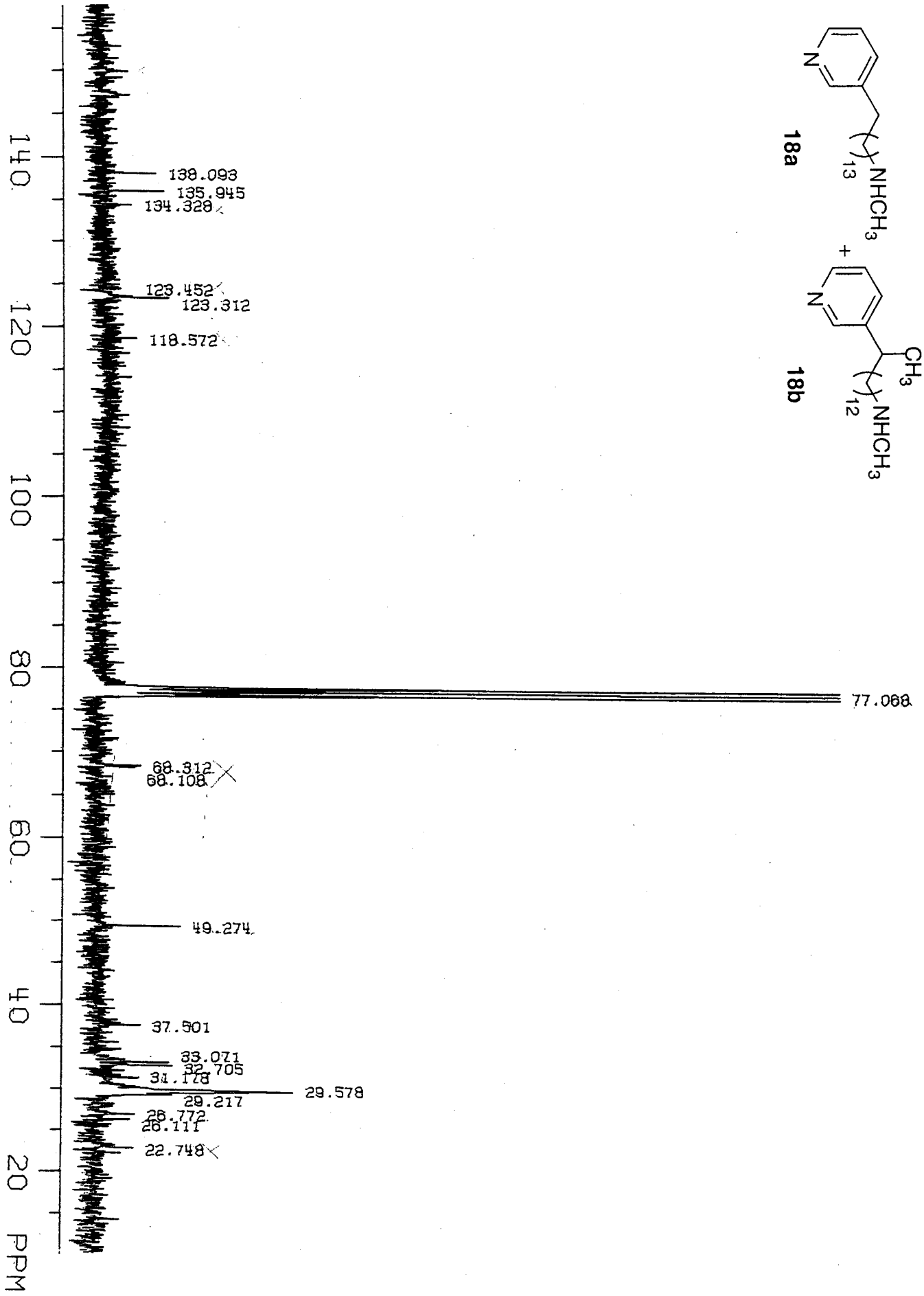
CH3
NHCH3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32.705
31.178
29.578
29.217
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26.111
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18b
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CH3
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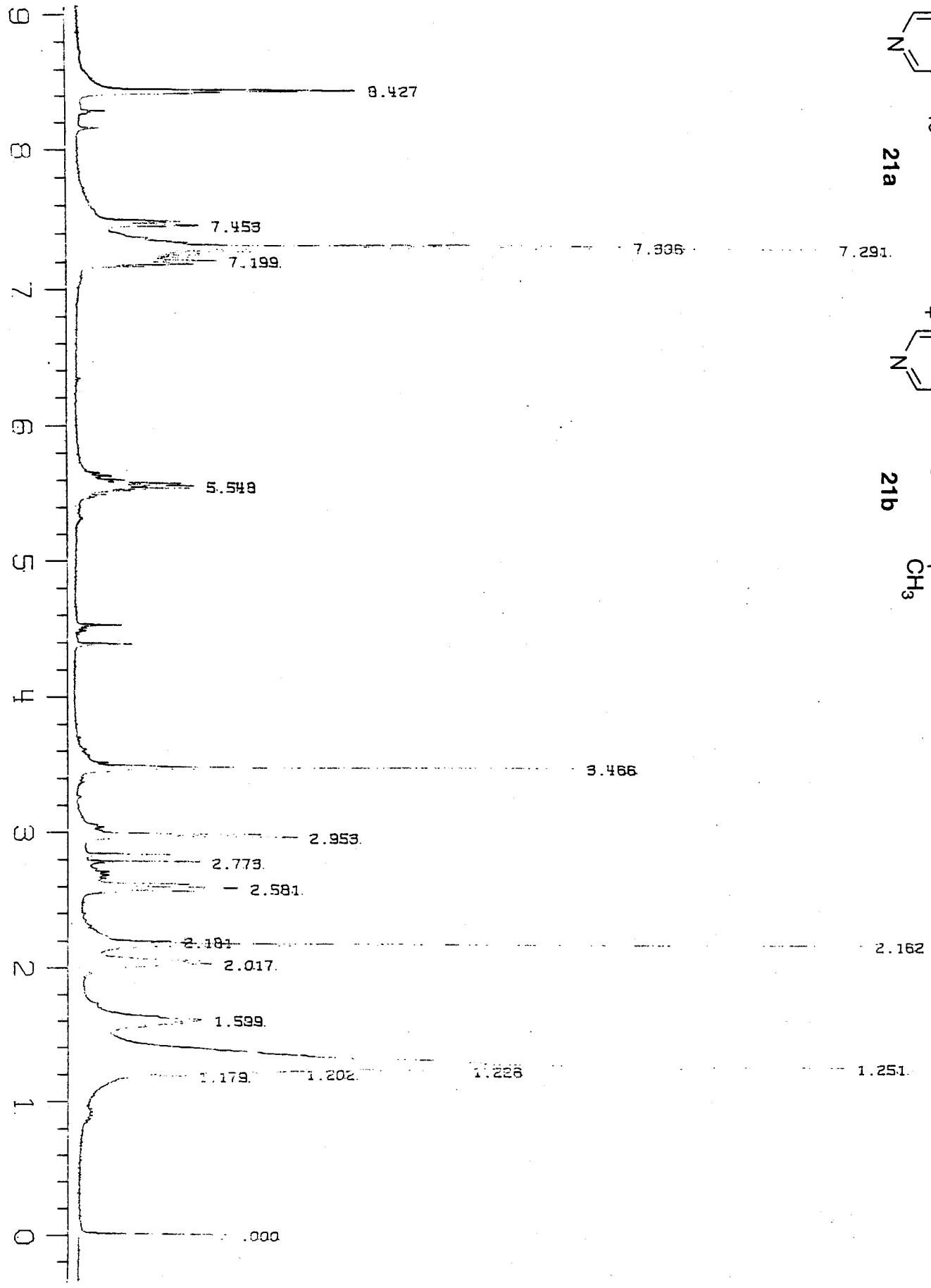
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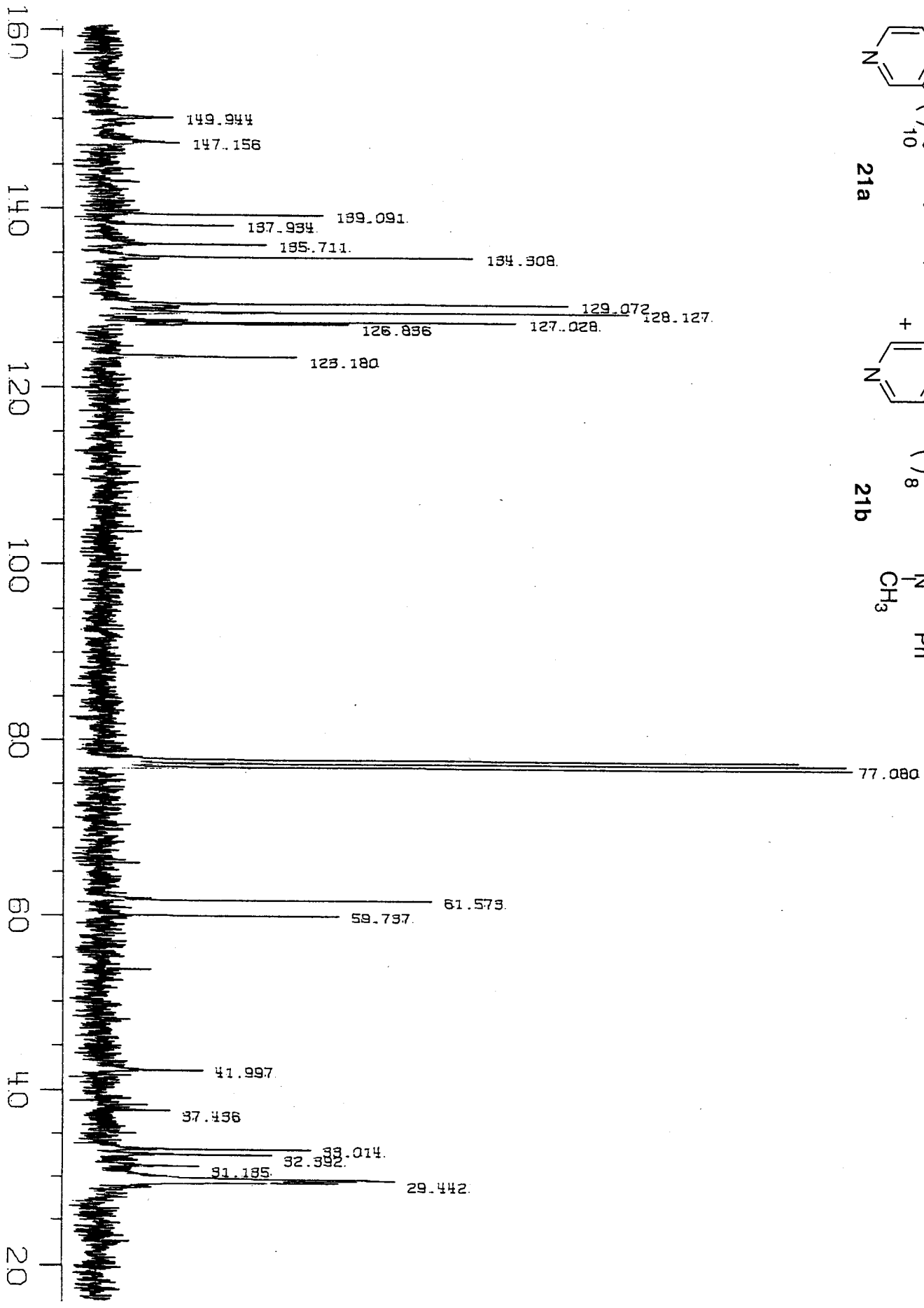
21b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128.127
127.028
126.836
123.180
77.080
61.573
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31.185
29.442
21a
21b
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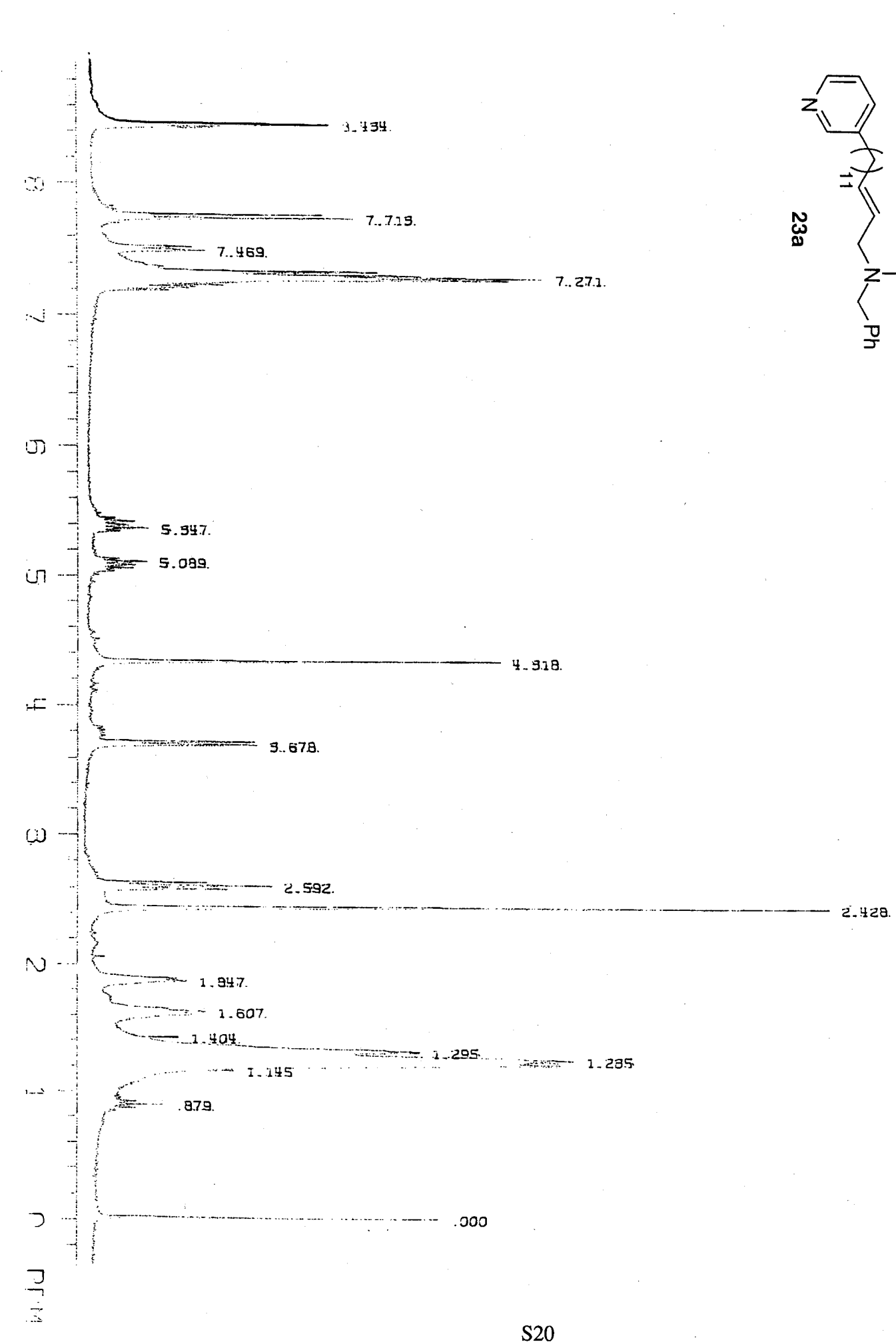
8
CH3
N
Ph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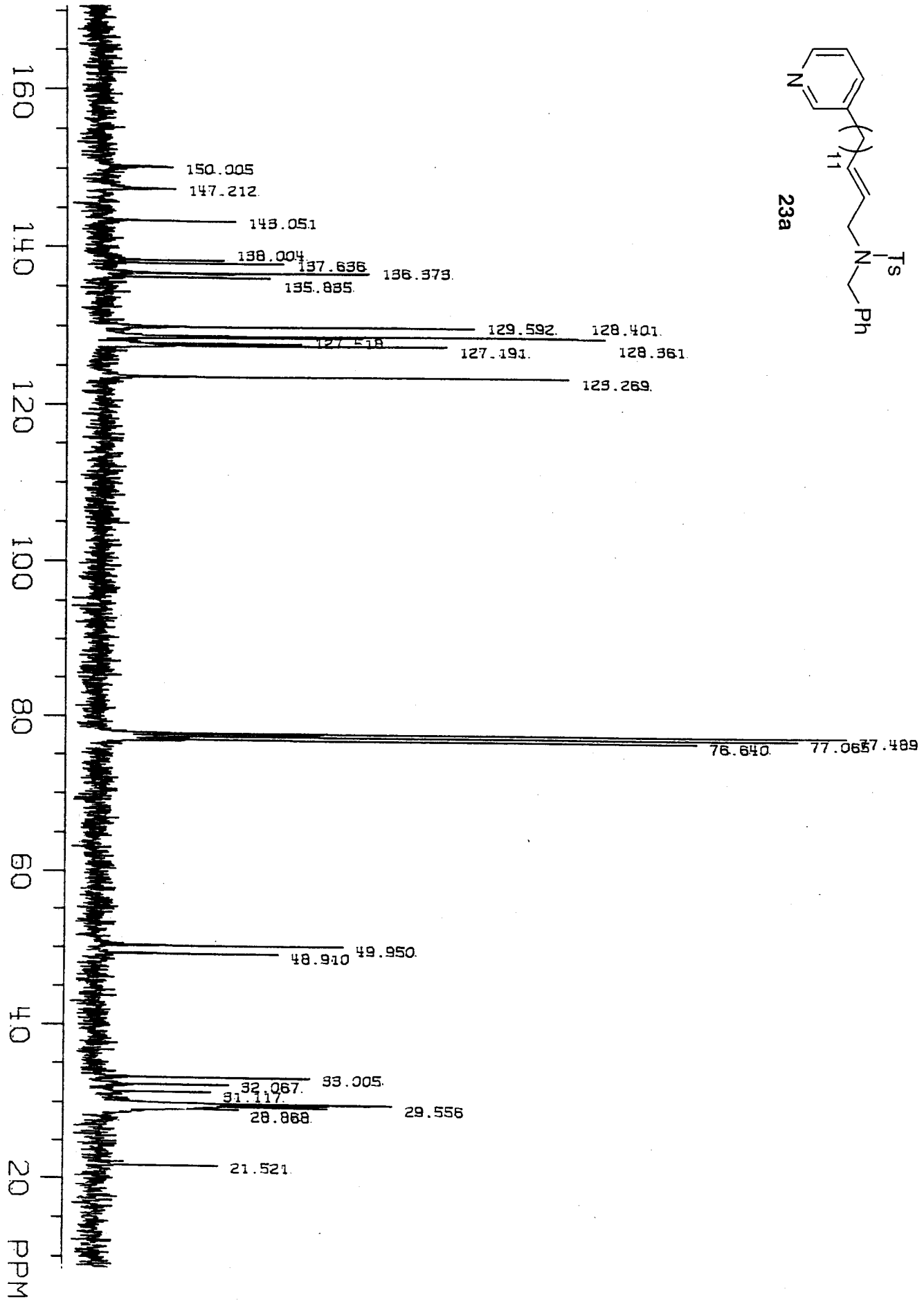
Ph
23a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127.191
128.361
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77.489
77.065
76.640
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Ts
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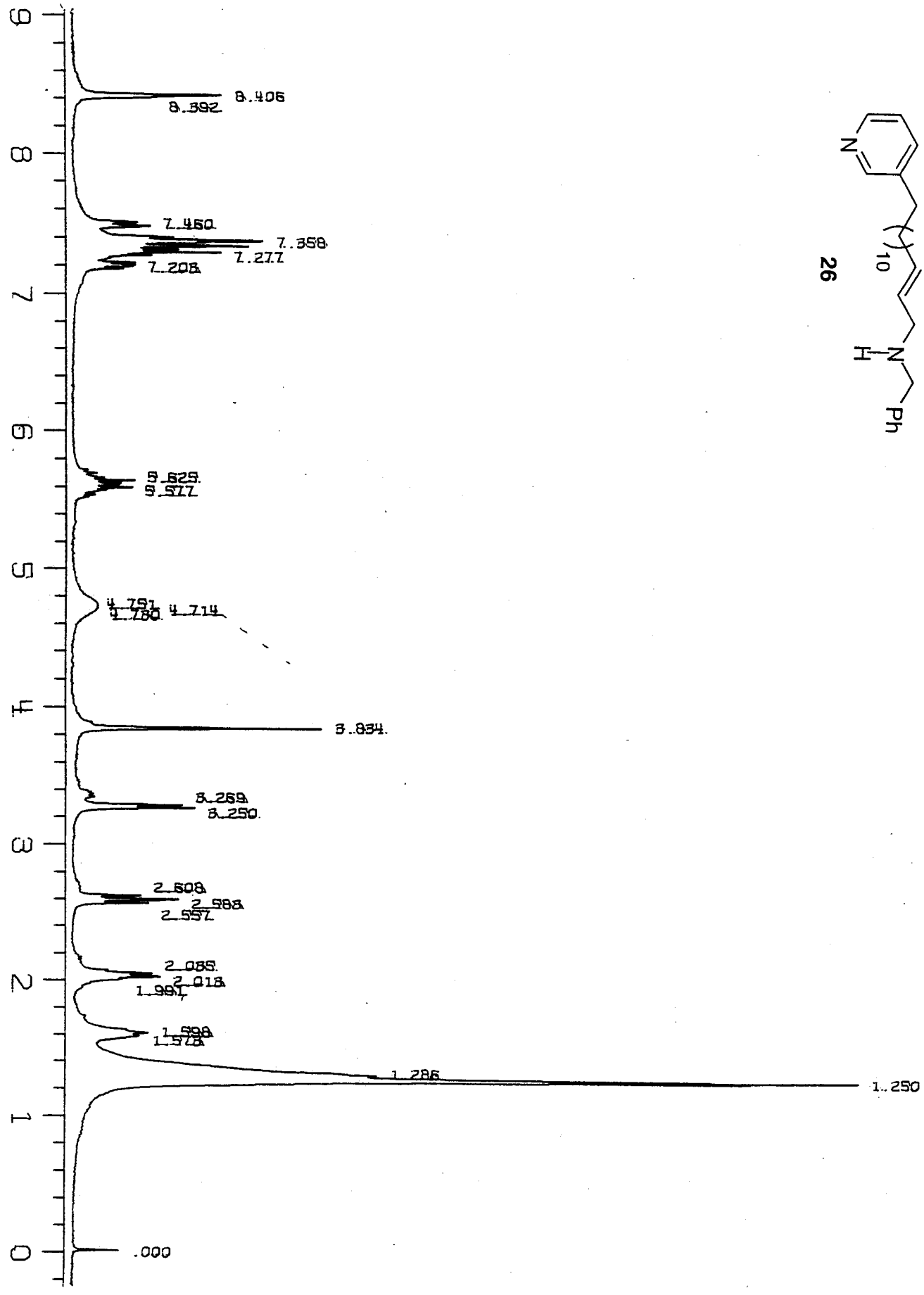
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5.577
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3.250
2.608
2.588
2.557
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1.598
1.578
1.286
1.250
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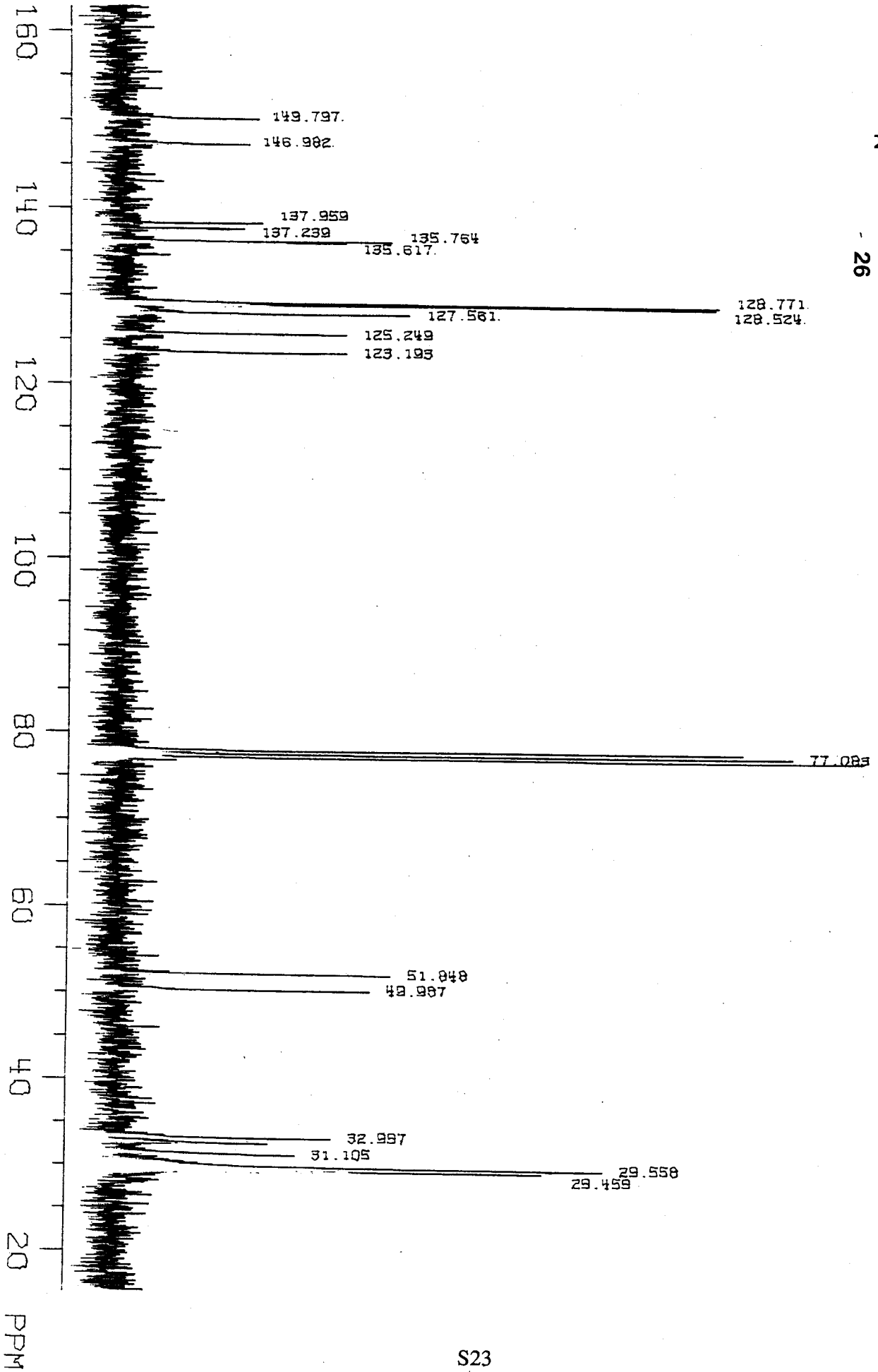
10
H
N
Ph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29.459
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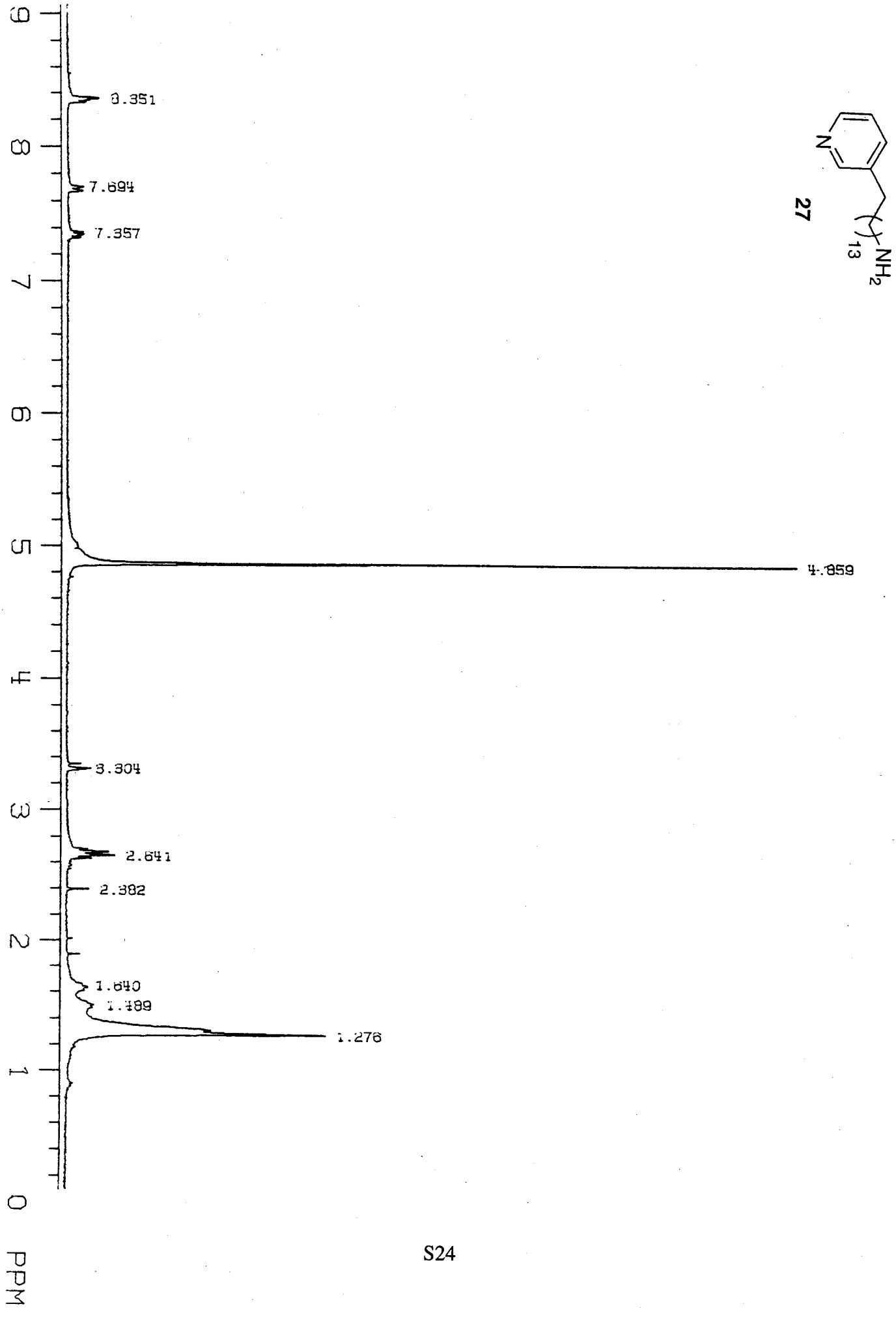
N
Ph
26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PPM
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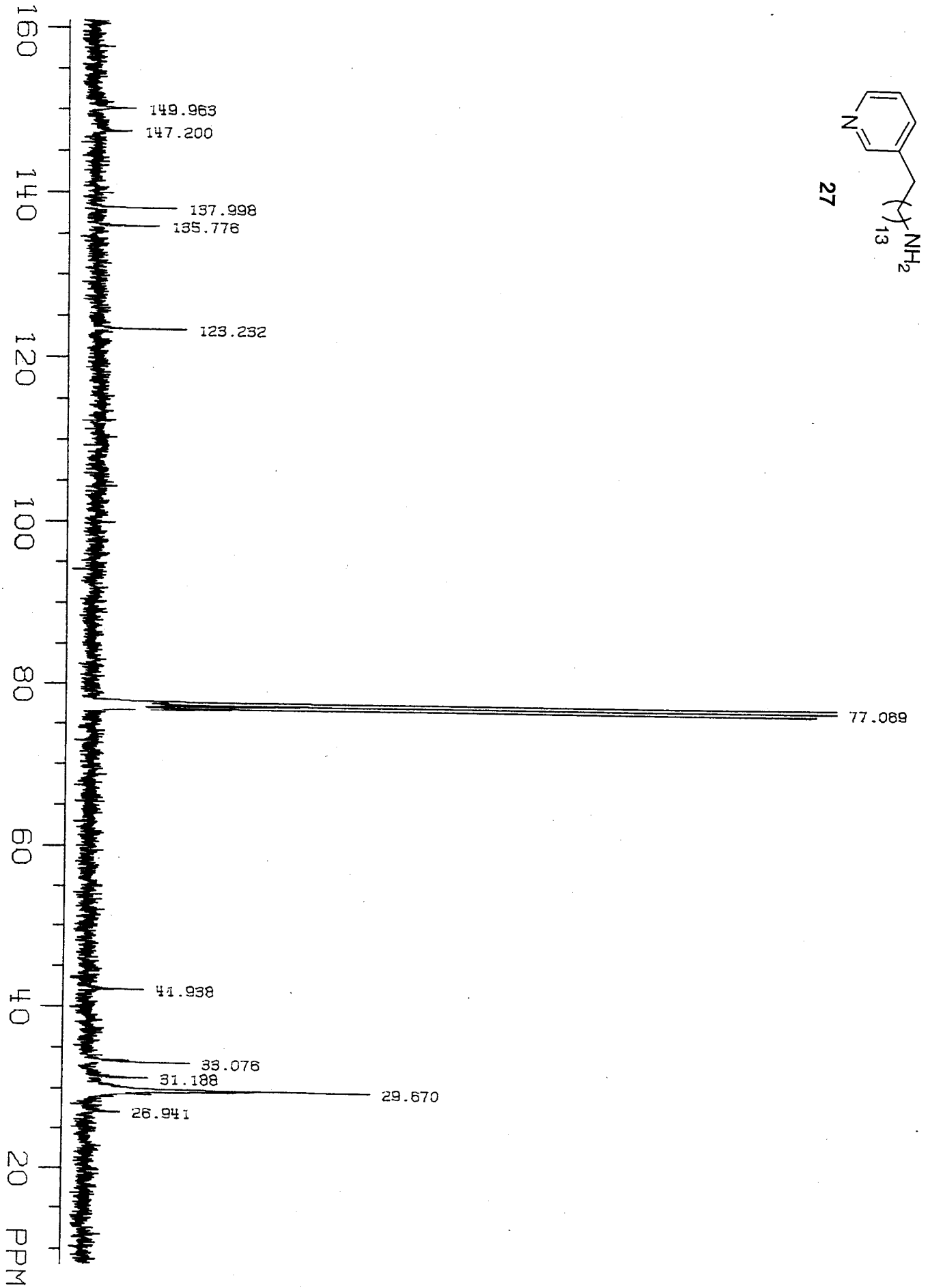
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NH2
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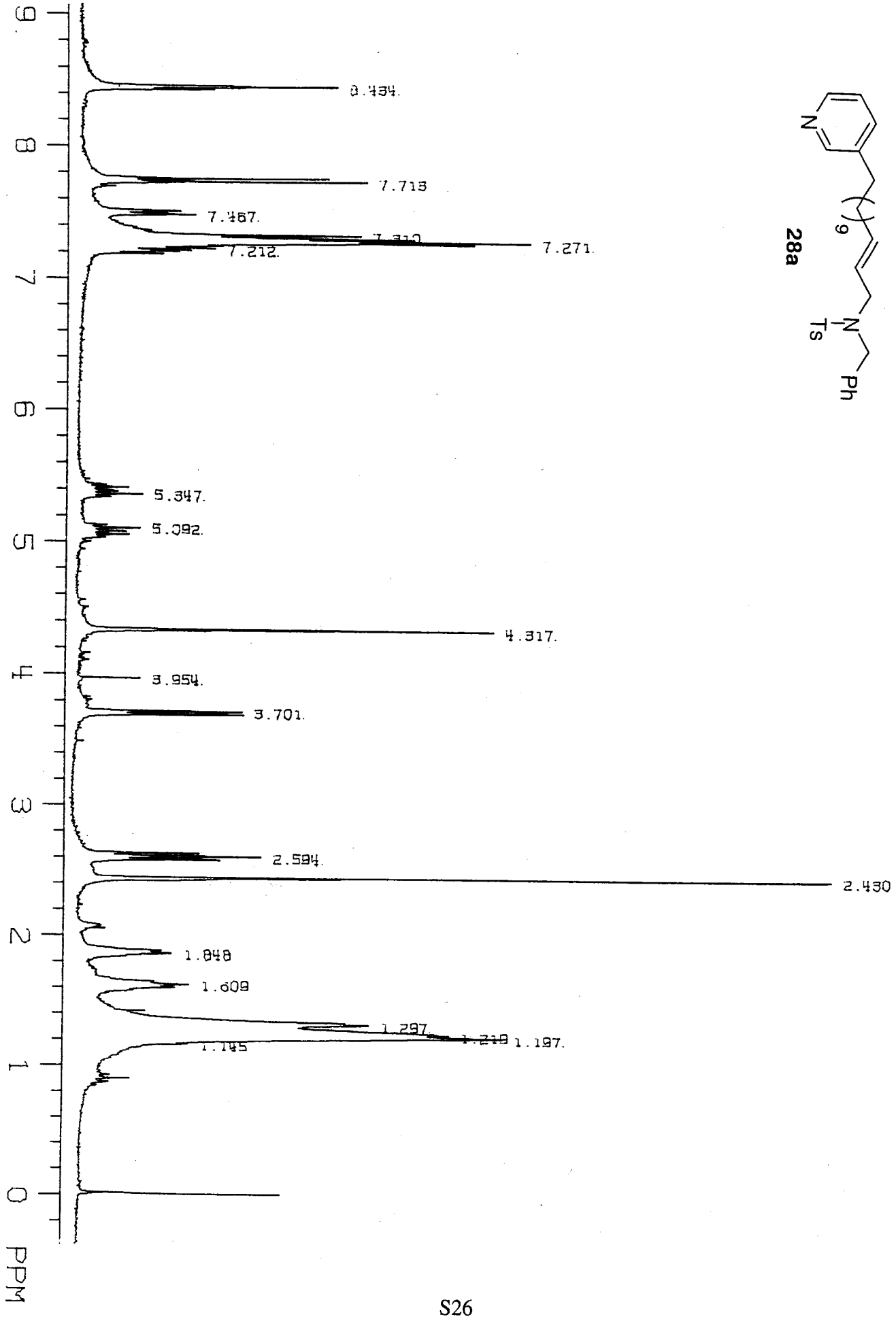
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1.197
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PPM
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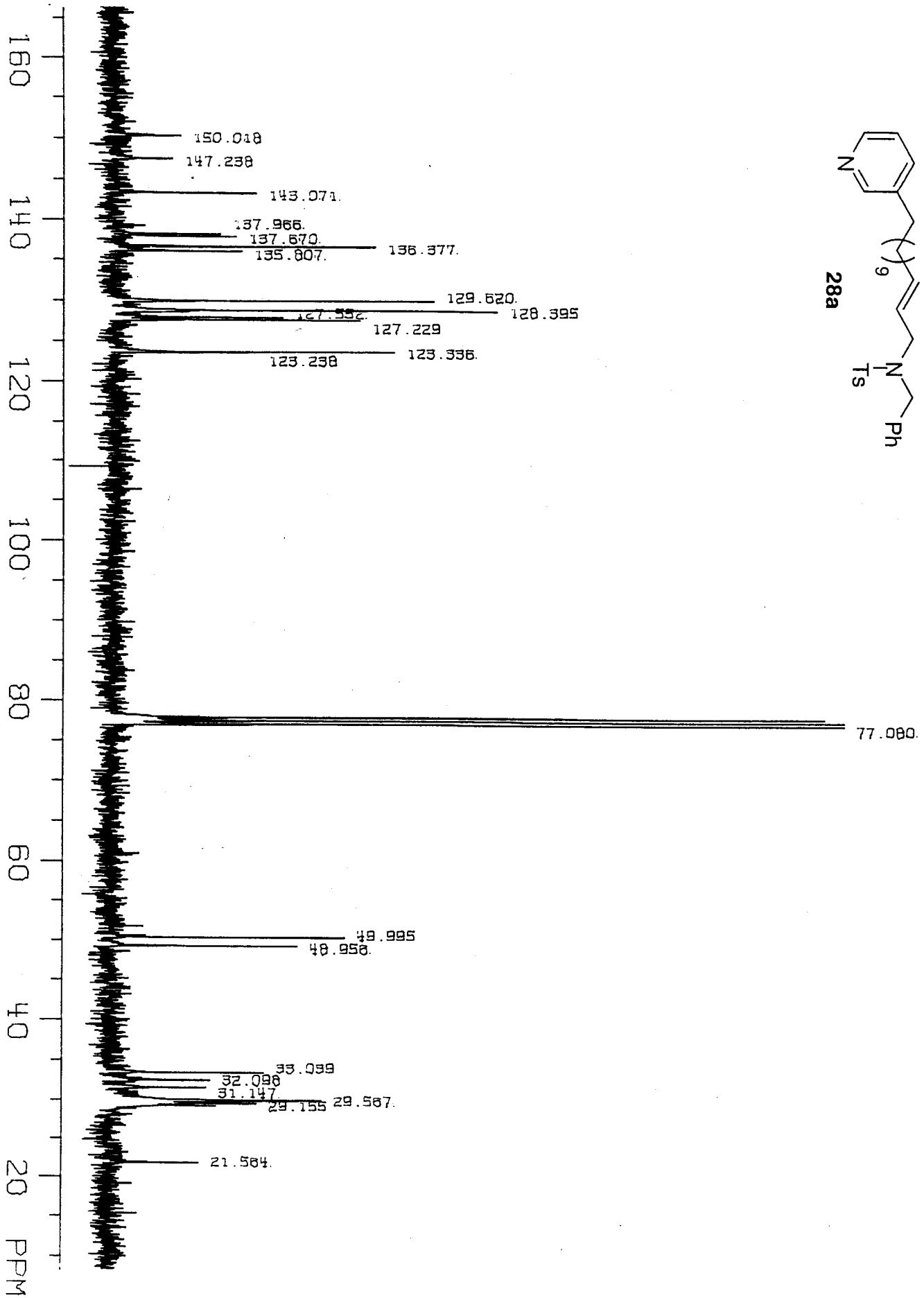
N
Ts
Ph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127.229
123.336
123.238
77.080
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N
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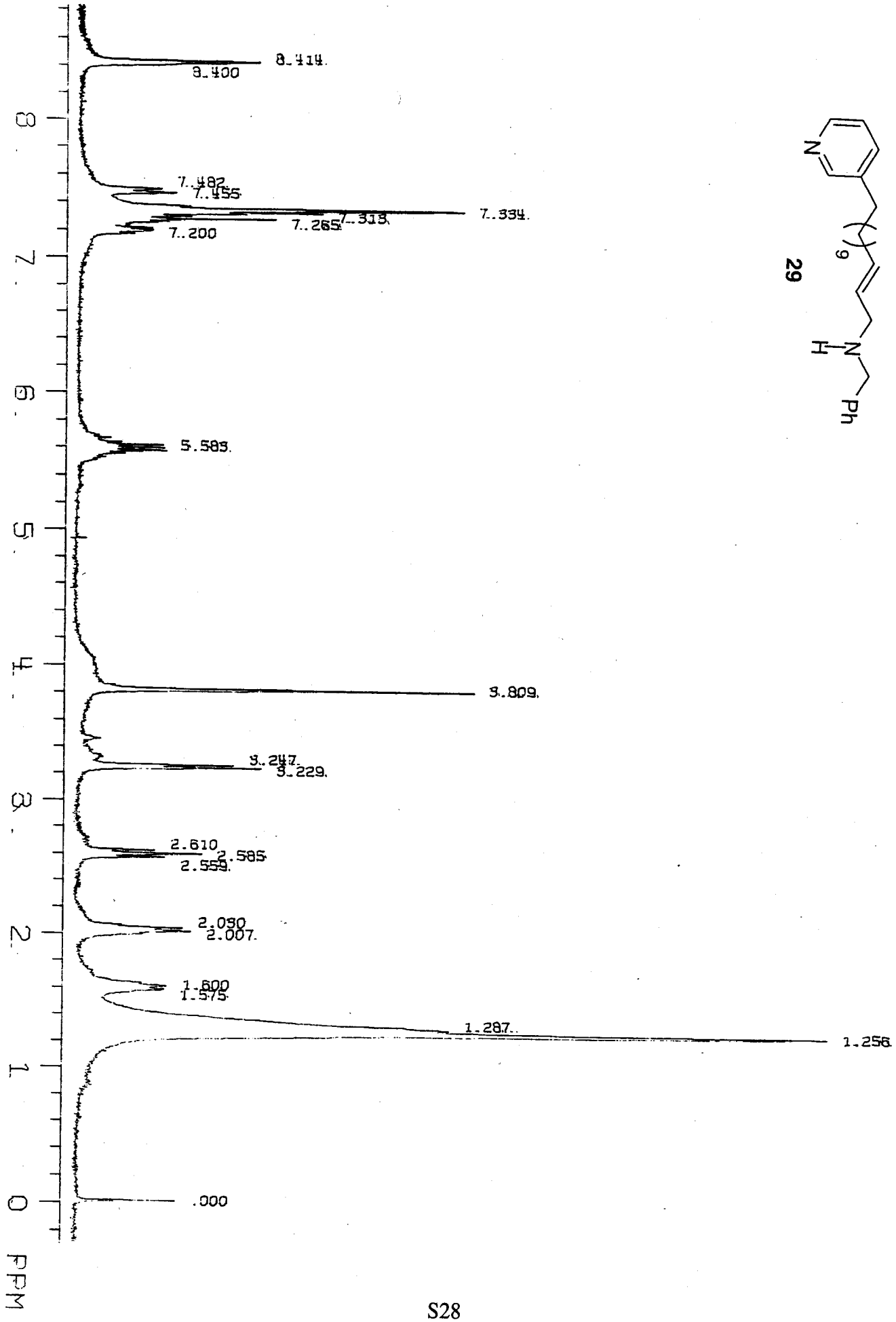
Ph
28a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2.610
2.585
2.559
2.090
2.007
1.600
1.575
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PPM
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7
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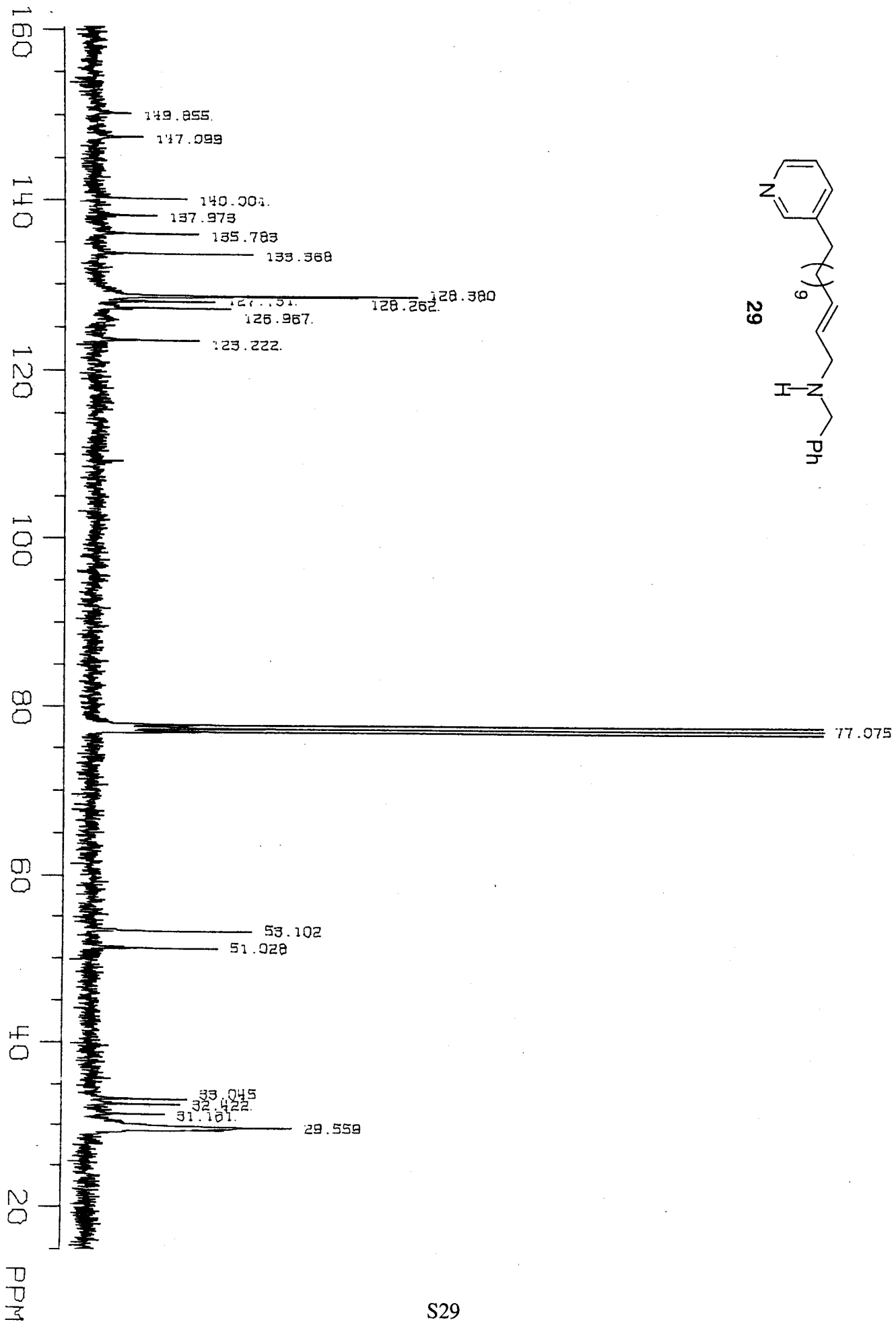
9
H
N
Ph

29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H
N
Ph
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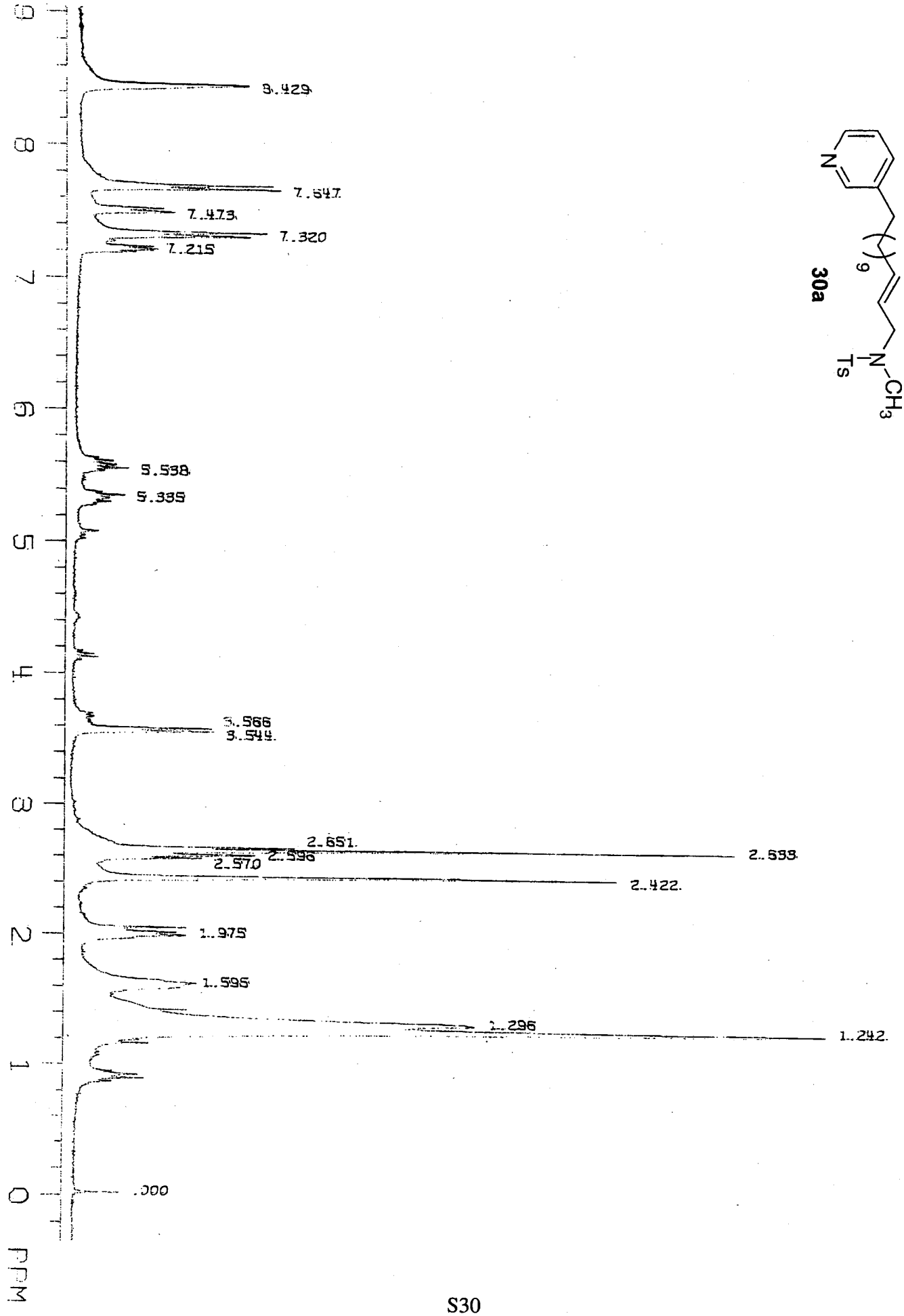
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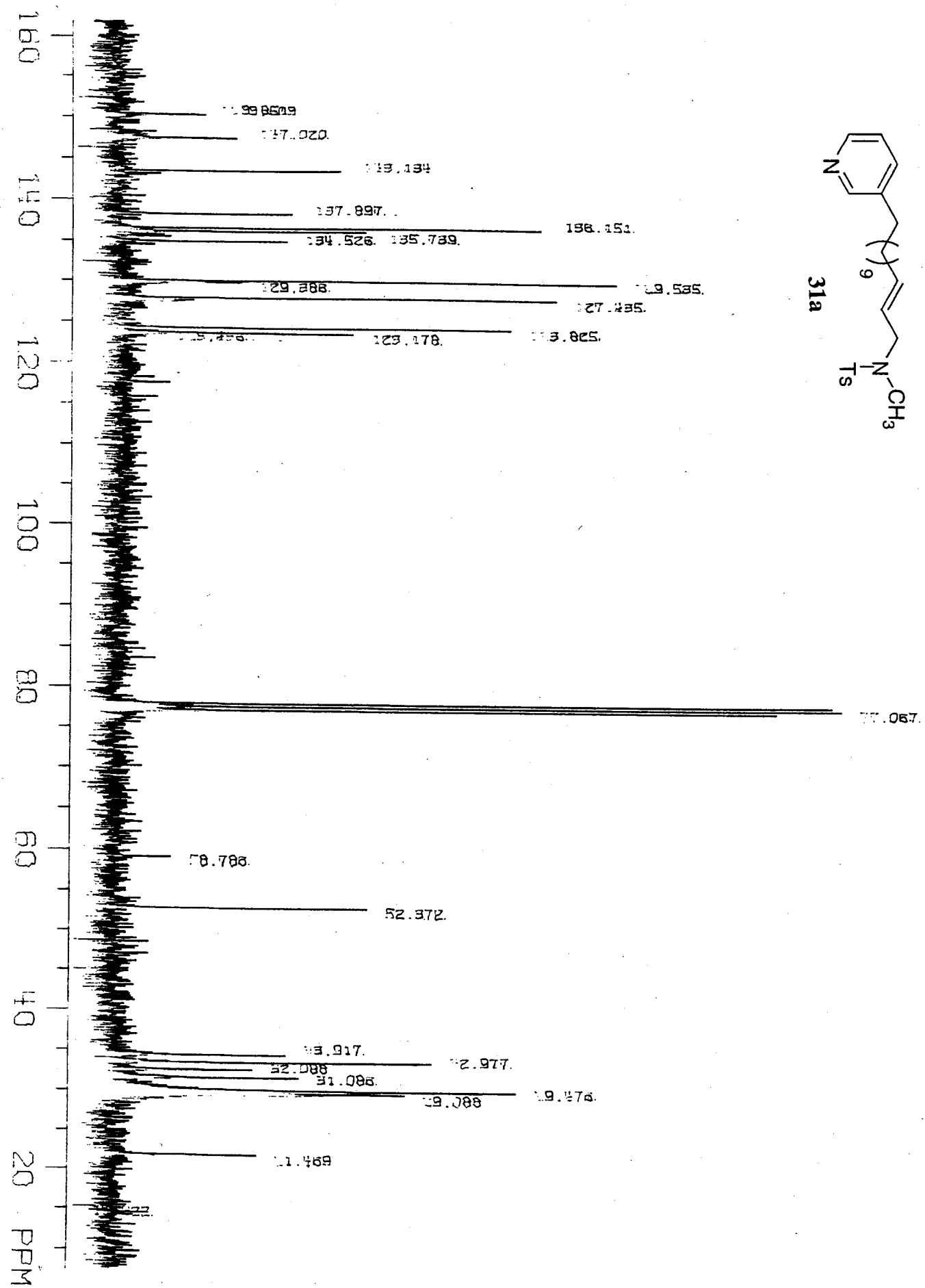
N
Ts
CH3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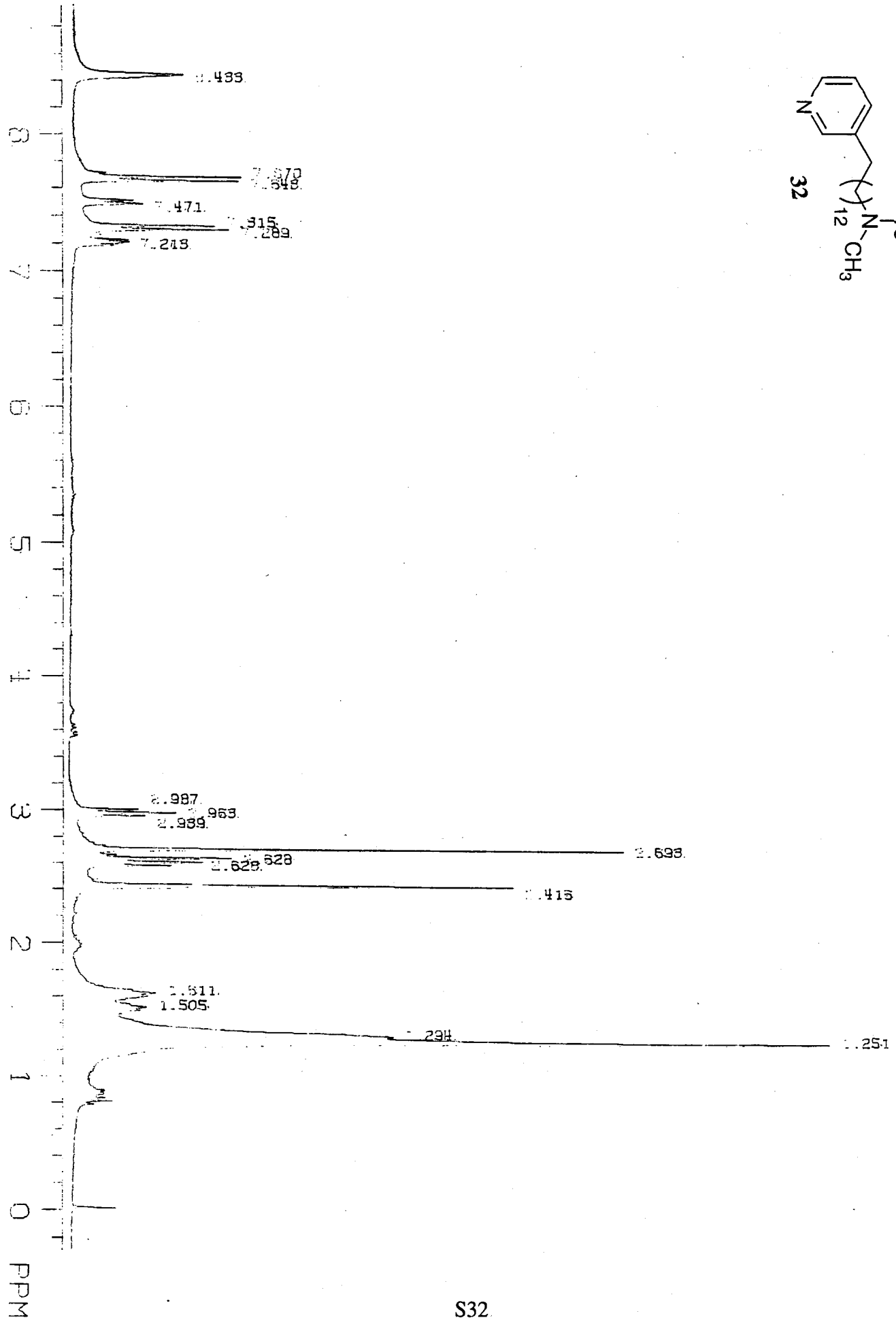
Ts
CH3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1.505
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PPM

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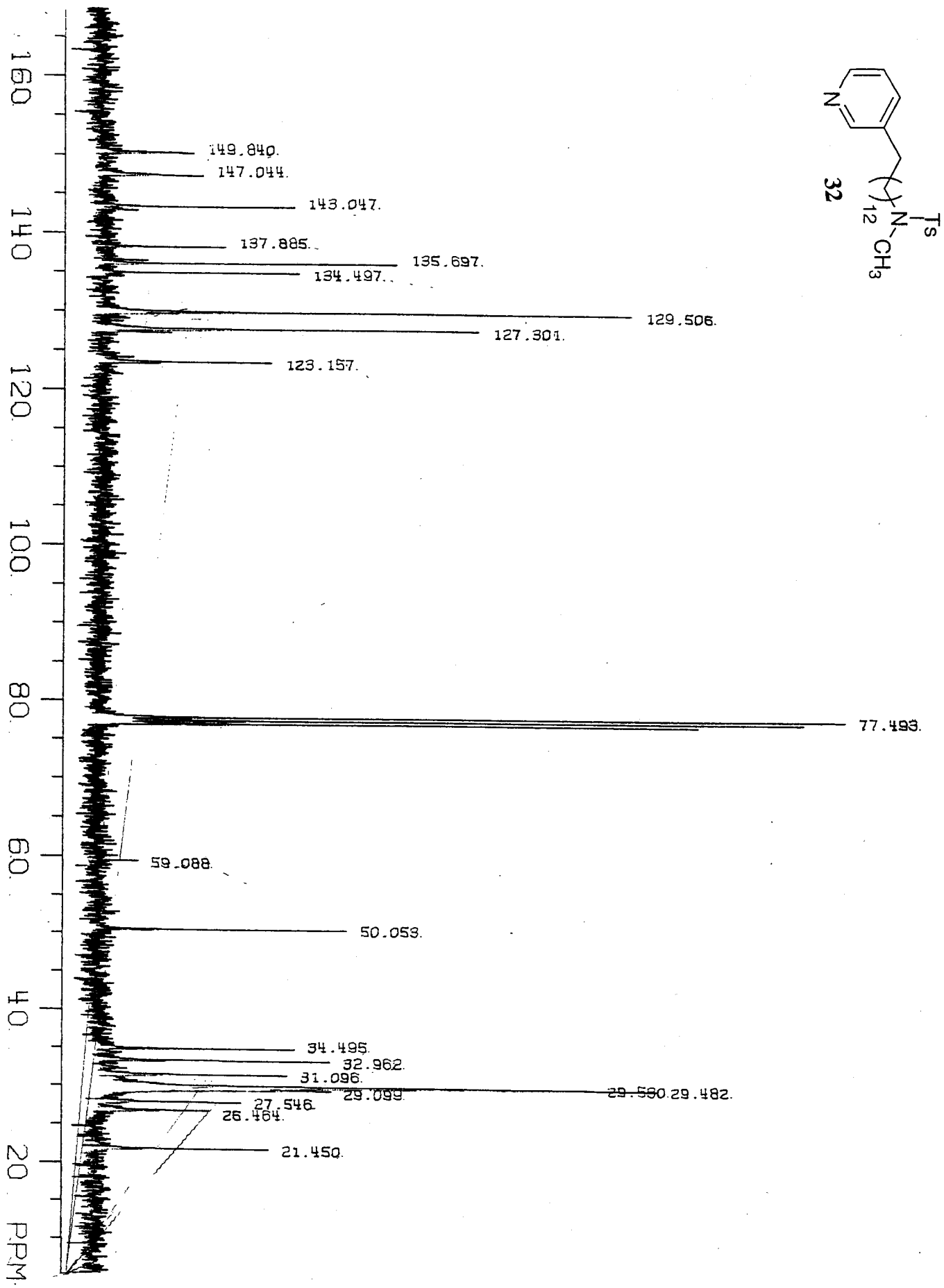
12
N
Ts
CH3

32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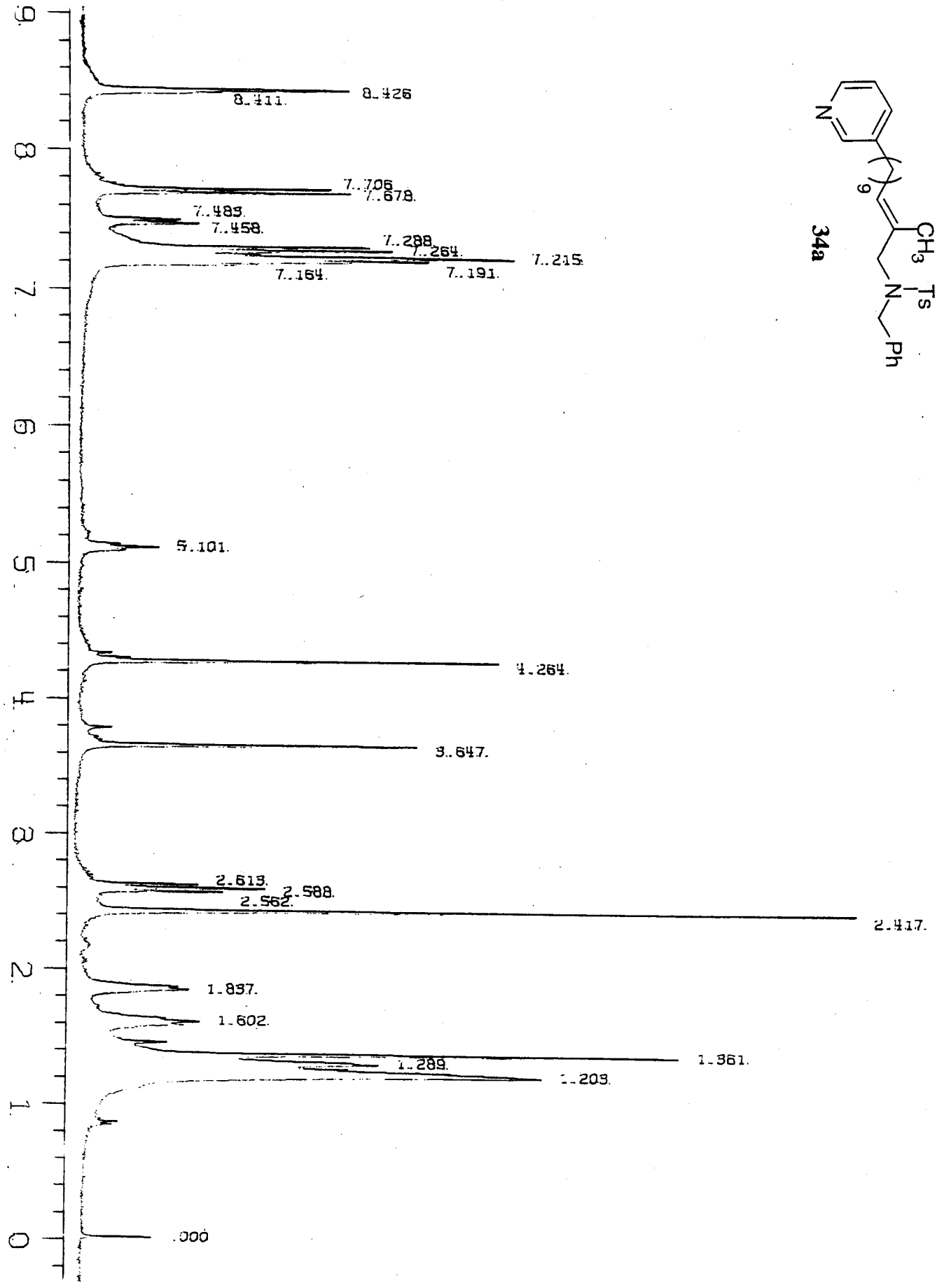
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Ph
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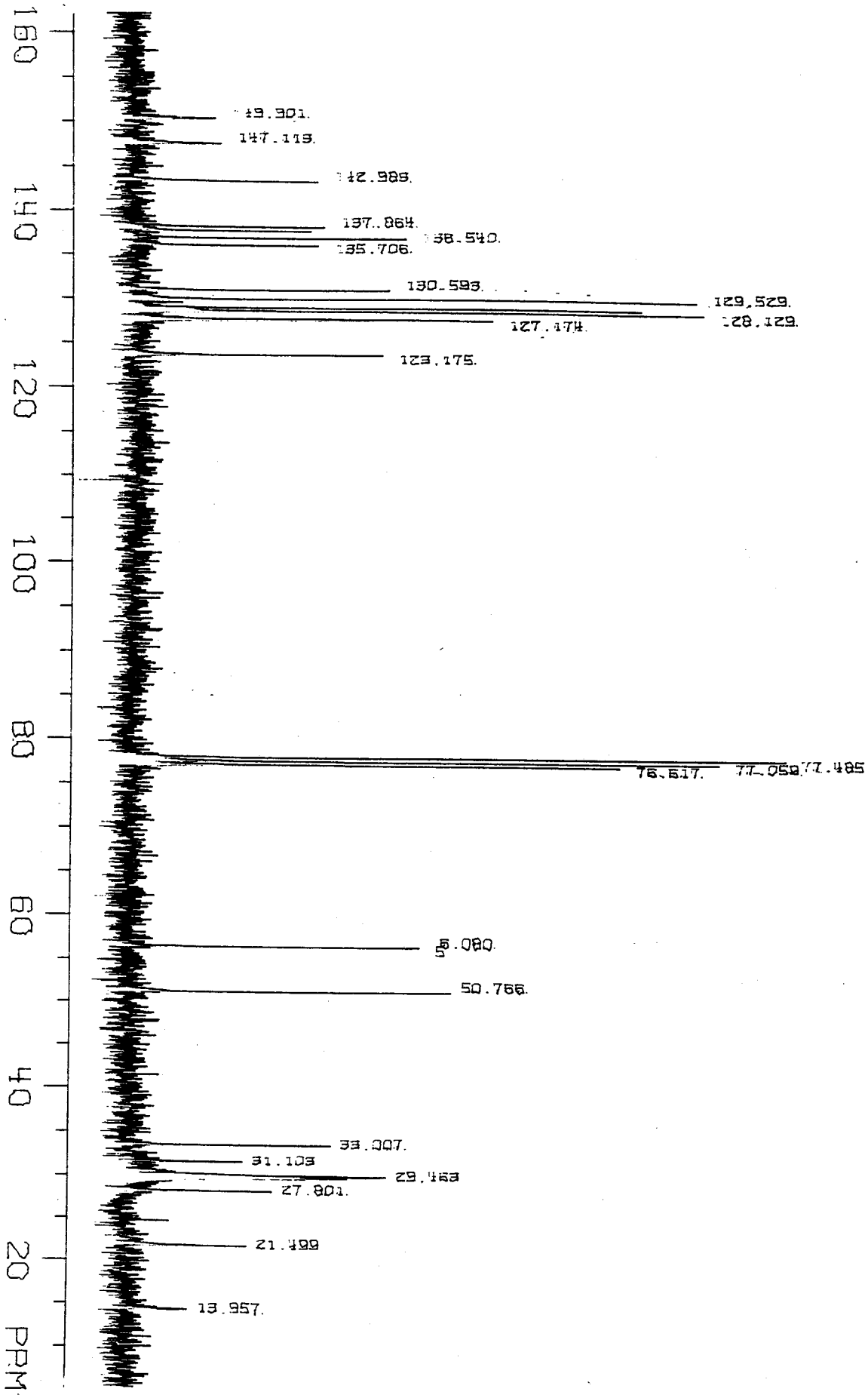
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Ph
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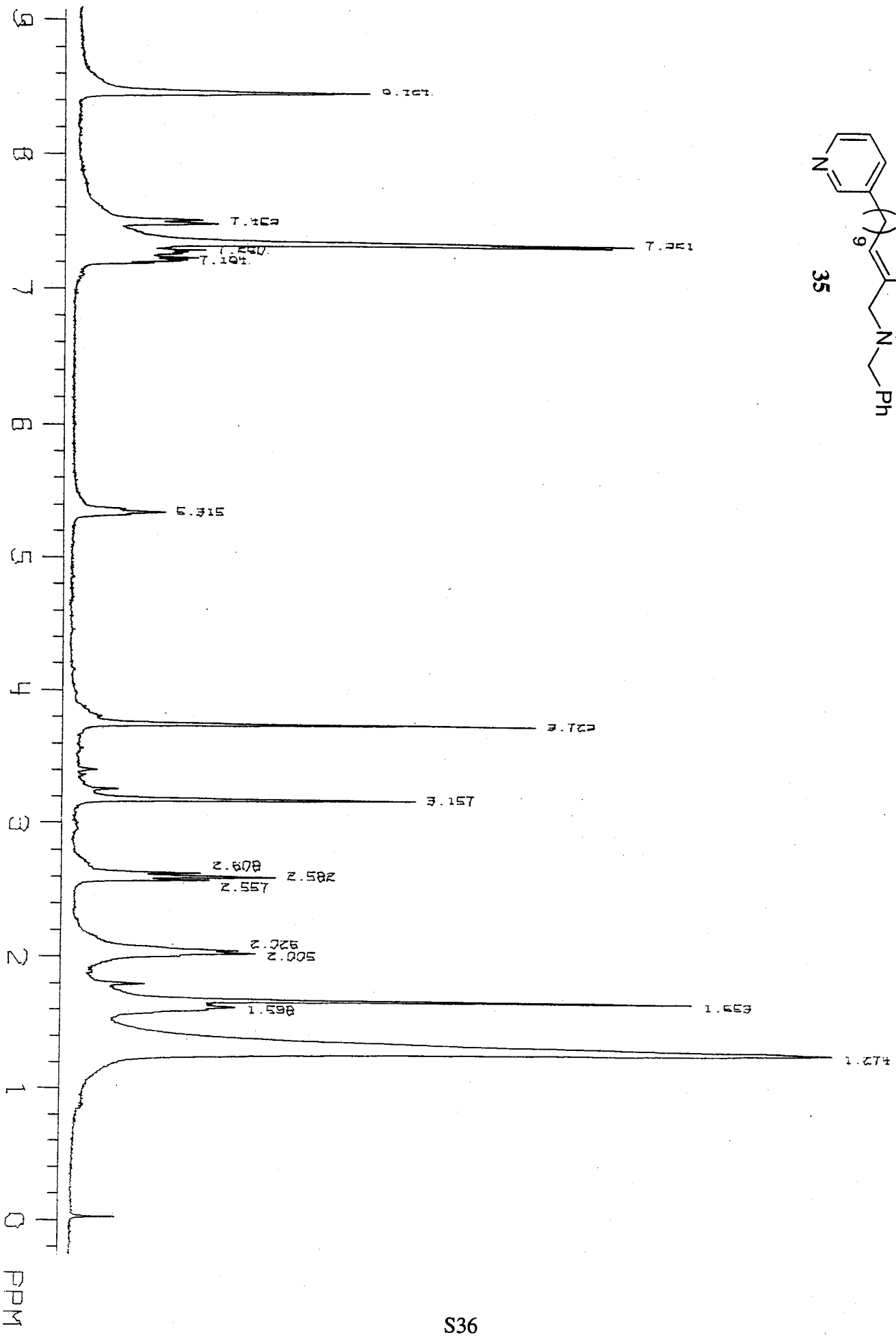
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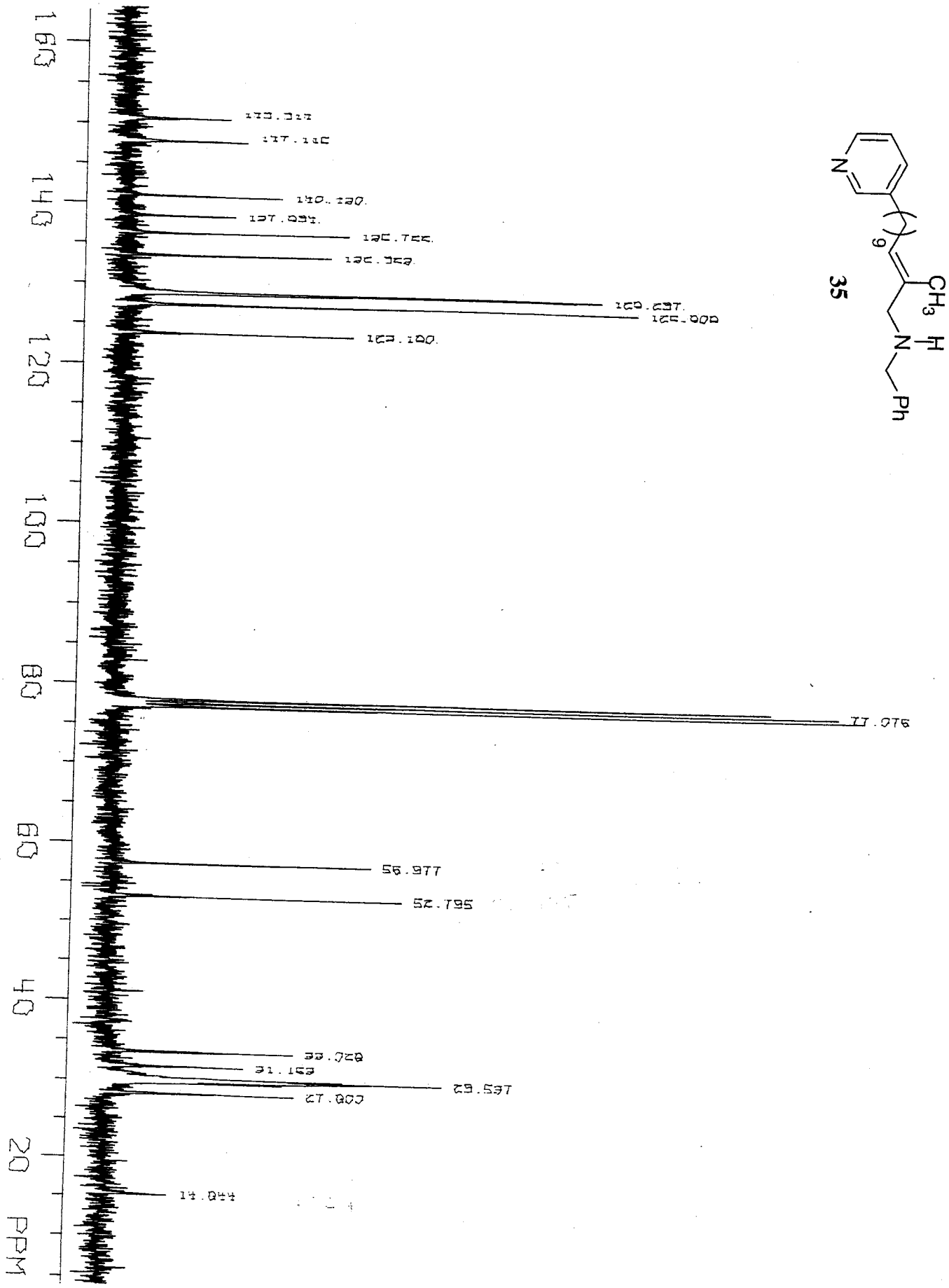
35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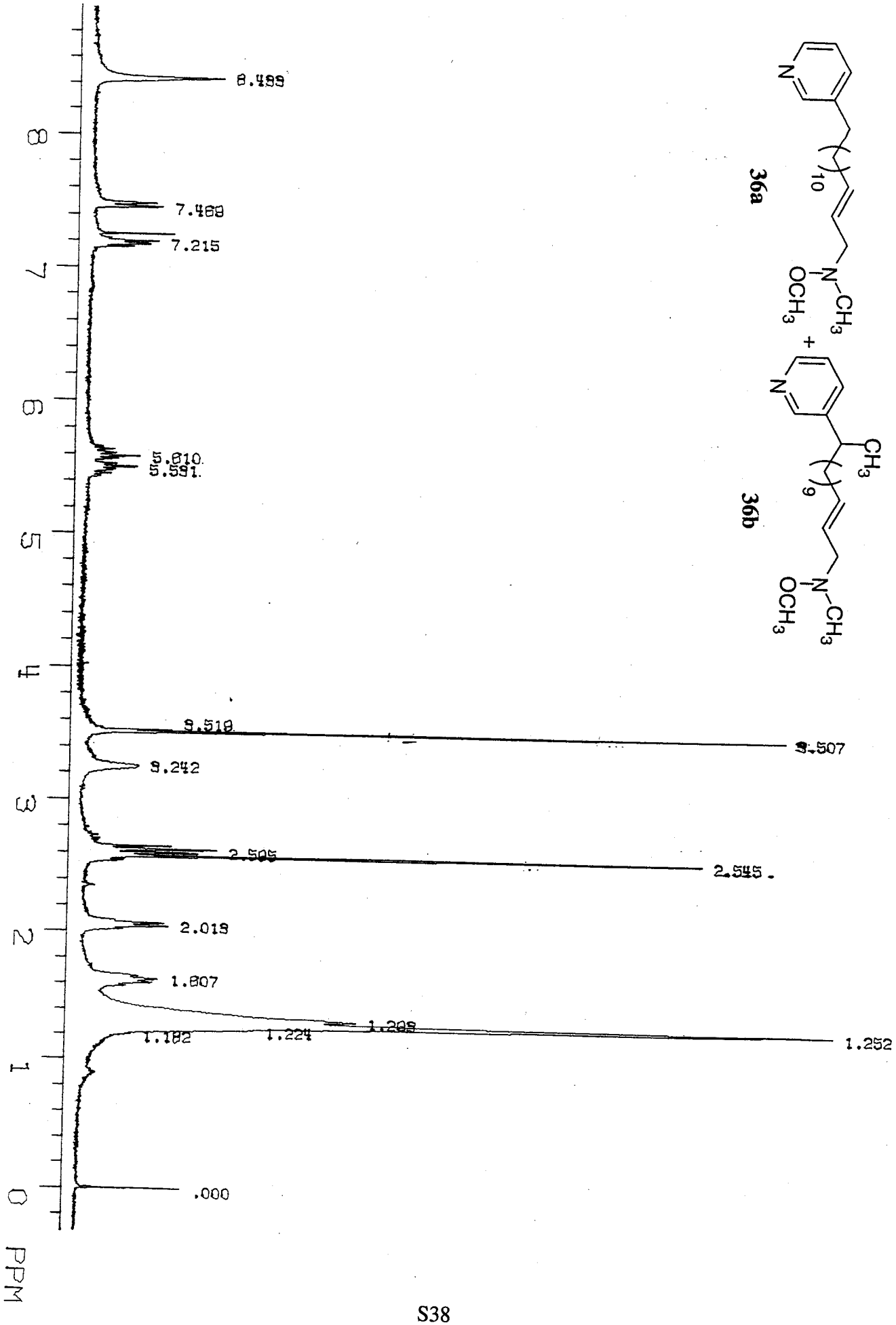
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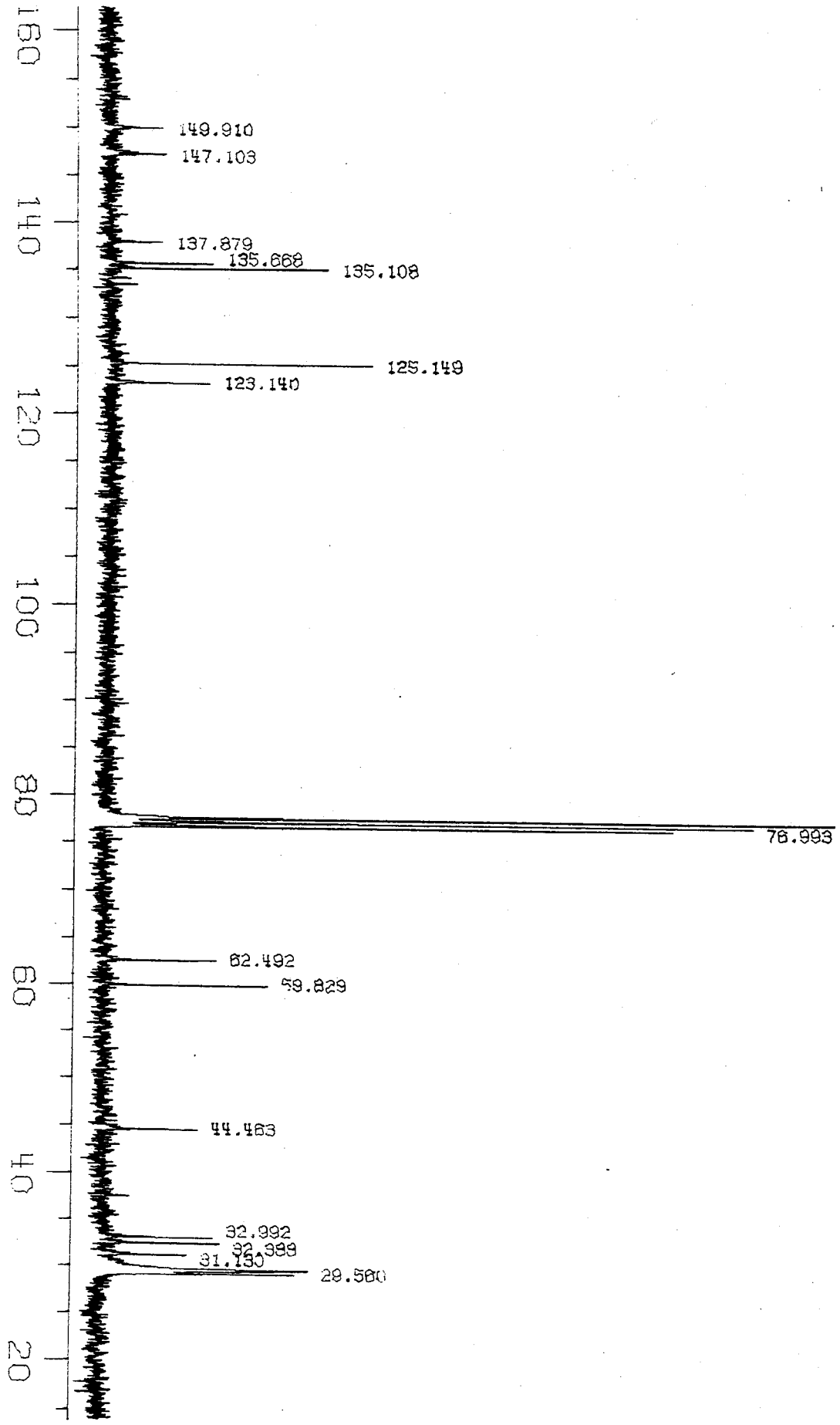
36a
36b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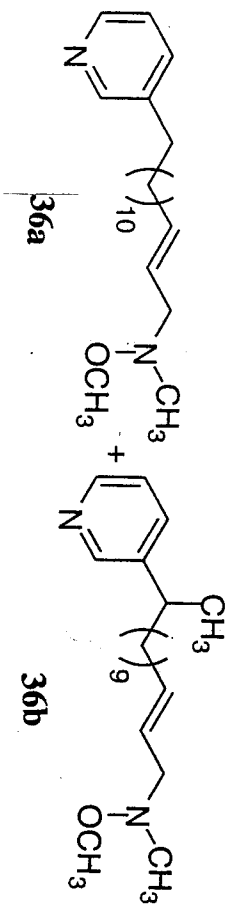
29.580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36b
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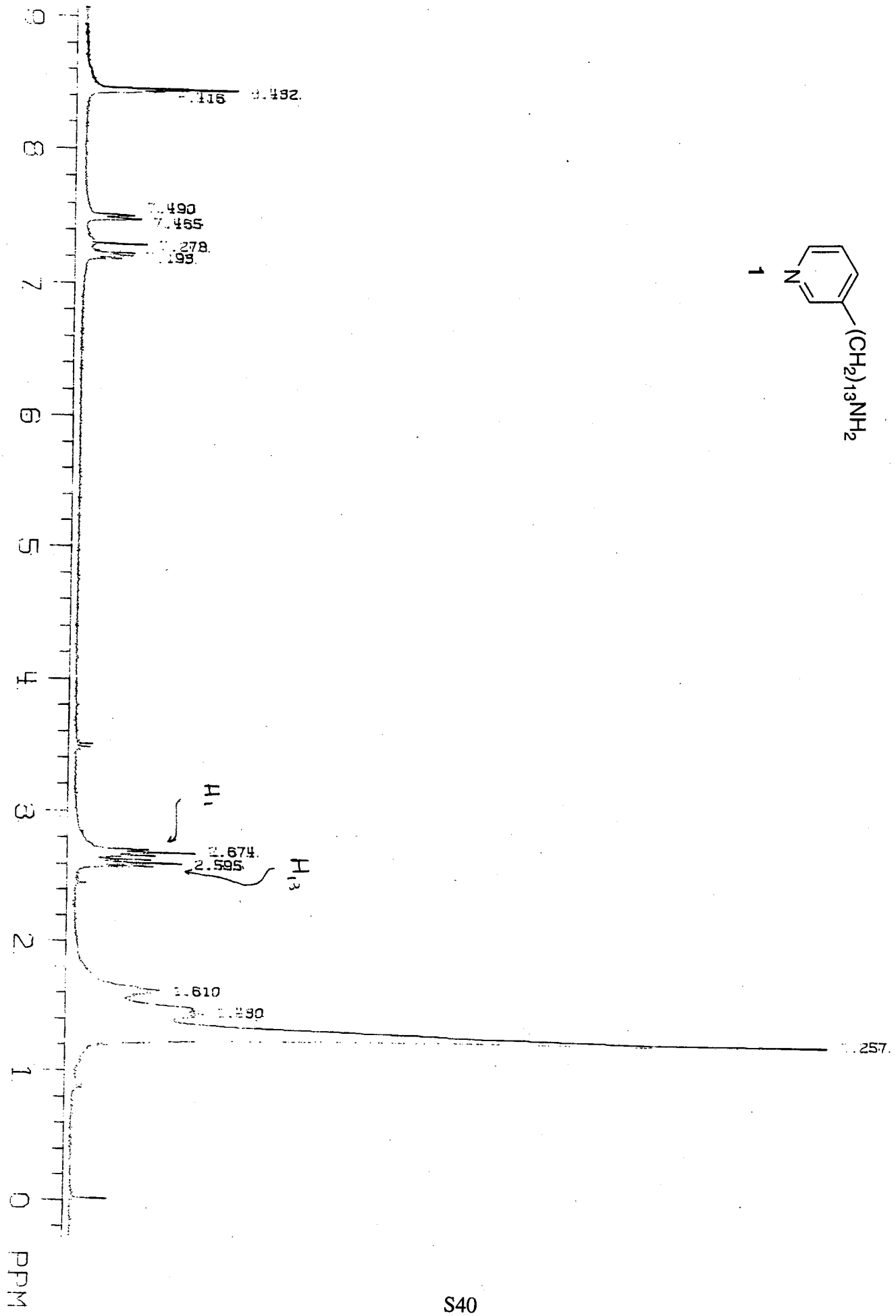
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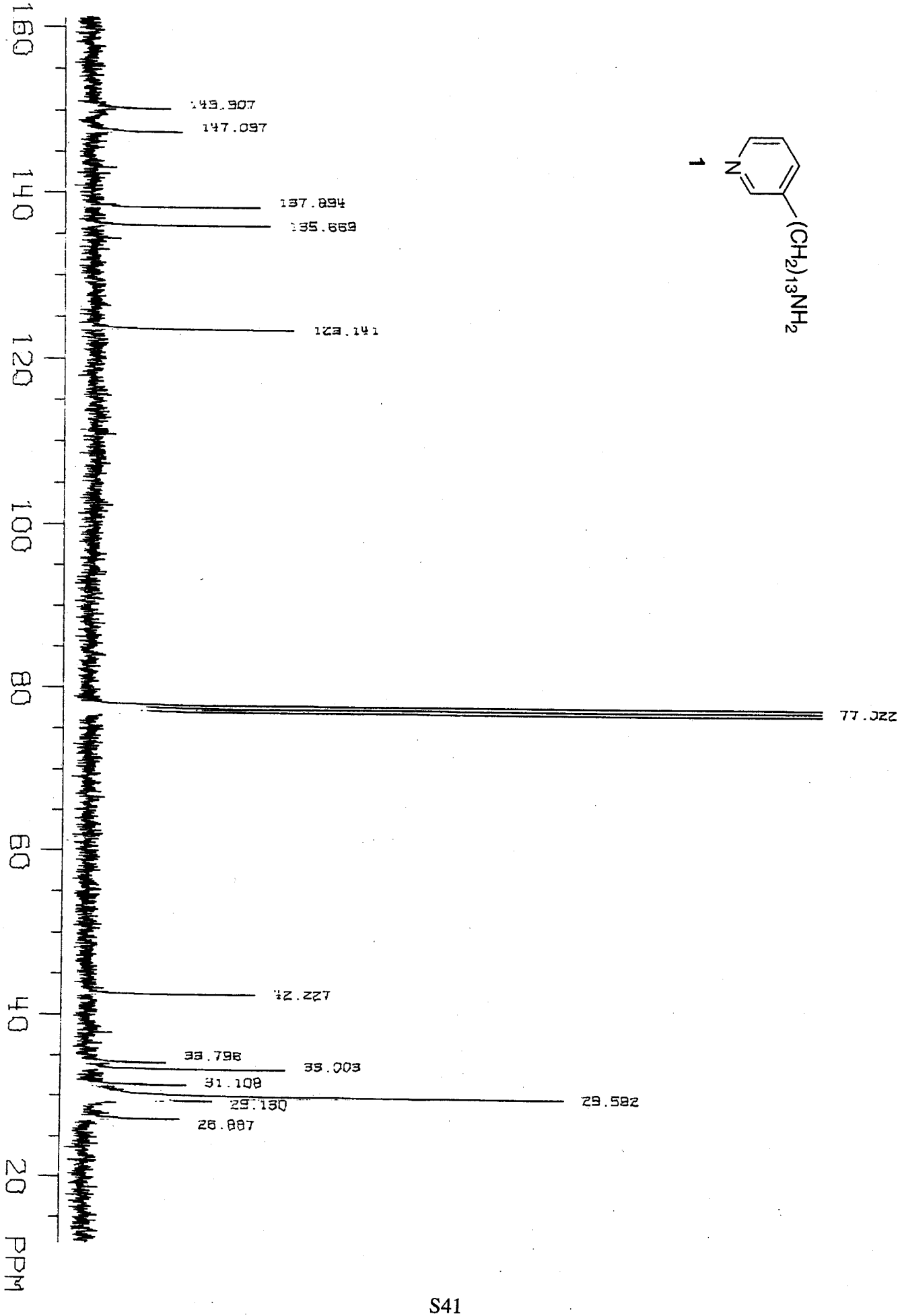
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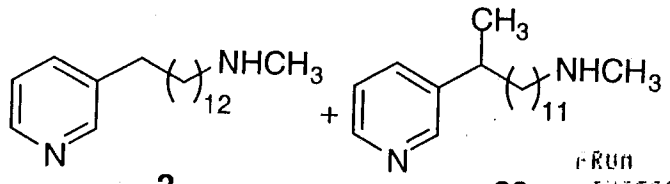

2

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22

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FROM	7.51	TO	7.43 PPM
INTEGRAL=	98.43		
FROM	7.22	TO	7.15 PPM
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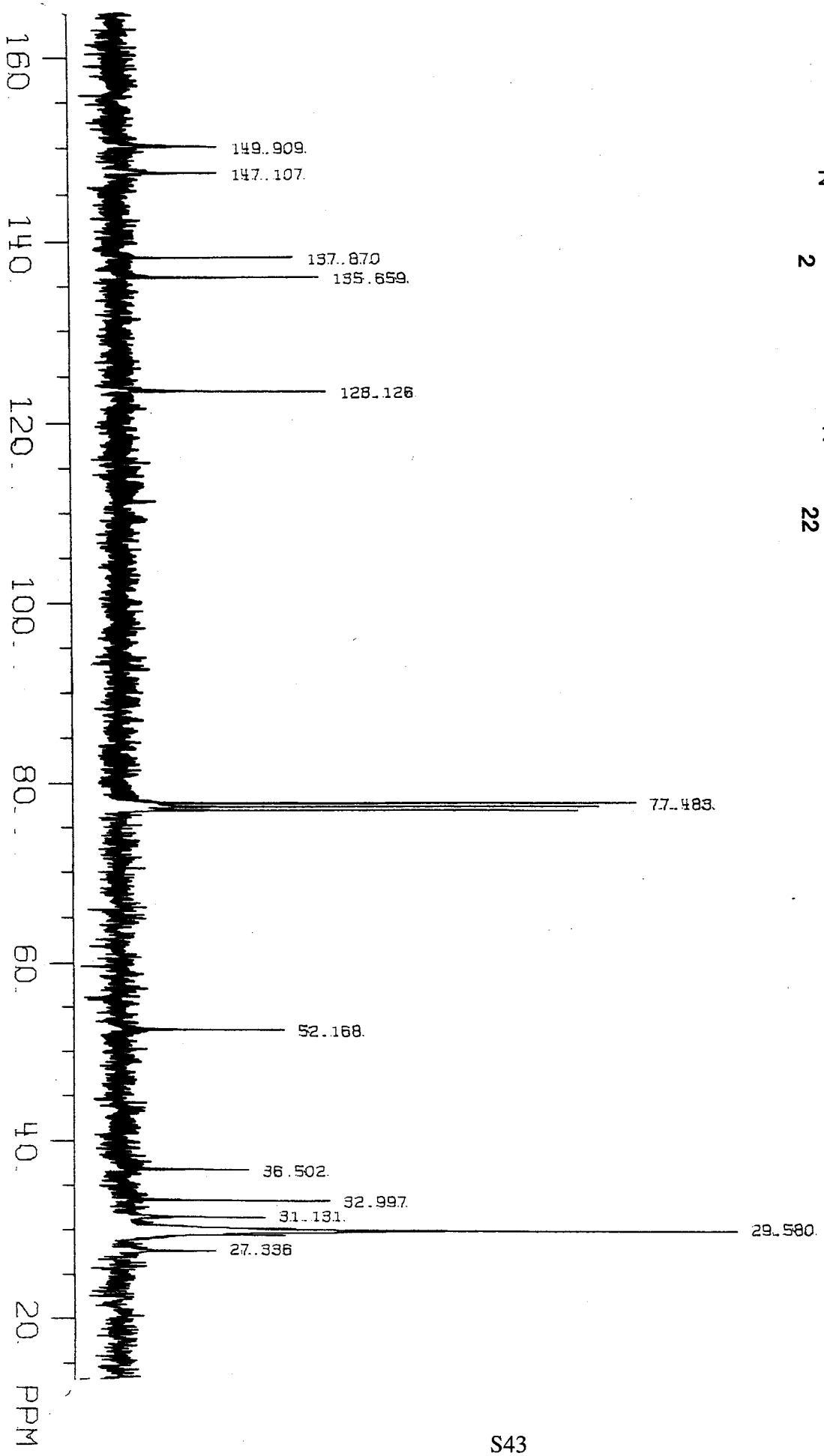
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32.997
31.131
29.580
27.336
2
22
NHCH3
CH3
NHCH3