Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

5-Position-selective C-H Trifluoromethylation of 8-Aminoquinoline Derivatives

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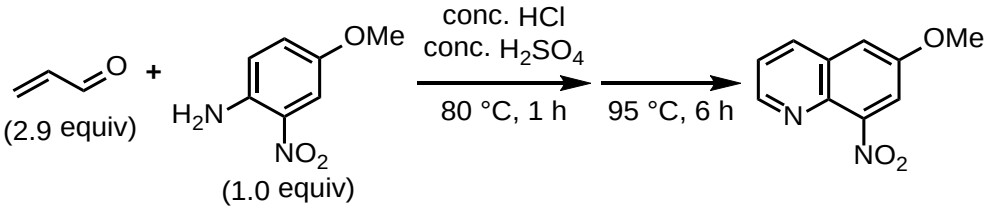
General.

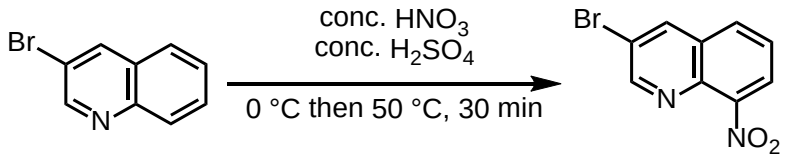
All reactions were carried out in a dry and degassed solvent under an argon atmosphere. All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Quinolylamides **1a**-**1d**,[1a] **1e**,[1b] **1f**,[1a] **1g**,[1c] **1h**,[1d] **1i**,[1e] **1j**,[1f] **1k**,[1g] **1l**,[1d] and **1m**-**1r**, carbamates **1s**[2a] and **1t**,[2b] urea **1u**, sulfonamides **1v**[3a] and **1w**,[3b] and *N*-benzylquinolylamines **4b**[4] and **4c**,[5] were prepared from 8-aminoquinoline according to the literature methods and identified by comparing the spectroscopic data with those of reported data. Trifluoromethylated products **5a** are known compounds.[6] Nitroquinolines[7] and aminoquinolines[7b] were synthesized according to the literature methods. 1-Trifluoromethyl-1,2-benziodoxol-3(1*H*)-one (**2**) (contains 60% diatomaceous earth), 8-aminoquinoline (**4a**), 5-methoxy-2-nitroaniline, 3-bromoquinoline, 2-methyl-8-aminoquinoline, 7-methyl-8-nitroquinoline, and 5-aminoquinoline were purchased from Tokyo Kasei Kogyo Co. Copper(I) chloride, 4-methoxy-2-nitroaniline, and 6-methoxycarbonylquinoline were purchased from Wako Co. 1,2-Dichloroethane was purchased from Sigma Aldrich Co and degassed before use. Column chromatography was performed with silica gel (230-400 mesh ASTM). Recycling preparative HPLC (LC-9210NEXT; column, JAIGEL-1H and JAIGEL-2H; solvent, $CHCl_3$) was used for isolation of trifluoromethylated products **5b** (as mixtures of 5- and 7- regioisomers) after removing metal wastes through a short pad of silica gel. NMR spectra were recorded on 500 MHz (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) and 400 MHz (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 368 MHz for ^{19}F NMR) spectrometers. Proton and carbon chemical shifts are reported relative to the solvent used as an internal reference. Fluorine chemical shifts are reported relative to trifluoroacetic acid (δ -76.55 ppm) as an external reference. Infrared (IR) spectra were recorded on Fourier transform infrared spectrophotometer. ESI-MS spectra were measured on a spectrometer for HRMS.

Synthesis and Characterisation of Quinolylamides, Carbamates, Urea, Sulfonamides, and Quinolylamines.

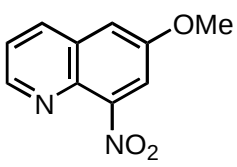
Synthesis of 8-nitroquinolines.



Method A:[7a] To a solution of 4-methoxy-2-nitroaniline (5.09 g, 33.0 mmol, 1.0 equiv) in conc. HCl (40 mL) and conc. H_3PO_4 (15 mL), acrolein (6.5 mL, 97 mmol, 2.9 equiv) was slowly added at 80 °C for 1 h. The mixture was stirred at 95 °C for 6 h, and then cooled to 0 °C. After neutralization with aq. NH_3, the resulting powder was filtered off and dissolved in acetone. The solvent was removed and 6-methoxy-8-nitroquinoline was obtained as a brown solid (4.68 g, 70% yield).

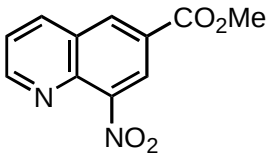


Method B:[7b] A cold mixture of conc. H_2SO_4 (20.0 mL) and conc. HNO_3 (10.0 mL) was added to the solution of 3-bromoquinoline (6.8 mL, 50.0 mmol, 1.0 equiv) in conc. H_2SO_4 (20.0 mL) at 0 °C, then heated to 50 °C. After 30 min, the reaction mixture was neutralized by slow addition of NaOH. Formed precipitate was filtered off and washed with water. A brown residue was dissolved in dichloromethane and dried over $MgSO_4$. The residue was purified by column chromatography on silica gel (hexane/dichloromethane = 1/2) to give 3-bromo-8-nitroquinoline (2.46 g, 19% yield).

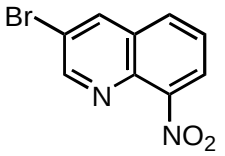


6-Methoxy-8-nitroquinoline. Method A; 70% yield; brown solid; R_f = 0.40 (hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.99 (s, 3H), 7.28 (d, *J* = 2.9 Hz, 1H), 7.50 (dd, *J* = 8.6, 4.6 Hz, 1H), 7.72 (d, *J* = 2.9 Hz, 1H), 8.14 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.92 (dd, *J* = 4.6, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.1, 109.3, 116.5, 122.9, 129.9, 134.8, 135.3, 148.6, 149.9, 156.0; IR (KBr, ν / cm^{-1}) 3009, 2973, 2936, 2833, 1632, 1598, 1525, 1496, 1449, 1360, 1335, 1244, 1156, 1047, 1032, 855, 786, 757, 635;

HRMS (ESI$^+$) Calcd for $C_{10}H_8N_2NaO_3$ ([M+Na]$^+$) 227.0433, Found 227.0432.

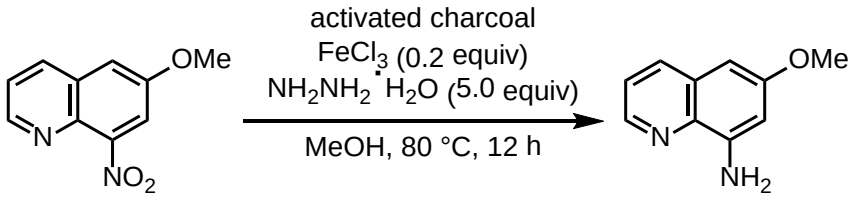


6-Methoxycarbonyl-8-nitroquinoline. Method B; 3% yield; light yellow solid; R_f = 0.25 (dichloromethane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 (s, 3H), 7.65 (dd, *J* = 8.6, 4.0 Hz, 1H), 8.38 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.60 (d, *J* = 1.8 Hz, 1H), 8.77 (d, *J* = 1.8 Hz, 1H), 9.15 (dd, *J* = 4.0, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.9, 123.0, 123.4, 127.1, 128.2, 134.1, 137.3, 140.8, 148.0, 154.3, 164.4; IR (KBr, ν / cm^{-1}) 3059, 2959, 1725, 1631, 1533, 1463, 1438, 1354, 1333, 1274, 1207, 1041, 981, 908, 794, 765, 736; HRMS (ESI$^+$) Calcd for $C_{11}H_8N_2NaO_4$ ([M+Na]$^+$) 255.0382, Found 255.0388.

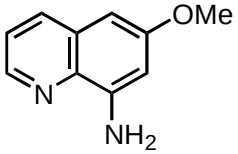


3-Bromo-8-nitroquinoline. Method B; 19% yield; pale yellow solid; R_f = 0.38 (hexane/dichloromethane = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.75 (m, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 8.44 (s, 1H), 9.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.2, 124.0, 126.6, 129.7, 131.1, 137.3, 137.5, 148.1, 153.6; IR (KBr, ν / cm^{-1}) 3094, 3049, 1620, 1585, 1531, 1483, 1349, 1322, 1189, 1090, 912, 896, 820, 793, 769, 730, 657; HRMS (ESI$^+$) Calcd for $C_9H_5BrN_2NaO_2$ ([M+Na]$^+$) 274.9432, Found 274.9442.

Synthesis of 8-aminoquinolines.[7b]



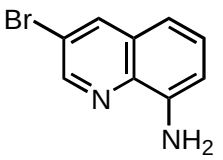
A mixture of 6-methoxy-8-nitroquinoline (2.82 g, 13.8 mmol, 1.0 equiv), activated charcoal (1.38 g), iron chloride (448 mg, 2.76 mmol, 0.20 equiv), and hydrazine monohydrate in methanol (80 mL) was stirred at 80 °C for 12 h. The reaction mixture was filtered through Celite and the solvent was removed under reduced pressure to give 8-amino-6-methoxyquinoline (2.00 g, 83% yield).



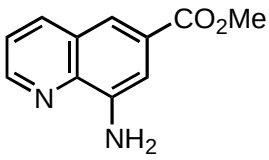
8-Amino-6-methoxyquinoline. 83% yield; dark brown oil; R_f = 0.50 (hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H), 5.09 (brs, 2H), 6.43 (d, *J* = 2.9 Hz, 1H), 6.60 (d, *J* = 2.9 Hz, 1H), 7.26 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.61 (dd, *J* = 4.0, 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 54.9, 94.2,

101.2, 121.5, 129.6, 134.5, 135.1, 144.7, 144.9, 158.5; IR (neat, ν / cm^{-1}) 3471, 3367, 3002, 2959, 2938, 2834, 1621, 1589, 1504, 1469, 1451, 1428, 1384, 1341, 1277, 1242, 1226, 1198, 1162, 1041, 1021, 900, 823, 791, 655; HRMS (ESI^+) Calcd for $C_{10}H_{11}N_2O$ ($[M+H]^+$) 175.0871, Found 175.0876.

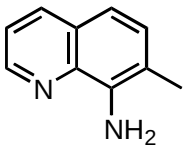
8-Amino-3-bromoquinoline. 96% yield; yellow solid; R_f = 0.30 (hexane/ethyl acetate = 5/1); ^1H NMR (400 MHz, $CDCl_3$) δ 4.96 (brs, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 7.33-7.37 (m, 1H), 8.22 (d, *J* = 1.8 Hz, 1H) 8.73 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.3, 115.0, 117.5, 128.7, 129.8, 136.2, 137.0, 144.1, 148.1; IR (KBr, ν / cm^{-1}) 3468, 3358, 1614, 1594, 1578, 1564, 1496, 1465, 1370, 1331, 1190, 1176, 1127, 909, 893, 824, 757; HRMS (ESI^+) Calcd for $C_9H_8BrN_2$ ($[M+H]^+$) 222.9871, Found 222.9862.



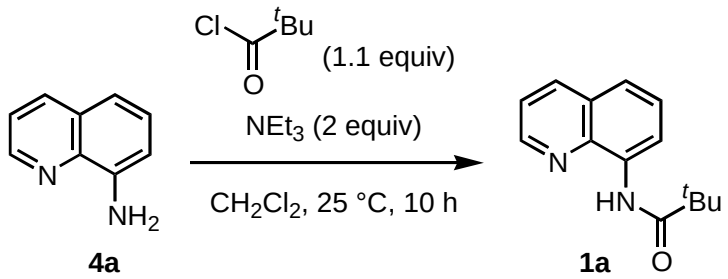
8-Amino-6-methoxycarbonylquinoline. 86% yield; yellow solid; R_f = 0.13 (hexane/ethyl acetate = 5/1); ^1H NMR (500 MHz, $CDCl_3$) δ 3.06 (s, 3H), 5.11 (brs, 2H), 7.39 (dd, *J* = 4.0, 8.0 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.87 (d, *J* = 1.7 Hz, 1H), 8.12 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.80 (dd, *J* = 4.0, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 108.9, 118.9, 122.0, 127.9, 128.7, 137.4, 140.0, 144.1, 149.4, 167.2; IR (KBr, ν / cm^{-1}) 3383, 3346, 3210, 1717, 1664, 1587, 1561, 1491, 1446, 1376, 1334, 1256, 1226, 992, 810, 763; HRMS (ESI^+) Calcd for $C_{11}H_{10}N_2NaO_2$ ($[M+Na]^+$) 225.0640, Found 225.0632.



8-Amino-7-methylquinoline. 95% yield; yellow solid; R_f = 0.50 (hexane/ethyl acetate = 1/1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 4.93 (brs, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 8.0, 4.0 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.75 (dd, *J* = 4.0, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.6, 115.3, 118.0, 120.4, 127.1, 129.9, 135.8, 138.0, 141.1, 147.4; IR (KBr, ν / cm^{-1}) 3418, 3326, 1616, 1590, 1506, 1469, 1369, 1100, 822, 793, 665; HRMS (ESI^+) Calcd for $C_{10}H_{11}N_2$ ($[M+H]^+$) 159.0922, Found 159.0923.

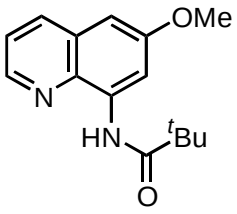


Typical procedure for the synthesis of quinolylamides 1.

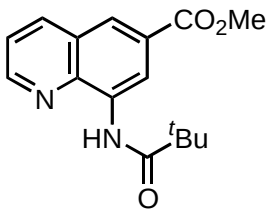


4a **1a**

To a solution of 8-aminoquinoline (**4a**, 721 mg, 5.00 mmol, 1.0 equiv) and Et_3N (1.4 mL, 10.0 mmol, 2.0 equiv) in dichloromethane (14 mL), pivaloyl chloride (0.67 mL, 5.5 mmol, 1.1 equiv) was added, and the reaction mixture was stirred at room temperature for 10 h. The mixture was diluted with dichloromethane (5.0 mL) and washed with water. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 5/1) to give **1a** (1.14 g, 99% yield).

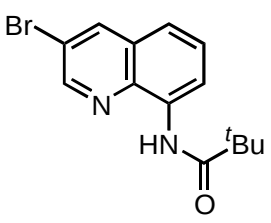


***N*-(6-Methoxyquinolin-8-yl)pivalamide (1m).** 98% yield; white solid; R_f = 0.23 (hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 3.92 (s, 3H), 6.78 (d, *J* = 2.3 Hz, 1H), 7.38 (dd, *J* = 8.6, 4.0 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 8.56 (d, *J* = 2.3 Hz, 1H), 8.64 (d, *J* = 4.0 Hz, 1H), 10.2 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 40.3, 55.5, 99.7, 108.3, 121.9, 128.8, 134.8, 135.2, 135.5, 145.5, 158.4, 177.2; IR (KBr, ν / cm^{-1}) 3369, 2965, 2939, 1672, 1629, 1595, 1524, 1482, 1454, 1423, 1391, 1337, 1270, 1247, 1207, 1195, 1179, 1157, 1136, 1049, 1032, 923, 891, 829, 795, 673; HRMS (ESI^+) Calcd for $C_{15}H_{18}N_2NaO_2$ ($[M+Na]^+$) 281.1266, Found 281.1274.

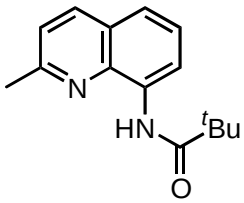


***N*-(6-Methoxycarbonylquinolin-8-yl)pivalamide (1n).** 12% yield; white solid; R_f = 0.80 (hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 9H), 3.96 (s, 3H), 7.51 (dd, *J* = 8.0, 4.0 Hz, 1H), 8.25 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.28 (d, *J* = 1.8 Hz, 1H), 8.89 (dd, *J* = 4.0, 1.8 Hz, 1H), 9.35 (d, *J* = 1.8 Hz, 1H), 10.2 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 40.4, 52.4, 115.3, 122.2, 124.3, 127.0, 128.9, 134.8, 137.7, 140.3, 150.2, 166.8, 177.3; IR (KBr, ν / cm^{-1}) 3357, 2962, 1717, 1673, 1542, 1481, 1437, 1423, 1274, 1253, 1236, 1199, 1186, 925, 895, 790, 689; HRMS (ESI^+) Calcd for $C_{16}H_{18}N_2NaO_3$ ($[M+Na]^+$) 309.1215, Found 309.1220.

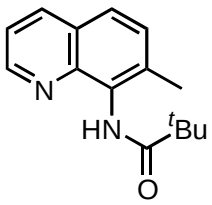
***N*-(3-Bromoquinolin-8-yl)pivalamide (1o).** 91% yield; light yellow solid; R_f = 0.45 (hexane/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 9H), 7.41 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.54-7.60 (m, 1H), 8.32 (d, *J* = 2.2 Hz, 1H), 8.79-8.83 (m, 2H), 10.1 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 40.4, 116.6, 117.7, 120.3, 128.8 (2C), 134.9, 136.8, 137.5, 149.2, 177.2; IR (KBr, ν / cm^{-1}) 3378, 3059, 2968, 2870, 1677, 1523, 1468, 1454, 1396, 1377, 1364, 1323, 1173, 1155, 1095, 924, 904, 824, 769, 636; HRMS (ESI^+) Calcd for $C_{14}H_{15}BrN_2NaO$ ($[M+Na]^+$) 329.0265, Found 329.0260.



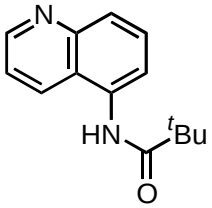
***N*-(2-Methylquinolin-8-yl)pivalamide (1p).** 88% yield; white solid; R_f = 0.43 (hexane/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 9H), 2.74 (s, 3H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.42-7.50 (m, 2H), 8.03 (d, *J* = 8.5 Hz, 1H), 8.74 (dd, *J* = 6.7, 2.7 Hz, 1H), 10.4 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 27.7, 40.3, 116.1, 120.9, 122.2, 126.0, 126.4, 134.0, 136.4, 138.1, 156.9, 177.1; IR (KBr, ν / cm^{-1}) 3351, 2959, 1674, 1604, 1533, 1493, 1481, 14347, 1393, 1338, 1160, 926, 838, 759, 697; HRMS (ESI^+) Calcd for $C_{15}H_{18}N_2NaO$ ($[M+Na]^+$) 265.1317, Found 265.1306.



***N*-(7-Methylquinolin-8-yl)pivalamide (1q).** 98% yield; pale orange solid; R_f = 0.11 (hexane/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H), 2.44 (s, 3H), 7.34 (dd, *J* = 8.1, 4.5 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 8.09 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.80 (dd, *J* = 4.5, 1.8 Hz, 1H), 8.96 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 27.8, 39.9, 120.5, 123.9, 126.4, 130.3, 131.7, 133.3, 135.7, 142.6, 149.0, 177.2; IR (KBr, ν / cm^{-1}) 3373, 2964, 2920, 2869, 1683, 1510, 1489, 1467, 1384, 1360, 1316, 1166, 898, 8.5, 825, 794, 655; HRMS (ESI^+) Calcd for $C_{15}H_{18}N_2NaO$ ($[M+Na]^+$) 265.1317, Found 265.1327.

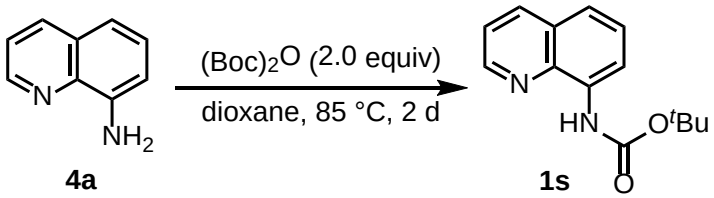


***N*-(Quinolin-5-yl)pivalamide (1r).** 36% yield; white solid; R_f = 0.10 (hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (s, 9H), 7.36 (dd, *J* = 8.6, 4.0 Hz, 1H), 7.61-7.67 (m, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.78 (brs, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.88 (dd, *J* = 4.0, 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.7, 39.6, 120.9, 122.3, 123.4, 127.5, 129.1, 129.9, 132.5, 148.6, 150.3, 177.4; IR



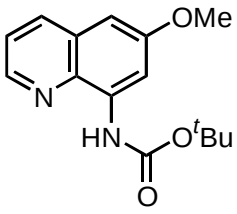
(KBr, ν / cm^{-1}) 3264, 2977, 2964, 1654, 1620, 1597, 1572, 1523, 1494, 1399, 1367, 1316, 1207, 1189, 1151, 939, 798; HRMS (ESI^+) Calcd for $C_{14}H_{16}N_2NaO$ ($[M+Na]^+$) 251.1160, Found 251.1170.

Synthesis of carbamates.[2b]



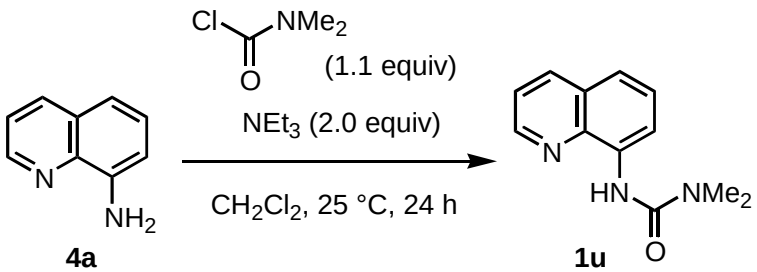
4a **1s**

A mixture of 8-aminoquinoline (**4a**, 0.72 g, 5.00 mmol, 1.0 equiv), di-*tert*-butyl dicarbonate (2.18 g, 10.0 mmol, 2.0 equiv), and dioxane (14 mL) was stirred at 85 °C for 2 d. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/dichloromethane = 1/2) to give **1s** (1.2 g, 98% yield).



***tert*-Butyl(6-methoxyquinolin-8-yl)carbamate (1t).** 97% yield; white solid; R_f = 0.43 (hexane/ethyl acetate = 5/1); ^1H NMR (400 MHz, $CDCl_3$) δ 1.57 (s, 9H), 3.91 (s, 3H), 6.71 (d, *J* = 2.7 Hz, 1H), 7.37 (dd, *J* = 8.5, 4.0 Hz, 1H), 8.00 (dd, *J* = 8.5, 1.8 Hz, 1H), 8.14 (s, 1H), 8.43 (dd, *J* = 4.0, 1.8 Hz, 1H), 8.97 (brs, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 28.4, 55.5, 80.5, 98.5, 106.8, 122.0, 129.1, 134.8, 134.9, 136.2, 145.4, 152.7, 158.6; IR (KBr, ν / cm^{-1}) 3352, 2985, 1726, 1627, 1525, 1479, 1454, 1427, 1389, 1368, 1338, 1255, 1229, 1159, 1120, 1057, 1033, 1001, 826, 787, 686, 662; HRMS (ESI^+) Calcd for $C_{15}H_{18}N_2NaO_3$ ($[M+Na]^+$) 297.1215, Found 297.1215.

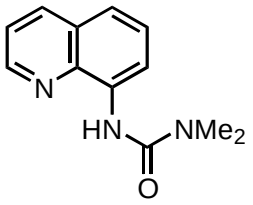
Synthesis of urea derivative 1u.



4a **1u**

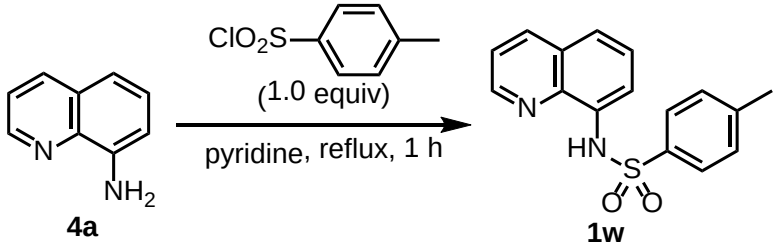
To a solution of 8-aminoquinoline (**4a**, 721 mg, 5.00 mmol, 1.0 equiv) and Et_3N (1.4 mL, 10.0 mmol, 2.0 equiv) in dichloromethane (14 mL), *N*,*N*-dimethylcarbamoyl chloride (0.50 mL, 3.50 mmol, 1.1 equiv) was added and the reaction mixture was

stirred at room temperature for 24 h. H_2O (5.0 mL) was added to the reaction mixture and the mixture was extracted with ethyl acetate (3×5.0 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 2/1) to give **1u** (296 mg, 27% yield).



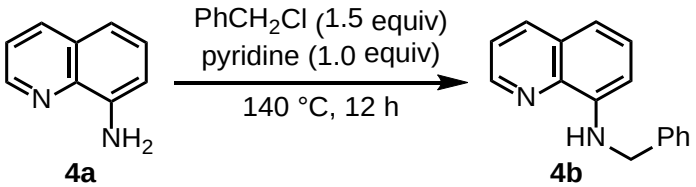
1,1-Dimethyl-3-(quinolin-8-yl)urea (1u). 27% yield; pale brown solid; R_f = 0.18 (hexane/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (s, 6H), 7.35-7.44 (m, 2H), 7.48-7.55 (m, 1H), 8.14 (dd, *J* = 8.5, 1.8 Hz, 1H), 8.57 (d, *J* = 6.7 Hz, 1H), 8.76 (dd, *J* = 4.0, 1.8 Hz, 1H), 9.36 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.4, 114.6, 119.4, 121.3, 127.6, 128.0, 136.0, 136.3, 138.5, 147.7, 155.6; IR (KBr, ν / cm^{-1}) 3369, 3062, 2922, 1662, 1530, 1490, 1463, 1427, 1387, 1350, 1329, 1262, 1186, 1167, 1007, 823, 794, 757, 639, 615; HRMS (ESI^+) Calcd for $C_{12}H_{13}N_3NaO$ ($[M+Na]^+$) 238.0956, Found 238.0966.

Synthesis of sulfonamides.[3a]

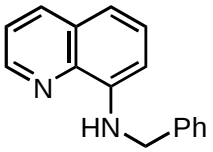


A mixture of 8-aminoquinoline (**4a**, 721 mg, 5.00 mmol, 1.0 equiv), *p*-toluenesulfonyl chloride (953 mg, 5.00 mmol, 1.0 equiv), and pyridine (10.0 mL), was stirred at 110 °C for 1 h. The reaction mixture was cooled to 70 °C and poured into water (10.0 mL). The resulting suspension was filtered and the precipitate was washed with water. The resulting solid was dried under reduced pressure at 50 °C to give sulfonamide **1w** (1.18 g, 79% yield).

Synthesis of aminoquinoline 4b.[4]

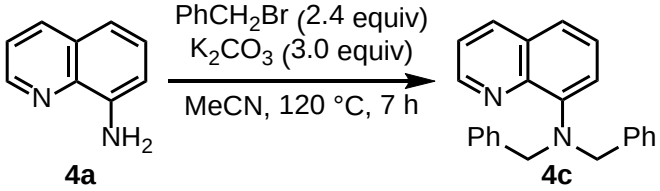


To a solution of 8-aminoquinoline (**4a**, 442 mg, 3.00 mmol, 1.0 equiv) in pyridine (0.24 mL, 3.00 mmol, 1.0 equiv), benzyl chloride (0.52 mL, 4.50 mmol, 1.5 equiv) was slowly added at 140 °C, then the mixture was heated at 140 °C for 12 h. Pyridine was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/ ethyl acetate = 5/1) to give **4b** (567 mg, 80% yield).



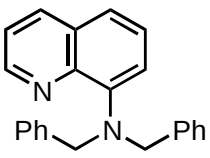
***N*-(quinolin-8-yl)benzylamine (4b).** 80% yield; pale yellow solid; R_f = 0.50 (hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.59 (d, *J* = 5.8 Hz, 2H), 6.66 (brs, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.28-7.33 (m, 1H), 7.34-7.42 (m, 4H), 7.48 (d, *J* = 7.5 Hz, 2H), 8.08 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.75 (dd, *J* = 4.0, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.6, 105.1, 114.1, 121.4, 127.1, 127.4, 127.7, 128.6 (2C), 136.0, 138.2, 139.2, 144.5, 146.9; IR (KBr, ν / cm^{-1}) 3420, 3060, 3021, 1605, 1573, 1520, 1478, 1451, 1439, 1420, 1380, 1360, 1337, 1296, 1274, 1121, 1026, 992, 821, 793, 746, 738, 692; HRMS (ESI^+) Calcd for $C_{16}H_{14}N_2Na$ ($[M+Na]^+$) 257.1055, Found 257.1047.

Synthesis of aminoquinoline 4c.[5]



4a **4c**

A mixture of 8-aminoquinoline (**4a**, 1.44 g, 10.0 mmol, 1.0 equiv), benzyl bromide (2.9 mL, 24.0 mmol, 2.4 equiv), K_2CO_3 (4.15 g, 30.0 mmol, 3.0 equiv), and acetonitrile (15 mL) was stirred at 120 °C for 7 h. H_2O (10 mL) was added to the reaction mixture and the mixture was extracted with ethyl acetate (3×10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ ethyl acetate = 5/1) to give **4c** (3.0 g, 93% yield).



***N*-(quinolin-8-yl)dibenzylamine (4c).** 93% yield; yellowish brown solid; R_f = 0.43 (hexane/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 4H), 6.89 (d, *J* = 7.5 Hz, 1H), 7.15-7.29 (m, 11H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.38 (dd, *J* = 8.1, 4.0 Hz, 1H), 8.10 (dd, *J* =

8.1, 1.3 Hz, 1H), 8.93 (dd, J = 4.0, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.6, 118.8, 120.6, 120.8, 126.3, 126.7, 128.1, 128.5, 129.8, 136.4, 138.7, 143.0, 146.9, 147.7; IR (KBr, ν / cm^{-1}) 3025, 2804, 1600, 1567, 1497, 1469, 1451, 1389, 1362, 1333, 1230, 1137, 1110, 1027, 1006, 946, 828, 809, 790, 749, 739, 705; HRMS (ESI^+) Calcd for $C_{23}H_{20}N_2Na$ ($[M+Na]^+$) 347.1524, Found 347.1530.

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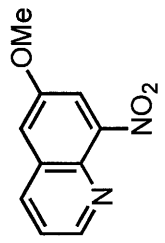
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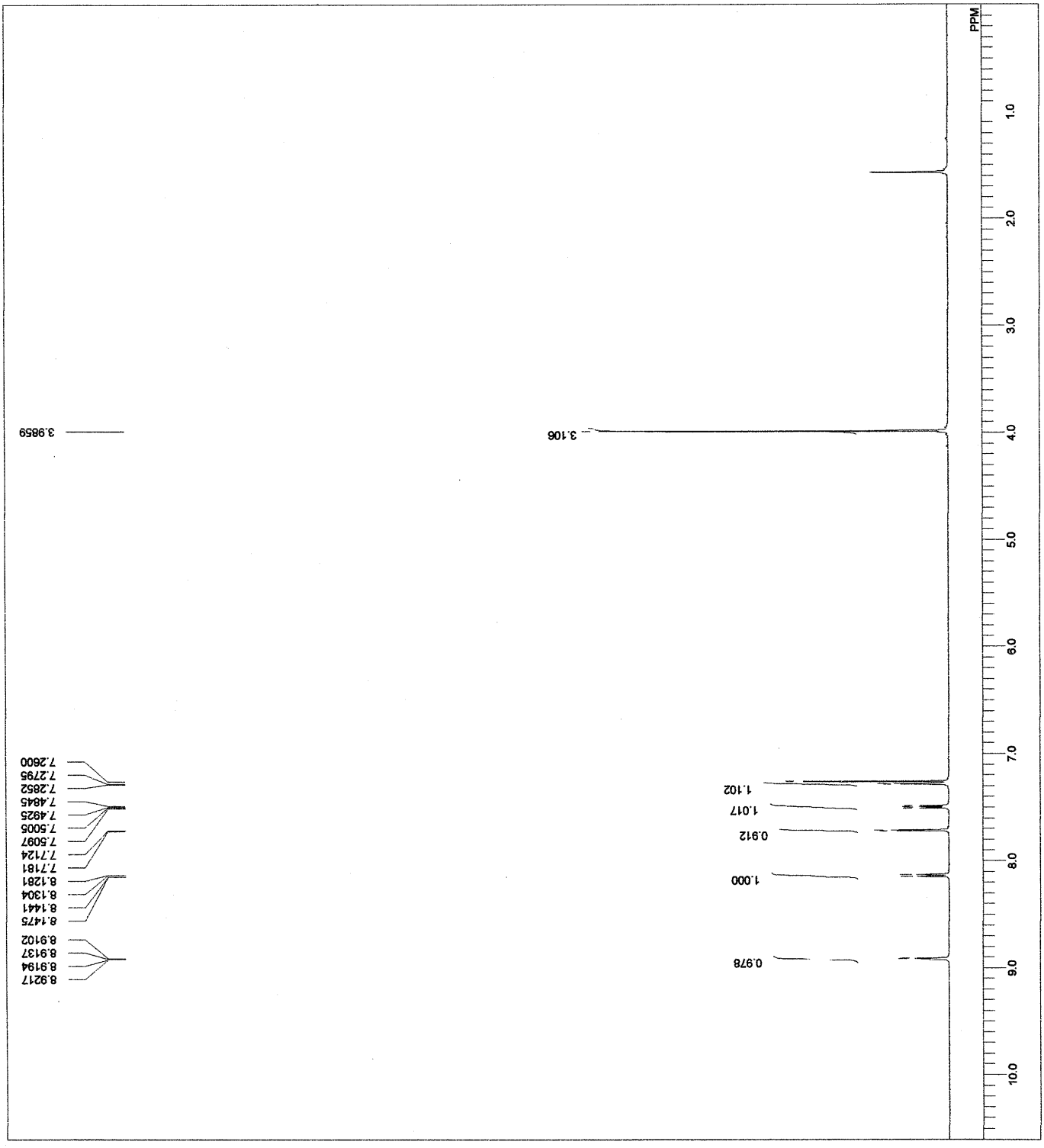
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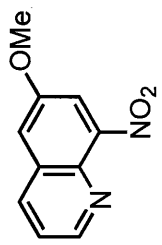
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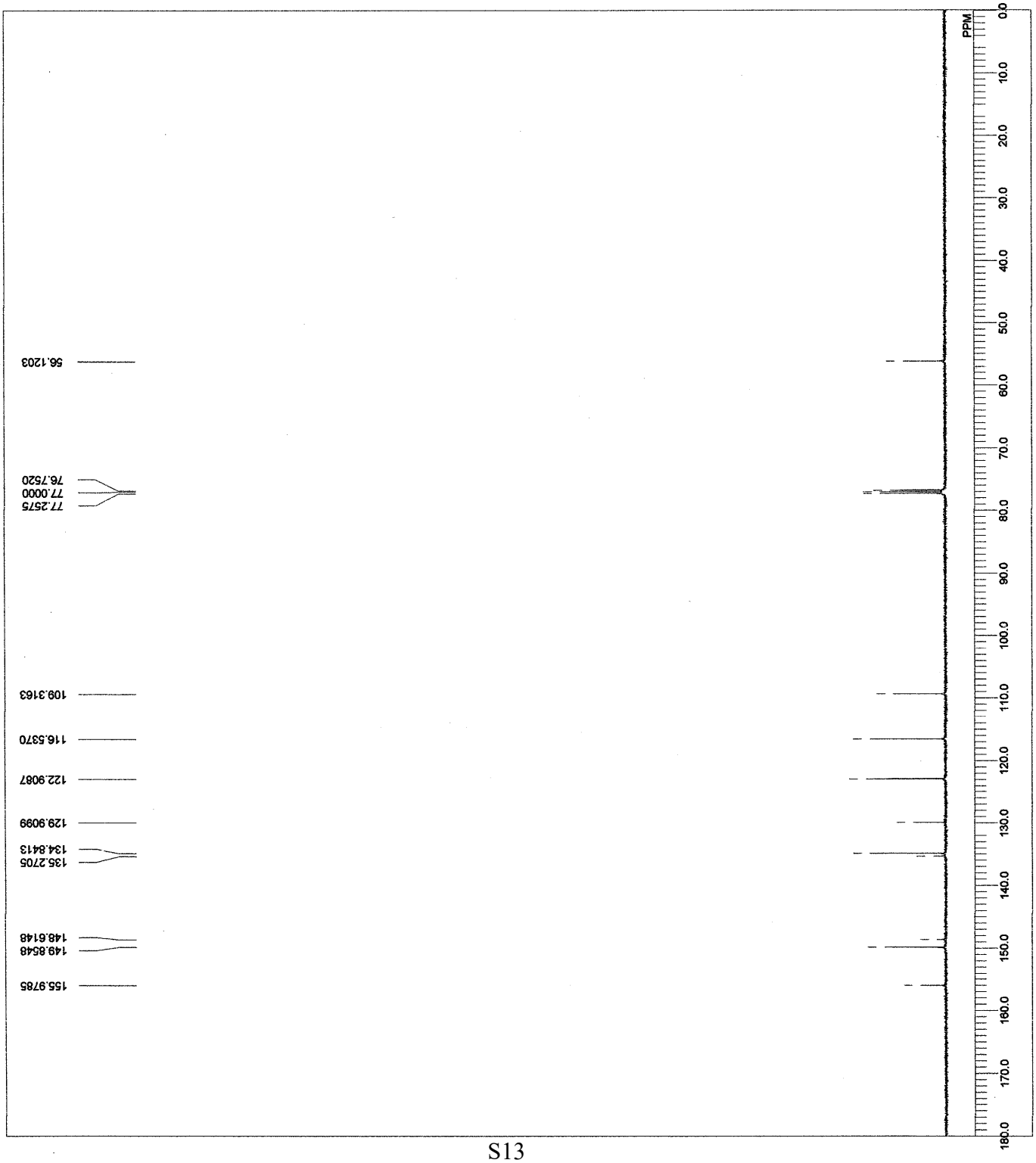
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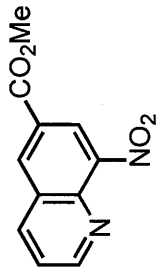
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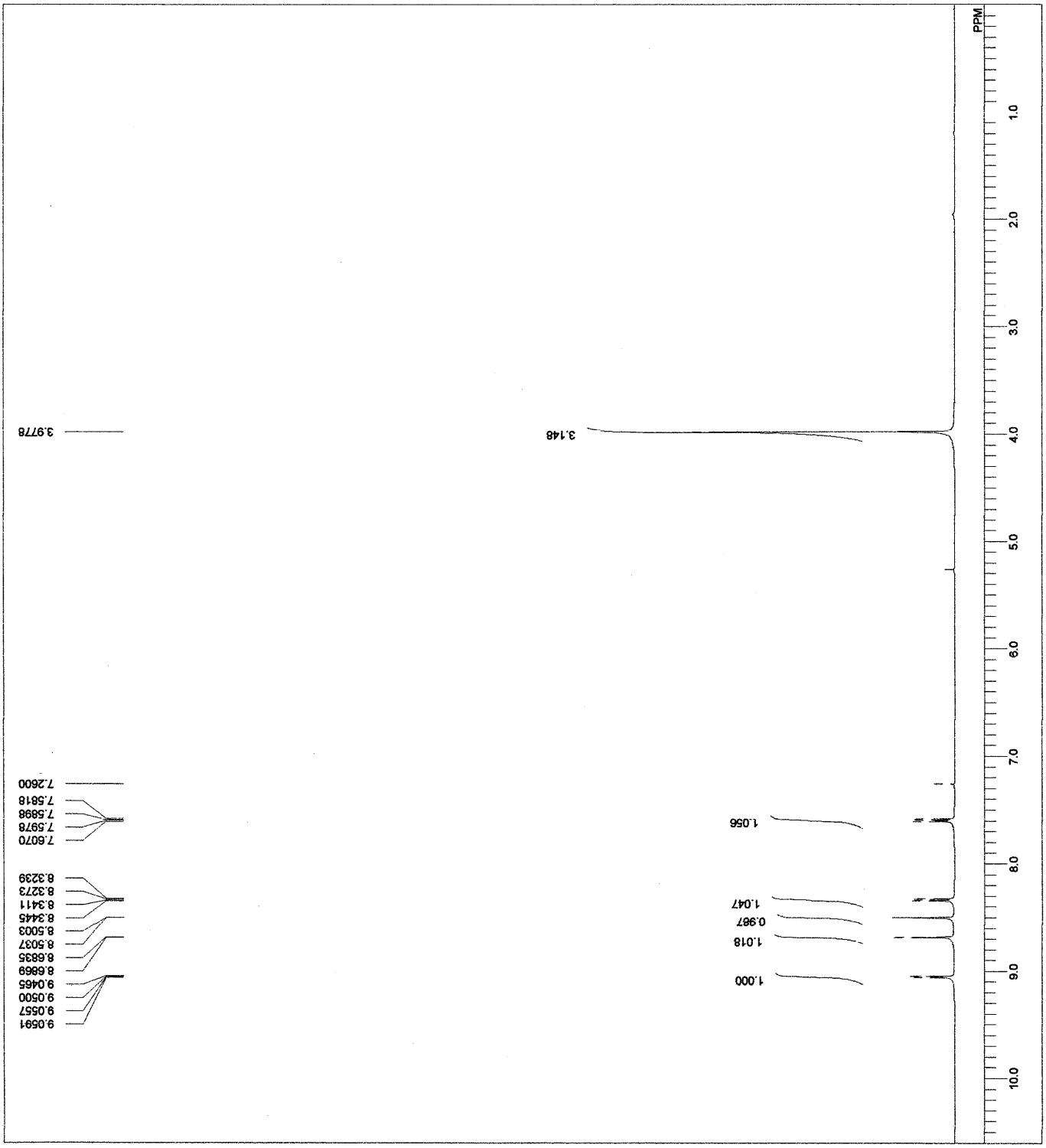
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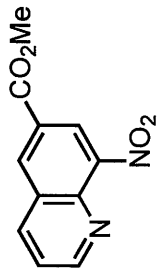
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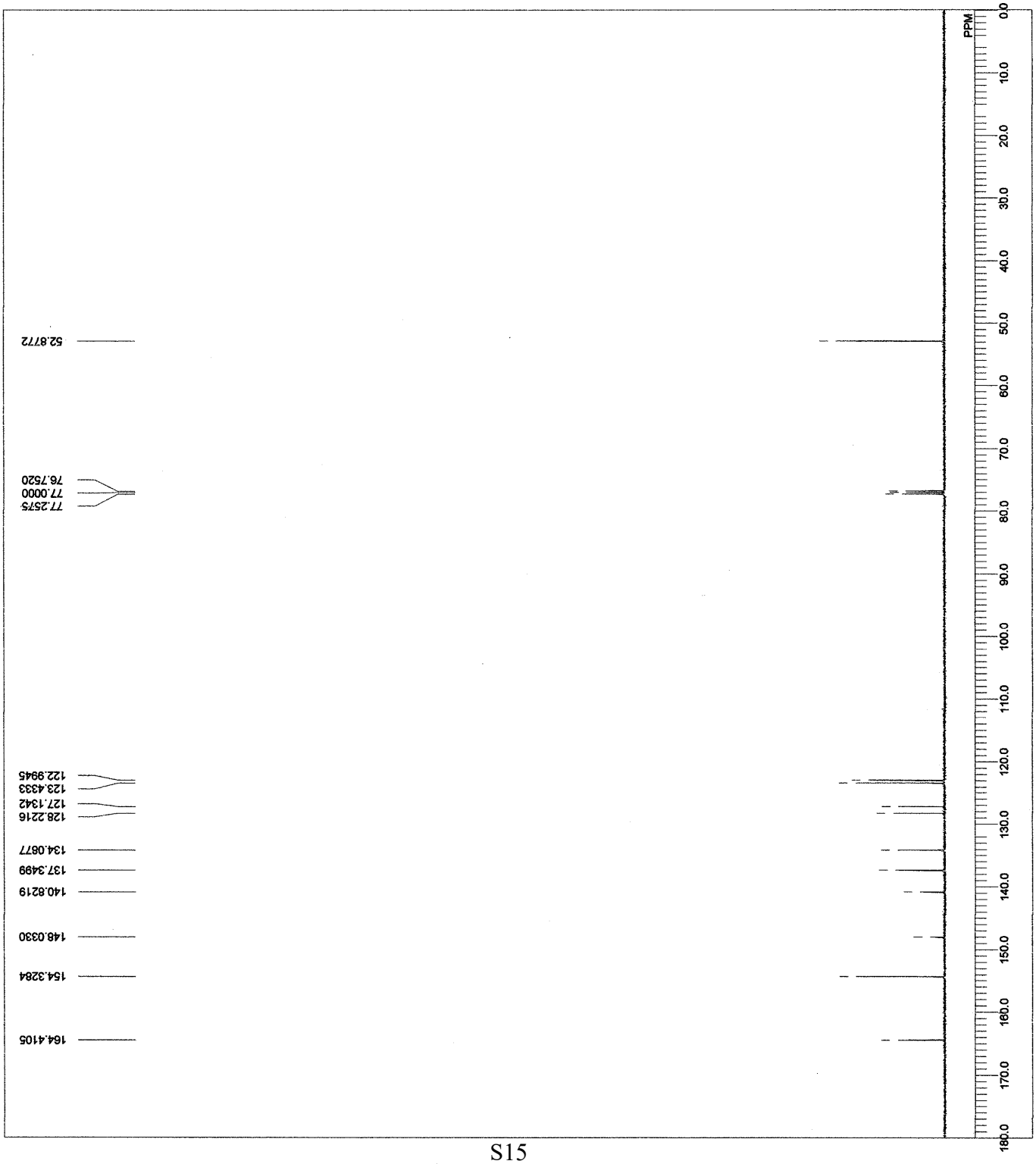
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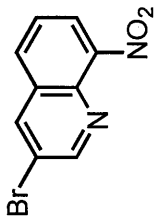
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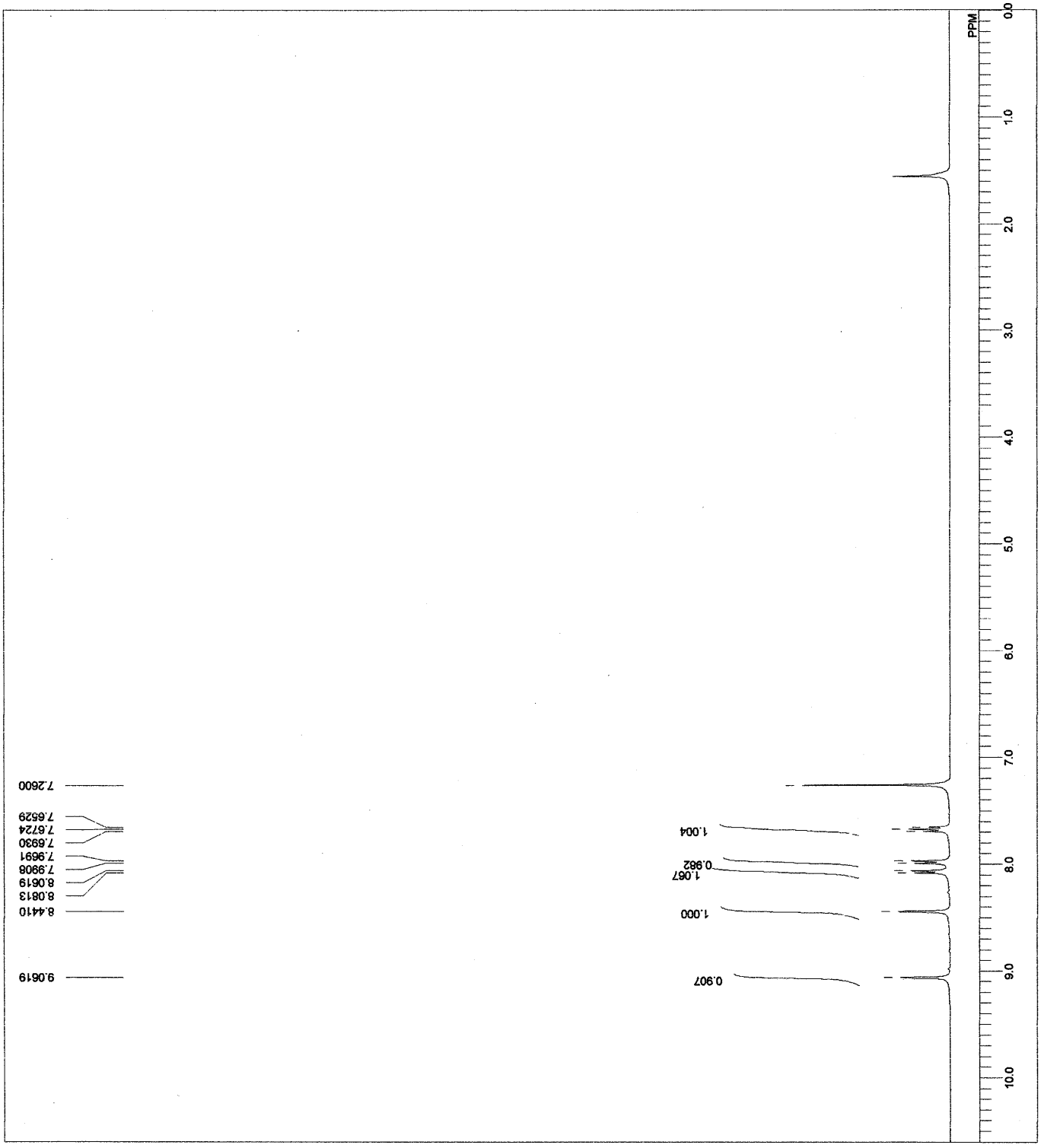
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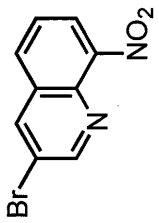
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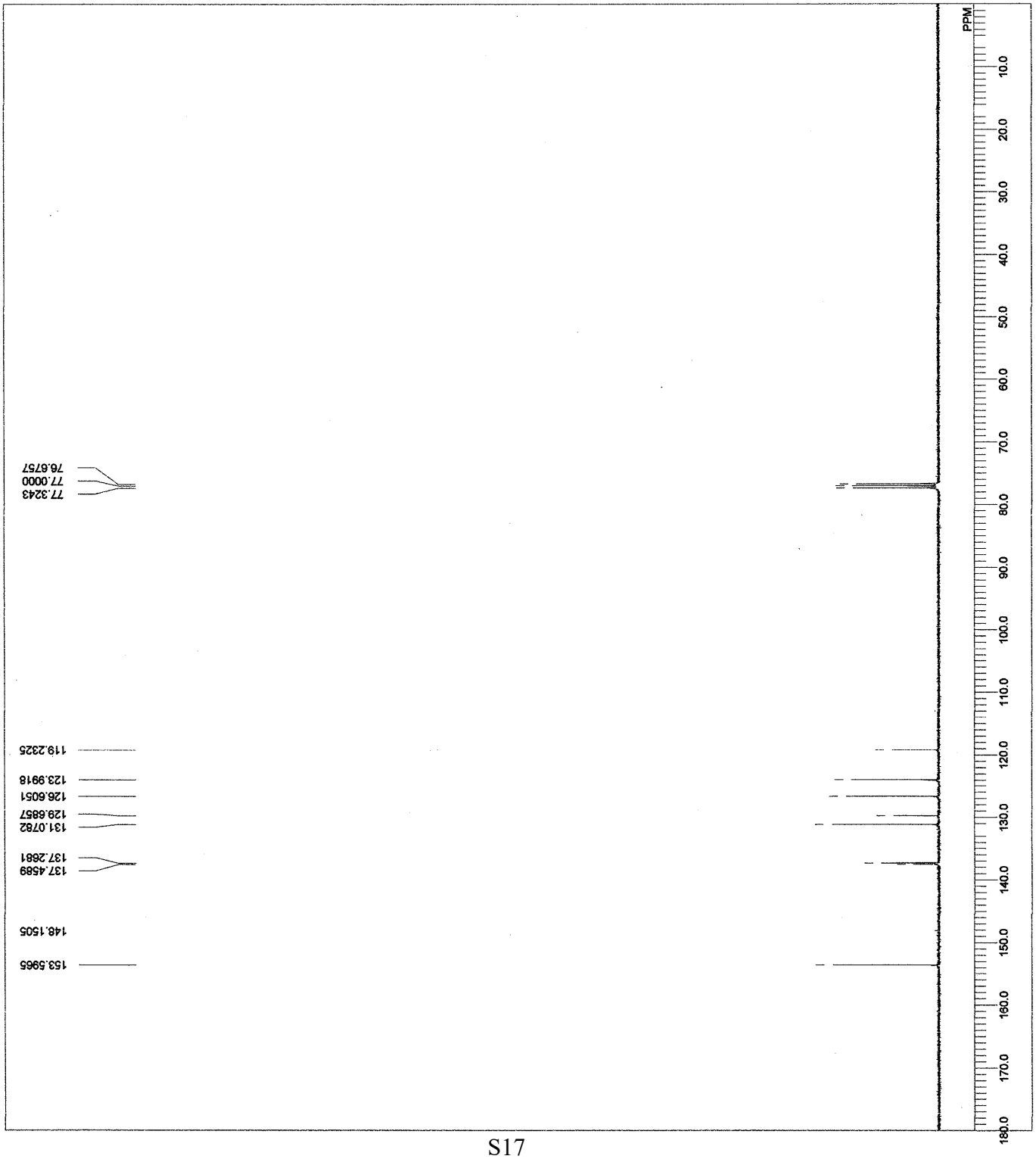
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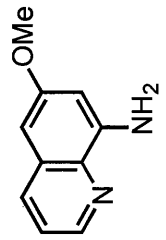
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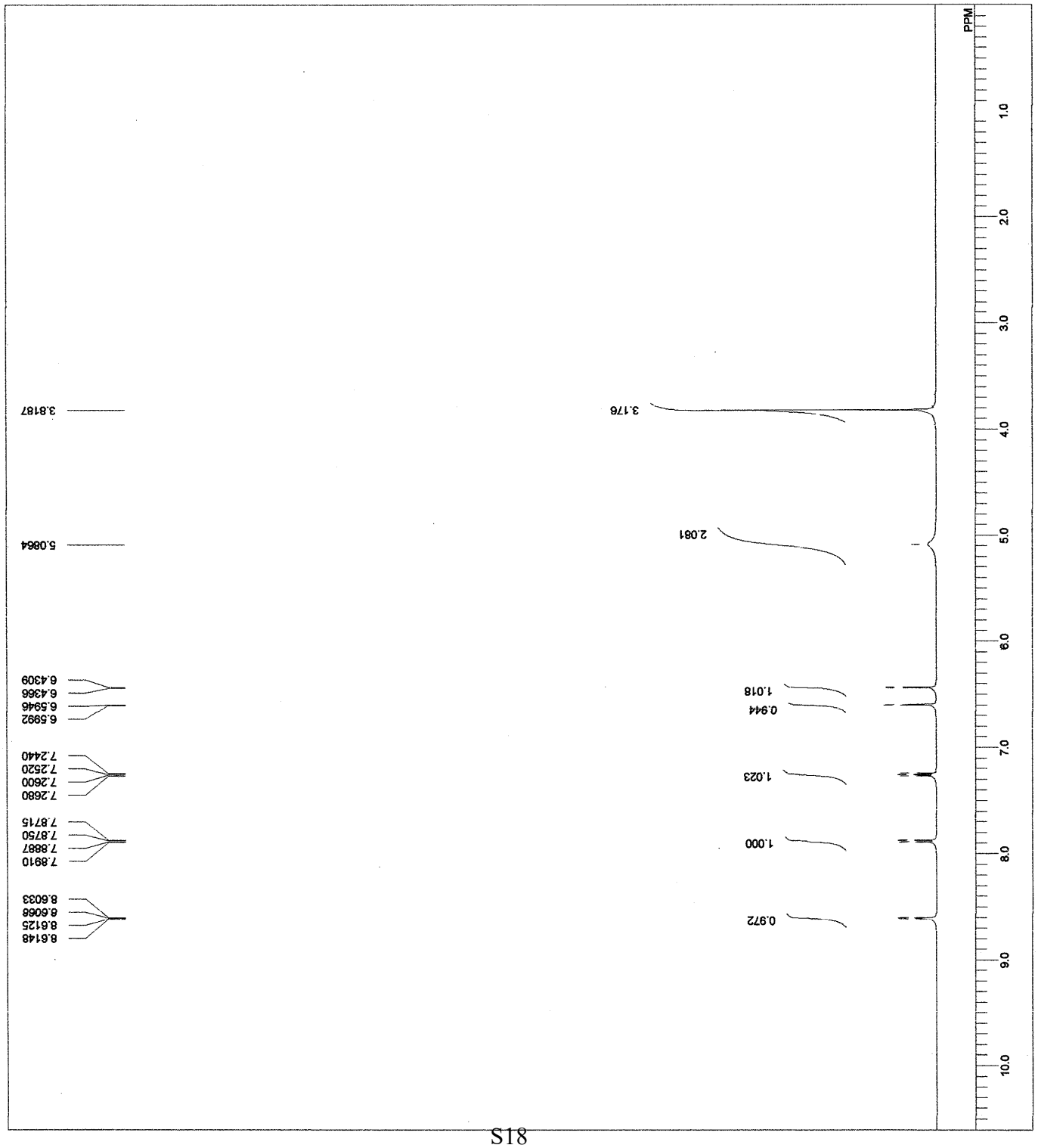
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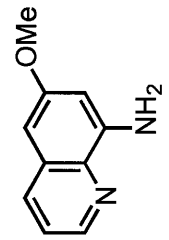
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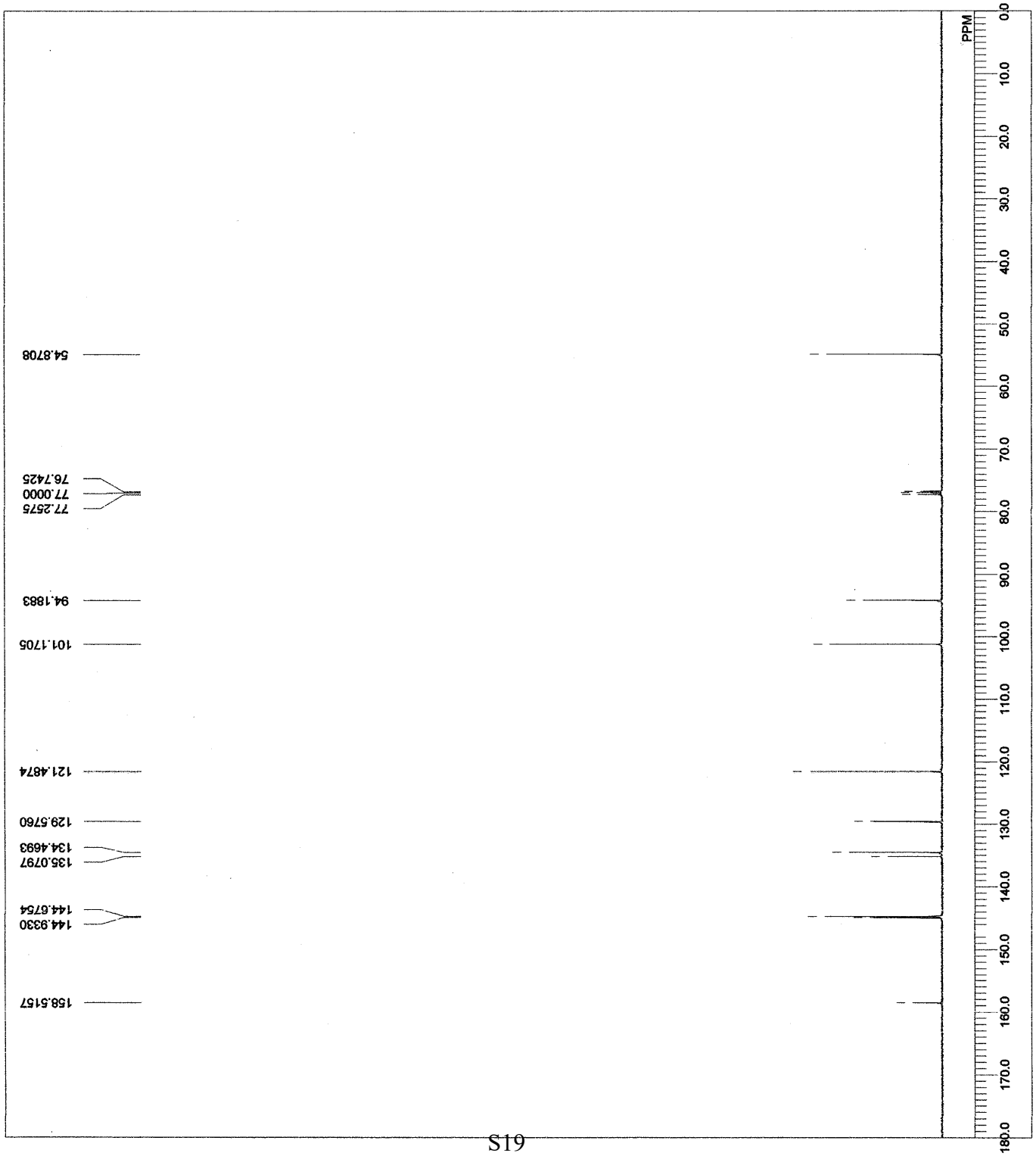
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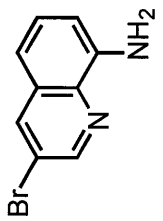
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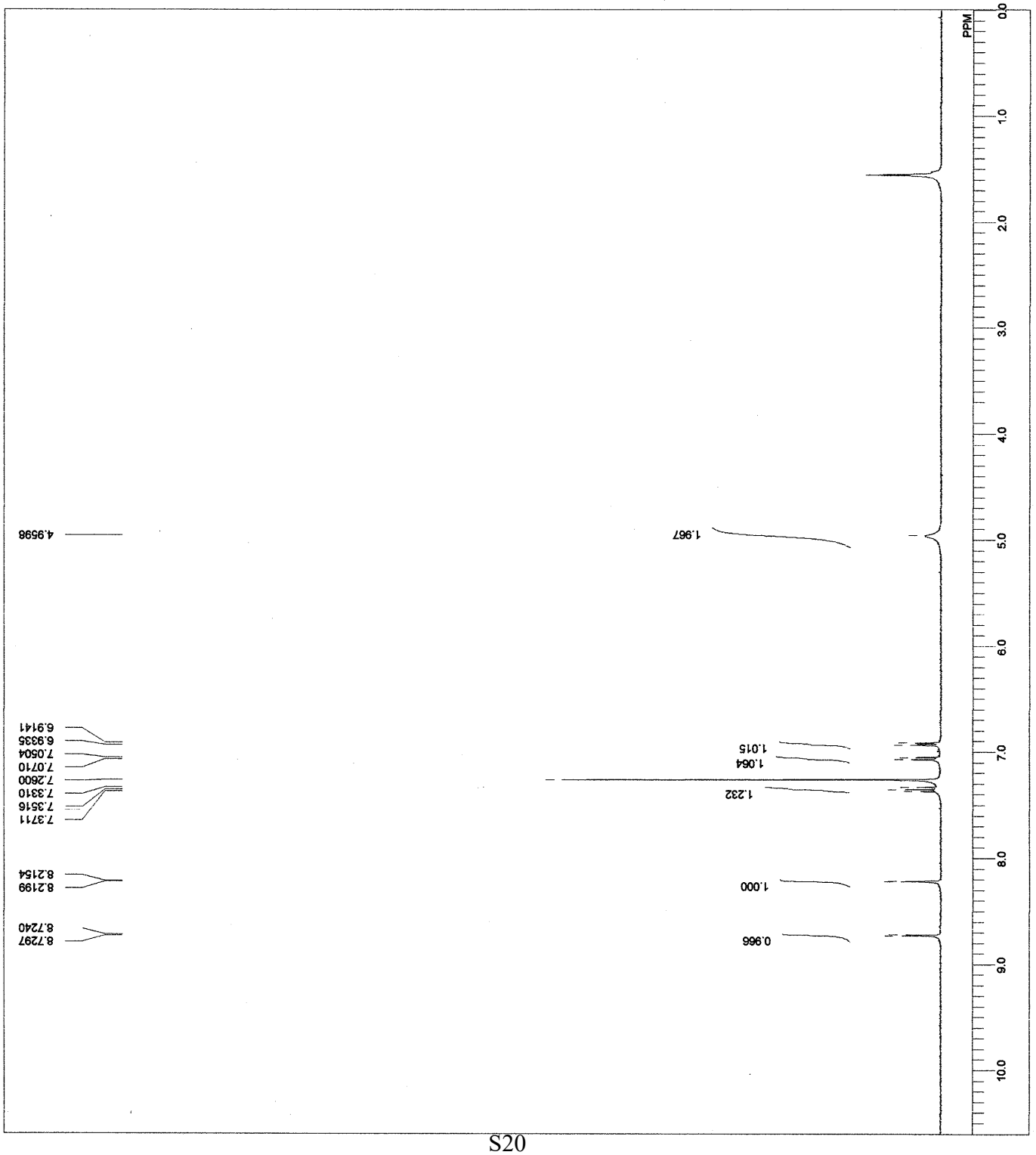
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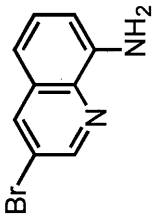
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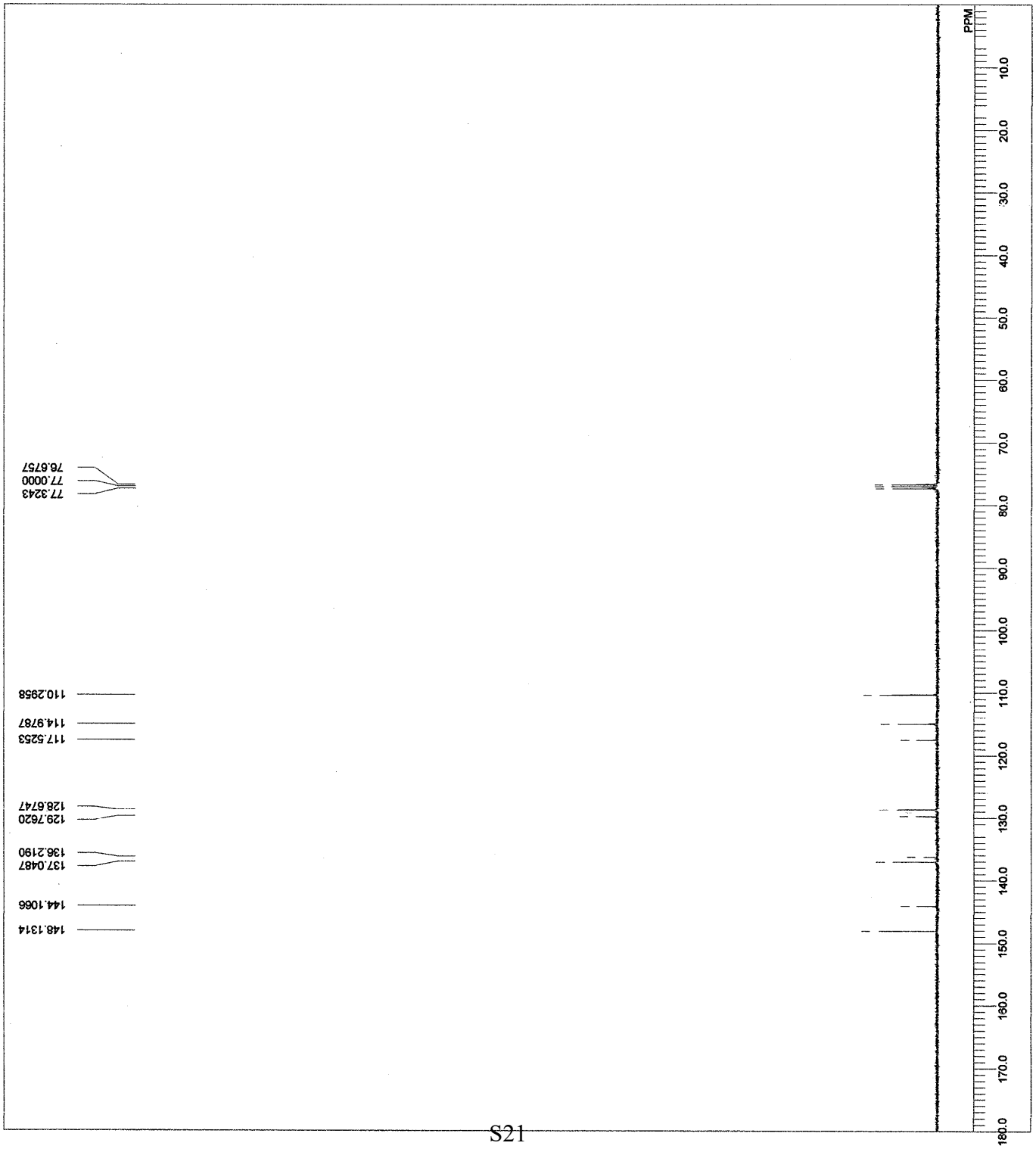
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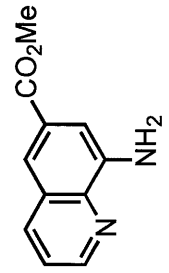
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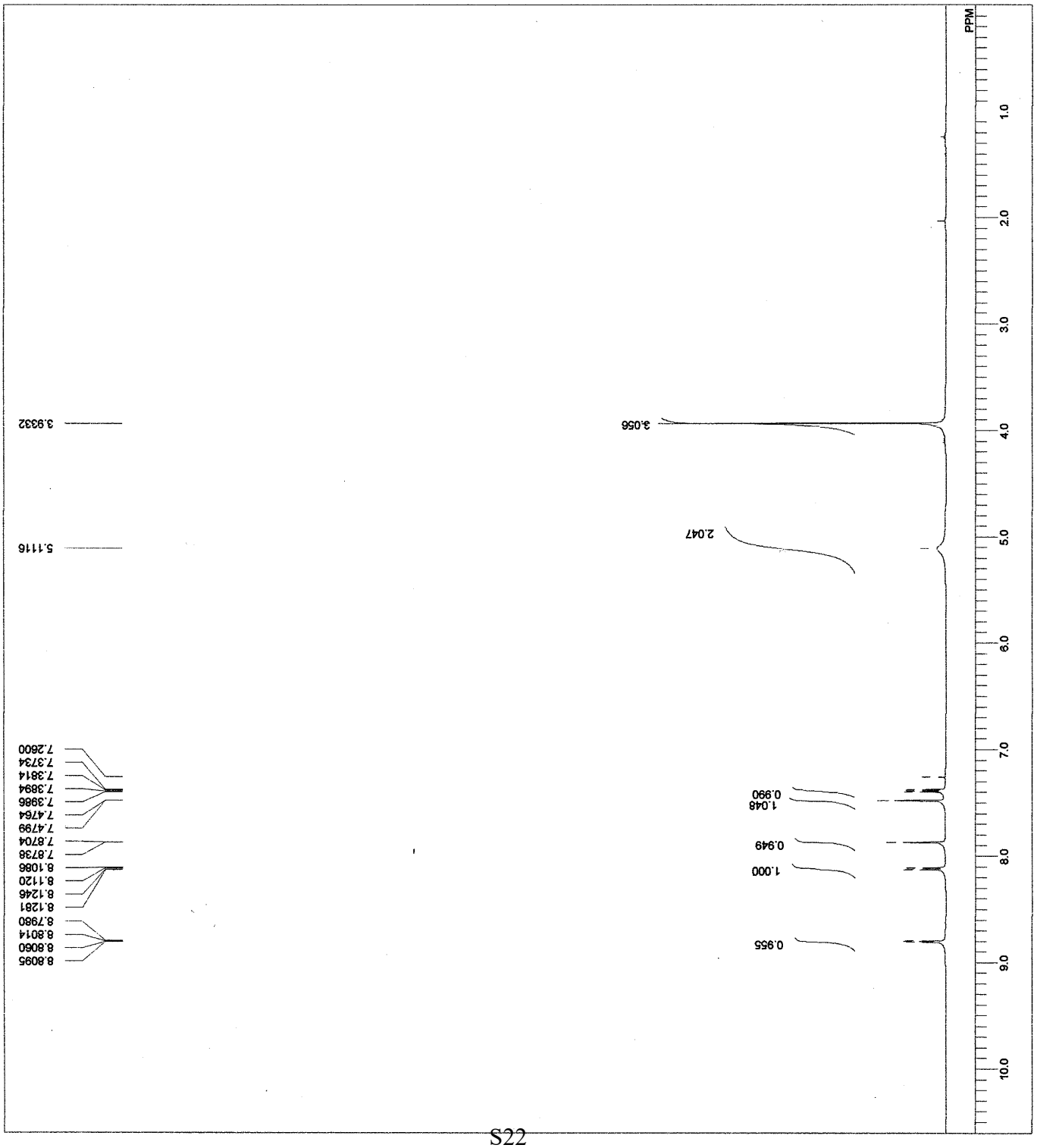
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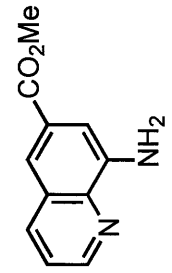
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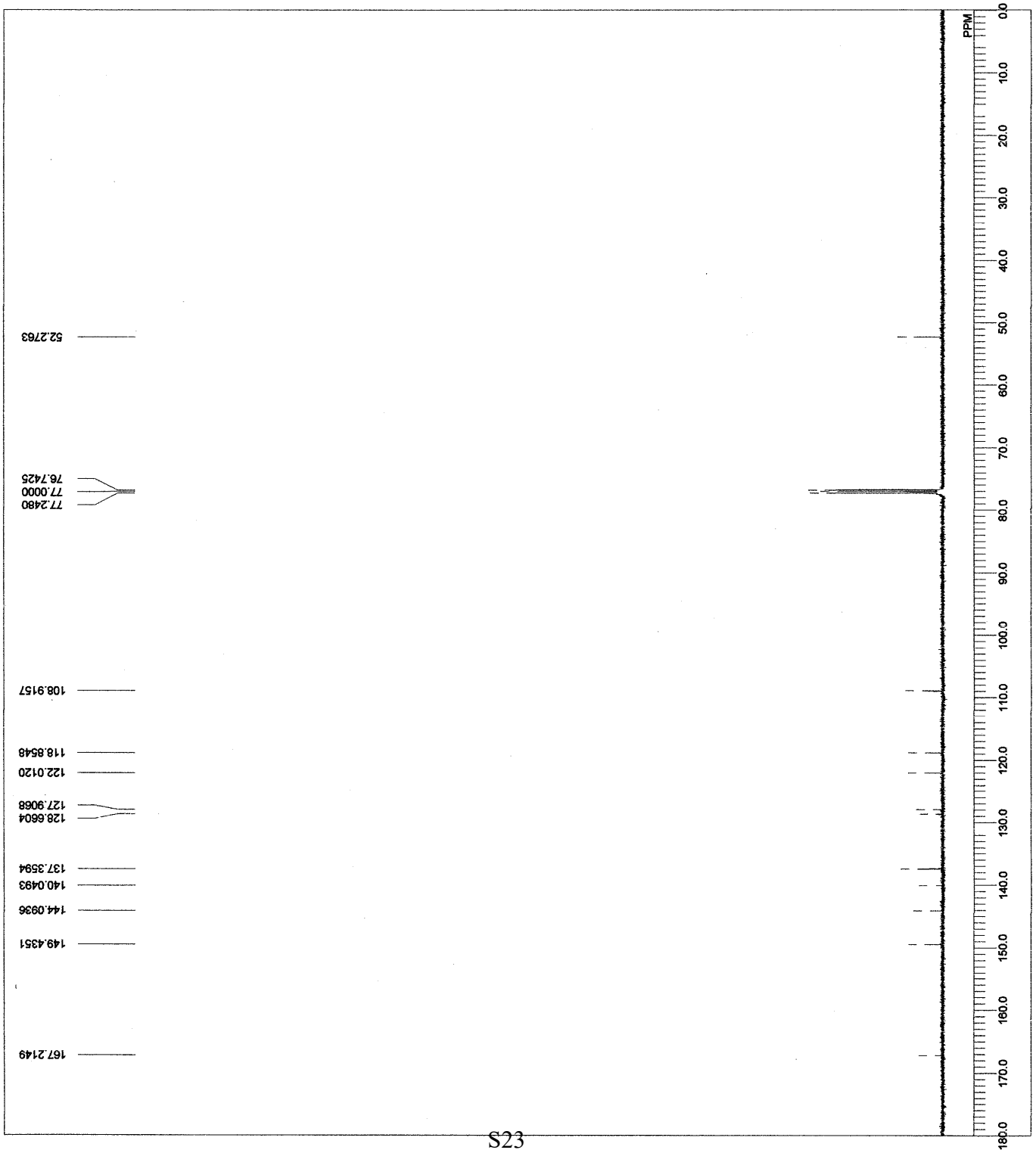
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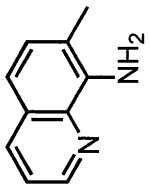
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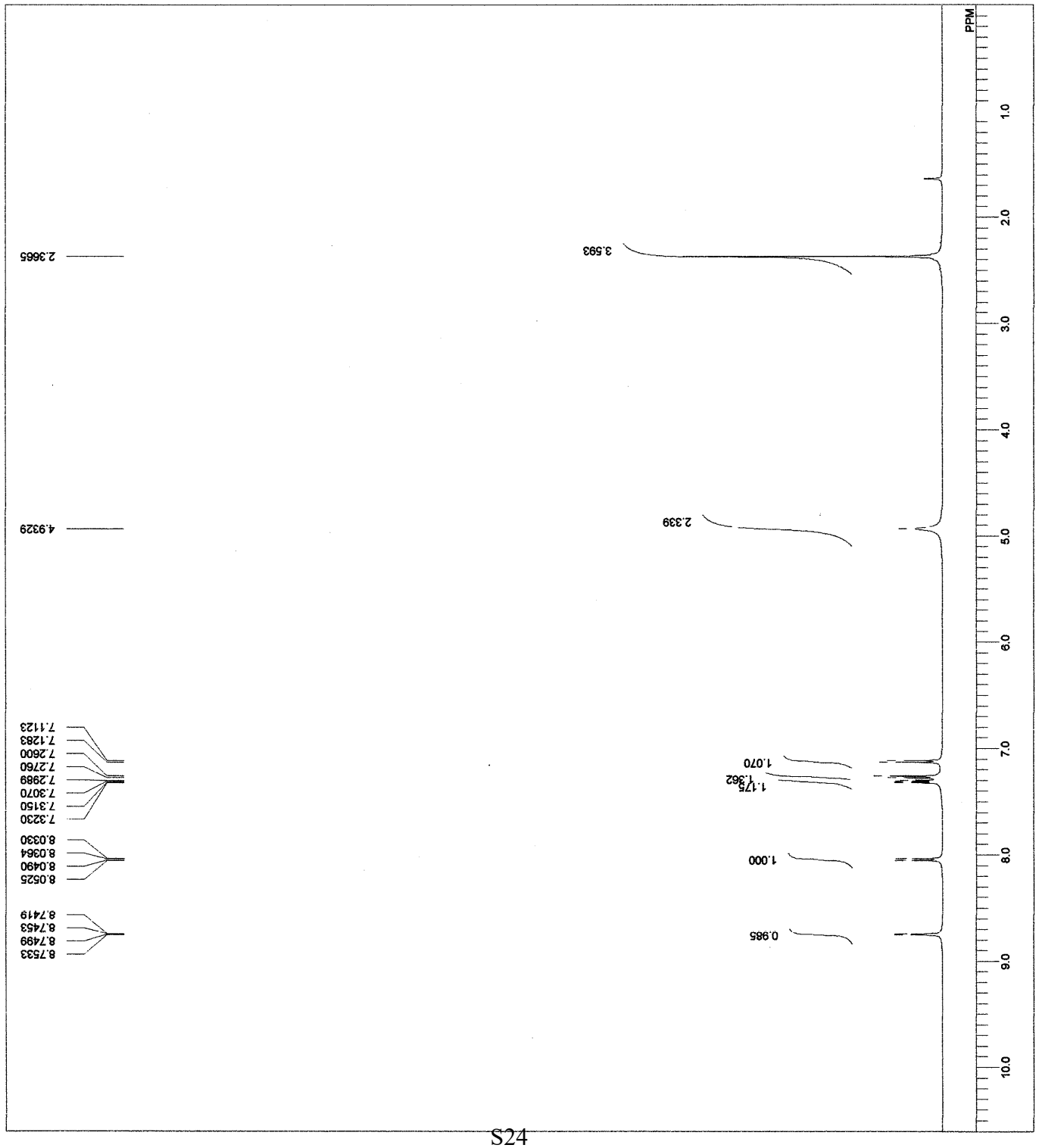
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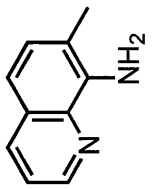
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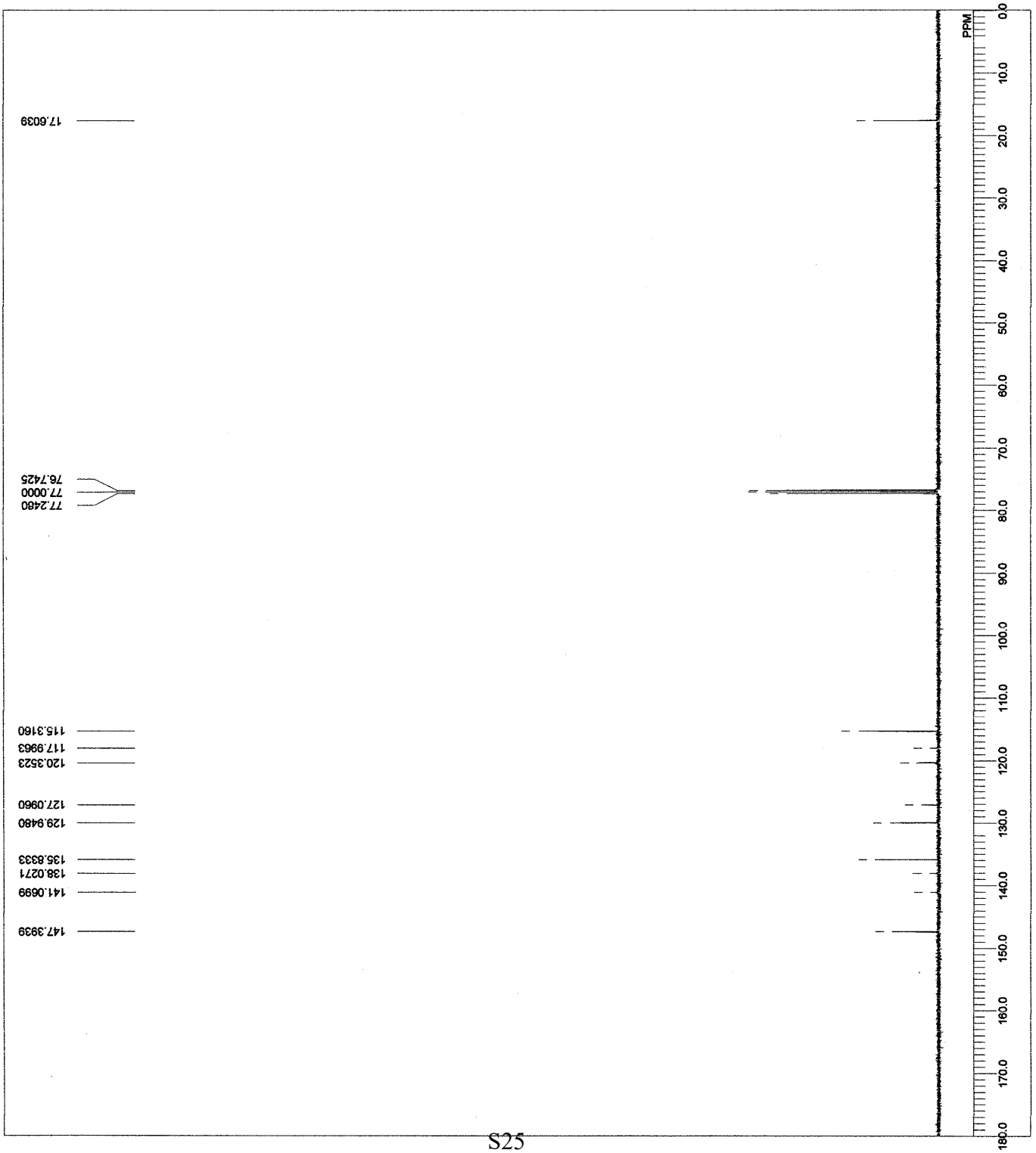
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129.9480
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138.0271
141.0699
147.3939
PPM
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40.0
50.0
60.0
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120.0
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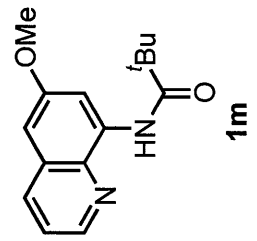
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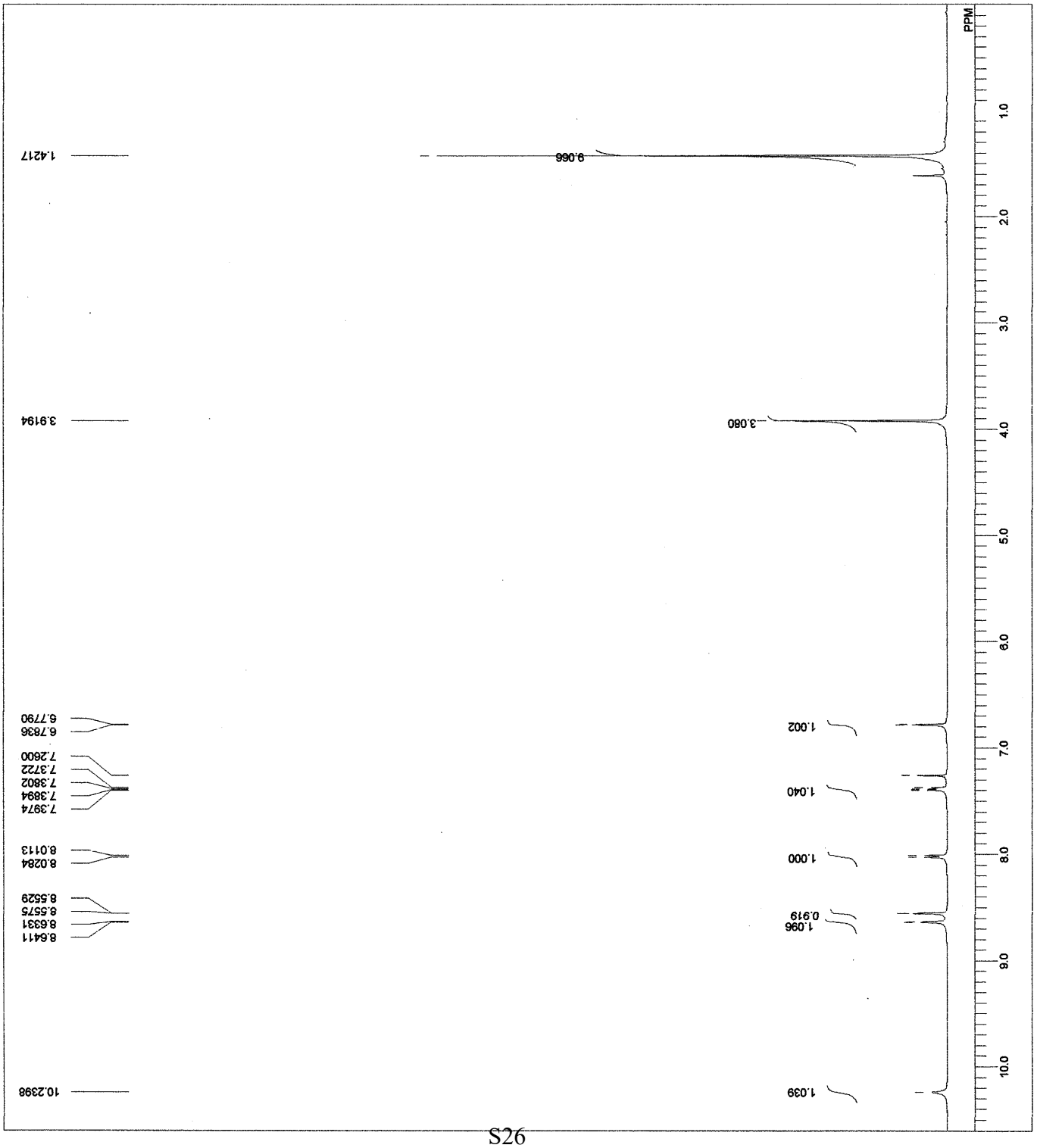
tBu
O
HN
N

1m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7.3722
7.2600
6.7836
6.7790
3.9194
1.4217
9.066
3.080
1.039
0.919
1.096
1.000
1.040
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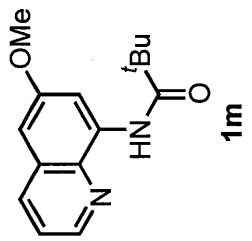
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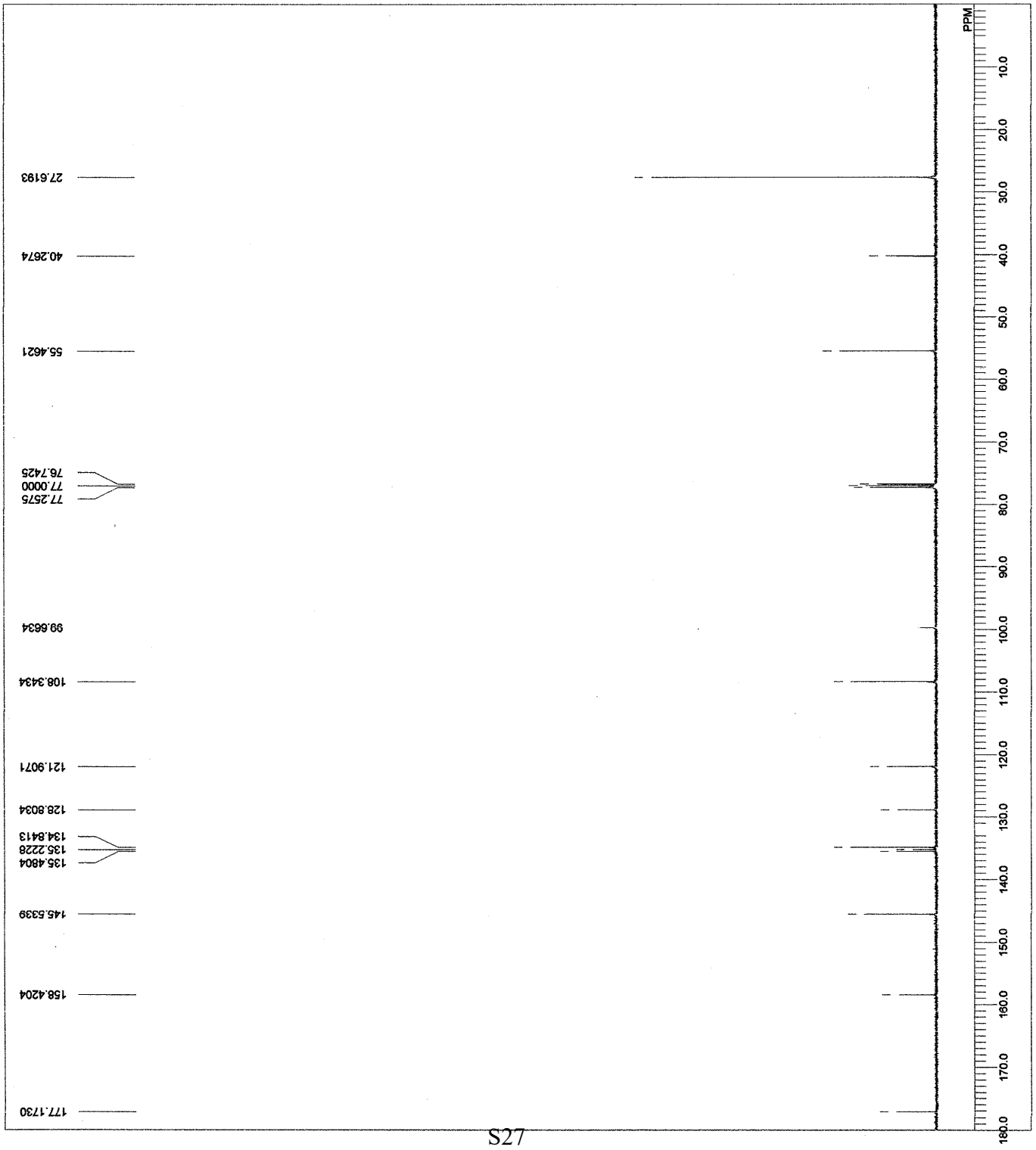
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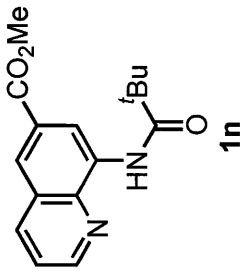
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HN
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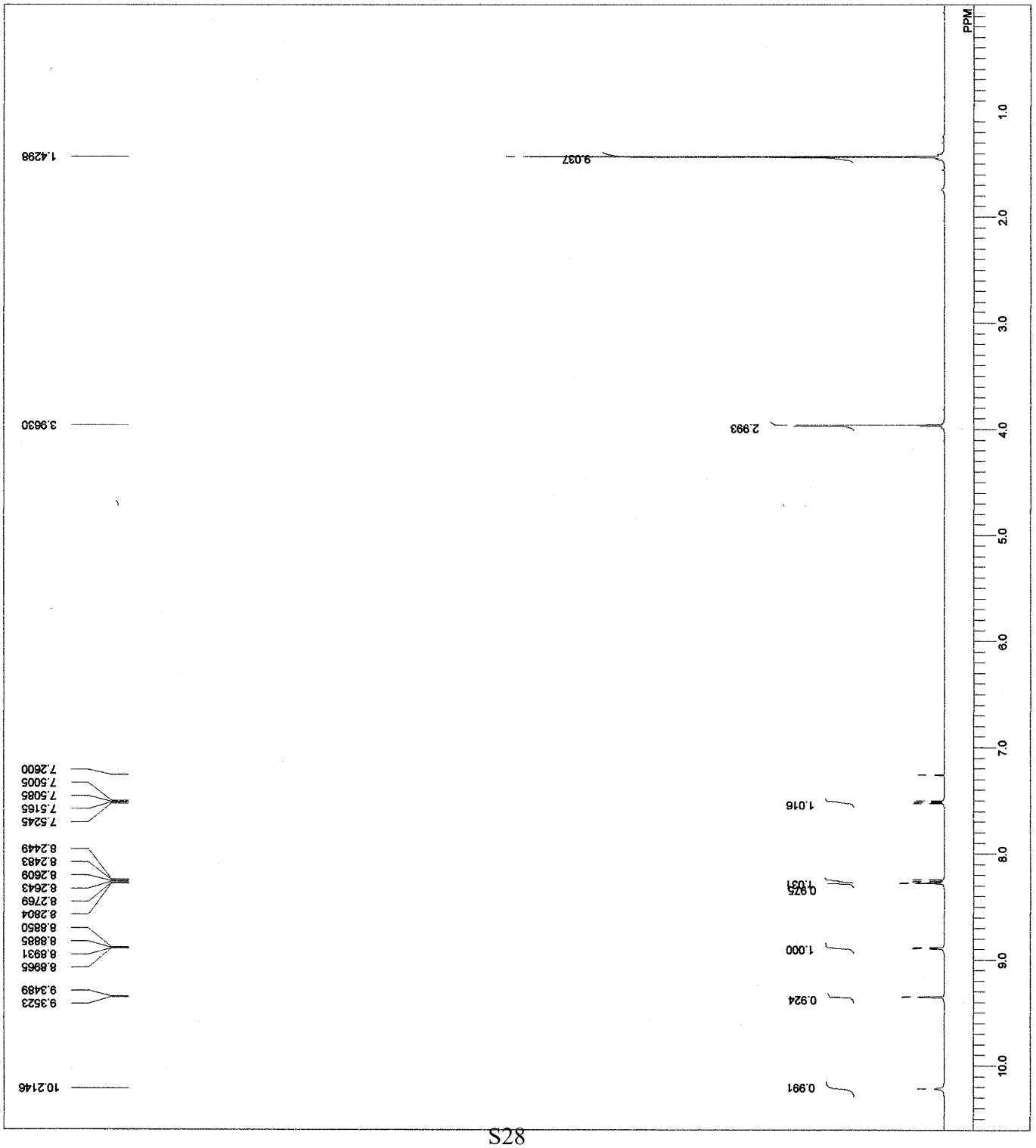
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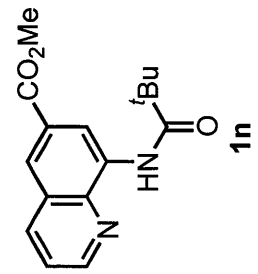
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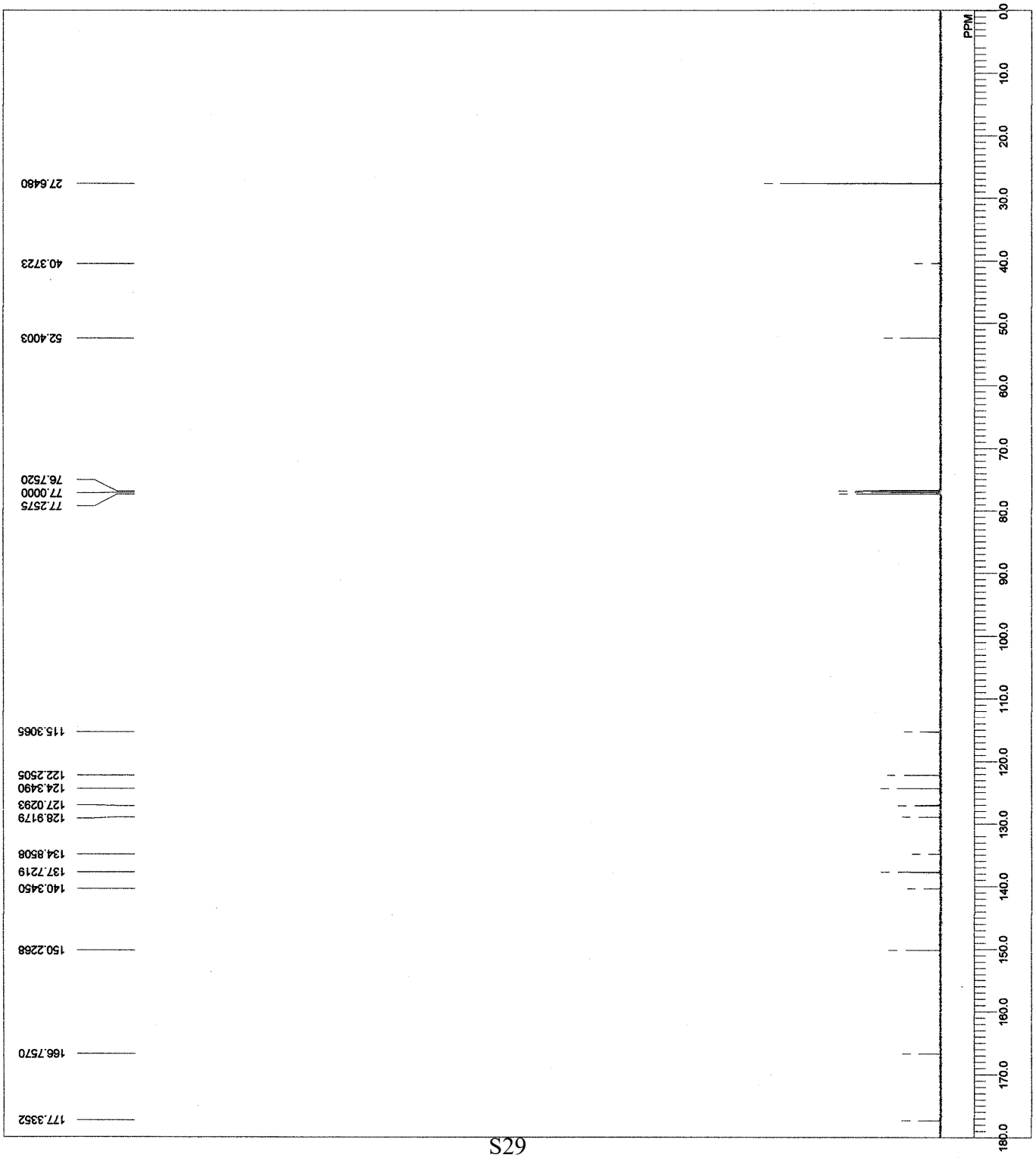
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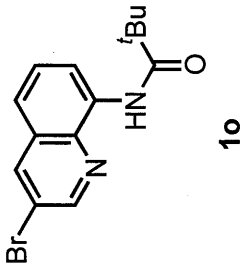
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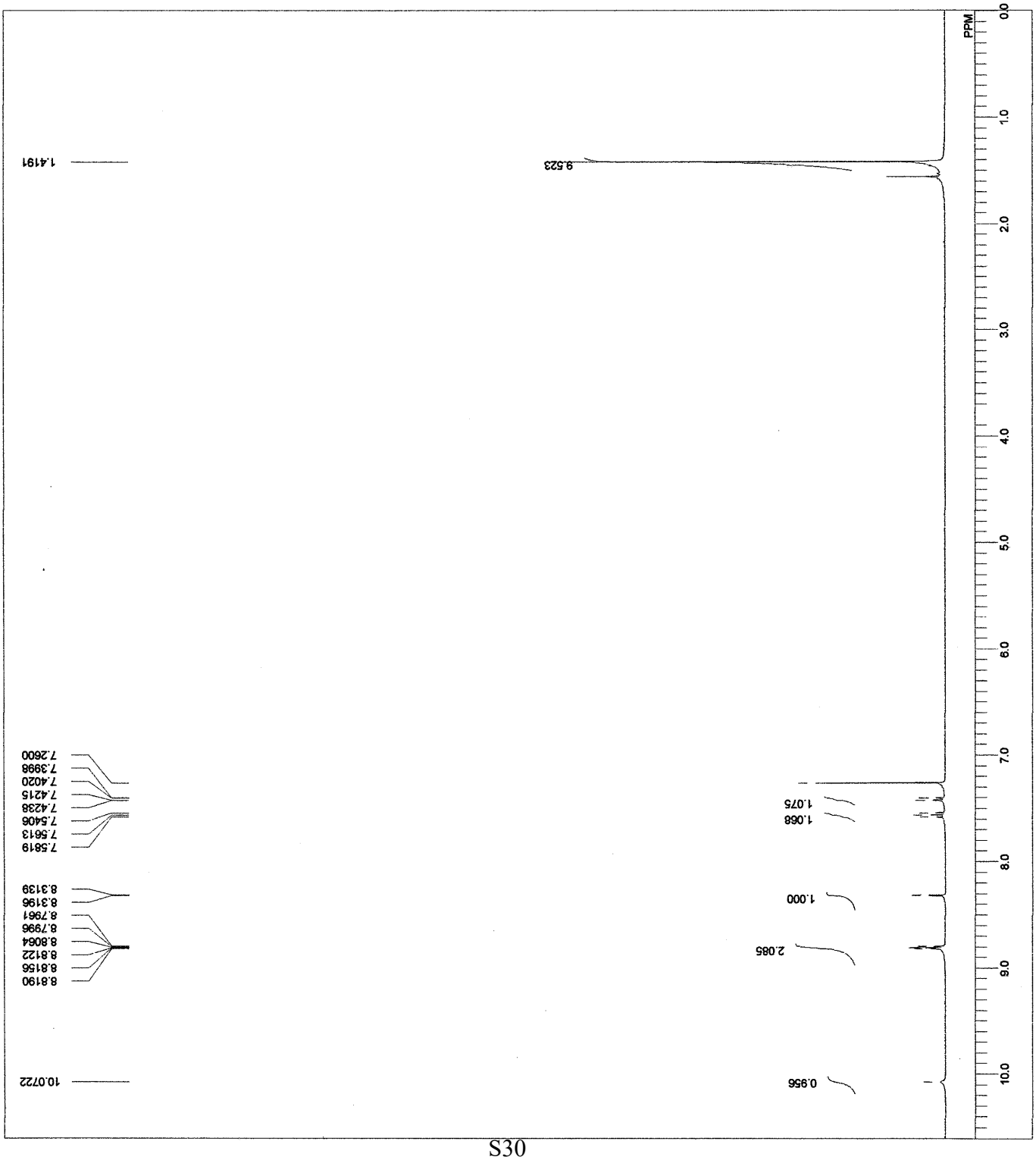
tBu

1o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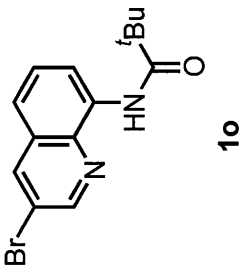
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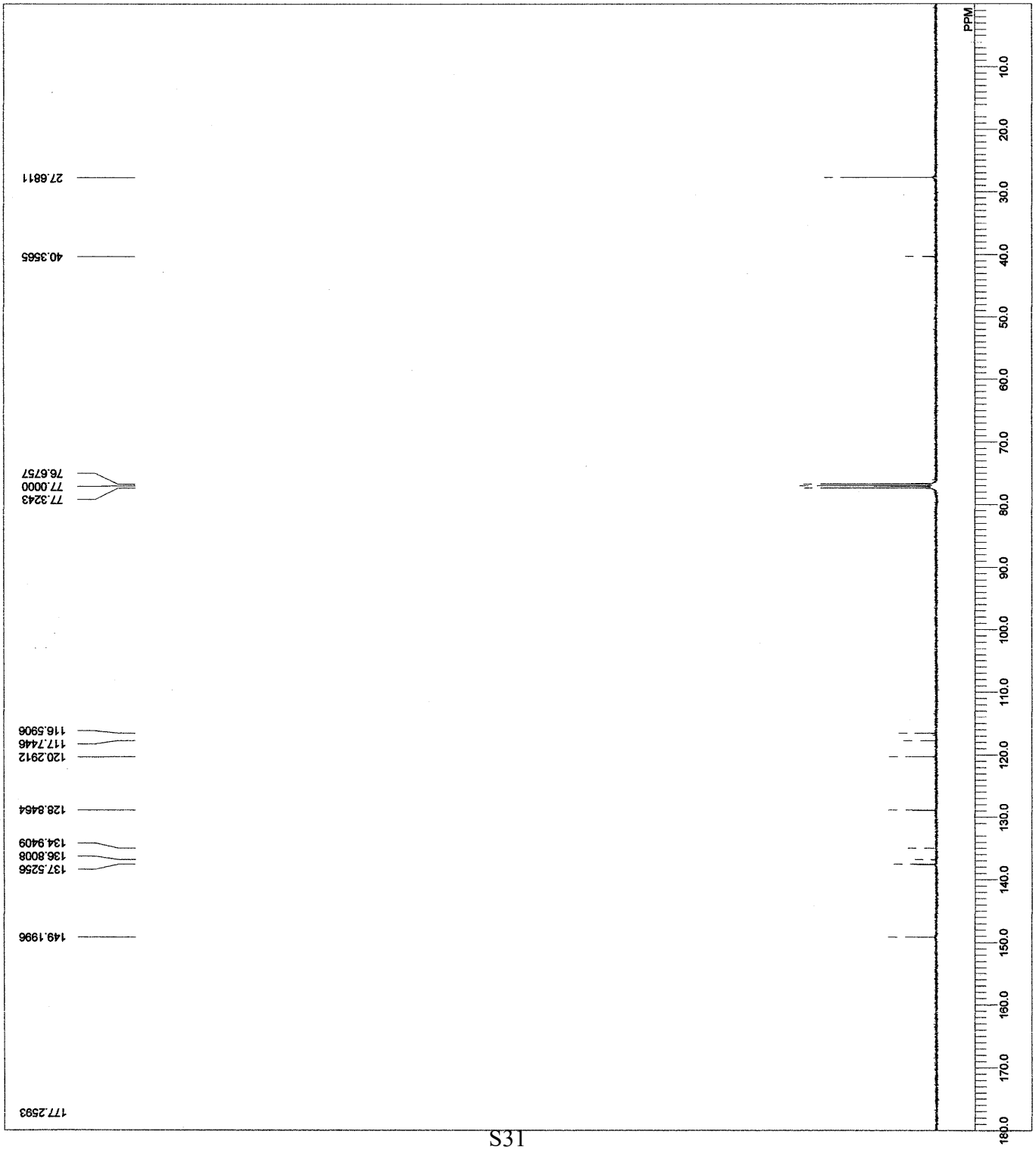
Br

1o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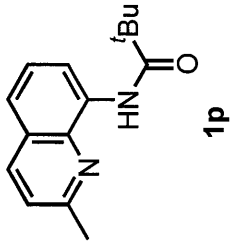
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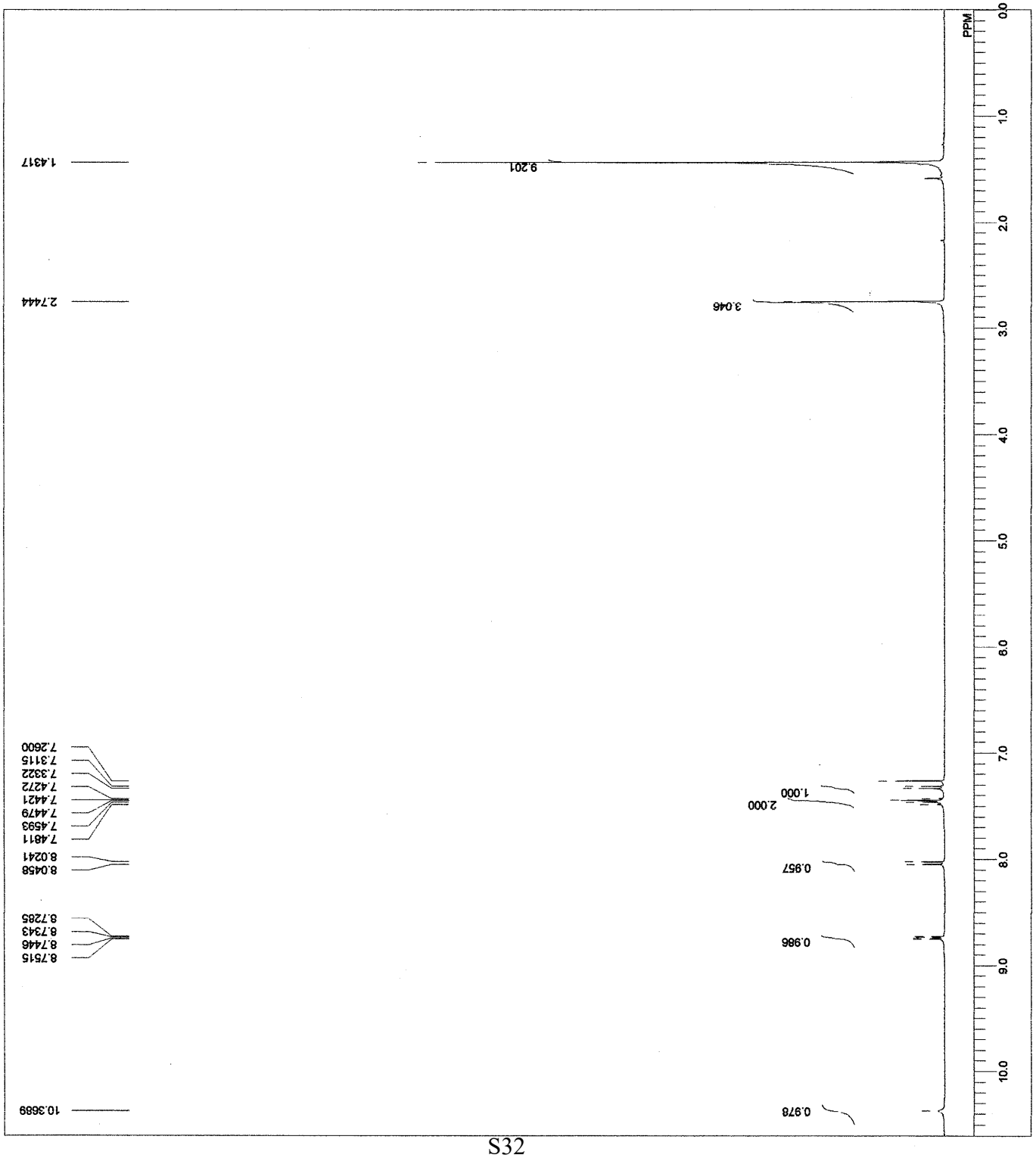
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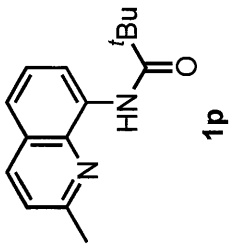
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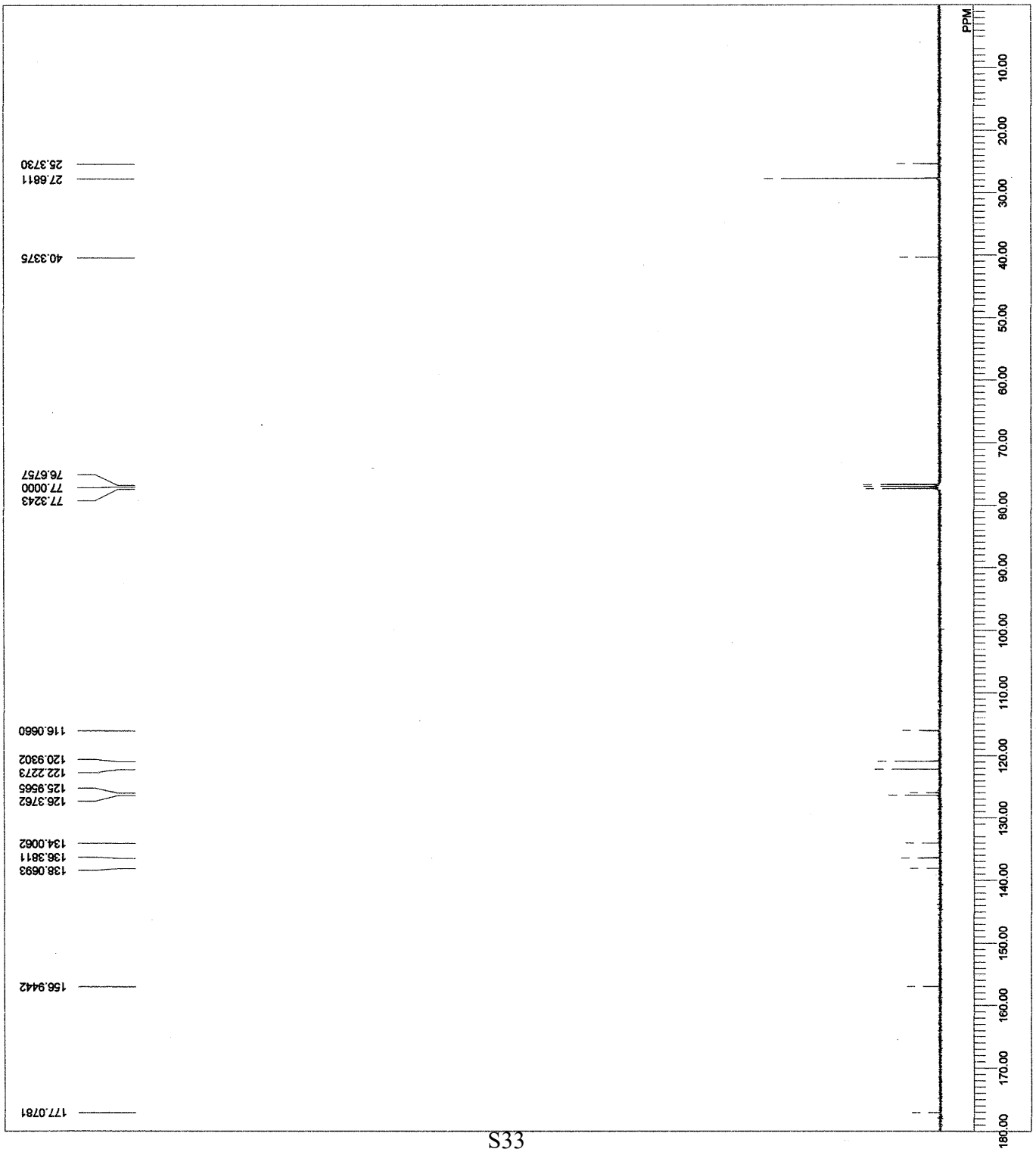
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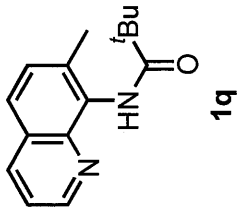
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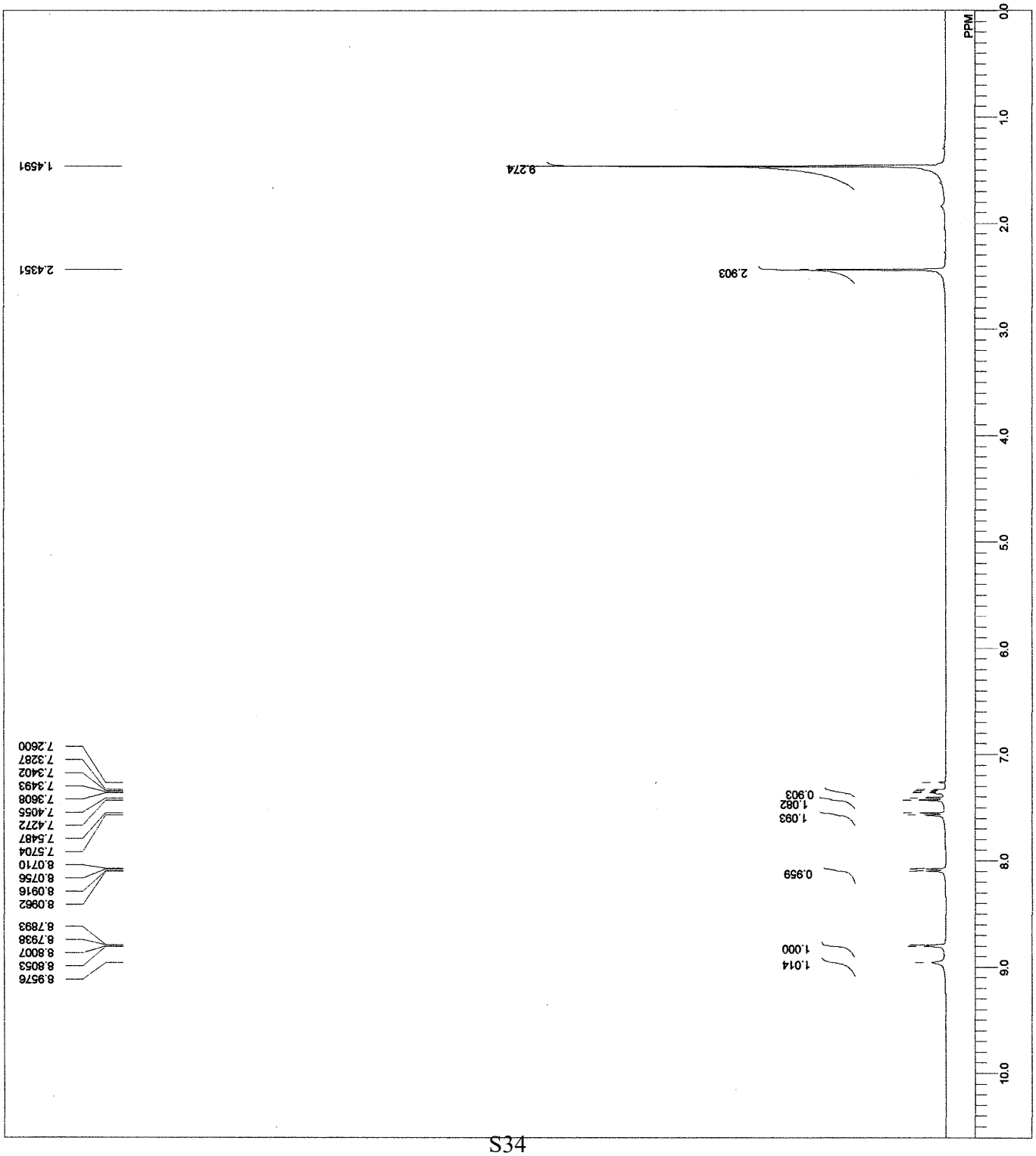
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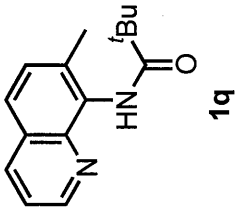
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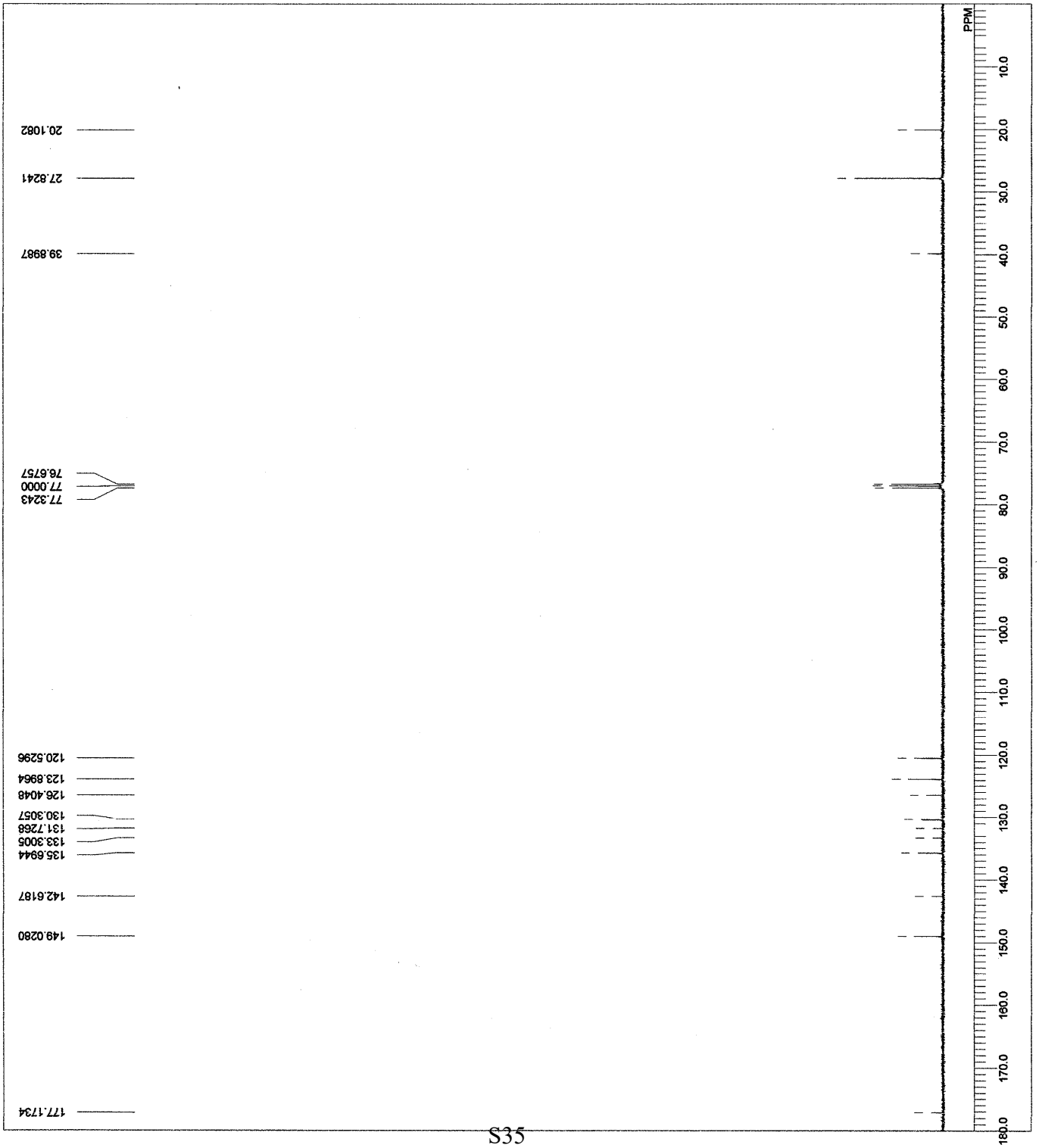
N

1q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39.8987
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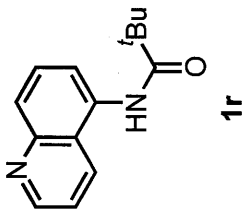
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HN
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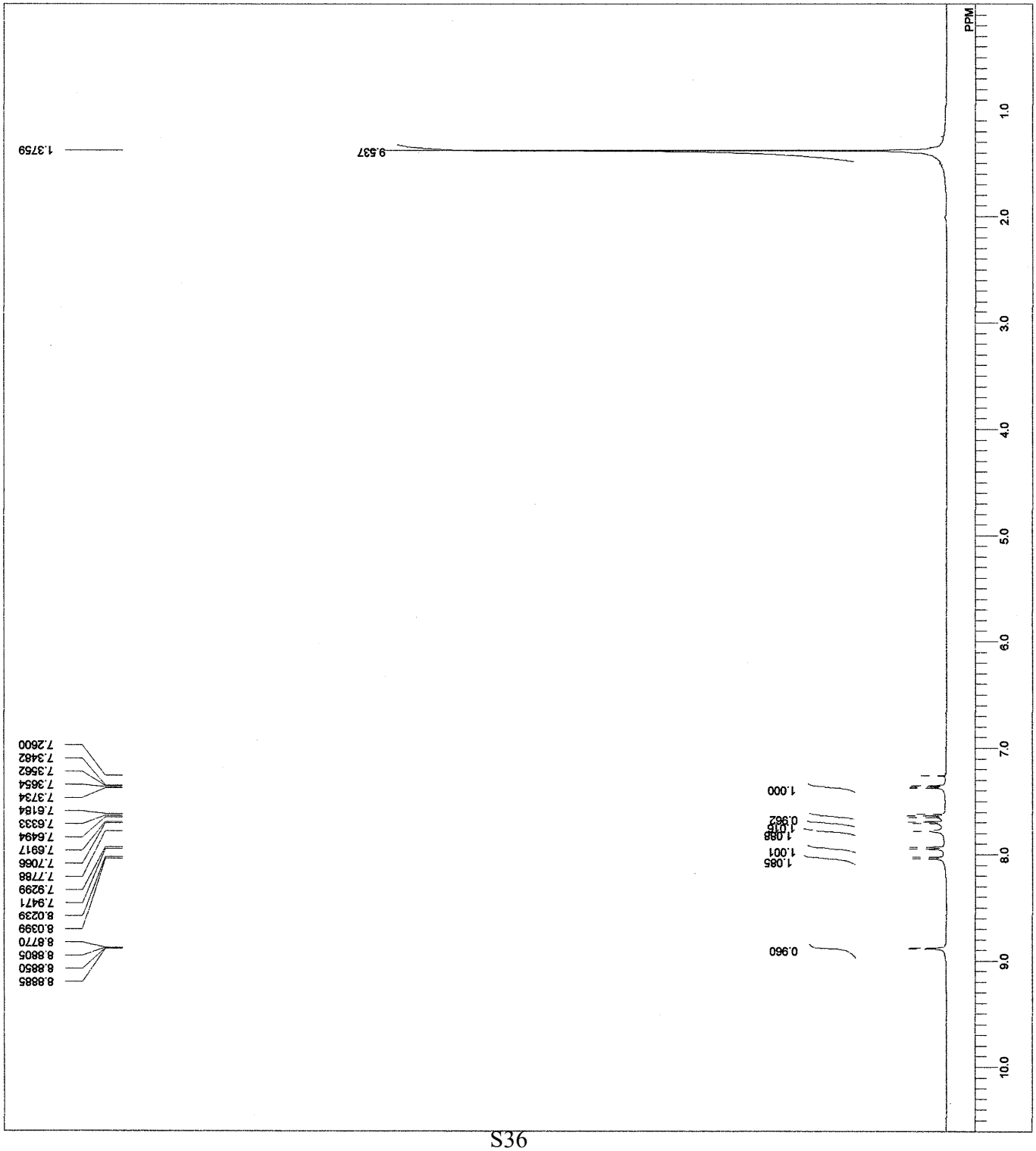
1r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7.3482
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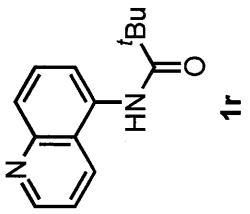
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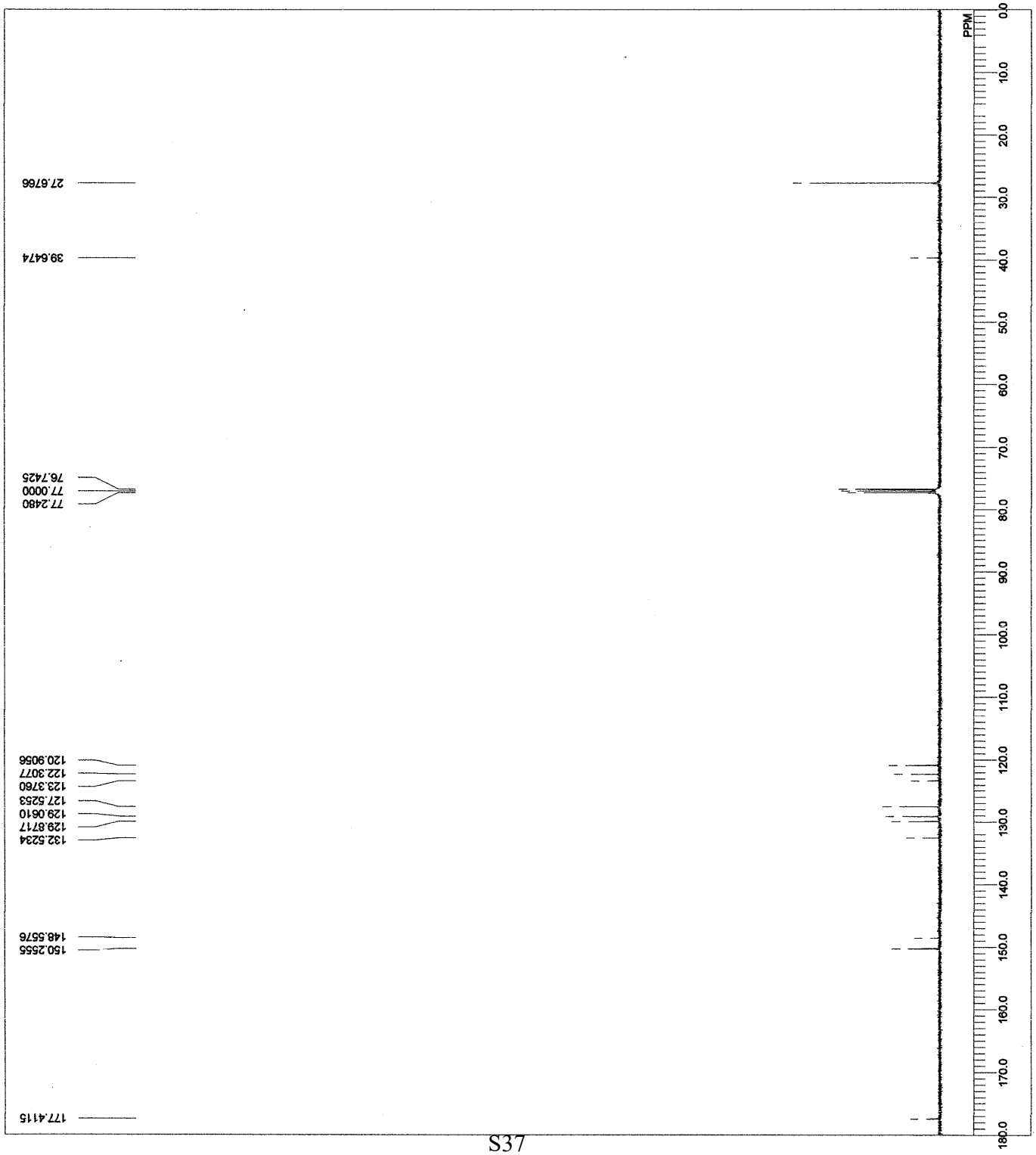
1r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76.7425
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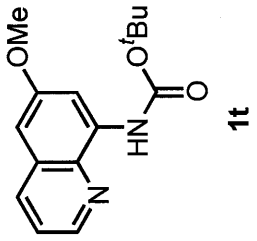
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O
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O
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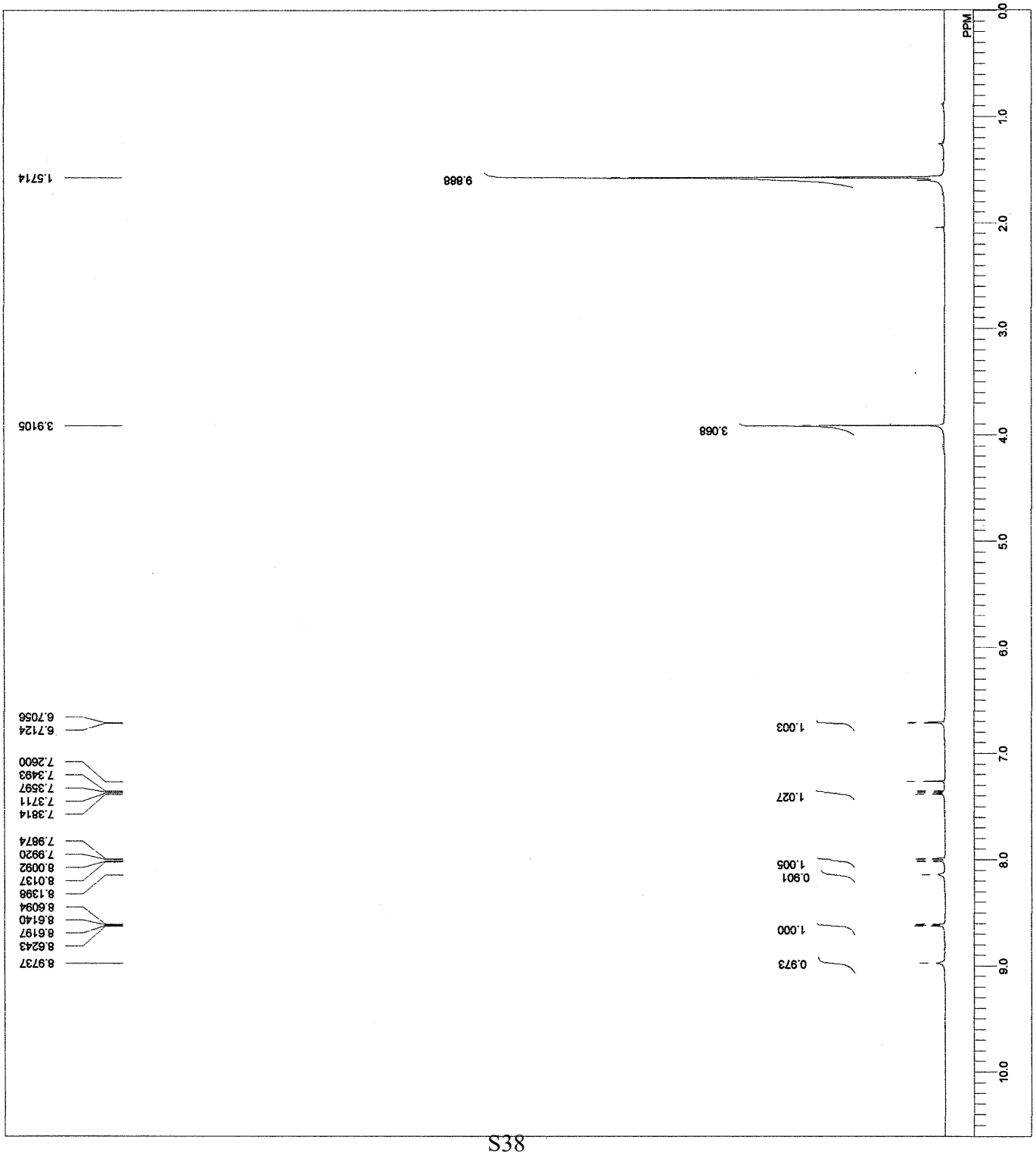
1t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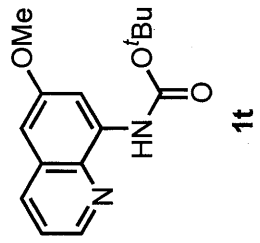
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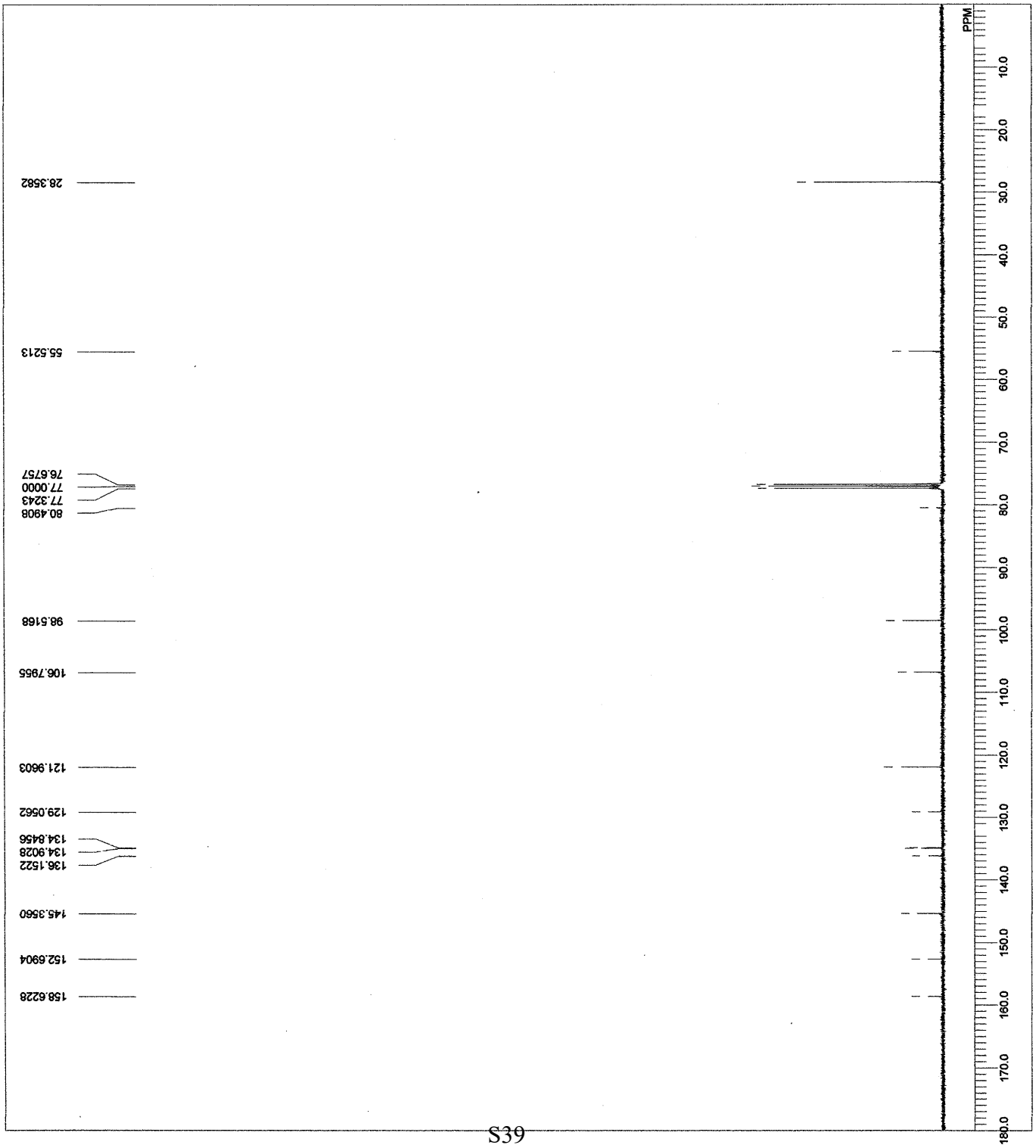
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PPM
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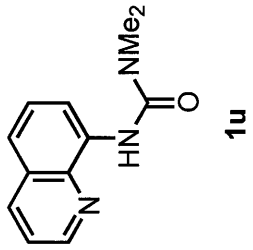
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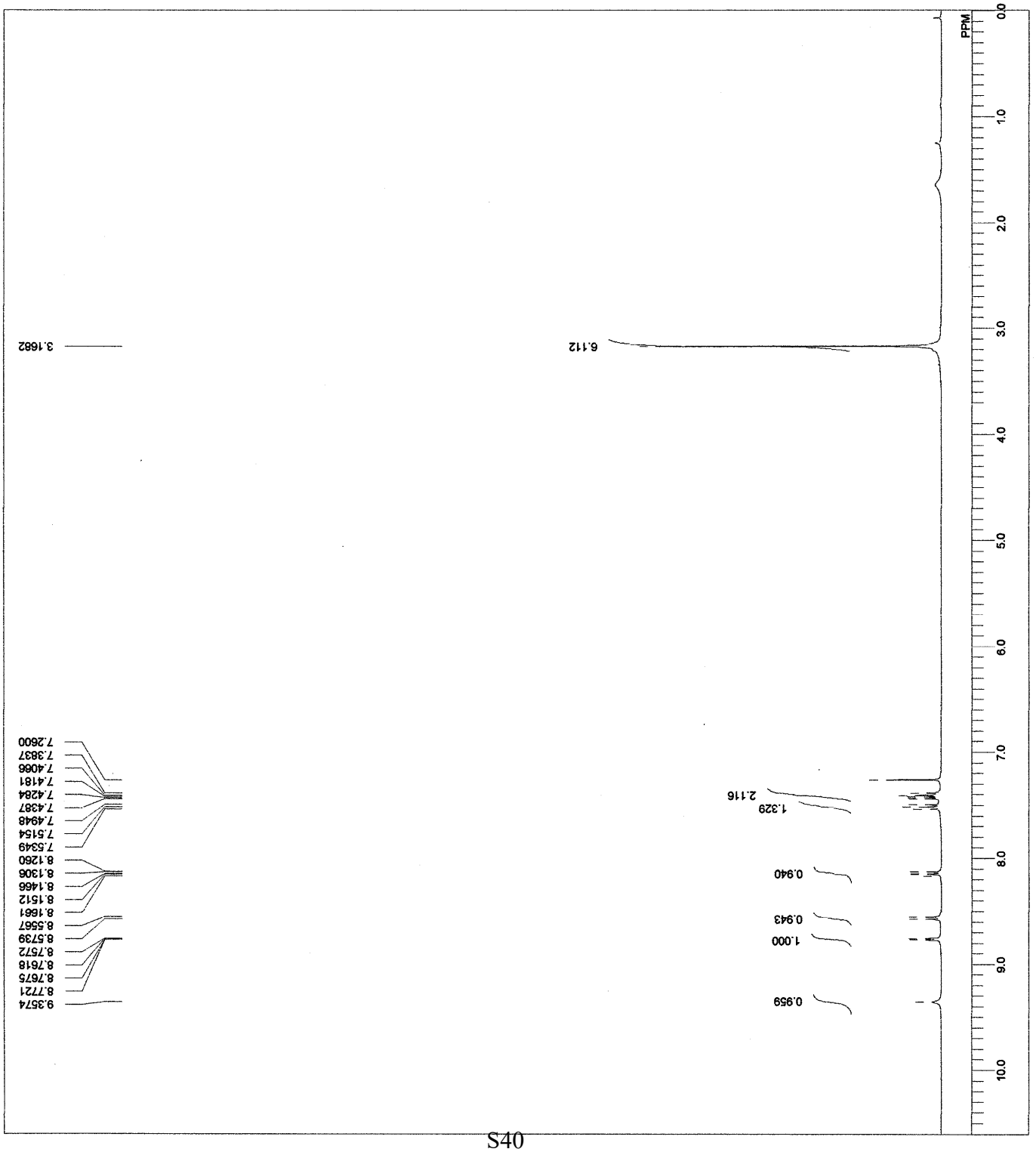
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8.1306
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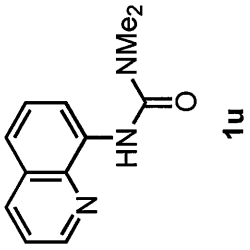
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O
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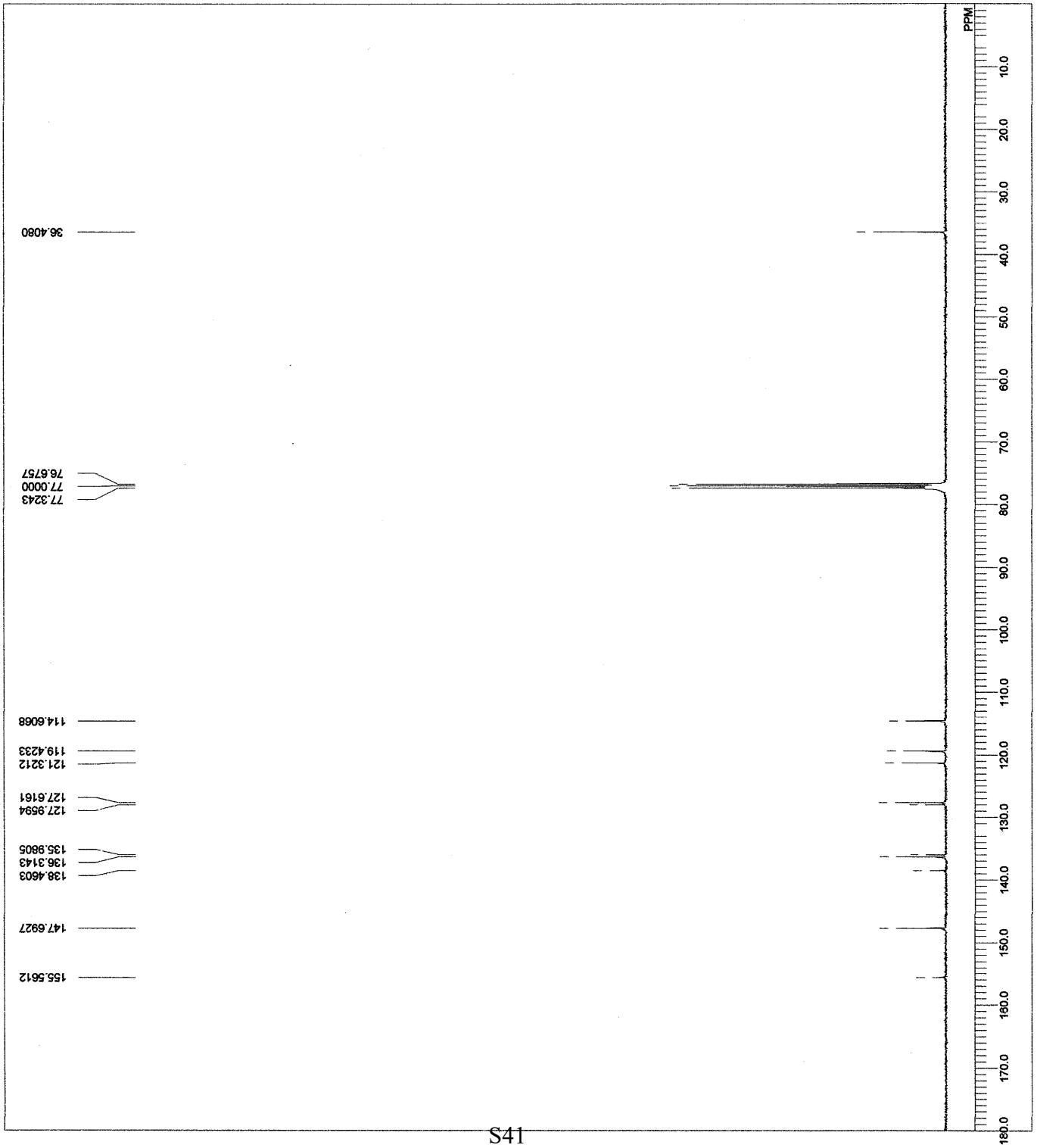
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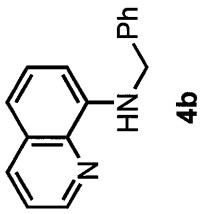
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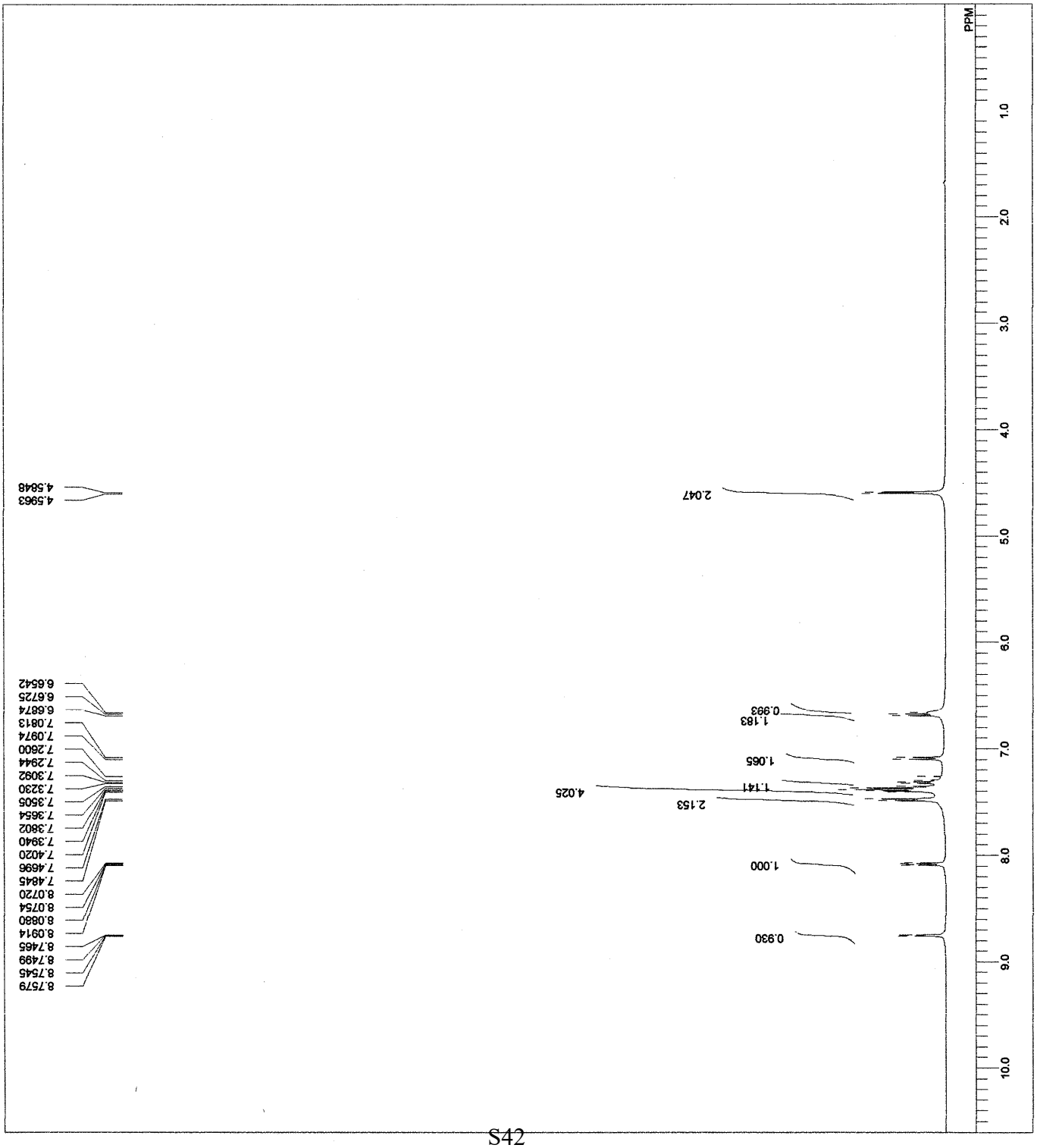
HN
N

4b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1.183
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8.0880
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7.4020
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7.3802
7.3654
7.3505
7.3230
7.3092
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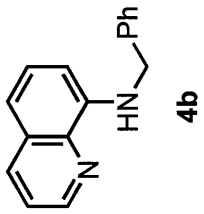
4.5848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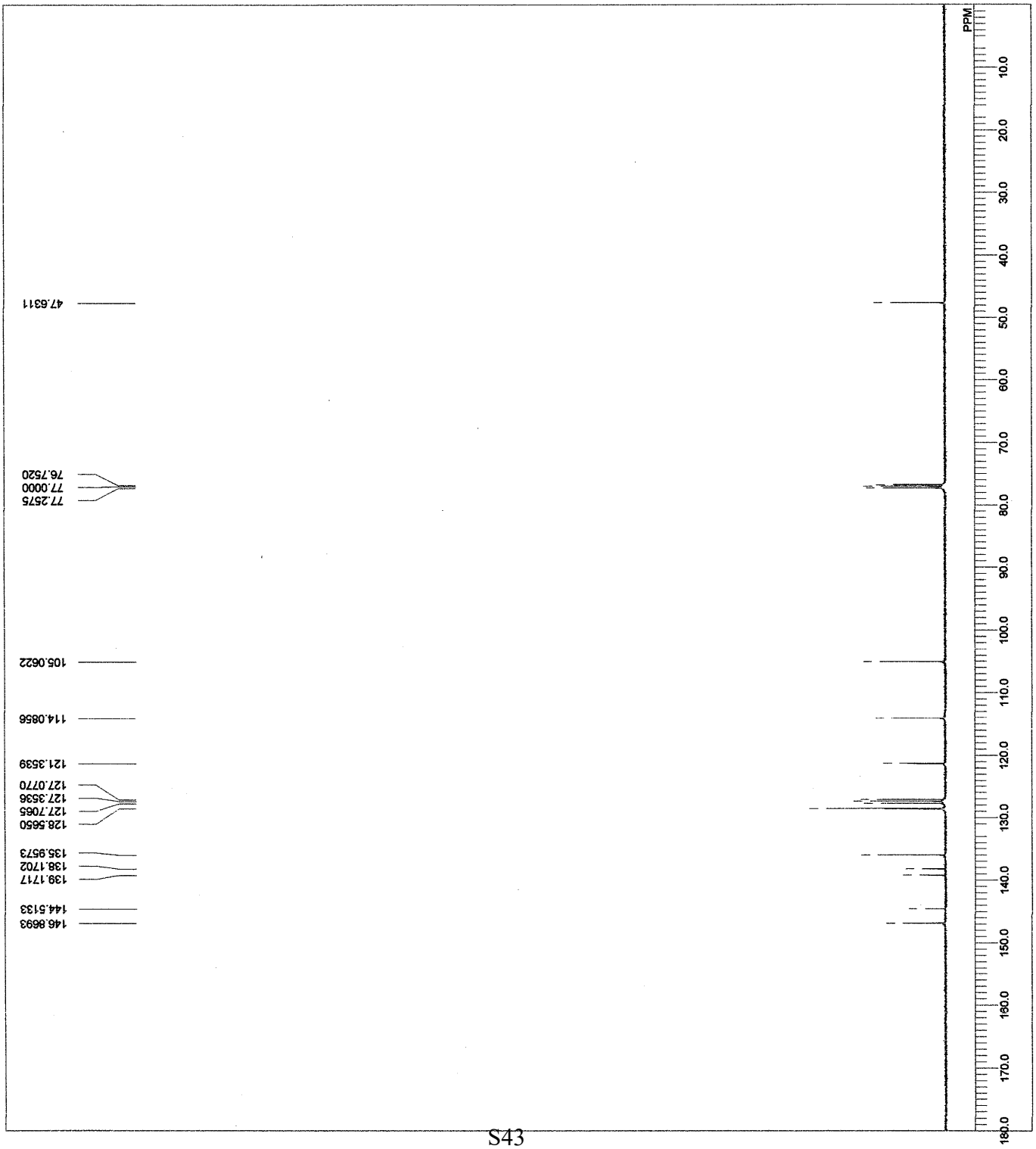
N

4b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120.0
130.0
140.0
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170.0
180.0
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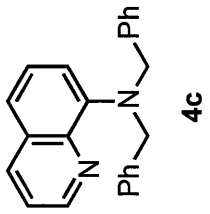
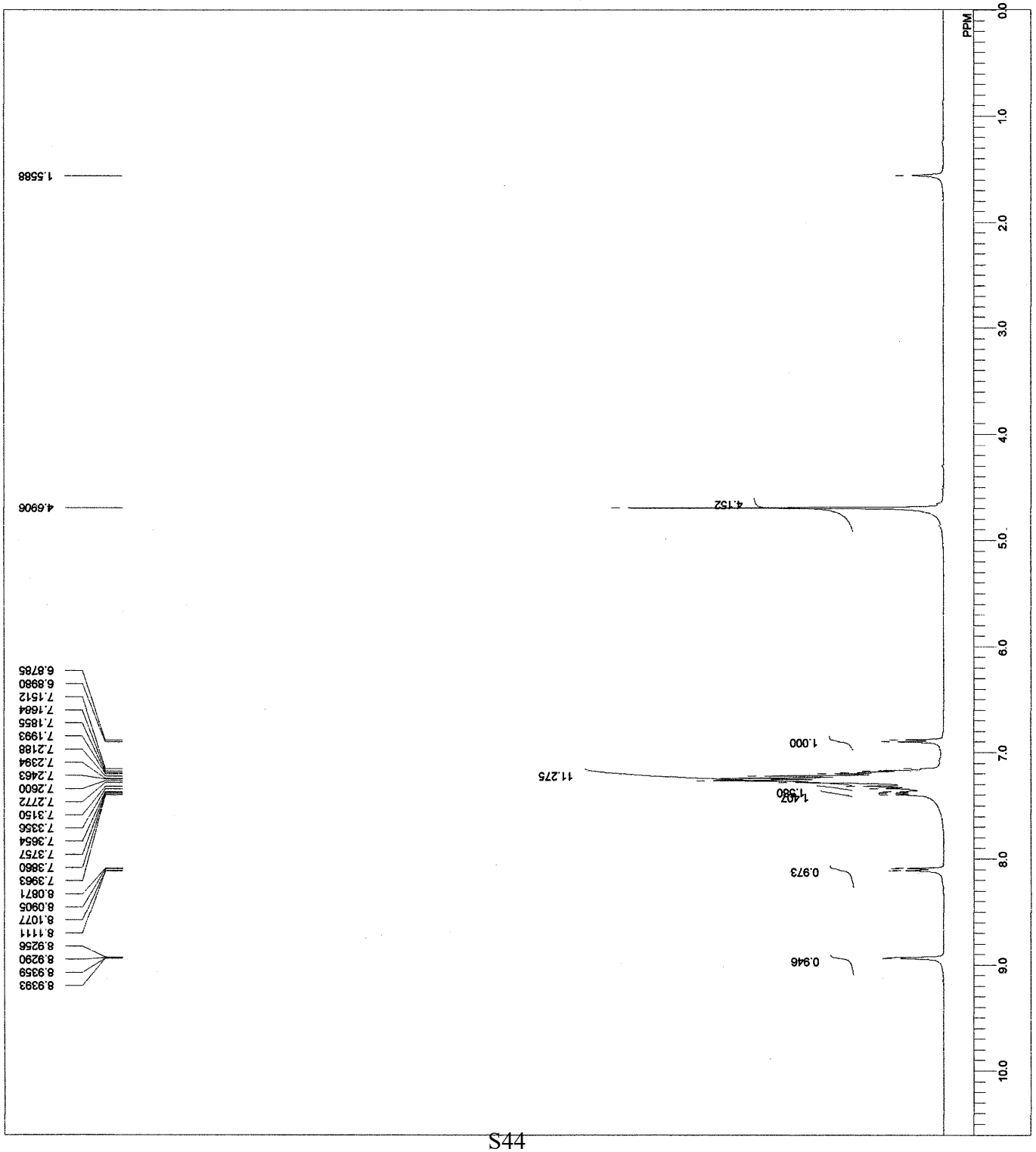

Ph
N
Ph
N

4c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1.580
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0.946
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7.1684
7.1855
7.1993
7.2188
7.2394
7.2463
7.2600
7.2772
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7.3654
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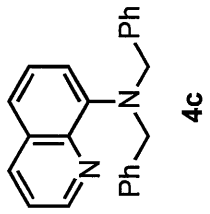
Ph
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Ph
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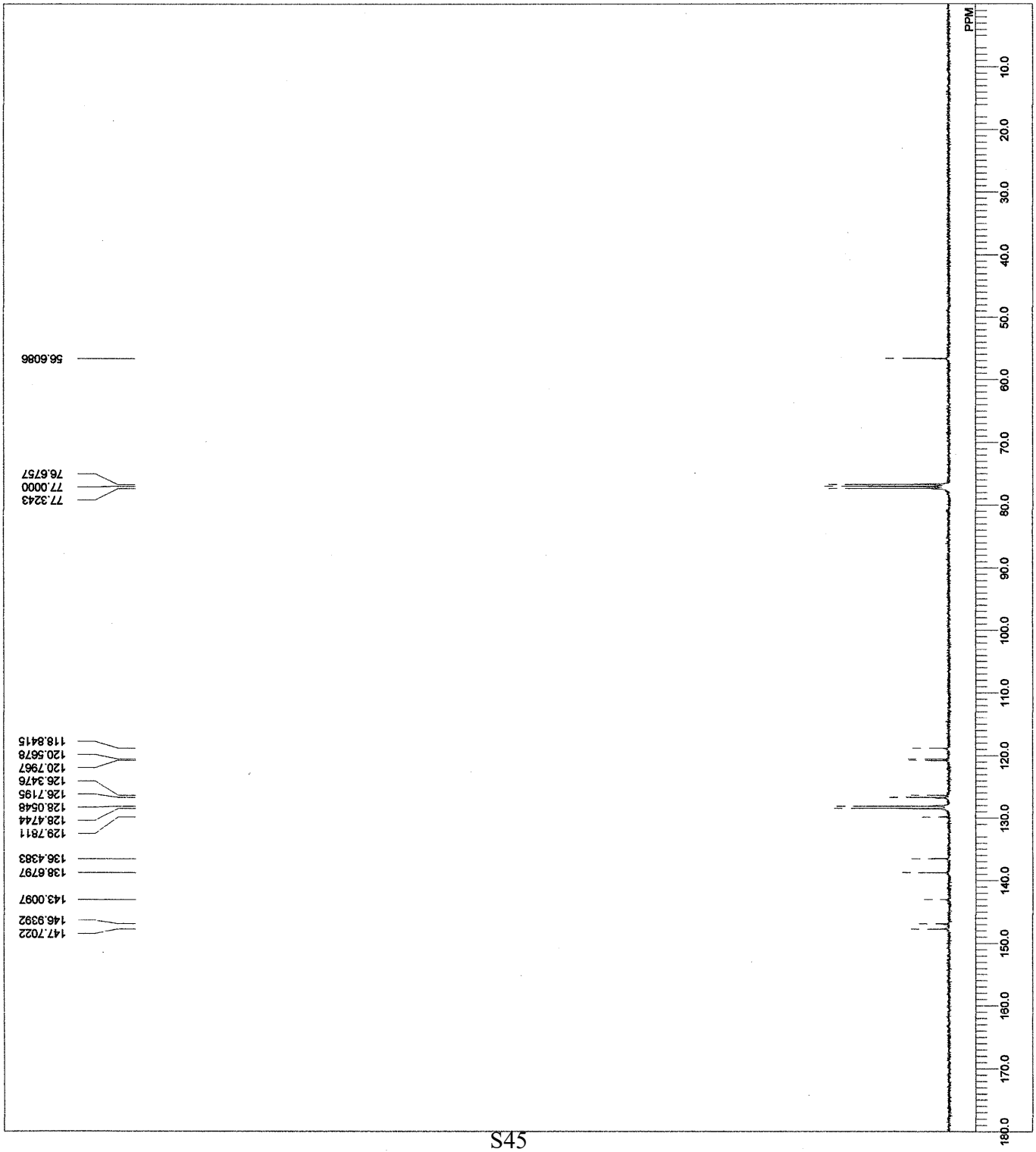
4c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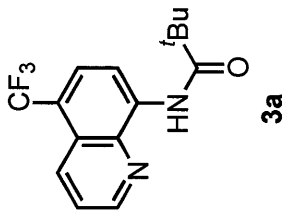
147.7022


CF3
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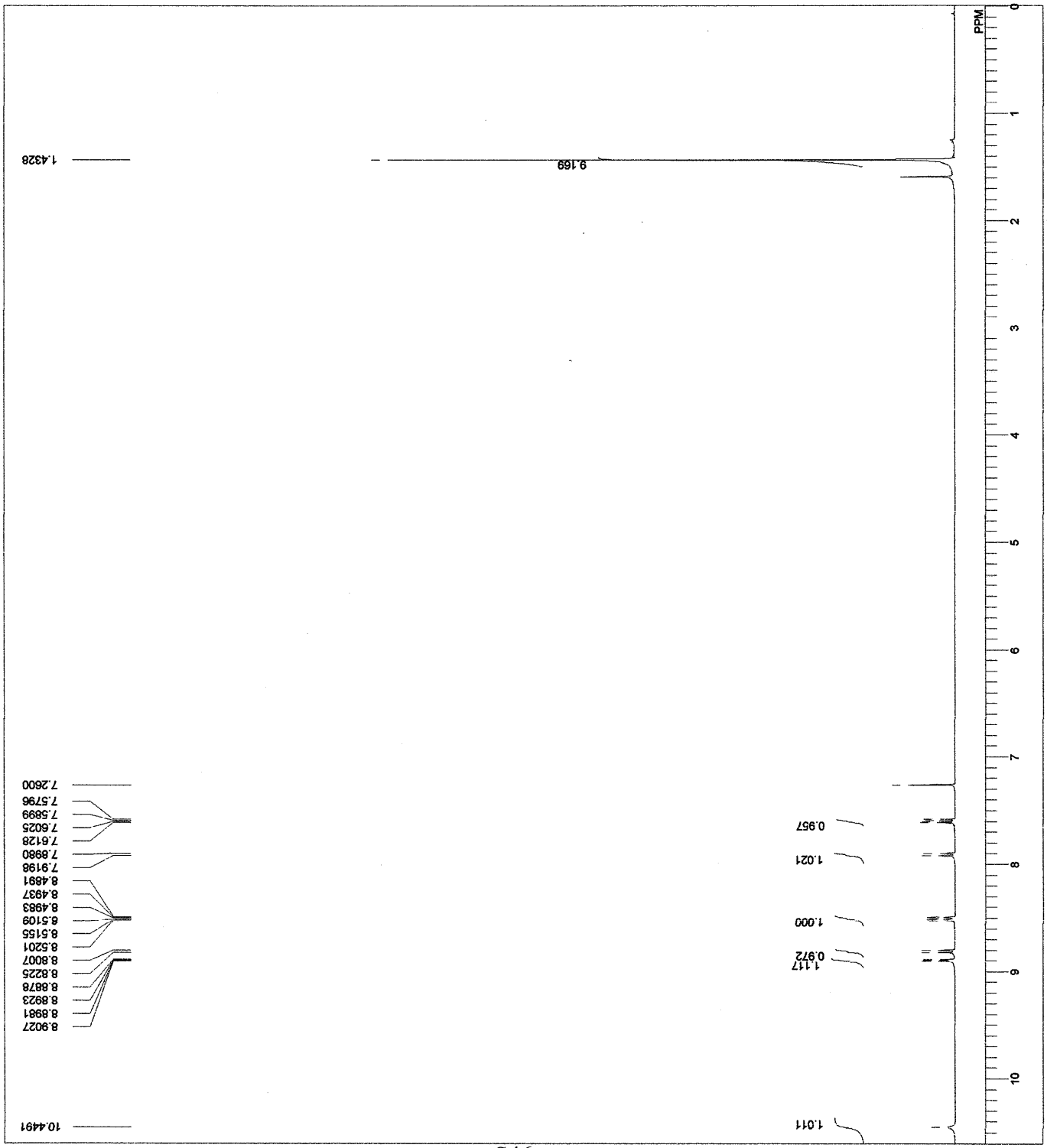
tBu
O
N

3a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7.8980
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8.5201
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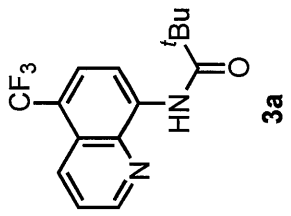
1.011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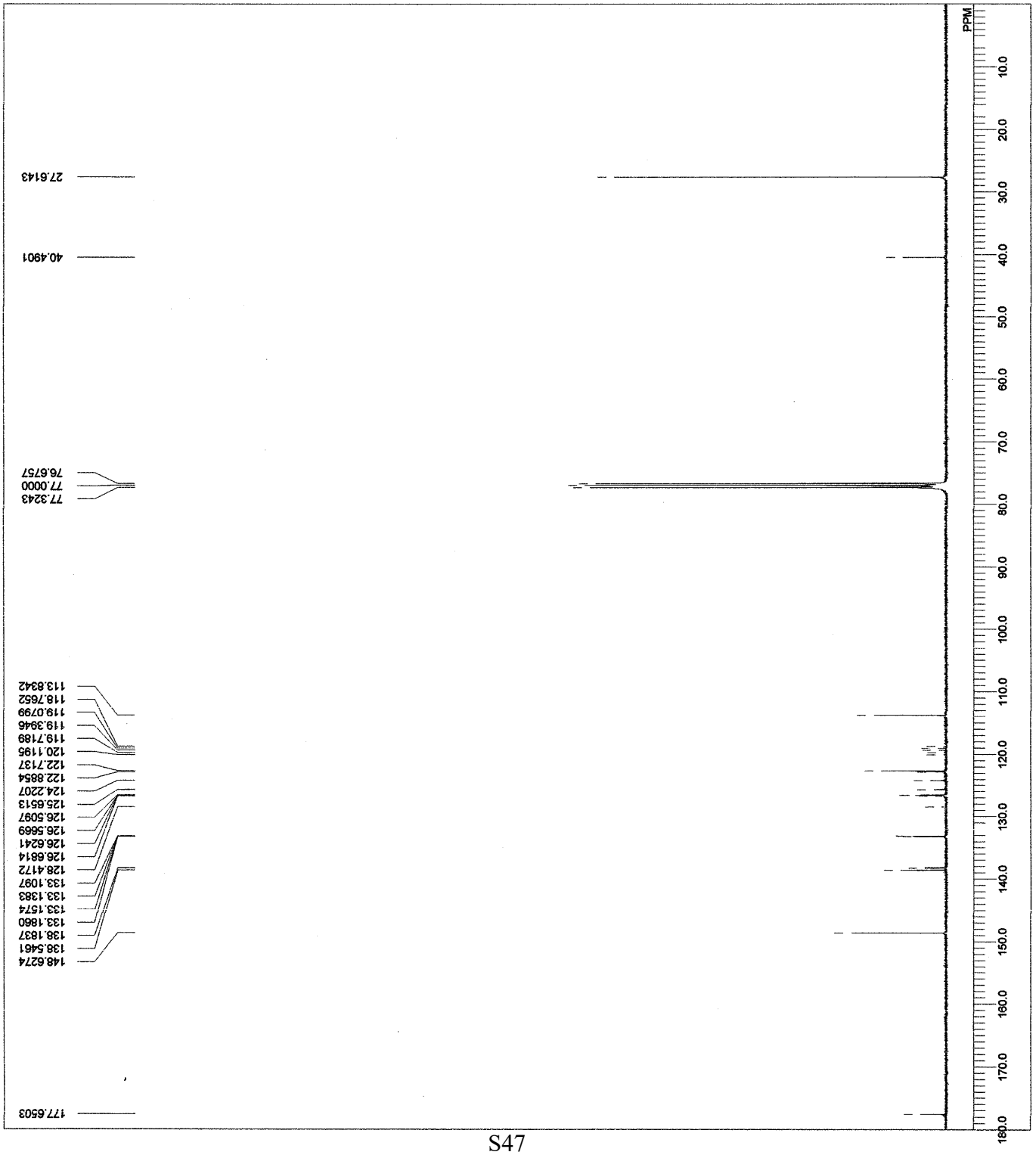
3a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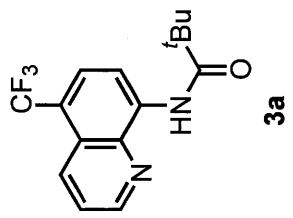
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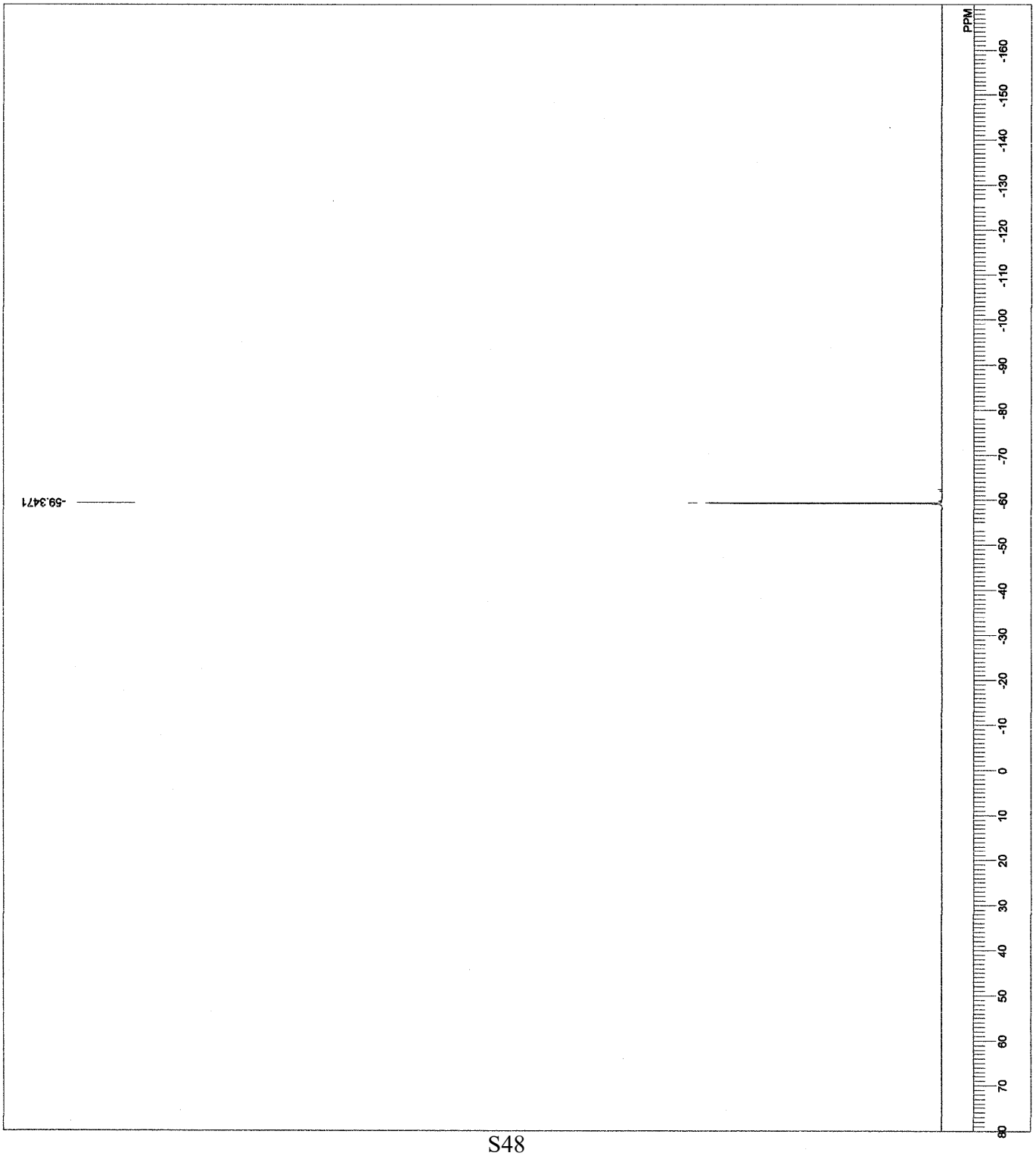
N

3a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PPM
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-140
-150
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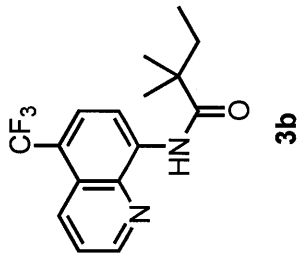
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O
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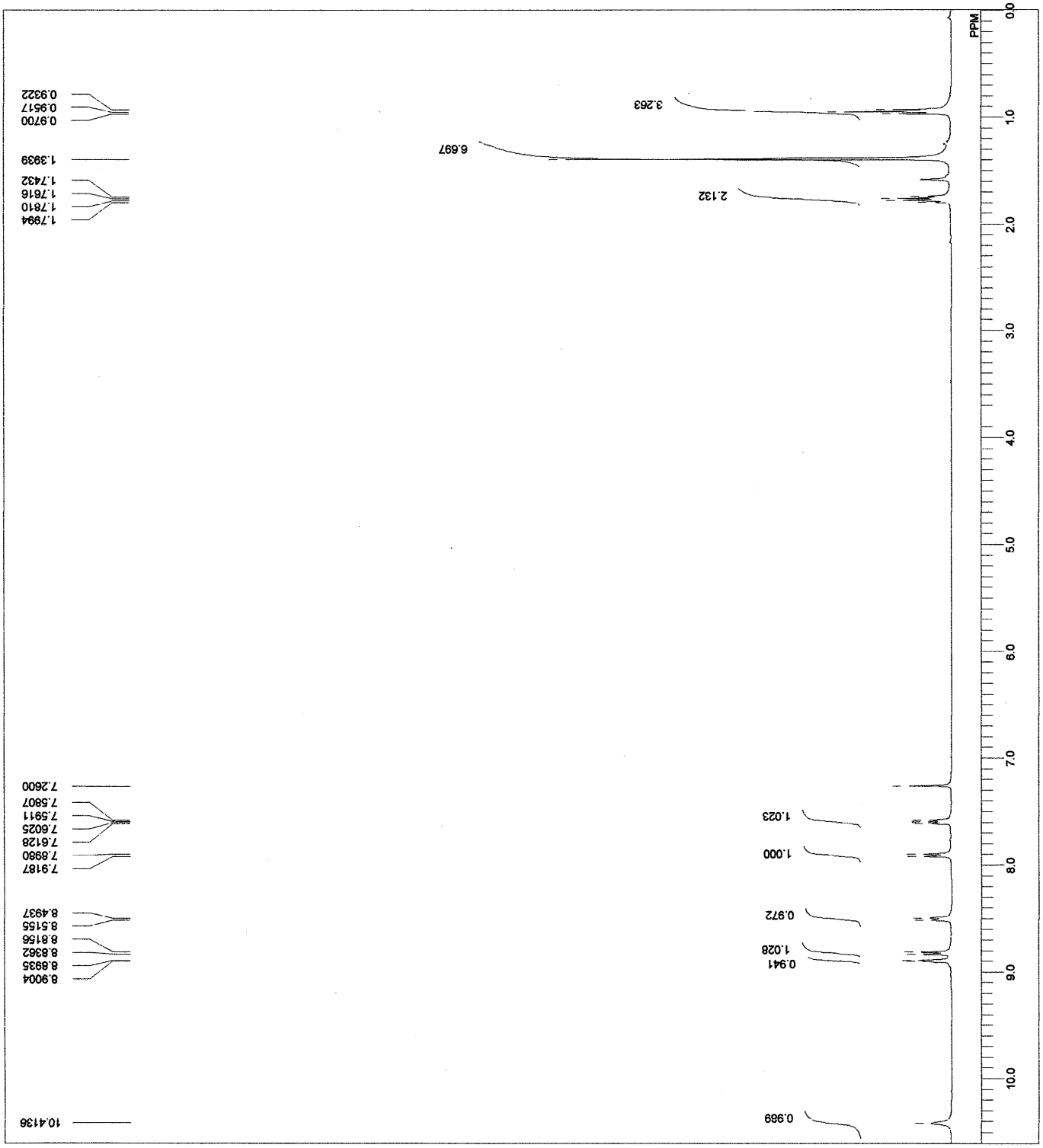
3b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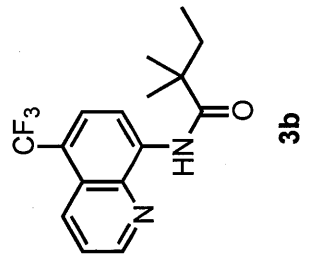
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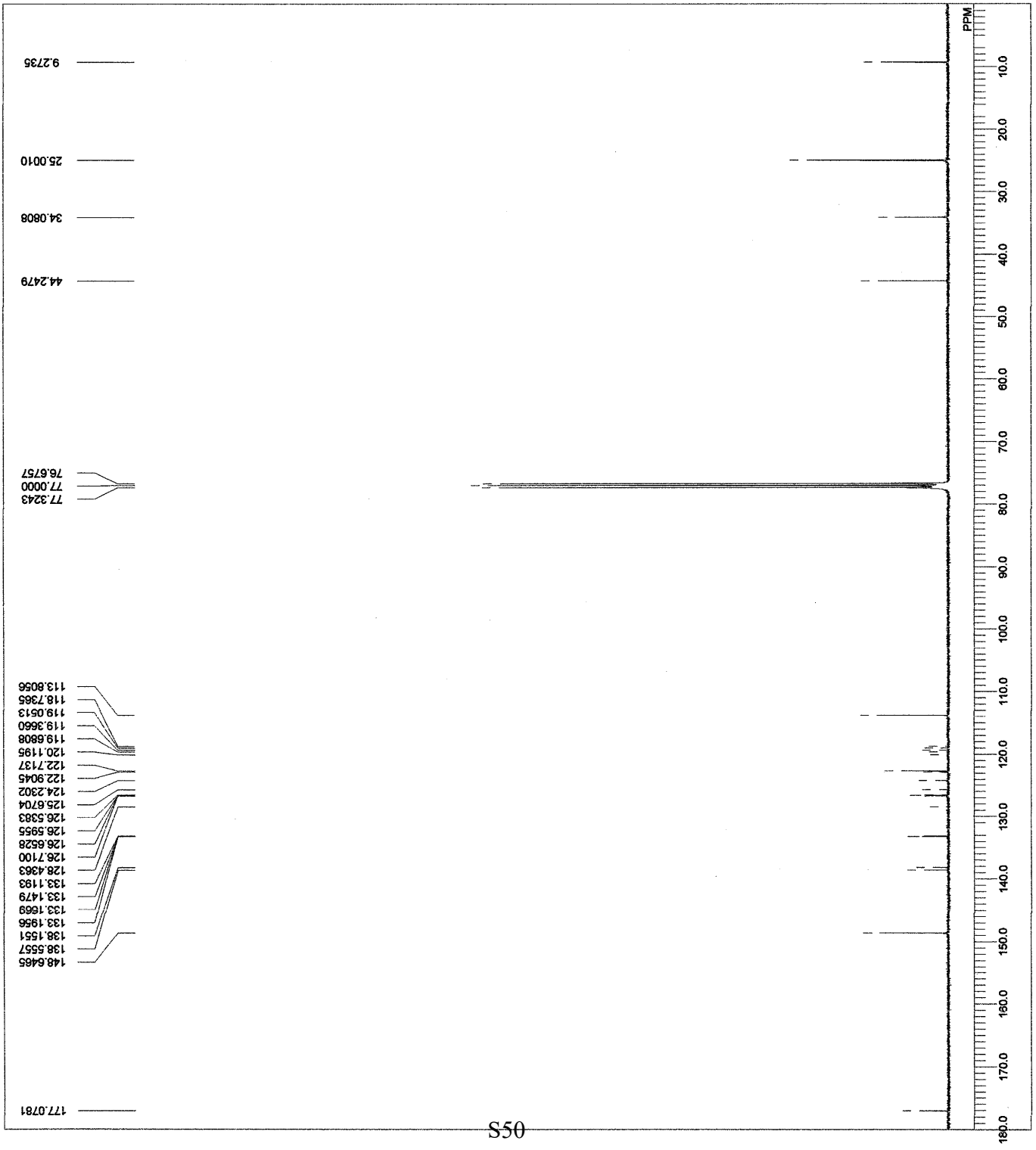
3b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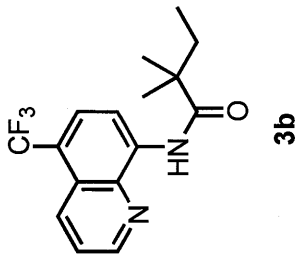

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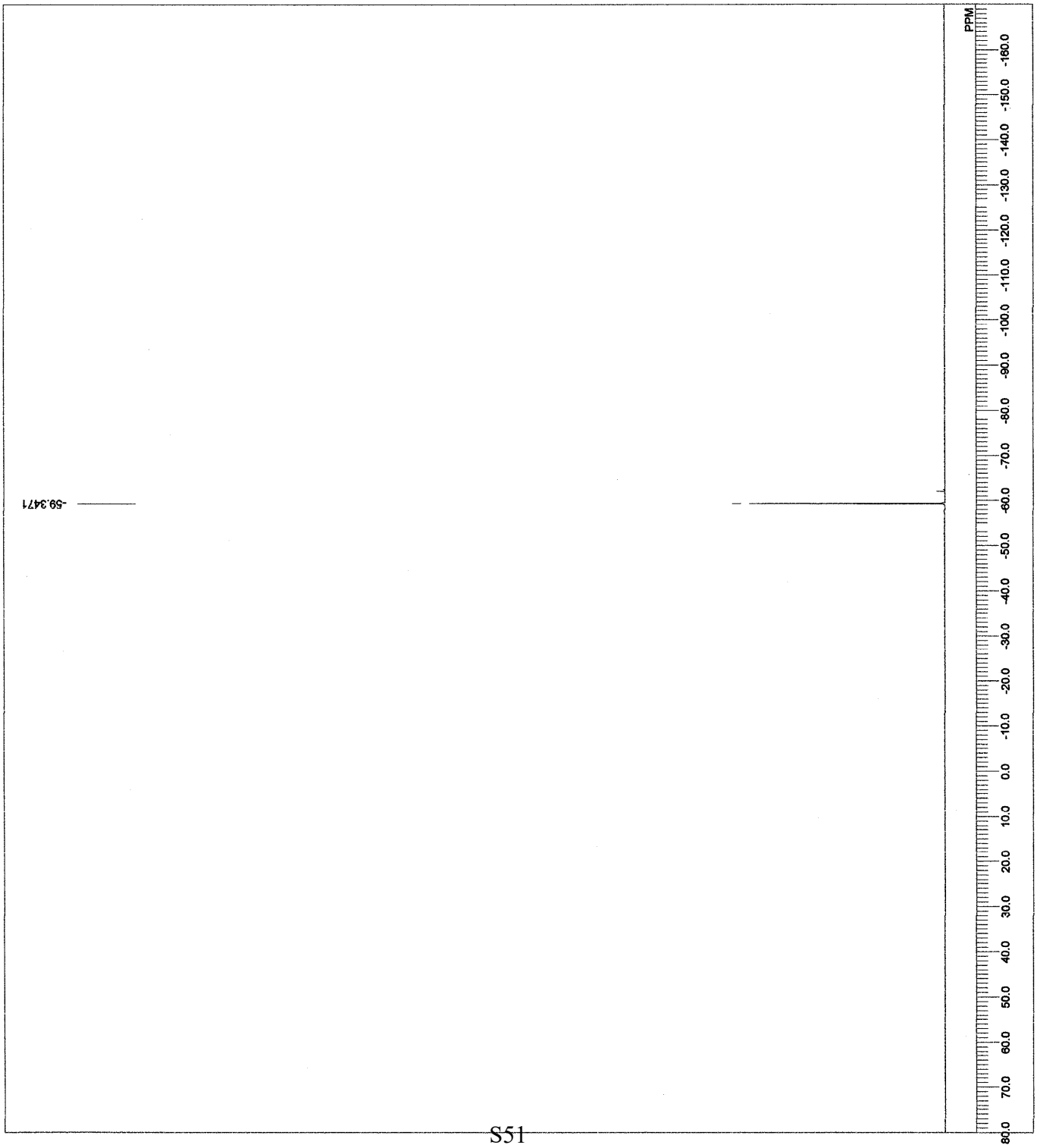
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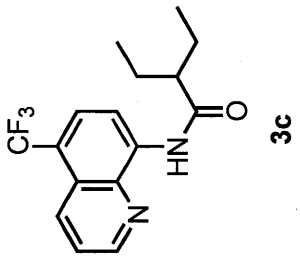
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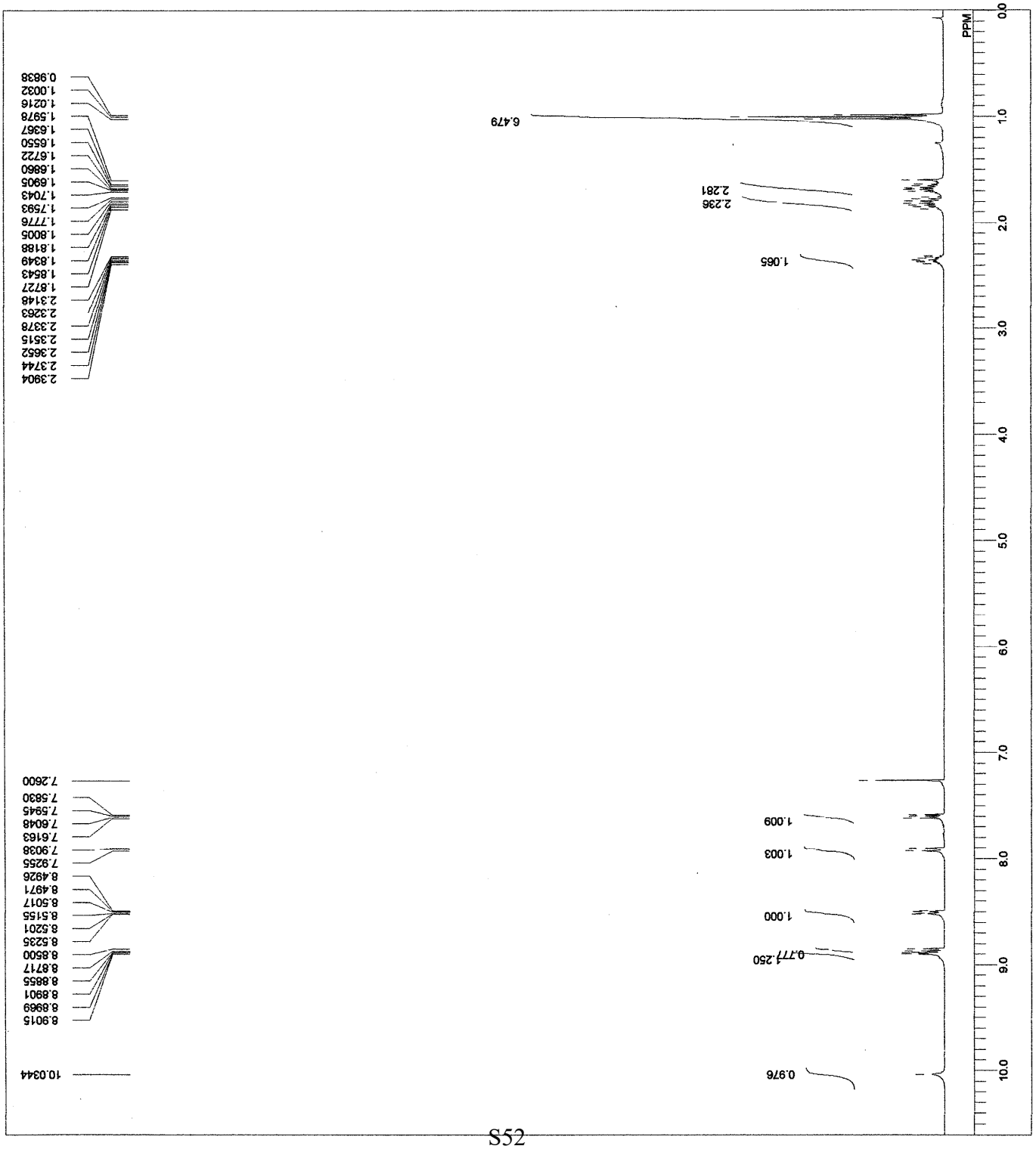
O
N

3c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1.000
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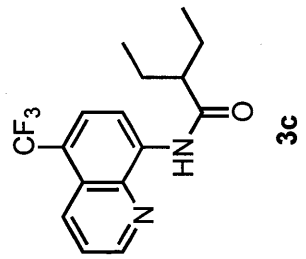
10.0344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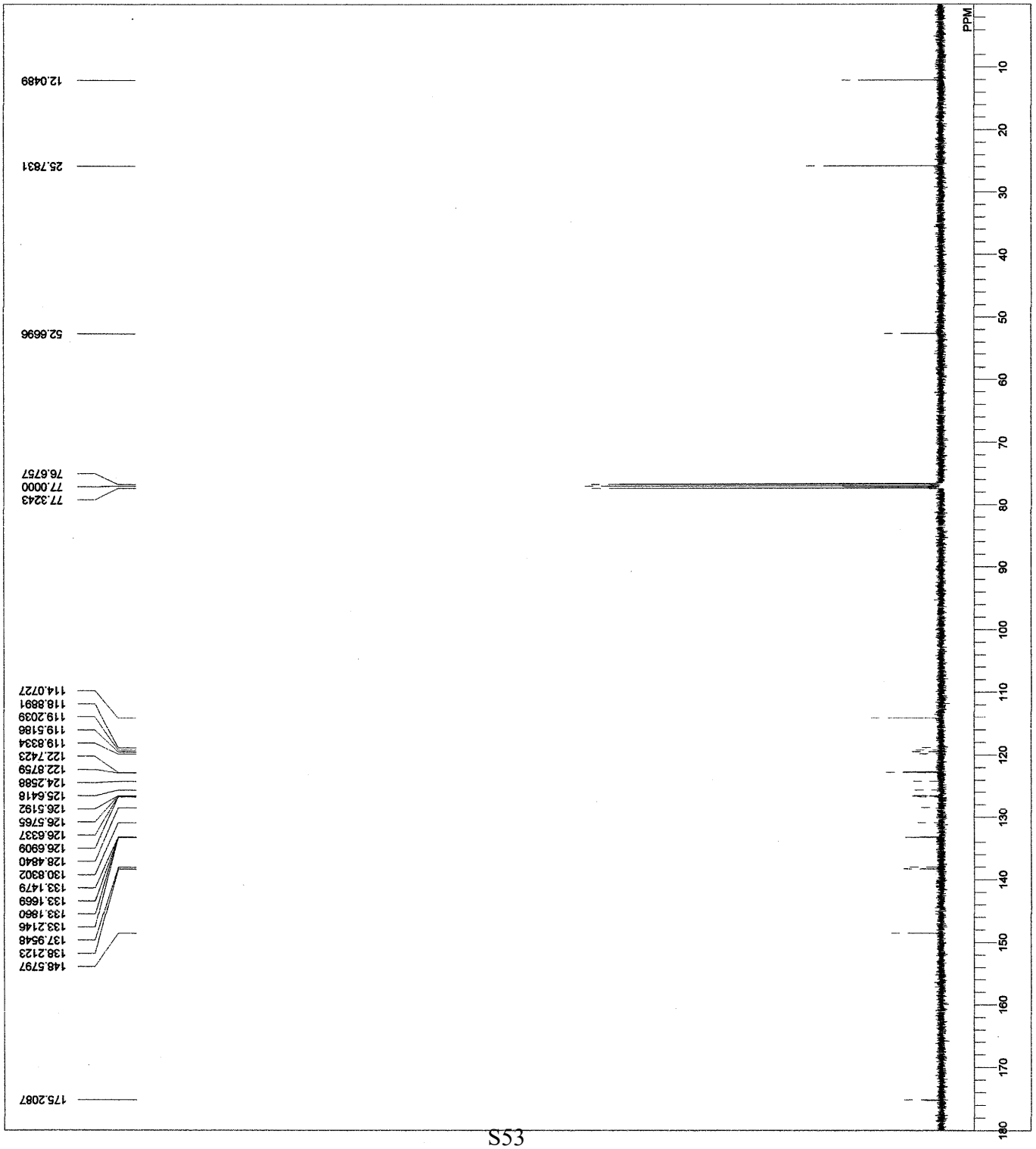
3c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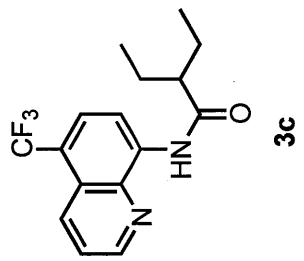
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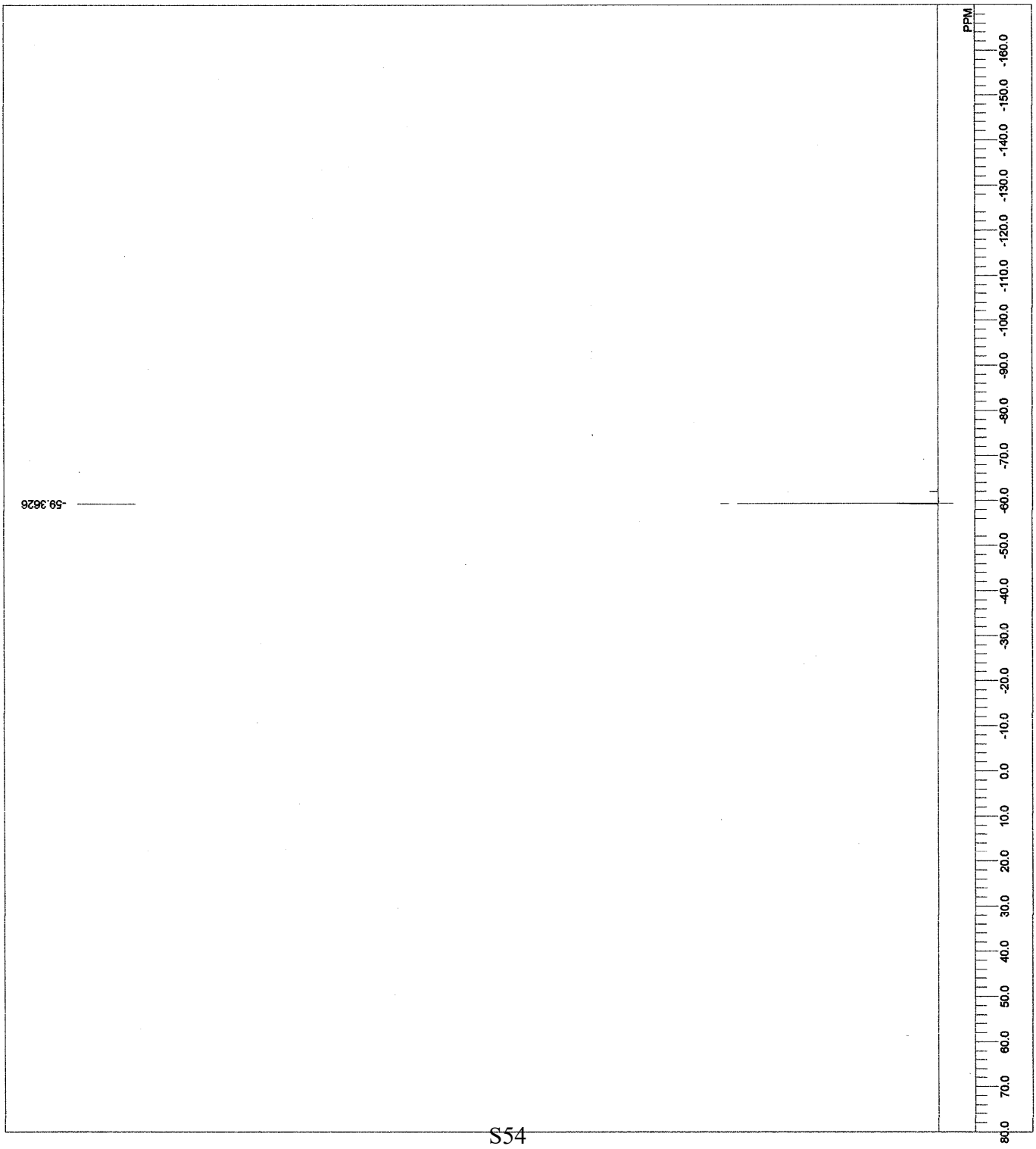
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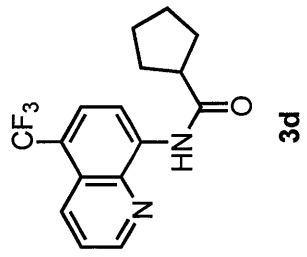
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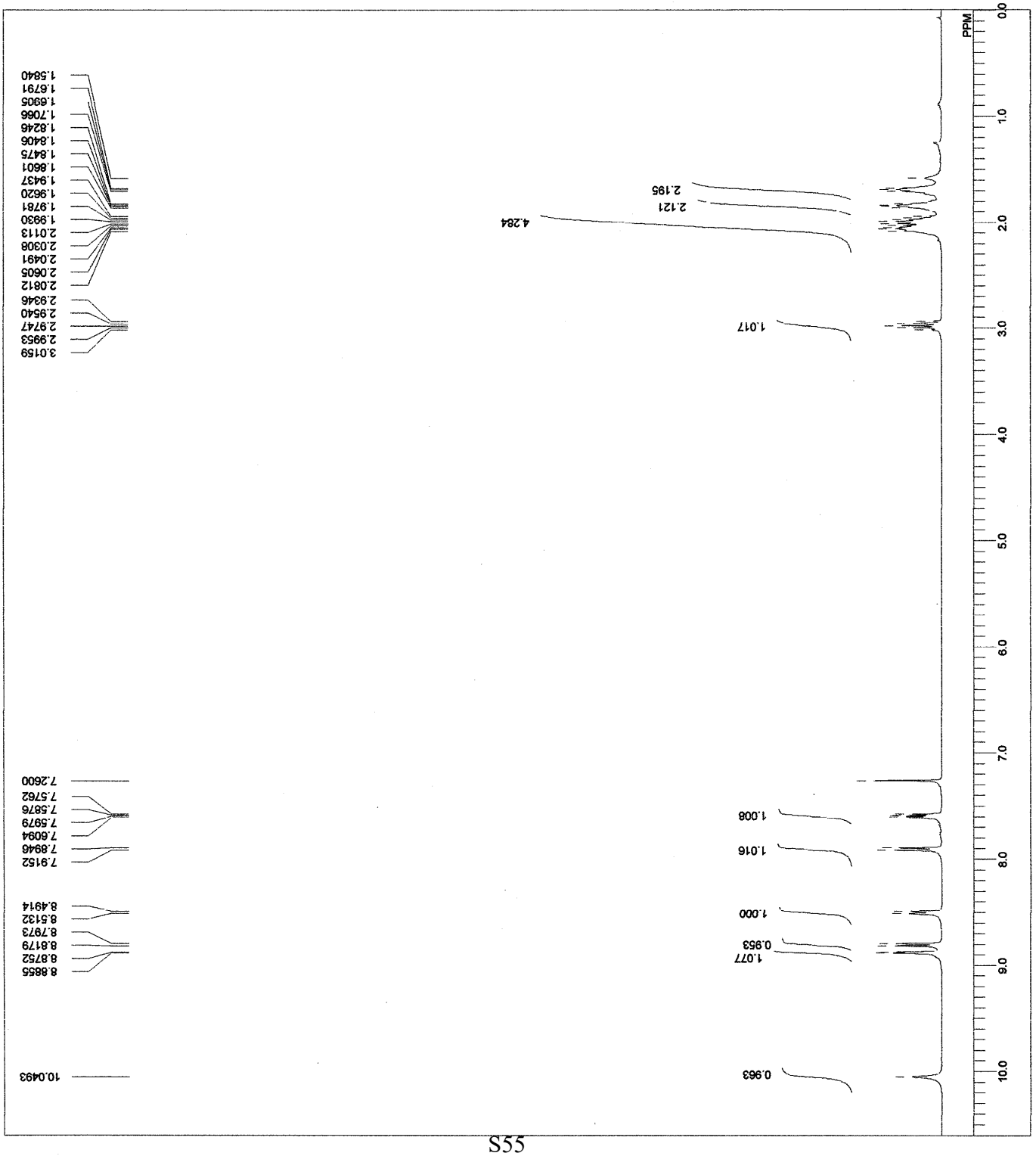
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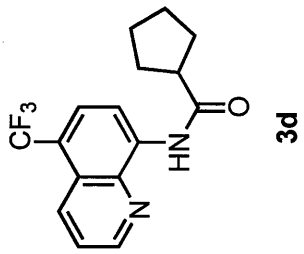
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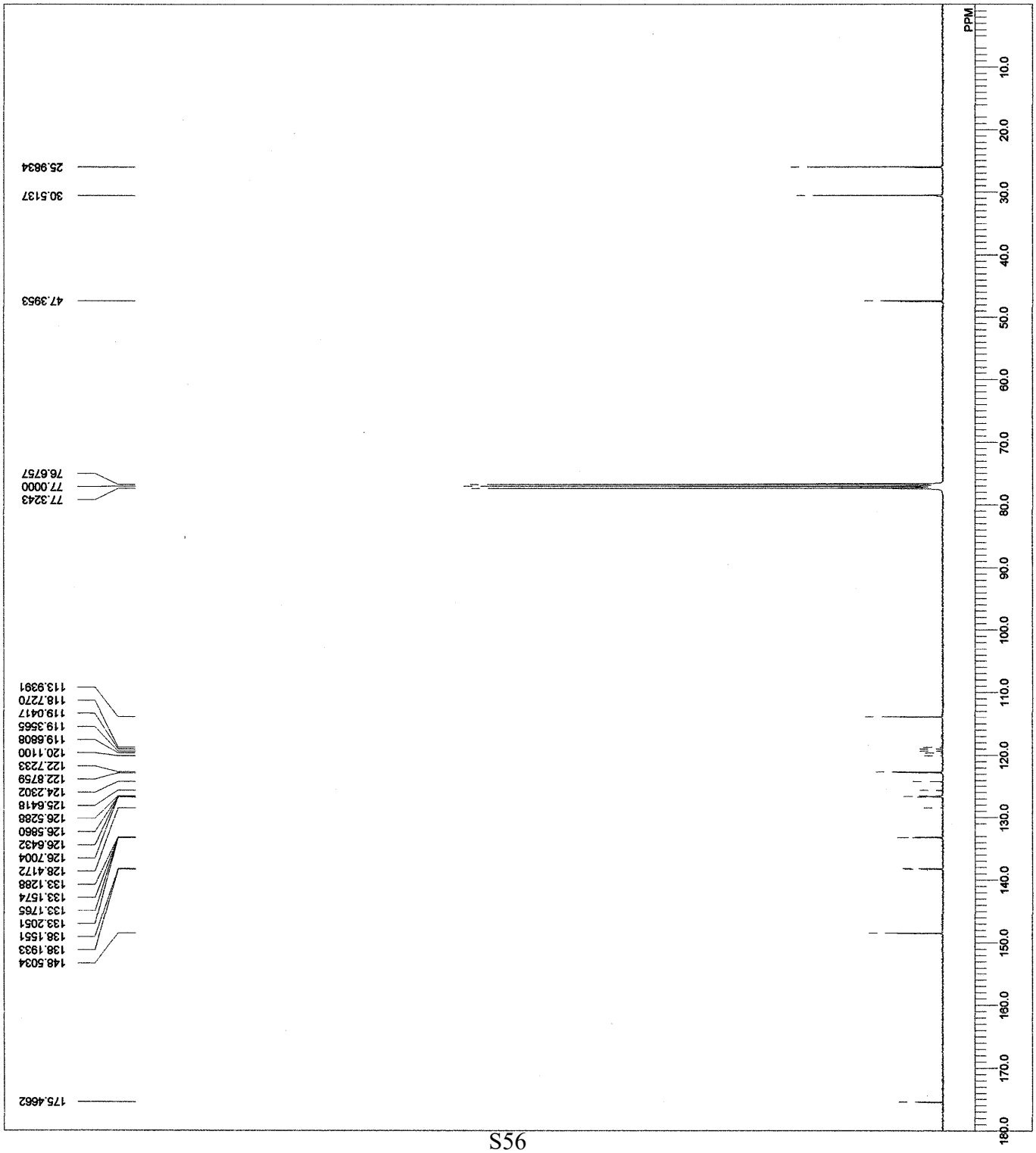
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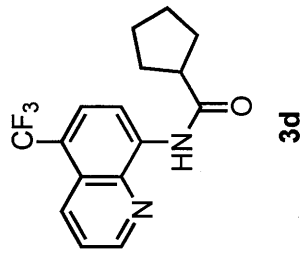
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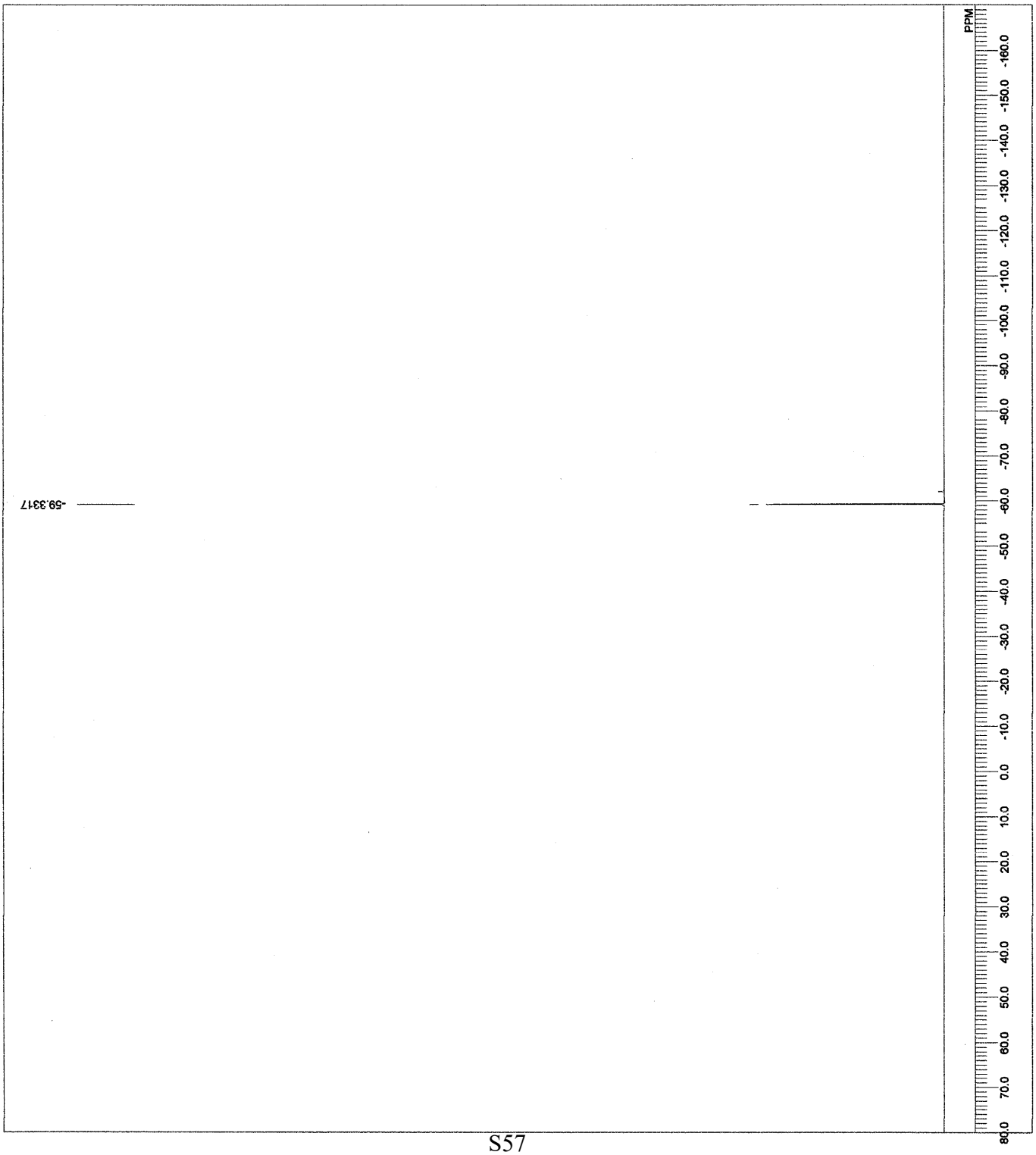
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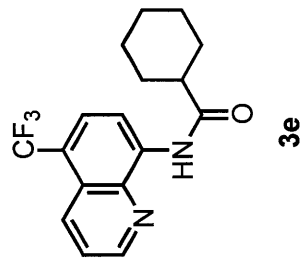
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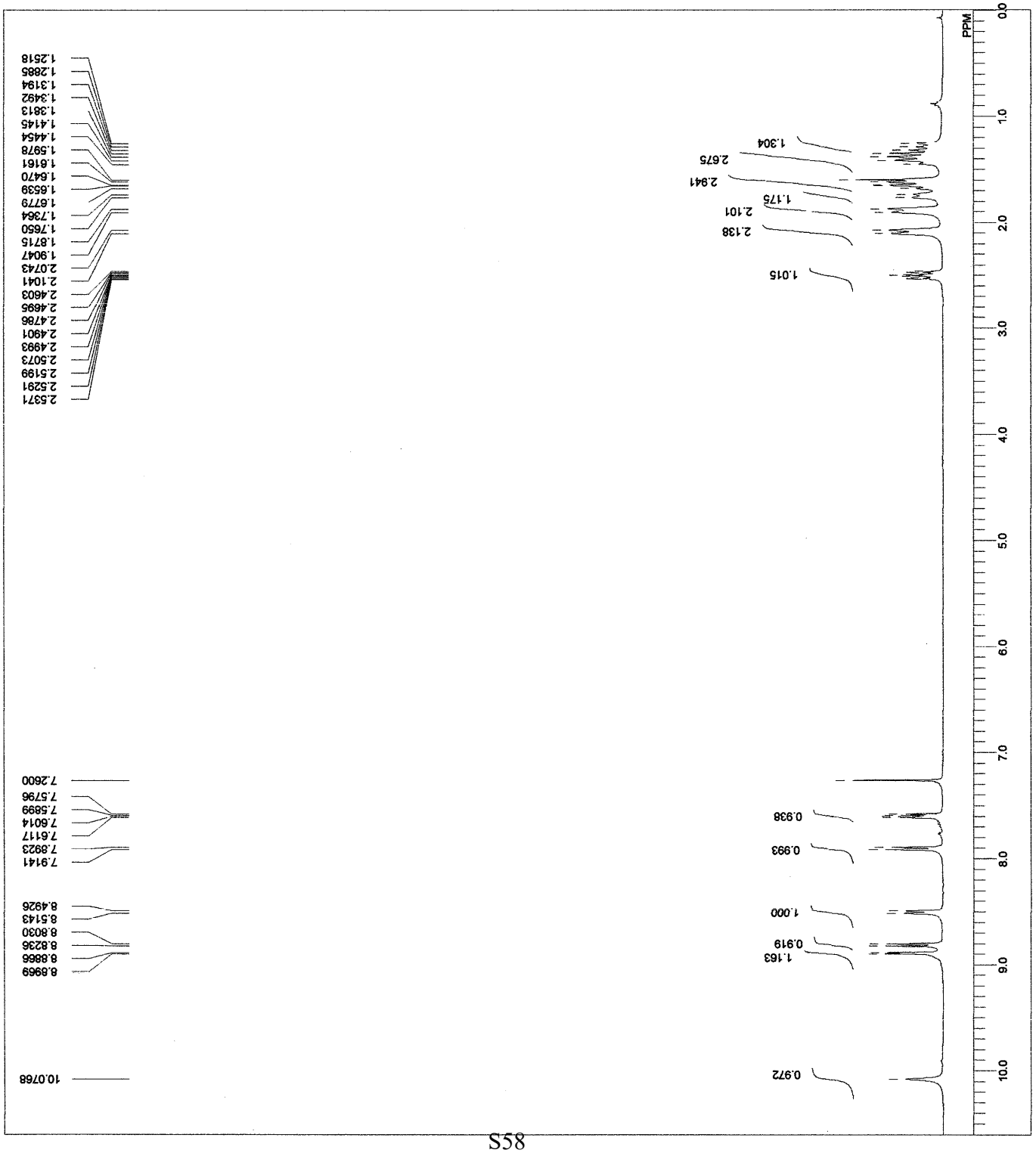
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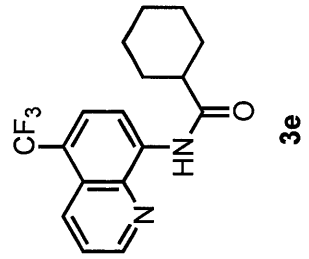

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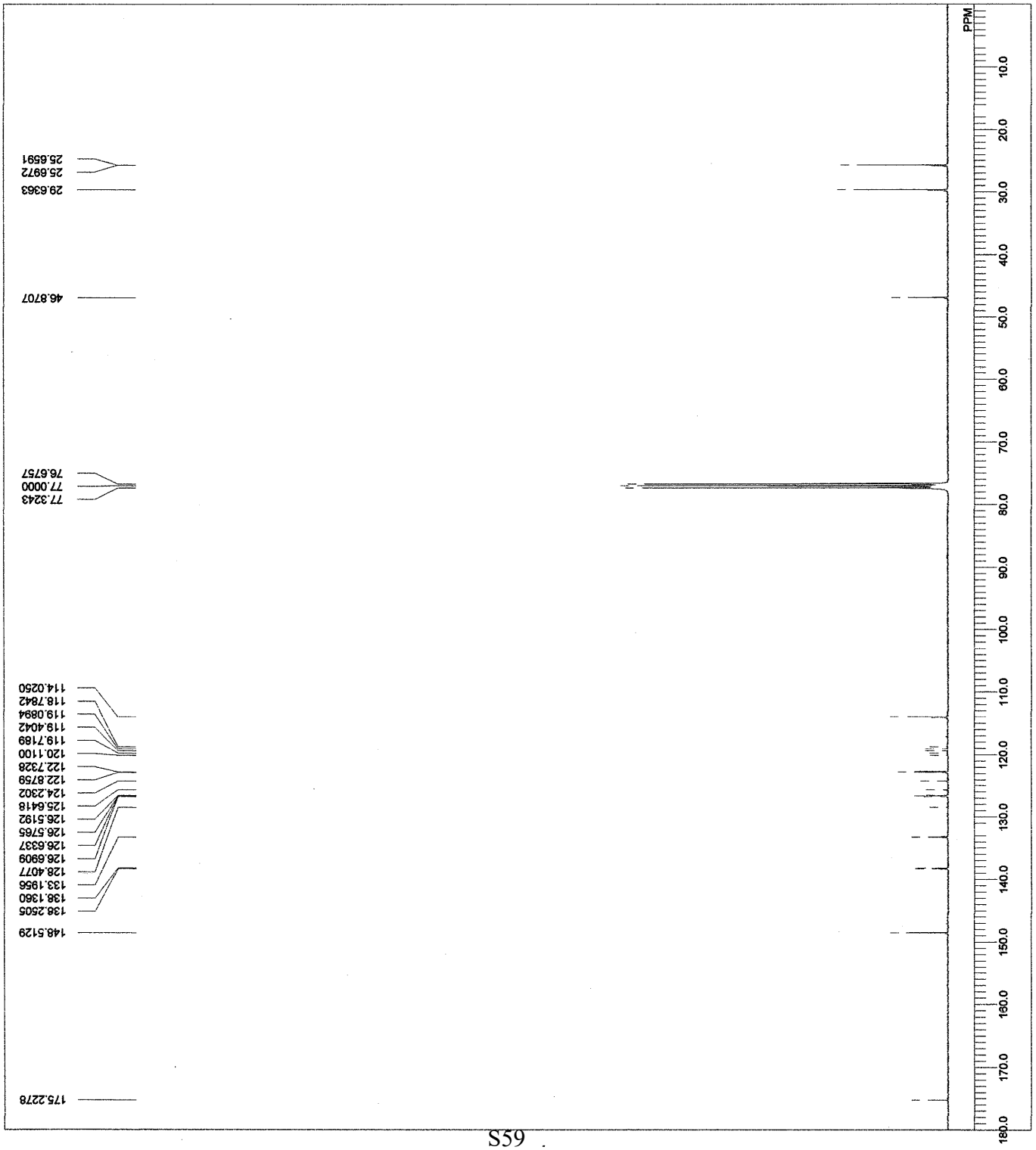
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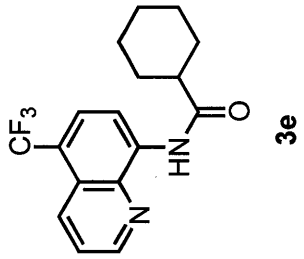
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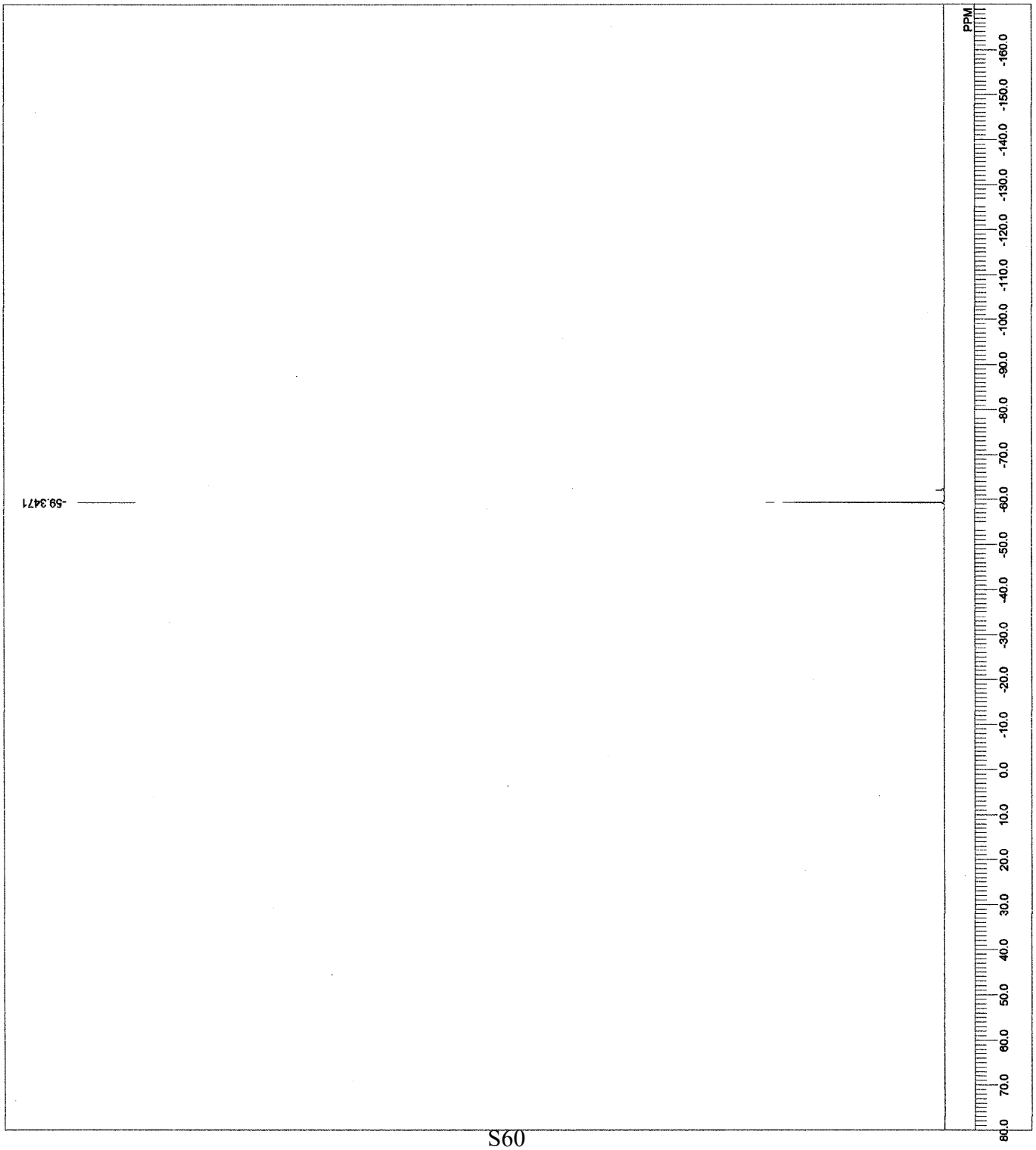
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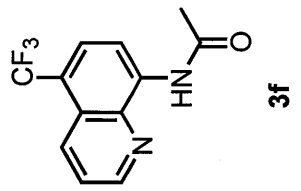
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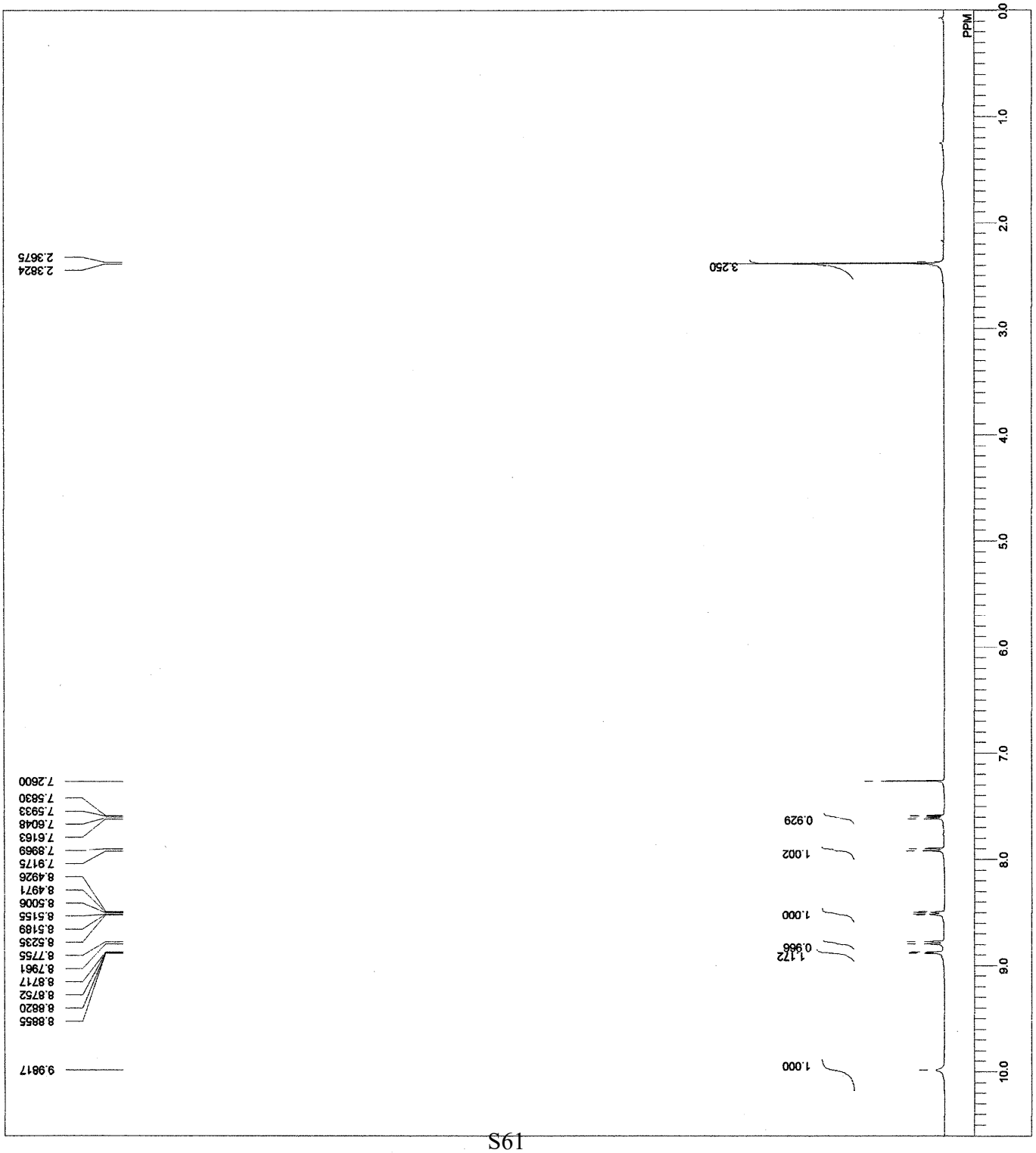
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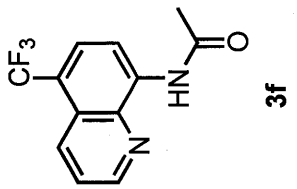
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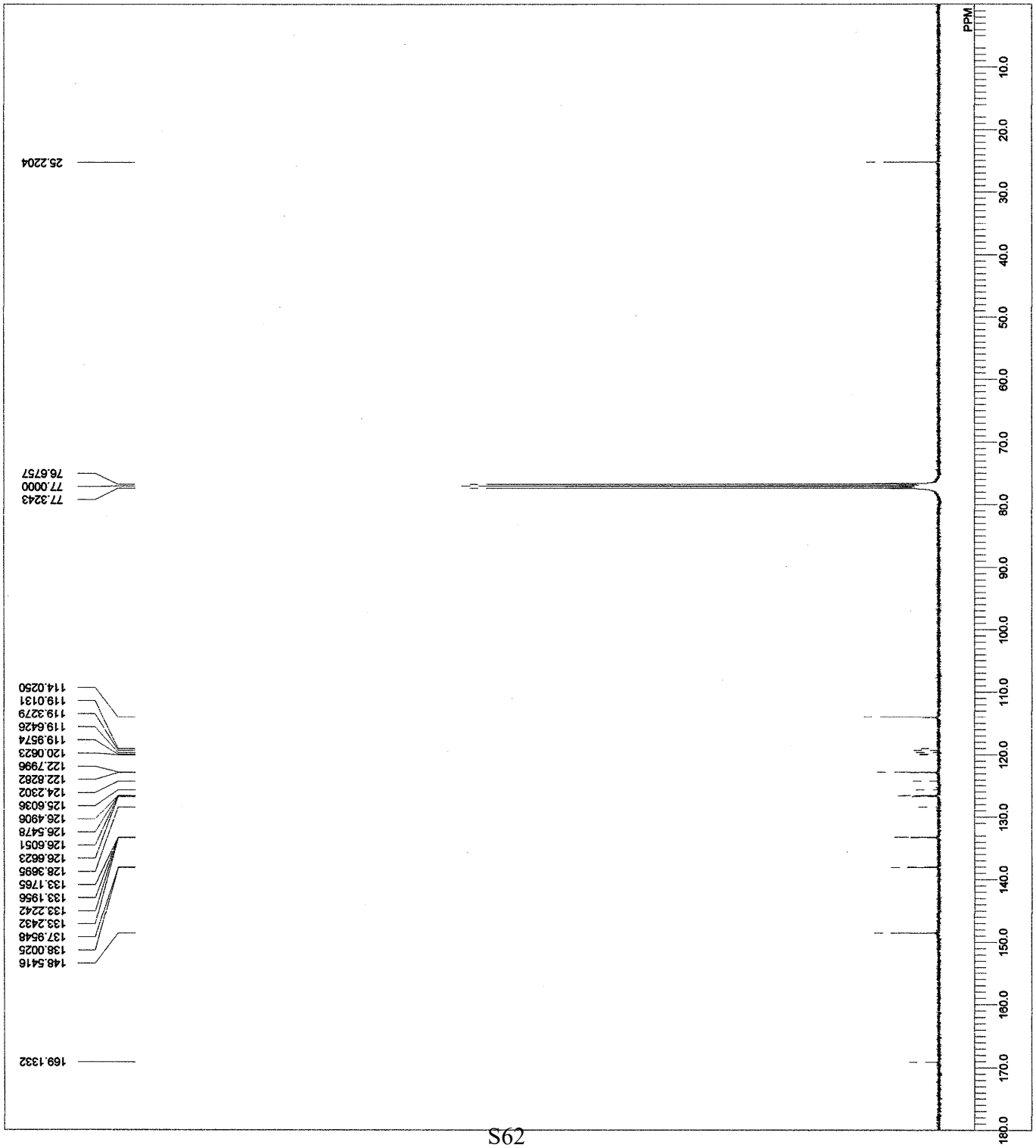
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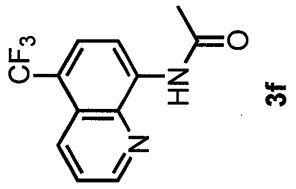

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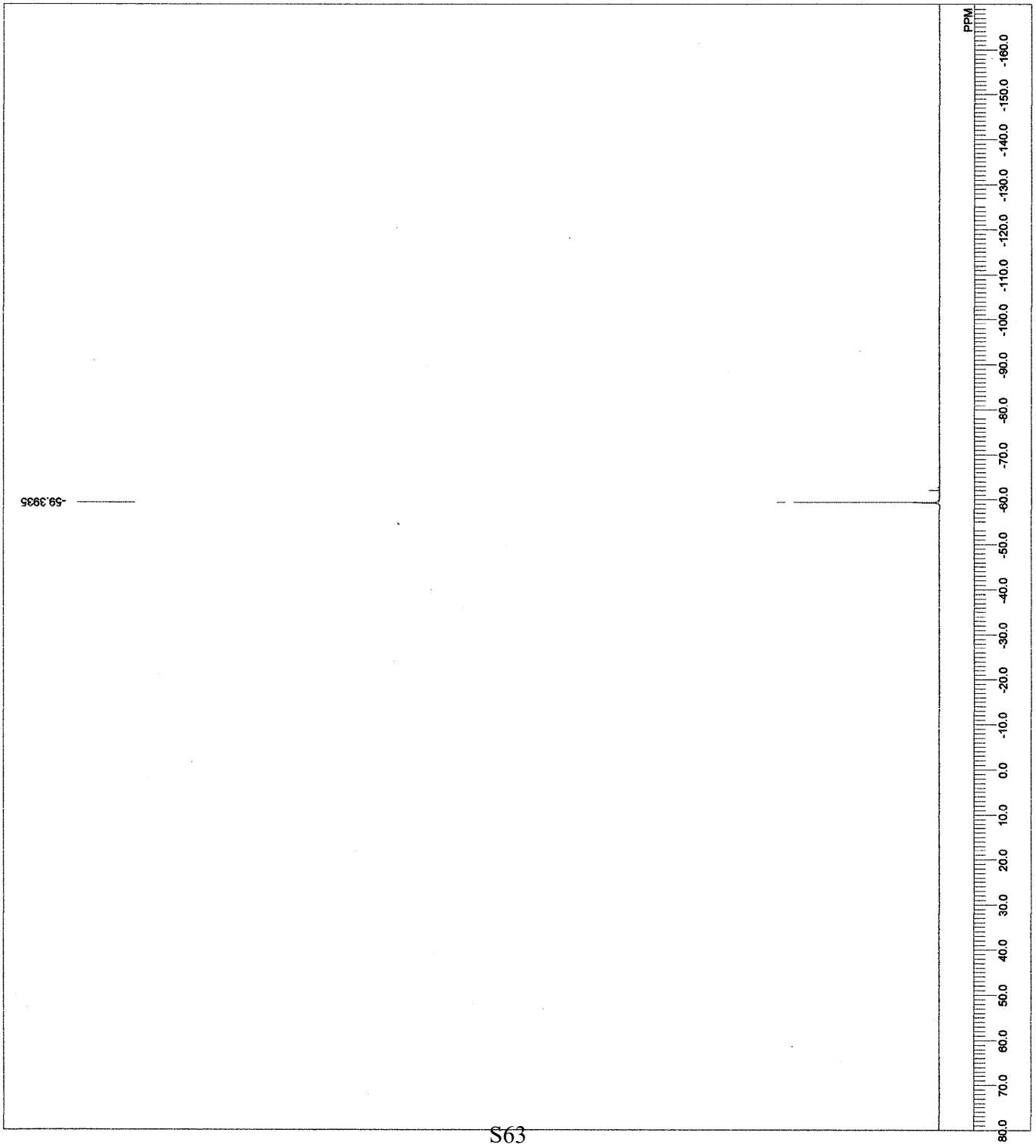
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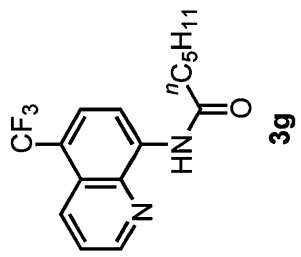
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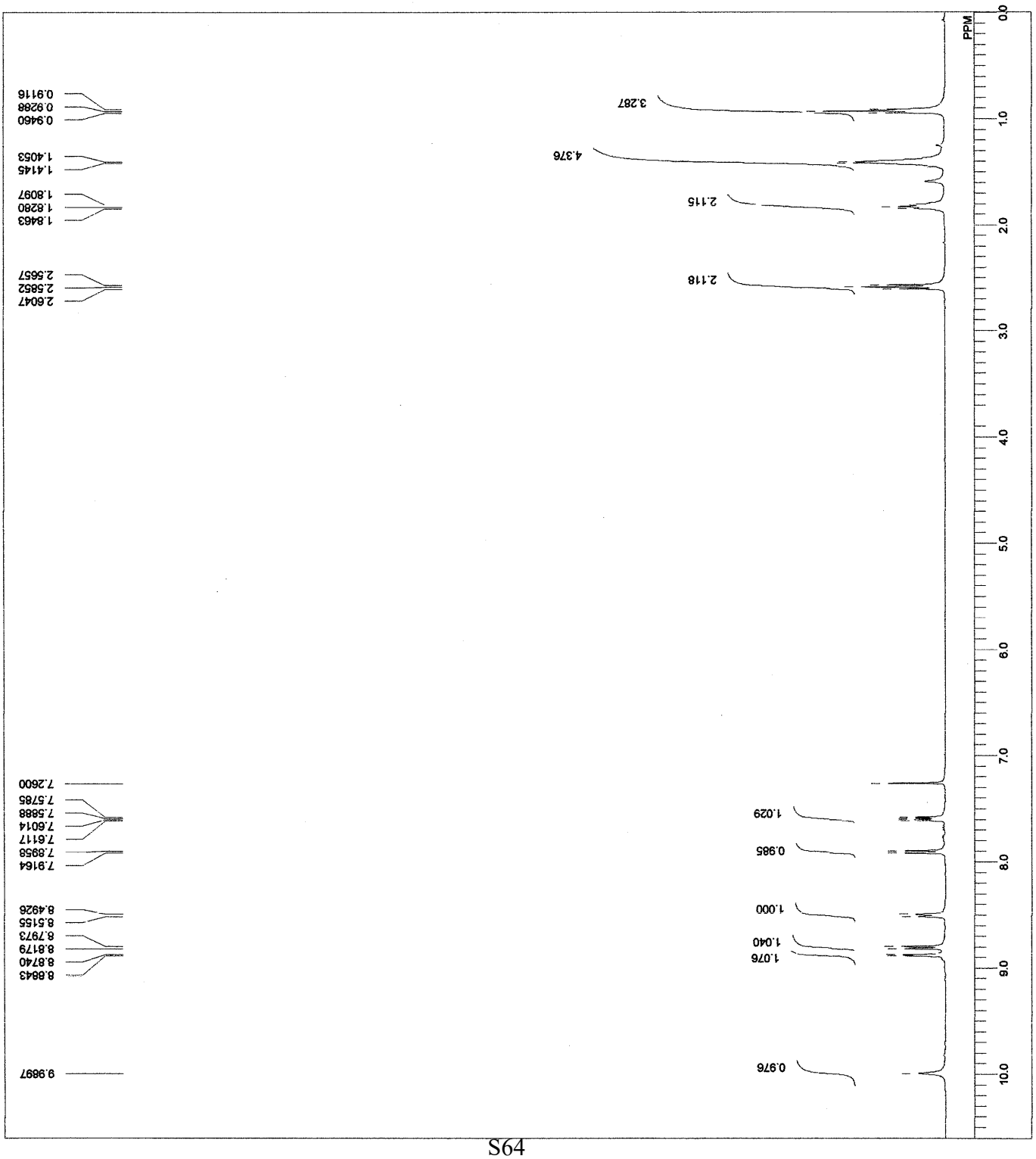
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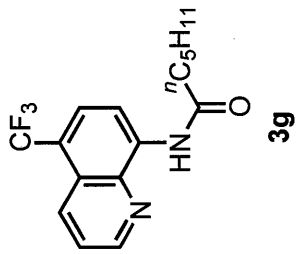
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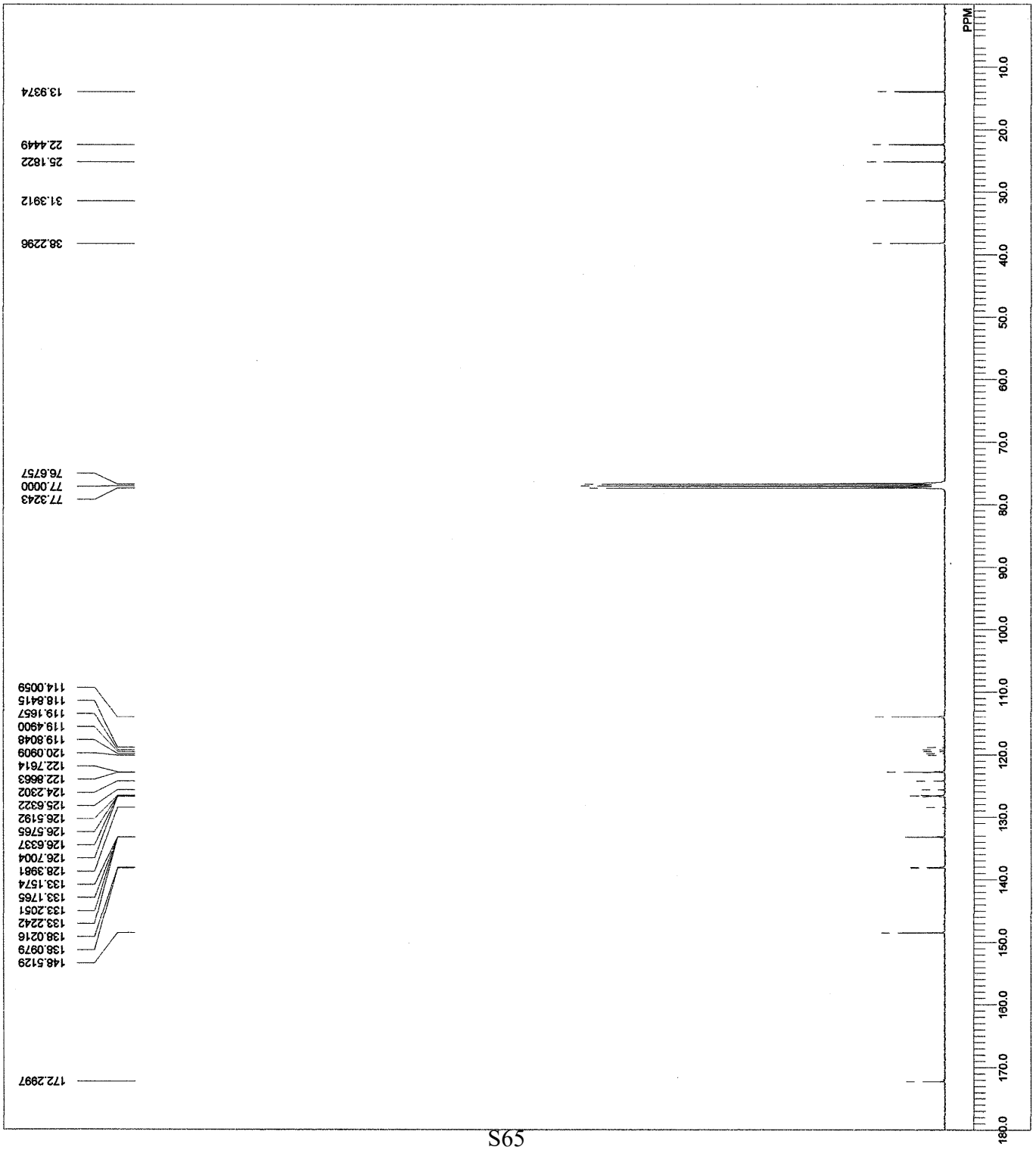
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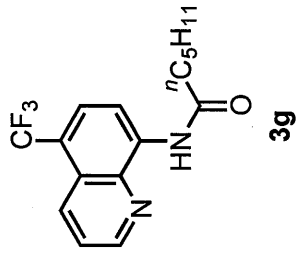
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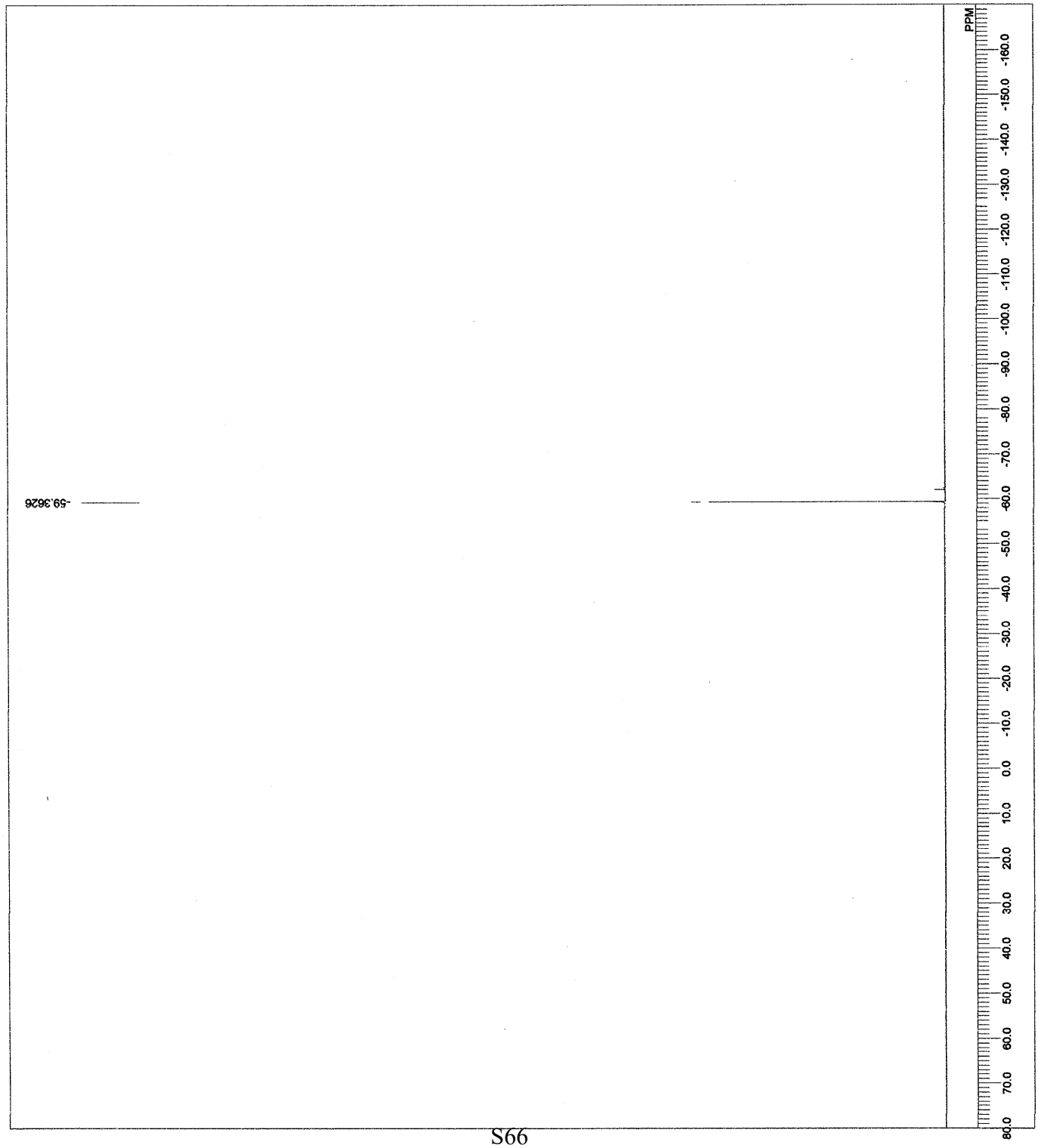
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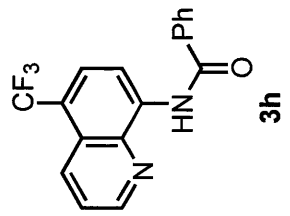
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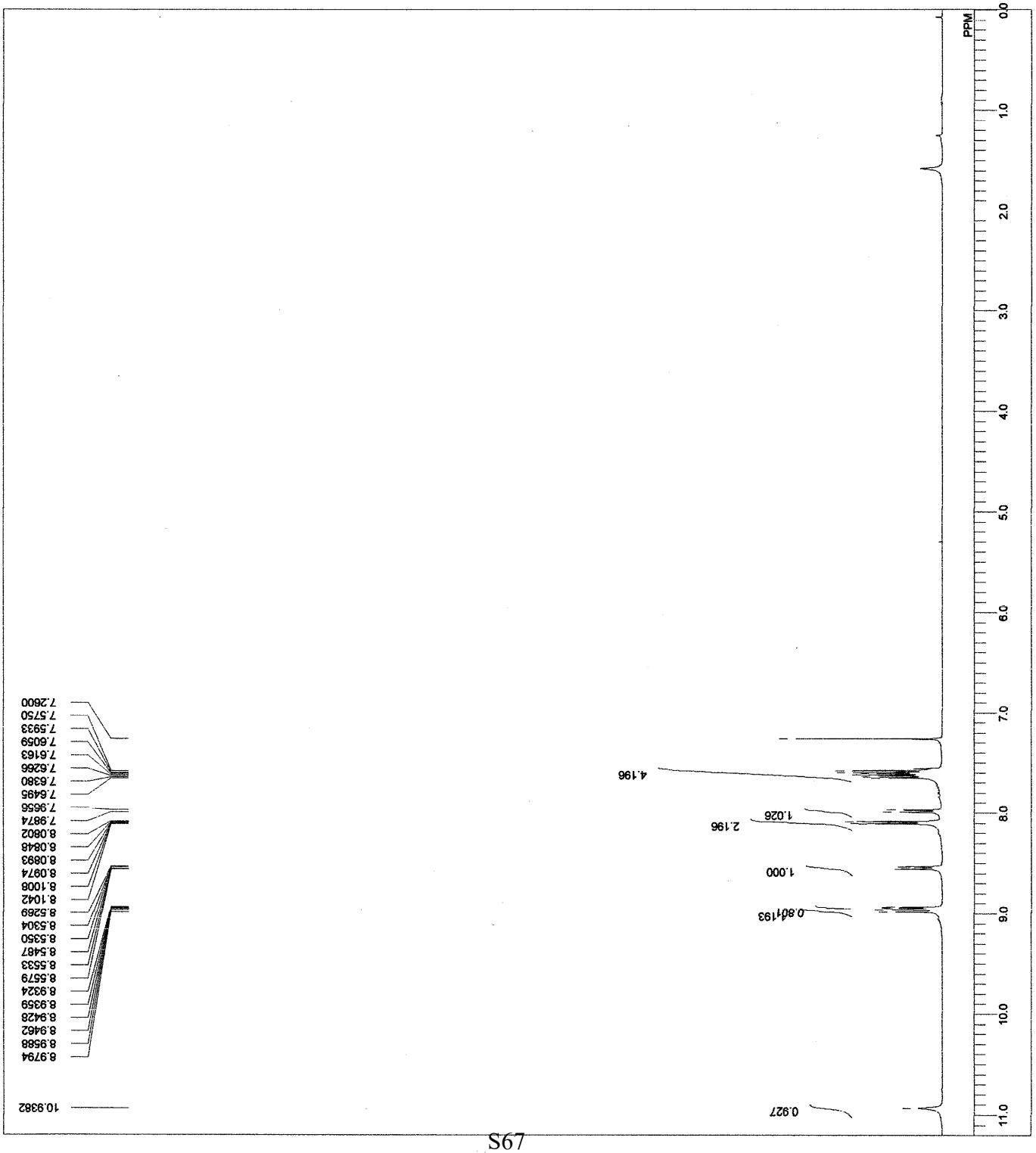
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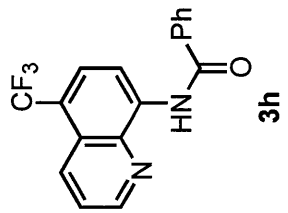
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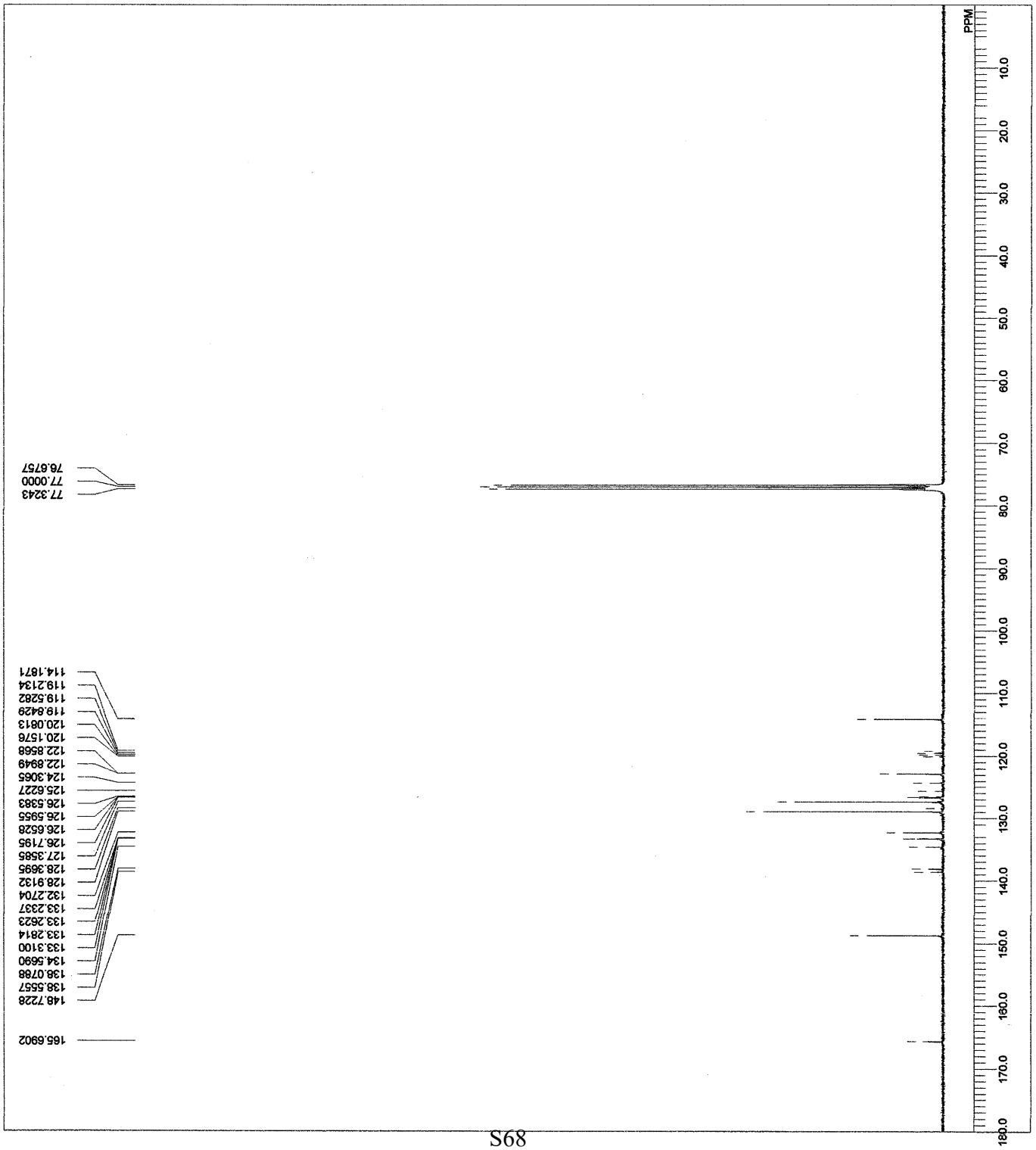
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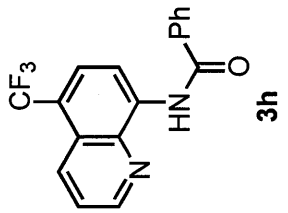
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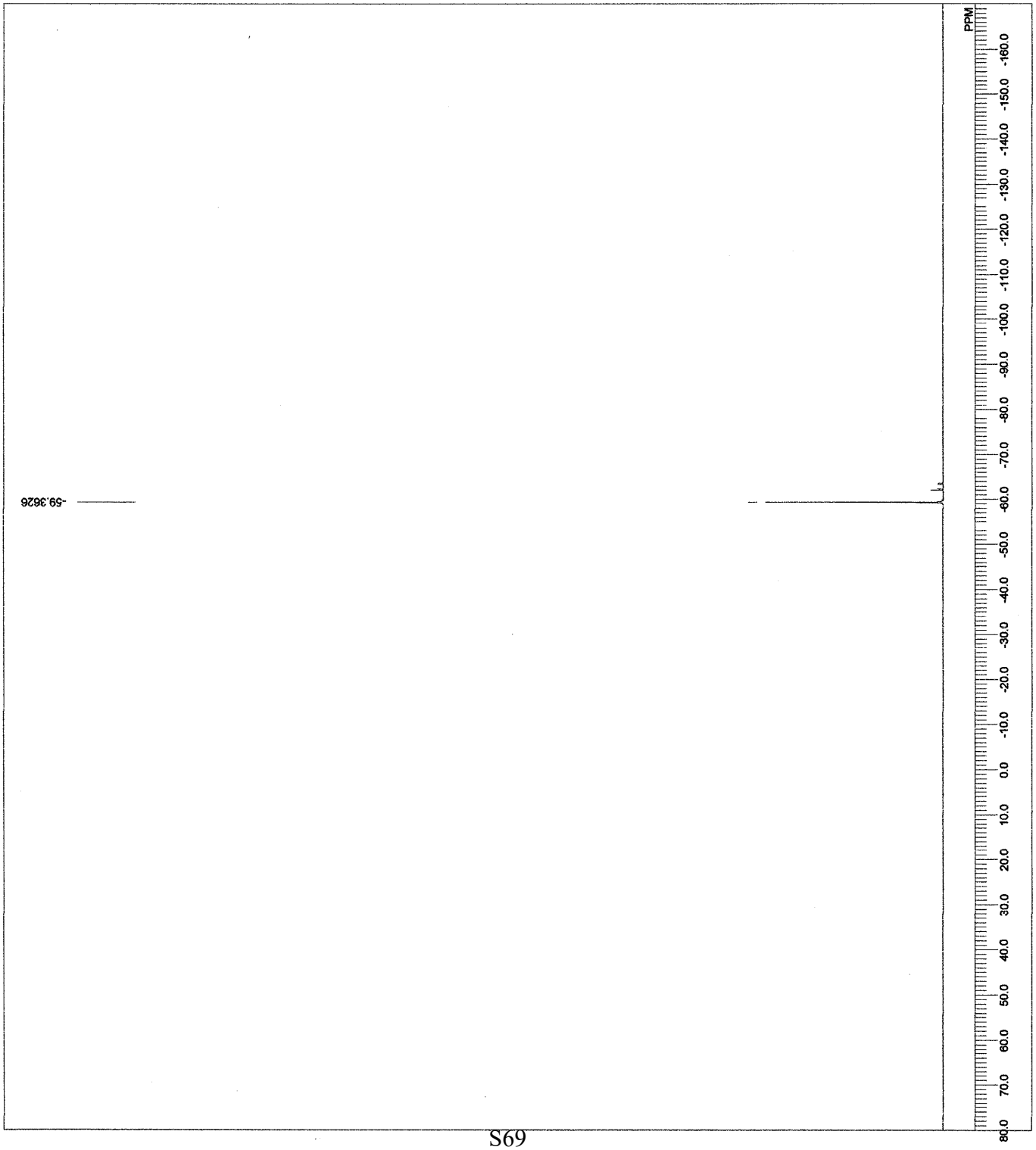
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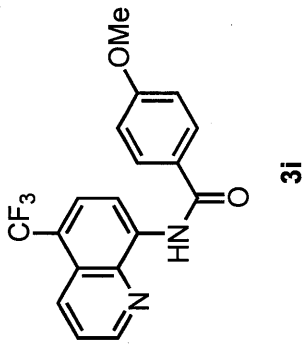
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N

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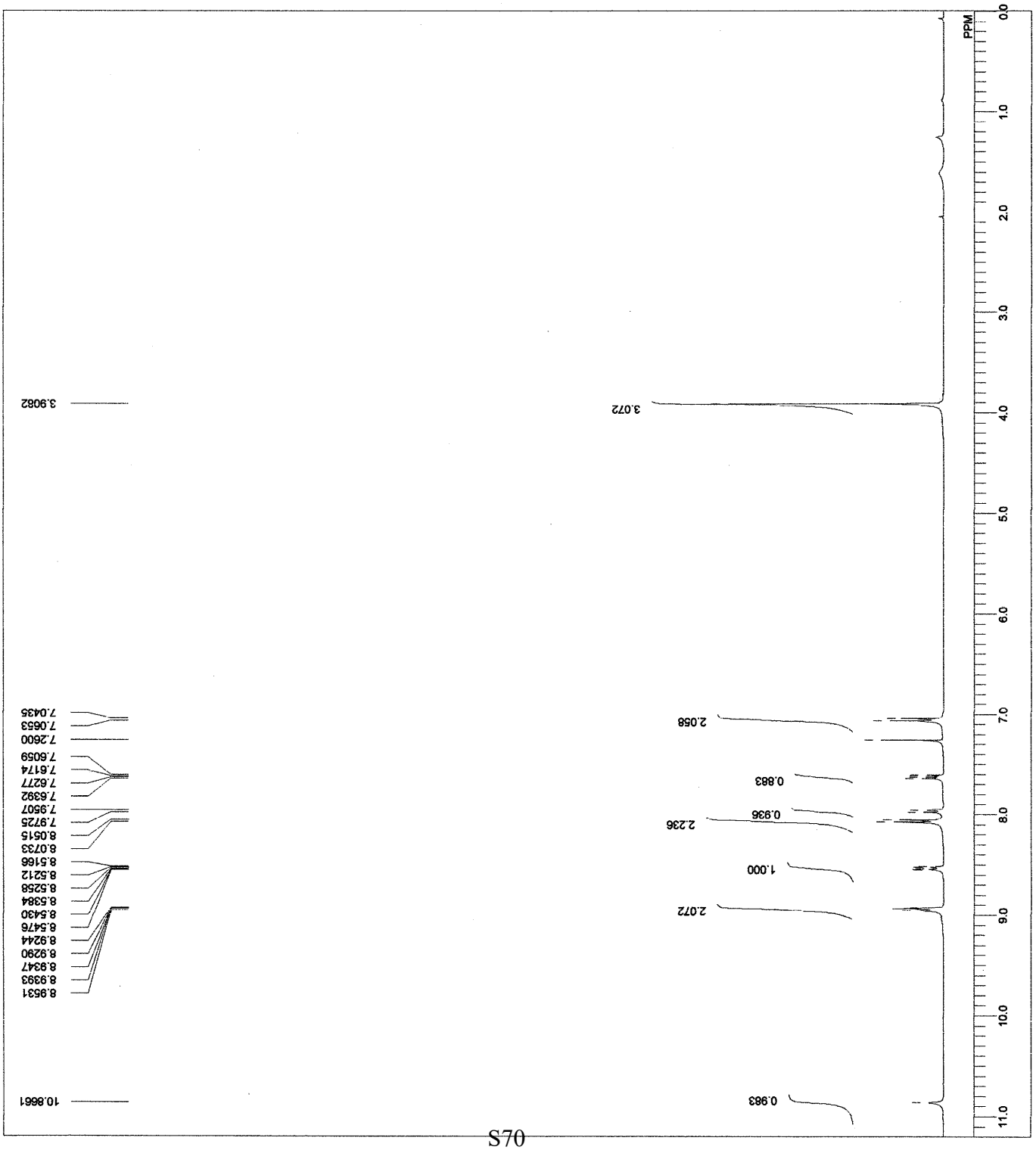
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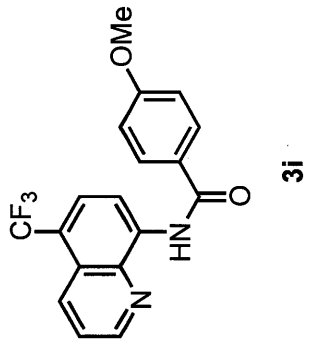
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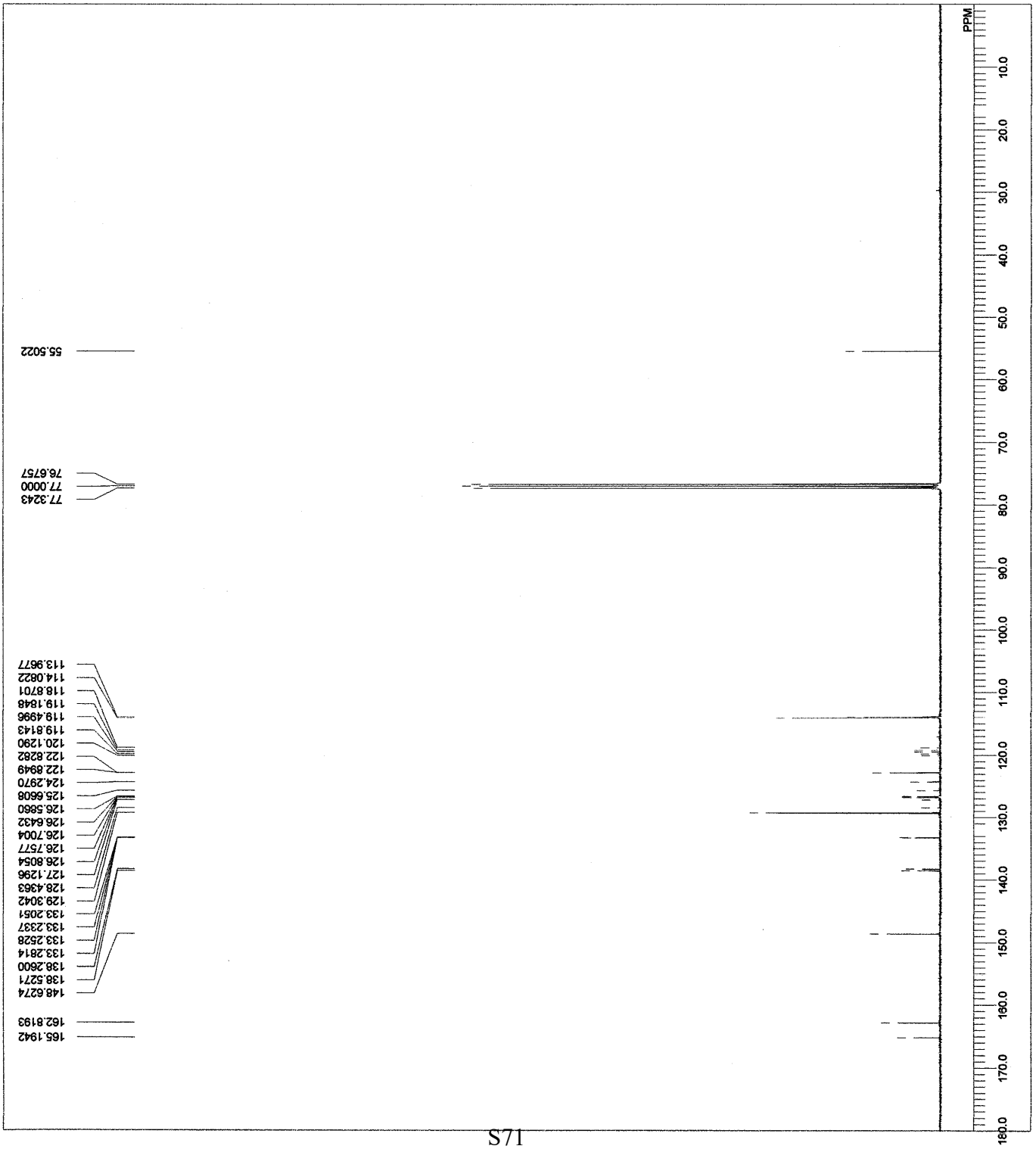
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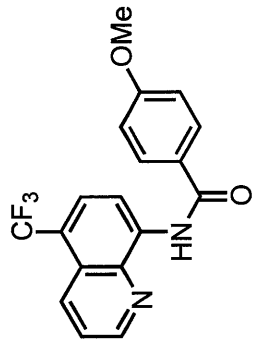
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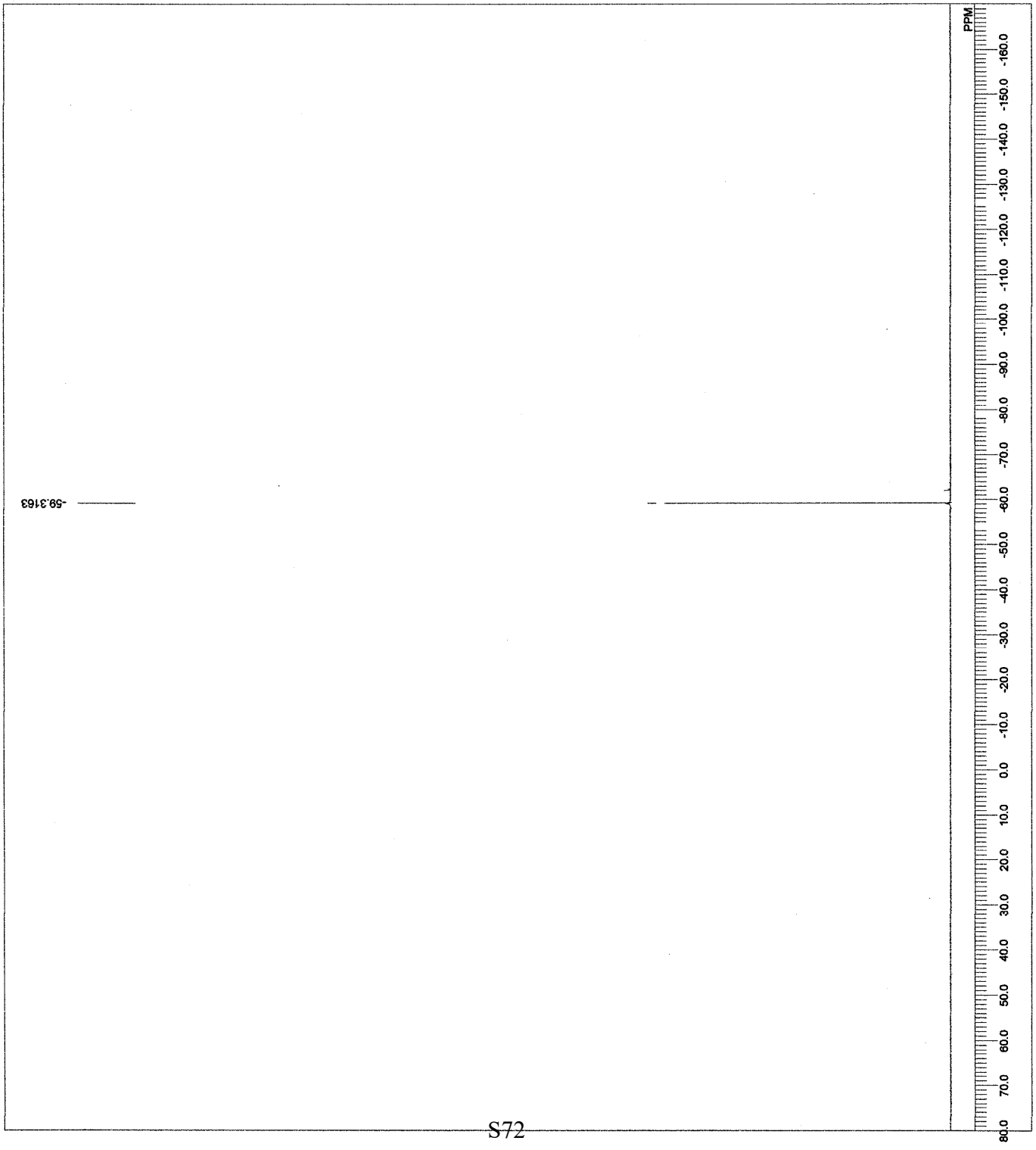
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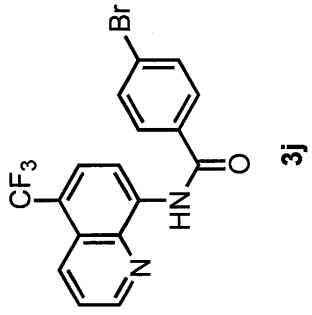
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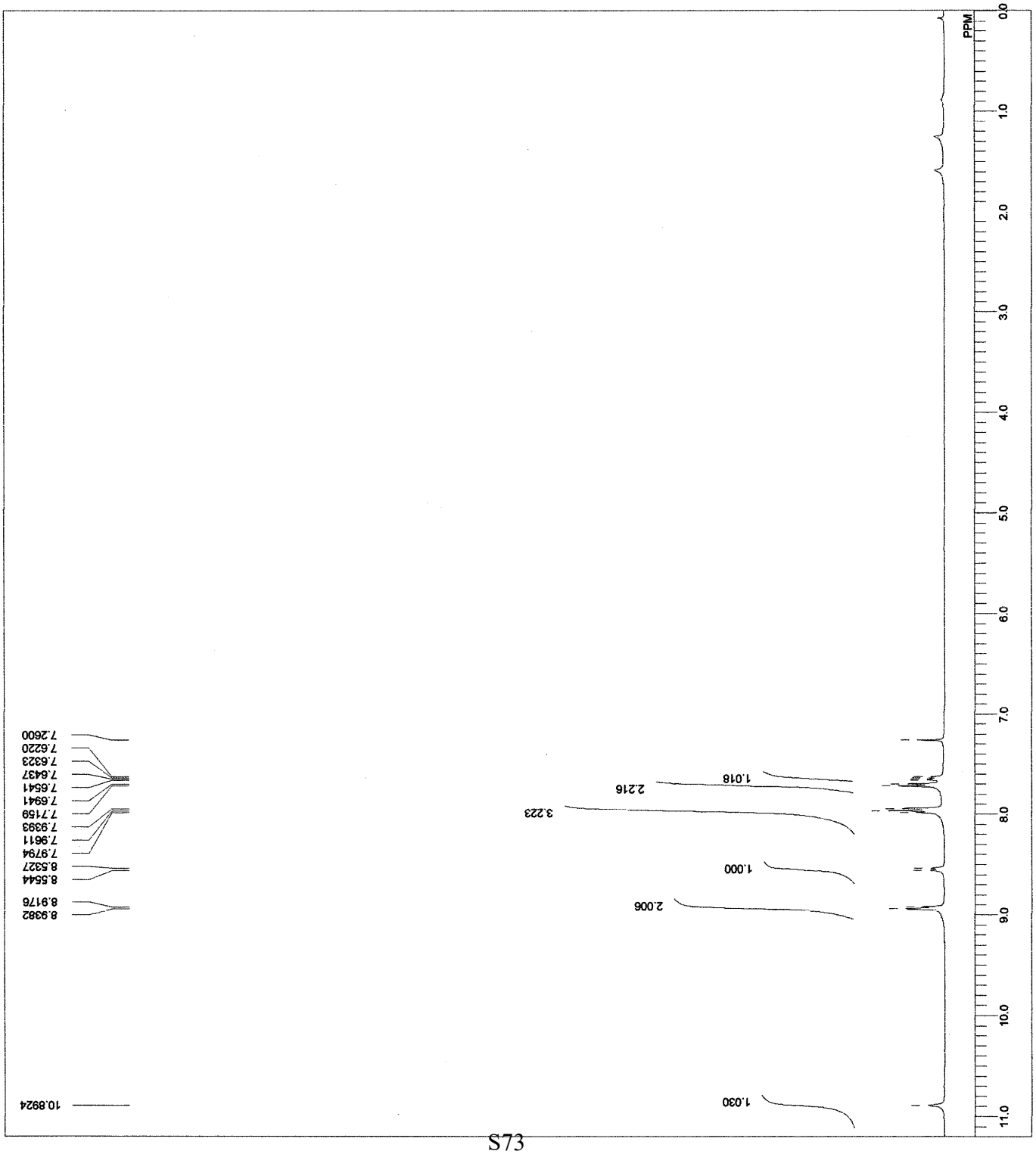
CF3

3j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1.000
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2.216
1.018
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8.9176
8.5544
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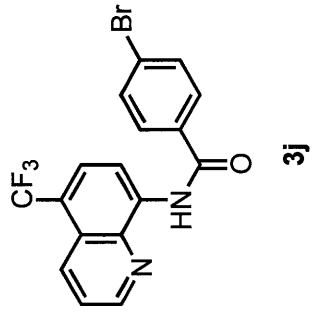
7.2600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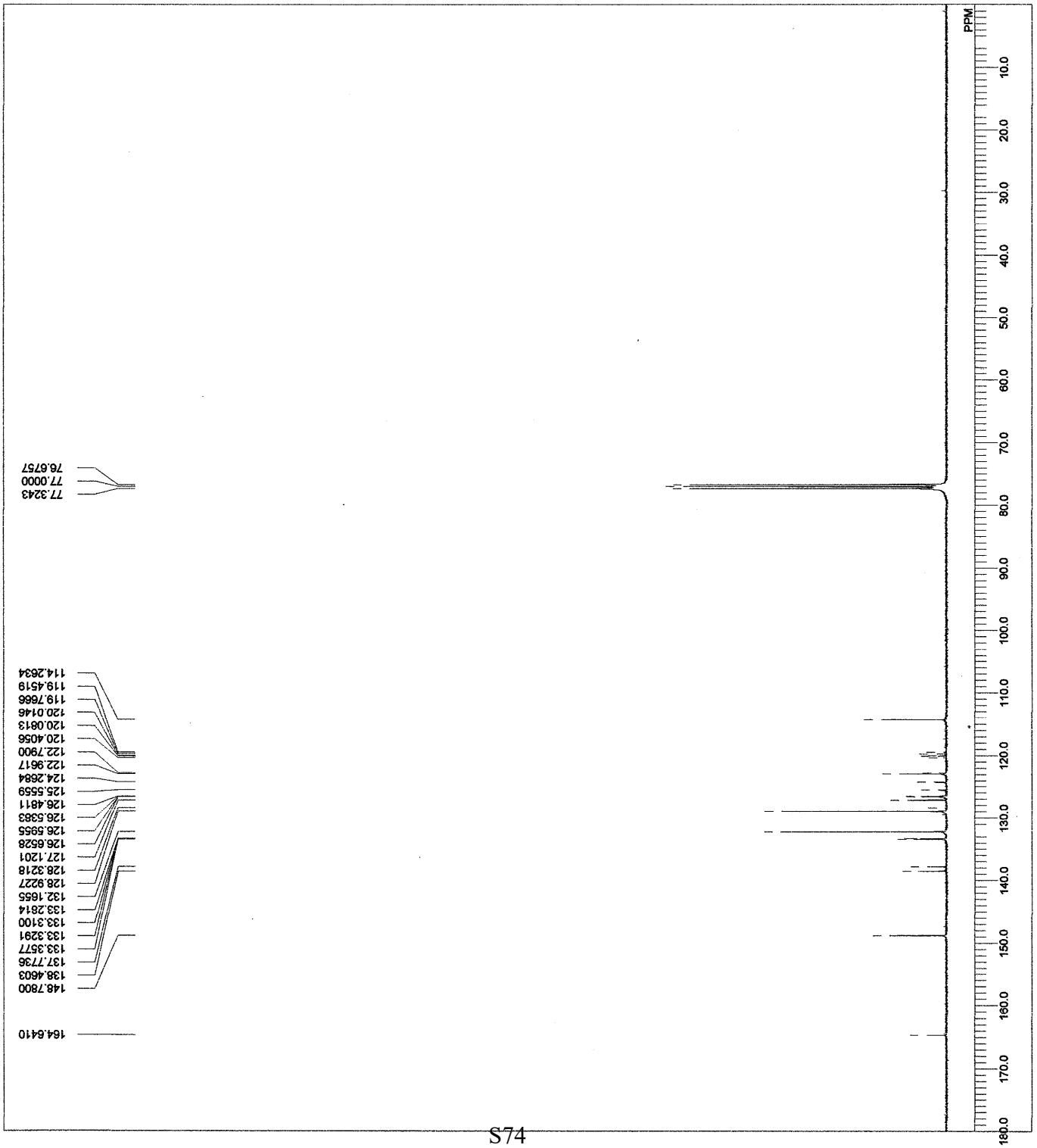
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133.3577
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50.0
60.0
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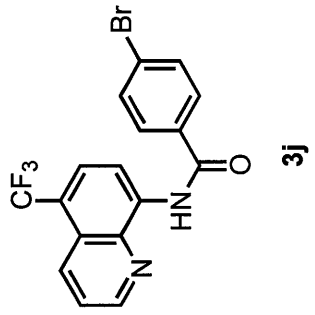
180.0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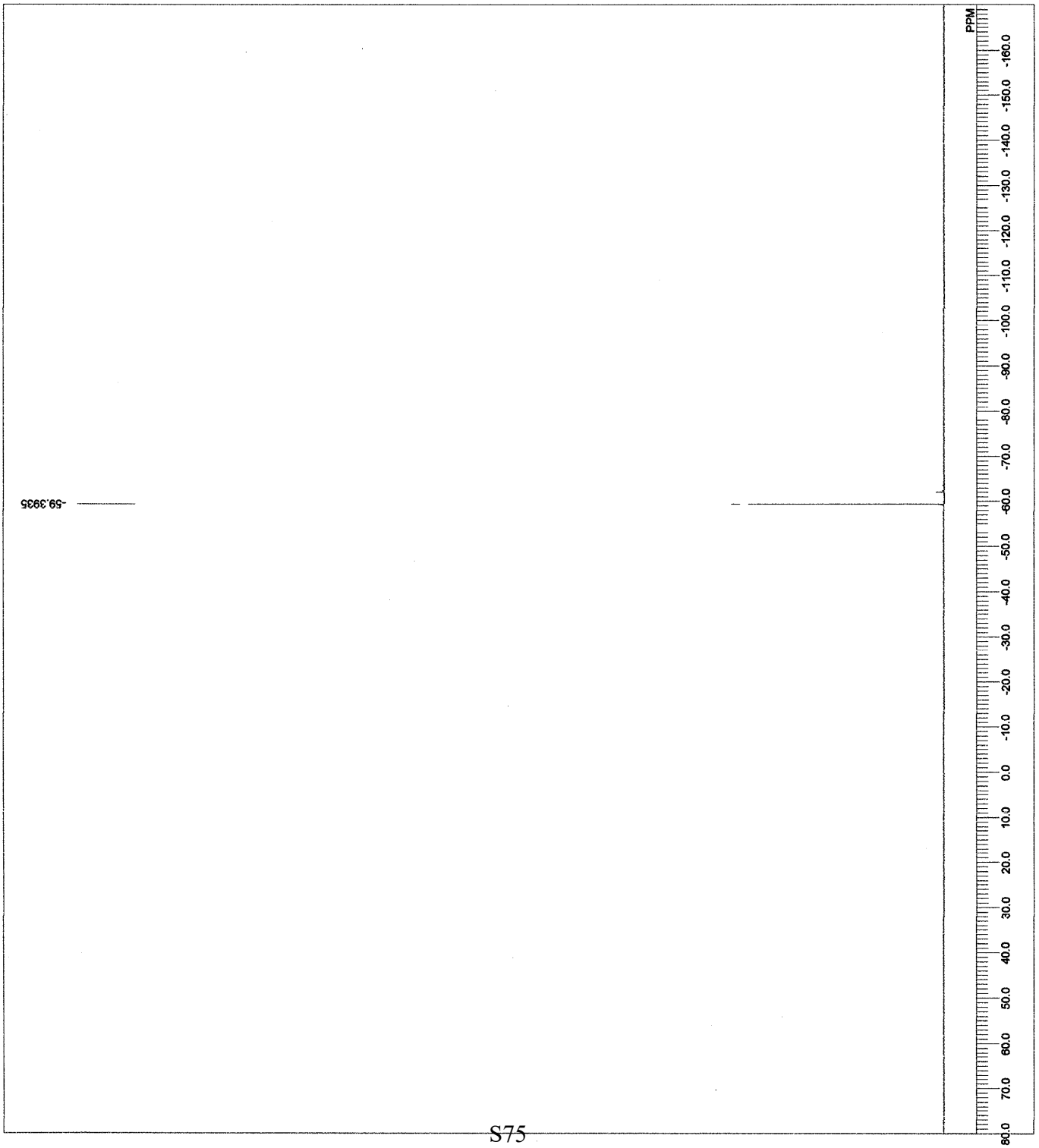
3j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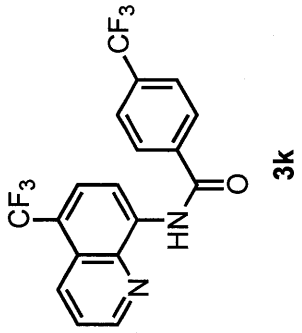

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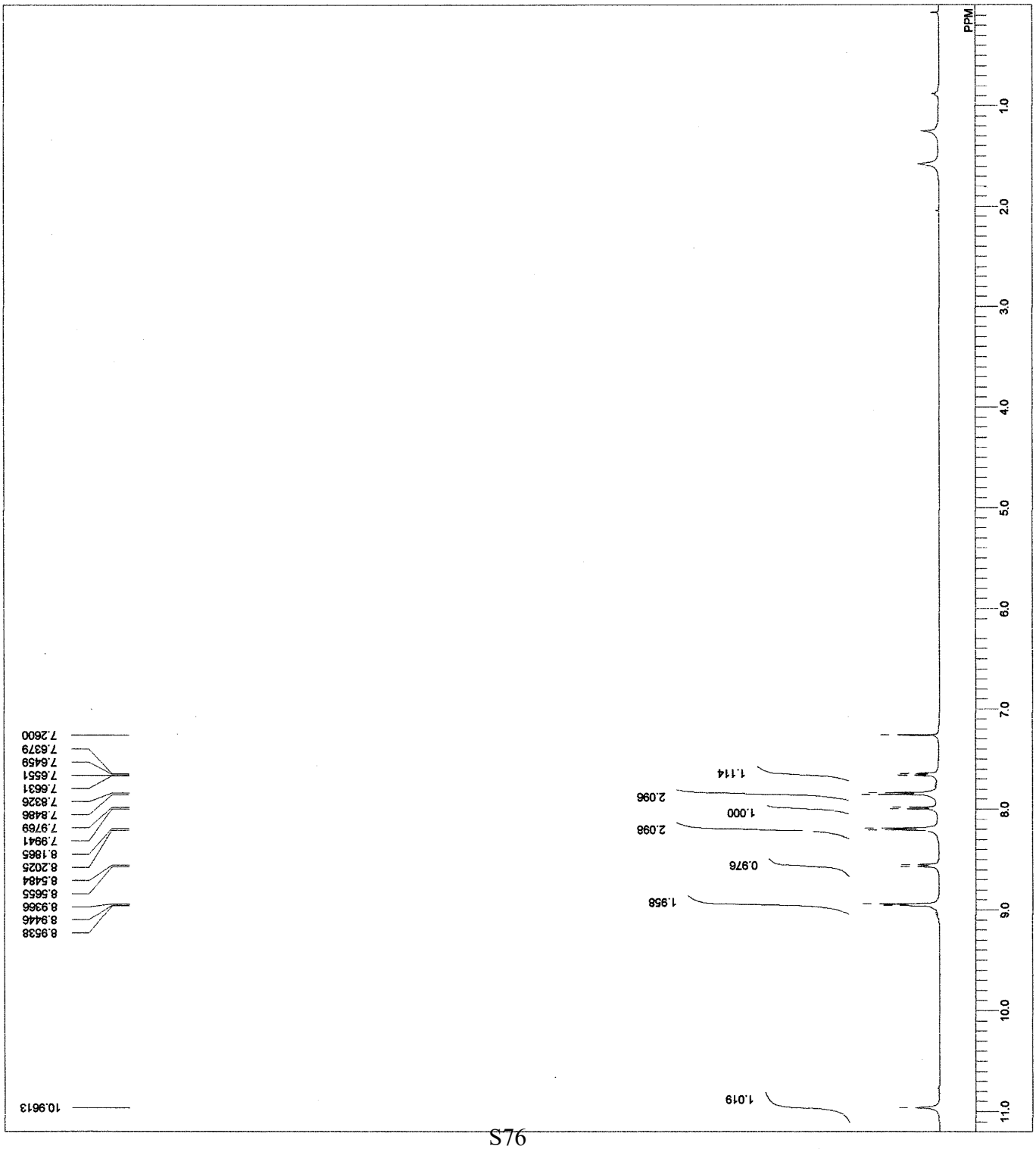
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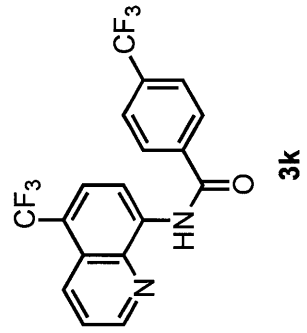
7.2600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HN
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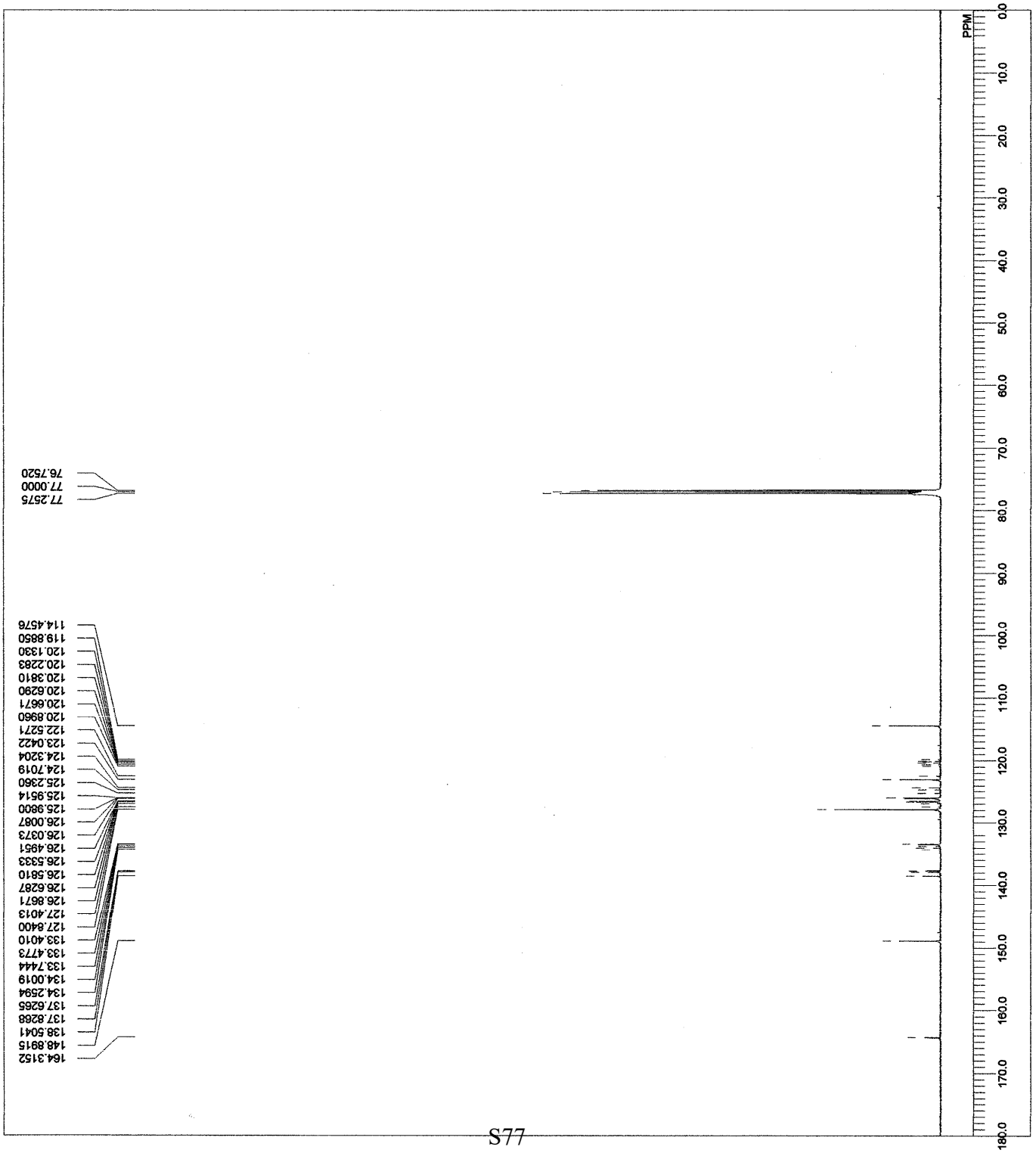
N
CF3

3k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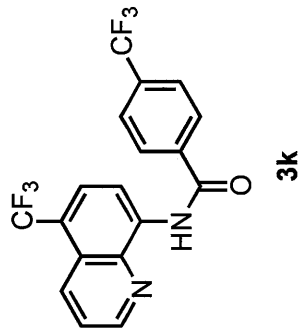

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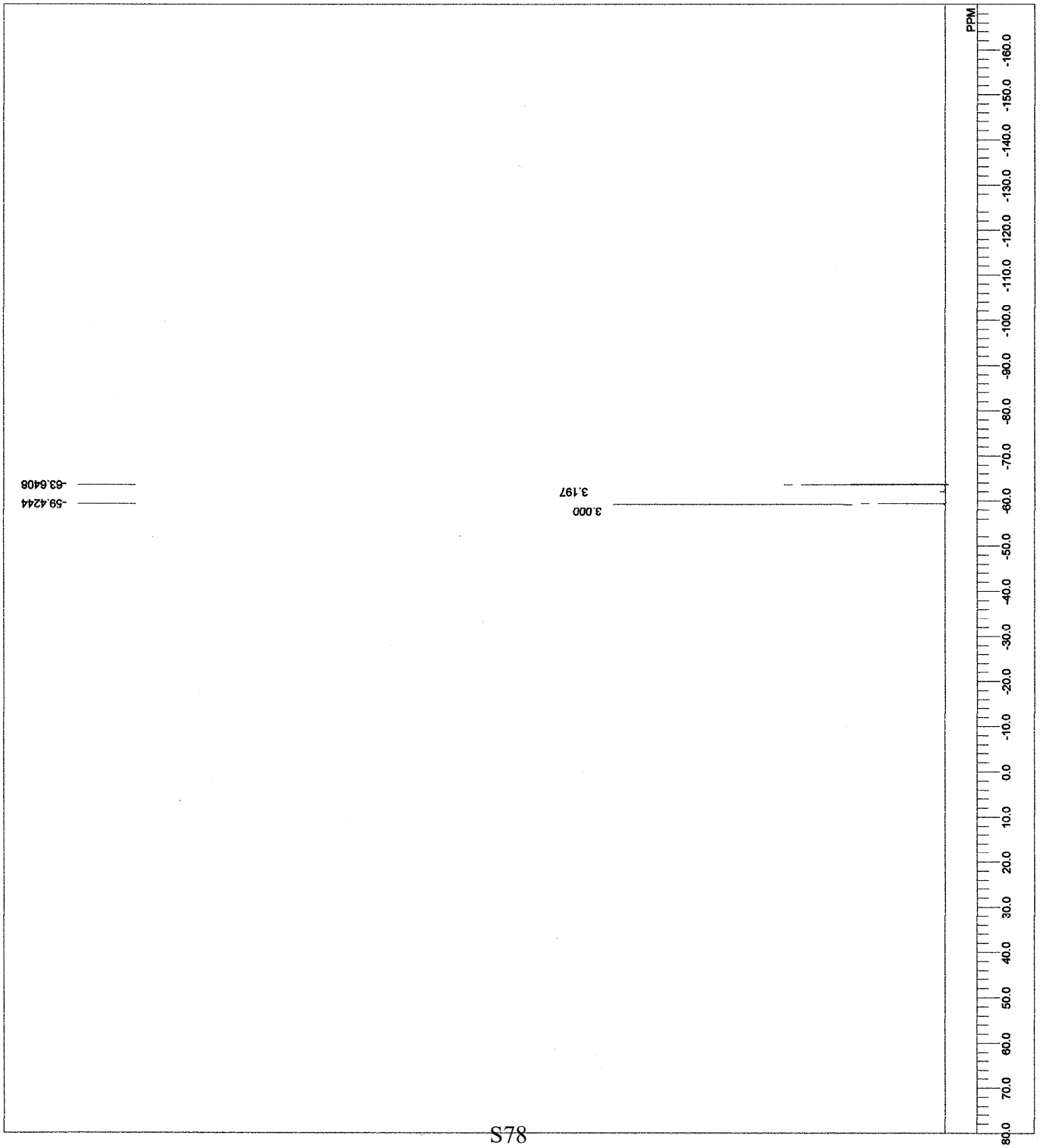

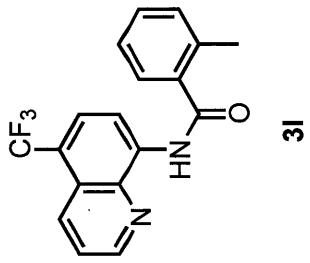
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O
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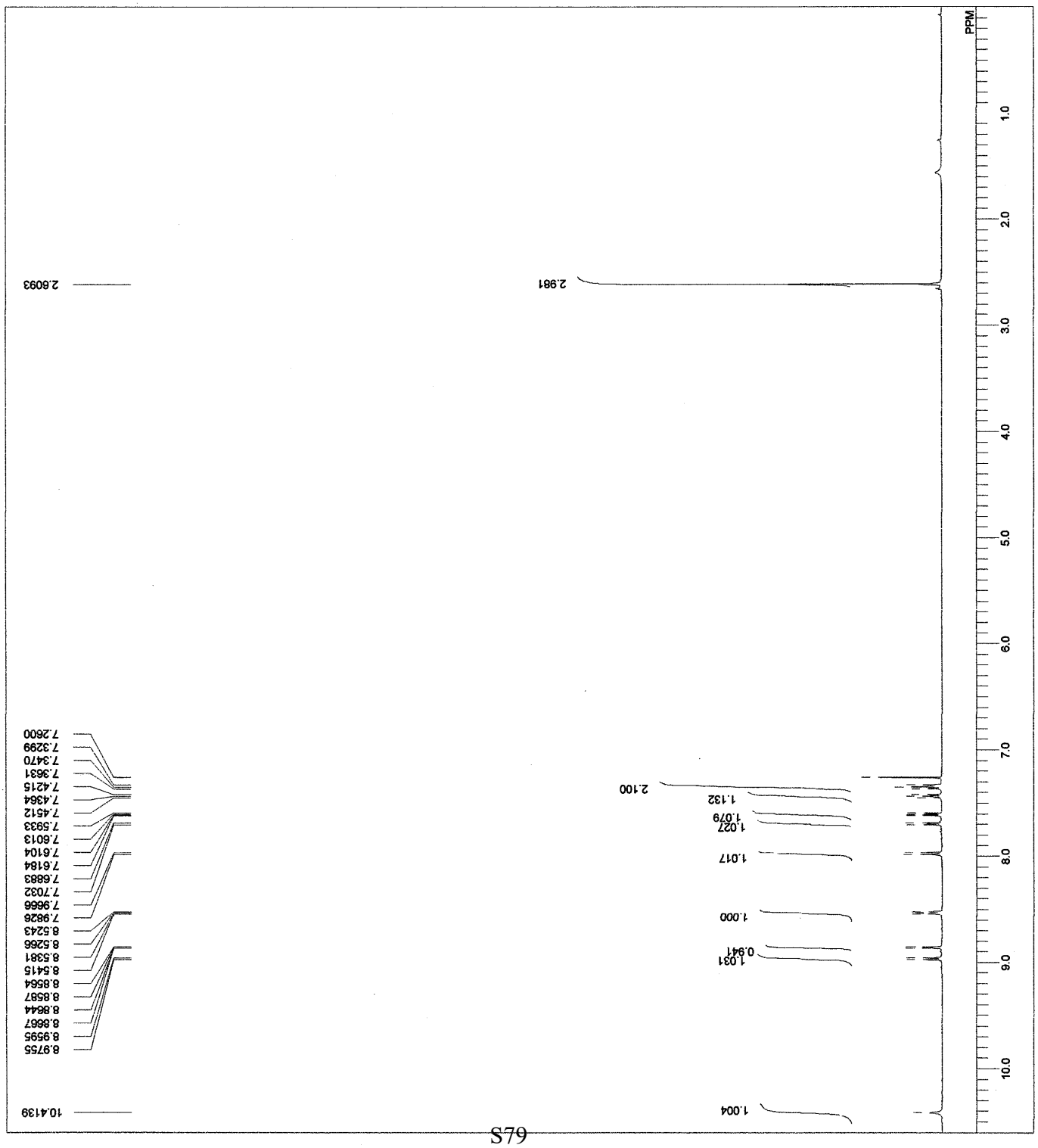
3l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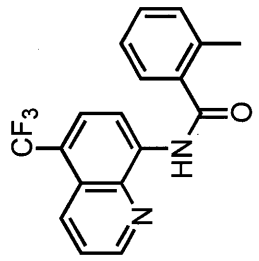
1.004



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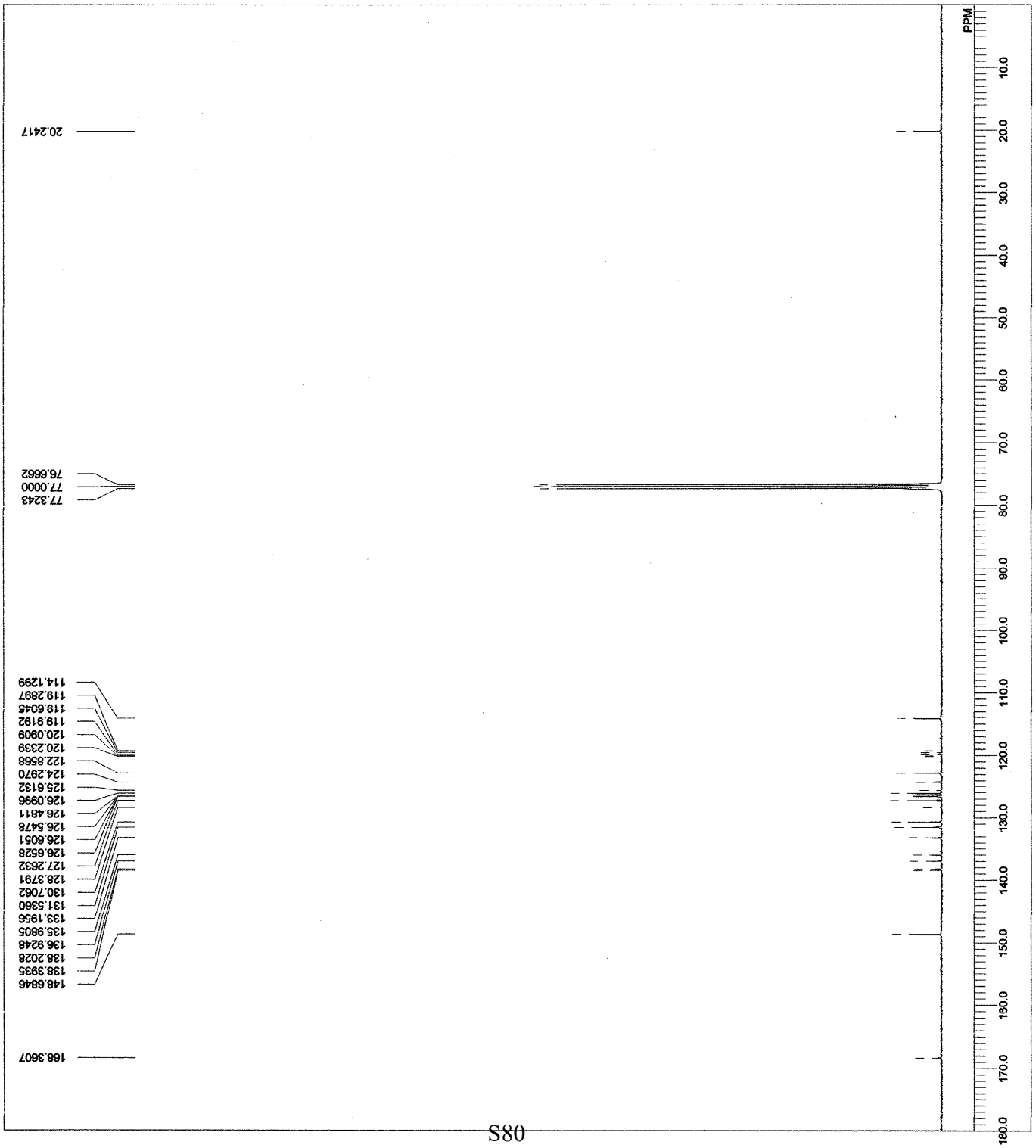
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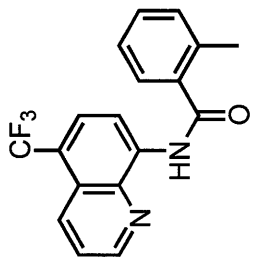

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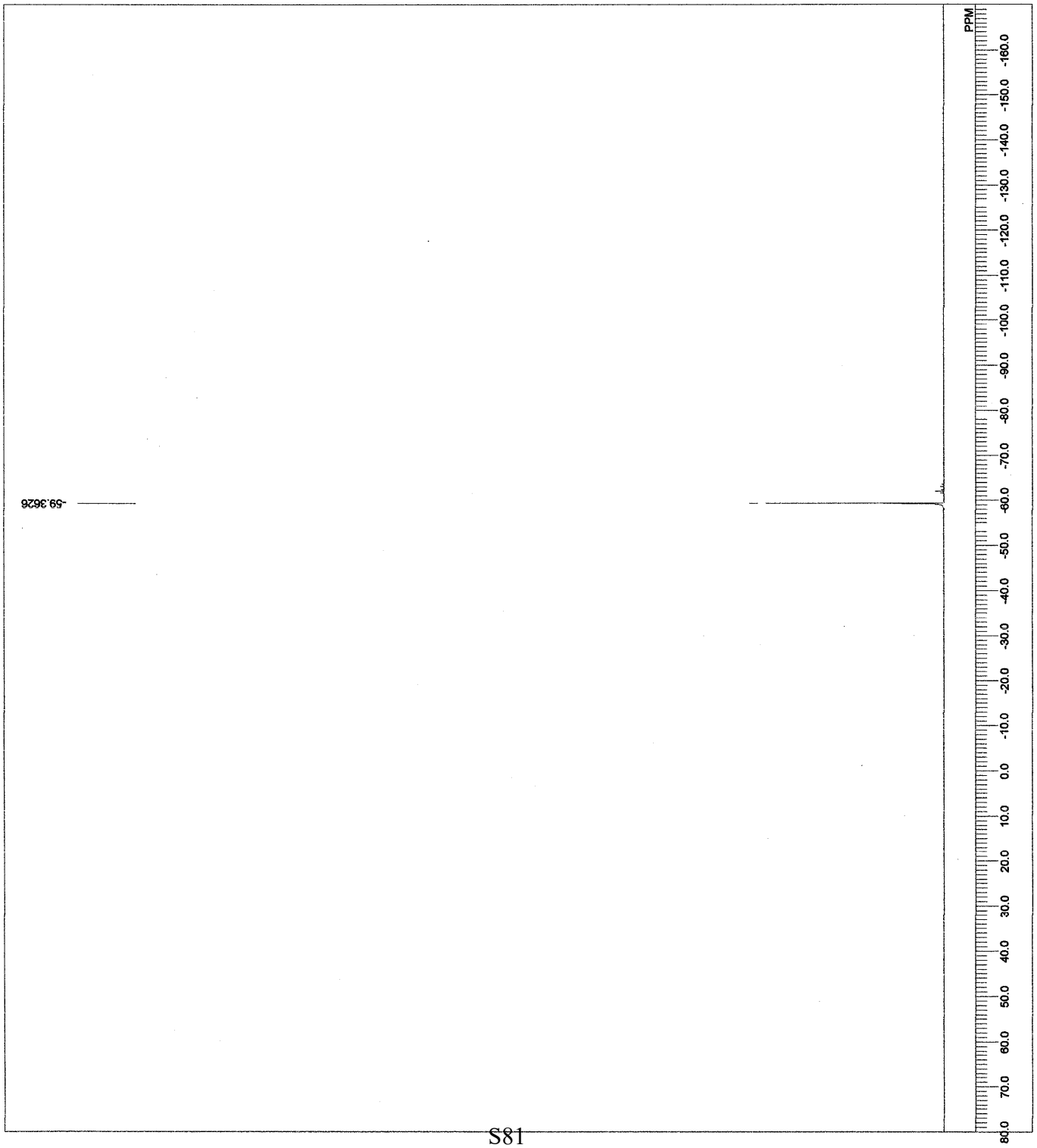
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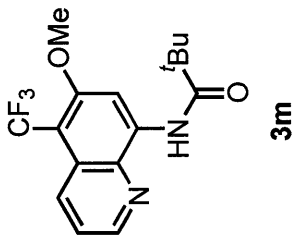
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^{t}Bu
CF_3
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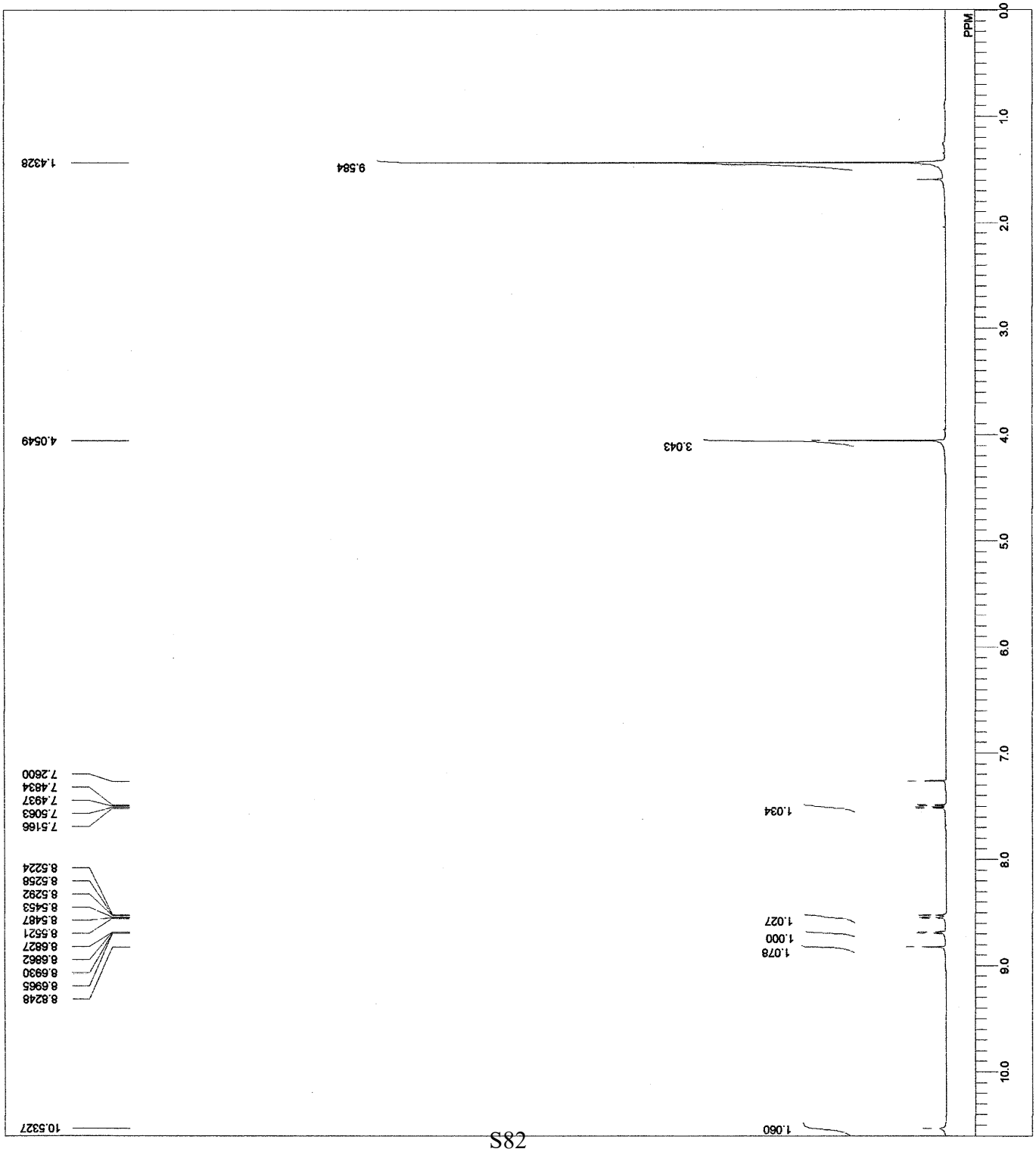
O
N

3m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1.000
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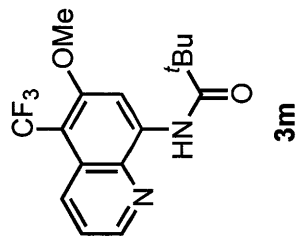
1.060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O
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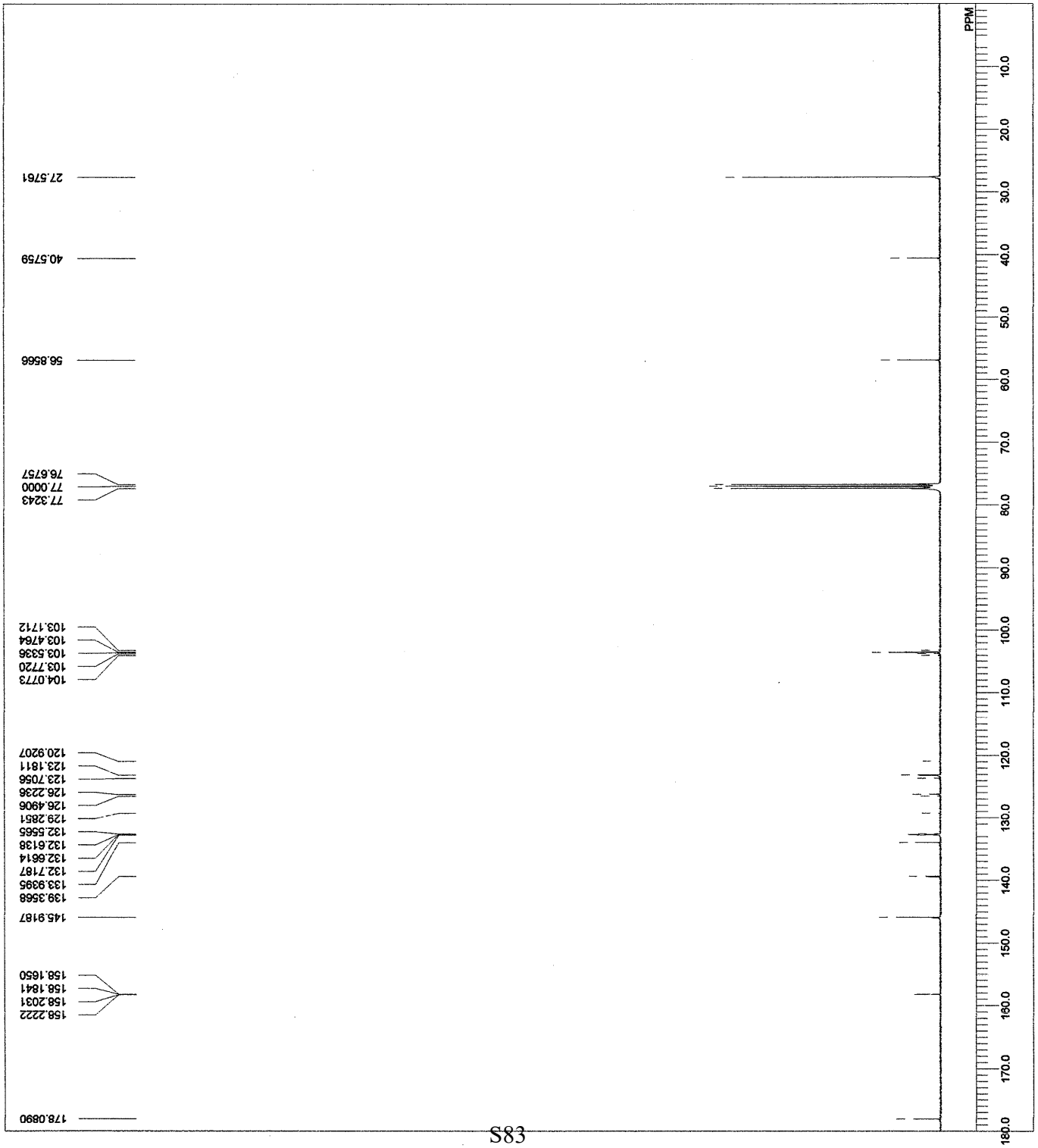
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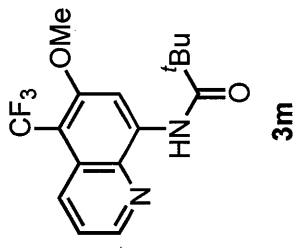
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CF_3
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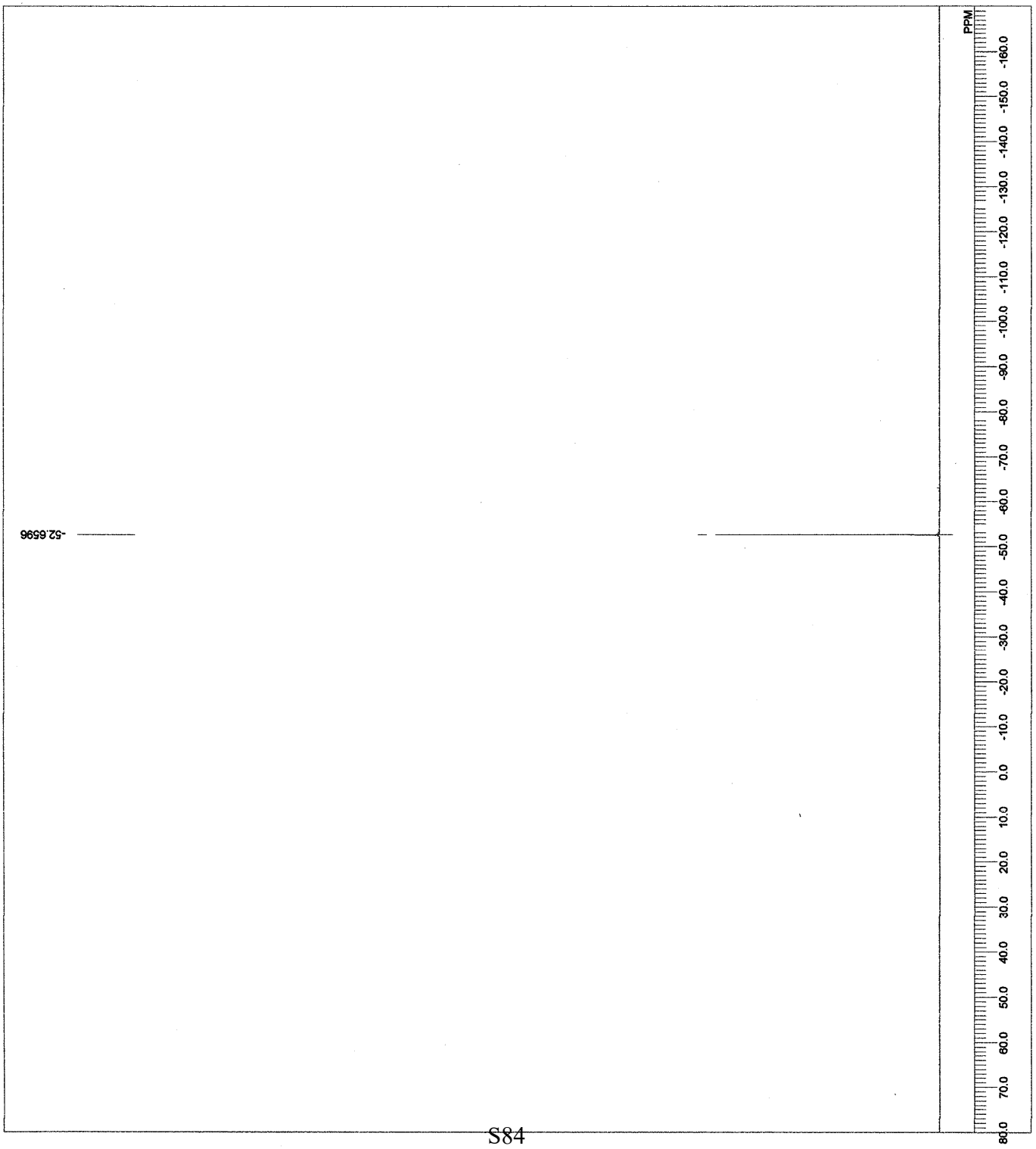
O
N

3m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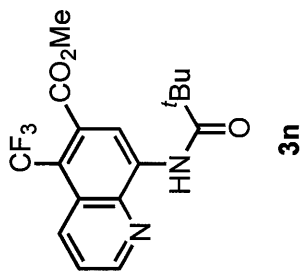
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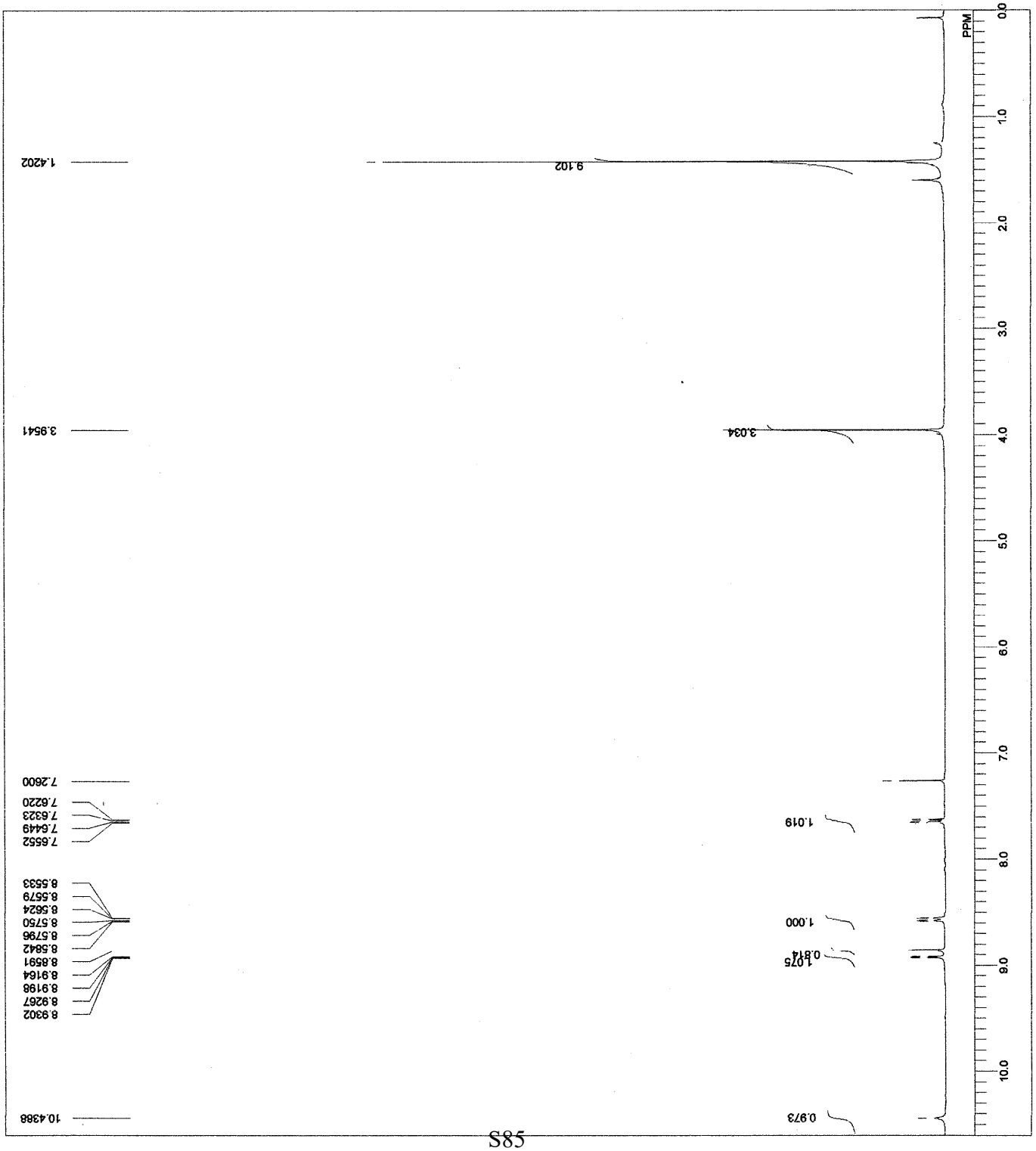
CF3
tBu
HN
O
N

3n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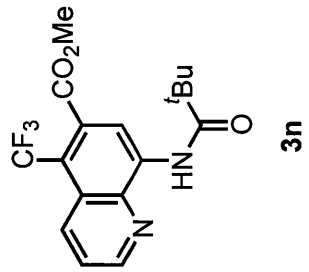
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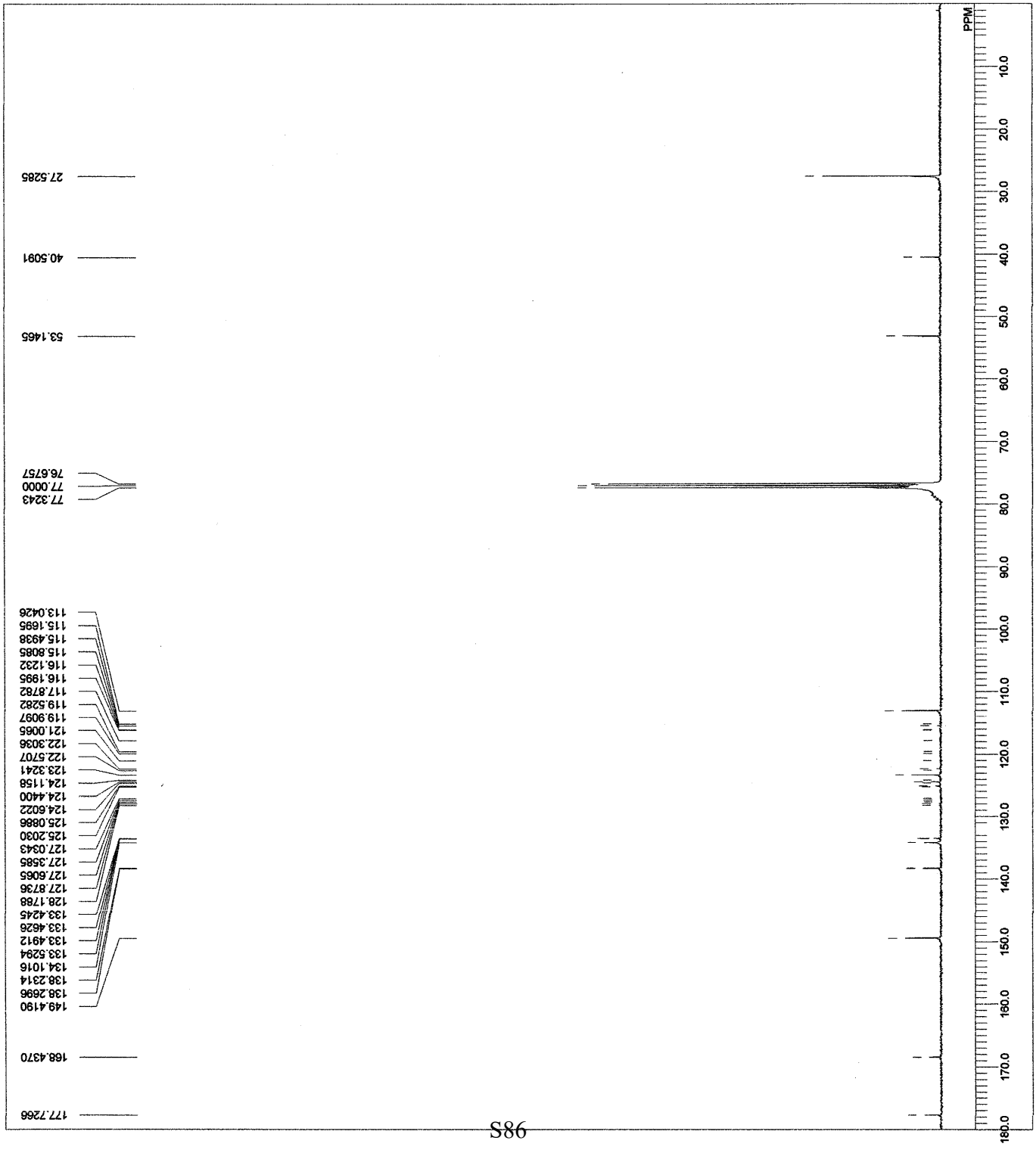
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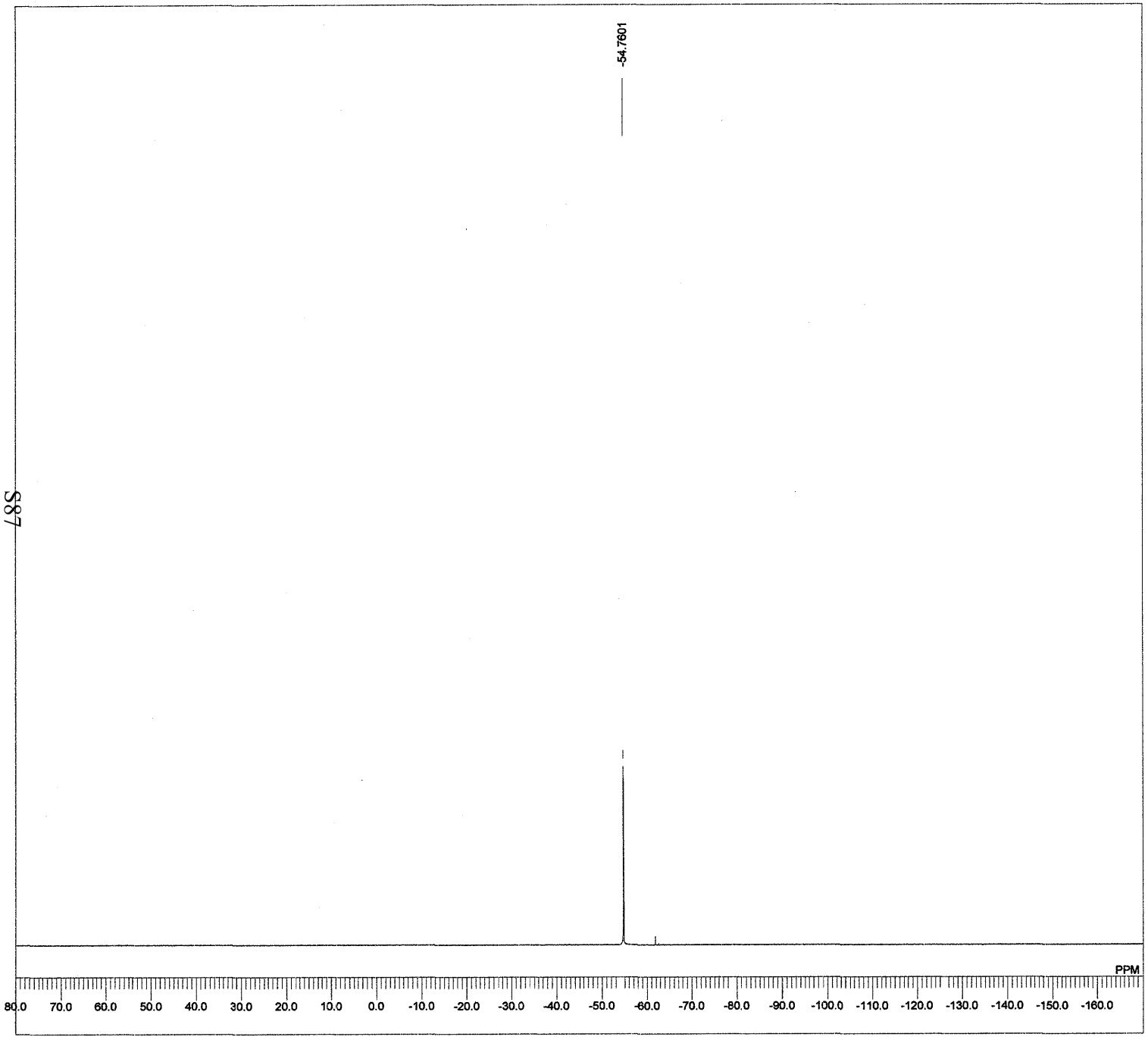
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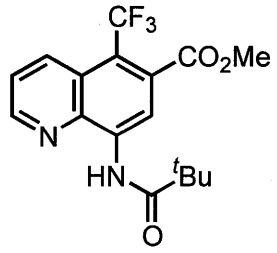
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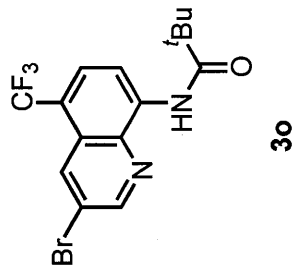
O

3n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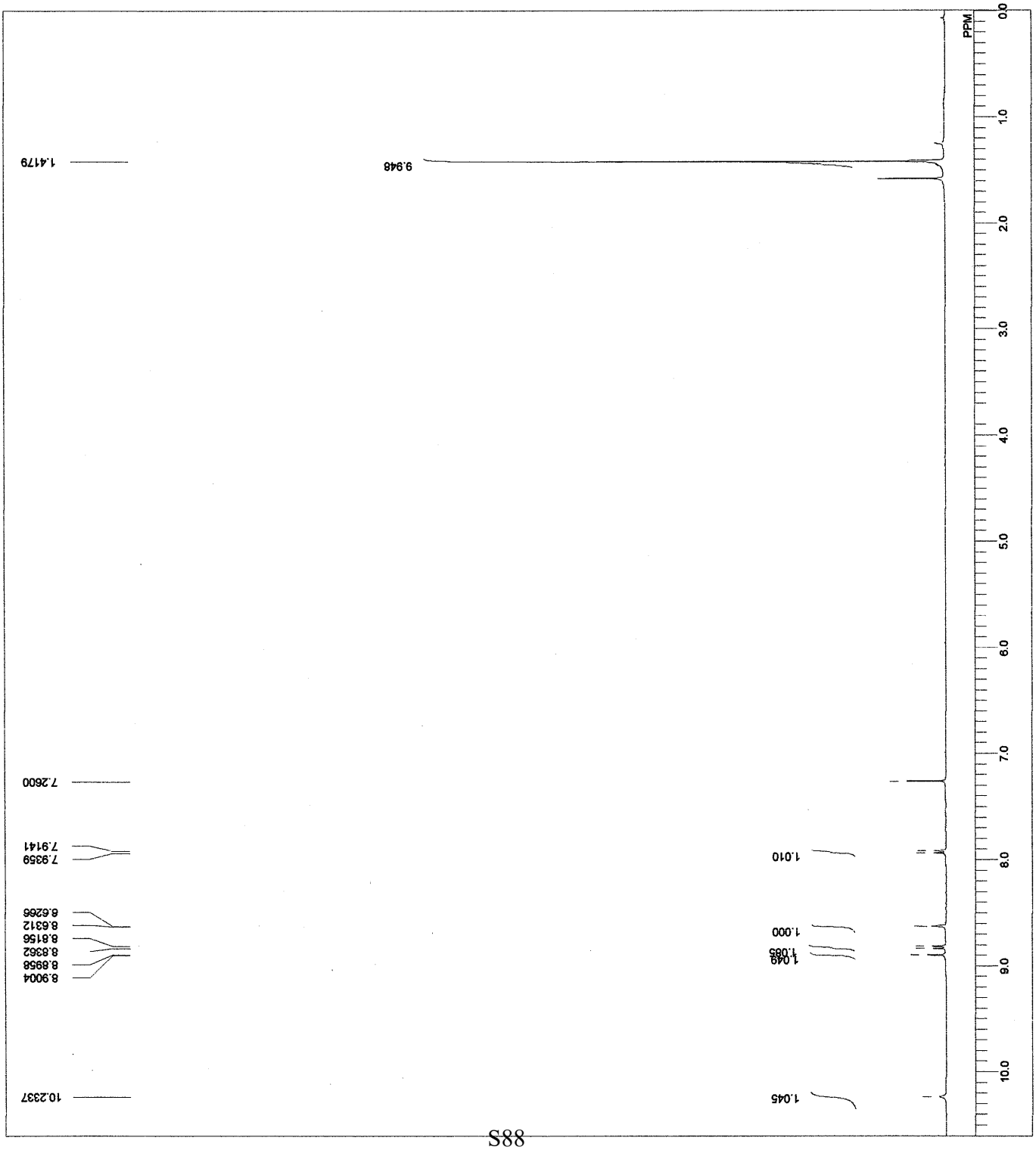
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1.045
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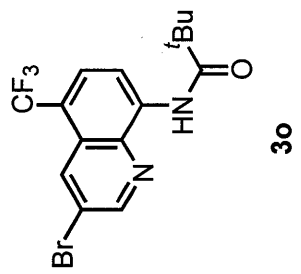

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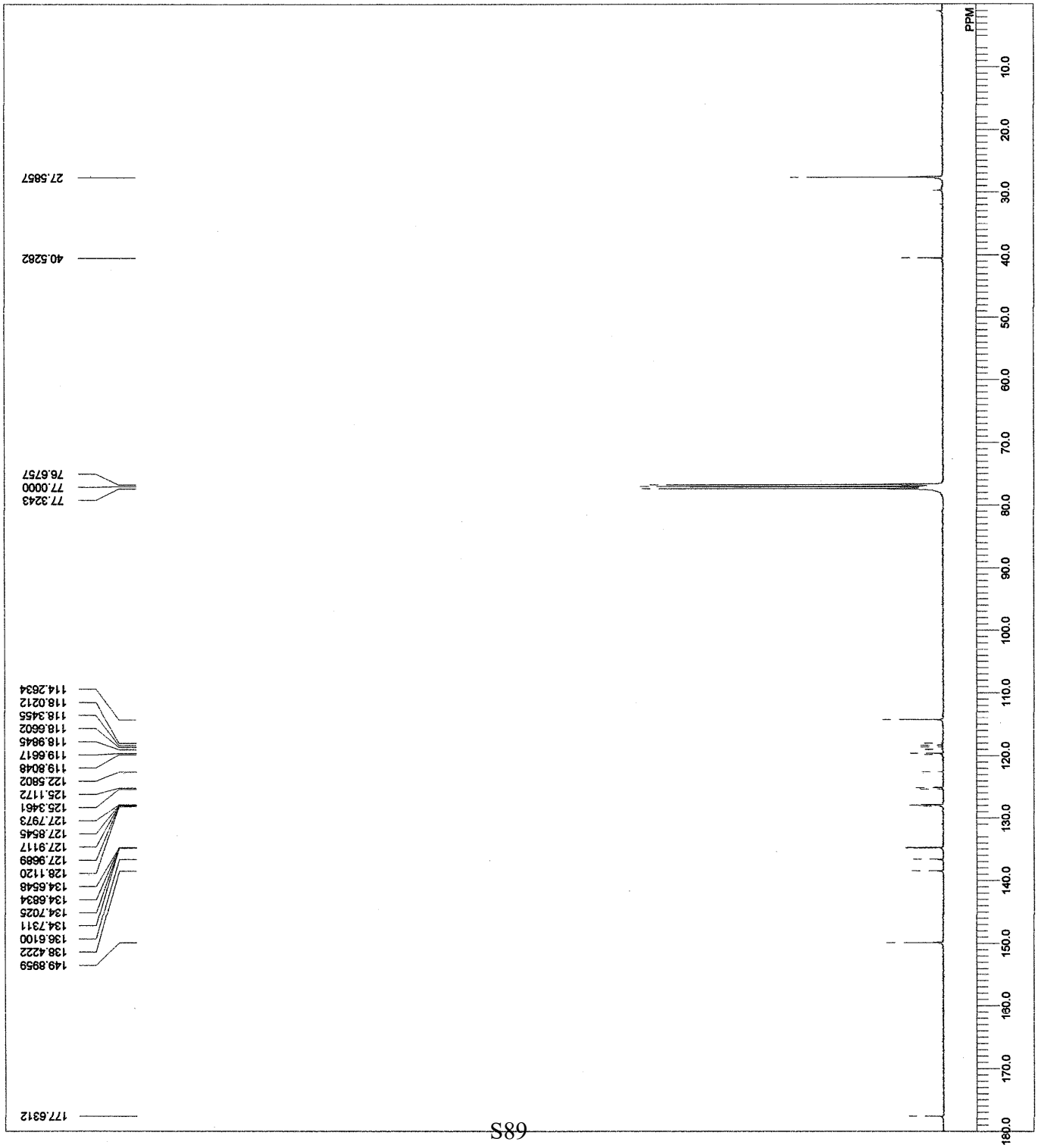
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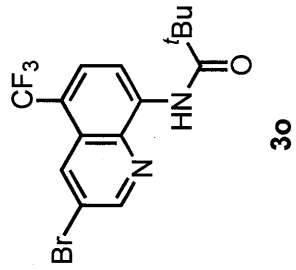
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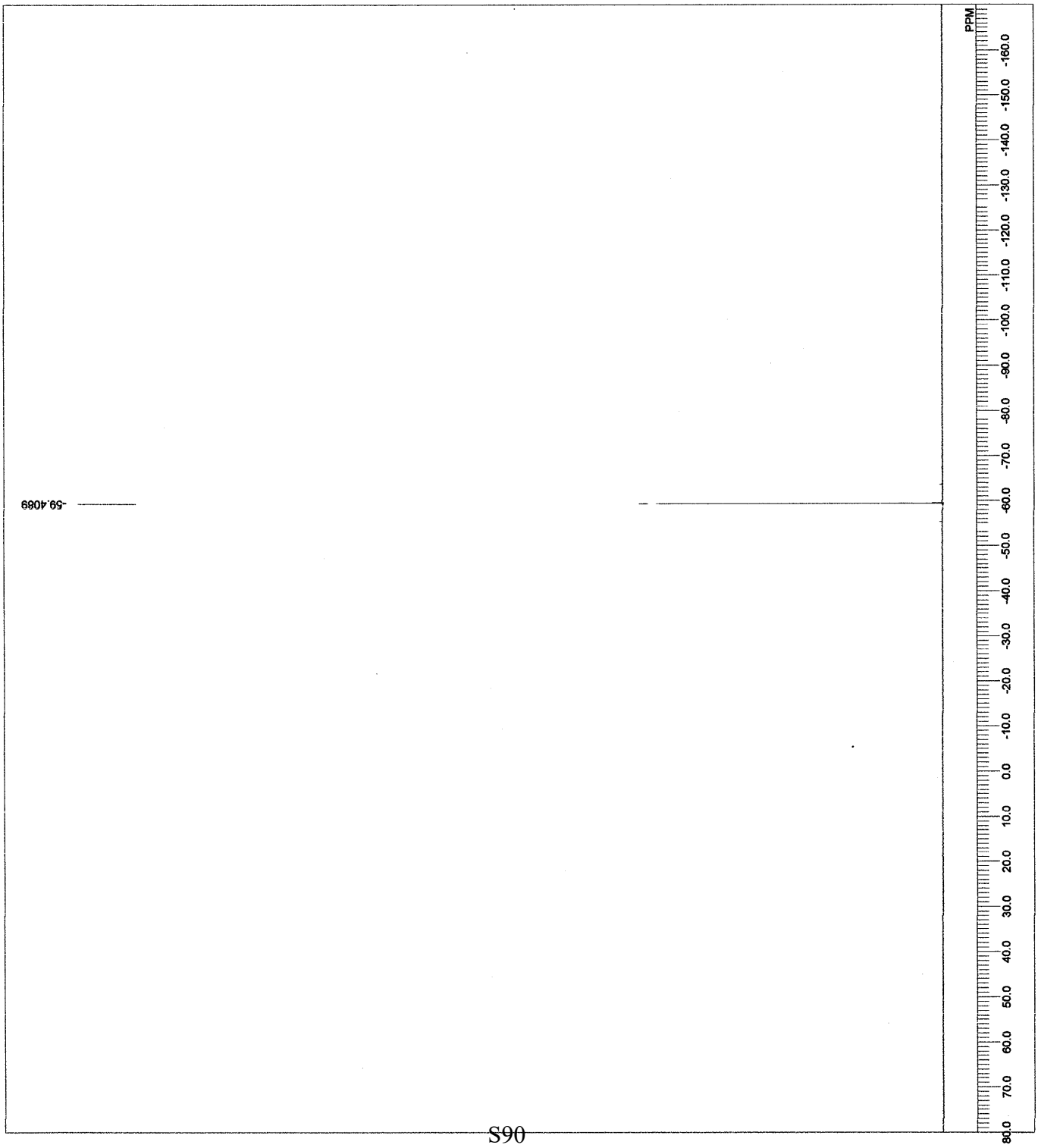
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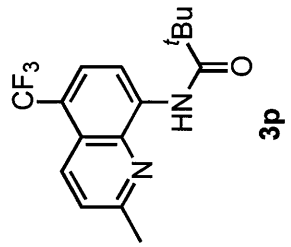
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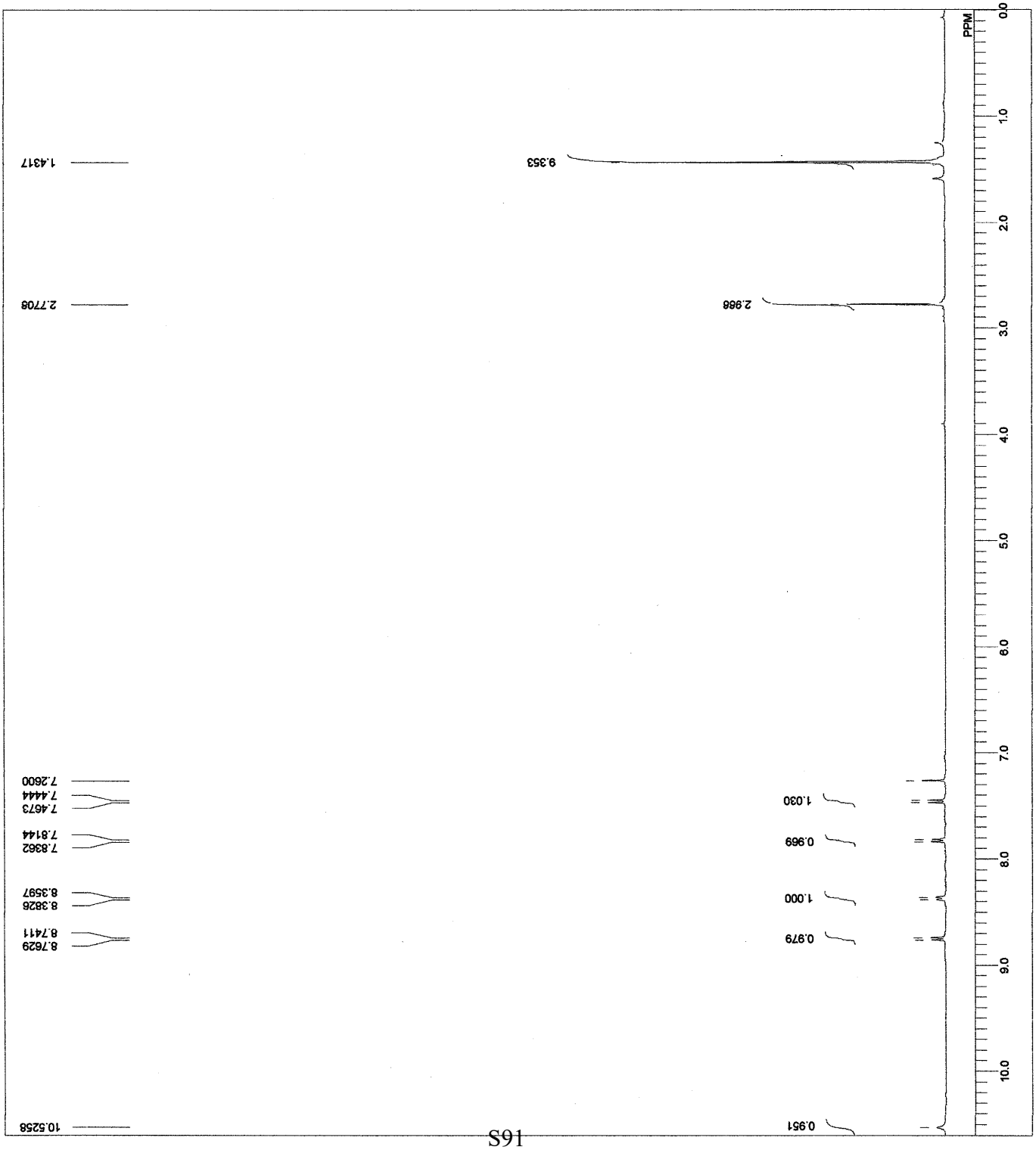
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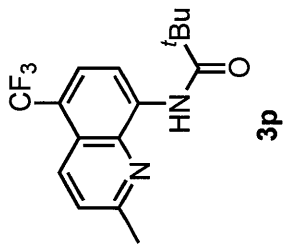
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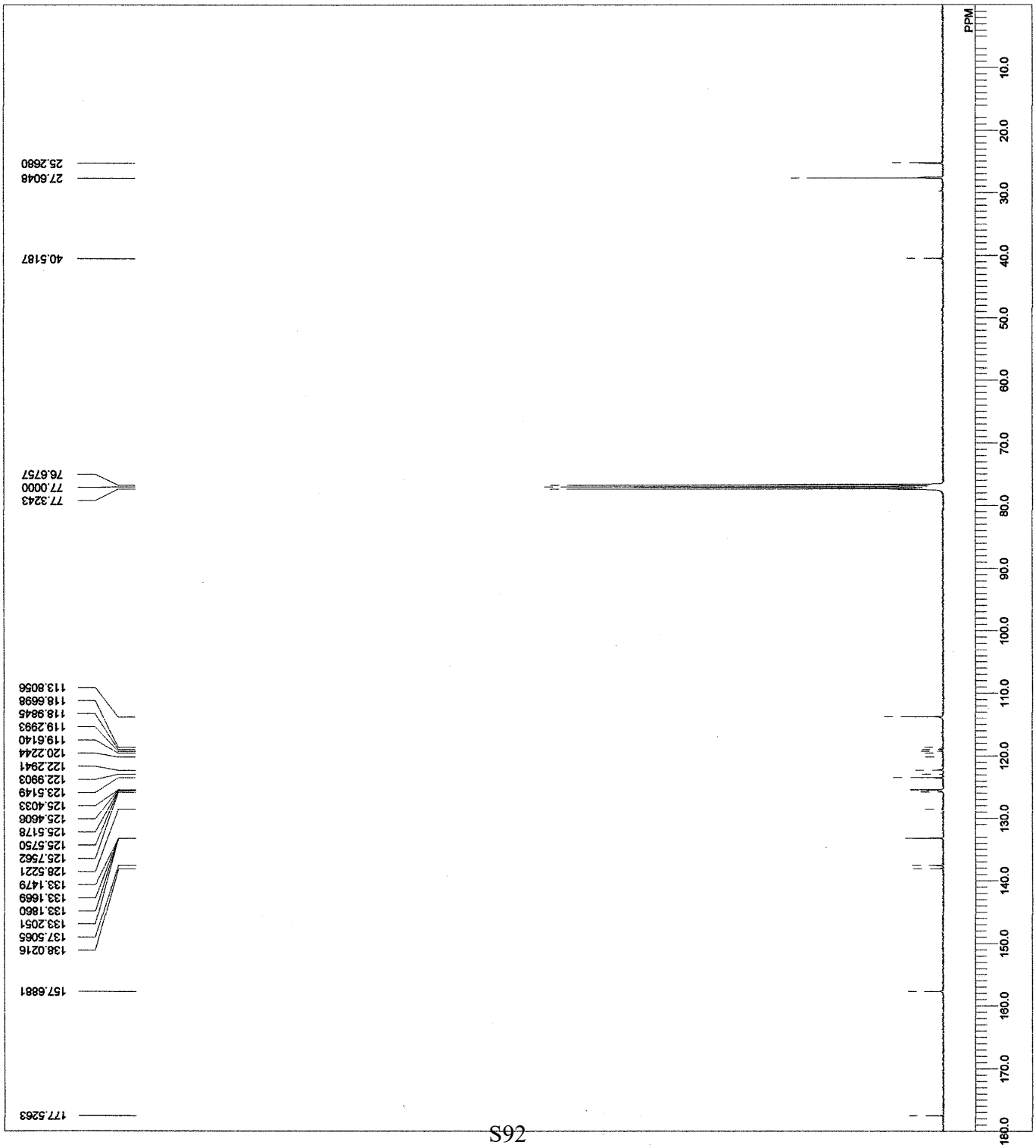
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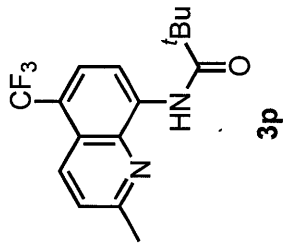
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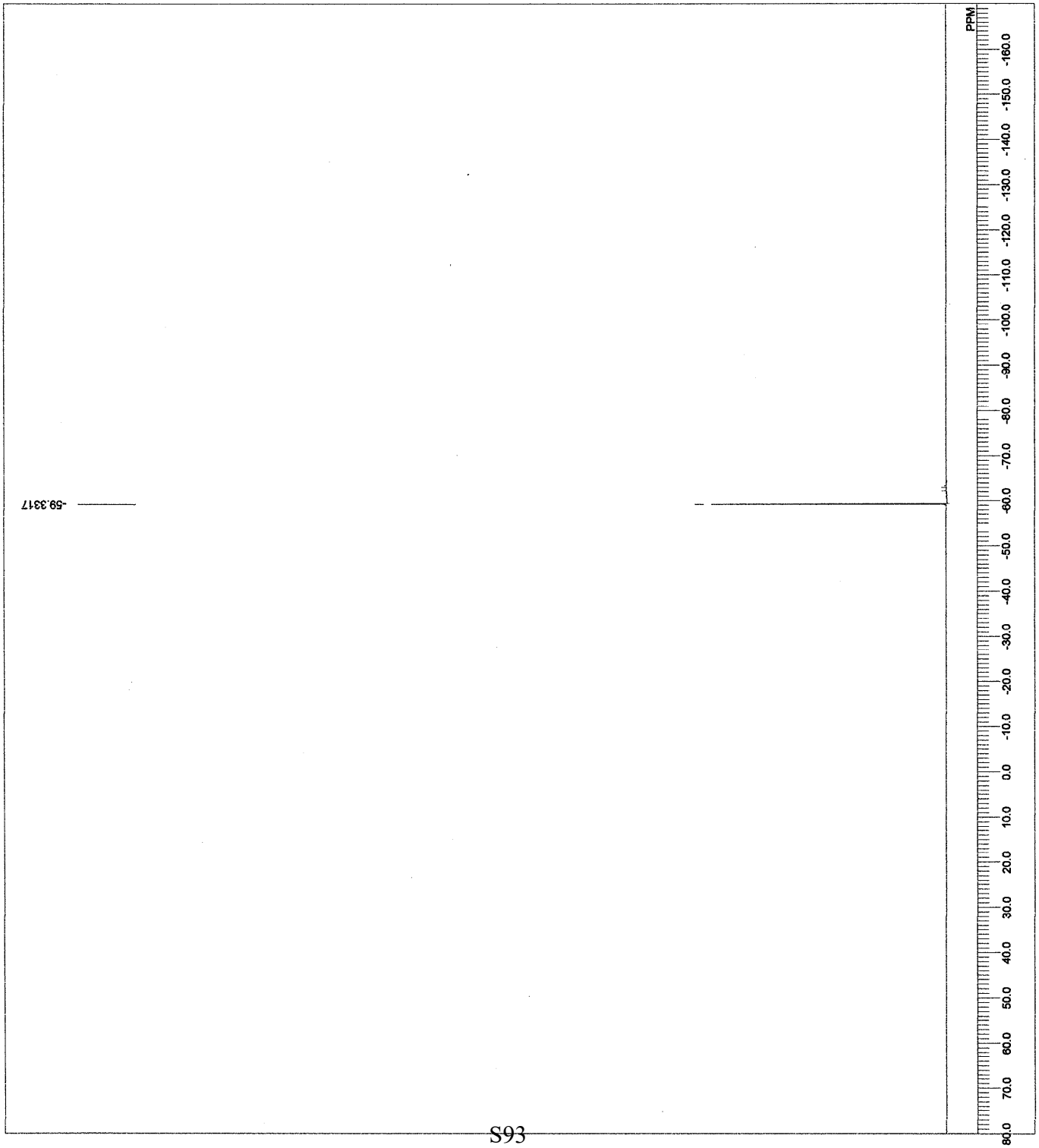
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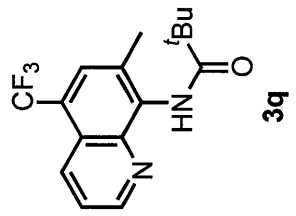
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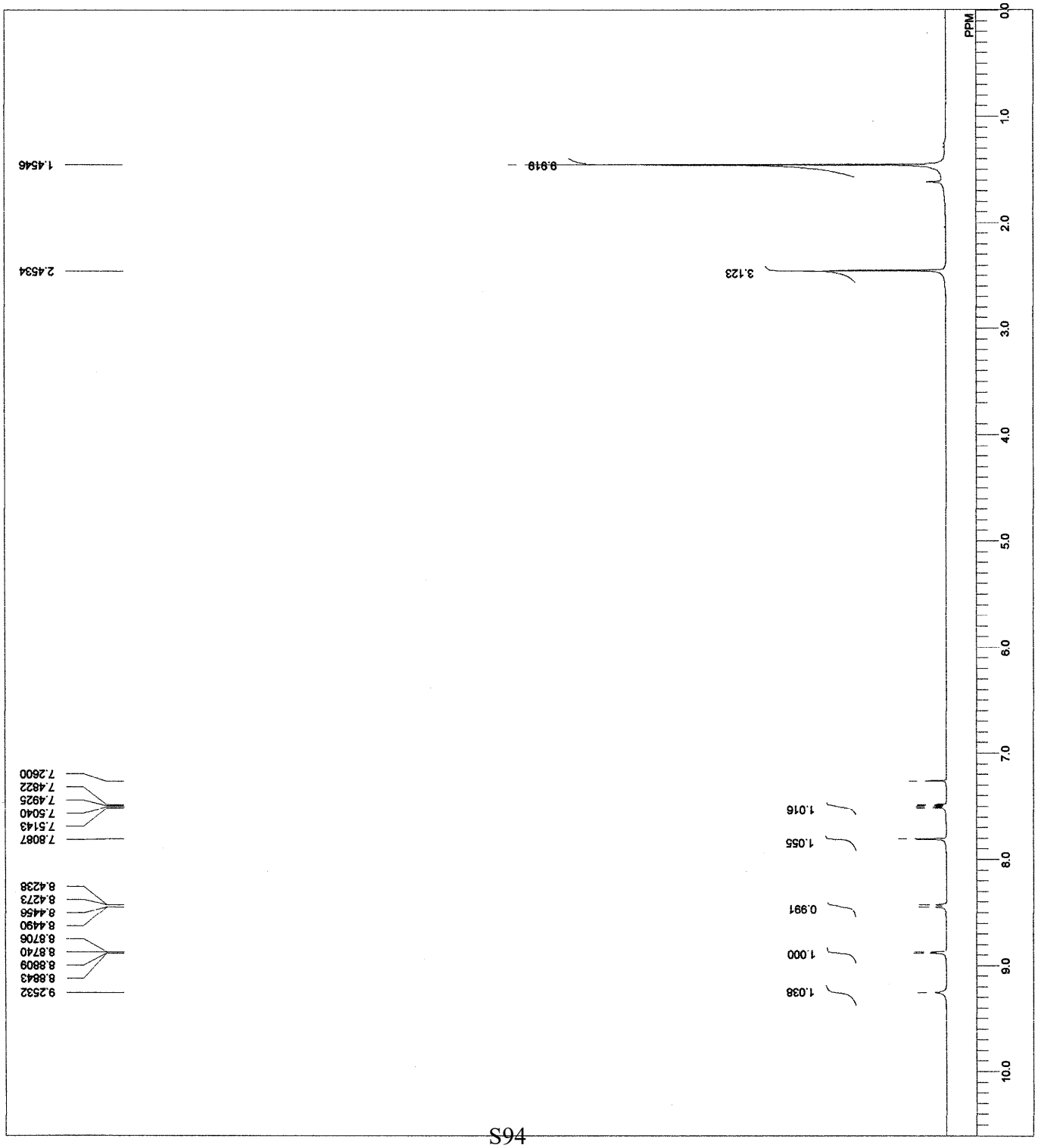
O
N

3q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8.4273
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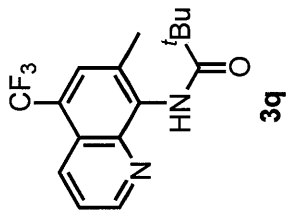
1.000
1.038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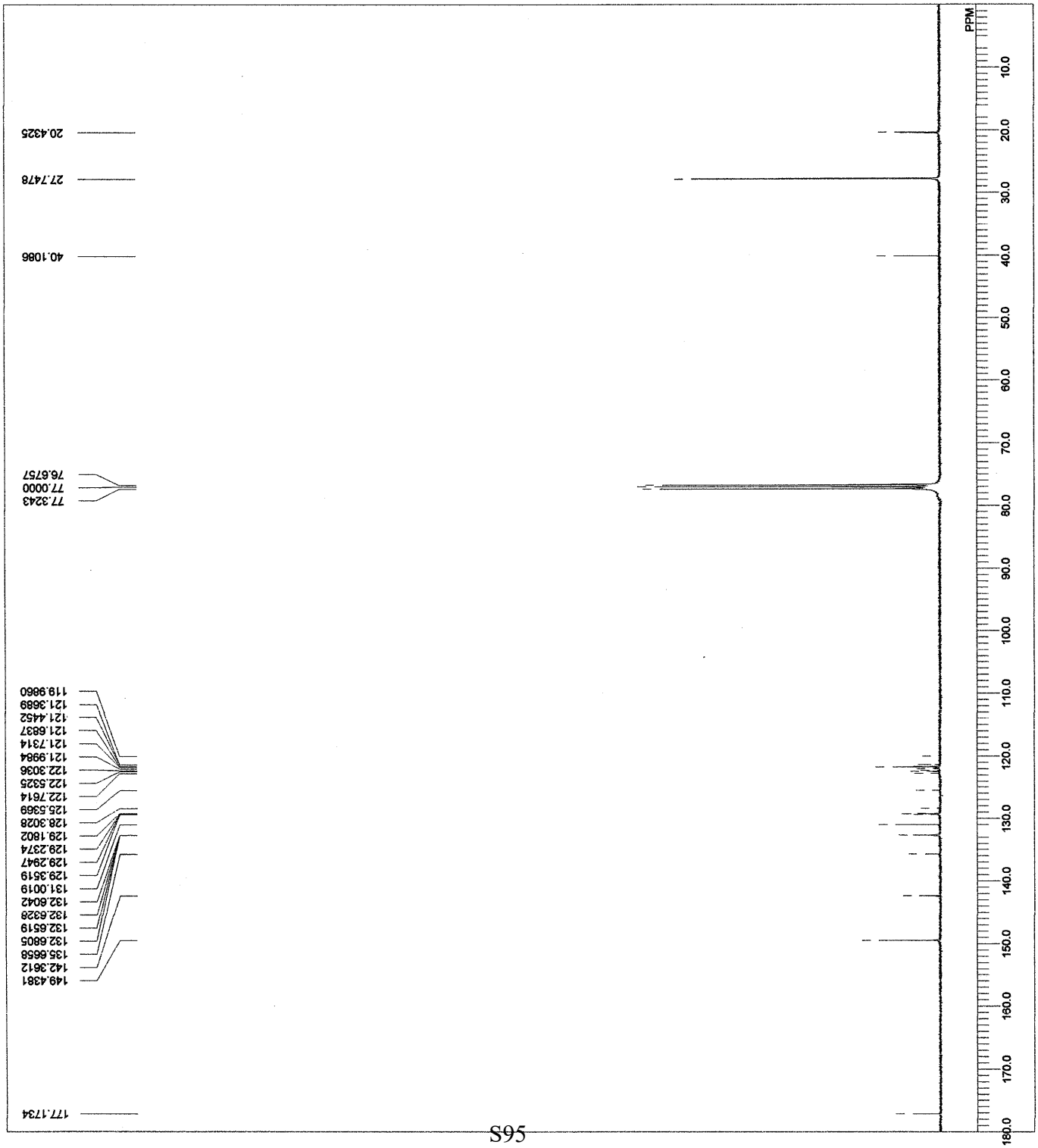
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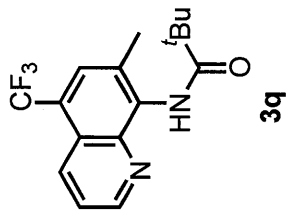

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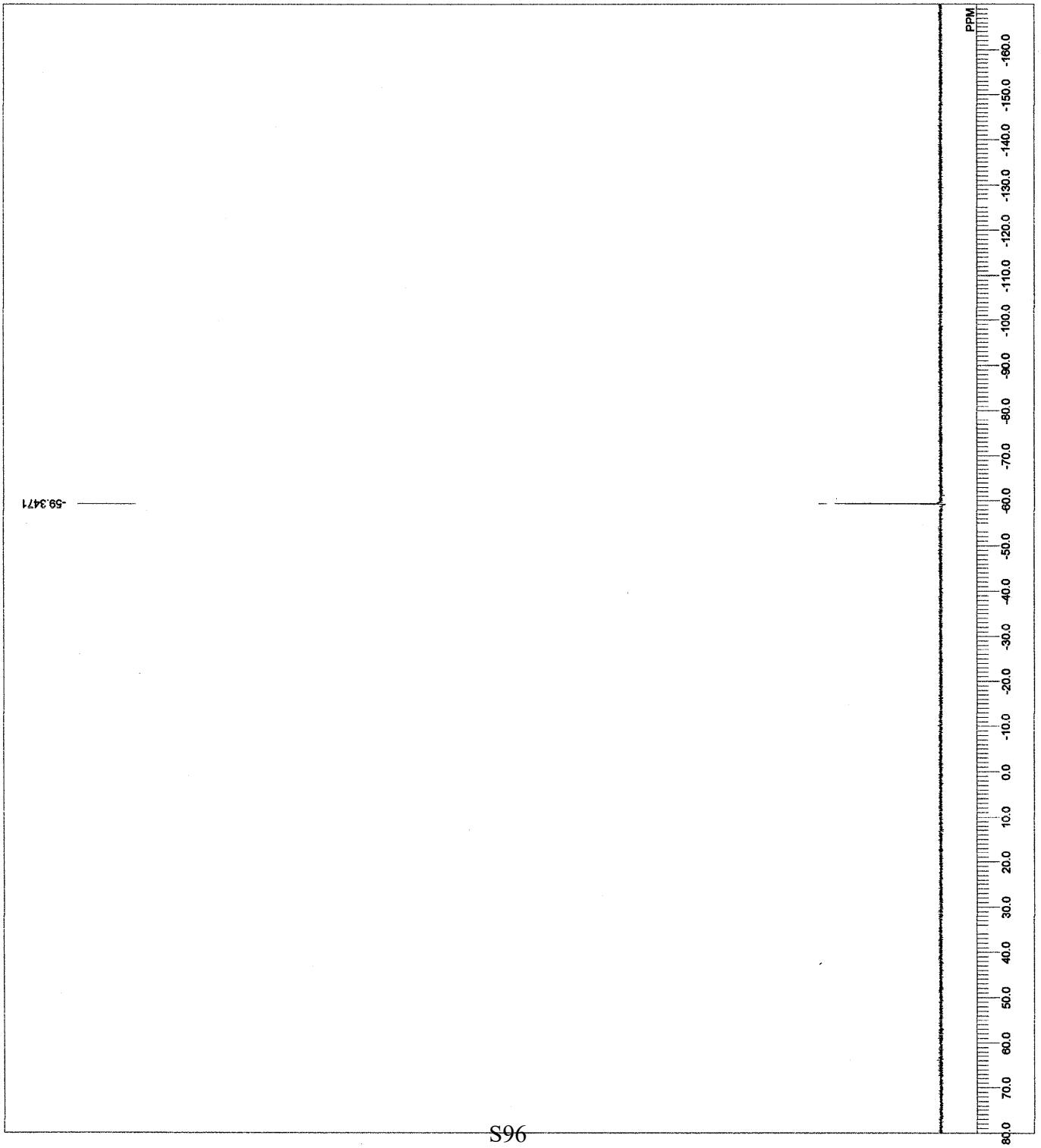
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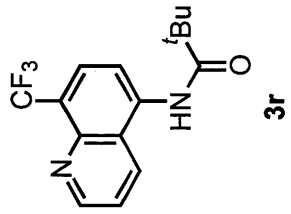
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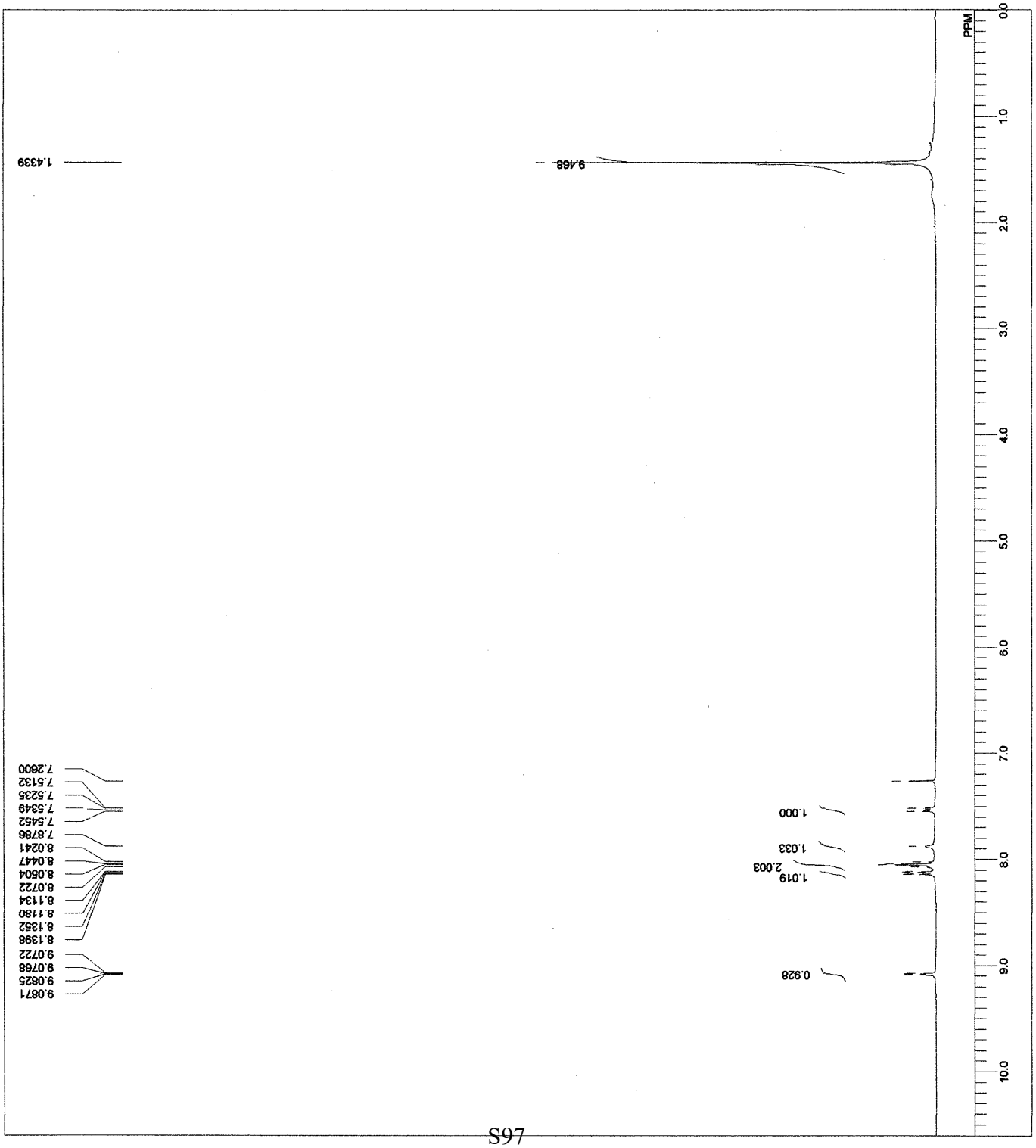
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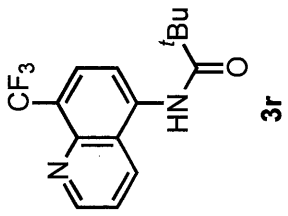
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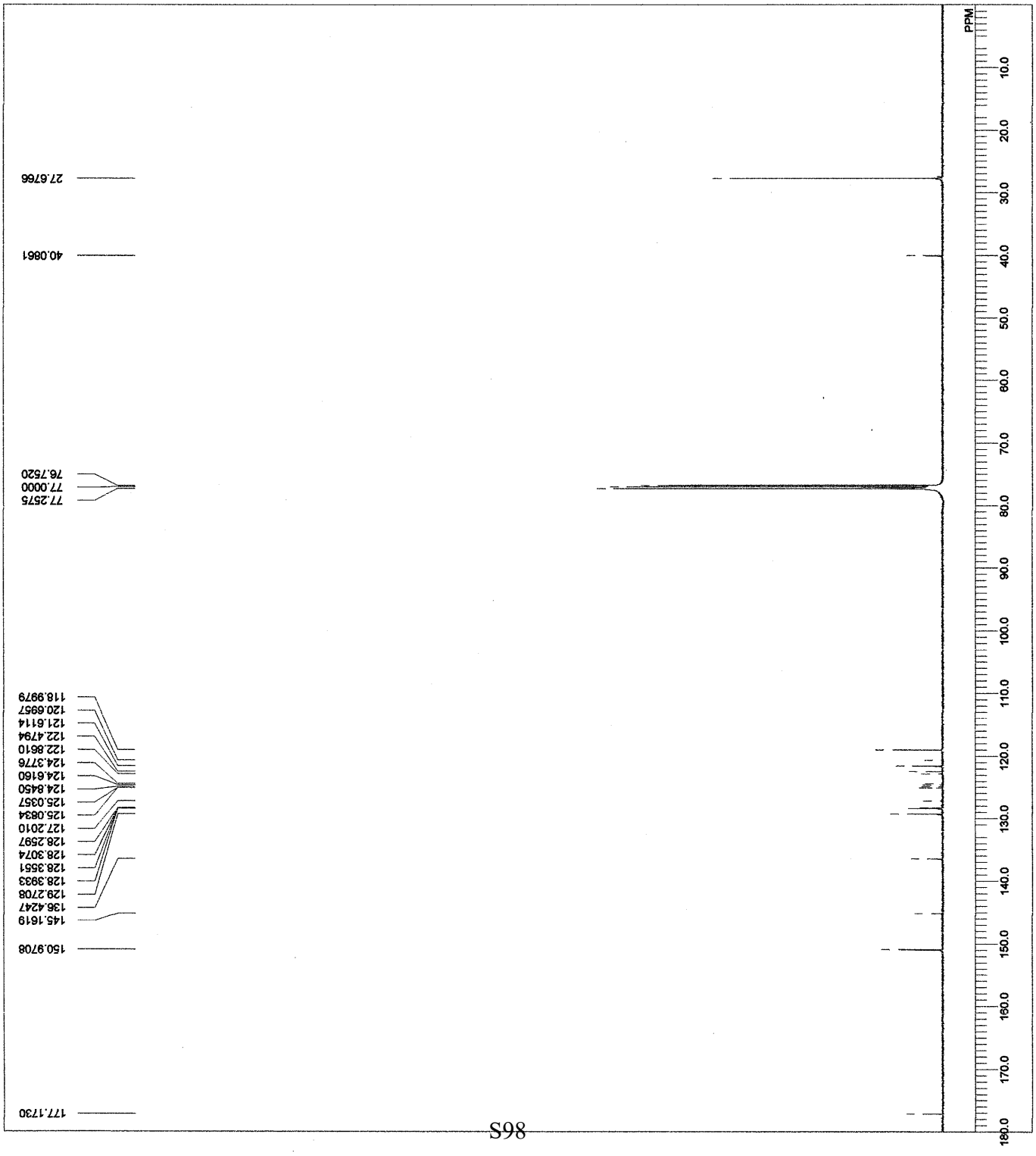
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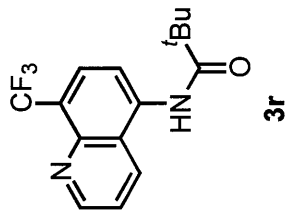

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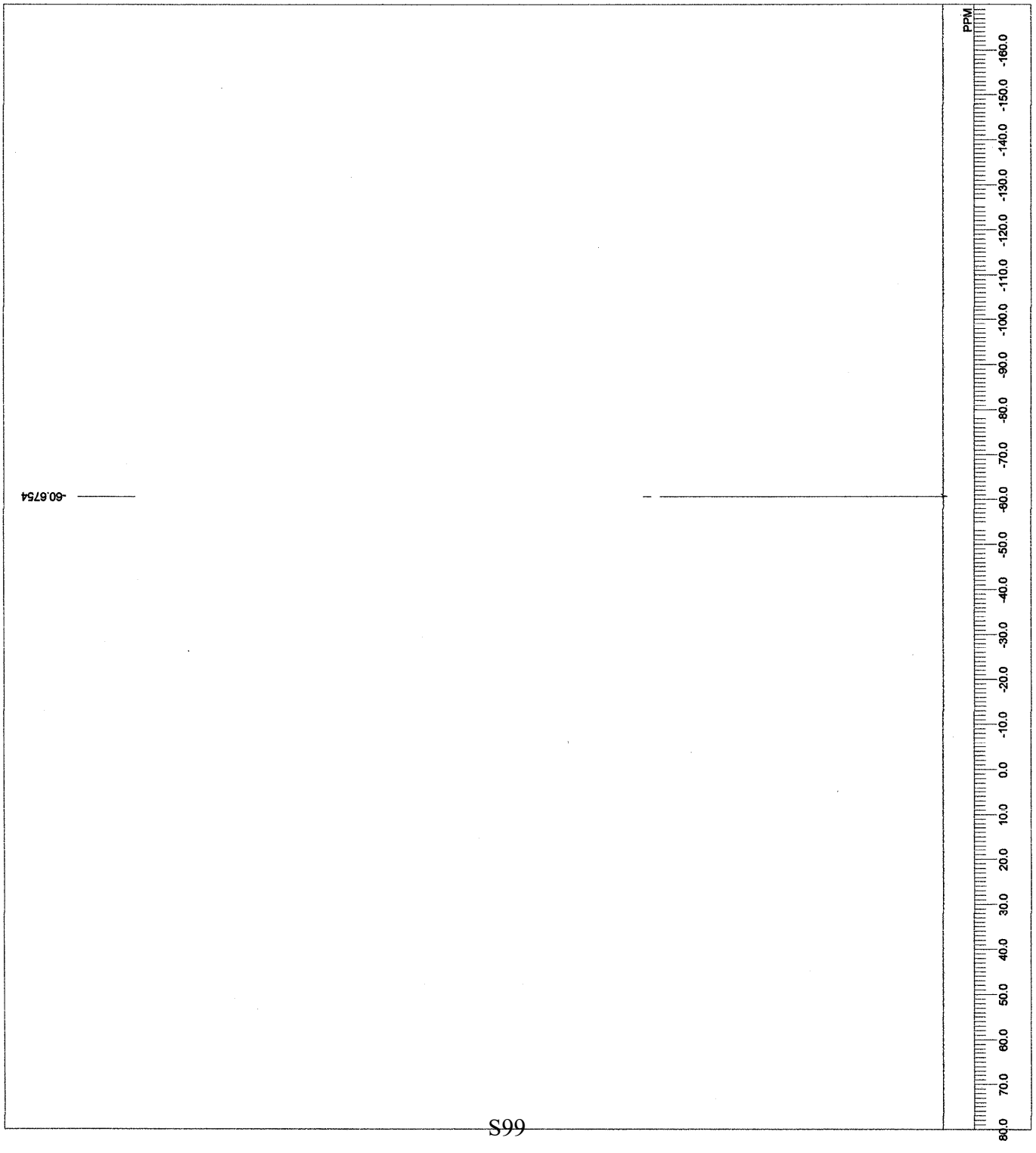
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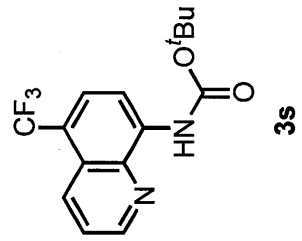
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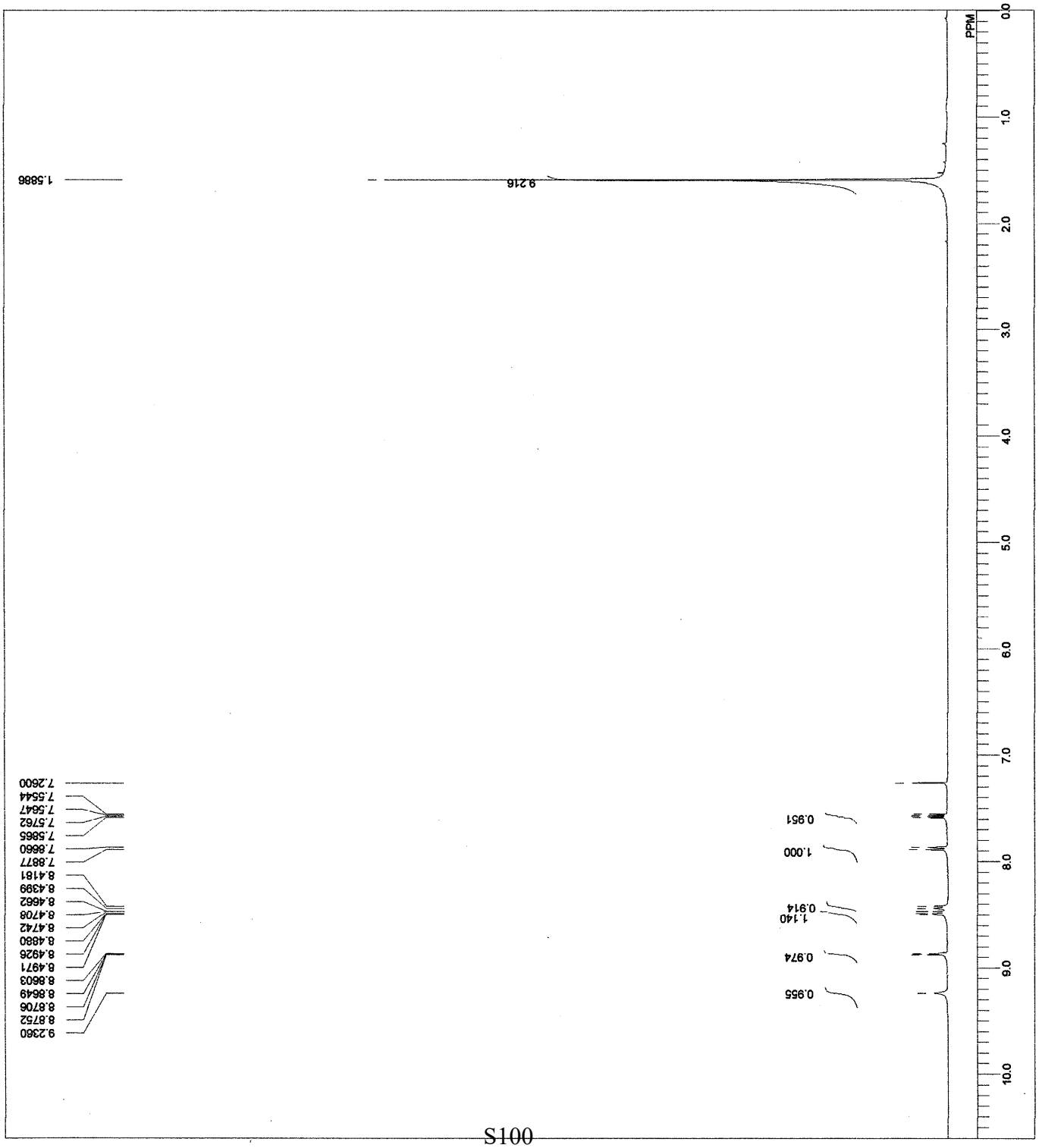
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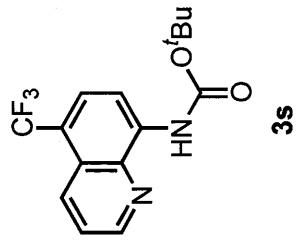
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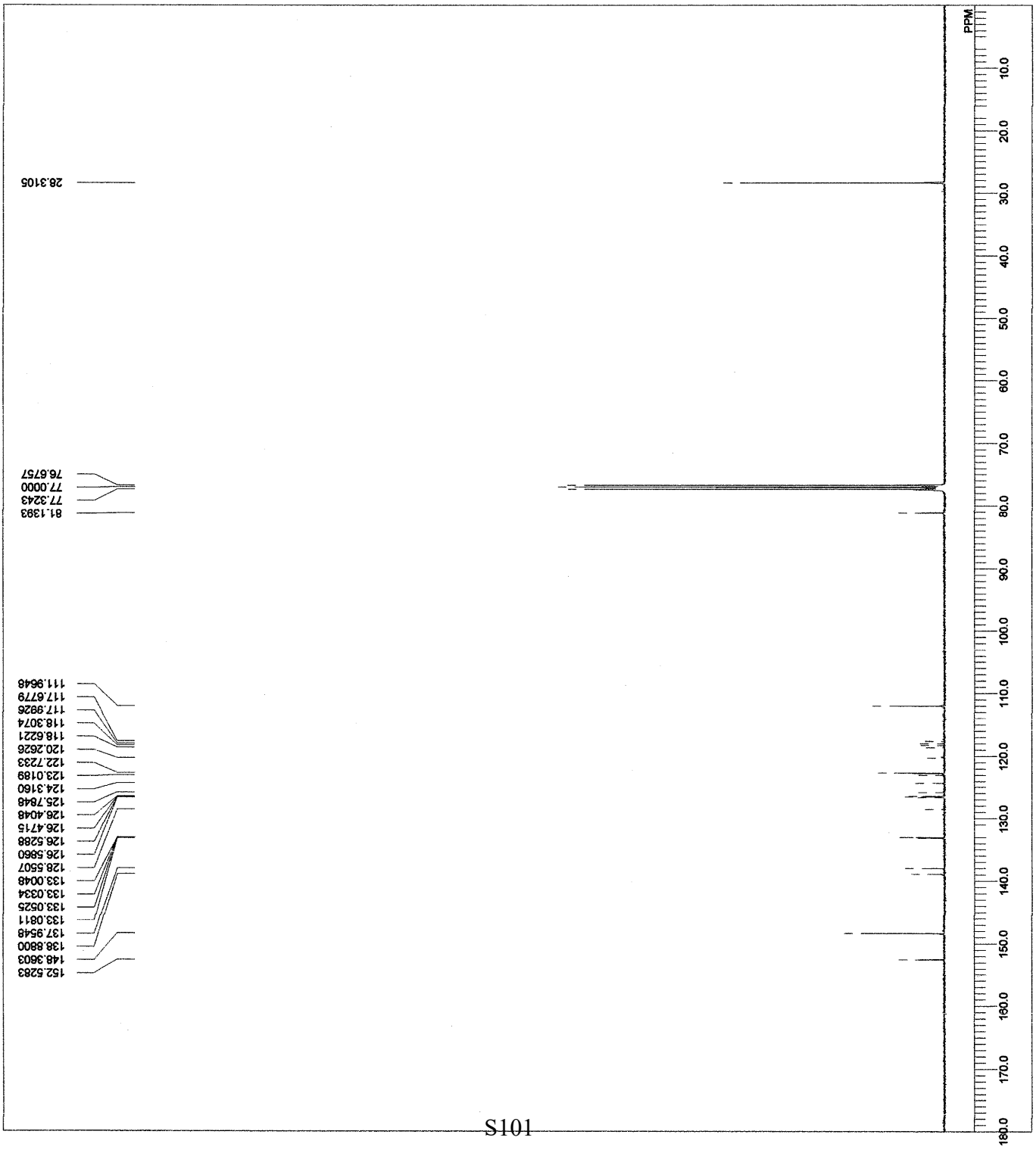
O
O
tBu
N

3s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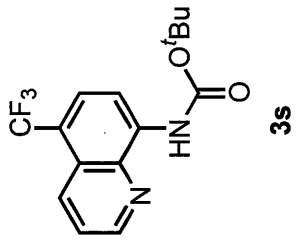

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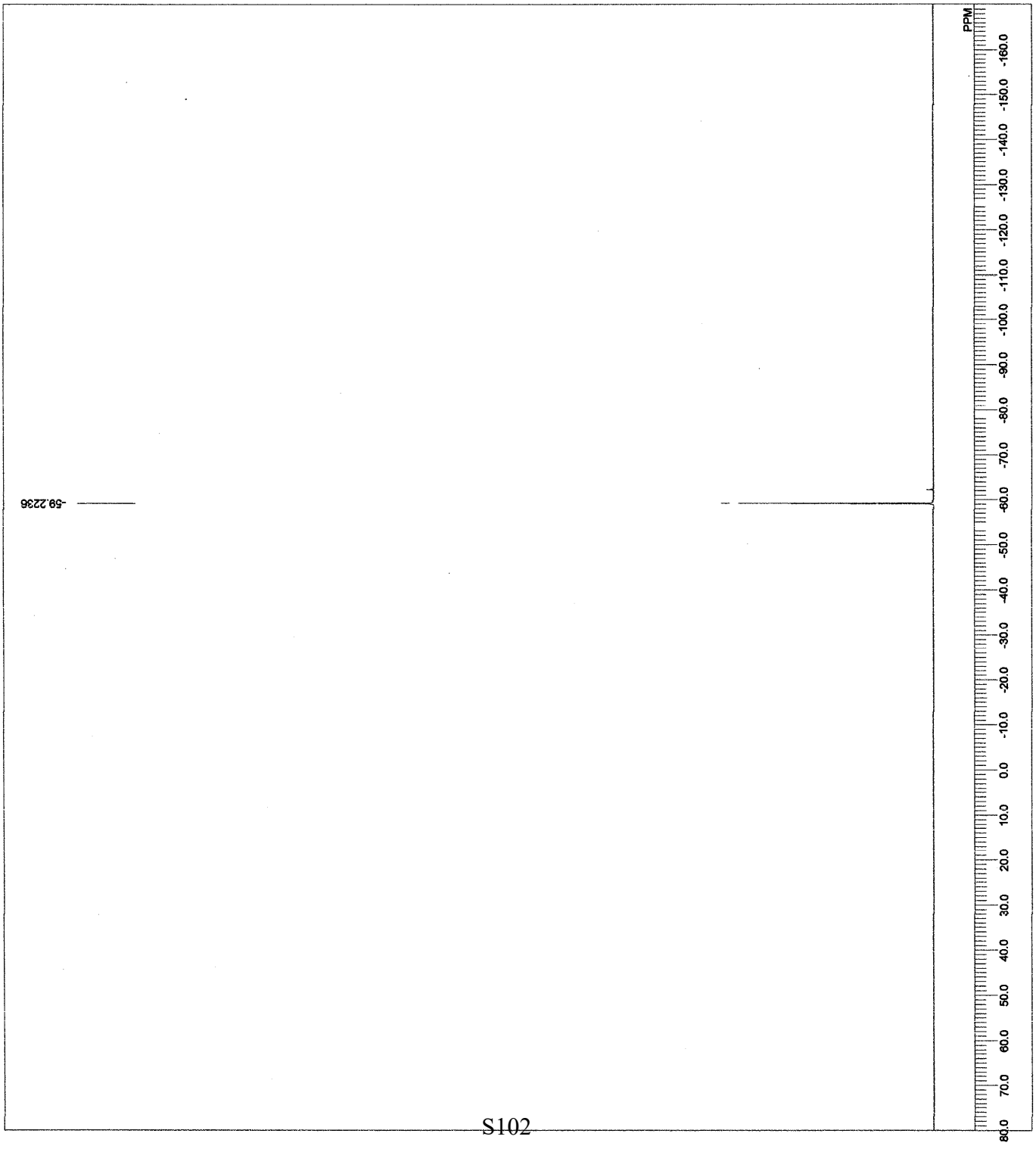
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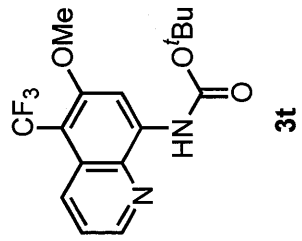
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O^tBu
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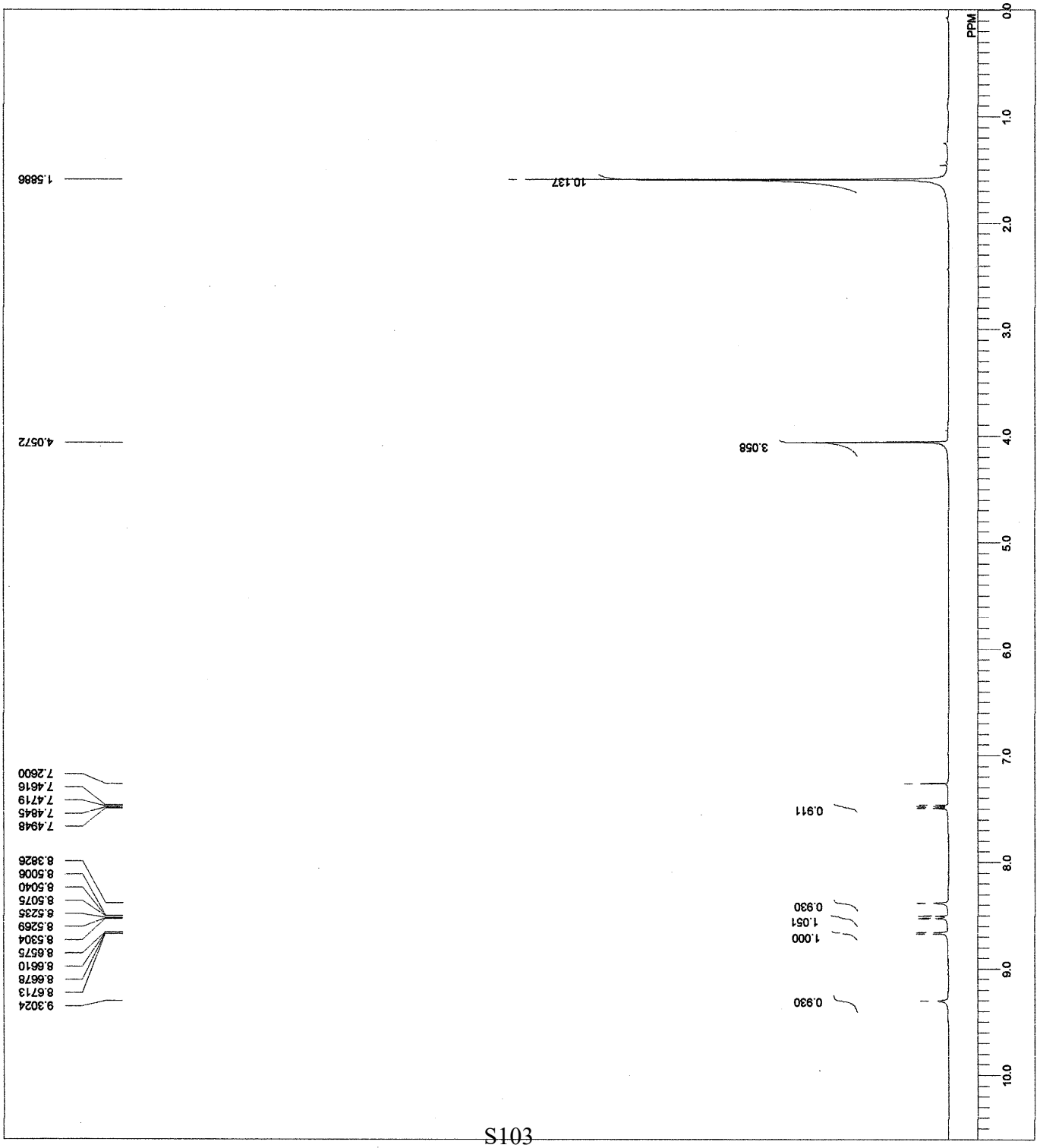
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8.5040
8.5075
8.5235
8.5269
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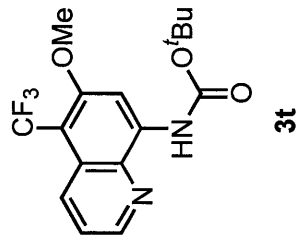
1.051
0.930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O
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CF_3
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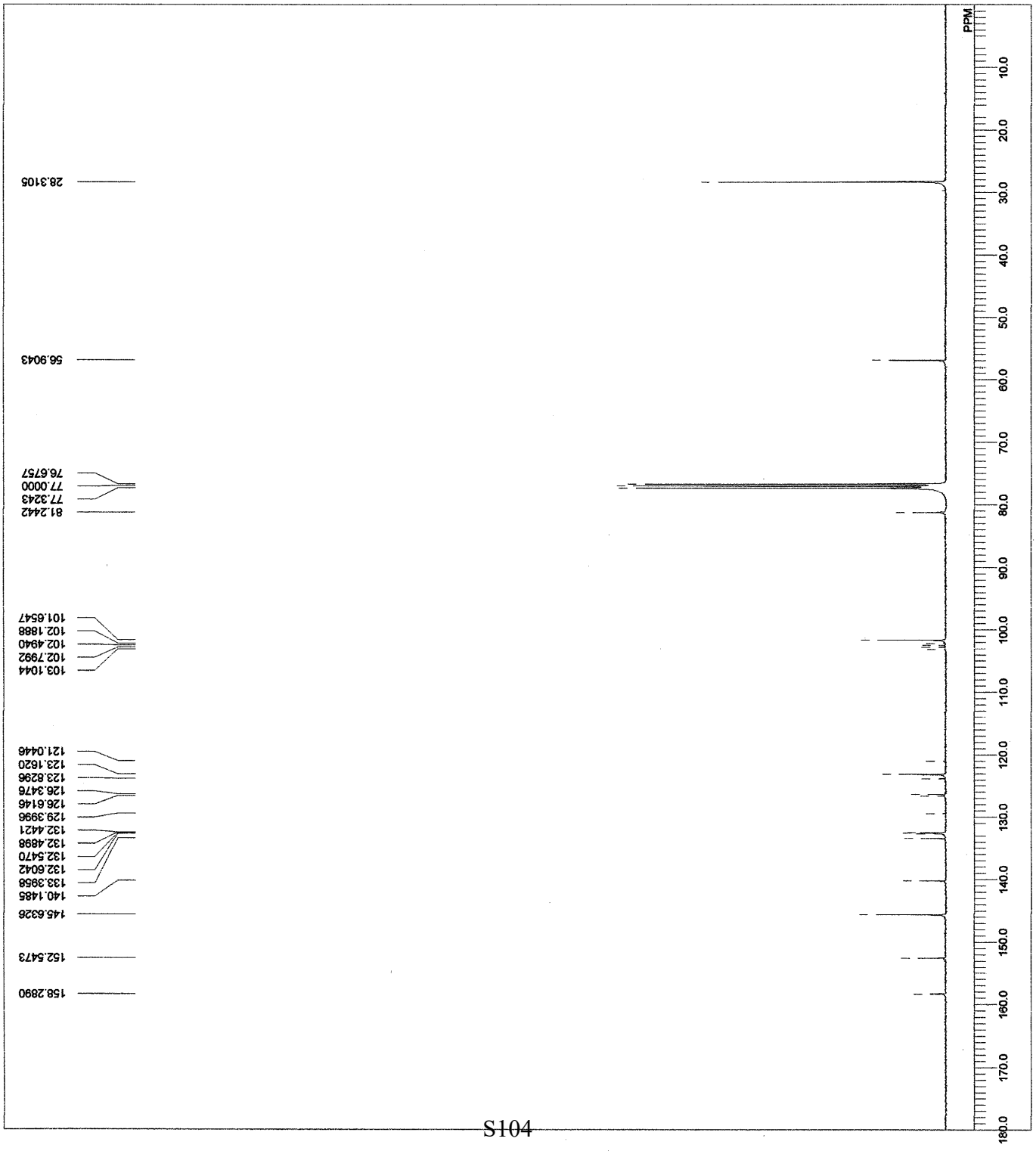
3t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PPM
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60.0
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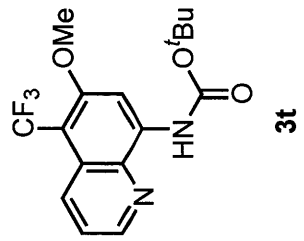
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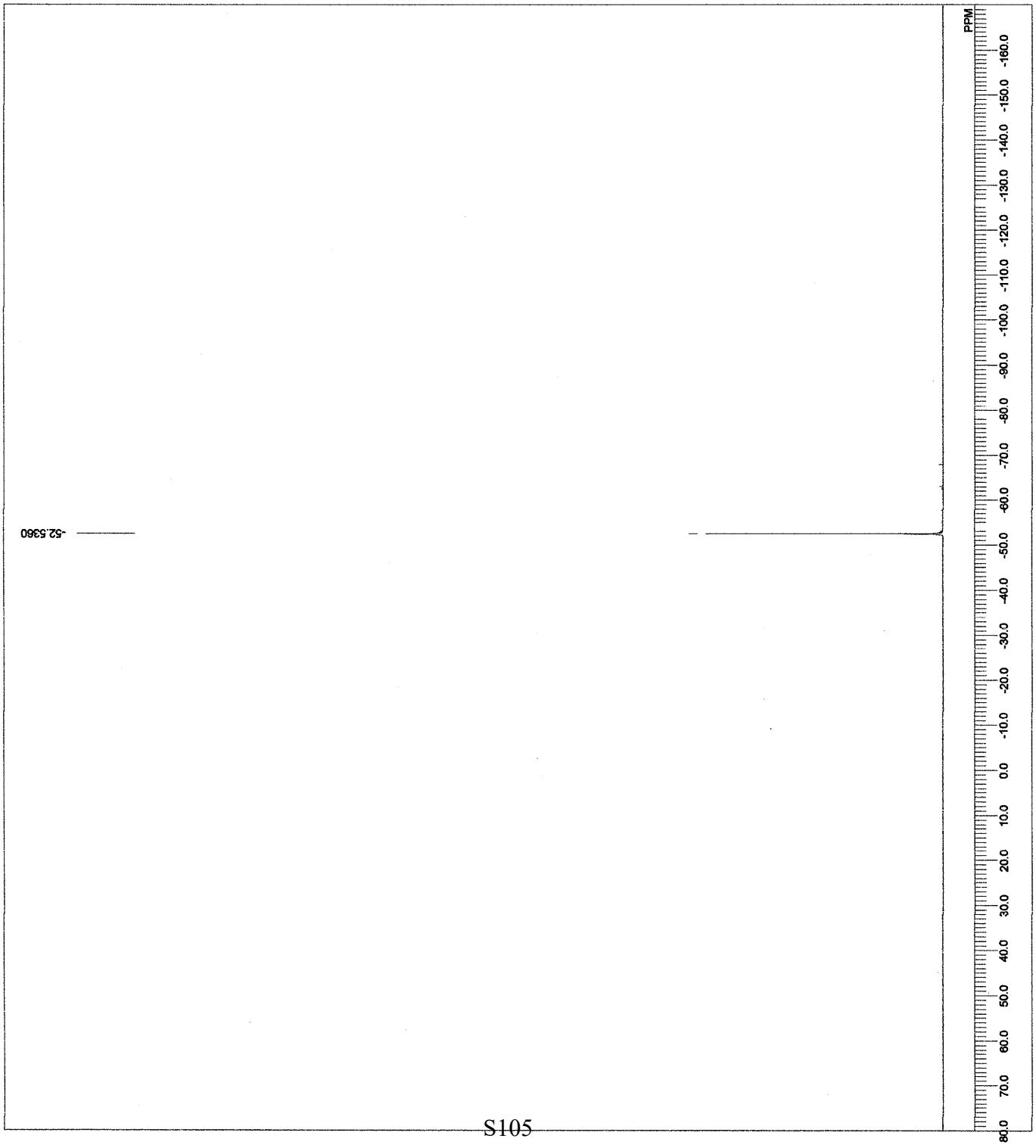
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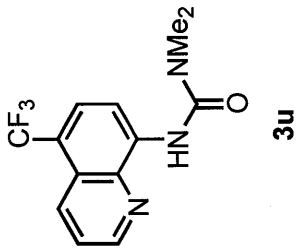
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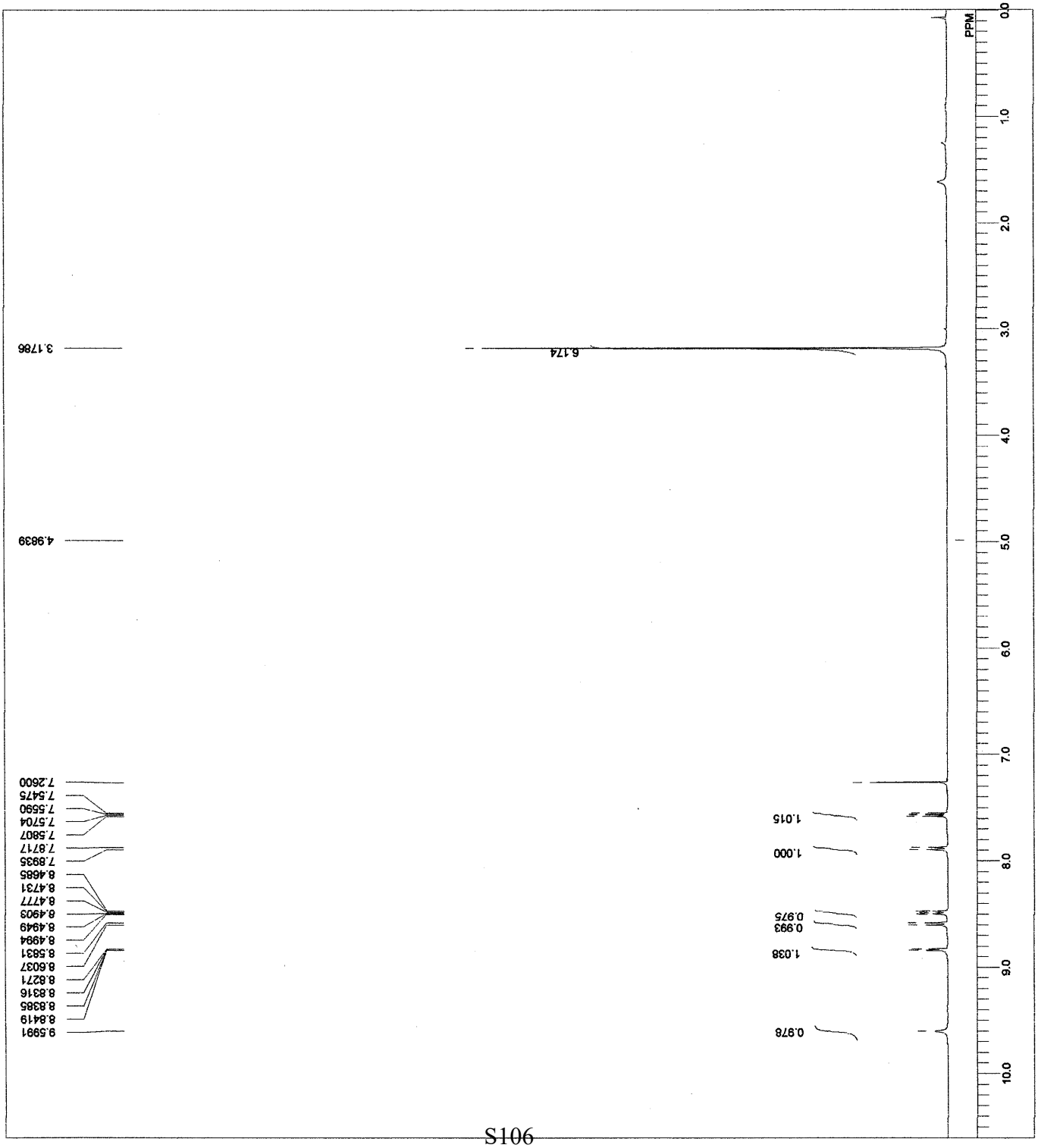
NMe2
N

3u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7.5590
7.5704
7.5807
7.8717
7.8935
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8.4731
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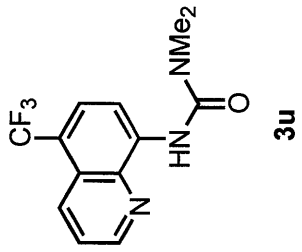
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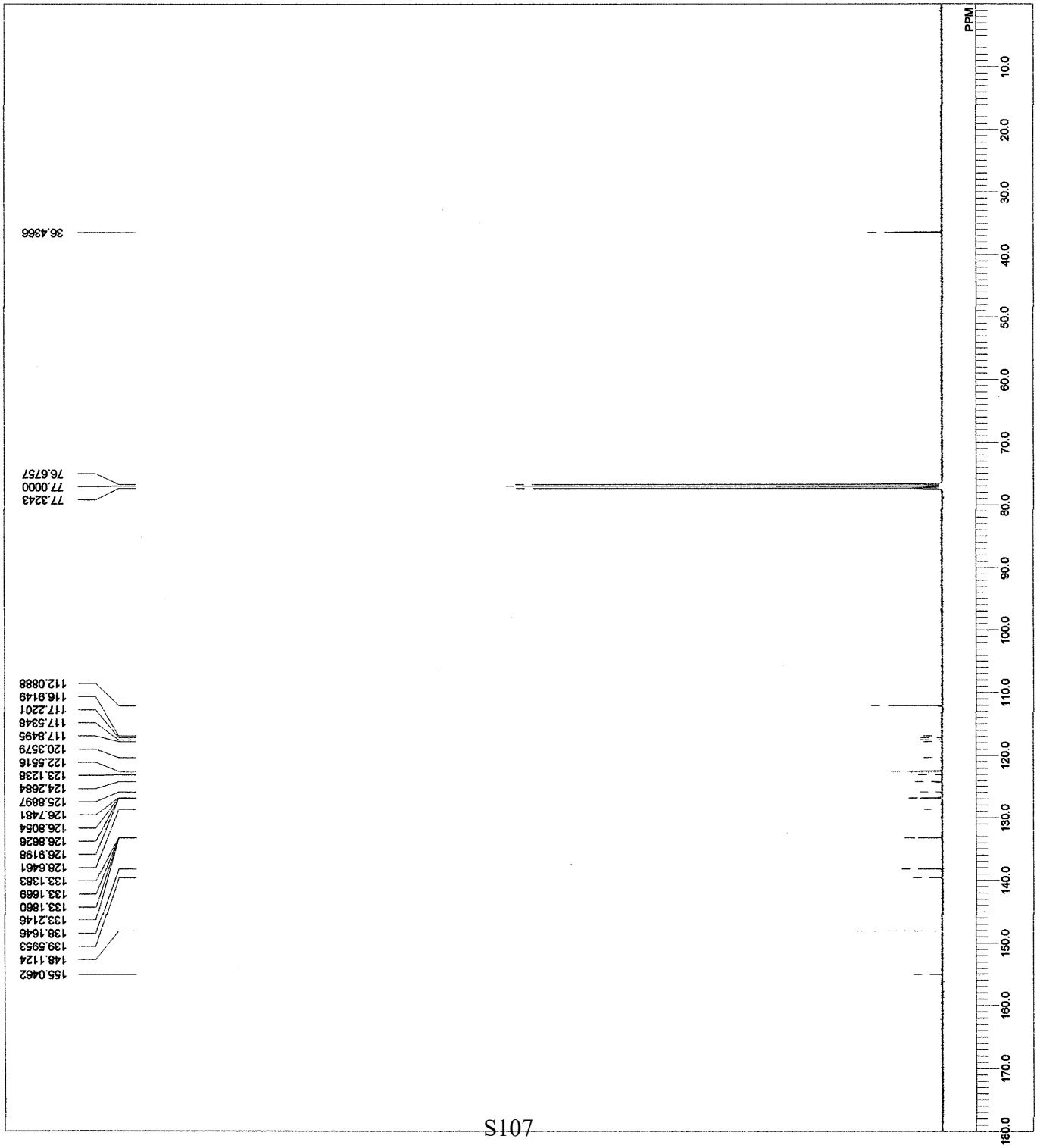
3u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125.8897
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126.9198
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133.1383
133.1669
133.1860
133.2146
138.1646
139.5953
148.1124
155.0462
PPM
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50.0
60.0
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100.0
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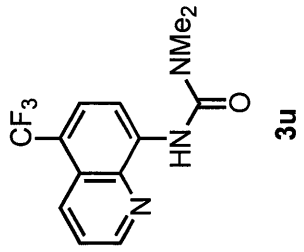
170.0
180.0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NMe2
HN
O
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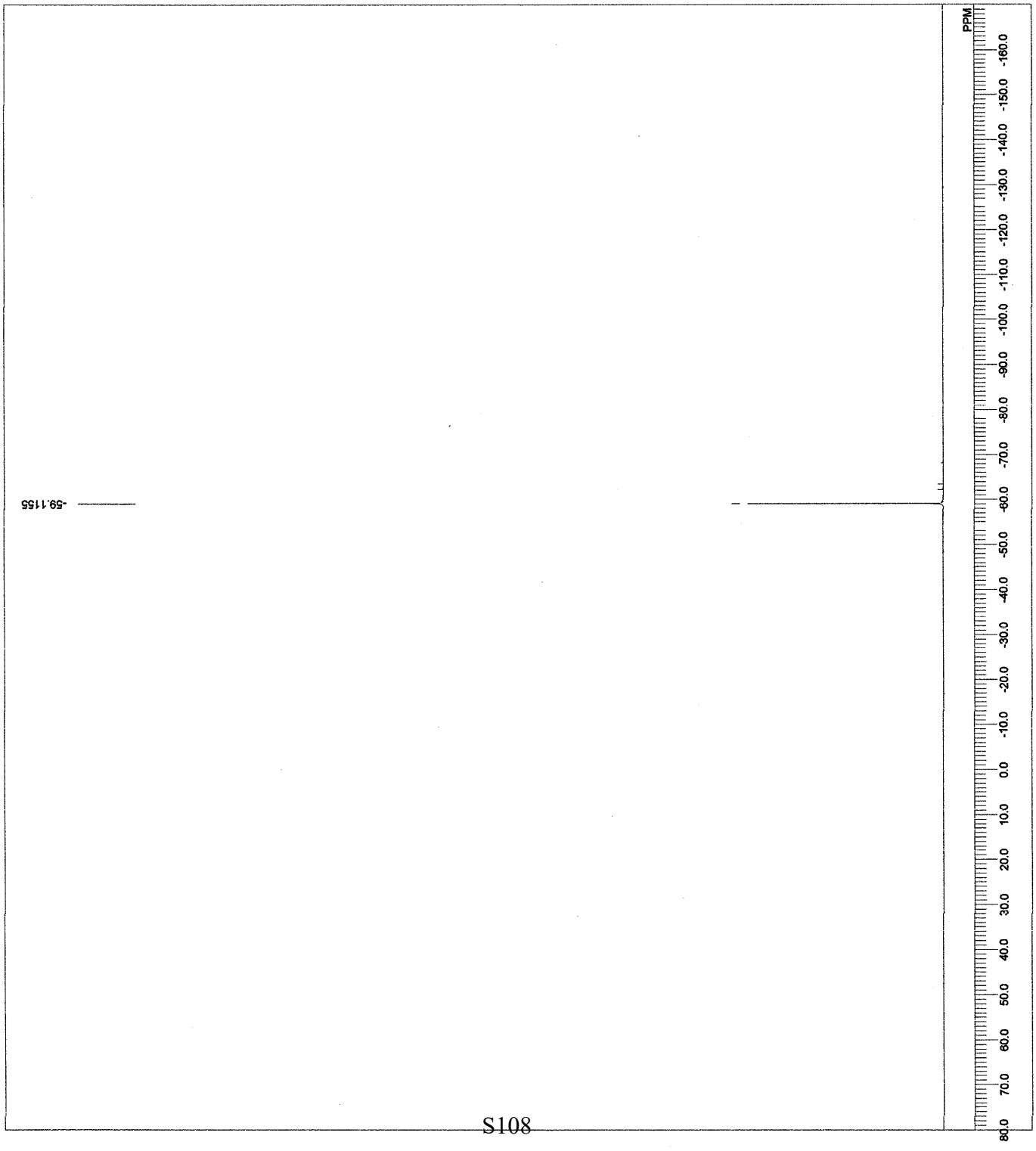
3u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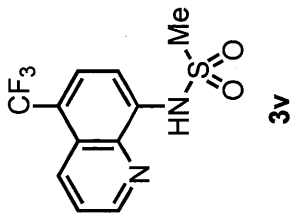
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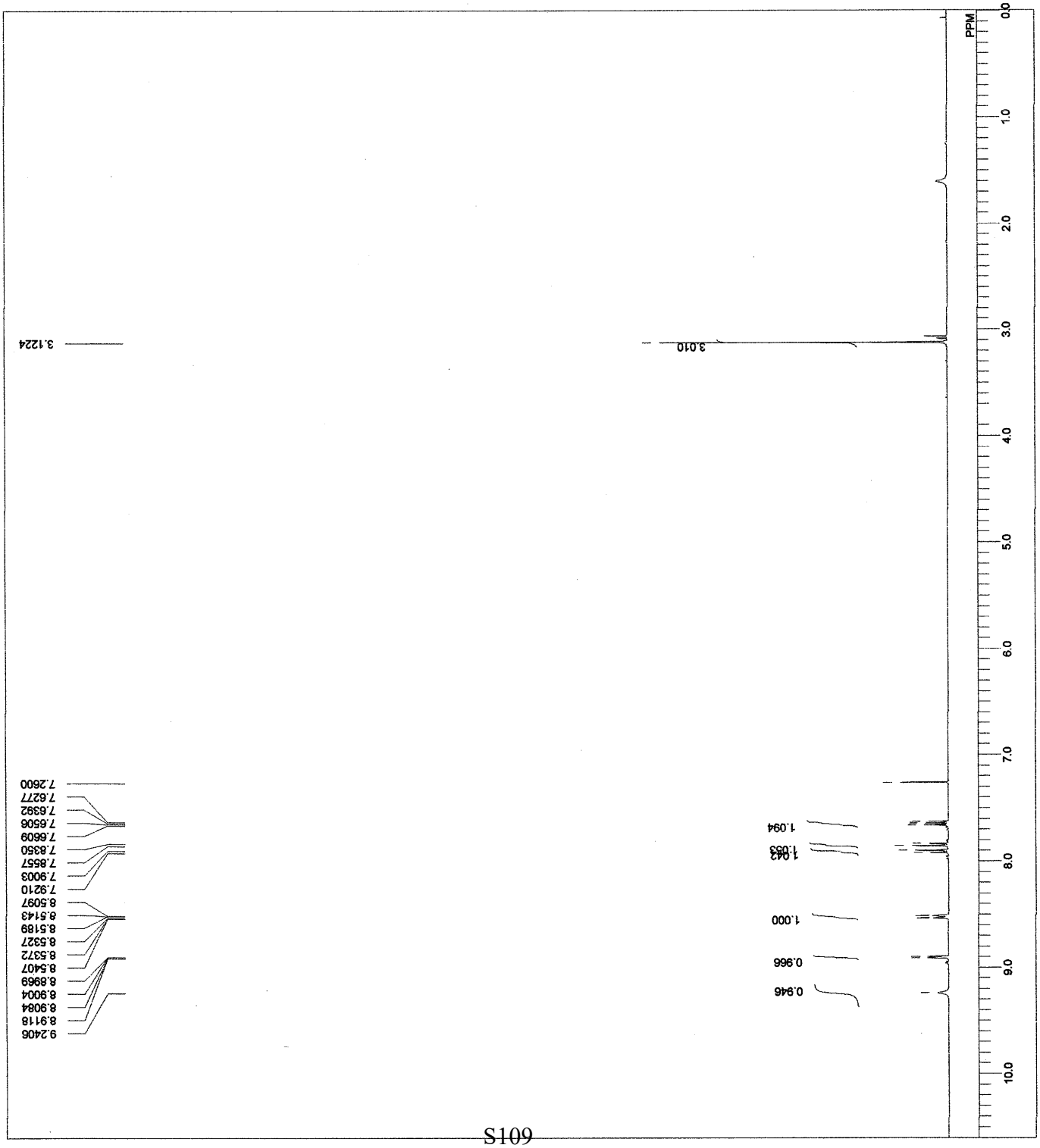
HN
S
Me
O
O
N

3v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1.053
1.043
1.000
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0.946
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8.9004
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8.5327
8.5189
8.5143
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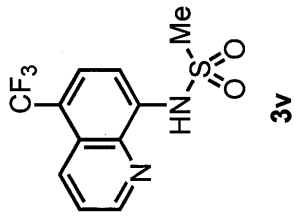
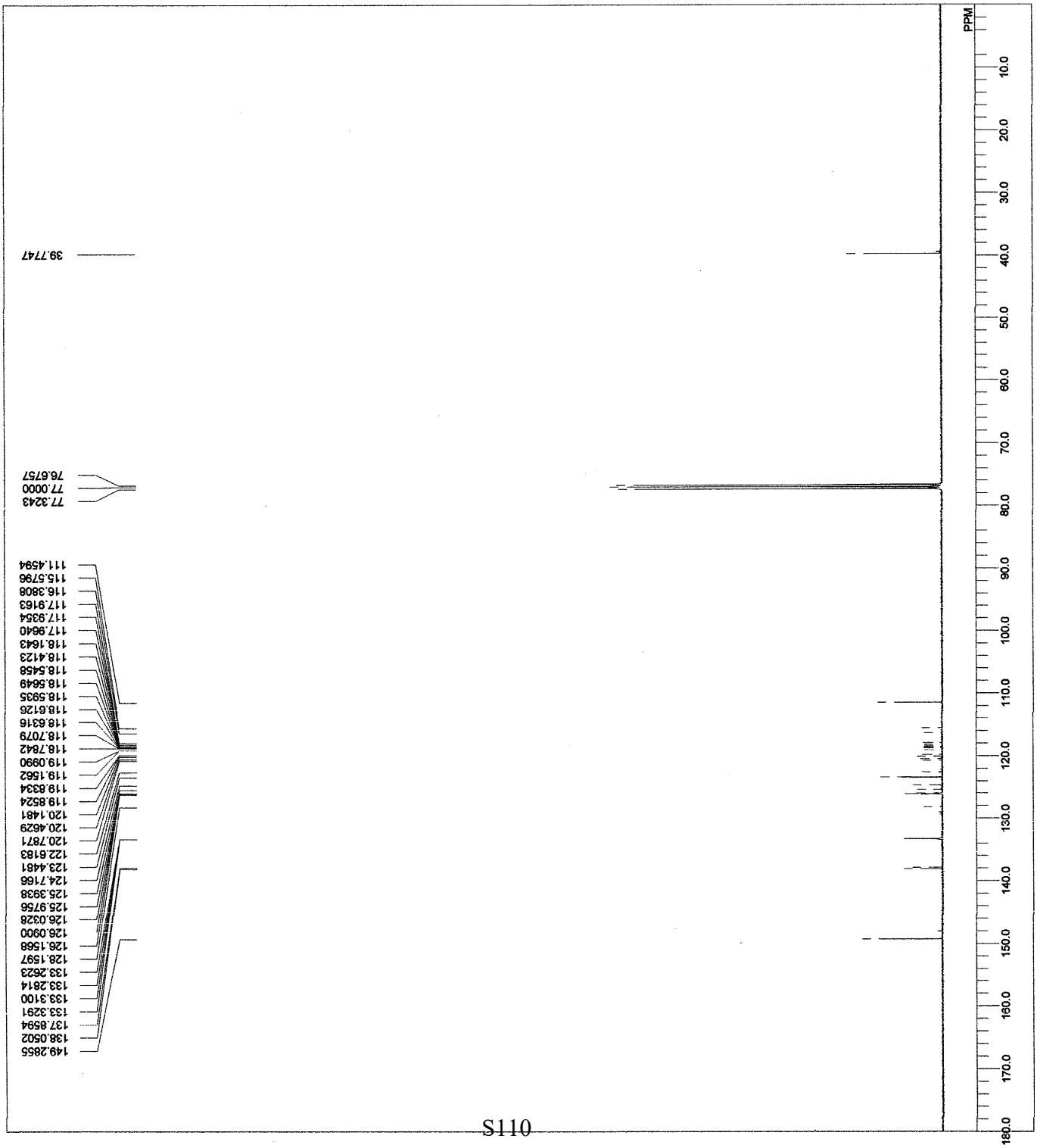
7.6277
7.2600


CF3
HN
S
Me
O
O
N

3v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125.9756
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126.1568
128.1597
133.2623
133.2814
133.3100
133.3291
137.8594
138.0502
149.2855
PPM
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20.0
30.0
40.0
50.0
60.0
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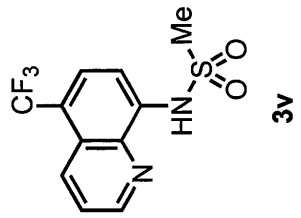
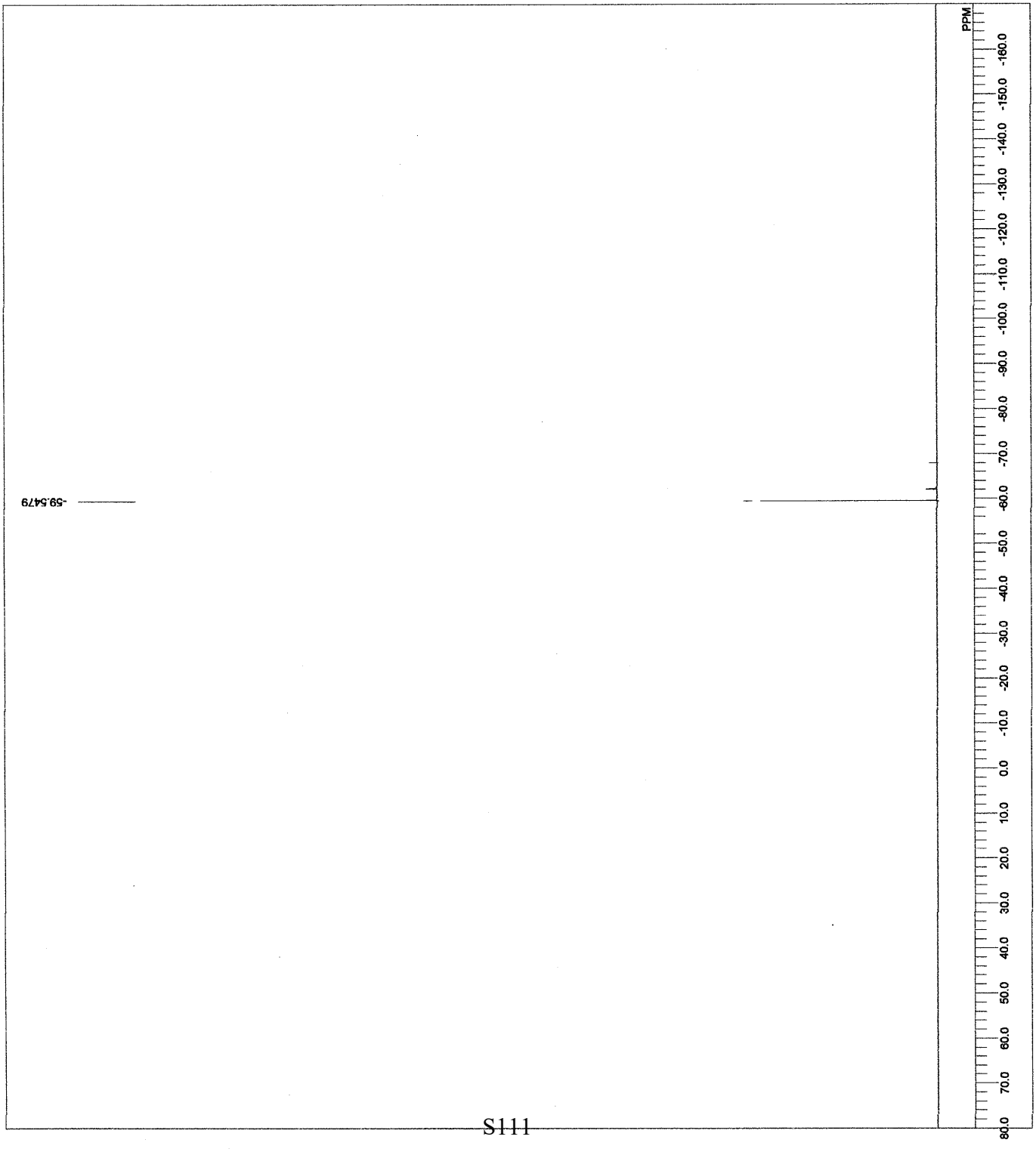


3v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-20.0
-30.0
-40.0
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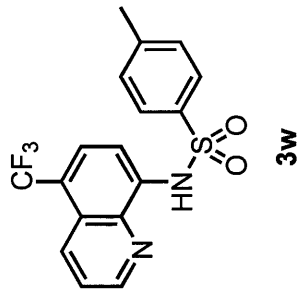
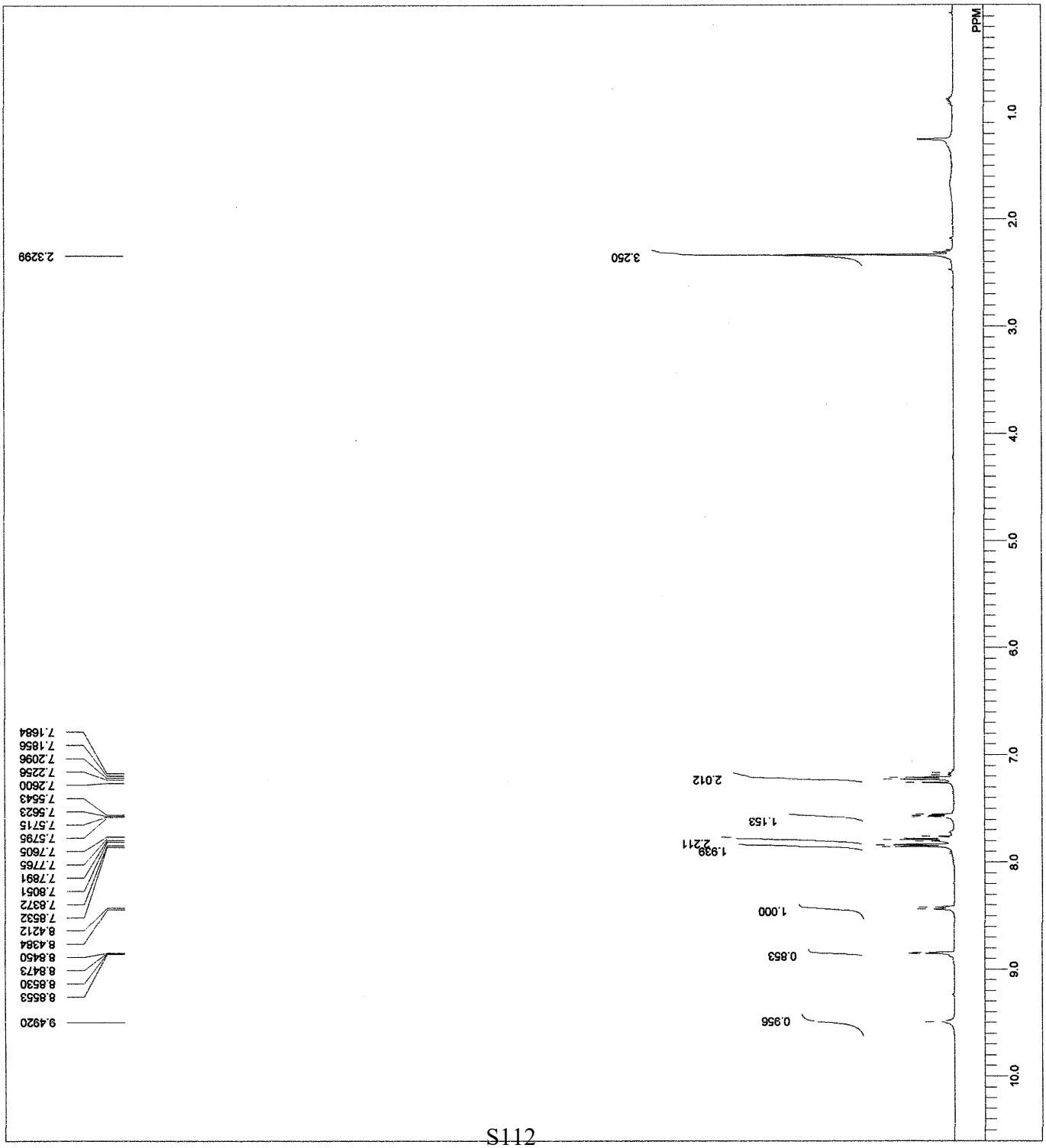

CF3
HN
S
O
O
N

3w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7.2096
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7.5795
7.7605
7.7765
7.7891
7.8051
7.8372
7.8532
8.4212
8.4384
8.8450
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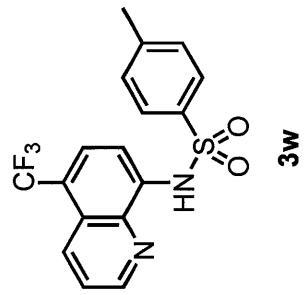
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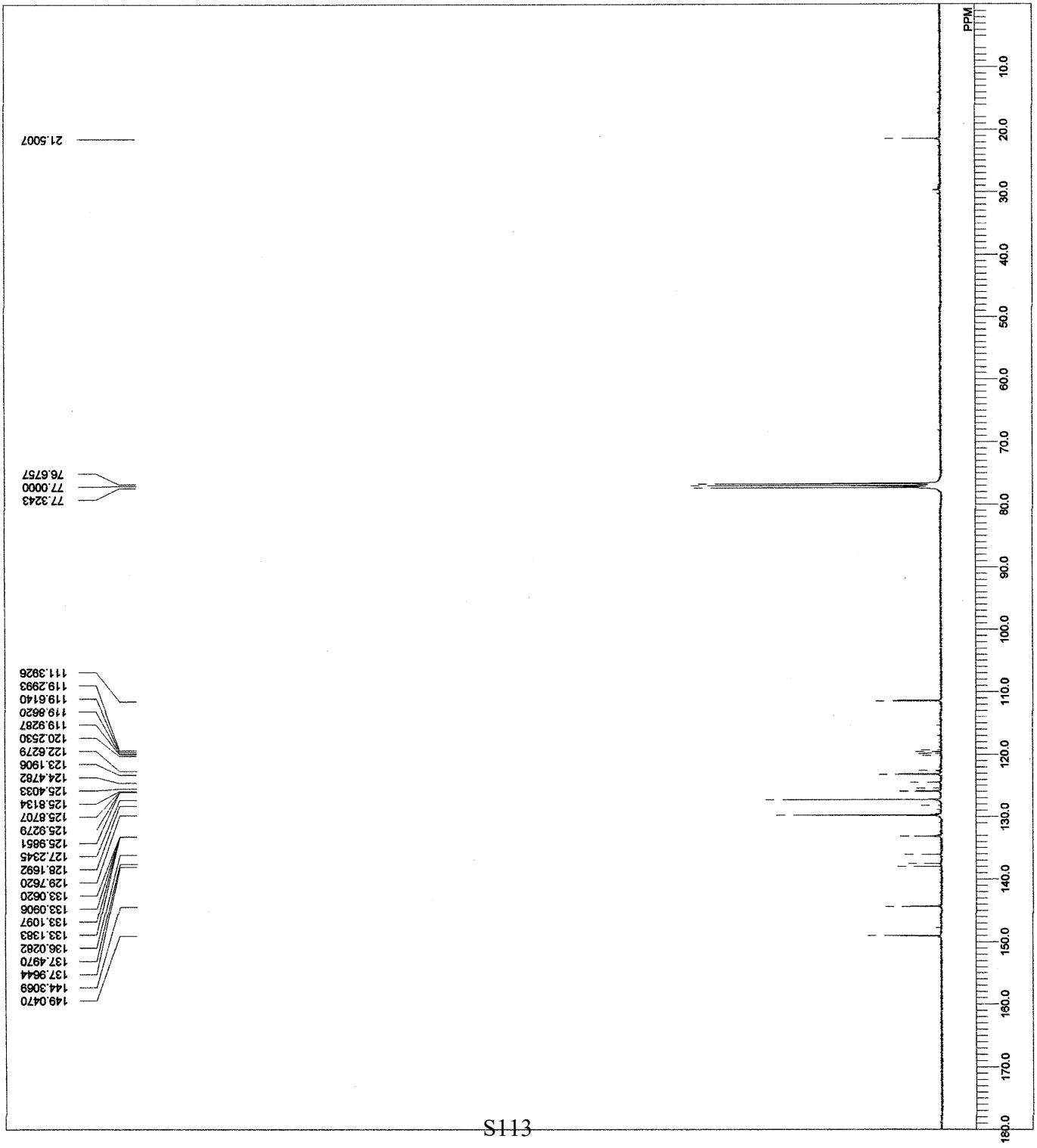
3w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129.7620
133.0620
133.0906
133.1097
133.1383
136.0282
137.4970
137.9644
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149.0470
PPM
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30.0
40.0
50.0
60.0
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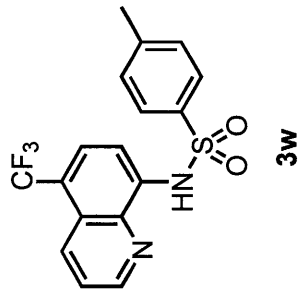

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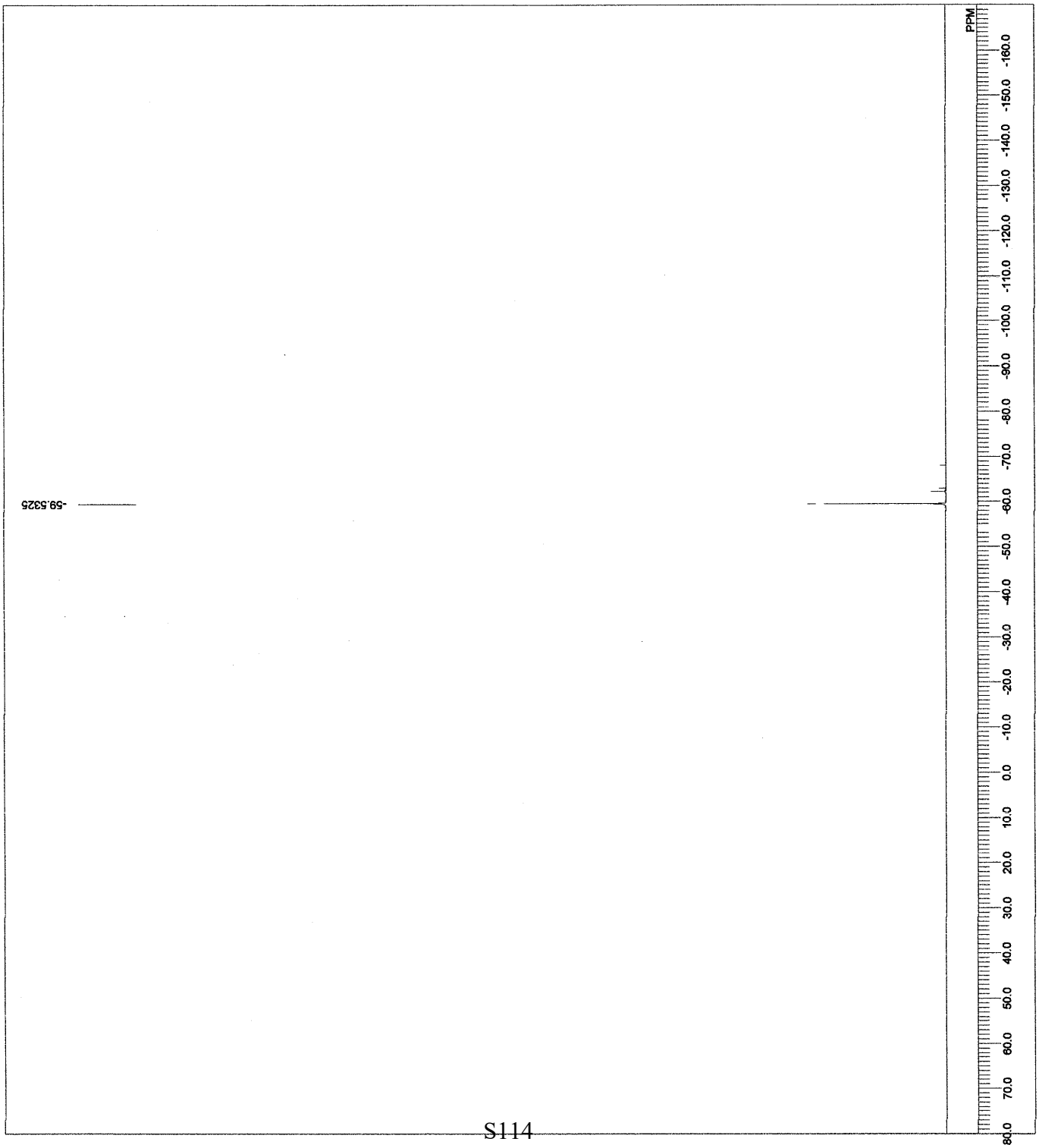
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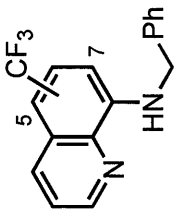
80.0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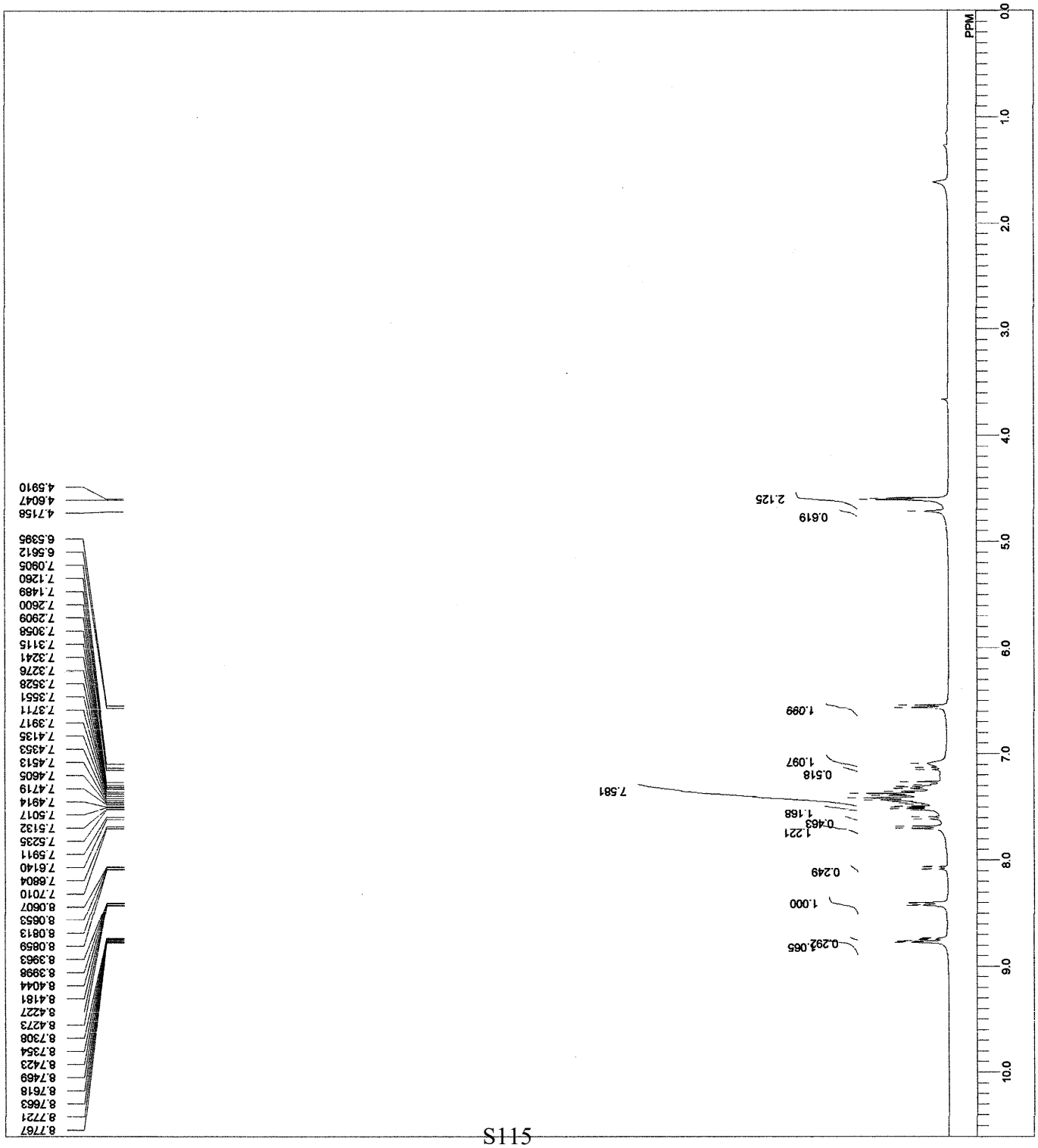
7
HN
Ph
N

5b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0.518
1.097
7.581
0.463
1.168
1.221
0.249
1.000
0.292
0.065
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4.7158
8.5385
8.5612
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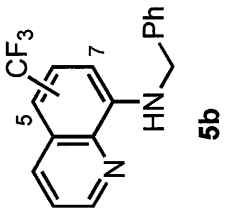
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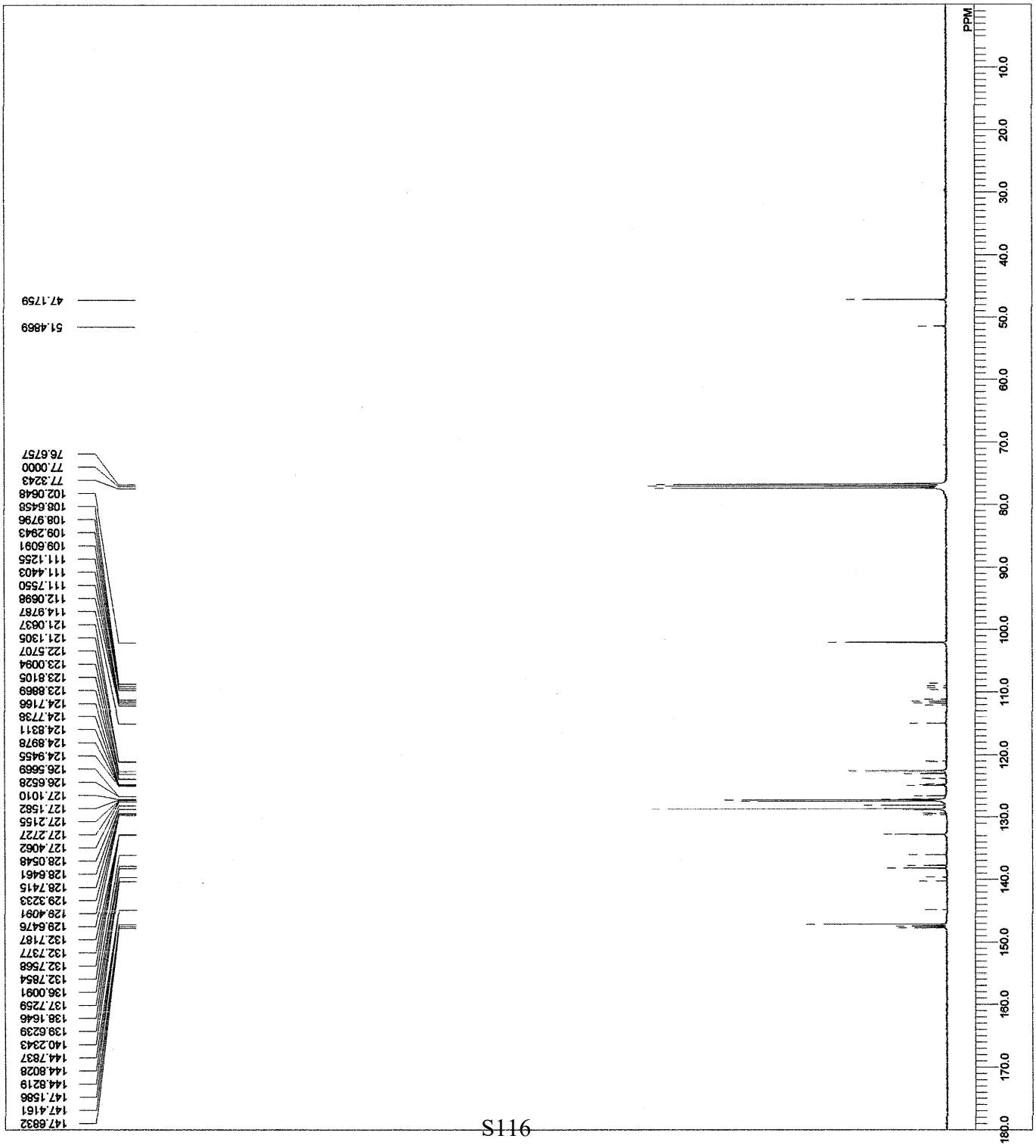
7
HN
Ph
N

5b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139.6239
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PPM
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20.0
30.0
40.0
50.0
60.0
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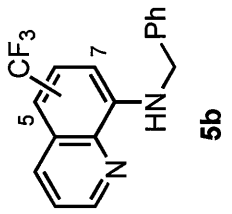
180.0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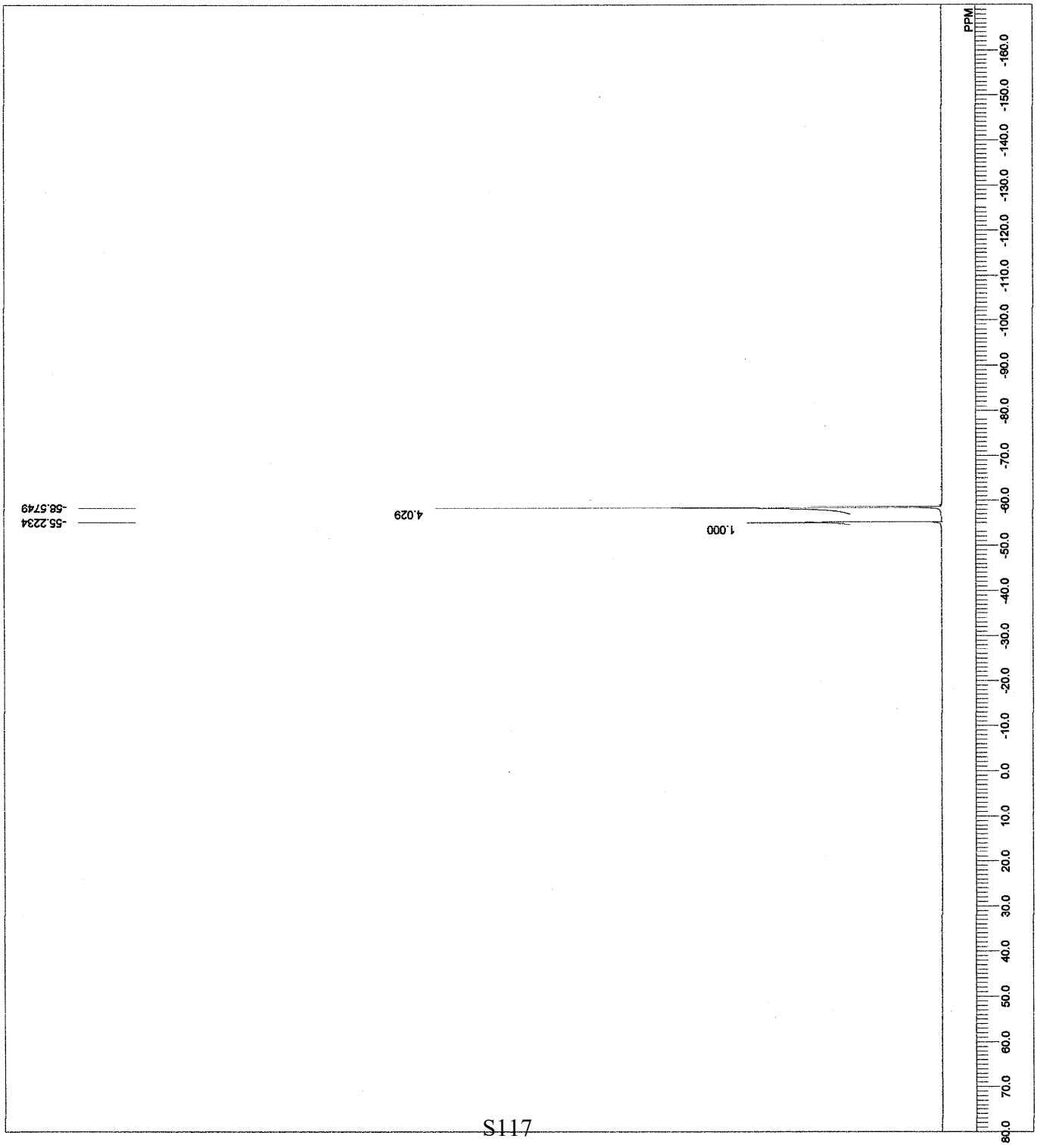
7
HN
Ph
N

5b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-100.0
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-70.0
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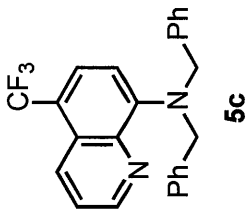
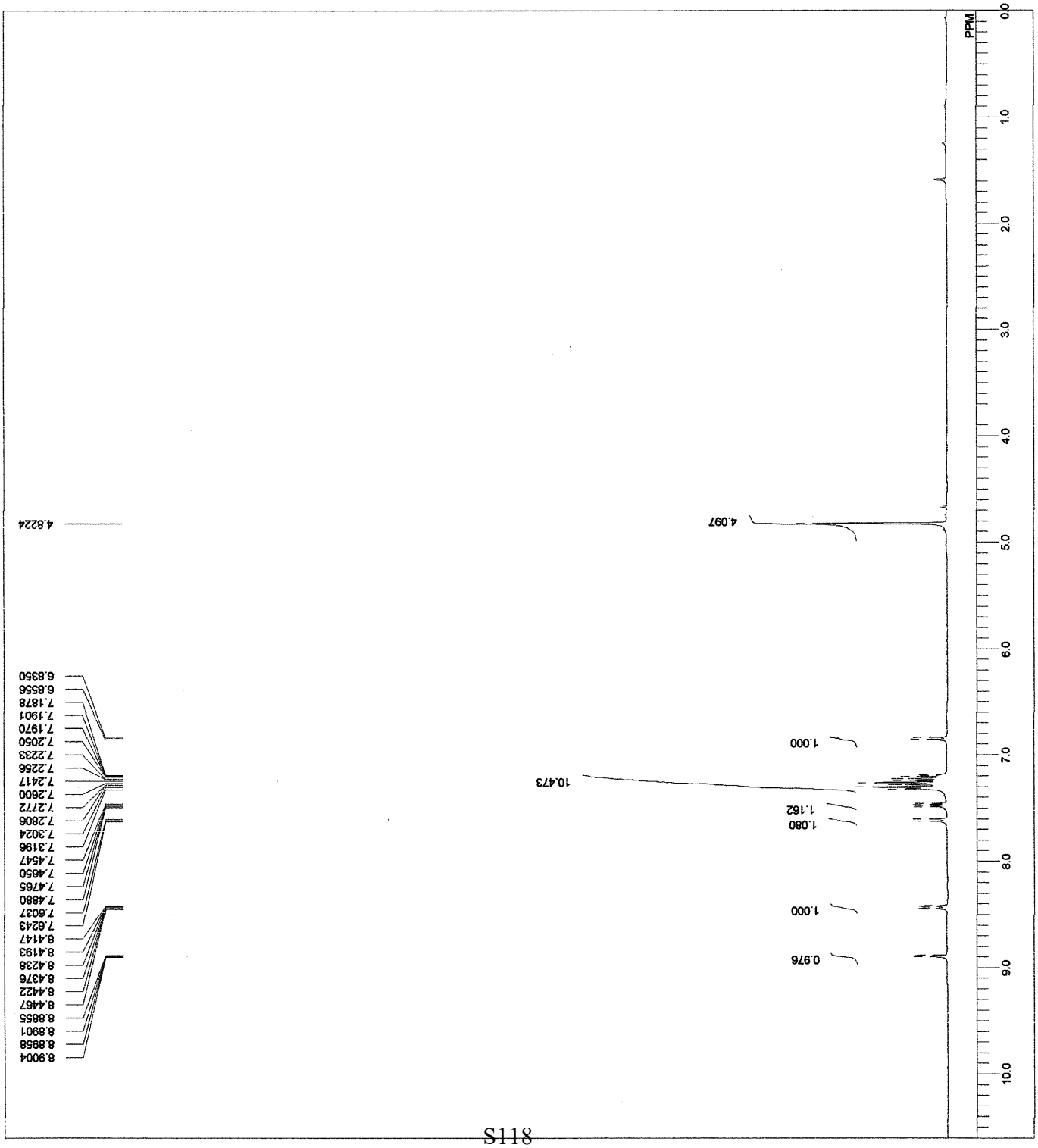
80.0


CF3
N
Ph
Ph
N

5c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10.473
1.162
1.080
1.000
0.976
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8.4422
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8.4147
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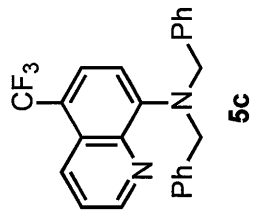
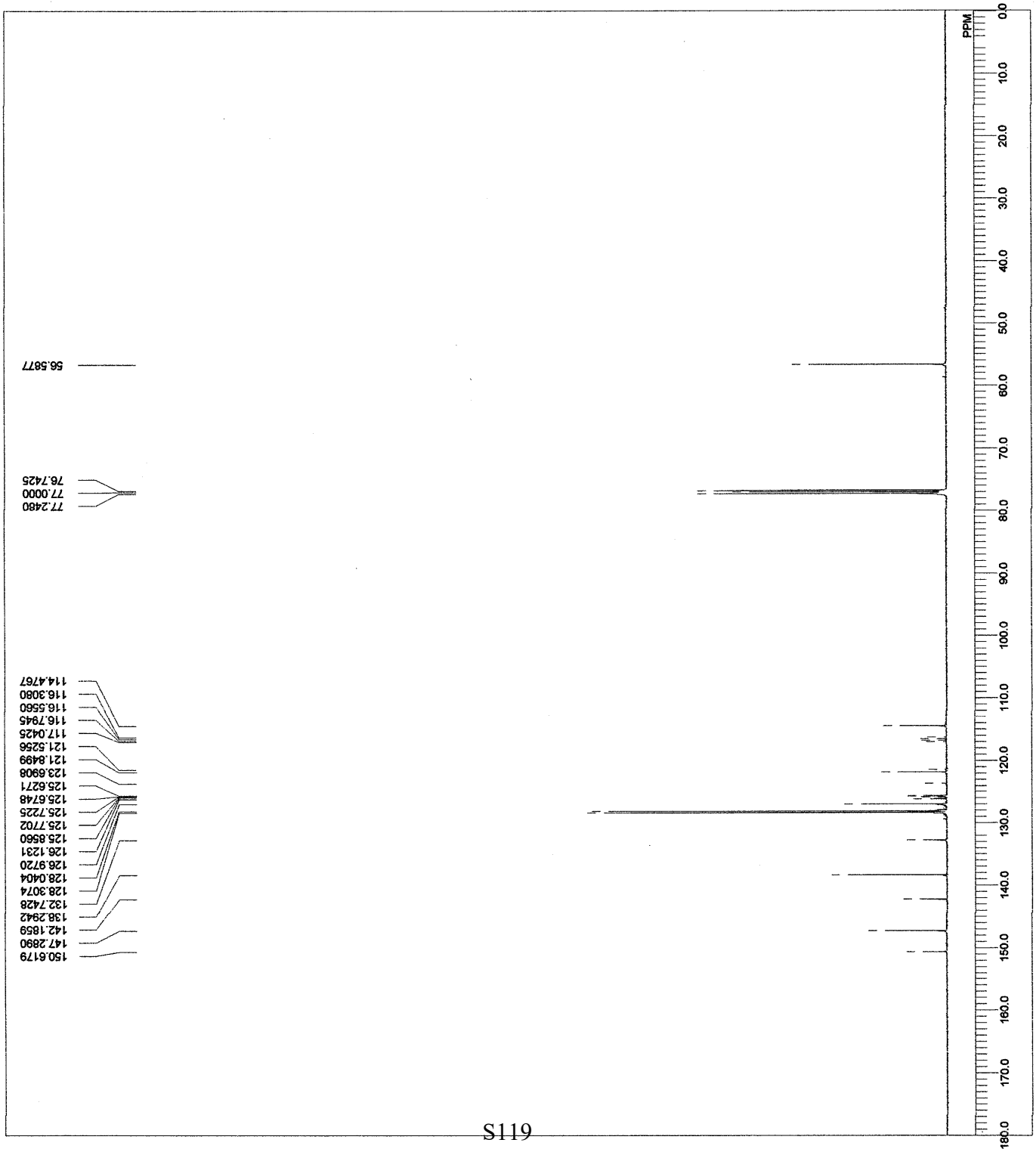

CF3
N
Ph
N
Ph

5c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125.7225
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125.8560
126.1231
126.9720
128.0404
128.3074
132.7428
138.2942
142.1859
147.2890
150.6179
PPM
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10.0
20.0
30.0
40.0
50.0
60.0
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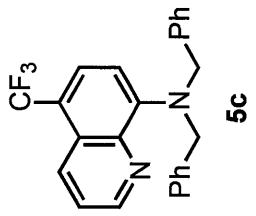
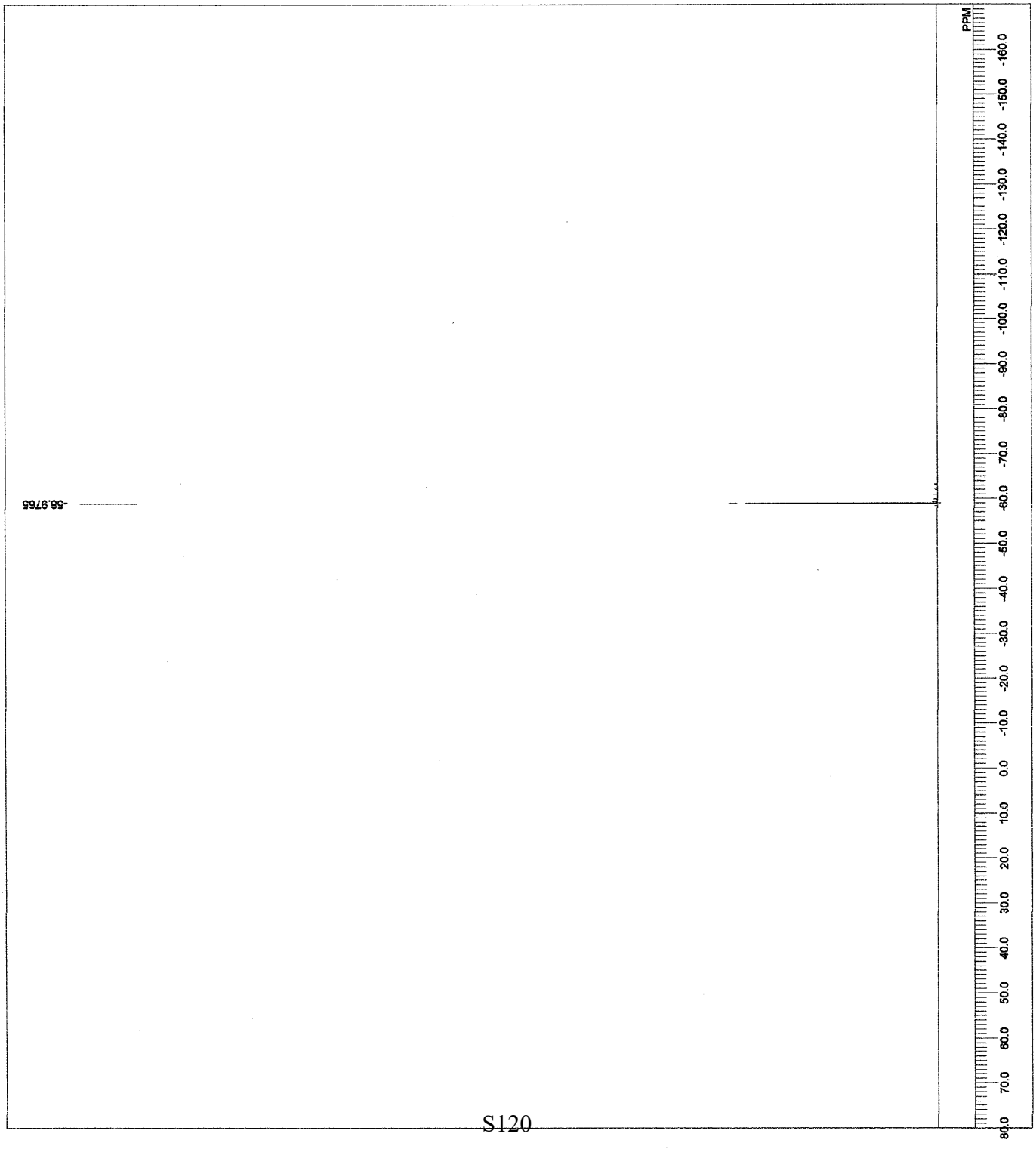

CF3
N
Ph
N
Ph

5c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80.0