Supporting Information

Copper-catalyzed synthesis of 2-aminophenyl benzothiazoles: A novel approach

S N Murthy Boddapati,[ab] Chandra Mohan Kurmarayuni,[a] Baby Ramana Mutchu,[a] Ramana Tamminana,[c] Hari Babu Bollikolla[a,*]

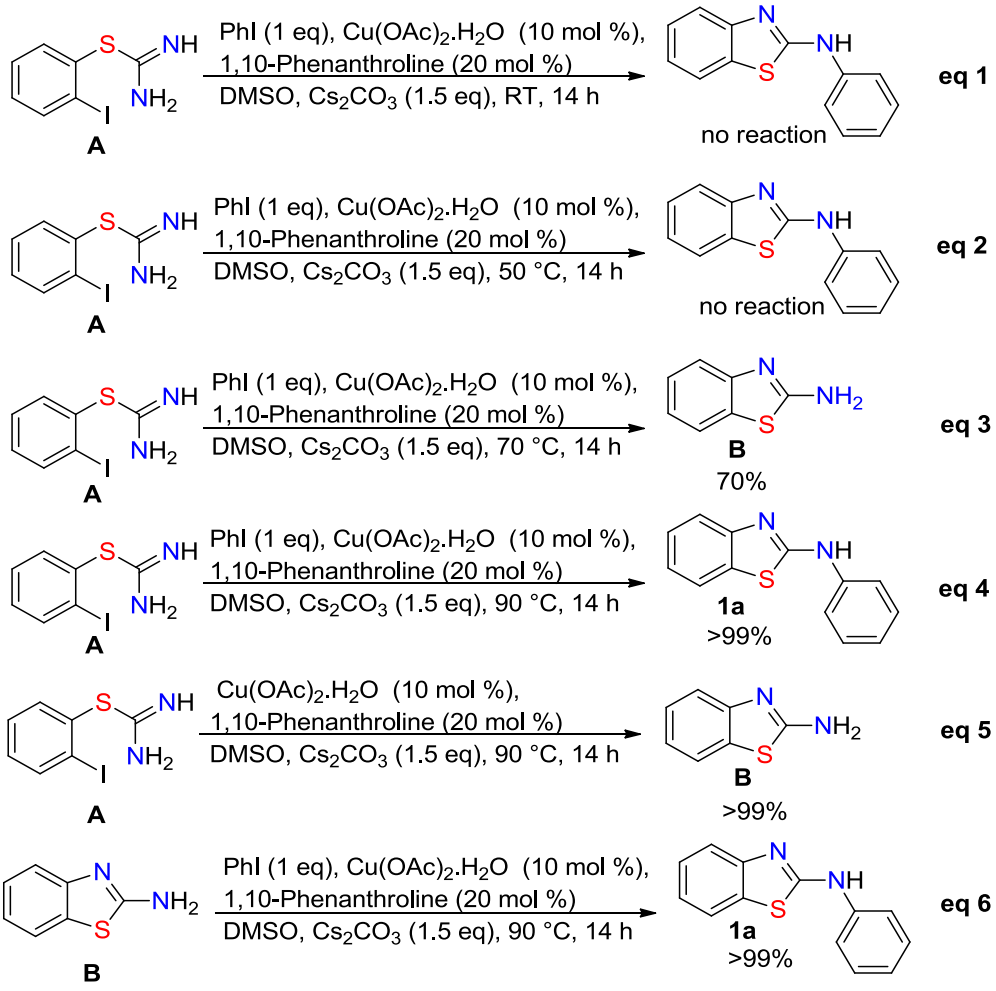
[a]*Department of Chemistry, Acharya Nagarjuna University, NNagar-522 510, Guntur, AP-India*

[b] *Department of Chemistry, C R Reddy P G College, Eluru-534002, AP-India*

[c]*Department of chemistry, GITAM Deemed to be University, Bengaluru Campu, Karnataka, India-562163.*

General Information: Thiourea, $CuSO_4 \cdot 5H_2O$ (98%), CuI (98%), CuBr (98%), Cu_2O (97%), CuCl (99%), $CuSO_4 \cdot 5H_2O$ (99%) and $Cu(OAc)_2 \cdot H_2O$ (98%), Et_3N, Pyridine, sodium bicarbonate, $K_3PO_4 \cdot 3H_2O$, KOH, K_2CO_3, Cs_2CO_3 were purchased from Aldrich and used without further purification. The solvents were purchased and dried according to standard procedure prior to use.[1] ^{1}H NMR (400 MHz) spectra were recorded with a Varian 400 spectrometer. Infrared (IR) spectra recorded on a Perkin Elmer Spectrum one FT-IR spectrometer. VKSI Medico Centrifuge machine was used for our experimental procedure for the synthesis of substituted 2-iodophenyl isothiourea.

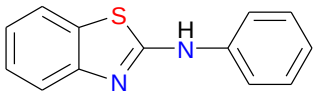
Control experiments:



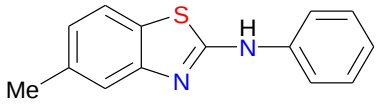
To reveal the mechanism control experiments were performed. When we have done the reaction at room temperature and 50 °C no target product could be occurred (eq 1 & eq 2), however, the reaction could give exclusively intra molecular *C-N* cyclised product 2-amino benzothiazole **B** in 70% (eq 3), whereas the reaction gave target product **1a** in complete conversion at 90 °C (eq 4). In addition, the reaction was also performed in the absence of aryl iodide under optimized reaction conditions and it gave intra molecular *C-N* cyclised product 2-amino benzothiazole **B** (eq 5). Furthermore, 2-amino benzothiazole readily underwent reaction with iodobenzene under optimized conditions to afford target product **1a** in complete conversion (eq 6). The above results clearly suggest that the 2-iodophenyl isothiourea **A** gave first intra molecular *C-N* cyclized product as 2-amino benzothiazole **B** that may react with iodo benzene to give final product **1a** by inter molecular *C-N* cross-coupling reaction.

General procedure for the synsthesis of 2-iodophenyl isothiourea: To a stirred solution of DMSO (2-3 ml), thiourea (1 mmol, 76 mg) was added in slowly and followed by Et_3N (1 mmol, 101 mg) and $CuSO_4.5H_2O$ (50 mol %, 125 mg) were added at room temperature. The whole reaction mixture stirred for one hour (until get the black colour) at room temperature. Later, to the previous solution, 2-iodothiophenol (2 mmol, 470 mg) was added. After completion of the reaction (monitored by TLC), the reaction mixture was transferred into centrifuged tubes and the mixture was centrifuged for 10 min by using centrifugation machine. Black colour solid was removed from the centrifuged tubes. The clear solution was concentrated by using rotary evaporator and the crude mixture was purified by silica gel (60-120 mesh) column chromatography using Ethylacetate in Hexane as eluent to obtain a 2-iodophenyl isothiourea as solid.

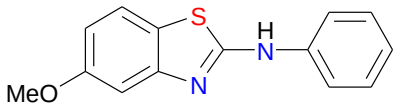
General Procedure for the synthesis of 2-(*N*-aryl)benzothiozole: To a stirred mixture of DMSO (2 ml) and *N*-2-iodoaryl isothiourea (1 mmol), iodobenzene (1 mmol, 204 mg), Cs_2CO_3 (1 mmol, 325 mg), $Cu(OAc)_2.H_2O$ (10 mol %, 20 mg) and 1,10-phenanthroline (20 mol %, 36 mg) were added consecutively in slowly for several min and the reaction mixture was stirred for 14 h at 90 °C. Progress of the reaction was monitored by TLC using ethyl acetate and hexane (1:9). After completion of the reaction, the reaction mixture was cooled to room temperature. Then, the solution was washed with ethyl acetate (7 ml) and water (3 mL) for 5 times. The organic layer was evoparated and crude reaction mixture was purified by by silica gel (60-120 mesh) column chromatography using ethylacetate in hexane as eluent to obtain final product 2-(*N*-arylamino)benzothiozole which was characterized by NMR (^1H and ^{13}C), IR and elemental analysis.



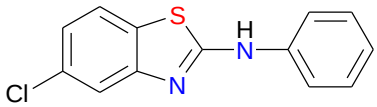
***N*-Phenylbenzo[*d*]thiazol-2-amine 1a**.[2] White solid; yield 96%; mp 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (dd, *J* = 1.6 Hz, 7.6 Hz**,** 1H), 7.49-7.45 (td, *J* = 1.6 Hz, 7.6 Hz, 1H), 7.34-7.31 (dd, *J* = 1.2 Hz, 8.4 Hz, 1H), 7.26-7.21 (m, 2H), 7.18-7.08 (m, 2H), 7.01-6.99 (m, 1H), 6.96-6.94 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 137.7, 135.1, 131.9, 129.6, 127.1, 126.7, 124.3, 117.5, 115.4, 110.3; FT-IR (KBr) 3148, 1590, 1578, 1490, 1438, 1409, 1288, 1261, 1078, 1023 cm^{-1}. Anal. Calcd. for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38; S, 14.17. Found: C, 69.11; H, 4.43; N, 12.35; S 14.11.



6-Methyl-*N*-phenylbenzo[*d*]thiazol-2-amine 1b.[2] White solid; yield 90%; mp 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.30-7.19 (m, 5H), 7.04-7.01 (m, 2H), 6.81 (br s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.4, 135.3, 134.1, 132.7, 129.6, 127.0, 126.7, 115.3, 110.0, 20.7; FT-IR (KBr) 3342, 3210, 2922, 1605, 1510, 1479, 1454, 1445, 1434, 1314, 1225, 1159, 1071, 1028 cm^{-1}. Anal. Calcd. for $C_{14}H_{12}N_2S$: C, 69.97; H, 5.03; N, 11.66; S, 13.34. Found: C, 70.07; H, 5.01; N, 11.62; S, 13.26.

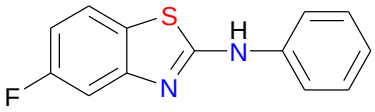


6-Methoxy-*N*-phenylbenzo[*d*]thiazol-2-amine 1c. White solid; yield 96%; mp 132-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.26-7.18 (m, 4H), 6.82-6.79 (m, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 138.4, 136.7, 134.0, 132.7, 132.1, 120.1, 116.4, 115.6, 115.0, 110.9, 55.5; FT-IR (KBr) 3288, 3153, 2919, 2873, 1572, 1486, 1455, 1408, 1384, 1284, 1260, 1100, 1017, 934 cm^{-1}. Anal. Calcd. for $C_{14}H_{12}N_2OS$: C, 65.60; H, 4.72; N, 10.93; O, 6.24; S, 12.51. Found: C, 65.76; H, 4.70; N, 10.88; S, 12.45.

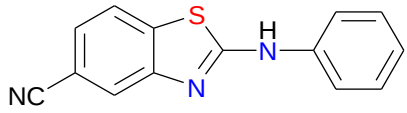


6-Chloro-*N*-phenylbenzo[*d*]thiazol-2-amine 1d.[3] White solid; yield 81%; mp 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.28-7.19 (m, 4H), 7.10-7.08 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.2, 134.3, 132.8, 131.1, 130.8, 130.0, 128.7, 115.2, 114.5, 110.7; FT-

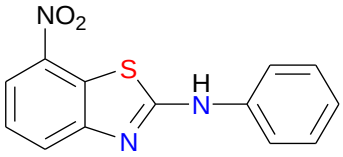
IR (KBr) 3255, 1677, 1607, 1581, 1548, 1453, 1401, 1367, 1265, 1155, 1018 cm^{-1}. Anal. Calcd. for $C_{13}H_9ClN_2S$: C, 59.88; H, 3.48; Cl, 13.60; N, 10.74; S, 12.30 Found: C, 60.02; H, 3.47; N, 10.69; S, 12.24.



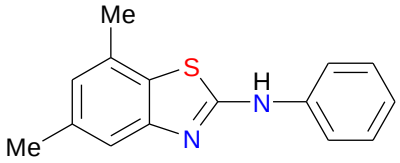
6-Fluoro-*N*-phenylbenzo[*d*]thiazol-2-amine 1e.[3] White solid; yield 70%; mp 109-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.26-7.08 (m, 2H), 6.57-6.55 (m, 3H), 6.92-6.90 (m, 2H), 6.74 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 137.9, 136.5, 133.8, 133.4, 131.6, 117.3, 116.7, 116.4, 114.9, 111.1; FT-IR (KBr) 3157, 1658, 1599, 1516, 1428, 1411, 1242, 1197, 1065, 1022 cm^{-1}. Anal. Calcd. for $C_{13}H_9FN_2S$: C, 63.92; H, 3.71; F, 7.78; N, 11.47; S, 13.13. Found: C, 64.08; H, 3.70; N, 11.40; S, 13.07.



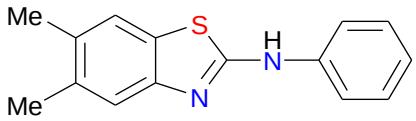
2-(Phenylamino)benzo[*d*]thiazole-6-carbonitrile 1f. White solid: yield 60%; mp 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.29-7.22 (m, 3H), 7.16 (d, *J* = 6.8 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.84 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.3, 134.2, 132.6, 130.5, 130.0, 129.7, 127.3, 115.0, 114.8, 111.0, 110.9, ; FT-IR (KBr) 3253, 3198, 1654, 1588, 1488, 1407, 1317, 1287, 1164, 1019, 927 cm^{-1}. Anal. Calcd. for $C_{14}H_9N_3S$: C, 66.91; H, 3.61; N, 16.72; S, 12.76. Found: C, 67.00; H, 3.60; N, 16.69; S, 12.71.



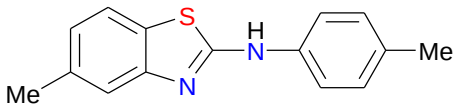
4-Nitro-*N*-phenylbenzo[*d*]thiazol-2-amine 1g. White solid; yield 55%; mp 130-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.04 (m, 2H), 7.55-7.26 (m, 6H), 6.80 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 139.4, 137.4, 134.8, 133.6, 133.1, 130.5, 124.0, 115.5, 113.1, 110.4; FT-IR (KBr) 3153, 1717, 1667, 1601, 1572, 1486, 1408, 1314, 1284, 1260, 1100, 1017, 924 cm^{-1}. Anal. Calcd. for $C_{13}H_9N_3O_2S$: C, 57.55; H, 3.34; N, 15.49; O, 11.79; S, 11.82. Found: C, 57.72; H, 3.32; N, 15.44; S, 11.75.



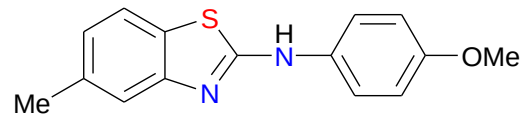
4,6-Dimethyl-*N*-phenylbenzo[*d*]thiazol-2-amine 1h. White solid; yield 85%; mp 94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.09 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.92-6.89 (m, 3H), 6.74 (br s, 1H), 2.28 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 138.4, 137.7, 136.9, 133.2, 132.4, 130.6, 127.5, 116.8, 114.9, 111.1, 21.4, 20.4; FT-IR (KBr) 3201, 2922, 2858, 1607, 1581, 1453, 1410, 1389, 1268, 1155, 1018 cm^{-1}. Anal. Calcd. for $C_{15}H_{14}N_2S$: C, 70.83; H, 5.55; N, 11.01; S, 12.61. Found: C, 70.95; H, 5.53; N, 10.96; S, 12.56.



5,6-Dimethyl-*N*-phenylbenzo[*d*]thiazol-2-amine 1i.[4] White solid; yield 87%; mp 95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.26-7.21 (m, 2H), 6.80 (d, *J* = 2.8 Hz, 2H), 6.64 (d, *J* = 1.6 Hz, 2H), 2.23 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 137.8, 137.3, 134.6, 134.0, 132.4, 128.7, 124.9, 117.6, 115.3, 110.6, 21.4, 20.7; FT-IR (KBr) 3157, 2917, 2845, 1608, 1567, 1498, 1411, 1272, 1197, 1081, 1022 cm^{-1}. Anal. Calcd. for $C_{15}H_{14}N_2S$: C, 70.83; H, 5.55; N, 11.01; S, 12.61. Found: C, 70.96; H, 5.53; N, 10.96; S, 12.55.

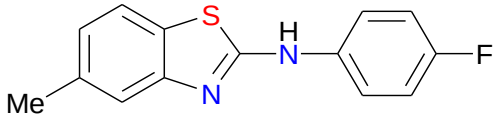


6-Methyl-*N*-p-tolylbenzo[*d*]thiazol-2-amine 1j.[2] White solid; yield 95 %; mp 136-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.26-7.12 (m, 4H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.57-6.56 (m, 1H), 6.40 (br s, 1H), 2.36 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 134.2, 133.4, 130.5, 130.0, 129.6, 129.0, 128.6, 122.6, 115.5, 111.1, 22.1, 20.9; FT-IR (KBr) 3210, 2968, 2877, 1752, 1656, 1599, 1578, 1489, 1365, 1272, 1154, 1011, 987 cm^{-1}. Anal. Calcd. for $C_{15}H_{14}N_2S$: C, 70.83; H, 5.55; N, 11.01; S, 12.61. Found: C, 70.96; H, 5.54; N, 10.95; S, 12.57.

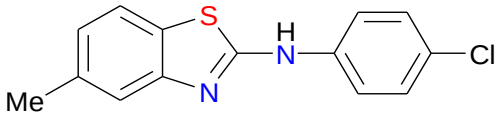


***N*-(4-Methoxyphenyl)-6-methylbenzo[*d*]thiazol-2-amine 1k**:[2] Gummy liquid; yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.23-7.18 (m, 2H), 7.10-7.07 (m, 2H), 6.83-6.80 (m,

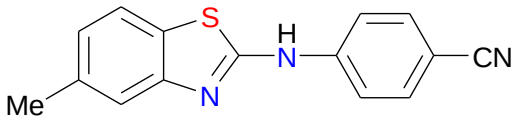
2H), 3.78 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 136.9, 136.6, 134.0, 131.9, 130.5, 125.3, 119.5, 115.3, 115.2, 110.7, 55.6, 20.7; FT-IR (KBr) 3222, 2925, 2851, 1594, 1492, 1283, 1247, 1173, 1097, 1031 cm^{-1}. Anal. Calcd. for $C_{15}H_{14}N_2SO$: C, 66.64; H, 5.22; N, 10.36; S, 11.86. Found: C, 66.76; H, 5.19; N, 10.31; S, 11.80.



***N*-(4-Fluorophenyl)-6-methylbenzo[*d*]thiazol-2-amine 1l**: White solid; yield 62%; mp 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.17 (d, J = 1.6 Hz, 2H), 7.03-7.01 (m, 2H), 6.84 (br s, 1H), 6.60 (d, J = 7.6 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 136.2, 133.8, 131.5, 131.3, 121.8, 120.6, 116.2, 115.2, 110.9, 20.7; FT-IR (KBr) 3199, 3132, 2923, 2853, 1711, 1683, 1604, 1523, 1495, 1449, 1290, 1154, 1115, 1028, 929 cm^{-1}. Anal. Calcd. for $C_{14}H_{11}FN_2S$: C, 65.10; H, 4.29; F, 7.35; N, 10.84; S, 12.41. Found: C, 65.25; H, 4.28; N, 10.80; S, 12.35.

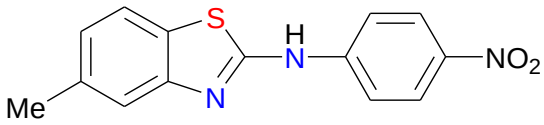


***N*-(4-Chlorophenyl)-6-methylbenzo[*d*]thiazol-2-amine 1m**: White solid; yield 70%; mp 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.29 (d, J = 0.8 Hz, 1H), 7.27-7.21 (m, 3H), 6.95 (d, J = 8.4 Hz, 2H), 6.78 (br s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.2, 134.4, 133.1, 133.0, 132.7, 129.8, 128.4, 116.9, 115.5, 110.4, 20.7; FT-IR (KBr) 3183, 3028, 2921, 2853, 1892, 1605, 1580, 1563, 1495, 1473, 1387, 1288, 1262, 1155, 1090, 1051, 1008 cm^{-1}. Anal. Calcd. for $C_{14}H_{11}N_2SCl$: C, 61.20; H, 4.04; N, 10.20; S, 11.67. Found: C, 61.32; H, 4.02; N, 10.14; S, 11.60.

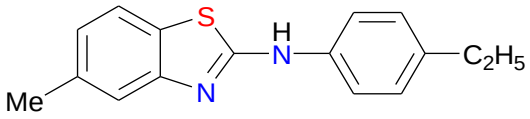


4-(6-Methylbenzo[*d*]thiazol-2-ylamino)benzonitrile 1n: White solid; yield 55%; mp 103-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8 Hz, 2H), 7.61-7.51 (m, 2H), 7.38 (s, 1H), 7.30-7.26 (m, 2H), 6.75 (br s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.3, 134.3, 134.1, 128.9, 127.1, 126.9, 126.8, 126.1, 124.4, 116.8, 115.5, 20.7; FT-IR (KBr) 3210, 3060,

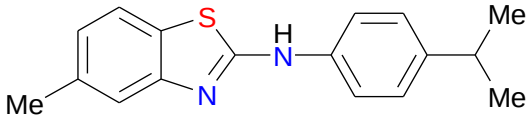
2899, 2222, 1717, 1670, 1579, 1488, 1413, 1388, 1270, 1243, 1023, 929 cm^{-1}. Anal. Calcd. for $C_{15}H_{11}N_3S$: C, 67.90; H, 4.18; N, 15.84; S, 12.08. Found: C, 68.04; H, 4.16; N, 15.79; S, 12.01.



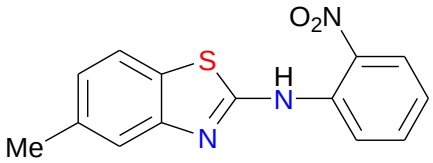
5-Methyl-*N*-(4-nitrophenyl)benzo[*d*]thiazol-2-amine 1o: White solid: yield 64%; mp 186-187 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.92 (br s, 1H), 8.09-8.05 (m, 2H), 7.78-7.75 (m, 2H), 7.26 (s, 1H), 7.07-7.04 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ 152.8, 146.3, 143.8, 141.8, 137.3, 129.6, 127.1, 125.6, 121.0, 120.7, 118.0, 21.5; FT-IR (KBr) 3314, 3109, 2892, 2115, 1619, 1509, 1330, 1250, 1112, 1088, 1025 cm^{-1}. Anal. Calcd. for $C_{14}H_{11}N_3O_2S$: C, 58.93; H, 3.89; N, 14.73; S, 11.24. Found: C, 60.08; H, 3.87; N, 14.68; S, 11.18



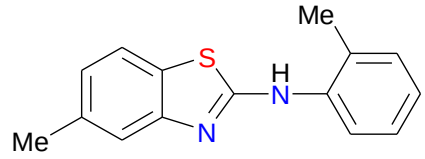
***N*-(4-Ethylphenyl)-5-methylbenzo[*d*]thiazol-2-amine 1p**: White solid; yield 93%; mp 139-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.37-7.35 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.00 (br s, 1H), 2.62-2.56 (q, 2H), 2.46 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ 151.5, 141.5, 136.3, 135.8, 132.4, 128.3, 128.1, 126.4, 122.8, 120.0, 117.1, 26.3, 19.3, 14.3; FT-IR (KBr) 3250, 3090, 2928, 2872, 1610, 1574, 1496, 1449, 1309, 1246, 1125, 1096 cm^{-1}. Anal. Calcd. for $C_{16}H_{16}N_2S$: C, 71.61; H, 6.01; N, 10.44; S, 11.95. Found C, 71.75; H, 5.99; N, 10.38; S, 11.89.



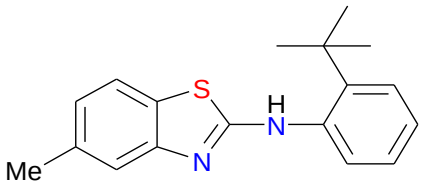
***N*-(4-Isopropylphenyl)-5-methylbenzo[*d*]thiazol-2-amine 1q**: White solid; yield 93%; mp 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.37-7.32 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.99 (br s, 1H), 2.88-2.83 (m, 1H), 2.46 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ 151.7, 141.6, 141.2, 135. 9, 132.5, 128.4, 128.2, 128.1, 125.0, 120.1, 117.2, 31.6, 22.6, 19.4; FT-IR (KBr) 3251, 3090, 2960, 1611, 1574, 1496, 1447, 1307, 1243, 1126, 1097 cm^{-1}. Anal. Calcd. for $C_{17}H_{18}N_2S$: C, 72.30; H, 6.42; N, 9.92; S, 11.35. Found: C, 72.42; H, 6.41; N, 9.87; S, 11.29.



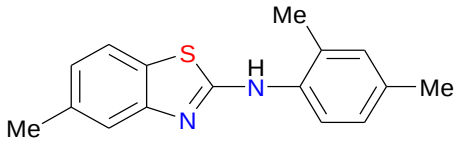
6-Methyl-*N*-(2-nitrophenyl)benzo[*d*]thiazol-2-amine 1r: White solid; yield 52%; mp 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 9.2 Hz, 2H), 7.66-7.63 (m, 2H), 7.38 (s, 1H), 6.50 (d, *J* = 8.4 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 141.9, 137.9, 132.9, 131.0, 129.3, 126.9, 125.2, 124.5, 122.7, 122.2, 110.0, 20.8; FT-IR (KBr) 3199, 3118, 2963, 2859, 1715, 1656, 1605, 1555, 1529, 1499, 1345, 1261, 1022, 929 cm^{-1}. Anal. Calcd. for $C_{14}H_{11}N_3O_2S$: C, 58.93; H, 3.89; N, 14.73; O, 11.22; S, 11.24. Found: C, 59.08; H, 3.87; N, 14.68; S, 11.20.



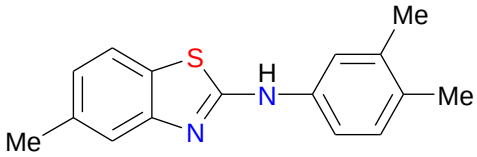
6-Methyl-*N*-o-tolylbenzo[*d*]thiazol-2-amine 1s. White solid; yield 82%; mp 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.26-7.19 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.87 (s, 1H), 6.83 (br s, 1H), 6.79-6.76 (m, 1H), 2.26 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.5, 137.1, 135.7, 134.0, 132.2, 131.6, 130.9, 129.0, 123.2, 118.2, 115.2, 20.7, 20.0; FT-IR (KBr) 3290, 3144, 2984, 2917, 2859, 1604, 1584, 1498, 1449, 1413, 1391, 1289, 1270, 1213, 1153, 1057, 934 cm^{-1}. Anal. Calcd. for $C_{15}H_{14}N_2S$: C, 70.83; H, 5.55; N, 11.01; S, 12.61. Found: C, 70.93; H, 5.54; N, 10.97; S, 12.56.



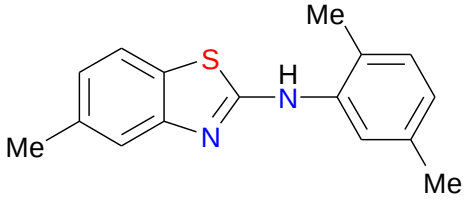
***N*-(2-Tert-butylphenyl)-6-methylbenzo[*d*]thiazol-2-amine 1t**: White solid; yield 74%; mp 112-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.26-7.20 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 1.2 Hz, 2H), 6.83 (br s, 1H), 6.79-6.76 (m, 1H), 2.26 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.5, 137.1, 135.7, 133.9, 132.2, 131.6, 130.9, 129.0, 125.3, 122.2, 118.2, 115.2, 34.5, 30.5, 20.7; FT-IR (KBr) 3280, 3198, 2961, 2895, 2819, 1721, 1621, 1597, 1496, 1385, 1388, 1262, 1177, 1032, 943 cm^{-1}. Anal. Calcd. for $C_{18}H_{20}N_2S$: C, 72.93; H, 6.80; N, 9.45; S, 10.82. Found: C, 73.05; H, 6.77; N, 9.41; S, 10.77.



6-Methyl-*N*-(2,4-dimethylphenyl)benzo[*d*]thiazol-2-amine 1u. White solid; yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.21 (m, 3H), 7.01 (s, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.72 (br s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 137.0, 136.7, 136.2, 134.2, 132.0, 131.7, 130.5, 127.9, 127.1, 117.8, 115.3, 110.7, 21.0, 20.7, 20.2; FT-IR (KBr) 3340, 3198, 2923, 2857, 1615, 1498, 1380, 1259, 1237, 1049 cm^{-1}. Anal. Calcd. for $C_{16}H_{16}N_2S$: C, 71.61; H, 6.01; N, 10.44; S, 11.95. Found: C, 71.72; H, 5.98; N, 10.39; S, 11.92.



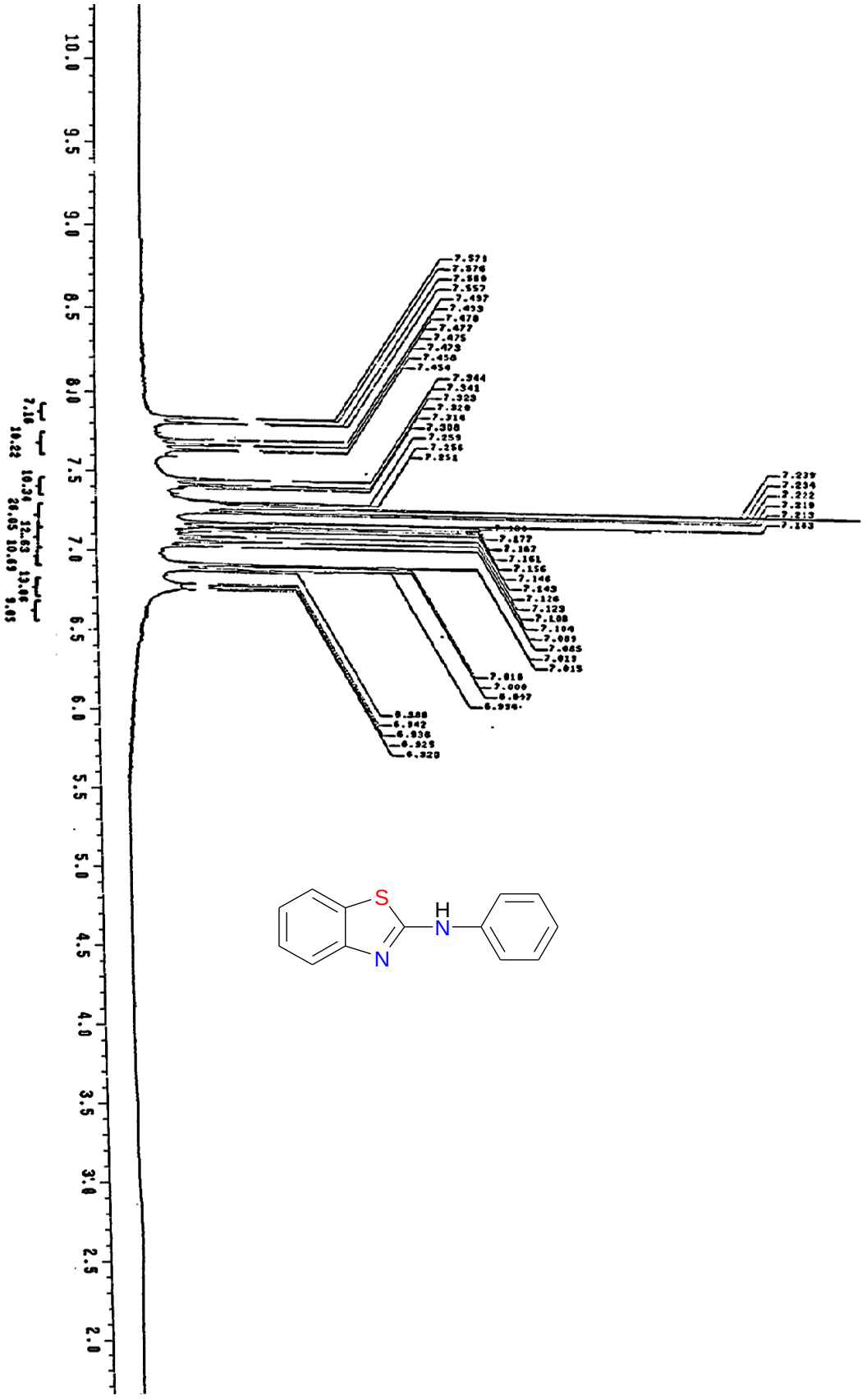
5-Methyl-*N*-(3,4-dimethylphenyl)benzo[*d*]thiazol-2-amine 1v: White solid; yield 90%; mp 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.30-7.22 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.59 (br s, 1H), 2.41 (s, 3H), 2.19 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ 151.4, 141.5, 135.7, 134.8, 132.2, 128.3, 128.0, 127.8, 119.9, 118.0, 114.2, 19.0, 18.1, 17.1; FT-IR (KBr) 3275, 2923, 2856, 1574, 1533, 1498, 1455, 1375, 1315, 1254, 1218, 1168, 1115, 1092, 1020 cm^{-1}. Anal. Calcd. for $C_{16}H_{16}N_2S$: C, 71.61; H, 6.01; N, 10.44; S, 11.95. Found: C, 71.72; H, 6.00; N, 10.40; S, 11.89.

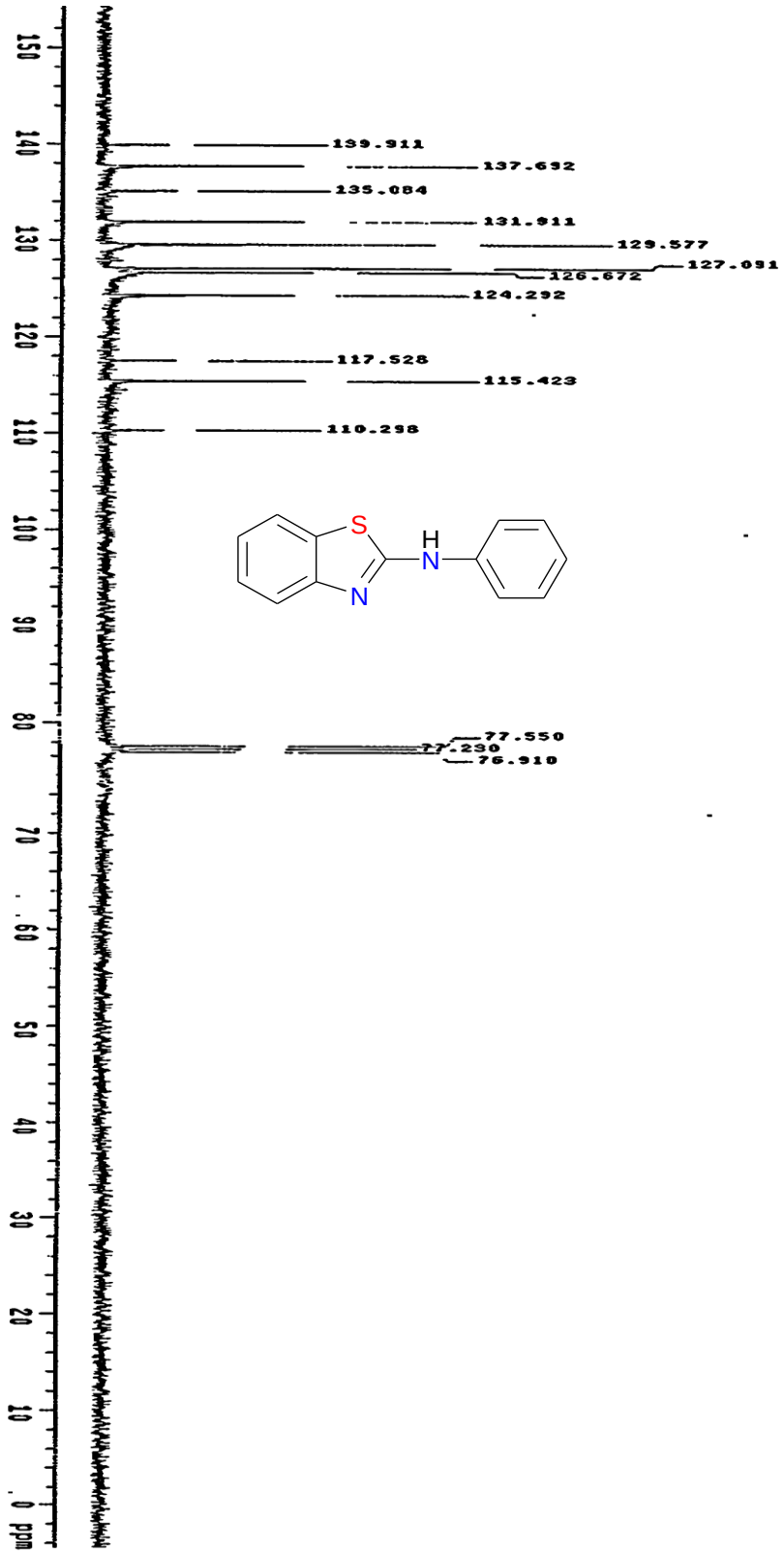


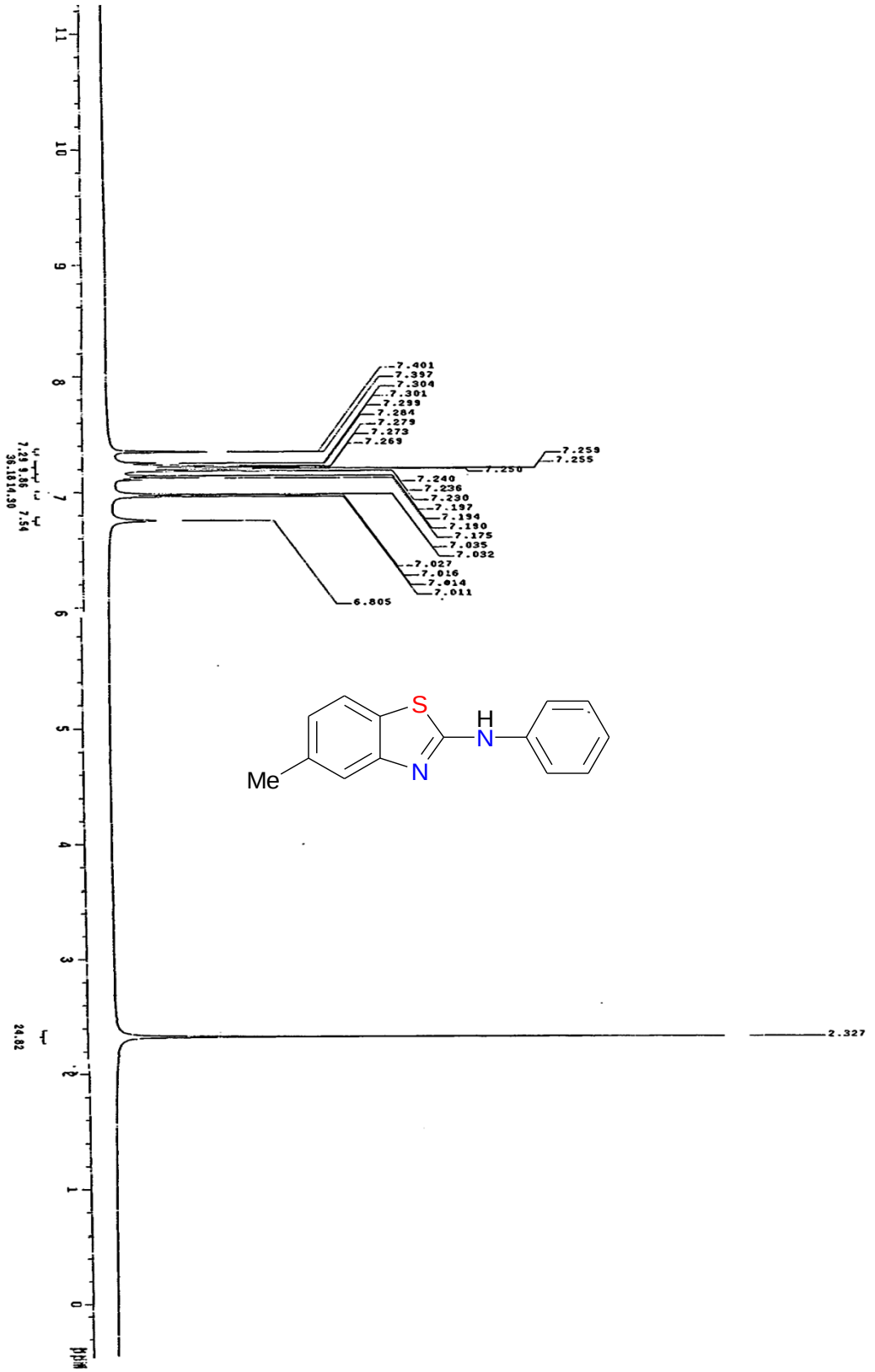
5-Methyl-*N*-(2,5-dimethylphenyl)benzo[*d*]thiazol-2-amine 1w: White solid; yield 90%; mp 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.65 (s, 1H), 7.38-7.33 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 5.90 (br s, 1H), 2.47 (s, 3H), 2.34 (s, 6H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ 154.2, 142.8, 136.7, 135.4, 133.7, 130.3, 129.6, 129.4, 129.3, 126.1, 125.2, 121.0, 20.6, 20.5, 17.4; FT-IR (KBr) 2921, 1587, 1527, 1492, 1462, 1381, 1306, 1263, 1088 cm^{-1}. Anal. Calcd. for $C_{16}H_{16}N_2S$: C, 71.61; H, 6.01; N, 10.44; S, 11.95. Found: C, 71.73; H, 5.99; N, 10.39; S, 11.90.

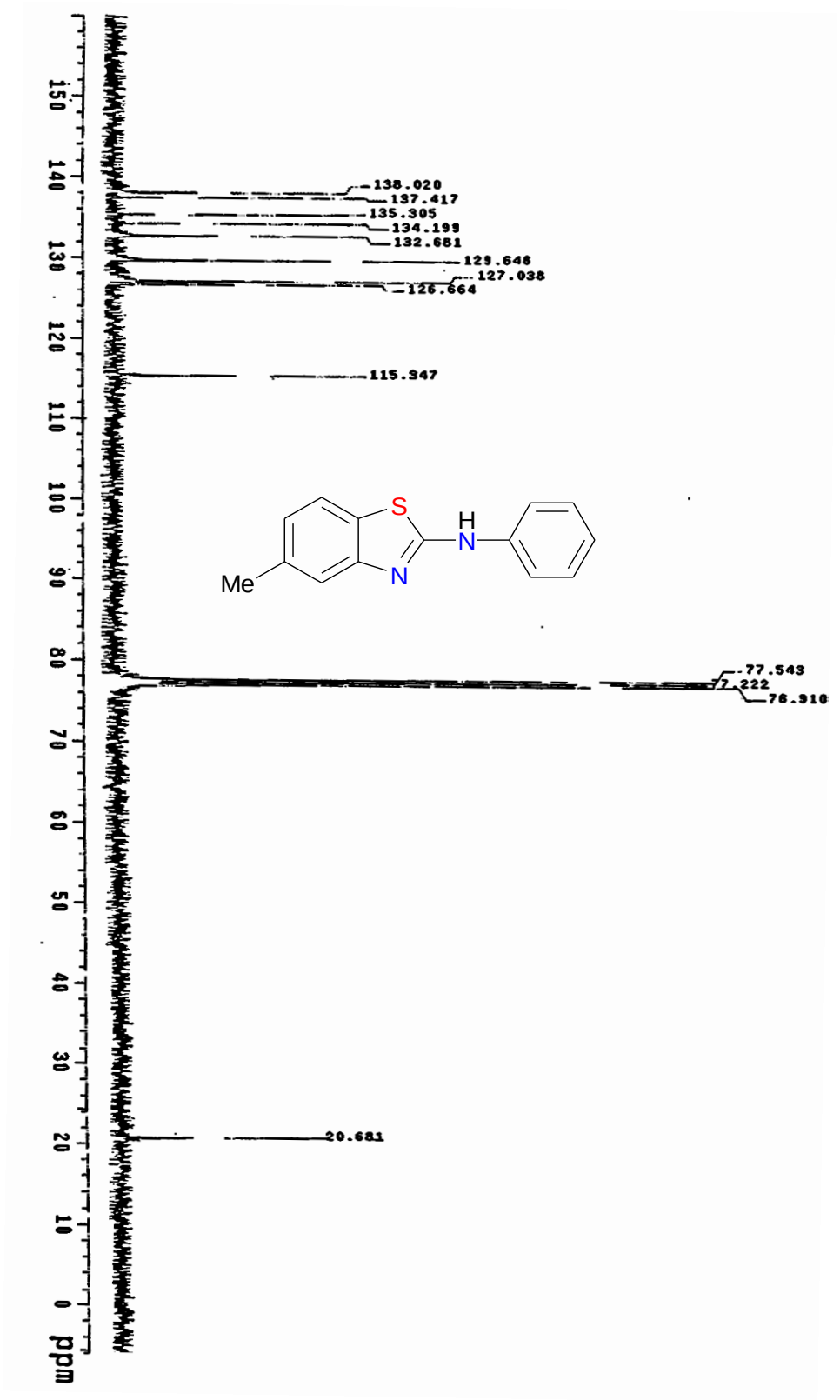
References:

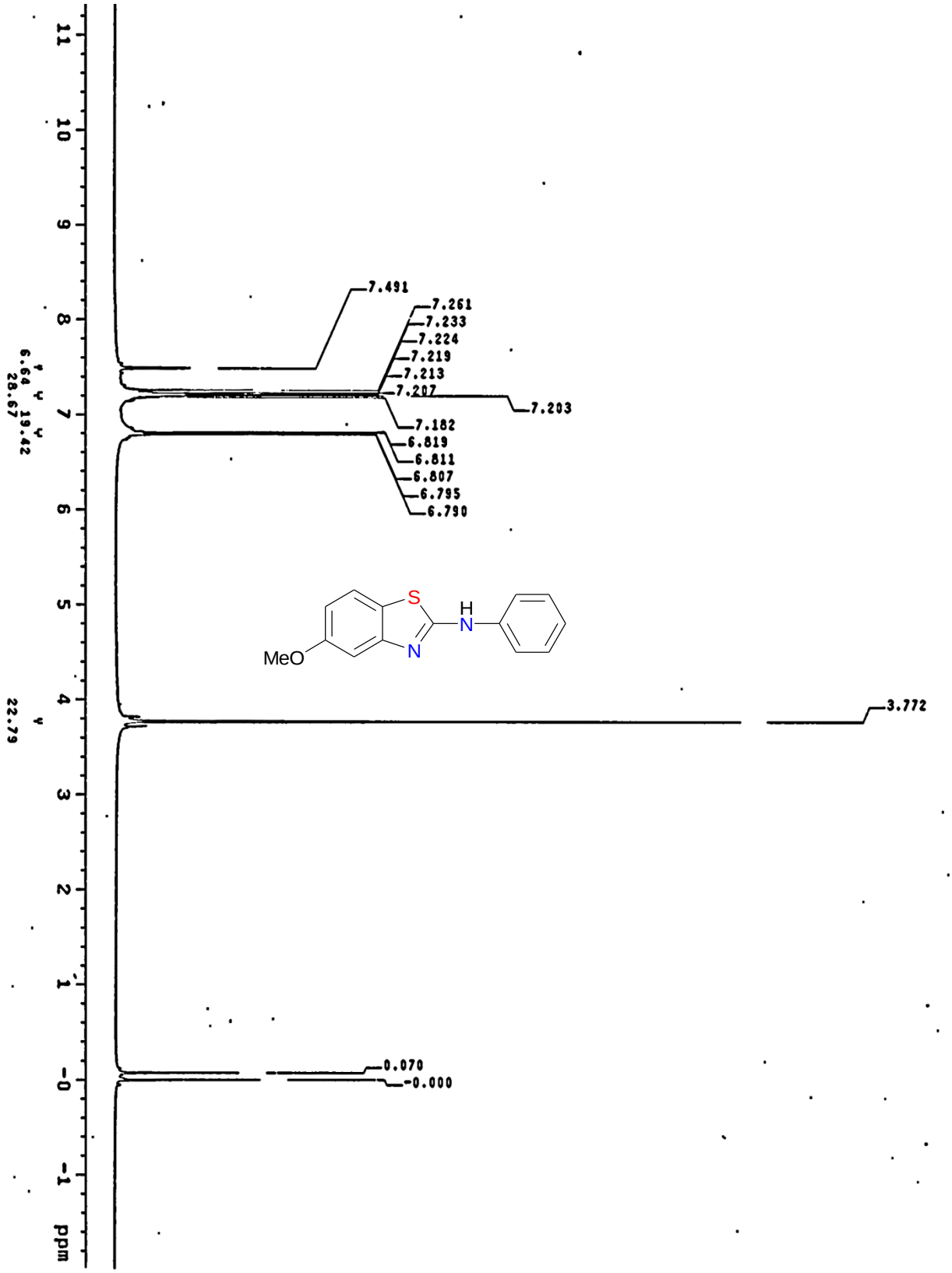
1. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. In *Vogel's Textbook of Practical Organic Chemistry*, Fifth Edition, Pearson Education Pte. Ltd., Indian Branch, Delhi, 2004, 928-929.
2. P. Saha, T. Ramana, N. Purkait, M. A. Ali, R. Paul, T. Punniyamurthy, *J. Org. Chem* 2009, **74**, 8719.
3. Y.-J. Guo, R.-Y. Tang, P. Zhong, J.-H. Li, *Tetrahedron Lett.*, 2010, **51**, 649.
4. R. Wang, W.-J. Yang, L. Yue, W. Pan, H.-Y. Zeng, *Synlett* 2012, **11**, 1643.

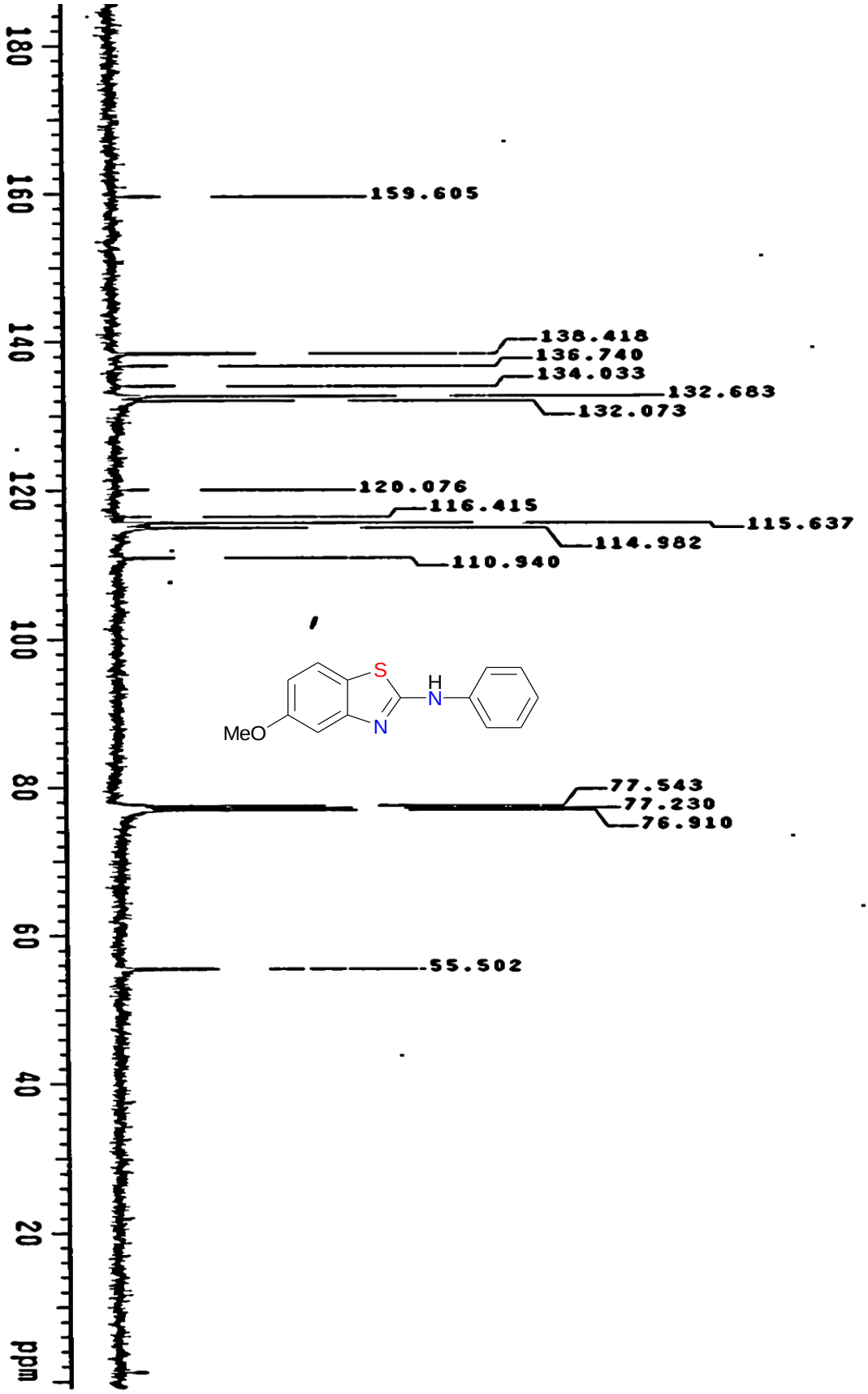

7.574
7.570
7.568
7.557
7.497
7.493
7.478
7.477
7.475
7.473
7.456
7.454
7.344
7.341
7.329
7.320
7.318
7.308
7.259
7.256
7.251
7.239
7.234
7.222
7.219
7.213
7.163
7.177
7.167
7.161
7.156
7.146
7.143
7.126
7.123
7.108
7.104
7.089
7.085
7.019
7.015
7.018
7.000
6.957
6.934
6.938
6.925
6.920
S
H
N
N

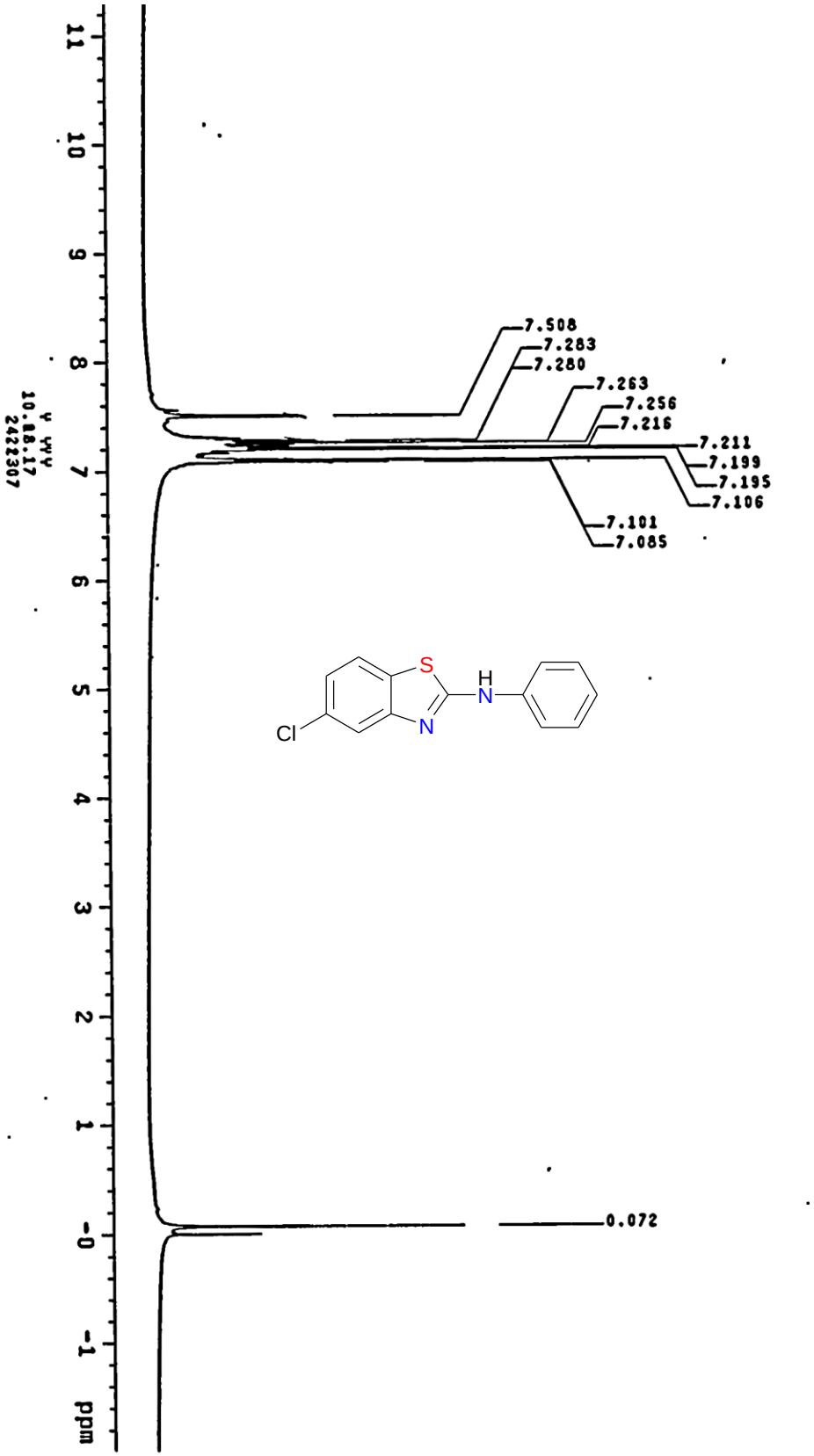

139.911
137.692
135.084
131.911
129.577
127.091
126.672
124.292
117.528
115.423
110.298
77.550
77.230
76.910
S
H
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

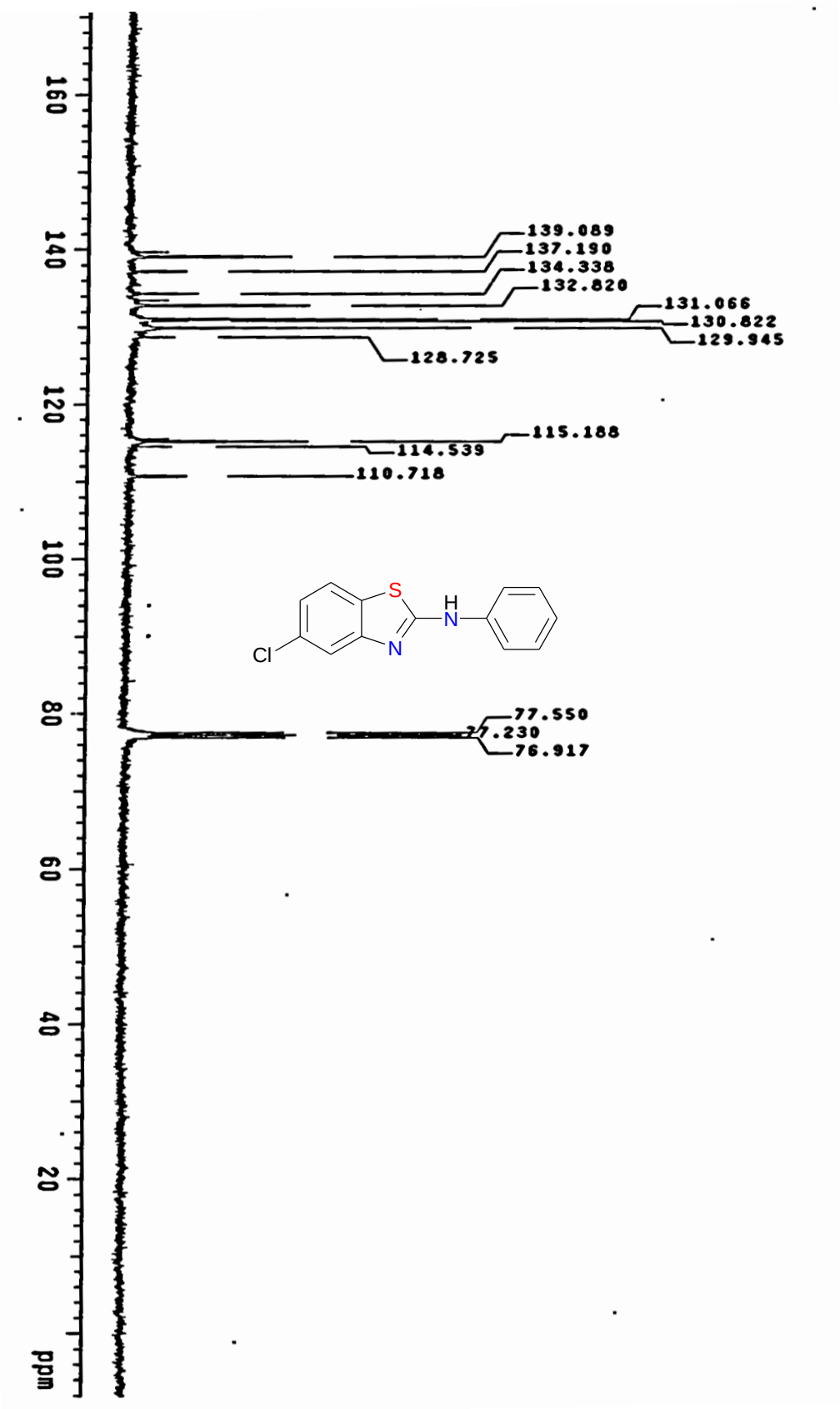

7.401
7.397
7.304
7.301
7.299
7.284
7.279
7.273
7.269
7.259
7.255
7.250
7.240
7.236
7.230
7.197
7.194
7.190
7.175
7.035
7.032
7.027
7.016
7.014
7.011
6.805
2.327
S
H
N
N
Me

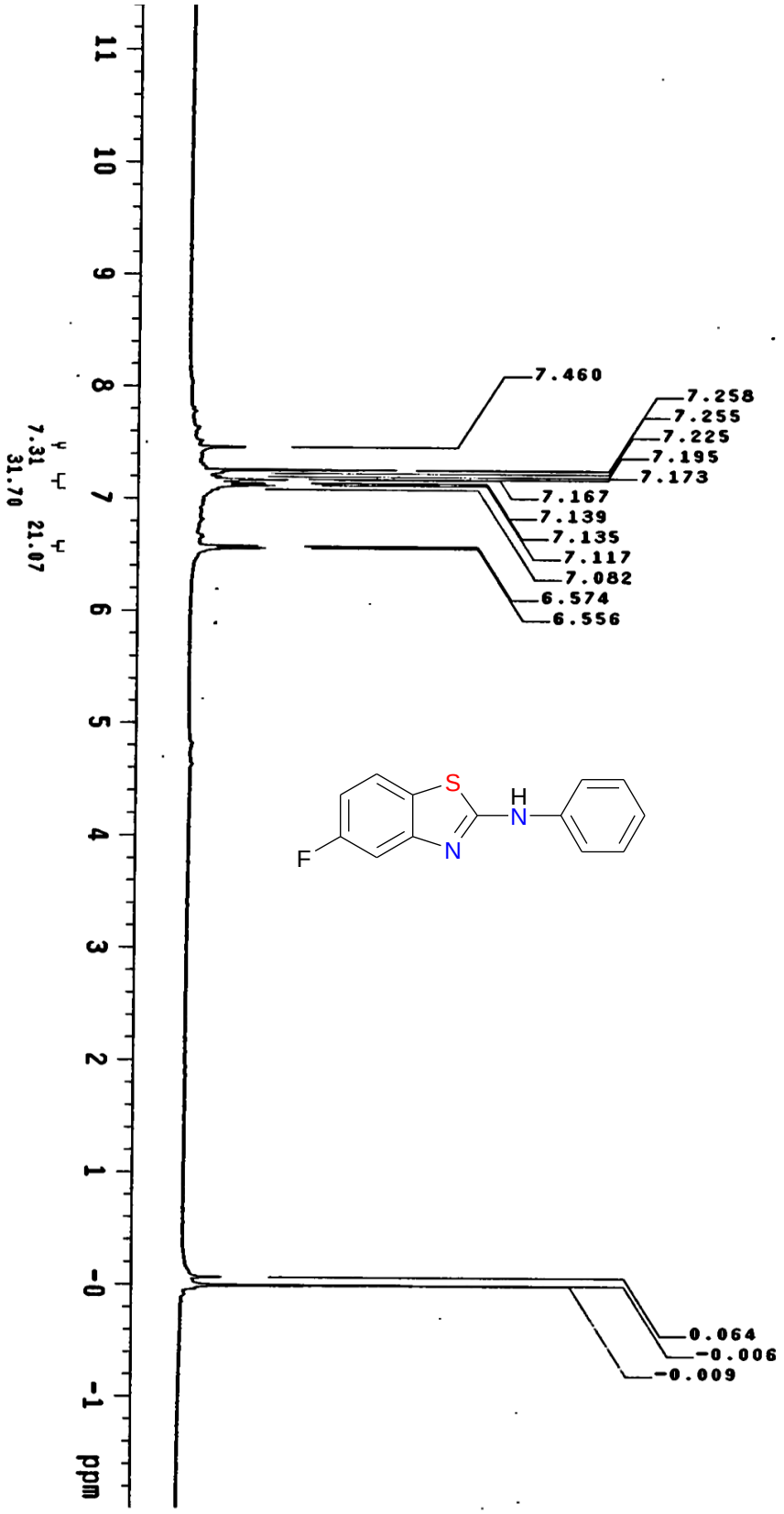

138.020
137.417
135.305
134.199
132.681
129.646
127.038
126.664
115.347
77.543
77.222
76.910
20.681
S
H
N
N
Me
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

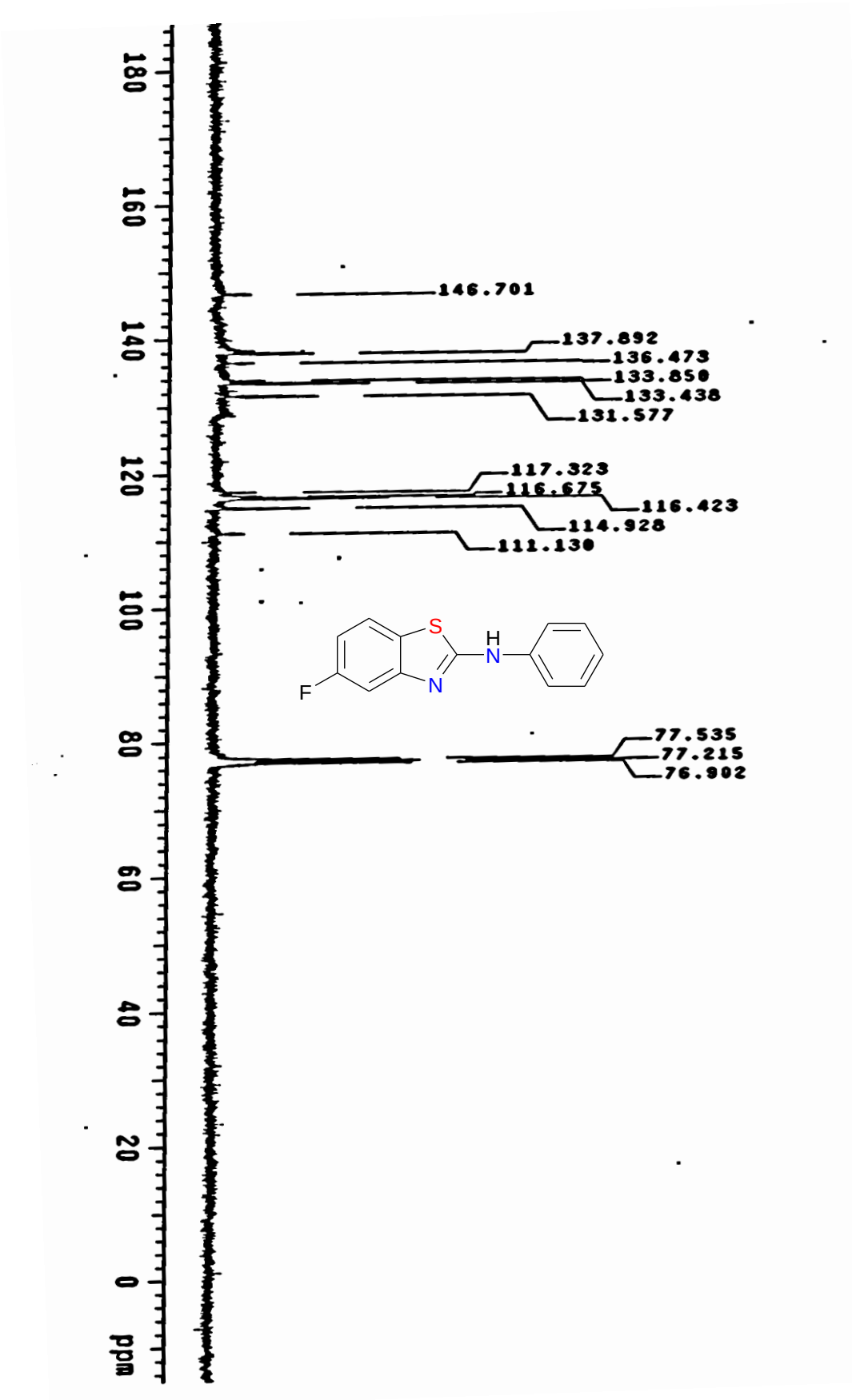

7.491
7.261
7.233
7.224
7.219
7.213
7.207
7.203
7.182
6.819
6.811
6.807
6.795
6.790
6.64
19.42
28.67
22.79
3.772
0.070
-0.000
S
H
N
N
MeO
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

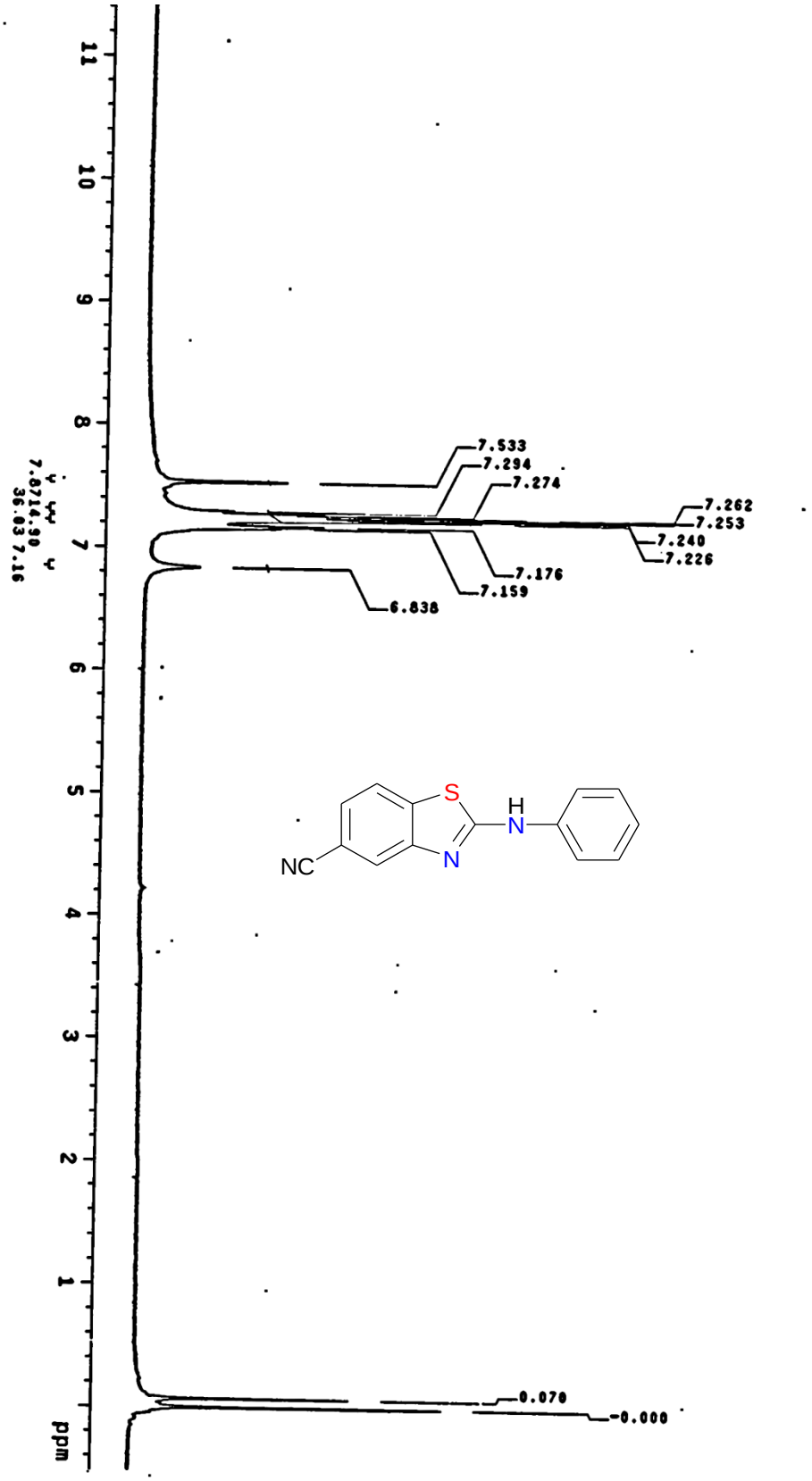

180
160
140
120
100
80
60
40
20
ppm
159.605
138.418
136.740
134.033
132.683
132.073
120.076
116.415
115.637
114.982
110.940
S
H
N
N
MeO
77.543
77.230
76.910
55.502

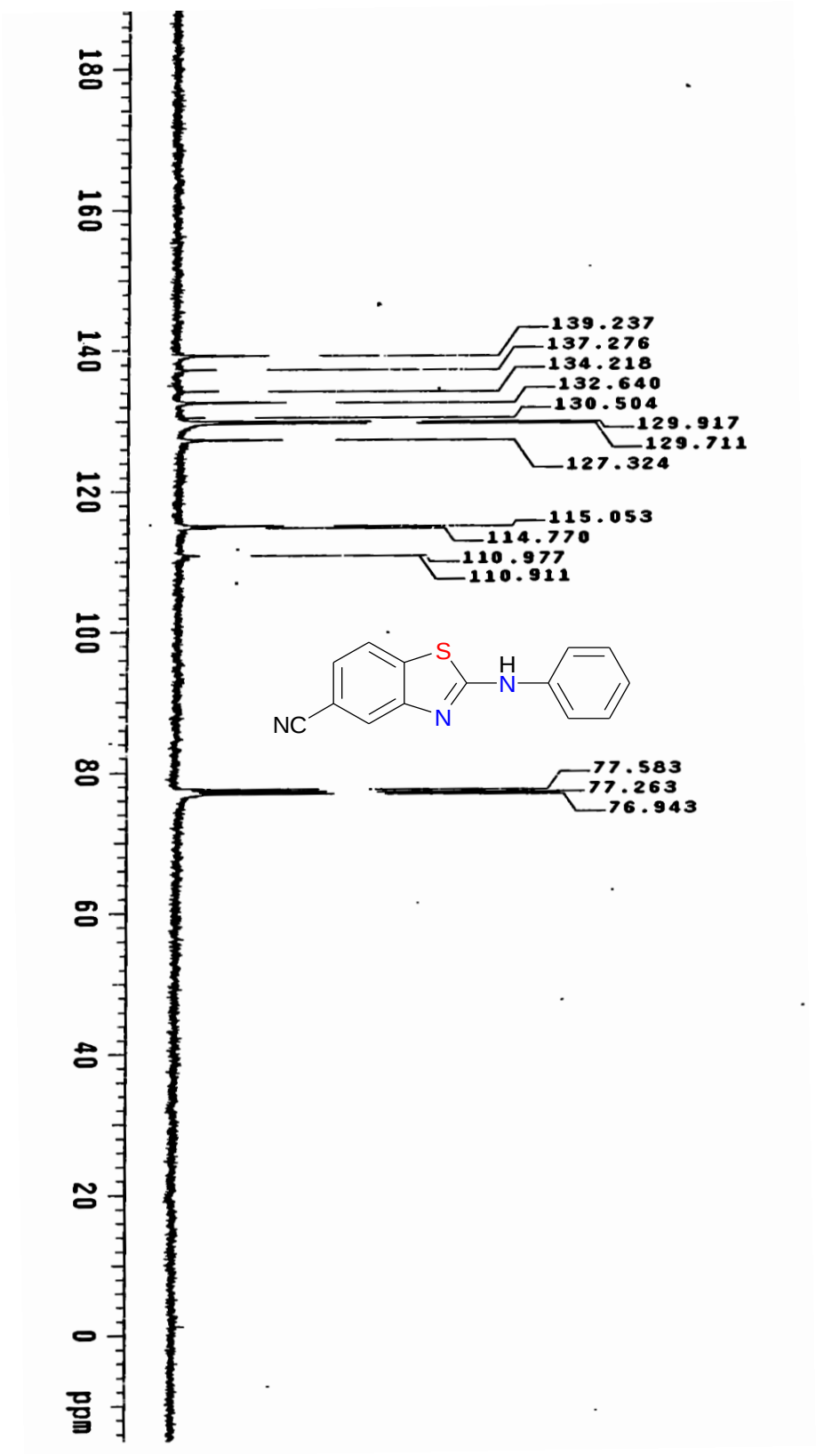

7.508
7.283
7.280
7.263
7.256
7.216
7.211
7.199
7.195
7.106
7.101
7.085
0.072
S
H
N
N
Cl
ppm

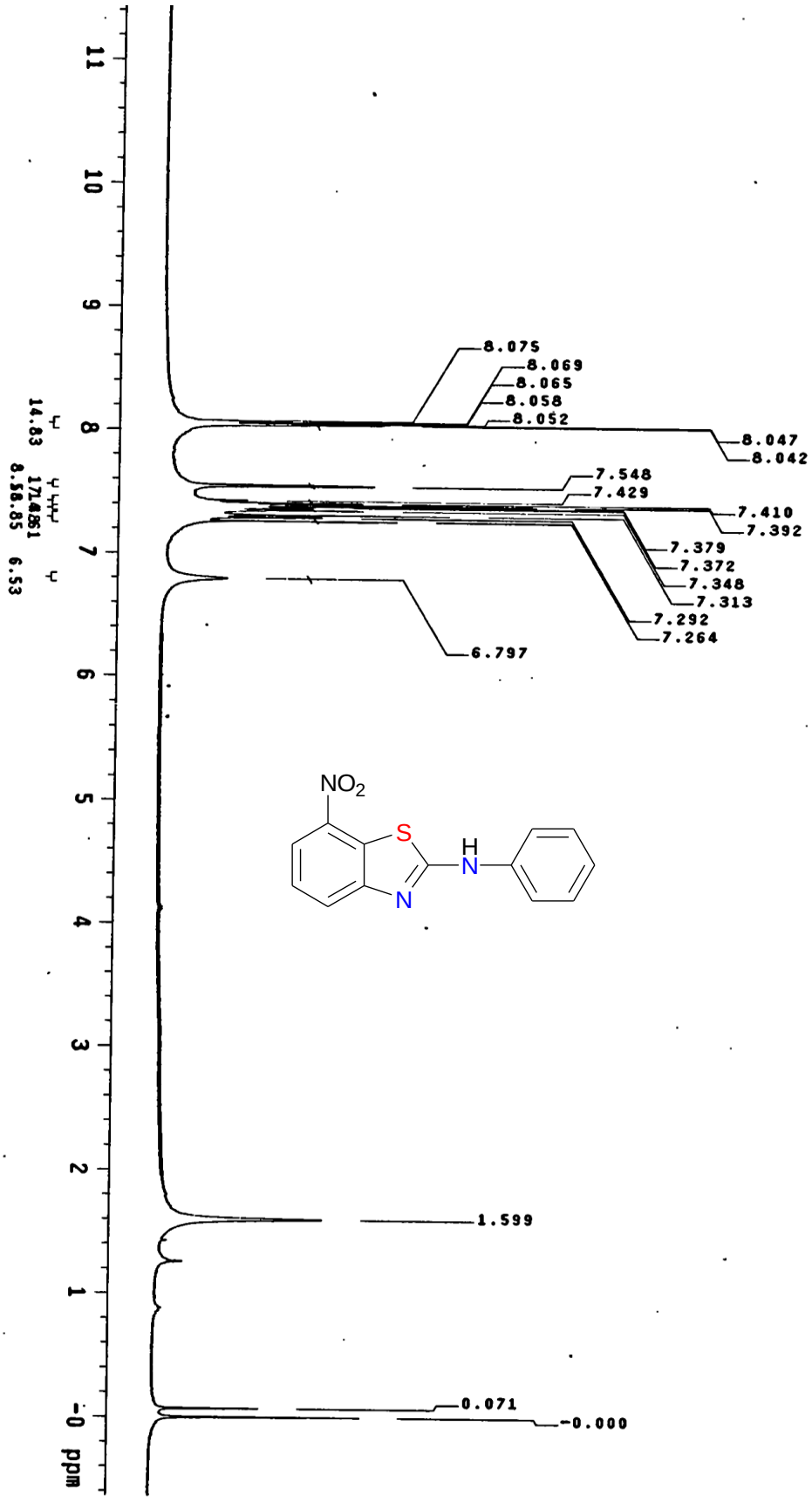

160
140
120
100
80
60
40
20
ppm
139.089
137.190
134.338
132.820
131.066
130.822
129.945
128.725
115.188
114.539
110.718
77.550
77.230
76.917
S
H
N
N
Cl

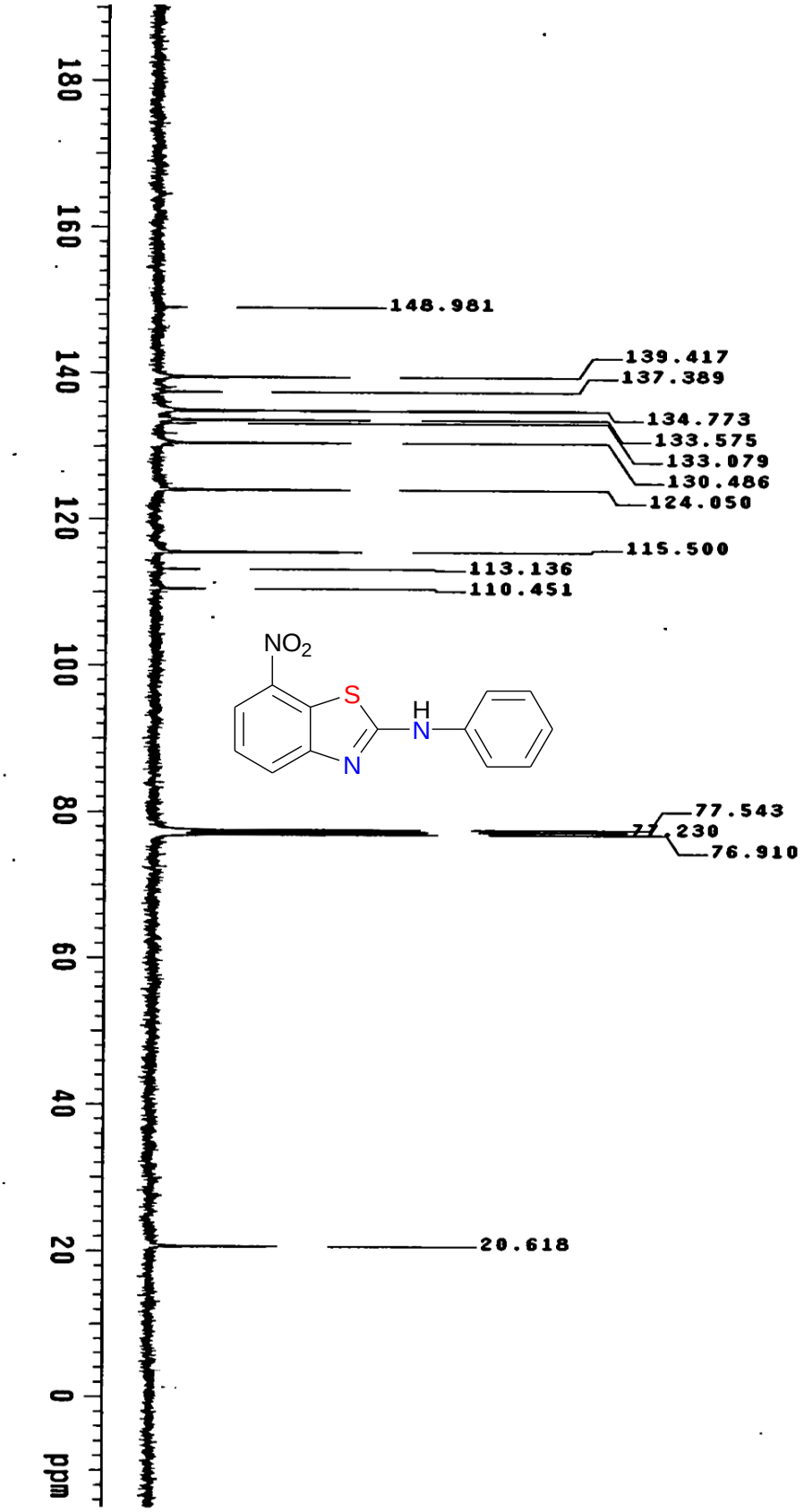

7.460
7.258
7.255
7.225
7.195
7.173
7.167
7.139
7.135
7.117
7.082
6.574
6.556
0.064
-0.006
-0.009
7.31
31.70
21.07
S
H
N
N
F
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

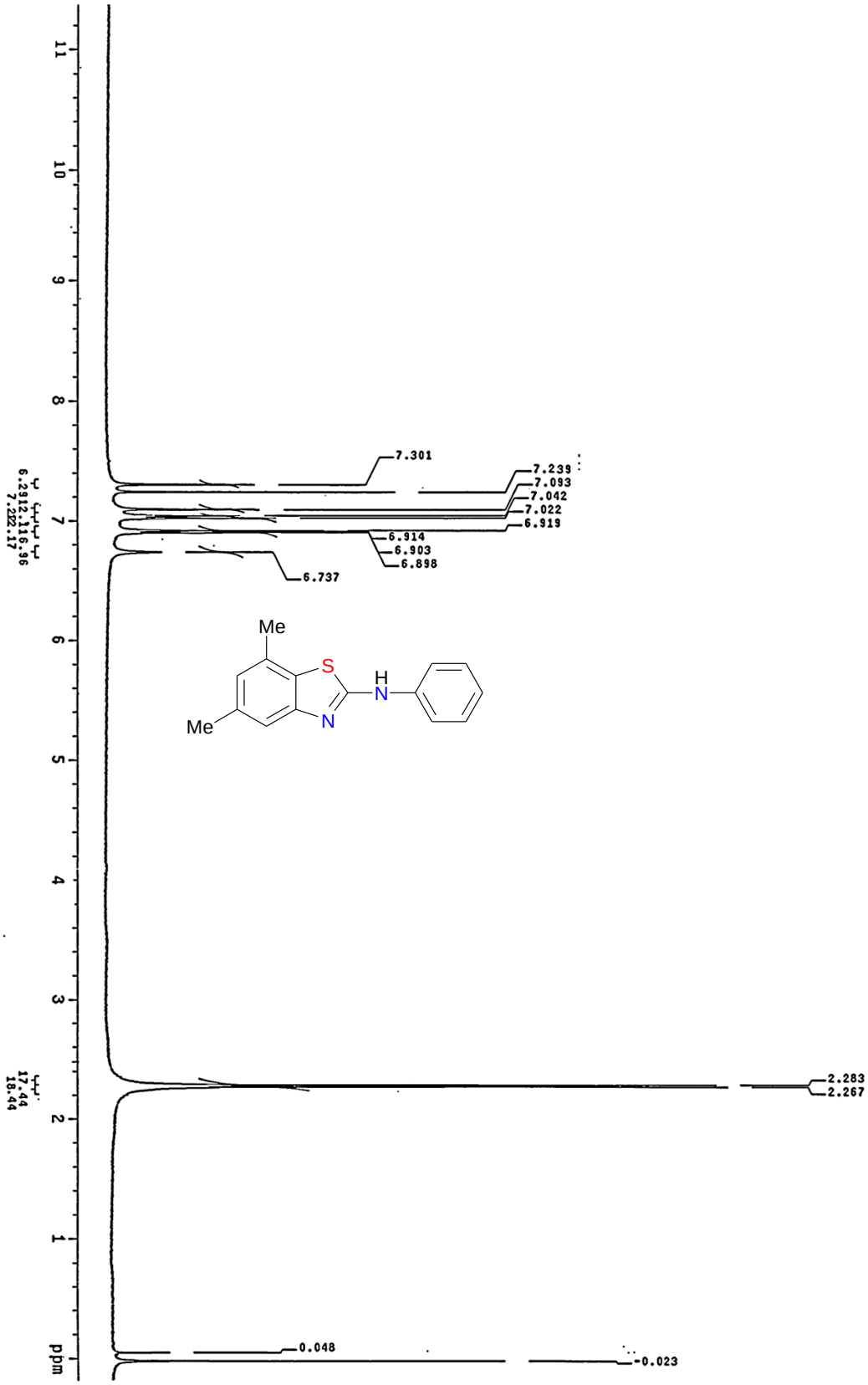

180
160
140
120
100
80
60
40
20
0
ppm
146.701
137.892
136.473
133.850
133.438
131.577
117.323
116.675
116.423
114.928
111.130
77.535
77.215
76.902
S
H
N
N
F

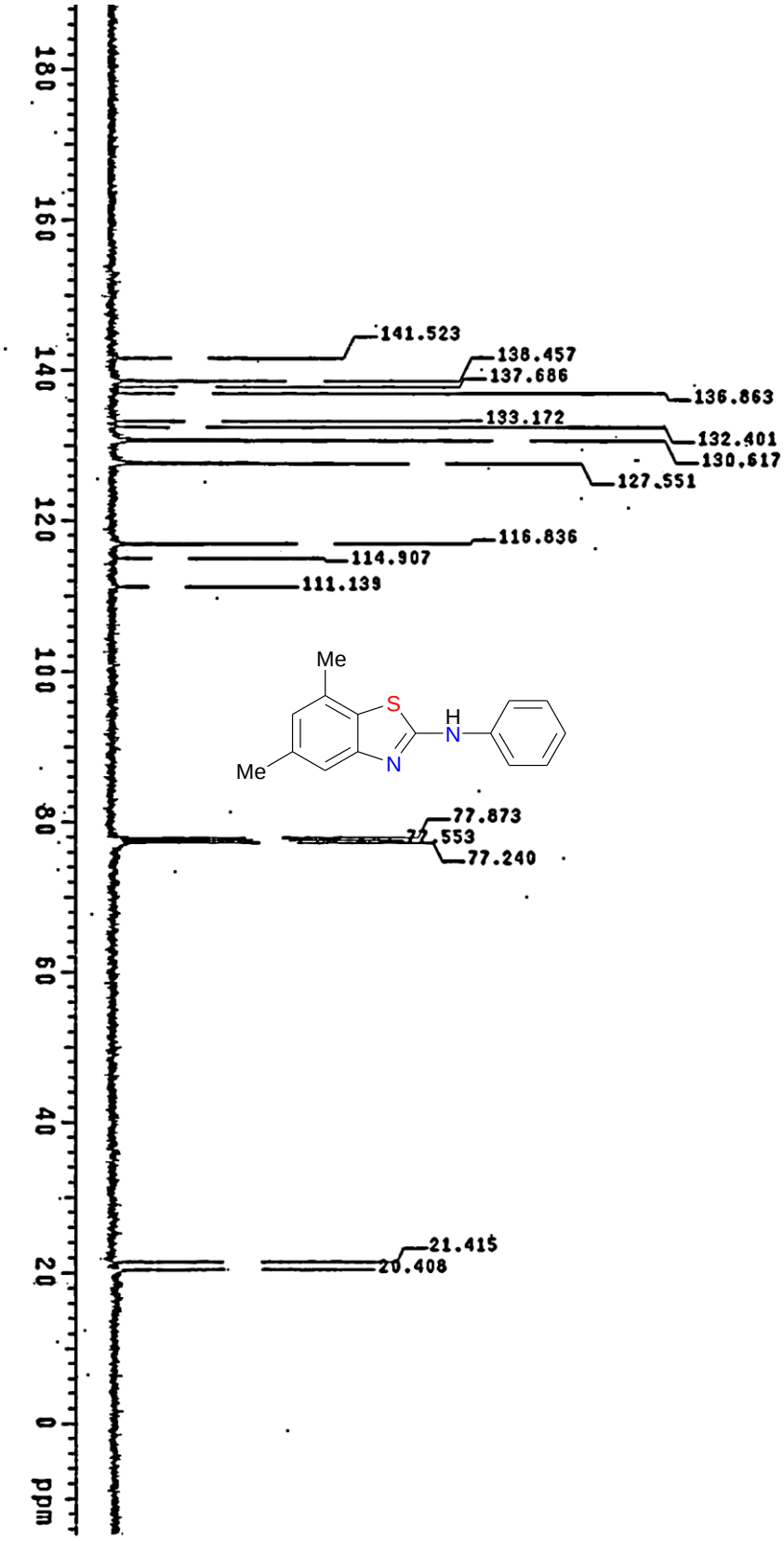

7.533
7.294
7.274
7.262
7.253
7.240
7.226
7.176
7.159
6.838
0.070
-0.000
ppm
S
H
N
N
NC

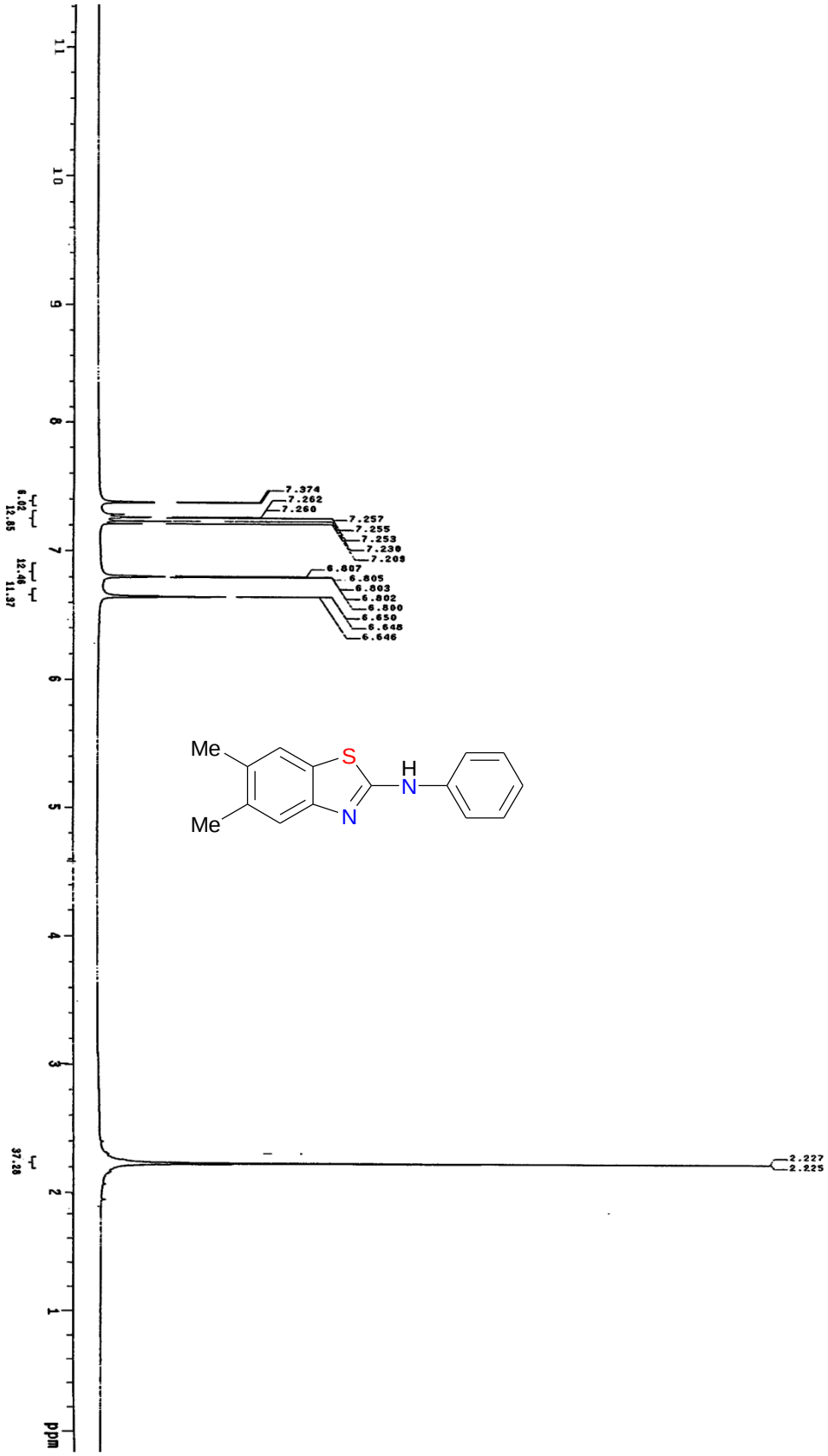

180
160
140
120
100
80
60
40
20
0
ppm
139.237
137.276
134.218
132.640
130.504
129.917
129.711
127.324
115.053
114.770
110.977
110.911
77.583
77.263
76.943
S
H
N
N
NC

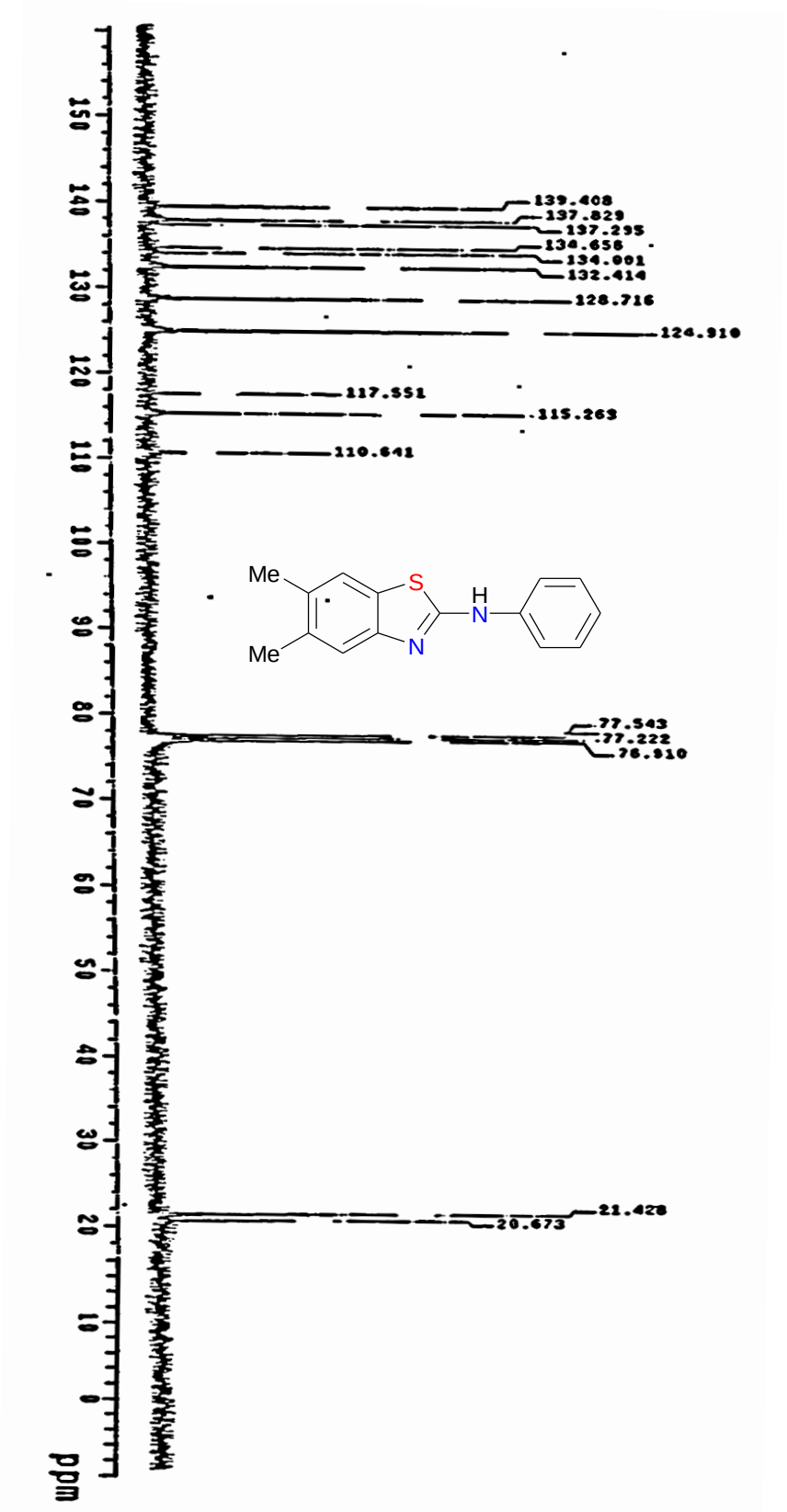

8.075
8.069
8.065
8.058
8.052
8.047
8.042
7.548
7.429
7.410
7.392
7.379
7.372
7.348
7.313
7.292
7.264
6.797
1.599
0.071
-0.000
NO2
S
H
N
N
11
10
9
8
7
6
5
4
3
2
1
-0 ppm

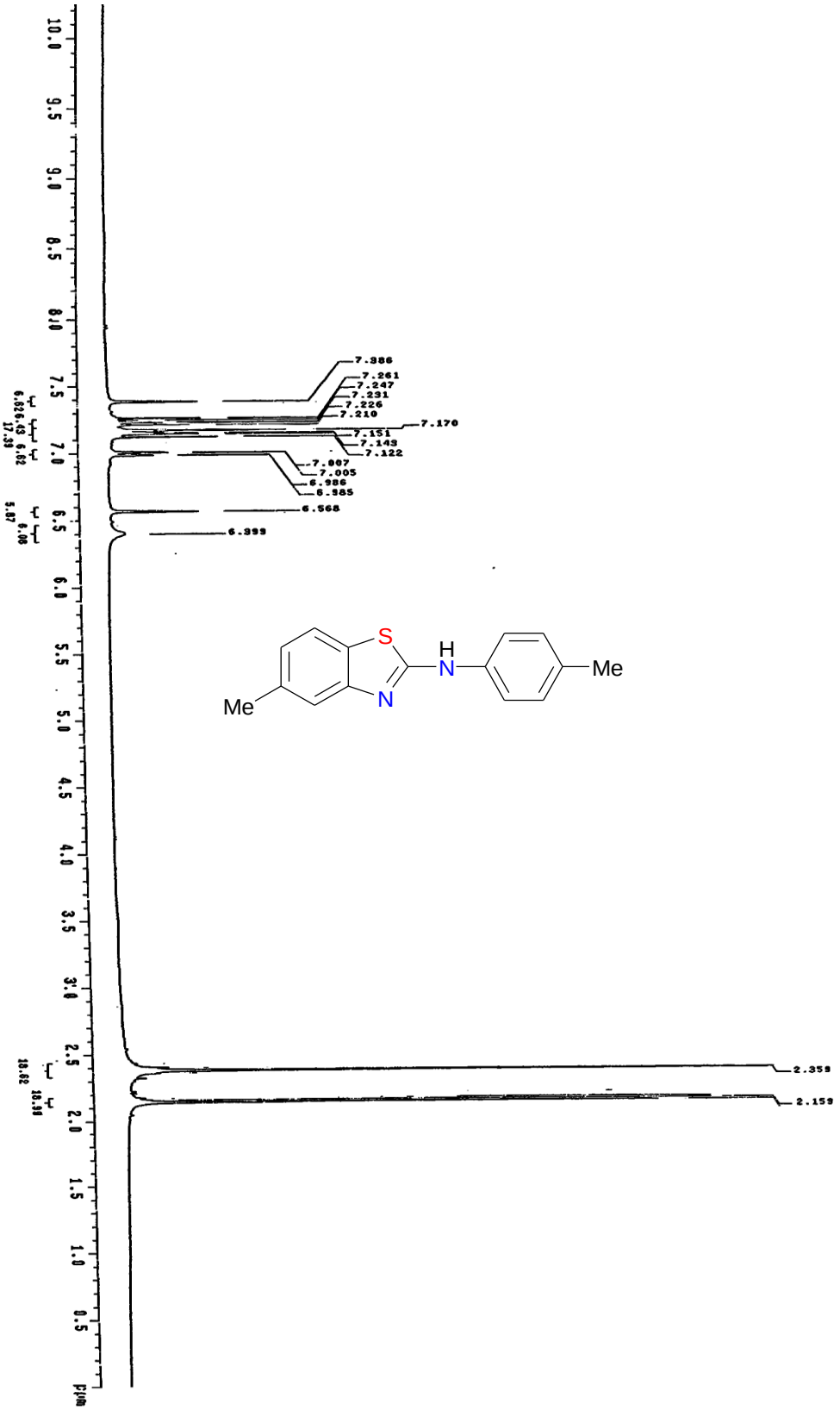

148.981
139.417
137.389
134.773
133.575
133.079
130.486
124.050
115.500
113.136
110.451
NO2
S
H
N
N
77.543
77.230
76.910
20.618
180
160
140
120
100
80
60
40
20
0
ppm

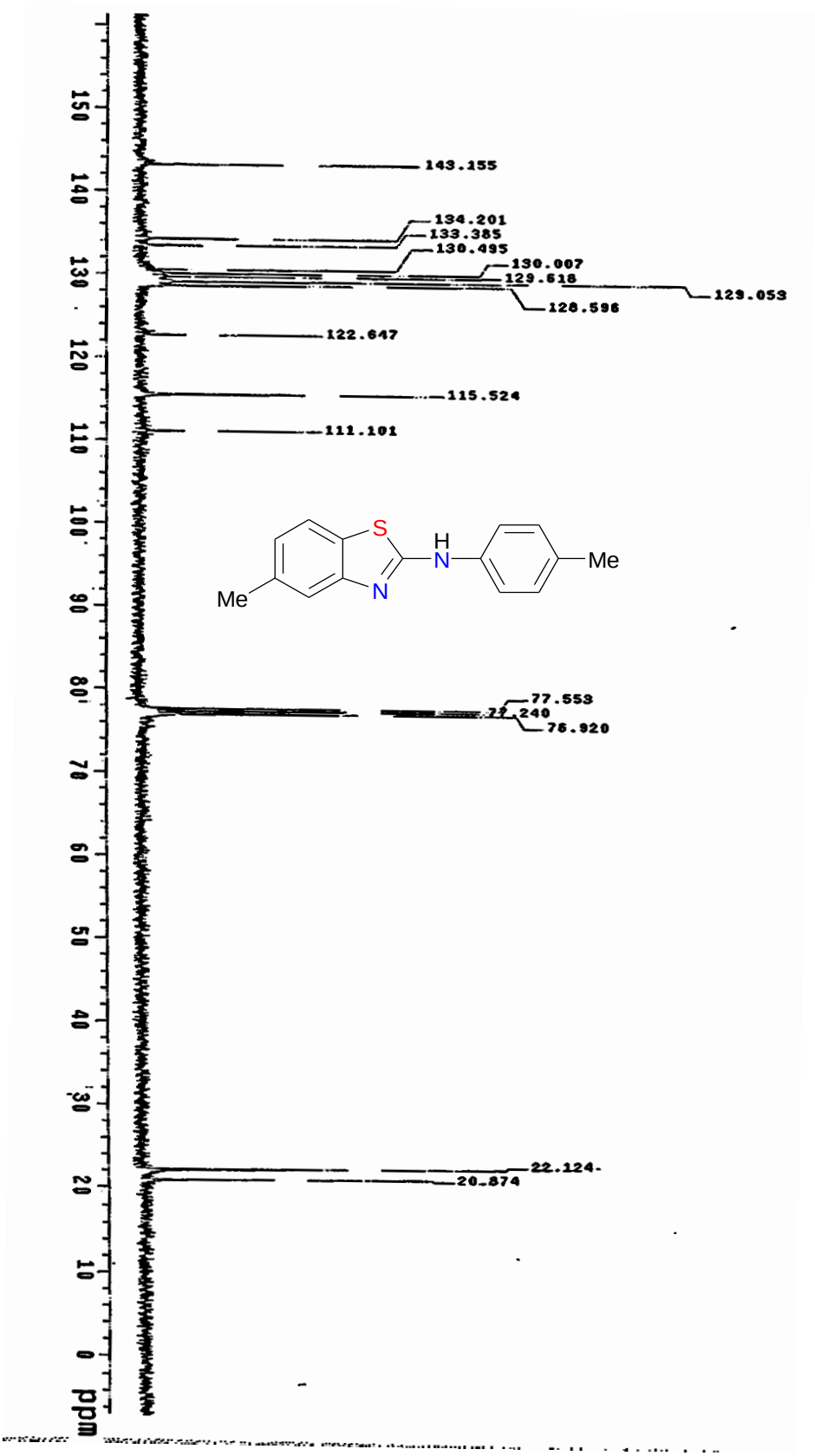

7.301
7.239
7.093
7.042
7.022
6.919
6.914
6.903
6.898
6.737
Me
S
H
N
N
Me
2.283
2.267
0.048
0.023
ppm

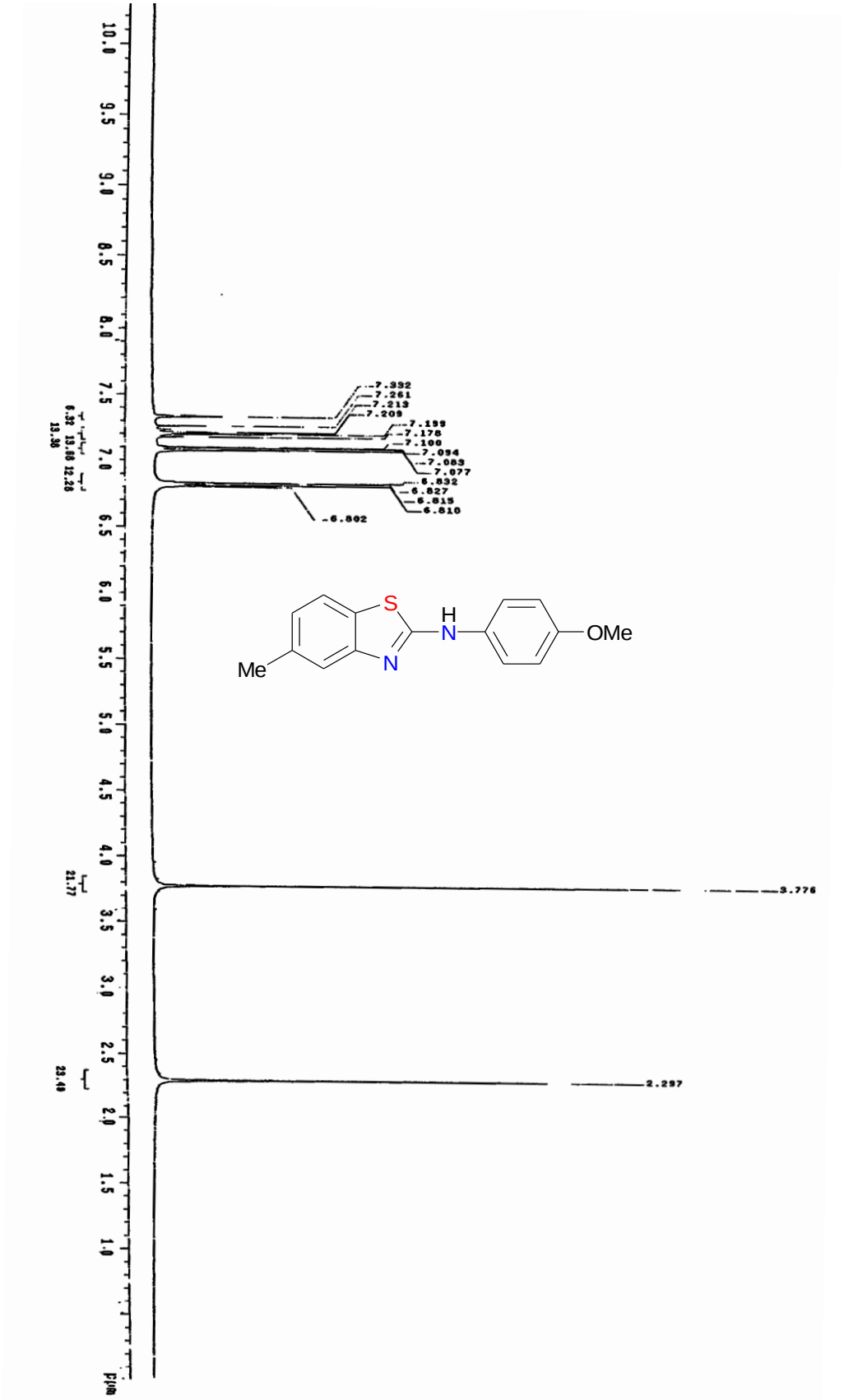

180
160
140
120
100
80
60
40
20
0
ppm
141.523
138.457
137.686
136.863
133.172
132.401
130.617
127.551
116.836
114.907
111.139
77.873
77.553
77.240
21.415
20.408
Me
Me
S
H
N
N

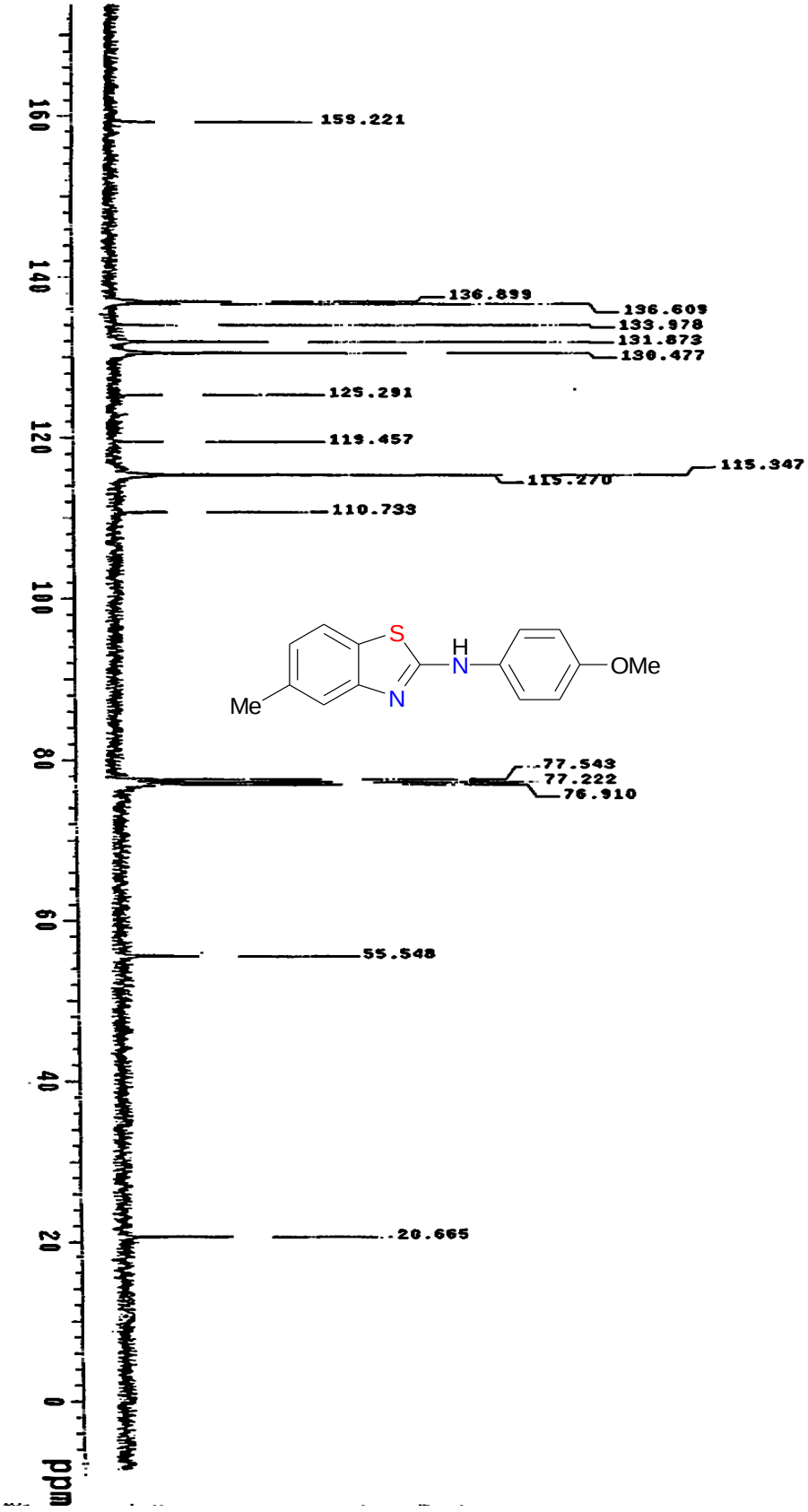

7.374
7.262
7.260
7.257
7.255
7.253
7.230
7.209
6.807
6.805
6.803
6.802
6.800
6.650
6.648
6.646
2.227
2.225
6.02
12.85
12.46
11.97
37.28
Me
Me
S
N
H
N
ppm

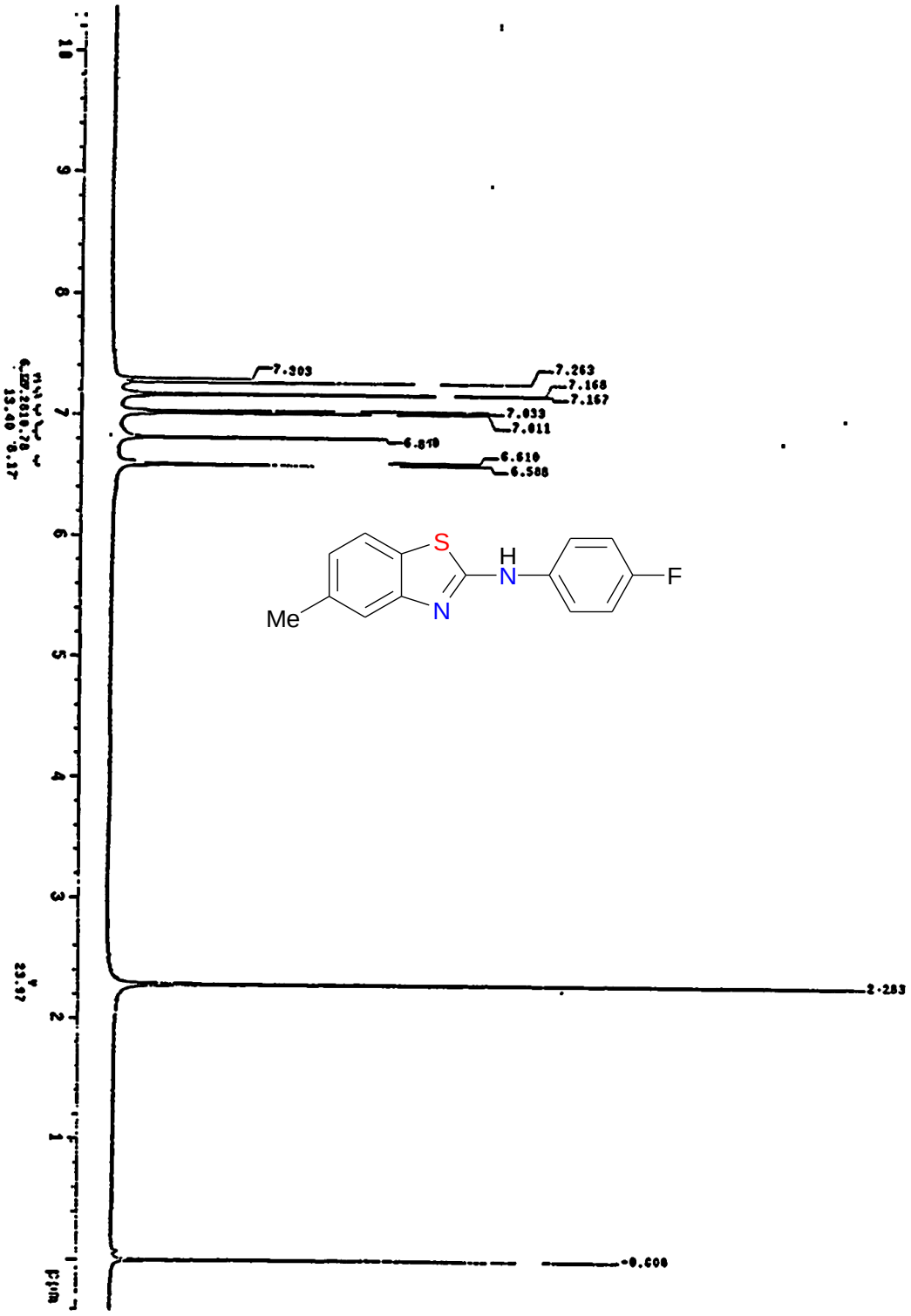

139.408
137.829
137.295
134.658
134.001
132.414
128.716
124.910
117.551
115.263
110.641
77.543
77.222
76.910
21.428
20.673
Me
Me
S
N
H
N
ppm

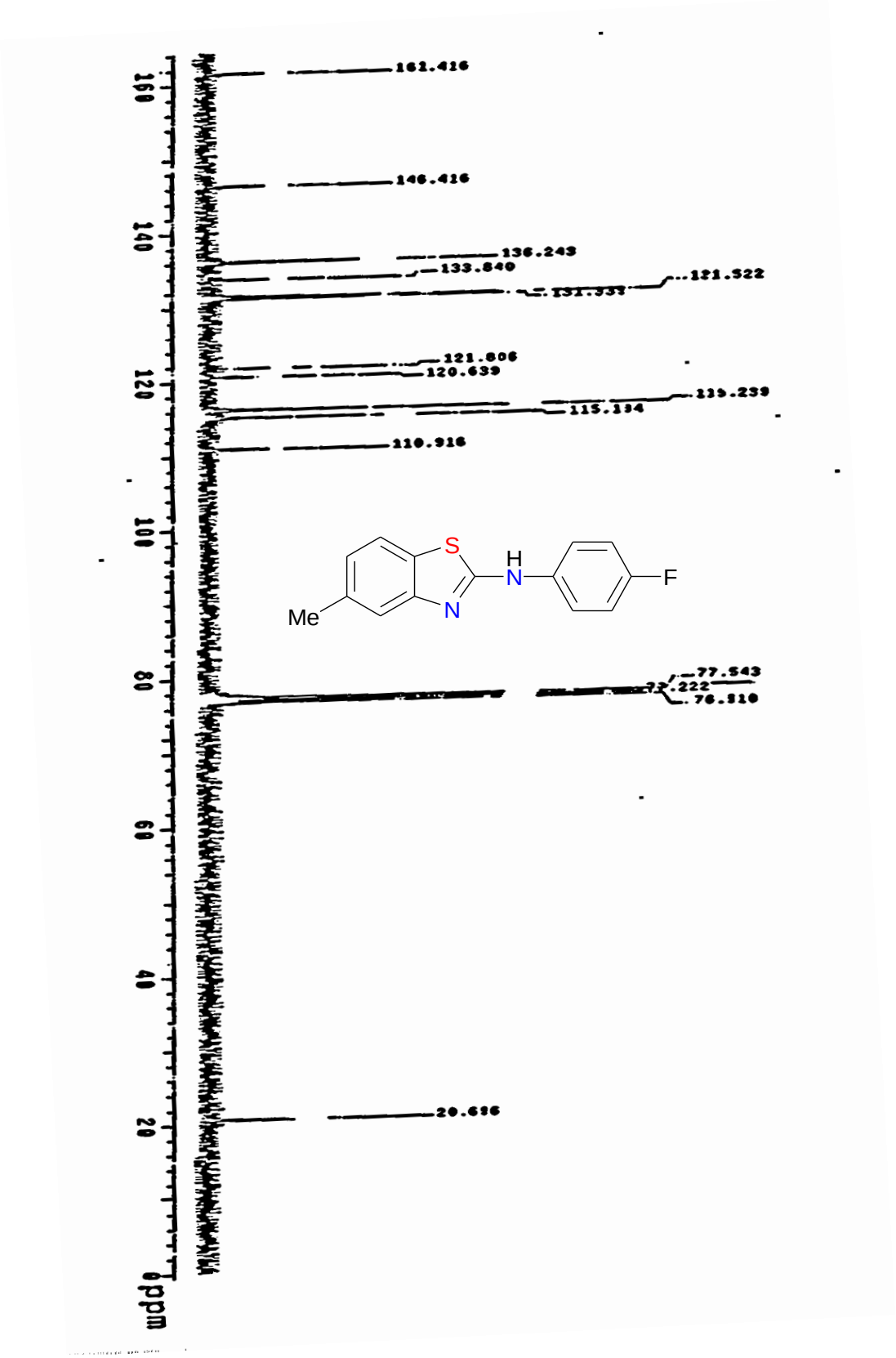

7.386
7.261
7.247
7.231
7.226
7.210
7.170
7.151
7.149
7.122
7.007
7.005
6.986
6.985
6.568
6.399
2.359
2.159
S
H
N
N
Me
Me

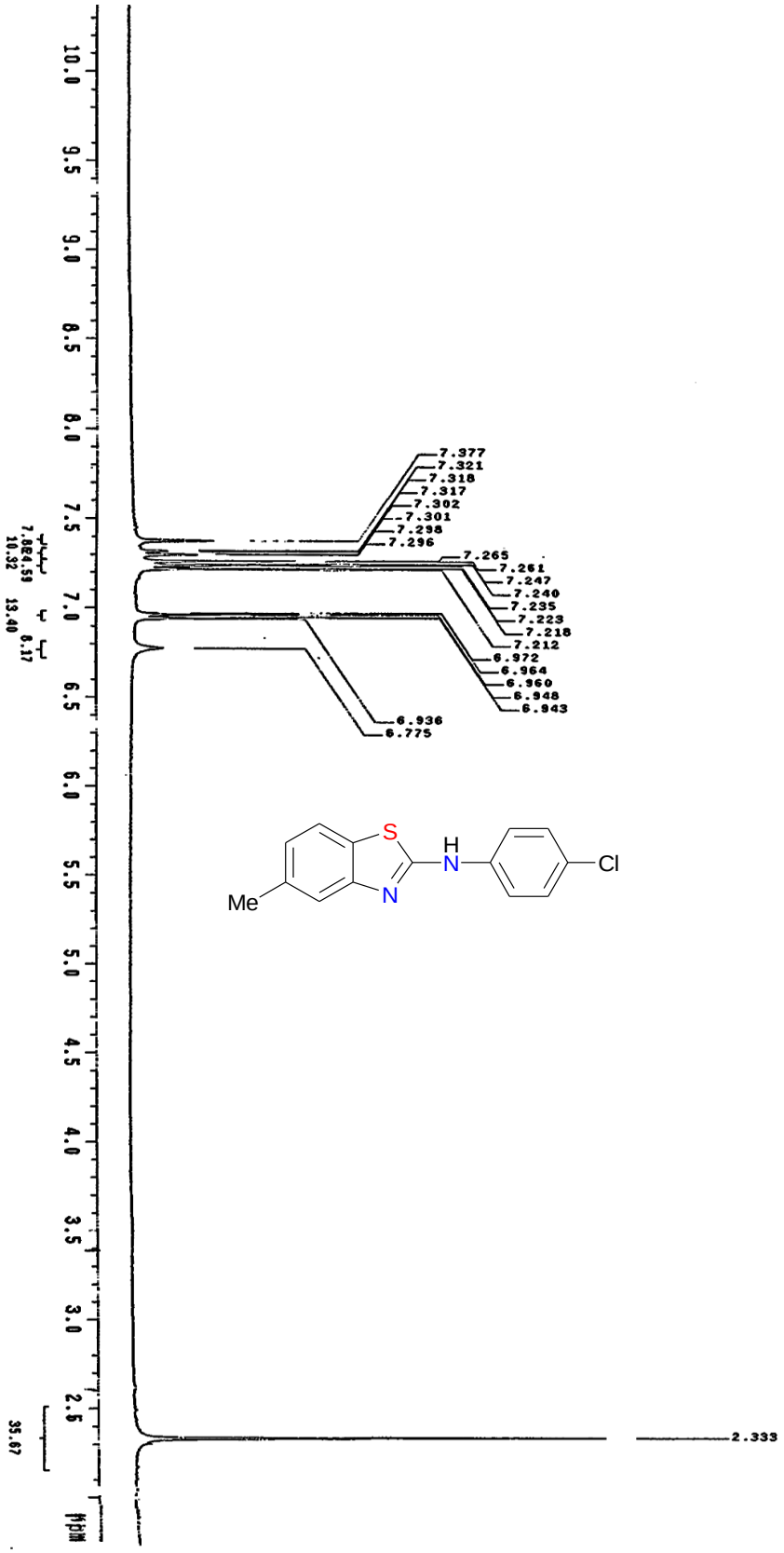

143.155
134.201
133.385
130.495
130.007
129.618
129.053
128.596
122.647
115.524
111.101
77.553
77.240
76.920
22.124
20.874
S
H
N
N
Me
Me
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

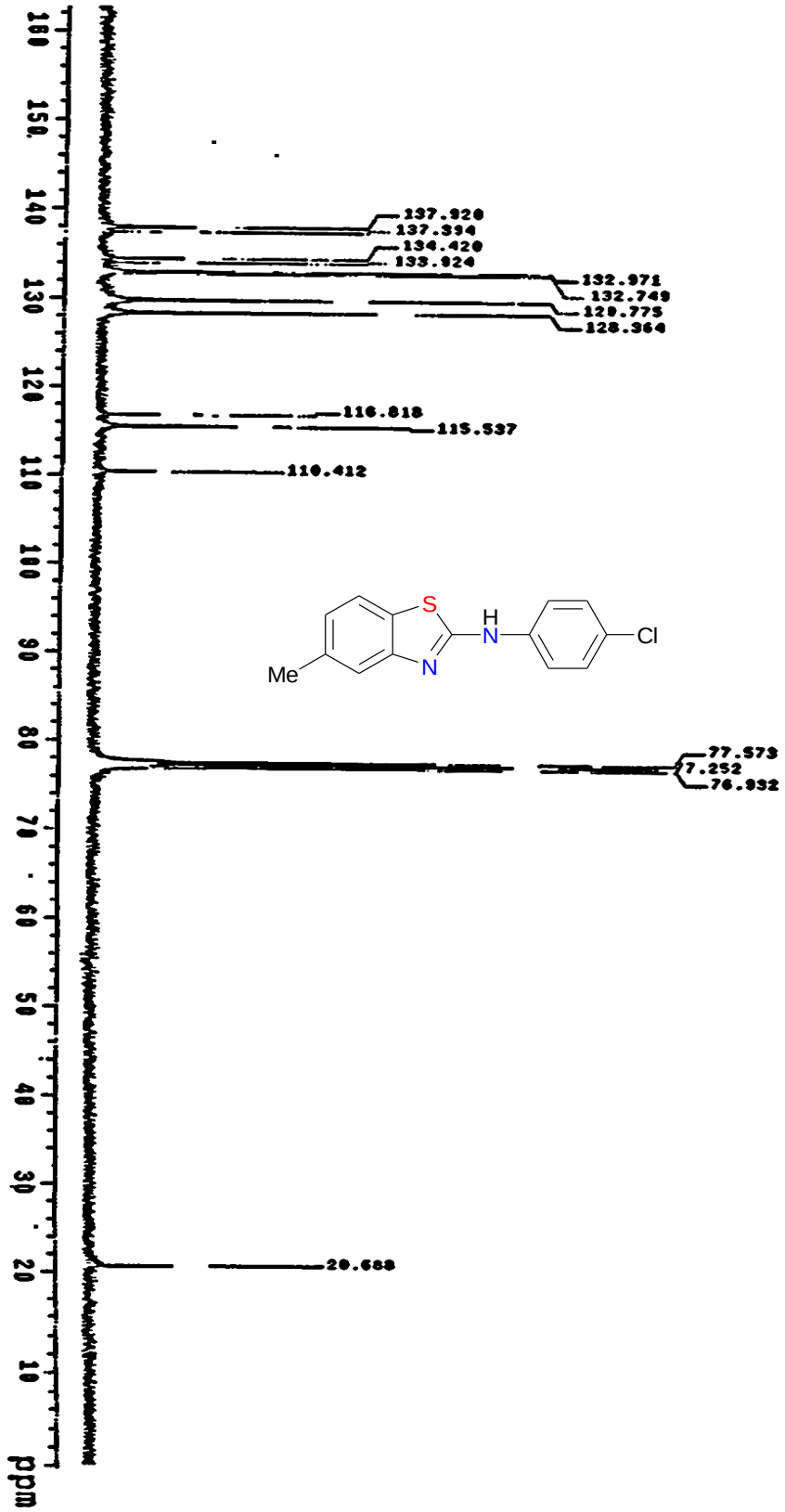

7.392
7.261
7.213
7.209
7.199
7.178
7.100
7.094
7.083
7.077
6.832
6.827
6.815
6.810
6.802
S
H
N
N
OMe
Me
3.776
2.297

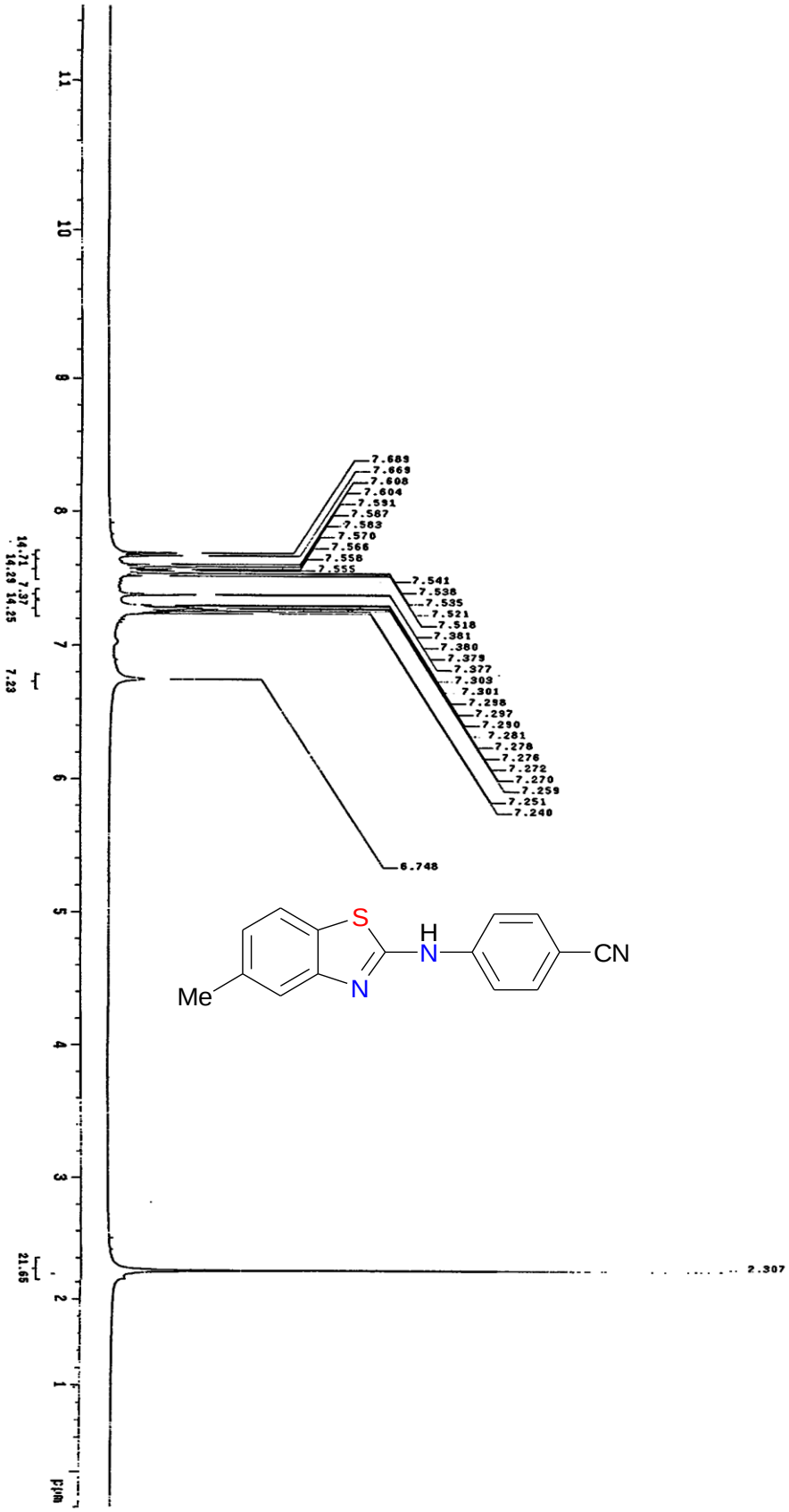

153.221
136.899
136.609
133.978
131.873
130.477
125.291
119.457
115.347
115.270
110.733
77.543
77.222
76.910
55.548
20.665
ppm
S
H
N
N
OMe
Me

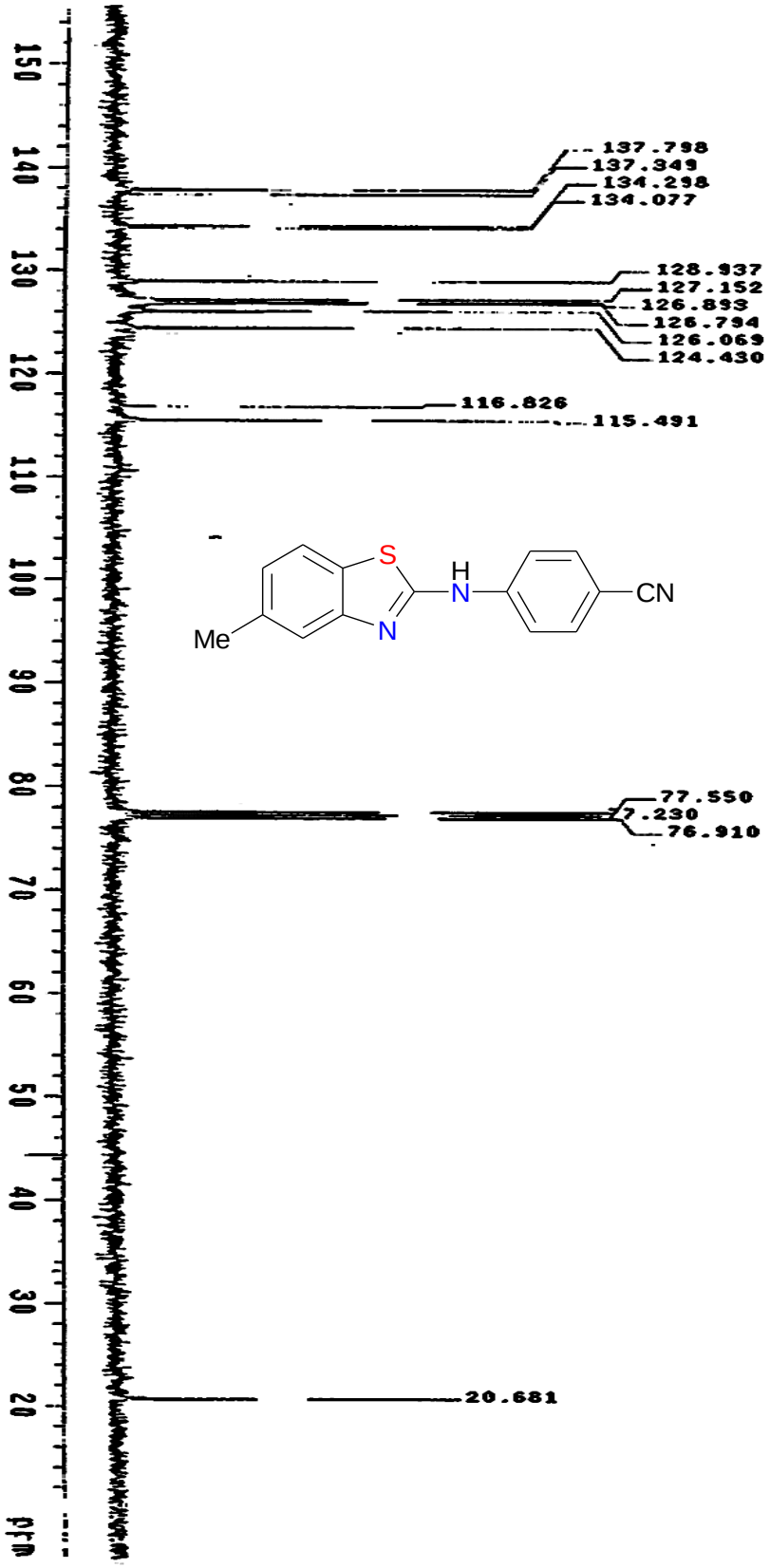

7.303
7.263
7.168
7.167
7.033
7.011
6.819
6.610
6.588
2.283
0.608
S
H
N
N
F
Me

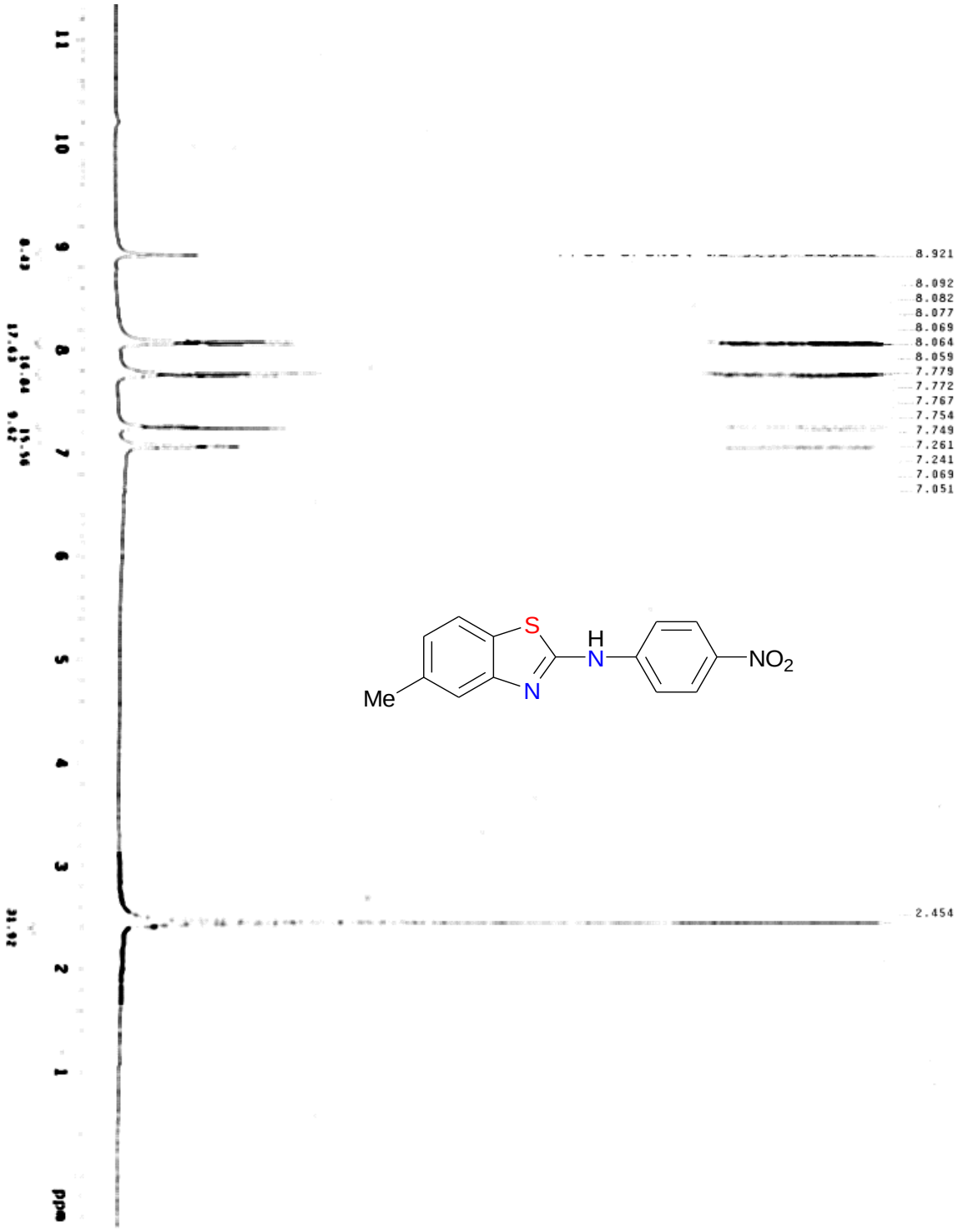

161.416
146.416
136.243
133.840
121.522
121.606
120.639
115.239
115.134
110.916
77.543
77.222
76.810
20.696
ppm
160
140
120
100
80
60
40
20
0
S
H
N
F
N
Me

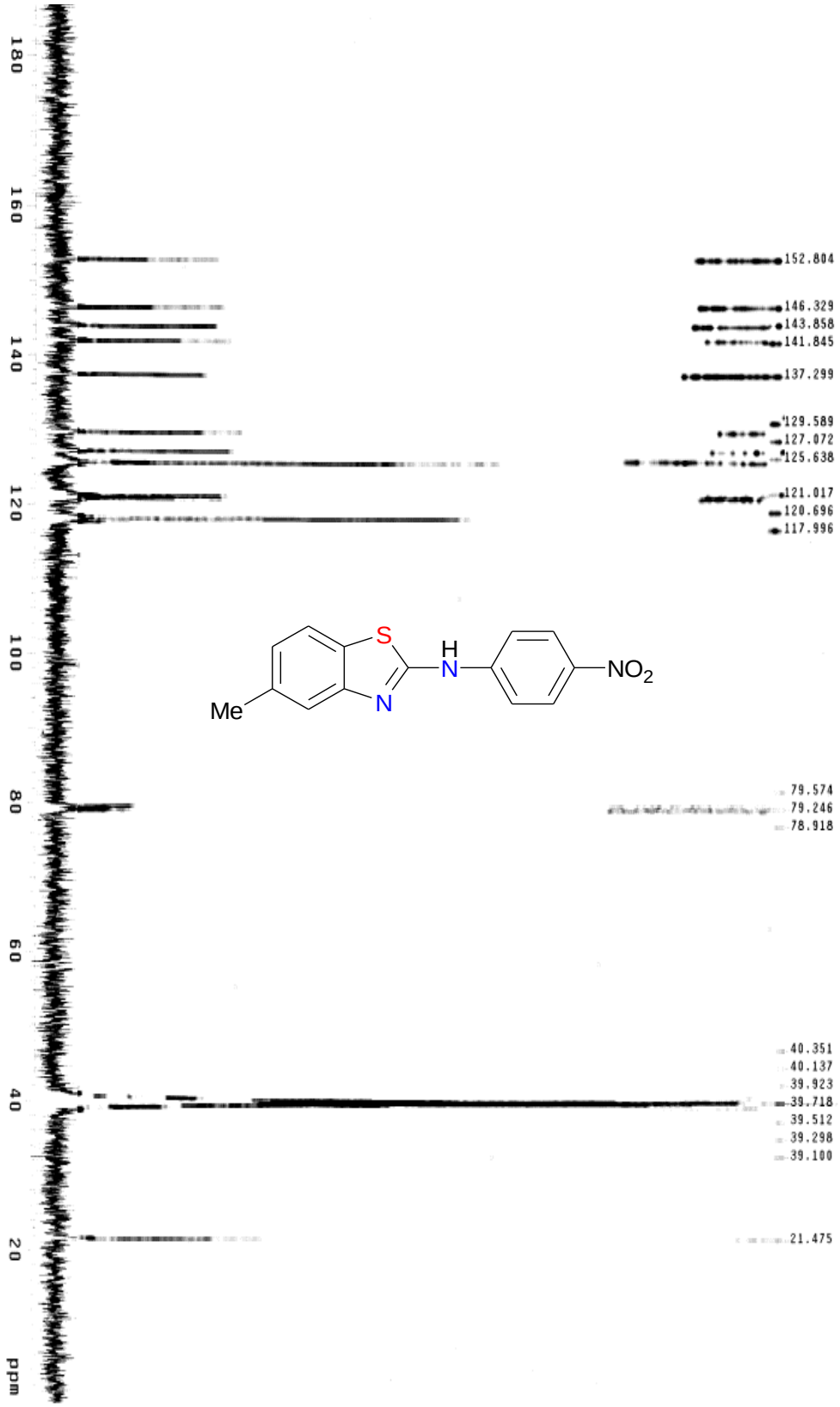

7.377
7.321
7.318
7.317
7.302
7.301
7.298
7.296
7.265
7.261
7.247
7.240
7.235
7.223
7.218
7.212
6.972
6.964
6.960
6.948
6.943
6.936
6.775
7.0844.59
10.32
13.40
8.17
35.67
2.333
S
H
N
Cl
Me
N
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
PPM

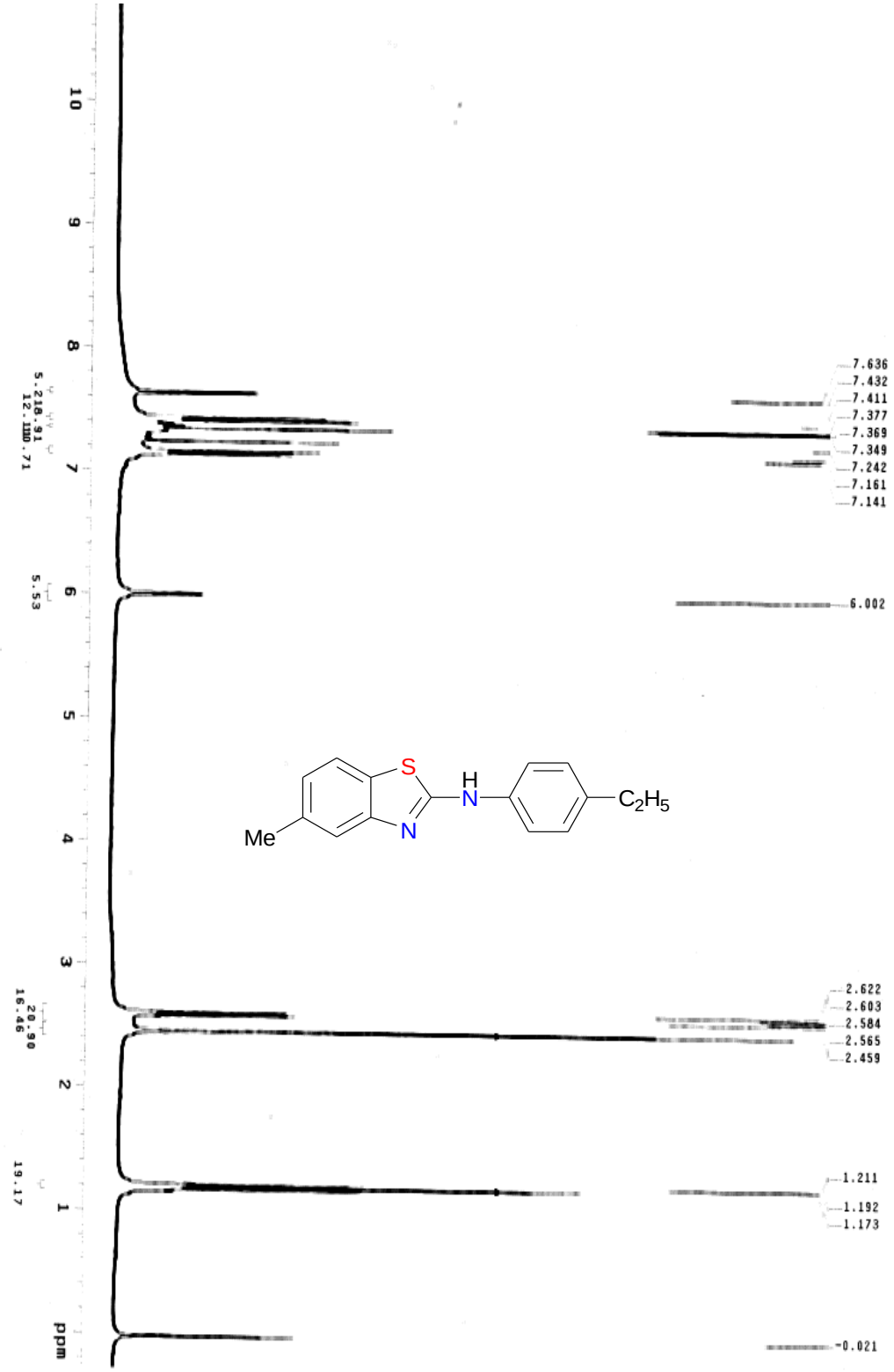

137.920
137.394
134.420
133.924
132.971
132.749
129.775
128.364
116.818
115.537
110.412
77.573
7.252
76.932
20.688
S
H
N
N
Cl
Me
ppm

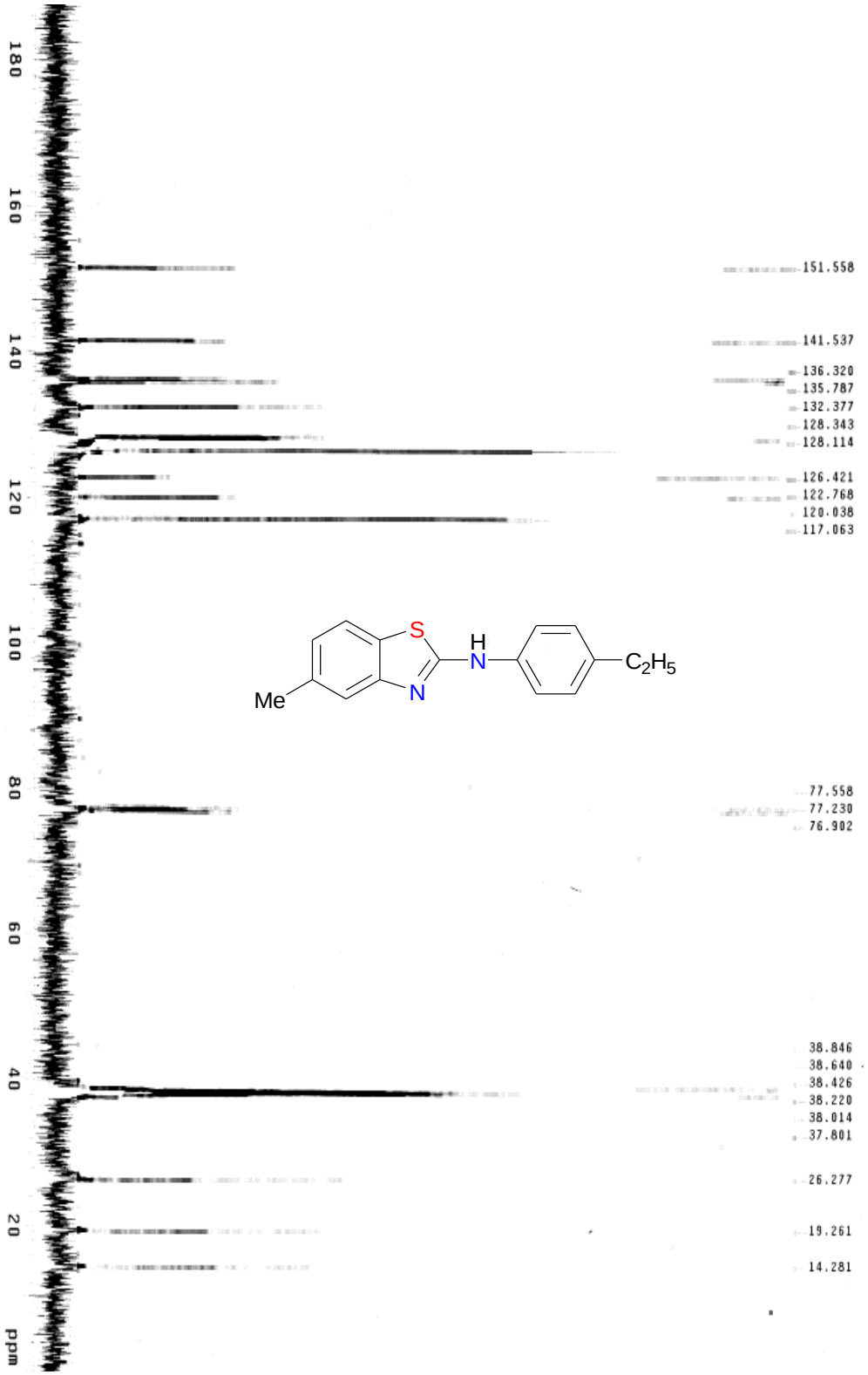

7.689
7.669
7.608
7.604
7.591
7.567
7.563
7.570
7.566
7.558
7.555
7.541
7.538
7.535
7.521
7.518
7.381
7.380
7.379
7.377
7.303
7.301
7.298
7.297
7.290
7.281
7.278
7.276
7.272
7.270
7.259
7.251
7.240
6.748
2.307
S
H
N
CN
Me
N

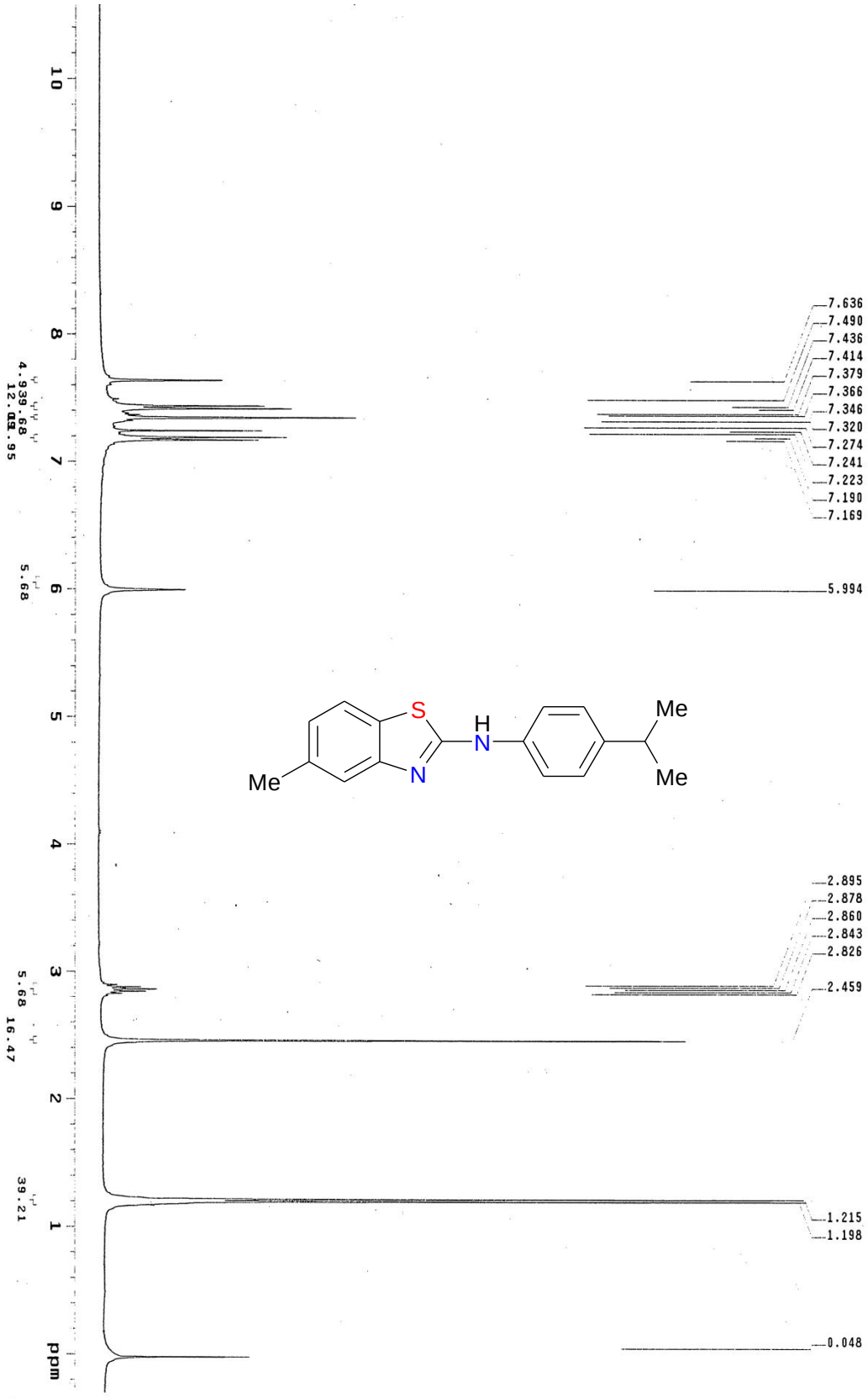

137.798
137.349
134.298
134.077
128.937
127.152
126.893
126.794
126.069
124.430
116.826
115.491
77.550
7.230
76.910
20.681
S
H
N
N
CN
Me

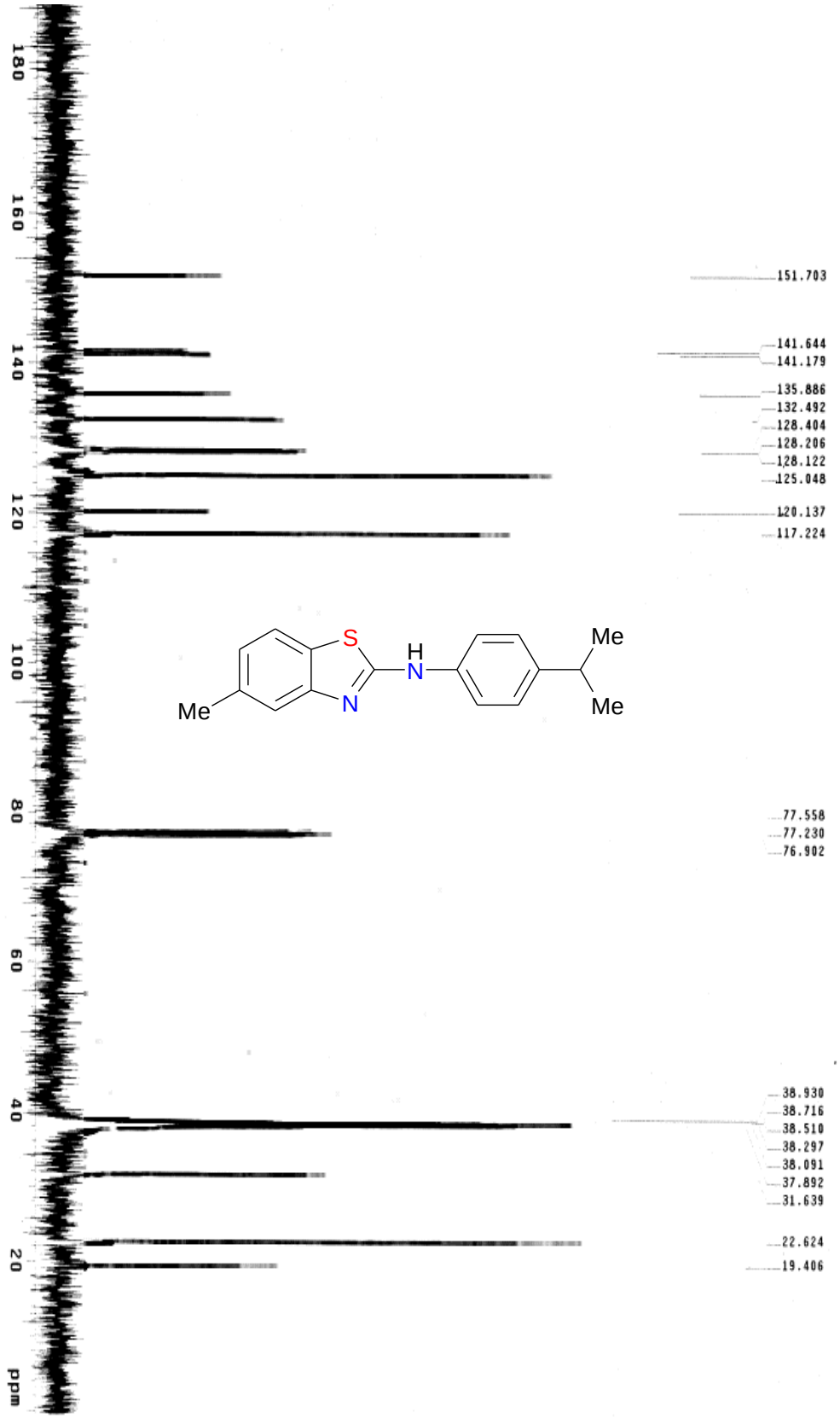

8.921
8.092
8.082
8.077
8.069
8.064
8.059
7.779
7.772
7.767
7.754
7.749
7.261
7.241
7.069
7.051
2.454
S
H
N
N
Me
NO2
ppm

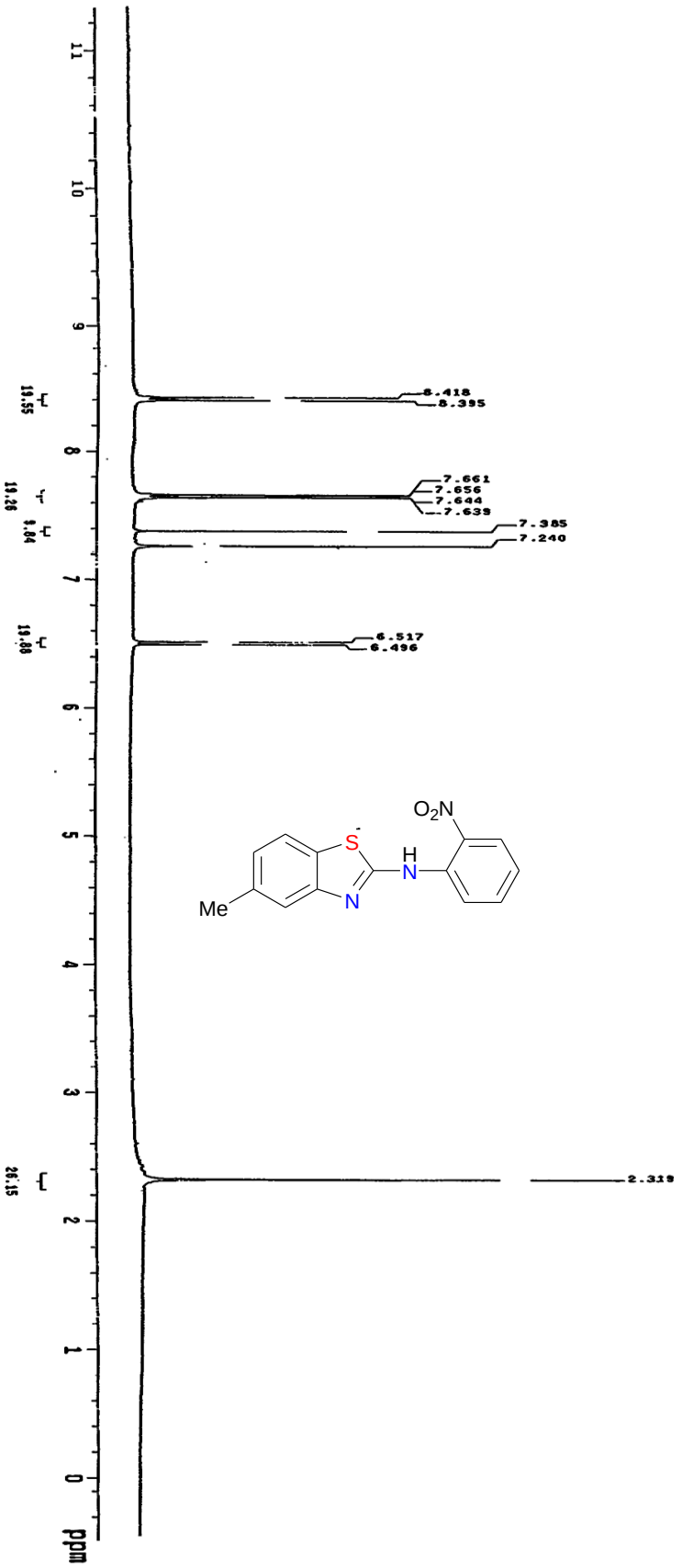

180
160
140
120
100
80
60
40
20
ppm
152.804
146.329
143.858
141.845
137.299
129.589
127.072
125.638
121.017
120.696
117.996
79.574
79.246
78.918
40.351
40.137
39.923
39.718
39.512
39.298
39.100
21.475
S
H
N
N
NO2
Me

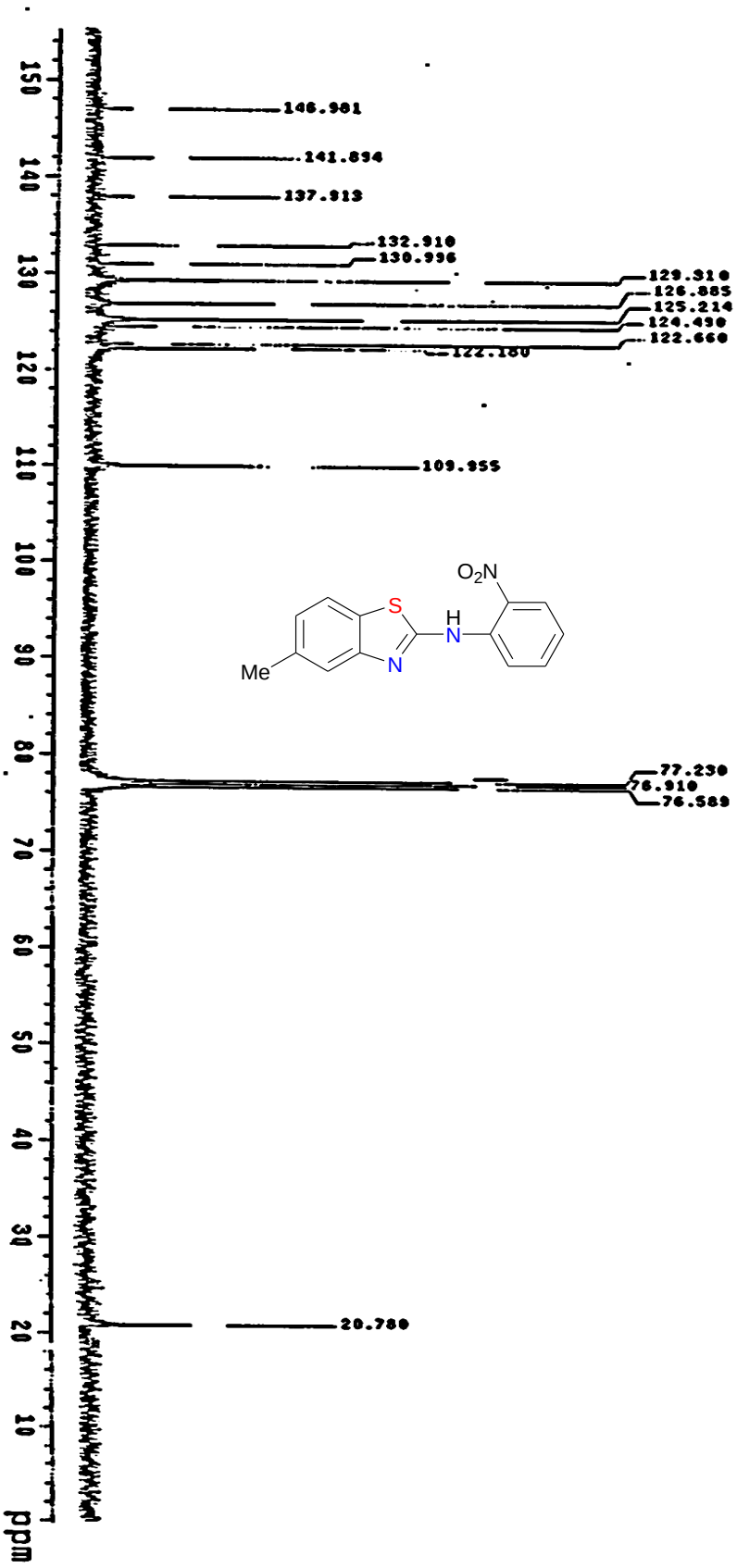

7.636
7.432
7.411
7.377
7.369
7.349
7.242
7.161
7.141
6.002
2.622
2.603
2.584
2.565
2.459
1.211
1.192
1.173
0.021
S
H
N
N
Me
C2H5
ppm

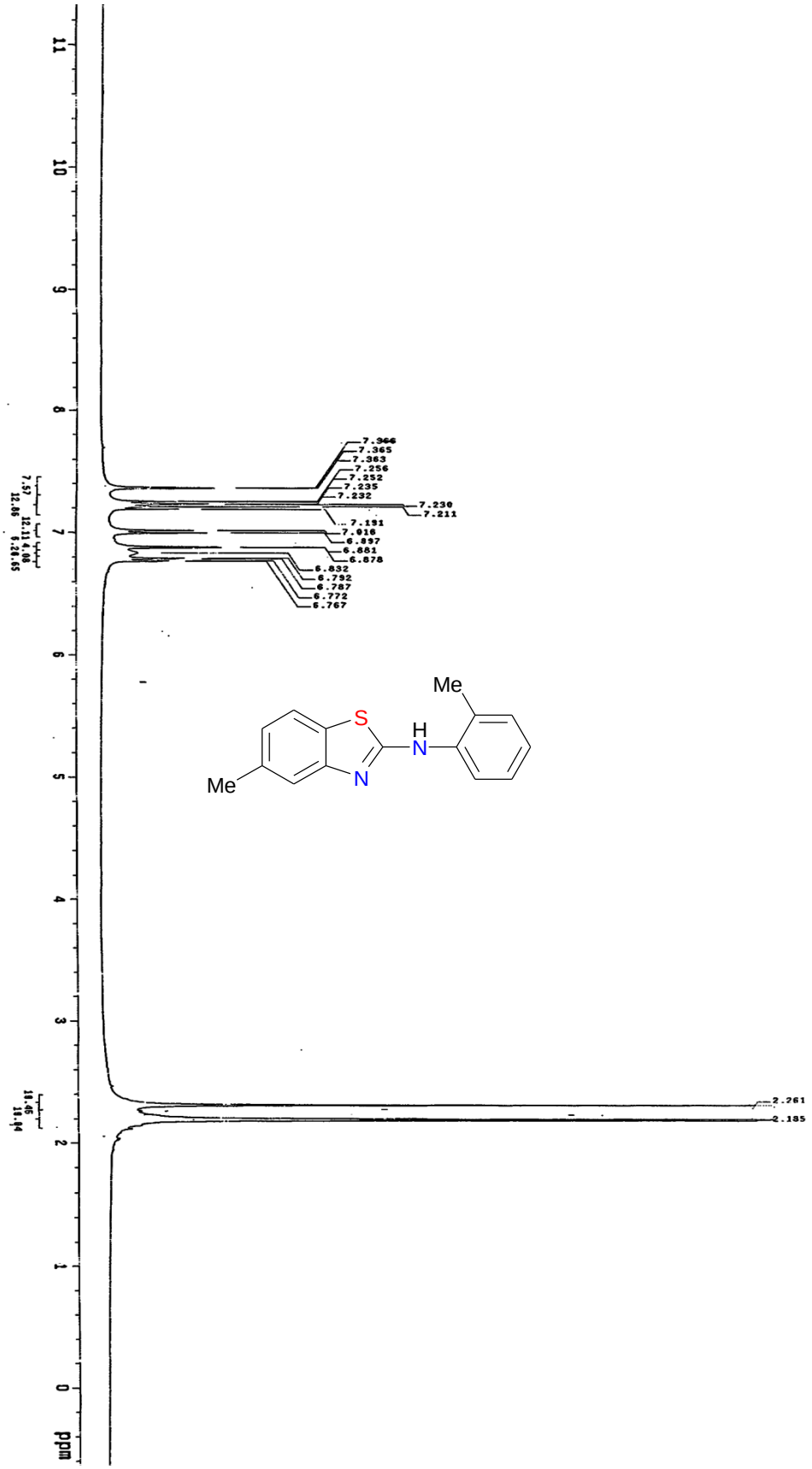

180
160
140
120
100
80
60
40
20
ppm
151.558
141.537
136.320
135.787
132.377
128.343
128.114
126.421
122.768
120.038
117.063
77.558
77.230
76.902
38.846
38.640
38.426
38.220
38.014
37.801
26.277
19.261
14.281
S
H
N
N
Me
C2H5

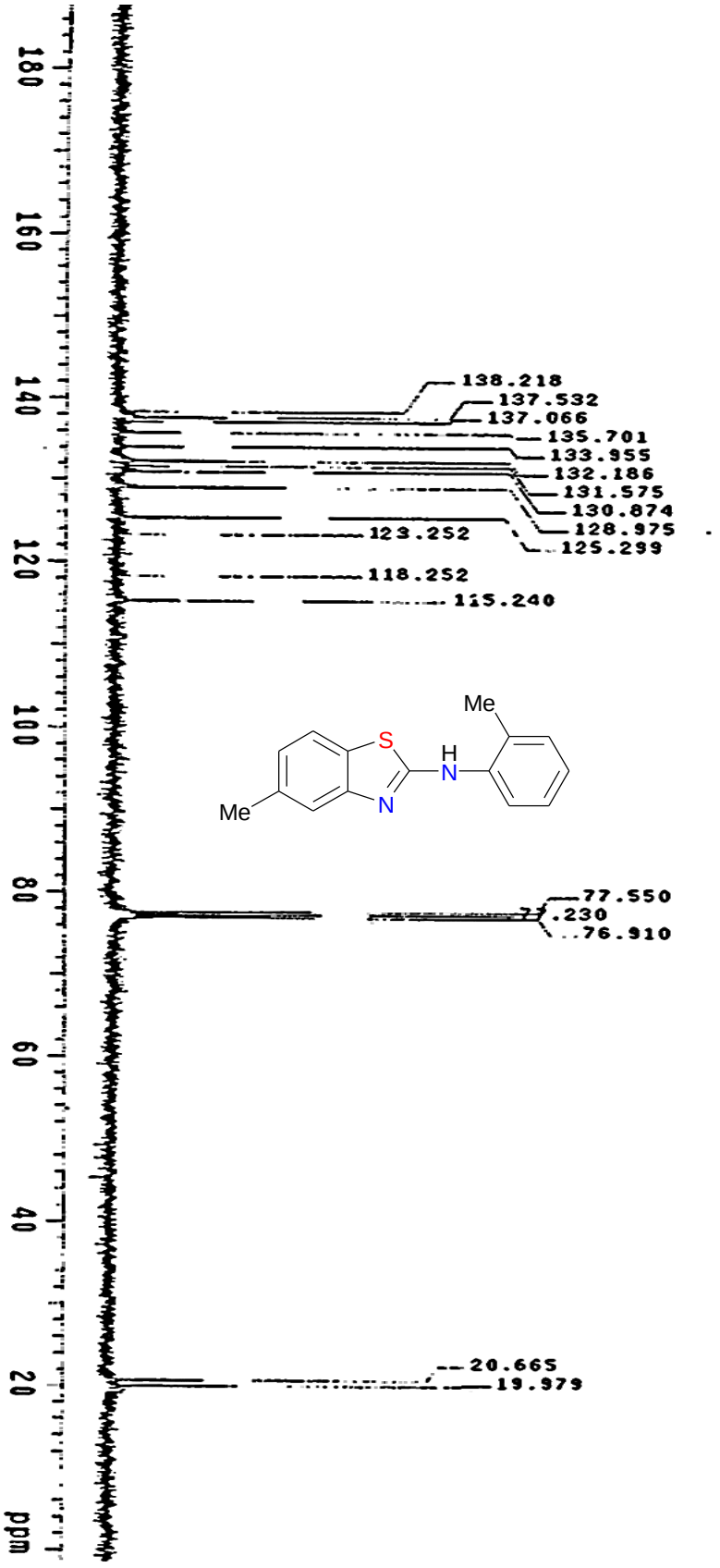

7.636
7.490
7.436
7.414
7.379
7.366
7.346
7.320
7.274
7.241
7.223
7.190
7.169
5.994
2.895
2.878
2.860
2.843
2.826
2.459
1.215
1.198
0.048
S
H
N
N
Me
Me
Me
ppm

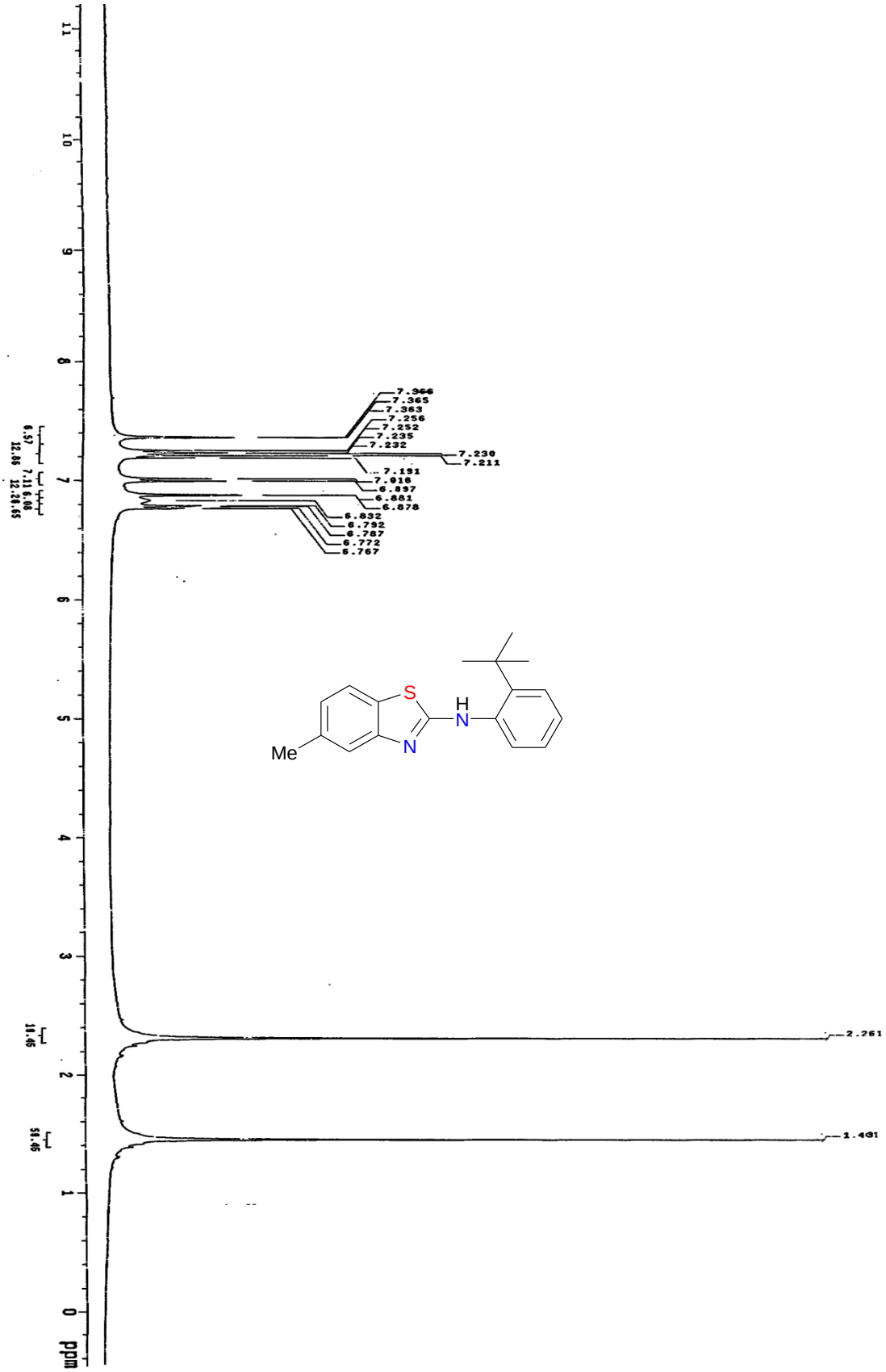

180
160
140
120
100
80
60
40
20
ppm
151.703
141.644
141.179
135.886
132.492
128.404
128.206
128.122
125.048
120.137
117.224
77.558
77.230
76.902
38.930
38.716
38.510
38.297
38.091
37.892
31.639
22.624
19.406
S
H
N
N
Me
Me
Me

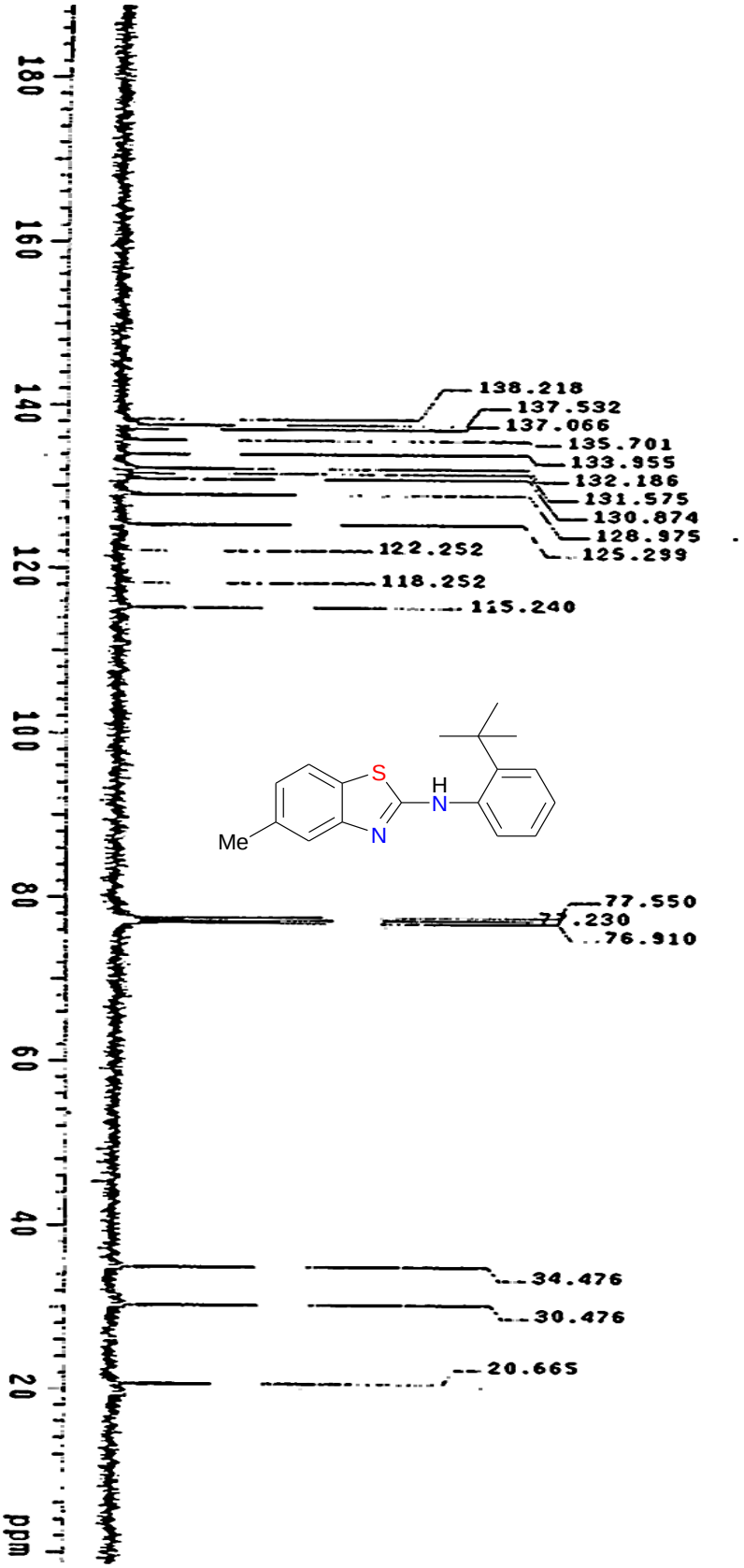

8.418
8.395
7.661
7.656
7.644
7.639
7.385
7.240
6.517
6.496
2.319
ppm
O2N
S
H
N
N
Me

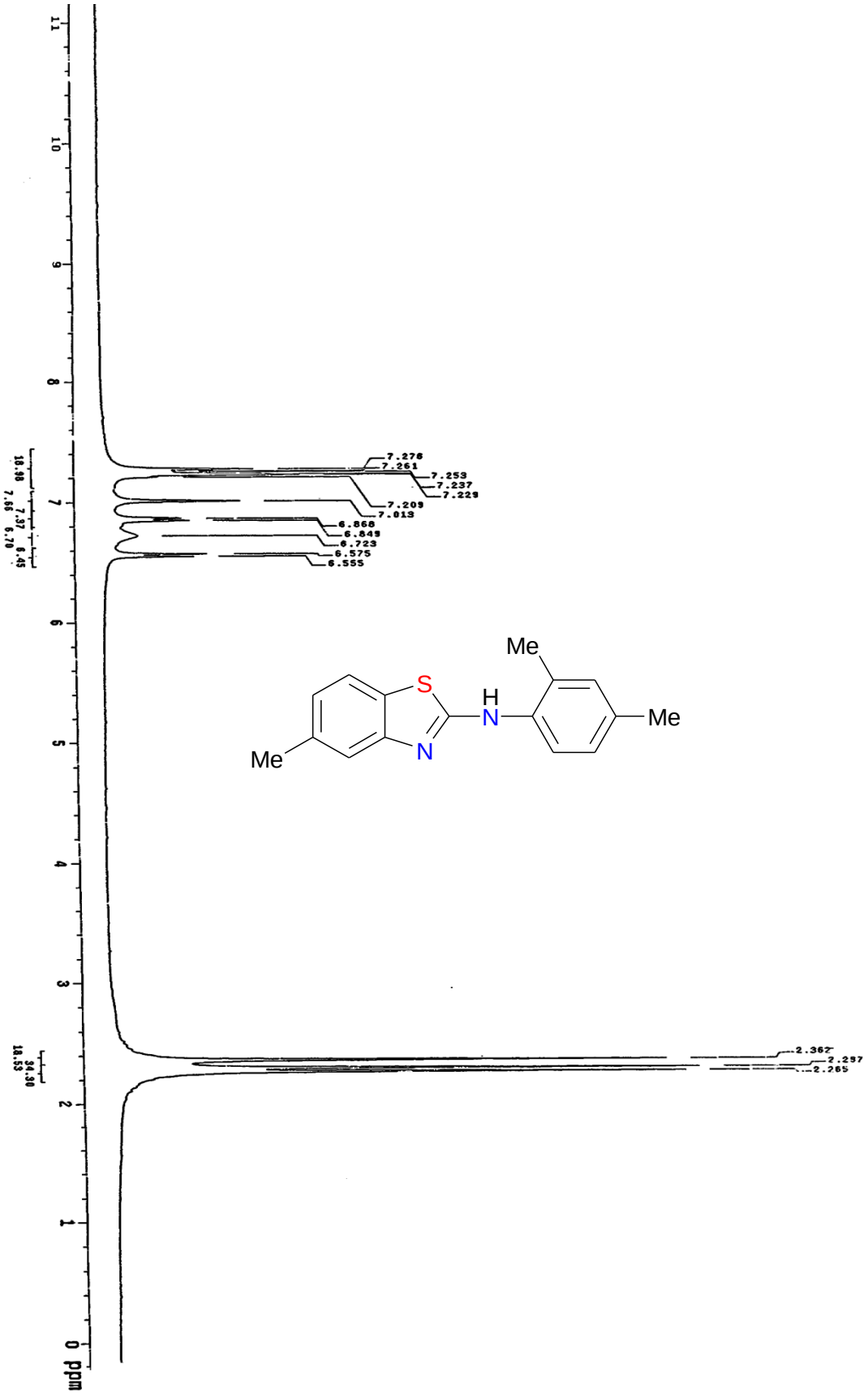

146.981
141.694
137.913
132.910
130.996
129.310
126.885
125.214
124.490
122.660
122.180
109.955
77.230
76.910
76.589
20.780
O2N
S
H
N
N
Me
ppm

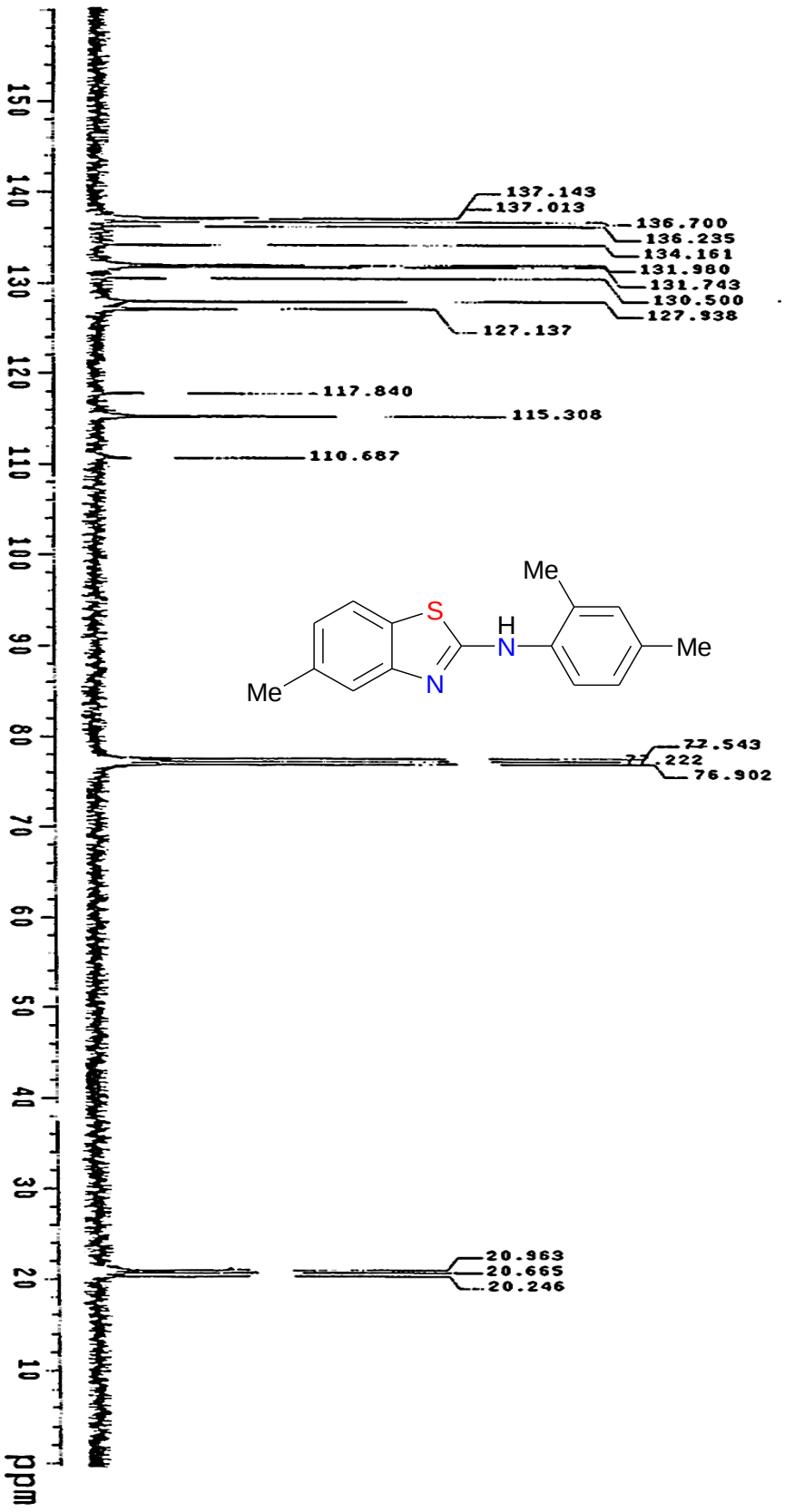

7.966
7.365
7.363
7.256
7.252
7.235
7.232
7.230
7.211
7.191
7.016
6.897
6.881
6.878
6.832
6.792
6.787
6.772
6.767
Me
S
H
N
N
Me
2.261
2.185
ppm

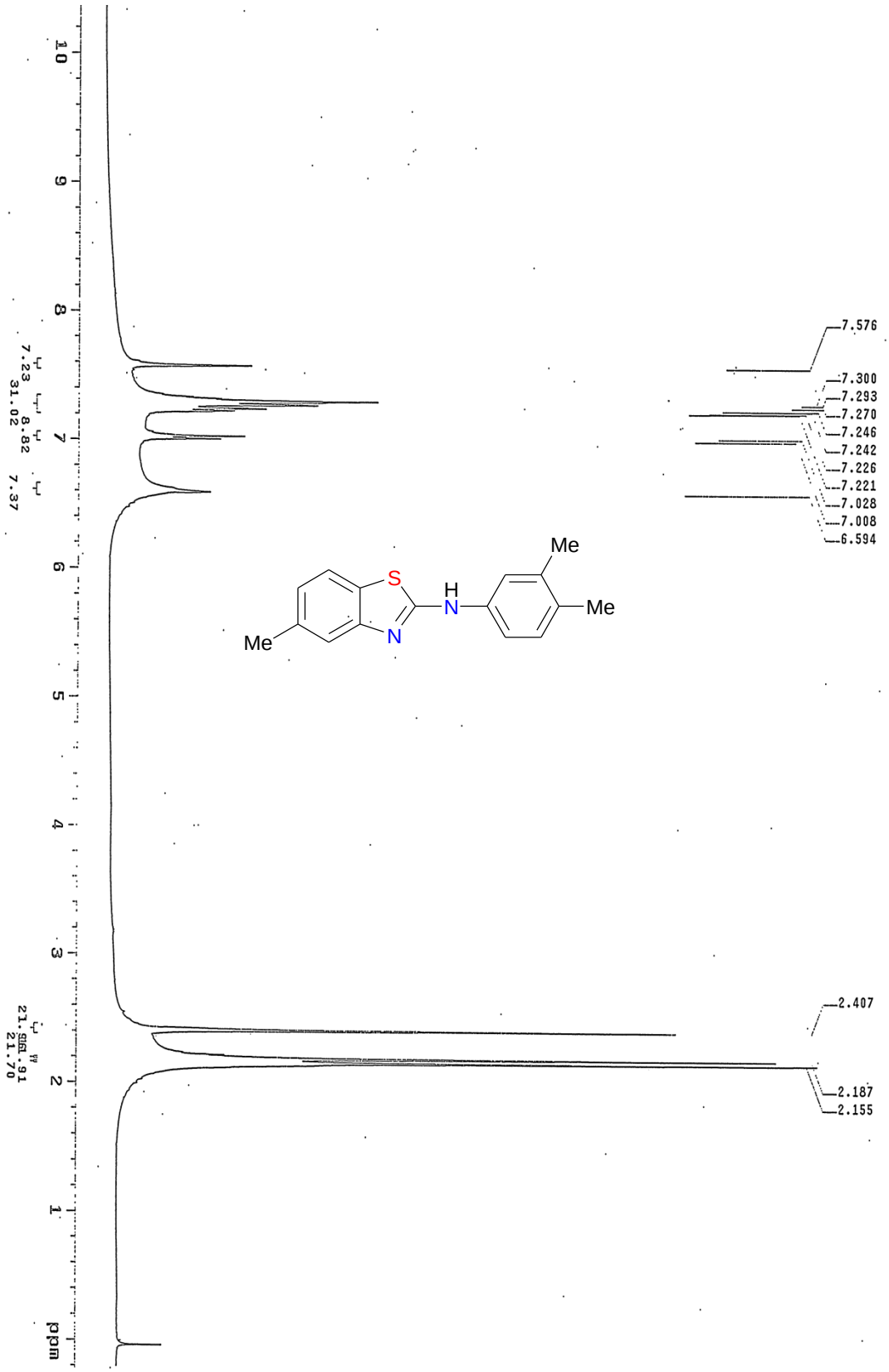

180
160
140
120
100
80
60
40
20
ppm
138.218
137.532
137.066
135.701
133.955
132.186
131.575
130.874
128.975
125.299
123.252
118.252
115.240
77.550
77.230
76.910
20.665
19.979
Me
S
H
N
N
Me

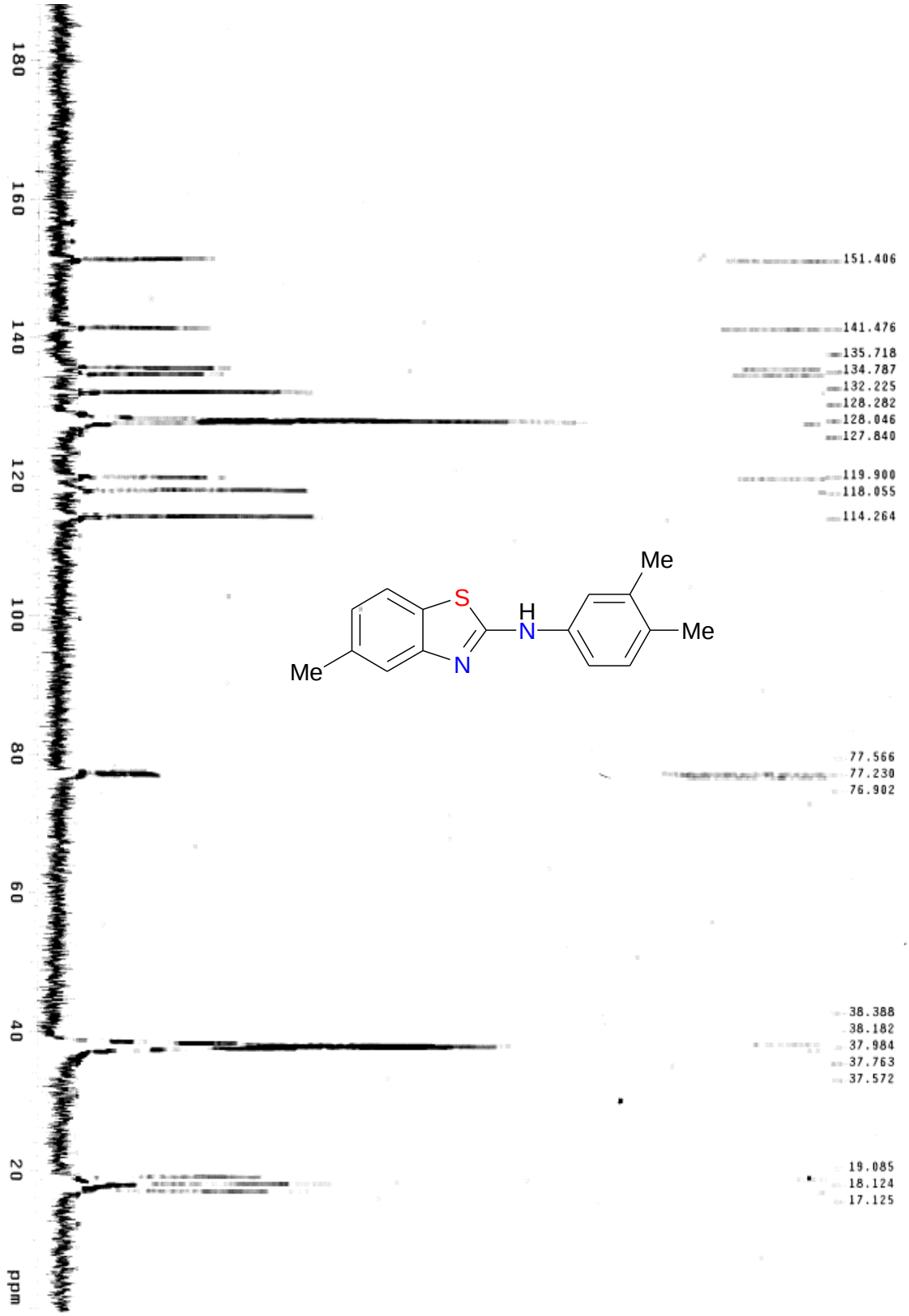

7.366
7.365
7.363
7.256
7.252
7.235
7.232
7.230
7.211
7.191
7.016
6.897
6.881
6.878
6.832
6.792
6.787
6.772
6.767
6.57
12.86
7.11
6.08
12.26
5.65
18.46
51.46
2.261
1.491
ppm
S
H
N
N
Me

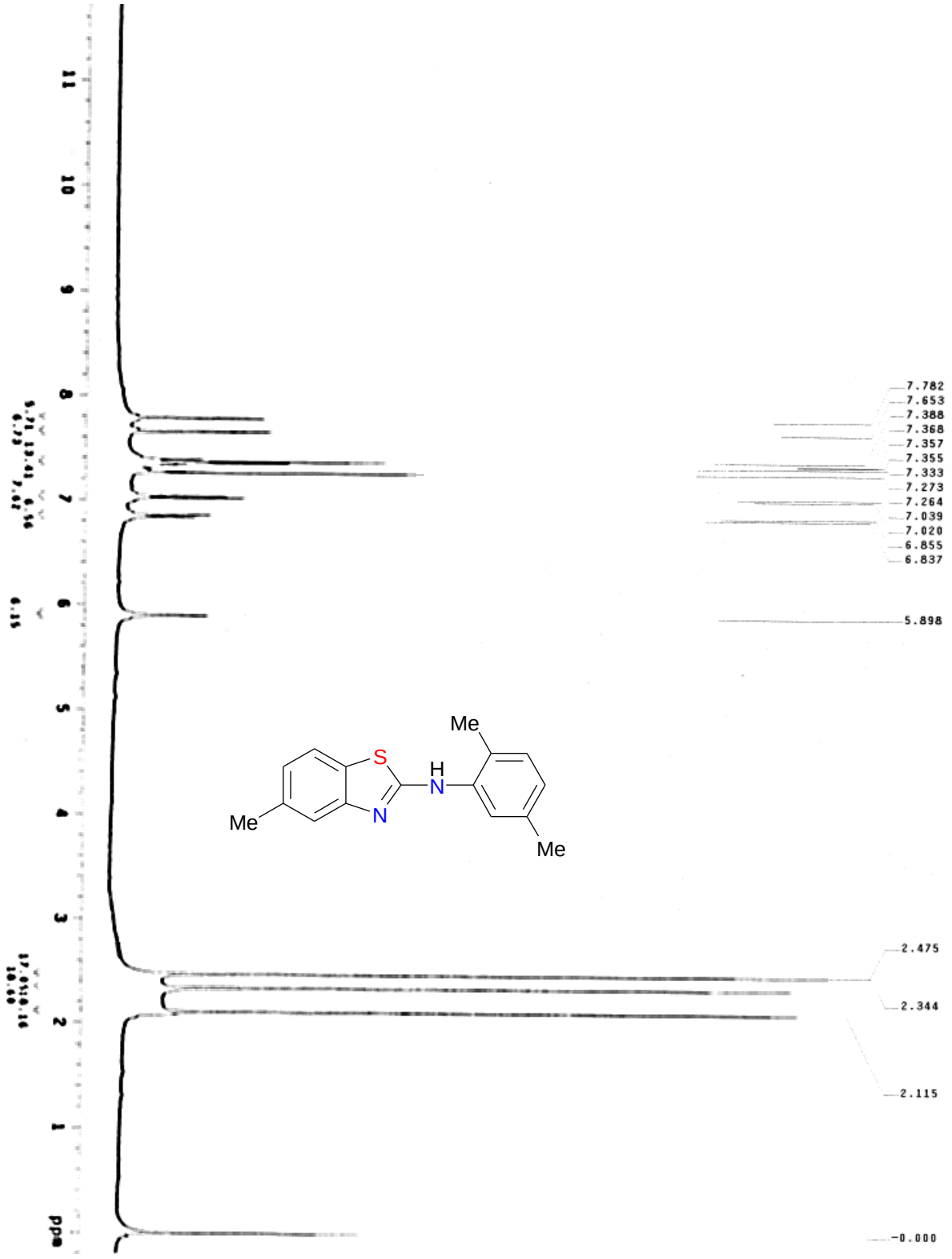

138.218
137.532
137.066
135.701
133.955
132.186
131.575
130.874
128.975
125.299
122.252
118.252
115.240
77.550
77.230
76.910
34.476
30.476
20.665
S
H
N
N
Me
180
160
140
120
100
80
60
40
20
ppm

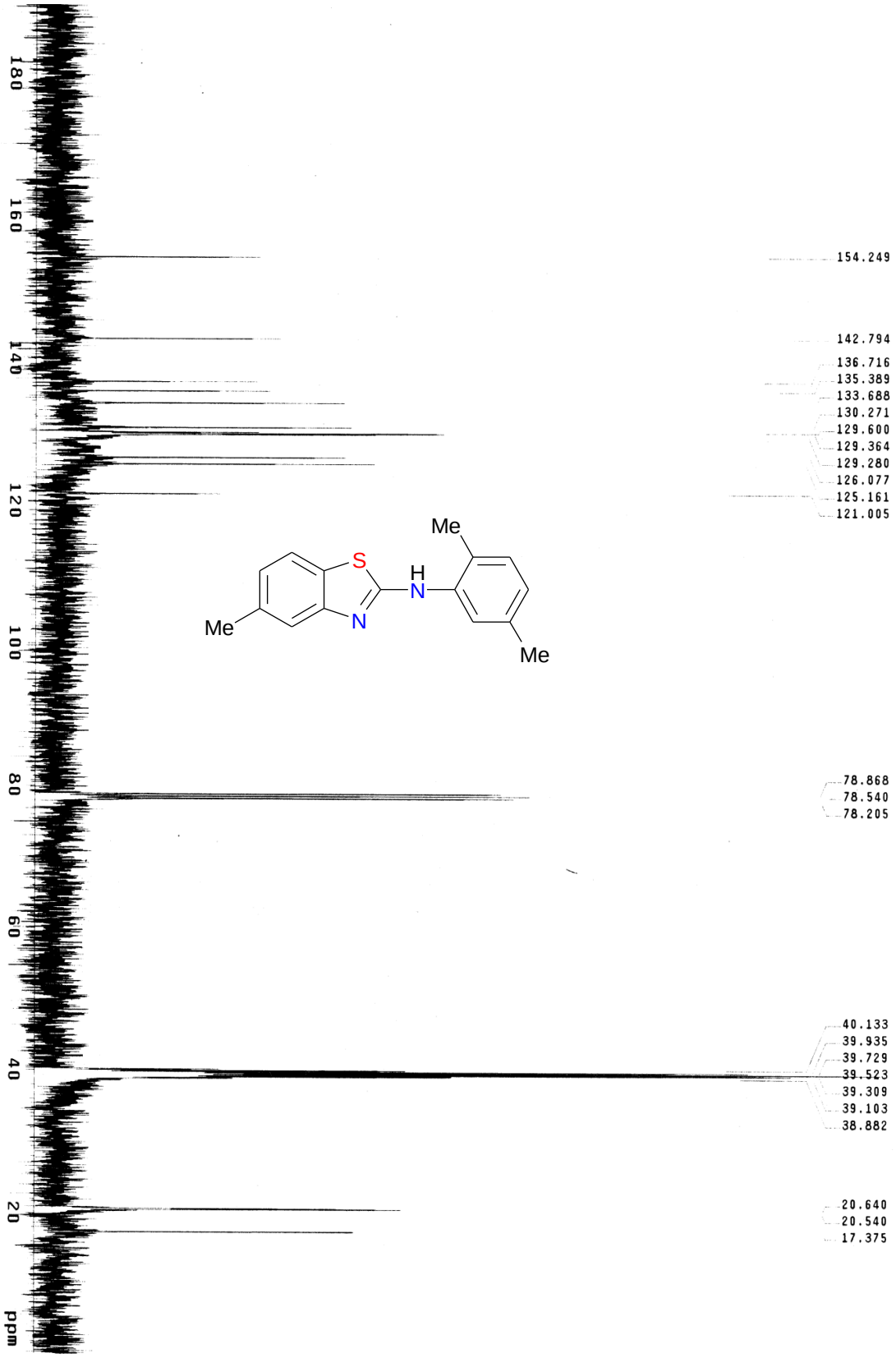

7.276
7.261
7.253
7.237
7.229
7.209
7.013
6.868
6.849
6.723
6.575
6.555
2.362
2.297
2.265
Me
S
H
N
Me
N
Me
ppm


137.143
137.013
136.700
136.235
134.161
131.980
131.743
130.500
127.938
127.137
117.840
115.308
110.687
77.543
77.222
76.902
20.963
20.665
20.246
ppm
Me
S
H
N
Me
N
Me


7.576
7.300
7.293
7.270
7.246
7.242
7.226
7.221
7.028
7.008
6.594
2.407
2.187
2.155
7.23
31.02
8.82
7.37
21.91
21.70
Me
S
H
N
N
Me
Me
ppm


180
160
140
120
100
80
60
40
20
ppm
151.406
141.476
135.718
134.787
132.225
128.282
128.046
127.840
119.900
118.055
114.264
77.566
77.230
76.902
38.388
38.182
37.984
37.763
37.572
19.085
18.124
17.125
Me
S
H
N
N
Me
Me


7.782
7.653
7.388
7.368
7.357
7.355
7.333
7.273
7.264
7.039
7.020
6.855
6.837
5.898
2.475
2.344
2.115
-0.000
Me
S
H
N
N
Me
Me


180
160
140
120
100
80
60
40
20
ppm
154.249
142.794
136.716
135.389
133.688
130.271
129.600
129.364
129.280
126.077
125.161
121.005
78.868
78.540
78.205
40.133
39.935
39.729
39.523
39.309
39.103
38.882
20.640
20.540
17.375
Me
S
H
N
N
Me
Me