Supporting Information for the manuscript entitled:

[1,2]-WITTIG REARRANGEMENT OF AROMATIC HETEROCYCLES

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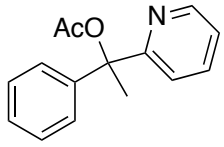
Table of Contents

General Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 400 MHz spectrometer from Bruker using $CDCl_3$ as the deuterated solvent. The chemical shifts (δ) are reported in parts per million (ppm) relative to internal TMS (0 ppm for ^{1}H-NMR) or the residual $CDCl_3$ peak (77.0 ppm for ^{13}C-NMR). The coupling constants (*J*) were reported in Hertz (Hz). IR spectra were recorded on an FT-IR spectrometer. Mass spectra were recorded using electron ionization (EI) or electrospray ionization (ESI). All chemicals were used as received unless otherwise stated. Tetrahydrofuran (THF) was purified by passing over a column of dry alumina or freshly distilled from sodium with benzophenone as an indicator. Dichloromethane (DCM) and diisopropylamine (DIA) were distilled from calcium hydride (CaH_2). Other solvents were used without any purification. Glassware, NMR tubes, stir bars, and needles were dried overnight in an oven heated at 130^{o}C. All reactions were performed under nitrogen atmosphere unless otherwise noted. Neutral organic compounds were purified by flash column chromatography using silica gel F-254 (230-499 mesh particle size) as the stationary phase and using ethyl acetate (EtOAc) and hexanes as the mobile phase. Yields refer to isolated material judged to be ≥95% pure by ^{1}H NMR spectroscopy. Enantiomeric excess values were determined using chiral OD column packed with Cellulose tris (3,5-dimethylphenylcarbamate) coated on 10µm silica gel, UV-detector detecting at 254nm, and mobile phase composed of HPLC grade n-hexane and 2-propanol.

Characterization Data

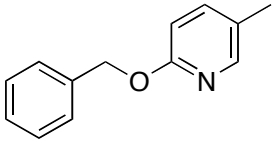
Equation 1:



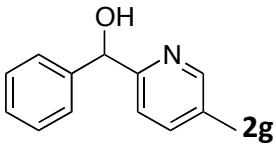
6

1-Phenyl-1-(pyridin-2-yl)ethyl acetate (6); white crystal, (67%); mp 91-93°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.57 (dq, *J* = 4.8, 0.88 Hz, 1H), 7.64 (td, *J* = 7.6, 1.88 Hz, 1H), 7.43 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.19 (m, 1H), 7.14 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 2.27 (s, 3H), 2.18 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.27, 162.89, 148.74, 144.77, 136.41, 128.16, 127.08, 125.28, 121.90, 120.12, 85.10, 22.58, 22.22; IR (cm^{-1}) 1736.54, 1588.32, 1470.62, 1447.42, 1431.47, 1368.50, 1247.49, 1217.85, 1118.98, 1059.76, 1015.07, 906.92, 780.89, 727.94, 698.50; HRMS (EI+) Calcd for $[C_{15}H_{15}O_2N]^{+}$: 241.1103, found: 241.1100.

Table 1, Entry 7:



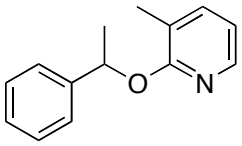
5-Methyl-2-(phenylmethoxy)-pyridine; white crystal, (78%); mp 30-31°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.46 (app. d, *J* = 7.3 Hz, 2H), 7.41-7.35 (m, 3H), 7.32-7.29 (m, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.34 (s, 2H), 2.25 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.88, 146.16, 139.67, 137.52, 128.39, 127.85, 127.70, 125.79, 110.61, 67.43, 17.39; IR (cm^{-1}) 2925.04, 1608.62, 1574.15, 1485.10, 1453.65, 1386.71, 1358.20, 1301.92, 1280.69, 1252.62, 1126.92, 1079.13, 1024.01, 1000.96, 913.27, 875.14, 822.05, 735.14, 695.37; HRMS (EI+) Calcd for $[C_{13}H_{13}ON]^{+}$: 199.0997, found: 199.0992.



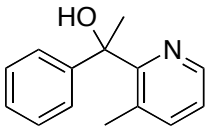
2g

5-Methyl-α-phenyl-2-pyridinemethanol (2g); yellow white powder, (86%); mp 65-67°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.40 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.37-7.35 (m, 2H), 7.33-7.29 (m, 2H), 7.26-7.23 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.71 (s, 1H), 5.35 (bs, 1H), 2.29 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.25, 147.92, 143.36, 137.39, 131.73, 128.35 127.52, 126.83, 120.61, 74.77, 17.91; IR (cm^{-1}) 3029.51, 1600.69, 1573.22, 1485.66, 1451.41, 1379.18, 1189.88, 1131.15, 1082.57, 1027.02, 918.31, 855.00, 813.31, 727.87, 697.66; HRMS (EI+) Calcd for $[C_{13}H_{13}ON]^{+}$: 199.0997, found: 199.0996.

Table 1, Entry 8:



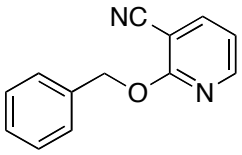
3-Methyl-2-(1-phenylethoxy)pyridine; colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 3.9 Hz, 1H), 7.45 (app. d, *J* = 7.4 Hz, 2H), 7.37-7.30 (m, 3H), 7.26-7.23 (m, 1H), 6.73 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.29 (q, *J* = 6.5 Hz, 1H), 2.25 (s, 3H), 1.63 (d, *J* = 6.5 Hz, 3H; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.36, 143.97, 143.75, 138.47, 128.26, 127.11, 125.84, 121.06, 116.43, 72.27, 23.17, 16.01; IR (cm^{-1}) 1594.72, 1448.99, 1421.62, 1304.19, 1252.06, 1187.11, 1115.57, 1063.46, 1010.13, 905.21, 784.98, 728.66, 699.01; HRMS (EI+) Calcd for $[C_{14}H_{15}ON]^{+}$: 213.1154, found: 213.1152.



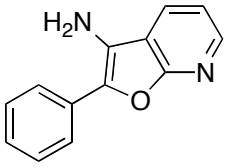
2h

1-(3-methylpyridin-2-yl)-1-phenylethanol (2h); light pink solid, (65%); mp 44-46°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.7 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.29 (app. d, *J* = 4.2 Hz, 4H), 7.25-7.19 (m, 3H), 1.93 (s, 6H), 1.89 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.39, 145.59, 143.72, 140.38, 130.57, 128.12, 127.09, 126.58, 122.78, 74.25, 25.77, 19.59; IR (cm^{-1}) 3287.05, 2978.30, 1574.79, 1494.36, 1445.85, 1383.65, 1364.15, 1277.58, 1224.09, 1101.99, 1067.56, 1027.04, 995.59, 910.80, 846.98, 791.09, 779.20, 759.72, 736.07, 698.22; HRMS (EI+) Calcd for $[C_{14}H_{15}ON]^{+}$: 213.1154, found: 213.1149.

Table 1, Entry 9:

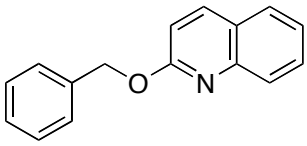


2-(Phenylmethoxy)-3-pyridinecarbonitrile; white crystal, (53%); mp 44-46°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.89 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.49 (app. d, *J* = 7.3 Hz, 2H), 7.38 (app. t, *J* = 7.6, 7.0 Hz, 2H), 7.34-7.30 (m, 1H), 6.99 (dd, *J* = 7.5, 5.0 Hz, 1H), 5.52 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.53, 151.20, 143.02, 136.01, 128.50, 128.07, 127.75, 116.64, 115.04, 97.09, 68.51; IR (cm^{-1}) 2230.30, 1575.02, 1497.86, 1462.96, 1433.74, 1361.49, 1306.75, 1261.58, 1179.39, 1105.78, 976.05, 918.50, 876.88, 797.96, 766.91, 739.10, 696.03; HRMS (EI+) Calcd for $[C_{13}H_{10}ON_2]^+$: 210.0793, found: 210.0792.

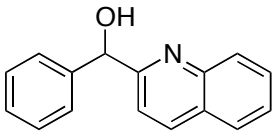


2-Phenylfuro[2,3-*b*]pyridin-3-amine (7); orange flakes, (75%); mp 120°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.84-7.81 (m, 3H), 7.50 (t, *J* = 7.78 Hz, 2H), 7.32 (t, *J* = 7.4, 1H), 7.22 (dd, *J* = 7.6, 4.9 Hz, 1H), 3.65 (bs, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.41, 144.20, 137.06, 130.69, 128.92, 127.19, 126.69, 124.92, 122.41, 118.36, 117.66; IR (cm^{-1}) 3203.19, 1746.32, 1640.10, 1614.66, 1497.36, 1445.97, 1423.68, 1405.67, 1303.50, 1265.12, 1225.04, 1172.95, 1131.88, 1103.98, 1058.38, 1021.94, 894.06, 756.54, 688.88, 659.60; HRMS (ESI+) Calcd for $[C_{13}H_{11}ON_2]^+$: 210.0871, found: 211.0875.

Table 1, Entry 13:



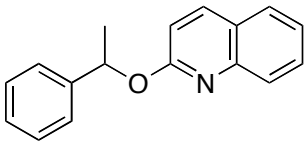
2-(Phenylmethoxy)-quinoline; yellow-white crystal; mp 46-48°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 (app. t, *J* = 8.1, 7.2 Hz, 1H), 7.53 (app. d, *J* = 7.3 Hz, 2H), 7.41-7.37 (m, 3H), 7.35-7.31 (m, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 5.56 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.76, 146.43, 138.71, 137.24, 129.43, 128.40, 128.23, 127.81, 127.37, 127.21, 125.12, 123.99, 113.15, 67.59; IR (cm^{-1}) 2924.43, 1618.06, 1604.92, 1573.68, 1507.02, 1475.37, 1427.61, 1393.77, 1369.48, 1343.15, 1309.35, 1275.33, 1257.27, 1239.00, 1208.07, 1111.19, 998.55, 820.68, 779.99, 754.51, 726.36, 695.14; HRMS (EI+) Calcd for $[C_{16}H_{13}ON]^{+}$: 235.0997, found: 235.0995.



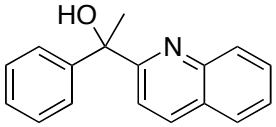
2i

α-Phenyl-2-quinolinemethanol (2i); light yellow crystal, (83%); mp 58-60°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.78-7.71 (m, 2H), 7.53 (app. t, *J* = 7.6, 7.4 Hz, 1H), 7.4 (app. d, *J* = 7.2 Hz, 2H), 7.34-7.30 (m, 2H), 7.28-7.23 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.11 (bs, 1H), 5.86 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.42, 145.95, 142.76, 136.99, 129.88, 128.78, 128.61, 127.96, 127.57, 127.46, 127.43, 126.59, 119.23, 75.15; IR (cm^{-1}) 3363.29, 3061.43, 1619.20, 1598.82, 1569.24, 1505.63, 1452.41, 1407.21, 1308.89, 1190.37, 1115.86, 1081.86, 1051.37, 1027.08, 966.36, 921.56, 850.83, 817.41, 772.08, 751.68, 726.73, 699.84; HRMS (EI+) Calcd for $[C_{16}H_{13}ON]^{+}$: 235.0997, found: 235.0994.

Table 1, Entry 14:



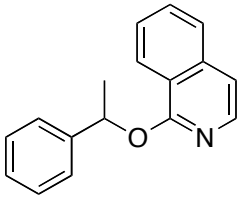
1-Phenyl-1-(quinolin-2-yl)ethanol (4g); colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.60-7.56 (m, 1H), 7.53 (app. d, *J* = 7.4 Hz, 2H), 7.34 (app. t, *J* = 7.8, 7.2 Hz, 3H), 7.27-7.23 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.51 (q, *J* = 6.5 Hz, 1H), 1.71 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.55, 143.16, 138.67, 129.32, 128.30, 127.36, 127.31, 126.35, 125.06, 123.86, 113.57, 72.65, 22.50; IR (cm^{-1}) 2926.42, 1618.36, 1603.83, 1572.36, 1507.91, 1472.01, 1426.22, 1392.50, 1343.35, 1303.47, 1273.91, 1254.97, 1239.06, 1208.03, 1111.28, 1063.69, 1029.86, 1009.71, 996.83, 979.66, 926.61, 887.31, 821.10, 754.73, 730.24, 697.20; HRMS (EI+) Calcd for $[C_{17}H_{15}ON]^{+}$: 249.1154, found: 249.1150.



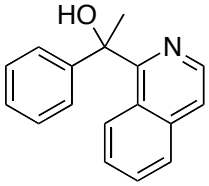
2j

α-Methyl-α-phenyl-2-quinolinemethanol (2j); yellow solid, (75%); mp 100-102°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (app. q, *J* = 8.6, 8.4, 8.2 Hz, 2H), 7.81-7.73 (m, 2H), 7.57-7.52 (m, 3H), 7.34-7.29 (m, 3H), 7.25-7.21 (m, 1H), 6.72 (bs, 1H), 2.01 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.32, 146.46, 145.53, 137.31, 129.94, 128.85, 128.30, 127.46, 127.20, 127.14, 126.64, 126.28, 118.49, 75.03, 28.63; IR (cm^{-1}) 3359.00, 2978.76, 1619.25, 1598.80, 1505.03, 1446.04, 1370.02, 1309.16, 1215.92, 1128.38, 1067.33, 912.82, 830.19, 764.68, 751.19, 701.94; HRMS (EI+) Calcd for $[C_{17}H_{15}ON]^{+}$: 249.1154, found: 249.1157.

Table 1, Entry 15:



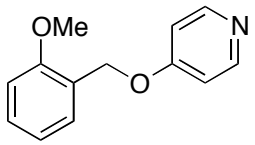
1-(1-Phenylethoxy)isoquinoline; yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 5.8 Hz, 1H), 7.71 (app. d, *J* = 8.0 Hz, 1H), 7.65 (app. t, *J* = 7.6, 7.2 Hz, 1H), 7.56-7.52 (m, 3H), 7.35 (app. t, *J* = 7.7, 7.4 Hz, 2H), 7.26-7.25 (m, 1H), 7.17 (d, *J* = 5.9 Hz, 1H), 6.51 (q, *J* = 6.5 Hz, 1H), 1.75 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.68, 143.27, 139.73, 138.00, 130.32, 128.34, 127.32, 126.46, 126.05, 125.95, 124.25, 120.06, 114.70, 72.91, 22.86; IR (cm^{-1}) 1627.97, 1568.83, 1497.75, 1451.39, 1391.76, 1320.90, 1302.56, 1205.73, 1158.69, 1076.91, 1028.73, 906.09, 812.05, 729.30, 698.08, 673.52; HRMS (EI+) Calcd for $[C_{17}H_{15}ON]^{+}$: 249.1154, found: 249.1152.



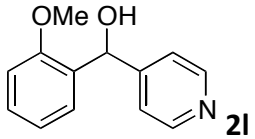
2k

α-Methyl-α-phenyl-1-isoquinolinemethanol (2k); yellow solid, (93%); mp 93-95°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.7 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 5.7 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.38 (app. d, *J* = 7.7 Hz, 2H), 7.34-7.28 (m, 4H), 7.25-7.21 (m, 1H), 2.12 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.87, 146.44, 138.73, 137.39, 129.70, 128.38, 127.46, 127.23, 126.79, 126.71, 126.43, 124.50, 121.48, 74.87, 28.18; IR (cm^{-1}) 3060.08, 2246.33, 1623.81, 1590.19, 1562.13, 1503.39, 1457.89, 1366.10, 1348.71, 1329.78, 1223.79, 1114.39, 1056.40, 1026.14, 1000.65, 905.48, 870.58, 826.16, 765.39, 727.26, 699.81; HRMS (EI+) Calcd for $[C_{17}H_{15}ON]^{+}$: (249.1154), found: (249.1153).

Table 1, Entry 16:



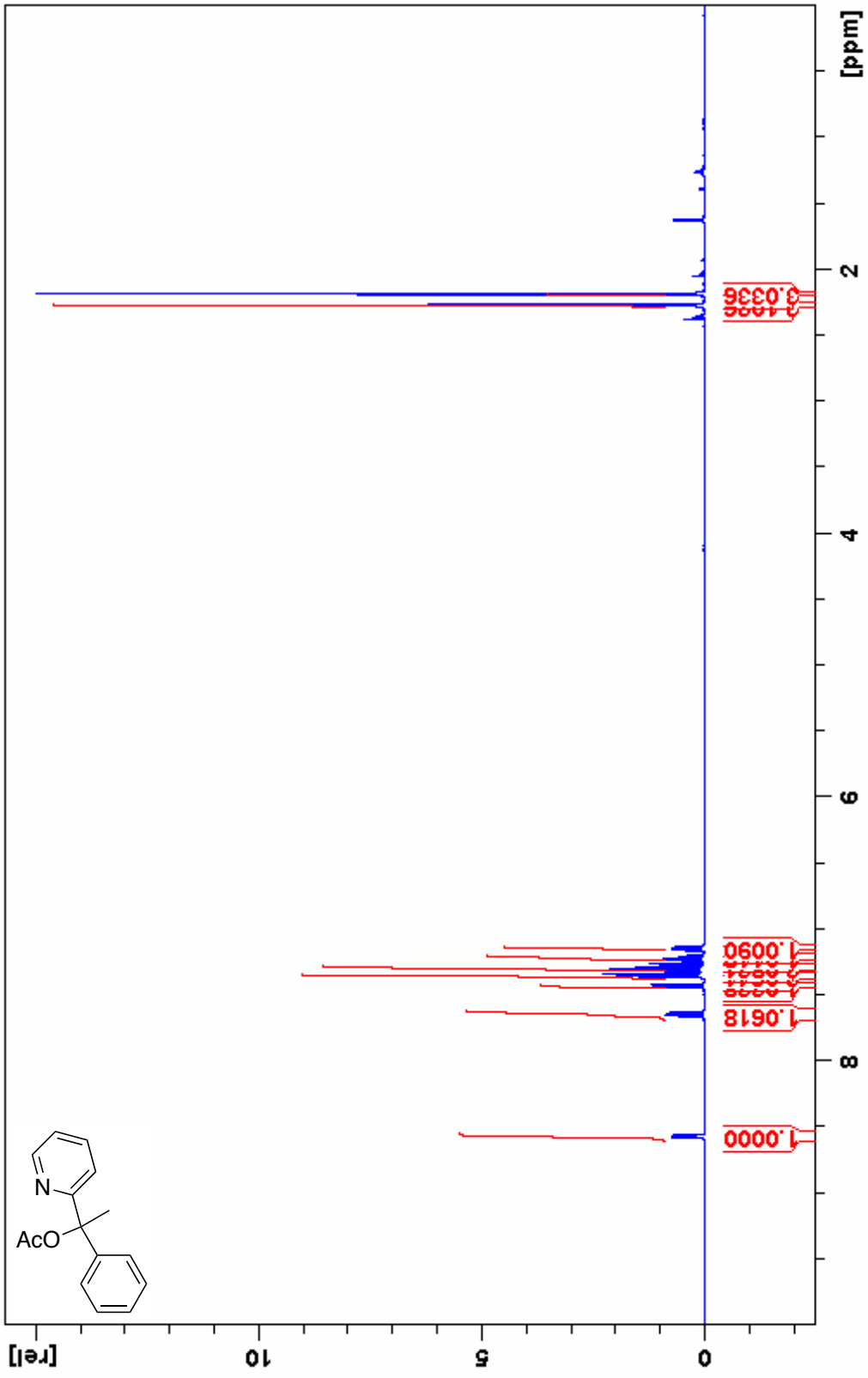
4-((2-Methoxybenzyl)oxy)pyridine; yellow-white solid, (92%); mp 90-92°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.0 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.33 (app. t, *J* = 8.0, 7.7 Hz, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.93-6.89 (m, 3H), 5.16 (s, 2H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.43, 156.44, 150.64, 129.06, 128.30, 123.54, 120.20, 110.16, 109.96, 64.40, 54.90; IR (cm^{-1}) 1589.67, 1569.50, 1495.07, 1463.87, 1439.07, 1420.83, 1381.05, 1281.76, 1245.30, 1211.13, 1176.56, 1122.90, 1031.03, 1001.03, 905.96, 879.52, 816.07, 754.83, 725.20; HRMS (EI+) Calcd for $[C_{13}H_{13}O_2N]^+$: 215.0946, found: 215.0948.

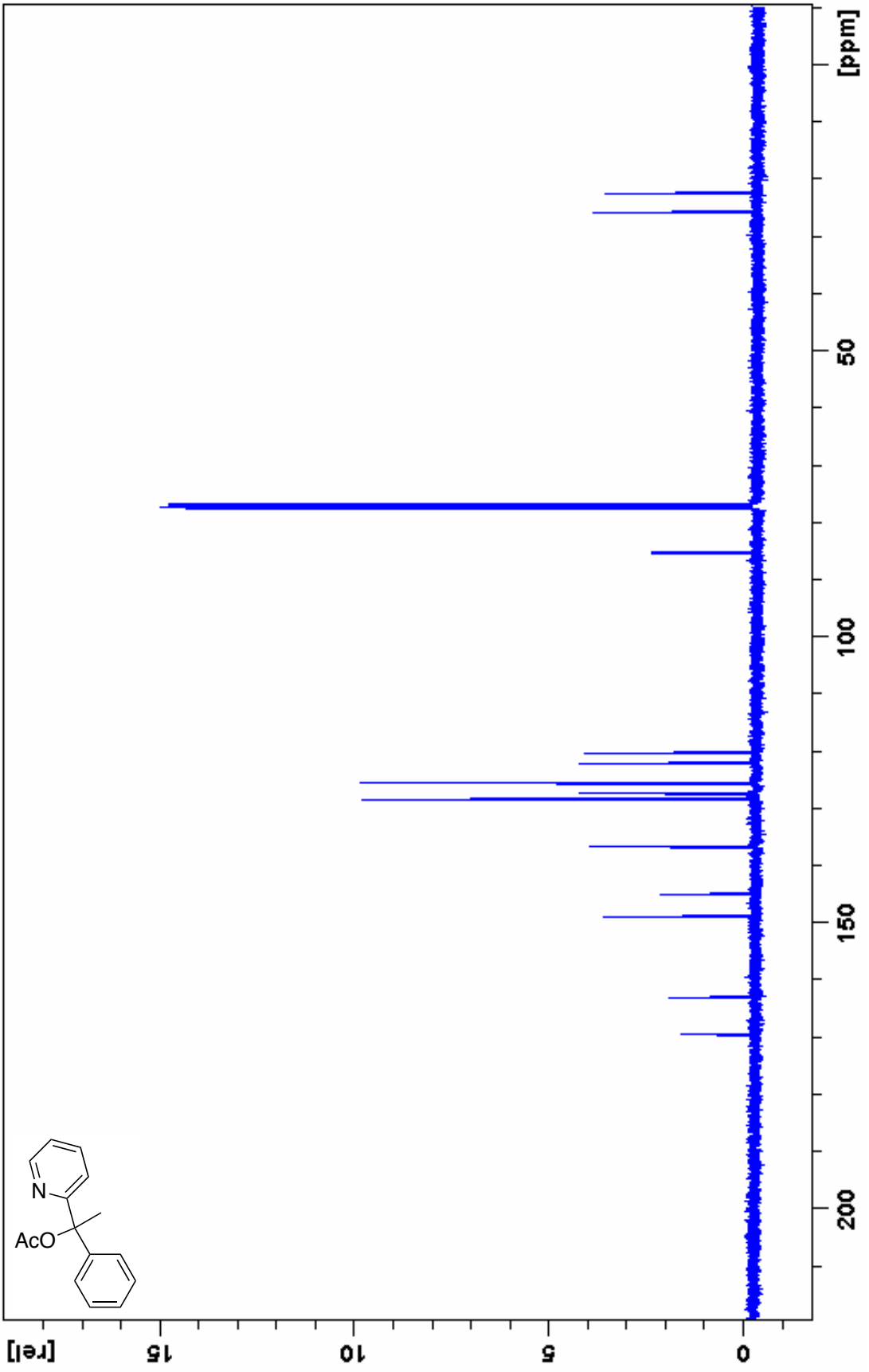


2l

α-(2-Methoxyphenyl)-4-pyridinemethanol (2l); white flakes, (83%); mp 154-156°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.8 Hz, 2H), 7.33-7.28 (m, 3H), 7.22 (d, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 5.99 (d, *J* = 6.1 Hz, 1H), 3.81 (s, 3H), 3.18 (bs, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.47, 152.79, 149.35, 130.73, 129.24, 127.90, 121.30, 120.97, 110.83, 70.76, 55.33; IR (cm^{-1}) 3079.58, 2841.51, 1597.62, 1561.53, 1487.52, 1463.36, 1438.54, 1418.30, 1350.28, 1335.02, 1287.59, 1237.31, 1189.10, 1115.35, 1091.63, 1046.86, 1028.81, 1002.78, 943.39, 798.82, 750.23; HRMS (EI+) Calcd for $[C_{13}H_{13}O_2N]^+$: 215.0946, found: 215.0942.

1H and 13C NMR Spectra

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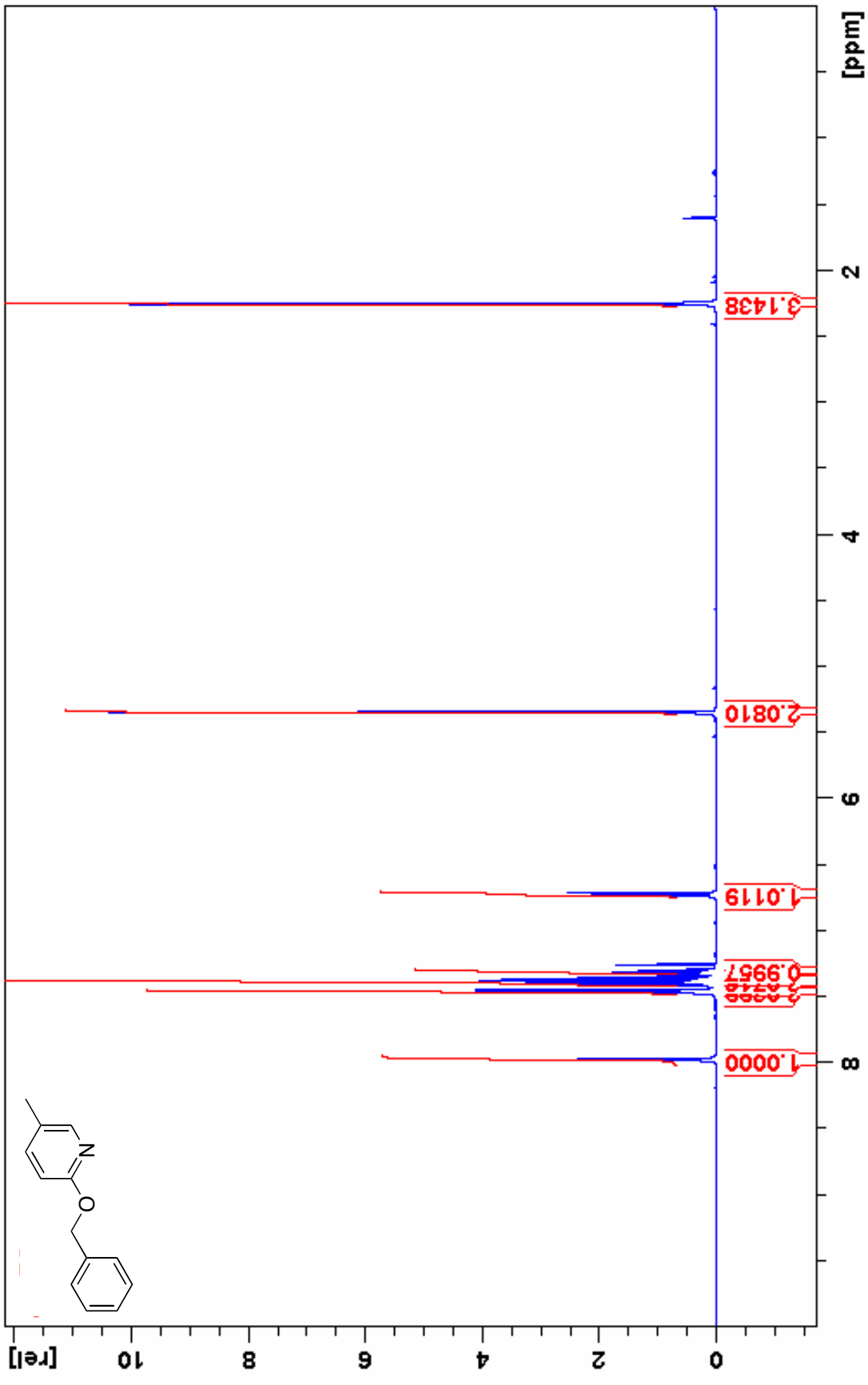
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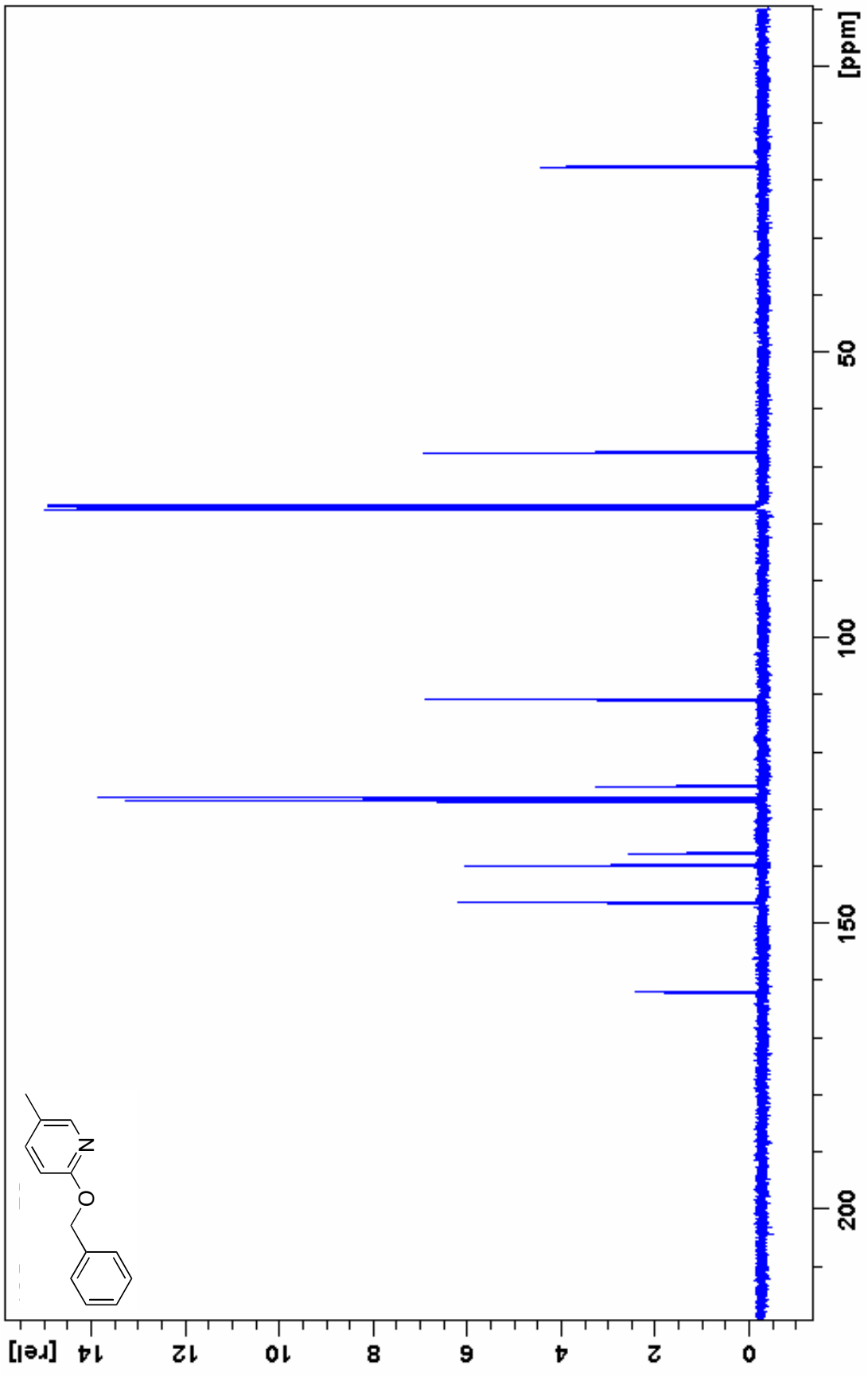
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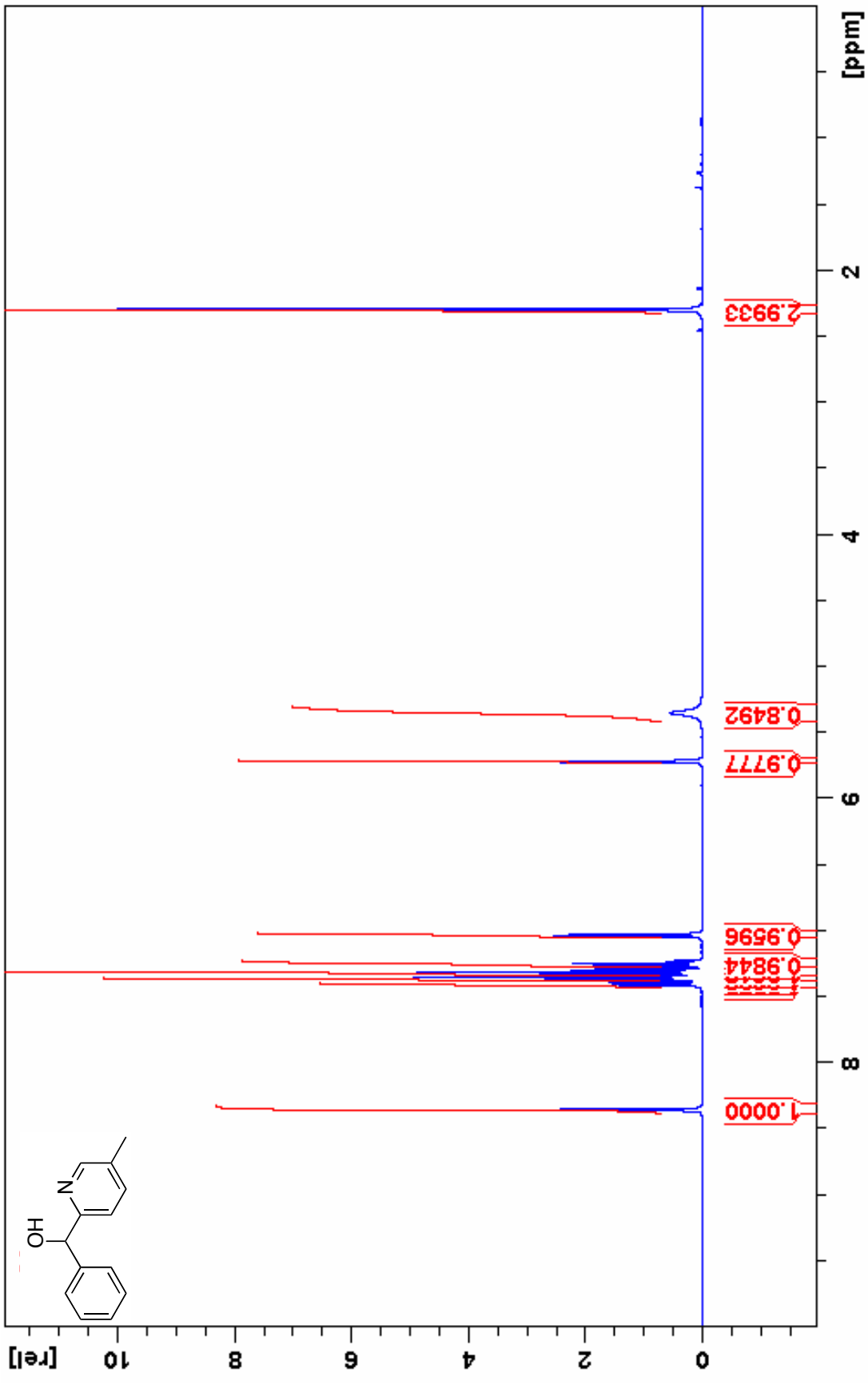
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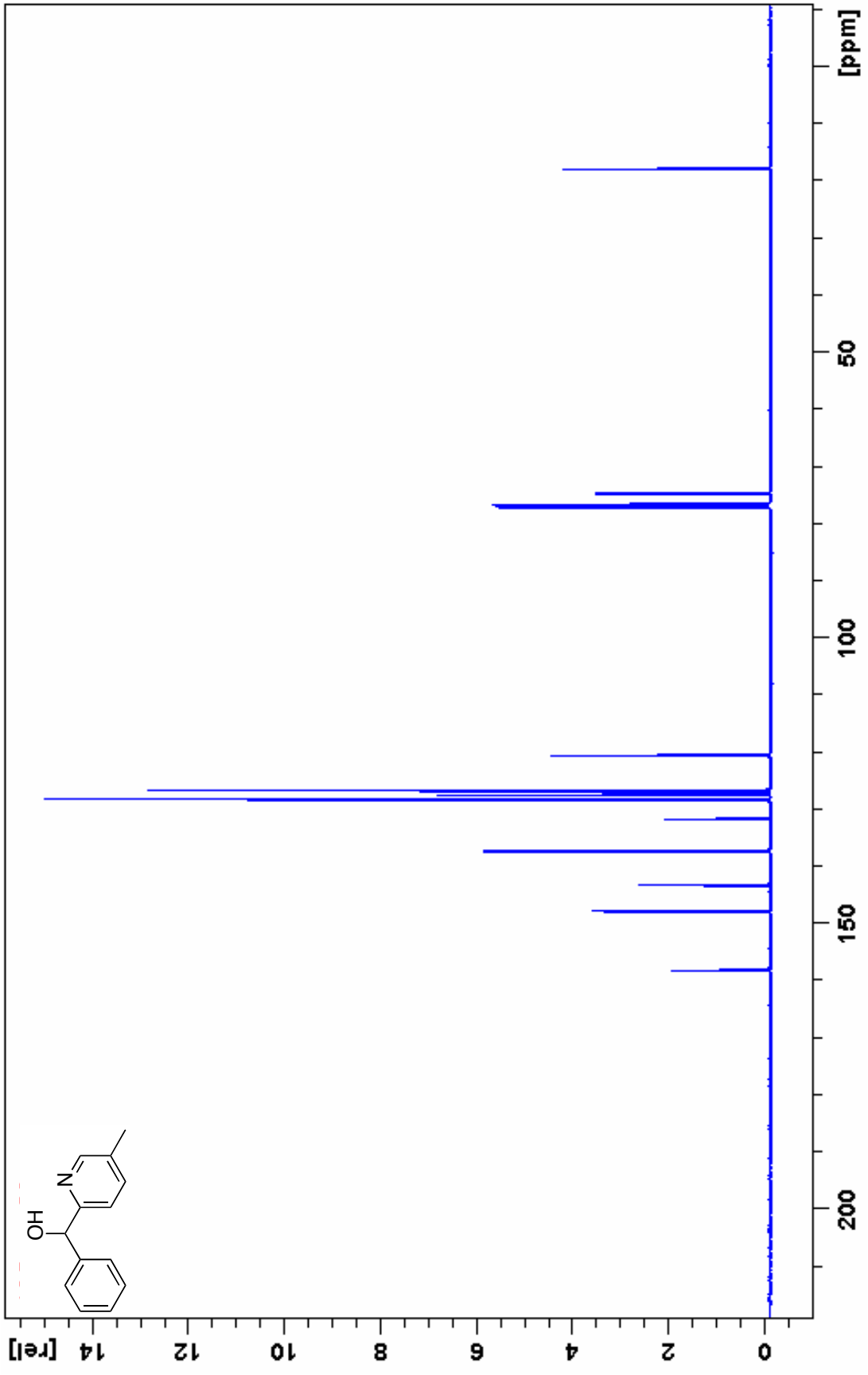
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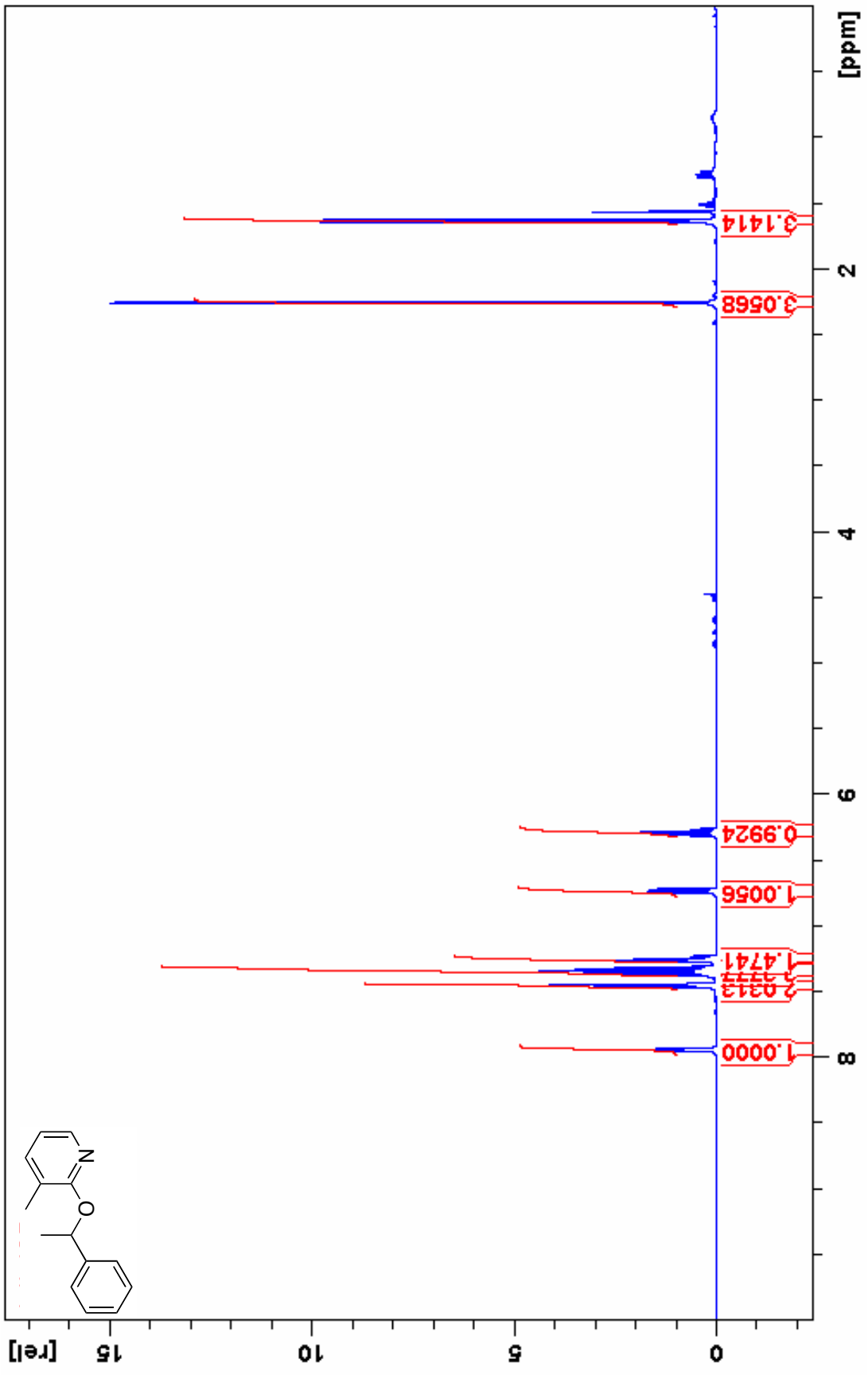
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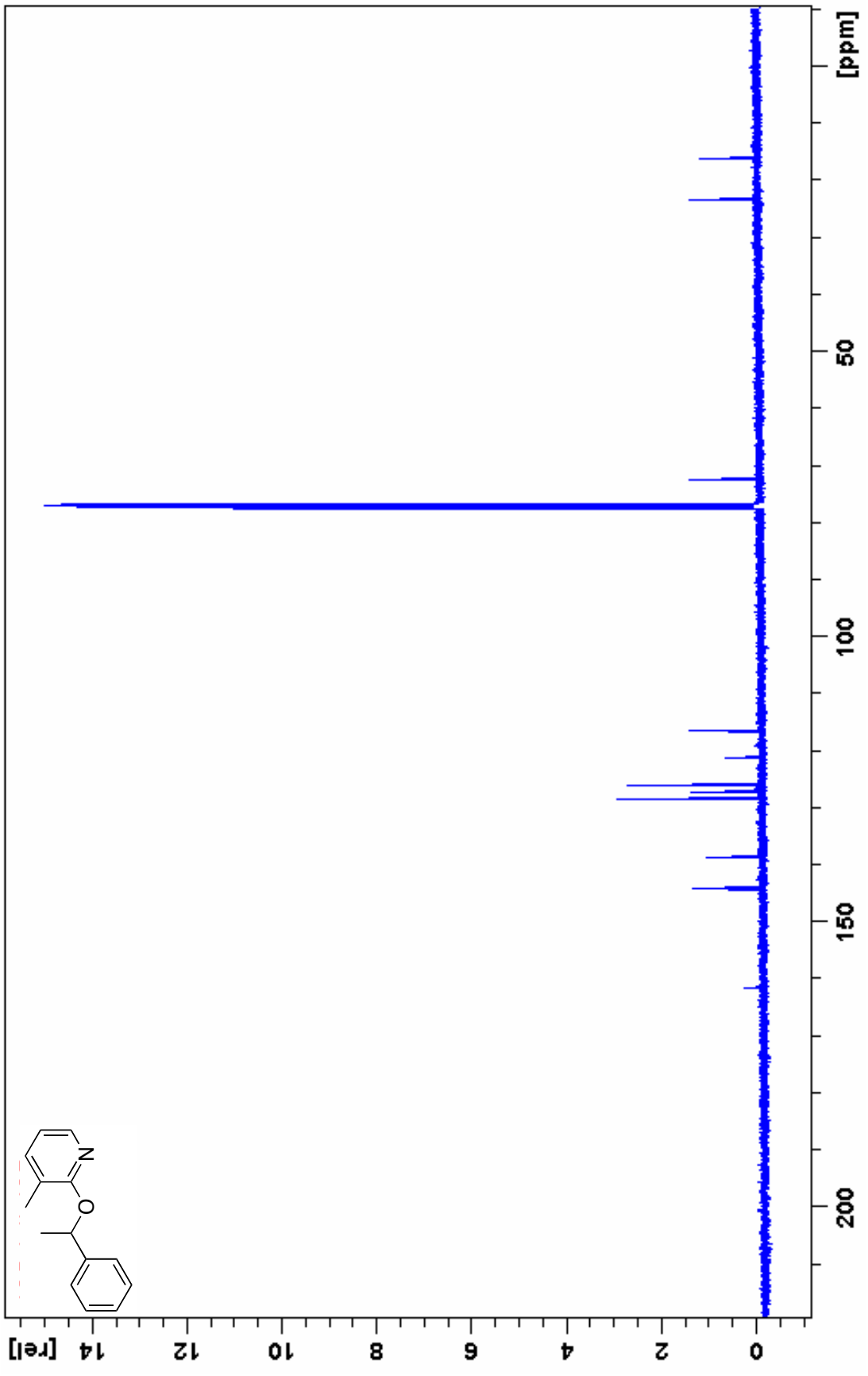
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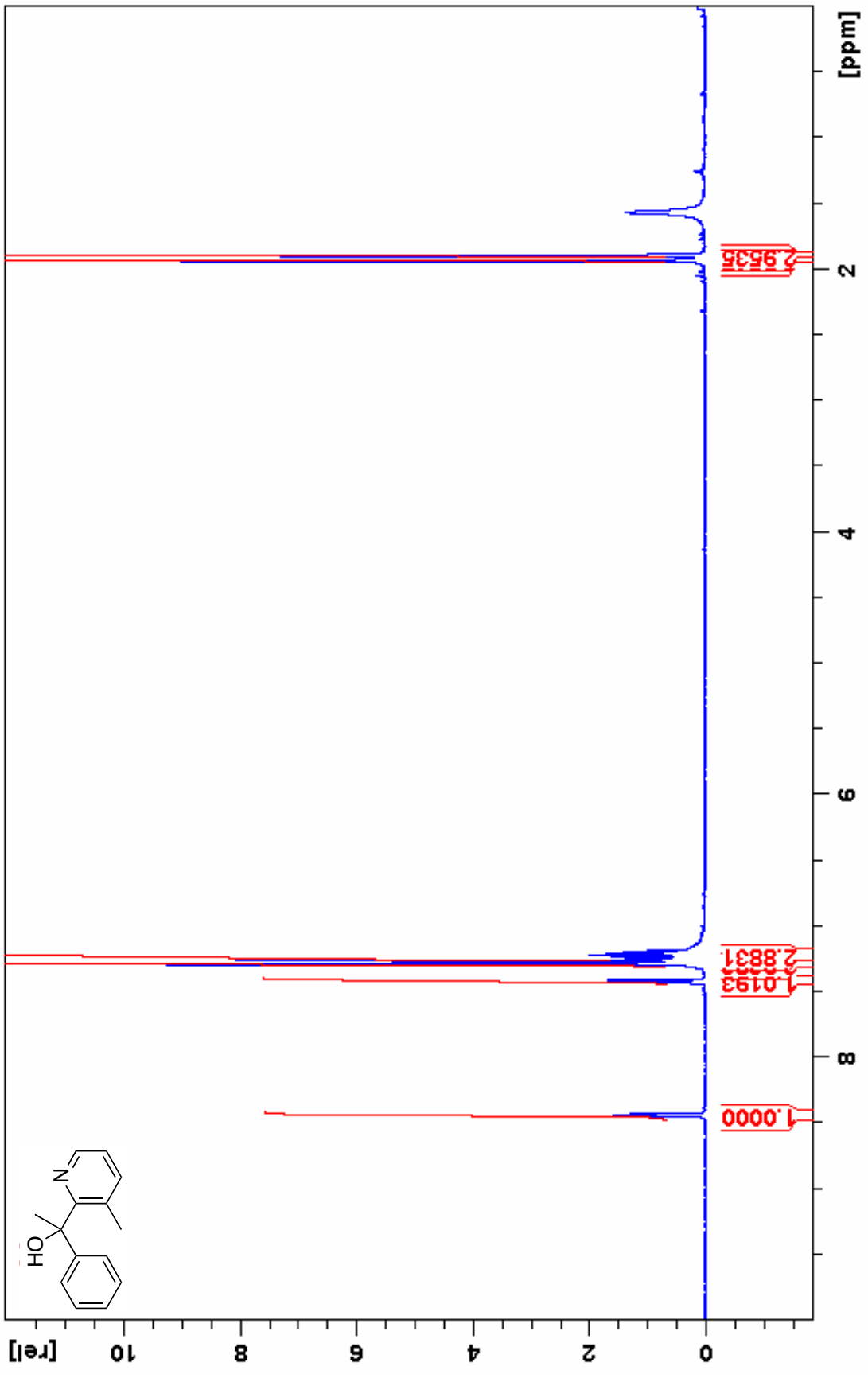
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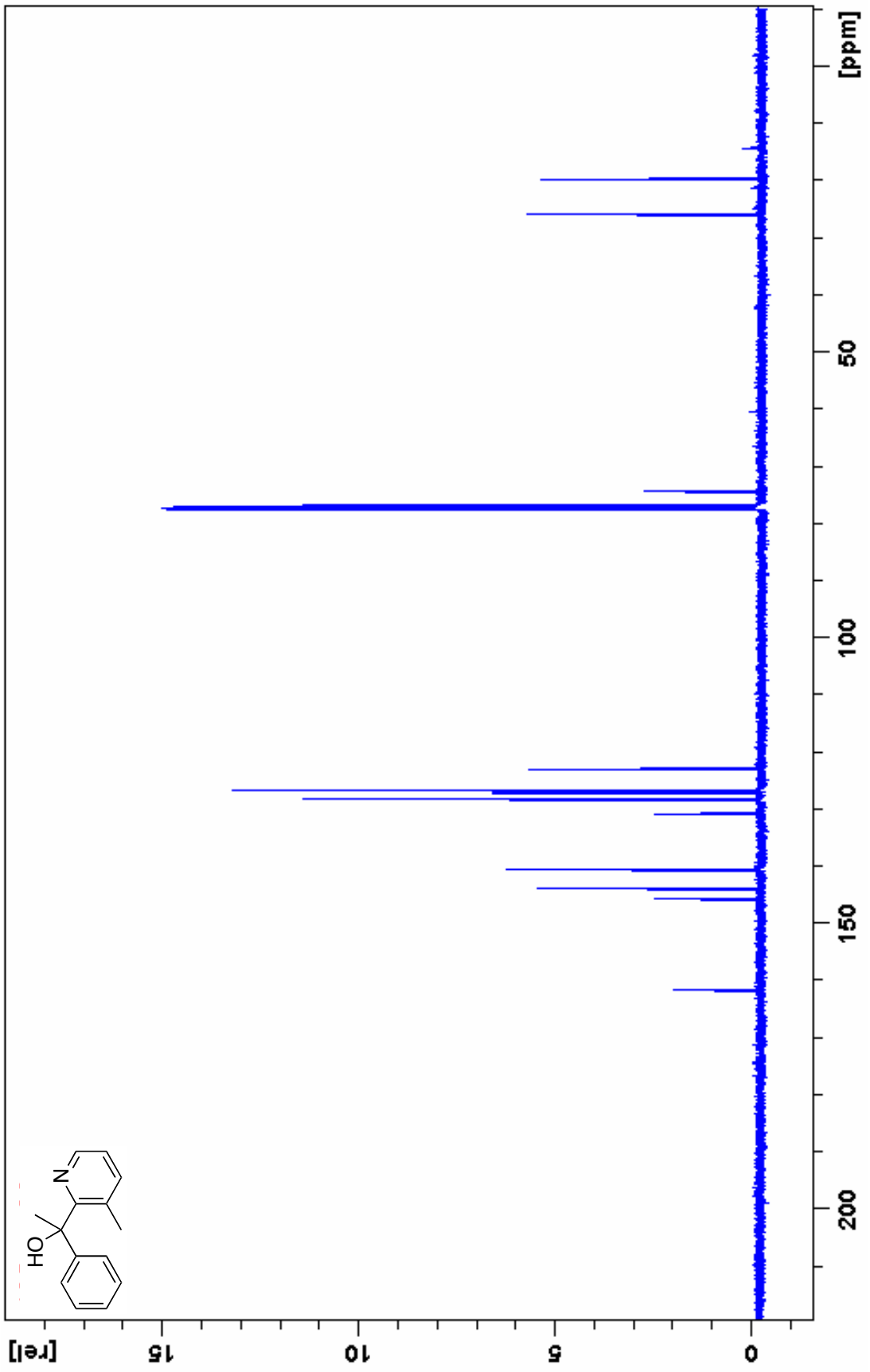
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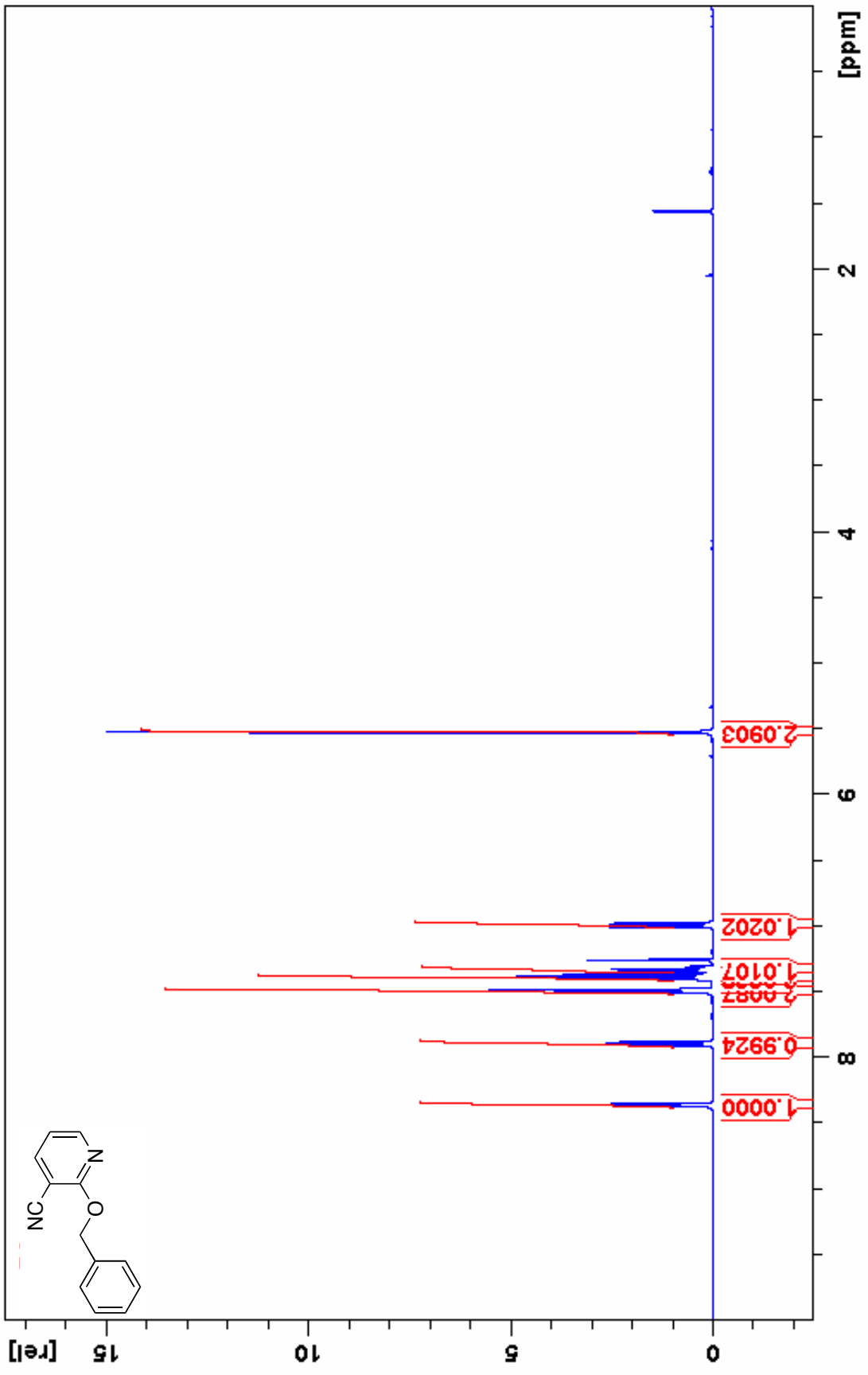
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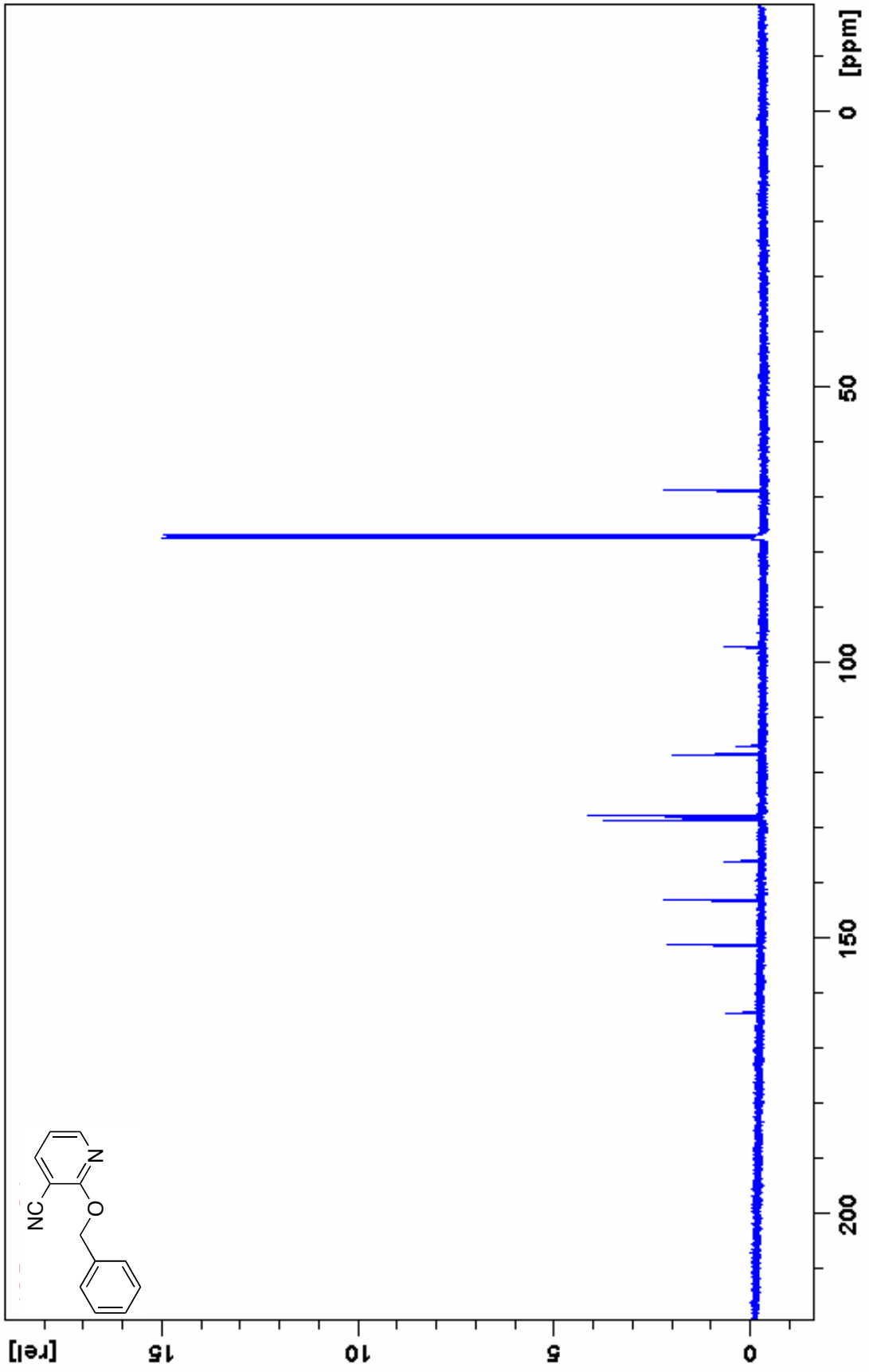
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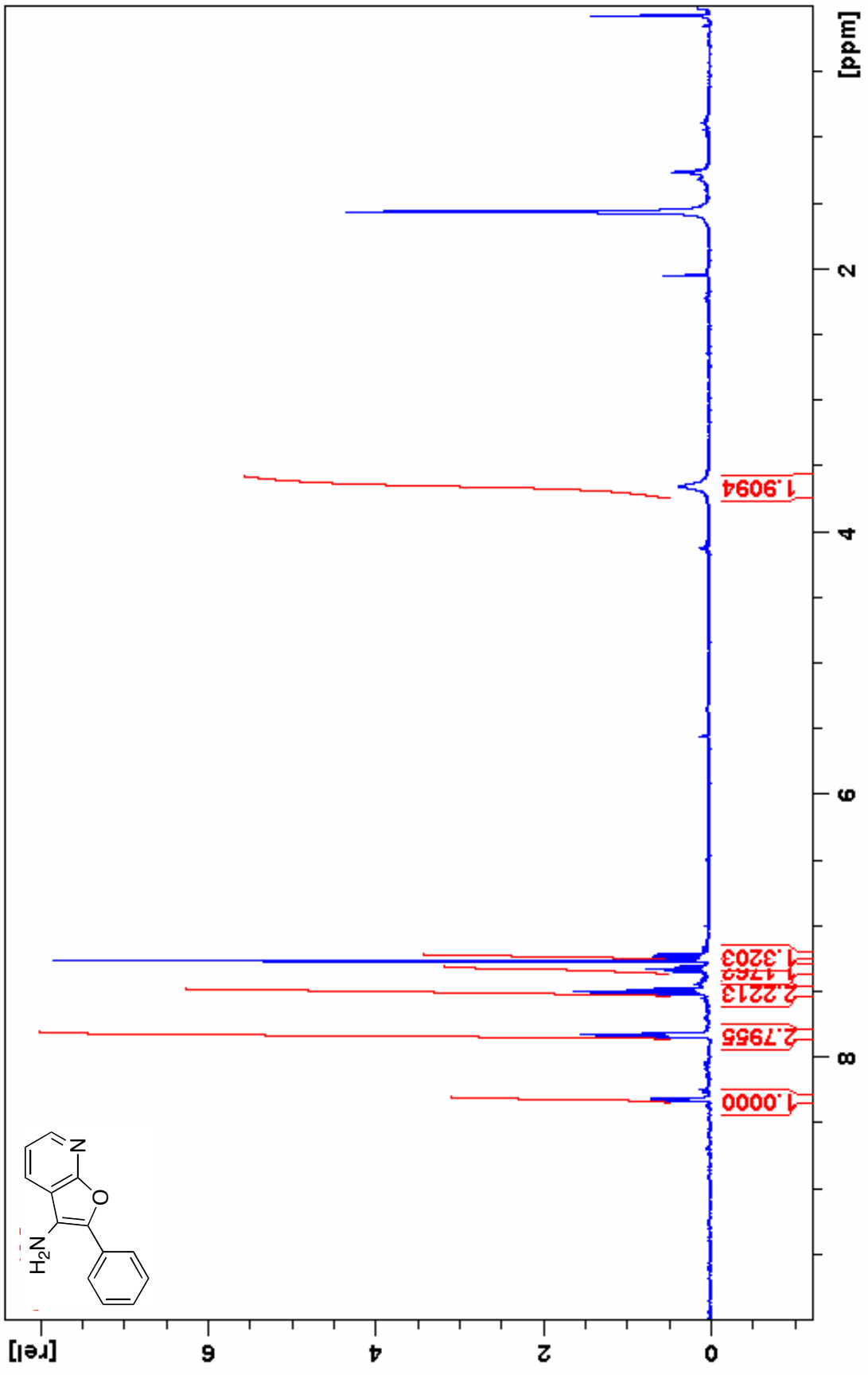
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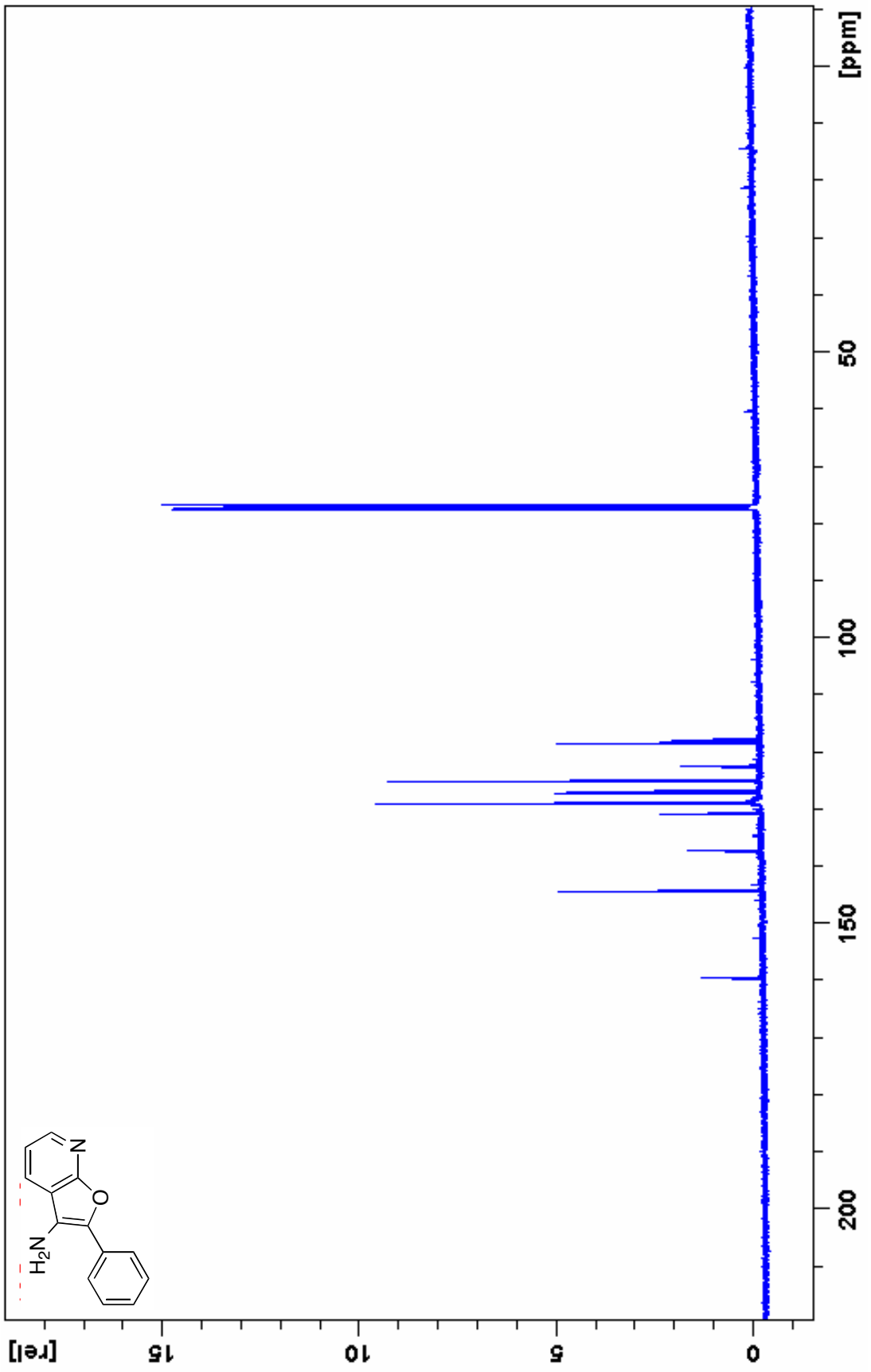
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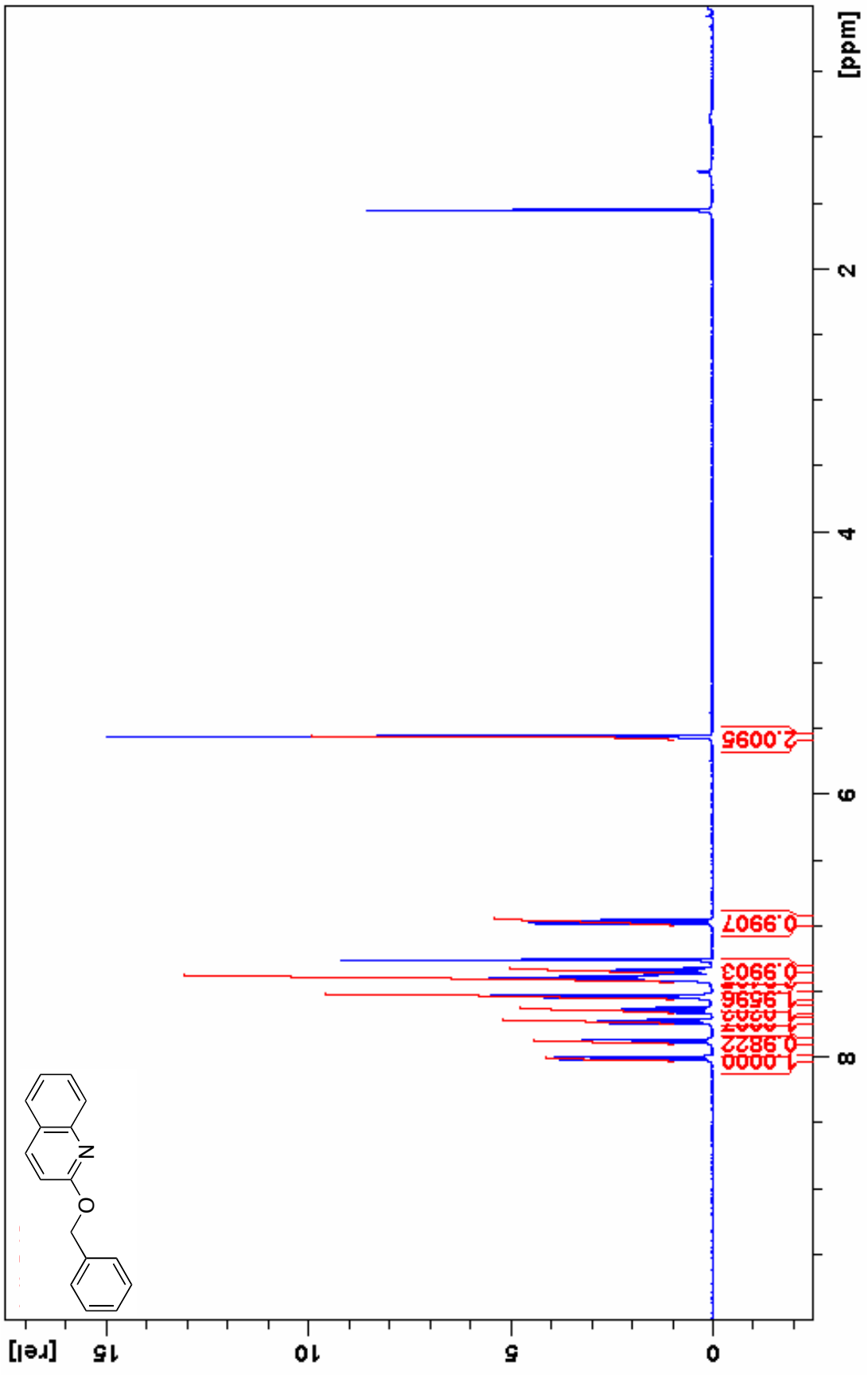
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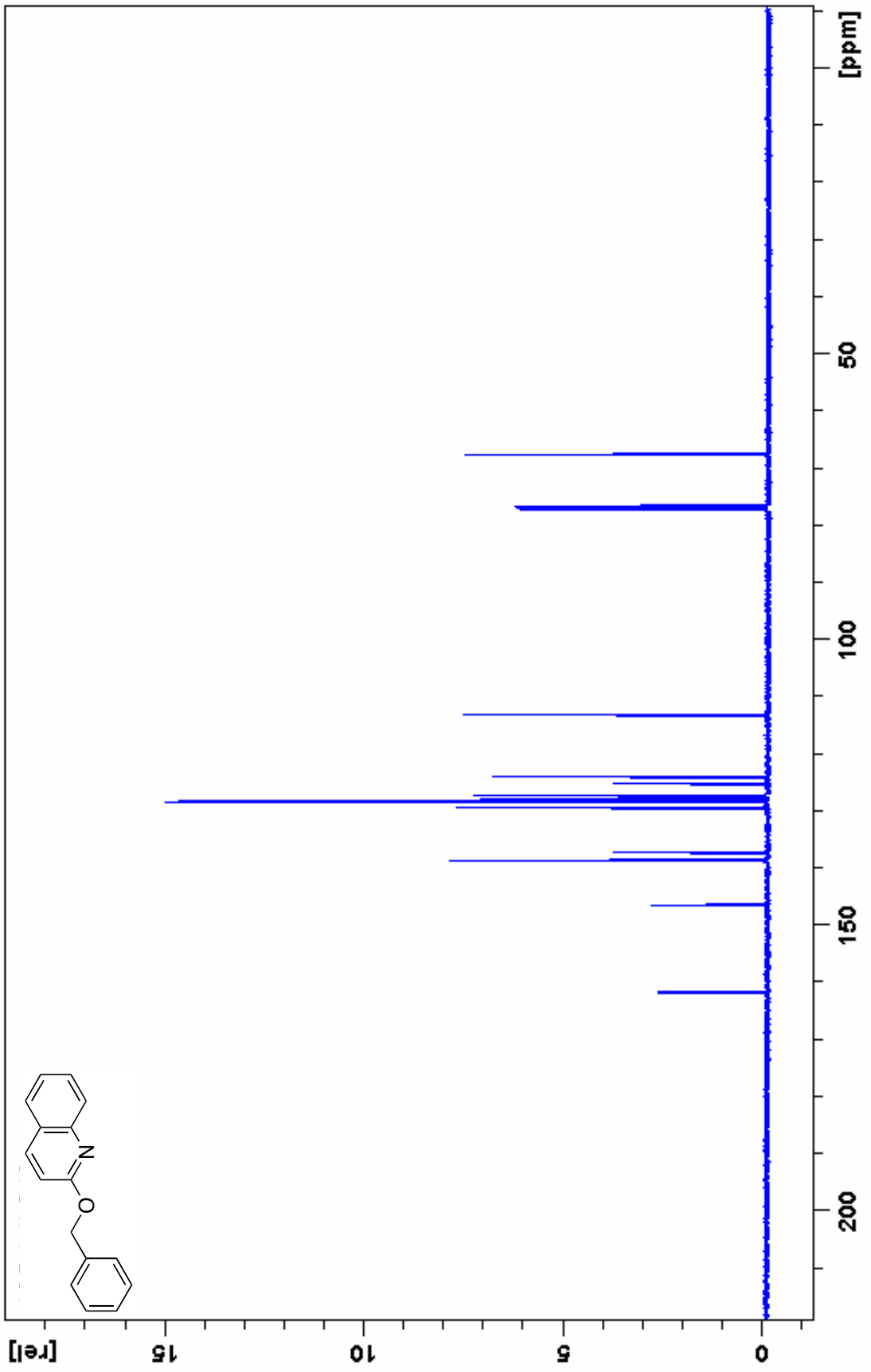
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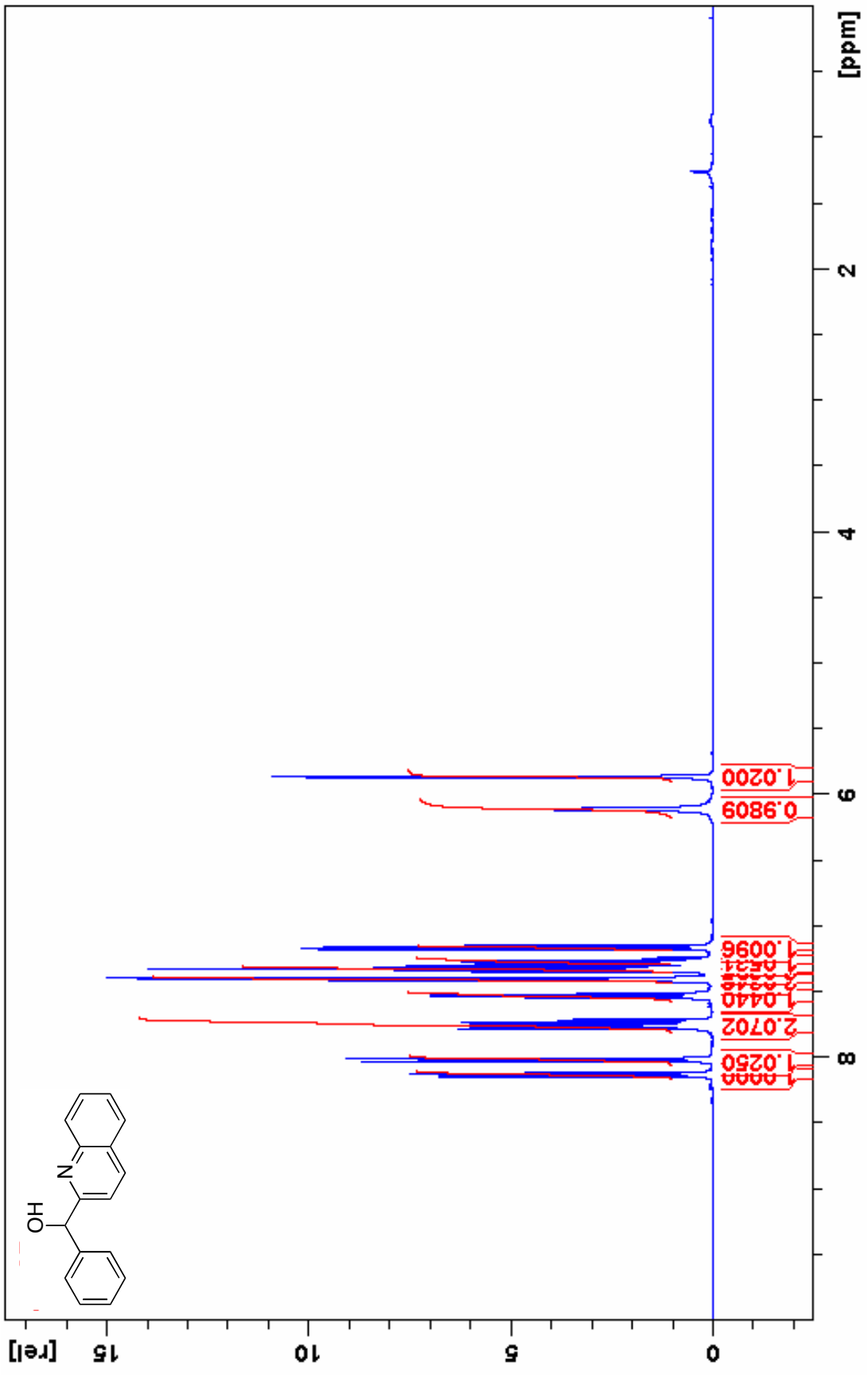
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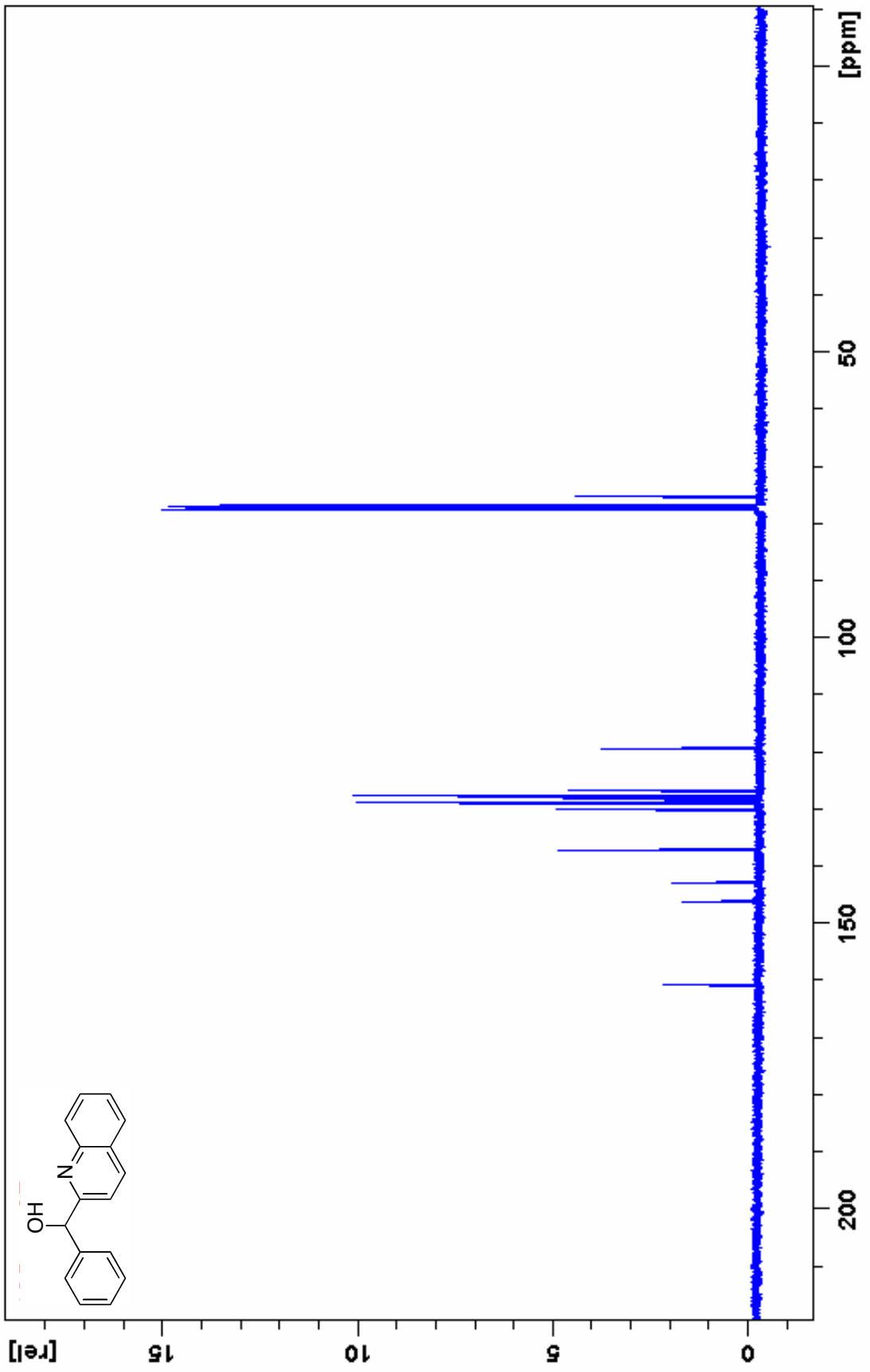
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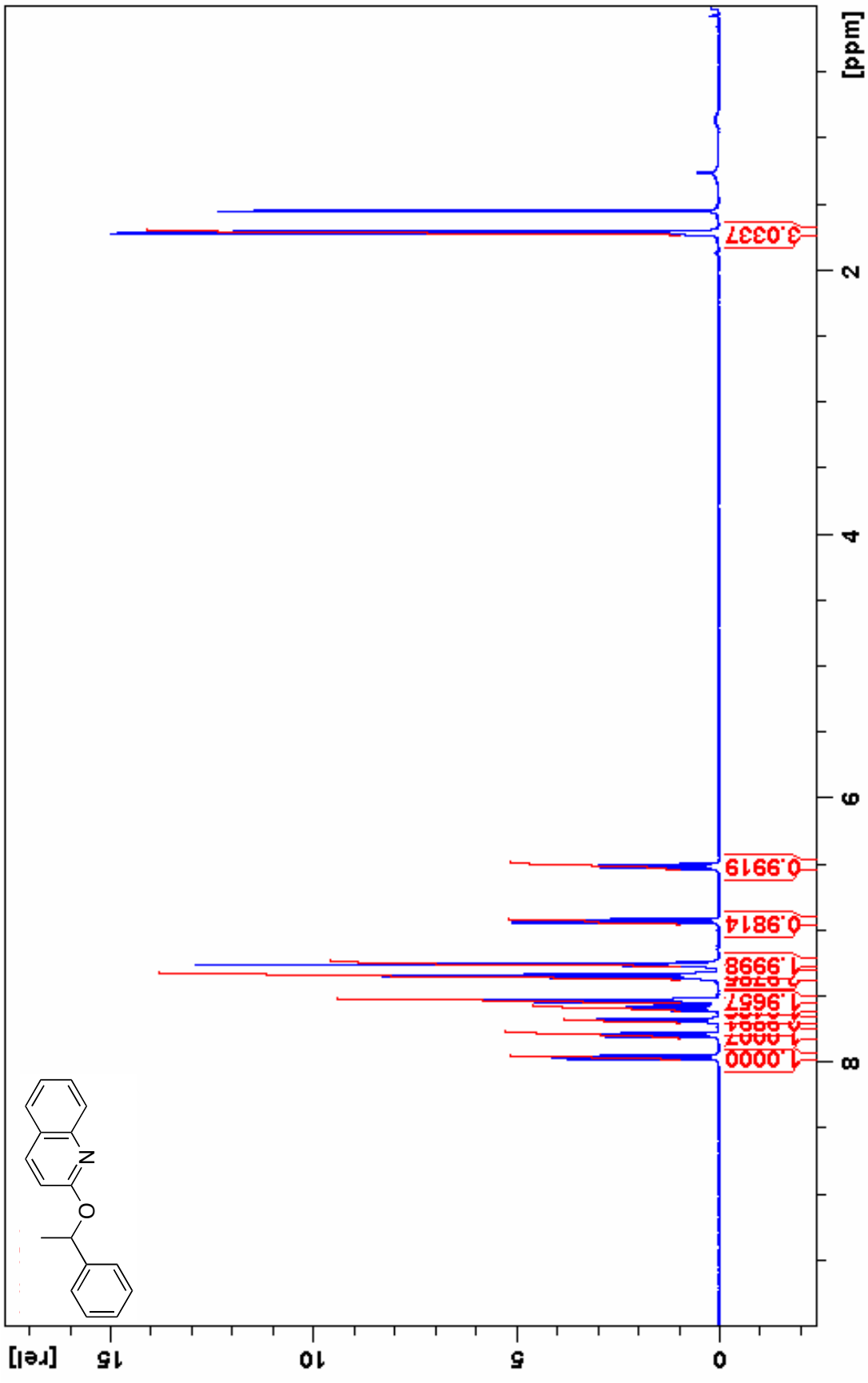
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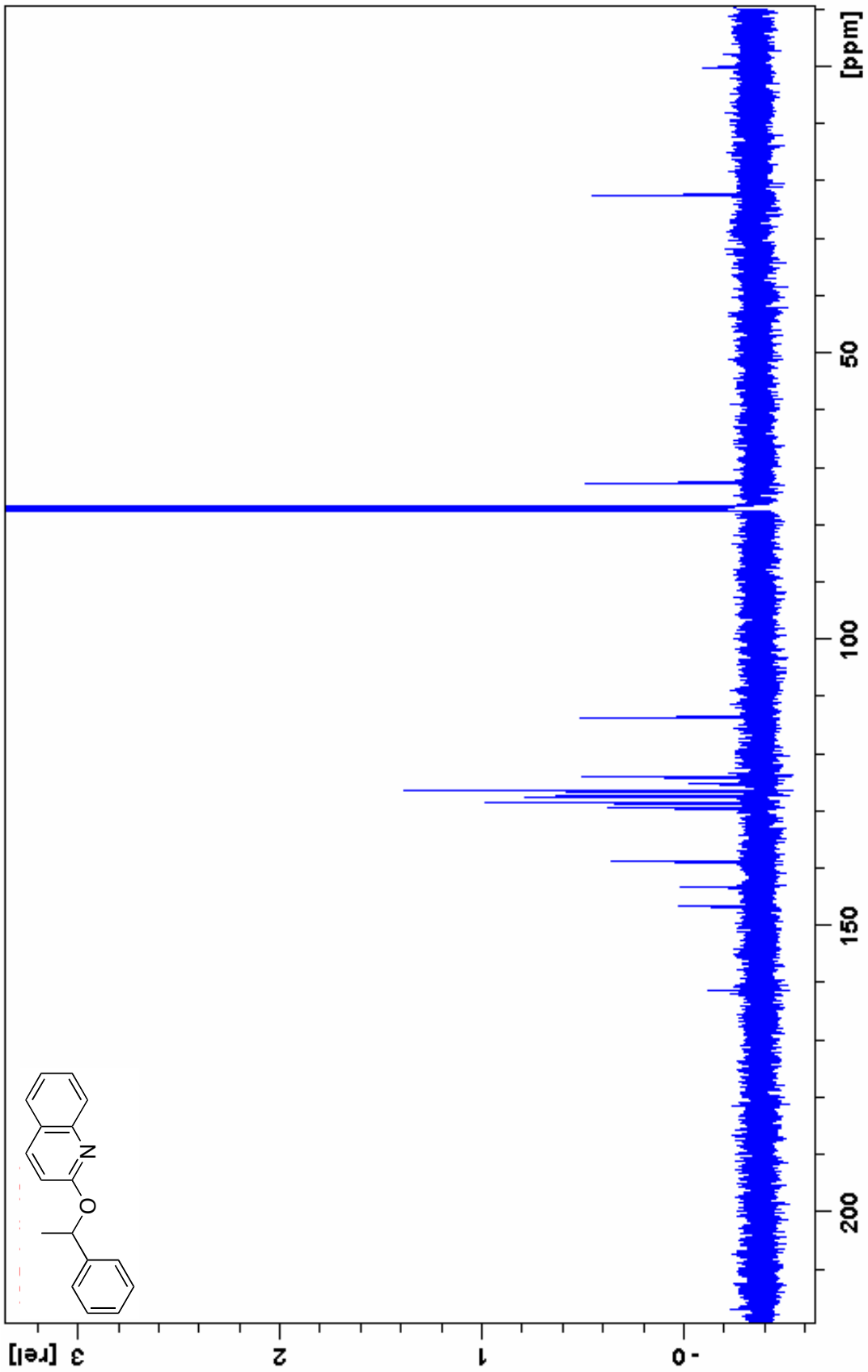
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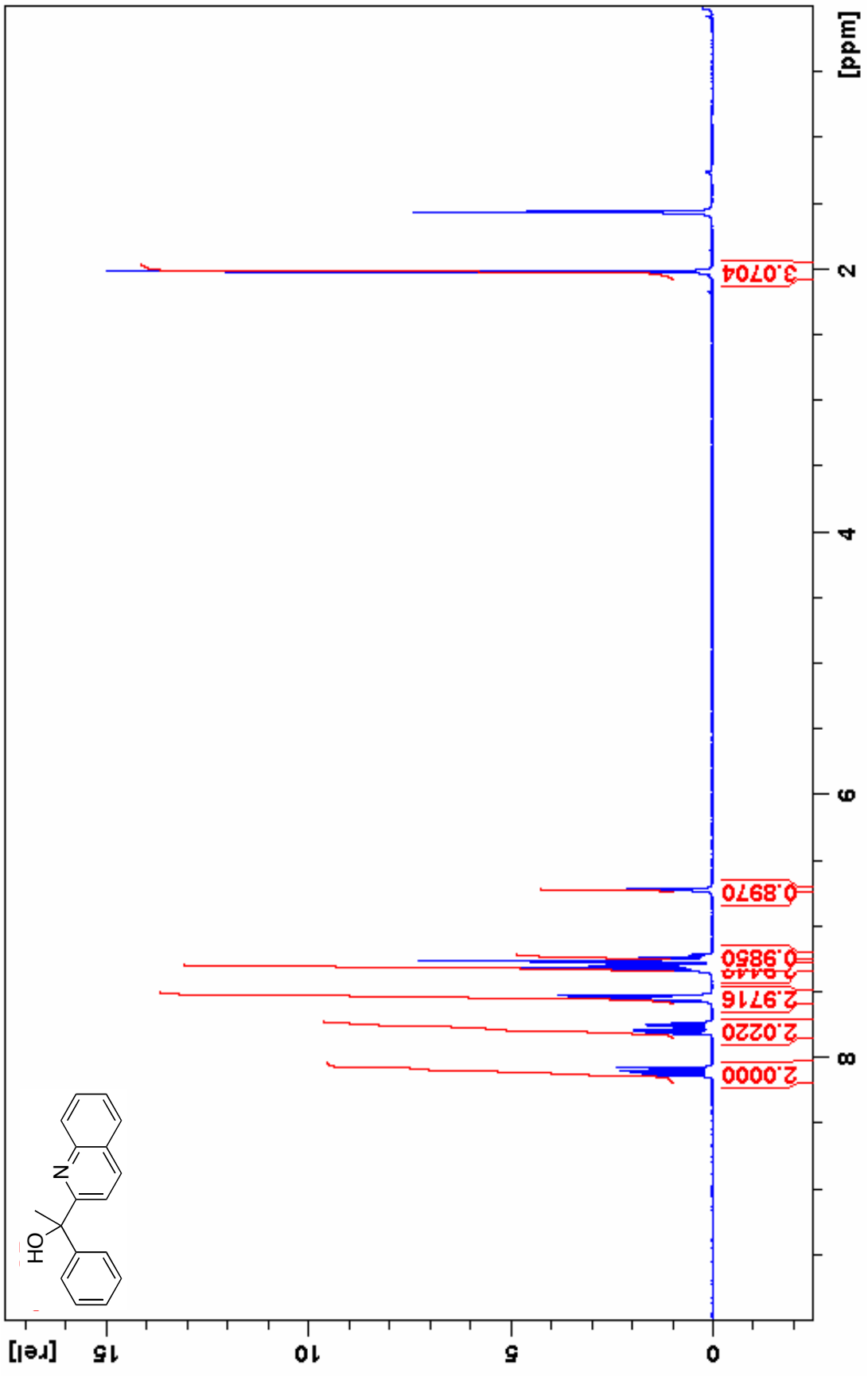
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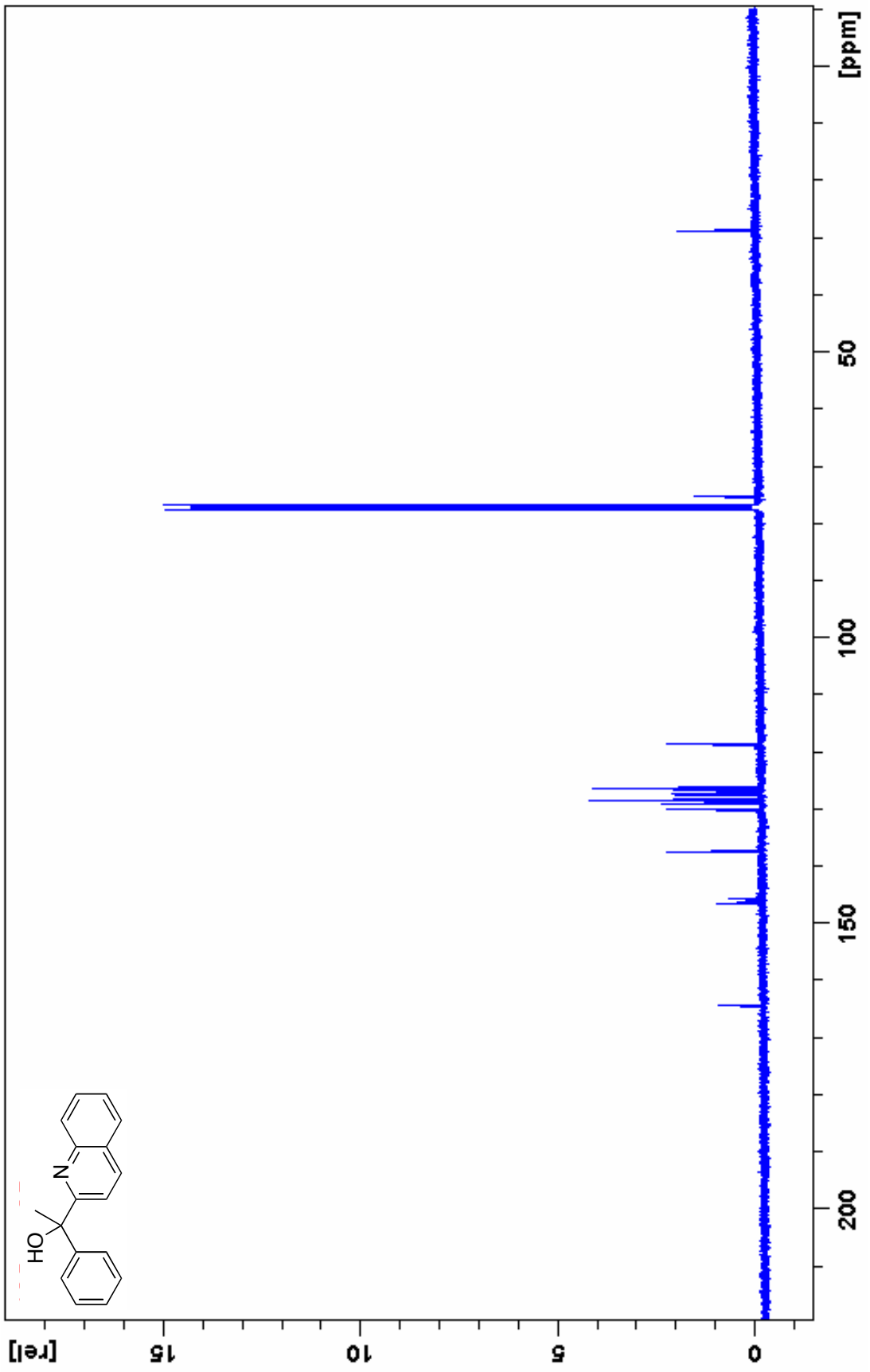
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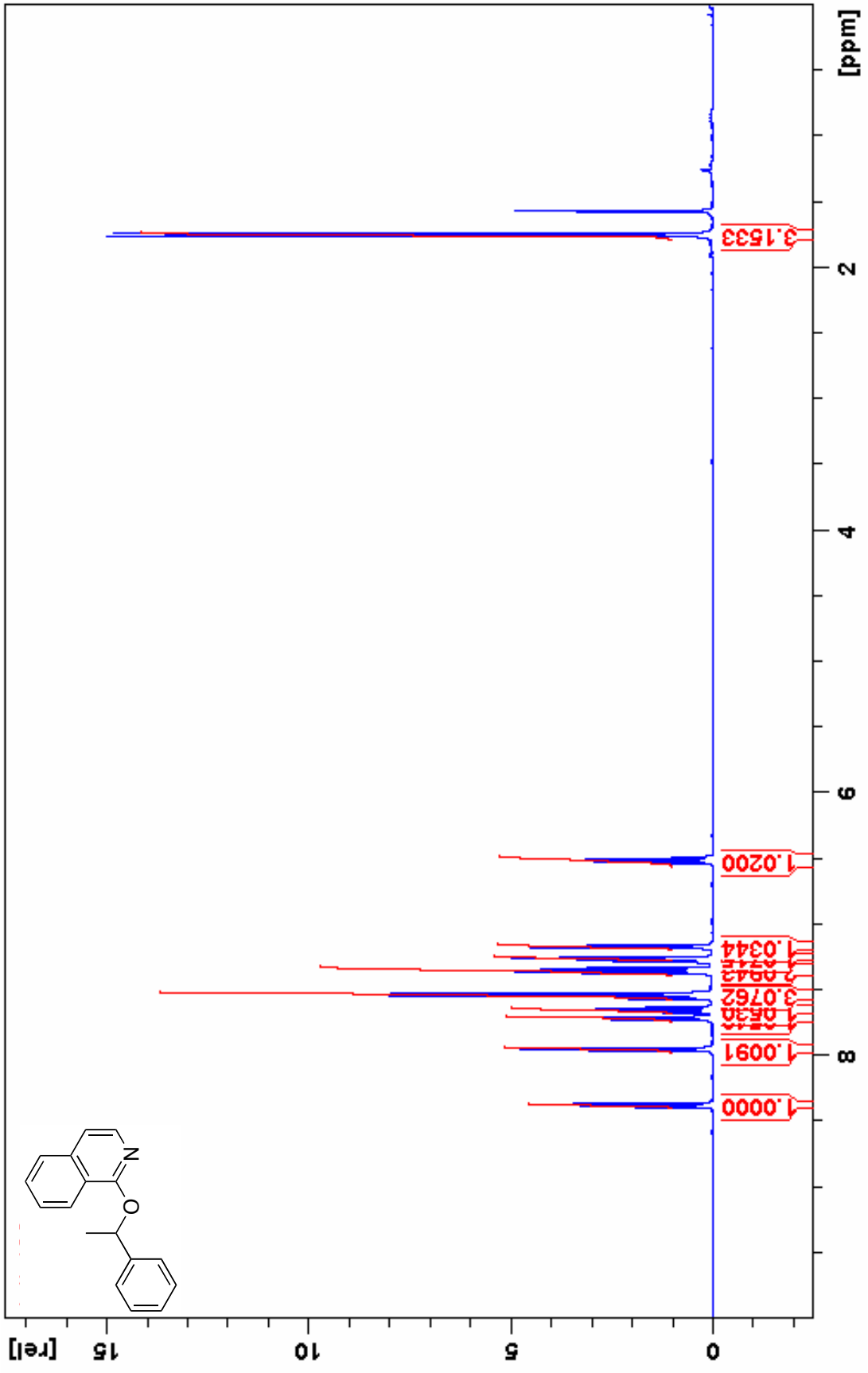
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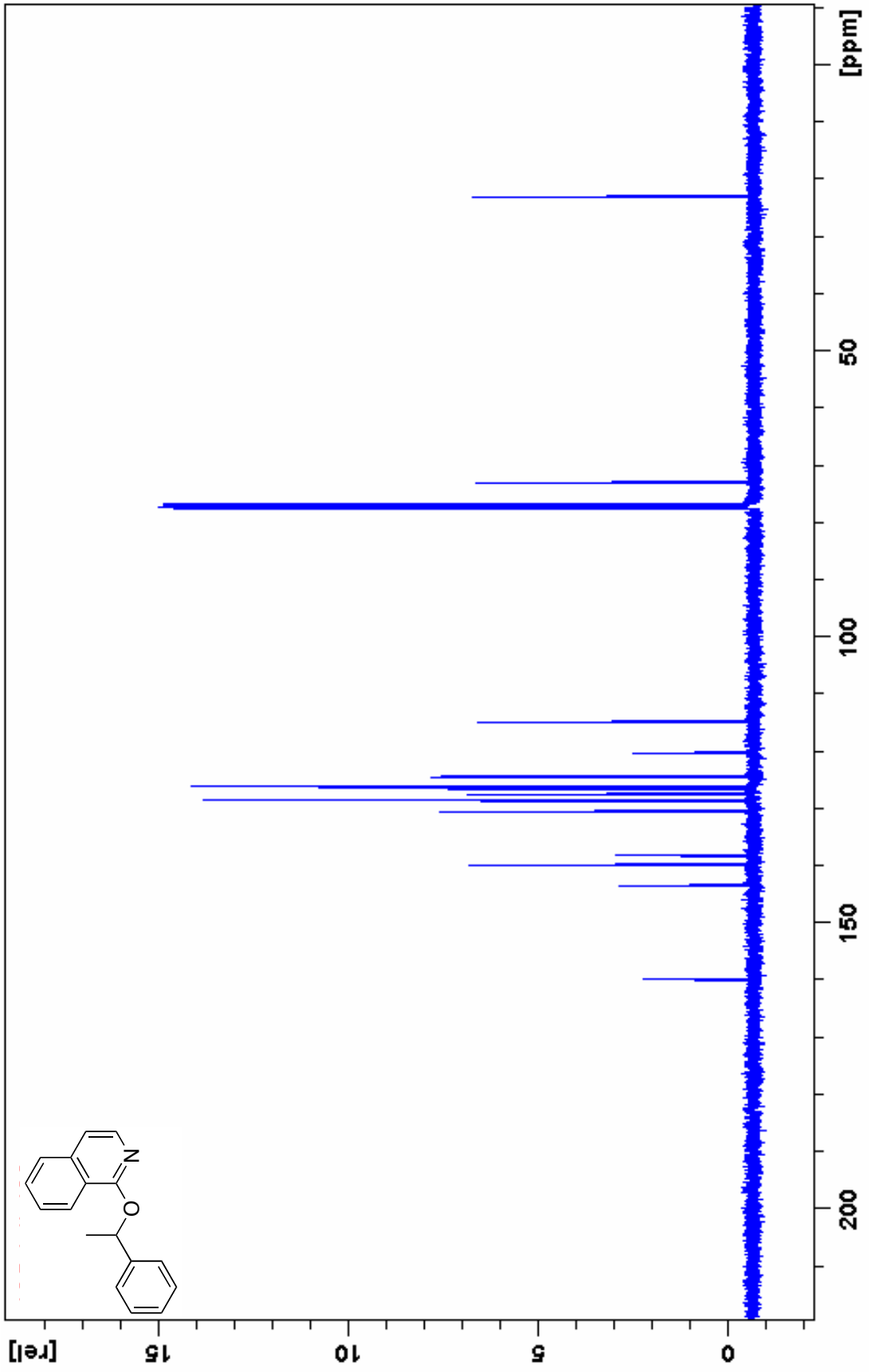
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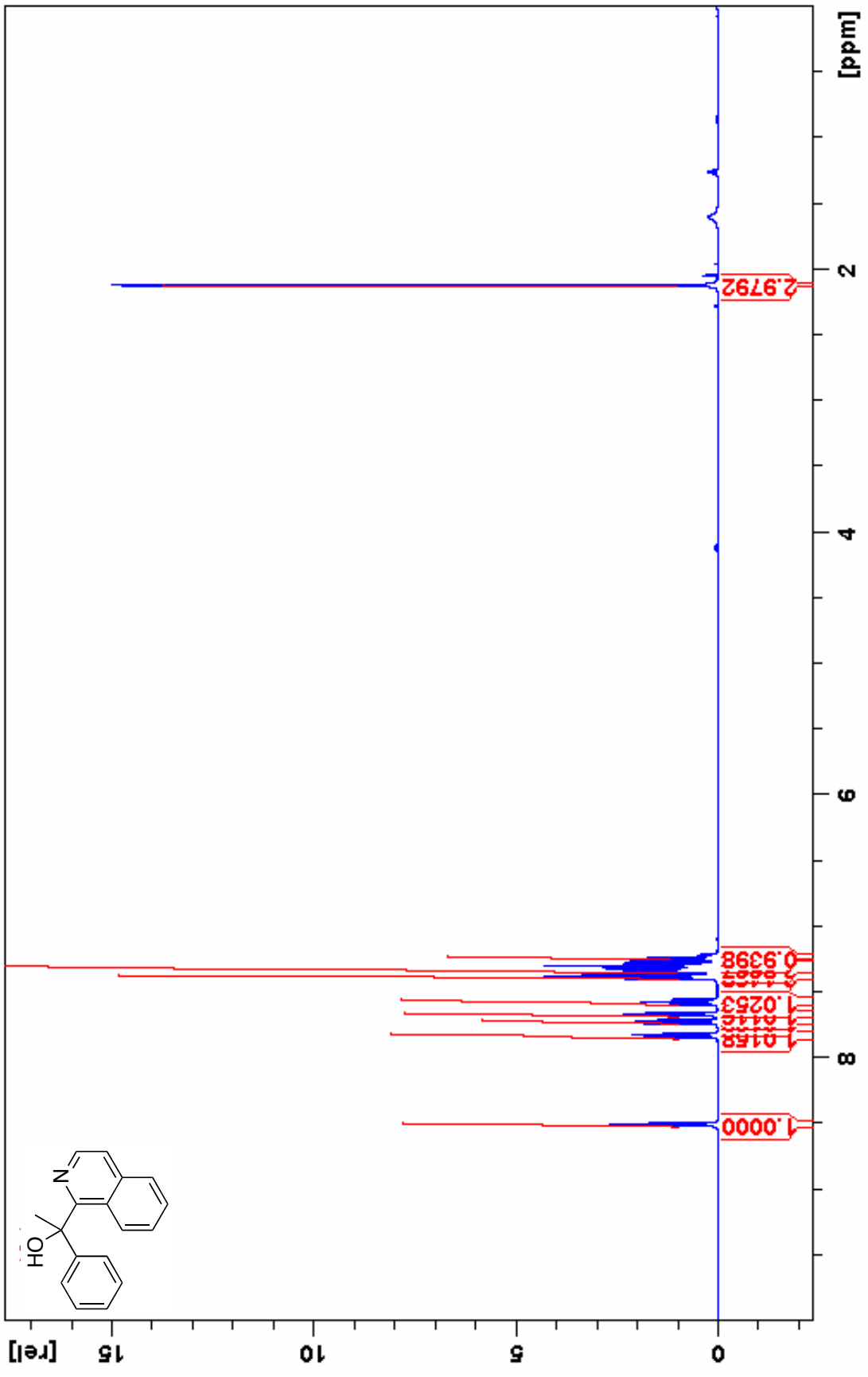
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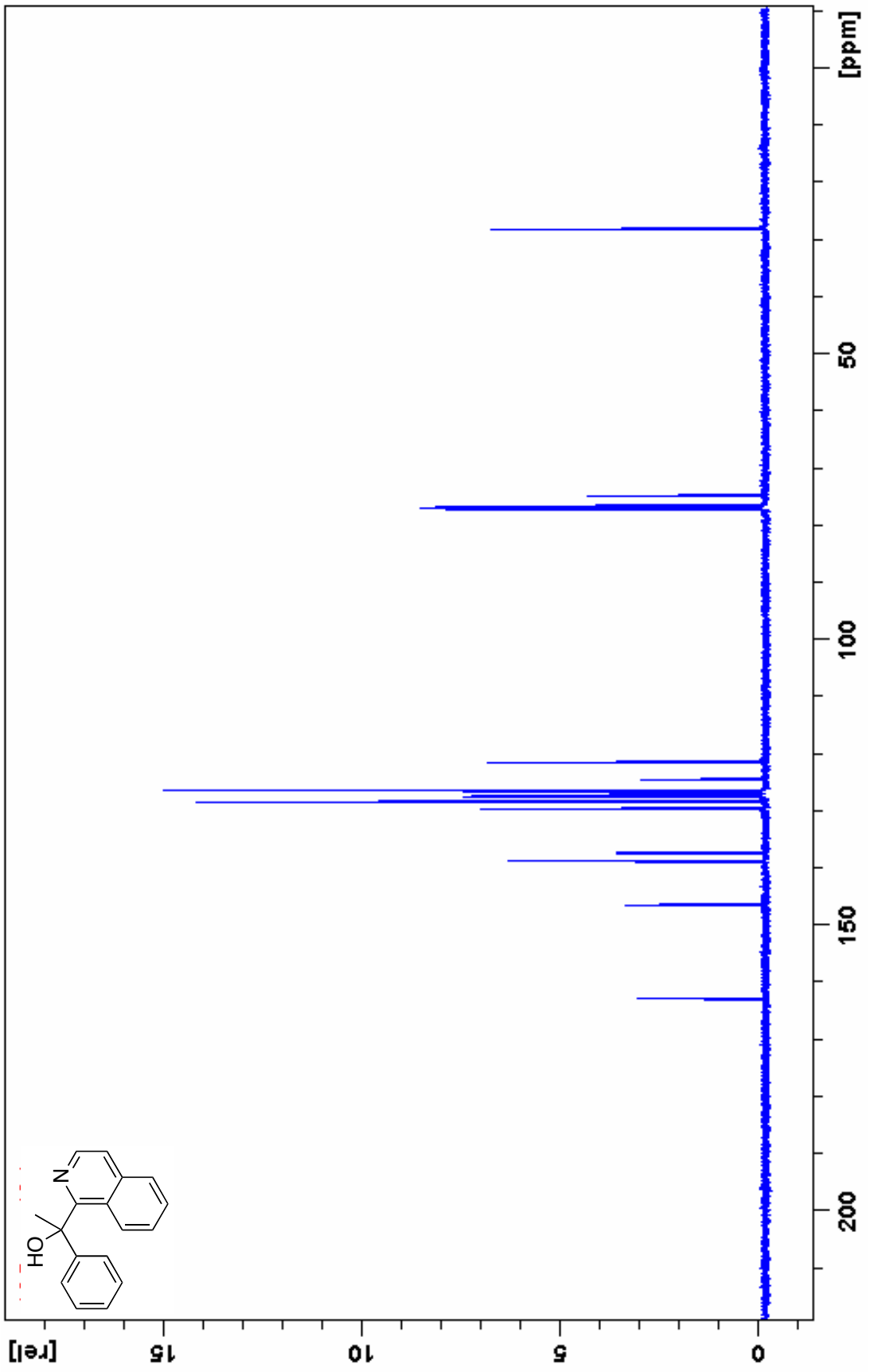
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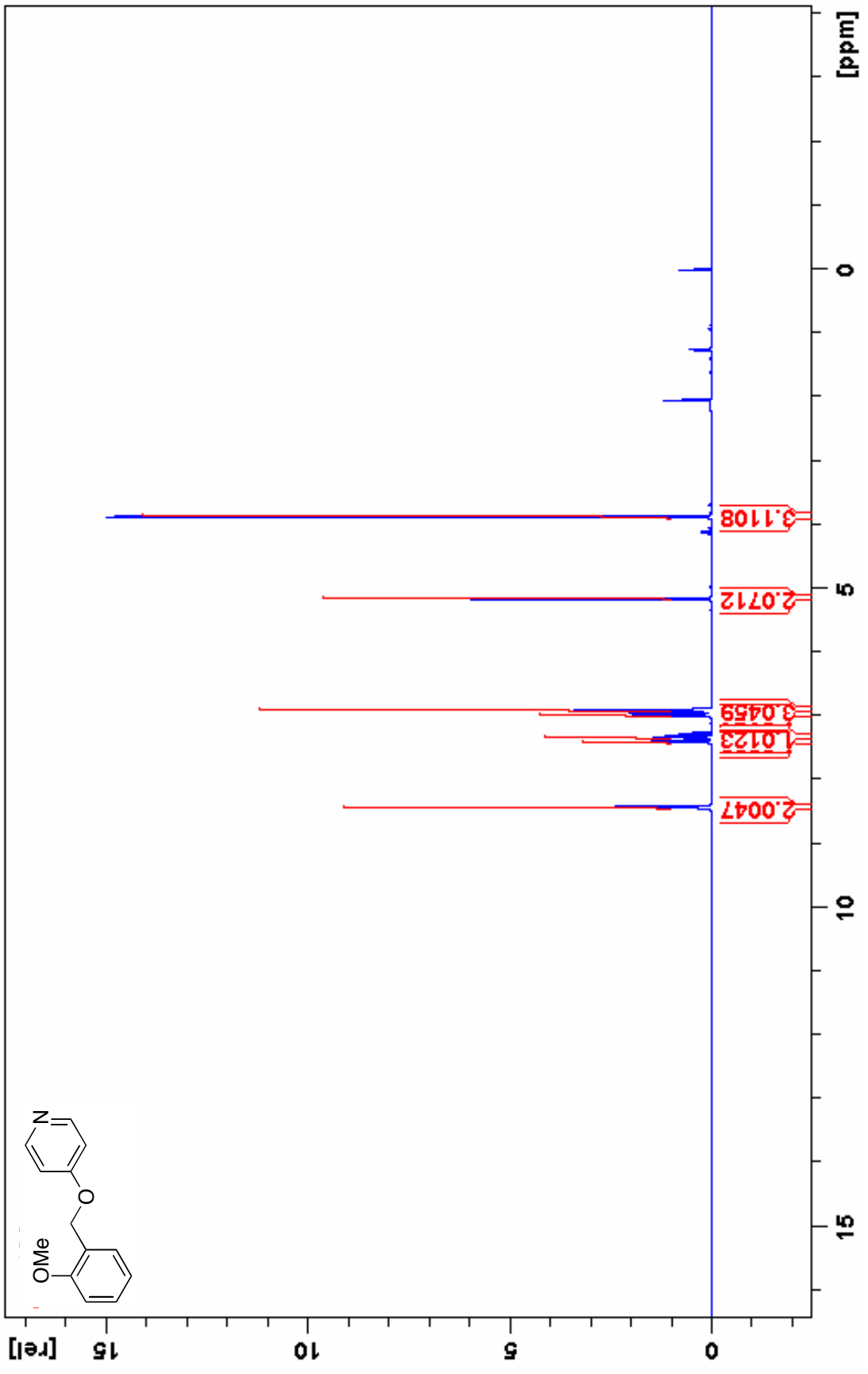
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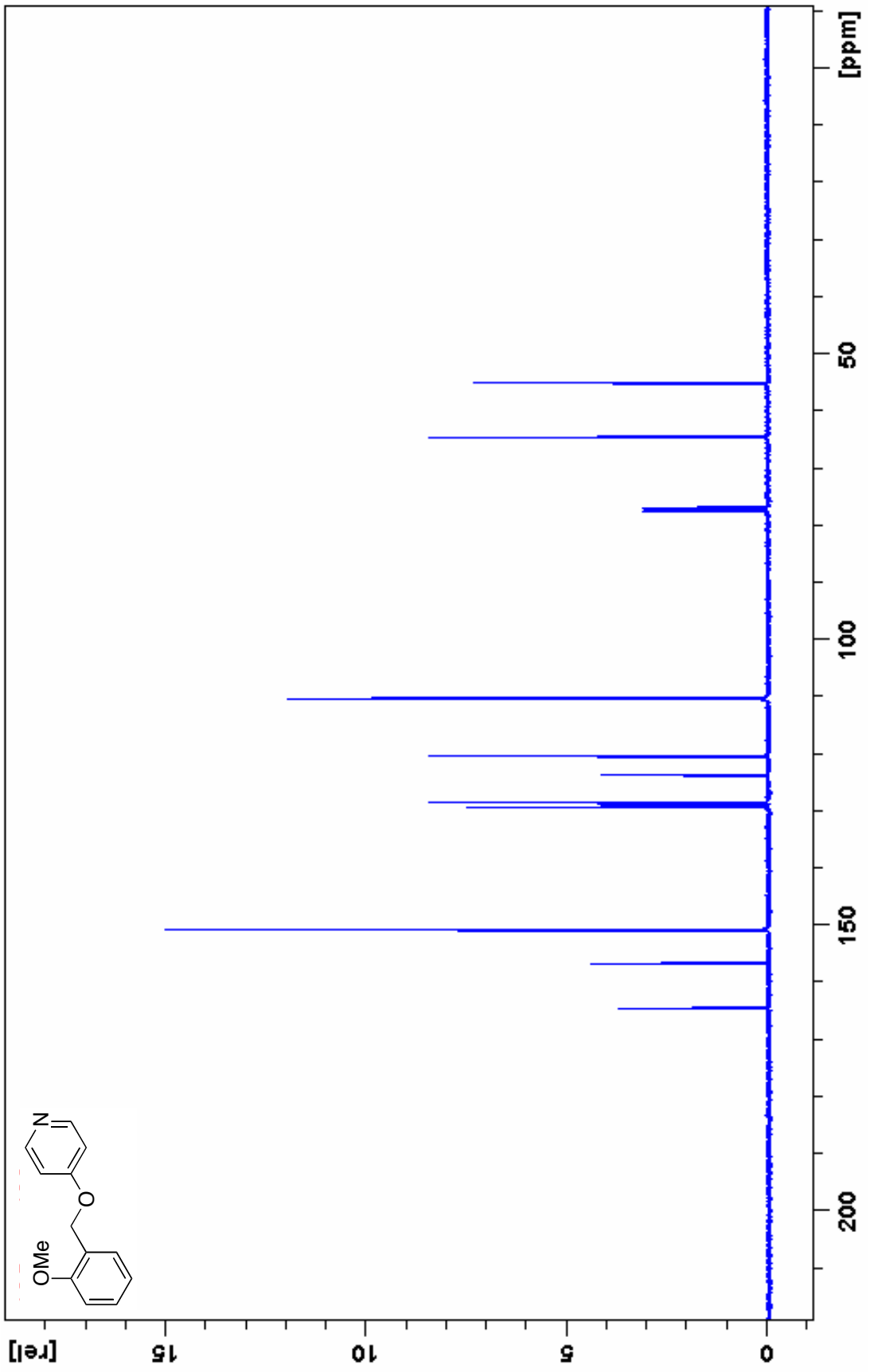
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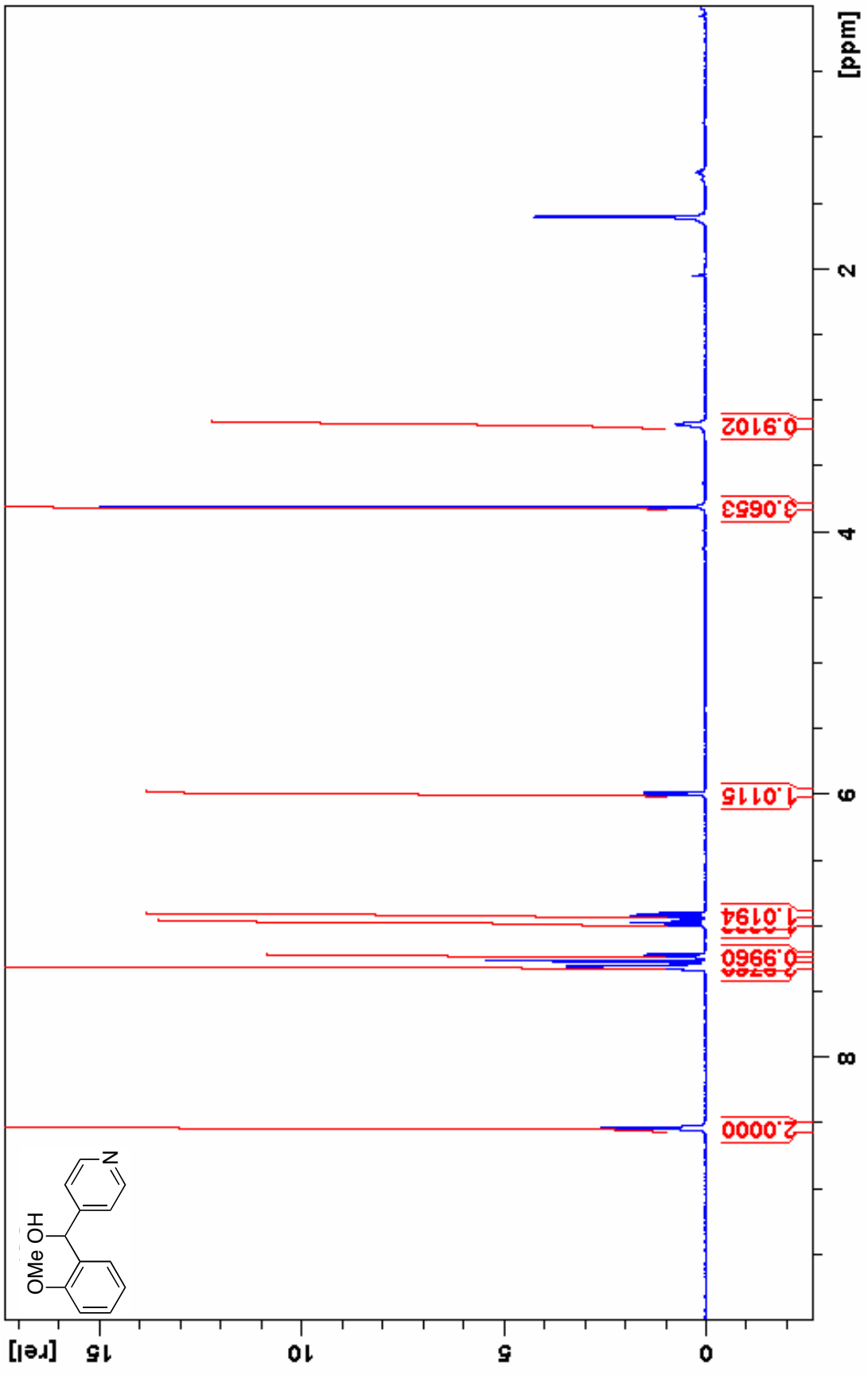
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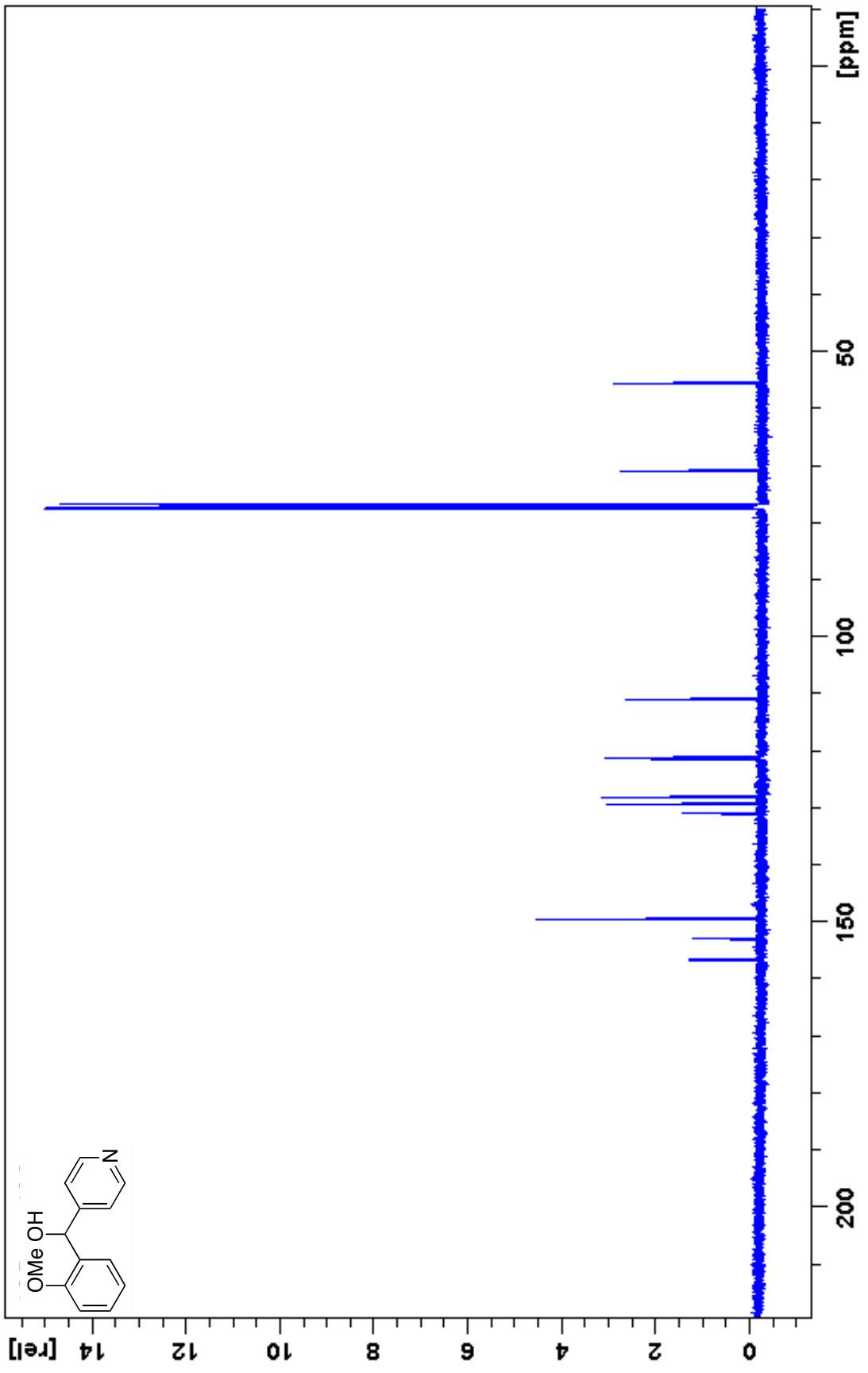
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