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Supporting Information

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Supporting Information

Convenient Synthesis of Pyrrolidine via Amphiphilic Allylation of Aldimine with 2-Methylenepropane-1,3-diol

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Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel $60F_{254}$). Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a

JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303.

Solvents and Reagents

Tetrahydrofuran was dried and distilled from benzophenone and sodium immediately prior to use under nitrogen atmosphere. $Pd(OAc)_2$ and *n*-Bu_3P (Aldrich), Et_3B and Et_2Zn (1.0 M hexane solution, KANTO), *p*-anisidine, *p*-chlorobenzaldehyde, *p*-hydroxybenzaldehyde were purchased and used without further purification. 2-Methylenepropane-1,3-diol, aniline, *p*-chloroaniline, benzylamine, benzaldehyde, *p*-anisaldehyde, 2-furfural, *n*-hexylaldehyde, cinnamaldehyde were purchased and distilled prior to use by Kugelrohr apparatus. 2-Methylenepropane-1,3-bisbenzyl ether was prepared from 2-methylenepropane-1,3-diol and benzyl bromide in the presence of NaH in DMF at 0 °C.

2-Methylenepropane-1,3-bisbenzyl Ether: IR (neat): 3352 (s), 3030 (m), 2876 (m), 1716 (m), 1654 (w), 1492 (m), 1452 (s), 1244 (m), 1191 (m), 1024 (m), 918 (m) 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.06 (s, 4 H), 4.51 (s, 4 H), 5.25 (s, 2 H), 7.24-7.39 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.8, (2 C) 72.1 (2 C), 114.1, 127.4 (2 C), 127.5 (2 C), 128.2 (4 C), 138.1 (2 C), 142.6. High-resolution MS, calcd for $C_{18}H_{20}O_2$: 268.1463, Found *m/z* (relative intensity): 268.1469 (M^+, 6), 197 (100).

Preparation of 2-Methylene-1-phenylpropane-1,3-diol

Into a flask containing a stirring bar purged with nitrogen were successfully added by MeOH (5 mL), 1,4-diazabicyclo[2.2.2]octane (673 mg, 9 mmol), benzaldehyde (4.8 g, 45 mmol), and methyl acrylate (6 mL, 60 mmol) via a syringe. The homogeneous mixture was stirred at room temperature for 3 days. After dilution with ethyl acetate (20 mL), the mixture was washed with water. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography over silica gel (hexane / ethyl acetate, 2/1, v/v) to provide 1-phenyl-2-methoxycarbonyl-2-propen-1-ol in 78% (6.7 g, 35 mmol). A 300-mL, two-necked round-bottomed flask, equipped with a rubber septum, an air condenser and a magnetic stir bar is charged under nitrogen atmosphere. A solution of 1-phenyl-2-methoxycarbonyl-2-propen-1-ol (3.8 g, 20 mmol) in diethyl ether (100 mL) was introduced via syringe and cooled to -78 ˚C, and DIBAL-H (60 mmol in 1M hexane solution) was added for 1 h. The reaction mixture was stirred at room temperature for 18 h and then 20 mL of water was added. The mixture was extracted with diethyl ether (30 mL x 3) and combined organic phases were washed with 2 M HCl (30 mL), and then brine, and dried over ($MgSO_4$) and concentrated in vacuo. The residue was subjected by means of column chromatography over silica gel (Ethyl acetate) to provide 2-methylene-1-phenylpropane-1,3-diol in 50% (1.7 g, 10 mmol).

2-Methylene-1-phenylpropane-1,3-diol: IR (neat): 3030 (m), 2855 (s), 1724 (w), 1657 (w), 1497 (m), 1454 (s), 1364 (m), 1205 (m), 1072 (s), 1028 (m), 914 (m) 737 (s) 696 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.98 (br s, 1 H), 2.72 (br s, 1 H), 4.04 (d, J = 13.2 Hz, 1 H), 4.15 (d, J = 13.2 Hz, 1 H), 5.21 (s, 2 H), 5.35 (s, 1 H), 7.26-7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 64.0, 69.8, 113.2, 126.2 (2 C), 127.6, 128.3 (2 C), 141.7, 149.3. High-resolution MS, calcd for $C_{10}H_{12}O_2$: 164.0837, Found *m/z* (relative intensity): 164.0802 (M^+, 5), 146 (100).

2-Methylene-1-phenylpropane-1,3-bisbenzyl ether was prepared from 2-methylene-1-phenylpropane-1,3-diol and benzyl bromide in the presence of NaH base in DMF at 0 ˚C.

2-Methylene-1-phenylpropane-1,3-bisbenzyl Ether: IR (neat): 3030 (m), 2923 (s), 2854 (s), 1740 (m), 1682 (w), 1494 (m), 1454 (s), 1363 (m), 1242 (m), 1205 (w), 1093 (s), 1069 (s), 1028 (m), 918 (m), 735 (s), 698 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (d, J = 13.1 Hz, 1 H), 4.00 (d, J = 13.1 Hz, 1 H), 4.39 (d, J = 12.0 Hz, 1 H), 4.43 (d, J = 12.0 Hz, 1 H), 4.50(s, 2 H), 4.97 (s, 1 H), 5.34 (s, 2 H), 7.28-7.37 (m, 15 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.1, 70.5, 72.1, 81.4, 113.6, 127.0 (2 C), 127.3 (2 C), 127.4 (2 C), 127.5 (3 C), 127.6 (3 C), 128.1 (4 C), 128.2, 138.2, 138.3, 139.9, 145.7. High-resolution MS, calcd for $C_{24}H_{24}O_2$: 344.1776, Found *m/z* (relative intensity): 344.1779 (M^+, 21), 277 (100).

2-Methylenebutane-1,3-diol was prepared from acetaldehyde and methyl acrylate according to the preparation of 2-methylene-1-phenylpropane-1,3-diol.

2-Methylenebutane-1,3-diol: IR (neat): 3329 (s), 2974 (m), 2880 (m), 1707 (w), 1654 (w), 1456 (m), 1373 (m), 1296 (m), 1080 (m), 1035 (m), 908 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.37 (d, J = 6.5 Hz, 3 H), 2.32 (br s, 2 H), 4.19 (d, J = 13.1 Hz, 1 H), 4.31 (d, J = 13.1 Hz, 1 H), 4.45 (d, J = 6.5 Hz, 1 H), 5.09 (s, 1 H), 5.11 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.2, 64.2, 69.9, 111.2, 150.9. High-resolution MS, calcd for $C_5H_{10}O_2$: 102.0681, Found *m/z* (relative intensity): 102.0630 (M^+, 100).

2-Methylenebutane-1,3-bisbenzyl Ether: IR (neat): 3030 (m), 2976 (m), 2860 (m), 1726 (m), 1497 (m), 1454 (s), 1367 (m), 1205 (w), 1097 (s), 1028 (m), 914 (m), 737 (s), 696 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (d, J = 6.6 Hz, 3 H), 4.04 (d, J = 13.2 Hz, 1 H), 4.06 (q, J = 6.6 Hz, 1 H), 4.10 (d, J = 13.2 Hz, 1 H), 4.36 (d, J = 12.1 Hz, 1 H), 4.52 (d, J = 11.6 Hz , 2 H), 4.55 (d, J = 12.1 Hz, 1 H), 5.24 (s, 1 H), 5.29 (s, 1 H), 7.24-7.36 (m, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.6, 69.6, 70.1, 72.3, 76.3, 112.9, 127.3, 127.5 (2 C), 127.6 (2 C), 127.7, 128.2 (2 C), 128.3 (2 C), 138.2, 138.6, 146.5. High-resolution MS, calcd for $C_{19}H_{22}O_2$: 282.1620, Found *m/z* (relative intensity): 282.1597 (M^+, 58), 259 (100).

General procedure for the amphiphilic allylation of *p*-anisidine-benzaldehyde imine with 2-methylenepropane-1,3-diol (run 2, Table 1): A solution of benzaldehyde (106 mg, 1.0 mmol) and *p*-anisidine (129 mg, 1.05 mmol) in dry THF (1 ml) was refluxed for 30 min under nitrogen, and then the solvent was removed by distillation (azeotropic removal of water). THF (1 ml) was added and distilled off under atmospheric pressure of nitrogen. Over the aldimine residue was successively added $Pd(OAc)_2$ (22.5 mg, 0.1 mmol), *n*-Bu_3P (50 μl, 0.2 mmol), 2-methylenepropane-1,3-diol (106 mg, 1.2 mmol), THF (1ml), and Et_3B (3.6 mmol, 1 M in hexane). The homogeneous mixture was stirred and heated for 18 hours at 50 °C under nitrogen. The mixture was diluted with EtOAc and washed with sat. $NaHCO_3$ and brine, and then the organic phases were dried ($MgSO_4$) and concentrated in vacuo to give brown oil, which was purified by column chromatography over silica gel (eluent; hexane) to give **1b** (242 mg, 91%). R_f = (0.70, EtOAc/hexane = 1/4); IR (neat): 2947 (m), 1620 (w), 1234 (s), 1042 (m), 810 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.51 (dd, J = 3.4, 15.1 Hz, 1 H), 3.20 (dd, J = 8.8, 15.1 Hz, 1 H), 3.70 (s, 3 H), 4.09 (d, J = 13.2 Hz, 1 H), 4.29 (d, J = 13.2 Hz, 1 H), 4.78 (dd, J = 3.4, 8.8 Hz, 1 H), 4.95 (s, 1 H), 5.08 (s, 1 H), 6.45 (d, J = 9.0 Hz, 2 H), 6.75 (d, J = 9.0 Hz, 2 H), 7.17-7.29 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 42.8, 54.7, 55.8, 63.1, 106.7, 113.3, 114.7, 125.7, 126.6, 128.4, 141.3, 144.5, 144.8, 151.1. High-resolution MS, calcd for $C_{18}H_{19}ON$: 265.1467; Found *m/z* (relative intensity): 265.1444 (100, M^+).

4-Methylene-1,2-diphenylpyrrolidine (**1a**): R_f = 0.80 (hexane:EtOAc = 4:1, v/v); IR (neat): 3024 (m), 2878 (m), 2831 (m), 1666 (w), 1597 (s), 1504 (s), 1450 (m), 1366 (s), 1242 (m), 1157 (m), 1072 (m), 1026 (m), 995 (w), 941 (w), 895 (m), 748 (s), 694 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.52 (dd, J = 2.7, 15.0 Hz, 1 H), 3.22 (dd, J = 8.9, 15.0 Hz, 1 H), 4.17 (d, J = 13.4 Hz, 1 H), 4.23 (d, J = 13.4 Hz, 1 H), 4.89 (dd, J = 2.7, 8.9 Hz, 1 H), 4.96 (s, 1 H), 5.11 (s, 1 H), 6.50 (d, J = 7.8 Hz, 2 H), 6.65 (d, J = 7.3 Hz, 2 H), 7.12-7.28 (m, 7 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.6, 53.8, 62.6, 107.1, 112.3 (2 C), 116.1, 125.6 (2 C), 126.6, 128.4 (2 C), 128.9 (2 C), 144.2, 144.4, 146.4. High-resolution MS, calcd for $C_{17}H_{17}N$: 235.1361, Found *m/z* (relative intensity): 235.1336 (M^+, 100).

1-(4-Methoxyphenyl)-4-methylene-2-phenylpyrrolidine (1b): R_f = 0.70 (hexane:EtOAc = 4:1, v/v); IR (neat) 3017 (m), 2947 (m), 2831 (m), 1796 (w), 1666 (w), 1620 (w), 1512 (s), 1450 (m), 1366 (m), 1234 (s), 1172 (m), 1042 (m), 895 (m), 810 (s), 748 (m), 694 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.51 (dd, J = 3.4, 15.1 Hz, 1 H), 3.20 (dd, J = 8.8, 15.1 Hz, 1 H), 3.70 (s, 3 H), 4.09 (d, J = 13.2 Hz, 1 H), 4.29 (d, J = 13.2 Hz, 1H), 4.78 (dd, J = 3.4, 8.8 Hz, 1 H), 4.95 (s, 1 H), 5.08 (s, 1 H), 6.45 (d, J = 9.0 Hz, 2 H), 6.75 (d, J = 9.0 Hz, 2 H), 7.17-7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.8, 54.7, 55.8, 63.1, 106.7, 113.3 (2 C), 114.7 (2 C), 125.7 (2 C), 126.6, 128.4 (2 C), 141.3, 144.5, 144.8, 151.1.

High-resolution MS, calcd for $C_{18}H_{19}ON$: 265.1467, Found *m/z* (relative intensity): 265.1444 (M^+, 100).

1-(4-Chlorophenyl)-4-methylene-2-phenylpyrrolidine (**1c**): R_f = 0.80 (hexane:EtOAc = 4:1, v/v); IR (neat): 3032 (w), 2970 (m), 2831 (m), 1735 (w), 1674 (m), 1597 (s), 1497 (s), 1466 (s), 1366 (s), 1242 (m), 1165 (m), 1096 (m), 1026 (w), 964 (w), 895 (m), 810 (s), 764 (m), 702 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.52 (dd, *J* = 2.7, 15.1 Hz, 1 H), 3.22 (dd, *J* = 8.8, 15.1Hz, 1 H), 4.12 (d, *J* = 13.4 Hz, 1 H), 4.20 (d, *J* = 13.4 Hz, 1 H), 4.84 (dd, *J* = 2.7, 8.8 Hz, 1 H), 4.97 (s, 1 H), 5.11 (s, 1 H), 6.40 (d, *J* = 8.9 Hz, 2 H), 7.07 (d, *J* = 8.9 Hz, 2 H), 7.12-7.29 (m, 7 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.7, 54.1, 62.8, 107.5, 113.4 (2 C), 121.1, 125.6 (2 C), 126.9, 128.6 (2 C), 128.7 (2 C), 143.8, 144.0, 145.0. High-resolution MS, calcd for $C_{17}H_{18}ClN$: 269.0971, Found *m/z* (relative intensity): 269.0975 (M^+, 100).

1,2-Bis(4-methoxyphenyl)-4-methylenepyrrolidine (**1d**): R_f = 0.50 (hexane:EtOAc = 4:1, v/v); IR (neat): 3055 (w), 2908 (m), 2870 (w), 2800 (m), 2052 (w), 1882 (w), 1666 (w), 1612 (m), 1512 (s), 1466 (m), 1288 (s), 1242 (s), 1180 (m), 1134 (m), 1034 (s), 964 (w), 872 (m), 826 (s), 732 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.47 (dd, *J* = 3.2, 15.1 Hz, 1 H), 3.17 (dd, *J* = 8.5, 15.1 Hz, 1 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 4.07 (d, *J* = 13.2 Hz, 1 H), 4.23 (d, *J* = 13.2 Hz, 1

H), 4.74 (dd, *J* = 3.2, 8.5 Hz, 1 H), 4.95 (s, 1 H), 5.08 (s, 1 H), 6.45 (d, *J* = 9.0 Hz, 2 H), 6.75 (d, *J* = 9.0 Hz, 2 H), 6.80 (d, *J* = 8.5 Hz, 2 H), 7.11 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 43.0, 54.6, 55.1, 55.8, 62.5, 106.6, 113.3 (2 C), 113.9 (2 C), 114.7 (2 C), 126.7 (2 C), 136.6, 141.4, 144.9, 151.0, 158.2. High-resolution MS, calcd for $C_{19}H_{21}O_2N$: 295.1572, Found *m/z* (relative intensity): 295.1558 (M^+, 100).

2-(4-Chlorophenyl)-1-(4-methoxyphenyl)-4-methylenepyrrolidine (**1e**): R_f = 0.80 (hexane:EtOAc = 4:1, v/v); IR (neat): 3086 (w), 3047 (w), 2939 (m), 2901 (m), 2862 (m), 2824 (m), 1899 (w), 1828 (w), 1674 (m), 1620 (w), 1512 (s), 1404 (m), 1350 (m), 1242 (s), 1165 (s), 1088 (m), 1034 (s), 957 (w), 902 (m), 810 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.45 (dd, *J* = 3.2, 15.1 Hz, 1 H), 3.19 (dd, *J* = 8.7, 15.1 Hz, 1 H), 3.70 (s, 3 H), 4.07 (d, *J* = 13.2 Hz, 1 H), 4.23 (d, *J* = 13.2 Hz, 1 H), 4.74 (dd, *J* = 3.2, 8.7 Hz, 1 H), 4.95 (s, 1 H), 5.09 (s, 1 H), 6.42 (d, *J* = 9.0 Hz, 2 H), 6.75 (d, *J* = 9.0 Hz, 2 H), 7.13 (d, *J* = 8.3 Hz, 2 H), 7.23 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.7, 54.6, 55.7, 62.5, 107.0, 113.4 (2 C), 114.7 (2 C), 127.1 (2 C), 128.6 (2 C), 132.3, 141.1, 143.1, 144.3, 151.2. High-resolution MS, calcd for $C_{18}H_{18}ClON$: 299.1077, Found *m/z* (relative intensity): 299.1031 (M^+, 100).

1-(4-Methoxyphenyl)-4-methylene-2-(4-hydroxyphenyl)pyrrolidine (**1f**): R_f =

0.30 (hexane:EtOAc = 4:1, v/v); IR (neat) 3375 (m), 2926 (m), 2831 (m), 1664 (w), 1612 (m), 1599 (m), 1514 (s), 1441 (m), 1364 (m), 1232 (s), 1182 (m), 1134 (m), 1038 (m), 963 (w), 887 (m), 814 (m), 789 (m) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 2.29 (ddd, J = 1.6, 3.5, 15.1 Hz, 1 H), 2.83 (dd, J = 8.5, 15.1 Hz, 1 H), 3.38 (s, 3 H), 3.85 (d, J = 13.3 Hz, 1 H), 4.02 (dd, J = 1.6, 13.3 Hz, 1 H), 4.51 (dd, J = 3.5, 8.5 Hz, 1 H), 4.78 (s, 1 H), 4.90 (s, 1 H), 6.48 (dd, J = 9.2 Hz, 2 H), 6.54 (d, J = 2.2, 8.5 Hz, 2 H), 6.79 (d, J = 9.2 Hz, 2 H), 6.95 (dd, J = 2.2, 8.5 Hz, 2 H); ^{13}C NMR (C_6D_6, 100 MHz) δ 43.2, 54.9, 55.3, 62.9, 106.4, 114.1 (2 C), 115.1 (2 C), 115.6 (2 C), 127.1 (2 C), 136.5, 141.8, 145.5, 152.0, 155.4. High-resolution MS, calcd for $C_{18}H_{19}O_2N$: 281.1416, Found *m/z* (relative intensity): 281.1418 (M^+, 100).

2-(Furan-2-yl)-1-(4-methoxyphenyl)-4-methylenepyrrolidine (**1g**): R_f = 0.60 (hexane:EtOAc = 4:1, v/v);IR (neat): 3071 (w), 2955 (m), 2909 (m), 2808 (m), 2021 (w), 1666 (m), 1612 (w), 1581 (w), 1512 (s), 1458 (m), 1350 (m), 1242 (s), 1180 (m), 1142 (m), 1034 (s), 964 (w), 895 (m), 818 (m), 733 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.72 (dd, J = 1.5, 15.4 Hz, 1 H), 3.07 (dd, J = 8.3, 15.4 Hz, 1 H), 3.72 (s, 3 H), 4.04 (s, 2 H), 4.93 (dd, J = 1.5, 8.1 Hz, 1 H), 5.02 (s, 1 H), 5.09 (s, 1 H), 5.96 (d, J = 3.0, Hz 1 H), 6.21 (dd, J = 1.0, 3.0 Hz, 1 H), 6.55 (d, J = 8.9 Hz, 2 H), 6.79 (d, J = 8.9 Hz, 2 H), 7.29 (d, J = 1.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.3, 53.1, 55.7, 56.5, 105.7, 106.8, 110.0, 113.4 (2 C), 114.7 (2 C), 141.0, 141.2, 144.9, 151.4, 155.8. High-resolution MS, calcd for $C_{16}H_{17}O_2N$: 255.1259,

Found *m/z* (relative intensity): 255.1250 (M^+, 100).

1-(4-Methoxyphenyl)-4-methylene-2-pentylpyrrolidine (**1h**): R_f = 0.73 (hexane:EtOAc = 4:1, v/v); IR (neat) 2924 (s), 2855 (m), 2793 (m), 1512 (s), 1465 (m), 1366 (m), 1242 (s), 1180 (w), 1041 (m), 887 (m), 810 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 6.7 Hz, 3 H), 1.19-1.30 (ddm, 7 H), 1.61-1.68 (m, 1 H), 2.40 (d, 15.4 Hz, 1 H), 2.79 (dd, 7.4, 15.4 Hz, 1 H), 3.74 (dm, 7.4 Hz, 1 H), 3.75 (s, 3 H), 3.81 (d, 13.4 Hz, 3 H), 3.89 (d, *J* = 13.4 Hz, 1 H), 5.02 (s, 1 H), 5.04 (s, 1 H), 6.51 (d, *J* = 9.0 Hz, 2 H), 6.84 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 22.7, 26.0, 31.5, 31.9, 37.6, 52.8, 55.9, 58.5, 106.3, 113.0 (2 C), 115.0 (2 C), 141.2, 146.4, 150.1. High-resolution MS, calcd for $C_{17}H_{18}ON$: 259.1936, Found *m/z* (relative intensity): 259.1911 (M^+, 32), 231 (69), 188 (100).

1-Benzyl-4-methylene-2-phenylpyrrolidine (1i): R_f = 0.80 (hexane:EtOAc = 4:1, v/v); IR (neat): 3032 (w), 2940 (s), 2909 (m), 2793 (s), 2716, (m), 1450 (s), 1366 (m), 1319 (m), 1242 (m), 1180 (w), 1142 (m), 1096 (m), 1026 (m), 980 (m), 887 (s), 756 (s), 694 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.49 (dd, *J* = 10.0, 16.1 Hz, 1 H), 2.82 (dd, *J* = 6.5, 16.1 Hz, 1 H), 2.91 (d, *J* = 13.7 Hz, 2 H), 3.02 (d, *J* = 13.1 H, 1 H), 3.55 (dd, *J* = 6.5, 10.1 Hz, 1 H), 3.64 (d, *J* = 13.7 Hz, 1 H), 3.86 (d, *J* = 13.1 Hz, 1 H), 4.84 (s, 1 H), 4.85 (s, 1 H), 7.19-7.51 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.8, 58.0, 58.7, 69.6, 104.5, 126.7, 127.2, 127.4 (2 C), 128.0 (2 C), 128.4

(2 C), 128.5(2 C), 139.2, 142.5, 146.7. High-resolution MS, calcd for $C_{18}H_{19}N$: 249.1517, Found *m/z* (relative intensity): 249.1491 (M^+, 100).

1-Benzyl-2-(4-chlorophenyl)-4-methylenepyrrolidine (1j): R_f = 0.80 (hexane:EtOAc = 4:1, v/v); IR (neat) 3071 (w), 3031 (w), 2939 (m), 2916 (m), 2793 (m), 1666 (w), 1489 (s), 1450 (m), 1366 (m), 1288 (w), 1141 (m), 1096 (s), 1018 (m), 880 (m), 826 (s), 702 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.42 (dd, *J* = 10.0, 16.1 Hz, 1 H), 2.80 (dd, *J* = 6.6, 16.1 Hz, 1 H), 2.91 (d, *J* = 13.7 Hz, 1 H), 3.03 (d, *J* = 13.0 Hz, 1 H), 3.53 (dd, *J* = 6.6, 10.0 Hz, 1 H), 3.63 (d, *J* = 13.7 Hz, 1 H), 3.80 (d, *J* = 13.0 Hz, 1 H), 4.84 (s, 2 H), 7.18-7.30 (m, 5 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.8, 57.9, 58.6, 68.9, 104.7, 126.8, 128.1 (2 C), 128.4 (2 C), 128.6 (2 C), 128.7 (2 C), 132.8, 138.9, 141.1, 146.2. High-resolution MS, calcd for $C_{18}H_{18}ClN$: 283.1128, Found *m/z* (relative intensity): 283.1117 (M^+, 100).

1-Benzyl-2-(furan-2-yl)-4-methylenepyrrolidine (1k): R_f = 0.70 (hexane:EtOAc = 4:1, v/v); IR (neat) 3092 (m), 3061 (w), 2943 (m), 2920 (m), 2800 (m), 2725 (m), 1663 (w), 1506 (m), 1497 (m), 1454 (m), 1375 (m), 1342 (m), 1151 (s), 1094 (m), 1018 (m), 866 (s), 734 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.77 (d, *J* = 8.0 Hz, 2 H), 2.98 (d, *J* = 13.8 Hz, 1 H), 3.24 (d, *J* = 13.0 Hz, 1 H), 3.54 (d, *J* = 13.8 Hz, 1 H), 3.75 (d, *J* = 8.0 Hz, 1 H), 3.87 (d, *J* = 13.0 Hz, 1 H), 4.85 (s, 1 H), 4.88 (s, 1 H),

6.29 (d, J = 3.0 Hz, 1 H), 6.33 (dd, J = 1.8, 3.0 Hz, 1 H), 7.18~7.32 (m, 5 H), 7.39 (d, J = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.3, 57.8, 58.0, 61.7, 105.1, 107.1, 109.9, 126.8, 128.0 (2 C), 128.7 (2 C), 138.6, 141.8, 145.9, 154.8. High-resolution MS, calcd for $C_{16}H_{17}ON$: 239.1310, Found *m/z* (relative intensity): 239.1301 (M^+, 100).

1-Benzyl-4-methylene-2-styrylpyrrolidine (**1l**): R_f = 0.70 (hexane:EtOAc = 4:1, v/v); IR (neat) 3065 (m), 3026 (m), 2957 (m), 2897 (m), 2772 (m), 2343 (w), 1663 (w), 1493 (s), 1448 (s), 1366 (m), 1315 (m), 1238 (m), 1120 (m), 1072 (m), 962 (s), 885 (s), 744(s), 694 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.40-2.54 (m, 1 H), 2.68 (dd, J = 6.2, 16.6 Hz, 1 H), 2.89 (d, J = 13.7 Hz, 1 H), 3.17 (d, J = 13.0 Hz, 1 H), 3.52 (d, J = 13.7 Hz, 1 H), 4.10 (d, J = 13.0 Hz , 1 H), 4.83 (s, 1 H), 4.86 (s, 1 H), 6.20 (dd, J =, 8.4, 15.9 Hz, 1 H), 6.60 (d, J = 15.9 Hz, 1 H) 7.18-7.44 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.5, 58.2, 58.4, 67.9, 104.9, 126.3 (3 C), 126.8, 127.4, 128.1 (2 C), 128.4 (2 C), 128.8 (2 C), 132.3, 136.7, 138.8, 138.9. High-resolution MS, calcd for $C_{20}H_{21}N$: 275.1674; Found *m/z* (relative intensity): 275.1649 (M^+, 100).

1-Benzyl-4-methylene-2-pentylpyrrolidine (**1m**): R_f = 0.80 (hexane:EtOAc = 4:1, v/v); IR (neat): 3028 (w), 2929 (s), 2856 (m), 1665 (w), 1495 (m), 1454 (m), 1072 (m), 878 (m), 736 (m), 698 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, J = 6.8

Hz, 3 H), 1.26-1.41 (m, 7 H), 1.80 (m, 1 H), 2.22 (ddt, *J* = 2.7, 6.6, 9.0 Hz, 1 H), 2.51 (ddd, *J* = 2.7, 9.0, 15.9 Hz, 1 H), 2.61 (dd, *J* = 6.6, 15.9 Hz, 1 H), 2.79 (dd, *J* = 2.7, 13.9 Hz, 1 H), 3.10 (d, *J* = 12.8 Hz, 1 H), 3.43 (d, *J* = 13.9 Hz, 1 H), 4.10 (d, *J* = 12.8 Hz, 1 H), 4.77 (s, 1 H), 4.80 (s, 1 H), 7.22-7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 22.7, 25.7, 32.2, 33.2, 38.1, 58.2, 59.5, 64.7, 104.4, 126.7, 128.0 (2 C), 128.7 (2 C), 139.2, 146.8. High-resolution MS, calcd for $C_{19}H_{21}N$: 243.1987, Found *m/z* (relative intensity): 243.1988 (M^+, 22), 172 (100).

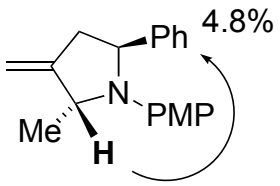
1-(4-Methoxyphenyl)-4-methylene-2-styrylpyrrolidine (**1n**): R_f = 0.67 (hexane:EtOAc = 4:1, v/v); mp = 114.0-116.0 ˚C; IR (KBr) 3024 (w), 2900 (m), 2831 (m), 1736 (w), 1674 (w), 1512 (s), 1450 (m), 1358 (m), 1250 (s), 1173 (m), 1142 (w), 1034 (m), 894 (m), 810 (m), 748 (m), 694 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *trans* isomer) δ 2.40 (d, *J* = 14.6, Hz, 1 H), 3.37 (ddd, *J* = 1.5, 8.7, 14.6 Hz, 1 H), 3.60 (s, 3 H), 4.82 (dd, *J* = 1.5, 2.6 Hz, 1 H), 5.19 (d, *J* = 2.6 Hz, 1 H), 5.29 (d, *J* = 8.7 Hz, 1 H), 6.32 (d, *J* = 9.0 Hz, 2 H), 6.58 (d, *J* = 9.0 Hz, 2 H), 7.14-7.37 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz, *trans* isomer) δ 40.5, 55.5, 62.7, 68.4, 107.9, 114.3 (2 C), 114.7 (2 C), 125.3 (2 C), 126.0 (2 C), 126.6, 126.9, 128.1 (2 C), 128.6 (2 C), 138.8, 143.4, 143.9, 148.7, 150.6. High-resolution MS, calcd for $C_{24}H_{23}ON$: 341.1780, Found *m/z* (relative intensity): 341.1771 (M^+, 66), 212 (100).

1-(4-Bromophenyl)-3-methylene-2,5-diphenylpyrrolidine (**1o**): R_f = 0.77

(hexane:EtOAc = 4:1, v/v); mp = 166.5-168.0 ˚C; IR (KBr) 3024 (w), 2900 (m), 2831 (m), 1736 (w), 1674 (w), 1512 (s), 1450 (m), 1358 (m), 1250 (s), 1173 (m), 1142 (w), 1034 (m), 894 (m), 810 (m), 748 (m), 694 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, *trans* isomer) δ 2.41 (dd, J = 0.8, 14.6, Hz, 1 H), 3.37 (dd, J = 8.8, 14.6 Hz, 1 H), 4.84 (d, J = 2.7 Hz, 1 H), 5.52 (d, J = 2.7 Hz, 1 H), 5.28 (d, J = 8.8 Hz, 1 H), 6.25 (d, J = 9.0 Hz, 2 H), 7.04 (d, J = 9.0 Hz, 2 H), 7.14-7.32 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz, *trans* isomer) δ 40.3, 62.7, 68.3, 108.4, 115.6, 125.2, 125.8, 126.9, 127.2, 128.5, 128.7, 131.3, 142.4, 143.1, 143.4, 148.0. Anal. calcd for $C_{23}H_{20}BrN$: C,70.78; H, 5.16; Br, 20.47; N, 3.59; Found: C, 71.05; H, 5.12, N, 3.42.

1-(4-Methoxyphenyl)-2-methyl-3-methylene-5-phenylpyrrolidine (**1p**): R_f = 0.70 (hexane:EtOAc = 4:1, v/v); mp = 89.5-91.5 ˚C; IR (KBr) 3026 (w), 2966 (m), 2930 (m), 2831 (m), 2361(w), 1514 (s), 1454 (m), 1356 (m), 1242 (s), 1180 (m), 1159 (w), 1041 (m), 887 (m), 814 (m), 761 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, *trans* isomer) δ 1.32 (d, J = 6.3, Hz, 3 H), 2.40 (dd, J = 1.5, 15.1 Hz, 1 H), 3.30 (dd, 8.5, 15.1 Hz, 1 H), 3.67 (s, 3 H), 4.63 (quint, J = 6.3 Hz, 1 H), 4.86 (s, 1 H), 4.91 (dd, J = 1.5, 8.5 Hz, 1 H), 5.04 (s, 1 H), 6.49 (d, J = 9.0 Hz, 2 H), 6.69 (d, J = 9.0 Hz, 2 H), 7.10-7.32 (m, 5 H); ^1H NMR ($CDCl_3$, 400 MHz, *cis* isomer) δ 1.53 (d, J = 6.1, Hz, 3 H), 2.40 (dd, J = 6.1, 15.1 Hz, 1 H), 3.08 (dd, 8.3, 15.1 Hz, 1 H), 3.70 (s, 3 H), 4.27 (dd, J = 6.1, 8.3 Hz, 1 H), 4.61 (quint, J = 6.1 Hz, 1 H), 4.89 (s,

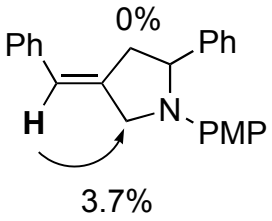
1 H), 4.92 (s, 1 H), 6.53 (d, J = 9.0 Hz, 2 H), 6.74 (d, J = 9.0 Hz, 2 H), 7.10-7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100 MHz, *trans* isomer) δ 19.9, 40.9, 55.6, 59.6, 61.9, 105.9, 114.5 (2 C), 115.6 (2 C), 126.0 (2 C), 126.5, 128.2 (2 C), 139.4, 144.2, 150.4, 150.7; ^{13}C NMR ($CDCl_3$, 100 MHz, *cis* isomer) δ 21.2, 42.1, 55.8, 60.1, 65.2, 105.3, 114.3 (2 C), 114.6 (2 C), 125.7 (2 C), 126.6, 128.5 (2 C), 141.9, 145.0, 150.8, 151.5. High-resolution MS, calcd for $C_{19}H_{21}ON$: 279.1623, Found *m/z* (relative intensity): 279.1611 (M^+, 67), 264 (100).



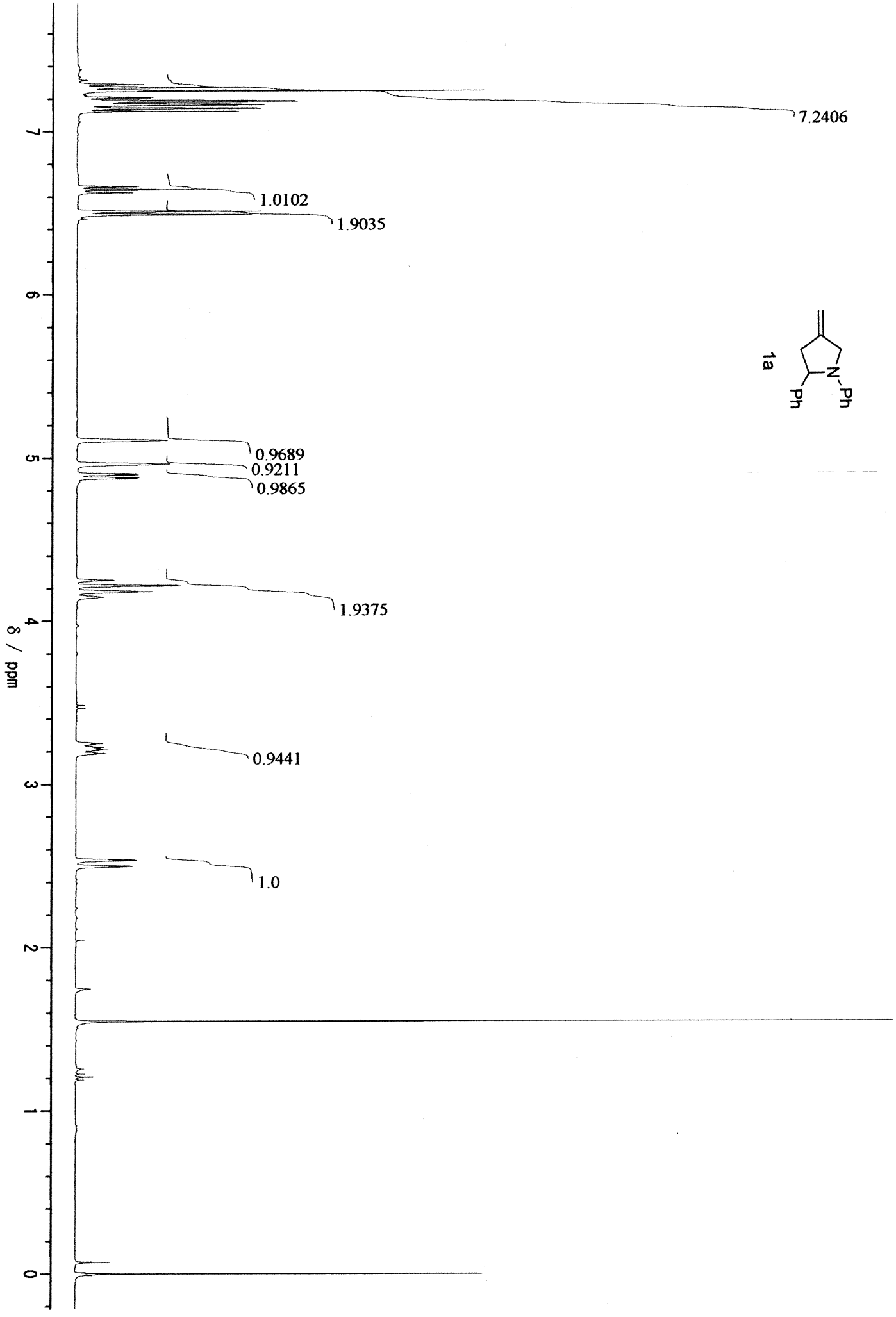
% Increment of area intensities for NOE of *trans*-1p

1-(4-Methoxyphenyl)-4-methylene-2-styrylpyrrolidine (**2a**): R_f = 0.67 (hexane:EtOAc = 4:1, v/v); mp = 132.3-135.0 ˚C; IR (KBr) 3022 (w), 2901 (m), 2787 (m), 2341 (w), 1510 (s), 1454 (m), 1348 (m), 1240 (s), 1178 (m), 1139 (w), 1036 (m), 910 (m), 864 (m), 810 (s), 783 (m), 698 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (dd, J = 4.5, 16.0 Hz, 1 H), 3.46 (dd, J = 8.7, 16.0 Hz, 1 H), 3.70 (s, 3 H), 4.27 (d, J = 13.8 Hz, 1 H), 4.53 (d, J = 13.8 Hz, 1 H), 4.82 (dd, J = 4.5, 8.7 Hz, 1 H), 6.51 (d, J = 8.9 Hz, 2 H), 7.15-7.30 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.9, 55.7, 57.2, 63.9, 114.0 (2 C), 114.6 (2 C), 121.7, 125.6 (2 C), 126.3, 126.7, 128.1 (4 C), 128.6 (2 C), 137.3, 138.2, 141.4, 144.6, 151.3. High-resolution

MS, calcd for $C_{24}H_{23}ON$: 341.1780, Found *m/z* (relative intensity): 341.1770 (M^+, 100).



% Increment of area intensities for NOE of 2a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1.0102
1.9035
0.9689
0.9211
0.9865
1.9375
0.9441
1.0
δ / ppm
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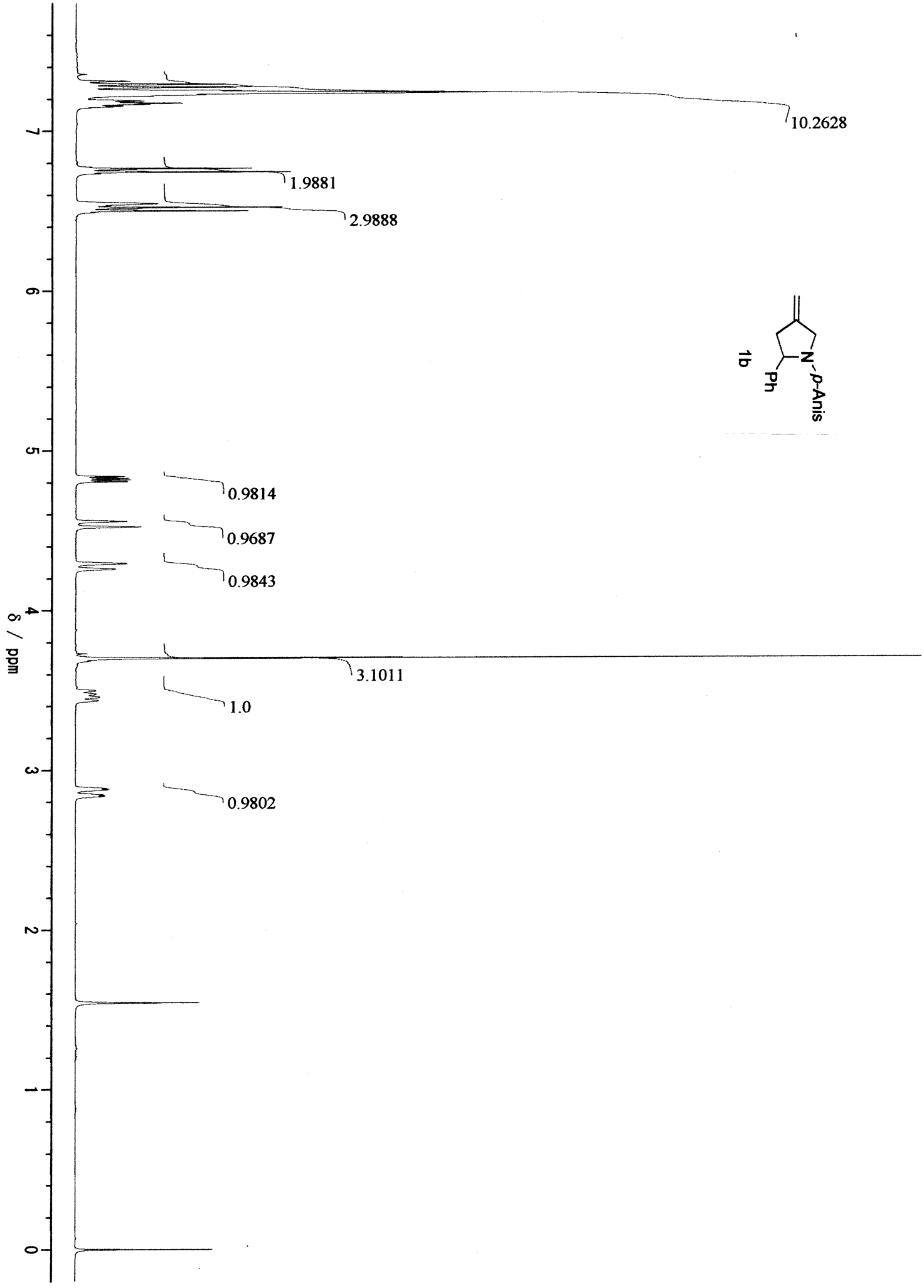
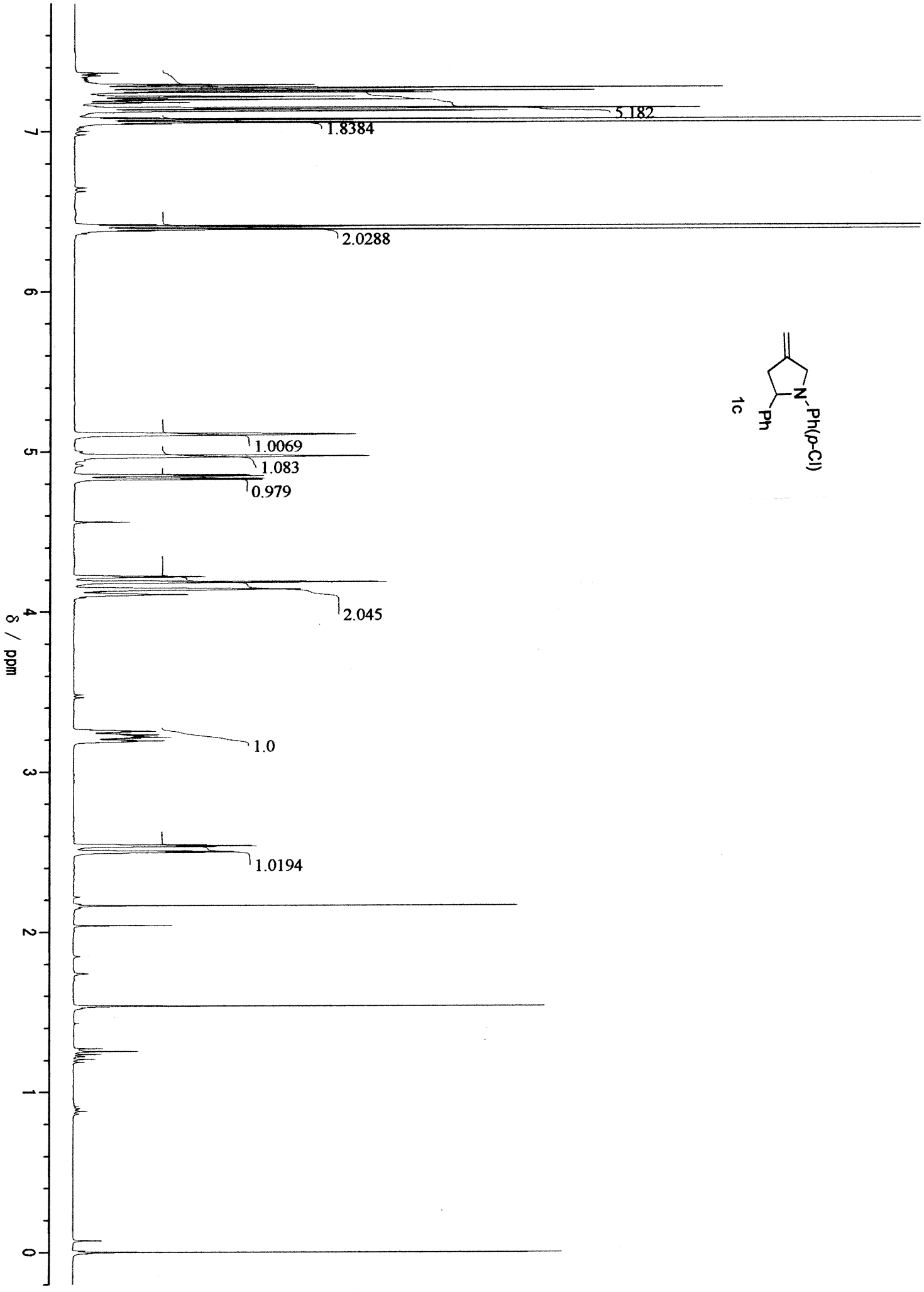
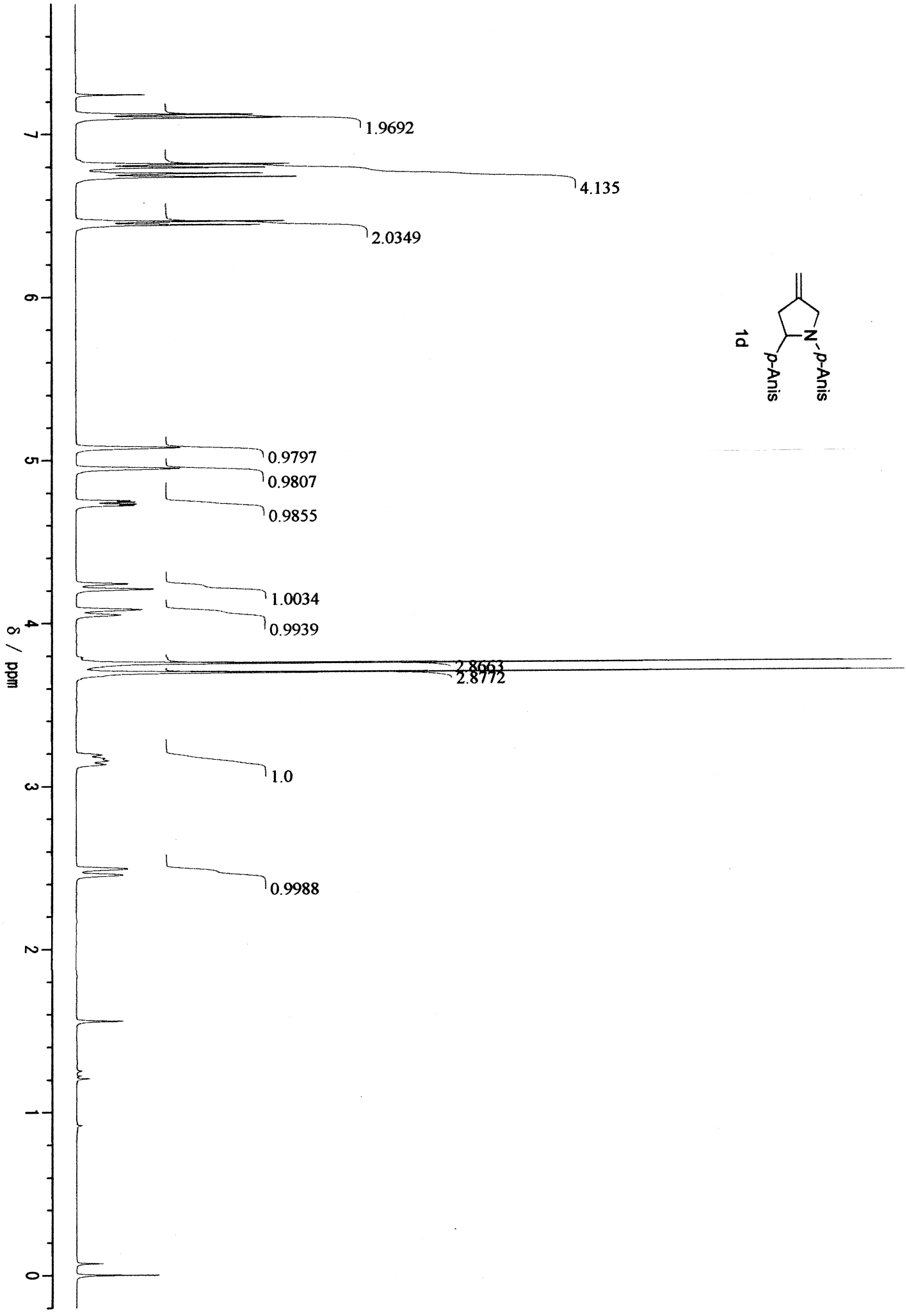
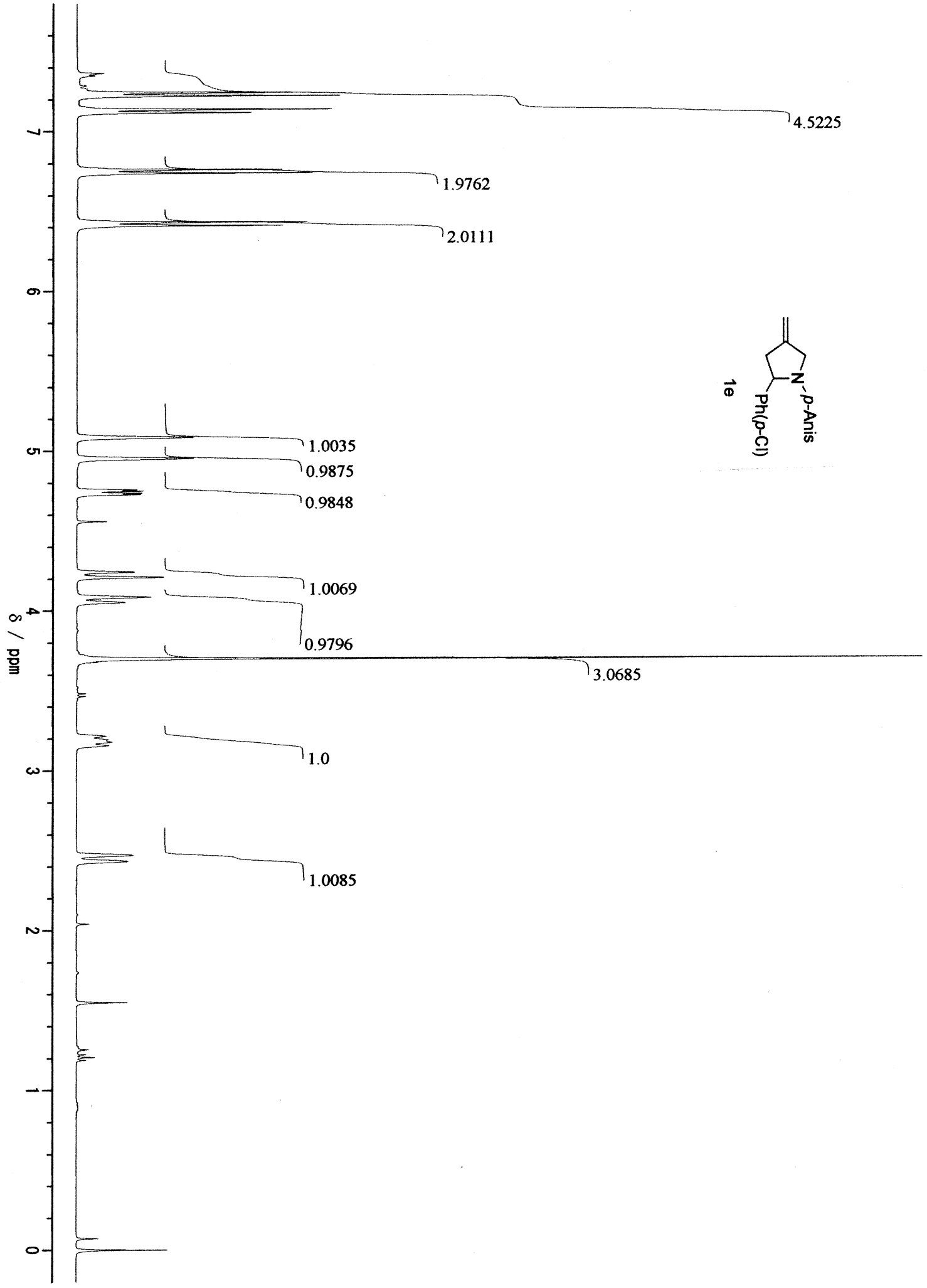
2
3
4
5
6
7
1a
Ph
N
Ph


10.2628
1.9881
2.9888
0.9814
0.9687
0.9843
3.1011
1.0
0.9802
δ / ppm
0
1
2
3
4
5
6
7
1b
Ph
N-p-Anis


5.182
1.8384
2.0288
1.0069
1.083
0.979
2.045
1.0
1.0194
δ / ppm
0
1
2
3
4
5
6
7
N-Ph(p-Cl)
Ph
1c


1.9692
4.135
2.0349
0.9797
0.9807
0.9855
1.0034
0.9939
2.8663
2.8772
1.0
0.9988
δ / ppm
0
1
2
3
4
5
6
7
1d
N-p-Anis
p-Anis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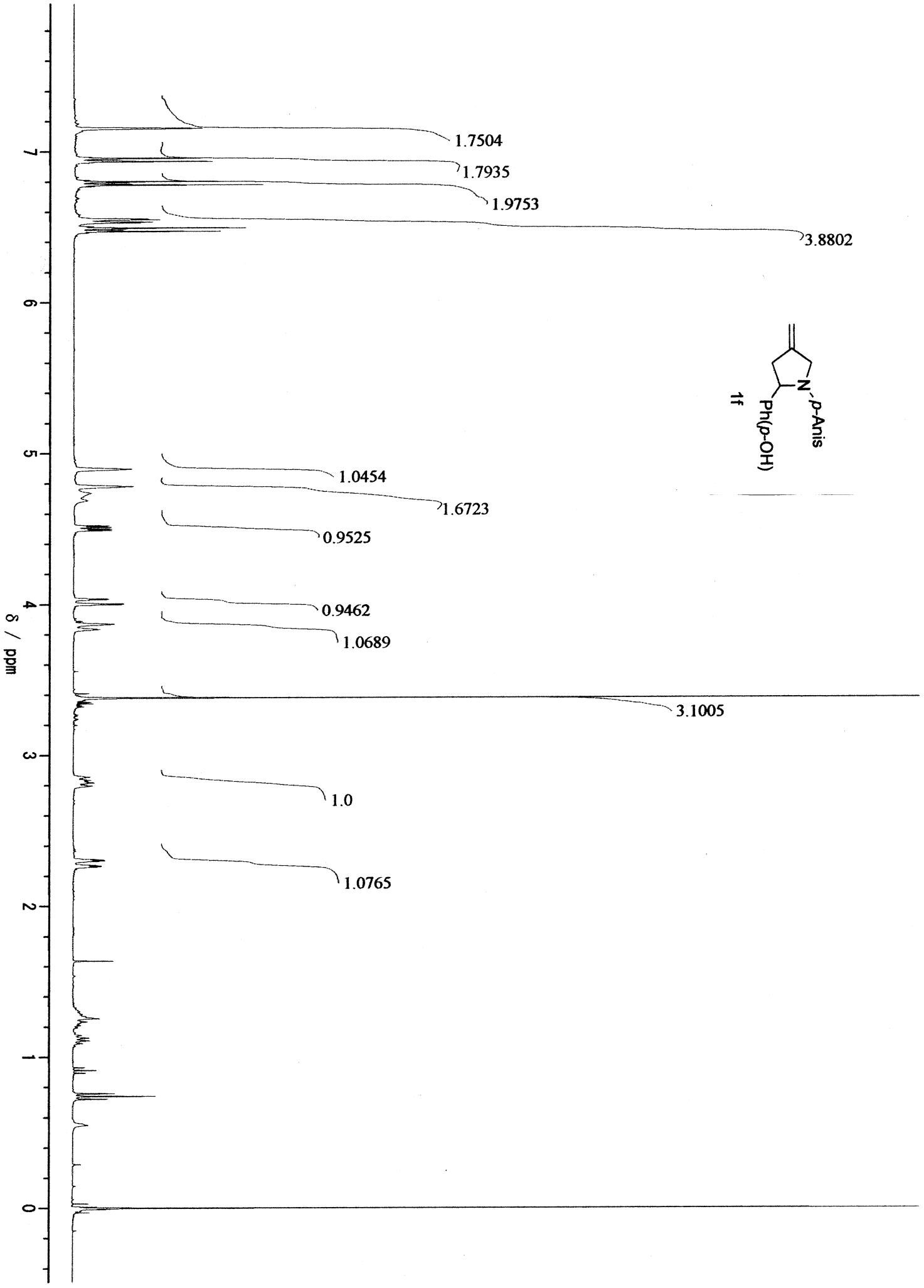
1.9762
2.0111
1.0035
0.9875
0.9848
1.0069
0.9796
3.0685
1.0
1.0085
δ / ppm
0
1
2
3
4
5
6
7
1e
Ph(p-Cl)
N-p-Anis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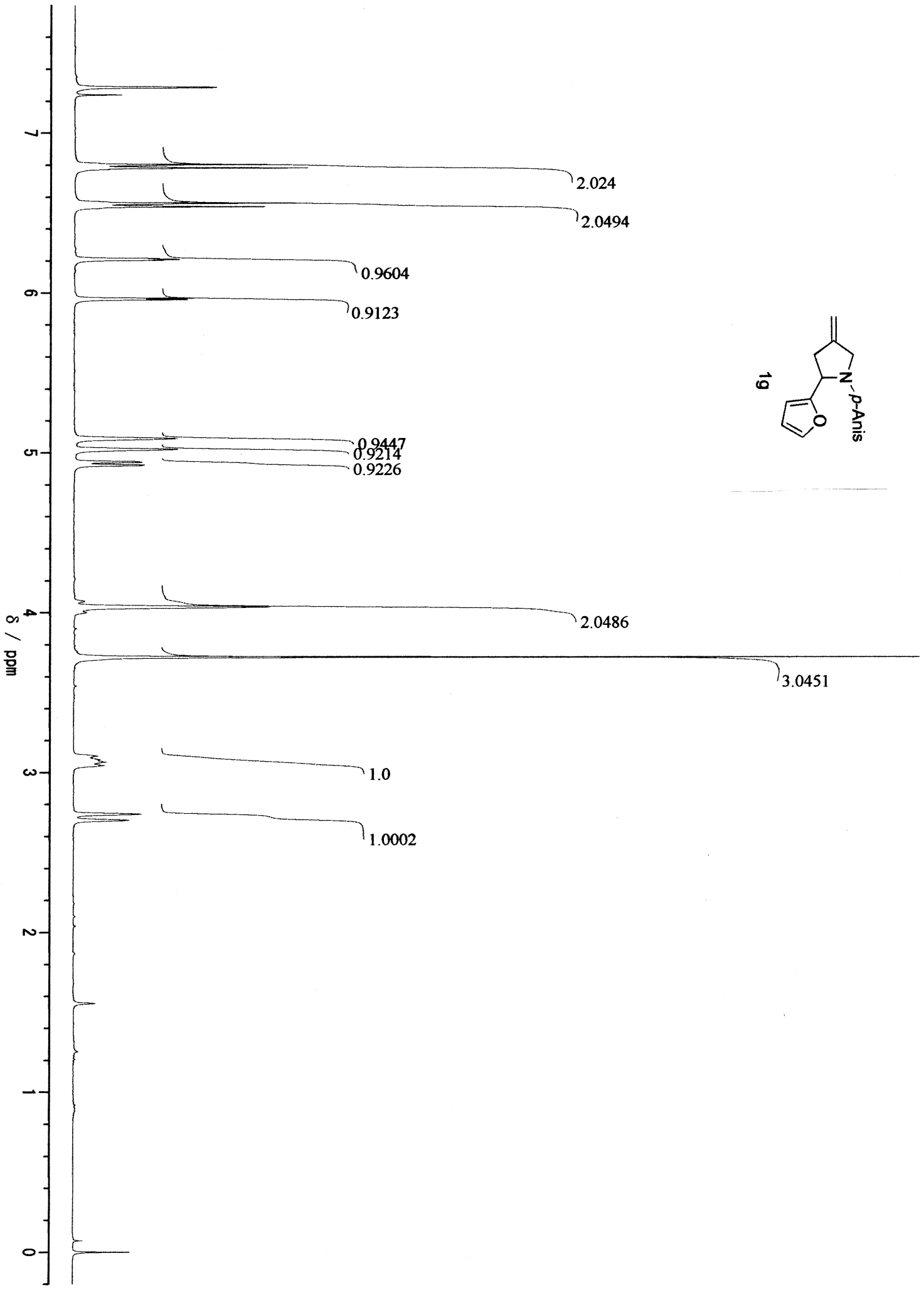
1.7935
1.9753
3.8802
1.0454
1.6723
0.9525
0.9462
1.0689
3.1005
1.0
1.0765
δ / ppm
1f
N-p-Anis
Ph(p-OH)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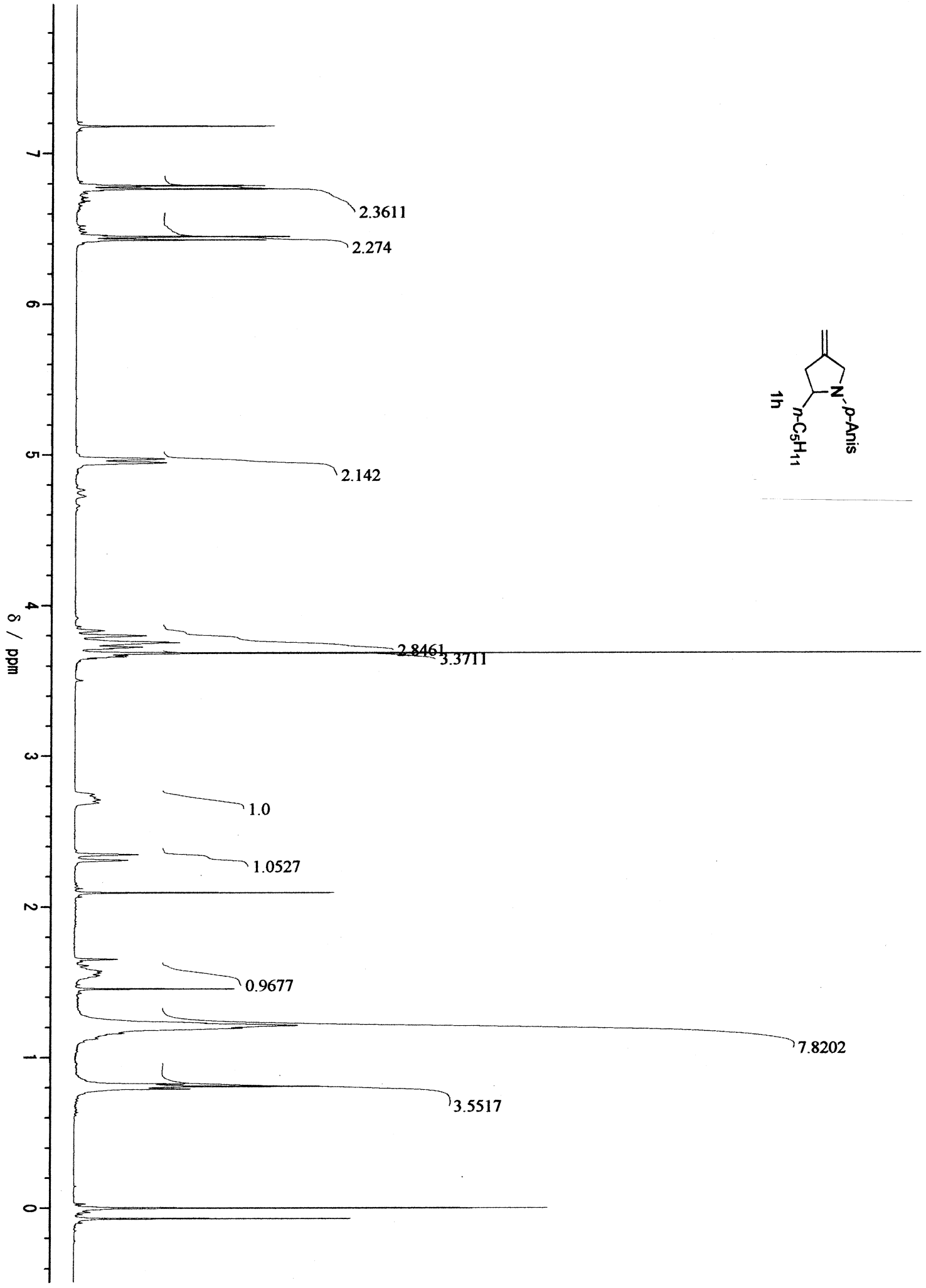
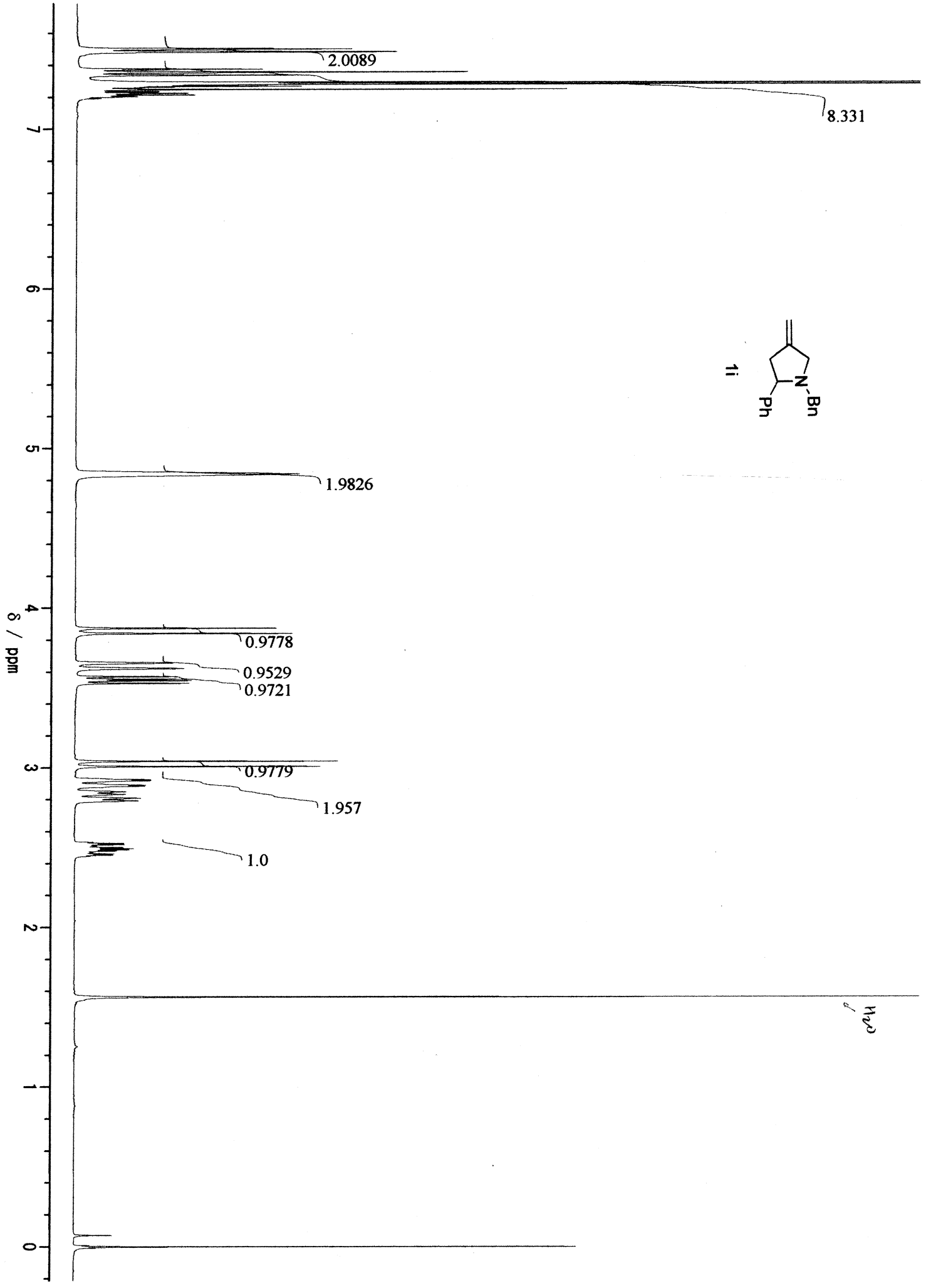
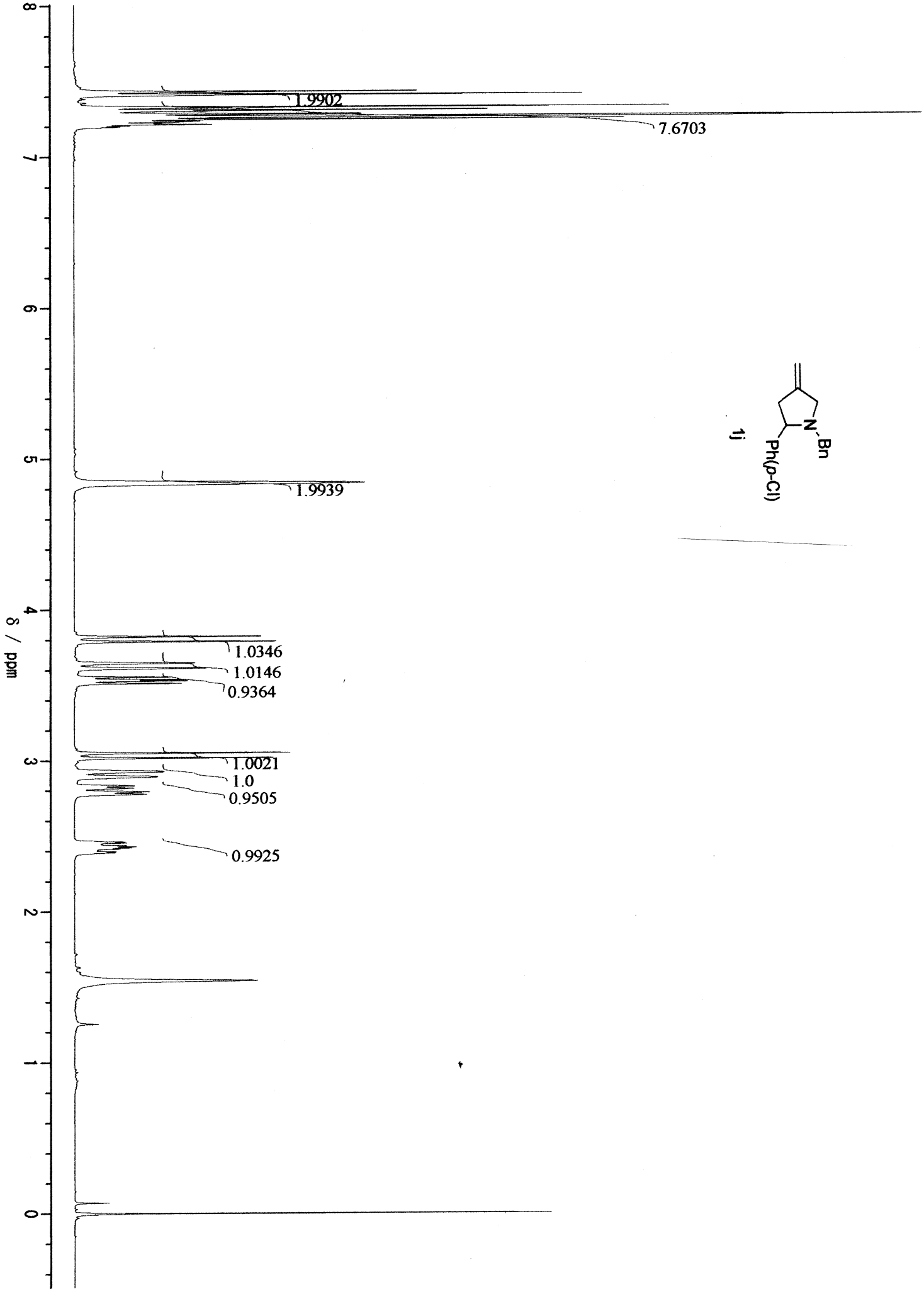
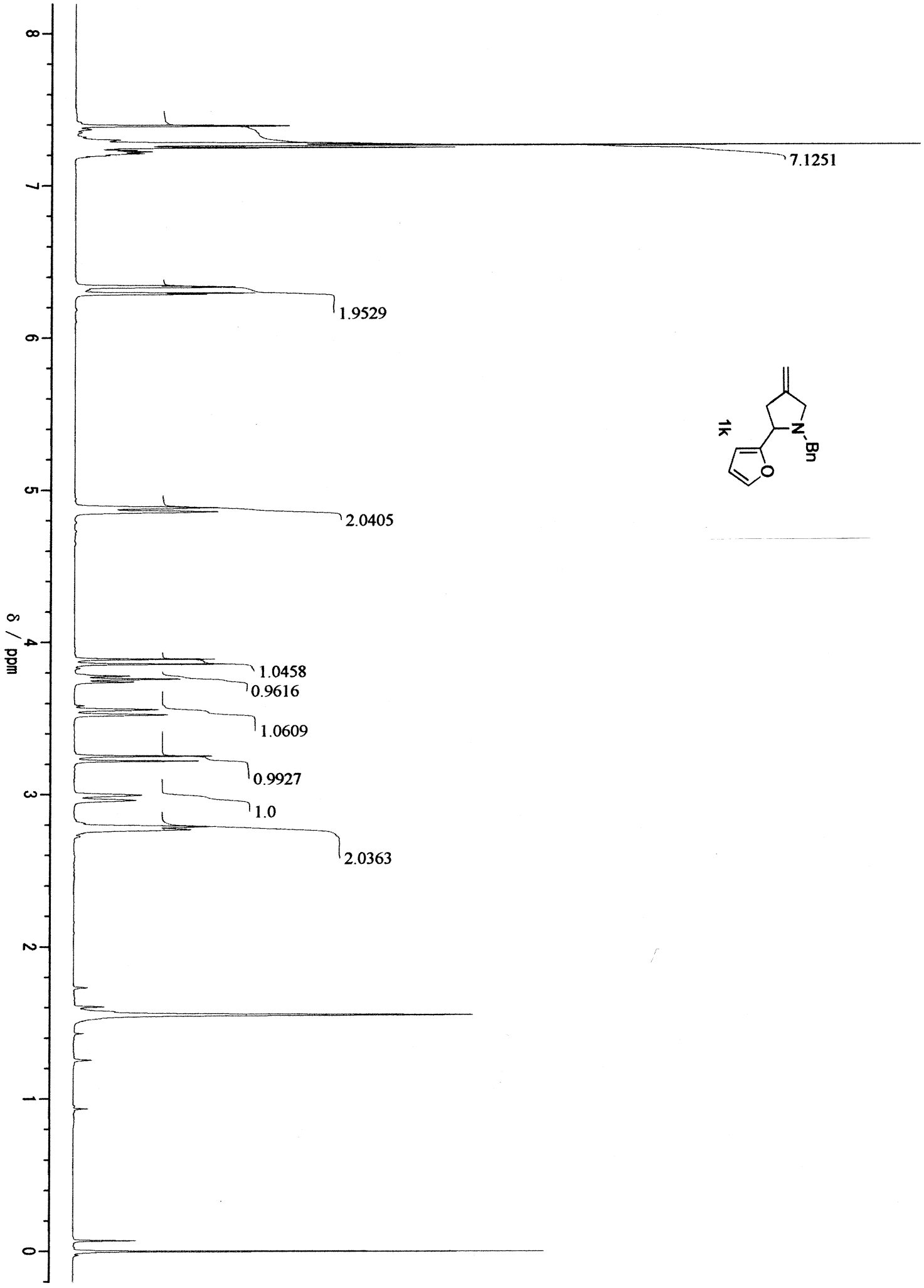
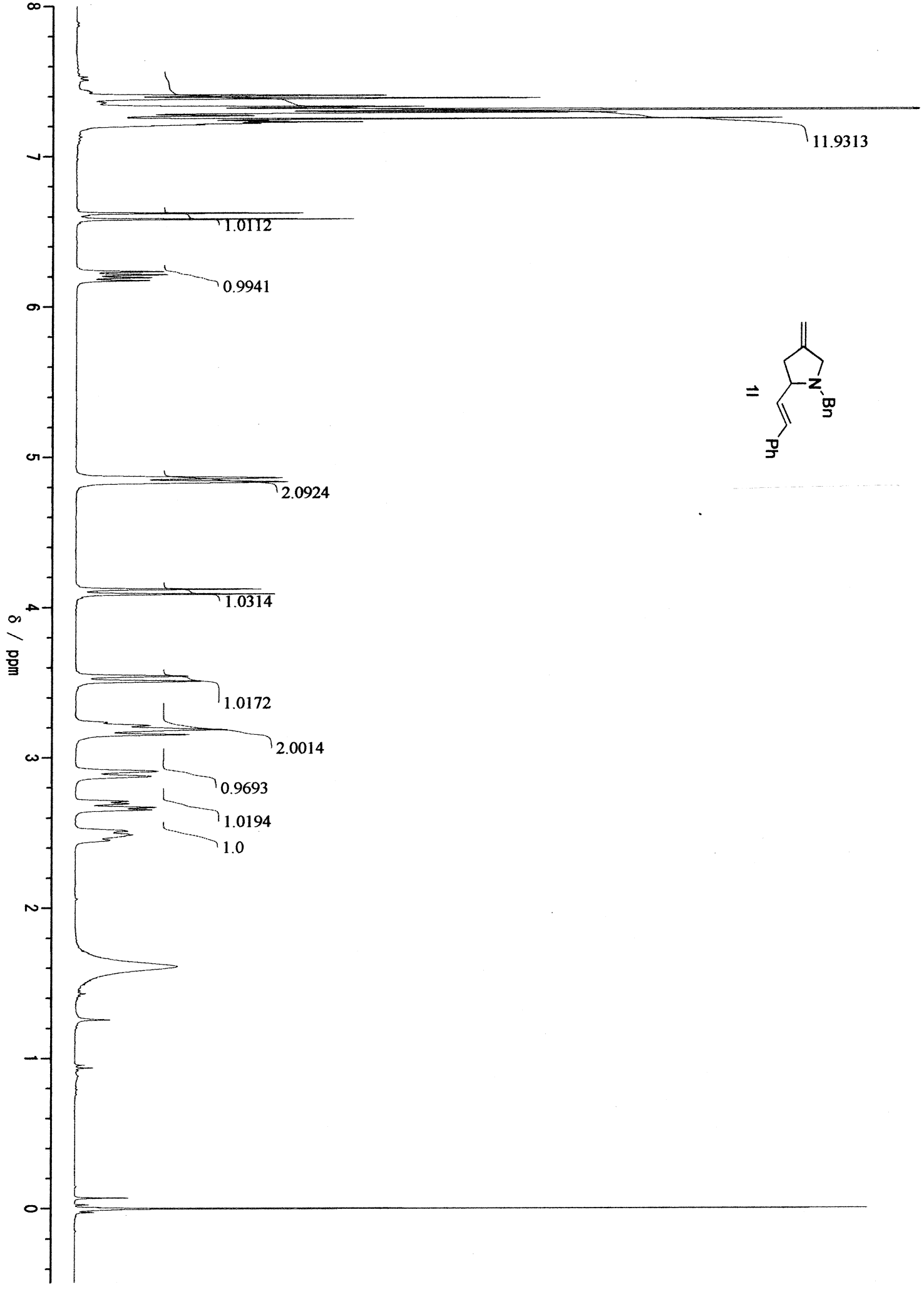
2.0494
0.9604
0.9123
0.9447
0.9214
0.9226
2.0486
3.0451
1.0
1.0002
δ / ppm
0
1
2
3
4
5
6
7
1g
N-p-Anis
O

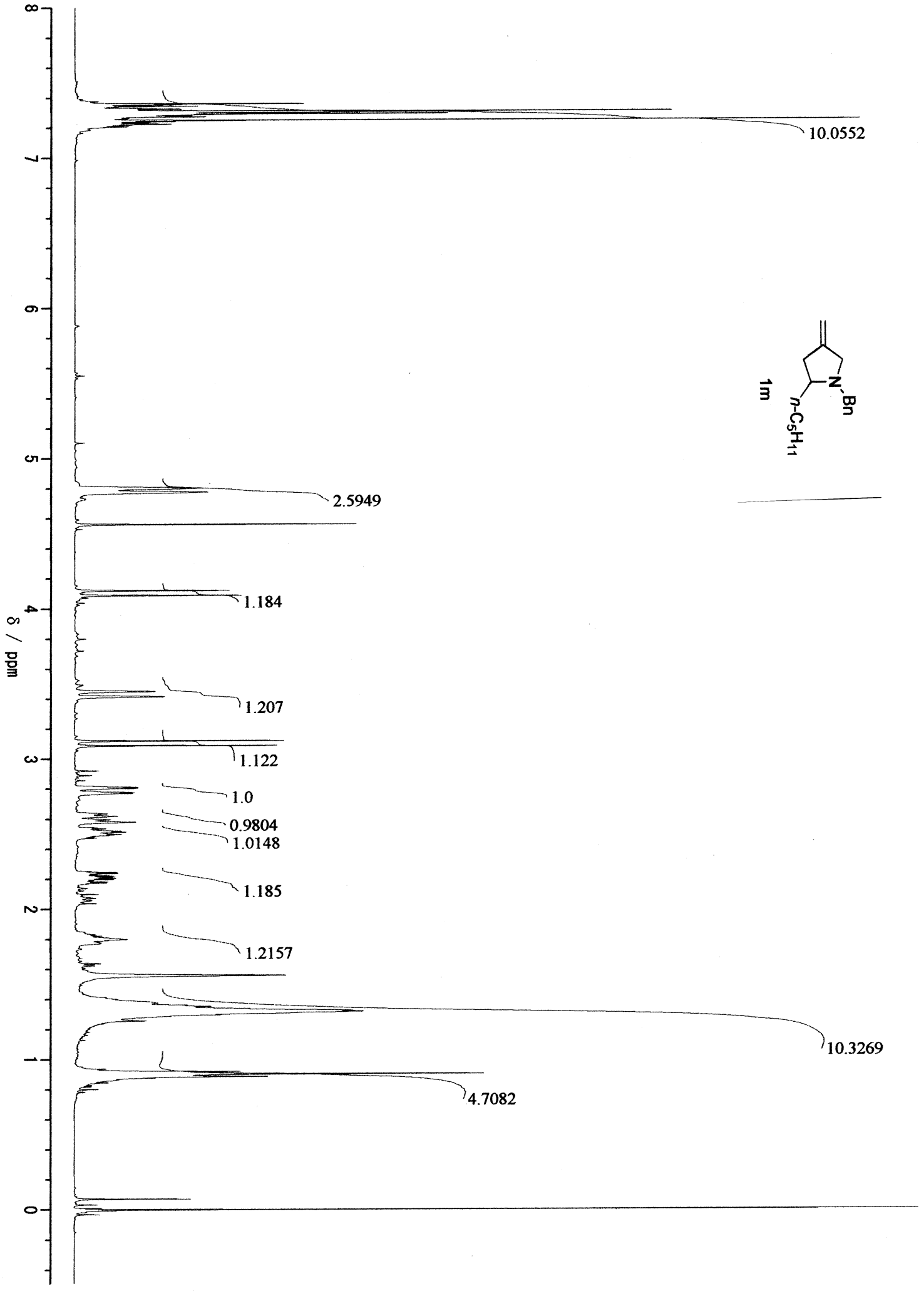

2.3611
2.274
2.142
2.8461
3.3711
1.0
1.0527
0.9677
7.8202
3.5517
δ / ppm
1h
n-C5H11
N
p-Anis

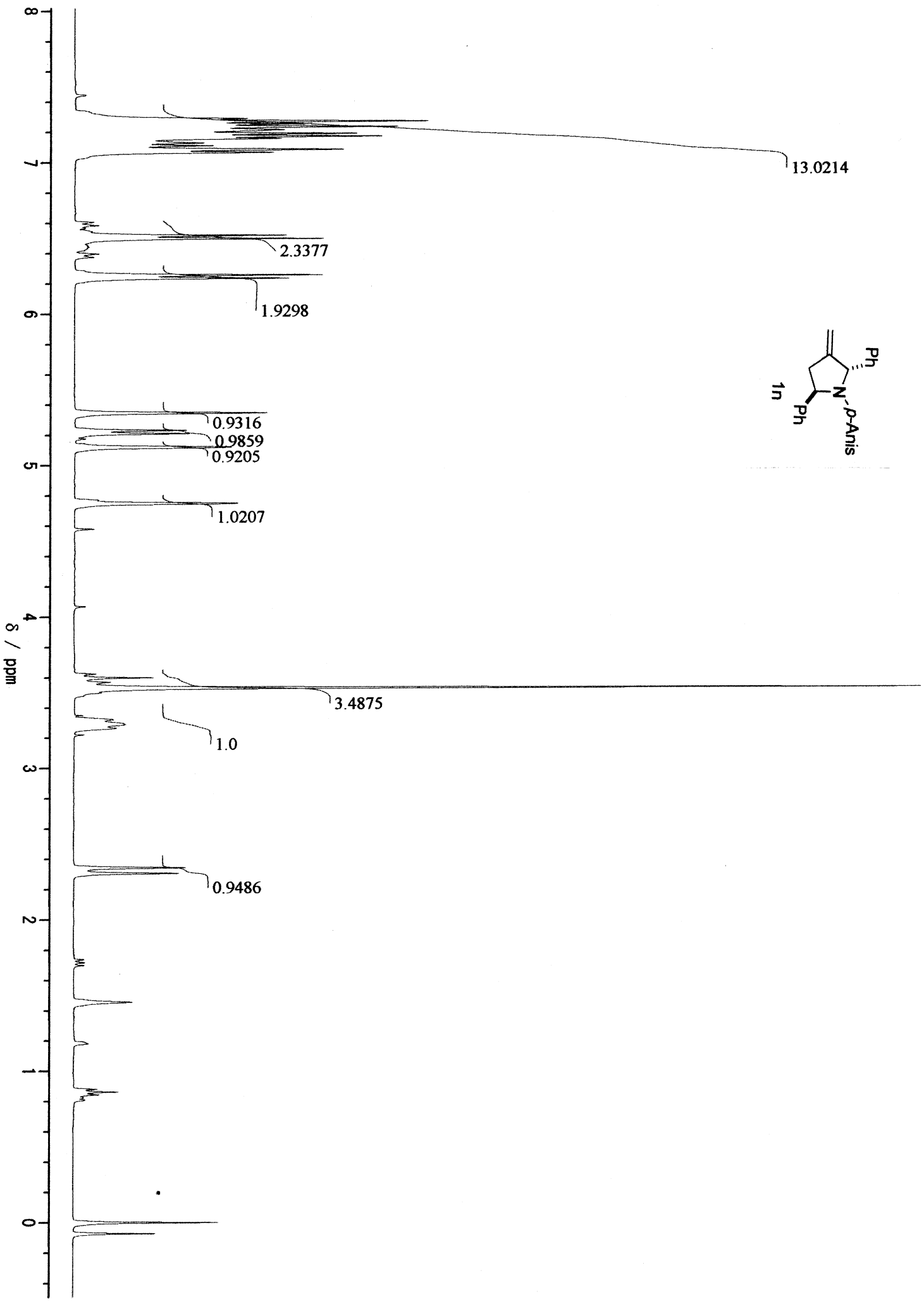

2.0089
8.331
1.9826
0.9778
0.9529
0.9721
0.9779
1.957
1.0
δ / ppm
0
1
2
3
4
5
6
7
1i
Ph
N-Bn

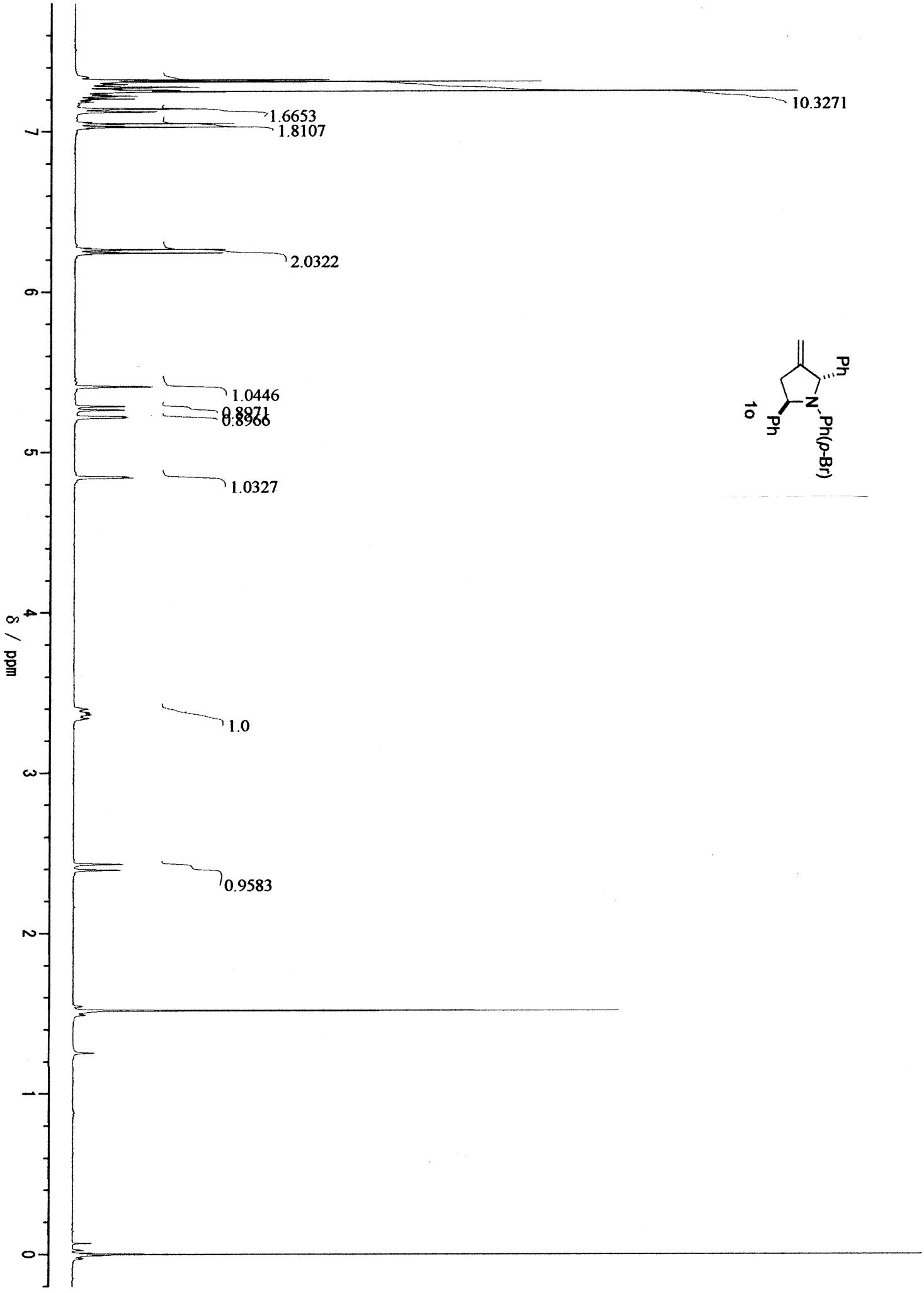

1.9902
7.6703
1.9939
1.0346
1.0146
0.9364
1.0021
1.0
0.9505
0.9925
δ / ppm
1j
N
Bn
Ph(p-Cl)

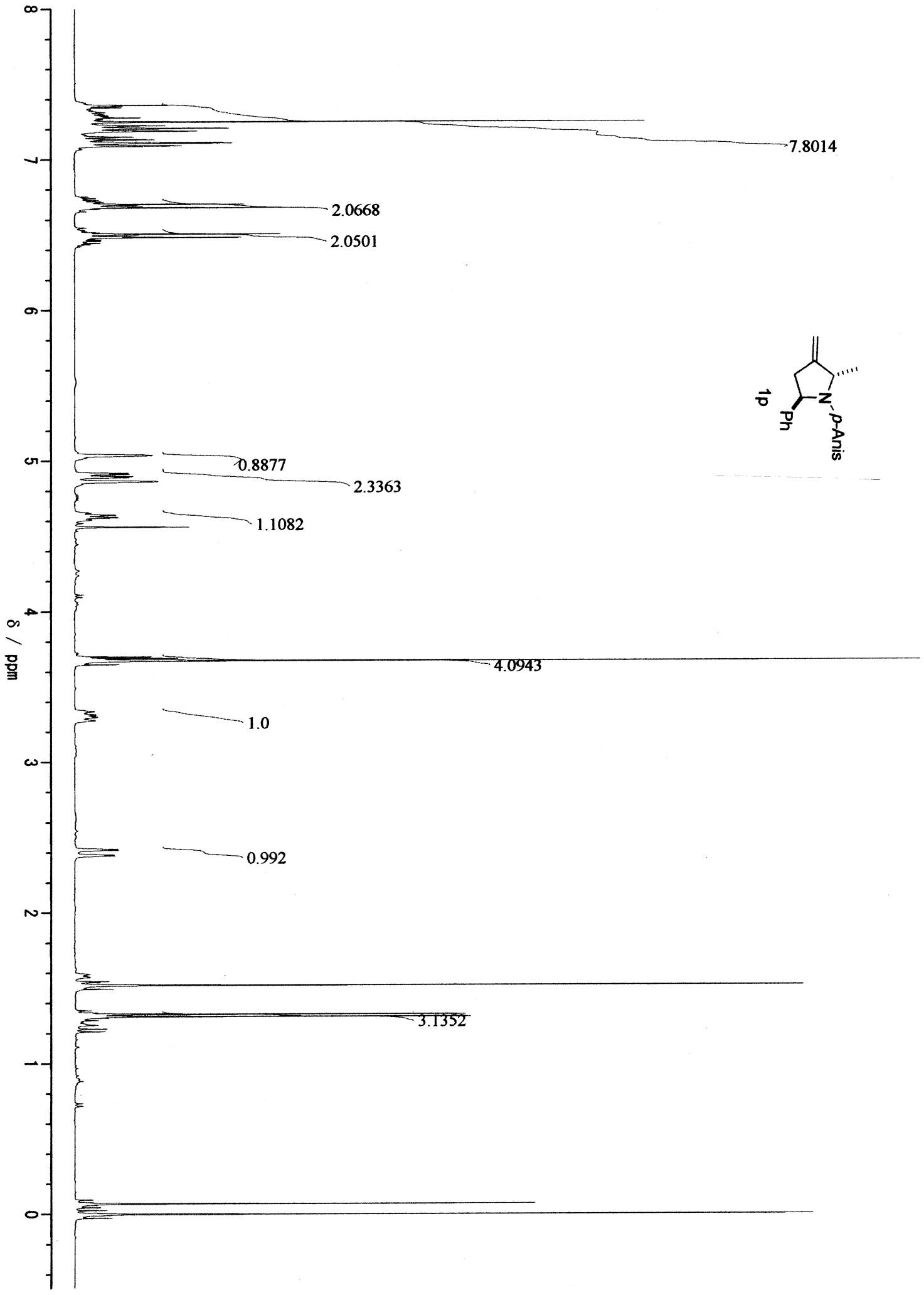

8
7
6
5
4
3
2
1
0
δ / ppm
7.1251
1.9529
2.0405
1.0458
0.9616
1.0609
0.9927
1.0
2.0363
1k
N
Bn
O

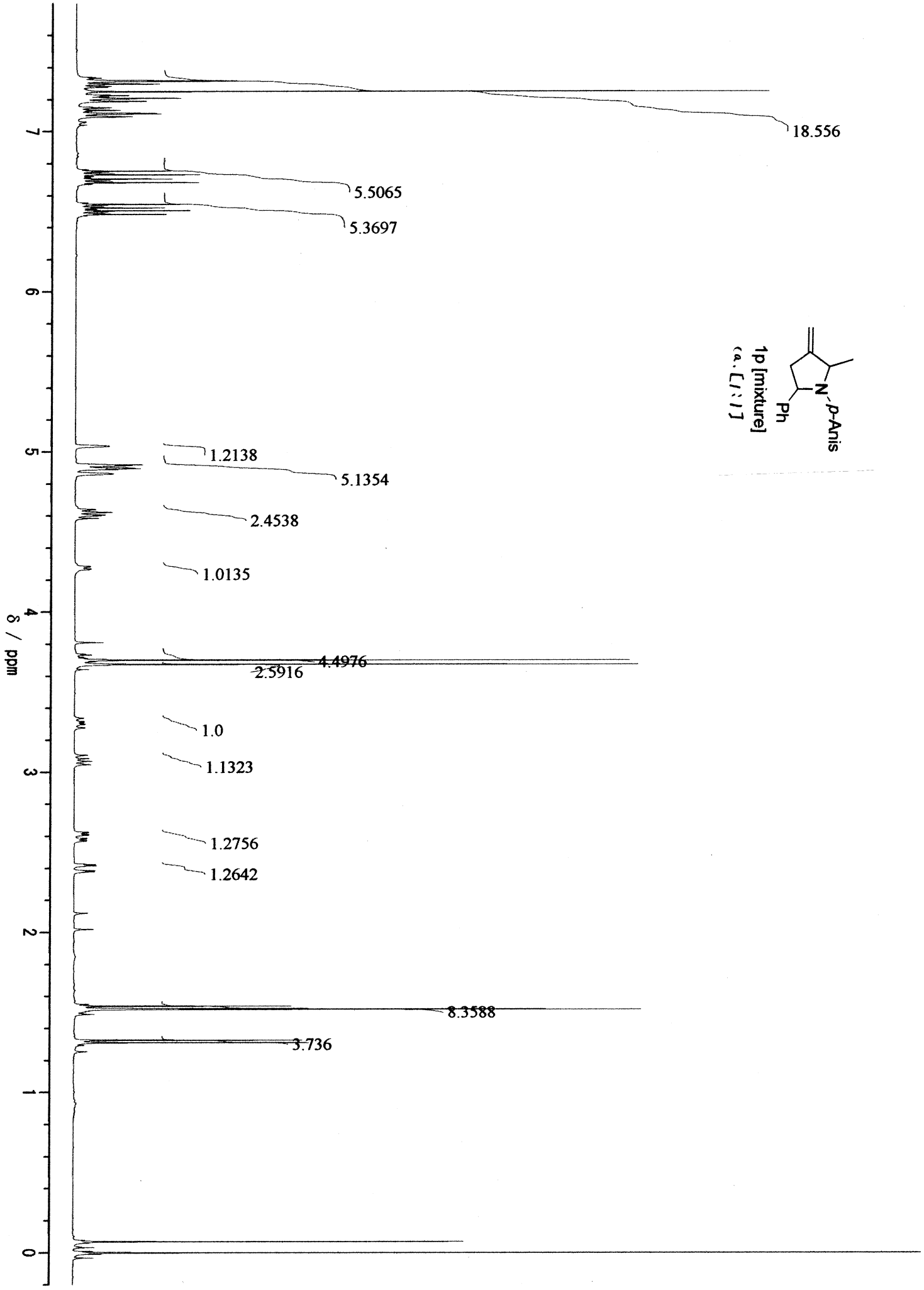

11.9313
1.0112
0.9941
2.0924
1.0314
1.0172
2.0014
0.9693
1.0194
1.0
δ / ppm
11
N
Bn
Ph

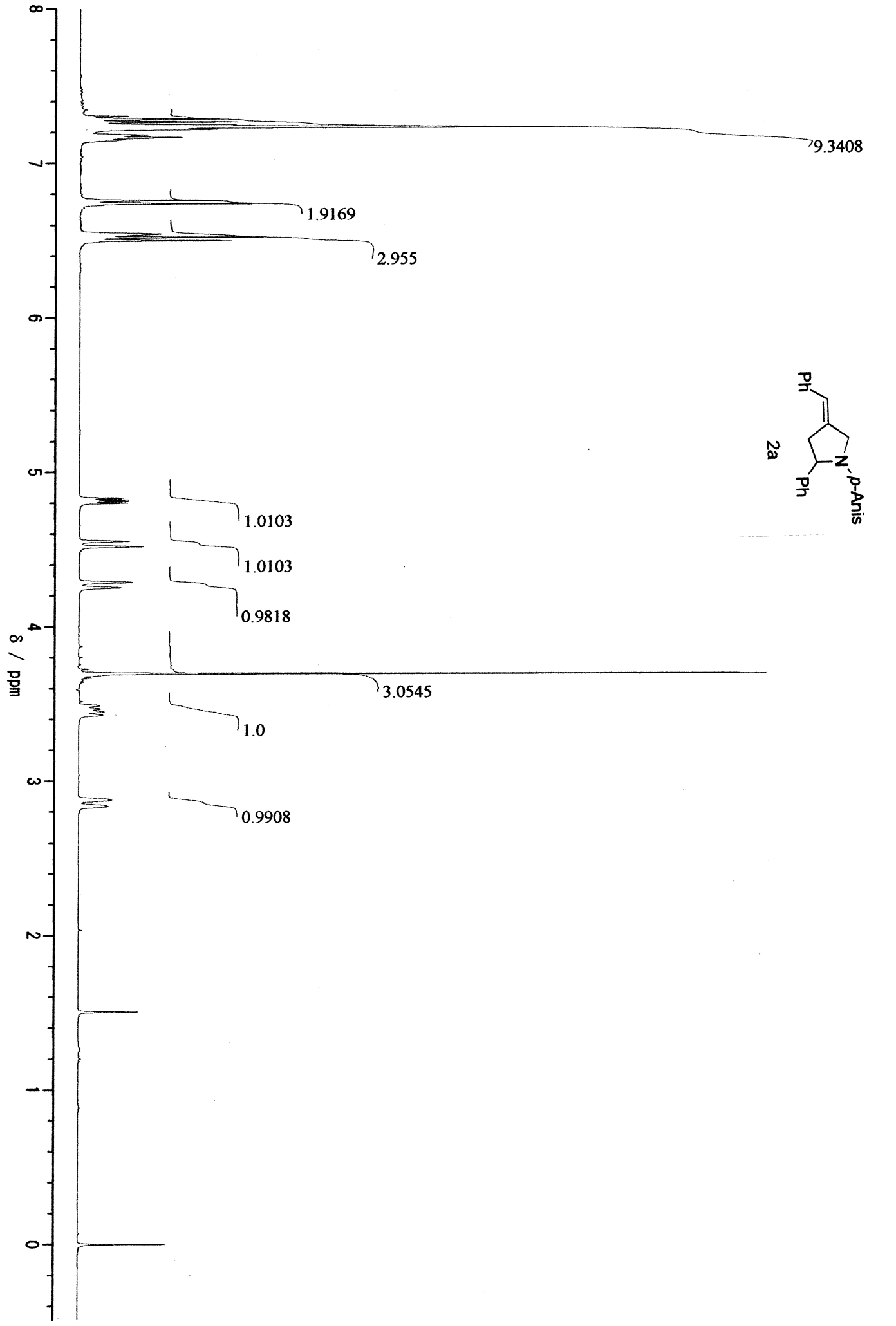

10.0552
2.5949
1.184
1.207
1.122
1.0
0.9804
1.0148
1.185
1.2157
10.3269
4.7082
δ / ppm
8
7
6
5
4
3
2
1
0
N
Bn
n-C5H11
1m

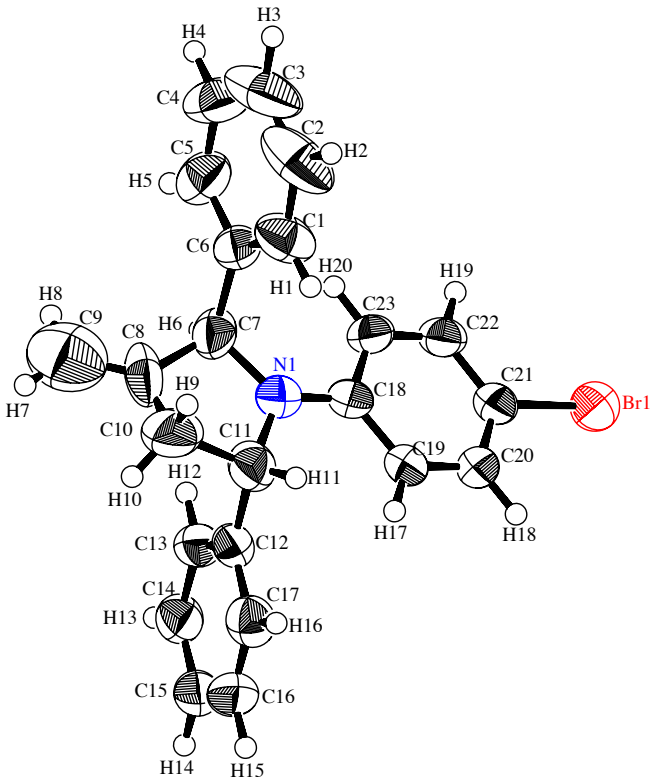

13.0214
2.3377
1.9298
0.9316
0.9859
0.9205
1.0207
3.4875
1.0
0.9486
δ / ppm
Ph
N
p-Anis
Ph
1n


10.3271
1.6653
1.8107
2.0322
1.0446
0.8971
0.8966
1.0327
1.0
0.9583
δ / ppm
0
1
2
3
4
5
6
7
Ph
N
Ph(p-Br)
Ph
1o


7.8014
2.0668
2.0501
0.8877
2.3363
1.1082
4.0943
1.0
0.992
3.1352
δ / ppm
1p
Ph
N
p-Anis


18.556
5.5065
5.3697
1.2138
5.1354
2.4538
1.0135
4.4976
2.5916
1.0
1.1323
1.2756
1.2642
8.3588
3.736
δ / ppm
0
1
2
3
4
5
6
7
1p [mixture]
Ph
N
p-Anis


9.3408
1.9169
2.955
1.0103
1.0103
0.9818
3.0545
1.0
0.9908
δ / ppm
Ph
Ph
N
p-Anis
2a



ORTEP representation of the crystal structure of **1o**