The Use of pH to Influence Regio- and Chemoselectivity in the Asymmetric Aminohydroxylation of Styrenes

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Supporting Information

Materials and methods.

^{1}H and ^{13}C NMR spectra were recorded on Varian Unity400 (400 MHz ^{1}H, 100 MHz ^{13}C) and on Varian Unity500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometers in deuterochloroform ($CDCl_3$). The data was reported as follows: chemical shifts in ppm ( ), multiplicities are indicated as s-singlet; d-doublet; t-triplet; q-quartet; m-multiplet, br - broad. Coupling constants, *J*, are reported in Hz. Infrared spectra were recorded on Mattson Galaxy Series FTIR 5000 spectrophotometer and the peaks reported in cm^{-1}. Mass spectra were recorded by the University of Illinois Mass Spectroscopy Center, and the data reported in *m/e* (intensity to 100%). Analytical thin-layer chromatography was performed on Merk silica gel plated with F254 indicator. Visualization of plates was by UV light and/or CAM stain. Optical rotations were obtained on Jasco DIP-30 Digital Polarimeter. Analytical chiral supercritical fluid chromatography (SFC) was performed on Berger Instruments SFC equipped with Diacel Chiracel OD column (250 x 4.5 mm). Internal spectrophotometric detector operated at wavelength 220 nM. Solvents for extraction and chromatography were reagent grade and were used without further purification. Melting points were determined on a Thomas-Hoover Capillary Melting Point Apparatus and are uncorrected. The pH of solutions was measured by Aquemet™ Research AR15 pH meter equipped with Corning semimicrocombo electrode (#476156), which was standardized by 5 buffer solutions (pH=4.0±0.01, 6.0±0.01, 7.0±0.01, 9.0±0.01 and 10.0±0.01) prior to measurements.

p-Acetoxystyrene, styrene, *p*-methoxystyrene, *p*-carboxystyrene, *p*-*t*butoxystyrene, *p*-nitrostyrene, *m*-methoxystyrene, *o*-methoxystryene, and *m*-nitrostryene were purchased from Aldrich. *p*-tosyloxystyrene, and *p*-*t*butyldimethylsilylstyrene were prepared by standard procedures[1] from *p*-hydroxystyrene.[2] All AA reactions were done on 0.62 mmol scale unless otherwise specified. Tert-butyl hypochlorite was prepared by procedure of Minz[3] and stored at -5 °C.[4]

General procedure for asymmetric aminohydroxylation of styrenes as described for *p*-acetoxystyrene.

Acetic acid 4-(2-benzyloxycarbonylamino-1-hydroxy-ethyl)-phenyl ester: In a 50 mL round bottom three neck flask, under an atmosphere of N_2,[5] benzyl carbamate (285.9 mg, 1.891 mmol) was dissolved in 6 mL of acetonitrile. The solution was cooled in a water-ice bath (0-4 °C) and under efficient stirring a cold solution of sodium hydroxide (52.1 mg NaOH in 5.38 g of water) was added. The reaction was stirred 2 minutes, and then the cold solution of *t*-butyl hypochlorite (134.4 mg, 1.24 mmol) in 1 mL of acetonitrile was added and stirred for 10 min. A solution of potassium osmate (8.9 mg, 0.0248 mmol) in 1 mL of cold water was then added. The pH at this point should not be below 12.5; if it is, it is necessary to add more NaOH. After 1 min a solution of DHQ_2AQN (28.0 mg, 0.031 mmol) in 4 mL of CH_3CN was added in one portion and stirred for 3 min. The cold acetonitrile/buffer mixture was then added to a total volume of 28 mL and allowed to stir for 5 min (solution turns light green immediately). At this point pH is checked and if necessary adjusted to pH=7.65±0.02 by addition of monobasic sodium phosphate solution. Styrene (100.6 mg, 0.62 mmol) in 2 mL of acetonitrile was then added in one portion. The reaction was stirred vigorously and allowed warming up to room temperature (18-20 °C). After 45-60 min the solution turned yellow, indicating completion.[6]

The reaction mixture was cooled down in an ice bath and 200 mg of sodium sulfite in 2 mL of water was added. After 15 min of stirring the organic layer was separated and the aqueous layer extracted with ethyl acetate (3x30 mL). The combined organic extracts were washed with water (2x100 mL) and brine (30 mL), and dried over anhydrous magnesium sulfate.

Solvent evaporation resulted in 459.2 mg of amorphous crystals, which was subjected to flash column chromatography (1.7 x 12 cm, 15 g of silica gel, 2:1=Hexane: EtOAc, 10 ml/min, 23 of 10 ml fractions, collected) to yield 161.2 mg of **acetic acid 4-(2-benzyloxycarbonylamino-1-hydroxy-ethyl)-phenyl ester** (78.9% isolated yield, 73% ee) as colorless crystals. R_f=0.36(EtOAc/Hexanes=10:7); mp 100-106 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.382-7.303 (m, 7H), 7.073 (dt, 2H, *J*=8.575, 2.57Hz), 5.204 (br t, 1H), 5.111 (s, 2H), 4.87 (br d, *J*=5 Hz), 3.544 (ddd, 1H, *J*=14, 6.9, 3.5 Hz), 3.283 (ddd, 1H, *J*=13.6, 7.7, 5.2 Hz), 2.907 (br s, 1H, OH, exchangeable), 2.296 (s, 3H, CH_3 of Ac), 1.634 (br s, 1H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 169.56, 157.24, 150.25, 139.14, 136.297, 128.552, 128.215, 128.14, 127.00, 121.69, 73.15, 67.00, 48.48, 21.08; IR (KBr , cm^{-1}) 3412, 3308, 3065, 1752, 1692, 1549, 1509, 1369, 1292, 1270, 1235, 1206, 1166, 1152, 1064, 1017, 992, 919, 851, 779, 752, 697; MS EI (m/z) 221(4.36), 179 (47.6), 165(9.27), 135(14.27), 134(13.36), 123(100), 121(11), 108(35.78), 107(33.11), 104(14.84), 95(14.31), 92(8.49), 91(45.16), 79(42), 78(11), 77(36.55), 74(10.17), 65(14.6); MS CI (m/z) 312(M-17), 268(11), 250(1), 222(10.6), 208(5.65), 206(4.13), 180(40.67), 178(75.8), 164(4.56), 162(8.76), 136(27.33), 123(8.13), 121(4.26), 108(6.52), 107(8.61), 91(100), 79(34.68); SFC(125psi CO_2, 12% , 3ml/min MeOH, Chiracel OD) 6.951 min (R), 7.384 (S) $[\alpha]^{25}_D$=21.24962 (c=.84, $CHCl_3$)

Detailed experimental protocols for graphs and figures.

Figure 1. Reaction mixture composition for the aminohydroxylation of styrene in the pH range from 5.5 to 11.3.

Procedure: All experiments were performed on 1mmol scale. In a 50 mL round bottom three neck flask, under an atmosphere of N_2 was dissolved benzyl carbamate (453.5 mg, 3 mmol) in 4 mL of acetonitrile. The solution was cooled in water-ice bath (0-4 ^{o}C) and under efficient stirring a cold solution of sodium hydroxide was added dropwise over 1-2 min (122.0 mg NaOH in 0.52 g of water, 3.05 mmol), stirred for 2 minutes, followed by the addition of a cold solution of tert-butyl hypochlorite (336.6 mg, 3.1 mmol) in 1 ml of acetonitrile. The resulting solution was stirred for 10 min. A solution of potassium osmate (14.3 mg, 0.04 mmol) in 1 mL of cold water was then added. After 1 min a solution of DHQ_2AQN (42.9 mg, 0.05 mmol) in 4 mL of CH_3CN was added in one portion and stirred for 3 min. The buffer of desired pH value (0.5 M, 8.5 mL) was added and allowed to stir for 5 min (solution turns light green immediately). At this point the pH is checked and if necessary adjusted to desired pH (±0.02) by addition of a monobasic sodium phosphate solution. A solution of styrene (104.2 mg, 1.0 mmol) in 2 mL of acetonitrile was then added in one portion, followed by vigorous stirring of the reaction mixture at 0-4 ^{o}C. After the solution turns yellow, which indicates completion,[8] 200 mg of sodium sulfite in 2 mL of water was added. After 15 min of stirring the organic layer was separated and the aqueous layer was extracted with ethyl acetate (3x30 mL). The combined organic extracts were washed with water (2x100 mL) and brine (30 mL), and dried over anhydrous magnesium sulfate. Solvent evaporation resulted in 598 ± 10 mg of amorphous crystals.

All reactions were worked up at least after 97% conversion. Reaction times under more acidic conditions were slightly longer as compared to neutral and basic conditions. For reactions at pH higher then 9.0 a mixture of 0.15 M Na_2HPO_4 and 0.1 N NaOH were used to prepare buffer.[9] The ratio of products of the reaction mixture was determined by integration of the ^{1}H NMR spectrum and normalizing all data to 100%. For all represented experiments 5 mol% ligand (DHQ_2AQN) and 4 mol % potassium osmate were used.

Figure 2. Effect of reaction temperature on the rate of aminohydroxylation of *p*-acetoxystyrene.

All experiments were performed as described in the general procedure. Experiments depicted in Figure 2 were worked up after at least 95% conversion. At low temperatures precipitation of the sodium phosphate occurs; at temperatures above 28 ^{o}C reaction mixtures were homogenous. For all represented experiments 5 mol% ligand (DHQ_2AQN) and 4 mol % potassium osmate were used. The reactions were monitored by TLC and the conversion was estimated from the ^{1}H NMR spectrum of crude reaction mixture.

Figure 3. Product formation as a function of time in the buffered asymmetric aminohydroxylation of *p*-acetoxystyrene.

The experiments were performed as described in general procedure with the following modifications. 2.5 mol% ligand (DHQ_2AQN) and 2 mol % potassium osmate were used. Reaction was performed on 1.25 mmol of *p*-acetoxy styrene and samples were withdrawn at 15, 30, 45, 60 min, as indicated on the graph. The data point at 90 min represents the reaction mixture composition upon complete conversion (>99%). All samples were worked up as described in the general procedure and the composition of the sample was determined from integration of the ^1H NMR spectrum and normalized to 100%. Enantioselectivity was determined for regioisomer B at each point after chromatography on silica gel and was constant during the reaction course (84:16 er).

Table 1. Ligand effect on regiomeric composition in the buffered aminohydroxylation of *p*-acetoxystyrene.

The experiments were performed as described in the general procedure. The experiments detailed in Table 2 were worked up after at least 95% conversion. Reaction mixtures were homogenous. For all experiments 5 mol% ligand and 4 mol % potassium osmate were used, and the solvent/buffer ratio was 1:1. The reactions were monitored by TLC and conversion was estimated from the ^1H NMR spectrum of crude reaction mixture. Enantioselectivity was determined after purification on silica gel (hexanes:ethyl acetate=1.6:1).

Table 2. Results of the pH controlled aminohydroxylation.

The styrenes in Table 2 were subjected to AA protocol as described in the general procedure. For all experiments solvent/buffer ratio was 1:1. The reactions were monitored by TLC and conversion was estimated from the ^1H NMR spectrum of crude reaction mixture. Enantioselectivity was determined after purification on silica gel.

Procedure for product inhibition experiments:

Addition of acetic acid 4-(2-benzyloxycarbonylamino-1-hydroxy-ethyl)-phenyl ester to the reaction mixture (Addition of regioisomer B).

In a 50 mL round bottom three neck flask, under an atmosphere of N_2, was dissolved benzyl carbamate (117.2 mg, 0.775 mmol) in 6 mL of acetonitrile. The solution was cooled down in water-ice bath (0-4 ^oC) and under efficient stirring a cold solution of tert-butyl hypochlorite (50.5 mg, 0.465 mmol) in 1 mL of acetonitrile was added and stirred 2 minutes; a cold solution of sodium hydroxide (18.6mg NaOH in 0.508 g of water, 0.465 mmol) was then added and stirred for 10 min. A solution of potassium osmate (8.9 mg, 0.0248 mmol) in 1 mL of cold water was then added. After 1 min a solution of DHQ_2AQN (28.0 mg, 0.031 mmol) in 4 mL of CH_3CN was added in one portion and stirred for 2 min. The phosphate buffer (0.25M, 10ml, pH 7.65) was then added and stirred for 5 min (solution turns light green immediately). At this point the pH is checked and if necessary adjusted to pH=7.65±0.02 by addition of monobasic sodium phosphate solution. A solution of **acetic acid 4-(2-benzyloxycarbonylamino-1-hydroxy-ethyl)-phenyl ester** (101.2 mg, 0.31 mmol) was then added in 2 mL of acetonitrile immediately followed by addition of the solution of styrene (50.1

mg, 0.31 mmol) in 1 mL of acetonitrile. The reaction mixture was stirred vigorously at room temperature (18-20 ^{o}C). After 2 h the reaction mixture was cooled down in an ice bath and 200 mg of sodium sulfite in 2 mL of water was added. After 15 min of stirring the organic layer was separated and the aqueous layer extracted with ethyl acetate (3x30 mL). Combined organic extracts were washed with water (2x100 mL) and brine (30 mL), and dried over anhydrous magnesium sulfate. Solvent evaporation resulted 294.3 mg (97.3 % yield) of amorphous crystals.

Conversion was determined to be 99% from ^{1}H NMR and regiomeric composition integrated as 7.95: 100=**A:B**. Effect of added product was determined as follows: theoretical yield of both aminohydroxylation products is 204.24 mg. at 99% conversion it is 203.22 mg. From integration **A:B**=14.97:188.25 mg, which is translated to 14.97:(188.25-101.2)mg ≈ 15: 87 mg=1:5.8=**A:B.**

Addition of A regioisomer to the reaction mixture.

The same protocol was used as above, with the exception that amount of **A regioisomer** added was 51.6 mg (0.155 mmol).

Solvent evaporation resulted 249.3 mg (96.8 % yield) of amorphous crystals.

Conversion was determined to be 95% from ^{1}H NMR and regiomeric composition integrated as 130.8: 100=**A:B**. Effect of added product was determined as follows: theoretical yield of both aminohydroxylation products is 158.28 mg. at 95% conversion. From integration **A:B**=89.7:60.6 mg, which is translated to (89.7-51.61) mg: 68.6 mg ≈ 38.1: 68.6 mg=1:1.6=**A:B.**

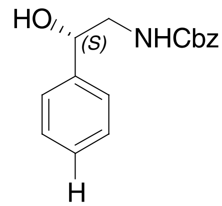
Clearly while addition of regioisomer **B** has little effect on the reaction outcome addition of **A** dramatically influenced the reaction outcome.

Procedure for determining enantiomeric ratios.

The enantiomeric composition of regioisomer **B** was determined (after purification on silica gel) by two methods. Diastereomeric Mosher esters were prepared by procedure of Ward[10] and analyzed by ^{1}H and ^{19}F NMR. The ratio of enantiomers was determined by integration. The results were identical to Supercritical Fluid Chromatography analysis, which was method of choice, as no chemical modification of the *N*-protected aminoalcohol was necessary. Samples for SCF were prepared as a solution in methyl alcohol of 1±0.4 mg/ml concentration and 5 µL of sample was analyzed. SCF chromatograms are attached.

Analytical data

(S)-(+)-(2-Hydroxy-2-phenyl-ethyl)-carbamic acid benzyl ester



white crystalline solid

R$_f$=0.47(EtOAc/Hexanes=10:7); **mp** 97-99 ^{o}C ; $[\alpha]^{25}_{D}$=27.16297 (c=.93, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.385-7.303 (m, 9H), 5.171 (br t, 1H), 5.109 (s, 2H), 4.83 (br dd, 1H *J*=8.0, 3.4 Hz), 3.56 (ddd, 1H, *J*=10.6, 7.1, 3.4 Hz), 3.315 (ddd, 1H, *J*=13.6, 8.0, 5.1 Hz), 2.89 (br s, 1H, OH, exchangeable);

^{13}C NMR (125 MHz, $CDCl_3$)

δ 157.15, 141.51, 136.33, 128.57, 128.53, 128.18, 128.12, 127.97, 125.86, 73.58, 66.93, 48.47

IR (KBr, cm^{-1})

3419, 3331, 3031, 1692, 1607, 1551, 1495, 1225, 1403, 1344, 1275, 1162, 1086, 910, 783, 733, 697;

MS (EI) (m/z)

180(M-91) (0.54), 163(6.79), 118(9.8), 108(33.77), 107(100), 105(12), 104(19), 91(51), 79(71), 77(38), 74(11), 65(13);

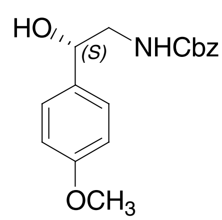
MS (CI) (m/z):

272(M+1), 254(M-17, 1.91) 238(1), 226(1), 192(1.09), 165(5), 164(47), 148(8.5), 146(17.91), 120(79.4), 107(16.8), 91(100), 79(29)

SFC (125psi CO_2, 12% , 3ml/min MeOH, Chiracel OD):

6.629 min (R), 6.990 (S); 64% ee (82:18 er)

(S)-(+)-[2-Hydroxy-2-(4-methoxy-phenyl)-ethyl]-carbamic acid benzyl ester



white crystalline solid

R$_f$=0.4 (EtOAc/Hexanes=10:7) **mp** 109-111 ^{o}C; $[\alpha]^{25}_{D}$=18.16585 (c=.995, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.381-7.266 (m, 7H), 5.17 (br t, 1H), 5.109 (s, 2H), 4.78 (br dd, 1H, *J*=8.0, 3.4 Hz), 3.79 (s, 3H), 3.52 (ddd, 1H, *J*=14.2, 7.1, 3.4 Hz), 3.315 (ddd, 1H, *J*=13.7, 8.0, 5.1 Hz), 2.62 (br s, 1H, OH, exchangeable), 1.62 (br s, 1H)

^{13}C NMR(125 MHz, $CDCl_3$)

δ 157.14, 141.52, 136.34, 128.56, 128.215, 128.18, 127.96, 125.86, 73.57, 66.93, 48.49

IR (KBr, cm^{-1})

3491, 3294, 3066, 2952, 2835, 1696, 1613, 1555, 1515, 1455, 1290, 1245, 1177, 1144, 1061, 1040, 992, 835, 752, 698;

MS (EI) (m/z):

283(0.62), 193(14.7), 175(2.56), 150(7.51), 149(14.56), 148(9.64), 137(100), 135(14.81), 134(15.44), 121(12.79), 109(21.58), 108(26.4), 107(22.07), 104(7.98), 91(45.99), 79(38.07), 78(12.27), 77(38.68), 65(13.84);

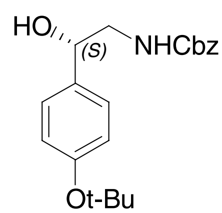
MS (CI) (m/z):

284(M-17, 2.29), 257(0.78), 240(9.95), 223(6.32), 194(39.6), 178(8.55), 176(18.38), 150(79.5), 137(15.84), 135(13.35), 121(5.29), 119(5.4), 109(10.1), 108(5.68), 107(7.78), 91(100), 79(32.78)

SFC (125psi CO_2, 12% , 3ml/min MeOH, Chiracel OD):

8.703 min (R), 9.336 (S); 69% ee (84.5:15.5 er)

(S)-(+)- [2-(4-tert-Butoxy-phenyl)-2-hydroxy-ethyl]-carbamic acid benzyl ester



white crystalline solid

R$_f$=0.51 (EtOAc/Hexanes=10:7); **mp**=119-125 °C (dec.); $[\alpha]^{25}_D$=17.49323 (c=1.3, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.381-7.266 (m, 5H), 7.24 (d, 2H, *J*=8.5 Hz), 6.96 (dt, 2H, *J*=8.5, 2.8), 5.26 (br t, 1H), 5.108 (s, 2H), 4.77 (br dd, 1H, *J*=8.2, 3.4 Hz), 3.53 (ddd, 1H, *J*=14.0, 6.8, 3.4 Hz), 3.27 (ddd, 1H, *J*=13.7, 8.2, 5.1 Hz), 2.93 (br s, 1H, OH, exchangeable), 1.33 (s, 9H)

^{13}C NMR(125 MHz, $CDCl_3$)

δ 157.08, 155.06, 136.35, 128.52, 128.15, 128.12, 126.45, 124.14, 78.59, 73.21, 66.88, 48.43, 28.77

IR (KBr, cm^{-1})

3419, 3332, 3062, 3033, 2975, 2954, 1691, 1608, 1544, 1498, 1446, 1403, 1344, 1278, 1234, 1162, 1120, 1085, 910, 732, 696;

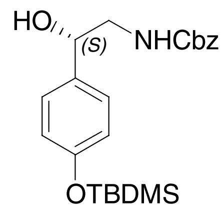
MS (CI) (m/z):

344(M+1, 16), 326(M-17, 66), 316(17), 298(5), 282(9), 270(91), 236(30), 226(61), 209(24), 180(100), 162(13), 136(57), 123(22), 91(68), 79(12)

SFC (125psi CO_2; 8% , 3ml/min MeOH, Chiracel OD):

4.873 min (R), 5.111 (S); 70% ee (85:15 er)

(S)-(+)-2-[4-(tert-Butyl-dimethyl-silanyloxy)-phenyl]-2-hydroxy-ethyl carbamic acid benzyl ester



white crystalline solid

R$_f$=0.58 (EtOAc/Hexanes=10:7); **mp**=142-149 °C (dec.); $[\alpha]^{25}_D$=9.969196 (c=.875, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.38-7.307 (m, 5H), 7.21 (d, 2H, *J*=8.3 Hz), 6.96 (dt, 2H, *J*=8.5, 2.8), 5.16 (br t, 1H), 5.11 (s, 2H), 4.76 (br d, 1H, *J*=5.9 Hz), 3.515(ddd, 1H, *J*=14.2, 7.4, 3.5 Hz), 3.315 (ddd, 1H, *J*=13.6, 8.2, 5.0 Hz), 2.58 (br s, 1H, OH, exchangeable), 1.613 (br s, 1H) 0.979(s, 9H), 0.189 (s, 6H)

^{13}C NMR(125 MHz, $CDCl_3$)

157.08, 155.51, 136.38, 134.22, 128.54, 128.17, 128.14, 127.05. 120.154, 73.29, 66.91, 48.45, 25.63, 18.15, -4.471;

IR (KBr, cm^{-1})

3383, 3263, 3063, 2957, 2930, 2886, 2858, 1695, 1608, 1548, 1509, 1471, 1406, 1341, 1281, 1249, 1167, 1079, 991, 918, 853, 840, 779, 746, 696

MS (FAB): 384(M-17)

MS (EI) (m/z):

384(0.2), 350(1.19), 293(18.6), 275(2.11), 249(31.0), 237(100), 236(82), 218(30.1), 192(84), 190(22), 181(11), 179(10), 165(9.8), 151(20), 135(8.8), 123(5.36), 119(27), 108(46), 107(34), 91(69), 79(55), 77(38), 75(43), 73(44), 65(11), 59(10), 57(16)

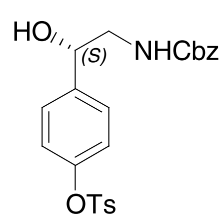
MS (CI) (m/z):

384(M-17, 2.64), 340(6.3), 323(5.4), 322(6.15), 294(48.5), 278(9.47), 276(7.76), 250(53.61), 237(11.46), 236(12.15), 209(6.48), 193(8.42), 192(6.91), 176(2.34), 119(4.61), 115(3.65), 107(9.33), 91(100), 79(42.54);

SFC (125psi CO_2; 8% , 3ml/min MeOH, Chiracel OD):

11.09 min (R), 11.508 (S); 73% ee (86.5:13.5 er)

(S)-(+)- Toluene-4-sulfonic acid 4-(2-benzyloxycarbonylamino-1-hydroxy-ethyl)-phenyl ester



white crystalline solid

R$_f$=0.36 (EtOAc/Hexanes=10:7); **mp** 132-134 °C; $[\alpha]^{25}_D$=18.5892 (c=.49, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.62 (dt, 2H, *J*=8.5, 2.1) 7.30-7.19 (m, 9H), 6.88 (dt, 2H, *J*=8.6, 2.6), 5.1 (br t, 1H, *J*=5.2 Hz), 5.11 (s, 2H), 4.73 (br dd, *J*=8.0, 3.0 Hz), 3.44 (ddd, 1H, *J*=14.2, 6.9, 3.0 Hz), 3.315 (ddd, 1H, *J*=13.3, 8.0, 5.2 Hz), 2.37 (s, 3H)

^{13}C NMR(125 MHz, $CDCl_3$)

δ 157.31, 149.09, 145.43, 140.47, 136.16, 132.29, 129.79, 128.58, 128.48, 128.28, 128.15, 127.19, 122.49, 73.13, 67.09, 48.55, 21.69

IR (KBr, cm^{-1})

3398, 3346, 3067, 3035, 2947, 2881, 1687, 1595, 1547, 1503, 1453, 1377, 1268, 1198, 1176, 1155, 1092, 1082, 870, 842, 818, 732, 694, 660, 579, 550

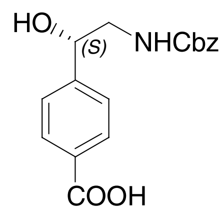
MS (CI) (m/z):

424(M-17, 0.52), 380(4.52), 334(8), 316(17), 290(100), 249(2.3), 180(2.16), 155(11), 136(10), 123(4), 107(12), 91(66), 79(28), 65(2.9);

SFC (125psi CO_2; 20% , 3ml/min MeOH, Chiracel OD):

6.336 min (R), 6.968 (S); 75% ee (87.5:12.5 er)

(S)-(+)-4-(2-Benzyloxycarbonyl-amino-1-hydroxy-ethyl)-benzoic acid[7]



p-vinylbenzoic acid was treated with 1.01 equvivalent of sodium hydroxide in 3 ml of acetonitrile/water mixture (2:1) prior to subjecting to aminohydroxylation protocol.

white crystalline solid

R_f=0.08 (EtOAc/Hexanes=10:7); **mp**180-186 °C (dec.) ;

^{1}H NMR (400 MHz, $DMSO_{d6}$)

δ 7.875 (d, 2H, *J*=8.2Hz), 7.41 (d, 2H, *J*=8.2Hz), 7.33-7.264 (m, 5H), 5.565 (br s, 1H), 4.971 (s, 2H), 4.66 (t, 1H, *J*=6 Hz), 3.21-3.12(m, 2H)

^{13}C NMR(125 MHz, $DMSO_{d6}$)

δ 167.35, 156.25, 148.64, 137.28, 129.56, 129.15, 128.34, 127.75, 127.64, 126.27, 71.123, 65.144, 48.22

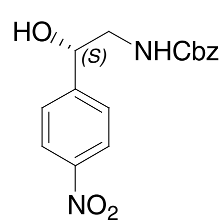
IR (KBr, cm^{-1})

3309, 3071, 3034, 2953, 2888, 2672, 2557, 1693, 1612, 1556, 1427, 1217, 1287, 1259, 1149, 1065, 988, 846, 751, 698

MS (CI) (m/z):

298(M-17, 1.12), 208(18), 192(6.4), 190(8), 164(78), 151(5.87), 146(5.9), 123(3.14), 120(5.4), 119(4.8), 108(6.25), 107(9.44), 105(4.35), 93(8.27), 91(100), 79(36), 65(1.12);

(S)-(+)- [2-Hydroxy-2-(4-nitro-phenyl)-ethyl]-carbamic acid benzyl ester



light yellow crystalline solid

R_f=0.38 (EtOAc/Hexanes=10:7); **mp** 97-99 ^oC (dec); $[\alpha]^{25}{}_D$=20.93949 (c=.815, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.18 (d, 2H, *J*=8.6 Hz), 7.52 (d, 2H, *J*=8.5 Hz), 7.38-7.31 (m, 5H), 5.21 (br s, 1H), 5.09 (s, 2H), 4.96 (br d, 1H, *J*=4.8 Hz), 3.58 (ddd, 1H, *J*=14.5, 6.8, 3.4 Hz), 3.44 (S, 1H, OH), 3.315 (ddd, 1H, *J*=13.7, 7.0, 6.0 Hz),

^{13}C NMR(125 MHz, $CDCl_3$)

δ 157.51, 148.79, 147.52, 135.99, 128.59, 128.39, 128.18, 126.71, 123.71, 73.07, 67.26, 48.47

IR (KBr, cm^{-1})

3426, 2279, 3275, 3075, 2961, 2894, 1691, 1603, 1516, 1455, 1349, 1299, 1275, 1237, 1142, 1090, 1049, 855, 749, 697

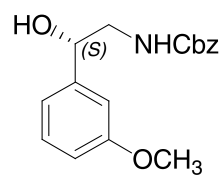
MS (CI) (m/z):

269(0.85), 257(1.35), 237(0.95), 209(M-Bn·, 33.4), 191(3.4), 179(6.2), 177(3.4), 165(27), 135(25), 120(11), 118(10), 107(13), 91(100), 79(34), 69(9), 61(16), 57(12), 55(11);

SFC (125psi CO_2; 15% , 3ml/min MeOH, Chiracel OD):

7.701 min (R), 9.889 (S); 70 % ee (85:15 er)

(S)-(+)- [2-Hydroxy-2-(3-methoxy-phenyl)-ethyl]-carbamic acid benzyl ester



white crystalline solid

R_f=0.5 (EtOAc/Hexanes=10:7); **mp** 78-80 ^oC; $[\alpha]^{25}{}_D$=17.29428 (c=.765, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.381-7.302 (m, 5H), 7.262 (t, 2H, *J*=8.1 Hz), 6.831(ddd, *J*=8.2, 2.5, 1.0 Hz), 5.17 (br t, 1H), 5.13 (s, 2H), 4.82 (br d, *J*=5.4 Hz), 3.79((s, 3H), 3.55(ddd, 1H, *J*=13.9, 6.9, 3.5 Hz), 3.315 (ddd, 1H, *J*=13.5, 7.9, 5.2 Hz), 2.78 (br s, 1H, OH, exchangeable), 1.62 (br s, 1H)

^{13}C NMR(125 MHz, $CDCl_3$)

δ 159.83, 157.17, 143.21, 136.32, 129.64, 128.54, 128.19, 128.12, 118.08, 113.55, 111.25, 66.95, 55.20, 48.46

IR (KBr, cm^{-1})

3406, 3341, 3065, 3023, 2963, 2928, 1682, 1602, 1545, 1487, 1466, 1454, 1432, 1361, 1319, 1239, 1159, 1059, 1038, 916, 878, 837, 786, 757, 697;

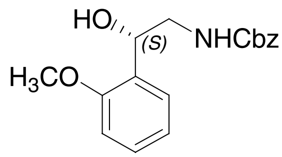
MS (CI) (m/z):

284(M-17, 1.74), 257(0.5), 240(7.4), 223(4.78), 194(34.8), 178(7.8), 176(11.98), 150(100), 137(7.1), 135(6.02), 109(5.3), 108(5.3), 107(6.6), 91(99.8), 79(24.3);

SFC (125psi CO_2; 15% , 3ml/min MeOH, Chiracel OD):

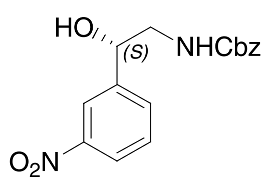
6.18 min (R), 7.060 (S); 72% ee (86:14 er)

(S)-(+)- [2-Hydroxy-2-(2-methoxy-phenyl)-ethyl]-carbamic acid benzyl ester



white crystalline solid
R_f=0.51 (EtOAc/Hexanes=10:7); **mp** 79-83 ^oC;
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.37-7.25 (m, 5H), 6.96 (dt, 2H, *J*=8.1, 1.0), 6.88(d, *J*=8.2), 5.17 (br t, 1H), 5.10 (s, 2H), 5.00(br d, *J*=4.7 Hz), 3.84 (s, 3H), 3.61(ddd, 1H, *J*=13.8, 6.8, 3.5 Hz), 3.315 (ddd, 1H, *J*=13.2, 7.7, 5.0 Hz), 3.17 (br s, 1H, OH, exchangeable), 1.62 (br s, 1H)
^{13}C NMR (125 MHz, $CDCl_3$)
δ 156.41, 136.49, 128.85, 128.51, 128.07, 127.18, 120.86, 110.41, 70.41, 66.80, 55.27, 46.57
IR (KBr, cm^{-1})
3404, 3318, 3065, 3005, 2940, 1701, 1599, 1586, 1547, 1489, 1453, 1433, 1287, 1266, 1238, 1150, 1068, 1027, 755, 729, 694;
MS (EI) (m/z):
260, 233, 193, 184, 168, 149, 137(100), 121, 119, 115, 107, 91, 79, 77, 65
MS (CI) (m/z):
284(M-17, 0.81), 257(0.5), 240(10.03), 223(1.84), 194(2.65), 178(5.31), 176(8.46), 150(100), 137(9.14), 135(6.85),119(4.39), 109(8.01), 107(7.23), 91(69.01), 79(23.3);
SFC (125psi CO_2; 15% , 3ml/min MeOH, Chiracel OD):
5.18 min (R), 5.997 (S); 23% ee (61.5:38.5 er)

(S)-(+)- [2-Hydroxy-2-(3-nitro-phenyl)-ethyl]-carbamic acid benzyl ester



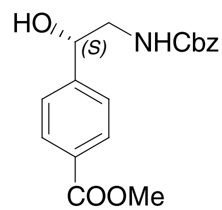
R_f=0.42 (EtOAc/Hexanes=10:7); oil $[\alpha]^{25}_D$=25.05022 (c=.86, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$)
δ 8.42, (br s, 1H), 8.14 (d, 1H, *J*=8.4 Hz), 7.69 (d, 1H, *J*=8.1 Hz), 7.49(t, 1H, *J*=7.9 Hz), 7.38-7.33 (m, 5H), 5.29 (br s, 1H), 5.10 (s, 2H), 4.98 (br d, 1H, *J*=5.4 Hz), 3.59 (ddd, 1H, *J*=14.3, 6.0, 2.6 Hz), 3.44 (S, 1H, OH), 3.315 (ddd, 1H, *J*=13.7, 7.0, 6.5 Hz), 1.64 (br s,1H)
^{13}C NMR (125 MHz, $CDCl_3$)
δ 157.53, 148.40, 143.74, 136.01, 132.033, 129.49, 128.60, 128.36, 128.17, 122.83, 120.94, 72.93, 67.26, 48.54;
IR (thin film from $CHCl_3$, cm^{-1})
3415, 3330, 3091, 3068, 3035, 2940, 2879, 1697, 1529, 1349, 1257, 1145, 1097, 1068, 738, 696;
MS (CI) (m/z):

209(M-Bn·, 13.1), 191(7.82), 179(6.4), 177(2.2), 165(45.92), 152(5.87), 135(37.1), 120(4.6), 119(5.8), 118(5), 117(5.8), 108(7.9), 107(9.7), 91(100), 79(31.4), 69(2.52), 61(3.68), 57(4.42), 55(4.07);

SFC (125psi CO_2; 15% , 3ml/min MeOH, Chiracel OD):

6.873 min (R), 8.196 (S); 69 % ee (84.5:15.5 er)

(S)-(+)-4-(2-Benzyloxycarbonyl-amino-1-hydroxy-ethyl)-benzoic acid methyl ester



white crystalline solid

R*f*=0.4 (EtOAc/Hexanes=10:7); **mp**= 98-116 °C (dec.); $[\alpha]^{25}_{D}$=19.60474 (c=.785, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.875 (d, 2H, *J*=8.2 Hz), 7.41 (d, 2H, *J*=8.2 Hz), 7.33-7.264 (m, 5H), 5.565 (br s, 1H), 4.971 (s, 2H), 4.66 (t, 1H, *J*=6 Hz), 3.21-3.12(m, 2H)

^{13}C NMR(125 MHz, $CDCl_3$)

δ 166.81, 157.30, 146.56, 136.13, 129.81, 129.65, 128.54, 128.24, 128.12, 125.80, 73.39, 67.08, 52.13, 48.46

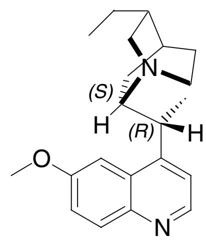
IR (KBr, cm^{-1})

3313, 3009, 3070, 2950, 2927, 2892, 1724, 1693, 1612, 1562, 1436, 1278, 1106, 1066, 773, 752, 698

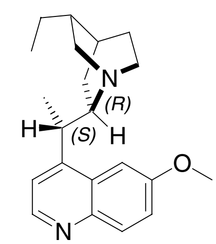
MS (CI) (m/z):

330(M+1, 20.76), 312(M-17, 48.41), 298(3), 286(5.4), 268(19.45), 250(2.9), 222(27.7), 206(4.35), 190(3.5), 178(52.6), 165(15), 146(3), 119(6.3), 105(5), 104(10), 91(100), 79(8)

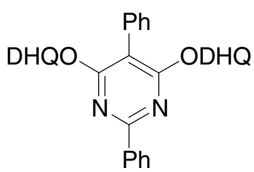
Structures of Ligands



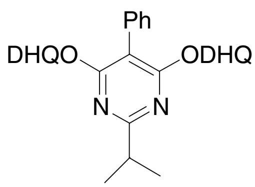
Dihydroquinyl(DHQ)



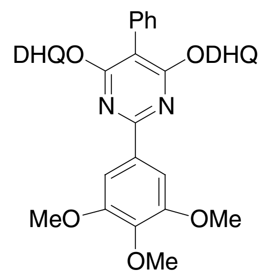
Dihydroquinidyl(DHQD)



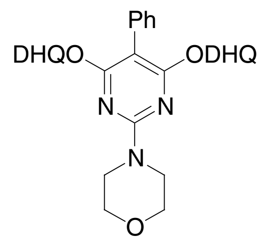
$(DHQ)_2$-PYR
CLogP = 11.0755



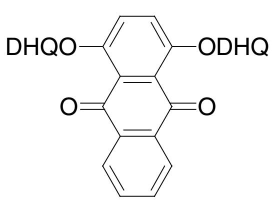
$(DHQ)_2$-PYR(*i*-Pr)
CLogP = 10.4045



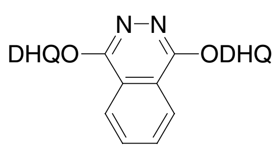
$(DHQ)_2$-PYR(*OMe*)$_3$
CLogP = 10.5269



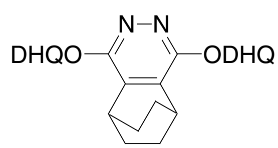
$(DHQ)_2$-PYR(*morph*)
CLogP = 9.53467



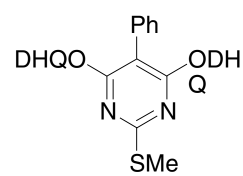
$(DHQ)_2$-AQN
CLogP = 10.091



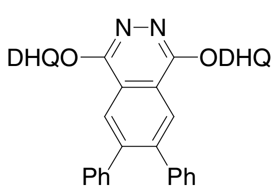
$(DHQ)_2$-PHAL
CLogP = 9.11949



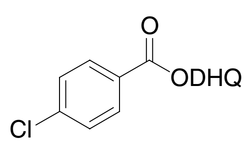
$(DHQ)_2$-[2.2.2]-bycyclo-PHAL
CLogP = 9.83149



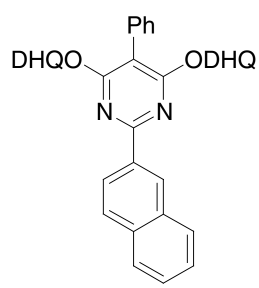
$(DHQ)_2$-PYR(SMe)
CLogP = 10.1797



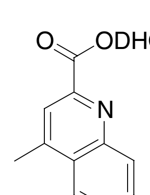
$(DHQ)_2$-PHAL-Ph_2
CLogP = 12.2955



DHQ-CLB
CLogP = 6.57785



$(DHQ)_2$-PYR(Naph)



DHQD-MEQ
CLogP = 6.00385

References and notes

(1) Grene T.W.; Wuts G.M. Protective groups in organic chemistry 3rd ed.; Wiley-Intersscience, 1999

(2) Available from Aldrich as propylene glycol solution, CAS# 2628-17-3. Prior to reaction p-hydroxy styrene was extracted with EtOAc (3x50 ml), washed with water(3x50 ml), brine and dried over magnesium sulfate.

(3) Mintz, M. J.; Walling, C. Organic Syntheses; Wiley: New York, 1983; Collect. Vol. V, p 183

(4) We noted that the reagent can be used even after several month of storing at -5 °C, without affecting regio- and enantioselectivity.

(5) Dobler C.; Gerald Mehltretter G.; Beller M.; Angew. Chem. Int. Ed. 1999, 38(20), 3026-3028

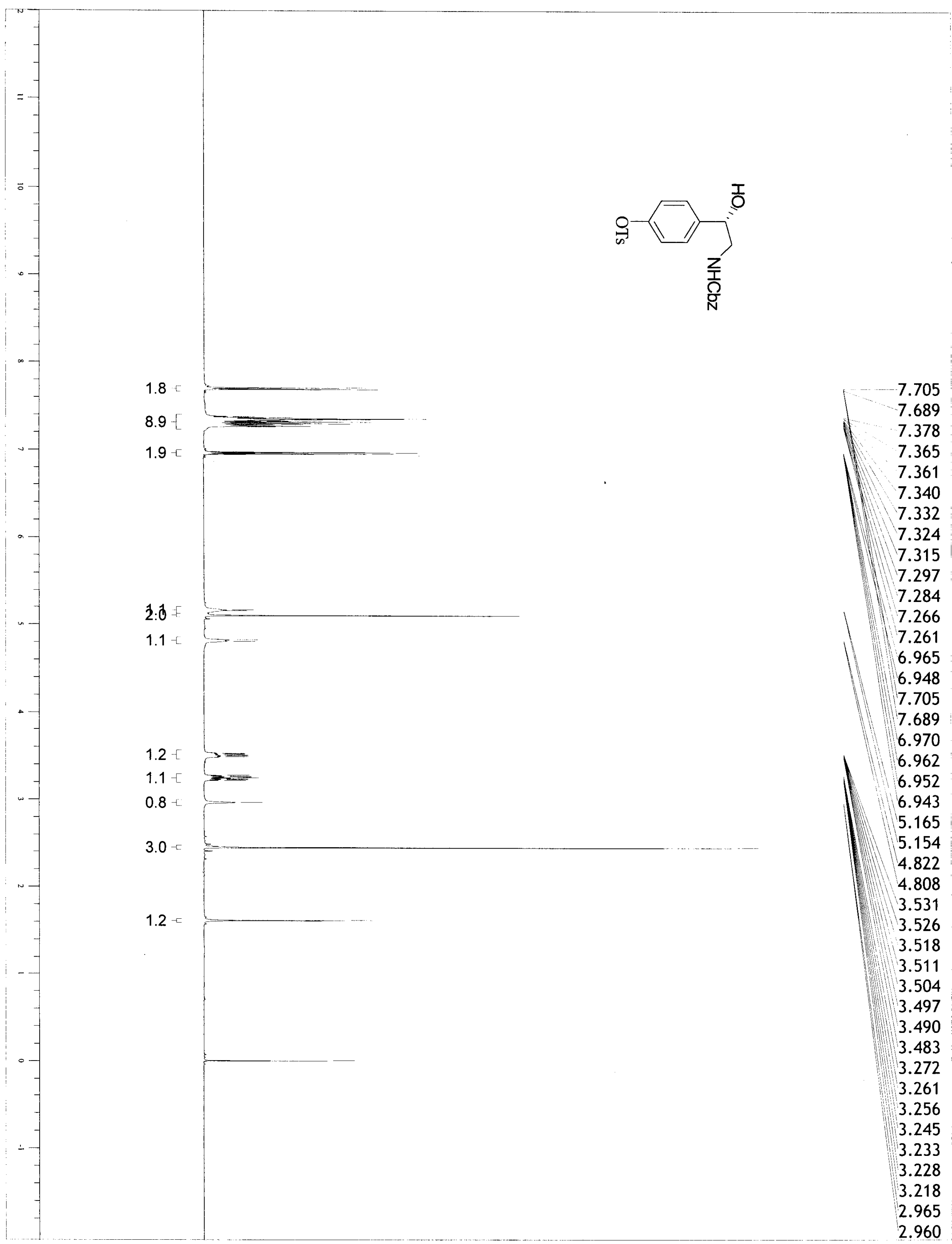
(6) Verified by TLC , by disappearance of starting material

(7) Enantioselectivity was determined for methyl ester.

(8) Verified by TLC , by disappearance of starting material

(9) Armarego W.L.F.; Perrin D.D; Purification of laboratory chemicals 4th ed.; 2000, Butterworth-Heineman; ISBN 0-7506-3761-7

(10) Ward D.E.; Rhee C.K.; Tetrrahedron Letters, 1991, 32(49), 7165-7166.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1.2
7.705
7.689
7.378
7.365
7.361
7.340
7.332
7.324
7.315
7.297
7.284
7.266
7.261
6.965
6.948
7.705
7.689
6.970
6.962
6.952
6.943
5.165
5.154
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3.531
3.526
3.518
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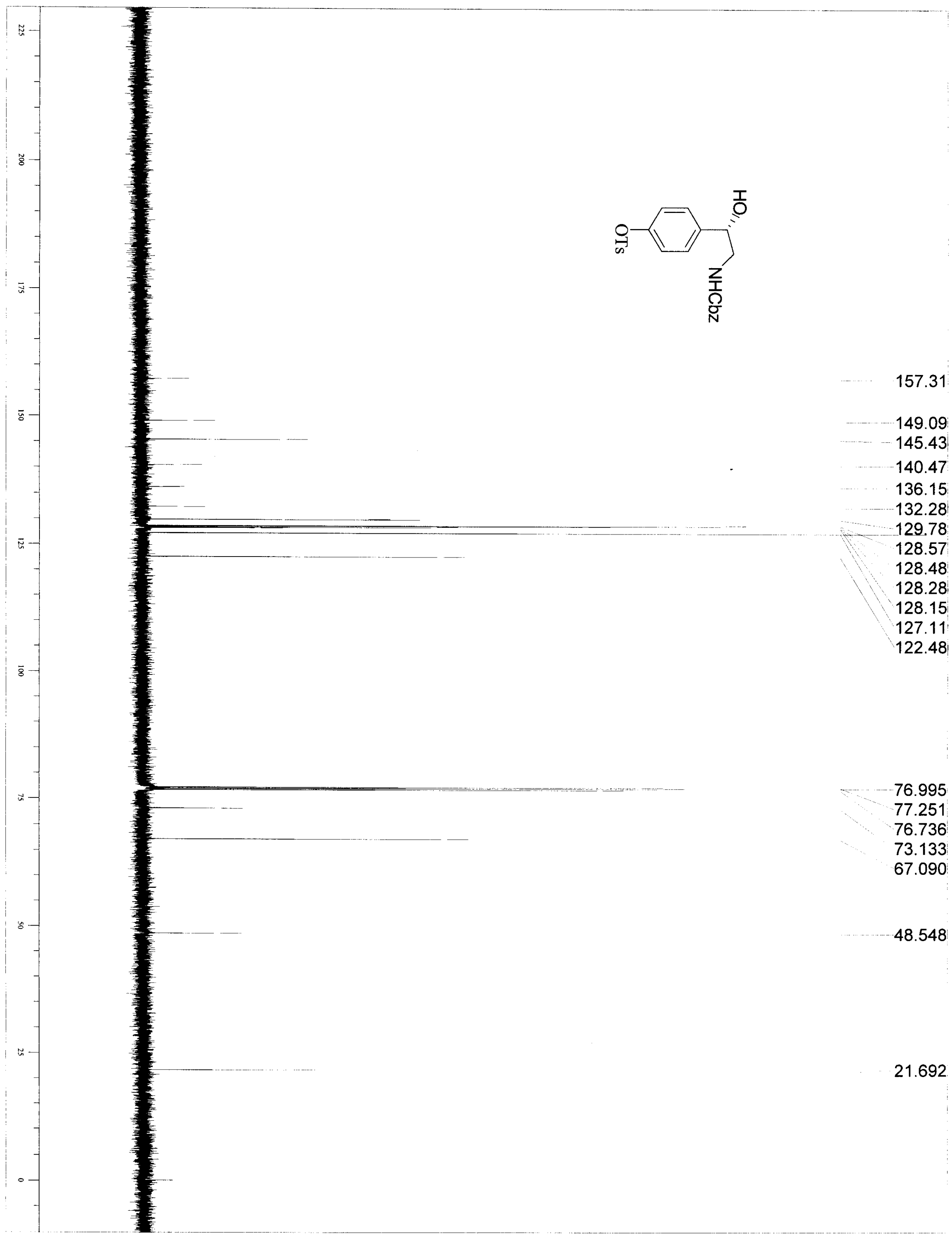
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127.11
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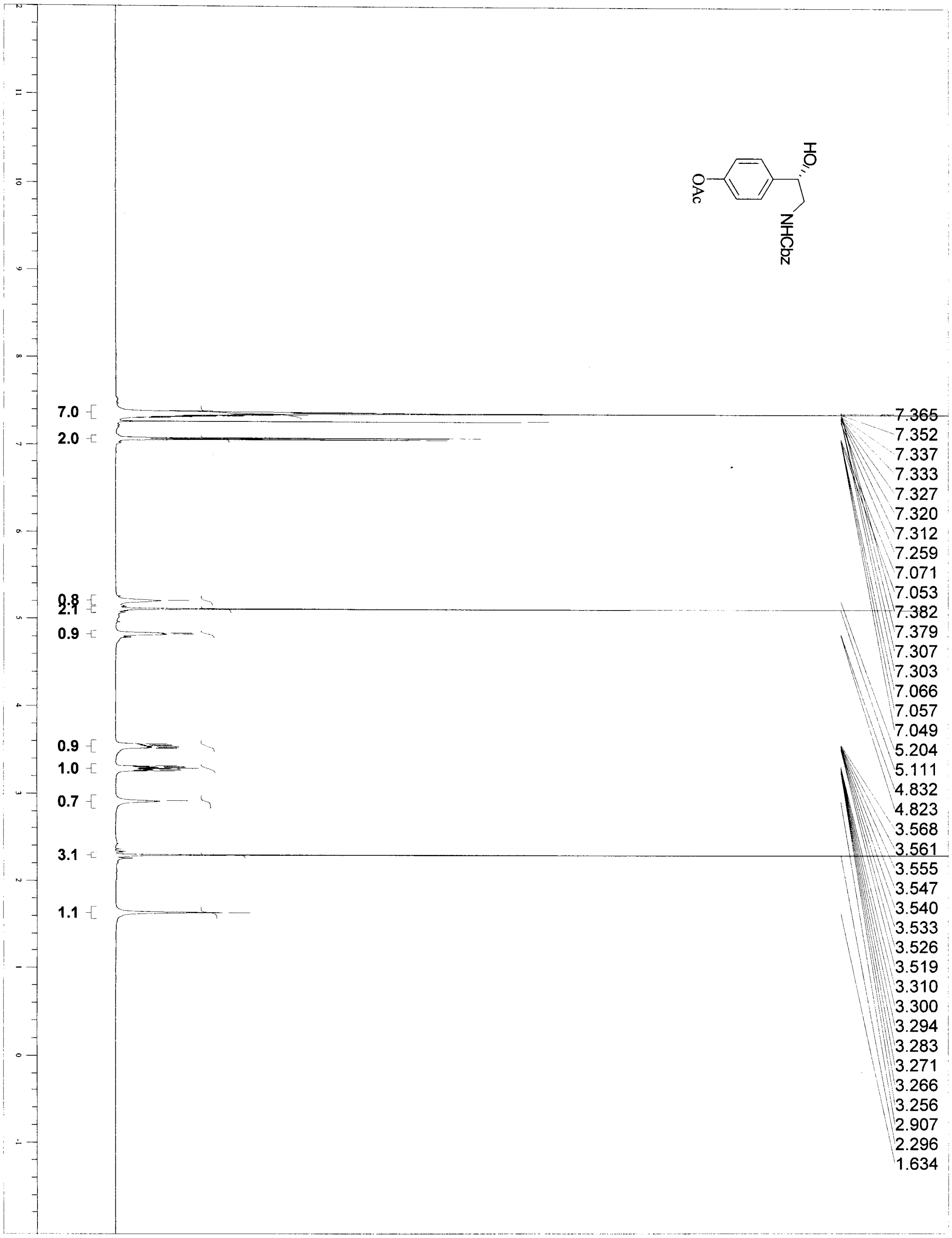
21.692



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0.9
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0.7
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1.1
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7.312
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7.303
7.066
7.057
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3.533
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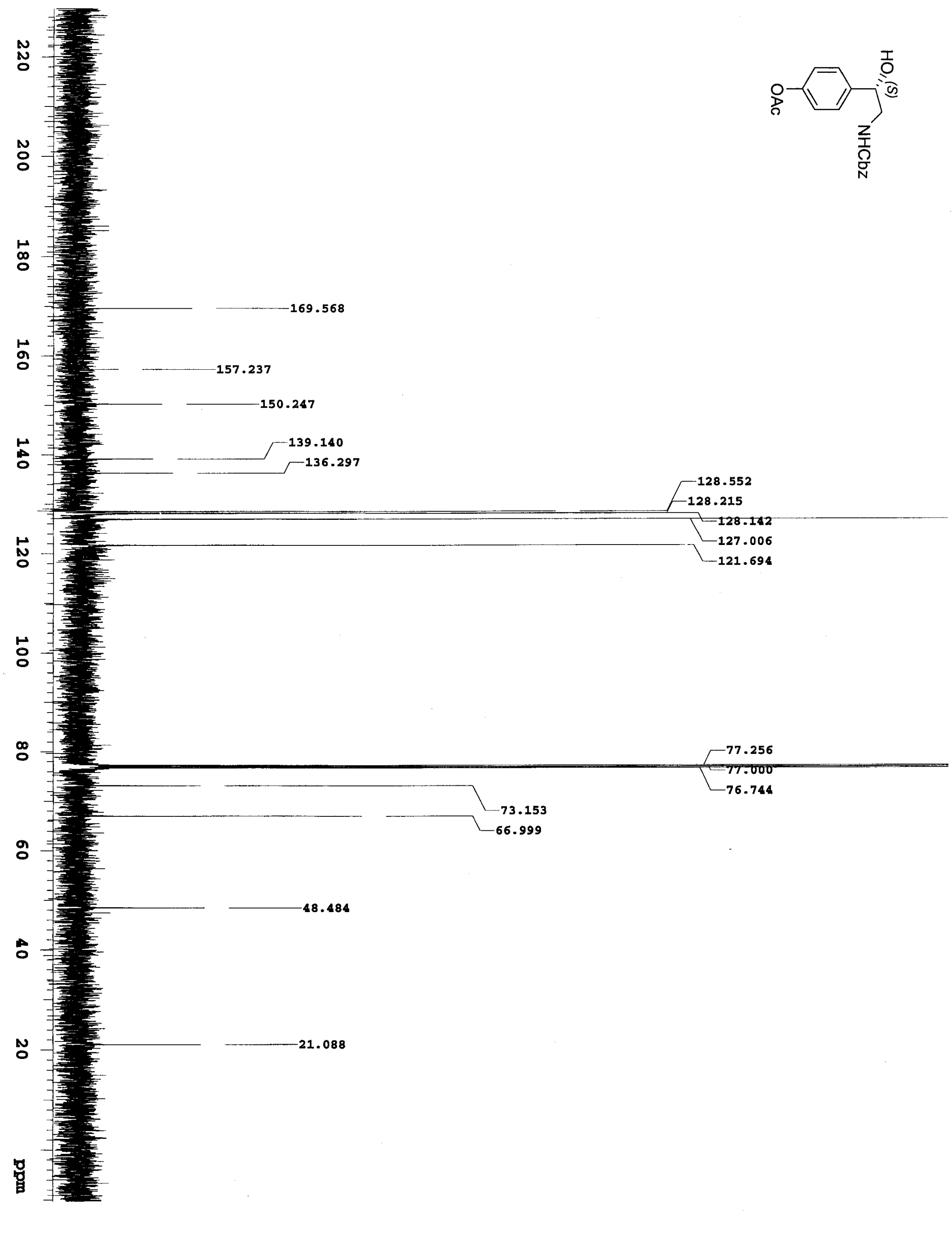
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77.000
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140
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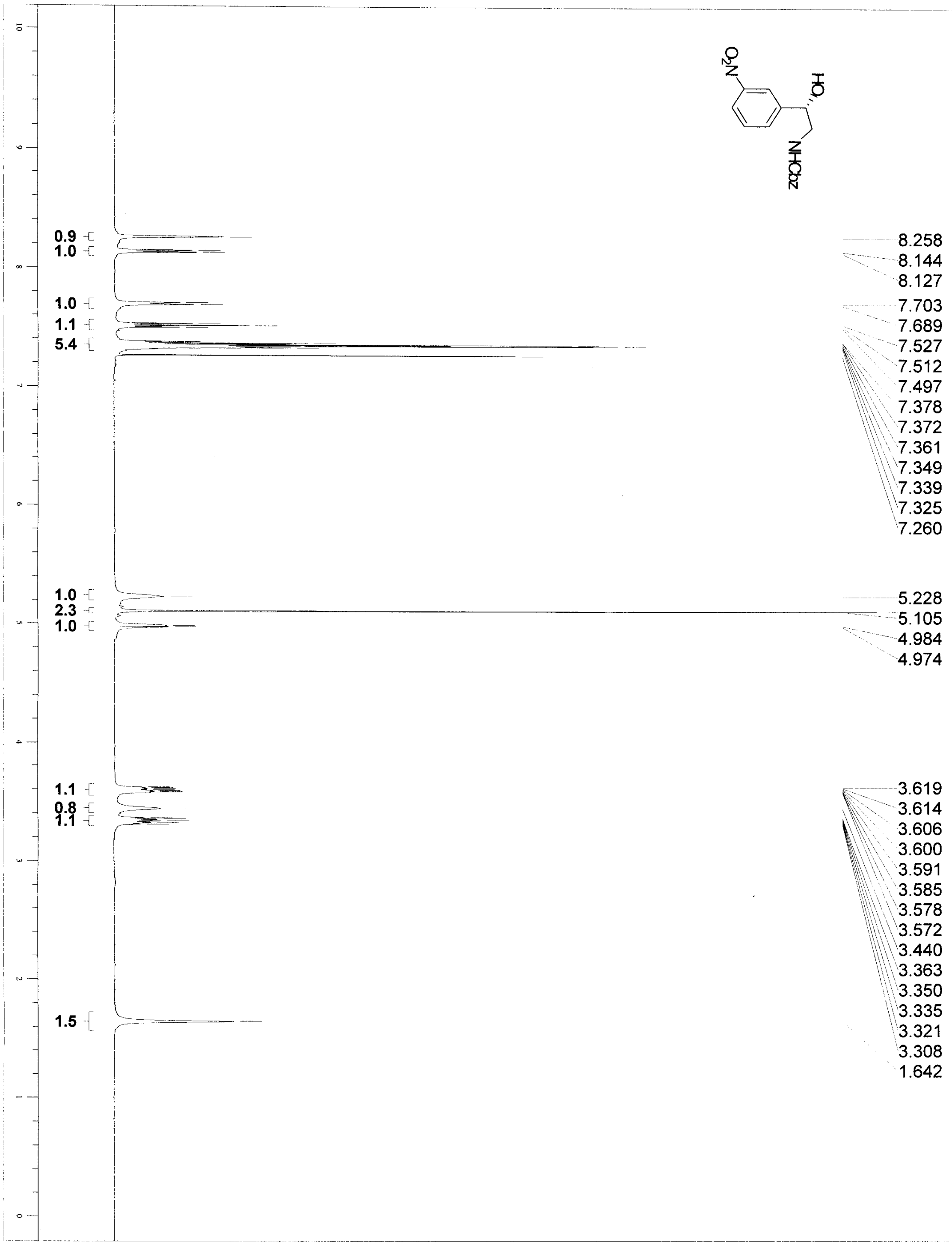
80
60
40
20
ppm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1.5
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8.144
8.127
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7.689
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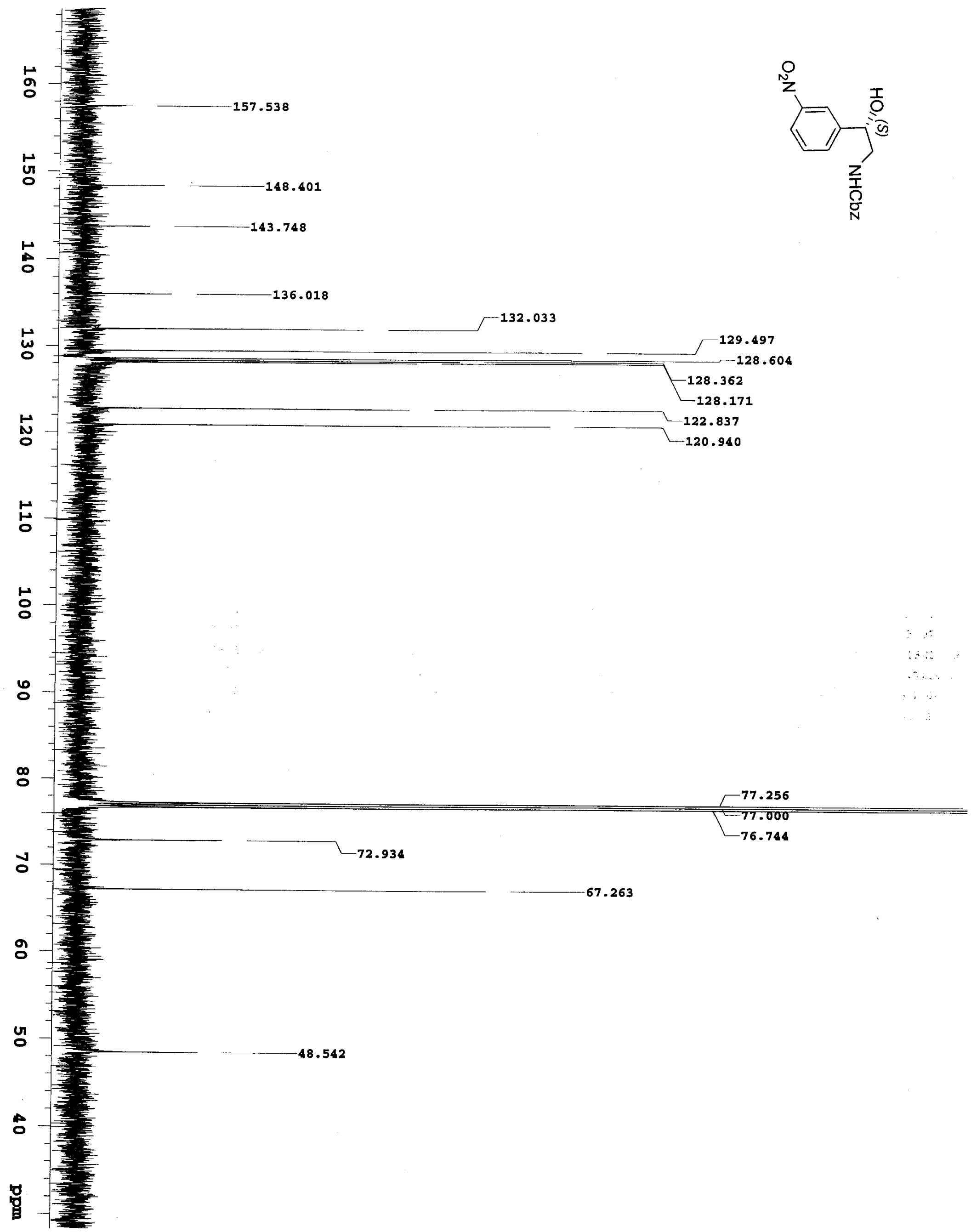
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72.934
67.263
48.542
160
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110
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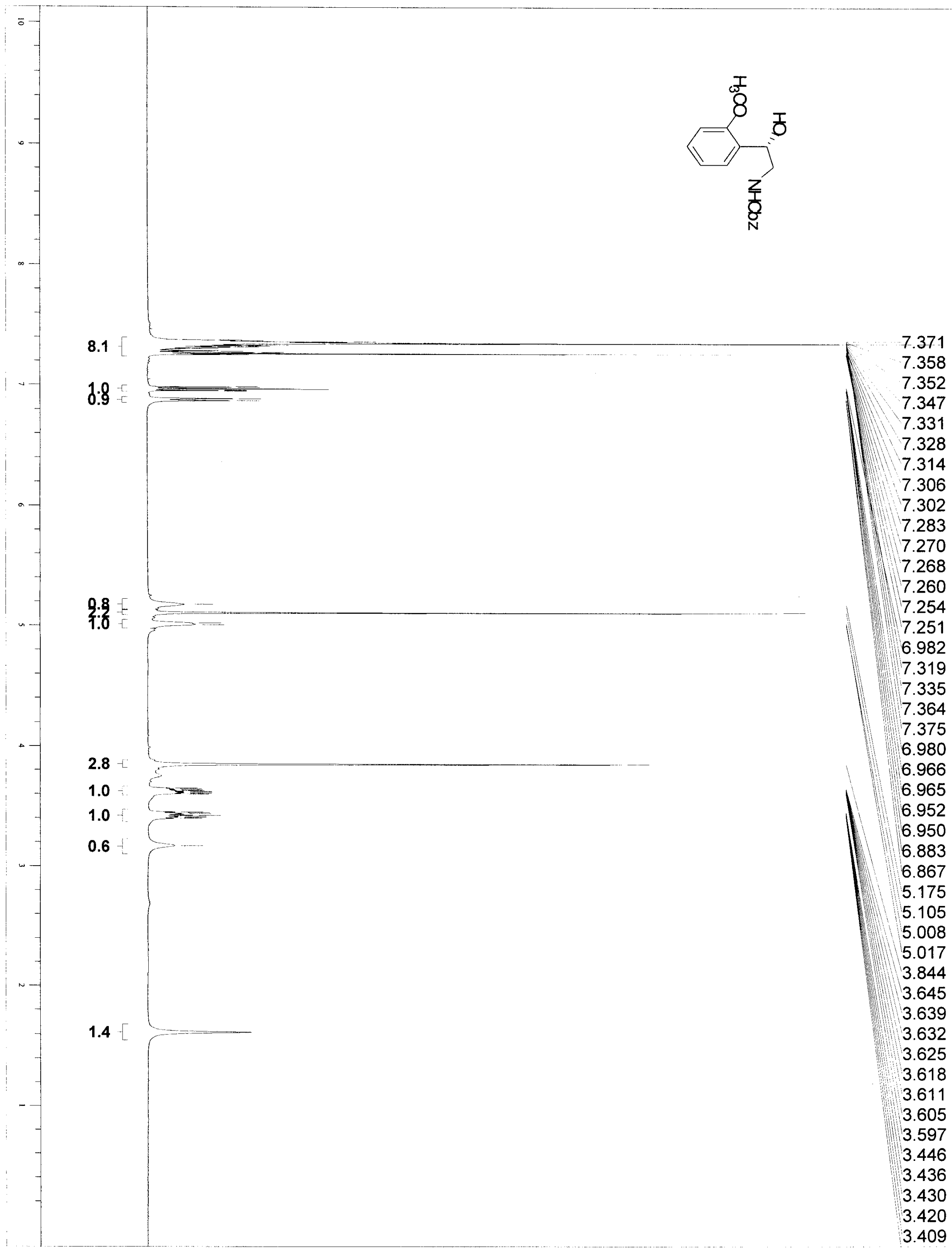
40
ppm
O2N
HO
(S)
NHCbz



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1.0
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1.4
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7.352
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7.331
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6.965
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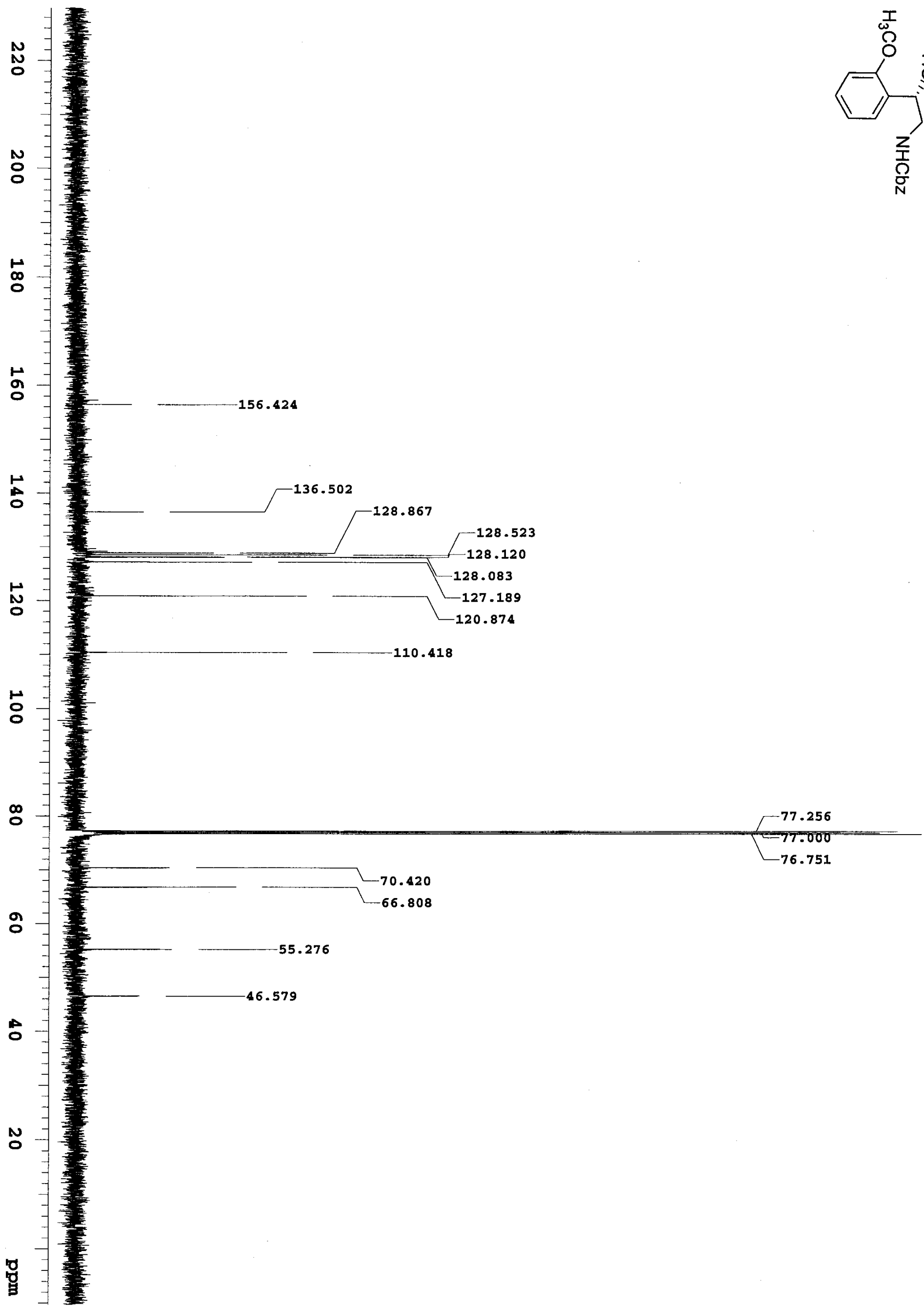
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55.276
46.579
220
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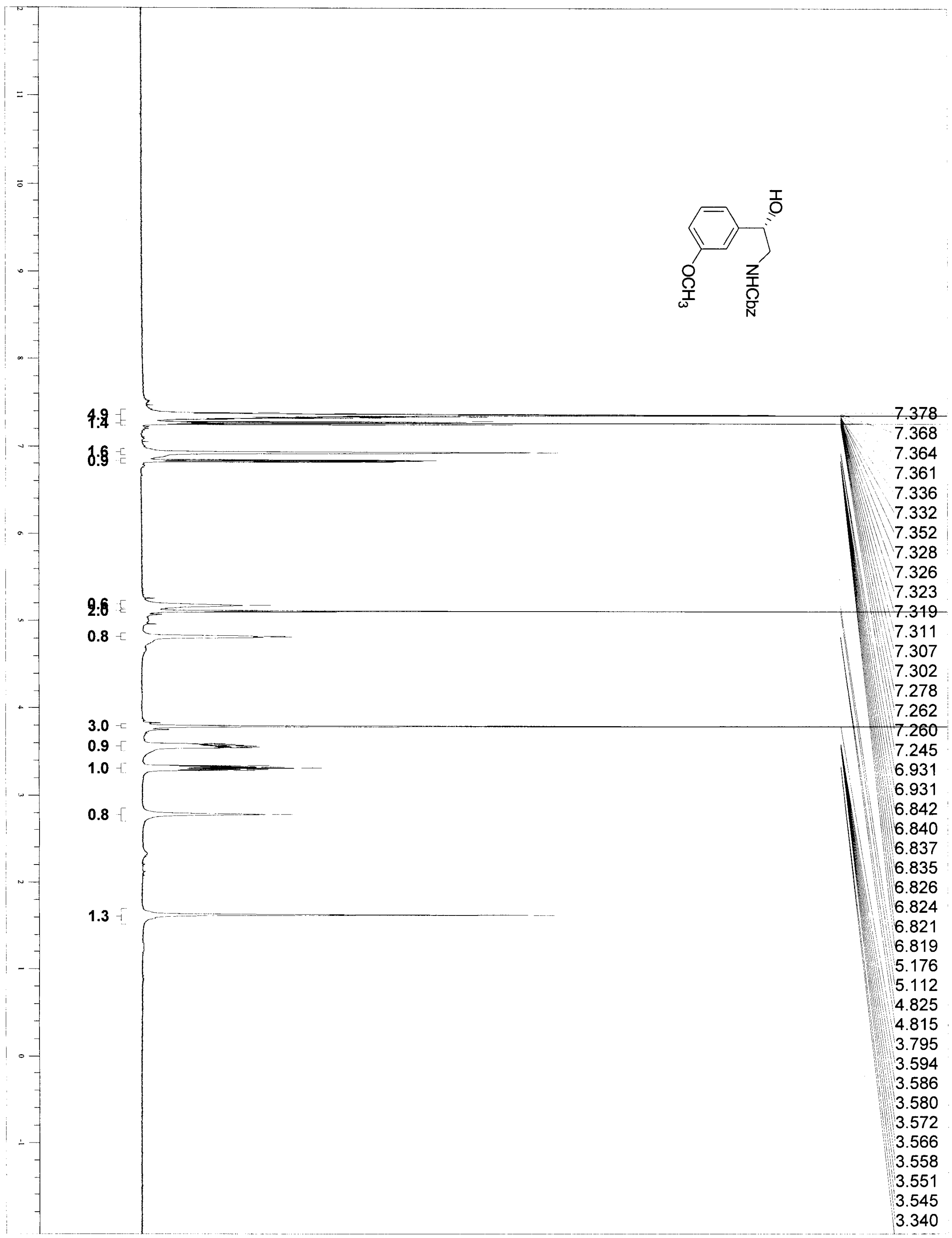
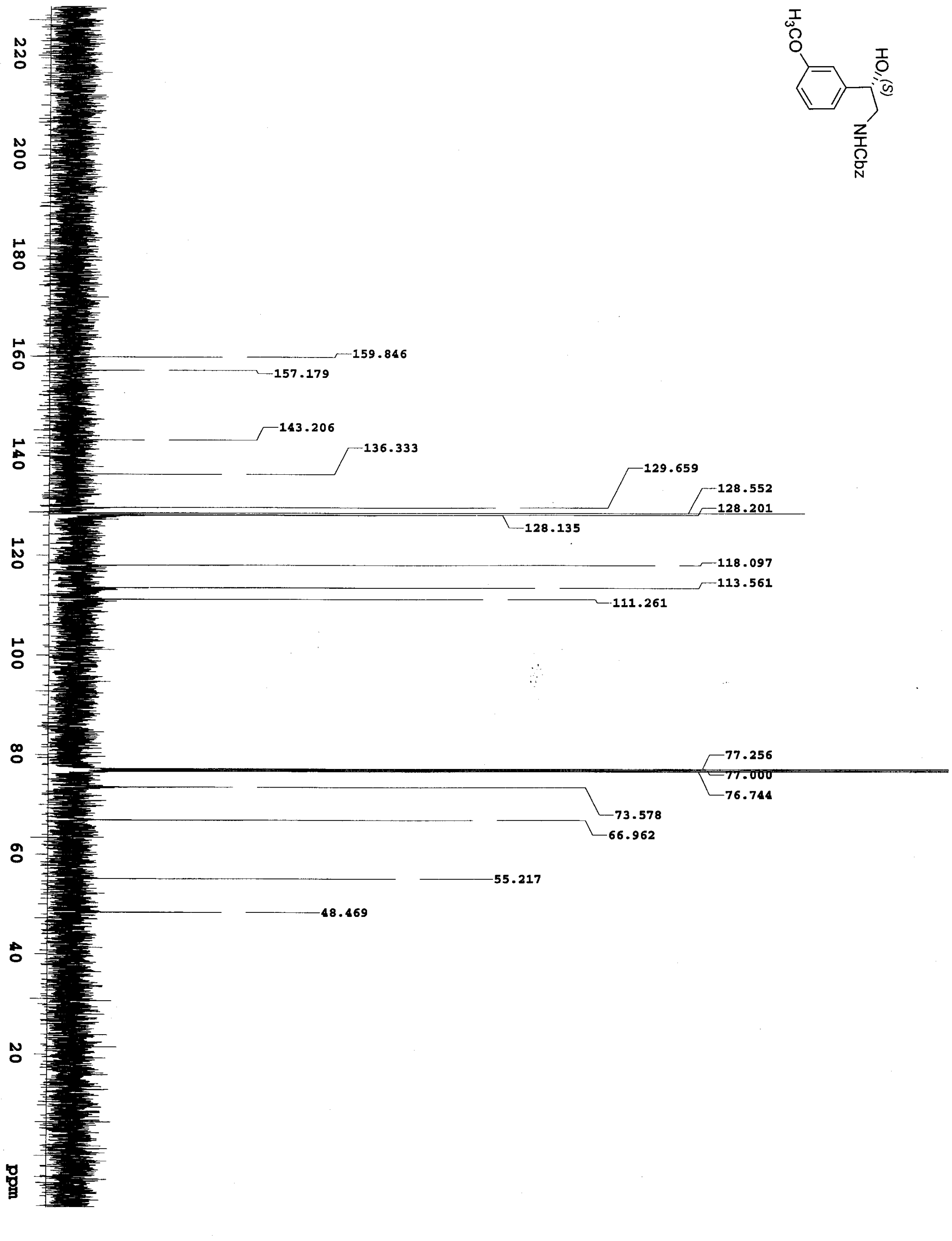
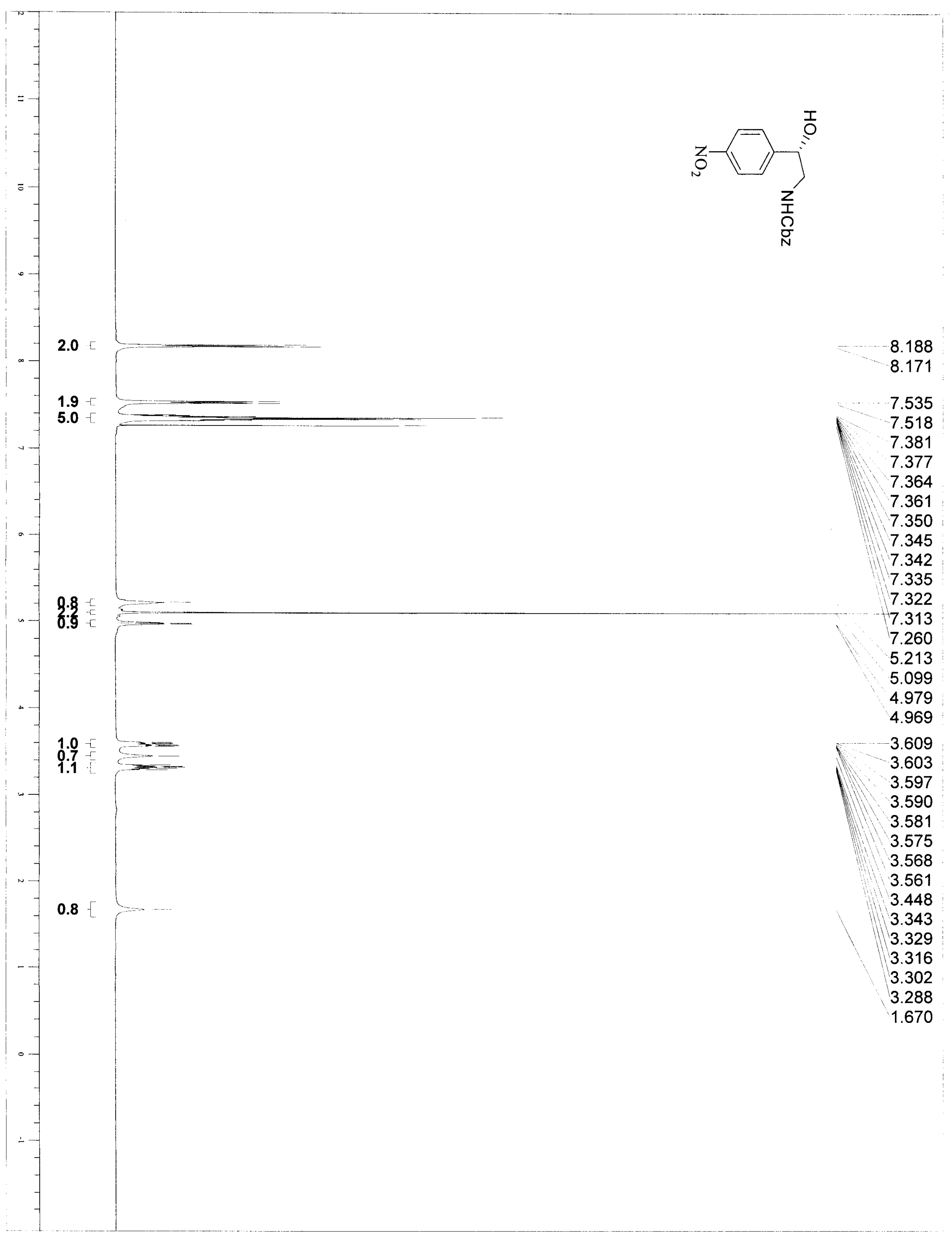
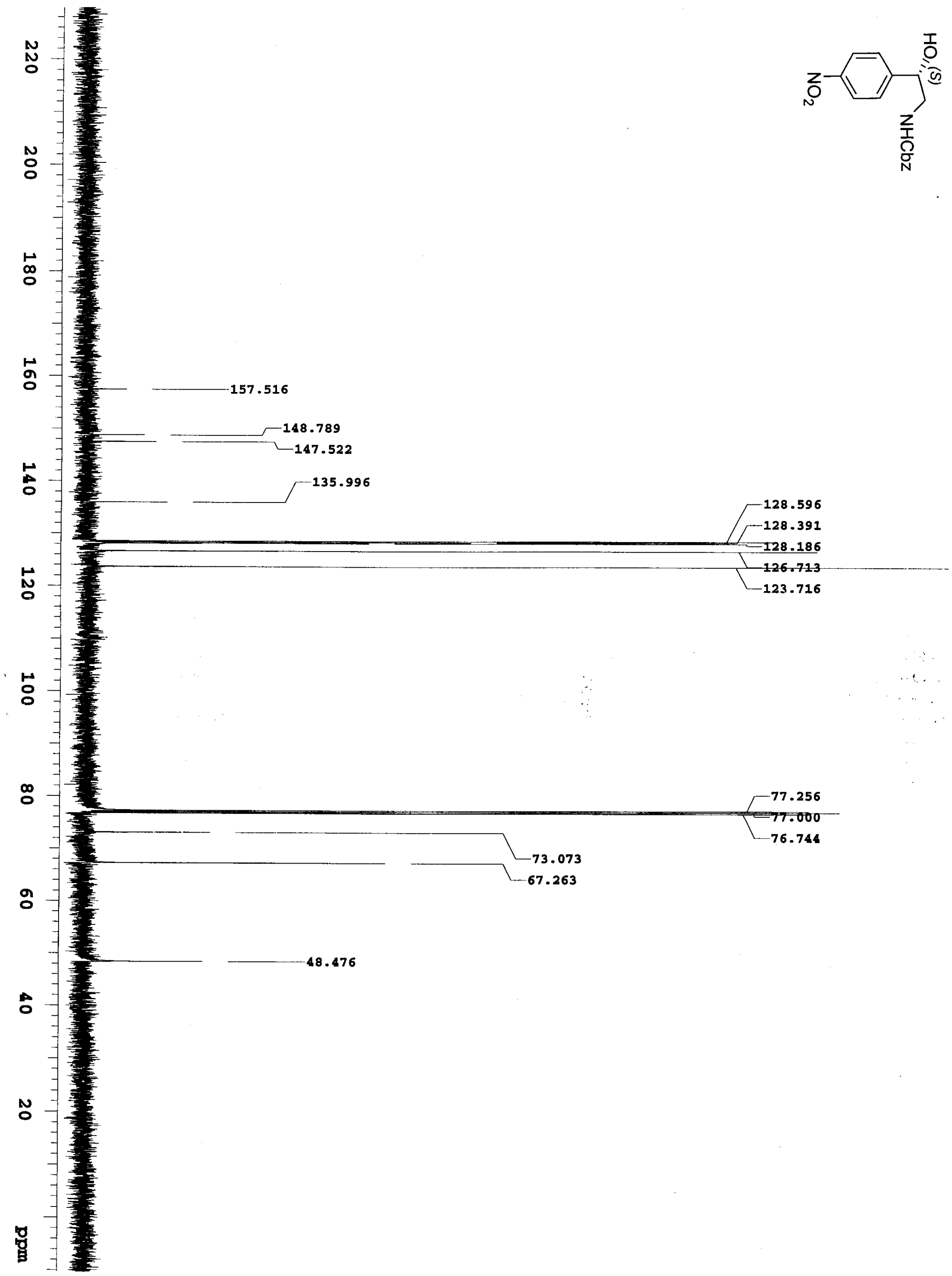
180
160
140
120
100
80
60
40
20
ppm

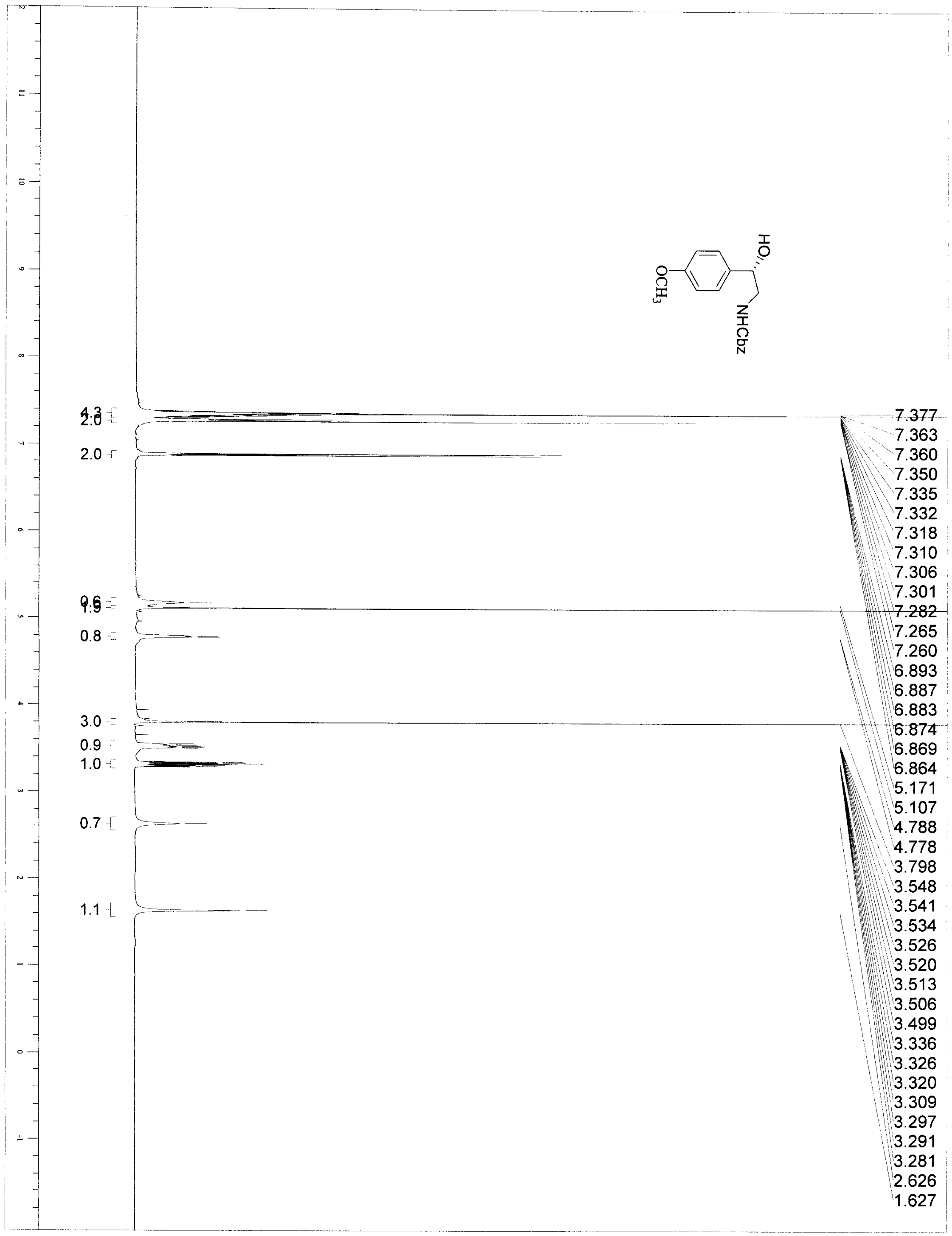

HO
NHCbz
OCH3
4.9
1.4
1.6
0.9
9.6
2.0
0.8
3.0
0.9
1.0
0.8
1.3
7.378
7.368
7.364
7.361
7.336
7.332
7.352
7.328
7.326
7.323
7.319
7.311
7.307
7.302
7.278
7.262
7.260
7.245
6.931
6.931
6.842
6.840
6.837
6.835
6.826
6.824
6.821
6.819
5.176
5.112
4.825
4.815
3.795
3.594
3.586
3.580
3.572
3.566
3.558
3.551
3.545
3.340

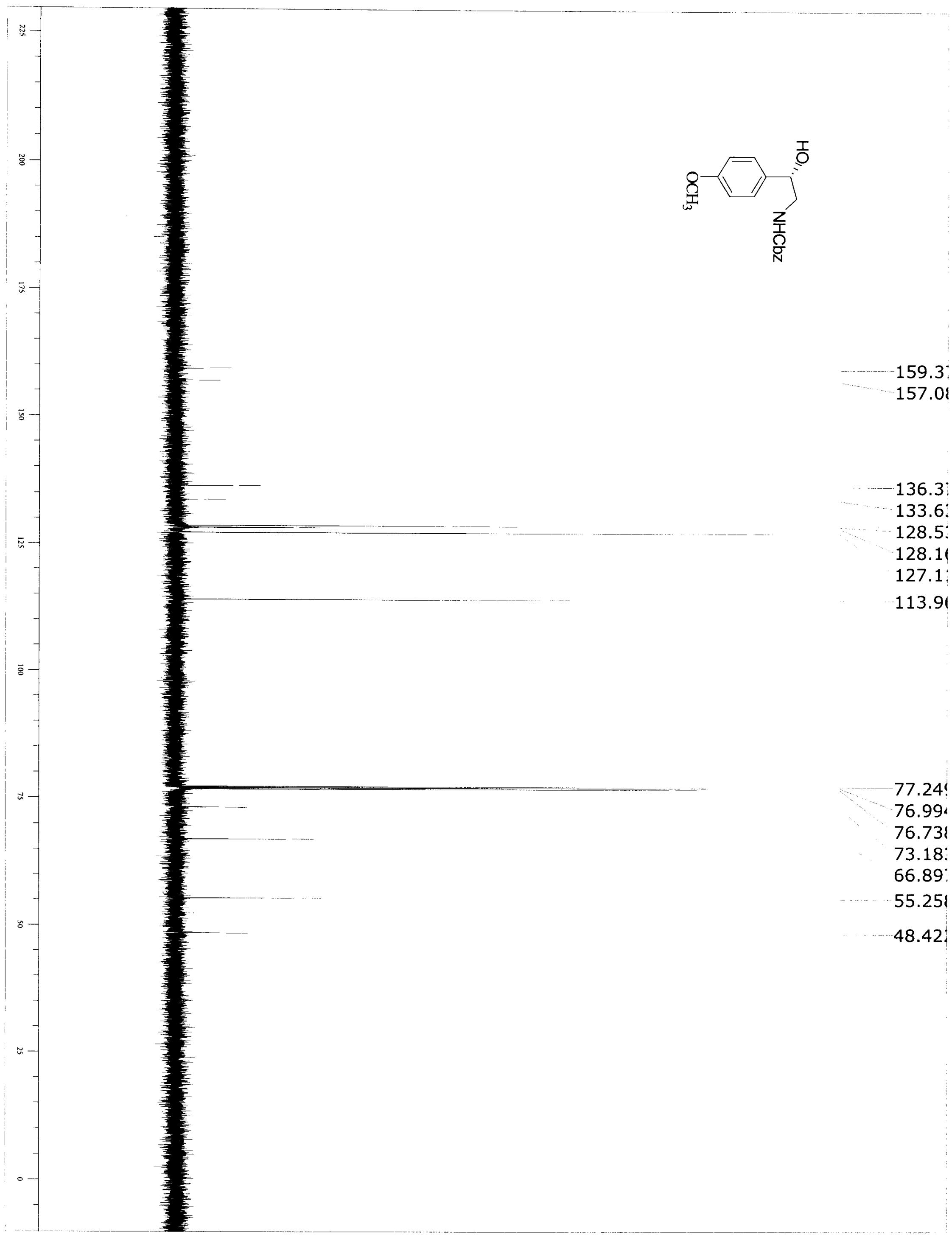


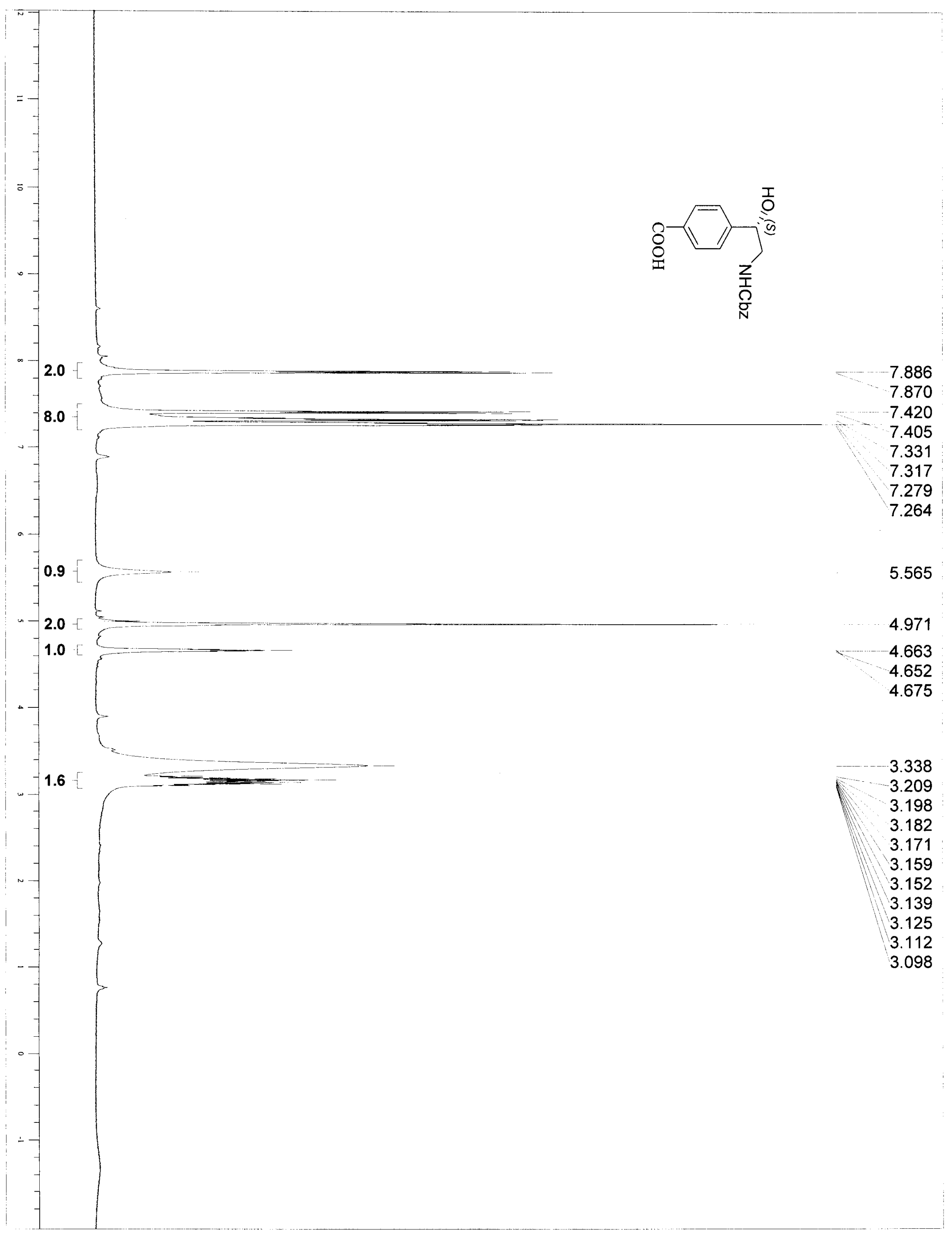
HO,,(S)
NHCbz
H3CO
159.846
157.179
143.206
136.333
129.659
128.552
128.201
128.135
118.097
113.561
111.261
77.256
77.000
76.744
73.578
66.962
55.217
48.469
220
200
180
160
140
120
100
80
60
40
20
ppm

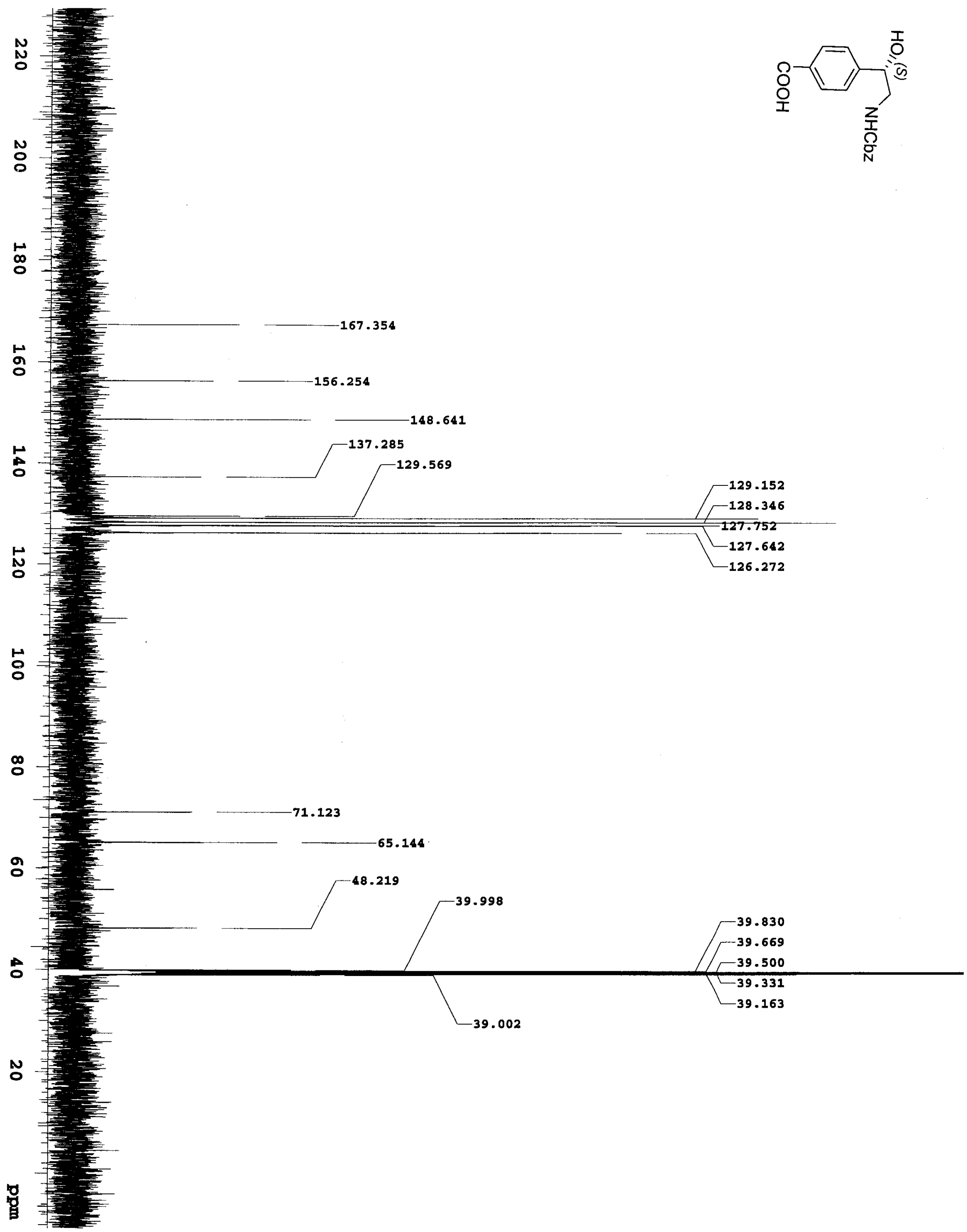

2.0
1.9
5.0
0.8
2.2
0.9
1.0
0.7
1.1
0.8
8.188
8.171
7.535
7.518
7.381
7.377
7.364
7.361
7.350
7.345
7.342
7.335
7.322
7.313
7.260
5.213
5.099
4.979
4.969
3.609
3.603
3.597
3.590
3.581
3.575
3.568
3.561
3.448
3.343
3.329
3.316
3.302
3.288
1.670

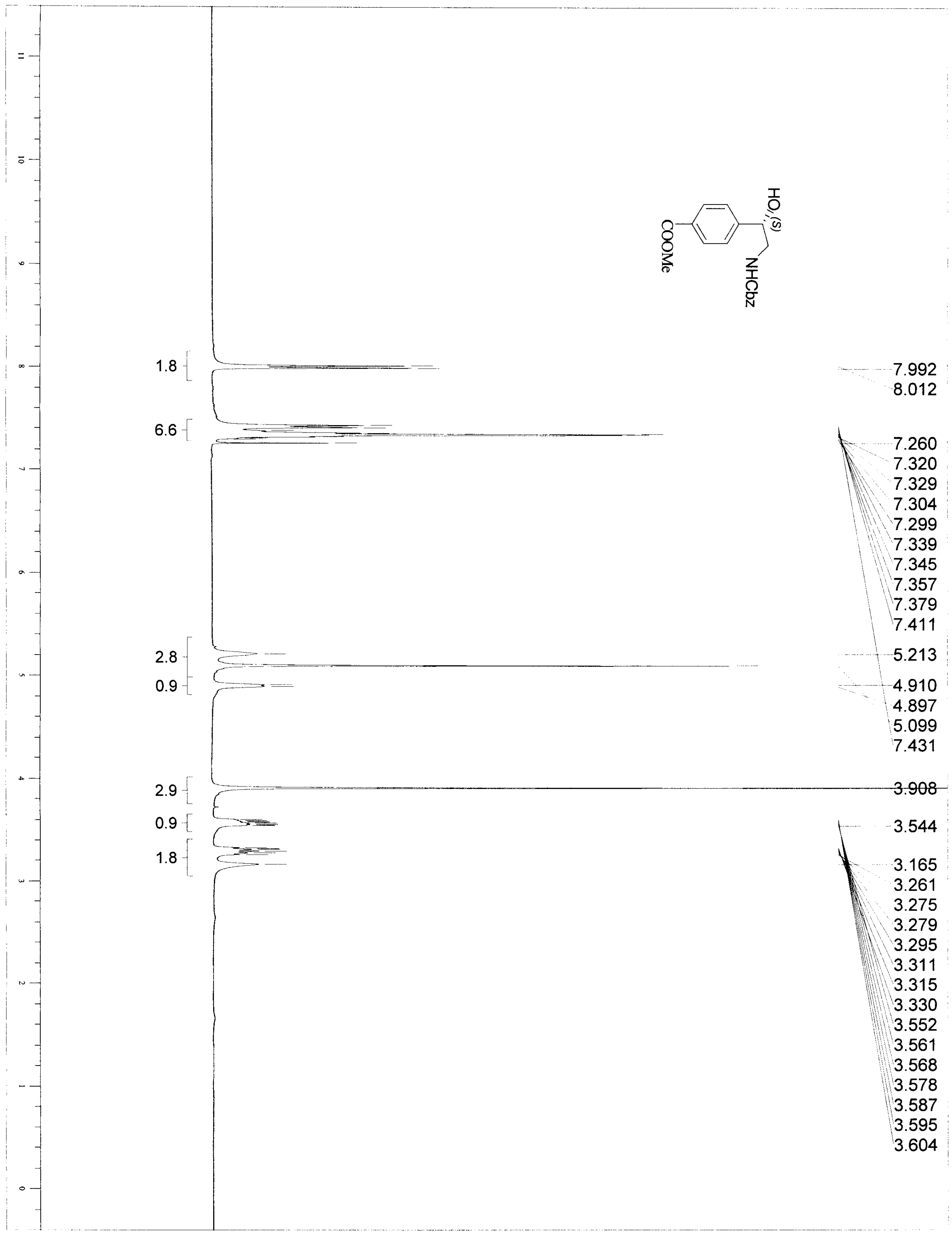

HO
(S)
NHCbz
NO2
157.516
148.789
147.522
135.996
128.596
128.391
128.186
126.713
123.716
77.256
77.000
76.744
73.073
67.263
48.476
220
200
180
160
140
120
100
80
60
40
20
ppm

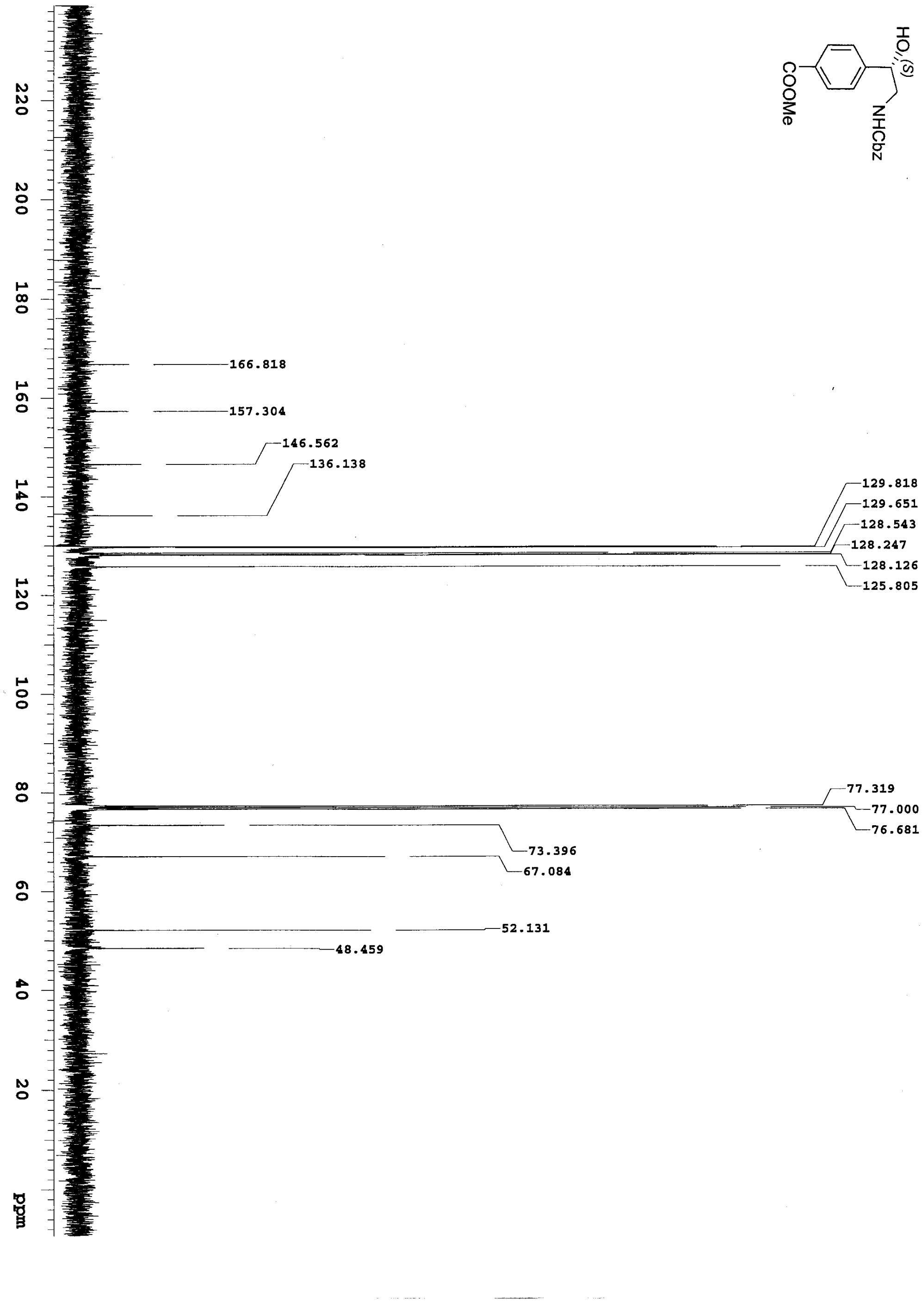

HO
NHCbz
OCH3
4.3
2.0
2.0
0.6
1.9
0.8
3.0
0.9
1.0
0.7
1.1
7.377
7.363
7.360
7.350
7.335
7.332
7.318
7.310
7.306
7.301
7.282
7.265
7.260
6.893
6.887
6.883
6.874
6.869
6.864
5.171
5.107
4.788
4.778
3.798
3.548
3.541
3.534
3.526
3.520
3.513
3.506
3.499
3.336
3.326
3.320
3.309
3.297
3.291
3.281
2.626
1.627

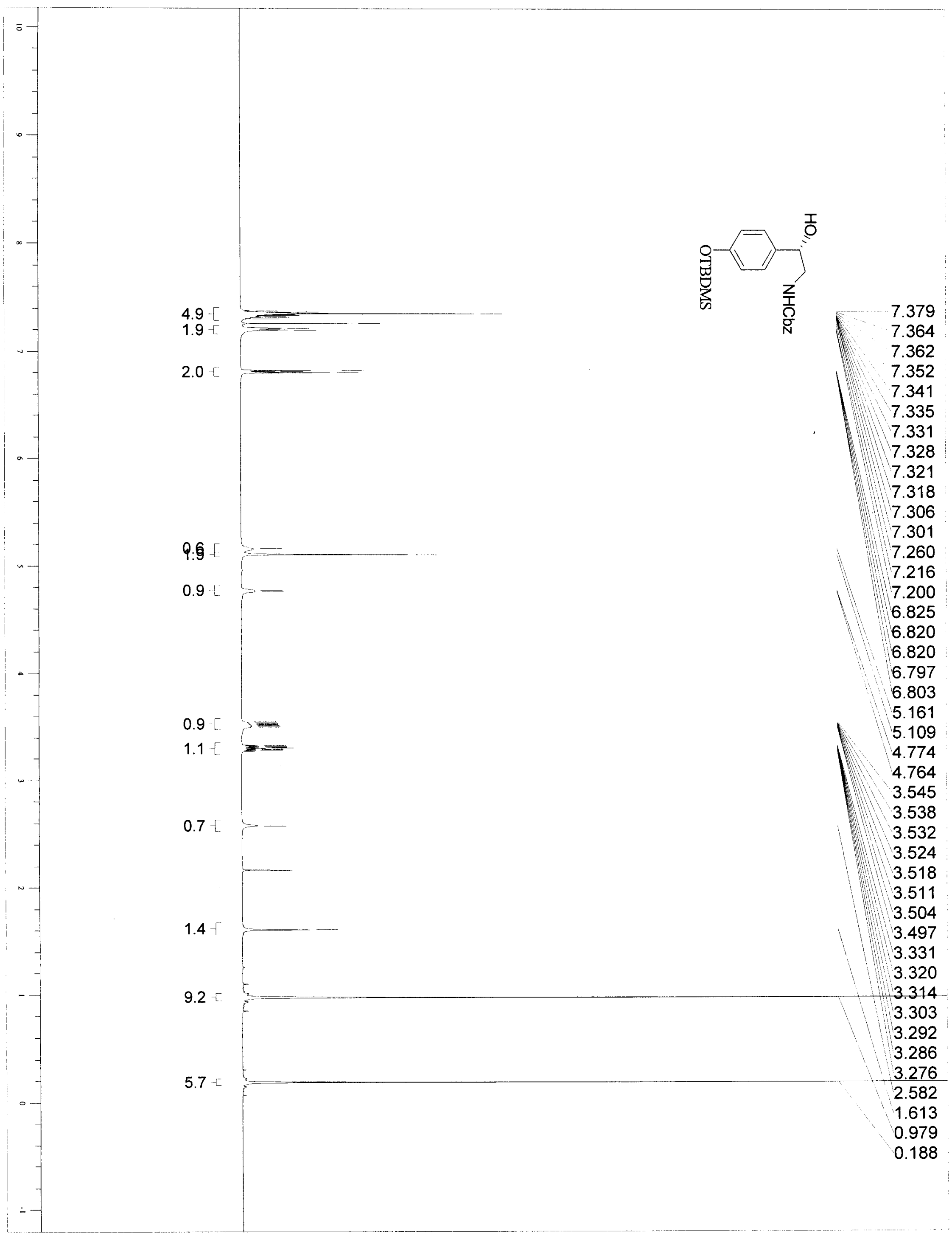

159.3
157.0
136.3
133.6
128.5
128.1
127.1
113.9
77.24
76.99
76.738
73.18
66.89
55.25
48.42
HO
NHCbz
OCH3

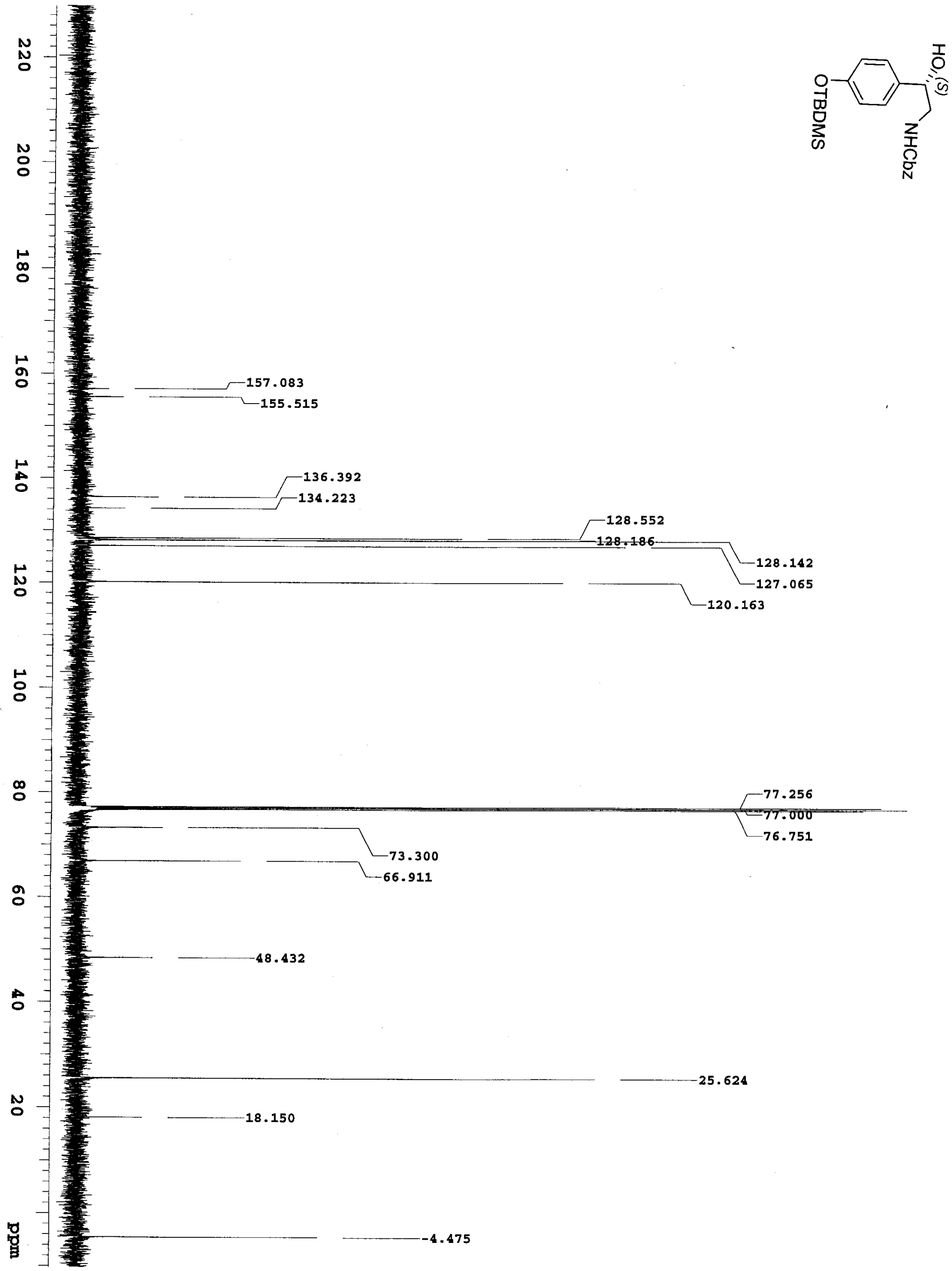

HO,,(S)
NHCbz
COOH
2.0
8.0
0.9
2.0
1.0
1.6
7.886
7.870
7.420
7.405
7.331
7.317
7.279
7.264
5.565
4.971
4.663
4.652
4.675
3.338
3.209
3.198
3.182
3.171
3.159
3.152
3.139
3.125
3.112
3.098

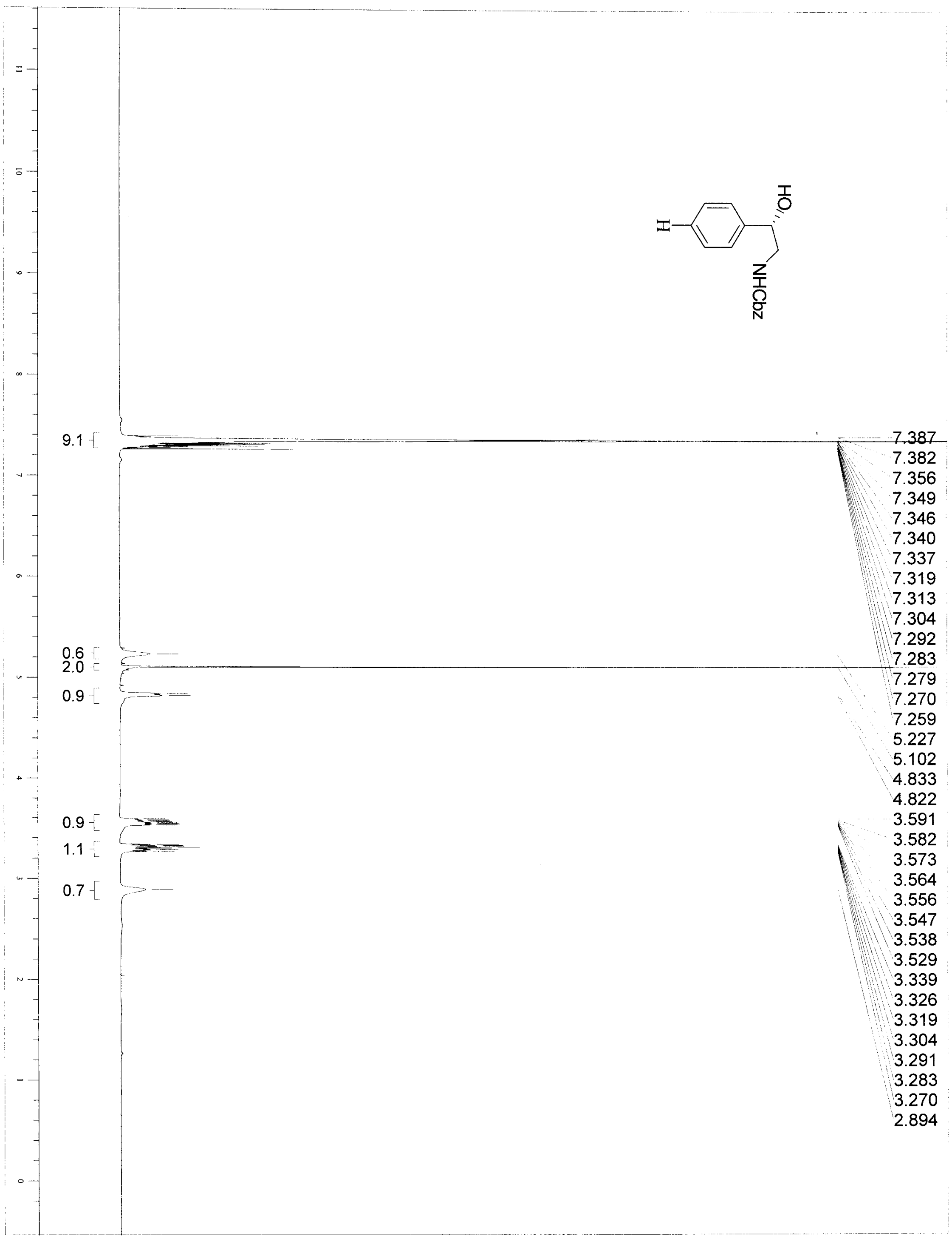

HO,,(S)
NHCbz
COOH
167.354
156.254
148.641
137.285
129.569
129.152
128.346
127.752
127.642
126.272
71.123
65.144
48.219
39.998
39.830
39.669
39.500
39.331
39.163
39.002
220
200
180
160
140
120
100
80
60
40
20
ppm

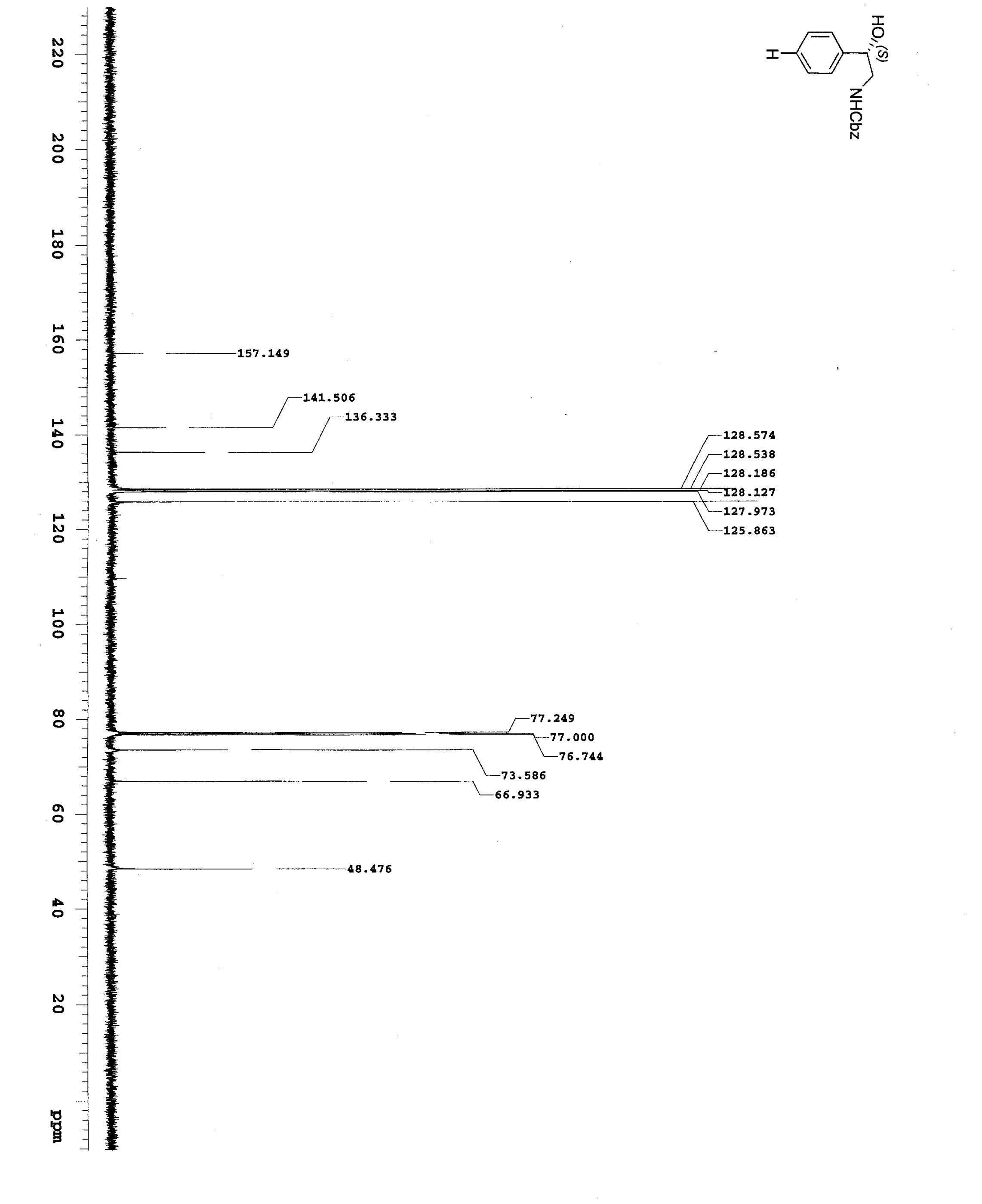

HO,,(S)
NHCbz
COOMe
1.8
6.6
2.8
0.9
2.9
0.9
1.8
7.992
8.012
7.260
7.320
7.329
7.304
7.299
7.339
7.345
7.357
7.379
7.411
5.213
4.910
4.897
5.099
7.431
3.908
3.544
3.165
3.261
3.275
3.279
3.295
3.311
3.315
3.330
3.552
3.561
3.568
3.578
3.587
3.595
3.604

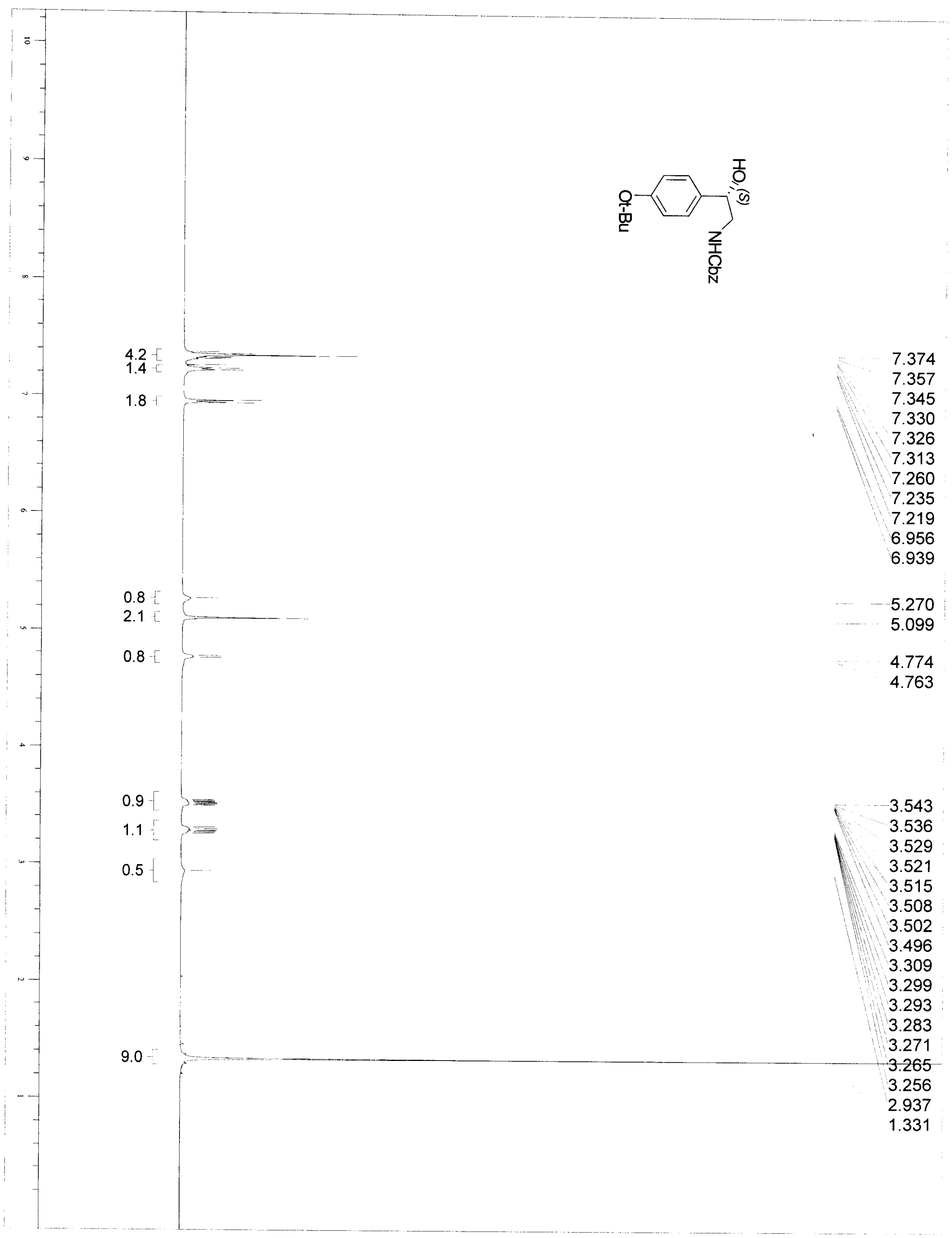

HO,,(S)
NHCbz
COOMe
166.818
157.304
146.562
136.138
129.818
129.651
128.543
128.247
128.126
125.805
77.319
77.000
76.681
73.396
67.084
52.131
48.459
220
200
180
160
140
120
100
80
60
40
20
ppm

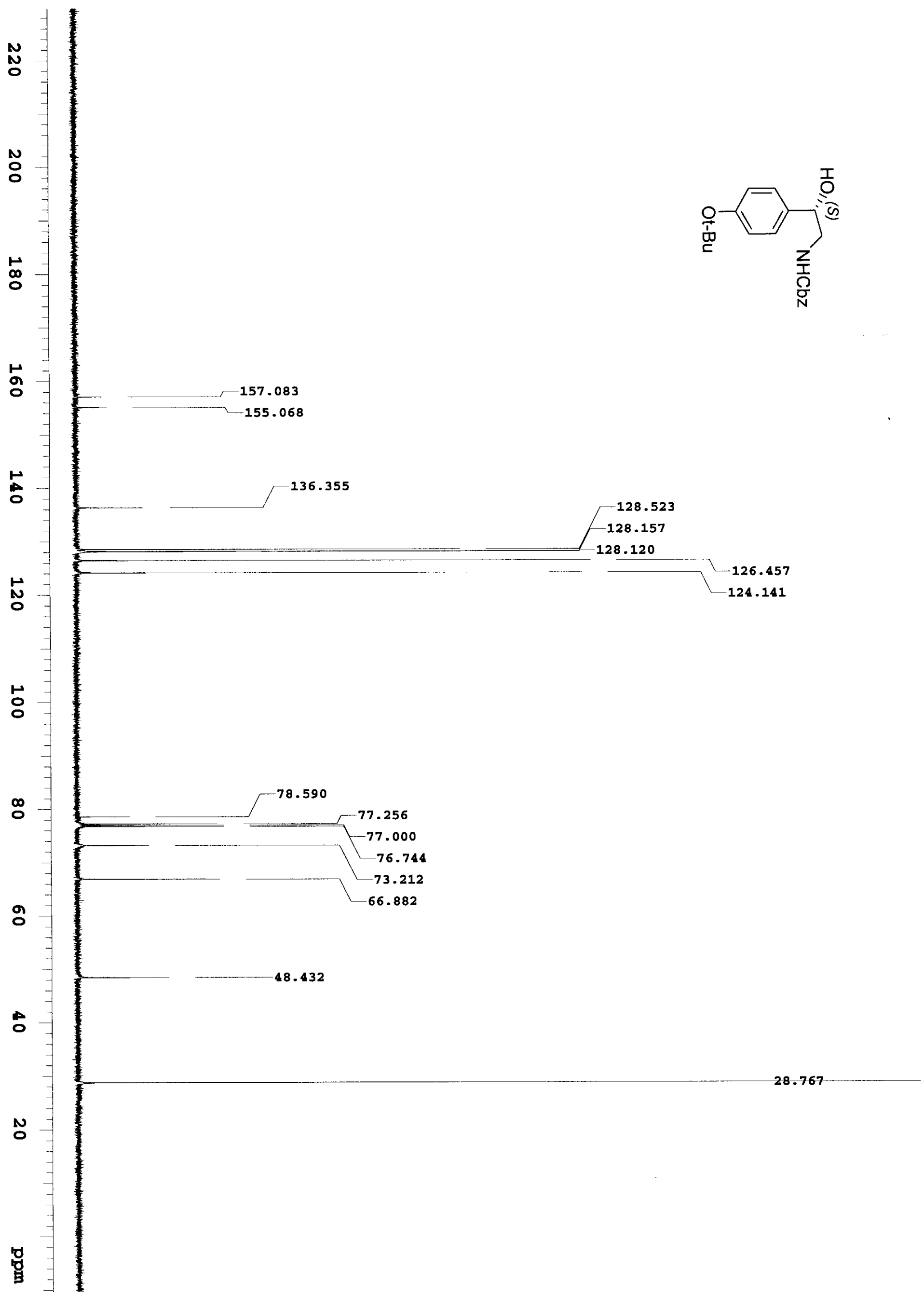

HO
NHCbz
OTBDMS
7.379
7.364
7.362
7.352
7.341
7.335
7.331
7.328
7.321
7.318
7.306
7.301
7.260
7.216
7.200
6.825
6.820
6.820
6.797
6.803
5.161
5.109
4.774
4.764
3.545
3.538
3.532
3.524
3.518
3.511
3.504
3.497
3.331
3.320
3.314
3.303
3.292
3.286
3.276
2.582
1.613
0.979
0.188
4.9
1.9
2.0
0.6
1.9
0.9
0.9
1.1
0.7
1.4
9.2
5.7


HO,,(S)
NHCbz
OTBDMS
157.083
155.515
136.392
134.223
128.552
128.186
128.142
127.065
120.163
77.256
77.000
76.751
73.300
66.911
48.432
25.624
18.150
-4.475
220
200
180
160
140
120
100
80
60
40
20
ppm


HO
NHCbz
H
9.1
0.6
2.0
0.9
0.9
1.1
0.7
7.387
7.382
7.356
7.349
7.346
7.340
7.337
7.319
7.313
7.304
7.292
7.283
7.279
7.270
7.259
5.227
5.102
4.833
4.822
3.591
3.582
3.573
3.564
3.556
3.547
3.538
3.529
3.339
3.326
3.319
3.304
3.291
3.283
3.270
2.894


HO,,(S)
NHCbz
H
157.149
141.506
136.333
128.574
128.538
128.186
128.127
127.973
125.863
77.249
77.000
76.744
73.586
66.933
48.476
220
200
180
160
140
120
100
80
60
40
20
ppm


HO,,(S)
NHCbz
Ot-Bu
4.2
1.4
1.8
0.8
2.1
0.8
0.9
1.1
0.5
9.0
7.374
7.357
7.345
7.330
7.326
7.313
7.260
7.235
7.219
6.956
6.939
5.270
5.099
4.774
4.763
3.543
3.536
3.529
3.521
3.515
3.508
3.502
3.496
3.309
3.299
3.293
3.283
3.271
3.265
3.256
2.937
1.331

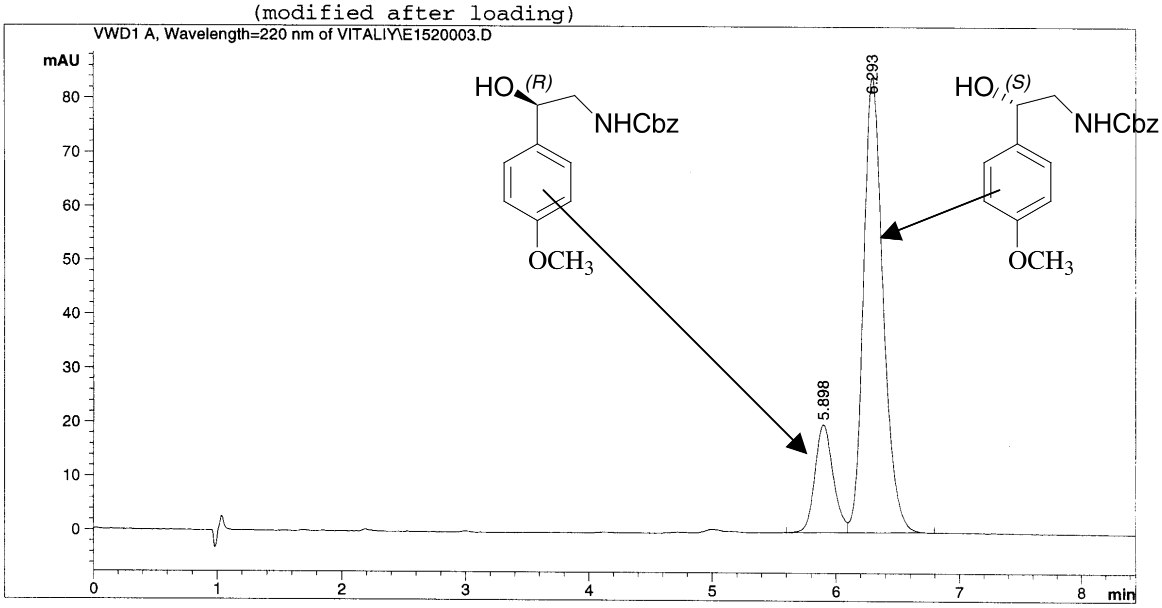

HO
(S)
NHCbz
Ot-Bu
157.083
155.068
136.355
128.523
128.157
128.120
126.457
124.141
78.590
77.256
77.000
76.744
73.212
66.882
48.432
28.767
220
200
180
160
140
120
100
80
60
40
20
ppm

OD Column, 3.0 mL/min, 15.0% MeOH, 125 psi, runtime 8 m
in

===

Acq. Method	: ODTEST.M	Seq. Line :	-
Acq. Operator	: Vitaliy	Vial :	2000
Injection Date	: 9/25/2002 3:36:37 PM	Inj :	-
Sample Name	: Exp 152.3	Inj Volume :	Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M
(modified after loading)



===

Area Percent Report

===

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	5.898	BF	0.156	205.83530	20.01750	18.0921
2	6.293	FB	0.168	931.87384	84.19759	81.9079

Totals : 1137.70911 104.21509

===

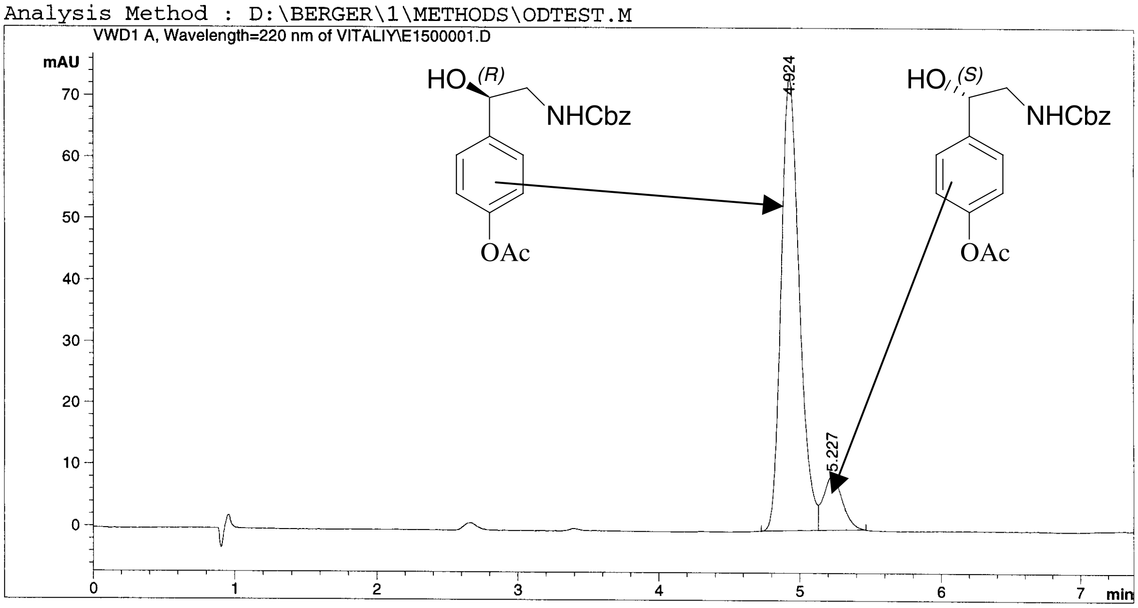
*** End of Report ***

OD column, 125 psi , 15.0 mol% MeOH, 3ml/min runtime 8 min

===

Acq. Method	: ODTEST.M	Seq. Line :	-
Acq. Operator	: Vitaliy	Vial :	2000
Injection Date	: 9/19/2002 11:36:20 PM	Inj :	-
Sample Name	: Exp150 f15-20	Inj Volume :	Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M



===

Area Percent Report

===

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.924	BV	0.138	659.31647	73.35968	88.8999
2	5.227	VB	0.142	82.32267	8.71021	11.1001

Totals : 741.63916 82.06989

===

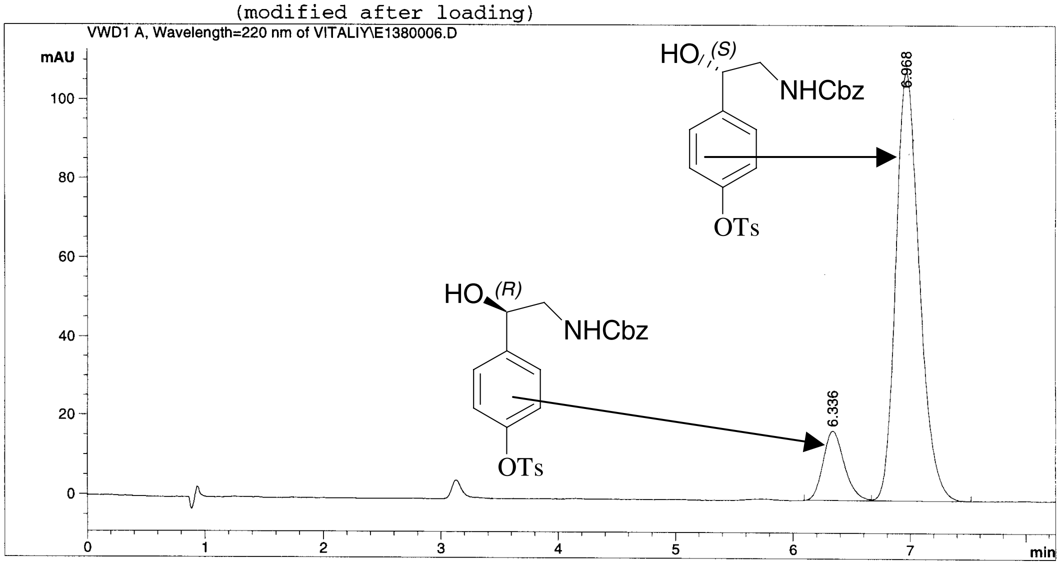
*** End of Report ***

This experiment was performed using the $(DHQD)_2AQN$ ligand.

OD column, 3.0 mL/min, 10.0 % MeOH, 125 psi 10 min run time

==
Acq. Method : ODTEST.M Seq. Line : -
Acq. Operator : Vitaliy Vial : 2000
Injection Date : 9/3/2002 10:42:13 PM Inj : -
Sample Name : Exp138.6 f9-13 Inj Volume : Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M
(modified after loading)



==
Area Percent Report
==

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	6.336	BF	0.178	217.84041	17.33973	12.4710
2	6.968	FB	0.216	1528.93652	108.25066	87.5290
Totals :				1746.77698	125.59039	

75.1% ee

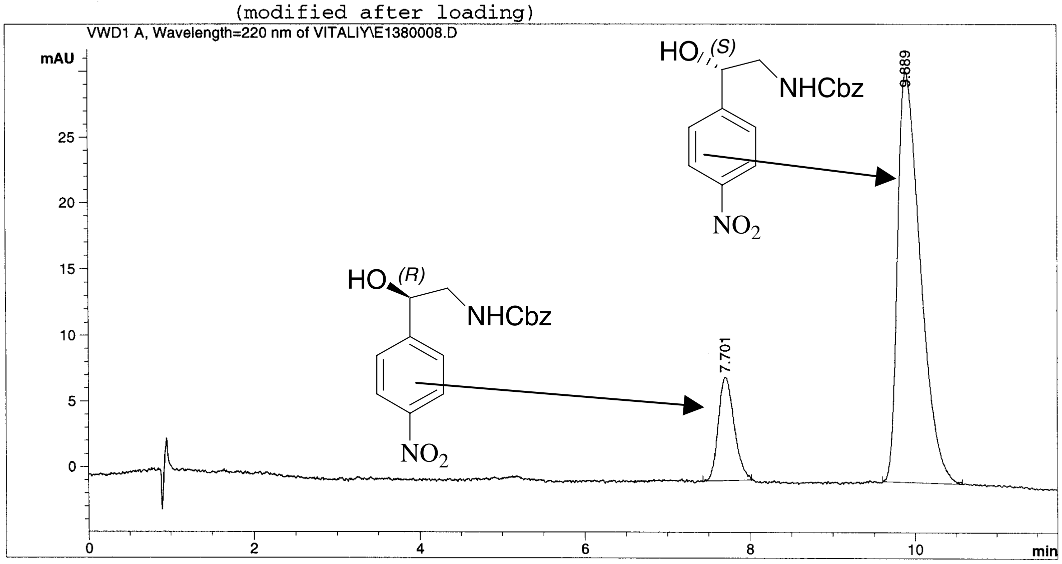
==
*** End of Report ***

OD column, 3 mL/min, 15 % MeOH, 125 bar 10 min runtime

10% ee

```
=====================================================================
Acq. Method      : ODTEST.M                          Seq. Line :  -
Acq. Operator    : Vitaliy                                Vial :  2000
Injection Date   : 9/10/2002 4:14:59 PM                    Inj :  -
Sample Name      : Exp138.8                         Inj Volume :  Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M
                  (modified after loading)
```




```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted by Signal
Multiplier              :      1.000000

Signal 1: VWD1 A, Wavelength=220 nm
```

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	7.701	BV	0.165	105.86246	7.90220	14.9079
2	9.889	BB	0.234	604.24872	31.14318	85.0921

Totals : 710.11121 39.04538

```
=====================================================================
                        *** End of Report ***
```

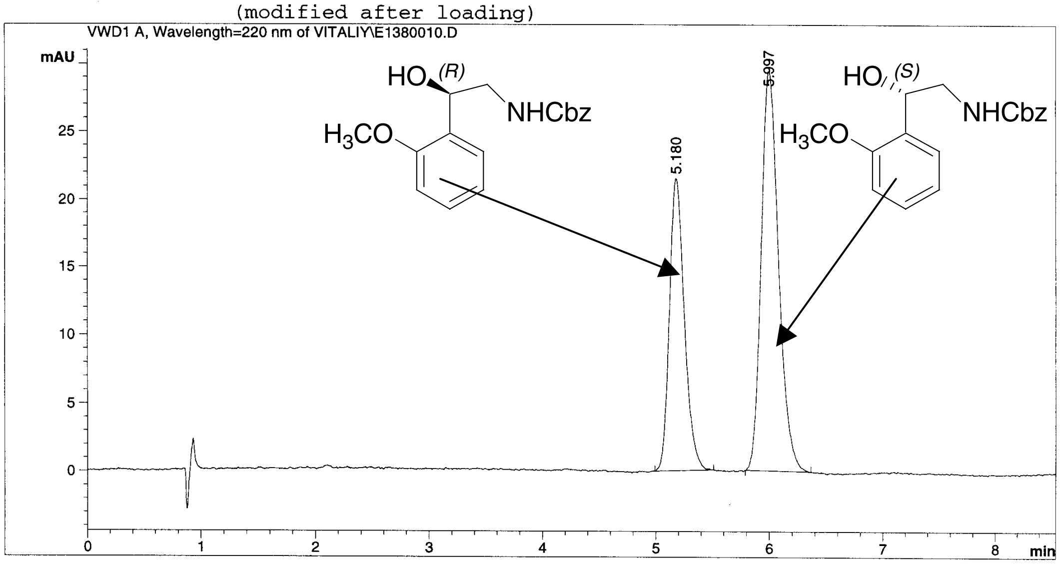
OD column, 3 mL/min, 15 % MeOH, 125 bar 15 min runtime

==

Acq. Method	: ODTEST.M	Seq. Line :	-
Acq. Operator	: Vitaliy	Vial :	2000
Injection Date	: 9/10/2002 4:39:20 PM	Inj :	-
Sample Name	: Exp138.10	Inj Volume :	Unknown

22.8% ee

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M
(modified after loading)



==
Area Percent Report
==

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	5.180	BB	0.132	196.99025	21.50577	38.6399
2	5.997	BB	0.153	312.81970	29.37704	61.3601
Totals :				509.80994	50.88281	

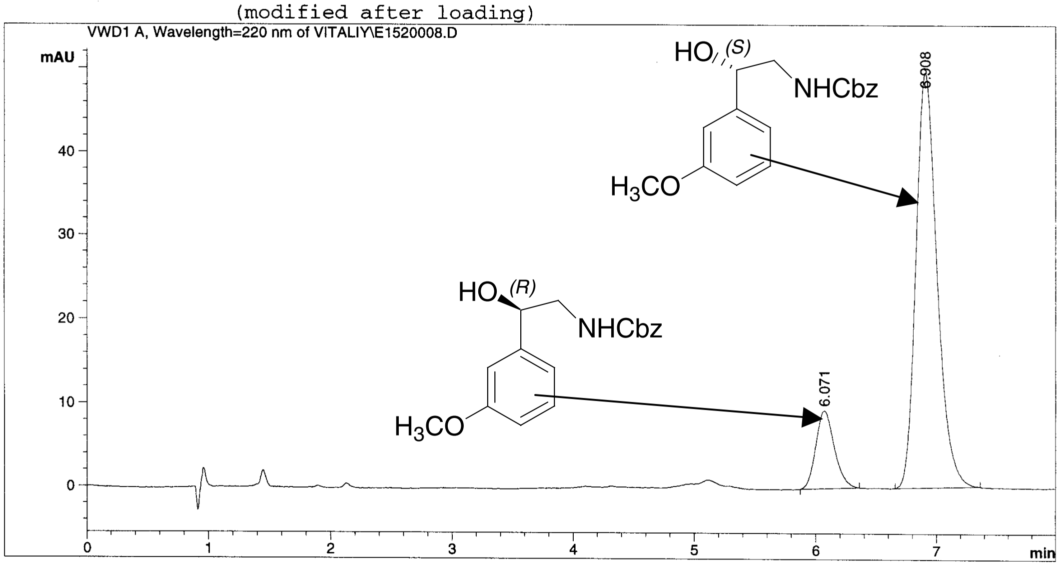
==
*** End of Report ***

OD column, 15mol% MeOH, 125 bar runtime 10 min

===

Acq. Method	: ODTEST.M	Seq. Line :	-
Acq. Operator	: Vitaliy	Vial :	2000
Injection Date	: 10/4/2002 8:48:42 PM	Inj :	-
Sample Name	: Exp 152.8 f22	Inj Volume :	Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M
(modified after loading)



===

Area Percent Report

===

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	6.071	BB	0.141	99.72226	9.35531	14.0542
2	6.908	BB	0.183	609.83044	49.56192	85.9458

Totals : 709.55273 58.91723

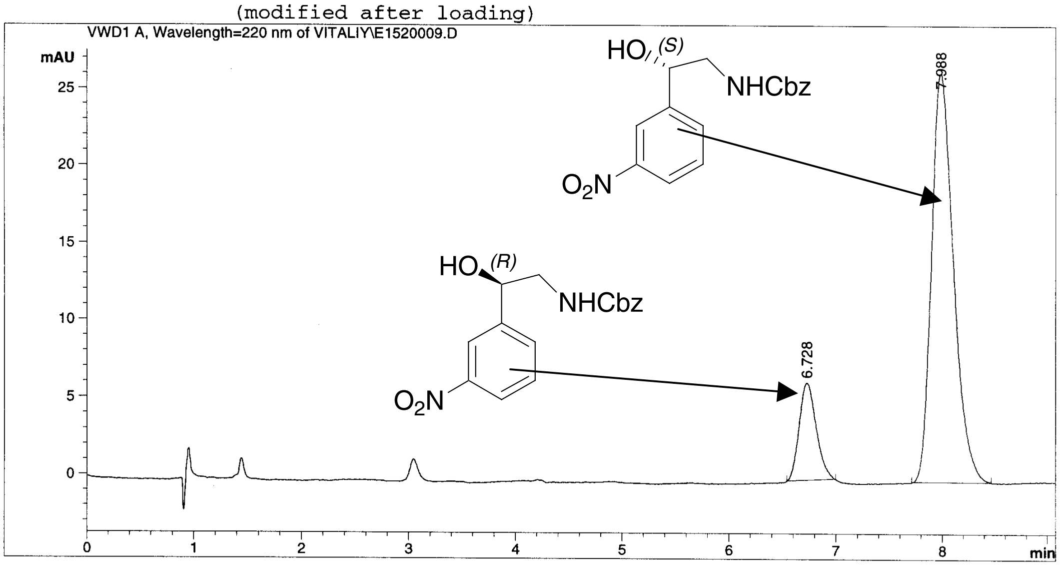
===

*** End of Report ***

```
OD column, 15mol% MeOH, 125 bar runtime 12 min

=====================================================================
Acq. Method      : ODTEST.M                          Seq. Line :  -
Acq. Operator    : Vitaliy                                Vial : 2000
Injection Date   : 10/4/2002 8:58:12 PM                    Inj :  -
Sample Name      : Exp 152.9  f16                   Inj Volume : Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M
                  (modified after loading)
```




```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted by Signal
Multiplier               :      1.000000

Signal 1: VWD1 A, Wavelength=220 nm
```

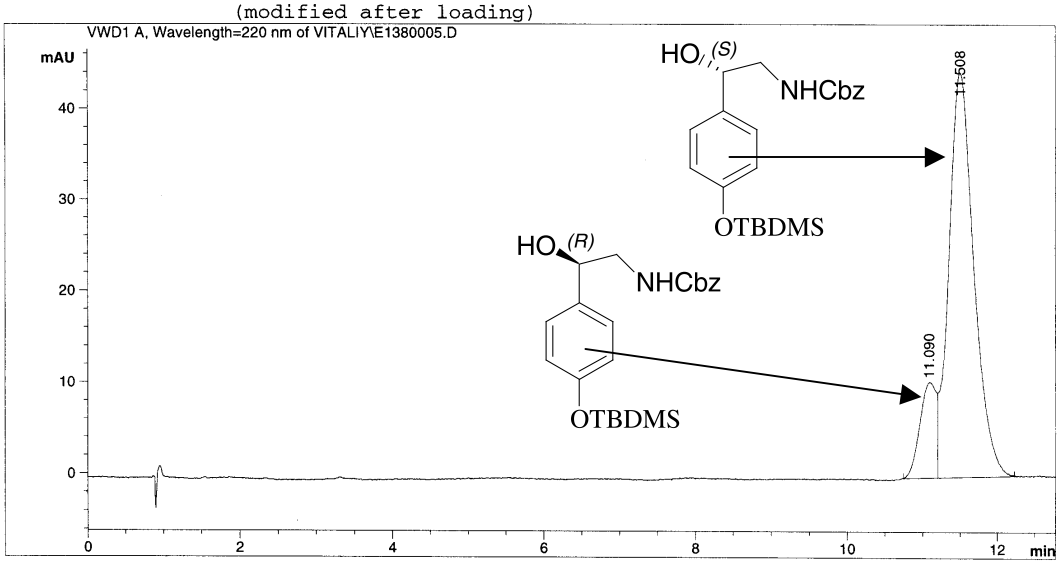
Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	6.728	BB	0.145	70.34304	6.29978	15.5069
2	7.988	BB	0.217	383.28058	26.47479	84.4931
Totals :				453.62363	32.77457	

```
=====================================================================
                         *** End of Report ***
```

OD column, 3.0 mL/min, 8.0 % MeOH, 125 psi 10 min runt
ime

```
=====================================================================
Acq. Method     : ODTEST.M                          Seq. Line :  -
Acq. Operator   : Vitaliy                                Vial : 2000
Injection Date  : 9/3/2002 10:54:10 PM                    Inj :  -
Sample Name     : Exp138.5 f11-15                  Inj Volume : Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M
                  (modified after loading)
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted by Signal
Multiplier          :     1.000000

Signal 1: VWD1 A, Wavelength=220 nm
```

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	11.090	BF	0.196	160.11591	10.49396	13.4621
2	11.508	FV	0.276	1029.26306	44.31294	86.5379

73.1% ee

Totals : 1189.37891 54.80691

```
=====================================================================
                      *** End of Report ***
```

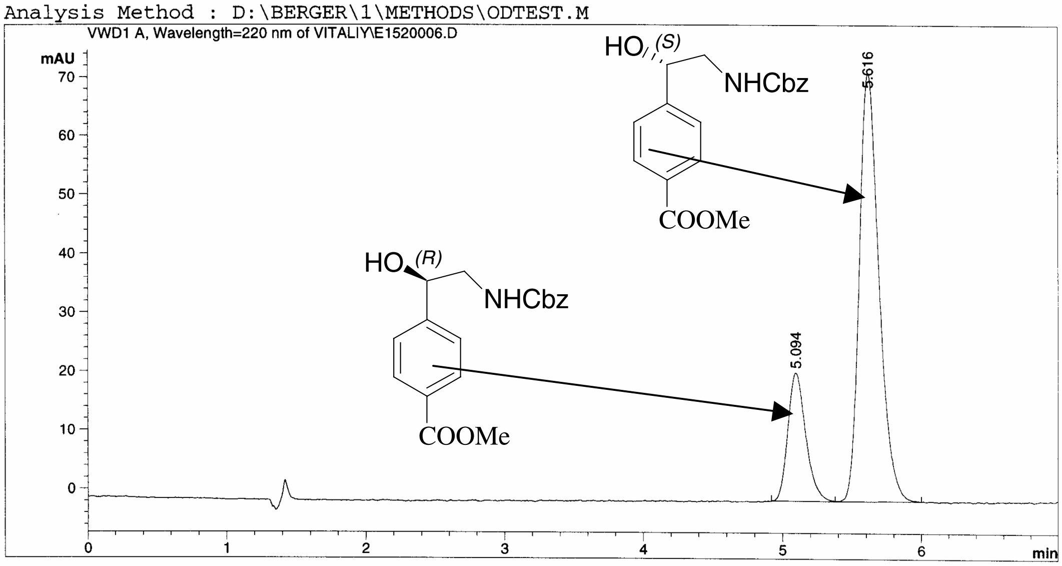
OD Column, 3.0 mL/min, 15.0% MeOH, 125 bar, runtime 7 min, after CH2N2 and column

==

Acq. Method : ODTEST.M
Acq. Operator : Vitaliy
Injection Date : 10/19/2002 7:12:56 PM
Sample Name : Exp152 f18-19

Seq. Line : -
Vial : 2000
Inj : -
Inj Volume : Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M



==

Area Percent Report

==

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	5.094	BV	0.113	193.44881	21.76159	21.2299
2	5.616	PV	0.143	717.76093	72.75037	78.7701

57.5 % ee

Totals : 911.20972 94.51197

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*** End of Report ***

OD Column, 3.0 mL/min; 15% MeOH, 125 ba

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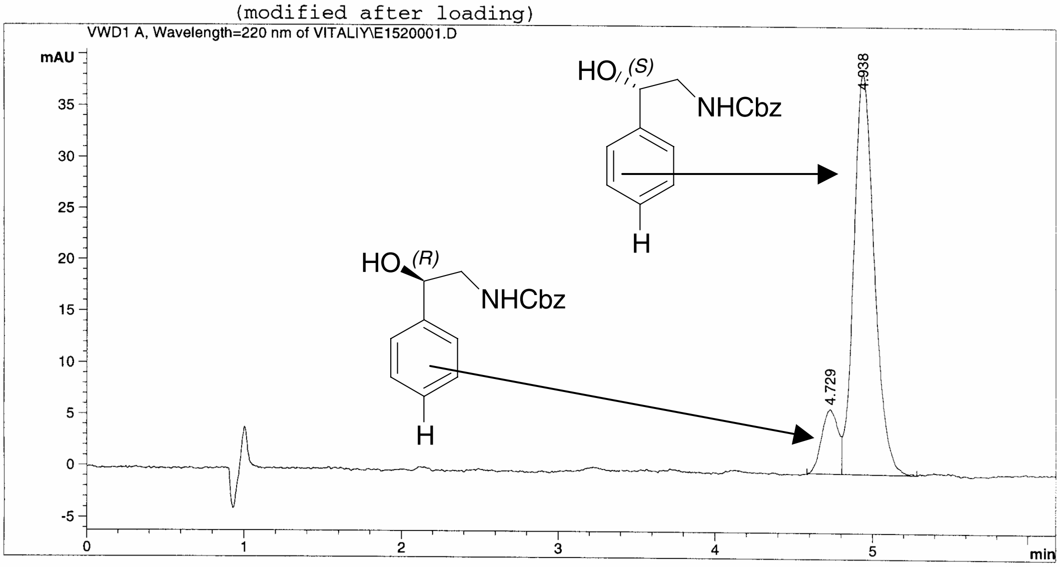
Acq. Method	: ODTEST.M	Seq. Line	: -
Acq. Operator	: Vitaliy	Vial	: 2000
Injection Date	: 11/1/2002 12:22:41 AM	Inj	: -
Sample Name	: Exp152.1	Inj Volume	: Unknown

Analysis Method : D:\BERGER\1\METHODS\ODTEST.M
(modified after loading)



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Area Percent Report

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Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.729	BF	0.090	46.13737	6.32001	11.4638
2	4.938	FB	0.132	356.32352	38.88392	88.5362
Totals :				402.46088	45.20393	

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*** End of Report ***