Table of Contents

1. Syntheses of starting materials

2. General procedure for the phosphoric acid catalyzed kinetic resolution and characterization data of secondary amines

3. Synthesis of (*R*)-Angustureine and (*R*)-Galipinine

3. ^{1}H NMR, ^{13}C NMR, and HPLC data of the reaction products and new compounds

General. NMR spectra were recorded on Unity Inova-400 instrument (Varian Inc., 400 MHz for ^{1}H, 100 MHz for ^{13}C) using $CDCl_3$ as a solvent. Tetramethylsilane (TMS) ($\delta = 0$) or $CHCl_3$ ($\delta = 7.26$) served as an internal standard for ^{1}H NMR, and $CDCl_3$ was used as an internal standard ($\delta = 77.0$) for ^{13}C NMR. Melting point (mp) determinations were performed by using a AS ONE ATM-01 instrument and are uncorrected. Infrared (IR) spectra were recorded on a FTIR-8600PC instrument (Shimadzu Co.). Electron spray ionization (ESI) mass spectra were recorded on a Shimadzu LCMS_2010 eV spectrometer or Bruker Daltonics microTOF_15 focus. EI mass spectra were recorded on JEOL GCmate™ II GC/MS Double-Focusing Mass Spectrometer. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. Purification of the products was performed by column chromatography on silica gel (Fuji sylisia PSQ-60B) or preparative TLC on silica gel (Wako gel B-5F). All solvents were purified according to the standard procedures.

1. Syntheses of starting materials

Syntheses of 2-alkyl substituted tetrahydroquinolines (2a-2d)

2-Alkyl substituted tetrahydroquinolines **2a-2d** were synthesized according to literature procedure.[1] 2-Aminobenzyl alcohol (10 mmol) and ketone (20 mmol), KOH (30 mmol), and $Pd(OAc)_2$ (0.20 mmol) was mixed in toluene (30 mL). After being stirred for 1 d at reflux, the mixture was filtered through Celite (washed with CH_2Cl_2). The filtrate was concentrated under reduced pressure and the residue was purified by silica-gel flash column chromatography to afford 2-alkyl substituted quinoline. The quinoline was dissolved to AcOH (0.2 M) and $NaBH_3CN$ (2.5 equiv) was added at room temperature. After being stirred for 1 day, the reaction was quenched by adding saturated Na_2CO_3 aq. The mixture was extracted with CH_2Cl_2 three times and the combined organic phase was dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography to afford 2-alkyl substituted

tetrahydroquinoline.

Syntheses of 2-aryl substituted tetrahydroquinolines (2e-2n)

2-Aryl substituted tetrahydroquinolines **2e-2n** were synthesized according to literature procedure.[2] 2-Chloro quinolone (5.3 mmol), aryl boronic acid (6.7 mmol), and Na_2CO_3 (26.5 mmol) was dissolved in distilled H_2O (10 mL) with 1,4-dioxane (40 mL) under inert atmosphere. $Pd(PPh_3)_4$ (0.050 mmol) was quickly added to the mixture and the mixture was refluxed for 1 day. After Celite filtration (washed with AcOEt), the mixture was extracted with AcOEt three times. The combined organic phase was washed with brine, dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue was directly used for next step without further purification.

The crude mixture was dissolved in AcOH (25 mL), and $NaBH_3CN$ (10.6 mmol) was added at room temperature. After being stirred for 1 day, the reaction was quenched by adding saturated Na_2CO_3 aq. The mixture was extracted with CH_2Cl_2 three times and the combined organic phase was dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography.

Syntheses of 2-substituted dihydrobenzoxazines (5a and 5b)

2-Substituted dihydrobenzoxazines **5a** and **5b** were synthesized according to literature procedure.[3] Phenacyl bromide derivative (4 mmol), K_2CO_3 (16 mmol), and tetrabutylammonium bromide were dissolved in CH_2Cl_2 (40 mL) and distilled H_2O (10 mL). 2-Aminophenol was added to the mixture and the mixture was warmed to 50 ^oC. After being stirred for 4 d, the mixture was extracted with CH_2Cl_2 three times, dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography to give benzoxazine derivative.

The benzoxazine derivative (3.0 mmol) was dissolved in EtOH (30 mL). $NaBH_4$ (9 mmol) was added to the solution and the mixture was stirred at reflux for 1 d. The reaction was quenched by adding H_2O. The mixture was extracted with CH_2Cl_2 three times, dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography to give dihydrobenzoxazine derivative.

Synthesis of 2-substituted dihydrobenzothiazine (5c)

2-Substituted dihydrobenzothiazine **5c** was synthesized by the following procedure.

Phenacyl bromide derivative (5 mmol) was dissolved in DMF (10 mL) and AcOH (0.2 mL). 2-Aminothiophenol (5 mmol) was added to the solution and the solution was stirred for 30 min. $NaBH_3CN$ was added to the mixture and the mixture was stirred for 14 h. The reaction was quenched by adding saturated $NaHCO_3$ aq and the mixture was extracted with AcOEt three times. The combined organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by silica-gel flash column chromatography.

Synthesis of 2-substituted tetrahydroazepine (5d)

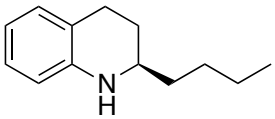
2-Substituted tetrahydroazepine **5d** was synthesized according to literature procedure.[4]

2-Iodoaniline (5 mmol), homoallyl alcohol (5 mmol), *i*-Pr_2NEt (40 mmol), LiCl (15 mmol) and Pd $(OAc)_2$ (0.25 mmol) were mixed in DMF (50 mL) under inert atmosphere. After being stirred at 120 ^oC for 12 h, water was added to the mixture. The mixture was extracted with AcOEt three times and the combined organic phase was concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography.

2. General procedure and for the phosphoric acid catalyzed kinetic resolution and characterization data of secondary amines

A typical procedure for the reaction of racemic **2a** is described.

A magnetic stirring bar and powdered molecular sieves 5Å (5Å MS) (50 mg) were placed in a test tube (TT) under nitrogen atmosphere. The 5Å MS were then dried with a heat gun under reduced pressure, and the TT was refilled with nitrogen. Ketimine **3c** (28.5 mg, 0.0999 mol), phosphoric acid (*R*)-**1** (7.6 mg, 0.0100 mol), and **2a** (19.0 mg, 0.100 mmol) were added to the TT successively under nitrogen atmosphere. Then, degassed toluene (1 mL) was added to the TT. After being stirred for 3 days at 110 ^oC, the mixture was cooled to room temperature and filtered through Celite pad (washed with CH_2Cl_2). The filtrate was concentrated under reduced pressure, and the residue was purified by preparative thin layer chromatography on silica gel (AcOEt/hexane = 1/10) to give 8.7 mg (0.0460 mmol, 46%, 98% ee) of (*R*)-**2a** as a pale yellow oil. The ee of (*R*)-**2a** was determined by HPLC analysis using a chiral stationary phase.

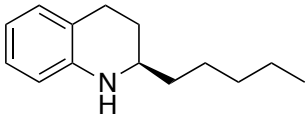


2a (3 d, Pale yellow oil, 46%, 98% ee)[5]

2a was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84-0.98 (m, 3H), 1.24-1.72 (m, 7H), 1.92-2.03 (m, 1H), 2.66-2.86 (m, 2H), 3.18-3.31 (m, 1H), 3.78 (brs, 1H), 6.49 (d, *J*=7.8 Hz, 1H), 6.61 (t, *J*=7.9 Hz, 1H), 6.96 (t, *J*=7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.8, 26.4, 27.9, 28.1, 36.4, 51.2, 114.1, 117.0, 121.4, 126.7, 129.2, 144.6; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 10/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R = 12.73 min; minor enantiomer: t_R = 14.17 min.

$[\alpha]_D^{22}$= 42.01 (c 1.0, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 90.4 (c 0.19, $CHCl_3$) for 99%ee of (*R*)-enantiomer][5]

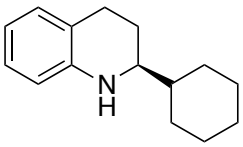


2b (3 d, Pale yellow oil, 50%, 98% ee)[5]

2b was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81-0.97 (m, 3H), 1.22-1.73 (m, 9H), 1.92-2.01 (m, 1H), 2.64-2.85 (m, 2H), 3.19-3.32 (m, 1H), 6.46 (d, *J*=7.9 Hz, 1H), 6.59 (t, *J*=7.4 Hz, 1H), 6.91-7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.5, 25.1, 26.2, 27.8, 31.8, 36.4, 51.3, 113.8, 116.5, 120.9, 126.4, 128.9, 144.5; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 9/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R = 10.97 min; minor enantiomer: t_R = 10.33 min.

$[\alpha]_D^{21}$ = 8.14 (c 1.3, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 87.3 (c 0.20, $CHCl_3$) for 99% ee of (*R*)-enantiomer][5]

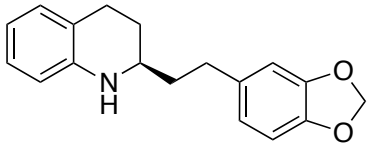


2c (3 d, Yellow oil, 50%, 98% ee)[6]

2c was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5 (twice), R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96-1.94 (m, 12H), 2.67-2.79 (m, 2H), 2.99-3.05 (m, 1H), 3.78 (brs, 1H), 6.45 (d, *J*=7.8 Hz, 1H), 6.57 (t, *J*=7.2 Hz, 1H), 6.88-7.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 16.3, 26.4, 26.5, 26.6, 28.7, 29.1, 42.4, 56.5, 114.0, 116.7, 121.4, 126.6, 129.1, 144.9; HPLC conditions: CHIRALCEL® OD-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 3.93 min; minor enantiomer: t_R = 4.37 min.

$[\alpha]_D^{20}$= 20.41 (c 1.0, $CHCl_3$)

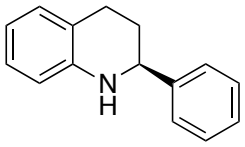


2d (3 d, Pale yellow oil, 53%, 97% ee)[5]

2d was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60-1.73 (m, 1H), 1.74-1.84 (m, 2H), 1.94-2.02 (m, 1H), 2.63-2.86 (m, 4H), 3.23-3.32 (m, 1H), 6.47 (d, *J*=8.2 Hz, 1H), 6.58-6.67 (m, 2H), 6.68-6.78 (m, 2H), 6.85-7.00 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.2, 27.9, 31.8, 38.4, 51.0, 100.8, 108.2, 108.8, 114.3, 117.2, 121.0, 121.4, 126.7, 129.2, 135.6, 144.2, 145.7, 147.6; HPLC conditions: CHIRALCEL® OD-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 8.72 min; minor enantiomer: t_R = 11.58 min.

$[\alpha]_D^{21}$= 75.23 (c 1.7, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 53.0 (c 0.20, $CHCl_3$) for 99% ee of (*R*)-enantiomer][5]

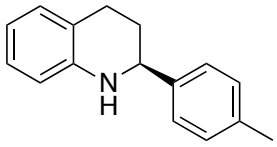


2e (2 d, Yellow oil, 50%, 81% ee)[5]

2e was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97-2.16 (m, 2H), 2.69-2.81 (m, 1H), 2.88-2.99 (m, 1H), 4.44 (dd, *J*=9.4, 3.6 Hz, 1H), 6.55 (d, *J*=8.2 Hz, 1H), 6.63 (td, *J*=8.2, 1.1 Hz, 1H), 6.99-7.06 (m, 2H), 7.19-7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 30.9, 56.2, 113.9, 117.1, 120.8, 126.5, 126.8, 127.4, 128.5, 144.6, 144.7; HPLC conditions: CHIRALCEL® OD-H column, hexane/2-propanol = 5/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R = 13.75 min; minor enantiomer: t_R = 15.34 min.

$[\alpha]_D^{21}$= -45.6 (c 1.1, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 36.8 (c 0.95, $CHCl_3$) for 92% ee of (*R*)-enantiomer][5]

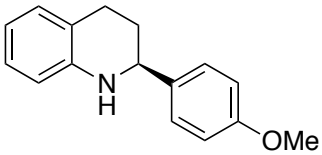


2f (2 d, Yellow oil, 55%, 96% ee)[7]

2f was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87-2.18 (m, 2H), 2.38 (s, 3H), 2.65-3.01 (m, 2H), 3.79-4.24 (brs, 1H), 4.41 (dd, *J*=9.4, 3.5 Hz, 1H), 6.52 (d, *J*=8.2 Hz, 1H), 6.63 (t, *J*=7.8 Hz, 1H), 6.96-7.03 (m, 2H), 7.17 (d, *J*=7.8 Hz, 2H), 7.22-7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 26.5, 31.0, 56.0, 114.0, 117.1, 120.9, 126.4, 126.8, 129.2, 129.3, 137.1, 141.8, 144.7; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 11.95 min; minor enantiomer: t_R = 13.34 min.

$[\alpha]_D^{21}$= -15.3 (c 1.2, $CHCl_3$) [lit. $[\alpha]_D^{20}$ = 24.3 (c 0.86, $CHCl_3$) for 90% ee of (*S*)-enantiomer][7]

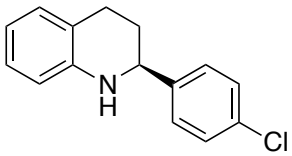


2g (2 d, Pale yellow oil, 52%, 99% ee)[5]

2g was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87-2.18 (m, 2H), 2.64-3.00 (m, 2H), 3.81 (s, 3H), 4.39 (dd, *J*=9.4, 3.4 Hz, 1H), 6.52 (d, *J*=8.1 Hz, 1H), 6.63 (t, *J*=7.7 Hz, 1H), 6.86-6.93 (m, 2H), 6.97-7.03 (m, 2H), 7.28-7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.5, 31.1, 55.3, 55.7, 113.9, 113.9, 117.1, 120.9, 126.8, 127.6, 129.2, 136.9, 144.8, 158.9; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 24.60 min; minor enantiomer: t_R = 21.45 min.

$[\alpha]_D^{21}$= -6.5 (c 1.2, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 31.9 (c 2.35, $CHCl_3$) for 92% ee of (*R*)-enantiomer][5]

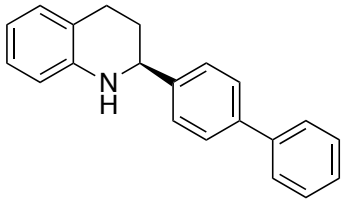


2h (4 d, Pale yellow oil, 44%, 89% ee)[5]

2h was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87-2.19 (m, 2H), 2.64-3.02 (m, 2H), 4.05 (brs, 1H), 4.44 (dt, *J*=9.4, 3.4 Hz, 1H), 6.57 (d, *J*=8.1 Hz, 1H), 6.66(t, *J*=7.9 Hz, 1H),6.97-7.06 (m, 1H), 7.26-7.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 30.9, 56.2, 113.9, 117.2, 120.9, 126.5, 126.9, 127.4, 128.5, 144.6, 144.7; HPLC conditions: CHIRALCEL® AD-H column, hexane/2-propanol = 5/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R = 11.07 min; minor enantiomer: t_R = 9.85 min.

$[\alpha]_D^{20}$= -31.69 (c 1.7, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 37.1 (c 1.75, $CHCl_3$) for 85% ee of (*R*)-enantiomer][5]

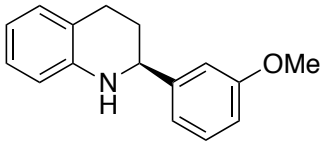


2i (3 d, Pale yellow oil, 56%, 95% ee)[2]

2i was isolated by preparative thin layer chromatography (CH_2Cl_2/Hexane = 1/4, R_f = 0.6).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00-2.23 (m, 2H), 2.75-3.01 (m, 2H), 4.47 (dd, *J*=9.4, 3.3 Hz, 1H), 6.59 (d, *J*=8.3 Hz, 1H), 6.64 (t, *J*=7.9 Hz, 1H), 6.97-7.07 (m, 2H), 7.35-7.39 (m, 1H) , 7.40-7.54 (m, 4H), 7.57-7.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 30.9, 55.9, 114.1, 117.3, 120.9, 126.9, 127.0, 127.0, 127.2, 127.3, 128.8, 129.3, 140.4, 140.8, 143.8, 144.5; HPLC conditions: CHIRALCEL® AD-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 8.38 min; minor enantiomer: t_R = 6.25 min.

$[\alpha]_D^{20}$= -17.25 (c 1.5, $CHCl_3$)[2]

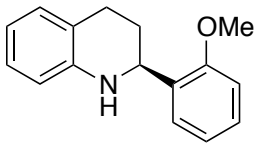


2j (3 d, Colorless solid, 53%, >99% ee)[5]

2j was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93-2.18 (m, 2H), 2.69-2.98 (m, 2H), 3.80 (s, 3H), 4.03 (brs, 1H), 4.41 (dd, *J*=9.3, 3.2 Hz, 1H), 6.54 (d, *J*=7.6 Hz, 1H), 6.65 (t, *J*=6.3 Hz, 1H), 6.74-6.85 (m, 1H), 6.95-7.03 (m, 4H), 7.22-7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.4, 30.9, 55.2, 56.2, 112.0, 112.8, 114.1, 117.3, 118.9, 120.9, 126.9, 129.3, 129.5, 144.5, 146.4, 159.8; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 21.36 min; minor enantiomer: t_R = 39.55 min.

$[\alpha]_D^{16}$= -51.86 (c 2.7, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 20.3 (c 1.0, $CHCl_3$) for 88% ee of (*R*)-enantiomer][5]



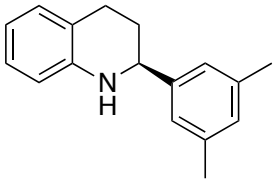
2k (3 d, Pale yellow oil, 52%, 77% ee)[5]

2k was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92-2.18 (m, 2H), 2.64-2.75 (m, 2H), 3.85 (s, 3H), 4.86 (dd, *J*=8.2,

3.5 Hz, 1H), 6.55 (d, *J*=7.8 Hz, 1H), 6.64 (t, *J*=7.3 Hz, 1H), 6.88 (d, *J*=8.2 Hz, 1H), 6.91-7.03 (m, 3H), 7.24 (t, *J*=8.1 Hz, 1H), 7.43 (d, *J*=7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.0, 18.0, 49.1, 55.3, 110.3, 114.1, 117.0, 120.6, 121.2, 126.8, 126.8, 128.0, 129.2, 132.6, 144.9, 156.4; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 11.75 min; minor enantiomer: t_R = 18.73 min.

$[\alpha]_D^{17}$= -37.98 (c 1.3, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 26.6 (c 0.6, $CHCl_3$) for 95% ee of (*R*)-enantiomer][5]



2l (3 d, Pale yellow oil, 50%, 97% ee)

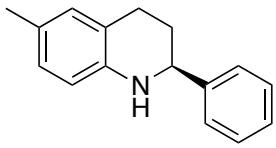
2l was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5 (twice), R_f = 0.9).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93-2.13 (m, 2H), 2.32 (s, 6H), 2.70-2.94 (m, 2H), 4.35 (dd, *J*=9.6, 3.3 Hz, 1H), 6.53 (dd, *J*=8.2, 1.2 Hz, 1H), 6.64(t, *J*=7.3 Hz, 1H),6.91-7.03 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 26.7, 31.0, 56.3, 114.0, 117.1, 121.0, 124.3, 126.8, 129.1, 129.2, 138.1, 144.7; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 6.48 min; minor enantiomer: t_R = 8.22 min.

$[\alpha]_D^{21}$= -25.53 (c 1.4, $CHCl_3$)

IR (film): 2918, 1607, 1585, 1480, 1338, 1309, 1274, 1249, 1155, 1113, 848, 745 cm^{-1}.

HRMS (EI) *m* / *z* calcd for $C_{17}H_{20}N$ $(M+H)^+$238.1596, found 238.1599.

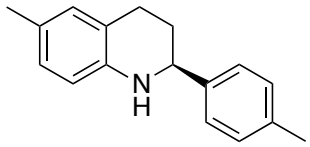


2m (3 d, Pale yellow oil, 46%, 97% ee)[8]

2m was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88-2.11 (m, 2H), 2.21 (s, 3H), 2.62-2.73 (m, 1H), 2.80-2.91 (m, 1H), 3.84 (brs, 1H), 4.35(dd, *J*=3.1, 9.4 Hz, 1H),6.41 (t, *J*=4.1 Hz, 1H), 6.78 (s, 1H), 7.21-7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 26.3, 31.1, 114.0, 120.8, 126.2, 126.5, 127.2, 127.3, 128.4, 142.3, 144.9; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 13.87 min; minor enantiomer: t_R = 16.50 min.

$[\alpha]_D^{20}$= -40.44 (c 1.2, $CHCl_3$)[8]



2n (3 d, Pale yellow oil, 49%, >99% ee)

2n was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.8).

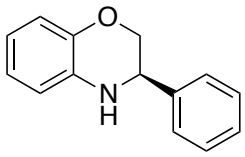
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92-2.10 (m, 2H), 2.22 (s, 3H), 2.34 (s, 3H), 2.63-2.76 (m, 1H), 2.82-2.90 (m, 1H), 4.34(dd, *J*=9.6, 3.1 Hz, 1H),6.44 (dd, *J*=3.1, 2.4 Hz, 1H), 6.81 (d, *J*=6.7 Hz, 2H), 7.14 (d, *J*=7.8 Hz, 2H) , 7.22-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 21.1, 26.5, 31.2, 56.1, 114.1, 120.9, 126.3, 126.4, 127.3, 129.2, 129.8, 137.0, 141.9, 142.4; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 5/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 13.91 min; minor enantiomer: t_R = 24.65 min.

$[\alpha]_D^{20}$= -16.12 (c 1.0, $CHCl_3$)

IR (film): 3399, 3006, 2920, 2855, 1619, 1509, 1471, 1442, 1335, 1303, 1274, 1253, 1214, 1167, 1132, 1104, 1045, 1020, 877, 809, 534 cm^{-1}.

HRMS (EI) *m* / *z* calcd for $C_{17}H_{20}N$ $(M)^+$238.1596, found 238.1595.

m. p. 106-108 ˚C

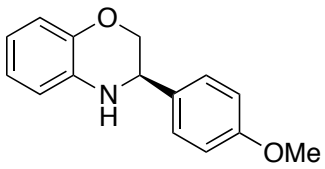


5a (8 d, Pale yellow oil, 53%, 84% ee)[7]

5a was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96 (dd, *J*=8.6, 10.6 Hz, 2H), 4.24 (dd, *J*=2.9, 10.6 Hz, 1H), 4.44 (dd, *J*=2.9, 8.6 Hz, 1H), 6.61-6.70 (m, 2H), 6.75-6.86 (m, 2H), 7.27-7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.1, 70.9, 115.3, 116.5, 118.8, 121.4, 127.1, 128.3, 128.7, 133.8, 139.1, 143.4; HPLC conditions: CHIRALCEL® OD-H column, hexane/2-propanol = 5/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R = 17.45 min; minor enantiomer: t_R = 21.25 min.

$[\alpha]_D^{21}$= -102.61 (c 0.9, $CHCl_3$) [lit. $[\alpha]_D^{16}$ = -137.9 (c 0.84, $CHCl_3$) for 92% ee of (*R*)-enantiomer][7]

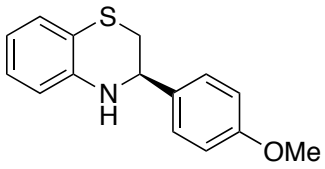


5b (7 d, Pale yellow oil, 40%, 72% ee)[3]

5b was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.6).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 3.96 (dd, *J*=8.8, 10.6 Hz, 1H), 4.24 (dd, *J*=10.6, 2.9 Hz, 1H), 4.45 (dd, *J*=2.9, 8.8 Hz, 1H), 6.63-6.74 (m, 2H), 6.77-6.87 (m, 2H), 6.89-6.94 (m, 2H), 7.29-7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 53.6, 55.3, 71.0, 114.2, 115.4, 116.6, 118.9, 121.4, 128.3, 131.1, 133.8, 143.5, 159.6; HPLC conditions: CHIRALCEL® OD-H column, hexane/2-propanol = 10/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 12.32 min; minor enantiomer: t_R = 21.49 min.

$[\alpha]_D^{22}$= -112.81 (c 0.8, $CHCl_3$) [lit. $[\alpha]_D^{25}$ = 53.2 (c 1.00, $CHCl_3$) for 91% ee of (*S*)-enantiomer][3]

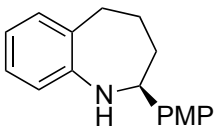


5c (7 d, Pale yellow oil, 48%, 73% ee)[9]

5c was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5 (twice), R_f = 0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (dd, *J*=2.7, 12.5 Hz, 2H), 3.17 (dd, *J*=12.3, 9.0 Hz, 1H), 3.82 (s, 3H), 4.62 (dd, *J*=2.6, 9.0 Hz, 1H), 6.53 (d, *J*=7.8 Hz, 1H), 6.67 (t, *J*=8.6 Hz, 1H), 6.88-6.96 (m, 3H), 7.06 (d, *J*= 7.6 Hz, 1H), 7.27-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.1, 55.3, 55.6, 114.2, 115.4, 118.4, 125.6, 127.4, 127.8, 134.8, 142.2, 159.5; HPLC conditions: CHIRALCEL® OD-H column, hexane/2-propanol = 10/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R = 16.09 min; minor enantiomer: t_R = 21.75 min.

$[\alpha]_D^{21}$= 5.67 (c 1.2, $CHCl_3$)



5d (7 d, Pale yellow oil, 55%, 62% ee)

5d was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43-1.53 (m, 1H), 1.90-2.08 (m, 3H), 2.82-2.92 (m, 2H), 3.74-3.81 (m, 1H), 3.82 (s, 3H), 6.74 (brs, 1H), 6.84-6.92 (m, 3H), 7.01-7.08 (m, 1H), 7.10-7.18 (m, 1H), 7.35-7.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6, 35.5, 40.0, 55.3, 63.2, 114.0, 114.0, 120.0, 121.3, 126.7, 127.6, 130.6, 133.8, 128.4, 158.9,; HPLC conditions: CHIRALCEL® OD-H column, hexane/2-propanol = 5/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R = 9.03 min; minor enantiomer: t_R = 14.37 min.

$[\alpha]_D^{18}$= 40.2 (c 1.4, $CHCl_3$)

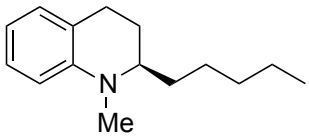
IR (film): 3345, 3006, 2925, 2834, 1890, 1609, 1586, 1512, 1471, 1438, 1350, 1336, 1303, 1291, 1245, 1176, 1097, 1063, 1035, 960, 930, 896, 870, 830, 812, 756, 722, 636, 812, 756, 722, 636, 812, 756, 722, 636, 613, 585, 550, 529 cm^{-1}.

HRMS (EI) *m* / *z* calcd for $C_{17}H_{20}NO$ $(M)^+$254.1545, found 254.1551.

m. p. 96-99 ˚C

3. Synthesis of (*R*)-Angustureine ((*R*)-2ba) and (*R*)-Galipinine ((*R*)-2da)

(*R*)-**2b** or (*R*)-**2d** (0.11 mmol) were dissolved in THF (5 mL), and K_2CO_3 (0.47 mmol), MeI (0.28 mmol) were added to the solution. After being stirred at 65 ^{o}C for 21 h, the mixture was diluted with water. The mixture was extracted with CH_2Cl_2 three times, the combined organic phase was concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography to give (*R*)-**2ba** or (*R*)-**2da**.

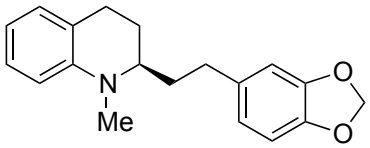


(*R*)-**2ba**: (*R*)-Angustureine (Pale yellow oil, 82%, 98% ee)[10]

(*R*)-**2ba** was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/10, R_f = 0.7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82-0.96 (m, 3H), 1.24-1.61 (m, 8H), 1.82-1.90 (m, 1H), 2.59-2.70 (m, 1H), 2.74-2.85 (m, 1H), 2.91 (s, 3H), 3.18-3.25 (m, 1H), 6.51 (d, *J*=8.2 Hz, 1H), 6.57 (t, *J*=7.2 Hz, 1H), 6.96 (d, *J*=7.2 Hz, 1H), 7.07 (t, *J*=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.7, 23.5, 24.4, 25.7, 31.1, 32.0, 37.9, 58.9, 110.3, 115.1, 121.8, 127.0, 128.6, 145.4; HPLC conditions: CHIRALCEL® OJ-H column, hexane/2-propanol = 95/5, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R = 11.37 min; minor enantiomer: t_R = 12.42 min.

$[\alpha]_D^{21}$= -13.16 (c 2.2, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ =-6.9 (c 1.0, $CHCl_3$) for 90% ee of (*R*)-enantiomer][10]



(*R*)-**2da**: (*R*)-Galipinine (Pale yellow oil, 86%, 98% ee)[10]

(*R*)-**2da** was isolated by preparative thin layer chromatography (AcOEt/Hexane = 1/5, R_f = 0.6).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67-1.96 (m, 4H), 2.48-2.55 (m, 3H), 2.58-2.71 (m, 1H), 2.90 (s, 3H), 3.23-3.29 (m, 1H), 5.92 (s, 2H), 6.52 (d, *J*=8.2 Hz, 1H), 6.56-6.64 (m, 2H), 6.66-6.77 (m, 2H), 6.97 (d, *J*= 7.0 Hz, 1H), 7.07 (t, *J*=7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.5, 24.3, 32.0, 33.1, 38.0, 58.2, 100.8, 108.1, 108.7, 110.6, 115.4, 120.9, 121.7, 127.1, 128.7, 135.8, 145.3, 145.6, 147.6; HPLC conditions: CHIRALCEL® OD-H column, hexane/2-propanol = 5/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R = 13.88 min; minor enantiomer: t_R = 16.75 min.

$[\alpha]_D^{20}$= 34.74 (c 2.4, $CHCl_3$) [lit. $[\alpha]_D^{RT}$ = 26.4 (c 1.0, $CHCl_3$) for 91% ee of (*R*)-enantiomer][10]

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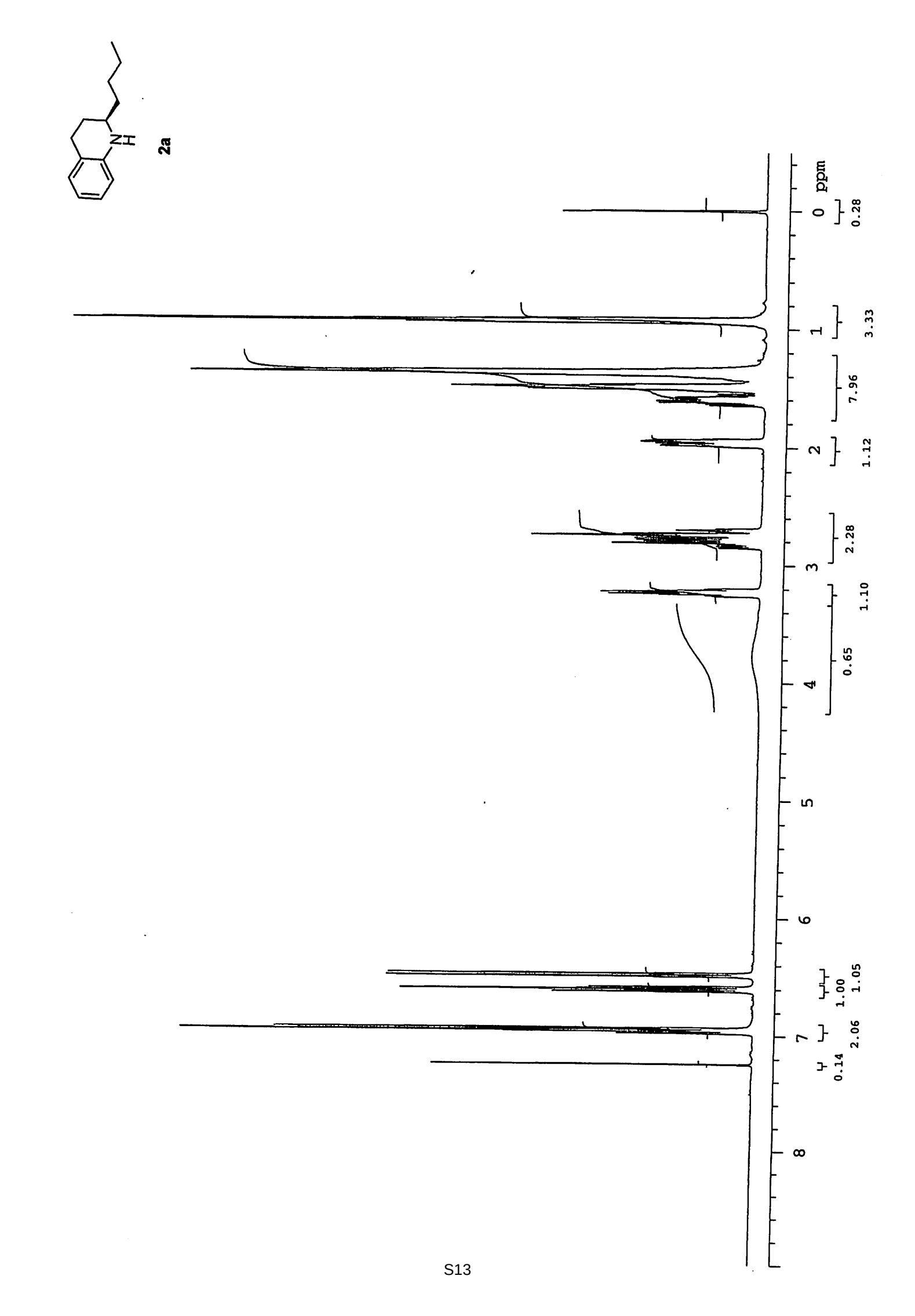
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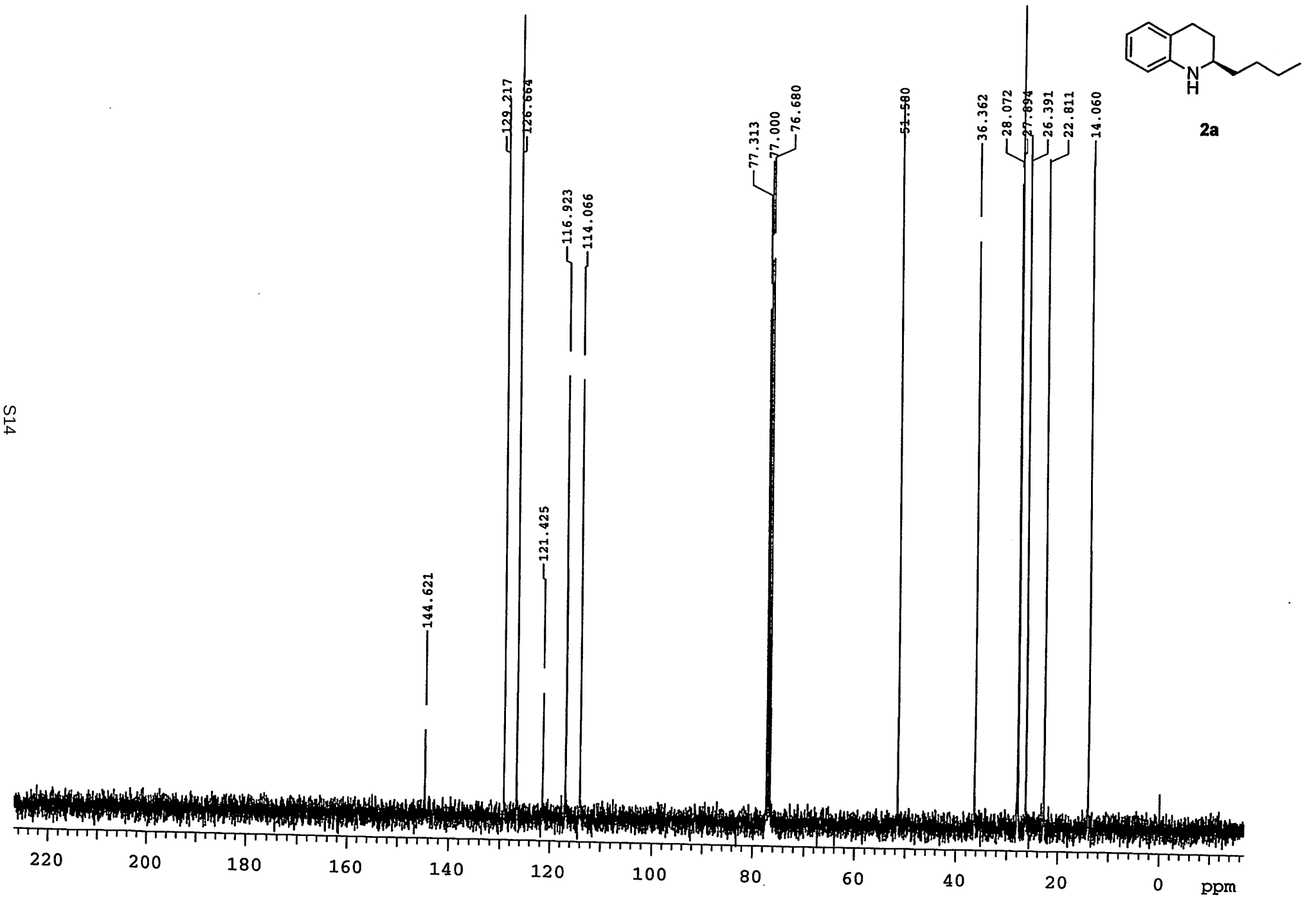
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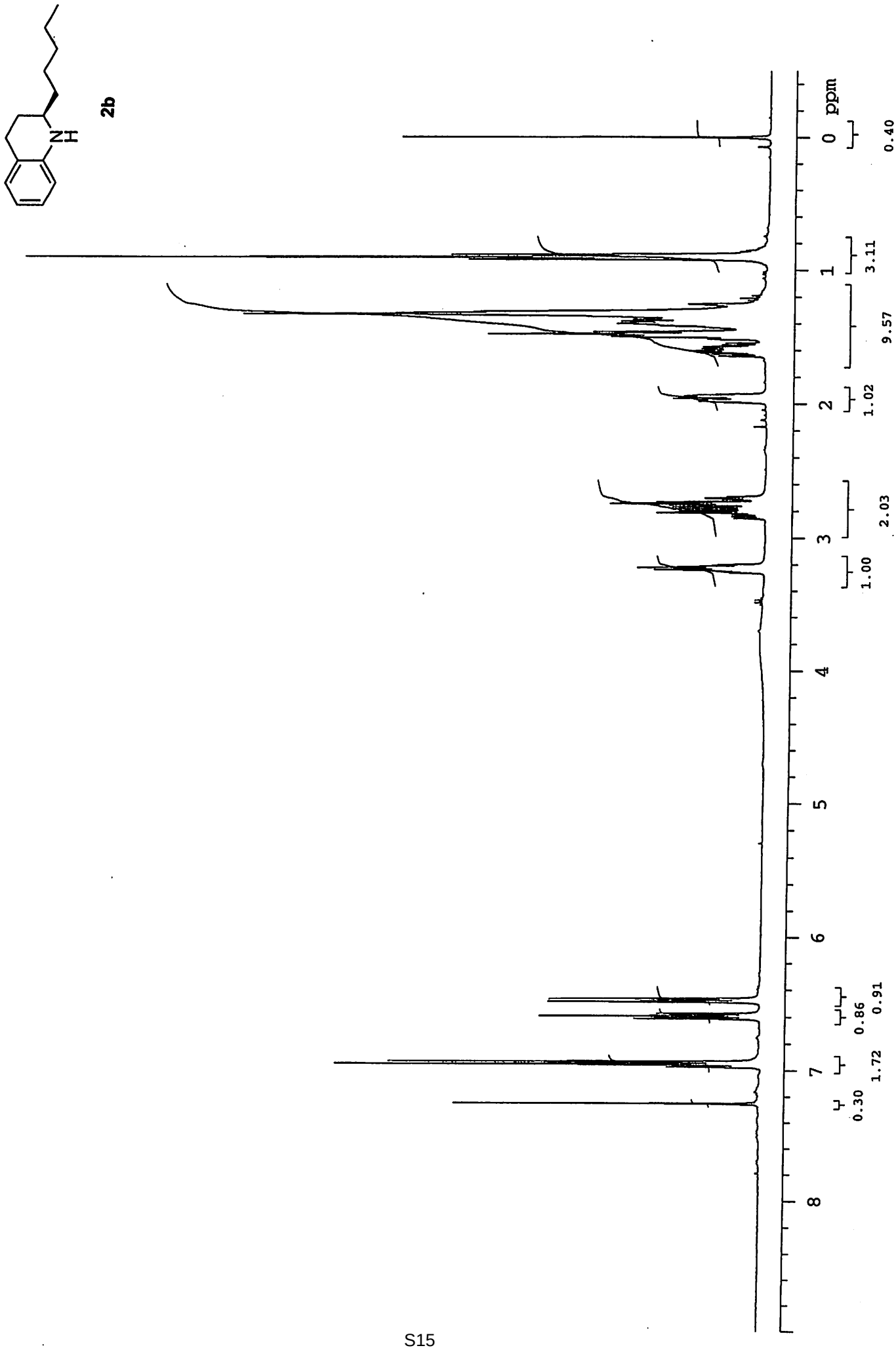
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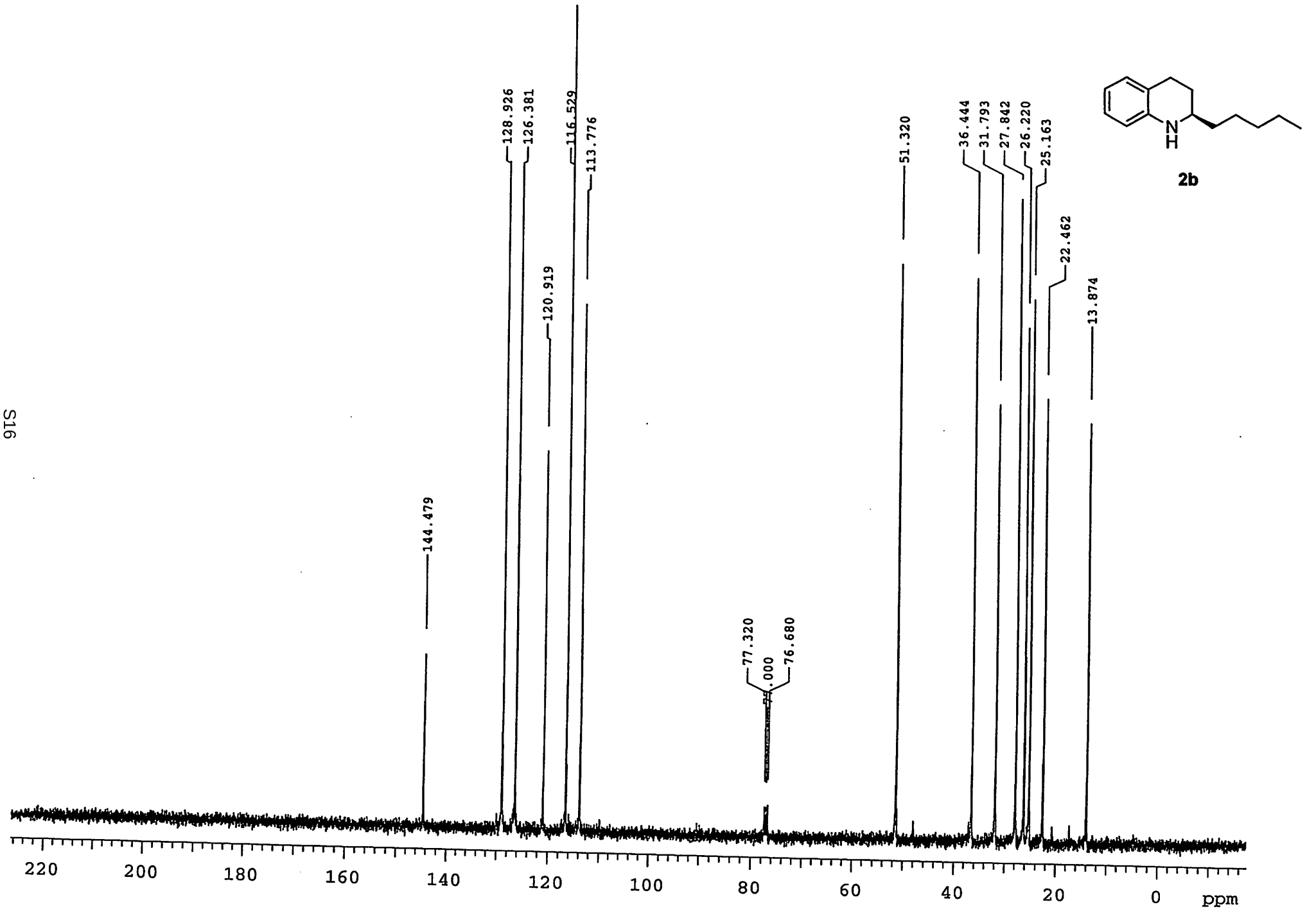
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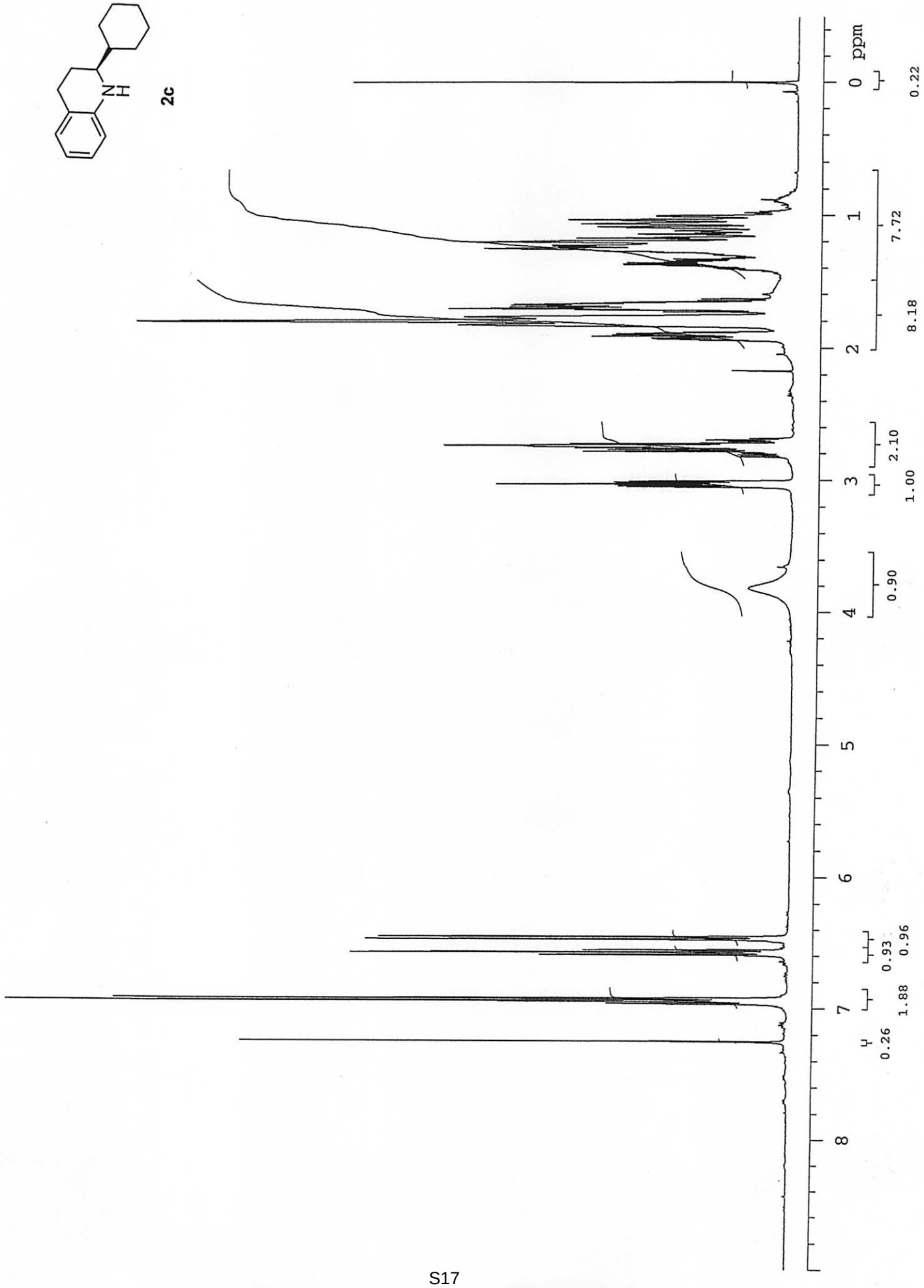
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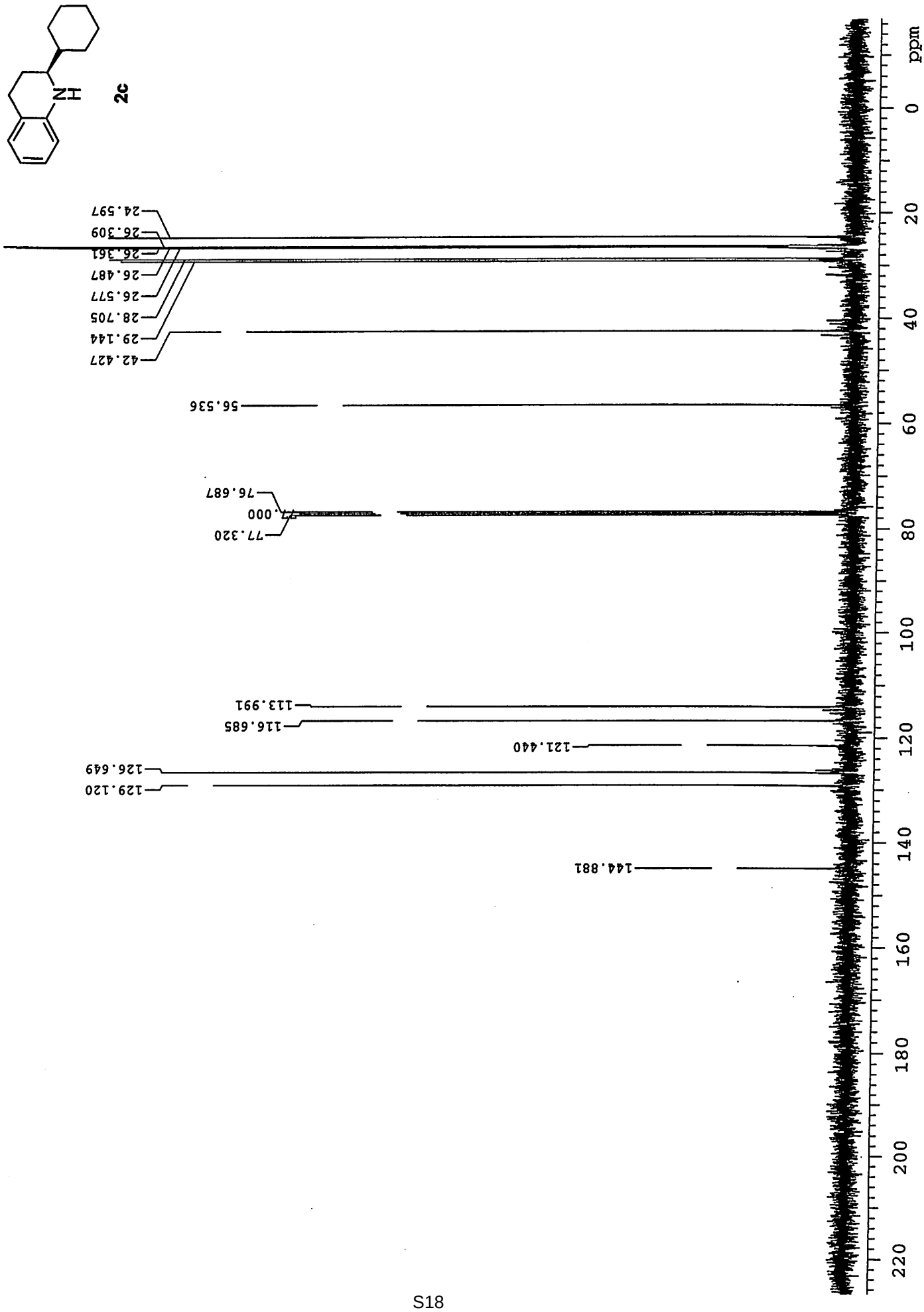
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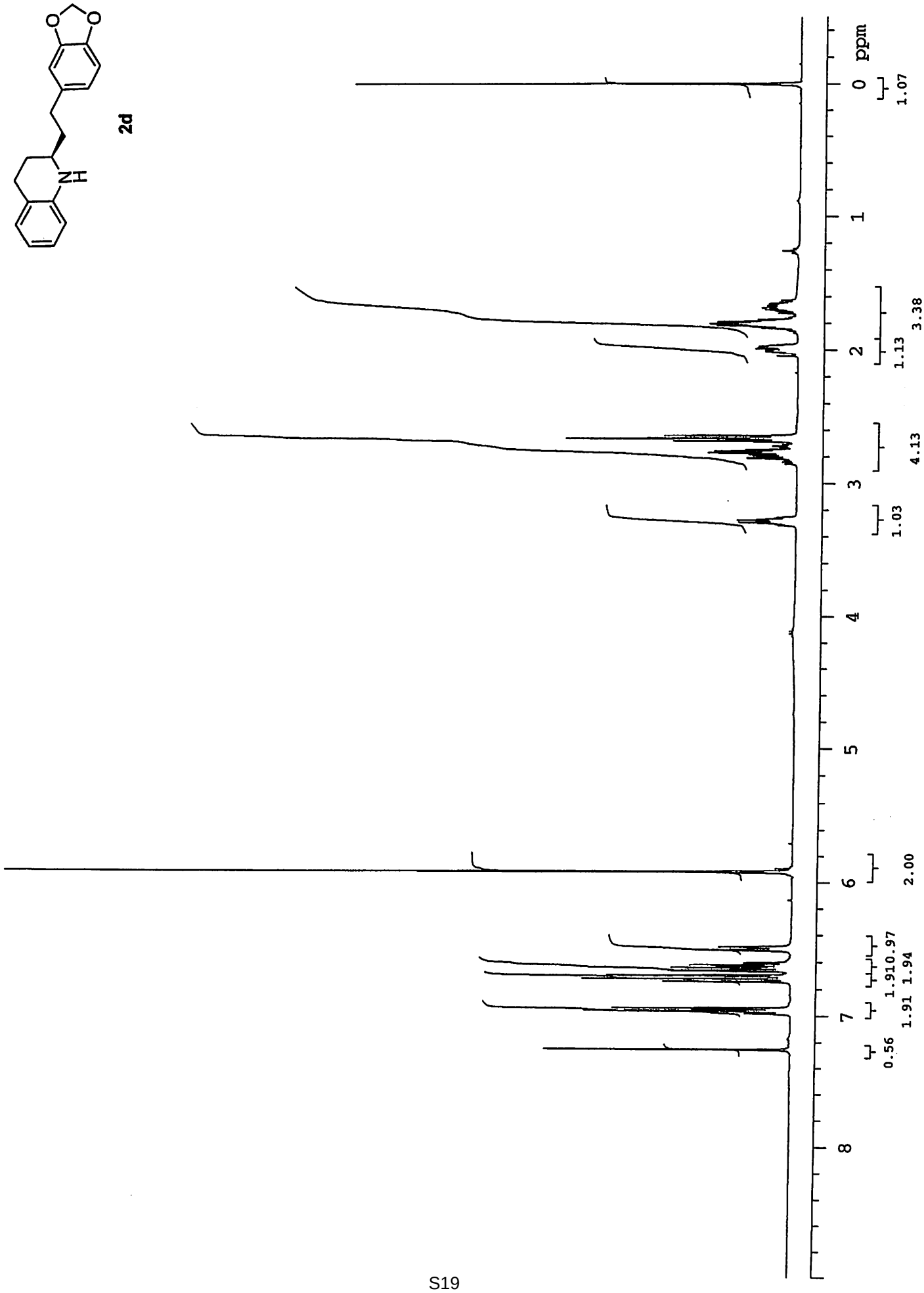
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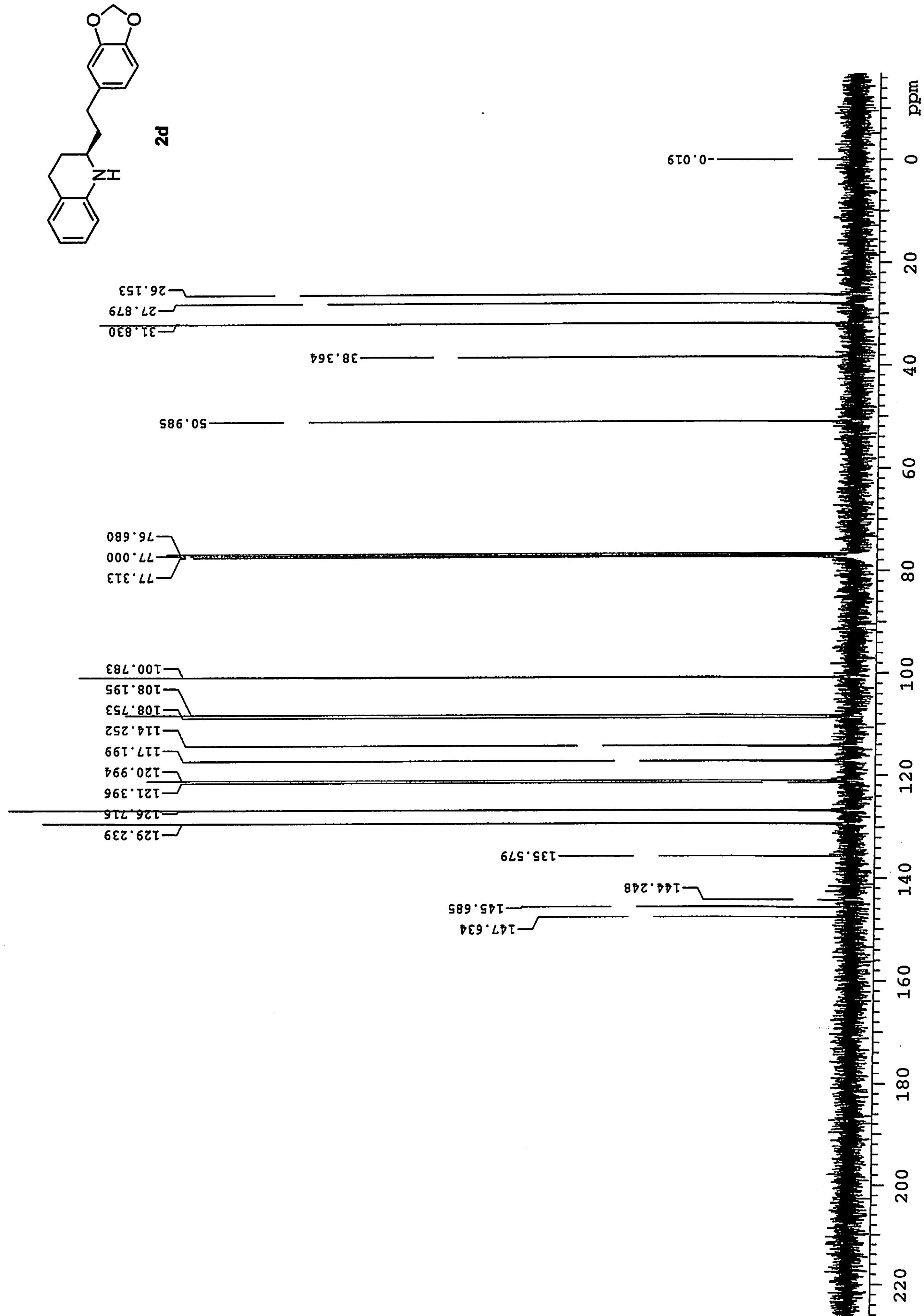
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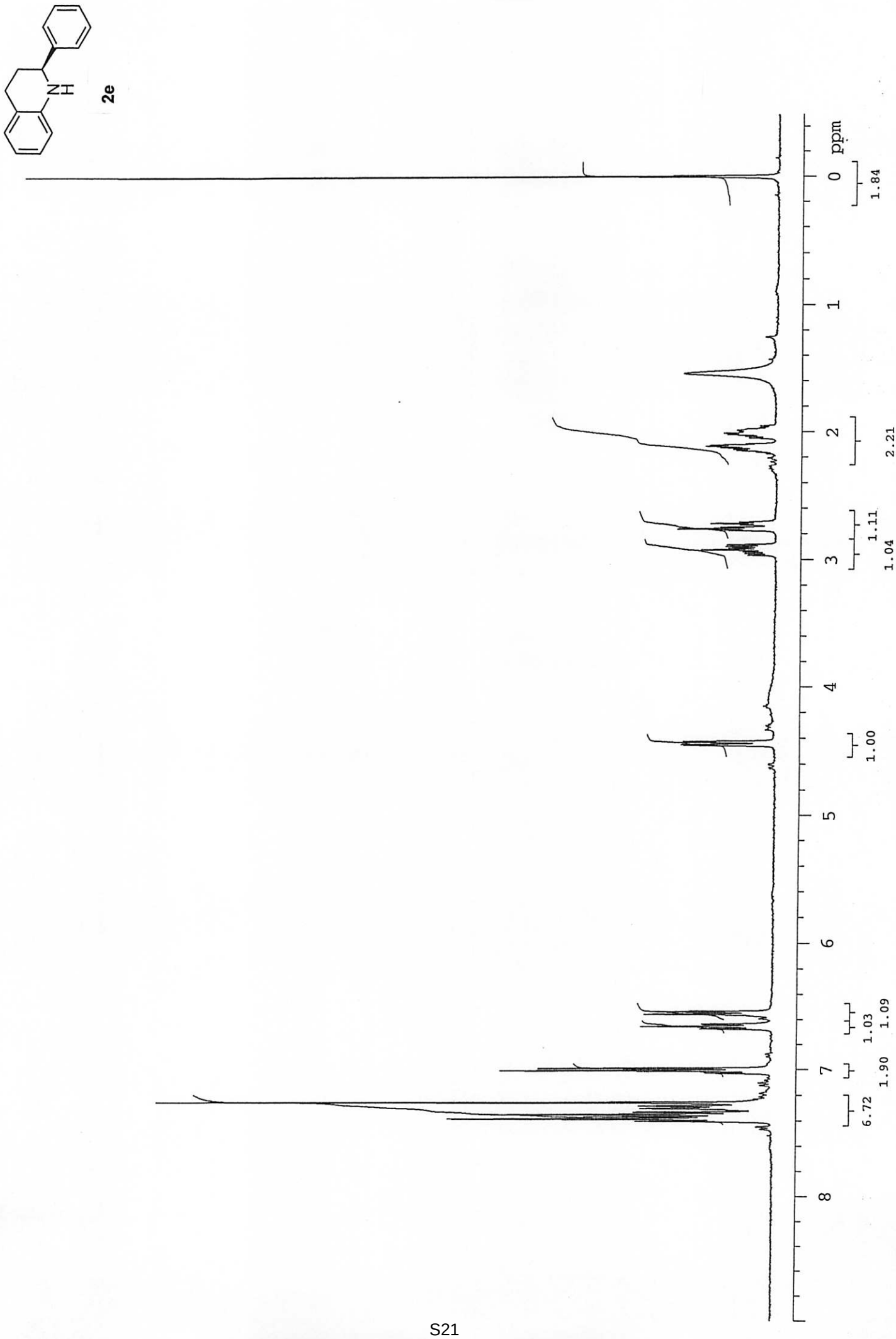
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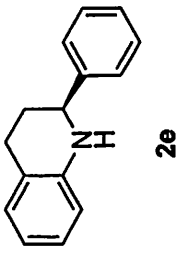
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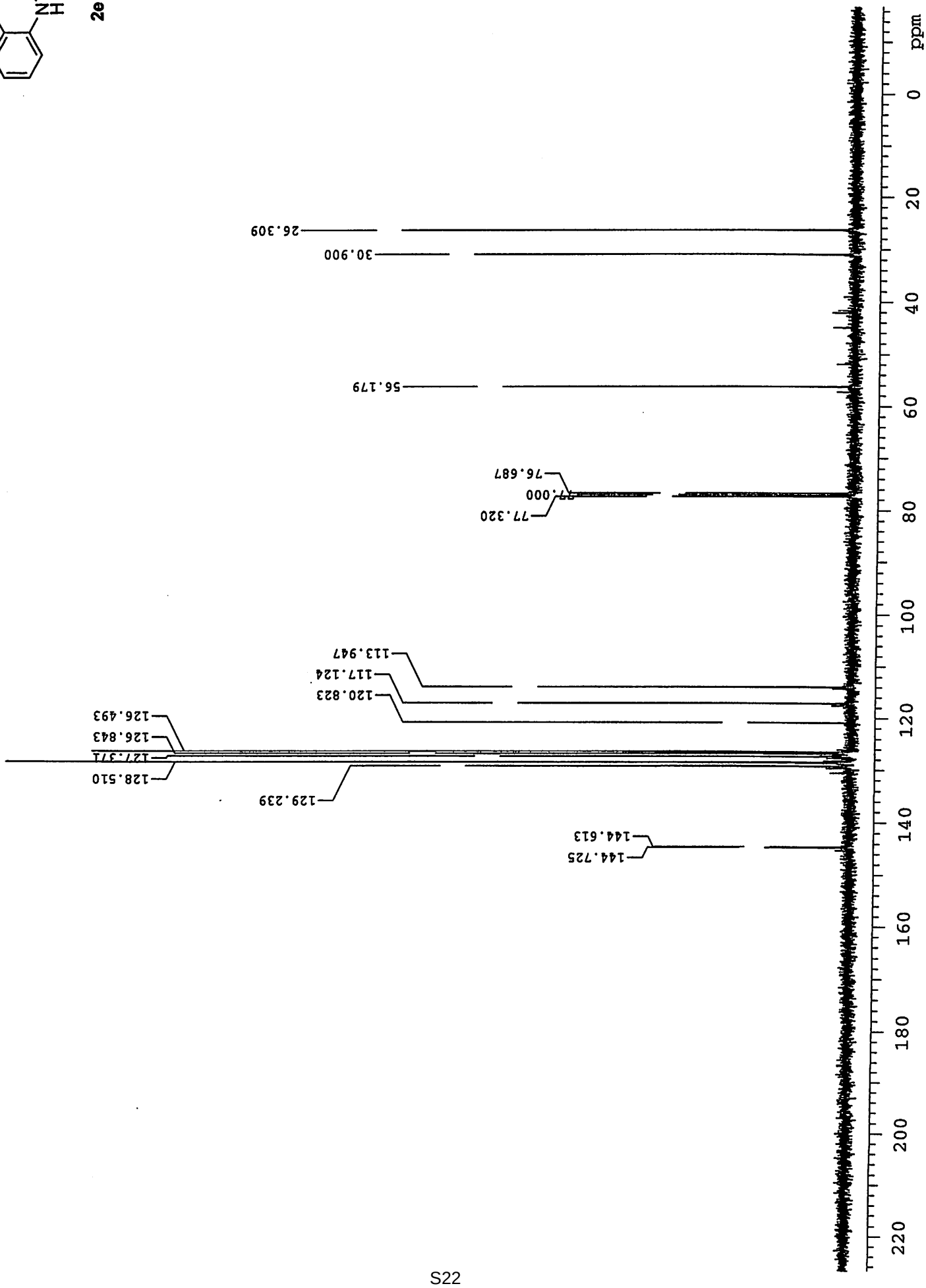
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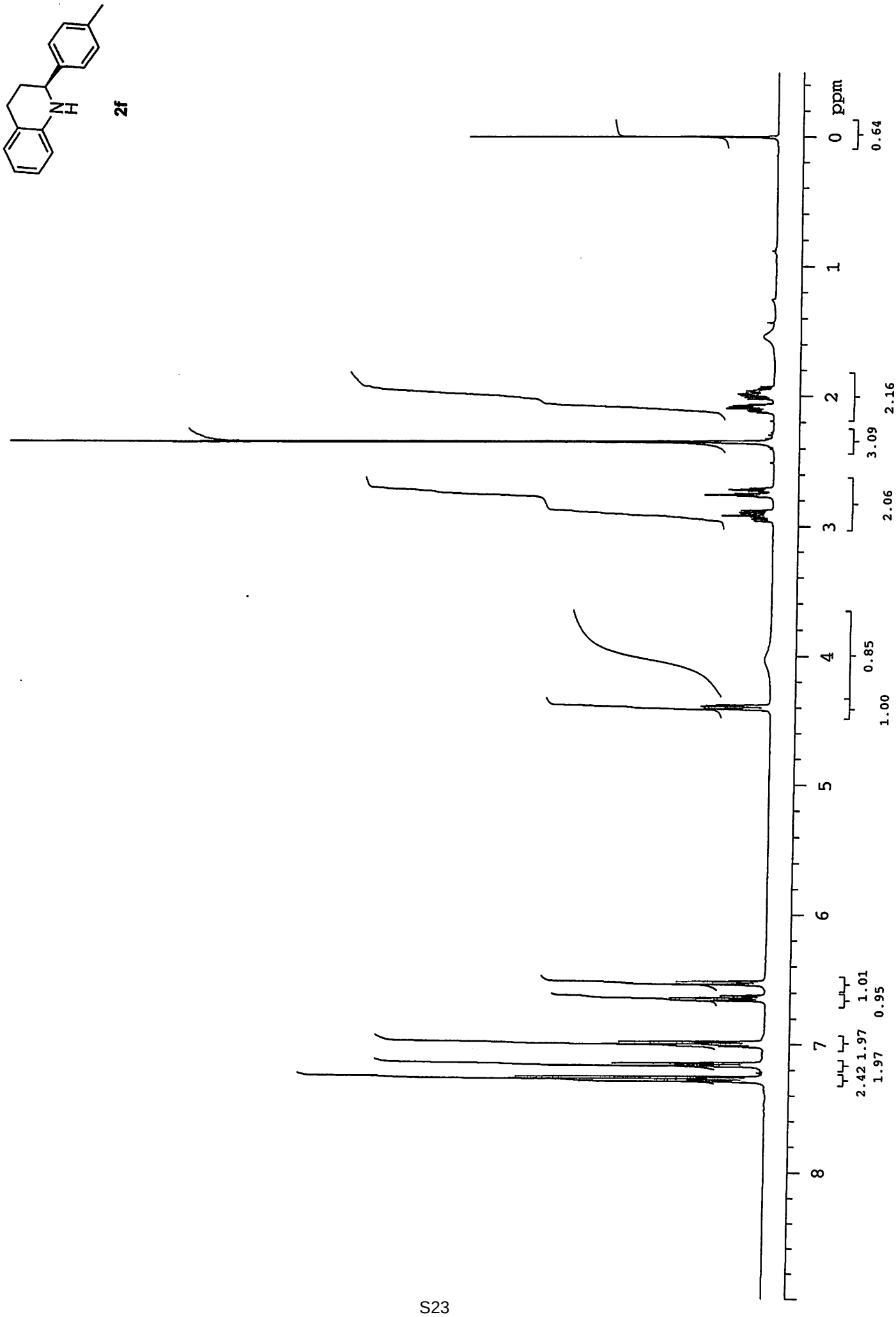
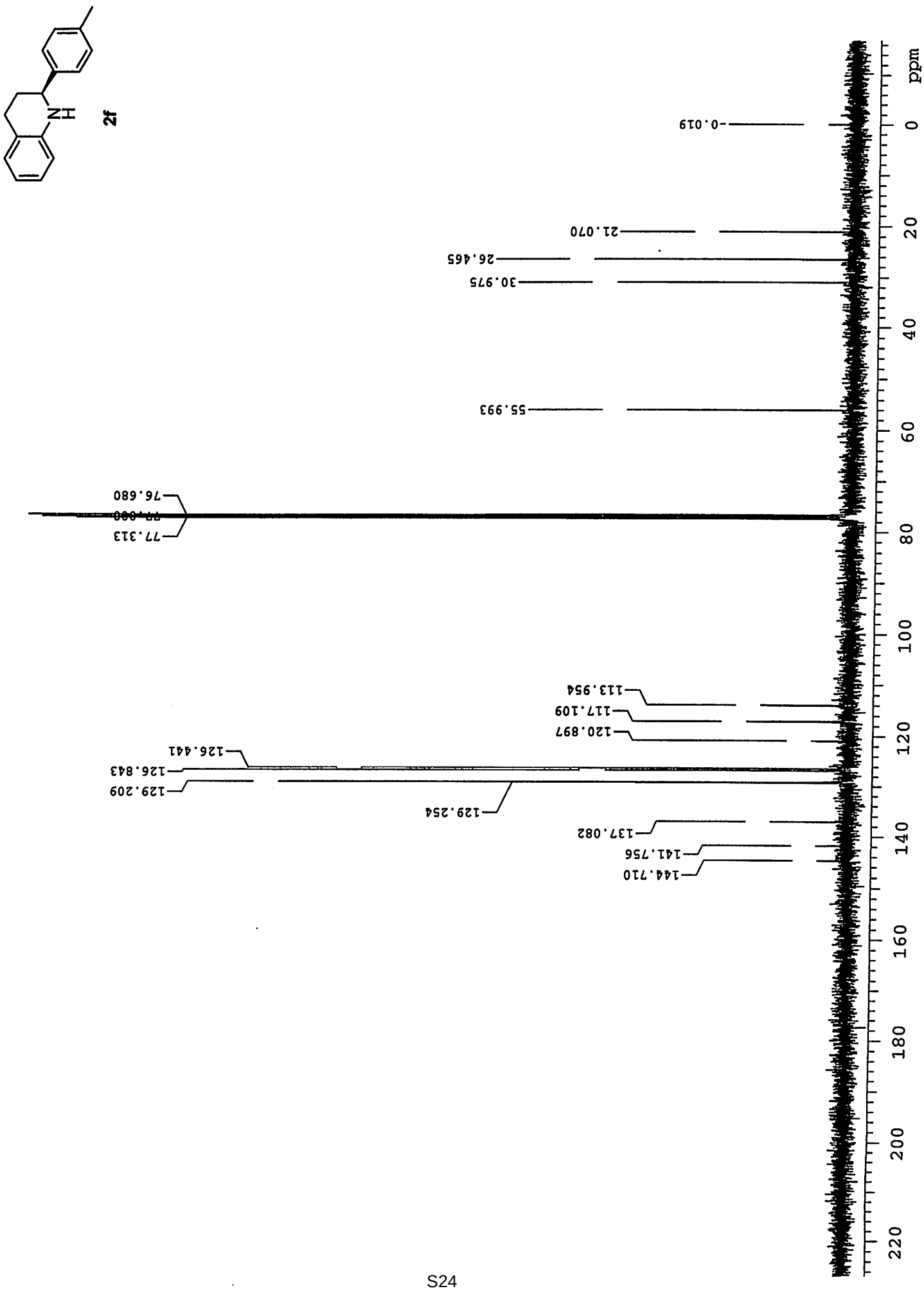
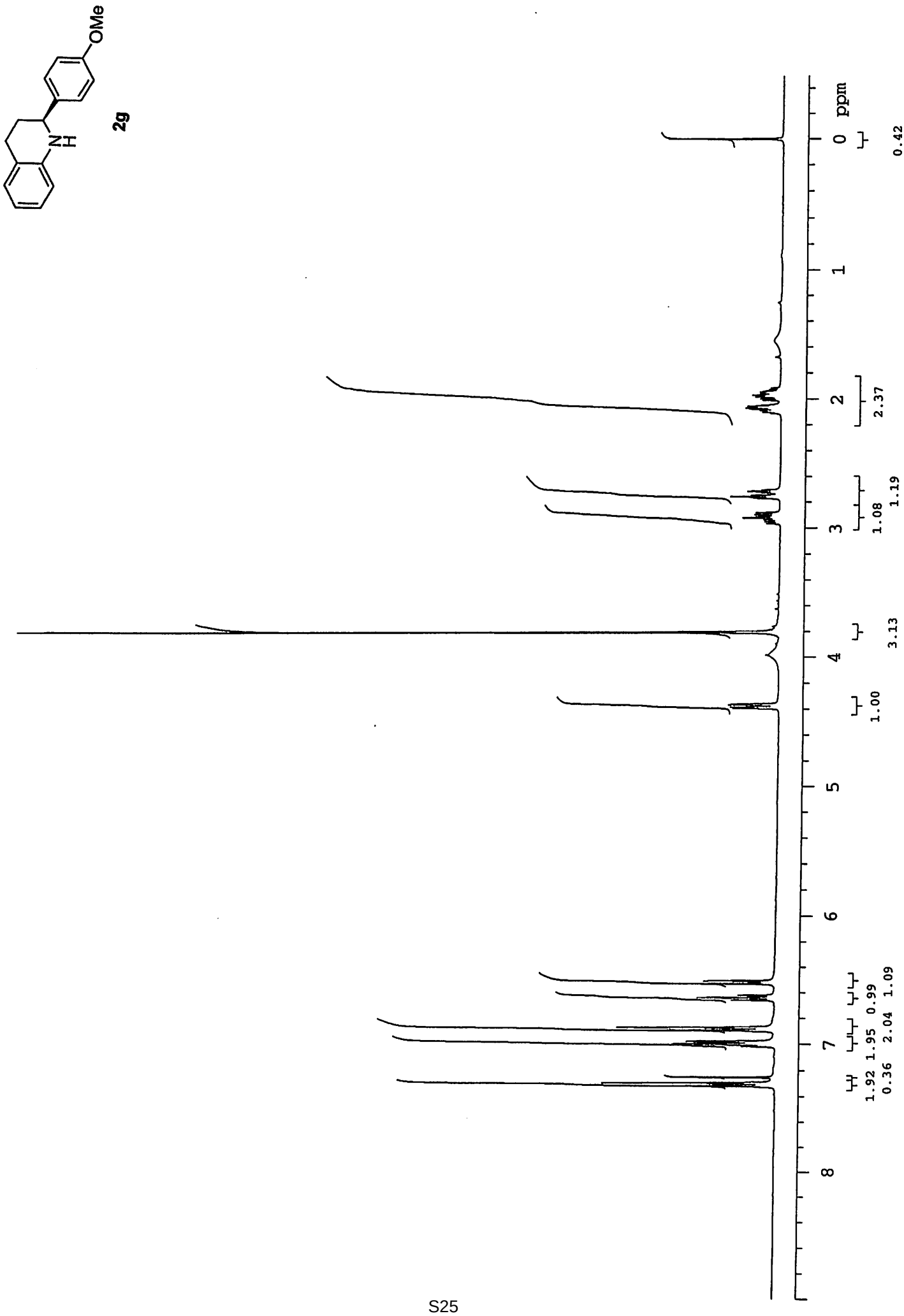
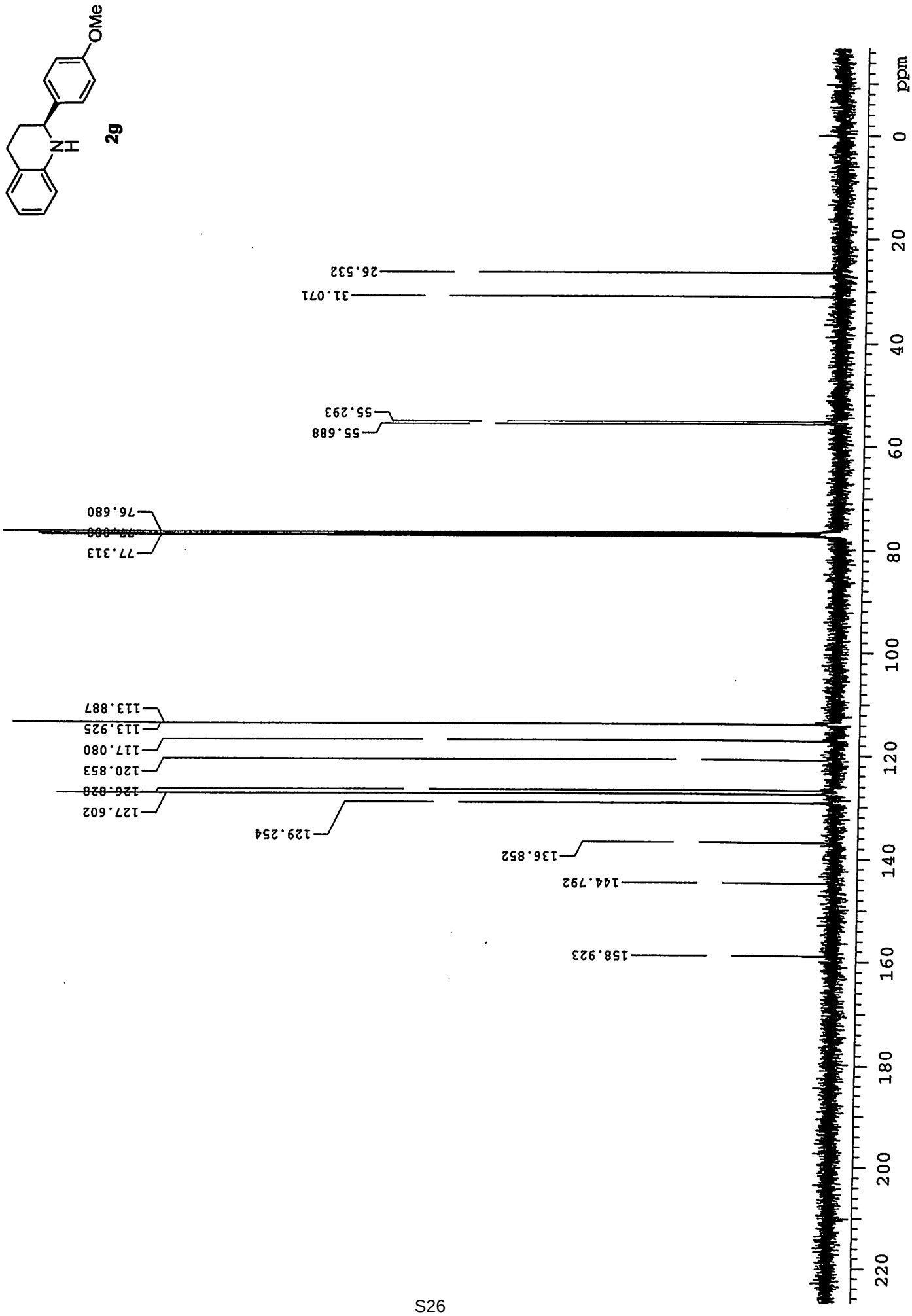
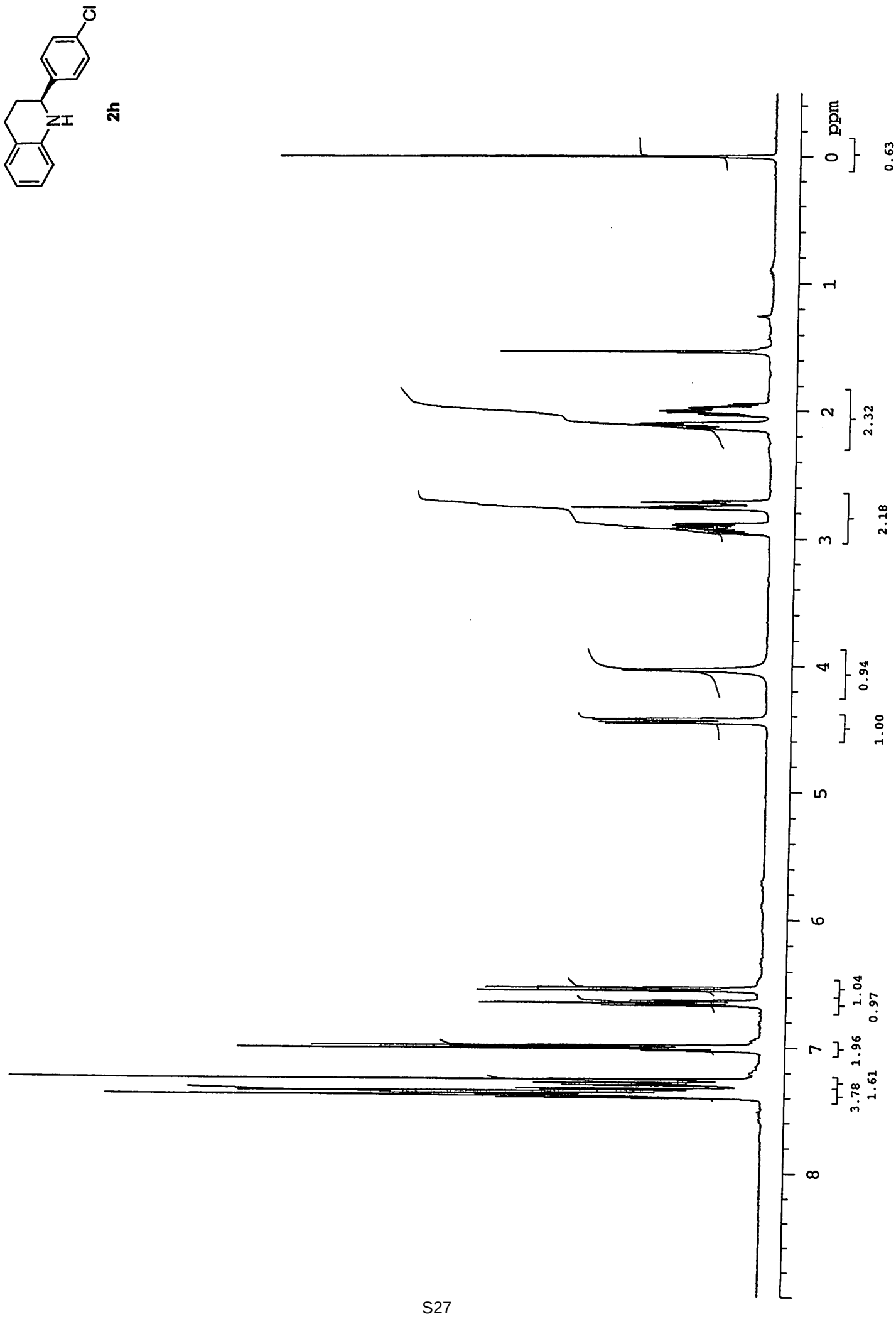
200
220

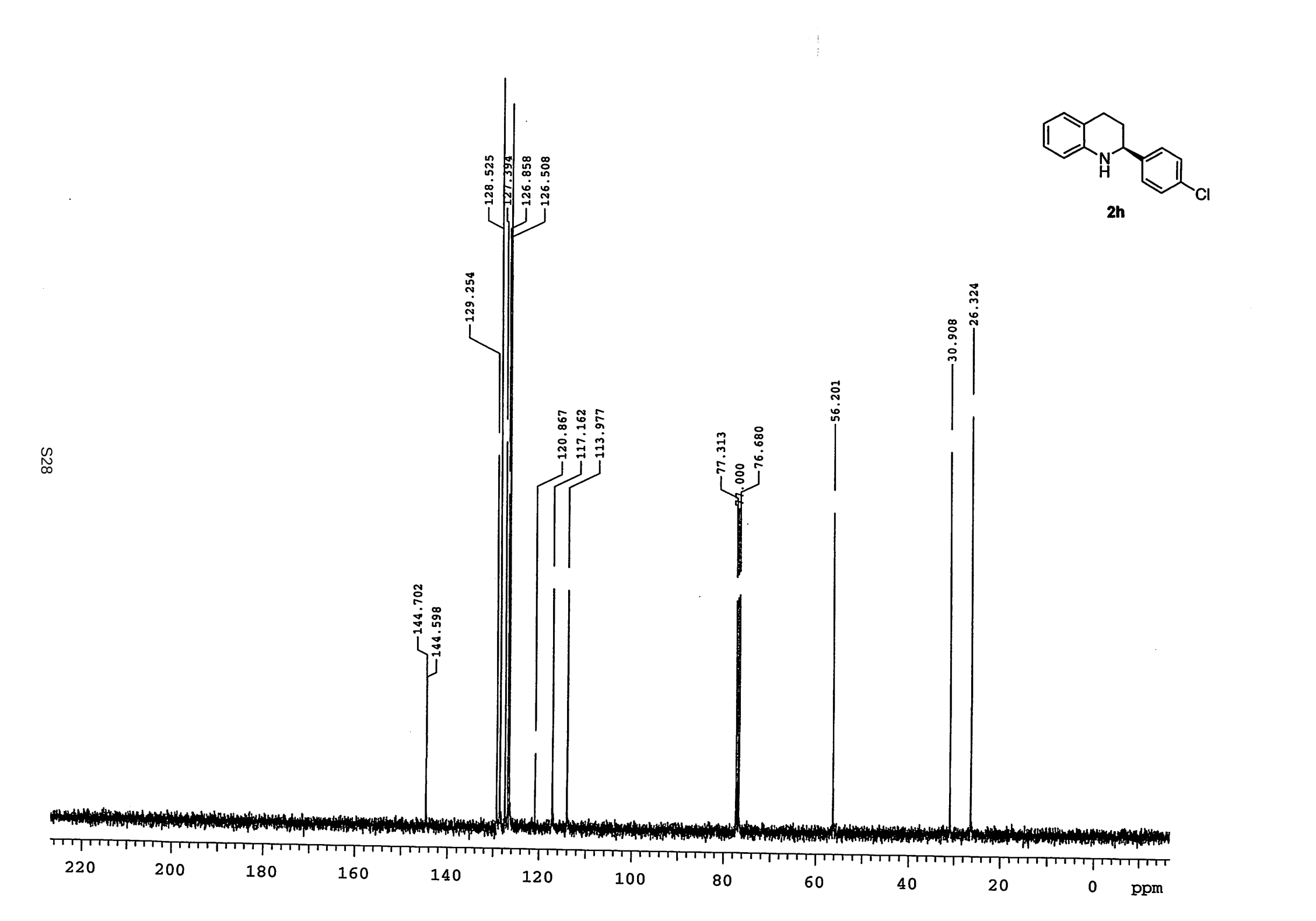

2f
NH
0 ppm
1
2
3
4
5
6
7
8
0.64
2.16
3.09
2.06
0.85
1.00
1.01
0.95
1.97
2.42 1.97

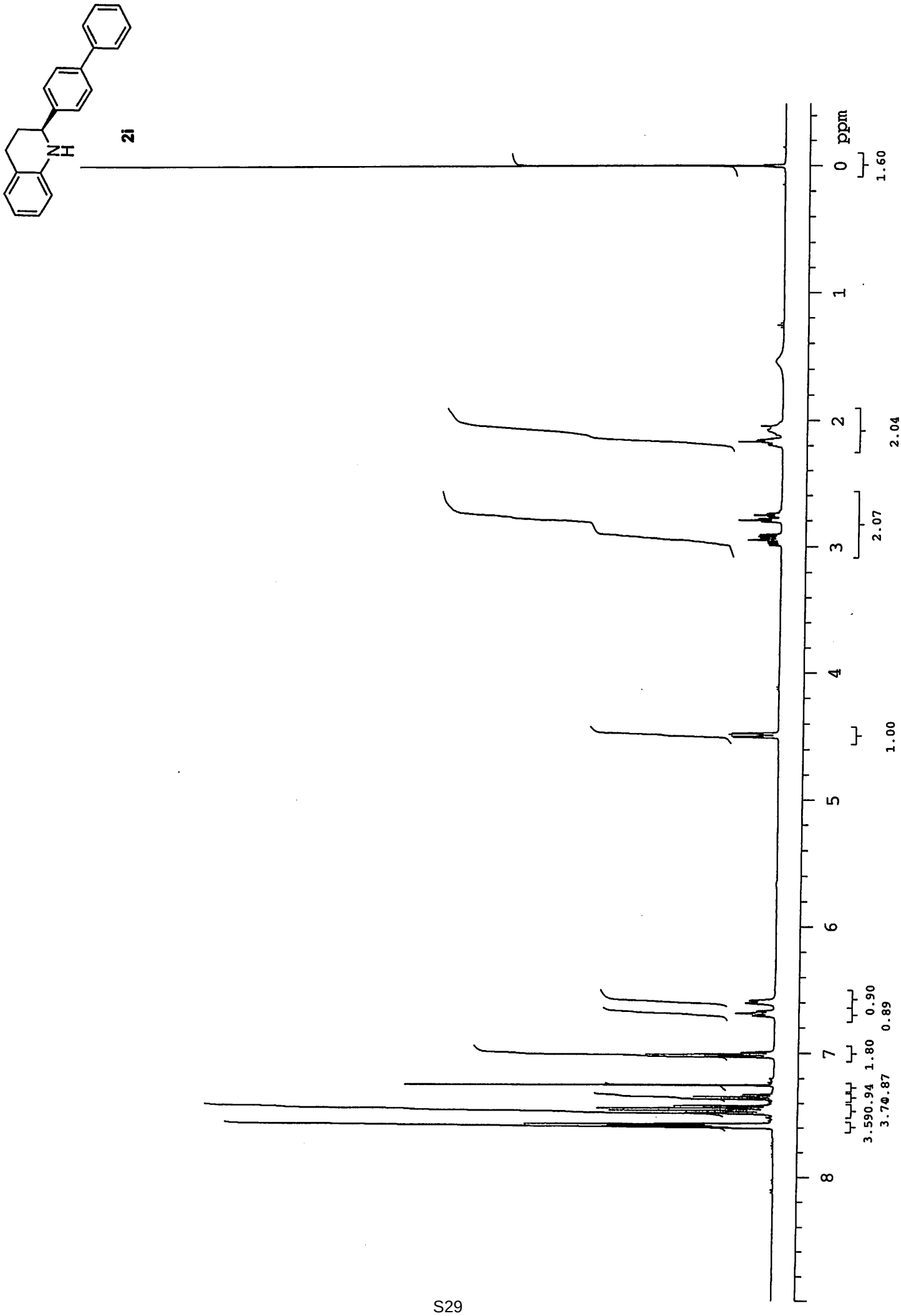

2f
NH
-0.019
21.070
26.465
30.975
55.993
76.680
77.000
77.313
113.954
117.109
120.897
126.441
126.843
129.209
129.254
137.082
141.756
144.710
ppm
0
20
40
60
80
100
120
140
160
180
200
220

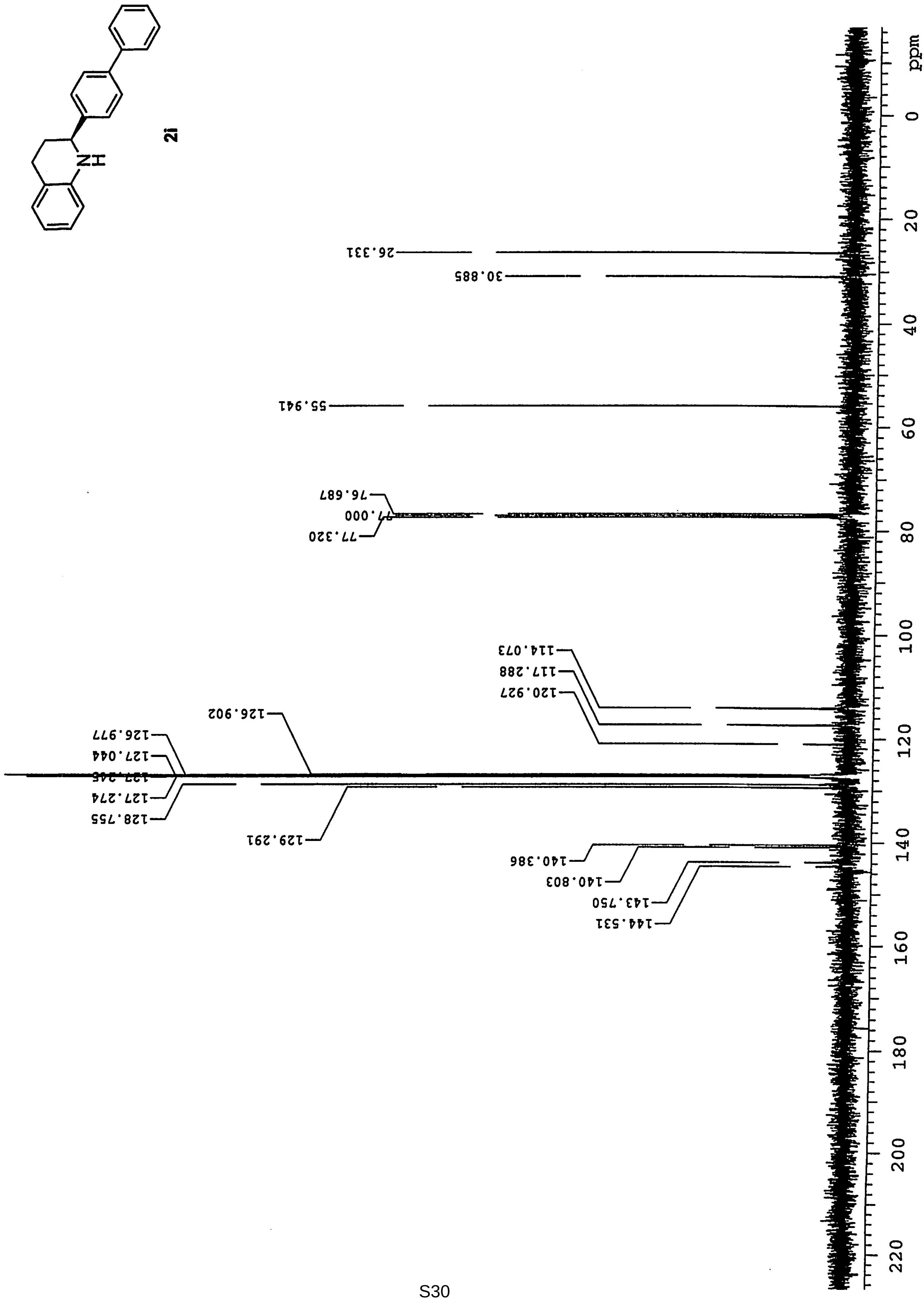

OMe
NH
2g
0 ppm
1
2
3
4
5
6
7
8
0.42
2.37
1.19
1.08
3.13
1.00
1.92 1.95 0.99
0.36 2.04 1.09

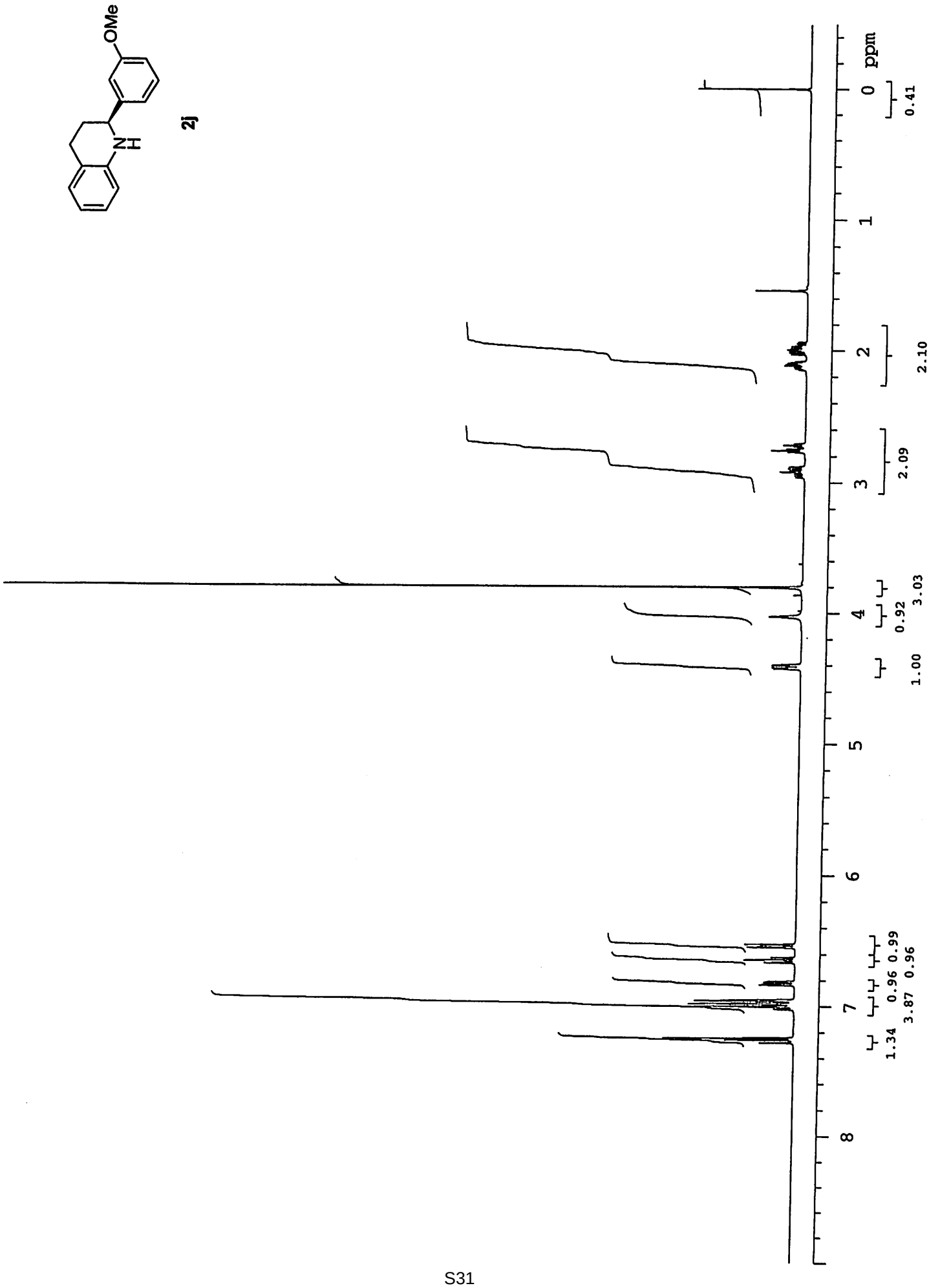

OMe
NH
2g
158.923
144.792
136.852
129.254
127.602
126.828
120.853
117.080
113.925
113.887
77.313
76.680
55.688
55.293
31.071
26.532
ppm
0
20
40
60
80
100
120
140
160
180
200
220

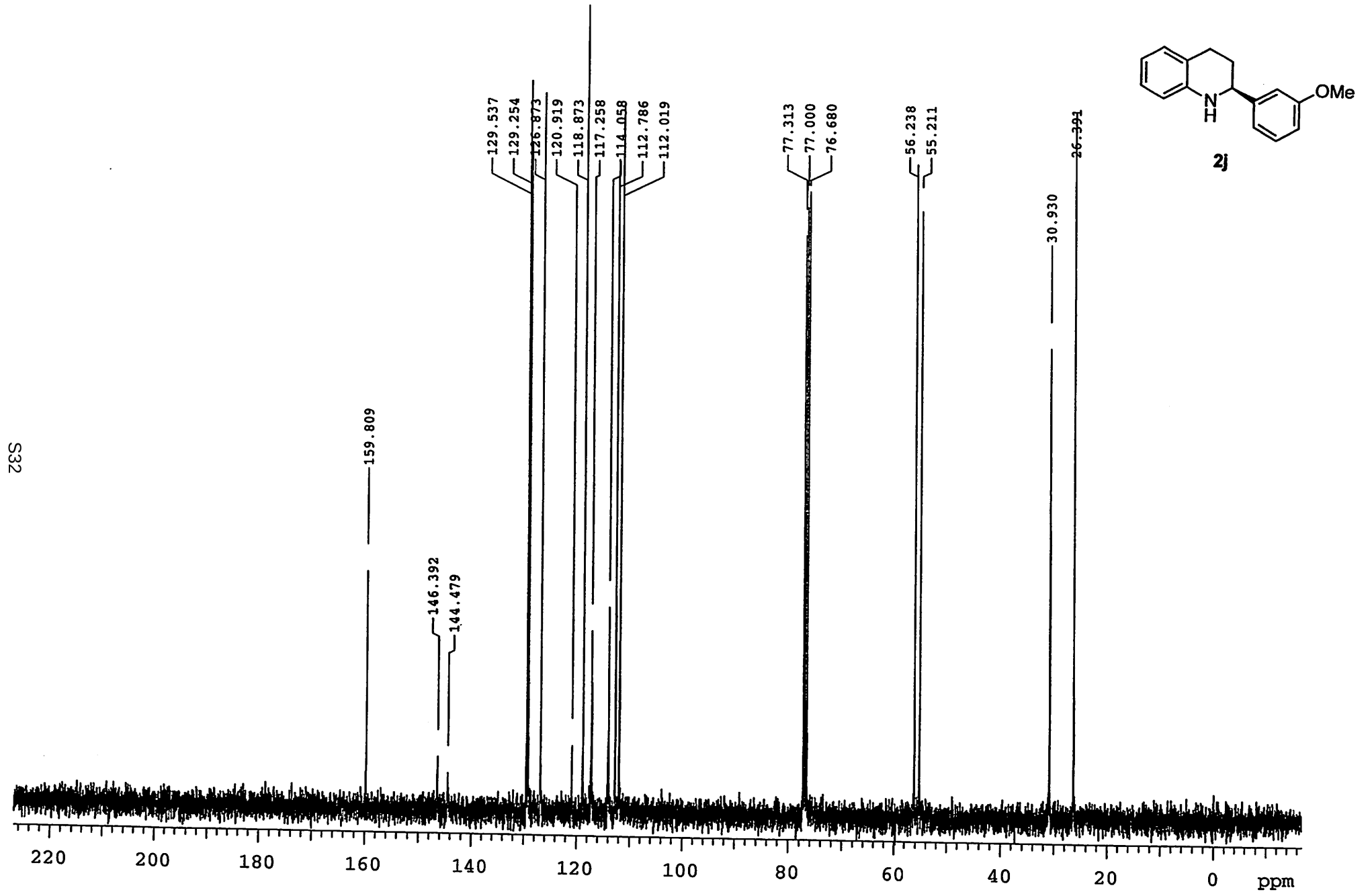

Cl
NH
2h
0 ppm
1
2
3
4
5
6
7
8
0.63
2.32
2.18
0.94
1.00
1.04
0.97
1.96
3.78
1.61

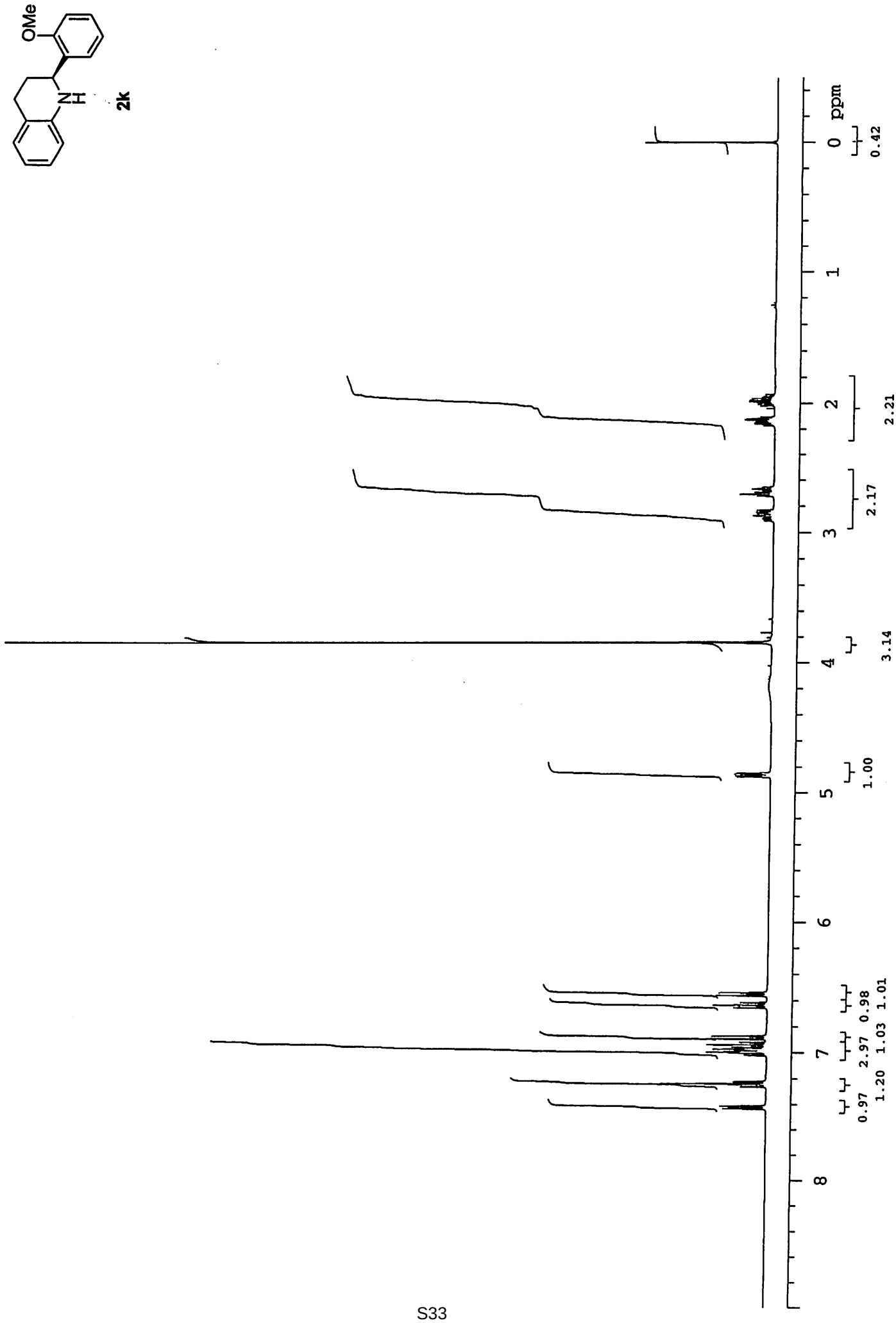

144.702
144.598
129.254
128.525
127.394
126.858
126.508
120.867
117.162
113.977
77.313
77.000
76.680
56.201
30.908
26.324
220
200
180
160
140
120
100
80
60
40
20
0
ppm
N
H
Cl
2h

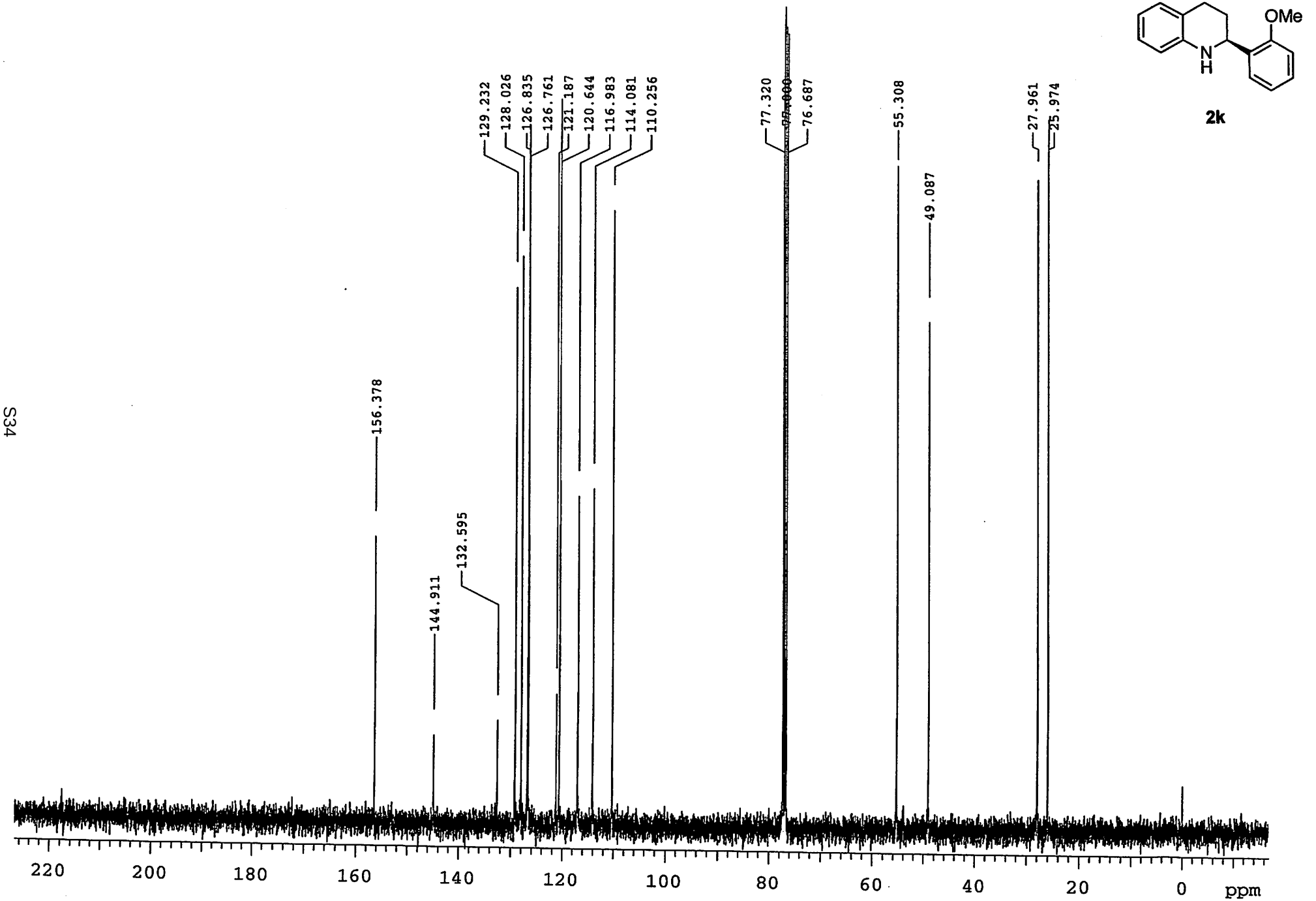

2i
NH
0 ppm
1
2
3
4
5
6
7
8
1.60
2.04
2.07
1.00
0.90
0.89
1.80
0.87

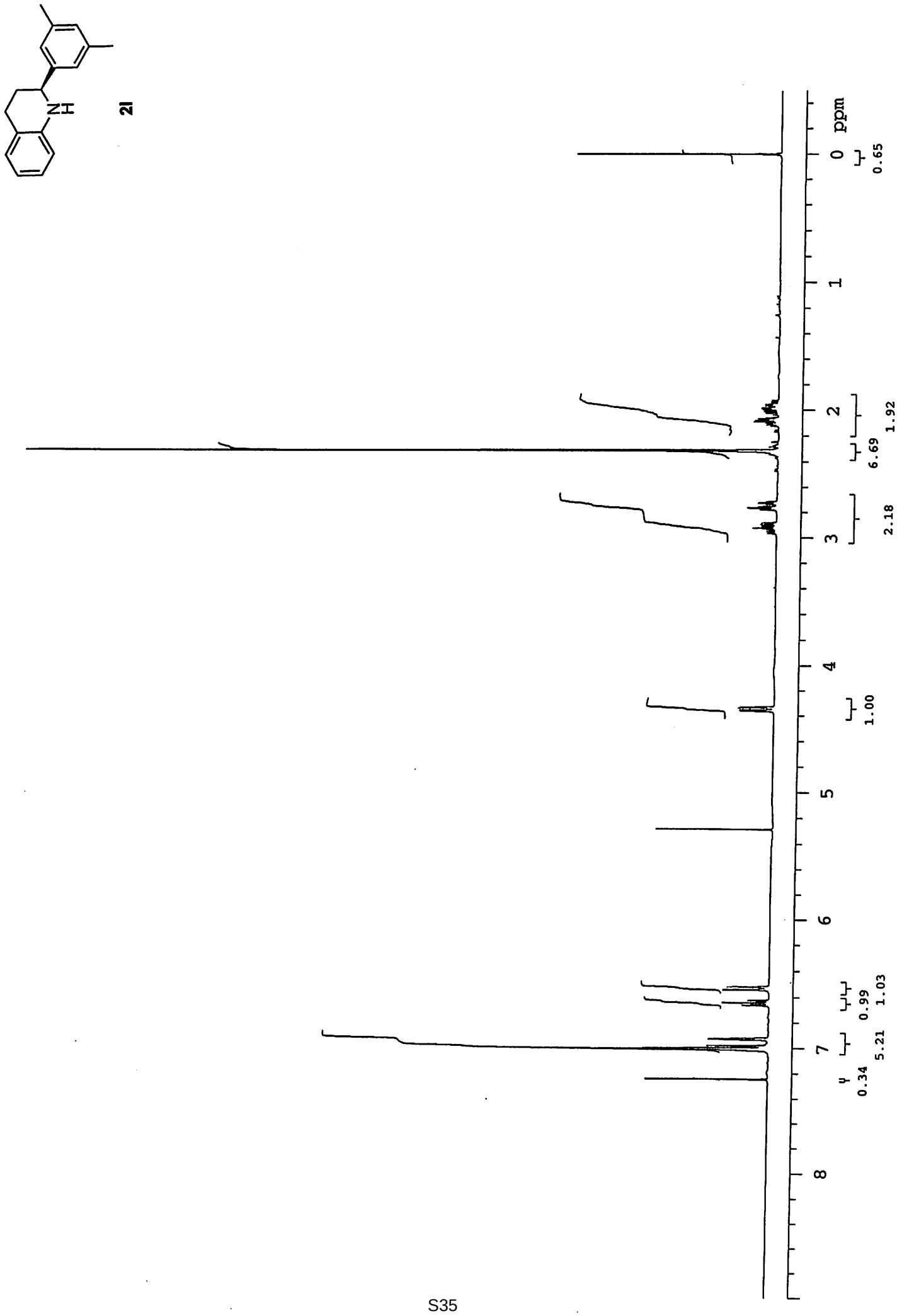

2i
26.331
30.885
55.941
76.687
77.000
77.320
114.073
117.288
120.927
126.902
126.977
127.044
127.245
127.274
128.755
129.291
140.386
140.803
143.750
144.531
ppm
0
20
40
60
80
100
120
140
160
180
200
220

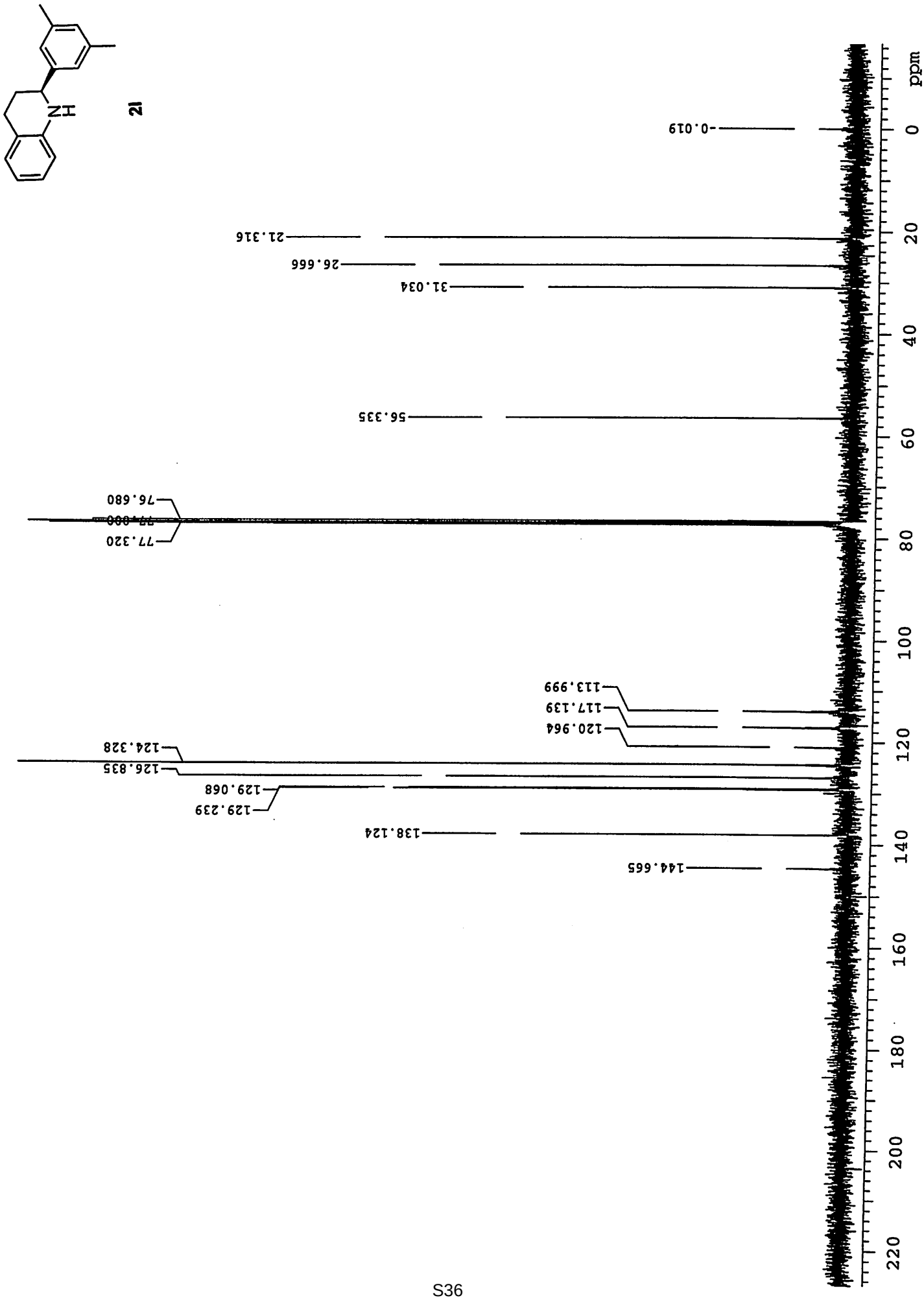

OMe
H
N
2j
0 ppm
0.41
1
2
2.10
3
2.09
4
0.92
3.03
1.00
5
6
7
1.34
0.96
0.99
3.87
0.96
8

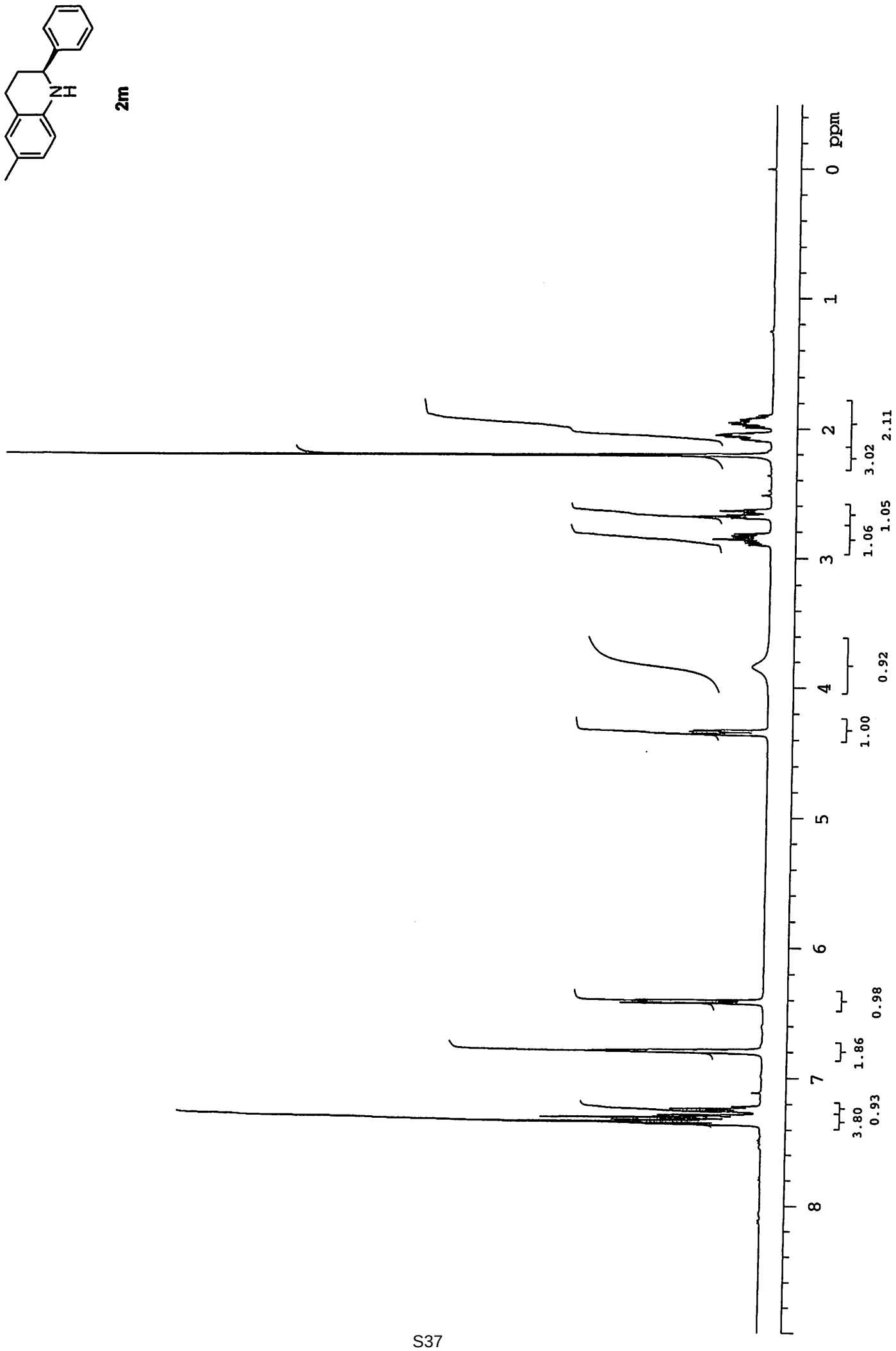

129.537
129.254
126.873
120.919
118.873
117.258
114.058
112.786
112.019
77.313
77.000
76.680
56.238
55.211
30.930
26.391
159.809
146.392
144.479
220
200
180
160
140
120
100
80
60
40
20
0
ppm
OMe
N
H
2j

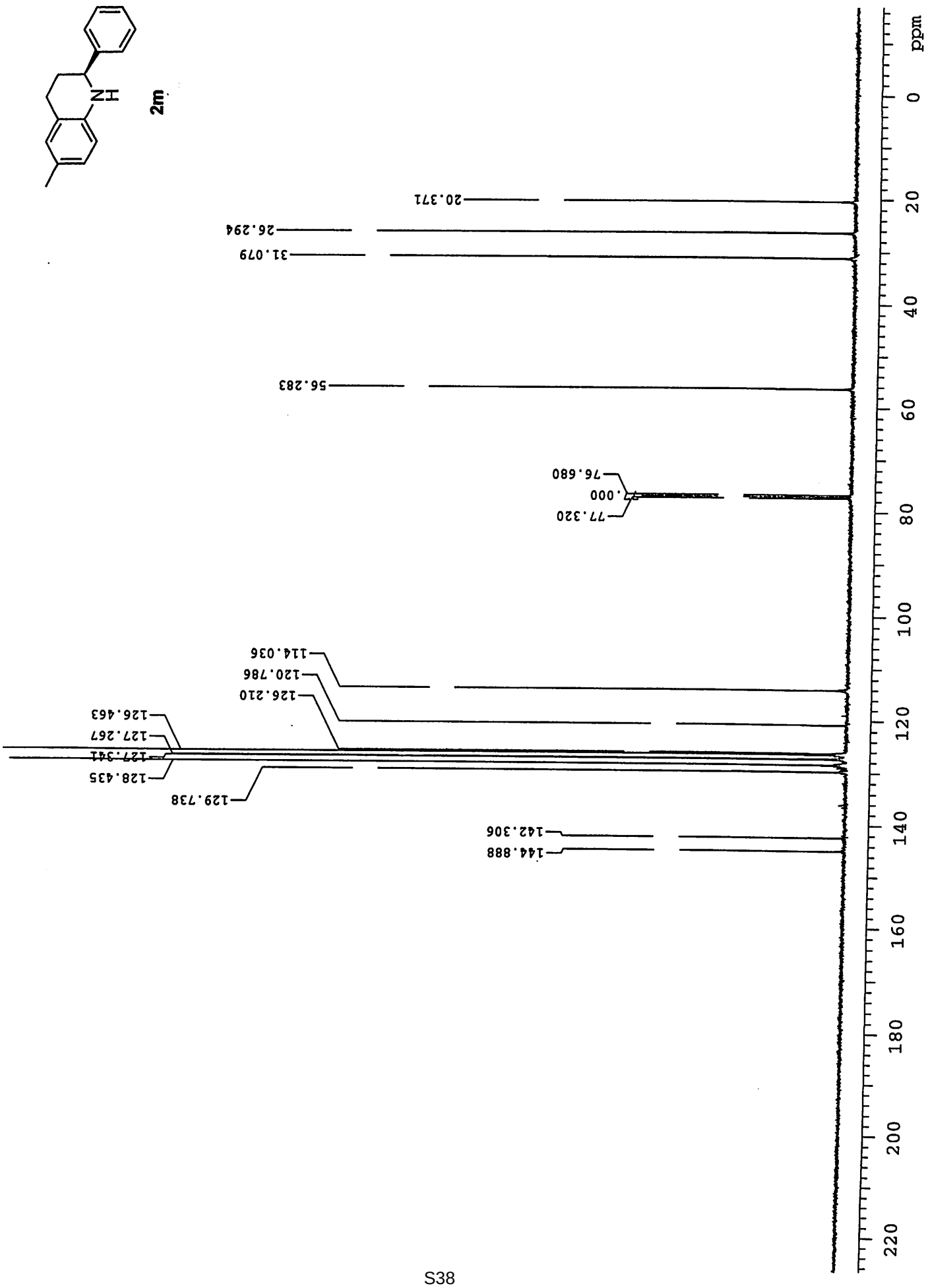

OMe
N
H
2k
0 ppm
1
2
3
4
5
6
7
8
0.42
2.21
2.17
3.14
1.00
0.97 2.97 0.98
1.20 1.03 1.01

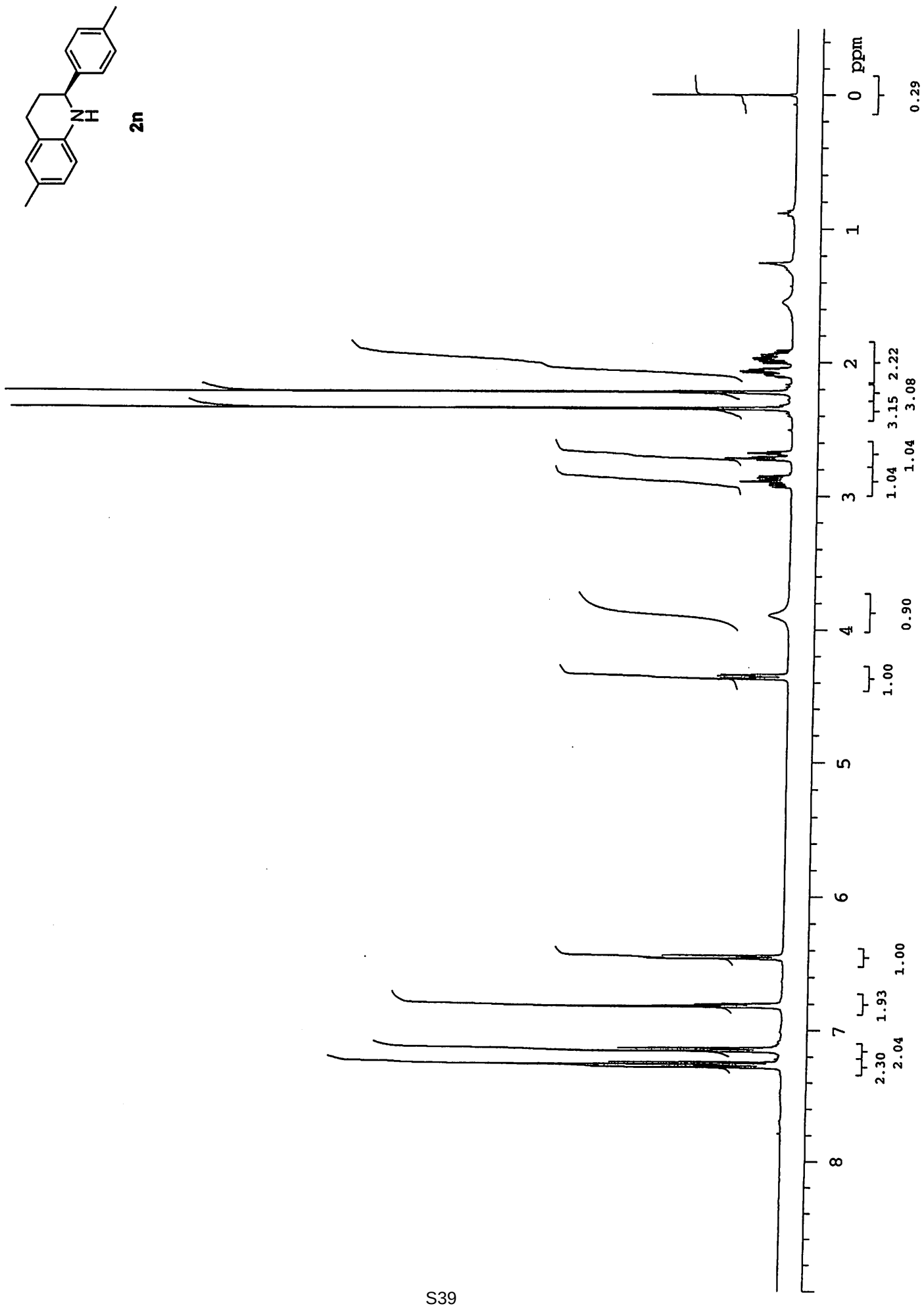

OMe
N
H
2k
156.378
144.911
132.595
129.232
128.026
126.835
126.761
121.187
120.644
116.983
114.081
110.256
77.320
77.000
76.687
55.308
49.087
27.961
25.974
220
200
180
160
140
120
100
80
60
40
20
0
ppm

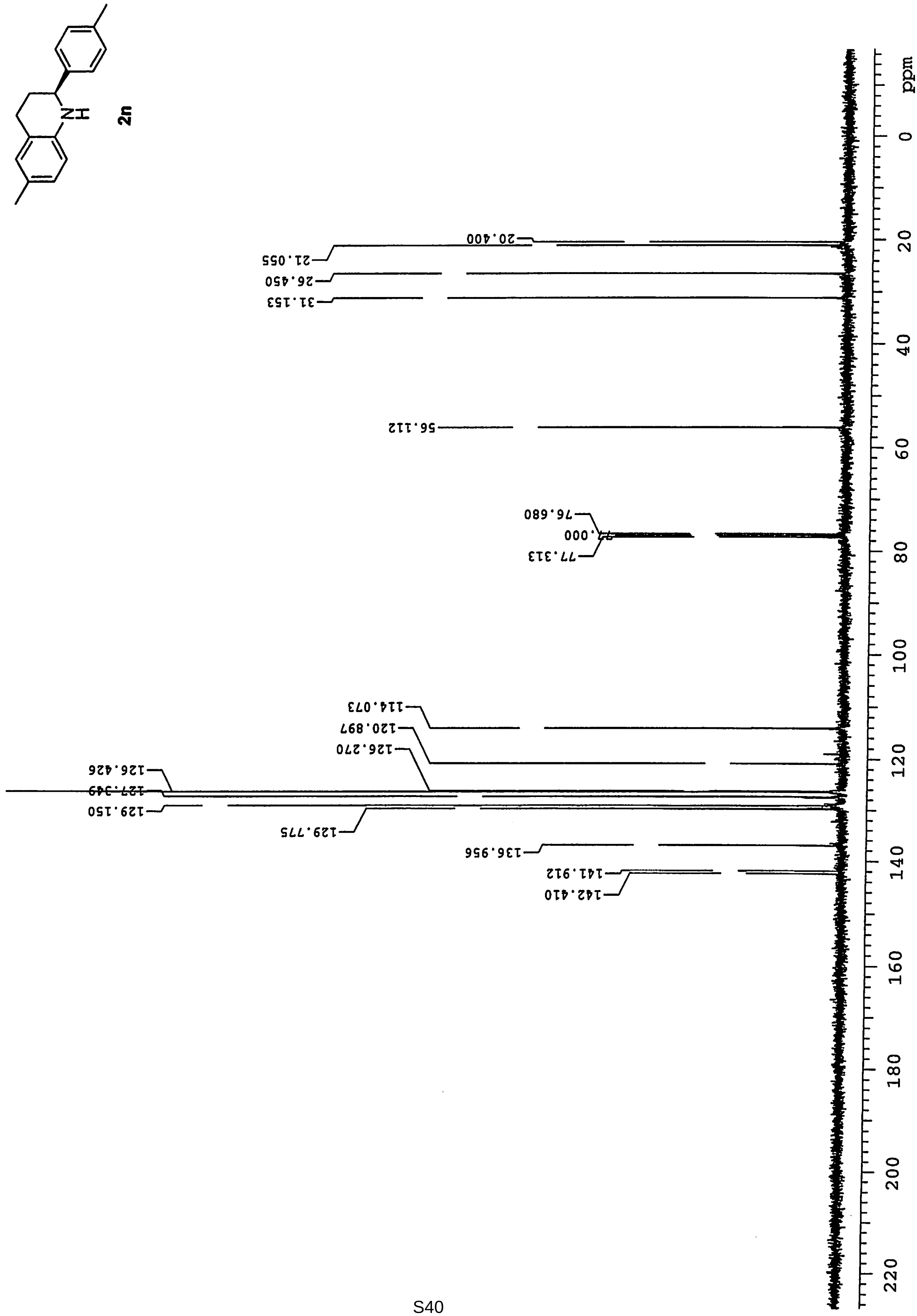

NH
2l
0 ppm
1
2
3
4
5
6
7
8
0.65
6.69
1.92
2.18
1.00
0.34
0.99
5.21
1.03

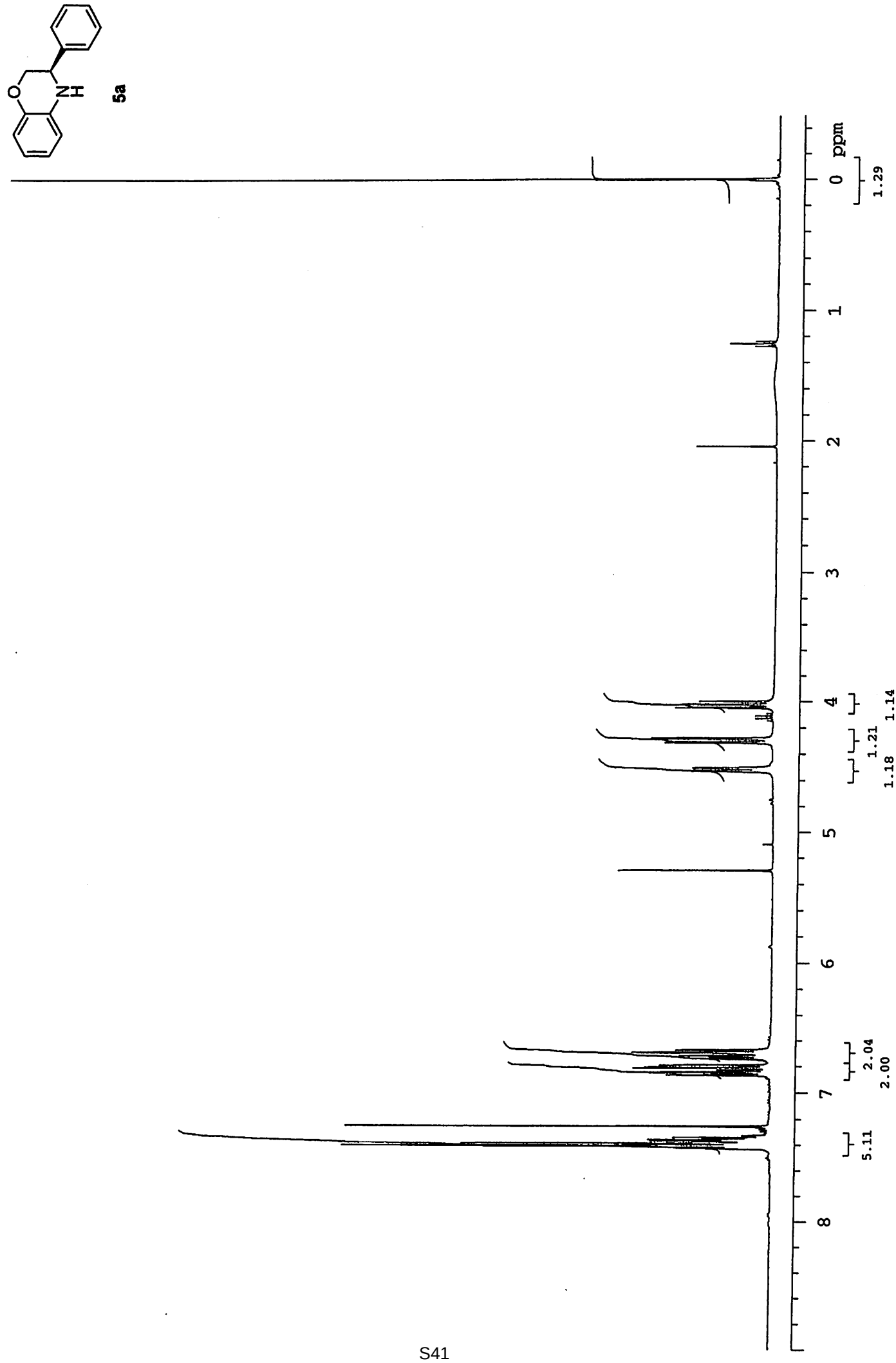

NH
2l
-0.019
21.316
26.666
31.034
56.335
76.680
77.000
77.320
113.999
117.139
120.964
124.328
126.835
129.068
129.239
138.124
144.665
ppm
0
20
40
60
80
100
120
140
160
180
200
220

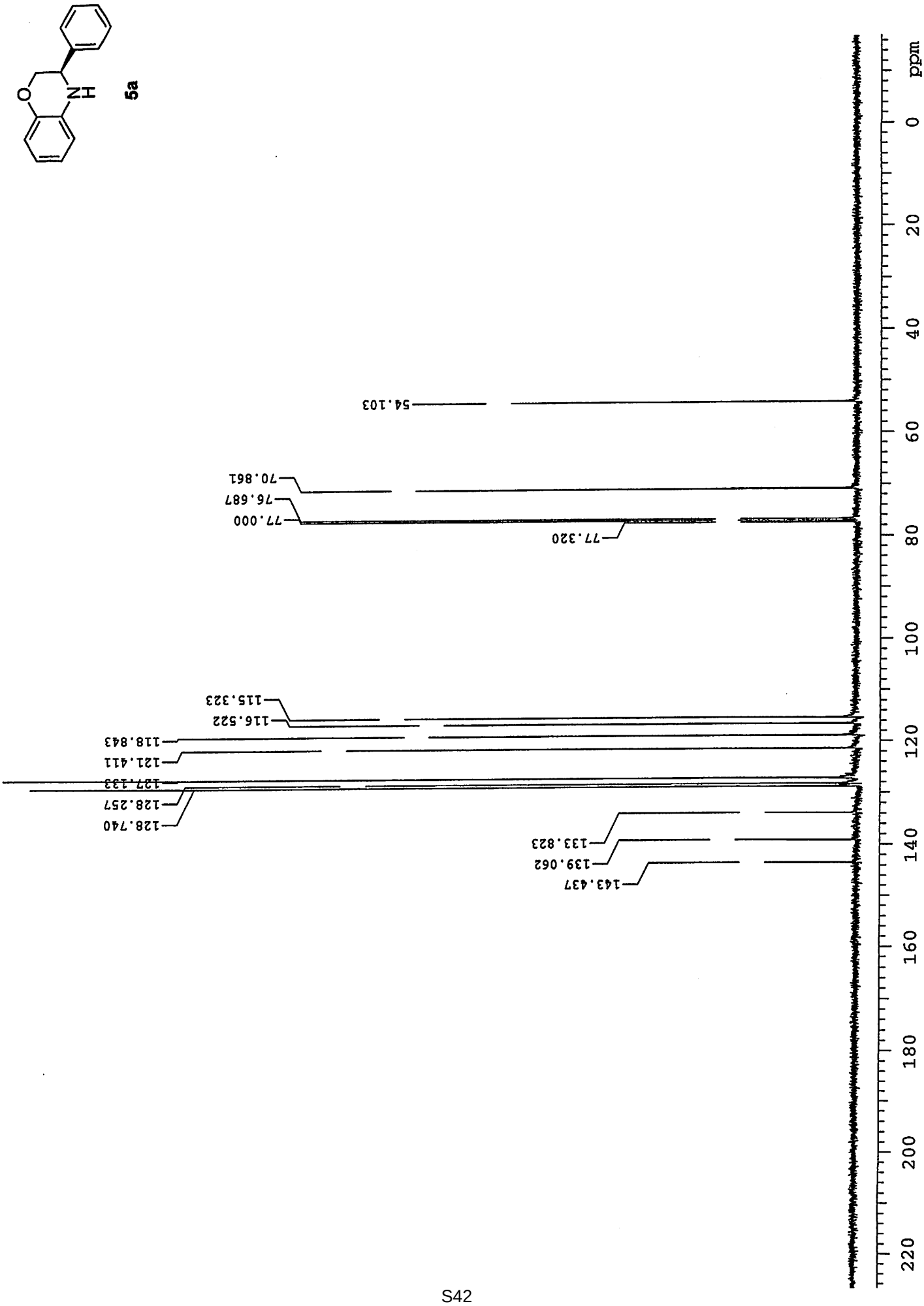

2m
NH
ppm
0
1
2
3
4
5
6
7
8
2.11
3.02
1.05
1.06
0.92
1.00
0.98
1.86
0.93
3.80

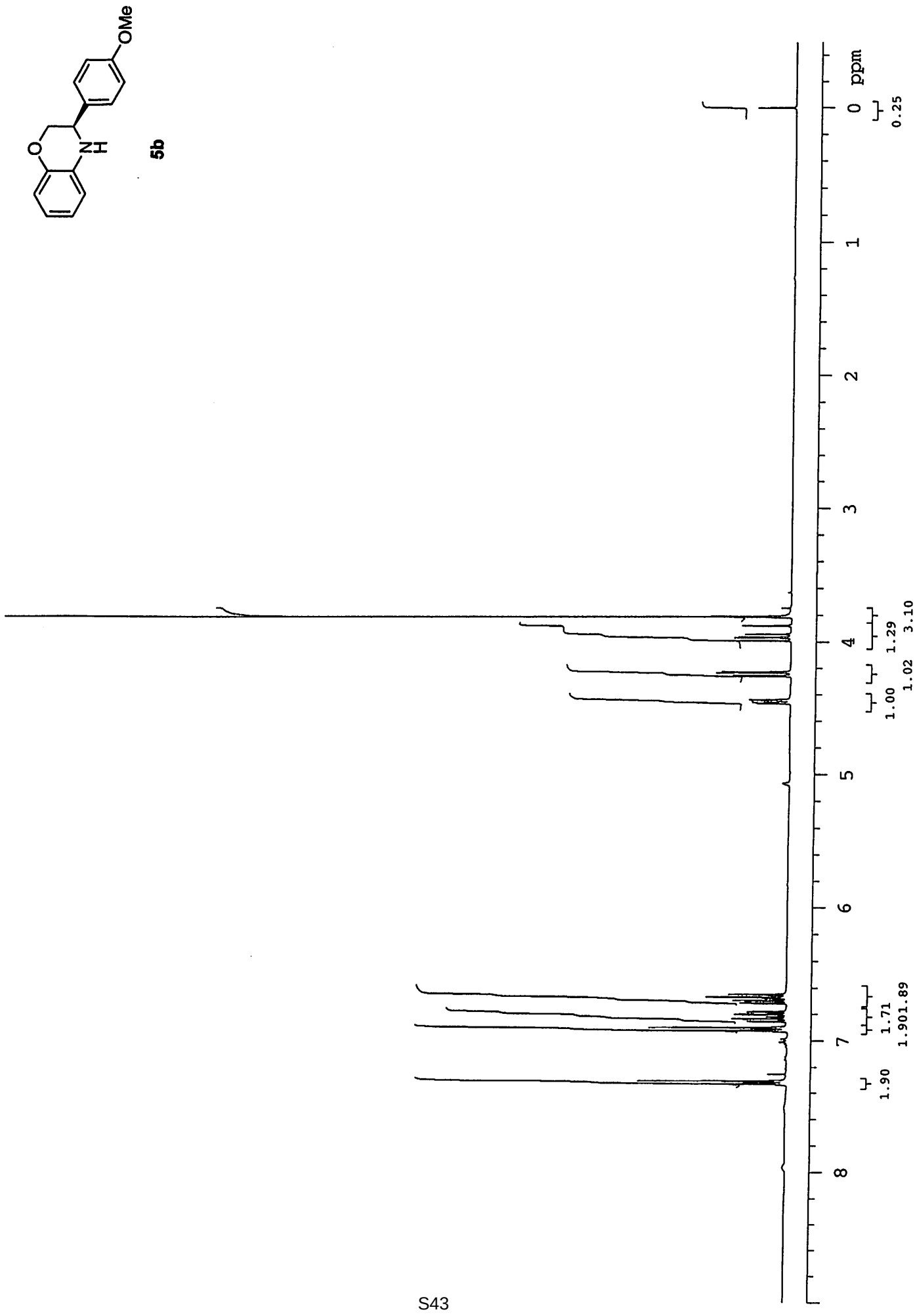

2m
NH
144.888
142.306
129.738
128.435
127.341
127.267
126.463
126.210
120.786
114.036
77.320
.000
76.680
56.283
31.079
26.294
20.371
ppm
0
20
40
60
80
100
120
140
160
180
200
220

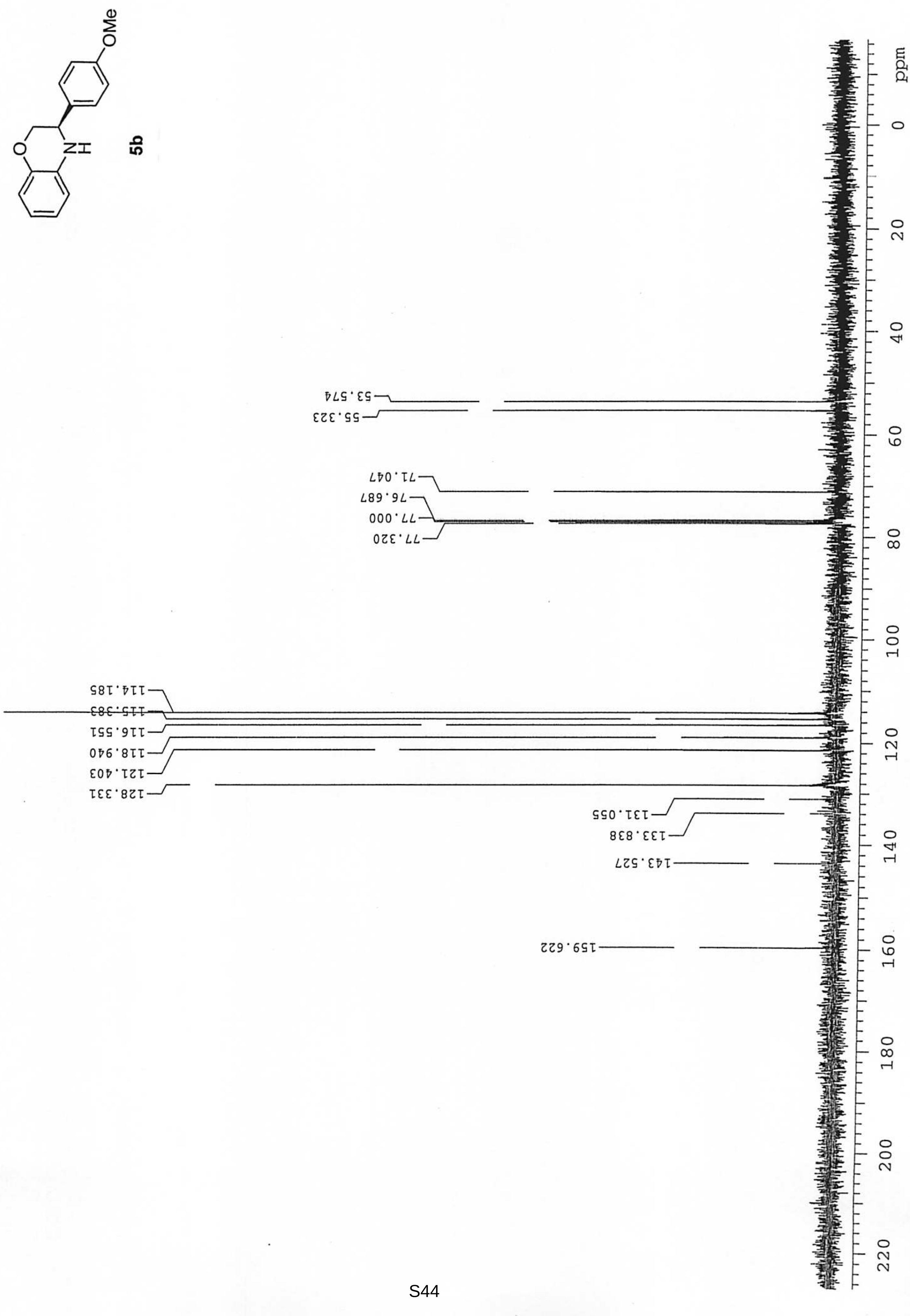

2n
NH
0 ppm
0.29
1.04
3.15
2.22
1.04
3.08
1.00
0.90
2.30
1.93
2.04
1.00

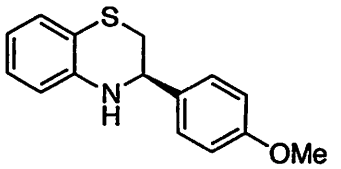

2n
20.400
21.055
26.450
31.153
56.112
76.680
77.000
77.313
114.073
120.897
126.270
126.426
127.349
129.150
129.775
136.956
141.912
142.410
ppm


O
NH
5a
0 ppm
1
2
3
4
5
6
7
8
1.29
1.14
1.21
1.18
2.04
2.00
5.11

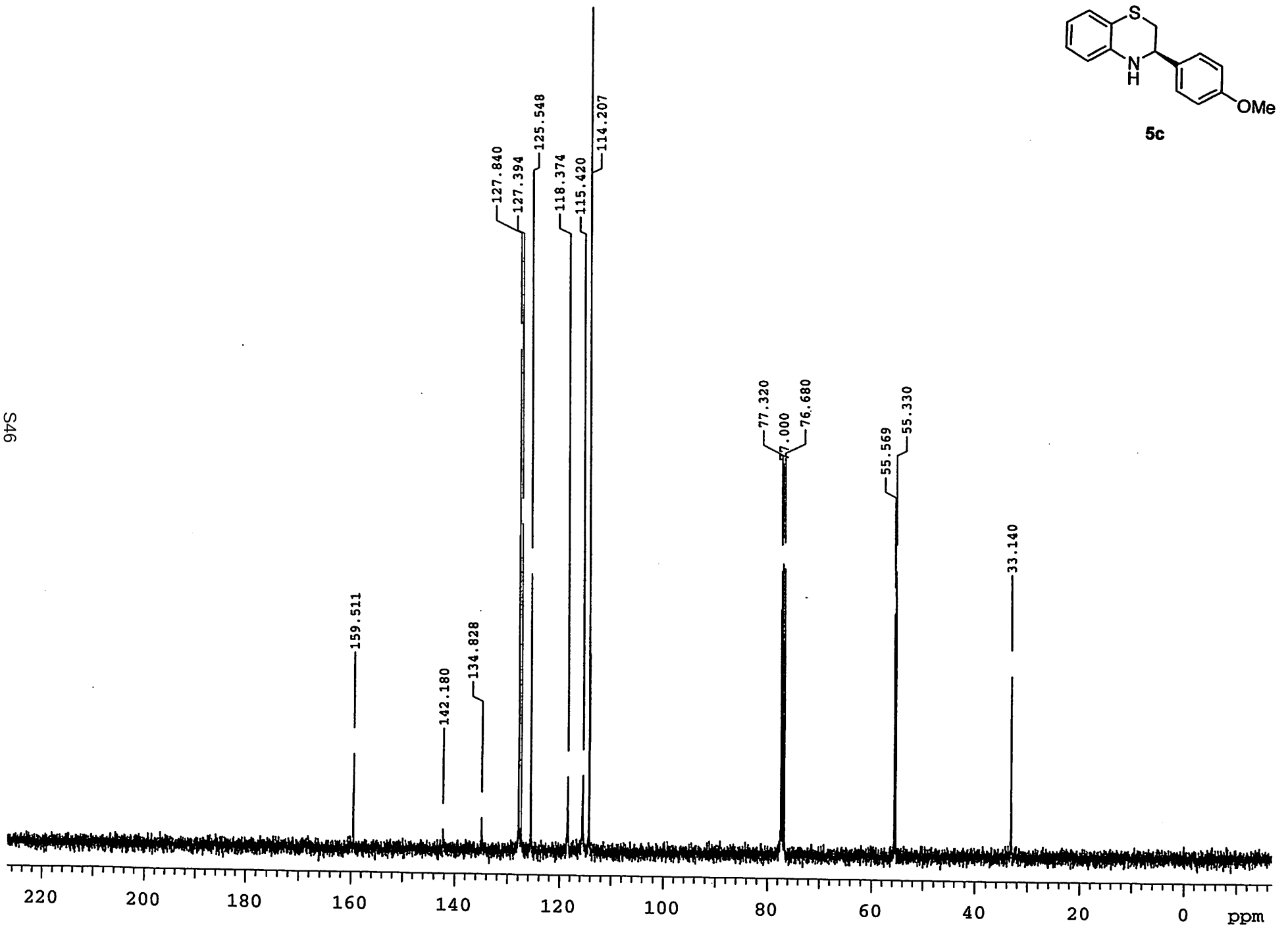

5a
143.437
139.062
133.823
128.740
128.257
127.133
121.411
118.843
116.522
115.323
77.320
77.000
76.687
70.861
54.103
ppm
0
20
40
60
80
100
120
140
160
180
200
220

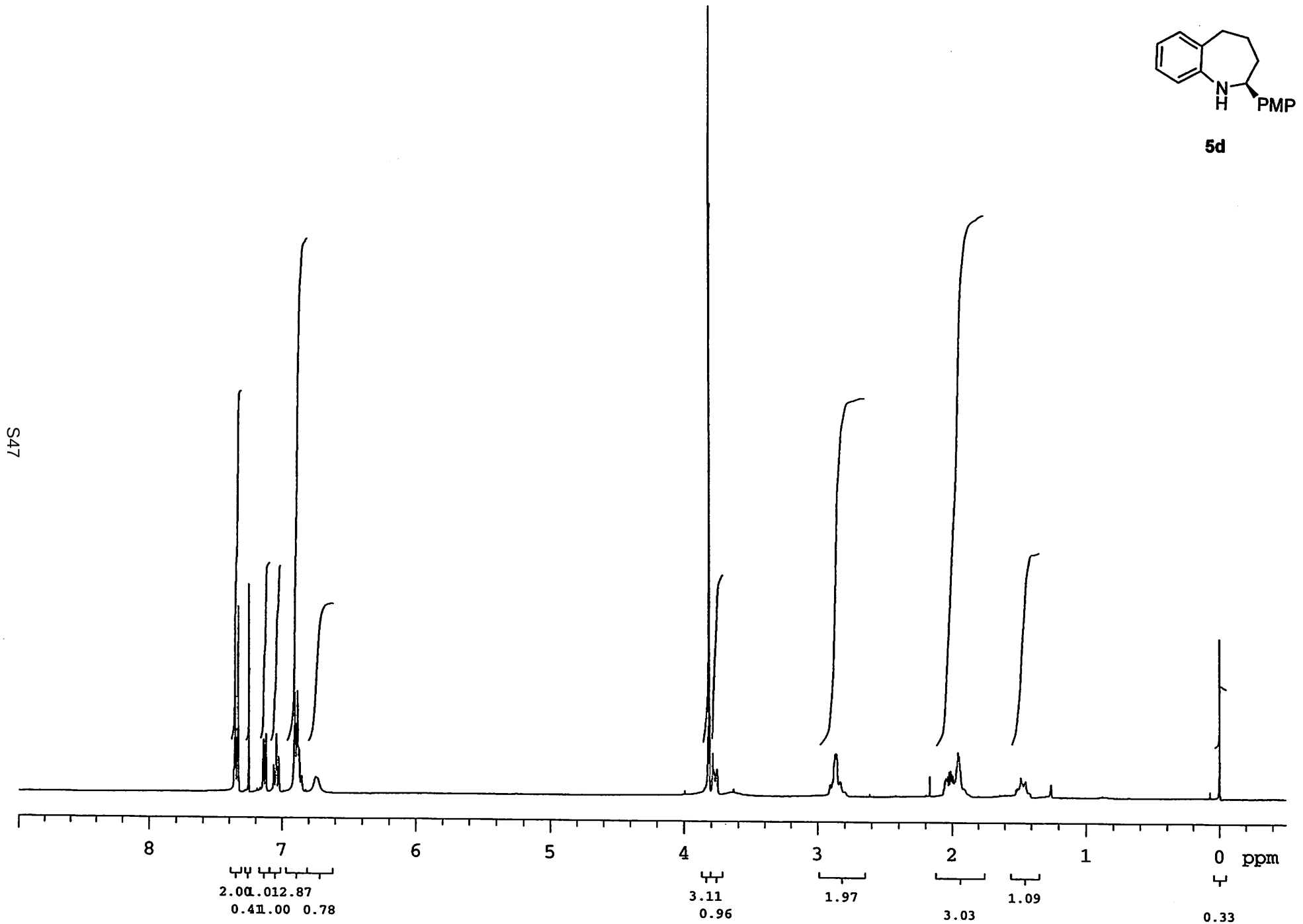

OMe
O
NH
5b
0 ppm
0.25
1.00
1.29
1.02
3.10
1.90
1.71
1.901.89

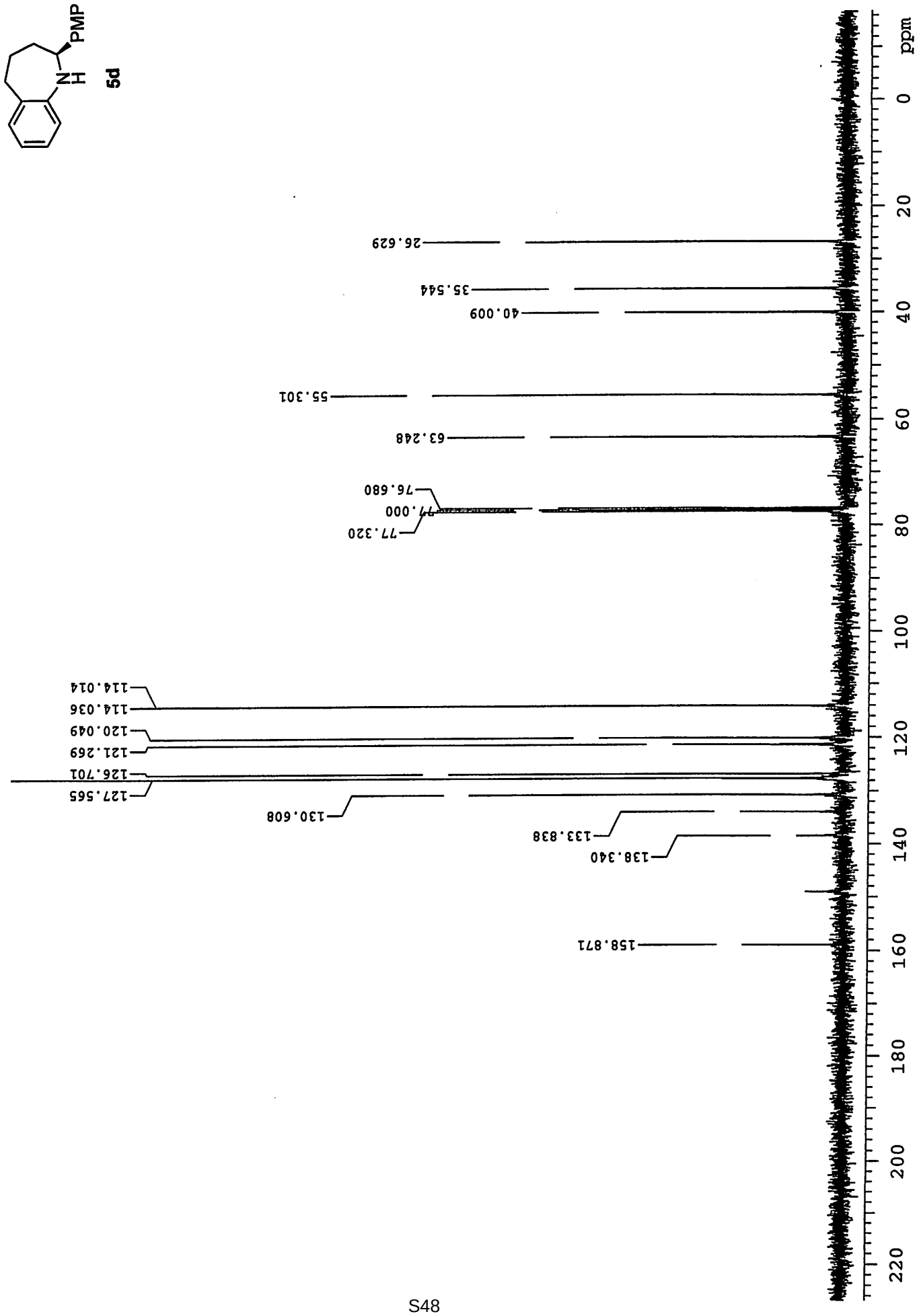

OMe
O
N
H
5b
53.574
55.323
71.047
76.687
77.000
77.320
114.185
115.383
116.551
118.940
121.403
128.331
131.055
133.838
143.527
159.622
ppm
0
20
40
60
80
100
120
140
160
180
200
220

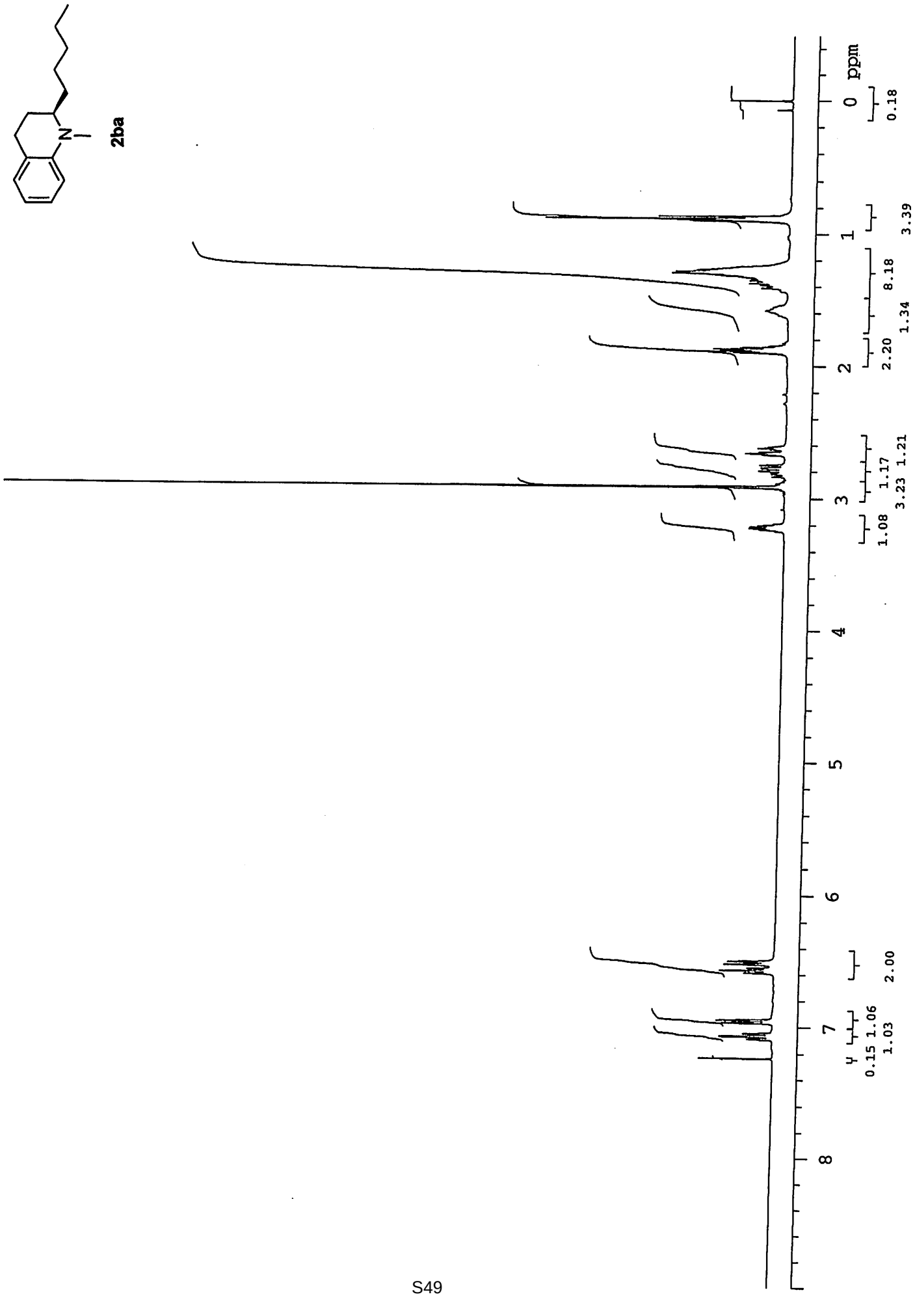


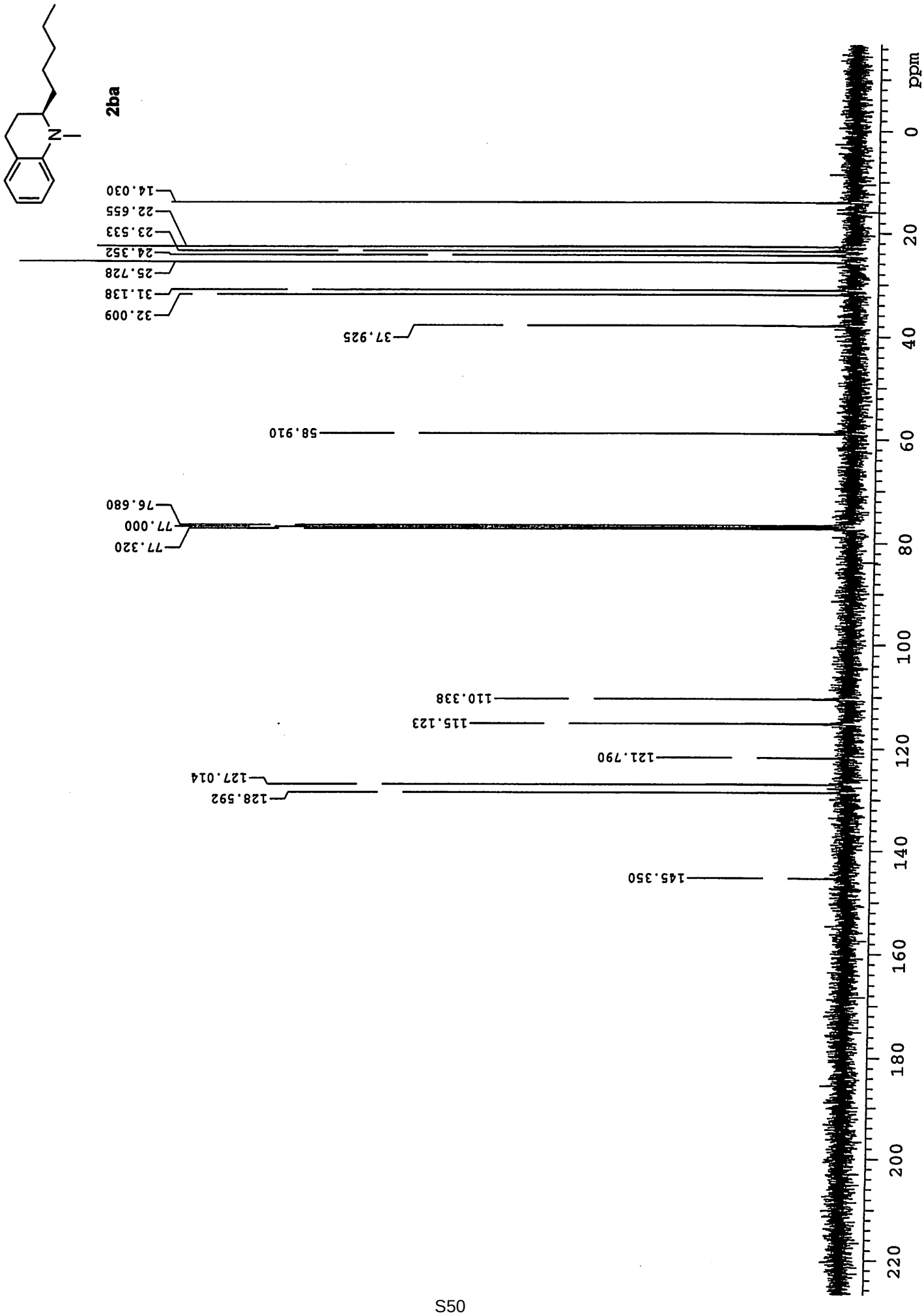
5c

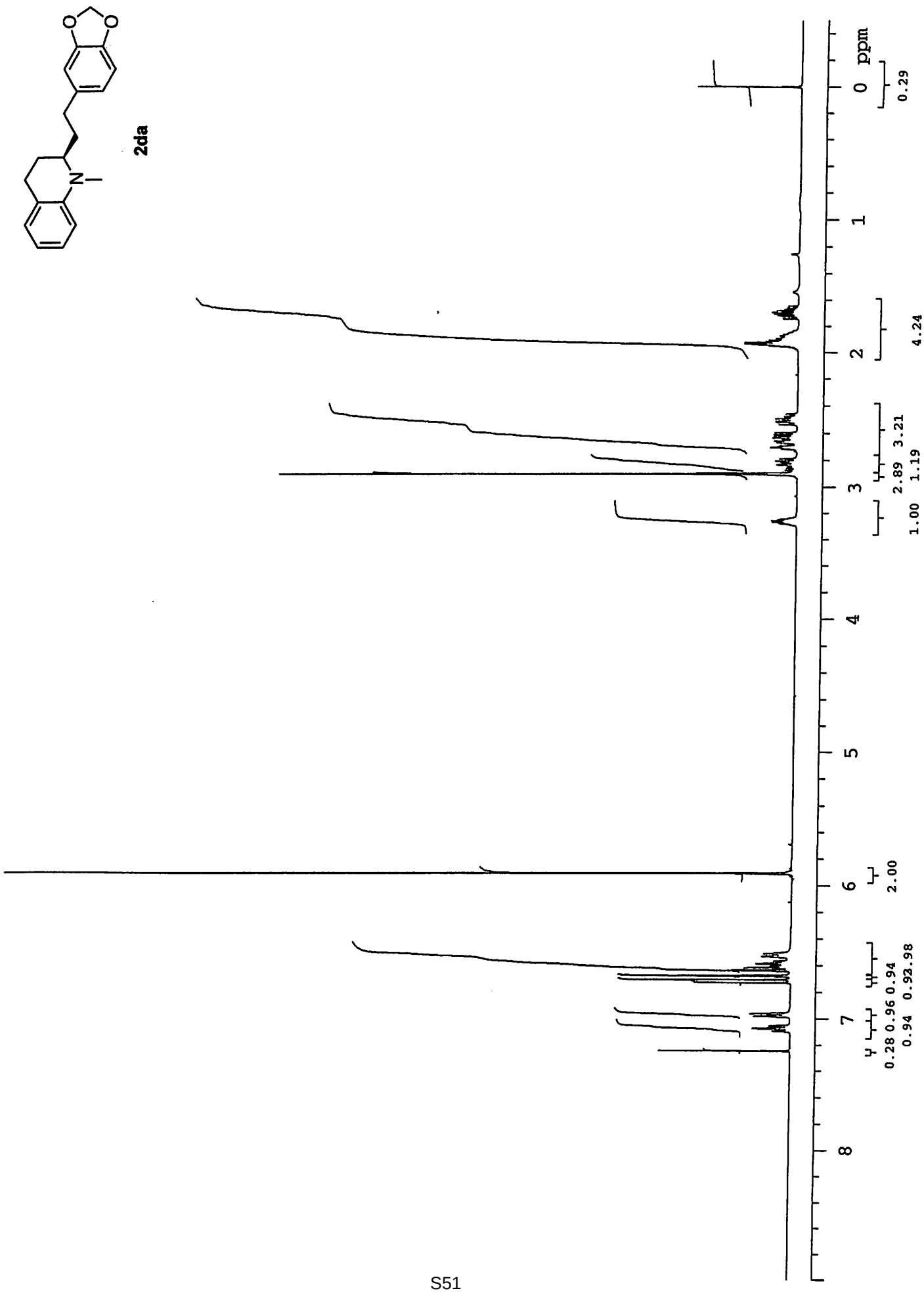

S
N
H
OMe
5c
159.511
142.180
134.828
127.840
127.394
125.548
118.374
115.420
114.207
77.320
77.000
76.680
55.569
55.330
33.140
220
200
180
160
140
120
100
80
60
40
20
0
ppm

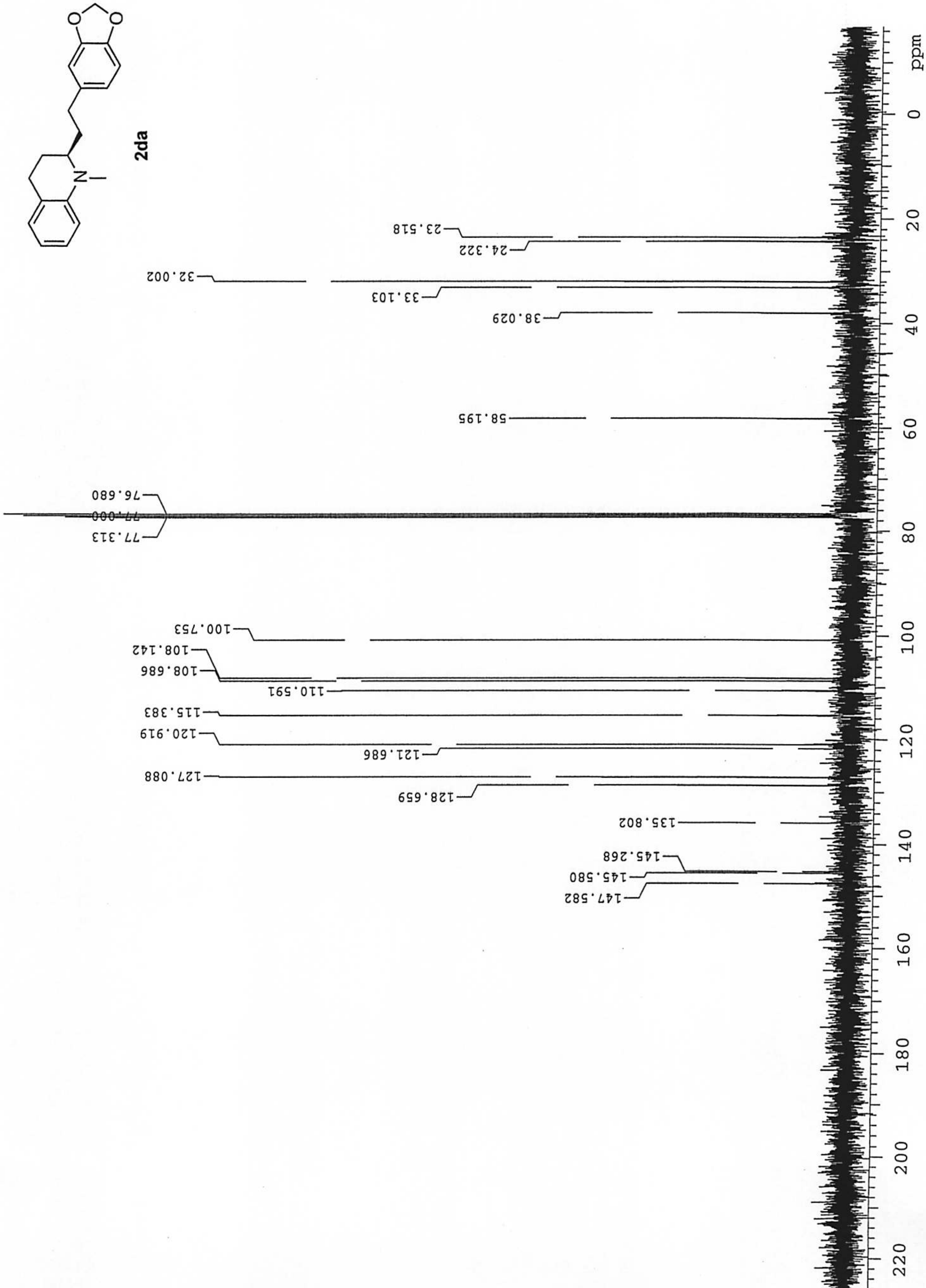

N
H
PMP
5d
8
7
6
5
4
3
2
1
0
ppm
2.00
1.01
2.87
0.41
1.00
0.78
3.11
0.96
1.97
3.03
1.09
0.33

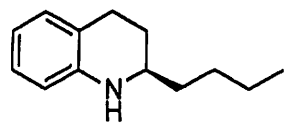

PMP
N
H
5d
158.871
138.340
133.838
130.608
127.565
126.701
121.269
120.049
114.036
114.014
77.320
77.000
76.680
63.248
55.301
40.009
35.544
26.629
ppm
0
20
40
60
80
100
120
140
160
180
200
220


2ba
N
0 ppm
0.18
3.39
8.18
1.34
2.20
1.21
1.17
3.23
1.08
2.00
1.06
1.03
0.15


2ba
14.030
22.655
23.533
24.352
25.728
31.138
32.009
37.925
58.910
76.680
77.000
77.320
110.338
115.123
121.790
127.014
128.592
145.350
ppm

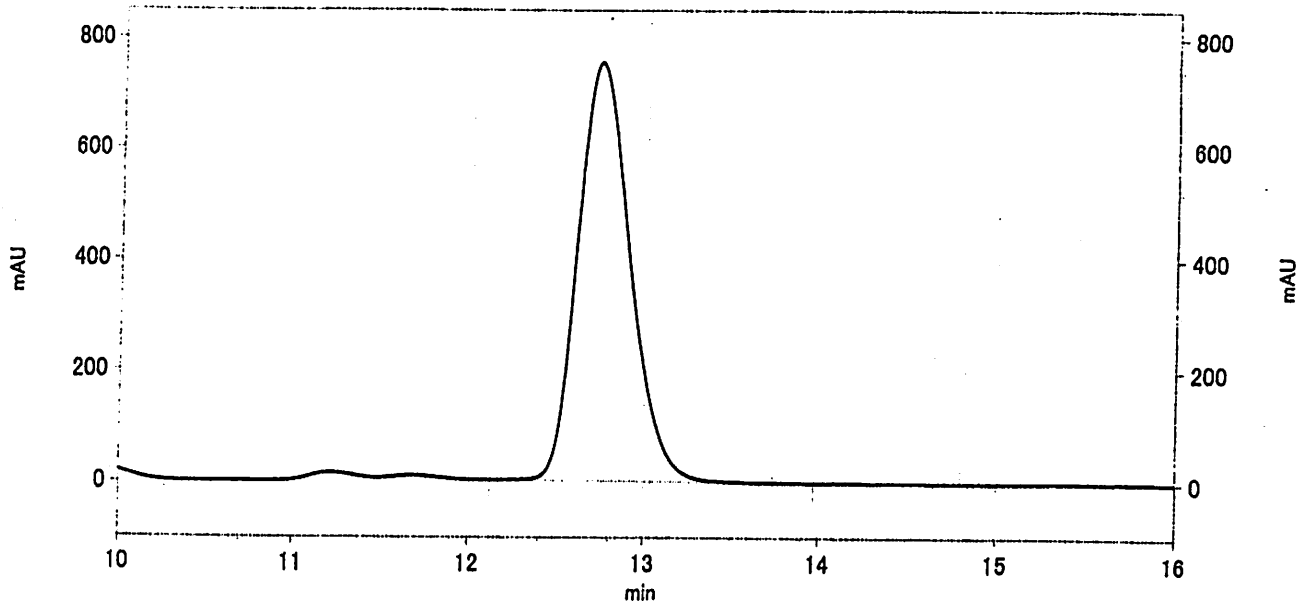

2da
0 ppm
0.29
4.24
2.89 3.21
1.00 1.19
2.00
0.28 0.96 0.94
0.94 0.92.98


2da
23.518
24.322
32.002
33.103
38.029
58.195
76.680
77.000
77.313
100.753
108.142
108.686
110.591
115.383
120.919
121.686
127.088
128.659
135.802
145.268
145.580
147.582
ppm
0
20
40
60
80
100
120
140
160
180
200
220

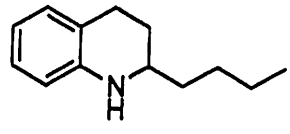


2a

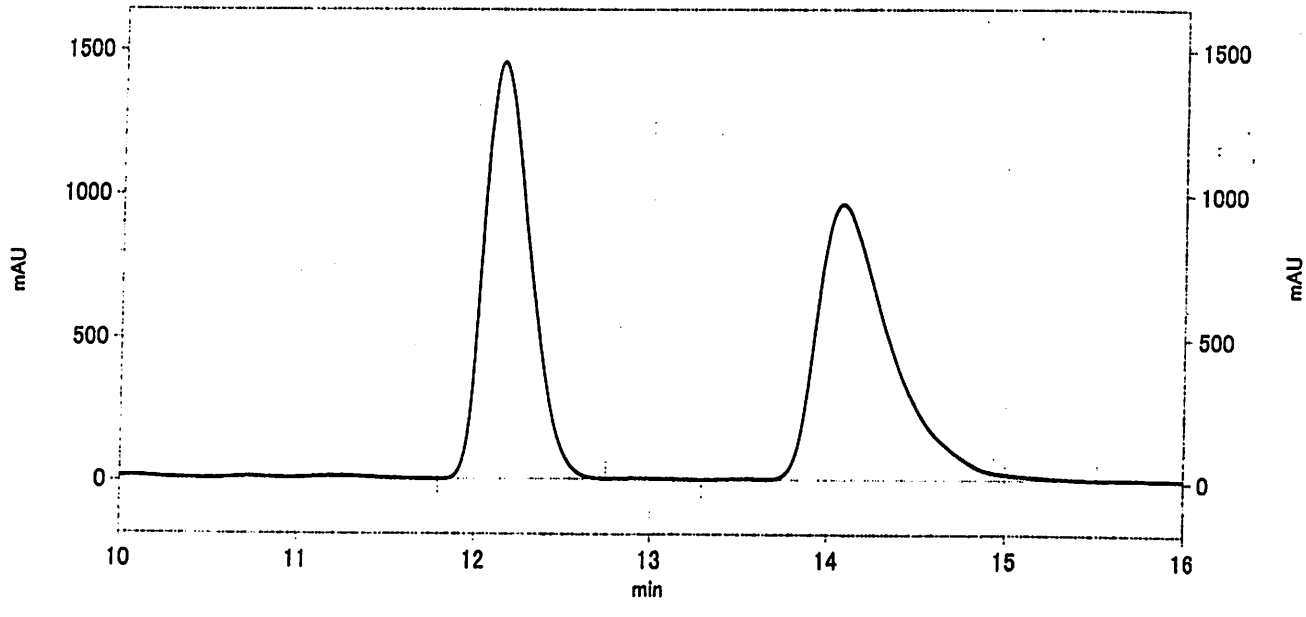
0.05



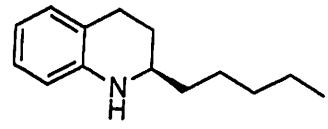
Peak #	Retention time	Type	Area	Area %
1	12.73	BB	62787775	99.949
2	14.17	BB	31849	0.051



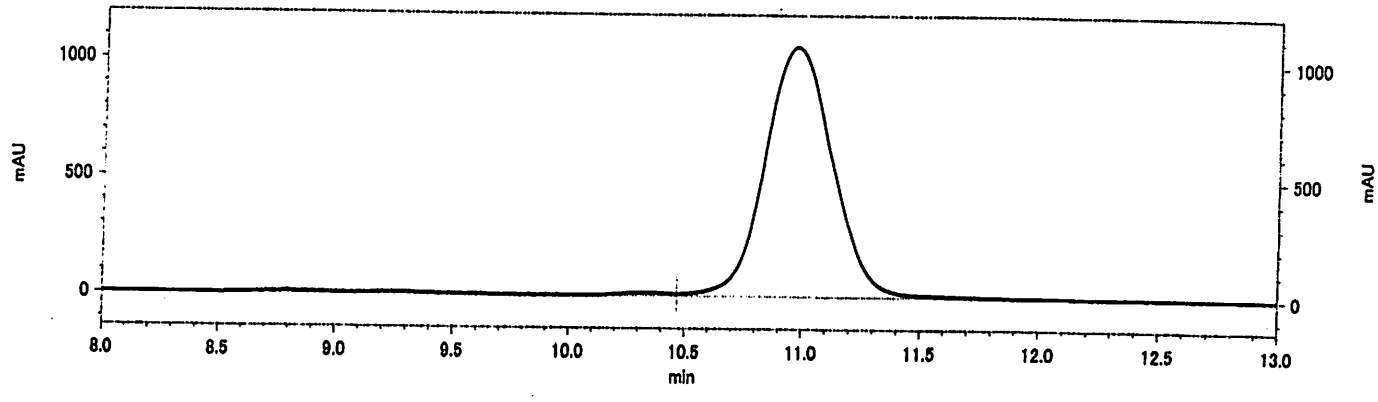
0.05



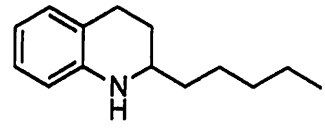
Peak #	Retention time	Type	Area	Area %
1	12.15	BB	105982098	48.872
2	14.08	BB S53	110875374	51.128

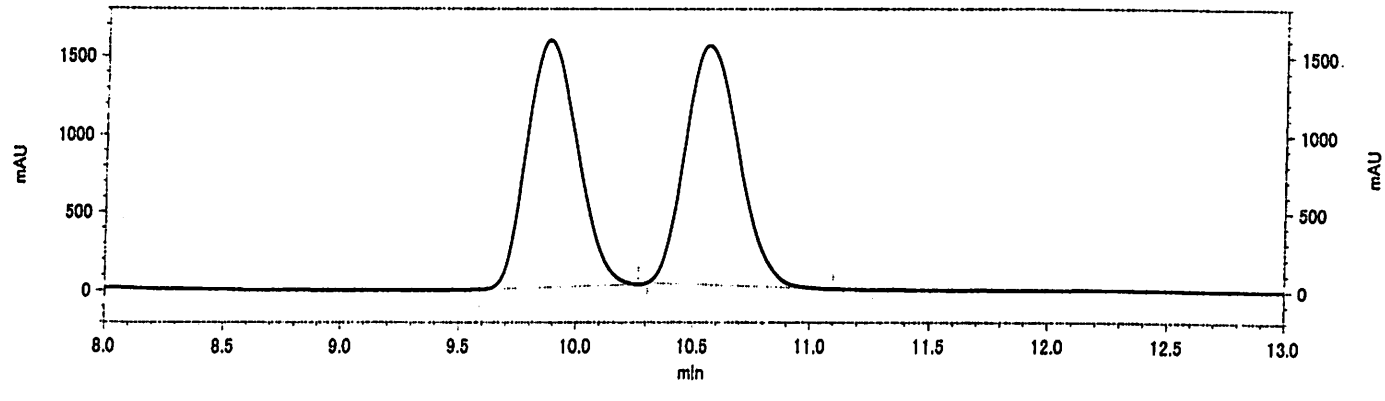


2b

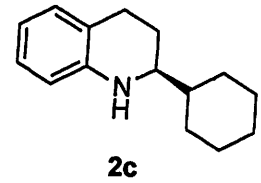


Pk #	Time	Area	Area%	Type
1	10.327	797469	0.926	BV
2	10.967	85319647	99.074	VB

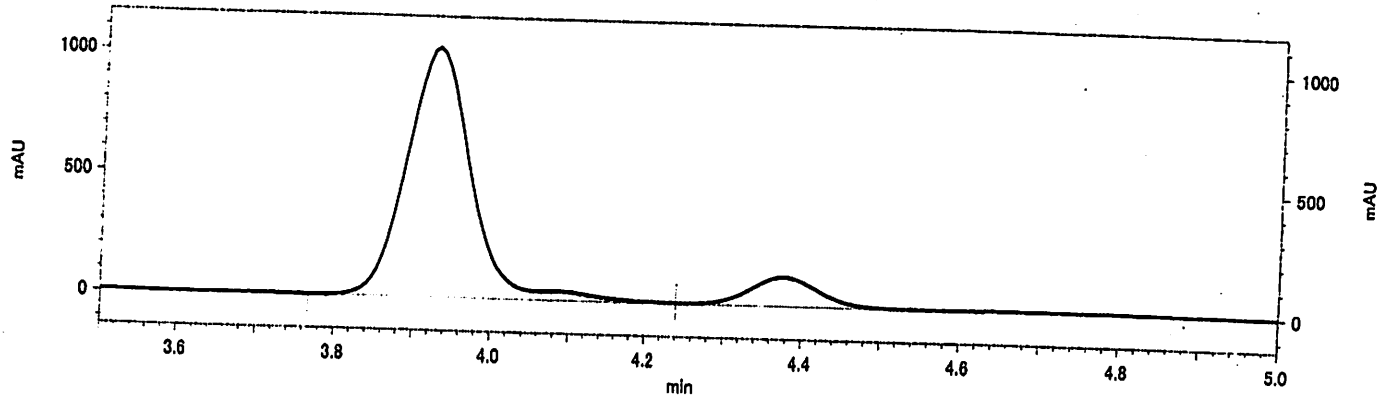




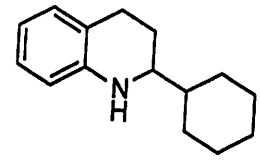
Pk #	Time	Area	Area%	Type
1	9.880	95365461	49.523	BB
2	10.560	97203551	50.477	IB

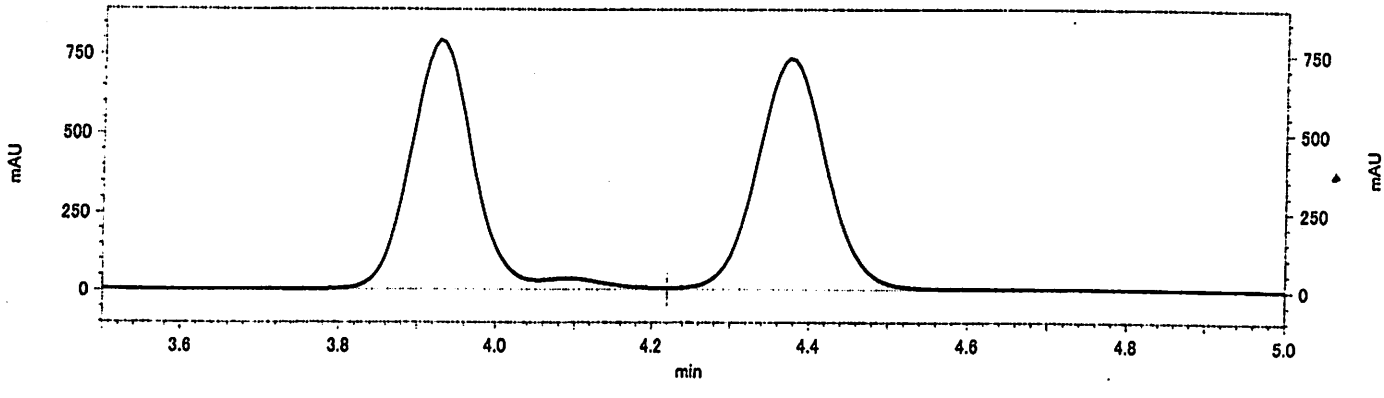


2c

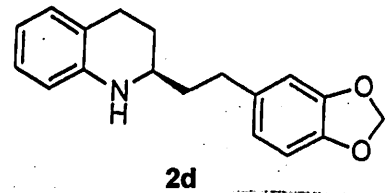


Pk #	Time	Area	Area%	Type
1	3.927	23618858	88.313	BV
2	4.373	3125481	11.687	VB





Pk #	Time	Area	Area%	Type
1	3.927	18105346	50.023	BV
2	4.373	18088714	49.977	VI



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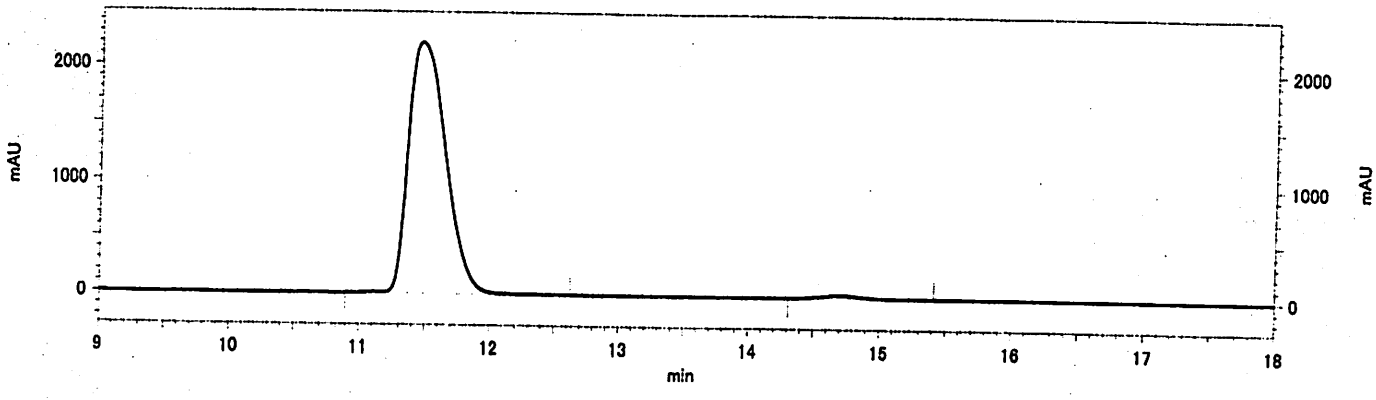
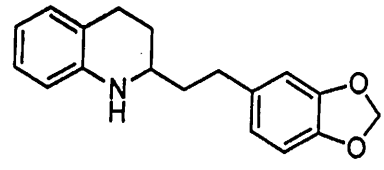
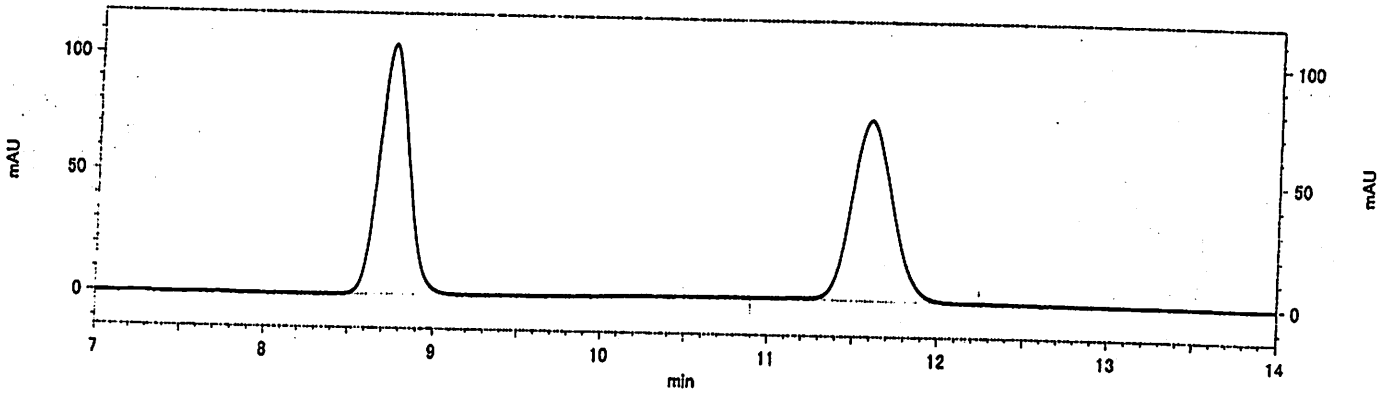
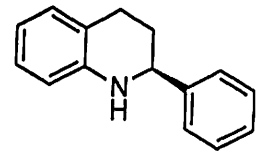


Pk #	Time	Area	Area%	Type
1	11.453	176806377	98.676	BB
2	14.700	2373010	1.324	BB





Pk #	Time	Area	Area%	Type
1	8.740	4955769	50.403	BB
2	11.587	4876551	49.597	BI



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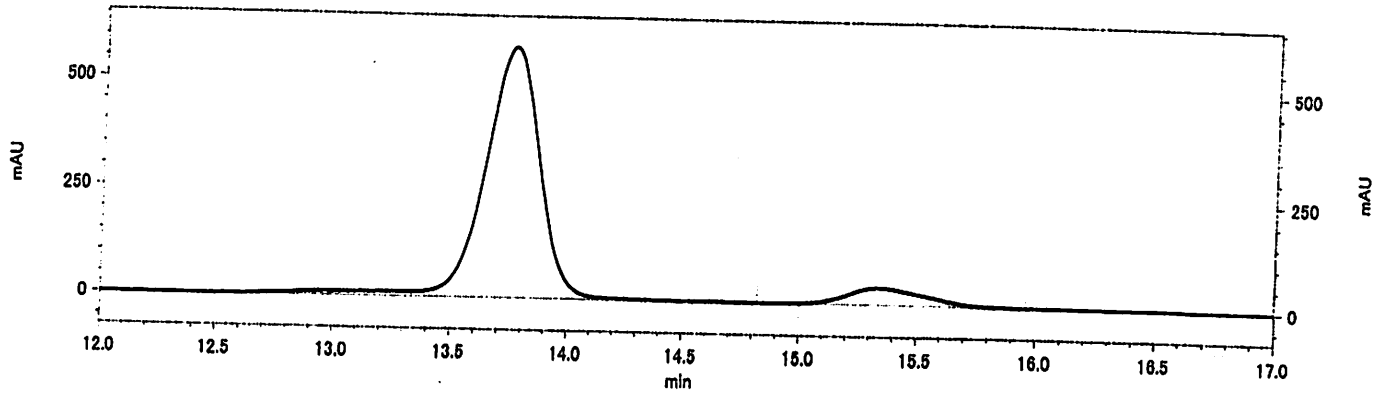
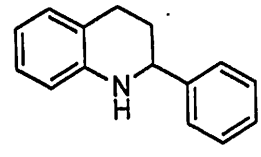
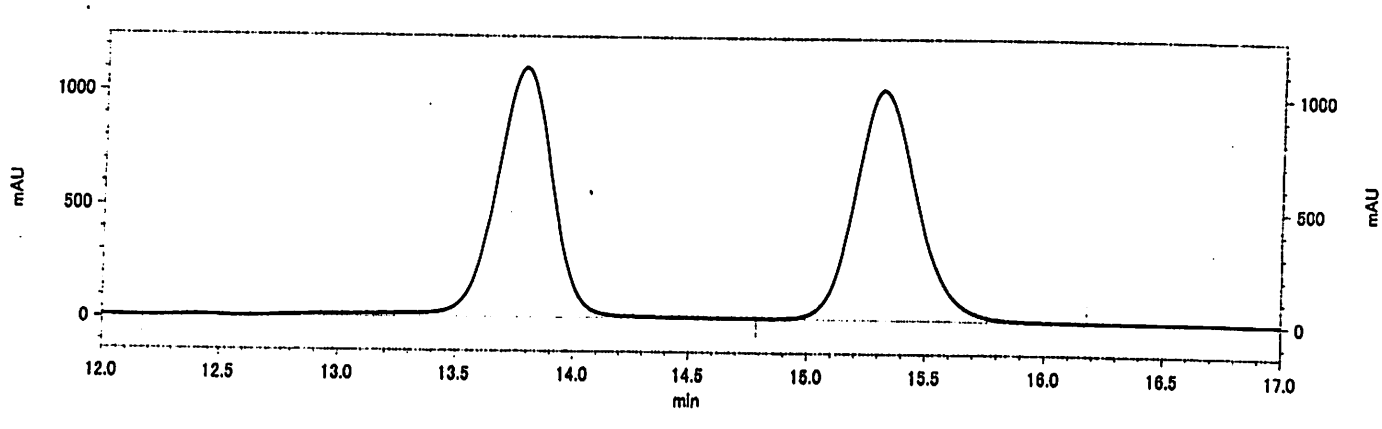
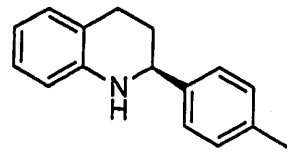


Pk #	Time	Area	Area%	Type
1	13.753	38570896	91.447	BB
2	15.340	3607589	8.553	IB





Pk #	Time	Area	Area%	Type
1	13.780	74162981	50.034	BB
2	15.313	74061417	49.966	IB



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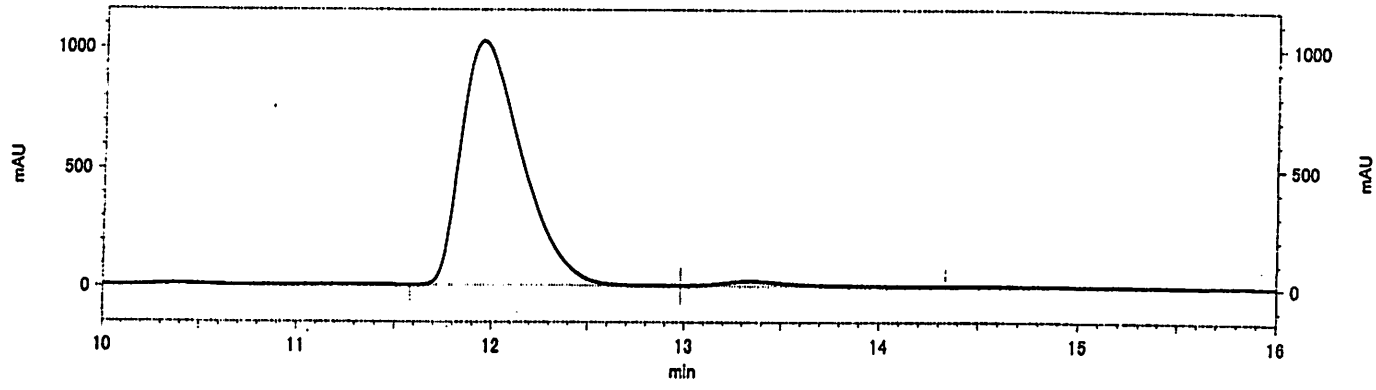
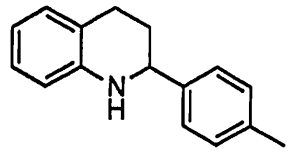
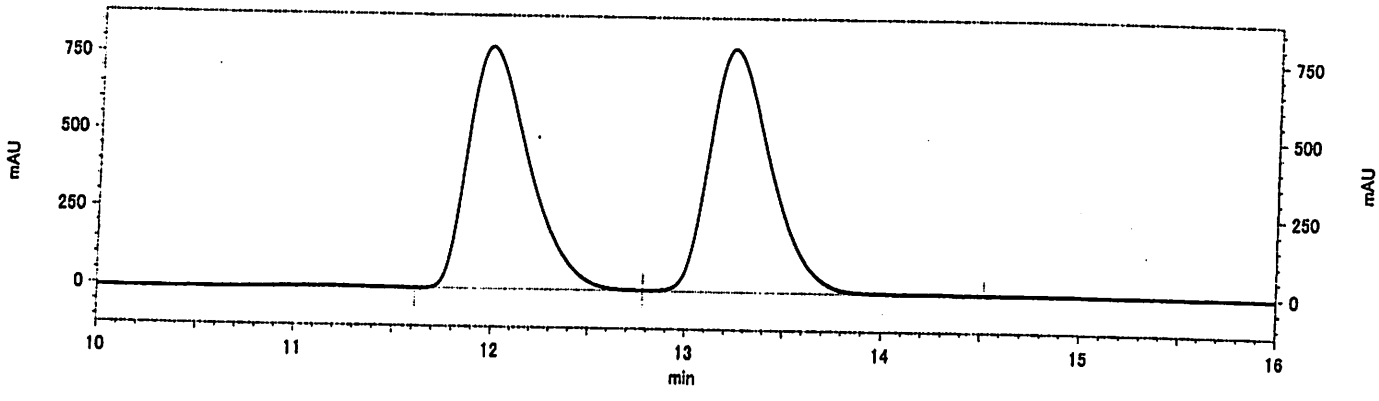
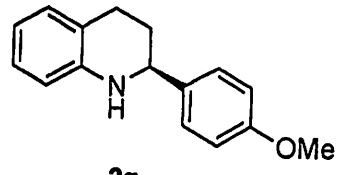


Pk #	Time	Area	Area%	Type
1	11.947	90296007	97.853	BV
2	13.340	1981546	2.147	VB





Pk #	Time	Area	Area%	Type
1	11.980	67532033	49.771	BV
2	13.233	68153335	50.229	VB



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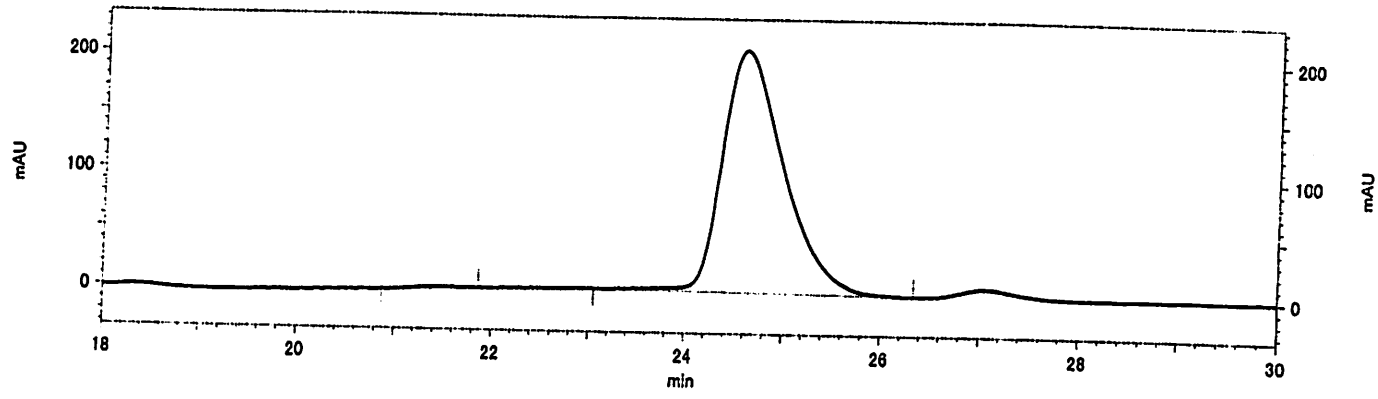
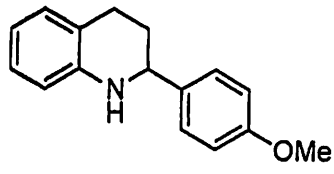
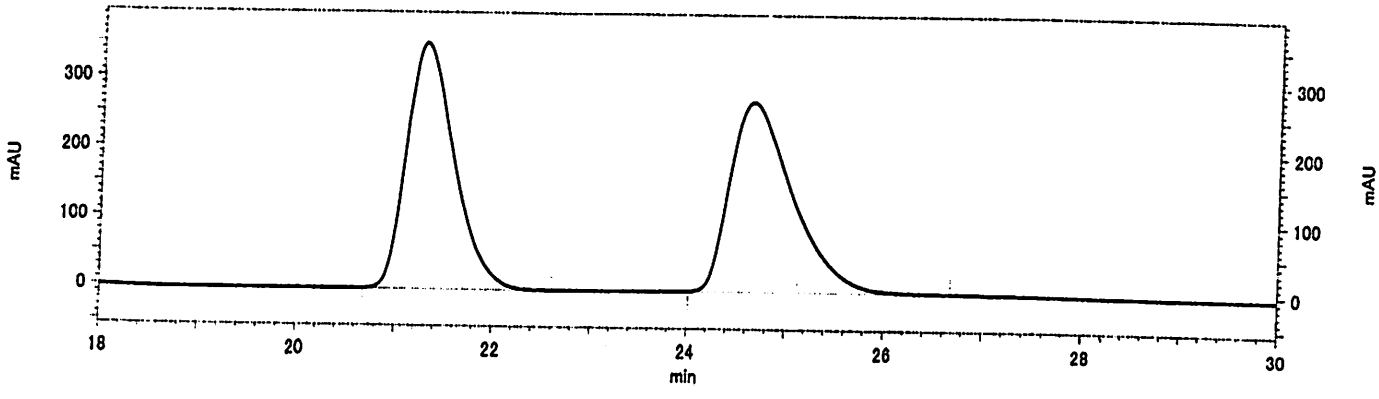
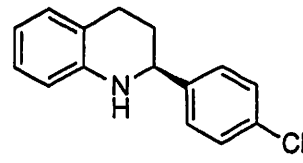


Pk #	Time	Area	Area%	Type
1	21.447	163463	0.455	BB
2	24.600	35734835	99.545	BB





Pk #	Time	Area	Area%	Type
1	21.287	47821967	49.820	BB
2	24.653	48168095	50.180	BB



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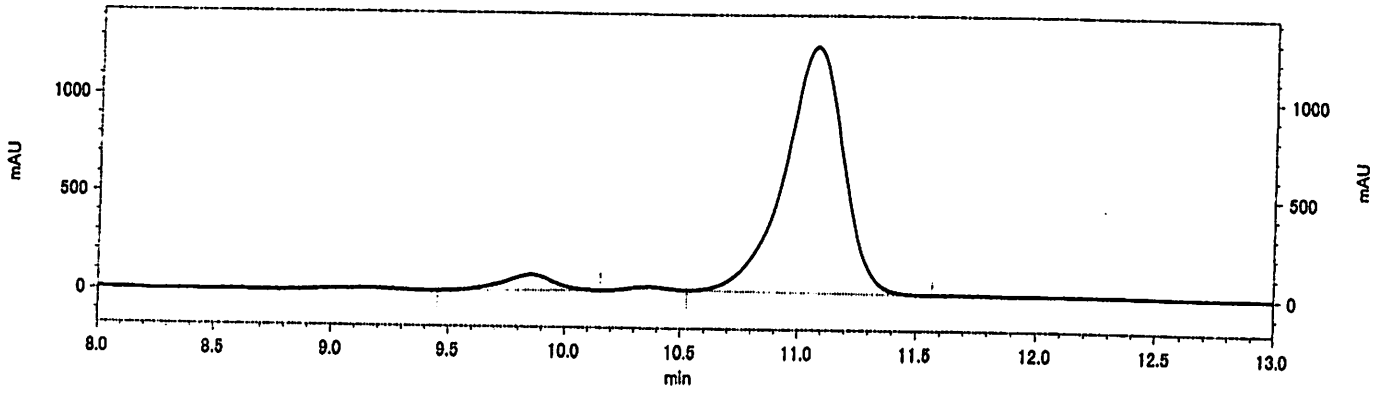
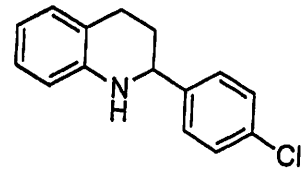
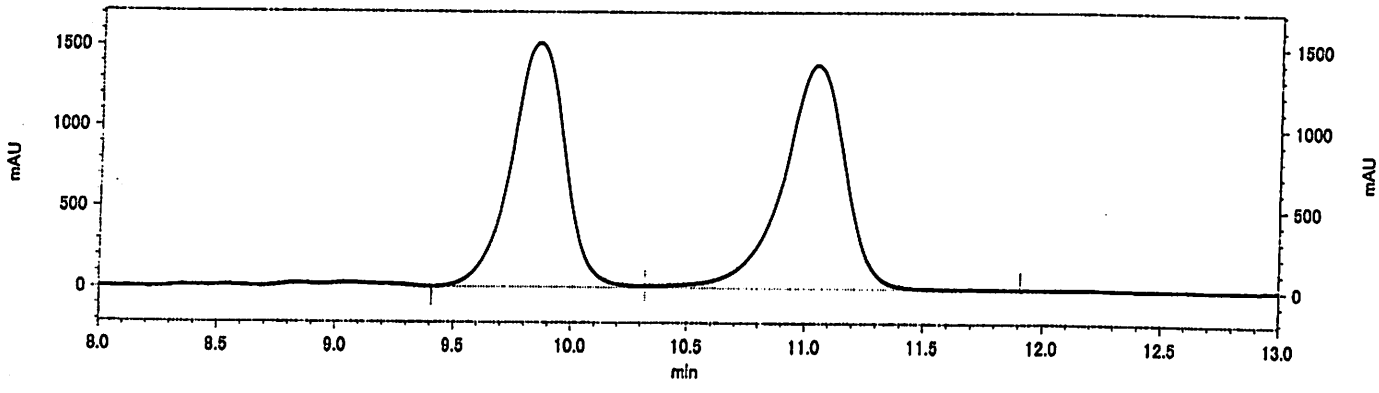
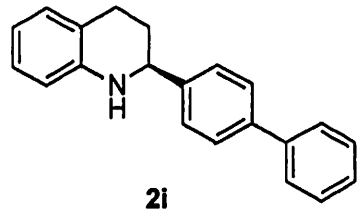


Pk #	Time	Area	Area%	Type
1	9.853	4829838	5.287	BB
2	11.073	86524462	94.713	BI

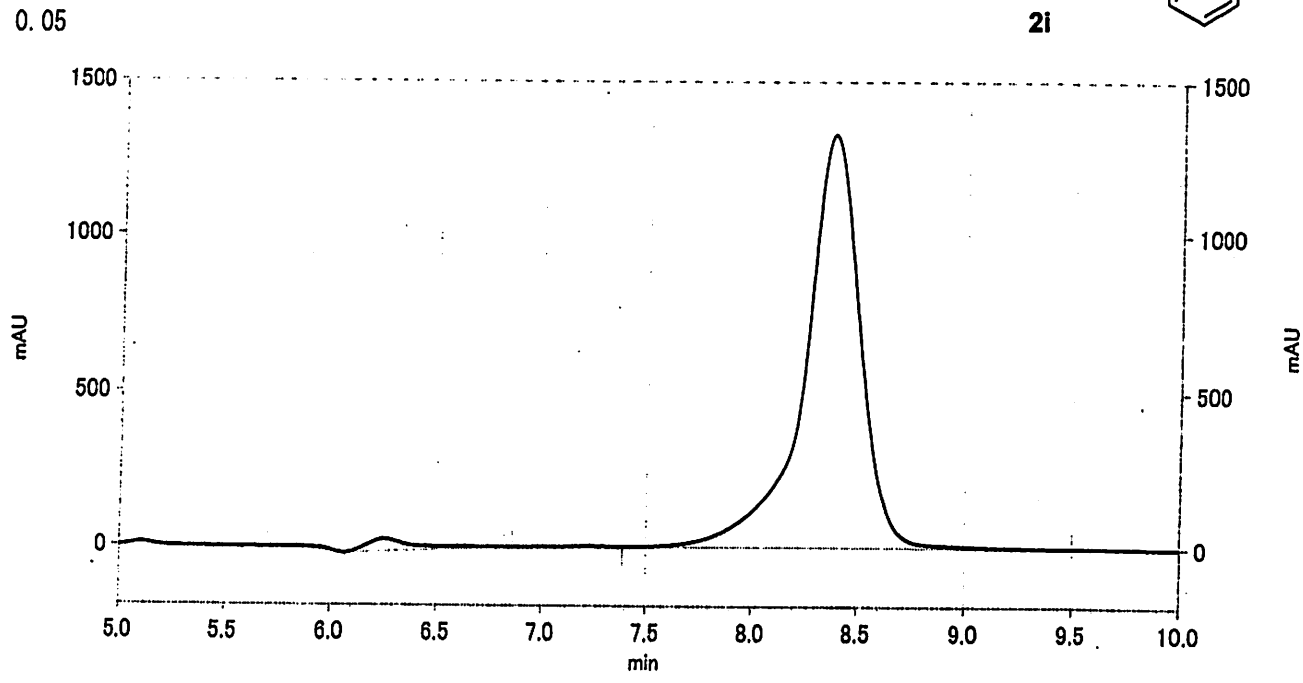




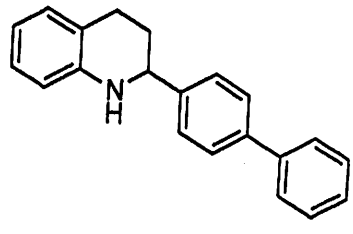
Pk #	Time	Area	Area%	Type
1	9.853	95773196	48.633	BV
2	11.047	101158578	51.367	VB

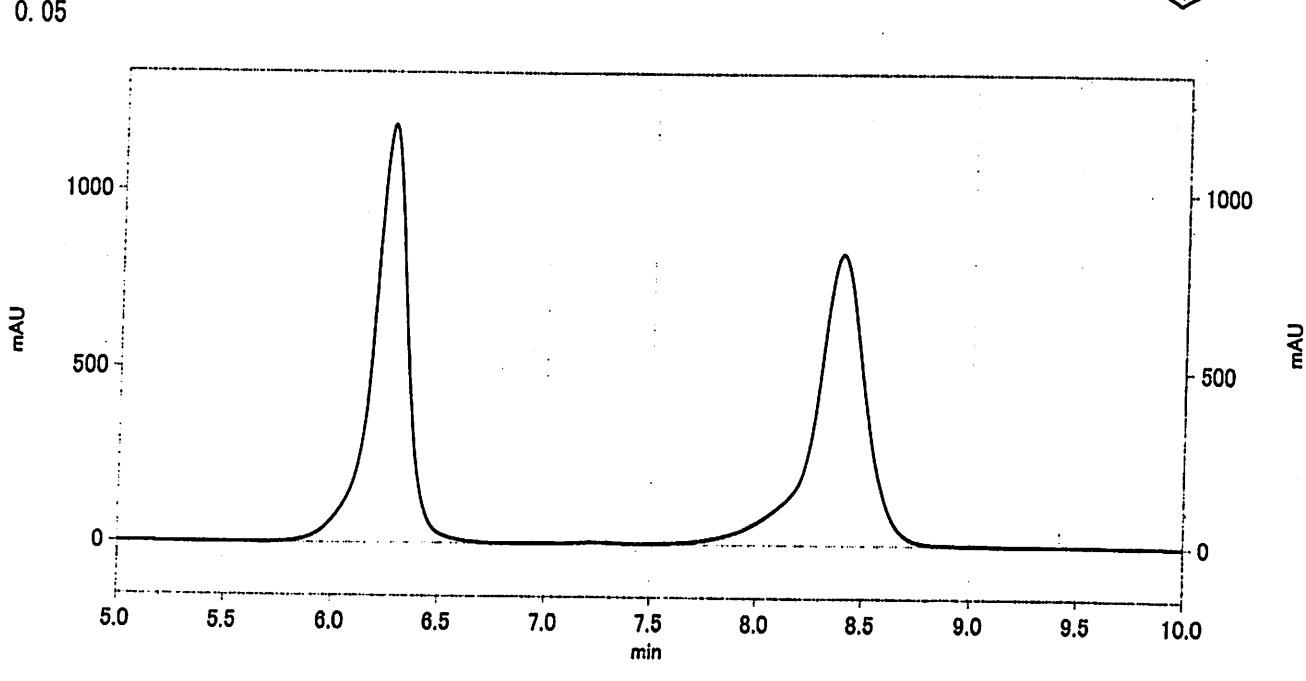


2i

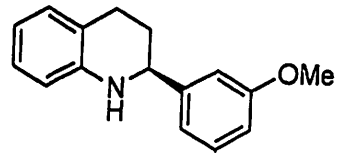


Peak #	Retention time	Type	Area	Area %
1	6.25	BB	2563886	2.567
2	8.38	II	97315526	97.433





Peak #	Retention time	Type	Area	Area %
1	6.26	BB S61	54411403	49.053
2	8.39	BI	56511782	50.947



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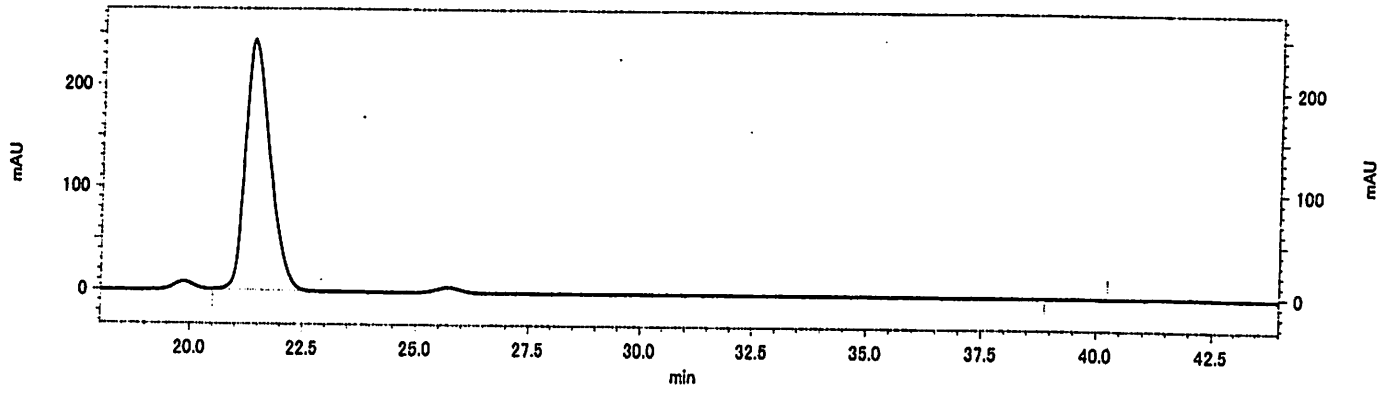
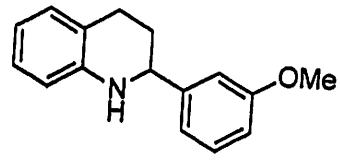
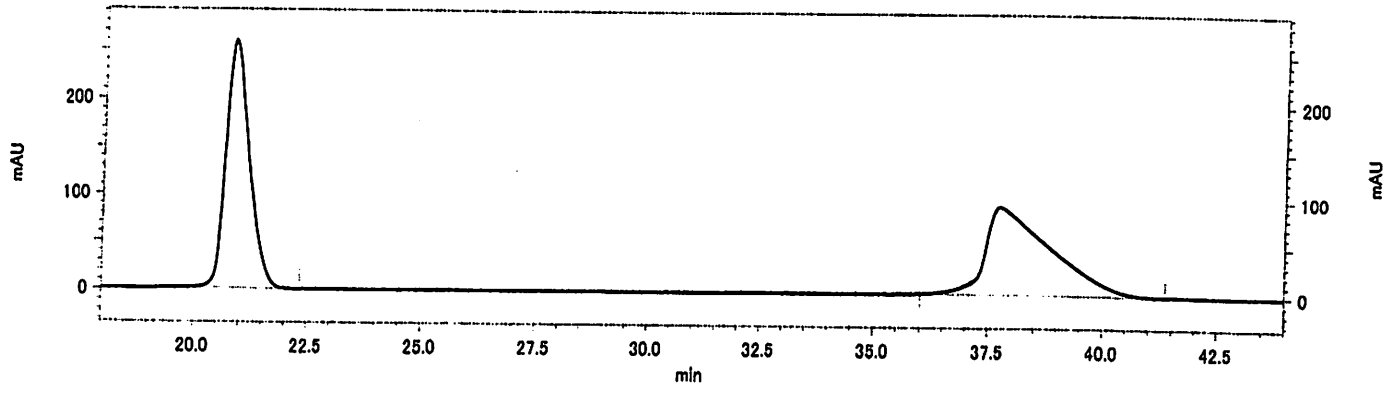
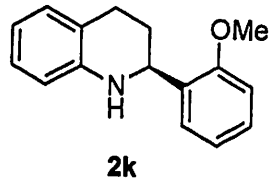


Pk #	Time	Area	Area%	Type
1	21.360	36930394	99.933	BI
2	39.547	24851	0.067	BB





Pk #	Time	Area	Area%	Type
1	20.833	36992590	50.593	BI
2	37.740	36125116	49.407	BB



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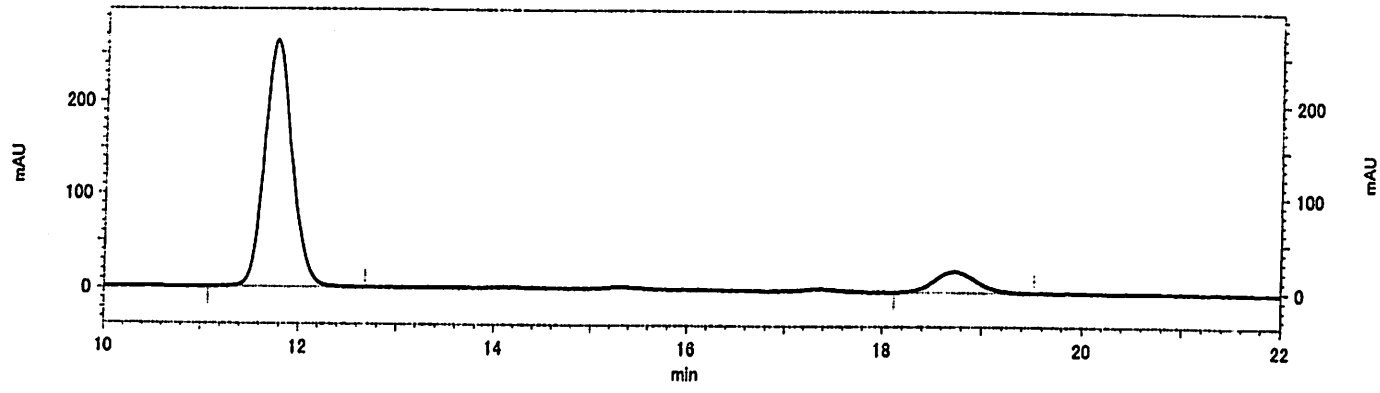
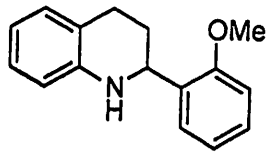
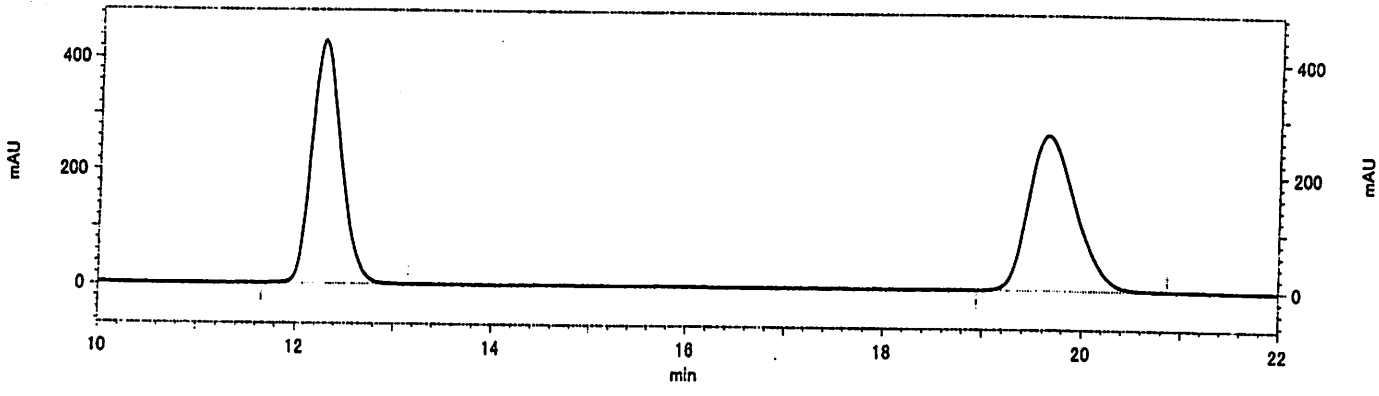
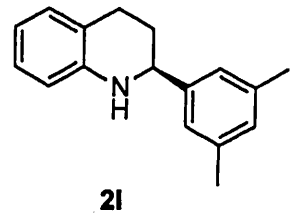


Pk #	Time	Area	Area%	Type
1	11.753	20471857	88.679	BB
2	18.727	2613482	11.321	BB





Pk #	Time	Area	Area%	Type
1	12.267	35737669	49.969	BB
2	19.647	35782135	50.031	BB



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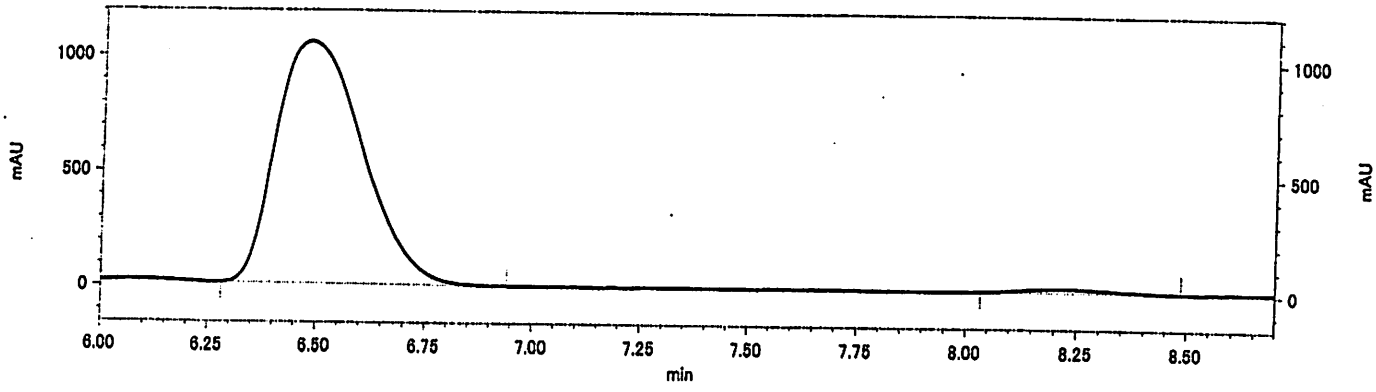
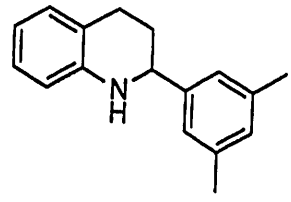
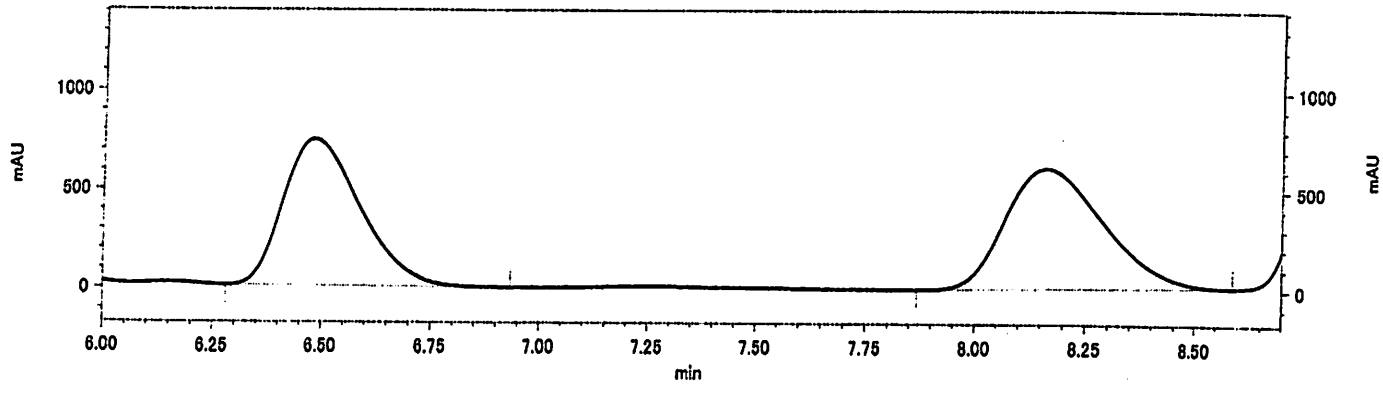
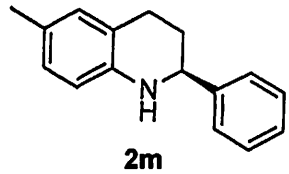


Pk #	Time	Area	Area%	Type
1	6.480	58171359	98.379	BB
2	8.220	958726	1.621	BB





Pk #	Time	Area	Area%	Type
1	6.480	36221385	49.326	BB
2	8.160	37211297	50.674	BB



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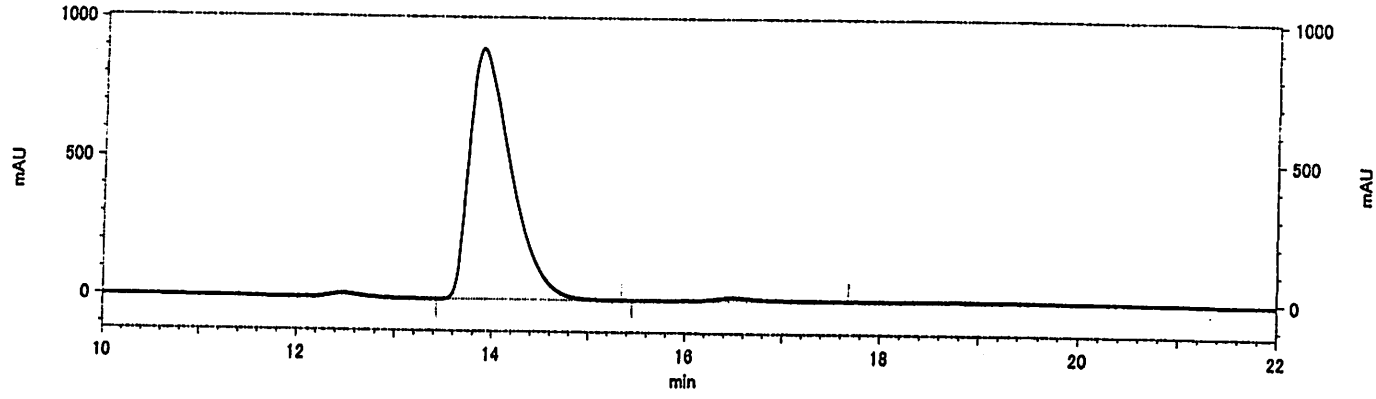
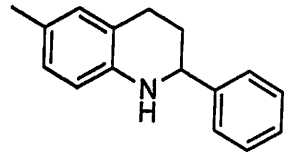
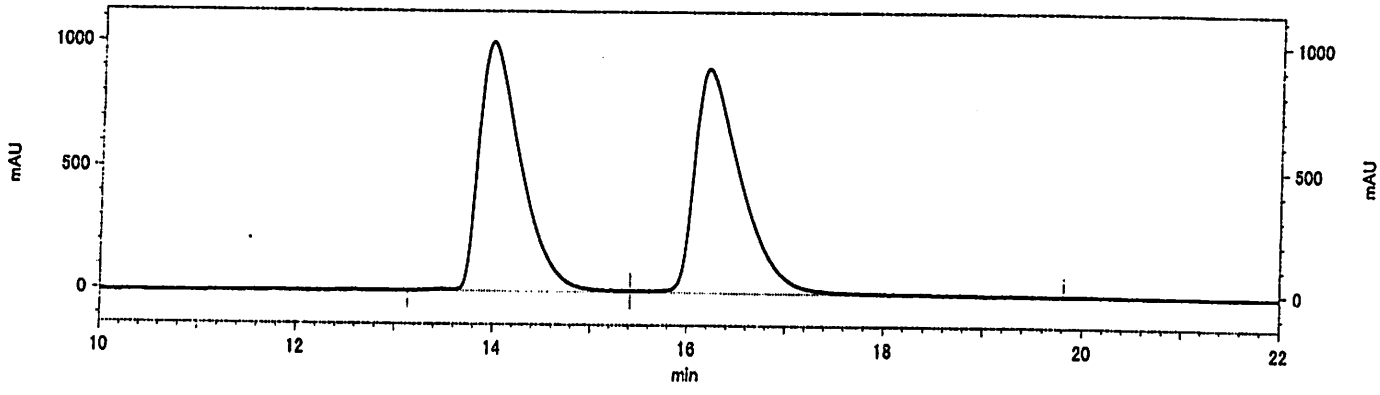
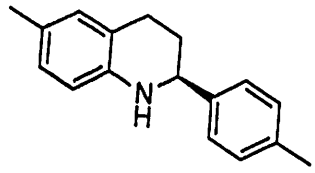


Pk #	Time	Area	Area%	Type
1	13.867	108370673	98.549	BB
2	16.500	1595054	1.451	BB





Pk #	Time	Area	Area%	Type
1	13.960	121509462	50.019	BV
2	16.193	121415049	49.981	VB



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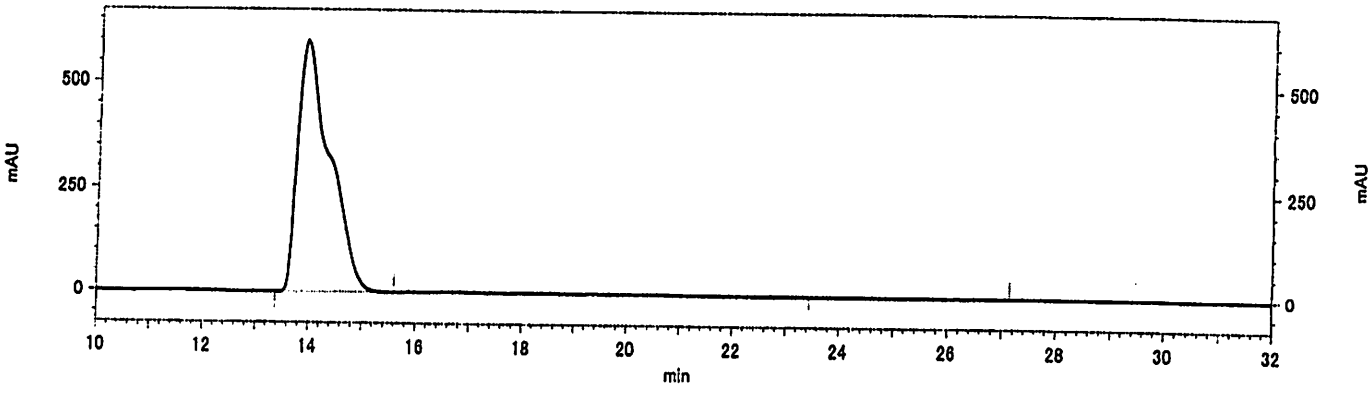
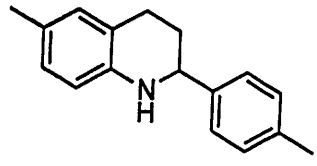
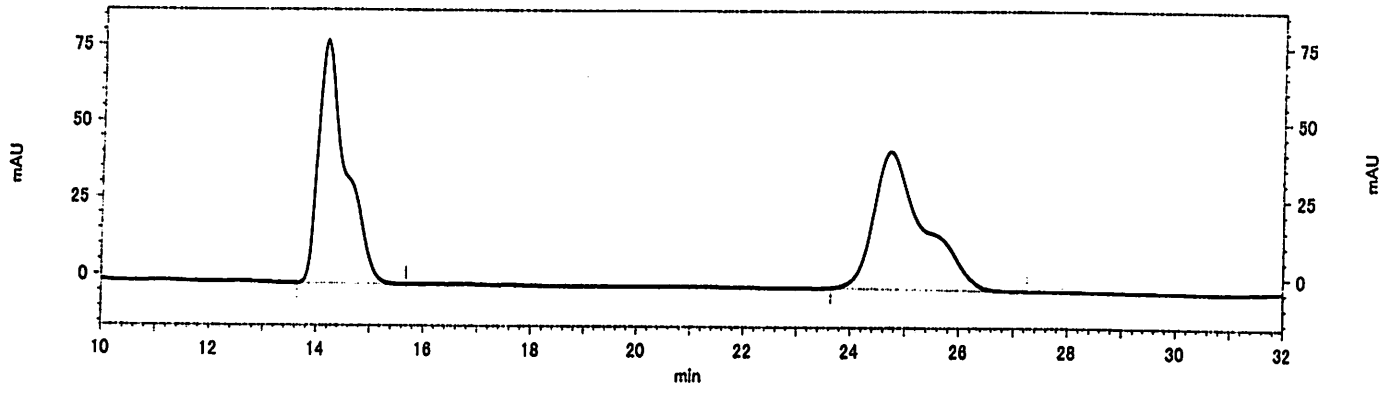
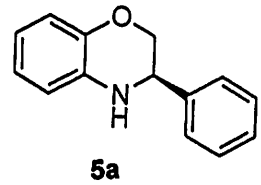


Pk #	Time	Area	Area%	Type
1	13.907	100899405	99.859	BB
2	24.653	142128	0.141	BB

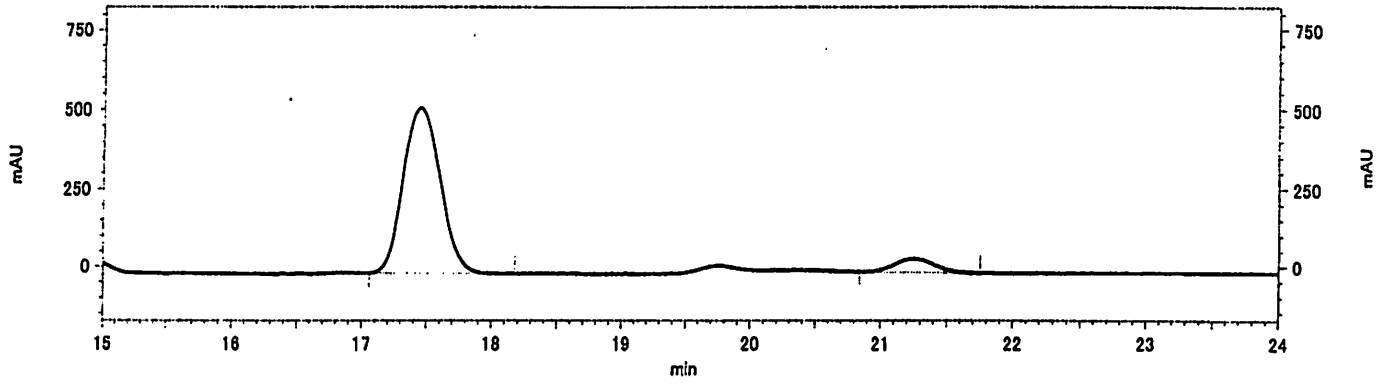




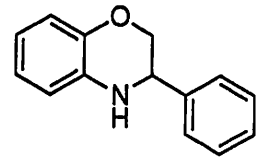
Pk #	Time	Area	Area%	Type
1	14.160	11359127	50.223	BB
2	24.720	11258100	49.777	BB

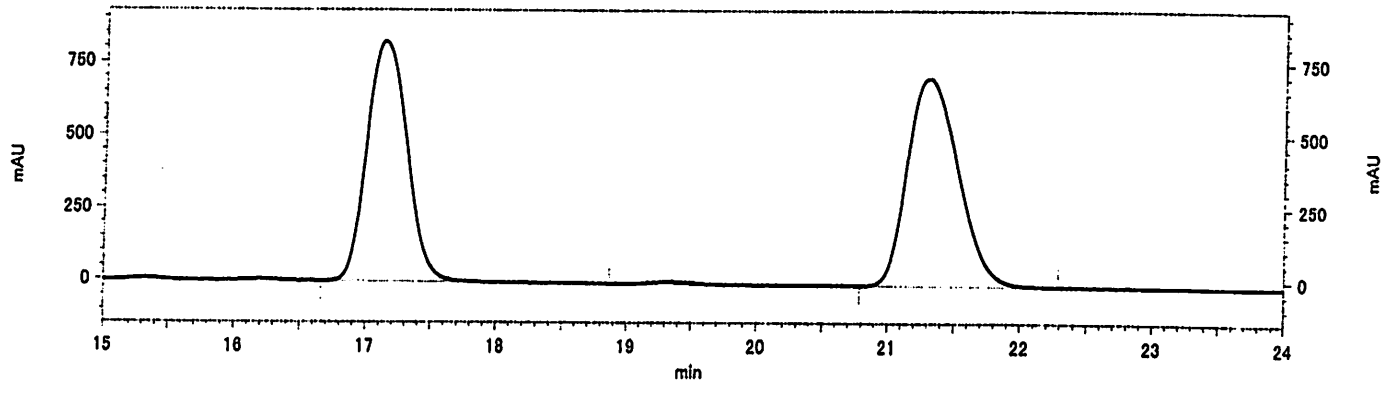


5a

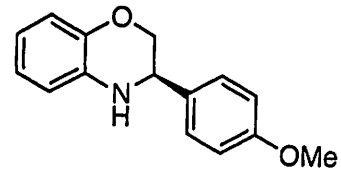


Pk #	Time	Area	Area%	Type
1	17.447	42306213	91.789	BB
2	21.247	3784672	8.211	BI

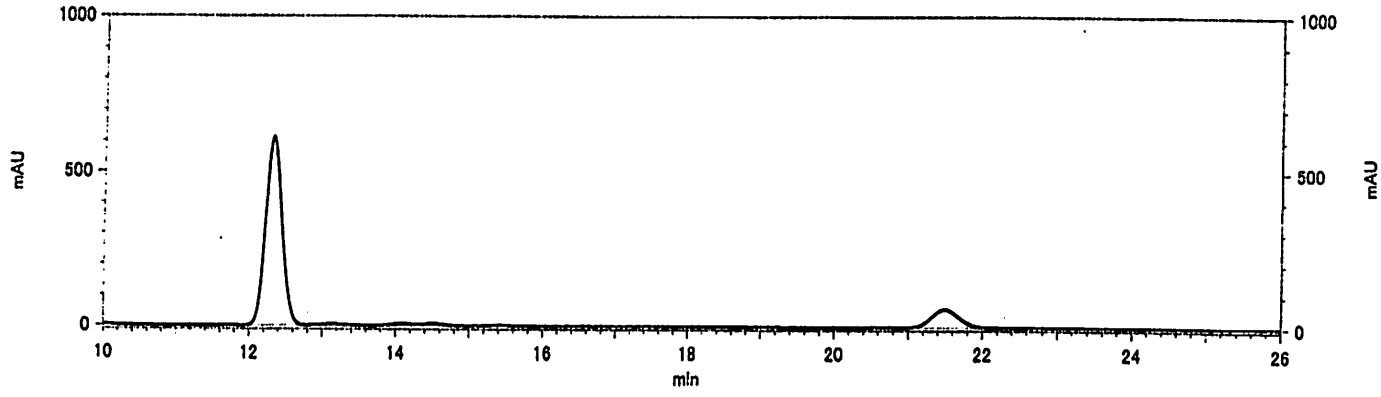




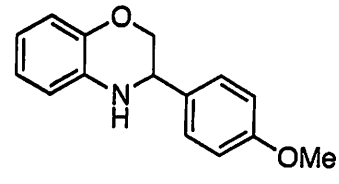
Pk #	Time	Area	Area%	Type
1	17.127	71469869	48.455	BB
2	21.307	76026852	51.545	BB

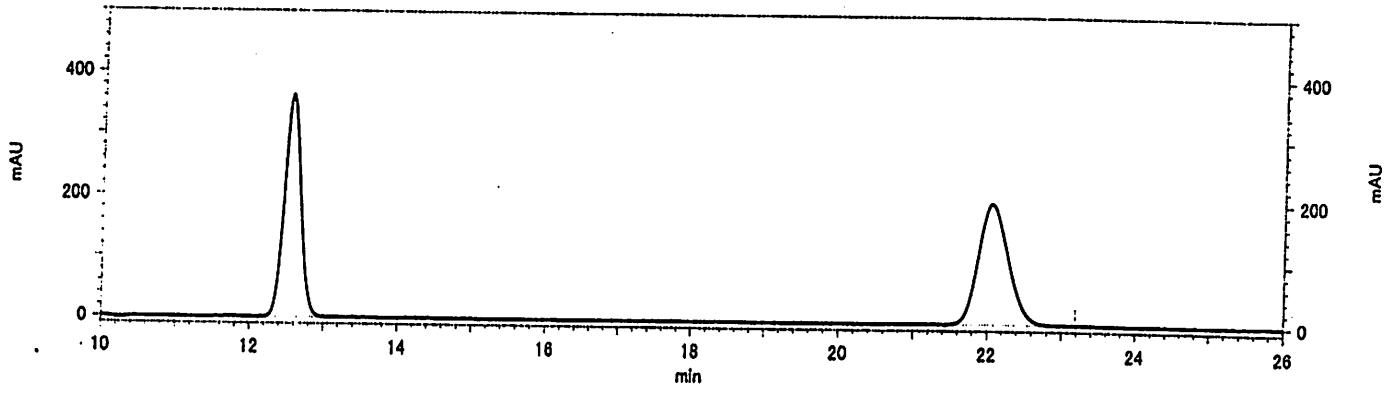


5b

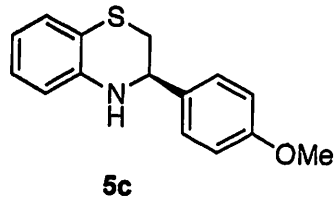


Pk #	Time	Area	Area%	Type
1	12.320	37917168	85.932	BB
2	21.493	6207247	14.068	BB

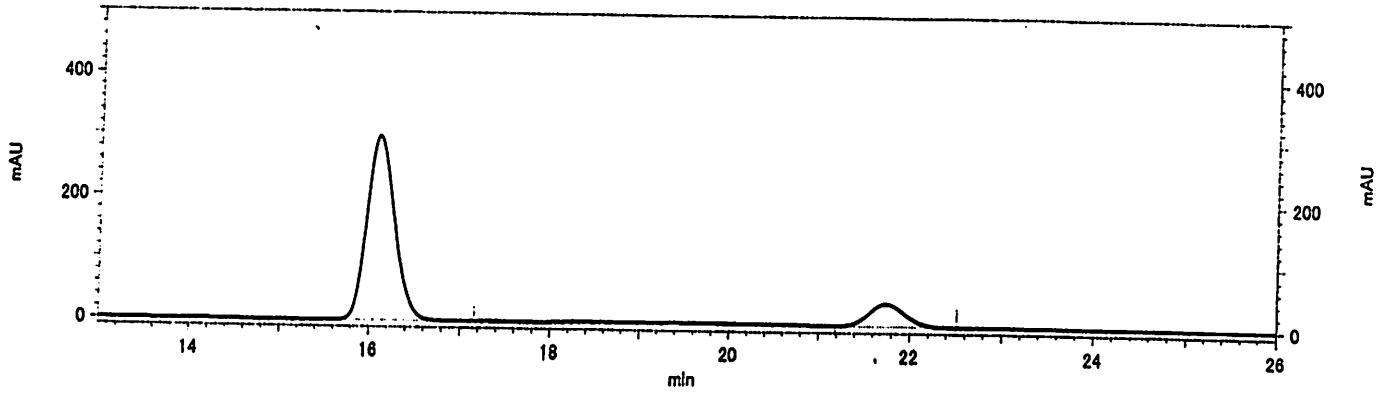




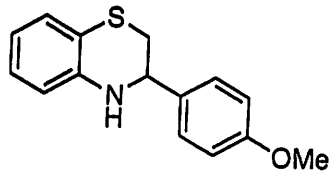
Pk #	Time	Area	Area%	Type
1	12.547	22409782	50.215	BB
2	22.047	22217489	49.785	BB

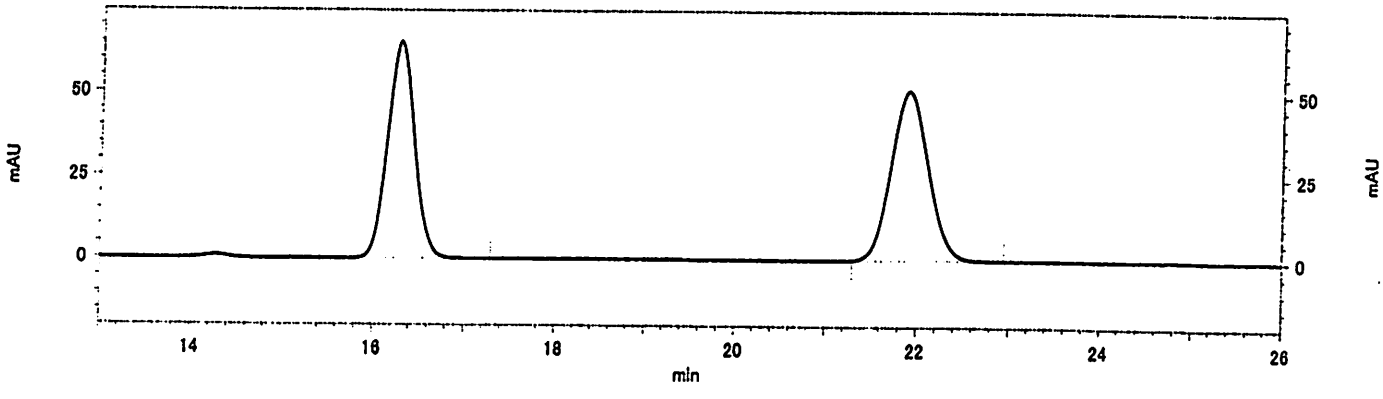


5c

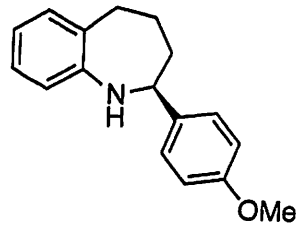


Pk #	Time	Area	Area%	Type
1	16.087	25322766	86.296	BB
2	21.747	4021374	13.704	BB





Pk #	Time	Area	Area%	Type
1	16.280	5366226	48.554	BB
2	21.900	5685956	51.446	BB



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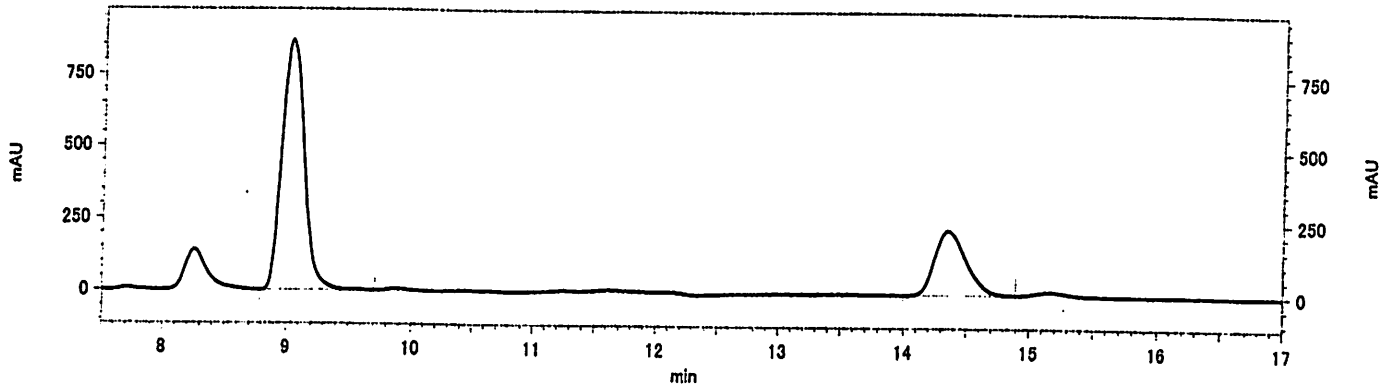
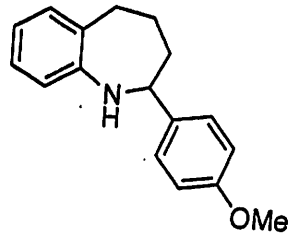
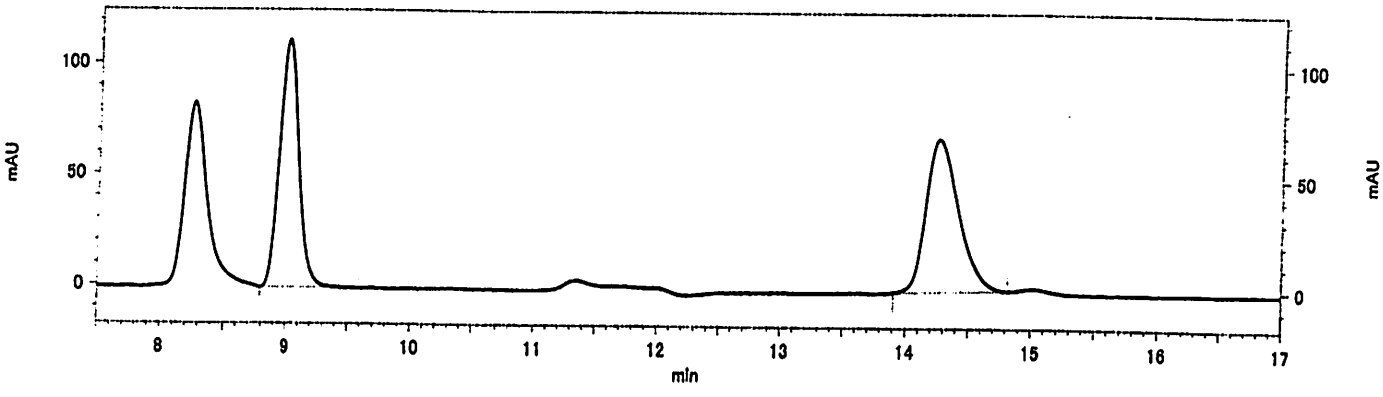
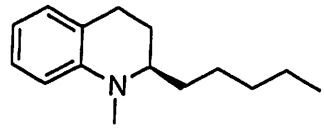


Pk #	Time	Area	Area%	Type
1	9.033	808964	81.090	BB
2	14.367	188646	18.910	BB





Pk #	Time	Area	Area%	Type
1	9.000	4817126	49.135	BI
2	14.253	4986819	50.865	BB



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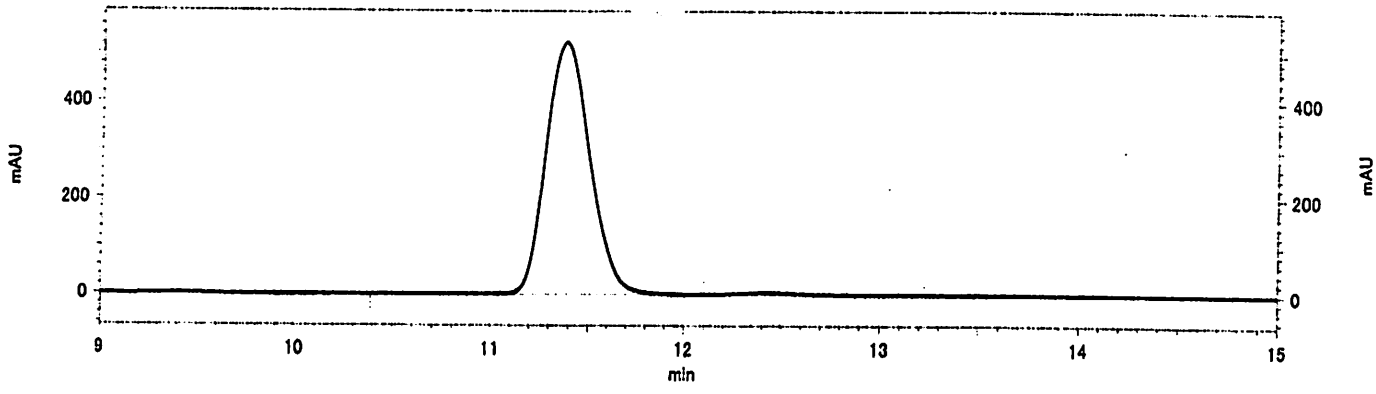
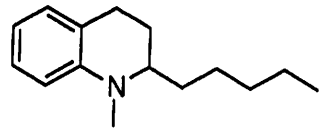
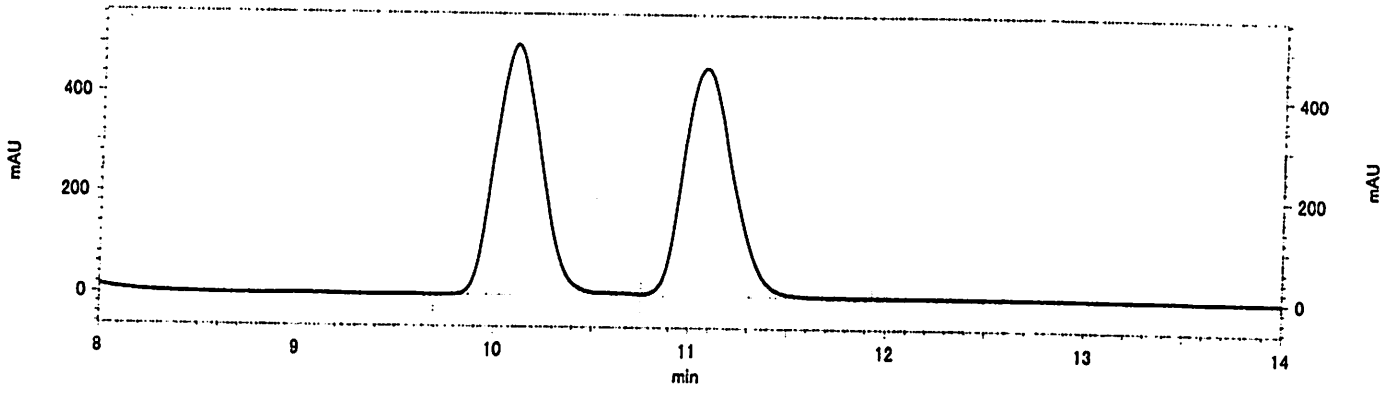
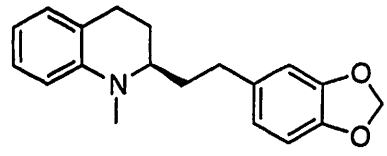


Pk #	Time	Area	Area%	Type
1	11.373	33086787	98.874	BV
2	12.420	376664	1.126	VB





Pk #	Time	Area	Area%	Type
1	10.100	32378584	50.657	BV
2	11.073	31539279	49.343	VB



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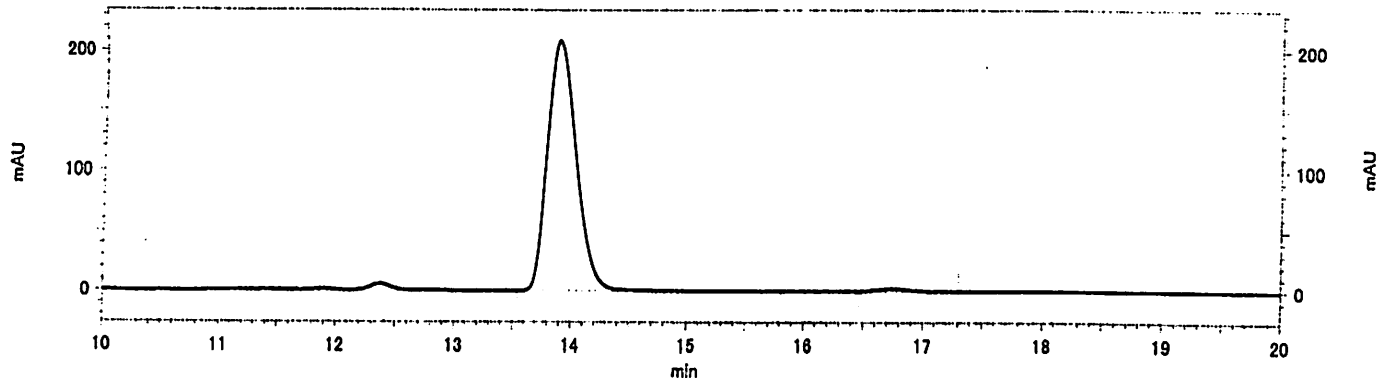
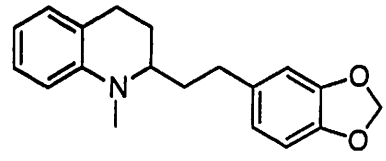
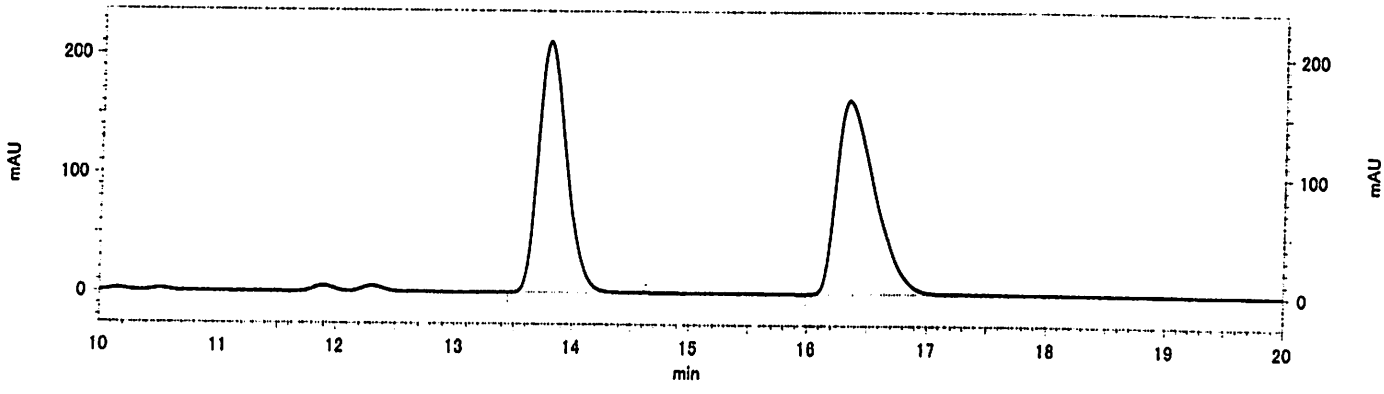


Pk #	Time	Area	Area%	Type
1	13.880	14238628	98.784	BI
2	16.747	175284	1.216	BB





Pk #	Time	Area	Area%	Type
1	13.780	14224634	49.494	BB
2	16.333	14515331	50.506	BB