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A Homo Diels-Alder Approach to Bicyclo[4.2.1]nonanes

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Supporting Information

Including:

Experimental Section

General Methods. Melting points were determined in capillaries and are uncorrected. ^1H NMR and ^{13}C NMR spectra data were recorded at 93.94 kG (^1H 400 MHz), 70.5 kG (^1H 300 MHz, ^{13}C 75 MHz) or 63.41 kG (^{13}C 67.5 MHz) at ambient temperature in $CDCl_3$. Proton chemical shifts (in ppm) are referenced to the residual $CHCl_3$ resonance at δ 7.24. For ^{13}C NMR, the center line of the $CDCl_3$ triplet was used as the internal reference: δ 77.0. Unless otherwise noted, each carbon resonance represents a single carbon (relative intensity). Mass spectra (HRMS) were recorded in either CI (140 eV) or EI (70 eV) mode as noted. Infrared spectra were recorded on NaCl plates. Solid samples were prepared by depositing a solution of the sample (typically in $CDCl_3$) on the plate and allowing the solvent to evaporate prior to recording the IR spectra.

All reaction solvents were anhydrous, and were distilled immediately prior to use (toluene, Et_2O, and THF from sodium with benzophenone ketyl radical anion as indicator, $ClCH_2CH_2Cl$ and CH_2Cl_2 from CaH_2);[1] chromatography solvents were distilled prior to use. Norbornadiene (**1a**) was distilled prior to use and stored under argon. Powdered zinc was activated prior to use by sequential washing with 5% aqueous HCl, EtOH, and Et_2O (twice with each solvent, with approximately twice the volume of the solid zinc) on a glass fritted funnel with vacuum filtration. Other commercially available reagents were used without further purification. All reactions were carried out in oven-dried (105 °C) glassware. The glass vessels used for reactions employing the low boiling reactants were heavy-walled tubes (25.4 X 102 mm) with Teflon Plugs, designated as "pressure tube" in the text. Reactions at –78 °C were maintained using dry

ice-acetone baths; reactions at –50 °C were maintained using dry ice-75% aqueous acetone baths, reactions at –30 °C were maintained using, dry ice-50% aqueous acetone baths. Flash chromatography was performed using silica gel-60 (43–60 μm); TLC was performed on silica gel plates, and visualization was accomplished with ammonium molybdate stain: ammonium molybdate (4 g)/H_2O (60 mL)/H_2SO_4 (4 mL). A silica gel plug is a disposable pipet filled with approximately 2 cm of silica gel.

Typical procedure for the [4 + 2 + 2] Cycloadditions of Norbornadienes. To a stirred, purple solution of CoI_2 (15.6 mg, 0.05 mmol) and dppe (19.9 mg, 0.05 mmol) in CH_2Cl_2 (1.0 mL) in a pressure tube at 0 °C under Ar, 1,3-butadiene (0.1 mL, 1.16 mmol) and 7-*tert*-butoxynorbornadiene[2] (164 mg in 1 mL CH_2Cl_2, 1 mmol) were added, then zinc powder (3.3 mg, 0.05 mmol) and ZnI_2 (47.9 mg, 0.15 mmol) were added quickly under Ar. The pressure tube was immediately capped and allowed to warm to rt. The dark brown cloudy solution was stirred at rt for 20 h. Then, the reaction mixture was passed through a silica gel plug washing with CH_2Cl_2 (3 X 5 mL) to remove the catalyst. The washings were collected, and the solvent removed in vacuo to give the crude oily product which was purified by flash chromatography (hexanes:EtOAc, 20:1) to give pure **7a**[3] (R_f = 0.3, 203 mg, 93%) as a colorless oil. Cycloadduct **7b** was obtained using the same method starting with *syn*-2-methyl-7-*tert*-butoxynorbornadiene.[3] Anything added after the formation of the dark brown solution indicative of the active catalyst has to be extremely air- free. 1,3-Butadiene (b.p. –5 °C) was transferred via cannula as a liquid trapped at –78 °C.

Tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecan-5-ol (2a). To a solution of H_2SO_4 (98%, 10.8 mg, 0.11 mmol) in CH_2Cl_2 (11 mL) under Ar at rt, **7a** (230 mg, 1.1 mmol) was added and the reaction mixture was stirred at rt for 20 h. Saturated $NaHCO_3$ (20 mL) was added to quench the acid, and the organic layer was washed with H_2O (20 mL) and brine (20 mL), then dried over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by flash chromatography (hexanes:EtOAc, 3:1) to give tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-en-5-ol (**2g**)[4] as a colorless oil (R_f = 0.4, 140 mg, 80% yield). The alcohol **2g** (96.0 mg, 0.55 mmol) and Pd-C (10% Pd on C, 32.7 mg, 1 mol%) in THF (5.5 mL) were kept under an H_2 atmosphere (balloon, 1 atm) at rt for 5 h with stirring. After removing the catalyst by passing through a silica gel plug eluting with CH_2Cl_2 (3 x 5 mL), the solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 3:1) to give **2a** (R_f = 0.4, 92 mg, 95% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 - 1.08 (m, 2H), 1.11 (dd, *J* = 5.6, 5.6 Hz, 1H), 1.23 - 1.34 (overlapped, 2H), 1.40 (br s, OH), 1.45 - 1.63 (overlapped, 5H), 1.74 - 1.83 (overlaped, 3H), 2.40 (br s, 1H), 3.77 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6, 17.0, 20.7, 26.4, 26.5, 30.3, 31.2, 39.1, 40.9, 43.4, 79.1; IR (NaCl) 3325 cm^{-1}; HRMS (EI, 70 eV) *m/z* 164.1200 ([M]$^+$, 2.6%), calcd for $C_{11}H_{16}O$ 164.1201.

***anti*-5-Acetoxy-1-methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-ene (7d).** To a solution of H_2SO_4 (98%, 4.9 mg, 0.05 mmol) in HOAc (1 mL), **7b** (106 mg, 0.457 mmol) was added and stirred under Ar for 2 days. Saturated $NaHCO_3$ (10 mL) was then added to the mixture with stirring until bubbling ceased. Then, Et_2O (10 mL) was added and the organic layer was separated and washed with saturated $NaHCO_3$ (5 mL), H_2O (5 mL) and brine (5 mL), then subsequently dried over Na_2SO_4. The solvent was removed in vacuo

and the residue was purified by flash chromatography (hexanes:EtOAc, 10:1) to give **7d** (R_f = 0.5, 79 mg, 79% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (overlapped, 1H), 1.09 (s, 3H), 1.14 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.29 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.57 (br s, 1H), 2.02 (s, 3H), 2.07 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.25 (m, 1H), 2.29 (m, 1H), 2.40 (ddd, *J* = 16.8, 7.2, 7.2 Hz, 1H), 2.48 (d, *J* = 5.6 Hz 1H), 5.05 (br s, 1H), 5.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 18.2, 21.4, 24.5, 24.6, 29.4, 38.9, 39.6, 43.2, 49.3, 80.5, 128.4, 128.7, 171.1; IR (NaCl) 1734 cm^{-1}; HRMS (EI, 70 eV) *m/z* 218.1293 ([M]$^+$, 1.1%), calcd for $C_{14}H_{18}O_2$ 218.1307. The relative stereochemistry of the 5-acetoxy and 1-methyl groups was established by the observation of a NOE between H-5 and 1-Me.

***anti*-1-Methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-en-5-ol (7e).** To a solution of **7d** (79 mg, 0.36 mmol) in THF/H_2O/MeOH (2:2:1, 2 mL), LiOH·H_2O (30.4 mg, 0.72 mmol) was added and the solution was stirred at rt for 1 h. The reaction mixture was neutralized to pH 7 with aqueous HCl (1N) and the aqueous layer was extracted with Et_2O (3 × 10 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by flash chromatography (hexanes:EtOAc, 10:1) to give **7e** (R_f = 0.3, 62 mg, 98% yield) as a white solid. Mp 89 - 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 3H), 1.04 (overlapped, 1H), 1.10 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.15 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.37 (br s, 1H), 1.43 (br s, 1H, OH), 2.05 (dd, *J* = 16.8, 7.6 Hz, 1H), 2.25 (ddd, *J* = 16.8, 6.8, 6.8 Hz, 1H), 2.31 (br d, *J* = 16.4 Hz, 1H), 2.44 (ddd, *J* = 16.4, 6.8, 6.8 Hz, 1H), 2.53 (br d, *J* = 6.0 Hz, 1H), 4.32 (br s, 1H), 5.54 - 5.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.1, 17.7, 24.2, 25.3, 29.5, 37.9, 39.9,

43.1, 51.4, 77.0, 128.3, 128.6; IR (NaCl) 3338 cm^{-1}; HRMS (EI, 70 eV) *m/z* 176.1186, calcd for $C_{12}H_{16}O$ 176.1201.

***syn*-1-Methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-en-5-ol (7f).** To a solution of **7e** (18.0 mg, 0.102 mmol) in CH_2Cl_2 (1 mL) was added PCC (48.0 mg, 0.12 mmol), and the reaction mixture was stirred for 22 h at rt. The solution was then passed through a short silica gel plug eluting with CH_2Cl_2 (3 × 5 mL). The solvent was removed in vacuo to give 1-methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-en-5-one which was >95% pure as judged by ^1H NMR, and used without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.48 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.84 (ddd, *J* = 5.2, 5.2, 0.8 Hz, 1H), 1.93 (dd, *J* = 5.2, 5.2 Hz, 1H), 2.28 - 2.46 (m, 6H), 5.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.2, 25.3, 26.9, 31.5, 31.9, 39.4, 41.0, 43.4, 56.0, 127.5, 127.8, 212.9; IR (NaCl) 1752 cm^{-1}; HRMS (EI, 70 eV) *m/z* 174.1039 ($[M]^+$, 3.1%), calcd for $C_{12}H_{14}O$ 174.1045. The ketone (17.8 mg, 0.101 mmol) was dissolved in THF (1 mL) and $LiAlH_4$ (4.0 mg, 0.105 mmol) was added under Ar at rt. After 10 min, TLC showed no starting material remaining. The solution was cooled to 0 °C and 15% KOH aqueous solution (1 mL) was added and stirred for 0.5 h. The aqueous solution was extracted with CH_2Cl_2 (3 x 5 mL), the combined organic layers were washed with saturated $NaHCO_3$ (5 mL), H_2O (5 mL) and brine (5 mL), and subsequently dried over Na_2SO_4. The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 3:1) to give **7f** (R_f = 0.2, 17.6 mg, 97% yield) as a white solid. Mp 57 - 58 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.08 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.19 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.38 (s, 3H), 1.45 (br s, 1H), 1.59 (br s, 1H), 1.78 (br s, 1H), 2.11 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.22 - 2.26 (m, 2H), 2.35 (br dd, *J* = 16.8, 2.4 Hz, 1H), 3.85 (br s, 1H), 5.56 (m,

1H), 5.62 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6, 18.0, 21.9, 25.5, 30.1, 39.7, 39.8, 43.9, 51.6, 81.1, 127.8, 129.4; HRMS (CI, NH_3, 140 eV) *m/z* 176.1215 ([M]$^+$, 16.6%), calcd for $C_{12}H_{16}O$ 176.1201.

***anti*-1-Methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecan-5-ol (2b).** Alcohol **7e** (20.5 mg, 0.116 mmol) and Pd-C (10 % Pd on C, 7.3 mg, 1 mmol%) in THF (1.2 mL) were kept under an H_2 atmosphere (balloon, 1 atm) at rt for 6 h with stirring. The reaction mixture was then passed through a short silica gel plug eluting with CH_2Cl_2 (3 × 5 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 3:1) to give **2b** (R_f = 0.3, 19.3 mg, 95% yield) as a white solid. Mp 65 - 66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 3H), 1.02 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.11 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.17 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.23 - 1.30 (m, 1H), 1.35 - 1.60 (m, 6H), 1.46 (br s, 1H), 1.71 (ddd, *J* = 14.4, 6.4, 6.4 Hz, 1H), 1.73 - 1.84 (m, 1H), 2.57 (br d, *J* = 4.0 Hz, 1H), 4.29 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4, 20.2, 25.0, 26.2, 26.7, 26.9, 30.1, 40.2, 42.0, 46.0, 48.0, 77.5 (overlapped with $CDCl_3$); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 18.8, 21.5, 26.1, 27.6, 28.1, 28.2, 31.5, 41.6, 43.4, 47.2, 49.6, 78.6; IR (NaCl) 3251 cm^{-1}; HRMS (EI, 70 eV) *m/z* 178.1346 ([M]$^+$, 15.8%), calcd for $C_{12}H_{18}O$ 178.1358.

***syn*-1-Methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undecan-5-ol (2c).** Alcohol **7f** (107 mg, 0.608 mmol) and Pd-C (10 % Pd on C, 36.5 mg, 1 mmol %) in THF (6 mL) were kept under an H_2 atmosphere (balloon, 1 atm) at rt for 5 h with stirring The reaction mixture was then passed through a short silica gel plug eluting with CH_2Cl_2 (3 × 5 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 3:1) to give **2c** (R_f = 0.2, 103 mg, 95% yield) as a colorless oil. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 1.03 (dd, J = 4.8, 4.8 Hz, 1H), 1.10 (dd, J = 4.8, 4.8 Hz, 1H), 1.14 (dd, J = 4.8, 4.8 Hz, 1H), 1.16 - 1.25 (m, 1H), 1.32 (s, 3H), 1.36 - 1.62 (m, 6H), 1.65 - 1.77 (m, 4H), 3.84 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.0, 21.2, 23.5, 26.1, 26.7, 27.2, 31.4, 42.6, 43.1, 47.2, 48.8, 82.5; IR (NaCl) 3337 cm^{-1}; HRMS (EI, 70 eV) m/z 178.1343 ($[M]^+$, 1.6%), calcd for $C_{12}H_{18}O$ 178.1358.

(1R*,5S*,9R*,11S*,12S*,13R*)-7,7-Dimethyl-6,8-dioxapentacyclo [9.2.1.$0^{2,14}$.$0^{3,12}$.$0^{5,9}$]tetradeca-13-ol (2d). To **7g**[4] (290 mg, 1.09 mmol) and NMO (204 mg, 1.74 mmol) in *tert*-BuOH-THF-H_2O (10:3:1, 10 mL) solution, OsO_4 (0.2 M in CH_2Cl_2, 0.273 mL, 5 mol %) was added at rt. After stirring for 3.5 h, saturated aqueous Na_2SO_3 (10 mL) was added and stirred for 1 h. The aqueous reaction mixture was extracted with CH_2Cl_2 (3x 30 mL), then the combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 1:3) to give 9-*endo*-10-*endo*-dihydroxytetracyclo-[5.4.0.$0^{2,4}$.$0^{3,7}$]undecan-5-ol benzoate (**A**) (R_f = 0.3, 272 mg, 83% yield) as a white solid. Mp 108 - 109 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 - 1.53 (overlapped, 3H), 1.56 (br s, 1H, OH), 1.82 (br s, 1H, OH), 1.85 - 1.96 (m, 3H), 2.04 (m, 1H), 2.08 (br d, J = 6.4 Hz, 1H), 2.16 (br s, 1H), 2.56 (br d, J = 6.0 Hz, 1H), 3.78 - 3.84 (m, 2H), 4.81 (br s, 1H), 7.42 (dd, J = 7.2, 7.2 Hz, 2H), 7.55 (dd, J = 7.2, 7.2 Hz, 1H), 8.00 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.9, 19.2, 21.6, 33.5, 34.3, 38.0, 38.6, 42.3, 75.5, 75.8, 82.0, 129.4 (2C), 130.6 (2C), 131.5, 133.9, 167.3; IR (NaCl) 3411, 1714 cm^{-1}; HRMS (EI, 70 eV) m/z 300.1378 ($[M]^+$, 55.2%), calcd for $C_{18}H_{20}O_4$ 300.1362. The stereochemistry was established by the observation of NOEs between H-9, H-10 with H-6. The *exo, exo*-diol was not isolated, but its production cannot be ruled out.

Diol **A** (272 mg, 0.906 mmol) was treated with a solution of 5% TsOH in dimethoxylpropane (20 mL) and stirred for 4.5 h at rt. Then, saturated $NaHCO_3$ (10 mL)was added to quench the acid, the organic layer was washed with water (20 mL) and brine (20 mL) followed by drying over Na_2SO_4. The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 10:1) to give the protected diol, (1R*,5S*,9R*,11S*,12S*,13R*)-7,7-dimethyl-6,8-dioxapentacyclo [9.2.1.$0^{2,14}$.$0^{3,12}$.$0^{5,9}$]tetradeca-13-yl benzoate (**B**) (R_f = 0.2, 302 mg, 98% yield) as a white solid. Mp 77 - 78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.40 (overlapped, dd, *J* = 5.2, 5.2 Hz, 1H), 1.41 (s, 3H), 1.49 - 1.55 (m, 2H), 1.57 - 1.61 (overlapped, m, 1H), 1.65 - 1.73 (m, 1H), 1.90 (br s, 1H), 1.98 - 2.08 (overlapped, m, 3H), 2.47 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.23 - 4.31 (m, 2H), 4.84 (br s, 1H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.54 (dd, *J* = 7.6, 7.6 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.7, 19.7, 21.2, 23.3, 26.7, 29.3, 30.6, 35.65, 35.88, 39.9, 75.3 (2C), 80.9, 105.9, 128.3 (2C), 129.6 (2C), 130.7, 132.8, 166.4; IR (NaCl) 1716 cm^{-1}; HRMS (EI, 70 eV) *m/z* 340.1708 ($[M]^+$, 0.7 %), calcd for $C_{21}H_{24}O_4$ 340.1675. The protected diol **B** (260 mg, 0.77 mmol) was dissolved in THF-H_2O-MeOH (2:2:1, 8 mL). Then, $LiOH{\cdot}H_2O$ (65 mg, 1.54 mmol) was added and the solution was stirred for 1 h. The solution was neutralized to pH 7 with 1N HCl, then extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (10 mL), H_2O (10 mL), brine (10 mL) and then dried over Na_2SO_4. The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 1:1) to give **2d** (R_f = 0.3, 176 mg, 97% yield) as a white solid. Mp 104 - 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (dd, *J* = 5.2, 5.2 Hz,

1H), 1.28 (s, 3H), 1.38 (overlapped, dd, J = 5.2, 5.2 Hz, 1H), 1.40 (s, 3H), 1.42 (overlapped, 1H), 1.47 - 1.55 (m, 3H), 1.66 (ddd, J = 17.6, 10.8, 6.8 Hz, 1H), 1.86 (dd, J = 9.2, 6.4 Hz, 1H), 1.96 (ddd, J = 13.6, 9.6, 4.0 Hz, 1H), 2.06 (ddd, J = 13.6, 9.2, 3.6 Hz, 1H), 2.37 (dd, J = 8.0, 8.0 Hz, 1H), 3.82 (s, 1H), 4.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0, 19.1, 22.0, 23.2, 26.7, 29.2, 30.6, 34.4, 35.6, 41.6, 75.2, 75.3, 78.1, 105.7; IR (NaCl) 3408 cm^{-1}; HRMS (EI, 70 eV) *m/z* 236.1417 ([M]$^+$, 2.3%), calcd for $C_{14}H_{20}O_3$ 236.1412.

(1S*,2S*,3S*,4S*,5R*,6R*,7R*,9S*,10S*)-9-Benzyloxy-7,10-dimethyl-tetracyclo[5.4.0.0^{2,4}.0^{3,7}]-undecan-5-ol (2e) and **(1S*,2S*,3S*,4S*,5S*,6R*,7R*,9S*, 10S*)-9-Benzyloxy-7,10-dimethyltetracyclo [5.4.0.0^{2,4}.0^{3,7}]undecan-5-ol (2f).** To a solution of **2i**[4] (120 mg, 0.455 mmol) and O-benzyl trichloroacetimide (0.116 mL, 0.592 mmol) in Et_2O (4.5 mL) cooled to 0 °C, TfOH (23 uL, 1M in Et_2O) solution was added. The resultant solution was allowed to warm to rt and stirred for 16 h. Then, saturated $NaHCO_3$ (3 mL) was added, the organic layer separated and dried over Na_2SO_4. The solution was concentrated and the residue dissolved in HOAc (1 mL) and treated with H_2SO_4 (4.2 mg, 0.04 mmol). The resultant solution was stirred at rt for 12 h, then saturated $NaHCO_3$ solutionwas added until bubbling ceased. Then, Et_2O (20 mL) was added and the organic layer was separated and washed with water (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvent was removed in vacuo and the residue was dissolved in THF/H_2O/MeOH (2:2:1, 5 mL) mixture, then LiOH (35.6 mg, 0.8 mmol) was added and stirred for 7 h. The reaction mixture was neutralized to pH 7 with aqueous HCl (1M) and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuo and the residue purified by

flash chromatography (hexanes:EtOAc, 3:1) to give **2e** (R_f = 0.25, 55 mg) and **2f** (R_f = 0.20, 55 mg) in 89% combined yield.

Compound **2e:** Mp 112 - 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (d, *J* = 6.4 Hz, 3H), 1.03 (s, 3H), 1.05 (dd, *J* = 4.8, 4.8 Hz, 1H), 1.16 (m, 2H), 1.43 (ddd, *J* = 14.2, 10.8, 2.0 Hz, 1H), 1.48 (br s, 1H), 1.52 (dd, *J* = 14.2, 10.8 Hz, 1H), 1.60 (m, 1H), 1.92 (dd, *J* = 14.2, 4.0 Hz, 1H), 1.97 (dd, *J* = 14.2, 5.6 Hz 1H), 2.55 (br d, *J* = 8.0 Hz, 1H), 3.21 (ddd, *J* = 10.4, 10.4, 2.8 Hz, 1H), 4.32 (br s, 1H), 4.41 (d, *J* = 11.2 Hz, 1H), 4.56 (d, *J* = 11.2 Hz, 1H), 7.24 - 7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5, 20.0, 21.1, 24.4, 26.1, 35.3, 38.8, 39.2, 43.8, 46.3, 47.6, 71.7, 76.9, 81.5, 127.4, 127.7 (2C), 128.3 (2C), 139.3; IR (NaCl) 3383 cm^{-1}; HRMS (EI, 70 eV) *m/z* 298.1943 ([M]$^+$, 75.5%), calcd for $C_{20}H_{26}O_2$ 298.1933.

Compound **2f:** Mp 101 - 102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (d, *J* = 6.4 Hz, 3H), 1.09 (m, 2H), 1.20 (overlapped, 2H), 1.39 (s, 3H), 1.57 (br s, 1H), 1.62 (overlapped, 2H), 1.67 (dd, *J* = 14.0, 9.6 Hz, 1H), 1.75 (br d, *J* = 7.6 Hz, 1H), 1.88 (ddd, *J* =14.0, 7.2, 7.2 Hz, 1H), 2.04 (dd, *J* = 14.0, 2.4 Hz, 1H), 3.24 (ddd, *J* = 9.6, 9.6, 2.4 Hz, 1H), 3.82 (brs, 1H), 4.41(d, *J* = 11.2 Hz, 1H), 4.59 (d, *J* = 11.2 Hz, 1H), 7.23 - 7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.6, 20.2, 21.1, 22.6, 25.4, 36.5, 39.1, 41.1, 44.8, 46.3, 47.5, 71.6, 81.3, 81.4, 127.3, 127.7 (2C), 128.3 (2C), 139.3; IR (NaCl) 3395 cm^{-1}; HRMS (EI, 70 eV) *m/z* 298.1946 ([M]$^+$, 75.5%), calcd for $C_{20}H_{26}O_2$ 298.1933.

Tricyclo[5.4.0.0^{3,7}]undecan-5-one (4a).[4] To a solution of **2a** (45 mg, 0.274 mmol) in toluene (2.7 mL) under Ar, was added $[Pt(C_2H_4)Cl_2]_2$ (16.7 mg, 0.027 mmol). The reaction mixture was refluxed for 48 h, then the cooled mixture was passed through a short silica gel plug eluting with CH_2Cl_2 (3 x 5 mL) and Et_2O (5 mL). The combined

solvents were removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 10:1) to give **4a**[4] as a colorless oil (R_f = 0.4, 44.5 mg, 99% yield).

7-Methyltricyclo[5.4.0.0^{3,7}]undecan-5-one (4b). To a solution of **2b** (14 mg, 0.084 mmol) in toluene (1 mL) was added $[Pt(C_2H_4)Cl_2]_2$ (5.2 mg, 0.0084 mmol, 0.1 eq) under Ar. The light yellow solution was refluxed for 48 h, then allowed to cool to rt. The solution was passed through a short silica gel plug eluting with CH_2Cl_2 (2 × 5 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 10:1) to give **4b** (R_f = 0.4, 13.8 mg, 99% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.31 (br ddd, *J* = 13.2, 12.4, 12.0 Hz, 1H), 1.46 - 1.62 (m, 6H), 1.67 - 1.75 (m, 3H), 1.83 (d, *J* = 18.0 Hz, 1H), 1.94 (dddd, *J* = 12.8, 6.4, 3.2, 3.2 Hz, 1H), 2.09 - 2.14 (m, 1H), 2.16 (br s, 1H), 2.31 (ddd, *J* = 18.0, 4.0, 4.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.4, 25.7, 26.7, 31.1, 32.4, 36.7, 39.6, 43.3, 46.3, 49.5, 63.7, 217.6; IR (NaCl) 1745 cm^{-1}; HRMS (EI, 70 eV) *m/z* 178.1344 ([M]$^+$, 79.6%), calcd for $C_{12}H_{18}O$ 178.1358.

1-Methyltricyclo[5.4.0.0^{3,7}]undecan-5-one (4c)[4]. To a solution of **2c** (107 mg, 0.608 mmol) in toluene (6 mL) was added $[Pt(C_2H_4)Cl_2]_2$ (37.0 mg, 0.06 mmol) under Ar. The light yellow solution was refluxed for 48 h, then allowed to cool to rt. The solution was passed through a short silica gel plug eluting with CH_2Cl_2 (3 × 10 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 10:1) to give **4c** [4](R_f = 0.4, 106 mg, 99% yield) as a colorless liquid.

(1S*,3S*,6R*,7S*,9S*,10R*)-11,11-Dimethyl-10,12-dioxytetracyclo-[8.4.0.0^{3,7}.0^{9,13}] tetradecan-5-one (4d). To a solution of **2d** (154 mg, 0.657 mmol) in toluene (6.5 mL) was added $[Pt(C_2H_4)Cl_2]_2$ (39.9 mg, 0.065 mmol) under Ar. The light

yellow solution was refluxed for 48 h, then allowed to cool to rt. The solution was passed through a short silica gel plug eluting with CH_2Cl_2 (3 × 10 mL). The solvents were removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 6:1,) to give **4d** (R_f = 0.2, 150 mg, 97% yield) as a white solid. Mp 150 - 151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 3H), 1.30 (overlapped, ddd, *J* = 11.6, 11.6, 3.2 Hz, 1H), 1.40 (overlapped, 1H), 1.41 (s, 3H), 1.75 (m, 1H), 1.83 (d, *J* = 14.4 Hz, 1H), 1.84 (dd, *J* = 13.2, 13.2 Hz, 1H), 2.02 (ddd, *J* = 18.0, 3.6, 3.6 Hz, 1H), 2.07 - 2.22 (m, 3H), 2.23 (br s, 1H), 2.48 (ddd, *J* = 14.4, 11.2, 6.0 Hz, 1H), 2.54 (br dd, *J* = 4.4, 4.4 Hz, 1H), 4.22 (ddd, *J* = 12.0, 7.2, 4.0 Hz, 1H), 4.33 (ddd, *J* = 12.0, 7.2, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 26.9, 28.7, 30.0, 38.2, 40.1, 40.2, 43.0, 46.7, 55.5, 74.7, 75.6, 106.4, 217.2; IR(neat) 1743 cm^{-1}; HRMS (EI, 70 eV) *m/z* 236.9400 ([M]$^+$, 14.3%), calcd for $C_{14}H_{20}O_3$ 236.1412.

(1S*,3S*,6R*,7S*,9R*,10S*)-9-Benzyloxy-7,10-Dimethyltricyclo[5.4.0.0^{3,7}]-undecan-5-one (4e). To a solution of **2e** (20 mg, 0.067 mmol) in toluene (1 mL) was added $[Pt(C_2H_4)Cl_2]_2$ (4.1 mg, 0.0067 mmol) under Ar. The light yellow solution was refluxed for 48 h, then allowed to cool to rt. The solution was passed through a short silica gel plug eluting with CH_2Cl_2 (3 × 10 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 6:1) to give **4e** (R_f = 0.31, 9.5 mg, 98% yield) as a white solid. Mp 65 - 66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (d, *J* = 6.8 Hz, 3H), 1.04 (s, 3H), 1.24 (br dd, *J* = 12.8, 12.8 Hz, 1H), 1.62 - 1.78 (overlapped, 4H), 1.83 (m, 1H), 1.97 (ddd, *J* = 6.4, 6.4, 6.2 Hz, 1H), 2.07-2.16 (overlapped, 2H), 2.23 (dd, *J* = 15.2, 4.0 Hz, 1H), 2.27 (br s, 1H), 2.34 (ddd, *J* = 17.6, 3.2, 3.2 Hz, 1H), 3.34 (ddd, *J* = 9.6, 9.6, 4.8 Hz, 1H), 4.44 (d, *J* = 11.2 Hz, 1H), 4.61 (d,

J = 11.2 Hz, 1H), 7.24 - 7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 24.0, 34.9, 37.7, 39.1, 39.4, 44.0, 45.0, 45.1, 47.9, 59.9, 72.2, 82.4, 127.4, 127.6 (2C), 128.3 (2C), 138.9, 217.3; IR (NaCl) 1745 cm^{-1}; HRMS (EI, 70 eV) *m/z* 298.1941 ($[M]^+$, 2.7%), calcd for $C_{20}H_{26}O_2$ 298.1933.

(1S*,3S*,6R*,7S*,9S*,10R*)-10-Benzyloxy-1,9-dimethyltricyclo[5.4.0.0^{3,7}]-undecan-5-one (4f). To a solution of **2f** (40 mg, 0.134 mmol) in toluene (2 mL) was added $[Pt(C_2H_4)Cl_2]_2$ (8.2 mg, 0.0134 mmol) under Ar. The light yellow solution was refluxed for 48 h, then allowed to cool to rt. The solution was passed through a short silica gel plug eluting with CH_2Cl_2 (3 × 10 mL). The solvents were removed in vacuo and the residue purified by flash chromatography (hexanes:EtOAc, 6:1) to give **4f** (R_f = 0.3, 39.2 mg, 98% yield) as a white solid. Mp 78 - 79 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (d, J = 6.4 Hz, 3H), 1.03 (s, 3H), 1.06 (overlapped, ddd, J = 13.6, 13.6, 3.6 Hz, 1H), 1.17 (d, J = 12.8 Hz, 1H), 1.44 (dd, J = 14.0, 10.4 Hz, 1H), 1.63 (m, 1H), 1.81 (d, J = 18.0 Hz, 1H), 1.92 (ddd, J = 12.8, 2.8, 2.8 Hz, 1H), 1.97 (ddd, J = 12.8, 2.8, 2.8 Hz, 1H), 2.08 (ddd, J = 18.0, 4.4, 2.4 Hz, 1H), 2.17 (dd, J = 9.2, 3.2 Hz, 1H), 2.19 (m, 1H), 2.20 (br s, 1H), 2.28 (br s, Hz, 1H), 3.03 (ddd, J = 10.4, 5.2, 5.2 Hz, 1H), 4.44 (d, J = 11.2 Hz, 1H), 4.61 (d, J = 11.2 Hz, 1H), 7.24 - 7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 30.5, 34.6, 37.0, 37.2, 37.4, 42.3, 45.4, 46.7, 47.0, 63.3, 72.3, 84.4, 127.5, 127.8 (2C), 128.3 (2C), 138.8, 215.5; IR (NaCl) 1746 cm^{-1}; HRMS (EI, 70 eV) *m/z* 298.1955 ($[M]^+$, 5.6%), calcd for $C_{20}H_{26}O_2$ 298.1933.

6-Oxatricyclo[5.5.0.0^{3,8}]dodecan-5-one (10). To a suspension of **4a** (61.7 mg, 0.376 mmol) and $NaHCO_3$ (632 mg, 7.52 mmol) in CH_2Cl_2 (37.6 mL) under Ar, was added *m*-CPBA (741 mg, 3.76 mmol), then the suspension was refluxed for 16 h. After

cooling to rt, saturated aqueous Na_2SO_3 (20 mL) was added and the mixture was stirred for 1 h to quench the peroxide. The organic layer was separated, then washed with saturated $NaHCO_3$ (3 x 20 mL), water (10 mL) and brine (10 mL), and subsequently dried over Na_2SO_4. The solvent was removed in vacuo and residue was purified by flash chromatography (hexanes:EtOAc, 3:1) to give **10** as a colorless oil (R_f = 0.25, 58 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 -1.46 (m, 3H), 1.50 - 1.54 (m, 3H), 1.63 - 1.68 (m, 1H), 1.78 - 1.84 (overlapped, 2H), 1.87 - 1.93 (m, 1H), 2.19 (br s, 1H), 2.36 (br d, *J* = 8.4 Hz, 1H), 2.49 (dd, *J* = 18.2, 1.6 Hz, 1H), 2.73 (ddd, *J* = 18.2, 4.5, 2.6 Hz, 1H), 2.78 (m, 1H), 4.53 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.4, 25.5, 29.5, 29.8, 34.8, 39.3, 42.7, 44.6, 45.2, 87.3, 171.2; IR (NaCl) 1735 cm^{-1}; HRMS (EI, 70 eV) *m/z* 180.1137 ($[M]^+$, 10.3%), calcd for $C_{11}H_{16}O_2$ 180.1150.

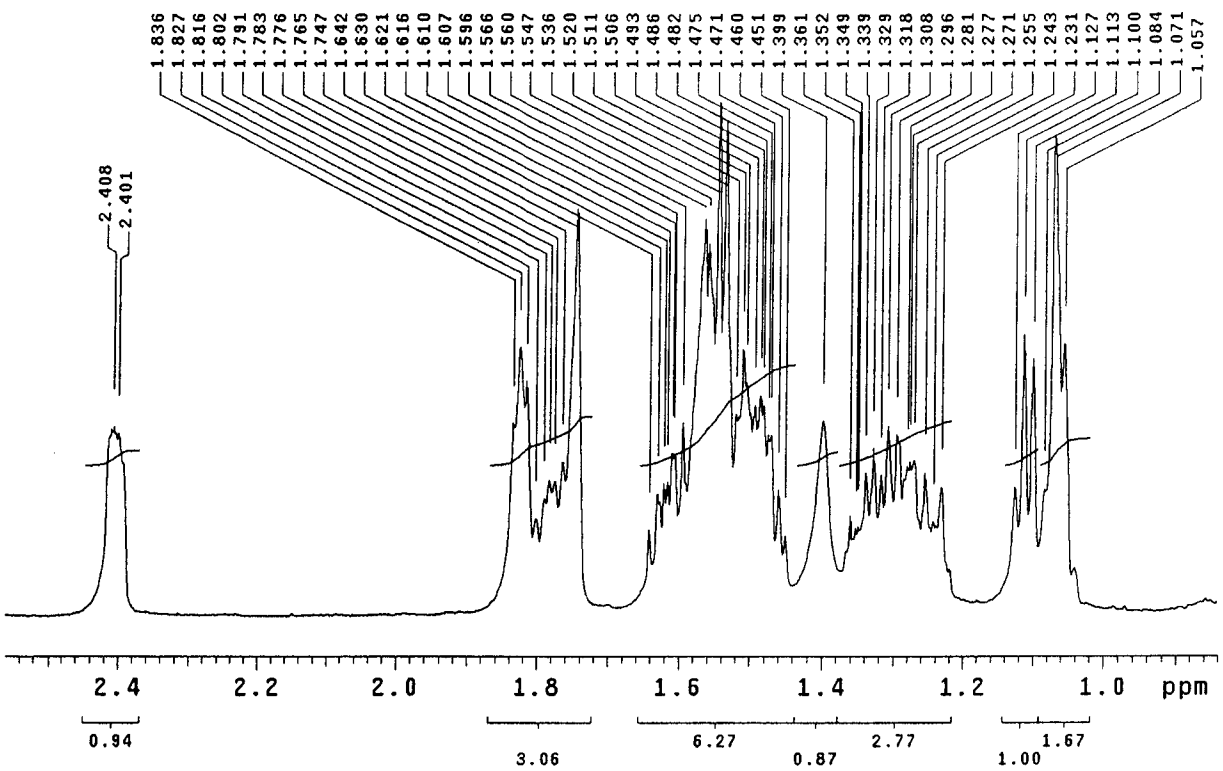
7-(2-Hydroxyethyl)-bicyclo[4.2.1]nonan-9-ol (11). To a solution of **10** (31.2 mg, 0.173 mmol) in THF (2 mL) under Ar, $LiAlH_4$ was added at rt and the suspension was refluxed for 1h. After cooling to rt, the reaction solution was quenched with 15% KOH aqueous solution (5 mL), and the aqueous solution was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, then the solvent removed in vacuo. The residue was purified by flash column (hexanes:EtOAc, 1:1) and **11** was obtained as a colorless solid (R_f = 0.21, 26.2 mg, 82% yield). Mp 124 - 125 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 - 1.55 (overlapped, 8H), 1.58 - 1.68 (overlapped, 2H), 1.71 - 1.78 (overlapped, 3H), 1.84 - 1.90 (overlapped, 2H), 1.99 (br d, *J* = 5.2 Hz, 1H), 2.27 (br s, 1H), 3.67 (AA'X, *J* = 10.8, 6.8 Hz, 2H), 4.02 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 25.9, 31.0, 32.9, 37.1, 42.0, 43.4, 47.6, 52.5, 61.9, 80.9; IR (NaCl) 3350 cm^{-1}; HRMS (EI, 70 eV) *m/z* 184.1453 ($[M]^+$, 1.1%), calcd for $C_{11}H_{20}O_2$ 184.1463.

[1] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. Purification of Laboratory Chemicals; 2nd ed.; Pergamon: New York, 1980.

[2] Story, P. R.; Fahrenholtz, S. R. *Org. Syn. Coll. Vol. V*, **1973**, 151.

[3] Chen, Y.; Snyder, *J.* K. *J Org. Chem.* **1998**, 63, 2060.

[4] Chen, Y.; Snyder, *J.* K. *J. Org. Chem.* **2001**, 66, 6943.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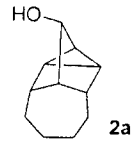
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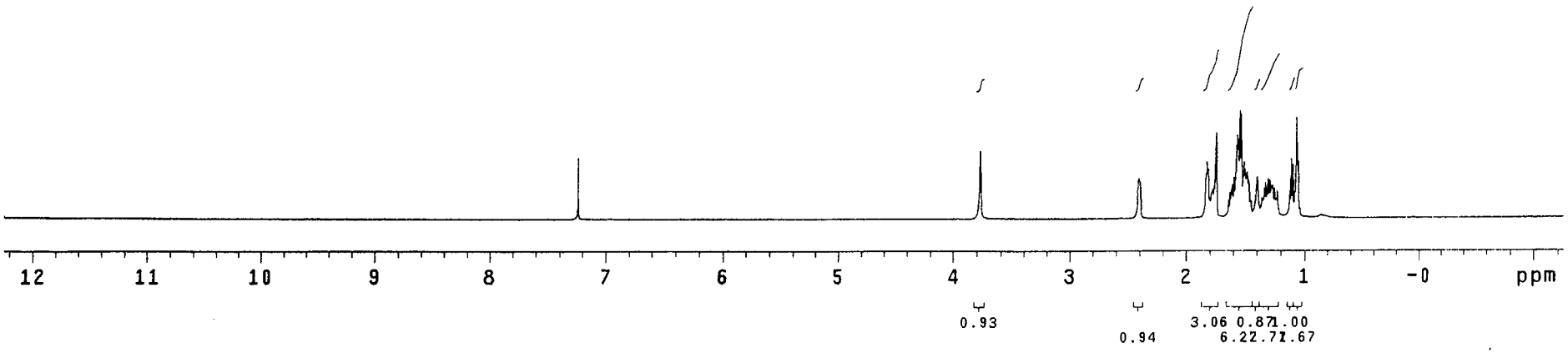
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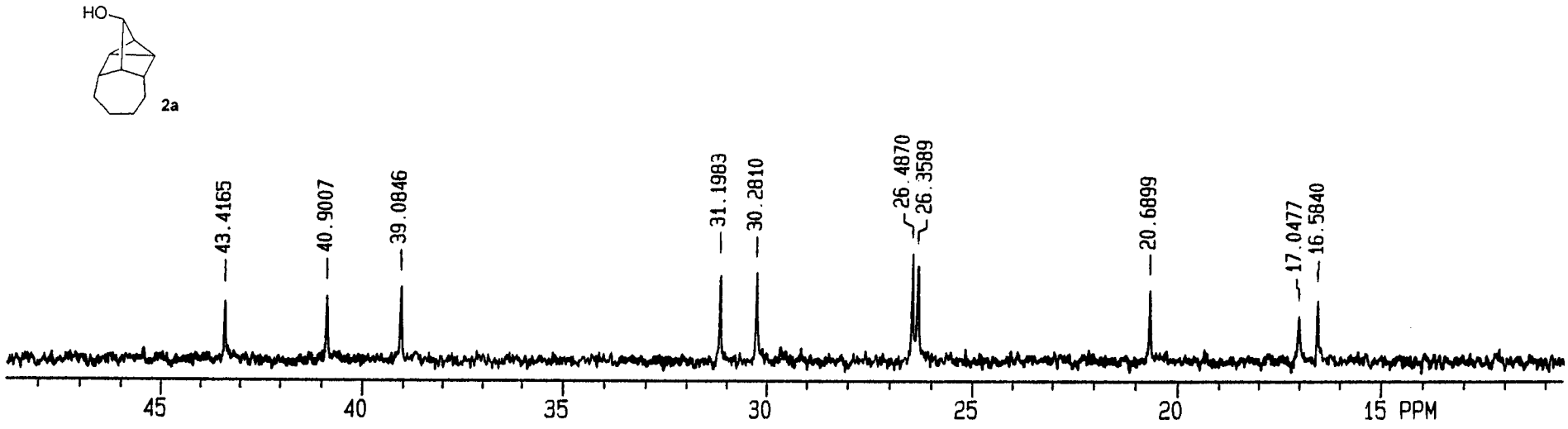
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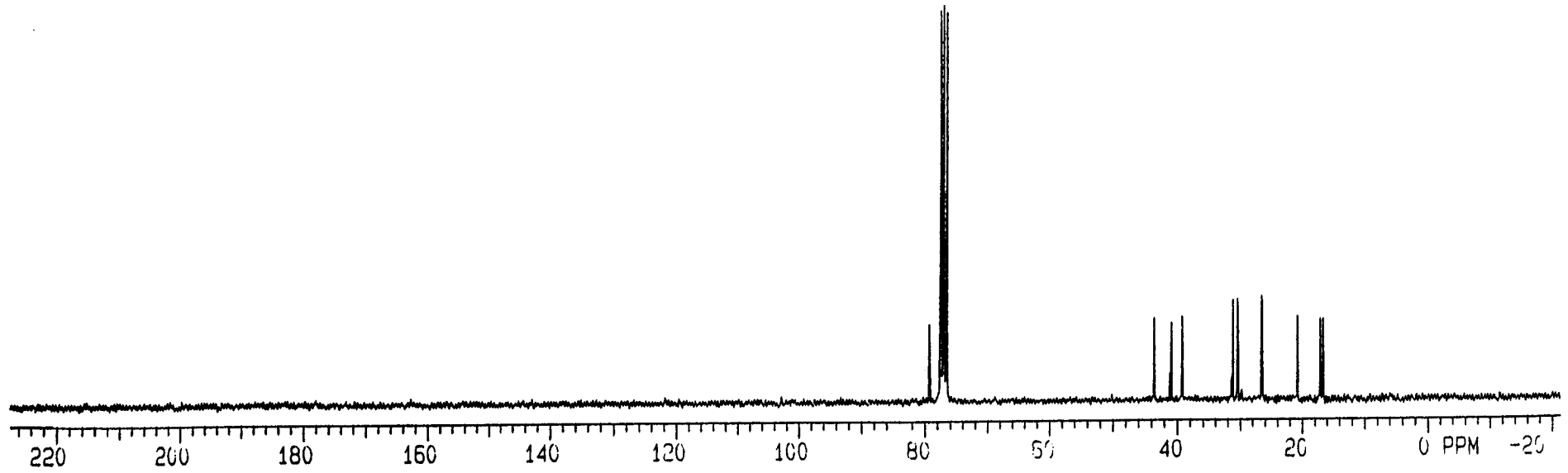
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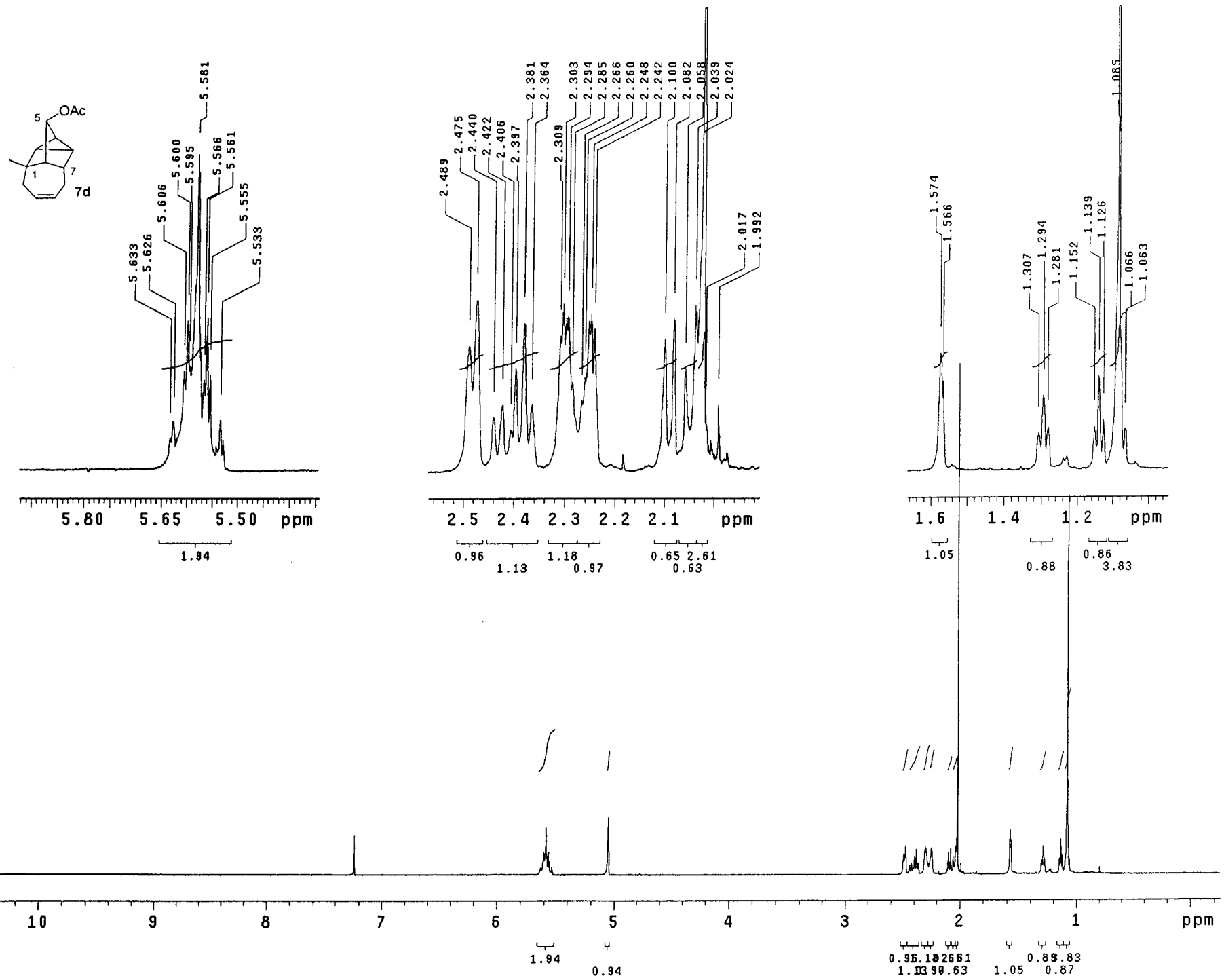
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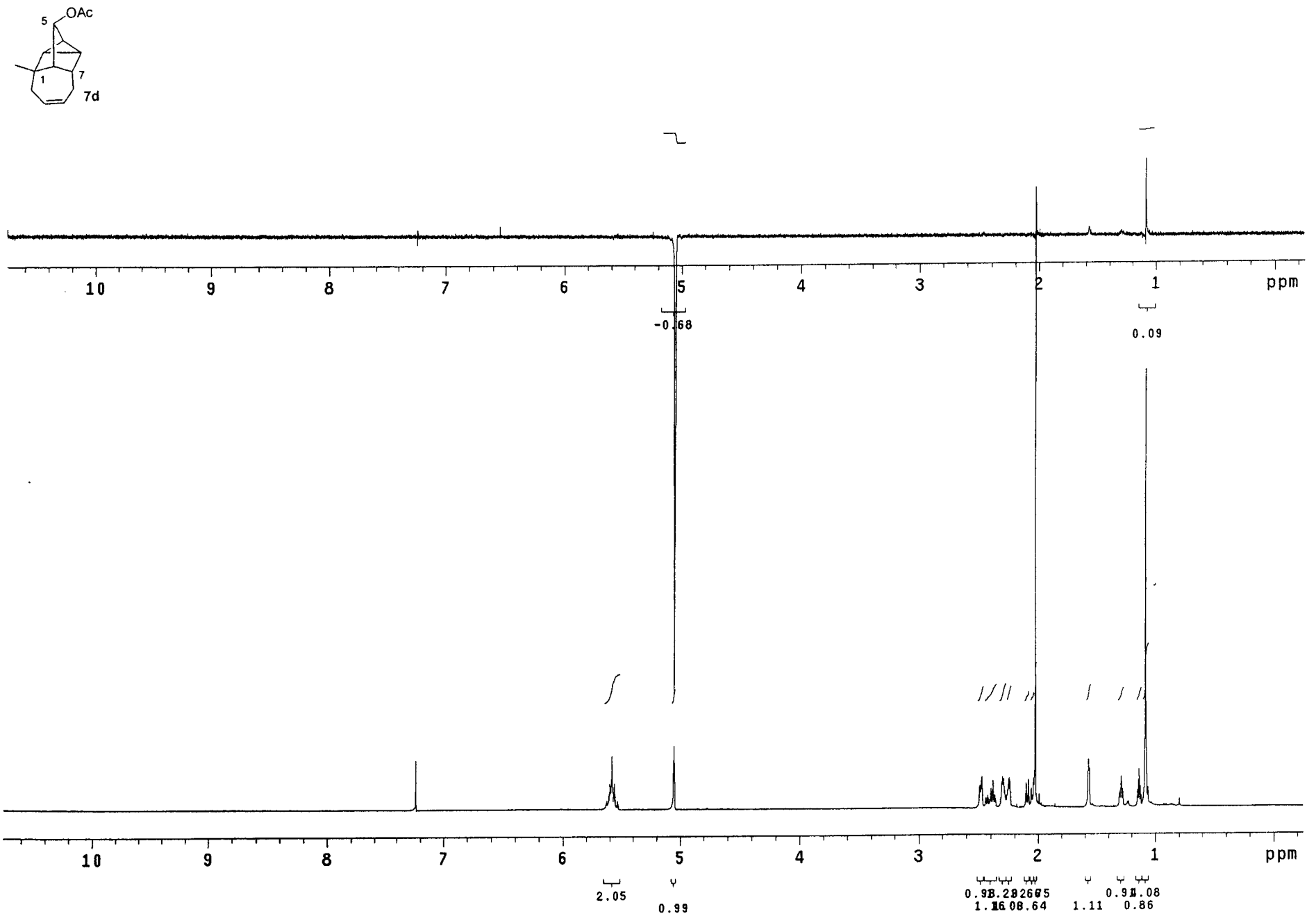
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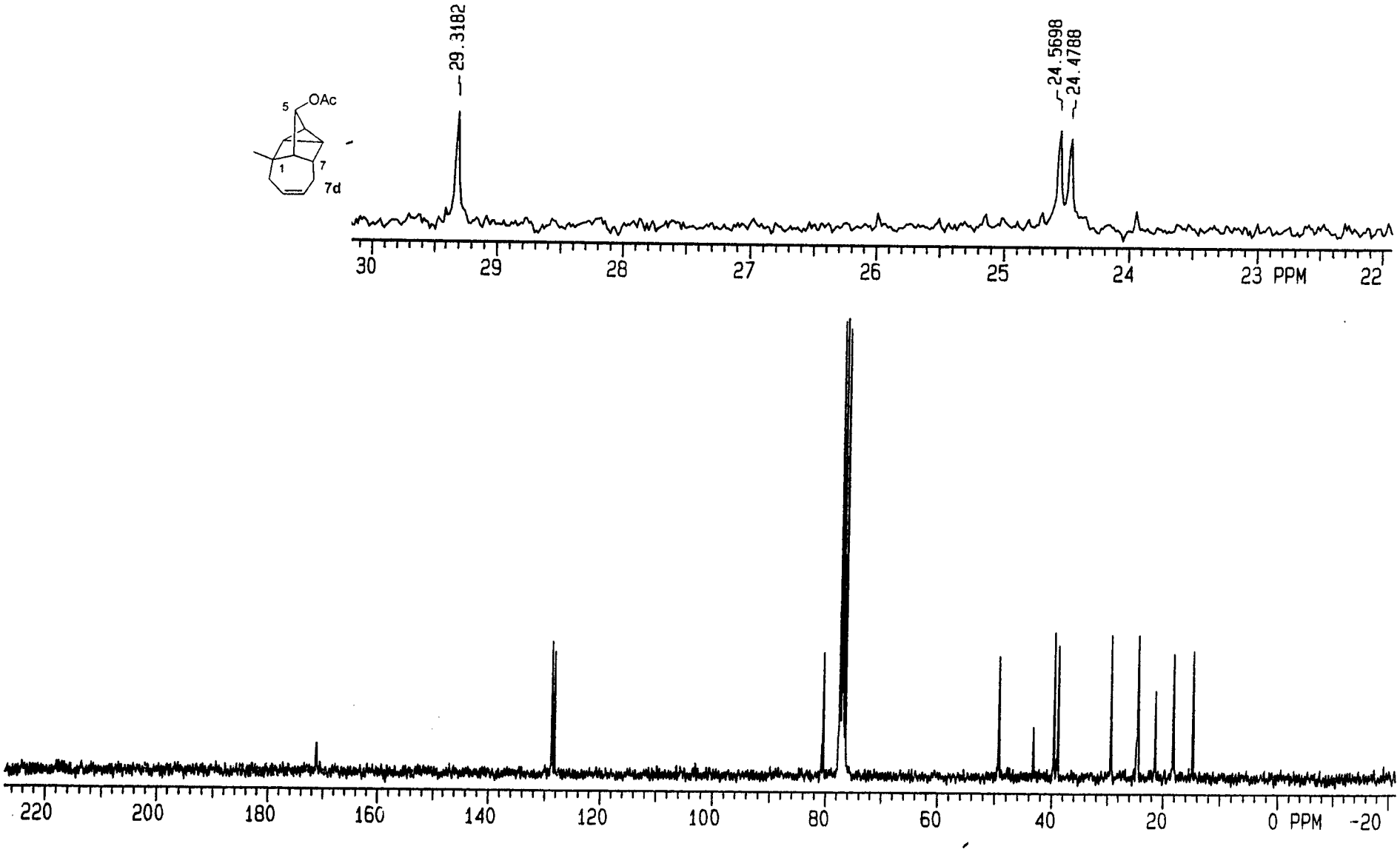
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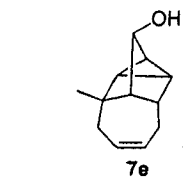
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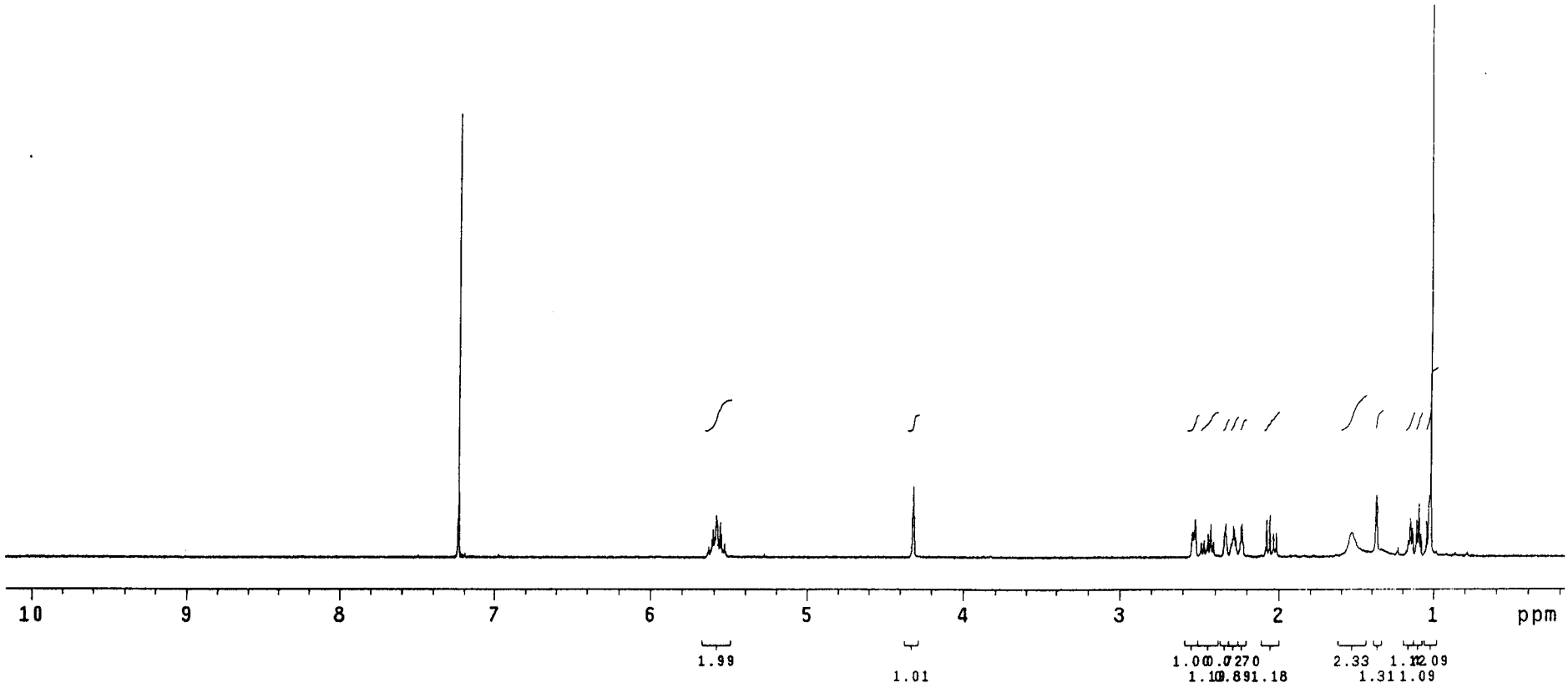
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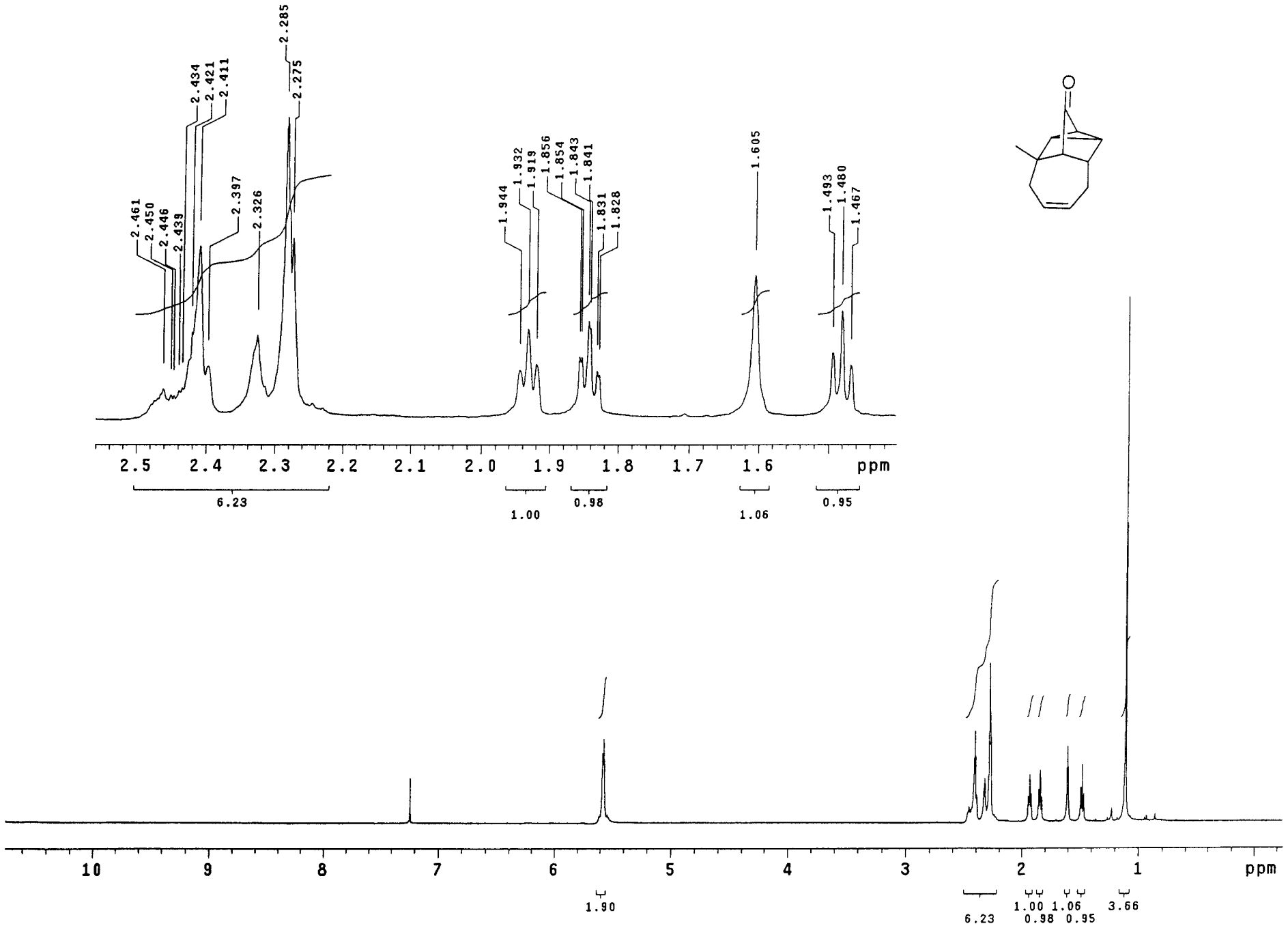
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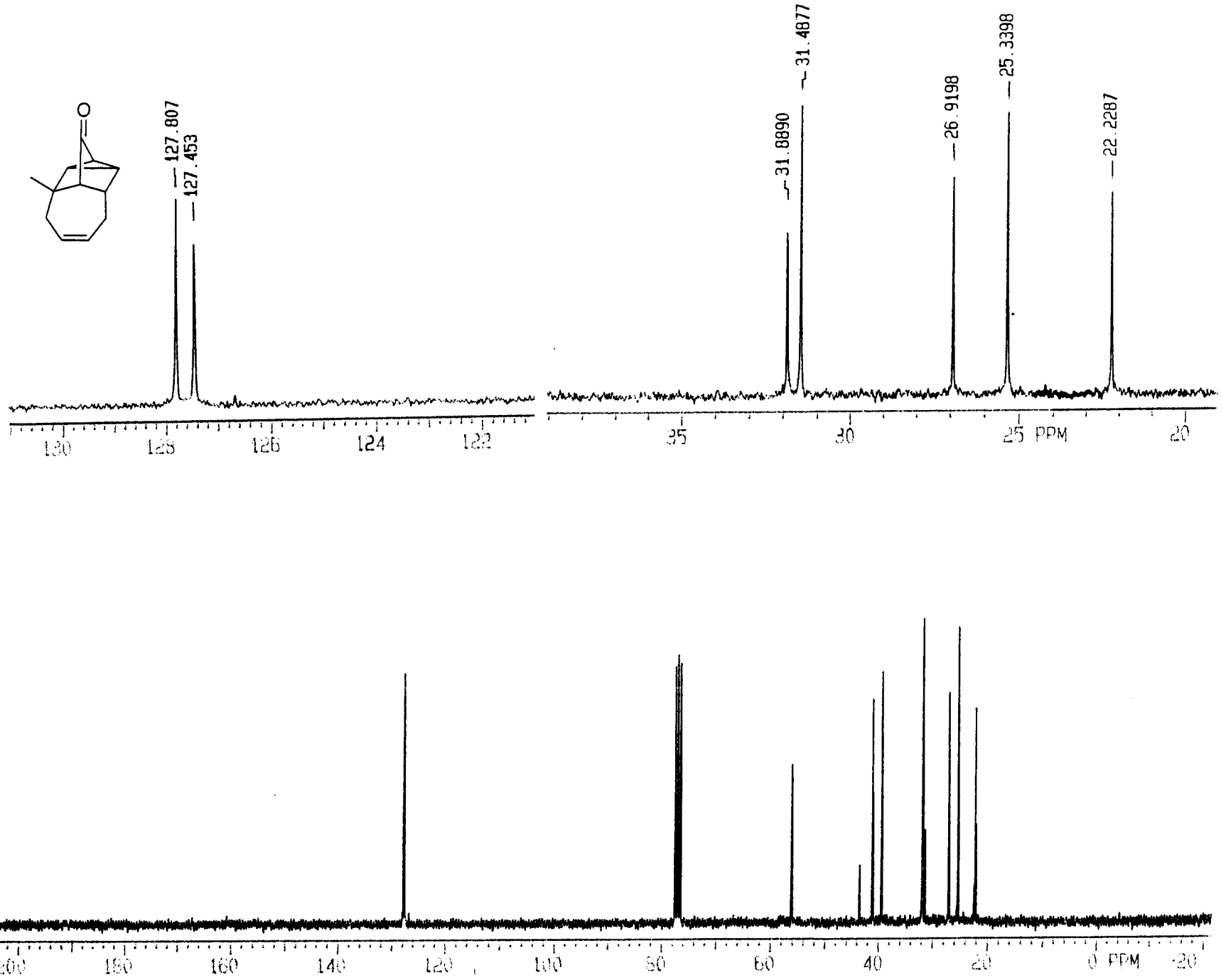
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100
80
60
40
20
0 PPM
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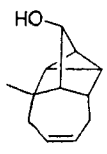
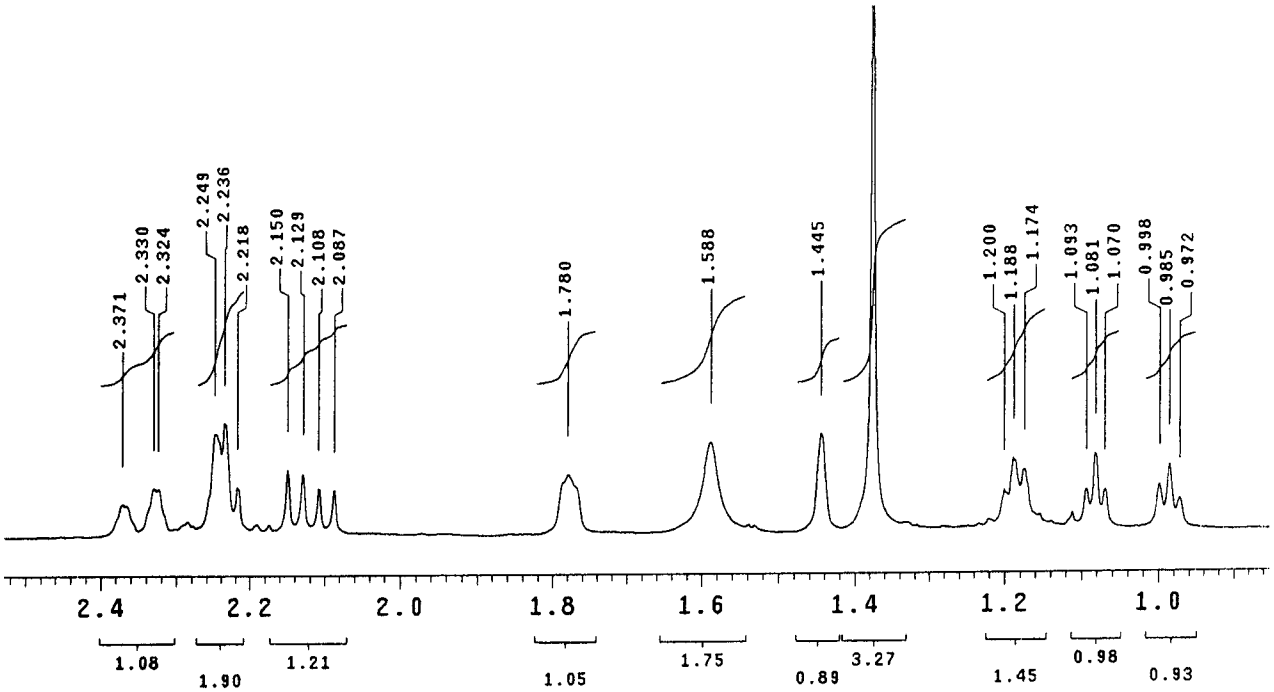

HO

7f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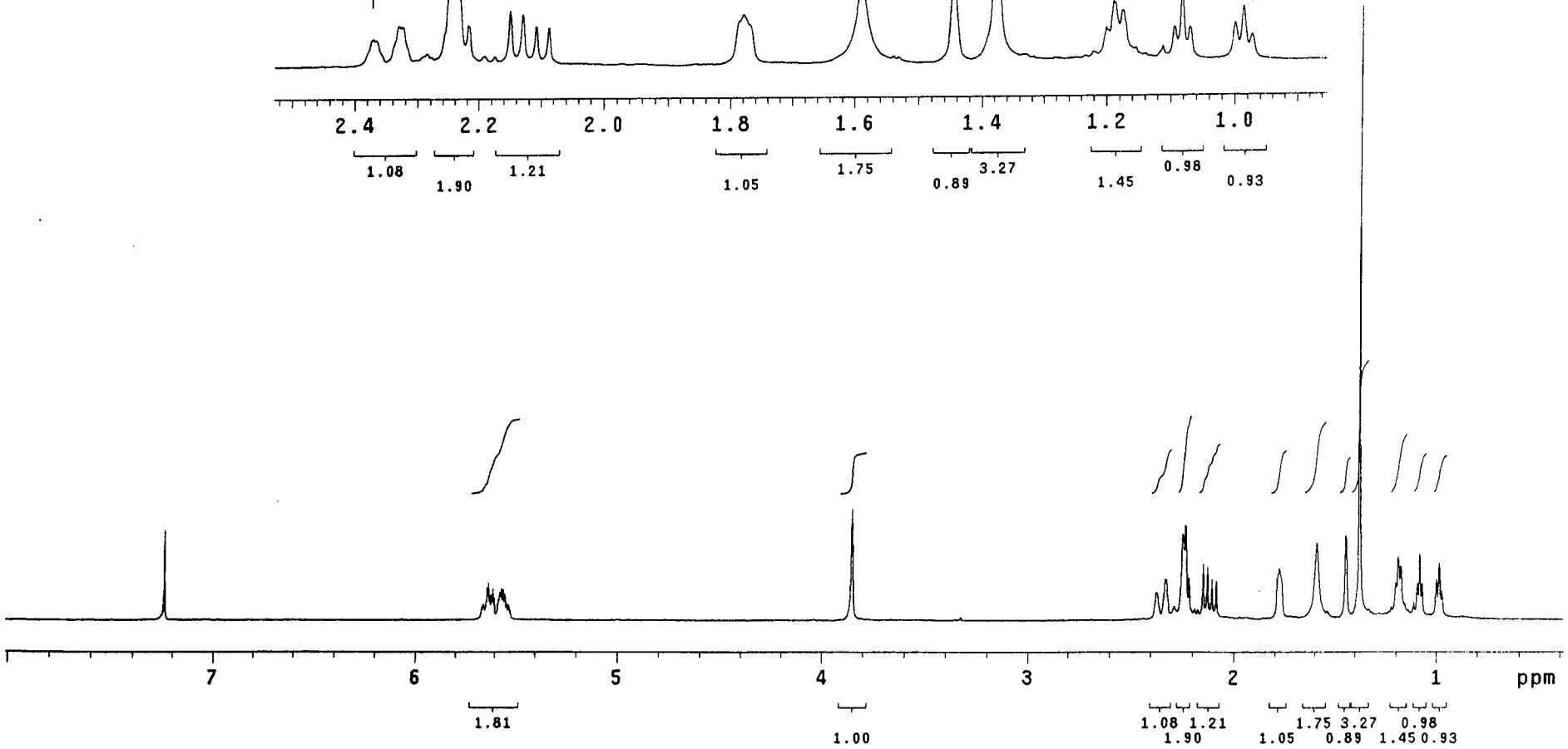
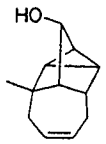
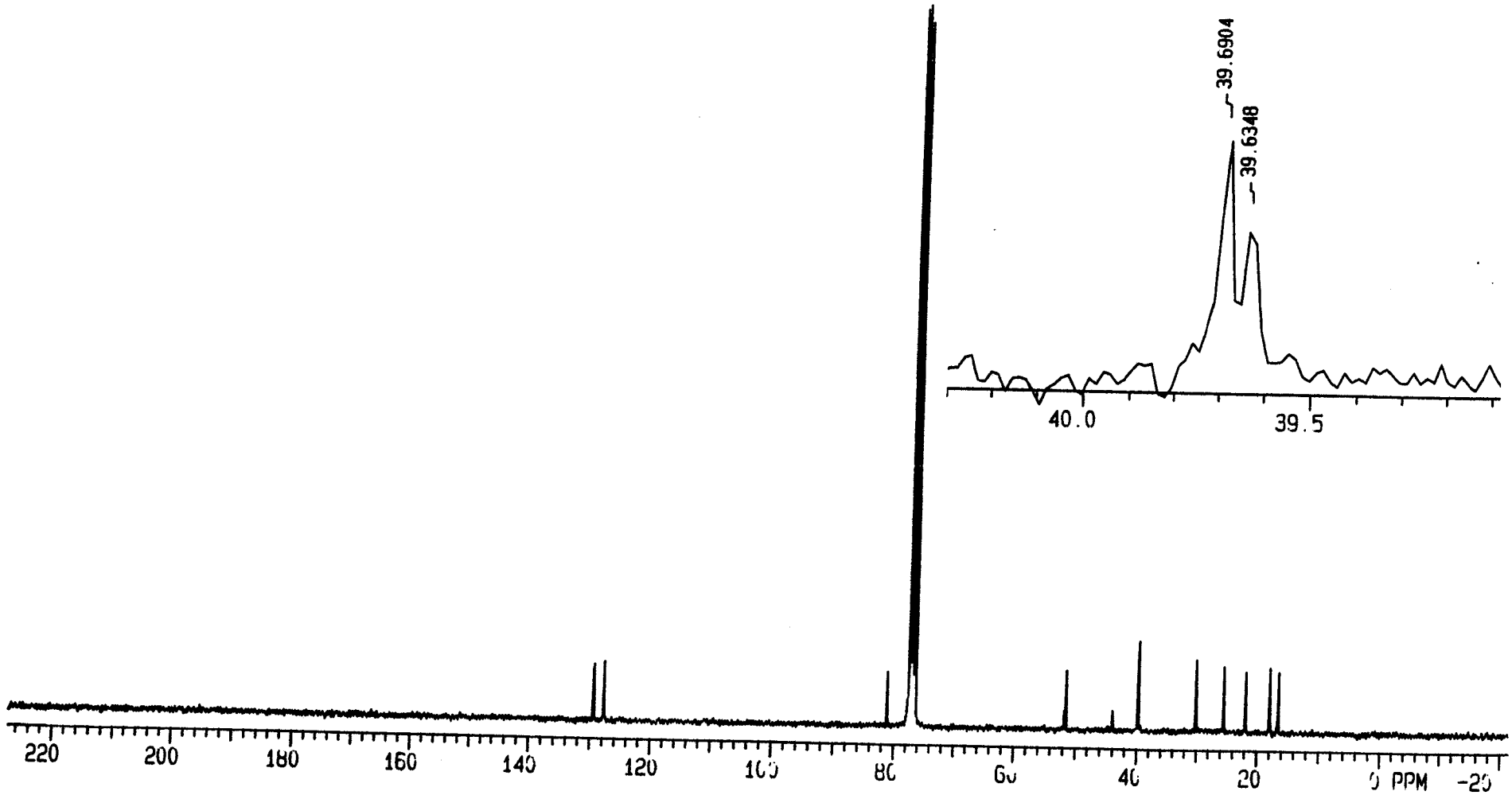
2.330
2.324
2.249
2.236
2.218
2.150
2.129
2.108
2.087
1.780
1.588
1.445
1.200
1.188
1.174
1.093
1.081
1.070
0.998
0.985
0.972
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
1.08
1.90
1.21
1.05
1.75
0.89
3.27
1.45
0.98
0.93


7
6
5
4
3
2
1
ppm
1.81
1.00
1.08
1.90
1.21
1.05
1.75
0.89
3.27
1.45
0.98
0.93


HO

7f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39.6348
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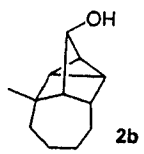
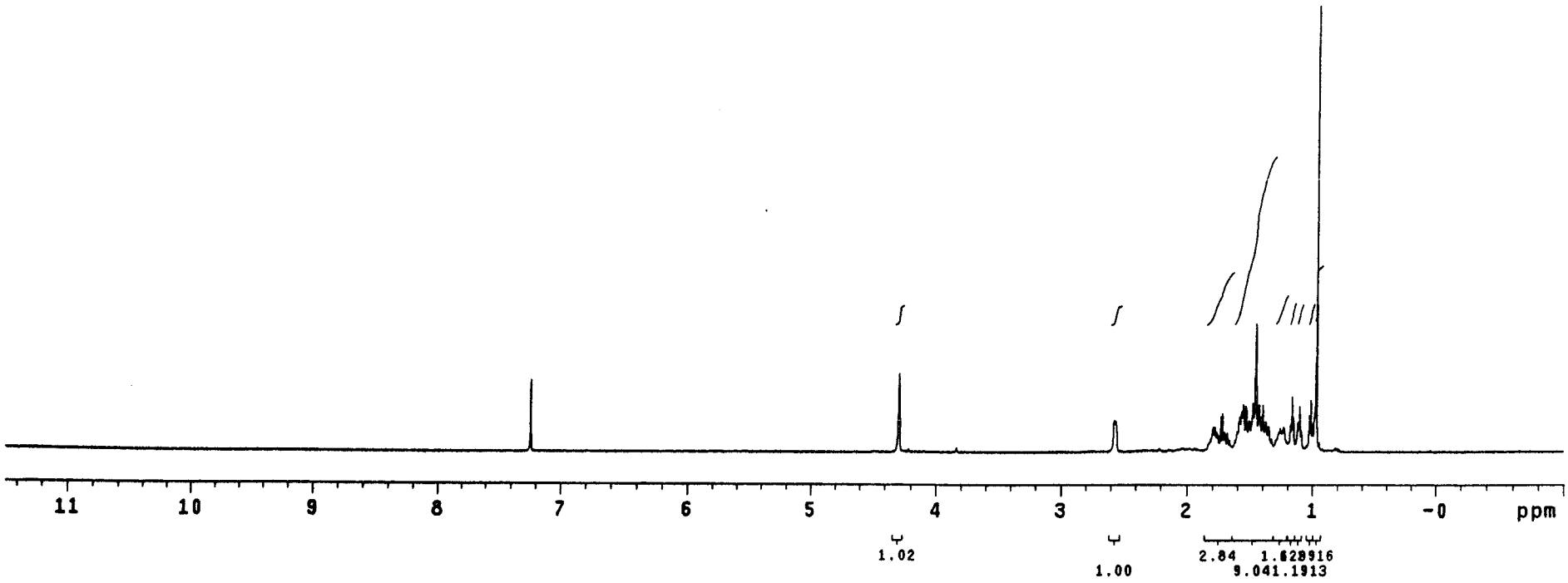
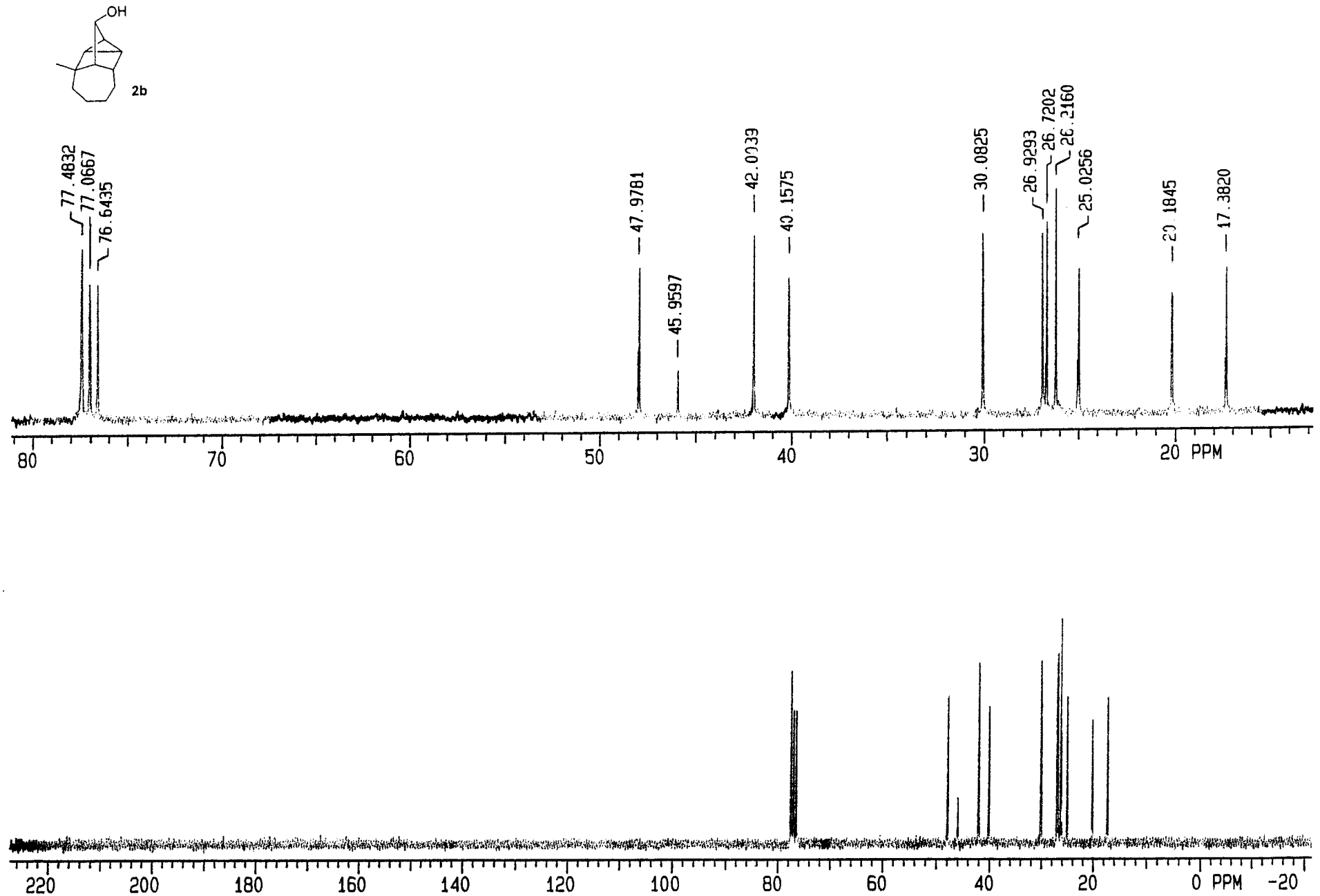
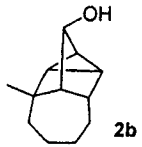
39.5
220
200
180
160
140
120
100
80
60
40
20
0 PPM
-20



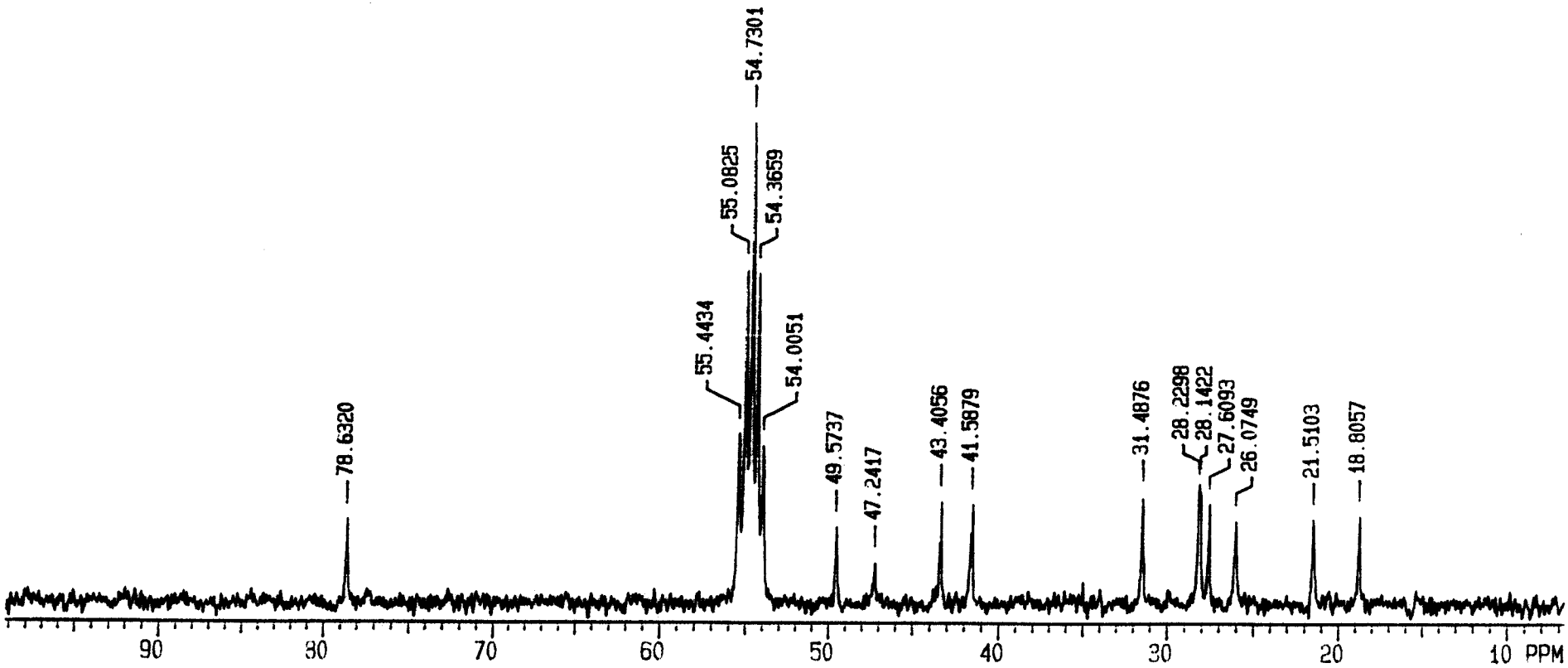
2b

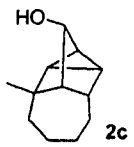



OH
2b
77.4832
77.0667
76.6435
47.9781
45.9597
42.0139
40.1575
30.0825
26.9293
26.7202
26.2160
25.0256
20.1845
17.3820
80
70
60
50
40
30
20 PPM
220
200
180
160
140
120
100
80
60
40
20
0 PPM
-20

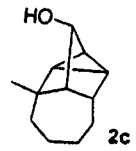

OH

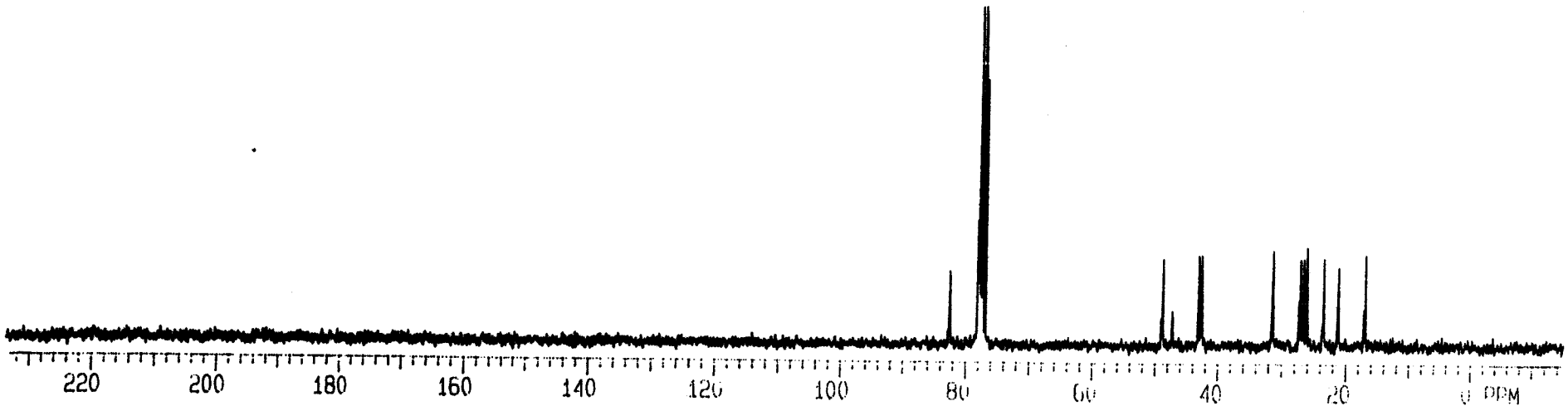
2b

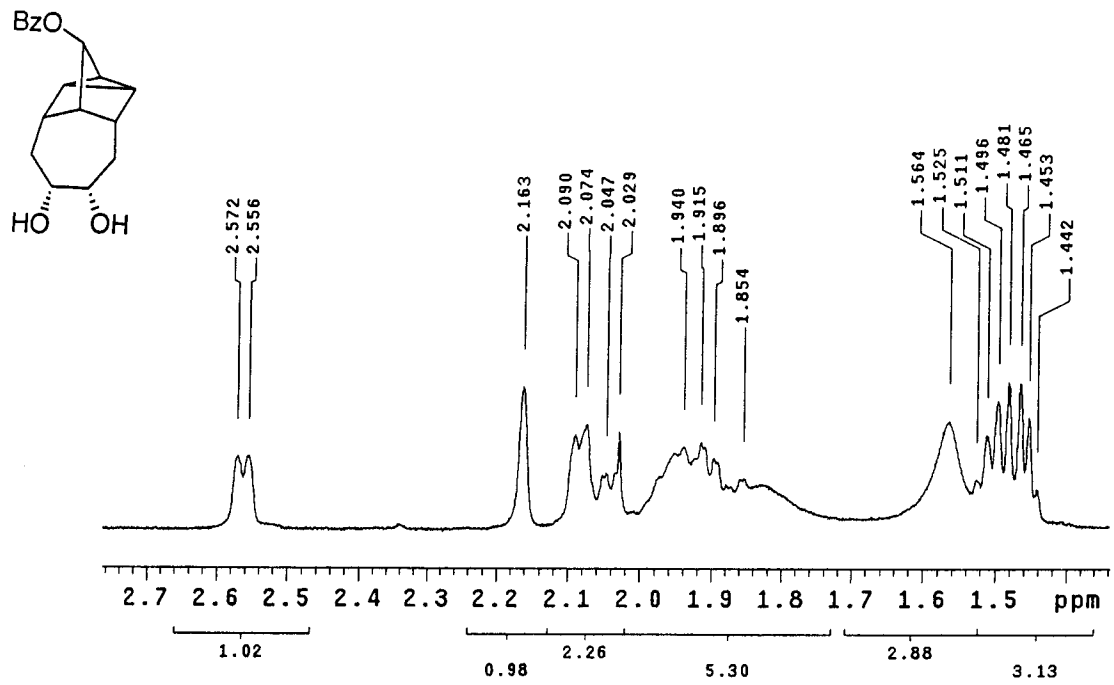

78.6320
55.4434
55.0825
54.7301
54.3659
54.0051
49.5737
47.2417
43.4056
41.5879
31.4876
28.2298
28.1422
27.6093
26.0749
21.5103
18.8057
90
80
70
60
50
40
30
20
10 PPM

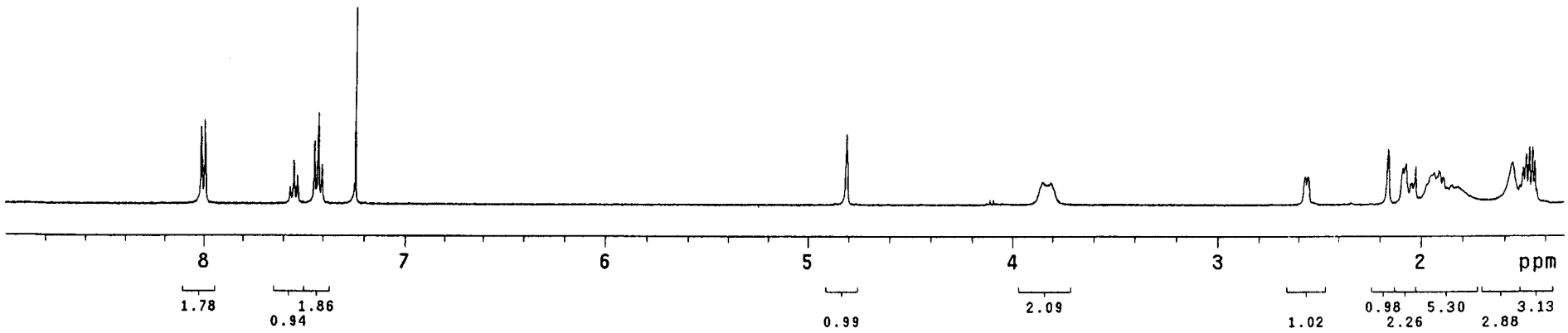


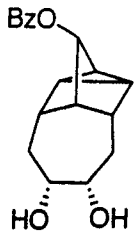
2c


HO
2c

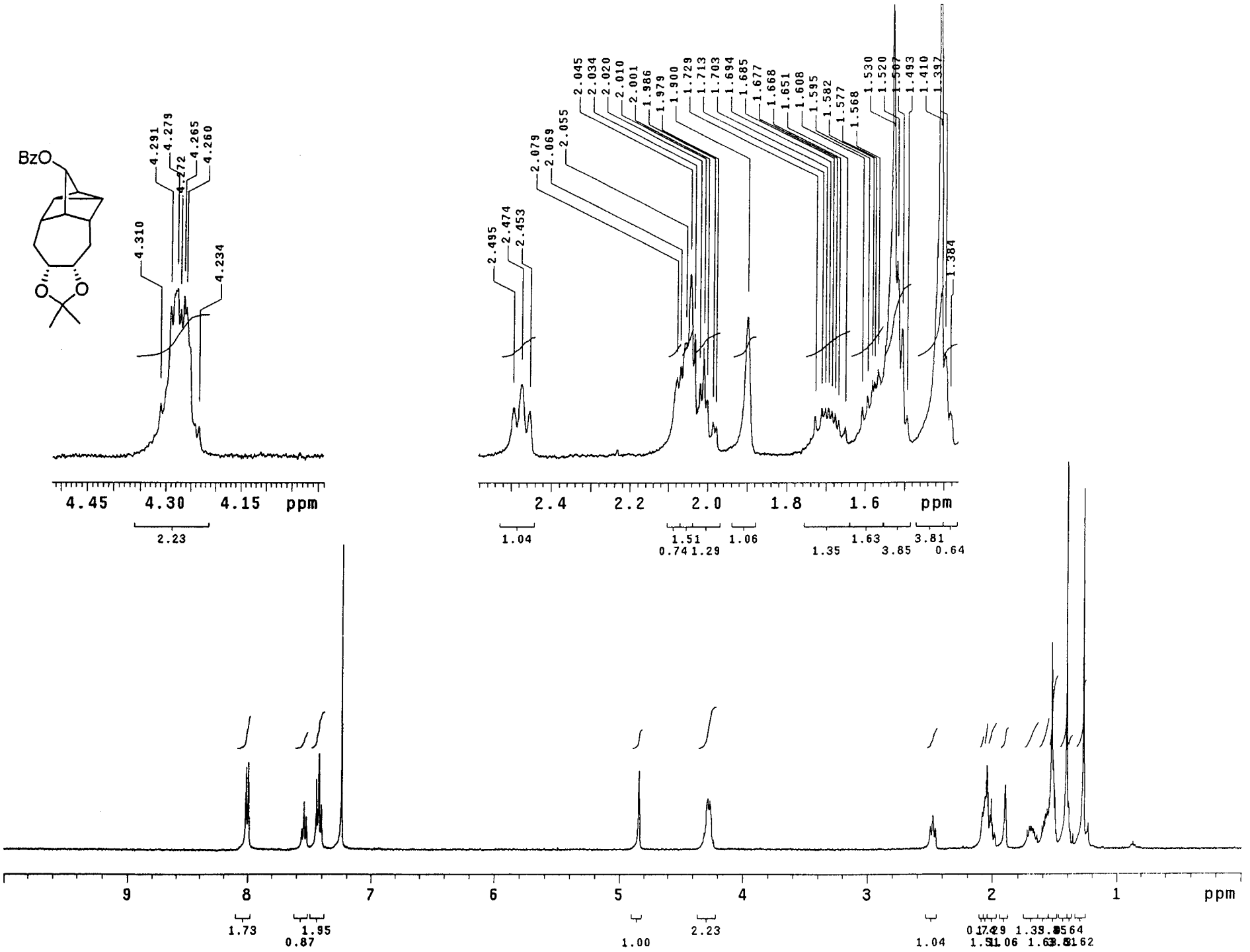

220
200
180
160
140
120
100
80
60
40
20
0 PPM

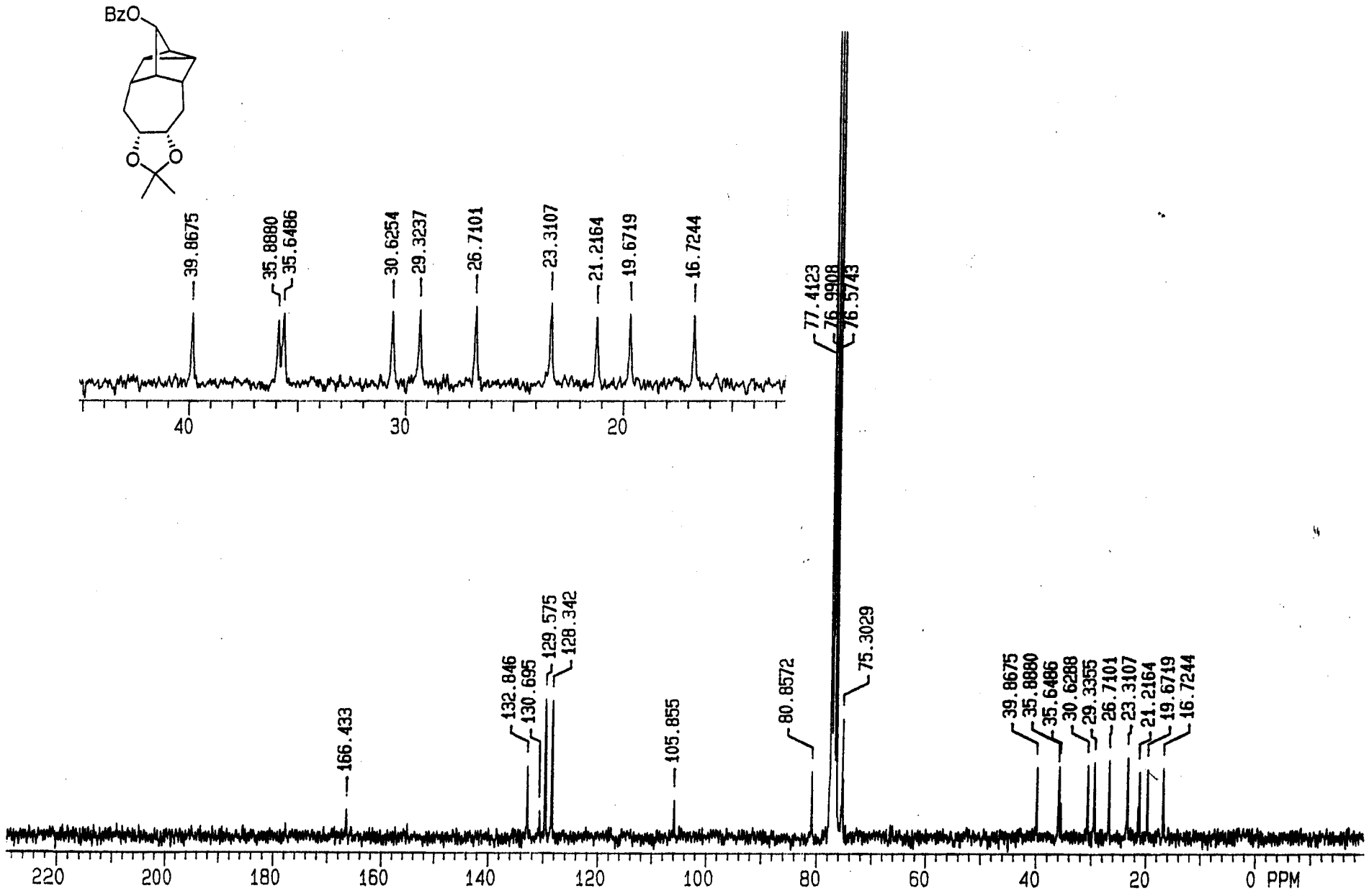

BzO
HO
OH
2.572
2.556
2.163
2.090
2.074
2.047
2.029
1.940
1.915
1.896
1.854
1.564
1.525
1.511
1.496
1.481
1.465
1.453
1.442
2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 ppm
1.02
0.98
2.26
5.30
2.88
3.13


8 7 6 5 4 3 2 ppm
1.78
0.94
1.86
0.99
2.09
1.02
0.98
2.26
5.30
2.88
3.13


BzO
HO
OH

220
200
180
160
140
120
100
80
60
40
20
0 PPM
-20

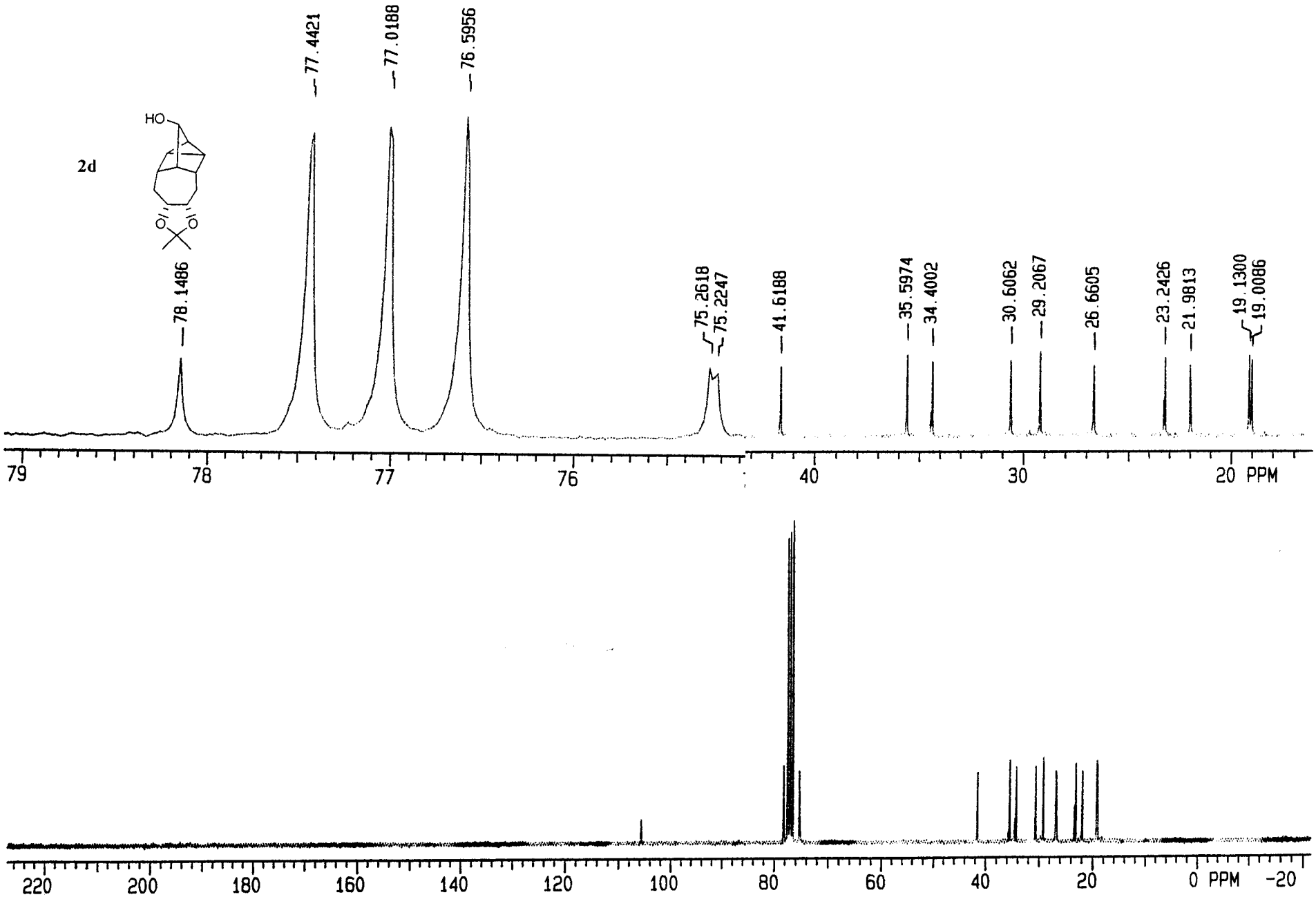

BzO
O
O
4.291
4.279
4.272
4.265
4.260
4.310
4.234
4.45
4.30
4.15
ppm
2.23
2.495
2.474
2.453
2.079
2.069
2.055
2.045
2.034
2.020
2.010
2.001
1.986
1.979
1.900
1.729
1.713
1.703
1.694
1.685
1.677
1.668
1.651
1.608
1.595
1.582
1.577
1.568
1.530
1.520
1.493
1.410
1.392
1.384
2.4
2.2
2.0
1.8
1.6
ppm
1.04
1.51
0.74
1.29
1.06
1.63
1.35
3.85
3.81
0.64
9
8
7
6
5
4
3
2
1
ppm
1.73
1.95
0.87
1.00
2.23
1.04

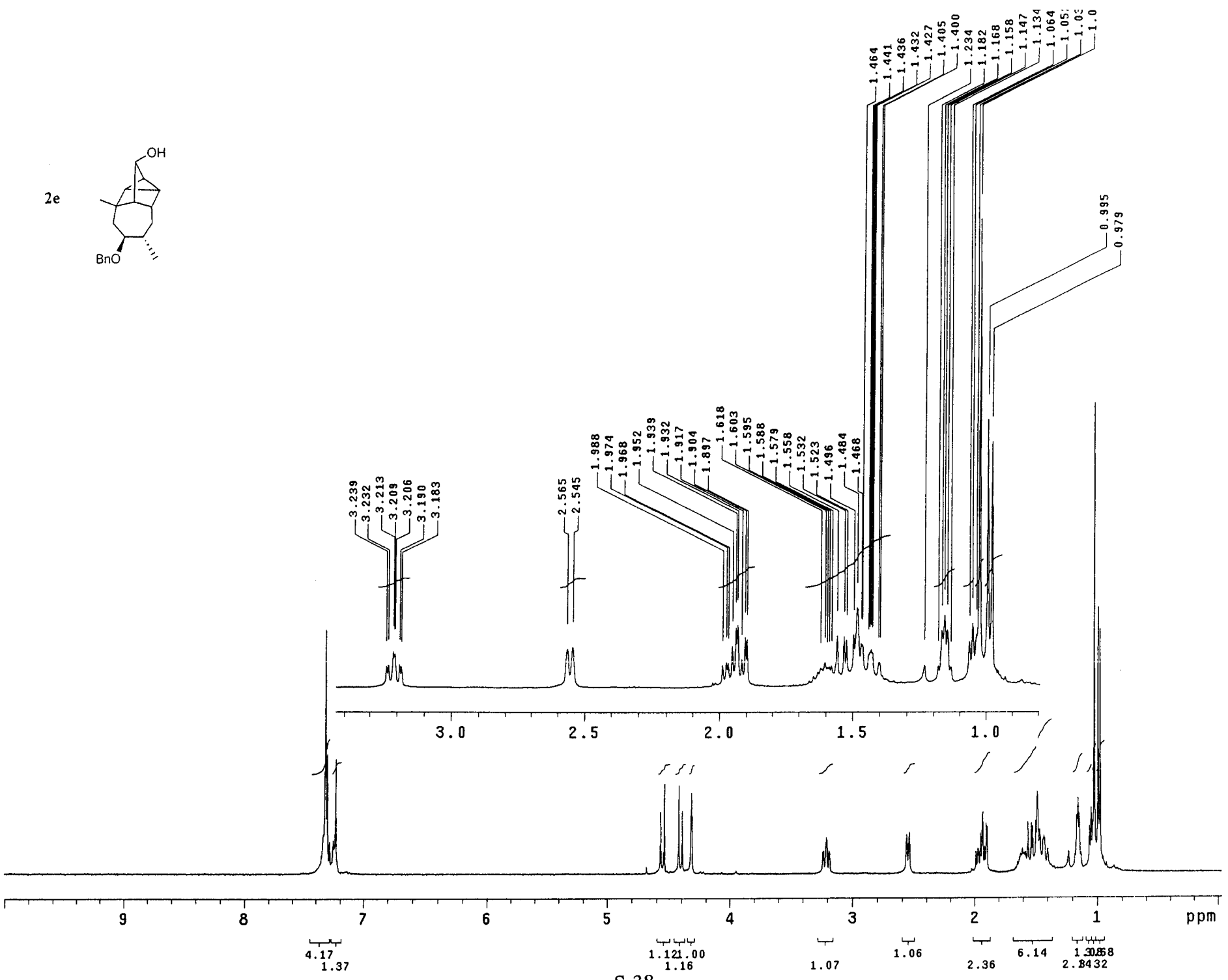

BzO
O
O
39.8675
35.8880
35.6486
30.6254
29.3237
26.7101
23.3107
21.2164
19.6719
16.7244
40
30
20
77.4123
76.9908
76.5743
166.433
132.846
130.695
129.575
128.342
105.855
80.8572
75.3029
39.8675
35.8880
35.6486
30.6288
29.3355
26.7101
23.3107
21.2164
19.6719
16.7244
220
200
180
160
140
120
100
80
60
40
20
0 PPM

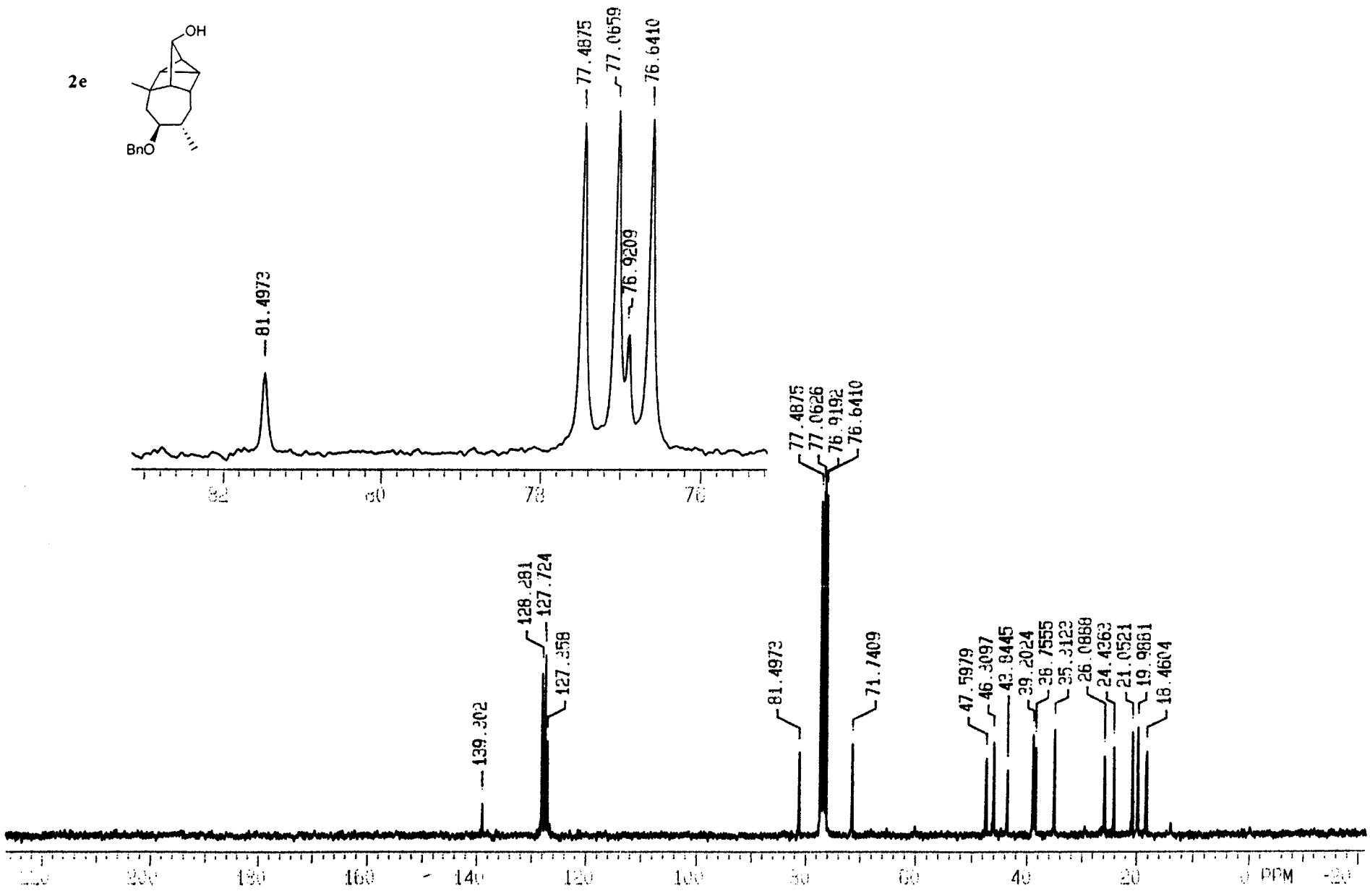
2d


HO
O
O

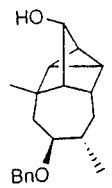
2.393
2.372
2.352
2.087
2.078
2.064
2.053
2.042
2.029
2.019
1.992
1.981
1.968
1.958
1.948
1.934
1.924
1.872
1.856
1.833
1.694
1.677
1.667
1.659
1.650
1.643
1.632
1.615
1.549
1.534
1.522
1.516
1.506
1.499
1.488
1.472
1.403
1.383
1.371
1.315
1.278
1.230
1.137
1.125
1.113
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
ppm
1.03
1.19
1.19
1.10
1.37
5.56
4.14
3.89
1.08
9
8
7
6
5
4
3
2
1
ppm
2.02
0.99
1.03
1.19
1.19
1.10
1.37
5.56
4.14
3.89
1.08

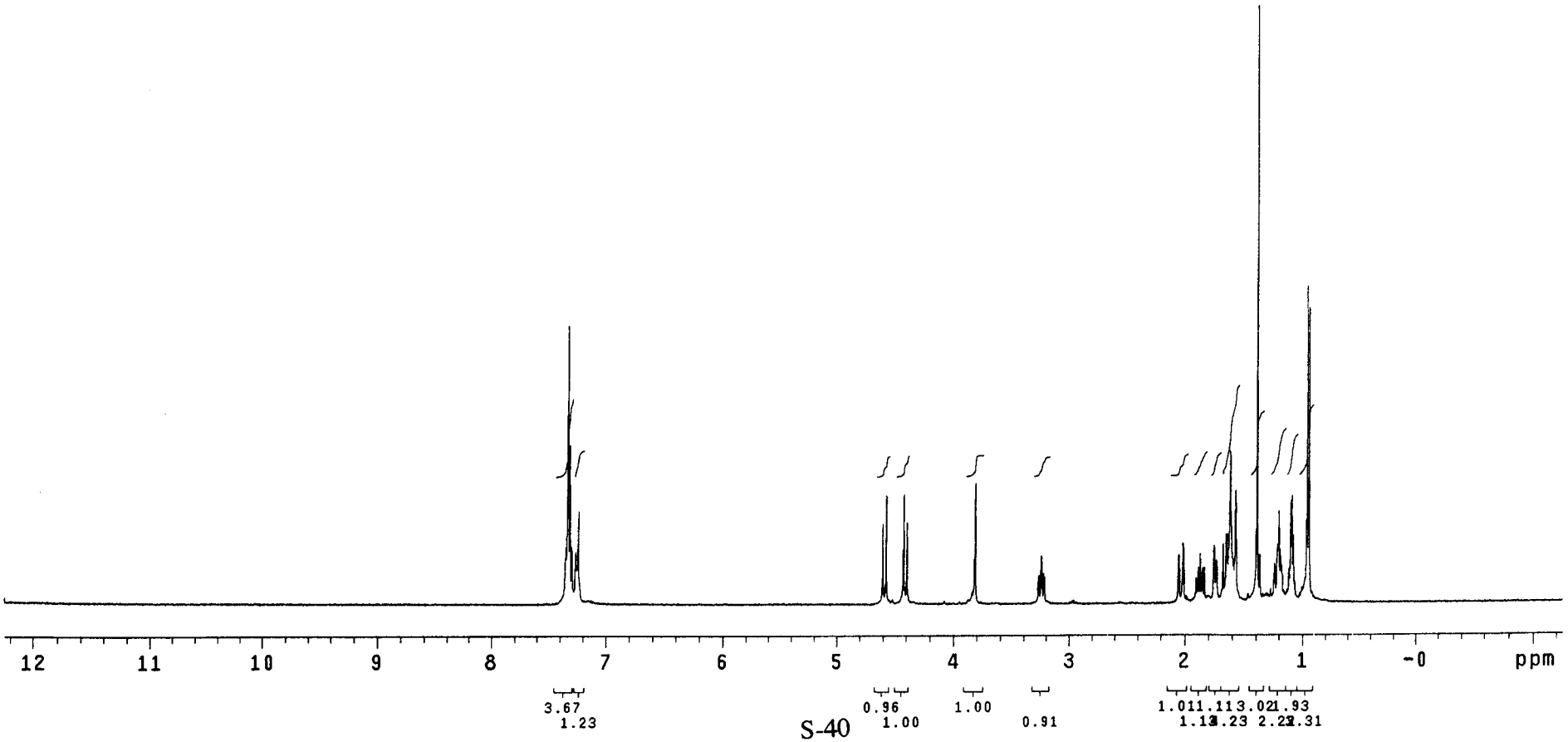

2d
HO
O
O
78.1486
77.4421
77.0188
76.5956
75.2618
75.2247
41.6188
35.5974
34.4002
30.6062
29.2067
26.6605
23.2426
21.9813
19.1300
19.0086
79
78
77
76
40
30
20 PPM
220
200
180
160
140
120
100
80
60
40
20
0 PPM
-20

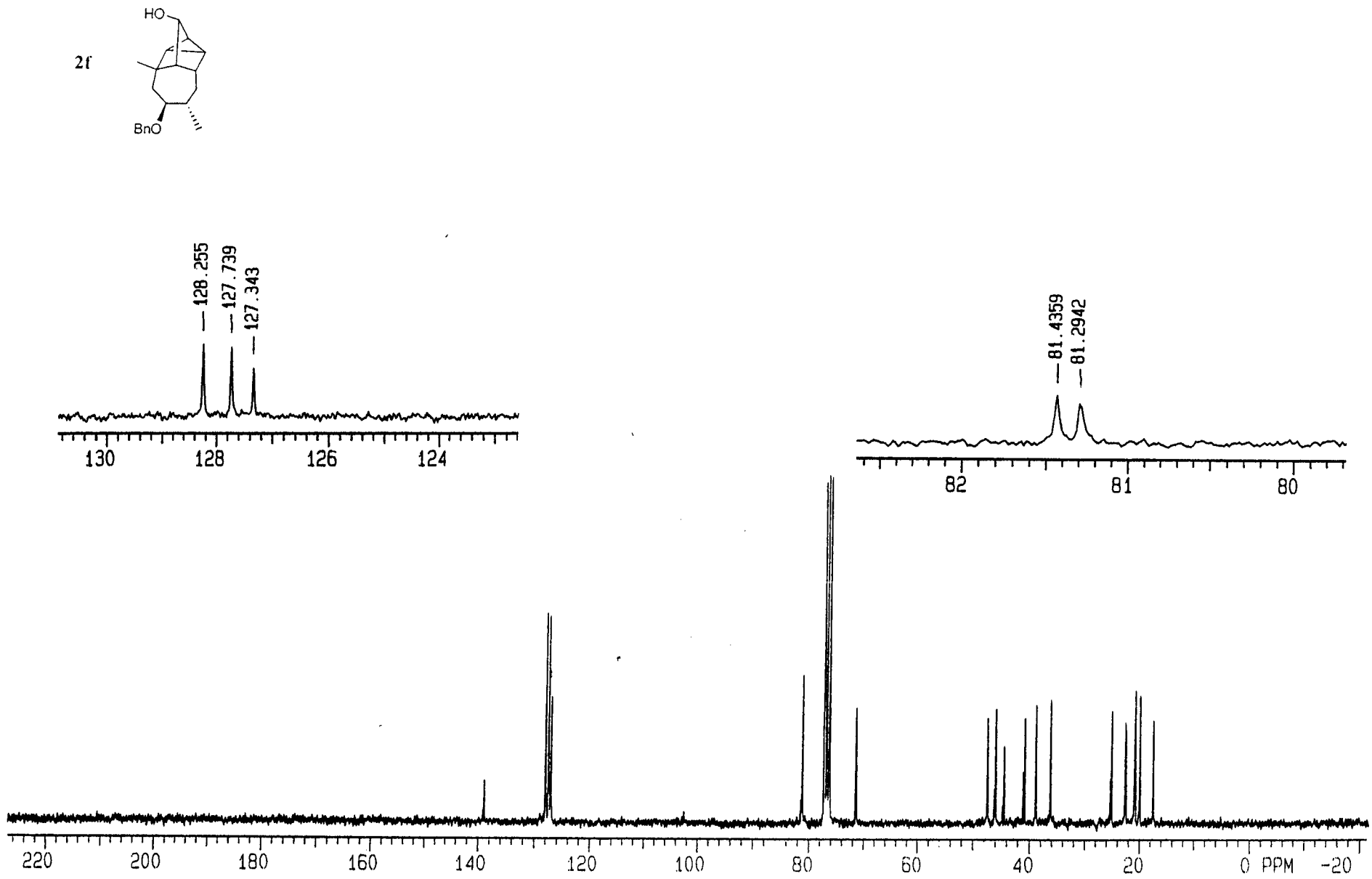

2e
OH
BnO
3.239
3.232
3.213
3.209
3.206
3.190
3.183
2.565
2.545
1.988
1.974
1.968
1.952
1.939
1.932
1.917
1.904
1.897
1.618
1.603
1.595
1.588
1.579
1.558
1.532
1.523
1.496
1.484
1.468
1.464
1.441
1.436
1.432
1.427
1.405
1.400
1.234
1.182
1.168
1.158
1.147
1.134
1.064
0.995
0.979
3.0
2.5
2.0
1.5
1.0
9
8
7
6
5
4
3
2
1
ppm
4.17
1.37
1.12
1.00
1.16
1.07
1.06
2.36
6.14

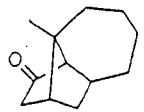

2e
OH
BnO
77.4875
77.0659
76.6410
81.4973
76.9209
77.4875
77.0626
76.9192
76.6410
128.281
127.724
127.358
139.302
81.4973
71.7409
47.5979
46.3097
43.8445
39.2024
36.7555
35.3123
26.0868
24.4363
21.0521
19.9861
18.4604
PPM

2f

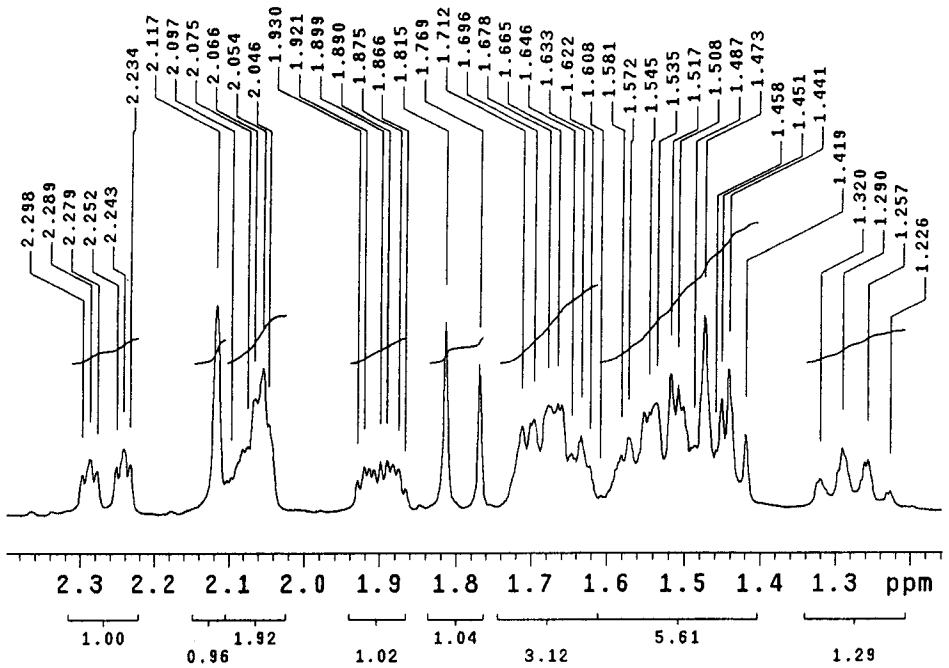

HO
BnO


12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.67
1.23
0.96
1.00
1.00
0.91
1.01
1.11
3.02
1.93
1.31

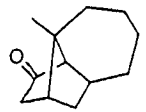

2f
HO
BnO
128.255
127.739
127.343
81.4359
81.2942
130
128
126
124
82
81
80
220
200
180
160
140
120
100
80
60
40
20
0 PPM
-20



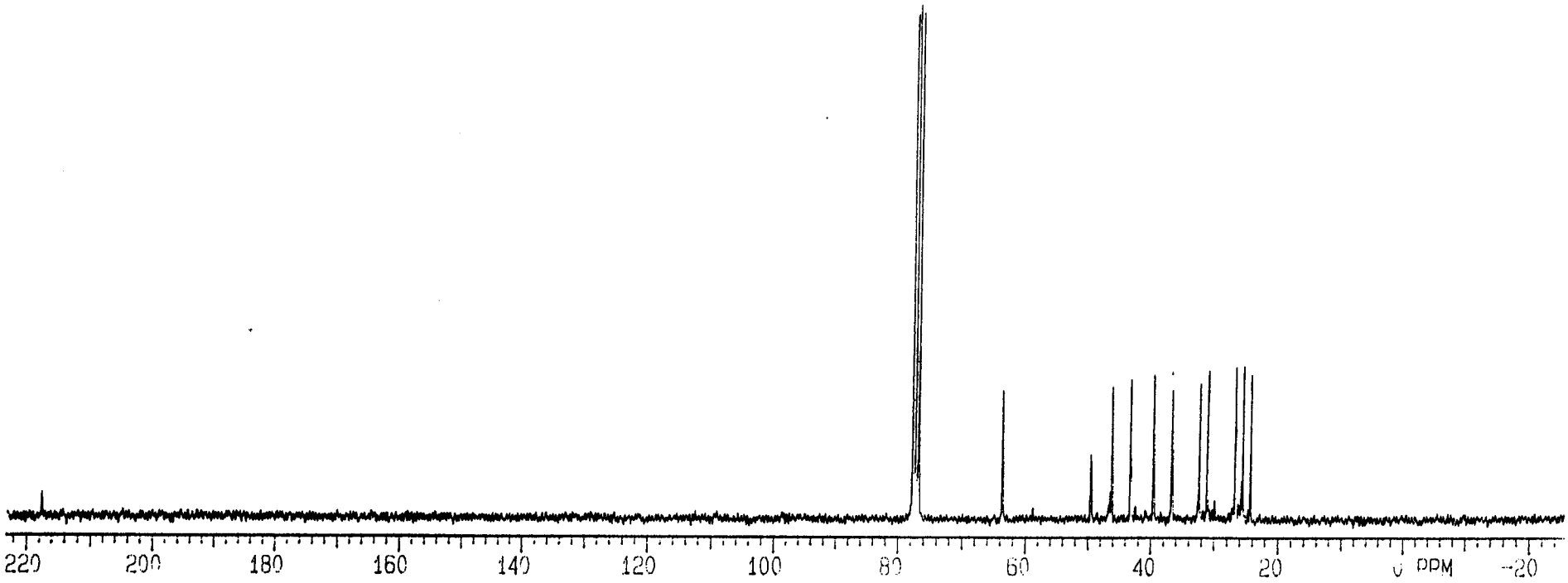
4b

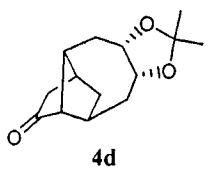

2.298
2.289
2.279
2.252
2.243
2.234
2.117
2.097
2.075
2.066
2.054
2.046
1.930
1.921
1.899
1.890
1.875
1.866
1.815
1.769
1.712
1.696
1.678
1.665
1.646
1.633
1.622
1.608
1.581
1.572
1.545
1.535
1.517
1.508
1.487
1.473
1.458
1.451
1.441
1.419
1.320
1.290
1.257
1.226
2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 ppm
1.00
0.96
1.92
1.02
1.04
3.12
5.61
1.29

10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.96
1.92
1.02
1.04
3.12
5.61
1.29
3.03

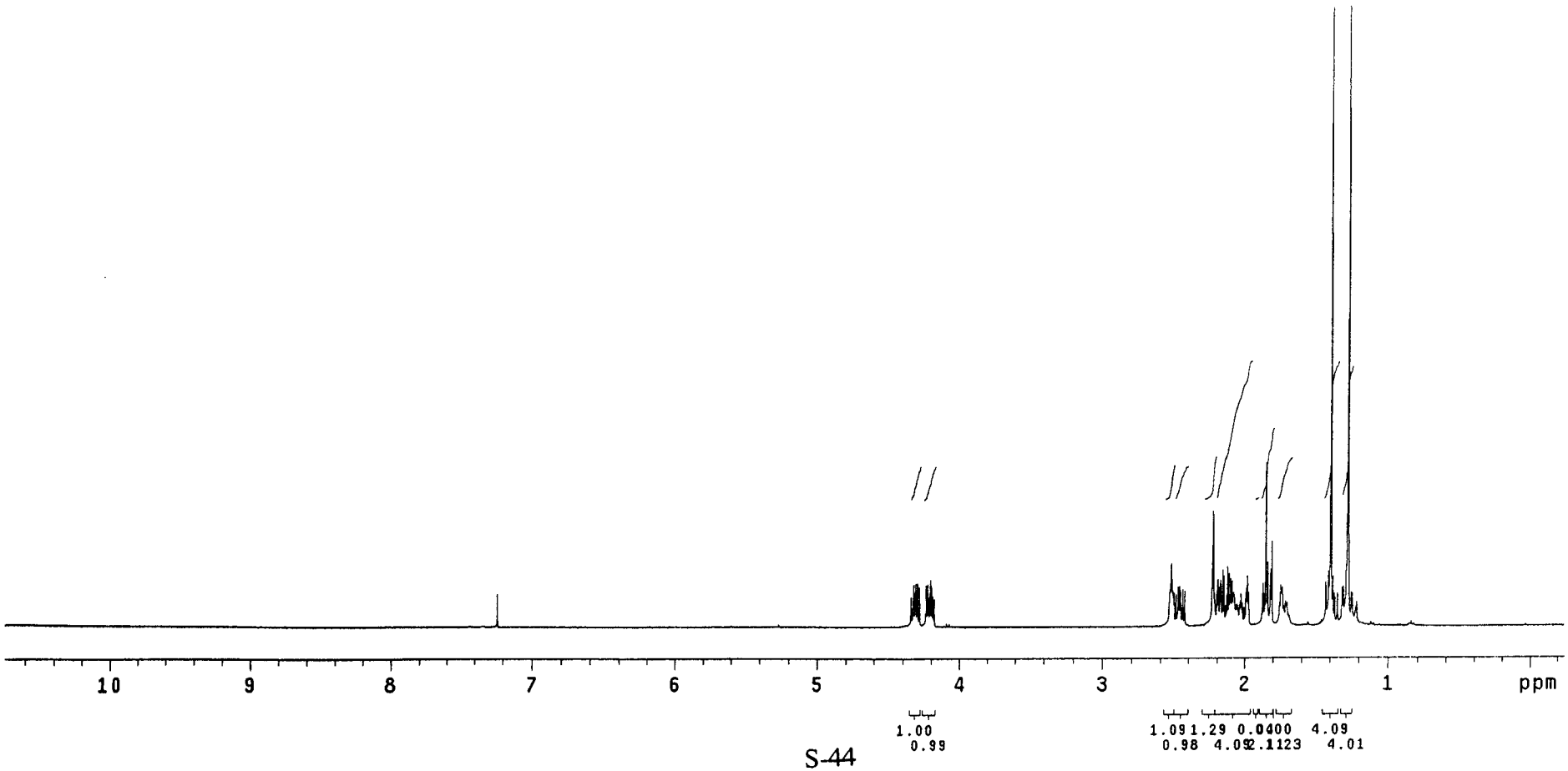


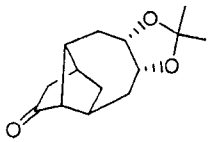
4b



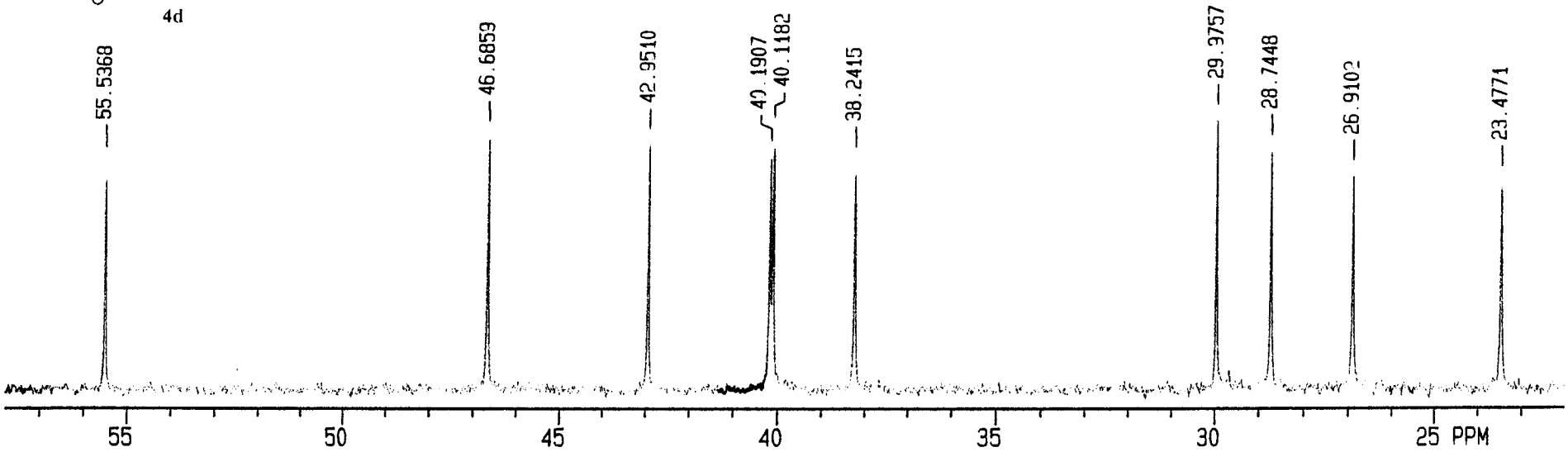


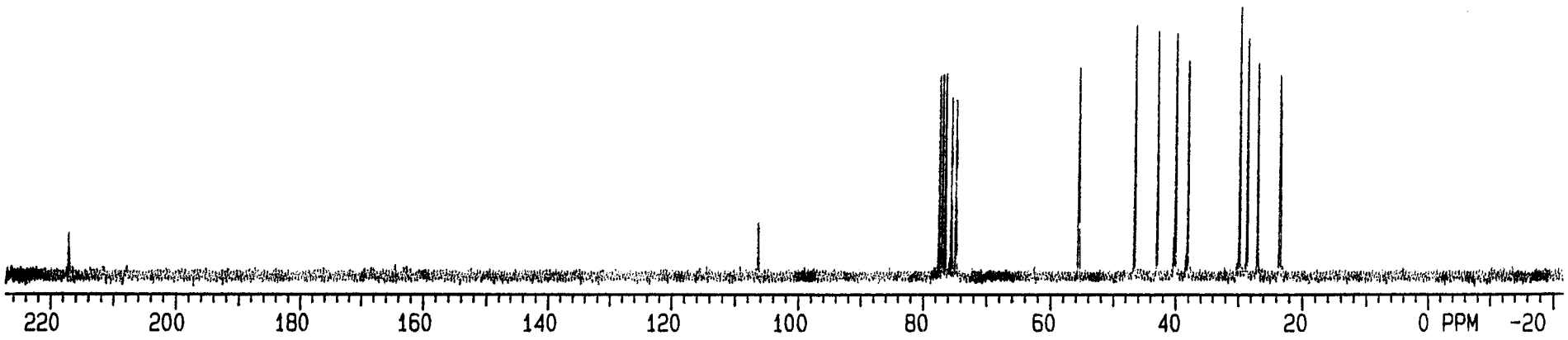
4d

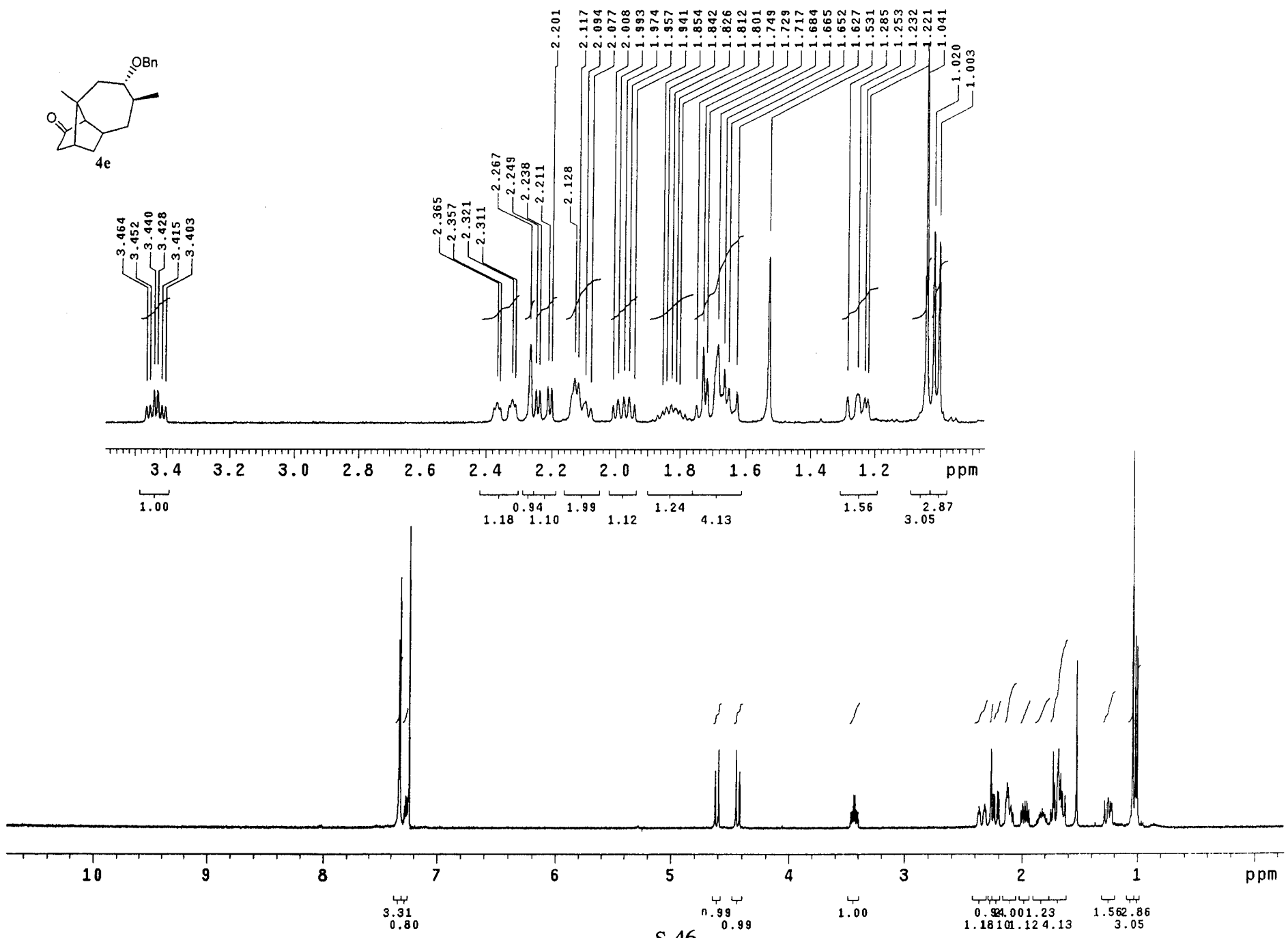




4d


55.5368
46.6859
42.9510
40.1907
40.1182
38.2415
29.9757
28.7448
26.9102
23.4771
55
50
45
40
35
30
25 PPM


220
200
180
160
140
120
100
80
60
40
20
0 PPM
-20


OBn
O
4e
3.464
3.452
3.440
3.428
3.415
3.403
2.365
2.357
2.321
2.311
2.267
2.249
2.238
2.211
2.201
2.128
2.117
2.094
2.077
2.008
1.993
1.974
1.957
1.941
1.854
1.842
1.826
1.812
1.801
1.749
1.729
1.717
1.684
1.665
1.652
1.627
1.531
1.285
1.253
1.232
1.221
1.041
1.020
1.003
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
ppm
1.00
1.18
0.94
1.10
1.99
1.12
1.24
4.13
1.56
2.87
3.05
10
9
8
7
6
5
4
3
2
1
ppm
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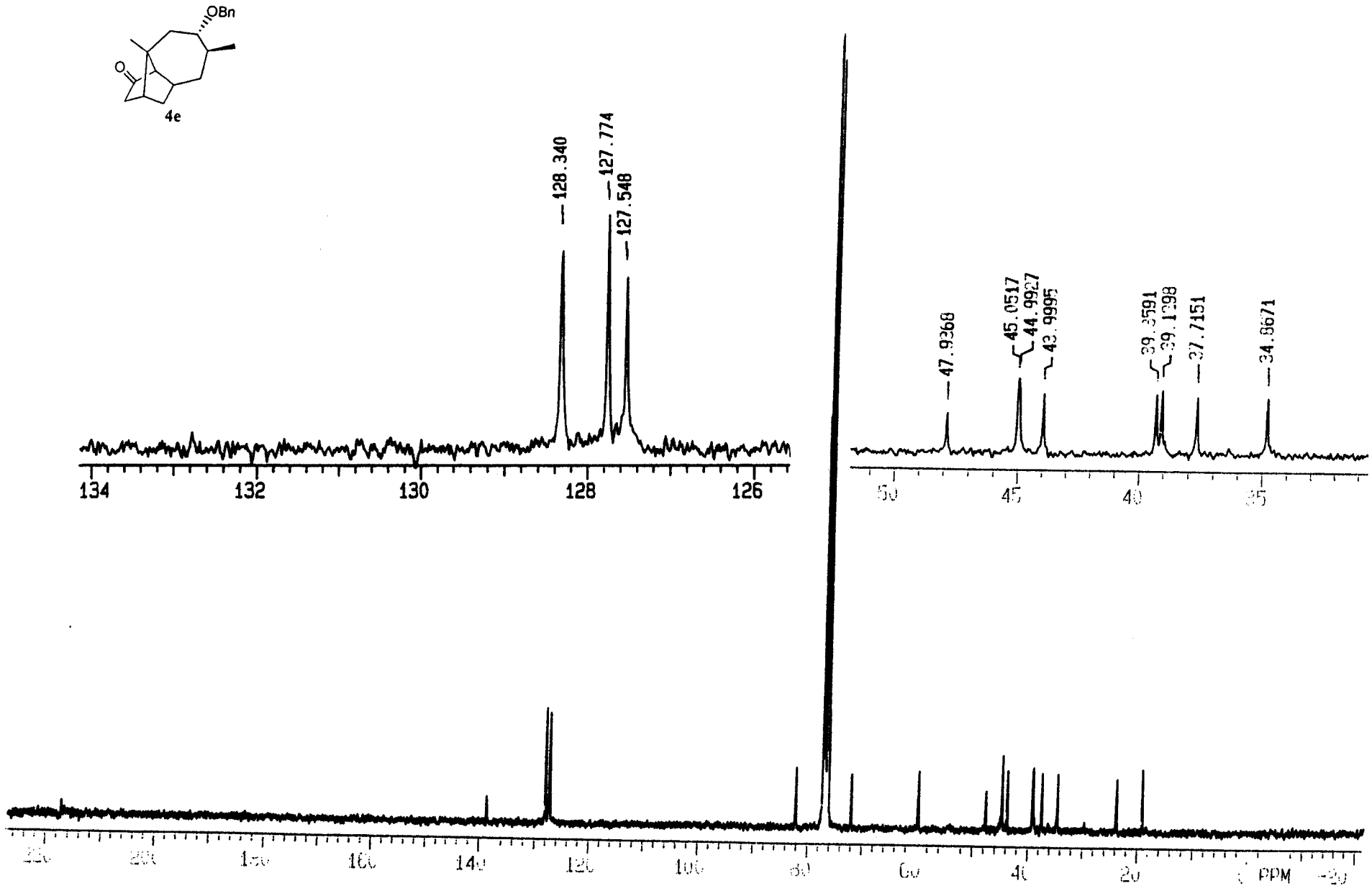
0.99
1.00
1.18
1.12
4.13
1.56
2.86
3.05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O
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134
132
130
128
126
50
45
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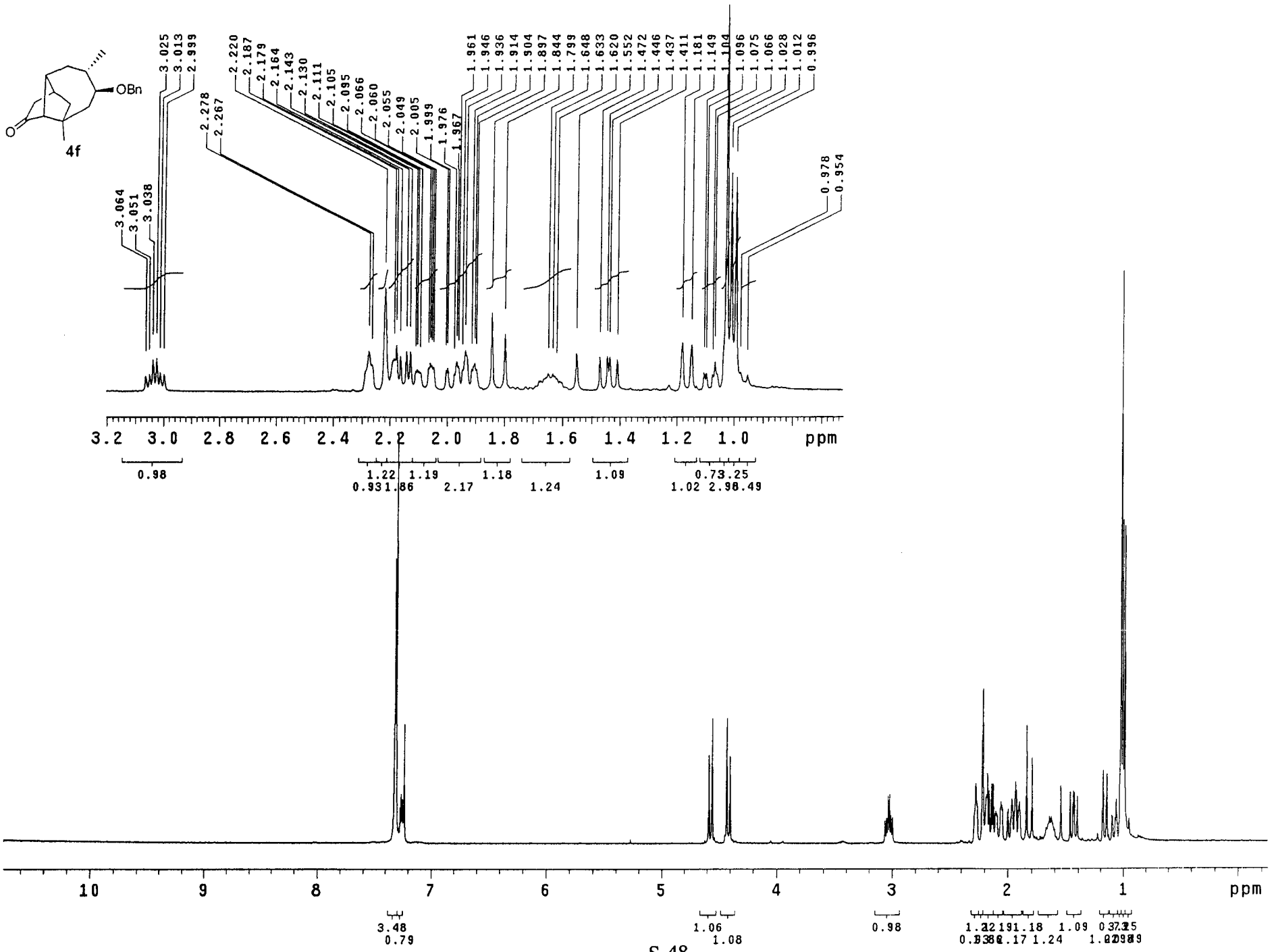
35
PPM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O
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2.267
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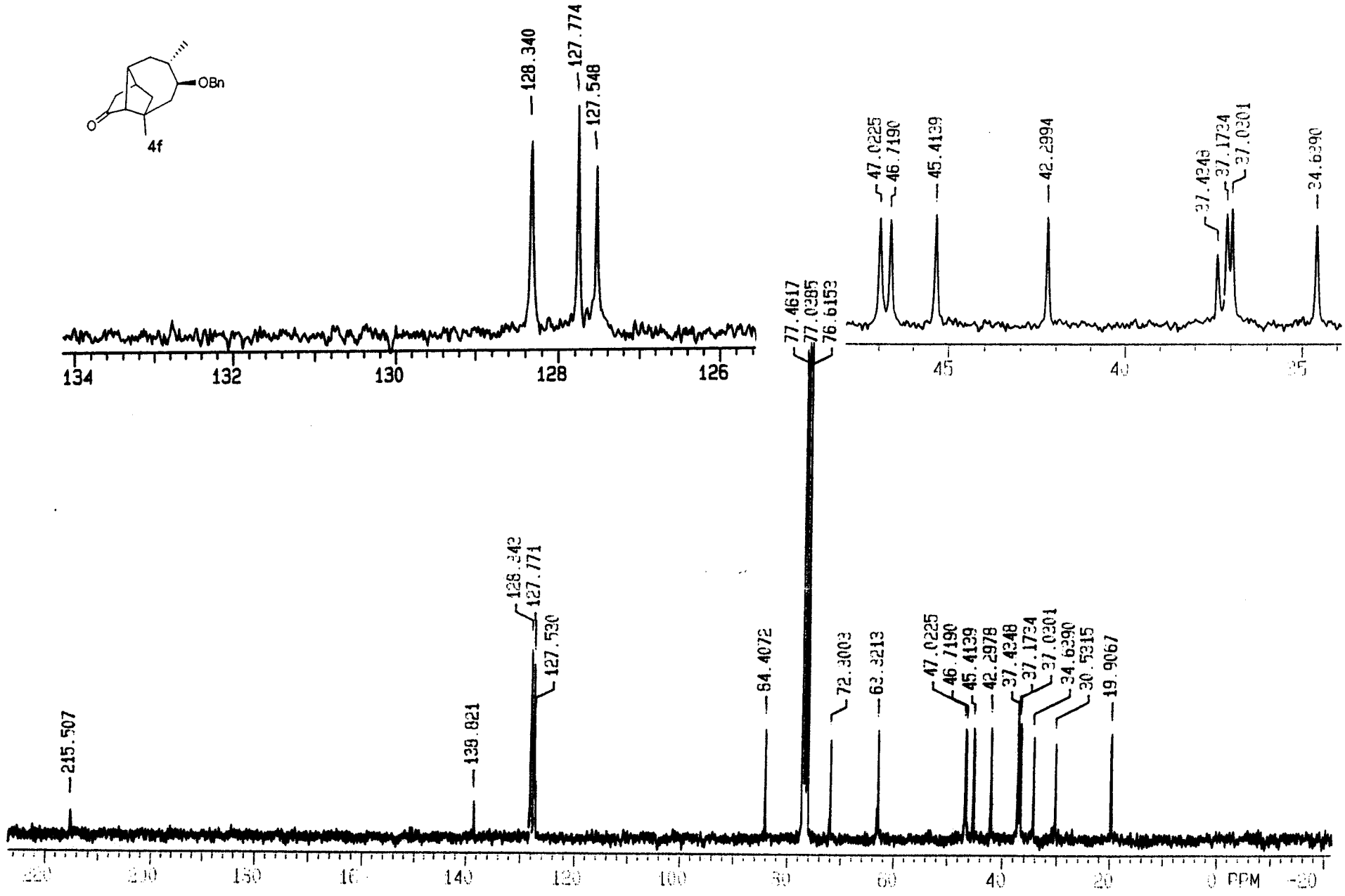
2.143
2.130
2.111
2.105
2.095
2.066
2.060
2.055
2.049
2.005
1.999
1.976
1.967
1.961
1.946
1.936
1.914
1.904
1.897
1.844
1.799
1.648
1.633
1.620
1.552
1.472
1.446
1.437
1.411
1.181
1.149
1.104
1.096
1.075
1.066
1.028
1.012
0.996
0.978
0.954
3.064
3.051
3.038
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 ppm
0.98
1.22 1.19 1.18 1.09 0.73 3.25
0.93 1.86 2.17 1.24 1.02 2.98 4.49
10 9 8 7 6 5 4 3 2 1 ppm
3.48
0.79
1.06
1.08
0.98
1.09
1.24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127.548
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37.4248
37.1734
37.0301
34.6390
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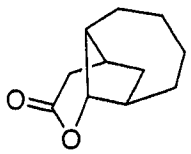
PPM



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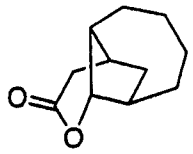

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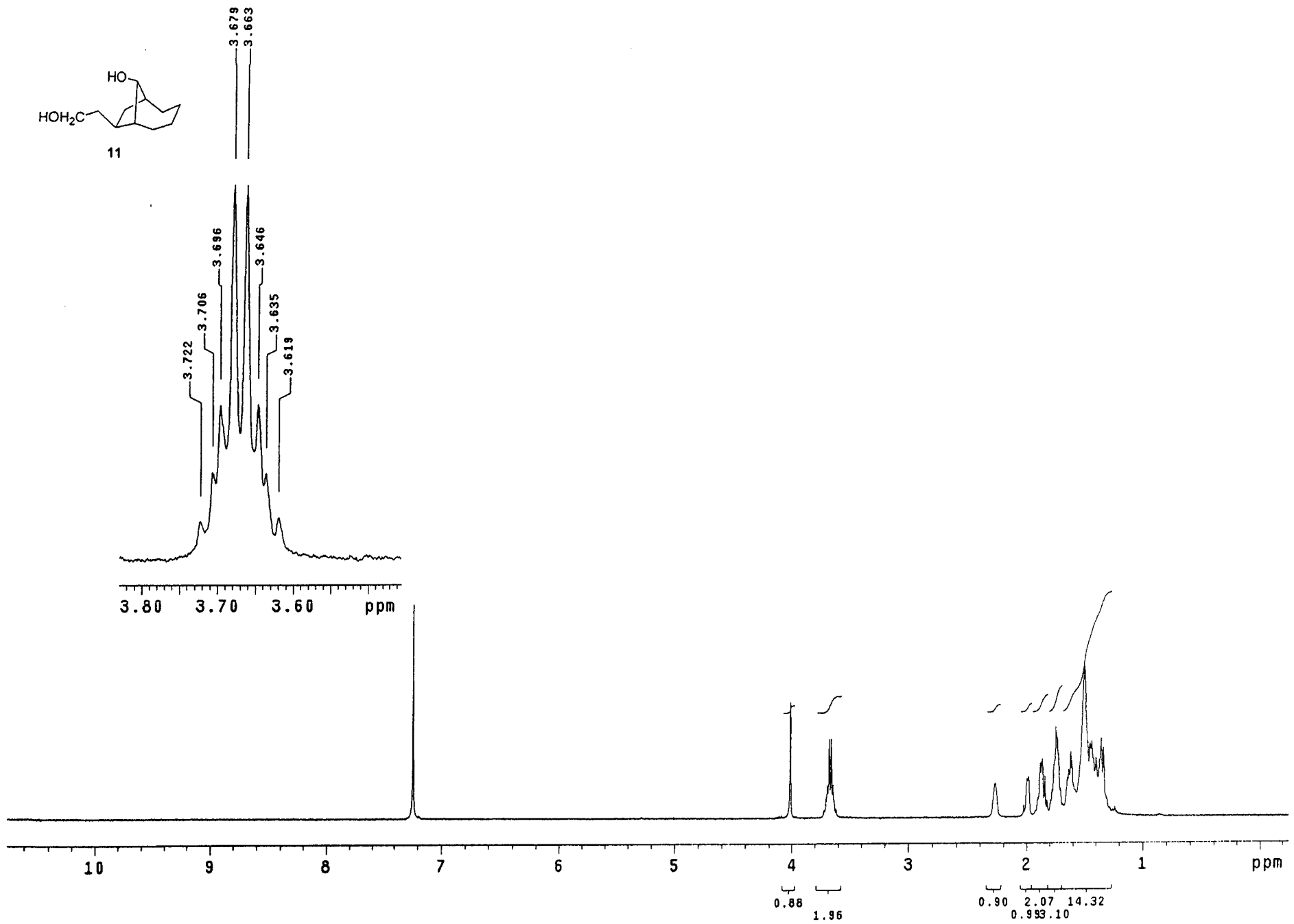
HO
HOH2C
11
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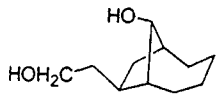
3.663
3.722
3.706
3.696
3.646
3.635
3.619
3.80
3.70
3.60
ppm
10
9
8
7
6
5
4
3
2
1
ppm
0.88
1.96
0.90
2.07
14.32
0.99
3.10



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