General Methodologies Toward *cis*-Fused Quinone Sesquiterpenoids. Enantiospecific Synthesis of the *epi*-Ilimaquinone Core Featuring Sc-Catalyzed Ring Expansion

Hilan Z. Kaplan, Victor L. Rendina, and Jason S. Kingsbury*

Supplementary Materials

Contact information, corresponding author:

Jason S. Kingsbury, Ph.D.
Assistant Professor of Chemistry
Ahmanson Center, California Lutheran University
60 West Olsen Road # 3700
Thousand Oaks, CA 91360

Phone: (805) 493-3026

Email: jkingsbu@callutheran.edu

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General Procedures

Unless stated otherwise, all reactions were carried out in flame-dried glassware under an atmosphere of argon passed through a tower of Drierite in dry and degassed solvents with standard Schlenk or vacuum-line techniques. Particularly air-sensitive manipulations were performed in an MBraun Unilab nitrogen atmosphere glovebox. Column chromatography was driven by compressed air and performed with ZEOPrep 60 Eco 40-63 μm silica gel. Analytical thin-layer chromatography (TLC) was performed with 0.25 mm silica gel 60 F254 plates from EMD Chemicals. TLC plates were visualized under UV light or by treatment with ceric ammonium molybdate, potassium permanganate, and *para*-anisaldehyde stains.

Materials

Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), acetonitrile (CH_3CN), and *N*,*N*-dimethylformamide (DMF) were dispensed under UHP argon from a Glass Contour solvent purification system manufactured by SG Waters, LLC (Nashua, NH). Dimethyl sulfoxide (DMSO), methanol, *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf), *tert*-butyldimethylsilyl chloride (TBSCl), triethylamine (Et_3N), imidazole, D-phenylalanine (D-Phe), pyridinium *p*-toluenesulfonate (PPTS), and chloroform ($CHCl_3$) were purified and dried in accordance with standard procedures.[1] Estrone 3-methylether, phosphorous pentoxide (P_2O_5), sodium borohydride ($NaBH_4$), sodium hydride (NaH), ethanol (EtOH), pyridinium chlorochromate (PCC), platinum(IV) oxide (PtO_2), tetra-*n*-butylammonium fluoride hydrate (TBAF·xH_2O), Celite 545, as well as HPLC-grade pentane, hexanes, and ethyl acetate (EtOAc) used in column chromatography were purchased from Sigma-Aldrich and used without purification. Sodium chloride (NaCl), ammonium chloride (NH_4Cl), sodium bicarbonate ($NaHCO_3$), potassium carbonate (K_2CO_3), sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), sodium thiosulfate ($Na_2S_2O_3$), and magnesium sulfate ($MgSO_4$) were purchased from Fisher Scientific and used without further purification. Methyltriphenylphosphonium iodide was prepared from triphenylphosphine (Sigma-Aldrich), and methyl iodide (Sigma-Aldrich) by stirring in dry benzene for 2 hours, filtering, washing with hexanes, and drying over P_2O_5 before use. Molecular sieves (3Å 4-8 mesh) were purchased from Sigma-Aldrich and activated by drying under vacuum (approx. 30 mm Hg) at 250 °C for at least 6 hours prior to use. Rhodium chloride hydrate ($RhCl_3·H_2O$) was purchased from Pressure Chemical Company and used without further purification.

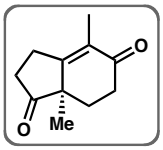
(1) Armarego, W. L. F.; Chai, C. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, 2003.

Dess-Martin Periodinane (DMP) was synthesized in accordance with a reported literature procedure.[2] Scandium triflate ($Sc(OTf)_3$, 99%) was purchased from Sigma-Aldrich, finely powdered, and then dried at 200 °C over P_2O_5 for 24 hours under high vacuum (0.1 mm Hg). The dry scandium triflate was then transported into a glovebox using rigorous Schlenk techniques. (Trimethylsilyl)diazomethane (TMSD) and (phenyldimethylsilyl)diazomethane (PDMSD) were obtained as discussed in the manuscript and stored over 3Å molecular sieves at −40 °C in a glovebox freezer. Note: TMSD is both non-explosive and non-mutagenic, but it is extremely toxic[3] and must be handled with the appropriate precautions.

Instrumentation

Infrared spectra were recorded on a Bruker Alpha-p spectrometer. Bands are reported as strong (s), medium (m), weak (w), broad strong (bs), broad medium (bm), and broad weak (bw). Optical rotation values were recorded on a Rudolph research Autopol IV automatic polarimeter and is reported as the average of five readings. Melting points were recorded on a Digimelt MPA160 SRS and are uncorrected. Sonication was performed with a Misonix Sonicator 3000 equipped with a Laude external circulator for temperature control. ^{1}H NMR spectra were recorded on a Varian VNMRS (500 MHz), INOVA (500 MHz), or VNMRS (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, t = triplet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian VNMRS (125 MHz), INOVA (125 MHz), or VNMRS (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with solvent as the internal reference ($CDCl_3$: δ 77.16). High-resolution mass spectra were obtained at the Boston College Mass Spectrometry Facility. Supercritical fluid chromatography (SFC) data were obtained on a Berger Instruments system using a Daicel CHIRALPAK AS-H column (ϕ 4.6 mm, 25 cm length). Gas chromatography (GC) analysis was performed on an Agilent Technologies 7890A system equipped with a flame ionization detector and HP-5 column (30 m x 0.320 mm x 0.25 μm).

(2) Meyer, S. D.; Schreiber, S. L. Acceleration of the Dess-Martin Oxidation by Water. *J. Org. Chem.* **1994**, *59*, 7549-7552.
(3) Murphy, N. G.; Varney, S. M.; Tallon, J. M.; Thompson, J. R.; Blanc, P. D. Fatal Occupational Exposure to Trimethylsilyl-Diazomethane. *Clin. Toxicol.* **2009**, *47*, 712.



(*R*)-4,7a-Dimethyl-2,3,7,7a-tetrahydro-1*H*-indene-1,5(6*H*)-dione (precursor to **8**). A 40 mL vial (95 mm x 25 mm) equipped with a magnetic stir bar and a rubber septum was charged with 2-methyl-2-(3-oxopentyl)cyclopentane-1,3-dione[4] (2.00 g, 10.2 mmol, 1.00 equiv), D-Phe (505 mg, 3.06 mmol, 0.300 equiv), and PPTS (1.28 g, 5.09 mmol, 0.499 equiv). DMSO (0.73 mL) was added through a syringe, and the resulting suspension was stirred for 5 minutes at room temperature. The vial was then tightly sealed with a Teflon-lined screw cap and sonicated (60 W) continuously at 50 °C for 24 hours. After 20 minutes of sonication at 50 °C, the reaction mixture was observed to be dark yellow and homogeneous. The crude reaction mixture was directly loaded onto a flash column and eluted with 50% Et_2O in pentane (v/v) to furnish the desired product as a colorless oil (1.61 g, 88.6%) with 91% ee (AS-H, 50 °C, 150 psi, 1.0 mL/min, 3% MeOH, λ = 220 nm; t_R = 10.06 min (minor), 10.80 min (major)).

R_f = 0.50 (60% Et_2O in pentane v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.96-2.87 (m, 1H), 2.85-2.73 (m, 2H), 2.60-2.37 (m, 3H), 2.07 (ddd, *J* = 13.4, 5.1, 2.2 Hz, 1H), 1.85 (ddd, *J* = 13.9, 13.9, 5.9 Hz, 1H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 217.74, 197.99, 162.55, 129.95, 48.99, 35.54, 32.92, 28.94, 24.60, 21.38, 10.89; HRMS (ESI+) Calcd. for $C_{11}H_{15}O_2$ $[M+H]^+$: 179.1072; Found 179.1076.

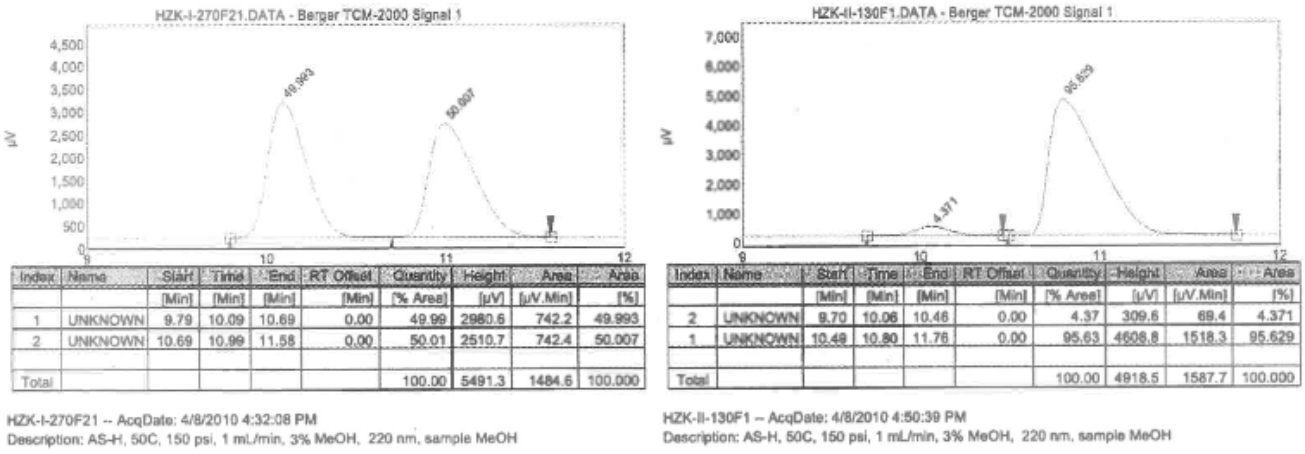
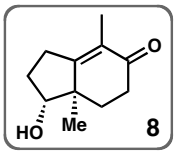


Figure S1. Supercritical fluid chromatography (SFC) trace for Hajos–Parrish ketone.

(4) Hajos, Z. G.; Parrish, D. R. (+)-(7*aS*)-7a-Methyl-2,3,7,7a-tetrahydro-1*H*-indene-1,5-(6*H*)-dione. *Org. Synth.* **1990**, *Coll. Vol. 7*, 363.



(1*R*,7a*R*)-1-Hydroxy-4,7a-dimethyl-2,3,7,7a-tetrahydro-1*H*-inden-5(6*H*)-one (**8**). The Hajos–Parrish ene-dione (3.49 g, 19.6 mmol, 1.00 equiv) was dissolved in 70 mL of EtOH, and the resulting homogeneous solution was cooled to −25 °C. Sodium borohydride (0.233 g, 6.16 mmol, 0.314 equiv) was added directly as a solid and the reaction was closely monitored by TLC. After 20 minutes, the reaction was judged to be complete and was quenched by the addition of saturated aqueous NaCl (30 mL) and H_2O (20 mL). The mixture was transferred to a separatory funnel and the product was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with saturated aqueous NaCl (50 mL), dried over Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (85% Et_2O in pentane v/v) afforded the desired product as a white solid (3.34 g, 94.5%). Enantioenrichment was achieved by a recrystallization from hot Et_2O and hexanes (approx. 3:1 v/v) to afford product **8** in optically pure form (2.14 g, 60.6%, 99% ee). (AS-H, 50 °C, 150 psi, 3.0 mL/min, 3% MeOH, λ = 220 nm; t_R = 16.27 min (major), 18.03 min (minor)).

R_f = 0.38 (60% EtOAc in hexanes v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.83 (ddd, *J* = 13.2, 7.3, 5.9 Hz, 1H), 2.62-2.52 (m, 2H), 2.46-2.36 (m, 2H), 2.19-2.11 (m, 1H), 2.07 (ddd, *J* = 12.7, 5.4, 2.0 Hz, 1H), 1.88-1.74 (m, 2H), 1.66 (dd, *J* = 1.2 Hz, 3H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 198.96, 168.10, 129.09, 81.05, 45.15, 34.11, 33.41, 29.60, 25.76, 15.34, 10.80; HRMS (ESI+) Calcd. for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.1229; Found 181.1220.

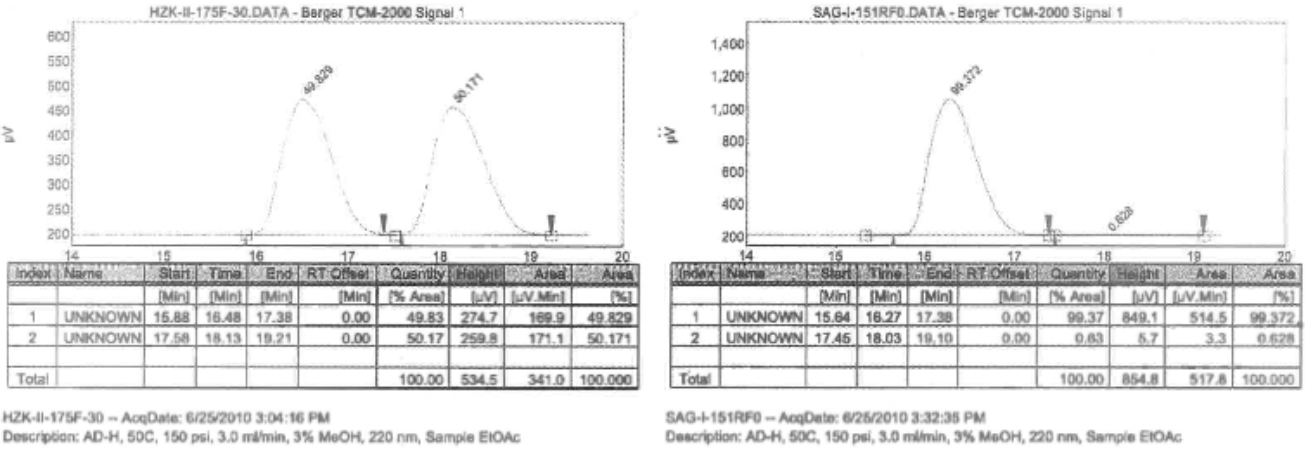
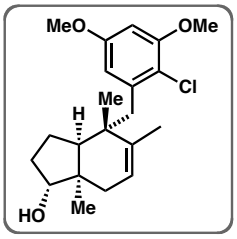
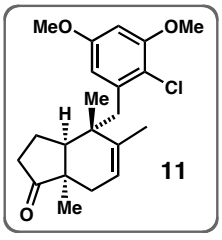


Figure S2. Supercritical fluid chromatography (SFC) trace for tetrahydroindanol **8**.



(1*R*,3a*S*,4*S*,7a*R*)-4-(2-Chloro-3,5-dimethoxybenzyl)-4,5,7a-trimethyl-2,3,3a,4,7,7a-hexahydro-1*H*-inden-1-ol (intermediate precursor to **11**). Exocyclic methylene **10**[5] (1.00 g, 2.09 mmol, 1.00 equiv) and $RhCl_3 \cdot H_2O$ (87.3 mg, 0.417 mmol, 0.200 equiv) were weighed into a 100 mL round bottom flask equipped with a magnetic stir bar and dissolved in 21 mL of $CHCl_3$ and 21 mL of EtOH. The resulting deep red solution was refluxed for a period of 2.5 days, during which time the solution got darker in color and a metallic precipitate formed. The reaction mixture was concentrated, and the crude residue was purified by flash column chromatography (60% Et_2O in pentane v/v) to afford the desired desilylated product as a white solid (749 mg, 98.2%), mp 44–48 °C.

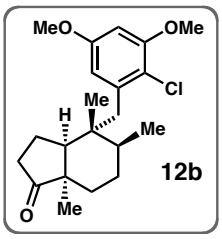
$[\alpha]^{20}_D = -130.65$ (c 0.39, $CHCl_3$); $R_f = 0.36$ (50% Et_2O in pentane v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.45 (d, *J* = 2.7 Hz, 1H), 6.38 (d, *J* = 2.7 Hz, 1H), 5.58-5.62 (m, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.56 (ddd, *J* = 8.8, 6.1, 6.1 Hz, 1H), 3.19 (d, *J* = 12.9 Hz, 1H), 2.75 (d, *J* = 13.2 Hz, 1H), 2.12-1.95 (m, 3H), 1.85 (dddd, *J* = 6.1, 6.1, 6.1, 6.1 Hz, 1H), 1.73-1.66 (m, 1H), 1.46 (s, 3H), 1.42-1.32 (m, 2H), 1.16 (s, 3H), 1.09-0.99 (m, 1H), 0.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.02, 155.65, 141.40, 139.51, 122.22, 116.08, 108.25, 97.96, 82.56, 56.29, 55.95, 55.53, 43.45, 42.90, 39.97, 34.98, 31.60, 26.58, 25.23, 22.14, 21.50; IR (neat) 3407 (bm), 2956 (m), 2873 (m), 1590 (s), 1455 (s), 1329 (m), 1202 (m), 1162 (s), 1118 (m), 1036 (m), 811 (w) cm^{-1}; HRMS (ESI+) Calcd. for $C_{21}H_{30}ClO_3$ $[M+H]^+$: 365.1884; Found 365.1879.



(3a*S*,4*S*,7a*R*)-4-(2-Chloro-3,5-dimethoxybenzyl)-4,5,7a-trimethyl-2,3,3a,4,7,7a-hexahydro-1*H*-inden-1-one (**11**). The endocyclic ene-carbinol (610 mg, 1.67 mmol, 1.00 equiv) and Celite 545 (720 mg) were weighed into a 25 mL round bottom flask equipped with a magnetic stir bar and suspended in 8.4 mL of CH_2Cl_2. PCC (721 mg, 3.34 mmol, 2.00 equiv) was then added directly as a solid, causing a black discoloration, and the mixture was stirred at room temperature for 2 hours. The reaction mixture was then diluted with 50 mL of Et_2O, filtered through Celite 545 on a sintered glass frit, and concentrated. The crude extract was purified by flash column chromatography (25% Et_2O in pentanes v/v) to furnish the desired cyclopentanone **11** as a white solid (561 mg, 92.6%), mp 130–135 °C.

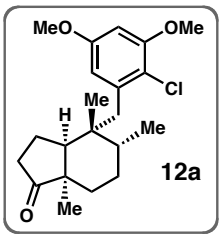
(5) Prepared as previously reported, see: Kaplan, H. Z.; Rendina, V. L.; Kingsbury, J. S. Diastereoselective synthesis of complex *cis*-hexahydroindanes by reductive alkylation. *J. Org. Chem.* **2013**, *78*, 4620-4626.

$[\alpha]^{20}_{D}$ = −99.36 (c 1.68, $CHCl_3$); R_f = 0.29 (20% Et_2O in pentane v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.41 (d, *J* = 2.7 Hz, 1H), 6.40 (d, *J* = 2.7 Hz, 1H), 5.51-5.47 (m, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 3.24 (d, *J* = 13.2 Hz, 1H), 2.80 (d, *J* = 13.2 Hz, 1H), 2.35-2.25 (m, 2H), 2.25-2.15 (m, 2H), 1.99-1.91 (m, 2H), 1.54-1.52 (m, 3H), 1.41-1.32 (m, 4H), 1.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 223.25, 158.10, 155.82, 139.81, 138.97, 120.87, 116.05, 108.61, 97.88, 56.30, 55.54, 53.45, 47.24, 42.34, 40.94, 36.15, 31.39, 26.91, 23.98, 21.51, 21.27; IR (neat) 2964 (m), 2937 (m), 2839 (w), 1737 (s), 1590 (s), 1455 (s), 1330 (m), 1205 (m), 1163 (s), 1086 (m), 1036 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{21}H_{28}ClO_3$ $[M+H]^+$: 363.1727; Found 363.1726.



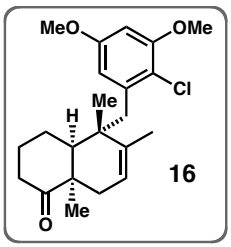
(3a*S*,4*R*,5*S*,7a*R*)-4-(2-Chloro-3,5-dimethoxybenzyl)-4,5,7a-trimethyloctahydro-1*H*-inden-1-one (**12b**). To a solution of racemic trisubstituted enone **11** (18.6 mg, 0.0513 mmol, 1.00 equiv) in 0.30 mL of CH_2Cl_2 at room temperature, PtO_2 (1.2 mg, 0.0051 mmol, 0.10 equiv) was added as a solid. With vigorous stirring, the suspension was purged for 1 minute with hydrogen from a balloon, at which point the brown PtO_2 catalyst turned black, signifying reduction to active Pt(0). The reaction was stirred for 3.5 hours under a positive pressure of hydrogen and then filtered through Celite 545. Upon removal of solvent, ^1H NMR analysis of the crude mixture showed incomplete conversion, so the material was re-subjected to the reaction conditions. Following another 6 hours of stirring under hydrogen, the suspension was again filtered and concentrated. Purification by silica gel chromatography (15% Et_2O, 75% pentane, 10% CH_2Cl_2 v/v/v) gave the desired β-methyl product **12b** as a white solid (12.1 mg, 64.6%), mp 131–133 °C. Single crystals for X-ray diffraction were obtained upon recrystallization from hot Et_2O and hexanes (approx. 5:1 v/v).

R_f = 0.43 (30% Et_2O in pentane v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.42 (d, *J* = 2.9 Hz, 1H), 6.41 (d, *J* = 2.7 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.02 (d, *J* = 13.7 Hz, 1H), 2.63 (d, *J* = 13.7 Hz, 1H), 2.32-2.23 (m, 1H), 2.09-1.97 (m, 3H), 1.88 (d, *J* = 7.6 Hz, 1H) 1.79-1.70 (m, 1H), 1.53-1.45 (m, 1H), 1.33-1.27 (m, 1H), 1.20-1.04 (m, 2H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.93 (s, 3H), 0.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 222.16, 158.01, 155.88, 138.93, 116.17, 108.63, 97.80, 56.33, 55.55, 49.60, 49.39, 42.14, 41.71, 37.07, 34.74, 30.23, 27.81, 27.41, 21.05, 17.37, 15.89; IR (neat) 2961 (m), 2926 (m), 1732 (s), 1589 (s), 1454 (s), 1329 (m), 1202 (s), 1164 (s), 1087 (m), 1038 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{21}H_{30}ClO_3$ $[M+H]^+$: 365.1884; Found 365.1895.



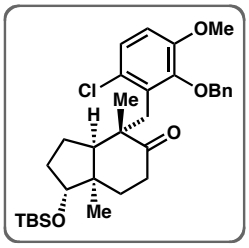
(3a*S*,4*R*,5*R*,7a*R*)-4-(2-Chloro-3,5-dimethoxybenzyl)-4,5,7a-trimethyloctahydro-1*H*-inden-1-one (**12a**). Recovered from the hydrogenation reaction above, the α-methyl diastereomer **12a** was isolated a white solid (6.3 mg, 33.7%), mp 147–149 °C. Single crystals for X-ray diffraction were obtained upon recrystallization from hot Et_2O and hexanes (approx. 5:1 v/v).

R_f = 0.31 (15% Et_2O, 10% CH_2Cl_2 in pentane v/v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.46 (d, *J* = 2.9 Hz, 1H), 6.40 (d, *J* = 2.9 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.07 (d, *J* = 13.4 Hz, 1H), 2.82 (d, *J* = 13.7 Hz, 1H), 2.41 (ddd, *J* = 19.3, 8.5, 2.4 Hz, 1H), 2.28 (ddd, *J* = 10.5, 7.0, 0 Hz, 1H), 2.19-2.10 (m, 1H), 1.87-1.74 (m, 2H), 1.74-1.65 (m, 1H), 1.51 (m, 3H), 1.38 (s, 3H), 1.27-1.21 (m, 1H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 222.87, 158.05, 156.01, 139.90, 116.15, 109.01, 97.26, 56.32, 55.58, 49.76, 48.71, 39.01, 37.49, 35.86, 35.01, 28.95, 26.32, 23.85, 22.18, 20.86, 16.19; IR (neat) 2963 (m), 2877 (m), 1732 (s), 1590 (s), 1455 (s), 1327 (m), 1201 (s), 1162 (s), 1092 (m), 1035 (m), 732 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{21}H_{30}ClO_3$ $[M+H]^+$: 365.1884; Found 365.1885.



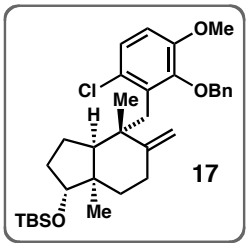
(4a*S*,5*S*,8a*R*)-5-(2-Chloro-3,5-dimethoxybenzyl)-5,6,8a-trimethyl-3,4,4a,5,8,8a-hexahydronaphthalen-1(2*H*)-one (**16**). In a glovebox $Sc(OTf)_3$ (5.2 mg, 0.011 mmol, 0.052 equiv) was weighed directly into a 1.5 mL vial equipped with a magnetic stir bar. A solution of cyclopentanone **11** (76.6 mg, 0.211 mmol, 1.00 equiv) in $CDCl_3$ (0.8 mL) was transferred directly to the solid $Sc(OTf)_3$. The cloudy gray suspension was stirred for 15 minutes, at which point TMSD (215 μL of a 1.96 M solution in hexanes, 0.422 mmol, 2.00 equiv) was added dropwise. The entire reaction mixture (including any residual solids) was transferred via glass pipette to a J. Young NMR tube, and the vial was rinsed with an additional 0.2 mL of $CDCl_3$. The vessel was removed from the glovebox, connected to a nitrogen manifold, and placed in an oil bath at 50 °C. After 16 hours of heating, the reaction was cooled to room temperature. ^{1}H NMR analysis indicated full conversion and an approximately 8.5:1 ratio of regioisomeric enoltrimethylsilane products. The mixture was rinsed from the NMR tube with Et_2O (5 mL) and concentrated to give a yellow oil. The residue was immediately dissolved in 4 mL of 1:1 (v/v) 1N HCl: THF and stirred for 2 hours. That solution was then poured into saturated $NaHCO_3$ (20 mL) and extracted with Et_2O (3 x 20 mL). The organic layer was washed with saturated aqueous NaCl (50 mL), dried over Na_2SO_4, filtered, and concentrated. Purification by chromatography (18% EtOAc in hexanes v/v) gave homologous cyclohexanone **16** (71.1 mg, 88.9%) and a minor amount of the minor regioisomer (8.6 mg, 10.8%) as colorless oils.

$[\alpha]^{20}_{D}$ = +4.12 (c 1.33, $CHCl_3$); R_f = 0.35 (18% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.46 (d, *J* = 2.7 Hz, 1H), 6.39 (d, *J* = 2.7 Hz, 1H), 5.54-5.51 (m, 1H), 3.87 (s, 3H), 3.74 (m, 3H), 3.22 (d, *J* = 14.4 Hz, 1H), 2.83 (d, *J* = 14.4 Hz, 1H), 2.63-2.56 (m , 1H), 2.48-2.44 (m, 1H), 2.12 (ddd, *J* = 8.1, 4.9, 0 Hz, 1H), 2.09-2.03 (m, 1H), 1.93-1.86 (m, 1H), 1.81-1.72 (m, 4H), 1.64-1.53 (m, 2H), 1.34 (s, 3H), 1.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 216.38, 158.10, 155.76, 139.31, 138.47, 121.64, 115.92, 107.47, 97.82, 56.29, 55.52, 49.03, 48.89, 42.66, 40.15, 36.66, 32.58, 26.44, 24.27, 24.05, 23.22, 20.19; IR (neat) 2963 (m), 2940 (m), 1701 (s), 1590 (s), 1454 (s), 1330 (m), 1203 (s), 1163 (s), 1087 (m), 1036 (w), 830 (w) cm^{-1}; HRMS (ESI+) Calcd. for $C_{22}H_{30}ClO_3$ $[M+H]^+$: 377.1884; Found 377.1891.



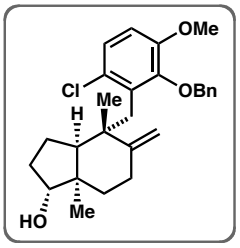
(1*R*,3a*R*,4*S*,7a*R*)-4-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-1-(*tert*-butyldimethylsilyloxy)-4,7a-dimethylhexahydro-1*H*-inden-5(6*H*)-one (precursor to **17**). To a solution of the corresponding keto carbinol[5] (1.03 g, 2.32 mmol, 1.00 equiv) in 12 mL of DMF were added imidazole (474 mg, 6.97 mmol, 3.00 equiv) and TBSCl (1.05 g, 6.97 mmol, 3.00 equiv) sequentially as solids. After 5 hours of stirring at room temperature, 5 mL of MeOH was added and the reaction was stirred for an additional 15 minutes. The reaction mixture was then poured into saturated NH_4Cl (20 mL) and the product was extracted with Et_2O (5 x 10 mL). The organic layer was washed with 1 N HCl (30 mL), H_2O (30 mL), and saturated aqueous NaCl (30 mL) before being dried over Na_2SO_4, filtered, and concentrated to give the target silyl ether as a thick oil that was used without further purification (1.14 g, 88.4%).

$[\alpha]^{20}_{D}$ = −31.95 (c 0.87, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.32 (m, 5H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 9.0 Hz, 1H), 5.02 (d, *J* =11.2 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 3H), 3.66 (dd, *J* = 7.3, 5.9 Hz, 1H), 3.42 (d, *J* = 13.4 Hz, 1H), 2.86 (d, *J* = 13.4 Hz, 1H), 2.61 (ddd, *J* = 17.4, 5.9, 5.9 Hz, 1H), 2.07-1.97 (m, 2H), 1.84-1.77 (m, 1H), 1.77-1.67 (m, 2H), 1.52-1.44 (m, 1H), 1.44-1.36 (m, 1H), 1.10 (s, 3H), 0.91 (s, 9H), 0.80 (s, 3H), 0.03-0.02 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 215.05, 151.19, 147.94, 137.56, 130.67, 128.79, 128.55, 128.32, 127.28, 124.39, 111.91, 80.62, 75.12, 56.89, 56.09, 52.03, 42.41, 37.09, 35.24, 32.13, 32.06, 27.20, 26.01, 25.26, 19.14, 18.24, −4.21, −4.77; IR (neat) 2956 (bs), 2876 (bm), 1705 (s), 1465 (bs), 1377 (bw), 1277 (s), 1214 (m), 1115 (bm), 1060 (s), 981 (bm), 836 (s), 775 (s), 698 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{32}H_{46}ClO_4Si$ $[M+H]^+$: 557.2854; Found 557.2836.



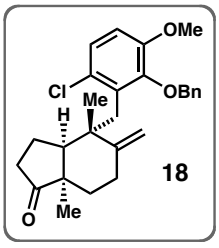
((1*R*,3a*S*,4*S*,7a*R*)-4-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-4,7a-dimethyl-5-methyleneoctahydro-1*H*-inden-1-yloxy)(*tert*-butyl)dimethylsilane (**17**). In a glovebox, NaH (92.6 mg, 3.86 mmol, 7.00 equiv) was added to a 2-neck, 25 mL round bottom flask equipped with a magnetic stir bar. Upon removing the flask from the glovebox, a reflux condenser was installed. DMSO (4.2 mL) was added and the suspension was heated at 75 °C for 1 hour. During this time, the reaction became homogeneous, forming a teal-colored, clear solution. This solution was cooled to ambient temperature and a solution of Ph_3PCH_3I (2.01 g, 4.96 mmol, 9.00 equiv) in 6.8 mL of DMSO was added over 30 minutes via syringe pump. After addition of the salt solution, the reaction mixture turned bright yellow. Upon completion of the addition, the mixture was stirred for an additional 30 minutes at room temperature, at which point a solution of the cyclohexanone (307 mg, 0.551 mmol, 1.00 equiv) in 1.5 mL of DMSO and 1.5 mL of THF was added dropwise. The reaction mixture was then heated to 75 °C and stirred for 16 hours. The resulting amber solution was cooled to room temperature and acidified by the addition of 5 mL of saturated aqueous NH_4Cl. The reaction mixture was then diluted with H_2O (15 mL), transferred to a separatory funnel, and extracted with Et_2O (3 x 20 mL). The organic layer was washed with H_2O (25 mL) and saturated aqueous NaCl (20 mL) before being dried over Na_2SO_4, filtered, and concentrated. Purification by silica gel chromatography (20% Et_2O in pentane v/v) afforded the desired compound **17** as a white solid (296 mg, 96.7%), mp 98–105 °C.

$[\alpha]^{20}_D$ = +15.37 (c 1.05, $CHCl_3$); R_f = 0.33 (3% Et_2O in pentane v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.43-7.29 (m, 5H), 7.04 (d, *J* = 8.8 Hz, 1H) 6.73 (d, *J* = 8.8 Hz, 1H), 4.98-4.81 (m, 2H), 4.75-4.71 (m, 1H), 4.35-4.30 (m, 1H), 3.84 (s, 3H), 3.51 (dd, *J* = 5.9, 2.0 Hz, 1H), 3.36 (d, *J* = 13.2 Hz, 1H), 2.76-2.65 (m, 1H), 2.73 (d, *J* = 12.9 Hz, 1H), 2.05-1.93 (m, 2H), 1.93-1.84 (m, 1H), 1.77-1.68 (m, 1H), 1.43-1.34 (m, 1H), 1.30-1.20 (m, 1H), 1.20-1.09 (m, 2H), 1.14 (s, 3H), 0.92 (s, 9H), 0.82 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.93, 151.25, 148.43, 137.74, 133.02, 128.62, 128.49, 128.10, 127.82, 124.31, 111.03, 110.56, 83.86, 75.02, 56.04, 55.78, 45.67, 43.81, 38.05, 33.26, 31.72, 30.03, 26.65, 26.12, 23.10, 22.71, 18.32, −4.26, −4.69; IR (neat) 2954 (bs), 2933 (bs), 2856 (bm), 1463 (s), 1438 (m), 1371 (bw), 1277 (bm), 1074 (bs), 1006 (m), 836 (s), 740 (m), 697 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{33}H_{48}ClO_3Si$ $[M+H]^+$: 555.3061; Found 555.3084.



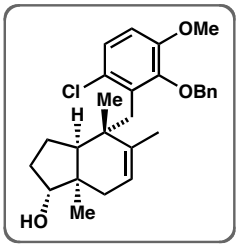
(1*R*,3a*S*,4*S*,7a*R*)-4-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-4,7a-dimethyl-5-methyleneoctahydro-1*H*-inden-1-ol (intermediate precursor to **18**). To a solution of TBS ether **17** (1.27 g, 2.29 mmol, 1.00 equiv) in 5.7 mL of THF was added TBAF·xH_2O (10.5 g, 37.5 mmol, 16.4 equiv) as a solid. The resulting suspension was then sonicated (60 W) continuously at 50 °C for 12 hours, a period shortly into which the reaction mixture became homogeneous. The residue was then directly loaded onto a pad of silica gel and eluted with EtOAc to afford the desired exocyclic ene carbinol as a solid that was used without further purification (1.01 g, quantitative), mp 122–125 °C.

$[\alpha]^{20}_D$ = +34.99 (c 0.96, $CHCl_3$); R_f = 0.48 (50% EtOAc in hexanes v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42-7.30 (m, 5H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 1H), 4.97-4.85 (m, 2H), 4.77-4.74 (m, 1H), 4.37-4.33 (m, 1H), 3.84 (s, 3H), 3.56 (ddd, *J* = 5.6, 4.2, 1.2 Hz, 1H), 3.33 (d, *J* = 12.9 Hz, 1H), 2.75-2.63 (m, 1H), 2.73 (d, *J* = 13.2 Hz, 1H), 2.04-1.92 (m, 3H), 1.81-1.72 (m, 1H), 1.46-1.38 (m, 1H), 1.37-1.27 (m, 2H), 1.20 (s, 3H), 1.19-1.12 (m, 1H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.56, 151.18, 148.45, 137.83, 132.73, 128.53, 128.47, 128.07, 127.77, 124.25, 111.06, 110.79, 83.99, 75.10, 56.02, 55.30, 45.32, 43.56, 37.89, 33.02, 30.71, 29.79, 26.45, 22.60, 21.87; IR (neat) 3377 (bw), 3058 (bw), 2917 (bw), 2848 (bw), 1647 (bw), 1479 (m), 1295 (bm), 1063 (bs), 925 (bm), 737 (s), 688 (bs) cm^{-1}; HRMS (ESI+) Calcd. for $C_{27}H_{34}ClO_3$ $[M+H]^+$: 441.2196; Found 441.2174.



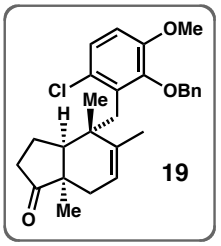
(3a*S*,4*S*,7a*R*)-4-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-4,7a-dimethyl-5-methyleneoctahydro-1*H*-inden-1-one (**18**). The ene cyclopentanol (1.01 g, 2.29 mmol, 1.00 equiv) was weighed into a 50 mL round bottom flask equipped with a magnetic stir bar and dissolved in 23 mL of wet CH_2Cl_2. The solution was cooled to 4 °C and DMP (2.91 g, 6.87 mmol, 3.00 equiv) was added as a solid. The reaction mixture was stirred for 12 hours at 4 °C, at which point additional DMP (2.02 g, 4.58 mmol, 2.00 equiv) and 50 μL of H_2O were added. The reaction was warmed to room temperature and stirred for an additional hour. The mixture was then poured over 100 mL of 1 N NaOH and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography (20% EtOAc in hexanes v/v) afforded cyclopentanone **18** as a white foam (1.00 g, quantitative), mp 95–98 °C.

$[\alpha]^{20}_{D}$ = +11.12 (c 1.17, $CHCl_3$); R_f = 0.27 (20% EtOAc in hexanes v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.30 (m, 5H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 4.98-4.86 (m, 2H), 4.80-4.77 (m, 1H), 4.43-4.39 (m, 1H), 3.86 (s, 3H), 3.34 (d, *J* = 12.9 Hz, 1H), 2.74 (d, *J* = 12.9 Hz, 1H), 2.71-2.60 (m, 1H), 2.38 (dd, *J* = 19.3, 8.5 Hz, 1H), 2.11-1.96 (m, 2H), 1.92-1.81 (m, 2H), 1.52-1.42 (m, 1H), 1.35 (ddd, *J* = 13.4, 13.4, 3.9 Hz, 1H), 1.23 (s, 3H), 1.20-1.12 (m, 1H), 0.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 222.21, 151.19, 150.50, 148.50, 137.64, 132.08, 128.64, 128.54, 128.27, 127.63, 124.34, 111.32, 111.24, 75.30, 57.35, 56.03, 48.82, 43.20, 38.17, 35.51, 30.61, 29.22, 21.81, 21.58, 21.49; IR (neat) 2935 (bm), 2856 (bw), 1734 (s), 1575 (w), 1464 (bs), 1406 (m), 1277 (s), 1234 (bm), 1072 (m), 978 (bm), 896 (bm), 798 (m), 698 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{27}H_{32}ClO_3$ $[M+H]^+$: 439.2040; Found 439.2024.



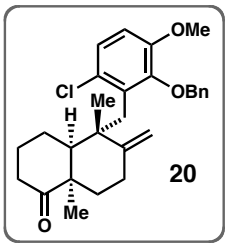
(1*R*,3a*S*,4*S*,7a*R*)-4-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-4,5,7a-trimethyl-2,3,3a,4,7,7a-hexahydro-1*H*-inden-1-ol (intermediate precursor to **19**). The TBS ether **17** (263 mg, 0.473 mmol, 1.00 equiv) and $RhCl_3 \cdot H_2O$ (14.7 mg, 0.0702 mmol, 0.148 equiv) were added to a 5 mL 2-neck round bottom flask equipped with a magnetic stir bar and a reflux condenser. The solids were dissolved in 1.2 mL of EtOH and 1.2 mL of $CHCl_3$, and the resulting deep red solution was heated at 55 °C for 15 hours. The reaction mixture was cooled to ambient temperature and concentrated. The crude residue was purified by column chromatography (25% EtOAc in hexanes) to give the desired alcohol as a colorless oil that was used directly in the next step (208 mg, quantitative).

$[\alpha]^{20}_{D}$ = −103.49 (c 0.85, $CHCl_3$); R_f = 0.38 (30% EtOAc in hexanes v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45-7.41 (m, 2H), 7.39-7.30 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 5.35-5.32 (m, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 3.86 (s, 3H), 3.52 (ddd, *J* = 6.1, 6.1, 0 Hz, 1H), 3.24 (d, *J* = 12.9 Hz, 1H), 2.75 (d, *J* = 12.9 Hz, 1H), 2.07-2.01 (m, 1H), 1.92-1.85 (m, 1H), 1.84-1.76 (m, 2H), 1.67 (dddd, *J* = 15.3, 7.6, 7.6, 2.0 Hz, 1H), 1.47-1.43 (m, 3H), 1.39-1.30 (m, 2H), 1.14 (s, 3H), 1.11-1.02 (m, 1H), 0.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.49, 148.35, 140.37, 137.71, 133.32, 128.45, 128.40, 128.09, 127.78, 124.63, 121.62, 111.00, 82.91, 74.81, 56.01, 55.17, 42.96, 42.51, 36.88, 34.60, 31.52, 26.91, 24.69, 22.15, 21.29; IR (neat) 3389 (bw), 3064 (bw), 2955 (bm), 2873 (bm), 1574 (w), 1464 (bs), 1373 (m), 1276 (s), 1178 (m), 1074 (bm), 981 (bm), 797 (m), 697 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{27}H_{33}ClO_3$ $[M+H]^+$: 441.2196; Found 441.2182.



(3a*S*,4*S*,7a*R*)-4-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-4,5,7a-trimethyl-2,3,3a,4,7,7a-hexahydro-1*H*-inden-1-one (**19**). The cyclopentanol above (208 mg, 0.473 mmol, 1.00 equiv) was weighed into a 10 mL round bottom flask equipped with a magnetic stir bar and dissolved in 4.7 mL of wet CH_2Cl_2. DMP (602 mg, 1.42 mmol, 3.00 equiv) was then added directly as a solid and the reaction mixture was stirred for 1.5 hours at room temperature. The mixture was then poured into 1 N NaOH (20 mL) and washed with CH_2Cl_2 (3 x 10 mL). The pooled organic layers were dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography (12% EtOAc in hexanes v/v) afforded the desired bicyclopentanone **19** as a colorless oil (203 mg, 97.8%, 2 steps).

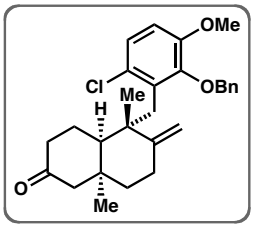
$[\alpha]^{20}_D = -84.42$ (c 0.95, $CHCl_3$); $R_f = 0.33$ (15% EtOAc in hexanes v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.30 (m, 5H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 5.29-5.26 (m, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 3.87 (s, 3H), 3.20 (d, *J* = 13.2, Hz, 1H), 2.77 (d, *J* = 13.0 Hz, 1H), 2.32 (dd, *J* = 18.6, 7.6 Hz, 1H), 2.18 (dd, *J* = 11.7, 6.4 Hz, 1H), 2.13- 2.05 (m, 1H), 2.05-1.98 (m, 1H), 1.91-1.83 (m, 1H), 1.72 (dddd, *J* = 18.1, 2.0, 2.0, 2.0 Hz, 1H), 1.50-1.45 (m, 3H), 1.34 (dddd, *J* = 12.2, 12.2, 12.2, 8.5 Hz, 1H), 1.25 (s, 3H), 0.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 223.13, 151.52, 148.33, 139.33, 137.56, 132.77, 128.51, 128.40, 128.22, 127.75, 124.73, 119.92, 111.18, 74.92, 56.03, 54.11, 47.07, 41.61, 37.68, 36.04, 30.82, 25.03, 23.58, 21.89, 21.05; IR (neat) 2966 (bm), 2935 (bw), 1736 (s), 1464 (bs), 1372 (m), 1277 (s), 1242 (bm), 1076 (m), 984 (bm), 798 (m), 698 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{27}H_{34}ClO_3$ $[M+H]^+$: 439.2040; Found 439.2037.



(4a*S*,5*S*,8a*R*)-5-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-5,8a-dimethyl-6-methyleneoctahydronaphthalen-1(2*H*)-one (**20**). In a glovebox, $Sc(OTf)_3$ (4.2 mg, 0.0086 mmol, 0.050 equiv) was weighed directly into a J. Young NMR tube. A solution of cyclopentanone **18** (75.2 mg, 0.171 mmol, 1.00 equiv) in 0.48 mL of $CDCl_3$ was transferred directly to the solid $Sc(OTf)_3$. The cloudy gray suspension was allowed to stand for 15 minutes, at which point TMSD (174 μL of a 2.47 M solution in hexanes, 0.342 mmol, 2.00 equiv) was introduced dropwise. The NRM tube was removed from the glovebox, connected to a nitrogen manifold, and allowed to stand at room temperature for 12 hours. The reaction mixture was then warmed to 50 °C for 48 hours. ^{1}H NMR analysis indicated 98% conversion and a 5:1 ratio of regioisomeric enoltrimethylsilane products. The mixture was poured into H_2O (5 mL) and extracted with

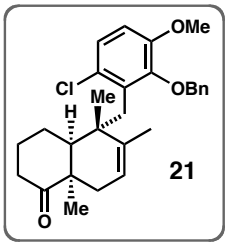
Et_2O (20 mL). The organic layers were washed with saturated aqueous NaCl (10 mL), dried over Na_2SO_4, filtered, and concentrated. The enol silane products were then purified away from trace amounts of starting material by column chromatography (7% EtOAc in hexanes v/v). The flashed product mixture was then dissolved in 2 mL of THF and TBAF·xH_2O (95.8 mg, 0.342 mmol, 2.00 equiv) was added as a solid, at which point the reaction mixture was allowed to stand for 10 minutes at room temperature. The solution was concentrated and purified by column chromatography (15 to 25% EtOAc in hexanes v/v) to give the desired homologous exocyclic ene decalone **20** as a white solid (53.4 mg, 68.8%), mp 88–92 °C.

$[\alpha]^{20}_D$ = +8.23 (c 0.65, $CHCl_3$); R_f = 0.34 (15% EtOAc in hexanes v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.30 (m, 5H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.77-4.74 (m, 1H), 4.46-4.43 (m, 1H), 3.86 (s, 3H), 3.37 (d, *J* = 12.9 Hz, 1H), 2.82 (d, *J* = 12.9 Hz, 1H), 2.63 (ddd, *J* = 13.9, 4.4, 4.4 Hz, 1H), 2.45-2.37 (m, 1H), 2.33-2.26 (m, 1H), 2.12 (ddd, *J* = 14.6, 5.1, 5.1 Hz, 1H), 1.95-1.76 (m, 4H), 1.59-1.49 (m, 1H), 1.38-1.31 (m, 2H), 1.33 (s, 3H), 0.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 216.60, 151.80, 151.31, 148.28, 137.69, 132.98, 128.55, 128.25, 127.59, 124.43, 111.07, 110.30, 75.16, 56.00, 55.82, 50.90, 44.72, 39.92, 37.07, 32.57, 29.70, 24.24, 24.16, 22.82; IR (neat) 3087 (bw), 2938 (bm), 2861 (bm), 1698 (s), 1575 (w), 1462 (s), 1438 (m), 1372 (m), 1276 (s), 1214 (bm), 980 (bm), 798 (m), 698 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{28}H_{34}ClO_3$ $[M+H]^+$: 453.2196; Found 453.2209.



(4a*R*,5*S*,8a*S*)-5-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-5,8a-dimethyl-6-methyleneoctahydronaphthalen-2(1*H*)-one (minor regioisomer in reaction of **18**). This material proved to be a colorless oil (6.5 mg, 8.4%).

$[\alpha]^{20}_D$ = +25.56 (c 0.59, $CHCl_3$); R_f = 0.25 (15% EtOAc in hexanes v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42-7.32 (m, 5H), 7.6 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 5.01 (d, *J* = 10.2, 1H), 5.01 (d, *J* = 10.2 Hz, 1H), 4.89 (d, *J* = 11.2 Hz, 1H), 4.76-4.72 (m, 1H), 4.43-4.39 (m, 1H), 3.86 (s, 3H), 3.38 (d, *J* = 12.9 Hz, 1H), 2.88 (d, *J* = 13.2 Hz, 1H), 2.67-2.58 (m, 1H), 2.24 (d, *J* = 13.9, 1H), 2.24-2.18 (m, 2H), 2.08 (ddd, *J* = 14.6, 4.4, 4.4 Hz, 1H), 2.03-1.96 (m, 1H), 1.97 (d, *J* = 13.7, 1H), 1.76-1.69 (m, 1H), 1.52-1.44 (m, 2H), 1.31-1.24 (m, 1H), 1.18 (s, 3H), 0.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.83, 151.32, 151.06, 148.34, 137.92, 132.92, 128.55, 128.48, 128.19, 127.63, 124.42, 111.14, 110.74, 75.12, 56.20, 56.05, 53.03, 44.95, 40.33, 40.24, 39.50, 34.10, 31.46, 29.98, 26.03, 23.18; IR (neat) 3086 (bw), 2936 (bm), 2853 (bm), 1716 (s), 1464 (s), 1438 (bm), 1373 (bw), 1275 (s), 1215 (bm), 1102 (bm), 985 (bm), 798 (m), 698 (m) cm^{-1}; HRMS (ESI+) Calcd. for $C_{28}H_{34}ClO_3$ $[M+H]^+$: 453.2196; Found 453.2218.



(4a*S*,5*S*,8a*R*)-5-(2-(Benzyloxy)-6-chloro-3-methoxybenzyl)-5,6,8a-trimethyl-3,4,4a,5,8,8a-hexahydronaphthalen-1(2*H*)-one (**21**). In a glovebox, $Sc(OTf)_3$ (6.5 mg, 0.015 mmol, 0.045 equiv) was added directly to a 1.5 mL vial equipped with a magnetic stir bar. A solution of bicyclopentanone **19** (128 mg, 0.292 mmol, 1.00 equiv) in $CDCl_3$ (0.53 mL) was added directly to the solid $Sc(OTf)_3$. The resulting cloudy gray suspension was stirred for 15 minutes, at which point TMSD (236 μL of a 2.47 M solution in hexanes, 0.583 mmol, 2.00 equiv) was added dropwise. The entire reaction mixture (including any residual solids) was then transferred via a glass pipette to a J. Young NMR tube, and the vial was rinsed with 0.2 mL of $CDCl_3$. The reaction tube was removed from the glovebox, connected to a nitrogen manifold, and submerged in an oil bath heated to 50 °C. After 16 hours of heating, the reaction was cooled to room temperature. ^{1}H NMR analysis indicated complete consumption of **19**. The reaction mixture was poured into H_2O (5 mL) and extracted with Et_2O (20 mL). The pooled organic layers were washed with saturated aqueous NaCl (10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was then dissolved in 2 mL of THF and after TBAF·xH_2O (164 mg, 0.584 mmol, 2.00 equiv) was added as a solid, the reaction mixture was allowed to stir for 10 minutes at 23 °C. The solution was concentrated and purified by chromatography (15% EtOAc in hexanes v/v) to give the desired homologous trisubstituted ene-decalone **21** as a colorless oil (124 mg, 93.4%).

$[\alpha]^{20}_D$ = −32.35 (c 0.83, $CHCl_3$); R_f = 0.57 (30% EtOAc in hexanes v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42-7.39 (m, 2H), 7.38-7.30 (m, 3H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 5.36-5.32 (m, 1H), 4.96 (d, *J* = 10.7 Hz, 1H), 4.88 (d, *J* = 10.7 Hz, 1H), 3.88 (s, 3H), 3.14 (d, *J* = 13.7 Hz, 1H), 2.99 (d, *J* = 13.9 Hz, 1H), 2.50 (ddd, *J* = 14.6, 12.6, 6.8, 1H), 2.46-2.40 (m, 1H), 2.39-2.35 (m, 1H), 2.27-2.21 (m, 1H), 1.93-1.86 (m, 1H), 1.78-1.72 (m, 1H), 1.68-1.66 (m, 3H), 1.64-1.58 (m, 1H), 1.35 (s, 3H), 1.34-1.18 (m, 2H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 216.42, 151.57, 148.21, 139.89, 137.28, 133.52, 128.72, 128.56, 128.29, 127.58, 124.82, 119.27, 111.02, 74.83, 55.97, 51.23, 49.70, 42.12, 37.94, 37.23, 32.88, 24.73, 24.47, 23.74, 20.49; IR (neat) 3030 (bw), 2955 (bm), 2861 (bm), 1698 (s), 1574 (m), 1462 (bs), 1371 (m), 1276 (s), 1214 (bm), 1080 (bs), 979 (bs), 924 (bm), 797 (s), 732 (s), 697 (s) cm^{-1}; HRMS (ESI+) Calcd. for $C_{28}H_{34}ClO_3$ $[M+H]^+$: 453.2196; Found 453.2210.

Sample Name:
VR-IV-014Fa
Archive directory:

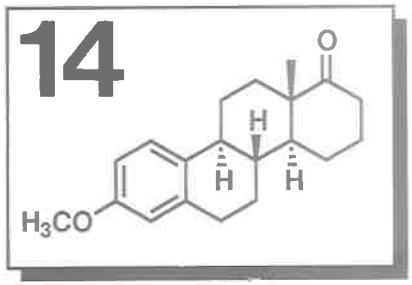
Sample directory:

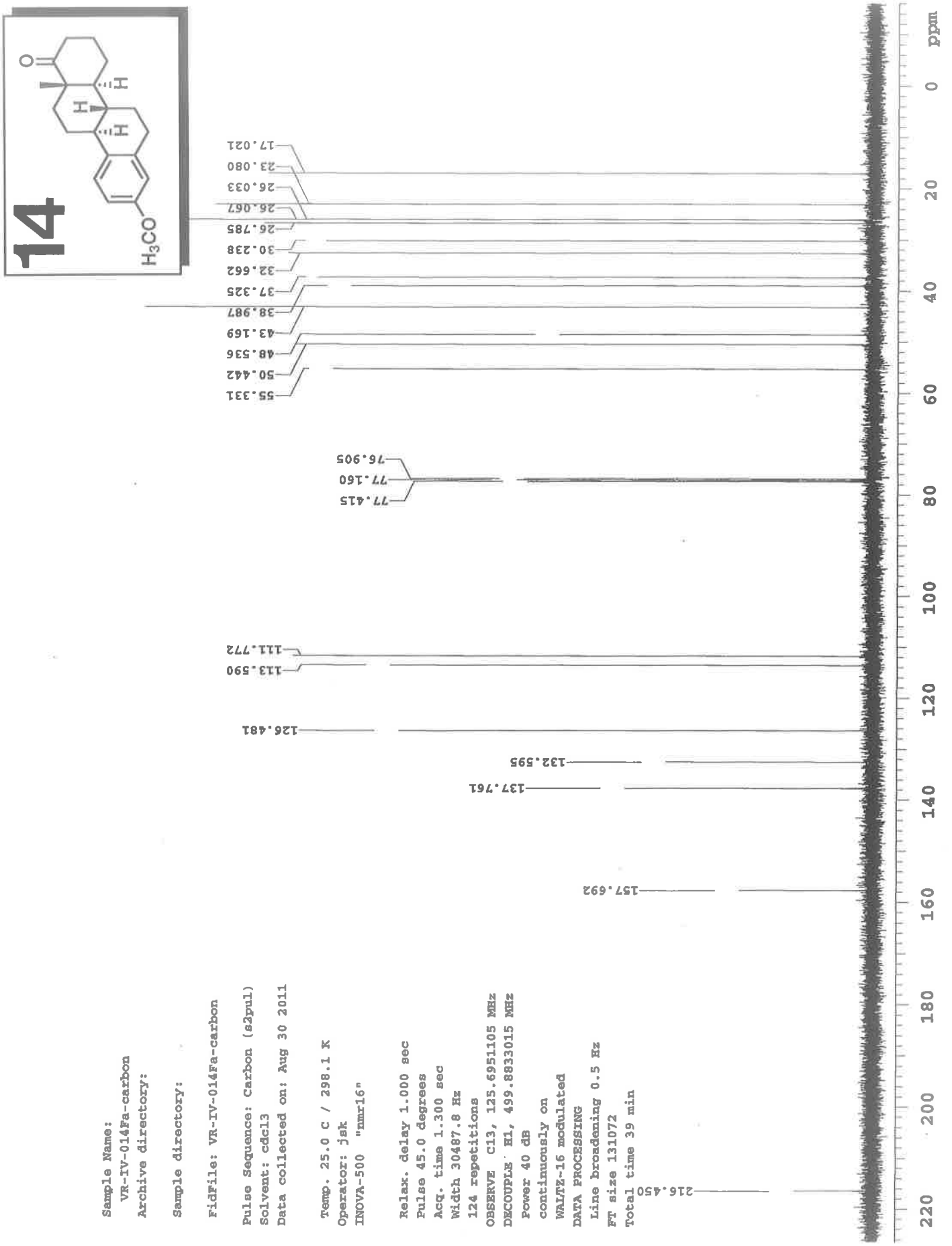
FidFile: VR-IV-014Fa

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Aug 30 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
9 repetitions
OBSERVE H1, 499.8808016 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 37 sec




14
H_3CO
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23.080
26.033
26.067
26.785
30.238
32.662
37.325
38.987
43.169
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50.442
55.331
76.905
77.160
77.415
111.772
113.590
126.481
132.595
137.761
157.692
216.450
ppm
0
20
40
60
80
100
120
140
160
180
200
220
Sample Name:
VR-IV-014Fa-carbon
Archive directory:
Sample directory:
FidFile: VR-IV-014Fa-carbon
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Aug 30 2011
Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30487.8 Hz
124 repetitions
OBSERVE C13, 125.6951105 MHz
DECOUPLE H1, 499.8833015 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 39 min

Sample Name:
VR-IV-014Fb
Archive directory:

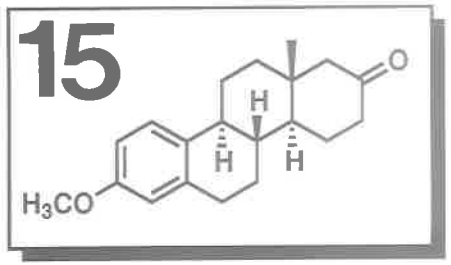
Sample directory:

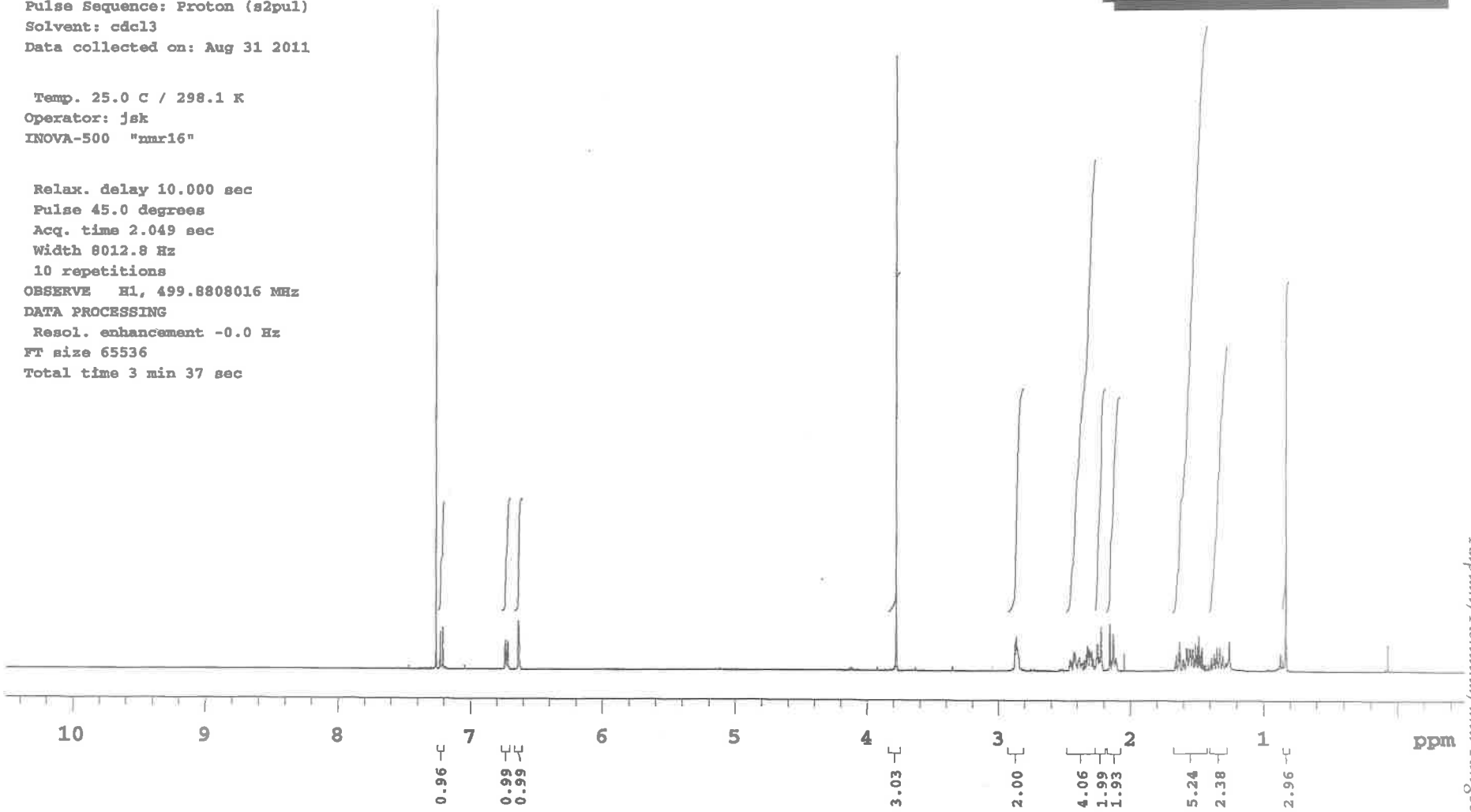
FidFile: VR-IV-014Fb

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Aug 31 2011

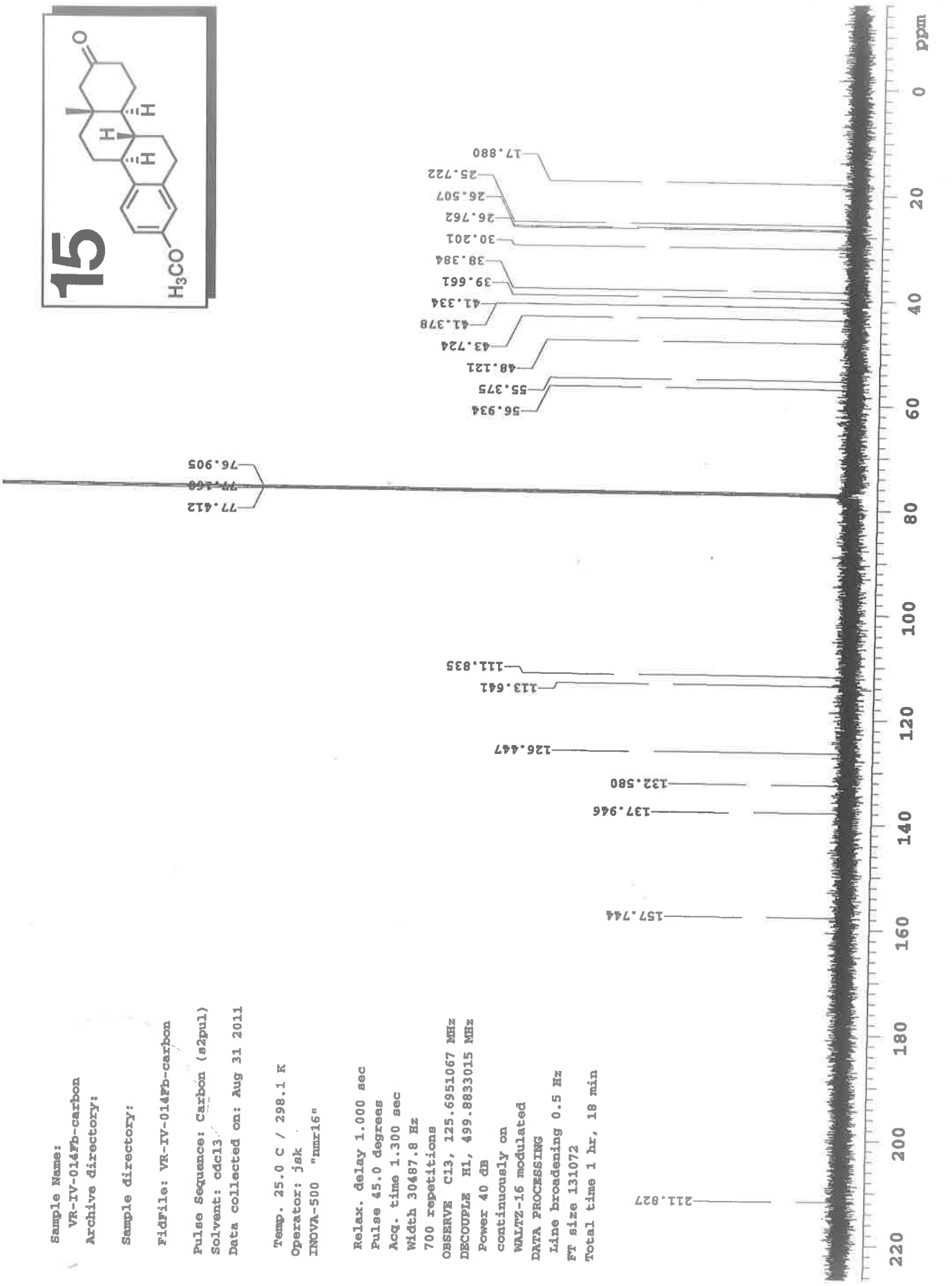
Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
10 repetitions
OBSERVE H1, 499.8808016 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 37 sec





*Kaplan, Rendina, and Kingsbury**



Sample Name:
VR-IV-014Fb-carbon
Archive directory:

Sample directory:

FidFile: VR-IV-014Fb-carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Aug 31 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30487.8 Hz
700 repetitions
OBSERVE C13, 125.6951067 MHz
DECOUPLE H1, 499.8833015 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 18 min

Sample Name:
HZK-II-144F
Archive directory:

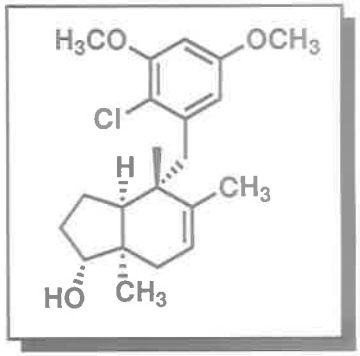
Sample directory:

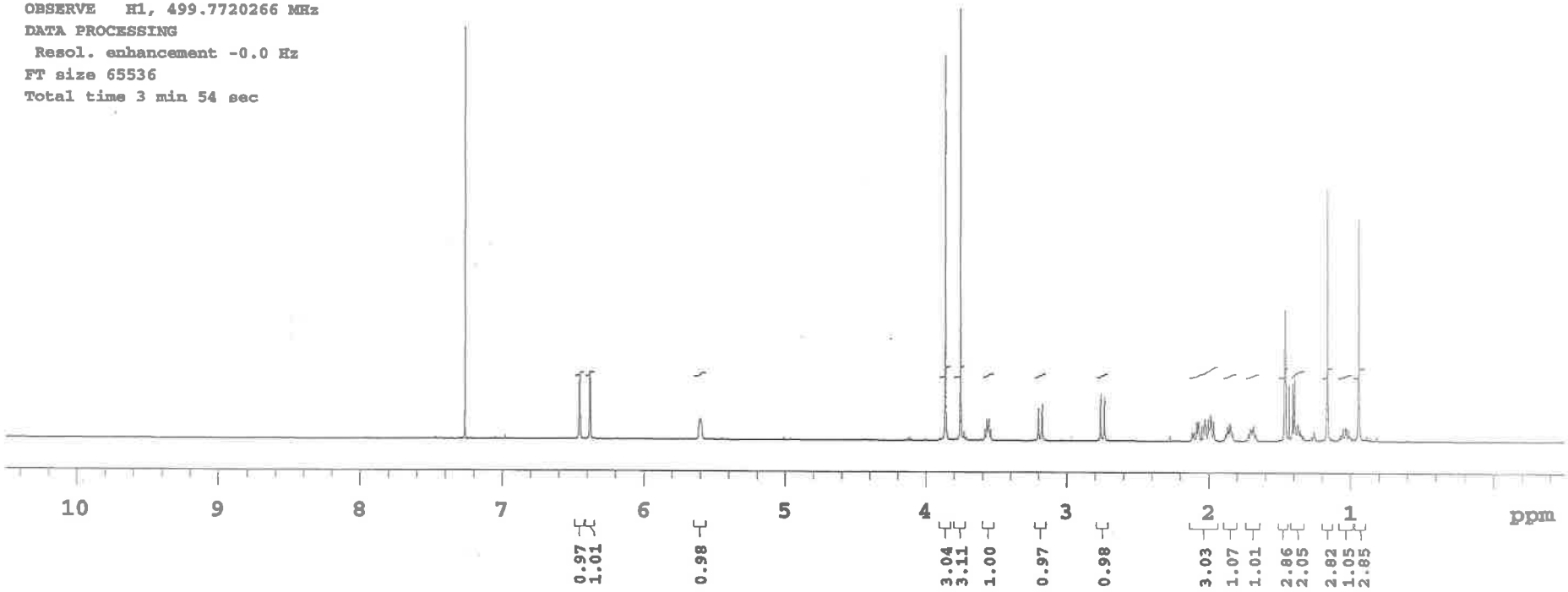
FidFile: HZK-II-144F

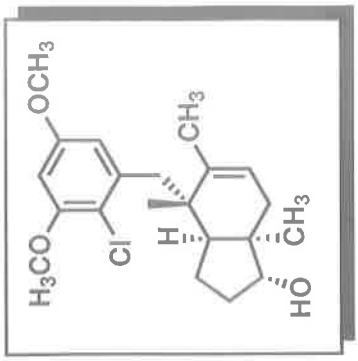
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 19 2011

Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7720266 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 54 sec







HZK-II-263F2-C

Sample Name:
HZK-II-263F2-C
Archive directory:

Sample directory:

FidFile: HZK-II-263F2-C

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Sep 6 2010

Temp. 25.0 C / 298.1 K
Operator: jak
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30487.8 Hz
500 repetitions
OBSERVE C13, 125.6951067 MHz
DECOUPLE H1, 499.8833015 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min

Sample Name:
HZK-II-290FPa
Archive directory:

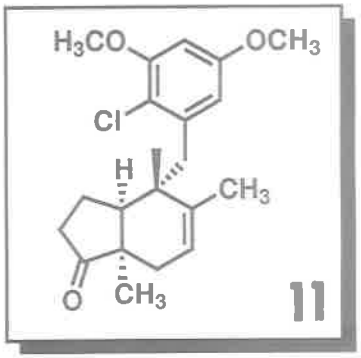
Sample directory:

FidFile: HZK-II-290FPa

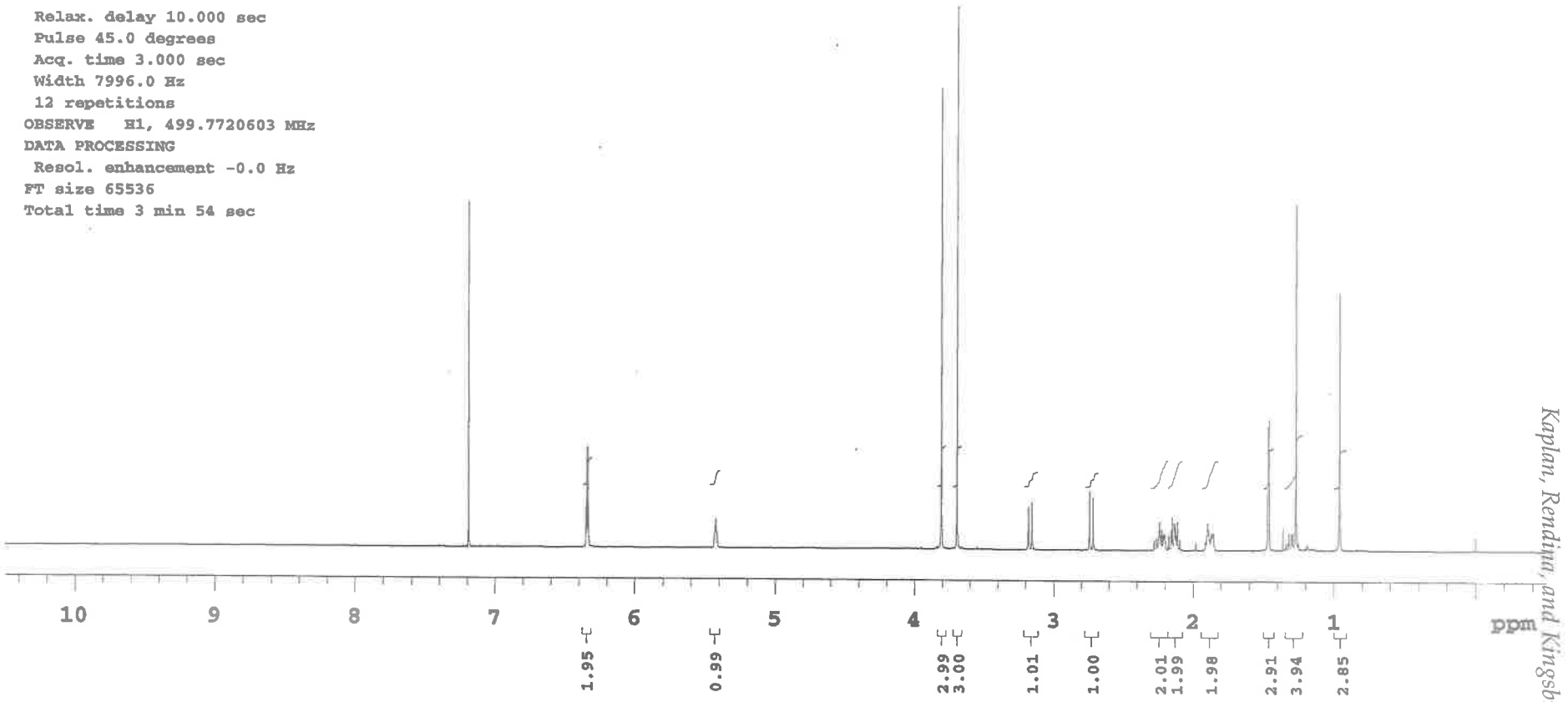
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 21 2011

Operator: jsk
INOVA-500 "nmr16"

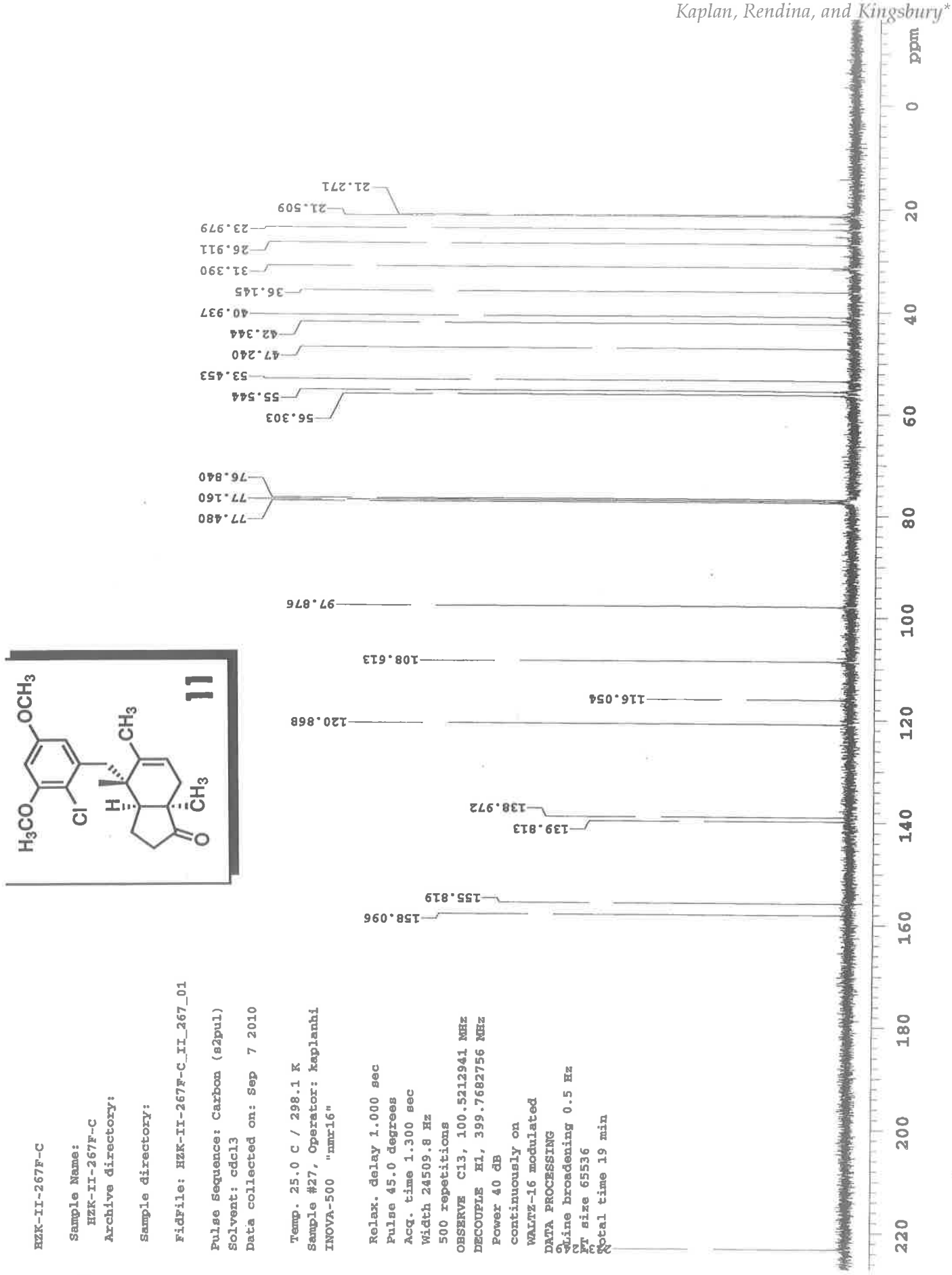
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
12 repetitions
OBSERVE H1, 499.7720603 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 54 sec



11



*Kaplan, Rendina, and Kingsbury**


HZK-II-267F-C
Sample Name:
HZK-II-267F-C
Archive directory:
Sample directory:
FidFile: HZK-II-267F-C_II_267_01
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Sep 7 2010
Temp. 25.0 C / 298.1 K
Sample #27, Operator: kaplanhi
INOVA-500 "nmr16"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
500 repetitions
OBSERVE C13, 100.5212941 MHz
DECOUPLE H1, 399.7682756 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min
11
OCH3
CH3
H3CO
Cl
H
CH3
O
21.271
21.509
23.979
26.911
31.390
36.145
40.937
42.344
47.240
53.453
55.544
56.303
76.840
77.160
77.480
97.876
108.613
116.054
120.868
138.972
139.813
155.819
158.096
ppm
0
20
40
60
80
100
120
140
160
180
200
220

Sample Name:
HZK-II-253F
Archive directory:

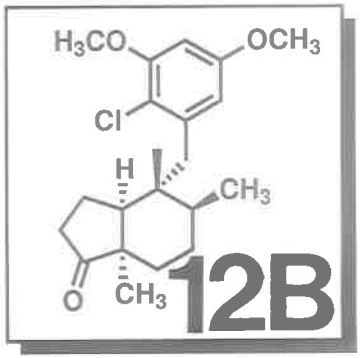
Sample directory:

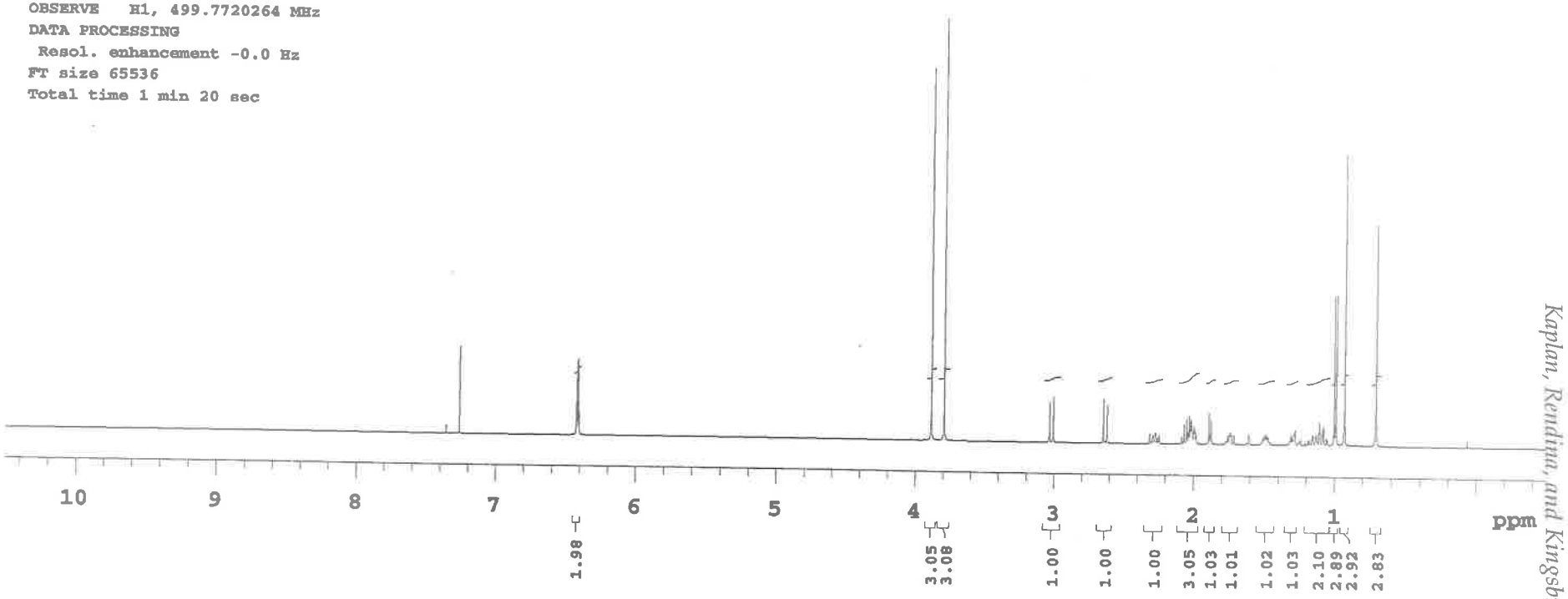
FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 18 2011

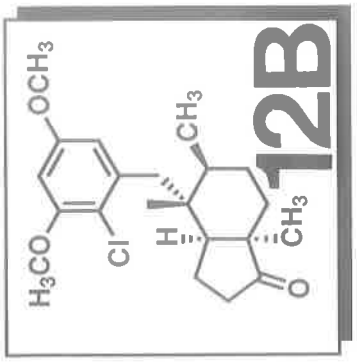
Operator: jsk
INOVA-500 "nmr16"

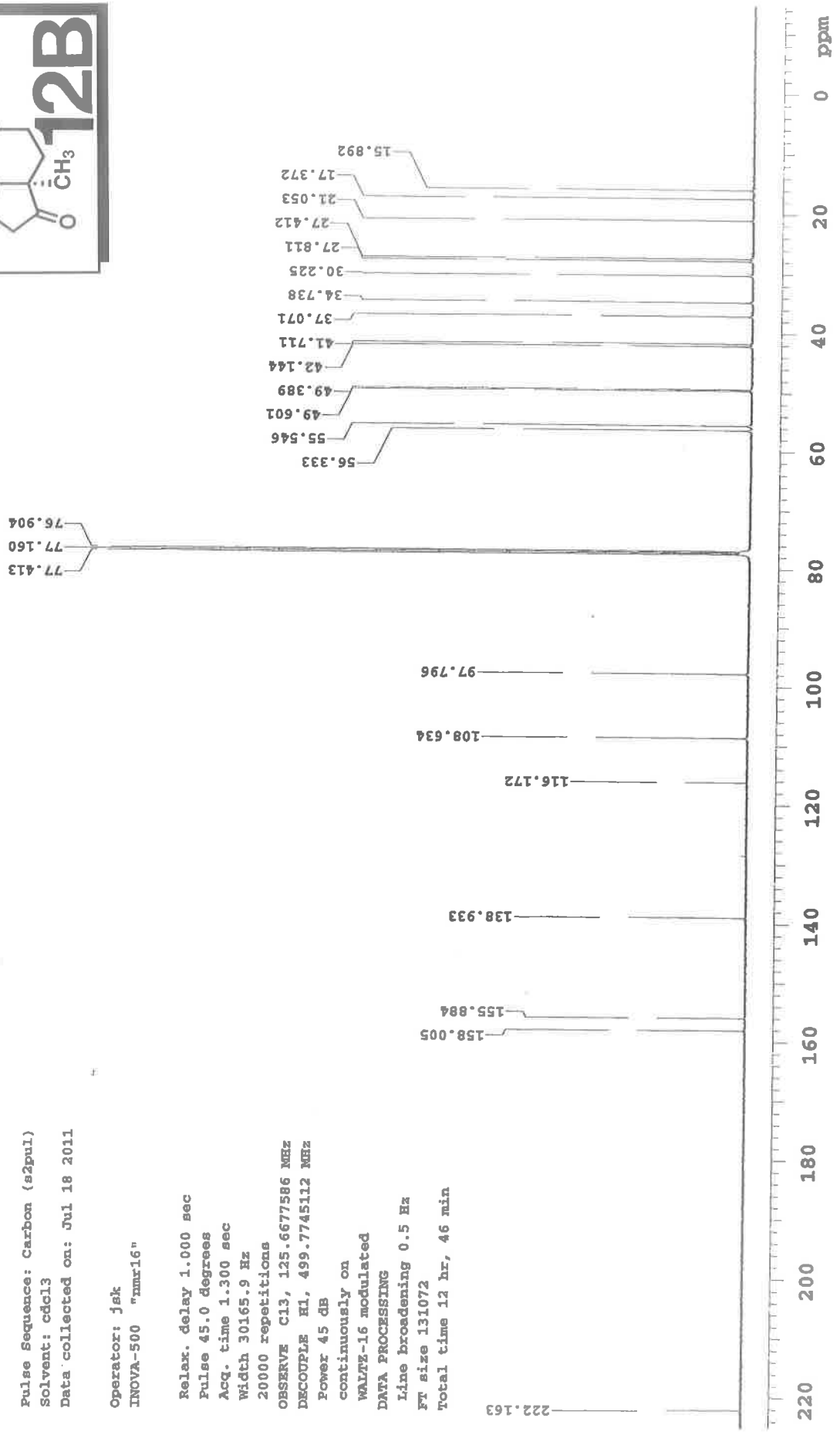
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7720264 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min 20 sec





*Kaplan, Rendina, and Kingsbury**





Sample Name:
HZK-II-253F-carbon
Archive directory:

Sample directory:

FidFile: HZK-II-253F-carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jul 18 2011

Operator: jak
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
20000 repetitions
OBSERVE C13, 125.6677586 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 hr, 46 min

Sample Name:
HZK-III-043Pb
Archive directory:

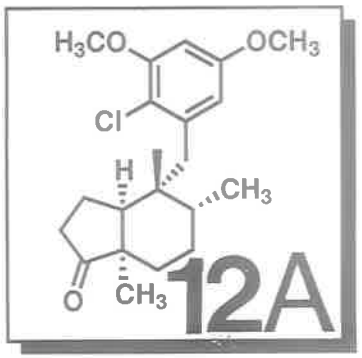
Sample directory:

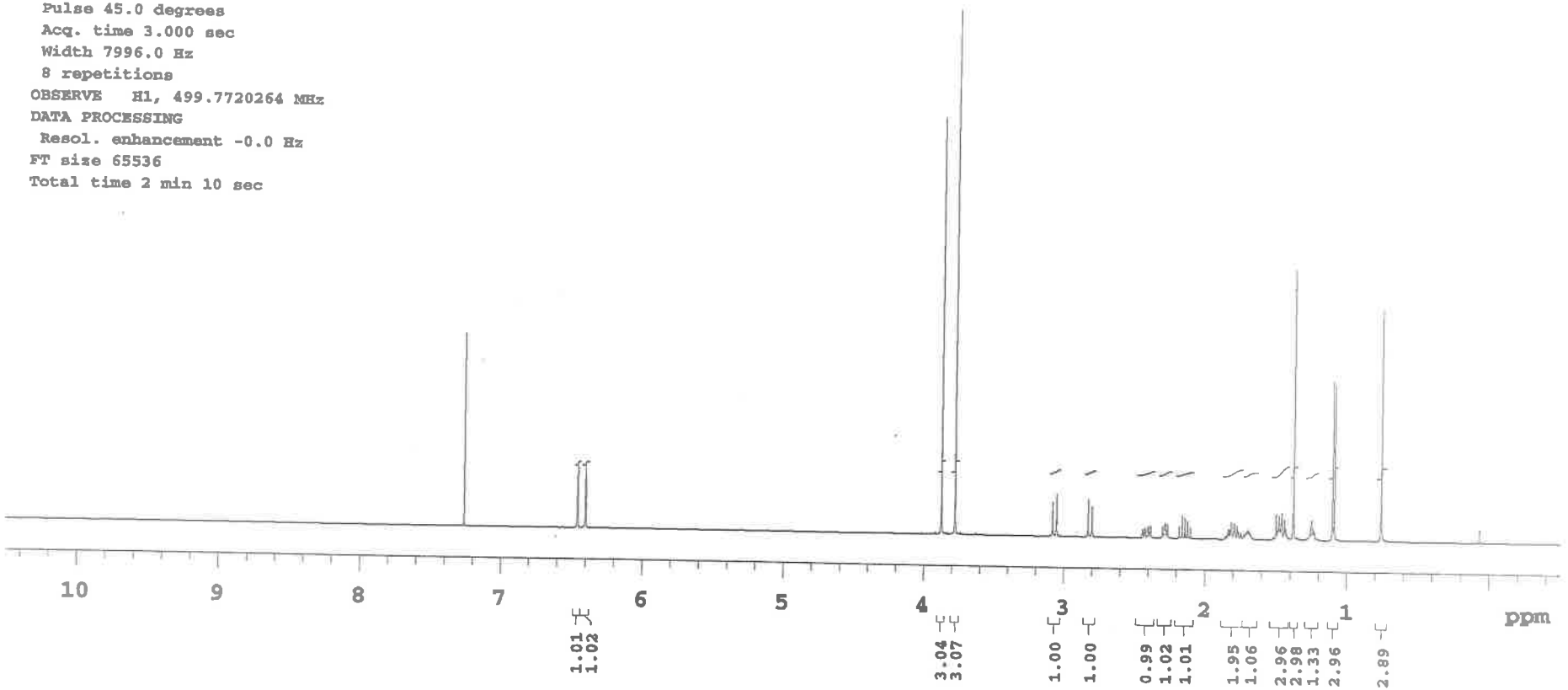
FidFile: HZK-III-043Pb

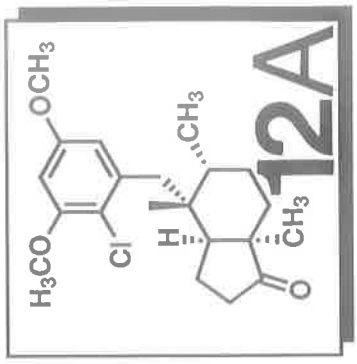
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 19 2011

Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7720264 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min 10 sec







Sample Name:
HZK-III-043Pb-carbon
Archive directory:

Sample directory:

FidFile: HZK-III-043Pb-carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jul 19 2011

Operator: jsk
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
19368 repetitions
OBSERVE C13, 125.6677576 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 hr, 46 min

HZK-III-118P

Sample Name:
HZK-III-118P
Archive directory:

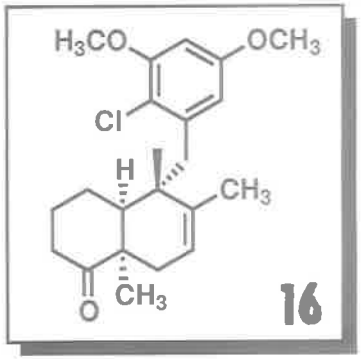
Sample directory:

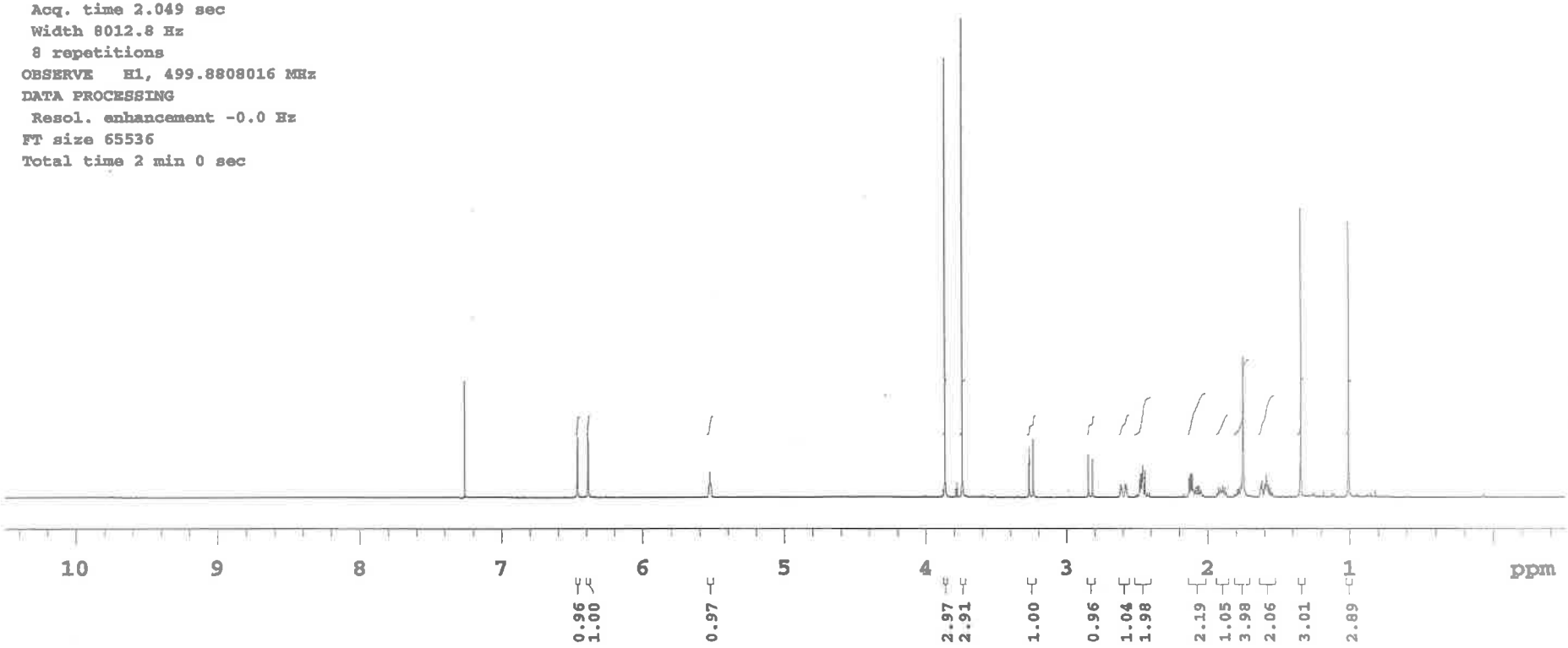
FidFile: HZK-III-118P

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 22 2011

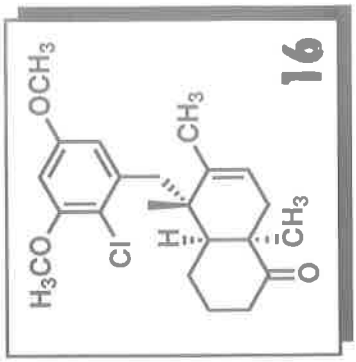
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8808016 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min 0 sec

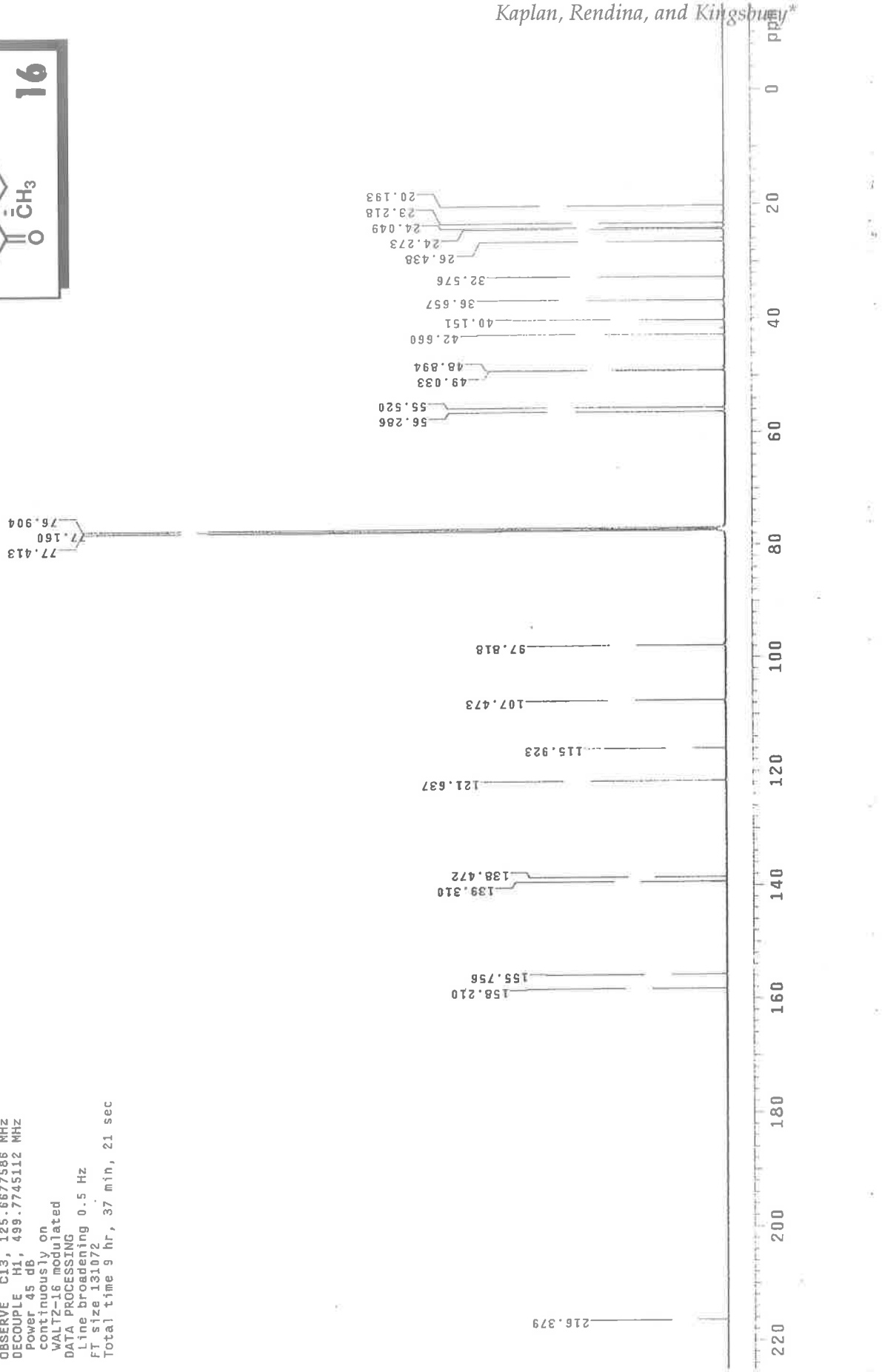




*Kaplan, Rendina, and Kingsbury**



16



HZK-III-118P-carbon

Sample: HZK-III-118P-carbon
File: exp

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: jsk
INOVA-500 "nmr11"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
15000 repetitions
OBSERVE C13, 125.6677586 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 131072
Total time 9 hr, 37 min, 21 sec

Sample Name:
HZK-III-213F
Archive directory:

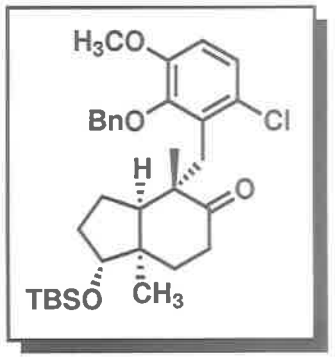
Sample directory:

FidFile: Proton

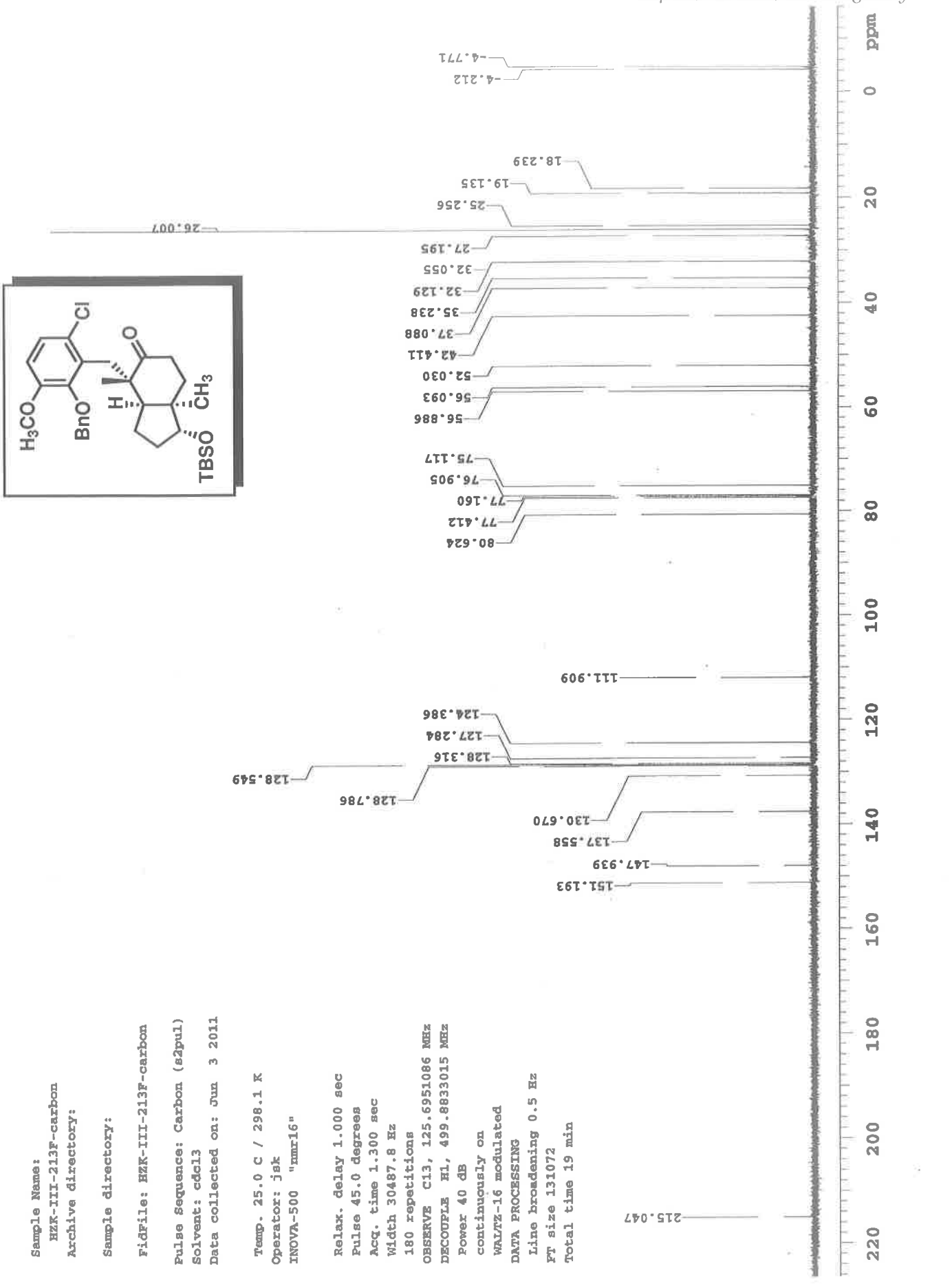
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jun 2 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
7 repetitions
OBSERVE H1, 499.8807991 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 37 sec



*Kaplan, Rendina, and Kingsbury**


Sample Name:
HZK-III-213F-carbon
Archive directory:
Sample directory:
FidFile: HZK-III-213F-carbon
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jun 3 2011
Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30487.8 Hz
180 repetitions
OBSERVE C13, 125.6951086 MHz
DECOUPLE H1, 499.8833015 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min
-4.771
-4.212
18.239
19.135
25.256
26.007
27.195
32.055
32.129
35.238
37.088
43.411
52.030
56.093
56.886
75.117
76.905
77.160
77.412
80.624
111.909
124.386
127.284
128.316
128.549
128.786
130.670
137.558
147.939
151.193
215.047
ppm
0
20
40
60
80
100
120
140
160
180
200
220
Cl
O
H3CO
BnO
H
CH3
TBSO

Sample Name:
HZK-III-233F
Archive directory:

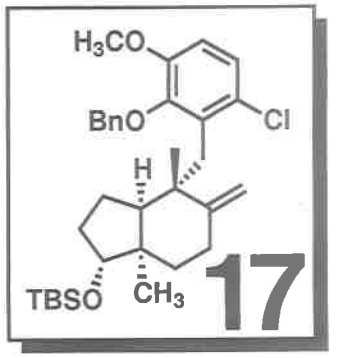
Sample directory:

FidFile: HZK-III-233F

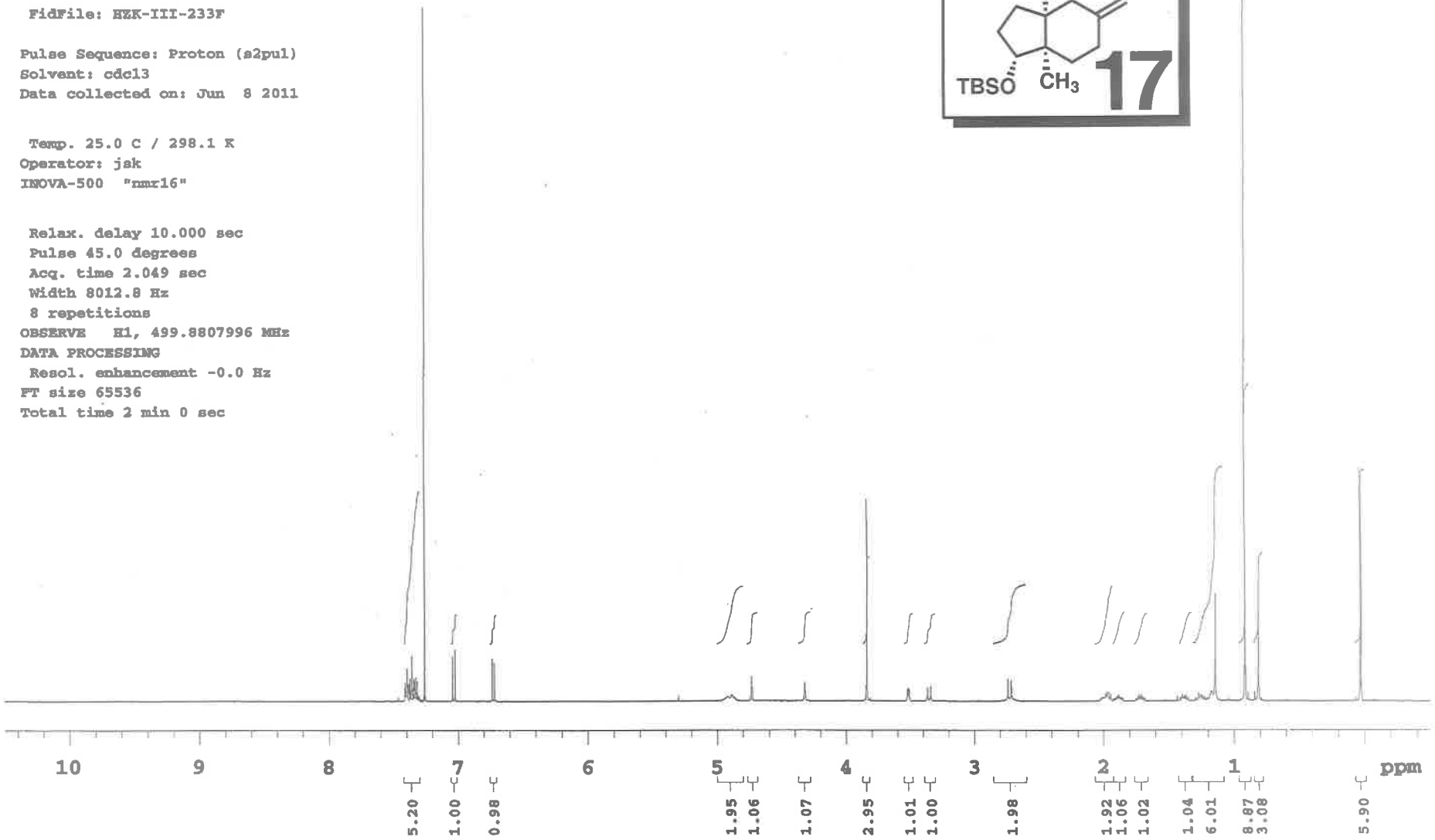
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jun 8 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

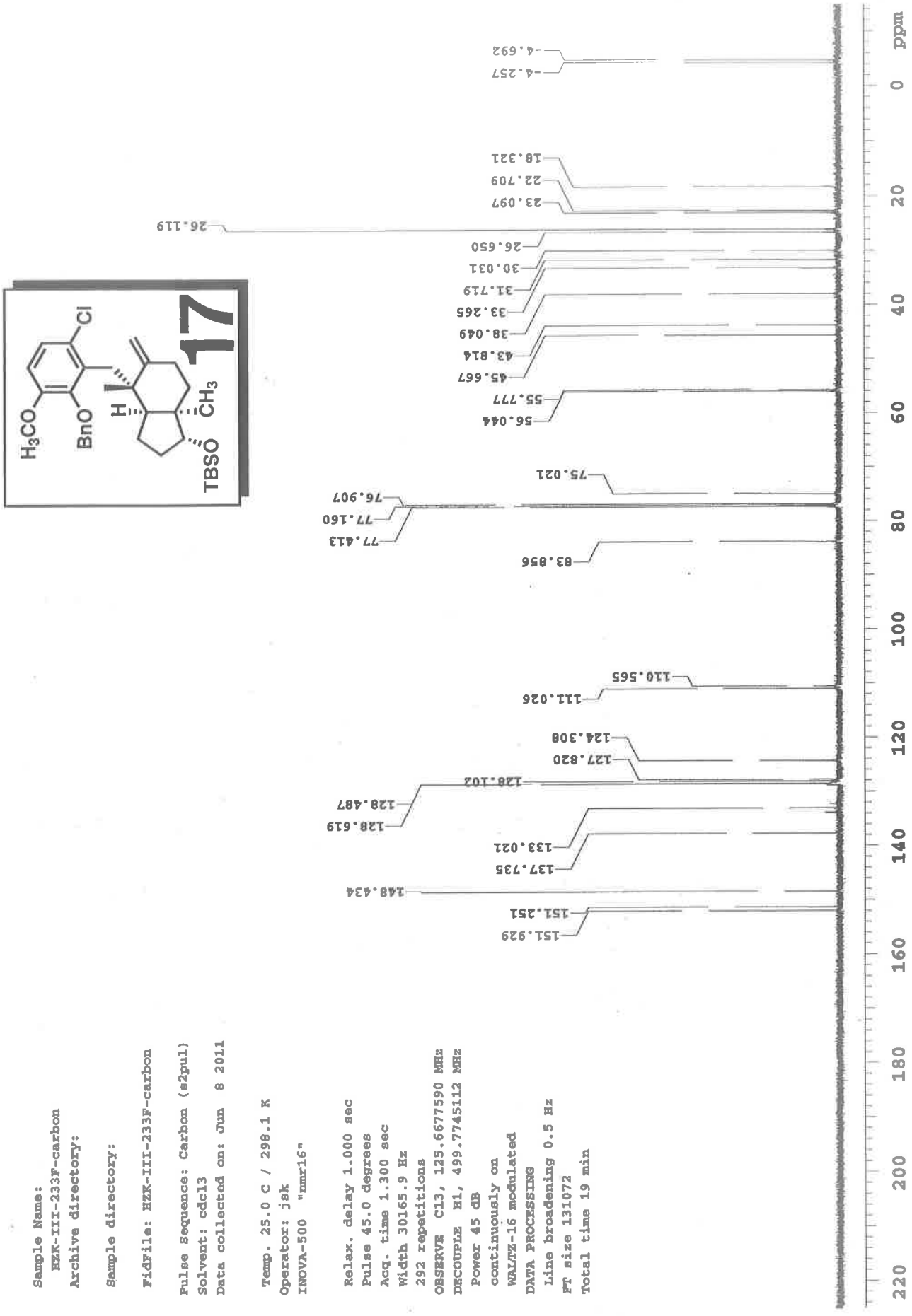
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8807996 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min 0 sec



17



*Kaplan, Rendina, and Kingsbury**



Sample Name:
HZK-III-233F-carbon
Archive directory:

Sample directory:

FidFile: HZK-III-233F-carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jun 8 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
292 repetitions
OBSERVE C13, 125.6677590 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min

Sample Name:
VR-III-279f
Archive directory:

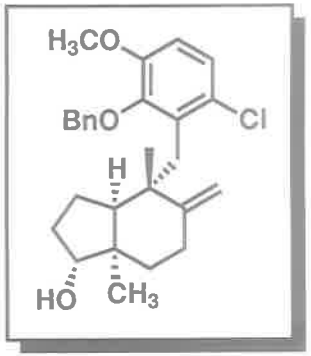
Sample directory:

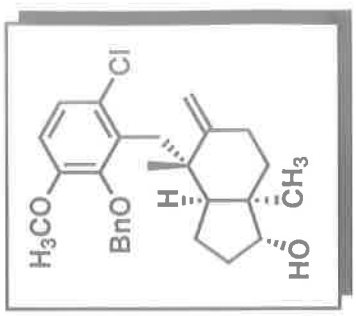
FidFile: VR-III-279f

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jun 22 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
16 repetitions
OBSERVE H1, 499.7720271 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 54 sec





Sample Name:
VR-III-279f-carbon
Archive directory:

Sample directory:

Fidfile: VR-III-279f-carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jun 22 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
160 repetitions
OBSERVE C13, 125.6677627 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 9 min 49 sec

HZK-III-253F

Sample Name:
HZK-III-253F
Archive directory:

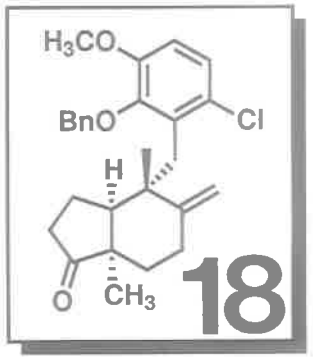
Sample directory:

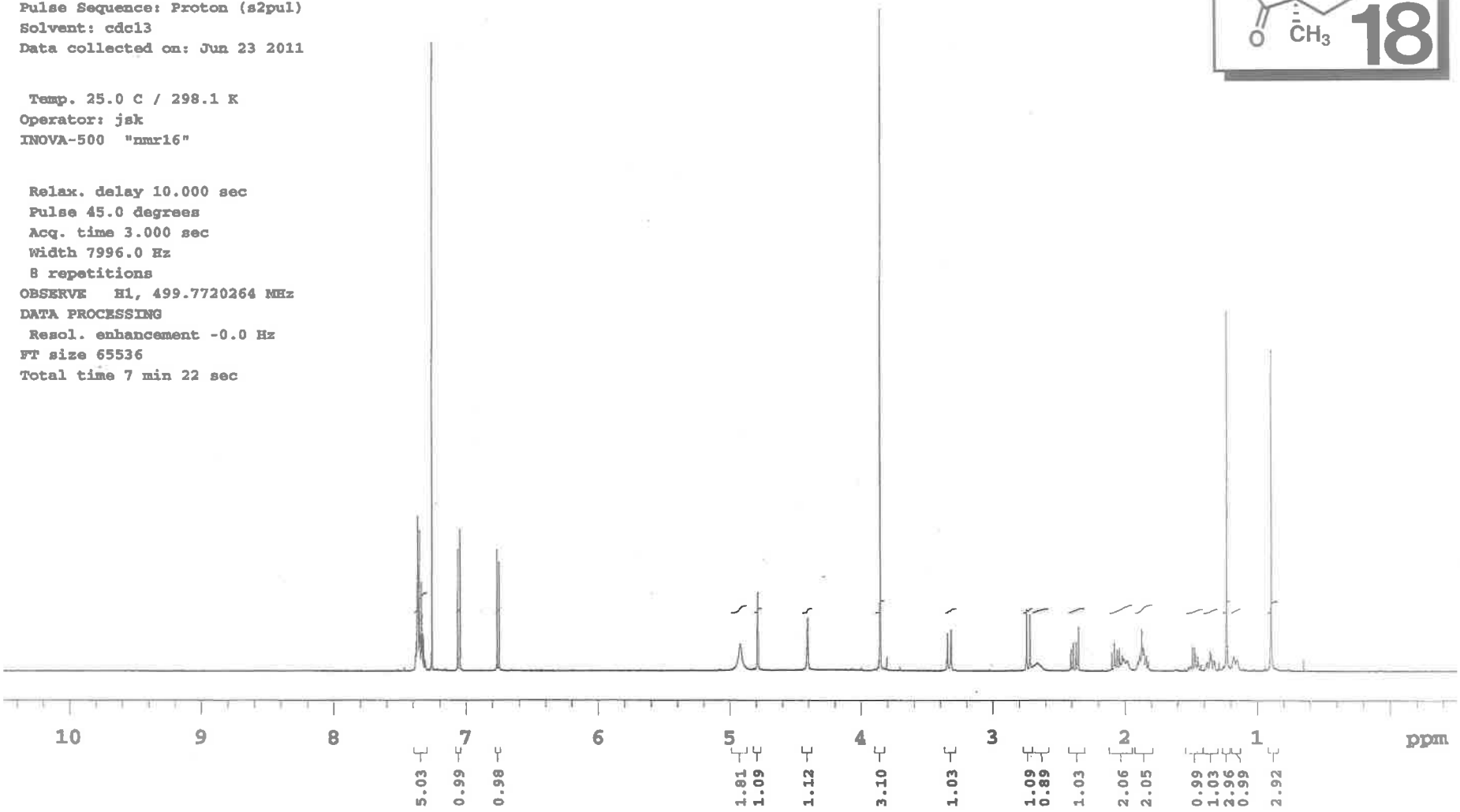
FidFile: HZK-III-253F

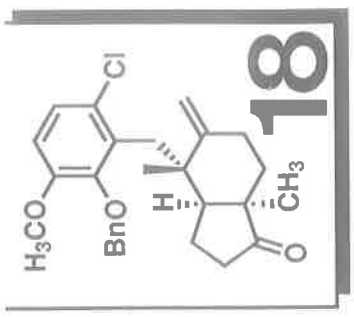
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jun 23 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

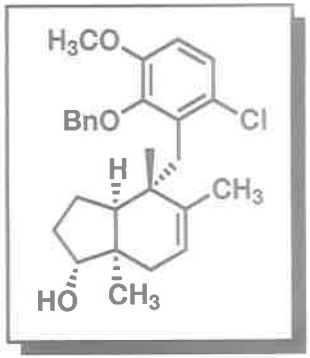
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7720264 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 7 min 22 sec






18
Cl
H3CO
BnO
H
CH3
O

ppm
0
20
40
60
80
100
120
140
160
180
200
220
21.489
21.581
21.811
29.225
30.610
35.507
38.170
43.195
48.825
56.029
57.348
75.296
76.907
77.160
77.416
111.239
111.316
124.340
127.630
128.274
128.538
128.637
132.084
137.644
148.500
150.500
151.192
222.214
HZK-III-253F-carbon
Sample Name:
HZK-III-253F-carbon
Archive directory:
Sample directory:
FidFile: HZK-III-253F-carbon
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jun 23 2011
Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
346 repetitions
OBSERVE C13, 125.6677609 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min



Sample Name:
HZK-III-250F
Archive directory:

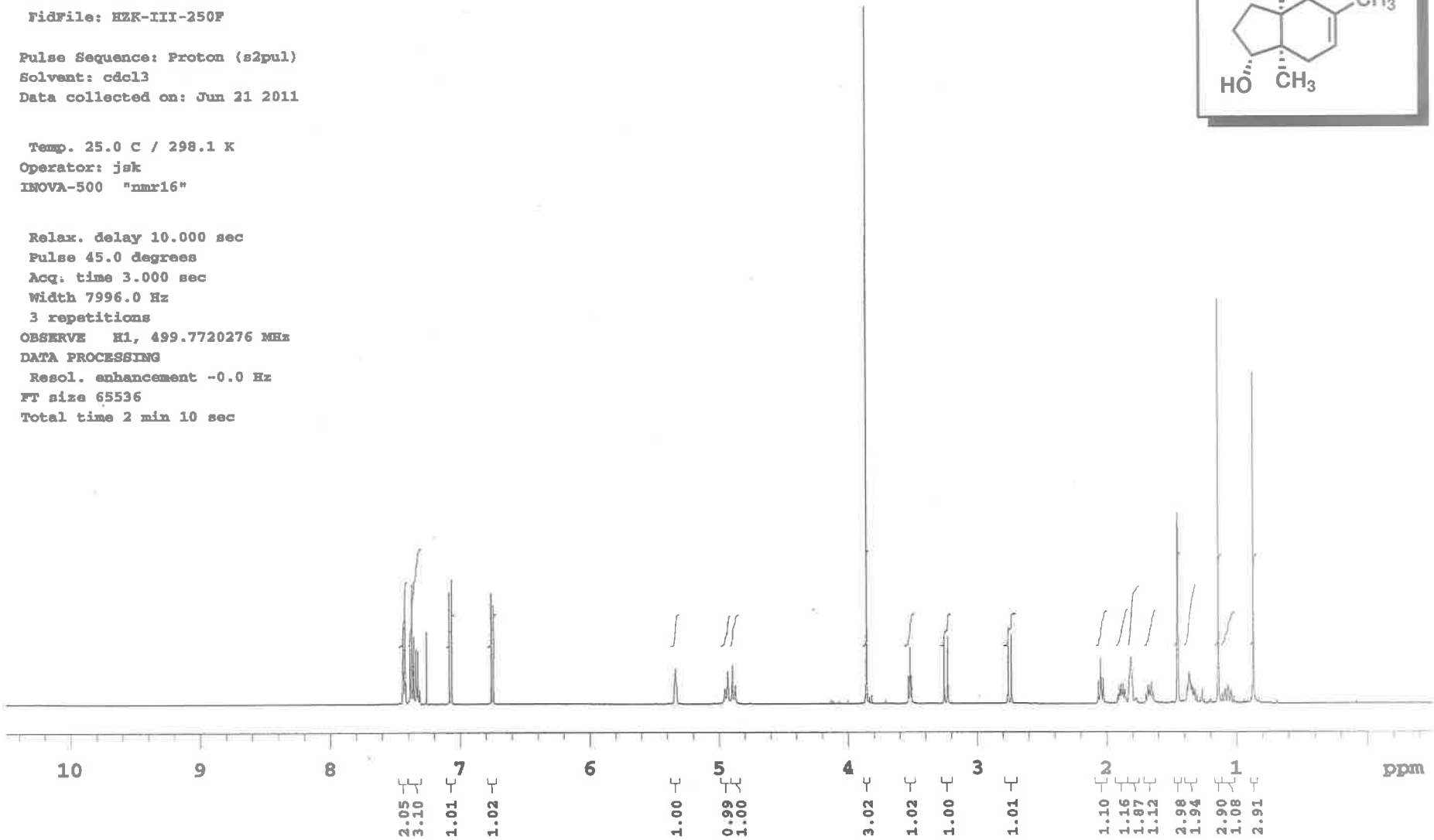
Sample directory:

FidFile: HZK-III-250F

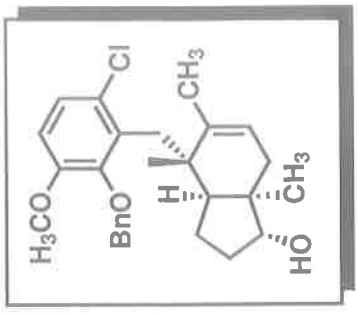
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jun 21 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
3 repetitions
OBSERVE H1, 499.7720276 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min 10 sec



*Kaplan, Rendina, and Kingsbury**



Sample Name:
HZK-III-250F-carbon
Archive directory:

Sample directory:

FidFile: HZK-III-250F-carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jun 21 2011

Temp. 25.0 C / 298.1 K
Operator: jak
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
92 repetitions
OBSERVE C13, 125.6677604 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 9 min 49 sec

Sample Name:
VR-III-281f
Archive directory:

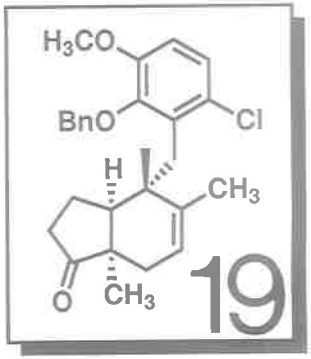
Sample directory:

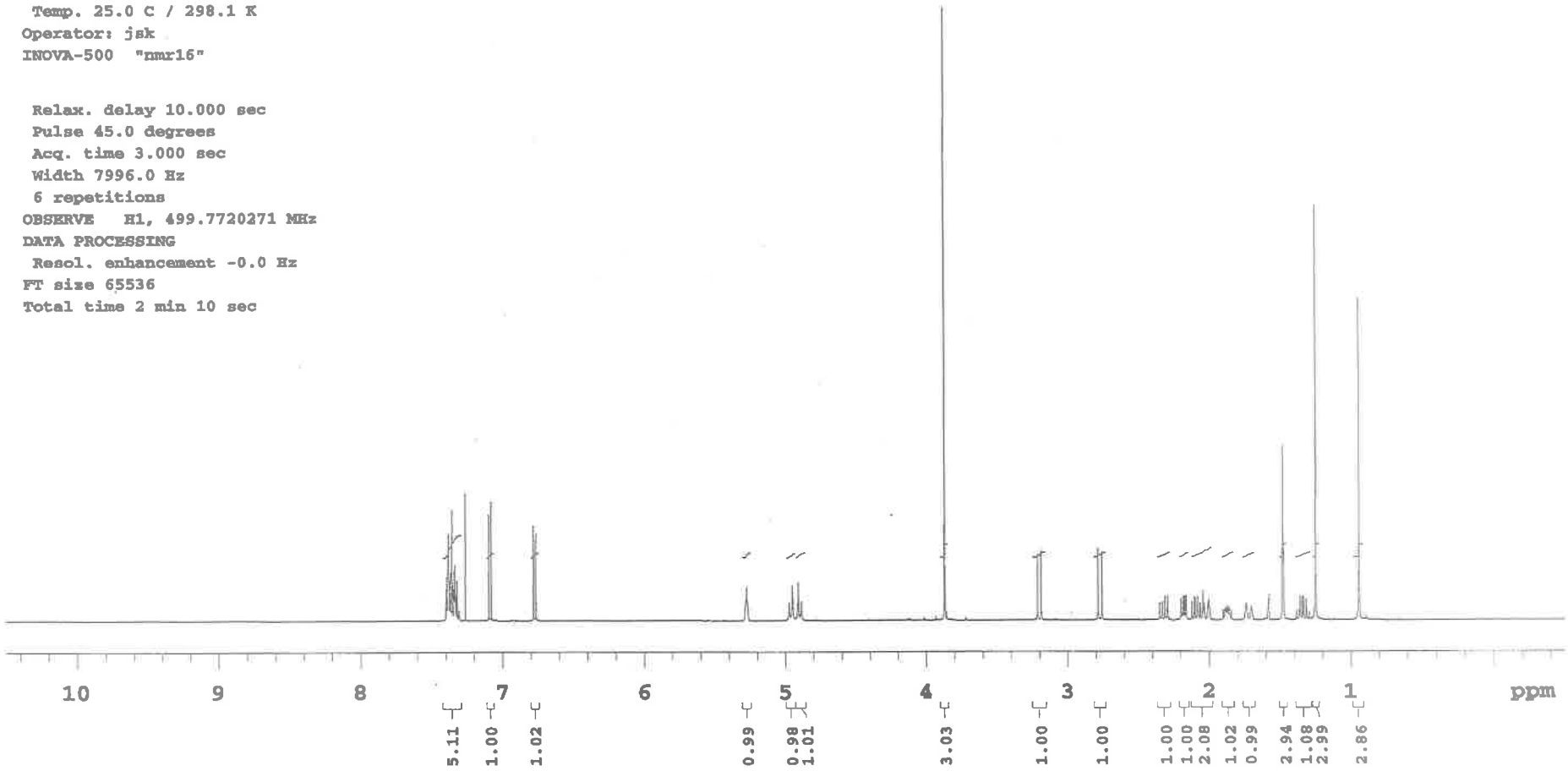
FidFile: VR-III-281f

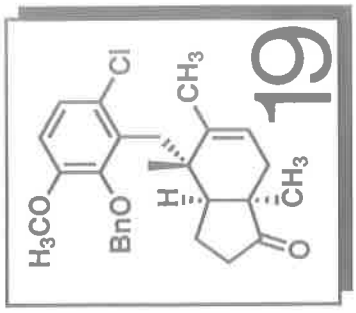
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jun 22 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
6 repetitions
OBSERVE H1, 499.7720271 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min 10 sec






19
Cl
CH3
H3CO
BnO
H
CH3
O

Sample Name:
VR-III-281f-carbon
Archive directory:
Sample directory:
FidFile: VR-III-281f-carbon
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jun 22 2011
Temp. 25.0 C / 298.1 K
Operator: jak
INOVA-500 "nmr16"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
308 repetitions
OBSERVE C13, 125.6677576 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min
21.050
21.888
23.584
25.031
30.822
36.038
37.675
41.613
47.074
54.110
56.029
74.922
76.907
77.160
77.413
111.176
119.923
124.732
127.754
128.216
128.403
128.512
132.772
137.556
139.329
148.328
151.522
223.130
ppm
0
20
40
60
80
100
120
140
160
180
200
220

Sample Name:
VR-III-283-2-fa
Archive directory:

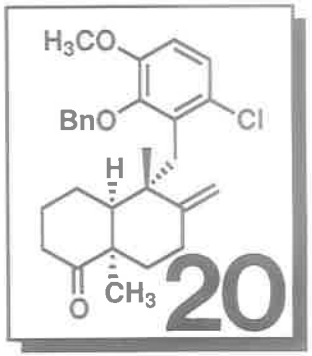
Sample directory:

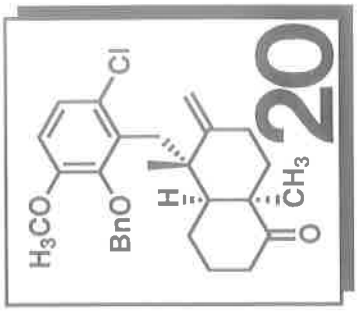
FidFile: VR-III-283-2-fa

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 10 2011

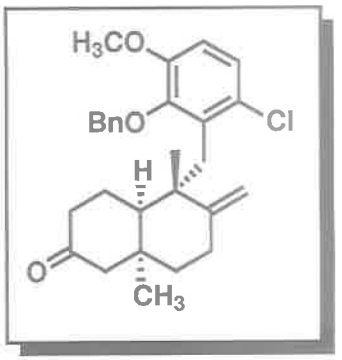
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
13 repetitions
OBSERVE H1, 499.7720269 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 54 sec




20
Cl
H_3CO
BnO
H
CH_3
O

Sample Name:
VR-III-283-2-fa-carbon
Archive directory:
Sample directory:
FidFile: VR-III-283-2-fa-carbon
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jul 10 2011
Operator: jak
INOVA-500 "nmr16"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
240 repetitions
OBSERVE C13, 125.6677599 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 9 min 49 sec
22.822
24.156
24.236
29.705
32.573
37.067
39.920
44.722
50.901
55.821
56.004
75.156
76.904
77.160
77.413
110.301
111.070
124.428
127.593
128.252
128.549
132.981
137.688
148.280
151.310
151.800
216.599
ppm
0
20
40
60
80
100
120
140
160
180
200
220



Sample Name:
VR-III-283fb
Archive directory:

Sample directory:

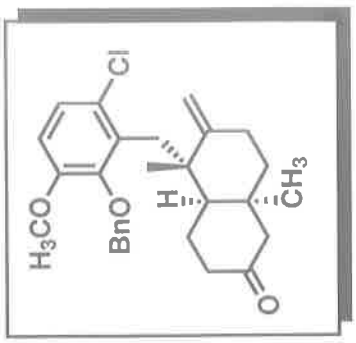
FidFile: VR-III-283fb

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 8 2011

Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
16 repetitions
OBSERVE H1, 499.7720266 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 54 sec

*Kaplan, Rendina, and Kingsbury**


Cl
H3CO
BnO
H
CH3
O

ppm
0
20
40
60
80
100
120
140
160
180
200
220
23.178
26.031
29.976
31.459
34.097
39.495
40.243
40.334
44.946
53.030
56.048
56.201
75.120
76.907
77.160
77.416
110.737
111.140
124.417
127.633
128.190
128.476
128.553
132.915
137.918
148.343
151.057
151.317
212.834
Sample Name:
VR-III-283fb-carbon
Archive directory:
Sample directory:
FidFile: VR-III-283fb-carbon
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jul 7 2011
Operator: jsk
INOVA-500 "nmr16"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
18184 repetitions
OBSERVE C13, 125.6677567 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 hr, 46 min

Sample Name:
VR-III-282f
Archive directory:

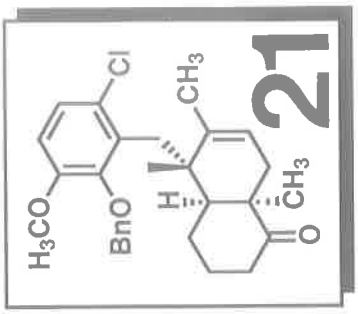
Sample directory:

FidFile: VR-III-282f

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 6 2011

Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
12 repetitions
OBSERVE H1, 499.7720266 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 54 sec


21
Cl
CH3
H3CO
BnO
H
CH3
O

Sample Name:
VR-III-282f-carbon
Archive directory:
Sample directory:
FidFile: VR-III-282f-carbon
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jul 6 2011
Temp. 25.0 C / 298.1 K
Operator: jsk
INOVA-500 "nmr16"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
204 repetitions
OBSERVE C13, 125.6677609 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min
20.486
23.738
24.467
24.731
32.884
37.232
37.935
42.122
49.704
51.231
55.971
74.834
76.904
77.160
77.413
111.019
119.271
124.824
127.578
128.293
128.564
128.725
133.523
137.285
139.889
148.211
151.566
216.423
ppm
0
20
40
60
80
100
120
140
160
180
200
220