MODULAR ASYMMETRIC SYNTHESIS OF 1,2-DIOLS BY SINGLE-POT ALLENE DIBORATION/HYDROBORATION/CROSS-COUPLING.

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Supplementary Material

General. ^{1}H NMR spectra were recorded on Bruker DRX 300 or 400 MHz spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.24 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, br = broad, m = multiplet), coupling constants (Hz) and assignment. ^{13}C NMR was recorded on a Bruker 400 MHz (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: 77.0 ppm). Low-resolution mass spectrometry was performed by the University of North Carolina, Department of Chemistry Mass Spectrometry Facility. Infrared (IR) spectra were obtained on an ASI ReactIR 1000.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 X 450 mesh) purchased from Sorbent Technologies. Thin layer chromatography was performed on 250 μm silica gel plates from EMD Chemicals Inc. Visualization was achieved using UV light, phosphomolybdic acid in ethanol, potassium permanganate in water, or cerium sulfate and ammonium molybdate in sulfuric acid, each followed by heating.

Analytical supercritical fluid chromatography (SFC) was performed on a Berger Instruments supercritical chromatograph equipped with an Alcott autosampler and a Knauer UV detector.

All reactions were conducted in oven or flame dried glassware under an inert atmosphere of nitrogen or argon. Toluene was distilled over CaH_2 and degassed by freeze-pump-thaw cycles prior to use. $Pd_2(dba)_3$ and tricyclohexylphosphine were purchased from Strem Chemical Company. Aromatic and vinylic halides were purchased from Aldrich and distilled prior to use. Phenyl triflate was purchased from Aldrich and used without prior purification. Bis(pinacolato)diboron was purchased from BASF. [(*R*,*R*)- xylylTADDOL]$PNMe_2$ was synthesized according to the literature (Woodward, A. R.; Burks, H. E.; Chan, L., K., M.; Morken, J. P. *Org. Lett.* **2005**, *7*, 5505). Allenes were synthesized according to the literature (Vermeer, P.; Meijer, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 112.). Acetic anhydride was purchased from Fisher Chemical and distilled under N_2. Starting material 4,4,5,5-tetramethyl-2-(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-2-yl)-1,3,2-dioxaborolane was synthesized via known protocol (Pelz, N.F.; Woodward, A.; Burks, H.; Sieber, J. *J. Am. Chem. Soc.* **2004**, *126*, 16328). Commercially available hydroborating reagents were used without further purification. Dimeric 9-BBN was purchased from Aldrich as a white crystalline solid. BH_3 SMe_2 was purchased as a solution in excess dimethylsulfide from Aldrich. All other reagents were purchased from either Fisher or Aldrich Chemical Companies and used directly.

Procedure for Hydroboration/Oxidation/Acylation with 9-BBN (Scheme 2).

An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 76 mg (0.198 mmol) of 4,4,5,5-tetramethyl-2-(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-2-yl)-1,3,2-dioxaborolane and 1 mL of toluene in a dry-box under an argon atmosphere. To this was added 27 mg (0.109 mmol) 9-BBN dimer. The vial was then sealed, removed from the drybox and stirred at ambient temperature for 14h. The vial was then cooled to 0 °C before the addition of 0.75 mL tetrahydrofuran, 0.75 mL 3M NaOH, and 0.75 mL H_2O_2 (30% solution by weight). The oxidation was stirred at 0 °C for 1h, and allowed to slowly warm to room temperature and stir for an additional 8 h. After this time period, the reaction was quenched with saturated aqueous sodium thiosulfate and transferred to a separatory funnel for extraction. The aqueous layer was acidified to pH 4 and extracted with ethyl acetate five times. The organics were combined, washed with brine, dried over sodium sulfate, and evaporated to dryness. The resultant crude material was then transferred to a flame dried 6 dram vial and evaporated to dryness. The vial, equipped with magnetic stir bar, was then charged with 14 mg (0.12 mmol) dimethylaminopyridine, 0.8 mL dry dichloromethane, and 1 mL triethylamine. The vial was sealed with a septum and cooled to 0 °C under an atmosphere of nitrogen for the addition of 280 μL (2.97 mmol) acetic anhydride. The reaction was held at 0 °C for 1 h and allowed to warm to room temperature and was stirred overnight. TheThe reaction was evaportated to dryness and passed through a pad of silica gel using 10:1 hexanes:ethyl acetate as the eluent. After concentration, a ^{1}H NMR spectrum was obtained for diastereomer ratio determination. Silica gel chromatography (hexanes/EtOAc) of this mixture afforded 37 mg (62 %) of pure 4-phenylbutane-1,2,3-triyl triacetate as a yellow oil.

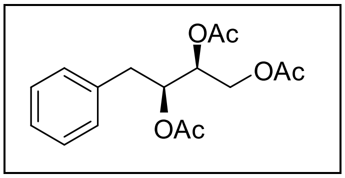
Procedure for Hydroboration/Oxidation/Acylation with $BH_3{\bullet}Me_2S$.

An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 50 mg (0.14 mmol) of 4,4,5,5-tetramethyl-2-(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-2-yl)-1,3,2-dioxaborolane and 0.6 mL of toluene in a dry-box under an argon atmosphere. The vial was then sealed with a septum, removed from the drybox and stirred at ambient temperature for the addition of 14 mg (0.18 mmol) of borane-dimethyl sulfide complex. The reaction was allowed to stir for 14 h. The vial was then cooled to 0 °C for alkali peroxide oxidation. The reaction was treated with 0.75 mL tetrahydrofuran, 0.75 mL 3M NaOH, and 0.75 mL H_2O_2 (30% solution by weight). The oxidation was stirred at 0 °C for 1h, and allowed to slowly warm to room temperature and stir for an additional 8 h. After this time period, the reaction was quenched with saturated aqueous sodium thiosulfate and transferred to a separatory funnel for extraction. The aqueous layer was acidified to pH 4 and extracted with ethyl acetate five times. The organics were combined, washed with brine, dried over sodium sulfate, and evaporated to dryness. The resultant crude material was then transferred to a flame dried 6 dram vial and evaporated to dryness. The vial, equipped with magnetic stir bar, was then charged with 14 mg (0.119 mmol) DMAP, 0.8 mL dry dichloromethane, and 1vmL triethylamine. The vial was sealed with a septum and cooled to 0 °C under an atmosphere of nitrogen for the addition of 280 μL (2.97 mmol) acetic anhydride. The reaction was held at 0 °C for 1 h and allowed to warm to room temperature. After stirring 14 h, the reaction was evaporated to dryness and passed through a pad of silica gel using 10:1 hexanes:ethyl acetate as the eluent. After evaporating to dryness, a ^{1}H NMR was taken for diastereomeric analysis.

Procedure for Sequential Diboration/Hydroboration/Cross-Coupling (Table 1 and 2).

An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 6 mg (0.007 mmol) of Pd_2dba_3, 11 mg (0.017 mmol) [(*R*,*R*)- xylylTADDOL]$PNMe_2$, and 1.4 mL toluene. The catalyst was allowed to stir for 45 minutes before the addition of 84 mg of

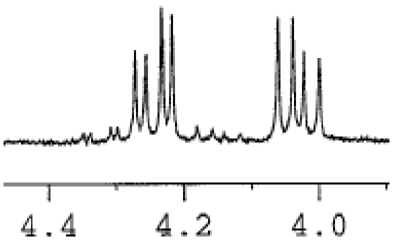
$B_2(pin)_2$ (0.33 mmol), and 50 mg allene. The vial was then sealed and stirred at ambient temperature for 14 h. At the end of that time period 44 mg (0.18 mmol) dimeric 9-BBN was added and the hydroboration sealed and stirred for 9 h. The vial was then charged with 203 mg Cs_2CO_3 (0.623 mmol) and 127 mg PhI (0.623 mmol). The vial was then sealed, removed from the drybox, and 100 mg H_2O (5.54 mmol) was added before resealing, and taping the reaction vial. The reaction was then placed in an 80 °C oil bath and allowed to react for 12 h. After the allotted time, the reaction was cooled to room temperature for alkali peroxide oxidation. The reaction was treated with air for the addition of 1.5 mL tetrahydrofuran, 1 mL 3M NaOH, and 1 mL H_2O_2 (30% solution by weight). The oxidation was stirred at 0 °C for 1h, and allowed to slowly warm to room temperature and stir for an additional 8 h. After this time period, the reaction was quenched with saturated aqueous sodium thiosulfate and transferred to a separatory funnel for extraction. The aqueous phase was extracted with ethyl acetate three times. The combined organics were then washed with brine, dried over magnesium sulfate, and evaporated to dryness. After evaporation, a ^1H NMR was obtained to determine diastereomer ratios. Silica gel chromatography (dichloromethane/ether) of this mixture was then employed for purification.



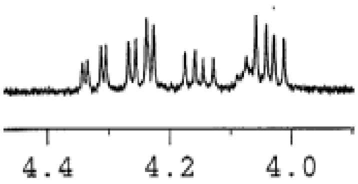
4-Phenylbutane-1,2,3-triyl triacetate (Compound SI-6). 19 mg of a yellow oil. R_f = 0.42 in 2:1 hexanes:ethyl acetate. IR ($CHCl_3$) 2956 (m), 1748 (s), 1497 (m), 1457 (m), 1372 (s), 1268 (s), 1063 (m), cm^{-1}; ^1H NMR: δ 7.29 – 7.14 (5 H, m, Ar), 5.30 (1 H, m), 5.16 (1H, m), 4.24 (1 H, dd, J = 12.0, 4.5 Hz), 4.03 (1 H, dd, J = 12.0, 6.6 Hz), 2.84 (2 H, d, J = 6.9 Hz), 2.12 (3 H, s), 2.01 (3 H, s), 1.98 (3 H, s); ^{13}C NMR: 170.5, 170.0, 169.9, 136.1, 129.2, 128.5, 126.7, 72.2, 70.7, 62.3, 36.9, 20.7, 20.7, 20.6. LRMS (ESI) Calc'd for $C_{16}H_{20}O_6$ $(M+Na)^+$: 331.3 Found $(M+Na)^+$: 331.2.

Diastereoselectivity. Diastereomeric ratio was determined by ^1H NMR of the unpurified triacetate.

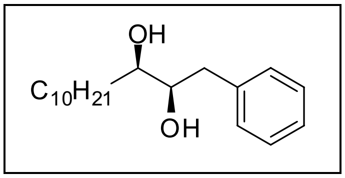
Portion of ^1H NMR of crude esterification product as taken on Bruker DRX 400MHz spectrometer.



9BBN Hydroboration



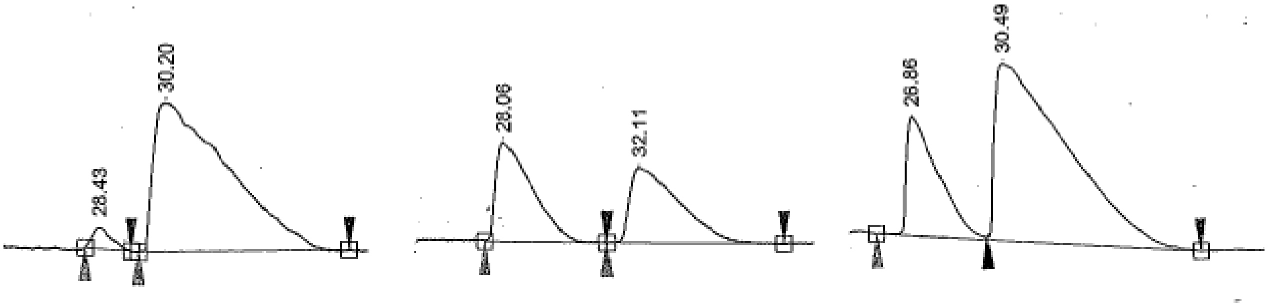
BH_3•Me_2S Hydroboration



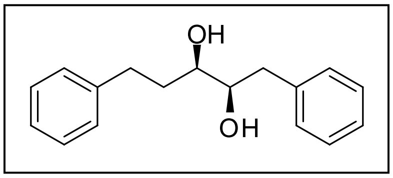
(2*R*,3*R*)-1-Phenyltridecane-2,3-diol (Compound SI-7). 50 mg of a white solid. R$_f$ = 0.26 in 20:1 dichloromethane:diethylether. IR (CHCl$_3$) 3579 (m), 2931 (s), 2856 (s), 1495 (m), 1466 (s), 1380 (m), 1302 (m) cm^{-1}; ^{1}H NMR: δ 7.31–7.21 (5 H, m, Ar), 3.67-3.63 (1 H, m), 3.46 (1 H, m) 2.85 (1 H, dd, J = 13.6, 4.4 Hz), 2.71 (1 H, dd, J = 13.6, 8.8 Hz), 2.15 (2 H, broad), 1.56-1.45 (2 H, m), 1.28-1.24 (16 H, m), 0.86 (3 H, t, J = 6.8 Hz); ^{13}C NMR: 138.2, 129.4, 128.7, 126.6, 75.0, 73.6, 40.3, 33.8, 31.9, 29.7 (2C), 29.3 (2C), 25.7, 22.7, 14.1. LRMS (ESI) Calc'd for $C_{19}H_{32}O_2$ (M+Na)$^+$: 315.2. Found (M+Na)$^+$: 315.2.

Stereochemistry. Enantiomeric excess was determined by chiral SFC of the diol in comparison to racemic material prepared by using tricyclohexylphosphine as the ligand. The identity of the major diastereomer was determined by ^{1}H NMR analysis in comparison to authentic material prepared via Sharpless dihydroxylation (Norrby, P.O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35).

Chiral SFC (Chiralpak AD-H, Daicel, 50℃,150psi, 3mL/min, 2% methanol, only the diastereomer corresponding to the syn diol is shown)



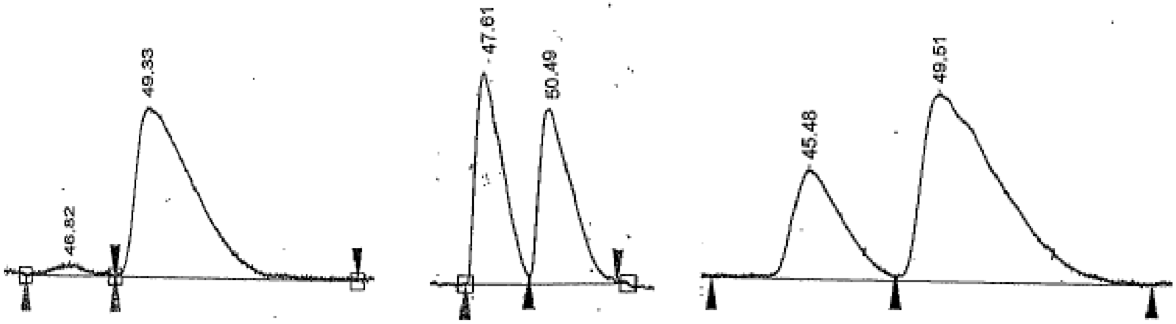
Asymmetric Reaction **Racemic Reaction** **Asymmetric + Racemic**



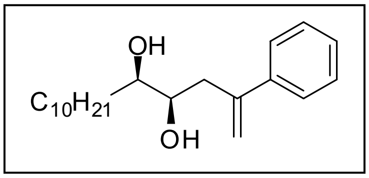
(2*R*,3*R*)-1,5-Diphenylpentane-2,3-diol (Compound SI-8). 50 mg of a white crystalline solid. R_f = 0.21 in 20:1 dichloromethane:diethyl ether. IR(CHCl$_3$) 3577 (s), 2929 (s), 2860 (m), 2360 (m), 2339 (m), 1603 (m), 1497 (s), 1455 (s), 1385 (m) cm^{-1}; ^{1}H NMR: δ 7.32-7.17 (10 H, m, Ar), 3.68 (1H, m), 3.51 (1H, m) 2.84 (2H, m), 2.70 (2H, m), 2.17 (2H, broad), 1.85 (2H, m); ^{13}C NMR: 141.9, 137.9, 129.4 (2C), 128.7 (2C), 126.6, 125.9, 75.0, 72.9, 40.2, 35.5, 31.9. LRMS (ESI) Calc'd for $C_{17}H_{20}O_2$ (M+Na)$^+$: 279.3. Found (M+Na)$^+$: 279.2.

Stereochemistry. Enantiomeric excess was determined by chiral SFC of the diol product. Racemic material was prepared by using tricyclohexylphosphine as the ligand as described in the general procedure. The identity of the major diastereomer was determined bycomparison to the the *syn*-diol prepared via Sharpless asymmetric dihydroxylation (Norrby, P.O,; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35).

Chiral SFC (Chiralpak AD-H, Daicel, 50℃, 150psi, 3mL/min, 2% methanol, only the diastereomer corresponding to the syn diol is shown)



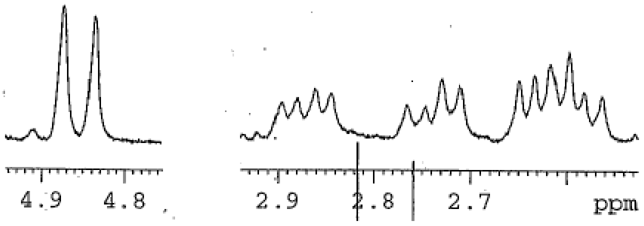
Asymmetric Reaction **Racemic Reaction** **Asymmetric + Racemic**



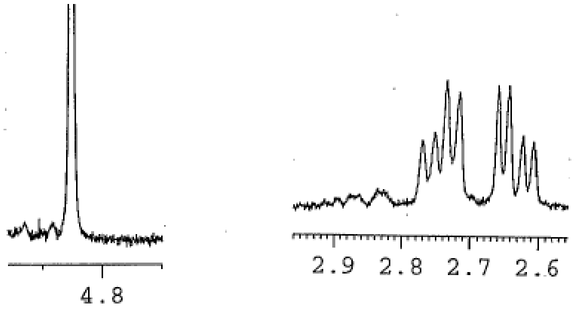
(4*R*,5*R*)-2-Phenylpentadec-1-ene-4,5-diol (Compound SI-9). 35 mg of a white solid. R_f = 0.19 in 20:1 dichloromethane:diethyl ether. IR ($CHCl_3$) 3579 (m), 2929 (s), 2858 (s), 1463 (m), 1380 (m) cm^{-1}; ^1H NMR: δ 7.40-7.25 (5H, m), 5.42 (1H, d, J = 1.2 Hz), 5.18 (1H, d, J = 1.2 Hz), 3.52-3.42 (2H, m), 2.82 (1H, dd, J = 14.4, 4.4 Hz), 2.60 (1H, dd, J = 14.4, 8.8 Hz), 2.06-1.83 (2H, broad), 1.53-1.1.4 (2 H, m), 1.29-1.18 (16 H, m), 0.86 (3 H, t, J = 6.8 Hz); ^{13}C NMR: 144.9, 140.1, 128.3, 127.6, 126.0, 115.4, 73.6, 71.7, 39.8, 33.5, 31.7, 29.4 (2C), 29.4, 29.2(2C), 25.5, 22.5, 13.9. LRMS (ESI) Calc'd for $C_{21}H_{34}O_2$ $(M+Na)^+$: 341.4 Found $(M+Na)^+$: 341.3.

Stereochemistry. Enantiomeric excess was determined by ^1H NMR analysis of the Mosher's ester derivativative prepared using (*S*)-Mosher's acid chloride. Authentic racemic material was prepared by using tricyclohexylphosphine as the ligand as described in the general procedure.

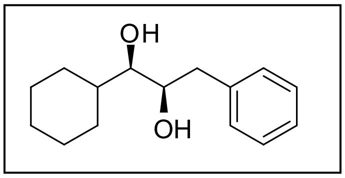
^1H NMR of unpurified Mosher's ester as taken on Bruker DRX 400MHz spectrometer.



Racemic Product



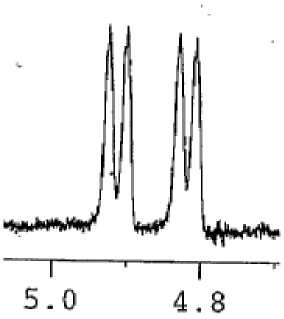
Asymmetric Reaction Product



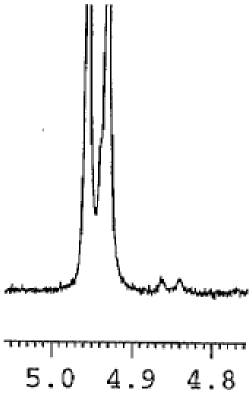
(1*R*,2*R*)-1-Cyclohexyl-3-phenylpropane-1,2-diol (Compound SI-10). 36 mg of a white solid. R_f = 0.43 in 20:1 dichloromethane:diethyl ether. IR ($CHCl_3$) 3572 (m), 2929 (s), 2856 (s), 2364 (m), 2339 (m), 1495 (m), 1453 (s), 1380 (m) cm^{-1}; Major Diastereomer: ^{1}H NMR: δ 7.31–7.21 (5H, m), 3.89 (1H, m), 3.19 (1H, dd, J = 7.5, 3.7 Hz) 2.85 (1 H, dd, J = 13.7, 4.5 Hz), 2.8 (1 H, dd, J = 13.7, 8.3 Hz), 1.86-1.47 (7 H, m), 1.31-0.99 (6H, m); ^{13}C NMR: 138.1, 129.2, 128.5, 126.3, 77.2, 71.3, 40.2, 39.3, 29.4, 27.9, 26.0, 25.9, 25.6. LRMS (ESI) Calc'd for $C_{19}H_{32}O_2$ $(M+Na)^+$: 257.3. Found $(M+Na)^+$: 257.1.

Stereochemistry. Enantiomeric excess was determined by ^{1}H NMR of the Mosher's ester derivative prepared using (*S*)-Mosher's acid chloride. Racemic material was prepared by using tricyclohexylphosphine as the ligand as described in the general procedure. The identity of the major diastereomer was determined by ^{1}H NMR analysis in comparison to authentic *syn*-diol prepared via Sharpless asymmetric dihydroxylation (Norrby, P.O,; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35).

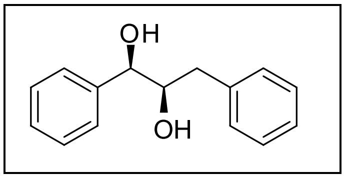
^{1}H NMR of crude Mosher's Esters as taken on Bruker DRX 400MHz spectrometer.



Racemic



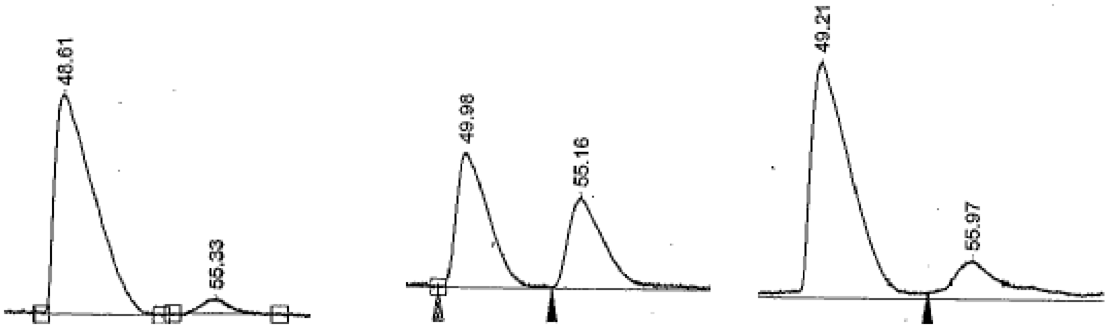
Enantioselective



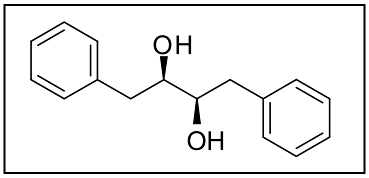
(1*R*,2*R*)-1,3-Diphenylpropane-1,2-diol (Compound SI-11). 44 mg of a white crystalline solid. $R_f = 0.38$ in 2:1 hexanes:ethyl acetate. IR($CHCl_3$) 3593 (s), 2927 (s), 2858 (m), 2366 (m), 2342 (m), 1603 (m), 1495 (s), 1455 (s), 1387 (s), 1324 (m), 1081 (m) cm^{-1}; Major Diastereomer: ^1H NMR: δ 7.42-7.15 (10 H, m), 4.51 (1 H, d, J = 6 Hz), 3.93 (1 H, m) 2.77-2.59 (2H, m), 2.44 (2H, broad); ^{13}C NMR: 140.1, 137.9, 129.2, 128.4, 128.3, 128.4, 126.7, 126.4, 76.1, 75.9, 37.4. LRMS (ESI) Calc'd for $C_{15}H_{16}O_2$ $(M+Na)^+$: 251.2. Found $(M+Na)^+$: 251.1.

Stereochemistry. Enantiomeric excess was determined by chiral SFC analysis of the chiral diol in comparison to authentic racemic material prepared using tricyclohexylphosphine as the ligand. The identity of the major diastereomer was determined by ^1H NMR analysis in comparison to the authentic *syn*-diol prepared via Sharpless asymmetric dihydroxylation (Norrby, P.O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35).

Chiral SFC (Chiralpak AD-H, Daicel, 50℃, 150psi, 3mL/min, 2.5% methanol, only the diastereomer corresponding to the syn diol is shown)



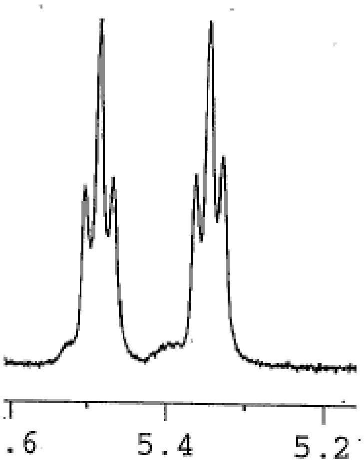
Asymmetric **Racemic** **Asymmetric+ Racemic**



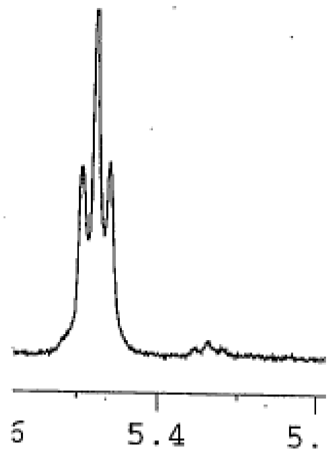
(2*R*,3*R*)-1,4-Diphenylbutane-2,3-diol (Compound SI-12). 52 mg of a white crystalline solid. R_f = 0.25 in 20:1 dichloromethane:diethyl ether. IR ($CHCl_3$) 3593 (s), 3579 (s), 3006 (m), 2927 (s), 2858 (m), 1603 (m), 1497 (s), 1455 (s), 1383 (s), 1088 (m) cm^{-1}; ^1H NMR: δ 7.32–7.19 (10 H, m), 3.74 (2 H, m), 2.86 (2 H, dd, J = 13.6, 4.4 Hz), 2.83 (2 H, dd, J = 13.6, 8.0 Hz), 1.955 (2H, broad, O**H**); ^{13}C NMR: 137.9, 129.2, 128.5, 126.4, 73.8, 40.2. LRMS (ESI) Calc'd for $C_{16}H_{18}O_2$ $(M+Na)^+$: 265.3. Found $(M+Na)^+$: 265.2.

Stereochemistry. Enantiomeric excess was determined by ^1H NMR of the Mosher's ester derivative prepared using (*S*)-Mosher's acid chloride. Racemic material was prepared by using tricyclohexylphosphine as the ligand as described in the general procedure. The identity of the major diastereomer was determined by ^1H NMR analysis in comparison to authentic *syn*-diol prepared via Sharpless asymmetric dihydroxylation (Norrby, P.O,; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35).

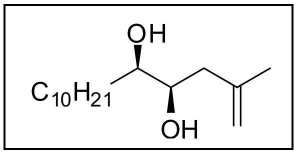
^1H NMR of crude Mosher's ester as taken on Bruker DRX 400MHz spectrometer.



Racemic



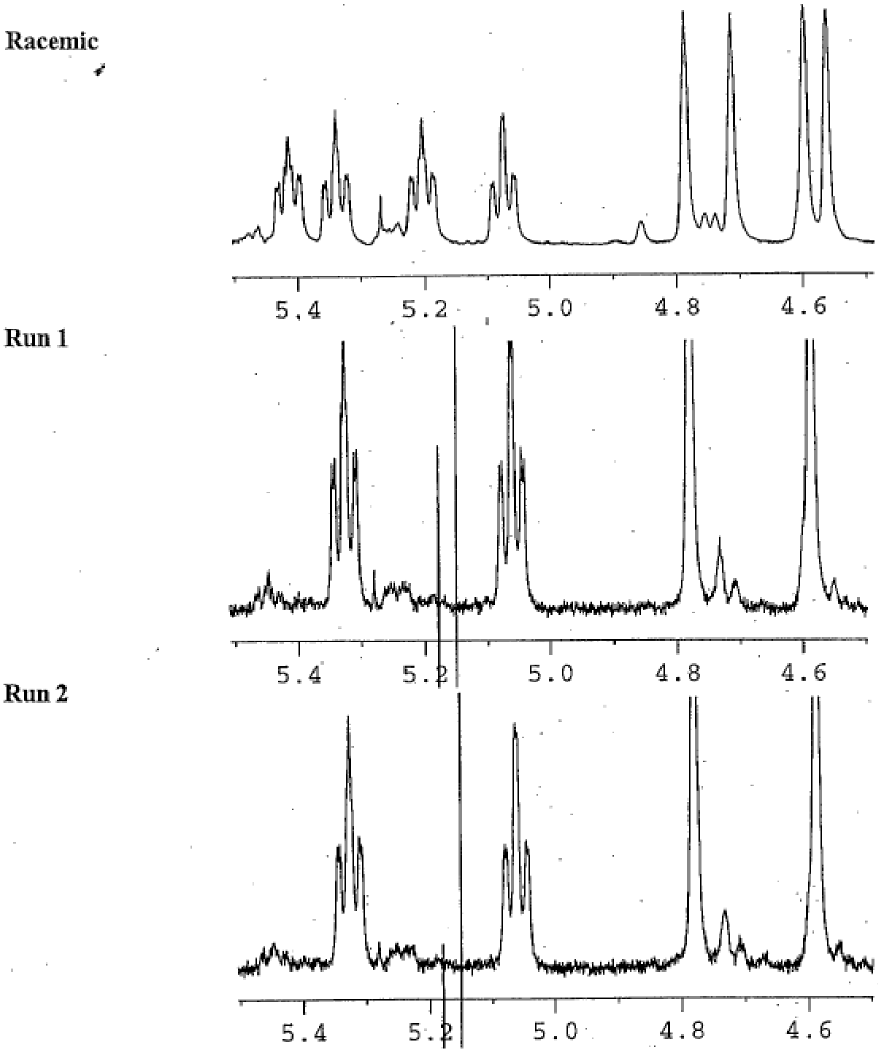
Enantioselective

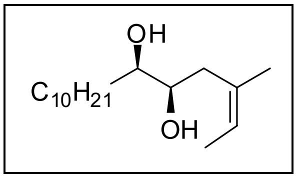


(4*R*,5*R*)-2-Methylpentadec-1-ene-4,5-diol (Compound SI-13). 33 mg of a white solid. $R_f = 0.15$ in 20:1 dichloromethane:diethyl ether. IR ($CHCl_3$) 3575 (m), 2929 (s), 2856 (s), 1463 (m), 1380 (m), 1090 (m) cm^{-1}; ^1H NMR: δ 4.89 (1 H, s), 4.81 (1 H, s), 3.57 (1 H, m), 3.41 (1 H, m), 2.23-2.12 (2H, m), 1.90-1.63 (2 H, broad), 1.76 (3 H, s), 1.51-1.41 (2H, m), 1.38-1.19 (16 H, s), 0.87-0.84 (3 H, t, J = 6.8 Hz); ^{13}C NMR: 142.2, 113.6, 74.1, 72.0, 42.2, 33.5, 31.7, 29.5, 29.4 (2C), 29.4, 29.1, 25.5, 22.5, 22.2, 13.9. HRMS (ESI) Calc'd for $C_{16}H_{32}O_2$ $(M+Na)^+$: 279.42 Found $(M+Na)^+$: 279.3.

Proof of Stereochemistry. Enantiomeric excess was determined by ^1H NMR of the Mosher's ester derivative prepared using (*S*)-Mosher's acid chloride. Racemic material was prepared by using tricyclohexylphosphine as the ligand as described in the general procedure.

^1H NMR of crude esterification as taken on Bruker DRX 400MHz spectrometer.



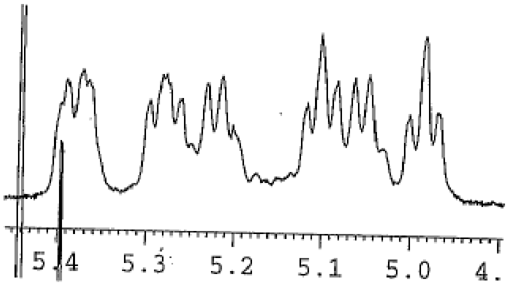


(5*R*,6*R*,Z)-3-Methylhexadec-2-ene-5,6-diol (Compound SI-14). 25 mg of a white solid. R_f = 0.16 in 20:1 dichloromethane:diethyl ether. IR ($CHCl_3$) 3579 (m), 2929 (s), 2858 (s), 1457 (m), 1380 (m), 1090 (m) cm^{-1}; ^1H NMR: δ 5.43 (1 H, q, J = 6.8 Hz), 3.57 (1 H, m), 3.41 (1 H, m), 2.41 (1 H, dd, J = 13.2, 9.4 Hz), 2.06 (1 H, dd, J = 13.6, 4.4 Hz), 1.71 (3H, s), 1.60 (3H, d, J = 6.8 Hz), 1.510-1.409 (2H, m), 1.35-1.17 (16H, s), 0.86 (3H, t, J = 6.8 Hz); ^{13}C NMR: 131.9, 122.9, 74.0, 71.7, 35.5, 33.6, 31.7, 29.5, 29.4 (2C), 29.2, 25.5, 23.5, 23.3, 22.5, 13.9, 13.4. LRMS (ESI) Calc'd for $C_{17}H_{34}O_2$ $(M+Na)^+$: 293.4. Found $(M+Na)^+$: 293.3.

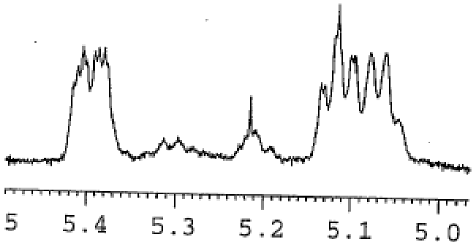
Proof of Stereochemistry. Enantiomeric excess was determined by ^1H NMR of the Mosher's ester derivative prepared using (*S*)-Mosher's acid chloride. Racemic material was prepared by using tricyclohexylphosphine as the ligand as described in the general procedure.

^1H NMR of crude Mosher's ester as taken on Bruker DRX 400MHz spectrometer.

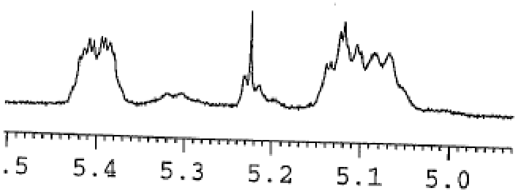
Racemic

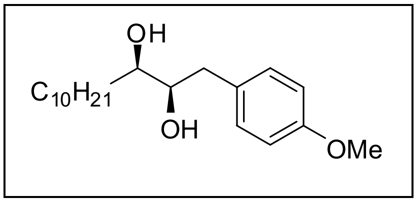


Run 1



Run 2

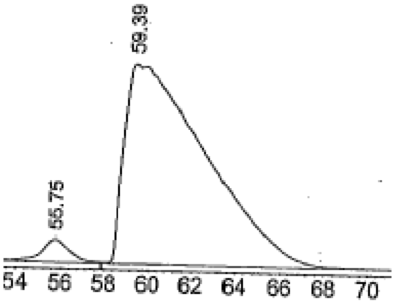




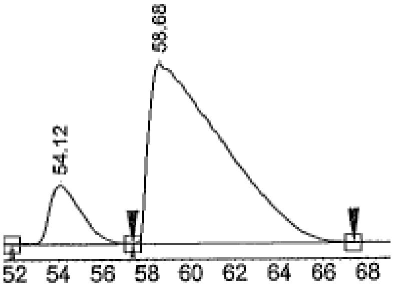
(2*R*,3*R*)-1-(4-Methoxyphenyl)tridecane-2,3-diol (Compound SI-15). 47 mg of a white solid. R_f = 0.17 in 20:1 dichloromethane:diethyl ether. IR ($CHCl_3$) 3579 (m), 2929 (s), 2858 (s), 1613 (m), 1513 (s), 1465 (m), 1380 (m), 1302 (m), 1250 (m), 1177 (m) cm^{-1}; ^{1}H NMR: δ 7.13 (2 H, d, J = 8.8 Hz), 6.84 (2 H, d, J = 8.8 Hz), 3.78 (3H, s), 3.60 (1H, m), 3.45 (1H, m), 2.82 (1H, dd, J = 14.0, 4.4 Hz), 2.66 (1H, dd, J = 14.0, 8.6 Hz), 1.82-1.55 (2H, broad), 1.55-1.48 (2H, m), 1.28-1.24 (16H, m), 0.88-0.84 (3H, t, J = 6.8 Hz); ^{13}C NMR: 158.2, 130.2, 129.8, 113.9, 74.9, 73.4, 55.1, 39.1, 33.6, 31.7, 29.5, 29.4(3C), 29.2, 25.5, 22.5, 13.9. HRMS (ESI) Calc'd for $C_{20}H_{34}O_3$ $(M+Na)^+$: 345.4. Found $(M+Na)^+$: 345.3.

Proof of Stereochemistry. Enantiomeric excess was determined by chiral SFC of the diol product. Racemic material was prepared by using tricyclohexylphosphine as the ligand as described in the general procedure.

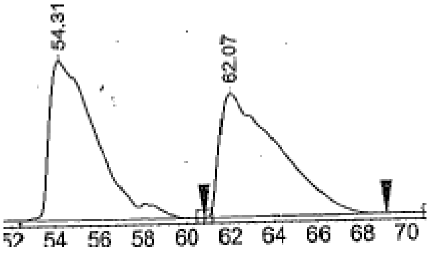
Chiral SFC (Chiralpak AD-H, Daicel, 50℃,150psi, 3mL/min, 2% methanol, only the diastereomer corresponding to the syn diol is shown)



Asymmetric Reaction

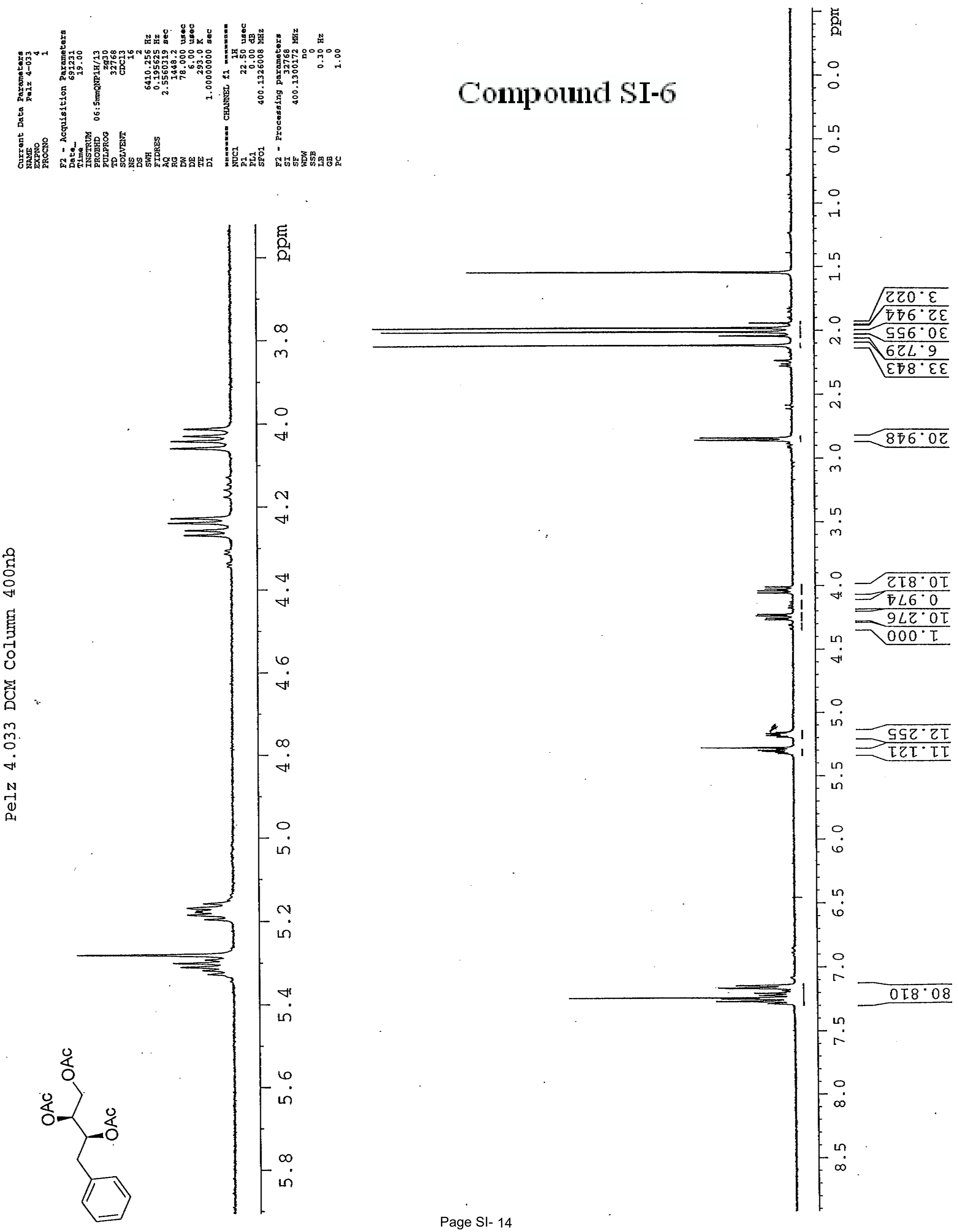


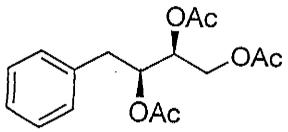
Asymmetric + Racemic



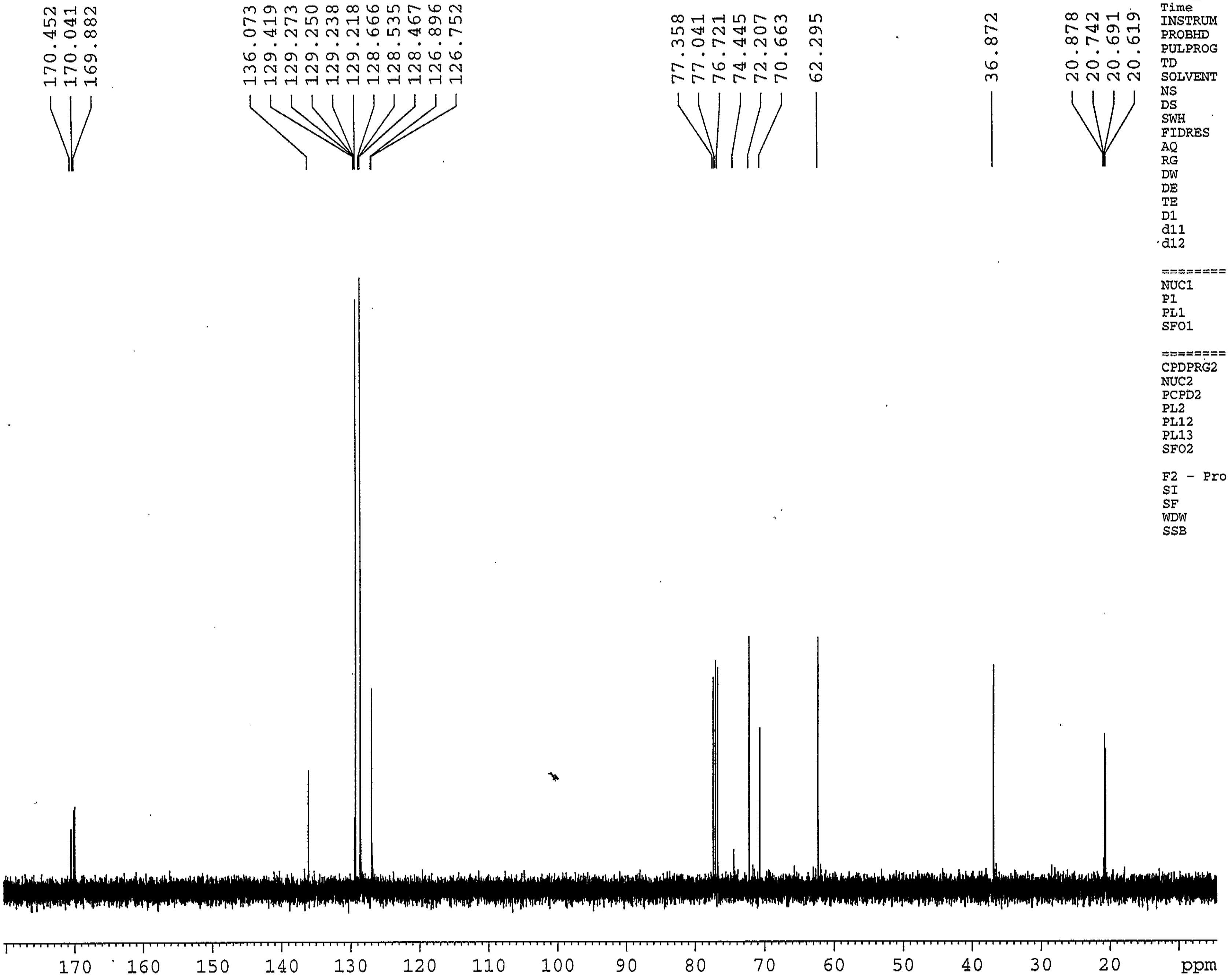
Racemic Reaction

Compound SI-6





Pelz 4.028 Supp Info 400nb



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EXPNO                    4
PROCNO                   1

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Time                 19.00
INSTRUM
PROBHD                  40
PULPROG               zg30
TD                   32768
SOLVENT              CDC13
NS                      16
DS                       2
SWH               5995.204 Hz
FIDRES            0.182959 Hz
AQ               2.7329011 sec
RG                    71.8
DW                  83.400 use
DE                    6.00 use
TE                   300.0 K
D1              1.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

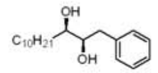
======== CHANNEL f1 =======
NUC1                    1H
P1                   10.10 use
PL1                  -3.00 dB
SFO1           399.8023988 MHz

======== CHANNEL f2 =======
CPDPRG2
NUC2                   off
PCPD2               100.00 use
PL2                 120.00 dB
PL12                120.00 dB
PL13                120.00 dB
SFO2           399.8000000 MHz

F2 - Processing parameters
SI                   32768
SF             100.5297927 MHz
WDW                     no
SSB                      0
```

Compound SI-6

Compound SI-7



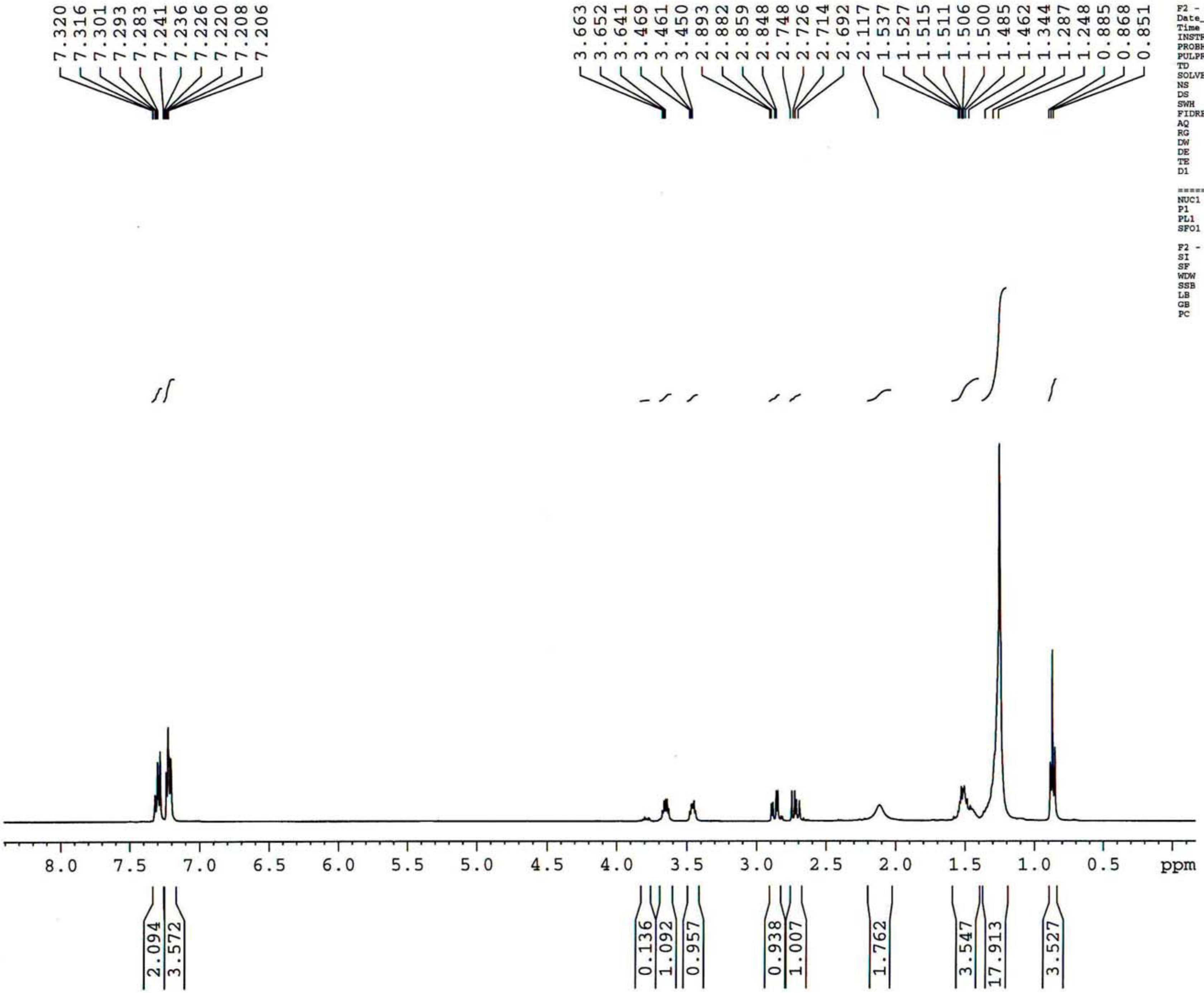
Pelz 4.058 Supp Info 400nb

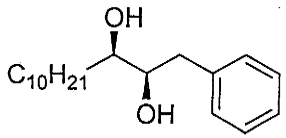
```
Current Data Parameters
NAME             Pelz 4-058
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20060227
Time                   8.56
INSTRUM               spect
PROBHD   5mm QNP 1H/13C
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       24
DS                        2
SWH              6410.256 Hz
FIDRES           0.195625 Hz
AQ              2.5559540 sec
RG                      128
DW                 78.000 usec
DE                   6.00 usec
TE                  293.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                  24.20 usec
PL1                  0.00 dB
SFO1         400.0524003 MHz

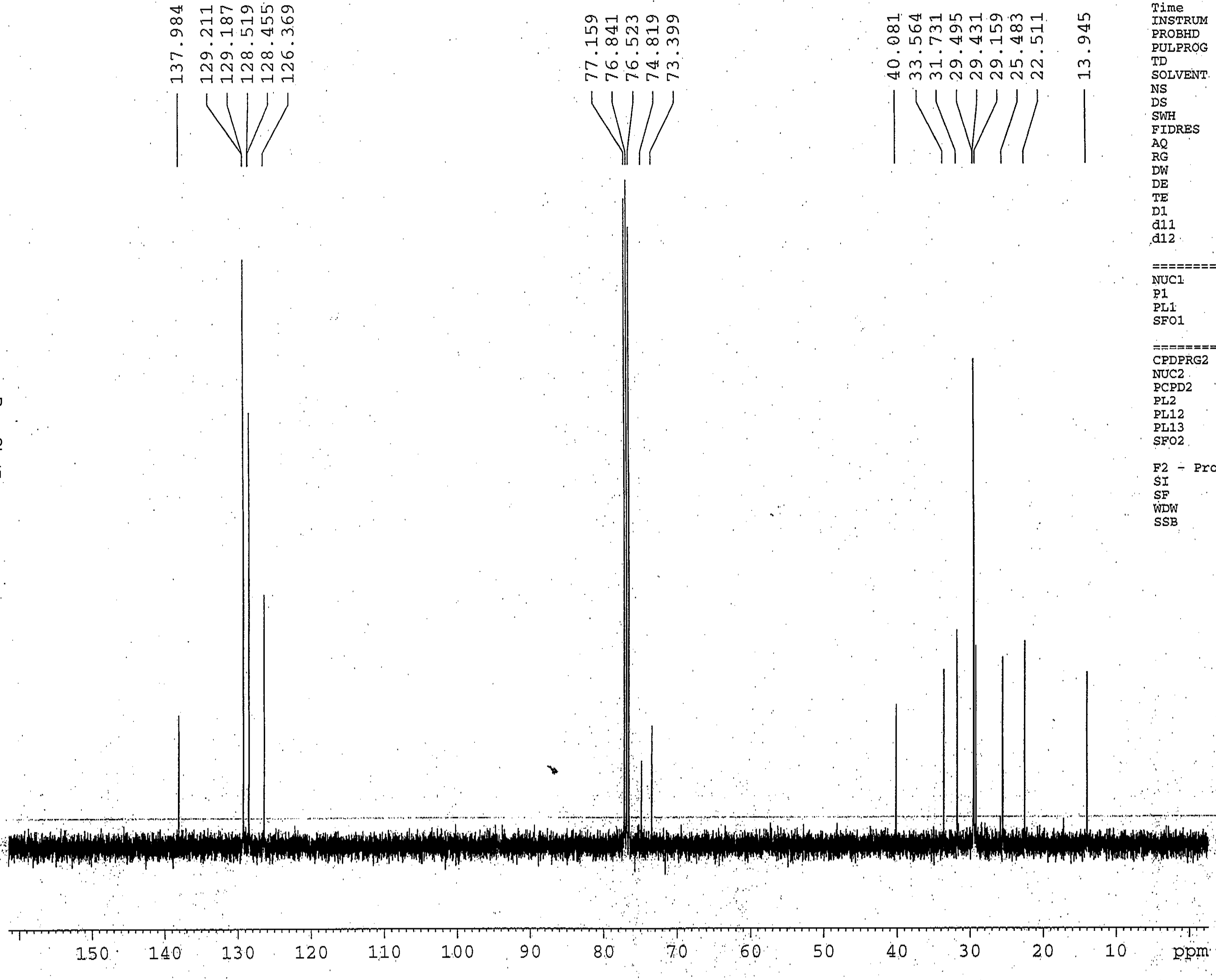
F2 - Processing parameters
SI                    32768
SF           400.0500200 MHz
WDW                      no
SSB                       0
LB                   0.00 Hz
GB                        0
PC                     1.00
```





Compound SI-7

Pelz 4.059 Supp Info 400nb



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Current Data Parameters
NAME             Pelz 4-059
EXPNO                     6
PROCNO                    1

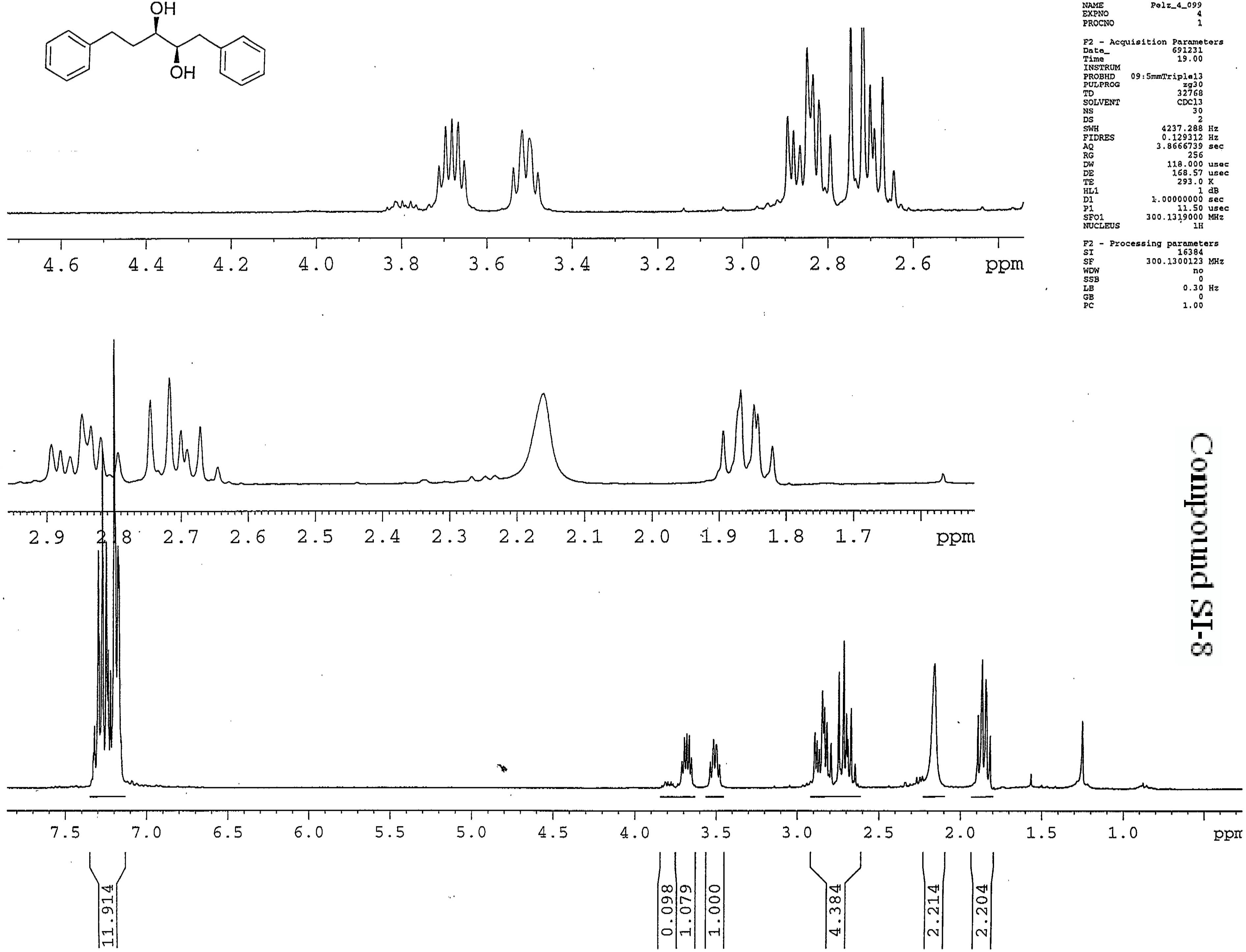
F2 - Acquisition Parameters
Date_              20050928
Time                  17.00
INSTRUM               spect
PROBHD   5mm QNP 1H/13C
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6410.256 Hz
FIDRES             0.195625 Hz
AQ                2.5560319 sec
RG                   1448.2
DW                   78.000 use
DE                     6.00 use
TE                    293.0 K
D1               1.00000000 sec
d11              0.03000000 sec
d12              0.00002000 sec

======== CHANNEL f1 =======
NUC1                     1H
P1                    24.20 use
PL1                    0.00 dB
SFO1         400.0524003 MHz

======== CHANNEL f2 =======
CPDPRG2
NUC2                    off
PCPD2                100.00 use
PL2                    0.00 dB
PL12                  14.50 dB
PL13                  14.50 dB
SFO2         400.0500000 MHz

F2 - Processing parameters
SI                    32768
SF           100.5926741 MHz
WDW                      no
SSB                       0
```

Pelz 4.099 Supp Info 300MHz



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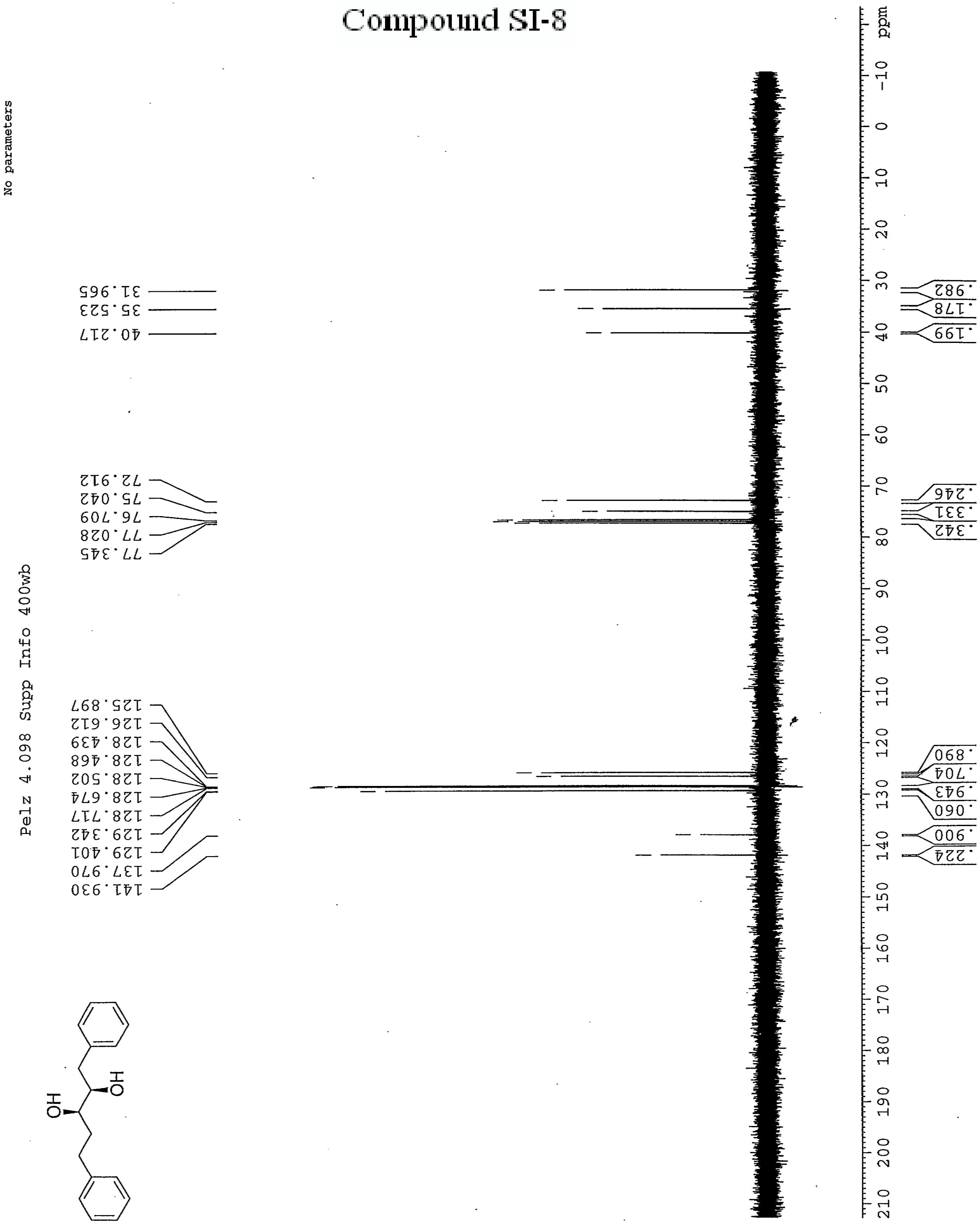
Current Data Parameters
NAME             Pelz_4_099
EXPNO                     4
PROCNO                    1

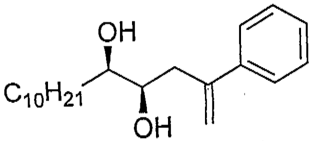
F2 - Acquisition Parameters
Date_                691231
Time                  19.00
INSTRUM
PROBHD    09:5mmTriple13
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      30
DS                       2
SWH            4237.288 Hz
FIDRES         0.129312 Hz
AQ           3.8666739 sec
RG                     256
DW             118.000 usec
DE              168.57 usec
TE                293.0 K
HL1                   1 dB
D1          1.00000000 sec
P1               11.50 usec
SFO1       300.1319000 MHz
NUCLEUS                 1H

F2 - Processing parameters
SI                   16384
SF         300.1300123 MHz
WDW                     no
SSB                      0
LB                 0.30 Hz
GB                       0
PC                    1.00
```

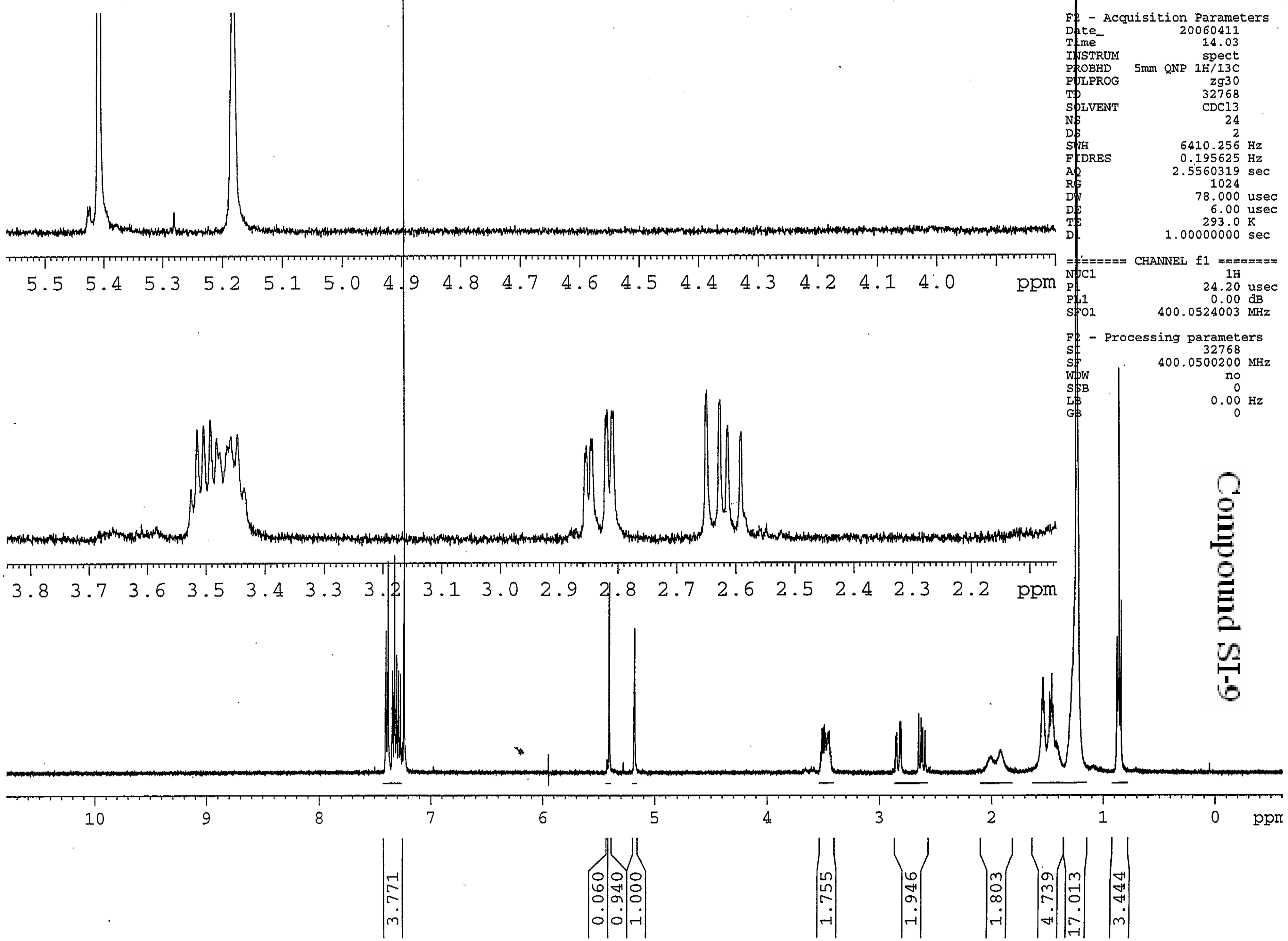
Compound SI-8

Compound SI-8





Pelz 4.133 Supp Info 400nb



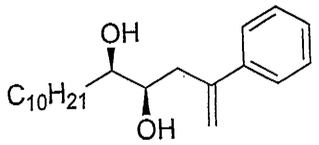
```
Current Data Parameters
NAME          Pelz 4-133
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060411
Time               14.03
INSTRUM            spect
PROBHD   5mm QNP 1H/13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    24
DS                     2
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ             2.5560319 sec
RG                  1024
DW                78.000 usec
DE                  6.00 usec
TE                 293.0 K
D1            1.00000000 sec

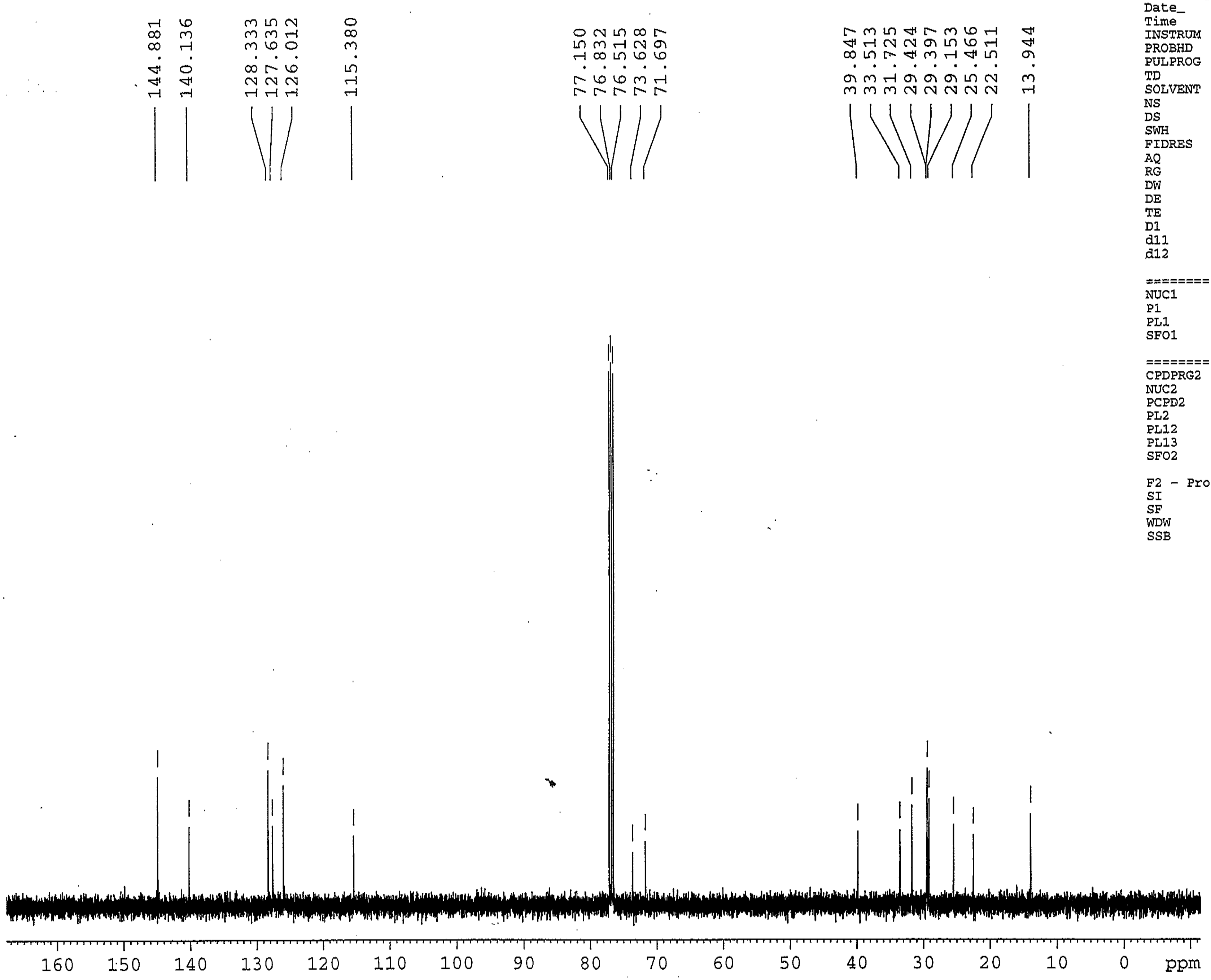
======== CHANNEL f1 ========
NUC1                  1H
P1                 24.20 usec
PL1                 0.00 dB
SFO1         400.0524003 MHz

F2 - Processing parameters
SI                 32768
SF           400.0500200 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
```

Compound SI-9



Pelz 4.133 13C Supp Info 400nb



```
Current Data Parameters
NAME          Pelz 4-133
EXPNO                  7
PROCNO                 1

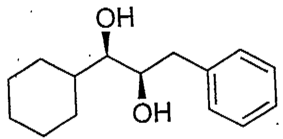
F2 - Acquisition Parameters
Date_             691231
Time               19.00
INSTRUM
PROBHD   06:5mmQNP1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    2
SWH           26246.719 Hz
FIDRES         0.400493 Hz
AQ            1.2485298 sec
RG               7298.2
DW               19.050 use
DE                 6.00 use
TE                300.0 K
D1           0.80000001 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 =======
NUC1                 13C
P1                  6.00 use
PL1                 0.00 dB
SFO1      100.6036782 MHz

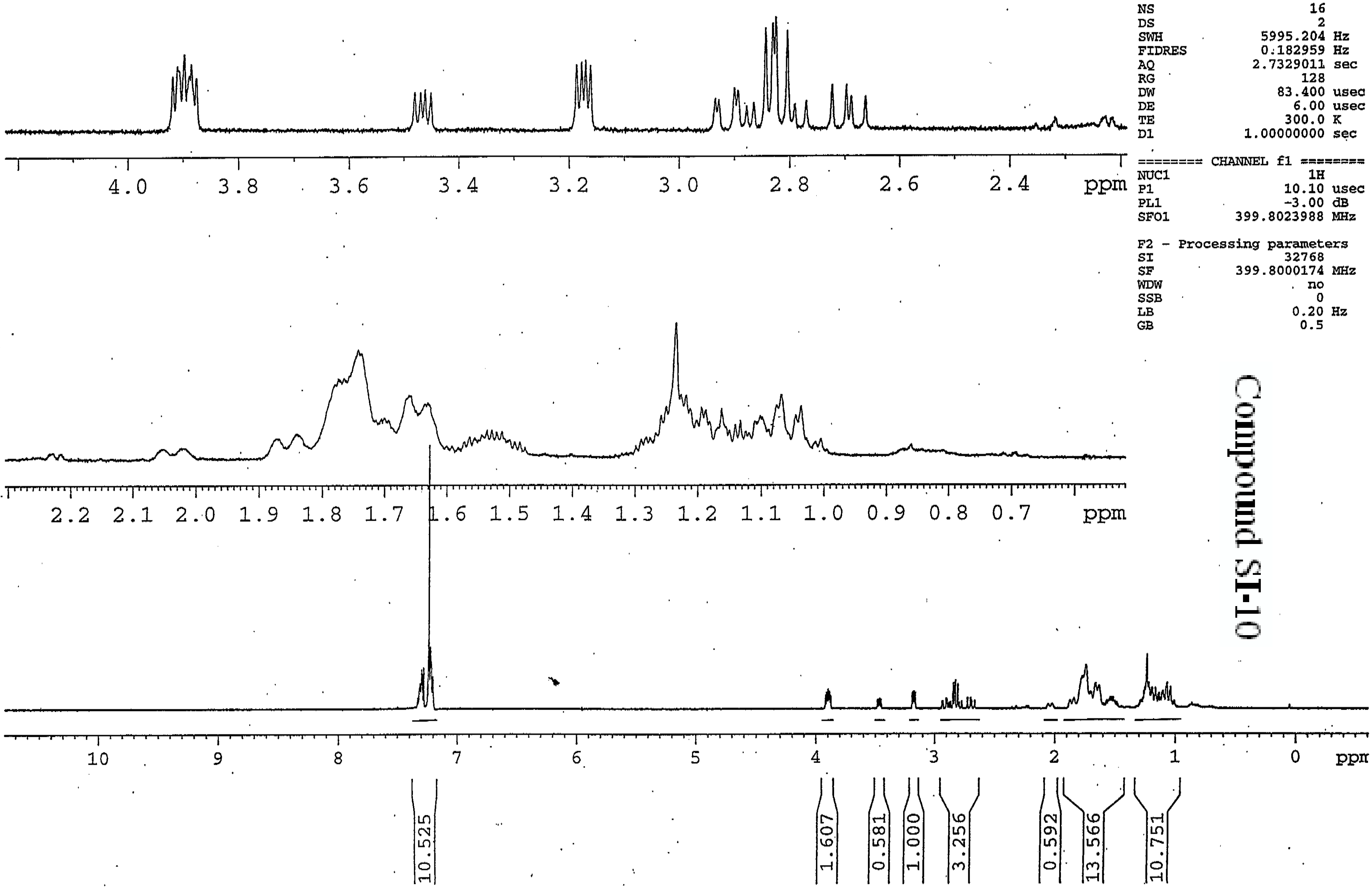
======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 use
PL2                -6.00 dB
PL12               13.80 dB
PL13               14.50 dB
SFO2      400.0516002 MHz

F2 - Processing parameters
SI                 32768
SF        100.5926741 MHz
WDW                   no
SSB                    0
```

Compound SI-9



Pelz 4.103 Column 400wb



```
Current Data Parameters
NAME          Pelz 4-103
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_             691231
Time               19.00
INSTRUM
PROBHD                40
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5995.204 Hz
FIDRES          0.182959 Hz
AQ             2.7329011 sec
RG                   128
DW                83.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.10 usec
PL1                -3.00 dB
SFO1         399.8023988 MHz

F2 - Processing parameters
SI                 32768
SF           399.8000174 MHz
WDW                   no
SSB                    0
LB                  0.20 Hz
GB                   0.5
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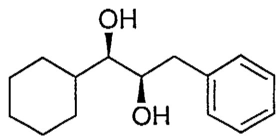
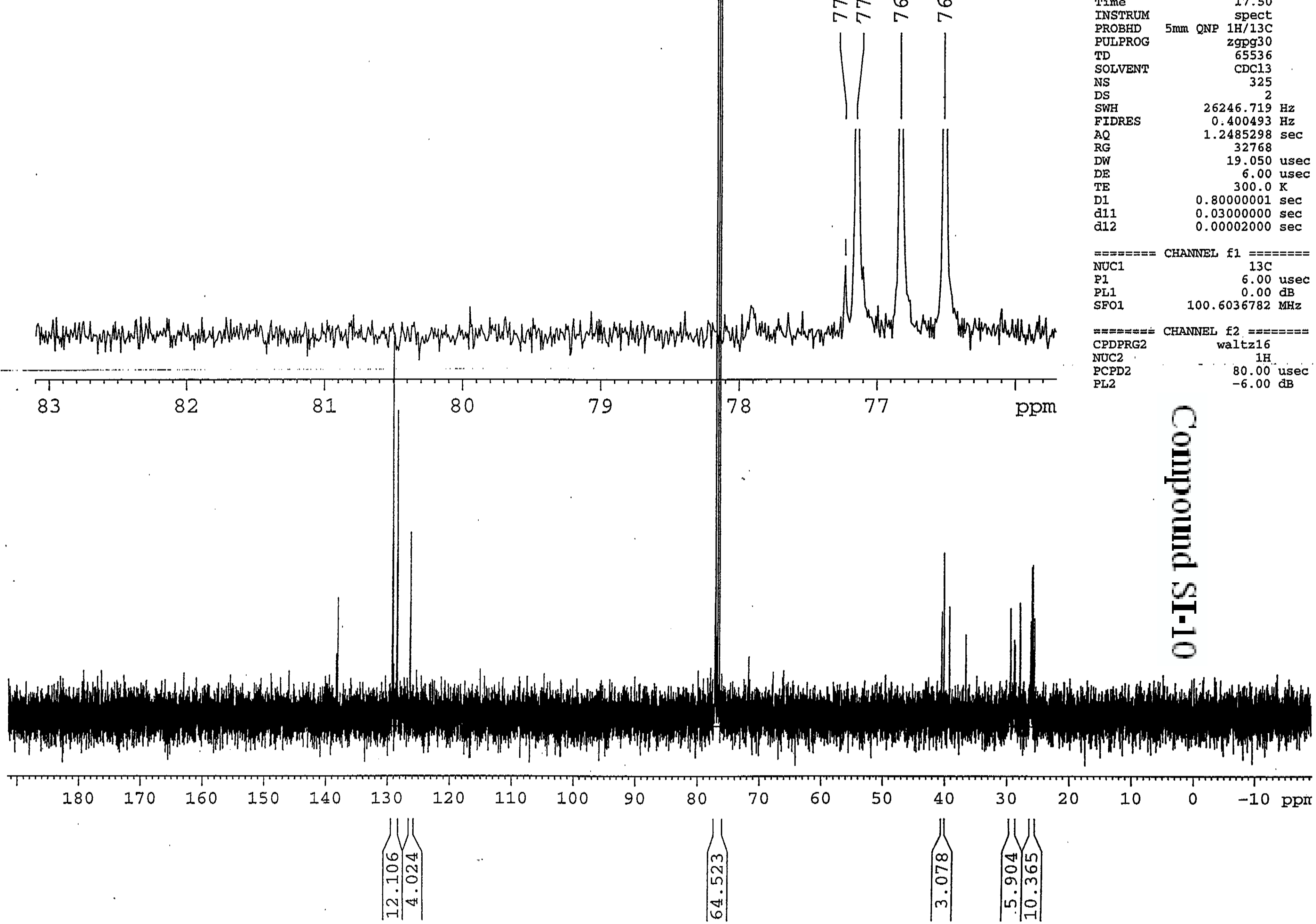
Compound SI-10



Pelz 4.104 Supp Info 400nb



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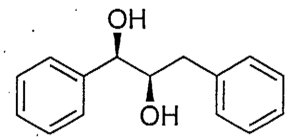
Current Data Parameters
NAME          Pelz 4-104
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060313
Time               17.50
INSTRUM            spect
PROBHD   5mm QNP 1H/13C
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   325
DS                     2
SWH            26246.719 Hz
FIDRES          0.400493 Hz
AQ             1.2485298 sec
RG                 32768
DW                19.050 usec
DE                  6.00 usec
TE                 300.0 K
D1            0.80000001 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.00 usec
PL1                 0.00 dB
SFO1         100.6036782 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
```

Compound SI-10



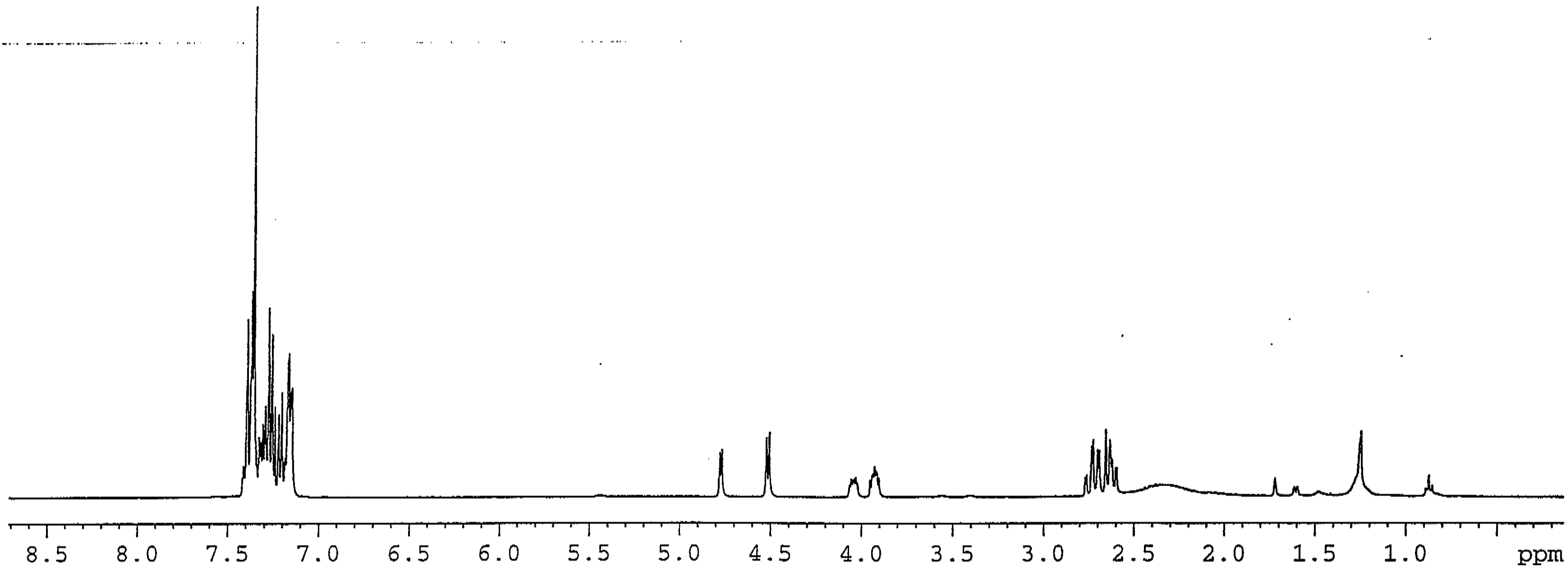
```
Current Data Parameters
NAME            Pelz 4-089
EXPNO                    3
PROCNO                   1

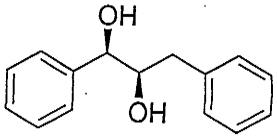
F2 - Acquisition Parameters
Date_             20060306
Time                  9.32
INSTRUM              spect
PROBHD   5mm QNP 1H/13C
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      30
DS                       2
SWH               6410.256 Hz
FIDRES            0.195625 Hz
AQ               2.5560319 sec
RG                   322.5
DW                  78.000 usec
DE                    6.00 usec
TE                   293.0 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   24.20 usec
PL1                   0.00 dB
SFO1           400.0524003 MHz

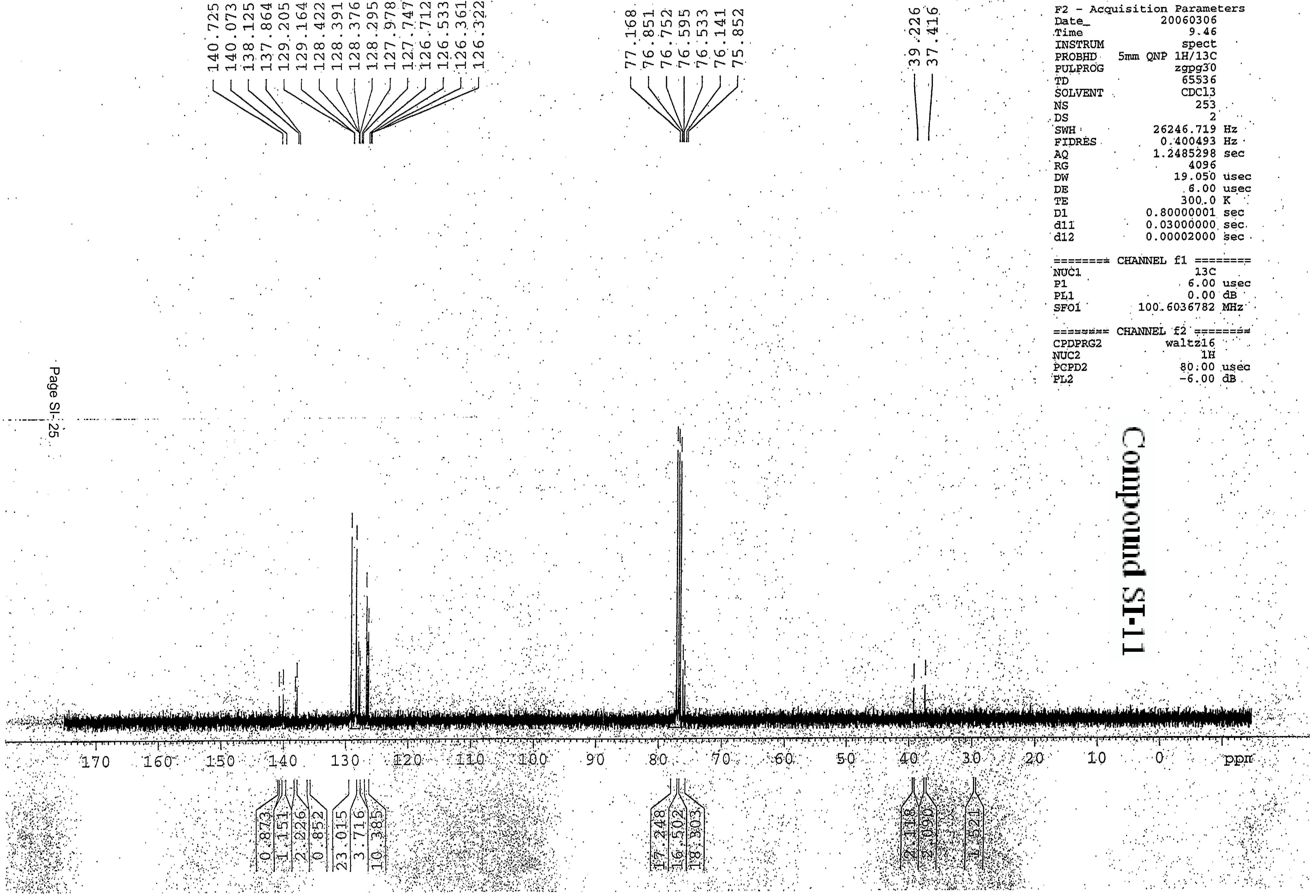
F2 - Processing parameters
SI                   32768
SF             400.0500200 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
```

Compound SI-11





Pelz 4.089 Supp Info 400nb



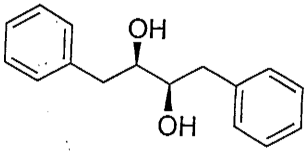
```
Current Data Parameters
NAME           Pelz 4-089
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060306
Time                 9.46
INSTRUM             spect
PROBHD   5mm QNP 1H/13C
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    253
DS                      2
SWH            26246.719 Hz
FIDRES          0.400493 Hz
AQ             1.2485298 sec
RG                   4096
DW                 19.050 usec
DE                   6.00 usec
TE                  300.0 K
D1             0.80000001 sec
d11            0.03000000 sec
d12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.00 usec
PL1                  0.00 dB
SFO1       100.6036782 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -6.00 dB
```

Compound SI-11



Pelz 4.111 Supp Info 400nb

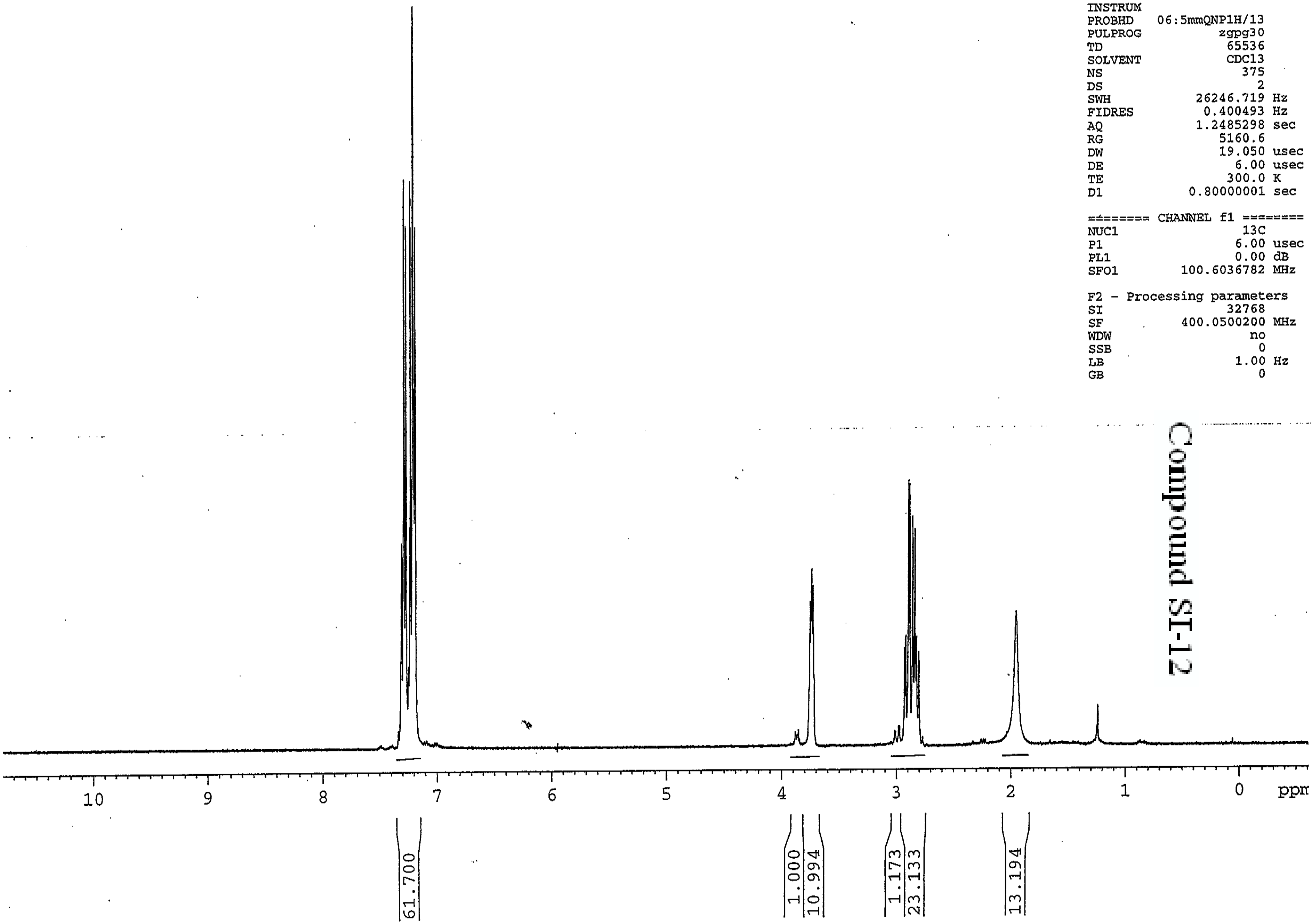
```
Current Data Parameters
NAME           Pelz 4-111
EXPNO                   2
PROCNO                  1

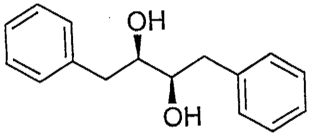
F2 - Acquisition Parameters
Date_              691231
Time                19.00
INSTRUM
PROBHD   06:5mmQNP1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   375
DS                     2
SWH            26246.719 Hz
FIDRES          0.400493 Hz
AQ             1.2485298 sec
RG                5160.6
DW                19.050 usec
DE                  6.00 usec
TE                 300.0 K
D1            0.80000001 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.00 usec
PL1                 0.00 dB
SFO1         100.6036782 MHz

F2 - Processing parameters
SI                 32768
SF           400.0500200 MHz
WDW                   no
SSB                    0
LB                  1.00 Hz
GB                     0
```

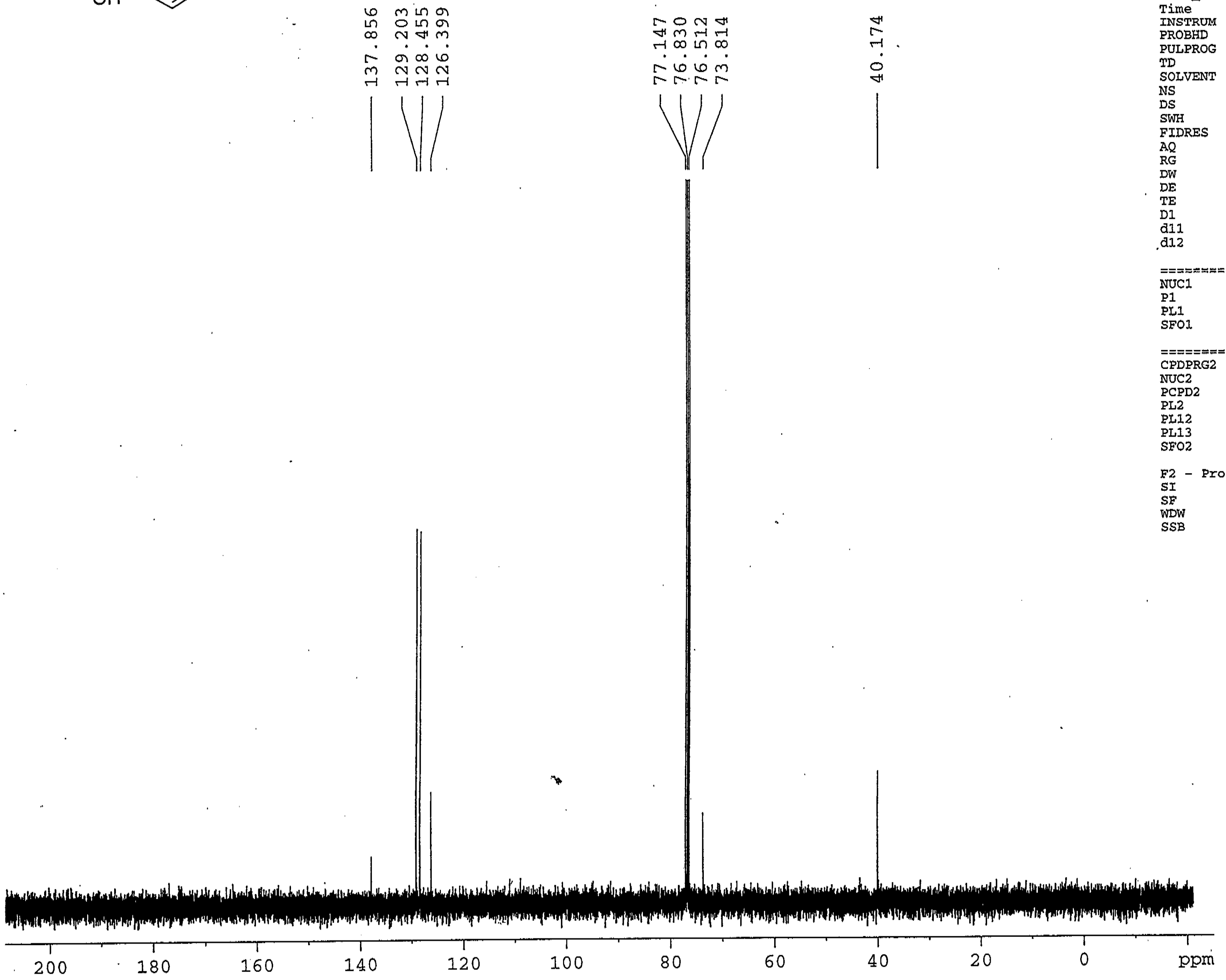
Compound SI-12





Compound SI-12

Pelz 4.110 Supp Info 400nb



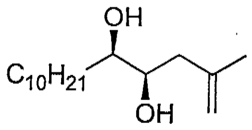
```
Current Data Parameters
NAME             Pelz 4-110
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20060315
Time                  18.37
INSTRUM               spect
PROBHD     5mm QNP 1H/13C
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     375
DS                       2
SWH              26246.719 Hz
FIDRES            0.400493 Hz
AQ               1.2485298 sec
RG                  5160.6
DW                  19.050 use
DE                    6.00 use
TE                   300.0 K
D1              0.80000001 sec
d11             0.03000000 sec
d12             0.00002000 sec

======== CHANNEL f1 =======
NUC1                   13C
P1                    6.00 use
PL1                   0.00 dB
SFO1        100.6036782 MHz

======== CHANNEL f2 =======
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 use
PL2                  -6.00 dB
PL12                 13.80 dB
PL13                 14.50 dB
SFO2        400.0516002 MHz

F2 - Processing parameters
SI                   32768
SF          100.5926741 MHz
WDW                     no
SSB                      0
```



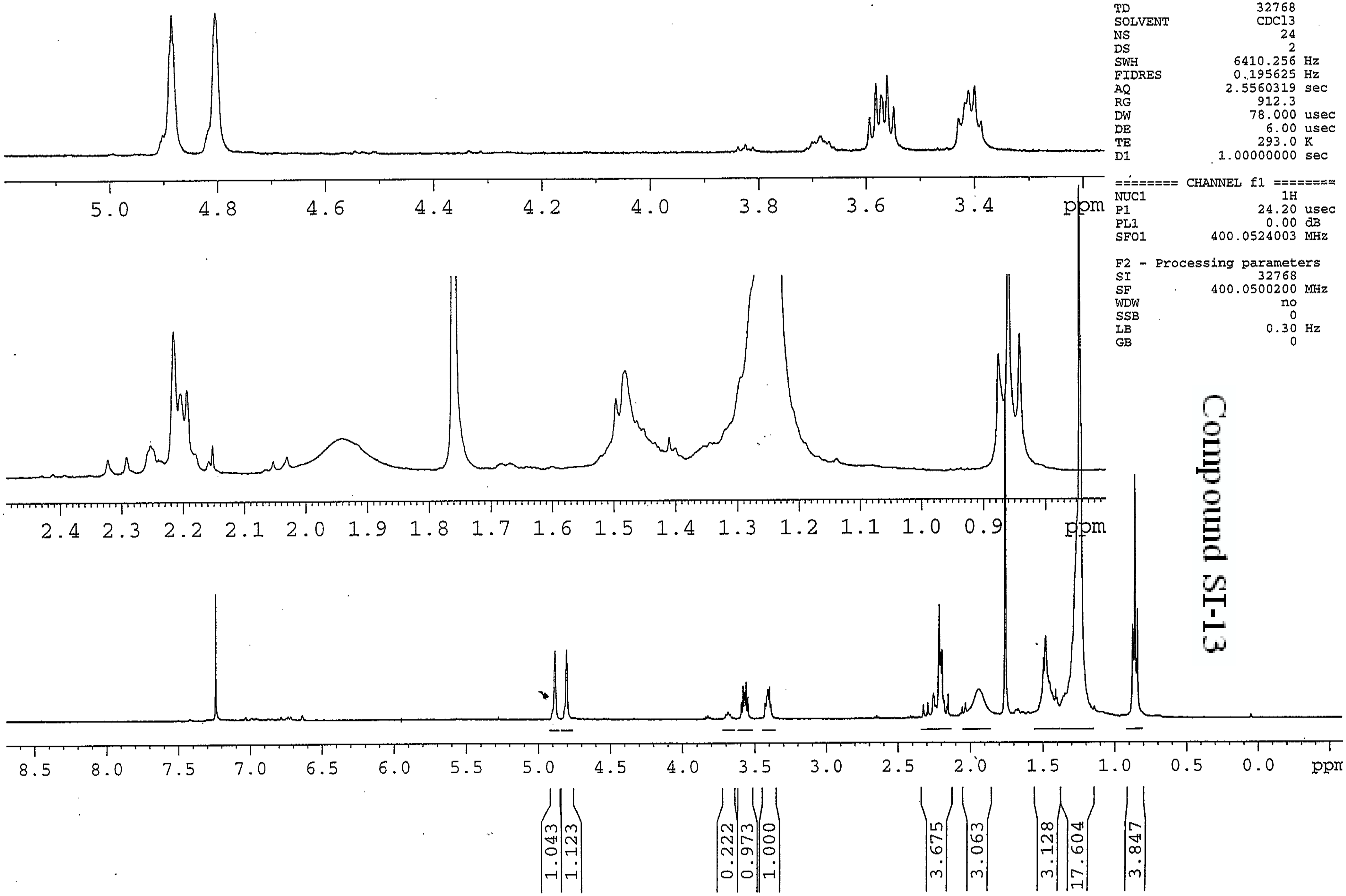
Pelz 4.119 Supp Info 400nb

```
Current Data Parameters
NAME          Pelz 4-119
EXPNO                  3
PROCNO                 1

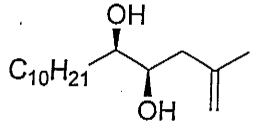
F2 - Acquisition Parameters
Date_             691231
Time               19.00
INSTRUM
PROBHD   06:5mmQNP1H/13
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    24
DS                     2
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ             2.5560319 sec
RG                 912.3
DW                78.000 usec
DE                  6.00 usec
TE                 293.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 24.20 usec
PL1                 0.00 dB
SFO1         400.0524003 MHz

F2 - Processing parameters
SI                 32768
SF           400.0500200 MHz
WDW                   no
SSB                    0
LB                  0.30 Hz
GB                     0
```



Compound SI-13



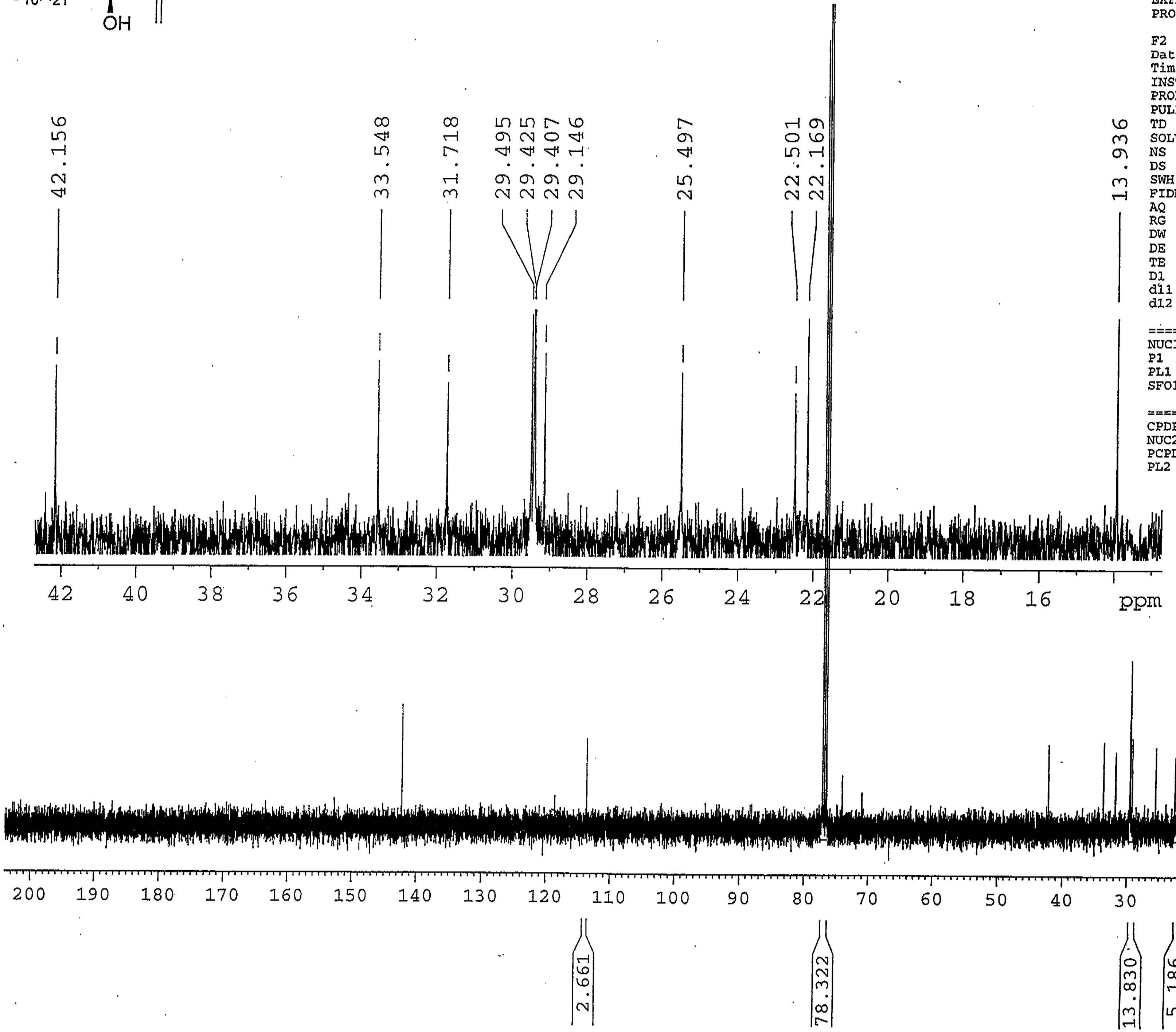
Pelz 4.119 13C Supp Info 400nb

```
Current Data Parameters
NAME             Pelz 4-119
EXPNO                     4
PROCNO                    1

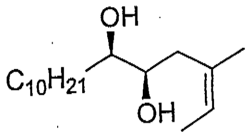
F2 - Acquisition Parameters
Date_                691231
Time                  19.00
INSTRUM
PROBHD    06:5mmQNP1H/13
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       24
DS                        2
SWH               6410.256 Hz
FIDRES            0.195625 Hz
AQ               2.5560319 sec
RG                    406.4
DW                   78.000 usec
DE                     6.00 usec
TE                    293.0 K
D1              1.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    24.20 usec
PL1                    0.00 dB
SFO1           400.0524003 MHz

======== CHANNEL f2 ========
CPDPRG2
NUC2                    off
PCPD2                100.00 usec
PL2                    0.00 dB
```

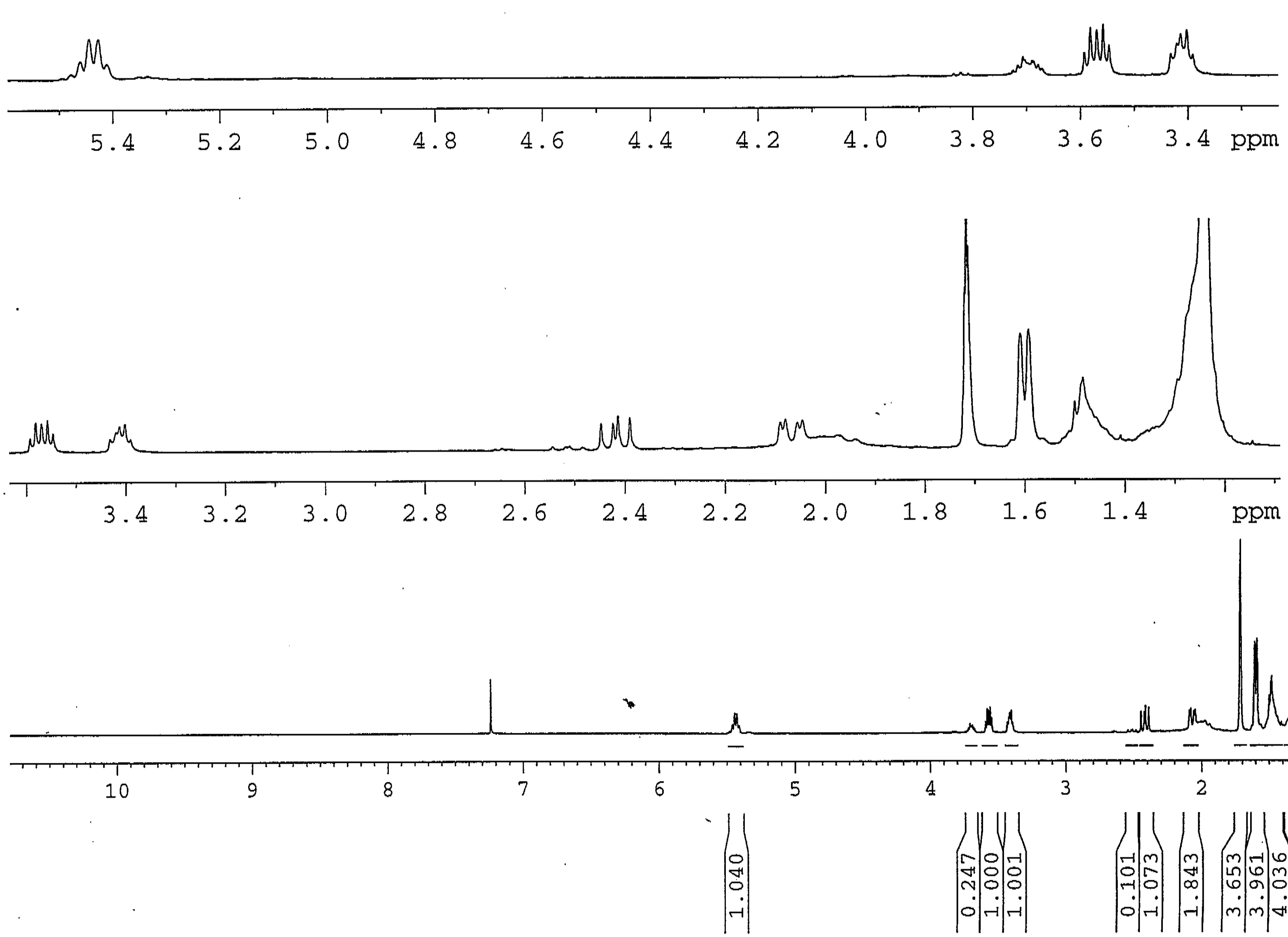


Compound SI-13



Compound SI-14

Pelz 4.162 Supp Info 400nb

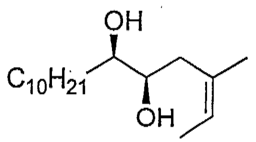


```
Current Data Parameters
NAME            Pelz 4-162
EXPNO                    3
PROCNO                   1

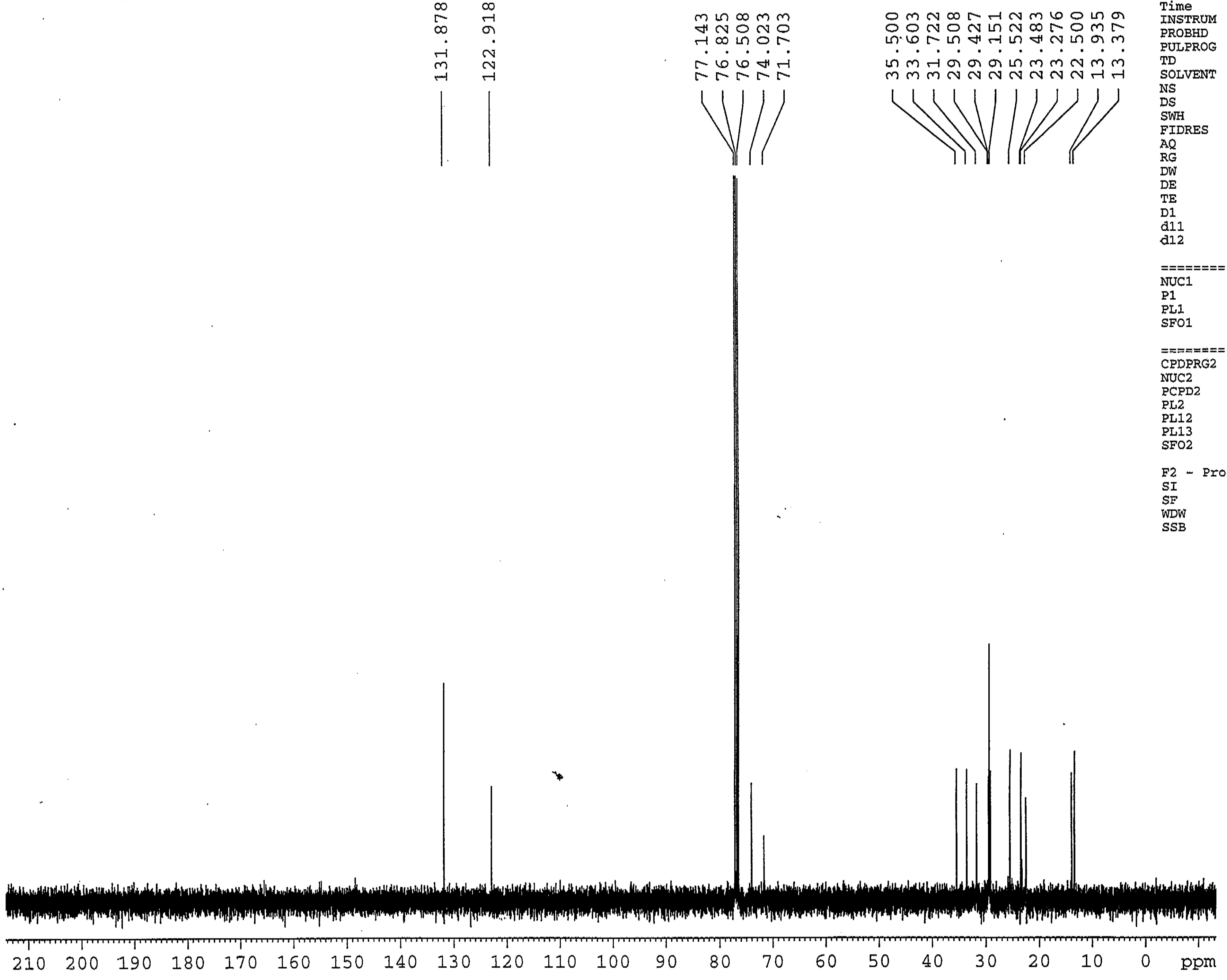
F2 - Acquisition Parameters
Date_             20060412
Time                 15.47
INSTRUM              spect
PROBHD    5mm QNP 1H/13C
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      24
DS                       2
SWH               6410.256 Hz
FIDRES            0.195625 Hz
AQ               2.5560319 sec
RG                   228.1
DW                  78.000 usec
DE                    6.00 usec
TE                   293.0 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   24.20 usec
PL1                   0.00 dB
SFO1          400.0524003 MHz

F2 - Processing parameters
SI                   32768
SF            400.0500200 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
```



Pelz 4.162 13C Supp Info 400nb



```
Current Data Parameters
NAME          Pelz 4-162
EXPNO                  4
PROCNO                 1

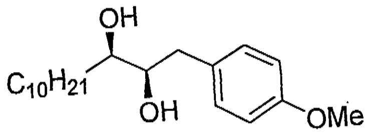
F2 - Acquisition Parameters
Date_           20060412
Time               16.33
INSTRUM            spect
PROBHD   5mm QNP 1H/13C
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     2
SWH           26246.719 Hz
FIDRES         0.400493 Hz
AQ            1.2485298 sec
RG                 32768
DW                19.050 use
DE                  6.00 use
TE                 300.0 K
D1            0.80000001 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 =======
NUC1                 13C
P1                  6.00 use
PL1                 0.00 dB
SFO1      100.6036782 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 use
PL2                -6.00 dB
PL12               13.80 dB
PL13               14.50 dB
SFO2      400.0516002 MHz

F2 - Processing parameters
SI                 32768
SF        100.5926741 MHz
WDW                   no
SSB                    0
```

Compound SI-14



Pelz 4.172 Supp Info 400-nb

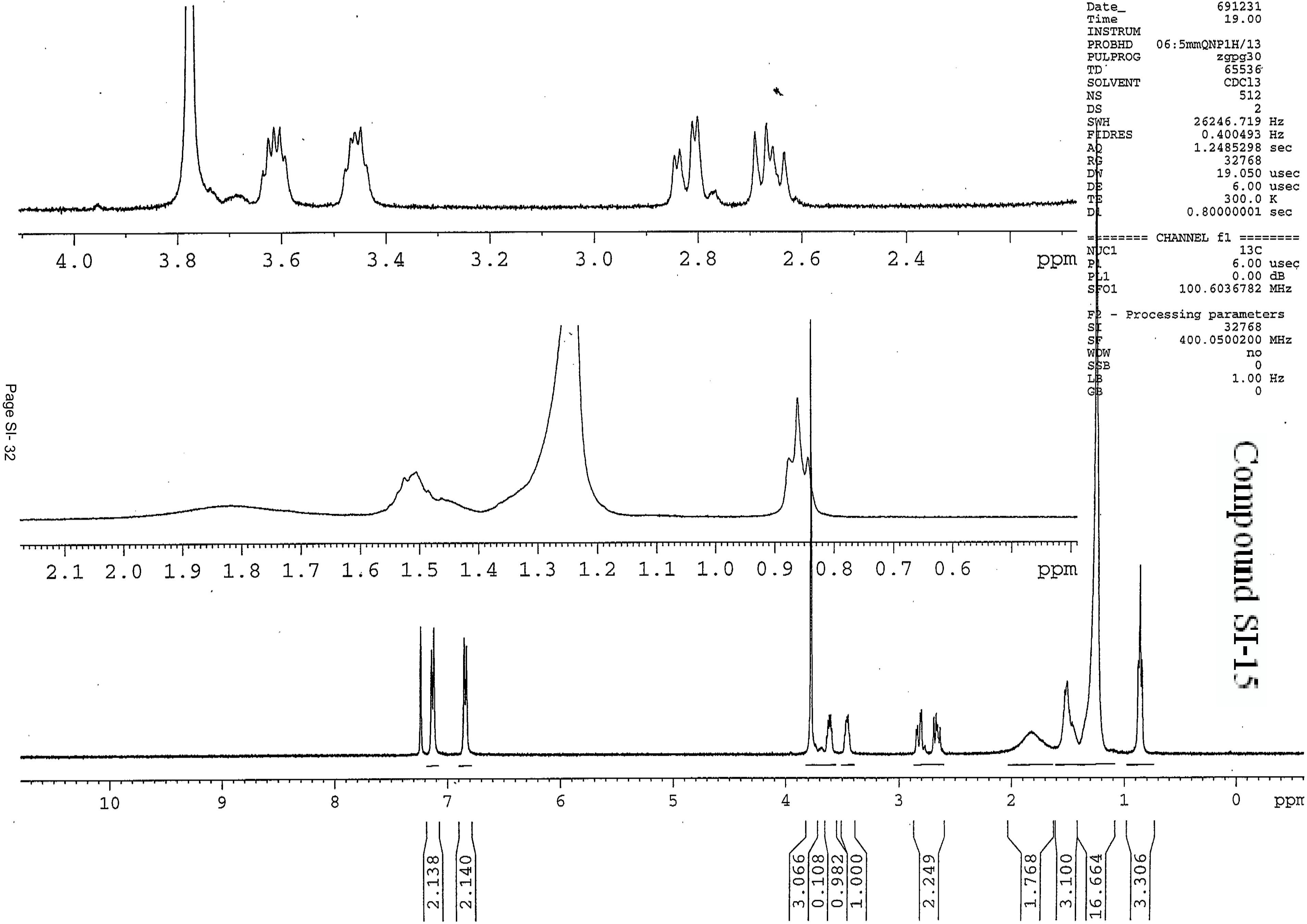
```
Current Data Parameters
NAME              Pelz 4-172
EXPNO                      2
PROCNO                     1

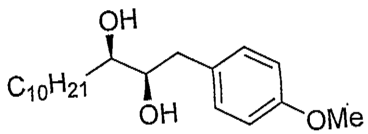
F2 - Acquisition Parameters
Date_                 691231
Time                   19.00
INSTRUM
PROBHD    06:5mmQNP1H/13
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       512
DS                         2
SWH              26246.719 Hz
FIDRES            0.400493 Hz
AQ               1.2485298 sec
RG                     32768
DW                  19.050 usec
DE                    6.00 usec
TE                   300.0 K
D1              0.80000001 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                      6.00 usec
PL1                     0.00 dB
SFO1          100.6036782 MHz

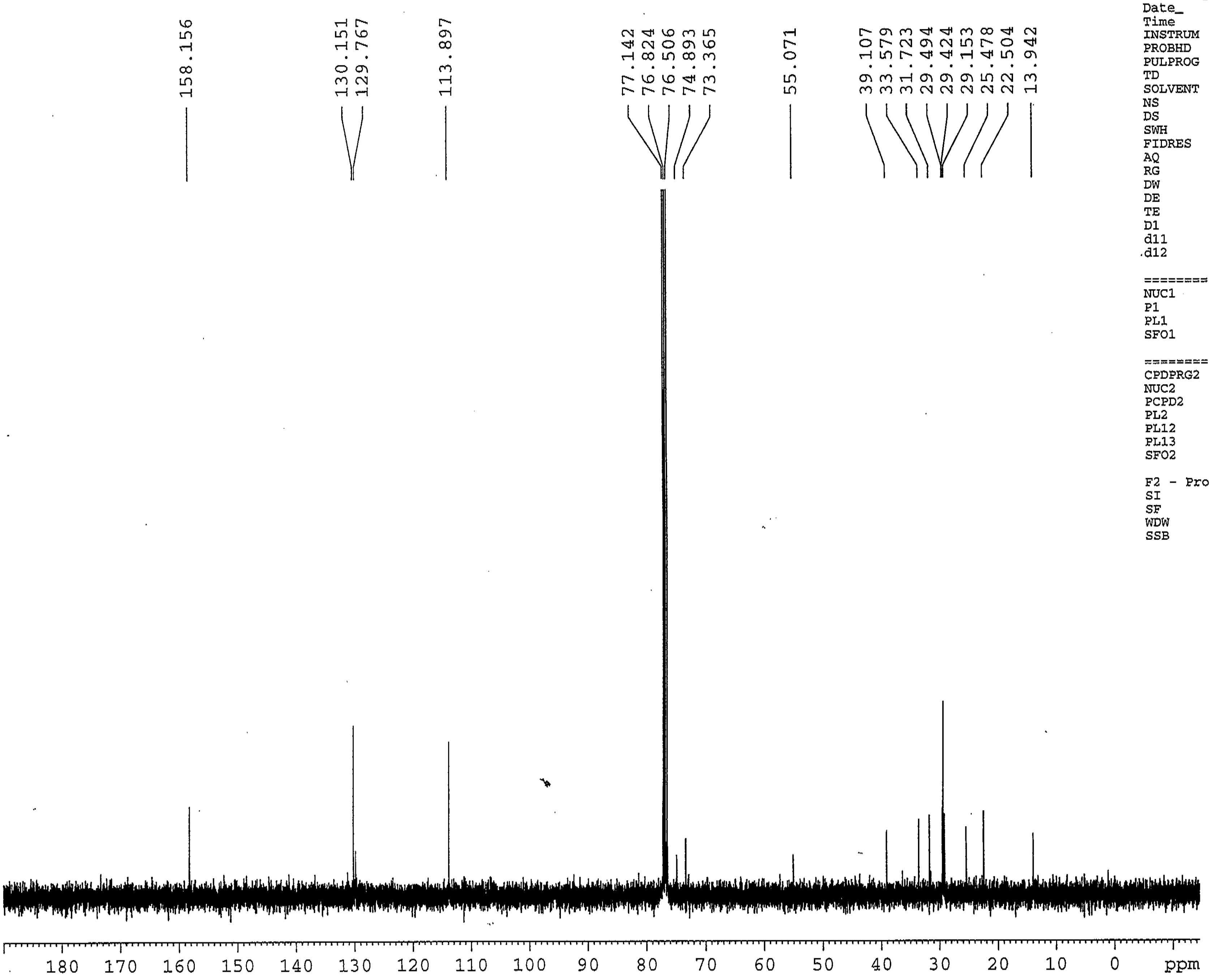
F2 - Processing parameters
SI                     32768
SF              400.0500200 MHz
WDW                       no
SSB                        0
LB                      1.00 Hz
GB                         0
```

Compound SI-15





Pelz 4.165 Carbon 400nb



```
Current Data Parameters
NAME          Pelz 4-176
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060412
Time               19.32
INSTRUM            spect
PROBHD   5mm QNP 1H/13C
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   650
DS                     2
SWH           26246.719 Hz
FIDRES         0.400493 Hz
AQ            1.2485298 sec
RG                3649.1
DW                19.050 use
DE                  6.00 use
TE                 300.0 K
D1            0.80000001 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 =======
NUC1                 13C
P1                  6.00 use
PL1                 0.00 dB
SFO1         100.6036782 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 use
PL2                -6.00 dB
PL12               13.80 dB
PL13               14.50 dB
SFO2         400.0516002 MHz

F2 - Processing parameters
SI                 32768
SF           100.5926741 MHz
WDW                   no
SSB                    0
```

Compound SI-15