

**Supporting Information for:**

**Palladium-Catalyzed Enantioselective Diboration of Prochiral Allenes.**

Nicholas F. Pelz, Angela R. Woodward, Heather E. Burks, Joshua D. Sieber and James P. Morken\*

*Department of Chemistry, Venable and Kenan Laboratories,*

*The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290.*

**General.**  $^1\text{H}$  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 ( $\text{CDCl}_3$ : 7.24 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and assignment.  $^{13}\text{C}$  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 ( $\text{CDCl}_3$ : 77.0 ppm). High-resolution mass spectrometry was performed by the University of Minnesota Mass Spectrometry Service Laboratory. Infrared (IR) spectra were obtained on an ASI ReactIR 1000 or a Nicolet 560 Magna-IR.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel ( $\text{SiO}_2$ , 230 X 450 mesh) purchased from Sorbent Technologies, Inc. Thin layer chromatography was performed on 25  $\mu\text{m}$  silica gel plates from Sorbent Technologies, 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 gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatography equipped with a CTC Analysis Combi Pal autosampler by Leap Technologies (Carrboro, NC), a split mode capillary injection system, a flame ionization detector and a Supelco  $\beta$ -dex 120 column with helium as the carrier gas. 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 and flame dried glassware under an inert atmosphere of nitrogen or argon. Toluene was distilled over  $\text{CaH}_2$  and degassed by freeze-pump-thaw cycles prior to use.  $\text{Pd}_2(\text{dba})_3$  and tricyclohexylphosphine were purchased from Strem Chemical Company. (*1R, 7R*)-4-Dimethylamino-9,9-dimethyl-2,2,6,6-tetraphenyl-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane, [ $\text{R},\text{R}$ ]- $(\text{TADDOL})\text{PNMe}_2$ ] was synthesized according to the literature (Alexakis, A.; Burton, J.; Vastra, J.; Benhaim, C.; Fournioux, X.; Heuvel, A. V. D.; Levêque, J. M.; Mazé, F.; Rosset, S. *Eur. J. Org. Chem.* **2000**, 4011). 1,2-Butadiene was purchased from ChemSampCo and used as a solution in toluene. All other allenes were synthesized via literature procedures (Myers, A. H.; Zhang, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492. Xu, L.; Fenggang, T.; Yu, T. *Tetrahedron Lett.* **1985**, *26*, 4231. Brandsma, L.; Verkruissee, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier Scientific Publishing Co.: Amsterdam, 1981; pp 157-161.). All other reagents were purchased from either Strem or Aldrich Chemical Companies and used directly.

### General Procedure for Catalytic Diboration of 1,2-Tridecadiene Followed by $^1\text{H}$ NMR Analysis:

In an inert atmospheres glovebox, an oven dried one dram vial was charged with 2.1 mg (0.0023 mmol)  $\text{Pd}_2(\text{dba})_3$  followed by subsequent addition of the required amount of ligand, using a stock solution whenever necessary. The mixture was then dissolved in 0.75mL toluene- $d_8$ . The metal and ligand were allowed to complex for 25 minutes, before the addition of 23 mg (0.092 mmol) bis(pinacolatodiboron). The reaction was then stirred to homogeneity before the addition of 20 mg (0.110 mmol) 1,2-tridecadiene. The reaction was then transferred to an oven dried NMR tube for analysis. All spectra were acquired 20 min after the allene was added.

### Representative Procedure for Catalytic, Enantioselective Diboration of Allenes:

An oven-dried 20-mL vial, with magnetic stir bar, was charged with tris(dibenzylideneacetone)dipalladium(0) (9.4 mg, 0.010 mmol), (R,R)-TADDOL-PNMe<sub>2</sub> (**3**) (13.2 mg, 0.024 mmol), and 2.5 mL toluene (0.16 M) in an inert atmosphere dry box. After stirring for 30 minutes, bis(pinacolato)diboron (124.6 mg, 0.490 mmol) was added to the mixture followed by cyclohexylallene (50 mg, 0.407 mmol). The vial was sealed with a Teflon-cap, removed from the dry box, and stirred at room temperature for 14 hours. The resulting solution was concentrated via rotary evaporation and chromatographed on silica gel (2% EtOAc/Hexanes) to provide 97 mg (60%) of a yellow oil in 87% ee.

### Modified Procedure for Diboration of 1,2-Butadiene:

Tris(dibenzylideneacetone)dipalladium (0) (8.7 mg, 0.010 mmol) and (R,R)-TADDOL-PNMe<sub>2</sub> (**3**) (12.6 mg, 0.023 mmol) were complexed for 30 minutes in 1.3 mL toluene, at which time the mixture was charged with bis(pinacolato)diboron (115.8 mg, 0.456 mmol) and 1 mL of 0.38 M solution of 1,2-butadiene in toluene (prepared by condensation of the allene into a toluene solution; concentration determined by  $^1\text{H}$  NMR). The vial was sealed with a Teflon-cap, removed from dry box, and stirred at room temperature for 14 hours. The resulting solution was concentrated via rotary evaporation and chromatographed on silica gel (4% EtOAc/Hexanes) to provide 74 mg (64% yield) of product (oil) with an enantiomeric purity of 92% ee.

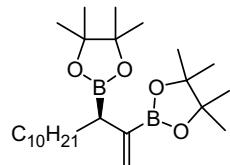
### General Procedure for the Diimide Reduction of Diboration Products:

A mixture of diboron (1 equiv., generally ca. 0.2 mmol scale)), nitrobenzenesulfonylhydrazide (10 equiv.), and triethylamine (15 equiv.) in dioxane (0.1 M in substrate) was placed in a flame-dried vial, then capped and sealed with electrical tape. The sealed reaction mixture was heated to 95 °C and stirred for 3 hours, and then cooled to 0 °C before the addition of aqueous NaOH (1 mL, 3 M) and H<sub>2</sub>O<sub>2</sub> (1 mL, 30 wt%). The oxidation was slowly allowed to warm to room temperature and stir overnight before placing in an ice bath and quenching with sodium thiosulfate (2 mL). The resulting mixture was extracted with ethyl acetate three times, and the organics were then washed with brine and dried over magnesium sulfate. The resultant oil was then purified by flash chromatography on silica gel to give the diol as a mixture of diastereomers.

### Procedure for One-pot Diboration/Allylation/Oxidation in Scheme 2:

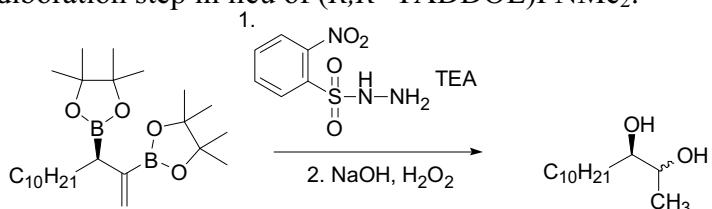
An oven-dried 20 mL vial equipped with a stir-bar was charged with 8 mg (0.009 mmol)  $\text{Pd}_2(\text{dba})_3$ , 11 mg (0.021 mmol) (*R,R*-TADDOL)PNMe<sub>2</sub>, and 2.1 mL of toluene under an inert atmosphere of argon in a dry-box. The purple solution was stirred until it appeared yellow (30 minutes). After this time, 107 mg (0.45 mmol) of bis(pinacolato)diboron was added to the solution. The solution was allowed to stir for 5 minutes. Next, 41 mg (0.350 mmol) of propa-1,2-dienyl-benzene was added to the solution. The vial was sealed with a screw-cap and allowed to stir for 14 hours at ambient temperature. After this time, 56 mg (0.52 mmol) of benzaldehyde was added to the solution, and the reaction was allowed to stir for 3 h. The vial was removed from the glovebox and cooled to 0 °C. Subsequently, 0.8 mL of 3 M NaOH was

added, followed by dropwise addition of 0.8 mL of 30% H<sub>2</sub>O<sub>2</sub> (for hazards associated with H<sub>2</sub>O<sub>2</sub>, see Encyclopedia of Reagents for Organic synthesis, L.A. Paquette, Ed. John Wiley and Sons, New York, 1995, Volume 4, 2731). The solution was allowed to stir at ambient temperature for 3 hours. The solution was then quenched with 1 mL of saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and 1 mL of 1 M NaOH. The mixture was extracted with ethyl acetate (3 x 5 mL) and the combined organic layers were washed with brine (1 x 5 mL). The organic layers were then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent removed by rotary evaporation. The crude material was purified by silica gel chromatography (5:1 hexanes:ethyl acetate) to provide 47.2 mg (56%) of 4-hydroxy-1,4-diphenyl-butan-2-one.

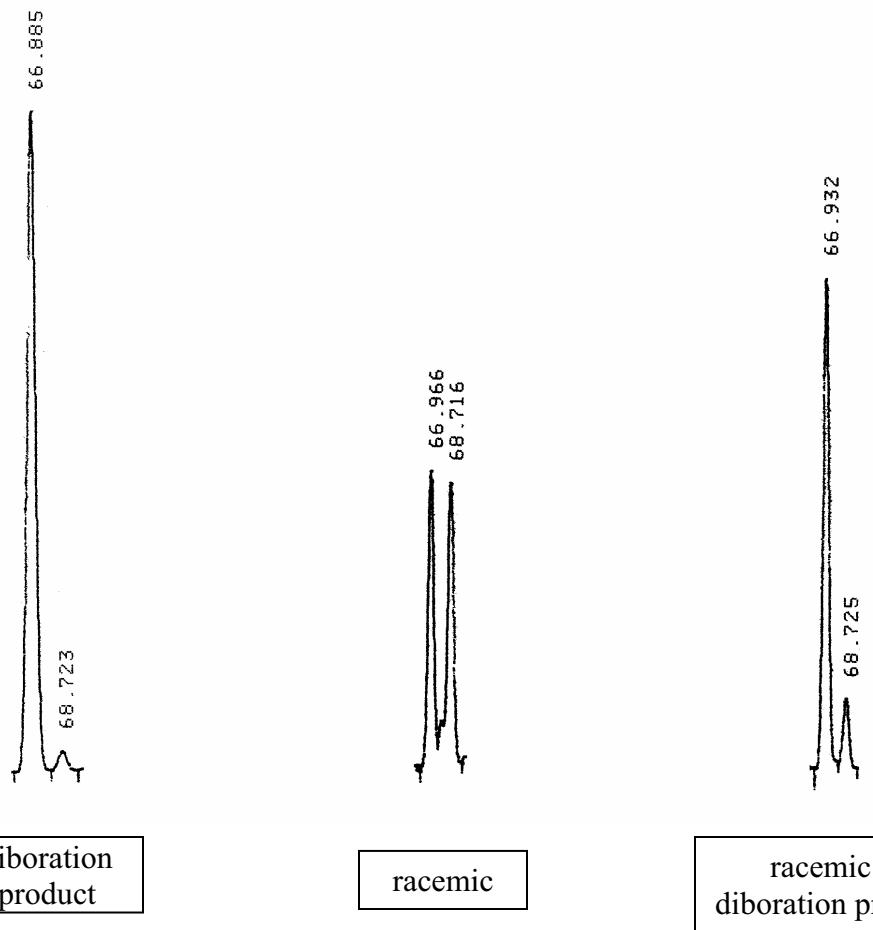


**(S)-2,3-di(pinacolatoboron)-1-tridecene.** IR (CH<sub>2</sub>Cl<sub>2</sub>): 2929 (s), 1349 (s), 1146 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$  5.76 (1H, d,  $J$  = 3.5 Hz, BCCH<sub>2</sub>), 5.55 (1H, d,  $J$  = 3.0 Hz, BCCCH<sub>2</sub>), 1.90 (2H, dd,  $J$  = 7.8 Hz, 7.5 Hz, CH<sub>2</sub>CHB), 1.16 – 1.48 (2H, m, BCHCH<sub>2</sub>), 1.24 (6H, s, BOC(CH<sub>3</sub>)<sub>2</sub>), 1.23 (6H, s, BOC(CH<sub>3</sub>)<sub>2</sub>), 1.22 (6H, s, BOC(CH<sub>3</sub>)<sub>2</sub>), 1.21 (6H, s, BOC(CH<sub>3</sub>)<sub>2</sub>), 0.86 (3H, t,  $J$  = 7 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR:  $\delta$  127.4, 83.1, 82.8, 31.8, 29.6, 29.6, 29.5, 29.5, 29.4, 29.2, 29.0, 24.7, 24.6, 24.5, 24.5, 22.5, 14.0; HRMS (ESI) Calc'd for C<sub>25</sub>H<sub>48</sub>B<sub>2</sub>O<sub>4</sub> (M+Na)<sup>+</sup>: 457.3631 Found (M+Na)<sup>+</sup>: 457.3626.

**Determination of Enantioselectivity.** Enantiomeric excess was determined by chiral GLC of the diol derivative formed by diimide reduction (see above) of the vinyl boronate ester followed by alkaline peroxide workup. Stereochemical ratios were determined in comparison to racemic material prepared by utilizing PCy<sub>3</sub> in the diboration step in lieu of (*R,R*-TADDOL)PNMe<sub>2</sub>.

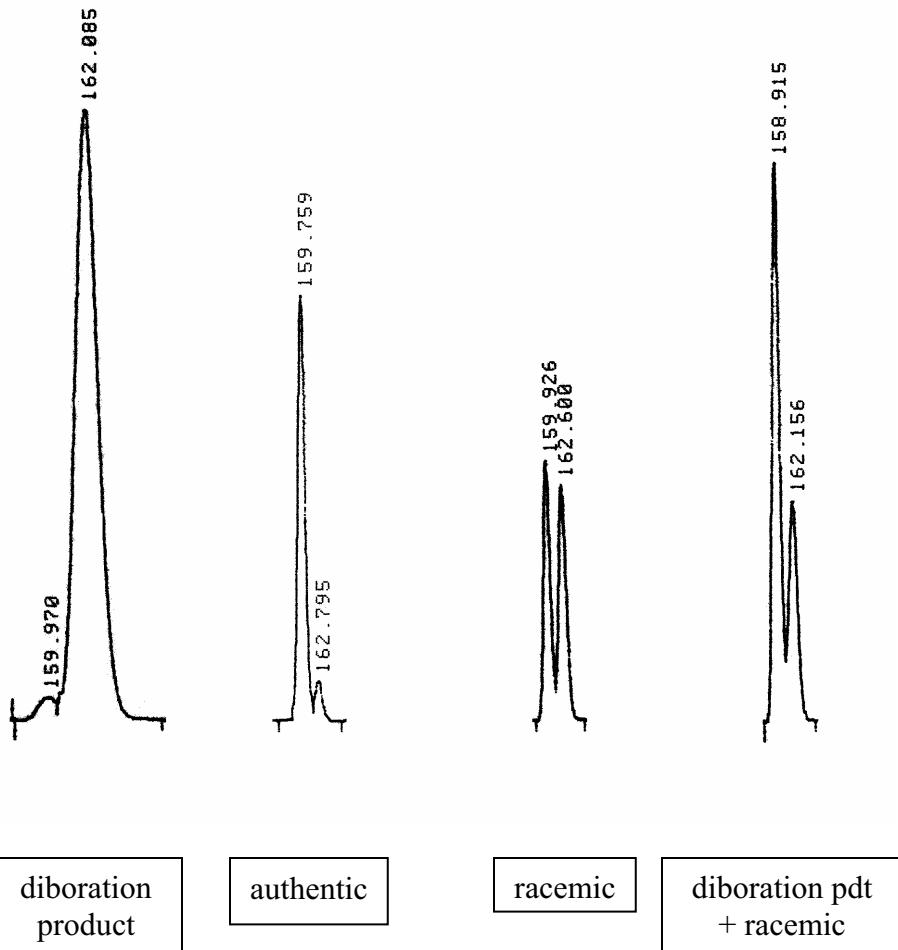


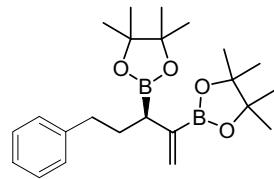
Chiral GLC ( $\beta$ -dex, Supelco, 120 °C, derived acetonide, cis diol is better resolved than the trans and is displayed below)



**Proof of Stereochemistry.** Absolute stereochemistry was established in comparison to acetonide of the authentic isomer prepared via Sharpless asymmetric dihydroxylation of the corresponding *trans*-alkene (Becker, H.; King, S. B.; Taniguchi, M.; Vanhessche, K.; Sharpless, K. B. *J. Org. Chem.* **1995**, *60*, 3940).

Chiral GLC ( $\beta$ -dex, Supelco, 100 °C, derived acetonide, *trans* diastereomer shown)

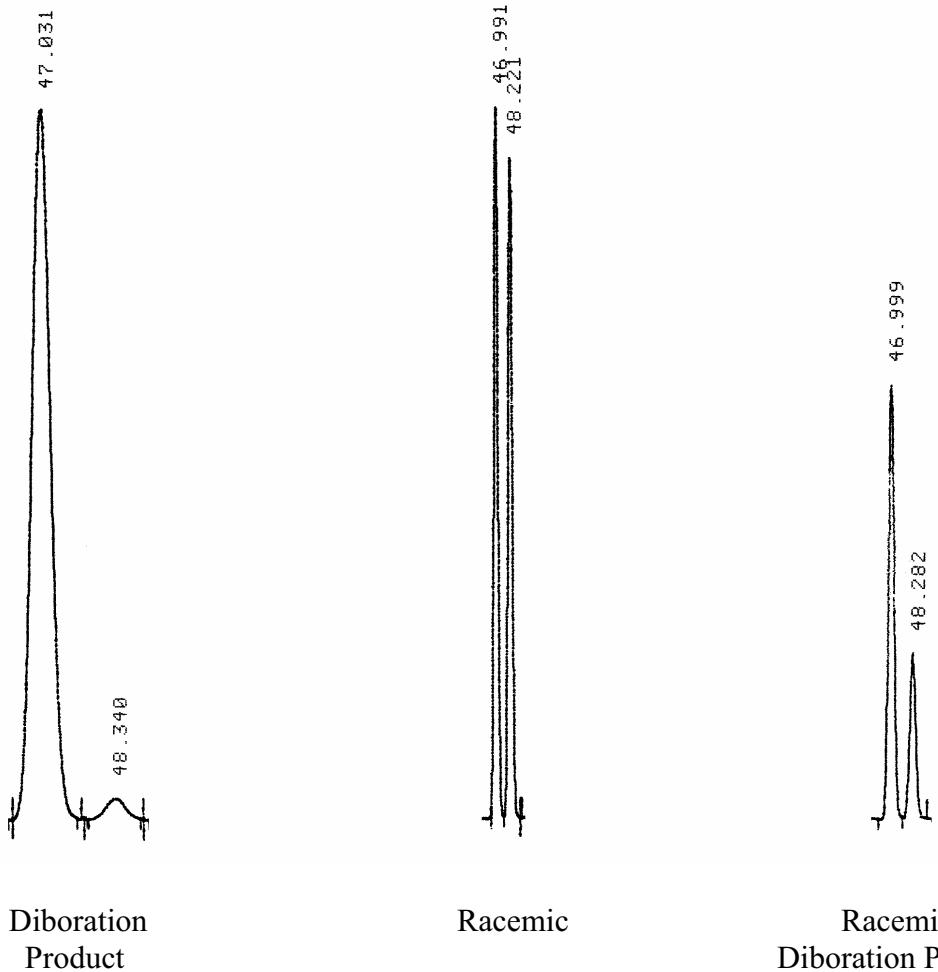


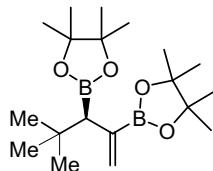


**(S)- 1-phenyl-3,4-dipinacolatoboron-4-pentene.** Isolated 90 mg of an oil.  $R_f = 0.49$  in 15:1 hexanes:EtOAc. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2929 (m), 1316 (s), 1133 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$  7.28-7.13 (5H, m, Ph), 5.85 (1H, d,  $J = 2.4$  Hz, BCCH<sub>2</sub>), 5.62 (1H, d,  $J = 2.4$  Hz, BCCH<sub>2</sub>), 2.64-2.54 (2H, m, PhCH<sub>2</sub>), 2.03-1.89 (3H, m, BCHCH<sub>2</sub>), 1.30 (6H, s, BOC(CH<sub>3</sub>)<sub>2</sub>), 1.28 (6H, s, BOC(CH<sub>3</sub>)<sub>2</sub>), 1.26 (6H, s, BOC(CH<sub>3</sub>)<sub>2</sub>), 1.26 (6H, s, BOC(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR:  $\delta$  143.1, 128.4, 128.1, 125.3, 83.2, 83.0, 35.3, 31.6, 24.8, 24.7, 24.6, 24.5. HRMS (ESI) Calc'd for C<sub>23</sub>H<sub>36</sub>B<sub>2</sub>O<sub>4</sub> (M+Na)<sup>+</sup>: 421.2692 Found (M+Na)<sup>+</sup>: 421.2685.

**Determination of Enantioselectivity.** Enantiomeric excess was determined by chiral GLC of the derivative formed by diimide reduction (see above) of the vinyl boronate ester followed by alkaline peroxide workup. Stereochemical ratios were determined in comparison to racemic material prepared by utilizing PCy<sub>3</sub> in the diboration step in lieu of (*R,R*-TADDOL)PNMe<sub>2</sub>.

*Chiral GLC ( $\beta$ -dex, Supelco, 120 °C, derived acetonide, one diastereomer shown)*

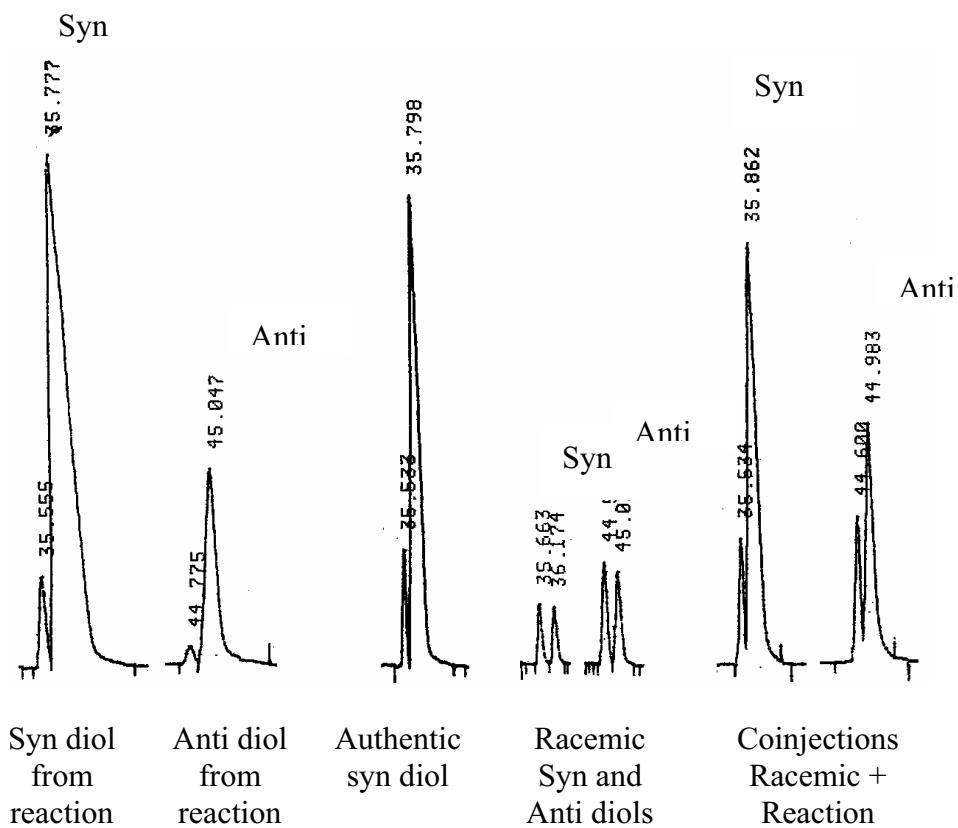


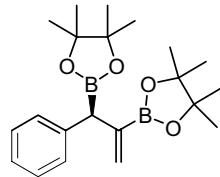


**(S)-2-4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.** 113 mg of a white solid.  $R_f = 0.25$  in 15:1 hexanes:EtOAc. IR (KBr pellet): 2986 (br, s), 2943 (br, s), 2866 (br, m) 1926 (w), 1600 (w), 1344 (br, m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  5.89 (1H, d,  $J = 3.6$  Hz, CBCHH), 5.71 (1H, d,  $J = 3.6$  Hz, CBCHH), 1.96 (1H, s,  $(\text{CH}_3)_3\text{CBH}$ ), 1.17-1.22 (24H, m, OCCH<sub>3</sub>), 0.89 (9H, s,  $(\text{CH}_3)_3\text{CB}$ );  $^{13}\text{C}$  NMR:  $\delta$  132.5, 83.7, 82.9, 33.4, 29.8, 25.3, 25.2, 25.1, 25.0 (Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. See Wrackmeyer, B. *Prog. NMR Spectrosc.* **1979**, 12, 227.). HRMS (ESI) Calc'd for C<sub>19</sub>H<sub>36</sub>B<sub>2</sub>O<sub>4</sub> (M + Na)<sup>+</sup>: 373.2692 Found (M + Na)<sup>+</sup>: 373.2701.

**Proof of Stereochemistry.** The olefin of the diboron product was reduced using diimide (generated in situ from 2-nitrobenzenesulfonylhydrazide and triethylamine in refluxing dioxane), and the reduction product was then oxidized with H<sub>2</sub>O<sub>2</sub> in basic media to afford the corresponding 1,2-diol. Stereochemical ratios were determined in comparison to authentic racemic materials prepared by the diboration of *t*-butylallene in the presence of PCy<sub>3</sub> as the achiral ligand, followed by the above reduction-oxidation sequence. The absolute stereochemistry was established in comparison to authentic (2*R*, 3*R*)-4,4-dimethylpentane-2,3-diol synthesized via a Sharpless asymmetric dihydroxylation of (*E*)-4,4-dimethyl-2-pentene (Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **2004**, 94, 2483).

*Chiral GLC (β-dex, Supelco, 80 – 140 °C at 1 °C/min) analysis of diol products resulting from the reduction-oxidation sequence described above:*

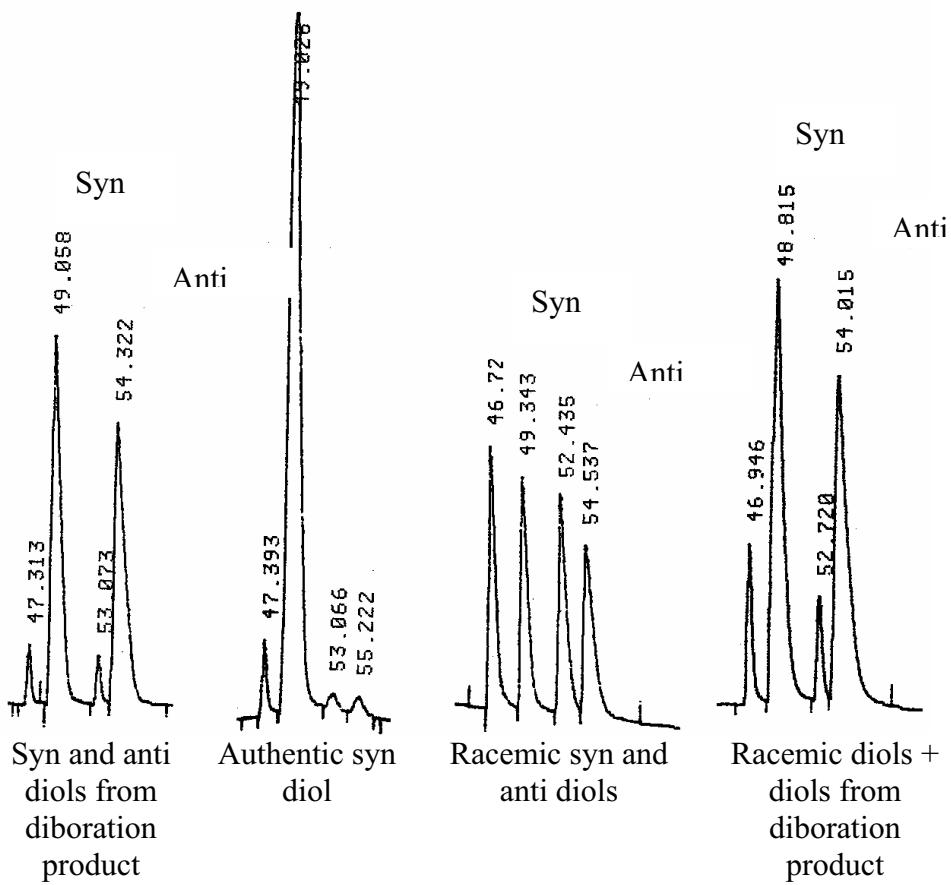


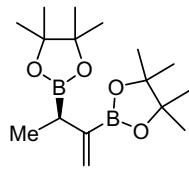


**(S)-4,4,5,5-tetramethyl-2-(1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-2-yl)-1,3,2-dioxaborolane.** 127 mg of a yellow oil.  $R_f = 0.33$  in 10:1 hexanes:EtOAc. IR (neat): 2970 (br, s), 2924 (br, m), 1604 (w), 1417 (br, m), 1313 (br, s), 1142 (br, s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  7.10-7.26 (5H, m, aromatic), 5.81 (1H, br s, CBCHH), 5.27 (1H, br s, CBCHH), 3.36 (1H, s, ArCHB), 1.20-1.25 (24H, m, OCCH<sub>3</sub>);  $^{13}\text{C}$  NMR:  $\delta$  141.0, 130.4, 128.6, 128.4, 125.8, 83.93, 83.89, 25.38, 25.23, 24.99, 24.93 (Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. See Wrackmeyer, B. *Prog. NMR Spectrosc.* **1979**, 12, 227.). HRMS (ESI) Calc'd for C<sub>21</sub>H<sub>32</sub>B<sub>2</sub>O<sub>4</sub> (M + Na)<sup>+</sup>: 393.2379 Found (M + Na)<sup>+</sup>: 393.2393.

**Proof of stereochemistry.** The olefin of the diboron product was reduced using diimide (generated in situ from 2-nitrobenzenesulfonylhydrazide and triethylamine in refluxing dioxane), and the reduction product was then oxidized with H<sub>2</sub>O<sub>2</sub> in basic media to afford the corresponding 1,2-diol. Stereochemical ratios were determined in comparison to authentic racemic materials prepared by the diboration of phenylallene in the presence of PCy<sub>3</sub> as the achiral ligand, followed by the above reduction-oxidation sequence. The absolute stereochemistry was established in comparison to authentic (1*R*, 2*R*)-1-phenylpropane-1,2-diol synthesized via a Sharpless asymmetric dihydroxylation of  $\beta$ -methylstyrene (Norrby, P-O.; Becker, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1996**, 118, 35).

*Chiral GLC (β-dex, Supelco, 140 °C) analysis of diol products resulting from the reduction-oxidation sequence described above:*

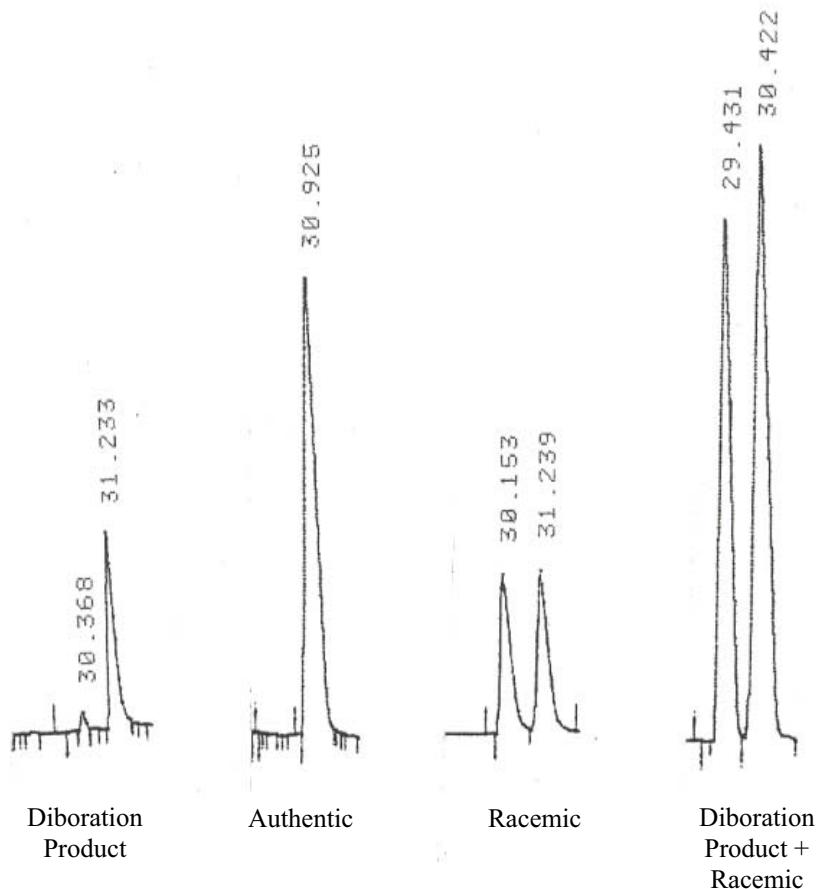


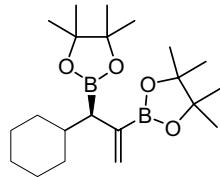


**(R)-4,4,5,5-tetramethyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-2-yl)-1,3,2-dioxaborolane.** 74 mg of a yellow oil.  $R_f = 0.32$  in 25:1 hexanes:EtOAc. IR: 2978 (s), 2933 (s), 1612 (s), 1464 (br, m), 1423 (br, m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.11 (3H, d,  $J = 7.2$  Hz,  $\text{CH}_3\text{CHB}$ ), 1.23 (12H, s,  $\text{OCCCH}_3$ ), 1.26 (12H, s,  $\text{OCCCH}_3$ ), 2.03 (1H, q,  $J = 7.2$  Hz,  $\text{CH}_3\text{CHB}$ ), 5.55 (1H, br s,  $\text{CHCB}$ ), 5.74 (1H,  $\text{CHCB}$ , d,  $J = 4$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.3, 24.8 (4C), 24.9 (4C), 83.2, 83.4, 125.9 (CB carbons cannot be elucidated due to the attached boron, see Wrackmeyer, B. *Progress in NMR Spectroscopy*, **1979**, 12, 227). IR (neat): 2978 (s), 2933 (s), 2874 (s), 1612 (s), 1464 (m, br), 1423 (m, br), 1378 (m, br)  $\text{cm}^{-1}$ . HRMS (ESI): Calc'd for  $\text{C}_{16}\text{H}_{30}\text{B}_2\text{O}_4$  ( $\text{M} + \text{Na}$ ) $^+$ : 331.2228. Found ( $\text{M} + \text{Na}$ ) $^+$ : 331.2229.

**Proof of Stereochemistry.** Stereochemistry was determined by diimide reduction (2-nitrobenzenesulfonylhydrazide, triethylamine, dioxanes, 95  $^{\circ}\text{C}$ ) of the diboron followed by basic hydrogen peroxide oxidation (3M NaOH,  $\text{H}_2\text{O}_2$ , quench with  $\text{Na}_2\text{S}_2\text{O}_3$ ). The resultant diol was compared to commercially available racemic 2,3-butanediol and (2*R*, 3*R*)-(-)-butanediol, available from Aldrich Chemical Company.

*Chiral GLC ( $\beta$ -dex, Supelco, 50  $^{\circ}\text{C}$ , 1 deg/min) – analysis of 2,3-butanediol – from reduction and oxidation of reaction product*

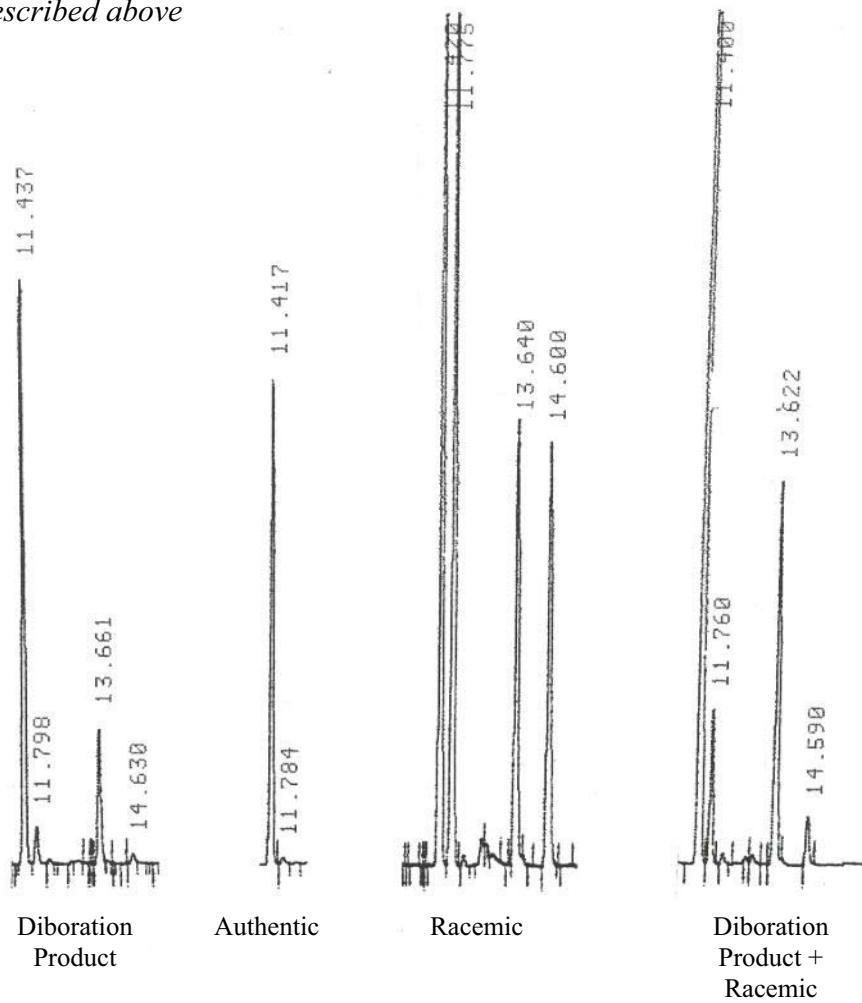


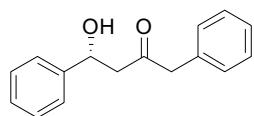


**(R)-2-(1-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.** 97 mg of a yellow oil.  $R_f = 0.18$  in 25:1 hexanes:EtOAc. IR: 3062 (s), 2978 (s), 2923 (s), 2850 (s), 1604 (s), 1371 (br, m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.80-1.4 (5H, m), 1.19 (6H, s,  $\text{OCCH}_3$ ), 1.20 (6H, s,  $\text{OCCH}_3$ ), 1.24 (12H, s,  $\text{OCCH}_3$ ), 1.60-1.80 (7H, m), 5.63 (1H, d,  $J = 2.8$  Hz,  $\text{CBCH}$ ), 5.82 (1H, d,  $J = 3.2$  Hz,  $\text{CBCH}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.9, 26.6 (2 C), 26.7 (1C), 26.9 (2C), 32.8, 33.7, 38.5, 82.9, 83.3, 129.3 (CB carbons cannot be elucidated due to the attached boron, see Wrackmeyer, B. *Progress in NMR Spectroscopy*, **1979**, 12, 227). IR (neat): 3062 (s), 2978 (s), 2923 (br), 2850 (s), 1604 (s), 1371 (br, m)  $\text{cm}^{-1}$ . HRMS (ESI): Calc'd for  $\text{C}_{21}\text{H}_{38}\text{B}_2\text{O}_4(\text{M} + \text{Na})^+$ : 399.2854 Found  $(\text{M} + \text{Na})^+$ : 399.2871.

**Proof of Stereochemistry.** Stereochemistry was determined by diimide reduction (2-nitrobenzenesulfonylhydrazide, triethylamine, dioxanes, 95 °C) of diboron followed by basic hydrogen peroxide oxidation (3M NaOH,  $\text{H}_2\text{O}_2$ , quench with  $\text{Na}_2\text{S}_2\text{O}_3$ ). The resultant diol was protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane). Racemic material was prepared from the diboration of cyclohexylallene as described in the general procedure using tricyclohexylphosphine. The diboron was then reduced, oxidized, and protected as described above. Absolute stereochemistry was established by hydrogenation of (1*R*, 2*R*)-1-phenyl-propane-1,2-diol (prepared via Sharpless asymmetric dihydroxylation – Norrby, P-O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, 118, 35) with rhodium on alumina (Degussa type), glacial acetic acid, and  $\text{H}_2$  (60 psi) - (Kolb, H.C.; Sharpless, K.B. *Tetrahedron*, **1992**, 48, 10515). The resultant diol was protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane).

*Chiral GLC (β-dex, Supelco, 120 °C) – analysis of acetonide derived from reduction and oxidation of reaction product as described above*

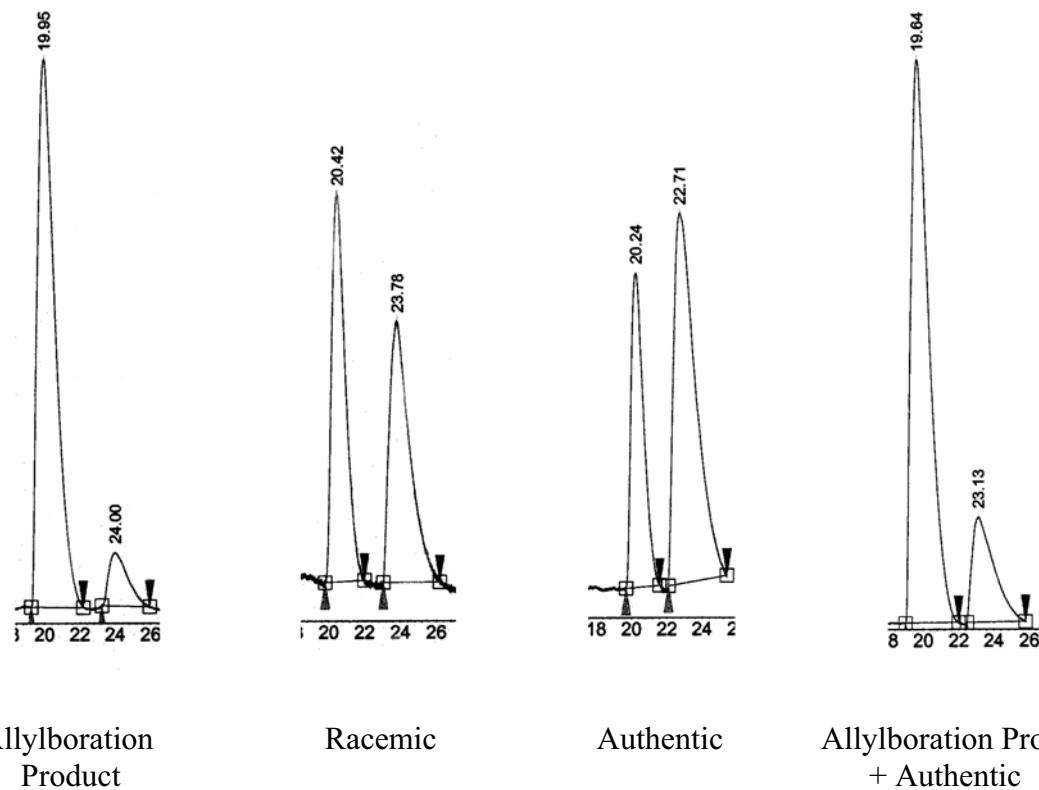




**(R)-4-Hydroxy-1,4-diphenyl-2-butanone.** IR (CH<sub>2</sub>Cl<sub>2</sub>) 2931 (br, m), 2368 (w), 1711 (s), 1497 (m), 1356 (br, m); <sup>1</sup>H NMR:  $\delta$  7.37 – 7.26 (8H, m, aromatic), 7.19 – 7.17 (2H, m, aromatic), 5.13 (1H, dd,  $J$  = 8.7, 3.6 Hz, HOCH), 3.71 (2H, s, benzylic), 3.25 (1H, br s, OH), 2.91 – 2.84 (1H, dd,  $J$  = 17.6, 8.7 Hz, OCCH<sub>a</sub>H<sub>b</sub>), 2.84 – 2.78 (1H, dd,  $J$  = 17.6, 3.6 Hz, OCCH<sub>a</sub>H<sub>b</sub>); <sup>13</sup>C NMR:  $\delta$  209.1, 143.0, 133.8, 129.9, 129.3, 128.9, 128.1, 127.7, 126.0, 70.4, 51.3, 50.8; HRMS (ESI) Calc'd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub> (M+Na)<sup>+</sup>: 263.1043 Found (M+Na)<sup>+</sup>: 263.1037.

**Proof of Stereochemistry.** Stereochemical ratios were determined in comparison to racemic material prepared by utilizing PCy<sub>3</sub> in the diboration step in lieu of (*R,R*-TADDOL)PNMe<sub>2</sub>. Absolute stereochemistry was established in comparison to material prepared by reaction benzaldehyde with the boron enolate derived chlorodiiisocampheylborane from phenylacetone. The reaction provided the methylketone aldol (*S*)-4-hydroxy-1,4-diphenyl-2-butanone in 50% ee accordingly to literature procedures [(a)Paterson, I.; Goodman, J. M.; Lister, M. A.; Schumann, R. C.; McClure, C. K.; Norcross, R. D. *Tetrahedron* **1990**, *46*, 4663. (b) Brown, H. C., Dhar, R. K., Ganesan, K., Singaram, B. *J. Org. Chem.* **1992**, *57*, 499.].

*SFC (Chiracel OD, Supelco) analysis of allylboration product and authentic material:*

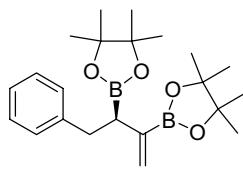


Allylboration Product

Racemic

Authentic

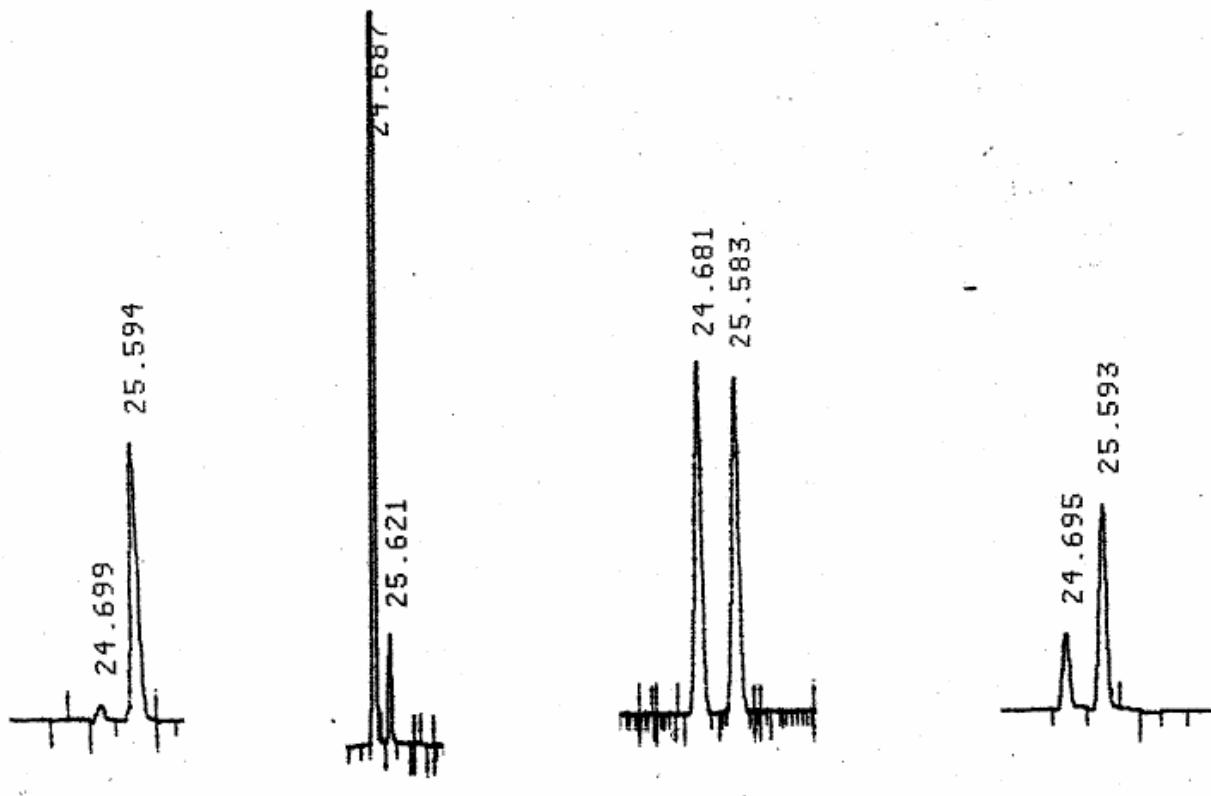
Allylboration Product + Authentic



**(R)-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** 90 mg of a yellow oil.  $R_f = 0.49$  in 15:1 hexanes:EtOAc. IR (CHCl<sub>3</sub>): 2985 (s), 1353 (s), 1146 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$  7.21-7.14 (4H, m, Ar), 7.12-7.07 (1H, m, Ar), 5.74 (1H, d,  $J = 3.2$  Hz, BCCH<sub>2</sub>), 5.51 (1H, d,  $J = 3.2$  Hz, BCCH<sub>2</sub>), 2.98 – 2.93 (1H, dd,  $J = 14, 7.7$  Hz, PhCH<sub>2</sub>), 2.86-2.81 (1H, dd,  $J = 14, 7.7$  Hz, PhCH<sub>2</sub>), 2.31 (1H, t,  $J = 7.7$  Hz, PhCH<sub>2</sub>CHB), 1.24 (6H, s, pinacol methyl), 1.23 (6H, s, pinacol methyl), 1.16 (6H, s, pinacol methyl), 1.15 (6H, s, pinacol methyl); <sup>13</sup>C NMR:  $\delta$  142.8, 129.4 (2C), 129.1, 128.3 (2C), 125.8, 83.8 (2C), 83.6 (2C), 36.5, 25.3 (2C), 25.12 (2C), 25.10 (2C), 25.3 (2C) (Boron bearing carbons were not detected, most likely due to quadrupolar relaxation. See Wrackmeyer, B. *Prog. NMR Spectrosc.* **1979**, *12*, 227.). HRMS (ESI) Calc'd for C<sub>22</sub>H<sub>34</sub>B<sub>2</sub>O<sub>4</sub> (M+Na)<sup>+</sup>: 384.1250 Found (M+Na)<sup>+</sup>: 384.1241.

**Proof of Stereochemistry.** Enantiomeric excess was determined by chiral GLC of the derivate formed via diimide reduction (see above) of the vinyl boronate ester followed by alkali hydrogen peroxide oxidation. The resultant diol was then converted to an acetonide (see above). Racemic material was prepared from benzylallene with tricyclohexylphosphine as the ligand as described in the general procedure. The diboron was then converted to the racemic acetonide as described above. Absolute stereochemistry was established from the acetonide of the (S,S) diol (prepared via Sharpless asymmetric dihydroxylation – Norrby, P.O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35).

*Chiral GLC (β-dex, Supelco, 120 °C, derived acetonide, only the diastereomer corresponding to the syn diol is shown)*

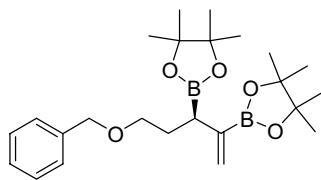


Diboration

Authentic

Racemic

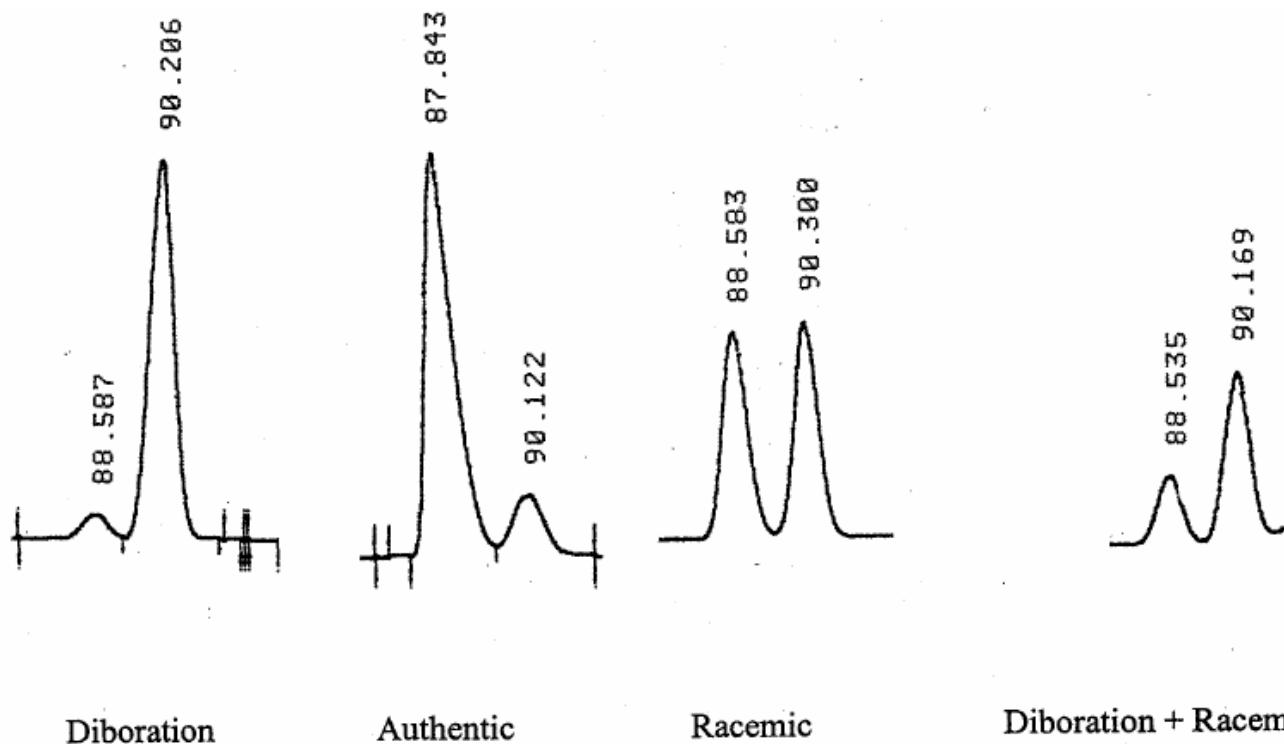
Diboration + Racemic



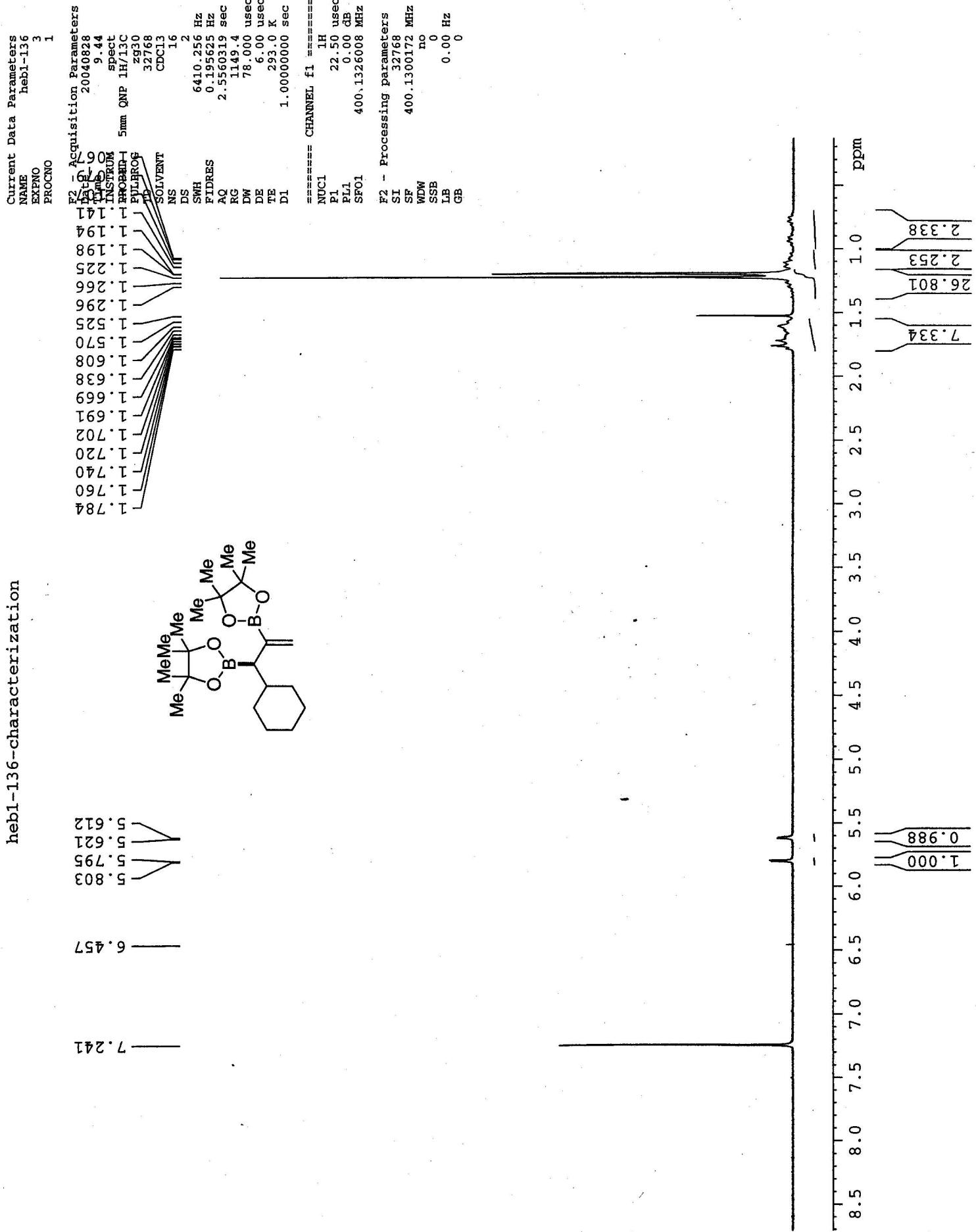
**(R)-2-(5-(benzyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.** 55 mg of a solid.  $R_f = 0.28$  in 10:1 hexanes:EtOAc. IR (CHCl<sub>3</sub>): 2985 (s), 1372 (s), 1146 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$  7.35-7.19 (5H, m, Ar), 5.76 (1H, d,  $J = 3.2$  Hz, BCCH<sub>2</sub>), 5.57 (1H, d,  $J = 2.8$  Hz, BCCH<sub>2</sub>), 4.46 (2H, s, PhCH<sub>2</sub>O), 3.47-3.38 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>), 2.06-1.95 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.87-1.77 (1H, m, CH<sub>2</sub>CHB), 1.220 (12H, s, pinacol methyl), 1.19 (6H, s, pinacol methyl), 1.18 (12H, s, pinacol methyl); <sup>13</sup>C NMR:  $\delta$  139.3, 128.6 (2C), 128.59, 128.1 (2C), 127.7, 83.7 (2C), 83.6 (2C), 73.1, 70.2, 30.2, 25.3 (2C), 25.12 (2C), 25.08 (2C), 25.0 (2C) (Boron bearing carbons were not detected, most likely due to quadrupolar relaxation. See Wrackmeyer, B. *Prog. NMR Spectrosc.* **1979**, *12*, 227.). HRMS (ESI) Calc'd for C<sub>24</sub>H<sub>38</sub>B<sub>2</sub>O<sub>5</sub> (M+Na)<sup>+</sup>: 428.1775 Found (M+Na)<sup>+</sup>: 428.1747.

**Proof of Stereochemistry.** Enantiomeric excess was determined by chiral GLC of the derivative formed via diimide reduction (see above) of the vinyl boronate ester followed by alkali hydrogen peroxide oxidation. The resultant diol was then converted to an acetonide (see above). Racemic material was prepared from benzyl protected allene with tricyclohexylphosphine as the ligand as described in the general procedure. The diboron was then converted to the racemic acetonide as described above. Absolute stereochemistry was established from the acetonide of the (S,S) diol (prepared via Sharpless asymmetric dihydroxylation of the trans alkene— Norrby, P.O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35).

*Chiral GLC ( $\beta$ -dex, Supelco, 125 °C, hold 90min, Ramp 5 °C/min to 150 °C derived acetonide, only the diastereomer corresponding to the syn diol is shown)*



heb1-136-characterization



heb1-136-c13 characterization data

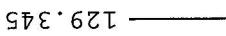
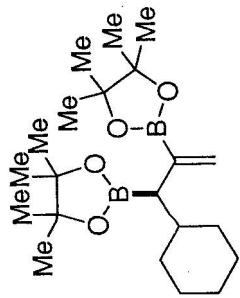
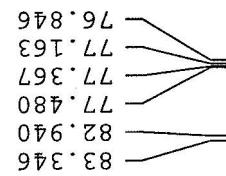
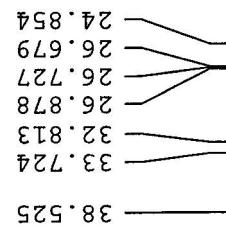
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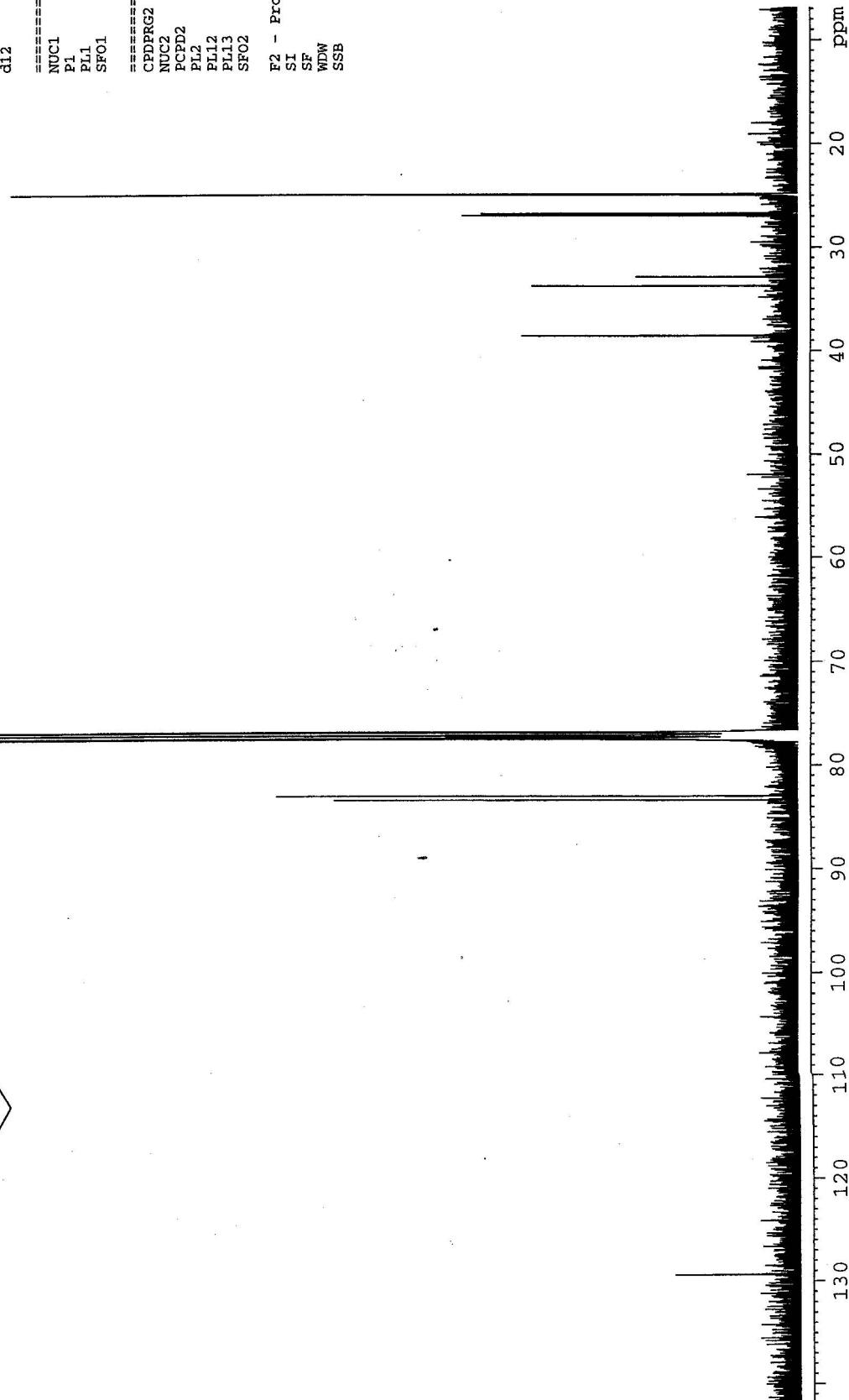
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S-15



heb1-134-clmned material characterization spectrum

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TIME 18:22

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TD CDCl3

SOLVENT NS

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RG 912.3

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DE 6.000 usec

TE 293.0 K

DI 1.0000000 sec

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F2 - Processing parameters

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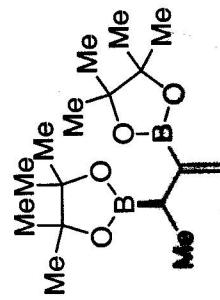
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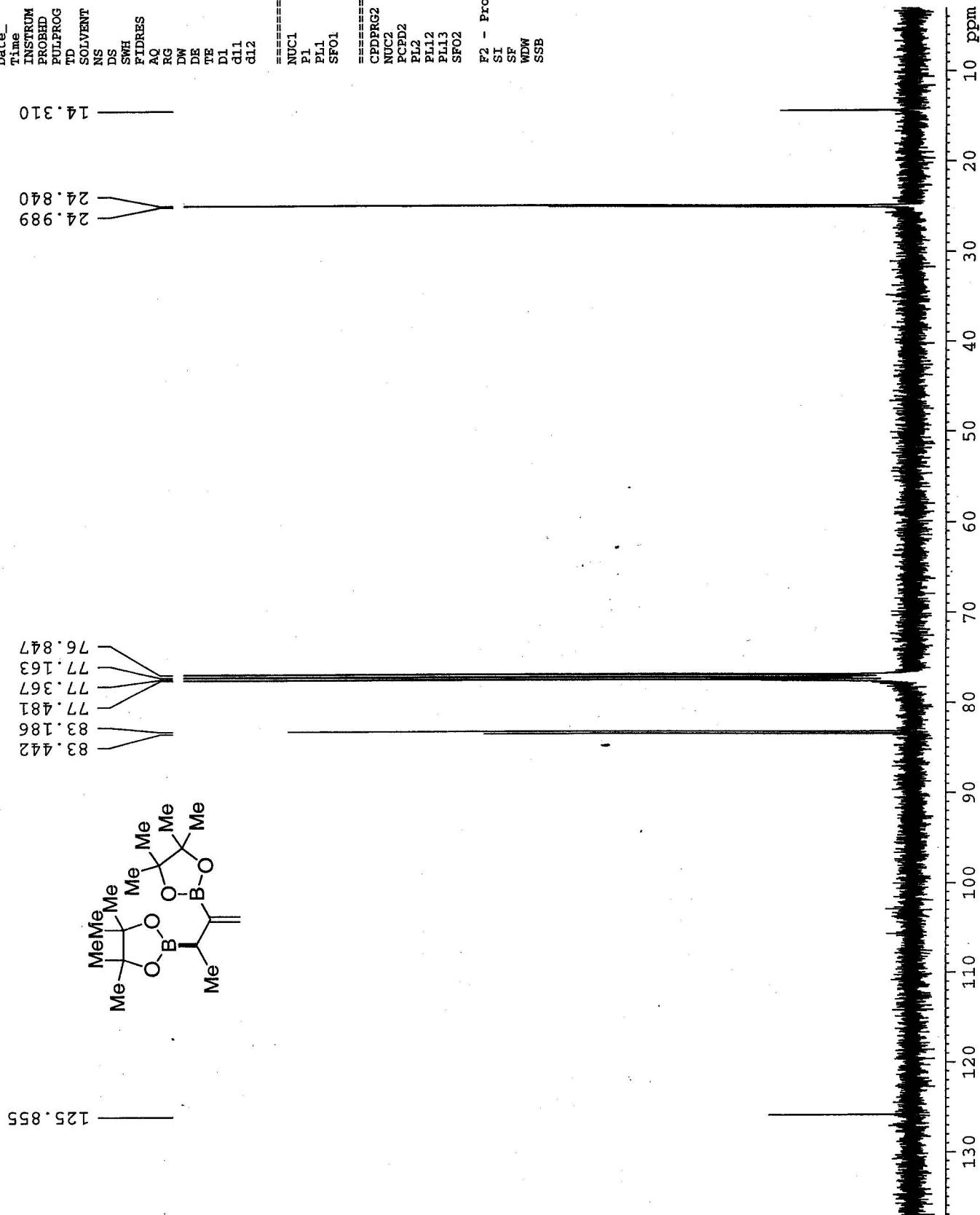
heb1-134-c13 characterization data

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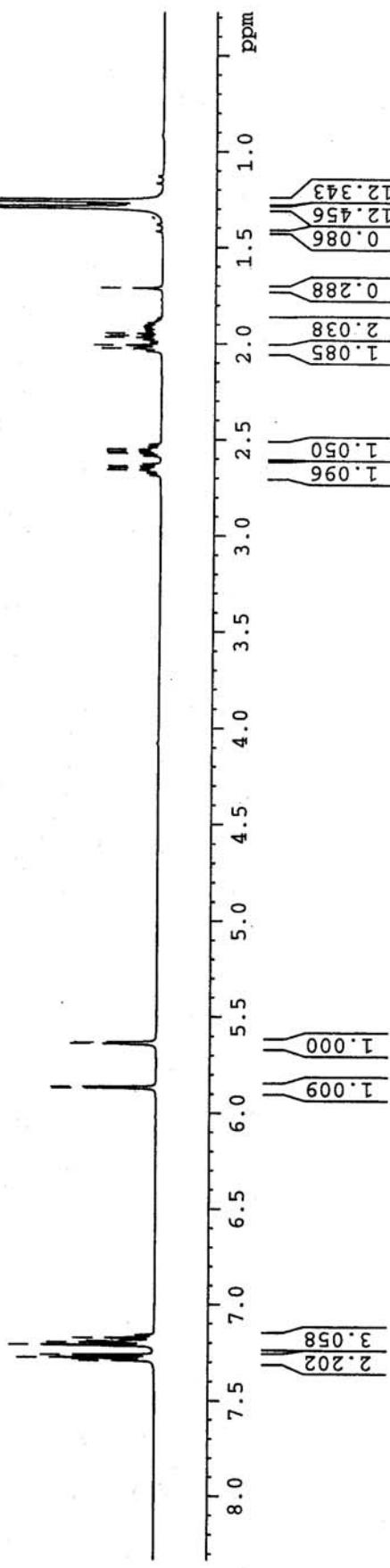
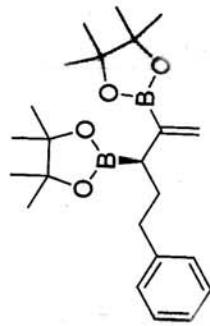
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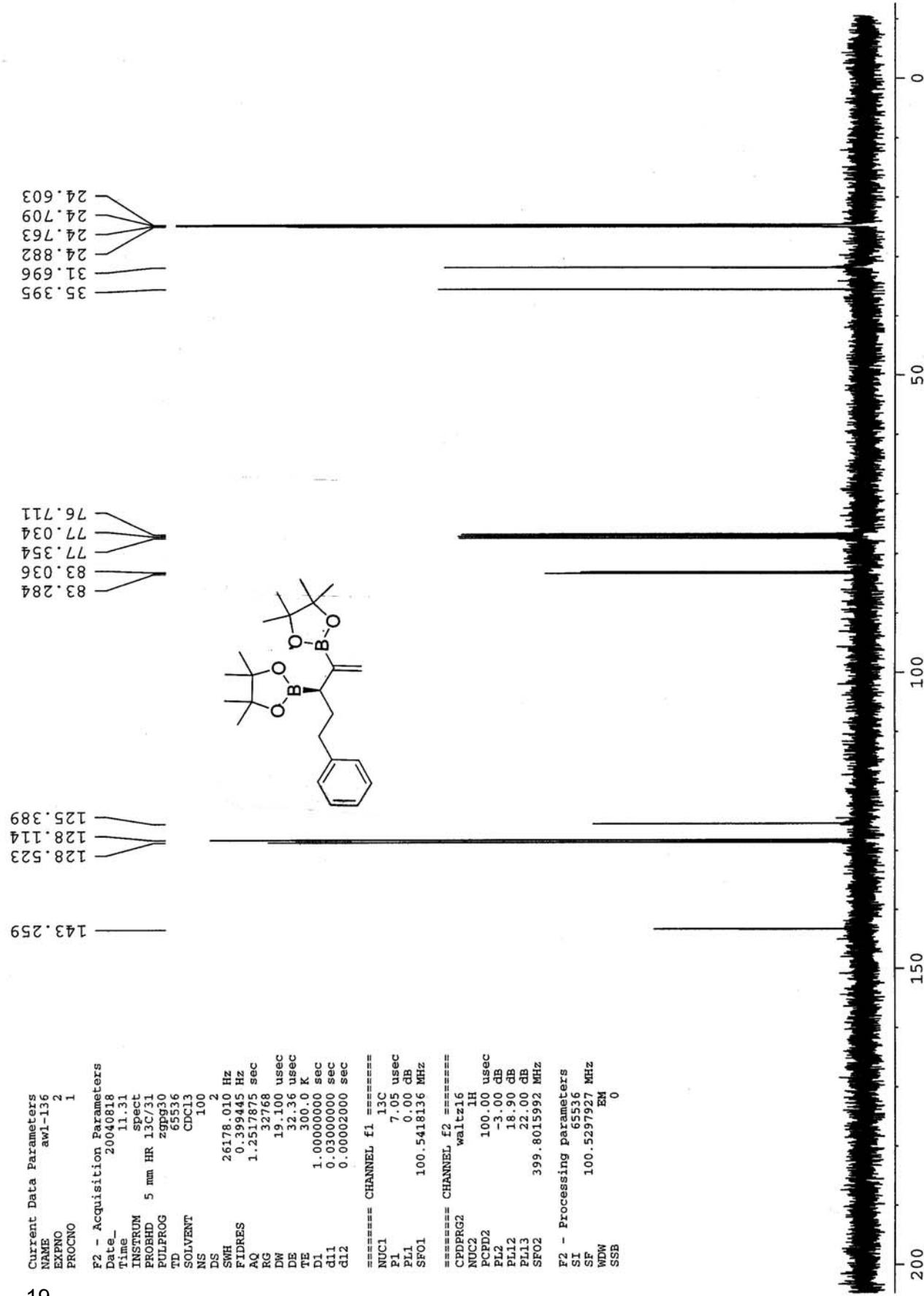
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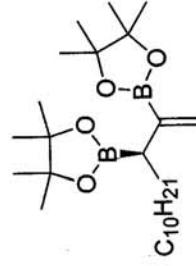
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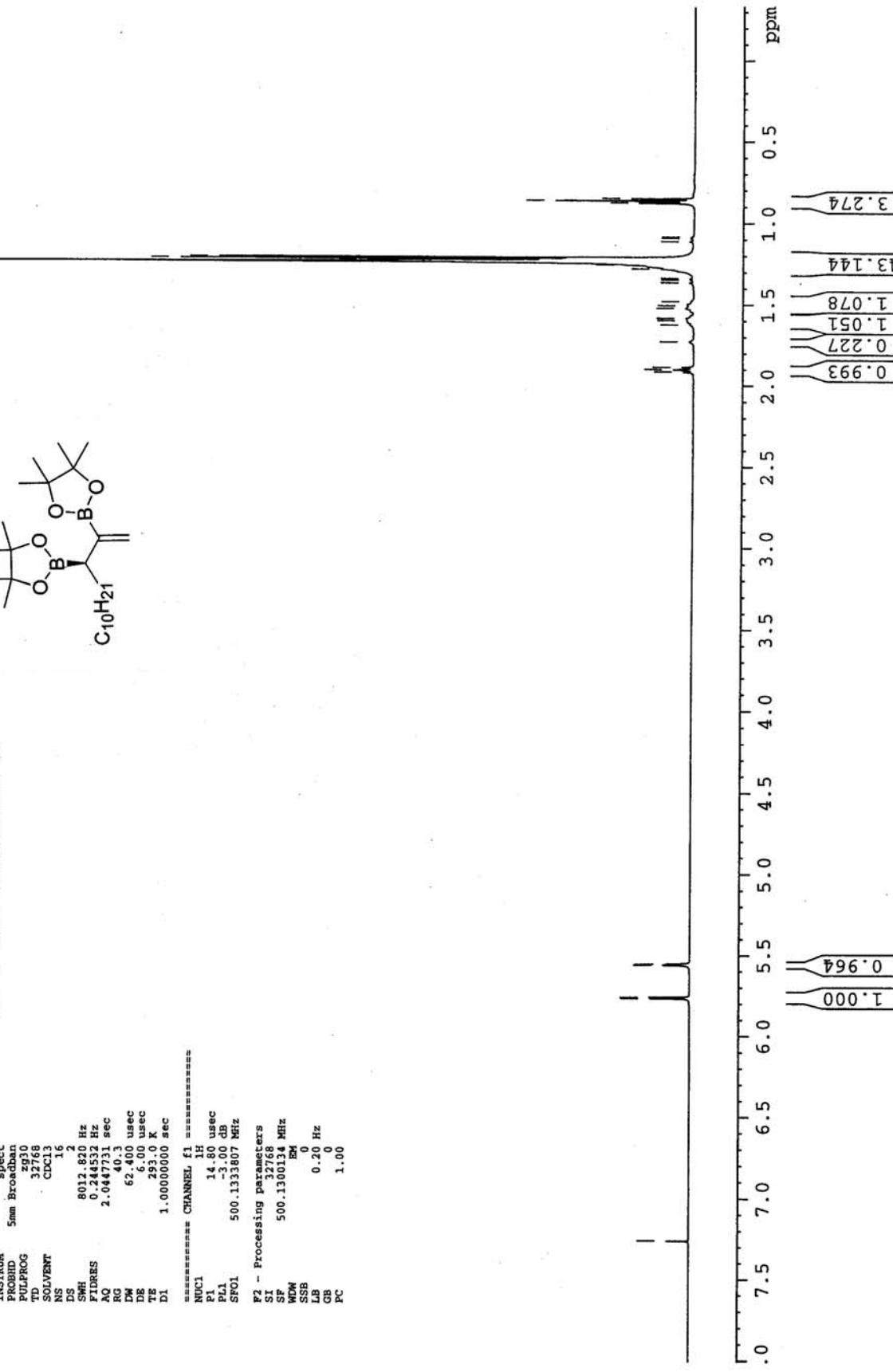
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aw 1-143 fraction 1



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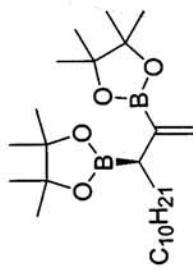
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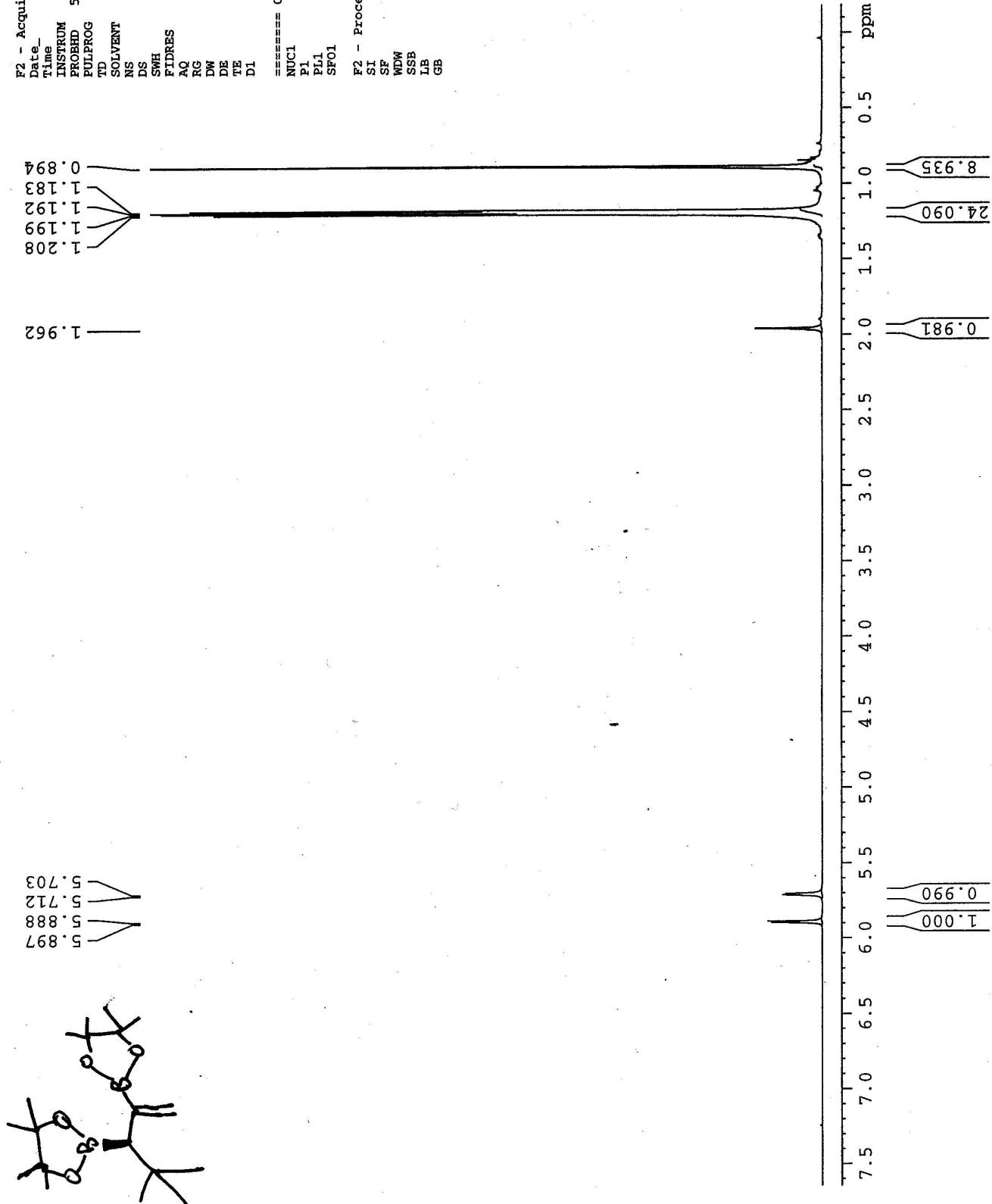
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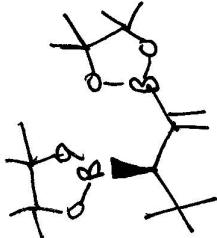
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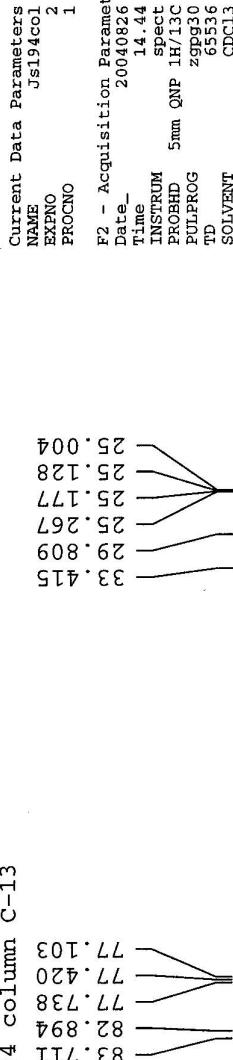


## JS194 column C-13

132.499



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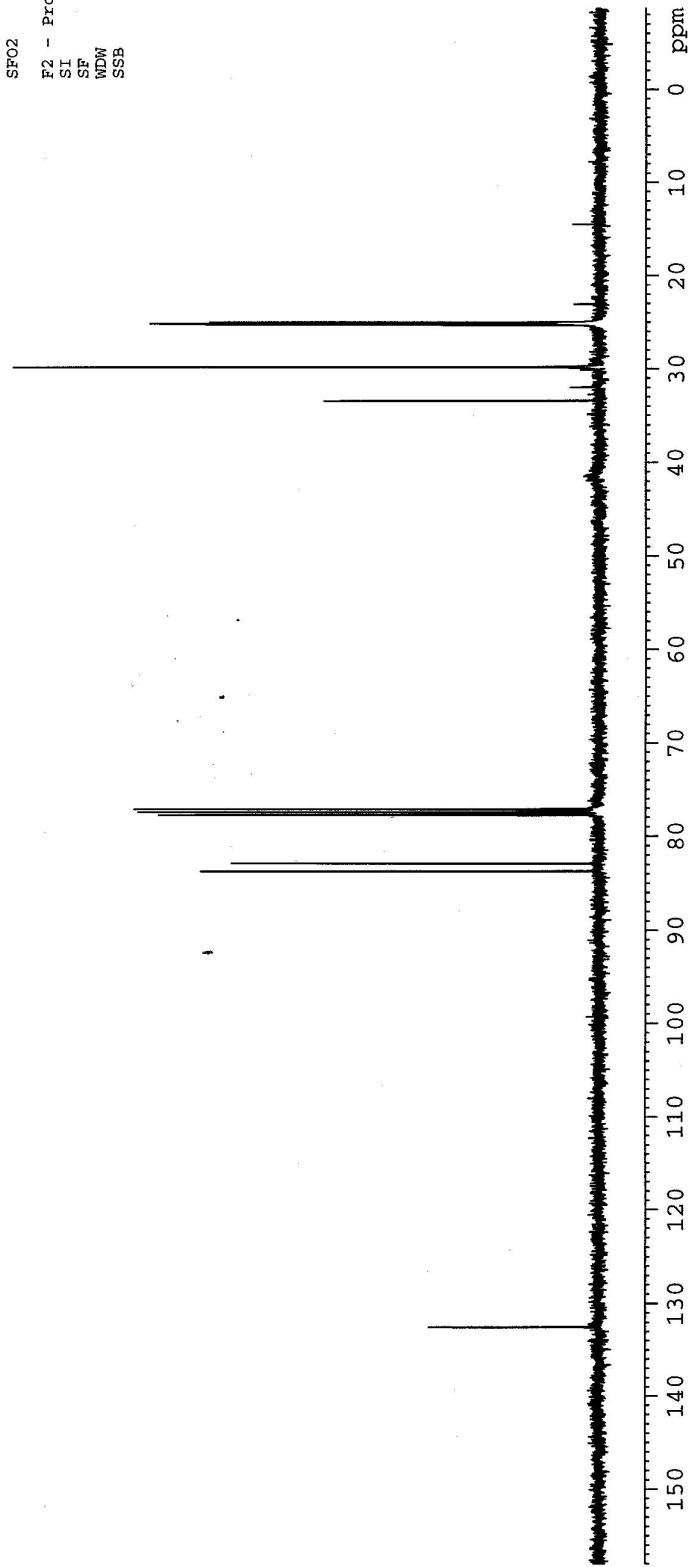
Current Data Parameters  
 NAME JS194col1  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameter  
 Date\_ 20040826  
 Time\_ 14.44  
 INSTRUM spect  
 PROBHD 5mm QNP 1H/13C  
 PULPROG zpp30  
 TD 65536  
 SOLVENT CDCl3  
 NS 107  
 DS 2  
 SWH 26246.719 Hz  
 FIDRES 0.400093 Hz  
 AQ 1.485298 sec  
 RG 9195.2  
 DW 19.050 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.80000001 sec  
 d11 0.03000000 sec  
 d12 0.000002000 sec

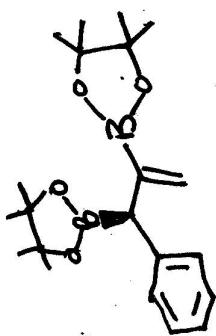
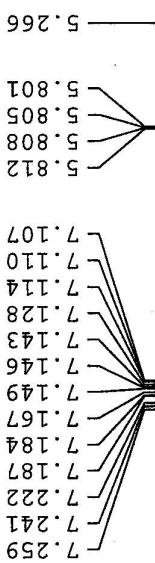
===== CHANNEL f1 =====  
 NUC1 13C  
 P1 5.70 usec  
 PLL 100.6237964 MHz  
 SFO1

===== CHANNEL f2 =====  
 CPDPRG2 walt16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -6.00 dB  
 PL12 13.80 dB  
 PL13 14.50 dB  
 SF02 400.1322200 MHz

F2 - Processing parameters  
 SI 32768  
 SF 100.6122790 MHz  
 WDW EM  
 SSB 0



J5s170 column



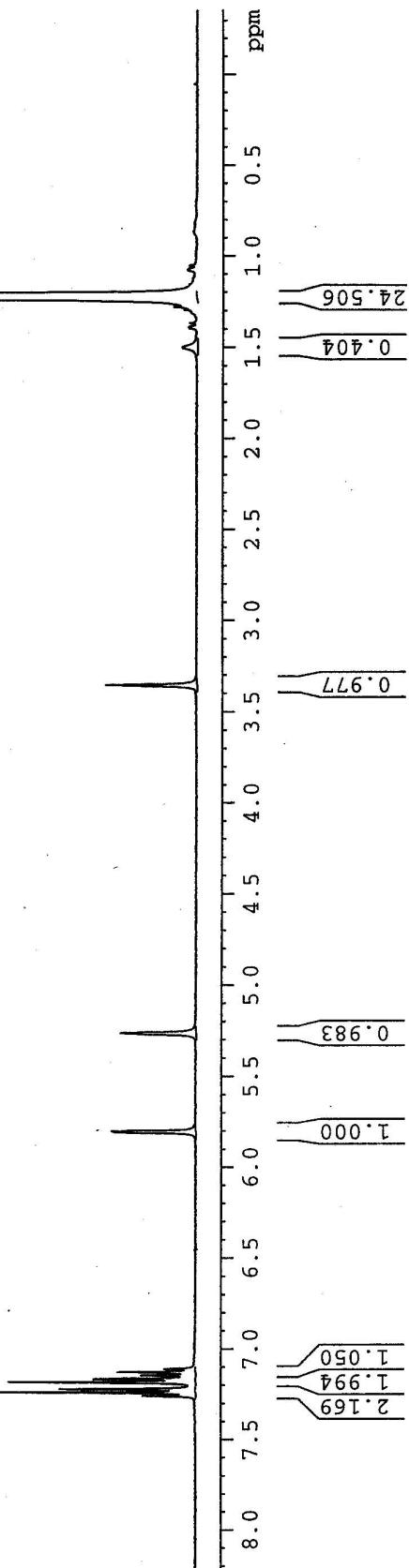
Current Data Parameters  
 NAME Jsi70co1  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameter  
 Date 20040811  
 Time 20:02  
 INSTRUM spect  
 PROBHD 5mm QNP 1H/13C  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDC13  
 NS 16  
 DS 2  
 SWH 6410.256 Hz  
 FIDRES 0.195625 Hz  
 AQ 2.5560319 sec  
 RG 574.7  
 DW 78.000 us  
 DE 6.000 us  
 TE 293.0 K  
 D1 1.00000000 sec

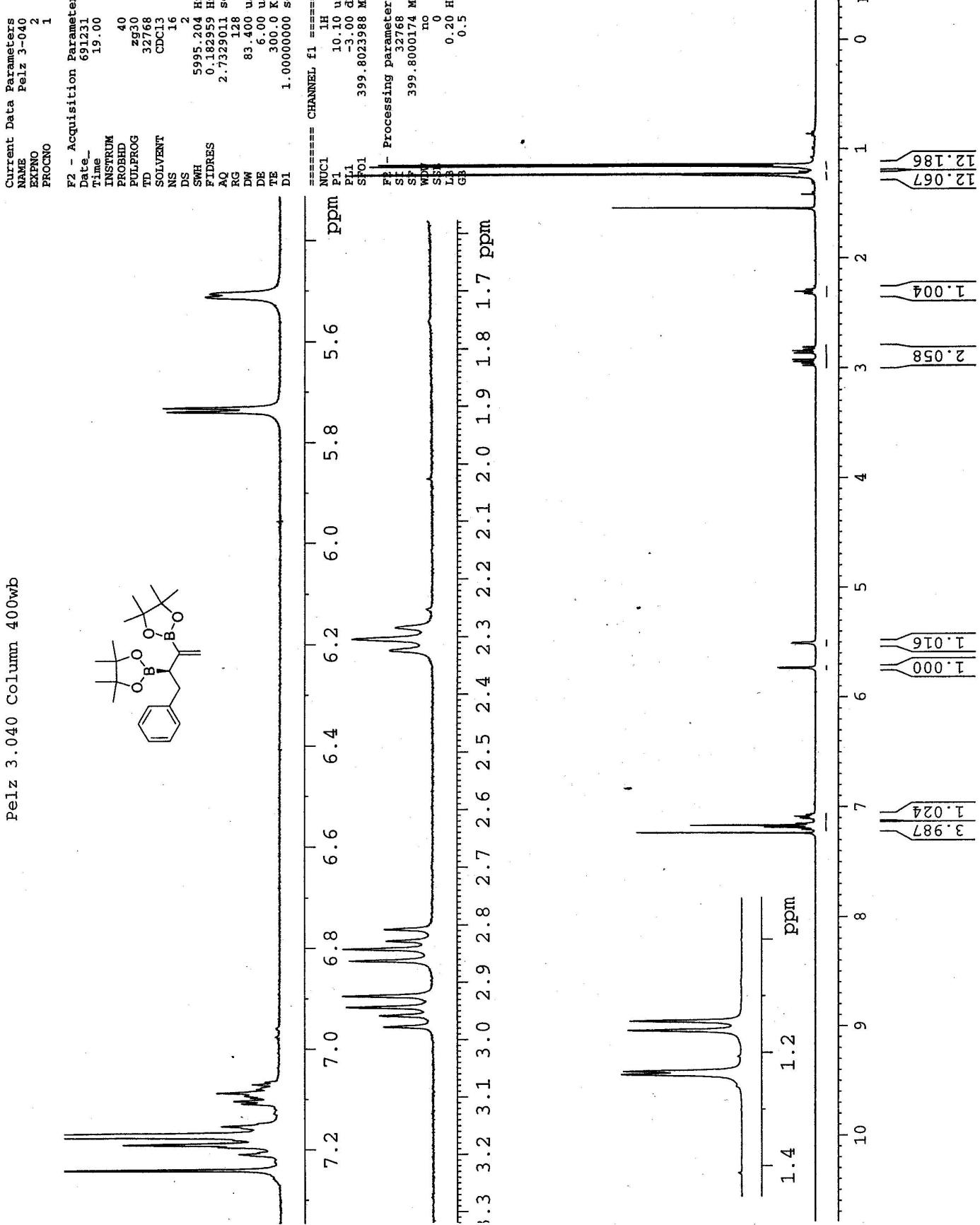
===== CHANNEL f1 =====

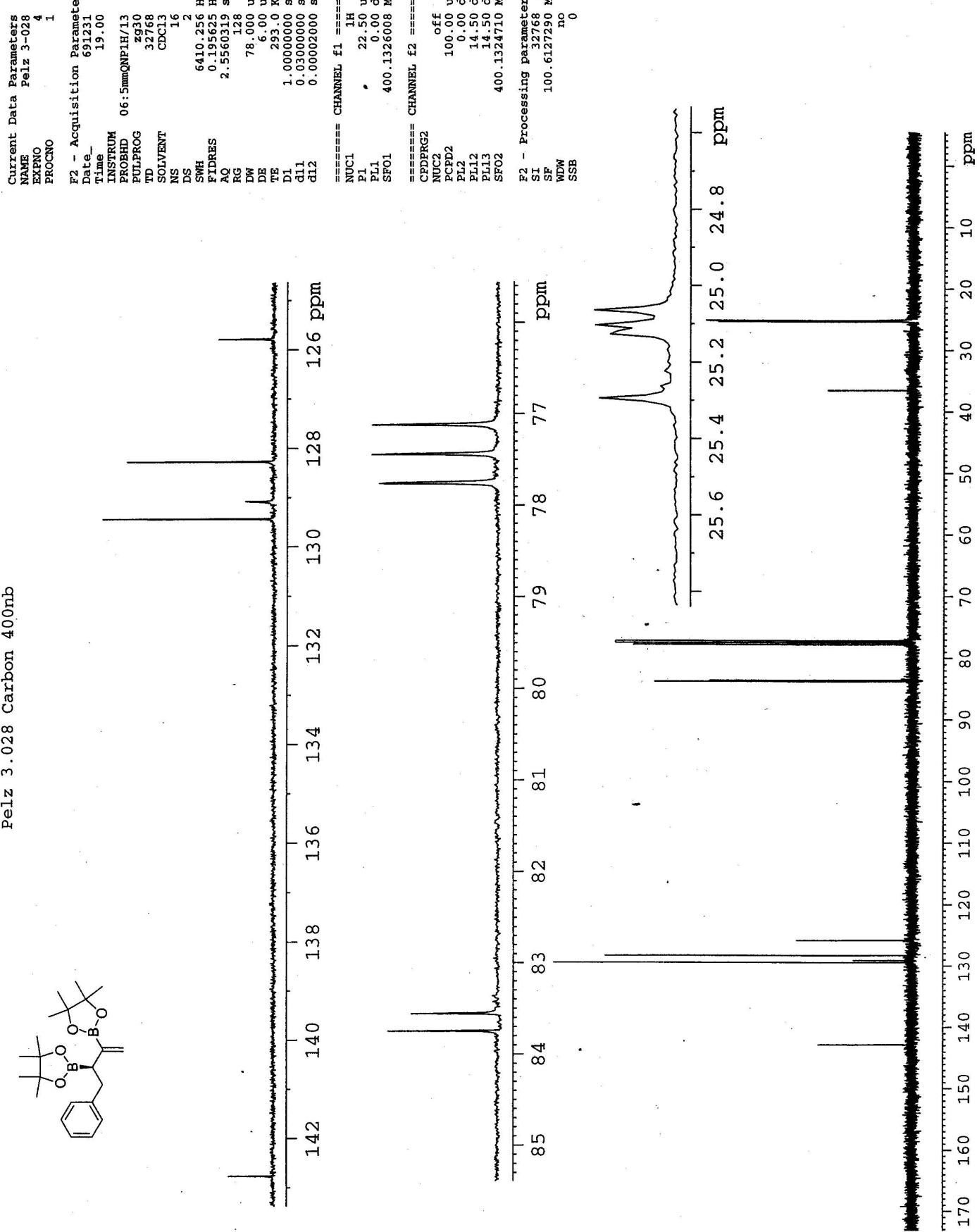
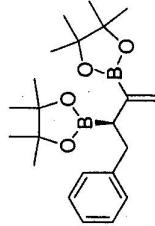
NUC1 1H  
 P1 22.50 us  
 PL1 0.00 deg  
 SF01 400.1346000 MHz

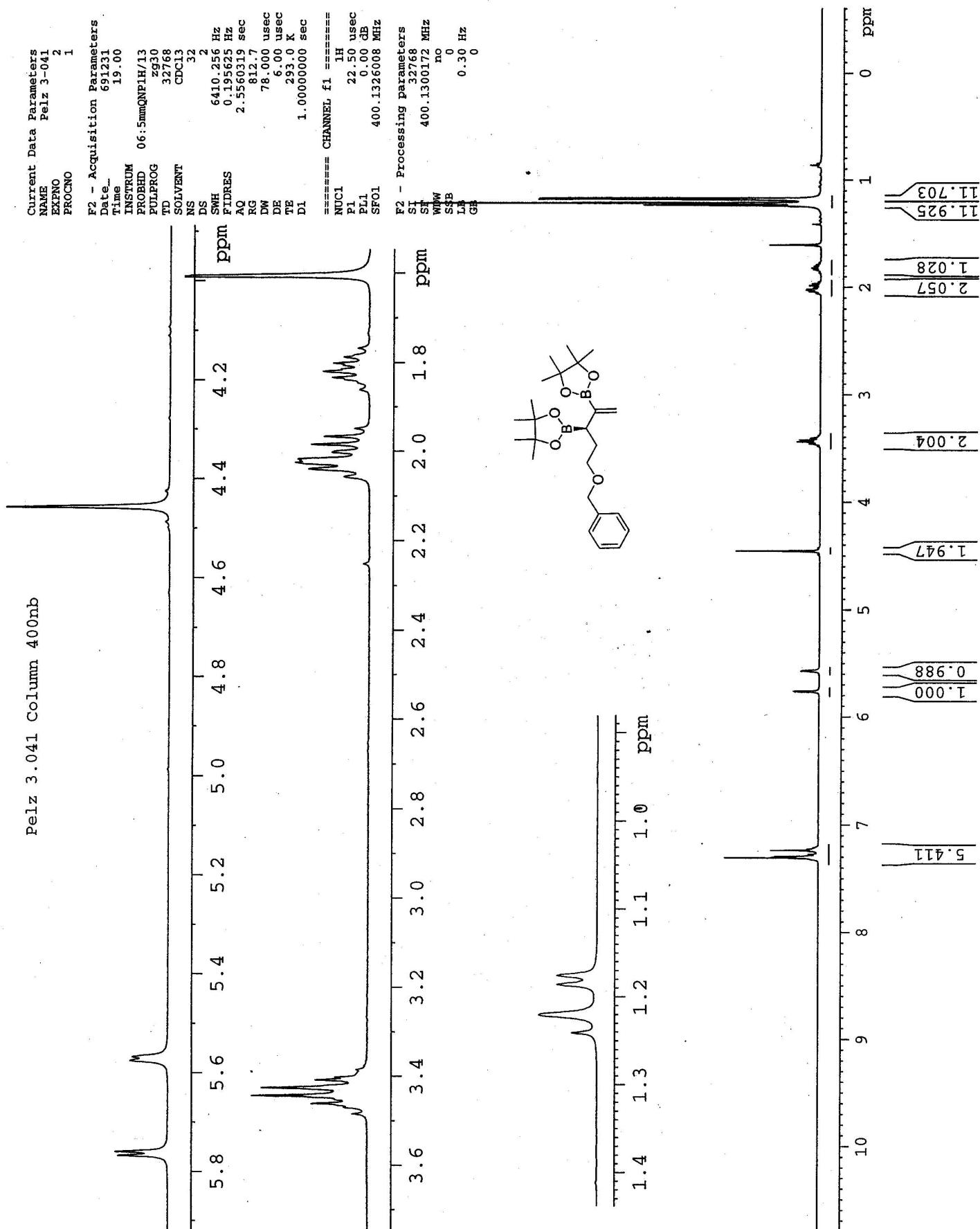
F2 - Processing parameter  
 SI 32768  
 SF 400.1300172 MHz  
 WDW 0  
 SSB 0  
 LB 0.30 Hz  
 GB 0

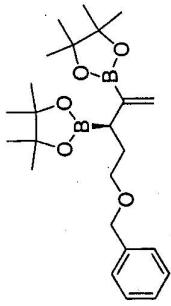




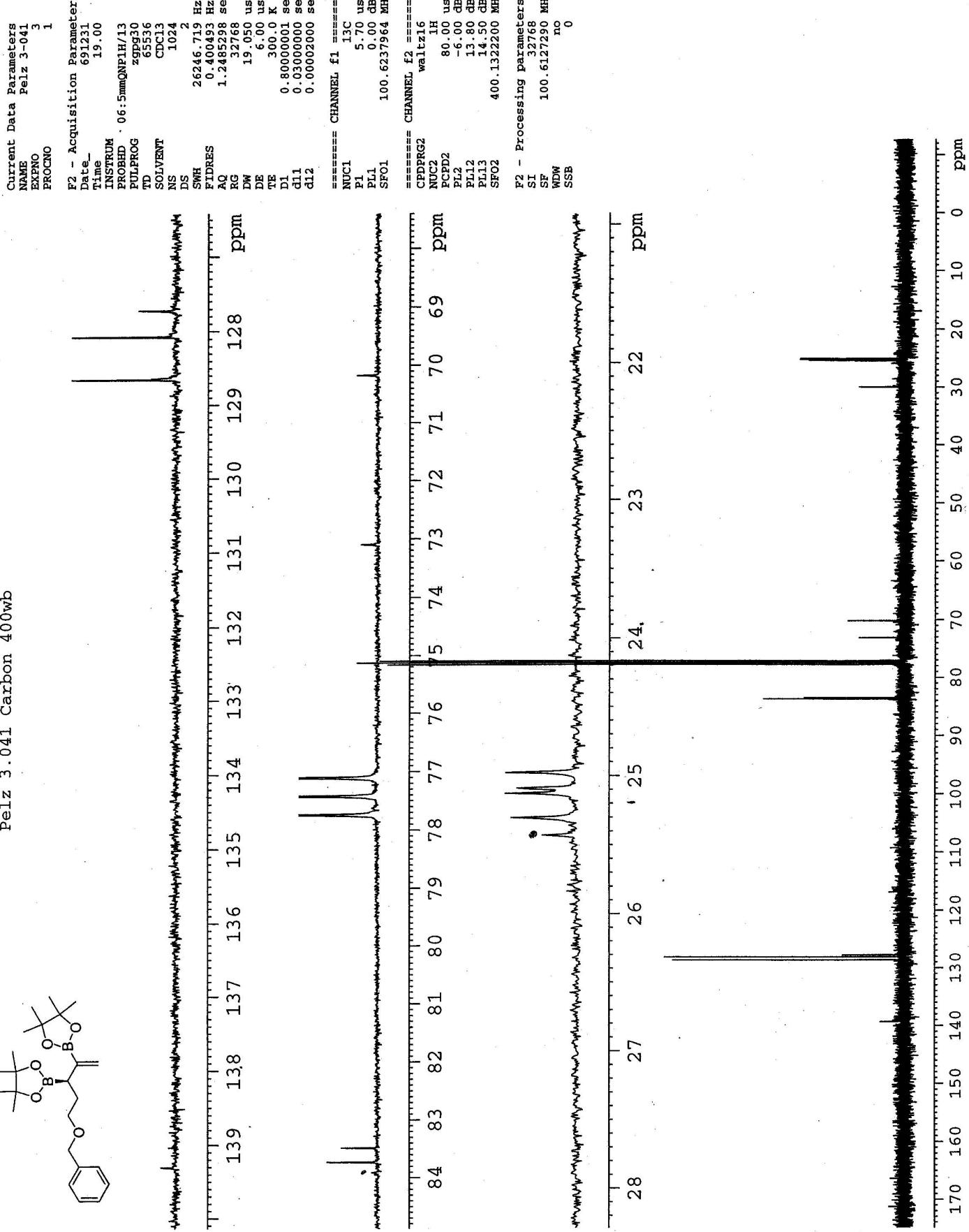








S- 29



1.294

2.956  
2.938  
2.921  
2.903  
2.878  
2.872  
2.843  
2.837

3.781  
3.748  
3.716

5.171  
5.165  
5.153  
5.147

7.198  
7.212  
7.288  
7.291  
7.294  
7.300  
7.303  
7.309  
7.313  
7.317  
7.321  
7.323  
7.326  
7.331  
7.338  
7.344  
7.356  
7.364  
7.378  
Current Data Parameters  
EXPNO  
PROCNO  
INSTRUM  
SPECTRUM  
PROBHD  
PULPROG  
TD  
SOLVENT  
NS  
DS  
SWH  
FIDRES  
AQ  
RG  
DW  
DE  
TE  
D1

2004922  
10.28  
5mm Broadband  
5mm  
32768  
CDCl<sub>3</sub>  
16  
2  
8012.820 Hz  
0.244532 Hz  
2.044731 sec  
181  
62.400 usec  
6.00 usec  
293.0 K  
1.0000000 sec

===== CHANNEL f1 =====

NUC1  
6.50 usec  
PL1  
500.1333607 kHz  
SP01

===== CHANNEL f2 =====

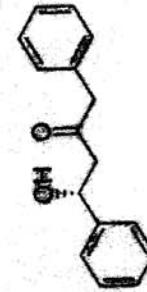
P2 - Acquisition Parameters

Time  
INSTRUM  
SPECTRUM  
PROBHD  
PULPROG  
TD  
SOLVENT  
NS  
DS  
SWH  
FIDRES  
AQ  
RG  
DW  
DE  
TE  
D1

P2 - Processing parameters

SI  
SF  
WDW  
SSB  
LB  
GB  
PC

137766  
500.1300000 Hz  
EM  
0  
0.20 Hz  
0  
1.00



aw 1-149 9/22/04

