

## Supporting Information for:

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

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**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. (1*R*, 7*R*)-4-Dimethylamino-9,9-dimethyl-2,2,6,6-tetraphenyl-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane, [(*R,R*)-(TADDOL)PNMe<sub>2</sub>] 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 allenenes 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.; Verkruijsse, 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 <sup>1</sup>H NMR Analysis:**

In an inert atmosphere glovebox, an oven dried one dram vial was charged with 2.1 mg (0.0023 mmol) Pd<sub>2</sub>(dba)<sub>3</sub> followed by subsequent addition of the required amount of ligand, using a stock solution whenever necessary. The mixture was then dissolved in 0.75 mL toluene-d<sub>8</sub>. 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 <sup>1</sup>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.

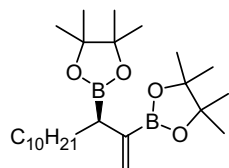
**General Procedure for the Diimide Reduction of Diboration Products:**

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:**

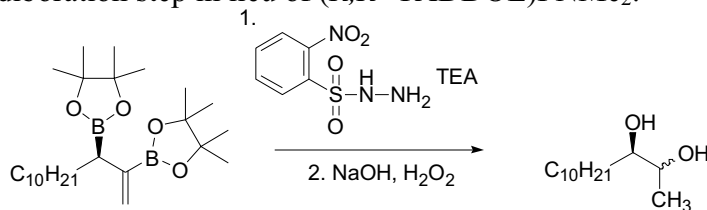
An oven-dried 20 mL vial equipped with a stir-bar was charged with 8 mg (0.009 mmol) Pd<sub>2</sub>(dba)<sub>3</sub>, 11 mg (0.021 mmol) (R,R)-TADDOL-PNMe<sub>2</sub>, and 2.1 mL of toluene under an inert atmosphere of argon in a dry-box. The purple solution was stirred until it appeared yellow (30 minutes). 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%  $\text{H}_2\text{O}_2$  (for hazards associated with  $\text{H}_2\text{O}_2$ , 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  $\text{Na}_2\text{S}_2\text{O}_3$  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  $\text{Na}_2\text{SO}_4$ , 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.

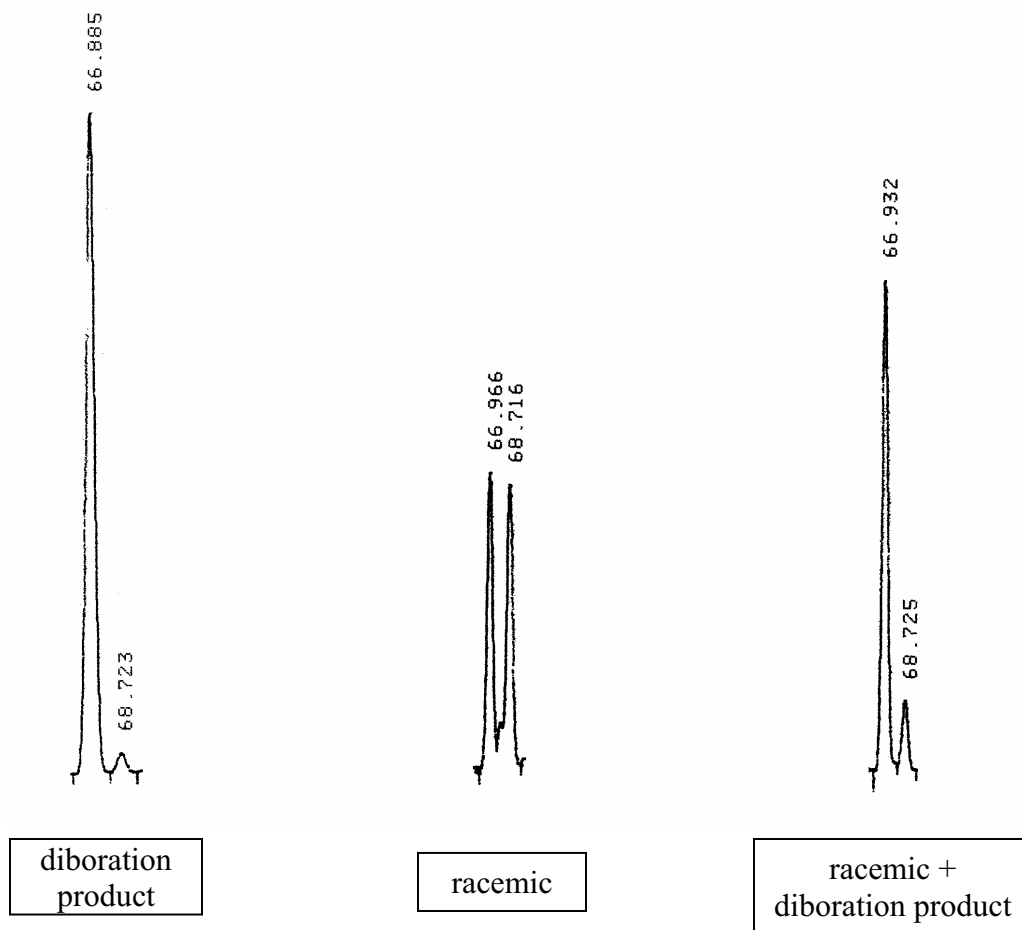


**(S)-2,3-di(pinacolatoboron)-1-tridecene.** IR (CH<sub>2</sub>Cl<sub>2</sub>): 2929 (s), 1349 (s), 1146 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR: δ 5.76 (1H, d, J = 3.5 Hz, BCCCH<sub>2</sub>), 5.55 (1H, d, J = 3.0 Hz, BCCCH<sub>2</sub>), 1.90 (2H, dd, J = 7.8 Hz, 7.5 Hz, CH<sub>2</sub>CHB), 1.16 – 1.48 (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: δ 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>.

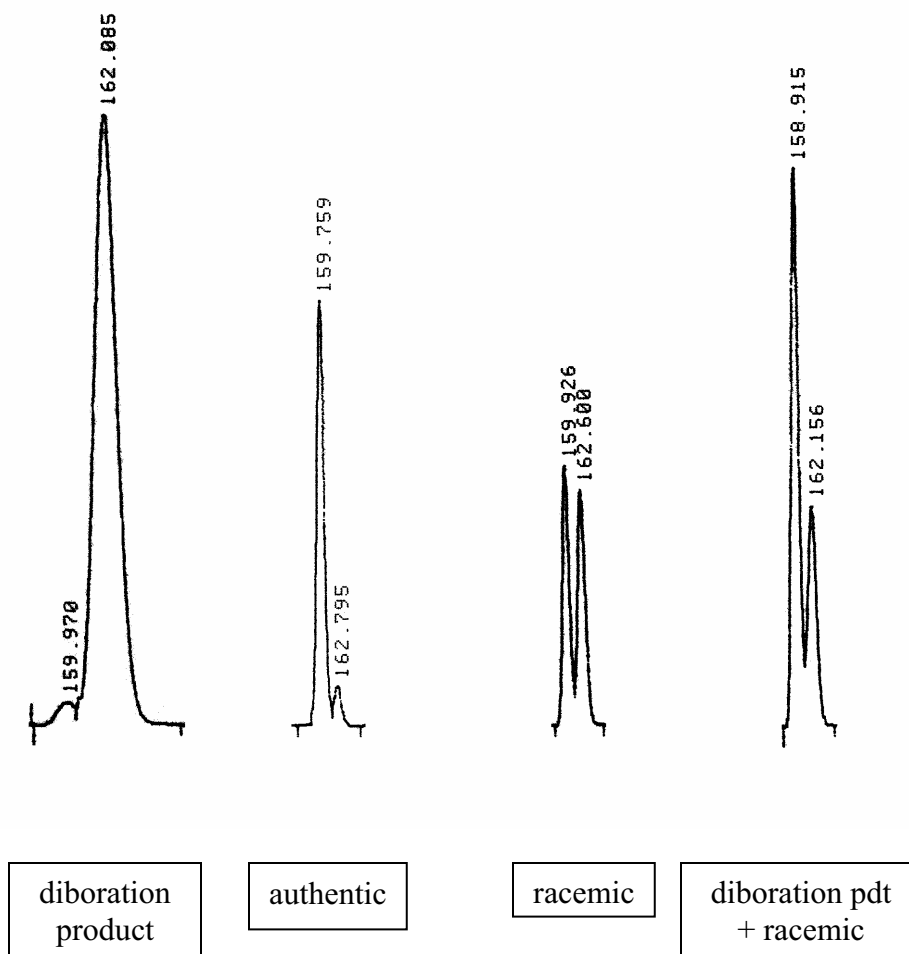


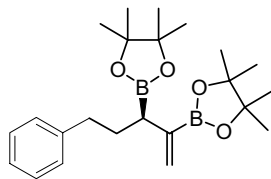
Chiral GLC (β-dex, Supelco, 120 °C, derived acetonide, *cis* diol is better resolved than the *trans* and is displayed below)



**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)*

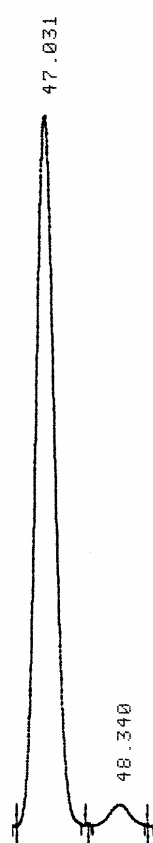




**(S)- 1-phenyl-3,4-dipinacolatoboron-4-pentene.** Isolated 90 mg of an oil.  $R_f = 0.49$  in 15:1 hexanes:EtOAc. IR ( $\text{CH}_2\text{Cl}_2$ ): 2929 (m), 1316 (s), 1133 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  7.28-7.13 (5H, m, Ph), 5.85 (1H, d,  $J = 2.4$  Hz,  $\text{BCCH}_2$ ), 5.62 (1H, d,  $J = 2.4$  Hz,  $\text{BCCH}_2$ ), 2.64-2.54 (2H, m,  $\text{PhCH}_2$ ), 2.03-1.89 (3H, m,  $\text{BCHCH}_2$ ), 1.30 (6H, s,  $\text{BOC}(\text{CH}_3)_2$ ), 1.28 (6H, s,  $\text{BOC}(\text{CH}_3)_2$ ), 1.26 (6H, s,  $\text{BOC}(\text{CH}_3)_2$ ), 1.26 (6H, s,  $\text{BOC}(\text{CH}_3)_2$ );  $^{13}\text{C}$  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  $\text{C}_{23}\text{H}_{36}\text{B}_2\text{O}_4$  ( $\text{M}+\text{Na}$ ) $^+$ : 421.2692 Found ( $\text{M}+\text{Na}$ ) $^+$ : 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  $\text{PCy}_3$  in the diboration step in lieu of (*R,R*-TADDOL)PNMe $_2$ .

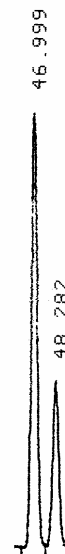
*Chiral GLC ( $\beta$ -dex, Supelco, 120  $^\circ\text{C}$ , derived acetone, one diastereomer shown)*



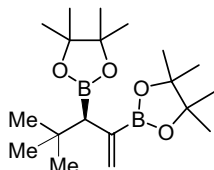
Diboration  
Product



Racemic



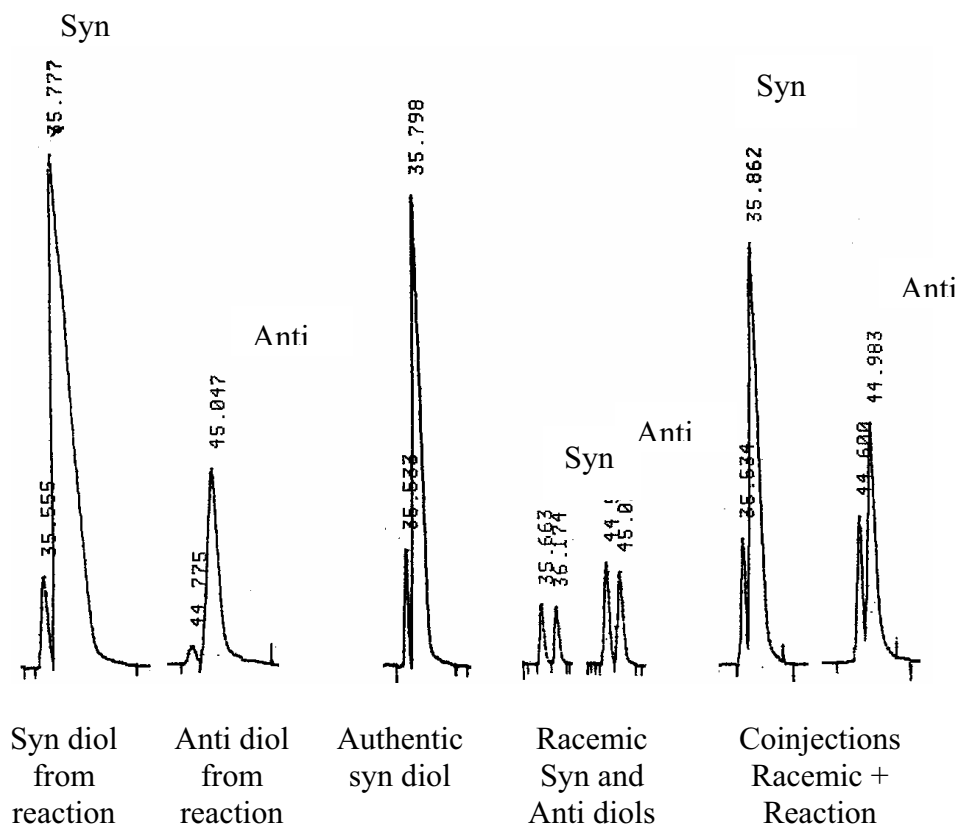
Racemic +  
Diboration Product

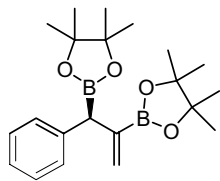


**(S)-2-4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.** 113 mg of a white solid.  $R_f = 0.25$  in 15:1 hexanes:EtOAc. IR (KBr pellet): 2986 (br, s), 2943 (br, s), 2866 (br, m) 1926 (w), 1600 (w), 1344 (br, m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  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,  $\text{OCCH}_3$ ), 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  $\text{C}_{19}\text{H}_{36}\text{B}_2\text{O}_4$  ( $\text{M} + \text{Na}$ ) $^+$ : 373.2692 Found ( $\text{M} + \text{Na}$ ) $^+$ : 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  $\text{H}_2\text{O}_2$  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  $\text{PCy}_3$  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 ( $\beta$ -dex, Supelco, 80 – 140  $^\circ\text{C}$  at 1  $^\circ\text{C}/\text{min}$ ) analysis of diol products resulting from the reduction-oxidation sequence described above:

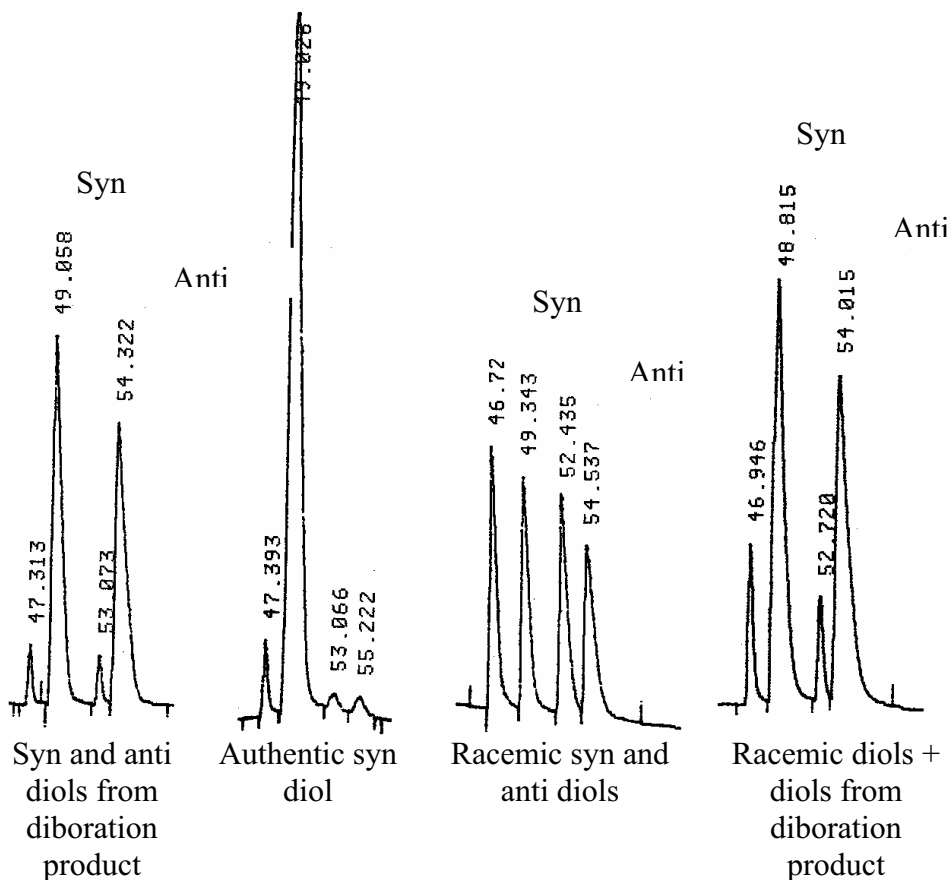




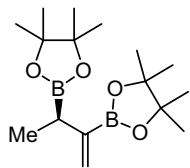
**(S)-4,4,5,5-tetramethyl-2-(1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-2-yl)-1,3,2-dioxaborolane.** 127 mg of a yellow oil.  $R_f = 0.33$  in 10:1 hexanes:EtOAc. IR (neat): 2970 (br, s), 2924 (br, m), 1604 (w), 1417 (br, m), 1313 (br, s), 1142 (br, s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  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,  $\text{OCCH}_3$ );  $^{13}\text{C}$  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  $\text{C}_{21}\text{H}_{32}\text{B}_2\text{O}_4$  ( $\text{M} + \text{Na}$ ) $^+$ : 393.2379 Found ( $\text{M} + \text{Na}$ ) $^+$ : 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  $\text{H}_2\text{O}_2$  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  $\text{PCy}_3$  as the achiral ligand, followed by the above reduction-oxidation sequence. The absolute stereochemistry was established in comparison to authentic (*1R*, *2R*)-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 ( $\beta$ -dex, Supelco, 140  $^\circ\text{C}$ ) analysis of diol products resulting from the reduction-oxidation sequence described above:



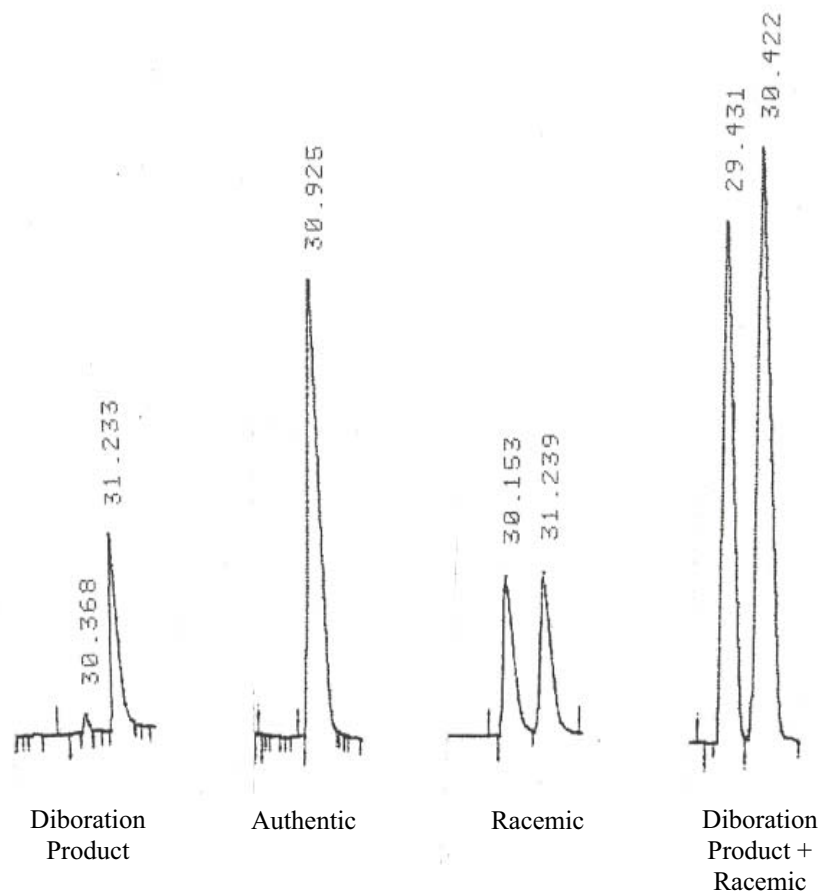


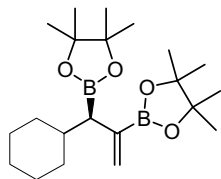


**(R)-4,4,5,5-tetramethyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-2-yl)-1,3,2-dioxaborolane.** 74 mg of a yellow oil.  $R_f = 0.32$  in 25:1 hexanes:EtOAc. IR: 2978 (s), 2933 (s), 1612 (s), 1464 (br, m), 1423 (br, m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.11 (3H, d,  $J = 7.2$  Hz,  $\text{CH}_3\text{CHB}$ ), 1.23 (12H, s,  $\text{OCCH}_3$ ), 1.26 (12H, s,  $\text{OCCH}_3$ ), 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*

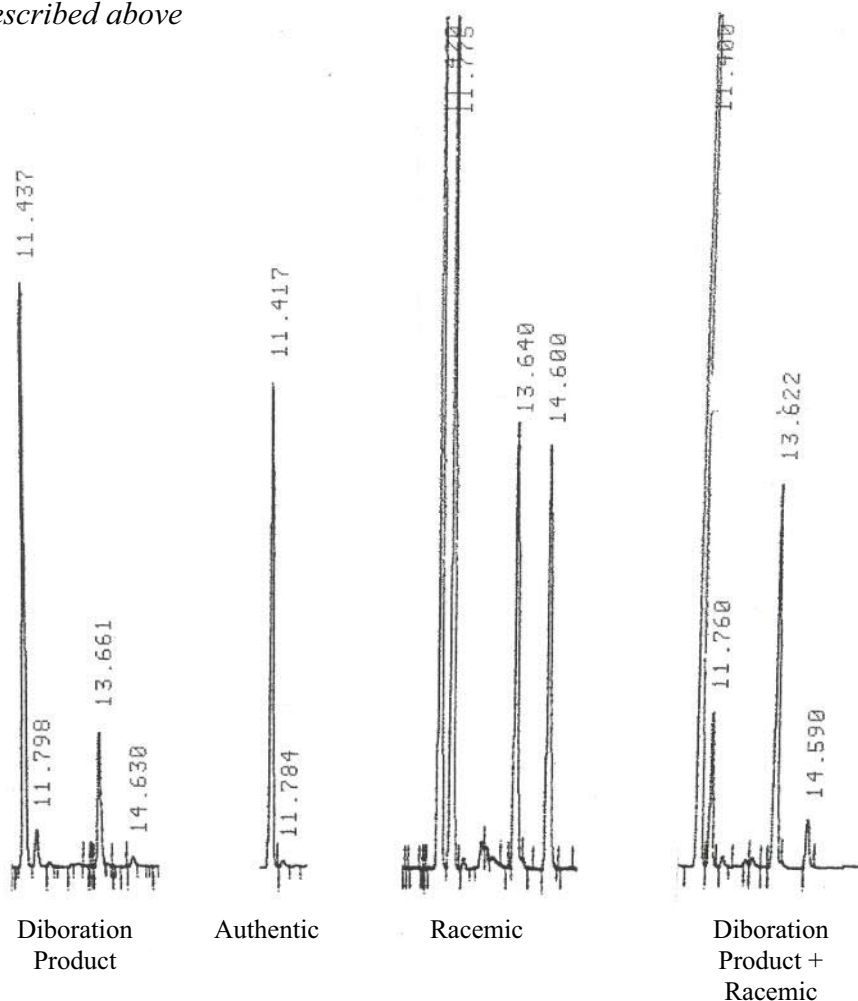


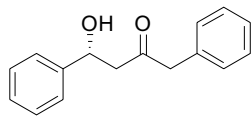


(*R*)-2-(1-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 97 mg of a yellow oil.  $R_f = 0.18$  in 25:1 hexanes:EtOAc. IR: 3062 (s), 2978 (s), 2923 (s), 2850 (s), 1604 (s), 1371 (br, m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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, CBCH), 5.82 (1H, d,  $J = 3.2$  Hz, 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 ( $\beta$ -dex, Supelco, 120 °C) – analysis of acetonide derived from reduction and oxidation of reaction product as described above

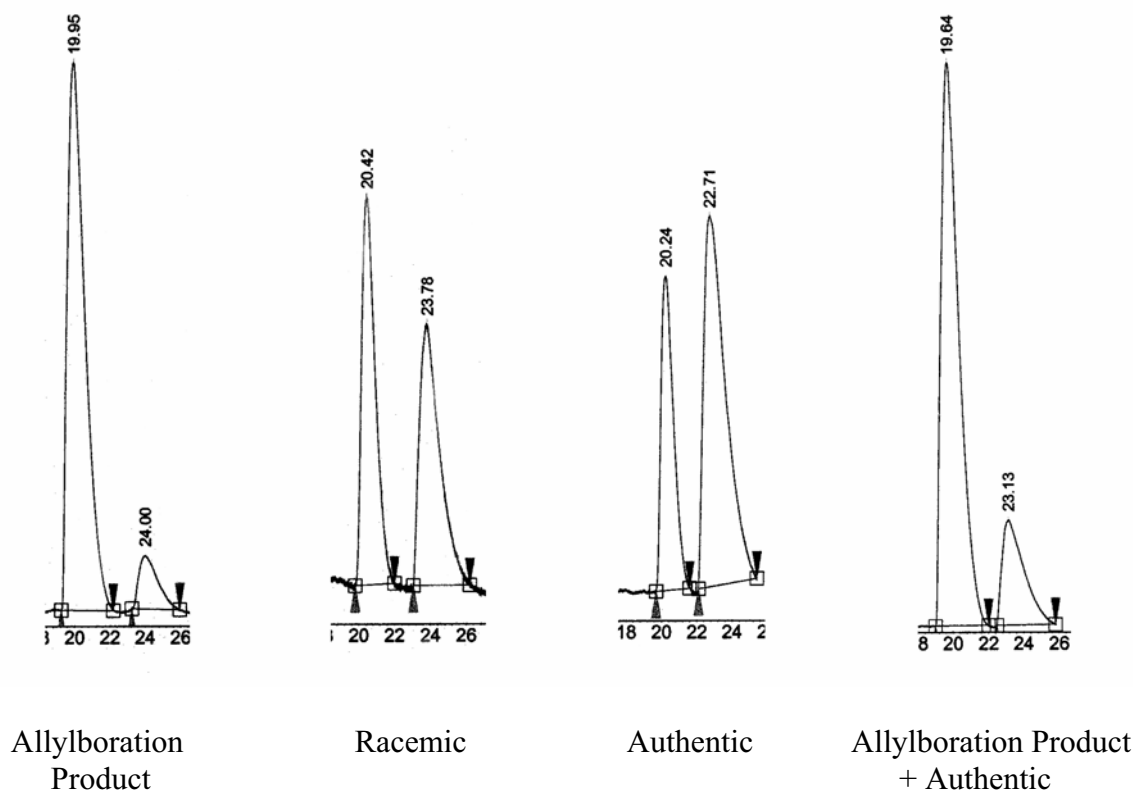


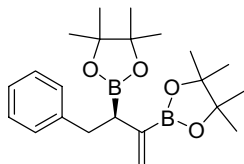


**(R)-4-Hydroxy-1,4-diphenyl-2-butanone.** IR (CH<sub>2</sub>Cl<sub>2</sub>) 2931 (br, m), 2368 (w), 1711 (s), 1497 (m), 1356 (br, m); <sup>1</sup>H NMR: δ 7.37 – 7.26 (8H, m, aromatic), 7.19 – 7.17 (2H, m, aromatic), 5.13 (1H, dd, J = 8.7, 3.6 Hz, HOCH), 3.71 (2H, s, benzylic), 3.25 (1H, br s, OH), 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: δ 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 chlorodiisocampheylborane 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:*

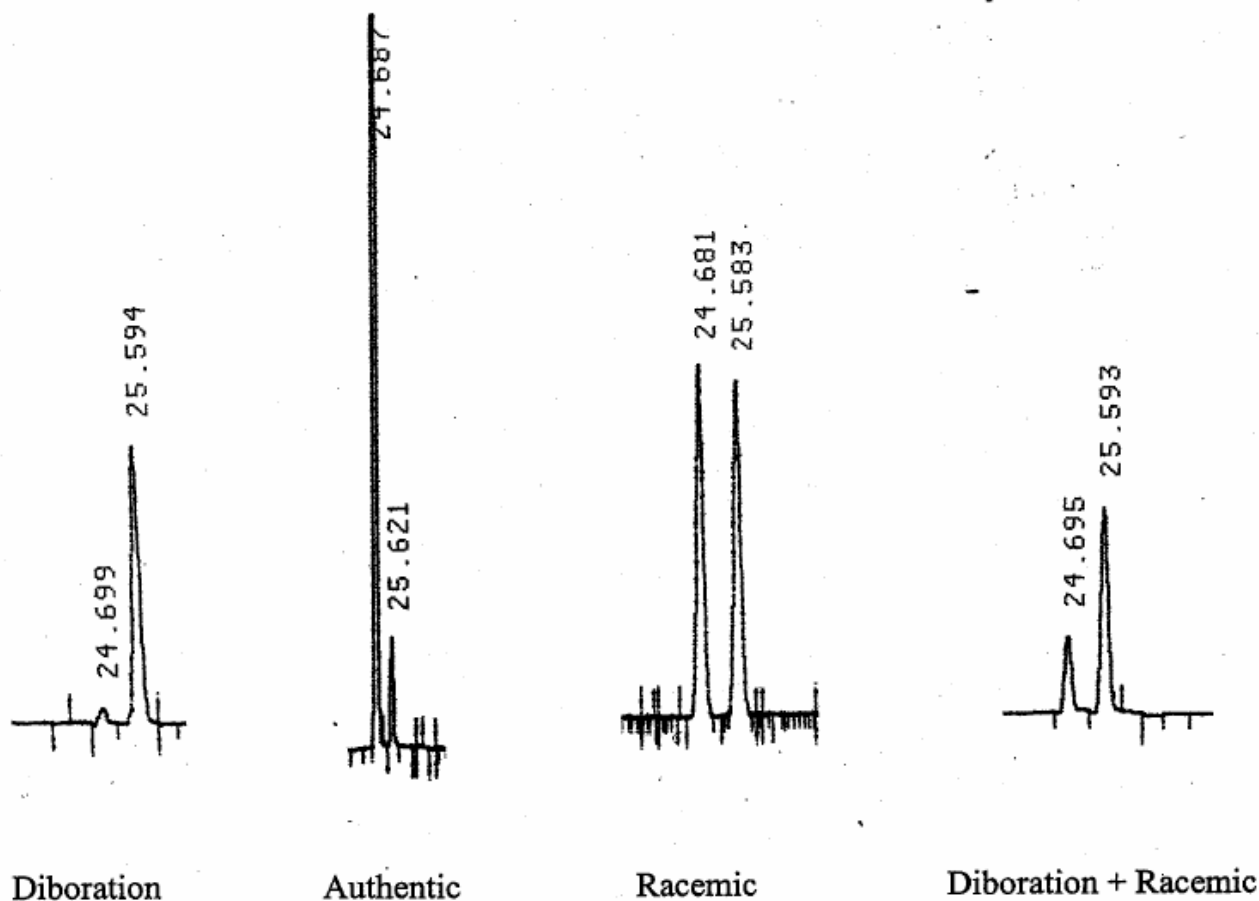


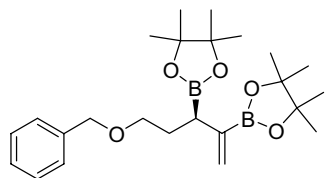


**(R)-4,4,5,5-tetramethyl-2-(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-2-yl)-1,3,2-dioxaborolane** 90 mg of a yellow oil.  $R_f = 0.49$  in 15:1 hexanes:EtOAc. IR ( $\text{CHCl}_3$ ): 2985 (s), 1353 (s), 1146 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  7.21-7.14 (4H, m, Ar), 7.12-7.07 (1H, m, Ar), 5.74 (1H, d,  $J = 3.2$  Hz,  $\text{BCCH}_2$ ), 5.51 (1H, d,  $J = 3.2$  Hz,  $\text{BCCH}_2$ ), 2.98 – 2.93 (1H, dd,  $J = 14, 7.7$  Hz,  $\text{PhCH}_2$ ), 2.86-2.81 (1H, dd,  $J = 14, 7.7$  Hz,  $\text{PhCH}_2$ ), 2.31 (1H, t,  $J = 7.7$  Hz,  $\text{PhCH}_2\text{CHB}$ ), 1.24 (6H, s, pinacol methyl), 1.23 (6H, s, pinacol methyl), 1.16 (6H, s, pinacol methyl), 1.15 (6H, s, pinacol methyl);  $^{13}\text{C}$  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  $\text{C}_{22}\text{H}_{34}\text{B}_2\text{O}_4$  ( $\text{M}+\text{Na}$ ) $^+$ : 384.1250 Found ( $\text{M}+\text{Na}$ ) $^+$ : 384.1241.

**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 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 ( $\beta$ -dex, Supelco, 120  $^\circ\text{C}$ , derived acetonide, only the diastereomer corresponding to the syn diol is shown)

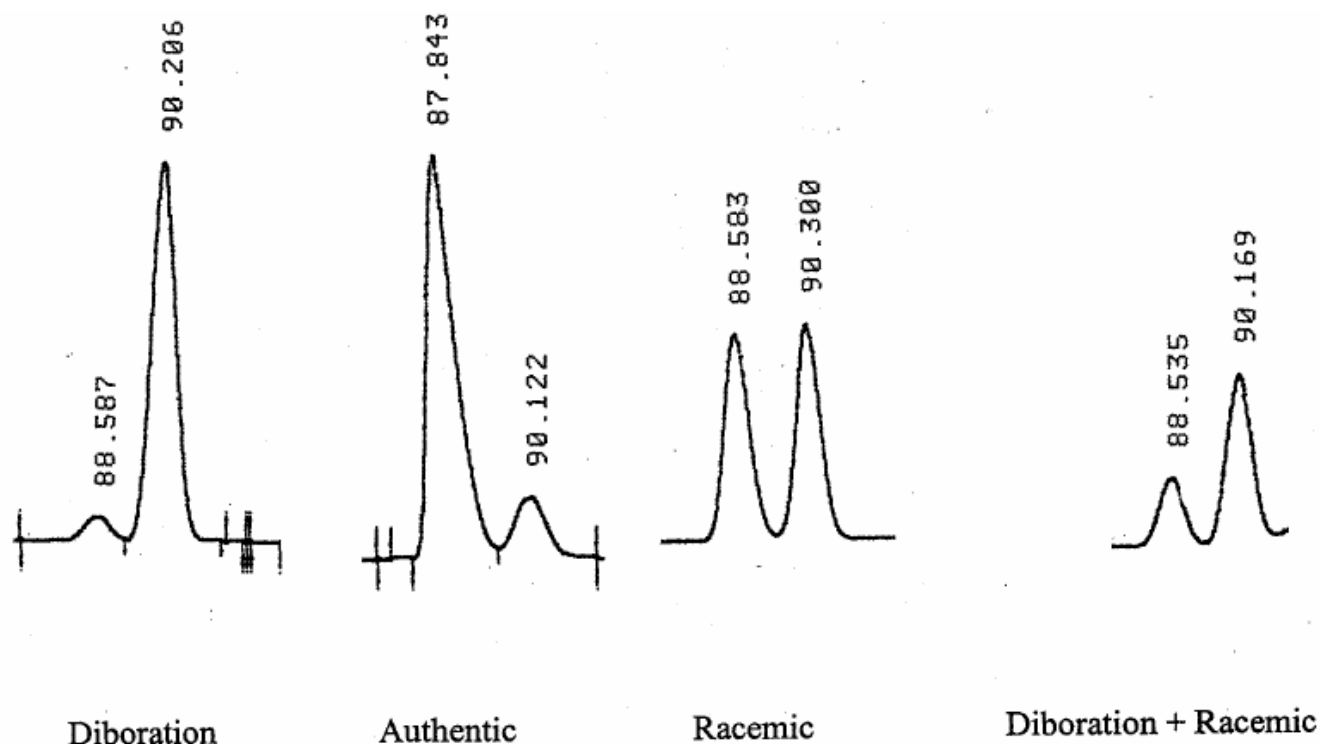




(*R*)-2-(5-(benzyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 55 mg of a solid.  $R_f = 0.28$  in 10:1 hexanes:EtOAc. IR ( $\text{CHCl}_3$ ): 2985 (s), 1372 (s), 1146 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  7.35-7.19 (5H, m, Ar), 5.76 (1H, d,  $J = 3.2$  Hz,  $\text{BCCH}_2$ ), 5.57 (1H, d,  $J = 2.8$  Hz,  $\text{BCCH}_2$ ), 4.46 (2H, s,  $\text{PhCH}_2\text{O}$ ), 3.47-3.38 (2H, m,  $\text{OCH}_2\text{CH}_2$ ), 2.06-1.95 (2H, m,  $\text{OCH}_2\text{CH}_2$ ), 1.87-1.77 (1H, m,  $\text{CH}_2\text{CHB}$ ), 1.220 (12H, s, pinacol methyl), 1.19 (6H, s, pinacol methyl), 1.18 (12H, s, pinacol methyl);  $^{13}\text{C}$  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  $\text{C}_{24}\text{H}_{38}\text{B}_2\text{O}_5$  ( $\text{M}+\text{Na}$ ) $^+$ : 428.1775 Found ( $\text{M}+\text{Na}$ ) $^+$ : 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 acetone (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 acetone as described above. Absolute stereochemistry was established from the acetone 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  $^\circ\text{C}$ , hold 90min, Ramp 5  $^\circ\text{C}/\text{min}$  to 150  $^\circ\text{C}$  derived acetone, only the diastereomer corresponding to the syn diol is shown)



heb1-136-characterization

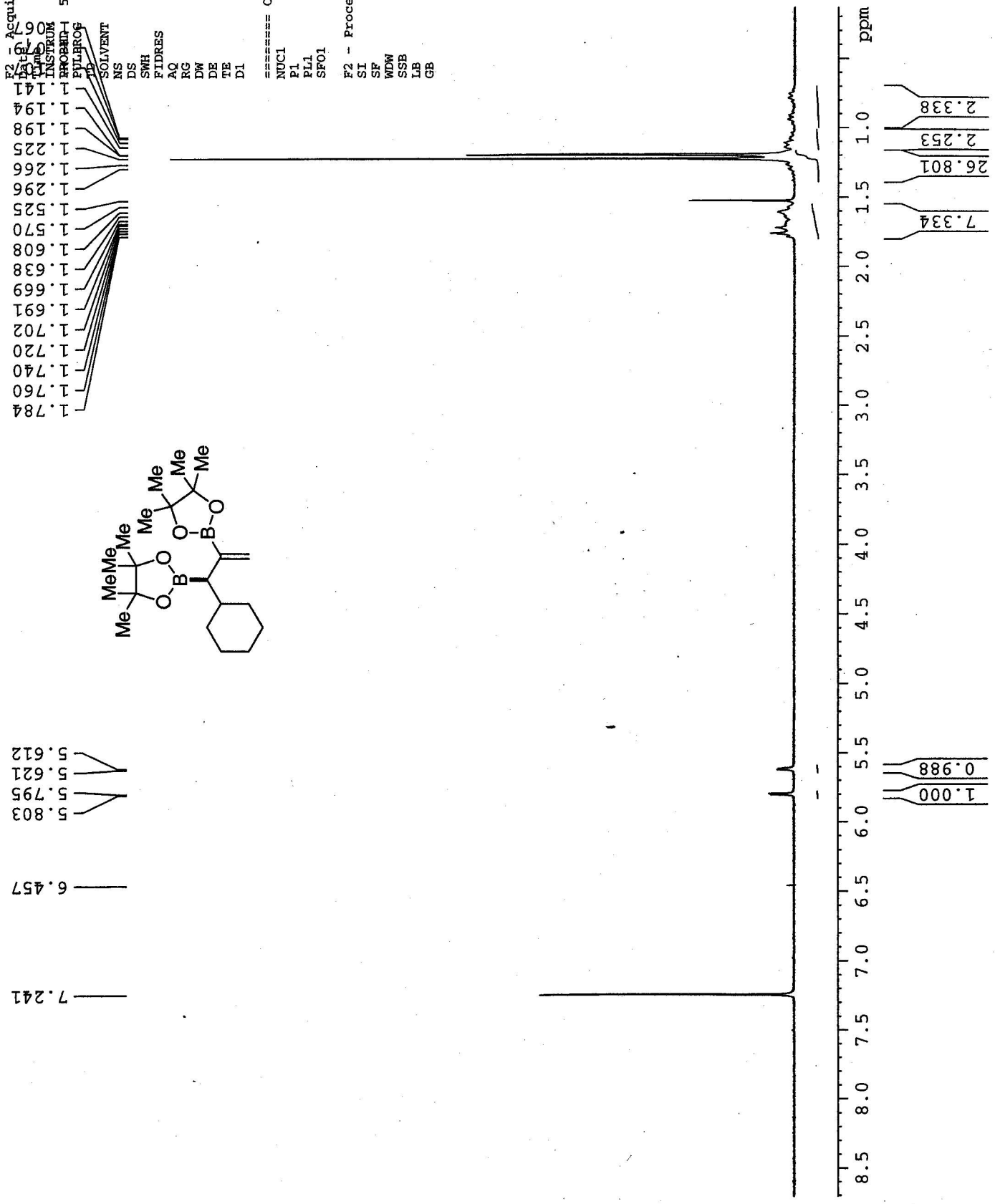
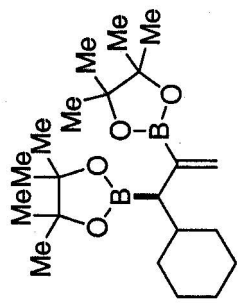
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 FIDRES 0.195625 Hz  
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 DE 6.00 usec  
 TE 293.0 K  
 D1 1.00000000 sec

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EXPNO 5  
PROCNO 1

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SOLVENT CDCl3  
NS 25257  
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SWH 26246.719 Hz  
FIDRES 0.400493 Hz  
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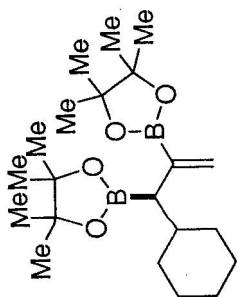
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PL13 14.50 dB  
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26.679  
24.854

83.346  
82.940  
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77.163  
76.846



129.345

130 120 110 100 90 80 70 60 50 40 30 20 ppm

heb1-134-clmned material characterization spectrum

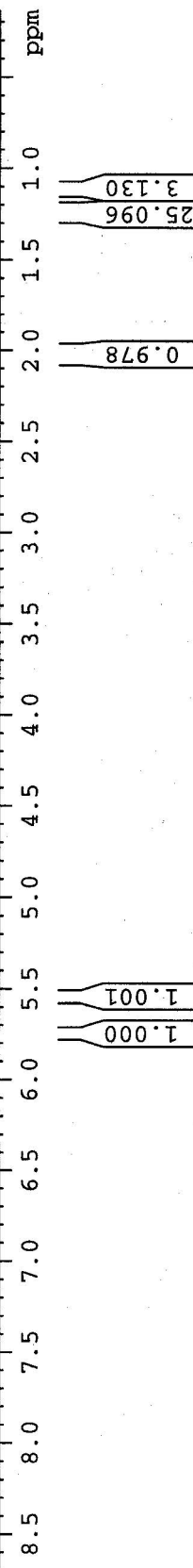
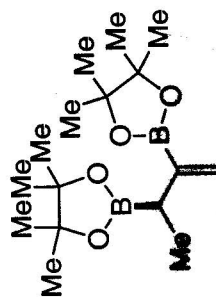
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TD 32768  
SOLVENT CDCl3  
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DS 2  
SWH 6410.256 Hz  
FIDRES 0.195625 Hz  
AQ 2.5559540 sec  
RG 912.3  
DW 78.000 usec  
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TE 293.0 K  
D1 1.00000000 sec

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WDW no  
SSB 0  
LB 0.00 Hz  
GB 0

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5.742  
5.551





F2 - Acquisition Parameters  
Date: 20040827

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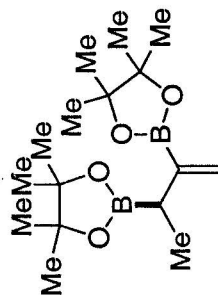
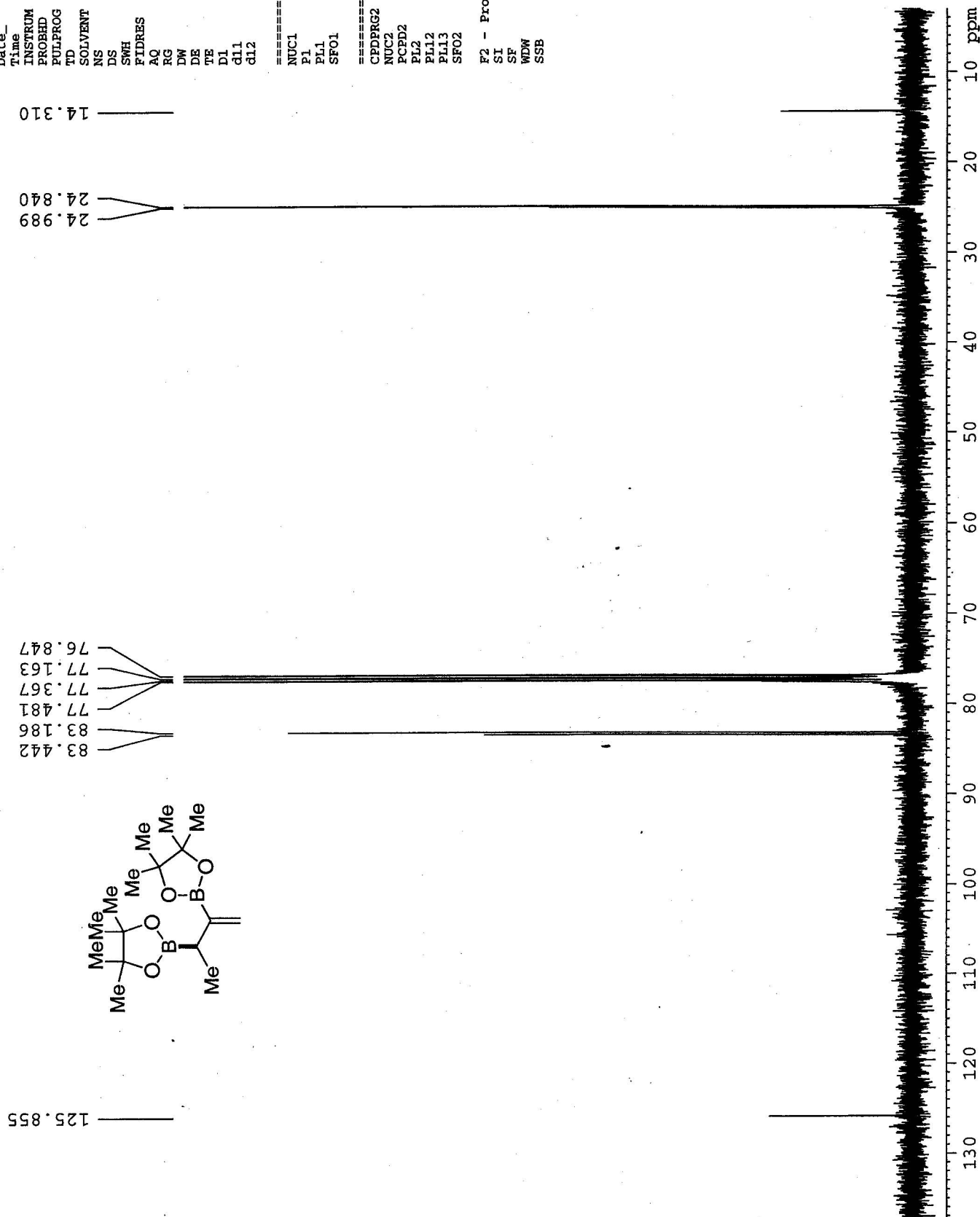
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SFO2

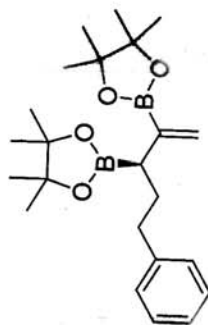
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 FIDRES 0.244532 Hz  
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aw 1-139 fraction 1



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7.200  
7.215  
7.219  
7.225  
7.295  
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5.642  
5.636

2.660  
2.649  
2.640  
2.574  
2.566  
2.554  
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1.296  
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2.202  
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1.000

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1.050

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0.086  
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ppm

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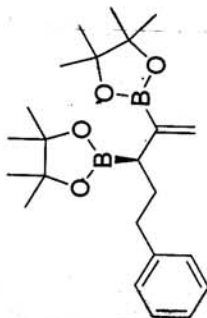
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143.259



200

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100

50

0

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Current Data Parameters  
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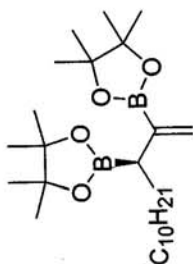
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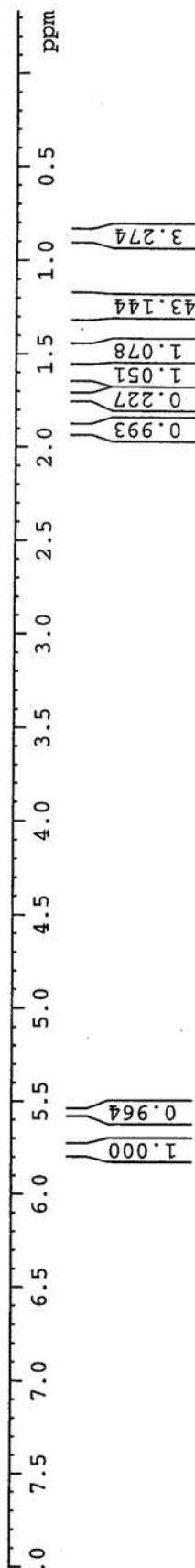
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aw 1-143 fraction 1



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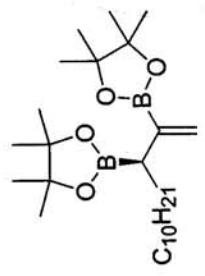
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 NUC2 1H  
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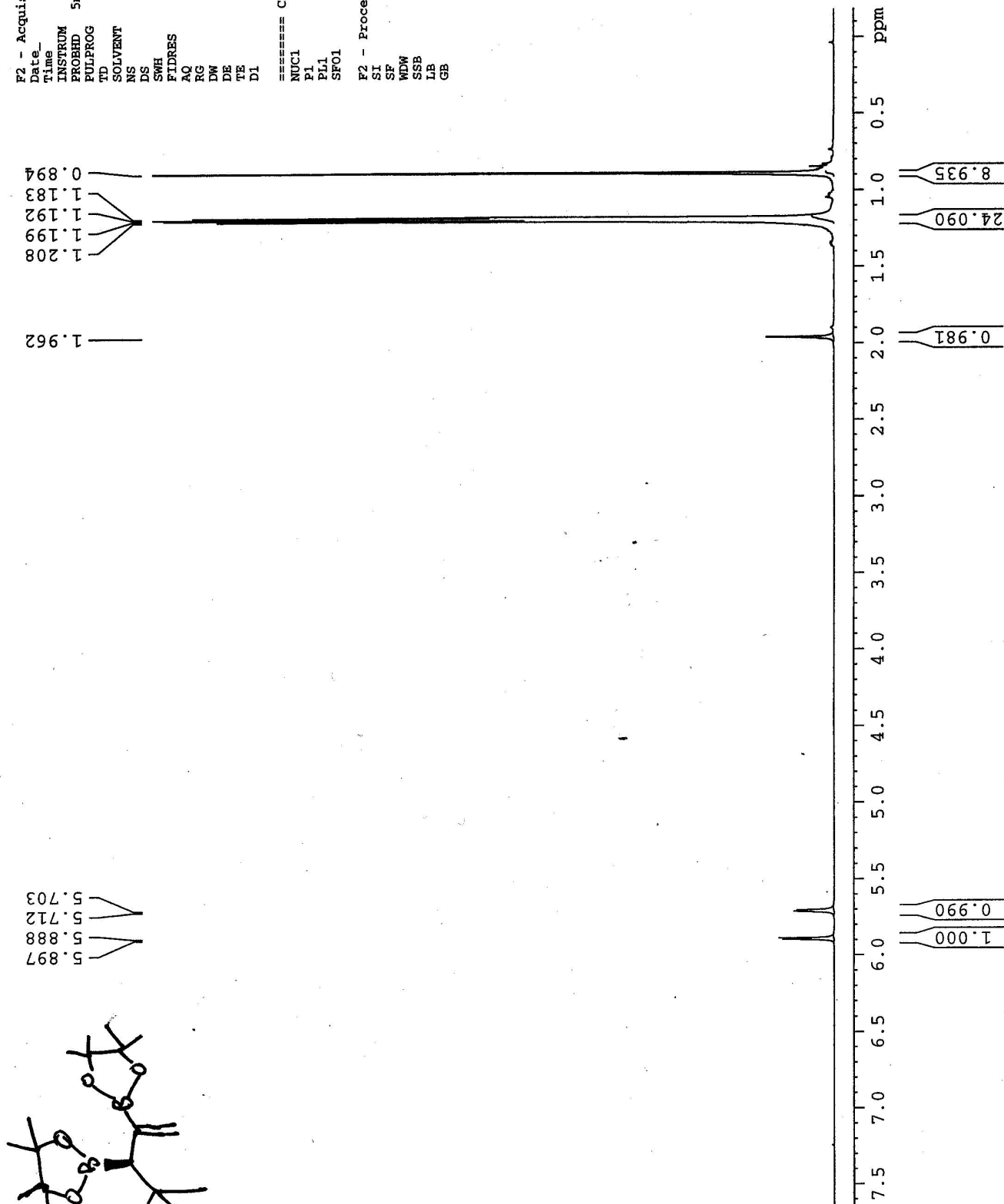
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 82.814  
 83.112

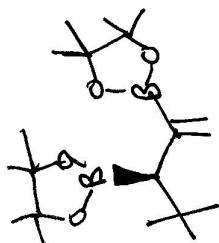
127.436



Current Data Parameters  
 NAME Js194col  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20040826  
 Time 14.39  
 INSTRUM spect  
 PROHD 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 57  
 DW 78.000 usec  
 DE 6.00 usec  
 TE 293.0 K  
 D1 1.0000000 sec  
 ===== CHANNEL f1 =====  
 NUC1 1H  
 P1 22.50 usec  
 PL1 0.00 dB  
 SFO1 400.1326008 MHz  
 F2 - Processing parameters  
 SI 32768  
 SF 400.1300172 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0





132.499

Js194 column C-13

83.711  
82.894  
77.738  
77.420  
77.103

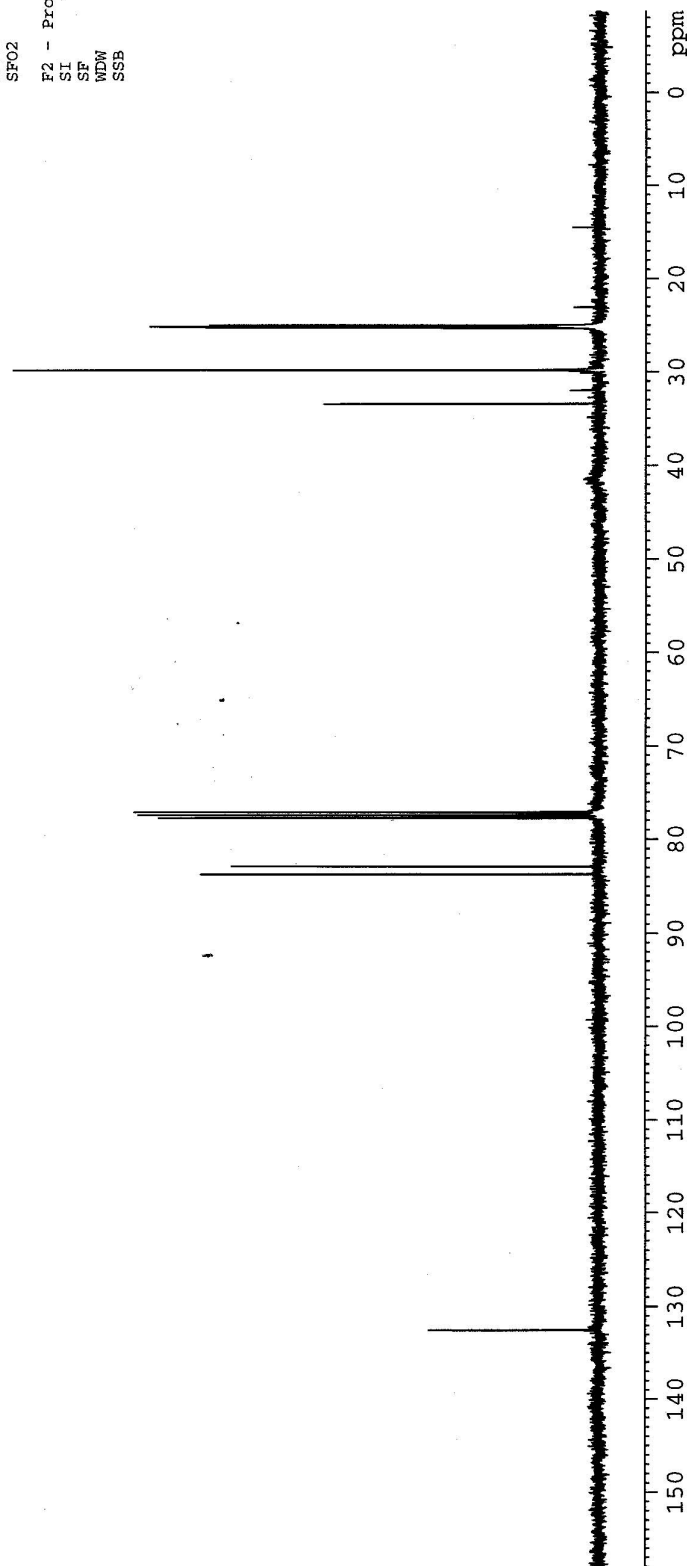
33.415  
29.809  
25.267  
25.177  
25.128  
25.004

Current Data Parameters  
NAME Js194col  
EXPNO 2  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20040826  
Time 14.44  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 107  
DS 2  
SWH 26246.719 Hz  
FIDRES 0.400493 Hz  
AQ 1.2485298 sec  
RG 9195.2  
DW 19.050 use  
DE 6.00 use  
TE 300.0 K  
D1 0.8000001 sec  
d11 0.0300000 sec  
d12 0.0000200 sec

===== CHANNEL f1 =====  
NUC1 13C  
P1 5.70 use  
PL1 0.00 dB  
SFO1 100.6237964 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 use  
PL2 -6.00 dB  
PL12 13.80 dB  
PL13 14.50 dB  
SFO2 400.1322200 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127290 MHz  
WDW EM  
SSB 0



Jsi170 column

Current Data Parameters  
 NAME Jsi170col  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20040811  
 Time 20.02  
 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 574.7  
 DW 78.000 usec  
 DE 6.00 usec  
 TE 293.0 K  
 D1 1.00000000 sec  
 ===== CHANNEL f1 =====  
 NUC1 1H  
 P1 22.50 usec  
 PL1 0.00 dB  
 SF01 400.1326008 MHz  
 F2 - Processing parameters  
 SI 32768  
 SF 400.1300172 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0

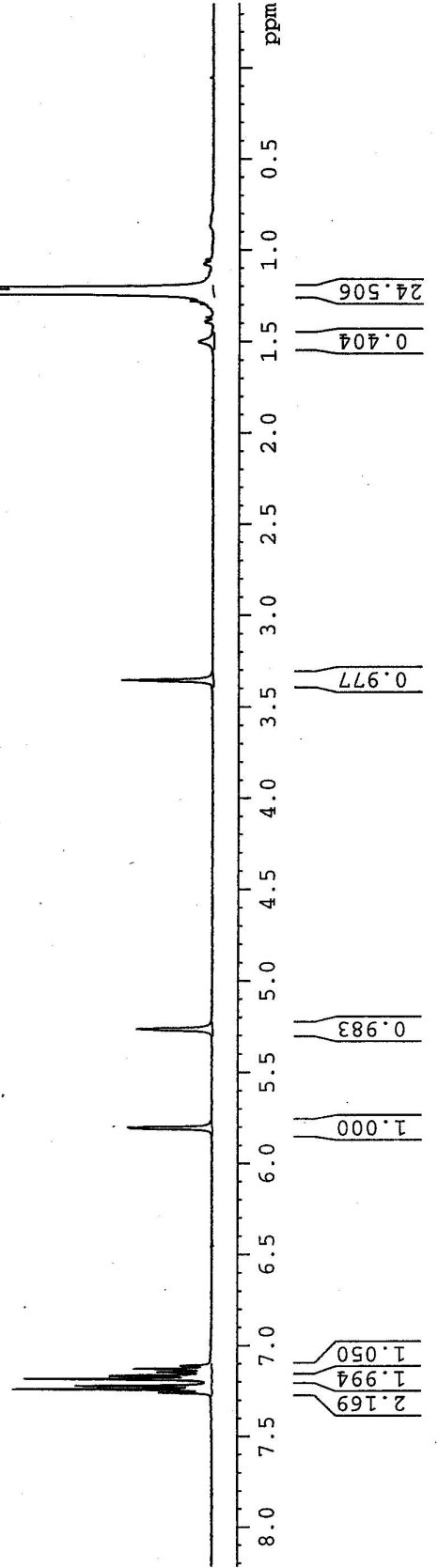
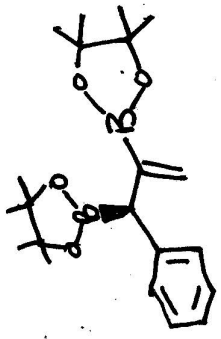
1.497  
1.296  
1.281  
1.240  
1.225  
1.228  
1.210

3.357

5.266

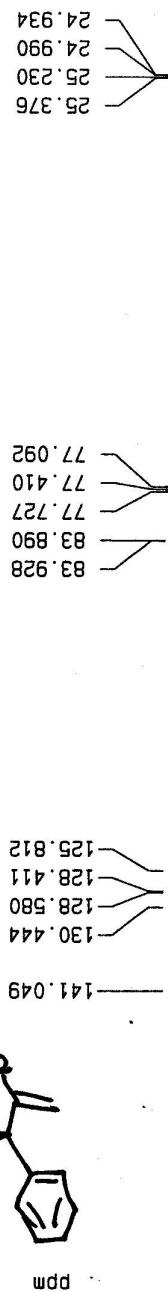
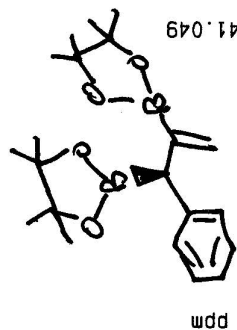
5.812  
5.808  
5.805  
5.801

7.259  
7.241  
7.222  
7.187  
7.184  
7.167  
7.149  
7.146  
7.143  
7.128  
7.114  
7.110  
7.107





JS170 column



Current Data Parameters  
NAME Js170col  
EXPNO 2  
PROCNO 1

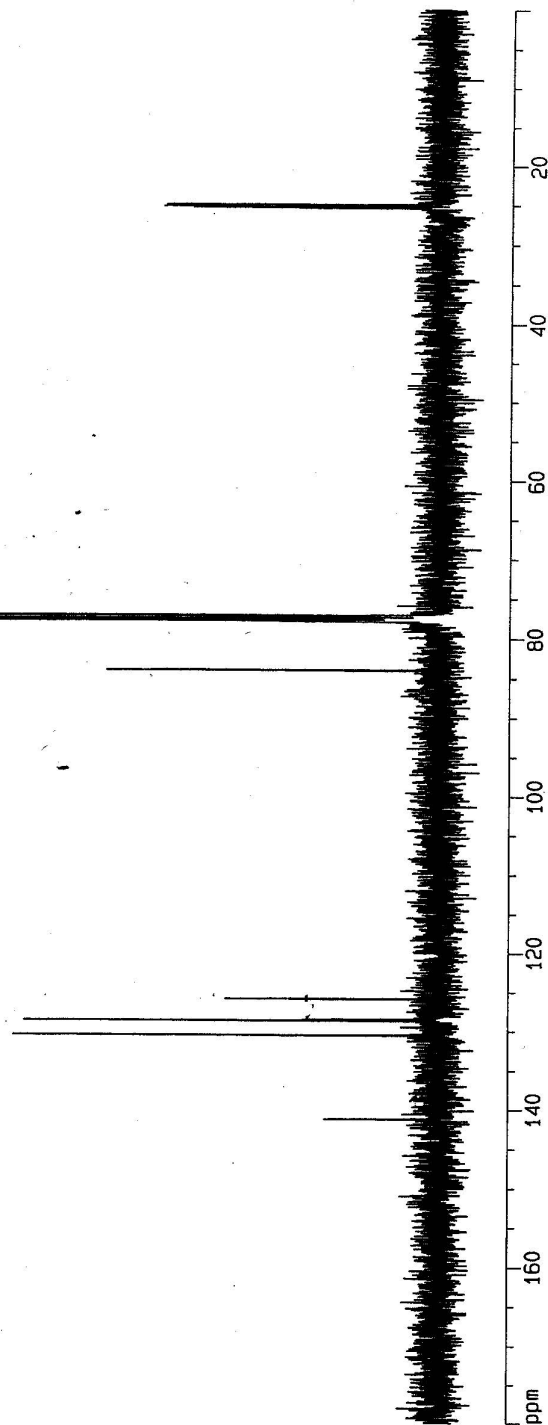
F2 - Acquisition Parameters  
Date\_ 20040811  
Time 20.08  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 1077  
DS 2  
SWH 26246.719 Hz  
FIDRES 0.400493 Hz  
AQ 1.2465298 sec  
RG 1149.4  
DW 19.050 usec  
DE 6.00 usec  
TE 300.0 K  
D1 0.80000001 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

===== CHANNEL f1 =====  
NUC1 13C  
P1 5.70 usec  
PL1 0.00 dB  
SF01 100.6237964 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
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 100.6127290 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

1D NMR plot parameters  
CX 20.00 cm  
CY 50.00 cm  
F1P 180.000 ppm  
F1 18110.29 Hz  
F2P 0.000 ppm  
F2 0.000 Hz  
PPMCM 9.00000 ppm/cm  
HZCM 905.51459 Hz/cm

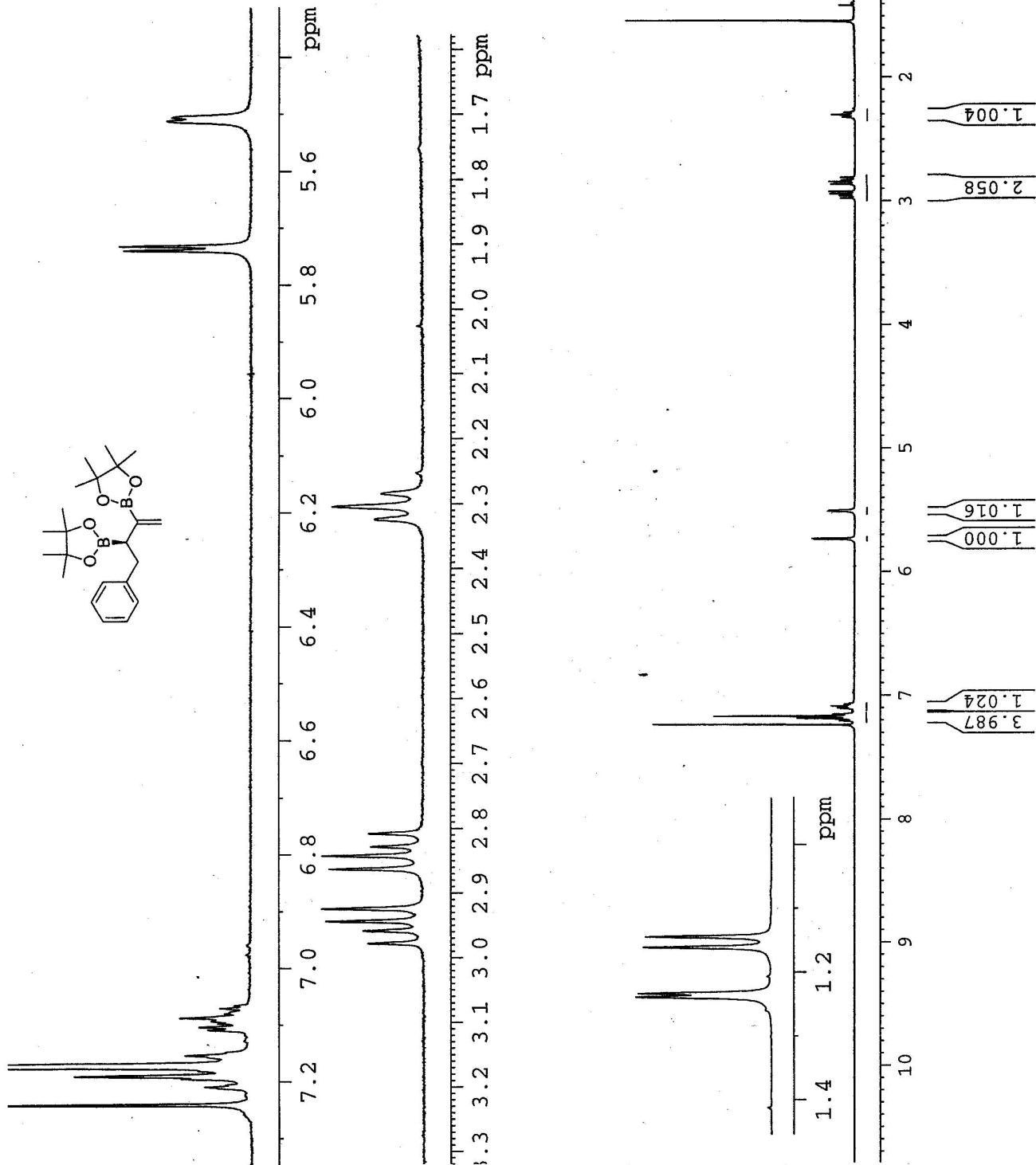


Pelz 3.040 Column 400wb

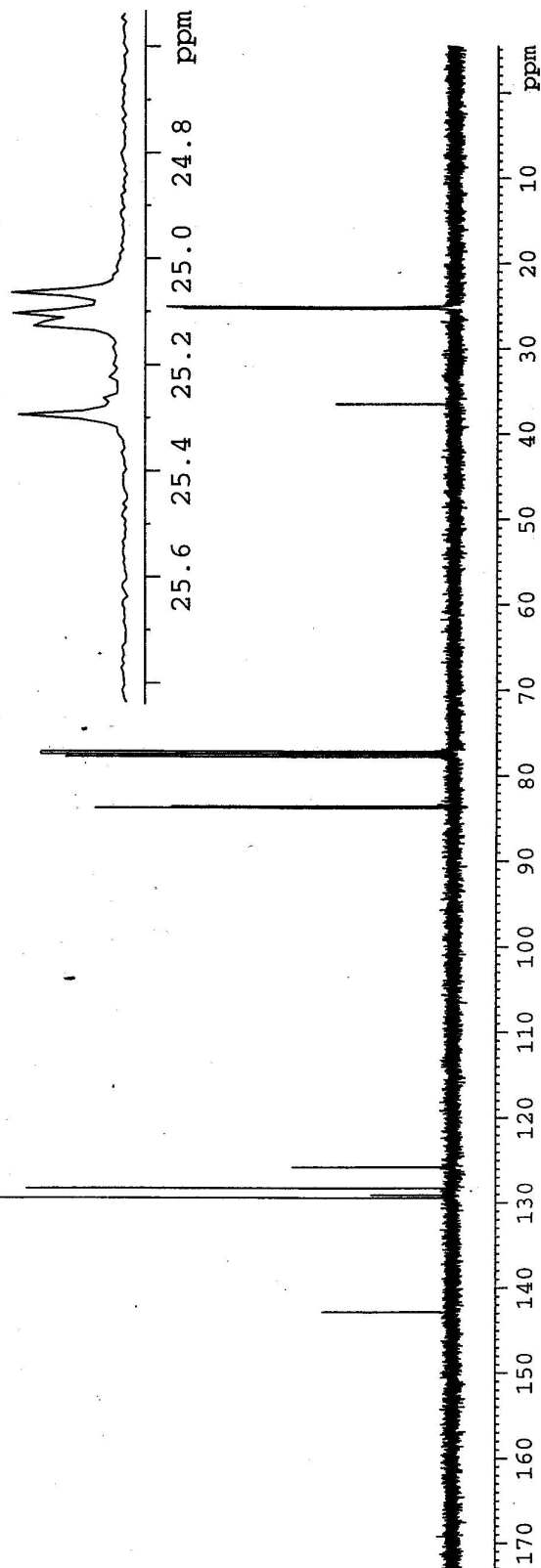
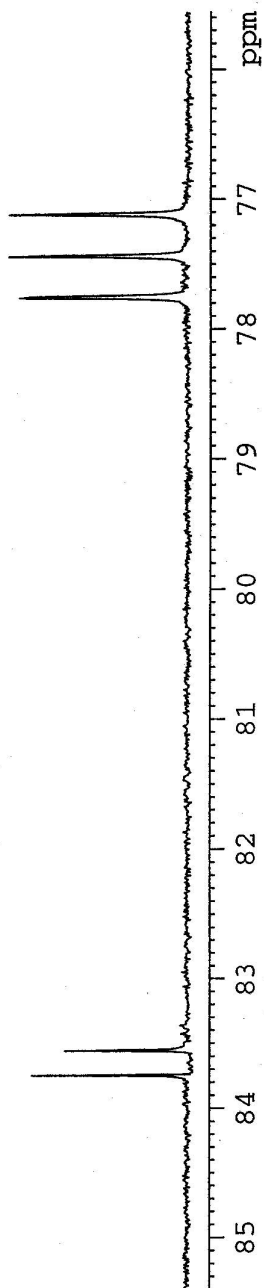
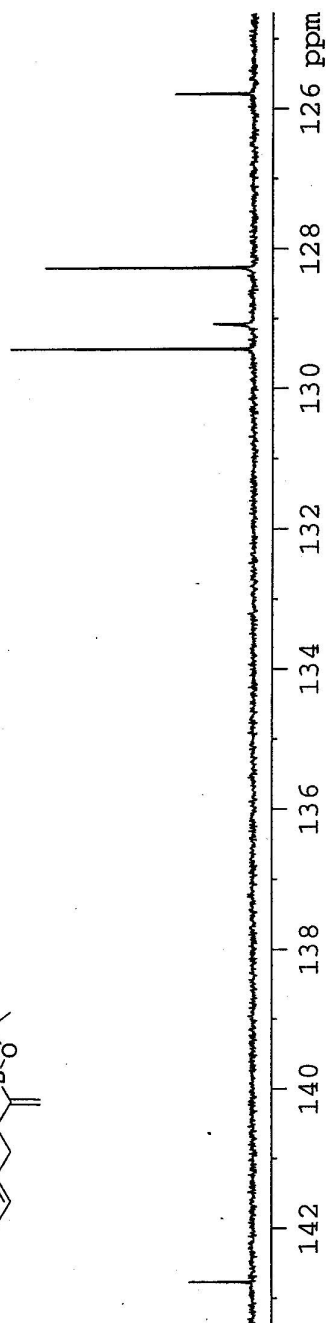
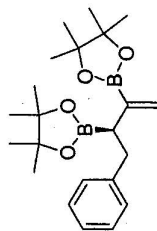
Current Data Parameters  
NAME Pelz 3-040  
EXPNO 2  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 691231  
Time 19.00  
INSTRUM 40  
PROBHD 2930  
PULPROG 32768  
TD CDC13  
SOLVENT 16  
NS 2  
DS 5995.204 Hz  
SWH 0.182359 Hz  
FIDRES 2.7329011 sec  
AQ 128  
RG 83.400 usec  
DW 6.00 usec  
DE 300.0 K  
TE 1.0000000 sec  
D1

===== 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



## Pelz 3.028 Carbon 400nb



Current Data Parameters  
NAME Pelz 3-028  
EXPNO 4  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 691231  
Time 19.00

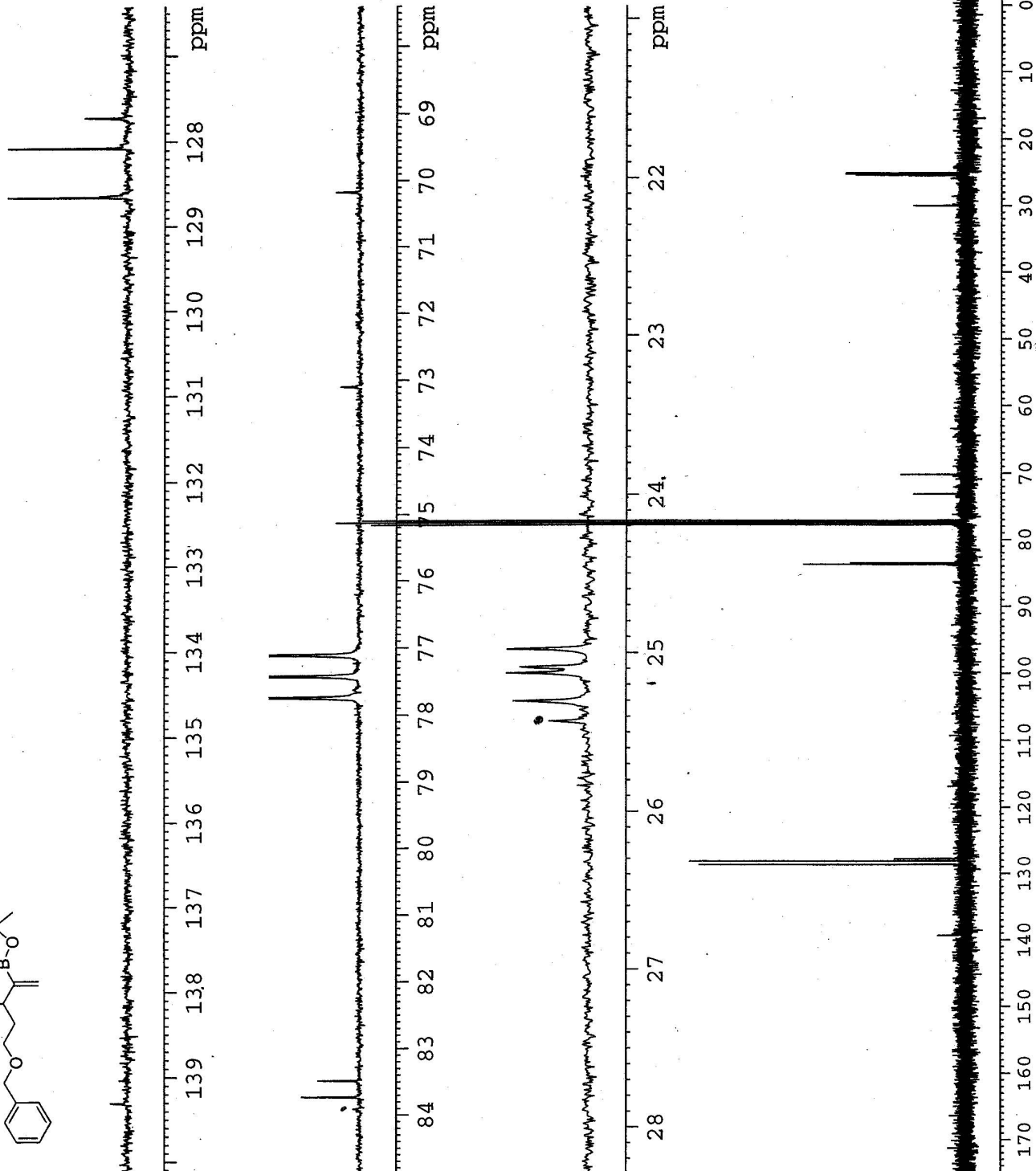
INSTRUM 06:5mmQNP1H/13  
PROBHD zg30  
PULPROG 32768  
TD 32768  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 6410.256 Hz  
FIDRES 0.195625 Hz  
AQ 2.5560319 sec  
RG 128  
DW 78.000 use  
DE 6.00 use  
TE 293.0 K  
D1 1.00000000 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

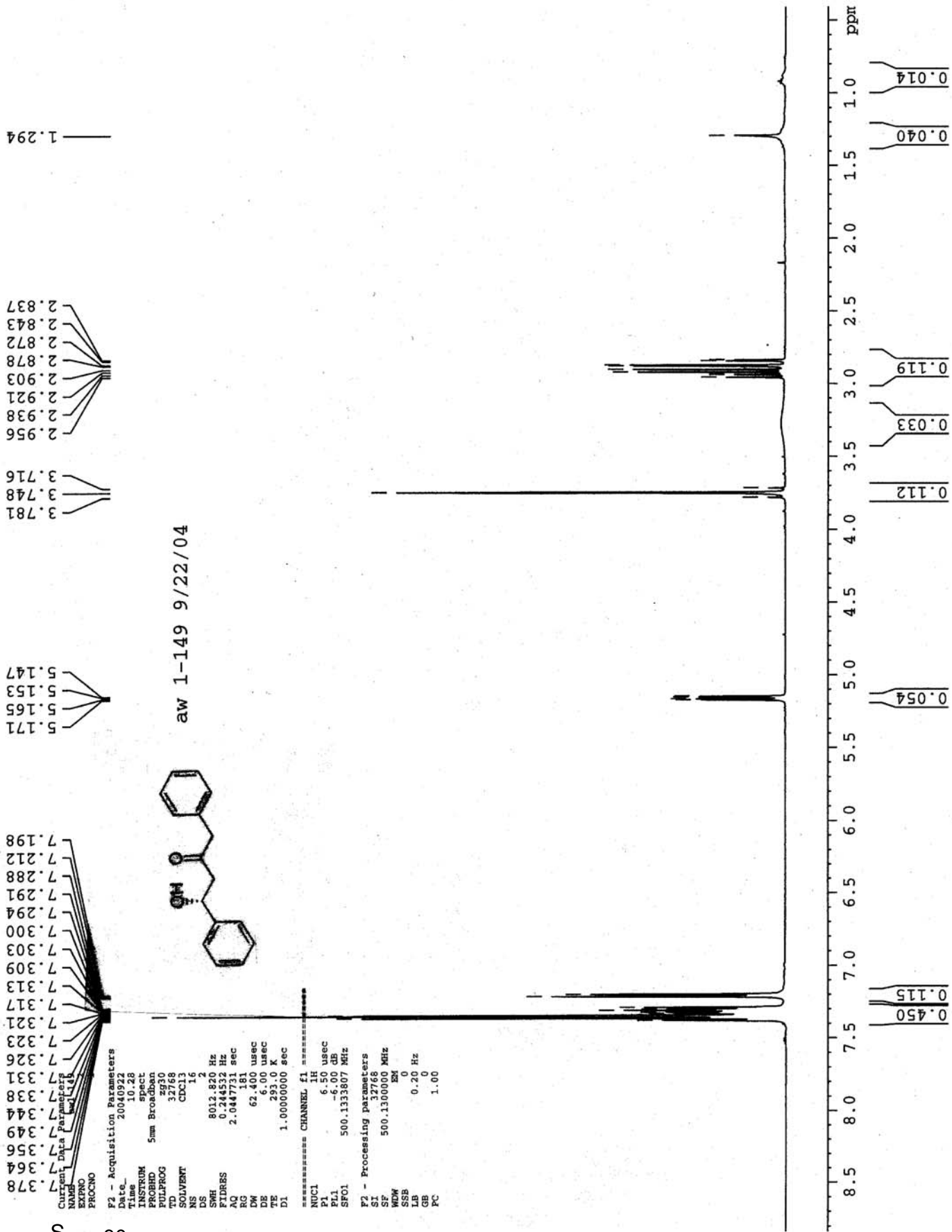
===== CHANNEL f1 =====  
NUC1 1H  
P1 22.50 use  
PL1 0.00 dB  
SF01 400.1326008 MHz

===== CHANNEL f2 =====  
CFPRG2 off  
NUC2 100.00 use  
PCPD2 0.00 dB  
PL2 0.00 dB  
PL12 14.50 dB  
PL13 14.50 dB  
SF02 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127290 MHz  
WDW no  
SSB 0







# Current Data Parameters

NAME aw1-163  
EXFNO 4  
PROCNO 1

## F2 - Acquisition Parameters

Date\_ 20040914  
Time 6.42  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 21080  
DS 2  
SWH 26246.719 Hz  
FIDRES 0.400493 Hz  
AQ 1.2485298 sec  
RG 1625.5  
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 5.70 usec  
PL1 0.00 dB  
SFO1 100.6237964 MHz

## ===== CHANNEL f2 =====

CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -6.00 dB  
PL12 13.80 dB  
PL13 14.50 dB  
SFO2 400.1322200 MHz

## F2 - Processing parameters

SI 32768  
SF 100.6127290 MHz  
WDW EM  
SSB 0

aw 1-163

143.062  
133.836  
129.871  
129.266  
128.946  
128.101  
127.681  
126.041

77.770  
77.453  
77.135  
70.382

51.278  
50.751

