

**Supporting Information for:**  
**Development, Mechanism, and Scope of the Palladium-Catalyzed Enantioselective Allene  
Diboration**

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## A. General.

$^1\text{H}$  NMR spectra were recorded on Bruker DRX 400 and 500 MHz spectrometer as well as a Varian Unity Inova 500 spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ( $\text{CDCl}_3$ : 7.26 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.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker DRX 400 (100 MHz), 500 (125 MHz) MHz, or Varian Gemini-500 MHz (125 MHz) spectrometers with chemical shifts are reported in ppm with the solvent resonance as the internal standard ( $\text{CDCl}_3$ : 77.16 ppm).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161 MHz or 202 MHz) were recorded on a Bruker DRX 400 or Varian Unity Inova 500 spectrometer. Chemical shifts are reported for  $^{31}\text{P}$  NMR spectra using phosphoric acid as an external standard.  $^{19}\text{F}$  NMR (376 MHz) and  $^2\text{H}$  spectra (61 MHz) were recorded on a Bruker DRX 400 MHz spectrometer. Low-resolution mass spectrometry was performed at The University of North Carolina at Chapel Hill Mass Spectrometry Facility. High-resolution CI-GC/MS, EI, and MALDI-TOF were recorded at Indiana University, Bloomington, IN.

Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel ( $\text{SiO}_2$ , 230 x 450 Mesh) purchased from Silicycle. Thin Layer Chromatography was performed on 25  $\mu\text{m}$  silica gel glass backed plates from EMD Chemicals, Inc. Visualization was performed using, ultraviolet light, phosphomolybdic acid (PMA), and potassium permanganate ( $\text{KMnO}_4$ ).

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, North Carolina), a split mode capillary injection system, a flame ionization detector and a Supleco  $\beta$ -Dex 120 column with helium as a carrier gas.

Tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2\text{dba}_3$ ), mercury(II) chloride ( $\text{HgCl}_2$ ), and chlorodicarbonylrhodium(I) dimer were purchased from Strem Chemicals, Inc. Bis(pinacolato)diboron ( $\text{B}_2(\text{pin})_2$ ) was obtained from Allychem Co., Ltd. and recrystallized from pentanes prior to use. Toluene- $d_8$  and acetone- $d_6$  were purchased from Cambridge Isotope Laboratories and dried and degassed prior to use. Methyl allene (1,2-butadiene) was purchased from Chem. Samp. Co. and used as a solution in toluene. All reactions were conducted in oven or flame-dried glassware under an inert atmosphere of nitrogen or argon. Toluene was distilled over calcium hydride and degassed by freeze-pump cycles prior to use. Tetrahydrofuran was distilled from sodium-benzophenone. Triethylamine was distilled from calcium hydride. Allenes were synthesized according to literature procedures.<sup>1</sup> Phosphoramidite ligands were prepared as described in the general procedure below. All other reagents were purchased from Aldrich and used without further purification.

## B. Diboration Procedures.

**Representative Procedure for Diboration of Allenes.** A 20 mL vial with magnetic stir bar was charged with  $\text{Pd}_2\text{dba}_3$  (7.62 mg, 0.0083 mmol), (*R,R*)-xylylTADDOL-PNMe<sub>2</sub> (**(*R,R*)-6**) (13.0 mg, 0.0199 mmol), and toluene (2.2 mL) in an inert atmosphere dry box. After stirring for 1 hour,  $\text{B}_2(\text{pin})_2$  (101.3 mg, 0.399 mmol) was added to the mixture followed by tridec-1,2-diene (60 mg, 0.3327 mmol). The vial was sealed with a polypropylene cap, removed from dry box, and stirred at room temperature for 12 hours. The resulting solution was concentrated via rotary evaporation and chromatographed on

<sup>1</sup> Myers, A.G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492. For aromatic allenenes: Huang, C.-W.; Shanmugasundaram, M.; Chang, H.-M.; Cheng, C.-H. *Tetrahedron*, **2003**, *59*, 3635. For OTBS protected allene: Trost, B.M.; Pinkerton, A.B.; Seidel, M. *J. Am. Chem. Soc.* **2001**, *123*, 12466.

silica gel (2% ethyl acetate/hexanes) to afford the 1,2-bis(boronate)ester product in 68% yield (99.7 mg).

**Modified Procedure for Diboration of 1,2-Butadiene.** Tris(dibenzylideneacetone)dipalladium(0) (16.3 mg, 0.0178 mmol) and (*R,R*)-**6** (27.7 mg, 0.0426 mmol) were complexed for 1 h in toluene (4.23 mL). The reaction was charged with B<sub>2</sub>(pin)<sub>2</sub> (216.3 mg, 0.852 mmol) and 0.5 mL of a 1.42 M solution of 1,2-butadiene in toluene (as determined by <sup>1</sup>H NMR). The vial was sealed with a polypropylene cap, removed from dry box, and stirred at room temperature for 14 hours. The resulting solution was concentrated via rotary evaporation and chromatographed (4% ethyl acetate/hexanes) on silica gel to afford 169.2 mg (77% yield) of the methyl allene diboration product.

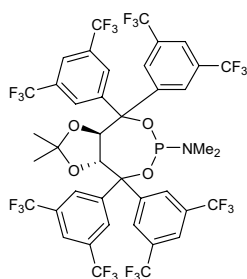
**Representative Procedure for Ligand Screening - Conversion by <sup>1</sup>H NMR.** In the dry box, a 6 dram vial with magnetic stir bar was charged with Pd<sub>2</sub>dba<sub>3</sub> (3.6 mg, 3.9 μmol) and (*R,R*)-TADDOLPNMe<sub>2</sub> (*R,R*)-**1** (5.3 mg, 9.9 μmol) in toluene-*d*<sub>8</sub> (1.10 mL, 0.15 M). The metal and ligand were complexed for 1 hour at which time B<sub>2</sub>(pin)<sub>2</sub> (50.6 mg, 0.199 mmol) was added following by tridec-1,2-diene (30 mg, 0.166 mmol). The reaction was allowed to stir for 2 minutes and then transferred to an oven dried NMR tube. The NMR tube was sealed with a cap and removed from the glove box. Single pulse <sup>1</sup>H NMR was used to determine the extent of reaction at 20 minutes.

### C. Phosphoramidite Ligand Synthesis.

**General Procedure for (*R,R*)-TADDOL Phosphoramidite Ligand Synthesis.** To an oven-dried flask with magnetic stir bar under nitrogen, was added flame-dried 4Å molecular sieves, the respective TADDOL derivative (1 equiv), and tetrahydrofuran (0.25 M). The flask was cooled to 0 °C (ice-water bath) and charged with triethylamine (3.4 equiv) and phosphorus trichloride (1.2 equiv). The mixture was warmed to ambient temperature and stirred for 30 minutes when it was cooled to 0 °C (ice-water bath) and charged with dimethylamine in tetrahydrofuran (10 equiv) or the respective amine (5 equiv, neat). The reaction was stirred overnight at ambient temperature, was diluted with diethyl ether, and filtered over celite. The solvent was removed via rotary evaporator and the crude mixture was chromatographed on silica gel.

**Procedure for the Preparation of 3,5-(CF<sub>3</sub>)<sub>2</sub>TADDOLPNMe<sub>2</sub>.** To a 100 mL round-bottom flask equipped with an oven-dried magnetic stir bar was added 4Å molecular sieves, followed by 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>TADDOL<sup>2</sup> (2.43 g, 2.40 mmol, 1 equiv) and tetrahydrofuran (9.6 mL, 0.25 M). The flask was cooled to 0 °C (ice-water bath) and charged with triethylamine (1.13 mL, 8.16 mmol) and phosphorus trichloride (251 μL, 2.88 mmol). The mixture was allowed to warm to ambient temperature and stirred for 30 minutes, at which time it was cooled to 0 °C (ice-water bath) and charged with dimethylamine (12 mL, 2.0 M in tetrahydrofuran). The mixture warmed to ambient temperature, stirred overnight, then diluted with diethyl ether and filtered over celite. The solvent was removed via rotary evaporator and the crude reaction mixture was chromatographed on silica gel (10% dichloromethane/hexanes) then recrystallized from dichloromethane to afford the desired phosphoramidite **8** (597 mg, 22% yield).

<sup>2</sup> 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>TADDOL was prepared from L-tartaric acid and 1,3-bis(trifluoromethyl)-5-bromobenzene. See: Seebach, D.; Beck, A.K.; Keckel, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 92.



**(3aR,8aR)-4,4,8,8-tetrakis(3,5-bis(trifluoromethyl)phenyl)-N,N,2,2-tetramethyl-tetrahydro-[1,3]dioxolo[9,4-b][1,3,2]dioxaphosphin-6-amine.**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.35 (3H, s,  $\text{CH}_3\text{CCH}_3$ ), 1.51 (3H, s,  $\text{CH}_3\text{CCH}_3$ ), 2.85 (6H, d,  $J = 11.0$  Hz,  $(\text{CH}_3)_2\text{N}$ ), 4.33 (1H, d,  $J = 8.5$  Hz, OCHC), 4.94 (1H, dd,  $J = 9.0, 3.5$  Hz, OCHC), 7.83-7.89 (8H, m, Ar-H), 8.03 (2H, s, Ar-H), 8.30 (2H, s, Ar-H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  25.4, 27.2, 35.2 (2C, d,  $^2J_{\text{CP}} = 20.2$  Hz), 79.7, 80.2 (1C, d,  $^2J_{\text{CP}} = 8.2$  Hz), 81.9 (1C, d,  $^3J_{\text{CP}} = 22.2$  Hz), 82.9 (1C, d,  $^3J_{\text{CP}} = 3.1$  Hz), 113.4, 122.5 (1C, q,  $^3J_{\text{CF}} = 3.5$  Hz), 122.6 (1C, q,  $^3J_{\text{CF}} = 3.6$  Hz), 122.9 (1C, q,  $^3J_{\text{CF}} = 3.7$  Hz), 123.0 (1C, q,  $^3J_{\text{CF}} = 3.5$  Hz), 123.24 (4C, q,  $^1J_{\text{CF}} = 272.6$  Hz), 123.25 (2C, q,  $^1J_{\text{CF}} = 272.7$  Hz), 123.3 (2C, q,  $^1J_{\text{CF}} = 272.2$  Hz), 126.8 (2C), 127.0 (2C), 128.7 (2C), 128.8 (2C), 131.6 (2C, q,  $^2J_{\text{CF}} = 33.5$  Hz), 132.12 (2C, q,  $^2J_{\text{CF}} = 33.5$  Hz), 132.15 (2C, q,  $^2J_{\text{CF}} = 33.2$  Hz), 132.6 (2C, q,  $^2J_{\text{CF}} = 34.2$  Hz), 141.8, 142.7, 146.5, 147.4.  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7.  $^{19}\text{F}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.8 (6F, s), -63.7 (6F, s), -63.6 (6F, s), -63.5 (6F, s). Purification Technique: very sensitive to silica gel, will decompose on the column, 10% dichloromethane/hexanes, silica gel, recrystallized from dichloromethane.  $R_f = 0.51$  (10% dichloromethane/hexanes). LRMS – (ESI $^+$ ): for  $\text{C}_{41}\text{H}_{27}\text{F}_{24}\text{NO}_4\text{P}$  calc'd: 1084.12 (M+H) $^+$ , observed: 1084.2 (M+H) $^+$ .

#### D. Preparation of Rhodium Complexes for analysis by IR:<sup>3</sup>

Chlorocarbonyl-bis(triphenylphosphine)rhodium and chlorocarbonylbis(tricyclohexylphosphine)-rhodium were prepared according to literature procedure and spectral data and analysis of the complexes by MALDI are in accordance with the literature.

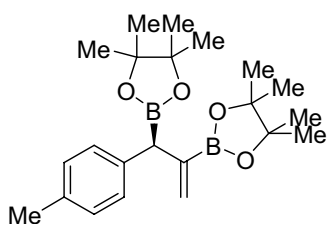
**Preparation of Chlorocarbonylbis((*R,R*)-1)rhodium:** In the dry box, a 25 mL round-bottom flask was charged with chlorodicarbonylrhodium(I) dimer (80 mg, 0.2057 mmol). To a separate 25-mL pear shaped flask was added (*R,R*)-TADDOLP $\text{NMe}_2$  (**(*R,R*)-1**) (444.1 mg, 0.8231 mmol). Both flasks were sealed with septa, removed from the glove box. Chlorodicarbonylrhodium(I) dimer was dissolved in benzene (1 mL) and (*R,R*)-TADDOLP $\text{NMe}_2$  was dissolved in benzene (5 mL) after mild heating. The solution of (*R,R*)-TADDOLP $\text{NMe}_2$  was cannulated into the chlorodicarbonylrhodium(I) dimer solution and CO evolution was immediate. The reaction mixture stirred at room temperature for 30 minutes when solvent was removed on the rotary evaporator. Residual solvent was removed overnight *in vacuo* to afford 473.6 mg (93% yield) of a yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.49 (6H, s,  $(\text{CH}_3)_2$ ), 0.58 (6H, s,  $(\text{CH}_3)_2$ ), 2.23 (12H, t,  $J = 5.2$  Hz, 2 x  $(\text{N}(\text{CH}_3)_2)$ ), 5.42 (2H, d,  $J = 8.0$  Hz, OCH), 5.49 (2H, d,  $J = 8.0$  Hz, OCH), 7.16-7.36 (28H, m, Ar-H), 7.45 (4H, t,  $J = 7.7$  Hz, Ar-H), 7.54-7.56 (4H, m, Ar-H), 7.70-7.72 (4H, m, Ar-H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  26.6 (2C), 26.9 (2C), 38.5 (4C, t,  $J_{\text{CP}} = 5.6$  Hz), 79.3 (2C), 79.5 (2C), 87.2 (2C), 88.1 (2C), 115.1 (2C), 126.8 (2C), 126.9 (4C), 127.2 (4C), 127.4 (4C), 127.7 (2C), 17.9 (2C), 128.0 (4C), 128.3 (4C), 128.4 (2C), 128.7 (4C), 129.0 (4C), 129.3 (4C).  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  117.6, 118.6. IR ( $\text{CH}_2\text{Cl}_2$ ): 1982 (s), 1607 (s), 1491 (m)  $\text{cm}^{-1}$ . MALDI-TOF with CAA overlay: calc'd for  $\text{C}_{66}\text{H}_{68}\text{N}_2\text{O}_8\text{P}_2\text{Rh}$  1181.35 (M-CO-Cl) $^+$ , observed 1181.488 (M-CO-Cl) $^+$ .

**Preparation of chlorocarbonylbis((*R,R*)-6)rhodium:** In the dry box, a 25 mL round-bottom flask was loaded with chlorodicarbonylrhodium(I) dimer (30 mg, 0.0771 mmol). To a separate 25-mL pear shaped flask was added (*R,R*)-xylylTADDOLP $\text{NMe}_2$  (**(*R,R*)-6**) (201.1 mg, 0.3086 mmol). Both flasks were sealed with septa and removed from the glove box. Chlorodicarbonylrhodium(I) dimer and (*R,R*)-xylylTADDOLP $\text{NMe}_2$  were dissolved in benzene (1 mL). The solution of (*R,R*)-xylylTADDOLP $\text{NMe}_2$

<sup>3</sup> Wilkinson, G.; McClevery, J.A. *Inorganic Syntheses*, **1966**, 8, 214-217.

in benzene was cannulated into the chlorodicarbonylrhodium(I) dimer solution and CO evolution was immediate. The reaction mixture was stirred at room temperature for 5 minutes when solvent was removed on the rotary evaporator. Residual solvent was removed overnight *in vacuo* and the crude reaction mixture was recrystallized from pentanes to afford 114 mg (50% yield) of a yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.44 (6H, s,  $(\text{CH}_3)_2$ ), 0.54 (6H, s,  $(\text{CH}_3)_2$ ), 2.04 (12H, t,  $J = 5.2$  Hz, 2 x  $(\text{N}(\text{CH}_3)_2)$ ), 2.21 (24H, s, Ar- $\text{CH}_3$ ), 2.25 (12H, s, Ar- $\text{CH}_3$ ), 2.42 (12H, s, Ar- $\text{CH}_3$ ), 5.26 (2H, d,  $J = 7.5$  Hz, OCH), 5.64 (2H, d,  $J = 8.0$  Hz, OCH), 6.80 (2H, s, Ar-H), 6.82 (2H, s, Ar-H), 6.85 (2H, s, Ar-H), 6.90 (4H, s, Ar-H), 6.94 (2H, s, Ar-H), 7.07 (4H, s, Ar-H), 7.10 (4H, s, Ar-H), 7.18 (4H, s, Ar-H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  21.5 (4C), 21.6 (4C), 21.7 (4C), 21.8 (4C), 26.5 (2C), 27.0 (2C), 38.2 (4C, t,  $J = 6.3$  Hz), 78.2 (2C), 79.7 (2C), 88.4 (2C), 86.7 (2C), 115.1 (2C), 125.3 (2C), 126.9 (4C), 127.2 (6C), 128.5 (2C), 128.6 (2C), 129.3 (4C), 129.7 (4C), 135.5 (4C), 135.9 (4C), 137.0 (4C), 137.1 (4C), 141.7 (2C), 142.3 (2C), 143.0 (2C), 144.9 (2C).  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  116.5, 117.5. MALDI-TOF with CAA overlay: calc'd for  $\text{C}_{82}\text{H}_{100}\text{N}_2\text{O}_8\text{P}_2\text{Rh}$  1405.601 ( $\text{M-CO-Cl}$ ) $^+$ , observed 1405.778 ( $\text{M-CO-Cl}$ ) $^+$ .

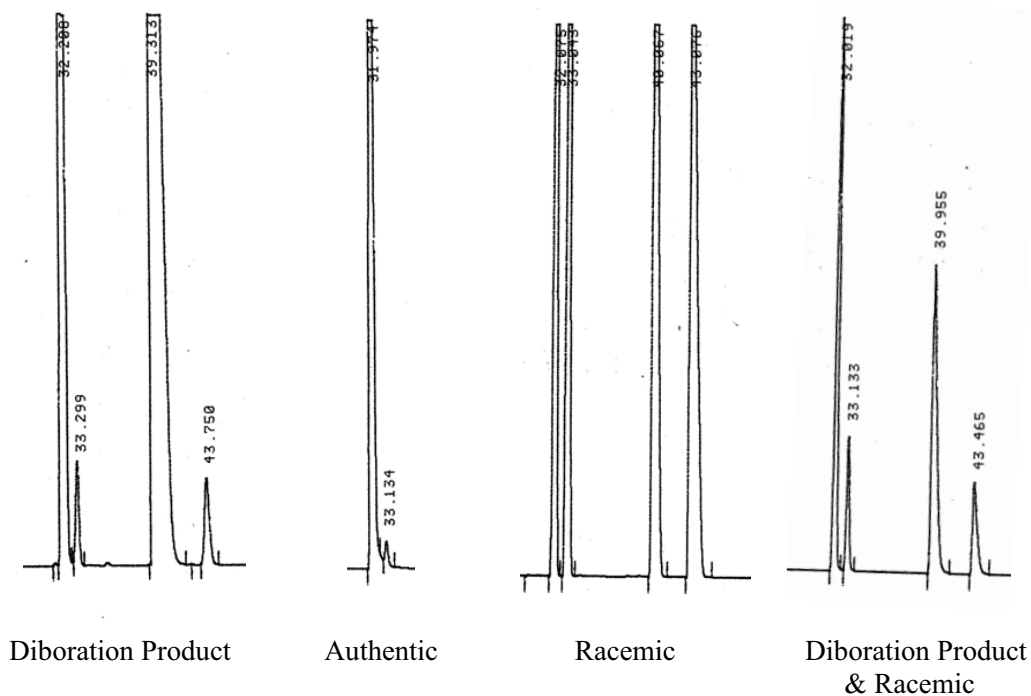
## E. Characterization of Substrates – Table 2, entries 6,8,9,10,11

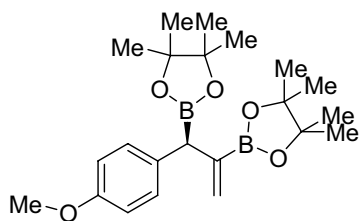


**(S)-4,4,5,5-tetramethyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-*p*-tolylprop-2-en-2-yl)-1,3,2-dioxaborolane.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24 (6H, s,  $\text{OCCH}_3$ ), 1.27 (12H, s,  $\text{OCCH}_3$ ), 1.28 (6H, s,  $\text{OCCH}_3$ ), 3.35 (1H, s, ArCHB), 5.28 (1H, t br,  $J = 2.4$  Hz, CBCH), 5.83 (1H, q br,  $J = 2.8, 1.6$  Hz, CBCH), 7.09 (4H, s, Ar-H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.1, 24.6 (2C), 24.7 (2C), 24.9 (2C), 25.0 (2C), 83.5 (2C), 83.6 (2C), 127.9, 129.0 (2C), 129.9 (2C), 134.8, 134.7. IR (neat): 2976 (s), 2926 (s), 2867 (w), 2731 (w), 2291 (w), 2244 (w), 1890 (w), 1610 (s), 1513 (s), 1412 (br)  $\text{cm}^{-1}$ . LRMS-(ESI $^+$ ): for  $\text{C}_{22}\text{H}_{35}\text{B}_2\text{O}_4$  calc'd: 385.2 (M+H) $^+$ , observed 385.2 (M+H) $^+$ . Purification Technique: silica gel, 2% ethyl acetate/hexanes.  $R_f = 0.24$  (4% ethyl acetate/hexanes).

**Proof of Stereochemistry.** Stereochemistry was determined by diimide reduction (2-nitrobenzenesulfonylhydrazide (3 equiv), triethylamine (6 equiv), dioxanes (0.1 M), 80  $^\circ\text{C}$ , overnight) 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 protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane). Racemic material was prepared from the diboration of 1-methyl-4-(propa-1,2-dienyl)benzene as described in the general procedure using tricyclohexylphosphine. Absolute stereochemistry was established in comparison to authentic material prepared by Sharpless asymmetric oxidation of 4-methyl-*trans*- $\beta$ -methylstyrene (Norrby, P-O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, 118, 35.). The resultant diol was protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane).

*Chiral GLC ( $\beta$ -dex, Supelco, 115  $^\circ\text{C}$ ) – analysis of acetonide derived from reduction and oxidation of reaction product as described above*

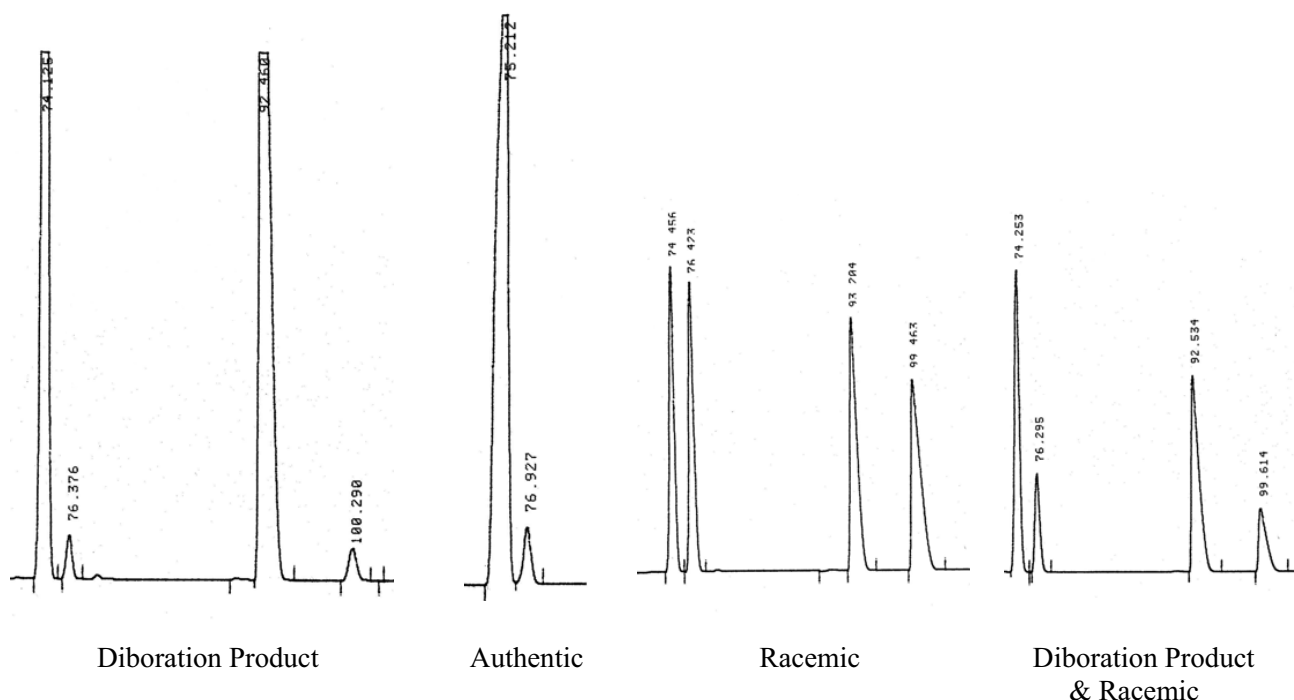


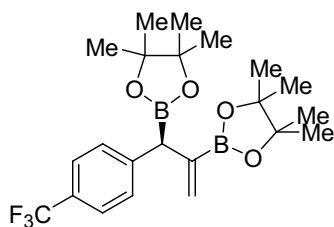


**(S)-2-(1-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.22 (6H, s,  $\text{OCCH}_3$ ), 1.25 (12H, s,  $\text{OCCH}_3$ ), 1.26 (6H, s,  $\text{OCCH}_3$ ), 3.31 (1H, s, ArCHB), 5.27 (1H, s, CBCH), 5.80 (1H, br, q,  $J = 1.2$  Hz, CBCH), 6.81 (2H, d,  $J = 8.8$  Hz, Ar-H), 7.11 (2H, d,  $J = 8.4$  Hz, Ar-H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.6, 24.7, 24.9, 25.0, 55.1, 83.4 (2C), 83.5 (2C), 113.7, 127.7, 130.9, 132.5, 157.6. IR (neat): 3069 (m), 2965 (s), 2922 (s), 2720 (w), 2589 (w), 2546 (w), 2421 (w), 2050 (w), 1876 (w), 1658 (w), 1609 (s), 1576 (s)  $\text{cm}^{-1}$ . LRMS-(ESI $^+$ ): for  $\text{C}_{22}\text{H}_{35}\text{B}_2\text{O}_5$  calc'd 401.2 (M+H) $^+$ , observed: 401.2 (M+H) $^+$ . Purification Technique: silica gel, 5% ethyl acetate/hexanes.  $R_f = 0.09$  (4% ethyl acetate/hexanes).

**Proof of Stereochemistry.** Stereochemistry was determined by diimide reduction (2-nitrobenzenesulfonylhydrazide (3 equiv), triethylamine (6 equiv), dioxanes (0.1 M), 80  $^\circ\text{C}$ , overnight) 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 protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane). Racemic material was prepared from the diboration of 1-methoxy-4-(propa-1,2-dienyl)benzene as described in the general procedure using tricyclohexylphosphine. Absolute stereochemistry was established in comparison to authentic material prepared by Sharpless asymmetric oxidation of anethole (Norrby, P-O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35) The resultant diol was protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane).

*Chiral GLC ( $\beta$ -dex, Supelco, 120  $^\circ\text{C}$ ) – analysis of acetonide derived from reduction and oxidation of reaction product as described above.*



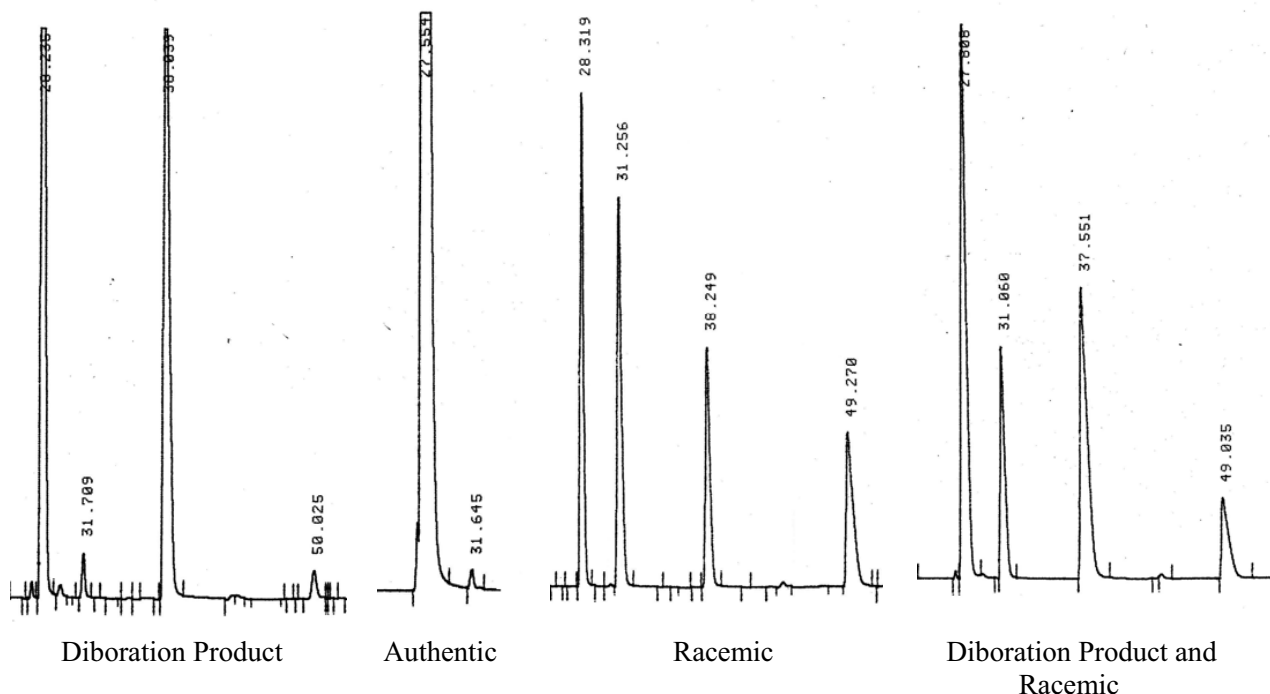


**(S)-4,4,5,5-tetramethyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-yl)-1,3,2-dioxaborolane.**

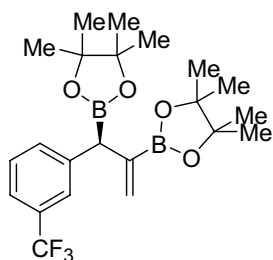
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24 (12H, s,  $\text{OCCCH}_3$ ), 1.25 (12H, s,  $\text{OCCCH}_3$ ), 3.44 (1H, s, ArCHB), 5.34 (1H, s, CBCH), 5.86 (1H, s, CBCH), 7.33 (2H, d,  $J = 8.0$  Hz, Ar-H), 7.51 (2H, d,  $J = 7.5$  Hz, Ar-H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.7 (2C), 24.8 (2C), 24.9 (2C), 25.0 (2C), 83.8 (2C), 83.9 (2C), 124.6 (1C, q,  $^1J_{\text{CF}} = 271$  Hz), 125.1 (2C, q,  $^3J_{\text{CF}} = 3.7$  Hz), 127.8 (1C, q,  $^2J_{\text{CF}} = 32.2$  Hz), 128.9, 130.3 (2C), 145.6.  $^{19}\text{F}$  NMR (376.4 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.8 (s). IR (neat): 2984 (s), 2930 (s), 2859 (w), 2354 (w), 1627 (m), 1366 (s), 1323 (s), 1133 (s)  $\text{cm}^{-1}$ . LRMS-(ESI $^+$ ): for  $\text{C}_{22}\text{H}_{31}\text{B}_2\text{F}_3\text{O}_4$  calc'd: 439.2 (M+H) $^+$ , observed: 439.2 (M+H) $^+$ . Purification Technique: silica gel, 4% ethyl acetate/hexanes.  $R_f = 0.23$  (4% ethyl acetate/hexanes).

**Proof of Stereochemistry.** Stereochemistry was determined by diimide reduction (2-nitrobenzenesulfonylhydrazide (3 equiv), triethylamine (6 equiv), dioxanes (0.1 M), 80  $^\circ\text{C}$ , overnight) 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 protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane). Racemic material was prepared from the diboration of 1-(propa-1,2-dienyl)-4-(trifluoromethyl)benzene as described in the general procedure using tricyclohexylphosphine. Absolute stereochemistry was established in comparison to authentic material prepared by Sharpless asymmetric oxidation of 4-trifluoromethyl-*trans*- $\beta$ -methylstyrene (Norrby, P.-O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35). The resultant diol was protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane).

Chiral GLC ( $\beta$ -dex, Supelco, 105  $^\circ\text{C}$ ) – analysis of acetonide derived from reduction and oxidation of reaction product as described above.



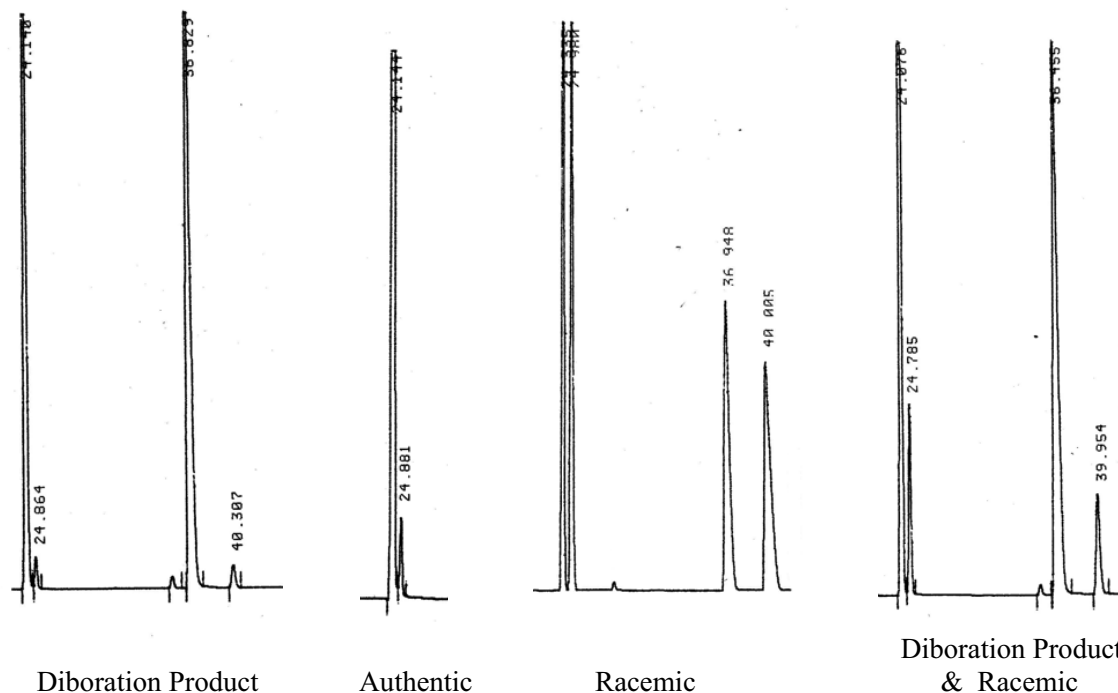


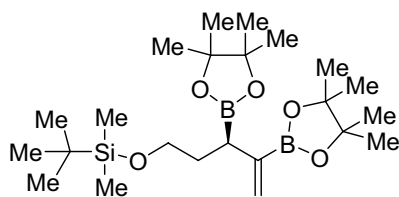


**(S)-4,4,5,5-tetramethyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(trifluoromethyl)phenyl)prop-2-en-2-yl)-1,3,2-dioxaborolane.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24 (6H, s,  $\text{OCCH}_3$ ), 1.24 (6H, s,  $\text{OCCH}_3$ ), 1.25 (6H, s,  $\text{OCCH}_3$ ), 1.26 (6H, s,  $\text{OCCH}_3$ ), 3.42 (1H, s, ArCHB), 5.33 (1H, s, CBCH), 5.85 (1H, s, CBCH), 7.36-7.42 (3H, m, Ar-H), 7.53 (1H, s, ortho-ArH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.6 (2C), 24.7 (2C), 24.9 (2C), 25.0 (2C), 83.8 (2C), 83.9 (2C), 122.4 (1C, q,  $^3J_{\text{CF}} = 3.8$  Hz), 124.6 (1C, q,  $^1J_{\text{CF}} = 272.3$  Hz), 126.9 (1C, q,  $^3J_{\text{CF}} = 3.8$  Hz), 128.6, 128.9, 130.4 (1C, q,  $^2J_{\text{CF}} = 32.2$  Hz), 133.5, 142.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.1. IR (neat): 3064 (w), 2978 (s), 2932 (s), 2357 (w), 1603 (m), 1445 (m), 1366 (s), 1320 (s)  $\text{cm}^{-1}$ . LRMS-ESI+: For  $\text{C}_{22}\text{H}_{31}\text{B}_2\text{F}_3\text{O}_4$  calc'd: 439.2 (M+H) $^+$ , observed: 439.2 (M+H) $^+$ . Purification Technique: silica gel, 4% ethyl acetate/hexanes.  $R_f = 0.18$  (4% ethyl acetate/hexanes).

**Proof of Stereochemistry.** Stereochemistry was determined by diimide reduction (2-nitrobenzenesulfonylhydrazide (3 equiv), triethylamine (6 equiv), dioxanes (0.1 M), 80  $^\circ\text{C}$ , overnight) 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 protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane). Racemic material was prepared from the diboration of 1-(propa-1,2-dienyl)-3-(trifluoromethyl)benzene as described in the general procedure using tricyclohexylphosphine. Absolute stereochemistry was established in comparison to authentic material prepared by Sharpless asymmetric oxidation of 3-trifluoromethyl-*trans*- $\beta$ -methylstyrene (Norrby, P.-O.; Becker, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1996**, *118*, 35) The resultant diol was protected as the acetonide (*p*-toluenesulfonic acid and 2,2-dimethoxypropane).

*Chiral GLC ( $\beta$ -dex, Supelco, 100  $^\circ\text{C}$ ) – analysis of acetonide derived from reduction and oxidation of reaction product as described above*

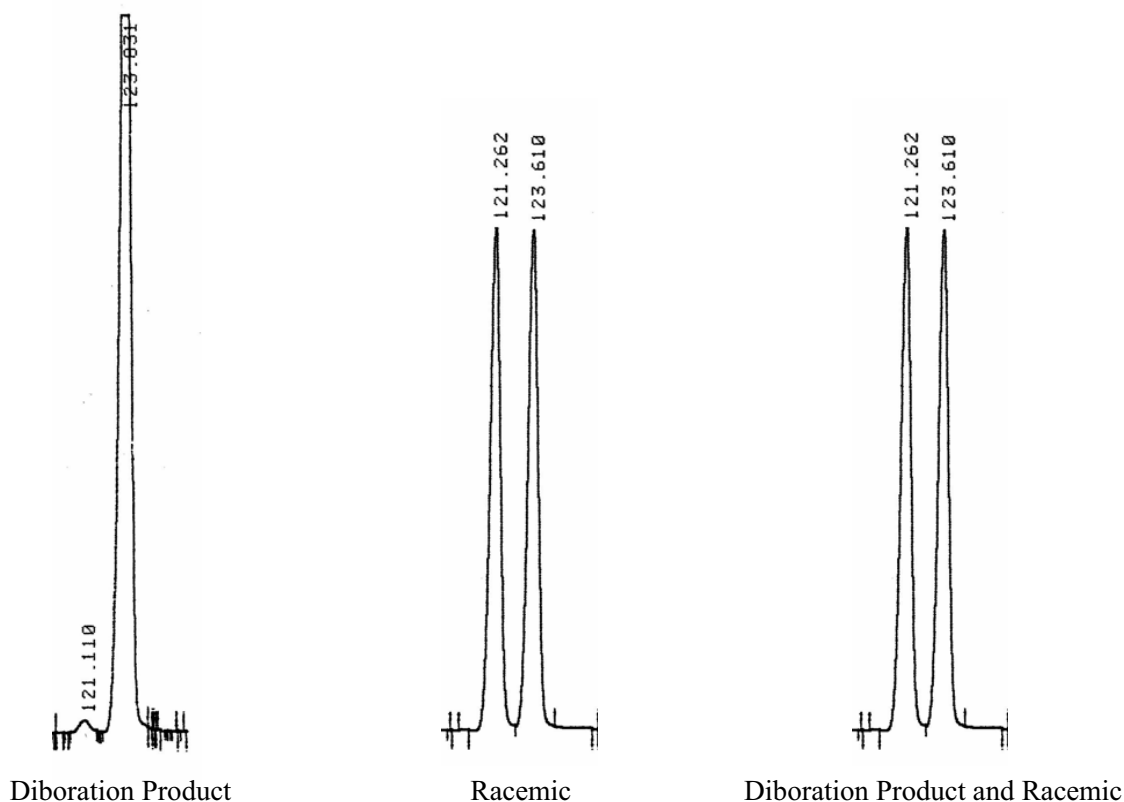




**(*R*)-(3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enyloxy)(*tert*-butyl)dimethylsilane.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.003 (6H, s,  $(\text{CH}_3)_2\text{Si}$ ), 0.89 (9H, s,  $(\text{CH}_3)_3\text{CSi}$ ), 1.19 (6H, s,  $\text{OCCH}_3$ ), 1.20 (6H, s,  $\text{OCCH}_3$ ), 1.22 (12H, s,  $\text{OCCH}_3$ ), 1.74 (1H, m,  $\text{CH}_2\text{CH}_A\text{H}_B\text{CHB}$ ), 1.85 (1H, m,  $\text{CH}_2\text{CH}_A\text{H}_B\text{CHB}$ ), 1.98 (1H, t,  $J = 7.4$  Hz,  $\text{CH}_2\text{CHBCB}$ ), 3.55 (2H, m,  $\text{OCH}_2\text{CH}_2$ ), 5.55 (1H, d,  $J = 2.4$  Hz,  $\text{CHCB}$ ), 5.75 (1H, d,  $J = 3.2$  Hz,  $\text{CHCB}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.1, -5.07, 18.5, 24.7 (2C), 24.8 (2C), 24.9 (2C), 25.0 (2C), 26.2 (3C), 32.7, 63.0, 83.1 (2C), 83.4 (2C), 128.0. IR (neat): 3055 (w), 2973 (s), 2848 (s), 2734 (w), 2289 (w), 1610 (s), 1475 (s), 1361 (s), 1274 (s), 1241 (s)  $\text{cm}^{-1}$ . LRMS-(ESI $^+$ ): for  $\text{C}_{23}\text{H}_{46}\text{B}_2\text{NaO}_5\text{Si}$  calc'd 475.3 ( $\text{M}+\text{Na}$ ) $^+$ , observed 475.3 ( $\text{M}+\text{Na}$ ) $^+$ . Purification Technique: silica gel, 5% ethyl acetate/hexanes.  $R_f = 0.33$  (5% ethyl acetate/hexanes).

**Proof of Stereochemistry.** Stereochemistry was determined by diimide reduction (2-nitrobenzenesulfonylhydrazide (3 equiv), triethylamine (6 equiv), dioxanes (0.1 M), 80  $^\circ\text{C}$ , overnight) 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 protected as the diacetate (acetic anhydride (1.2 equiv), triethylamine (3 equiv), and 4-dimethylaminopyridine (cat) in dichloromethane (0.25 M). Racemic material was prepared from the diboration of *tert*-butyldimethyl(penta-3,4-dienyloxy)silane as described in the general procedure using tricyclohexylphosphine.

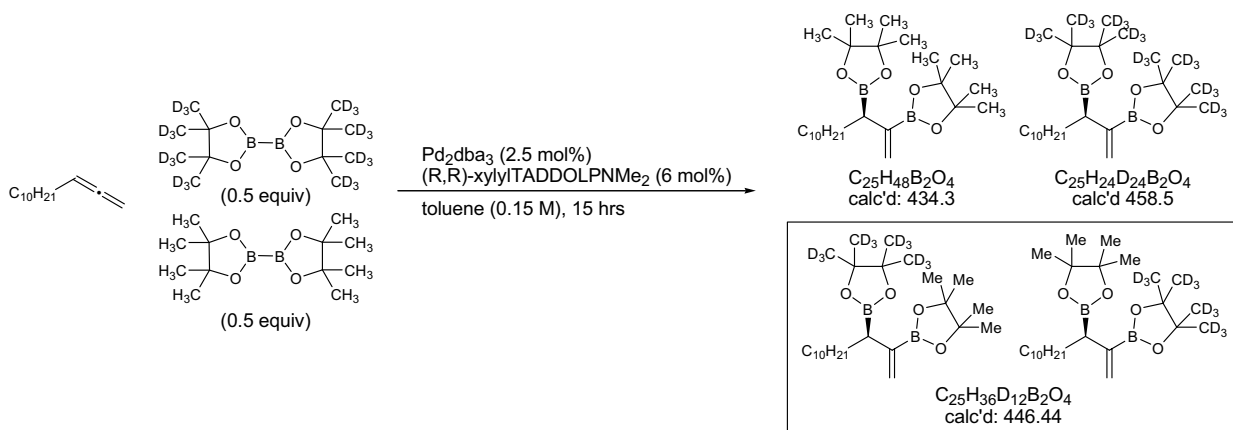
*Chiral GLC ( $\beta$ -dex, Supelco, 100  $^\circ\text{C}$  for 25 minutes then 0.5 deg/min to 120  $^\circ\text{C}$ ) – analysis of acetate derived from reduction and oxidation of reaction product as described above*



## F. Preparation of pinacol- $d_{12}$ and $B_2(\text{pin-}d_{12})_2$ , and subsequent Crossover Experiment.

**Pinacol- $d_{12}$ .**<sup>4</sup> To a 1 L two-neck flask equipped with a magnetic stir bar was added magnesium turnings (3.08 g, 127 mmol), which were flame-dried under vacuum. Under nitrogen,  $\text{HgCl}_2$  (3.45 g, 12.71 mmol) was added, followed by benzene (500 mL, 0.025 M). The flask was charged with acetone- $d_6$  (65.5 mL, 890 mmol) and the resultant mixture stirred for 24 hours at 60 °C under nitrogen. The mixture was cooled to ambient temperature, quenched with distilled water (200 mL) and stirred at 60 °C for an additional three hours. The suspension was extracted with diethyl ether and the organic layers combined and filtered on a Büchner funnel. The solvent was removed by distillation to afford a yellow oil which was purified on silica gel (30% ethyl acetate/hexanes) to afford 2.27 g (13% yield) of a clear oil. Spectral data are in accordance with those in the literature.

$B_2(\text{pin-}d_{12})_2$  was prepared according to literature procedure without deviation.<sup>5</sup>

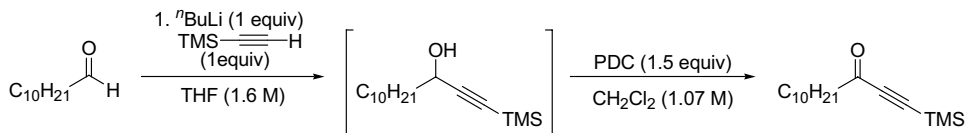


**Crossover experiment.** In the dry box, a 6 dram vial with a magnetic stir bar was charged with  $\text{Pd}_2\text{dba}_3$  (7.6 mg, 8.3  $\mu\text{mol}$ ),  $(R,R)$ -xylylTADDOLPNMe<sub>2</sub> (**( $R,R$ )-6**, 13.2 mg, 19.9  $\mu\text{mol}$ ), and toluene (2.21 mL, 0.15 M). The metal and ligand were complexed for 1 hour, at which time  $B_2(\text{pin})_2$  (43.2 mg, 0.170 mmol) and  $B_2(\text{pin-}d_{12})_2$  (46.3 mg, 0.166 mmol) were added simultaneously to the reaction mixture. Tridec-1,2-diene (60.3 mg, 0.332 mmol) was added to the reaction mixture, the vial was sealed with a polyethylene cap and electrical tape then removed from the dry box. The reaction stirred at room temperature for 15 hours when it was concentrated to dryness. Residual solvent was removed *in vacuo* and the material was purified with by passage through a short column of silica gel (5% ethyl acetate/hexanes). All fractions were pooled, concentrated, and submitted for LRMS-ESI<sup>+</sup> analysis. For  $C_{25}H_{48}B_2O_4$  ( $M+H$ )<sup>+</sup> calc'd: 435.3, observed: 435.3 ( $M+H$ )<sup>+</sup>. For  $C_{25}H_{25}D_{24}B_2O_4$  ( $M+H$ )<sup>+</sup> calc'd: 459.5, observed: 459.5.  $C_{25}H_{36}D_{12}B_2O_4$  was not observed.

<sup>4</sup> Boller, T.M.; Murphy, J.M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J.F. *J. Am. Chem. Soc.* **2005**, *127*, 14263.

<sup>5</sup> Ishiyama, T.; Murata, M.; Ahiko, T.-A.; Miyaura, N. *Organic Syntheses*, **2000**, *77*, 176-185.

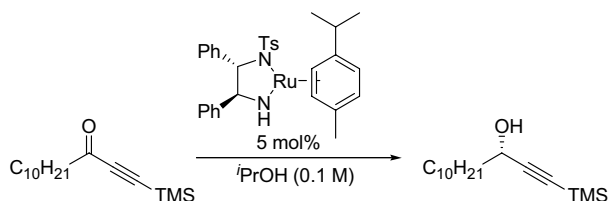
## G. Synthesis of (*R*)-9-*d*<sub>1</sub>



**1-(Trimethylsilyl)-tridec-1-yn-3-one.**<sup>6</sup> To a 25 mL round-bottom flask equipped with magnetic stir bar and sealed with a septum, was added trimethylsilylacetylene (1 mL, 7.07 mmol) and THF (4.4 mL). The flask was cooled to 0 °C (ice-water bath) and charged with 1.54 M *n*BuLi (4.59 mL). After stirring for 30 min at 0 °C, undecanal was added slowly over 30 min and the reaction allowed to stir at 0 °C for an additional 60 min. The reaction was quenched with water (10 mL) and extracted with ethyl acetate (3 times). The organic layers were combined, washed with 0.5 M HCl, saturated NaHCO<sub>3</sub>, and brine. Organic extracts were dried (MgSO<sub>4</sub>) and concentrated on a rotary evaporator to afford 1-trimethylsilanyl-tri-dec-1-yl-ol as an oil.

**PDC Oxidation:** To a septum-sealed 100 mL round-bottom flask with a magnetic stir bar and 4Å MS (1.27 g) was added CH<sub>2</sub>Cl<sub>2</sub> (10 mL, 1.07 M) and pyridinium dichromate (3.98 g). In a separate flask, 1-trimethylsilanyl-tri-dec-1-yl-ol was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4.4 mL) and transferred by cannula into the reaction flask. After the reaction stirred for 16 hours, it was diluted with diethyl ether and filtered over celite. The filtrate was concentrated to afford a clear oil, which was purified by silica gel chromatography (2% ethyl acetate/hexanes) to afford 1.17 g (62% yield) of a clear oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.24 (9H, s, (CH<sub>3</sub>)<sub>3</sub>Si), 0.85 (3H, t, *J* = 6.8 Hz, CH<sub>3</sub>CH<sub>2</sub>), 1.24-1.27 (14H, m, br, (CH<sub>2</sub>)<sub>7</sub>), 1.63 (2H, p, *J* = 7.2 Hz, CH<sub>2</sub>CH<sub>2</sub>CO), 2.52 (2H, t, *J* = 7.4 Hz, CH<sub>2</sub>CH<sub>2</sub>CO). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -0.67 (3C), 14.2, 22.8, 24.0, 29.0, 29.4, 29.5, 29.6, 31.9, 97.5, 102.2, 188.0. IR (neat): 2942 (s), 2843 (s), 2148 (m), 2089 (w), 1681 (s), 1459 (s), 1404 (w), 1241 (s) cm<sup>-1</sup>. LRMS-(ESI<sup>+</sup>): for C<sub>16</sub>H<sub>30</sub>NaOSi calc'd 289.2 (M+Na)<sup>+</sup>, observed 289.3 (M+Na)<sup>+</sup>. Purification: silica gel, 2% ethyl acetate/hexanes, R<sub>f</sub> = 0.45 (10% ethyl acetate/hexanes), stains in PMA.



**(*S*)-1-(trimethylsilyl)tridec-1-yn-3-ol.**<sup>7</sup> To a 100 mL round-bottom flask with magnetic stir bar was added 1-(trimethylsilyl)-tridec-1-yn-3-one (1 g, 3.76 mmol) in isopropanol (37.6 mL). Next, Ru[(1*S*,2*S*)-*p*-TsNCH(C<sub>6</sub>H<sub>5</sub>)CH(C<sub>6</sub>H<sub>5</sub>)NH](η<sup>6</sup>-*p*-cymene) (112.6 mg, 0.187) was added. The reaction was stirred for 16 hours after which time the crude reaction mixture was concentrated, and purified on silica gel to afford 1.00 g (91% yield, 99% *ee*) of a clear oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.15 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 0.86 (3H, t, *J* = 6.7 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.24 (14 H, s, br, (CH<sub>2</sub>)<sub>7</sub>), 1.38-1.44 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CHOH), 1.63-1.69 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CHOH), 2.20 (1H, s br, OH), 4.32 (1H, t, *J* = 6.6 Hz, CHOH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -0.008 (3C), 14.2, 22.8, 25.2, 29.3, 29.4, 29.6, 29.7, 29.8, 32.0, 37.8, 62.9, 89.2, 107.2. IR (neat): 3315 (s), 2935 (s), 2859 (s), 2164 (s), 1453 (s), 1399 (m), 1252 (s) cm<sup>-1</sup>. LRMS-(ESI<sup>+</sup>) for C<sub>16</sub>H<sub>31</sub>NaOSi calc'd 290.2042

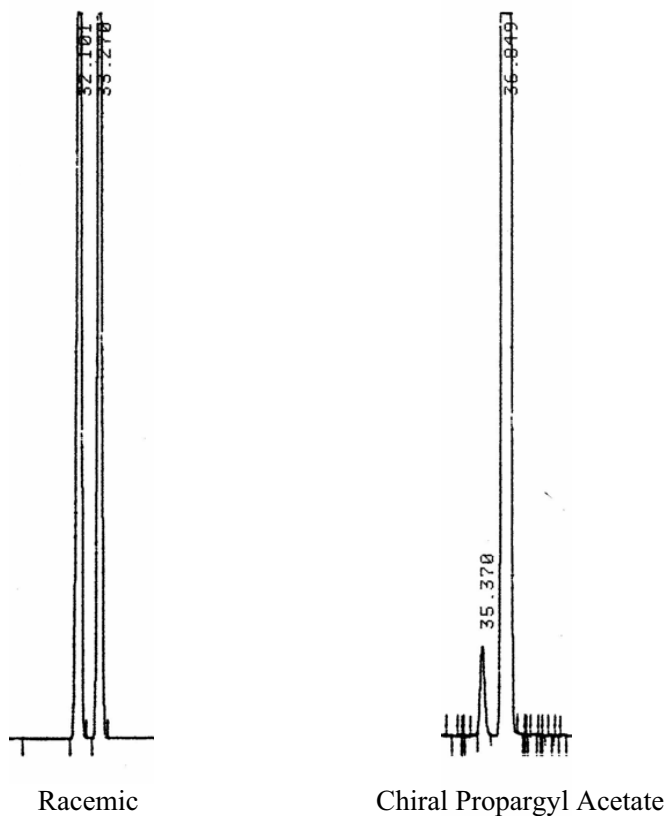
<sup>6</sup> Matsumara, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738-8739.

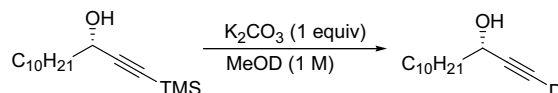
<sup>7</sup> Catalyst Preparation: Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem. Int. Ed. Eng.* **1997**, *36*, 285-287. Transfer Hydrogenation: Matsumara, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738-8739.

(M+Na)<sup>+</sup>, observed 291.3 (M+Na)<sup>+</sup>. Purification Technique: silica gel, 5% ethyl acetate/hexanes, R<sub>f</sub> = 0.45 (10% ethyl acetate/hexanes), stains in PMA.

**Determination of Enantioselectivity.** The trimethylsilyl group of (S)-1-(trimethylsilyl)tridec-1-yn-3-ol was deprotected with potassium carbonate (1 equiv) in methanol (1.0 M). The hydroxyl group was then protected using acetic anhydride (1.2 equiv), triethylamine (3 equiv), and 4-dimethylaminopyridine (cat) in dichloromethane (0.25 M). The enantiomerically enriched material was compared to racemic product.

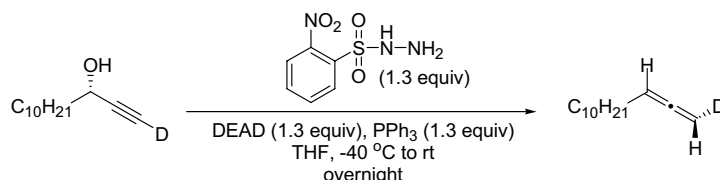
*Chiral GLC (β-dex, Supelco, 140 °C) – analysis of acetate derived from TMS deprotection and alcohol protection of the reaction product as described above*





**(S)-1-Deuteriotridec-1-yn-3-ol.** To a 50 mL round-bottom flask with magnetic stir bar, was added (S)-1-(trimethylsilyl)tridec-1-yn-3-ol (2.23 mg, 8.31 mmol) in methanol-OD (8.3 mL). Potassium carbonate (anhydrous) (1.132 g, 8.314 mmol) was added under nitrogen. The reaction was stirred for 3 hours when it was quenched with water and diluted with ethyl acetate. The aqueous layer was washed twice with ethyl acetate, then the organic extracts were combined and washed with brine and dried ( $\text{MgSO}_4$ ). The organic layer was filtered over celite and concentrated on a rotary evaporator. The reaction mixture was purified on silica gel (10% ethyl acetate/hexanes) to afford 1.548 g (94% yield) of a white solid.

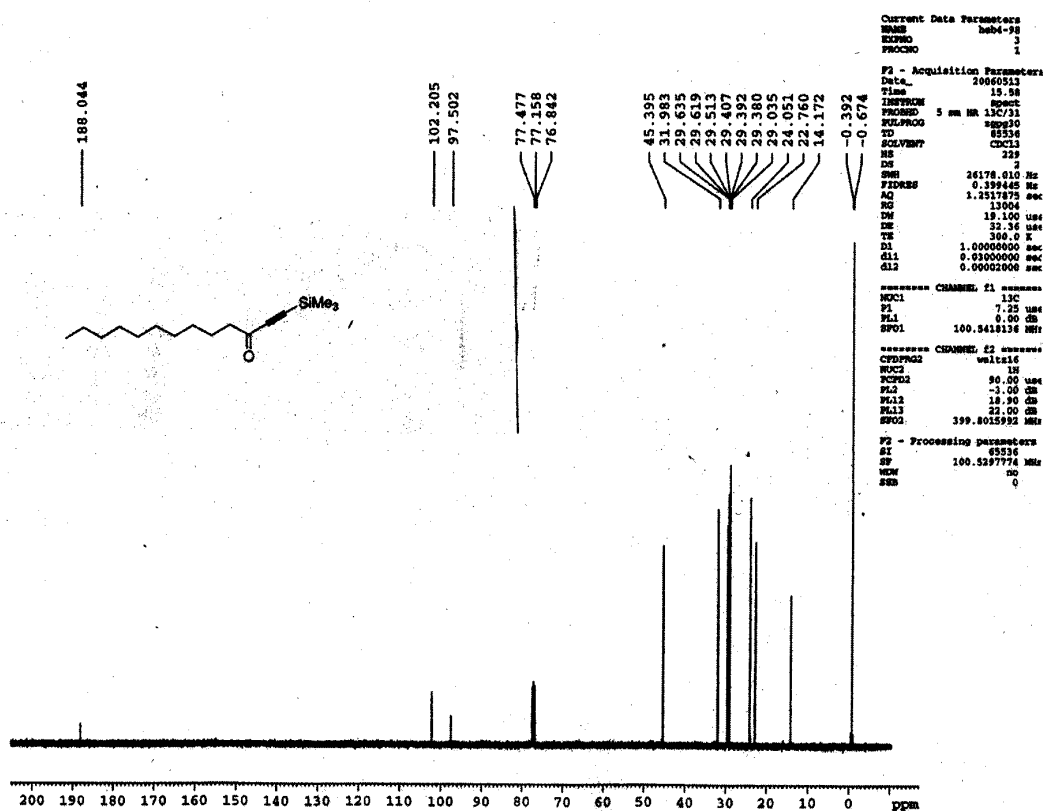
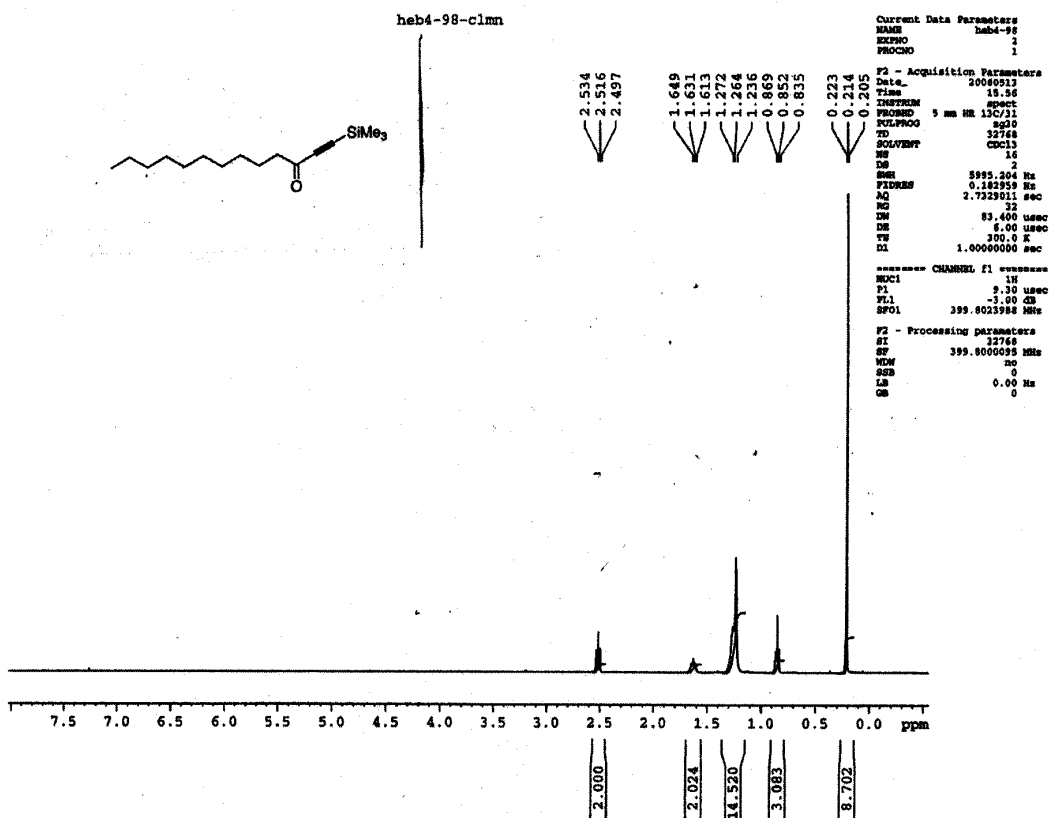
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (3H, t,  $J = 6.8$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.24 (14H, m,  $(\text{CH}_2)_7$ ), 1.42 (2H, m,  $\text{CH}_2\text{CH}_2\text{CHOH}$ ), 1.68 (2H, m,  $\text{CH}_2\text{CH}_2\text{CHOH}$ ), 2.53 (1H, s, OH), 4.34 (1H, t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CHOH}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.2, 22.8, 25.1, 29.3, 29.4, 29.6, 29.7, 29.8, 31.9, 37.7, 62.3 (1C,  $^3J_{\text{CD}} = 2.3$  Hz), 72.6 (1C,  $^1J_{\text{CD}} = 38.1$  Hz), 84.8 (1C,  $^2J_{\text{CD}} = 7.2$  Hz). IR ( $\text{CH}_2\text{Cl}_2$ ): 3364 (s), 2952 (s), 2843 (s), 2593 (s), 1980 (s), 1632 (w), 1464 (s)  $\text{cm}^{-1}$ . LRMS-(ESI $^+$ ) for  $\text{C}_{13}\text{H}_{23}\text{DNaO}$  calc'd 220.1 ( $\text{M}+\text{Na}$ ) $^+$ , observed 220.1 ( $\text{M}+\text{Na}$ ) $^+$ . Purification Technique: silica gel, 10% ethyl acetate/hexanes,  $R_f = 0.21$  (10% ethyl acetate/hexanes), developed with PMA.

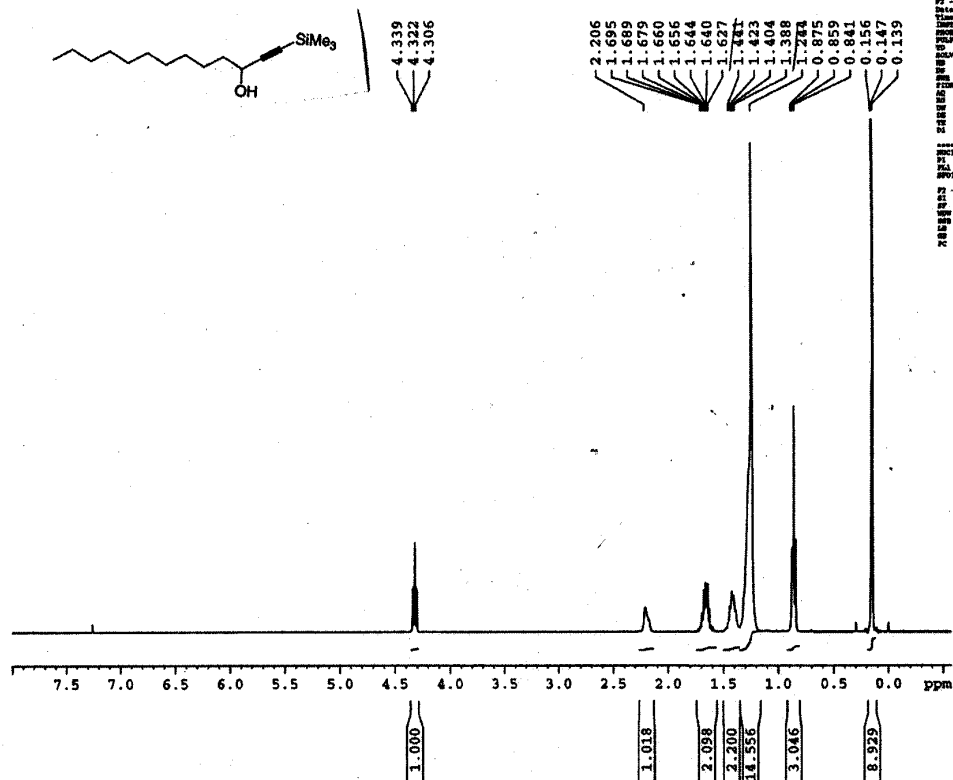


**(R)-1-Deuteriotridec-1,2-diene.**<sup>8</sup> To a two neck 100 mL round-bottom flask with a magnetic stir bar, was added triphenylphosphine (1.01 g, 3.86 mmol) in THF (12 mL). This was cooled to  $-40$  °C (ethylene glycol:ethanol, dry ice) and diethyl azodicarboxylate (607  $\mu\text{L}$ , 3.86 mmol) was added slowly. The reaction stirred for 15 minutes at  $-40$  °C when the labeled alkyne (586 mg, 2.662 mmol) was transferred by cannula as a solution in THF (9.1 mL). After an additional 15 minutes at  $-40$  °C, *o*-nitrobenzenesulfonylhydrazine (NBSH, 838.2 mg, 3.860 mmol) was added as a solution in THF (12 mL). The reaction was stirred at  $-40$  °C for an additional 2 hours, then was allowed to gradually warm to ambient temperature and stir overnight. The crude reaction mixture was concentrated, dissolved in methylene chloride and purified on silica gel (pentanes) to afford 263 mg (50% yield) of a clear oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.90 (3H, t,  $J = 6.8$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.29 (14H, s, br,  $(\text{CH}_2)_7$ ), 1.38-1.45 (2H, m,  $\text{CH}_2\text{CH}_2\text{CH}$ ), 2.00 (2H, qd,  $J = 7.2, 7.2, 7.1, 3.0$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}$ ), 4.65-4.62 (1H, m, CHD), 5.09 (1H, q,  $J = 7.2, 6.8$  Hz,  $\text{CH}_2\text{CHC}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.2, 22.9, 28.5, 29.3, 29.4, 29.5, 29.6, 28.9, 32.1, 74.4 (1C, t,  $^1J_{\text{CD}} = 25.6$  Hz), 90.3, 208.73.  $^2\text{H}$  NMR (61.4 MHz,  $\text{CHCl}_3$ ):  $\delta$  4.68. IR (neat) 2962 (s), 2924 (s), 2848(s), 1958 (s), 1458 (s), 1372 (m)  $\text{cm}^{-1}$ . HRMS-CI GC/MS: for  $\text{C}_{13}\text{H}_{23}\text{D}$  calc'd 181.194 ( $\text{M}^+$ ), observed 181.193 ( $\text{M}^+$ ). Purification: silica gel, pentanes,  $R_f = 0.92$  (pentanes), developed with  $\text{KMnO}_4$ .

<sup>8</sup> Myers, A.G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492-4493.





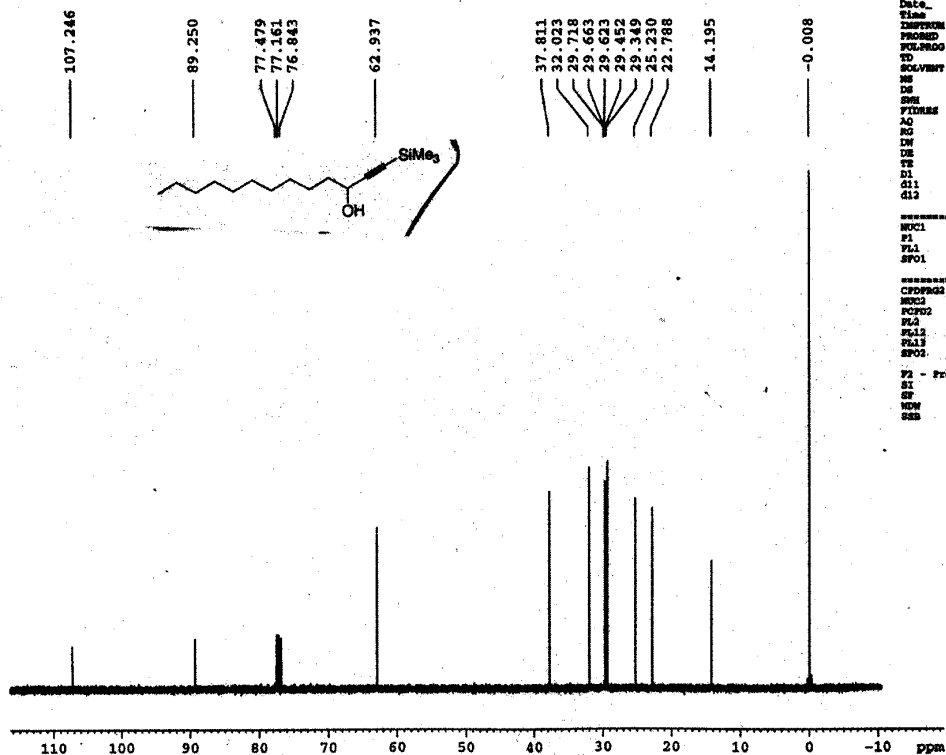
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EXPNO 7  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060511  
Time 20.06  
INSTRUM spect  
PROBHD 5 mm HR 13C/31  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 110  
DS 2  
SWH 26178.010 Hz  
FIDRES 0.339445 Hz  
AQ 1.2517875 sec  
RG 13004  
DW 19.100 usec  
DE 32.36 usec  
TE 300.0 K  
D1 1.00000000 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

===== CHANNEL f1 =====  
NUC1 13C  
P1 7.25 usec  
PL1 0.00 dB  
SFO1 100.5418134 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 31P  
PCPD2 90.00 usec  
PL2 -3.00 dB  
PL12 18.00 dB  
PL13 22.00 dB  
SFO2 125.7611992 MHz

F2 - Processing parameters  
SI 65536  
SF 100.5297770 MHz  
WDW no  
SSB 0



Current Data Parameters  
NAME heb2-268  
EXPNO 7  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060511  
Time 20.06  
INSTRUM spect  
PROBHD 5 mm HR 13C/31  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 110  
DS 2  
SWH 26178.010 Hz  
FIDRES 0.339445 Hz  
AQ 1.2517875 sec  
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TE 300.0 K  
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d11 0.03000000 sec  
d12 0.00002000 sec

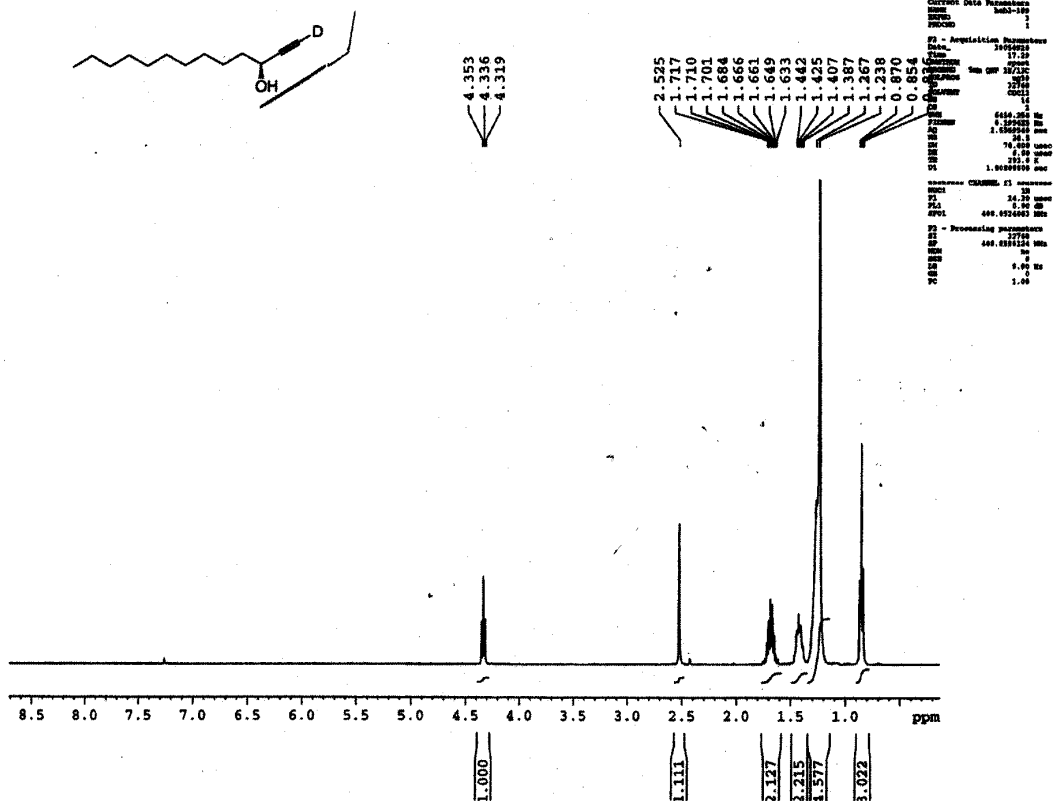
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NUC1 13C  
P1 7.25 usec  
PL1 0.00 dB  
SFO1 100.5418134 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 31P  
PCPD2 90.00 usec  
PL2 -3.00 dB  
PL12 18.00 dB  
PL13 22.00 dB  
SFO2 125.7611992 MHz

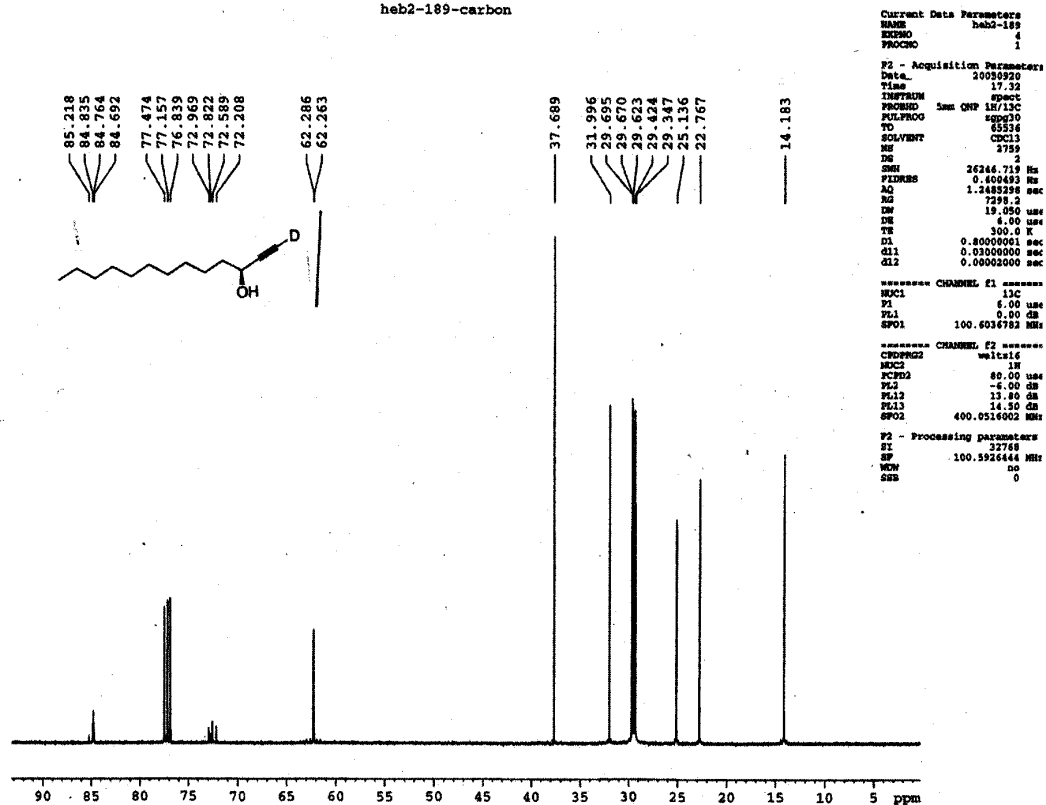
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SF 100.5297770 MHz  
WDW no  
SSB 0



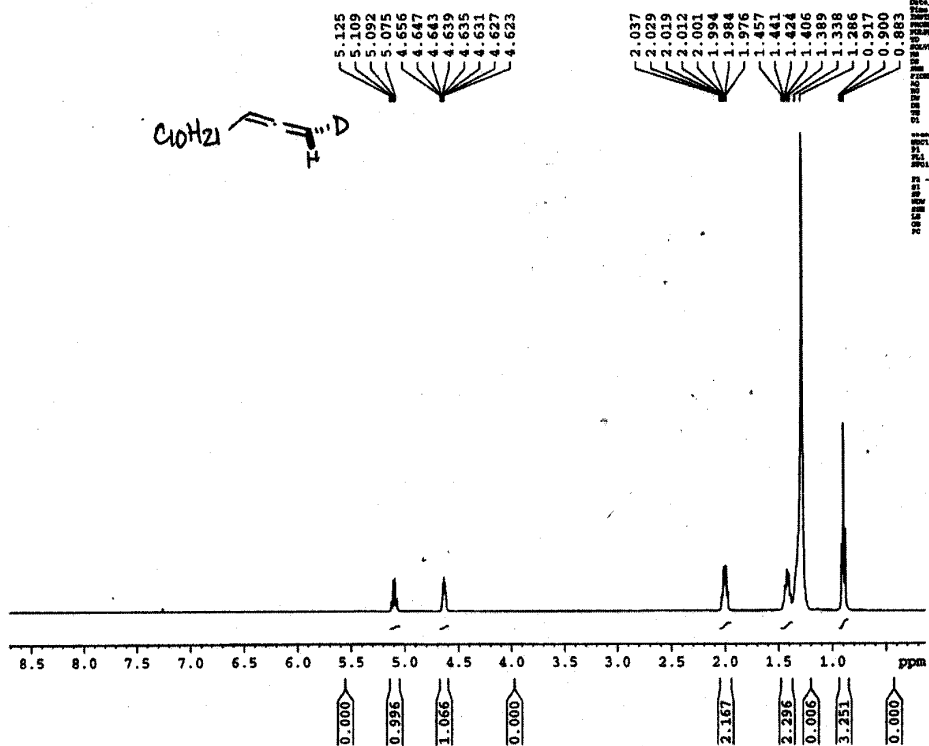
heb2-189-proton



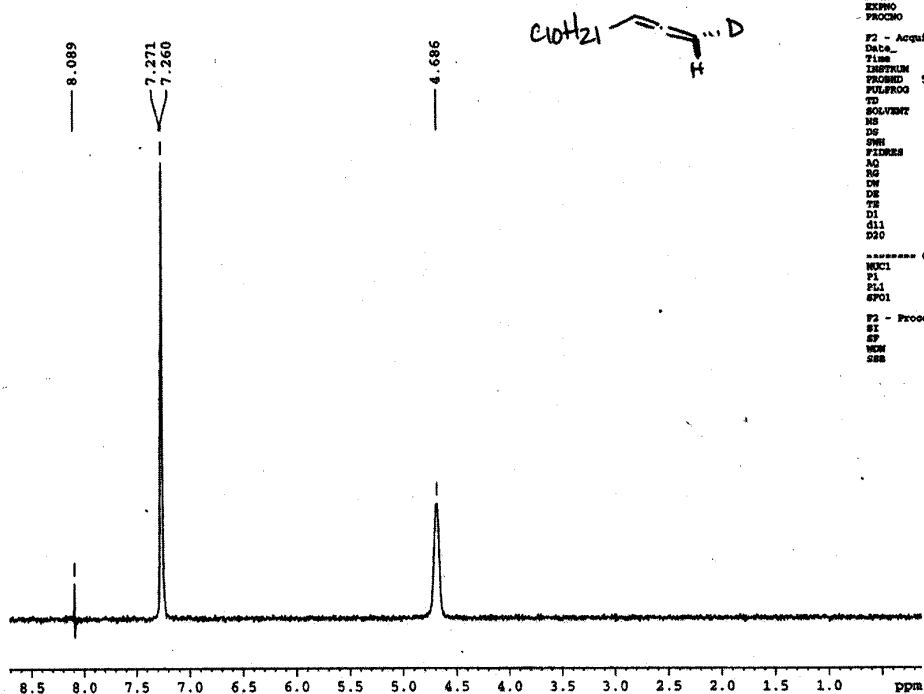
heb2-189-carbon



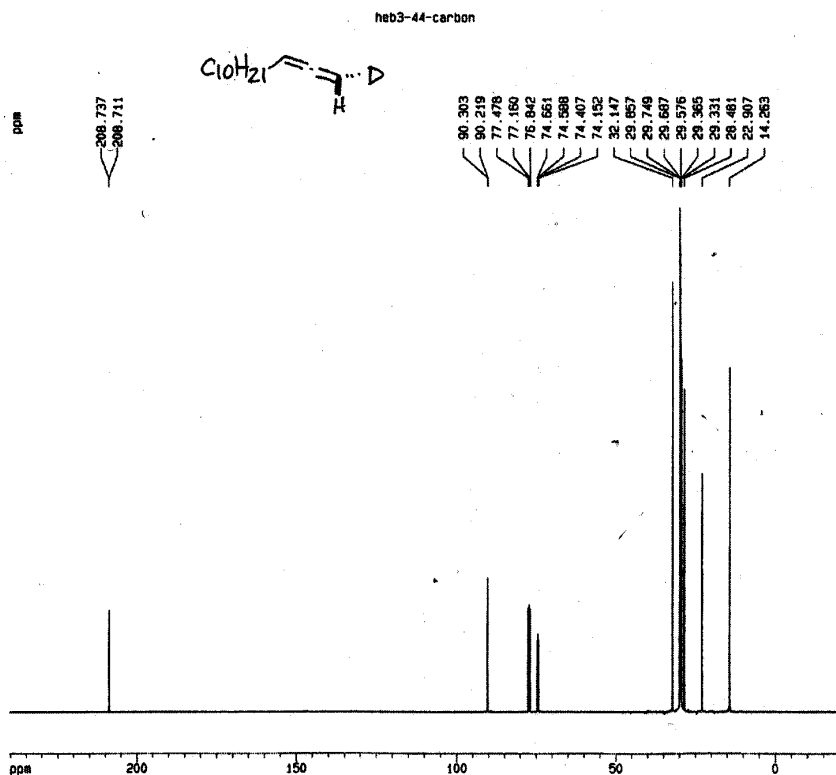
heb3-44-clmn



Current Data Parameters  
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PROCNO 1  
F2 - Acquisition Parameters  
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INSTRUM spect  
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PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 2  
SWH 513.743 Hz  
FIDRES 0.223082 Hz  
AQ 2.2415283 sec  
RG 512  
CW 547.200 usec  
DE 6.00 usec  
TE 293.0 K  
D1 1.00000000 sec  
d11 0.01000000 sec  
D20 0.20000000 sec  
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
NUC1 13C  
P1 400.60 usec  
PL1 -3.00 dB  
SFO1 61.4105050 MHz  
F2 - Processing parameters  
SI 16384  
SF 61.4105050 MHz  
WDW no  
SSB 0



Current Data Parameters  
NAME heb3-44  
EXPNO 5  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20060527  
Time 21.05  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 2  
SWH 513.743 Hz  
FIDRES 0.223082 Hz  
AQ 2.2415283 sec  
RG 512  
CW 547.200 usec  
DE 6.00 usec  
TE 293.0 K  
D1 1.00000000 sec  
d11 0.01000000 sec  
D20 0.20000000 sec  
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
NUC1 13C  
P1 400.60 usec  
PL1 -3.00 dB  
SFO1 61.4105050 MHz  
F2 - Processing parameters  
SI 16384  
SF 61.4105050 MHz  
WDW no  
SSB 0



Current Data Parameters  
NAME heb3-44  
EXPNO 4  
PROCNO 1

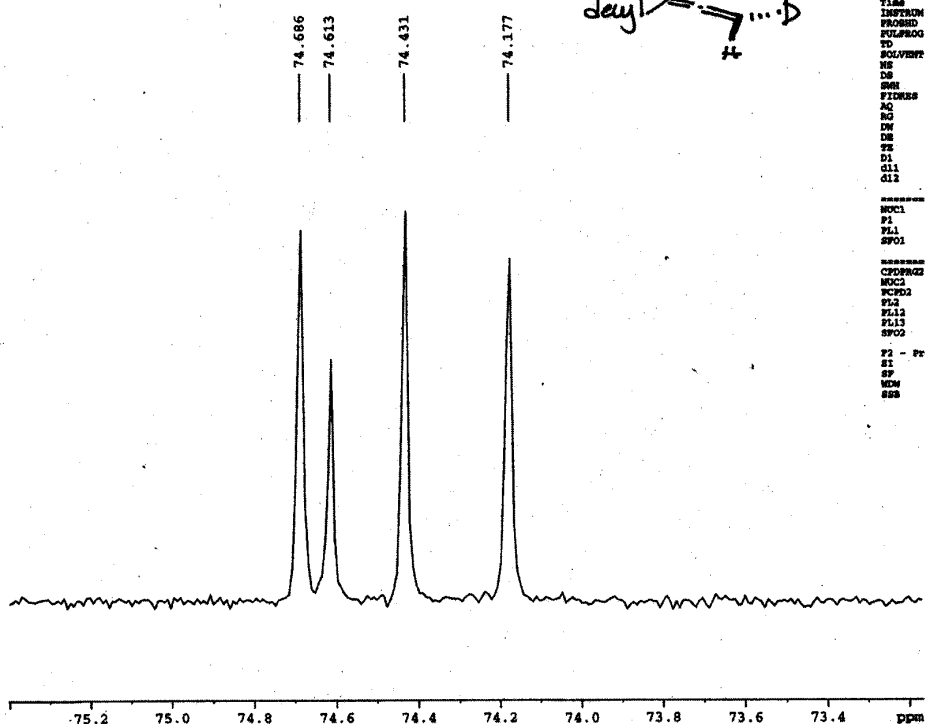
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PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 21019  
DS 2  
SWH 26246.719 Hz  
FIDRES 0.400493 Hz  
AQ 1.2485108 sec  
RG 6502  
DN 19.050 usec  
DE 8.00 usec  
TE 300.0 K  
D1 0.80000001 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

===== CHANNEL f1 =====  
NUC1 13C  
P1 8.00 usec  
PL1 0.00 dB  
SFO1 100.626182 MHz

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

F2 - Processing parameters  
SI 32768  
SF 100.626182 MHz  
WDW no  
SSB 0  
LB 0.00 Hz  
GB 0  
PC 1.40

1D 1H plot parameters  
CX 20.00 cm  
CY 12.50 cm  
FIP 240.238 ppm  
F1 24185.13 Hz  
F2 -208.558 Hz  
PPMCH 13.84804 ppm/cm  
PCMH 1312.35994 Hz/cm



Current Data Parameters  
NAME heb3-209  
EXPNO 7  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20050812  
Time 18.07  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 24185  
DS 2  
SWH 26246.719 Hz  
FIDRES 0.400493 Hz  
AQ 1.2485108 sec  
RG 6502  
DN 19.050 usec  
DE 8.00 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 100.626182 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

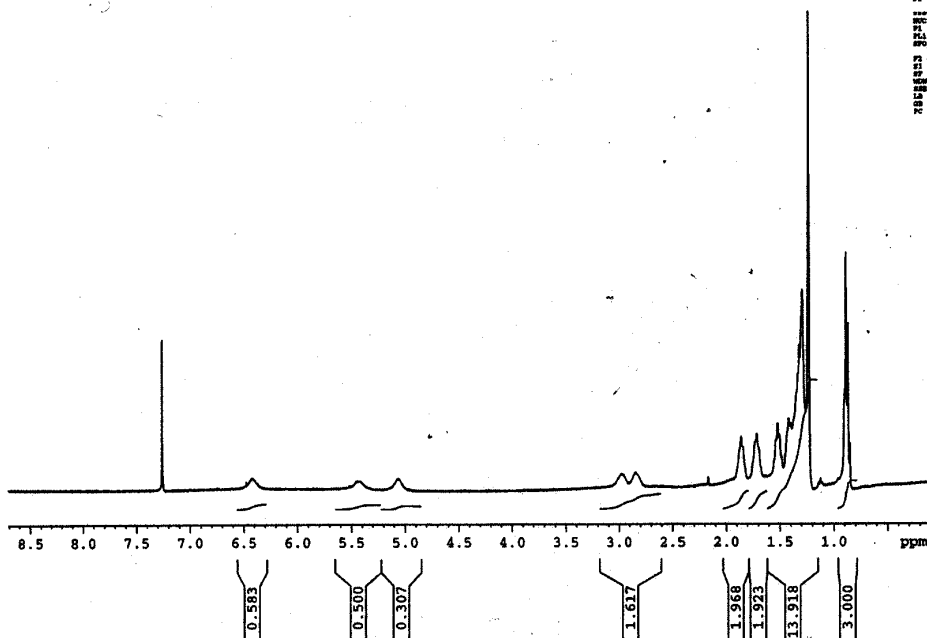
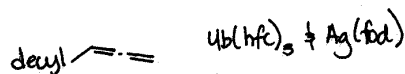
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SI 32768  
SF 100.6127523 MHz  
WDW no  
SSB 0

**Enantiomeric purity determination of (*R*)-9-*d*<sub>7</sub>.**<sup>9</sup> To a 1 dram vial was added ytterbium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (Yb(hfc)<sub>3</sub>) (23.4 mg, 0.019 mmol) and (6,6,7,7,8,8-Heptafluoro-2,2-dimethyl-3,5-octandionato)silver (Ag(fod)) (8.0 mg, 0.019 mmol). To this was added 750  $\mu$ L of CDCl<sub>3</sub> and decyl allene (5.8 mg, 0.0321 mmol). <sup>1</sup>H NMR of the reference unlabeled decyl allene is below. The signals at  $\delta$  5.0 and 5.5 ppm correspond to the two terminal protons on the allene. A small amount of protonation was observed in the labeled decyl allene ( $\delta$  5.2 ppm).

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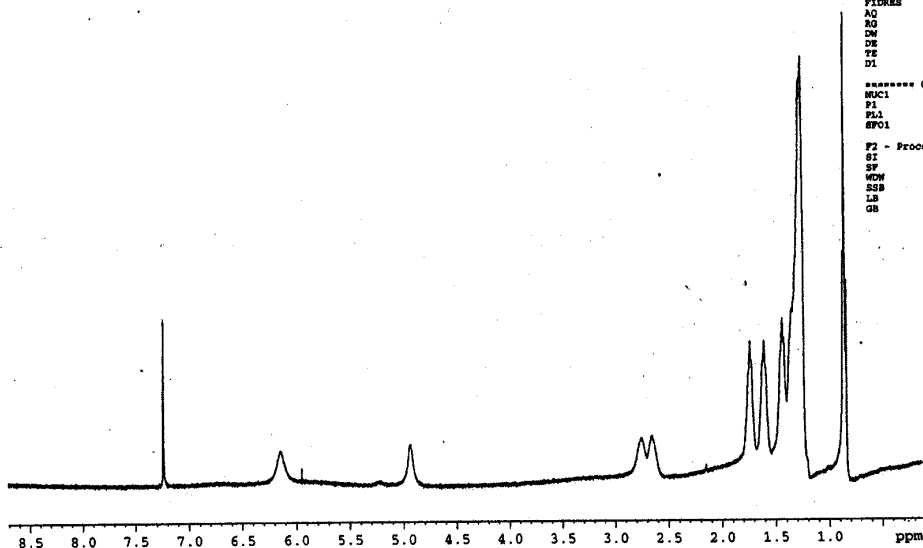
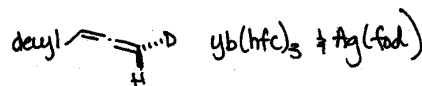
<sup>9</sup> Chirality of Allene. Reference: Offermann, W.; Mannschreck, A. *Organic Magnetic Resonance*. **1984**, 22, 355-363. Mannschreck, A.; Munninger, W.; Burgemeister, T.; Gore, J.; Cazes, B. *Tetrahedron*, **1986**, 42, 399-408.

heb2-129-ag/yb



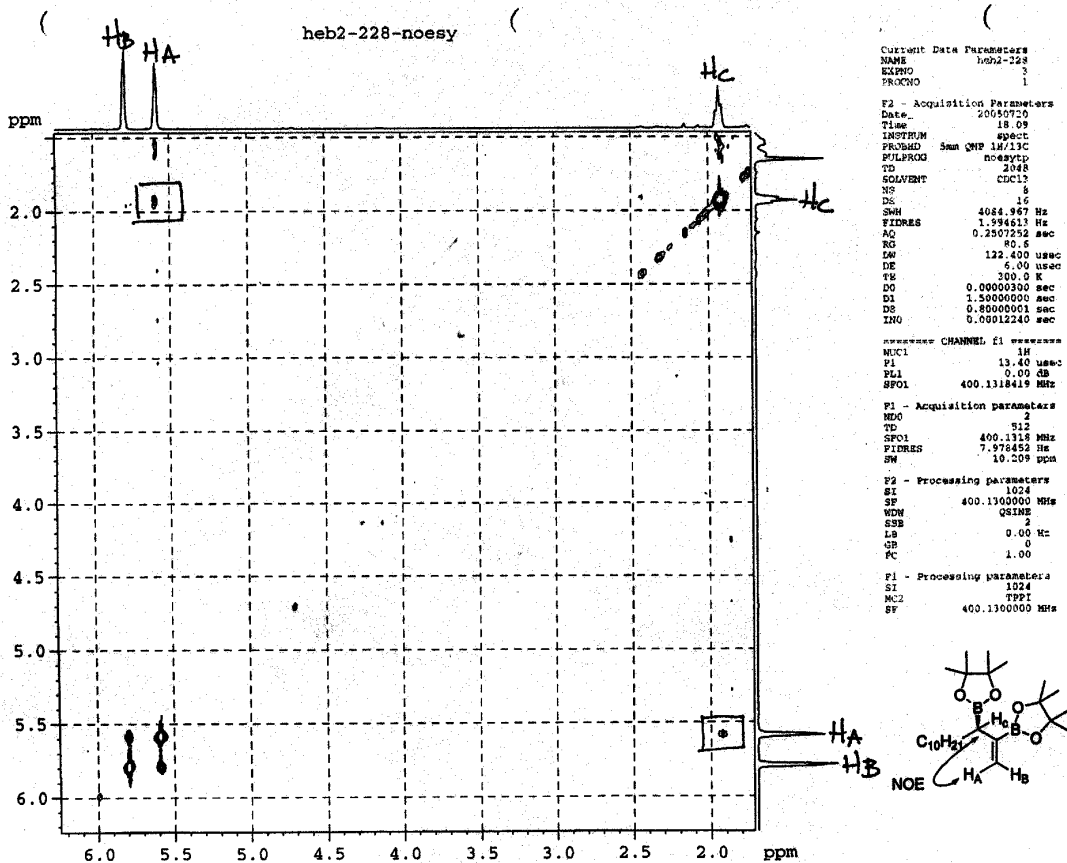
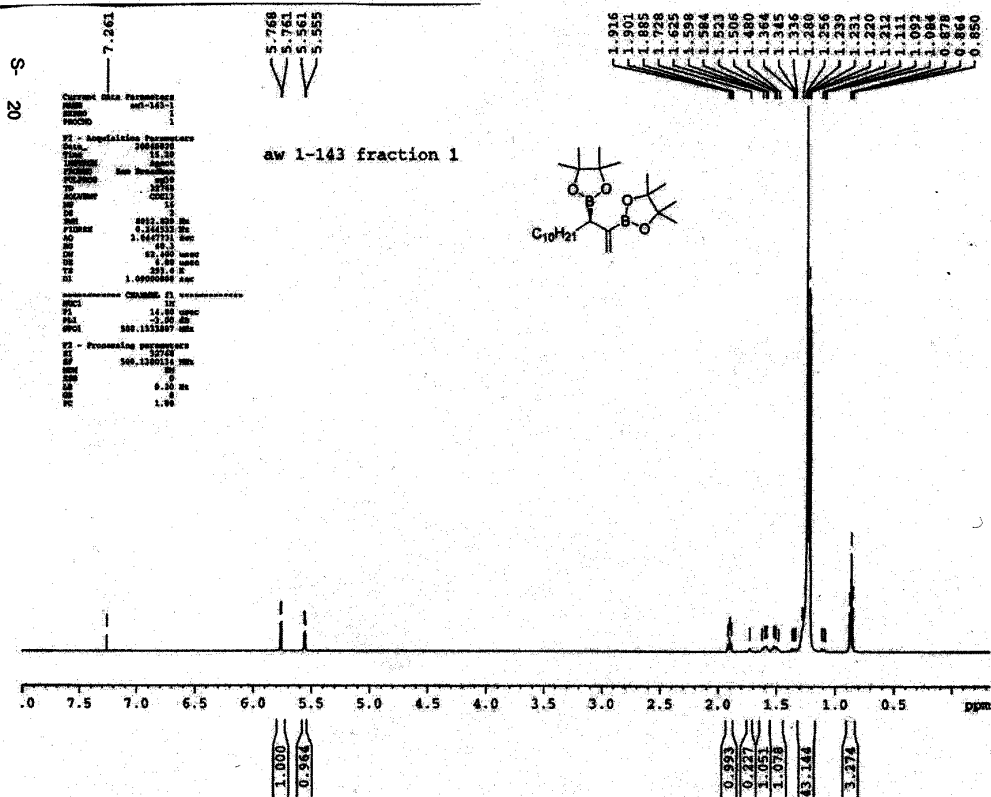
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EXPNO 1  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20050123  
Time 17.25  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 32768  
SOLVENT CDCl3  
NS 15  
DS 2  
SWH 6410.354 Hz  
FIDRES 0.195425 Hz  
AQ 0.195425 sec  
RG 203.2  
IN 78.000 usec  
DE 6.00 usec  
TE 300.2 K  
D1 1.00000000 sec  
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
NUC1 1H  
P1 24.20 usec  
PL1 0.00 dB  
SFO1 400.1524003 MHz  
F2 - Processing parameters  
SI 32768  
SF 400.0500300 MHz  
WDW no  
SSB 0  
LB 0.00 Hz  
GB 0

heb3-52-



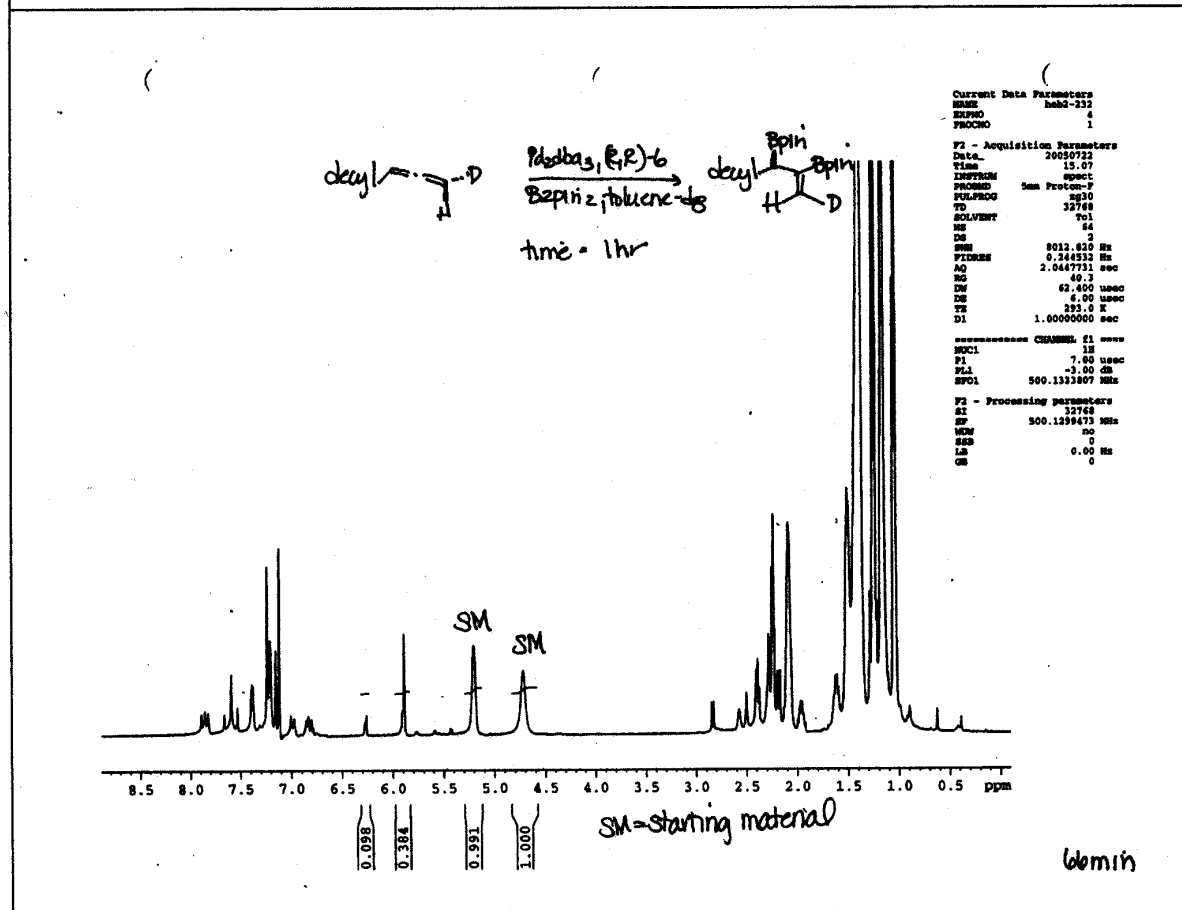
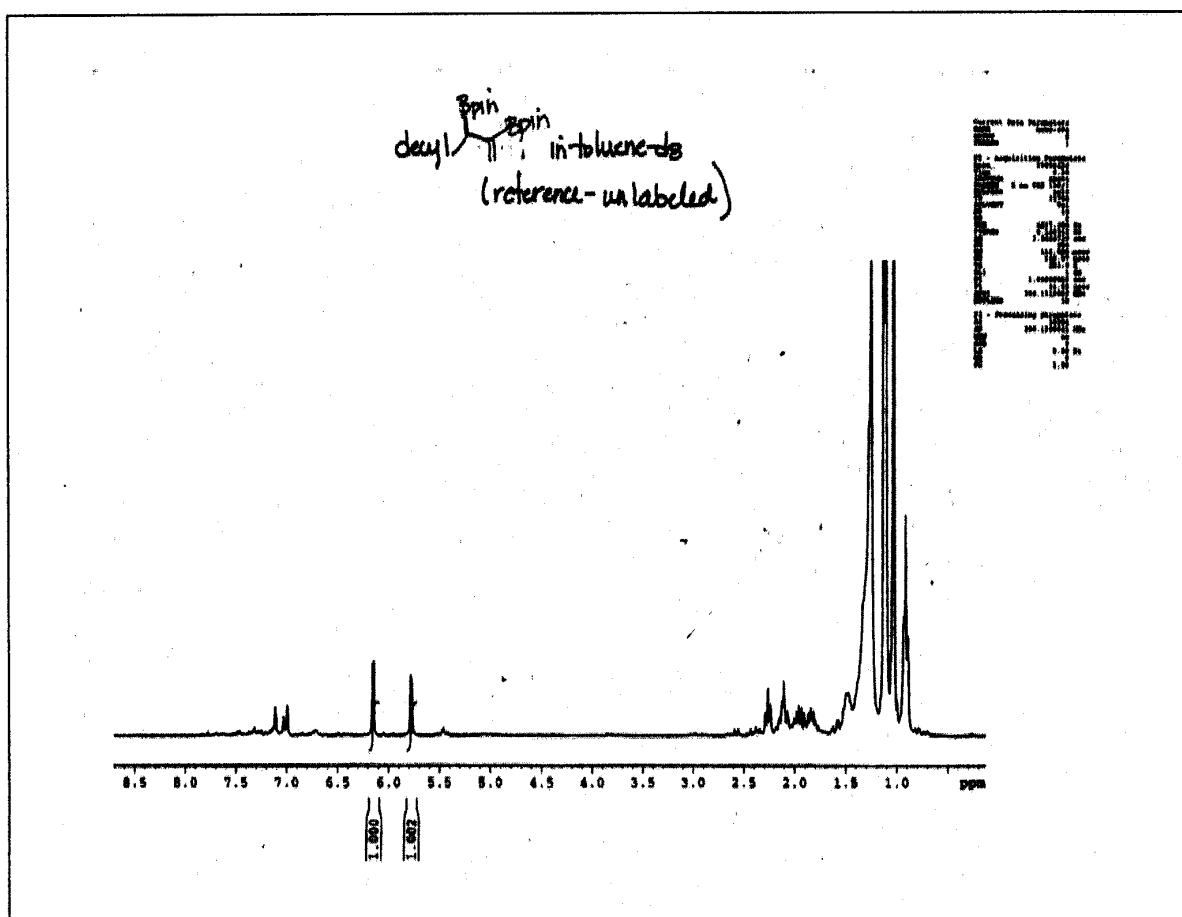
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EXPNO 1  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20051002  
Time 12.48  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 32768  
SOLVENT CDCl3  
NS 15  
DS 2  
SWH 6410.354 Hz  
FIDRES 0.195425 Hz  
AQ 0.195425 sec  
RG 203.2  
IN 78.000 usec  
DE 6.00 usec  
TE 300.2 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 400.0500300 MHz  
WDW no  
SSB 0  
LB 0.00 Hz  
GB 0

#### H. NOESY - reference and NOESY in CDCl<sub>3</sub>

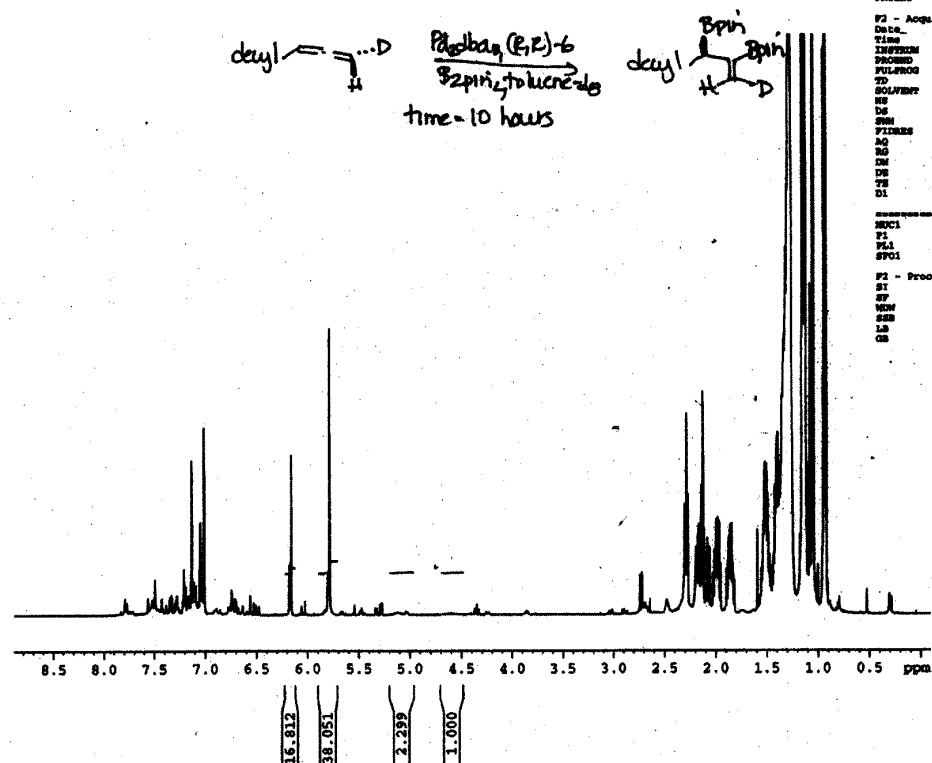


## I. Diboration of (*R*)-9-*d*<sub>1</sub>

**Diboration with(*R*)-9-*d*<sub>1</sub>** In the dry box, a 1 dram vial equipped with a stir bar was loaded with Pd<sub>2</sub>dba<sub>3</sub> (4.0 mg, 0.0043 mmol) and (*R,R*)-**6** (6.6 mg, 0.010 mmol). To this was added 300 μL of toluene-*d*<sub>8</sub>. The metal/ligand mixture stirred for 1 hour at which time B<sub>2</sub>(pin)<sub>2</sub> (46.3 mg, 0.1824 mmol) was added followed by the labeled allene (27.5 mg, 0.152 mmol). The reaction mixture was transferred to an oven-dried J-Young tube and diluted with the remaining 700 μL of toluene-*d*<sub>8</sub>. The reaction progress was monitored by <sup>1</sup>H NMR every 17 minutes. After completion of the reaction, solvent was removed *in vacuo* and the crude material was purified on silica gel (2% ethyl acetate/hexanes) to afford 45.5 mg (68% yield) of the labeled product.





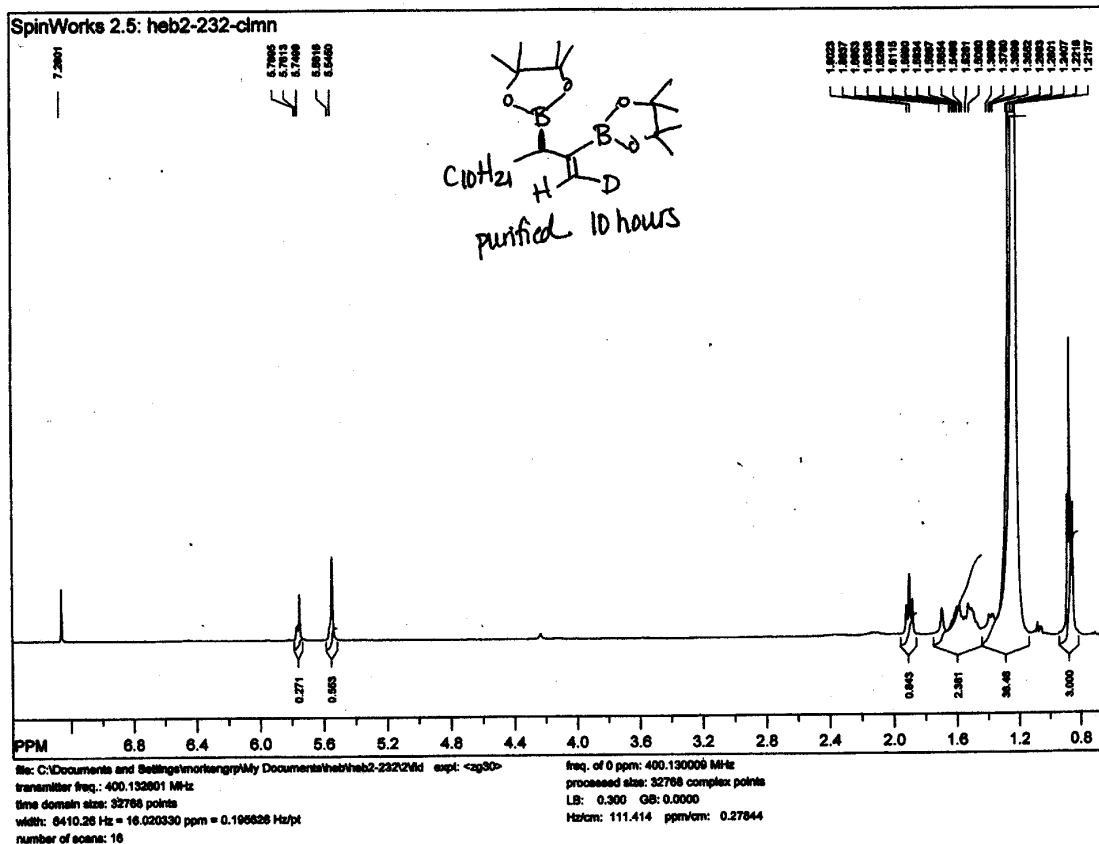


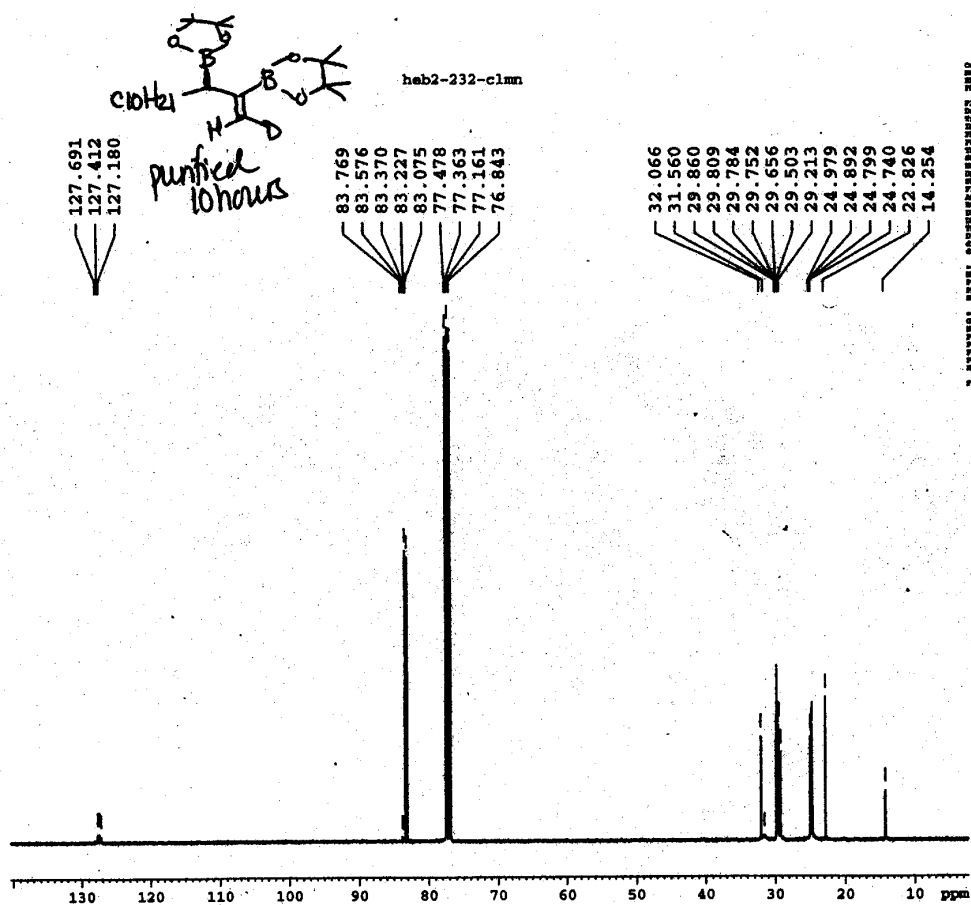
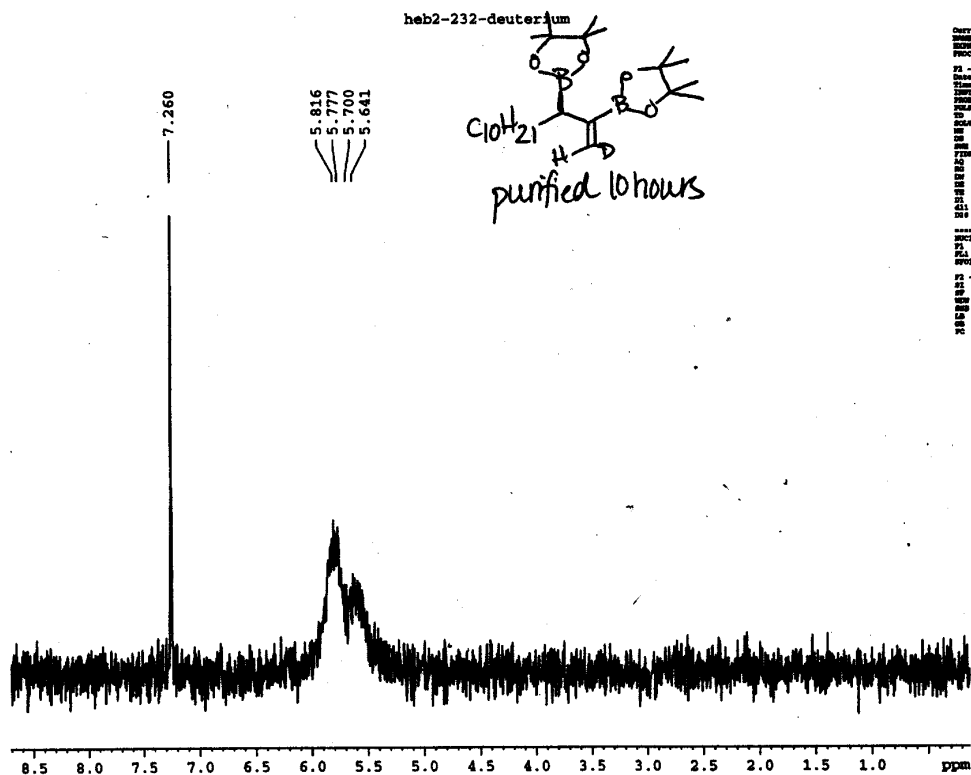
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 EXPNO 16  
 PROCNO 1

F2 - Acquisition Parameters  
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 Time 0.17  
 INSTRUM spect  
 PROCNO 16  
 PULPROG sm  
 TD 32768  
 SOLVENT Tol  
 NS 64  
 DS 2  
 SWH 8013.840 Hz  
 FIDRES 0.244532 Hz  
 AQ 2.0447731 sec  
 RG 40.0  
 CW 62.400 usec  
 DE 4.00 usec  
 TE 293.0 K  
 D1 1.00000000 sec

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.50 usec  
 PL1 -3.00 dB  
 SFO1 500.1333807 MHz

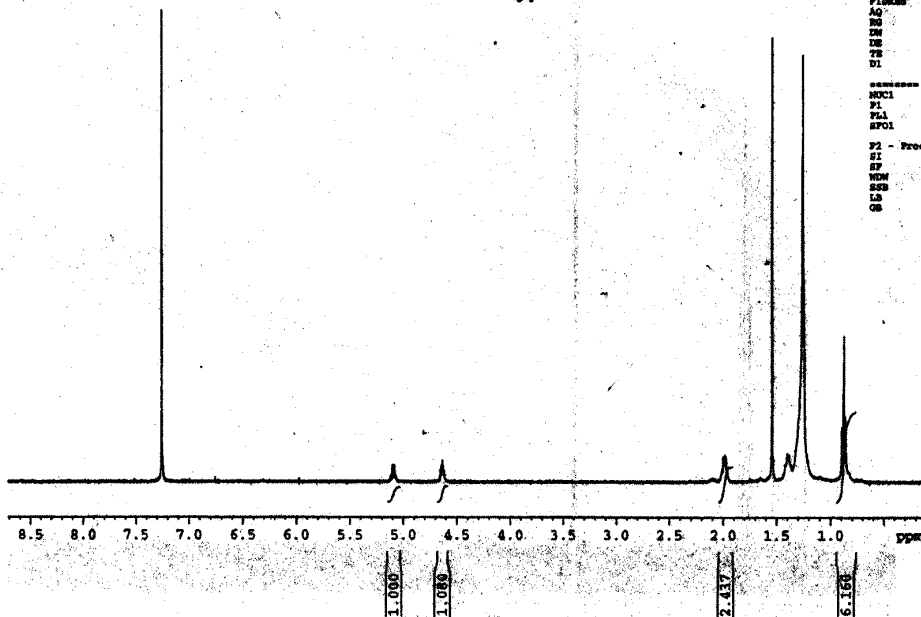
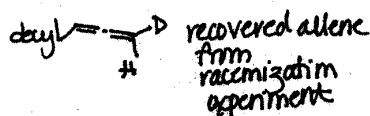
F2 - Processing parameters  
 SI 32768  
 SF 500.1330000 MHz  
 WDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0





**J. Racemization experiment with labeled allene.** In the dry box, a 2 dram vial equipped with a stir bar was charged Pd<sub>2</sub>dba<sub>3</sub> (3.5 mg, 0.0038 mmol) and **(*R,R*)-6** (6 mg, 0.0091 mmol). To this was added 1 mL of toluene and the metal/ligand mixture complexed for 1 hour at which time the labeled allene (27.5 mg, 0.152 mmol) was added. The vial was sealed with a polypropylene cap and removed from the glove box. After a reaction time of 1 hour, solvent was removed in vacuo and the crude reaction mixture was purified on silica gel (pentanes) to afford 7.4 mg (27%) of the recovered allene. Analysis by Yb(hfc)<sub>3</sub> and Ag(fod) indicates that the allene has racemized under the reaction conditions in the absence of B<sub>2</sub>(pin)<sub>2</sub>.

heb2-251-recovered allene



Current Data Parameters

NAME	heb2-251
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20020829
Time	17.16
INSTRUM	spect
PROBHD	5 mm BB 13C/1H
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5995.204 Hz
FIDRES	0.182259 Hz
AQ	2.7329011 sec
RG	161.3
DM	43.400 usec
DE	8.00 usec
TE	300.0 K
D1	1.00000000 sec

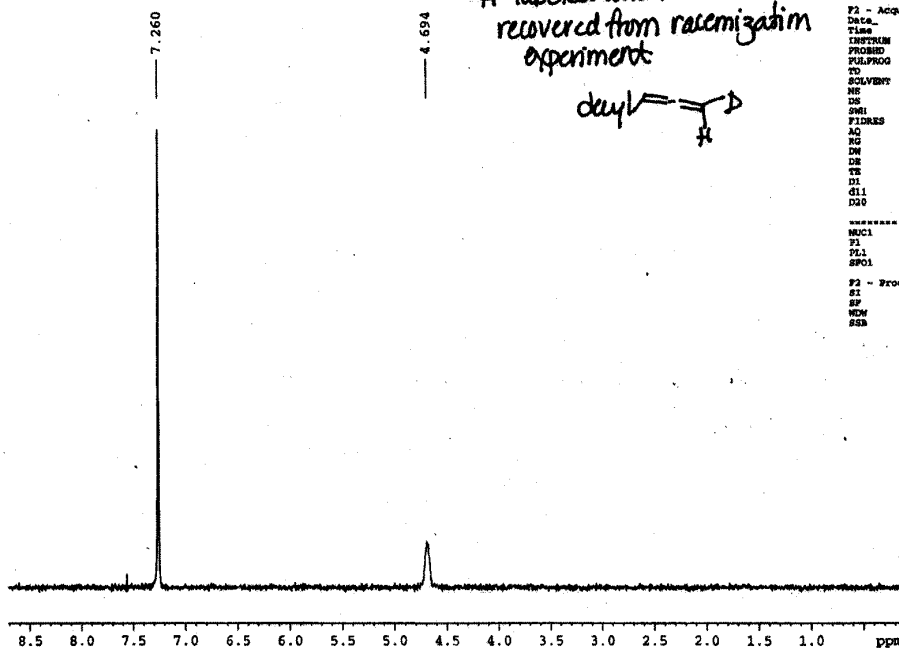
===== CHANNEL f1 =====

MUCL	1H
PL	9.30 usec
PL1	-0.00 dB
RFQ1	399.8023988 MHz

F2 - Processing parameters

SI	32768
SP	399.8000092 MHz
WDW	no
SF	0
LB	0.00 Hz
GB	0

CC=C=C 2H labeled allene  
 recovered from racemization  
 experiment



Current Data Parameters

NAME	heb2-253
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050804
Time	13.28
INSTRUM	spect
PROBHD	5 mm QNP 1H/13C
PULPROG	zgpg30
TD	4096
SOLVENT	CDCl3
NS	72
DS	2
SWH	913.742 Hz
FIDRES	0.213082 Hz
AQ	2.2418291 sec
RG	574.7
DM	547.200 usec
DE	4.00 usec
TE	283.0 K
D1	1.00000000 sec
d11	0.03000000 sec
D10	0.20000000 sec

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

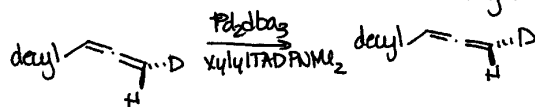
MUCL	2H
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RFQ1	61.4227851 MHz

F2 - Processing parameters

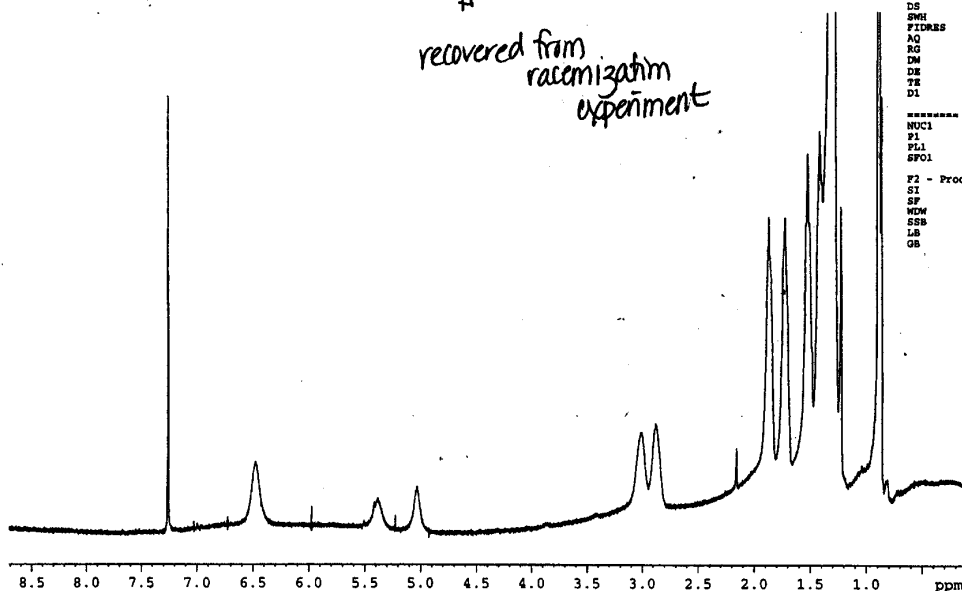
SI	16384
SP	61.4223710 MHz
WDW	no
SF	0

heb3-55-allene after clmn

4b(hfc)<sub>3</sub> 7 tg(fed)



recovered from  
racemization  
experiment



Current Data Parameters  
NAME heb3-55  
EXPNO 2  
PROCNO 1

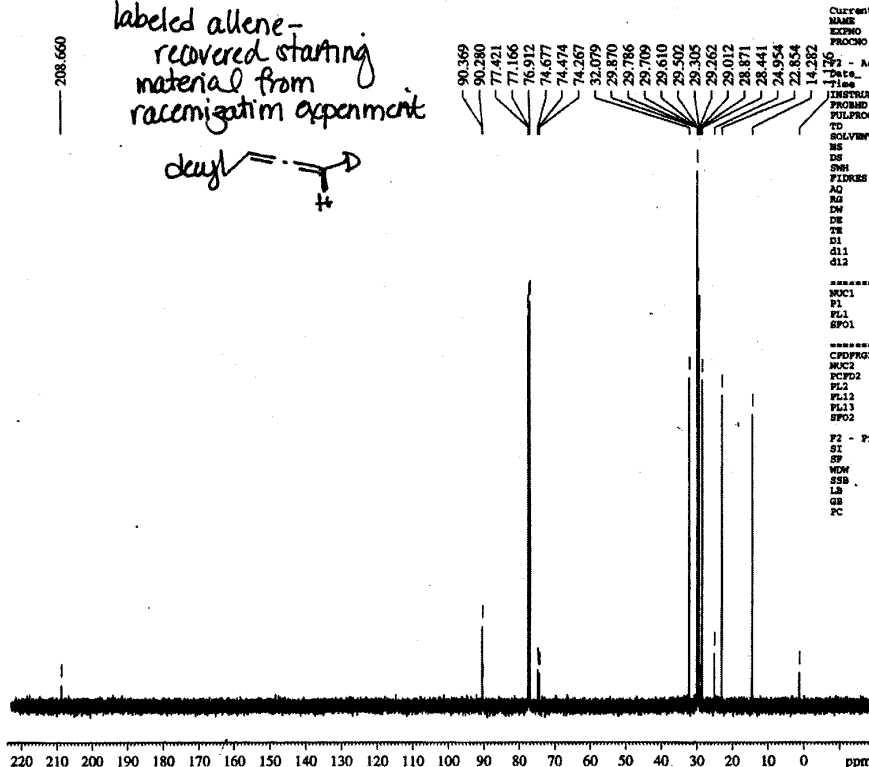
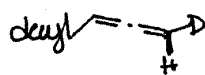
F2 - Acquisition Parameters  
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PROBHD 5 mm HR 13C/31  
PULPROG zg30  
TD 32768  
FIDRES 0.182959 Hz  
AQ 2.7329011 sec  
RG 71.8  
DM 83.400 usec  
DE 6.00 usec  
TE 300.0 K  
D1 1.00000000 sec

===== CHANNEL f1 =====  
NUC1 1H  
P1 9.30 usec  
PL1 -3.00 dB  
SFO1 399.8023988 MHz

F2 - Processing parameters  
SI 32768  
SF 399.8000093 MHz  
WDW no  
SSB 0  
LB 0.00 Hz  
GB 0

208.660

labeled allene-  
recovered starting  
material from  
racemization experiment



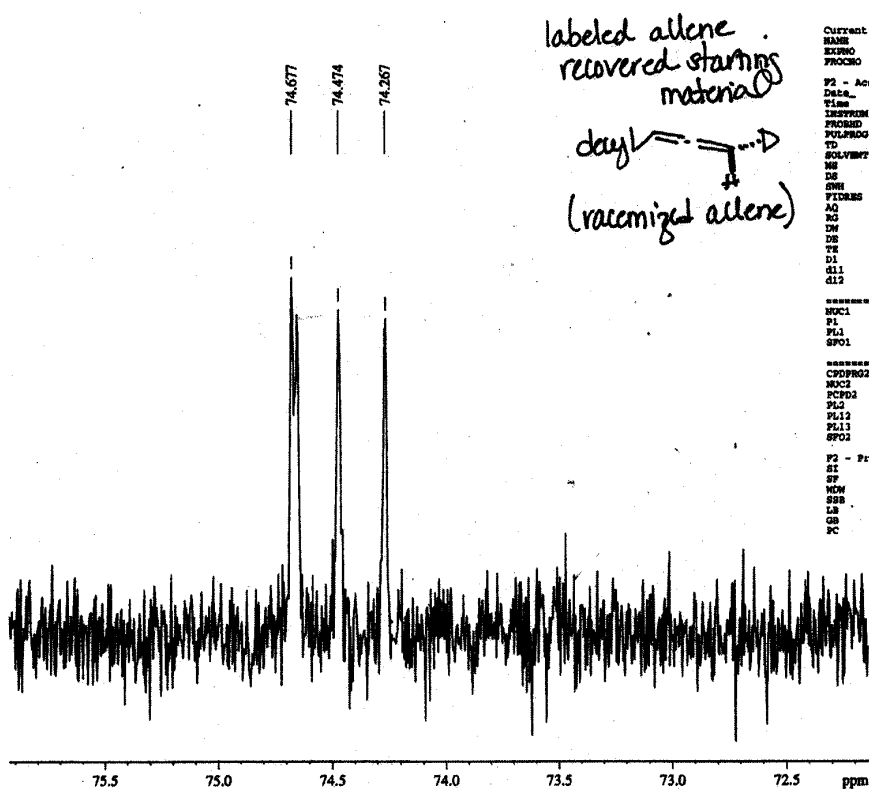
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NAME heb3-291  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20050831  
Time 18.39  
INSTRUM spect  
PROBHD 3mm Micro Du  
PULPROG zgpg30  
TD 65536  
FIDRES 0.466630 Hz  
AQ 1.0713636 sec  
RG 4096  
DM 16.350 usec  
DE 6.00 usec  
TE 303.0 K  
D1 1.00000000 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.50 usec  
PL1 -3.00 dB  
SFO1 125.7705006 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 103.00 usec  
PL2 -3.00 dB  
PL12 20.00 dB  
PL13 20.00 dB  
SFO2 500.1320005 MHz

F2 - Processing parameters  
SI 65536  
SF 125.7577715 MHz  
WDW no  
SSB 0  
LB 0.00 Hz  
GB 0  
PC 1.40



Current Data Parameters  
NAME heb2-251  
EXNO 1  
PROCNO 1

F2 - Acquisition Parameters  
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PL1 -3.00 dB  
SFO1 125.7705006 MHz

===== CHANNEL f2 =====  
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PCPD2 103.00 usec  
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F2 - Processing parameters  
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## K. Kinetics Studies for Allene Diboration

**A. Preparation of capillary tubes containing 1,3-dimethoxybenzene.** A stock solution of 1,3-dimethoxybenzene (100  $\mu\text{L}$ , 0.7635 mmol) in toluene- $d_8$  (5 mL) was prepared. A 6-inch 22 gauge needle attached to a 100  $\mu\text{L}$  gas-tight syringe was used to transfer 70  $\mu\text{L}$  of the stock solution to a capillary tube. Each capillary was flame-sealed and its accuracy checked by  $^1\text{H}$  NMR against a stock solution of tridec-1,2-diene.

### B. Initial Rate Studies with varied $[\text{B}_2(\text{pin})_2]$ :

**Preparation of stock solutions:** All operations were performed in the dry box, all glassware was oven-dried overnight prior to use, and gas-tight microliter syringes were used for all operations. Stock solutions were prepared immediately before use.

**Tridec-1,2-diene solution:** To a 6 dram vial was added 405.3 mg (2.247 mmol) of tridec-1,2-diene and this was diluted with toluene- $d_8$  (1.5 mL).

**Catalyst solution:** To a 6 dram vial was added  $\text{Pd}_2\text{dba}_3$  (11.8 mg, 0.0128 mmol), (*R,R*)-xylylTADDOLPNMe $_2$  (18.8 mg, 0.0288 mmol), and toluene- $d_8$  (4 mL). This mixture was allowed to incubate for 1 hour prior to use.

**$\text{B}_2(\text{pin})_2$  solution:** To a 6 dram vial was added bis(pinacolato)diboron (457.7 mg, 1.802 mmol) and toluene- $d_8$  (3 mL).

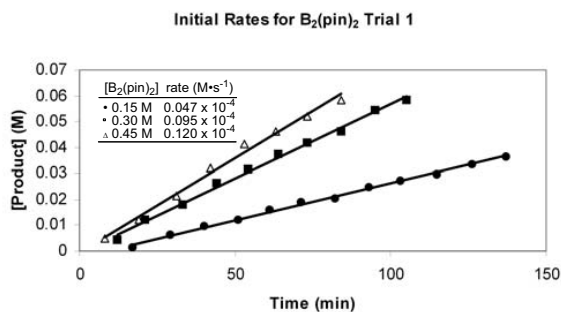
### Kinetic Runs:

**$[\text{B}_2(\text{pin})_2] = 0.45 \text{ M}$ :** To a J-Young tube was added 200  $\mu\text{L}$  of the catalyst solution. To this was added 100  $\mu\text{L}$  of toluene- $d_8$  and 1.5 mL of  $\text{B}_2(\text{pin})_2$  solution. The J-Young tube was sealed with a Teflon cap and inverted several times. The Teflon cap was removed, the flame-sealed capillary inserted, and 200  $\mu\text{L}$  of tridec-1,2-diene solution was added. The J-Young tube was sealed with the Teflon cap and inverted several more times.

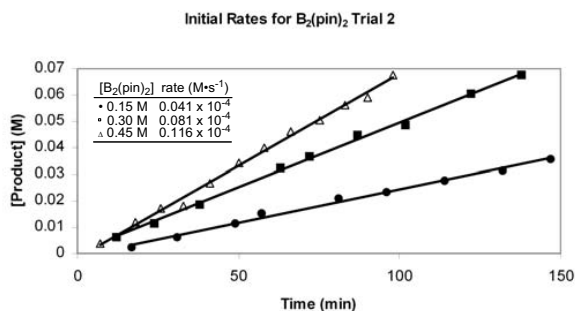
**$[\text{B}_2(\text{pin})_2] = 0.30 \text{ M}$ :** This experiment was conducted as above except that 1 mL of  $\text{B}_2(\text{pin})_2$  solution and 600  $\mu\text{L}$  of toluene were employed.

**$[\text{B}_2(\text{pin})_2] = 0.15 \text{ M}$ :** This experiment was conducted as above except that 0.5 mL of  $\text{B}_2(\text{pin})_2$  solution and 1.1 mL of toluene were employed.

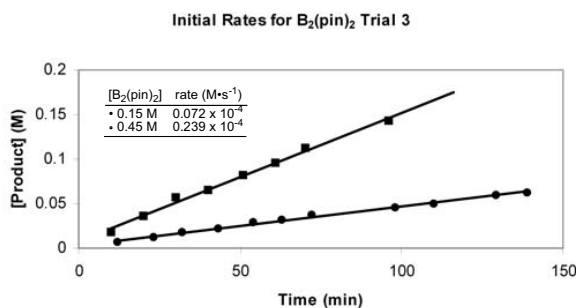
**Results.** Single-pulse  $^1\text{H}$  NMR was utilized to measure the formation of product (in comparison to the internal standard) versus time.



**Figure S1.** Initial Rates for  $\text{B}_2(\text{pin})_2$  Trial 1: 0.2 mol %  $\text{Pd}_2\text{dba}_3$  and 0.48 mol % (*R,R*)-6



**Figure S2.** Initial Rates for  $B_2(\text{pin})_2$  Trial 2: Catalyst loading: 0.2 mol %  $\text{Pd}_2\text{dba}_3$  and 0.48 mol %  $(R,R)\text{-6}$



**Figure S3.** Initial Rates for  $B_2(\text{pin})_2$  Trial 3: Catalyst loading: 0.5 mol %  $\text{Pd}_2\text{dba}_3$  and 1.2 mol %  $(R,R)\text{-6}$

### C. Initial Rate Studies with varied [Allene]:

**Preparation of stock solutions:** All operations were performed in the dry box, all glassware was oven-dried overnight prior to use, and gas-tight microliter syringes were used for all operations. Stock solutions were prepared immediately before each kinetic run.

**Tridec-1,2-diene solution:** To a 6 dram vial was added 324.4 mg (1.799 mmol) of tridec-1,2-diene and this was diluted with toluene- $d_8$  (3 mL).

**Catalyst solution:** To a 6 dram vial was added  $\text{Pd}_2\text{dba}_3$  (12.0 mg, 0.0131 mmol),  $(R,R)$ -xylylTADDOLP $\text{NMe}_2$  (19.8 mg, 0.0303 mmol), and toluene- $d_8$  (4 mL). The metal and ligand were incubated for 1 hour in the dry box prior to use.

**$B_2(\text{pin})_2$  solution:** To a 6 dram vial was added bis(pinacolato)diboron (571.0 mg, 2.248 mmol) and toluene- $d_8$  (1.5 mL).

#### Kinetic Runs:

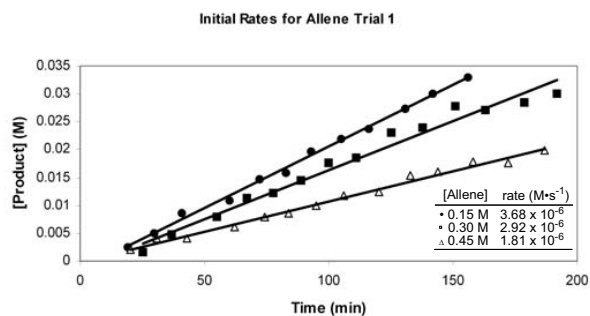
**[tridec-1,2-diene] = 0.45 M:** To a J-Young tube was added 200  $\mu\text{L}$  of the catalyst solution. To this was added 100  $\mu\text{L}$  of toluene- $d_8$  and 200  $\mu\text{L}$  of  $B_2(\text{pin})_2$  solution. The J-Young tube was sealed with a Teflon cap and inverted several times. The Teflon cap was removed, the flame-sealed capillary inserted, and 1.5 mL of tridec-1,2-diene solution was added. The J-Young tube was sealed with the Teflon cap and the NMR tube inverted several more times.

**[tridec-1,2-diene] = 0.30 M:** This was carried out as above except that 1 mL of the tridec-1,2-diene solution and 600  $\mu\text{L}$  of toluene were used.

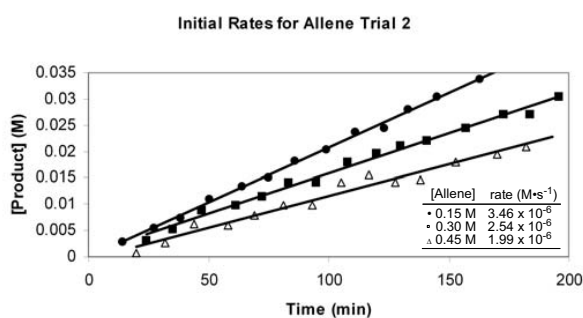
**[tridec-1,2-diene] = 0.15 M:** This was carried out as above except that 0.5 mL of the tridec-1,2-diene solution and 1.1 mL of toluene were used.



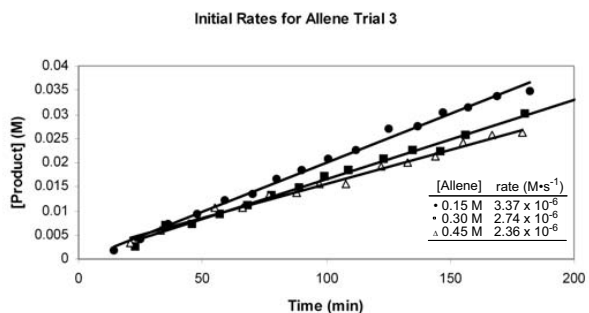
**Results.** Single-pulse  $^1\text{H}$  NMR was utilized to measure the formation of product (in comparison to the internal standard) versus time.



**Figure S4.** Initial Rates for Allene – Trial 1: Catalyst loading: 0.2 mol %  $\text{Pd}_2\text{dba}_3$  and 0.48 mol %  $(R,R)\text{-6}$



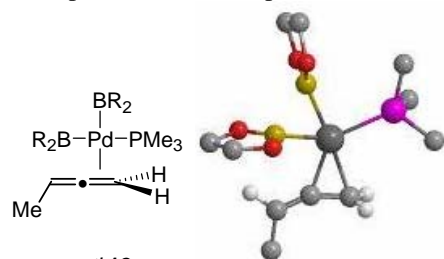
**Figure S5.** Initial Rates for Allene – Trial 2: Catalyst loading: 0.2 mol %  $\text{Pd}_2\text{dba}_3$  and 0.48 mol %  $(R,R)\text{-6}$



**Figure S6.** Initial Rates for Allene – Trial 3: Catalyst loading: 0.2 mol %  $\text{Pd}_2\text{dba}_3$  and 0.48 mol %  $(R,R)\text{-6}$

## L. DFT Calculations.

**Computational Methods:** DFT calculations were performed using B3LYP<sup>10,11</sup> with the basis set of Stuttgart RSC 1997 ECP<sup>12</sup> for Pd, 6-311+G\*<sup>13</sup> for others. All calculations were conducted using Gaussian 03 C02 package<sup>14</sup> with tight SCF convergence and ultra fine integration grids on the 128-CPU SGI Altix 3700 SMP machine<sup>15</sup> at University of North Carolina at Chapel Hill. In search for the transition state structure, a single-point frequency calculation has been performed to ensure that the final structure obtained (i) has only one imaginary frequency and (ii) the vibration mode of the negative frequency corresponds to the anticipated bond formation.



*anti-12*

Total energy = -1253.29080684 a.u.

C	-2.62500	-2.13300	-0.75800	C	3.08300	-2.08800	1.46700
C	-1.39800	-2.12000	-0.27200	H	4.17500	-2.15900	1.47500
C	-0.26300	-2.77100	0.13800	H	2.74100	-1.81000	2.46600
H	0.35800	-3.29600	-0.58500	H	2.66600	-3.06800	1.23000
H	-0.13700	-3.07400	1.17500	C	1.10700	3.64500	-0.07200
B	0.32200	1.49100	-0.27600	H	0.57800	4.54700	0.24100
O	0.56500	2.51400	0.63100	H	2.16400	3.75200	0.19600
O	0.61700	1.89800	-1.57100	C	0.90600	3.30500	-1.56000
Pd	0.09800	-0.58100	0.04500	H	0.05700	3.83900	-1.99900
P	2.49100	-0.84000	0.23800	H	1.79100	3.49700	-2.17100
B	-1.55000	0.70400	0.31000	C	-3.24500	1.56400	1.59800
O	-1.99100	0.86600	1.60900	H	-3.96800	1.01000	2.20200
O	-2.47200	1.19200	-0.60400	H	-3.10000	2.55200	2.04600
C	3.52000	0.62400	0.69900	C	-3.63900	1.64000	0.10800
H	4.57200	0.35300	0.82300	H	-4.47600	0.98000	-0.13900
H	3.44100	1.38300	-0.08100	H	-3.88700	2.65200	-0.22100
H	3.14600	1.05800	1.62800	C	-3.43000	-3.39200	-0.96500
C	3.32100	-1.39900	-1.31400	H	-3.71800	-3.50200	-2.01700
H	3.12200	-0.67800	-2.11000	H	-2.87100	-4.28200	-0.66900
H	4.40200	-1.49900	-1.18300	H	-4.36000	-3.36600	-0.38600
H	2.91100	-2.36100	-1.62700	H	-3.10000	-1.20000	-1.04600

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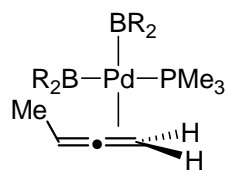
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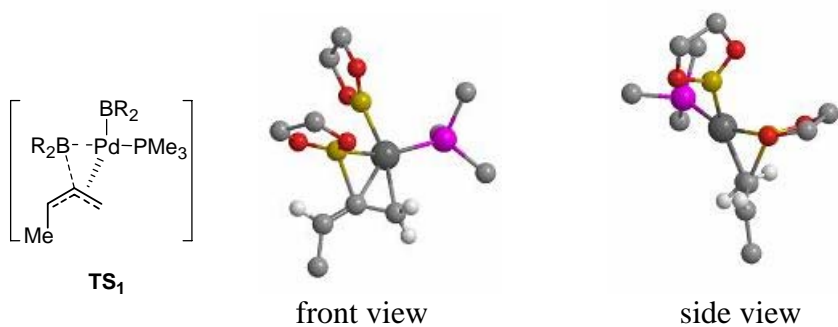
(15) <http://its.unc.edu/hpc/hardware/#Cedar/Cypress/outline>



***syn-12***

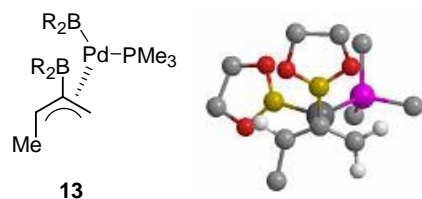
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H	-1.33600	-2.89200	-1.35400
H	0.33200	-2.46600	-2.03400
B	0.23600	1.53300	0.13100
O	0.58100	2.53400	-0.76700
O	0.03900	2.06100	1.40400
Pd	-0.22300	-0.43000	-0.30200
P	-2.63100	-0.06000	-0.18700
B	1.83700	-0.13800	-0.35900
O	2.49300	-0.31400	-1.56800
O	2.74200	0.04600	0.67600
C	0.98000	-2.41700	2.45100
H	2.03000	-2.52500	2.74300
H	0.77300	-1.35600	2.32300
H	0.37700	-2.80000	3.28200
H	0.90400	-4.26600	1.23000
C	-3.27100	1.36700	-1.17100
H	-4.34100	1.52600	-1.01300
H	-2.73000	2.27300	-0.89400
H	-3.09100	1.19000	-2.23400
C	-3.19300	0.36200	1.52000
H	-2.59400	1.19200	1.89900
H	-4.25300	0.62900	1.55000
H	-3.02400	-0.49300	2.17900
C	-3.84300	-1.38100	-0.65700
H	-4.87700	-1.05900	-0.50000
H	-3.71800	-1.64400	-1.71000
H	-3.66500	-2.28000	-0.06100
C	0.54600	3.80400	-0.09000
H	1.44600	4.36800	-0.34100
H	-0.32600	4.36700	-0.44000
C	0.45200	3.43900	1.40100
H	1.41700	3.51600	1.91100
H	-0.28100	4.03600	1.94800
C	3.90400	-0.11500	-1.36800
H	4.45300	-0.91900	-1.86200
H	4.19200	0.83800	-1.82300
C	4.07700	-0.11200	0.16200
H	4.48900	-1.05400	0.53800
H	4.69800	0.70900	0.52500



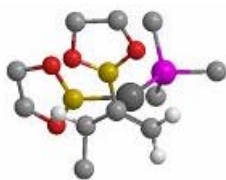
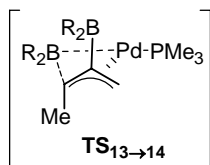
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C	-1.56100	-1.71200	-0.28000
C	-0.68100	-2.56400	0.41300
H	-0.25200	-3.41400	-0.11100
H	-0.74300	-2.65900	1.49400
B	0.48300	1.47400	-0.36400
O	0.32200	2.52800	0.52700
O	0.93200	1.94000	-1.59500
Pd	0.19800	-0.56800	0.02500
P	2.51100	-0.85700	0.27000
B	-1.76000	0.18900	0.35800
O	-2.13100	0.22500	1.69200
O	-2.53500	1.03900	-0.41700
C	3.31600	0.24000	1.51400
H	4.39400	0.06100	1.56700
H	3.13500	1.28400	1.25800
H	2.87700	0.06000	2.49700
C	3.47400	-0.52700	-1.26500
H	3.21900	0.46400	-1.64200
H	4.55100	-0.59400	-1.08700
H	3.19500	-1.25300	-2.03200
C	3.14000	-2.51900	0.77800
H	4.23200	-2.53600	0.84700
H	2.71900	-2.78800	1.74800
H	2.81700	-3.26900	0.05400
C	0.71300	3.75700	-0.11200
H	-0.06600	4.50600	0.04500
H	1.63900	4.11700	0.35000
C	0.89900	3.38000	-1.59300
H	0.06400	3.71200	-2.21600
H	1.82900	3.76100	-2.02200
C	-3.10100	1.27400	1.85100
H	-3.89600	0.92900	2.51500
H	-2.60800	2.14100	2.30000
C	-3.58300	1.55700	0.41800
H	-4.51700	1.03200	0.18400
H	-3.71500	2.62000	0.20800
C	-3.24900	-3.09000	-1.52200
H	-3.10000	-3.38200	-2.57000
H	-2.92100	-3.91300	-0.88600
H	-4.32900	-2.96000	-1.38900
H	-2.80000	-0.94000	-1.78700



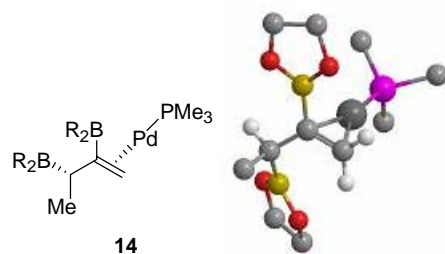
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C	-1.86300	-0.12900	1.22500
C	-1.57100	1.10000	1.82900
H	-1.06100	1.16800	2.78400
H	-2.11000	1.98800	1.51900
B	1.43700	-1.27400	-0.25300
O	1.76400	-1.37800	-1.60400
O	2.05500	-2.28000	0.47500
Pd	0.21500	0.18700	0.54600
P	1.56900	1.90000	-0.22400
B	-2.83800	-0.14800	0.00300
O	-3.41700	0.98000	-0.53500
O	-3.23700	-1.30100	-0.63000
C	1.55400	2.05600	-2.05900
H	2.25600	2.82100	-2.40400
H	1.81300	1.09100	-2.49500
H	0.54900	2.32000	-2.39300
C	3.37100	1.76000	0.15100
H	3.75800	0.83200	-0.27300
H	3.93400	2.60300	-0.25900
H	3.52200	1.72300	1.23200
C	1.21000	3.62800	0.32400
H	1.89700	4.34900	-0.13000
H	0.18600	3.89000	0.05200
H	1.29300	3.69500	1.41100
C	2.65400	-2.49400	-1.80100
H	2.23700	-3.15100	-2.56700
H	3.61800	-2.11700	-2.15700
C	2.75400	-3.16700	-0.41700
H	2.26600	-4.14600	-0.39100
H	3.78300	-3.28400	-0.07000
C	-4.34000	0.56600	-1.55600
H	-5.35900	0.74600	-1.19900
H	-4.17300	1.16400	-2.45300
C	-4.04100	-0.93500	-1.76200
H	-4.94000	-1.55400	-1.77700
H	-3.46700	-1.12700	-2.67300
C	-0.51700	-1.67500	2.84200
H	0.33900	-2.34400	2.73200
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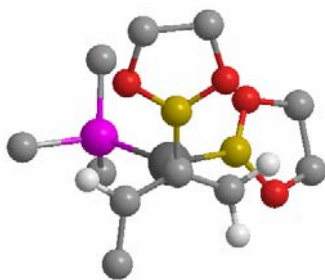
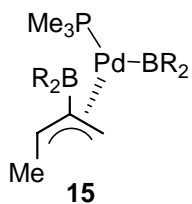
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H	0.13000	1.02500	3.18100
H	-1.46900	1.75800	3.31800
C	-1.00200	1.11300	1.30500
H	-1.59300	1.83400	0.73900
C	-1.68400	-0.21200	1.27500
C	-1.46300	-1.20500	2.19600
H	-1.96600	-2.16000	2.10300
H	-0.87000	-1.05500	3.09200
B	-2.69400	-0.49300	0.11700
O	-3.13800	-1.74600	-0.24000
O	-3.27500	0.50700	-0.62500
Pd	0.44700	-0.39300	0.49300
P	2.29900	-1.40200	-0.38700
B	0.46700	1.60300	-0.05600
O	0.04000	1.95000	-1.33700
O	1.30600	2.58300	0.46700
C	2.32300	-1.48200	-2.23200
H	2.22200	-0.47600	-2.64200
H	3.24700	-1.93400	-2.60600
H	1.47300	-2.07000	-2.58300
C	2.67600	-3.15800	0.06400
H	1.84100	-3.79900	-0.22700
H	3.58800	-3.51900	-0.42300
H	2.79600	-3.24000	1.14600
C	3.91400	-0.58400	-0.01800
H	4.08400	-0.58100	1.06100
H	4.75000	-1.09300	-0.50800
H	3.88000	0.45500	-0.34800
C	-4.07300	-0.10400	-1.65100
H	-5.04400	0.39200	-1.69400
H	-3.56600	0.03000	-2.61100
C	-4.16500	-1.58700	-1.23300
H	-5.13000	-1.83500	-0.78100
H	-3.97600	-2.27900	-2.05600
C	0.48400	3.28500	-1.62200
H	0.87700	3.32700	-2.64000
H	-0.37000	3.96700	-1.55000
C	1.54800	3.57000	-0.54700
H	1.46200	4.56700	-0.10700
H	2.56800	3.44600	-0.92900



Total energy = -1253.36071508 a.u.

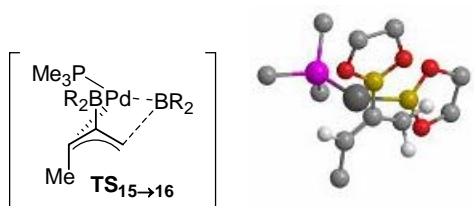
C	2.52600	2.87600	0.12900
H	2.51200	3.71900	0.82800
H	2.47600	3.27900	-0.88500
H	3.49100	2.37200	0.24400
C	1.35500	1.89500	0.40300
H	1.46000	1.54600	1.43500
C	1.48900	0.66600	-0.50900
C	0.96900	0.62600	-1.78900
H	1.30100	-0.13100	-2.49300
H	0.42700	1.46700	-2.21100
B	2.44500	-0.47300	-0.05300
O	2.98000	-1.43000	-0.89400
O	2.91000	-0.59900	1.24100
Pd	-0.38000	-0.56900	-0.48500
P	-2.18600	-1.86900	0.16100
B	-0.03000	2.63500	0.31200
O	-0.88700	2.76700	1.38200
O	-0.48600	3.30100	-0.80600
C	-1.97200	-2.82800	1.72800
H	-2.86600	-3.40900	1.97300
H	-1.12300	-3.50800	1.62900
H	-1.75600	-2.14400	2.55100
C	-2.72200	-3.19800	-1.00900
H	-1.88700	-3.87600	-1.19500
H	-3.56700	-3.77000	-0.61500
H	-3.00800	-2.75400	-1.96400
C	-3.79100	-1.00700	0.48900
H	-4.11600	-0.48000	-0.41000
H	-4.57600	-1.70700	0.79400
H	-3.65000	-0.26600	1.27800
C	3.86500	-1.66900	1.27500
H	3.64100	-2.32400	2.11900
H	4.86300	-1.24200	1.41800
C	3.71300	-2.36700	-0.09300
H	4.66900	-2.58100	-0.57600
H	3.13900	-3.29600	-0.02400
C	-1.98900	3.59900	0.98900
H	-2.92500	3.09300	1.23400
H	-1.93900	4.53500	1.55300
C	-1.80000	3.81100	-0.53000
H	-1.84300	4.86200	-0.82600
H	-2.52500	3.24900	-1.12500



Total energy = -1253.33702854 a.u.

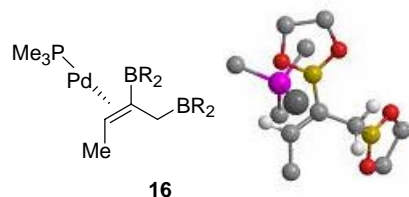
C	-1.11800	1.56400	2.94700
H	-0.71800	2.57700	2.84500
H	-0.31000	0.92100	3.30200
H	-1.87400	1.60500	3.74400
C	-1.74100	1.08700	1.66000
H	-2.38400	1.81000	1.16300
C	-1.84500	-0.23500	1.23000
C	-0.92100	-1.26200	1.64800
H	-1.07800	-2.26200	1.26400
H	-0.49000	-1.24300	2.64600
B	-2.80700	-0.54200	0.03900
O	-3.07900	-1.81500	-0.40300
O	-3.50600	0.42000	-0.65900
Pd	0.22900	0.14600	0.48600
P	1.31500	1.81000	-0.71200
B	1.69900	-1.24000	0.12500
O	2.11300	-1.62500	-1.15000
O	2.43200	-1.90100	1.09800
C	1.35600	1.47600	-2.52300
H	1.93000	2.23500	-3.06300
H	1.79600	0.49100	-2.68600
H	0.33600	1.45800	-2.91300
C	3.09700	2.09200	-0.32000
H	3.65400	1.16900	-0.48600
H	3.52600	2.88500	-0.94000
H	3.20500	2.36400	0.73100
C	0.64600	3.53300	-0.64300
H	0.66900	3.89600	0.38700
H	1.22200	4.21900	-1.27100
H	-0.39400	3.53400	-0.97400
C	3.43800	-2.71400	0.46600
H	4.42100	-2.26900	0.65300
H	3.41900	-3.71200	0.90800
C	3.06000	-2.70500	-1.02600
H	2.57500	-3.63500	-1.34000
H	3.90900	-2.51400	-1.68600
C	-3.92500	-1.71900	-1.55900
H	-3.33800	-1.98800	-2.44300
H	-4.75100	-2.42600	-1.45800
C	-4.38500	-0.24500	-1.58000
H	-5.41500	-0.12300	-1.23200
H	-4.29100	0.22000	-2.56400





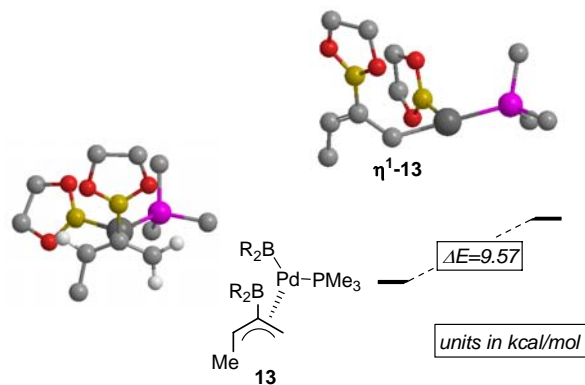
Total energy = -1253.32837014 a.u.

C	1.04900	-0.58500	3.44300
H	0.73200	-1.59100	3.73400
H	0.16000	0.04500	3.39100
H	1.67500	-0.20900	4.26500
C	1.82800	-0.61500	2.16000
H	2.57900	-1.39800	2.08500
C	1.77200	0.29000	1.13400
C	0.79300	1.41600	1.05900
H	1.16700	2.22400	0.43300
H	0.45900	1.79600	2.02100
B	2.79600	0.12500	-0.02700
O	3.03100	1.10200	-0.96700
O	3.59500	-0.98500	-0.21100
Pd	-0.35700	-0.29700	0.32900
P	-1.86700	-1.79600	-0.52800
B	-1.01600	1.62600	0.06800
O	-0.97900	2.25500	-1.17400
O	-1.92300	2.25700	0.91700
C	-1.99500	-1.79400	-2.37000
H	-2.76400	-2.48700	-2.72400
H	-2.23000	-0.78600	-2.71600
H	-1.03400	-2.07700	-2.80500
C	-3.62400	-1.52700	-0.02500
H	-3.93300	-0.52000	-0.30900
H	-4.29600	-2.25400	-0.49000
H	-3.71100	-1.60400	1.06100
C	-1.66400	-3.60300	-0.17200
H	-1.69300	-3.76800	0.90700
H	-2.44800	-4.20500	-0.64300
H	-0.69100	-3.94200	-0.53400
C	-2.61700	3.27000	0.17400
H	-3.63600	2.92500	-0.03500
H	-2.67600	4.18100	0.77500
C	-1.78500	3.44100	-1.11000
H	-1.12700	4.31600	-1.06500
H	-2.39500	3.51300	-2.01300
C	3.96500	0.58800	-1.92700
H	3.43300	0.39700	-2.86400
H	4.73900	1.33600	-2.11100
C	4.51000	-0.70400	-1.28100
H	5.51200	-0.57000	-0.86000
H	4.53000	-1.55300	-1.96800



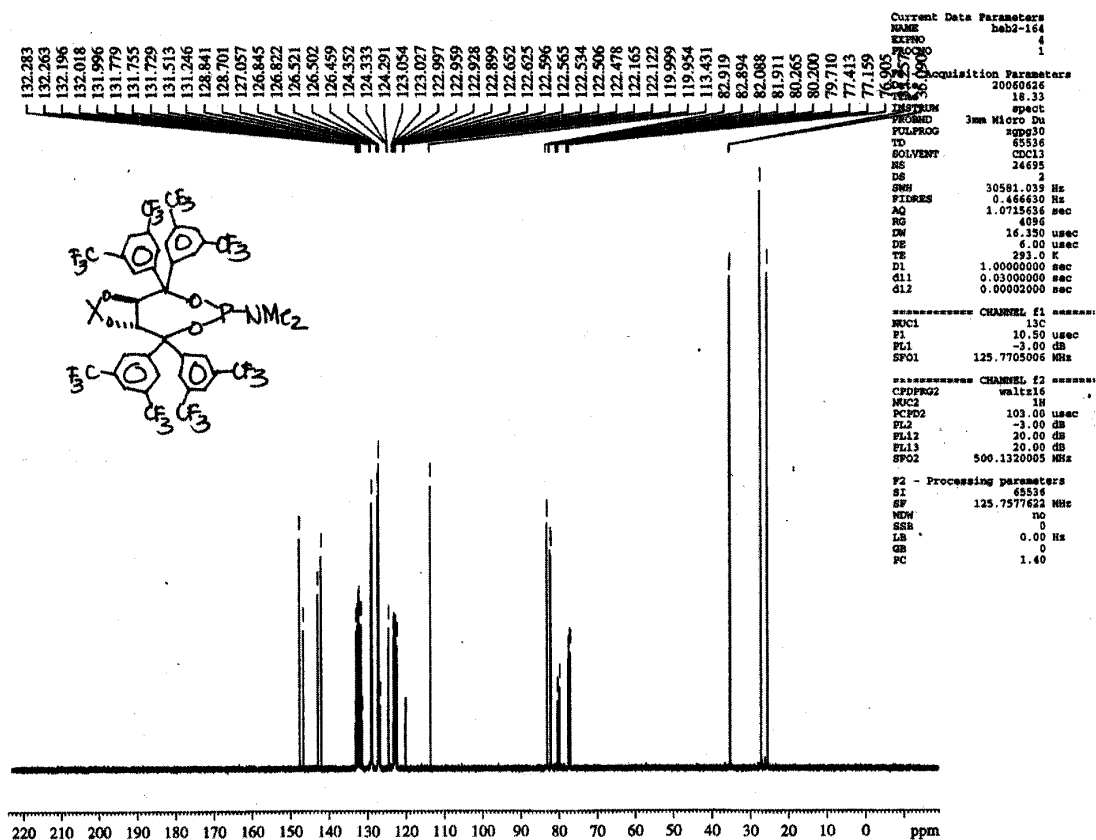
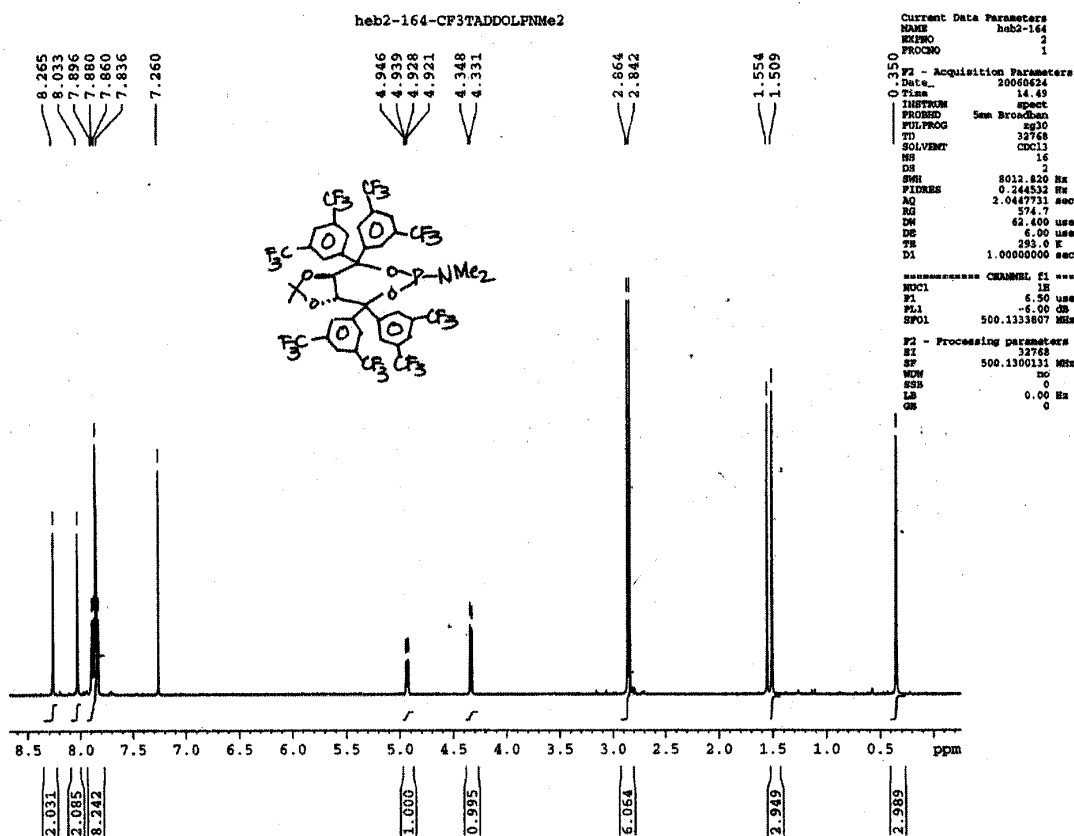
Total energy = -1253.36450257 a.u.

C	0.34200	1.50100	2.96700
H	-0.23000	0.86700	3.65100
H	-0.34600	2.20600	2.50100
H	1.04900	2.07400	3.58400
C	1.09400	0.66600	1.96700
H	1.60800	-0.19900	2.38400
C	1.46300	1.05400	0.68900
C	1.09800	2.42500	0.10100
H	1.75700	2.62100	-0.74900
H	1.30800	3.20100	0.84800
B	2.48700	0.17300	-0.07400
O	2.85700	0.40400	-1.38600
O	3.21300	-0.86200	0.49400
Pd	-0.15500	-0.50200	0.48800
P	-1.71000	-2.08600	-0.13900
B	-0.38600	2.58700	-0.39000
O	-0.78700	2.41000	-1.69400
O	-1.41500	3.01600	0.42200
C	-1.90100	-2.35900	-1.96000
H	-2.64700	-3.13100	-2.17900
H	-2.19900	-1.42800	-2.44400
H	-0.94300	-2.66000	-2.38700
C	-3.47200	-1.84100	0.37400
H	-3.84200	-0.89400	-0.02300
H	-4.11600	-2.65100	0.01900
H	-3.53300	-1.79100	1.46300
C	-1.41100	-3.81400	0.45100
H	-1.40300	-3.83300	1.54300
H	-2.17700	-4.50700	0.08800
H	-0.43200	-4.15300	0.10700
C	-2.63100	3.01000	-0.34000
H	-3.28600	2.22700	0.05200
H	-3.13000	3.97400	-0.22200
C	-2.18100	2.73500	-1.79500
H	-2.29000	3.60900	-2.44200
H	-2.71100	1.89600	-2.25200
C	3.93400	-0.48400	-1.71300
H	3.73500	-0.95200	-2.67900
H	4.85900	0.09700	-1.79000
C	3.97000	-1.49200	-0.54600
H	4.97900	-1.69700	-0.18300
H	3.49100	-2.44300	-0.80500

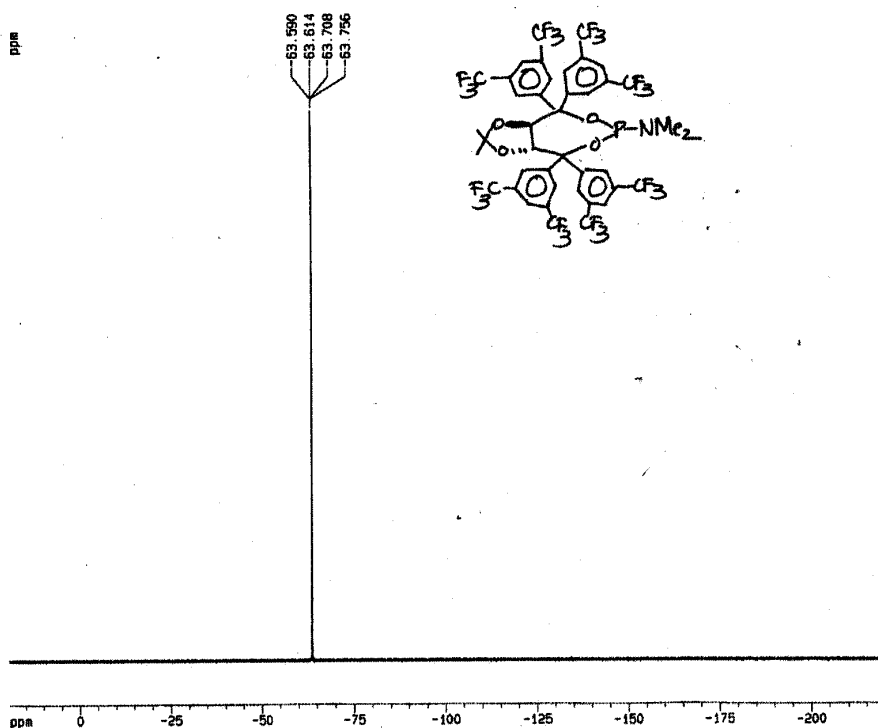


**$\eta^1\text{-13}$**  Total Energy = -1253.3207049 a.u.

C	2.62000	2.69200	-1.76800
H	3.30700	3.50200	-1.50700
H	1.60100	3.03000	-1.55500
H	2.68500	2.55300	-2.85400
C	2.95800	1.42700	-1.02400
H	3.88500	1.43300	-0.45600
C	2.21900	0.29300	-1.01300
C	0.92900	0.14300	-1.74800
H	0.89700	-0.83600	-2.25400
H	0.77400	0.92900	-2.49100
B	2.75500	-0.91200	-0.19900
O	2.25700	-2.19500	-0.31200
O	3.79800	-0.84000	0.70700
Pd	-0.94600	-0.18200	-0.85300
P	-3.06300	-0.61200	0.11000
B	-0.23400	1.11800	0.47400
O	0.26100	0.71900	1.70100
O	-0.24000	2.49100	0.33300
C	-2.98800	-1.37300	1.78800
H	-2.38000	-0.74700	2.44300
H	-3.98300	-1.49800	2.22500
H	-2.50200	-2.34800	1.72300
C	-4.21900	-1.75400	-0.77700
H	-3.74600	-2.72900	-0.91100
H	-5.15500	-1.89000	-0.22800
H	-4.44900	-1.35400	-1.76700
C	-4.13800	0.86200	0.39200
H	-4.35600	1.34500	-0.56200
H	-5.07900	0.59200	0.88000
H	-3.60900	1.58700	1.01400
C	4.10300	-2.16900	1.14900
H	5.05000	-2.48300	0.69900
H	4.21500	-2.17100	2.23500
C	2.91100	-3.02000	0.66100
H	3.21700	-3.95800	0.19300
H	2.20200	-3.24300	1.46500
C	0.81700	1.87900	2.35400
H	0.51200	1.88000	3.40300
H	1.90600	1.81600	2.29700
C	0.25600	3.07300	1.55600
H	1.01500	3.81700	1.31000
H	-0.57300	3.57100	2.06900



heb3-264-19F



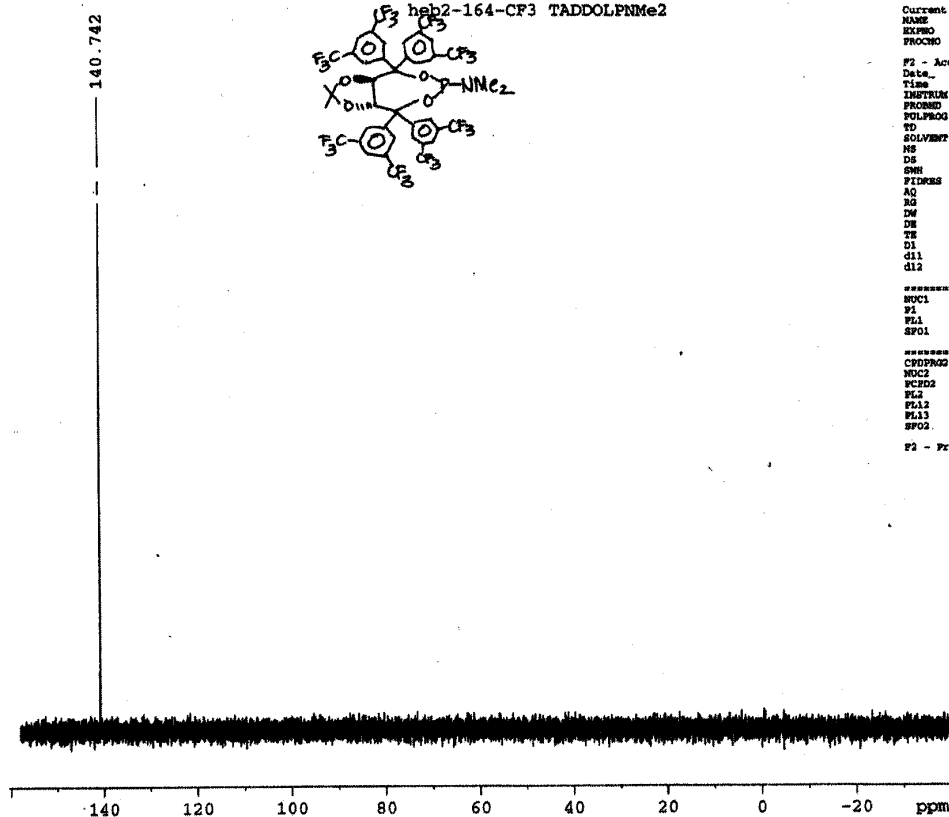
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NAME heb2-164  
EXPNO 22  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060625  
Time 11.55  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 131072  
SOLVENT CDCl3  
NS 16  
DS 4  
SWH 90090.084 Hz  
FIDRES 0.567333 Hz  
AQ 0.7270051 sec  
RG 2886.3  
DW 5.550 usec  
DE 6.00 usec  
TE 300.0 K  
D1 1.00000000 sec

===== CHANNEL f1 =====  
NUC1 19F  
P1 18.00 usec  
PL1 0.00 dB  
SFO1 376.3856157 MHz

F2 - Processing parameters  
SI 65536  
SF 376.4233185 MHz  
WDW no  
SSB 0  
LB 0.00 Hz  
GB 0  
PC 1.00

1D NMR plot parameters  
CX 20.00 cm  
CY 12.50 cm  
F1P 19.506 ppm  
F1 7343.21 Hz  
F2P -219.824 ppm  
F2 -82746.98 Hz  
PPMCH 11.98859 ppm/cm  
HZCM 4504.50439 Hz/cm



Current Data Parameters  
NAME heb2-164  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060625  
Time 14.47  
INSTRUM spect  
PROBHD 5mm Broadband  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 64  
DS 2  
SWH 64102.562 Hz  
FIDRES 0.978127 Hz  
AQ 0.5112308 sec  
RG 18190.4  
DW 7.800 usec  
DE 6.00 usec  
TE 293.0 K  
D1 2.00000000 sec  
d11 0.05000000 sec  
d12 0.00002000 sec

===== CHANNEL f1 =====  
NUC1 19F  
P1 12.70 usec  
PL1 0.00 dB  
SFO1 202.4561427 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 89.00 usec  
PL2 -3.00 dB  
PL12 14.00 dB  
PL13 14.00 dB  
SFO2 500.1320005 MHz

F2 - Processing parameters

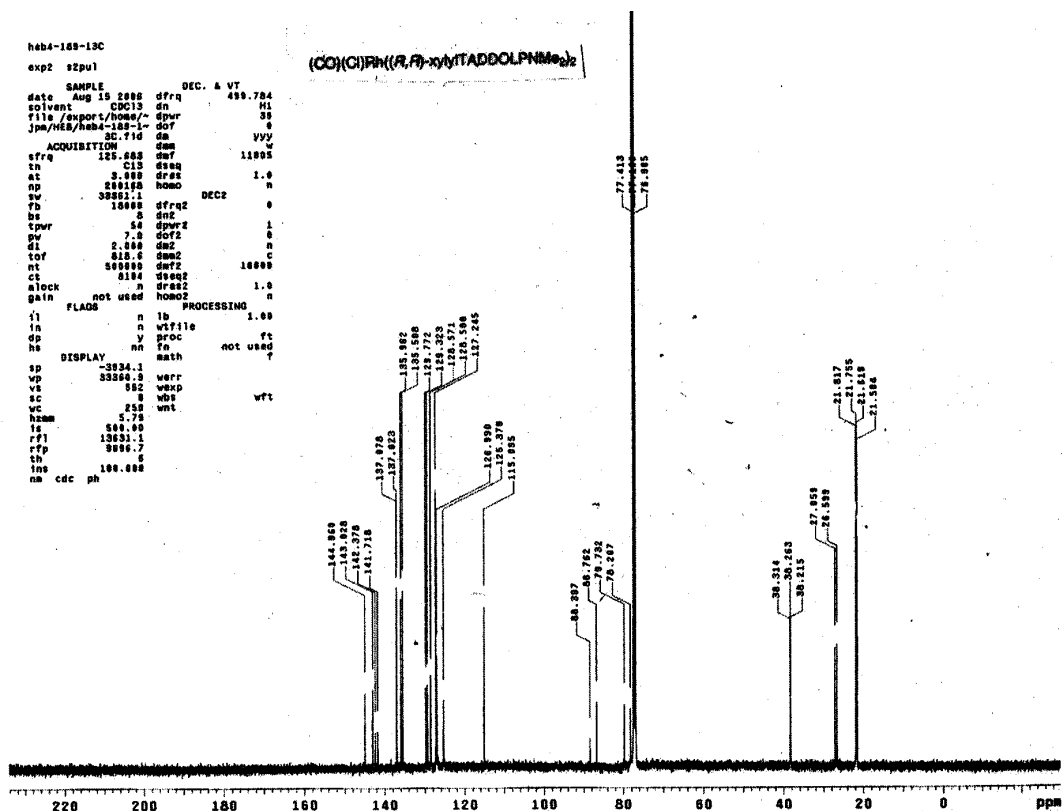




heba-188-13C  
exp2 s2pu1

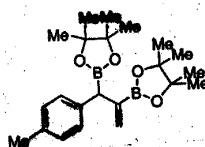
(CO)(C)Rn(R,R)-xyTADDOLPnMe<sub>2</sub>

SAMPLE DEC. & VT  
date Aug 15 2008 dfrq 499.784  
solvent CDCl<sub>3</sub> dn H1  
file /export/home/~  
jpw/heba/heba-188-13C-1-  
30.710 dm VVV  
ACQUISITION  
f1 125.682 dm 11895  
t1 C13 dssq  
at 2.000 dssq 1.0  
np 200000 homo n  
sv 300000.0 dssq DEC2 0  
fb 100000 dfrq2  
bs 8 dssq  
tpur 7.0 dssq2 1  
dl 2.000 dssq2 0  
tof 0.100 dssq2 C  
nt 500000 dssq2 10000  
ct 0.100 dssq2  
atock 0 dssq2 1.0  
gain not used homo2 n  
FLAGS n lb PROCESSING 1.00  
in n vtfile  
dp y proc ft  
hs nn fn not used f  
DISPLAY  
sp -3034.1  
vp 30300.0 werr  
vs 582 wexp  
sc 0 wnt  
vc 250 wnt  
hnm 5.75  
ls 500.00  
rf1 13031.1  
rfp 9000.7  
th 100.000  
ins  
nb cdc ph





heb3-245-clmm

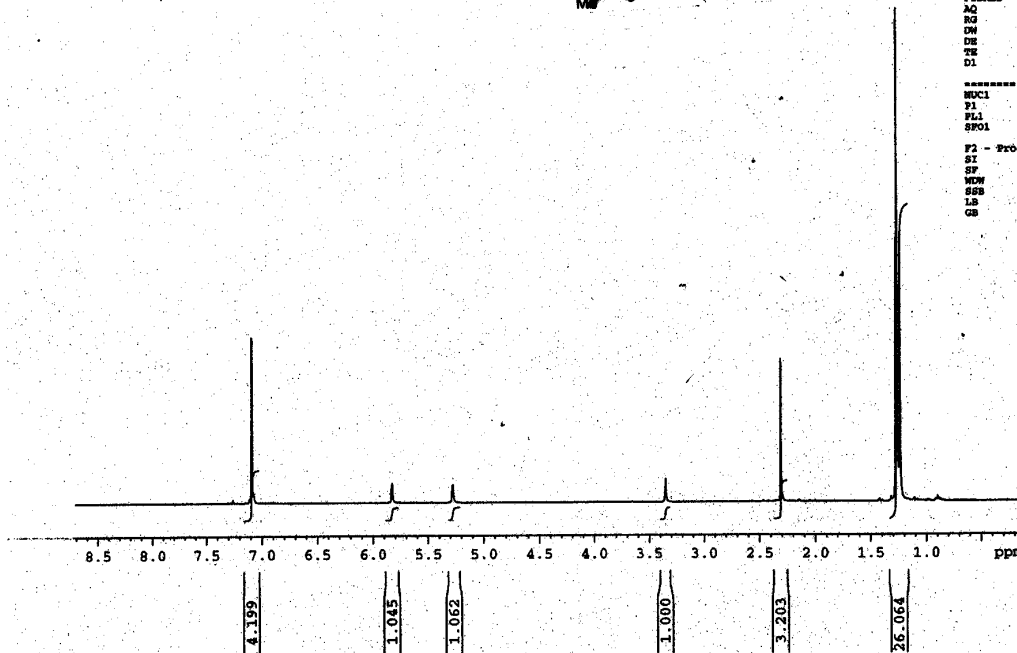


Current Data Parameters  
NAME heb3-245  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060127  
Time 10.59  
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 50.8  
DW 78.000 usec  
DE 6.00 usec  
TE 293.0 K  
D1 1.00000000 sec

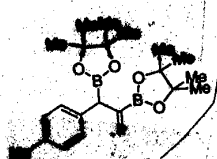
===== CHANNEL f1 =====  
NUC1 1H  
P1 24.20 usec  
PL1 0.00 dB  
SFO1 400.0524003 MHz

F2 - Processing parameters  
SI 32768  
SF 400.0500122 MHz  
WDW no  
SSB 0  
LB 0.00 Hz  
GB 0



137.445  
134.794  
129.983  
129.036  
127.903

83.565  
83.506  
77.479  
77.161  
76.842



25.078  
24.929  
24.678  
24.602  
21.117

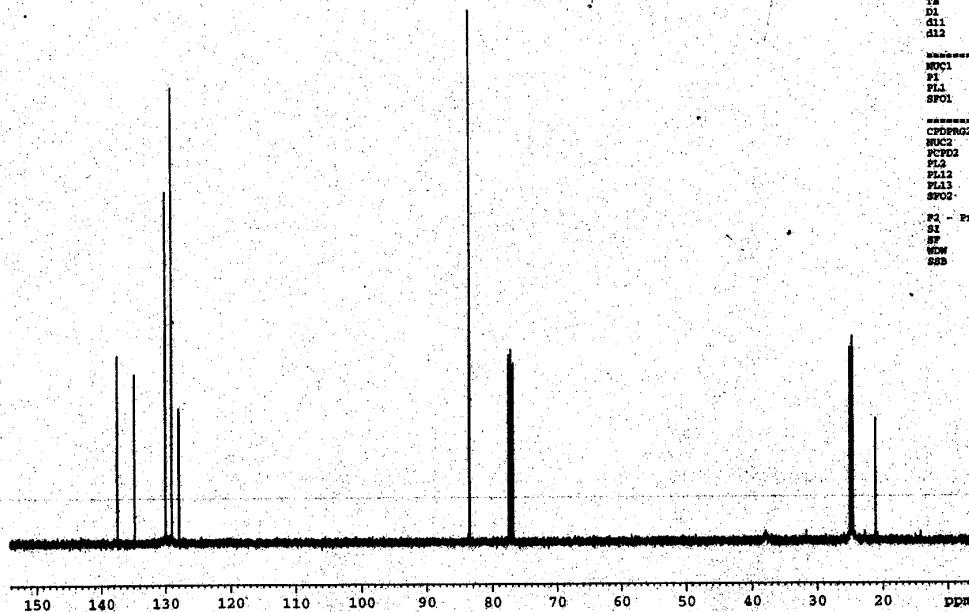
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NAME heb3-245  
EXPNO 4  
PROCNO 1

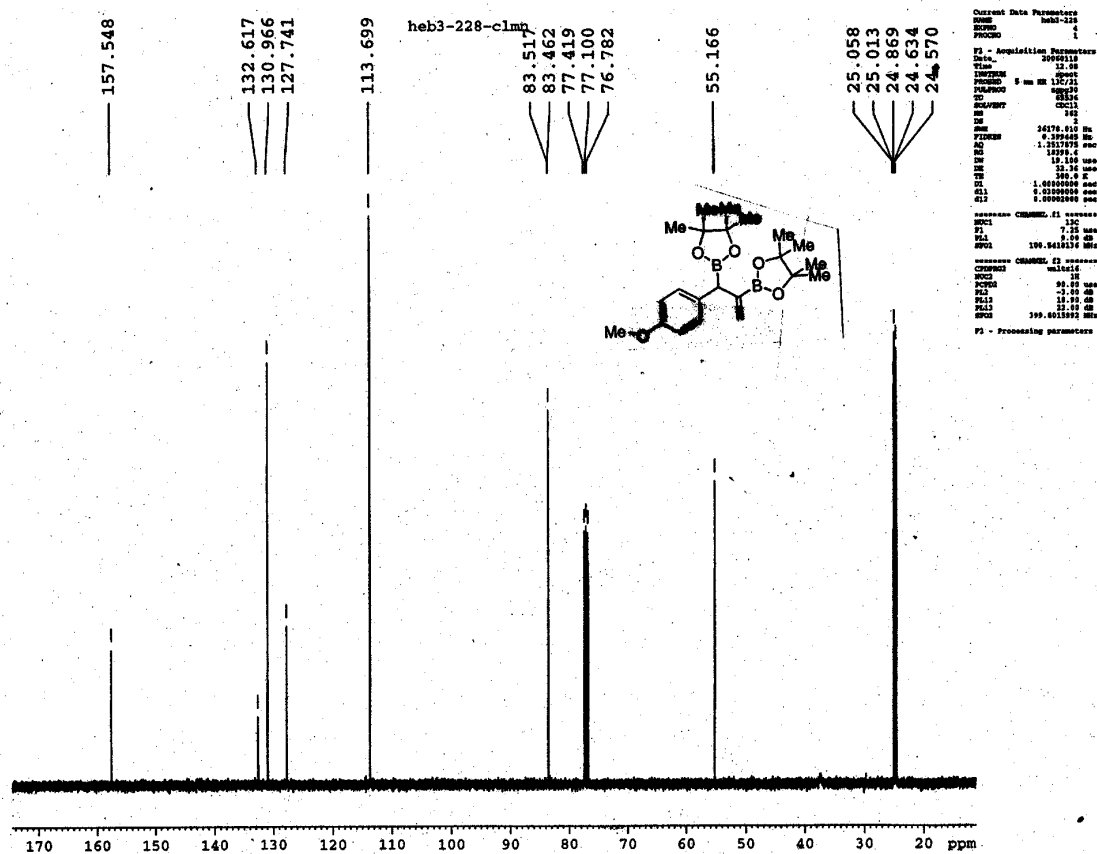
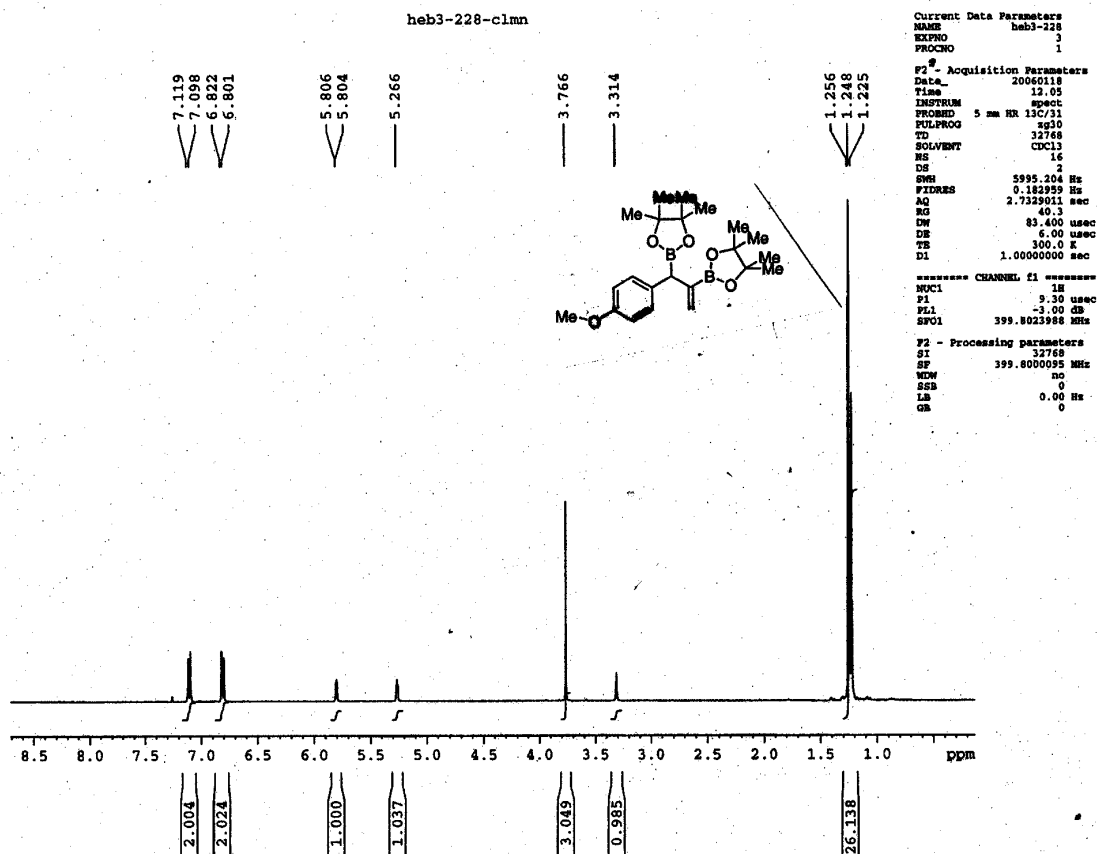
F2 - Acquisition Parameters  
Date\_ 20060127  
Time 11.01  
INSTRUM spect  
PROBHD 5mm QNP 1H/13C  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 275  
DS 2  
SWH 26246.719 Hz  
FIDRES 0.400493 Hz  
AQ 1.2485298 sec  
RG 13004  
DW 19.090 usec  
DE 6.00 usec  
TE 300.0 K  
D1 0.80000001 sec  
d11 0.03000000 sec  
d12 0.00000000 sec

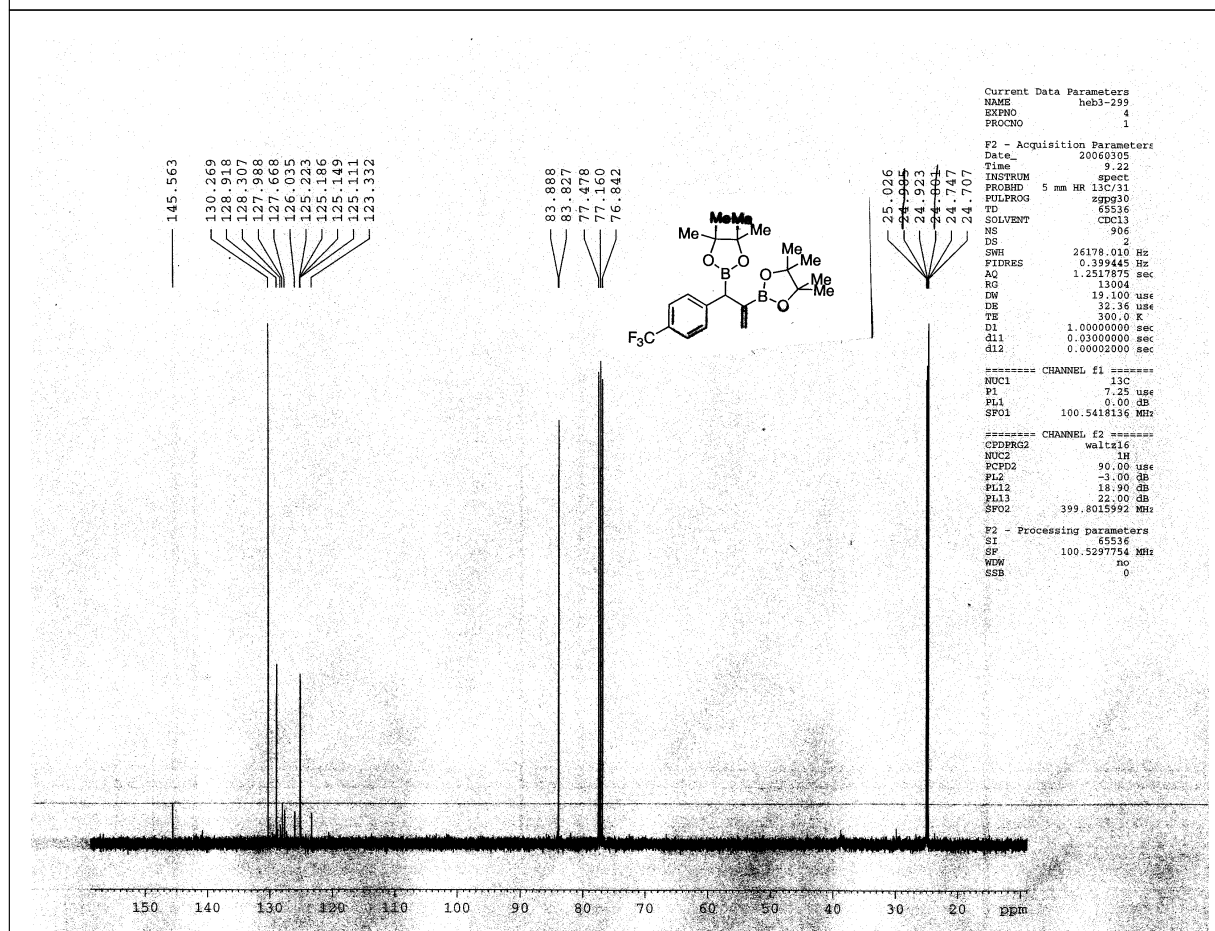
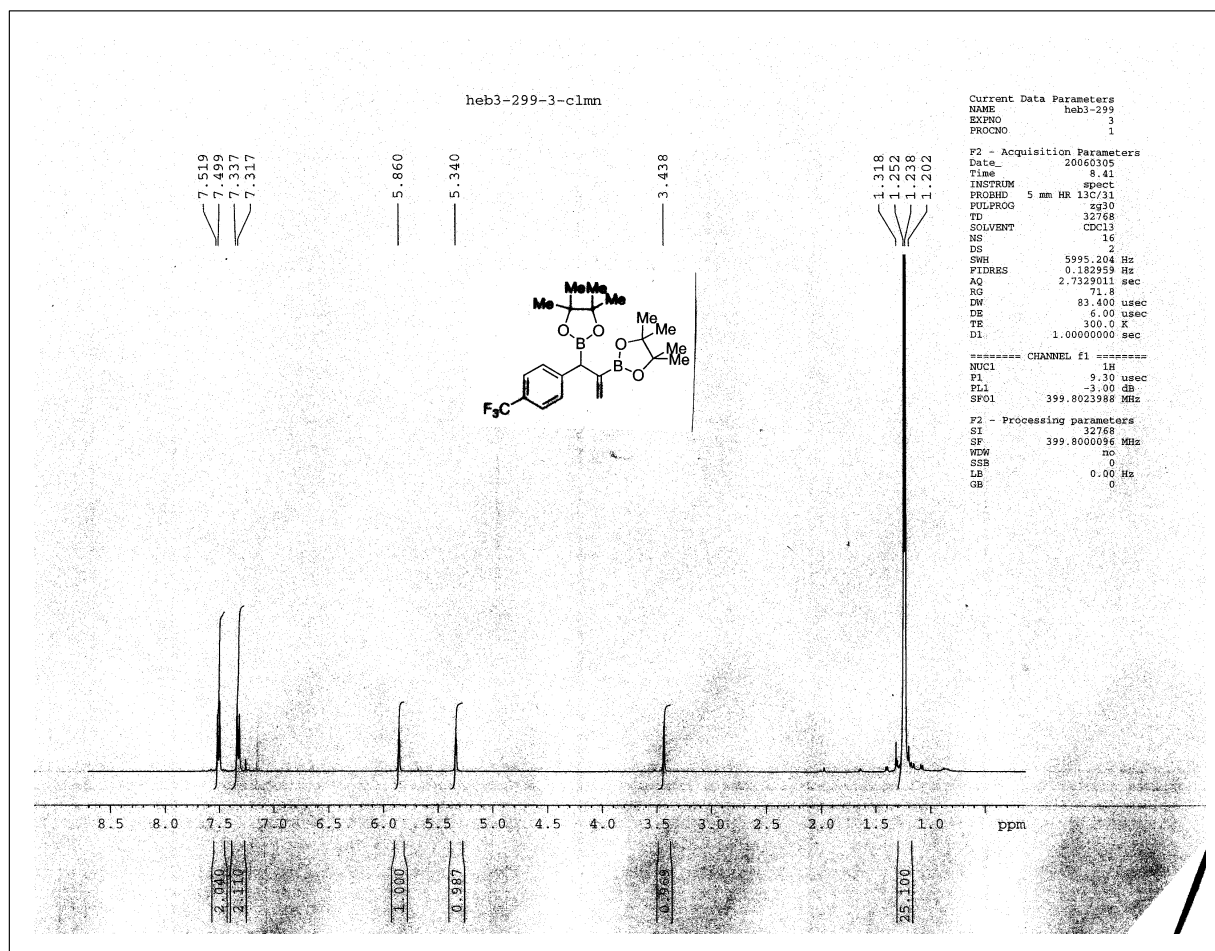
===== CHANNEL f1 =====  
NUC1 13C  
P1 6.00 usec  
PL1 0.00 dB  
SFO1 100.626782 MHz

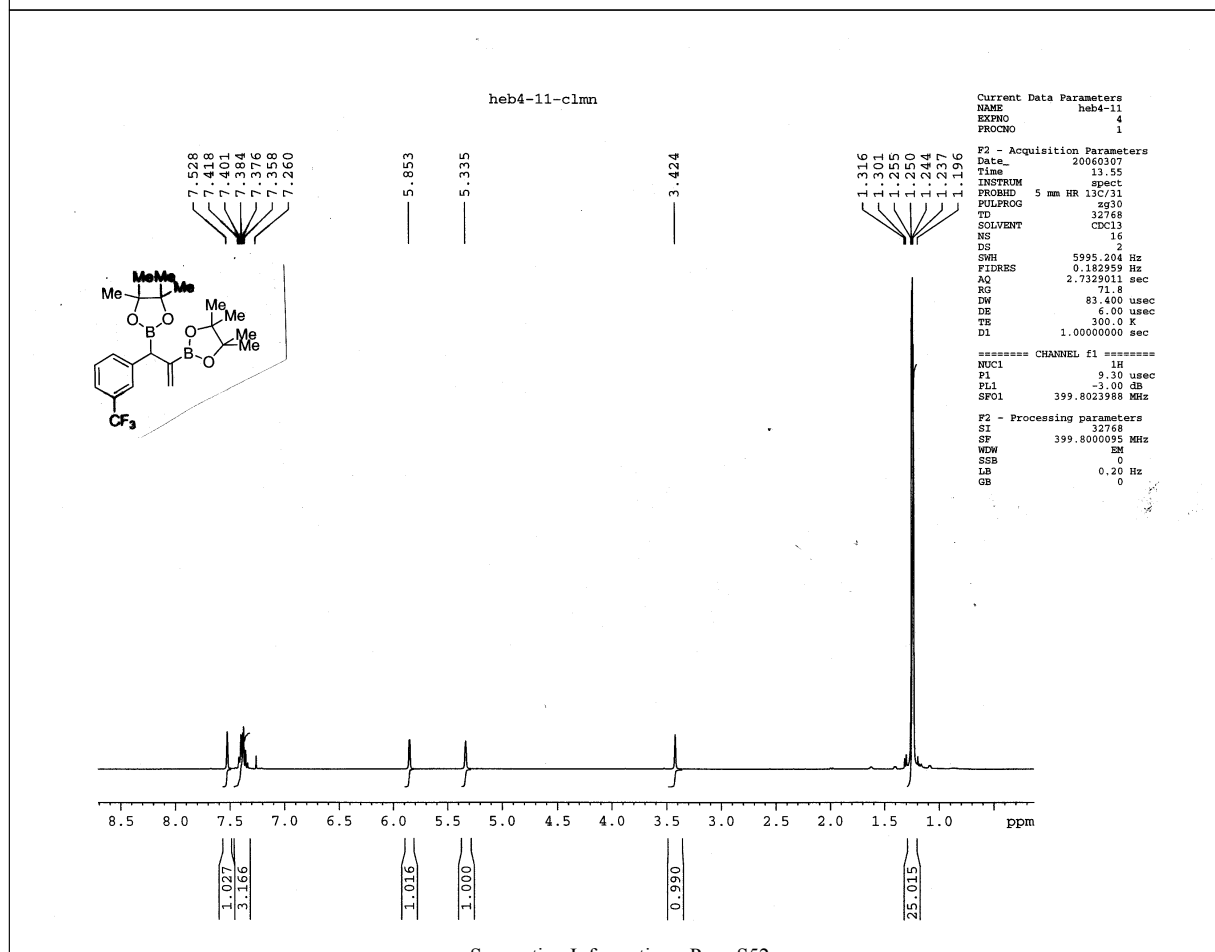
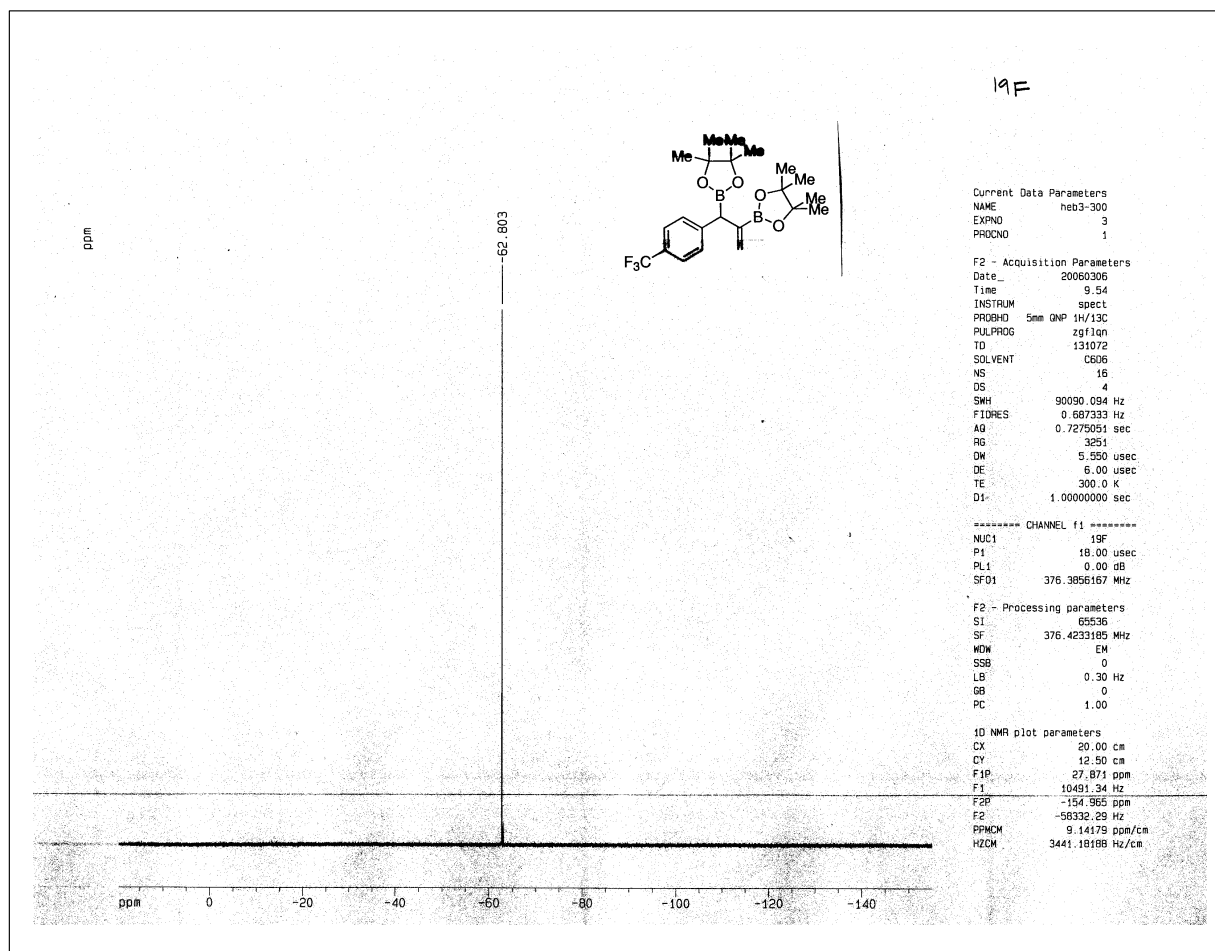
===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -4.00 dB  
PL12 13.80 dB  
PL13 14.30 dB  
SFO2 400.0516002 MHz

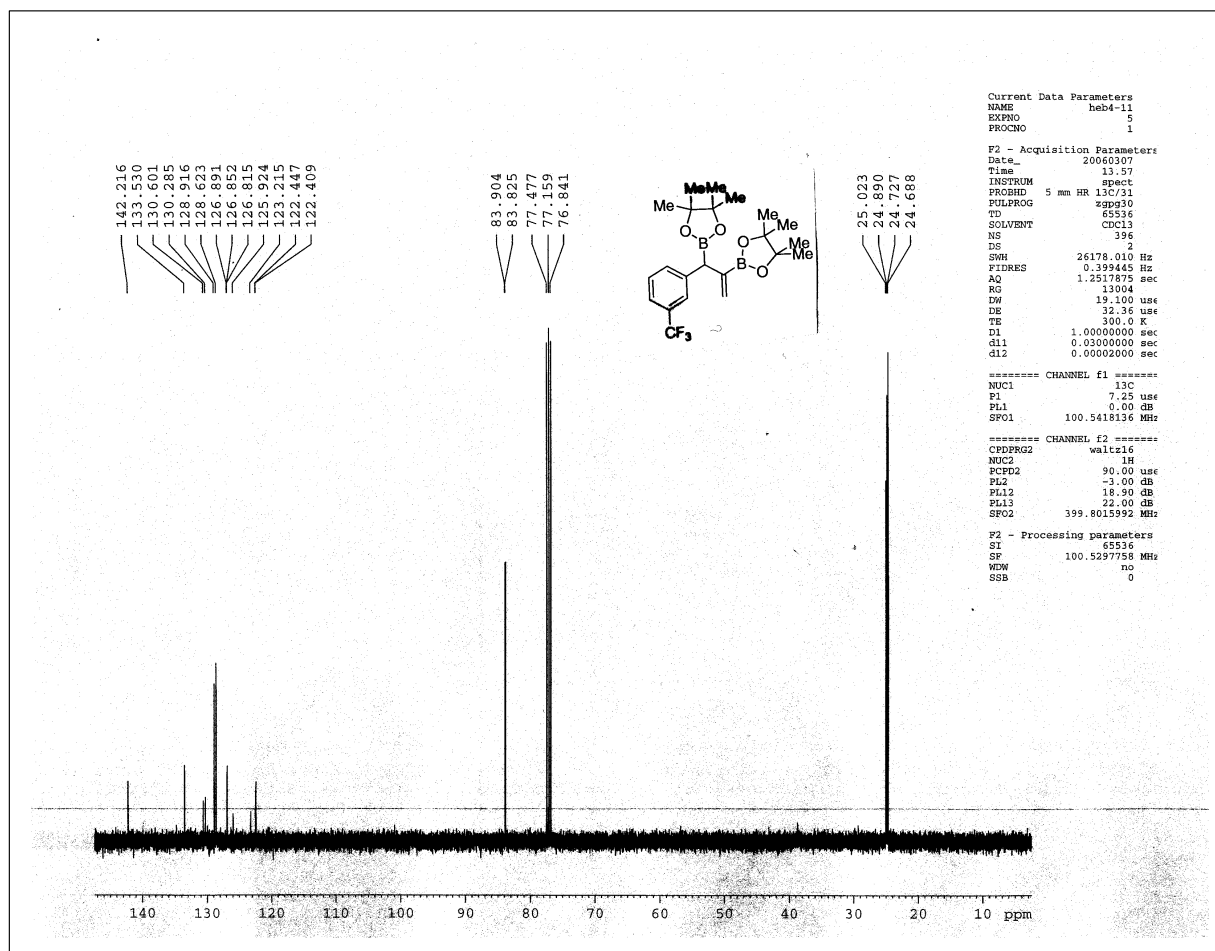
F2 - Processing parameters  
SI 32768  
SF 100.5926684 MHz  
WDW no  
SSB 0











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Current Data Parameters
NAME          beb4-108
EXPNO         2
PROCNO        1
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