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Supporting Information

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Asymmetric Synthesis of Isomerically Pure Allenylboranes from Alkynylboranes through a Novel 1,2-Insertion, 1,3-Borotropic Rearrangement

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General Information. All experiments were carried out in pre-dried glassware (1 h, 150 °C) under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were also employed for all the operations. Nuclear magnetic resonance (NMR) spectra were obtained using General Electric DPX-300 spectrometer. ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{11}B (96.5 MHz) NMR were recorded in $CDCl_3$ or C_6D_6, unless otherwise used, and the chemical shift as were expressed in ppm relative to $CDCl_3$ (δ 7.26 and 77.0 for ^{1}H and ^{13}C NMR, respectively) and of C_6D_6 (δ 7.15 and 128.0 ppm for ^{1}H and ^{13}C NMR, respectively) as the internal standard. Infrared spectra were recorded on a Perkin-Elmer 282 or a Nicolet Series 6000 FT-IR spectrophotometer. Mass spectral data were obtained with a Hewlett-Packard 5995A GC/MS spectrometer (70 eV) or a Hewlett-Packard 5971A Mass Selective Ion Detector. High-resolution mass spectral data were obtained from Atlantic Microlabs, Emory University. Optical rotations were measured employing a Perkin-Elmer 243B Polarimeter.

***B*-Methoxy-10-trimethylsilyl-9-borabicyclo[3.3.2]decane.** To a solution of *B*-MeO-9-BBN (18.0 g, 118 mmol) in hexanes (110 mL), $TMSCHN_2$ in hexanes (130 mmol, 2 M) was added at room temperature. The mixture was refluxed for 10 h and the solvent was removed under vacuum. The residue was distilled to give 27.2 g of *B*-MeO-10-TMS-9-BBD (97%, bp 80 °C, 0.10 mm Hg): ^{1}H NMR (300 MHz, C_6D_6) δ 0.21 (s, 9H), 1.45-1.68 (m, 15H), 3.34 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.1, 22.3, 22.5, 24.9, 25.8, 28.0, 29.2, 32.0, 33.2, 33.6, 52.5; ^{11}B NMR (96 MHz, C_6D_6) δ 54.9. IR (neat) 2950, 1466, 1324, 1092, 688 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{13}H_{27}BOSi$ 238.1924, found 238.1929.

Figure 1. Pictures of the crystalline **(-)-6*S*.**

9-(1*S*,2*S*-Pseudoephedrinyl)-(10*R*)-(trimethylsilyl)-9-borabicyclo[3.3.2]decane ((+)-6*R*). To a solution of 1*S*,2*S*-pseudoephedrine (8.28 g, 50 mmol) in acetonitrile (110 mL) was added *B*-MeO-10-TMS-9-BBD (23.85 g, 100 mmol) dropwise. The reaction mixture was refluxed for 6 h and slowly cooled to room temperature resulting in large crystals. The supernatant was decanted via cannula and the crystals were washed with hexanes (3 X 10 mL) to remove residual MeCN and organoborane impurities and dried *in vacuo* to give 14.1 g *of* (+)-**6*R*** (38% yield, mp 106-109 °C) (Fig. 1): $[\alpha]_D^{28}$ = + 54.2 (*c* 4.5, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 0.95 (d, *J* = 6.4 Hz, 3 H), 1.25 (m, 2 H), 1.40-1.67 (m, 13H), 1.8 (br s, 1 H), 2.45 (s, 3H), 2.62 (m, 1 H), 4.18 (d, *J* = 8.2 Hz, 1 H), 7.29 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.7, 15.1, 22.6, 23.1, 26.4, 27.6, 29.3, 31.0, 33.1, 35.4, 38.4, 65.0, 80.8, 127.0, 127.4, 128.1, 141.7; ^{11}B NMR (96 MHz, C_6D_6) δ 55.2, 17.4; HRMS *m/z* calcd for $C_{22}H_{38}BNOSi$ 371.2816, found 371.2825.

9-(1*R*,2*R*-Pseudoephedrinyl)-(10*S*)-(trimethylsilyl)-9-borabicyclo[3.3.2]decane ((-)-6*S*)). The above supernatant together with the hexane washings were concentrated. The resulting residue was dissolved in acetonitrile (100 mL) and mixed with 1*R*,2*R*-pseudoephedrine (8.28 g, 50 mmol). The reaction mixture was refluxed for 6 h, whereupon it was slowly cooled to room temperature forming large crystals. The supernatant was removed and the crystals were washed as above and dried *in vacuo* to give 10.4 g of (-)-**6*S*** (28% yield): $[\alpha]_D^{28}$ = - 54.4 (*c* 4.3, $CDCl_3$).

Determination of enantiomeric purity of 6 using ^{13}C NMR. The enantiomeric purity of the crystals can be determined utilizing ^{13}C NMR by analyzing the TMS signal of the complex in $CDCl_3$ (Fig. 2). The enantiomerically pure **6** is wholly complexed in the solid state, but exists in an open and closed forms in solution. Analysis of the complex shows two signals, δ 1.7 (open) and δ 0.7 (closed). During the transesterification minor amounts of the undesired diastereomer can precipitate. This is easily detected by ^{13}C NMR (δ 1.1). The impure complex is recrystallized using fresh acetonitrile (0.5 M), heating at reflux until all the precipitant is in solution (20-40 h). This can be facilitated by adding CH_2Cl_2 (up to 10 mL/ 40 mmol).

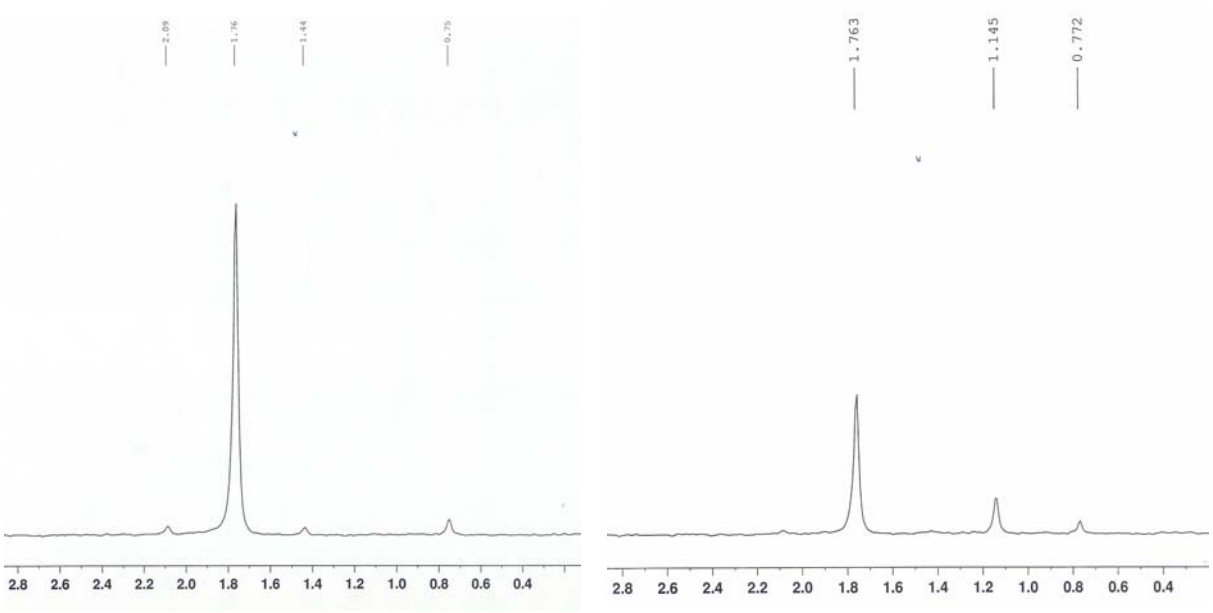


Figure 2. (left) ^{13}C NMR spectrum of optically pure **6** -Si**C**H_3 signal of the open (δ 1.7) and closed (δ 0.7) form plus the Si-satellites. (right) ^{13}C NMR spectrum of optically pure **6** –Si**C**H_3 signal of the open (δ 1.7) and closed (δ 0.7) form plus the diastereomeric impurity (δ 1.1).

General procedure for the preparation of *B*-alkynyl-10-TMS-9-BBD (2) reagents.

B*-Propynyl-10*R*-trimethylsilyl-9-borabicyclo[3.3.2]decane (+)-2a** A suspension of (+)-**6*R (1.19 g, 3.0 mmol) in Et_2O (10 mL) was cooled to -78 °C and a solution of propynylmagnesium bromide (4 mL, 1.0 M in Et_2O) was added dropwise. The solution was allowed to reach room temperature for an additional 0.5 h before TMSCl was added (0.8 mL) at -78 ºC removing the bath 10 min after the addition. Using standard techniques to prevent the exposure of the borane to the open atmosphere, the solution was concentrated under vacuum, the residue was washed with pentane (6 x 10 mL) and these washings were filtered through a Celite pad. The filtrate was concentrated to obtain (+)-**2a** in 98% yield (0.73 g, 2.96 mmol); $[\alpha]_D^{20}$ = + 46.0 (*c* 1.5 , $CDCl_3$); ^{11}B NMR ($CDCl_3$, 96 MHz) δ 75 (Fig. 3); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.19 (s, 9 H), 0.97- 2.37 (m, 18 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 1.1, 5.5, 21.9, 24.7, 25.5, 28.8, 31.2, 33.0, 33.4, 34.5, 41.5, 91.6, 117.4. (-)-**2a** is prepared by the same procedure starting with (-)-**6*S***. $[\alpha]_D^{20}$= - 46.4 (*c* 1.5 , $CDCl_3$). Other data are essentially identical to (+)-**2a**. (")-**2a** is also prepared by essentially the same procedure starting with (")-*B*-MeO-10-TMS-9-BBD.

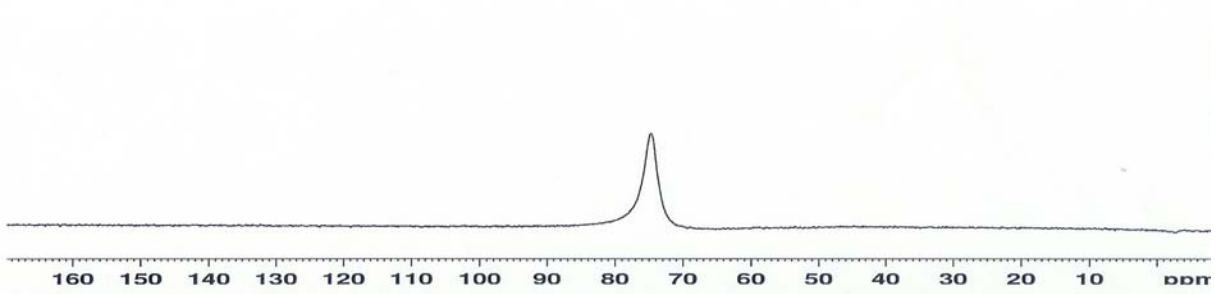


Figure 3. ^{11}B NMR spectrum of **2a**.

B*-(5-Chloropent-1-ynyl)-10*R*-trimethylsilyl-9-borabicyclo[3.3.2]decane ((+)-2b).** A suspension of (+)-**4*R (1.19 g, 3.0 mmol) in Et_2O (10 mL) was cooled to -78 °C and a solution of 5-chloro-1-pentynylmagnesium bromide (4 mL, 1.0 M in Et_2O) was added dropwise. The solution was allowed to reach room temperature for an additional 0.5 h before TMSCl was added (0.8 mL) at -78 ºC removing the bath 10 min after the addition. Using standard techniques to prevent the exposure of the borane to the open atmosphere, the solution was concentrated under vacuum, the residue was washed with pentane (6 x 10 mL) and these washings were filtered through a celite pad. The filtrate was concentrated once more to obtain (+)-**2b** 96% yield (2.78 mmol, 0.89 g); $[\alpha]_D^{20}$ = + 55.9 (*c* 1.6 , C_6D_6; ^{11}B (C_6D_6, 96 MHz) δ 68; ^1H NMR (C_6D_6, 300 MHz) δ 0.35 (s, 9 H), 1.54-1.72 (m, 15 H), 1.88-1.97 (m, 2 H), 2.33 (t, *J*= 6.9 Hz, 2 H), 1.87 (m, 2H), 3.29 (t, *J*= 6.4 Hz, 2H); ^{13}C NMR (C_6D_6, 75 MHz) δ 1.2, 17.9, 22.0, 25.0, 25.7, 29.1, 31.2, 31.2, 33.6, 33.8, 34.7, 41.5, 43.2, 93.6, 120.1. (-)-**2b** is prepared by the same procedure starting with (-)-**6*S***. $[\alpha]_D^{20}$= - 55.5 (*c* 1.5, C_6D_6). Other data are essentially identical to (+)-**2b**. (")-**2b** is also prepared by essentially the same procedure starting with (")-*B*-MeO-10-TMS-9-BBD.

B*-(Cyclopropylacetylenyl)-10*R*-trimethylsilyl-9-borabicyclo[3.3.2]decane ((+)-2c).** A suspension of (+)-**6*R (1.19 g, 3.0 mmol) in Et_2O (10 mL) was cooled to -78 °C and a solution of 5-Cl-pentynylmagnesium bromide (4 mL, 1.0 M in Et_2O) was added dropwise. The solution was allowed to reach room temperature for an additional 0.5 h before TMSCl was added (0.8 mL) at -78 ºC removing the bath 10 min after the addition. Using standard techniques to prevent the exposure of the borane to the open atmosphere, the solution was concentrated under vacuum, the residue was washed with pentane (6 x 10 mL) and these washings were filtered through a celite pad. The solvents were concentrated once more to obtain (+)-**2c** in 99% yield (0.81 g, 2.97 mmol); $[\alpha]_D^{20}$ = + 24.6 (*c* 0.66, CH_2Cl_2); ^{11}B NMR (C_6D_6, 96 MHz) δ 71; ^1H NMR (C_6D_6, 300 MHz) δ 0.31 (s, 9 H), 0.58- 0.62 (m, 2 H), 0.77- 0.80 (m, 2 H), 1.23- 1.30 (m, 2 H), 1.45- 1.69 (m, 10 H), 1.71- 2.0 (m, 2 H), 2.25- 2.28 (m, 1 H), 2.43 (s, 1 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 1.2, 1.3, 9.5, 9.6, 22.1, 25.0, 25.8, 29.0, 31.4, 33.3, 33.6, 34.7, 41.0, 9.3, 126.9. (-)-**2c** is prepared by the same procedure starting with (-)-**6*S***; $[\alpha]_D^{20}$ = -23.4 (*c* 0.56, CH_2Cl_2). Other data are essentially identical to (-)-**2c**. (")-**2c** is also prepared by essentially the same procedure starting with (")-*B*-MeO-10-TMS-9-BBD.

General procedure for the preparation of *B*-(γ-trimethylsilyl-α-alkylallenyl-10-TMS-9-BBD (1a-1c).

***B*-(α-Methyl-γ-trimethylsilylallenyl)-10*R*-trimethylsilyl-9-borabicyclo[3.3.2]decane ((-)-1a).** To a pentane solution of (+)-**2a** (2.9 mmol in 5 mL of pentane) trimethylsilyldiazomethane was added (4 mmol, 2 M solution in hexanes) dropwise at room temperature. The reaction was complete after 3 h as shown by ^{11}B NMR (pentane, 96 MHz) δ 78. The solvents were removed to obtain (-)-**1a** in quantitative yield (2.9 mmol, 0.78 g); $[\alpha]_D^{20}$ = -14.2 (*c* 1.2 , C_6D_6); ^1H NMR (C_6D_6, 300 MHz) δ 0.16 (s, 9 H), 0.23 (s, 9 H), 1.49-1.95 (m, 18 H), 4.71 (t, *J*= 3.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -0.6, 1.5, 15.7, 21.9, 24.7, 25.4, 29.2, 29.9, 31.3, 34.1, 35.1, 36.5, 74.8, 92.7, 214.0 (Fig. 4); (+)-**1a** is prepared by the same procedure starting with (-)-**2a**. $[\alpha]_D^{20}$= +14.0 (*c* 1.2, C_6D_6). (")-**2a** gives (")-**1a**. Other data are essentially identical to (-)-**1a.**

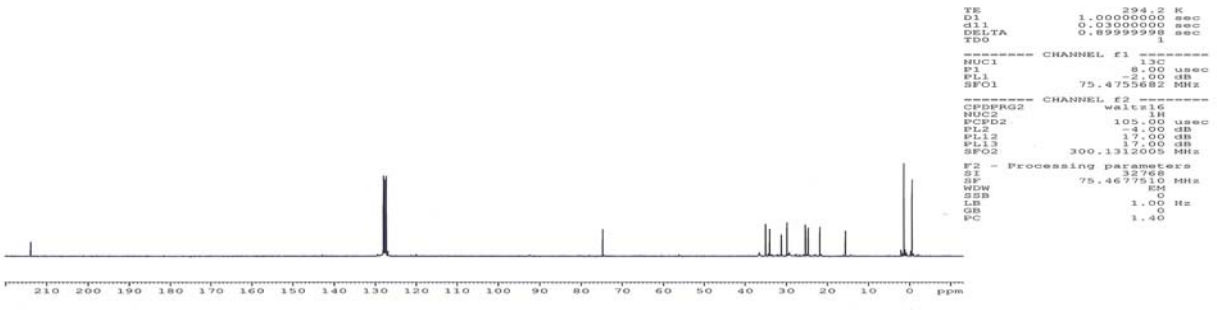


Figure 4. ^{13}C NMR spectrum of **1a**. No diastereomers are observed.

***B*-[α-(γ-Chloropropyl)-γ-trimethylsilylallenyl]-10*R*-trimethylsilyl-9-borabicyclo[3.3.2]decane ((-)-1b).** To a pentane solution of **(+)-2b** (2.9 mmol in 5 mL of pentane) trimethylsilyldiazomethane ($TMSCHN_2$) was added (2.0 mL, 2 M solution in hexanes) dropwise at room temperature. The reaction is completed after 3 h as shown in by ^{11}B NMR (pentane, 96 MHz) δ 78. The solvents were removed to obtain (-)-**1b** in quantitative yield (2.9 mmol, 1.14 g); $[\alpha]_D^{20}$ = - 16.0 (*c* 1.9, C_6D_6); ^1H NMR (C_6D_6, 300 MHz) δ 0.13 (s, 9 H), 0.20 (s, 9 H), 1.48- 2.26 (m, 19 H), 3.31 (t, *J*= 6.63 Hz, 2 H), 4.73 (t, *J*= 3.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: -0.6, 1.5, 21.8, 24.7, 25.3, 26.4, 29.1, 29.8, 31.2, 33.1, 34.0, 34.9, 36.9, 44.4, 77.0, 97.1, 212.9 (Fig. 5). (+)-**1b** is prepared by the same procedure starting with (-)-**2b** $[\alpha]_D^{20}$ = + 15.5 (*c* 2.0 , C_6D_6). (")-**2b** gives (")-**1b**. Other data are essentially identical to (-)-**1b**

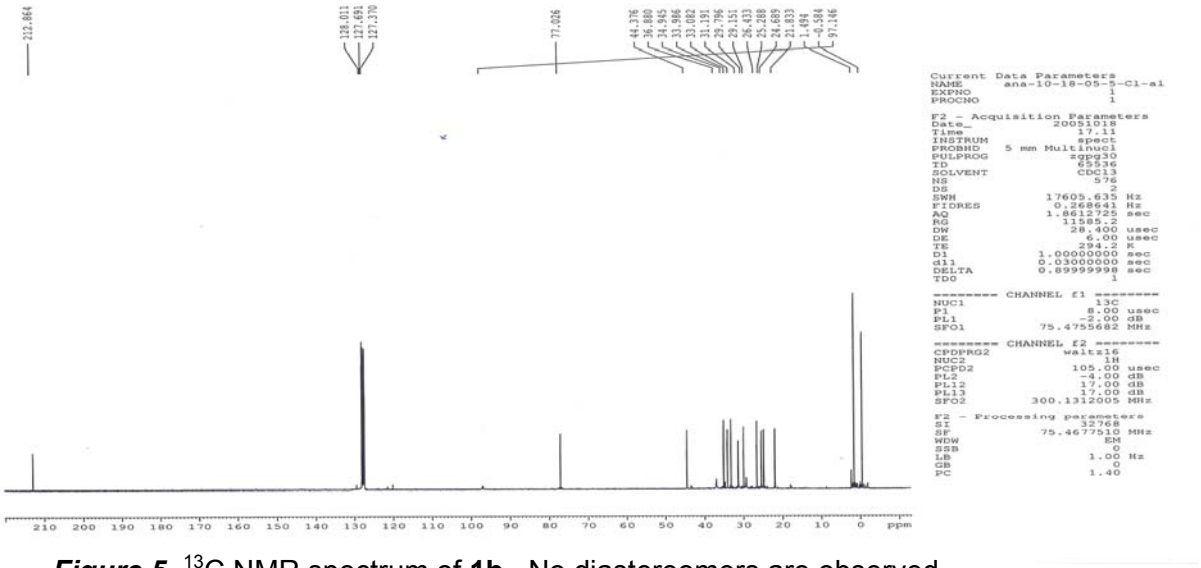


Figure 5. ^{13}C NMR spectrum of **1b**. No diastereomers are observed.

***B*-(α-Cyclopropyl-γ-trimethylsilylallenyl)-10*R*-trimethylsilyl-borabicyclo[3.3.2] decane (-)-1c.** To a pentane solution of (+)-**2c** (3.0 mmol in 5 mL of pentane) trimethylsilyldiazomethane ($TMSCHN_2$) was added (2.0 mL, 2 M solution in hexanes) dropwise at room temperature. The reaction is completed after 3 h as shown in by ^{11}B NMR (pentane, 96 MHz) δ 78. The solvents were removed to obtain (-)-**1c** in quantitative yield (2.9 mmol, 1.07 g); $[\alpha]_D^{20}$ = - 36.1 (*c* 1.7, C_6D_6); ^1H NMR (C_6D_6, 300 MHz) δ 0.16 (s, 9 H), 0.23 (s, 9 H), 0.71- 0.73 (m, 2 H), 0.73- 0.74 (m, 2 H), 1.20-1.84 (m, 15 H), 2.50-2.53 (m, 1 H), 4.81 (d, *J*= 1.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -0.6, 1.5, 7.7, 8.5, 9.1, 21.9, 24.8, 25.5, 29.5, 30.0, 31.2, 34.1, 35.0, 36.9, 78.9, 102.3, 211.5 (Fig. 6). (+)-**1c** is prepared by the same procedure starting with (-)-**2c**; $[\alpha]_D^{20}$ = + 36.2 (*c* 1.7 , C_6D_6). (")-**2c** gives (")-**1c**. Other data are essentially identical to (-)-**1c**.

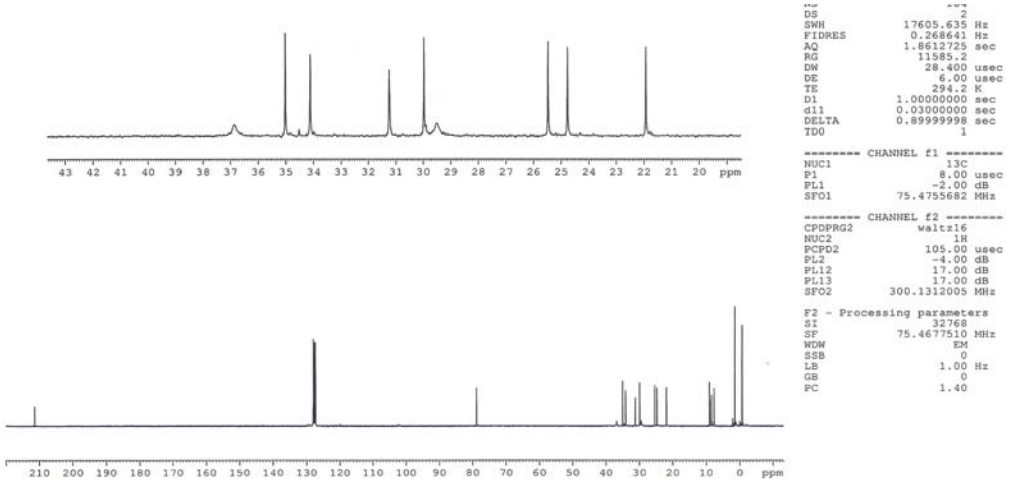


Figure 6. ^{13}C NMR spectrum of **1c**. No diastereomers are observed.

General Procedure for the synthesis of β-TMS homopropargylic alcohols 7a-g.

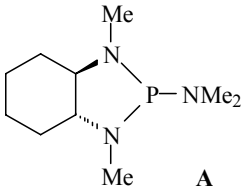
A solution of (+)-**1a** (2.9 mmol) in THF (10 mL) was cooled to -78 ºC and butyraldehyde (2.7 mmol) was added dropwise and the mixture was stirred for 3 h. For the racemic alcohols, only the oxidative workup was used.

Oxidative workup: The reaction mixture was raised to 25 ºC and pH 7.2 phosphate buffer solution in water was added (10 mL) followed by NaOH (2.0 mL, 3 M solution in water) and H_2O_2 (0.9 mL, 30 wt% in water). The biphasic solution was refluxed for 2 h followed by an aqueous workup (3 x 20 mL of brine solution). The combined organic phase was dried over $MgSO_4$ and filtered. The crude product was then purified by silica gel column chromatography (95:4:1, hexane: ether: NEt_3) to obtain **6b** in 90% yield (2.43 mmol, 0.48 g).

Pseudoephedrine work-up: The reaction mixture was raised to 25 ºC and concentrated under vacuum. The crude borinate **5a** was then diluted in CH_3CN (7 mL) and (1*R*, 2*R*)-pseudoephedrine was added. The mixture was refluxed for 12 h and cooled slowly resulting in the precipitation of crystalline **(-)-6*S***. The crystals were washed with pentane (3 x 5 mL) and dried under vacuum resulting in 80% yield (2.32 mmol, 0.86 g) of recovered **(-)-6*S***. The supernatant was then purified by silica gel column chromatography (95:4:1, hexane: ether: NEt_3) to obtain **7b** in 90% yield (2.43 mmol, 0.48 g).

Determination of the enantiomeric purity:

The enantiomeric purity was determined by the ^{31}P NMR CDA reagent developed by Alexakis using the reported procedures.[1] All samples were calibrated with the phosphoramide **A** (δ 122.5).



A

(*R*)-3-Trimethylsilylhex-4-yn-2-ol (+)-7a. Prepared from **1a*S***: $[\alpha]_D^{20}$ = +2.5 (*c* 2.5, CH_2Cl_2, 94% ee); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -2.2, 3.6, 22.2, 30.9, 68.0, 76.4, 78.9; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9 H), 1.25 (d, *J*= 6.2 Hz, 3 H), 1.82 (d, *J*= 2.7 Hz, 3 H), 1.96-2.02 (m, 1 H), 2.32 (bs, 1 H), 3.81-3.92 (m, 1 H) (Fig. 7); HRMS $[M+H]^+$ calcd. 171.1199 found 171.1199. ^{31}P NMR ($CDCl_3$, 121.5 MHz) **7a**-CDA analysis δ 144.37 (97), δ 138.96 (3).

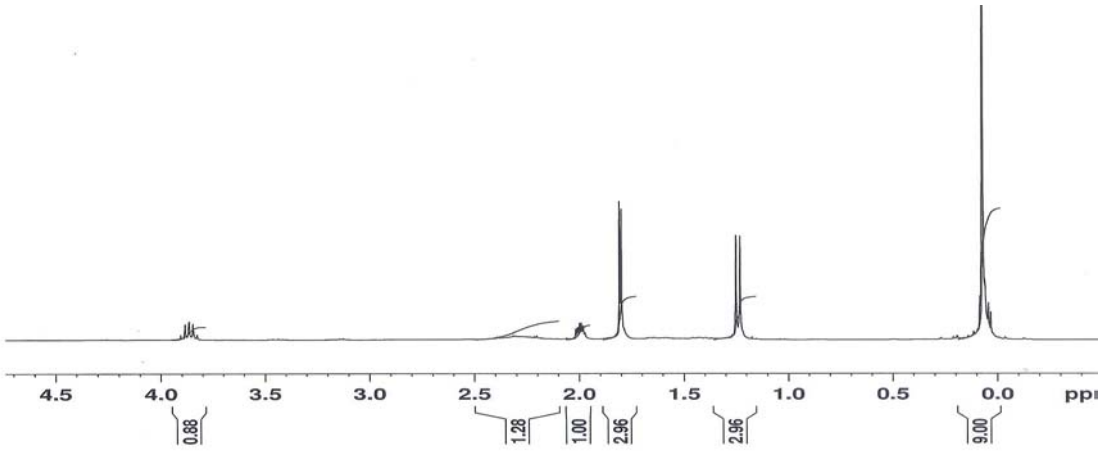


Figure 7. ^{1}H NMR spectrum of **7a**. No diastereomers are observed.

(*R*)-5-Trimethylsilyloct-6-yn-4-ol (+)-7b. Prepared from **1a*S***: $[\alpha]_D^{28}$ = + 21.3º (*c* 1.2, CH_2Cl_2, 99% ee); ^{13}C NMR (C_6D_6, 75 MHz) δ -1.9, 3.3, 13.9, 19.0, 29.7, 39.4, 72.2, 77.8, 78.0 (Fig. 9); ^{1}H NMR (C_6D_6, 300 MHz) δ 0.27 (s, 9 H), 0.99 (t, *J*= 7.2 Hz, 3 H), 1.34-1.44 (m, 1 H), 1.53 (bs, 1 H), 1.60-1.69 (m, 5 H), 1.72-1.79 (m, 1 H), 1.97-2.08 (m, 1 H), 3.75-3.85 (m, 1 H); HRMS $[M+H]^+$ calcd. 197.1356 found 197.1356. ^{31}P NMR ($CDCl_3$, 121.5 MHz) **7b**-CDA analysis δ 145.29 (<0.5), δ 142.81 (>99.5) (Fig. 8).

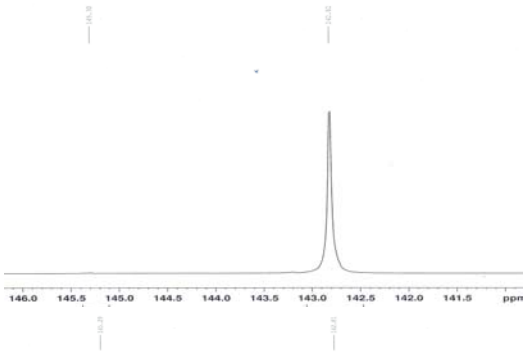


Figure 8. ^{31}P NMR of (+)-**7b-CDA** (top) and (±)-**7b-CDA** (bottom).

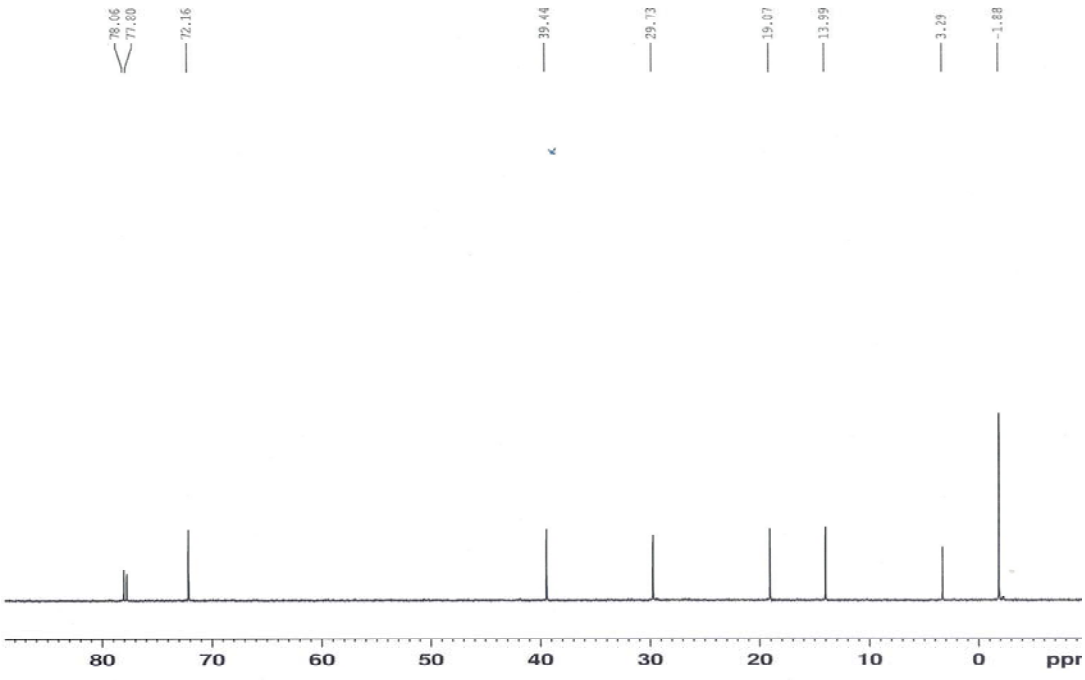


Figure 9. ^{13}C NMR of (+)-**7b**.

(*R*)-2-Methyl-4-trimethylsilylhept-5-yn-3-ol (+)-7c. Prepared from **1a*S***: $[\alpha]_D^{20}$ = +9.5 (*c* 1.3, CH_2Cl_2, 98% ee); ^{13}C NMR (C_6D_6, 75 MHz) δ -1.99, 3.3, 14.1, 19.9, 25.9, 31.9, 77.0, 77.2, 78.6 (Fig. 10); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.34 (s, 9 H), 0.93 (d, *J*= 7.0 Hz, 3 H), 0.98 (d, *J*= 7.0 Hz, 3 H), 1.65 (d, *J*= 2.7 Hz, 3 H), 1.73 (bs, 1 H), 1.98-2.15 (m, 1 H), 2.20-2.34 (m, 1 H), 3.56-3.65 (m, 1 H); HRMS $[M+H]^+$ calcd. 199.1518 found 199.1512. ^{31}P NMR ($CDCl_3$, 121.5 MHz) **7c**-CDA analysis δ 146.33 (1), δ 145.82 (99).

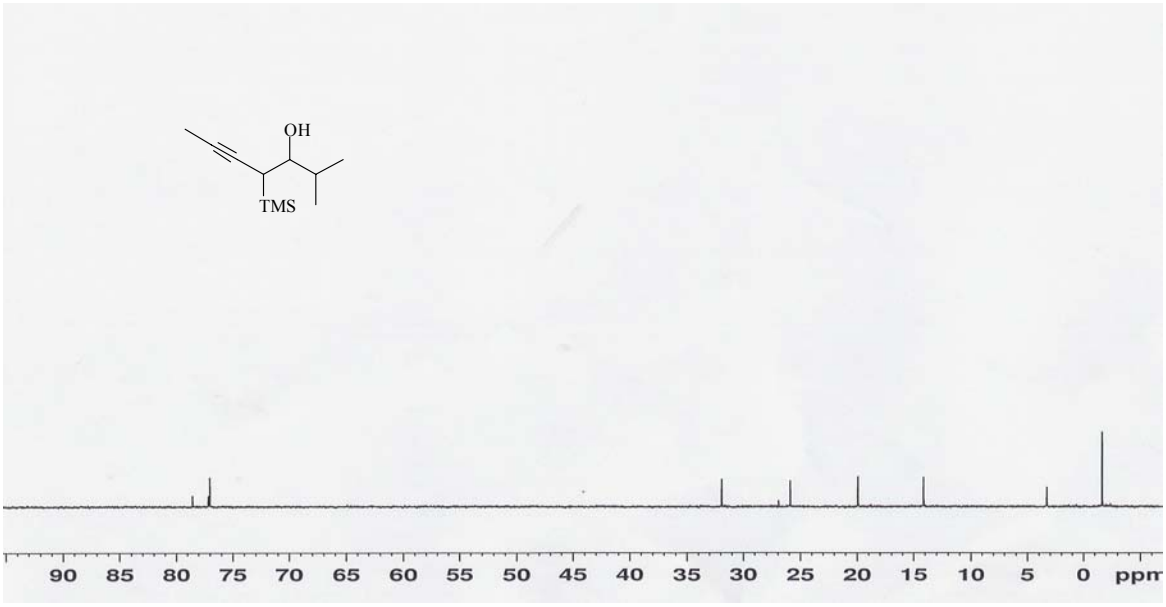


Figure 10. ^{13}C NMR of **7c**.

(*R*)-2-Methyl-5-trimethylsilyloct-6-yn-4-ol (+)-7d. Prepared from **1a*S***: $[\alpha]_D^{20}$ = + 25.0 (*c* 5.2, CH_2Cl_2, 98% ee); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.92, 3.7, 21.4, 23.9, 24.6, 30.5, 45.4, 70.0, 76.8, 78.7 (Fig. 11); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9 H), 0.90 (d, *J*= 6.5 Hz, 3 H), 0.94 (d, *J*=6.5 Hz, 3 H), 1.14-1.27 (m, 2 H), 1.50-1.61 (m, 1 H), 1.66 (bs, 1 H), 1.82 (d, *J*= 2.7 Hz, 3 H), 1.98-2.04 (m, 1 H), 3.75 (ddd, *J*= 2.4, 5.3, 7.6,1 H); HRMS $[M+H]^+$ calcd. 213.1674 found 213.1677. ^{31}P NMR ($CDCl_3$, 121.5 MHz) **7d**-CDA analysis δ 141.13 (99), δ 140.21 (1).

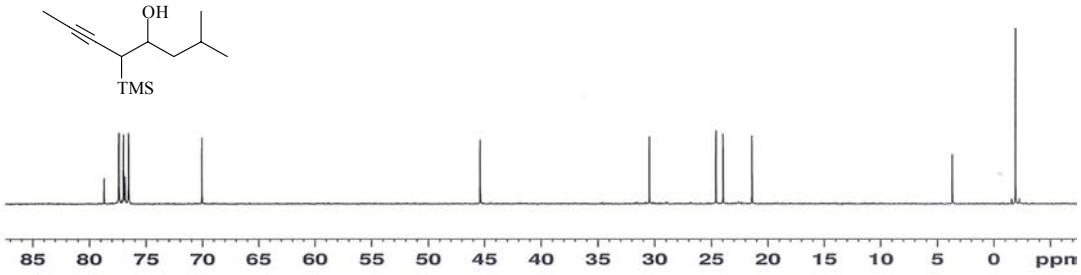


Figure 11. ^{13}C NMR of **7d**.

(*R*)-1-Phenyl-2-trimethylsilylpen-3-yn-1-ol (-)-7e. Prepared from **1a*S***: $[\alpha]_D^{20}$ = - 30.9 (*c* 2.8 CH_2Cl_2, 99% ee); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.84, 3.3, 26.9, 30.8, 75.4, 78.1, 78.4, 126.6, 127.9, 129.4, 144.9 (Fig. 13); ^{1}H NMR ($CDCl_3$, 300 MHz) δ -0.10 (s, 9 H), 1.80 (d, *J*= 2.7 Hz, 3 H), 2.25-2.30 (m, 2 H), 2.33 (bs, 1 H), 4.77 (d, *J*= 6.7 Hz, 1 H), 7.23-7.40 (m, 5 H); HRMS $[M+H]^+$ calcd. 233.1361 found 233.1356. ^{31}P NMR ($CDCl_3$, 121.5 MHz) **7e**-CDA analysis δ 146.70 (>99.5), δ 136.11 (<0.5) (Fig. 12).

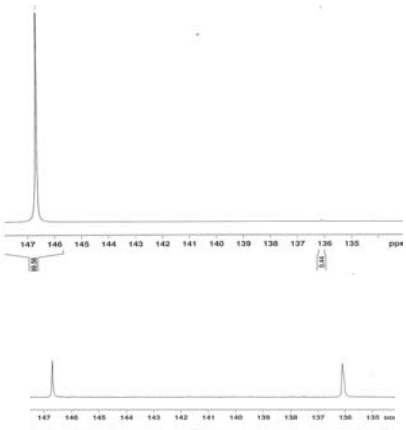


Figure 12. ^{31}P NMR of (-)-**7e-CDA** (top) and (±)-**7e-CDA** (bottom).

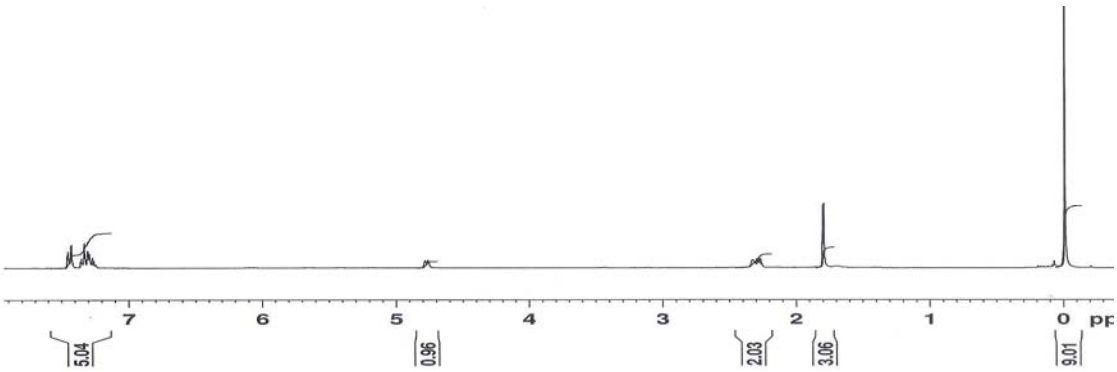


Figure 13. ^{1}H NMR spectrum of **7e**. No diastereomers are observed.

(*S*)-10-Chloro-5-trimethylsilyldec-6-yn-4-ol (-)-7f. Prepared from **1b*R***: $[\alpha]_D^{20}$ = - 25.1 (*c* 1.1, CH_2Cl_2, 99% ee); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.9, 14.0, 16.3, 18.9, 29.6, 31.9, 39.5, 43.4, 72.1, 80.3, 80.77 (Fig. 15); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.25 (s, 9 H), 0.98 (t, *J*= 6.9 Hz, 3 H), 1.4 (m, 1 H), 1.50-1.77 (m, 6 H), 1.94-2.01 (m, 1 H), 2.15-2.25 (m, 2 H), 3.34-3.42 (m, 2 H), 3.72-3.80 (m, 1 H); HRMS $[M+H]^+$ calcd. 275.1228 found 275.1228. ^{31}P NMR ($CDCl_3$, 121.5 MHz) **7f**-CDA analysis δ 145.38 (>99.5), δ 142.95 (<0.5) (Fig. 14).

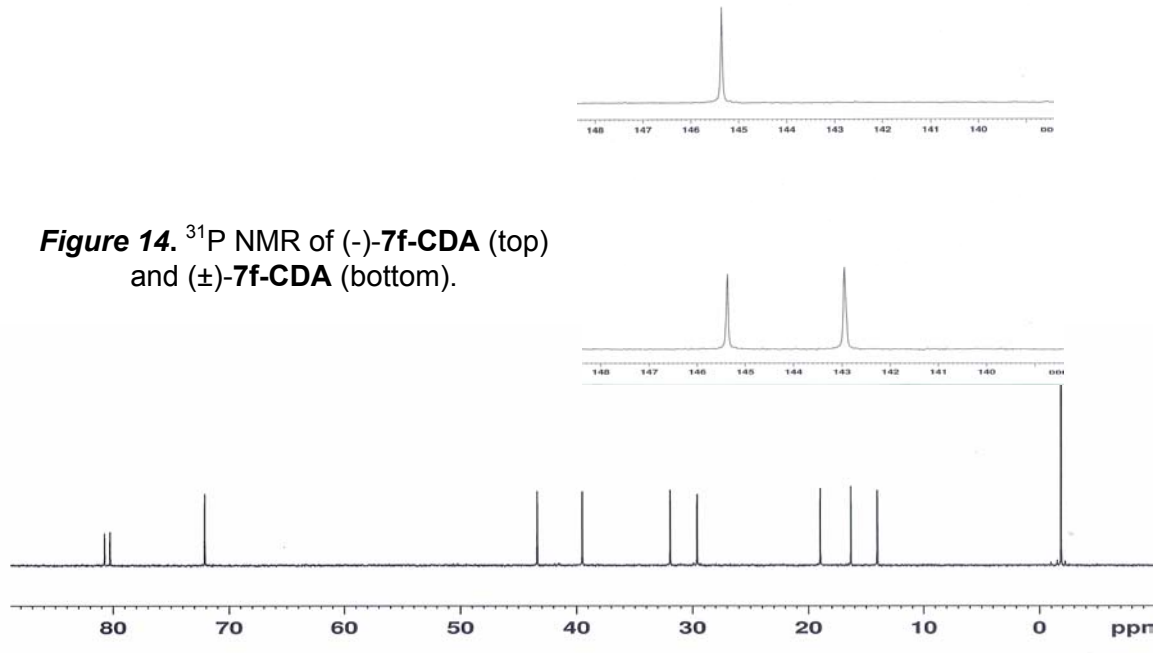


Figure 14. ^{31}P NMR of (-)-**7f-CDA** (top) and (±)-**7f-CDA** (bottom).

Figure 15. ^{1}HNMR spectrum of **7f**. No diastereomers are observed.

(*R*)-1-Cyclopropyl-3-trimethylsilylhept-1-yne-4-ol (+)-7g. Prepared from **1c*S***: $[\alpha]_D^{20}$ = + 25.5º (*c* 3.0, CH_2Cl_2, 96% ee); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.5, 0.12, 8.2, 13.9, 19.0, 29.6, 39.6, 72.3, 74.5, 86.3 (Fig. 17); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.25 (s, 9 H), 0.40-0.50 (m, 2 H), 0.58-0.65 (m, 2 H), 0.96 (t, *J*= 7.1 Hz, 3 H), 1.10-1.20 (m, 1 H), 1.35-1.44 (m, 2 H), 1.53-1.68 (m, 2 H), 1.70-1.83 (m, 1 H), 1.95-2.00 (m, 1 H) 3.74-3.82 (m, 1 H); HRMS $[M+H]^+$ calcd. 225.1674 found 225.1675. ^{31}P NMR ($CDCl_3$, 121.5 MHz) **6g**-CDA analysis δ 145.06 (2), δ 143.01 (98) (Fig. 16).

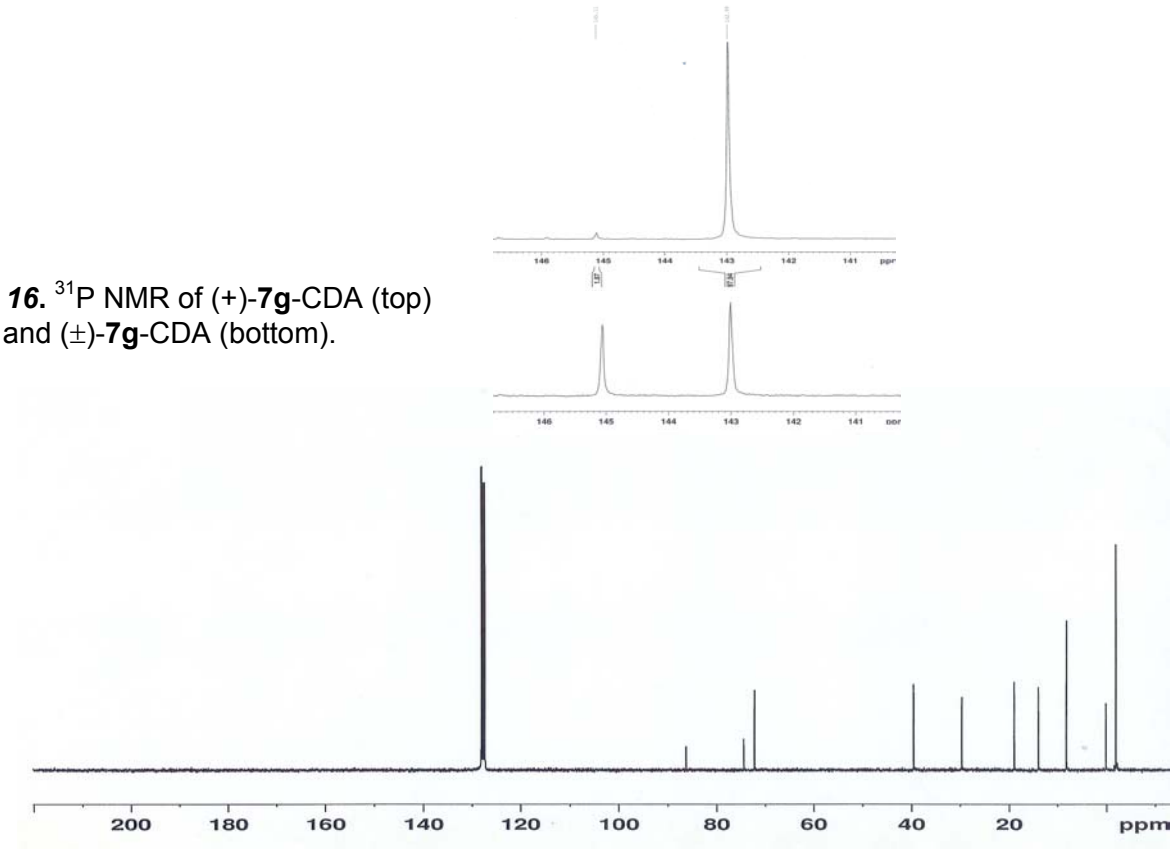
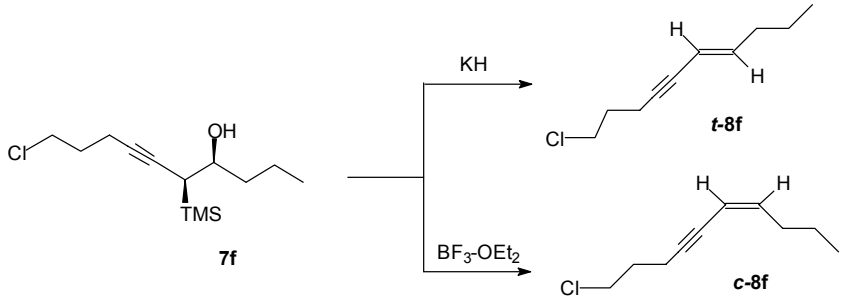


Figure 16. ^{31}P NMR of (+)-**7g**-CDA (top) and (±)-**7g**-CDA (bottom).

Figure 17. ^{13}C NMR spectrum of **7g**. No diastereomers are observed.

Determination of the absolute stereochemistry: (*R*)-4-octanol ((-)-*R*-9b): Prepared by the homo-Brook rearrangement of **7b**:[2] To a solution of (+)-**7b** in pentane (1.0 mmol, 0.198 g in 10 mL of pentane) Pd/C (0.06 g, 10 wt %) was added and the reaction mixture was flushed with $N_{2(g)}$. A balloon filled with $H_{2(g)}$ was inserted into the septum of the sealed reaction flask and the reaction was stirred for 3 h at 25 ºC. The reaction mixture was then dried over $MgSO_4$, filtered, and concentrated to yield 5-TMS-4-octanol in 98% yield (0.197 g, 0.98 mmol). To the crude reaction mixture, 30 mL of a 5% solution of KO(Bu-*t*) in 19:1 DMSO:H_2O solution was added at 25 ºC and stirred for 4 d. The reaction mixture was then poured over an ammonium chloride solution (1 M in water) over laid with ether. The ethereal phase was dried with $MgSO_4$, filtered, and concentrated to yield the known **(-)-*R*-9b** in 85% yield (0.83 mmol, 0.11 g). $[\alpha]_D^{22}$ = -0.65 (neat); lit.[3] for (*S*)-octanol: $[\alpha]_D^{25}$ = + 0.75º (neat).

Determination of the relative stereochemistry: *trans*-1-Chlorodec-6-en-4-yne (*t*-8f): Prepared by the KH mediated Hudrlik elimination.[4] To a solution of **7f** (2.0 mmol, 0.52 g) in Et_2O (10 mL) KH (2 mL, 1.0 M in pentane) was added at 25 ºC. The reaction was stirred for 1 h and quenched by the slow addition of water (10 mL). The reaction mixture was washed with water (3 x 20 mL) and the combined organic phase was dried over $MgSO_4$ and concentrated to yield ***t*-8f** in 95% yield (0.33 g, 1.9 mmol). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 16.9, 29.8, 29.8, 31.6, 35.1, 43.8, 80.3, 86.4, 109.7, 143.9 (Fig. 18); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, *J*= 7.3 Hz, 3 H), 1.35-1.49 (m, 2 H), 1.90-2.00 (m, 2 H), 2.00-2.15 (m, 2 H), 2.48-2.51 (m, 2 H), 3.66 (t, *J*= 6.4 Hz, 2 H), 5.34 (dt, *J* = 15.8, 1.0 Hz, 1 H), 5.96 (dt, *J*= 15.8, 7.9 Hz, 1 H) (Fig. 19). Anal cald. for $C_{10}H_{15}Cl$ C: 70.37 H: 8.86 Found C: 70.52 H: 8.78.



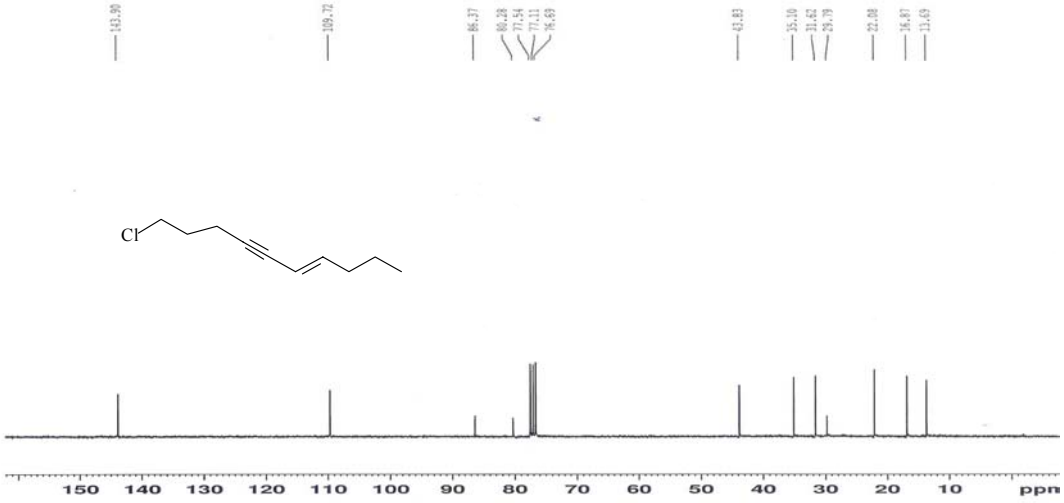


Figure 18. ^{13}C NMR spectrum of ***t*-8f**.

***cis*-1-Chlorodec-6-en-4-yne (*c*-8f):** Prepared by the $BF_3{\cdot}OEt_2$ mediated Hudrlik elimination.[4] To a solution of **7f** (2.0 mmol, 0.52 g) in Et_2O (10 mL), $BF_3{\cdot}OEt_2$ (0.5 mL) was added at 0 ºC and stirred for 1 h. The reaction mixture was allowed to slowly reach 25 ºC over a period of 1 h and the organic phase was washed with Na_2CO_3 (3 x 20 mL, 1.0 M in water,). The combined organic phase was concentrated to yield ***c*-8f** in 97% yield (1.94 mmol, 0.33 g). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.8, 17.0, 22.2, 43.8, 78.5, 92.1, 109.2, 143.1; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94 (t, *J*= 7.36 Hz, 3 H), 1.35-1.48 (m, 2 H), 1.90-2.11 (m, 2 H), 2.25-2.30 (m, 2 H), 2.51-2.59 (m, 2 H), 3.70 (t, *J*= 6.4 Hz, 2 H), 5.33 (ad, *J*= 10.7 Hz, 1 H), 5.75 (dt, *J*= 10.7, 4.5 Hz, 1 H) (Fig. 19).

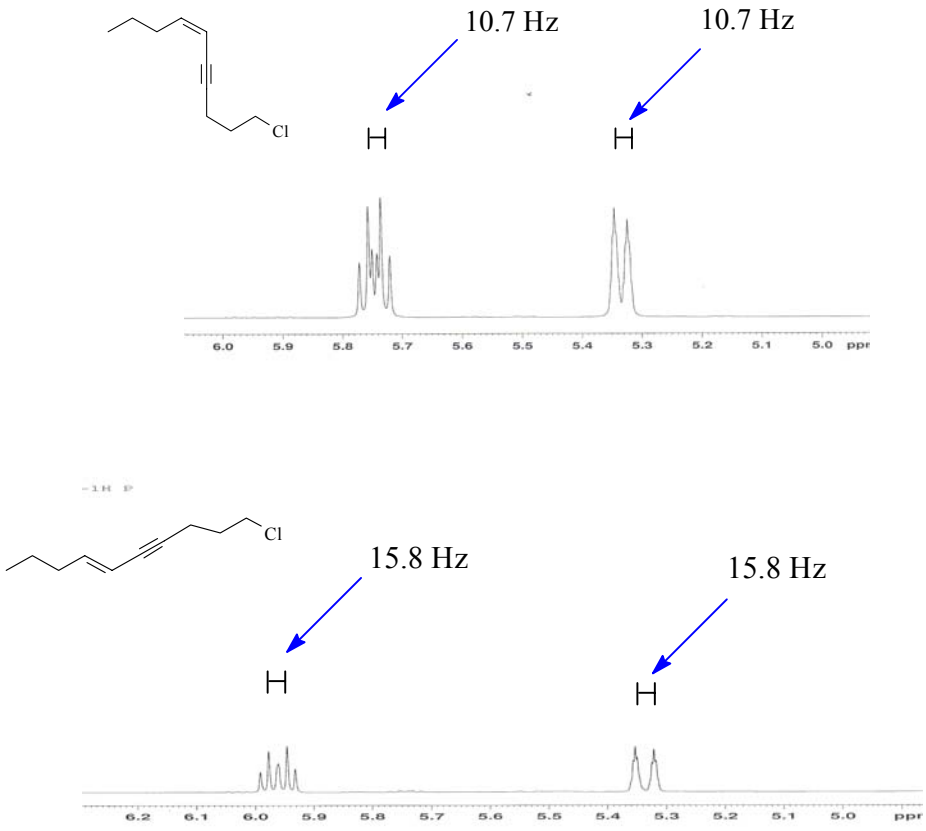


Figure 19. Expansion of alkene region in the ^{1}H NMR spectra of ***c*-8f** (top) and ***t*-8f** (bottom).

Procedure for the preparation of 10: ***B*-(3-Methylbut-3-en-1-ynyl)-10*S*-trimethylsilyl-9-borabicyclo[3.3.2]decane (-)-2d*S*:** To a 1 M suspension of (-)-**6*S*** (3 mmol, 1.19 g) in Et_2O (10 mL) 3-methylbut-3-en-1-ynylmagnesium bromide (3.0 mmol, 3 M, in Et_2O) was transferred via cannula at -78 ºC and stirred for 1 h. The solution was allowed to reach room temperature for an additional 0.5 h before TMSCl was added (0.8 mL) at -78 ºC removing the bath 10 min after the addition. After 0.5 h, the solvents were removed under vacuum and the crude was washed with pentane (3 x 20 mL) and filtered through a Celite plug. The solvents were concentrated once more to obtain (-)-**2d** in 98% yield (0.80 g, 2.94 mmol). $[\alpha]_D^{20}$ = -102.8 (*c* 2.6 , C_6D_6); ^{11}B NMR (C_6D_6, 96 MHz) δ 72; ^1H NMR (C_6D_6, 300 MHz) δ 0.36 (s, 9 H), 1.53- 1.77 (m, 12 H), 1.87 (m, 3 H), 1.89- 1.96 (m, 2 H), 2.37- 2.46 (m, 2 H), 5.14 (t, *J*= 1.8 Hz, 1 H), 5.48 (q, *J*= 0.9 Hz, 1 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 1.4, 22.3, 23.1, 25.3, 25.9, 29.3, 31.5, 33.8, 35.1, 42.0, 99.9, 120.4, 123.1 (Fig. 20).

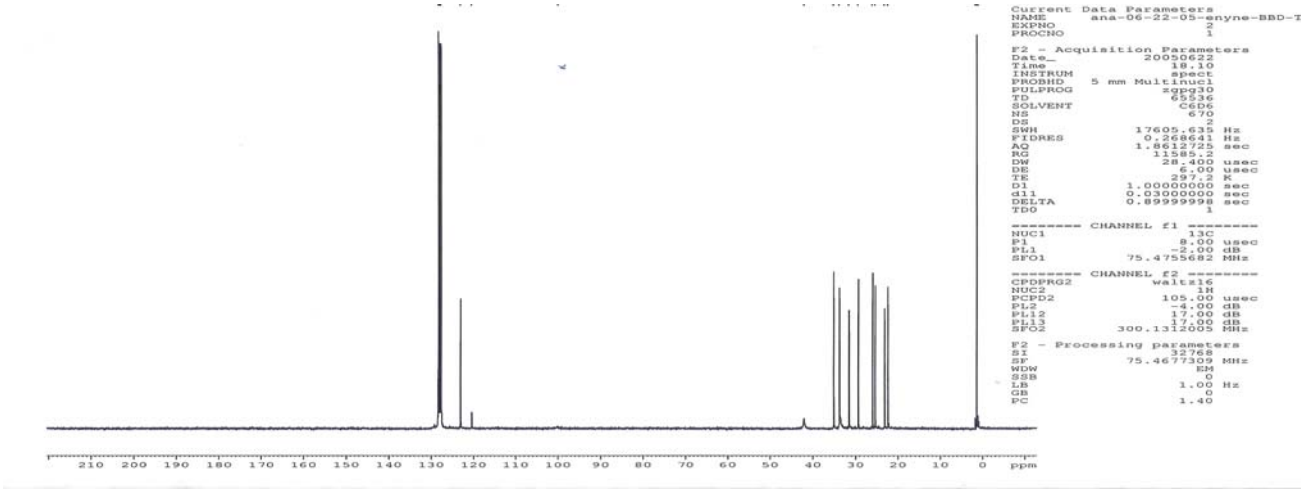


Figure 20. ^{13}C NMR of **2d**.

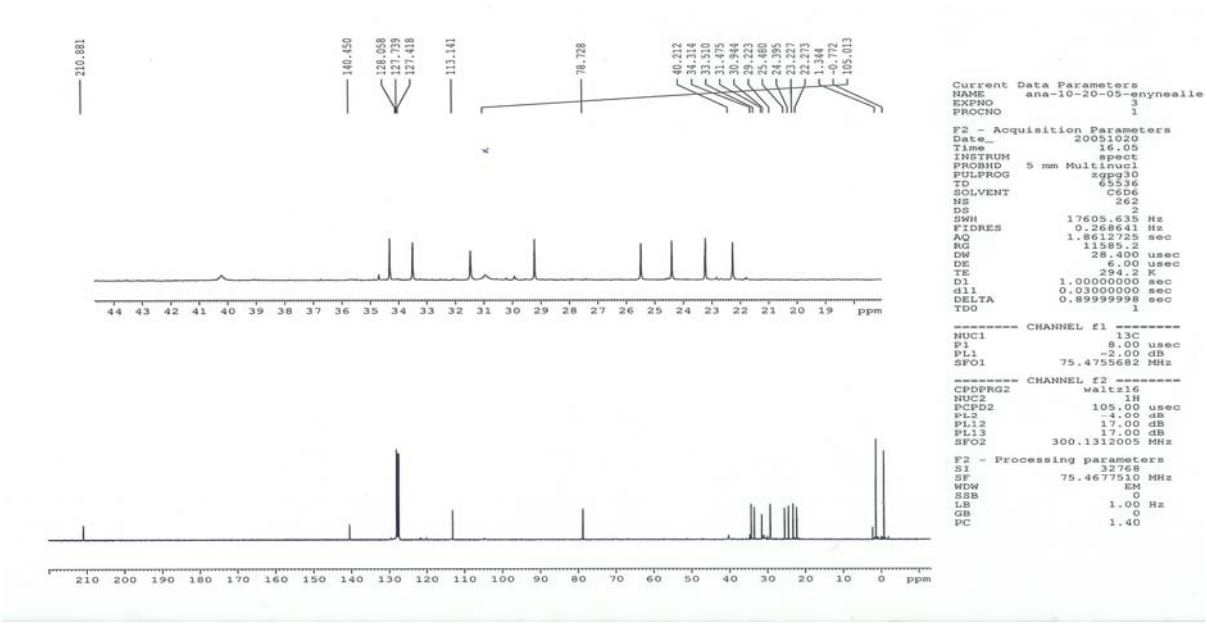


Figure 21. ^{13}C NMR of **1d**.

B*-(α-Isopropenyl-γ-trimethylsilylallenyl)-10*S*-trimethylsilyl-9-borabicyclo[3.3.2]decane ((+)-1d*S*)).** To a 1.0 M solution of (+)-**2d** in pentane (2.94 mmol) trimethylsilyldiazomethane ($TMSCHN_2$) was added (1.7 mL, 2M solution in hexanes) dropwise at room temperature. The reaction was complete after 3 h as revealed by ^{11}B NMR analysis (pentane, 96 MHz) δ 78. The solvents were removed to obtain (+)-**1d** in quantitative yield (0.78 g, 2.94 mmol). $[\alpha]_D^{20}$ = + 9.4 (*c* 1.4 , C_6D_6); ^{1}H NMR (C_6D_6, 300 MHz) δ 0.16 (s, 9 H), 0.23 (s, 9 H), 1.49- 1.95 (m, 18 H), 4.71 (t, *J*= 3.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -0.6, 1.5, 15.7, 21.9, 24.7, 25.4, 29.2, 29.9, 31.3, 34.1, 35.1, 36.5, 74.8, 92.7, 214.0 (Fig. 21). (")-**2d** gives (")-**1d** and (-)-**2d** gives (-)-**1d*R.

(+)-(*R*)-*E*-1-Phenyl-3-methyl-6-trimethsilylhexa-4,5,6-triene-1-ol (10). Prepared from **1d*R***. To a 1 M solution of **1d*R*** (2.94 mmol) in THF cooled to -78 ºC , benzaldehyde (3.0 mmol) was added dropwise. After 3 h, the reaction mixture was raised to 25 ºC and 7.2 phosphate buffer solution in water was added followed by NaOH (2.0 mL, 3 M in water) and H_2O_2 (0.9 mL, 30 wt% in water) and the mixture was refluxed for 2 h. Upon cooling the crude was poured over water (30 mL) overlaid with Et_2O (10 mL). The organic phase was washed with brine (3 x 20 mL) and the organic phase was dried over $MgSO_4$, concentrated, and purified by silica gel column chromatography (95:4:1 Hexane: Et_2O: TEA) to obtain **10** in 70% yield (2.05 mmol, 0.53 g). ^{13}C NMR ($CDCl_3$, 75 MHz) δ –1.00, 25.2, 48.5, 72.4, 105.7, 122.1, 125.8, 127.5, 128.4, 143.7, 158.5, 171.9 (Fig. 22); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10-0.30 (s, 9 H), 2.01 (s, 3 H), 2.52 (bs, 1 H), 2.55-2.60 (m, 2 H), 5.00 (bs, 1 H), 6.52 (s, 1 H),7.23-7.39 (m, 5 H). $[\alpha]_D^{25}$= + 25.0 (*c* 5.0, $CDCl_3$). **10**-CDA Analysis ^{31}P NMR δ145.37 (>99.5) and 135.74 (<0.5).

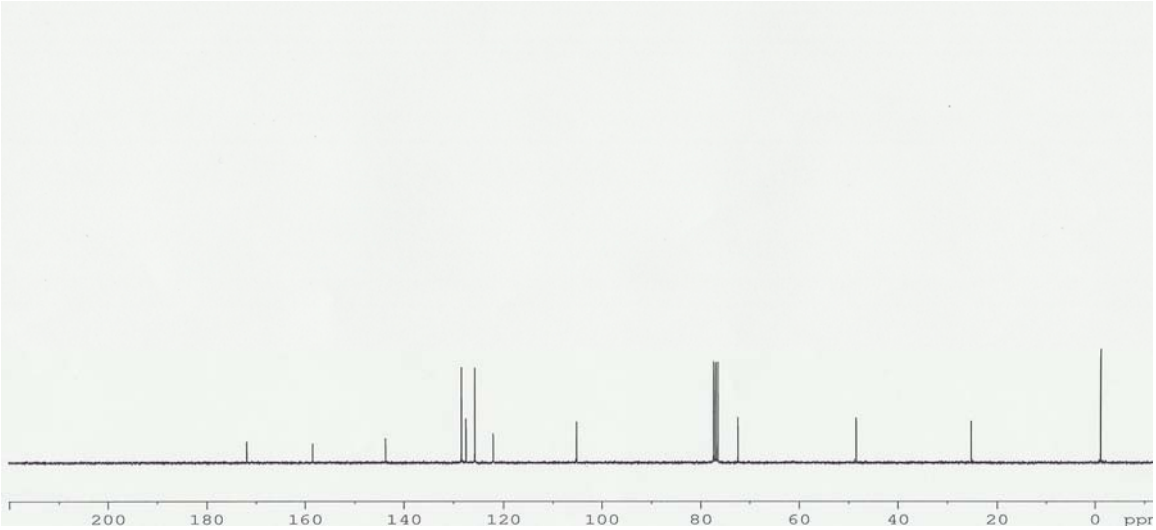


Figure 22. ^{13}C NMR of **10**.

Determination of the absolute stereochemistry of 10. (*R*)-4-hydroxy-4-phenyl-2-butanone (11): A 0.25 M solution of **10** (2.0 mmol) in CH_2Cl_2 was cooled to -78 ºC and ozone was bubbled through the solution until a consistent blue color was observed. The solution was maintained at -78 ºC and stirred for an additional 0.5 h. The solution was raised to room temperature and flushed with $N_{2(g)}$ to remove excess ozone. Upon concentration the β-hydroxy ketone **11** was obtained in 90% yield. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.7, 51.9, 69.8, 125.6, 127.6, 128.5, 142.7, 209.0 (Fig. 23); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, 3 H), 2.82-2.89 (m, 2 H), 3.43 (bs, 1 H), 5.16 (dd, *J*= 3.6, 8.7 Hz, 1H). $[\alpha]_D^{22}$= + 54.2 (*c* 10.0, $CHCl_3$) lit:[5] for the (*R*)-4-hydroxy-4-phenyl-2-butanone $[\alpha]_D^{20}$= + 40.9 (*c* 10.3 $CHCl_3$, 57% ee).

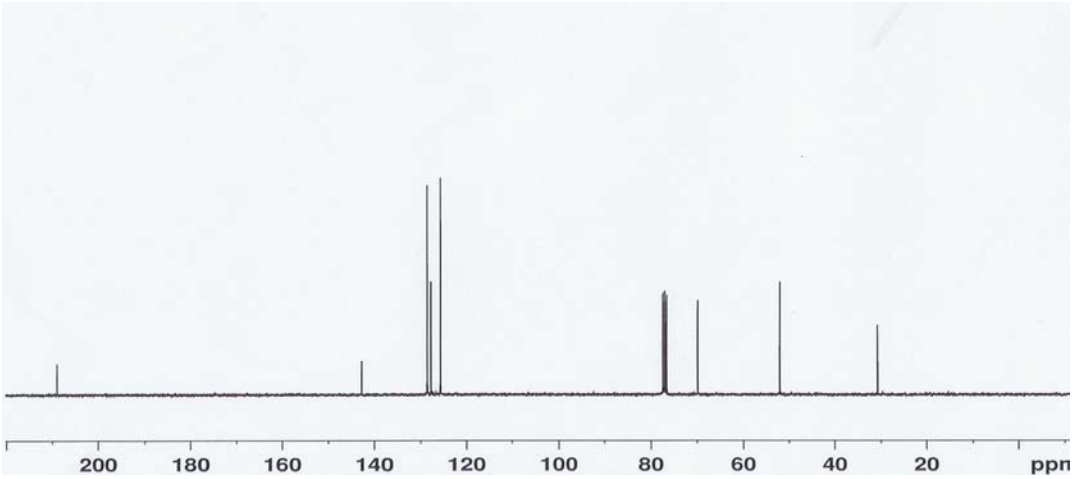


Figure 23. ^{13}C NMR of **11**.

Preparation of (")-*syn/anti* mixtures of 7f. *B*-(5-chloropent-1-ynyl)-10-phenyl-9-borabicyclo-[3.3.2]decane. A solution of *B*-MeO-10-Ph-BBD[6] (1.19 g, 3.0 mmol) in Et_2O (10 mL) was cooled to -78 ºC and a solution of 5-chloropentynylmagnesium bromide (3 mL, 1.0 M in Et_2O) was added dropwise. The solution was stirred for 1h at -78 ºC. The ^{11}B NMR (Et_2O, 96 MHz) spectra of the crude reaction mixture showed two peaks δ 72 (~ 75%) and the ''double addition'' product δ -15 (25%). Using standard techniques to prevent the exposure of the borane to the open atmosphere, the solution was concentrated under vacuum, the residue was washed with pentane (6 x 10 mL) and these washings were filtered through a celite pad. The filtrate was concentrated once more to obtain the crude mixture. ***B*-[α-(γ-chloropropyl)-γ-trimethylsilylallenyl]-10-phenyl-9-borabicyclo[3.3.2]decane.** To a pentane solution of the above mixture of *B*-(5-chloropent-1-ynyl)-10-Ph-borabicyclo[3.3.2]decane (~75%)**,** $TMSCHN_2$ was added (2.0 mL, 2 M solution in hexanes) dropwise at 0 ºC. The reaction is complete after 1 h as shown by ^{11}B NMR analysis (hexane, 96 MHz) δ 78 (~75%, the double addition product was still present in the reaction mixture). The solvents were removed to obtain *B*-[α-(γ-chloropropyl)-γ-trimethylsilylallenyl]-10-Ph-9-borabicyclo [3.3.2]decane quantitatively based upon the starting material purity. ***syn/anti* – (")-7f** (Fig. 24). In a 1 M solution of *B*-[α-(γ-chloropropyl)-γ-trimethylsilylallenyl]-10-phenyl-9-borabicyclo[3.3.2]decane in THF, butyraldehyde (2.25 mmol) was added dropwise at 25 ºC and the reaction mixture was stirred for 1 h. Upon oxidative work-up the diastereomeric mixture was obtained in 76% yield.

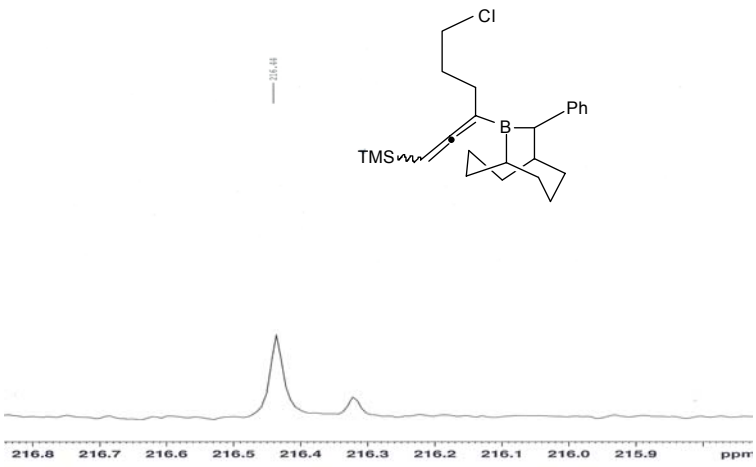


Figure 24. ^{13}C NMR spectra of the center carbon allenyl signals for the isomeric (")-*B*-[α-(γ-chloropropyl)-γ-trimethylsilylallenyl]-10-phenyl-9-borabicyclo[3.3.2]decane.

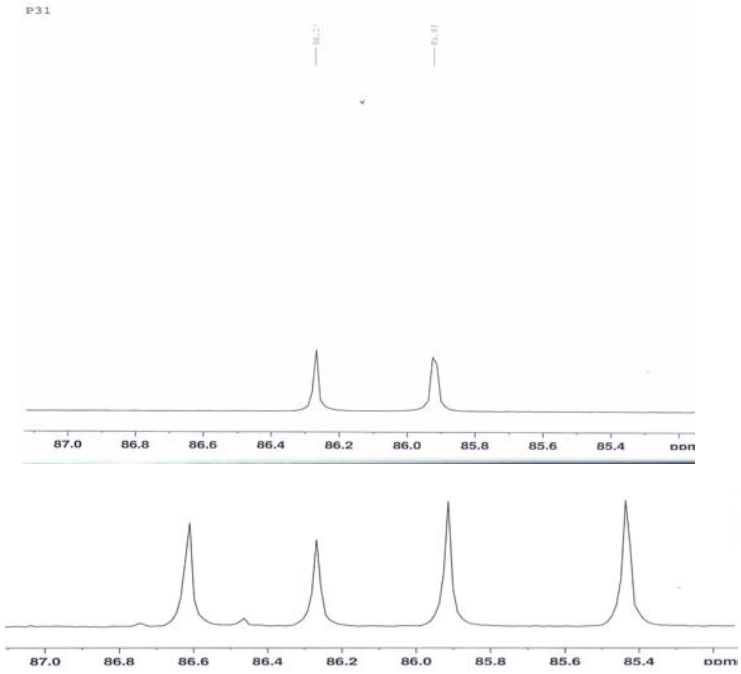


Figure 25. ^{31}P NMR spectra of **7f-**CDA derivatives resulting from the allenylboration of butyraldehyde with (")-**1b** (top) and its 10-Ph analogue (bottom). The above spectrum reveals the signals derived from the (")-*syn*-**7f** while the bottom spectrum shows additional signals derived from the (")-*anti* alcohols.

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