Supplementary Material

B-Allenyl- and *B*-(γ-Trimethylsilylpropargyl)-10-Ph-9-borabicyclo[3.3.2]decanes: Asymmetric Synthesis of Propargyl and α-Allenyl 3E-Carbinols from Ketones

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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 and DRX-500 spectrometers. ^{1}H (300 MHz), ^{13}C (75 MHz), ^{31}P (121.5 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. Standard COSY, HETCOR and DEPT experiments were performed to establish NMR assignments for the compounds discussed in this work. We use the term ad (apparent doublet) for ab patterns where δ and *J* values can not be directly determined from the spectra. Infrared spectra were recorded on a Nicolet 740 GC FT-IR, 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), Fisons VG Autospect or a Hewlett-Packard 5971A Mass Selective Ion Detector. High-resolution mass spectral data were obtained with a Micromass VG AutoSpec magnetic sector mass spectrometer (70 eV). Optical rotations were measured employing a Perkin-Elmer 243B polarimeter. Ozonolyses were conducted with a Polymetrics Laboratory Ozonator Model T-408 operating at 70 V (O_2 pressure = 8 psig, flow rate = 0.46 (nominal)). Literature citations are provided for all known compounds together with a repeat of the spectral data with data obtained in this study to consolidate this information herein.

(±)-*B*-Methoxy-10-phenyl-9-borabicyclo[3.3.2]decane ((±)-3).[1] To a solution of *B*-MeO-9-BBN (18.0 g, 118 mmol) in hexanes (110 mL), $PhCHN_2$[2] in hexanes (130 mmol, 2 M) was added dropwise at 0 °C. The mixture was stirred for 10 h and the solvents were removed under vacuum. The residue was distilled to give 25.7 g of (±)-**3** (90%, bp 120 °C, 0.10 mm Hg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30-2.0 (m, 14H), 2.40 (m, 1H), 3.51 (s, 3H), 7.1-7.4 (m, 5H) ^{13}C NMR (75 MHz, C_6D_6) δ 21.5, 24.3, 26.5, 28.0, 29.1, 31.6, 38.8, 43.1, 53.7, 125.0, 128.1, 129.0, 130.4, 145.0; (Figure 1); IR (cm $^{-1}$) 3020. 2908, 2851, 1467, 1323, 1288, 1254, 749, 717, 697; ^{11}B NMR (96 MHz, C_6D_6) δ 55.5. HRMS $[M+H]^+$calcd. 242.18 found 242.15

(+)-(1*S*,2*S*)-*N*-Methylpseudoephedrinyl)-(10*S*)-phenyl-9-borabicyclo[3.3.2]decane ((+)-4*S*).[1] To a solution of 1*S*, 2*S*-*N*-methylpseudoephedrine (5.0 g, 27.9 mmol) in hexane (60 mL) was added to (±)-**3** 13.5 g, 55.8 mmol) dropwise. The reaction mixture was refluxed for 6 h and slowly cooled to room temperature resulting in small square, clear crystals. The supernatant was decanted via cannula and the crystals were washed with hexane (3 x 20 mL) and dried *in vacuo* to give 4.2 g (10.8 mmol) of **(+)-4*S*** (38% yield). The supernatant was concentrated, fresh hexane (60 mL) was added and the mixture was refluxed for an additional 6 h. Upon cooling, a second batch of crystals are obtained following the before mentioned work-up. The second collection gives 4.4 g (11.2 mmol) of **(+)-4*S***. The overall yield of **(+)-4*S*** is 79 % (39.5% based upon (±)-**3**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (s, 3H), 1.32 (m, 2H), 1.75-2.0 (m, 11H) 2.45 (m, 7H), 2.85 (m, 1H), 4.28 (m, 1H), 6.95-7.66 (m, 10H); ^{11}B NMR (96 MHz, $CDCl_3$) δ 55.5, 10.0; mp = 130- 140 °C; Anal. calcd for C 80.20, H 9.32, found C 79.99, H 9.44. $[\alpha]_D^{22}$ = + 66.3 (*c* = 4.5, CH_2Cl_2). In the recovery processes described below, (-)-**8*S*** ($[\alpha]_D^{20}$ = -22.6 (*c* = 1.3, CH_2Cl_2)) was obtained as an air-stable crystalline compound which can be used for the generation of either (+)-**1*S*** or (+)-**2*S***.

(-)-(1*R*,2*R*)-*N*-Methylpseudoephedrinyl)-(10*R*)-phenyl-9-borabicyclo[3.3.2]decane ((-)-4*R*).[1] The above supernatant was concentrated and the resulting residue was dissolved in hexane (60 mL) and mixed with 1*R*,2*R*-*N*-methylpseudoephedrine (5.0 g, 27.9 mmol).[3] The reaction mixture was refluxed for 6 h, whereupon it was slowly cooled to room temperature forming small square, clear crystals. The supernatant was decanted via cannula and the crystals were washed (3 x 20 mL) with hexane and dried *in vacuo* to give 4.1 g (10.5 mmol) of **(-)-4*R***. The supernatant was concentrated, fresh hexane (60 mL) was added and the mixture was refluxed for an additional 6 h. Upon cooling, a second batch of crystals (2.0 g) were obtained following the above work-up. The overall yield of **(-)-4*R*** is 56 % (28 % based upon (±)-**3**). mp = 135-140 °C; $[\alpha]_D^{25}$ = - 66.6 (*c* = 4.5, CH_2Cl_2). The 1*S*,2*S*-pseudoephedrine can also be used to convert the residual ***3R*** into crystalline (+)-**8*R***.[1]

B*-Allenyl-(10*S*)-phenyl-9-borabicyclo[3.3.2]decane ((+)-1*S*)** To a solution of (+)-**4*S (3.7 g, 9.4 mmol) in ether (47 mL), a solution of freshly prepared allenylmagnesium bromide (11.0 mL) was added (dropwise) at 25°C. The solution was allowed to stir for 1 h. Using standard techniques to prevent exposure of the borane to the open atmosphere, the solution was concentrated under vacuum, the residue was washed with hexane (5 x 10mL) and

these washings were filtered through a celite pad. Solvents were removed to obtain 1.9 g (84%) of (+)-**1*S***. ^{13}C NMR (C_6D_6, 75 MHz) δ 23.5, 27.4, 28.1 (broad singlet), 28.2, 29.0, 34.4, 40.5, 52.3 (broad singlet), 68.6, 90.6 (broad singlet), 124.7, 128.1, 130.0, 146.6, 220.7 (Fig. 1); ^{11}B NMR (C_6D_6, 96 MHz) δ 80.1; HRMS (M^+ + 2H) *m/z* calcd for $C_{18}H_{23}B$ 252.20, found 252.19; $[\alpha]_D^{20}$ = +29.8 (c 1.92, C_6D_6). Alternatively, (+)-**1*S*** can be prepared from (-)-**8*S***.

B*-Allenyl-(10*R*)-phenyl-9-borabicyclo[3.3.2]decane** ((-)-**1*R) is prepared by the same procedure starting with **(-)-4*R*;** $[\alpha]_D^{20}$ = -29.2 (c 1.92, C_6D_6). Alternatively, (-)-**1*R*** can be prepared from (+)-**8*R***. Other data are essentially identical to (+)-**1*S***.

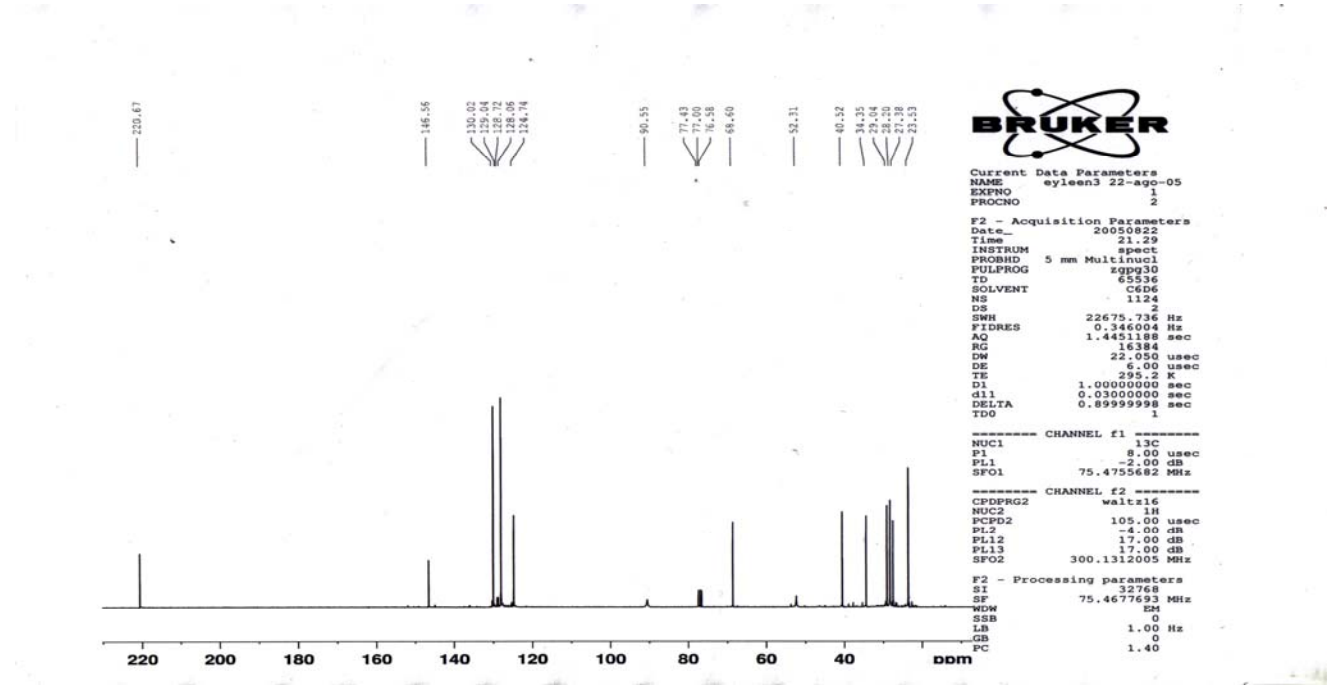
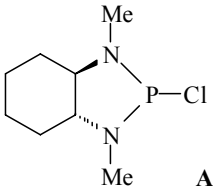


Figure 1. ^{13}C NMR of *B*-Allenyl-10-phenyl-9-borabicyclo[3.3.2]decane (**1**).

General procedure for the recovery of *N*-methylpseudoephedrine from the generation of 1. The white solid obtained from the Celite filtration is transferred to a flask containing 100 mL of water and stirred for 5 h. The aqueous solution is washed with Et_2O (4 X 30 mL) and concentrated to obtain 0.46 g (86%) of recovered *N*-methylpseudoephedrine.

Determination of enantiomeric purity: The enantiomeric purity was determined by the ^{31}P NMR (121 MHz, $CDCl_3$) CDA reagent developed by Alexakis using the reported procedures.[4] All samples were calibrated with the phosphoramide **A** (δ 184.0).



A

General procedure for the preparation of racemic homopropargylic alcohols (")-6a-i. A 1 M solution of allenylmagnesium bromide in Et_2O (5 mmol) was cooled to 0°C and the ketone (3.0 mmol) was added *via* syringe dropwise. After stirring for 4 h at 25 ºC, the reaction mixture was poured over ammonium chloride solution (1 M, 20 mL) and washed with Et_2O (3 X 10 mL). The combined organic phase was washed with brine solution (3 X 20 mL) and was dried over $MgSO_4$. Upon the removal of solvents under vacuum, (")-**6** was obtained in ~95% yield.

Procedures for the allenylation of ketones with (+)-1*S* or (-)-1*R*:

(+)-(*S*)-2-Phenyl-4-pentyn-2-ol (6a*S*).[5] A solution of **(+)-1*S*** (0.75 g, 3 mmol) in ethyl ether (30 mL) was cooled to -78 °C and acetophenone (0.36 g, 3.0 mmol) was added. After 3 h the solution was warmed to room temperature

and treated with NaOH (3 M, 9 mmol) and H_2O_2 (30%, 6.0 mmol). This mixture was heated at reflux for 1 h. The residue was extracted with ethyl ether (3x 10 mL) and distilled (100 °C at 15 mm Hg (kugelrohr)) to obtain 0.36 g (74%) of **6a*S*** (91% ee). $[\alpha]_D^{27}$ = + 25.0 (c = 2.2, $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 3H), 2.06 (t, *J* = 2.6 Hz), 1H), 2.41 (s, 1H), 2.66-2.81 (m, 2H), 7.26-7.30 (m, 1H), 7.34-7.39 (m, 2H), 7.50-7.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.2, 34.6, 71.7, 73.2, 80.4, 124.7, 127.1, 128.2, 146.3 (Fig. 2). All experimental data for these compounds were in complete agreement with those reported.[5] The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphopholidine derivative **CDA-6a**. Analysis of the peaks areas for δ 138.4 and 139.5 ppm revealed a 50:50 ratio for the racemic diazaphopholidine and a 95.5:4.5 ratio (91% ee) for the non-racemic material.

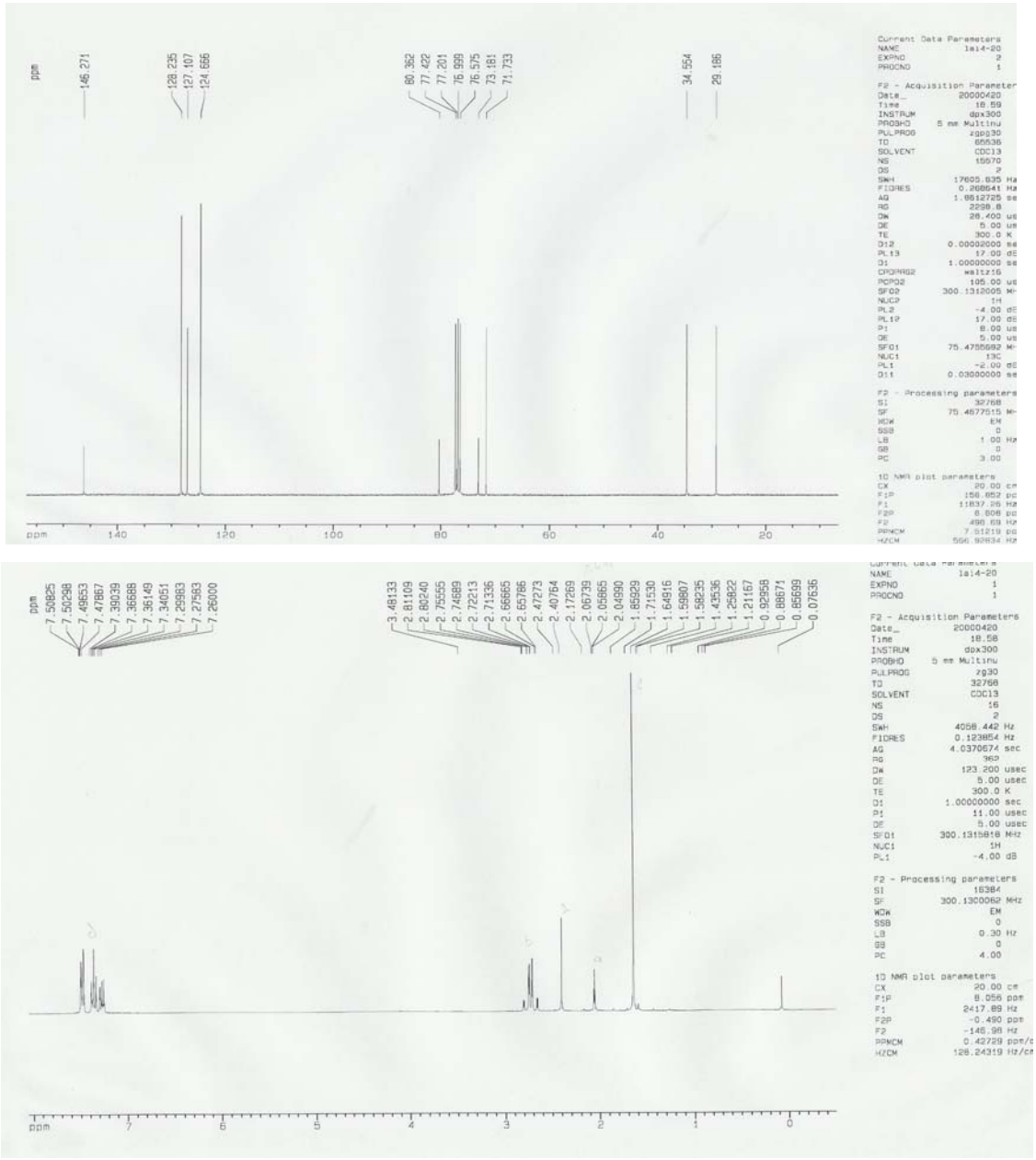


Figure 2. ^{13}C and ^{1}H NMR of homopropargylic alcohol **6a**.

(*R*)-2-Phenyl-4-pentyn-2-ol (6a*R*): A solution of **(-)-1*R*** (1.25 g, 5.0 mmol) in ethyl ether (50 mL) was cooled to -78 °C and acetophenone (0.18 g, 2.5 mmol) was added dropwise. After 3 h, the reaction solution was warmed to room temperature and the solvents were removed to yield the borinate intermediate **5**. The (1*S,2S*)-

pseudoephedrine (0.83 g, 5.0 mmol) was added followed by hexane (8 mL) and the mixture was heated to reflux for 3 h. The solution was allowed to cool while complex **(-)-8*R*** precipitated out of solution. These crystals were separated and washed with hexane (3 x 10 mL) to yield 1.51 g (80%) of **(+)-8*R***. The residue was distilled to obtain 0.61 g (85%) of **6a*R*.** The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphospholidine derivative **CDA-6a**. Analysis of the peaks areas for δ138.4 and 139.5 ppm revealed a 50:50 ratio for the racemic diazaphospholidine and 3.5:96.5 ratio (93% ee) for the non-racemic material (Fig. 3).

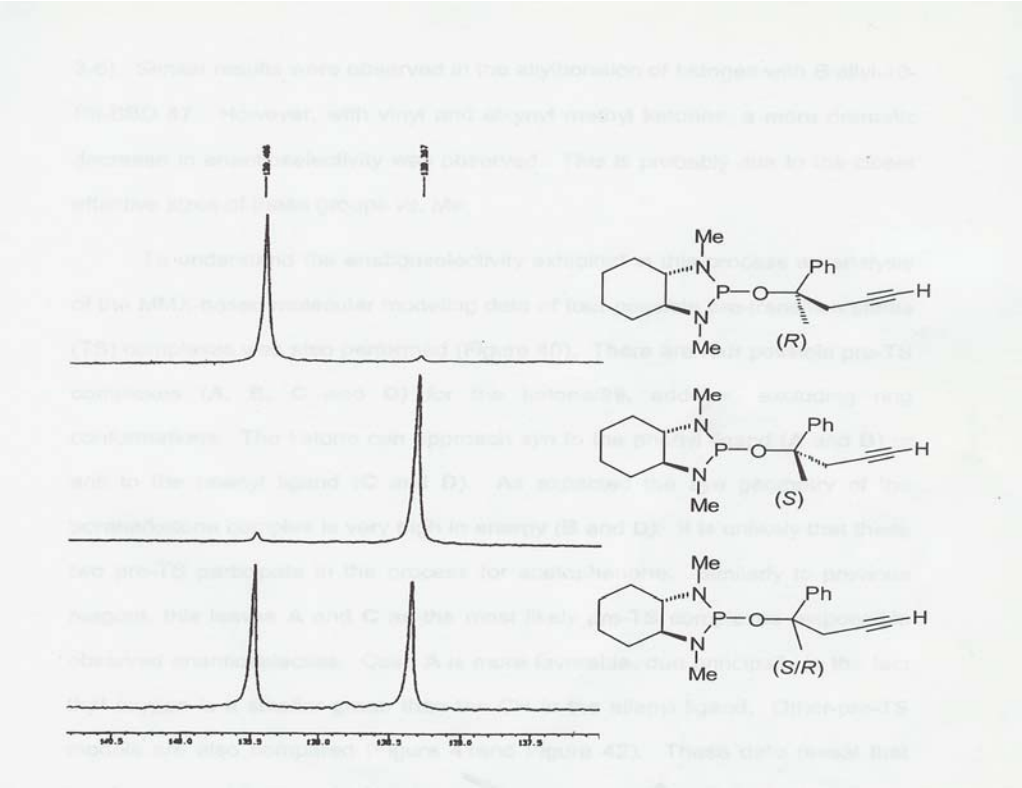
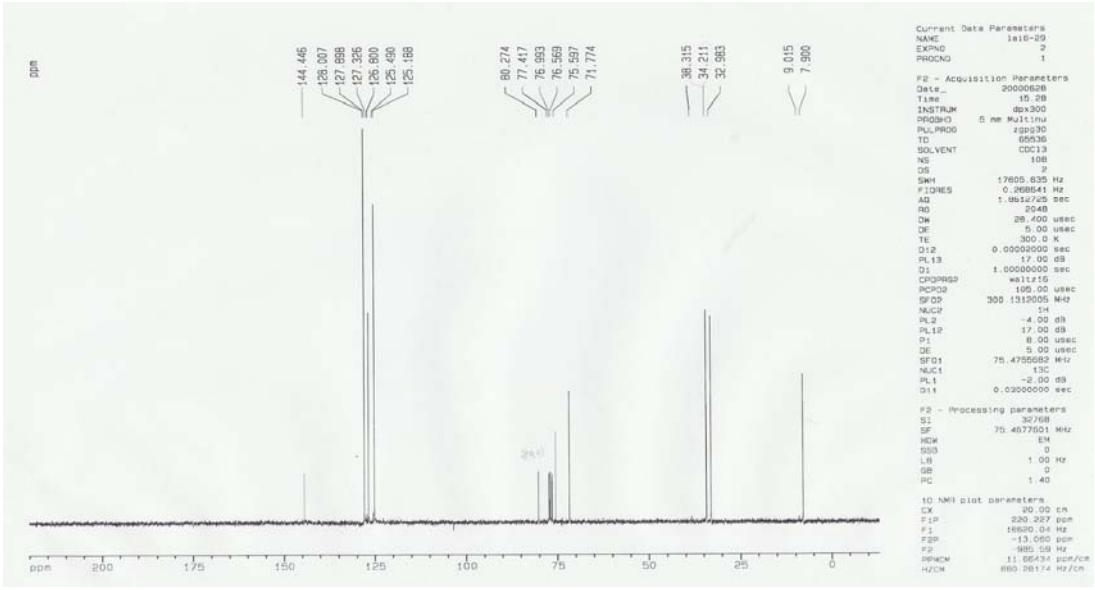


Figure 3. ^{31}P NMR of CDA-**6a*R*** (top), CDA-**6a*S*** (middle), and CDA-**6a-rac** (bottom).

(+)-(*R*)-3-Phenyl-5-hexyne-3-ol (6b*R*).[6] A solution of **(-)-1*R*** (0.71 g, 2.8 mmol) in ethyl ether (30 mL) and propiophenone (0.32. g, 2.4 mmol) was added dropwise at room temperature. After 2 da, NaOH (3 mL of 3 M) and H_2O_2 (6 mmol, 30 %) was added to the borinate **5b** and the mixture was refluxed for 1 h. The organic layer was washed with water (3 x 10 mL) and dried over magnesium sulfate. The residue was distilled (82-85 °C at 1.2 mm Hg) to obtain 0.27 g (65%) of **6b** (76% ee). $[\alpha]_D^{28}$ = +19.4 (c 1.2, $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (t, *J* = 7.5 Hz, 3H), 1.85-2.04 (m, 3H), 2.45 (br s, 1H), 2.69-2.83 (m, 2H), 7.25-7.30 (m, 1H), 7.35-7.39 (m, 2H), 7.40-7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.8, 33.0, 34.2, 71.8, 75.6, 80.3, 125.2, 126.9, 128.1, 144.5 (Fig. 4). All experimental data for these compounds were in complete agreement with those reported.[6] The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphospholidine derivative **CDA-6b**. Analysis of the peaks areas for δ 137.7 and 138.9 ppm revealed a 50:50 ratio for the racemic diazaphospholidine and 88:12 ratio (76% ee) for the non-racemic material.



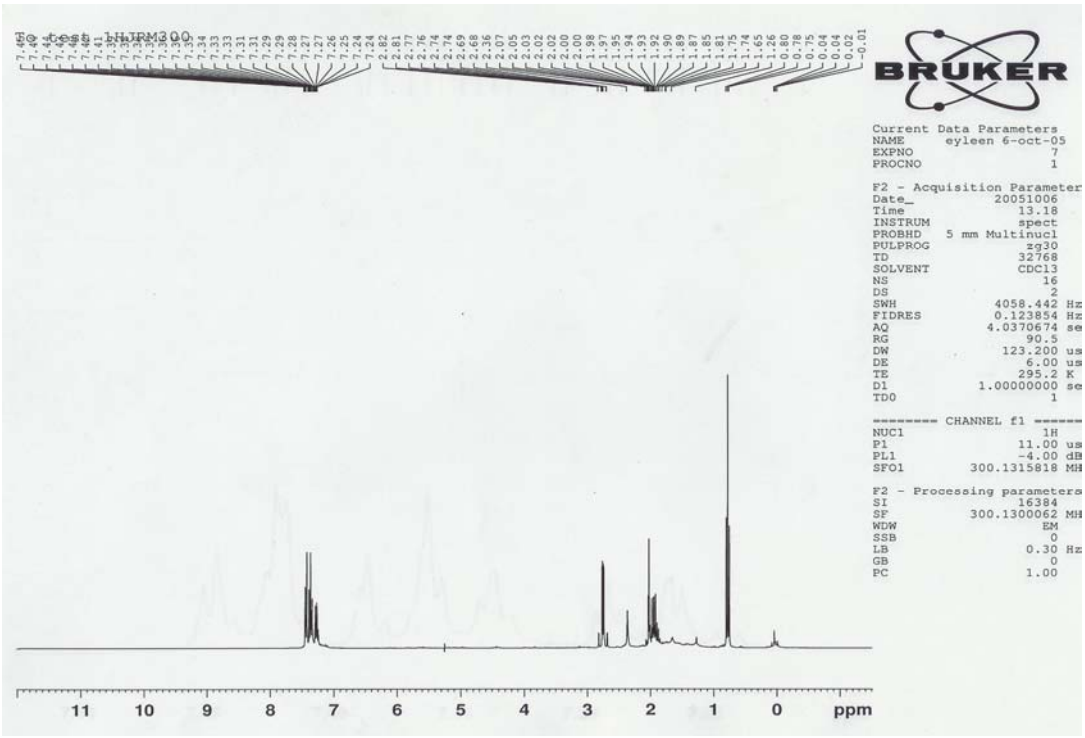


Figure 4. ^{13}C and ^{1}H NMR of homopropargylic alcohol **6b**.

(+)-(*S*)-3-Methyl-5-hexyn-3-ol (6c*S*).[7] A solution of **(-)-1*R*** (1.25 g, 5.0 mmol) in ethyl ether (50 mL) was cooled to -78 °C and 2-butanone (0.18 g, 2.5 mmol) was added dropwise. After 3 h, the reaction solution was warmed to room temperature and the solvents were removed to yield the borinate intermediate **5c**. The (1*S,2S*)-pseudoephedrine (0.83 g, 5.0 mmol) was added followed by hexane (8 mL) and the mixture was heated at reflux for 2 h. The solution was allowed to cool and complex **(-)-8*R*** precipitates from solution. These crystals were separated and washed with hexane (3 x 10 mL) to yield 1.53 g (81%) of **(+)-8*R***. The residue was distilled (86-88 °C at 74 mmHg) to obtain 0.20 g (71%) of **6c*S*** (74% ee). $[\alpha]_D^{28}$ = +6.2 (c = 0.8, $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.6 Hz, 3H), 1.25 (s, 3H), 1.54-1.64 (m, 2H), 1.77 (s, 1H), 2.07 (t, *J* = 2.7 Hz, 1H), 2.35-2.36 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.3, 25.6, 31.7, 33.5, 71.0, 71.7, 80.9 (Fig. 5). All experimental data for these compounds were in complete agreement with those reported.[7] The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphospholidine derivative after addition of S_8 **CDA-6c**. Analysis of the peaks areas for δ 79.9 and 80.1 ppm revealed a 50:50 ratio for the racemic diazaphospholidine and 13:87 ratio (74% ee) for the non-racemic material.

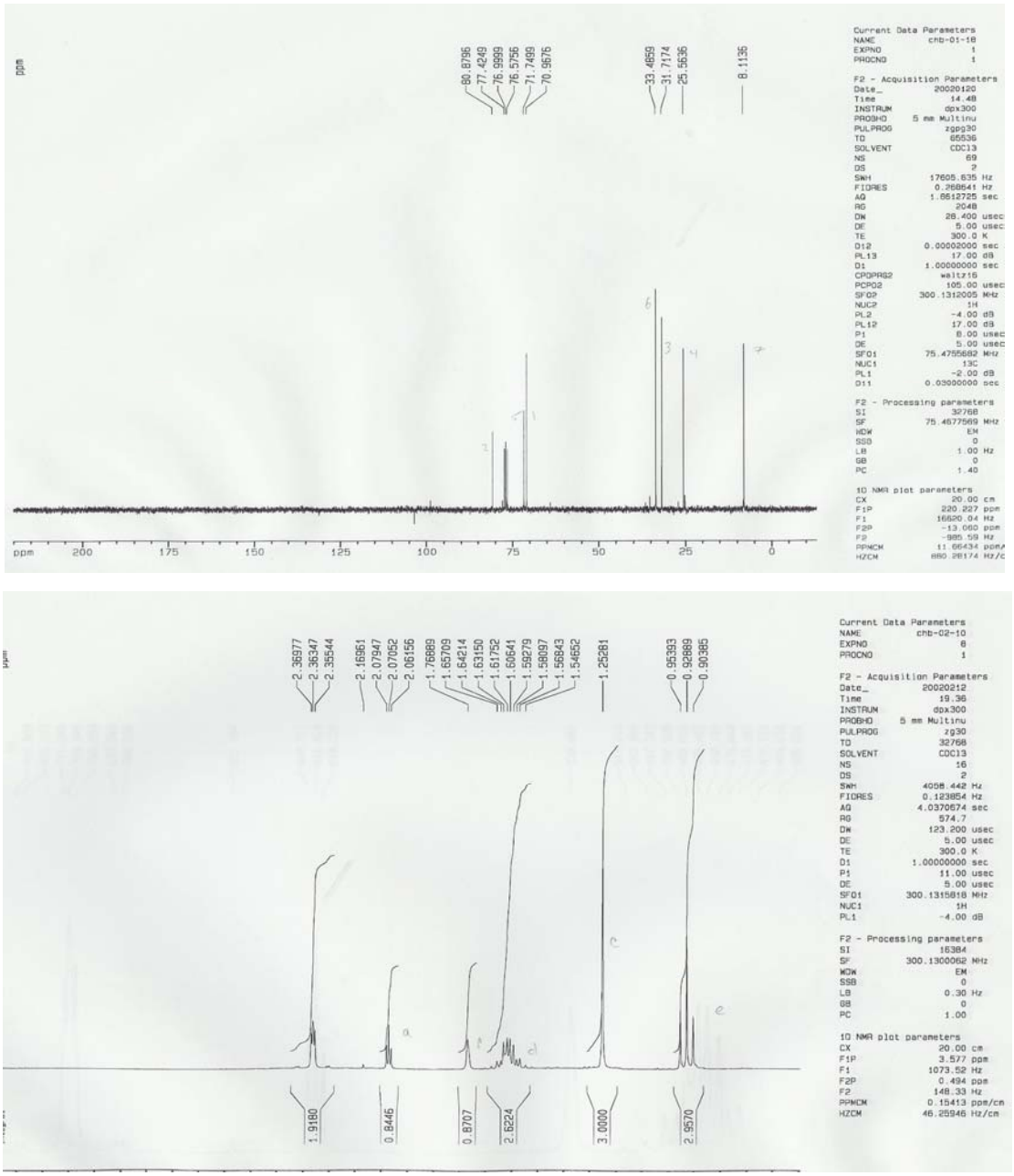


Figure 5. ^{13}C and ^{1}H NMR of homopropargylic alcohol **6c**.

(-)-(*R*)-4-Methyl-1-octyn-4-ol (6d*R*).[8] A solution of **(+)-1*S*** (1.25 g, 5.0 mmol) in ethyl ether (50 mL) was cooled to -78 °C and 2-hexanone (0.45 g, 4.5 mmol) was added dropwise. After 3 h, the reaction solution was warmed to room temperature and the solvents were removed to yield the borinate intermediate **5**. The (1*R,2R*)-pseudoephedrine (0.83 g, 5.0 mmol) was added followed by hexane (8 mL) and the mixture was heated to reflux for 2 h. The solution was allowed to cool while complex **(+)-8*S*** precipitated out of solution. The crystals were separated and washed with pentane (3 x 10 mL) to yield 1.32 g (69%) of **(+)-8*S***. The residue was distilled (72 °C at 6 mm Hg) to obtain 0.50 g (80%) of **6d*R*** (81% ee). $[\alpha]_D^{26}$ = -2.0 (c = 3.0, $CDCl_3$); lit.[8] $[\alpha]_D^{28}$ = -1.1 (c = 3.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, *J* = 6.9 Hz, 3H), 1.26 (s, 3H), 1.30-1.34 (m, 4H), 1.53-1.59 (m, 2H), 1.81 (s, 1H), 2.07 (t, *J* = 2.6 Hz, 1H), 2.29-2.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 23.1, 26.1, 26.2, 32.3, 40.8, 71.0, 71.5, 80.9 (Fig. 6). The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphospholidine derivative after addition of S_8 **CDA-6d**. Analysis of the peaks areas for δ 80.8 and 81.0 ppm revealed 50:50 ratio for the racemic diazaphospholidine and 90.5:9.5 ratio (81% ee) for the non-racemic material.

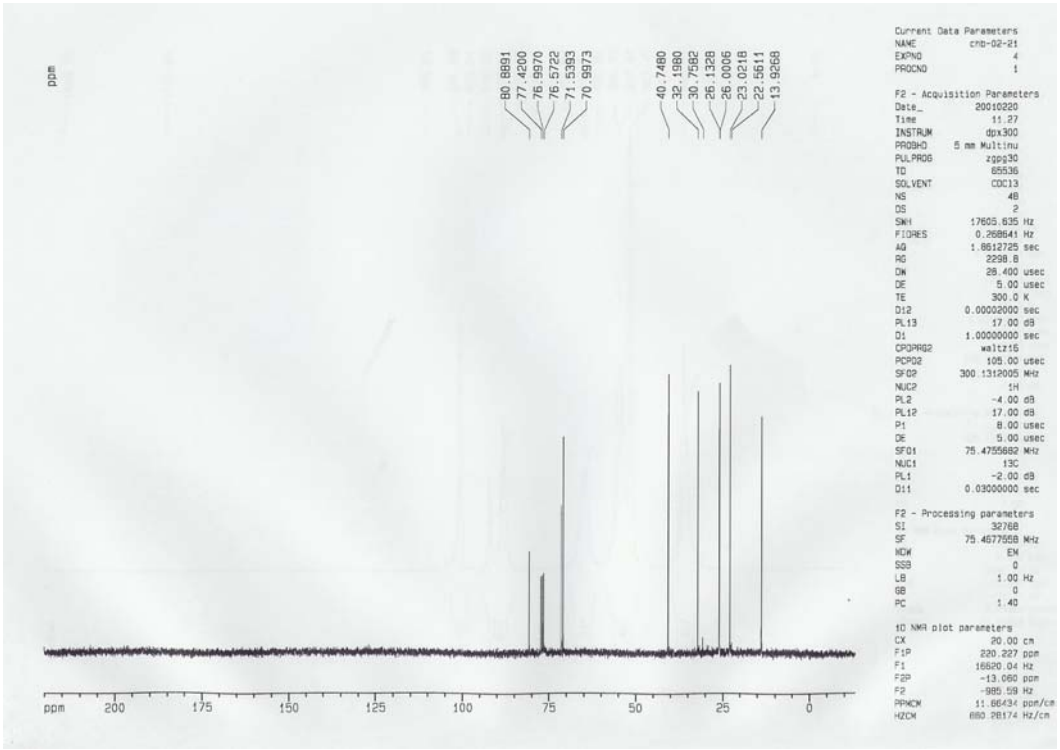


Figure 6. ^{13}C NMR of homopropargylic alcohol **6d**.

(-)-(*R*)-2,3-Dimethyl-5-hexyn-3-ol (6e*R*). A solution of **(-)-1*R*** (1.25 g, 5.0 mmol) in ethyl ether (50 mL) was cooled to -78 °C and 3-methyl-2-butanone (0.39 g, 4.5 mmol) was added dropwise. After 6 h, the reaction solution was warmed to room temperature and the solvents were removed to yield the borinate intermediate **5e**. The (1*R,2R*)- pseudoephedrine (0.83 g, 5.0 mmol) was added followed by hexane (10 mL) and the mixture was heated to reflux for 3 h. The solution was allowed to cool while complex **(-)-8*R*** precipitated out of solution. The crystals were separated and washed with hexane (3 x 10 mL) to yield 1.46 g (77%) of **(-)-8*R***. The residue was distilled (90-91 °C at 55 mm Hg) to obtain 0.40 g (71%) of **6e*R*** (84% ee). $\alpha]_D^{27}$ = -4.6 (c 3.2, $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.9 Hz, 3H), 1.18 (s, 3H), 1.79 (br s, 1H), 1.81-1.96 (m, 1H), 2.07 (t, J = 2.6 Hz, 1H), 2.32-2.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.9, 17.6, 22.4, 30.6, 36.2, 71.3, 73.7, 80.9 (Fig. 7). All experimental data for these compounds were in complete agreement with those reported.[9] The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphospholidine derivative after addition of S_8 **CDA-6e**. Analysis of the peaks areas for δ 79.9 and 80.1 ppm revealed a 50:50 ratio for the racemic diazaphospholidine and 92:8 ratio (84% ee) for the non-racemic material.

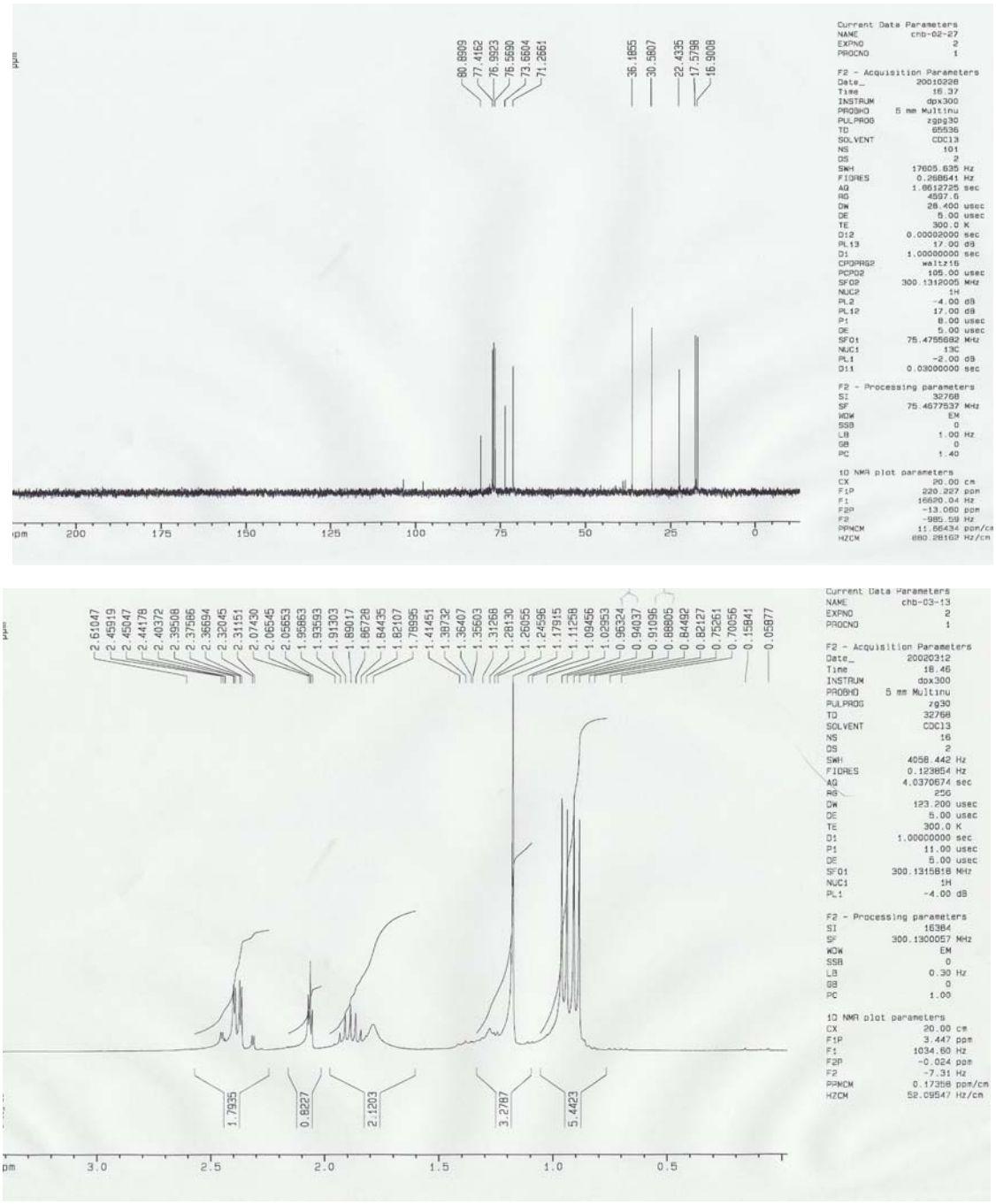


Figure 7. ^{13}C and ^{1}H NMR of homopropargylic alcohol **6e**.

(-)-(*S*)-2,2,3-Trimethyl-5-hexyn-3-ol (6f*S*). A solution of **(+)-1S** (0.75, 3.0 mmol) in ethyl ether (30 mL) was cooled to -78 °C and pinacolone (0.30. g, 3.0 mmol) was added dropwise. After 12 h, the reaction solution was warmed to room temperature and treated with NaOH (3 M, 9 mmol) and H_2O_2 (30%, 6.0 mmol). This mixture was heated to reflux for 1 h. The residue was extracted with ether (3x 10 mL) and distilled (174-176 °C) to obtain 0.28 g (66 %) of **6f*S*** (83% ee). $\alpha]_D^{27}$ = -20.0 (c = 1.4, $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (s, 9H), 1.29 (s, 3H), 1.79 (s, 1H), 2.08 (t, *J* = 2.7 Hz, 1H), 2.29-2.61 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 22.3, 25.4, 28.3, 37.4, 71.9, 74.7, 82.1 (Fig. 8). All experimental data for these compounds were in complete agreement with those reported.[10] The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphopholidine derivative after addition of S_8 **CDA-6f**. Analysis of the peaks areas for δ 79.8 and 80.0 ppm revealed 50:50 ratio for the racemic diazaphopholidine and 8.5:91.5 ratio (83% ee) for the non-racemic material.

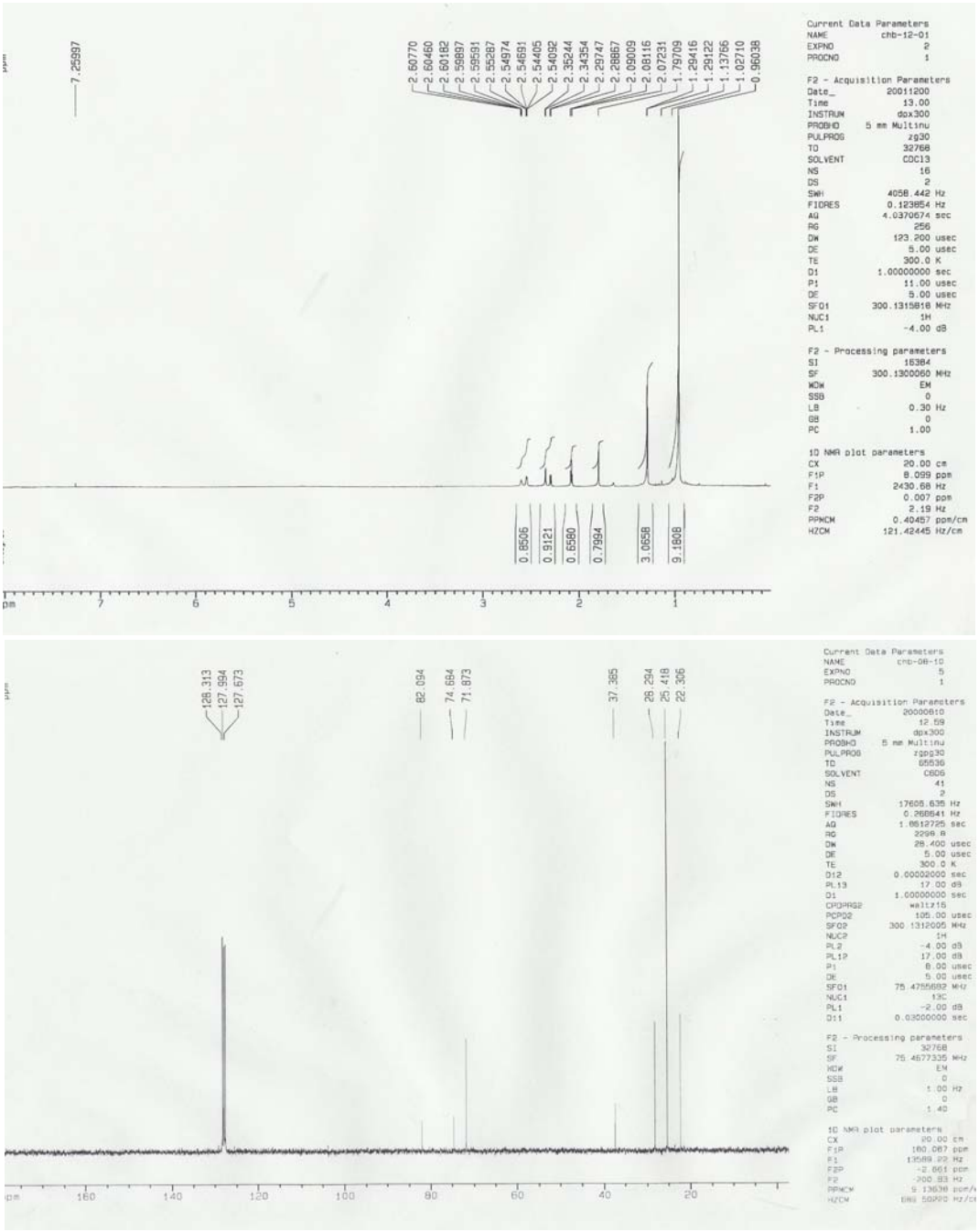


Figure 8. ^{13}C and ^{1}H NMR of homopropargylic alcohol **6f**.

(-)-(*R*)-2-Trimethylsilyl-4-pentyn-2-ol (6g*R*): A solution of **(+)1*S*** (0.87 g, 3.5 mmol) in ethyl ether (40 mL) was cooled to -78 °C and acetyltrimethylsilane (0.35 g, 3.0 mmol) was added dropwise. After 3 h, the reaction solution was warmed to room temperature and the solvents were removed to yield the borinate intermediate **5g**. The (1*R*,2*R*)-pseudoephedrine (0.58 g, 3.5 mmol) was added followed by hexane (8 mL) and the mixture was heated to reflux for 2 h. The solution was allowed to cool while complex **(+)-8S** precipitated out of solution. The crystals were separated and washed with hexane (3 x 10 mL) to yield 0.83 g (74%) of **(+)-8S**. The residue was distilled (60 °C at 35 mm Hg) to obtain 0.29 g (62%) of **6g*R*** (90% ee,). $[\alpha]_D^{28}$ = -5.0 (c = 1.8. $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.24 (s, 3H), 1.58 (s, 1H), 2.07 (t, *J* = 2.6 Hz, 1H), 2.23-2.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -4.1, 23.9, 29.8, 63.7, 71.9, 80.2 (Fig. 9). HRMS calculated for $C_8H_{16}OSi$ = 156.0970, found 156.0981. The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphopholidine derivative after addition of S_8 **CDA-6g**. Analysis of the peaks areas for δ 81.7 and 81.8 ppm revealed 50:50 ratio for the racemic diazaphopholidine and 95:5 ratio (90% ee) for the non-racemic material.

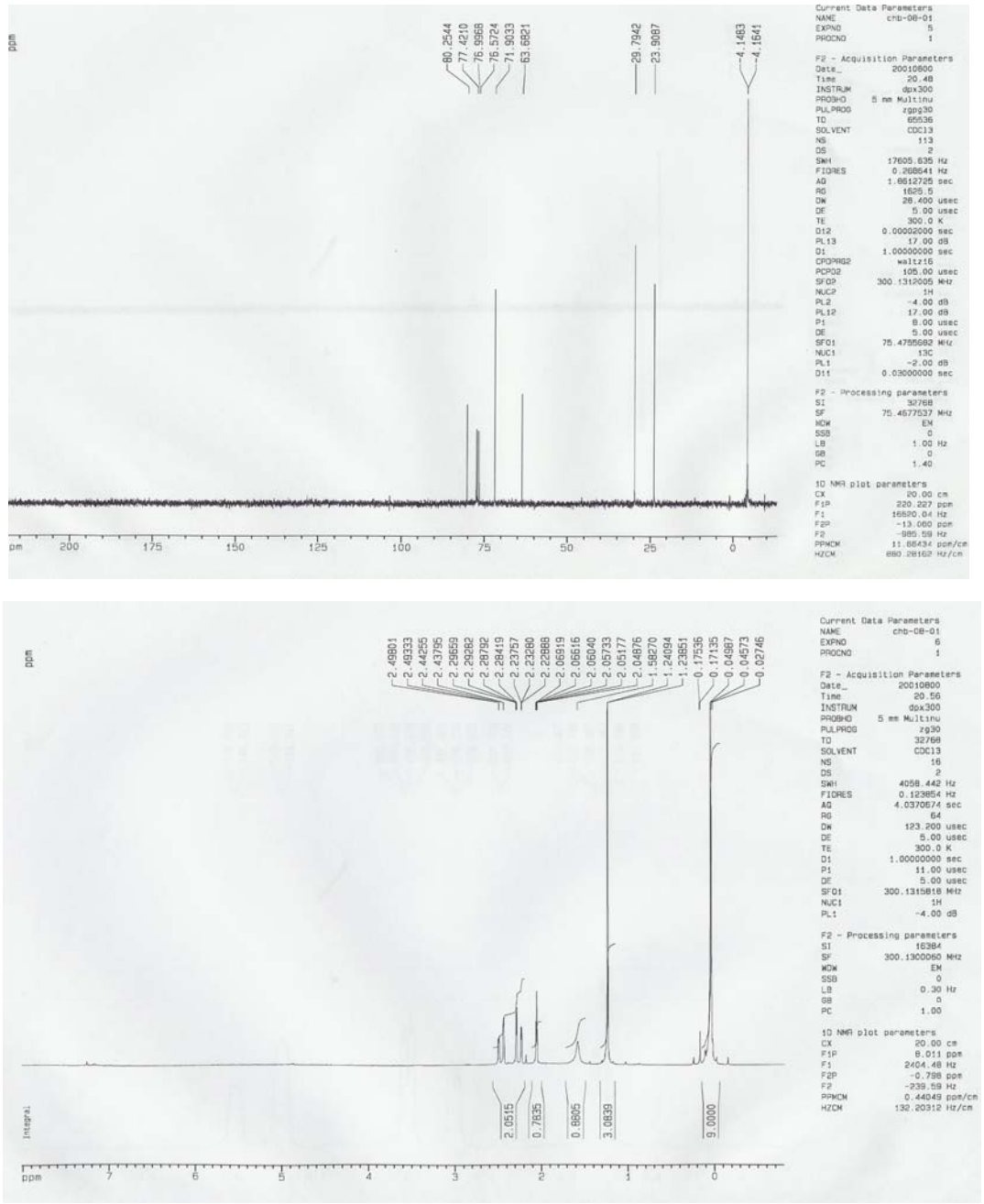


Figure 9. ^{13}C and ^{1}H NMR of homopropargylic alcohol **6g**.

(+)-(*S*)-3-Methyl-1-hexen-5-yn-3-ol (6h*S*): A solution of **(+)-1*S*** (1.00, 4.0 mmol) in ethyl ether (40 mL) was cooled to -78 °C and 3-buten-2-one (0.25 g, 3.5 mmol) was added dropwise. After 3 h, the solution was warmed to room temperature and treated with NaOH (3 M, 15 mmol) and H_2O_2 (10.0 mmol, 1.0 mL, 30%). This mixture was heated to reflux for 1 h. The residue was extracted with ether (3x 10 mL) and distilled (88-92 °C at 75 mm Hg) to obtain 0.25 g (64%) of **6h*S*** (61% ee). $[\alpha]_D^{27}$ = +18.3 (c = 1.2, $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 3H), 2.01 (br s, 1H), 2.09 (t, *J* = 2.6 Hz, 1H), 2.46 (d, *J* = 2.6 Hz, 2H), 5.11-5.15 (dd, *J* = 10.7 Hz, *J* = 1 Hz, 1H), 5.28-5.35 (dd, *J* = 17.3, *J* = 1 Hz, 1H), 5.94-6.04 (dd, *J* = 17.3 Hz, *J* = 10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.7, 32.7, 71.2, 71.8, 80.3, 112.7, 143.1 (Fig. 10). All experimental data for these compounds were in complete agreement with those reported.[7] The ee value was determined from the ^{31}P NMR analysis of the corresponding diazaphopholidine derivative after addition of S_8 **CDA-6h**. Analysis of the peaks areas for δ 80.4 and 80.5 ppm revealed a 50:50 ratio for the racemic diazaphopholidine and 80.5:19.5 ratio (61% ee) for the non-racemic material.

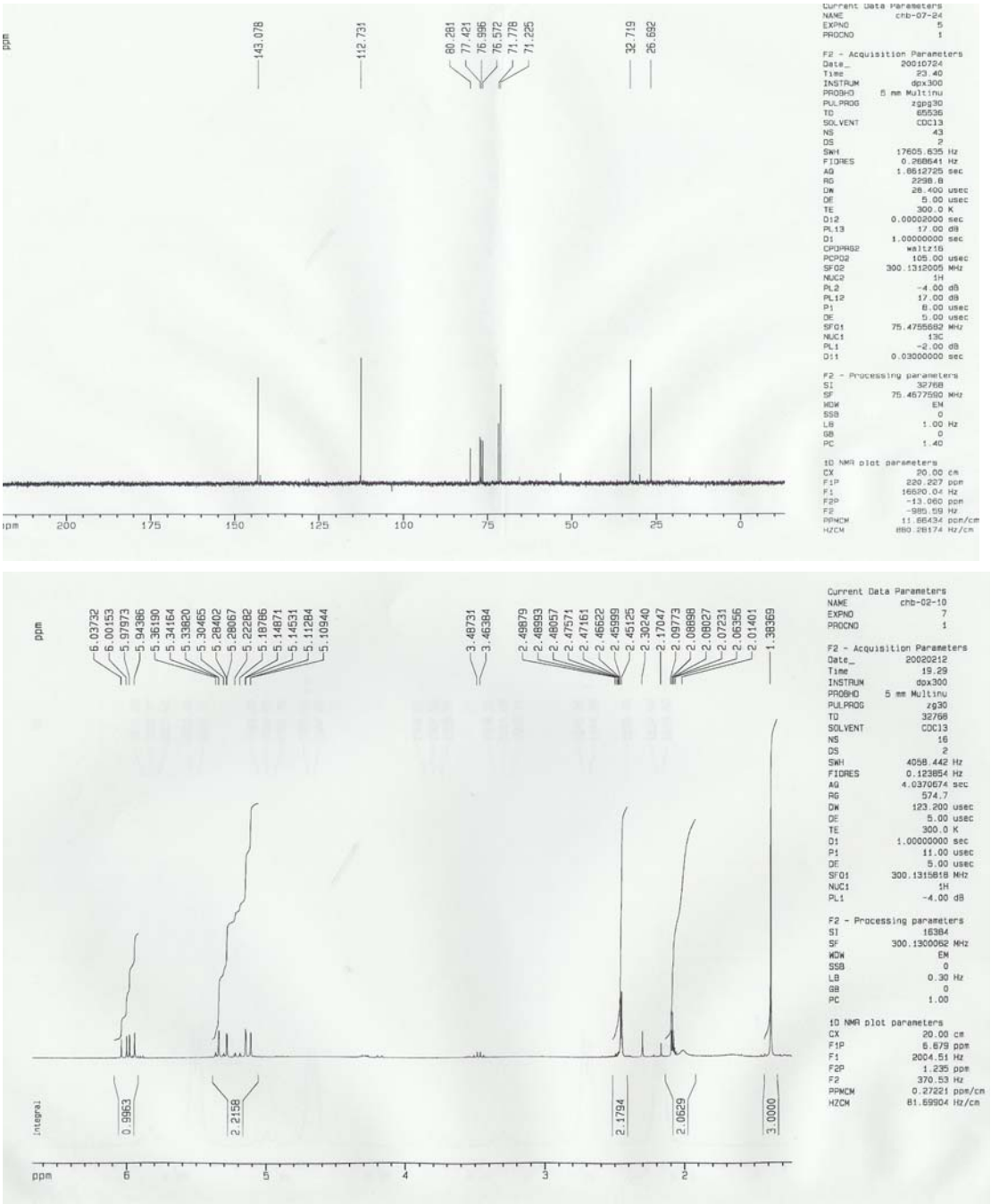


Figure 10. ^{13}C and ^{1}H NMR of homopropargylic alcohol **6h**.

(+)-*B*-[γ-(Trimethylsilyl)propargyl]-10*S*-phenyl-9-borabicyclo[3.3.2]decane ((+)-2*S*). A solution of (+)-**4*S*** (1.17 g, 3.0 mmol) in Et_2O (15 mL) was cooled to -78 °C and a solution of freshly prepared trimethylsilylpropynylmagnesium bromide[11] (5.0 mL, 0.67M) in Et_2O was added dropwise and stirred for 1 h. The solution was allowed to reach room temperature and was stirred overnight (8-10 h). The reaction mixture was quenched with TMSCl (0.054 g). 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 hexane (3 x 20 mL) and these washings were filtered through a celite pad. Concentration gives 0.94 g (97%) of **(+)-2*S*)**. $[\alpha]_D^{20}$ = +31.7 (*c* 2.05, C_6D_6); ^{1}H NMR (C_6D_6, 300 MHz) δ 0.18 (s, 9H), 1.19-1.45 (m, 3H), 1.50-1.80 (m, 9H), 1.93 (ad, *J* = 18.2 Hz, 1H), 2.13 (ad, *J* = 18.2 Hz, 1H), 2.29 (m, 1H), 2.41 (m, 1H), 2.51 (s, 1H), 6.85 (m, 1H), 7.04 (m, 1H), 7.10-7.15 (m, 3H), ^{13}C NMR (75 MHz, C_6D_6) δ 0.5, 20.1, 23.7, 23.8, 26.8, 27.2, 28.4, 29.3, 30.2, 31.2, 34.3, 40.8, 52.7, 84.5, 105.8, 125.4, 128.1, 130.0, 146.0 (Fig. 11); IR (neat) 3022, 2912, 2853, 2178 (C≡C), 1490, 1468, 1449, 1379, 1327, 1298 (C-B-C), 1248 (Si-C), 981, 838 (Si-C), 758, 698, 637 cm^{-1}; ^{11}B NMR (C_6D_6, 96 MHz) δ 86.6. Alternatively, (+)-**2*S*** can be prepared from (-)-**8*S***.

(-)-*B*-[γ-(Trimethylsilyl)propargyl]-10-phenyl-9-borabicyclo[3.3.2]decane ((-)-2*R*) is prepared by the same procedure employing **(-)-4*R***. $[\alpha]_D^{20}$ = -29.8 (*c* 2.0, C_6D_6). Alternatively, (-)-**2*R*** can be prepared from (+)-**8*R***. Other data is essentially identical to that of **(+)-2*S***.

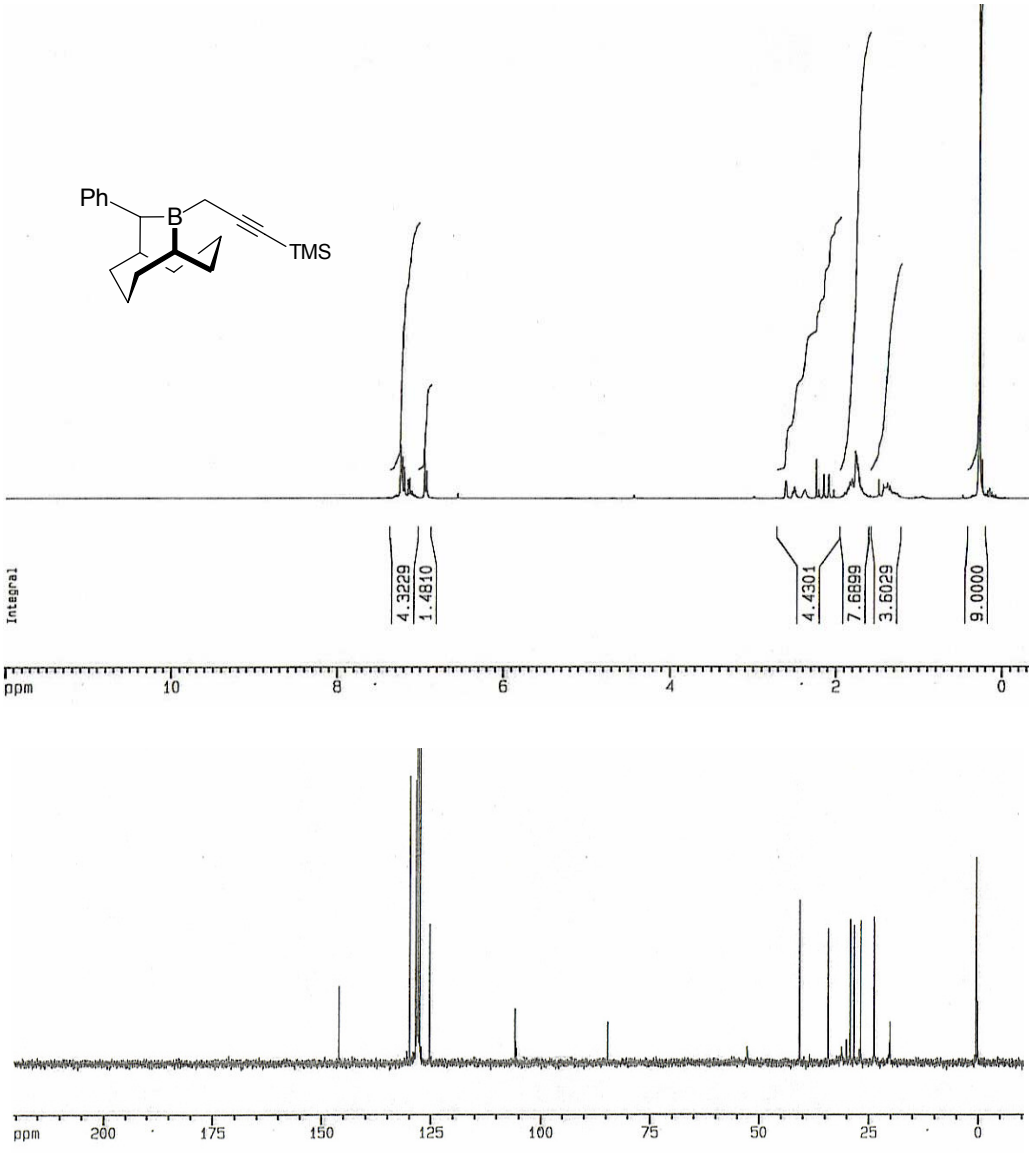


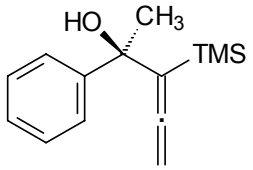
Figure 11. ^{13}C and ^{1}H NMR of propargylborane **2**.

(±)-*B*-[γ-(Trimethylsilyl)propargyl]-10-phenyl-9-borabicyclo[3.3.2]decane ((±)-2). A solution of **(±)-3** (0.73 g, 3.0 mmol) in Et_2O (15 mL) was cooled to -78° and a solution of freshly prepared 3-trimethylsilyl-2-propynylmagnesium bromide (5.0 mL, 0.67M)[11] in Et_2O was added dropwise and stirred for 1 h. The solution was allowed to reach room temperature and was stirred overnight (8-10 h). The reaction mixture was quenched with TMSCl (0.054 g) 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 hexane (3 x 20 mL) and these washings were filtrated through a celite pad. Concentration gives 0.94 g (97%) of **(±)-2**. Spectral data were as above.

Representative Procedure for the Propargylboration of Ketones with (±)-2.

(±)-2-Phenyl-3-(trimethylsilyl)-3,4-pentadien-2-ol ((±)-9a). A solution of **(±)-2** (0.73 g, 3.0 mmol) in THF (3 mL) was cooled to -78 °C and acetophenone (0.3 mL, 2.5 mmol) was added dropwise. After 12 h, the solvents were removed under vacuum to yield the borinate **7a**. To the reaction mixture MeOH was added (15 mL) and refluxed for 3 h. The mixture was cooled to room temperature and the volatiles removed *in vacuo*. The reaction crude was purified by silica gel chromatography (hexane-ether, 98:2) to give 0.59 g (87%) of **(±)-9a**. The spectral data is identical to that of **(+)-9a*R***.

General procedure for the propargylboration of ketones with (-)-2*R* or (+)-2*S*:



(+)-(2*R*)-2-Phenyl-3-(trimethylsilyl)-3,4-pentadien-2-ol (9a*R*). A solution of **(+)-2*S*** (0.94 g, 3.0 mmol) in THF (3 mL) was cooled to -78 °C and acetophenone (0.3 mL, 2.5 mmol) was added dropwise. After 12 h, the solvents were removed under vacuum to yield the borinate. (1*R*,2*R*)-(-)-pseudoephedrine (0.49 g, 3.0 mmol) and hexane (10 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.75 g (80%) of **(-)-8*S***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane:ether, 98-2) to afford 0.47 g (81%) (97% ee) of **9a*R***. R_f = 0.29. $[\alpha]_D^{23}$ = +106.3 (*c* 2.19, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.95 (s, 9H), 1.71 (s, 3H), 2.10 (s, 1H), 4.61 (bs, 2H), 7.20-7.28 (tt, *J* = 1.3, 7.3 Hz, 2H), 7.30-7.35 (m, 1H), 7.46-7.50 (dt, *J* = 1.5, 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.9, 32.5, 71.5, 75.9, 105.2, 125.2, 126.5, 127.7, 147.5, 208.0 (Fig. 12); IR (neat) 3454 (O-H), 3059, 3028, 2958, 2896, 1922 (C=C=C), 1446, 1246 (Si-C), 1067, 837 (Si-C), 760, 698 cm^{-1}; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 137.5 (1.3%), 137.3 (98.6%) (Fig. 21). Anal. calcd for C 72.36, H 8.67, found C 72.10, H 8.66.

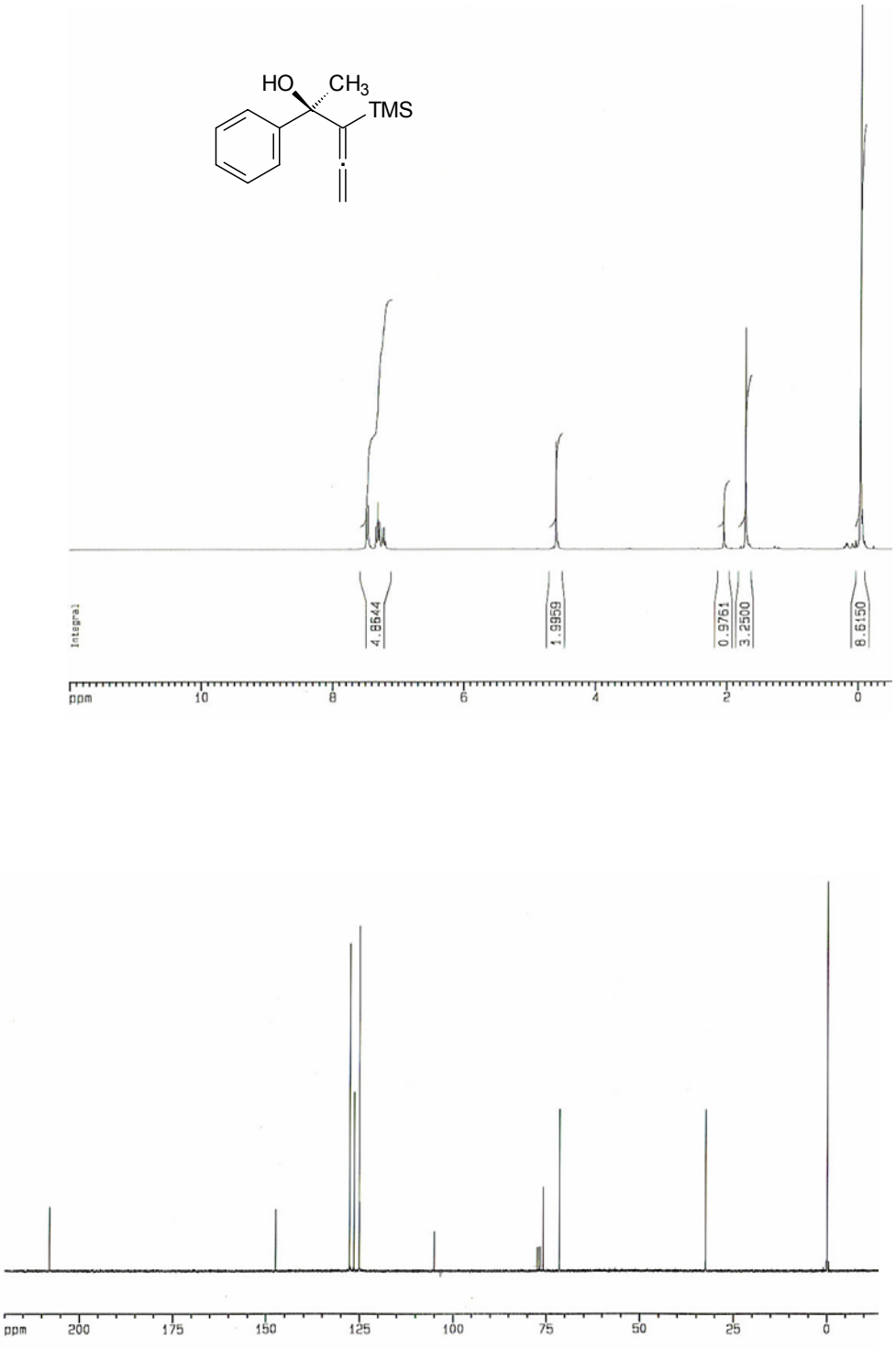


Figure 12. ^{13}C and ^{1}H NMR of **9a*R***.

(+)-(4*R*)-4-Methyl-3-(Trimethylsilyl)-1,2-octadien-4-ol (9b*R*). A solution of **(+)-2*S*** (0.95 g, 3.0 mmol) in THF (5 mL) was cooled to -78 ^{o}C and 2-hexanone (0.31 mL, 2.5 mmol) was added dropwise. After 3 h, the solvents were removed under vacuum to yield the borinate **7b**. The (1*R*,2*R*)-(-)-pseudoephedrine (0.49 g, 3.0 mmol) and hexane (20 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.71 g (76%) of **(-)-8*S***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane-ether, 97:3) to afford 0.33 g, (62%) of **9b*R***. R_f = 0.24. $[\alpha]_D^{20}$ = +9.8 (*c* 2.24, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 9H), 0.90 (t, *J* = 6.8 Hz, 3H), 1.25 (m, 4H), 1.30 (s, 3H), 1.50-1.60 (m, 2H), 1.80 (bs, 1H), 4.44 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.3, 14.0, 22.9, 26.2, 29.7, 42.9, 70.9, 74.4, 104.8, 206.9 (Fig. 13); IR (neat) 3475 (O-H), 2956, 2934, 2862, 1924 (C=C=C), 1457, 1371, 1246 (Si-C), 1118, 1047, 835 (Si-C), 809, 758, 690, 633, 592 cm^{-1}; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 136.1 (92%), 134.2 (8%) (Fig. 22). Anal. calcd for C 67.86, H 11.39, found C 67.88, H 11.38.

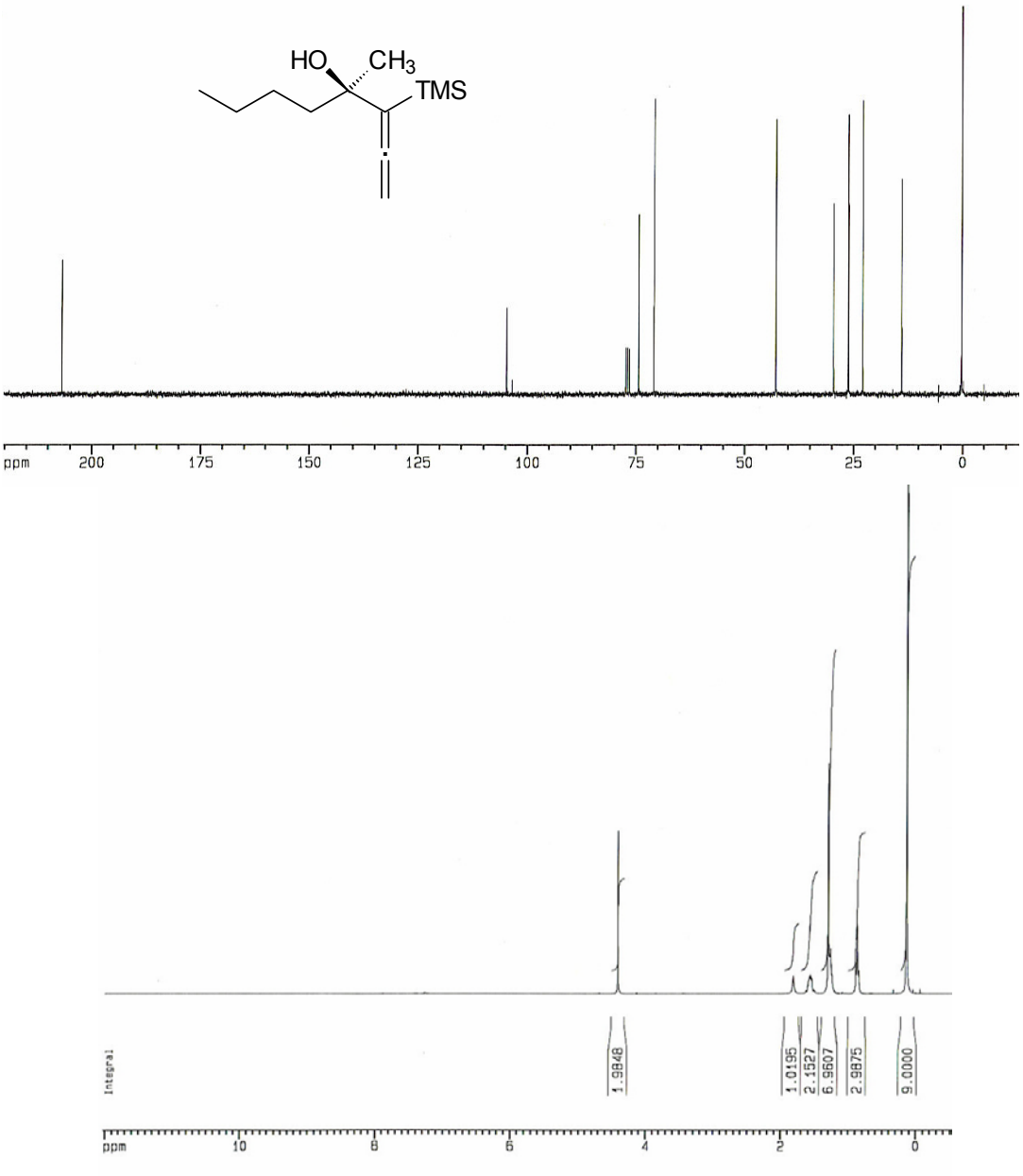


Figure 13. ^{13}C and ^{1}H NMR of **9b*R***.

(+)-(2*R*)-2-Cyclohexenyl-3-(trimethylsilyl)-3,4-pentadien-2-ol (9c*R*). A solution of **(+)-2*S*** (0.96 g, 3.0 mmol) in THF (5 mL) was cooled to -78 °C and 1-acetyl-1-cyclohexene (0.15 mL, 1.5 mmol) was added dropwise. After 3 h, the solvents were removed under vacuum to yield the borinate **7c**. The (1*R*,2*R*)-(-)-pseudoephedrine (0.33 g, 2.0 mmol) and hexane (7 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.57 g (85%) of **(-)-8*S***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane-ether, 97:3) to afford 0.22 g, (67%) of **9c*R***. R_f = 0.24. $[\alpha]_D^{20}$ = +45.6 (*c* 2.08, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 9H), 1.45 (s, 3H), 1.48-1.65 (m, 4H), 1.86 (s, 1H), 1.90-2.01 (m, 2H), 2.02-2.07 (m, 2H), 4.50 (s, 2H), 5.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.20, 22.29, 22.88, 24.4, 25.1, 28.7, 77.5, 76.2, 103.9, 120.6, 141.9, 207.8 (Fig. 14); IR (neat) 3465 (O-H), 3051, 2927, 2858, 2936, 1922 (C=C=C), 1627, 1447, 1366, 1313, 1245 (Si-C), 1208, 1141, 1072, 835 (Si-C), 807, 757, 691, 623 cm^{-1}; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 77.3 (95.5%), 74.2 (4.5%) (Fig. 23). Anal. calcd for C 71.12, H 10.23, found C 70.83, H 10.29.

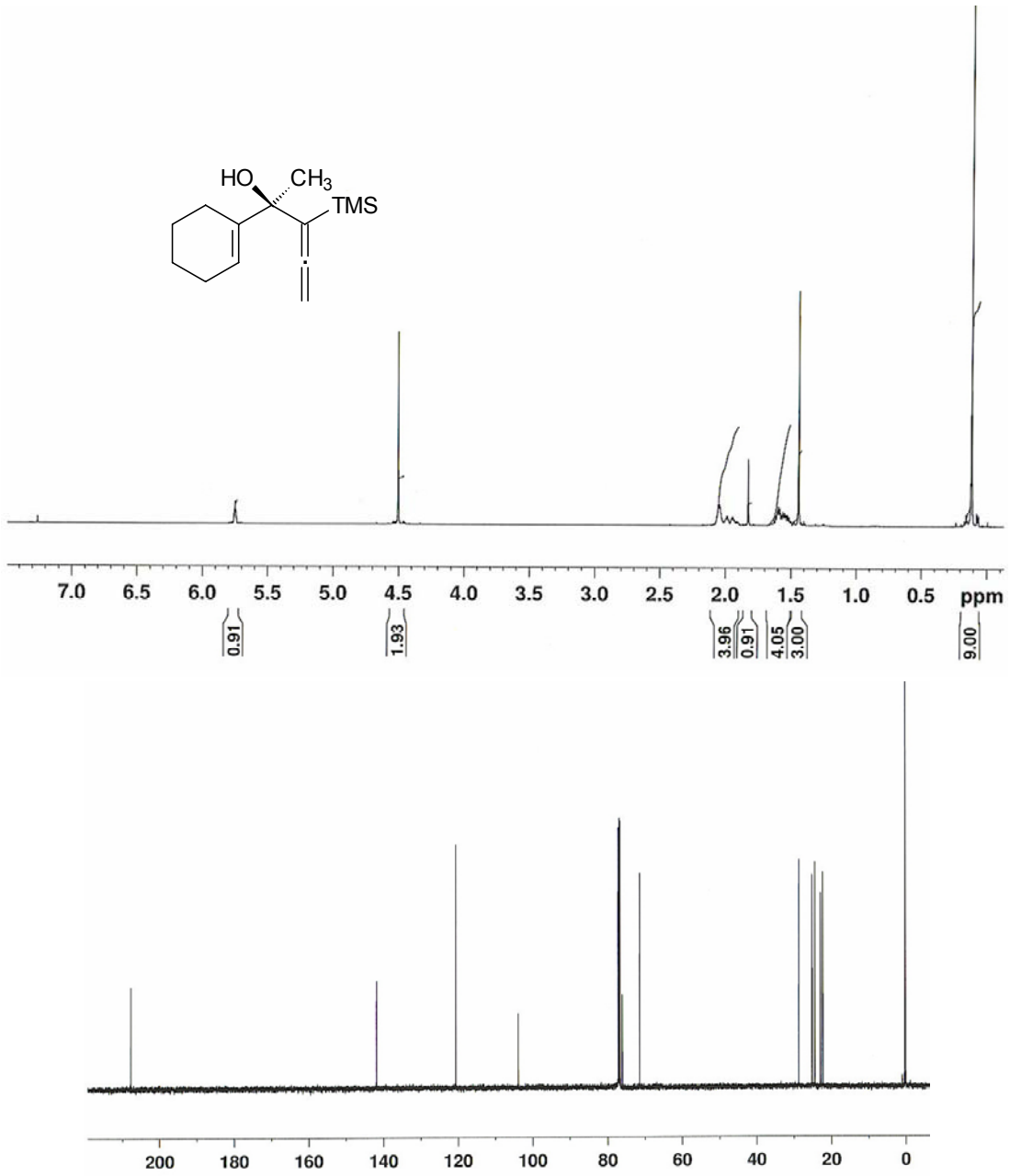


Figure 14. ^{13}C and ^{1}H NMR of **9c*R***.

(-)-(2*S*)-2-(4-Methoxyphenyl)-3-(trimethylsilyl)-3,4-pentadien-2-ol (9d*S*). A solution of **(-)-2*R*** (0.94 g, 3.0 mmol) in THF (3 mL) was cooled to -78 °C and 4-methoxyacetophenone (0.4 g, 2.6 mmol) in THF (1 mL) was added dropwise. After 6 h, the solvents were removed under vacuum to yield the borinate **7d**. The (1*S*,2*S*)-(+)-pseudoephedrine (0.43 g, 2.6 mmol) and hexane (10 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.77 g (79%) of **(+)-8*R***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane-ether, 98:2) to afford 0.65 g (95%) of **9d*S***. R_f = 0.10. $[\alpha]_D^{20}$ = -73.7 (*c* 1.92, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ -0.97 (s, 9H), 1.70 (s, 3H), 2.11 (s, 1H), 3.75 (s, 3H), 4.61 (bs, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.08, 32.4, 55.1, 71.5, 75.5, 105.4, 113.0, 126.4, 139.8, 158.2, 207.9 (Fig. 15); IR (neat) 3495 (O-H), 2956, 2897, 2835, 1921 (C=C=C), 1699, 1608, 1583, 1509, 1245 (Si-C), 1170, 1092, 1033, 904, 831 (Si-C), 809, 760 cm^{-1}; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 137.5 (96%), 137.0 (4%) (Fig. 24). Anal. calcd for C 68.65, H 8.45, found C 68.64, H 8.64.

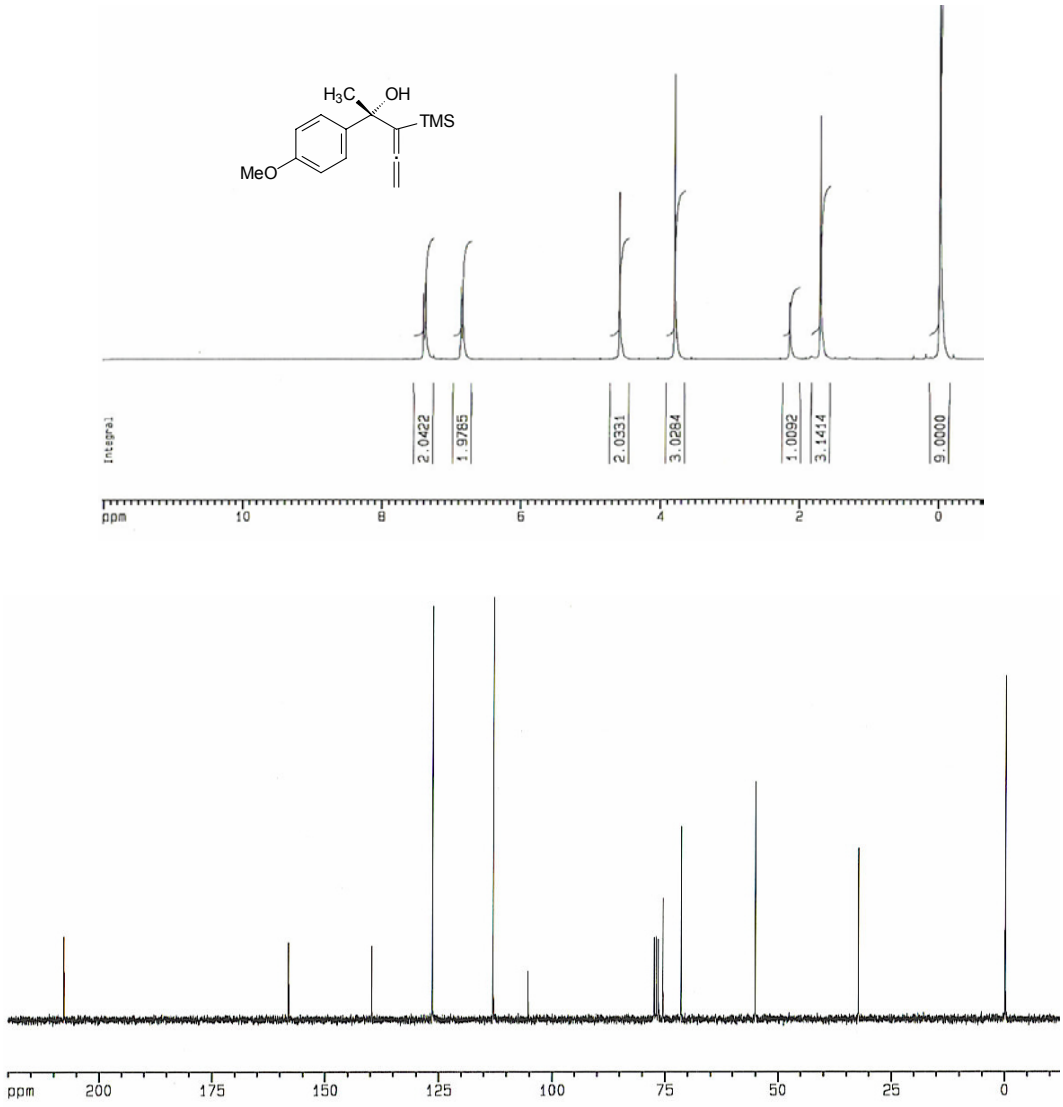


Figure 15. ^{13}C and ^1H NMR of **9d*S***.

(+)-(2*R*)-2-(4-Bromophenyl)-3-(trimethylsilyl)-3,4-pentadien-2-ol (9e*R*). A solution of **(+)-2*S*** (0.96 g, 3.0 mmol) in THF (3 mL) was cooled to -78 ºC and 4-bromoacetophenone (0.44 g, 2.2 mmol) in THF (1 mL) was added dropwise. After 36 h, the solvents were removed under vacuum to yield the borinate **7e**. (1*R*,2*R*)-(-)-pseudoephedrine (0.36 g, 2.2 mmol) and hexane (10 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.35 g (50%) of **(-)-8*S***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane:ether, 98-2) to afford 0.55 g (80%) of **(+)-6**. R_f = 0.15. $[\alpha]_D^{20}$ = +119.4 (*c* 1.72, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.0 (s, 9H), 1.71 (s, 3H), 2.15 (s, 1H), 4.63 (bs, 2H), 7.35 (d, *J* = 7.1 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.02, 32.6, 71.7, 75.6, 104.9, 120.4, 127.1, 130.8, 146.7, 208.1 (Fig. 16); IR (neat) 3465 (O-H), 2958, 2896, 1921 (C=C=C), 1485, 1394, 1246 (Si-C), 1008, 903, 838 (Si-C), 824, 757, 692, 620, 557 cm^{-1}; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 138.2 (1%), 137.6 (99%) (Fig. 25). Anal. calcd for C 54.02, H 6.15, found C 54.24, H 6.25.

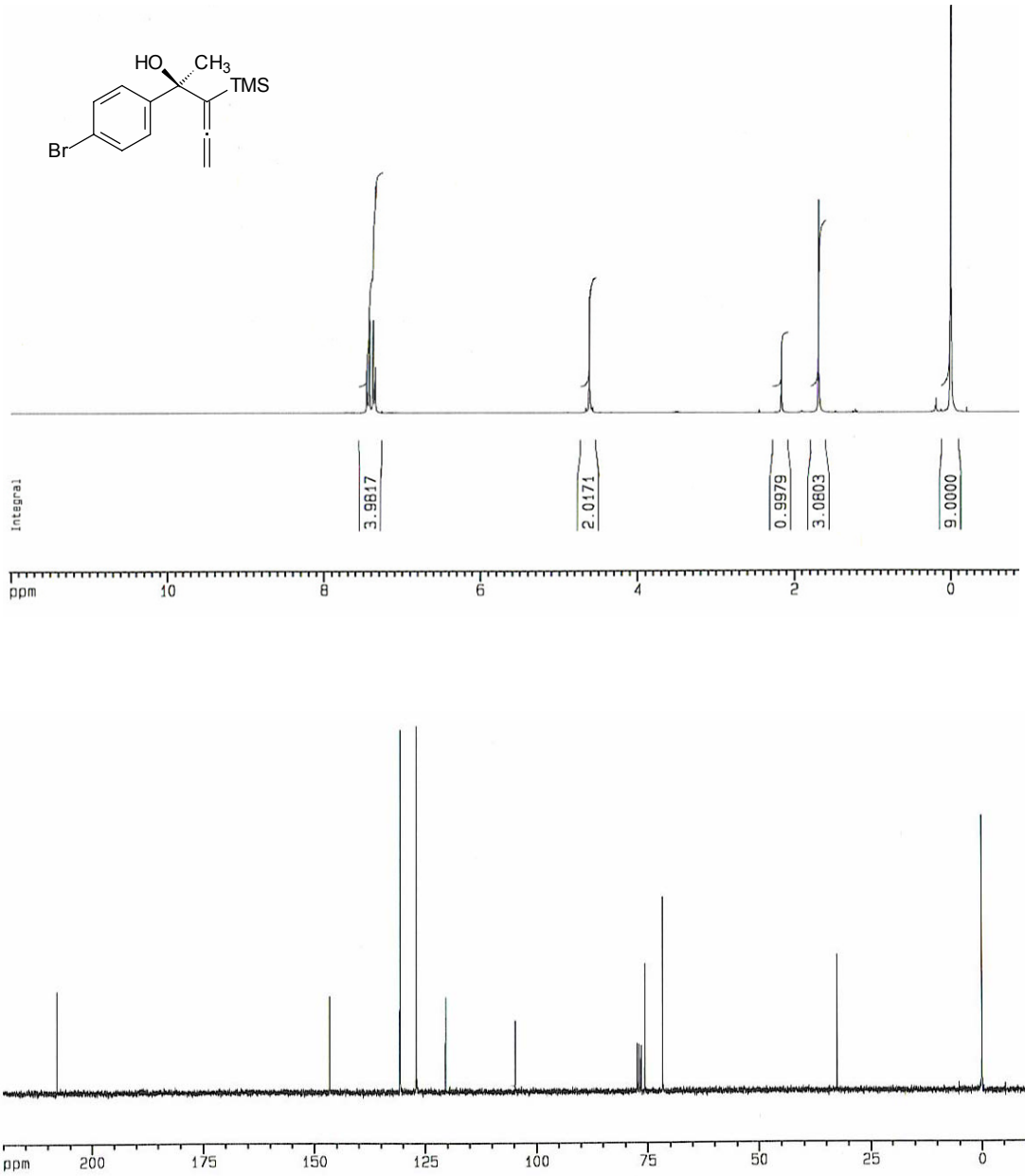


Figure 16. ^{13}C and ^{1}H NMR of **9e*R***.

(+)-(2*R*)-2-(4-Nitrophenyl)-3-(trimethylsilyl)-3,4-pentadien-2-ol (9f*R*). A solution of **(+)-2*S*** (0.95 g, 3.0 mmol) in THF (5 mL) was cooled to -78 °C and 4-nitroacetophenone (0.33 g, 2.0 mmol) in THF (1 mL) was added dropwise. After 36 h, the solvents were removed under vacuum to yield the borinate **7f**. The (1*R*,2*R*)-(-)-pseudoephedrine (0.33 g, 2.0 mmol) and hexane (10 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.49 g (65%) of **(-)-8*S***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane-ether, 95:5) to afford 0.40 g (73%) of **9f*R***. R_f = 0.17. $[\alpha]_D^{20}$ = +188.7 (*c* 1.20, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.90 (s, 9H), 1.68 (s, 3H), 2.45 (s, 1H), 4.45 (add, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 8.13 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.16, 32.5, 71.8, 75.8, 104.5, 122.9, 126.2, 146.4, 155.4, 208.4 (Fig. 17); IR (neat) 3398 (O-H), 2974, 2897, 1924 (C=C=C), 1597, 1518, 1447, 1344, 1246 (Si-C), 1094, 838 (Si-C), 755, 701, 620 cm-1; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 139.1 (1%), 138.2 (99%) (Fig. 26). Anal. calcd for C 60.62, H 6.90, found C 60.75, H 7.03.

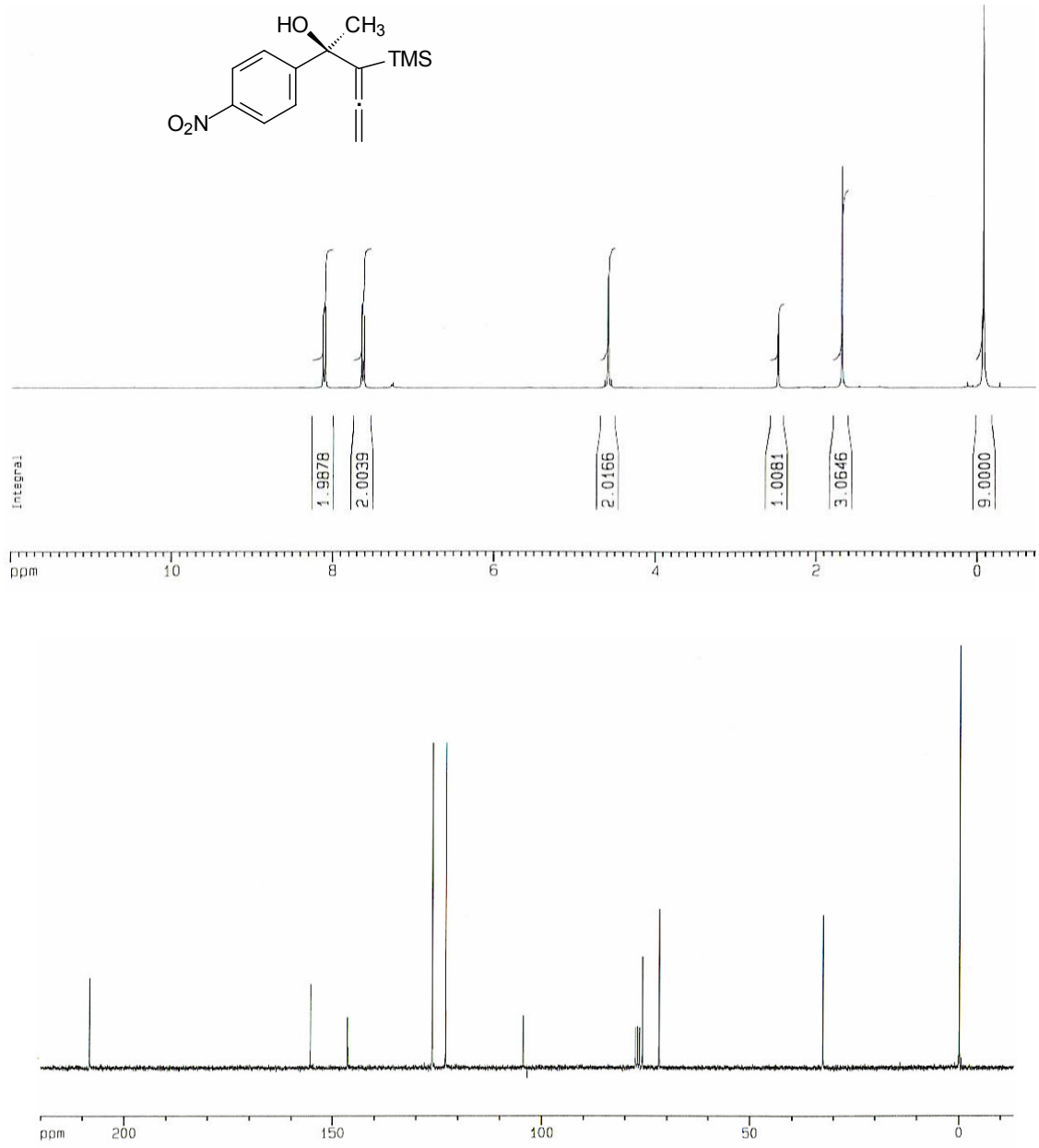


Figure 17. ^{13}C and ^{1}H NMR of **9f*R***.

(-)-(2*S*)-2-Thienyl-3-(trimethylsilyl)-3,4-pentadien-2-ol (9g*S*). A solution of **(+)-2*S*** (0.35 g, 1.1 mmol) in THF (3 mL) was cooled to -78 °C and 2-acetylthiophene (0.11 mL, 1.0 mmol) was added dropwise. After 3 h, the solvents were removed under vacuum to yield the borinate **7g**. The (1*R*,2*R*)-(-)-pseudoephedrine (0.16 g, 1.0 mmol) and hexane (10 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.72 g (70%) of **(-)-8*S***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane-ether, 97:3) to afford 0.17 g, (71%) of **9g*S***. R_f = 0.2. $[\alpha]_D^{20}$ = +26.5 (*c* 1.65, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 9H), 1.81 (s, 3H), 2.36 (s, 1H), 4.60 (s, 2H), 6.91 (dd, *J* = 3.5, 4.9 Hz, 1H), 6.94 (dd, *J* = 1.4, 3.5 Hz, 1H), 7.18 (dd, *J* = 1.4, 4.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.09, 32.4, 72.6, 74.3, 105.9, 123.0, 124.2, 126.4, 153.5, 207.6 (Fig. 18); IR (neat) 3445 (O-H), 3071, 2955, 2896, 1922 (C=C=C), 1694, 1528, 1446, 1350, 1246 (Si-C), 1130, 1090, 1047, 1023, 965, 836 (Si-C), 760, 693, 626, 469 cm^{-1}; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 136.4 (89%), 136.2 (11%) (Fig. 27); HRMS [M+H]+ calcd. 239.2244 found 239.2246.

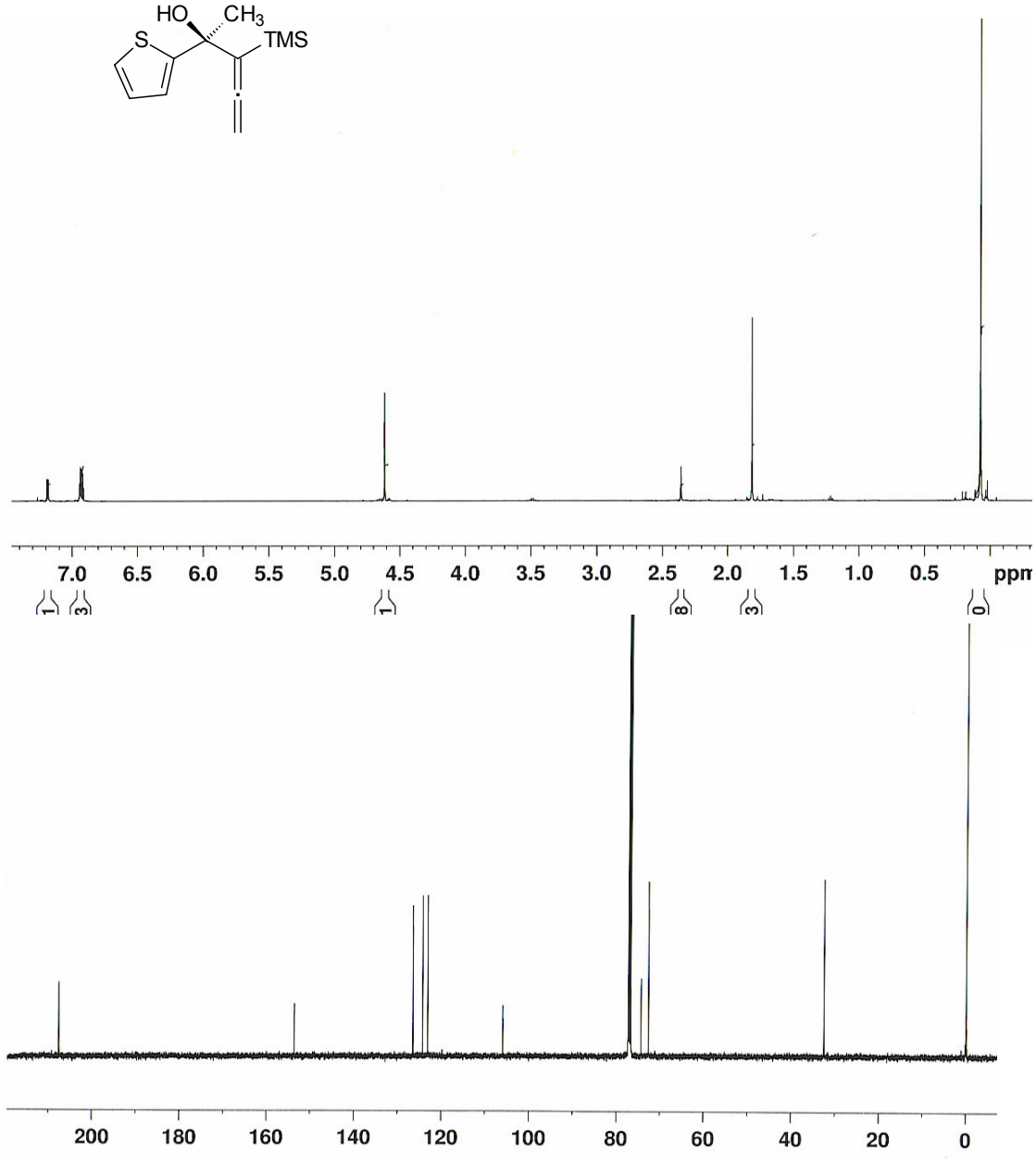


Figure 18. ^{13}C and ^{1}H NMR of **9h*S***.

(-)-(2*R*)-2-Furyl-3-(trimethylsilyl)-3,4-pentadien-2-ol (9h*R*). A solution of **(+)-2*S*** (0.64 g, 2.0 mmol) in THF (3 mL) was cooled to -78 °C and 2-acetylfuran (0.15 mL, 1.5 mmol) was added dropwise. After 3 h, the solvents were removed under vacuum to yield the borinate **7h**. The (1*R*,2*R*)-(-)-pseudoephedrine (0.29 g, 1.8 mmol) and hexane (15 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.60 g (80%) of **(-)-8*S***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane-ether, 90:10) to afford 0.23 g, (82%) of **9h*R***. R_f = 0.12. $[\alpha]_D^{20}$ = -10.5° (*c* 2.48, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.60 (s, 3H), 2.49 (s, 1H), 4.60 (ab, 2H), 6.19 (dd, *J* = 0.8, 3.2 Hz, 1H), 6.30 (dd, *J* = 1.8, 3.3 Hz, 1H), 7.34 (dd, *J* = 0.8, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.3, 28.4, 71.6, 72.8, 104.2, 105.1, 110.1, 141.4, 158.8, 207.5 (Fig. 19); IR (neat) 3453 (O-H), 3118, 3062, 2956, 2897, 1924 (C=C=C), 1448, 1406, 1247 (Si-C), 1155, 1136, 1098, 1070, 836 (Si-C), 812, 759, 732, 691 cm^{-1}; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 136.9 (10%), 136.5 (90%) (Fig. 28). Anal. calcd for C 64.82, H 8.16, found C 65.04, H 8.40.

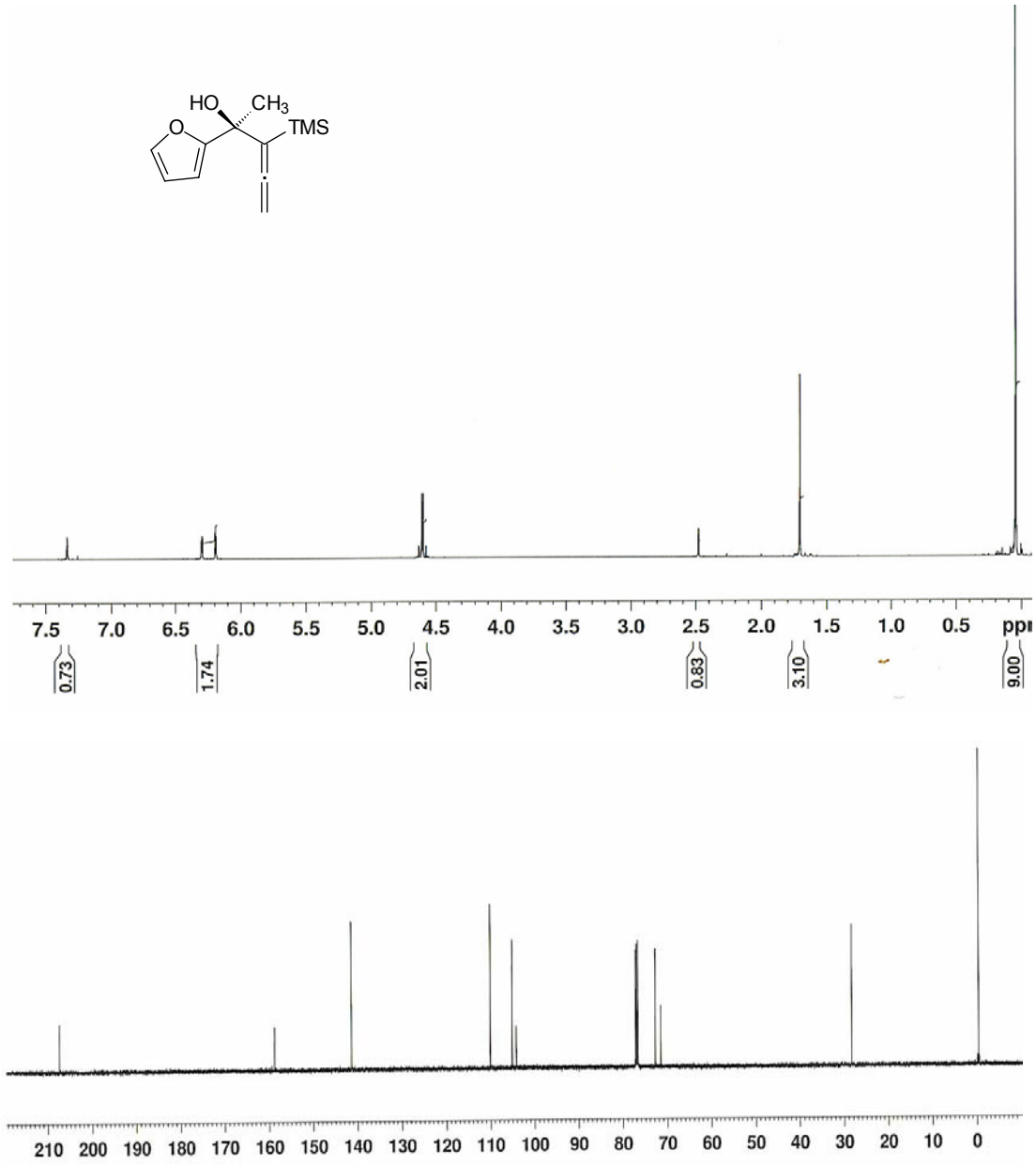


Figure 19. ^{13}C and ^{1}H NMR of **9i*R***.

(+)-(4*R*)-4-Phenyl-3-(trimethylsilyl)-1,2-hexadien-4-ol (9i*R*). A solution of **(+)-2*S*** (0.64 g, 2.0 mmol) in THF (3 mL) was cooled to -78 °C and propiophenone (0.21 mL, 1.6 mmol) was added dropwise. After 52 h, the solvents were removed under vacuum to yield the borinate **7i**. The (1*R*,2*R*)-(-)-pseudoephedrine (0.36 g, 2.2 mmol) and hexane (10 mL) were added and the mixture was heated at reflux temperature for 12 h and slowly cooled. The resulting crystals were separated and washed with hexane (3 x 5 mL) to yield 0.50 g (83%) of **(-)-8*S***. The supernatant was concentrated and the residue was purified by silica gel chromatography (hexane-ether, 95:5) to afford 0.22 g, (63%) of **9i*R***. R_f = 0.37. $[\alpha]_D^{20}$ = +41.3° (*c* = 2.66, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.0 (s, 9H), 0.82 (t, *J* = 7.3, 3H), 1.90 (s, 1H), 1.98-2.10 (m, 2H), 4.60 (dd, *J* = 11.1, 18.9 Hz, 2H), 7.20-7.24 (m, 2H), 7.28-7.33 (m, 2H), 7.42-7.45 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.05, 8.0, 36.4, 71.3, 78.3, 104.4, 125.7, 126.4, 127.7, 146.2, 208.1 (Fig. 20); IR (neat) 3483 (O-H), 3086, 3059, 3027, 2965, 2897, 1924 (C=C=C), 1601, 1446, 1342, 1246 (Si-C), 1166, 1073, 971, 837 (Si-C), 814, 755, 699, 626, 476 cm^{-1}; CDA ^{31}P NMR (121 MHz, $CDCl_3$) δ 138.7 (82%), 137.6 (18%) (Fig. 29). Anal. calcd for C 73.11, H 9.00, found C 73.33, H 9.22.

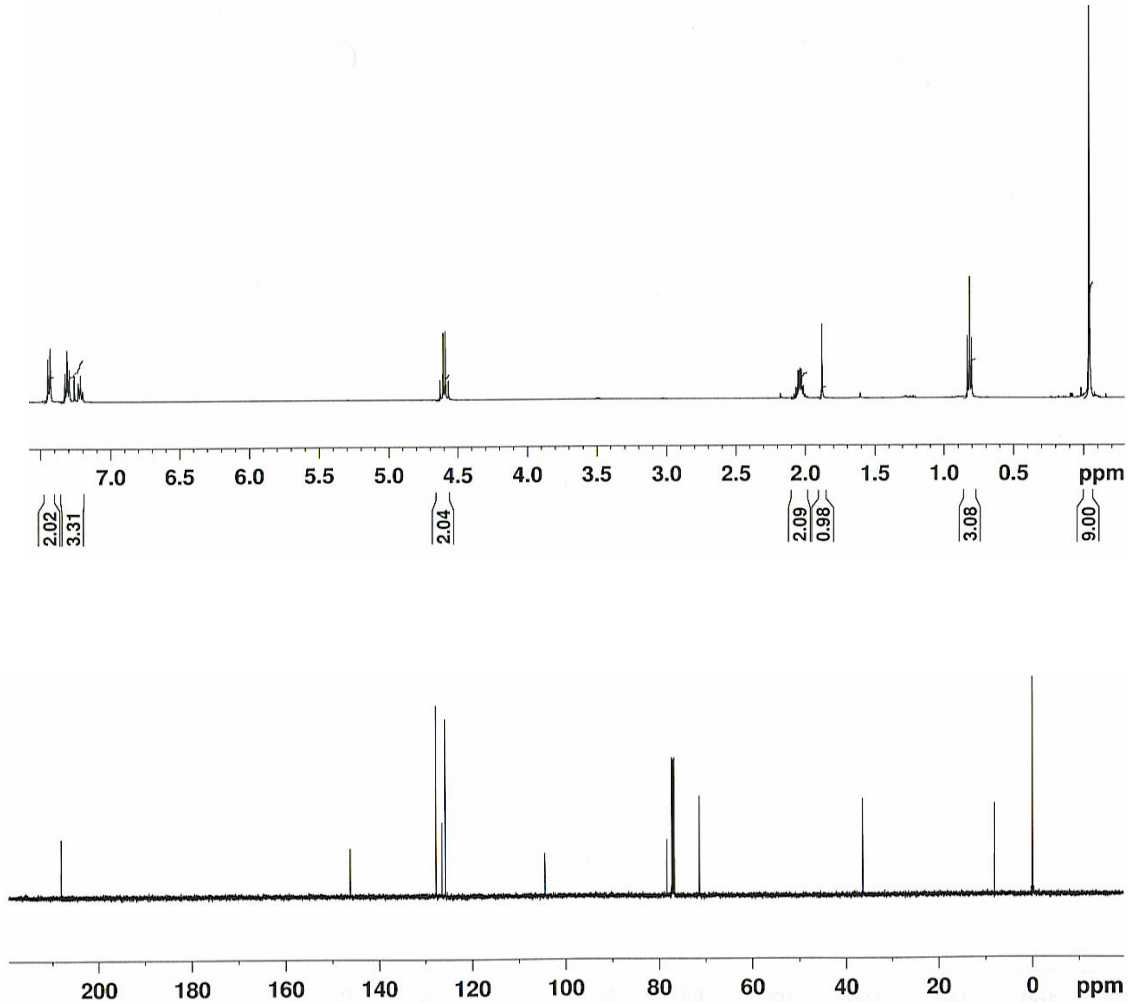
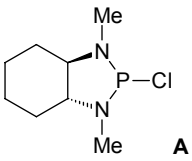


Figure 20. ^{13}C and ^{1}H NMR of **9j*R***.

Determination of enantiomeric purity.

The enantiomeric purity was determined by the ^{31}P NMR CDA method developed by Alexakis using the reported procedure.[12] All examples were calibrated with the phosphoramide **A**. (δ 184.0).



A

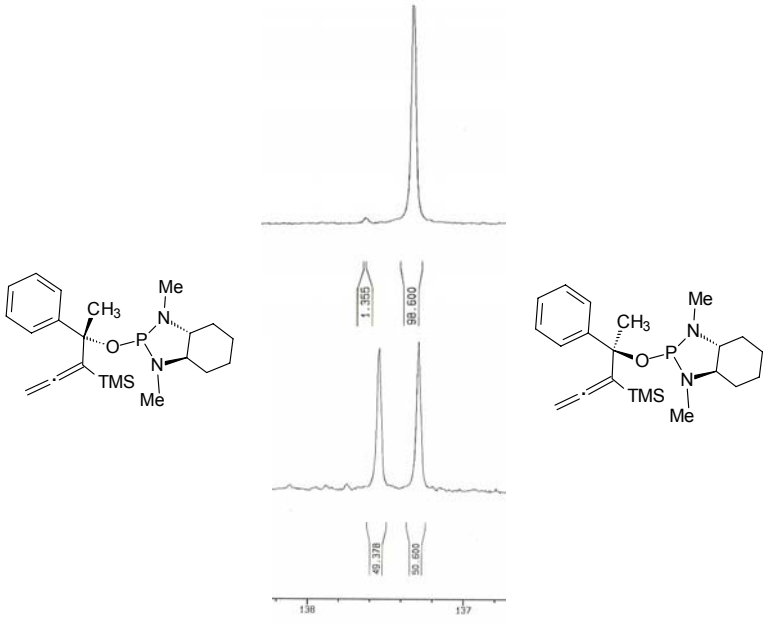


Figure 21. ^{31}P NMR of CDA derivative of **9a*R***.

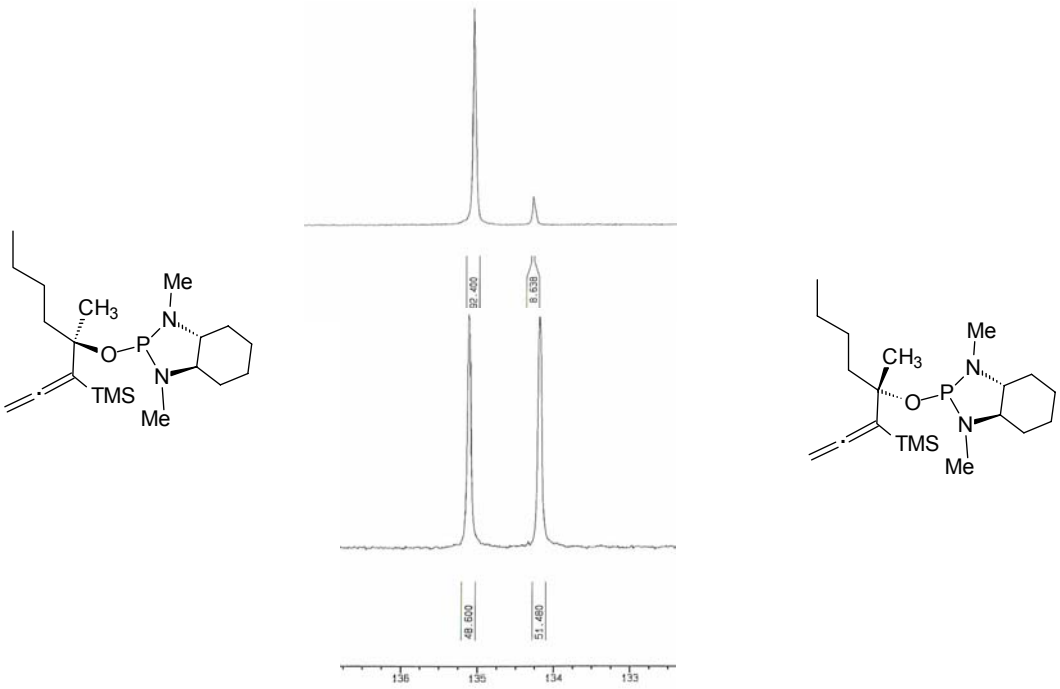


Figure 22. ^{31}P NMR of CDA derivative of **9b*R***

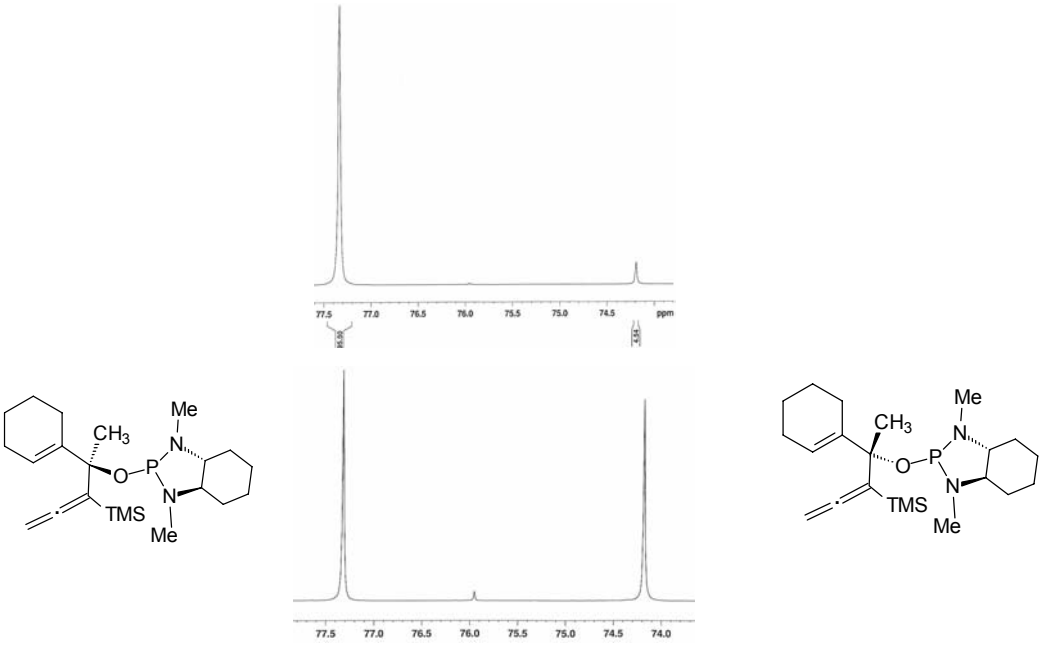


Figure 23. ^{31}P NMR of CDA derivative of **9c*R***

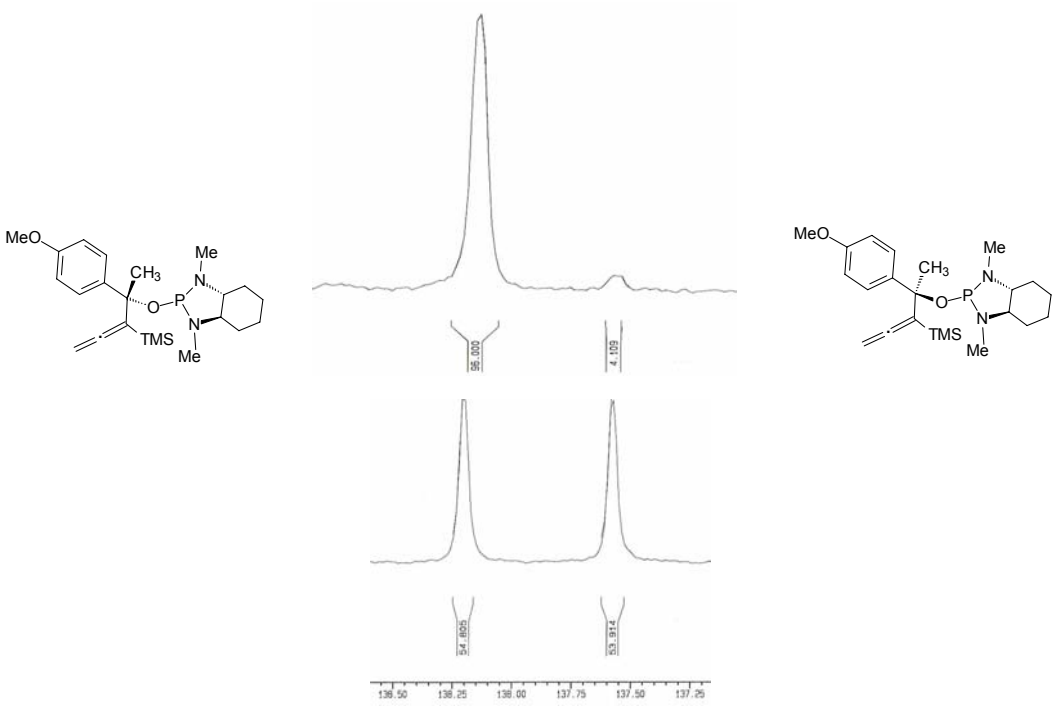


Figure 24. ^{31}P NMR of CDA derivative of **9d*S***.

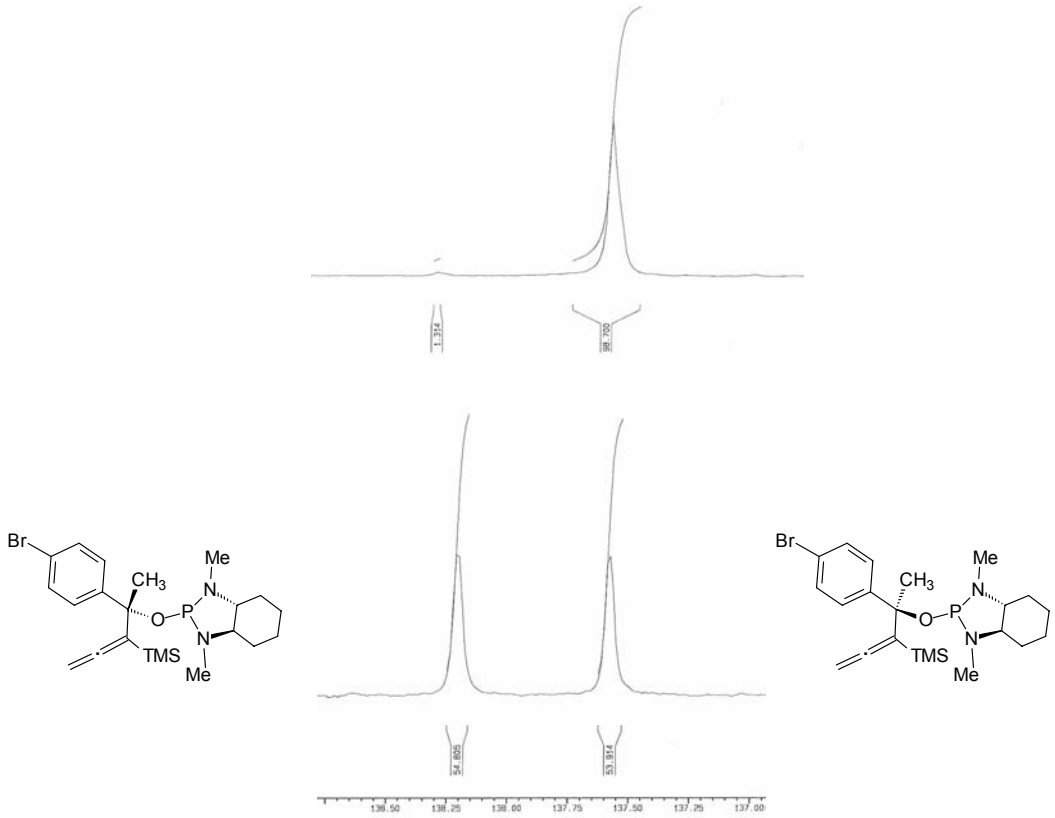


Figure 25. ^{31}P NMR of CDA derivative of **9e*R***.

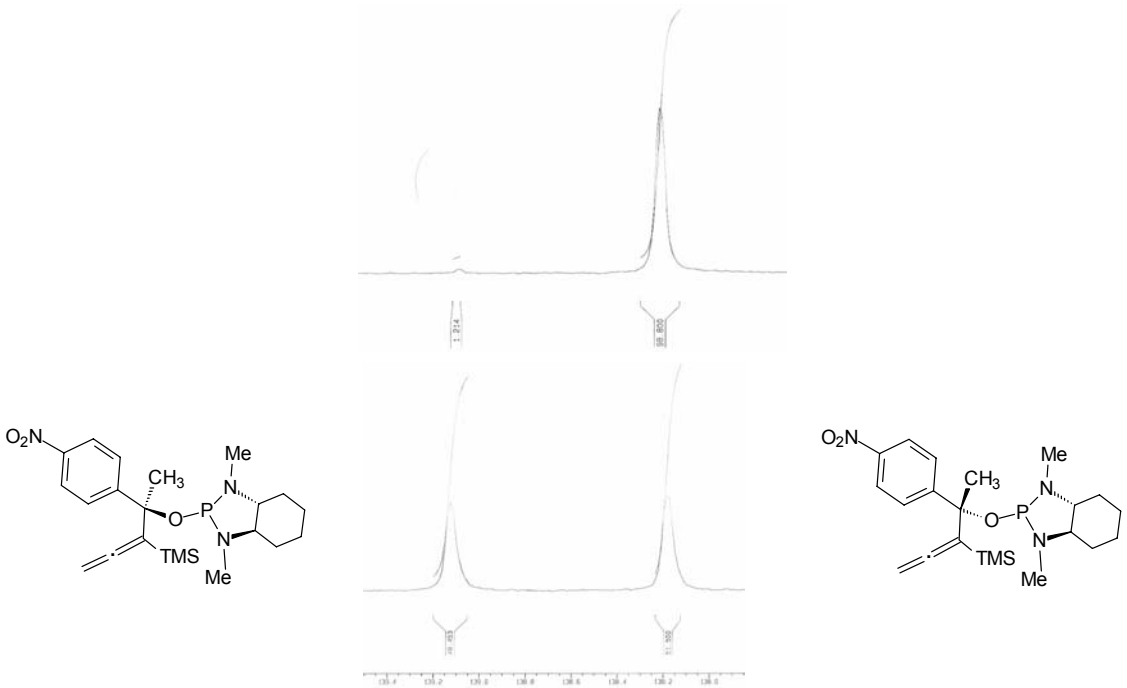


Figure 26. ^{31}P NMR of CDA derivative of **9f*R***

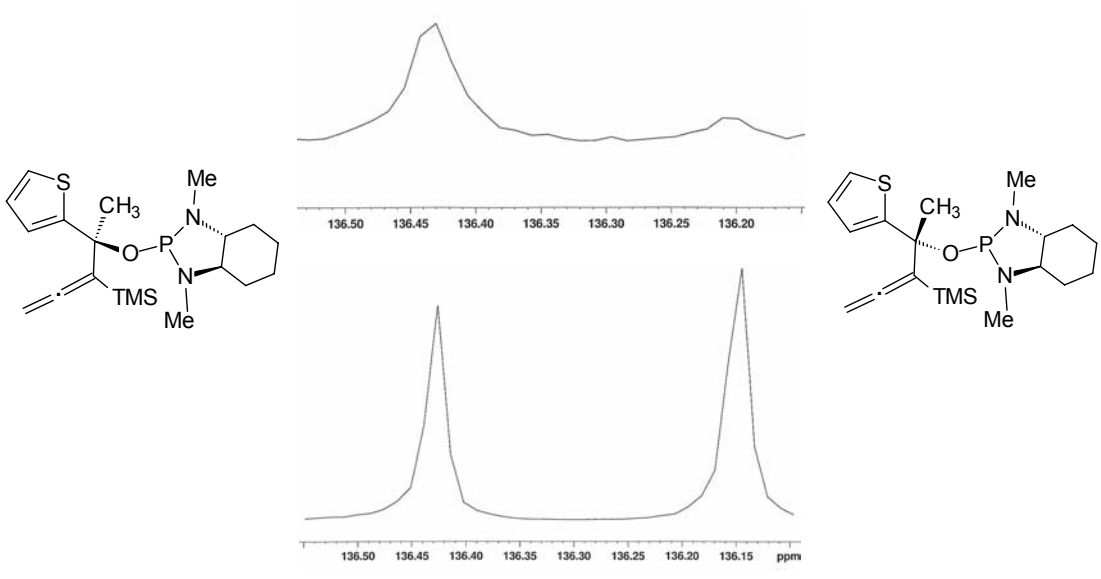


Figure 27. ^{31}P NMR of CDA derivative of **9h*S***

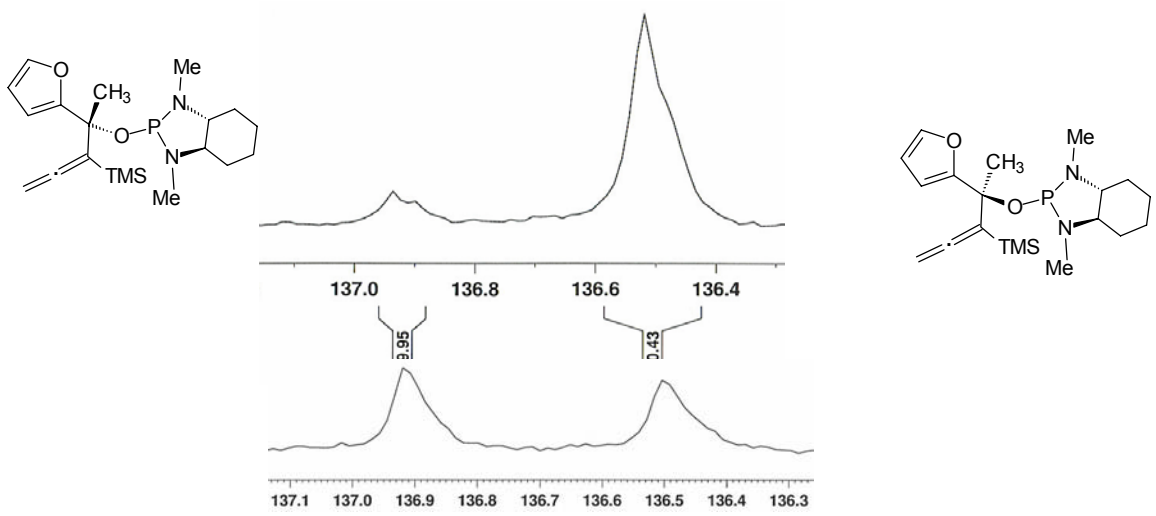


Figure 28. ^{31}P NMR of CDA derivative of **9i*R***

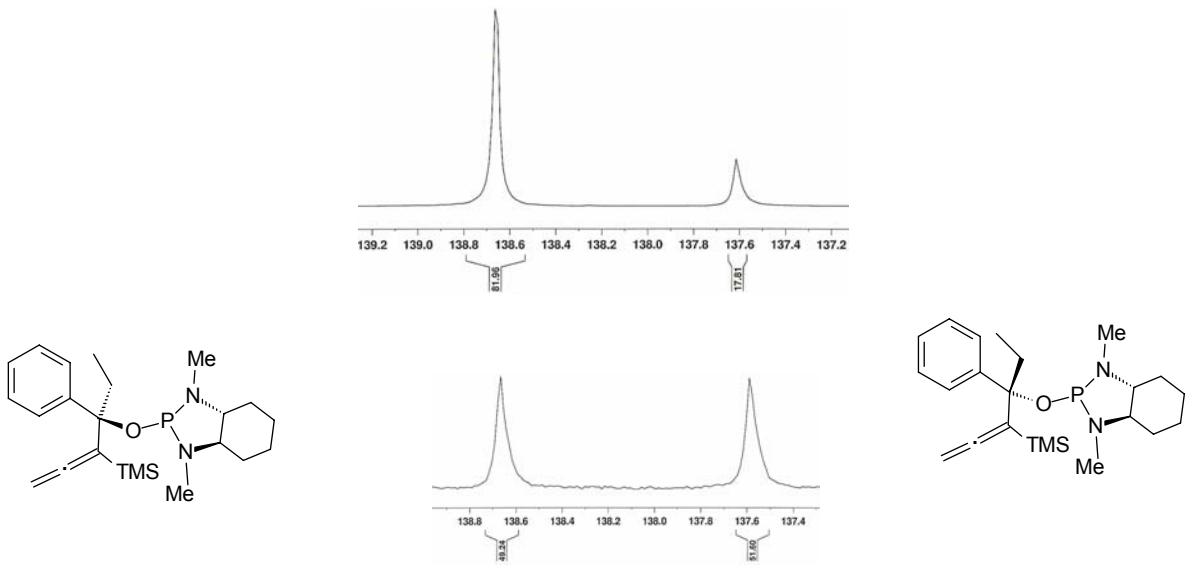
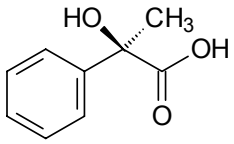


Figure 29. ^{31}P NMR of CDA derivative of **9j*R***



(*R*)-(-)-2-Hydroxy-2-phenylpropionic acid (Atrolactic acid, 12). The **(+)-9a*R*** (0.097 g, 0.42 mmol) was dissolved in dichloromethane (30 mL), and the solution was cooled to -78 ºC. Ozone was bubbled through the solution until a blue color persisted (10 min). The solvents were removed to reveal the formation of the silyl ester intermediate **11** (^{13}C NMR δ 179.1 (SiOC=O), 1.88 (TMS)) (Fig 30). THF (3 mL) was added followed by water (0.08 g, 0.42 mmol). The mixture was stirred for 3 h at room temperature and the solvents were removed *in vacuo* to give **12** (0.069 g, 100%). $[\alpha]_D^{25}$ = -37 (*c* 2.0 H_2O), lit.[12] (2*S*) $[\alpha]_D^{25}$ = +49 (*c* 2 H_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21 (s, 1H), 1.92 (s, 3H), 7.30-7.40 (m, 3H), 7.55-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.6, 75.7, 125.2, 128.12, 128.44, 141.8, 180.3 (Fig. 33). In a separate experiment, the ozonolysis was interrupted after 3 min, the mixture was concentrated and its ^{13}C NMR spectrum was recorded to clearly reveal the acylsilane intermediate **10** (*i.e.* δ 241.6 (TMSC=O); -1.82 (TMS)) (Fig. 31 and 32).

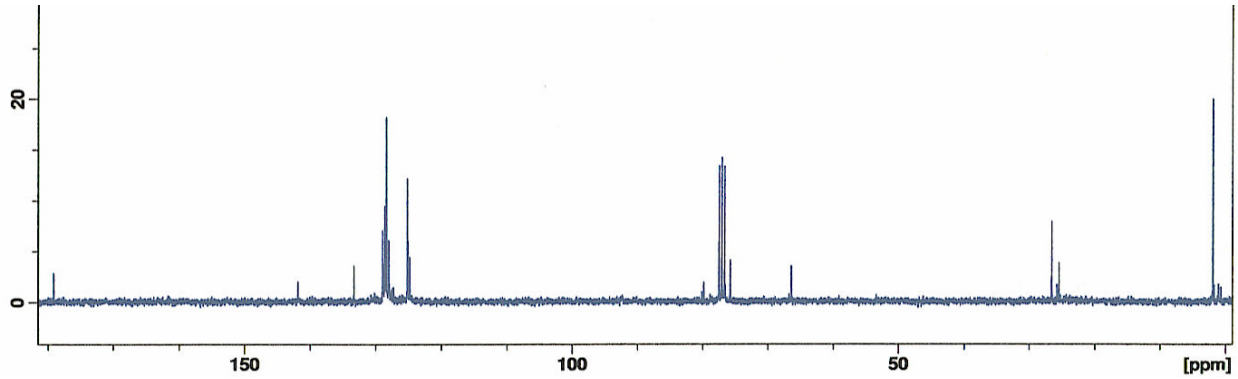


Figure 30. ^{13}C NMR of crude trimethylsilyl ester intermediate **11**.

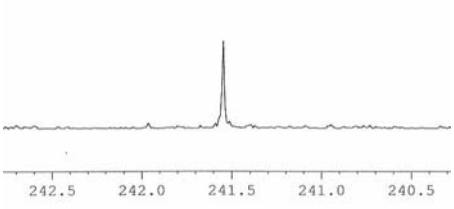


Figure 31. ^{13}C NMR of TMSC=O for intermediate **10**.

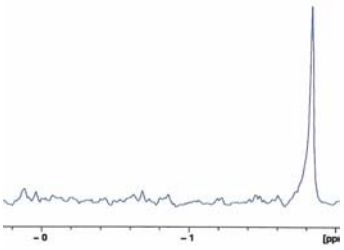


Figure 32. ^{13}C NMR of TMS for intermediate **10**.

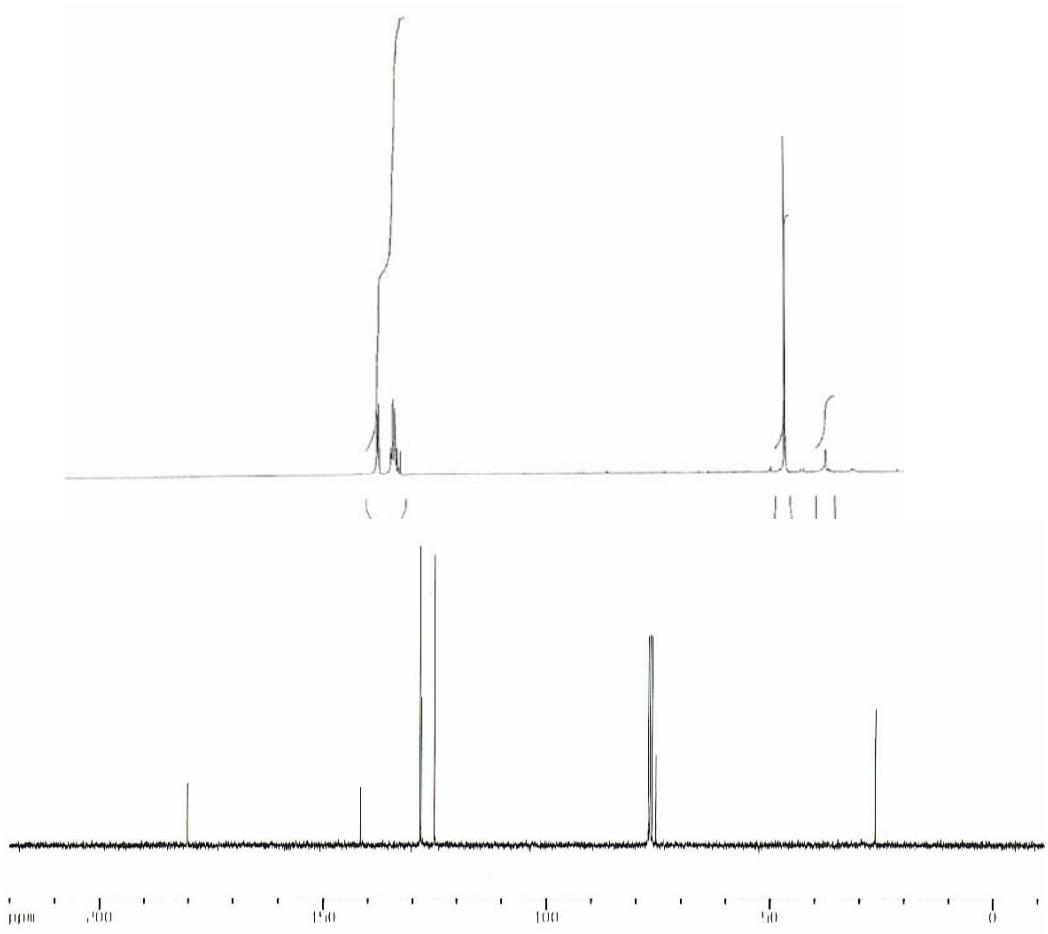
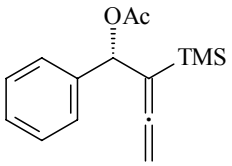
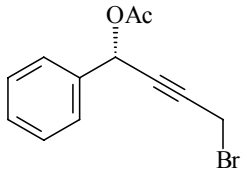


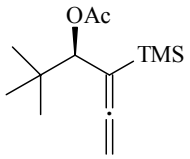
Figure 33. ^{1}H and ^{13}C NMR of 2-hydroxy-2-phenylpropionic acid **12**.



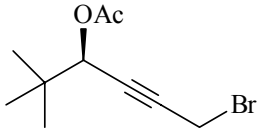
1-Acetoxy-1-phenyl-2-(trimethylsilyl)-2,3-butadiene (9k*S*).[11] The (+)-(1*S*)-1-phenyl-2-(trimethylsilyl)-2,3-butadien-1-ol (0.096 g, 0.44 mmol)[13] was dissolved in 5 mL of dry THF. DMAP (0.12 g, 1 mmol) was added followed by AcCl (0.1 mL, 1 mmol) at 0 °C and stirred for 1 h. The solution was allowed to reach room temperature and was stirred overnight. The organic layer was extracted with water (4 X 3 mL) to remove the excess of precipitated salts. The organic layer was dried with $MgSO_4$, filtrated and concentrated to give 0.10 g (89%) of **9k*S***. ^{1}H NMR ($CHCl_3$, 300 MHz) δ 0.02 (s, 9H), 2.09 (s, 3H), 4.53 (d, 2H), 6.29 (t, 1H), 7.27-7.37 (m, 5H); ^{13}C NMR ($CHCl_3$, 75 MHz) δ -1.14, 21.2, 71.64, 71.68, 97.6, 127.5, 128.1, 128.2 139.5, 169.9, 209.0.



(-)-(1*S*)-4-Bromo-1-(acetoxy)-1-phenyl-2-butyne (13k*S*). The **9k*S*** (0.0813 g, 0.31 mmol) was added to a solution of NBS (0.056 g, 0.31 mmol) in THF at 0 °C and stirred for 1 h. The reaction was allowed to reach room temperature and stirred for 3 h. The organic layer was extracted with water (3 X 5 mL), dried with $MgSO_4$, filtrated and concentrated. The crude oil was purified by silica gel column chromatography (hexane-ethyl ether, 80:20) to afford 0.0190 g (38 %) of **13k*S***. R_f = 0.47. ^{1}H NMR ($CHCl_3$, 300 MHz) δ 2.11 (s, 3H), 3.97 (d, *J* = 2.0 Hz, 2H), 6.49 (t, *J* = 2.0 Hz. 1H), 7.31-7.40 (m, 3H), 7.50 (dd, *J* = 4.0, 7.0 Hz, 2H); ^{13}C NMR ($CHCl_3$, 75 MHz) δ 13.8, 21.0, 65.5, 82.22, 83.11, 127.7, 128.7, 129.1, 136.5, 169.7 (Fig. 34); IR (neat) cm^{-1} 3033, 2924, 2868, 2361 (C≡C), 1739 (C=O), 1495, 1369, 1222, 1209, 1149, 1015, 957, 753, 696, 615, 555 (C-Br) cm^{-1}. HRMS $[M+H]^+$ calcd. 208.9783 found 208.9784. $[\alpha]_D^{20}$ = -28.6 (*c* 1.18, $CHCl_3$).

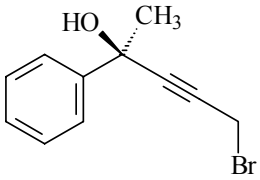


(+)-(3*R*)-3-Acetoxy-2,2-dimethyl-4-(trimethylsilyl)-4,5-hexadiene (9l*R*). The (+)-(3*R*)-2,2-dimethyl-4-(trimethylsilyl)-4,5-hexadien-3-ol (0.079 g, 0.40 mmol) was dissolved in 5 mL of dry THF. The DMAP (0.12 g, 1 mmol) was added followed by AcCl (0.1 mL, 1 mmol) at 0 °C and stirred for 1 h. The solution was allowed to reach room temperature and stirred overnight. The organic layer was extracted with water (4 X 3 mL) to remove the excess of precipitated salts, dried with $MgSO_4$, filtered twice through silica and concentrated to give 0.043 g (50%) of **9l*R***. $[\alpha]_D^{20}$ = +32.3 (*c* 0.60, $CHCl_3$). ^{1}H NMR ($CHCl_3$, 300 MHz) δ 0.12 (s, 9H), 0.95 (s, 9H), 2.03 (s, 3H), 4.42 (s, 2H); ^{13}C NMR ($CHCl_3$, 75 MHz) δ -0.6, 20.9, 26.2, 36.5, 70.3, 79.0, 94.9, 170.1, 210.1. HRMS $[M+H]^+$ calcd. 241.1618 found 241.1618.

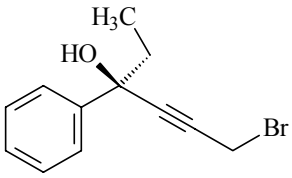


(+)-(3*S*)-3-Acetoxy-2,2-dimethyl-6-bromo-4-hexyne (13l*S*). A solution of **9l*R*** (0.043 g, 0.20 mmol) in THF at -78 °C was added to a solution of NBS (0.036 g, 0.20 mmol) in THF at -78 °C and stirred for 1 h. The reaction was allowed to reach room temperature and stirred for 12 h. The organic layer was extracted with water (3 X 5 mL), dried with $MgSO_4$, filtered and concentrated. The crude oil was purified by silica gel chromatography (hexane-AcOEt, 90:10) to afford product 0.030 g (61%) of **13l*S***. R_f = 0.45. ^{1}H NMR ($CHCl_3$, 300 MHz) δ 1.01 (s,

9H), 2.10 (s, 3H), 3.93 (d, *J* = 1.9 Hz, 2H), 5.12 (t, *J* = 1.9 Hz, 1H); ^{13}C NMR ($CHCl_3$, 75 MHz) δ 14.1, 20.8, 25.5, 35.3, 71.7, 80.8, 83.3. 170.1 (Fig. 35). $[\alpha]_D^{20}$ = +38.2 (*c* 2.26, $CHCl_3$). HRMS $[M+H]^+$ calcd. 233.1719 found 233.1719.



(-)-(2*S*)-5-Bromo-2-phenyl-3-pentyn-2-ol (13a*S*). A solution of **9a*R*** (0.072 g, 0.31 mmol) in THF at -78 °C was added *via cannula* to a solution of NBS (0.055 g, 0.31 mmol) in THF at -78 °C and stirred for 1 h. The reaction was allowed to reach room temperature and stirred for 3 h. The organic layer was extracted with water (3 x 5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by silica gel chromatography (hexane-EtOAc, 95:5) to afford 0.067 g (90%) of **13a*S***. R_f = 0.18. ^{1}H NMR ($CHCl_3$, 300 MHz) δ 1.77 (s, 3H), 2.48 (bs, 1H), 4.01 (s, 2H), 7.27-7.40 (m, 3H), 7.63 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CHCl_3$, 75 MHz) δ 14.1, 32.9, 70.0, 80.1, 90.1, 124.8, 127.86, 128.37, 145.0 (Fig. 36); IR (neat) cm^{-1} 3377, 3061, 3027, 2984, 2928, 2857, 2366 (C≡C), 1446, 1367, 1233, 1209, 1096, 1062, 1027, 762, 698, 601, 577 (C-Br) cm^{-1}. HRMS $[M+H]^+$ calcd. 236.9910 found 236.9910. $[\alpha]_D^{20}$ = -2.4 (*c* 1.59, $CHCl_3$).



(+)-(3*S*)-6-Bromo-3-phenyl-4-hexyn-3-ol (13b*S*). A solution of **9b*S*** (0.075 g, 0.30 mmol) in THF at -78 °C was added *via cannula* to a solution of NBS (0.062 g, 0.35 mmol) in THF at -78 °C and stirred for 1 h. The reaction was allowed to reach room temperature and was stirred for 12 h. The organic layer was extracted with water (3 x 5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by silica gel chromatography (hexane-EtOAc, 95:5) to afford 0.051 g (67%) of **13b*S***. R_f = 0.19. ^{1}H NMR ($CHCl_3$, 300 MHz) δ 0.95 (t, *J* = 7.4 Hz, 3H), 1.40 (s, 1H), 1.85-2.08 (m, 2H), 4.0 (s, 2H), 7.27-7.40 (m, 3H), 7.55-7.62 (m, 2H); ^{13}C NMR ($CHCl_3$, 75 MHz) δ 8.9, 14.3, 38.1, 73.9, 81.2, 89.0, 125.4, 127.79, 128.18, 143.9 (Fig. 37); IR (neat) cm^{-1} 3384, 2970, 2934, 2878, 2360 (C≡C), 1447, 1377, 1325, 1210, 1096, 1049, 757, 699, 569 (C-Br) cm^{-1}. $[\alpha]_D^{20}$ = +3.5 (*c* 1.90, $CHCl_3$). HRMS $[M-OH]^+$ calcd. 235.0117 found 235.0115.

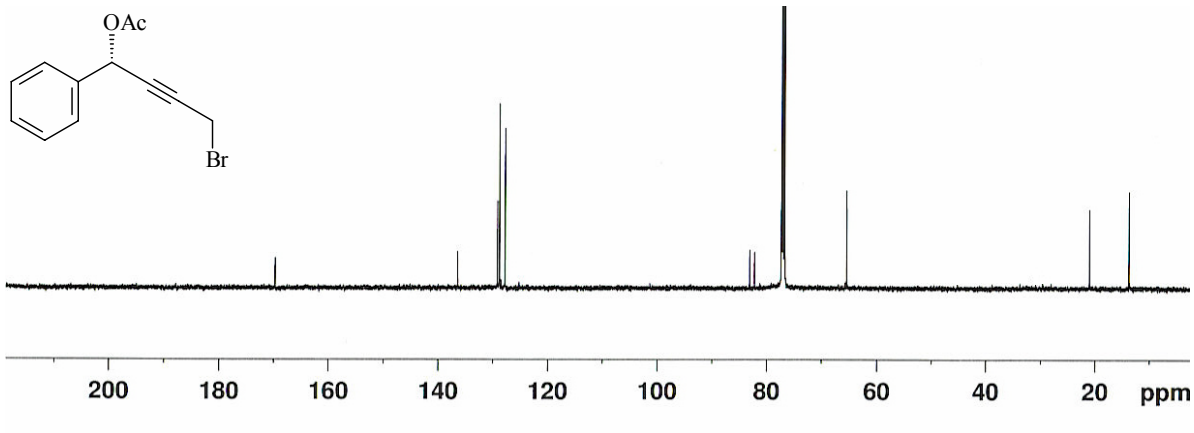


Figure 34. ^{13}C NMR of **13k*S***.

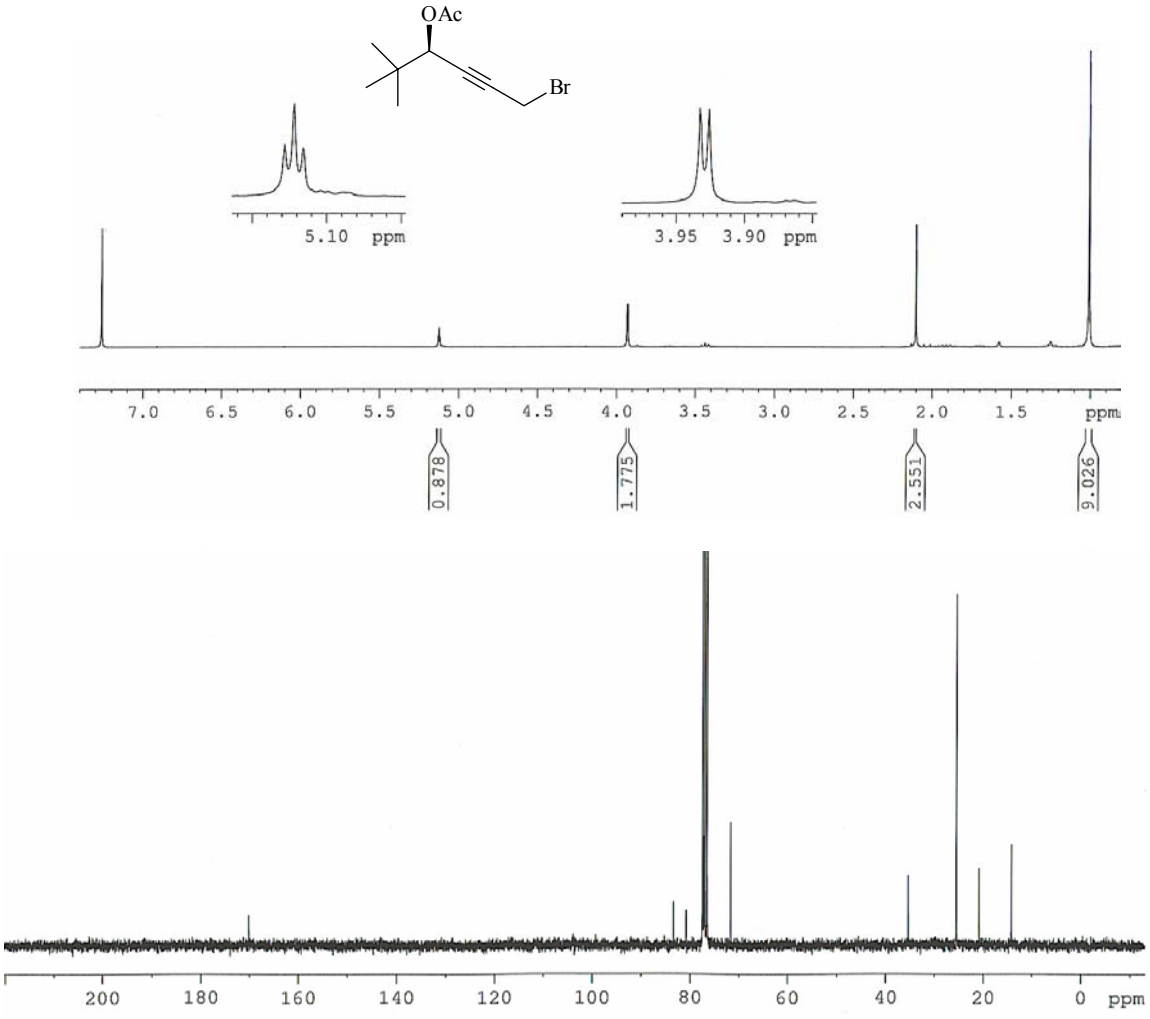


Figure 35. ^{13}C and ^{1}H NMR of **13I*S***.

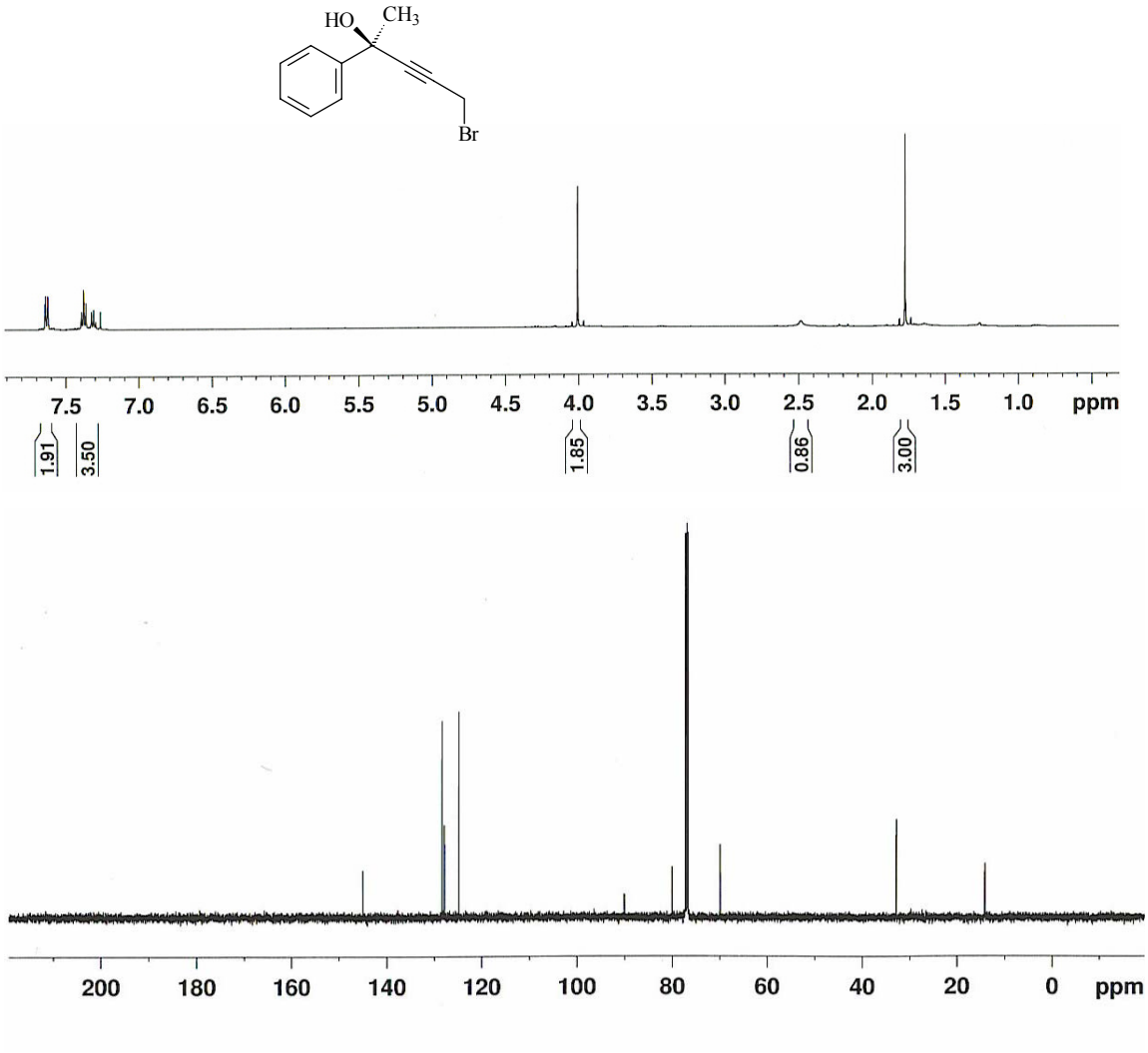


Figure 36. ^{13}C and ^{1}H NMR of **13aS**.

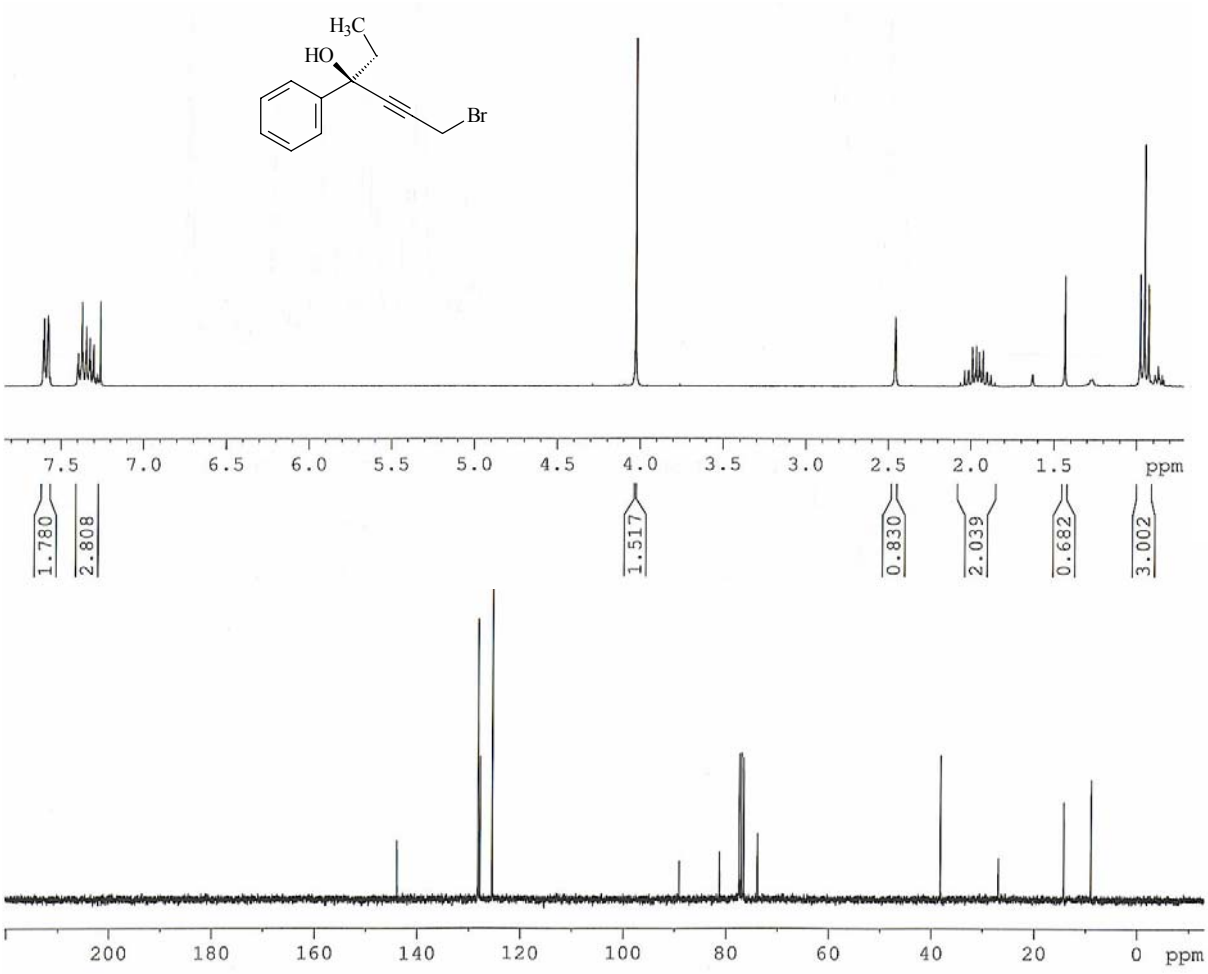


Figure 37. ^{13}C and ^{1}H NMR of **13b*S***. Note! Sample contains a small amount of cyclohexane impurity which was in the $CDCl_3$.

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(13) Lancaster Synthesis Catalog Research Chemicals 2004-2005, Lancaster Synthesis Inc.: Windham, NH (2004). Note! The synthesis of **12** was conducted on a small scale to determine the sign of rotation to assign the stereochemistry of **9a**. We made no attempt to rigorously remove water from our sample of **12** whose specific rotation is somewhat lower than the reported value (vide ultra). However, no loss of optically purity with the ozonolysis should be inferred from this data.