Supplementary Material

9-Borabicyclo[3.3.2]decanes and the Asymmetric Hydroboration of 1,1-Disubstituted Alkenes

Ana Z. González, Jose G. Román, Eduvigis González, Judith Martinez, Jesus R. Medina, Kart Matos and John A. Soderquist*

University of Puerto Rico, Department of Chemistry, Rio Piedras, PR 00931-3346

.

Table of Contents

List of Figures

I. 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 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. Several reported procedures are included herein to consolidate the information for future researchers.

II. General procedures for the synthesis of reagents.

(±)-*B*-Methoxy-10-trimethylsilyl-9-borabicyclo[3.3.2]decane (8b).[1] 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 **8b** (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 (+)-2bR.

(+)-*B*-((1*S*,2*S*-Pseudoephedrinyl))-(10*R*)-trimethylsilyl-9-borabicyclo[3.3.2]decane ((+)-2b*R*). To a solution of (1*S*,2*S*)-pseudoephedrine (8.28 g, 50 mmol) in acetonitrile (110 mL) was added **8b** (23.85 g, 100 mmol) dropwise. The reaction mixture was refluxed for 6 h and slowly cooled to room temperature resulting in large crystals (Figure 1). 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* (+)-**2b*R*** (38% yield, mp 106-109 °C): $[\alpha]_D^{28}$ = + 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.

(-)-*B*-((1*R*,2*R*-Pseudoephedrinyl))-(10*S*)-trimethylsilyl-9-borabicyclo[3.3.2]decane ((-)-2b*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, $CDCl_3$).

(±)-*B*-Methoxy-10-phenyl-9-borabicyclo[3.3.2]decane (8a).[2] To a solution of *B*-MeO-9-BBN (18.0 g, 118 mmol) in hexanes (110 mL), $PhCHN_2$ 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 **9a** (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; 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 calcd. 242.18 found 242.15.

(+)-*B*-((1*S*,2*S*)-*N*-Methylpseudoephedrinyl))-(10*S*)-phenyl-9-borabicyclo[3.3.2]decane ((+)-2a*S*). To a solution of (1*S*, 2*S*)-*N*-methylpseudoephedrine

(5.0 g, 27.9 mmol) in hexane (60 mL) was added **8a** (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 (+)-**2a*S*** (38% yield). The supernatant is concentrated and fresh hexane (60 mL) is added the mixture is then 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 (+)-**2a*S***. The overall yield of (+)-**2a*S*** is 79 % (39.5% based upon **8a**). ^{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, CDCl3) 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).

(-)-*B*-((1*R*,2*R*)-*N*-Methylpseudoephedrinyl))-(10*R*)-phenyl-9-borabicyclo[3.3.2]decane((-)-2a*R*)). The above supernatant was concentrated. The resulting residue was dissolved in hexane (60 mL) and mixed with (1*R*,2*R*)-*N*-methylpseudoephedrine (5.0 g, 27.9 mmol). The reaction mixture was refluxed for 6 h, whereupon it was slowly cooled to room temperature forming small square and 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 (-)-**2a*R***. The supernatant is concentrated and fresh hexane (60 mL) is added the mixture is then refluxed for an additional 6 h. Upon cooling a second batch of crystals (2.0 g) are obtained following the above work-up. The overall yield of (-)-**2a*R*** is 56 % (28 % based

upon **8a**). mp = 135- 140 ° $[\alpha]^{D}_{25}$ = - 66.6° (c = 4.5, CH_2Cl_2). Pseudoephedrine can also be used to precipitate the residual isomer.

(+)-*B*-((1*S*,2*S*)-Pseudoephedrinyl))-(10*R*)-phenyl-9-borabicyclo [3.3.2]-decane ((+)-7*R*). As above, with (1*S*,2*S*)-pseudoephedrine, 29%, $[\alpha]^{D}_{28}$ = + 25.45° (c= 1.1, CH_2Cl_2).

III. General Procedure for the preparation of *B*-H-10-trimethylsilyl(phenyl)-9-BBD reagents (1).

Note! The (+/-)-**1** reagents used for the synthesis of (+/-)-**3** were prepared through the following procedures substituting **8** for **2**.

Lithium-*B*-H_2-(10*R*)-trimethylsilyl-9-borabicyclo[3.3.2]decane (3b*R*). To (+)-**2b*R*** (1.11 g, 3.0 mmol) in Et_2O (3 mL) at 0 °C, EtOAc (0.15 mL, 1.5 mmols) was added followed by the dropwise addition of $LiAlH_4$ (3 mL, 1.0 M in ether). The solution was allowed to reach room temperature and was stirred for 12 h. Using standard techniques to prevent the exposure of the borohydride to the open atmosphere, the solution was transferred to a centrifuge tube, the residue was washed with pentane (10 mL) and the biphasic solution was centrifuged. The clear supernatant was decanted into a clean, cooled under N_2, 100 mL round bottom flask, and fresh pentane (10 mL) was added to the remaining salts to be washed and centrifuged again (this process is repeated two more times). These washings were concentrated to obtain **3b*R*** in 98% yield (0.64 g, 2.96 mmol); ^{11}B NMR (C_6D_6, 96 MHz) δ -20.0 (t, *J* = 67 Hz); ^{1}H NMR ($CDCl_3$, 300 MHz) δ -0.05 (s, 9 H), 1.49- 1.89 (m, 17 H) (Figure 3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 2.4, 19.5, 24.1, 24.9, 26.4, 33.9, 34.6, 36.2, 36.3, 38.0. **3b*S*** is prepared by the same procedure starting with (-)-**2b*S***.

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

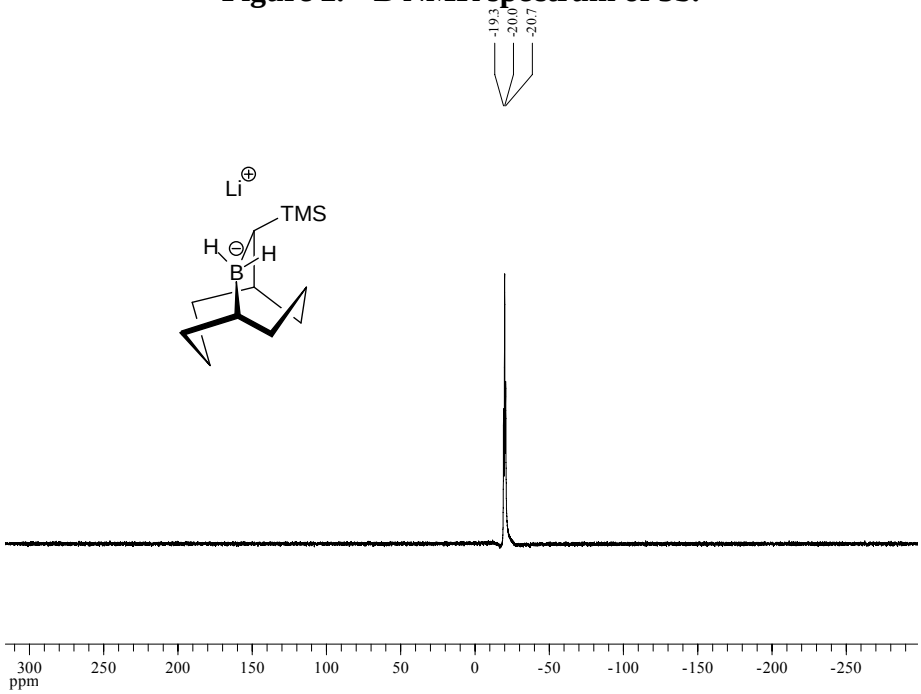


Figure 3. ^{1}H NMR spectrum of **3b** (additional peaks corresponding to Et_2O are shown).

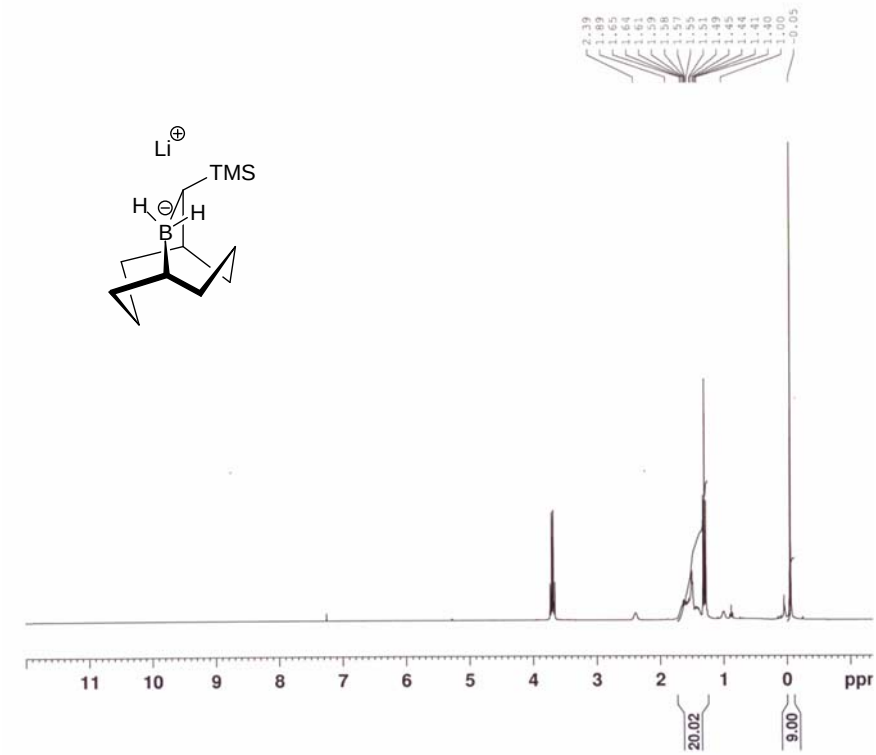
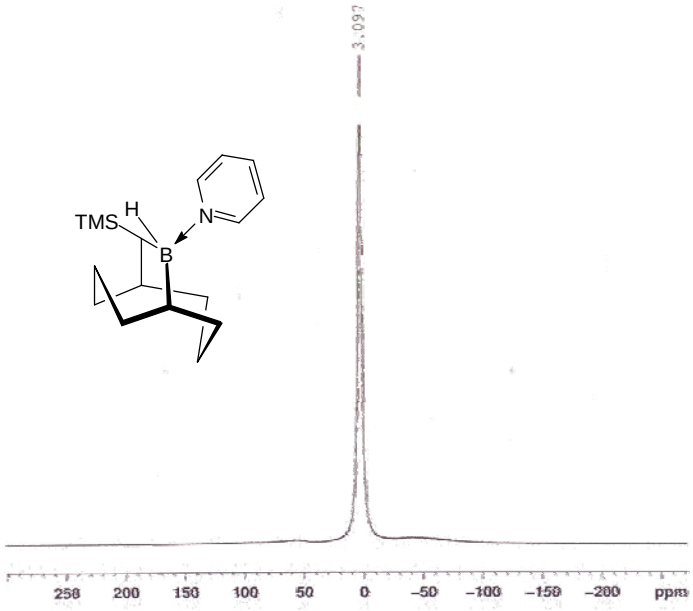


Figure 4. ^{11}B NMR spectrum of 4bS.

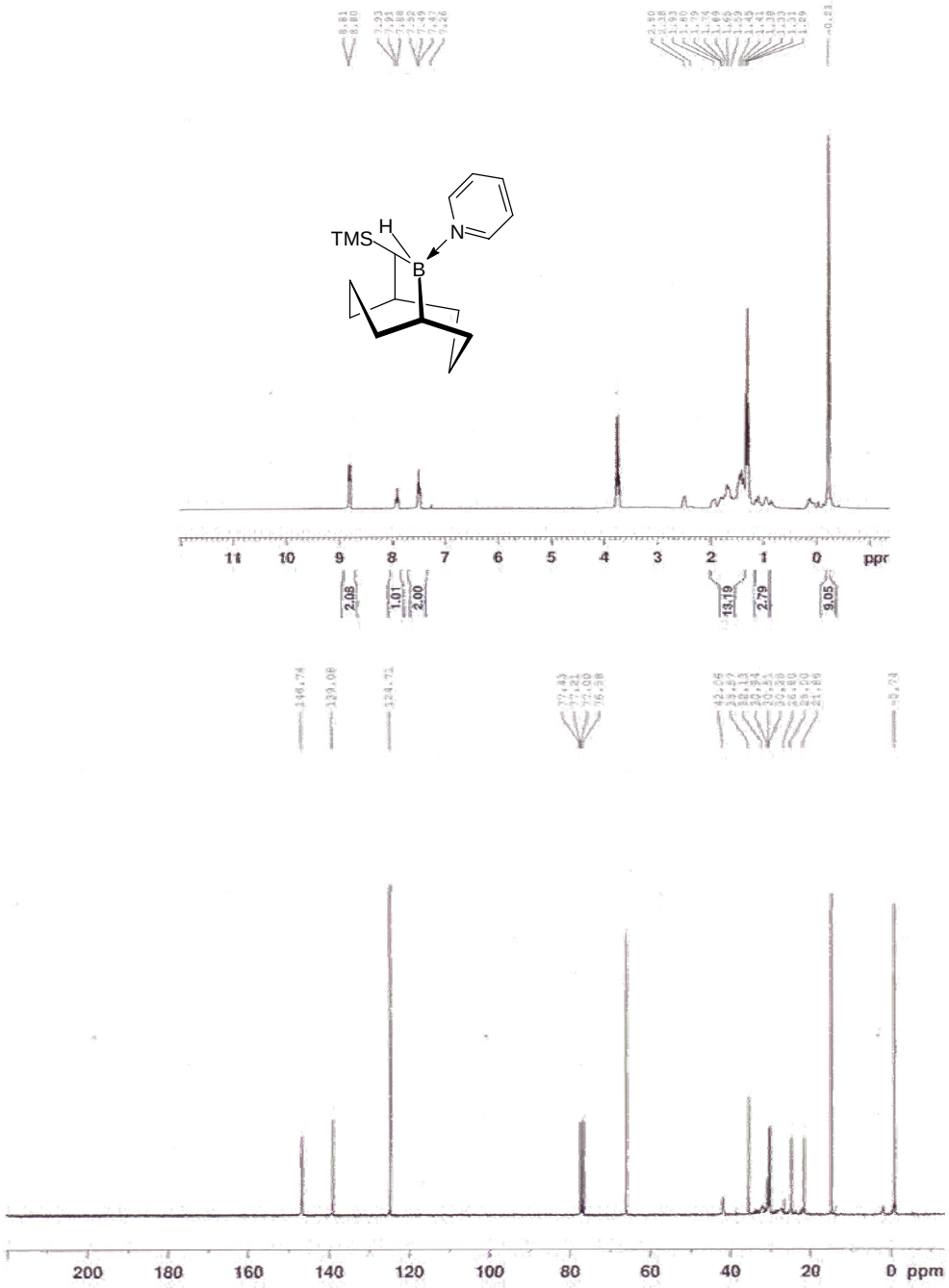


(±)-*B*-H-TMS-9-borabicyclo[3.3.2]decane ((±)-1b). A 50 mL centrifuge vial fitted with a rubber septum and a magnetic stirring bar was charged with a solution of **3b** (0.64 g, 2.96 mmol) in ether (6 mL). To this solution chlorotrimethylsilane (0.45 mL, 3.5 mmols) was added and then, the reaction mixture was centrifuged. The clear supernatant solution was transferred to an oven-dried, cooled under N_2, round-bottomed flask. The LiCl precipitate was washed with ether (2 × 2.5 mL) and the washings were combined with the supernatant solution which was concentrated *in vacuo* to give (±)-**1b** in 79% yield (0.46 g, 2.2 mmols). ^{11}B NMR ($CDCl_3$, 96 MHz) δ 24.6, 79.0)[3]; IR (cm^{-1}, solution): 2918, 2496, 1378, 841.

B*-H-(10*S*)-trimethylsilyl-9-borabicyclo[3.3.2]decane · pyridine (4b*S*).** In an NMR tube, to **3b*S (0.11 g, 0.5 mmol) in $CDCl_3$ (0.5 mL) at 25 °C was added pyridine (0.5 mmol, 0.04 mL) followed by the dropwise addition of MeI (0.06 mL, 1 mmol). ^{11}B NMR ($CDCl_3$, 96 MHz) δ 3.1 (Figure 4); ^{1}H NMR ($CDCl_3$, 300 MHz) δ -0.23 (s, 9H),

1.29- 1.45 (m, 3H), 1.59- 1.93 (m, 13H), 7.47 (t, *J* = 6.8 Hz, 2H), 7.91 (t, *J* = 7.6 Hz, 1H), 8.81 (d, *J* = 5.4 Hz, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.7, 21.9, 25.0, 26.8, 30.3, 30.5, 30.9, 32.1, 35.6, 42.1, 124.7, 139.1, 146.7 (Figure 5).

Figure 5. ^{13}C (top) and ^{1}H NMR (bottom) spectra of 4bS (additional diethyl ether peaks are also observed).



Lithium-*B*-H_2-(10*R*)-phenyl-9-borabicyclo[3.3.2]decane (3a*R*). To (+)-**2a*R*** (1.17 g, 3.0 mmol) in Et_2O (3 mL) at 0 °C, EtOAc (0.15 mL, 1.5 mmols) was added followed by the dropwise addition of $LiAlH_4$ (3 mL, 1.0 M in ether). The solution was allowed to reach room temperature and stirred for 12 h. Using standard techniques to prevent the exposure of the borohydride to the open atmosphere, the solution was transferred to a centrifuge vial fitted with a rubber septum, the residue was washed with pentane (10 mL) and the biphasic solution was then centrifuged. The clear supernatant was decanted *via* cannula into a clean, cooled under N_2, 100 mL round-bottomed flask. The diethoxyalane precipitate was washed with fresh pentane (2 × 10 mL) and centrifuged. These washings were combined and concentrated *in vacuo* to obtain **3a*R*** in 95% yield (0.64 g, 2.9 mmol); ^{11}B NMR ($CDCl_3$, 96 MHz) δ -12.4 (t, J = 67 Hz) (Figure 6); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.36- 1.94 (m, 13H), 2.20 (s, 1H), 2.48 (s, 1H), 6.98 (t, J = 7.3 Hz, 1H), 7.19 (t, J = 7.2, 2H), 7.36 (d, J = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 25.0, 26.1, 30.7, 32.6, 34.1, 37.0, 41.8, 42.2, 122.2, 127.3, 128.8, 138.2 (Figure 7). **3a*S*** is prepared by the same procedure starting with (-)-**2aS**.

Figure 6. ^{11}B NMR spectrum of 3a.

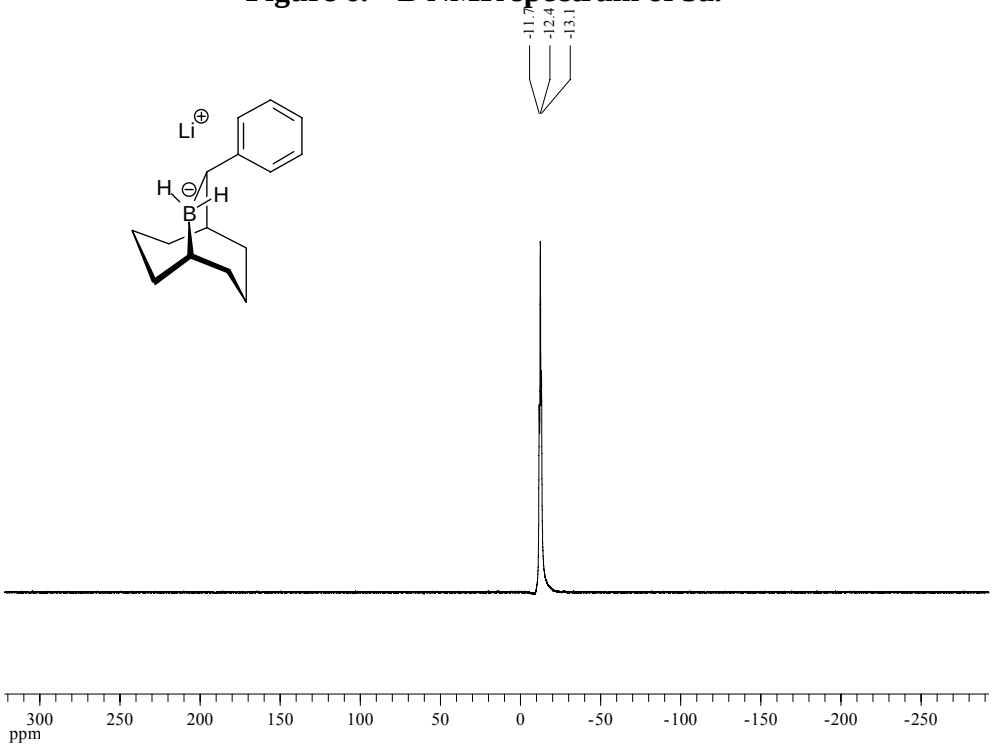
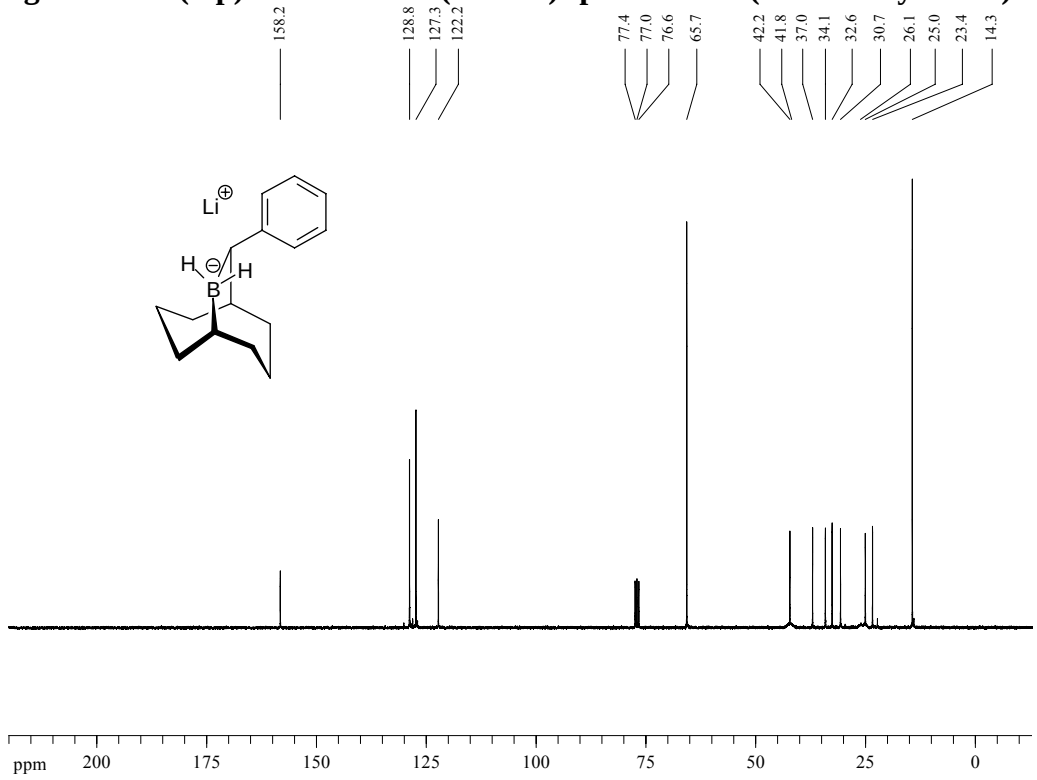
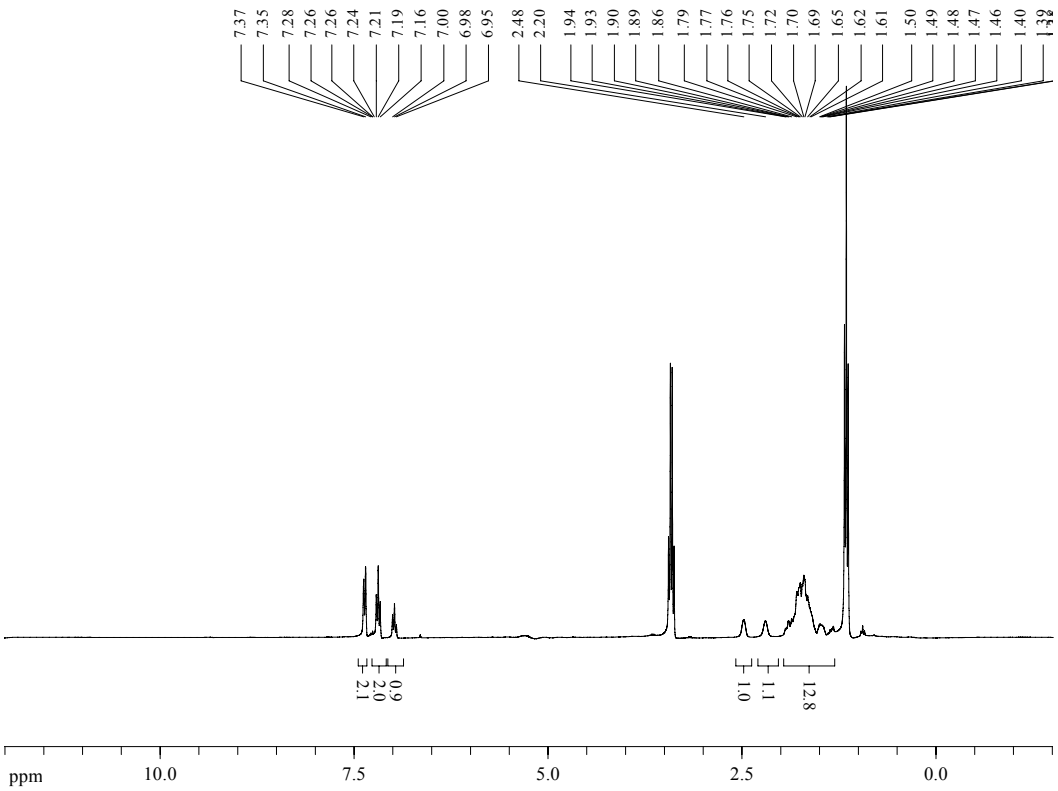


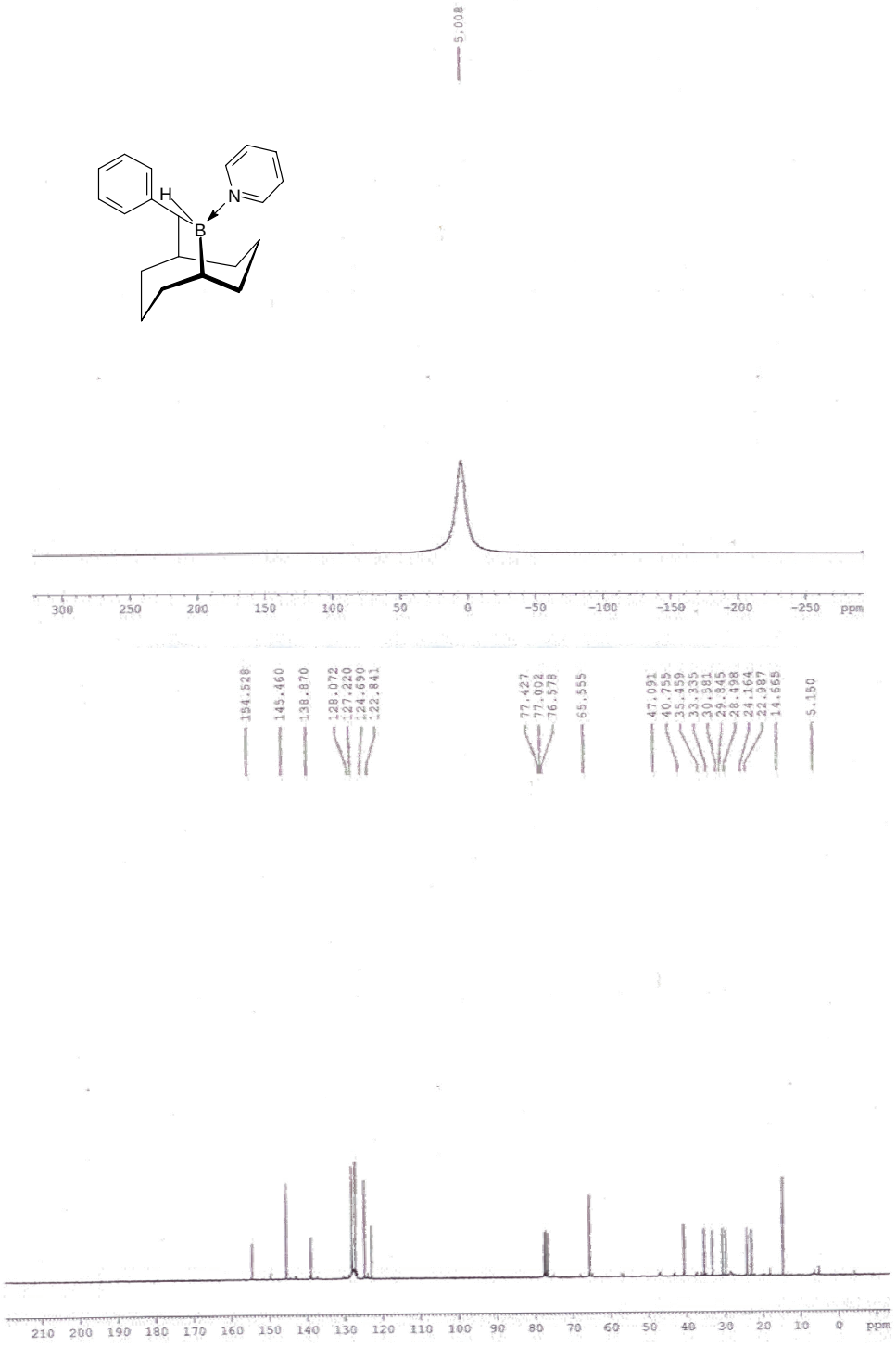
Figure 7. ^{13}C (top) and ^{1}H NMR (bottom) spectra of 3a (with diethyl ether).

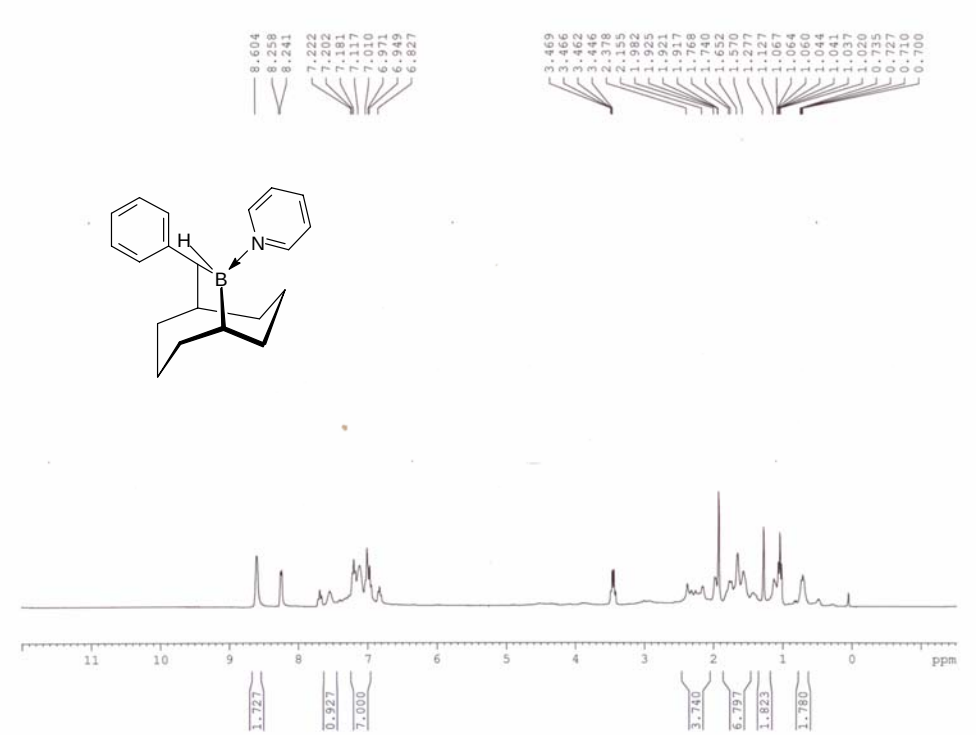




B*-H-(10*S*)-phenyl-9-borabicyclo[3.3.2]decane · pyridine (4a*S*).** In an NMR tube, to **3a*S (0.11 g, 0.5 mmol) in $CDCl_3$ (0.5 mL) at 25 °C was added pyridine (0.5 mmol, 0.04 mL) followed by the dropwise addition of MeI (0.06 mL, 1 mmol). ^{11}B NMR ($CDCl_3$, 96 MHz) δ 5.0; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.70-0.74 (m, 2H), 1.28 (s, 2H), 1.58-1.92 (m, 7H), 2.15-2.38 (m, 4H), 6.95-7.22 (m, 7H), 7.57 (s, 1H), 8.60 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 24.2, 28.5, 29.8, 30.6, 33.3, 35.5, 40.8, 47.1, 122.8, 124.7, 127.2, 128.1, 138.9, 145.5, 154.5 (Figure 8).

Figure 8. ^{11}B (top), ^{13}C (bottom) and ^{1}H (top, next page) spectra of 4a.





B*-H-(10*S*)-phenyl-9-borabicyclo[3.3.2]decane (1a*S*).** In an NMR tube, to **3a*S (0.11 g, 0.5 mmol) in $CDCl_3$ (0.5 mL) at 25 °C MeI (0.06 mL, 1 mmol) was added followed by the dropwise. ^{11}B NMR ($CDCl_3$, 96 MHz) δ 27.4 (Figure 9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.0, 23.4, 24.7, 24.9, 27.6, 28.3, 28.9, 29.0, 29.1, 29.8, 30.7, 31.3, 31.4, 41.4, 41.6, 124.4, 125.5, 127.4, 127.5, 127.8, 127.9, 147.2, 149.5 (Figure 10) **.**

Figure 9. ^{11}B NMR spectrum of 1aS.

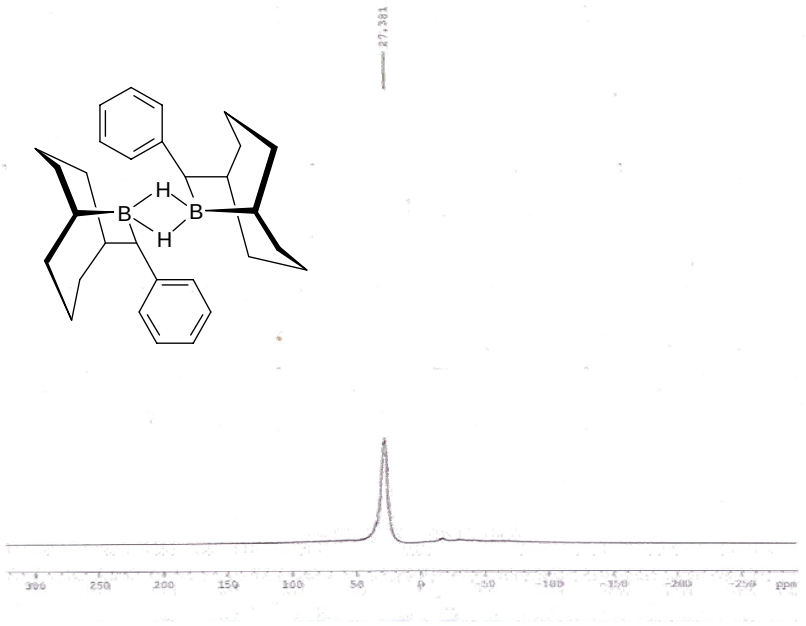
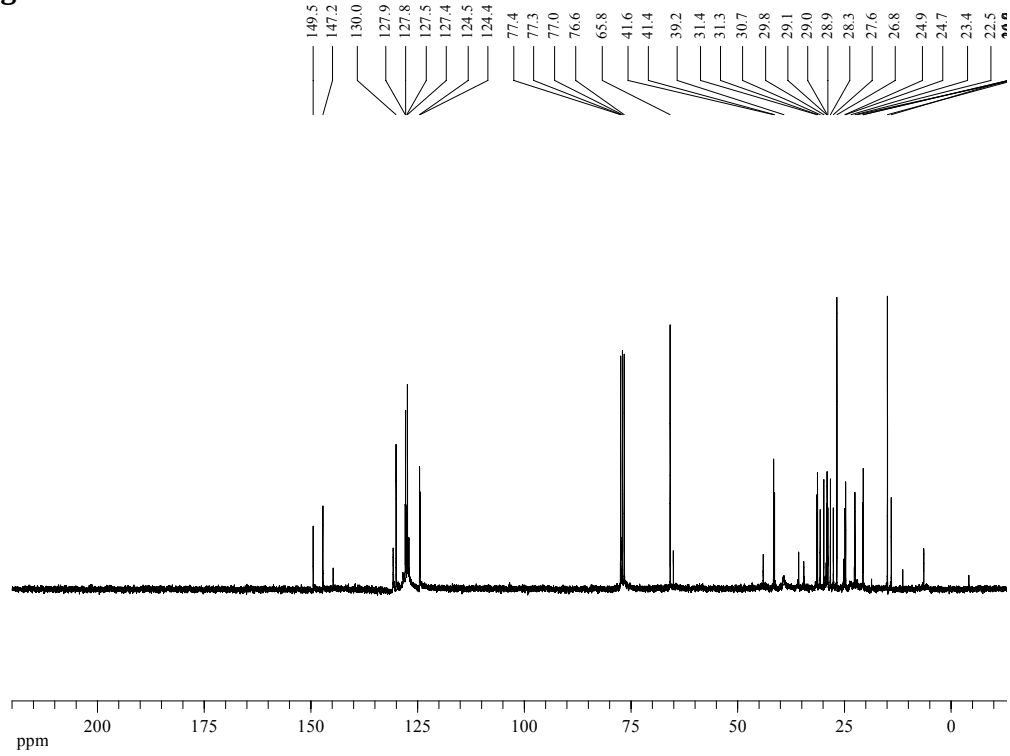
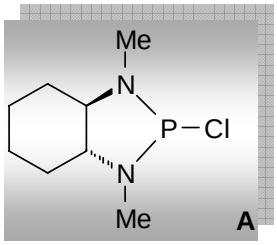


Figure 10. ^{13}C NMR spectrum of 1aS (Additional peaks corresponding to MeI and diethyl ether are also shown; the complexity of the spectrum is due to configurational isomers of dimeric 1aS.



IV. Determination of the enantiomeric purity:



The enantiomeric purity for most samples (**6c, 6d, 6h**) was determined by ^{31}P NMR by derivatization of the corresponding carbinols with the CDA reagent developed by Alexakis[4] using the reported procedures. All samples were calibrated with the phosphoramide **A** (see Figure to the left) (δ 184).

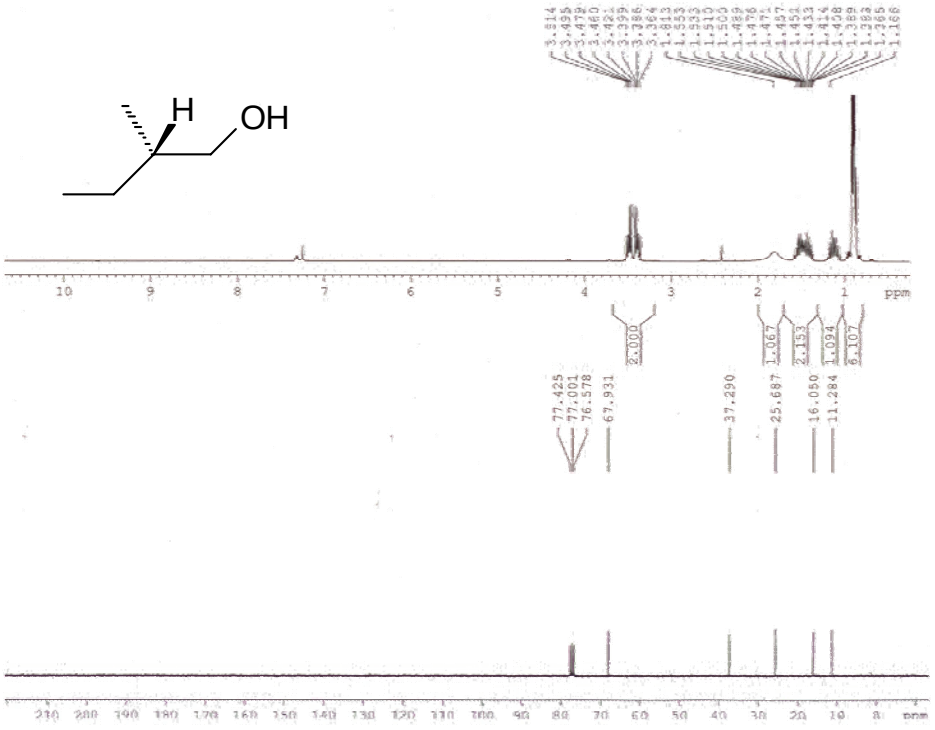
V. General Procedure for the synthesis of primary carbinols 6c-i.

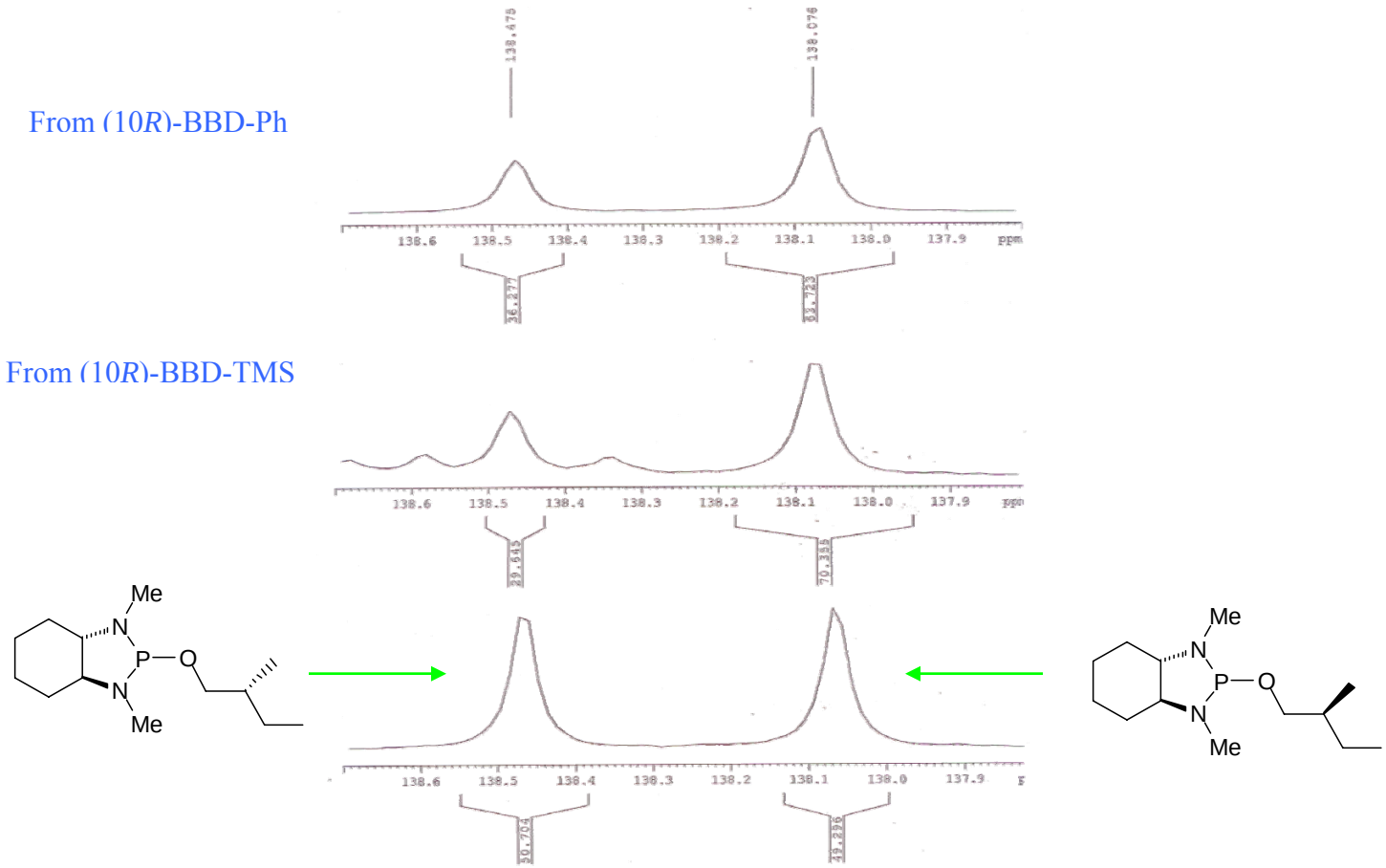
(*S*)-(-)-2-Methyl-1-butanol (6c).[5] To a solution of **3a*R*** (0.64 g, 2.9 mmol) in ether (3 mL) at -40 °C, 2-methyl-1-butene (0.38 mL, 3.5 mmols) was added followed by the addition of TMSCl (0.58 mL, 4.5 mmols). The reaction mixture was allowed to slowly reach 25 °C and allowed to react for 12 h.[6] Using standard techniques to prevent the exposure of the trialkylborane to the open atmosphere, the solution was concentrated *in vacuo*, diluted in pentane (20 mL) and filtered through a celite pad washing the remainings with pentane (2 × 20 mL). The resulting trialkylborane (**5**) was diluted in 10 mL of THF followed by the addition of NaOH (2.0 mL, 3 M) and then H_2O_2 (0.9 mL, 30 %). The biphasic mixture 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 product distilled at 125 °C to obtain 0.22 g (83%) of **6c*S*.** ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, J = 4.4 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H), 1.08-1.20 (m, 1H), 1.45 (dq, J = 13.1, 7.4 Hz, 1H), 1.53 (dq, J = 13.0 Hz J = 6.4 Hz, 1H), 1.81(s, broad OH, 1H), 3.45 (dt, J = 10.4, 5.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.3, 16.1, 25.7, 37.3, 67.9 (Figure 11). These data were in complete agreement with literature values.[5]

From **3b*R***: 0.23 g (87 % yield, 3 mmols scale) $[\alpha]_D^{25}$ = -1.7° (*c* = 1.00, CH_2Cl_2, 40% ee) [Lit.[5] (for **6c*S***): $[\alpha]_D^{25}$ = -5.8° (neat, 99% ee)] . The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 138.1 (major), 138.5 (minor) compared with the racemic derivative (50:50) (Figure 11).

From **3a*R***: $[\alpha]_D^{25}$ = -1.1° (*c* = 1.00, CH_2Cl_2, 28% ee). The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 138.1 (major), 138.5 (minor) compared with the racemic derivative (50:50) (Figure 11).

Figure 11. ^{1}H (top), ^{13}C (bottom) NMR spectra of 6c and ^{31}P NMR spectrum (top, next page) of 6c-CDA.





2,3-Dimethyl-1-butanol (6d).[7] The product distilled at 68 °C @ 30 mmHg to obtain 0.25g (82% from **3b*S***, 3 mmols scale) of **6d**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ δ 0.83 (t, *J* = 7.1 Hz, 6H), 0.89 (d, *J* = 6.8 Hz, 3H), 1.43-1.52 (m, 1H), 1.62- 1.73 (m, 1H), 1.99 (s, broad OH, 1H), 3.41 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.56 (dd, *J* = 10.5, 5.9 Hz, 1H) (Fig.13); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.4, 17.9, 20.6, 28.7, 41.3, 67.9 (Figure 12). These data were in complete agreement with literature values**.**

From **3b*S***: $[\alpha]_D^{25}$ = -4.8° (*c* = 1.0, CH_2Cl_2, 52% ee) [Lit.[7] (**6d*S*)**: $[\alpha]_D^{25}$ = +4.8° (neat, 99% ee)]. The enantiomeric purity was determined by analysis of the diastereotopic CH_2-hydrogens by ^{1}H NMR (C_6D_6, 500 MHz) from the Mosher[8] ester derivative of **6d*R***: δ

4.04 (dd, *J* = 13.1, 7.4 Hz, 1H), 4.29 (dd, *J* = 13.1, 7.4 Hz, 1H) (major diastereomer) and 4.13-4.23 (m, 2H) (minor diastereomer) with a 38+38:24 ratio respectively resulting in a 52% ee. Compared with the Mosher ester derivative from (±)-**6d** which gives a 25+25:50 ratio respectively for the aforementioned protons (Figure 13).

From **3a*R***: 0.30 g (97% yield, 3 mmols scale). $[\alpha]_D^{25}$ = + 3.9° (*c* = 1.1, CH_2Cl_2, 38% ee). The enantiomeric purity was determined by analysis of the diastereotopic CH_2-hydrogens by ^{1}H NMR (C_6D_6, 500 MHz) from the Mosher ester derivative of **6dS**: δ 4.04 (dd, *J* = 13.1, 7.4 Hz, 1H), 4.29 (dd, *J* = 13.1, 7.4 Hz, 1H) (major diastereomer) and 4.13-4.23 (m, 2H) (minor diastereomer) with a 15+15:70 ratio respectively resulting in a 40% ee. Compared with the Mosher ester derivative from (±)-**6d** which gives a 25+25:50 ratio respectively for the aforementioned ^{1}H NMR signals (Figure 13).

Figure 12. ^{13}C NMR spectrum of 6d.

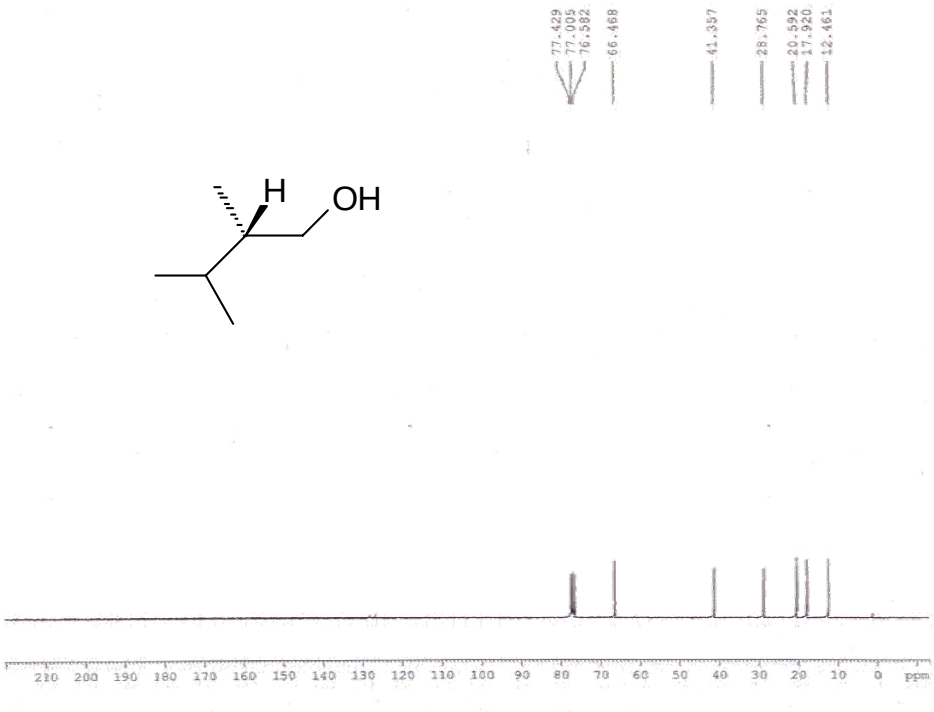
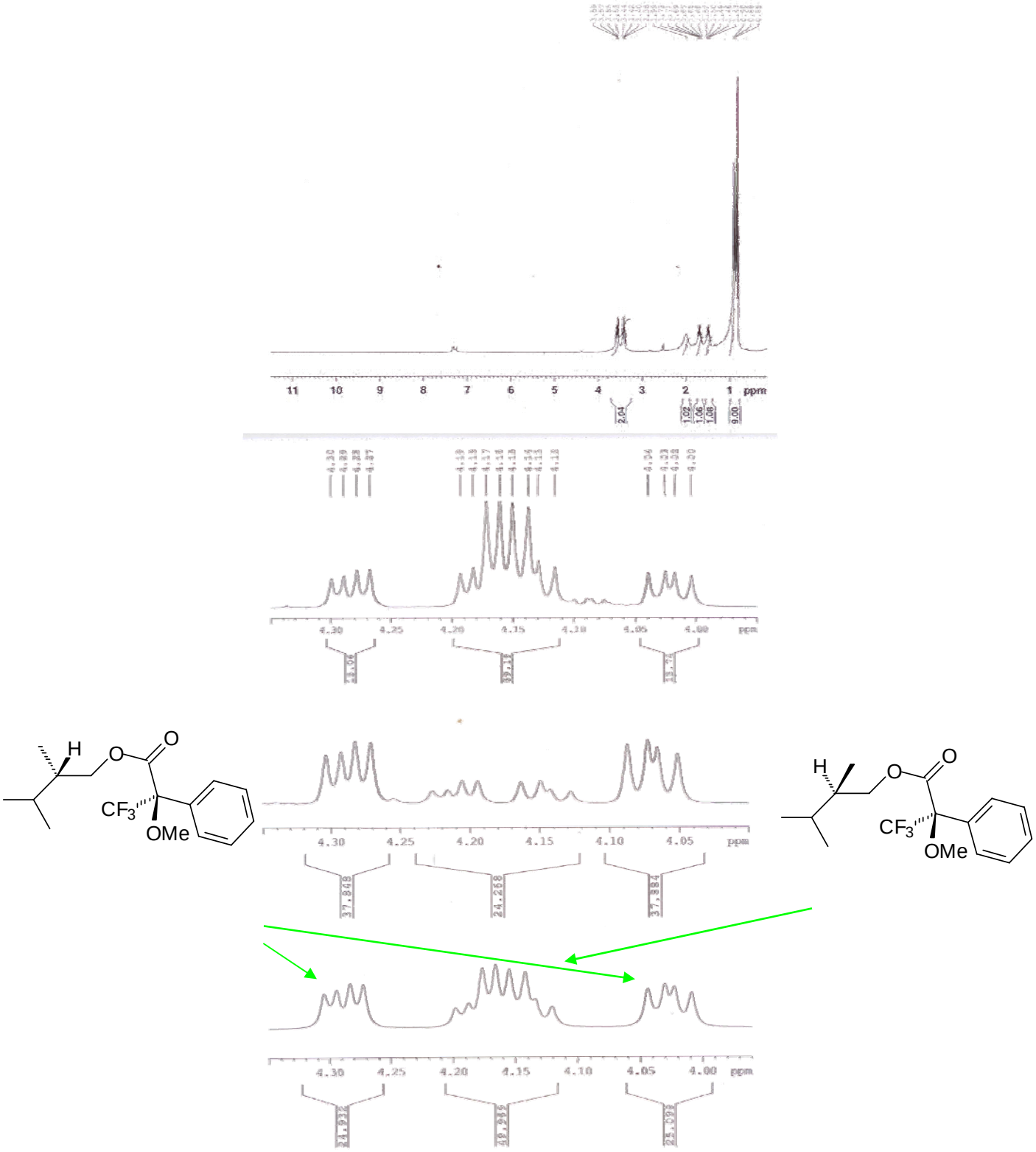


Figure 13. ^{1}H NMR spectrum of 3b (top) and ^{1}H NMR spectrum of 6d-CDA.



(*S*)-(+)-2,3,3-trimethyl-1-butanol (6e). The crude product was distilled at 110 °C at 120 mmHg to obtain 0.29 g (84% yield from **3a*S***, 3 mmols scale) of **6e**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (s, 9H), 0.91 (d, *J*= 6.7 Hz, 3H) 1.35 (s, broad OH, 1H), 3.24 (dd, app t, *J* = 9.4 Hz, 1H), 3.77 (d, *J*= 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.3, 27.6, 31.9, 45.4, 65.0 (Figure 14). These data were in complete agreement with literature values.[9]

From **3b*R***: 0.21 g (60% yield, 3 mmols scale) $[\alpha]_D^{25}$ = +35.4° (*c* = 1.00, CH_2Cl_2, 56% ee) [Lit.[9] (**6e*S***): $[\alpha]_D^{25}$ = +8.93° (EtOH, 22% ee)]. The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 136.3 (major), 139.6 (minor) compared with the racemic derivative (50:50) (Figure 15).

From **3a*S***: $[\alpha]_D^{25}$ = -35.8° (*c* = 2.00, EtOH, 92% ee) [Lit.[10] (**6e*R***): $[\alpha]_D^{25}$ = -11.0° (*c* = 3.2, EtOH, 27% ee)]. The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 139.6 (major), 136.3 (minor) compared with the racemic derivative (50:50) (Figure 15).

Figure 14. ^{1}H (bottom) and ^{13}C (top) NMR spectra of 6e.

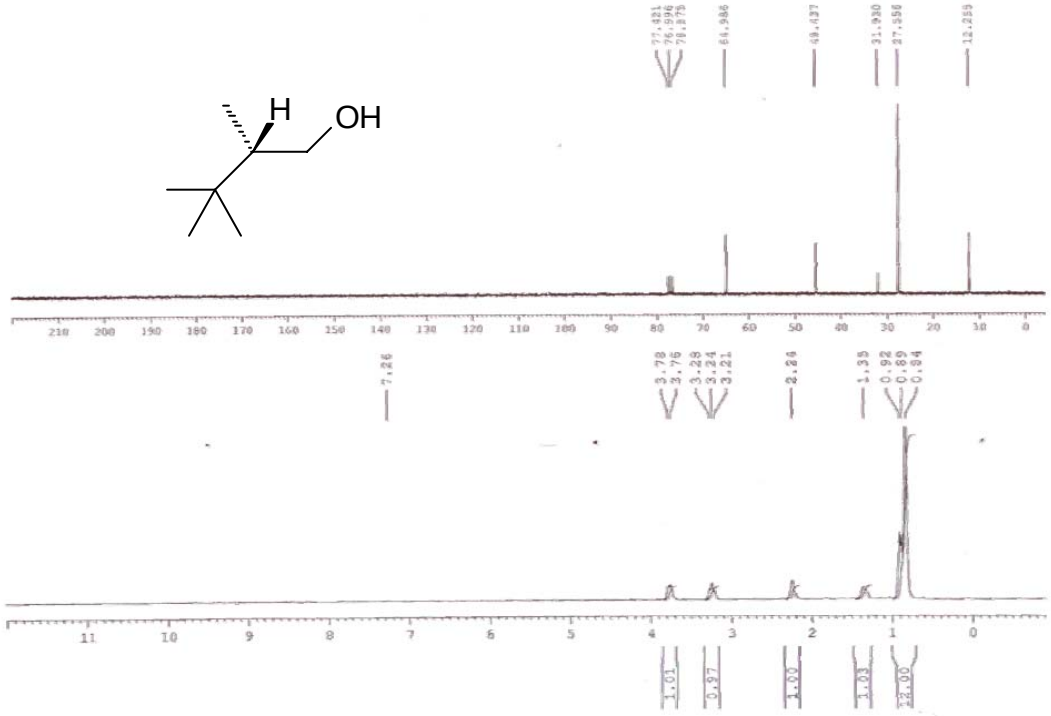
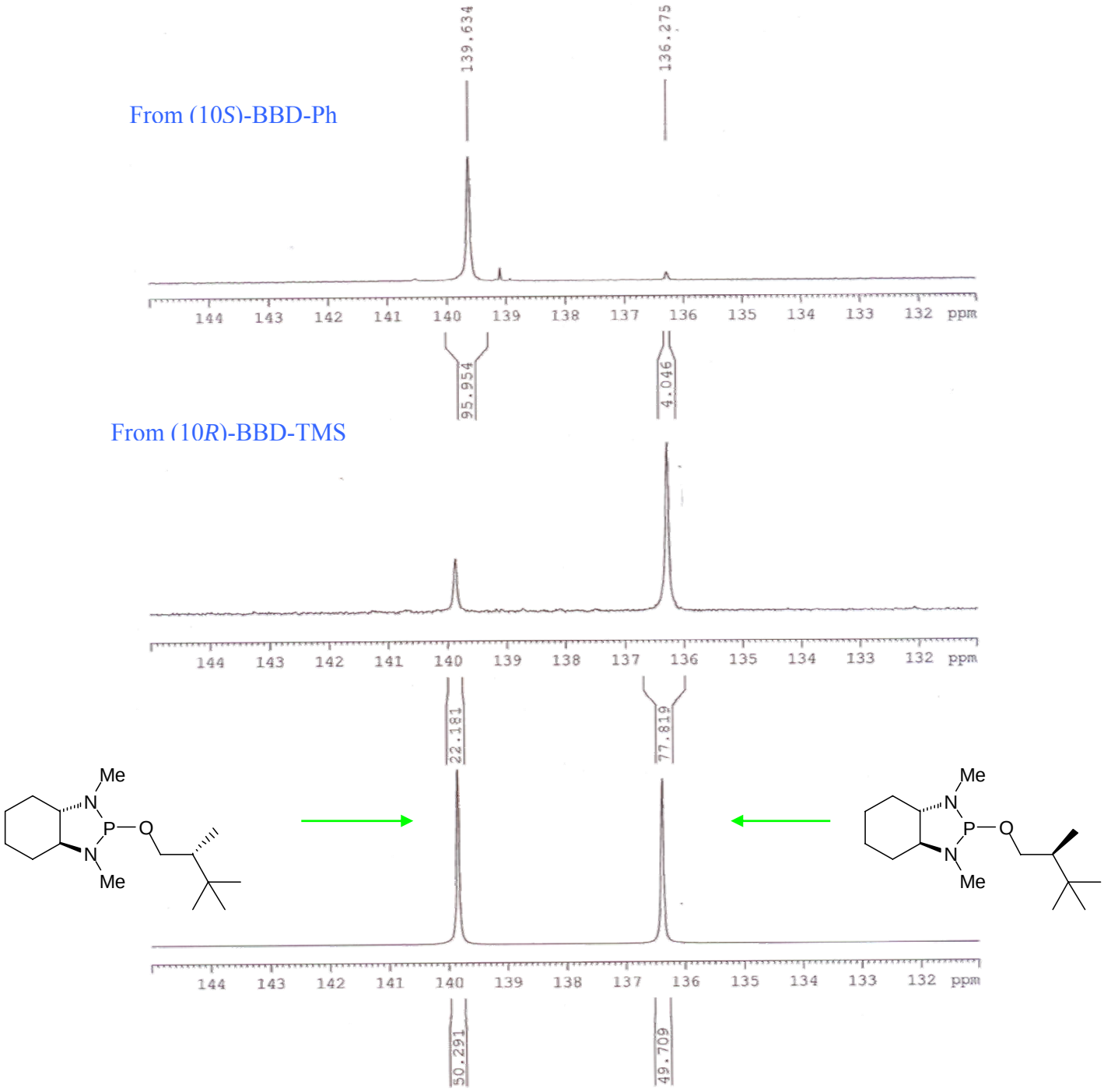


Figure 15. ^{31}P NMR spectrum of 6e-CDA.



2-Phenyl-1-propanol (6f). The crude product was purified by silica gel column chromatography (4:1, hexanes: diethyl ether) to obtain 0.34 g (83% yield from **3b*R***, 3 mmols scale) of **6f**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.35 (d, *J* = 7.0 Hz, 3H), 2.91-3.02 (m, 1H), 3.12 (s, OH, 1H), 3.67 (ddd, *J* = 10.7, 7.2, 3.5 Hz, 2H), 7.28-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.4, 42.0, 68.1, 126.2, 127.2, 128.2, 143.8 (Figure 16). These data were in complete agreement with literature values**.**[11]

From **3b*R***: $[\alpha]_D^{25}$ = -10.2° (*c* = 1.00, CH_2Cl_2, 66% ee). The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 137.8 (major), 139.5 (minor) compared with the racemic derivative (50:50) (Figure 17).

From **3a*S***: 0.39 g (95% yield, 3 mmols scale) ($[\alpha]_D^{25}$ = +11.0° (neat, 78% ee). [Lit.[11] (**6f*R***): $[\alpha]_D^{25}$ = +14.3° (*c* = 1.65, $CHCl_3$, 99% ee)]. The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 139.5 (major), 137.8 (minor) compared with the racemic derivative (50:50) (Figure 17).

Figure 16. ^{1}H (top) and ^{13}C NMR (bottom) spectra of 6f.

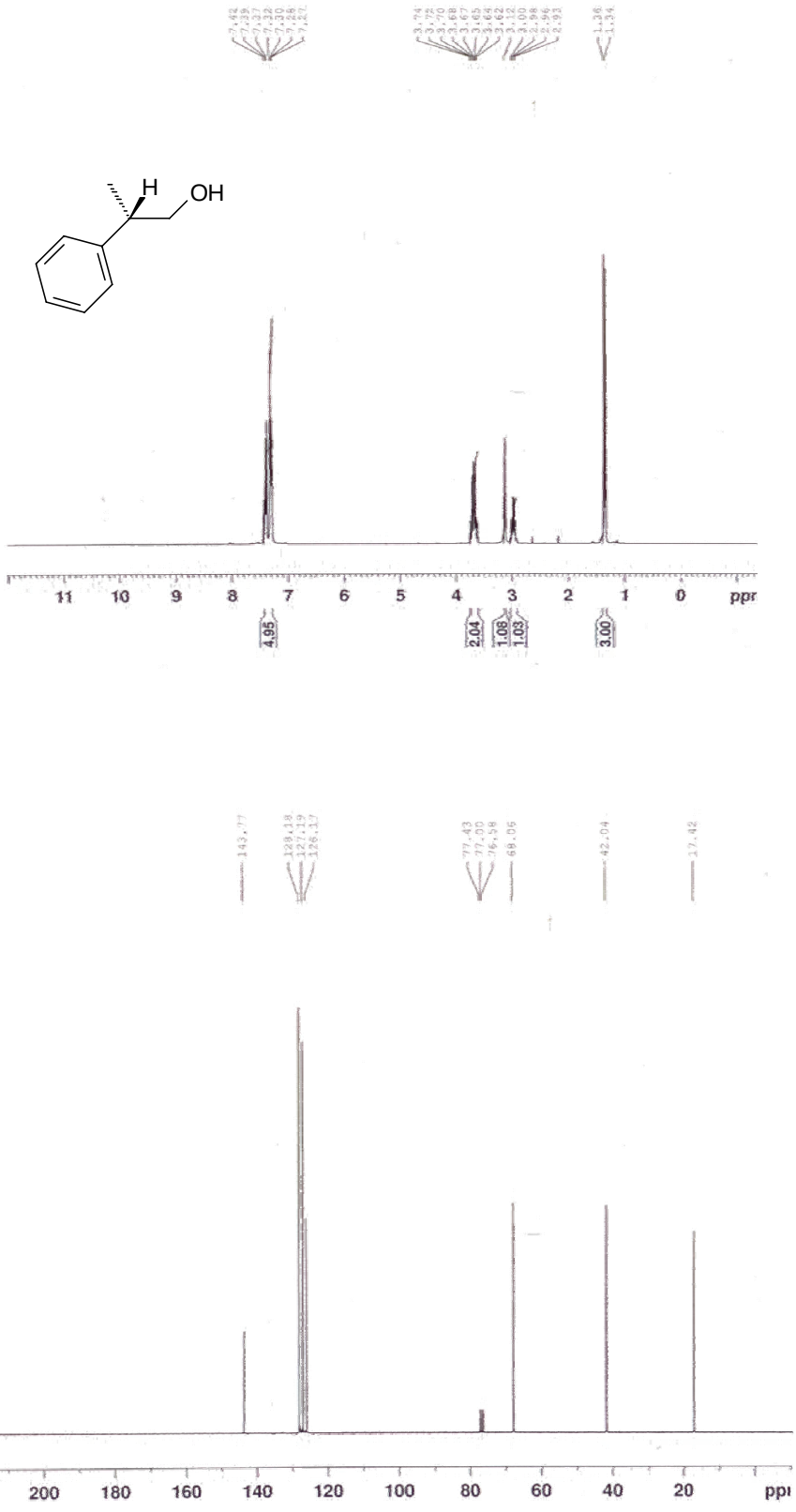
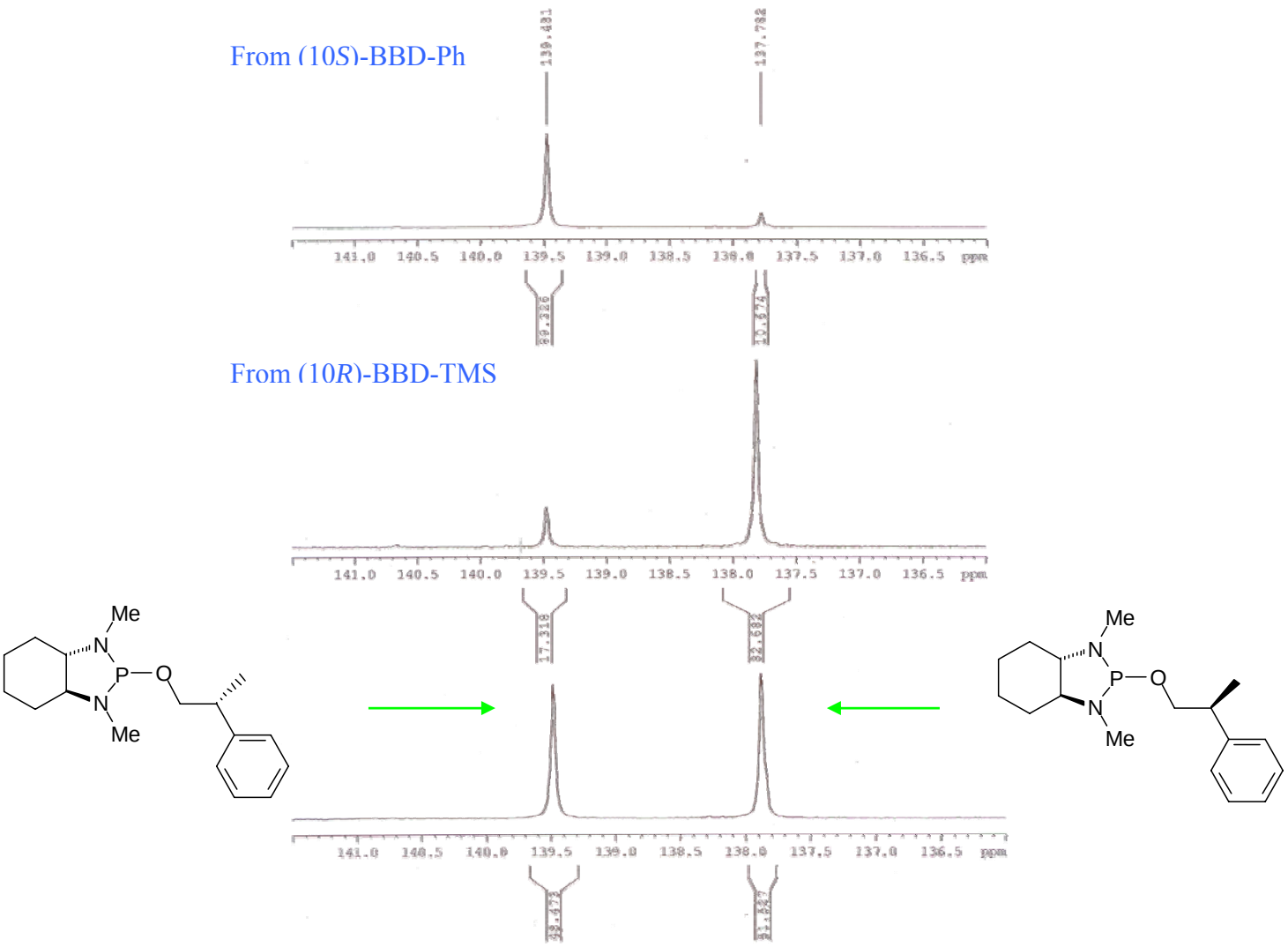


Figure 17. ^{31}P NMR spectra of 6f-CDA.



(*R*)-(+)-2-Deuterio-2-phenyl-1-ethanol (6g). The crude product was purified by silica gel column chromatography (4:1, hexanes: diethyl ether) to obtain 0.32 g (86% yield from **3b*S***, 3 mmols scale) of **6g**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.13 (s, 1H), 2.84 (dt, *J* = 3.3 Hz *J* = 1.7 Hz, 1H), 3.82 (s, 2H), 7.19-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.4, 38.7, 39.0, 63.5, 126.4, 128.2, 128.9, 138.4 (Figure 18). These data were in complete agreement with literature values.[12]

From **3b*S***: $[\alpha]_D^{24}$ = + 1.2 (*c* = 1.00, CH_2Cl_2, 98% ee). The enantiomeric purity was determined from ^{13}C NMR analysis of the trialkylborane **5gb** δ 34.9(major):34.7(minor), 99:1 (Figure 20).

From **3a*S***: 0.36 g (97% yield, 3 mmols scale) $[\alpha]_D^{24}$ = + 1.2 (*c* = 1.00, CH_2Cl_2, 92% ee) [Lit.[12](**6g*R***): $[\alpha]_D^{25}$ = +1.52° (neat, 99% ee)]. The enantiomeric purity was determined from ^{13}C NMR analysis of the trialkylborane **5ga** δ 130.4(major):130.3(minor), 96:4 (Figure 19).

Figure 18. ^{1}H (bottom) and ^{13}C (top) NMR spectra of 6g.

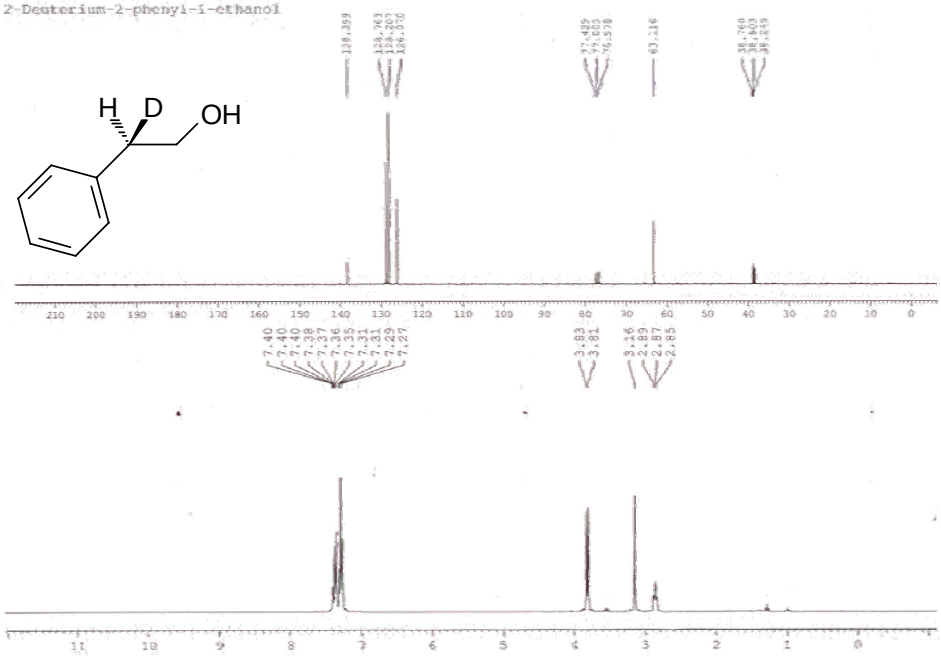


Figure 19. ^{11}B (top right) and ^{13}C NMR spectra of 5ga.

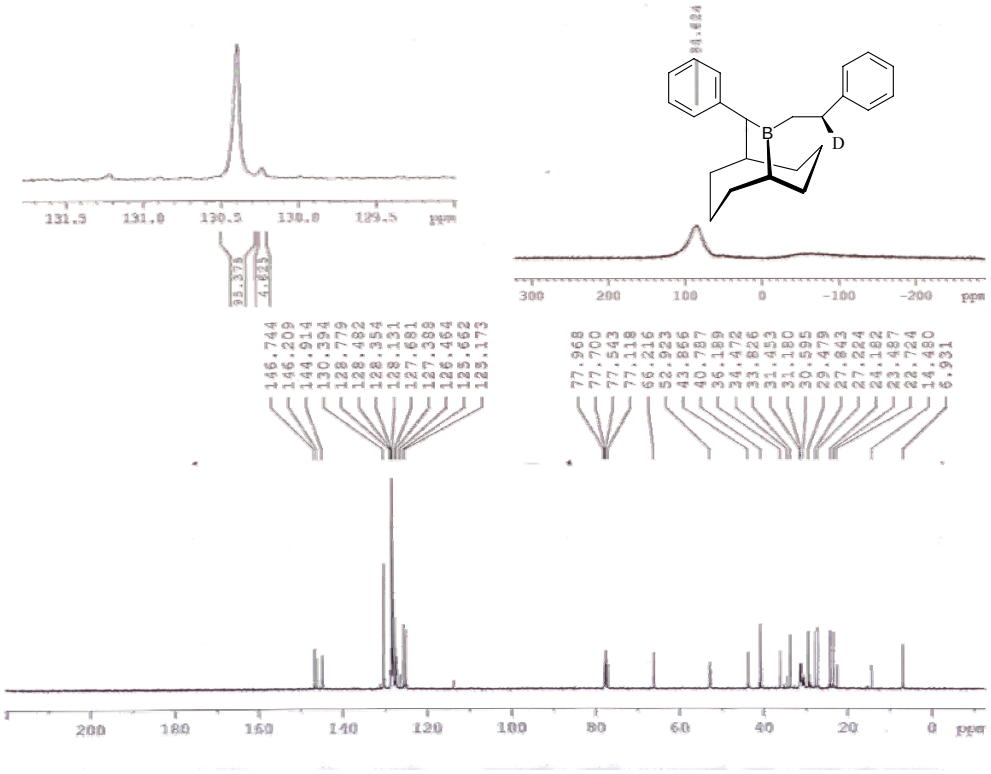
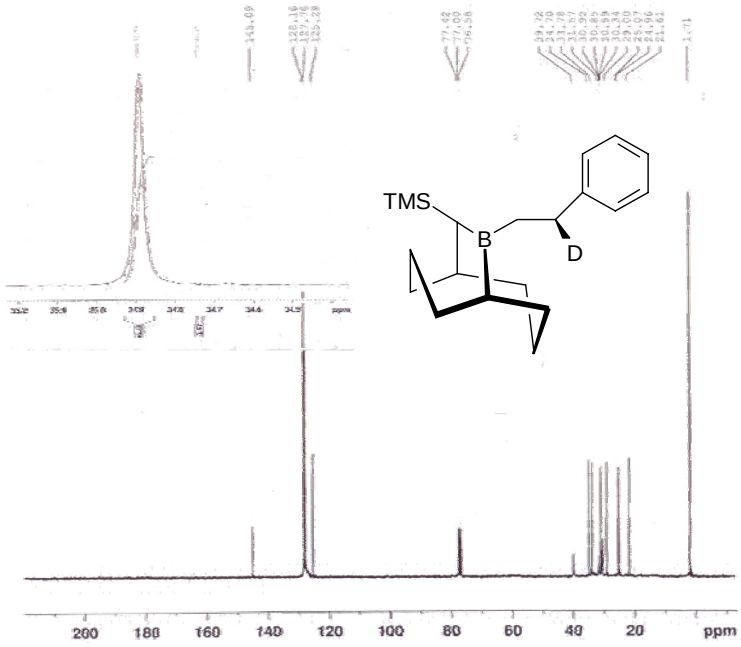


Figure 20. ^{11}B (top right) and ^{13}C NMR spectra of 5gb.



(1*S*, 2*R*, 5*S*)-(-)-Myrtanol (6h).[13] The crude product was purified by silica gel column chromatography (4:1, hexanes: diethyl ether) to obtain 0.43 g (94% yield from **3a*S*** *and* **3a*R***, 3 mmols scale) of **6h**. $[\alpha]_D^{24}$ = - 19.0 (*c* = 1.00, $CHCl_3$, >99% ee) [From **3a*S***] $[\alpha]_D^{24}$ = - 21.8 (*c* = 1.00, $CHCl_3$, >99% ee) [From **3a*R***] [Lit.[14] **6h (1*S*, 2*R*, 5*S*)**: $[\alpha]_D^{20}$ = - 19.5° (neat). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81-0.85 (m, 2H), 0.92 (s, 3H) 1.13 (s, 3H), 1.36-1.45 (m, 2H), 1.79-1.98 (m, 5H), 2.11-2.24 (m, 1H), 2.27-2.35 (m, 1H), 2.97 (s (broad), 1H), 3.41-3.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.8, 23.3, 26.0, 27.9, 33.1, 38.6, 41.4, 42.8, 44.2, 67.4 (Figure 21). These data were in complete agreement with literature values.[13, 15]

Figure 21. ^{13}C NMR (top) and ^{1}H (bottom) spectra of 6h.

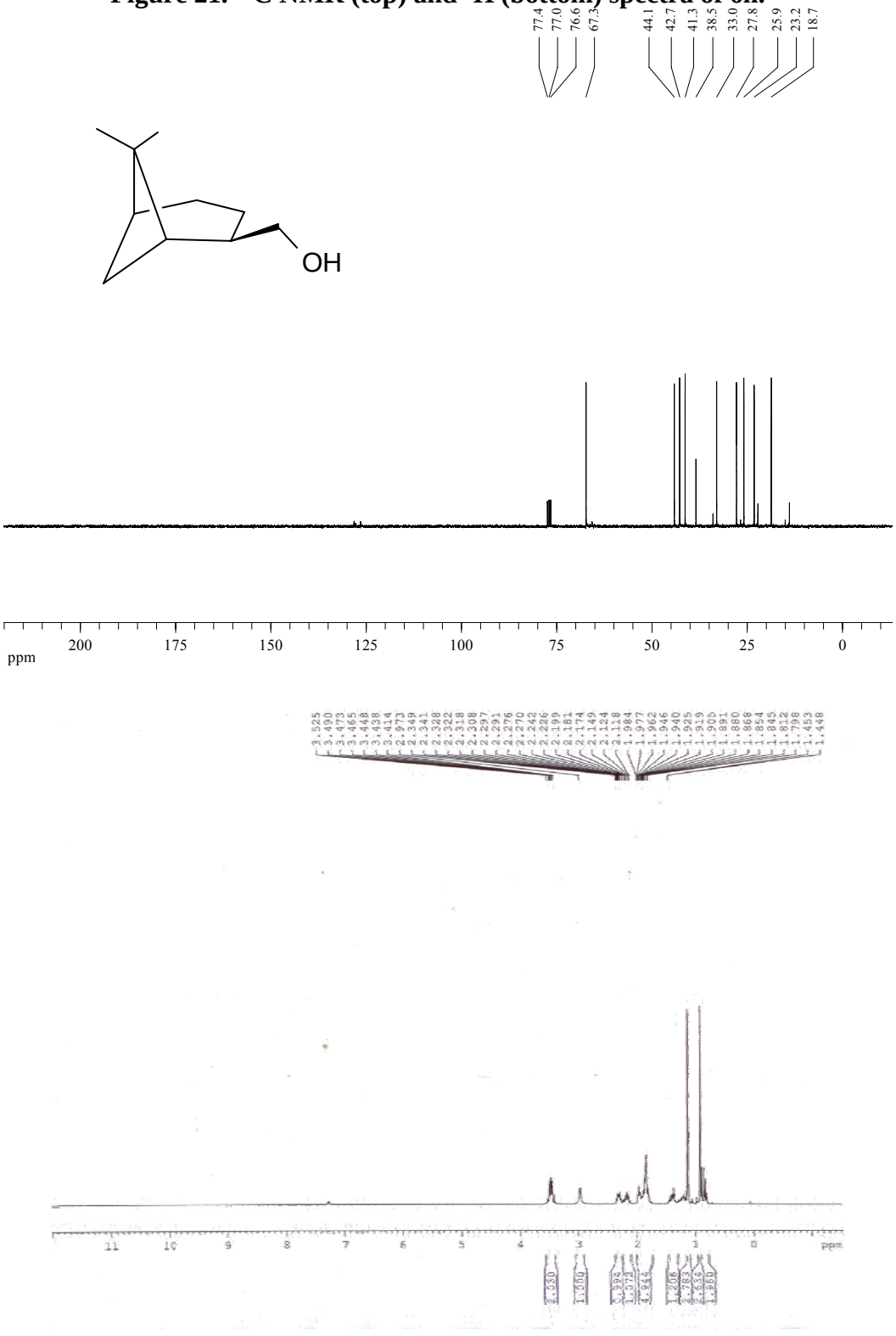
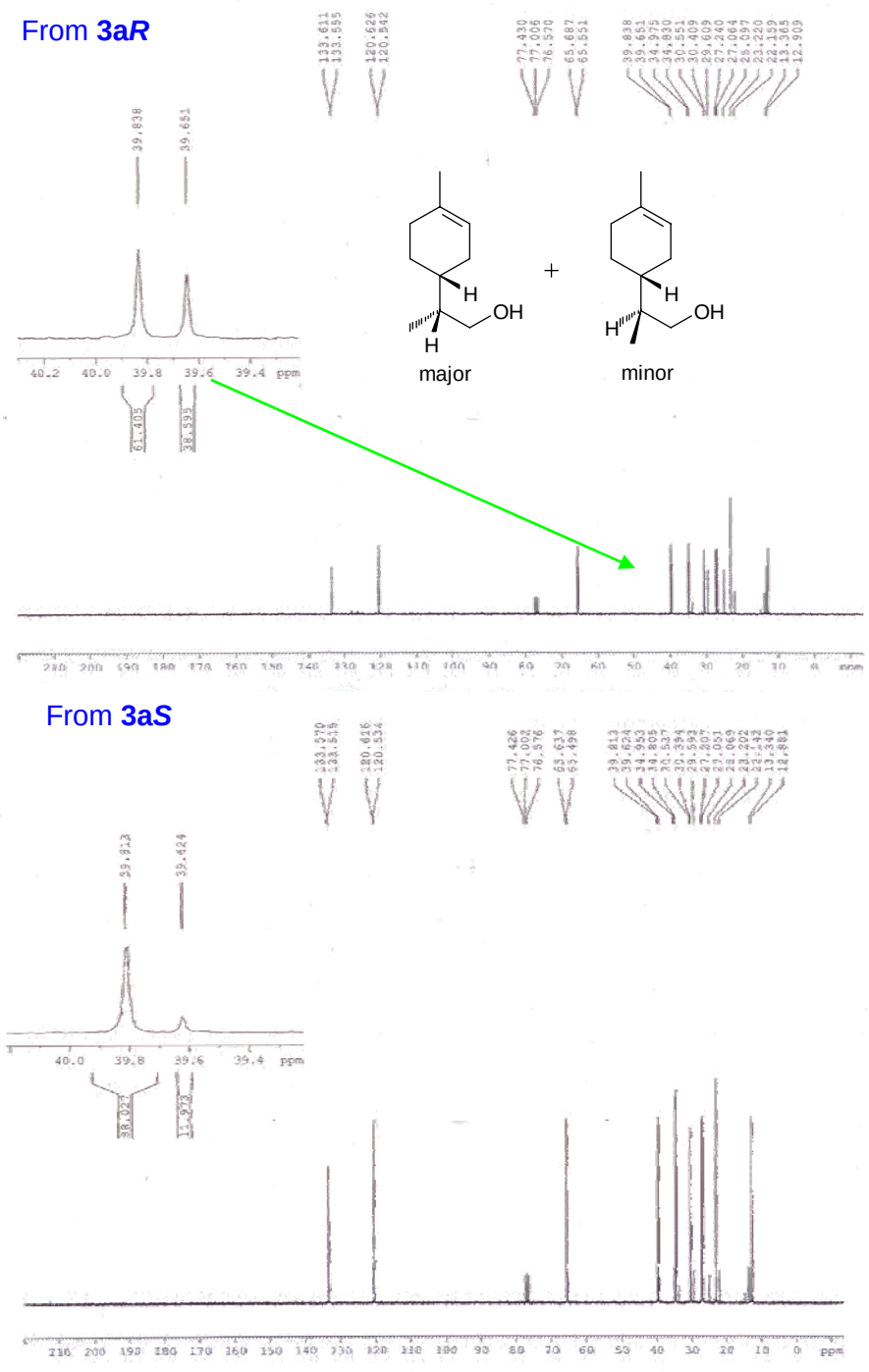
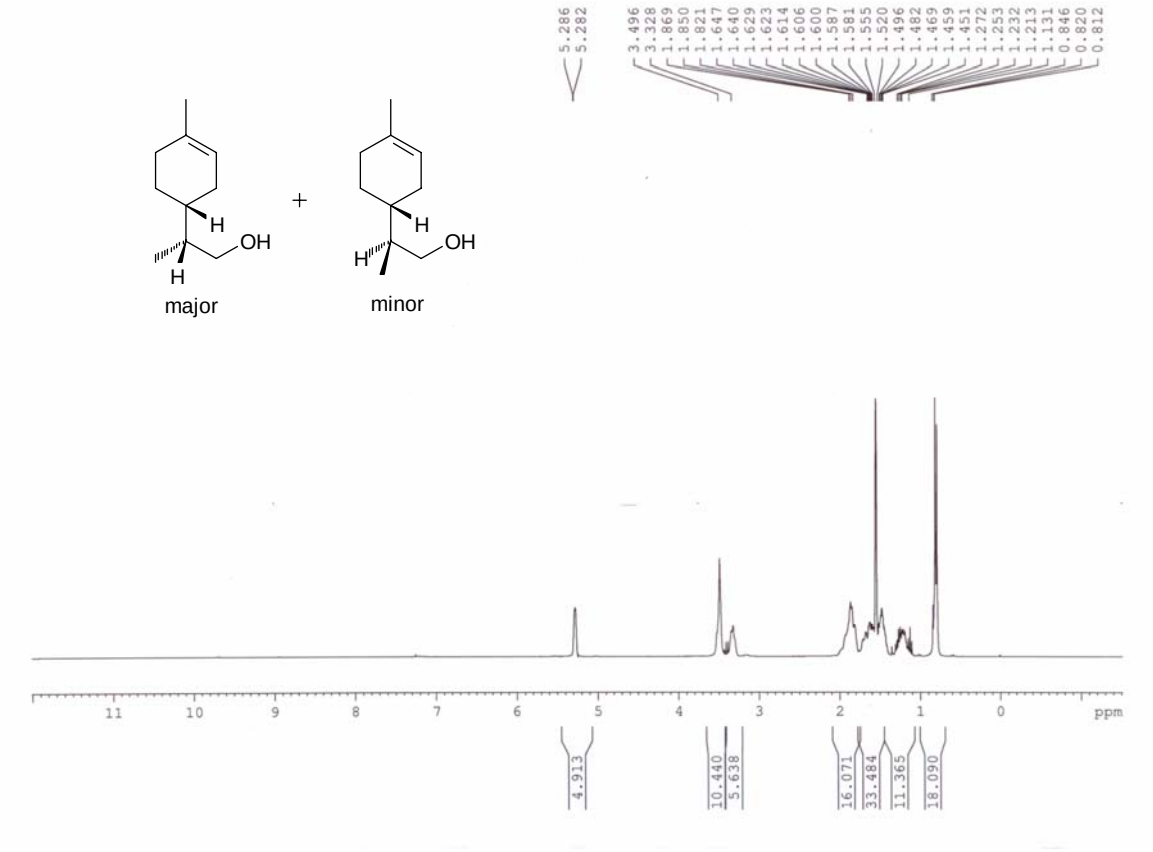


Figure 22. ^{13}C NMR spectra of 6i (4*R*, 8*R*) (major, see also below) and 6i (4*R*, 8*S*) (minor).



(4*R*,8*R*)-*p*-Ment-1-en-9-ol {(2*R*)-2-[(1*R*)-4-methyl-cyclohenen-1-yl]-1-propanol (6i).[16] The crude product was purified by silica gel column chromatography (4:1, hexanes: diethyl ether) to obtain 0.40 g (93% yield from **3a*S*** and **3a*R***, 3 mmols scale) of **3g**. From **3a*S*:** $[\alpha]_D^{24}$ = + 75.5 (*c* = 2.2, CH_2Cl_2, 76% de), from **3a*R*:** $[\alpha]_D^{24}$ = + 65.4 (*c* = 2.5, CH_2Cl_2, 22% de), [Lit.[16] [**6i** (2:1 of (4*R*, 8*R*):(4*R*, 8*S*)]: $[\alpha]_D^{20}$ = + 99.0° (*c* = 4.2, toluene)]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81-0.85 (m, 3H), 1.13-1.27 (m, 2H), 1.45-1.65 (m, 6H), 1.82- 1.87 (m, 3H), 3.33 (s, 1H), 3.50 (s, 2H), 5.28 (d, *J* = 1.2 Hz, 1H) (Figure 23); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.9, 23.2, 27.1, 27.2, 30.5, 34.8, 39.8, 65.6, 120.5, 133.5 (Figure 22). These data were in complete agreement with literature values**.**[16]

Figure 23. ^{1}H NMR spectrum of 3g(4R, 8R) (major, see below) and 3g(4R, 8S) (minor)

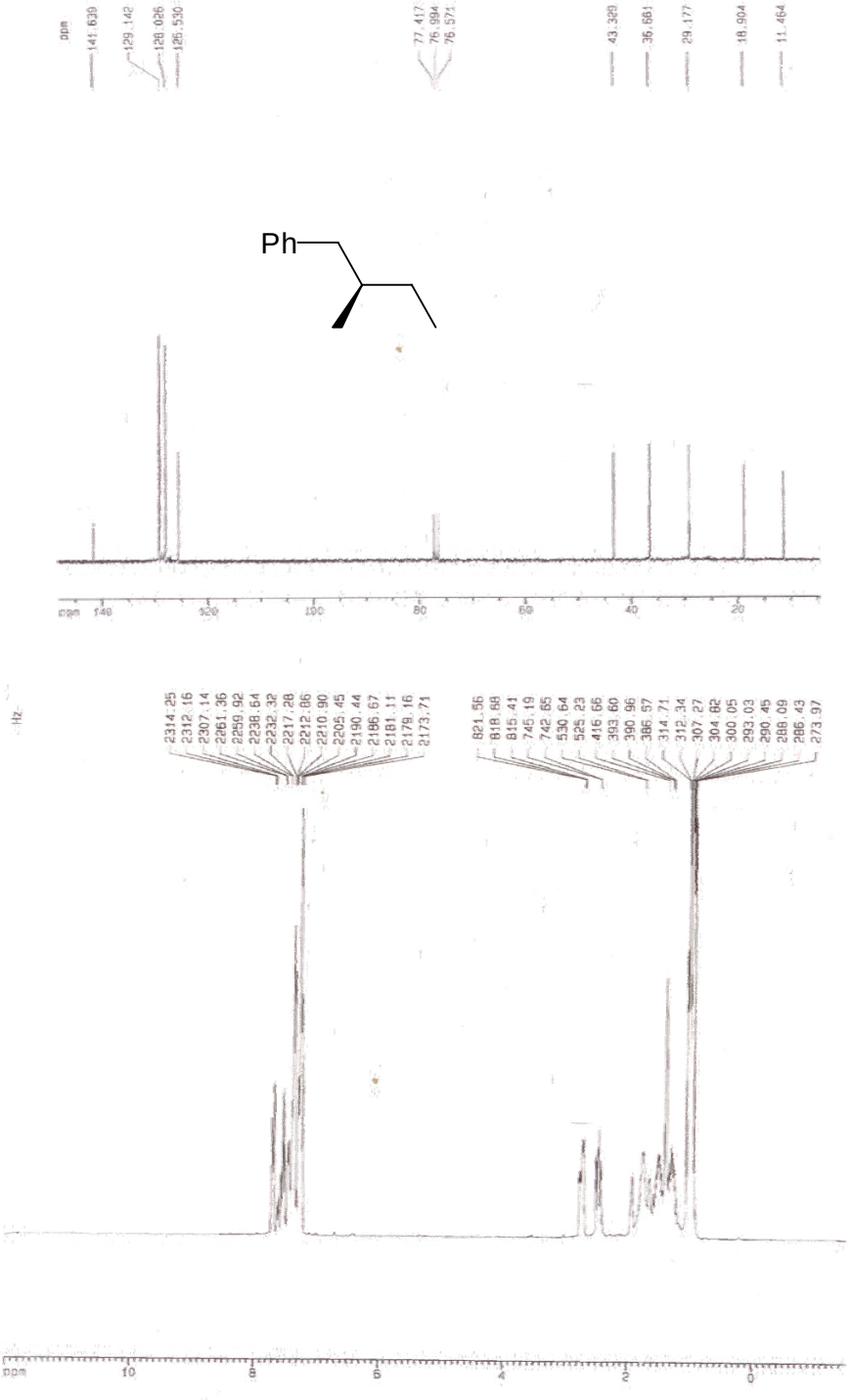


VI. General Procedure for the synthesis of hydrocarbons 7a-g.

(*R*)-(-)-2-Methyl-1-phenylbutane (7a*R*).[17] To **5c*S*** (1.41 g, 5.0 mmols) in THF (5 mL) was added previously degassed NaOH/H_2O (5.0 mL, 3.0 M). This solution was transferred *via cannula* to a beforehand prepared mixture of $Pd(PPh_3)_4$ (0.17 g, 3.0 mol %) and bromobenzene (0.79 g, 5.0 mmol) in THF (5 mL). The reaction mixture was refluxed overnight, and then quenched with water (10.0 mL). The mixture was extracted with pentane (3 x 10 mL) and the combined organic layer was filtered through a silica gel plug with pentane and concentrated. The crude was purified by fractional distillation affording 0.59 g of **7a** (80%, bp = 85-87 ^oC @ 20 mmHg). ^{1}H NMR ($CDCl_3$, 300 MHz) δ

0.94-1.10 (m, 5 H), 1.4 (m, 2 H), 2.74-2.48 (m, 1 H), 2.71-2.78 (m, 2 H), 7.2-7.7 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.5, 18.9, 29.2, 36.7, 43.3, 125.5, 128.0, 129.1, 141.6 (Figure 24). $[\alpha]_D^{24}$ = - 2.4 (neat, 28% ee) [Lit.[17] (**7aS**): $[\alpha]_D^{25}$ = +10.7° (neat, > 93% ee)].

Figure 24. ^{13}C (top) and ^{1}H (bottom) NMR spectra of 7a*R*.



(S)-(-)-1-Phenyl-2,3,3-trimethylbutane (7b*S*).[18] Following the above mentioned procedure starting from **5e*S*** (3 mmols scale) the crude product was purified by silica gel column chromatography (hexanes) affording 0.37 g of **7b*S*** (70% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.73 (d, *J* = 6.8 Hz, 3H), 0.98 (s, 9H), 2.03 (d, *J* = 13.0 Hz, 1H), 2.07 (d, *J* = 13.0, 1H), 2.98 (dd, *J* = 13.1, 2.3 Hz, 1H); 13C NMR ($CDCl_3$, 75 MHz) δ 13.7, 27.4, 33.1, 38.3, 45.6, 125.4, 128.1, 129.2, 142.9 (Figure 25). $[\alpha]_D^{24}$ = - 21.6° (*c* = 1.0, CH_2Cl_2, 92% ee).

(*S*)-(+)-1,2-Diphenylpropane (7c*S*).[19] Following the above mentioned procedure starting from **5f*S*** (3 mmols scale) the crude product was purified by silica gel column chromatography (hexanes) affording 0.47 g of **7c*S*** (80% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26 (d, *J* = 6.9 Hz, 3H), 2.74-2.83 (m, 1H), 2.93-3.08 (m, 2H), 7.08-7.33 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 41.8, 45.0, 125.8, 126.0, 127.0, 128.1, 128.3, 129.1, 140.8, 146.9 (Figure 26). $[\alpha]_D^{24}$ = + 53.0° (*c* = 2.3, $CHCl_3$, 78% ee) [Lit. value for **7c*R***: $[\alpha]_D^{25}$ = - 78.6° (*c* = 2.0, $CHCl_3$, 99% ee)].

(*S*)-(+)-2-Phenyl-1-(*p*-methoxyphenyl)propane (7d*S*).[20] Following the above mentioned procedure starting from **5f*S*** (3 mmols scale) the crude product was purified by silica gel column chromatography (hexanes) affording 0.57 g of **7d*S*** (50% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (d, *J* = 3.1 Hz, 3H), 2.75-2.79 (m, 1H), 2.89-2.97 (m, 2H), 3.80 (s, 3H), 6.82 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 7.21-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 42.1, 44.2, 55.2, 113.5, 126.0, 127.1, 128.3, 130.1, 132.9, 147.1, 3.8 (Figure 27). $[\alpha]_D^{24}$ = + 3.9° (*c* = 1.2, CH_2Cl_2, 78% ee).

Figure 25. ^{13}C (top) and ^{1}H (bottom) NMR spectra of 7b*S*.

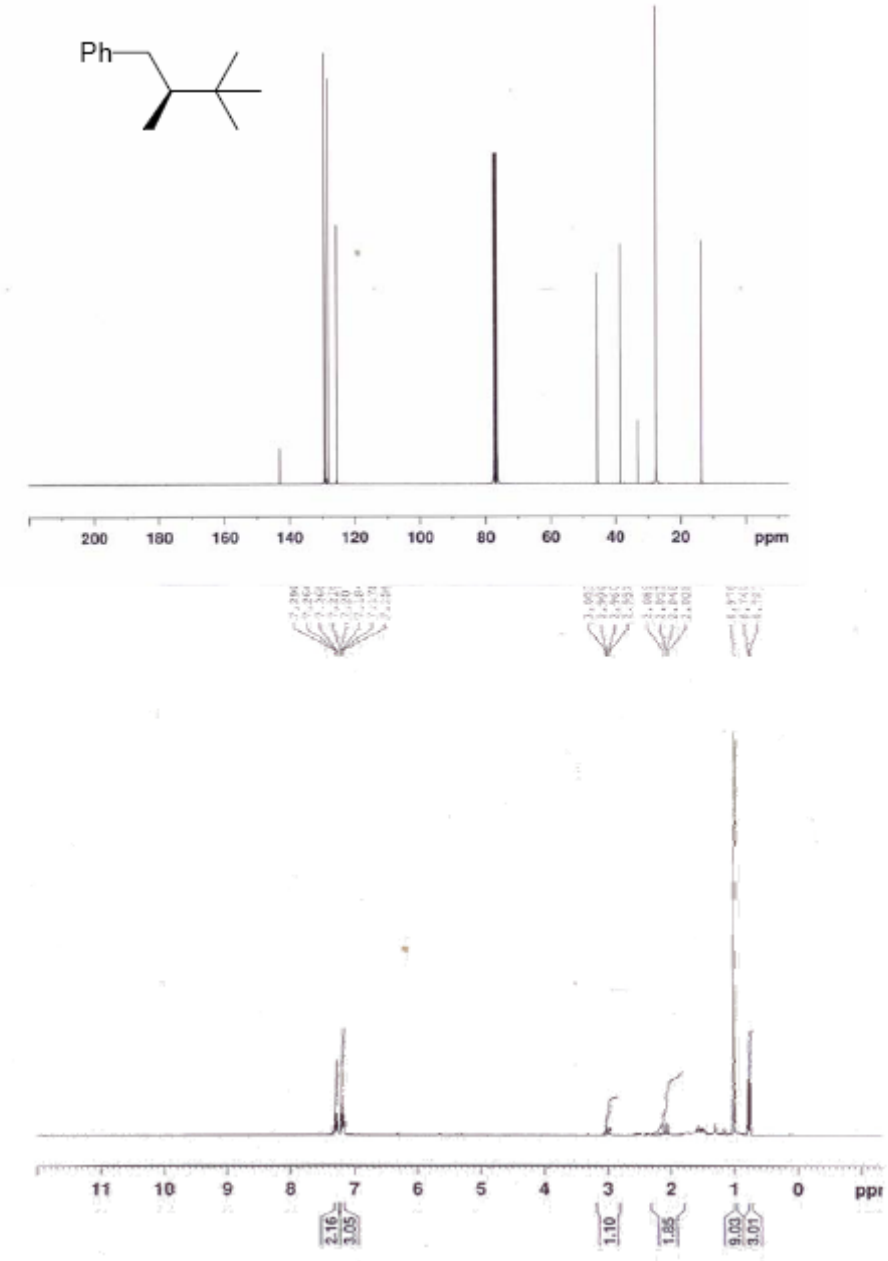
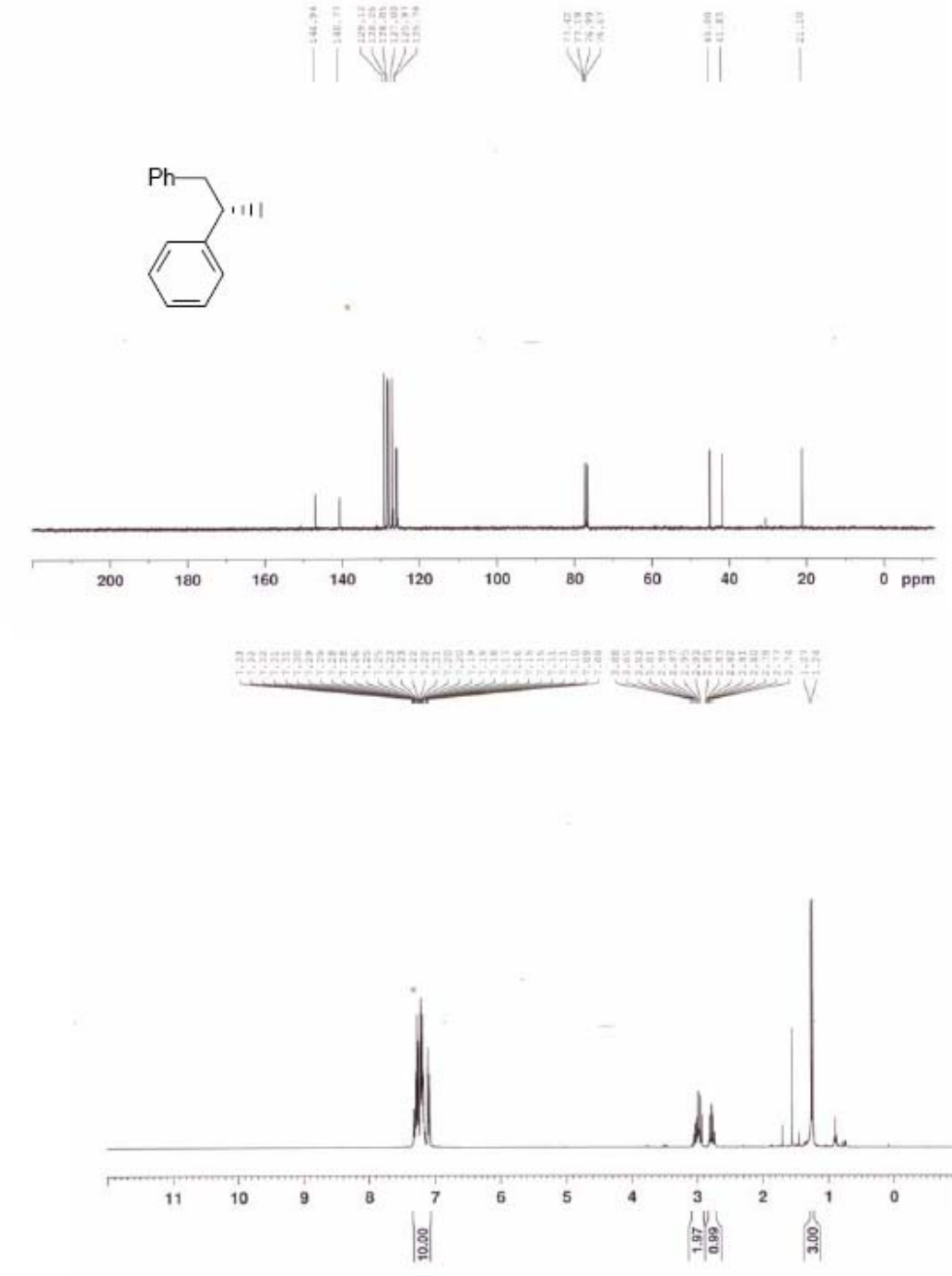


Figure 26. ^{13}C (top) and ^{1}H (bottom) NMR spectra of 7c*S*.



(*S*)-(+)-2-Methyl-5-phenyl-2-hexene (7e*S*).[21] Following the above mentioned procedure starting from **5f*S*** (5 mmols scale) the crude product was distilled (137 °C @ 5.9 mmHg) affording 0.73 g of **7e*S*** (84% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (d, *J* = 6.9 Hz, 3H), 1.59 (s, 3H), 1.70 (s, 3H), 2.27-2.32 (m, 2H), 2.71-2.80 (m, 1H), 7.23-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9, 21.5, 25.9, 37.0, 40.5, 123.1, 125.9, 127.1, 128.3, 132.4, 147.7 (Figure 18). $[\alpha]_D^{24}$ = + 7.4° (*c* = 2.0, CH_2Cl_2, 78% ee) [Lit.[21] **7e*S***: $[\alpha]_D^{25}$ = + 3.6° (*c* = 2.3, CH_2Cl_2, 38% ee)].

(1*S*, 2*R*, 5*S*)-(-)-2-Benzyl-6,6-dimethylbicyclo[3.1.1]heptane (7f). Following the above mentioned procedure starting from **5h*R*** (3 mmols scale) the crude product was purified by silica gel column chromatography (hexanes) affording 0.45 g of **7f** (70% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, *J* = 9.6 Hz, 1H), 0.99-1.44 (m, 6H), 1.52-1.62 (m, 3H), 1.73-1.94 (m, 3H), 2.05-2.15 (m, 2H), 2.27-2.71 (m, 1H), 7.15- 7.20 (m, 3H), 7.26- 7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3, 23.5, 26.4, 28.2, 33.8, 38.7, 41.4, 43.3, 43.4, 45.2, 125.5, 128.1, 129.1, 141.9 (Figure 19). IR cm^{-1}: 2959.4, 2913.9, 1588.5, 1568.4, 1473.4, 1433.3, 794.4, 749.8. HRMS $[M]^+$ calcd. 215.1794, found 215.1799. $[\alpha]_D^{24}$ = - 11.3° (*c* = 1.1, CH_2Cl_2, 99% ee).

(4*R*)-(-)1-Methyl-4-[(1*S*)-1-methyl-2-phenylethyl]-1-cyclohexene (7g). Following the above mentioned procedure starting from **5i*S*** (3 mmols scale) the crude product was purified by silica gel column chromatography (hexanes) affording 0.64 g of **7g** (64% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.91-0.94 (m, 3H), 1.46-1.61 (m, 3H), 1.77-2.15 (m, 8H), 2.37-2.47 (m, 1H), 2.88-2.94 (dd, *J* = 5.0, 13.3 Hz, 1H), 7.25-7.30 (m, 3H), 7.35-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.4, 23.5, 27.3, 27.5, 30.9, 38.0, 39.6, 40.8, 120.9, 125.5, 128.1, 129.1, 133.9, 141.9 (Figure 30). IR cm^{-1}: 2914.4, 1452.5,

1376.4, 714.1, 697.8. MS *m/z*: 214 (M^+) (Fig.34). Anal. Calcd. for $C_{16}H_{22}$: C 89.65 H 10.35; Found: C 89.55 H 10.30. $[\alpha]_D^{24}$ = - 47.7° (*c* = 2.7, CH_2Cl_2, 76% de).

Figure 27. ^{13}C (top) and ^{1}H (bottom) NMR spectra of 7d*S*.

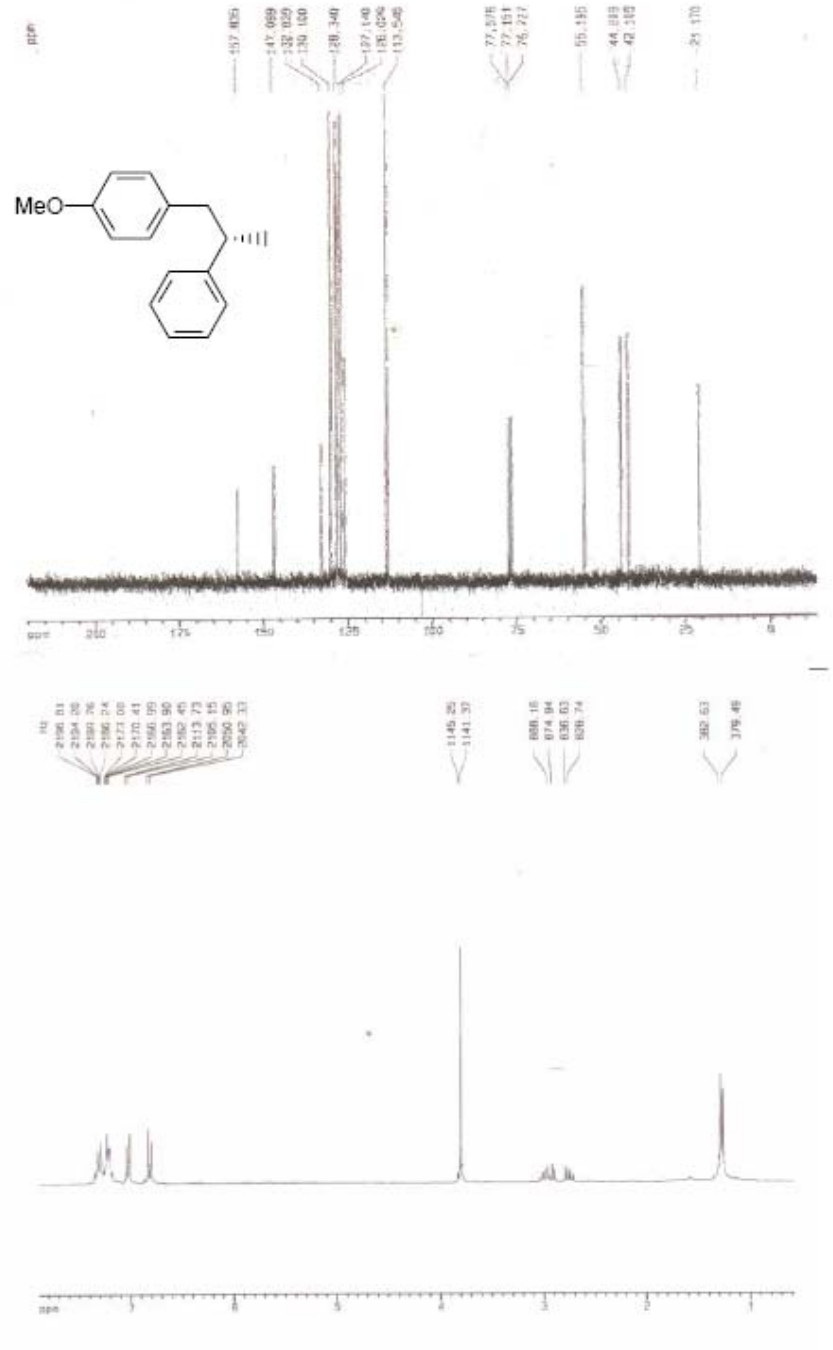


Figure 28. ^{13}C (top) and ^{1}H (bottom) NMR spectra of 7e*S*.

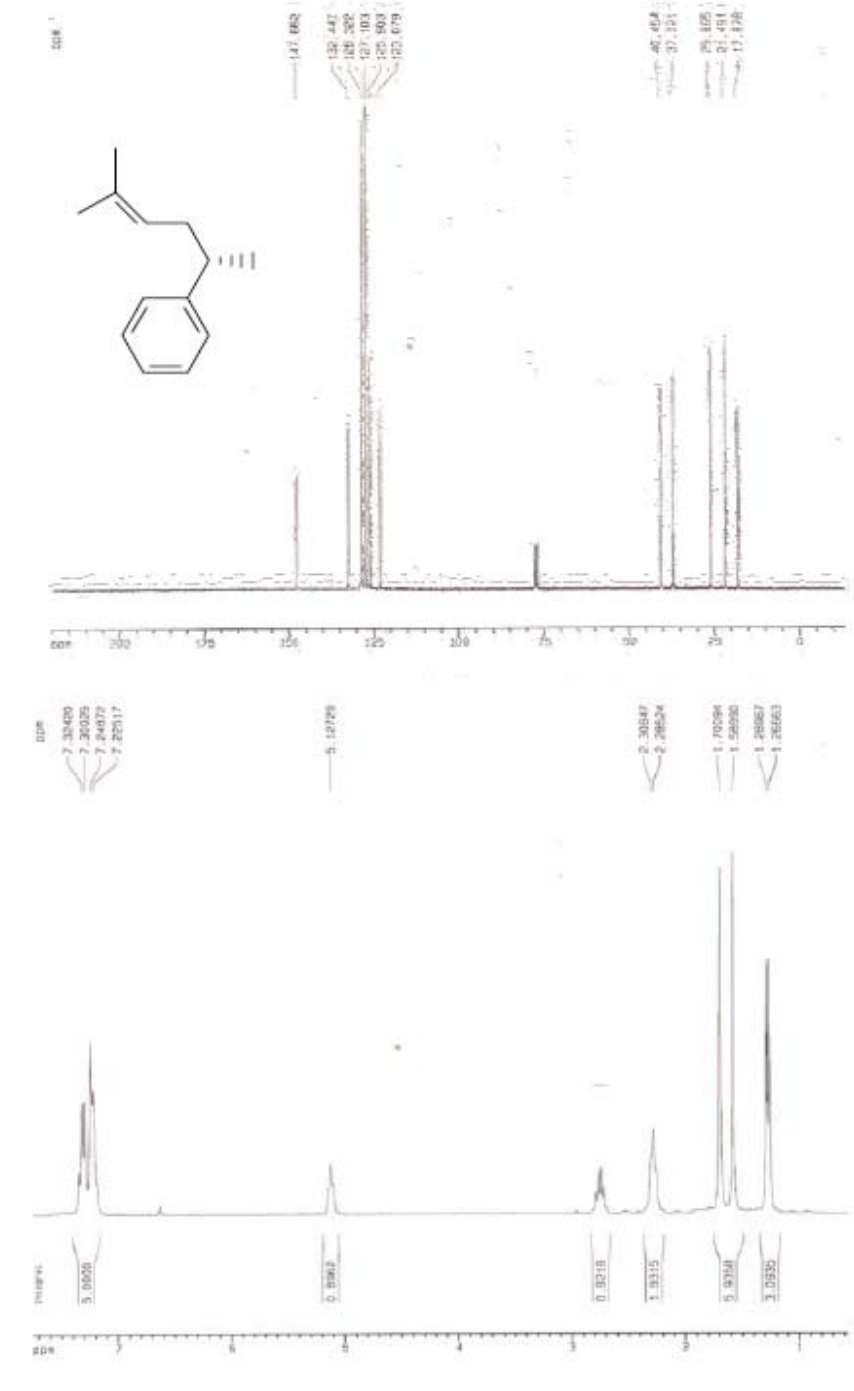


Figure 29. ^{13}C (top) and ^{1}H (bottom) NMR spectra of 7f.

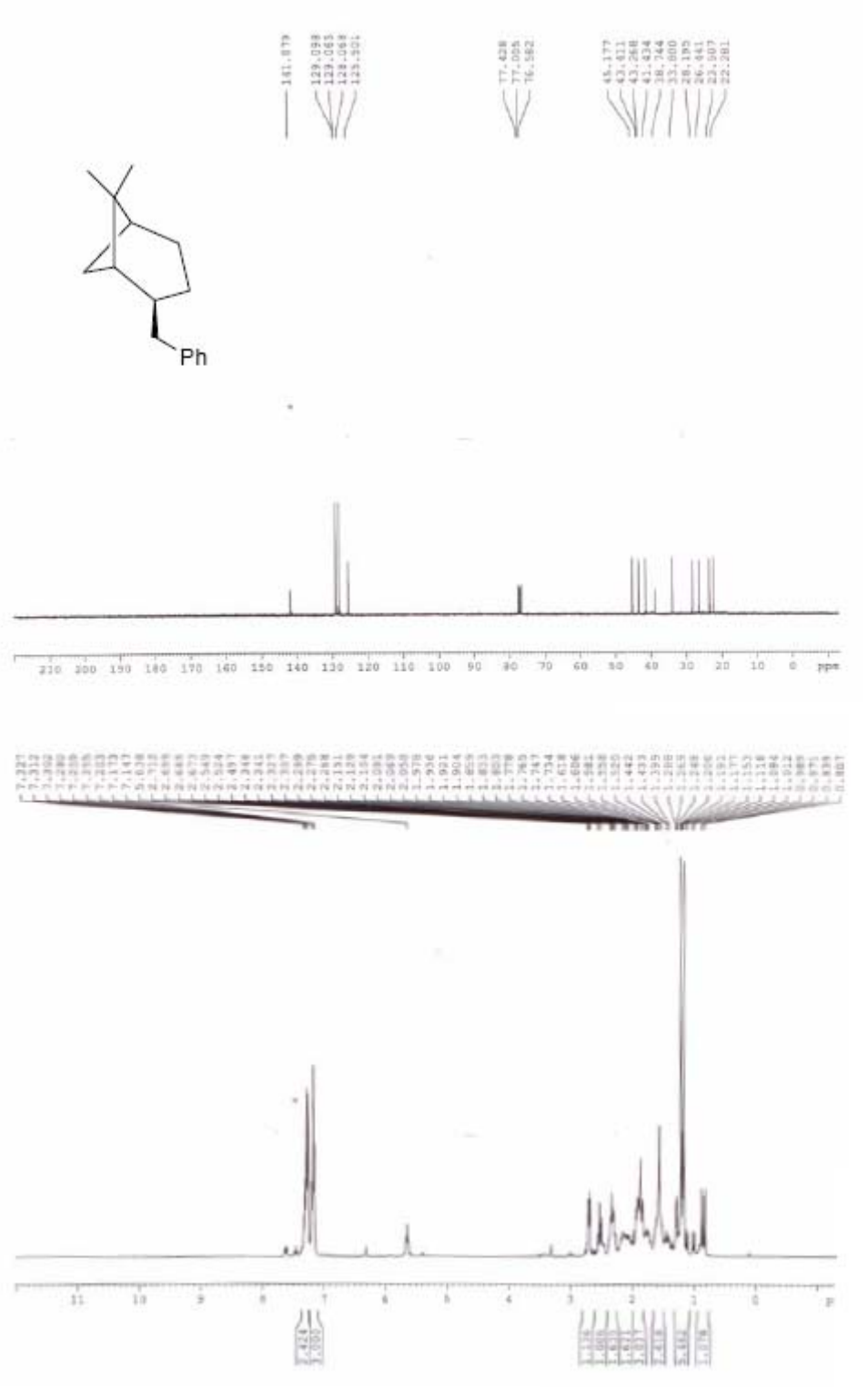
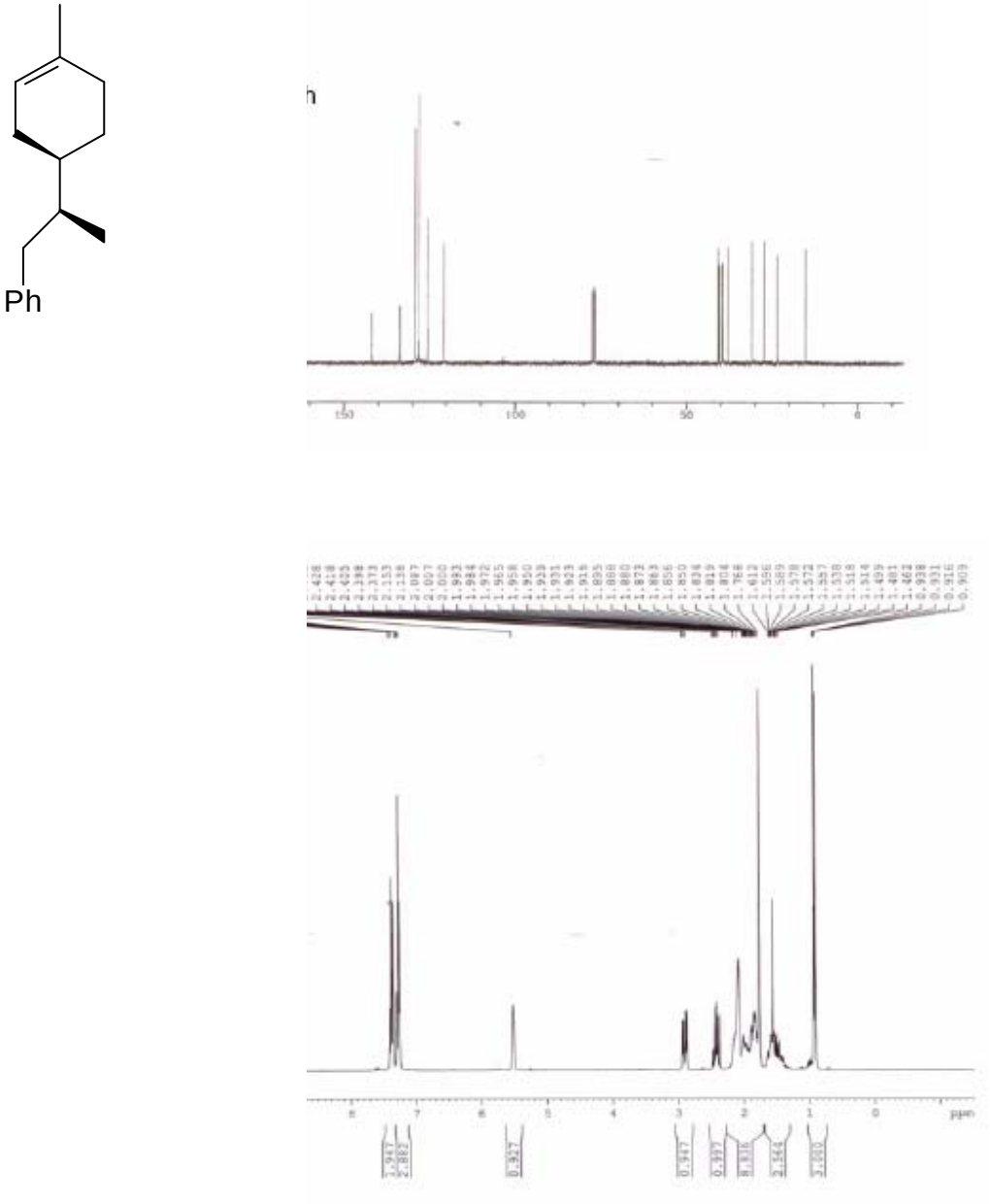


Figure 30. ^{13}C (top) and ^{1}H (bottom) NMR spectra of 7g.



(4*R*)-(+)1-Methyl-4-((1*S*)-1-methyl-2-*o*-pyridinylethyl)-1-cyclohexene (7h).

Following the above mentioned procedure starting from **5i*S*** (3 mmols scale) the crude

product was purified by silica gel column chromatography (hexanes) affording 0.36 g of 7**h** (55% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.80 (d, *J* = 6.8 Hz, 3H), 1.30-1.52 (M, 2H), 1.64 (s, 3H), 1.72-2.04 (m, 6H), 2.50 (dd, *J* = 9.6, 13.2 Hz, 1H), 2.93 (dd, *J* = 5.1, 13.2, 1H), 7.06- 7.12 (m, 2H), 7.56 (dt, *J* = 1.7, 7.7 Hz, 1H), 8.53 (d, *J* = 4.1 Hz, 1H) (Figure 31); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.3, 23.5, 27.2, 27.4, 30.9, 38.2, 38.3, 43.1, 120.8, 120.9, 123.6, 134.0, 136.0, 149.2, 161.9 (Figure 32). IR cm^{-1}: 2908.2, 2868.8, 1453.3, 1365.6, 1030.0, 738.6, 697.6. HRMS $[M+H]^+$ calcd. 216.1752, found 216.1746. $[\alpha]_D^{24}$ = + 62.9° (*c* = 1.0, CH_2Cl_2, 76% ee).

Figure 31. ^{1}H NMR spectrum of 7h.

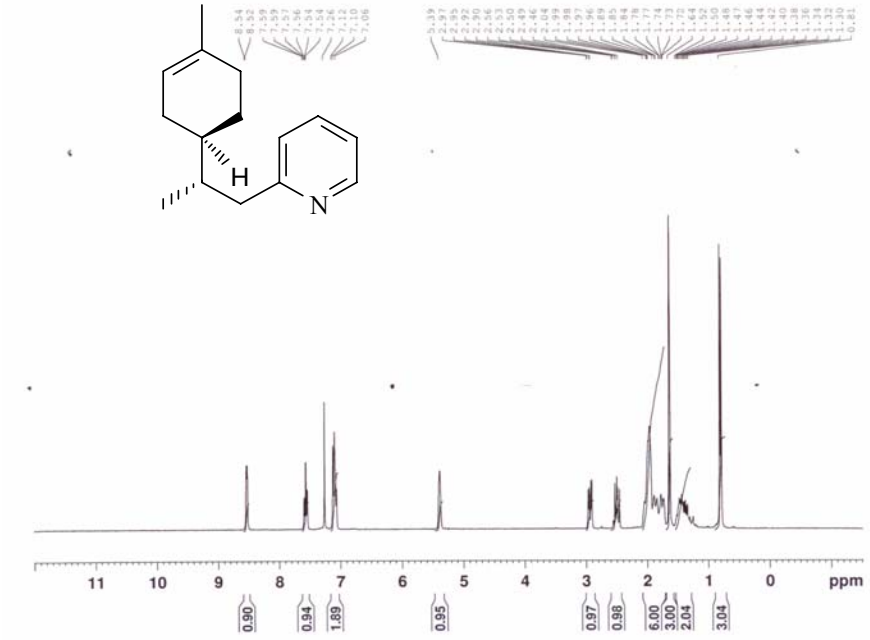
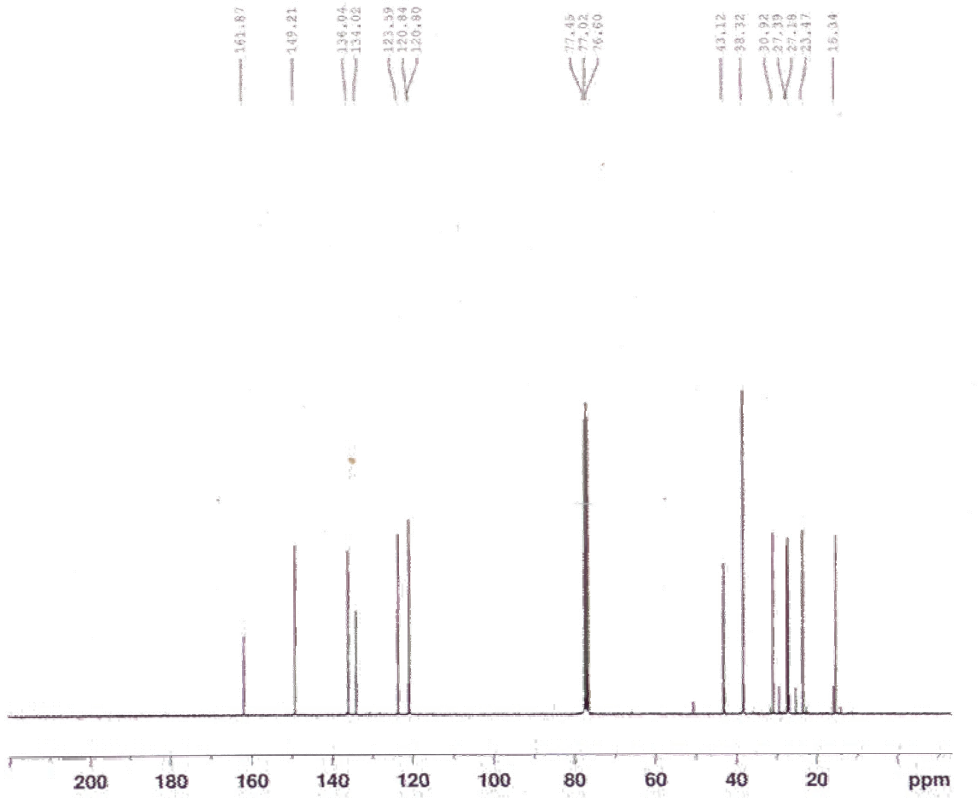


Figure 32. ^{13}C NMR spectrum of 7h.

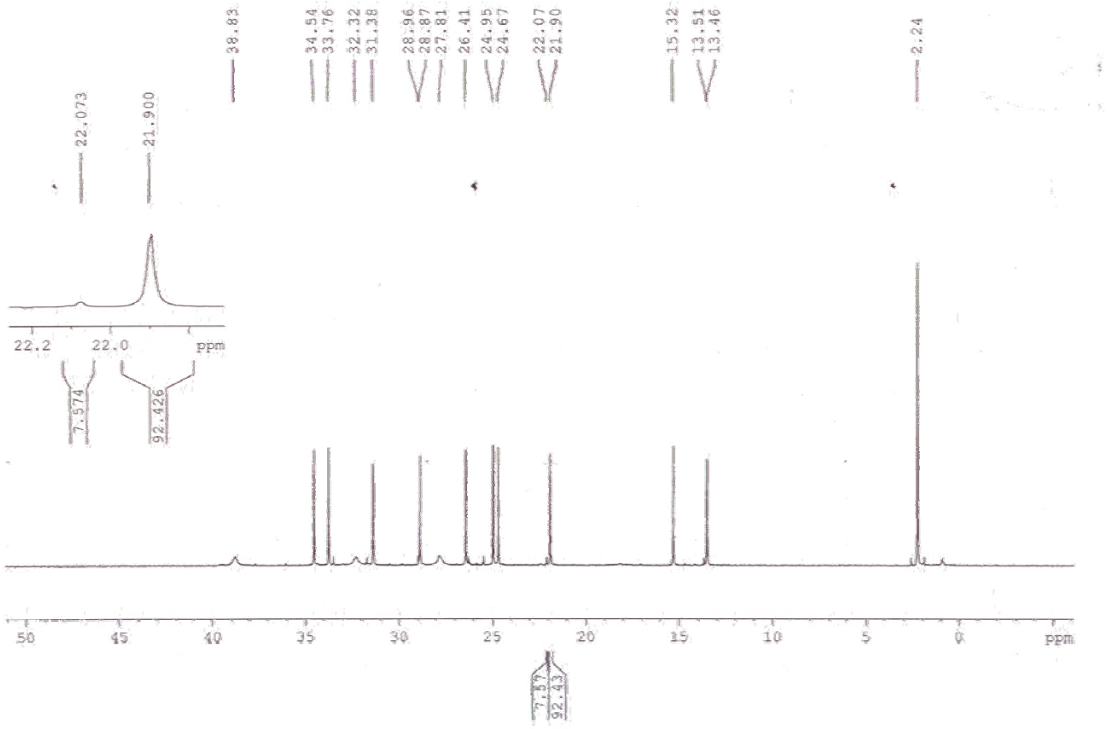


VII. General Procedure for the hydroboration of *cis*- and *trans*-2-butene.

B*-[(*S*)-*sec*-butyl]-(10*R*)-trimethylsilyl-9-borabicyclo[3.3.1]decane from *cis*-2-butene (*S*-5b*R*).** To a solution of **3b*R (3 mmols, 0.66 g) in diethyl ether (3 mL) at -78 ^{o}C was added *via* cannula an excess of condensed *cis*-2-butene (1 mL of *cis*-2-butene in 1 mL of diethyl ether), followed by the addition of TMSCl (0.58 mL, 4.5 mmols). The reaction was allowed to slowly reach room temperature (25 °C) over a period of 2 hours when the reaction reached completion as revealed by ^{11}B NMR δ 87. The solution was concentrated *in vacuo,* diluted in pentane (20 mL) and filtered through a celite pad washing the residue with pentane (2 × 20 mL) and the filtered solution was concentrated again producing ***S*-5b*R*** (97% yield, 0.77 g, 2.9 mmols). ^{13}C NMR ($CDCl_3$, 75 MHz) δ

2.2, 13.5, 15.3, 21.9, 24.7, 25.0, 26.4, 27.8, 28.9, 31.4, 32.3, 33.8, 34.5, 38.8 (92:8 dr) (Figure 33). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H) 0.96 (d, *J* = 7.2 Hz, 3H), 1.17-1.67 (m, 18H).

Figure 33. ^{13}C NMR spectrum of *S*-5b*R*.



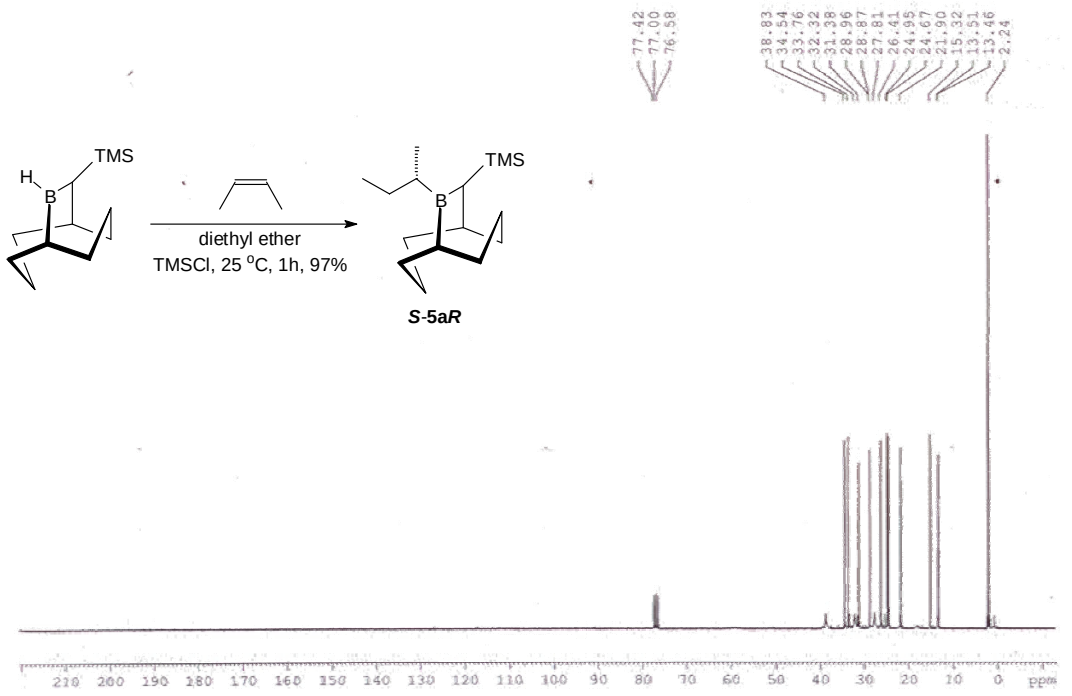


Figure 34. ^{1}H NMR spectrum of *S*-5b*R*.

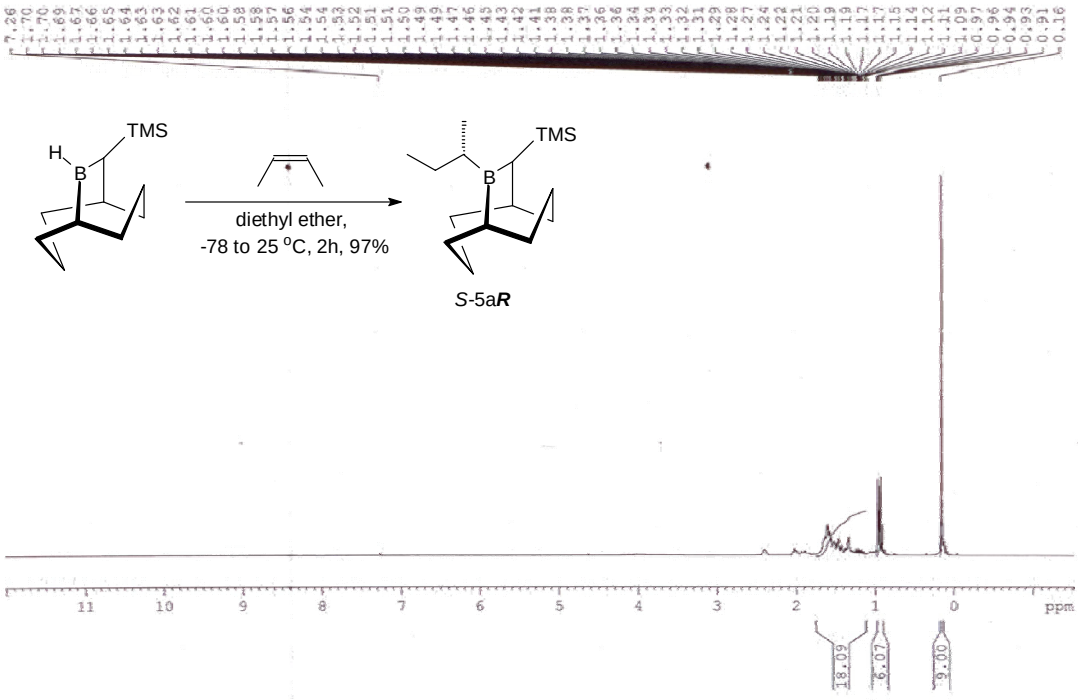
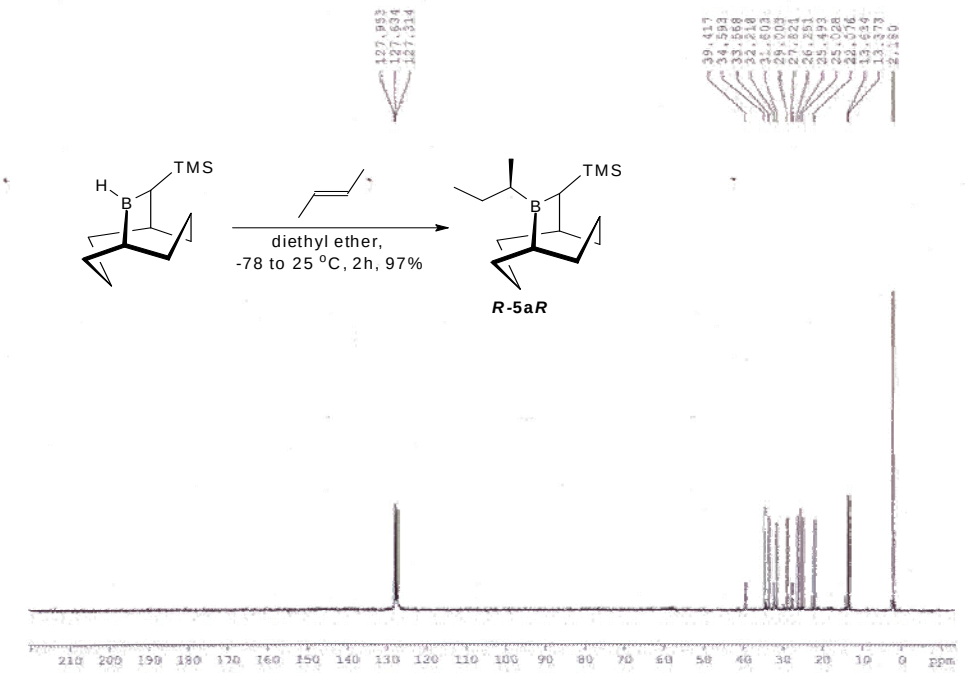


Figure 35. ^{13}C NMR spectrum of *R*-5b*R*.



B*-[(*R*)-*sec*-butyl]-(10*R*)-trimethylsilyl-9-borabicyclo[3.3.1]decane from *trans*-2-butene (*R*-5b*R*).** To a solution of **3b*R (3 mmols, 0.66 g) in diethyl ether (3 mL) at -78 °C was added *via* cannula an excess of condensed *trans*-2-butene (1 mL of *trans*-2-butene in 1 mL of diethyl ether), followed by the addition of TMSCl (0.58 mL, 4.5 mmols). The reaction was allowed to slowly reach room temperature (25 °C) over a period of 2 hours when the reaction reach completion as shown by ^{11}B NMR δ 87. The solution was concentrated *in vacuo,* diluted in pentane (20 mL) and filtered through a celite pad washing the remainings with pentane (2 × 20 mL) and the filtered solution was concentrated again producing ***R*-5b*R*** (97% yield, 0.77 g, 2.9 mmols). ^{13}C NMR (C_6D_6, 75 MHz) δ 2.2, 13.4, 13.6, 22.1, 25.0, 25.5, 26.3, 27.8, 29.0, 31.6, 32.2, 33.6, 34.6, 39.4 (92:8 dr) (Figure 35). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H) 0.96 (d, *J* = 7.2 Hz, 3H), 1.17-1.67 (m, 18H).

2-butanol (6a).[22] To the previously prepared ***S*-5b*R*** from the above procedure was diluted in dry THF (6 mL) at -78 °C a solution of NaOH/MeOH (6 mL, 5 M) was added dropwise followed by the also dropwise addition of H_2O_2 solution (0.93 mL, 30 wt. %). The reaction mixture was refluxed for 2 hrs, cooled and extracted with ether (3 × 20 mL) from brine. The combined organic phase was dried over $MgSO_4$ and filtered. The solvents were distilled out of the filtered solution and then **6a** was distilled out of the crude mixture. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.6, 22.3, 31.6, 68.7 (Fig.42). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 (t, J = 7.5 Hz, 3H), 1.18 (d, J = 6.2 Hz, 3H), 1.40 (s (broad, OH), 1H), 1.42-1.52 (m, 2H), 3.67-3.78 (m, 1H) (Figure 36).

From ***S*-5b*R* (6a*S*)**: $[\alpha]_D^{25}$ = +11.8° (*c* = 1.0, diethyl ether, 84% ee). The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 139.7 (major), 143.8 (minor) compared with the racemic derivative (50:50) (Figure 37).

From ***R*-5b*R* (6a*R*)**: 0.39 g (95% yield, 3 mmols scale) $[\alpha]_D^{25}$ = -13.6° (*c* = 1.0, diethyl ether, 96% ee). [Lit.[22] (**6a*R***): $[\alpha]_D^{25}$ = -13.3° (*c* = 0.63, CH_3OH, 95% ee)]. The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 143.8 (major), 139.7 (minor) compared with the racemic derivative (50:50) (Figure 37).

Figure 36. ^{13}C NMR spectrum of 6a.

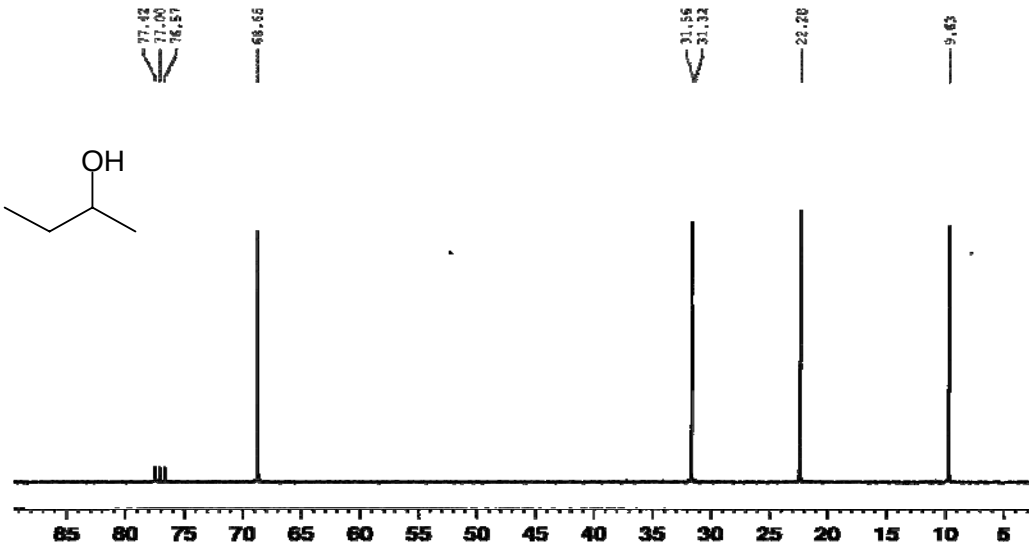
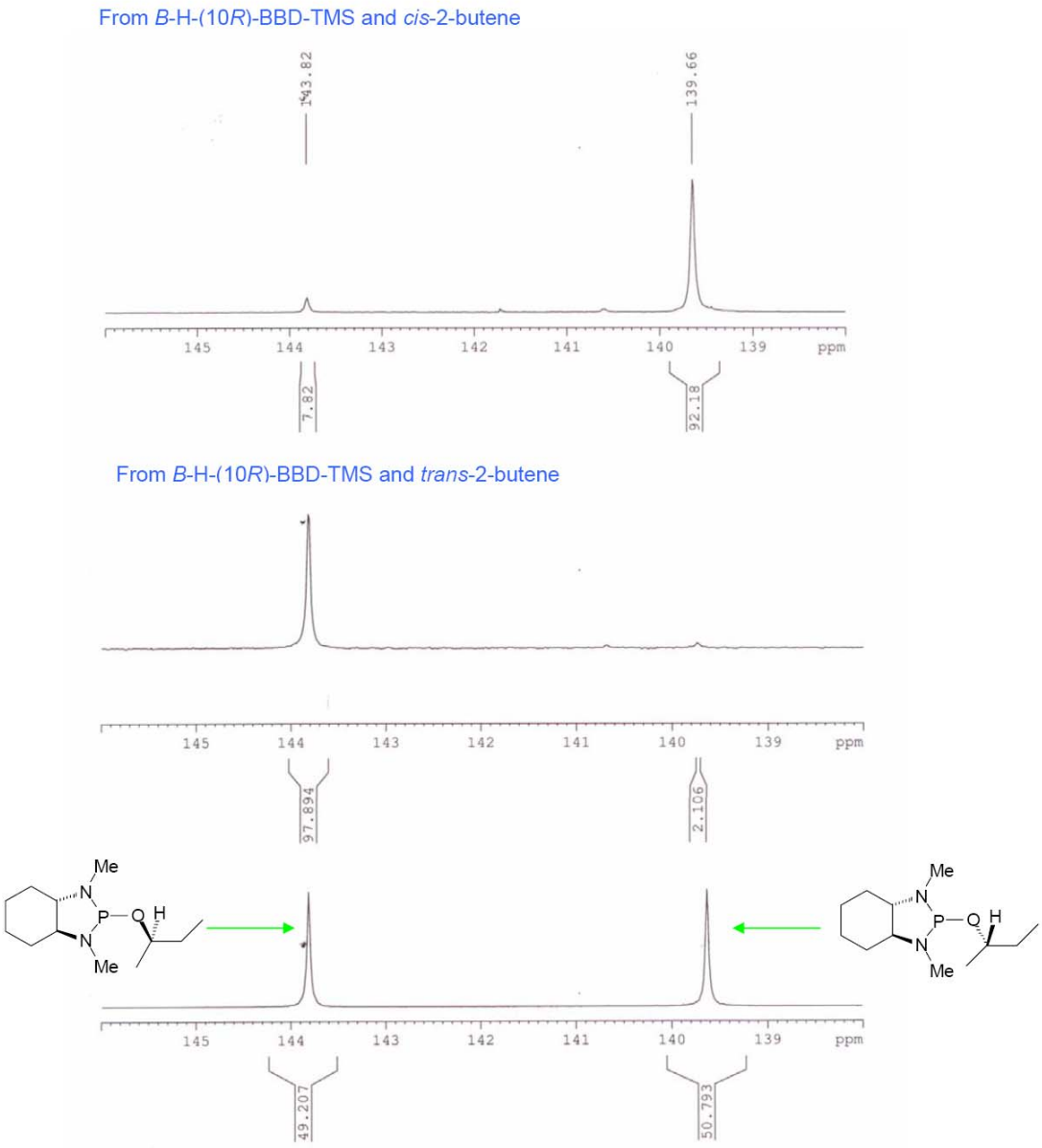


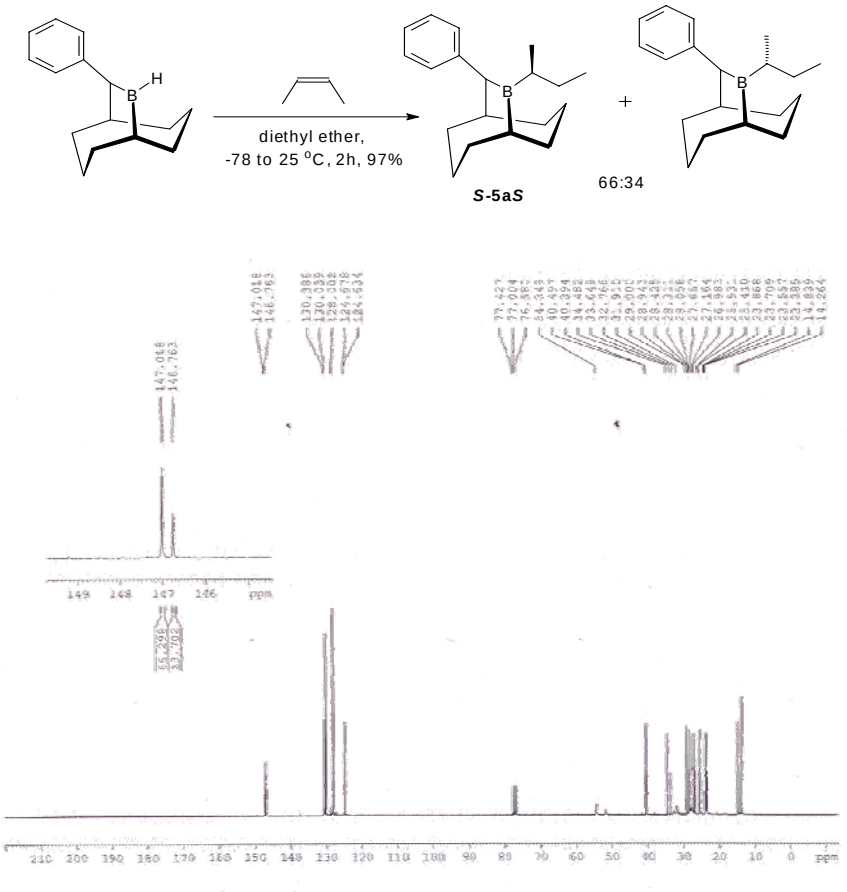
Figure 37. ^{31}P NMR spectrum of 6a-CDA.



B*-[(*S*)-sec-butyl]-(10R)-phenyl-9-borabicyclo[3.3.1]decane from *cis*-2-butene (*S*-5a*S*).** To a solution of **5a*S (3 mmols, 0.66 g) in diethyl ether (3 mL) at -78 ^{o}C was added *via* cannula an excess of condensed *cis*-2-butene (1 mL of *cis*-2-butene in 1 mL of diethyl ether), followed by the addition of TMSCl (0.58 mL, 4.5 mmols). The reaction was allowed to slowly reach room temperature (25 °C) over a period of 2 hours when the

reaction reach completion as shown by ^{11}B NMR δ 86. The solution was concentrated *in vacuo,* diluted in pentane (20 mL) and filtered through a celite pad washing the remainings with pentane (2 × 20 mL) and the filtered solution was concentrated again producing ***S*-5a*S*** (97% yield, 0.76 g, 2.9 mmols). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 14.8, 23.6, 23.7, 25.4, 27.0, 28.3, 28.9, 31.9, 34.5, 40.5, 54.3, 124.6, 128.0, 130.0, 147.0 (66:34 dr) (Figure 38). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87-1.03 (m, 5H), 1.21-2.10 (m, 16H), 2.33 (s, 1H), 2.45 (s, 1H), 2.66-2.78 (m, 1H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 2H).

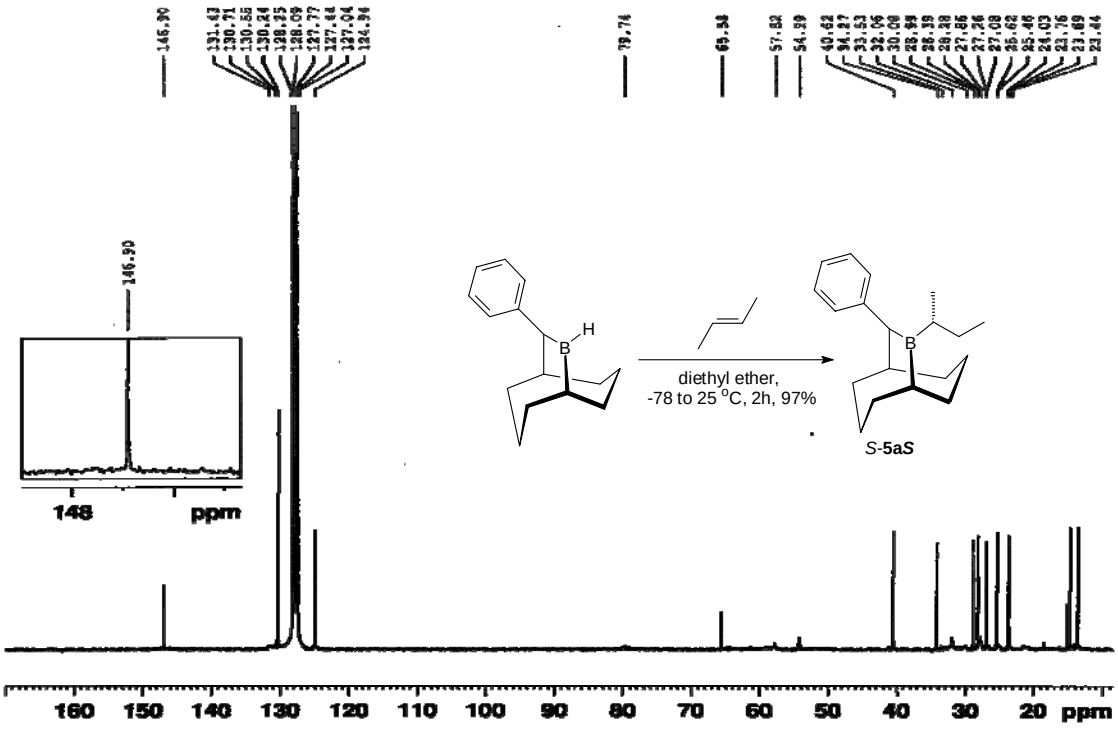
Figure 38. ^{13}C NMR spectrum of *S*-5a*S*.



B*-[(*S*)-sec-butyl]-(10*S*)-phenyl-9-borabicyclo[3.3.1]decane from *trans*-2-butene (*S*-5a*S*).** To a solution of **3a*S (3 mmols, 0.66 g) in diethyl ether (3 mL) at -78 °C was

added *via* cannula an excess of condensed *cis*-2-butene (1 mL of *cis*-2-butene in 1 mL of diethyl ether), followed by the addition of TMSCl (0.58 mL, 4.5 mmols). The reaction was allowed to slowly reach room temperature (25 °C) over a period of 2 hours when the reaction reach completion as shown by ^{11}B NMR δ 87. The solution was concentrated *in vacuo,* diluted in pentane (20 mL) and filtered through a celite pad washing the remainings with pentane (2 × 20 mL) and the filtered solution was concentrated again producing ***S*-5a*S*** (97% yield, 0.76 g, 2.9 mmols). ^{13}C NMR (C_6D_6, 75 MHz) δ 13.7, 14.8, 23.6, 23.7, 25.4, 27.0, 28.3, 28.9, 31.9, 34.5, 40.5, 54.3, 124.6, 128.0, 130.0, 147.0 (66:34 dr) (Figure 39). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87-1.03 (m, 5H), 1.21-2.10 (m, 16H), 2.33 (s, 1H), 2.45 (s, 1H), 2.66-2.78 (m, 1H), 7.17 (d, J = 7.1 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.3 Hz, 2H).

Figure 39. ^{13}C NMR spectrum of *S*-5a*S'*.



2-butanol (6a). To the previously prepared ***S*-5a*S*** from the above procedure was diluted in dry THF (6 mL) at -78 °C a solution of NaOH/MeOH (6 mL, 5 M) was added dropwise followed by the also dropwise addition of H_2O_2 solution (0.93 mL, 30 wt. %). The reaction mixture was refluxed for 2 hrs, cooled and extracted with ether (3 × 20 mL) from brine. The combined organic phase was dried over $MgSO_4$ and filtered. The solvents were distilled out of the filtered solution and then **6a** was distilled out of the crude mixture. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.6, 22.3, 31.6, 68.7 (Fig.42). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 (t, J = 7.5 Hz, 3H), 1.18 (d, J = 6.2 Hz, 3H), 1.40 (s (broad, OH), 1H), 1.42-1.52 (m, 2H), 3.67-3.78 (m, 1H).

From ***S*-5a*S* (6a*S*)**: $[\alpha]_D^{25}$ = +2.7° (*c* = 1.0, diethyl ether, 32% ee). The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**:

^{31}P NMR ($CDCl_3$, 122 MHz) δ 139.7 (major), 143.8 (minor) compared with the racemic derivative (50:50).

From ***S*-5a*S* (6a*S*)**: $[\alpha]_D^{25}$ = +12.8° (*c* = 1.0, diethyl ether, 96% ee). [Lit. value for **6a*S***: $[\alpha]_D^{25}$ = +13.3° (*c* = 0.63, CH_3OH, 95% ee)]. The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 139.7 (major), 143.8 (minor) compared with the racemic derivative (50:50).

VIII. General procedure for the synthesis of secondary carbinol 6b.

(*S*)-(+)-3-Methyl-2-butanol (6b). To a solution of **3a*S*** (0.66 g, 3.0 mmol) in ether (3 mL) at -40 °C, 2-methyl-2-butene (0.37 mL, 3.5 mmols) was added followed by the addition of TMSCl (0.58 mL, 4.5 mmols). The reaction mixture was allowed to quickly reach 25 °C and react for 15 min (over a total period of 30 min). Using standard techniques to prevent the exposure of the trialkylborane to the open atmosphere, the solution was concentrated *in vacuo,* diluted in pentane (20 mL) and filtered through a celite pad washing the remainings with pentane (3 × 15 mL). The resulting trialkylborane was diluted in dry THF (6 mL) at -78 °C a solution of NaOH/MeOH (6 mL, 5 M) was added dropwise followed by the also dropwise addition of H_2O_2 solution (0.93 mL, 30 wt. %). The reaction mixture was refluxed for 2 hrs, cooled and extracted with ether (3 × 20 mL) from brine. The combined organic phase was dried over $MgSO_4$ and filtered. The solvents were distilled out of the filtered solution and then **(3i*S*)** was distilled out of the crude mixture. The product distilled at 95-110 °C to obtain 0.21 g (79%) of **6b.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (dq, app t, J = 7.2 Hz, 6H), 1.78 (d, J = 6.4 Hz, 3H), 1.55 (dq, J = 6.6, 6.7 Hz, 1H), 2.04 (s, broad OH, 1H), 3.47-3.52 (m, 1H) (Figure 40); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.8, 18.0, 19.8, 34.9, 72.6. $[\alpha]_D^{24}$ = + 7.91° (*c* = 1.0, CH_2Cl_2, 74% ee) (Figure 41). The enantiomeric purity was determined by ^{31}P NMR by derivatization of the carbinol with Alexakis reagent **A**: ^{31}P NMR ($CDCl_3$, 122 MHz) δ 139.1 (minor), 144.6 (major) compared with the racemic derivative (50:50) (Figure 42). These data were in complete agreement with literature values.[23]

Figure 40. ^{1}H NMR sectrum of 6b.

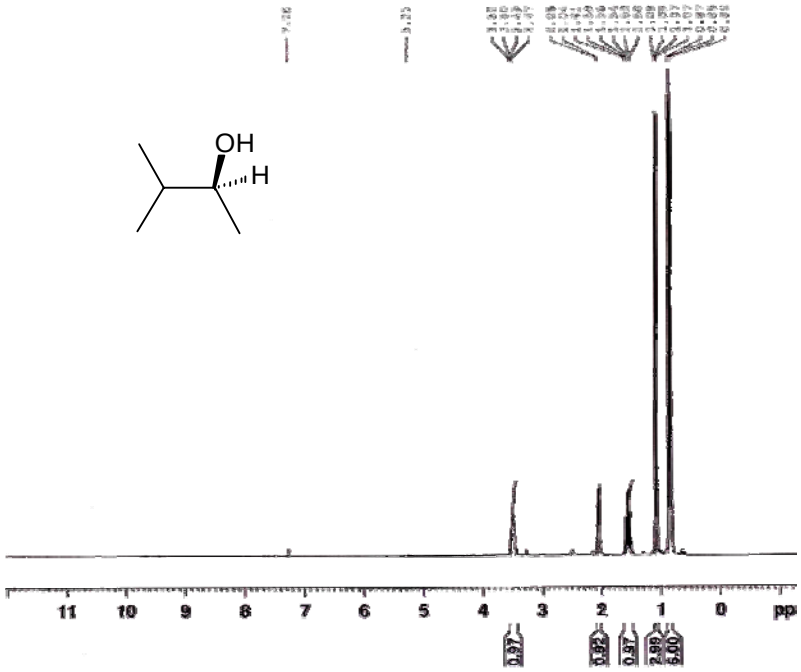


Figure 41. ^{13}C NMR spectrum of 6b.

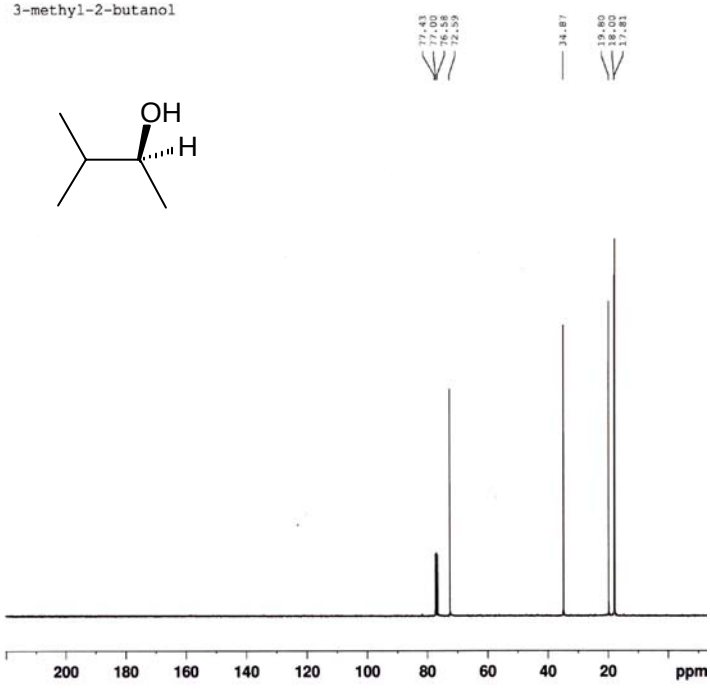
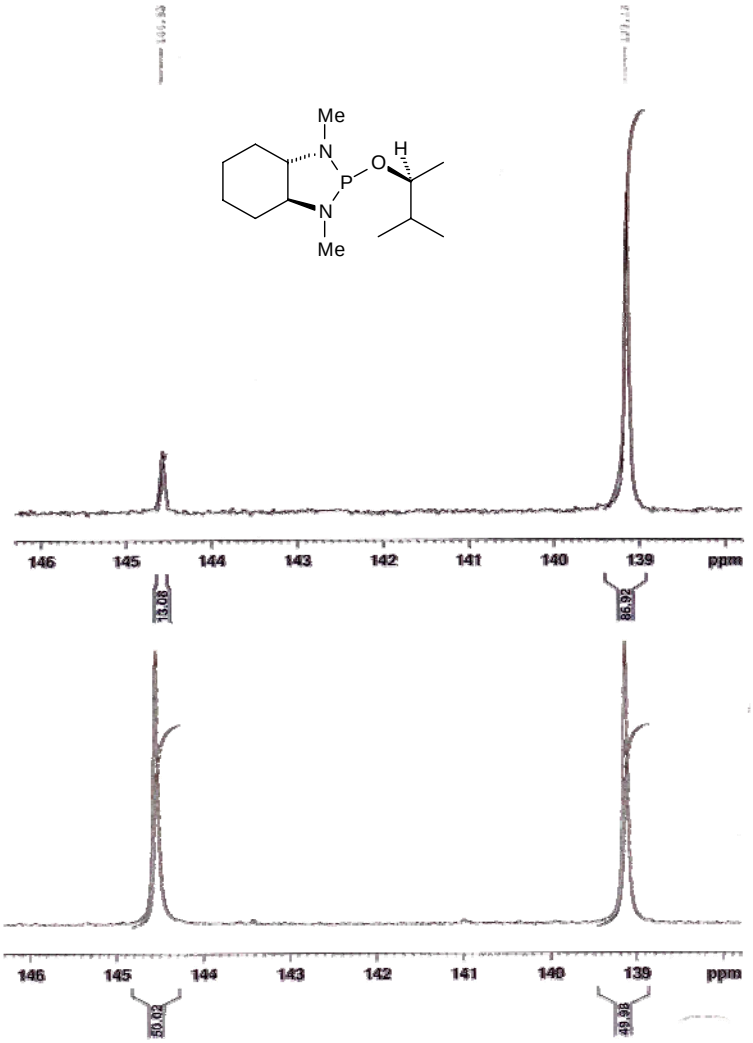


Figure 42. ^{31}P NMR spectra of 6b-CDA.



IX. References:

[1] Burgos, C.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044.

[2] Canales, E.; Prasad, K. G.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 11572-11573.

[3] Soderquist, J. A.; Matos, K.; Burgos, C. H.; Lai, C.; Vaquer, J.; Medina, J. R. in *Contemporary Boron Chemistry*, Davidson M. G.; Hughes A. K.; Marder, T. B.; Wade, K. (eds) Royal Society of Chemistry: Cambridge, UK (2000) pp 472-482. (b) Soderquist, J. A.; Matos, K.; Burgos, C. H.; Lai, C.; Vaquer, J.; Medina, J. R.; Huang, S. D. in *Organoboranes for Syntheses*, A. C. S. Symposium Series 783, Ramachandran, P. V.; Brown, H. C. (Eds.) American Chemical Society, Washington, D. C., 2000. Chapter 13, pp 176-194.

[4] Alexakis, A.; Furtos, J. C.; Mutti, S.; Mangeney, P. *J. Org. Chem.* **1994**, *59*, 3326.

[5] Organ, M. G.; Bilokin, Y. V.; Bratovanov, S. *J. Org. Chem.* **2002**, *67*, 5176- 5183.

[6] All reactions carried out with the Li-*B*-H_2-10-phenyl-9-BBD (**3a**) reagent followed the described procedure. However, the reactions that utilized the Li-*B*-H_2-10-trimethylsilyl-9-BBD (**3b**) reagent as the hydroborating agent were done at 25 °C and their reaction times showed a dramatic dependence on the alkene substrate.

[7] Brown, H. C.; Imai, T.; Desai, M. C.; Singaram, B. *J. Am. Chem. Soc.* **1985**, *107*, 4980-4985.

[8] Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512- 519.

[9] Giancomelli, G.; Rosini, C.; Caporusso, A. M.; Palla, F. *J. Org. Chem.* **1983**, *48*, 4887-4891.

[10] Giancomelli, G.; Bertero, L.; Lardicci, L. *Terahedron. Lett.* **1981**, *22*, 883- 886.

[11] Spino, C.; Beaulier, C. *J. Am. Chem. Soc.* **1998**, *120*, 11832- 11833.

[12] Elsenbaumer, R. L.; Mosher, H. S. *J. Org. Chem.* **1979**, *44*, 600-604.

[13] *Beil.* 6 IV 278.

[14] G. Giancomelli *et.* al. *J. Org. Chem.* **1984**, *49*, 310.

[15] Kim, K.-Y.; Lee, S.-G. *Magnetic Resonance in Chemistry*, **1997**, *35*, 451- 454.

[16] Barlett, P. A.; Pizzo, C. F. *J. Org. Chem.* **1981**, *46*, 3896-3900.

[17] Letsinger, R. L. *J. Am. Chem. Soc.* **1948**, *70*, 406- 409.

[18] Grovenstein, E.; Rhee, J-U. *J. Am. Chem. Soc.* **1975**, *97*, 764- 769.

[19] Broene R. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 12569- 12570.

[20] Royer, R.; Demerseman, P.; Lechartier, J.; Cheutin, A. *J. Org. Chem.* **1962**, *27*, 3808-3814.

[21] Paquette, L. A.; Gilday, J. P. *J. Org. Chem.* **1988**, 53, 4972- 4978.

[22] Masamune, S.; Kim, B.; Petersen, J. S. *J. Am.Chem. Soc.* **1985**, *107*, 4549-4551.

[23] Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *J. Org. Chem.* **1982,** *47***,** 5074-5083.