Supplementary Material

Non-Racemic α-Allenyl Carbinols from Asymmetric Propargylboration with the 10-Trimethylsilyl-9-borabicyclo[3.3.2]decanes

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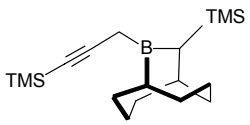
General Information. All experiments were carried out in pre-dried glassware (1 h, 150 °C) under a nitrogen atmosphere. Standard handing techniques for air-sensitive compounds were employed for all the operations. Nuclear magnetic resonance (NMR) spectra were obtained using General Electric DPX-300 spectrometer. ^{1}H (300 MHz), ^{13}C (75 MHz), ^{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. Infrared spectra were recorded on a Perkin-Elmer 282 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 the scanned spectra obtained in this study to consolidate more complete information herein.

Experimental Procedures

3-Trimethylsilyl-2-propynylmagnesium bromide In a 100 mL three neck round bottom flask equipped with a stirring bar, a dry-ice condenser and a 50 mL addition funnel, To pulverized Mg powder (0.177 g, 7.3 mmol) was added and $HgCl_2$ 1-2% (0.02 g, 0.073 mmol) as the initiator. Dry ether (from Na/Ph_2CO) (ca. 1 mL) was added and 3-bromo-1-(trimethylsilyl)-1-propyne (1.0 mL, 7.0 mmol) in ether (6.3 mL) was added dropwise from the addition funnel with the contents of the flask being stirred vigorously. After the addition was complete the solution is refluxed for 2 h. A dark-green color indicates the formation of the Grignard reagent. The reaction is cooled at room temperature under positive pressure of nitrogen to produce the Grignard reagent (6.0 mL, 0.67 M, 4.0 mmol) (55%).



(±)-*B*-[γ-(Trimethylsilyl)propargyl]-10-trimethylsilyl-9-borabicyclo[3.3.2]-decane (1). Method A. To a stirred solution of (±)-**3**[1] (Fig. 1) (0.952 g, 4.0 mmol) in ether (110 mL) at -78 °C, was added a solution of freshly prepared γ-

(trimethylsilyl)propargylmagnesium bromide in ether (6.0 mL, 0.67 M) and the mixture was stirred for 1 h at -78 °C. The solution was allowed to slowly warm to room temperature and the solvents were removed *in vacuo* and hexane (10 mL) was added to the residue. The slurry was filtered under a nitrogen atmosphere through a celite pad employing a double-ended needle to effect the transfer. This washing/filtration procedure was repeated two more times and the combined filtrates were concentrated at reduced pressure to obtain 1.25 g (98%) of **1**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.13 (s, 3H), 0.14 (s, 3H), 1.4-1.8 (m, 15H), 2.2 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.06, 1.5, 20.0, 21.7, 24.8, 25.1, 27.8, 29.2, 30.9, 31.4, 33.6, 34.9, 40.1, 84.0, 127.4 (Fig. 3); ^{11}B NMR ($CDCl_3$, 96 MHz) δ 84.5. IR (neat) 2913, 2852, 2172, 1278, 1247, 835, 758 cm^{-1}. **Method B.** To a stirred solution of 1-(trimethylsilyl)propyne (0.74 mL, 5.0 mmol) in THF (5 mL) at 0 °C was added *tert*-butyllithium in pentane (1.7 M, 5.0 mmol) dropwise, and the reaction mixture was stirred for 1 h. The mixture was cooled to -78 °C and added dropwise *via* double ended needle to a solution of (±)-**3**[1] (1.2 g, 5.0 mmol) in ether (10 mL) at -78 °C. After 30 min, trimethylsilyl triflate (1.0 mL, 5.3 mmol) was added dropwise, and the solution was stirred for 1 h at -78 °C, allowed to slowly warm to room temperature, and concentrated at reduced pressure. Hexane (10 mL) was added to the residue and the lithium salts were removed by filtration as above to give 1.1 g (85%) of **1**. **Note!** The lithium triflate salt was difficult to remove and several filtrations were sometimes required which both lowered the yield and introduced the possibility of minor amounts of oxidation in **1**. **Note!** Both methods were used to obtain (-)-**1*R*** from (-)-**3*R*** and (+)-**1*S*** from (+)-**3*S***.[1]

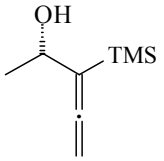
(-)-(10*R*)-*B*-[γ-(Trimethylsilyl)propargyl]-10-TMS-9-borabicyclo[3.3.2]decane ((-)-1*R*). To a stirred solution of (+)-**2*R*** (Fig. 2) (1.5 g, 4.0 mmol) in ether (16 mL, 0.25 M) at -78 °C was added dropwise to a solution of freshly prepared trimethylsilylpropynemagnesium bromide (6.0 mL, 0.67 M) in dry ether and the mixture was stirred for 1 h. The reaction mixture was allowed to slowly warm to room temperature. The solvent was removed *in vacuo* and hexane was added to the residue. The magnesium salts were filtered through a celite pad employing a double-ended needle to effect the transfer. The filtrate was dissolved in water and extracted with ether to give 0.602 g (92%) recovered (1*S*,2*S*)-(+)-pseudoephedrine. The eluent was concentrated to obtain 1.25 g (98%) of (-)-**1*R***. $[\alpha]^{20}_{D}$ = -10.5° (*c* 4.2, C_6D_6). (+)-**1*S*** was similarly prepared from (-)-**2*S***. $[\alpha]^{20}_{D}$ = +11.3° (*c* 4.2, C_6D_6).

Representative Procedure for the Propargylboration of Aldehydes with (±)-1.

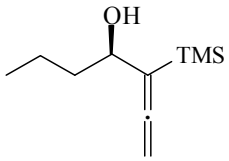
1-Phenyl-2-(trimethylsilyl)-2,3-butadien-1-ol (±)-(6e). Representative procedure: A solution of **1** (1.27 g, 4.0 mmol) in dry THF (5 mL) was cooled to -78 °C and PhCHO (0.3 mL, 4.0 mmol), was added. After 3 h, the solvents were removed *in vacuo*, to give borinate **5e** (1.68 g, 3.96 mmol) in 99% yield. 8-Hydroxyquinoline (0.581 g, 4.0 mmol), was added followed by dry acetonitrile (6 mL) and refluxed for 10 h. The mixture is cooled slowly and the supernatant is decanted into another flask. The precipitated bright-yellow crystals were dried at reduced pressure (54% yield, 0.758 g, 2.16 mmol). The

solution was distilled to give 0.762 g (87%) of (±)-(**6e**) in 87% yield. bp 125 ^{o}C 1.0 mm Hg. The spectral data is identical to that of **6e**.

Propargylboration of Representative Aldehydes with (-)-1*R* or (+)-1*S*.

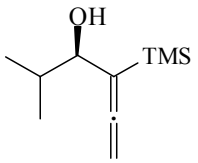


(-)-(2*S*)-3-(Trimethylsilyl)-3,4-pentadien-2-ol (6a). A solution of (-)-**1*R*** (1.27 g, 4.0 mmol) in dry THF (16 mL) was cooled to -78 $^{\circ}$C and MeCHO (0.22 mL, 4.0 mmol) was added dropwise. After 3 h, the solvents were removed at reduced pressure to give borinate **5a** (1.43 g). The (1*S*, 2*S*)-(+)-pseudoephedrine (0.66 g, 4.0 mmol) and freshly distilled acetonitrile (8 mL) were added and the mixture was heated at reflux temperature for 4 h. The solution was slowly cooled to room temperature and decanted into another flask and the precipitated white crystals were washed with hexane (3×5 mL) to yield 1.04 g (71%) of **(+)-2*R***. The residue was distilled to obtain 0.49 g (78%) of **6a**, bp 125 ^{o}C, 60 mm Hg. ^{1}H NMR ($CDCl_3$, 300MHz) δ 0.10 (s, 9H), 1.30 (d, 3H), 2.15 (br s, 1H), 4.30 (m, 1H), 4.50 (d, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -0.95, 24.2, 66.6, 71.9, 101.8, 206.7 (Fig. 4). IR (neat) 3349, 1925, 1247, 1076, 835, 810 cm^{-1}. $[\alpha]^{26}_{D}$ = -8.9^{o} (*c* 1.31, $CHCl_3$), lit[3] (2*R*): $[\alpha]^{25}_{D}$ = +11.9^{o} (*c* 1.27, $CHCl_3$); LRGCMS *m/z* $[M]^{+}$ 155, 141, 117, 97, 75, 73, 75, 66.

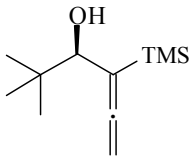


(-)-(4*R*)-3-(Trimethylsilyl)-1,2-heptadien-4-ol (6b).[2] A solution of (+)-**1*S*** (1.27 g, 4.0 mmol) in dry THF (16 mL) was cooled to -78 ^{o}C and *n*-PrCHO (0.36 mL, 4.0 mmol) was added dropwise. After 3 h, the solvents were removed at reduced pressure to give cleanly borinate **5b** (1.39 g). The (1*R*, 2*R*)-(-)-pseudoephedrine (0.61 g, 3.7 mmol) and freshly distilled acetonitrile (8 mL) were added and the mixture was heated at reflux temperature for 9 h. The solution was slowly cooled to room temperature and decanted into another flask and the precipitated white crystals were washed with hexane (3×5 mL) to yield 1.16 g (85%) of **(-)-2*S***. The residue was distilled to obtain 0.64 g (87%) of **6b**, bp 100 ^{o}C, 1.0 mm Hg. Anal. calcd for $C_{10}H_{20}OSi$: C 65.15, H 10.94; found: C 65.09, H 10.90. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9H), 0.85 (t, 3H), 1.3-1.65 (m, 4H), 1.75 (br s, 1H), 4.15 (t, 1H), 4.5 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.3, 13.9, 18.8, 40.0, 70.4, 71.7, 100.7, 207.2 (Fig. 5). IR (neat) 3417, 1928, 1249, 1100, 839 cm^{-1}. $[\alpha]^{20}_{D}$ = -6.0^{o} (*c* 1.54, $CHCl_3$); LRGCMS *m/z* $[M]^{+}$ ($C_{10}H_{20}OSi$)183, 169, 145, 79, 75, 73, 55. This experiment

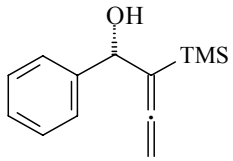
was repeated with (-)-**1*R*** which gave **6b'** whose spectral properties were identical to those of **6b**, but exhibited the opposite specific rotation.



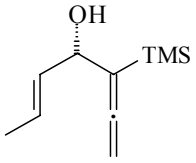
(-)-(**3*R*)-2-Methyl-4-(trimethylsilyl)-4,5-hexadien-3-ol (6c).** A solution of (+)-**1*S*** (1.11 g, 3.5 mmol) in dry THF (16 mL) was cooled to -78 °C and *i*-PrCHO (0.32 mL, 3.5 mmol) was added dropwise. After 3 h, the solvents were removed at reduced pressure to give borinate **5c** (1.23 g). The (1*R*, 2*R*)-(-)-pseudoephedrine (0.54 g, 3.3 mmol) and freshly distilled acetonitrile (7 mL) were added and the mixture was heated at reflux temperature for 10 h. The solution was slowly cooled to room temperature and decanted into another flask and the precipitated white crystals were washed with hexane (3×5 mL) to yield 0.94 g (78%) of **(-)-2*S***. The solution was distilled to obtain 0.49 g (77%) of **6c**, bp 85 °C, 1.0 mm Hg. ^{1}H ($CDCl_3$, 300 MHz) δ 0.10 (s, 9H), 0.85 (d, 3H), 0.90 (d, 3H), 1.75 (m, 1H), 1.80 (br s, 1H), 3.85 (d, 1H), 4.50 (d, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.3, 16.2, 20.0, 33.6, 71.6, 75.4, 99.8, 207.3 (Fig. 6). IR (neat) 3446, 1926, 1248, 1020, 837 cm^{-1}. $[\alpha]^{23.5}_D$ = -5.4° (*c* 1.94, $CHCl_3$), lit[3] $[\alpha]^{26}_D$ = -5.3° (*c* 1.96, $CHCl_3$); LRGCMS *m/z* $[M]^+$ 184, 168, 145, 125, 79, 73, 75.



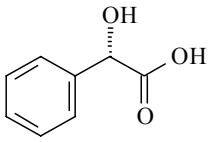
(+)-(3*R*)-2,2-Dimethyl-4-(trimethylsilyl)-4,5-hexadien-3-ol (6d). A solution of (+)-**1*S*** (1.25 g, 3.92 mmol) in dry THF (16 mL) was cooled to -78 °C and *t*-BuCHO (0.38 mL, 3.5 mmol) was added dropwise. After 3 h, the solvents were removed at reduced pressure to give borinate **5d** (1.58 g). The (1*R*, 2*R*)-(-)-pseudoephedrine (0.64 g, 3.88 mmol) and freshly distilled acetonitrile (8 mL) were added and the mixture was heated at reflux temperature for 10 h. The solution was slowly cooled to room temperature and decanted into another flask and the precipitated crystals were washed with hexane (3 × 5 mL) to yield 1.00 g (70%) of **(-)-2*S***. The residue was distilled to obtain 0.56 g (80%) of **6d**, bp 105 °C, 1.0 mm Hg. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9H), 0.92 (s, 9H), 1.8 (br s, 1 H), 3.75 (s, 1H), 4.5 (dd, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -0.6, 26.1, 37.4, 71. 4, 77. 6, 98.4, 208.6 (Fig. 7). IR (neat) 3479, 1921, 1248, 1050, 1007, 836, 803 cm^{-1}. $[\alpha]^{25}_D$ = +5.0° (*c* 1.13, $CHCl_3$), lit[3] $[\alpha]^{25}_D$ = +5.4° (*c* 2.60, $CHCl_3$); LRGCMS *m/z* $[M]^+$ 197, 141, 125, 93, 75, 73, 57.



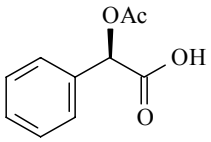
(-)-(**1*S*)-1-Phenyl-2-(trimethylsilyl)-2,3-butadien-1-ol (6e).** A solution of (-)-**1*R*** (0.96 g, 3.0 mmol) in dry THF (16 mL) was cooled to -78 °C and PhCHO (0.30 mL, 3.0 mmol) was added dropwise. After 3 h, the solvents were removed at reduced pressure to give borinate **5e** (1.23 g). The (1*S*, 2*S*)-(+)-pseudoephedrine (0.48 g, 2.91 mmol) and freshly distilled acetonitrile (8 mL) were added and the mixture was heated at reflux temperature for 15 h. The solution was slowly cooled to room temperature and decanted into another flask and the precipitated white crystals were washed with hexane (3×5 mL) to yield 0.76 g (70%) of **(+)-2*R***. The solution was distilled to obtain 0.40 g (60%) of **6e**, bp 125 °C, 1.0 mm Hg. ^{1}H ($CDCl_3$, 300 MHz) δ 0.0 (s, 9H), 2.61 (d, 1H), 4.65 (dd, 2H), 5.25 (s, 1H), 7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.2, 72.5, 72.8, 99.5, 126.8, 127.6, 128.1, 143.0, 207.0 (Fig. 8). IR (neat) 3393, 3029, 1955, 1267, 1024, 905, 843, 749, 698 cm^{-1}. $[\alpha]^{20}_D$ = -122.8° (*c* 1.40, $CHCl_3$), lit[3] $[\alpha]^{25}_D$ = -139.4° (*c* 1.40, $CHCl_3$); LRGCMS *m/z* $[M]^+$ 218, 179, 128, 107, 79, 77, 75, 73, 51. This experiment was repeated with (+)-**1*S*** which gave **6e'** whose spectral properties were identical to those of **6e**, but exhibited the opposite specific rotation.



(+)-(**4*S*)-(*E*)-3-(Trimethylsilyl)-1,2,5-heptatrien-4-ol (6f).** A solution of (-)-**1*R*** (1.11 g, 3.5 mmol) in dry THF (16 mL) was cooled to -78 °C and (*E*)-crotonaldehyde (0.3 mL, 3.5 mmol) was added dropwise. After 3 h, the solvents were removed at reduced pressure to give borinate **5f** (1.35 g). The (1*R*, 2*R*)-(-)-pseudoephedrine (0.58 g, 3.5 mmol) and freshly distilled acetonitrile (8 mL) were added and the mixture was heated at reflux temperature for 10 h. The solution was slowly cooled to room temperature and decanted into another flask and the precipitated white crystals were washed with hexane (3×5 mL) to yield 1.10 g (85%) of **(-)-2*S***. The solution was distilled to obtain 0.56 g (87%) of **6f**, bp 80 °C, 1.0 mm Hg. ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.70 (dd, *J* = 6.4 Hz, *J* = 1.4 Hz, 3H), 1.89 (br s, 1H), 4.60 (m, 3 H), 5.50 (ddq, *J* = 15.3 Hz, *J* = 7.4 Hz, *J* = 1.5 Hz, 1H), 5.70 (dq, *J* = 15.4 Hz, *J* = 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.0, 17.4, 71.4, 72.3, 100.3, 126.9, 133.2, 206.8 (Fig. 9). IR (neat) 3308, 3044, 2084, 1639, 1247, 1025, 977, 851 cm^{-1}. $[\alpha]^{25}_D$ = +57.7° (*c* 1.60, $CHCl_3$), lit[3] (4*R*) $[\alpha]^{25}_D$ = -87.8° (*c* 1.96, $CHCl_3$); LRGCMS *m/z* $[M]^+$ 182, 167, 143, 112, 75, 73, 71, 53.



(*S*)-(+)-α-Hydroxyphenylacetic acid (Mandelic acid, 9). 6e (0.060 g, 0.27 mmol) was dissolved in dichloromethane (30 mL), and the solution was cooled to -78 ^{o}C. Ozone was bubbled through the solution until a blue color persisted (11 min). The solvents were removed to give the trimethylsilyl ester intermediate **8** (^{13}C NMR δ 176 (SiOC=O), 1.8 (TMS)). THF (3 mL) was added followed by 1 equiv of water (0.005 g, 0.27 mmol). The mixture was stirred for 3 h at room temperature and the solvents were removed *in vacuo* to give **9** (0.041 g, 100%). $[\alpha]^{20}_{D}$ = +149^{o} (*c* 2.5 H_2O), lit.[4] $[\alpha]^{25}_{D}$ = +155^{o} (*c* 5 H_2O); ^{1}H NMR (CD_3OD) δ 4.90 (s, 1H), 7.10-7.35 (m, 5H); ^{13}C NMR (CD_3OD, 75 MHz) δ 72.6, 126.6, 127.6, 127.7, 138.2, 175.4 (Fig. 10). In a separate experiment, the ozonolysis was interrupted after 2.5 min, the mixture was concentrated and its ^{13}C NMR spectrum was recorded to clearly reveal the acylsilane intermediate **7** (*i.e.* δ 240.6 (TMSC=O); -2.8 (TMS) (Fig. 17).



(*R*)-(-)-α-(Acetoxy)phenylacetic acid (*O*-Acetylmandelic acid, 9') (0.978 g, 0.45 mmol) was dissolved in 3 mL of dry THF. Pyridine (1.0 mL, 12.4 mmol) was added followed by acetic anhydride (1.0 mL, 10.6 mmol) at room temperature. The solution was allowed to react overnight. The mixture was extracted with water (4 X 3 mL) to remove the precipitated salts. The organic layer was dried with $MgSO_4$, filtrated and concentrated to give the acetylated product (0.117 g, 0.45 mmol) quantitatively. ^{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. This material was dissolved in dichloromethane (25 mL) and cooled to -78 ^{o}C. Ozone was bubbled through the solution until a blue solution persisted (10 min.). The mixture was concentrated and dissolved in THF (5 mL). Hydrogen peroxide (1 mL of 30%) was added and the mixture was stirred at room temperature for 3 h. Water (3 mL) was added and the layers were separated and the organic layer was dried ($MgSO_4$), filtered and the solvents were removed *in vacuo* to afford 0.087 g (100%) of **9'**. $[\alpha]^{21}_{D}$ = -145.5 (*c* 1.78, CH_3COCH_3), lit.[5] $[\alpha]^{25}_{D}$ = -152.4 (*c* 2, CH_3COCH_3). ^{1}H NMR

($CHCl_3$, 300 MHz) δ 2.22 (s, 3H), 5.90 (s, 1H), 7.31-7.50 (m, 5H), 8.80 (bs, 1H); ^{13}C NMR ($CHCl_3$, 75 MHz) δ 20.5, 74.1, 127.55, 128.50, 128.74, 133.11, 170.6, 173.4 (Fig. 10).

General procedure for the preparation of Mosher esters.

3-(Trimethylsilyl)-3,4-pentadien-2-yl (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate (10a^{S}). In a 25 mL round bottom flask dried at 150 ^{o}C and cooled under N_2, **6a** (0.062 g, 0.40 mmol) is added with 4-(dimethylamino)pyridine (DMAP) (0.10 g, 0.80 mmol) in 4.0 mL of THF at room temperature. With a constant stirring (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (Mosher's acid chloride)[6] (0.126 g, 0.50 mmol) was added *via* syringe dropwise at the same temperature for 10 h. Water (ca. 5 mL) is added and the layers are separated. The aqueous layer is washed with dichloromethane (3 X ca. 5 mL) and the organic layers combined and concentrated. Hexane is added and the solution was eluted through an alumina gel chromatographic column to afford **10a^{S}** (0.132g, 0.35 mmol, 70%). ^1H NMR ($CDCl_3$, 300 MHz) δ 0.13 (s, 9H), 1.5 (d, 3H), 3.61 (q, 3H), 4.35 (d, 1H), 4.5 (d, 1H), 5.6 (q, *J* = 6 Hz, 1H), 7.3-7.6 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -0.9, 20.9, 55.5, 72.4, 84.2 (q, *J* = 27.4 Hz), 97.1, 126.8 (q, *J* = 288.8 Hz), 127.2, 128.4, 130.5, 132.4, 165.8, 209.5. This was determined from the analysis, by ^1H NMR of the O**CH$_3$** with δ 3.61 and 3.55 in 50:50 ratio for **10a** from (±)-(**6a**) and 97:3 from **6a** (Fig. 11). This was confirmed by analysis of the ^{13}C NMR spectrum of **10a** for C-2 in CH_3**C**H(OMosher)C(TMS)=C=CH_2 with signals at δ 72.0 and 71.6 ppm in a 50:50 ratio and 3:97 for **10a^{S}**.

3-(Trimethylsilyl)-1,2-heptadien-4-yl (*R*)-α-methoxy-α-(trifluoromethyl)-phenylacetate (10b^{R}). 80% yield, ^1H NMR ($CDCl_3$, 300 MHz) δ 0.08 (s, 9H), 0.75 (t, 3H), 1.25 (m, 2H), 1.70 (m, 2H), 3.56 (q, 3H), 4.5 (d, 1H), 4.6 (d, 1H), 5.4 (dd, *J* = 5.1, 8.3 Hz, 1H), 7.3-7.4 (m, 3H), 7.6-7.7 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.2, 13.5, 18.5, 37.2, 55.4, 71.7, 75.7, 84.4 (q, *J* = 27.5 Hz), 96.2, 123.4 (q, *J* = 288.6 Hz), 127.5, 128.9, 129.4, 165.9, 210.0. The % ee was determined from the analysis by ^{13}C NMR, methylene carbons at C-6 (CH_3**C**H$_2$$CH_2$CH(OMosher)C(TMS)=C=$CH_2$) with δ 18.8 and 18.5 a peak area ratio of 50:50 for **10b** from (±)-(**6b**), and 1:99 from **6b**, and 99:1 from **6b'** (Fig. 12). This was confirmed by analysis of C-1 (PrCH(OMosher)C(TMS)=C=**CH$_2$**) with δ 71.7 and 71.5 ppm in a peak area ratio of 50:50 for **10b** from (±)-(**6b**), and 99:1 for **10b^{R}**.

2-Methyl-4-(trimethylsilyl)-4,5-hexadien-3-yl (*R*)-α-methoxy-α-(trifluoro-methyl)phenylacetate (10c^{R}). 73% yield, ^1H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9H), 0.9 (dd, 6H), 2.0 (m, 1H), 3.57 (q, 3H), 4.2 (dd, 1H), 4.4 (dd, 1H), 5.1 (d, 1H), 7.4 (m, 3H), 7.5-7.6(m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.1, 19.5, 32.7, 38.7, 71.3, 75.3, 84.5 (q, *J* = 27.7 Hz), 95.5, 124.2 (q, *J* = 288.1 Hz), 127.6, 128. 8, 129.5, 165.6, 210.2. The % ee was determined from the analysis by ^{13}C NMR, of C-6 ($CH_3CH(CH_3)$CH(OMosher)**C**(TMS)=C=**CH$_2$**) with δ 71.5 and 71.3 in a peak ratio of

50:50 for **10c** from (±)-(**6c**), and 1:99 from **6c** (Fig. 13). This was confirmed by analysis of C-4 ($CH_3CH(CH_3)CH(OMosher)\mathbf{C}(TMS)=C=CH_2$) with 95.6 and 95.5 in a peak area ratio of 50:50 for **10c** from (±)-(**6c**), and 1:99 from **6c** for **10c**$^{\boldsymbol{R}}$.

2,2-Dimethyl-4-(trimethylsilyl)-4,5-hexadien-3-yl (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate (10d$^{\boldsymbol{R}}$). 82% yield, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.13 (s, 9H), 0.9 (s, 9H), 3.58 (q, 3H), 4.46 (d, 1H), 4.55 (d, 1H), 4.95 (s, 1H), 7.4-7.6 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -0.4, 25.9, 36.5, 55.3, 67.8, 71.4, 81.1, 84.1 (q, J = 27.8 Hz), 94.5, 123.4 (q, J = 288.4 Hz), 127.5, 128.1, 129.4, 132.5, 165.7, 211.0. The % ee was determined from the analysis by ^{1}H NMR, of the C-3 methine proton ($(CH_3)_3C\mathbf{C}\mathbf{H}(OMosher)C(TMS)=C=CH_2$) with δ 4.95 and 4.90 in a 50:50 peak area ratio for **10d** from (±)-(**6d**) and 99:1 from **6d** (Fig. 14). This was confirmed by analysis of ^{13}C NMR, of C-6 ($(CH_3)_3CCH(OMosher)C(TMS)=\mathbf{C}=CH_2$) with δ 211.0 and 210.8 ppm in a 50:50 peak area ratio for **10d** from (±)-(**6d**) and 99:1 for **10d**$^{\boldsymbol{R}}$.

1-Phenyl-2-(trimethylsilyl)-2,3-butadien-1-yl (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate (10e$^{\boldsymbol{S}}$). 78% yield, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.01 (s, 9H), 3.55 (bs, 3H), 4.6 (d, 2H), 6.5 (bs, 1H), 7.2-7.4 (m, 6H), 7.45-7.55 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.3, 55.5, 72.8, 77.2, 84.6 (q, J = 27.7 Hz), 96.6, 123.3 (q, J = 288.4 Hz), 127.5, 127.5, 128.1, 128.2, 128.5, 128.8, 130.5, 132.9, 138.3, 165.6, 209.5. The % ee was determined from the analysis by ^{13}C NMR, of C-1 ((Ph)$\mathbf{C}\mathbf{H}$(OMosher)C(TMS)=C=CH_2) with δ 72.8 and 72.4 ppm in a peak area ratio of 50:50 for **10e** from (±)-(**6e**), and 99:1 from **6e** (Fig. 15). This was confirmed by analysis of C-3 (PhCH(OMosher)C(TMS)=$\mathbf{C}$=CH_2) with δ 209.5 and 209.0 ppm in a peak area ratio of 50:50 for **10e** from (±)-(**6e**), and 99:1 for **10e**$^{\boldsymbol{S}}$.

(*E*)-3-(Trimethylsilyl)-1,2,5-heptatrien-4-yl (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate (10f$^{\boldsymbol{S}}$). 75% yield, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.2 (s, 9H), 1.81 (dd, J = 6.4, 1.5 Hz, 3H), 3.6 (bs, 3H), 4.7 (d, 2H), 5.6 (ddq, J = 15.2, 7.4, 1.4 Hz, 1H), 5.8 (dq, J = 15.3, 6.4 Hz, 1H), 5.9, (d, J = 7.2 Hz, 1H), 7.2-7.4 (m, 3H), 7.5-7.6 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.1, 20.0, 55.4, 69.8, 74.1, 85.5, (q, J = 28.2 Hz), 95.6, 123.3 (q, J = 288.6 Hz), 127.3, 128.5, 128.6, 129.5, 130.6, 130.8, 165.7, 213.2. The % ee was determined from the analysis by ^{13}C NMR, of the ester C=O signal with δ 165.69 and 165.61 ppm in a peak area ratio of 50:50 for **10f** from (±)-(**6f**), and <1.5:98.5 from **6f** (Fig. 16). This was confirmed by analysis of C-5 (MeHC=$\mathbf{C}\mathbf{H}$CH(OMosher)-C(TMS)=C=CH_2) with δ 130.8 and 130.5 ppm in a peak area ratio of 50:50 for **10f** from (±)-(**6f**), and 99:1 for **10f**$^{\boldsymbol{S}}$. Unfortunately, this clearer spectral comparison was lost in a hurricane-related laboratory fire (September 18, 2004).

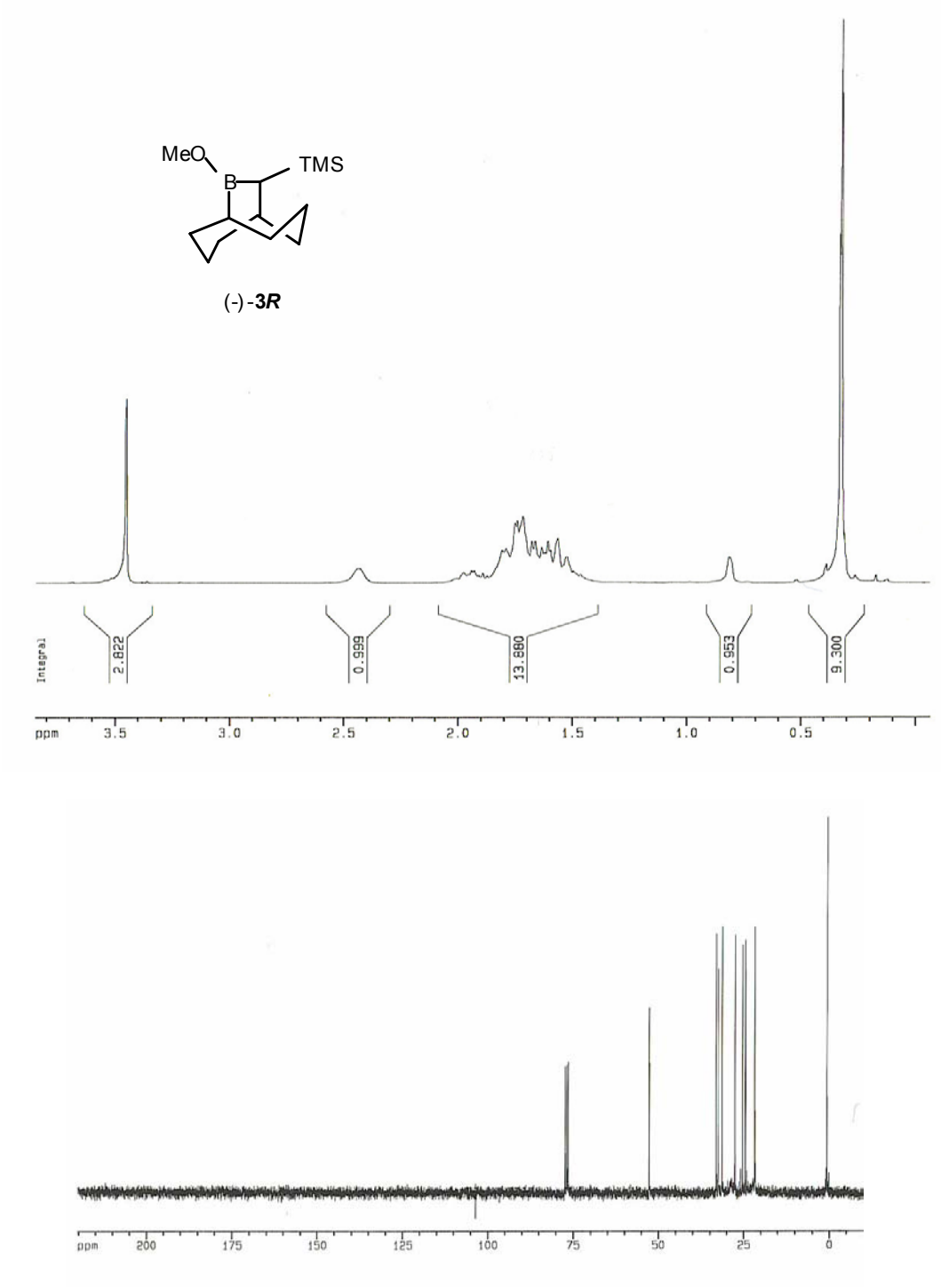


Figure 1. ^{1}H and ^{13}C NMR Spectra of *B*-Methoxy-10-trimethylsilyl-9-borabicyclo[3.3.2]decane (3)

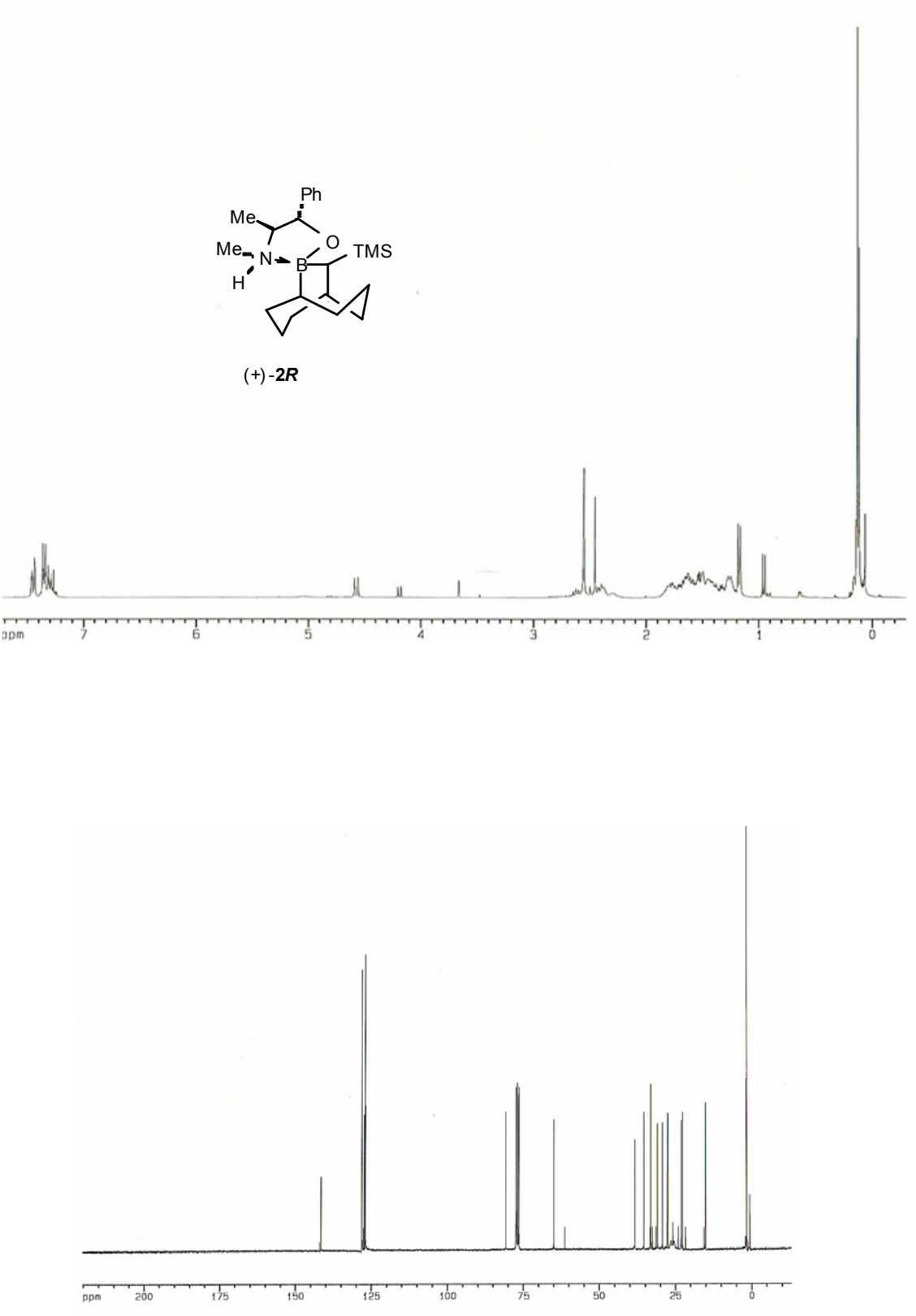


Figure 2. ^{1}H and ^{13}C NMR Spectra of (+)-(10*R*)-*B*-(1*S*,2*S*)-Pseudoephedrinyl-10-trimethylsilyl-9-borabicyclo[3.3.2]decane ((+)-2*R*)

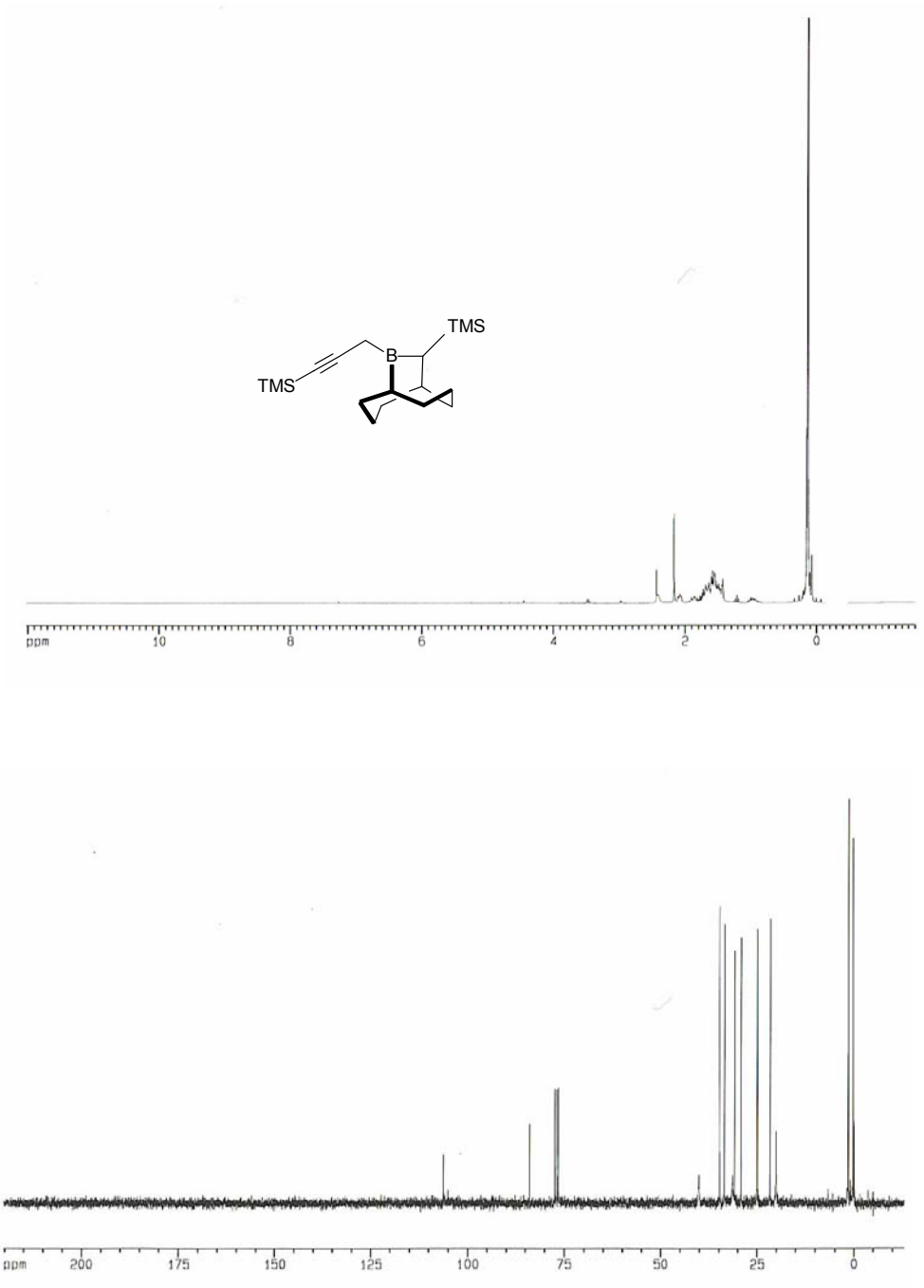


Figure 3. ^{1}H and ^{13}C NMR Spectra of (-)-(10*R*)-*B*-[γ-(Trimethylsilyl)propargyl]-10-TMS-9-borabicyclo[3.3.2]decane ((-)-1*R*)

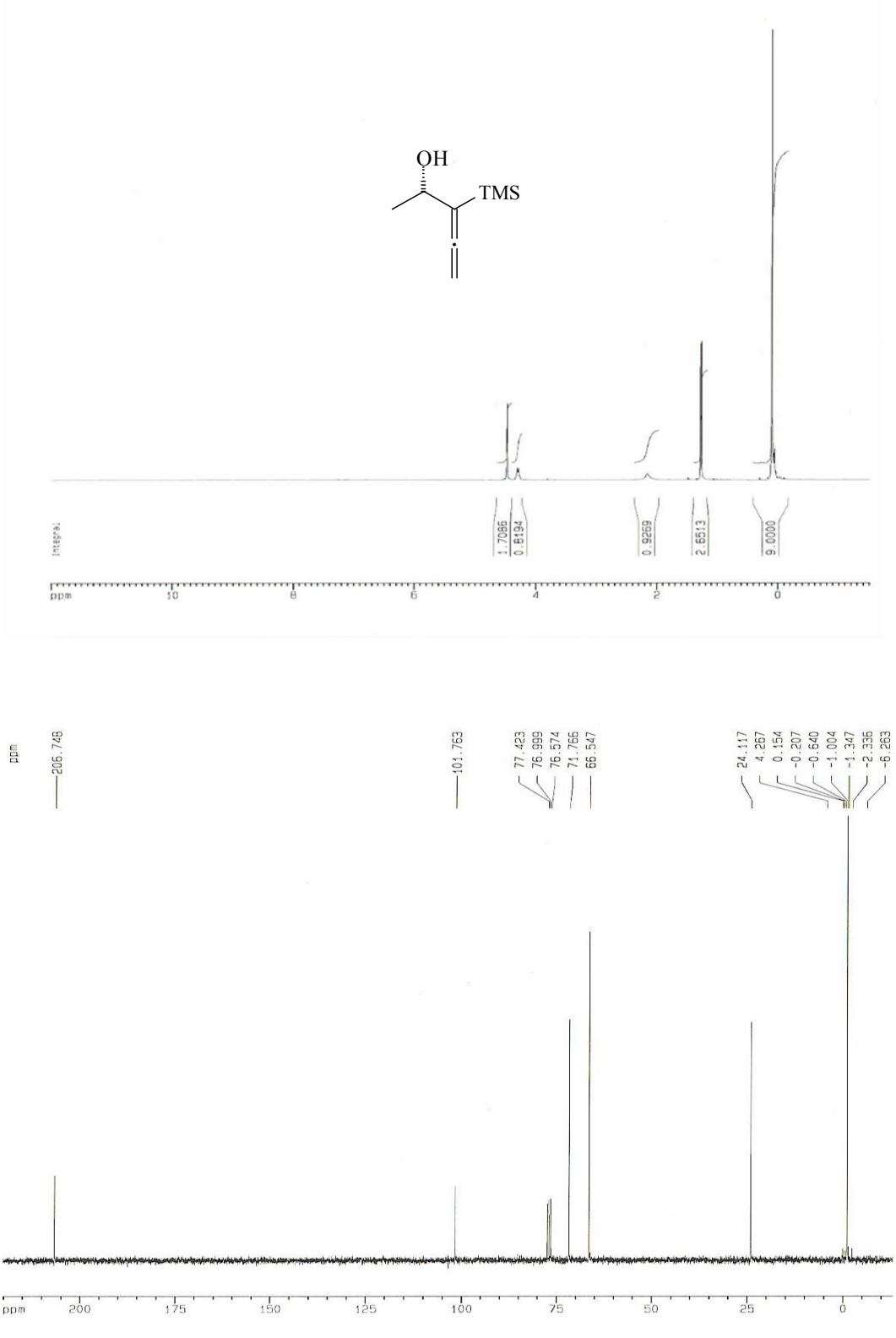


Figure 4. ^{1}H and ^{13}C NMR Spectra of (-)-(2*S*)-3-(Trimethylsilyl)-3,4-pentadien-2-ol (6a).

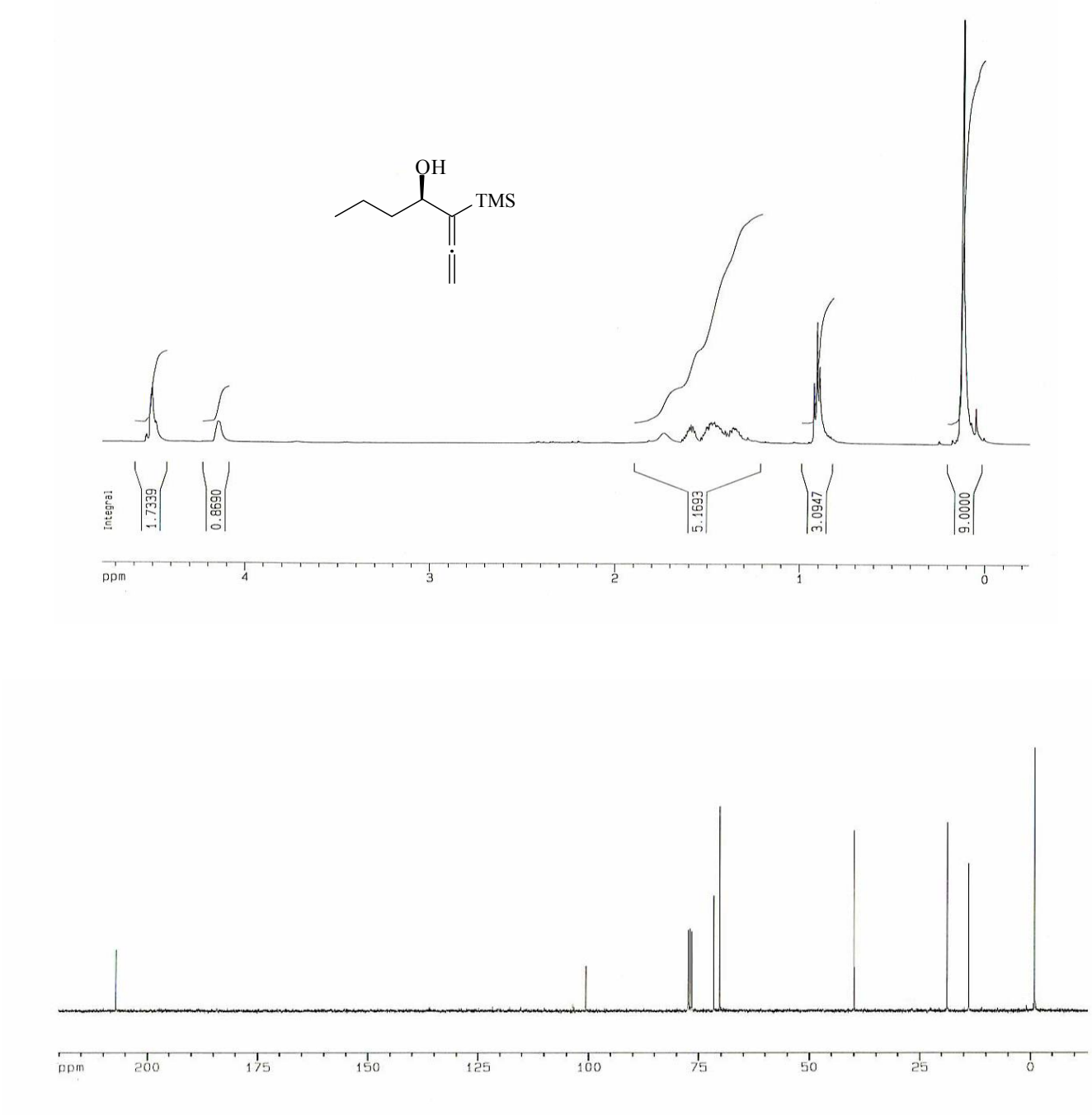


Figure 5. ^{1}H and ^{13}C NMR Spectra of (-)-(4*R*)-3-(Trimethylsilyl)-1,2-heptadien-4-ol (6b).

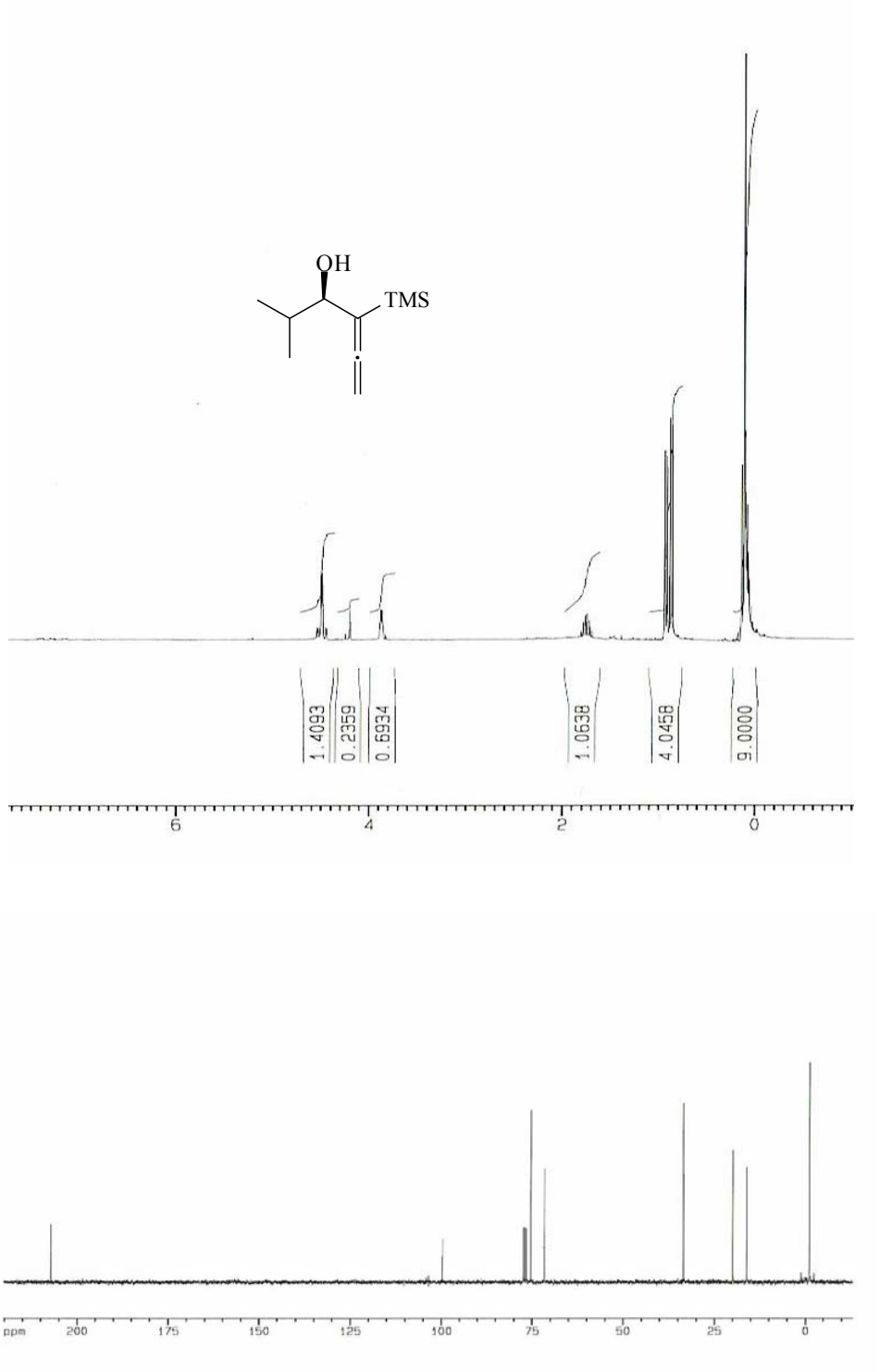


Figure 6. ^{1}H and ^{13}C NMR Spectra of (-)-(3*R*)-2-Methyl-4-(trimethylsilyl)-4,5-hexadien-3-ol (6c).

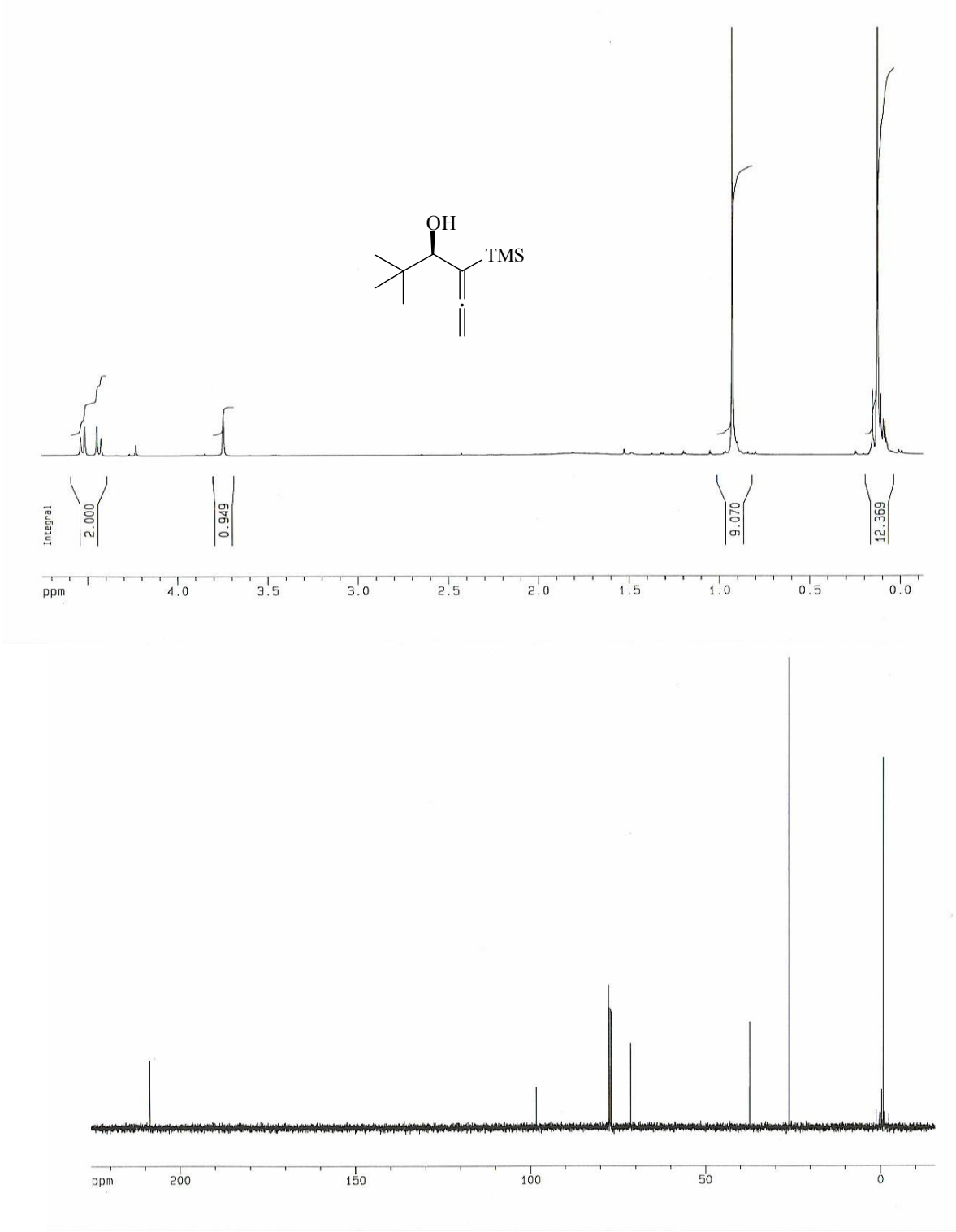


Figure 7. ^{1}H and ^{13}C NMR Spectra of (+)-(3*R*)-2,2-Dimethyl-4-(trimethylsilyl)-4,5-hexadien-3-ol (6d).

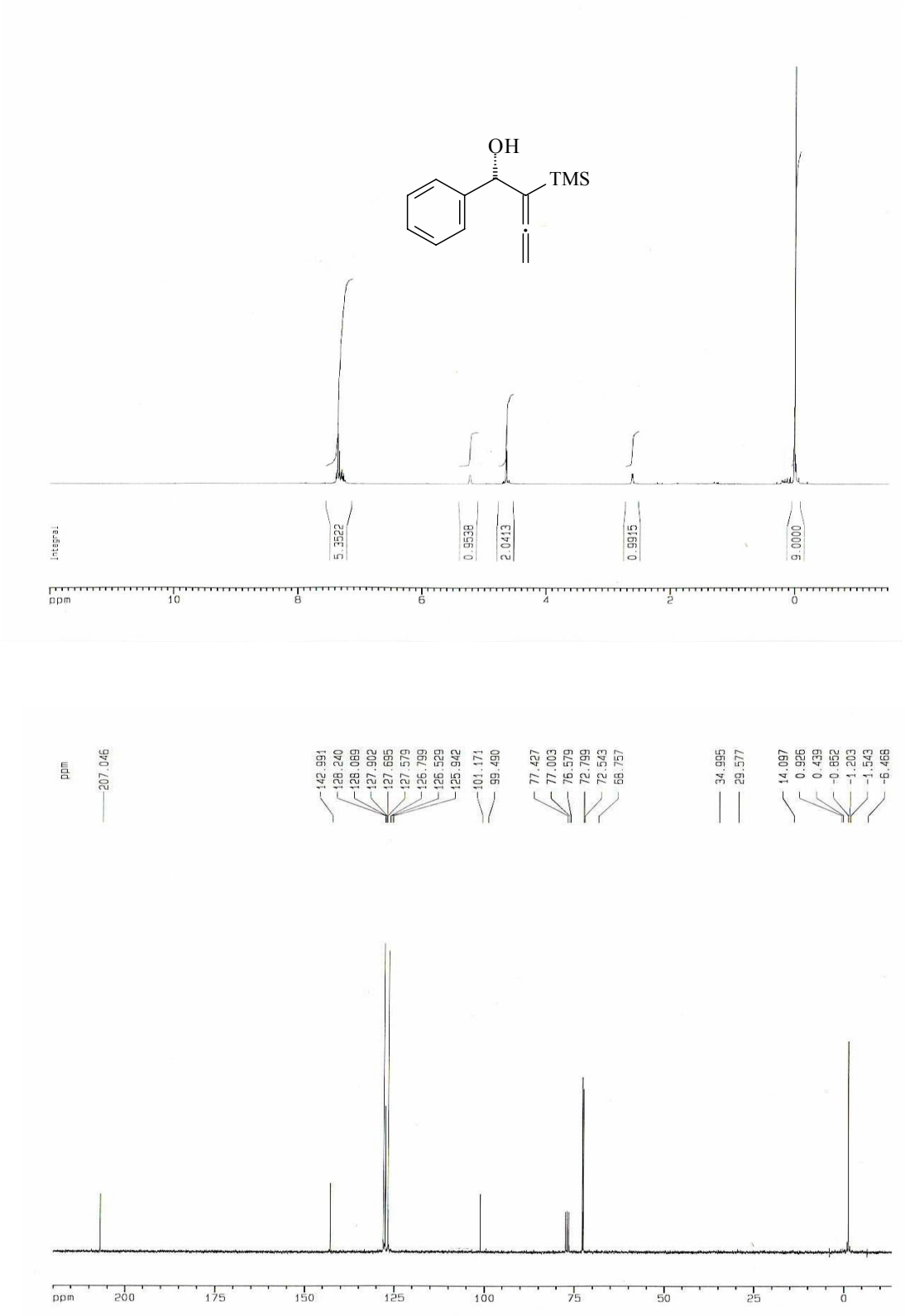


Figure 8. ^{1}H and ^{13}C NMR Spectra of (-)-(1*S*)-1-Phenyl-2-(trimethylsilyl)-2,3-butadien-1-ol (6e).

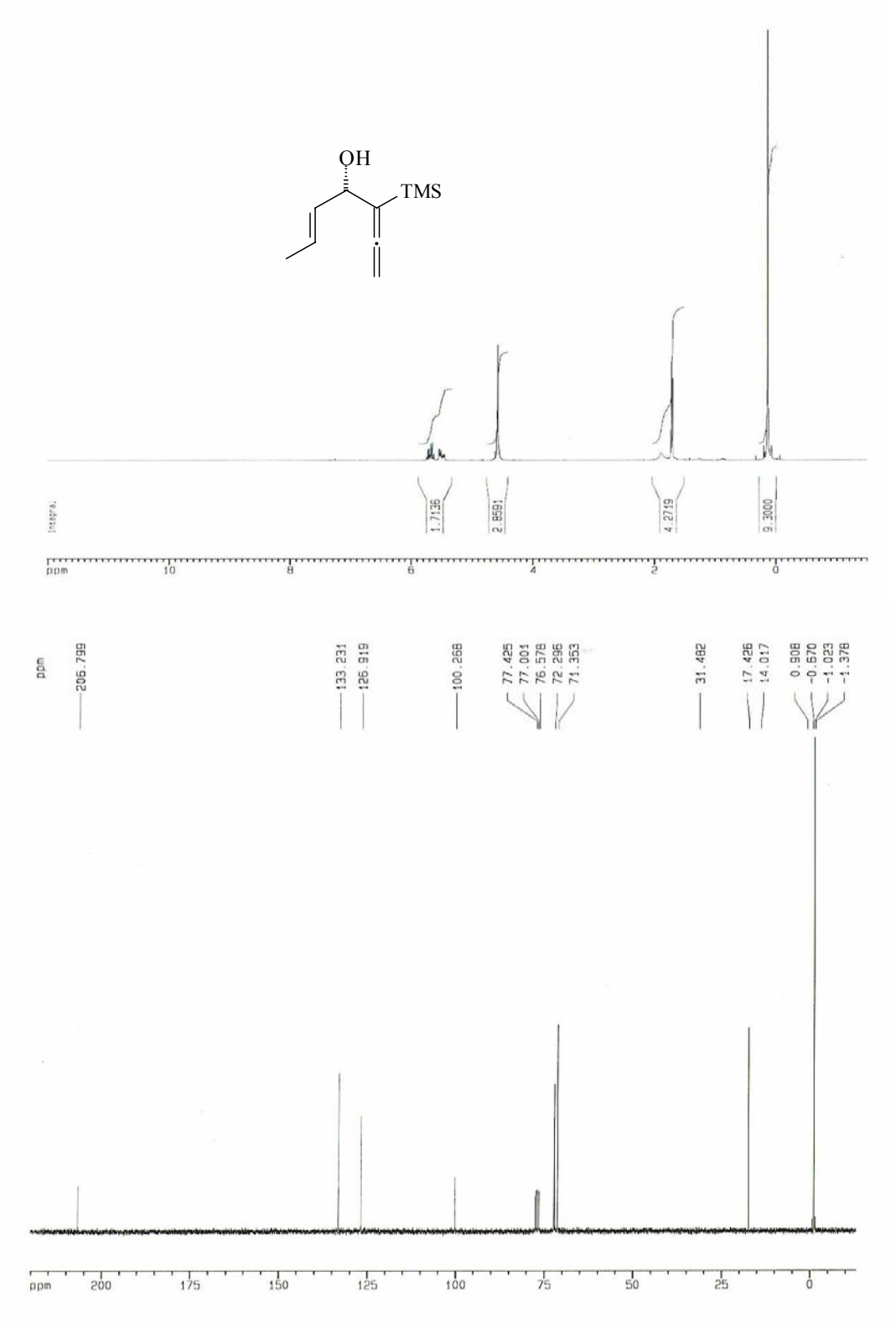


Figure 9. ^{1}H and ^{13}C NMR Spectra of (+)-(4*S*)-(*E*)-3-(Trimethylsilyl)-1,2,5-heptatrien-4-ol (6f).

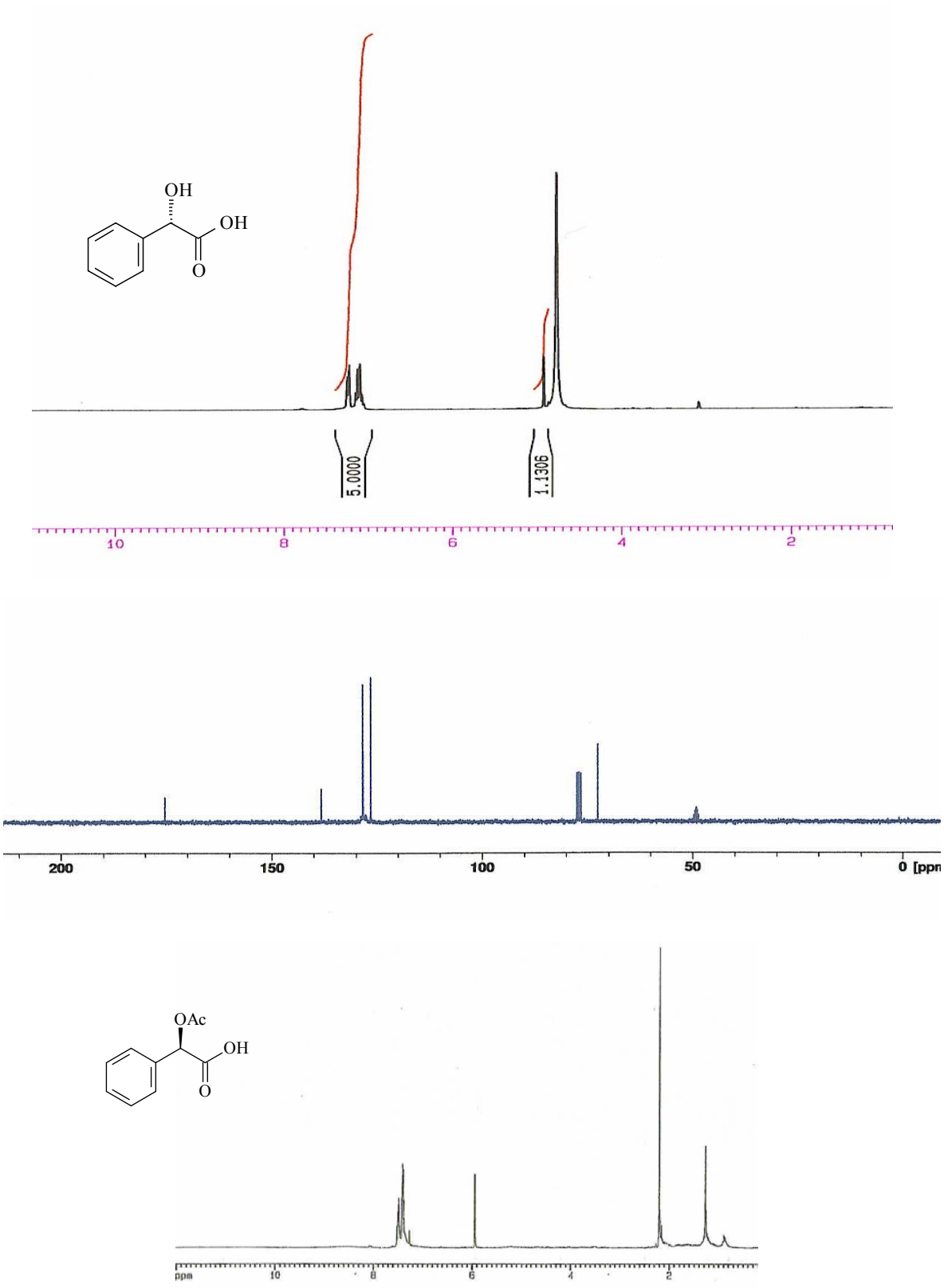


Figure 10. ^{1}H and ^{13}C NMR Spectra of *S*-(+)-Mandelic acid (9) (CD_3OD) (above). ^{1}H NMR Spectrum of *R*-(-)-*O*-Acetylmandelic acid (9') ($CDCl_3$) (below).

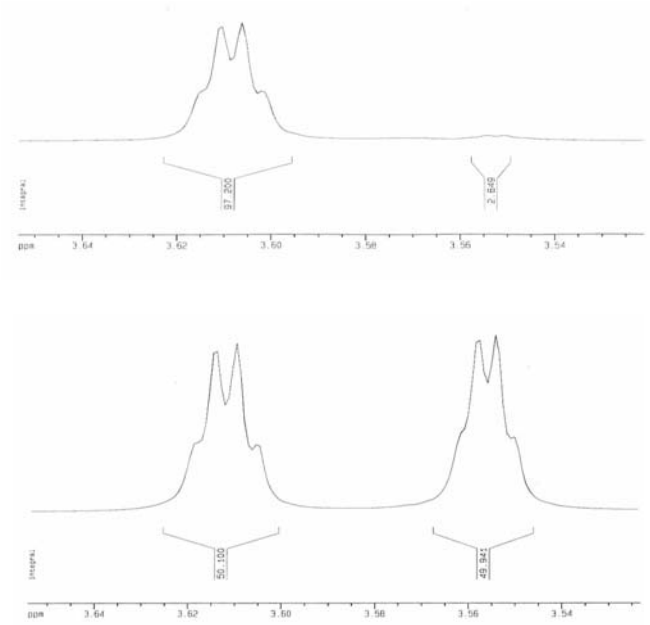


Figure 11. ^{1}H NMR of OMe Region for 3-(Trimethylsilyl)-3,4-pentadien-2-yl (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate (10a^{S}).

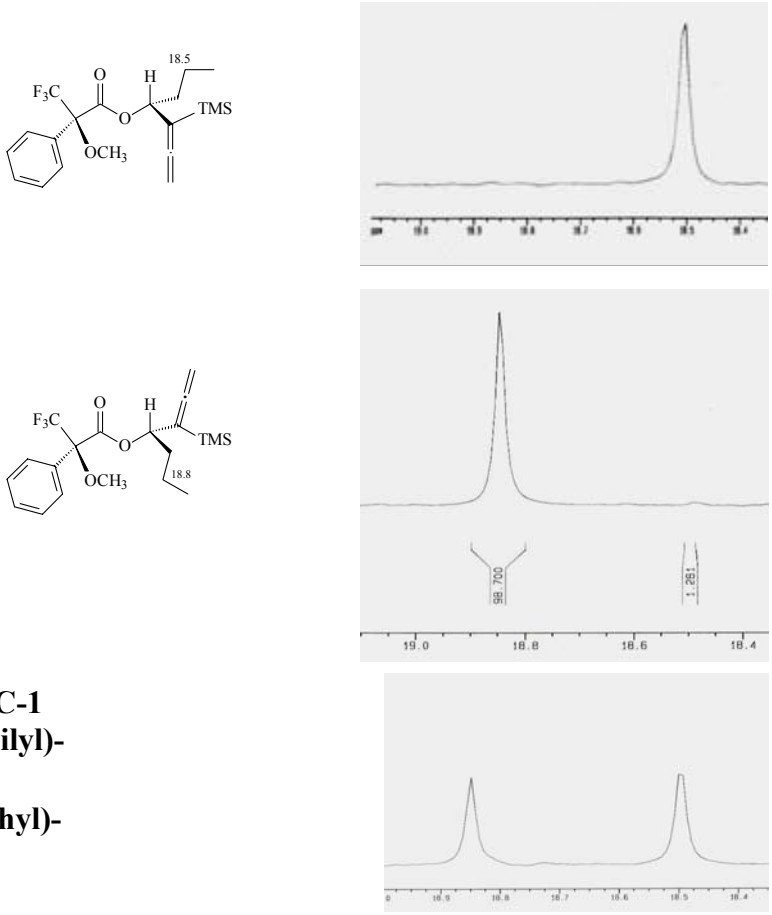


Figure 12. ^{13}C NMR of C-1 Region for 3-(Trimethylsilyl)-1,2-heptadien-4-yl (*R*)-α-methoxy-α-(trifluoromethyl)-phenylacetate (10b^{R}).

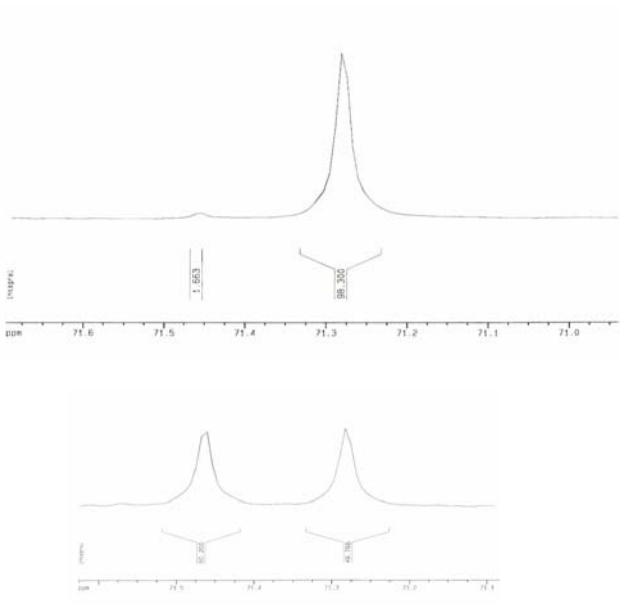


Figure 13. ^{13}C NMR of C-6 Region for 2-Methyl-4-(trimethylsilyl)-4,5-hexadien-3-yl (*R*)-α-methoxy-α-(trifluoro-methyl)phenylacetate (10c^{R}).

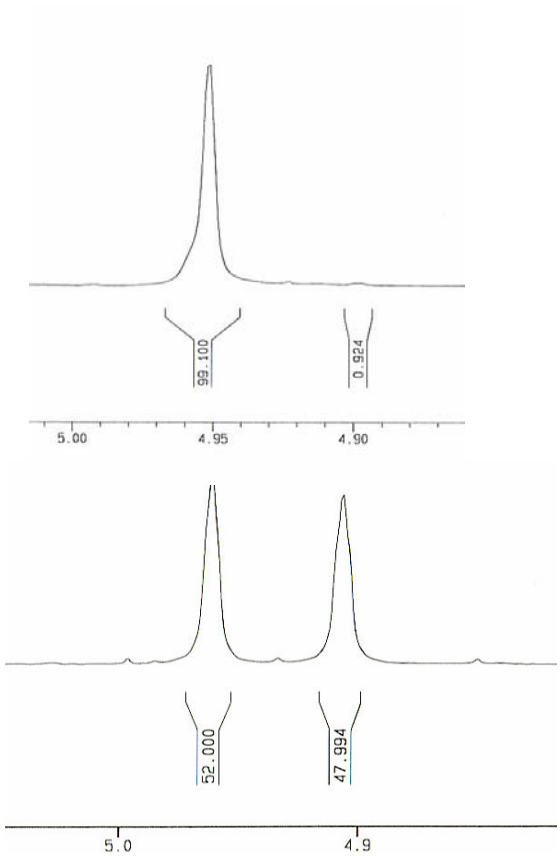


Figure 14. ^{1}H NMR of C-3 Methine Region for 2,2-Dimethyl-4-(trimethylsilyl)-4,5-hexadien-3-yl (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate (10d^{R}).

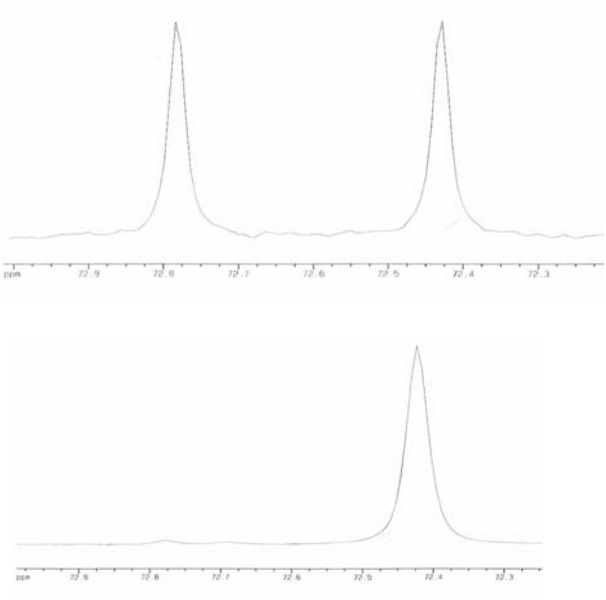


Figure 15. ^{13}C NMR of C-1 Region for 1-Phenyl-2-(trimethylsilyl)-2,3-butadien-1-yl (*R*)-α-methoxy-α-(trifluoro-methyl)phenylacetate (10e^{S}).

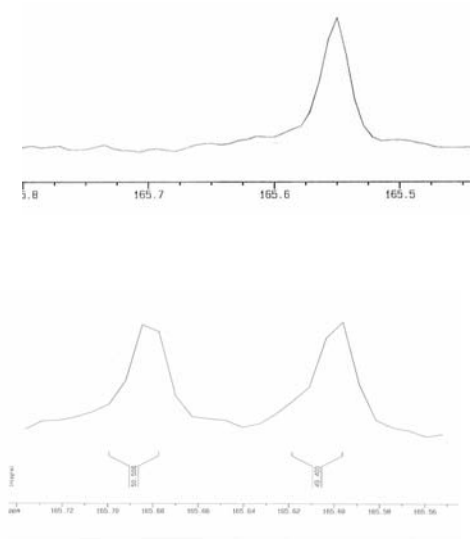


Figure 16. ^{13}C NMR of C=O Region for (*E*)-3-(Trimethylsilyl)-1,2,5-heptatrien-4-yl (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate (10f^{S}).

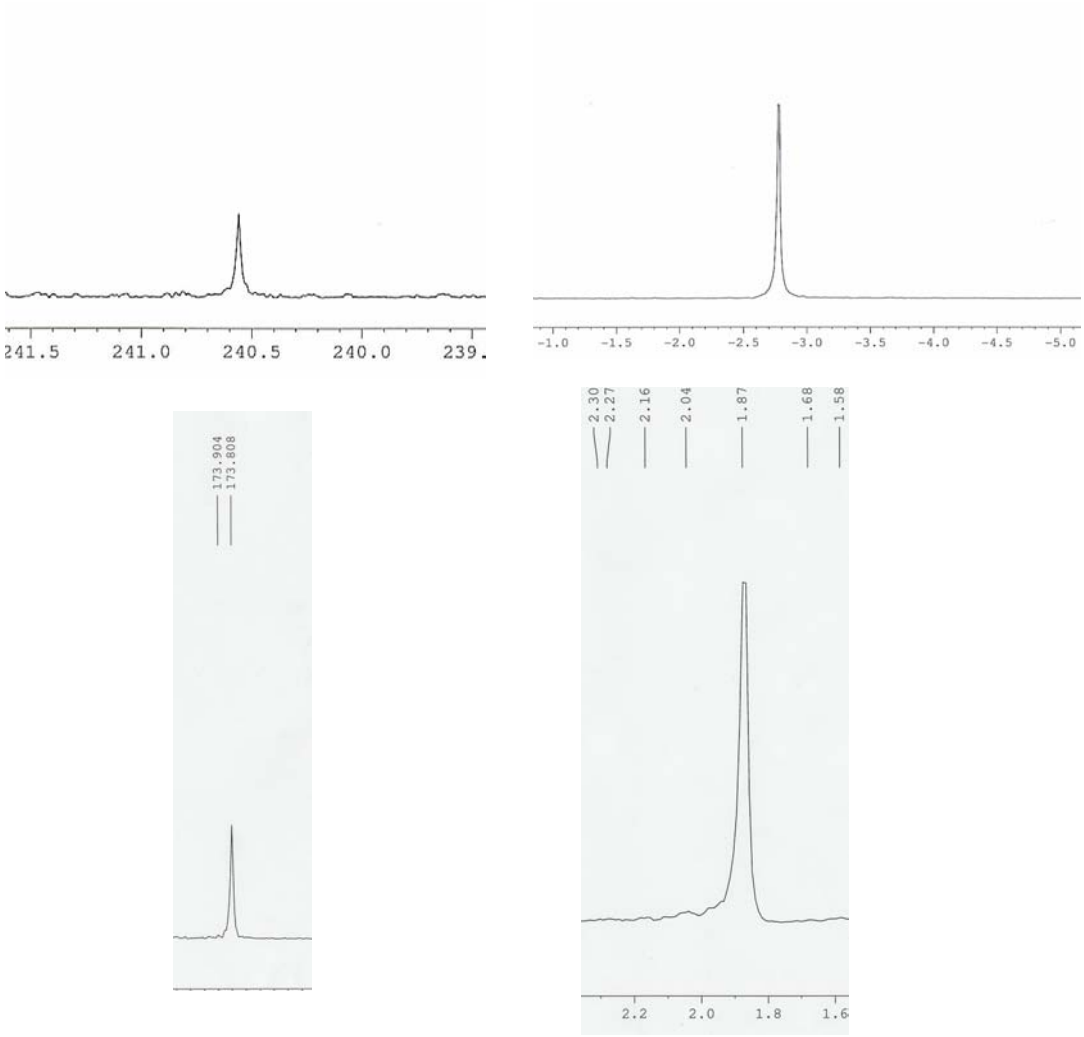


Figure 17. (Above): ^{13}C NMR of TMSC=O (left) and TMS (right) for 7. (Below): ^{13}C NMR of TMSOC=O (left) and TMS (right) for 8.

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