Supplementary Material

Non-Racemic Homopropargylic Alcohols via Asymmetric Allenylboration with the Robust and Versatile 10-TMS-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 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. ^1H (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 ^1H and ^{13}C NMR, respectively) and of C_6D_6 (δ 7.15 and 128.0 ppm for ^1H and ^{13}C NMR, respectively) as the internal standard. Standard COSY, HETCOR and DEPT experiments were performed to establish NMR assignments for all of the compounds discussed in this work. 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). Gas Chromatographic analyzes were performed with a Perkin-Elmer 8320 instrument or Perkin-Elmer Autosystem XL capillary column using 30 m x 0.23 mm. I.D. 20% SE-30 vitreous silica open tubular columns and for % ee determinations, a Supelcowax-10 fused silica capillary column (30 m x 0.25 mm x 0.25 μm). Optical rotations were measured employing a Perkin-Elmer 243B polarimeter.

B-Methoxy-10-trimethylsilyl-9-borabicyclo[3.3.2]decane (3). 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 **3** (97%, bp 80 °C, 0.10 mm Hg, >98% purity by $^1\text{H}/^{13}\text{C}$ NMR): ^1H 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 $\text{C}_{13}\text{H}_{27}\text{BOSi}$ 238.1924, found 238.1929.

9-(1*S*,2*S*-Pseudoephedriny)-(10*R*)-(trimethylsilyl)-9-borabicyclo[3.3.2]decane ((+)-4*R*). To a solution of 1*S*,2*S*-pseudoephedrine (8.28 g, 50 mmol) in acetonitrile (110 mL) was added **3** (23.85 g, 100 mmol) dropwise. The reaction mixture was refluxed for 6 h and slowly cooled to room temperature resulting in large crystals. The supernatant was decanted via cannula and the crystals were dried *in vacuo* to give 14.1 g of (+)-**4*R*** (38% yield,

Figure 1. Pictures of the X-ray structure and crystalline (+)-**4*R***.

mp 106-109 °C, >98% purity by ^{13}C NMR): $[\alpha]_{\text{D}}^{28} = +54.2^\circ$ (c = 4.5, CDCl_3) ^1H 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 $\text{C}_{22}\text{H}_{38}\text{BNOSi}$ 371.2816, found 371.2825; Crystal data: $\text{C}_{22}\text{H}_{38}\text{BNOSi}$, $M = 371.44$; orthorhombic (space group P212121 (#19)); $a = 7.259(3)$ Å, $b = 10.343(2)$ Å; $V = 2264.3(9)$ Å³; D_{calc} 1.090 g/cm³; $A = 4$ (Figure 1).

9-(1*R*,2*R*-Pseudoephedriny)-(10*S*)-(trimethylsilyl)-9-borabicyclo[3.3.2]decane ((-)-4*S*)). The above supernatant was 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 dried in vacuo to give 10.4 g of (-)-4*S* (28% yield, >98% purity by ^{13}C NMR): $[\alpha]_{\text{D}}^{28} = -54.4^\circ$ (c = 4.3, CDCl_3).

B-Chloro-10-trimethylsilyl-9-borabicyclo[3.3.2]decane (8).¹ A BCl_3 solution (20 mmol, 1 M in hexanes) was added dropwise to a well-stirred solution of **2** (8.2 g, 34.5 mmol) in hexanes (25 mL) at 0 °C. After stirring for 30 minutes at room temperature, the solvent was removed *in vacuo* and the residue was distilled to give 7.9 g of **8** (95 %, bp 88-90 °C, 0.20 mm Hg, colorless liquid, >98% purity by $^{13}\text{C}/^{11}\text{B}$ NMR): ^1H NMR (300 MHz, C_6D_6) δ 2.22 (m, 1 H), 2.03 (m, 1 H), 1.30-1.77 (m, 13H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 52.5, 33.6, 33.2, 32.0, 29.2, 28.0, 25.8, 24.9, 22.5, 22.3, 1.1; ^{11}B NMR (96 MHz, C_6D_6) δ 54.9.

B-Bromo-10-trimethylsilyl-9-borabicyclo[3.3.2]decane (9).¹ The reaction was carried out in the same manner as described for the preparation of **26**, except that BBr_3 solution (6.0 mmol, 1 M in hexanes) was added dropwise to a well-stirred solution of **2** (2.36 g, 9.9 mmol) in hexanes (15 mL) at 0 °C. Distillation gave 2.33 g of **9** (82 %, bp 86-88 °C, 0.15 mm Hg, colorless liquid, >98% purity by $^{13}\text{C}/^{11}\text{B}$ NMR): ^1H NMR (300 MHz, C_6D_6) δ 2.31 (m, 1 H), 2.23 (m, 1 H), 1.24-1.76 (m, 13 H), 0.20 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) δ 43.2, 38.2, 35.0, 33.5, 30.9, 28.5, 24.6, 24.5, 21.6, 1.3; ^{11}B NMR (96 MHz, C_6D_6) δ 77.1.

Tributylallenyltin (10). Following the literature procedure,² allenylmagnesium bromide was obtained by dropwise addition (2 h) of a solution of propargyl bromide (112.5 mmol, 12.5 mL (80 % in toluene)) in diethyl ether (50 mL) to magnesium turnings (337.5 mmol, 8.25 g) amalgamated with mercury (II) chloride (0.6 mmol, 0.14 g). The solution was decanted from the residue and a solution of tributyltin chloride (37.5 mmol, 12.15 g) in diethyl ether (25 mL) was slowly added (1.5 h) to it. After hydrolysis with ice, the ethereal layer was separated and dried over Na_2SO_4 . Most of the solvent was distilled off and methanol (15 mL) was added. The solution was refluxed for 15 min to bring about the isomerization of the product to the allenic form. Distillation under reduced pressure gave 6.2 g of **10** (bp 94-96 °C, 0.15 mm Hg). Purification by column chromatography on silica gel (hexanes-acetone, 20:1) afforded pure **10** (>98% purity by ^{13}C NMR) as a colorless liquid (4.0 g, 32 %): ^1H NMR (300 MHz, C_6D_6) δ 5.04 (t, $J = 7.1$ Hz, 2 H), 4.20 (d, $J = 7.1$ Hz, 3 H), 1.50-1.55 (m, 2 H), 1.28-1.35 (m, 2 H), 0.92-0.98 (m, 2 H), 0.89 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 210.7, 74.2 (t, $J = 153$ Hz), 63.6, 29.3, 27.6, 13.9, 10.6 (t, $J = 171$ Hz); IR (neat) 1930 (C=C=C) cm^{-1} .

((±)-B-Allenyl-10-trimethylsilyl-9-borabicyclo[3.3.2]decane ((±)-1).

Method A. Freshly prepared allenylmagnesium bromide in ethyl ether (40 mmol, 1 M) was added dropwise to a well-stirred solution of **2** (40 mmol, 9.25 g) in ethyl ether (80 mL) at 0 °C. Following the addition, the reaction mixture was vigorously stirred for 30 min at 0 °C and then stirred at room temperature for 2 h. Solvents were evaporated under vacuum and the residue was washed with hexane (6 x 30 mL). These washings were filtered through a celite pad *via* double ended needle. The filtrate was evaporated and the residue was distilled to give 8.85 g of ((±)-1 (90 %, bp 88-91 °C, 0.10 mm Hg, >97% purity by ^{13}C NMR (Figs. 2,3): ^1H NMR (300 MHz, CDCl_3) δ 5.53 (t, $J = 6.5$ Hz, 1H), 4.57 (d, $J = 6.5$ Hz, 2H), 2.41 (br s, 1 H), 2.11 (m, 1 H), 0.90-1.92 (m, 13 H), 0.12 (s, 9 H) (Figure 2); ^{13}C NMR (75 MHz, CDCl_3) δ 218.4, 91.0, 68.5, 39.6, 34.9, 33.9, 30.9, 29.4, 28.7, 25.8, 25.0, 21.7, 1.6 (Figure 3); ^{11}B NMR (96 MHz, CDCl_3) δ 75.0 IR (neat) 2943, 2911, 2852, 1927(C=C=C), 1243, 837 cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{27}\text{BSi}$ (M^+) 246.1975, found 246.1963.

Method B. To a stirred solution of **9** (4.0 mmol, 1.16 g) in CH_2Cl_2 (10 mL) at room temperature was added tributylallenyltin (4.0 mmol, 1.32 g). The reaction mixture was stirred at room temperature for 28 h. An aliquot was analyzed by ^{11}B and ^{13}C NMR which indicated the formation of ((±)-1. ^{13}C NMR (75 MHz, C_6D_6) δ 219.0, 91.9, 68.7, 39.8, 35.5, 34.3, 31.3, 29.9, 29.2, 26.3, 25.4, 22.1, 1.8; ^{11}B NMR (96 MHz, C_6D_6) δ 74.9.

(10*R*)-*B*-Allenyl-10-trimethylsilyl-9-borabicyclo[3.3.2]decane (1*R*) and 1*S*.

To a solution of (+)-**4*R*** (20 mmol, 7.42 g) in EE (100 mL) at -78 °C was added dropwise, a solution of freshly prepared allenylmagnesium bromide (20.0 mmol, 1.0 M solution in EE). After stirring for 15 min, the cold bath was removed and the reaction mixture was allowed to reach room temperature and stirred for 1 h. Solvents were stripped off and the residue was washed with hexane (5 x 30 mL). These washings were filtered through a celite pad *via* a double ended needle. The solvents were removed, and the residue gave, after distillation, 4.57 g of **1*R*** (93 %, bp 88-90 °C, 0.10 mm Hg, >97% purity by ¹³C NMR). The spectroscopic data were identical to that of (±)-**1**.

1*S*: The reaction was carried out in the same way as described for the preparation of **1*R*** except that (-)-**4*S*** was used. The product **1*S*** was obtained in 90 % yield (bp 88-91 °C, 0.10 mm Hg, >97% purity by ¹³C NMR). The spectroscopic data were identical to that of (±)-**1**.

General procedure for the recovery of pseudoephedrine from the precipitated magnesium salts. The salts from several runs were combined, weighed and dissolved in 1.0 M HCl (> 2 equiv). The volume was doubled with EtOAc and 1.0 N NaOH was slowly added until the aqueous phase was basic. The layers were separated and the aqueous phase was washed with EtOAc (2 X equal vol). The organic phases were combined, dried (Na₂SO₄), and concentrated *in vacuo* to give pseudoephedrine (90%, >98% purity by ¹³C NMR).

General procedure for the allenylation of aldehydes with reagent 1*R*. The allenylation of *n*-PrCHO with **1*R*** is representative. A solution of **1*R*** (1.23 g, 5.0 mmol) in EE (25 mL) was cooled to -78 °C and a solution of *n*-butyraldehyde (0.46 mL, 5.0 mmol) in EE (5 mL) at -78 °C was added to it slowly *via* a double ended needle. After 3 h at -78 °C, the solvents were removed under vacuum to yield essentially pure borinate **5a**. The (1*S*,2*S*)-(+)-pseudoephedrine (0.83 g, 5.0 mmol.) and acetonitrile (15 mL) were added, and the mixture was refluxed for 4 h. The crystals were separated and washed with acetonitrile (2 x 3 mL) to afford 1.55 g (84%) of (+)-**4*R***. The residue was distilled to give 0.45g of (-)-**(*S*)-5-hexyn-3-ol (6a)** (82%) bp 27-28 °C, 1.5 mm Hg, >98% GC purity (30 m x 0.23 mm. I.D. 20% SE-30 vitreous silica open tubular column, 100 °C (init), programmed at

Figure 2. ¹H NMR of **1**.

Figure 3. ¹³C NMR of **1**.

Figure 4. ¹³C NMR of **5a**.

10 °C/min), >98% ^{13}C NMR purity, $[\alpha]_{\text{D}}^{28} = -28.18$ (2.2, MeOH); ^1H NMR (300 MHz, CDCl_3) δ 3.81-3.73 (m, 1H), 2.47-1.27 (m, 8H), 0.93 (t, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 80.9, 70.7, 69.6, 38.3, 27.3, 18.8, 13.9. The intermediate borinate **5a** was analyzed by NMR. **(10R)-B-((4S)-1-Heptyn-4-oxy)-10-trimethylsilyl-9-borabicyclo[3.3.2]-decane (5a)**: (>98% purity by ^{13}C NMR) ^1H NMR (300 MHz, CDCl_3) δ 4.25 (quintet, $J = 5.9$ Hz, 1H), 2.34 (dd, $J = 4.8, 1.4$ Hz, 2H), 2.23 (br s, 1H), 1.95 (s, 1H), 1.84-1.25 (m, 17H), 0.92 (t, $J = 7.3$ Hz, 3H), 0.60 (d, $J = 2.1$ Hz, 1H), 0.06 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 81.4, 72.6, 69.7, 38.4, 33.4, 32.9, 31.3, 29.1, 27.7, 26.9, 26.0, 24.6, 22.6, 21.9, 18.6, 14.0, 0.9 (see Figure 4); ^{11}B NMR (96 MHz, CDCl_3) δ 54.4.

(-)-(R)-2-Methyl-5-hexyn-3-ol (6b): 81 % yield, bp 31-32 °C, 2.0 mm Hg [lit.³ bp 82-84 °C, 60 mm Hg], >98% GC purity, $[\alpha]_{\text{D}}^{28} = -3.45$ (1.2, MeOH); ^1H NMR (300 MHz, C_6D_6) δ 3.24 (m, 1H), 2.11-2.08 (m, 2H), 1.81 (br s, 1H, OH), 1.74 (t, $J = 2.7$ Hz, 1H), 1.65-1.58 (m, 1H), 0.83 (d, $J = 6.8$ Hz, 3H), 0.72 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 81.6, 74.6, 70.7, 32.8, 25.1, 18.9, 17.3. **(10R)-B-(2-Methyl-5-hexyn-3-oxy)-10-trimethylsilyl-9-borabicyclo[3.3.2]decane (5b)**: (>98% purity by ^{13}C NMR) ^1H NMR (300 MHz, CDCl_3) δ 4.14-4.08 (m, 1H), 2.35-1.44 (m, 19H), 0.93 (d, $J = 6.8$ Hz, 6H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 81.8, 77.6, 69.5, 33.2, 33.0, 32.6, 31.6, 29.0, 27.7, 26.0, 24.7, 24.3, 22.7, 21.9, 18.6, 17.4, 1.1; ^{11}B NMR (96 MHz, CDCl_3) δ 54.9.

(+)-(R)-2,2-Dimethyl-5-hexyn-3-ol (6c): 75 % yield, bp 76-77 °C, 59 mm Hg, >98% GC purity, [lit.³ bp 90-91 °C, 70 mm Hg]; $[\alpha]_{\text{D}}^{28} = +45.37$ (1.1, MeOH) [(S) lit.⁴ -38.28 (3.6), 93 % ee]; ^1H NMR (300 MHz, CDCl_3) δ 3.42-3.39 (m, 1H), 2.43-2.36 (m, 1H), 2.31-2.10 (m, 2H), 2.03-1.90 (m, 1H), 0.88 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 82.4, 77.4, 70.3, 34.5, 25.5, 20.2. **(10R)-B-(2,2-Dimethyl-5-hexyn-3-oxy)-10-trimethylsilyl-9-borabicyclo[3.3.2]decane (5c)**: (>98% purity by ^{13}C NMR), ^1H NMR (300 MHz, CDCl_3) δ 4.03 (dd, $J = 9.4, 2.5$ Hz, 1H), 2.43-1.40 (m, 17H), 0.91 (s, 9H), 0.61 (m, 1H), 0.10 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 83.0, 81.2, 69.4, 34.8, 33.8, 32.7, 31.5, 29.1, 27.3, 26.5, 26.0, 24.3, 22.9, 22.3, 22.2, 1.2; ^{11}B NMR (96 MHz, CDCl_3) δ 54.7.

(+)-(R)-1-Phenyl-3-butyn-1-ol (6d): 78 % yield, bp 68-70 °C, 2.0 mm Hg, >98% GC/ ^{13}C NMR purity, [lit.³ bp 70 °C, 2.0 mm Hg]; $[\alpha]_{\text{D}}^{28} = +11.18$ (1.7, MeOH) [lit.^{4,5} $[\alpha]_{\text{D}}^{24} = +7.36$ (3.8, MeOH, 63% ee), +12.9 (1.55, MeOH), 98% ee]; ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.29 (m, 5H), 4.86 (t, $J = 6.4$ Hz, 1H), 2.64 (dd, $J = 6.3, 2.5$ Hz, 2H), 2.52 (br s, 1H), 2.07 (t, $J = 2.7$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 142.4, 128.4, 127.9, 125.7, 80.7, 72.3, 70.0, 29.3 (Figures 5, 6).

(-)-(R)-1-Hexen-5-yn-3-ol (6e): 74 % yield, bp 40-42 °C, 60 mm Hg, >98% GC/ ^{13}C NMR purity [lit.⁶ bp 105 °C, 200 mm Hg]; $[\alpha]_{\text{D}}^{28} = -36.79$ (2.1, MeOH); ^1H NMR (300 MHz, CDCl_3) δ 5.97-5.87 (m, 1H), 5.35-5.16 (m, 2H), 4.32-4.26 (m, 1H), 2.48-2.43 (m, 2H), 2.16 (br s, 1H), 2.07-2.05 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 138.8, 115.6, 80.2, 70.9, 70.7, 27.7. **(10R)-B-((3S)-Hex-1-en-5-yn-3-oxy)-10-trimethylsilyl-9-borabicyclo[3.3.2]-decane (5e)**: (>98% purity by ^{13}C NMR), ^1H NMR (300 MHz, CDCl_3) δ 5.97-5.85 (m, 1H), 5.25-5.14 (m, 2H), 4.72-4.66 (m, 1H), 2.47-2.43 (m, 2H), 2.27 (m, 1H), 1.98-1.05 (m, 14H), 0.64 (m, 1H), 0.07 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.8, 115.6, 80.8, 74.2, 70.0, 33.1, 32.9, 31.6, 29.1, 27.5, 27.4, 25.9, 24.6, 23.1, 21.9, 1.0; ^{11}B NMR (96 MHz, CDCl_3) δ 55.3.

(-)-(R)-1-(2-Furyl)-3-butyn-1-ol (6f): 80 % yield, bp 70-72 °C, 1.5 mm Hg, >98% GC/ ^{13}C NMR purity, [lit.³ bp 62 °C, 0.6 mm Hg]; $[\alpha]_{\text{D}}^{28} = -6.61$ (2.4, MeOH); ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.36 (m, 1H), 6.34-6.32 (m, 2H), 4.85 (t, $J = 6.3$ Hz, 1H), 2.75 (dd, $J = 6.3, 2.6$ Hz, 2H),

Figure 5. ^{13}C NMR of **6d**.

Figure 6. Assigned ^{13}C NMR spectra for **6**.

2.05 (t, $J = 2.6$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.6, 142.2, 110.2, 106.5, 79.9, 71.0, 65.9, 25.9. **(10R)-B-((1S)-2-Furyl)-3-butyn-1-oxy)-10-trimethylsilyl-9-borabicyclo-[3.3.2]decane (5f)**: (>98% purity by ^{13}C NMR), ^1H NMR (300 MHz, CDCl_3) δ 7.36 (m, 1H), 6.33-6.26 (m, 2H), 5.28 (t, $J = 6.8$ Hz, 1H), 2.81-2.77 (m, 2H), 2.27 (m, 1H), 1.98 (t, $J = 2.6$ Hz, 1H), 1.81-1.19 (m, 13H), 0.68 (d, $J = 2.3$ Hz, 1H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.6, 141.8, 110.1, 106.5, 80.4, 70.1, 68.7, 33.1, 32.8, 31.5, 29.0, 27.4, 25.9, 25.8, 24.5, 22.9, 21.8, 0.6; ^{11}B NMR (96 MHz, CDCl_3) δ 55.7.

(+)-(R)-1-Heptyn-4-ol (6a'). A solution of **1S** (1.23 g, 5.0 mmol) in EE (25 mL) was cooled to -78°C and a solution of $n\text{-PrCHO}$ (0.46 mL, 5.0 mmol) in EE (5 mL) at -78°C was added to it slowly *via* a double ended needle. After 3 h at -78°C , the solvents were removed under vacuum to yield essentially pure **5a'**. The (1*R*,2*R*)-(-)-pseudoephedrine (0.83 g, 5.0 mmol) and acetonitrile (15 mL) were added, and the mixture was refluxed for 4 h. The crystals were separated and washed with acetonitrile (2 x 3 mL) to afford 1.55 g (84%) of (-)-**4S**. The residue was distilled to give 0.43 g (80%) of **6a'** (bp $27\text{--}28^\circ\text{C}$, 1.5 mm Hg, >98% GC/ ^{13}C NMR purity). $[\alpha]_{\text{D}}^{28} = +28.10$ (2.2, MeOH). The spectroscopic data were identical to those of **6a**.

(R)-(+)- α -methoxy- α -trifluoromethylphenylacetyl chloride (11R): MPTA-Cl was prepared by a procedure analogous to that reported by Mosher.⁷ A dry 2-necked 100 mL round-bottom flask, equipped with a magnetic stirring bar, water condenser, and addition funnel, was charged with NaCl (0.1 g) and (R)-(+)-MPTA (4.88 g, 21 mmol) at room temperature. Thionyl chloride (10 mL) was added dropwise. The mixture was allowed to reflux for 96 h, the excess thionyl chloride was removed *in vacuo*, and the residue was distilled to give 4.3 g (88 %), bp $40\text{--}43^\circ\text{C}$, 0.2 mm Hg (lit.⁷ $54\text{--}56^\circ\text{C}$, 1 mm Hg).

General procedure for the preparation of

Mosher esters of optically active homopropargylic alcohols (12a-f). The preparation of the Mosher ester(s) of (S)-1-heptyn-4-ol (**6a**) is representative. To a well-stirred solution of (-)-(S)-1-heptyn-4-ol (**1a**) (45 mg, 0.4 mmol) and 4-(dimethylamino)pyridine (61 mg, 0.5 mmol) in THF (3 mL) at 25°C was added dropwise (R)-(+)- α -methoxy- α -(trifluoromethyl)phenylacetic acid chloride (131 mg, 0.5 mmol). After 12 h at 25°C , the solvents were removed under vacuum and the residue was extracted with ethyl ether. The combined extracts were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. Chromatography on silica gel (hexanes-acetone, 10:1) gave (S)-1-heptyn-4-yl (R)- α -methoxy- α -(trifluoromethyl)phenylacetate (**12a**) as a colorless liquid (121 mg, 90% yield, >98% ^{13}C NMR purity): R_f 0.32 (hexanes-acetone, 2:1); ^1H NMR (300 MHz, CDCl_3) δ 7.57-7.55 (m, 2H), 7.42-7.38 (m, 3H), 5.22-5.14 (m, 1H), 3.55 (s, 3H), 2.53-2.50 (m, 2H), 1.93 (t, $J = 2.7$ Hz, 1H), 1.80-1.69 (m, 2H), 1.44-1.34 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.2, 132.0, 129.5, 128.3, 127.5, 123.2 (q, $J = 288.5$ Hz), 84.6 (q, $J = 27.6$ Hz), 78.9, 74.5, 70.8, 55.4, 34.9, 23.5, 18.3, 13.7 (Figures 7-9).

(R)-1-Heptyn-4-yl (R)- α -methoxy- α -(trifluoromethyl)phenylacetate (12a'). 88 % yield, >98% ^{13}C NMR purity. ^1H NMR (300 MHz, CDCl_3) δ 7.61-7.58 (m, 2H), 7.41-7.34 (m, 3H), 5.24-5.15 (m, 1H), 3.61 (s, 3H), 2.67-2.49 (m, 2H), 2.03 (t, $J = 2.7$ Hz, 1H), 1.80-1.57 (m, 2H), 1.31-1.16 (m, 2H), 0.86 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.1, 132.3, 129.5, 128.3, 127.3, 123.3 (q, $J = 288.7$ Hz), 84.5 (q, $J = 27.7$ Hz), 79.2, 74.4, 71.0, 55.6, 34.9, 23.7, 18.0, 13.5.

(R)-2-Methyl-5-hexyn-3-yl (R)- α -methoxy- α -(trifluoromethyl)phenylacetate (12b): 88 % yield, >98% ^{13}C NMR purity. ^1H NMR (300 MHz, CDCl_3) δ 7.57-7.55 (m,

Figure 7. Upfield region in the ^{13}C NMR spectra of **12** derived from ($\pm$)-**1**, **1R**, and **1S** (bottom to top).

Figure 8. ^{13}C NMR of **12a**.

2H), 7.42-7.39 (m, 3H), 5.06-5.00 (m, 1H), 3.54 (s, 3H), 2.54-2.51 (m, 2H), 2.18-2.11 (m, 1H), 1.90 (t, $J = 2.6$ Hz, 1H), 0.95 (t (2 doublets), $J = 6.5$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.2, 131.9, 129.6, 128.3, 127.6, 123.3 (q, $J = 288.3$ Hz), 84.8 (q, $J = 27.9$ Hz), 79.1, 79.0, 70.6, 55.4, 30.3, 21.1, 18.6, 17.0.

(*R*)-2,2-Dimethyl-5-hexyn-3-yl (*R*)- α -methoxy- α -(tri-fluoromethyl)phenylacetate (12c): 84 % yield, >98% ^{13}C NMR purity. ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.61 (m, 2H), 7.42-7.37 (m, 3H), 5.14-5.10 (m, 1H), 3.53 (s, 3H), 2.62-2.38 (m, 2H), 1.86 (t, $J = 2.7$ Hz), 0.95 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.0, 131.7, 129.5, 128.3, 128.1, 123.3 (q, $J = 288.1$ Hz), 84.9 (q, $J = 27.8$ Hz), 81.4, 80.3, 70.5, 55.3, 34.8, 25.8, 20.0.

(*R*)-1-Phenyl-3-butyn-1-yl (*R*)- α -methoxy- α -(trifluoro-methyl)phenylacetate (12d): 90 % yield, >98% ^{13}C NMR purity. ^1H NMR (500 MHz, CDCl_3) δ 7.48-7.32 (m, 10H), 6.15-6.12 (m, 1H), 3.47 (s, 3H), 2.85-2.71 (m, 2H), 1.92 (t, $J = 2.6$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.7, 137.6, 132.1, 129.5, 128.9, 128.6, 128.3, 127.5, 126.8, 123.3 (q, $J = 288.5$ Hz), 84.7 (q, $J = 27.7$ Hz), 78.7, 76.0, 71.0, 55.4, 26.2.

(*R*)-Hex-1-en-5-yn-3-yl (*R*)- α -methoxy- α -(trifluoromethyl)phenylacetate (12e): 91 % yield, >98% ^{13}C NMR purity. ^1H NMR (300 MHz, CDCl_3) δ 7.56-7.53 (m, 2H), 7.41-7.38 (m, 3H), 5.98-5.82 (m, 1H), 5.62-5.57 (m, 1H), 5.48-5.33 (m, 2H), 3.55 (s, 3H), 2.60-2.56 (m, 2H), 1.96 (t, $J = 2.7$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.7, 133.5, 132.1, 129.6, 128.4, 127.5, 123.3 (q, $J = 288.4$ Hz), 119.8, 84.7 (q, $J = 27.7$ Hz), 78.4, 74.8, 71.0, 55.4, 24.3.

(*R*)-1-(2-Furyl)-3-butyn-1-yl (*R*)- α -methoxy- α -(trifluoromethyl)phenylacetate (12f): 88 % yield, >98% ^{13}C NMR purity. ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.32 (m, 5H), 6.52-6.51 (m, 1H), 6.39-6.37 (m, 1H), 6.25-6.21 (m, 1H), 3.48 (s, 3H), 2.93-2.86 (m, 2H), 1.94 (t, $J = 2.6$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.6, 149.7, 143.2, 132.1, 129.5, 128.3, 127.4, 123.3 (q, $J = 288.5$ Hz), 110.5, 110.3, 84.6 (q, $J = 27.8$ Hz), 78.2, 71.0, 68.5, 55.4, 22.5.

Figure 9. Assigned ^{13}C NMR for **12** made through DEPT, APT, COSY and HETCOR experiments.

Racemic Homopropargylic alcohols ((±)-6) The reaction was carried out in the same way as described for the preparation of optically active homopropargylic alcohols (**6a-f**), except that (±)-**1** was used. The products (±)-**6a-f** were obtained in 75-84 % yield, >98% ¹³C NMR purity. The spectroscopic data were identical to that of the non-racemic homopropargylic alcohols (**6a-f**).

Mosher esters of (±)-6 (12R) (Chemical purities of diastereomers were ≥ 98% (¹³C NMR)). The reaction was carried out in the same way as described for the preparation of **12**, except that (±)-**6** was used with **11R**. All resolved signals are listed individually.

1-Heptyn-4-yl (R)-α-methoxy-α-(trifluoromethyl)phenylacetate (12Ra): 87 % yield. ¹H NMR (300 MHz, CDCl₃) δ 7.61-7.54 (m, 2H), 7.42-7.37 (m, 3H), 5.22-5.16 (m, 1H), 3.61, 3.55 (s, 3H), 2.61-2.49 (m, 2H), 2.03, 1.93 (t, *J* = 2.7 Hz, 1H), 1.80-1.59 (m, 2H), 1.44-1.17 (m, 2H), 0.94, 0.86 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 166.2, 132.3, 132.0, 129.5, 128.3, 127.5, 127.2, 123.2 (q, *J* = 288.6 Hz), 84.6 (q, *J* = 27.7 Hz), 79.3, 78.9, 74.5, 74.4, 71.0, 70.8, 55.6, 55.4, 34.9, 34.8, 23.7, 23.5, 18.3, 18.0, 13.7, 13.6.

2-Methyl-5-hexyn-3-yl (R)-α-methoxy-α-(trifluoromethyl)phenylacetate (12Rb): 86 % yield. ¹H NMR (300 MHz, CDCl₃) δ 7.62-7.55 (m, 2H), 7.43-7.37 (m, 3H), 5.06-4.98 (m, 1H), 3.62, 3.54 (s, 3H), 2.60-2.51 (m, 2H), 2.18-2.06 (m, 1H), 2.01, 1.91 (t, *J* = 2.6 Hz, 1H), 0.96 (ct, *J* = 6.4 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 166.3, 166.2, 132.3, 131.9, 129.5, 128.3, 127.7, 127.4, 123.3 (q, *J* = 288.7 Hz), 84.8 (q, *J* = 27.7 Hz), 79.4, 79.1, 79.0, 70.8, 70.6, 55.6, 55.4, 30.4, 30.3, 21.2, 21.1, 18.5, 18.2, 17.1, 17.0.

2,2-Dimethyl-5-hexyn-3-yl (R)-α-methoxy-α-(trifluoromethyl)phenylacetate (12Rc): 85 % yield. ¹H NMR (300 MHz, CDCl₃) δ 7.66-7.61 (m, 2H), 7.42-7.37 (m, 3H), 5.16-5.10 (m, 1H), 3.63 (s), 3.53 (s), 2.62-2.38 (m, 2H), 1.97, 1.86 (t, *J* = 2.7 Hz, 1H), 0.95, 0.88 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 166.0, 132.2, 131.7, 129.5, 128.3, 128.1, 127.6, 123.4 (q, *J* = 288.1 Hz), 84.9 (q, *J* = 27.8 Hz), 81.4, 80.6, 80.3, 70.8, 70.5, 55.6, 55.3, 34.8, 25.8, 25.7, 20.1, 20.0.

1-Phenyl-3-butyn-1-yl (R)-α-methoxy-α-(trifluoromethyl)phenylacetate (12Rd): 90 % yield. ¹H NMR (500 MHz, CDCl₃) δ 7.48-7.48 (m, 10H), 6.15-6.12, 6.09-6.06 (m, 1H), 3.63, 3.48 (s, 3H), 2.85-2.73 (m, 2H), 2.04, 1.92 (t, *J* = 2.4, 2.6 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 165.7, 165.7, 137.6, 132.1, 129.5, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 127.6, 127.4, 126.8, 126.5, 123.3 (q, *J* = 288.5 Hz), 84.7 (q, *J* = 27.7 Hz), 79.4, 78.7, 76.5, 76.0, 71.0, 70.9, 55.8, 55.4, 26.5, 26.2.

1-Hexen-5-yn-3-yl (R)-α-methoxy-α-(trifluoromethyl)phenylacetate (12Re): 88 % yield. ¹H NMR (300 MHz, CDCl₃) δ 7.58-7.47 (m, 2H), 7.41-7.36 (m, 3H), 5.98-5.75 (m, 1H), 5.63-5.57 (m, 1H), 5.48-5.25 (m, 2H), 3.62, 3.55 (s, 3H), 2.64-2.56 (m, 2H), 2.04, 1.96 (t, *J* = 2.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 165.7, 165.6, 133.5, 133.4, 132.2, 132.1, 129.6, 128.4, 128.3, 127.5, 127.4, 123.3 (q, *J* = 288.6 Hz), 119.8, 119.3, 84.7 (q, *J* = 27.7 Hz), 78.9, 78.4, 74.8, 71.0, 55.4, 55.4, 24.4, 24.3.

1-(2-Furyl)-3-butyn-1-yl (R)-α-methoxy-α-(trifluoromethyl)phenylacetate (12Rf): 87 % yield. ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.25 (m, 5H), 6.51-6.18 (m, 3H), 3.60, 3.47 (s, 3H), 2.99-2.85 (m, 2H), 2.04, 1.93 (t, *J* = 2.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 165.7, 149.7, 149.6, 143.2, 143.0, 132.1, 129.6, 129.5, 128.3, 128.2, 127.4, 127.3, 123.2 (q, *J* = 288.5 Hz), 110.5, 110.3, 110.0, 84.7 (q, *J* = 27.5 Hz), 84.6 (q, *J* = 27.8 Hz), 78.8, 78.2, 71.0, 69.0, 68.5, 55.7, 55.4, 22.7, 22.5.

Figure 10. The C-4 position in the ¹³C NMR of **12a** (from **1R**). (δ 70.9 (area = 1.0); 70.8 (area = 31.5) dr = 3:97, **6a** (94% ee).

Determination of the enantiomeric excess for 6 through 12 by NMR. As can be seen from the above NMR data for **12**, several sets of signals both in the ^1H and ^{13}C NMR spectra, are well resolved for the diastereomeric esters derived from ($\pm$)-**6** which integrate as 50:50 ratio. However, from **6** derived from either **1R** or **1S**, the areas of several sets, and those from resolved ^1H NMR signals, were measured to determine the dr comparing these to arrive ultimately at the reported ee of **6** (Figures 7, 10).

Procedure for the determination of chemoselectivity of toward benzaldehyde and acetophenone. To a solution of PhCHO (0.53 g, 5 mmol) and PhCOMe (0.60 g, 5 mmol) in EE (30 mL) at $-78\text{ }^\circ\text{C}$ was added ($\pm$)-**1** (1.23 g, 5 mmol) in a dropwise manner. After the mixture was stirred for 3h at $-78\text{ }^\circ\text{C}$, the solvents were removed *in vacuo* and the residue was analyzed by NMR revealing that only **6d** and unreacted PhCOMe were present. In a separate experiment, ($\pm$)-**1** failed to react with PhCOMe even at $25\text{ }^\circ\text{C}$ after one week.

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