Stereoisomerically Pure Trisubstituted Vinylaluminum Reagents and their Utility in Cu-Catalyzed Enantioselective Synthesis of 1,4-Dienes Containing *Z*- and *E*-Alkenes

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SUPPORTING INFORMATION, PART A

General. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septuplet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomer ratios were determined by analytical liquid chromatography (HPLC) on a Shimadzu chromatograph (Chiral Technologies Chiralpak AS (4.6 x 250 mm), Chiral Technologies Chiralpak OD (4.6 x 250 mm), Chiral Technologies Chiralpak OD-R (4.6 x 250 mm) or Chiral Technologies Chiralpak AD (4.6 x 250 mm)) in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 ºC) and flame-dried glassware with standard dry box or vacuum-line techniques. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Doe & Ingalls) in air. Substrates were prepared by known procedures.[1] All allylic phosphates are of *E*-olefin geometry (>98%); the stereochemical purity of the allylic alkylation substrates was established through ^1H NMR analysis (400 MHz).

■ **Reagents and Ligands:**

Acetic acid: Purchased from Fisher and used as received.

Acetic anhydride: Purchased from Acros and used as received.

9-Borabicyclo[3.3.1]nonane: Purchased from Aldrich and used without further purification.

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[1] C. A. Luchaco-Cullis, H. Mizutani, K. E. Murphy, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2001**, *40*, 1456–1460.

Chlorodiethylphosphate: Purchased from Aldrich and used as received.

Chloroform: Purchased from Fisher Scientific and distilled from CaH_2 under N_2.

Copper (II) chloride dihydrate: Purchased from Aldrich and used without further purification.

Di-*t*-butyl dicarbonate: Purchased from Advanced Chem Tech and used as received.

Diisobutyl aluminum hydride (neat): Purchased from Aldrich and used as received.

2,6-Diisopropylaniline: Purchased from Aldrich and used as received.

4-Dimethylaminopyridine: Purchased from Advanced Chem Tech used as received.

***N*,*N'*-Dimethylformamide** (anhydrous): Purchased from Aldrich and used as received.

***N*,*N'*-Dimethylmethylene ammonium iodide**: Purchased from Lancaster and used as received.

1-(Dimethylsilyl)-2-phenylacetylene: Purchased from Aldrich and used after distillation from CaH_2 under N_2.

1,4-Dioxane (anhydrous): Purchased from Aldrich and used as received.

[(4-Fluorophenyl)ethynyl]trimethylsilane: Purchased from Aldrich and used after distillation from CaH_2 under N_2.

Hydrogen peroxide (35% wt solution in water): Purchased from Aldrich and used without further purification.

4-Iodophenol: Purchased from Aldrich and used without further purification.

Methanol (extra dry with molecular sieves**)**: Purchased from Acros and used as received.

Palladium acetate: Purchased from Strem (99% purity) and used as received.

Phenylethynyltrimethylsilane: Purchased from Aldrich and used after distillation from CaH_2 under N_2.

Potassium carbonate: Purchased from Aldrich and used as received.

Pyridine (anhydrous): Purchased from Aldrich and used as received.

Racemic-2,2'-bis(diphenylphosphino)-1,1'-binapthyl (*rac*-binap): Purchased from Aldrich (99% purity) and used as received.

Silver (I) oxide: Prepared by previously reported methods.[2]

Sodium *tert*-butoxide (98%): Purchased from Strem and used as received.

Sodium hydride (60% dispersion): Purchased from Strem and used as received.

Tetrahydrofuran: Distilled under N_2 from sodium benzophenone ketyl.

Triethylamine: Purchased from Aldrich and distilled from CaH_2 under N_2.

Trifluoroacetic acid: Purchased from Acros and used as received.

Trimethylsilyl acetylene: Purchased from Acros and used without further purification.

2-(Trimethylsilylethynyl)anisole: Purchased from Aldrich and used after distillation from CaH_2 under N_2.

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[2] T. L. May, M. K. Brown, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2008**, *47*, 7358–7362.

4-(Trimethylsilylethynyl)toluene: Prepared by a previously reported procedure.[3]

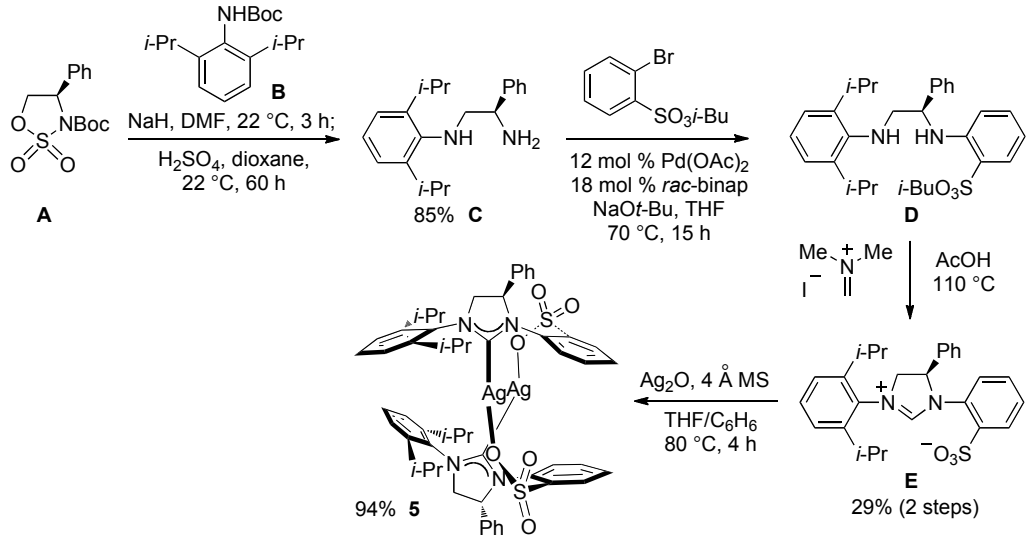
3-(Trimethylsilylethynyl)toluene: Prepared by a previously reported procedure.[3]

1-(Trimethylsilylethynyl)-4-(trifluoromethyl)benzene: Purchased from Aldrich and used after distillation from CaH_2 under N_2.

Benzene, Dichloromethane, Diethyl ether, and Hexanes: Purified by being passed through two alumina columns under a positive pressure of dry argon with a modified Advanced ChemTech purification system.

Synthesis Chiral NHC Complex 5: Chiral NHC•Ag complex **5** was prepared according to the route illustrated in Scheme 1.

Scheme 1. Synthesis of NHC-Ag **5**



(2,6-Diisopropylphenyl)-carbamic acid *tert*-butyl ester (B):[4] To a solution of 2,6-diisopropylaniline (3.80 mL, 20.0 mmol) in water (100 mL) was added $(Boc)_2O$ (4.36 g, 22.0 mmol) in one portion. The solution was allowed to stir for 48 hours, after which was washed with Et_2O (3 x 100 mL). The combined organic layers were washed with 1N HCl (100 mL x 3), dried over $MgSO_4$, and the volatiles were evaporated under reduced pressure. The resulting residue was dried under vacuum to afford a light red solid in 73% yield (4.03 g, 14.5 mmol). IR (neat): 3310 (w), 2960 (m), 2929 (w), 2868 (w), 1686 (s), 1591 (w), 1503 (s), 1390 (w), 1364 (m), 1248 (s), 1164 (s), 1055 (s), 1025 (m), 937 (w), 918 (w), 840 (w), 801 (w), 774 (w), 721 (m), 617 (m), 458 (w), 417 (w) cm^{-1}; this compound was isolated as a mixture of rotamers. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (1H, t, J = 7.2 Hz, Ar**H**), 7.13 (2H, d, J = 7.2 Hz, Ar**H**) 5.80 (0.6H, brs, ArN**H**), 5.63 (0.4H, brs, ArN**H**), 3.30-3.10 (2H, m, ArC**H**$(CH_3)_2$), 1.49 (5.4H, s, ArOCOC(C**H**$_3)_3$), 1.35 (3.6H, s, ArOCOC(C**H**$_3)_3$), 1.20 (12H, d, J = 6.8 Hz, ArCH(C**H**$_3)_2$); ^{13}C

[3] N. Leventis, A. M. Rawashdeh, I. A. Elder, J. Yang, A. Dass, C. Sotiriou-Leventis, *Chem. Mater.* **2004**, *16*, 1493-1506.

[4] S. V. Chankeshwara, A. K. Chakraborti, *Org. Lett.* **2006**, *8*, 3259-3262.

NMR (100 MHz, $CDCl_3$): δ 154.6, 146.8, 131.1, 127.9, 123.3, 79.6, 28.6, 28.2, 23.5; HRMS (ESI+) Calcd for $C_{17}H_{28}N_1O_2$ $[M+H]^+$: 278.2120. Found: 278.2118.

(*R*)-N2-(2,6-Diisopropyl-phenyl)-1-phenyl-ethane-1,2-diamine (C): To a two-necked, 100-mL flask was added NaH (60% dispersion, 640 mg, 16.0 mmol), *tert*-butyl-2,6-diisopropylphenylcarbamate **B** (3.88 g, 14.0 mmol) and DMF (35.0 mL) under N_2. The solution was allowed to stir at 22 °C for 30 min, after which sulfonamide **A**[5] (2.99 g, 10.0 mmol) was added as a solid in one portion and the resulting mixture was allowed to stir for an additional 15 hours. The reaction flask was equipped with a distillation head and DMF was removed under reduced pressure (~3 mmHg) with gentle heating (<60 °C). Dioxane (35.0 mL) was added followed by concentrated H_2SO_4 (2.0 mL, ~18 M). The resulting mixture was allowed to stir at 22 °C for 60 hours. Reaction progress was monitored by TLC analysis and an additional portion of H_2SO_4 (1.0 mL) was added after 18 hours. A saturated aqueous solution of Na_2CO_3 was added until pH = ~10. CH_2Cl_2 (100 mL) was added and the organic layer was separated. The aqueous layer was washed with CH_2Cl_2 (3 x 100 mL), and the organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting dark brown oil residue was purified by silica gel column chromatography (petroleum ether/EtOAc from 20/1 to 1/1) to afford the desired product in 85% yield (2.53 g, 8.53 mmol). IR (neat): 3368 (w), 2959 (s), 2866 (w), 1760 (w), 1692 (w), 1588 (w), 1491 (w), 1449 (s), 1382 (w), 1362 (w), 803 (m), 751 (s), 699 (s), 575 (w), 529 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.27 (5H, m, Ar**H**), 7.09-6.98 (3H, m, Ar**H**), 4.20 (1H, t, J = 6.2 Hz, $NH_2C\mathbf{H}Ph$), 3.13 (2H, dsept, J = 6.8, 1.0 Hz, $ArC\mathbf{H}(CH_3)_2$), 3.07-3.02 (2H, m, $ArNHC\mathbf{H}_2$), 2.21 (brs, 3H, $N\mathbf{H}CH_2CH(Ph)N\mathbf{H}_2$) 1.17 (12H, d, J = 6.8 Hz, $ArCH(C\mathbf{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 143.0, 142.5, 128.6, 127.4, 126.3, 123.7, 123.4, 59.1, 56.3, 27.4, 24.1; HRMS (ESI+) Calcd for $C_{20}H_{29}N_2$ $[M+H]^+$: 297.2330. Found: 297.2328; $[\alpha]^{20}_D$ –24.9 (c = 1.19, $CHCl_3$).

Imidazolinium salt E: To a 150-mL round bottom flask in a N_2-filled glove box was added $Pd(OAc)_2$ (308 mg, 1.37 mmol), *rac*-binap (1.28 g, 2.05 mmol), and NaO*t*-Bu (1.97 g, 20.5 mmol). The flask was fitted with a reflux condenser, capped with a septum and removed from the glove box. A solution of diamine **C** (3.40 g, 11.4 mmol) and *iso*-butyl-2-bromobenzenesulfonate[6] (4.02 g, 13.7 mmol) in THF (50 mL) was added through a syringe and the resulting red solution was allowed to stir at 60 °C for 20 hours. The mixture was allowed to cool to 22 °C before being filtered (filter paper), and concentrated under reduced pressure. The **resulting residue** was purified by silica gel chromatography (petroleum ether/Et_2O from 100/1 to 20/1) to afford a mixture of diamine **D** and isobutylbenzenesulfonate (3.89 g). The resulting mixture was used in next step. A 150 mL round bottom flask was charged with a mixture of diamine **D** and isobutylbenzenesulfonate (3.89 g) and *N*,*N*'-dimethylmethylene ammonium iodide (5.46 g, 29.5 mmol), and acetic acid (40 mL); the flask was equipped with a reflux condenser and the solution was allowed to stir at 110 °C for 2.5 h. The reaction mixture was

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[5] Sulfonamide **A** was prepared by previously reported procedure; see: Ref. 2.

[6] The compound was prepared by a previously reported procedure; see; M. K. Brown, T. L. May, C. A. Baxter, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2007**, *46*, 1097–1100.

transfered to a 500 mL flask, and neutralized by the addition of a saturated solution of $NaHCO_3$. The aqueous layer was washed with CH_2Cl_2 (3 x 100 mL), and the combined organic layers were washed with a saturated solution of Na_2SO_3, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH from100/1 to 20/1). The yellow residue was further purified by trituration with pentane to afford imidazolinium salt **E** as a white solid in 29% yield (over two steps, 1.54 g, 3.33 mmol). IR (neat): 3457 (br), 2962 (w), 2927 (w), 2869 (w), 1619 (s), 1585 (m), 1458 (w), 1386 (w), 1365 (w), 1333 (w), 1234 (s), 1199 (s), 1141 (w), 1090 (m), 1055 (w), 1022 (m), 935 (w), 888 (w), 865 (w), 808 (w), 757 (s), 729 (w), 703 (m), 651 (w), 610 (s), 564 (m), 537 (w), 498 (w), 451 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.81 (1H, s, N=C**H**N), 8.12 (1H, dd, *J* = 8.0, 1.6 Hz, Ar**H**), 7.50-7.43 (6H, m, Ar**H**), 7.30-7.25 (3H, m, Ar**H**), 7.08 (1H, td, *J* = 8.0, 1.6 Hz, Ar**H**), 6.65 (1H, dd, *J* = 8.0, 1.2 Hz, Ar**H**), 6.25 (1H, dd, *J* = 12.0, 10.0 Hz, NCH_2C**H**(Ph)N), 4.81 (1H, t, *J* = 12.0 Hz, NC**H**$_2$CH(Ph)N), 4.11 (1H, dd, *J* = 11.6, 9.6 Hz, NC**H**$_2$CH(Ph)N), 3.64 (1H, sept, *J* = 6.8 Hz, ArC**H**$(CH_3)_2$), 3.18 (1H, sept, *J* = 6.8 Hz, ArC**H**$(CH_3)_2$), 1.40 (3H, d, *J* = 6.8 Hz, ArCH(C**H**$_3)_2$), 1.32 (3H, d, *J* = 6.8 Hz, ArCH(C**H**$_3)_2$), 1.29 (3H, d, *J* = 6.8 Hz, ArCH(C**H**$_3)_2$), 1.24 (3H, d, *J* = 6.8 Hz, ArCH(C**H**$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 148.1, 145.6, 143.7, 135.9, 131.2, 130.5, 130.0, 129.7, 129.6, 129.5, 128.2, 126.6, 125.5, 124.5, 68.2, 61.3, 28.8, 28.0, 24.8, 24.7, 24.7, 24.6; HRMS (ESI+) Calcd for $C_{27}H_{31}N_2O_3S_1$ $[M+H]^+$: 463.2044. Found: 463.2055; $[\alpha]^{20}_D$ –130.0 (*c* = 0.96, $CHCl_3$).

NHC•Ag complex 5: Imidazolinium salt **E** (50.0 mg, 0.108 mmol), Ag_2O (50.0 mg, 0.215 mmol), and oven-dried 4 Å molecular sieves (powdered) were weighed into an oven-dried 25-mL vial wrapped with aluminum foil. Tetrahydrofuran (1.0 mL), followed immediately by benzene (1.0 mL), were added through a syringe resulting in a black heterogeneous mixture. The vial was capped and sealed with electrical tape; the solution was allowed to stir at 80 °C. After 4 hours, the mixture was allowed to cool to 22 °C and filtered through a short plug of Celite 545 eluted with THF (~4 mL). The solution was concentrated under vacuum to afford the desired product as a white solid in 94% yield (57.9 mg, 0.0508 mmol). IR (neat): 3435 (br), 3059 (w), 3027 (w), 2960 (w), 2923 (w), 2867 (w), 1479 (s), 1445 (w), 1333 (w), 1274 (w), 1194 (s), 1137 (m), 1091 (m), 1055 (w), 1022 (s), 867 (w), 805 (w), 756 (s), 700 (m), 663 (w), 608 (s), 564 (m), 548 (m), 458 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (1H, br, Ar**H**), 8.12 (1H, dd, *J* = 8.0, 1.6 Hz, Ar**H**), 7.34-7.17 (6H, m, Ar**H**), 7.08-7.06 (2H, m, Ar**H**), 6.94 (1H, d, *J* = 6.4 Hz, Ar**H**), 6.60 (1H, br, Ar**H**), 6.06-5.98 (2H, br, Ar**H**, NCH_2C**H**(Ph)N), 4.29 (1H, br, NC**H**$_2$CH(Ph)N), 3.65 (1H, dd, *J* = 11.2, 7.2 Hz, NC**H**$_2$CH(Ph)N), 3.21 (1H, br, ArC**H**$(CH_3)_2$), 3.23 (1H, br, ArC**H**$(CH_3)_2$), 1.42 (3H, br, ArCH(C**H**$_3)_2$), 1.23-1.10 (6H, br, ArCH(C**H**$_3)_2$), 0.73 (3H, br, ArCH(C**H**$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 205.5, 148.5, 145.9, 143.5, 139.8, 135.4, 134.7, 130.6, 130.0, 129.4, 128.9, 128.5, 128.2, 128.0, 125.3, 123.3, 68.3, 62.7, 28.3, 27.3, 25.6, 25.1, 24.6, 24.2; HRMS (ESI+) Calcd for $C_{27}H_{29}N_2O_3S_1Ag_1Na_1$ $[M+Na]^+$: 591.0848. Found: 591.0859; $[\alpha]^{20}_D$ –106.1 (*c* = 0.36, $CHCl_3$).

NHC•Ag complex 12: Prepared according to the same procedure as described above for NHC-Ag complex **5** in 87% yield as a pale yellow solid. The imidazolinium salt is prepared according

to a previously disclosed procedure.[7] IR (neat): 3448 (br), 3065 (w), 2961 (w), 2927 (w), 2923 (w), 2870 (w), 2247 (w), 1473 (m), 1450 (m), 1226 (m), 1197 (m), 1138 (w), 1093 (w), 1022 (w), 905 (s), 725 (s), 698 (s), 646 (m), 612 (m), 561 (w), 540 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (1H, d, *J* = 7.6 Hz, Ar**H**), 7.26-7.18 (6H, m, Ar**H**), 7.09-7.07 (4H, m, Ar**H**), 6.97-6.95 (2H, m, Ar**H**), 6.51-6.45 (3H, m, Ar**H**), 6.22 (1H, d, *J* = 7.6 Hz, NCH(Ph)C**H**(Ph)N), 4.97 (1H, d, *J* = 12.0 Hz, NC**H**(Ph)CH(Ph)N), 3.29 (1H, brs, ArC**H**$(CH_3)_2$), 2.89 (2H, brs, ArC**H**$(CH_3)_2$), 1.54 (6H, brs, ArCH(C**H**$_3)_2$), 1.27 (6H, brs, ArCH(C**H**$_3)_2$), 0.60 (3H, brs, ArCH(C**H**$_3)_2$), 0.22 (3H, brs, ArCH(C**H**$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7, 204.9, 149.0, 148.4, 145.2, 143.5, 138.6, 135.5, 133.6, 131.0, 130.6, 130.2, 129.7, 128.9, 128.8, 128.6, 128.4, 128.0, 122.2, 121.1, 79.5, 72.7, 68.1, 33.9, 28.7, 28.0, 27.5, 26.6, 24.9, 24.0, 23.9, 21.5; HRMS (ESI+) Calcd for $C_{36}H_{39}N_2O_3S_1Ag_1Na_1$ $[M+Na]^+$: 709.1630. Found: 709.1646; $[\alpha]^{20}_D$ –11.75 (*c* = 0.80, $CHCl_3$).

Preparation of ethynyldimethylsilanes: A variety of aryl-substituted ethylnyldimethylsilanes were prepared according to a previously reported protocol.[8]

Preparation of allylic phosphate substrates: Allylic alcohols were synthesized from the corresponding aldehydes by a two-step Horner-Wadsworth-Emmons olefination[9]/dibal–H reduction sequence.[10] Allylic alcohols were converted to the corresponding allylic phosphates based on well-established methods.[1] Physical attributes of compounds that have not been reported in the past are presented below.

2-Methoxycinnamyl diethyl phosphate (4c; Table 1, entry 3): IR (neat): 2982 (w), 2909 (w), 2838 (w), 1597 (w), 1489 (m), 1462 (m), 1438 (w), 1242 (s), 1163 (w), 1022 (s), 964 (s), 817 (m), 750 (s), 732 (s), 528 (m), 462 (m), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (1H, dd, *J* = 8.0, 2.0 Hz, Ar**H**), 7.28 (1H, dt, *J* = 8.0, 1.5 Hz, Ar**H**), 7.02 (1H, d, *J* = 16.0 Hz, ArC**H**=CH), 6.96 (1H, dt, *J* = 8.0, 1.0 Hz, Ar**H**), 6.90 (1H, dd, *J* = 8.0, 1.0 Hz, Ar**H**), 6.36 (1H, dt, *J* = 16.5, 6.0 Hz, ArCH=C**H**), 4.74 (2H, ddd, *J* = 8.0, 6.5, 1.5 Hz, CH=CHC**H**$_2$), 4.17 (4H, dq, *J* = 7.5, 7.5 Hz, PO(OC**H**$_2$CH$_3)_2$), 3.88 (3H, s, ArOC**H**$_3$), 1.37 (6H, td, *J* = 7.5, 1.0 Hz, PO(OCH$_2$C**H**$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 129.4, 129.2, 127.4, 125.2, 124.3 (d, *J* = 6.7 Hz), 120.8, 111.0, 68.7 (d, *J* = 5.2 Hz), 63.9 (d, *J* = 6.0 Hz), 55.5, 16.3 (d, *J* = 6.7 Hz); HRMS (ESI+) Calcd for $C_{14}H_{25}N_1O_5P_1$ $[M+NH_4]^+$: 318.1470. Found: 318.1471.

Phosphoric acid 3-(3-bromo-phenyl)-allyl ester diethyl ester (4e; Table 1, entry 5): IR (neat): 2982 (w), 1591 (w), 1562 (w), 1475 (w), 1261 (s), 1165 (w), 1010 (s), 960 (s), 816 (m), 773 (m), 680 (m), 522 (m), 433 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (1H, t, *J* = 1.8 Hz, Ar**H**), 7.39 (1H, dq, *J* = 8.0, 0.8 Hz, Ar**H**), 7.29 (1H, d, *J* = 7.6 Hz, Ar**H**), 7.19 (1H, t, *J* = 7.8 Hz, Ar**H**), 6.60 (1H, d, *J* = 16.0 Hz, ArC**H**=CH), 6.30 (1H, dt, *J* = 16.0, 6.0 Hz, ArCH=C**H**), 4.69 (2H, ddd, *J* = 7.8, 7.2, 1.6 Hz, CH=CH-C**H$_2$**), 4.13 (4H, dq, *J* = 7.6, 7.2 Hz, PO(C**H$_2$**CH$_3)_2$), 1.34

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[7] Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 3160–3161.

[8] S. V. Maifeld, D. Lee, *Org. Lett.* **2005**, *7*, 4995–4998.

[9] B. M. Nestl, S. M. Glueck, M. Hall, W. Kroutil, R. Stuermer, B. Hauer, K. Faber, *Eur. J. Org. Chem.* **2006**, 4573–4577.

[10] D. L. J. Clive, E. J. L. Stoffman, *Chem. Comm.* **2007**, *21*, 2151–2153.

(6H, td, J = 7.2, 0.8 Hz, PO($CH_2C\mathbf{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 132.0, 130.9, 130.1, 129.4, 125.2, 125.1, 122.7, 67.4 (d, J = 5.3 Hz), 63.8 (d, J = 5.6 Hz), 16.1 (d, J = 6.9 Hz); HRMS (ESI+) Calcd for $C_{13}H_{19}Br_1O_4P_1$ [M+H]$^+$: 349.0204. Found: 349.0201.

Phosphoric acid 3-(4-chloro-phenyl)-allyl ester diethyl ester (4f; Table 1, entry 6): IR (neat): 2982 (w), 1491 (w), 1262 (s), 1007 (s), 962 (s), 795 (m), 747 (w), 679 (w), 505 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (2H, dd, J = 6.4, 2.8 Hz, Ar**H**), 7.29 (2H, dd, J = 6.4, 2.8 Hz, Ar**H**), 6.63 (1H, dt, J = 16.0, 1.2 Hz, ArC**H**=CH), 6.28 (1H, dt, J = 16.0, 5.8 Hz, ArCH=C**H**), 4.68 (2H, ddd, J = 16.0, 6.4, 1.4 Hz, CH=CHC**H**$_2$), 4.13 (4H, dq, J = 8.0, 7.0 Hz, PO(OC**H**$_2$CH$_3$)$_2$), 1.34 (6H, td, J = 7.0, 0.8 Hz, PO($OCH_2C\mathbf{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 133.8, 132.4, 128.8, 127.8, 124.2 (d, J = 6.5 Hz), 67.6 (d, J = 5.7 Hz), 63.8 (d, J = 5.7 Hz), 16.1 (d, J = 6.4 Hz); HRMS (ESI+) Calcd for $C_{13}H_{19}Cl_1O_4P_1$ [M+H]$^+$: 305.0709. Found: 305.0706.

Toluene-4-sulfonic acid 4-[3-(diethoxy-phosphoryloxy)-propenyl]-phenyl ester (4h; Table 1, entry 8): IR (neat): 2983 (w), 1597 (w), 1501 (m), 1370 (m), 1264 (m), 1197 (m), 1176 (m), 1152 (m), 1091 (m), 1011 (s), 965 (s), 860 (s), 811 (s), 731 (m), 708 (m), 659 (m), 548 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (2H, d, J = 8.0 Hz, Ar**H**), 7.30 (2H, d, J = 8.0 Hz, Ar**H**), 7.29 (2H, d, J = 8.8 Hz, Ar**H**), 6.93 (2H, d, J = 8.8 Hz, Ar**H**), 6.61 (1H, d, J = 15.6 Hz, ArC**H**=CH), 6.24 (1H, dt, J = 16.0, 6.0 Hz, ArCH=C**H**), 4.67 (2H, ddd, J = 8.4, 6.0, 1.2 Hz, CH=CHC**H**$_2$), 4.13 (4H, dq, J = 6.8, 6.8 Hz, PO(OC**H**$_2$CH$_3$)$_2$), 2.44 (3H, s, ArC**H**$_3$), 1.33 (6H, td, J = 7.0, 0.8 Hz, PO($OCH_2C\mathbf{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 145.3, 135.0, 132.3, 132.1, 129.7, 128.4, 127.7, 124.7 (d, J = 6.5 Hz), 122.5, 67.5 (d, J = 5.3 Hz), 63.8 (d, J = 5.7 Hz), 21.6, 16.1 (d, J = 6.5 Hz); HRMS (ESI+) Calcd for $C_{20}H_{29}N_1O_7P_1S_1$ [M+NH_4]$^+$: 458.1402. Found: 458.1404.

Representative procedure for the synthesis of *E*-vinylaluminum reagents (Table 1-2): [11] Under a N_2 atmosphere, phenylethynyltrimethylsilane (1.18 mL, 6.00 mmol) and hexanes (3.75 mL) were added to 10-mL round bottom flask equipped with a reflux condenser. The resulting solution was allowed to cool to 0 °C and dibal–H (1.07 mL, 6.00 mmol) was added through a syringe. The mixture was allowed to stir at 55 °C (oil bath) for 2 hours. The vinylaluminum reagent was used without purification.

General Procedure for Cu-catalyzed Enantioselective Vinyl Additions to Allylic Phosphates (Table 1-2): A 10 mL test tube equipped with a stir bar was charged with NHC•Ag complex **5** (2.3 mg, 0.0020 mmol) in an N_2-filled glovebox. The test tube was sealed with a septum and removed from the glovebox. Tetrahydrofuran (2.0 mL) and a solution of $CuCl_2$•$2H_2O$ (0.01M in THF, 400 μL, 0.004 mmol) were added to the test tube at 22 °C. The resulting blue solution was allowed to cool to –78 °C (dry ice/acetone), followed by the addition of the vinylaluminum reagent (1.0 M in hexane, 300 μL, 0.300 mmol) and the substrate (0.200 mmol). The mixture was allowed to warm to –15 °C and stir for 6 h, after which time, the reaction was quenched by addition of a saturated aqueous solution of Rochelle's salt (3.0 mL) and allowed to stir for 1 h at

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[11] E. Negishi, T. Takahashi, S. Baba, *Org. Synth. Coll.* **1993**, *8*, 295–297.

22 °C. The organic layer was separated, and the aqueous layer was washed with Et_2O (1.0 mL x 3). The combined organic layers were passed through a short plug of $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil was purified by silica gel chromatography to give products as colorless oil.

General Procedure for Cu-catalyzed Enantioselective Vinyl Additions to Allylic Phosphates (Table 3): A 10-mL Schlenk tube equipped with a stir bar was charged with dibal–H (71 μL, 0.40 mmol) and tetrahydrofuran (65 μL, 0.80 mmol) under N_2. Alkynyldimethylsilanes (0.40 mmol) in hexanes (325 μL) were added. After allowing the mixture to stir at 55 °C for 2 hours, it was allowed to cool to –78 °C and a solution of NHC•Ag **12** (2.7 mg, 0.0020 mmol) and $CuCl_2$•$2H_2O$ (0.68 mg, 0.0040 mmol) in THF (2.4 mL) was added through a syringe. After allowing the solution to stir for 10 min, the substrate (0.20 mmol) was added and the resulting solution was allowed to warm to –15 °C (freezer) and stand for 12 hours. The reaction was quenched with a saturated aqueous solution of Rochelle's salt (3.0 mL) and allowed to stir for one hour at 22 °C. The organic layer was separated and the aqueous layer was washed with Et_2O (1 mL x 3). The combined organic layers were passed through a short plug of $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil residue was purified by silica gel chromatography to afford the desired products as colorless oil.

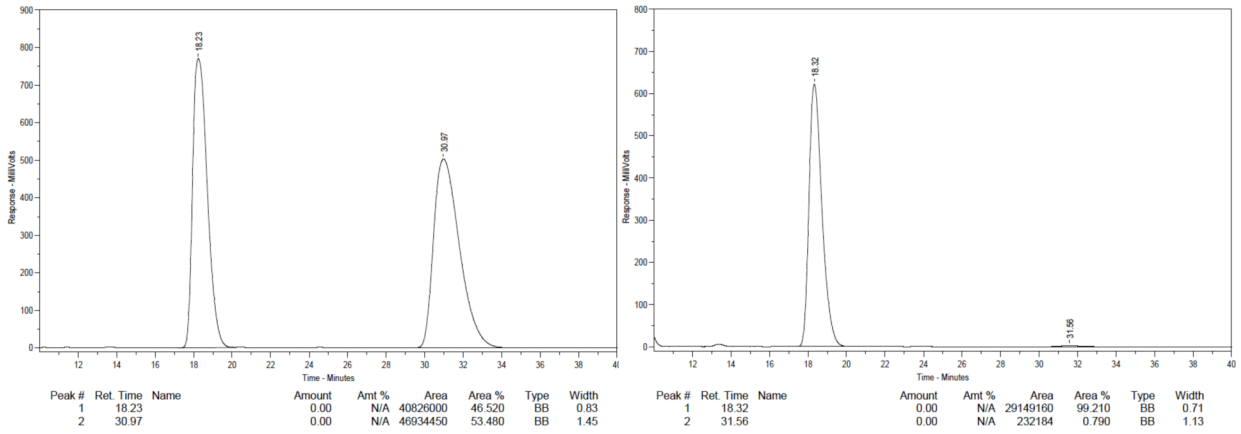
General Procedure for Hydroboration/Oxidation of 1,4-Dienes: To a 10-mL test tube charged with 1,4-diene **6b** (27.6 mg, 0.0900 mmol) in THF (1.0 mL) was added a 0.1 M THF solution of 9-BBN (1.0 mL, 0.100 mmol) under N_2 at 22 °C. The mixture was allowed to stir for 15 h. The mixture was quenched by the addition of 30% wt H_2O_2 solution (300 μL), and 2 N NaOH (300 μL), and allowed to stir for 30 min. A saturated solution of NaCl (1 mL) was added and the resulting mixture was washed with Et_2O (3 x 2 mL). Combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The colorless oil residue was purified by silica gel chromatography (Et_2O/Hexanes 1/4) to afford the desired alcohol in 73% yield (21.2 mg, 0.0653 mmol) as colorless oil.

(*S*,*E*)-(1-Benzylidene-2-phenyl-but-3-enyl)-trimethylsilane (6a, Table 1, entry 1): IR (neat): 3078 (w), 3058 (w), 3024 (w), 2953 (w), 2895 (w), 1634 (w), 1599 (w), 1491 (m), 1446 (m), 1405 (w), 1247 (s), 1062 (w), 1020 (w), 955 (w), 916 (m), 832 (s), 755 (s), 695 (s), 628 (m), 550 (w), 494 (w), 476 (w), 452 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.19 (10H, m, Ar**H**), 7.10 (1H, s, C=C**H**Ph), 6.31 (1H, ddd, J = 17.2, 10.0, 7.2 Hz, CC**H**=CHH), 5.31 (1H, dt, J = 10.4, 1.6 Hz, CH=C**H**H), 5.17 (1H, dt, J = 16.8, 1.6 Hz, CH=C**H**H), 4.95 (1H, d, J = 7.2 Hz, PhC**H**CH=CH_2), –0.02 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 142.8, 139.7, 139.2, 138.2, 128.3, 128.1, 128.0, 128.0, 126.8, 126.0, 117.1, 50.1, 0.7; HRMS (ESI+): Calcd for $C_{20}H_{25}Si_1$ $[M+H]^+$: 293.1726. Found: 293.1717. Specific rotation: $[\alpha]_D^{20}$ –67.2 (c = 0.64, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

(*S*,*E*)-3,5-Diphenyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared through hydroboration/oxidation of **6a** with 9-BBN, as described above. IR (neat): 3334 (br), 3057 (w), 3024 (w), 2950 (w), 2892 (w), 1599 (w), 1491 (w), 1445 (w), 1406 (w), 1247 (m), 1053 (w), 1025 (w), 911 (w), 831 (s), 753 (s), 696 (s), 634 (w), 582 (w), 519 (w), 486 (w), 443 (w) cm^{-1}; ^1H

NMR (400 MHz, $CDCl_3$): δ 7.37-7.18 (10H, m, Ar**H**), 7.06 (1H, s, C=C**H**Ph), 4.41 (1H, dd, *J* = 9.2, 6.0 Hz, ArC**H**CH_2CH_2OH), 3.67-3.55 (2H, m, $ArCHCH_2C\mathbf{H}_2OH$), 2.32 (1H, dddd, *J* = 14.4, 7.2, 7.2, 7.2 Hz, $ArCHC\mathbf{H}_2CH_2OH$), 2.01-1.92 (1H, m, $ArCHC\mathbf{H}_2CH_2OH$), –0.07 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 143.0, 139.8, 138.4, 128.4, 128.1, 127.7, 126.9, 126.0, 61.2, 41.0, 34.9, 0.6; HRMS (ESI+): Calcd for $C_{20}H_{27}OSi_1$ $[M+H]^+$: 311.1831. Found: 311.1841. Specific rotation: $[\alpha]_D^{20}$ –318.3 (*c* = 1.19, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 18.32 min, minor peak at 31.56 min.

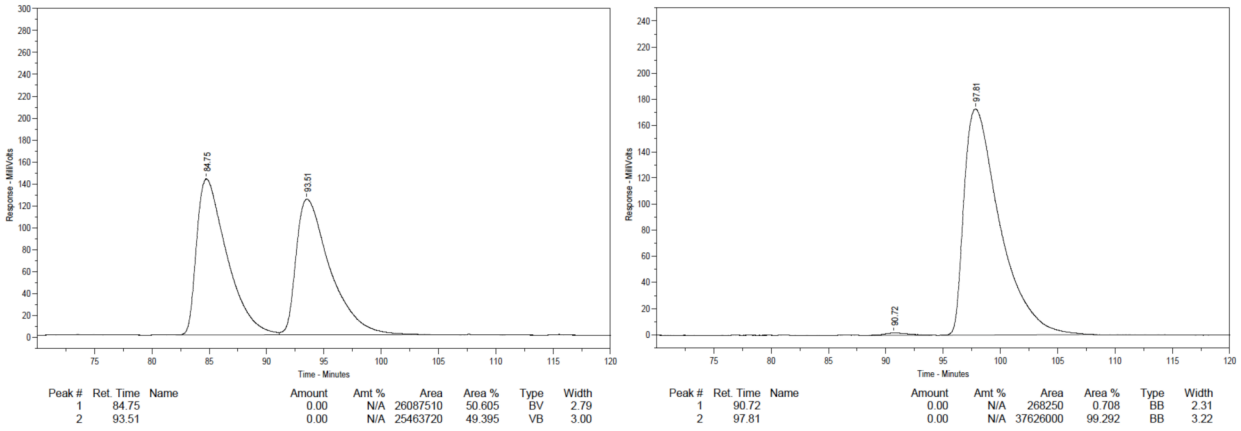


(*S*,*E*)-(1-Benzylidene-2-*o*-tolyl-but-3-enyl)-trimethylsilane (6b; Table 1, entry 2): IR (neat): 3058 (w), 3020 (w), 2951 (w), 2925 (w), 2895 (w), 2854 (w), 1634 (w), 1568 (w), 1487 (w), 1459 (w), 1443 (w), 1404 (w), 1246 (m), 1133 (w), 1018 (m), 942 (m), 833 (s), 754 (s), 728 (w), 697 (s), 628 (m), 571 (w), 495 (w), 446 (w), 396 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.30 (5H, m, Ar**H**), 7.30-7.22 (1H, m, Ar**H**), 7.15 (1H, td, *J* = 7.2, 1.6 Hz, Ar**H**), 7.10 (1H, td, *J* = 7.2, 1.6 Hz, Ar**H**), 7.09 (1H, s, PhC**H**=C), 7.03 (1H, d, *J* = 7.6 Hz, Ar**H**), 6.36 (1H, ddd, *J* = 17.6, 10.4, 4.4 Hz, CC**H**=CHH), 5.39 (1H, ddd, *J* = 10.8, 2.4, 2.0 Hz, CH=C**H**H), 5.24 (1H, ddd, *J* = 17.6, 2.2, 1.8 Hz, CH=C**H**H), 4.79-4.77 (1H, m, ArC**H**CH=CH_2), 1.85 (3H, s, Ar$C\mathbf{H}_3$), -0.16 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 141.2, 140.8, 138.1, 130.2, 128.2, 128.0, 126.9, 126.5, 125.4, 116.8, 47.9, 19.3, 0.2; HRMS (ESI+): Calcd for $C_{21}H_{27}Si_1$ $[M+H]^+$: 307.1882. Found: 307.1892. Specific rotation: $[\alpha]_D^{20}$ +35.7 (*c* = 0.74, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

(*S*,*E*)-5-Phenyl-3-*o*-tolyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **6b** using 9-BBN as described above. IR (neat): 3320 (br), 3060 (w), 3020 (w), 2949 (w), 2892 (w), 1488 (w), 1459 (w), 1443 (w), 1245 (m), 1026 (m), 918 (w), 832 (s), 754 (s), 697 (s), 636 (w), 624 (w), 511 (w), 477 (w), 441 (w), 406 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.37 (5H, m, Ar**H**), 7.29-7.25 (1H, m, Ar**H**), 7.18 (1H, t, *J* = 7.2 Hz, Ar**H**), 7.10 (1H, t, *J* = 7.2 Hz, Ar**H**), 7.05 (1H, d, *J* = 7.2 Hz, Ar**H**), 6.90 (1H, s, C=C**H**Ph), 4.30 (1H, dd, *J* = 11.2, 4.0 Hz, ArC**H**CH_2CH_2OH), 3.74-3.57 (2H, m, $ArCHCH_2C\mathbf{H}_2OH$), 2.66-2.56 (1H, m, $ArCHC\mathbf{H}_2CH_2OH$), 2.12-2.04 (1H, m, $ArCHC\mathbf{H}_2CH_2OH$), 1.89 (3H, s, Ar$C\mathbf{H}_3$), –0.15 (9H, s,

$Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 139.3, 139.0, 138.9, 138.4, 130.7, 128.5, 128.1, 126.8, 126.3, 126.2, 125.5, 60.9, 39.7, 36.6, 19.7, 0.2; HRMS (ESI+): Calcd for $C_{21}H_{29}O_1Si_1$ $[M+H]^+$: 325.1988. Found: 325.1997. Specific rotation: $[\alpha]_D^{20}$ –36.0 (*c* = 1.19, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

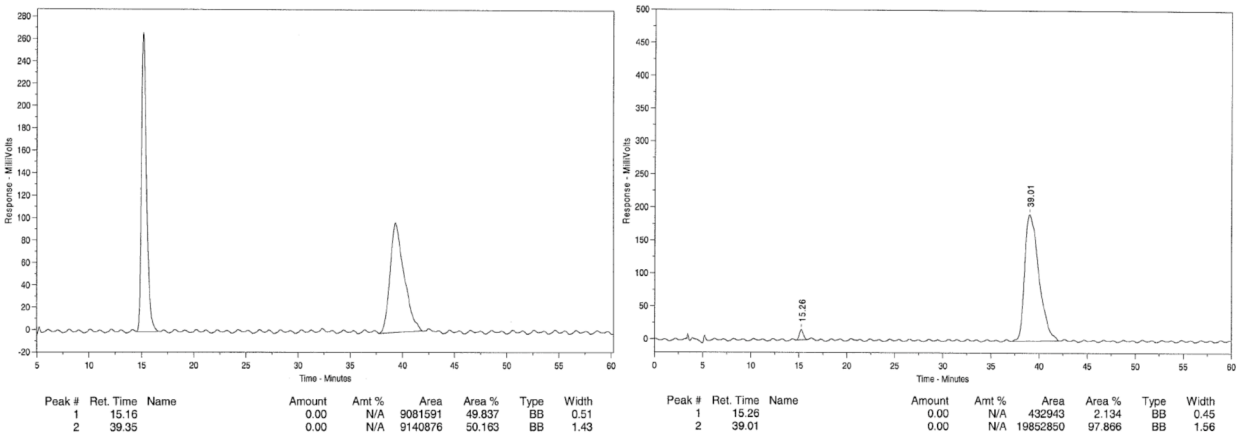
Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD-R column (25 cm x 0.46 cm), 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm). Retention time: minor peak at 90.72 min, major peak at 97.81 min.



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	84.75		0.00	N/A	26087510	50.605	BV	2.79
2	93.51		0.00	N/A	25463720	49.395	VB	3.00

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	90.72		0.00	N/A	268250	0.708	BB	2.31
2	97.81		0.00	N/A	37626000	99.292	BB	3.22

(*S*,*E*)-(3-(2-Methoxyphenyl)-1-phenylpenta-1,4-dien-2-yl)trimethylsilane (6c; Table 1, entry 3): IR (neat): 3057 (w), 2952 (w), 2833 (w), 1585 (w), 1489 (m), 1462 (m), 1241 (s), 1111 (w), 1020 (m), 916 (m), 832 (s), 752 (s), 697 (s), 627 (m), 581 (w), 485 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.31 (4H, m, Ar**H**), 7.24-7.22 (2H, m, Ar**H**), 7.19 (1H, dt, *J* = 8.0, 1.0 Hz, Ar**H**), 7.03 (1H, s, C=C**H**Ph), 6.90 (1H, dt, *J* = 7.5, 1.0 Hz, Ar**H**), 6.75 (1H, dd, *J* = 7.5, 1.0 Hz, Ar**H**), 6.26 (1H, ddd, *J* = 17.5, 10.5, 5.0 Hz, ArCHC**H**=CHH), 5.27 (1H, dt, *J* = 11.0, 2.0 Hz CH=C**H**H), 5.14 (1H, dt, *J* = 17.0, 2.0 Hz, CH=CH**H**), 5.04 (1H, d, *J* = 2.0 Hz, ArC**H**CH=CH_2), 3.63 (3H, s, ArOC$\mathbf{H}_3$), –0.13 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 143.6, 140.7, 140.3, 139.3, 131.5, 129.0, 128.3, 127.9, 127.7, 126.6, 120.0, 116.4, 110.3, 55.0, 44.8, 0.5; HRMS (ESI+): Calcd for $C_{21}H_{27}O_1Si_1$ $[M+H]^+$: 323.1831. Found: 323.1842. Specific rotation: $[\alpha]_D^{20}$ –90.5 (*c* = 1.24, $CHCl_3$) for an enantiomerically enriched sample of 96% *ee*.
Enantiomeric purity was determined by HPLC analysis of the derived primary alcohol after



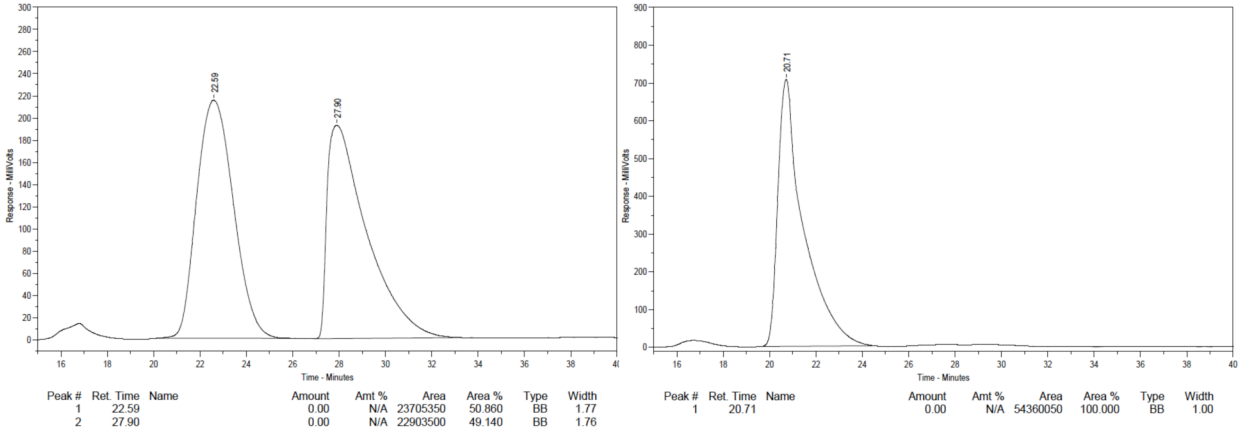
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	15.16		0.00	N/A	9081591	49.837	BB	0.51
2	39.35		0.00	N/A	9140876	50.163	BB	1.43

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	15.26		0.00	N/A	432943	2.134	BB	0.45
2	39.01		0.00	N/A	19852850	97.866	BB	1.56

hydroboration of the title compound with 9-BBN in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: minor peak 15.26 min, major peak 39.01 min.

(*S*,*E*)-[1-Benzylidene-2-(2-nitrophenyl)-but-3-enyl]-trimethylsilane (6d; Table 1, entry 4): IR (neat): 3078 (w), 3023 (w), 2953 (w), 2895 (w), 1605 (w), 1525 (s), 1443 (w), 1406 (w), 1354 (s), 1247 (s), 1018 (m), 921 (m), 833 (s), 781 (m), 756 (s), 743 (s), 695 (s), 648 (w), 626 (m) 566 (w), 492 (w), 459 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (1H, dd, *J* = 7.6, 0.8 Hz, Ar**H**), 7.48-7.42 (2H, m, Ar**H**), 7.32-7.20 (6H, m, Ar**H**), 7.04 (1H, s, C=C**H**Ph), 6.21 (1H, ddd, *J* = 17.2, 10.4, 6.0 Hz, ArCHC**H**=CHH), 5.48 (1H, d, *J* = 6.0 Hz, ArC**H**CH=CH_2), 5.38 (1H, dt, *J* = 10.4, 1.2 Hz, CH=C**H**H), 5.22 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), -0.04 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 142.5, 141.7, 138.1, 137.8, 136.6, 131.6, 130.2, 128.2, 127.8, 127.3, 127.0, 124.3, 118.2, 45.6, 0.4; HRMS (ESI+): Calcd for $C_{20}H_{24}N_1O_2Si_1$ $[M+H]^+$: 338.1576. Found: 338.1572. Specific rotation: $[\alpha]_D^{20}$ +178.3 (*c* = 0.70, $CHCl_3$) for an enantiomerically enriched sample of >98% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak AD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 0.2 mL/min, 220 nm). Retention time: major peak at 20.71, minor peak is too small to integrate.

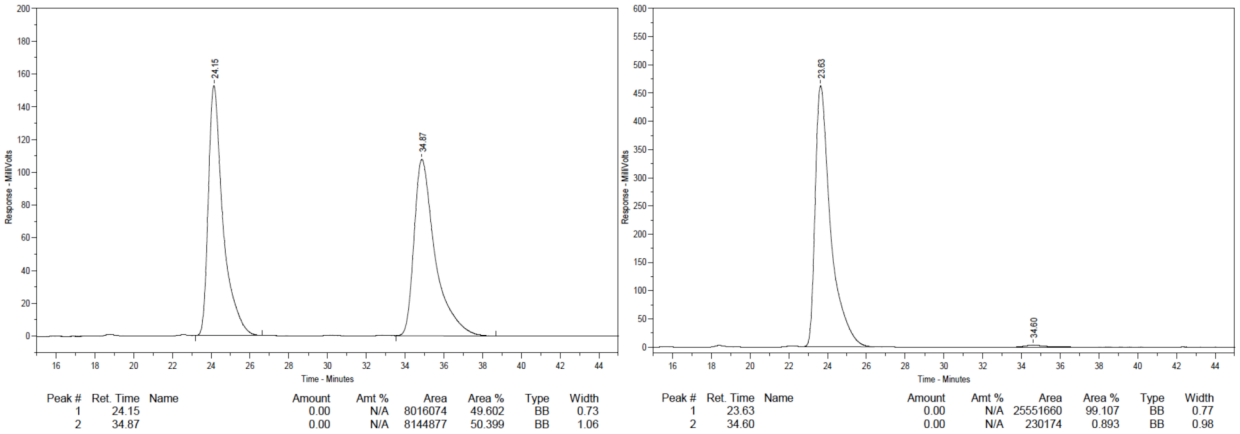


(*S*,*E*)-[1-Benzylidene-2-(3-bromophenyl)-but-3-enyl]-trimethylsilane (6e; Table 1, entry 5): IR (neat): 3077 (w), 3058 (w), 3020 (w), 2953 (w), 2894 (w), 1590 (w), 1563 (w), 1491 (w), 1470 (w), 1443 (w), 1419 (w), 1406 (w), 1247 (m), 1073 (w), 1021 (w), 995 (w), 919 (m), 832 (s), 778 (m), 758 (s), 695 (s), 630 (m), 570 (w), 491 (w), 433 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (4H, m, Ar**H**), 7.26-7.22 (3H, m, Ar**H**), 7.14-7.12 (2H, m, Ar**H**), 7.09 (1H, s, C=C**H**Ph), 6.21 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, CHC**H**=CHH), 5.30 (1H, dt, *J* = 10.4, 1.2 Hz, CH=C**H**H), 5.14 (1H, dt, *J* = 17.2, 1.2 Hz, CH=C**H**H), 4.87 (1H, d, *J* = 7.2 Hz, ArC**H**CH=CH_2), –0.02 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 144.8, 140.4, 138.4, 137.9, 131.1, 129.5, 129.1, 128.3, 128.2, 126.9, 126.6, 122.3, 117.8, 49.9, 0.7; HRMS (ESI+): Calcd for $C_{20}H_{24}Br_1Si_1$ $[M+H]^+$: 373.0810. Found: 373.0804. Specific rotation: $[\alpha]_D^{20}$ –71.2 (*c* = 0.80, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

(*S*,*E*)-3-(3-Bromophenyl)-5-phenyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **6e** with 9-BBN, as described above. IR (neat): 3344 (br), 3057 (w),

3021 (w), 2950 (w), 2892 (w), 1590 (w), 1563 (w), 1473 (w), 1442 (w), 1415 (w), 1247 (m), 1027 (m), 832 (s), 777 (w), 758 (s), 697 (s), 664 (w), 634 (m), 590 (w), 426 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (1H, brs, Ar**H**), 7.38-7.14 (8H, m, Ar**H**), 7.09 (1H, s, C=C**H**Ph), 4.37 (1H, dd, *J* = 9.6, 6.0 Hz, ArC**H**CH_2CH_2OH), 3.66-3.53 (2H, m, $ArCHCH_2C\mathbf{H}_2OH$), 2.27 (1H, dddd, *J* = 13.6, 6.8, 6.8, 6.8 Hz, $ArCHC\mathbf{H}_2CH_2OH$), 1.98-1.89 (1H, m, $ArCHC\mathbf{H}_2CH_2OH$), –0.04 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 145.7, 140.5, 138.1, 130.9, 129.6, 129.1, 128.5, 128.0, 127.0, 126.3, 122.4, 60.9, 40.9, 34.9, 0.7; HRMS (ESI+): Calcd for $C_{20}H_{26}Br_1O_1Si_1$ $[M+H]^+$: 391.0916. Found: 391.0926. Specific rotation: $[\alpha]_D^{20}$ –283.8 (*c* = 1.49, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 23.63 min, minor peak at 34.60 min.



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	24.15		0.00	N/A	8016074	49.602	BB	0.73
2	34.87		0.00	N/A	8144877	50.399	BB	1.06

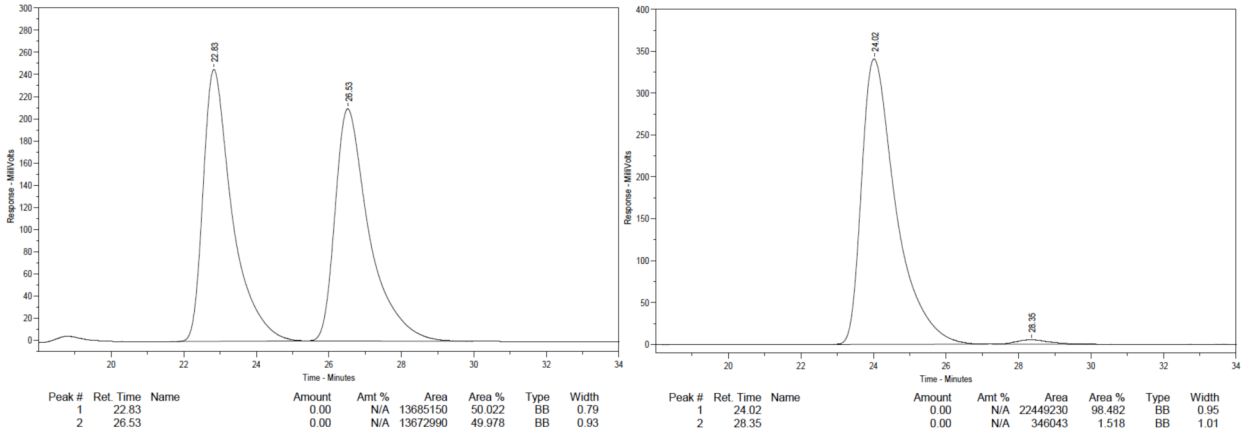
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	23.63		0.00	N/A	25551660	99.107	BB	0.77
2	34.60		0.00	N/A	230174	0.893	BB	0.98

(*S*,*E*)-[1-Benzylidene-2-(4-chlorophenyl)-but-3-enyl]-trimethylsilane (6f; Table 1, entry 6): IR (neat): 3077 (w), 3022 (w), 2954 (w), 2895 (w), 1634 (w), 1588 (m), 1571 (w), 1488 (s), 1443 (w), 1404 (w), 1247 (s), 1091 (m), 1070 (w), 1014 (m), 995 (w), 918 (m), 832 (s), 757 (s), 725 (w), 696 (s), 630 (m), 574 (m), 472 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (2H, m, Ar**H**) 7.26-7.21 (5H, m, Ar**H**), 7.15-7.11 (2H, m, Ar**H**), 7.07 (1H, s, C=C**H**Ph), 6.21 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, CC**H**=CHH), 5.28 (1H, dt, *J* = 10.4, 1.4 Hz, CH=C**H**H), 5.14 (1H, dt, *J* = 17.2, 1.4 Hz, CH=C**H**H), 4.85 (1H, d, *J* = 7.2 Hz, ArC**H**$CH=CH_2$), -0.03 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 141.4, 140.2, 138.7, 138.0, 131.9, 129.4, 128.3, 128.2, 128.1, 126.9, 117.5, 49.6, 0.7; HRMS (ESI+): Calcd for $C_{20}H_{24}Cl_1Si_1$ $[M+H]^+$: 327.1336. Found: 327.1344. Specific rotation: $[\alpha]_D^{20}$ –107.7 (*c* = 0.86, $CHCl_3$) for an enantiomerically enriched sample of 97% *ee*.

(*S*,*E*)3-(4-Chlorophenyl)-5-phenyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **6f** with 9-BBN as described above. IR (neat): 3331 (br), 2950 (w), 1489 (m), 1442 (w), 1403 (w), 1248 (m), 1091 (m), 1050 (w), 1027 (w), 1012 (m), 832 (s), 758 (s), 696 (s), 633 (w), 581 (w), 546 (w), 469 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (7H, m, Ar**H**), 7.20 (2H, d, *J* = 8.8 Hz, Ar**H**), 7.07 (1H, s, C=C**H**Ph), 4.35 (1H, dd, *J* = 9.2, 6.0 Hz, ArC**H**CH_2CH_2OH), 3.66-3.53 (2H, m, $ArCHCH_2C\mathbf{H}_2OH$), 2.27 (1H, dddd, *J* = 13.6, 6.8, 6.8, 6.8 Hz, $ArCHC\mathbf{H}_2CH_2OH$), 1.99-1.90 (1H, m, $ArCHC\mathbf{H}_2CH_2OH$), –0.05 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 147.1, 141.7, 140.3, 138.2, 131.7, 129.1, 128.5, 128.2, 128.0, 127.0, 61.0, 40.5, 34.9, 0.7; HRMS (ESI+): Calcd for $C_{20}H_{26}Cl_1O_1Si_1$ $[M+H]^+$: 345.1441. Found: 345.1441. Specific rotation: $[\alpha]_D^{20}$ –346.5 (*c* = 1.58, $CHCl_3$) for an enantiomerically enriched sample of 97% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 24.02 min, minor peak at 28.35 min.

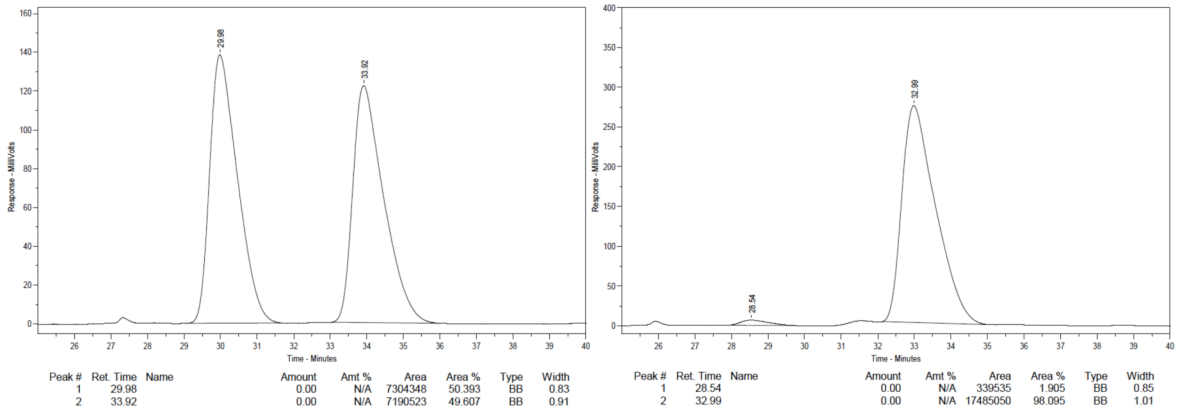


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	22.83		0.00	N/A	13685150	50.022	BB	0.79
2	26.53		0.00	N/A	13672990	49.978	BB	0.93

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	24.02		0.00	N/A	22449230	98.482	BB	0.95
2	28.35		0.00	N/A	346043	1.518	BB	1.01

(*S*,*E*)-[1-Benzylidene-2-(4-nitrophenyl)-but-3-enyl]-trimethylsilane (6g; Table 1, entry 7): IR (neat): 3077 (w), 3057 (w), 3020 (w), 2954 (w), 2895 (w), 1594 (m), 1516 (s), 1490 (m), 1443 (w), 1407 (w), 1342 (s), 1248 (s), 1108 (w), 1070 (w), 1014 (w), 995 (w), 920 (m), 831 (s), 757 (s), 696 (s), 629 (m), 573 (m), 547 (w), 481 (w), 461 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (2H, dt, *J* = 8.8, 2.2 Hz, Ar**H**), 7.38-7.30 (4H, m, Ar**H**), 7.27-7.22 (3H, m, Ar**H**), 7.13 (1H, s, C=C**H**Ph), 6.24 (1H, ddd, *J* = 17.2, 10.0, 7.6 Hz, ArCHC**H**=CHH), 5.36 (1H, dt, *J* = 10.0, 1.2 Hz, CH=C**H**H), 5.20 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.95 (1H, d, *J* = 7.6 Hz, ArC**H**CH=CH_2), –0.02 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 146.4, 144.2, 141.1, 137.7, 128.7, 128.3, 128.1, 127.1, 123.2, 118.5, 50.3, 0.7; HRMS (ESI+): Calcd for $C_{20}H_{24}NO_2Si_1$ $[M+H]^+$: 338.1576. Found: 338.1572. Specific rotation: $[\alpha]_D^{20}$ –166.1 (*c* = 0.89, $CHCl_3$) for an enantiomerically enriched sample of 96% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic



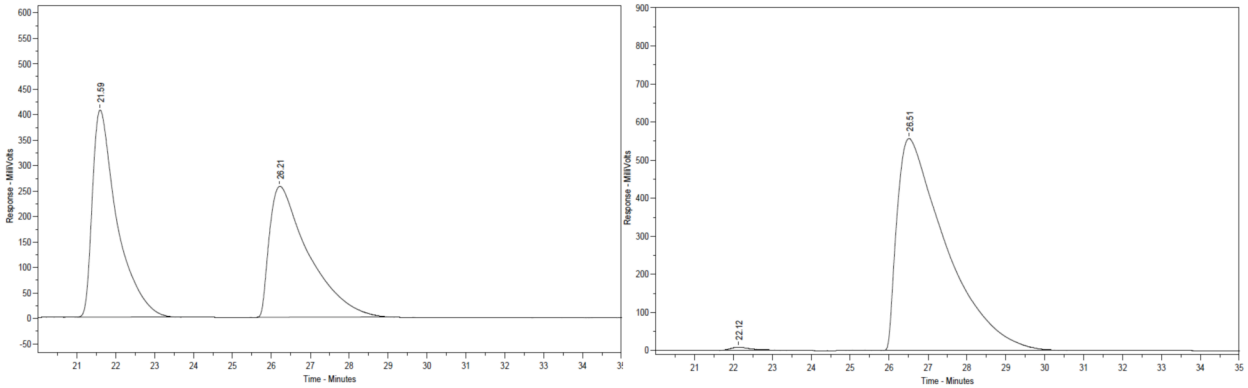
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	29.98		0.00	N/A	7304348	50.393	BB	0.83
2	33.92		0.00	N/A	7190523	49.607	BB	0.91

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	28.54		0.00	N/A	339535	1.905	BB	0.85
2	32.99		0.00	N/A	17485050	98.095	BB	1.01

material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 0.2 mL/min, 220 nm). Retention time: minor peak at 28.54 min, major peak at 32.99 min.

(*S*,*E*)-Toluene-4-sulfonic acid 4-(3-phenyl-2-trimethylsilanyl-1-vinyl-allyl)-phenyl ester (6h, Table 1, entry 8): IR (neat): 3076 (w), 3056 (w), 2954 (br), 2895 (w), 1597 (w), 1497 (s), 1444 (w), 1405 (w), 1373 (s), 1248 (m), 1198 (s), 1176 (s), 1153 (s), 1092 (s), 1017 (m), 919 (m), 833 (s), 812 (w), 755 (s), 722 (w), 698 (s), 666 (s), 631 (m), 550 (s), 514 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (2H, dt, *J* = 8.4, 1.6 Hz, Ar**H**), 7.34-7.20 (7H, m, Ar**H**), 7.08 (2H, dd, *J* = 8.8, 0.8 Hz, Ar**H**), 7.04 (1H, s, C=C**H**Ph), 6.86 (2H, dt, *J* = 8.8, 2.0 Hz, Ar**H**), 6.20 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, ArCHC**H**=CHH), 5.28 (1H, dt, *J* = 10.0, 1.2 Hz, CH=C**H**H), 5.13 (1H, dt, *J* = 17.2, 1.2 Hz, CH=C**H**H), 4.85 (1H, d, *J* = 6.8 Hz, ArC**H**CH=CH_2), 2.42 (3H, s, ArC$\mathbf{H}_3$), -0.09 (9H, s, Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 145.1, 145.0, 142.0, 140.2, 138.5, 137.9, 132.1, 129.6, 129.1, 128.6, 128.2, 128.1, 126.9, 121.9, 117.6, 49.5, 21.6, 0.7; HRMS (ESI+): Calcd for $C_{27}H_{31}O_3S_1Si_1$ $[M+H]^+$: 463.1763. Found: 463.1752. Specific rotation: $[\alpha]_D^{20}$ –62.1 (*c* = 0.69, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm). Retention time: minor peak at 22.12 min, major peak at 26.51 min.



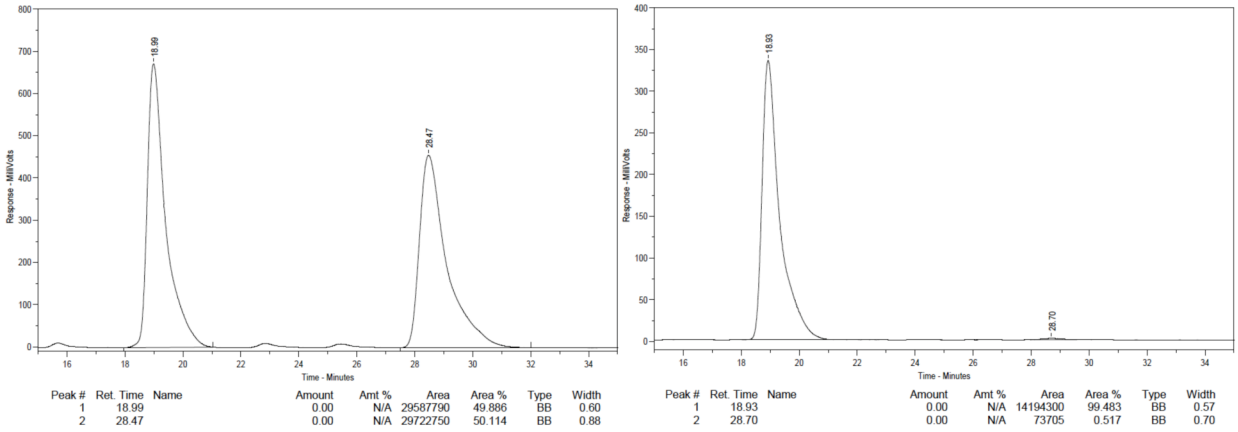
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	21.59		0.00	N/A	17902000	49.920	BB	0.62
2	26.21		0.00	N/A	17959370	50.080	BB	1.02

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	22.12		0.00	N/A	357545	0.731	BB	0.60
2	26.51		0.00	N/A	48559890	99.269	BB	1.30

(*S*,*E*)-(1-Benzylidene-2-*p*-tolyl-but-3-enyl)-trimethylsilane (6i; Table 1, entry 9): IR (neat): 3077 (w), 3054 (w), 3020 (w), 2953 (w), 2922 (w), 2895 (w), 1634 (w), 1588 (w), 1509 (w), 1491 (w), 1443 (w), 1405 (w), 1247 (m), 1070 (w), 1019 (w), 995 (w), 916 (m), 832 (s), 783 (w), 756 (s), 697 (s), 631 (m), 601 (w), 561 (w), 548 (w), 488 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (5H, m, Ar**H**), 7.12-7.07 (4H, m, Ar**H**), 7.06 (1H, s, C=C**H**Ph), 6.27 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, ArCHC**H**=CHH), 5.26 (1H, ddd, *J* = 10.0, 2.0, 1.2 Hz, CH=C**H**H), 5.13 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.89 (1H, d, *J* = 7.2 Hz, ArC**H**CH=CH_2), 2.32 (3H, s, ArC$\mathbf{H}_3$), -0.02 (9H, s, Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 139.7, 139.6, 139.5, 138.2, 135.5, 128.7, 128.3, 128.1, 127.9, 126.7, 116.8, 49.8, 20.9, 0.7; HRMS (ESI+): Calcd for $C_{21}H_{27}Si_1$ $[M+H]^+$: 307.1882. Found: 307.1873. Specific rotation: $[\alpha]_D^{20}$ –102.0 (*c* = 0.80, $CHCl_3$) for an enantiomerically enriched sample of >98% *ee*.

(*S*,*E*)-5-Phenyl-3-*p*-tolyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **6i** with 9-BBN, as described previously. IR (neat): 3337 (br), 3053 (w), 3020 (w), 2949 (w), 2892 (w), 1586 (w), 1511 (w), 1489 (w), 1442 (w), 1406 (w), 1247 (m), 1027 (m), 831 (s), 756 (s), 698 (s), 633 (w), 604 (w), 515 (w), 470 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.22 (5H, m, Ar**H**), 7.17 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.10 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.05 (1H, s, C=C**H**Ph), 4.36 (1H, dd, *J* = 9.2, 6.0 Hz, ArC**H**CH_2CH_2OH), 3.66-3.54 (2H, m, $ArCHCH_2C\mathbf{H}_2OH$), 2.33 (3H, s, $ArC\mathbf{H}_3$), 2.35-2.27 (1H, m, $ArCHC\mathbf{H}_2CH_2OH$), 1.99-1.90 (1H, m, $ArCHC\mathbf{H}_2CH_2OH$), –0.05 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 139.9, 139.6, 138.4, 135.5, 128.8, 128.4, 128.1, 127.6, 126.8, 61.3, 40.6, 35.0, 20.9, 0.7; HRMS (ESI+): Calcd for $C_{21}H_{29}O_1Si_1$ $[M+H]^+$: 325.1988. Found: 325.1973. Specific rotation: $[\alpha]_D^{20}$ –362.5 (*c* = 1.11, $CHCl_3$) for an enantiomerically enriched sample of >98% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 18.93 min, minor peak at 28.70 min.

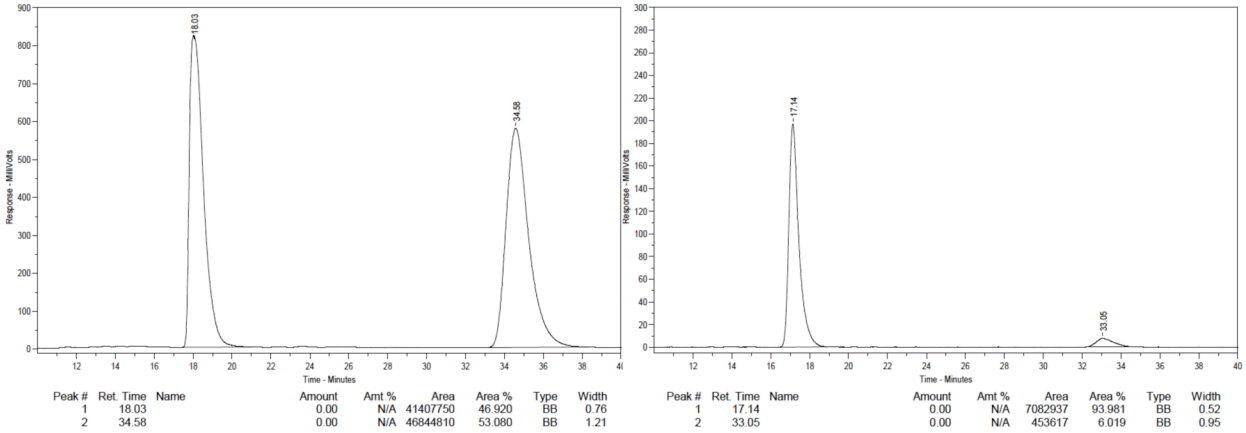


(*R*,*E*)-(1-Benzylidene-2-phenethyl-but-3-enyl)-trimethylsilane (6j; Table 1, entry 10): IR (neat): 3060 (w), 3025 (w), 2950 (w), 2858 (w), 1632 (w), 1602 (w), 1586 (w), 1493 (w), 1453 (w), 1443 (w), 1407 (w), 1247 (m), 1070 (w), 1028 (w), 993 (w), 960 (w), 912 (m), 831 (s), 758 (s), 695 (s), 632 (m), 569 (w), 487 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.04 (10H, m, Ar**H**), 6.95 (1H, s, C=C**H**Ph), 5.94 (1H, ddd, *J* = 17.2, 10.4, 6.4 Hz, CC**H**=CHH), 5.06 (1H, dt, *J* = 10.4, 1.6 Hz, CH=C**H**H), 5.00 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 3.59 (1H, q, *J* = 7.2 Hz, $ArCH_2CH_2C\mathbf{H}CH=CH_2$), 2.55-2.39 (2H, m, $PhC\mathbf{H}_2CH_2$), 1.90-1.76 (2H, m, $PhCH_2C\mathbf{H}_2$), 0.02 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 142.3, 141.8, 139.7, 138.7, 128.4, 128.3, 128.2, 128.0, 126.4, 125.5, 114.8, 45.4, 36.1, 33.9, 1.3; HRMS (ESI+): Calcd for $C_{22}H_{29}Si_1$ $[M+H]^+$: 321.2039. Found: 321.2025. Specific rotation: $[\alpha]_D^{20}$ +77.7 (*c* = 1.03, $CHCl_3$) for an enantiomerically enriched sample of 88% *ee*.

(*R*,*E*)-3-Phenethyl-5-phenyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **6j** using 9-BBN as described above. IR (neat): 3339 (br), 3059 (w), 3024 (w), 2944 (w), 2859 (w), 1601 (w), 1584 (w), 1492 (w), 1453 (w), 1406 (w), 1248 (m), 1051 (w), 1028 (w), 915 (w), 831 (s), 760 (s), 696 (s), 634 (m), 574 (w), 515 (w), 486 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.08 (10H, m, Ar**H**), 7.00 (1H, s, C=C**H**Ph), 3.56-3.44 (2H, m, $CHCH_2C\mathbf{H}_2OH$),

3.03 (1H, ddd, *J* = 14.8, 8.8, 6.4 Hz, $PhCH_2CH_2C\mathbf{H}CH_2CH_2OH$), 2.59 (1H, ddd, *J* = 14.0, 9.6, 6.8 Hz, $PhC\mathbf{H_2}CH_2CHCH_2CH_2OH$), 2.46 (1H, ddd, *J* = 14.0, 9.6, 6.8 Hz, $PhC\mathbf{H_2}CH_2CHCH_2CH_2OH$), 1.81-1.62 (4H, m, $PhCH_2C\mathbf{H_2}CHC\mathbf{H_2}CH_2OH$), 0.25 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 142.4, 140.7, 138.8, 128.3, 128.2, 126.5, 125.7, 61.3, 37.8, 37.1, 34.3, 1.4; HRMS (ESI+): Calcd for $C_{22}H_{30}O_1Si_1Na$ $[M+Na]^+$: 361.1964. Found: 361.1960. Specific rotation: $[\alpha]_D^{20}$ –89.0 (*c* = 1.31, $CHCl_3$) for an enantiomerically enriched sample of 88% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD-R column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 17.14 min, minor peak at 33.05 min.

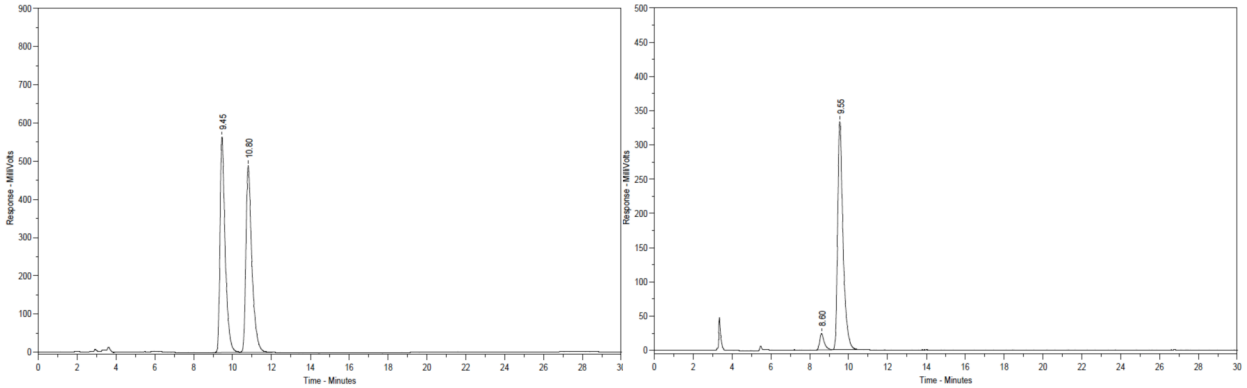


(*S*,*E*)-(1-Benzylidene-2-cyclohexyl-but-3-enyl)-trimethylsilane (6k; Table 1, entry 11): IR (neat): 3074 (w), 2921 (m), 2849 (m), 1490 (w), 1447 (w), 1407 (w), 1247 (m), 1061 (w), 1028 (w), 933 (w), 909 (m), 889 (w), 831 (s), 758 (s), 721 (w), 697 (s), 657 (w), 633 (w), 480 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (2H, m, Ar**H**), 7.21-7.15 (3H, m, Ar**H**), 6.90 (1H, s, C=C**H**Ph), 5.86 (1H, ddd, *J* = 17.2, 10.4, 8.6 Hz, CyCHC**H**=CHH), 4.97 (1H, ddd, *J* = 10.0, 2.0, 0.8 Hz, CyCH=C**H**H), 4.89 (1H, ddd, *J* = 17.2, 2.0, 1.2 Hz, CyCH=C**H**H), 3.14 (1H, t, *J* = 7.2 Hz, Cy**H**CH=CH_2), 1.76-1.50 (5H, m, Cy**H**), 1.34 (1H, qt, *J* = 11.2, 3.2 Hz, Cy**H**) 1.20-0.95 (3H, m, Cy**H**), 0.70-0.50 (2H, m, Cy**H**), 0.20 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 140.8, 139.6, 139.3, 128.4, 127.9, 126.2, 114.8, 53.1, 39.9, 32.0, 31.6, 26.4, 26.3, 1.3; HRMS (ESI+): Calcd for $C_{20}H_{31}Si_1$ $[M+H]^+$: 299.2195. Found: 299.2201. Specific rotation: $[\alpha]_D^{20}$ +168.8 (*c* = 0.70, $CHCl_3$) for an enantiomerically enriched sample of 88% *ee*.

(*S*,*E*)-3-Cyclohexyl-5-phenyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **6k** with 9-BBN, as described above. IR (neat): 3314 (br), 2921 (m), 2849 (w), 1585 (w), 1490 (w), 1447 (w), 1406 (w), 1247 (m), 1051 (w), 1030 (w), 1009 (w), 974 (w), 956 (w), 914 (w), 890 (w), 831 (s), 759 (s), 700 (s), 685 (w), 634 (m), 567 (w), 526 (w), 490 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.16 (5H, m, Ar**H**), 7.00 (1H, s, C=C**H**Ph), 3.53-3.48 (1H, m, $CyCHCH_2C\mathbf{H}_2OH$), 3.43-3.36 (1H, m, $CyCHCH_2C\mathbf{H}_2OH$), 2.61 (1H, td, *J* = 10.8, 3.6 Hz, Cy**H**CH_2CH_2OH), 1.91-1.60 (7H, m, **Cy**$CHC\mathbf{H}_2CH_2OH$), 1.47-1.09 (4H, m, **Cy**$CHCH_2CH_2OH$), 0.87-0.68 (2H, m, **Cy**$CHCH_2CH_2OH$), 0.22 (9H, s, $Si(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 140.6, 138.9, 128.3, 128.1, 126.4, 61.7, 43.8, 41.2, 34.7, 33.2, 31.3,

26.7, 26.5, 1.4; HRMS (ESI+): Calcd for $C_{20}H_{33}O_1Si_1$ $[M+H]^+$: 317.2301. Found: 317.2299. Specific rotation: $[\alpha]_D^{20}$ –109.1 (*c* = 1.05, $CHCl_3$) for an enantiomerically enriched sample of 88% *ee*.

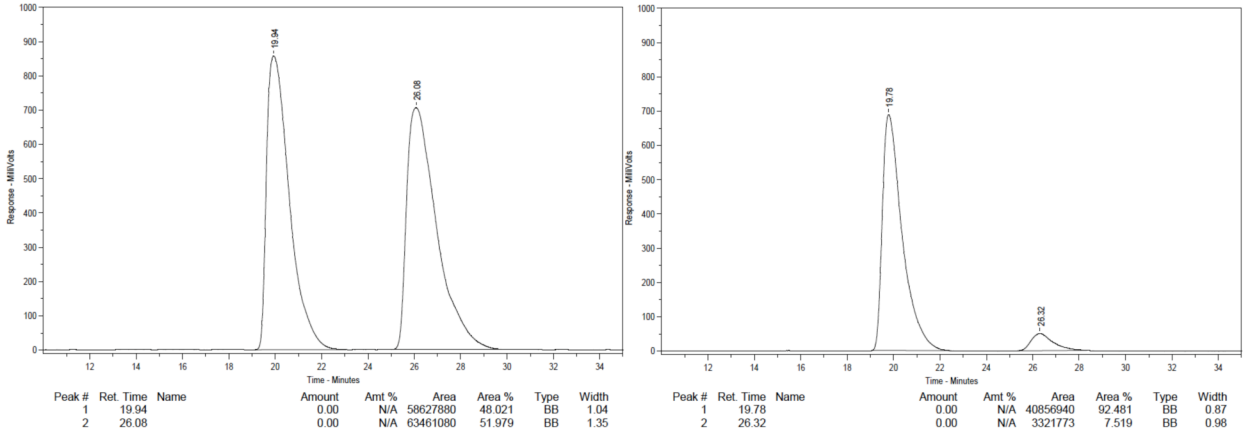
Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD-R column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: minor peak at 8.60 min, major peak at 9.55 min.



(*S*,*E*)-[1-(2-Methoxybenzylidene)-2-phenyl-but-3-enyl]-trimethylsilane (7a; Table 2, entry 1): IR (neat): 3077 (w), 3059 (w), 3024 (w), 2953 (w), 2895 (w), 2834 (w), 1598 (w), 1484 (w), 1462 (w), 1434 (w), 1406 (w), 1291 (w), 1246 (s), 1175 (w), 1161 (w), 1108 (w), 1048 (w), 1028 (w), 996 (w), 916 (w), 831 (s), 746 (s), 698 (s), 630 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.14 (7H, m, Ar**H**), 7.05 (1H, s, C=C**H**Ar), 6.88-6.83 (2H, m, Ar**H**), 6.26 (1H, ddd, *J* = 17.2, 10.4, 7.2 Hz, PhCHC**H**=CHH), 5.25 (1H, dt, *J* = 10.0, 1.2 Hz, CH=C**H**H), 5.11 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.81 (1H, d, *J* = 7.6 Hz, PhC**H**CH=CH_2), 3.83 (3H, s, ArOC**H**$_3$), -0.05 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 145.0, 143.1, 139.4, 136.2, 129.4, 128.2, 128.1, 127.9, 127.3, 125.8, 119.9, 116.8, 110.6, 55.5, 50.5, 0.8; HRMS (ESI+): Calcd for $C_{21}H_{27}O_1Si_1$ $[M+H]^+$: 323.1831. Found: 323.1828. Specific rotation: $[\alpha]_D^{20}$ –38.7 (*c* = 0.80, $CHCl_3$) for an enantiomerically enriched sample of 84% *ee*.

(*S*,*E*)-5-(2-Methoxyphenyl)-3-phenyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **7a** with 9-BBN, as described before. IR (neat): 3369 (br), 3059 (w), 3025 (w), 2950 (w), 1599 (w), 1484 (w), 1462 (w), 1434 (w), 1289 (w), 1241 (s), 1174 (w), 1160 (w), 1109 (w), 1048 (w), 1025 (m), 831 (s), 746 (s), 698 (s), 634 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.15 (7H, m, Ar**H**), 6.96 (1H, s, C=C**H**Ar), 6.93-6.89 (2H, m, Ar**H**), 4.20 (1H, dd, *J* = 9.6, 5.6 Hz, PhC**H**CH_2CH_2OH), 3.83 (s, 3H, ArOC**H**$_3$), 3.57 (2H, t, *J* = 6.4 Hz, PhCHCH_2C**H**$_2$OH), 2.28-2.20 (1H, m, PhCHC**H**$_2CH_2$OH), 1.99-1.90 (1H, m, PhCHC**H**$_2CH_2$OH), -0.08 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 147.8, 143.5, 136.4, 129.4, 128.4, 128.0, 127.8, 127.4, 125.9, 120.3, 110.7, 61.4, 55.4, 42.0, 35.0, 0.7; HRMS (ESI+): Calcd for $C_{21}H_{29}O_2Si_1$ $[M+H]^+$: 341.1937. Found: 341.1938. Specific rotation: $[\alpha]_D^{20}$ –290.4 (*c* = 0.23, $CHCl_3$) for an enantiomerically enriched sample of 84% *ee*.

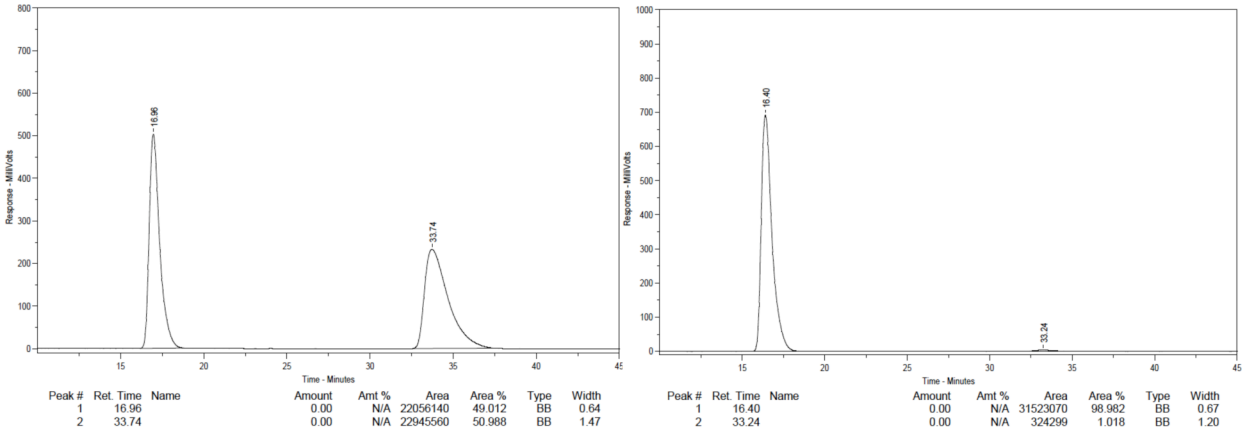
Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 19.78 min, minor peak at 26.32 min.



(*S*,*E*)-Trimethyl-[1-(3-methyl-benzylidene)-2-phenyl-but-3-enyl]-silane (7b, Table 2, entry 2): IR (neat): 3080 (w), 3058 (w), 3025 (w), 2953 (w), 2921 (w), 2895 (w), 1599 (w), 1491 (w), 1447 (w), 1405 (w), 1246 (m), 1023 (w), 995 (w), 915 (m), 831 (s), 788 (w), 753 (s), 735 (w), 696 (s), 633 (w), 575 (w), 554 (w), 480 (w), 457 (w), 438 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.03 (9H, m, Ar**H**), 7.02 (1H, s, C=C**H**Ar), 6.27 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, PhCHC**H**=CHH), 5.27 (1H, ddd, *J* = 10.4, 2.0, 1.2 Hz, CH=C**H**H), 5.13 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.92 (1H, d, *J* = 7.2 Hz, PhC**H**CH=CH_2), 2.30 (3H, s, ArC$\mathbf{H}_3$), -0.07 (9H, s, Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 143.0, 139.9, 139.3, 138.1, 137.6, 129.1, 128.1, 128.0, 127.5, 126.0, 125.2, 117.0, 50.1, 21.4, 0.7; HRMS (ESI+): Calcd for $C_{21}H_{27}Si_1$ $[M+H]^+$: 307.1882. Found: 307.1871. Specific rotation: $[\alpha]_D^{20}$ –55.4 (*c* = 0.66, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

(*S*,*E*)-3-Phenyl-5-*m*-tolyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **7b** in the presence of 9-BBN, as described above. IR (neat): 3332 (br), 3085 (w), 3057 (w), 3025 (w), 2950 (w), 2892 (w), 1600 (w), 1493 (w), 1447 (w), 1406 (w), 1247 (m), 1024 (w), 907 (w), 831 (s), 752 (s), 732 (m), 697 (s), 636 (w), 592 (w), 438 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.04 (9H, m, Ar**H**), 7.02 (1H, s, C=C**H**Ar), 4.41 (1H, dd, *J* = 9.6, 6.4 Hz, PhC**H**CH_2CH_2OH), 3.64-3.57 (2H, m, PhCHCH_2C$\mathbf{H}_2$OH), 2.33 (3H, s, ArC$\mathbf{H}_3$), 2.38-2.26 (1H, m, PhCHC$\mathbf{H}_2CH_2OH$), 1.99-1.91 (1H, m, PhCHC$\mathbf{H}_2CH_2OH$), -0.09 (9H, s, Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 143.1, 139.9, 138.3, 138.0, 128.8, 128.3, 128.1, 127.8, 127.6, 126.0, 125.1, 61.2, 41.0, 34.9, 21.4, 0.6; HRMS (ESI+): Calcd for $C_{21}H_{29}O_1Si_1$ $[M+H]^+$: 325.1988. Found: 325.1988. Specific rotation: $[\alpha]_D^{20}$ –304.0 (*c* = 1.21, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

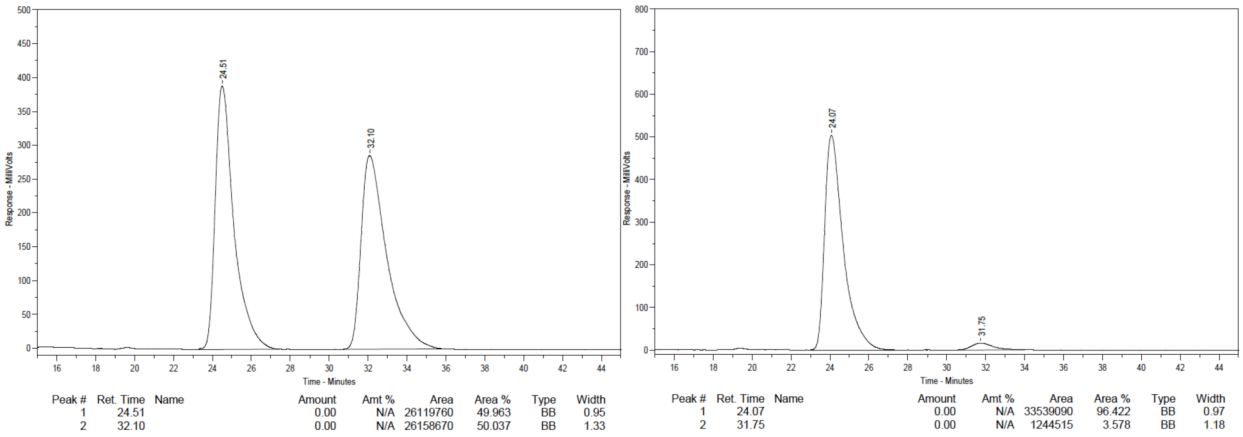
Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 16.40 min, minor peak at 33.24 min.



(*S*,*E*)-[1-(4-Fluoro-benzylidene)-2-phenyl-but-3-enyl]-trimethylsilane (7c; Table 2, entry 3): IR (neat): 3080 (w), 3060 (w), 2954 (w), 2895 (w), 1635 (w), 1601 (w), 1504 (s), 1448 (w), 1407 (w), 1247 (m), 1221 (m), 1157 (w), 1093 (w), 1062 (w), 1021 (w), 995 (w), 918 (w), 830 (s), 782 (w), 755 (m), 739 (s), 698 (s), 617 (w), 554 (w), 521 (w), 495 (w), 458 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.16 (7H, m, Ar**H**), 7.01-6.96 (3H, m, Ar**H**, C=C**H**Ar), 6.27 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, CHC**H**=CHH), 5.28 (1H, dt, *J* = 10.4, 1.6 Hz, CH=C**H**H), 5.13 (1H, dt, *J* = 16.8, 1.6 Hz, CH=C**H**H), 4.85 (1H, d, *J* = 7.2 Hz, PhC**H**CH=CH_2), –0.05 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, *J* = 244.8 Hz), 145.7, 142.7, 139.1, 138.6, 134.1 (d, *J* = 3.4 Hz), 129.9 (d, *J* = 8.0 Hz), 128.1, 128.0, 126.2, 117.1, 115.0 (d, *J* = 21.3 Hz), 50.1, 0.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.7 (tt, *J* = 9.0, 5.3 Hz); HRMS (ESI+): Calcd for $C_{21}H_{24}F_1Si_1$ $[M+H]^+$: 311.1631. Found: 311.1619. Specific rotation: $[\alpha]_D^{20}$ –57.2 (*c* = 1.06, $CHCl_3$) for an enantiomerically enriched sample of 93% *ee*.

(*S*,*E*)-5-(4-Fluorophenyl)-3-phenyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **7c** with 9-BBN, as described above. IR (neat): 3332 (br), 3085 (w), 3059 (w), 3027 (w), 2950 (w), 2893 (w), 1601 (w), 1503 (s), 1447 (w), 1406 (w), 1247 (m), 1221 (m), 1156 (w), 1093 (w), 1054 (w), 1024 (w), 972 (w), 910 (w), 831 (s), 754 (m), 739 (s), 697 (s), 640 (w), 622 (w), 571 (w), 533 (w), 494 (w), 443 (w), 421 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.15 (7H, m, Ar**H**), 7.02 (2H, tt, *J* = 8.8, 2.0 Hz, Ar**H**), 6.97 (1H, s, C=C**H**Ar), 4.29 (1H, dd, *J* = 8.8, 6.4 Hz, PhC**H**CH_2CH_2OH), 3.67-3.54 (2H, m, PhCHCH_2C**H**$_2$OH), 2.33 (1H, dddd, *J* = 13.6, 6.8, 6.8, 6.8 Hz, PhCHC**H**$_2CH_2OH$), 2.00-1.92 (1H, m, PhCHC**H**$_2CH_2OH$), -0.08 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, *J* = 244.8 Hz), 148.0, 142.8, 138.6, 134.3 (d, *J* = 3.2 Hz), 129.9 (d, *J* = 8.0 Hz), 128.2, 127.7, 126.1, 115.3 (d, *J* = 20.9 Hz), 61.3, 41.1, 35.0, 0.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ –115.6 (tt, *J* = 8.8, 5.3 Hz); HRMS (ESI+): Calcd for $C_{20}H_{26}F_1O_1Si_1$ $[M+H]^+$: 329.1737. Found: 329.1743. Specific rotation: $[\alpha]_D^{20}$ –267.5 (*c* = 1.17, $CHCl_3$) for an enantiomerically enriched sample of 93% *ee*.

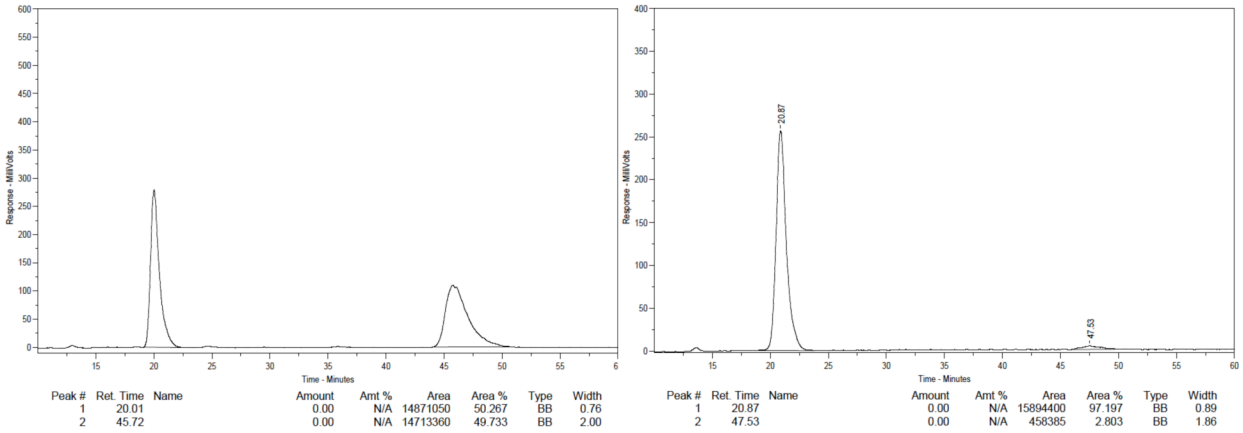
Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 24.07 min, minor peak at 31.75 min.



(*S*,*E*)-Trimethyl-[2-phenyl-1-(4-trifluoromethyl-benzylidene)-but-3-enyl]-silane (7d, Table 2, entry 4): IR (neat): 3082 (w), 3061 (w), 2955 (w), 2897 (w), 1616 (w), 1600 (w), 1492 (w), 1448 (w), 1408 (w), 1321 (s), 1248 (m), 1163 (m), 1123 (s), 1107 (w), 1066 (s), 1016 (m), 919 (w), 832 (s), 756 (s), 699 (m), 641 (m), 597 (w), 554 (w), 507 (w), 458 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.37 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.29-7.24 (2H, m, Ar**H**), 7.20-7.15 (3H, m, Ar**H**), 7.05 (1H, s, C=C**H**Ar), 6.26 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, CHC**H**=CHH), 5.29 (1H, ddd, *J* = 10.4, 1.6, 1.2 Hz, CH=C**H**H), 5.12 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.80 (1H, d, *J* = 7.2 Hz, PhC**H**CH=CH_2), –0.03 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 142.3, 141.9, 138.9, 138.2, 128.6, 128.5 (q, *J* = 32.3 Hz), 128.1, 127.9, 126.3, 125.0 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.6 Hz), 117.4, 50.3, 0.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.87; HRMS (ESI+): Calcd for $C_{21}H_{24}F_3Si_1$ $[M+H]^+$: 361.1599. Found: 361.1591. Specific rotation: $[\alpha]_D^{20}$ –46.7 (*c* = 0.81, $CHCl_3$) for an enantiomerically enriched sample of 94% *ee*.

(*S*,*E*)-3-Phenyl-5-(4-trifluoromethylphenyl)-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration-oxidation of **7d** in the presence of 9-BBN, as described above. IR (neat): 3337 (br), 3086 (w), 3060 (w), 2952 (w), 2894 (w), 1615 (w), 1600 (w), 1494 (w), 1447 (w), 1407 (w), 1321 (s), 1248 (m), 1163 (m), 1122 (s), 1065 (s), 1016 (m), 833 (s), 755 (m), 697 (m), 640 (m), 596 (w), 525 (w), 443 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.41 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.29-7.16 (5H, m, Ar**H**), 7.00 (1H, s, C=C**H**Ar), 4.29 (1H, t, *J* = 7.6 Hz, PhC**H**CH_2CH_2OH), 3.66-3.52 (2H, m, $PhCHCH_2C$**H**$_2OH$), 2.27 (1H, dddd, *J* = 13.6, 6.8, 6.8, 6.8 Hz, $PhCHC$**H**$_2CH_2OH$), 2.04-1.95 (1H, m, $PhCHC$**H**$_2CH_2OH$), -0.05 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 142.4, 142.2, 138.1, 128.8 (q, *J* = 32.2 Hz), 128.6, 128.2, 127.7, 126.2, 125.2 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 270.6 Hz), 61.3, 41.4, 35.0, 0.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.87; HRMS (ESI+): Calcd for $C_{21}H_{26}F_3O_1Si_1$ $[M+H]^+$: 379.1705. Found: 379.1705. Specific rotation: $[\alpha]_D^{20}$ –224.1 (*c* = 0.96, $CHCl_3$) for an enantiomerically enriched sample of 94% *ee*.

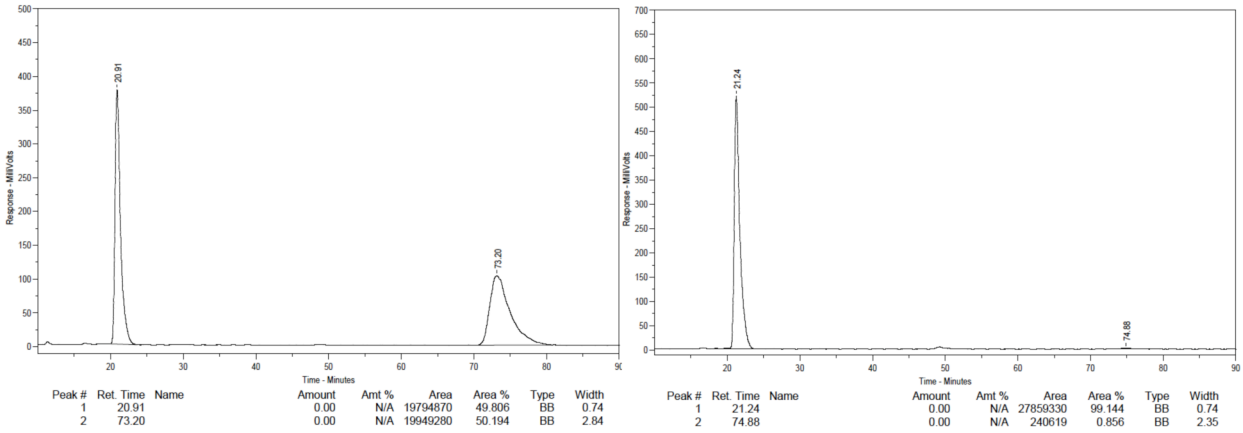
Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 20.87 min, minor peak at 47.53 min.



(*S*,*E*)-Trimethyl-[1-(4-methyl-benzylidene)-2-phenyl-but-3-enyl]-silane (7e; Table 2, entry 5): IR (neat): 3079 (w), 3058 (w), 3023 (w), 2953 (w), 2920 (w), 2894 (w), 1635 (w), 1599 (w), 1507 (w), 1492 (w), 1447 (w), 1406 (w), 1246 (s), 1020 (w), 995 (w), 950 (w), 916 (m), 830 (s), 807 (m), 773 (m), 754 (s), 737 (m), 698 (s), 620 (w), 554 (w), 492 (w), 455 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.15 (7H, m, Ar**H**) 7.11 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.03 (1H, s, C=C**H**Ar), 6.28 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, PhCHC**H**=CHH), 5.27 (1H, dt, *J* = 10.0, 1.6 Hz, CH=C**H**H), 5.14 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.94 (1H, d, *J* = 7.2 Hz, PhC**H**CH=CH_2), 2.32 (3H, s, ArC$\mathbf{H}_3$), –0.06 (9H, s, Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 142.9, 139.7, 139.3, 136.5, 135.2, 128.8, 128.3, 128.1, 128.0, 126.0, 117.0, 50.1, 21.1, 0.7; HRMS (ESI+): Calcd for $C_{21}H_{27}Si_1$ $[M+H]^+$: 307.1882. Found: 307.1876. Specific rotation: $[\alpha]_D^{20}$ –63.3 (*c* = 0.73, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

(*S*,*E*)-3-Phenyl-5-*p*-tolyl-4-trimethylsilanyl-pent-4-en-1-ol: Prepared by hydroboration/oxidation of **7e** in the presence of 9-BBN, as described above. IR (neat): 3321 (br), 3053 (w), 3023 (w), 2891 (w), 1600 (w), 1507 (w), 1494 (w), 1446 (w), 1406 (w), 1246 (m), 1021 (m), 831 (s), 752 (s), 737 (m), 697 (s), 643 (w), 626 (w), 572 (w), 539 (w), 493 (w), 441 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.13 (9H, m, Ar**H**), 7.02 (1H, s, C=C**H**Ar), 4.42 (1H, dd, *J* = 9.6, 5.6 Hz, PhC**H**CH_2CH_2OH), 3.65-3.56 (2H, m, PhCHCH_2C$\mathbf{H}_2$OH), 2.32 (3H, s, ArC$\mathbf{H}_3$), 2.37-2.26 (1H, m, PhCHC$\mathbf{H}_2CH_2$OH), 1.98-1.89 (1H, m, PhCHC$\mathbf{H}_2CH_2$OH), -0.09 (9H, s, Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 143.1, 139.8, 136.6, 135.4, 129.1, 128.1, 128.0, 127.7, 126.0, 61.2, 40.9, 34.9, 21.1, 0.6; HRMS (ESI+): Calcd for $C_{21}H_{29}O_1Si_1$ $[M+H]^+$: 325.1988. Found: 325.1986. Specific rotation: $[\alpha]_D^{20}$ –346.9 (*c* = 1.21, $CHCl_3$) for an enantiomerically enriched sample of 98% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 21.24 min, minor peak at 74.88 min.



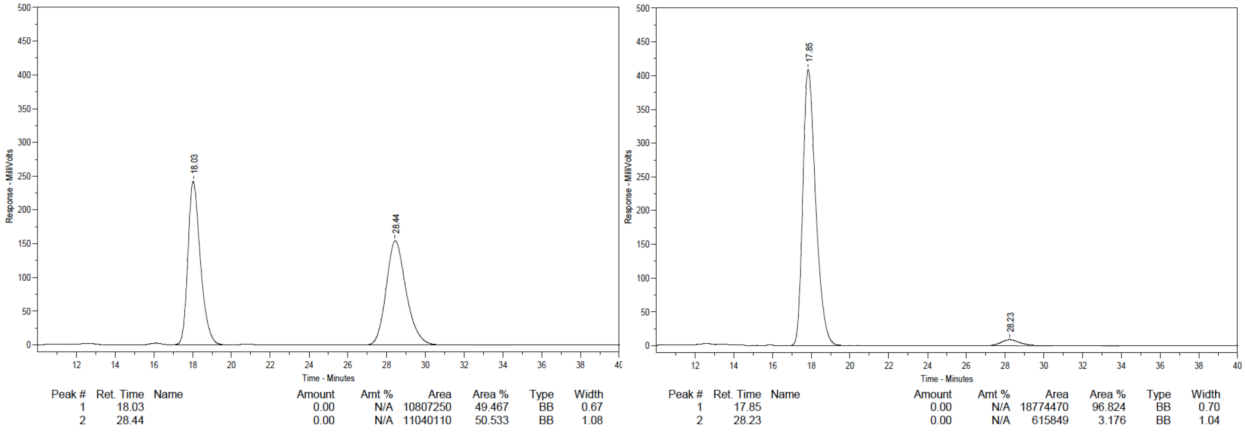
(*R*,*Z*)-(1-Benzylidene-2-phenyl-but-3-enyl)-dimethylsilane (14; Table 3, entry 1): IR (neat): 3079 (w), 3058 (w), 3024 (w), 2957 (w), 2122 (w), 1633 (w), 1598 (w), 1491 (w), 1449 (w), 1247 (m), 1073 (w), 1029 (w), 999 (w), 886 (s), 834 (m), 747 (s), 695 (s), 665 (w), 637 (w), 598 (w), 560 (w), 495 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.22 (11H, m, Ar**H**, C=C**H**Ph), 6.21 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, CC**H**=CHH), 5.23 (1H, ddd, *J* = 10.4, 1.6, 1.2 Hz, CH=C**H**H), 4.99 (1H, dt, *J* = 17.2, 1.6Hz, C=C**H**H), 4.42 (1H, d, *J* = 6.8 Hz, PhC**H**CH=CH_2), 4.07 (1H, dq, *J* = 4.0, 4.0 Hz, $Si(CH_3)_2$**H**), –0.03 (3H, d, *J* = 4.0 Hz, $Si(CH_3)_2H$), –0.13 (3H, d, *J* = 3.6 Hz, $Si(CH_3)_2H$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 143.6, 142.0, 140.8, 139.6, 129.0, 128.5, 128.2, 127.8, 127.0, 126.4, 116.2, 55.9, –2.8, –2.9; HRMS (ESI+): Calcd for $C_{19}H_{23}Si_1$ $[M+H]^+$: 279.1569. Found: 279.1578. Specific rotation: $[\alpha]_D^{20}$ +20.7 (*c* = 0.30, $CHCl_3$) for an enantiomerically enriched sample of 94% *ee*.

(*S*,*E*)-Penta-1,4-diene-1,3-diyldibenzene (24): A 5-mL vial was charged with **14** (14.8 mg, 0.067 mmol), and $CHCl_3$ (0.5 mL). The solution was allowed to cool to 0 °C, and trifluoroacetic acid (0.5 mL) was added. The mixture was allowed to stir at 4 °C for 15 hours. At this time, the solution was diluted with Et_2O (1 mL), and carefully neutralized by the addition of a saturated aqueous solution of $NaHCO_3$ (~5 mL). The aqueous layer was washed with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting yellow oil was purified by silica gel chromatography (hexane/Et_2O = 20/1) to afford the desired product in 89% yield (8.3 mg, 0.035 mmol). IR (neat): 3080 (w), 3059 (w), 3025 (w), 2976 (w), 2924 (w), 2855 (w), 1634 (w), 1598 (w), 1492 (w), 1448 (w), 1406 (w), 1073 (w), 1028 (w), 965 (m), 915 (m), 741 (s), 691 (s), 594 (w), 552 (w), 491 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.18 (10H, m, Ar**H**), 6.46-6.36 (2H, m, C**H**=C**H**Ph), 6.11 (1H, ddd, *J* = 17.2, 10.0, 6.8 Hz, CHC**H**=CHH), 5.18 (1H, dt, *J* = 10.4, 1.6 Hz, CH=C**H**H), 5.13 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.42 (1H, d, *J* = 6.4 Hz, PhC**H**CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 140.0, 137.3, 131.7, 130.6, 128.5, 128.4, 128.0, 127.2, 126.5, 126.2, 115.6, 52.3; HRMS (ESI+): Calcd for $C_{17}H_{17}$ $[M+H]^+$: 221.1330. Found: 221.1331. Specific rotation: $[\alpha]_D^{20}$ +3.3 (*c* = 0.60, $CHCl_3$) for an enantiomerically enriched sample of 94% *ee*.

(*S*)-3,5-Diphenyl-pent-4-en-1-ol: Prepared by hydroboration/oxidation of **24** with 9-BBN, as described above. The resulting alcohol product serves as the proof of absolute stereochemistry of

1,4-dienes from *Z*-vinylaluminum additions to allylic phosphates.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.16 (10H, m, Ar**H**), 6.43 (1H, d, *J* = 16.0 Hz, CH=C**H**Ph), 6.33 (1H, dd, *J* = 16.0, 7.6 Hz, C**H**=CHPh), 3.68-3.61 (3H, m, PhC**H**CH_2CH_2OH, $PhCHCH_2C\mathbf{H}_2OH$), 2.14-2.00 (2H, m, $PhCHC\mathbf{H}_2CH_2OH$); HRMS (ESI+): Calcd for $C_{17}H_{19}O_1$ $[M+H]^+$: 239.1436. Found: 239.1437. Specific rotation: $[\alpha]_D^{20}$ –10.5 (*c* = 0.21, $CHCl_3$) for an enantiomerically enriched sample of 94% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 17.85 min, minor peak at 28.23 min.



(*R*,*Z*)-(1-(2-Methoxyphenyl)-3-phenylpenta-1,4-dien-2-yl)dimethylsilane (15, Table 3, entry 2): IR (neat): 3059 (w), 3025 (w), 3001 (w), 2955 (w), 2926 (w), 2853 (w), 2834 (w), 2126 (w), 1592 (w), 1485 (m), 1462 (m), 1243 (s), 1075 (m), 999 (m), 884 (s), 836 (m), 750 (s), 700 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.19 (8H, m, Ar**H**, C=C**H**Ar), 6.92-6.84 (2H, m, Ar**H**), 6.24 (1H, ddd, *J* = 17.2, 10.0, 6.0 Hz, CHC**H**=CHH), 5.21 (1H, dt, *J* = 10.0, 1.2 Hz, CH=C**H**H), 4.98 (1H, dt, *J* = 17.2, 1.2 Hz, CH=CH**H**), 4.41 (1H, d, *J* = 6.0 Hz, PhC**H**CH=CHH), 3.96 (1H, dq, *J* = 4.0, 4.0 Hz, CH_3CH_3SiH), 3.83 (3H, s, $OC\mathbf{H}_3$), -0.10 (3H, d, *J* = 4.0 Hz, $C\mathbf{H}_3CH_3SiH$), -0.21 (3H, d, *J* = 4.0 Hz, $CH_3C\mathbf{H}_3SiH$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 143.8, 142.7, 141.5, 140.3, 130.7, 129.6, 129.5, 129.1, 128.7, 126.8, 120.3, 116.5, 110.6, 56.3, 55.9, –2.5, –2.6; HRMS (ESI+): Calcd for $C_{20}H_{25}O_1Si_1$ $[M+H]^+$: 309.1675. Found: 309.1661. Specific rotation: $[\alpha]_D^{20}$ +31.8 (*c* = 0.81, $CHCl_3$) for an enantiomerically enriched sample of 95% *ee*.

Enantiomeric purity was determined by HPLC analysis of the derived primary alcohol after hydroboration of title compound with 9-BBN in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: Major peak at 52.36 min, minor peak at 81.12 min.

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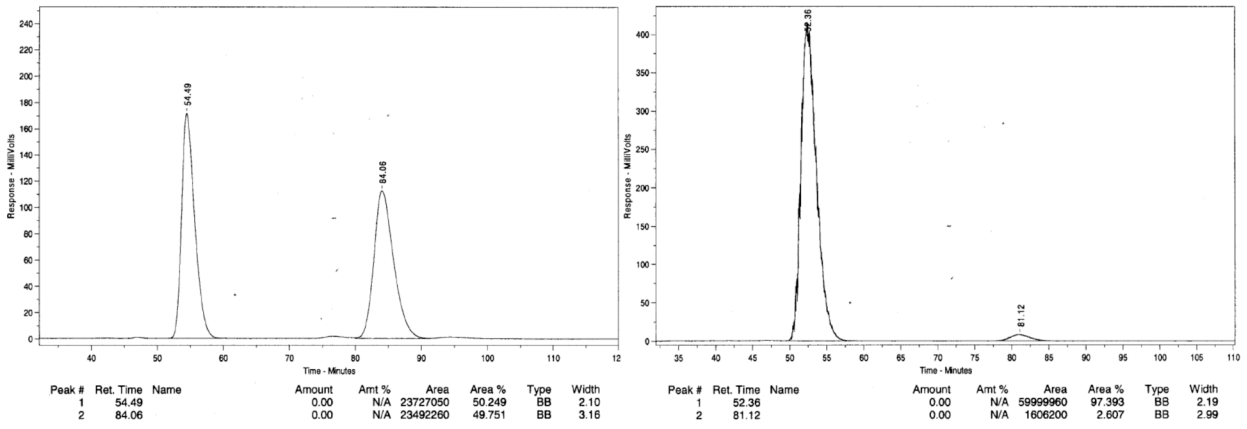
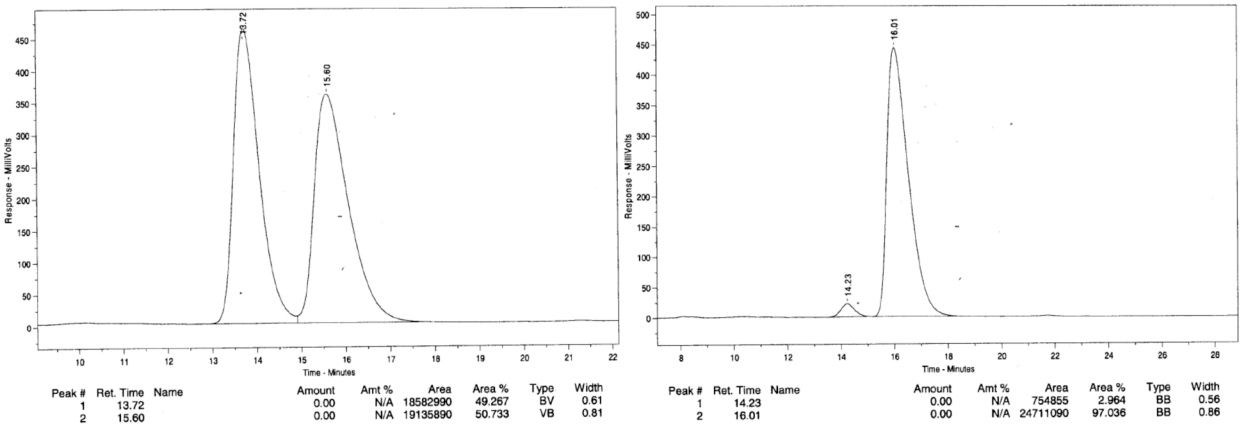
[12] The analytical data for the compound is identical with that previously reported; see: P. von-Matt, G. C. Lloyd-Jones, A. B. E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Rueegger, P. S. Pregosin, *Helv. Chim. Acta* **1995**, *78*, 265–284.



(*R*,*Z*)-Dimethyl(3-phenyl-1-*o*-tolylpenta-1,4-dien-2-yl)silane (16; Table 3, entry 3): IR (neat): 3060 (w), 3024 (w), 2956 (w), 2902 (w), 2118 (w), 1633 (w), 1599 (w), 1490 (w), 1450 (w), 1246 (m), 883 (s), 836 (m), 760 (m), 746 (s), 698 (s), 454 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (5H, m, Ar**H**), 7.27-7.14 (5H, m, Ar**H**, C=C**H**Ar), 6.25 (1H, ddd, *J* = 17.2, 10.4, 6.4 Hz, CHC**H**=CHH), 5.24 (1H, dt, *J* = 10.4, 1.2 Hz, CH=C**H**H), 5.04 (1H, dt, *J* = 17.2, 1.2 Hz, CH=CH**H**), 4.43 (1H, d, *J* = 6.4 Hz, PhC**H**CH=CHH), 3.92 (1H, dq, *J* = 4.0, 4.0 Hz, CH_3CH_3Si**H**), 2.23 (3H, s, PhC**H**$_3$), –0.14 (3H, d, *J* = 4.0 Hz, C**H**$_3$$CH_3SiH$), –0.23 (3H, d, *J* = 4.0 Hz, CH_3C**H**$_3$SiH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 143.6, 142.4, 140.9, 139.5, 136.2, 129.5, 129.2, 129.1, 128.4, 127.5, 126.5, 125.3, 116.3, 56.0, 20.1, -2.9, -3.0; HRMS (ESI+): Calcd for $C_{20}H_{25}O_1$ $[M+H]^+$: 293.1726. Found: 293.1712. Specific rotation: $[\alpha]_D^{20}$ +17.9 (*c* = 1.31, $CHCl_3$) for an enantiomerically enriched sample of 94% *ee*.

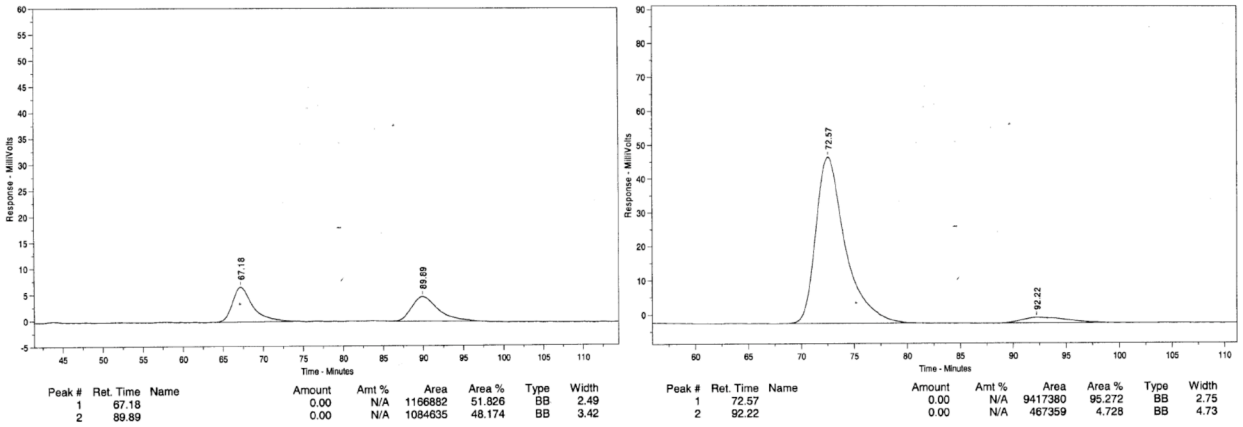
Enantiomeric purity was determined by HPLC analysis of the derived primary alcohol after hydroboration of title compound with 9-BBN in comparison with authentic racemic material (chiralpak AS column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: minor peak 14.23 min, major peak 16.01 min.



(*R*,*Z*)-Dimethyl(3-phenyl-1-(3-(trifluoromethyl)phenyl)penta-1,4-dien-2-yl)silane: (17; Table 3, entry 4): IR (neat): 3061 (w), 3027 (w), 2960 (w), 2903 (w), 2130 (w), 1634 (w), 1600 (w), 1491 (w), 1450 (w), 1428 (w), 1328 (s), 1250 (w), 1205 (w), 1163 (m), 1123 (s), 1071 (m), 999 (w), 878 (s), 837 (m), 797 (m), 754 (m), 698 (s), 514 (w), 458 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.51 (2H, m, Ar**H**), 7.46-7.43 (2H, m, Ar**H**), 7.38-7.34 (2H, m, Ar**H**), 7.28-7.24

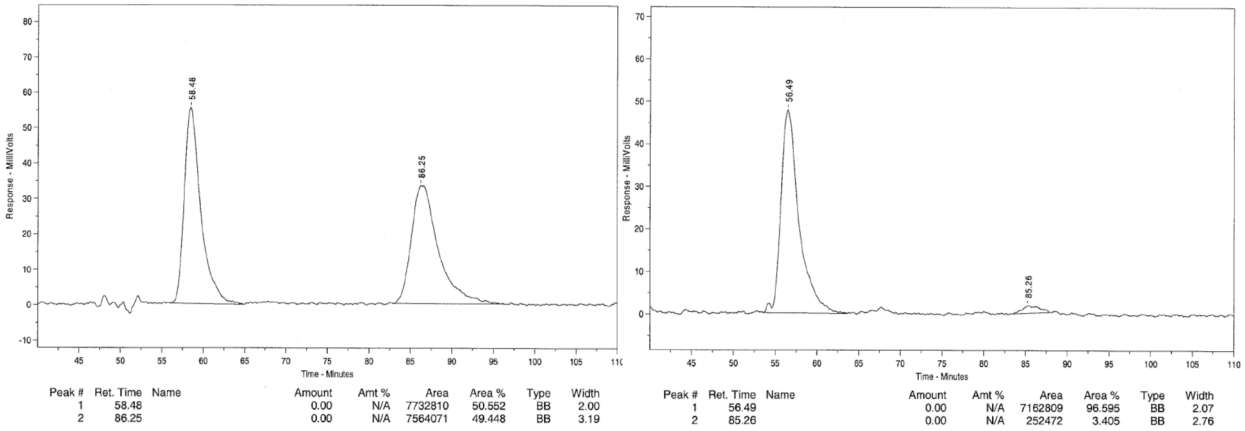
(3H, m, Ar**H**), 7.20 (1H, s, C=C**H**Ar), 6.20 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, CHC**H**=CHH), 5.25 (1H, dt, *J* = 10.0, 1.2 Hz, CH=C**H**H), 5.02 (1H, dt, *J* = 17.2, 1.2 Hz, CH=CH**H**), 4.44 (1H, d, *J* = 7.2 Hz, PhC**H**CH=CHH), 4.04 (1H, dq, *J* = 4.0, 4.0 Hz, CH_3CH_3Si**H**), -0.01 (3H, d, *J* = 4.0 Hz, C**H**$_3$$CH_3SiH$), –0.13 (3H, d, *J* = 4.0 Hz, CH_3C**H**$_3$SiH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 142.4, 142.1, 140.9, 140.8, 132.3, 129.5, 128.9, 128.8, 127.1, 125.9, 125.8, 124.2, 124.1, 117.1, 56.4, –2.5, –2.7; HRMS (ESI+): Calcd for $C_{20}H_{22}F_3Si_1$ $[M+H]^+$: 347.1443. Found: 347.1431. Specific rotation: $[\alpha]_D^{20}$ +22.7 (*c* = 2.56, $CHCl_3$) for an enantiomerically enriched sample of 91% *ee*.

Enantiomeric purity was determined by HPLC analysis of the derived primary alcohol after hydroboration of title compound with 9-BBN in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 72.57 min, minor peak at 92.22 min.



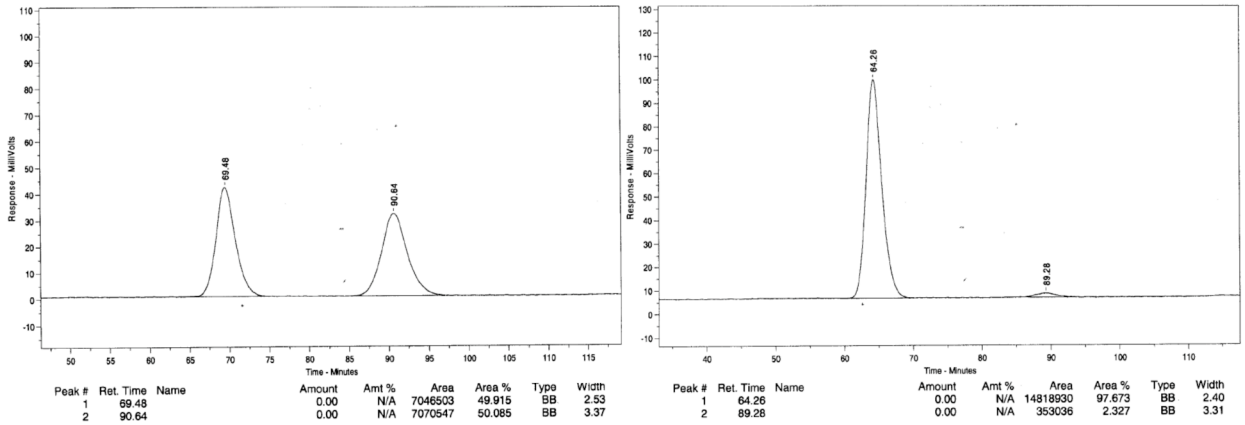
(*R*,*Z*)-Dimethyl(3-phenyl-1-(4-(trifluoromethyl)phenyl)penta-1,4-dien-2-yl)silane: (18, Table 3, entry 5): IR (neat): 3062 (w), 3027 (w), 2960 (w), 2904 (w), 2137 (w), 1616 (w), 1491 (w), 1406 (w), 1321 (s), 1250 (w), 1163 (m), 1122 (s), 1065 (s), 1017 (m), 881 (s), 834 (s), 765 (m), 699 (s), 599 (m), 511 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (2H, d, *J* = 8.5 Hz, Ar**H**), 7.38-7.33 (4H, m, Ar**H**), 7.26-7.24 (3H, m, Ar**H**), 7.19 (1H, s, C=C**H**Ar), 6.19 (1H, ddd, *J* = 17.0, 10.5, 7.0 Hz, CHC**H**=CHH), 5.25 (1H, dt, *J* = 10.5, 1.5 Hz, CH=C**H**H), 5.00 (1H, dt, *J* = 17.0, 1.5 Hz, CH=CH**H**), 4.43 (1H, d, *J* = 7.5 Hz, PhC**H**CH=CHH), 4.04 (1H, dq, *J* = 4.0, 4.0 Hz, CH_3CH_3Si**H**), –0.02 (3H, d, *J* = 4.0 Hz, C**H**$_3$$CH_3SiH$), –0.14 (3H, d, *J* = 4.0 Hz, CH_3C**H**$_3$SiH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 143.4, 142.2, 141.8, 140.6, 129.3, 129.2, 129.0, 128.5, 126.8, 124.9 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270.9 Hz), 116.8, 56.0, –2.8, –2.9; HRMS (ESI+): Calcd for $C_{20}H_{22}F_3Si_1$ $[M+H]^+$: 347.1443. Found: 347.1458. Specific rotation: $[\alpha]_D^{20}$ +18.7 (*c* = 2.22, $CHCl_3$) for an enantiomerically enriched sample of 93% *ee*.

Enantiomeric purity was determined by HPLC analysis of the derived primary alcohol after hydroboration of title compound with 9-BBN in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 56.49 min, minor peak at 85.26 min.



(*R*,*Z*)-(1-(4-fluorophenyl)-3-phenylpenta-1,4-dien-2-yl)dimethylsilane: (19; Table 3, entry 6): IR (neat): 3060 (w), 3026 (w), 2959 (w), 2901 (w), 2131 (w), 1601 (w), 1503 (s), 1450 (w), 1248 (m), 1222 (s), 1155 (m), 881 (s), 833 (s), 757 (s), 698 (s), 510 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.31 (2H, m, Ar**H**), 7.26-7.21 (5H, m, Ar**H**), 7.14 (1H, s, C=C**H**Ar), 7.02-6.98 (2H, m, Ar**H**), 6.18 (1H, ddd, *J* = 17.2, 10.4, 7.2 Hz, CHC**H**=CHH), 5.22 (1H, dt, *J* = 10.4, 1.2 Hz, CH=C**H**H), 4.98 (1H, dt, *J* = 17.2, 1.2 Hz, CH=CH**H**), 4.39 (1H, d, *J* = 6.8 Hz, PhC**H**CH=CHH), 4.04 (1H, dq, *J* = 4.0, 4.0 Hz, CH_3CH_3Si**H**), –0.04 (3H, d, *J* = 4.0 Hz, C**H**$_3$$CH_3SiH$), –0.15 (3H, d, *J* = 4.0 Hz, CH_3C**H**$_3$SiH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, *J* = 244.8 Hz), 144.4, 142.6, 142.1, 140.9, 135.9, 130.3 (d, *J* = 7.6 Hz), 129.2, 128.5, 126.6, 116.5, 114.9 (d, *J* = 21.3 Hz), 56.0, –2.7, –2.9; HRMS (ESI+): Calcd for $C_{19}H_{20}F_1Si_1$ $[M-H]^+$: 295.1318. Found: 295.1313. Specific rotation: $[\alpha]_D^{20}$ +25.7 (*c* = 0.52, $CHCl_3$) for an enantiomerically enriched sample of 96% *ee*.

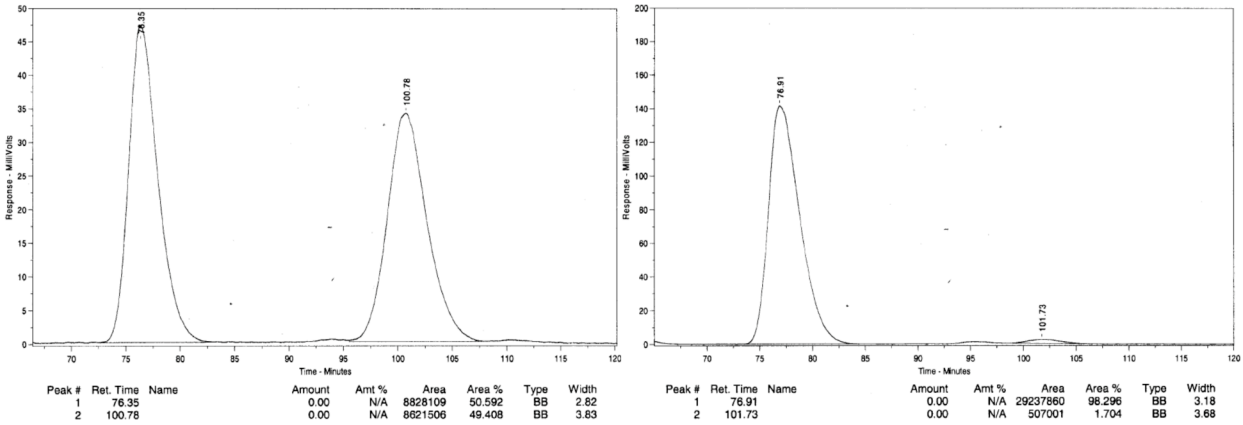
Enantiomeric purity was determined by HPLC analysis of the derived primary alcohol after hydroboration of title compound with 9-BBN in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 64.26 min, minor peak at 89.28 min.



(*R*,*Z*)-(1-(4-Methoxyphenyl)-3-phenylpenta-1,4-dien-2-yl)dimethylsilane: (20; Table 3, entry 7): The data were collected from a sample containing ~10% of the inseparable *E* vinylaluminum addition product. IR (neat): 3059 (w), 3026 (w), 2955 (w), 2904 (w), 2834 (w), 2123 (w), 1607 (m), 1491 (s), 1297 (w), 1245 (s), 1173 (m), 1034 (m), 999 (w), 882 (s), 830 (s), 755 (s), 698 (s),

552 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (2H, m, Ar**H**), 7.28-7.20 (5H, m, Ar**H**), 7.14 (1H, s, C=C**H**Ar), 6.88-6.84 (2H, m, Ar**H**), 6.20 (1H, ddd, *J* = 17.2, 10.4, 6.8 Hz, CHC**H**=CHH), 5.21 (1H, dt, *J* = 10.4, 1.2 Hz, CH=C**H**H), 4.97 (1H, dt, *J* = 17.2, 1.2 Hz, CH=CH**H**), 4.39 (1H, d, *J* = 6.8 Hz, PhC**H**CH=CHH), 4.09 (1H, dq, *J* = 4.0, 3.6 Hz, CH_3CH_3Si**H**), 3.81 (3H, s, OC**H**$_3$), –0.02 (3H, d, *J* = 4.0 Hz, C**H**$_3$$CH_3SiH$), –0.12 (3H, d, *J* = 3.6 Hz, CH_3C**H**$_3$SiH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 143.4, 142.4, 141.2, 132.4, 130.0, 129.2, 128.4, 126.5, 116.2, 113.8, 113.4, 56.1, 55.4, –2.6, –2.8; HRMS (ESI+): Calcd for $C_{20}H_{25}O_1Si_1$ $[M+H]^+$: 309.1675. Found: 309.1659. Specific rotation: $[\alpha]_D^{20}$ +47.7 (*c* = 2.31, $CHCl_3$) for an enantiomerically enriched sample of 97% *ee*.

Enantiomeric purity was determined by HPLC analysis of the derived primary alcohol after hydroboration of title compound with 9-BBN in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 76.91 min, minor peak at 101.73 min.

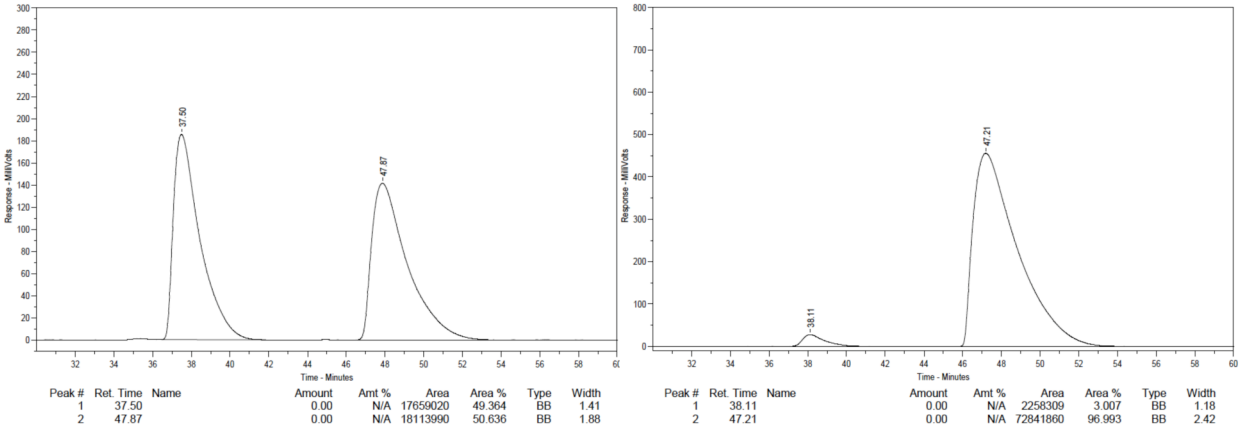


(*R*,*Z*)-[1-Benzylidene-2-(4-nitrophenyl)-but-3-enyl]-dimethylsilane (21; Table 3, entry 8): The data was measured with 7% unseparable *iso*-butyl addition product. IR (neat): 3078 (w), 3057 (w), 3020 (w), 2957 (w), 2920 (w), 2854 (w), 2121 (m), 1594 (m), 1516 (s), 1490 (m), 1342 (s), 1248 (m), 1108 (w), 888 (s), 833 (s), 850 (s), 835 (s) 748(s), 696 (s), 605 (w), 506 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (2H, d, *J* = 8.8 Hz, Ar**H**), 7.42 (2H, d, *J* = 8.8 Hz, Ar**H**), 7.31-7.22 (5H, m, Ar**H**), 7.19 (1H, s, C=C**H**Ph), 6.16 (1H, ddd, *J* = 17.2, 10.4, 6.8 Hz, CHC**H**=CHH), 5.28 (1H, dt, *J* = 10.4, 1.2 Hz, CH=C**H**H), 4.98 (1H, dt, *J* = 17.2, 1.2 Hz, CH=C**H**H), 4.50 (1H, d, *J* = 6.8 Hz, PhC**H**CH=CH_2), 4.03 (1H, dq, *J* = 4.0, 4.0 Hz, $Si(CH_3)_2$**H**), –0.04 (3H, d, *J* = 3.6 Hz, $Si(CH_3)_2H$), –0.13 (3H, d, *J* = 4.0 Hz, $Si(CH_3)_2H$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 146.7, 145.1, 142.6, 139.3, 139.0, 129.7, 128.4, 127.9, 127.4, 123.5, 117.5, 55.7, –2.8, –2.9; HRMS (ESI+): Calcd for $C_{19}H_{21}N_1O_2Si_1$ $[M]^+$: 323.1356. Found: 323.1354. Specific rotation: $[\alpha]_D^{20}$ +8.1 (*c* = 0.37, $CHCl_3$) for an enantiomerically enriched sample of 94% *ee*.

(*S*,*Z*)-1-Nitro-4-(1-phenylpenta-1,4-dien-3-yl)benzene: Prepared by proto-desilylation of **21** in TFA/$CHCl_3$ as described above. IR (neat): 3079 (w), 3025 (w), 2925 (w), 2850 (w), 1634 (w), 1596 (m), 1514 (s), 1447 (w), 1409 (w), 1341 (s), 1179 (w), 1108 (w), 1014 (w), 966 (m), 921 (m), 850 (m), 798 (w), 744 (m), 691 (s), 604 (w), 513 (w), 490 (w) cm^{-1}; ^1H NMR (400 MHz,

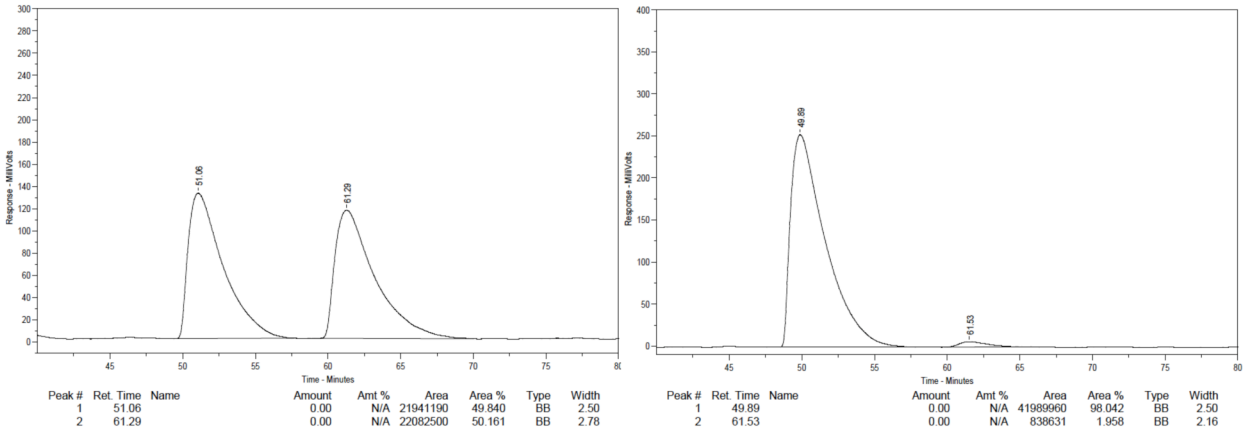
$CDCl_3$): δ 8.17 (2H, dt, *J* = 8.8, 2.4 Hz, Ar**H**), 7.42 (2H, dt, *J* = 8.8, 2.4 Hz, Ar**H**), 7.37-7.21 (5H, m, Ar**H**), 6.45 (1H, d, *J* = 16.4 Hz, CH=C**H**Ph), 6.33 (1H, dd, *J* = 16.0, 6.8 Hz, C**H**=CHPh), 6.06 (1H, ddd, *J* = 17.2, 10.4, 6.8 Hz, CHC**H**=CHH), 5.26 (1H, dt, *J* = 10.0, 1.2 Hz, CH=C**H**H), 5.16 (1H, dt, *J* = 17.2, 1.2 Hz, CH=C**H**H), 4.32 (1H, t, *J* = 6.8 Hz, PhC**H**CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 146.7, 138.4, 136.7, 131.9, 129.8, 128.9, 128.6, 127.7, 126.3, 123.8, 117.0, 52.0; HRMS (ESI+): Calcd for $C_{17}H_{16}N_1O_2$ $[M+H]^+$: 266.1181. Found: 266.1174. Specific rotation: $[\alpha]_D^{20}$ +2.1 (*c* = 0.55, $CHCl_3$) for an enantiomerically enriched sample of 94% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm). Retention time: minor peak at 38.11 min, major peak at 47.21 min.



(*R*,*Z*)-Toluene-4-sulfonic acid 4-(2-dimethylsilanyl-3-phenyl-1-vinyl-allyl)-phenyl ester (22; Table 3, entry 9): The data was measured with 10% unseparable *iso*-butyl addition product. IR (neat): 3076 (w), 3054 (w), 3024 (w), 2958 (w), 2924 (w), 2870 (w), 2129 (w), 1633 (w), 1597 (w), 1497 (m), 1372 (w), 1248 (w), 1197 (m), 1175 (s), 1151 (s), 1092 (m), 1017 (w), 860 (s), 812 (m), 749 (m), 697 (s), 663 (s), 564 (m), 549 (s), 503 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.31-7.19 (7H, m, Ar**H**), 7.14 (2H, d, *J* = 8.8 Hz, Ar**H**), 7.13 (1H, s, C=C**H**Ph), 6.92 (2H, d, *J* = 8.4 Hz, Ar**H**), 6.11 (1H, ddd, *J* = 17.2, 10.4, 6.8 Hz, CHC**H**=CHH), 5.20 (1H, d, *J* = 10.0 Hz, CH=C**H**H), 4.91 (1H, dt, *J* = 17.2, 1.2 Hz, CH=C**H**H), 4.34 (1H, d, *J* = 7.2 Hz, PhC**H**CH=CH_2), 3.98 (1H, dq, *J* = 4.0, 4.0 Hz, Si$(CH_3)_2$**H**), 2.41 (3H, s, ArC**H**$_3$), –0.10 (3H, d, *J* = 4.0 Hz, Si(C**H**$_3)_2$H), –0.22 (3H, d, *J* = 3.6 Hz, Si(C**H**$_3)_2$H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 145.2, 144.0, 143.4, 141.1, 140.2, 139.3, 132.2, 130.1, 129.6, 128.5, 128.4, 127.8, 127.1, 122.1, 116.6, 55.2, 21.6, –2.8, –2.9; HRMS (ESI+): Calcd for $C_{26}H_{27}O_3S_1Si_1$ $[M-H]^+$: 447.1450, Found: 447.1456. Specific rotation: $[\alpha]_D^{20}$ +4.3 (*c* = 0.33, $CHCl_3$) for an enantiomerically enriched sample of 96% *ee*.

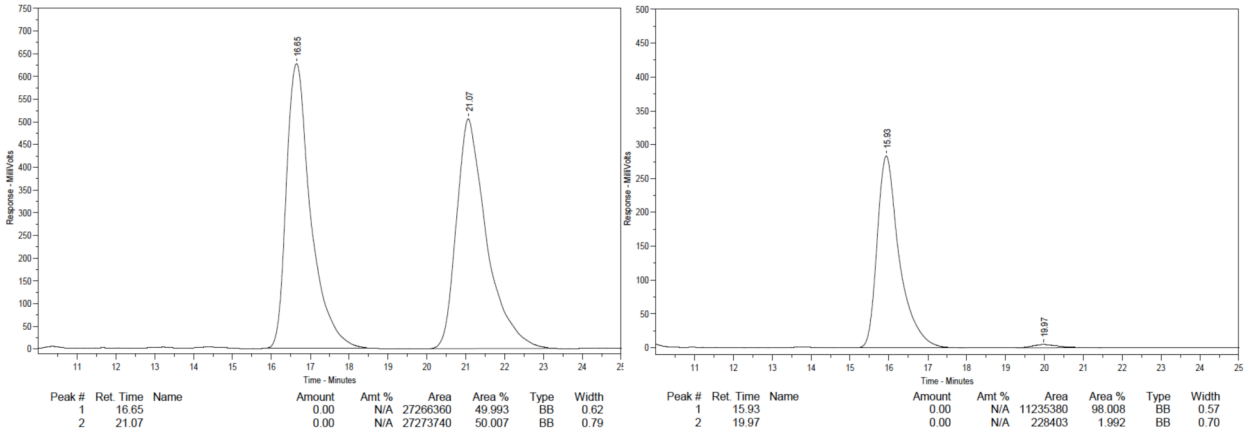
Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm). Retention time: major peak at 49.89 min, minor peak at 61.53 min.



(*R*,*Z*)-(1-Benzylidene-2-*p*-tolyl-but-3-enyl)-dimethylsilane (23; Table 3, entry 10): IR (neat): 3077 (w), 3053 (w), 3020 (w), 2973 (w), 2956 (w), 2920 (w), 2901 (w), 2864 (w), 2125 (w), 1632 (w), 1592 (w), 1572 (w), 1509 (w), 1491 (w), 1443 (w), 1406 (w), 1247 (m), 998 (w), 888 (s), 833 (s), 815 (w), 746 (s), 696 (s), 661 (w), 640 (w), 591 (w), 555 (w), 525 (w), 491 (m), 450 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33-7.14 (10H, m, Ar**H**, C=C**H**Ph), 6.19 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, CHC**H**=CHH), 5.20 (1H, ddd, *J* = 10.4, 1.6, 1.2 Hz, CH=C**H**H), 4.98 (1H, dt, *J* = 17.2, 1.2 Hz, CH=C**H**H), 4.37 (1H, dd, *J* = 7.2, 1.2 Hz, PhC**H**CH=CH_2), 4.05 (1H, dq, *J* = 4.0, 4.0 Hz, $Si(CH_3)_2$**H**), 2.34 (3H, s, ArC**H**$_3$), –0.03 (3H, d, *J* = 3.6 Hz, $Si(C$**H**$_3)_2H$), –0.13 (3H, d, *J* = 4.0 Hz, $Si(C$**H**$_3)_2H$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 143.4, 141.0, 139.7, 139.0, 135.9, 129.0, 128.9, 128.5, 127.7, 126.9, 115.9, 55.5, 21.0, –2.7, –2.9; HRMS (ESI+): Calcd for $C_{20}H_{25}Si_1$ $[M+H]^+$: 293.1726. Found: 293.1719. Specific rotation: $[\alpha]_D^{20}$ +34.4 (*c* = 0.98, $CHCl_3$) for an enantiomerically enriched sample of 96% *ee*.

(*R*,*Z*)-4-Dimethylsilanyl-5-phenyl-3-*p*-tolyl-pent-4-en-1-ol: Prepared by hydroboration/oxidation of **23** with 9-BBN, as described above. IR (neat): 3317 (br), 3051 (w), 3020 (w), 2923 (w), 2857 (w), 2128 (w), 1728 (w), 1592 (w), 1510 (w), 1491 (w), 1442 (w), 1042 (m), 884 (s), 834 (m), 815 (m), 655 (w), 638 (w), 566 (w), 486 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.20 (6H, m, Ar**H**, C=C**H**Ph), 7.15 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.10 (2H, d, *J* = 8.0 Hz, Ar**H**), 3.96 (1H, dq, *J* = 4.0, 4.0 Hz, $Si(CH_3)_2$**H**), 3.75 (1H, t, *J* = 7.6 Hz, ArC**H**CH_2CH_2OH), 3.70-3.59 (2H, m, $ArCHCH_2C$**H**$_2OH$), 2.31 (3H, s, ArC**H**$_3$), 2.22 (1H, dddd, *J* = 13.6, 6.8, 6.8, 6.8 Hz, $ArCHC$**H**$_2CH_2OH$), 2.10-2.01 (1H, m, $ArCHC$**H**$_2CH_2OH$), -0.11 (3H, d, *J* = 3.6 Hz, $Si(C$**H**$_3)_2H$), -0.24 (3H, d, *J* = 4.0 Hz, $Si(C$**H**$_3)_2H$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 141.1, 140.0, 139.7, 135.9, 129.0, 128.6, 128.4, 127.8, 126.9, 61.4, 47.9, 37.5, 21.0, –2.7, –2.9; HRMS (ESI+): Calcd for $C_{20}H_{28}O_1Si_1$ $[M+H]^+$: 311.1831. Found: 311.1822. Specific rotation: $[\alpha]_D^{20}$ –40.0 (*c* = 0.31, $CHCl_3$) for an enantiomerically enriched sample of 96% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 15.93 min, minor peak at 19.97 min.



■ ENANTIOSELECTIVE SYNTHESIS *of* (–)-NAYSOL

(*E*)-Acetic acid 4-[3-(diethoxy-phosphoryloxy)-propenyl]-phenyl ester (10; Scheme 4): A 10-mL test tube was charged with (*E*)-acetic acid 4-(3-hydroxy-propenyl)-phenyl ester[13] (192 mg, 1.00 mmol), 4-dimethylaminopyridine (24.4 mg, 0.200 mmol), CH_2Cl_2 (2.0 mL), and triethylamine (170 μL, 1.20 mmol). The mixture was allowed to cool to 0 °C, and chlorodiethylphosphate (173 μL, 1.20 mmol) was added. After allowing the solution to stir at 22 °C for 15 hours, the reaction was quenched by the addition of a saturated solution of NH_4Cl (2.0 mL). The layers were separated; the aqueous layer was washed with Et_2O (3 x 1.0 mL). The combined organic layers were passed through a short column of $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil was purified by silica gel chromatography (hexanes/EtOAc = 1/1) to give the product as light yellow oil in 92% yield (303 mg, 0.920 mmol). IR (neat): 2984 (w), 2931 (w), 1757 (m), 1501 (m), 1601 (w), 1506 (m), 1443 (w), 1369 (m), 1262 (m), 1190 (s), 1165 (s), 1097 (w), 1007 (s), 963 (s), 909 (s), 853 (m), 800 (m), 746 (w), 658 (w), 593 (w), 517 (m), 454 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (2H, dt, J = 8.8, 2.4 Hz, Ar**H**), 7.03 (2H, dt, J = 8.8, 2.4 Hz, Ar**H**), 6.64 (1H, d, J = 16.0 Hz, ArC**H**=CH), 6.23 (1H, dt, J = 15.6, 6.0 Hz, ArCH=C**H**), 4.66 (2H, ddd, J = 8.4, 6.0, 1.2 Hz, CH=CHC**H**$_2$), 4.11 (4H, dq, J = 7.2, 7.2 Hz, PO(OC**H**$_2$CH$_3$)$_2$), 2.27 (3H, s, ArOCOC**H**$_3$), 1.32 (6H, td, J = 7.2, 1.2 Hz, PO(OCH$_2$C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 150.4, 133.8, 132.7, 127.6, 123.8 (d, J = 6.5 Hz), 121.7, 67.7 (d, J = 5.4 Hz), 63.8 (d, J = 5.7 Hz), 21.0, 16.1 (d, J = 6.8 Hz); HRMS (ESI+) Calcd for $C_{15}H_{22}O_6P_1$ $[M+H]^+$:329.1154. Found: 329.1153.

(*S*,*E*)-Acetic acid 4-[3-(4-hydroxyphenyl)-2-trimethylsilanyl-1-vinyl-allyl]-phenyl ester (11; Scheme 4): A 10-mL Schlenk tube equipped with a stir bar was charged with 4-hydroxyphenylethynyltrimethylsilane **8**[14] (76.1 mg, 0.400 mmol) under N_2. Hexanes (1.0 mL) and dibal–H (143 μL, 0.80 mmol) were added to the vessel at 0 °C. The mixture was allowed to stir at 55 °C for 2 hours, after which it was allowed to cool to –78 °C and a solution of NHC•Ag

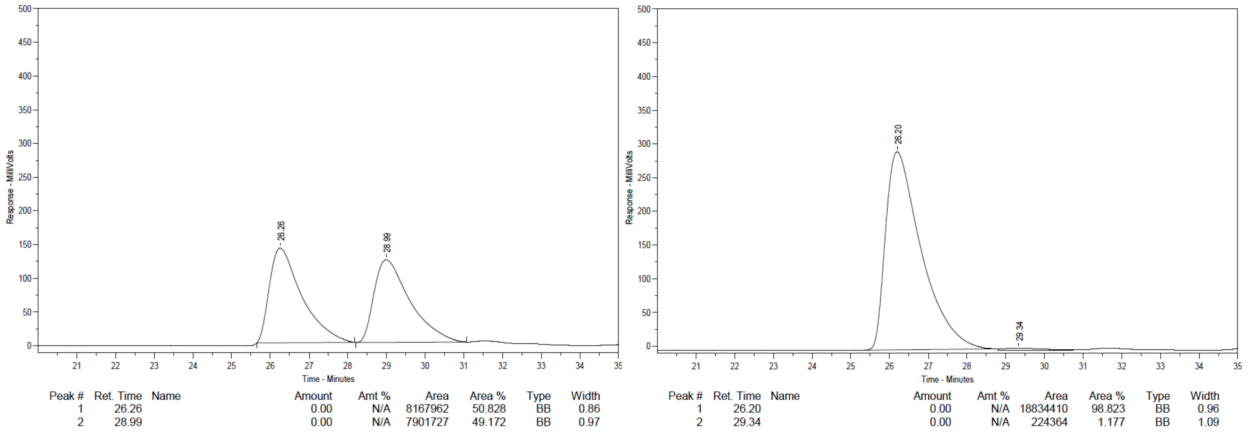
[13] Prepared as described in the literature by Mizoroki-Heck reaction from 4-iodophenyl acetate and allyl alcohol. See: A. S. Paraskar, A. Sudalai, *Tetrahedron*, **2006**, *62*, 5756–5762.

[14] Prepared by Sonogashira coupling from 4-iodophenol and trimethylsilylacetylene; see: E. Yashima, S. Huang, T. Matsuhima, Y. Okamoto, *Macromolecules*, **1995**, *28*, 4184–4193.

5 (2.3 mg, 0.002 mmol) and $CuCl_2 \bullet 2H_2O$ (0.68 mg, 0.004 mmol) in THF (2.4 mL) were added with a syringe. After allowing the solution to stir for 10 minutes, substrate **10** (65.7 mg, 0.200 mmol) was added (at –78 °C). The mixture was allowed to warm to –15 °C and stand for 12 hours. The reaction was quenched by addition of a saturated aqueous solution of Rochelle's salt (3.0 mL) and the resulting mixture was allowed to stir for one hour at 22 °C. The layers were separated and the aqueous layer was washed with Et_2O (3 x 1.0 mL). The combined organic layers were passed through a short plug of $MgSO_4$ and concentrated under reduced pressure. The resulting yellow residue was purified by silica gel chromatography (hexane/Et_2O = 10/1) to give the product as clear oil (55.7 mg, 0.152 mmol, 76% yield). IR (neat): 3405 (w), 3077 (w), 3033 (w), 2954 (w), 2895 (w), 1757 (w), 1735 (w), 1608 (w), 1505 (m), 1433 (w), 1369 (w), 1196 (s), 1165 (m), 1100 (w), 1072 (w), 1016 (w), 909 (m), 888 (w), 832 (s), 780 (w), 755 (w), 729 (s), 687 (w), 647 (w), 582 (w), 551 (w), 508 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.13 (2H, d, *J* = 8.0 Hz, Ar**H**), 6.98 (2H, dt, *J* = 8.8, 2.4 Hz, Ar**H**), 6.97 (1H, s, C=C**H**Ar), 6.74 (2H, dt, *J* = 8.8, 2.4 Hz, Ar**H**), 6.23 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, ArCHC**H**=CHH), 5.26 (1H, dt, *J* = 10.0, 1.6 Hz, CH=C**H**H), 5.12 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.88 (1H, d, *J* = 7.2 Hz, ArC**H**CH=CH_2), 2.27 (3H, s, ArOCOC**H**$_3$), -0.06 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 154.5, 148.9, 143.8, 140.6, 139.5, 139.1, 130.5, 129.8, 128.9, 121.0, 117.3, 115.0, 49.6, 21.1, 0.7; HRMS (ESI+): Calcd for $C_{22}H_{27}O_3Si_1$ $[M+H]^+$: 367.1723. Found: 367.1745. Specific rotation: $[\alpha]_D^{20}$ –63.7 (*c* = 2.85, $CHCl_3$) for an enantiomerically enriched sample of 97% *ee*.

(*S*,*E*)-Acetic acid 4-[3-(4-acetoxy-phenyl)-2-trimethylsilanyl-1-vinyl-allyl]-phenyl ester (S1): A 10-mL test tube was charged with **11** (37.5 mg, 0.102 mmol), pyridine (0.7 mL), and acetic anhydride (19.2 μL, 0.204 mmol) under N_2. The mixture was allowed to stir at 22 °C for 2 h. The reaction was quenched by addition of 1N aqueous solution of HCl (1.5 mL), washed with Et_2O (3 x 1.0 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil was purified by silica gel chromatography (hexane/Et_2O = 20/1) to afford the desired product in 94% yield (39.3 mg, 0.096 mmol). IR (neat): 3077 (w), 3034 (w), 2954 (w), 2896 (w), 1760 (s), 1634 (w), 1602 (w), 1501 (s), 1409 (w), 1367 (m), 1247 (w), 1187 (s), 1164 (s), 1103 (w), 1072 (w), 1044 (w), 1015 (m), 910 (s), 834 (s), 756 (m), 687 (w), 631 (w), 613 (w), 592 (w), 582 (w), 551 (w), 511 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.18 (2H, d, *J* = 8.8 Hz, Ar**H**), 7.04-6.97 (5H, m, Ar**H**, C=C**H**Ar), 6.23 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz, ArCHC**H**=CHH), 5.27 (1H, dt, *J* = 10.0, 1.6 Hz, CH=C**H**H), 5.13 (1H, dt, *J* = 17.2, 1.6 Hz, CH=C**H**H), 4.86 (1H, d, *J* = 7.2 Hz, ArC**H**CH=CH_2), 2.27 (3H, s, ArOCOC**H**$_3$), 2.26 (3H, s, ArOCOC**H**$_3$), –0.04 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 149.4, 149.0, 145.7, 140.2, 139.0, 138.9, 135.6, 129.3, 128.9, 121.2, 121.0, 117.4, 49.6, 21.1, 0.7; HRMS (ESI+): Calcd for $C_{24}H_{29}O_4Si_1$ $[M+H]^+$: 409.1835. Found: 409.1843. Specific rotation: $[\alpha]_D^{20}$ –60.7 (*c* = 0.57, $CHCl_3$) for an enantiomerically enriched sample of 97% *ee*.

Enantiomeric purity was determined by HPLC analysis of the derived primary alcohol after hydroboration of title compound with 9-BBN in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: major peak at 26.20 min, minor peak at 29.34 min.



(*R*,*Z*)Acetic acid 4-[3-(4-acetoxy-phenyl)-1-vinyl-allyl]-phenyl ester (S2): A 5-mL vial was charged with **S1** (37.7 mg, 0.092 mmol), $CHCl_3$ (1.5 mL), and trifluoroacetic acid (1.5 mL). The mixture was allowed to stir at 22 °C for 48 hours. After 48 hours, the mixture was diluted with Et_2O, and carefully neutralized by addition of a saturated solution of $NaHCO_3$. The organic layer was extracted with Et_2O (3 x 1.0 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting yellow oil was purified by silica gel chromatography (hexane/Et_2O = 20/1) to afford the desired product in 73% yield (22.6 mg, 0.067 mmol). IR (neat): 3079 (w), 3012 (w), 2960 (w), 2927 (w), 2855 (w), 1755 (s), 1633 (w), 1601 (w), 1503 (m), 1429 (w), 1367 (m), 1187 (s), 1163 (s), 1143 (w), 1014 (m), 908 (s), 875 (w), 846 (m), 749 (w), 684 (w), 594 (w), 562 (w), 540 (w), 511 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (2H, dt, *J* = 8.4, 2.4 Hz, Ar**H**), 7.22 (2H, dt, *J* = 8.8, 2.4 Hz, Ar**H**), 7.04 (2H, dt, *J* = 8.4, 2.0 Hz, Ar**H**), 7.01 (2H, dt, *J* = 8.4, 2.0 Hz, Ar**H**), 6.58 (1H, d, *J* = 11.2 Hz, ArC(CH=CH_2)CH=C**H**Ar), 6.00 (1H, ddd, *J* = 17.6, 10.0, 6.0 Hz, C**H**=CHH), 5.76 (1H, dd, *J* = 11.6, 10.0, ArC(CH=CH_2)C**H**=CHAr), 5.21-5.16 (2H, m, ArCH=C**HH**), 4.54 (1H, dd, *J* = 10.0, 6.0 Hz, ArC**H**CH=CH_2), 2.29 (3H, s, ArOCOC**H**$_3$), 2.27 (3H, s, ArOCOC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 169.4, 149.5, 149.2, 140.5, 139.9, 134.6, 132.7, 129.5, 128.6, 121.5, 121.3, 115.7, 46.9, 21.1; HRMS (ESI+): Calcd for $C_{21}H_{21}O_4$ $[M+H]^+$: 337.1440. Found: 337.1454. Specific rotation: $[\alpha]_D^{20}$ –181.7 (*c* = 0.95, $CHCl_3$) for an enantiomerically enriched sample of 97% *ee*.

(–)-Nyasol (*cis*-hinokiresinol):[15] To a 10-mL test tube charged with **S2** (14.2 mg, 0.042 mmol) in MeOH (2.0 mL) was added a solution of K_2CO_3 (100 mg in 1.0 mL H_2O). The mixture was allowed to stir at 22 °C for one hour, after which it was charged with solution of 1N HCl (2.0 mL) was added dropwise. The solution was washed with Et_2O (3 x 1.0 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The brown oil residue was purified by silica gel column chromatography (hexane/EtOAc = 4/1) to give (–)-nyasol in >98% yield (10.7 mg, 0.042 mmol). IR (neat): 3300 (br), 3011 (w), 2975 (w), 2960 (w), 2927 (w), 1633 (m), 1508 (s),

[15] Analytical data regarding this compound is identical with the previously reported data, for ^1H and ^{13}C; see: Y. Iida, K-B. Oh, M. Saito, H. Matsuoka, H. Kurata, M. Natsume, H. Abe, *J. Agric. Food Chem.* **1999**, *47*, 584–587. For a report on the specific rotation: $[\alpha]_D^{22}$= –198 (*c* = 0.13, MeOH). See: S-J. Jeong, R. Higuchi, M. Ono, M. Kuwano, Y-C. Kim, T. Miyamoto, *Biol. Pharm. Bull.* **2003**, *26*, 1721–1724.

1440 (w), 1365 (w), 1225 (s), 1169 (s), 1098 (m), 994 (w), 913 (m), 874 (w), 829 (s), 732 (m), 647 (w), 622 (w), 584 (w), 541 (w), 513 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (2H, dt, *J* = 8.4, 2.4 Hz, Ar**H**), 7.11 (2H, dt, *J* = 8.8, 2.4 Hz, Ar**H**), 6.79 (2H, dt, *J* = 8.8, 2.4 Hz, Ar**H**), 6.78 (2H, dt, *J* = 8.4, 2.4 Hz, Ar**H**), 6.52 (1H, d, *J* = 11.6 Hz, ArC(CH=CH_2)CH=C**H**Ar), 6.01 (1H, ddd, *J* = 16.8, 10.4, 6.0 Hz, C**H**=CHH), 5.68 (1H, dd, *J* = 11.6, 10.0 Hz, ArC(CH=CH_2)C**H**=CHAr), 5.17-5.14 (2H, m, ArCH=C**HH**), 4.76 (1H, s, ArO**H**), 4.67 (1H, s, ArO**H**), 4.49 (1H, dd, *J* = 10.0, 6.0 Hz, ArC**H**CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 153.9, 140.6, 135.6, 131.7, 130.0, 129.9, 128.8, 128.5, 115.3, 115.1, 115.0, 46.8; HRMS (ESI+): Calcd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1229. Found: 253.1233. Specific rotation: $[\alpha]_D^{20}$ –201.9 (*c* = 0.42, $CHCl_3$) for an enantiomerically enriched sample of 97% *ee*.

(*R,Z*)-4,4'-(5-hydroxypent-1-ene-1,3-diyl)diphenol: Prepared by hydroboration/oxidation of (–)-nyasol in the presence of 9-BBN (3.0 equiv), as described above. IR (neat): 3270 (br), 2927 (w), 2443 (br), 1607 (m), 1508 (s), 1443 (w), 1382 (w), 1242 (s), 1170 (m), 1102 (w), 1013 (w), 829 (s), 728 (w), 701 (w), 624 (w), 577 (w), 550 (w), 517 (w) cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ 7.10 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.08 (2H, d, *J* = 8.4 Hz, Ar**H**), 6.74-6.70 (4H, m, Ar**H**), 6.36 (1H, d, *J* = 11.2 Hz, CH=C**H**Ar), 5.69 (1H, t, *J* = 11.0 Hz, C**H**=CHAr), 3.91 (1H, dt, *J* = 10.0, 7.2 Hz, ArC**H**CH_2CH_2OH), 3.44 (2H, td, *J* = 6.8, 2.0 Hz, ArCHCH_2C**H**$_2$OH), 1.91-1.81 (2H, m, ArCHC**H**$_2CH_2$OH); ^{13}C NMR (100 MHz, CD_3OD): δ 157.3, 156.6, 137.2, 135.1, 131.0, 130.1, 129.3, 129.2, 116.3, 115.9, 60.9, 41.8, 40.7; HRMS (ESI+): Calcd for $C_{17}H_{18}O_3$ $[M]^+$: 270.1256. Found: 270.1246. Specific rotation: $[\alpha]_D^{20}$ –324.2 (*c* = 0.71, CH_3OH) for an enantiomerically enriched sample of 97% *ee*.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (chiralpak OD column (25 cm x 0.46 cm), 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm). Retention time: minor peak at 130.38 min, major peak at 149.84 min.