Supporting Information
Part 1: Procedures and Characterization

One-Pot Multicomponent Coupling Methods for the Synthesis of Diastereo- and Enantioenriched (*Z*)-Trisubstituted Allylic Alcohols

*Michael H. Kerrigan, Sang-Jin Jeon, Young K. Chen, Luca Salvi, Patrick J. Carroll, and Patrick J. Walsh**

Contributions from the P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323

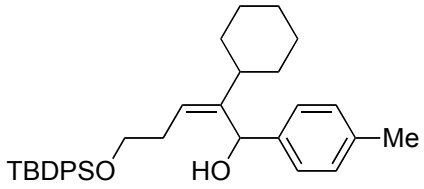
pwalsh@sas.upenn.edu

General Methods. All reactions were performed under a nitrogen atmosphere with oven-dried glassware using standard Schlenk or vacuum line techniques. Toluene was dried through an alumina column. THF was distilled from Na/benzophenone. Thin-layer chromatography (TLC) and ^{11}B NMR were used to monitor reaction progress. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained on Bruker AM-500, DMX-360 and DMX 300 Fourier transform NMR spectrometers at 500, 360, and 300 MHz for ^{1}H and 125, 90, 75 MHz for ^{13}C{^{1}H} NMR, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane or residual protonated solvent for ^{1}H

and $^{13}C\{^{1}H\}$ NMR; ^{11}B NMR is calibrated to an external $BF_3 \bullet OEt_2$ standard. All coupling constants are reported in Hz. A vertical asymptote at 4.5 ppm appears on some ^{1}H NMR spectra, while in some ^{13}C NMR it appears at 100 ppm. In both cases it is due to the iNMR processing software (ver. 0.7). The infrared spectra were obtained using a Perkin-Elmer 100 series FT-IR spectrometer. All reagents were purchased from Aldrich or Acros unless otherwise described. 1-Haloalkynes were prepared according to known procedures.[1-5] Chiral aldehydes were prepared by literature methods;[6-9] either Swern oxidation of the primary alcohol or DIBAL-H reduction of the methyl ester was performed just prior to reaction to generate the crude chiral aldehydes, which were used without further purification. All commercially available aldehyde substrates were distilled prior to use. Diastereomeric ratios were determined by crude ^{1}H NMR. Silica gel (230-400 mesh, Silicycle) was used for air-flashed chromatography. Analysis of enantiomeric excess was performed using a Hewlett-Packard 1050 or 1100 Series HPLC and a Chiralcel OD-H, Chiralpak AD, AD-H, AS, or AS-H column. Note that the compounds in Table 1 were reporteted in the initial communication.[10]

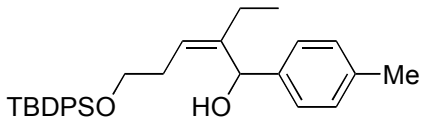
Cautionary Note: Dialkylzinc reagents are pyrophoric and must be handled with caution. In experiments involving removal of volatile materials that contain pyrophoric alkyl boron and/or alkyl zinc species, a cold trap was inserted into the hose of the Schlenk line and cooled with liquid nitrogen. After the volatile materials had been removed, the liquid nitrogen trap was removed and the trap backfilled and then purged with nitrogen gas. A dilute solution of isopropanol in hexanes was then added followed by dropwise addition of water to destroy the alkyl boron and alkyl zinc species.

Examination of the Impact of Dialkylborane and Dialkylzinc Reagents on the 1,2-Metallate Rearrangement (Table 2).



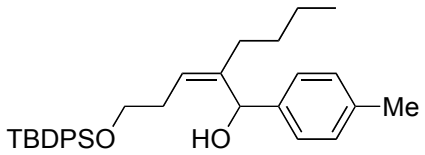
(*Z*)-5-(tert-butyldiphenylsilyloxy)-2-cyclohexyl-1-p-tolylpent-2-en-1-ol. A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N_2 (g) three times, was charged with dicyclohexylborane (1 mmol) and toluene (1 mL) under a nitrogen atmosphere. The solution was cooled to 0 ^oC followed by addition of (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (386.4 mg, 1 mmol). The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to –78 °C and diethylzinc (3 mL, 3 mmol, 1.0 M in toluene). After stirring for 20 min, the reaction flask was warmed to 0 ^oC. Under a steady flow of N_2 (g), the rubber septum was replaced with a glass stopper coated with silicon grease and high vacuum was gradually applied to remove the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL) followed by addition of *p*-tolualdehyde (0.67 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred until no aldehyde remained by TLC (usually 7-16 hrs). Quenching by saturated aq. NH_4Cl (2 mL), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were successively washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on

silica gel to yield a mixture of the title compound (173 mg, 50.7%) and (*Z*)-5-(tert-butyldiphenylsilyloxy)-2-ethyl-1-p-tolylpent-2-en-1-ol (11.0 mg, 3.6%) in a 14:1 ratio, respectively. When was diethylzinc added to the reaction solution at 0 °C, the ratio changed to 4:1. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (m, 4H), 7.44 (m, 6H), 7.31 (d, J = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.54 (d, 4.0 Hz, 1H), 5.48 (t, *J* = 7.8 Hz, 1H), 3.69 (m, 2H), 2.61 (m, 1H), 2.37 (s, 3H), 1.96 (m, 1H), 1.79 (m, 2H), 1.68 (m, 2H), 1.51 (d, *J* = 9.4 Hz, 1H), 1.28 (m, 2H), 1.11 (s, 9H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 149.9, 140.5, 136.4, 135.9, 133.7, 129.9, 128.9, 127.9, 126.1, 123.2, 72.6, 63.9, 41.6, 34.6, 34.3, 31.4, 27.2, 26.5, 21.3, 19.4 ppm; HRMS-CI calcd for $C_{34}H_{44}O_2SiCl$ $(M+Cl)^-$: 547.2797, found 547.2799.



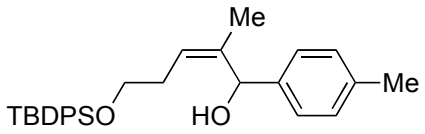
(*Z*)-5-(tert-butyldiphenylsilyloxy)-2-ethyl-1-p-tolylpent-2-en-1-ol. A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N_2 (g) three times, was charged with (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (128.13 mg, 0.33 mmol) and toluene (1 mL) under a nitrogen atmosphere. The solution was cooled to 0 ^{o}C followed by slow addition of diethylborane (0.33 mL, 1.0 M in toluene, 0.33 mmol). The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to –78 °C and diisopropylzinc (1 mL, 1.0 M in toluene 1 mmol). After stirring for 20 min, the reaction flask was warmed to 0 ^{o}C. Under a steady flow of N_2 (g), the rubber septum was replaced with a glass stopper coated with silicon grease and high vacuum was gradually applied to

remove the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL) followed by addition of *p*-tolualdehyde (0.22 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred until no aldehyde remained by TLC (usually 7-16 hrs). Quenching by saturated aq. NH_4Cl (2 ml), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were successively washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel to yield a mixture of the title compound (48 mg, 47.5%) and (*Z*)-5-(tert-butyldiphenylsilyloxy)-2-isopropyl-1-p-tolylpent-2-en-1-ol (10.0 mg, 9.6%) in a 5:1 ratio, respectively. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, J = 7.8 Hz, 4H), 7.44 (m, 6H), 7.26 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.63 (d, J = 3.0 Hz, 1H), 5.42 (t, J =7. 6 Hz, 1H), 3.74 (t, J = 6.4 Hz, 2H), 2.6 (m, 1H), 2.51 (m, 1H), 2.37 (s, 3H), 2.30 (d, J = 3.5 Hz, 1H), 2.10 (m, 1H), 1.87 (m, 1H), 1.10 (s, 9H), 0.99 (t, J = 7.4 Hz, 3H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 144.9, 140.0, 136.6, 133.8, 129.9, 129.0, 127.9, 126.7, 126.0, 122.8, 72.1, 64.0, 31.2, 27.1, 24.6, 21.3, 19.4, 13.0 ppm.



(*Z*)-2-(3-(tert-butyldiphenylsilyloxy)propylidene)-1-p-tolylhexan-1-ol. A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N_2 (g) three times, was charged with (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (386.4 mg, 1 mmol) and toluene (1 mL) under a nitrogen

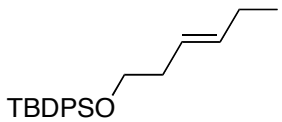
atmosphere. The solution was cooled to 0 °C followed by slow addition of diethylborane (1 mL, 1.0 M in toluene, 1 mmol). The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to −78 °C and dibutylzinc (3 mL, 1.0 M in heptane, 3 mmol). After stirring for 20 min, the reaction flask was warmed to 0 °C. Under a steady flow of N_2 (g), the rubber septum was replaced with a glass stopper coated with silicon grease and high vacuum was gradually applied to remove the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL) followed by addition of *p*-tolualdehyde (0.67 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred until no aldehyde remained by TLC (usually 7-16 hrs). Quenching by saturated aq. NH_4Cl (2 ml), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were successively washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel to yield a mixture of the title compound (55 mg, 15.7%) and (*Z*)-5-(tert-butyldiphenylsilyloxy)-2-ethyl-1-p-tolylpent-2-en-1-ol (205 mg, 62%) in a 1:4 ratio, respectively. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (d, J = 7.6 Hz, 4H), 7.42 (m, 6H), 7.26 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 5.59 (d, J = 2.7 Hz, 1H), 5.42 (t, J = 7.4 Hz, 1H), 3.73 (t, J = 6.2 Hz, 2H), 2.59 (m, 1H), 2.49 (m, 1H), 2.36 (s, 3H), 2.29 (d, 3.5 Hz, 1H), 2.03 (m, 1H), 1.88 (m, 1H), 1.29 (m, 4H), 1.09 (s, 9H), 0.86 (t, J = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 143.6, 140.0, 136.6, 135.9, 133.8, 129.9, 129.0, 127.9, 126.0, 123.9, 72.2, 64.0, 31.9, 31.3, 31.2, 27.1, 22.9, 21.3, 19.4, 14.2 ppm.



(*Z*)-5-(tert-butyldiphenylsilyloxy)-2-methyl-1-p-tolylpent-2-en-1-ol. A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N_2 (g) three times, was charged with (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (386.4 mg, 1 mmol) and toluene (1 mL) under a nitrogen atmosphere. The solution was cooled to 0 ^oC followed by slow addition of diethylborane (1 mL, 1.0 M in toluene, 1 mmol). The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to –78 °C and dimethylzinc (3 mL, 1.0 M, in toluene, 3 mmol). After stirring for 20 min, the reaction flask was warmed to 0 ^oC. Under a steady flow of N_2 (g), the rubber septum was replaced with a glass stopper coated with silicon grease and high vacuum was gradually applied to remove the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL) followed by addition of *p*-tolualdehyde (0.67 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred until no aldehyde remained by TLC (usually 7-16 hrs). Quenching by saturated aq. NH_4Cl (2 mL), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were successively washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel to yield a mixture of the title compound (67.6 mg, 23%)

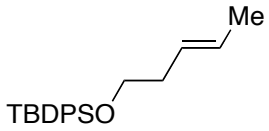
and (*Z*)-5-(tert-butyldiphenylsilyloxy)-2-ethyl-1-p-tolylpent-2-en-1-ol (172.2 mg, 56.7%) in a 1:2.5 ratio, respectively. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75 (d, *J* = 7.1 Hz, 4H), 7.45 (m, 6H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.62 (s, 1H), 5.40 (t, *J* = 7.4 Hz, 1H), 3.76 (m, 2H), 2.55 (dt, *J* = 6.7 Hz, 6.4 Hz, 2H), 2.37 (s, 3H), 2.08 (d, *J* = 3.1 Hz, 1H), 1.62 (s, 3 H), 1.12 (s, 9H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 139.6, 139.1, 136.6, 135.8, 133.9, 129.9, 129.1, 127.9, 125.9, 124.7, 71.5, 64.0, 31.3, 27.1, 21.3, 19.4, 18.5 ppm; HRMS-CI calcd for $C_{29}H_{36}O_2SiCl$ ($M+Cl^+$): 479.2195, found 479.2189.

Protonolysis of Intermediates in the Generation of Trisubstituted Vinylzinc Species (Scheme 7).



(*E*)-*tert*-butyl(hex-3-enyloxy)diphenylsilane. A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N_2 (g) three times, was charged with (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (386.4 mg, 1 mmol) and toluene (1 mL) under a nitrogen atmosphere. The solution was cooled to 0 ^{o}C followed by slow addition of diethylborane (1mL, 1.0 M in toluene, 1 mmol). The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to –78 °C and dimethylzinc (3 mL, 1.0 M, in toluene, 3 mmol). After stirring for 20 min, the reaction was quenched with MeOH. Warming to ambient temperature, saturated aq. NH_4Cl (2 ml) was added and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were successively washed with saturated $NaHCO_3$

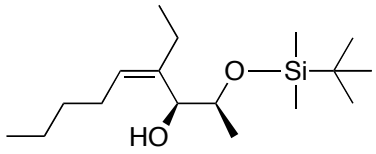
and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel to yield a mixture of the title compound and (*Z*)- (*E*)-*tert*-butyl(pent-3-enyloxy)diphenylsilane in a 1:2.7 ratio, respectively. For comparison, (*E*)-*tert*-butyl(hex-3-enyloxy)diphenylsilane was also prepared using the same procedure and diethylzinc in the place of dimethylzinc. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70 (d, *J* = 6.5 Hz, 4H), 7.41 (m, 6H), 5.52 (dt, *J* = 15.3, 6.1 Hz, 1H), 5.41 (dt, *J* = 15.3, 6.7 Hz, 1H), 3.70 (t, *J* = 6.7 Hz, 2H), 2.28 (dt, *J* = 6.5, 6.7 Hz, 2H), 2.02 (dq, *J* = 6.5, 7.0 Hz, 2H), 1.08 (s, 9H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 135.8, 134.4, 134.3, 129.7, 127.8, 125.7, 64.3, 36.2, 27.1, 25.9, 19.5, 14.0 ppm.



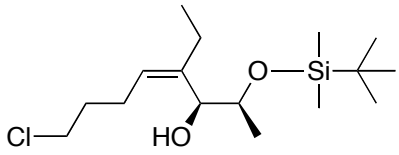
(*E*)-*tert*-butyl(pent-3-enyloxy)diphenylsilane. For comparison the title compound was synthesized applying general procedure C to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (386.4 mg, 1 mmol), $Br_2BH{\bullet}SMe_2$ (166 μL, 1 mmol), Me_2Zn (2.25 mL, 2.0 M in PhMe), and *p*-tolualdehyde (78.5 μL, 0.67 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, *J* = 7.8 Hz, 4H), 7.41 (m, 6H), 5.45 (m, 2H), 3.69 (t, *J* = 6.8 Hz, 2H), 2.27 (dt, *J* = 6.6, 6.3 Hz, 2H), 1.66 (d, 5.4 Hz, 3H), 1.07 (s, 9H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): 135.8, 134.3, 129.7, 127.9, 127.8, 127.2, 64.2, 36.2, 27.1, 19.4, 18.2 ppm.

Diastereoselective Synthesis of (*Z*)-Trisubstituted Allylic Alcohols via Addition to Chiral or Racemic Aldehydes

General Procedure A: Synthesis of (*Z*)-Trisubsitituted Allylic Alcohols with Ethyl Installation. A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N_2 (g) three times, was charged with 1-bromoalkyne (1 mmol) and toluene (1 mL) under a nitrogen atmosphere. The solution was cooled to 0 ^oC followed by slow addition of diethylborane (Et_2BH) (1 mL, 1 M solution in toluene). The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to −78 ^oC and diethylzinc (Et_2Zn) (2.2 mL, 1 M solution in toluene) was added. After stirring at this temperature for 20 min, the reaction flask was warmed to 0 ^oC. Under a steady flow of N_2 (g), the rubber septum was replaced with a glass stopper coated with silicon grease and high vacuum was gradually applied to remove the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL) followed by addition of aldehyde (0.67 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred until no aldehyde remained by TLC (usually 7-16 hrs). Quenching by saturated aq. NH_4Cl (2 ml), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were successively washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel.

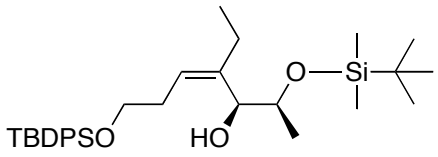


(2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-4-ethylnon-4-en-3-ol (19). General Procedure A was applied to 1-bromohex-1-yne (64 μL, 0.50 mmol), Et_2BH (0.50 mL, 1M in PhMe), Et_2Zn (1.1 mL, 1M in PhMe), and (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (72 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (81.6 mg, 82% yield) as a colorless oil. $[\alpha]_D^{20}$ = 9.12 (*c* = 0.970, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.35 (t, *J* = 7.3 Hz, 1H), 4.26 (d, *J* = 7.9 Hz, 1H), 3.82 (dq, *J* = 7.9 Hz, *J* = 6.2 Hz, 1H), 2.65 (s, 1H), 2.19 (m, 2H), 2.05 (m, 1H), 1.94 (m, 1H), 1.36 (m, 4H), 1.08 (d, *J* = 6.3 Hz, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.94 (s, 9H), 0.91 (t, *J* = 6.6 Hz, 3H), 0.13 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 138.9, 128.7, 75.4, 71.7, 32.5, 27.7, 26.1, 23.7, 22.7, 20.1, 18.4, 14.2, 13.5, -3.8, -4.5 ppm; IR (neat): 3574, 3486, 2958, 2931, 2858, 1464, 1254, 1135, 1092, 1064, 967, 835, and 777 cm^{-1}; HRMS-CI calcd for $C_{17}H_{36}O_2Si$ $(M)^+$: 300.2485, found 300.2496.



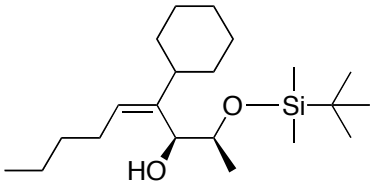
(2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-8-chloro-4-ethyloct-4-en-3-ol (20). General Procedure A was applied to 1-bromo-5-chloropent-1-yne (60 μL, 0.5 mmol), Et_2BH (500 μL, 0.5 mmol), Et_2Zn (1.15 mL, 1.15 mmol), and (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (72 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (98.2 mg, 93% yield) as a colorless oil. $[\alpha]_D^{20}$ = 29.2 (*c* 4.37, $CHCl_3$); ^1H NMR ($CDCl_3$, 500

MHz): δ 5.30 (t, *J* = 7.5 Hz, 1H), 4.25 (d, *J* = 8.1 Hz, 1H), 3.83 (dq, *J* = 7.9, 6.2 Hz, 1H), 3.57 (m, 2H), 2.64 (s, 1H), 2.36 (m, 1H), 2.22 (m, 2H), 1.95 (m, 1H), 1.87 (m, 2H), 1.08 (d, *J* = 6.2 Hz, 3H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.94 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.9. 126.4. 75.4. 71.7. 44.8. 33.1. 26.1. 25.3. 24.0. 20.1. 18.3. 13.4. –3.4. and –4.5 ppm; IR (neat): 3568, 2958, 2932, 2858, 1463, 1257, 1075, 836, and 777 cm^{-1}; HRMS-CI calcd for $C_{16}H_{32}OSi$ $(M–OH)^+$: 303.1911, found 303.1908.

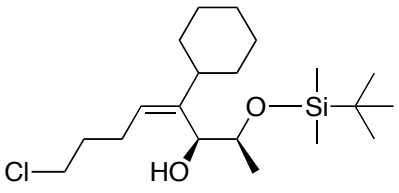


(5*S*,6*S*,*Z*)-7-ethyl-2,2,3,3,5,13,13-heptamethyl-12,12-diphenyl-4,11-dioxa-3,12-disilatetradec-7-en-6-ol (21). General Procedure A was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (160 μL, 0.50 mmol), Et_2BH (0.50 mL, 1.0 M in PhMe), Et_2Zn (1.2 mL, 1.0 M in PhMe), and (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (72 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (166.6 mg, 96% yield) as a colorless oil. $[\alpha]_D^{20}$ = 20.0 (*c* 0.365, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, *J* = 7.9 Hz, 4H), 7.41 (m, 6H), 5.38 (t, *J* = 7.2 Hz, 1H), 4.18 (d, *J* = 7.9 Hz, 1H), 3.77 (dq, *J* = 7.9 Hz, 6.2 Hz, 1H), 3.69 (t, *J* = 7.0 Hz, 2H), 2.66 (s, 1H), 2.42 (m, 2H), 2.05 (m, 2H), 1.07 (s, 9H), 1.05-1.00 (m, 6H), 0.94 (s, 9H), 0.12 (s, 6H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 141.1, 135.8, 134.2, 129.8, 127.8, 124.2, 75.5, 71.6, 61.0, 31.5, 27.1, 26.1, 24.0, 20.1, 19.4, 14.4, 13.2, –3.9, and –4.5 ppm; IR (neat): 3468, 2957, 2930, 2858, 1472, 1428, 1253 ,1112, 1084, 832, and 701 cm^{-1}; HRMS-ESI calcd for $C_{31}H_{51}O_3Si_2$ $(MH)^+$: 527.3377, found 527.3402.

General Procedure B: Synthesis of (*Z*)-Trisubsitituted Allylic Alcohols with Cyclohexyl Installation. In the glovebox, dicyclohexylborane (Cy_2BH) (1 mmol) was added to a dry 10 mL Schlenk flask, fitted with a rubber septum and stirbar and was removed from the box. Under a nitrogen atmosphere (via Schlenk line by was evacuated under vacuum and backfilled with N_2 (g) three times), the flask was charged with toluene (1 mL) and bromoalkyne (1 mmol) at 0 ˚C. The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min when the white solid Cy_2BH dissolved to make a clear solution. The solution was cooled to −78 ^{o}C and Et_2Zn (2.25 mL, 1 M solution in toluene) was added. After stirring at this temperature for 20 min, the reaction flask was warmed to 0 ^{o}C. Under a steady flow of N_2 (g), the rubber septum was replaced with a glass stopper coated with silicon grease and high vacuum was gradually applied to remove the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL) followed by addition of aldehyde (0.67 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred until no aldehyde remained by TLC (usually ~16 hrs). Quenching by saturated aq. NH_4Cl (2 ml), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were successively washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel.

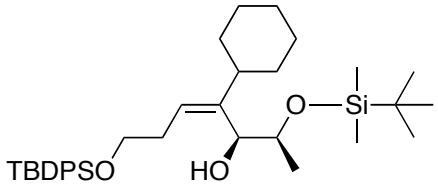


(2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-4-cyclohexylnon-4-en-3-ol (22). General Procedure B was applied to 1-bromohex-1-yne (128 μL, 1.0 mmol), Cy_2BH (180 mg, 1.0 mmol), Et_2Zn (2.2 ml, 1.0 M in PhMe), and (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (144 μL, 0.66 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (149.4 mg, 75% yield) as a colorless oil. $[\alpha]_D^{20}$ = 17.5 (*c* 3.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.39 (t, *J* = 7.3 Hz, 1H), 4.23 (d, *J* = 8.6 Hz, 1H), 3.77 (dq, *J* = 8.5, 6.2 Hz, 1H), 2.72 (s, 1H), 2.10 (m, 3H), 1.71 (m, 4H), 1.28 (m, 10H), 1.07 (d, *J* = 6.1 Hz, 3H), 0.95 s, 9H, overlapping with t, 3H), 0.16 (s, 3H), 0.15 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 143.3, 129.0, 76.0, 71.7, 39.4, 35.6, 35.0, 32.5, 27.7, 27.5, 27.4, 26.6, 26.1, 22.6, 20.3, 14.3, 1.2, –3.8, and –4.5 ppm; IR (neat): 3565, 2957, 2928, 2855, 1464, 1449, 1259, 1079, and 835 cm^{-1}; HRMS-ESI calcd for $C_{21}H_{42}O_2NaSi$ $(M)^+$: 377.2852, found 377.2795.



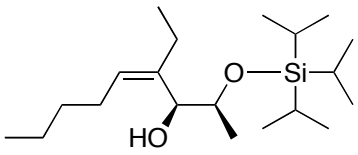
(2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-8-chloro-4-cyclohexyloct-4-en-3-ol (23). General Procedure B was applied to 1-bromo-5-chloropent-1-yne (60 μL, 0.5 mmol), Cy_2BH (90 mg, 0.5 mmol), Et_2Zn (1.1 ml, 1.0 M in PhMe), (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (72μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound

(66.6 mg, 54% yield) as a colorless oil. $[\alpha]_D^{20}$ = –1.3 (*c* 0.28, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.35 (t, *J* = 7.3 Hz, 1H), 4.21 (d, *J* = 8.6 Hz, 1H), 3.77 (dq, *J* = 8.4, 6.2 Hz, 1H), 3.55 (dt, *J* = 2.0, 6.5 Hz, 2H), 2.74 (s, 1H), 2.29 (m, 2H), 2.00 (t, *J* = 11.3 Hz, 1H), 1.85 (m, 2H), 1.75 (m, 4H), 1.24 (m, 6H), 1.07 (d, *J* = 6.1 Hz, 3H), 0.94 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 145.3, 126.6, 76.1, 71.6, 44.8, 39.7, 35.5, 24.9, 33.1, 29.9, 27.5, 27.3, 26.5, 26.1, 25.3, 20.3, –3.8, and –4.5 ppm; IR (neat): 3569, 2955, 2928, 2855, 1448, 1258, 1072, and 835 cm^{-1}; HRMS-ESI calcd for $C_{20}H_{39}ClO_2NaSi$ $(M+Na)^+$: 397.2306, found 397.2302.

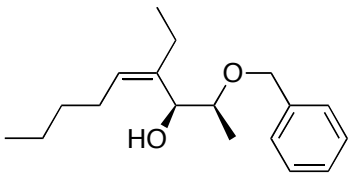


(5*S*,6*S*,*Z*)-7-cyclohexyl-2,2,3,3,5,13,13-heptamethyl-12,12-diphenyl-4,11-dioxa-3,12-disilatetradec-7-en-6-ol (24). General Procedure B was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (160 µL, 0.5 mmol), Cy_2BH (90 mg, 0.5 mmol), Et_2Zn (1.1 ml, 1.0 M in PhMe), and (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (72 µL, 0.5 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (380.5 mg, 74% yield) as a colorless oil. $[\alpha]_D^{20}$ = 7.23 (*c* 10.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.70 (d, *J* = 6.5 Hz, 4H), 7.42 (m, 6H), 5.45 (t, *J* = 7.3 Hz, 1H), 4.16 (d, *J* = 8.5 Hz, 1H), 3.78 (dq, *J* = 8.3, 6.2 Hz, 1H), 3.68 (t, *J* = 6.5 Hz, 2H) 2.74 (s, 1H), 2.44 (m, 2H), 1.99 (m, 1H), 1.83 – 1.60 (m, 4H), 1.31 – 1.16 (m, 6H), 1.08 (s, 9H), 1.03 (d, *J* = 6.1 Hz, 3H), 0.96 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 145.5, 135.8, 134.2, 129.8, 127.8, 124.6, 76.2, 71.6, 64.0, 39.9, 35.4, 35.0, 31.5, 27.5, 27.4, 27.1,

26.6, 26.1, 20.3, 17.4, 18.3, –3.8 and –4.5 ppm; IR (neat): 3565, 2956, 2928, 2857, 1472, 1428, 1257, 1112, and 701 cm^{-1}; HRMS-ESI calcd for $C_{35}H_{56}O_3NaSi_2$ $(M+Na)^+$: 603.3666, found 603.3686.

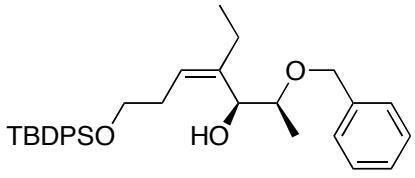


(2*S*,3*S*,*Z*)-4-ethyl-2-(triisopropylsilyloxy)non-4-en-3-ol (25). General Procedure A. 1-bromohex-1-yne (288 μL, 2.25 mmol), Et_2BH (2.25 mL, 1.0 M in PhMe), Et_2Zn (4.5 mL, 1.0 M in PhMe), and (*S*)-2-(triisopropylsilyloxy)propanal (346 mg, 1.5 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (380.5 mg, 74% yield) as a colorless oil. $[\alpha]_D^{20}$ = 34.49 (*c* 1.265, CHCl3); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.34 (t, 7.1 Hz, 1H), 4.27 (d, *J* = 8.4 Hz, 1H), 3.98 (d1, *J* = 8.4 Hz, 6.1 Hz, 1H), 2.85 (s, 1H), 2.21 (m, 2H), 2.07 (m, 1H), 1.94 (m, 1H), 1.36 (m, 4H), 1.11 (m, 24 H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 138.8, 129.0, 75.8, 71.8, 32.5, 27.8, 23.7, 22.7, 20.2, 18.4, 18.3, 14.3, 13.5, 12.9 ppm; IR (film): 3582, 2960, 2945, 2868, 1464, 1373, 1134, 1094, 1062, 883, and 679 cm^{-1}; HRMS-ESI calcd for $C_{20}H_{42}O_2SiNa$ $(M+Na)^+$: 365.2876, found 365.2866.



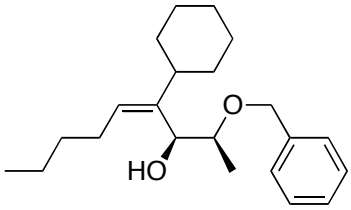
(2*S*,3*S*,*Z*)-2-(benzyloxy)-4-ethylnon-4-en-3-ol (26). General Procedure A. 1-bromohex-1-yne (64 μL, 0.5 mmol), Et_2BH (0.5 mL, 1.0 M in PhMe), Et_2Zn (1.1 mL, 1.0 M in PhMe), and (*S*)-2-(benzyloxy)propanal (53 μL, 0.33 mmol).

The crude product was purified by column chromatography on silica gel to yield the title compound (68 mg, 75% yield) as a colorless oil. $[\alpha]_D^{20}$ = 54.7 (*c* = 0.92, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.39 (d, *J* = 4.4 Hz, 4H), 7.33, (m, 1H), 5.38 (t, *J* = 7.2 Hz, 1H), 4.72 (d, *J* = 11.3, 1H), 4.51 (d, *J* = 11.3 Hz, 1H), 4.45 (d, *J* = 8.7 Hz, 1H), 3.64 (d quart, *J* = 8.6, 6.2 Hz, 1H), 2.83 (s, 1H), 2.20 (m, 2H), 2.07 (m, 1H), 1.95 (m, 1H), 1.35 (m, 4H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.92 (t, 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 138.5, 138.4, 129.2, 128.7, 128.1, 128.0, 78.3, 74.2, 71.6, 32.5, 27.7, 23.5, 22.7, 15.6, 14.2, 13.4 ppm; IR (neat): 3563, 3470, 2960, 2930, 2873, 1455, 1375, 1094, 1069, 1029, 735, and 698 cm^{-1}; HRMS-CI calcd for $C_{18}H_{28}O_2$ $(M)^+$: 276.2089, found 276.2087.

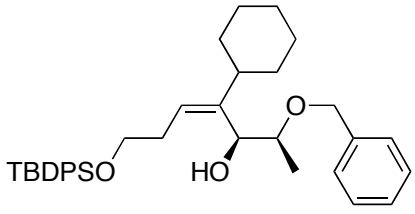


(2*S*,3*S*,*Z*)-2-(benzyloxy)-7-(*tert*-butyldiphenylsilyloxy)-4-ethylhept-4-en-3-ol (27). General Procedure A was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (160 μL, 0.5 mmol), Et_2BH (0.5 mL, 1.0 M in PhMe), Et_2Zn (1.2 mL, 1.0 M in PhMe), and (*S*)-2-(benzyloxy)propanal (53 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (124.8 mg, 75% yield) as a colorless oil. $[\alpha]_D^{20}$ = 29.3 (*c* 6.23, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.69 (m, 4H), 7.44 – 7.33 (m, 11H), 5.43 (t, *J* = 7.3 Hz, 1H), 4.70 (d, *J* = 11.3 Hz, 1H), 4.49 (d, *J* = 11.3 Hz, 1H), 4.37 (d, *J* = 8.5 Hz, 1H), 3.69 (t, *J* = 6.9 Hz, 2H), 3.61 (dq, *J* = 8.5, 6.2 Hz, 1H), 2.49 – 2.38 (m, 2H), 2.20 (m, 1H), 1.94 (m, 1H), 1.07 (s, 1H), 1.05 (d, *J* = 7.7 Hz, 3H0, 0.91 (t, *J* = 6.9 Hz, 3H)

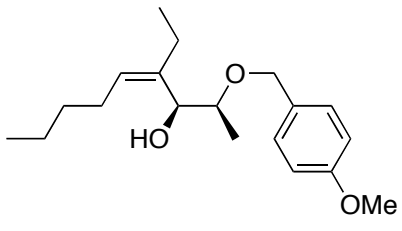
ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 140.6, 135.8, 134.1, 129.8, 128.7, 128.0, 127.9, 124.8, 78.1, 74.4, 71.5, 64.0, 31.5, 27.1, 23.8, 19.4, 15.6, and 13.2 ppm; IR (neat): 3564, 2962, 2932, 2858, 1472, 1428, 1112, and 701 cm^{-1}; HRMS-ESI calcd for $C_{32}H_{42}O_3NaSi$ $(M+Na)^+$: 525.2801, found 525.2827.



(2*S*,3*S*,*Z*)-2-(benzyloxy)-4-cyclohexylnon-4-en-3-ol (28). General Procedure B was applied to 1-bromohex-1-yne (64 μL, 0.5 mmol), Cy_2BH (90 mg, 0.5 mmol), Et_2Zn (1.2 mL, 1.0 M in PhMe), and (*S*)-2-(benzyloxy)propanal (53 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (74.2 mg, 68% yield) as a colorless oil. $[\alpha]_D^{20}$ = 10.6 (*c* 3.60, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71-7.31 (m, 5H), 5.42 (t, *J* = 7.3 Hz, 1H), 4.62 (dd, *J* = 11.2, 98.3 Hz, 2H), 4.43 (d, *J* = 8.8 Hz, 1H), 3.59 (dq, *J* = 8.8, 6.1 Hz, 1H), 2.88 (d, 1H), 2.17 (m, 1H), 2.04 (m, 2H), 1.85-1.67 (m, 4H), 1.35-1.17 (m, 10H), 1.13 (d, *J* = 6.2 Hz, 3H), 3H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 143.0, 138.5, 129.3, 128.7, 128.1, 128.0, 78.3, 74.7, 71.6, 39.1, 35.8, 35.0, 32.4, 27.7, 27.5, 27.4, 26.6, 22.6, 15.9, and 14.2 ppm; IR (neat): 3436, 2927, 2853, 1450, 1274, 1095, and 1070 cm^{-1}; HRMS-ESI calcd for $C_{22}H_{34}ONa$ $(M+Na)^+$: 353.2457, found 353.2434.

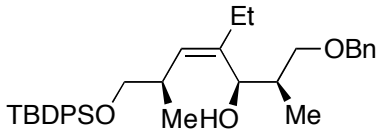


(2*S*,3*S*,*Z*)-2-(benzyloxy)-7-(*tert*-butyldiphenylsilyloxy)-4-cyclohexylhept-4-en-3-ol (29). General Procedure B was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (160 μL, 0.5 mmol), Cy_2BH (90 mg, 0.5 mmol), Et_2Zn (1.2 mL, 1.0 M in PhMe), and (*S*)-2-(benzyloxy)propanal (53 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (95.6 mg, 52% yield) as a colorless oil. $[\alpha]_D^{20}$ = 4.33 (*c* 4.37, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, *J* = 7.7 Hz, 4H), 7.44 - 7.38 (m, 10 H), 7.33 (m, 1H), 5.46 (t, *J* = 7.2 Hz, 1H), 4.61 (dd, *J* = 11.2, 94.9 Hz, 2H), 4.34 (d, *J* = 8.7 Hz, 1H), 3.68 (t, *J* = 6.6 Hz, 2H), 3.59 (dq, *J* = 8.6, 6.2 Hz, 1H), 2.89 (s, 1H), 2.43 (m, 2H), 2.01 (t, *J* = 11.6 Hz, 1H), 1.83 – 1.67 (m, 4H), 1.20 (m, 6H), 1.08 (d, *J* = 6.3 Hz, 3H), 1.07 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 145.2, 138.6, 135.8, 134.1, 129.8, 128.7, 128.1, 128.0, 127.8, 125.0, 78.2, 75.0, 71.6, 64.0, 39.7, 35.5, 34.9, 31.5, 27.5, 27.3, 27.1, 26.6, 21.3, and 16.0 ppm; IR (neat): 3448, 2928, 2856, 1449, 1428, 1112, and 702 cm^{-1}; HRMS-ESI calcd for $C_{36}H_{48}O_3NaSi$ $(M+Na)^+$: 579.3270, found 579.3266.



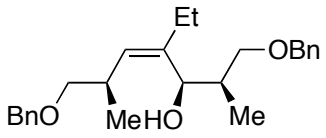
(2*S*,3*S*,*Z*)-4-ethyl-2-(4-methoxybenzyloxy)non-4-en-3-ol (30). General Procedure A was applied to 1-bromohex-1-yne (157 μL, 1.23 mmol),

Et_2BH (1.23 mL, 1.0 M in PhMe), Et_2Zn (2.50 mL, 1.0 M in PhMe), and (*S*)-2-(4-methoxybenzyloxy)propanal (159 mg, 0.821 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (179 mg, 71% yield) as a colorless oil. $[\alpha]_D^{20}$ = 53.8 (*c* = 2.29 , $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.37 (t, *J* = 7.3 Hz, 1H), 4.64 (d, *J* = 10.9 Hz, 1H), 4.43 (d, 11.0 Hz, 1H), 4.42 (d, *J* = 8.3 Hz, 1H), 2.06 (m, 1H), 1.94 (m, 1H) 1.34 (m, 4H), 1.11 (d, *J* = 6.2 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 159.6, 138.4, 130.6, 129.7, 129.2, 114.2, 78.0, 74.2, 71.2, 55.5, 32.4, 27.7, 23.5, 22.7, 15.6, 14.2, 13.4 ppm; IR (neat): 3553, 2959, 2930, 2872, 1613, 1514, 1464, 1249, and 1037 cm^{-1}; HRMS-ESI calcd for $C_{19}H_{30}O_3Na$ $(M+Na)^+$: 329.2093, found 329.2093.

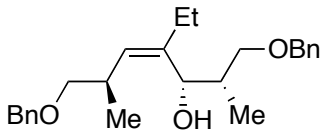


(2*R*,3*R*,6*R*,*Z*)-1-(benzyloxy)-7-(*tert*-butyldiphenylsilyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (31). General Procedure D was applied to (*R*)-(4-bromo-2-methylbut-3-ynyloxy)(*tert*-butyl)diphenylsilane (106 μL, 0.3 mmol), Et_2BH (300 μL, 1.0M in PhMe), Et_2Zn (0.6 mL, 1.0 M in PhMe), and (*R*)-3-(benzyloxy)-2-methylpropanal (34 μL, 0.2 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (143 mg, 74%) as a colorless oil. $[\alpha]_D^{20}$ = –25.8 (*c* 3.42, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.68 (m, 4H), 7.44 – 7.33 (m, 11H), 5.12 (d, *J* = 9.9 Hz, 1H), 4.57 (d, *J* = 3.6 Hz, 2H), 4.31 (d, *J* = 9.0 Hz, 1H), 3.55 (m, 2H), 3.45 (dd, *J* = 1.6 , 6.8 Hz, 2H), 1.06 (s, 9H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.64 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 141.6,

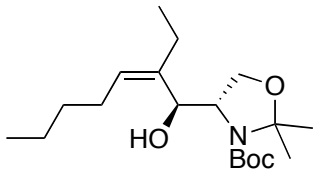
138.2, 135.9, 135.8, 134.0, 133.9, 129.8, 129.7, 128.7, 127.98, 127.96, 127.83, 127.81, 76.0, 75.8, 73.7, 69.1, 37.3, 34.8, 27.1, 23.9, 19.5, 18.3, 14.1, and 13.1 ppm; IR (neat): 3480, 3071, 2961, 2931, 2858, 1455, 1428, 1112, and 701 cm^{-1}; HRMS-ESI calcd for $C_{34}H_{46}O_3NaSi$ $(M+Na)^+$: 553.3114, found 553.3128.



(2*R*,3*R*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (32). General Procedure D was applied to (*R*)-((4-bromo-2-methylbut-3-ynyloxy)methyl)benzene (70 μL, 0.358 mmol), Et_2BH (0.358 ml, 1.0 M), Et_2Zn (0.75 mL, 1.0 M in PhMe), and (*R*)-3-(benzyloxy)-2-methylpropanal (40 μL, 0.236 mmol). The crude product was purified by column chromatography on silica gel to yield the desired product (78.5 mg, 87%) as a colorless oil. $[\alpha]_D^{20}$ = –37.7 (*c* 1.55, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.37 – 7.30 (m, 10H), 5.07 (d, *J* = 10.0 Hz, 1H), 4.56 (d, *J* = 3.4 Hz, 2H), 4.51 (s, 2H), 4.33 (d, *J* = 9.0 Hz, 1H), 3.59 (m, 2H), 3.28 (dd, *J* = 6.5, 6.9 Hz, 2H), 2.97 (dq, *J* = 9.8, 6.7 Hz, 1H), 2.19 (m, 1H), 2.08 (m, H), 1.97 (m, 1H), 1.07 (t, *J* = 7.4 H, 3H) 1.02 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 142.0, 138.7, 138.2, 129.7, 128.7, 128.5, 127.9, 127.7, 127.7, 75.9, 75.8, 75.5, 73.7, 73.2, 37.6, 32.7, 24.5, 18.5, 14.1, and 13.2 ppm; IR (neat): 3429, 2962, 2927, 1644, 1094, 735, and 697 cm^{-1}; HRMS-ESI calcd for $C_{25}H_{34}O_3Na$ $(M+Na)^+$: 405.2406, found 405.2391.

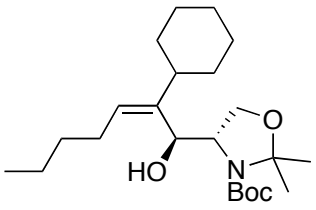


(2*S*,3*S*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (33). General Procedure D was applied to (*S*)-((4-bromo-2-methylbut-3-ynyloxy)methyl)benzene (70 μL, 0.358 mmol), Et_2BH (0.358 ml, 1.0 M), Et_2Zn (0.75 mL, 1.0 M in PhMe), and (*R*)-3-(benzyloxy)-2-methylpropanal (40 μL, 0.236 mmol). The crude product was purified by column chromatography on silica gel to yield the desired product (58.4 mg, 65%) as a colorless oil. $[\alpha]_D^{20}$ = -1.19 (*c* 1.35, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.37 – 7.29 (m, 10H), 5.05 (d, *J* = 9.8 Hz, 1H) 4.57 (d, *J* = 7.9 Hz, 2H), 4.53 (s, 2H), 4.42 (d, *J* = 9.8 Hz, 1H) 3.62 (m, 2H) 3.30 (dd, 6.2, 6.5 Hz,, 2H), 2.24 (m, 2H, overlaps w/ OH) 2.08 (m, 1H), 1.98 (m, 1H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 142.1, 138.6, 138.4, 129.6, 128.6, 128.6, 127.9, 127.9, 127.8, 75.6, 75.4, 74.2, 73.7, 73.3, 36.3, 32.4, 22.8, 18.1, 14.1, and 13.2 ppm; IR (neat): 34.36, 2962, 2928, 1638, 1454, 1092, 735, and 697 cm^{-1}; HRMS-ESI calcd $C_{25}H_{35}O_3$ for $(MH)^+$: 383.2586, found 383.2597.



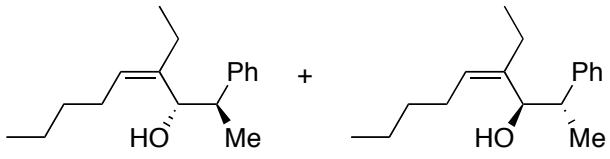
(*S*)-*tert*-butyl 4-((*S*,*Z*)-2-ethyl-1-hydroxyhept-2-enyl)-2,2-dimethyloxazolidine-3-carboxylate (34). General Procedure A was applied to 1-bromohex-1-yne (64 μL, 0.5 mmol), Et_2BH (0.5 mL, 1.0 M in PhMe), Et_2Zn (1.05 mL, 1.0 M in PhMe), and (*S*)-*tert*-butyl 4-formyl-2,2-dimethyloxazolidine-3-carboxylate (73 μL, 0.33 mmol). The crude product was purified by column chromatography on silica

gel to yield the title compound (103.8 mg, 92% yield) as a colorless oil. $[\alpha]_D^{20} = -42.4$ (*c* 4.42, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ 5.38 (t, *J* = 7.2 Hz, 1H), 4.66 9d, *J* = 9.5 Hz, 1H), 4.15 (m, 1H), 3.84 (dd, *J* = 6.1, 9.3 Hz, 1H), 3.69 (dd, *J* = 1.2, 9.3 Hz, 1H), 2.22 (m, 2H), 2.06 (m, 1H), 1.96 (m, 1H), 1.64 (s, 3H), 1.53 (s, 12H (*t*-butyl overlaps with Me)), 1.36 (m, 4H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 156.1, 139.5, 128.5, 94.6, 81.9, 71.2, 65.3, 64.0, 32.4, 28.6, 28.6, 27.5, 27.4, 23.0, 22.6, 14.2, and 13.5 ppm; IR (neat): 3402, 2961, 2933, 2874, 1696, 1662, 1402, 1256, 1173, 1107, and 1064 cm^{-1}; HRMS-ESI calcd for $C_{19}H_{36}NO_4$ $(MH)^+$: 342.2644, found 342.2636.

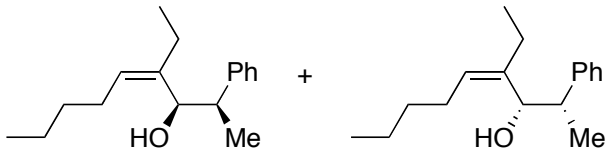


(*S*)-*tert*-butyl 4-((*S*,*Z*)-2-cyclohexyl-1-hydroxyhept-2-enyl)-2,2-dimethyloxazolidine-3-carboxylate (35). General Procedure B was applied to 1-bromohex-1-yne (128 μL, 1.0 mmol), Cy_2BH (180 mg, 1.0 mmol), Et_2Zn (2.05 mL, 1.0 M in PhMe), and (*S*)-*tert*-butyl 4-formyl-2,2-dimethyloxazolidine-3-carboxylate (146 μL, 0.66 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (75.4 mg, 29% yield) initially as a colorless oil, which became a white solid. $[\alpha]_D^{20} = -33.9$ (*c* 0.44, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.40 (t, *J* = 7.3 Hz, 1H), 4.65 (d, *J* = 9.3 Hz, 1H), 4.14 (m, 1H), 3.83 (dd, *J* = 6.1, 9.2 Hz, 1H), 3.68 (d, *J* = 9.2 Hz, 1H), 2.18 (m, 1H), 2.06 (m, 2H), 1.86 – 1.71 (m, 4H), 1.65 (s, 6H), 1.54 (s, 9H), 1.36 – 1.22 (m, 10H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 155.7, 128.7, 126.6, 97.8, 65.4, 61.5, 38.4, 35.7, 35.0, 32.7, 32.4, 29.9, 28.6,

27.9, 27.4, 27.3, 27.2, 26.5, 24.4, 22.5, and 14.2 ppm; IR (neat): 3408, 2926, 1695, 1667, 1402, 1367, 1257, 1173, 1107, and 1054 cm^{-1}; HRMS-ESI calcd for $C_{23}H_{41}NO_4Na$ $(M+Na)^+$: 418.2933, found . CIF file is also available of the X-ray crystal structure of this compound later in the supporting information.

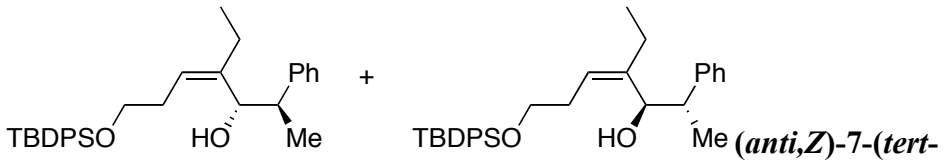


(*anti,Z*)-4-ethyl-2-phenylnon-4-en-3-ol (major diastereomer) **(36)**. General Procedure A was applied to 1-bromohex-1-yne (64 μL, 0.5 mmol), Et_2BH (0.5 mL, 1.0 M in PhMe), Et_2Zn (1.2 mL, 1.0 M in PhMe), 2-phenylpropanal (45 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (81.3 mg, 91% yield) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.26 (d, J = 7.5 Hz, 2H), 7.18 (m, 3H), 5.05 (t, J = 7.2 Hz, 1H), 4.63 (dd, J = 3.1, 8.8 Hz, 1H), 2.98 (dq, J = 8.6, 7.0 Hz, 1H), 2.15 (m, 1H), 1.96 (m, 2H), 1.73 (m, 1H), 1.44 (d, J = 3.4 Hz, 1H), 1.42 (d, J = 6.9 Hz, 3H), 1.20 (m, 4H), 0.99 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 144.4, 140.4, 128.3, 127.9, 127.2, 126.5, 75.7, 44.4, 32.2, 27.5, 23.4, 22.7, 18.3, 14.2, and 13.4 ppm; IR (neat): 3431, 2960, 2929, 2873, 1453, 1005, 996, and 699 cm^{-1}; HRMS calcd for $C_{17}H_{25}$ $(M)^+$: 229.1956, found 229.1948.



(*syn,Z*)-4-ethyl-2-phenylnon-4-en-3-ol (minor diastereomer) **(36)**. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.34 (m, 5H), 5.42 (t, J = 7.2

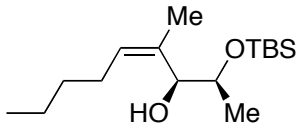
Hz, 1H), 4.64 (dd, *J* = 2.2, 9.7 Hz, 1H), 2.92 (dq, *J* = 9.7, 7.1 Hz), 2.25 (m, 2H), 2.15 (m, 1H), 2.06 (m, 1H), 1.40 (m, 4H), 1.33 (d, *J* = 2.4 Hz, 1H), 1.14 d, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 7.3 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H) ppm.



(*anti,Z*)-7-(*tert*-butyldiphenylsilyloxy)-4-ethyl-2-phenylhept-4-en-3-ol (37). General Procedure A was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (160 μL, 0.5 mmol), Et_2BH (0.5 mL, 1.0 M in PhMe), Et_2Zn (1.2 mL, 1.0 M in PhMe), and 2-phenylpropanal (45 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (142.8 mg, 95% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.39 (m, 6H), 7.20 (m, 2H), 7.13 (m, 3H), 5.11 (t, *J* = 7.6 Hz, 1H), 4.48 (d, *J* = 8.8 Hz, 1H), 3.50 (t, *J* = 6.5 Hz, 1H), 2.97 (dq, *J* = 8.5, 7.1 Hz, 1H), 2.31 – 2.17 (m, 2H), 2.06 (m, 1H), 1.86 (m, 1H), 1.73 (s, 1H), 1.41 (d, *J* = 6.9 Hz, 3H), 1.06 (s, 9H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ ppm; IR (neat): 3435, 2961, 2931, 2858, 1450, 1428, 1111, 997, and 700 cm^{-1}; HRMS-ESI calcd for $C_{31}H_{40}ClO_2Si$ $(M+Cl)^-$: 507.2486, found 507.2462.

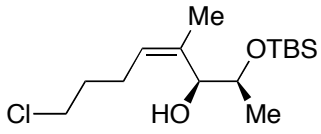
General Procedure C: Synthesis of (*Z*)-Trisubsitituted Allylic Alcohols with Methyl Installation using Dihaloborane. A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N_2 (g) three times, was charged with bromoalkyne (1 mmol) and toluene (1 mL) under a nitrogen atmosphere. The solution was cooled to 0 °C followed by slow addition of either $Br_2BH•SMe_2$ or $Cl_2BH•SMe_2$ (1 mmol). The reaction

was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to −78 °C and Et_2Zn (2.25 mL, 1.0 M solution in toluene) was added. After stirring at this temperature for 20 min, the reaction flask was warmed to 0 °C. Under a steady flow of N_2 (g), the rubber septum was replaced with a glass stopper coated with silicon grease and high vacuum was gradually applied to remove the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL) followed by addition of aldehyde (0.67 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred until no aldehyde remained by TLC (usually ~16 hrs). Quenching by saturated aq. NH_4Cl (2 ml), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were washed with saturated $NaHCO_3$ followed by saturated NaCl, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography on silica gel.

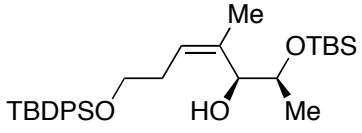


(2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-4-methylnon-4-en-3-ol (41). General Procedure C was applied to 1-bromohex-1-yne (97 μL, 0.75 mmol), $Cl_2BH•SMe_2$ (87 μL, 0.75 mmol), Me_2Zn (1.50 mL, 2.0 M in PhMe), and (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (108 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (97.5 mg, 68% yield) as a colorless oil. $[\alpha]_D^{20}$ = 37.6 (*c* 2.33, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.37 (t, *J* = 7.0 Hz, 1H), 4.22 (d, *J* = 8.0 Hz, 1H), 3.81 (dq, *J* = 8.0 Hz, *J* = 6.2 Hz, 1H), 2.64 (d, *J* =

1.7 Hz, 1H), 2.15 (m, 1H), 2.00 (m, 1H), 1.70 (s, 3H), 1.34 (m, 4H), 1.09 (d, J = 6.2 Hz, 3H), 0.94 (s, 9H), 0.91 (t, J = 7.0 Hz, 3H), 0.14 (s, 3H), 0.13 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 133.4, 131.0, 74.8, 71.4, 32.3, 27.7, 26.1, 22.7, 20.0, 18.5, 18.3, 14.2, -3.8, and -4.5 ppm; IR (neat): 3575, 2957, 2930, 2858, 1464, 1374, 1255, 1135, 1091, 1052, 835, and 777 cm^{-1}; HRMS-CI calcd for $C_{16}H_{33}OSi$ $(M\text{-}OH)^+$: 269.2301, found 269.2278.

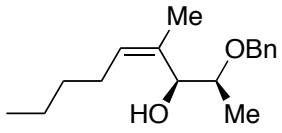


(2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-8-chloro-4-methyloct-4-en-3-ol (42). General Procedure C was applied to 1-bromo-5-chloropent-1-yne (60 μL, 0.5 mmol), $Cl_2BH{\bullet}SMe_2$ (58 μL, 0.5 mmol), Me_2Zn (1.75 mL, 1.2 M in PhMe), and (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (72 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (67.4 mg, 67% yield) as a colorless oil. $[\alpha]_D^{20}$ = 22.5 (*c* 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.33 (t, J = 7.1 Hz, 1H), 4.22 (d, J = 8.0 Hz, 1H), 3.81 (dq, J = 7.9, 6.2 Hz, 1H), 3.57 (m, 2H), 2.32 (m, 1H), 2.20 (m, 1H), 1.86 (tt, J = 7.0, 6.9 Hz, 2H), 1.28 (s, 3H), 1.09 (d, J = 6.2 Hz, 3H), 0.94 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H) ppm; ^{13}C), NMR ($CDCl_3$, 125 MHz): δ 128.6, 97.8, 74.8, 71.3, 44.7, 32.4, 29.9, 26.1, 25.1, 20.0, 18.7, 1.3, –4.5 ppm; IR (neat): 3431, 2956, 2931, 2858, 1463, 1257, 1095, 836, and 777 cm^{-1}; HRMS-ESI calcd for $C_{15}H_{31}Cl_2O_2Si$ $(M+Cl)^-$: 341.1470, found 341.1471.



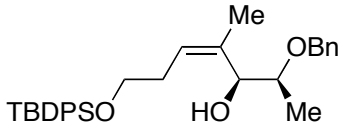
(5*S*,6*S*,*Z*)-2,2,3,3,5,7,13,13-octamethyl-12,12-diphenyl-4,11-dioxa-3,12-disilatetradec-7-en-6-ol (43). General Procedure C was applied to (4-

bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (160 μL, 0.5 mmol), $Cl_2BH•SMe_2$ (87 μL, 0.5 mmol), Me_2Zn (1.1 mL, 2.0 M in PhMe), and (*S*)-2-(*tert*-butyldimethylsilyloxy)propanal (72 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (131.6 mg, 78% yield) as a colorless oil. $[\alpha]_D^{20}$ = 16.2 (*c* 6.79, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (D, *J* = 7.2 Hz, 4H), 7.42 (m, 6H), 5.37 (t, *J* = 7.1 Hz, 1H), 4.13 (d, *J* = 7.6 Hz, 1H), 3.77 (dq, *J* = 7.6, 6.9 Hz, 1H), 3.67 (t, *J* = 7.0 Hz, 2H), 2.62 (s, 1H), 2.38 (m, 2H), 1.69 (s, 3H), 1.07 (s, 9H), 1.03 (d, *J* = 6.2 Hz, 3H), 0.94 (s, 9H), 0.12 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 135.8, 135.6, 134.2, 129.8, 127.8, 126.4, 74.9, 71.3, 64.0, 36.3, 31.5, 27.1, 26.1, 20.0, 18.7, -3.9, and –4.5 ppm; IR (neat): 3574, 3480, 2929, 2857, 1472, 1428, 1257, 1112, 834, and 701 cm^{-1}; HRMS-ESI calcd for $C_{30}H_{48}O_3NaSi_2$ $(M+Na)^+$: 535.3040, found 535.3032.



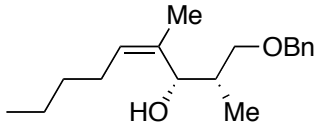
(2*S*,3*S*,*Z*)-2-(benzyloxy)-4-methylnon-4-en-3-ol (44). General Procedure C was applied to 1-bromohex-1-yne (64 μL, 0.5 mmol), $Cl_2BH•SMe_2$ (58 μL, 0.5 mmol), Me_2Zn (1.0 mL, 2.0 M in PhMe), and (*S*)-2-(benzyloxy)propanal (53 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (43.8 mg, 51% yield) as a colorless oil. $[\alpha]_D^{20}$ = 59.3 (*c* 2.56, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (d, *J* = 4.4 Hz, 4H), 7.33 (m, 1H), 5.40 (t, 7.00 Hz, 1H), 4.72 (d, *J* = 11.3 Hz, 1H), 4.51 (d, *J* = 11.3 Hz, 1H), 4.42 (d, *J* = 8.6 Hz, 1H), 3.62 (dq, *J* = 8.5 Hz, 6.2 Hz, 1H), 2.82 (s, 1H), 2.15 (m, 1H), 2.04 (m, 1H), 1.70 (s, 3H), 1.34 (m, 4H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$,

125 MHz): δ 138.5, 132.9, 131.4, 128.7, 128.0, 128.0, 78.0, 73.6, 71.6, 32.3, 27.6, 22.6, 18.3, 15.5, and 14.2 ppm; IR (neat): 3564, 3469, 2957, 2928, 2872, 1454, 1375, 1135, 1094, 1058, 1029, 736, and 698 cm^{-1}; HRMS-CI calcd for 262.1933 $(M)^+$: , found 262.1944.



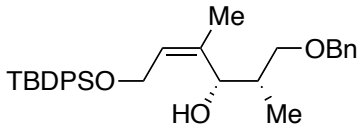
(2*S*,3*S*,*Z*)-2-(benzyloxy)-7-(*tert*-butyldiphenylsilyloxy)-4-methylhept-4-en-3-ol (45). General Procedure C was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (160 μL, 0.5 mmol), $Cl_2BH•SMe_2$ (58 μL, 0.5 mmol), Me_2Zn (1.0 mL, 2.0 M in PhMe), and (*S*)-2-(benzyloxy)propanal (53 μL, 0.33 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (92.3 mg, 57% yield) as a colorless oil. $[\alpha]_D^{20}$ = 4.43 (*c* 4.34, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.68 (d, *J* = 6.4 Hz, 4H), 7.43 – 7.33 (m, 11H), 5.40 (t, *J* = 7.3 Hz, 1H), 4.69 (d, *J* = 11.3 Hz, 1H), 4.49 (d, *J* = 11.3 Hz, 1H) 4.32 (d, *J* = 8.4 Hz, 1H), 3.67 (t, *J* = 7.0 Hz, 2H), 3.58 (dq, *J* = 8.3, 6.2 Hz, 1H), 2.78 (s, 1H), 2.44 (m, 1H), 2.34 (m, 1H), 1.70 (s, 3H), 1.07 (s, 9H), 1.05 (d, *J* = 6.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 138.5, 135.8, 135.1, 134.1, 129.8, 128.7, 128.0, 128.0, 127.9, 126.9, 77.9, 73.7, 71.5, 64.0, 31.4, 29.9, 27.1, 18.5, and 15.5 ppm; IR (neat): 3420, 2959, 2931, 2858, 1428, 1112, and 702 cm^{-1}; HRMS-ESI calcd for $C_{31}H_{40}O_3NaSi$ $(M+Na)^+$: 511.2644, found 511.2648.

General Procedure D: Synthesis of (*Z*)-Trisubsitituted Allylic Alcohols with Methyl Installation, Additions to (*R*)- and (*S*)-3-(benzyloxy)-2-methylpropanal.

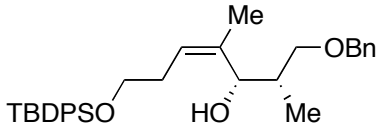


(2*S*,3*S*,*Z*)-1-(benzyloxy)-2,4-dimethylnon-4-en-3-ol (46). A dry and thoroughly purged (N_2) 10 mL Schlenk flask capped with a rubber septum was charged with 1-bromohex-1-yne (128 μL, 1.0 mmol) and PhMe (1 mL). $Br_2BH•SMe_2$ (1.0 mL, 1.0 M in PhMe) was added at ambient temperature. The reaction was warmed to 70 ^oC. After 1 hour, the reaction was cooled to –78 ^oC and Me_2Zn (2.0 mL, 2.0 M in PhMe) was added dropwise and stirred at this temperature for 15 min then warmed to 0 ^oC. Under a steady flow of N_2, the rubber septum was replaced with a glass stopper coated with silicon grease and high vacuum was gradually applied. After most of the volatile contents were evacuated (approximately 1.0 mL remained), the resulting vinylzinc reagent was diluted with an additional 1 mL of PhMe and (*R*)-3-(benzyloxy)-2-methylpropanal (116 mg, 0.65 mmol) in PhMe (1.0 mL) was added. The reaction was transferred to a –40 ^oC bath and stirred for 24 hrs. The reaction was quenched by dropwise addition of NH_4Cl, followed by the 2 N HCl (1.0 mL), and 5 mL of ethyl acetate. The clear biphasic layers were partitioned and the aqueous layer was successively extracted with ethyl acetate (3 X 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ followed by saturated NaCl, dried over anhydrous $MgSO_4$, and concentrated. (*R*)-3-(benzyloxy)-2-methylpropanal (116 mg, 0.65 mmol, 1.0 M in PhMe). The crude product was purified by column chromatography on silica gel to yield the title compound (126 mg, 70% yield) as a colorless oil. $[\alpha]_D^{20}$ = 19.7 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.38-7.44 (m, 4H), 5.38 (t, *J* = 7.43 Hz, 1H),

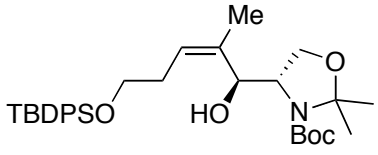
4.60 (d, *J* = 6.0 Hz, 2H), 4.46 (d, *J* = 9.5 Hz, 1H), 3.68 (dd, *J* = 9.22, *J* = 9.25 Hz, 1H), 3.60 (dd, *J* = 8.3 9.1 Hz, 1H), 2.0-2.2 (m, 3H), 1.71 (d, 1 Hz, 3H), 1.34 (m, 4H), 0.89 (m, 3H) and 0.73 (d, *J* = 7.0 Hz, 3H) ppm, ^{13}C() NMR ($CDCl_3$, 125 MHz): δ 113.0, 110.7, 106.0, 105.3, 104.8, 104.6, 61.5, 60.2, 59.5, 28.5, 25.0, 20.8, 16.8, 12.8, 9.8, and 9.3 ppm, IR (neat): 3436, 1715, 1602, 1495, and 1454 cm^{-1}. HRMS-ESI calcd for $C_{18}H_{28}O_2Na$ $(M+Na)^+$: 299.1973, found 299.1973.



(2*S*,3*S*,*Z*)-1-(benzyloxy)-6-(*tert*-butyldiphenylsilyloxy)-2,4-dimethylhex-4-en-3-ol (47). General Procedure D was applied to (3-bromoprop-2-ynyloxy)(*tert*-butyl)diphenylsilane (472 mg, 1.5 mmol), $Cl_2BH•SMe_2$ (173 μL, 1.5 mmol), Me_2Zn (3.0 mL, 2.0 M in PhMe), and (*S*)-3-(benzyloxy)-2-methylpropanal (178 mg, 0.65 mmol) that was dissolved in PhMe (1.0 mL). The crude product was purified by column chromatography on silica gel to yield the title compound (290 mg, 59% yield) as a colorless oil. $[\alpha]_D^{20}$ = 8.80 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79 (m, 4H), 7.35-7.53 (m, 11H), 5.63 (t, *J* = 6.6 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 2H), 4.36 (dd, *J* = 7.1, 12.8 Hz, 1H), 4.25 (dd, *J* = 6.0, 12.9 Hz, 1H), 4.20 (d, *J* = 9.3 Hz, 1H), 3.57-3.60 (dd, *J* = 4.5, 9.2 Hz, 1H), 3.48 (dd, *J* = 8.2, 8.6 Hz, 1H), 3.23 (s, 1H), 1.99 (m, 1H), 1.74 (s, 3H), 1.06 (s, 9H), and 0.66 (d, *J* = 7.0 Hz, 3H) ppm, ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 138.2, 137.9, 136.0, 134.2, 130.0, 128.9, 128.5, 128.2, 128.1, 128.0, 76.0, 74.7, 73.9, 60.3, 36.8, 27.2, 19.5, 18.0, and 13.8 ppm, IR (neat): 3445, 1721, 1667, 1588, 1471, and 1453 cm^{-1}. HRMS-ESI calc for $C_{31}H_{40}O_3NaSi$ $(M+Na)^+$: 511.2644, found 511.2650.

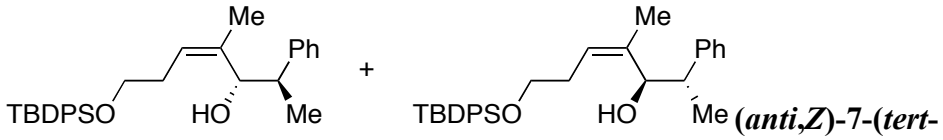


(2*S*,3*S*,*Z*)-1-(benzyloxy)-7-(*tert*-butyldiphenylsilyloxy)-2,4-dimethylhept-4-en-3-ol (48). General Procedure D was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (472 mg, 1.5 mmol), Br_2BH (1.08 mL, 1.4 M in PhMe), Me_2Zn (3.0 mL, 2.0 M in PhMe), and (*S*)-3-(benzyloxy)-2-methylpropanal (178 mg, 0.65 mmol) that was dissolved in PhMe (1.0 mL). The crude product was purified by column chromatography on silica gel to yield the title compound (316 mg, 63% yield) as a colorless oil. $[\alpha]_D^{20}$ = 8.10 (c 1.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75 (m, 4H), 7.43-7.49 (m, 11H), 5.36 (t, *J* = 6.3 Hz, 1H), 4.60 (d, *J* = 3.0 Hz, 2H), 4.34-4.36 (d, *J* = 9.4 Hz, 1H), 3.48 (m, 2H), 3.68 (dd, *J* = 4.6, 9.2 Hz, 1H), 3.36 (dd, *J* = 8.1, 9.2 Hz, 1H), 3.3 (s, 1H), 2.30-2.44 (m, 2H), 2.0 (m, 1H), 1.70 (d, *J* =1.2 Hz, 3H), 1.05 (s, 9H), and 0.65 (d, *J* = 7.0 Hz, 3H) ppm, ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 138.2, 137.5, 135.9, 135.8, 134.2, 129.8, 128.7, 128.0, 127.9, 127.8, 125.0, 76.0, 74.5, 73.8, 64.0, 36.7, 31.3, 27.1, 19.5, 18.0, and 13.6 ppm, IR (neat): 3477, 1704, 1666, 1588, 1495, and 1471 cm^{-1}. HRMS-ESI calc for $C_{32}H_{42}O_3NaSi$ $(M+Na)^+$: 525.2801, found 525.2816.



(*S*)-*tert*-butyl 4-((*S*,*Z*)-5-(*tert*-butyldiphenylsilyloxy)-1-hydroxy-2-methylpent-2-enyl)-2,2-dimethyloxazolidine-3-carboxylate (49). General Procedure C was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (163 μL, 0.5 mmol), $Cl_2BH{\bullet}SMe_2$ (87 μL, 0.5 mmol), Me_2Zn (2.05 mL, 1.0 M in PhMe), and (*S*)-*tert*-butyl 4-formyl-2,2-dimethyloxazolidine-3-carboxylate (73 μL, 0.33 mmol). The

crude product was purified by column chromatography on silica gel to yield the title compound (85.6 mg, 47%) as a colorless oil. $[\alpha]_D^{20}$ = –22.3 (*c* 4.23, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.68 (d, *J* = 6.6 Hz, 4H), 7.45 – 7.37 (m, 6H), 5.43 (t, *J* = 6.8 Hz, 1H), 4.58 (d, *J* = 9.2 Hz, 1H), 4.14 (m, 1H), 3.82 (dd, *J* = 6.1, 9.3 Hz, 1H), 3.70 (m, 3H), 2.41 (m, 2H), 1.73 (s, 3H), 1.63 (s, 3H), 1.54 (s, 9H), 1.52 (s, 3H), 1.05 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 156.0, 135.8, 134.2, 130.0, 129.7, 127.9, 127.8, 94.5, 73.9, 65.1, 64.0, 61.1, 60.6, 31.2, 28.6, 27.1, 21.3, 19.4, 18.1, and 14.4 ppm; IR (neat): 3407, 2962, 2932, 2859, 1695, 1661, 1402, 1173, 1110, and 703 cm^{-1}; HRMS-ESI calcd for $C_{32}H_{48}NO_5Si$ $(M+H)^+$: 554.3302, found 554.3294.



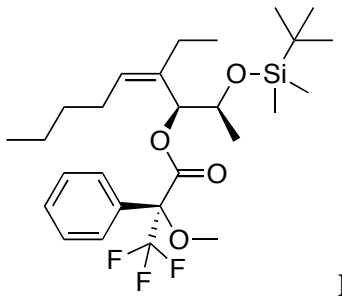
(*anti*,*Z*)-7-(*tert*-butyldiphenylsilyloxy)-4-methyl-2-phenylhept-4-en-3-ol (50). General Procedure C was applied to (4-bromobut-3-ynyloxy)(*tert*-butyl)diphenylsilane (240 μL, 0.75 mmol), $Cl_2BH{\bullet}SMe_2$ (87 μL, 0.75 mmol), Me_2Zn (1.5 mL, 2.0 M in PhMe), and 2-phenylpropanal (67 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel to yield the title compound (126.2 mg, 55% yield) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.67 (m, 4H), 7.46 – 7.38 (m, 6H), 7.22 – 7.10 (m, 5H), 5.07 (t, *J* = 7.3 Hz, 1H), 4.48 (d, *J* = 9.0 Hz, 1H), 3.44 (dt, *J* = 2.8, 6.8 Hz, 2H), 2.94 (dq, *J* = 8.9, 6.9 Hz, 1H), 2.24 (m, 1H), 2.01 (m, 1H), 1.65 (s, 3H), 1.40 (d, *J* = 6.9 Hz, 3H), 1.06 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 144.2, 137.6, 135.8, 134.1, 129.8, 128.4, 127.9, 127.8, 126.5, 125.1, 75.0, 63.8, 44.1, 31.1, 27.1, 19.4, 18.8,

and 18.7 ppm; IR (neat): 3437, 2961, 2931, 2858, 1428, 1112, and 701 cm^{-1}; HRMS-ESI calcd for $C_{30}H_{38}O_2NaSi$ $(M+Na)^+$: 481.2539, found 481.2532.

Determination of Relative (or Absolute) Configuration (Z)-Trisubstituted Allylic Alcohols from Diastereoselective Additions to Chiral or Racemic Aldehydes

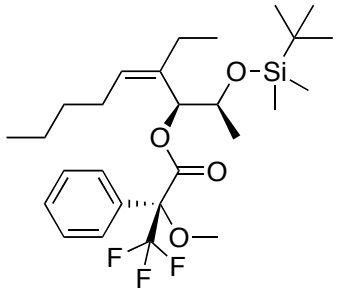
Mosher's Method for the Determination of Absolute Stereochemistry[11,12]

General Procedure F. Synthesis of *O*-Mosher Ester from (Z)-Trisubstituted Allylic Alcohol. A solution of allylic alcohol (0.02 mmol) and 4-dimethylamino-pyridine (12.3 mg, 0.1 mmol) in 1 mL CH_2Cl_2 was treated with (*R*)-(–)-α-methoxy-α-(trifluoromethyl(phenylacetyl chloride ((*R*)-MTPA-Cl) (19 μL, 0.1 mmol). The mixture was allowed to stand at rt for 2 h. After removal of solvent by rotary evaporation, the crude product was purified by column chromatography on silica gel to prepare the (*S*)-*O*-Mosher ester.. The same procedure was used with (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride ((*S*)-MTPA-Cl) in the preparation of the analogous (*R*)-*O*-Mosher ester.

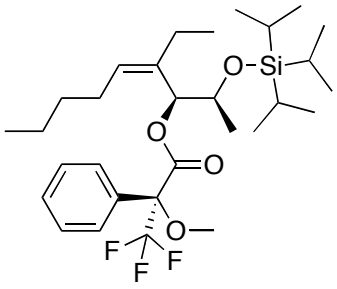


Preparation of *(S)-O*-Mosher Ester of (2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-4-ethylnon-4-en-3-ol (19). General Procedure F was applied to (2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-4-ethylnon-4-en-3-ol (7 μL, 0.02 mmol) with

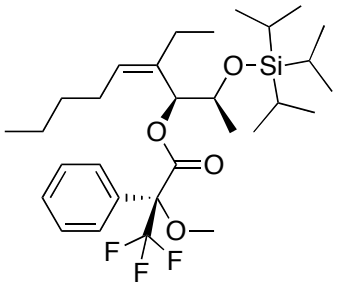
DMAP (12.3 mg, 0.10 mmol) and (*R*)-MTPA-Cl (19 μL, 0.10 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (d, *J* = 7.7 Hz, 2H), 7.39 (m, 3 H), 5.68 (d, *J* = 7.8 Hz, 1H), 5.37 (t, *J* = 7.2 Hz, 1H), 4.12 (dq, *J* = 6.3, 7.3 Hz, 1H), 3.55 (s, 3H), 2.33 (m, 1H), 2.17 (m, 1H), 1.86 (m, 2H), 1. 39 (m, 4H), 1.11 (d, *J* = 6.3 Hz, 3H), 0.93 (t, *J* = 7.8 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.03 s, 3H) ppm, HRMS-ESI calcd for $C_{27}H_{43}F_3O_4NaSi$ $(M+Na)^+$: 539.2780, found 539.2756.



Preparation of *(R)-O*-Mosher Ester of (2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-4-ethylnon-4-en-3-ol (19). General Procedure F was applied to (2*S*,3*S*,*Z*)-2-(*tert*-butyldimethylsilyloxy)-4-ethylnon-4-en-3-ol (9 μL, 0.027 mmol) with DMAP (26 mg, 0.214 mmol) and (*S*)-MTPA-Cl (40 μL, 0.214 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (d, *J* = 7.7 Hz, 2H), 7.39 (m, 3H), 5.74 (d, *J* = 7.6 Hz, 1H), 5.42 (t, J = 7.2 Hz, 1H), 4.11 (dq, 6.3, 7.1 Hz, 1H), 3.55 (s, 3H), 2.33 (m, 1H), 2.20 (m, 1H), 2.03 (m, 1H), 1.37 (m, 4H), 1.10 (d, *J* = 6.3 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.85 (s, 9H), 0.04 (s, 3H), –0.07 (s, 3H) ppm, HRMS-ESI calcd for $C_{27}H_{43}F_3O_4NaSi$ $(M+Na)^+$: 539.2780, found 539.2756.

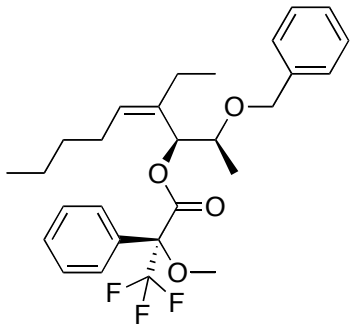


Preparation of *(S)-O*-Mosher Ester of (2*S*,3*S*,*Z*)-4-ethyl-2-(triisopropylsilyloxy)non-4-en-3-ol (25). General Procedure F was applied to (2*S*,3*S*,*Z*)-4-ethyl-2-(triisopropylsilyloxy)non-4-en-3-ol (5.3 mg, 0.016 mmol), DMAP (10 mg, 0.08 mmol), and (*R*)-MTPA-Cl (15 μL, 0.08 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (d, J = 7.6 Hz, 2H), 7.38 (m, 3H), 5.73 (d, J = 7.6 Hz, 1H), 5.36 (t, J = 7.2 Hz, 1H), 4.29 (dq, J = 6.4, 7.1 Hz, 1H), 3.55 (s, 3H), 2.34 (m, 1H), 2.16 (m, 1H), 1.85 (m, 2H), 1.37 (m, 4H), 1.15 (d, J = 6.3 Hz, 3H), 1.08 (m, 21 H), 0.93 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H) ppm, HRMS-ESI calcd for $C_{30}H_{49}F_3O_4NaSi$ $(M)^+$: 581.3250, found 581.3209.

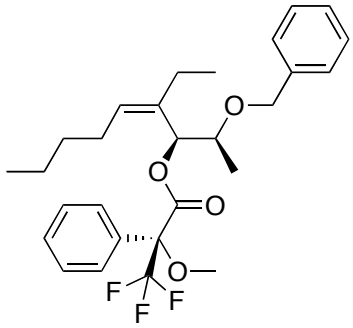


Preparation of *(R)-O*-Mosher Ester of (2*S*,3*S*,*Z*)-4-ethyl-2-(triisopropylsilyloxy)non-4-en-3-ol (25). General Procedure F was applied to (2*S*,3*S*,*Z*)-4-ethyl-2-(triisopropylsilyloxy)non-4-en-3-ol (6.5 mg, 0.019 mmol), DMAP (12 mg, 0.095 mmol), and (*S*)-MTPA-Cl (18 μL, 0.095 mmol). The crude product was purified

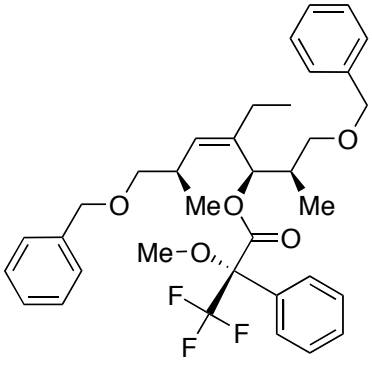
by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (d, *J* = 7.0 Hz, 2H), 7.38 (m, 3H), 5.77 (d, *J* = 7.4 Hz, 1H), 5.42 (t, *J* = 7.1 Hz, 1H), 4.29 (dq, *J* = 6.3, 6.6 Hz, 1H), 3.55 (s, 3H), 2.34 (m, 1H), 2.19 (m, 1H), 2.03 (m, 2H), 1.35 (m, 4H), 1.13 (d, *J* = 5.8 Hz, 3H), 1.02 (m, 24 H), 0.91 (t, *J* = 6.6 Hz, 3H) ppm, HRMS-ESI calcd for $C_{30}H_{49}F_3O_4NaSi$ $(M)^+$: 581.3250, found 581.3209.



Preparation of *(S)-O*-Mosher Ester of (2*S*,3*S*,*Z*)-2-(benzyloxy)-4-ethylnon-4-en-3-ol (26). General Procedure F was applied to (2*S*,3*S*,*Z*)-2-(benzyloxy)-4-ethylnon-4-en-3-ol (8.7 mg, 0.032), DMAP (20 mg, 0.16 mmol), and (*R*)-MTPA-Cl (30 μL, 0.16 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.43 (m, 1H), 7.33 (m, 5H) 7.24 (m, 2H), 5.89 (d, *J* = 9.2 Hz, 1H), 5.43 (t, *J* = 7.2 Hz, 1H), 4.57 (dd, *J* = 11.6, 67.9 Hz, 2H), 3.88 (dq, *J* = 6.1, 9.3 Hz, 1H), 3.50 (s, 3H), 2.37 (m, 1H), 2.23 (m, 1H), 1.86 (m, 2H), 1.38 (m, 4H), 1.14 (d, *J* = 6.3 Hz, 3H), 0.93 (m, 6H) ppm, HRMS-ESI calcd for $C_{28}H_{36}F_3O_4$ $(M+H)^+$: 493.2566, found 493.2574.

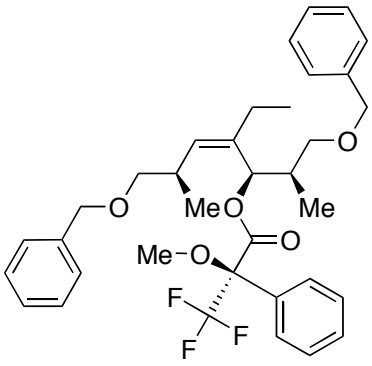


Preparation of *(R)-O*-Mosher Ester of (2*S*,3*S*,*Z*)-2-(benzyloxy)-4-ethylnon-4-en-3-ol (26). General Procedure F was applied to (2*S*,3*S*,*Z*)-2-(benzyloxy)-4-ethylnon-4-en-3-ol (9 mg, 0.033 mmol), DMAP (20 mg, 0.16 mmol), and (*S*)-MTPA-Cl (30 μL, 0.16 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (d, *J* = 7.7 Hz, 2H), 7.45-7.23 (m, 8H), 6.00 (d, *J* = 9.0 Hz, 1H), 5.48 (t, *J* = 7.3 Hz, 1H), 4.42 (dd, *J* = 11.7, 54.5 Hz, 2H), 3.81 (dq, *J* = 6.4, 9.0 Hz, 1H), 3.46 (s, 3H), 2.36 (m, 1H), 2.24 (m, 1H), 2.11 (m, 1H), 1.96 (m, 1H), 1.36 (m, 4H), 1.10 (d, *J* = 6.3 Hz, 3H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm, HRMS-ESI calcd for $C_{28}H_{35}F_3O_4Cl$ $(M+Cl)^+$: 527.2176, found 527.2117.

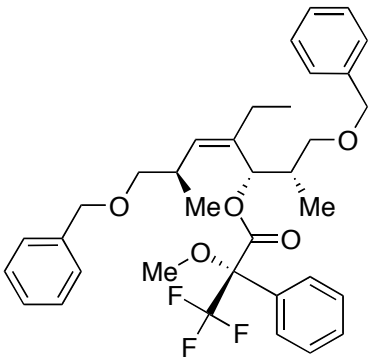


Preparation of *(S)-O*-Mosher Ester of (2*R*,3*R*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (32). General Procedure F was applied to (2*R*,3*R*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (10.2 mg, 0.027 mmol), DMAP (16.3 mg, 0.13 mmol), and (*R*)-MTPA-Cl (25 μL, 0.13 mmol). The

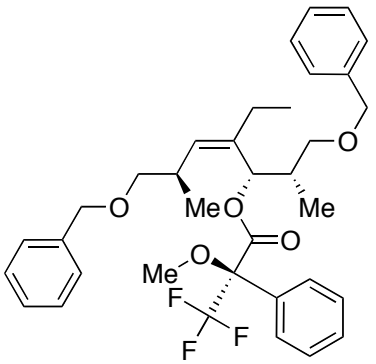
crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.35 (m, 13H), 5.94 (d, *J* = 10.7 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 4.50 (dd, *J* = 12.3, 19.1 Hz, 2H), 4.39 (dd, *J* = 12.0, 28.7 Hz, 2H), 3.49 (s, 3H), 3.32 (m, 3H), 3.25 (dd, *J* = 6.3, 8.8 Hz, 1H), 3.18 (m, 1H), 2.17 (m, 1H), 2.02 (m, 2H), 1.04 (d, *J* = 6.1 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H).



Preparation of *(R)-O*-Mosher Ester of (2*R*,3*R*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (32). General Procedure F was applied to (2*R*,3*R*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (12.0 mg, 0.031 mmol), DMAP (19.1 mg, 0.16 mmol), and (*S*)-MTPA-Cl (29 μL, 0.16 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.37 (m, 13H), 5.86 (d, *J* = 10.6 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 4.51 (dd, *J* = 12.3, 8.6 Hz, 2H), 4.47 (dd, 12.1, 7.9 Hz, 2H), 3.53 (dd, *J* = 17.4, 19.4, 1H), 3.44 (s, 3H), 3.40 (m, 1H), 3.32 (t, *J* = 5.9 Hz, 2H), 3.16 (m, 1H), 2.18 (m, 1H), 1.80 (m, 2H), 1.10 (d, *J* – 6.5 Hz, 3H), 0.89 (t, *J* = 8.2 Hz, 3H), 0.88 (d, *J* = 7.2 Hz, 3H).



Preparation of *(S)-O*-Mosher Ester of (2*S*,3*S*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (33). General Procedure F was applied to (2*S*,3*S*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (7.5 mg, 0.020 mmol), DMAP (12 mg, 0.10 mmol), and (*R*)-MTPA-Cl (18 μL, 0.10 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.32 (m, 13H), 5.85 (d, *J* = 10.6 Hz, 1H), 5.28 (d, *J* = 10.1 Hz, 1H), 4.67 (dd, *J* = 12.2, 26.1 Hz, 2H), 4.48 (dd, *J* = 12.2, 23.7 Hz, 2H), 3.52 (m, 1H), 3.45 (m, 2H), 3.41 (s, 3H), 3.33 (dd, *J* = 7.5, 8.9 Hz, 1H), 3.17 (m, 1H), 2.20 (m, 1H), 1.84 (m, 1H), 1.74 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H).

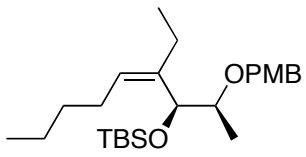


Preparation of *(R)-O*-Mosher Ester of (2*S*,3*S*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (33). General Procedure F was applied to (2*S*,3*S*,6*R*,*Z*)-1,7-bis(benzyloxy)-4-ethyl-2,6-dimethylhept-4-en-3-ol (4.5 mg,

0.012 mmol), DMAP (7.2 mg, 0.06 mmol), and (*S*)-MTPA-Cl (11 μL, 0.06 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 97.5 / 2.5) to give the title compound as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.35 (m, 13H), 5.93 (d, *J* = 10.7 Hz, 1H), 5.35 (d, *J* = 10.1 Hz, 1H), 4.51 (dd, *J* = 12.3, 30.9 Hz, 2H), 4.40 (dd, *J* = 12.1 33.0 Hz, 2H), 3.45 (s, 3H), 3.30 (m, 4H), 3.17 (m, 1H), 2.17 (m, 1H), 2.01 (m, 2H), 1.05 (d, *J* = 6.7 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H).

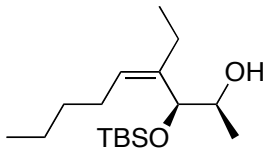
Second Method to Confirm that Vinyl Additions to TBS, TIPS, and OPMB Aldehydes were of the Same Stereochemistry

In an effort to confirm the relative stereochemistry of the molecules, **19**, **25**, and **30** were all converted to a common molecule, **38**. Due to the likelihood that these linear chained diols would exhibit similar spectra dispite dissimilar stereochemistry, they were converted to the corresponding acetonides and carbonates. All spectra for the diols, acetonides, and carbonates matched for each product, leading us to believe that the *anti*-Felkin product was actually being formed in all cases.



***tert*-butyl((2*S*,3*S*,*Z*)-4-ethyl-2-(4-methoxybenzyloxy)non-4-en-3-yloxy)dimethylsilane (30a).** To a dry, N_2 flushed 25 mL round-bottom flask was added (2*S*,3*S*,*Z*)-4-ethyl-2-(4-methoxybenzyloxy)non-4-en-3-ol (**30**) (45.7 mg, 0.15 mmol), 2,6-lutidine (65.2 µL, 0.563 mmol), and TBSOTf (55.1 µL, 0.24 mmol) in dry THF (3 mL) at ambient temperature. The reaction was stirred until all of the secondary

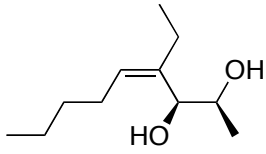
alcohol was consumed (monitored by TLC, 1/9 EtOAc to hexanes). The reaction was quenched with water and extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated, and the crude product was purified by column chromatography (10% ethyl acetate in hexanes) to yield the desired product (56.2 mg, 90% yield) as a colorless oil. $[\alpha]_D^{20} = -10.14$ (*c* 2.81, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.18 (t, *J* = 7.1 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.48 (d, *J* = 7.9 Hz, 1H), 3.82 (s, 3H), 3.54 (dq, *J* = 7.6 Hz, 6.6 Hz, 1H), 2.22 (m, 1H), 2.14 (m, 1H), 2.07 (m, 1H), 1.92 (m, 1H), 1.36 (m, 4H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.92 (m, 12 H), 0.09 (s, 3H), 0.02 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 159.2, 140.6, 131.7, 129.5, 126.1, 113.8, 78.7, 76.1, 72.5, 55.5, 32.5, 28.0, 26.2, 23.9, 18.4, 16.7, 14.3, 12.8, -4.4, -4.6 ppm; IR (neat): 2957, 2929, 2856, 1614, 1514, 1463, 1248, 1072 and 836 cm^{-1}; HRMS-ESI calcd for $C_{25}H_{44}O_3SiNa$ $(M+Na)^+$: 443.2957, found 443.2946.



(2*S*,3*S*,*Z*)-3-(*tert*-butyldimethylsilyloxy)-4-ethylnon-4-en-2-ol (30b). In a dry, N_2 flushed 25 mL round-bottom flask $NaHCO_3$ (112.6 mg, 1.34 mmol) was added to *tert*-butyl((2*S*,3*S*,*Z*)-4-ethyl-2-(4-methoxybenzyloxy)non-4-en-3-yloxy)dimethylsilane (**30a**) (53.2 mg, 0.133 mmol) in CH_2Cl_2 (3 mL) and H_2O (3 drops) to make a cloudy white mixture. DDQ (150 mg, 0.66 mmol) was then added to make an initially black mixture. The mixture color faded to green and yellow while stirring for 1 h. The reaction mixture was poured onto a 1:1 mixture of saturated $NaHCO_3$ (aq)

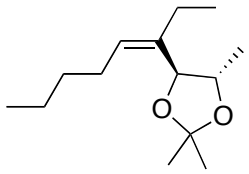
solution and 10% sodium thiosulfate (aq) solution (10 mL) and extracted with ether (2 x 10 mL). The combined organic layers were washed with water, saturated $NaHCO_3$ (aq), brine, dried with $MgSO_4$ and filtered. The filtrate was concentrated, and the crude product was purified by column chromatography to yield the desired product (36.1 mg, 90% yield) as a colorless oil. $[\alpha]_D^{20}$ = –5.21 (*c* 1.81, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.27 (t, *J* = 7.1 Hz, 1H), 4.26 (d, *J* = 8.2 Hz, 1H), 3.74 (dq, *J* = 6.6 Hz, 7.4 Hz, 1H), 2.69 (s, 1H), 2.12 (m, 3H), 1.95 (m, 1H), 1.37 (m, 4H), 1.05 (d, *J* = 6.3 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.94 (m, 12 H), 0.11 (s, 3H), 0.02 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 139.6, 127.6, 77.0, 69.9, 32.4, 30.6, 27.8, 26.0, 22.8, 18.4, 17.9, 14.2, 13.0, -4.4, -4.9 ppm; IR (neat): 3585, 3495, 2958, 1463, 1252, 1051, 837 and 777 cm^{-1}; HRMS-ESI calcd for $C_{17}H_{36}O_2SiNa$ $(M+Na)^+$: 323.2382, found 323.2382.

General Procedure E. Removal of TBS or TIPS groups from secondary allylic alcohols using TBAF.

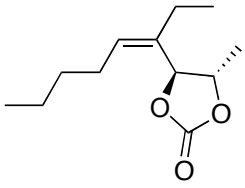


(2*S*,3*S*,*Z*)-4-ethylnon-4-ene-2,3-diol (38). To a stirring solution of (2*S*,3*S*,*Z*)-3-(*tert*-butyldimethylsilyloxy)-4-ethylnon-4-en-2-ol (**19**) (36.1 mg, 0.12 mmol) in THF (2 mL) was added tetra-*n*-butylammonium fluoride (TBAF) (0.132 mL, 1.0 M in THF containing ~5% H_2O) dropwise at ambient temperature. After completion, the reaction was quenched with H_2O (5 mL) and extracted with CH_2Cl_2 (3 x 7 mL). The combined organic layers were dried with $MgSO_4$ and filtered. The filtrate was concentrated, and the crude product was purified by column chromatography to yield the desired product (19.0 mg, 85% yield) as a colorless oil. $[\alpha]_D^{20}$ = 9.58 (*c* 0.95, $CHCl_3$); ^1H

NMR ($CDCl_3$, 500 MHz): δ 5.36 (t, *J* = 7.3 Hz, 1H), 4.31 (d, *J* = 8.6 Hz, 1H), 3.86 (dq, *J* = 8.6 Hz, 6.3 Hz, 1H), 2.45 (s, 1H), 2.17 (m, 2H), 2.08 (m, 1H), 1.97 (m, 1H), 1.72 (m, 1H), 1.35 (m, 4H), 1.10 (d, *J* = 6.3 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 139.1, 129.1, 75.9, 70.0, 32.5, 27.6, 23.6, 22.6, 18.8, 14.2, 13.6 ppm; IR (neat): 3387, 2961, 2929, 2874, 1462, 1376, 1272, and 1030 cm^{-1}; HRMS-ESI calcd for $C_{11}H_{22}O_2Na$ $(M+Na)^+$: 209.1517, found 209.1522.



(4*S*,5*S*)-2,2,4-trimethyl-5-((*Z*)-oct-3-en-3-yl)-1,3-dioxolane (39). To a stirred solution of (2*S*,3*S*,*Z*)-4-ethylnon-4-ene-2,3-diol (**38**) (41.3 mg, 0.22 mmol) in CH_2Cl_2 (2 mL) in a 25 mL round bottom flask was added TsOH•H_2O (4.2 mg, 0.022 mmol) and 2,2-dimethoxypropane (203 μL, 1.65 mmol) sequentially. The reaction was stirred for 3 h at ambient temperature. After completion, the reaction was concentrated, and the crude product was purified by column chromatography to yield the desired product (42.8 mg, 86% yield) as a colorless oil. $[\alpha]_D^{20}$ = 8.3 (*c* 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.44 (t, *J* = 7.3 Hz, 1H), 4.50 (d, *J* = 8.7 Hz, 1H), 3.90 (dq, *J* = 8.7, 6.0 Hz, 1H), 2.19 (m, 2H), 2.04 (m, 2H), 1.45 (s, 6H), 1.37 (m, 4H), 1.23 (d, *J* = 6.0 Hz, 3H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 135.5, 130.3, 108.1, 81.0, 74.9, 32.6, 27.7, 27.4, 27.3, 23.7, 22.6, 17.1, 14.2, and 13.8 ppm; IR (neat): 2961, 2929, 2874, 1457, 1377, 1241, 1176, 1098, 1038, and 865 cm^{-1}; HRMS-ESI calcd for $C_{14}H_{26}O_2Na$ $(M+Na)^+$: 249.1831, found 249.1821.



(4*S*)-4-methyl-5-((*Z*)-oct-3-en-3-yl)-1,3-dioxolan-2-one (40). To a stirred solution of (2*S*,3*S*,*Z*)-4-ethylnon-4-ene-2,3-diol (**38**) (20.5 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) was added carbonyldiimidazole (27 mg, 0.165 mmol). After completion, the reaction was concentrated, and the crude product was purified by column chromatography to yield the desired product (22.4 mg, 96% yield) as a colorless oil. $[\alpha]_D^{20}$ = –42.42 (*c* 0.855, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.54 (t, *J* = 7.4 Hz, 1H), 5.14 (d, *J* = 7.8 Hz, 1H), 4.48 (dq, *J* = 7.7 Hz, 6.2 Hz, 1H), 2.15 (m, 2H), 2.03 (m, 1H), 1.48 (d, *J* = 6.2 Hz, 3H), 1.36 (m, 4H), 1.10 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 155.0, 134.0, 132.2, 81.9, 77.4, 32.2, 27.5, 23.1, 22.5, 19.0, 14.0, and 13.0 ppm; IR (neat): 2961, 2932, 2874, 1809, 1459, 1366, 1289, 1183, 1071, and 1027 cm^{-1}; HRMS-ESI calcd for $C_{12}H_{20}O_3Na$ $(M+Na)^+$: 235.1310, found 235.1299.

Determination of the Relative Stereochemistry of the Addition Products to 2-Phenylpropanal via Heathcock's Analysis

Major and minor diastereomers were determined through analysis and observation of ^{1}H NMR and Fisher projections in accordance with literature precident.[13,14] In the lowest energy conformations, a relative upfield shift would be observed on the vinyl group when a gauche interaction occurs between the vinyl group and the phenyl group; this is predicted for the Felkin Product. This is due to the shielding effect of the aromatic group

on the vinyl group. In contrast, the *anti*-Felkin product would show a relative downfield shift for the vinyl group (see figures below). Through this analysis, it was determined that the major diastereomer was produced through Felkin addition to 2-phenylpropanal.

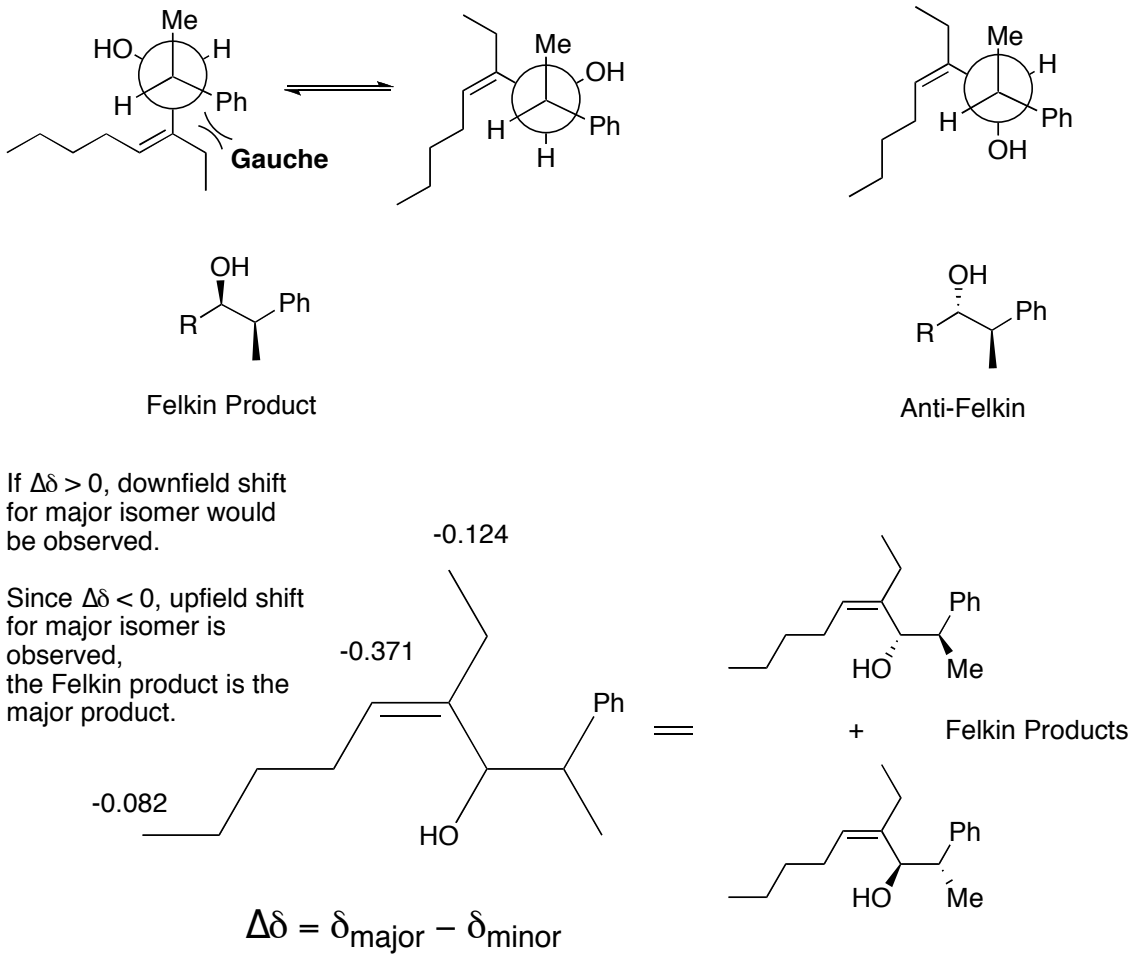
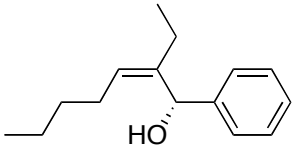


Figure SI-1. Determination of the relative stereochemistry of the vinyl addition to 2-phenylpropanal.

Enantioselective Synthesis of (*Z*)-Trisubstituted Allylic Alcohols via Asymmetric Catalysis to Prochiral Aldehydes

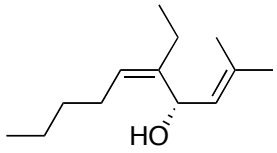
General Procedure G. Catalytic Asymmetric Synthesis of (*Z*)-Trisubstituted Allylic Alcohols with Ethyl Group Installation. A dry and thoroughly purged (N_2) 10 mL Schlenk flask was charged with bromoalkyne (1 equiv) and toluene (1 mL/mmol). The

solution was cooled to 0 °C followed by slow addition of Et_2BH (1 equiv, 1 M solution in toluene). The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to −78 °C and Et_2Zn (2.4 equiv, 1 M solution in toluene) was added. After stirring at this temperature for 20 min, the reaction flask was warmed to 0 °C. High vacuum was gradually applied to evacuate most of the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL/mmol) and TMEDA (1 equiv) was added at 0 °C. After 2 min, (−)-MIB (5 mol%) was added to the reaction solution followed by addition of aldehyde substrate (0.5 equiv). The reaction mixture was then allowed to warm to ambient temperature and stirred for 24 h before quenching by saturated aq. NH_4Cl (2 mL), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was extracted successively with EtOAc (2 x 10 mL). The combined organic layers were washed with saturated $NaHCO_3$ followed by saturated NaCl, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography on silica gel.

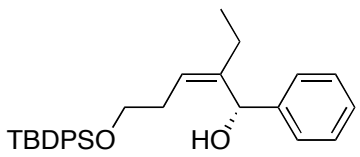


Preparation of (*Z*)-2-Ethyl-1-phenylhept-2-en-1-ol (51). General Procedure G was applied to benzaldehyde (51 μL, 0.5 mmol) and 1-bromohex-1-yne (128 μL, 1.0 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **51** (71 mg, 65% yield, 95% ee) as an oil. $[\alpha]_D^{20}$ = +143.6 (*c* 0.7, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89-1.01 (m, 6H), 1.32-1.47 (m, 4H), 1.74-1.84 (m, 2H), 2.03-2.12 (m, 1H), 2.17-2.32 (m, 2H), 5.39 (t, *J* = 7.3

Hz, 1H), 5.81 (s, 1H), 7.21-7.42 (m, 5H) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 13.4, 14.4, 22.9, 23.4, 27.9, 32.8, 71.7, 126.0, 127.2, 127.6, 128.6, 142.0, 143.3 ppm; IR (neat): 3381, 3086, 3061, 3028, 2958, 2929, 2872, 1946, 1879, 1804, 1603, 1493, 1450, 1378 cm^{-1}; HRMS calcd for $C_{15}H_{22}O$ $(M)^+$: 218.1671, found 218.1665.

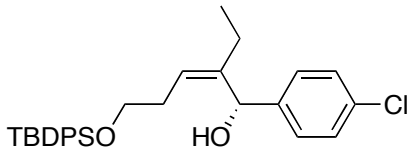


Preparation of (*Z*)-5-Ethyl-2-methyldeca-2,5-dien-4-ol (52). General Procedure G was applied to 3-methylbut-2-enal (48 μL, 0.5 mmol) and 1-bromohex-1-yne (128 μL, 1.0 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) that had been pretreated with triethylamine (2.5% v/v Et_3N) to give **52** (88 mg, 90% yield, 94% ee) as an oil. $[\alpha]_D^{20}$ = +20.1 (*c* 1.73, CH_2Cl_2); ^1H NMR (C_6D_6, 500 MHz): δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 7.4 Hz, 3H), 1.24-1.37 (m, 4H), 1.57 (s, 6H), 2.05-2.23 (m, 3H), 2.26-2.36 (m, 1H), 5.20 (t, *J* = 7.3 Hz, 1H), 5.30 (d, *J* = 8.4 Hz, 1H), 5.43-5.47 (m, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz): δ 13.8, 14.2, 18.1, 22.7, 24.4, 25.8, 27.5, 32.7, 67.5, 125.2, 127.5, 133.3, 143.1 ppm; IR (neat): 3349, 2959, 2923, 2872, 1715, 1674, 1456, 1376, 1261, 1097 cm^{-1}; HRMS calcd for $C_{13}H_{23}$ $(M - OH)^+$: 179.1800, found 179.1808.

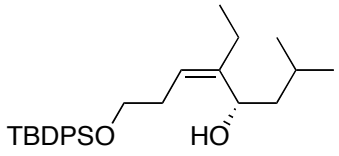


Preparation of (*Z*)-2-Ethyl-5-(*tert*-butyl-diphenyl-silanyloxy)-1-phenylpent-2-en-1-ol (53). General Procedure G was applied to benzaldehyde (26 μL, 0.25 mmol) and 1-bromo-4-(*tert*-butyl-diphenyl-silanyloxy)-but-1-

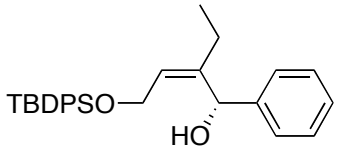
yne (160 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 90 / 10) to give **53** (100 mg, 90% yield, 97% ee) as an oil. $[\alpha]_D^{20}$ = +50.0 (*c* 2.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.99 (t, *J* = 7.4 Hz, 3H), 1.13 (s, 9H), 1.82-1.92 (m, 1H), 2.06-2.15 (m, 1H), 2.38 (br, 1H), 2.51-2.64 (m, 2H), 3.77 (t, *J* = 6.4 Hz, 2H), 5.45 (t, *J* = 7.7 Hz, 1H), 5.67 (s, 1H), 7.25-7.78 (m, 15H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 13.1, 19.5, 24.6, 27.2, 31.3, 64.1, 72.2, 123.2, 126.1, 127.1, 128.0, 128.4, 130.0, 133.9, 135.9, 143.0, 144.9 ppm; IR (neat): 3443, 3069, 3028, 2957, 1958, 1888, 1823, 1715, 1602, 1589, 1493, 1428, 1386, 1361 cm^{-1}; HRMS calcd for $C_{29}H_{36}O_2NaSi$ $(M + Na)^+$: 467.2382, found 467.2374.



Preparation of (*Z*)-1-(4-Chlorophenyl)-2-ethyl-5-(*tert*-butyl-diphenyl-silanyloxy)- pent- 2-en-1-ol (54). General Procedure G was applied to 4-chlorobenzaldehyde (36 mg, 0.25 mmol) and 1-bromo-4-(*tert*-butyl-diphenyl-silanyloxy)-but-1-yne (160 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 90 / 10) to give **54** (89 mg, 75% yield, 93% ee) as an oil. $[\alpha]_D^{20}$ = +47.8 (*c* 1.75, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.08 (s, 9H), 1.78-1.85 (m, 1H), 1.09-2.09 (m, 1H), 2.42-2.60 (m, 3H), 3.72 (t, *J* = 6.2 Hz, 2H), 5.42 (t, *J* = 7.7 Hz, 1H), 5.58 (s, 1H), 7.24-7.73 (m, 14H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 13.3, 19.6, 24.9, 27.3, 31.4, 64.1, 71.7, 123.8, 127.7, 128.2, 128.6, 130.2, 132.9, 133.84, 133.86, 136.03, 136.06, 141.7, 144.9 ppm; IR (neat): 3444, 3067, 2964, 1962, 1902, 1823, 1590, 1488, 1428, 1393 cm^{-1}; HRMS calcd for $C_{29}H_{35}O_2NaClSi$ $(M + Na)^+$: 501.1993, found 501.1989.



Preparation of (*Z*)-5-Ethyl-8-(*tert*-butyl-diphenyl-silanyloxy)-2-methyloct-5-en-4-ol (55). General Procedure G was applied to isovaleraldehyde (27 μL, 0.25 mmol) and 1-bromo-4-(*tert*-butyl-diphenyl-silanyloxy)-but-1-yne (160 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 90 / 10) to give **55** (92 mg, 87% yield, 95% ee) as an oil. $[\alpha]_D^{20} = -1.5$ (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 0.92 (d, *J* = 2.4 Hz, 3H), 0.93 (d, *J* = 2.4 Hz, 3H), 1.07 (s, 9H), 1.25-1.31 (m, 1H), 1.54-1.71 (m, 2H), 1.98-2.07 (m, 1H), 2.11-2.20 (m, 1H), 2.39-2.44 (m, 2H), 3.63-3.72 (m, 2H), 4.57-4.63 (m, 1H), 5.26 (t, *J* = 7.6 Hz, 1H), 7.35-7.74 (m, 10H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 13.4, 19.4, 22.6, 23.6, 23.9, 25.1, 27.1, 30.9, 44.7, 64.1, 68.9, 121.9, 127.9, 129.8, 133.9, 135.8, 145.3 ppm; IR (neat): 3409, 3070, 2954, 1958, 1889, 1824, 1728, 1589, 1471, 1428, 1386, 1362 cm^{-1}; HRMS calcd for $C_{27}H_{40}O_2NaSi$ $(M + Na)^+$: 447.2695, found 447.2688.

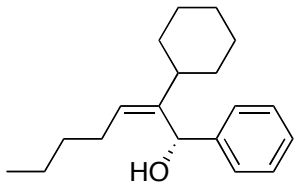


Preparation of (*Z*)-2-Ethyl-4-(*tert*-butyl-diphenyl-silanyloxy)-1-phenylbut-2-en-1-ol (56). General Procedure G was applied to benzaldehyde (26 μL, 0.25 mmol) and 1-bromo-3-(*tert*-butyl-diphenyl-silanyloxy)prop-1-yne (153 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 90 / 10) to give **56** (67 mg, 63% yield, 94% ee) as an oil.

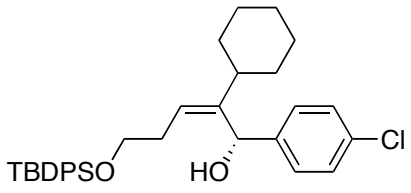
$[\alpha]_D^{20}$ = +50.6 (*c* 2.83, CH_2Cl_2); ^1H NMR ($CDCl_3$, 500 MHz): δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.11 (s, 9H), 1.79-1.86 (m, 1H), 2.04-2.13 (m, 2H), 4.42 (dd, *J* = 12.8, 5.9 Hz, 1H), 4.49 (dd, *J* = 12.8, 5.9 Hz, 1H), 5.49 (s, 1H), 5.63 (t, *J* = 6.5 Hz, 1H), 7.22-7.80 (m, 15H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 13.1, 19.6, 24.2, 27.3, 60.8, 72.3, 125.7, 126.2, 127.4, 128.1, 128.2, 128.6, 130.1, 130.17, 130.19, 134.1, 134.2, 135.3, 136.1, 136.2, 142.6, 145.5 ppm; IR (neat): 3419, 3069, 2967, 2933, 2898, 2856, 1959, 1890, 1822, 1664, 1600, 1587, 1493, 1472, 1427, 1390, 1264 cm^{-1}; HRMS calcd for $C_{28}H_{34}O_2NaSi$ $(M+Na)^+$: 453.2226, found 453.2239.

General Procedure H. Catalytic Asymmetric Synthesis of (*Z*)-Trisubstituted Allylic Alcohols with Cyclohexyl Group Installation. A dry and thoroughly purged (N_2) 10 mL Schlenk flask was charged Cy_2BH (1 mmol), toluene (1mL/mmol) and bromoalkyne (1 equiv). The solution was cooled to 0 ^oC followed by slow addition of Et_2BH (1 equiv, 1 M solution in toluene). The reaction was stirred for 5 min, warmed to room temperature, and stirred for 15 min. The solution was cooled to −78 ^oC and Et_2Zn (2.4 equiv, 1 M solution in toluene) was added. After stirring at this temperature for 20 min, the reaction flask was warmed to 0 ^oC. High vacuum was gradually applied to evacuate most of the volatile contents. The resulting vinylzinc reagent was redissolved in toluene (1 mL/mmol) and TMEDA (1 equiv) was added at 0 ^oC. After 2 min, (–)-MIB (5 mol%) was added to the reaction solution followed by addition of aldehyde substrate (0.5 equiv). The reaction mixture was then allowed to warm to ambient temperature and stirred for 24 h before quenching by saturated aq. NH_4Cl (2 mL), followed by addition of 2 N HCl (1 mL) and 5 mL of EtOAc. The organic layer was separated and the aqueous layer was

extracted successively with EtOAc (2 x 10 mL). The combined organic layers were washed with saturated $NaHCO_3$ followed by saturated NaCl, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography on silica gel.

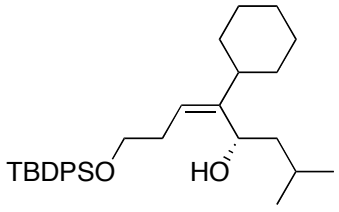


Preparation of (*Z*)-2-Cyclohexyl-1-phenylhept-2-en-1-ol (57). General Procedure H was applied to benzaldehyde (52 μL, 0.5 mmol) and 1-bromohex-1-yne (128 μL, 1.0 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 90 / 10) to give **57** (68 mg, 50% yield, 95% ee) as an oil. $[\alpha]_D^{20}$ = +89.0 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.91 (t, *J* = 7.1 Hz, 3H), 0.97-1.12 (m, 3H), 1.13-1.28 (m, 3H), 1.29-1.46 (m, 4H), 1.51-1.65 (m, 2H), 1.69-1.83 (m, 2H), 1.88-1.96 (m, 1H), 2.14-2.27 (m, 2H), 5.43 (t, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 7.18-7.44 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 14.4, 22.8, 26.7, 27.39, 27.47, 27.8, 32.8, 35.0, 35.8, 39.4, 72.0, 126.1, 127.1, 127.8, 128.4, 143.2, 146.7 ppm; IR (neat): 3432, 3086, 3060, 2918, 1945, 1882, 1805, 1602, 1493, 1448, 1378 cm^{-1}; HRMS calcd for $C_{19}H_{28}O$ $(M)^+$: 272.2140, found 272.2125.



Preparation of (*Z*)-1-(4-Chlorophenyl)-2-cyclohexyl-5-(*tert*-butyl-diphenyl-silanyloxy)pent-2-en-1-ol (58). General Procedure H was applied

to 4-chlorobenzaldehyde (36 mg, 0.25 mmol) and 1-bromo-4-(*tert*-butyl-diphenyl-silanyloxy)- but-1-yne (160 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 90 / 10) to give **58** (106.5 mg, 80% yield, 92% ee) as an oil. $[\alpha]_D^{20}$ = +17.6 (*c* 1.3, CH_2Cl_2); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.09 (s, 9H), 1.09-1.20 (m, 2H), 1.21-1.33 (m, 3H), 1.44-1.50 (m, 1H), 1.60-1.69 (m, 2H), 1.72-1.81 (m, 2H), 1.85-1.93 (m, 1H), 2.23-2.31 (m, 1H), 2.50-2.59 (m, 1H), 2.85 (br, 1H), 3.60-3.70 (m, 2H), 5.44-5.53 (m, 2H), 7.22-7.74 (m, 14H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 19.5, 26.7, 27.2, 27.3, 31.5, 34.4, 34.7, 42.0, 63.9, 72.2, 124.1, 127.9, 128.14, 128.17, 128.6, 130.2, 132.7, 133.7, 136.04, 136.09, 142.3, 150.0 ppm; IR (neat): 3430, 3070, 3049, 2930, 2854, 1959, 1902, 1824, 1706, 1589, 1488, 1428, 1391 cm^{-1}; HRMS calcd for $C_{33}H_{41}O_2ClNaSi$ $(M + Na)^+$: 555.2462, found 555.2472.



Preparation of (*Z*)-5-Cyclohexyl-8-(*tert*-butyl-diphenyl-silanyloxy)-2-methyloct-5-en- 4-ol (59). General Procedure G was applied to isovaleraldehyde (27 μL, 0.25 mmol) and 1-bromo-4-(*tert*-butyl-diphenyl-silanyloxy)-but-1-yne (160 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 90 / 10) to give **59** (62.2 mg, 52% yield, 77% ee) as an oil. $[\alpha]_D^{20}$ = –4.06 (*c* 1.65, CH_2Cl_2); ^1H NMR ($CDCl_3$, 500 MHz): δ 0.92 (d, *J* = 3.9 Hz, 3H), 0.94 (d, *J* = 3.9 Hz, 3H), 1.05 (s, 9H), 1.12-1.35 (m, 6H), 1.54-1.64 (m, 1H), 1.65-1.79 (m, 6H), 1.96-2.04 (m, 1H), 2.31-2.40 (m, 1H), 2.46-2.54 (m, 1H), 3.66 (t, *J* = 6.2 Hz, 2H), 4.54 (dd, *J* = 8.6, 5.0 Hz, 1H), 5.29 (t, *J* = 7.6 Hz, 1H), 7.37-

7.72 (m, 10H) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 19.6, 22.7, 23.9, 25.3, 26.8, 27.3, 27.5, 27.6, 31.1, 35.1, 35.4, 40.2, 45.3, 64.2, 69.8, 122.03, 128.05, 128.07, 130.04, 134.1, 136.04, 136.07, 150.3 ppm; IR (neat): 3465, 3070, 2942, 1959, 1889, 1824, 1740, 1589, 1472, 1428, 1384, 1264 cm^{-1}; HRMS calcd for $C_{31}H_{46}O_2NaSi$ $(M + Na)^+$: 501.3165, found 501.3188.

Conditions for the Determination of Enantiomeric Excesses. The racemic (*Z*)-trisubstituted allylic alcohols were prepared by General Procedure G, but without addition of additives (TMEDA, etc.). **51-59** were analyzed by chiral HPLC. The chiral column used for resolution of each compound is specified below.

(*Z*)-2-Ethyl-1-phenylhept-2-en-1-ol (51). Chiralcel OD-H, t_1 = 11.4 min, t_2 = 12.4 min (hexanes/2-propanol : 97/3, 0.5 mL/min).

(*Z*)-5-Ethyl-2-methyldeca-2,5-dien-4-ol (52). Chiralpak AD-H, t_1 = 13.5 min, t_2 = 16.3 min (hexanes/2-propanol : 99/1, 0.5 mL/min).

(*Z*)-2-Ethyl-5-(*tert*-butyl-diphenyl-silanyloxy)-1-phenylpent-2-en-1-ol (53). Chiralpak AS, t_1 = 10.8 min, t_2 = 11.8 min (hexanes/2-propanol : 99/1, 0.5 mL/min).

(*Z*)-1-(4-Chlorophenyl)-2-ethyl-5-(*tert*-butyl-diphenyl-silanyloxy)-pent- 2-en-1-ol (54). Chiralpak AD-H, t_1 = 18.0 min, t_2 = 19.4 min (hexanes/2-propanol : 99/1, 0.5 mL/min).

(*Z*)-5-Ethyl-8-(*tert*-butyl-diphenyl-silanyloxy)-2-methyloct-5-en-4-ol (55). Chiralpak AS, t_1 = 10.7 min, t_2 = 11.7 min (hexanes/2-propanol : 99/1, 0.5 mL/min).

(*Z*)-2-Ethyl-4-(*tert*-butyl-diphenyl-silanyloxy)-1-phenylbut-2-en-1-ol (56). Chiralpak AD, t_1 = 18.1 min, t_2 = 19.5 min (hexanes/2-propanol : 99/1, 0.5 mL/min).

(*Z*)-2-Cyclohexyl-1-phenylhept-2-en-1-ol (57). Chiralpak AD-H, t_1 = 10.1 min, t_2 = 11.5 min (hexanes/2-propanol : 99/1, 0.5 mL/min).

(*Z*)-1-(4-Chlorophenyl)-2-cyclohexyl-5-(*tert*-butyl-diphenyl-silanyloxy)pent-2-en-1-ol (58). Chiralpak AD-H, t_1 = 16.7 min, t_2 = 21.9 min (hexanes/2-propanol : 99/1, 0.5 mL/min).

(*Z*)-5-Cyclohexyl-8-(*tert*-butyl-diphenyl-silanyloxy)-2-methyloct-5-en-4-ol (59). Chiralpak AD-H, t_1 = 37.7 min, t_2 = 42.0 min (hexanes/2-propanol : 99.9/0.1, 0.3 mL/min).

X-Ray Crystallography

See CIF file for structure of **35** determined by X-Ray Crystallography.

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