A Convenient Synthesis of γ-Hydroxy-α-methylene Silanes

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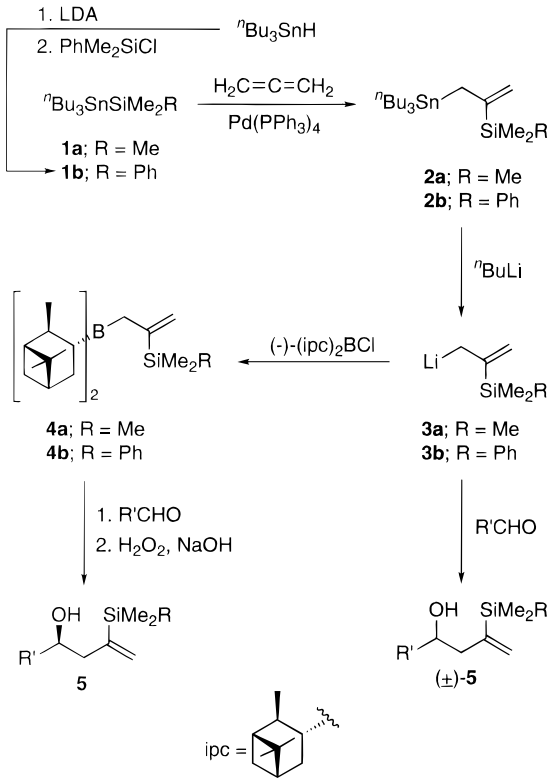
γ-Hydroxy-α-methylene silanes are useful intermediates in synthesis that may be prepared *via* the silylmetalation of allenes and subsequent condensation with aldehydes.[1] Synthetic variations on this theme include the use of allylchromium and allylzinc reagents, respectively, derived from silylallyl phosphates[2] and silylallyl and vinyl bromides[3] and the fluoride ion-mediated condensation of 2,3-bis(trimethylsilyl)alkenes with aldehydes.[4] However, in most cases, these procedures are inconvenient since the reagents require multistep syntheses for their elaboration. We now report a convenient experimental procedure for the preparation of γ-hydroxy-α-methylene silanes from an aldehyde, allene, and a silylstannane.

Both (trimethylsilyl)tributylstannane (**1a**)[5] and (dimethylphenylsilyl)tributylstannane (**1b**) were, respectively, prepared by the reaction of (tributylstannyl)-lithium with chlorotrimethylsilane and chlorodimethylphenylsilane (98%) (Scheme 1). Alternatively, reagent **1a** is commercially available. $(Ph_3P)_4Pd$-catalyzed[6] addition of the silylstannanes **1a** and **1b** to allene gave the corresponding adducts **2a** (85%) and **2b** (66%). These transformations are experimentally easy on account of the air stability of both the silylstannanes **1** and 3-stannyl-2-silyl-1-propenes **2**, and both series of compounds can be stored for long periods without decomposition. Reaction of **2a** and **b** with butyllithium generated the corresponding allyllithium reagents **3a** and **b**, which were trapped with aldehydes to afford the desired γ-hydroxy-α-methylene silanes **5** in moderate to good yields (Scheme 1, Table 1). This convenient experimental procedure was extended to the synthesis of scalemic hydroxy silanes using a variation of Brown asymmetric allylboration.[7] Reaction of the allyllithium reagents **3a** and **b** with (−)-*B*-chlorodiisocamphenylborane easily provided the novel allylboranes **4a** and **b**. *In situ* condensation of boranes **4a** and **b** with aldehydes gave the enantiomerically enriched silyl homoallylic alcohols **5** in moderate to good yields and moderate enantiomeric excesses (Scheme 1, Table 1). In each case, enantioiselectivities were estimated either by chiral HPLC or *via* formation of the corresponding Mosher esters[8] and ^1H NMR spectroscopy.

Scheme 1



It is clear from these results that the sequential reaction of silylstannanes with allene, butyllithium, and an aldehyde provides a convenient procedure for the synthesis of γ-hydroxy-α-methylene silanes **5**. The method is amenable for asymmetric synthesis with moderate enantioselectivities.

Experimental Section

General Procedures. Solvents were dried by distillation under N_2 or Ar, from sodium benzophenone ketyl (THF, Et_2O); CaH_2 (CH_2Cl_2); KOH (*i*-Pr_2NH). Hexanes refers to the petroleum fraction bp 40−60 °C. All other reagents were used as commercially supplied. All reactions were performed in oven-dried (110 °C) glassware under N_2. TLC was carried out on E. Merck precoated silica gel 60 F_{254} plates. Plates were visualized using UV radiation (254 nm) or with $KMnO_4$ or vanillin reagents. Chromatography refers to flash chromatography on E. Merck silica gel 60, 40−60 μm. Unless stated otherwise, products were obtained as colorless oils. HPLC was performed on an ATI Unicam Crystal 200 series liquid chromatograph using a Chiralpak AD column.

2-(Trimethylsilyl)-3-(tributylstannyl)prop-1-ene (2a). $Me_3SiSnBu_3$ (2 mL, 5.73 mmol) and $(Ph_3P)_4Pd$ (66 mg, 0.57 mmol) in THF (6 mL) in a Fisher-Porter tube was stirred under N_2 at 0 °C, evaporated (*ca.* 20 mmHg), and recharged with allene (14 psi). The evacuation and recharging process was repeated 4× at 0 °C, and the mixture was warmed to 55 °C for 3 h until there was no further pressure reduction. Evaporation and chromatography (neutral alumina, hexanes) gave **2a** (1.97 g, 85%) as a colorless oil: R_f 0.50 (hexanes); IR (film) 2957, 2926, 2853, 1580, 1460, 1247, 1074 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 9H, Me_3Si), 0.75−0.95 (m, 15H, Bu), 1.25−1.36 (m, 6H, Bu), 1.42−1.54 (m, 6H, Bu), 1.89 (dt, 2H, J = 30.8, 1.1 Hz, 3-H), 5.07 (dt, 1H, J = 10.2, 2.9 Hz, 1-H), 5.34 (dt, 1H, J = 2.9, 1.3 Hz,

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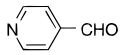
Table 1. Reactions of Lithioallylsilanes 3 and Allylboranes 4 with Aldehydes

Entry	Lithioallyl silane	Aldehyde	(±)-Product [Yield (%)]	Allylboration Product [Yield (%)]	ee (%)[a]	$[\alpha]_D^{25}$ [b]	Abs. Config.[c]
1	**3a**	PhCHO	**5a** [96]	**5a** [46]	75	-30.7	(*S*)
2	**3a**	$^nC_5H_{11}CHO$	**5b** [79]	**5b** [62]	28	-0.5	(*R*)
3	**3a**	4-$CF_3C_6H_4CHO$	**5c** [89]	**5c** [76]	51	-15.8	(*S*)
4	**3a**	2-$CF_3C_6H_4CHO$	**5d** [70]	**5d** [51]	34	-16.7	(*S*)
5	**3a**	4-$O_2NC_6H_4CHO$	**5e** [27]	**5e** [72]	33	-12.5	(*S*)
6	**3a**		**5f** [58][d]	**5f** [31]	de 70[d]	+11.2	(1′*S*,4*R*)
7	**3a**		**5g** [27]	**5g** [36]	54[e]	-23.2	(*S*)
8	**3b**	PhCHO	**5h** [67]	**5h** [63]	22[e]	-5.0	(*S*)
9	**3b**	4-$CF_3C_6H_4CHO$	**5i** [59]	**5i** [69]	48	-8.8	(*S*)
10	**3b**	$^nC_5H_{11}CHO$	**5j** [75]	**5j** [43]	30[e]	-1.0	(*R*)

[a] Enantiomeric excesses determined using chiral HPLC. [b] Optical rotations were measured in $CHCl_3$ ($c = 1$). [c] The absolute configurations of the enriched enantiomers were assigned by analogy with other Brown allylboration reactions.[7] [d] Diastereomeric excess, de = 56%, determined using GCMS. [e] Enantiomeric excesses of these products were determined from ^{1}H NMR spectra of the corresponding Mosher's esters.

1-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.6, 9.7, 13.7, 17.1, 27.4, 29.1, 120.0, 152.1; MS (EI) *m*/*z* 389 $[M - CH_3]^+$, 347, 291, 235; HRMS (EI) calcd for $C_{14}H_{31}SiSn$ $[M - C_4H_9]^+$, 347.1217, found $[M - C_4H_9]^+$, 347.1223. Anal. Calcd for $C_{18}H_{40}SiSn$: C, 53.44; H, 9.97. Found: C, 53.22; H, 9.78.

(Phenyldimethylsilyl)tributylstannane (1b). *n*-BuLi (2.5 M solution in hexane; 2 mL, 5 mmol) was added with stirring to *i*-Pr_2NH (0.66 mL, 5 mmol) in THF (10 mL) at −20 °C under N_2. After 15 min, Bu_3SnH (1.34 mL, 5 mmol) was added dropwise and stirring continued at 0 °C for 15 min. After the mixture was cooled to −78 °C, $Me_2PhSiCl$ (1.0 mL, 6 mmol) was added dropwise and stirring continued at at −78 °C for 2 h. The mixture was quenched with saturated aqueous NH_4Cl (15 mL) and allowed to warm to room temperature. The mixture was extracted with Et_2O (3 × 20 mL), and the combined extracts were washed with brine (20 mL). The organic extract was dried ($MgSO_4$), evaporated, and chromatographed (hexanes) to provide **1b** (2.07 g, 98%) as a colorless oil: R_f 0.54 (hexanes); IR 3068, 3052, 2955, 2924, 2871, 2853, 1463, 1427, 1376, 1244, 1109 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.29 (s, 6H, Me_2Si), 0.50−0.80 (m, 15H, Bu), 0.95−1.11 (m, 6H, Bu), 1.11−1.30 (m, 6H, Bu), 7.05−7.15 (m, 3H, Ph), 7.20−7.30 (m, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.3, 8.2, 13.7, 27.6, 30.2, 127.8, 128.4, 133.6, 140.9; MS (EI) *m*/*z* 426, 369, 313, 257; HRMS (EI) calcd for $C_{16}H_{29}SiSn$ $[M - C_4H_9]^+$ 369.1061, found $[M - C_4H_9]^+$ 369.1061. Anal. Calcd for $C_{20}H_{38}SiSn$: C, 56.31; H, 8.99. Found: C, 56.61; H, 8.76.

2-(Phenyldimethylsilyl)-3-(tributylstannyl)prop-1-ene (2b). $PhMe_2SiSnBu_3$ (4.80 g, 11.30 mmol) and $(Ph_3P)_4Pd$ (130 mg, 0.11 mmol) in THF (11 mL) in a Fisher-Porter tube was stirred under N_2 at 0 °C, evaporated (*ca.* 20 mmHg), and recharged with allene (14 psi). The evacuation and recharging process was repeated 4× at 0 °C, and the mixture was warmed to 45 °C for 3 h until there was no further pressure reduction. Evaporation and chromatography (neutral alumina, hexanes) gave **2b** (3.46 g, 66%) as a colorless oil: R_f 0.50 (hexanes); IR 3068, 3050, 2956, 2926, 2871, 2853, 1580, 1463, 1427, 1376, 1248, 1112 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20 (s, 6H, Me_2-Si), 0.45−0.65 (m, 6H, Bu), 0.65−0.75 (m, 9H, Bu), 1.00−1.35 (m, 12H, Bu), 1.60-1.90 (m, 2H, 3-H), 5.01 (dt, 1H, J = 10.2, 2.7 Hz, 1-H), 5.31 (m, 1H, 1-H), 7.10−7.25 (m, 3H, Ph), 7.30−7.40 (m, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.0, 9.7, 13.7, 17.4, 27.4, 29.1, 122.2, 127.7, 129.0, 134.1, 138.4, 150.1; MS (EI) *m*/*z* 409, 291, 255, 235; HRMS (EI) calcd for $C_{19}H_{33}SiSn$ $[M - C_4H_9]^+$ 409.1374, found $[M - C_4H_9]^+$ 409.1383. Anal. Calcd for $C_{23}H_{42}SiSn$: C, 59.20; H, 9.08. Found: C, 59.04; H, 9.31.

General Procedure for the Synthesis of Racemic Homoallylic Alcohols 5. *n*-BuLi (2.5 M in hexane; 0.11 mL, 0.27 mmol) was added dropwise to stannane **2a** or **2b** (0.25 mmol) in THF (1 mL) at −78 °C under N_2. After 2 h, the aldehyde (0.3 mmol) in THF (0.3 mL) was added dropwise, and the mixture was stirred at −78 °C for 3 h and quenched by the addition of saturated aqueous NH_4Cl (5 mL) at −78 °C. After being warmed to room temperature, the mixture was extracted with Et_2O (3 × 5 mL), and the combined extracts were washed with brine (5 mL) and dried ($MgSO_4$). Evaporation and chromatography gave the adducts **5**.

General Procedure for the Synthesis of Enantiomerically Enriched Homoallylic Alcohols. *n*-BuLi (2.5 M in hexane; 0.22 mL, 0.55 mmol) was added dropwise to stannane **2a** or **2b** (0.5 mmol) in THF (2 mL) at −78 °C under N_2. After 2 h, (−)-*B*-chlorodiisopinocampheylborane (192 mg, 0.6 mmol) in THF (0.6 mL) was added dropwise, and the mixture was stirred at −78 °C for 2 h. The aldehyde (0.6 mmol) in THF (0.6 mL) was added dropwise over 15 min, and the mixture was stirred at −78 °C for 3 h and quenched by the addition of hydrogen peroxide (0.25 mL, 2 mmol, 27% w/w) and 2.5 M sodium hydroxide solution (0.24 mL, 0.6 mmol) at −78 °C. The mixture was allowed to warm to room temperature, stirred overnight, diluted with water (5 mL), and extracted with Et_2O (3 × 10 mL). The combined extracts were washed with brine (10 mL) and dried ($MgSO_4$). Evaporation and chromatography gave the adducts **5**.

1-Phenyl-3-(trimethylsilyl)-3-buten-1-ol (5a): R_f 0.26 (4:1 hexanes:Et_2O); IR (film) 3412, 3031, 2955, 2900, 1603, 1494, 1453, 1408, 1248, 1050 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H, Me_3Si), 2.13 (d, 1H, J = 1.9 Hz, OH), 2.46 (dd, 1H, J = 14.0, 9.9 Hz, 2-H), 2.65 (ddd, 1H, J = 14.0, 3.6, 0.8 Hz, 2-H), 4.76 (ddd, 1H, J = 9.9, 3.6, 1.5 Hz, 1-H), 5.56 (d, 1H, J = 2.8 Hz, 4-H), 5.75 (ddd, 1H, J = 2.8, 1.5, 0.8 Hz, 4-H), 7.24−7.44 (m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.4, 46.9, 72.2, 125.8, 127.4, 128.3, 128.4, 144.1, 149.2; MS (CI, NH_3) *m*/*z* 238, 220, 203; HRMS (CI, NH_3) calcd for $C_{13}H_{24}NOSi$ $[M + NH_4]^+$ 238.1627, found $[M + NH_4]^+$ 238.1633. Anal. Calcd for $C_{13}H_{20}$-OSi: C, 70.87; H, 9.16. Found: C, 70.55; H, 8.92.

2-(Trimethylsilyl)-1-nonen-4-ol (5b): R_f 0.26 (4:1 hexanes:Et_2O); IR (film) 3369, 3049, 2956, 2930, 2860, 1456, 1407, 1248, 1124, 1074, 1036 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9H, Me_3Si), 0.70−1.50 (m, 11H, $Me(CH_2)_4$), 1.58 (d, 1H, J = 2.3 Hz, OH), 2.02 (dd, 1H, J = 13.6, 9.7 Hz, 3-H), 2.34 (dd, 1H, J = 13.6, 3.1 Hz, 3-H), 3.53 (m, 1H, 4-H), 5.39 (d, 1H, J = 2.8 Hz, 1-H), 5.57 (m, 1H, 1-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.3, 14.1, 22.7, 25.5, 31.9, 37.1, 45.0, 69.6, 127.8, 149.6; MS (CI, NH_3) *m*/*z* 232, 214, 197, 186; HRMS (CI, NH_3) calcd for $C_{12}H_{30}NOSi$ $[M + NH_4]^+$ 232.2097, found $[M + NH_4]^+$ 232.2089.

1-[4-(Trifluoromethyl)phenyl]-3-(trimethylsilyl)-3-buten-1-ol (5c): R_f 0.26 (4:1 hexanes:Et_2O); IR (film) 3410, 3050, 2956, 2905, 1621, 1417, 1327, 1251, 1165, 1128, 1067, 1016 cm^{-1}; ^{1}H

NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9H, Me_3Si), 2.12 (s, 1H, OH), 2.24 (dd, 1H, J = 14.0, 10.0 Hz, 2-H), 2.49 (ddd, 1H, J = 14.0, 3.4, 1.0 Hz, 2-H), 4.63 (m, 1H, 1-H), 5.43 (d, 1H, J = 2.7 Hz, 4-H), 5.59 (m, 1H, 4-H), 7.33 (d, 2H, J = 8.2 Hz, Ph), 7.45 (d, 2H, J = 8.2 Hz, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.4, 47.0, 71.6, 125.3, 125.4, 126.1, 128.8, 148.1, 148.8; MS (CI, NH_3) m/z 306, 288, 271; HRMS (CI, NH_3) calcd for $C_{14}H_{23}F_3NOSi$ [M + NH_4]$^+$ 306.1501, found [M + NH_4]$^+$ 306.1497. Anal. Calcd for $C_{14}H_{19}F_3OSi$: C, 58.31; H, 6.65. Found: C, 58.60; H, 6.77.

1-[2-(Trifluoromethyl)phenyl]-3-(trimethylsilyl)-3-buten-1-ol (5d): R_f 0.26 (4:1 hexanes:Et_2O); IR (film) 3465, 3052, 2957, 2904, 1609, 1454, 1409, 1313, 1251, 1162, 1121, 1036 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9H, Me_3Si), 2.03 (br s, 1H, OH), 2.18 (dd, 1H, J = 14.0, 10.7 Hz, 2-H), 2.54 (d, 1H, J = 14.0 Hz, 2-H), 5.01 (d, 1H, J = 10.7 Hz, 1-H), 5.46 (d, 1H, J = 2.9 Hz, 4-H), 5.66 (m, 1H, 4-H), 7.21 (t, 1H, J = 7.5 Hz, Ph), 7.43 (t, 1H, J = 7.5 Hz, Ph), 7.46 (d, 1H, J = 7.5 Hz, Ph), 7.67 (d, 1H, J = 7.5 Hz, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.5, 47.1, 67.3, 122.7, 125.3, 125.4, 127.4, 127.8, 129.1, 132.3, 143.4, 149.3; MS (CI, NH_3) m/z 306, 288, 271, 247; HRMS (CI, NH_3) calcd for $C_{14}H_{23}F_3NOSi$ [M + NH_4]$^+$ 306.1501, found [M + NH_4]$^+$ 306.1491.

1-(4-Nitrophenyl)-3-(trimethylsilyl)-3-buten-1-ol (5e): R_f 0.26 (4:1 hexanes:EtOAc); IR (film) 3551, 3442, 3051, 2954, 2902, 1603, 1521, 1408, 1347, 1249, 1190, 1109, 1060, 1013 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9H, Me_3Si), 2.15 (d, 1H, J = 1.9 Hz, OH), 2.20 (dd, 1H, J = 13.9, 10.1 Hz, 2-H), 2.50 (dd, 1H, J = 13.9, 2.3 Hz, 2-H), 4.67 (m, 1H, 1-H), 5.45 (d, 1H, J = 2.6 Hz, 4-H), 5.59 (m, 1H, 4-H), 7.38 (d, 2H, J = 8.7 Hz, Ph), 8.04 (d, 2H, J = 8.7 Hz, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.3, 47.0, 71.4, 123.7, 126.5, 129.2, 147.3, 148.5, 151.5; MS (CI, NH_3) m/z 283, 265, 250, 234, 218; HRMS (CI, NH_3) calcd for $C_{13}H_{23}N_2O_3Si$ [M + NH_4]$^+$ 283.1478, found [M + NH_4]$^+$ 283.1477. Anal. Calcd for $C_{13}H_{19}NO_3Si$: C, 58.84; H, 7.22; N, 5.28. Found: C, 59.07; H, 6.94; N, 5.28.

(4*R*)-2,2-Dimethyl-4-[(1*S*/*R*)-1-hydroxy-3-(trimethylsilyl)-3-buten-1-yl]-1,3-dioxolane (5f). Mixture of isomers (1*S*:1*R* 85:15): R_f 0.26 (4:1 hexanes:EtOAc); IR (film) 3482, 3048, 2986, 2954, 2897, 1439, 1408, 1375, 1250, 1216, 1156, 1065 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9H, Me_3Si), 1.25 (s, 3H, Me), 1.32 (s, 3H, CH_3), 1.88 (d, 0.85H, J = 1.9 Hz, OH), 2.03 (dd, 1H, J = 13.9, 9.9 Hz, 2-H), 2.18 (d, 0.15H, J = 6.6 Hz, OH), 2.42 (dd, 1H, J = 13.9, 3.4 Hz, 2-H), 3.52 (m, 0.15H, 1-H), 3.63 (m, 0.85H, 1-H), 3.80−4.00 (m, 3H, dioxolane-H), 5.38 (d, 1H, J = 2.8 Hz, 4-H), 5.57 (m, 0.85H, 4-H), 5.60 (m, 0.15H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.3, 25.3, 26.6, 40.4, 40.5, 65.5, 66.1, 69.8, 70.6, 78.5, 109.1, 127.9, 148.2, 148.6; MS (CI, NH_3) m/z 262, 227, 209, 204, 187; HRMS (CI, NH_3) calcd for $C_{12}H_{25}O_3Si$ [M + H]$^+$ 245.1573, found [M + H]$^+$ 245.1562. Anal. Calcd for $C_{12}H_{24}O_3Si$: C, 58.97; H, 9.90. Found: C, 58.75; H, 9.67.

1-(4-Pyridyl)-3-(trimethylsilyl)-3-buten-1-ol (5g): R_f 0.28 (EtOAc); IR (film) 3205, 3049, 2954, 2901, 1603, 1414, 1248, 1063, 1004 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9H, Me_3Si), 2.24 (dd, 1H, J = 14.0, 10.0 Hz, 2-H), 2.48 (dd, 1H, J = 14.0, 3.0 Hz, 2-H), 2.77 (br s, 1 H, OH), 4.59 (dd, 1H, J = 10.0, 3.5 Hz, 1-H), 5.43 (d, 1H, J = 2.6 Hz, 4-H), 5.58 (s, 1H, 4-H), 7.15 (d, 2H, J = 5.5 Hz, py), 8.37 (d, 2H, J = 5.5 Hz, py); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.3, 46.5, 70.9, 120.8, 128.9, 148.5, 149.7, 153.3; MS (CI, NH_3) m/z 222, 206, 108; HRMS (CI, NH_3) calcd for $C_{12}H_{20}NOSi$ [M + H]$^+$ 222.1314, found [M + H]$^+$ 222.1322. Anal. Calcd for $C_{12}H_{19}NOSi$: C, 65.12; H, 8.66; N, 6.33. Found: C, 64.83; H, 8.44; N, 6.50.

1-Phenyl-3-(phenyldimethylsilyl)-3-buten-1-ol (5h): R_f 0.26 (4:1 hexanes:Et_2O); IR (film) 3403, 3064, 3050, 2956, 2922, 1602, 1492, 1452, 1428, 1251, 1112, 1047 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.36 (s, 3H, CH_3Si), 0.37 (s, 3H, CH_3Si), 1.91 (d, 1H, J = 2.3 Hz, OH), 2.36 (dd, 1H, J = 14.0, 9.7 Hz, 2-H), 2.52 (ddd, 1H, J = 14.0, 3.6, 1.0 Hz, 2-H), 4.46 (ddd, 1H, J = 9.7, 3.6, 2.3 Hz, 1-H), 5.57 (d, 1H, J = 2.8 Hz, 4-H), 5.78 (m, 1H, 4-H), 7.10−7.25 (m, 5H, Ph), 7.25−7.35 (m, 3H, Ph), 7.45−7.55 (m, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.8, −2.7, 47.1, 72.4, 125.9, 127.4, 128.1, 128.4, 129.4, 130.1, 134.0, 137.8, 144.3, 147.5; MS (CI, NH_3) m/z 300, 282, 265, 204; HRMS (CI, NH_3) calcd for $C_{18}H_{26}NOSi$ [M + NH_4]$^+$ 300.1784, found [M + NH_4]$^+$ 300.1807. Anal. Calcd for $C_{18}H_{22}OSi$: C, 76.56; H, 7.86. Found: C, 76.26; H, 7.66.

1-[4-(Trifluoromethyl)phenyl]-3-(phenyldimethylsilyl)-3-buten-1-ol (5i): R_f 0.26 (4:1 hexanes:Et_2O); IR (film) 3433, 3052, 2957, 2907, 1620, 1424, 1326, 1253, 1164, 1125, 1067, 1016 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.36 (s, 3H, CH_3Si), 0.37 (s, 3H, CH_3Si), 2.00 (d, 1H, J = 2.2 Hz, OH), 2.28 (dd, 1H, J = 14.0, 9.9 Hz, 2-H), 2.49 (dd, 1H, J = 14.0, 2.5 Hz, 2-H), 4.44 (m, 1H, 1-H), 5.59 (d, 1H, J = 2.7 Hz, 4-H), 5.76 (m, 1H, 4-H), 7.19 (d, 2H, J = 8.0 Hz, Ph), 7.25−7.35 (m, 3H, Ph), 7.40−7.50 (m, 4H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.0, −2.9, 47.2, 71.6, 125.0, 125.2, 125.3, 126.0, 128.1, 129.5, 130.4, 133.9, 137.4, 147.2, 148.0; MS (CI, NH_3) m/z 368, 350, 333, 290, 272; HRMS (CI, NH_3) calcd for $C_{19}H_{25}F_3NOSi$ [M + NH_4]$^+$ 368.165, found [M + NH_4]$^+$ 368.1655. Anal. Calcd for $C_{19}H_{21}F_3OSi$: C, 65.12; H, 6.04. Found: C, 65.16; H, 5.89.

2-(Phenyldimethylsilyl)-1-nonen-4-ol (5j): R_f 0.26 (4:1 hexanes:Et_2O); IR (film) 3391, 3068, 3050, 2955, 2929, 2871, 2859, 1458, 1428, 1411, 1378, 1250, 1111, 1069, 1038 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 3H, CH_3Si), 0.20 (s, 3H, CH_3-Si), 0.66 (t, 3H, J = 7.0 Hz, 9-H), 0.90−1.25 (m, 8H, 4 × CH_2), 1.35 (d, 1H, J = 2.7 Hz, OH), 1.93 (dd, 1H, J = 13.7, 9.4 Hz, 3-H), 2.19 (ddd, 1H, J = 13.7, 3.5, 0.9 Hz, 3-H), 3.27 (m, 1H, 4-H), 5.38 (d, 1H, J = 2.9 Hz, 1-H), 5.59 (m, 1H, 1-H), 7.10−7.20 (m, 3H, Ph), 7.25−7.35 (m, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.9, −2.8, 14.1, 22.6, 25.3, 31.8, 37.0, 45.0, 69.6, 127.9, 129.2, 129.5, 133.8, 137.8, 147.8; MS (CI, NH_3) m/z 294, 276, 259, 199; HRMS (CI, NH_3) calcd for $C_{17}H_{32}NOSi$ [M + NH_4]$^+$ 294.2253, found [M + NH_4]$^+$ 294.2246. Anal. Calcd for $C_{17}H_{28}$-OSi: C, 73.86; H, 10.22. Found: C, 73.59; H, 9.97.

General Procedure for the Synthesis of Mosher Esters. DMAP (cat.), pyridine (40 μL, 0.5 mmol), and (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (11 μL, 0.06 mmol) were added to alcohol **5** (0.05 mmol) in CH_2Cl_2 (0.1 mL) under N_2. The mixture was stirred at room temperature until the reaction was complete (TLC, *ca.* 4 h), diluted with Et_2O (5 mL), and washed sequentially with saturated aqueous $CuSO_4$ (2 × 2 mL), saturated aqueous $NaHCO_3$ (2 × 2 mL), 1 M HCl (2 mL), and brine (2 mL). The organic phase was dried ($MgSO_4$), evaporated, dissolved in Et_2O, and filtered through silica gel, which was further washed with Et_2O, and reevaporated under reduced pressure to give the Mosher ester(s), which was analyzed directly by ^{1}H NMR.

(4*R*/*S*)-4-[(*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetoxy]-4-(4-pyridyl)-2-(trimethylsilyl)-1-butene. 1:1 Mixture of diastereoisomers: R_f 0.45 (1:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.02 (s, 9H, Me_3Si), 0.00 (s, 9H, Me_3Si), 2.35−2.50 (m, 2H, 3-H), 2.55−2.70 (m, 2H, 3-H), 3.33 (s, 3H, CH_3O), 3.41 (s, 3H, CH_3O), 5.24 (d, 1H, J = 2.2 Hz, 1-H), 5.34 (m, 1H, 1-H), 5.38 (d, 1H, J = 2.2 Hz, 1-H), 5.51 (m, 1H, 1-H), 5.85−6.00 (m, 2H, 2 × 4-H), 6.98 (d, 2H, J = 6.0 Hz, Py), 7.14 (d, 2H, J = 6.0 Hz, Py), 7.20−7.35 (m, 10H, Ph), 8.44 (d, 2H, J = 6.0 Hz, Py), 8.51 (d, 2H, J = 6.0 Hz, Py); MS (CI, NH_3) m/z 438, 292, 220; HRMS (CI, NH_3) calcd for $C_{22}H_{27}F_3NO_3Si$ [M + H]$^+$ 438.1712, found [M + H]$^+$ 438.1735.

(4*R*/*S*)-4-[(*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetoxy]-2-(phenyldimethylsilyl)-1-nonene. 1:1 mixture of diastereoisomers: R_f 0.70 (4:1 hexanes:Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 3H, CH_3Si), 0.33 (s, 3H, CH_3Si), 0.35 (s, 3H, CH_3Si), 0.37 (s, 3H, CH_3Si), 0.65−1.50 (m, 22H, 2 × CH_3-$(CH_2)_4$), 2.18 (dd, 1H, J = 14.1, 6.5 Hz, 3-H), 2.25 (dd, 1H, J = 14.1, 6.5 Hz, 3-H), 2.36 (dd, 1H, J = 14.1, 7.1 Hz, 3-H), 2.46 (dd, 1H, J = 14.1, 7.1 Hz, 3-H), 3.44 (q, 6H, J = 1.1 Hz, 2 x CH_3O), 5.02 (m, 2H, 2 × 4-H), 5.23 (d, 1H, J = 2.5 Hz, 1-H), 5.44 (d, 1H, J = 2.5 Hz, 1-H), 5.53 (m, 1H, 1-H), 5.65 (m, 1H, 1-H), 7.20−7.50 (m, 20H, Ph); MS (CI, NH_3) m/z 510, 386; HRMS (CI, NH_3) calcd for $C_{27}H_{39}F_3NO_3Si$ [M + NH_4]$^+$ 510.2651, found [M + NH_4]$^+$ 510.2644.

(4*R*/*S*)-4-[(*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetoxy]-4-phenyl-2-(phenyldimethylsilyl)-1-butene. 1:1 mixture of diastereoisomers: R_f 0.54 (4:1 hexanes:Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 3H, CH_3Si), 0.30 (s, 3H, CH_3Si), 0.31 (s, 3H, CH_3Si), 0.32 (s, 3H, CH_3Si), 2.43 (dd, 1H, J = 14.6, 5.0 Hz, 3-H), 2.46 (dd, 1H, J = 14.6, 4.6 Hz, 3-H), 2.64 (dd, 1H, J = 14.6, 9.0 Hz, 3-H), 2.68 (dd, 1H, J = 14.6, 9.3 Hz, 3-H), 3.32

(s, 3H, CH_3O), 3.38 (s, 3H, CH_3O), 5.30 (d, 1H, $J = 2.2$ Hz, 1-H), 5.48 (m, 2H, 2 × 1-H), 5.67 (m, 1H, 1-H), 5.79 (dd, 1H, $J = 9.3$, 4.6 Hz, 4-H), 5.85 (dd, 1H, $J = 9.0$, 5.0 Hz, 4-H), 6.90−7.70 (m, 30H, Ph); MS (CI, NH_3) m/z 516, 291, 282; HRMS (CI, NH_3) calcd for $C_{28}H_{33}F_3NO_3Si$ $[M + NH_4]^+$ 516.2182, found $[M + NH_4]^+$ 516.2194.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra of **5b** and **5d** and ^1H NMR spectra of the Mosher esters derived from racemic **5g**, **5h**, and **5j** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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