Carboxylate Methylenation with a Functionalized Silylmethyl Anion: A Two-Step Synthesis of 2-Substituted Allylic Alcohols from Esters

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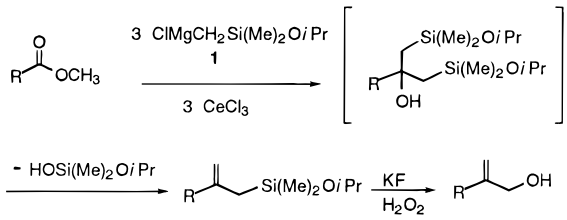
Allylic silanes have proven to be very useful intermediates in organic synthesis.[1] A reliable method for the synthesis of substituted allylic silanes is the double addition of silylmethyl nucleophiles to carboxylic acid derivatives followed by Peterson-type elimination.[2−6] Because the carbon−silicon bonds of aryl- and heteroatom-substituted[7,8] silanes may be cleaved under mild oxidative conditions to afford the corresponding alcohols, we envisioned that the synthetic utility of the double addition−Peterson elimination sequence could be extended conveniently by the use of appropriately substituted silylmethyl nucleophiles. The derived aryl- or heteroatom-substituted allylic silane products should provide ready access to a variety of additional allylic functionality via the derived allylic alcohols. In particular, we have found that the use of a $CeCl_3$-modified, oxygen-substituted silylmethyl nucleophile does allow for a direct and general two-step conversion of carboxylic acid esters into highly functionalized allylic alcohol products via a Peterson olefination−Tamao oxidation process. The details of this novel two-step transformation of carboxylic acid esters into 1,1-disubstituted ethylene products are reported here.

A key factor for successful conversion of carboxylic acid derivatives into allylic trimethylsilanes via the double addition−Peterson elimination sequence is the use of silylmethyl nucleophiles of low basicity. In 1978 Demuth showed that monoaddition of [(trimethylsilyl)methyl]-lithium to simple esters gave α-trimethylsilyl ketones.[9] Because the α-trimethylsilyl ketone products undergo facile enolization in the presence of excess [(trimethylsilyl)methyl]lithium, the addition of a second equivalent of the basic lithium anion does not occur to an appreciable extent. However, double addition to esters and subsequent Peterson-type elimination can be accomplished using the less basic reagents derived from [(trimethylsilyl)methyl]magnesium chloride[6] or with [(trimethylsilyl)methyl]lithium and $CeCl_3$.[2] From esters, however, the best yields of allylic trimethylsilanes have been obtained using [(trimethylsilyl)methyl]magnesium chloride in conjunction with $CeCl_3$.[3−5,10] We have found that a reagent



derived from Tamao's hydroxymethyl anion equivalent, [(dimethylisopropoxysilyl)methyl]magnesium chloride (**1**),[11,12] and $CeCl_3$ provides good yields of the isopropoxy-substituted allylic silanes. Furthermore, these products can be converted into the corresponding allylic alcohols in high yields.

The utility of this two-step ester to allylic alcohol transformation was examined initially using methyl (*S*)-3-(benzyloxy)-2-methylpropionate (**2**),[13] a substrate that is susceptible to potential base-induced α-epimerization and *β*-elimination. Treatment of **2** with the reagent prepared from 3 equiv each of **1** and carefully prepared $CeCl_3$ in THF at −65 °C to rt over 4 h, followed by workup and chromatography, reproducibly gave allylic silane **3** in >80% yield (Table 1). In contrast to the multistep protocols developed to induce Peterson elimination in reactions of carboxyl derivatives and (trialkylsilyl)methyl nucleophiles, double addition *as well as elimination* occurred spontaneously under the reaction conditions. A simple aqueous NH_4Cl quench and extractive workup gave the allylic (dimethylisopropoxy)silane **3** directly. The observed in situ Peterson-type elimination may be facilitated by the cerium salts formed in the reaction mixture. The success of this process was highly dependent upon the purity and handling of the reagents and products. In modifying the recently published procedure for the preparation of **1**,[12] we found that the use of magnesium activated by the method of Baker and co-workers[14] gave consistently good results. Also, proper preparation and handling of the $CeCl_3$ was critical to the success of this procedure.[2−4] As previously noted,[5] partial dehydration of $CeCl_3(H_2O)_7$ under somewhat rigorous drying conditions was necessary for the generation of a viable silylmethyl nucleophile. Although the conditions we used for $CeCl_3$ dehydration (0.3 Torr and 150 °C for 7 h) have been shown to give the monohydrate $CeCl_3 \cdot H_2O$,[15] the use of 3 equiv each of the $CeCl_3$ prepared this way and the Grignard reagent gave very reproducible and satisfactory results. Less vigorous dehydrating conditions or the use of commercially available "anhydrous" $CeCl_3$ generally resulted in little or no carboxylate addition/elimination. Prolonged reaction times or exposure of the

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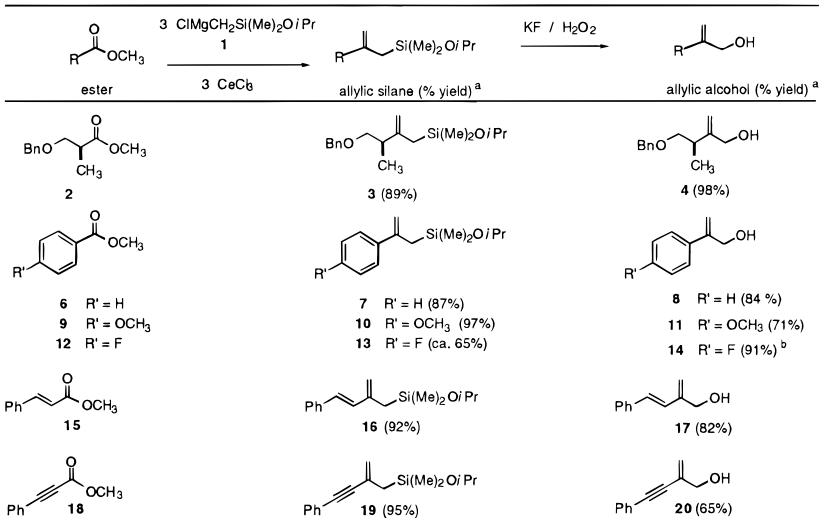
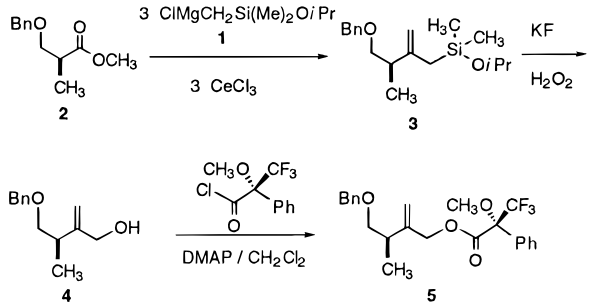
Table 1. Methyl Ester Methylenation with 1 and $CeCl_3$, and the Derived Alcohol Oxidation Products



[a] Yields are of isolated and chromatographically homogeneous products. [b] Yield for **14** is based on recovered starting material; the isolated yield is 56%.

crude reaction product to aqueous acidic conditions led to cleavage of the isopropyl silyl ether of **3**. The resultant silanol condensed readily to afford the corresponding disiloxane, which proved to be only somewhat less useful synthetically.[16] Chromatographically purified **3** could be oxidized under Tamao's conditions[12] to give allylic alcohol **4** cleanly and in excellent yield. A convenient alternative, however, involved oxidative treatment of the crude product mixture containing allylic silane **3** to give **4** in similar overall yields from **2**. The two-step ester to allylic alcohol transformation could thus be accomplished reproducibly in ca. 80% yield.

To determine whether in situ enolization and epimerization of the stereogenic center α to the carboxylic acid ester occurred, the allylic alcohol products (+)- and (−)-**4** derived from each enantiomer of **2** were derivatized and analyzed as the Mosher esters. Separate treatment of (+)- and (−)-**4** with (*S*)-α-methoxy-α-(trifluoromethyl)-phenylacetyl chloride and DMAP in CH_2Cl_2 gave (*R,R*)- and (*R,S*)-MTPA esters **5**. Although these diastereomers



could not be distinguished readily by chromatography, the allylic methylene proton resonances in their ^1H NMR displayed unique splitting patterns. No trace of the corresponding epimeric was detected in either (*R,R*)- or (*R,S*)-**5** by 500 MHz ^1H NMR spectroscopy. Thus, the integrity of the α-stereogenic center of **2** was largely, if not entirely, retained in the conversion to **4**.

(16) The resultant disiloxanes could be oxidized to the corresponding allylic alcohols under the same conditions as used for **3**, but lower yields of allylic alcohol products were obtained.

The scope of this carboxylate methylenation procedure was surveyed with a variety of different methyl esters, including methyl benzoates (**6**, **9**, and **12**), methyl cinnamate (**15**), and methyl 2-phenylpropiolate (**18**, Table 1). Using the same procedures as for the conversion of **2** into **3** and **4**, each of these esters was converted efficiently into the corresponding allylic silanes and alcohols, respectively. Consistent with previous use of Ce(III)-modified nucleophiles, only 1,2-addition and no 1,4-addition was observed in the case of the α,β-unsaturated esters **15** and **18**. The resultant silylmethyl-substituted 1,3-diene **16** and the enyne **19** underwent smooth oxidation to the corresponding allylic alcohols **17** and **20**. Although silylmethyl methylenation with **1** and $CeCl_3$ works well for a number of highly functionalized esters, nucleophilic addition to methyl 4-nitrobenzoate resulted in a complex mixture of chromatographically unstable products. In contrast, methyl 4-fluorobenzoate (**12**) underwent satisfactory methylenation, and subsequent Tamao oxidation of the resultant silane **13** also proceeded well. Silylmethyl methylenation of methyl 4-methoxybenzoate (**9**) with **1** and $CeCl_3$ gave the expected allylic siloxane **10** in excellent yield. Thus, aryl esters with either electron-withdrawing or electron-donating substituents as well as α,β-unsaturated esters are good substrates for the methylenation−oxidation sequence.

In summary, the use of Tamao's hydroxymethyl anion equivalent **1** with stoichiometric $CeCl_3$ is effective for the facile conversion of a variety of methyl esters into the corresponding isopropoxy-substituted allylic silanes without the necessity of inducing a Peterson-type elimination in a discrete step. The isopropyl silyl ether is stable under the reaction conditions, yet allows oxidative cleavage of the functionalized allylic silanes to give the corresponding allylic alcohols in high yields.[17] The conditions for each step are both mild and general. If care is taken to avoid silyl ether cleavage of the allylic silane intermediates, then both methylenation and oxidation may be accomplished without appreciable side reactions. Carboxylic acid esters are converted into substituted allylic alcohols without detectable α-epimerization or β-elimination (**2**), and neither 1,4-addition (**15**,

18) nor overoxidation occurs under these conditions. Because of the ease of execution, mild reaction conditions, and overall efficiency, this sequence should prove to be generally useful for the conversion of carboxylic acid esters into highly functionalized derivatives of the common 1,1-disubstituted ethylene moiety.

Experimental Section

General Methods. Unless otherwise noted, all reactions were carried out under an argon or nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa techniques. Diethyl ether and tetrahydrofuran were distilled from Na/benzophenone ketyl under N_2. Dichloromethane, 2-propanol, and triethylamine were distilled from CaH_2 under N_2. All other solvents were used as received. (Chloromethyl)-dimethylsilyl chloride and $CeCl_3 \cdot 7H_2O$ (99%) were purchased from Aldrich Chemical Co., Milwaukee, WI. (Chloromethyl)-dimethylisopropoxysilane (**21**) was prepared from (chloromethyl)dimethylsilyl chloride as previously described[12] and was distilled immediately prior to use. Flash chromatography was performed using Baker flash silica gel 60 (40 μm) and the solvent systems indicated. Analytical and preparative TLC was performed with 0.25 and 0.50 mm EM silica gel 60 F_{254} plates, respectively. NMR spectra are referenced to residual $CHCl_3$ at 7.25 (^{1}H) and 77.0 ppm (^{13}C). HRMS data were obtained by CI using a Finnigan MAT 95 spectrometer and isobutane or NH_3. Combustion analyses were performed by M-H-W Laboratories (Phoenix, AZ).

(*R*)-4-(Benzyloxy)-3-methyl-2-(isopropoxydimethylsilyl)-1-butene ((*R*)-3). $CeCl_3 \cdot 7H_2O$ (3.00 g, 8.05 mmol) was stirred in a 100 mL round bottom flask at 0.3 Torr and 150 °C for 7 h. The $CeCl_3$ was then cooled to 0 °C and stirred while THF (15 mL) was slowly added. The resulting suspension was allowed to warm to rt and stir for ca. 12 h. The homogeneous white suspension was then cooled to −78 °C prior to addition of the Grignard reagent, which was prepared from **21** as follows.

Mg turnings were placed in a 50 mL round bottom flask and stirred with a 1.6 × 3.0 cm Teflon-coated magnetic stir bar under argon for 3 d, at which time the Mg was pulverized to a black powder. A portion (783 mg, 32.21 mmol) was removed and placed in a 50 mL two-necked round bottom flask fitted with a reflux condenser. The whole apparatus was heated with a heat gun while under vacuum (0.3 Torr). After the apparatus was cooled to rt under argon, 2 mL of a solution of **21** (1.33 g, 8.05 mmol) in THF (10 mL) followed by 1,2-dibromoethane (100 μL) was added to the charcoal-colored Mg powder. The remaining THF solution of **21** was added over 30 min, allowing the black Mg suspension to reflux vigorously without external heating. After complete addition, the suspension was externally heated and maintained at reflux for 30 min. After the suspension was cooled to rt, the black supernatant was transferred via syringe over 10 min to the previously prepared, −78 °C, stirred THF suspension of $CeCl_3$. The resulting dark gray mixture was stirred at −78 °C for an additional 15 min before neat **2**[13] (558 mg, 2.68 mmol) was added dropwise over 3 min. The resulting mixture was allowed to warm slowly to rt and stir for 4 h. TLC indicated complete disappearance of **2**. The reaction mixture was cooled to 0 °C and diluted with diethyl ether (35 mL) before a 0 °C saturated aqueous solution of NH_4Cl (5 mL) was added. The organic layer was separated and washed with water (20 mL) and brine (20 mL). The combined aqueous phases were extracted with diethyl ether (2 × 50 mL). The combined organic extracts were dried over anhyd $MgSO_4$, filtered, and concentrated to an oil by rotary evaporation. Silica gel chromatography (hexanes−ethyl acetate, 20:1) gave (*R*)-**3** (732 mg, 2.39 mmol, 89%) as a colorless oil: $[\alpha]^{23}_D$ −46° (*c* 0.12, $CHCl_3$); IR (neat) 3200−3550, 2866, 1649, 1453 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.2−7.35 (m, 5H), 4.68 (s, 2H), 4.51 (s, 2H), 4.00 (m, 1H), 3.53 (dd, *J* = 5.2, 9.1 Hz, 1H), 3.27 (dd, *J* = 7.9, 9.1 Hz, 1 H), 2.36 (m, 1H), 1.64 (s, 2H), 1.14 (d, *J* = 6.4 Hz, 6 H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.13 (s, 6H); ^{13}C NMR (75 MHz) δ 148.81, 138.84, 128.30 (2C), 127.52 (2C), 127.41, 107.58, 74.90, 72.94, 65.01, 41.03, 26.54, 25.78, 17.13, −1.31 (2C); MS 307.2 $(M + H)^+$; HRMS calcd for $C_{18}H_{31}O_2Si$ $[M + H]^+$ 307.2093, found 307.2081, calcd for $C_{18}H_{34}NO_2Si$ $(M + NH_4)^+$ 324.2359, found 324.2350.

(*S*)-3 $[[\alpha]^{23}_D$ +49° (*c* 0.12, $CHCl_3$)] was similarly prepared from (*S*)-**2**.

(*R*)-4-(Benzyloxy)-2-(hydroxymethyl)-3-methyl-1-butene (4). Oxidative cleavage of the isopropoxysilane to the allylic alcohol was accomplished by slight modification of the literature procedure.[12] To a stirred solution of (*R*)-**3** (182 mg, 596 μmol) in THF and methanol (2.5 mL each) at rt were added $KHCO_3$ (237 mg, 2.37 mmol) and $KF \cdot 2H_2O$ (446 mg, 4.74 mmol). After the mixture was stirred for 5 min, an aqueous solution of 30% H_2O_2 (400 μL, 2.85 mmol) was added, forming a milky suspension. The reaction mixture was allowed to stir at rt for 22 h, at which point TLC showed no remaining **3**. An aqueous 50% solution of $Na_2S_2O_3$ (5 mL) was added over 30 min to the reaction mixture, the resulting mixture was filtered through a fritted glass funnel under vacuum, and the organic solvents were removed by rotary evaporation. The residual aqueous suspension was extracted with diethyl ether (4 × 10 mL), and the combined ether extracts were washed with brine. The organic phase was dried over anhyd $MgSO_4$, filtered, and concentrated. Silica gel chromatography (hexanes−ethyl acetate, 4:1) gave (*R*)-**4** (120 mg, 582 mmol, 98%) as a clear, volatile oil: $[\alpha]^{23}_D$ −278° (*c* 0.134, $CHCl_3$); IR (neat) 2971, 2927, 2871, 1632 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.2−7.39 (m, 5H), 5.10 (d, *J* = 1.2 Hz, 1H), 4.95 (s, 1H), 4.52 (s, 2H), 4.09 (br s, 2H), 3.44 (m, 2H), 2.57 (m, 1 H), 2.50 (br s, 1H), 1.10 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz) δ 151.71, 137.97, 128.45 (2C), 127.70 (2C), 110.99, 75.39, 73.23, 65.68, 37.40, 16.85; HRMS calcd for $C_{13}H_{19}O_2$ $(M + H)^+$ 207.1386, found 207.1375. Anal. Calcd for $C_{13}H_{18}O$: C, 75.685; H, 8.8128; O, 15.562. Found: C, 75.90; H, 8.55; O, 15.73.

(*S*)-4 was similarly prepared from (*S*)-**3**: $[\alpha]^{23}_D$ +273° (*c* 0.107, $CHCl_3$); HRMS calcd for $C_{13}H_{19}O_2$ $(M + H)^+$ 207.1386, found 207.1388.

[(*R*)-4-(Benzyloxy)-2-(hydroxymethyl)-3-methyl-1-buten-2-yl]methyl (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetate [(*R*,*R*)-5]. To a stirred rt solution of (*R*)-**4** (49.0 mg, 238 μmol) in CH_2Cl_2 (2 mL) were sequentially added 4-(*N*,*N*-dimethylamino)pyridine (34.8 mg, 285 μmol) and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (72.0 mg, 285 μmol). After 10 min, TLC showed no remaining **4**. The reaction mixture was diluted with CH_2Cl_2 (2 mL) and sequentially washed with saturated aqueous $NaHCO_3$, H_2O, and saturated aqueous NaCl (2 mL each). The organic phase was dried (anhyd $MgSO_4$), filtered, and concentrated. Purification by silica gel column chromatography (hexanes−ethyl acetate, 8:1) gave (*R*,*R*)-**5** (94.5 mg, 224 μmol, 94%) as a colorless oil: ^{1}H NMR (300 MHz) δ 7.20−7.55 (m, 10H), 5.12 (s, 1H), 5.03 (s, 1H), 4.84, (d, *J* = 13.1 Hz, 1H), 4.78, (d, *J* = 13.1 Hz, 1H), 4.47 (s, 2H), 3.54 (s, 3H), 3.27−3.43 (m, 2H), 2.49 (m, 1H), 1.08 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz) δ 145.2, 138.4, 129.6, 128.8, 128.41, 128.37, 127.5, 127.4, 113.9, 74.4, 73.0, 68.2, 55.5, 37.2, 16.6; HRMS calcd for $C_{23}H_{29}F_3NO_4$ $(M + NH_4)^+$ 440.2050, found 440.2065.

(*S*,*R*)-5 was similarly prepared from (*S*)-**4**: ^{1}H NMR (300 MHz) δ 7.25−7.51 (m, 10H), 5.12 (s, 1H), 5.03 (s, 1H), 4.86 (d, *J* = 13.0 Hz, 1H), 4.73 (d, *J* = 13.0 Hz, 1H), 4.45 (s, 2H), 3.53 (s, 3H), 3.37 (m, 2H), 2.48 (m, 1H), 1.06 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz) δ 166.6, 145.2, 138.2, 129.6, 128.42, 128.38, 127.6, 127.3, 113.9, 74.4, 73.0, 68.2, 55.8, 37.2, 16.6; HRMS calcd for $C_{23}H_{29}F_3NO_4$ $(M + NH_4)^+$ 440.2050, found 440.2040.

Allylic Silanes 7, 10, 13, 16, and 19. Treatment of methyl benzoate (**6**), methyl 4-methoxybenzoate (**9**), methyl 4-fluorobenzoate (**12**), methyl cinnamate (**15**), and methyl 2-phenylpropiolate (**18**) with the reagent derived from **21** (3.0 equiv), Mg (12 equiv), and $CeCl_3$ (3.0 equiv) under the conditions described for the preparation of **3** gave, after workup and chromatography, the corresponding allylic silanes **7, 10, 13**, **16**, and **19**, respectively, as colorless oils.

3-(Isopropoxydimethylsilyl)-2-phenylpropene (7). Ester **6** (654 mg, 4.80 mmol) gave **7** (981 mg, 4.19 mmol, 87% yield): IR (neat) 3083, 2970, 1617, 1028 cm^{-1}; ^{1}H NMR (300 MHz) δ

(17) The stability of the isopropyl silyl ether proved useful for demonstrating the utility of this methodology; however, the scope of this chemistry may be expanded by the use of functionalized alkyl groups in place of the isopropyl group of **1**. For example, methyl carboxylate methylenation using the reagent derived from (chloromethyl)dimethyl(allyloxy)silane also gave the corresponding allylic silane (data not shown). Such alternatively functionalized silylmethyl anions may lead to allylic silanes suitable for a variety of subsequent intramolecular transformations via this new type of temporary silicon connection.

7.41 (m, 2H), 7.29 (m, 3H), 5.20 (s, 1H), 4.98 (s, 1H), 3.95 (m, 1H), 2.14 (s, 2H), 1.09 (d, J = 6.1 Hz, 6H), −0.01 (s, 6H); ^{13}C NMR (75 MHz) δ 145.5, 142.6, 128.1, 127.3, 126.4, 111.0, 65.1, 26.4, 25.8, −1.4; HRMS calcd for $C_{14}H_{22}OSi$ $(M + H)^+$ 235.1520, found 235.1524.

3-(Isopropoxydimethylsilyl)-2-(4-methoxyphenyl)propene (10). Ester **9** (482 mg, 2.9 mmol) gave **10** (744 mg, 2.82 mmol, 97%): IR (neat) 3084, 3040, 2970, 2837, 1610, 1512, 1029 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.36 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 5.10 (s, 1H), 4.86 (s, 1H), 3.96 (m, J = 6.0 Hz, 1H), 3.81 (s, 3H), 2.08 (s, 2H), 1.11 (d, J = 6.0 Hz, 6H), 0.00 (s, 6H); ^{13}C NMR (75 MHz) δ 158.9, 144.7, 135.0, 113.4, 109.5, 102.8, 65.0, 55.2, 26.3, 25.7, −1.4; HRMS calcd for $C_{15}H_{24}O_2Si$ (M^+) 264.1546, found 264.1547, calcd for $C_{15}H_{25}O_2Si$ $(M + H)^+$ 265.1624, found 265.1618.

2-(4-Fluorophenyl)-3-(isopropoxydimethylsilyl)propene (13). Ester **12** (252 mg, 1.8 mmol) gave **13** (0.35 g, 1.4 mmol, 77% yield, 12:1 mixture with disiloxane). An analytical sample was obtained by preparative TLC: IR (neat) 3084, 2971, 2930, 2875, 1617, 1603, 1028 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.40 (dd, J = 5.4, 9.0 Hz, 2H), 6.98 (dd, J = 8.7, 9.0 Hz, 2H), 5.11 (d, J = 1.5 Hz, 1H), 4.92 (d, J = 0.9 Hz, 1H), 3.94 (septet, J = 6 Hz, 1H), 2.08 (s, 2H), 1.04 (d, J = 6 Hz, 6H), 0.00 (s, 6H); ^{13}C NMR (75 MHz) δ 144.5, 138.6, 127.9, 114.8, 110.9, 102.9, 65.1, 26.6, 25.7, −1.4; HRMS calcd for $C_{14}H_{22}OSiF$ $(M + H)^+$ 253.1424, found 253.1413.

***(E)*-3-[(Isopropoxydimethylsilyl)methyl]-1-phenyl-1,3-butadiene (16).** Ester **15** (454 mg, 2.8 mmol) gave **16** (668 mg, 2.57 mmol, 92% yield): IR (neat) 3027, 2969, 1596, 1026 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.41 (d, J = 7.4 Hz, 2H) 7.31 (t, J = 7.4 Hz, 2H), 7.21 (m, 1H), 6.86 (d, J = 16.2 Hz, 1H), 6.60 (d, J = 16.2 Hz, 1H), 5.11 (s, 1H), 4.98 (s, 1H), 4.04 (dt, J = 6.0 , 0.6 Hz, 1H), 1.97(s, 2H), 1.16 (d, J = 6.2 Hz, 6H), 0.14 (s, 6H); ^{13}C NMR (75 MHz) δ 143.1, 137.4, 131.9, 129.0, 128.7, 128.6, 127.7, 126.7, 126.5, 115.7, 65.2, 25.8, 22.6, −1.2; HRMS calcd for $C_{16}H_{24}OSi$ $(M + H)^+$ 261.1676, found 261.1673.

2-[(Isopropoxydimethylsilyl)methyl]-4-phenyl-1-buten-3-yne (19). Ester **18** (448 mg, 2.8 mmol) gave **19** (686 mg, 2.66 mmol, 95%): IR (neat) 3085, 1600, 1490, 1028 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.43 (m, 2H), 7.31 (m, 2H), 5.32 (d, J = 1.8 Hz, 1H), 5.17 (d, J = 1.8 Hz, 1H), 4.07 (septet J = 6.0 Hz, 1H), 1.89 (s, 2H), 1.16 (d, J = 6.0 Hz, 6H), 0.25 (s, 6H); ^{13}C (75 MHz) 131.42, 128.26, 128.06, 127.79, 123.37, 120.00, 91.36, 88.45, 65.16, 28.48, 25.81, −1.39; HRMS calcd for $C_{16}H_{23}OSi$ $(M + H)^+$ 259.1518, found 259.1526.

Allylic Alcohols 8, 11, 14, 17, and 20. Treatment of allylic silanes **7**, **10**, **13**, **16**, and **19** with $KHCO_3$ (4 equiv), $KF{\cdot}2H_2O$ (8 equiv), and 30% H_2O_2 (4.8 equiv) under the conditions described for the preparation of **4** above gave, after workup and chromatography, allylic alcohols **8**, **11**, **14**, **17**, and **20**, respectively.

2-Phenyl-2-propen-1-ol (8). Silane **7** (55 mg, 0.23 mmol) gave **8** as a colorless oil (26 mg, 0.19 mmol, 84% yield): IR (neat) 3372, 1631, 1599, 1047, 1026 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.43−7.48 (m, 2H), 7.26−7.39 (m, 3H), 5.48 (s, 1H), 5.36 (s, 1H), 4.56 (s, 2H), 1.62 (br s, 1H); ^{13}C NMR (75 MHz) δ 142.3, 138.5, 128.5, 128.0, 126.1, 112.6, 65.1; HRMS calcd for $C_9H_{14}ON$ $(M + NH_4)^+$ 152.1075, found 152.1078.

2-(4-Methoxyphenyl)-2-propen-1-ol (11). Silane **10** (50 mg, 0.19 mmol) gave **11** as a white solid (22 mg, 0.13 mmol, 71% yield): IR (thin film) 3236, 1624, 1609, 1028 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.41 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.39 (s, 1H), 5.26 (s, 1H), 4.52 (d, J = 3.9 Hz, 2H), 3.82 (s, 3H), 1.60 (d, J = 3.9 Hz, 1H); ^{13}C NMR (75 MHz) δ 159.4, 146.5, 127.2, 113.9, 111.1, 65.2, 55.3; mp 75−77 °C (lit.[18] mp 76−78 °C); HRMS calcd for $C_{14}H_{13}O_2$ $(M + H)^+$ 165.0916, found 165.0910.

2-(4-Fluorophenyl)-2-propen-1-ol (14). Silane **13** (107 mg, 0.42 mmol) gave **14** as a white solid (36 mg, 0.24 mmol, 56% yield): IR (thin film) 3317, 1715, 1632, 1602, 1043 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.42 (dd, J = 5.4, 9.0 Hz, 2H), 7.06 (dd, J = 8.8, 9.0 Hz, 2H), 5.42 (s, 1H), 5.33 (s, 1H), 4.51 (s, 2H), 1.72 (s, 1H); ^{13}C NMR (75 MHz) δ 146.2, 134.5, 127.8, 127.7, 115.5, 115.2, 112.7, 65.1; mp 29−30 °C; HRMS calcd for $C_9H_{14}FON$ $(M + NH_4)^+$ 170.0981, found 170.0988.

3-(Hydroxymethyl)-1-phenyl-1,3-butadiene (17). Silane **16** (100 mg, 0.38 mmol) gave **17** as a white solid (51 mg, 0.39 mmol, 82% yield): IR (thin film) 3412, 1640, 1448 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.43 (dd, J = 1.3, 8.0 Hz, 2H), 7.34 (dt, J = 1.5, 6.8 Hz, 2H), 7.25 (m, 1H), 7.24 (m, 1H), 6.82 (d, J = 16.5 Hz, 1H), 6.67 (d, J = 16.5 Hz, 1H), 5.36 (s, 1H), 5.29 (s, 1H), 4.47 (d, J = 4 Hz, 2H), 1.57 (m, 1H); ^{13}C NMR (75 MHz) δ 145.1, 128.9, 128.7, 128.2, 127.8, 126.5, 120.5, 116.3, 63.3; mp 78−80 °C; HRMS calcd for $C_{11}H_{13}O$ $(M + H)^+$ 161.0966, found 161.0961, calcd for $C_{11}H_{16}NO$ $(M + NH_4)^+$ 178.1232, found 178.1228.

2-(Hydroxymethyl)-4-phenyl-1-buten-3-yne (20). Silane **19** (100 mg, 0.39 mmol) gave **20** as a colorless oil (40 mg, 0.25 mmol, 65% yield): IR (neat) 3401, 2203, 1645, 1058 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.45−7.48 (m, 2H), 7.31−7.35 (m, 3H), 5.61 (d, J = 1.8 Hz, 1H), 5.58 (d, J = 1.5 Hz, 1H), 4.25 (s, 2H), 1.80 (br s, 1H); ^{13}C NMR (75 MHz) δ 131.7, 131.2, 128.5, 128.3, 122.7, 120.5, 90.9, 86.9, 65.4; HRMS calcd for $C_{11}H_{11}O$ $(M + H)^+$ 159.0810, found 159.0808, calcd for $C_{11}H_{14}NO$ $(M + NH_4)^+$ 176.1075, found 176.1079.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds (*R*)-**3**, (*R*)-**4**, (*R*,*R*)-**5**, and (*S*,*R*)-**5** and ^{1}H NMR spectra of compounds **7**, **8**, **10**, **11**, **13**, **14**, **16**, **17**, **19**, and **20** (15 pages). This material is contained in libraries on microfiche, immediatley 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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