Highly Diastereoselective Intramolecular Allylation Reactions of Mixed Silyl-Substituted Acetals

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The reaction of preformed mixed acetals derived from (α-hydroxyalkyl)dimethylallylsilane with a number of aromatic and aliphatic aldehydes in the presence of Lewis acids results in a highly diastereoselective intramolecular allylation reaction. The reaction proceeds through a cyclic synclinal $S_{E'}$ addition of the allylsilane to an intermediate oxocarbenium ion. The reaction occurs exclusively by an intramolecular process as determined by means of a cross-over experiment. The relative stereochemistry was determined by the conversion of one of the allylation products to a known (stereodefined) aldol-type product. A greater degree of diastereoselectivity is obtained by in-situ formation of an oxocarbenium ion from (α-hydroxyhexyl)dimethylallylsilane and an aldehyde in the presence of boron trifluoride etherate. The diastereoselectivity of the in-situ allylation reaction typically exceeds 100:1 in favor of the *syn* adduct. However, reactions with electron rich aryl aldehydes resulted in a diminished degree of diastereoselectivity. The initial product of the in-situ reaction is an unstable silyl fluoride which is readily hydrolyzed to a silanol derivative upon reaction with methanolic potassium hydroxide. The overall yield of the two-step process is greater than 80%. A method for the synthesis of more highly substituted (α-alkoxyalkyl)dimethylallylsilanes by allyl anion displacement of methoxide from silicon is also described. The methyl siloxane derivatives were obtained by ozonolytic cleavage of an unsubstituted allyl group in methanol.

Introduction

Allylsilanes comprise a very useful class of functionalized nucleophilic reagents that have enjoyed a considerable degree of application in synthesis. A number of intermolecular and intramolecular regiospecific and stereoselective reactions have been reported.[1] In addition to the synthetic applications of allylsilanes, a number of investigations have probed the mechanism of reaction with acetals and carbonyl compounds.[2] In general, current and previous work has focused on transformations in which the silyl reagent undergoes an acyclic antiperiplanar $S_{E'}$ reaction with an electrophile. The antiperiplanar reaction manifold is also commonly observed in intramolecular reactions of allylsilanes which incorporate a trimethylsilyl-substituted allyl group. There are few examples in the literature in which the silicon atom serves as a template to bring the allyl moiety and the electrophile together in an intramolecular reaction. To our knowledge, there are only two examples of an allylsilane addition reaction in which the silicon atom is "endocyclic" within a closed cyclic transition state for intramolecular delivery of the allyl group.[3]

Earlier work from our laboratory revealed that (α-alkoxyalkyl)silyl- and -stannyl-substituted mixed acetals undergo diastereoselective nucleophilic addition reactions with a number of enol ethers and ketene silyl acetals.[4] The relative stereochemistry (across the ether linkage) of the aldol type products was determined to be *anti* as illustrated in Figure 1. As part of a program designed to fully investigate the synthetic utility of (α-alkoxyalkyl)-silanes, we sought to develop a stereocomplementary process which would lead to products bearing a *syn* stereochemical relationship of the substituents across the ether linkage. In this paper, we describe details of the study of an intramolecular allyl transfer reaction via an (α-alkoxyalkyl)dimethylallylsilane. We also note that the silane derivative is a bis-functionalized reagent that serves to bring together both the electrophilic and nucleophilic reactive centers via an "endocyclic" silicon template.

Synthesis of Allylsilane Substituted Mixed Acetals

The (α-hydroxyalkyl)allyldimethylsilanes **1a**−**c** were easily prepared by the reverse Brook methodology developed earlier in this group, Scheme 1.[5] Initial condensation of the aldehyde with (tributylstannyl)lithium followed by O-silylation of the alcohol with commercially available chlorodimethylallylsilane provided the intermediate (tributylstannyl)silyl ether. Rearrangement of silicon from oxygen to carbon was then accomplished by treatment of the stannane with an excess of butyllithium.

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(1) (a) Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83. (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (c) Majetich, G. In *Organic Synthesis: Theory and Application*; Hudlicky, T., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, p 173. (d) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

(2) For examples of mechanistic studies, see: (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963. (c) Yamamoto, T.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239. (d) Heathcock, C. H.; Kiyooka, S.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214. (e) Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Willson, T. M. *Tetrahedron* **1989**, *45*, 1053. (f) Panek, J. S.; Cirillo, P. F. *J. Org. Chem.* **1993**, *58*, 999. (g) Denmark, S. E.; Almstead, N. G. *J. Org. Chem.* **1994**, *59*, 5130. (h) For an example of a syn $S_{E'}$ addition from a bis-silyl-substituted species, see: Wetter, H.; Scherer, P.; Schweizer, W. B. *Helv. Chim. Acta* **1979**, 1985. (i) Mayr, H.; Gorath, G. *J. Am. Chem. Soc.* **1995**, *117*, 7862.

(3) (a) Reetz, M. T.; Jung, A.; Bolm, C. *Tetrahedron* **1988**, *44*, 3889. (b) Uyeo, S.; Itani, H. *Tetrahedron Lett.* **1991**, *32*, 2143.

(4) (a) Linderman, R. J.; Anklekar, T. V. *J. Org. Chem.* **1992**, *57*, 5078. (b) Linderman, R. J.; Viviani, F. G.; Kwochka, W. R. *Tetrahedron Lett.* **1992**, *33*, 3571.

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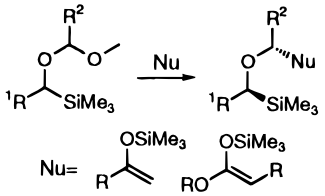
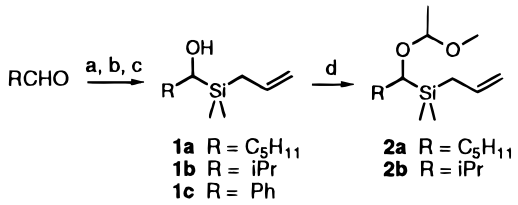


Figure 1. Diastereoselective nucleophilic addition reactions to (α-alkoxyalkyl)trimethylsilanes.

Scheme 1[a]

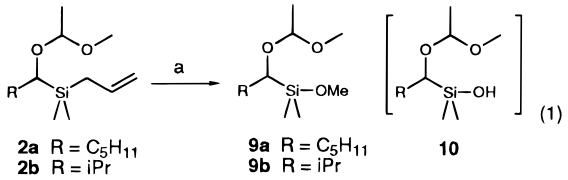


[a] Reagents: (a) Bu_3SnLi, THF −78 °C; (b) $CH_2CHCH_2Si(CH_3)_2Cl$, (c) 3 equiv of BuLi, THF, −78 °C; (d) 1-chloroethyl methyl ether, iPr_2NEt, CH_2Cl_2.

Conversion of the dimethylallylsilyl substituted carbinol to the mixed acetal was straightforward via reaction with an α-chloro ether in the presence of Hunig's base.[5] The mixed silyl-substituted acetals were each obtained as a 1:1 mixture of diastereoisomers.

The synthesis of mixed acetals containing more highly substituted allyl silanes was then pursued. Unfortunately, chlorodimethyl-substituted allylsilanes which could be employed in the reverse Brook rearrangement method are not readily available. A number of approaches to the synthesis of bifunctional silanes have been reported from dichlorodialkylsilanes[6] or (dialkylamino)alkoxydialkylsilane[7] derivatives; however, earlier studies in our group had indicated that nucleophilic addition of α-alkoxy anions to silyl halides or silyl ethers was not a synthetically useful process.[5] Our initial attempts to solve this problem involved chemoselective functionalization of dimethylphenyl(α-hydroxyhexyl)silane **3**. The requisite starting material was prepared by the reverse Brook rearrangement method rather than direct addition of the dimethylphenylsilyl anion[8] to hexanal, Scheme 2. In our hands this three-step procedure provided very good overall yields of the product and obviated the need to prepare the silyl anion. In addition, we have found that the reverse Brook approach for the synthesis of (α-hydroxyalkyl)silanes can be easily carried out on relatively large scales (≥4 g). The hydroxy group of the silane was then protected as the acetate **4** in excellent yield. Chemoselective removal of the phenyl group of **4** was then effected by reaction with tetrafluoroboric acid under the conditions reported by Fleming and co-workers.[9] It is interesting to note in this example that no competing cleavage of the α-acetoxyalkyl group from silicon was observed. The silyl fluoride **5** could be obtained in 80−87% yield by Kugelrohr distillation. Unfortunately, the electrophilic cleavage of the phenyl group could not be accomplished on an acetal-protected derivative of **3** without concomitant loss of the acetal protecting group. Reaction of the silyl fluoride **5** with methallyllithium or Grignard reagents did not result in the anticipated free (α-hydroxyhexyl)dimethylmethallylsilane. The reaction led instead to a diastereomeric mixture of the unstable dimeric product **6** (tentatively identified by NMR data) along with the expected bishomoallylic ether **7** resulting from addition of the anion to the acetate, Scheme 3. We were unable to find reaction conditions that would allow for the conversion of the dimeric product **6** to the desired addition product in reasonable yield. Interestingly, treatment of the dimer **6** with excess methyllithium resulted in cleavage of the silyl ether as well as loss of the methallyl group, providing only the known trimethylsilyl derivative **8**.[5]

Given the fact that alkoxy groups are readily displaced from silicon by reaction with alkyllithio species,[7] we then explored an alternative route to synthesize a methoxy substituted (α-alkoxyalkyl)dimethylsilane. We anticipated that ozonolysis of allyl silane **2a** or **2b** in methanol would result in an unstable α−trialkylsilyl aldehyde.[10] Methanolysis of the α-silyl aldehyde or rearrangement to a silyl enol ether prior to methanolysis could then result in the silyl ether product. In the event, ozonolysis of acetal **2a** or **2b** in methanol provided the silyl methyl ether derivatives **9a** and **9b**, respectively, in good yields (1). It must be pointed out that the ozonolysis reaction



(1)

Reagents (a) O_3, MeOH, -78°C to rt

of the silyl acetal can be tempermental. Extended ozonolysis reaction times can result in loss of the acetal protecting group with subsequent oxidation of the (α-hydroxyhexyl)dimethylsilane derivative to hexanoic acid.[11] Overoxidation can be minimized by monitoring the ozonolysis reaction for loss of starting material. Longer reaction times are required for larger scale reactions (>2 g) which can lead to an increase in the extent of overoxidation. The methoxy ether **9** is somewhat unstable to chromatography on silica gel and is best purified by rapidly passing the crude ozonolysis reaction mixture through a short plug of silica gel. The fairly unstable silanol acetal **10** may be obtained as a byproduct by hydrolysis on the column. Nevertheless, silyl ether **9a** or **9b** can be reproducibly obtained in 70−80% yield.

Substituted allylsilanes were then prepared by displacement of the methoxy group of **9** by allyllithio regents which were in turn generated by transmetalation of the corresponding allylstannane; see Table 1. The stannanes

(6) Dihalodialkylsilanes have been employed in the preparation of a wide variety of bisfunctionalized silane derivatives. The "temporary silicon connection" methodology of Stork provides an example of this approach. See, for example: (a) Stork, G.; Suh, H. S.; Kim, G. *J. Am. Chem. Soc.* **1991**, *113*, 7054. (b) Stork, G.; Kim, G. *J. Am. Chem.* **1992**, *114*, 1087. (c) Matsumoto, Y.; Ohno, A.; Hayashi, T. *Organometallics* **1993**, *12*, 4051.

(7) Aminosilanes are also useful intermediates in the synthesis of bisfunctionalized silanes. See: (a) Stork, G.; Keitz, P. F. *Tetrahedron Lett.* **1989**, *30*, 6981. (b) Tamao, K.; Kawachi, A.; Ito, Y. *Organometallics* **1993**, *12*, 580.

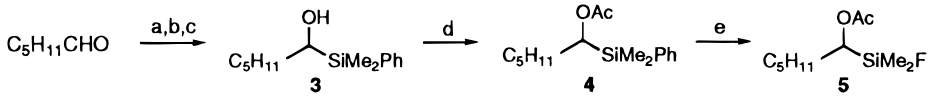
(8) (a) George, M. V.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 403. (b) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkins Trans. 1* **1984**, 1805.

(9) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29.

(10) For a recent report on the isolation of a stable α-trialkylsilyl substituted aldehyde, see: Duhamel, L.; Gralak, J.; Bouyanzer, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1763.

(11) Linderman, R. J.; Chen, K. Y. *Tetrahedron Lett.* **1992**, *33*, 6767.

Scheme 2[a]



[a] Reagents: (a) Bu_3SnLi, THF, −78 °C; (b) $PhMe_2SiCl$, iPr_2NEt, DMAP, CH_2Cl_2, rt; (c) 3 equiv of nBuLi, THF, −78 °C (69%); (d) Ac_2O, py, DMAP, CH_2Cl_2, rt (91%); (e) 2 equiv of $HBF_4{\cdot}Et_2O$, CH_2Cl_2, rt (87%).

Scheme 3

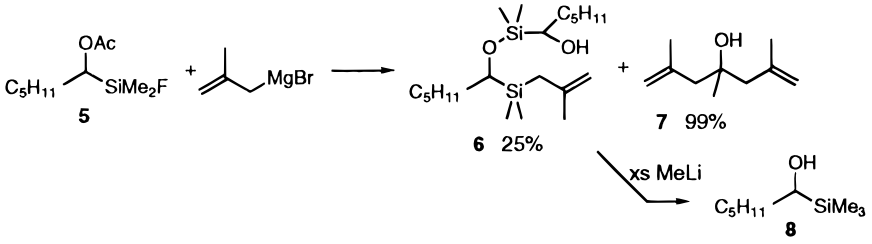
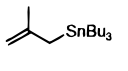
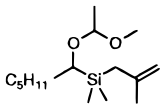
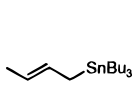
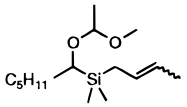
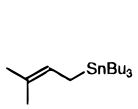
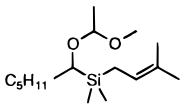
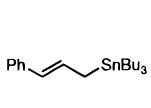
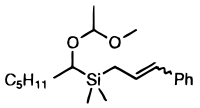
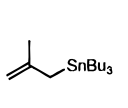
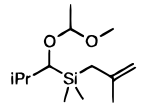


Table 1. Synthesis of Substituted Allylsilanes

Entry	Stannane	Silane (number)[a]	Yield, %[b]
1		 **11**	65
2		 **12**[c]	71
3		 **13**	75
4		 **14**[d]	75
5		 **15**	64

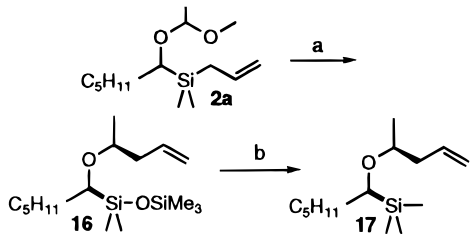
[a] Each acetal was obtained as a 1:1 mixture of diastereomers. [b] Isolated yields after chromatography. [c] Silane **12** was obtained as an approximately 2:1 ratio of *E*:*Z* isomers. [d] Silane **14** was obtained as an approximately 6:1 ratio of *E*:*Z* isomers.

were prepared from the appropriate allyl halide and tributyltin chloride using Barbier reaction conditions.[12] Tributylcrotylstannane prepared in this fashion from 3-chloro-1-butene was isolated as an *E*/*Z* mixture of alkenes. The best yields of the allylsilane derivatives **11**−**15** were obtained from reaction of **9a** or **9b** with 3 equiv of the allyllithium reagent.

Intramolecular Allylation Reactions

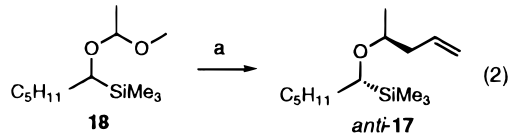
Our initial investigations of the allylsilane-functionalized mixed acetals focused on an intramolecular allylation reaction using mixed acetal **2a**. On the basis of our earlier work on aldol reactions of trimethylsilyl-substituted mixed acetals, we first chose to examine reactions catalyzed by trimethylsilyl triflate. Reaction of the mixed acetal **2a** with 1.1 equiv of trimethylsilyl triflate at −78 °C resulted in the somewhat hydrolytically

Scheme 4[a]



[a] Reagents: (a) Me_3SiOTf, CH_2Cl_2, −78 °C (70%); (b) 8 equiv of MeLi, THF, 0 °C (91%).

unstable allyl transfer product **16** in good yield after chromatography, Scheme 4. Verification of the structural assignment was realized upon reaction of the trimethylsilyl ether derivative **16** with an excess of methyllithium, providing the trimethylsilyl-substituted derivative **17** as a 34:1 diastereomeric mixture. The derived trimethylsilyl substituted allylation product was the same as that obtained by intermolecular reaction of the corresponding trimethylsilyl substituted mixed acetal **18** with allyltrimethylsilane,[4a] (2), except that the diaster-



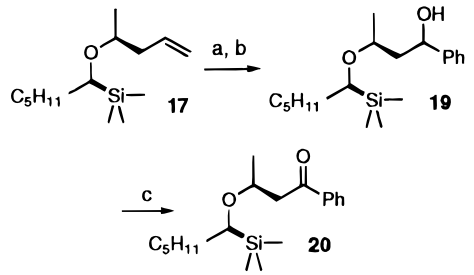
Reagents (a) Allyltrimethylsilane, $TiCl_4$, CH_2Cl_2 -78°C (70%)

eomeric ratio of the product, as determined by capillary GC, was reversed. Significantly, the intermolecular allylation reaction only produced **17** as a 1:5 (*syn:anti*) mixture of diastereomers. The *syn*- and *anti*-isomers of **17** were also readily distinguished by ^{13}C NMR spectral data. The relative stereochemistry of *syn*-**17** obtained from the intramolecular reaction (Scheme 4) was then verified by chemical conversion to the aldol product **20** as shown in Scheme 5. Ozonolysis of the allyl group followed by Grignard addition to the aldehyde provided alcohol **19** in 56% overall yield. Swern oxidation[13] provided the ketone **20** in very good yield. Comparison of ketone **20** with that derived from the known *anti* selective Mukaiyama aldol reaction[4a] clearly indicated that the intramolecular allylation product **16** bears the

(12) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079.

(13) Mancuso, A. J.; Brownfair, D. S.; Swern, D. *J. Org. Chem.* **1979**, *44*, 4148.

Scheme 5[a]



[a] Reagents: (a) O_3, then Me_2S, (b) PhMgCl (56%), (c) Swern (89%).

Table 2. Intramolecular Allylation Reactions of Substituted Allyl Silanes

entry	R^1	R^2	R^3	silane **A**[a]	siloxane **B**	selectivity[b]	silanol **C**	yield[c] (%)
1	C_5H_{11}	H	H	**2a**	**3**	34:1	**26**	85
2	iPr	H	H	**2b**	**21**	38:1	**27**	69
3	C_5H_{11}	CH_3	H	**11**	**22**	25:1	**28**	70
4	C_5H_{11}	H	CH_3	**12**	**23**	1.6:1[d]	**29**	78
5	C_5H_{11}	H	Ph	**14**	**24**	6.4:1[d]	**30**	78
6	iPr	CH_3	H	**15**	**25**	37:1	**31**	71

[a] Structures shown in Figure 2. [b] Diastereoselectivity (syn:anti) of the initially formed trimethylsilyl ether of the silanol determined by capillary GC analysis of the crude reaction mixture. [c] Isolated overall yield of the silanol. [d] The diastereoselectivity reported reflects the ratio of isomers determined by the stereochemistry of R^3 relative to the vicinal methyl group. Diastereoselectivity across the ether linkage could not be accurately determined but is estimated as >20:1 by NMR data.

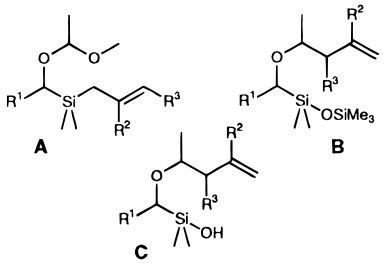
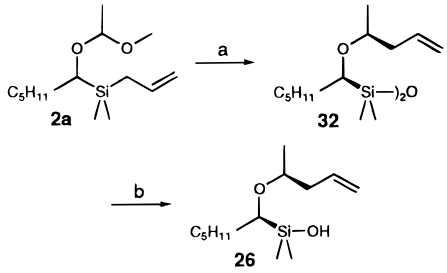


Figure 2. Structures of substituted allylsilanes **A**, siloxanes **B**, and silanols **C**.

syn stereochemical relationship for the substituents across the ether linkage.

The yields and selectivities of the intramolecular allylation reaction of mixed acetals **2a**, **2b**, **11**, **12**, **14**, and **15** are given in Table 2. The structures of the mixed acetal silane **A**, siloxane **B**, and silanol **C** are shown in Figure 2. Each acetal provided the allylation product with an excellent degree of diastereoselectivity (as determined by capillary GC analysis of the initial (trimethylsilyl)siloxane derivative **B**). Reactions using less than stoichiometric amounts of trimethylsilyl triflate led to substantial amounts of symmetric siloxane derivatives, such as **32**, Scheme 6. The symmetric siloxanes were difficult to purify due to partial hydrolysis upon silica gel column chromatography. The spectral data (^1H and ^{13}C NMR) for the symmetric siloxane were virtually identical to that for the corresponding silanol with the only distinction being observation of an absorption for a free OH in the IR spectrum of the silanol. Symmetric siloxanes can also be obtained in reactions using 1.1 equiv of trimethylsilyl triflate if the reaction mixture is allowed to stir for >2 h at room temperature. To prevent this problematic side reaction, the crude allylation products

Scheme 6[a]



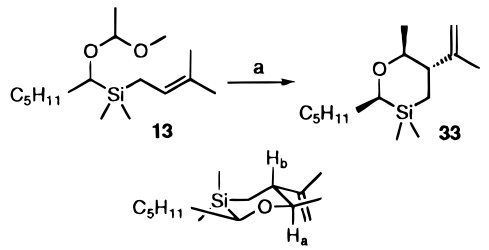
[a] Reagents: (a) 0.1 equiv of TMSOTf, CH_2Cl_2, −78 °C; (b) SiO_2/H_2O (observed incomplete hydrolysis under these conditions).

were treated under the relatively strong basic conditions of 10% KOH in MeOH/THF to effect complete conversion to the relatively stable silanol. The silanols could be readily purified by flash chromatography. Symmetric siloxanes or (trimethylsilyl)siloxanes (such as **16**) were converted to the silanol in >95% yield in all cases examined. A number of milder basic hydrolysis conditions were examined but found not to be as effective. Over time the silanols are found to dehydrate to once again produce the corresponding symmetric siloxane.

The initial experiments using mixed acetal **2a** were carried out at room temperature; however, the substituted allyl species **11**−**15** were found to be more reactive, and the allylation reaction was therefore carried out at −78 °C. Acetal **2a** also provides the silanol **26** in good yield upon treatment with trimethylsilyl triflate at −78 °C (Table 2, entry 1). Both β-substituted silanes **12** and **14** provide the product resulting from γ-allylation, silanols **29** and **30**, respectively, as anticipated. The selectivities of the allylation reaction of silanes **12** and **14** were much more difficult to assess due to the fact that the starting silanes were diastereomeric mixtures at the acetal carbon as well as an *E*/*Z* isomeric mixture at the double bond. In the case of silane **12**, all four isomers were resolved by GC, providing assessment of the acetal diastereomeric mixture as 1:1.2 and the alkene isomeric ratio as 1.6:1. GC analysis of the (trimethylsilyl)siloxane derivative of silanol **29** indicated two diastereomers in a ratio of 1.6:1, reflecting the ratio of double bond isomers in the starting material. A comparison of spectral data from the series of compounds produced by this study indicated that the ratio was due to the relative stereochemistry of the R^3 (see Figure 2) group and the vicinal methyl substituent, rather than the relative stereochemistry across the ether linkage. Similarly, silane **14** was produced as a roughly 6:1 ratio of alkene isomers and a 1:1 ratio of diastereomers at the acetal carbon (relative to the silyl-substituted carbon). The allylation product was isolated as a 6.4:1 mixture of isomers, again due to the relative stereochemistry of R^3 and the vicinal methyl group. The actual diastereoselectivity across the ether linkage could not be accurately determined for either **29** or **30**, but is estimated as >20:1 from ^1H NMR spectral data. Unfortunately, attempts to obtain a single alkene isomer of silane **12** or **14** for use in the allylation reaction were not successful.

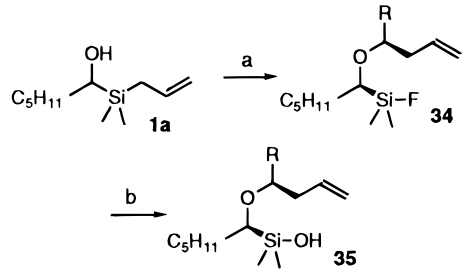
The reaction of silane **13** with trimethylsilyl triflate was unique in that the reaction did not provide the expected allyl transfer product, but rather the cyclic silane **33** in 76% yield, Scheme 7. Significantly, **33** was isolated as a single isomer in which all of the substituents are equatorial. The diaxial orientation of H_a and H_b (Scheme 7) was readily apparent from the observed

Scheme 7[a]



[a] Reagents: (a) 1.1 equiv of TMSOTf, CH_2Cl_2, −78 °C.

Scheme 8[a]



[a] Reagents: (a) RCHO, 0.5 equiv of BF_3Et_2O, CH_2Cl_2, rt; (b) 10% KOH MeOH/THF.

Table 3. Intramolecular Allylation Reaction of RCHO with 1a

entry	aldehyde R	selectivity[a]	SiF	SiOH	yield[b] (%)
1	CH_3	>120:1	**34a**	**35a** (**26**)	49
2	$CH(CH_3)_2$	118:1	**34b**	**35b**	81
3	nC_5H_{11}	113:1	**34c**	**35c**	82
4	cyclo-C_6H_{11}	114:1	**34d**	**35d**	85
5	C_6H_5	>120:1	**34e**	**35e**	93
6	4-PhC_6H_4	>120:1	**34f**	**35f**	77
7	2-naphthaldehyde	>120:1	**34g**	**35g**	75
8	2-BrC_6H_4	>120:1	**34h**	**35h**	72
9	4-$NO_2C_6H_4$	>120:1	**34i**	**35i**	85
10	4-$CF_3C_6H_4$	>120:1	**34j**	**35j**	80
11	3-$CF_3C_6H_4$	>120:1	**34k**	**35k**	73
12	2-$CF_3C_6H_4$	>120:1	**34l**	**35l**	72
13	4-MeC_6H_4	24:1	**34m**	**35m**	78
14	2,4,6-$(CH_3)_3C_6H_2$	4:1	**34n**	**35n**	34
15	4-$MeOC_6H_4$	c			

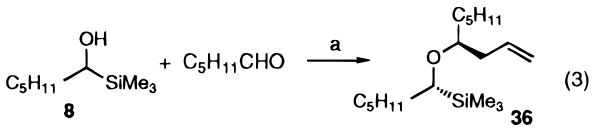
[a] Diastereoselectivity (*syn:anti*) of the silyl fluoride **34**, determined by capillary GC analysis of the crude reaction mixture. [b] Isolated overall yield of the silanol **35** from the aldehyde. [c] No silyl containing allylation product was obtained. 4-(Diallylmethyl)anisole **38** was isolated in 31% yield with 48% recovered 4-methoxybenzaldehyde.

vicinal coupling constant of 3 Hz. Additional NOE and 2D NMR data served to confirm the stereochemical assignment.

The intramolecular allylation reaction does not require the prior synthesis of a mixed acetal. The direct combination of (α−hydroxyhexyl)dimethylallylsilane (**1a**), an aldehyde, and boron trifluoride etherate also results in the desired allylation product in very good yield, Scheme 8 and Table 3. In this case, the initial product of the reaction is the silyl fluoride **34**. More significantly, the diastereoselectivity of the reaction is enhanced over that observed in reactions with preformed mixed acetals, from roughly a >20:1 mixture to a >100:1 mixture. As in the reactions using preformed mixed acetals, we believe that the free alcohol forms an intermediate oxocarbenium ion which then undergoes intramolecular allylation in very good yield with excellent selectivity; see the mechanism discussion below. As shown in Table 3 , the allylation product is obtained with greater than 100:1 selectivity for the *syn* isomer in nearly all of the cases examined. The diastereoselectivity of the allylation reaction was determined by GC analysis of the crude silyl fluoride product **34**. The high degree of diastereoselectivity is also reflected in the ^{19}F NMR of the fluoride**.** For example, the ^{19}F NMR spectrum of **34c** revealed only a singlet at −164 ppm. The relatively unstable silyl fluoride partially hydrolyzes upon attempted column chromatography on silica gel. Similar to the trimethylsilyl ethers (siloxanes) discussed above, neutral pH aqueous hydrolysis of the fluoride leads to a mixture of silanol and siloxane dimers which is difficult to separate. Clean hydrolysis of the silyl fluoride was then routinely accomplished with 10% potassium hydroxide in MeOH/THF in the same manner as discussed above for the siloxanes. The silanols **35** obtained in this fashion are remarkably stable and easily chromatographed on silica gel. The yields of isolated silanols given in Table 3 are for the overall two-step process (allyl transfer and hydrolysis). The silanols tail upon attempted GC analysis, preventing an accurate determination of diastereomeric ratios by this analytical method at this stage; however, NMR data (^1H and ^{13}C) of the silanols **35a**−**l** indicate a single diastereomeric product in good agreement with the GC data from the silyl fluorides.

Trimethylsilyl triflate is not as effective a catalyst in the reaction of the free alcohol **1a** with aldehydes as in the reactions of preformed acetals with this Lewis acid. For example, the reaction of benzaldehyde and silane **1a** catalyzed by trimethylsilyl triflate at room temperature produced silanol **35e** in 35−40% yield (after hydrolysis of the initially formed (trimethylsilyl)siloxane). In contrast, boron trifluoride etherate consistently provided silanol **35e** in yields over 85%. Other Lewis acids such as titanium tetrachloride or tin tetrachloride did not cleanly provide the allylation products from reactions of **1a** with aldehydes. A slight excess of the silane **1a** is required to optimize the yield of the allylation product **35**. The examples shown in Table 3 were obtained using 1.4 equiv of silane to aldehyde. The yield of the allyl transfer product is also dependent on the reaction time and temperature. Reactions using silane **1a** at room temperature for periods longer than 10 min resulted in a significant reduction in the yield of the adduct. However, reaction times using the hydroxysilane at lower temperatures (<−40 °C) were much longer (>2 h for completion) and, therefore, did not provide any advantage over the shorter reaction time at room temperature.

For a direct comparison of the diastereoselectivity of the intramolecular allyl transfer reaction with an intermolecular allylation reaction, the in-situ reaction of allyltrimethylsilane, hexanal, and (1-hydroxyhexyl)trimethylsilane (**8**) was carried out (3). In this reaction,

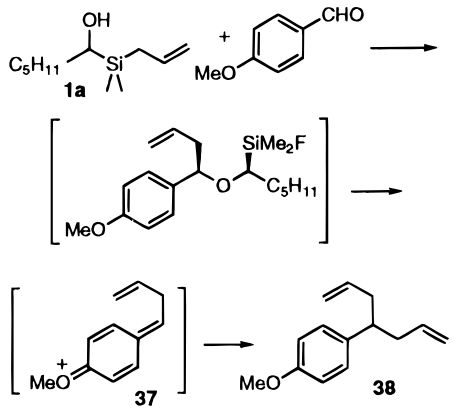


(3)

Reagents (a) Allyltrimethylsilane, TMSOTf, CH_2Cl_2 -78°C (74%)

the intermolecular allylation product **36** was obtained in good yield, but with only 1:3.4 selectivity. In contrast to the intermolecular reaction, note the extent of selectivity realized for the intramolecular process, Table 3, entry 3, of 113:1. Given the data presented within this study, we

Scheme 9



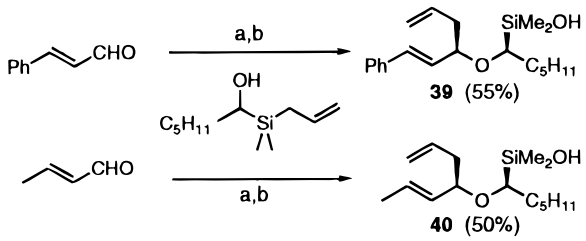
have assigned the relative stereochemistry of **36** derived from the intermolecular allylation process *anti* as shown in (3). In a related reaction, Marko and co-workers have realized diastereoselectivity as high as 10:1 for intermolecular allylation reactions employing mixed acetals derived in-situ from aryl-substituted alcohols.[14] There are other examples of high degrees of diastereoselection in reactions of acyclic acetals[15] and trimethylallylsilane; however, there are no other examples of addition reactions to silyl-substituted mixed acetals such as those reported here. The observed diastereoselectivity for this intramolecular allylation process provides an example of one of the highest degrees of "acyclic" 1,3-asymmetric induction reported to date.[16]

The reactions of silane **1a** and substituted aromatic aldehydes reveal that electron-rich aryl aldehydes result in silanols **35** with diminished diastereoselectivity relative to silanols obtained from reaction with electron poor aryl aldehydes. The substitution of a methyl group for hydrogen in the para position dramatically reduces the diastereoselectivity of the reaction (compare Table 3, entries 5 and 13) from >120:1 to 24:1. The incorporation of three alkyl groups on the aromatic ring further reduce the selectivity to 4:1, see Table 3, entry 14. Anisaldehyde does not result in the formation of the silyl fluoride product at all, but rather undergoes a second allylation reaction to form **38**, presumably through a quinone methide intermediate **37** formed by Lewis acid catalyzed expulsion of the benzylic oxygen present in the initial allylation product, Scheme 9.

The reaction of silane **1a** with two unsaturated aldehydes has also been examined. Reaction with cinnamaldehyde provided the 1,2-addition product **39** in reasonable yield (55%), Scheme 10.

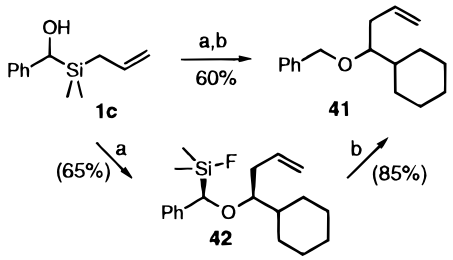
The possible 1,4-addition product was not observed in the reaction mixture, but given the attenuated yield of the reaction relative to the other examples discussed above, this possible reaction pathway cannot be completely ruled out. Intermolecular reactions of unsaturated aldehyde acetals with allyltrimethylsilane result in products derived from multiple allylations by 1,2- and 1,4-additions.[17] The somewhat sensitive diene **40** was obtained as a 100:1 ratio of diastereomers. In contrast, crotonaldehyde also provided the 1,2-addition reaction product **40** in similar yield (50%), but as a 22:1 diastereomeric mixture. Closer examination of the products revealed that the observed ratio of isomers reflected a mixture of *cis*- and *trans*-alkene isomers rather than a diastereomeric mixture across the ether linkage. However, we cannot be certain of complete resolution of the mixture and therefore can only presume that the actual diastereoselectivity of the allylation reaction in this particular example is as high as that observed for cinnamaldehyde (>100:1).

Scheme 10[a]



[a] Reagents: (a) 0.5 equiv of $BF_3{\cdot}Et_2O$, CH_2Cl_2, −78 to −20 °C; (b) 10% KOH, MeOH/THF.

Scheme 11[a]



[a] Reagents: (a) c-$C_6H_{11}CHO$, 0.5 equiv of $BF_3{\cdot}OEt_2$, CH_2Cl_2, −78 °C; (b) 10% KOH, MeOH/THF.

The intramolecular allylation reaction was also examined for a phenyl-substituted silane **1c** and cyclohexylcarboxaldehyde. In this case the normal reaction conditions did not result in a product that contained the dimethylsilanol moiety, but rather the benzyl ether **41**, Scheme 11.

Cleavage of C−Si bonds of benzylic silanes under strongly basic conditions is a well-known process.[18] Indeed, if the allylation reaction of **1c** is repeated without the secondary base treatment step, the sensitive silyl fluoride **42** was obtained as a single diastereomer (>120:1 selectivity). Submission of the fluoride to methanolic potassium hydroxide then resulted in the benzyl ether **41** in very good yield.

Attempted intramolecular allylation reaction of silane **1a** or **1b** with ketones, such as acetophenone and cyclohexanone, did not result in any allylation products. The ketone and silane were recovered from the reaction mixture. This result is not unexpected given the lower propensity of a ketone to form a hemiketal with the free alcohol (and therefore an oxocarbenium ion) under the reaction conditions employed.

Mechanism of the Reaction

Given the fact that each silyl-substituted mixed acetal initially exists as a 1:1 mixture of diastereomers, but produces a product with typically >25:1 stereoselectivity,

(14) Mekhalfia, A.; Marko, I. E. *Tetrahedron Lett.* **1991**, *32*, 4779.
(15) (a) Imwinkelreid, R.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 591. (b) Mukaiyama, T.; Ohshima, M.; Muyishi, N. *Chem. Lett.* **1987**, 1121.
(16) Hoffman, R. W. *Chem. Rev.* **1989**, *89*, 1841.
(17) Allylsilane additions to unsaturated aldehydes result in mixtures of 1,2- and 1,4-addition products as well as diaddition products; see: Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1978**, 499.
(18) Linderman, R. J.; Ghannam, A.; Badejo, I. *J. Org. Chem.* **1991**, *56*, 5213.

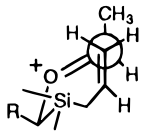
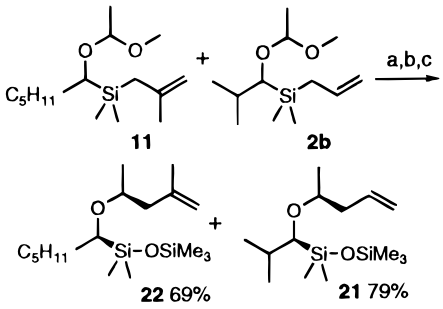


Figure 3. Cyclic $S_{E'}$ synclinal transition state.

implies that the reaction proceeds through an oxocarbenium ion intermediate. This mechanism is consistent with our previous data on aldol reactions of silyl-substituted mixed acetals[4] and is also supported by recent mechanistic studies of Lewis acid-catalyzed nucleophilic addition reactions to acyclic acetals not containing silicon.[19] Trialkylallylsilanes generally react via an anti $S_{E'}$ mechanism through either an antiperiplanar or synclinal acyclic transition state.[1,2] Reactions through a syn $S_{E'}$ mechanism are typically disfavored for stereoelectronic reasons.[2g,h] Reactions of allylsilanes through cyclic (or closed) transition states are fairly uncommon and are typically only observed for pentacoordinate allylsilicate[20] species or allylsilanes bearing inductively withdrawing substituents such as allyltrifluorosilane.[21] Intramolecular allyl transfer reactions proceeding by an anti $S_{E'}$ mechanism are well known for the construction of carbocyclic and heterocyclic systems.[1c] The stereoselectivity of the intramolecular allylation reactions can be very high, such as the tetrahydrofuran synthesis reported by Mohr.[22] Marko and co-workers have examined an intramolecular Sakurai reaction of functionalized allylsilanes that leads to tetrahydropyran derivatives.[23] Lee and co-workers have also studied reactions of functionalized allylsilanes that react via in-situ formation of an oxocarbenium ion.[24] However, these reactions are distinct from the intramolecular allyl transfer reaction reported herein in that the silicon in the previous studies is present as a trimethylsilyl moiety and is "exocyclic" to the forming ring in the transition state.

A reasonable transition state for the intramolecular process is depicted in Figure 3 in which a synclinal $S_{E'}$ attack of the allylsilane occurs on the intermediate oxocarbenium ion through a seven-membered cyclic transition state. Note in this case that the silicon atom is "endocyclic" within the cyclic transition state. This constraint apparently precludes the adoption of an antiperiplanar approach of the electrophile to the allylsilane. Indeed, examination of molecular models indicates that an antiperiplanar $S_{E'}$ approach is not favorable. Reetz and co-workers have reported a novel intramolecular allyl transfer reaction to provide *syn*-1,3-diols.[3a] In this example, a dimethylallylsilyl moiety is used to derivatize an aldol product with subsequent intramolecular delivery of the allyl group via a cyclic 10-membered ring induced by chelation to titanium. The seven-membered ring intermediate, shown in Figure 3, provides for a possible dual role for silicon in that the C−Si σ bond α to the oxocarbenium ion can adopt an antiperiplanar geometry to the developing π^* orbital of the oxocarbenium ion.[4a] This orientation will facilitate ionization of the acetal via a stereoelectronic effect similar to hyperconjugative stabilization of a β-carbocation.[25] The allylic C−Si σ bond is also situated *anti* (or nearly so) to the C=C π-system for the "normal" mode of reaction (stereoelectronic control) for the allylsilane. The cyclic nature of the transition state is strongly supported not only by the data from a cross-over reaction (described below), but also by the results of the reactions of substituted silanes **12** and **14**. An intermolecular antiperiplanar mechanism would be expected to give a high degree of stereoselection independent of the double bond geometry, whereas the stereoselectivity of a closed or cyclic transition state allylsilane reaction is known to be dependent on the alkene geometry[1,20,21] as is observed in our study.

Scheme 12[a]



[a] Reagents: (a) 1.1 equiv of TMSOTf, CH_2Cl_2, −78 °C; (b) 10% KOH MeOH/THF; (c) 5 equiv of Me_3SiCl, 10 equiv of Et_3N, CH_2Cl_2, rt.

The question of whether the reaction mechanism for the allylation process was solely an intramolecular pathway or potentially also involved a degree of intermolecular reaction was then probed in detail by the design of a cross-over experiment, Scheme 12. An equimolar amount of acetals **11** and **2b** was combined with trimethylsilyl triflate at −78 °C. GC analysis of the crude reaction mixture revealed siloxanes **21** and **22** and dimeric siloxanes as discussed above (Scheme 6). To remove the dimeric siloxane byproducts, the crude reaction mixture was hydrolyzed with KOH and the silanols thus obtained were reprotected as the (trimethylsilyl)-siloxanes using an excess of trimethylsilyl chloride.[26] Interestingly, trimethylsilyl chloride does not promote dimeric siloxane formation as noted previously for trimethylsilyl triflate. Upon careful GC analysis of the crude reaction mixture, only the products of intramolecular allyl transfer (siloxanes **21** and **22:** diastereoselectivity >25:1 in each case) were observed. The products

(19) For recent mechanistic investigations into the reaction of nonsilyl-substituted acyclic acetals, see: Sammakia, T.; Smith, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 7915 and references therein.

(20) (a) Hosomi, A.; Kohra, S.; Ogata, K.; Yanagi, T.; Tominaga, Y. *J. Org. Chem.* **1990**, *55*, 2415. (b) Hosomi, A.; Kohra, S.; Tominaga, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1517.

(21) (a) Kira, M.; Hino, T.; Sakurai, H. *Tetrahedron Lett.* **1989**, *30*, 1099. (b) Sato, K.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 6429.

(22) (a) Mohr, P. *Tetrahedron Lett.* **1993**, *34*, 6251. (b) For a diastereoselective synthesis of tetrahydrofurans via an intermolecular allylsilane addition, see: Panek, J. S.; Beresis, R. *J. Org. Chem.* **1993**, *58*, 809.

(23) (a) Marko, I. E.; Bailey, M.; Murphy, F.; Declercq, J.-P.; Tinant, B.; Feneau-Dupont, J.; Krief, A.; Dumont, W. *Synlett* **1995**, 123. (b) Marko, I. E.; Bayston, D. J. *Tetrahedron* **1994**, *50*, 7141 and earlier references therein.

(24) (a) Lee, T. V.; Ellis, K. L.; Richardson, K. A.; Visani, N. *Tetrahedron* **1989**, *45*, 1167. (b) Lee, T. V.; Boucher, R. J.; Porter, J. R.; Taylor, D. A. *Tetrahedron* **1988**, *44*, 4233.

(25) (a) For a review of hyperconjugation effects of silicon, see: Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. For additional recent studies, see: (b) Lambert, J. B.; Emblidge, R. W.; Malany, S. *J. Am. Chem. Soc.* **1993**, *115*, 1317. (c) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 962. (d) Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609.

(26) A control reaction indicated that the deprotection/reprotection sequence did not effect the diastereomeric ratio of the product.

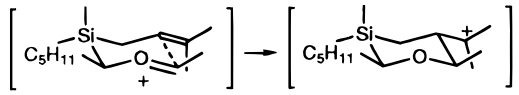


Figure 4. Transition state for formation of **33**.

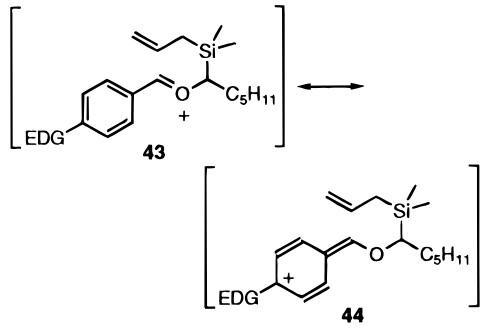


Figure 5. Possible intermediates in the allylation of electron rich aromatic aldehydes.

21 and **22** were isolated by careful column chromatography in good overall yields.[27]

The reaction of silane **13** to form the cyclic silane **33** (Scheme 7) is interesting in that reaction at the β-position of an allyl silane is very uncommon.[1] Akiba and coworkers have reported alkylation at the β-carbon in reactions of (γ,γ-dimethylallyl)trimethylsilane.[28] In the case of silane **13**, a six-membered ring transition state can be adopted in which all of the substituents, with the exception of a methyl group on silicon, are equatorial; see Figure 4. The ring closure results in formation of a tertiary carbocation which may not be significantly higher in energy than the cyclic β-silyl carbocation formed in the intramolecular allyl transfer process. The end result is competitive ring closure via the smaller ring (six vs seven) with ultimate loss of a proton to provide the isopropenyl group.

Stabilization of the forming intermediate benzylic cation by the aromatic ring also provides a reasonable explanation for the lower degrees of selectivity observed for electron-rich aryl aldehydes. A quinone methide intermediate **44** can arise as the reactive species rather than the oxocarbenium ion **43**, Figure 5. The quinone methide resonance form must not provide the same degree of stereochemical control in the transition state for the intramolecular allyl transfer reaction as that enjoyed by the oxocarbenium ion. One must also note that the possibility of intermolecular reactions in allylation of the aryl aldehydes cannot be completely ruled out from the data in hand.

Conclusions

In summary, we have described a novel method for stereochemical complementarity in nucleophilic addition reactions to silyl-substituted mixed acetals. In intermolecular nucleophilic addition reactions the silyl group serves to block one face of the oxocarbenium ion, directing addition to the face of the oxocarbenium ion opposite the silyl group. In the intramolecular variant, a stereoelectronic effect of silicon to accentuate oxocarbenium ion formation positions the silyl group such that delivery of an internal nucleophile occurs from the same face of the oxocarbenium ion as the silyl substituent. The resulting intramolecular allyl transfer reaction results in one of the most diastereoselective allylsilane reactions for acyclic acetals ever reported. Further work will explore the potential for extension of this approach for intramolecular delivery of other nucleophiles from bis-functionalized silanes.

Experimental Section

General. All reagents were purchased from Aldrich, unless otherwise noted, and were purified prior to use. Amines and trialkylsilyl chlorides were distilled from CaH_2. Methanol was refluxed for 2 h over magnesium turnings and then distilled and stored over 3A molecular sieves. Alkyllithium reagents were titrated in ether with 2-propanol using 1,10-phenanthroline as an indicator. Tetrahydrofuran (THF) was freshly distilled from sodium−benzophenone. Methylene chloride was distilled from phosphorous pentoxide. Unless specifically stated, all reactions were performed in flame-dried glassware under an argon atmosphere. Infrared spectra were recorded on a FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer, and chemical shifts are reported relative to TMS. ^{19}F NMR spectra were recorded on a 300 MHz spectrometer and chemical shifts are reported relative to $CFCl_3$. Capillary gas chromatographic analyses were carried out on a 30 m SE-30 fused silica capillary column using a temperature ramp program of 100 °C for 10 min, rate increase of 10 °C/min to 250 °C and a final temperature of 250 °C for 5 min. Flash chromatography was performed on silica gel 60, 230−400 mesh ASTM, obtained from American Scientific Products or Baxter Scientific. Elemental analyses were carried out by Atlantic Microlab, Inc., Atlanta, GA.

A. Synthesis of α-Hydroxy Silanes by the Reverse Brook Rearrangement. Known compounds **1a** and **3** were prepared as described in ref 5 in 74% and 89% yields, respectively. Compounds **1b** and **1c** were also prepared by the published procedure for **1a**.

1-[Dimethyl(3-propen-1-yl)silyl]-2-methylpropan-1-ol, 1b (63%): ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 3 H), 0.05 (s, 3 H), 0.92 (d, 3 H, J = 5 Hz), 0.95 (d, 3 H, J = 5 Hz), 1.40 (s, 1 H), 1.60 (t, 2 H, J = 7 Hz), 1.83 (m, 1 H), 3.12 (t, 1 H, J = 5 Hz), 4.83 (m, 2 H), 5.79 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −4.97, −4.49, 18.97, 20.36, 22.20, 31.96, 71.02, 113.03, 134.94; IR (neat) (cm^{-1}) 3470, 3100, 1640, 1470, 1250, 835, 820. Anal. Calcd for $C_9H_{20}OSi$: C, 62.73; H, 11.79. Found: C, 62.62; H, 11.65.

[Dimethyl(3-propen-1-yl)silyl]phenylmethanol, 1c (51%): ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 3 H), 0.01 (s, 3 H), 1.61 (t, 2 H, J = 7 Hz), 1.81 (s, 1 H), 4.60 (s, 1 H), 4.89 (m, 2 H), 5.79 (m, 1 H), 7.19−7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm −6.49, −6.03, 20.72, 69.50, 113.51, 124.95, 125.95, 125.88, 128.18, 134.54, 143.85; IR (neat) (cm^{-1}) 3440, 3180, 1630, 1490, 1250, 840, 700. Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.56; H, 8.74.

B. General Procedure for Mixed Acetal Formation. A solution of (α-hydroxyalkyl)silane (10 mmol), diisopropylethylamine (5.23 mL, 30 mmol), and 4-(dimethylamino)-pyridine (12 mg, 0.1 mmol) in 25 mL of CH_2Cl_2 was cooled to 0 °C (ice/water bath). Methyl methoxymethyl chloride (1.57 g, 20 mmol) was then added dropwise via syringe. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The mixture was diluted with 100 mL of petroleum ether and washed successively with 0.1 N hydrochloric acid (2 × 30 mL), water (30 mL), saturated sodium bicarbonate (30 mL), and saturated aqueous sodium chloride solution (30 mL). The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel by a gradient elution using 100% hexanes or a 1%, 2%, and 3% diethyl ether/hexanes system.

Methoxyethyl 1-[dimethyl(3-propen-1-yl)silyl]hexyl ether, 2a (87%): GC t_R 17.00 and 17.12 min (1:1); ^{1}H NMR

(27) The silica gel must be deactivated by treatment with triethylamine (2%)/hexane prior to chromatography of **28** or **29** (see Experimental Section).

(28) Wada, M.; Shigehisa, T.; Kitani, H.; Akiba, K.-Y. *Tetrahedron Lett.* **1983**, *24*, 1715.

($CDCl_3$) δ −0.01 (s, 3 H), 0.01 (s, 3 H), 0.84 (t, 3 H, J = 6 Hz), 1.19−1.58 (m, 13 H), 3.24 (d, 3 H, J = 12 Hz), 3.33 (t, 1 H, J = 6 Hz), 4.54 (q, 1 H, J = 5 Hz), 4.80 (m, 2 H), 5.74 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −5.01, 13.99, 19.71, 21.75, 22.52, 26.75, 31.47, 32.12, 51.76, 70.41, 101.40, 113.13, 134.61; IR (neat) (cm^{-1}) 3100, 1635, 1460, 1250, 840. Anal. Calcd for $C_{14}H_{30}O_2Si$: C, 65.06; H, 11.70. Found: C, 65.17; H, 11.67.

Methoxyethyl 1-[dimethyl(3-propen-1-yl)silyl]-2-methylpropyl ether, 2b (94%): GC t_R 12.82 and 13.22 min (1:1); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.07 (s, 3 H), 0.90 (d, 3 H, J = 7 Hz), 0.95 (d, 3 H, J = 7 Hz), 1.26 (d, 3 H, J = 6 Hz), 1.62 (m, 2H), 1.96 (m, 1 H), 3.25 (t, 1 H, J = 4 Hz), 3.26 (s, 3 H), 4.57 (q, 1 H, J = 6 Hz), 4.83 (m, 2 H), 5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −3.59, −3.39, 19.16, 19.58, 20.84, 22.94, 31.34, 52.09, 76.55, 101.95, 113.19, 134.87; IR (neat) (cm^{-1}) 3180, 1625, 1240, 830. Anal. Calcd for $C_{12}H_{26}O_2Si$: C, 62.54; H, 11.37. Found: C, 62.66; H, 11.36.

C. Attempted Conversion of Dimethylphenylsilane to Substituted Allylsilanes. Synthesis of 4. A solution of **3** (2.36 g, 10 mmol), pyridine (4.0 mL, 50 mmol), and 4-(dimethylamino)pyridine (12 mg, 0.1 mmol) in 25 mL of CH_2Cl_2 was cooled to 0 °C (ice/water bath). Acetic anhydride (2.0 mL, 21 mmol) was then added dropwise via syringe. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was diluted with 100 mL of CH_2Cl_2 and washed sequentially with 0.1 N HCl (2 × 30 mL), water (30 mL), and saturated aqueous sodium chloride solution (30 mL). The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel by a gradient elution using a 1%, 2%, 3%, and 5% diethyl ether/hexanes system.

1-(Dimethylphenylsilyl)hexyl acetate, 4 (91%): ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 3 H), 0.24 (s, 3 H), 0.74 (t, 3 H, J = 7 Hz), 1.05−1.60 (m, 8 H), 1.90 (s, 3 H), 4.88 (dd, 1 H, J = 4 Hz, J' = 13 Hz), 7.26 (m, 3 H), 7.43 (m, 2 H); ^{13}C NMR ($CDCl_3$) ppm −5.36, −5.07, 13.93, 20.91, 22.43, 26.59, 30.79, 31.41, 68.37, 127.73, 129.31, 133.97, 135.97, 171.06; IR (neat) (cm^{-1}) 3070, 3050, 1730, 1240, 830, 690. Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 68.90; H, 9.37.

Synthesis of 5. A sample of 85% HBF_4·OEt_2 (0.3 mL, 1.8 mmol) was added via syringe to a solution of **4** (230 mg, 0.827 mmol) in 5 mL of CH_2Cl_2 at room temperature. The reaction mixture was stirred for 2 h and then quenched by the addition of 5 mL of water. The layers were separated and the aqueous phase extracted with ether (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate and the solvents removed under reduced pressure to provide the crude fluorosilane in 90−95% yield. (GC and NMR data showed that the Si−F intermediate was pure enough to carry out the next reaction.) Crude product was purified by vacuum distillation, 50−55 °C/4 mmHg, to provide a colorless liquid in 85% yield.

1-(Dimethylfluorosilyl)-1-hexyl acetate, 5: ^{1}H NMR ($CDCl_3$) δ 0.23 (d, 3 H, J = 7 Hz), 0.25 (d, 3 H, J = 8 Hz), 0.86 (t, 3 H, J = 7 Hz), 1.25-1.65 (m, 8 H), 2.04 (s, 3 H), 4.26 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −2.91 (-3.13), −1.94 (-2.13), 13.96, 20.45, 22.43, 26.43, 29.95, 31.47, 69.31 (69.05), 172.26; ^{19}F NMR ($CDCl_3$) −158.64; IR (neat) (cm^{-1}) 1730, 1710, 1255, 840, 795.

Synthesis of 6 and 7. Compound **5** (160 mg, 0.73 mmol) was dissolved in 15 mL of THF, and Mg metal (583 mg, 24 mmol) and a crystal of iodine were added. A THF solution (10 mL) of methallyl chloride (0.8 mL, 8.1 mmol) was then added dropwise at room temperature over a period of approximately 30 min. After being stirred for 90 min at room temperature, the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride (10 mL). The reaction mixture was diluted with ether (100 mL) and washed sequentially with saturated aqueous sodium bisulfate (20 mL), saturated aqueous sodium bicarbonate (20 mL), water (20 mL), and saturated aqueous sodium chloride (20 mL). The organic phase was then dried over anhydrous magnesium sulfate, and the solvents were removed under reduced pressure. Purification of the crude product mixture provided **6** and **7** in 25% and 99% yield, respectively.

Compound 6: ^{1}H NMR ($CDCl_3$) δ 0.04−0.13 (m, 12H), 0.8−1.8 (m, 25H), 2.08 (d, 1H, J = 6 Hz), 2.17 (d, 1H, J = 6 Hz), 3.25 (m, 1H), 4.00 (s, 1H), 4.71 (s, 1H), 4.78 (s, 1H); ^{13}C NMR ($CDCl_3$) ppm −4.52, −3.62, −3.56, −2.84, 14.06, 22.62, 23.81, 26.40, 26.50, 31.80, 32.67, 32.83, 48.15, 65.34, 67.37, 112.87, 143.18; IR (neat) (cm^{-1}) 3460, 3080, 1250, 1080, 835.

2,4,6-Trimethylhepta-1,6-dien-4-ol, 7: ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 3H), 1.83 (s, 6H), 2.19 (dd, 4H, J = 13 and 23 Hz), 4.73 (s, 2H), 4.91 (s, 4H); ^{13}C NMR ($CDCl_3$) ppm 24.95, 27.05, 50.15, 71.96, 114.87, 142.89; IR (neat) (cm^{-1}) 3460, 3080, 1250, 1095, 890.

D. General Procedure for Ozonolysis of Silanes 2a and 2b. A solution of silane **2a** or **2b** in methanol (1 mmol/20 mL) was cooled to −78 °C. Ozone was passed through the solution until a blue coloration persisted. Excess ozone was purged from the reaction with argon, and dimethyl sulfide (2 mL) was then added. The reaction mixture was allowed to warm to room temperature, stirred for 6 h, and then concentrated under reduced pressure. The residue was taken up in ether (100 mL), the solution dried over anhydrous magnesium sulfate, and the solvent removed under reduced pressure. The crude product was purified by rapid filtration of a hexane solution through a plug of silica gel.

Methoxyethyl 1-(dimethylmethoxysilyl)hexyl ether, 9a (70%): GC t_R 14.85 and 14.97 min (1:1); ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 3 H), 0.12 (s, 3 H), 0.85 (t, 3 H, J = 7 Hz), 1.22−1.60 (m, 11 H), 3.25 (s, 3 H), 3.33 (t, 1 H, J = 6 Hz), 3.42 (s, 3 H), 4.59 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −4.17, −3.98, 13.99, 19.81, 22.49, 26.33, 31.47, 32.18, 50.67, 51.57, 69.47, 101.23; IR (neat) (cm^{-1}) 1250, 1090, 830. Anal. Calcd for $C_{12}H_{28}O_3Si$: C, 58.02; H, 11.36. Found: C, 58.17; H, 11.34.

Methoxyethyl 1-(dimethylmethoxysilyl)-2-methylpropyl ether, 9b (68%): GC t_R 7.81 and 8.38 min (1:1); ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 3H), 0.17 (s, 3H), 0.98 (m, 6H), 1.25 (d, J = 6 Hz, 3H), 2.02 (m, 1H), 3.25 (d, J = 5 Hz, 1H), 3.32 (s, 3H), 3.45 (s, 3H), 4.59 (m, 1H); ^{13}C NMR ($CDCl_3$) ppm −2.62, −2.46, 19.52, 19.74, 20.45, 30.79, 50.60, 51.96, 76.42, 101.91; IR (neat) (cm^{-1}) 1245, 1140, 1080, 995, 830. Anal. Calcd for $C_{10}H_{24}O_3Si$: C, 54.50; H, 10.98. Found: C, 54.21; H, 10.78.

E. General Procedure for the Synthesis of Substituted Allylsilanes. Butyllithium (2.6 M in hexanes, 1.2 mL, 3.0 mmol) was added dropwise via syringe to a solution of a substituted allyltributylstannane (3 mmol) in 5 mL of THF at −78 °C. The reaction mixture was stirred for 20 min at −78 °C to provide a bright yellow or red solution. Silane **9a** or **9b** (0.32 mmol) in 1 mL of THF was then added dropwise at −78 °C. The reaction mixture was allowed to warm to 0 °C and stirred for 2 h. The reaction mixture was then quenched by the addition of 2 mL of water. The layers were separated, and the aqueous phase was extracted with ether (2 × 30 mL). The combined organic phases were then washed with water (20 mL) and dried over anhydrous sodium sulfate, and the solvents were removed under reduced pressure. The crude product was purified by flash chromatography using 2% petroleum ether/hexane as eluent.

Methoxyethyl 1-[dimethyl(2-methyl-3-propen-1-yl)silyl]hexyl ether, 11 (65%): GC t_R 18.48 and 18.58 min (1:1); ^{1}H NMR ($CDCl_3$) δ (mixture of diastereomers) 0.06 (m, 6 H), 0.86 (t, 3 H, J = 7 Hz), 1.20−1.85 (m, 16 H), 3.24 (s, 3 H), 3.34 (t, 1 H, J = 6 Hz), 4.48 (s, 1 H), 4.58 (s, 1 H), 4.60 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm (major diastereomer) −4.30, −4.17, 14.02, 19.55, 22.55, 25.30, 26.88, 31.57, 32.12, 32.25, 51.67, 69.89, 100.59, 108.54, 143.56; IR (neat) (cm^{-1}) 3080, 1630, 1250, 840, 730. Anal. Calcd for $C_{15}H_{32}O_2Si$: C, 66.11; H, 11.84. Found: C, 65.93; H, 11.78.

Methoxyethyl 1-[dimethyl(4-buten-2-yl)silyl]hexyl ether, 12 (71%): GC t_R (a) 18.26 and 18.36 min (1:1.2), (b) 18.64 and 18.75 min (1.2:1); a:b = 1:1.6; ^{1}H NMR ($CDCl_3$) δ (mixture of diastereomers) 0.15 (m, 6 H), 0.87 (t, 3 H, J = 7 Hz), 1.20−1.65 (m, 14 H), 3.27 (m, 4 H), 4.56 (m, 1 H), 5.33 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm (major diastereomer) −4.88, −4.78, 13.99, 17.97, 19.52, 22.52, 26.69, 26.82, 31.54, 32.22, 51.76, 70.73, 100.46, 121.72, 126.05; IR (neat) (cm^{-1}) 1450, 1090. 837, 734. Anal. Calcd for $C_{15}H_{32}O_2Si$: C, 66.11; H, 11.84. Found: C, 66.28; H, 11.79.

Methoxyethyl 1-[dimethyl(2-methyl-4-buten-2-yl)silyl]-hexyl ether, 13 (75%): GC t_R 19.45 and 19.55 min (1:1); ^{1}H NMR ($CDCl_3$) δ (mixture of diastereomers) 0.02 (s, 3 H), 0.03 (s, 3 H), 0.89 (t, 3 H, J = 7 Hz), 1.20−1.75 (m, 19 H), 3.29 (s, 3 H), 3.33 (m, 1 H), 4.54 (q, 0.5 H, J = 5 Hz), 4.64 (q, 0.5 H, J = 5 Hz), 5.14 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm (major diastereomer) −4.65, 14.06, 15.63, 17.64, 19.78, 22.55, 25.69, 26.72, 31.60, 32.28, 51.73, 70.86, 100.52, 119.52, 129.02; IR (neat) (cm^{-1}) 1456, 1090, 836, 773, 720. Anal. Calcd for $C_{16}H_{34}O_2Si$: C, 67.07; H, 11.96. Found: C, 67.16; H, 11.93.

Methoxyethyl 1-[dimethyl(1-phenyl-3-propen-1-yl)silyl]hexyl ether, 14 (75%): GC t_R 25.55 and 25.64 min (1:1); ^{1}H NMR ($CDCl_3$) δ (mixture of diastereomers) 0.03 (s, 3 H), 0.04 (s, 3 H), 0.83 (t, 3 H, J = 7 Hz), 1.15−1.65 (m, 11 H), 1.70 (m, 2 H), 3.20−3.28 (m, 3 H), 3.36 (m, 1 H), 4.55 (m, 1 H), 6.20 (m, 2 H), 7.07−7.26 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm (major diastereomer) −4.78, −4.72, 14.02, 19.74, 21.06, 22.52, 26.66, 31.47, 32.18, 51.54, 69.44, 100.49, 125.40, 126.12, 127.54, 128.34, 138.23, 146.41; IR (neat) (cm^{-1}) 3060, 3025, 1642, 1090, 832, 695. Anal. Calcd for $C_{18}H_{34}O_2Si$: C, 71.80; H, 10.24. Found: C, 71.76; H, 10.20.

Methoxyethyl 1-[dimethyl(2-methyl-4-buten-2-yl)silyl]-2-methylpropyl ether, 15 (64%): GC t_R 14.78 and 15.14 min (1:1); ^{1}H NMR ($CDCl_3$) δ (mixture of diastereomers) 0.08 (s, 3H), 0.09 (s, 3H), 0.95 (m, 6H), 1.25 (d, 3H, J = 6 Hz), 1.61 (d, 1H, J = 1.5 Hz), 1.65 (d, 1H, J = 5 Hz), 1.70 (s, 3H), 2.00 (m, 1H), 3.10 (d, 1H, J = 5 Hz), 3.26 (s, 3H), 4.47 (m, 1H), 4.52 (m, 1H), 4.58 (m, 1H); ^{13}C NMR ($CDCl_3$) ppm −2.91, −2.84, 19.19, 19.65, 21.10, 25.40, 26.21, 31.08, 52.09, 77.16, 102.04, 108.73, 143.79; IR (neat) (cm^{-1}) 3060, 1080, 990, 830.

F. Allylsilane Reactions from Preformed Mixed Acetals. Trimethylsilyl triflate (44 μL, 0.23 mmol) was added dropwise to a solution of silane **A** (0.2 mmol) in 5 mL of CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 2 h at −78 °C and then quenched by the addition of 2 mL of water. The crude reaction mixture was washed with water (2 × 10 mL), and the combined aqueous layers were extracted with petroleum ether (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, and the solvents were removed under reduced pressure. The crude siloxane product could be purified by flash chromatography on deactivated silica gel (2% triethylamine/hexane) using petroleum ether as eluent. Alternatively, the crude siloxane was directly hydrolyzed to the silanol by dissolving the siloxane in a mixture of 2 mL of 10% methanolic KOH, 2 mL of H_2O, and 5 mL of THF and stirring overnight at room temperature. The mixture was diluted with water (10 mL) and extracted with ether (3 × 20 mL). The combined ether phases were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by silica gel flash chromatography using 5% ether/petroleum ether as eluent.

4-[[[1-[(Dimethyltrimethylsilyl)oxy]silyl]hexyl]oxy]-1-pentene, 16: GC t_R 17.80 and 17.97 min (1:34); ^{1}H NMR ($CDCl_3$) δ 0.07−0.11 (m, 15 H), 0.89 (t, 3 H, J = 6 Hz), 1.10 (d, 3 H, J = 6 Hz), 1.20−1.60 (m, 8 H), 2.11 (m, 1 H), 2.29 (m, 1 H), 2.97 (t, 1 H, J = 7 Hz), 3.43 (q, 1 H, J = 6 Hz), 5.01 (m, 2 H), 5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −1.42, −0.61, 1.94, 14.09, 20.00, 22.65, 26.69, 31.47, 32.25, 41.55, 71.60, 75.03, 116.36, 135.68; IR (neat) (cm^{-1}) 3080, 1640, 1250, 1060, 840.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-1-pentene, 26 (85%): ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.86 (t, 3 H, J = 7 Hz), 1.11 (d, 3 H, J = 7 Hz), 1.20−1.55 (m, 8 H), 2.12 (m, 1 H), 2.26 (m, 2 H), 3.02 (t, 1 H, J = 7 Hz), 3.45 (m, 1 H), 5.05 (m, 2 H), 5.81 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −1.91, −1.33, 14.06, 20.49, 22.55, 26.53, 31.47, 32.22, 41.33, 71.90, 75.68, 117.00, 135.74; IR (neat) (cm^{-1}) 3384, 3078, 1250, 862. Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55. Found: C, 63.90; H, 11.49.

4-[[1-[[(Dimethyltrimethylsilyl)oxy]silyl]-2-methylpropyl]oxy]-1-pentene, 21: GC t_R 14.35 and 14.78 min (1:38). ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 0.10 (s, 6 H), 0.92 (d, 3 H, J = 7 Hz), 0.95 (d, 3 H, J = 7 Hz), 1.07 (d, 3 H, J = 6 Hz), 1.92 (m, 1 H), 2.05 (m, 1 H), 2.30 (m, 1 H), 2.81 (d, 1 H, J = 5 Hz), 3.40 (m, 1 H), 5.00 (m, 2 H), 5.77 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm 0.19, 0.87, 1.97, 19.74, 19.90, 20.49, 30.79, 41.49, 75.48, 77.29, 116.42, 135.68; IR (neat) (cm^{-1}) 3070, 1250, 1040, 830, 740.

4-[[1-(Hydroxydimethylsilyl)-2-methylpropyl]oxy]-1-pentene, 27 (69%): ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 3 H), 0.17 (s, 3 H), 0.94 (t, 6 H, J = 7 Hz), 1.12 (d, 3 H, J = 7 Hz), 1.97 (m, 1 H), 2.05 (s, 1 H), 2.10 (m, 1 H), 2.27 (m, 1 H), 2.88 (d, 1 H, J = 6 Hz), 3.46 (m, 1 H), 5.08 (m, 2 H), 5.80 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −0.26, 0.36, 19.78, 20.13, 20.42, 30.50, 41.30, 75.97, 76.55, 117.13, 135.68; IR (neat) (cm^{-1}) 3420, 3075, 1646, 861, 735. Anal. Calcd for $C_{11}H_{24}O_2Si$: C, 61.06; H, 11.18. Found: C, 61.17; H, 11.15.

4-[[1-[[(Dimethyltrimethylsilyl)oxy]silyl]hexyl]oxy]-2-methyl-1-pentene, 22: GC t_R 18.81 and 18.93 min (1:25); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 0.054 (s, 3 H), 0.08 (s, 3 H), 0.87 (t, 3 H, J = 7 Hz), 1.06 (d, 3 H, J = 6 Hz), 1.20−1.65 (m, 8 H), 1.69 (s, 3 H), 1.95 (m, 1 H), 2.33 (dd, 1 H, J = 4 Hz, J' = 13 Hz), 2.96 (t, 1 H, J = 6 Hz), 3.50 (m, 1 H), 4.67 (s, 1 H), 4.72 (s, 1 H); ^{13}C NMR ($CDCl_3$) ppm −1.52, −0.61, 1.94, 14.09, 19.84, 22.62, 22.91, 26.69, 31.57, 32.25, 45.66, 71.54, 74.06, 112.38, 143.14; IR (neat) (cm^{-1}) 3080, 1250, 1050, 830.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-2-methyl-1-pentene, 28 (70%): ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.87 (t, 3 H, J = 7 Hz), 1.11 (d, 3 H, J = 6 Hz), 1.20−1.60 (m, 8 H), 1.73 (s, 3 H), 1.97 (dd, 1 H, J = 7 Hz, J' = 13 Hz), 2.17 (s, 1 H), 2.29 (dd, 1 H, J = 7 Hz, J' = 13 Hz), 3.00 (t, 1 H, J = 7 Hz), 3.53 (m, 1 H), 4.74 (s, 1 H), 4.79 (s, 1 H); ^{13}C NMR ($CDCl_3$) ppm −2.07, −1.29, 14.06, 20.74, 22.55, 23.01, 26.50, 31.76, 32.18, 45.79, 72.19, 75.00, 112.71, 143.95; IR (neat) (cm^{-1}) 3423, 3053, 1265, 741. Anal. Calcd for $C_{14}H_{30}O_2Si$: C, 65.06; H, 11.70. Found: C, 64.87; H, 11.63.

4-[[1-[[(Dimethyltrimethylsilyl)oxy]silyl]hexyl]oxy]-3-methyl-1-pentene, 23: GC t_R 18.89 and 18.98 min (1.6:1); ^{1}H NMR ($CDCl_3$) δ (mixture of diastereomers) 0.05 (s, 9 H), 0.06 (s, 3 H), 0.08 (s, 3 H). 0.87 (t, 3 H, J = 7 Hz), 0.97 (m, 6 H), 1.20−1.55 (m, 8 H), 2.29 (m, 1 H), 2.97 (m, 1 H), 3.32 (m, 1 H), 4.96 (m, 2 H), 5.77 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm (major diastereomer) −1.26, −0.42, 1.94, 13.80, 14.09, 16.29, 22.65, 26.53, 31.38, 32.31, 42.23, 71.70, 78.29, 113.77, 141.79; IR (neat) (cm^{-1}) 3089, 1253, 1059, 842.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-3-methyl-1-pentene, 29 (78%): ^{1}H NMR ($CDCl_3$) δ (mixture of diastereomers) 0.14 (s, 6 H), 0.87 (t, 3 H, J = 7 Hz), 0.97 (t, 3 H, J = 7 Hz), 1.04 (d, 3 H, J = 6 Hz), 1.20−1.60 (m, 8 H), 2.05 (s, 1 H), 2.13 (m, 1 H), 3.04 (q, 1 H, J = 7 Hz), 3.33 (m, 1 H), 5.01 (d, 2 H, J = 15 Hz), 5.83 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm (major diastereomer) −1.81, −1.10, 14.02, 15.35, 17.35, 22.55, 26.37, 31.38, 32.25, 42.43, 71.90, 79.10, 114.42, 141.24; IR (neat) (cm^{-1}) 3406, 3079, 1251, 1092, 837. Anal. Calcd for $C_{14}H_{30}O_2Si$: C, 65.06; H, 11.70. Found: C, 65.00; H, 11.79.

4-[[1-[[(Dimethyltrimethylsilyl)oxy]silyl]hexyl]oxy]-3-phenyl-1-pentene, 24: GC t_R 24.47 and 24.76 min (6.4:1); ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 3 H), 0.03 (s, 3 H), 0.05 (s, 9 H), 0.86 (t, 3 H, J = 7 Hz), 0.96 (d, 3 H, J = 7 Hz), 1.20−1.55 (m, 8 H), 2.96 (t, 1 H, J = 6 Hz), 3.24 (t, 1 H, J = 7 Hz), 3.66 (m, 1 H), 4.93, (d, 1 H, J = 18 Hz), 5.06 (d, 1 H, J = 10 Hz), 5.26 (m, 1 H), 7.14−7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm −1.26, −0.26, 1.97, 14.09, 18.71, 22.62, 26.59, 31.67, 32.25, 57.03, 71.86, 78.39, 115.97, 126.15, 128.15, 128.64, 139.52, 142.56; IR (neat) (cm^{-1}) 3054, 3018, 1452, 1249, 843, 694.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-3-phenyl-1-pentene, 30 (78%): ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 6 H), 0.87 (t, 3 H, J = 7 Hz), 1.05 (d, 3 H, J = 6 Hz), 1.20−1.55 (m, 8 H), 1.58 (s, 1 H), 2.97 (t, 1 H, J = 7 Hz), 3.26 (dd, 1 H, J = 7 Hz, J' = 9 Hz), 3.67 (m, 1 H), 5.07 (d, 1 H, J = 18 Hz), 5.16 (dd, 1 H, J = 1.5 Hz, J' = 10 Hz), 6.28 (m, 1 H), 7.18−7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm −2.26, −1.26, 14.02, 19.10, 22.52, 26.43, 31.89, 32.15, 57.26, 72.67, 79.59, 116.94, 126.47, 128.31, 128.44, 138.78, 142.82; IR (neat) (cm^{-1}) 3427, 3068, 3027, 1250, 836, 700. Anal. Calcd for $C_{19}H_{32}O_2Si$: C, 71.19; H, 10.06. Found: C, 71.47; H, 10.07.

4-[[1-[[(Dimethyltrimethylsilyl)oxy]silyl]-2-methylpropyl]oxy]-2-methyl-1-pentene, 25: GC t_R 16.27 and 16.40 min (1:37); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 0.10 (s, 6 H), 0.93 (d, 3 H, J = 7 Hz), 0.96 (d, 3 H, J = 7 Hz), 1.05 (d, 3 H, J = 7 Hz), 1.69 (s, 3 H), 1.93 (m, 2 H), 2.35 (m, 1 H), 2.80 (d, 1 H, J = 5

Hz), 3.49 (m, 1 H), 4.66 (s, 1 H), 4.72 (s, 1 H); ^{13}C NMR ($CDCl_3$) ppm 0.03, 0.87, 1.94, 19.74, 20.52, 22.94, 29.70, 30.83, 45.59, 74.48, 77.23, 112.35, 143.24; IR (neat) (cm^{-1}) 3060, 1240, 1050, 830.

4-[[1-(HydroxyDimethylsilyl)-2-methylpropyl]oxy]-2-methyl-1-pentene, 31 (71%): ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 3 H), 0.17 (s, 3 H), 0.93 (d, 3 H, J = 6 Hz), 0.95 (d, 3 H, J = 5 Hz), 1.11 (d, 3 H, J = 7 Hz), 1.73 (s, 3 H), 1.96 (m, 2 H), 2.20 (s, 1 H), 2.30 (m, 1 H), 2.86 (d, 1 H, J = 6 Hz), 3.55 (m, 1 H), 4.73 (s, 1 H), 4.79 (s, 1 H); ^{13}C NMR ($CDCl_3$) ppm −0.32, 0.42, 19.81, 20.13, 20.62, 23.01, 30.66, 45.82, 75.16, 77.91, 112.77, 143.95; IR (neat) (cm^{-1}) 3420, 3075, 1075, 862, 780.

G. Anomalous Reaction Product From Silane 13. 3-(Dimethylsilyl)-2-hexyl-6-methyl-5-(2-methyl-2-ethen-1-yl)-1-oxacyclohexane, 33 (76%): ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 3 H), 0.07 (s, 3 H), 0.65−0.85 (m, 2 H). 0.86 (t, 3 H, J = 7 Hz), 1.05 (d, 3 H, J = 7 Hz), 1.20−1.60 (m, 8 H), 1.61, (s, 3 H), 2.12 (m, 1 H), 3.07 (m, 1 H), 3.17 (m, 1 H), 4.59 (s, 1 H), 4.67 (s, 1 H); ^{13}C NMR ($CDCl_3$) ppm −7.37, −3.75, 14.06, 18.29, 18.52, 20.65, 22.62, 26.46, 31.76, 31.83, 51.15, 74.96, 78.81, 110.38, 149.70; IR (neat) (cm^{-1}) 3072, 1248, 1094, 838, 781. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.79; H, 11.88. Found: C, 70.87; H, 11.77.

H. Verification of the Relative Stereochemistry. (a) Synthesis of 17 from 16. MeLi (1.4 M in ether, 4.2 mL, 10 equiv) was added dropwise to a solution of **16** (130 mg, 0.41 mmol) in 5 mL of dry THF at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. Water (6 mL) was then added and the mixture stirred for an additional 20 min. The layers were separated, and the aqueous layer was extracted with petroleum ether (3 × 10 mL). The combined organic phases were dried over anhydrous magnesium sulfate, and the solvent was then removed under reduced pressure. The crude product was purified by column chromatography.

4-[[1-(Trimethylsilyl)hexyl]oxy]-1-pentene, 17 (91%): ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.88 (t, 3 H, J = 7 Hz), 1.08 (d, 3 H, J = 6 Hz), 1.23−1.59 (m, 8 H), 2.08 (m, 1 H), 2.27 (m, 1 H), 3.00 (t, 1 H, J = 6 Hz), 3.36 (m, 1 H), 5.00 (m, 2 H), 5.77 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −2.78, 14.09, 20.07, 22.62, 26.92, 32.09, 32.25, 41.55, 71.60, 75.19, 116.42, 135.65; IR (neat) (cm^{-1}): 3080, 1640, 1240, 830. Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.34; H, 12.47. Found: C, 69.25; H, 12.41.

(b) Conversion of 17 to the Aldol Product 20. Synthesis of 19. Ozone was passed through a solution of *syn*-**17** (163.5 mg, 0.67 mmol) in 10 mL of MeOH at −78 °C until a blue color persisted. Excess ozone was then purged from the reaction with argon. Dimethyl sulfide (2 mL) was then added and the mixture allowed to warm to room temperature. The reaction mixture was concentrated under reduced pressure, and the residue was taken up in ether (50 mL). The ether layer was washed with water (2 × 5 mL) and dried over anhydrous magnesium sulfate. The solvent was then removed under reduced pressure. PhMgCl (2 M in THF, 1.7 mL, 3.4 mmol) was added dropwise to a solution of the crude aldehyde in dry THF (10 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature, stirred for 2 h, and then quenched by the addition of 5 mL water. The layers were separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic phases were washed sequentially with 0.1N HCl (5 mL), water (10 mL), and saturated aqueous sodium chloride solution (10 mL) and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to provide crude alcohol which was purified by silica gel column chromatography. The overall yield for two steps was 56%.

1-Phenyl-3-[[1-(trimethylsilyl)hexyl]oxy]butan-2-ol, 19: ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9 H), 0.90 (t, 3 H, J = 6 Hz), 1.18 (d, 3 H, J = 6 Hz), 1.91−1.21 (m, 10 H), 3.20 (t, 1 H, J = 6 Hz), 3.89 (m, 1 H), 4.60 (s, 1 H), 4.93 (d, 1 H, J = 9 Hz), 7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm −2.62, 14.09, 20.16, 22.59, 26.88, 32.09, 32.60, 47.24, 71.38, 74.25, 125.63, 125.99, 127.08, 128.22, 144.73; IR (neat) (cm^{-1}) 3450, 3040, 1250, 1120, 840, 730.

Synthesis of 20.[4a] Oxalyl chloride (0.014 mL, 0.162 mmol) was dissolved in 1 mL of CH_2Cl_2 and cooled to −60 °C. A solution of dimethyl sulfoxide (0.023 mL, 0.323 mmol dissolved in 0.5 mL CH_2Cl_2) was added dropwise over a period of 2 min. The reaction mixture was stirred at −60 °C for 10 min followed by addition of **6** (15.8 mg, 0.049 mmol in 0.5 mL CH_2Cl_2) over a period of 2 min. The reaction mixture was then stirred for 15 min at −60 °C. Triethylamine (0.068 mL, 0.49 mmol) was then added dropwise over a period of 2 min, and the reaction mixture was stirred at −60 °C for 30 min. The reaction mixture was allowed to warm to room temperature, and water (5 mL) was then added. Stirring was continued for 10 min, and the layers were then separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic phases were washed sequentially with 0.5 N HCl (5 mL), water (10 mL), saturated aqueous sodium bicarbonate (5 mL), and water (10 mL). The organic phase was dried over anhydrous magnesium sulfate, and the solvents were then removed under reduced pressure. The crude product was purified by silica gel chromatography using 2% ether/petroleum ether as eluent (89%).

1-Phenyl-3-[[1-(trimethylsilyl)hexyl]oxy]butan-1-one, 20: GC t_R 24.39 and 24.64 min (1:30); ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9 H), 0.88 (t, 3 H, J = 6 Hz), 1.18−1.64 (m, 11 H), 2.94 (dd, 1 H, J = 7.5 Hz, J' = 15 Hz), 3.09 (t, 1 H, J = 6 Hz), 4.25 (dd, 1 H, J = 5 Hz, J' = 16 Hz), 4.04 (m, 1 H), 7.45 (m, 2 H), 7.56 (m, 1 H), 7.95 (d, 2 H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) ppm −2.88, 14.06, 21.16, 22.59, 26.79, 32.15, 32.25, 46.24, 72.19, 72.61, 128.25, 128.51, 132.97, 137.46, 199.14; IR (neat) (cm^{-1}) 3070, 1740, 1680, 1250, 855, 730. The GC t_R for the minor isomer matches that for *syn*-**20**.[4a]

I. General Procedure for Intramolecular Allylation Using 1a. (a) Aliphatic and Aryl Aldehydes. The aldehyde (0.1 mmol) and **1a** (281 mg, 0.14 mmol) were dissolved in 2 mL of CH_2Cl_2. A neat sample of $BF_3{\cdot}OEt_2$ (6.2 μL, 0.5 mmol) was then added dropwise via syringe at room temperature. The reaction mixture was stirred for 10 min at room temperature and then quenched by the addition of 5 mL of water. The reaction mixture was extracted with diethyl ether (3 × 10 mL). The combined ether phases were washed with water (10 mL) and dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The crude Si−F compound was dissolved in a mixture of 2 mL of 10% methanolic KOH, 2 mL of H_2O, and 5 mL of THF and stirred overnight at room temperature. The reaction mixture was diluted with water (10 mL) and extracted with ether (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The crude Si−OH compound was purified by flash chromatography on silica gel using 5% ether/petroleum ether as eluent.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-1-pentene, 35a (26) (49%): GC t_R 13.36 and 13.69 min (1:73); ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.87 (t, 3 H, J = 6 Hz), 1.24 (d, 3 H, J = 6 Hz), 1.23−1.60 (m, 8 H), 2.13 (m, 1 H), 2.25 (m, 1 H), 3.02 (t, 1 H, J = 7 Hz), 3.47 (m, 1 H), 5.06 (m, 2 H), 5.81 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −1.94, −1.29, 14.06, 20.52, 22.55, 26.53, 31.50, 32.22, 41.33, 71.83, 75.68, 117.00, 135.81; IR (neat) (cm^{-1}) 3400, 3070, 1660, 1250, 1080, 850. Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55. Found: C, 63.95; H, 11.47.

4-[1-(Dimethylfluorosilyl)hexyl]oxy]-5-methyl-1-hexene, 34a: GC t_R 16.73 and 16.79 min. (118:1); ^{1}H NMR ($CDCl_3$) δ 0.22 (m, 6 H), 0.86 (m, 9 H), 1.23−1.61 (m, 8 H), 1.77 (m, 1 H), 2.18 (m, 2 H), 3.17 (m, 2 H), 5.01 (m, 2 H), 5.79 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −3.17 (−3.33), −2.29 (−2.49), 14.02, 17.48, 18.64, 22.52, 26.01, 30.28, 32.28, 34.87, 68.89 (68.66), 82.24, 116.32, 135.68; ^{19}F NMR ($CFCl_3$) −163.44; IR (neat) (cm^{-1}) 3080, 1640, 1250, 1040, 870.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-5-methyl-1-hexene, 35b (81%): ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.87 (m, 9 H), 1.23−1.57 (m, 8 H), 1.80 (m, 1 H), 2.02 (s, 1 H), 2.19 (t, 2 H, J = 6 Hz), 3.05 (t, 1 H, J = 6 Hz), 3.15 (q, 1 H, J = 5 Hz), 5.06 (m, 2 H), 5.82 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −1.94, −1.16, 14.02, 18.00, 18.29, 22.52, 26.33, 30.31, 30.73, 32.34, 34.64, 70.47, 82.40, 116.81, 136.26; IR (neat) (cm^{-1}) 3400, 3080, 1640, 1250, 1040, 860. Anal. Calcd for $C_{15}H_{32}O_2Si$: C, 66.11; H, 11.84. Found: C, 66.38; H, 11.77.

4-[[1-(Dimethylfluorosilyl)hexyl]oxy]-1-nonene, 34c: GC t_R 19.72 and 19.80 min (113:1); ^{1}H NMR ($CDCl_3$) δ 0.23 (t, 6 H, J = 8 Hz), 0.87 (m, 6 H), 1.20−1.60 (m, 16 H), 2.18 (m, 2 H), 3.16 (t, 1 H, J = 6.6 Hz), 3.31 (m, 1 H), 5.05 (m, 2 H), 5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −3.07 (−3.26), −2.36 (−2.55), 14.06, 22.55, 22.65, 25.04, 26.11, 30.70, 32.02, 32.28, 33.93, 38.39, 69.37 (69.60), 78.49, 116.62, 135.32; ^{19}F NMR ($CFCl_3$) −163.8; IR (neat) (cm^{-1}): 3080, 1640, 1250, 1040, 870.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-1-nonene, 35c (82%): ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 6 H), 0.89 (t, 6 H, J = 6 Hz), 1.20−1.60 (m, 16 H), 2.22 (m, 2 H), 3.07 (t, 1 H, J = 6 Hz), 3.36 (m, 1 H), 5.08 (m, 2 H), 5.83 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −1.91, −1.20, 14.02, 22.55, 22.62, 25.14, 26.37, 30.99, 31.99, 32.31, 34.22, 38.36, 70.93, 78.36, 116.94, 135.74; IR (neat) (cm^{-1}) 3400, 3080, 1640, 1250, 1035, 860. Anal. Calcd for $C_{17}H_{36}O_2Si$: C, 67.94; H, 12.07. Found: C, 68.03; H, 12.04.

4-Cyclohexyl-4-[[1-(hydroxydimethylsilyl)hexyl]oxy]-1-butene, 35d (85%): ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.87 (t, 3 H, J = 7 Hz), 1.00−1.72 (m, 19 H), 2.05 (s, 1 H), 2.20 (m, 2 H), 3.04 (t, 1 H, J = 6 Hz), 3.14 (q, 1 H, J = 5 Hz), 5.06 (m, 2 H), 5.82 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −1.91, −1.16, 14.02, 22.52, 26.30, 26.40, 26.66, 28.60, 28.89, 30.66, 32.31, 34.67, 40.46, 70.38, 81.85, 116.78, 136.20; IR (neat) (cm^{-1}) 3350, 3070, 1240, 1030, 860. Anal. Calcd for $C_{18}H_{36}O_2Si$: C, 69.17; H, 11.61. Found: C, 69.01; H, 11.53.

4-Phenyl-4-[[1-(hydroxydimethylsilyl)hexyl]oxy]-1-butene, 35e (93%): ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 3 H), 0.22 (s, 3 H), 0.78 (t, 3 H, J = 6 Hz), 0.87−1.50 (m, 8 H), 2.02 (s, 1 H), 2.42 (m, 1 H), 2.58 (m, 1 H), 3.08 (t, 1 H, J = 6 Hz), 4.32 (t, 1 H, J = 6 Hz), 5.07 (m, 2 H), 5.81 (m, 1 H), 7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm −0.93, −0.28, 14.65, 23.11, 26.89, 32.06, 32.48, 43.18, 73.10, 83.56, 117.91, 127.83, 128.18, 128.76, 136.32, 143.63; IR (neat) (cm^{-1}) 3450, 3070, 3030, 1250, 1060, 830, 700. Anal. Calcd for $C_{18}H_{30}O_2Si$: C, 70.53; H, 9.87. Found: C, 70.60; H, 9.89.

4-(4′-Biphenylyl)-4-[[1-(hydroxydimethylsilyl)hexyl]-oxy]-1-butene, 35f (77%): ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.21 (s, 3 H), 0.74 (t, 3 H, J = 7 Hz), 0.80−1.50 (m, 8 H), 2.12 (s, 1 H), 2.43 (m, 1 H), 2.60 (m, 1 H), 3.10 (t, 1 H, J = 6 Hz), 4.35 (dd, 1 H, J = 5 Hz, J' = 8 Hz), 5.07 (m, 2 H), 5.86 (m, 1 H), 7.32−7.60 (m, 9 H); ^{13}C NMR ($CDCl_3$) ppm −1.68, −1.00, 13.96, 22.39, 26.17, 31.34, 31.76, 42.43, 72.41, 82.56, 117.33, 126.79, 127.02, 127.15, 127.54, 128.70, 135.58, 140.36, 140.91, 141.98; IR (neat) (cm^{-1}) 3503, 3065, 3029, 1787, 1696, 734. Anal. Calcd for $C_{24}H_{34}O_2Si$: C, 75.34; H, 8.96. Found: C, 75.12; H, 8.93.

4-(2′-Naphthyl)-4-[[1-(hydroxydimethylsilyl)hexyl]oxy]-1-butene, 35g (75%): ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 3 H), 0.22 (s, 3 H), 0.64 (t, 3 H, J = 7 Hz), 0.80−1.45 (m 8 H), 2.05 (s, 1 H), 2.48 (m, 1 H), 2.65 (m, 1 H), 3.11 (dd, 1 H, J = 6 Hz, J' = 7 Hz), 4.47 (dd, 1 H, J = 5 Hz, J' = 8 Hz), 5.06 (m, 2 H), 5.83 (m, 1 H), 7.47 (m, 3 H), 7.71 (s, 1 H), 7.81 (m, 3 H); ^{13}C NMR ($CDCl_3$) ppm −1.68, −0.97, 13.80, 22.36, 26.21, 31.38, 31.70, 42.39, 72.14, 83.01, 117.33, 124.95, 125.66, 125.95, 126.18, 127.63, 127.80, 127.92, 133.00, 133.06, 135.55, 140.27; IR (neat) (cm^{-1}) 3406, 3058, 1250, 1069, 858, 778, 746. Anal. Calcd for $C_{22}H_{32}O_2Si$: C, 74.10; H, 9.05. Found: C, 74.38; H, 9.28.

4-(2′-Bromophenyl)-4-[[1-(hydroxydimethylsilyl)hexyl]-oxy]-1-butene, 35h (72%): ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.20 (s, 3 H), 0.76 (t, 3 H, J = 8 Hz), 0.80−1.55 (m, 8 H), 2.15 (s, 1 H), 2.41 (t, 2 H, J = 8 Hz), 3.09 (t, 1 H, J = 7 Hz), 4.83 (m, 1 H), 5.07 (m, 2 H), 5.87 (m, 1 H), 7.11 (m, 1 H), 7.28 (m, 1 H), 7.49 (m, 2 H); ^{13}C NMR ($CDCl_3$) ppm −1.65, −1.03, 13.89, 22.33, 26.27, 31.31, 31.80, 41.72, 73.87, 80.88, 117.49, 122.50, 127.28, 128.64, 132.16, 135.19, 142.56; IR (neat) (cm^{-1}) 3412, 3074, 1072, 910, 865, 735. Anal. Calcd for $C_{18}H_{29}BrO_2Si$: C, 56.09; H, 7.58. Found: C, 55.84; H, 7.59.

4-(4′-Nitrophenyl)-4-[[1-(hydroxydimethylsilyl)hexyl]-oxy]-1-butene, 35i (85%): ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 3 H), 0.20 (s, 3 H), 0.75 (t, 3 H, J = 7 Hz), 0.99−1.45 (m, 8 H), 1.92 (s, 1 H), 2.39 (m, 1 H), 2.51 (m, 1 H), 3.06 (t, 1 H, J = 7 Hz), 4.56 (m, 1 H), 5.01 (m, 2 H), 5.73 (m, 1 H), 7.47 (d, 2 H, J = 8 Hz), 8.17 (d, 2 H, J = 9 Hz); ^{13}C NMR ($CDCl_3$) ppm −1.75, −1.31, 13.89, 22.36, 26.27, 31.25, 31.83, 42.30, 73.61, 81.69, 118.17, 123.40, 127.63, 134.23, 147.28, 150.93; IR (neat) (cm^{-1}) 3411, 3074, 1251, 1072, 865, 735. Anal. Calcd for $C_{18}H_{29}NO_4Si$: C, 61.50; H, 8.32. Found: C, 61.26; H, 8.37.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-4-[4′-(α′,α′,α′-trifluoromethyl)phenyl]-1-butene, 35j (80%): ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 3 H), 0.20 (s, 3 H), 0.74 (t, 3 H, J = 7 Hz), 0.90−1.45 (m, 8 H), 2.04 (s, 1 H), 2.38 (m, 1 H), 2.53 (m, 1 H), 3.05 (t, 1 H, J = 7 Hz), 4.37 (dd, 1 H, J = 6 Hz, J = 7 Hz), 5.06 (m, 2 H), 5.74 (m, 1 H), 7.49 (dd, 4 H, J = 9 Hz, J' = 14 Hz); ^{13}C NMR ($CDCl_3$) ppm −1.71, −1.10, 13.83, 22.36, 26.21, 31.25, 31.76, 42.36, 73.09, 82.14, 117.78, 125.05, 127.28, 129.86, 134.81, 147.25; ^{19}F NMR ($CFCl_3$) −62.93; IR (neat) (cm^{-1}) 3375, 1068, 865, 839. Anal. Calcd for $C_{19}H_{29}F_3O_2Si$: C, 60.93; H, 7.80. Found: C, 61.09; H, 7.85.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-4-[3′-(α′,α′,α′-trifluoromethyl)phenyl]-1-butene, 35k (73%): ^{1}H NMR ($CDCl_3$) δ 0.17, (s, 3 H), 0.20 (s, 3 H), 0.74 (t, 3 H, J = 7 Hz), 0.90−1.40 (m, 8 H), 2.05 (s, 1 H), 2.38 (m, 1 H), 2.53 (m, 1 H), 3.03 (t, 1 H, J = 6 Hz,), 4.37 (dd, 1 H, J = 5 Hz, J' = 8 Hz), 5.06 (m, 2 H), 5.77 (m, 1 H), 7.39−7.58 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm −1.75, −1.10, 13.86, 22.33, 26.33, 31.28, 31.80, 42.49, 73.12, 82.27, 117.81, 123.72, 123.79, 124.31, 125.95, 128.51, 130.41, 134.90, 144.77; ^{19}F NMR ($CFCl_3$) −64.07; IR (neat) (cm^{-1}) 3388, 3077, 1253, 1129, 567. Anal. Calcd for $C_{19}H_{29}F_3O_2Si$: C, 60.93; H, 7.80. Found: C, 61.07; H, 7.92.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-4-[2′-(α′,α′,α′-trifluoromethyl)phenyl]-1-butene, 35l (72%): ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 3 H), 0.18 (s, 3 H), 0.72 (t, 3 H, J = 7 Hz), 0.80−1.40 (m, 8 H), 2.03 (s, 1 H), 2.38 (m, 2 H), 3.05 (t, 1 H, J = 7 Hz), 4.75 (m, 1 H), 5.08 (m, 2 H), 5.92 (m, 1 H), 7.33 (t, 1 H, J = 8 Hz), 7.55 (m, 2 H), 7.75 (d, 1 H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) ppm −1.71, −1.04, 13.89, 22.30, 26.11, 31.25, 31.73, 43.59, 74.16, 78.23, 117.58, 124.92, 125.02, 127.18, 128.73, 131.71, 135.68, 143.34; ^{19}F NMR ($CFCl_3$) −59.20; IR (neat) (cm^{-1}) 3417, 3075, 1313, 1123, 834, 769.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-4-(4′-methylphenyl)-1-butene, 35m (78%): ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 3 H), 0.19 (s, 3 H), 0.76 (t, 3 H, J = 8 Hz), 0.90−1.45 (m, 8 H), 2.29 (s, 1 H), 2.33 (s, 3 H), 2.36 (m, 1 H), 2.56 (m, 1 H), 3.04 (t, 1 H, J = 6 Hz), 4.26 (dd, 1 H, J = 6 Hz, J' = 7 Hz), 5.05 (m, 2 H), 5.81 (m, 1 H), 7.15 (dd, 4 H, J = 8 Hz, J' = 24 Hz); ^{13}C NMR ($CDCl_3$) ppm −1.65, −0.97, 13.96, 21.10, 22.46, 26.17, 31.38, 31.76, 42.43, 71.99, 82.59, 117.13, 127.08, 128.76, 135.81, 137.10, 139.82; IR (neat) (cm^{-1}) 3405, 3076, 1251, 1069, 846, 833, 780, 735. Anal. Calcd for $C_{19}H_{32}O_2Si$: C, 71.19; H, 10.06. Found: C, 70.95; H, 9.97.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-4-(2′,4′,6′-trimethylphenyl)-1-butene, 35n (34%): ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 3 H), 0.17 (s, 3 H), 0.73 (t, 3 H, J = 7 Hz), 0.87−1.60 (m, 8 H), 2.04 (s, 1 H), 2.20 (s, 3 H), 2.25−2.50 (m, 7 H), 2.71 (m, 1 H), 3.05 (t, 1 H, J = 6 Hz), 4.68 (dd, 1 H, J = 6 Hz, J' = 8 Hz), 5.07 (m, 2 H), 5.80 (m, 1 H), 6.78 (m, 2 H); ^{13}C NMR ($CDCl_3$) ppm (major diastereomer) −1.65, −1.10, 13.89, 20.71, 20.84, 22.36, 26.04, 31.12, 31.96, 39.94, 75.00, 80.52, 116.91, 128.89, 130.12, 131.22, 135.71, 136.10, 136.16, 136.46; IR (neat) (cm^{-1}) 3405, 3076, 1612, 1250, 1057, 851, 782. Anal. Calcd for $C_{21}H_{36}O_2Si$: C, 72.36; H, 10.41. Found: C, 72.62; H, 10.31.

4-[4-(Methyloxy)phenyl]-1,6-heptadiene, 38 (31%): ^{1}H NMR ($CDCl_3$) δ 2.33 (m, 4 H), 2.65 (m, 1 H), 3.77 (s, 3 H), 4.92 (m, 2 H), 5.63 (m, 1 H), 6.81 (d, 2 H, J = 9 Hz), 7.05 (d, 2 H, J = 9 Hz); ^{13}C NMR ($CDCl_3$) ppm 40.46, 44.69, 55.13, 113.55,113.71, 115.97, 128.54, 136.65, 136.91; IR (neat) (cm^{-1}) 3067, 3032, 1602, 1240, 1030, 821; HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1347.

(b) α,β-Unsaturated Aldehydes. A slightly modified reaction procedure compared to that described above was employed for reactions of **1a** with *trans*-cinnamaldehyde or *trans*-crotonaldehyde. The reaction mixture was stirred at −78 °C for 1 h after the addition of the Lewis acid, gradually warmed to −40 °C, stirred at −40 °C for 1 h, and then warmed to −20 to −10 °C, and stirred for an additional 1.5 h. Reaction progress was monitored by TLC until the starting aldehyde was consumed.

3-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-1-phenyl-1,5-hexadiene, 39 (55%): ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.20 (s, 3 H), 0.79 (t, 3 H, J = 7 Hz), 1.15−1.65 (m, 8 H), 2.04 (s, 1

H), 2.35 (m, 1 H), 2.43 (m, 1 H), 3.14 (dd, 1 H, $J = 6$ Hz, $J' = 8$ Hz), 3.89 (m, 1 H), 5.11 (m, 2 H), 5.89 (m, 1 H), 6.09 (dd, 1 H, $J = 8$ Hz, $J' = 15$ Hz), 6.50 (d, 1 H, $J = 16$ Hz), 7.20−7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm −1.84, −1.26, 13.96, 22.59, 26.56, 31.63, 31.96, 40.58, 71.57, 81.75, 117.36, 126.41, 127.60, 128.54, 131.09, 131.77, 135.26, 136.65; IR (neat) (cm^{-1}) 3407, 3079, 3027, 1641, 1450, 1250, 1058, 858, 748, 692. Anal. Calcd for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.70. Found: C, 72.30; H, 9.72.

4-[[1-(Hydroxydimethylsilyl)hexyl]oxy]-1,5-heptadiene, 40 (50%): GC t_R 16.54 and 16.74 min (22:1); ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 6 H), 0.80−1.60 (m, 11 H), 1.68 (d, 3 H, $J = 7$ Hz), 1.93 (s, 1 H), 2.19 (m, 1 H), 2.82 (m, 1 H), 3.03 (dd, 1 H, $J = 6$ Hz, $J' = 8$ Hz), 3.61 (q, 1 H, $J = 7$ Hz), 5.05 (m, 2 H), 5.31 (m, 1 H), 5.55 (m, 1 H), 5.81 (m, 1 H); ^{13}C NMR ($CDCl_3$) ppm −1.84, −1.26, 14.06, 17.64, 22.59, 26.37, 31.57, 31.92, 40.49, 70.86, 81.75, 116.94, 128.09, 132.71, 135.71; IR (neat) (cm^{-1}) 3419, 3077, 1250, 1058, 863, 782. Anal. Calcd for $C_{15}H_{30}O_2Si$: C, 66.61; H, 11.18. Found: C, 66.72; H, 11.13.

***J*. Intermolecular Allylation Reaction. Synthesis of 36.** Silanol **8** (53 mg, 0.30 mmol), hexanal (30 mg, 0.31 mmol), and allyltrimethylsilane (38 mg, 0.33 mmol) were dissolved in 3 mL of CH_2Cl_2, and the mixture was cooled to −78 °C. Trimethylsilyl triflate (64 μL, 0.33 mmol) was then added, and the reaction mixture was stirred for 30 min. The reaction mixture was then quenched by the addition of 1 mL of water and allowed to warm to room temperature. The mixture was then diluted with ether (25 mL) and washed with water (5 mL). The organic phase was dried over anhydrous magnesium sulfate, and the solvents were removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using hexane as eluent.

4-[[(1-Trimethylsilyl)hexyl]oxy]nonene, 36 (74%): GC t_R 20.36 and 20.45 min (3.4:1); ^{1}H NMR ($CDCl_3$) δ (mixture of diastereomers) 0.02 (s, 9H), 0.85−1.60 (m, 22H), 2.22 (m, 2H), 3.05 (m, 1H), 3.28 (m, 1H), 5.05 (m, 2h), 5.85 (m, 1H); ^{13}C NMR ($CDCl_3$) ppm −2.65, −2.33, 14.06, 22.65, 24.98, 26.72, 26.82, 29.70, 31.50, 31.67, 31.83, 32.09, 32.18, 32.34, 33.77, 33.93, 38.39, 38.58, 70.50, 70.96, 77.65, 78.25, 116.10, 116.29, 135.65, 135.81; IR (neat) (cm^{-1}) 3095, 2925, 1640, 1450, 1250. Anal. Calcd for $C_{18}H_{38}OSi$: C, 72.40; H, 12.83. Found: C, 72.51; H, 12.79.

K. Attempted Intramolecular Allylation Using 1C. The same procedure as described above for the reactions of **1a** was employed. The benzyl ether **41** was obtained after the basic hydrolysis step; however, removal of the solvents and careful column chromatography on deactivated silica gel provided the silyl fluoride **42** in excellent yield and in >90% purity. The main contaminant is the silanol. Resubjection of the silyl fluoride **42** to the basic hydrolysis conditions provided the benzyl ether in nearly quantitative yield.

Benzyl 4-cyclohexylbuten-1-yl ether, 41: ^{1}H NMR ($CDCl_3$) δ 0.90−2.00 (m, 11 H), 2.31 (m, 2 H), 3.18 (m, 1 H), 4.52 (dd, 2 H, $J = 11$ Hz, $J' = 30$ Hz), 5.05 (m, 2 H), 5.86 (m, 1 H), 7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm 26.27, 26.33, 26.59, 28.66, 28.95, 35.25, 41.04, 71.83, 83.27, 116.49, 127.34, 127.73, 128.25, 135.61, 139.04; IR (neat) (cm^{-1}) 3066, 3030, 1097, 1069, 734, 696. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.36; H, 9.95.

4-[[1-[(Dimethylfluorosilyl)phenyl]methyl]oxy]-4-cyclohexyl-1-butene, 42 (93%): GC t_R 22.76 and 22.86 min (>120:1); ^{1}H NMR ($CDCl_3$) δ 0.14 (d, 3 H, $J = 8$ Hz), 0.27 (d, 3 H, $J = 8$ Hz), 0.90−1.90 (m, 10 H), 1.95 (d, 1 H, $J = 11$ Hz), 2.28 (m, 1 H), 2.37 (m, 1 H), 3.16 (q, 1 H, $J = 5$ Hz), 4.41 (s, 1 H), 5.07 (m, 2 H), 5.81 (m, 1 H), 7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$) ppm −3.91 (−4.10), −3.56 (−3.75), 26.30, 26.37, 26.59, 28.44, 29.34, 33.06, 40.58, 72.22 (71.99), 79.94, 116.58, 126.37, 126.86, 128.18, 134.90, 139.46; ^{19}F NMR ($CFCl_3$) −166.66; IR (neat) (cm^{-1}) 3426, 3078, 3024, 1252, 1047, 886, 700.

L. The Crossover Reaction. Trimethylsilyl triflate (60 μL, 0.31 mmol) was added dropwise to a solution of **2b** (37.5 mg, 0.163 mmol) and **11** (41.1 mg, 0.150 mmol) in 3 mL of CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 2 h at −78 °C, and then quenched by the addition of 6 mL of water. The reaction mixture was then allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with petroleum ether (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, and the solvents were removed under reduced pressure. The crude product was then added to a mixture of 2 mL of 10% methanolic KOH, 2 mL of H_2O, and 5 mL of THF and the resulting mixture stirred overnight at room temperature. The crude silanol mixture was then dissolved in 3 mL of CH_2Cl_2, and 10 equiv triethylamine and 5 equiv trimethylsilyl chloride were added at 0 °C. The reaction mixture was allowed to warm to room temperature and the resulting mixture stirred overnight. Water (6 mL) was then added, and the layers were separated. The aqueous layer was extracted with petroleum ether (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the solvents were removed under reduced pressure. GC analysis was performed at this stage to determine the overall composition of the reaction mixture. The crude products were purified by silica gel chromatography as described above. Siloxane **21** was obtained in 79% yield as a 1:38 mixture of diastereomers. Siloxane **22** was obtained in 69% yield as a 1:25 mixture of diastereomers.

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