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Synthesis of Optically Pure Arylsilylcarbinols and Their Use as Chiral Auxiliaries in Oxacarbenium Ion Reactions

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A family of arylsilylcarbinols was synthesized and investigated as chiral auxiliaries for oxacarbenium ion reactions. The optically pure arylsilylcarbinols were prepared using Noyori's transfer hydrogenation catalyst **11**. The transfer hydrogenation shows very good enantioselectivities and turnover efficiency for the aryl silyl ketones and is the method of choice for preparing these optically pure alcohols. The diastereoselective addition of allyltrimethylsilane to an in situ generated oxacarbenium ion was explored using Marko's conditions. The selectivity for a representative aliphatic aldehyde was very good, but the selectivity was significantly reduced with unsaturated and aromatic aldehydes. The range of selectivities with different auxiliaries was narrow, and the most practical auxiliary is the phenylsilylcarbinol **2**.

Introduction

Oxacarbenium ions are intermediates in a variety of useful synthetic transformations including Johnson's polyene cyclizations,[1] Prins cyclizations,[2] and many nucleophilic addition reactions that form new carbon−carbon bonds.[3] Oxacarbenium ions are very reactive intermediates that are generated with the aid of Lewis acids but are not covalently bound to the Lewis acid. Thus, the very desirable strategy of controlling enantiofacial addition to an aldehyde with a chiral, catalytic Lewis acid is not generally feasible with an oxacarbenium ion intermediate. An alternative strategy for introducing enantiofacial addition to oxacarbenium ions uses chiral auxiliaries, and this approach has been developed by a number of research groups. Several alkylarylcarbinols have been used as auxiliaries with some success.[4] Tietze has developed the very selective norpseudoephedrine auxiliary,[5] and Johnson's group and others have used chiral cyclic acetals as oxacarbenium ion precursors.[6] Although a number of these methods have led to good diastereoselectivity with the addition of carbon nucleophiles, most of them suffer from harsh or multistep deprotection conditions. We set out to develop a practical and general chiral auxiliary for oxacarbenium ion reactions. An ideal chiral auxiliary would fulfill several requirements: both enantiomers would be readily accessible, it would be easily incorporated into oxacarbenium ion intermediates, and it would promote the addition of various nucleophiles to one diastereotopic face of the oxacarbenium ion. Additionally, the auxiliary should be easily removed from the ether products to afford alcohols of high enantiopurity. Our initial strategy used the α-(trimethylsilyl)benzyl alcohol (**1**) auxiliary, which was inspired by Linderman's work.[7] In this paper, we present a systematic investigation of the synthesis of other optically pure arylsilylcarbinols and their use as oxacarbenium ion auxiliaries.

Mixed acetals prepared from racemic **1** were shown by Linderman to react with enol ethers in the presence of Lewis acids to produce Mukaiyama aldol-type adducts

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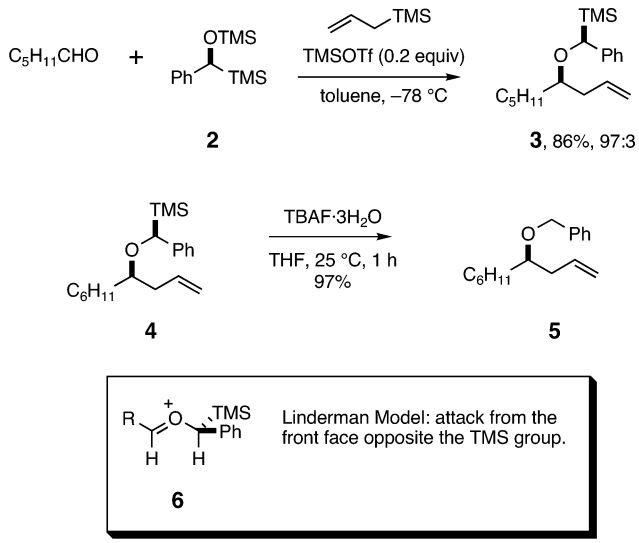
SCHEME 1. Use of 2 as an Oxacarbenium Ion Chiral Auxiliary



with good diastereoselectivities.[7a] We have developed this alcohol as a chiral auxiliary for oxacarbenium ion reactions.[8] This α-silyl alcohol appeared to have a number of very desirable properties as a potential chiral auxiliary. An efficient enantioselective synthesis of this auxiliary was developed based on Noyori's enantioselective reduction[9] that made both enantiomers readily available. The auxiliary led to high diastereoselectivity in allylsilane additions to aliphatic aldehydes under Marko's conditions,[4c] Scheme 1. Thus, the reaction of hexanal with the TMS ether of **1** gave adduct **3** in good yield and with 97:3 diastereoselectivity. The diastereoselectivity with aromatic or α,β-unsaturated aldehydes was lower, however. The scope of auxiliary-modified oxacarbenium ions was expanded by our recent synthesis of α-acetoxy ethers derived from **1** and their diastereoselective reactions with a variety of carbon nucleophiles.[10] Deprotection of the auxiliary could be carried out in one pot by Na/NH_3 reduction.[8] A more powerful transformation was the conversion of the auxiliary product **4** to a simple benzyl-protected product **5** in excellent yield on treatment with TBAF.[8] The direct introduction of a protected alcohol, rather than the free alcohol, often has strategic advantages in a total synthesis.[11] Alcohol **1** is an interesting and potentially useful auxiliary for oxacarbenium ion intermediates, and we are continuing to explore its chemistry. The success of this strategy led us to explore other arylsilylcarbinols as auxiliaries, and the results of these studies are described below.

In exploring the potential of other arylsilylcarbinols as auxiliaries, we considered the synthetic accessibility of the optically pure alcohols and their diastereoselectivities in oxacarbenium ion additions. There are a number of possible routes to the synthesis of these alcohols, but we focused on the preparation and enantioselective reduction of acylsilanes. Acylsilanes can be prepared by many different routes; we selected Brook's route based on its generality and the wide availability of starting materials.[12] The enantioselective reduction of acylsilanes has been accomplished by *B*-chlorodiisopinocamphenylborane (DIPCl) reduction,[13] Baker's yeast reduction,[14] and CBS reduction.[15] In the preparation of auxiliary **2**, we had found that Noyori's ruthenium-catalyzed transfer hydrogenation[9] was both highly enantioselective and very practical. It gave better enantioselectivity than either DIPCl or CBS reductions in this case. We chose to explore this transfer hydrogenation with all of the acylsilane substrates because of its superior practicality compared with the other methods considered. This systematic study of acylsilane reduction extends the scope of Noyori's transfer hydrogenation method.

The diastereoselectivity of the new chiral oxacarbenium ion auxiliaries was investigated using the addition of allyltrimethylsilane to aldehydes under Marko's in situ conditions[4c] (e.g., Scheme 1). Three classes of aldehydes were selected for evaluation: aliphatic, aromatic, and α,β-unsaturated. Auxiliary **2** showed good selectivity with aliphatic aldehydes (ca. 32:1) and moderate selectivity with aromatic aldehydes (10:1) and α,β-unsaturated aldehydes (6:1). There was clearly room for improvements in the diastereoselectivity with the new auxiliaries.

Results and Discussion

Acylsilane Synthesis and Reduction. The preparations of acylsilanes are outlined in Scheme 2. Our route was based on Brook's synthesis of aryl silyl ketones.[12] The benzyl chloride or bromide was converted into the corresponding Grignard reagent and silylated with the appropriate chlorotrialkylsilane. Free-radical bromination with NBS produced the dibromide **9** in good yields.[16] Silver-assisted hydrolysis of the dibromide generated the acylsilane **10**.[16] The route worked well for each of the six acylsilanes prepared, and the overall yields ranged from 33% to 77%. Experimental details and characterization of **10a**−**10f** are presented with the Supporting Information. Although the route may not be the most economical for a particular acylsilane, it was an effective and expedient method to prepare the range of acylsilanes required for our studies.

The enantioselective reductions of acylsilanes **10a**−**10f** are shown in Table 1. The previously reported reduction

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(16) The experimental details and characterization of new compounds are included in the Supporting Information.

SCHEME 2. Preparation of the Acylsilanes 10a−10f

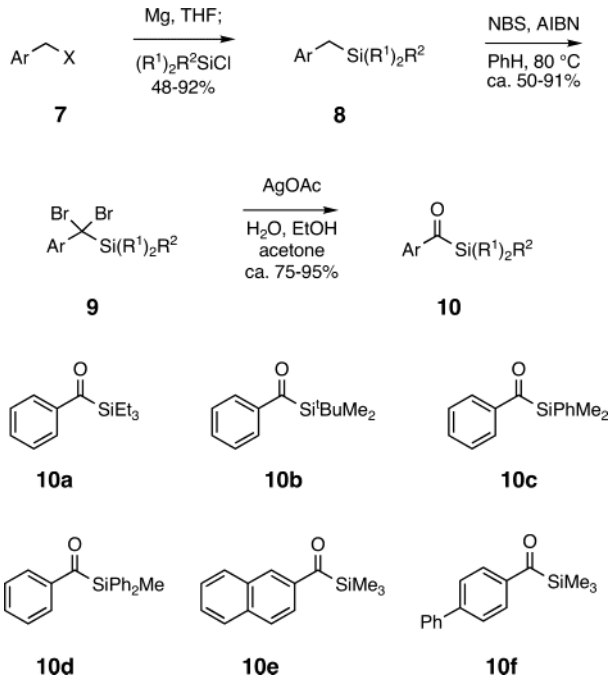
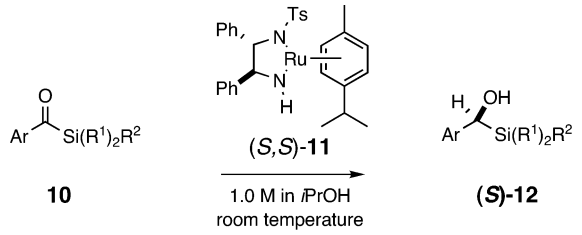


TABLE 1. Enantioselective Reduction of the Acylsilanes Using Noyori's Catalyst

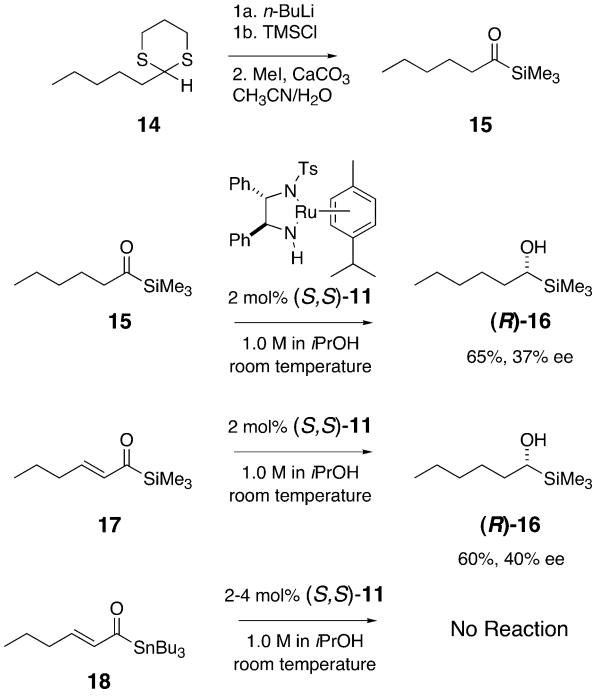


entry	substrate	mol % (*S*,*S*)-**11**	time (h)	ee (%)[a]	yield (%)
1	**13**	0.5	3.4	98	91
2	**10a**	3	6	91	95
3	**10b**	2	10	82	57
4	**10c**	0.5	4	92	93
5[b]	**10c**	2	12	95	92
6	**10d**	2	6	65	87
7	**10e**	1	10	96	98
8	**10f**	0.5	4	96	98
9[c]	**10f**	2	12	98	100

[a] The ee values were determined by HPLC analysis on a Chiracel OD-H column. [b] The reaction was performed at 0 °C. [c] The reaction was performed at 0 °C in an 80:20 mixture of *i*-PrOH and THF.

of benzoyltrimethylsilane (**13**) to **1** is included in entry 1 for comparison.[8] The reactions were very clean. The moderate yields observed in some cases reflect incomplete conversion of the starting materials, which could be recovered. Typical catalyst loadings were 1−3 mol %. In each case, reduction of the acylsilane with the (*S*,*S*)-**11** catalyst led to the predominant enantiomer of the product that was identified as the *S* enantiomer by analogy to **1**.[17] The majority of the substrates generated arylsilylcarbinols with >90% ee. The two exceptions were *tert*-butyldimethylsilane **10b** and the diphenylmethylsilane **10d** that proceeded with 82% ee and 65% ee, respectively. These are the two largest silyl groups investigated, and

SCHEME 3. Synthesis and Enantioselective Reduction of the Aliphatic Acylsilanes



presumably their steric bulk is responsible for the reduced enantioselectivity in the reaction. These two substrates also showed the lowest conversions, suggesting that the steric bulk in the silane inhibited the reduction. The dimethylphenylsilane **10c** was noteworthy because it led to a rapid reduction, entry 4. Reducing the temperature to 0 °C, entry 5, gave almost complete reduction of this substrate in 12 h with 2 mol % catalyst loading and led to a small but preparatively useful increase in enantioselectivity. Similar conditions were applied to acylsilane **10f**, where they also led to a useful increase in enantioselectivity. The reactions were very convenient to run, and analytically pure products were easily isolated from the reaction mixtures by silica gel chromatography. On the basis of these results, we believe that Noyori's transfer hydrogenation is the method of choice for enantioselective reduction of most aromatic acylsilanes.

The enantioselective reduction of aliphatic and α,*β*-unsaturated acylsilanes and acylstannanes was briefly investigated. Scheme 3 presents the synthesis of acylsilane **15** using Corey's procedure.[18] Unsaturated acylsilane **17** was prepared from (*E*)-2-hexen-1-ol by in situ silylation and anti-Brook rearrangement,[19] followed by Narasaka oxidation.[20] Enantioselective reduction of acylsilane **15** using catalyst **11** did not proceed to completion and gave the alcohol **16** in only 37% ee.[21] The enantioselective reduction of the α,*β*-unsaturated acylsilane **17** unexpect-

(17) All of the arylsilylcarbinols **12** and compound **1** showed negative optical rotations, and in each case the major enantiomer eluted first on a Chiracel OD-H column. These physical properties are consistent with the proposal that all of the reduction products share the *S* configuration.

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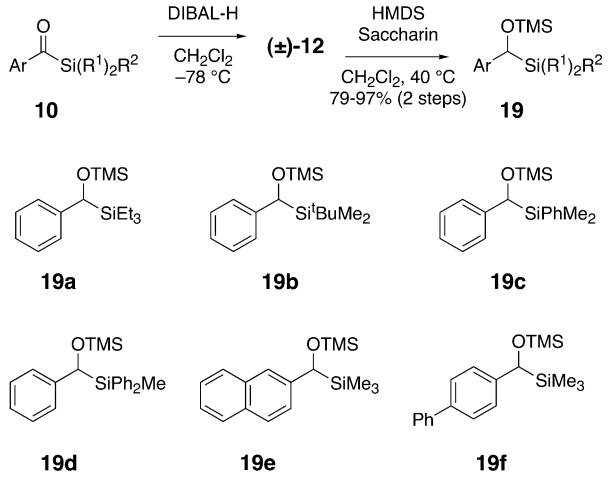
SCHEME 4. Preparation of the Racemic Auxiliaries 19a−19f



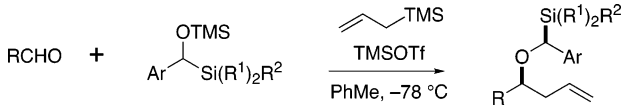
edly gave the same saturated alcohol **16** with essentially identical optical purity. The catalyst **11** with 2-propanol apparently reduces the double bond before reduction of the ketone. The results of these reductions are inferior to all of the aromatic acylsilane examples and suggest that the aryl group is necessary for high selectivity. An enantioselective reduction of acylstannane **18**[22] was attempted but failed. In this case, no reduction was observed. Adding the acylsilane substrate **10f** to a mixture of **18** and catalyst **11** did not lead to reduction of either the acylsilane or the acylstannane, suggesting that the acylstannane deactivates the catalyst. Noyori's transfer hydrogenation of aromatic acylsilanes is a very effective method to prepare optically pure arylsilylcarbinols. The method is not appropriate for aliphatic acylsilanes or for acylstannanes.

Diastereoselectivity of the New Oxacarbenium Ion Auxiliaries. Evaluation of these arylsilylcarbinols as oxacarbenium ion auxiliaries was the next step. For this purpose, we used racemic auxiliaries and analyzed the diastereoselectivity of the reactions by GC or NMR analysis. The racemic auxiliaries **19a−19f** were prepared by DIBALH reduction of the corresponding acylsilane, and the resulting alcohols were protected as TMS ethers, Scheme 4.[16] This route worked well for all of the substrates and generated the silylated alcohols in 79−97% yield over the two steps.

Marko's in situ allylsilane addition was used as a model reaction to evaluate the selectivity of the oxacarbenium ion auxiliaries.[4c] The results are presented in Table 2. The three aldehyde substrates, hexanal, benzaldehyde, and cinnamaldehyde, were chosen to test the selectivity for oxacarbenium ion additions in a representative set of aldehydes. In each case, the selectivity for the original auxiliary **2** was included for comparison (entries 1, 8, and 15). All of the reactions used 1.1 equiv of aldehyde, 1.0 equiv of silyl auxiliary **19**, 1.1 equiv of allyltrimethylsilane, and 0.2 equiv of TMSOTf as the catalyst.

The most remarkable outcome in the additions to hexanal was the lack of variation in the selectivity. The

TABLE 2. Diastereoselective Additions of Allyltrimethylsilane to Aldehydes Using Chiral Auxiliaries 19a−19f



entry	auxiliary	RCHO	product	yield (%)[a]	dr[b]
1	**2**	*n*-C_5H_{11}CHO	**3**[d]	86	32:1
2	**19a**	*n*-C_5H_{11}CHO	**20a**	80	35:1
3	**19b**	*n*-C_5H_{11}CHO	**20b**	75	>20:1[c]
4	**19c**	*n*-C_5H_{11}CHO	**20c**	96	>20:1[c]
5	**19d**	*n*-C_5H_{11}CHO	**20d**	57	>20:1[c]
6	**19e**	*n*-C_5H_{11}CHO	**20e**	87	47:1
7	**19f**	*n*-C_5H_{11}CHO	**20f**	92	36:1
8	**2**	PhCHO	*d*	96	10:1
9	**19a**	PhCHO	**20g**	98	14:1
10	**19b**	PhCHO	**20h**	100	16:1
11	**19c**	PhCHO	**20i**	93	6:1
12	**19d**	PhCHO	**20j**	92	5:1[c]
13	**19e**	PhCHO	**20k**	97	12:1
14	**19f**	PhCHO	**20l**	90	7:1
15	**2**	PhCH=CHCHO	*d*	69	6:1
16	**19a**	PhCH=CHCHO	**20m**	96	8:1
17	**19b**	PhCH=CHCHO	**20n**	76	8:1
18	**19c**	PhCH=CHCHO	**20o**	61	5:1[c]
19	**19d**	PhCH=CHCHO	**20p**	60	5:1[c]
20	**19e**	PhCH=CHCHO	**20q**	54	7:1[c]
21	**19f**	PhCH=CHCHO	**20r**	58	5:1[c]

[a] Yield of the purified product. [b] dr based on the GC analysis of the crude product. [c] dr based on the ^{1}H NMR analysis of the crude product. [d] These examples are described in ref 8.

selectivity ranged from 32:1 to 47:1 as analyzed by GC. Unfortunately, three of the product diastereomeric ratios could not be analyzed by GC and instead were analyzed by ^{1}H NMR. These three substrates, **19b−19d**, all showed better than 20:1 selectivities, but limitations of the analytical method obscured the precise ratios. The best measured selectivity was found with **19e**, the 2-naphthyl(trimethylsilyl)carbinol, and the lowest selectivity was found with the original auxiliary **2**. Increased silyl bulk, e.g., TES, **19a**, did not improve the ratio significantly, but increased aryl bulk, e.g., naphthyl, **19e**, showed a modest increase in selectivity. The selectivity was surprisingly insensitive to the structure of the arylsilylcarbinol in the Marko allyl transfer reaction.

The reactions with benzaldehyde are listed in Table 2, entries 8−14. The most selective auxiliaries had bulky silyl groups, but the range only varied from 7:1 to 16:1. The original phenyl TMS auxiliary **2** produced an acceptable 10:1 ratio. The yields in all cases were excellent. None of the new auxiliaries were significantly better than the original auxiliary **2**.

The allylsilane addition reactions with the unsaturated aldehyde (*E*)-cinnamaldehyde are shown in Table 2, entries 15−19. The selectivities in addition to cinnamaldehyde are modest and show little variation. The selectivities range from 5:1 to 8:1, but the yields are more diverse. The best yield and selectivity were found with the phenyl TES auxiliary **19a**. Compound **19a** is the best auxiliary for the cinnamaldehyde substrate in this study, but the modest selectivity with this unsaturated aldehyde compromises its usefulness.

(21) The *R* configuration of acylsilane **16** was assigned by Mosher's ester analysis. Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092−4096.

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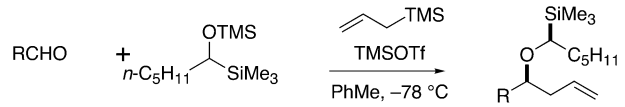
TABLE 3. Diastereoselective Additions of Allyltrimethylsilane to Aldehydes Using Aliphatic Auxiliary 21

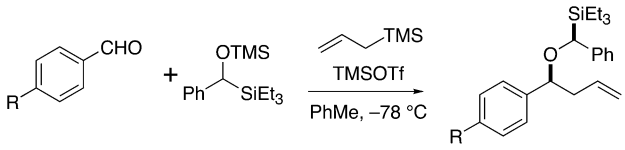


21 **22**

entry	RCHO	yield (%)[a]	dr[b]
1	n-$C_5H_{11}CHO$	45	3.2:1
2	PhCHO	62	3.0:1
3	PhCH=CHCHO	20	2.3:1

[a] Yield of the purified product. [b] dr based on the GC analysis of the crude product.

TABLE 4. Diastereoselective Additions to Substituted Benzaldehydes Using Auxiliary 19a



23 **19a** **24**

entry	R	σ_p^+	yield (%)[a]	dr[b]
1	OMe	−0.648	60	11:1
2	F	−0.247	99	14:1
3	H	0.000	98	14:1
5	CN	0.674	76	22:1
6	NO_2	0.740	64[c]	19:1[c]

[a] Yield of the purified product. [b] dr based on the GC analysis of the crude product. The ratio is the average of the two experiments. [c] This reaction was very messy, and many side products were observed.

An alkylsilylcarbinol was investigated in the Marko allylsilane addition to evaluate the importance of the aryl group versus the silyl group. The auxiliary **21** was prepared by DIBALH reduction and silylation of the acylsilane **15**. The addition of allylsilane to hexanal, benzaldehyde, and cinnamaldehyde is compared in Table 3. In each case, the addition proceeds in modest yield with low selectivity, ranging from 2.3:1 to 3.2:1. The result with hexanal, entry 1, stands in contrast to the results with all of the aromatic auxiliaries that proceed in better yield and with much higher selectivity. Alkylsilylcarbinols lead to low diastereoselectivities in these oxacarbenium ion reactions.

Oxacarbenium Ion Additions with Substituted Benzaldehydes. Aliphatic aldehydes lead to very good yields and diastereoselectivities in the allylsilane addition reactions with the auxiliaries listed in Table 2, but the selectivities with aromatic aldehydes are less impressive. One effect of the aromatic ring is to spread out the charge and stabilize the oxacarbenium ion. Does this stabilization of the intermediate correlate with the reduced selectivity? A systematic investigation of the substituent effect on diastereoselectivity was designed to answer this question, and the results are presented in Table 4. A group of para-substituted benzaldehydes were investigated using Marko's in situ allylsilane transfer reaction with the phenyl TES auxiliary **19a**. The electron-donating substituent methoxy gave the lowest diastereoselectivity, whereas the electron-withdrawing substituent CN gave the highest selectivity. The general trend clearly follows the σ_p^+ parameter, with only the nitro group falling out of order. Even the best case, however, is less selective than the 35:1 selectivity observed with hexanal using this auxiliary.

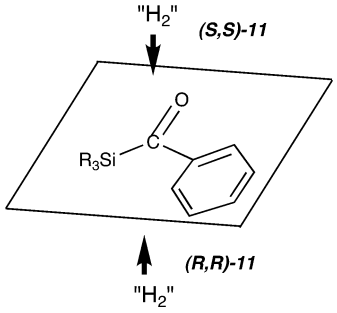


FIGURE 1. Mnemonic for the reduction of the acylsilanes with the transfer hydrogenation catalyst **11**.

Discussion

The transfer hydrogenation catalyst **11** has proven highly effective in the enantioselective reduction of alkyl aryl ketones. For ketones of this class, Noyori has proposed a mnemonic that predicts the sense of selectivity in these reductions. A similar mnemonic, shown in Figure 1, predicts the absolute configuration of the products in each of the reactions presented in Table 1. In both models, the aromatic ring occupies the right-hand position and the alkyl or silyl group occupies the left-hand position. Acetophenone is reduced with 97% ee, quite comparable to the 98% ee observed with **13**. The enantioselectivity is slightly improved by lowering the temperature. We see no evidence that the optical purity of the product is reduced by long reaction times, as found in the reduction of alkyl aryl ketones because of the reversibility of the hydrogen-transfer reaction. Indeed, the optical purity of **12f** did not change, and no oxidation was observed on treatment with catalyst (*S*,*S*)-**11** and acetone. The reduction of *n*-pentyl trimethylsilyl ketone **15** is not very selective, and the configuration of the product does not follow the silyl mnemonic. For aryl silyl ketones, the Noyori transfer hydrogenation is both enantioselective and predictable.

The arylsilylcarbinols show good facial discrimination as oxacarbenium ion auxiliaries. Linderman proposed a model to explain the observed selectivity that was based on a hyperconjugative effect of the carbon−silicon bond stabilizing the oxacarbenium ion (Scheme 1). Addition would come from the face of the oxacarbenium ion away from the silyl substituent. This model predicts the correct product for all of the auxiliaries presented in Table 2. Linderman's model predicts that bulky silyl groups should be more selective, but this trend was not reflected in our data. The troubling aspect of Linderman's model is that it does not reflect a realistic conformational minimum for these oxacarbenium ions. Figure 2 shows the minimum-energy structure of the oxacarbenium ion derived from the phenyl TMS auxiliary **2** and acetaldehyde calculated at B3LYP/6-31G*. In this conformation, the C−H of the carbenium ion is aligned parallel to the phenyl group, and the partial positive charge on this

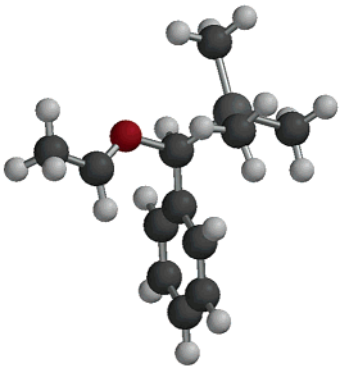


FIGURE 2. Minimum-energy conformation of the oxacarbenium ion **6** at B3LYP/6-31G*.

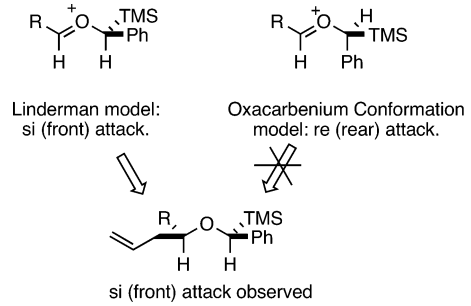


FIGURE 3. Linderman's model with the auxiliary (*S*)-**2**.

proton is probably stabilized by interaction with the electron-rich face of the aryl ring. The silyl hyperconjugative stabilization effect proposed by Linderman does not manifest itself. This conformation is at least 4 kcal/mol more stable than Linderman's conformation. Unfortunately, analysis of this conformation suggests that the most accessible face is the one opposite the silyl substituent, but that does not match the experimental outcome.[23] Figure 3 compares Linderman's model to the calculated oxacarbenium ion model. Linderman's model predicts *si* face attack as is observed, whereas a more realistic conformation incorrectly predicts *re* face attack. The failure of the calculated model is presumably due to the limitations of a "ground-state" analysis of the problem. A similar problem was found in ketone reactions. Ground-state conformations do not explain the selectivity in addition to chiral ketones, and transition-state analyses that include the ketone and the nucleophile were necessary to develop the Felkin−Ahn model.[24] Similarly, ground-state oxacarbenium ion analysis fails to predict the correct product, and a transition-state analysis would be more appropriate. The qualitative success of the Linderman model to predict facial selectivity suggests that it will share features with a more sophisticated transition-state analysis.

The effects of aromatic aldehyde substituents on the Marko addition selectivity were examined in Table 3. Substituents that stabilize a positive charge such as methoxy have the effect of lowering the selectivity of the reaction. Substituents that destabilize a benzylic cation enhance the selectivity of the reaction. The effect accounts for a 2-fold increase in selectivity, going from cation-stabilizing substituents to cation-destabilizing substituents. The selectivity with an aliphatic aldehyde using the same auxiliary is slightly better than that in the aromatic cases. Delocalization of the positive charge is clearly detrimental to the selectivity of the reaction, which is consistent with the lower selectivity with α,β-unsaturated aldehydes as well. Another trend that we have observed with auxiliary **2** is that the selectivity is often higher in toluene than in dichloromethane.[10] In fact, a wider range of selectivities was observed with solvent variations using auxiliary **2** than those using the auxiliary variations described in Table 3.[10] A well-stabilized cation in a polar solvent does not lead to the best selectivity in these oxacarbenium ion addition reactions. This observation taken together with the failure of the calculated oxacarbenium ion conformation model to predict the correct product suggests that free oxacarbenium ions are not the best way to analyze the reaction. The best selectivities arise under conditions that would produce tight ion pairs, which is consistent with Sammakia's conclusion on the role of solvation in Lewis acid induced reactions of chiral acetals.[25] Future efforts to model the selectivity of these oxacarbenium ion reactions should consider the actual transition states and the role of tight ion pairs in the reaction.

Conclusions

We have developed a family of arylsilylcarbinols as chiral auxiliaries for oxacarbenium ion reactions. The optically pure auxiliaries were prepared using Noyori's transfer hydrogenation catalyst **11**. The transfer hydrogenation shows very good enantioselectivities and turnover efficiency for the aryl silyl ketones and is the method of choice for preparing these optically pure alcohols. The reduction shows modest enantioselectivity with an alkyl silyl ketone, and a stannyl ketone appears to poison the catalyst.

The original phenyl trimethylsilyl auxiliary **2** leads to good selectivities in the allylsilane addition to aliphatic aldehydes. The synthesis of optically pure auxiliary **2** works particularly well. Slightly better selectivities were found with several of the new auxiliaries, notably the 2-naphthyl TMS auxiliary **19e**. On the balance, the phenyl silyl auxiliary **2** shows the best compromise between simplicity, selectivity, and ease of synthesis. Deprotection of the resulting phenyl silyl ethers was previously demonstrated,[8] and similar strategies have been applied to ethers derived from auxiliary **19c**. Oxacarbenium ion auxiliaries work well for additions to aliphatic aldehydes, but the selectivities are lower for aromatic and α,β-unsaturated aldehydes. Although these auxiliaries were investigated with allyltrimethylsilane nucleophiles, we expect them to be effective with a variety of carbon nucleophiles.[10]

(23) A similar problem was found with a model of the phenylmethylcarbinol auxiliary, where the model did not predict the observed product. Broeker, J. L.; Hoffmann, R. W.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5006−5017.

(24) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199−2204. (b) Nguyen, T. A.; Eisenstein, O. *Tetrahedron Lett.* **1976**, 155−158. (c) Nguyen, T. A.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61−70. (d) Ahn, N. T. *Top. Curr. Chem.* **1980**, *88*, 145−162.

(25) Sammakia, T.; Smith, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 10998−10999. (b) Sammakia, T.; Smith, R. S. *J. Org. Chem.* **1992**, *57*, 2997−3000. (c) Sammakia, T.; Smith, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 7915−7979.

Experimental Section

General Procedure for the Preparation of Chiral Alcohols from Acylsilanes. The general procedure established by Noyori was followed.[9] The acylsilane (1.0 equiv) was added to an aluminum foil wrapped flask and dissolved in 2-propanol to make a 1.0 M solution. Catalyst (*S*,*S*)-**11** (0.01−0.03 equiv) was added, and the mixture was maintained at either ambient temperature or 0 °C until conversion was deemed sufficient (typically 1.5−12 h). The mixture was then placed on a column of silica and purified by flash chromatography, which afforded the title compounds. The ee values were determined by either HPLC using a Chiralcel OD-H column at a flow rate of 0.93−1.0 mL/min in hexane/IPA (90:10) or chiral capillary GC analysis using a 30 m × 0.25 μm Chiraldex γ-cyclodextrin trifluoroacetyl column and flame ionization detector. Retention times (t_R) for the major and minor enantiomers are given in minutes. *J* values are given in hertz.

(*S*)-1-Phenyl-1-(triethylsilyl)methanol (12a). The general procedure above was applied to 0.30 g (1.3 mmol) of **10a** and 0.024 g (40 μmol) of (*S*,*S*)-**11**. After 6.0 h at ambient temperature, 0.28 g (95%) of (*S*)-**12a** was obtained upon flash chromatography (5% Et_2O/hexanes) as a pale yellow oil: 91% ee (HPLC, 1.0 mL/min; t_R major = 6.8; t_R minor = 11.2); $[\alpha]^{24}_D$ −78.3 (*c* 1.07, CH_2Cl_2); IR (neat) 3434, 3050, 2953, 1451, 1239, 1009, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.24−7.22 (m, 2H), 7.19−7.16 (m, 1H), 4.68 (d, *J* = 2.8, 1H), 1.63 (d, *J* = 3.0, 1H), 0.94 (t, *J* = 7.9, 9H), 0.58 (dq, *J* = 7.9, 4.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 128.4, 126.0, 125.2, 69.1, 7.5, 1.6. HRMS (CI/NH_3) *m*/*z* calcd for $C_{13}H_{22}OSi$ $[M]^+$ 222.1440, found 222.1440. Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 69.97; H, 9.75.

(*S*)-1-Phenyl-1-(*tert*-butyldimethylsilyl)methanol (12b). The general procedure above was applied to 0.27 g (1.2 mmol) of **10b** and 0.015 g (25 μmol) of (*S*,*S*)-**11**. After 10.0 h at ambient temperature, 0.16 g (57%) of (*S*)-**12b** was obtained after flash chromatography (6% Et_2O/hexanes) as a pale yellow oil: 82% ee (HPLC, 0.93 mL/min; t_R major = 7.9; t_R minor = 13.9); $[\alpha]^{24}_D$ −81.6 (*c* 1.02, CH_2Cl_2); IR (neat) 3436, 3025, 2929, 1598, 1471, 1248, 1007, 837 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33−7.30 (m, 2H), 7.23−7.22 (m, 2H), 7.20−7.17 (m, 1H), 4.69 (d, *J* = 2.6, 1H), 1.65 (d, *J* = 2.9, 1H), 0.97 (s, 9H), 0.014 (s, 3H), −0.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 128.4, 126.1, 125.7, 69.3, 27.2, 17.3, −7.0, −9.2. HRMS (CI/NH_3) *m*/*z* calcd for $C_{13}H_{22}OSi$ $[M]^+$ 222.1440, found 222.1433. Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.46; H, 9.83.

(*S*)-1-Phenyl-1-(dimethylphenylsilyl)methanol (12c). The general procedure above was applied to 0.25 g (1.0 mmol) of **10c** and 0.012 g (20 μmol) of (*S*,*S*)-**11**. After 12.0 h at 0 °C, 0.23 g (92%) of (*S*)-**12c** was obtained after flash chromatography (10% Et_2O/hexanes) as a pale yellow oil: 95% ee (HPLC, 1.0 mL/min; t_R major = 8.2; t_R minor = 10.3); $[\alpha]^{24}_D$ −66.1 (*c* 1.06, CH_2Cl_2); IR (neat) 3429, 3069, 2959, 1598, 1427, 1249, 1113, 999, 813 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51−7.48 (m, 2H), 7.42−7.34 (m, 3H), 7.28−7.25 (m, 2H), 7.18−7.15 (m, 1H), 7.10−7.09 (m, 2H), 4.71 (s, 1H), 1.68, (s, 1H), 0.31 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 136.2, 134.6, 129.7, 128.2, 128.0, 126.1, 125.4, 70.2, −5.2, −6.1. HRMS (CI/NH_3) *m*/*z* calcd for $C_{15}H_{18}OSi$ $[M]^+$ 242.1127, found 242.1117. Anal. Calcd for $C_{15}H_{18}OSi$: C, 74.33; H, 7.49. Found: C, 74.25; H, 7.41.

(S)-1-Phenyl-1-(diphenylmethylsilyl)methanol (12d). The general procedure above was applied to 0.27 g (0.89 mmol) of **10d** and 0.011 g (18 μmol) of (*S*,*S*)-**11**. After 6.0 h at ambient temperature, 0.24 g (87%) of (*S*)-**12d** was obtained after flash chromatography (10% Et_2O/hexanes) as a white solid: mp = 76.5−78 °C; 65% ee (HPLC, 1.0 mL/min; t_R major = 9.0; t_R minor = 11.0); $[\alpha]^{24}_D$ −35.8 (*c* 1.04, CH_2Cl_2); IR (KBr) 3538, 3449, 3050, 2960, 1426, 1112, 784 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.57 (m, 2H), 7.53−7.50 (m, 2H), 7.45−7.32 (m, 6H), 7.23−7.13 (m, 3H), 7.04−7.02 (m, 2H), 5.09 (s, 1H), 1.81 (s, br, 1H), 0.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 135.6, 135.4, 134.6, 133.9, 130.0, 129.8, 128.2, 128.1, 128.0, 126.3, 125.9, 69.4, −6.6. HRMS (CI/NH_3) *m*/*z* calcd for $C_{20}H_{20}OSi$ $[M]^+$ 304.1283, found 304.1286. Anal. Calcd for $C_{20}H_{20}OSi$: C, 78.90; H, 6.62. Found: C, 79.30; H, 6.64.

(*S*)-1-(2-Naphthyl)-1-(trimethylsilyl)methanol (12e). The general procedure above was applied to 0.21 g (0.93 mmol) of **10e** and 0.006 g (9 μmol) of (*S*,*S*)-**11**. After 10.0 h at ambient temperature, 0.21 g (98%) of (*S*)-**12e** was obtained after flash chromatography (5% EtOAc/hexanes) as a white solid: mp = 38−42 °C; 96% ee (HPLC, 0.97 mL/min; t_R major = 10.9; t_R minor = 17.4); $[\alpha]^{24}_D$ −88.7 (*c* 1.04, CH_2Cl_2); IR (film) 3413, 3055, 2956, 1600, 1247, 1006, 842 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83−7.78 (m, 3H), 7.66 (s, 1H), 7.49−7.42 (m, 2H), 7.31 (d,d, *J* = 8.4, 1.7, 1H), 4.71 (s, 1H), 1.83 (s, br, 1H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 133.7, 132.3, 127.9, 127.8, 127.8, 126.2, 125.3, 124.4, 122.7, 71.0, −3.8. HRMS (CI/NH_3) *m*/*z* calcd for $C_{14}H_{18}OSi$ $[M]^+$ 230.1127, found 230.1132. Anal. Calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.88. Found: C, 72.80; H, 8.06.

(*S*)-1-Biphenyl-1-(trimethylsilyl)methanol (12f). The general procedure above was applied to 0.27 g (1.1 mmol) of **10f** and 0.003 g (5 μmol) of (*S*,*S*)-**11**. After 4.0 h at ambient temperature, 0.27 g (98%) of (*S*)-**12f** was obtained after flash chromatography (10% Et_2O/hexanes) as a white solid: mp = 58−59 °C; 96% ee (HPLC, 1.0 mL/min; t_R major = 8.9; t_R minor = 11.8); $[\alpha]^{24}_D$ −111.5 (*c* 1.00, CH_2Cl_2); IR (KBr) 3343, 3027, 2961, 1488, 1248, 1001, 847 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.55−7.54 (m, 2H), 7.44−7.41 (m, 2H), 7.33−7.30 (m, 1H), 7.26−7.24 (m, 2H), 4.57 (s, 1H), 1.72 (s, 1H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 141.2, 138.8, 129.0, 127.2, 127.1, 127.1, 125.5, 70.6, −3.9. HRMS (CI/NH_3) *m*/*z* calcd for $C_{16}H_{20}OSi$ $[M]^+$ 256.1283, found 256.1287. Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86. Found: C, 75.19; H, 7.97.

(*R*)-1-Hexyl-1-(trimethylsilyl)methanol (16). The general procedure above was applied to 0.18 g (1.0 mmol) of **15** and 0.012 g (20 μmol) of (*S*,*S*)-**11**. After 12.0 h at ambient temperature, 0.12 g (65%) of (*R*)-**16** was obtained after flash chromatography (10% Et_2O/hexanes) as a pale yellow oil: 37% ee (GC, init temp = 60 °C, ramp = 1.0 °C/min; t_R major = 21.9; t_R minor = 22.7); $[\alpha]^{24}_D$ −3.2 (*c* 0.98, CH_2Cl_2); IR (neat) 3369, 2928, 1248, 840 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.32−3.29 (m, 1H), 1.58−1.49 (m, 3H), 1.34−1.26 (m, 5H), 1.16 (s, 1H), 0.90 (t, *J* = 7.0, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.3, 33.7, 32.0, 26.7, 22.9, 14.3, −3.7. HRMS (EI/isobutane) *m*/*z* calcd for $C_9H_{21}OSi$ $[M - H]^+$ 173.1362, found 173.1359.

General Procedure for the Preparation of (±)-Auxiliaries from Acylsilanes. The acylsilane (1.0 equiv) was added to an aluminum foil wrapped flask, dissolved in CH_2Cl_2 to make a 0.25 M solution, and then cooled to −78 °C. DIBALH (1.0 M in PhMe, 1.1−1.7 equiv) was added dropwise, and the mixture was maintained at −78 °C for 1 h. The mixture was warmed to 0 °C for 10 min, and then the reaction was quenched with saturated aqueous sodium potassium tartrate. The mixture was allowed to warm to ambient temperature, maintained for 2 h, diluted with CH_2Cl_2, and washed three times with brine. The combined aqueous phases were extracted twice with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$ and then concentrated in vacuo. Purification by flash chromatography afforded the (±)-alcohols.

The general procedure of Bruynes[26] was then followed for silylation of the alcohols. To a 0.25 M solution of the (±)-alcohol (1.0 equiv) in CH_2Cl_2 was added saccharin (0.05 equiv). The mixture was heated to reflux, and HMDS (0.75−2.0 equiv) was added dropwise. The mixture was maintained at reflux for 24 h, and then it was allowed to cool to ambient temperature. The mixture was diluted with CH_2Cl_2 and washed three times with brine. The combined aqueous phases were extracted twice with CH_2Cl_2, and the combined organic layers were dried over

(26) Bruynes, C. A.; Jurriens, T. K. *J. Org. Chem.* **1982**, *47*, 3966−3969.

$MgSO_4$ and then concentrated in vacuo. Purification by flash chromatography using silica gel neutralized with 2% triethylamine afforded the title compounds.

(±)-1-Phenyl-1-(triethylsilyl)methanol TMS Ether (19a). The general procedure above was applied to 0.29 g (1.3 mmol) of acylsilane **10a** and 1.9 mmol of DIBALH to provide after flash chromatography (5% EtOAc/hexanes) 0.28 g (96%) of (±)-**12a** as a pale yellow oil: All data matched that reported for (*S*)-**12a**. Continued application of the general procedure to 0.21 g (0.94 mmol) of (±)-**12a** and 0.4 mL (2 mmol) of HMDS afforded after flash chromatography (4% EtOAc/hexanes) 0.24 g (87%) of **19a** as a pale yellow oil: IR (neat) 3055, 2954, 1450, 1250, 1050, 873 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.23 (m, 2H), 7.17−7.15 (m, 2H), 7.13−7.09 (m, 1H), 4.60 (s, 1H), 0.91 (t, J = 7.9, 9H), 0.52 (dq, J = 7.9, 3.0, 6H), 0.00 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 128.0, 125.3, 125.2, 69.0, 7.6, 1.6, 0.32. HRMS (CI/NH_3) m/z calcd for $C_{16}H_{30}OSi_2$ $[M]^+$ 294.1835, found 294.1829.

(±)-1-Phenyl-1-(*tert*-butyldimethylsilyl)methanol TMS Ether (19b). The general procedure above was applied to 0.74 g (3.4 mmol) of acylsilane **10b** and 5.7 mmol of DIBALH to provide after flash chromatography (6% Et_2O/hexanes) 0.64 g (85%) of (±)-**12b** as a pale yellow oil: All data matched that reported for (*S*)-**12b**. Continued application of the general procedure to 0.59 g (2.7 mmol) of (±)-**12b** and 1.2 mL (5.3 mmol) of HMDS afforded after flash chromatography (10% CH_2Cl_2/hexanes) 0.73 g (93%) of **19b** as a pale yellow oil: IR (neat) 3025, 2956, 1471, 1251, 1051, 844 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26−7.23 (m, 2H), 7.18−7.16 (m, 2H), 7.14−7.11 (m, 1H), 4.63 (s, 1H), 0.91 (s, 9H), −0.01 (s, 9H), −0.04 (s, 3H), −0.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 127.9, 126.1, 125.6, 69.7, 27.3, 17.5, 0.5, −7.2, −8.7. HRMS (CI/NH_3) m/z calcd for $C_{16}H_{30}OSi_2$ $[M]^+$ 294.1835, found 294.1849.

(±)-1-Phenyl-1-(dimethylphenylsilyl)methanol TMS Ether (19c). The general procedure above was applied to 0.76 g (3.1 mmol) of acylsilane **10c** and 3.8 mmol of DIBALH to provide after flash chromatography (10% Et_2O/hexanes) 0.76 g (99%) of (±)-**12c** as a cloudy oil: All data matched that reported for (*S*)-**12c**. Continued application of the general procedure to 0.72 g (3.0 mmol) of (±)-**12c** and 1.0 mL (4.4 mmol) of HMDS afforded after flash chromatography (10% CH_2Cl_2/hexanes) 0.89 g (96%) of **19c** as a pale yellow oil: IR (neat) 3069, 2959, 1428, 1250, 1050, 842 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45−7.43 (m, 2H), 7.38−7.35 (m, 1H), 7.33−7.30 (m, 2H), 7.20 (t, J = 7.5, 2H), 7.10 (t, J = 7.3, 1H), 7.02 (d, J = 7.2, 2H), 4.60 (s, 1H), 0.27 (s, 3H), 0.20 (s, 3H), −0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 137.0, 134.7, 129.3, 127.8, 127.6, 125.5, 125.4, 70.3, 0.1, −5.6, −6.0. HRMS (CI/NH_3) m/z calcd for $C_{18}H_{26}OSi_2$ $[M]^+$ 314.1522, found 314.1521.

(±)-1-Phenyl-1-(diphenylmethylsilyl)methanol TMS Ether (19d). The general procedure above was applied to 0.75 g (2.5 mmol) of acylsilane **10d** and 3.7 mmol of DIBALH to provide after flash chromatography (10% Et_2O/hexanes) 0.75 g (98%) of (±)-**12d** as a white solid: mp = 67−68 °C; all other data matched that reported for (*S*)-**12d**. Continued application of the general procedure to 0.66 g (2.2 mmol) of (±)-**12d** and 0.9 mL (4 mmol) of HMDS afforded after flash chromatography (5% Et_2O/hexanes) 0.80 g (99%) of **19d** as a colorless oil: IR (neat) 3070, 2958, 1448, 1428, 1251, 1113, 1050, 872, 841 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.48−7.46 (m, 2H), 7.42−7.30 (m, 6H), 7.16−7.13 (m, 2H), 7.10−7.07 (m, 1H), 7.00 (d, J = 7.0, 2H), 4.95 (s, 1H), 0.49 (s, 3H), −0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 135.8, 135.5, 135.3, 134.7, 129.6, 129.5, 127.7, 127.7, 127.7, 126.0, 125.7, 70.1, 0.2, −6.6. HRMS (CI/NH_3) m/z calcd for $C_{22}H_{25}OSi_2$ $[M - CH_3]^+$ 361.1444, found 361.1446.

(±)-1-(2-Naphthyl)-1-(trimethylsilyl)methanol TMS Ether (19e). The general procedure above was applied to 0.27 g (1.2 mmol) of acylsilane **10e** and 1.4 mmol of DIBALH to provide after flash chromatography (5% EtOAc/hexanes) 0.27 g (99%) of (±)-**12e** as a colorless oil: All data (except mp) matched that reported for (*S*)-**12e**. Continued application of the general procedure to 0.18 g (0.76 mmol) of (±)-**12e** and 0.1 mL (0.6 mmol) of HMDS afforded after flash chromatography (5% EtOAc/hexanes) 0.21 g (91%) of **19e** as a white solid: mp = 70−72 °C; IR (KBr) 3058, 2958, 1600, 1507, 1245, 1043, 842 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81−7.78 (m, 2H), 7.74 (d, J = 8.4, 1H), 7.58 (s, 1H), 7.45−7.40 (m, 2H), 7.30 (dd, J = 8.5, 1.7, 1H), 4.62 (s, 1H), 0.04 (s, 9H), −0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 133.7, 132.1, 127.8, 127.8, 127.3, 125.9, 124.9, 124.5, 122.7, 70.7, 0.3, −3.8. HRMS (CI/NH_3) m/z calcd for $C_{17}H_{26}OSi_2$ $[M]^+$ 302.1522, found 302.1515.

(±)-1-Biphenyl-1-(trimethylsilyl)methanol TMS Ether (19f). The general procedure above was applied to 0.76 g (3.0 mmol) of acylsilane **10f** and 3.3 mmol of DIBALH to provide after flash chromatography (10% Et_2O/hexanes) 0.75 g (99%) of (±)-**12f** as a white solid: mp = 75−76 °C; all other data matched that reported for (*S*)-**12f**. Continued application of the general procedure to 0.62 g (2.4 mmol) of (±)-**12f** and 0.4 mL (2 mmol) of HMDS afforded after flash chromatography (5% Et_2O/hexanes) 0.77 g (98%) of **19f** as a colorless oil: IR (neat) 3028, 2957, 1486, 1249, 1052, 871, 841 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64−7.61 (m, 2H), 7.53−7.51 (m, 2H), 7.45−7.42 (m, 2H), 7.34−7.30 (m, 1H), 7.22 (d, J = 8.0, 2H), 4.51 (s, 1H), 0.06 (s, 9H), 0.00 (s, 9H); ^{13}C NMR (125 MHz, CD_3OD) δ 144.9, 142.6, 139.8, 129.9, 128.1, 127.9, 127.6, 126.7, 71.6, 0.2, −3.8. HRMS (CI/NH_3) m/z calcd for $C_{19}H_{28}OSi_2$ $[M]^+$ 328.1679, found 328.1673.

(±)-1-Hexyl-1-(trimethylsilyl)methanol TMS Ether (21). The general procedure above was applied to 0.89 g (5.1 mmol) of acylsilane **15** and 5.7 mmol of DIBALH to provide after flash chromatography (15% Et_2O/petroleum ether) 0.78 g (87%) of (±)-**16** as a pale yellow oil: All data matched that reported for (*S*)-**16**. Continued application of the general procedure to 0.73 g (4.2 mmol) of (±)-**16** and 0.7 mL (3 mmol) of HMDS afforded after flash chromatography (2% Et_2O/hexanes) 0.96 g (92%) of **21** as a colorless oil: IR (neat) 2958, 1251, 1072, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.36−3.33 (m, 1H), 1.53−1.45 (m, 3H), 1.34−1.23 (m, 5H), 0.90 (t, J = 7.1, 3H), 0.09 (s, 9H), 0.00 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 67.1, 34.3, 32.3, 27.1, 22.9, 14.3, 0.8, −3.0. HRMS (EI/isobutane) m/z calcd for $C_8H_{21}OSi_2$ $[M - C_4H_9]^+$ 189.1131, found 189.1133.

General Procedure for the Preparation of Homoallylic Ethers Using Auxiliaries. The general procedure established by Marko was followed.[4c] A 0.1 M solution of the (±)-auxiliary (1.0 equiv) in PhMe was cooled to −78 °C. To the solution was added the indicated aldehyde (1.1 equiv), allyltrimethylsilane (1.1 equiv), and TMSOTf (0.2 equiv). The mixture was maintained at −78 °C for 1 h, and then the reaction was quenched by the addition of saturated aqueous $NaHCO_3$. The mixture was allowed to warm to ambient temperature, diluted with CH_2Cl_2, and washed once with saturated $NaHCO_3$ and then three times with brine. The combined aqueous phases were extracted twice with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$ and then concentrated in vacuo. Purification by flash chromatography afforded the title compounds as mixtures of diastereomers. NMR data are reported for the major diastereomer, while IR and combustion analysis data are reported for the mixtures of diastereomers.

Triethyl[(1-pentylbut-3-enyloxy)phenylmethyl]silane (20a). The general procedure above was applied to 0.11 g (0.38 mmol) of auxiliary **19a** and 52 μL (0.42 mmol) of hexanal to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.10 g (80%) of **20a** as a colorless oil: IR (neat) 3070, 2933, 1459, 1210, 1104, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28−7.25 (m, 2H), 7.20−7.18, (m, 2H), 7.16−7.12 (m, 1H), 5.80 (dddd, J = 16.6, 10.7, 7.1, 7.1, 1H), 5.00−4.96 (m, 2H), 4.35 (s, 1H), 3.32−3.28 (m, 1H), 2.20−2.17 (m, 2H), 1.51−1.42 (m, 2H), 1.33−1.21 (m, 6H), 0.91 (t, J = 7.9, 12H), 0.56−0.48 (m, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 143.3, 136.7, 128.4,

127.0, 126.0, 116.4, 77.8, 73.6, 39.8, 32.8, 32.2, 24.7, 23.3, 14.4, 7.7, 2.1. HRMS (CI/NH_3) *m*/*z* calcd for $C_{22}H_{39}OSi$ $[M + H]^+$ 347.2770, found 347.2777. Anal. Calcd for $C_{22}H_{38}OSi$: C, 76.23; H, 11.05. Found: C, 76.36; H, 11.22.

***tert*-Butyldimethyl[(1-pentylbut-3-enyloxy)phenylmethyl]silane (20b).** The general procedure above was applied to 0.16 g (0.56 mmol) of auxiliary **19b** and 75 μL (0.61 mmol) of hexanal to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.14 g (75%) of **20b** as a colorless oil: IR (neat) 3070, 2930, 1463, 1246, 1045, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28−7.25 (m, 2H), 7.19−7.13 (m, 3H), 5.84 (dddd, J = 17.4, 10.2, 7.0, 7.0, 1H), 5.01−4.97 (m, 2H), 4.41 (s, 1H), 3.32−3.27 (m, 1H), 2.23−2.13 (m, 2H), 1.57−1.52 (m, 1H), 1.45−1.38 (m, 1H), 1.31−1.17 (m, 6H), 0.91 (s, 9H), 0.88 (t, J = 7.1, 3H), −0.02 (s, 3H), −0.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 136.2, 128.0, 127.1, 125.9, 116.3, 76.4, 72.8, 39.4, 32.4, 31.6, 27.2, 24.6, 22.9, 17.4, 14.3, −7.1, −8.5. HRMS (CI/NH_3) *m*/*z* calcd for $C_{22}H_{38}OSi$ $[M]^+$ 346.2692, found 346.2696. Anal. Calcd for $C_{22}H_{38}OSi$: C, 76.23; H, 11.05. Found: C, 76.02; H, 10.85.

Dimethylphenyl[(1-pentylbut-3-enyloxy)phenylmethyl]silane (20c). The general procedure above was applied to 0.18 g (0.58 mmol) of auxiliary **19c** and 78 μL (0.64 mmol) of hexanal to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.20 g (96%) of **20c** as a colorless oil: IR (neat) 3071, 2931, 1641, 1599, 1451, 1428, 1247, 1115, 1046, 832 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45−7.43 (m, 2H), 7.37−7.34 (m, 1H), 7.31−7.28 (m, 2H), 7.22−7.19 (m, 2H), 7.14−7.11 (m, 1H), 7.04−7.02 (m, 2H), 5.82−5.74 (m, 1H), 4.99−4.95 (m, 2H), 4.36 (s, 1H), 3.31 (quintet, J = 5.6, 1H), 2.23−2.13 (m, 2H), 1.40−1.38 (m, 2H), 1.25−1.16 (m, 6H), 0.86 (t, J = 7.2, 3H), 0.29 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 137.0, 136.1, 134.7, 129.2, 127.9, 127.6, 126.7, 125.8, 116.3, 77.7, 74.8, 39.4, 32.4, 31.9, 24.2, 22.8, 14.3, −5.0, −5.7. HRMS (CI/NH_3) *m*/*z* calcd for $C_{24}H_{34}OSi$ $[M - H]^+$ 365.2301, found 365.2294. Anal. Calcd for $C_{24}H_{34}OSi$: C, 78.63; H, 9.35. Found: C, 78.74; H, 9.27.

Methyldiphenyl[(1-pentylbut-3-enyloxy)phenylmethyl]silane (20d). The general procedure above was applied to 0.16 g (0.43 mmol) of auxiliary **19d** and 58 μL (0.47 mmol) of hexanal to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.10 g (57%) of **20d** as a colorless oil: IR (neat) 3071, 2930, 2859, 1641, 1598, 1451, 1428, 1250, 1113, 1044, 913 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60−7.56 (m, 2H), 7.50−7.46 (m, 2H), 7.42−7.38 (m, 1H), 7.37−7.32 (m, 3H), 7.30−7.28 (m, 2H), 7.16−7.09 (m, 3H), 7.00−6.98 (m, 2H), 5.80−5.72 (m, 1H), 5.00−4.98 (m, 1H), 4.97−4.96 (m, 1H), 4.72 (s, 1H), 3.34 (quintet, J = 5.6, 1H), 2.24−2.14 (m, 2H), 1.45−1.38 (m, 2H), 1.23−1.08 (m, 6H), 0.84 (t, J = 7.2, 3H), 0.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 136.1, 135.9, 135.6, 135.4, 134.4, 129.5, 129.4, 127.9, 127.7, 127.6, 127.4, 126.1, 116.4, 77.6, 74.4, 39.3, 32.4, 31.8, 24.2, 22.8, 14.3, −6.2. HRMS (CI/NH_3) *m*/*z* calcd for $C_{29}H_{36}OSi$ $[M]^+$ 428.2535, found 428.2538.

Trimethyl[naphth-2-yl(1-pentylbut-3-enyloxy)methyl]silane (20e). The general procedure above was applied to 0.14 g (0.47 mmol) of auxiliary **19e** and 64 μL (0.52 mmol) of hexanal to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.14 g (87%) of **20e** as a yellow oil: IR (neat) 3058, 2931, 1457, 1248, 1048, 848 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82−7.75 (m, 3H), 7.61 (s, 1H), 7.47−7.40 (m, 2H), 7.33 (dd, J = 8.4, 1.7 1H), 5.82 (dddd, J = 17.5, 10.1, 7.0, 7.0, 1H), 5.01−4.97 (m, 2H), 4.35 (s, 1H), 3.36 (quintet, J = 5.6, 1H), 2.71−2.17 (m, 2H), 1.50−1.48 (m, 2H), 1.34−1.28 (m, 6H), 0.09 (t, J = 7.1, 3H), −0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 136.2, 133.6, 132.3, 127.8, 127.7, 127.5, 126.0, 125.6, 125.0, 124.2, 116.4, 78.0, 75.3, 39.4, 32.4, 32.1, 24.3, 22.9, 14.3, −3.6. HRMS (CI/NH_3) *m*/*z* calcd for $C_{23}H_{34}OSi$ $[M]^+$ 354.2379, found 354.2384. Anal. Calcd for $C_{23}H_{34}OSi$: C, 77.90; H, 9.66. Found: C, 77.63; H, 9.41.

[Biphenyl-4-yl(1-pentylbut-3-enyloxy)methyl]trimethylsilane (20f). The general procedure above was applied to 0.21 g (0.65 mmol) of auxiliary **19f** and 88 μL (0.71 mmol) of hexanal to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.23 g (92%) of **20f** as a pale yellow oil: IR (neat) 3077, 3028, 2931, 2859, 1641, 1486, 1247, 1047, 911, 844 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63−7.61 (m, 2H), 7.53−7.52 (m, 2H), 7.45−7.42 (m, 2H), 7.34−7.30 (m, 1H), 7.23 (d, J = 8.1, 2H), 5.87−5.79 (m, 1H), 5.02−5.01 (m, 1H), 4.99−4.98 (m, 1H), 4.24 (s, 1H), 3.37 (quintet, J = 5.6, 1H), 2.28−2.20 (m, 2H), 1.50−1.48 (m, 2H), 1.35−1.28 (m, 6H), 0.91 (t, J = 7.1 3H), 0.00 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 141.4, 138.5, 136.2, 128.9, 127.1, 127.1, 126.8, 126.7, 116.4, 77.8, 74.9, 39.5, 32.5, 32.1, 24.3, 22.9, 14.3, −3.6. HRMS (CI/NH_3) *m*/*z* calcd for $C_{24}H_{33}OSi$ $[M - CH_3]^+$ 365.2301, found 365.2297.

Trimethyl[1-(1-pentylbut-3-enyloxy)hexyl]silane (22a). The general procedure above was applied to 0.18 g (0.72 mmol) of auxiliary **21** and 98 μL (0.80 mmol) of hexanal to afford, after flash chromatography (2% CH_2Cl_2/hexanes), 0.10 g (45%) of **22a** as a pale yellow oil: IR (neat) 3077, 2930, 1464, 1247, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.88−5.80 (m, 1H), 5.06−5.00 (m, 2H), 3.28 (quintet, J = 5.8, 1H), 3.05 (q, J = 6.4, 1H), 2.25−2.21 (m, 2H), 1.59−1.50 (m, 2H), 1.42−1.26 (m, 14H), 0.91−0.87 (m, 6H), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1, 116.4, 78.5, 71.2, 38.8, 34.0, 32.6, 32.4, 32.1, 27.1, 25.3, 22.9, 22.8, 14.3, 14.3, −2.4. HRMS (CI/NH_3) *m*/*z* calcd for $C_{18}H_{39}OSi$ $[M + H]^+$ 299.2770, found 299.2765.

Triethyl[phenyl(1-phenylbut-3-enyloxy)methyl]silane (20g). The general procedure above was applied to 0.11 g (0.36 mmol) of auxiliary **19a** and 41 μL (0.40 mmol) of benzaldehyde to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.12 g (98%) of **20g** as a colorless oil: IR (neat) 3072, 2952, 1456, 1238, 1015, 845 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34−7.27 (m, 5H), 7.22−7.16 (m, 3H), 7.13 (d, J = 7.3, 2H), 5.85−5.76 (m, 1H), 5.00−4.97 (m, 2H), 4.22 (dd, J = 7.8, 5.7, 1H), 4.03 (s, 1H), 2.62−2.56 (m, 1H), 2.40−2.35 (m, 1H), 0.83 (t, J = 7.9, 9H), 0.53−0.45 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 141.9, 135.6, 128.4, 128.3, 127.8, 127.7, 126.7, 125.9, 116.8, 79.3, 72.8, 43.1, 7.5, 1.6. HRMS (CI/NH_3) *m*/*z* calcd for $C_{23}H_{33}OSi$ $[M + H]^+$ 353.2300, found 353.2304. Anal. Calcd for $C_{23}H_{32}OSi$: C, 78.35; H, 9.15. Found: C, 78.12; H, 9.26.

***tert*-Butyldimethyl[phenyl(1-phenylbut-3-enyloxy)-methyl]silane (20h).** The general procedure above was applied to 0.10 g (0.35 mmol) of auxiliary **19b** and 40 μL (0.38 mmol) of benzaldehyde to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.12 g (100%) of **20h** as a pale yellow oil: IR (neat) 3080, 3027, 2929, 2856, 1642, 1492, 1454, 1247, 1055, 1023, 913, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35−7.28 (m, 5H), 7.21−7.18 (m, 3H), 7.14 (s, br, 2H), 5.85−5.77 (m, 1H), 5.03−5.01 (m, 1H), 4.99, (s, 1H), 4.22 (dd, J = 5.8, 7.9, 1H), 4.05 (s, 1H), 2.67−2.62 (m, 1H), 2.43−2.38 (m, 1H), 0.83 (s, 9H), 0.01 (d, J = 2.0, 3H), −0.27 (d, J = 2.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 141.5, 135.6, 128.3, 128.3, 128.2, 127.9, 127.4, 126.0, 116.7, 78.8, 72.7, 42.5, 27.1, 17.4, −7.1, −8.3. HRMS (CI/NH_3) *m*/*z* calcd for $C_{22}H_{29}OSi$ $[M - CH_3]^+$ 337.1987, found 337.1987. Anal. Calcd for $C_{23}H_{32}OSi$: C, 78.35; H, 9.15. Found: C, 78.48; H, 8.99.

Dimethylphenyl[phenyl(1-phenylbut-3-enyloxy)methyl]silane (20i). The general procedure above was applied to 0.12 g (0.40 mmol) of auxiliary **19c** and 45 μL (0.44 mmol) of benzaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.14 g (93%) of **20i** as a pale yellow oil: IR (neat) 3069, 3026, 2961, 1642, 1600, 1492, 1428, 1247, 1115, 1058, 913, 832 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45−7.39 (m, 3H), 7.36−7.32 (m, 2H), 7.30−7.18 (m, 6H), 7.03−7.02 (m, 4H), 5.87−5.77 (m, 1H), 5.05−5.04 (m, 1H), 5.02−5.01 (m, 1H), 4.27 (dd, J = 7.7, 5.6, 1H), 4.11 (s, 1H), 2.62−2.55 (m, 1H), 2.41−2.35 (m, 1H), 0.31 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 143.0, 142.0, 137.7, 136.6, 135.7, 130.4, 129.4, 129.1, 128.7, 128.7, 128.6, 128.0, 127.2, 117.2, 80.9, 75.3, 44.3, −4.7, −5.8. HRMS (CI/NH_3) *m*/*z* calcd for $C_{22}H_{23}OSi$ $[M - C_3H_5]^+$ 331.1518, found 331.1518. Anal. Calcd for $C_{25}H_{28}OSi$: C, 80.59; H, 7.57. Found: C, 80.56; H, 7.68.

Methyldiphenyl[phenyl(1-phenylbut-3-enyloxy)methyl]silane (20j). The general procedure above was applied to 0.13 g (0.42 mmol) of auxiliary **19d** and 48 μL (0.47 mmol) of benzaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.14 g (93%) of **20j** as a colorless oil: IR (neat) 3069, 2903, 2837, 1642, 1489, 1250, 913 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57−7.55 (m, 2H), 7.44−7.41 (m, 1H), 7.37−7.33 (m, 5H), 7.28−7.14 (m, 8H), 6.98−6.94 (m, 4H), 5.76 (dddd, *J* = 17.2, 10.1, 7.0, 7.0, 1H), 5.03−4.99 (m, 2H), 4.40 (s, 1H), 4.26 (dd, *J* = 7.9, 5.5, 1H), 2.61−2.55 (m, 1H), 2.39−2.33 (m, 1H), 0.43 (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 141.8, 140.6, 136.2, 136.0, 135.8, 135.7, 134.5, 130.0, 129.8, 128.7, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 126.7, 116.9, 79.9, 74.0, 43.3, −6.2. HRMS (CI/NH_3) *m*/*z* calcd for $C_{27}H_{25}OSi$ [M − C_3H_5]$^+$ 393.1675, found 393.1674.

Trimethyl[naphth-2-yl(1-phenylbut-3-enyloxy)methyl]silane (20k). The general procedure above was applied to 0.12 g (0.39 mmol) of auxiliary **19e** and 45 μL (0.43 mmol) of benzaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.14 g (97%) of **20k** as a colorless oil: IR (neat) 3050, 2910, 1247, 1055, 844 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9, 1H), 7.80−7.78 (m, 2H), 7.54 (s, 1H), 7.49−7.42 (m, 2H), 7.37−7.30 (m, 4H), 7.23−7.22 (m, 2H), 5.86 (dddd, *J* = 17.3, 10.1, 7.0, 7.0, 1H), 5.05−5.00 (m, 2H), 4.30 (dd, *J* = 7.8, 5.7, 1H), 4.10 (s, 1H), 2.66−2.61 (m, 1H), 2.43−2.37 (m, 1H), −0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 139.5, 135.6, 133.7, 132.5, 128.4, 127.9, 127.8, 127.8, 127.8, 127.7, 126.1, 125.7, 125.2, 124.6, 116.9, 79.7, 74.5, 43.4, −3.6. HRMS (CI/NH_3) *m*/*z* calcd for $C_{24}H_{28}OSi$ [M]$^+$ 360.1909, found 360.1912. Anal. Calcd for $C_{24}H_{28}OSi$: C, 79.95; H, 7.83. Found: C, 79.79; H, 7.96.

[Biphenyl-4-yl(1-phenylbut-3-enyloxy)methyl]trimethylsilane (20l). The general procedure above was applied to 0.16 g (0.47 mmol) of auxiliary **19f** and 52 μL (0.52 mmol) of benzaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.16 g (90%) of **20l** as a white solid: mp = 102−104 °C; IR (KBr) 3028, 2962, 1484, 1247, 1060, 846 cm^{-1};^1H NMR (500 MHz, $CDCl_3$) δ 7.64−7.62 (m, 2H), 7.54 (d, *J* = 8.4, 2H), 7.44 (t, *J* = 7.7, 2H), 7.36−7.29 (m, 4H), 7.25−7.23 (m, 2H), 7.17 (d, *J* = 8.0, 2H), 5.88−5.79 (m, 1H), 5.03−5.02 (m, 1H), 5.00−4.99 (m, 1H), 4.30 (dd, *J* = 7.7, 5.6, 1H), 3.96 (s, 1H), 2.64−2.58 (m, 1H), 2.42−2.37 (m, 1H), −0.03 (s, 9H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 142.9, 141.8, 141.6, 139.4, 136.3, 129.8, 129.2, 128.6, 128.4, 128.0, 127.8, 127.6, 127.5, 117.1, 80.4, 74.7, 43.9, −3.6. HRMS (CI/NH_3) *m*/*z* calcd for $C_{25}H_{27}OSi$ [M − CH_3]$^+$ 371.1831, found 371.1834.

Trimethyl[1-(1-phenylbut-3-enyloxy)hexyl]silane (22b). The general procedure above was applied to 0.18 g (0.73 mmol) of auxiliary **21** and 83 μL (0.80 mmol) of benzaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.14 g (62%) of **22b** as a colorless oil: IR (neat) 3077, 2930, 1455, 1247, 1062, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35−7.32 (m, 2H), 7.29−7.26 (m, 3H), 5.80 (dddd, *J* = 17.2, 10.2, 7.0, 7.0, 1H), 5.04−4.97 (m, 2H), 4.38 (dd, *J* = 7.6, 6.0, 1H), 2.93 (dd, *J* = 6.6, 4.3, 1H), 2.59−2.53 (m, 1H), 2.40−2.34 (m, 1H), 1.73−1.68 (m, 1H), 1.55−1.49 (m, 1H), 1.43−1.29 (m, 6H), 0.92 (t, *J* = 7.1, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 135.9, 128.2, 127.7, 127.6, 116.5, 79.6, 69.6, 43.1, 32.7, 30.2, 26.6, 22.8, 14.3, −2.5. HRMS (CI/NH_3) *m*/*z* calcd for $C_9H_{21}OSi$ [M − $C_{10}H_{11}$]$^+$ 173.1362, found 173.1359.

Triethyl[phenyl(1-styrylbut-3-enyloxy)methyl]silane (20m). The general procedure above was applied to 0.08 g (0.3 mmol) of auxiliary **19a** and 37 μL (0.30 mmol) of *trans*-cinnamaldehyde to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.09 g (96%) of **20m** as a yellow oil: IR (neat) 3025, 2876, 1492, 1020, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40−7.24 (m, 7H), 7.20−7.16 (m, 3H), 6.33 (d, *J* = 16.0, 1H), 6.01 (dd, *J* = 15.9, 8.6, 1H), 5.92−5.84 (m, 1H), 5.08−5.03 (m, 2H), 4.43 (s, 1H), 3.83 (ddd, *J* = 8.6, 6.3, 6.3, 1H), 2.47−2.41 (m, 1H), 2.39−2.33 (m, 1H), 0.90 (t, *J* = 7.9, 9H), 0.59−0.47 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 136.9, 135.2, 133.4, 130.2, 128.8, 128.3, 127.8, 126.7, 126.5, 125.8, 116.9, 78.0, 72.1, 41.2, 7.6, 1.7. HRMS (CI/NH_3) *m*/*z* calcd for $C_{23}H_{29}OSi$ [M − C_2H_5]$^+$ 349.1988, found 349.1992. Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.47; H, 9.26.

***tert*-Butyldimethyl[phenyl(1-styrylbut-3-enyloxy)methyl]silane (20n).** The general procedure above was applied to 0.22 g (0.73 mmol) of auxiliary **19b** and 103 μL (0.81 mmol) of *trans*-cinnamaldehyde to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.21 g (76%) of **20n** as a colorless oil: IR (neat) 3026, 2928, 1599, 1247, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39−7.25 (m, 7H), 7.20−7.15 (m, 3H), 6.29 (d, *J* = 15.9, 1H), 6.03 (dd, *J* = 15.9, 9.0, 1H), 5.88 (dddd, *J* = 17.1, 10.1, 7.0, 7.0, 1H), 5.07−5.03 (m, 2H), 4.46 (s, 1H), 3.81 (ddd, *J* = 8.5, 6.5, 6.5, 1H), 2.47−2.41 (m, 1H), 2.38−2.33 (m, 1H), 0.93 (s, 9H), −0.02 (s, 3H), −0.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 136.9, 135.2, 133.8, 130.0, 128.8, 128.2, 127.9, 127.0, 126.7, 125.9, 116.9, 77.8, 72.0, 41.2, 27.3, 17.4, −7.0, −8.8. HRMS (CI/NH_3) *m*/*z* calcd for $C_{25}H_{34}OSi$ [M − H]$^+$ 377.2301, found 377.2301. Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.40; H, 8.96.

Dimethylphenyl[phenyl(1-styrylbut-3-enyloxy)methyl]silane (20o). The general procedure above was applied to 0.18 g (0.59 mmol) of auxiliary **19c** and 82 μL (0.65 mmol) of *trans*-cinnamaldehyde to afford, after flash chromatography (5% CH_2Cl_2/hexanes), 0.14 g (61%) of **20o** as a pale yellow oil: IR (neat) 3025, 2959, 1599, 1428, 1247, 1045, 832 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.46 (m, 2H), 7.41−7.36 (m, 1H), 7.34−7.29 (m, 4H), 7.27−7.23 (m, 5H), 7.18−7.14 (m, 1H), 7.06−7.04 (m, 2H), 6.25 (d, *J* = 16.0, 1H), 5.91−5.80 (m, 2H), 5.08−5.03 (m, 2H), 4.46 (s, 1H), 3.84 (ddd, *J* = 8.3, 6.3, 6.3, 1H), 2.48−2.40 (m, 1H), 2.38−2.31 (m, 1H), 0.28 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 137.0, 136.9, 135.1, 134.7, 133.0, 130.2, 129.3, 128.7, 128.1, 127.8, 127.6, 126.7, 126.6, 125.9, 117.0, 78.3, 73.4, 41.2, −4.9, −5.9. HRMS (CI/NH_3) *m*/*z* calcd for $C_{24}H_{25}OSi$ [M − C_3H_5]$^+$ 357.1675, found 357.1677. Anal. Calcd for $C_{27}H_{30}OSi$: C, 81.35; H, 7.59. Found: C, 81.50; H, 7.63.

Methyldiphenyl[phenyl(1-styrylbut-3-enyloxy)methyl]silane (20p). The general procedure above was applied to 0.21 g (0.55 mmol) of auxiliary **19d** and 78 μL (0.61 mmol) of *trans*-cinnamaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.15 g (60%) of **20p** as a pale yellow oil: IR (neat) 3069, 2930, 1598, 1428, 1251, 1113, 846 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 1.4, 2H), 7.46−7.38 (m, 3H), 7.36−7.25 (m, 10H), 7.21−7.13 (m, 3H), 7.01−6.99 (m, 2H), 6.29 (d, *J* = 16.0, 1H), 5.92 (dd, *J* = 16.0, 8.6, 1H), 5.87−5.78 (m, 1H), 5.09−5.02 (m, 2H), 4.82 (s, 1H), 3.88 (ddd, *J* = 8.5, 6.3, 6.3, 1H), 2.50−2.42 (m, 1H), 2.39−2.32 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 136.8, 135.9, 135.6, 135.4, 135.1, 134.4, 133.5, 129.9, 129.6, 129.4, 128.8, 128.1, 127.9, 127.7, 127.7, 127.3, 126.7, 126.2, 117.0, 78.4, 72.9, 41.2, −6.3. HRMS (CI/NH_3) *m*/*z* calcd for $C_{29}H_{27}OSi$ [M − C_3H_5]$^+$ 419.1831, found 419.1830.

Trimethyl[naphth-2-yl(1-styrylbut-3-enyloxy)methyl]silane (20q). The general procedure above was applied to 0.05 g (0.2 mmol) of auxiliary **19e** and 24 μL (0.19 mmol) of *trans*-cinnamaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.04 g (54%) of **20q** as a yellow oil: IR (neat) 3055, 2926, 1427, 1048, 842 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85−7.79 (m, 3H), 7.60 (s, 1H), 7.50−7.26 (m, 8H), 6.35 (d, *J* = 16.0, 1H), 6.05 (dd, *J* = 16.0, 8.4, 1H), 5.97−5.87 (m, 1H), 5.10−5.06 (m, 2H), 4.46 (s, 1H), 3.90 (dd, *J* = 14.7, 6.4, 1H), 2.54−2.47 (m, 1H), 2.43−2.36 (m, 1H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 137.0, 135.2, 133.7, 133.2, 132.4, 130.4, 128.8, 127.9, 127.8, 127.7, 126.7, 126.6, 126.0, 125.5, 125.2, 124.3, 117.0, 78.5, 74.0, 41.2, −3.6. HRMS (CI/NH_3) *m*/*z* calcd for $C_{26}H_{30}OSi$ [M]$^+$ 386.2066, found 386.2069. Anal. Calcd for $C_{26}H_{30}OSi$: C, 80.78; H, 7.82. Found: C, 80.73; H, 7.62.

[Biphenyl-4-yl(1-styrylbut-3-enyloxy)methyl]trimethylsilane (20r). The general procedure above was applied to 0.15 g (0.46 mmol) of auxiliary **19f** and 65 μL (0.41 mmol) of *trans*-cinnamaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.11 g (58%) of **20r** as a colorless oil:

IR (neat) 3027, 2957, 1642, 1487, 1247, 1044, 842 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65−7.63 (m, 2H), 7.56 (d, J = 8.3, 2H), 7.47−7.40 (m, 4H), 7.37−7.32 (m, 3H), 7.29−7.25 (m, 1H), 7.22 (d, J = 8.1, 2H), 6.39 (d, J = 15.9, 1H), 6.39 (dd, J = 15.9, 8.4, 1H), 5.91 (dddd, J = 17.2, 10.1, 7.1, 7.1, 1H), 5.11−5.05 (m, 2H), 4.33 (s, 1H), 3.91 (ddd, J = 8.2, 6.4, 6.4, 1H), 2.52−2.45 (m, 1H), 2.42−2.36 (m, 1 H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 141.2, 138.6, 137.0, 135.2, 133.2, 130.4, 128.9, 128.8, 127.9, 127.1, 127.1, 126.9, 126.8, 126.7, 117.0, 78.4, 73.6, 41.2, −3.7. HRMS (CI/NH_3) m/z calcd for $C_{27}H_{29}OSi$ $[M - CH_3]^+$ 397.1988, found 397.1991.

Trimethyl[1-(1-styrylbut-3-enyloxy)hexyl]silane (22c). The general procedure above was applied to 0.20 g (0.80 mmol) of auxiliary **21** and 113 μL (0.88 mmol) of *trans*-cinnamaldehyde to afford, after flash chromatography (10% CH_2Cl_2/hexanes), 0.11 g (58%) of **22c** as a pale yellow oil: IR (neat) 3028, 2929, 1451, 1247, 1055, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40−7.38 (m, 2H), 7.33 (t, J = 7.7, 2H), 7.26−7.23 (m, 1H), 6.47 (d, J = 16.0, 1H), 6.00 (dd, J = 15.9, 8.3, 1H), 5.87 (dddd, J = 17.2, 10.2, 7.1, 7.1, 1H), 5.09−5.02 (m, 2H), 3.93 (ddd, J = 8.0, 6.4, 6.4, 1H), 3.15 (t, J = 6.1, 1H), 2.45−2.40 (m, 1H), 2.35−2.30 (m, 1H), 1.65−1.51 (m, 2H), 1.41−1.27 (m, 6H), 0.92 (t, J = 7.0, 3H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 135.4, 132.1, 131.7, 128.8, 127.7, 126.6, 116.7, 79.6, 69.8, 41.0, 32.6, 31.2, 27.0, 22.9, 14.3, −2.6. HRMS (CI/NH_3) m/z calcd for $C_{21}H_{35}OSi$ $[M + H]^+$ 331.2457, found 331.2467.

Triethyl{[1-(4-methoxyphenyl)but-3-enyloxy]phenylmethyl}silane (24a). The general procedure above was applied to 0.11 g (0.36 mmol) of auxiliary **19a** and 49 μL (0.40 mmol) of *p*-anisaldehyde to afford, after flash chromatography (2% NEt_3/3−10% CH_2Cl_2/hexanes), 0.08 g (60%) of **24a** as a colorless oil: IR (neat) 3072, 2953, 1512, 1247, 1039, 831 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.23 (d, J = 4.7, 4H), 7.10−7.06 (m, 3H), 6.80−6.78 (m, 2H), 5.96−5.88 (m, 1H), 5.06−5.03 (m, 1H), 5.02 (t, J = 1.2, 1H), 4.36 (dd, J = 7.7, 5.9, 1H), 4.22 (s, 1H), 3.30 (s, 3H), 2.75−2.69 (m, 1H), 2.48−2.42 (m, 1H), 0.93 (t, J = 7.9, 9H), 0.65−0.44 (m, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.9, 142.2, 135.8, 134.0, 129.2, 128.6, 126.9, 126.2, 116.8, 114.1, 79.1, 72.7, 54.8, 43.4, 7.6, 2.0. HRMS (CI/NH_3) m/z calcd for $C_{22}H_{29}O_2Si$ $[M - C_2H_5]^+$ 353.1937, found 353.1941.

Triethyl{[1-(4-fluorophenyl)but-3-enyloxy]phenylmethyl}silane (24b). The general procedure above was applied to 0.15 g (0.52 mmol) of auxiliary **19a** and 62 μL (0.57 mmol) of *p*-fluorobenzaldehyde to afford, after flash chromatography (2−5% CH_2Cl_2/hexanes), 0.19 g (100%) of **24b** as a colorless oil: IR (neat) 3078, 2954, 1510, 1225, 1013, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.7, 2H), 7.20−7.11 (m, 5H), 7.02 (t, J = 8.7, 2H), 5.76 (dddd, J = 17.5, 10.1, 7.0, 7.0, 1H), 5.00−4.96 (m, 2H), 4.21 (dd, J = 7.5, 6.0, 1H), 3.99 (s, 1H), 2.60−2.54 (m, 1H), 2.38−2.33 (m, 1H), 0.84 (t, J = 7.9, 9H), 0.53−0.45 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 161.5, 141.7, 137.8, 137.8, 135.2, 129.4, 129.3, 128.3, 126.7, 126.0, 117.0, 115.3, 115.1, 78.6, 72.9, 43.1, 7.4, 1.6. HRMS (CI/NH_3) m/z calcd for $C_{21}H_{26}OFSi$ $[M - C_2H_5]^+$ 341.1737, found 341.1726.

4-[1-(Phenyltriethylsilanylmethoxy)but-3-enyl]benzonitrile (24c). The general procedure above was applied to 0.14 g (0.47 mmol) of auxiliary **19a** and 0.07 g (0.5 mmol) of *p*-cyanobenzaldehyde to afford, after flash chromatography (1−5% Et_2O/hexanes), 0.13 g (76%) of **24c** as a colorless oil: IR (neat) 3079, 2953, 2230, 1602, 1453, 1238, 1013, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1, 2H), 7.32−7.28 (m, 4H), 7.20 (t, J = 7.3, 1H), 7.10 (d, J = 7.3, 2H), 5.73 (dddd, J = 17.2, 10.2, 7.1, 7.1, 1H), 5.02−4.94 (m, 2H), 4.30 (dd, J = 7.0, 6.3, 1H), 3.95 (s, 1H), 2.57−2.52 (m, 1H), 2.38−2.33 (m, 1H), 0.84 (t, J = 7.9, 9H), 0.50 (q, J = 7.9, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 141.1, 134.3, 132.3, 128.5, 128.4, 126.6, 126.3, 119.1, 117.8, 111.6, 78.8, 73.9, 42.9, 7.4, 1.6. HRMS (CI/NH_3) m/z calcd for $C_{24}H_{32}NOSi$ $[M + H]^+$ 378.2253, found 378.2248.

Triethyl[3-(4-nitrophenyl)-1-phenylhex-5-enyl]silane (24d). The general procedure above was applied to 0.12 g (0.42 mmol) of auxiliary **19a** and 0.07 g (0.5 mmol) of *p*-nitrobenzaldehyde to afford, after flash chromatography (1−5% Et_2O/hexanes), 0.11 g (65%) of **24d** as a yellow oil: IR (neat) 3080, 2954, 1525, 1291, 1011, 854 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, 2H), 7.39−7.36 (m, 2H), 7.33−7.29 (m, 2H), 7.22−7.07 (m, 3H), 5.74 (dddd, J = 17.2, 10.1, 7.1, 7.1, 1H), 5.05−4.94 (m, 2H), 4.37 (dd, J = 7.1, 6.1, 1H), 3.96 (s, 1H), 2.60−2.53 (m, 1H), 2.41−2.35 (m, 1H), 0.85 (t, J = 7.9, 9H), 0.59−0.44 (m, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 149.2, 141.2, 134.4, 128.8, 128.3, 127.9, 126.8, 126.7, 123.6, 117.7, 78.6, 74.2, 43.0, 7.5, 1.8. HRMS (CI/NH_3) m/z calcd for $C_{24}H_{32}NOSi$ $[M + H]^+$ 398.2151, found 398.2148.

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Supporting Information Available: Syntheses of the acylsilanes **10a**−**10f** and of the other compounds not described in the Experimental Section are reported. This material is available free of charge via the Internet at http//pubs.acs.org.

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