The 2,4,6-Trimethoxyphenyl Unit as a Unique Protecting Group for Silicon in Synthesis and the Silylation Potential of (2,4,6-Trimethoxyphenyl)silanes

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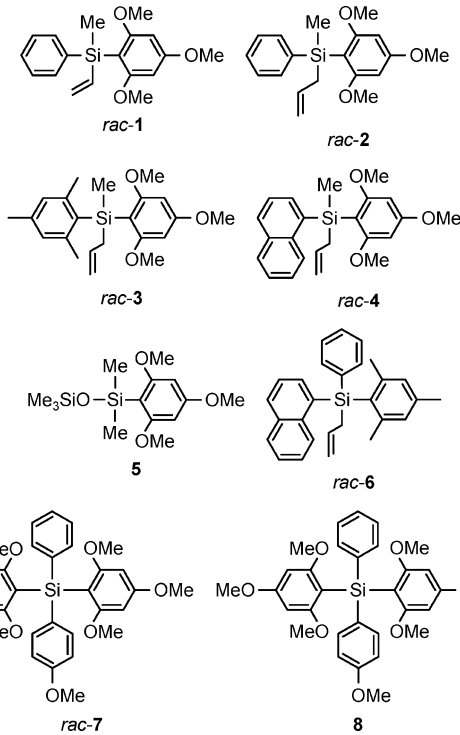
A series of triorganyl(2,4,6-trimethoxyphenyl)silanes containing various combinations of acid-labile protecting groups for silicon, including allyl, 2,6-dimethoxyphenyl, mesityl, 4-methoxyphenyl, 1-naphthyl, and phenyl, were synthesized and characterized. These compounds served as reagents in a series of experiments to determine the selectivity of the cleavage of the 2,4,6-trimethoxyphenyl group in the presence of the aforementioned groups using an ethereal hydrogen chloride solution to obtain synthetically useful chlorosilanes. Additionally, the silylation potential of trimethyl-, methyldiphenyl-, and triethyl(2,4,6-trimethoxyphenyl)silane under mild (0−35 °C), acidic conditions with *O*-, *N*-, and *S*-nucleophiles was examined. These silylation reagents exhibit both chemo- and regioselectivity with respect to the tested nucleophiles, are neither moisture nor air sensitive and thus easy to handle, and produce a relatively inert byproduct, 1,3,5-trimethoxybenzene, which is recyclable.

Introduction

Several years ago, we discovered that the 2,4,6-trimethoxyphenyl unit can be effectively used as a protecting group for silicon during the synthesis of the serotonin/noradrenaline reuptake inhibitor sila-venlafaxine.[1] In the course of this study, it was found that the protecting group could be efficiently and selectively cleaved in the presence of a silicon-bound substituted vinyl group under mild conditions (0 °C) using an ethereal hydrogen chloride solution to give the corresponding chlorosilane. The electrophilic cleavage of various unsaturated organic groups, such as aryl groups,[2] has already been studied extensively. However, in many cases, very strong acids, such as perchloric acid,[3] trifluoromethanesulfonic acid,[4] or trifluoroacetic acid,[5] have been used to cleave the less labile groups. Since chlorosilanes are very useful reactive building blocks for the synthesis of organosilicon compounds, we wished to investigate the selectivity with which the 2,4,6-trimethoxyphenyl group may be removed with hydrogen chloride in the presence of other common silicon protecting groups to produce chlorosilanes. In the following work, we present the synthesis and characterization of a series of new silanes (**1**−**8**) with varying silicon-bound organyl substituents, including the allyl (All), 2,6-dimethoxyphenyl (DMOP), mesityl (Mes), 4-methoxyphenyl (MOP), methyl (Me), 1-naphthyl (Np), phenyl (Ph), 2,4,6-trimethoxyphenyl (TMOP), trimethylsilyloxy (TMSO), and vinyl (Vi)



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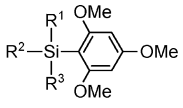
group, as well as a series of reactions of these model compounds in which certain groups are selectively cleaved using hydrogen chloride. Except for the achiral compounds **5** and **8**, all these silanes were synthesized and studied as racemates.

During the course of these studies, it was found that the TMOP group could also be cleaved with catalytic amounts of acid in the presence of methanol to give the respective methoxysilanes. The question arose as to whether this is a general reaction, which can also be applied to other alcohols. In other words, rather than simply understanding this particular reaction as the cleavage of a protecting group with the simultaneous formation of a reactive Si−alkoxy group, one may also view such triorganyl(2,4,6-trimethoxyphenyl)silanes as reagents with the general ability to transfer silyl groups, in the presence of catalytic amounts of acid, to *O*- or even perhaps *N*- and *S*-nucleophiles. Therefore, we also synthesized the triorganyl(2,4,6-trimethoxyphenyl)silanes **9**−**11**, which are



9–**11**

9: $R^1 = R^2 = R^3 = Me$
10: $R^1 = Me$, $R^2 = R^3 = Ph$
11: $R^1 = R^2 = R^3 = Et$

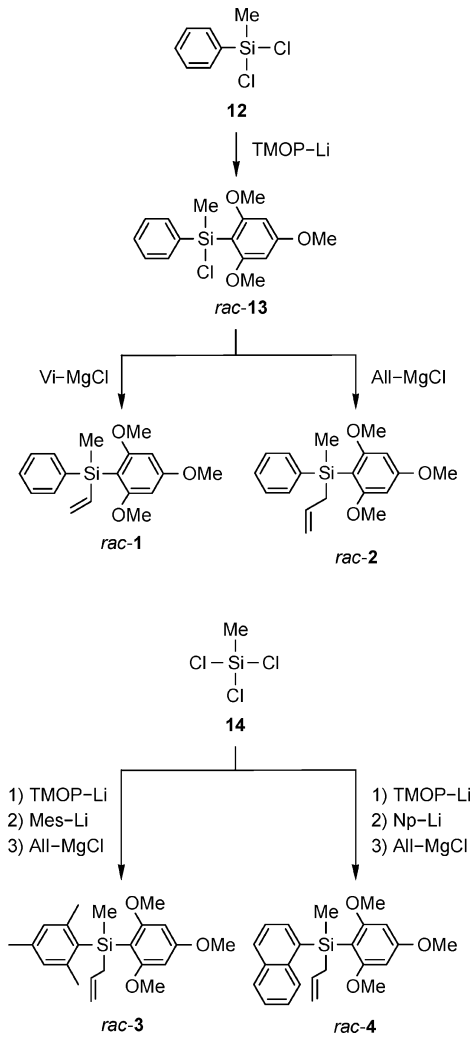
derivatives of commonly used chlorosilane-based silylation reagents,[6] complemented by a study of their silylation potential with respect to *O*-, *N*-, and *S*-nucleophiles.

Results and Discussion

Syntheses of the Model Compounds for the Cleavage Reactions. The model compounds *rac*-**1**−*rac*-**4**, **5**, *rac*-**6**, *rac*-**7**, and **8** were synthesized by reaction of organolithium and Grignard reagents with the respective chlorosilanes (Schemes 1−4). To the best of our knowledge, these silanes have not yet been described in the literature. Where applicable, the TMOP group was introduced first by reaction of stoichiometric amounts of the respective chlorosilane and a suspension of (2,4,6-trimethoxyphenyl)lithium (TMOP−Li), produced by reaction of *n*-butyllithium with 1,3,5-trimethoxybenzene in hexanes, in the presence of *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA), to give selective substitution of a single chlorine atom. The other organyl groups were then introduced by sequential reaction with the respective organometallic reagents.

The model compounds *rac*-**1**−*rac*-**4** were synthesized (Scheme 1) to make a comparison of the relative acid lability of the TMOP unit and other unsaturated hydrocarbon-based silicon protecting groups possible. Reaction of dichloro(methyl)-phenylsilane (**12**) with 1 mol equiv of TMOP−Li gave *rac*-chloro(methyl)phenyl(2,4,6-trimethoxyphenyl)silane (*rac*-**13**) in 73% yield, which was then treated with an excess of vinylmagnesium chloride (Vi–MgCl) or allylmagnesium chloride (All-MgCl) to give *rac*-methyl(phenyl)(2,4,6-trimethoxyphenyl)-vinylsilane (*rac*-**1**) in 63% yield and *rac*-allyl(methyl)phenyl-(2,4,6-trimethoxyphenyl)silane (*rac*-**2**) in 84% yield, respectively. Although it is in principle possible to obtain the chloro(2,4,6-trimethoxyphenyl)silane intermediates, as demonstrated by the characterization of *rac*-**13**, **17**, *rac*-**18**, **19**, and *rac*-**27** (see below), during these syntheses it was found that

Scheme 1



chlorodiorganyl(2,4,6-trimethoxyphenyl)silanes and dichloro-(organyl)(2,4,6-trimethoxyphenyl)silanes with only small organic groups are very sensitive to hydrolysis and cannot be easily isolated and handled. Therefore, the target compounds, which had to be synthesized through such chloro(2,4,6-trimethoxyphenyl)silane intermediates, were obtained from one-pot syntheses. Thus, sequential treatment of trichloro(methyl)-silane (**14**) with 1 mol equiv of TMOP−Li, followed by 1 mol equiv of mesityllithium (Mes–Li) or 1-naphthyllithium (Np−Li) and finally an excess of All−MgCl, gave *rac*-allyl(mesityl)-methyl(2,4,6-trimethoxyphenyl)silane (*rac*-**3**) in 36% yield and *rac*-allyl(methyl)(1-naphthyl)(2,4,6-trimethoxyphenyl)silane (*rac*-**4**) in 52% yield, respectively. It was also discovered during the syntheses of *rac*-**3** and *rac*-**4** that the chlorosilane intermediates following the introduction of the mesityl or 1-naphthyl groups tenaciously retain the TMEDA necessary for the previous reaction, as it could not be completely removed in vacuo (0.01 mbar, 60 °C, 3 h).

Since the disiloxane linkage may also be regarded as a type of protecting unit, which may be used in the synthesis of organosilicon compounds, we synthesized the model compound **5** (Scheme 2) to compare the acid lability of the Si−O−Si unit with that of the Si−TMOP group. Thus, reaction of dichlorodimethylsilane (**15**) with 1 mol equiv of TMOP−Li, followed by addition of lithium trimethylsilanolate (TMSO−Li), gave dimethyl(2,4,6-trimethoxyphenyl)(trimethylsilyloxy)silane (**5**) in 73% yield.

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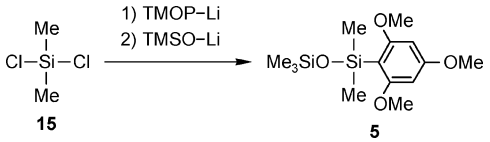
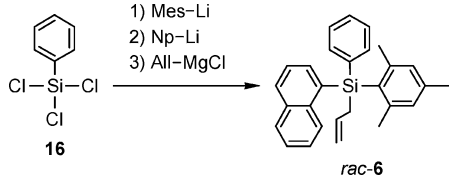
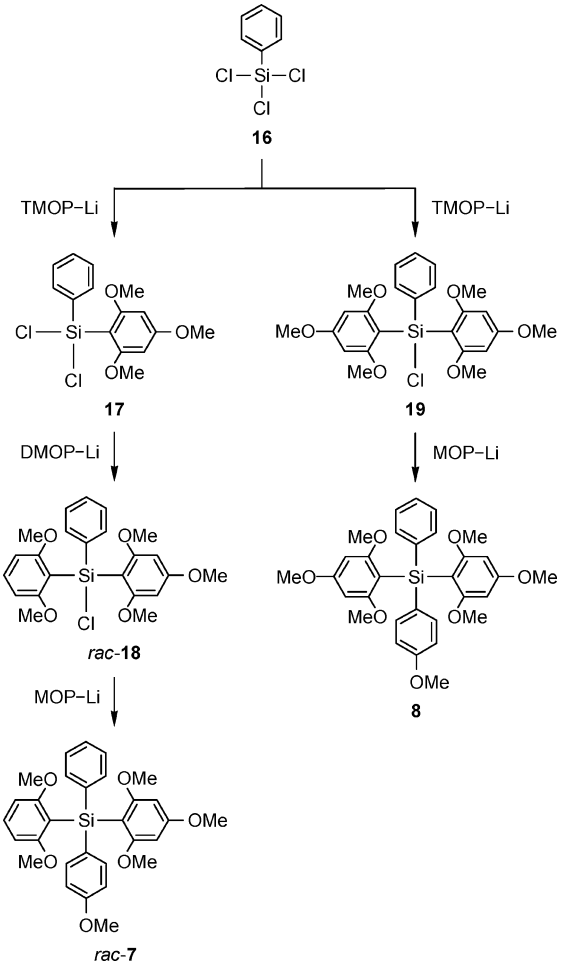
Scheme 2



Scheme 3



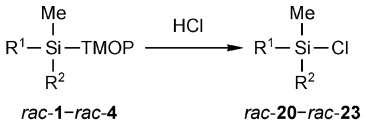
Scheme 4



To make a comparison of the behavior of the unsaturated hydrocarbon protecting groups for silicon that lie in the middle of the spectrum of acid lability possible, the model compound *rac*-**6** was synthesized (Scheme 3). Thus, trichloro(phenyl)silane (**16**) was treated sequentially with 1 mol equiv of Mes–Li, then with 1 mol equiv of Np−Li, and finally with an excess of All–MgCl to give *rac*-allyl(mesityl)(1-naphthyl)phenylsilane (*rac*-**6**) in 33% yield.

Two model compounds, *rac*-**7** and **8**, containing only phenyl and various methoxyphenyl groups, intended to test the effect of the methoxy substitution pattern of the phenyl groups on their acid lability, were also synthesized (Scheme 4). Thus, reaction of **16** with 1 mol equiv of TMOP−Li gave dichloro(phenyl)-(2,4,6-trimethoxyphenyl)silane (**17**) in 48% yield, which was then treated with 1 mol equiv of (2,6-dimethoxyphenyl)lithium (DMOP−Li) to give *rac*-chloro(2,6-dimethoxyphenyl)phenyl-(2,4,6-trimethoxyphenyl)silane (*rac*-**18**) in 25% yield. Finally, reaction of *rac*-**18** with an excess of 4-methoxyphenyllithium (MOP−Li) gave *rac*-(2,6-dimethoxyphenyl)(4-methoxyphenyl)-phenyl(2,4,6-trimethoxyphenyl)silane (*rac*-**7**) in 30% yield. Similarly, treatment of **16** with 2 mol equiv of TMOP−Li gave chloro(phenyl)bis(2,4,6-trimethoxyphenyl)silane (**19**) in 33% yield. Subsequent reaction with an excess of MOP−Li gave (4-methoxyphenyl)phenylbis(2,4,6-trimethoxyphenyl)silane (**8**) in 51% yield. Due to the poor solubility of *rac*-**7**, **8**, **17**, *rac*-**18**, and **19** in solvents such as *n*-hexane or diethyl ether in which lithium salts are almost insoluble, the separation of these silanes from the lithium salts during workup was problematic. In these cases, the isolated yields were somewhat low, even though GC control showed nearly quantitative conversion.

Scheme 5



rac-**1**−*rac*-**4** *rac*-**20**−*rac*-**23**

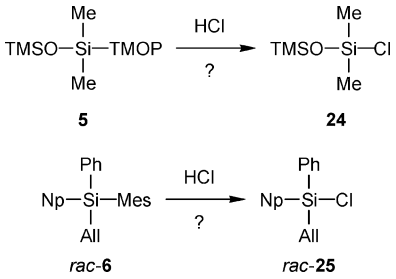
	rac-**1**, *rac*-**20**	*rac*-**2**, *rac*-**21**	*rac*-**3**, *rac*-**22**	*rac*-**4**, *rac*-**23**
R^1	Ph	Ph	Mes	Np
R^2	Vi	All	All	All

The identities of the model compounds *rac*-**1**−*rac*-**4**, **5**, *rac*-**6**, *rac*-**7**, and **8** as well as the intermediates *rac*-**13**, **17**, *rac*-**18**, and **19** were established by elemental analyses (C, H) and solution NMR studies (^{1}H, ^{13}C, ^{29}Si). In addition, compounds *rac*-**1**−*rac*-**3**, *rac*-**6**, and *rac*-**18** were structurally characterized by single-crystal X-ray diffraction.

Selective Cleavage of the Protecting Groups with Hydrogen Chloride in Diethyl Ether. In a series of experiments designed to demonstrate the high selectivity with which the TMOP group may be cleaved with the simultaneous formation of a reactive Si−Cl bond under mild conditions in the presence of other hydrocarbon-based silicon protecting groups, model compounds *rac*-**1**−*rac*-**4** were each treated with 1 mol equiv of hydrogen chloride in diethyl ether at 0 °C to give *rac*-chloro-(methyl)phenyl(vinyl)silane (*rac*-**20**), *rac*-allyl(chloro)methyl-(phenyl)silane (*rac*-**21**), *rac*-allyl(chloro)mesityl(methyl)silane (*rac*-**22**), and *rac*-allyl(chloro)methyl(1-naphthyl)silane (*rac*-**23**), respectively (Scheme 5). The identities of these compounds were verified by elemental analyses (C, H) and solution NMR studies (^{1}H, ^{13}C, ^{29}Si). No cleavage of allyl, mesityl, methyl, 1-naphthyl, phenyl, or vinyl groups could be observed in any of these experiments. The reactions gave essentially quantitative conversion (by GC) to the desired chlorotriorganylsilanes *rac*-**20**−*rac*-**23**.

Compounds **5** and *rac*-**6** were also treated with 1 mol equiv of hydrogen chloride in diethyl ether in similar experiments (Scheme 6). In the case of the reaction of **5** with hydrogen chloride at −20 °C, the desired product, chlorodimethyl-(trimethylsilyloxy)silane (**24**), could be observed by mass spectrometry for a short time at the beginning of the experiment. However, with longer reaction times, significant amounts of byproducts corresponding to cleavage of the disiloxane linkage were observed, so that the desired product **24** could not be isolated under the tested experimental conditions. The experiment using *rac*-**6** demonstrated the behavior of the less acid labile unsaturated hydrocarbon protecting groups mesityl, allyl, 1-naphthyl, and phenyl in the presence of one another. Although

Scheme 6



the reaction was incomplete and very slow, of the four groups, the mesityl group is most easily removed with 1 mol equiv of hydrogen chloride in diethyl ether at 20 °C. Using these conditions, mesitylene, *rac*-allylchloro(1-naphthyl)phenylsilane (*rac*-**25**), and small amounts of the hydrogen chloride adduct to the allyl double bond of *rac*-**25** could be observed by GC/EI-MS; no observable cleavage of the other groups occurred (for further experimental details, see the Supporting Information).

These results, in conjuction with previous work,[4a,c,f] demonstrate that the various tested groups in order of decreasing acid lability are:

$$\text{TMOP} \geq \text{TMSO} \gg \text{mesityl} > \text{allyl} > \text{1-naphthyl} > \text{phenyl} > \text{vinyl} > \text{methyl}.$$

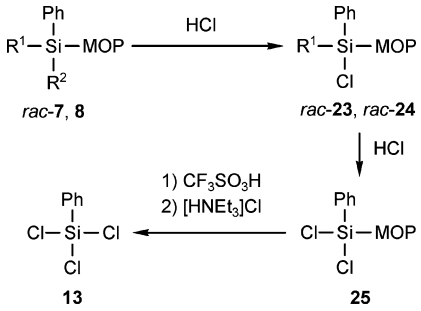
To investigate the relative lability of the TMOP, DMOP, and MOP protecting groups in the presence of one another, the protecting groups of model compounds *rac*-**7** and **8** were removed successively in a series of reactions with hydrogen chloride (Schema 7). Compound *rac*-**7** was treated with 1 mol equiv of hydrogen chloride in diethyl ether at 0 °C to give the chlorosilane *rac*-**26** in 80% yield; only cleavage of the TMOP group was detected by GC. Compound *rac*-**26** was then treated with 2 mol equiv of hydrogen chloride in diethyl ether at 20 °C to give the dichlorosilane **28** in 47% yield; only negligible amounts of methoxybenzene from cleavage of the MOP group were observed by GC. The reactions gave essentially quantitative conversion (by GC) to the desired products *rac*-**26** and **28**.

The model compound **8** was treated with 1 mol equiv of hydrogen chloride in diethyl ether at 0 °C to give the chlorosilane *rac*-**27** in 39% yield. No cleavage of the second TMOP group could be observed by GC. Therefore, it is possible to cleave a single TMOP group in the presence of another on the same silicon atom by stoichiometric use of hydrogen chloride in diethyl ether. Compound *rac*-**27** was further treated with 1 mol equiv of hydrogen chloride in diethyl ether at 20 °C to give the dichlorosilane **28** in 34% yield. Again, the reactions showed essentially quantitative conversion by GC to the desired products *rac*-**27** and **28**.

The identities of the cleavage products *rac*-**26**, *rac*-**27**, and **28** were verified by solution NMR studies (^{1}H, ^{13}C, ^{29}Si) and by comparison with the NMR data of authentic samples synthesized starting with **16** by subsequent treatment with the respective organometallic reagents (TMOP−Li, DMOP−Li, and MOP−MgBr) (Scheme 8). The reaction of **16** according to ref 7 with 0.45 mol equiv of 4-methoxyphenylmagnesium bromide (MOP−MgBr) gave **28** in 70% yield. The reaction of **28** with 1 mol equiv of DMOP−Li gave *rac*-**26** in 40% yield, and reaction with 1 mol equiv of TMOP−Li gave *rac*-**27** in 50% yield. Compound *rac*-**26** was additionally characterized by single-crystal X-ray diffraction.

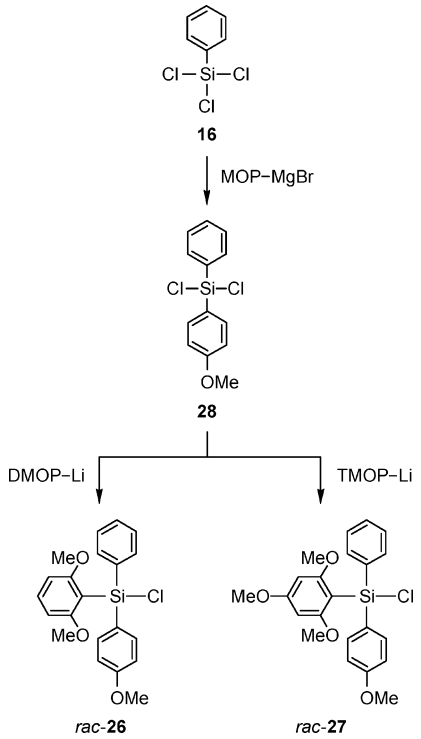
It was also possible to cleave the MOP group in the presence of a phenyl unit, which confirms observations reported in ref

Scheme 7



	rac-**7**	**8**	*rac*-**23**	*rac*-**24**
R^1	DMOP	TMOP	DMOP	TMOP
R^2	TMOP	TMOP		

Scheme 8



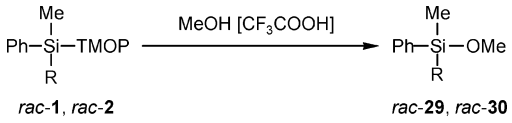
4f. Thus, treatment of **28** with 1.1 mol equiv of trifluoromethanesulfonic acid in *n*-hexane at 0 °C, followed by treatment with 1.2 mol equiv of triethylammonium chloride, gave **16** in 52% yield (Scheme 7). Only small amounts of benzene from cleavage of the phenyl group were observed by GC. The identification of **16** was made by comparison of its NMR data with those of commercially available trichloro(phenyl)silane.

These results demonstrate that the TMOP, DMOP, and MOP groups are a useful set of protecting groups for silicon as they may be highly selectively removed and replaced by other functional groups in the course of a synthesis. The order of these three protecting groups, in order of decreasing acid lability compared to phenyl, is:

$$\text{TMOP} \gg \text{DMOP} > \text{MOP} > \text{Ph}.$$

Though it is in principle possible to convert any of the isolated chlorosilanes into methoxysilanes by methanolysis in the presence of triethylamine, we also wanted to determine if it is

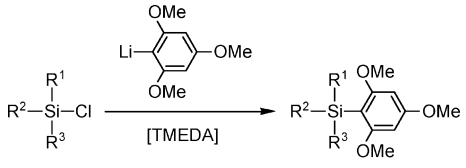
Scheme 9



rac-**1**, *rac*-**2** *rac*-**29**, *rac*-**30**

	rac-**1**	*rac*-**2**	*rac*-**29**	*rac*-**30**
R	Vi	All	Vi	All

Scheme 10



31–**33** **9**–**11**

	9, **31**	**10**, **32**	**11**, **33**
R^1	Me	Me	Et
R^2	Me	Ph	Et
R^3	Me	Ph	Et

possible to selectively cleave the TMOP group by methanolysis in the presence of catalytic amounts of acid to give the synthetically useful methoxysilanes directly. When compounds *rac*-**1** and *rac*-**2** were treated with an excess of methanol in the presence of catalytic amounts of trifluoroacetic acid (ca. 7 mol %), the desired products *rac*-methoxy(methyl)phenyl(vinyl)-silane (*rac*-**29**) and *rac*-allyl(methoxy)methyl(phenyl)silane (*rac*-**30**) could be isolated in 51 and 40% yield, respectively (Scheme 9).

It is important to note that the experiments involving the cleavages of the protecting groups with hydrogen chloride were carried out with the intention of isolating analytically pure samples. As a result, the *isolated yields* were somewhat modest in some cases due to difficult distillations resulting from coincidentally similar boiling points between the product and 1,3,5-trimethoxybenzene. The isolated yields were not a reflection of the *efficiency of conversion* to the desired product, as all reactions proceeded smoothly without byproducts (GC control). In addition, one must remember that the systems tested were only *model systems*; with other systems, the removal of 1,3,5-trimethoxybenzene may pose no problem at all. It is also conceivable that a 1,3,5-trimethoxybenzene impurity would not hinder further synthetic steps taken with the deprotected product without its isolation.

Syntheses of the Silylation Agents 9−**11**. The syntheses of compounds **9**−**11** were carried out similarly to procedures already reported for the synthesis of **9**.[8] In each case, a stoichiometric amount of the respective chlorosilane (**31**−**33**) in *n*-hexane was treated with a suspension of (2,4,6-trimethoxyphenyl)lithium, produced by reaction of *n*-butyllithium with 1,3,5-trimethoxybenzene in hexanes, in the presence of TMEDA (Scheme 10). In contrast to the reported syntheses of **9**, the products were conveniently isolated in high yields by crystallization from *n*-hexane solutions at −20 °C. The identities of **9**−**11** were established by elemental analyses (C, H), solution NMR studies (^{1}H, ^{13}C, ^{29}Si), and single-crystal X-ray diffraction.

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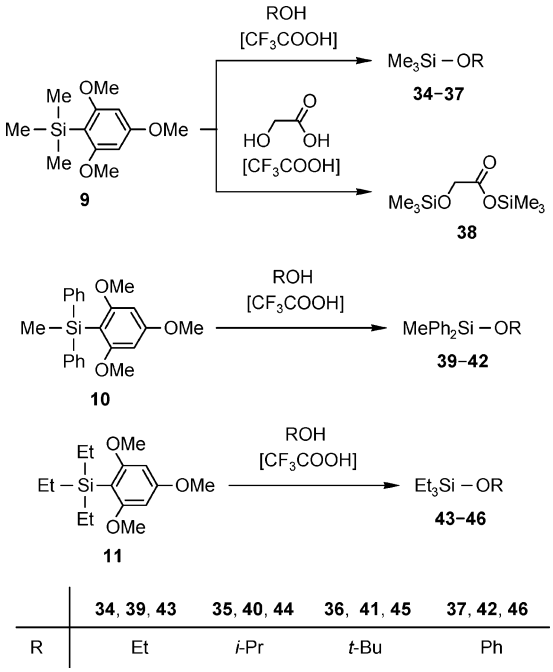
Scheme 11



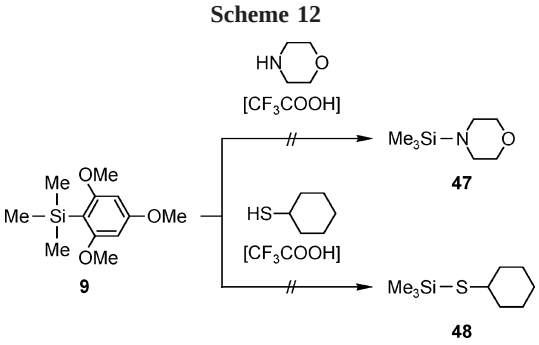
	34, **39**, **43**	**35**, **40**, **44**	**36**, **41**, **45**	**37**, **42**, **46**
R	Et	*i*-Pr	*t*-Bu	Ph

Studies on the Utility of Compounds 9−**11 as Silylation Agents.** Each of the compounds **9**−**11** was tested with the series of alcohols consisting of ethanol, isopropanol, *tert*-butanol, and phenol, which served as models for primary, secondary, tertiary, and aromatic alcohols (*O*-nucleophiles), respectively. A stoichiometric amount of the alcohol to be silylated was treated with the respective (2,4,6-trimethoxyphenyl)silane in the presence of catalytic amounts of trifluoroacetic acid (typically 5−7 mol %) (Scheme 11). In all cases, the expected silylated alcohol could be identified as the only product, along with 1,3,5-trimethoxybenzene. The identities of the silylated alcohols **34**−**37** and **39**−**46** were verified by solution NMR studies (^{1}H, ^{13}C, ^{29}Si) and/or mass spectrometric analyses.

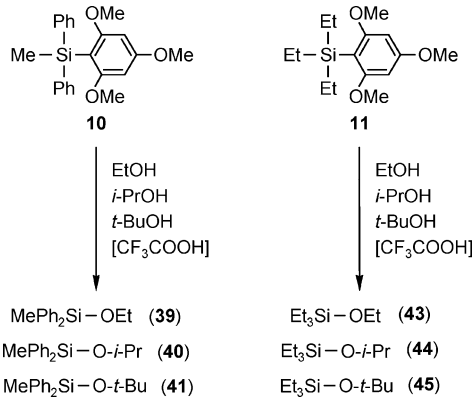
Although in all silylations trifluoroacetic acid was added as a catalyst, it was observed that the acidic OH function of phenol can catalyze the reaction without additional acid, albeit very slowly. Therefore, compound **9** was also tested with glycolic acid giving a positive result, showing that (2,4,6-trimethoxyphenyl)silanes are capable of silylating carboxylic acid functions in the absence of an additional acid catalyst.

It was found that the byproduct of the silylations, 1,3,5-trimethoxybenzene, is recyclable, as it could be reisolated in up to 85% yield to be reused in the syntheses of **9**−**11**. In some cases, the complete removal of 1,3,5-trimethoxybenzene was difficult due to similarities in the boiling points of product and byproduct. To address this problem, a convenient workup method was developed, whereby the major portion of 1,3,5-trimethoxybenzene was first removed by crystallization out of *n*-pentane solution at −20 °C, to make the final distillative purification of the products more efficient. Despite this workup strategy, some of the isolated yields were somewhat low. However, as was the case with the cleavage experiments, these yields were not a reflection of the efficiency of the reaction, as the conversion to the desired silylated products was always essentially quantitative (by GC). In cases in which silylated products have much higher boiling points than 1,3,5-trimethoxybenzene (e.g., high molecular mass silylated intermediates in the synthesis of natural products), this presents no problem. Once again, should the complete removal of the 1,3,5-trimethoxybenzene be impossible, it is conceivable that a small impurity

Scheme 12



Scheme 13



would not hinder further synthetic steps undertaken with the silylated product, as 1,3,5-trimethoxybenzene is likely relatively inert except in the presence of very strong bases and very strong electrophiles.

Silylations with **9** of *N*- and *S*-nucleophiles using morpholine and cyclohexanethiol, respectively, in the presence of catalytic amounts of trifluoroacetic acid were also attempted (Scheme 12). In neither case could the silylated products **47** and **48**, respectively, be identified in the reaction mixture.

In the case of morpholine, the conditions are too basic for the reaction to occur; the amine simply reacts with the protons of the trifluoroacetic acid, eliminating the catalyst necessary for the reaction. The most probable explanation for the failure of the silylation of cyclohexanethiol is that the trifluoroacetic acid itself was preferentially silylated by **9**. This would likewise result in a consumption of the catalytic protons (as 1,3,5-trimethoxybenzene). The reaction of **9** with glycolic acid also confirms the feasibility of this explanation. Silylations with **9**−**11** in the presence of catalytic amounts of trifluoroacetic acid therefore show chemoselectivity for *O*- and against *N*-and *S*-nucleophiles under the tested reaction conditions.

During the experimental work concerning the silylations of primary, secondary, and tertiary alcohols with **10** and **11**, a significant difference in the speed of the reactions was observed. This was so pronounced that the silylated products of the reactions with *tert*-butanol were not formally isolated, but were identified by mass spectrometry, because the reactions were not complete even over a period of several weeks. This selectivity was examined more closely in "competitive" silylations using a mixture of alcohols. Equimolar mixtures of ethanol, isopropanol, and *tert*-butanol were each treated with three molar equivalents of **10** and **11**, respectively, in the presence of catalytic amounts of trifluoroacetic acid (Scheme 13).

The relative concentrations of the respective silylation products were monitored by gas chromatography and plotted against the reaction time (Figure 1). If one assumes that the

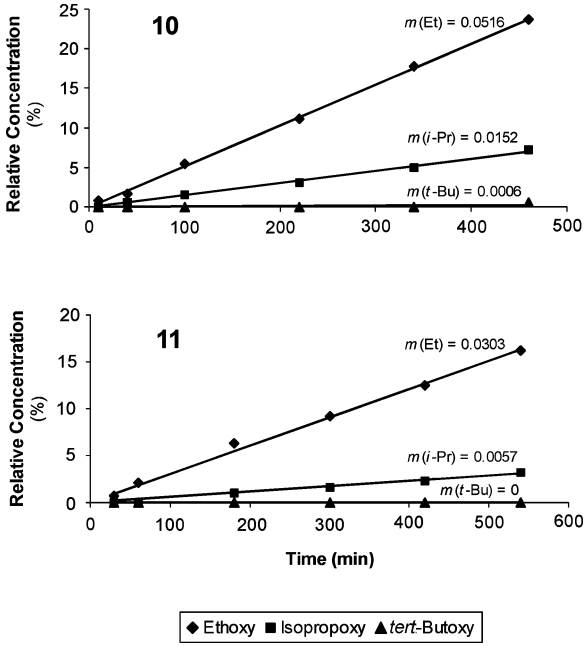


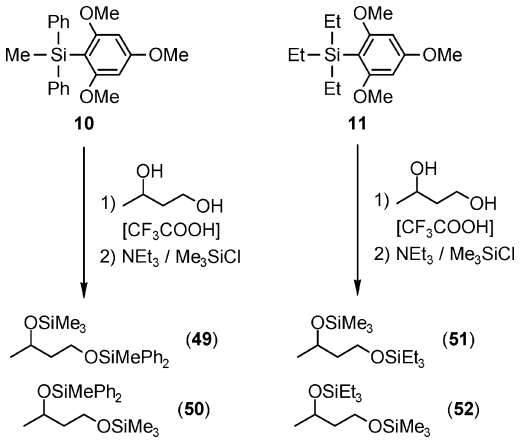
Figure 1. Selectivity of silylations with **10** (above) and **11** (below) using a mixture of primary (ethanol), secondary (isopropanol), and tertiary (*tert*-butanol) alcohols. The relative concentrations of the respective silylation products **39**−**41** and **43**−**45** were measured by gas chromatography (given in percent; the remainder of each mixture was composed of the unused portion of the respective silylation reagent **10** or **11** and the byproduct, 1,3,5-trimethoxybenzene). The slopes of the best-fit lines determined by linear regression are given by *m*.

slope of the best-fit line determined by linear regression can be used as a rough approximation for the speed of the reaction (particularly true at the beginning of the reaction when all three alcohols are present in about the same concentration), compound **10** silylates a primary alcohol ca. 3.4 times more quickly than a secondary alcohol, while **11** is able to silylate a primary alcohol ca. 5.3 times faster than a secondary alcohol. In both cases, the silylation of the tertiary alcohol was significantly slower, giving, in order of decreasing reactivity, the series one would expect based on steric arguments: primary > secondary ≫ tertiary.

To determine the extent to which this selectivity could potentially be utilized as a regioselectivity in the course of an actual synthesis, two experiments were performed using **10** and **11** to selectively silylate the primary hydroxyl function of a diol containing both a primary and a secondary hydroxyl group. Butane-1,3-diol was chosen as a model system because it probably represents a relatively difficult selectivity test, as there is no long or bulky alkyl rest at the α-position to the secondary hydroxyl function (Scheme 14).

In each case, butane-1,3-diol was treated with a stoichiometric amount of **10** or **11** in the presence of a catalytic amount of trifluoroacetic acid at 0 °C. To eliminate the possibility of the exchange of the silyl group between hydroxyl functions during the somewhat thermally harsh conditions of distillative purification, an excess of triethylamine was added and the remaining hydroxyl group was silylated in a standard procedure using chlorotrimethylsilane. (Triethylamine served to remove the trifluoroacetic acid by salt formation and thus to stop the first silylation reaction with **10** or **11**, and also to capture the hydrogen chloride formed in the second silylation with chlorotrimethylsilane.) The isomeric ratio of the mixtures isolated was determined by NMR analysis. In both experiments, the

Scheme 14



(2,4,6-trimethoxyphenyl)silanes **10** and **11** preferentially silylated the primary hydroxyl function as expected. In the case of **10**, the ratio *rac*-**49**/*rac*-**50** was ca. 82:18, giving an isomeric excess of 64%. For **11**, the ratio *rac*-**51**/*rac*-**52** was ca. 90:10, giving an isomeric excess of 80%. For comparison, the chlorosilane **32** silylated the primary hydroxyl group of butane-1,3-diol at 0 °C under basic conditions (in the presence of triethylamine), rather than acidic conditions as is the case with (2,4,6-trimethoxyphenyl)silanes, with a somewhat higher selectivity to give the ratio *rac*-**49**/*rac*-**50** of ca. 92:8.

Conclusions

This work has demonstrated that the TMOP group is indeed a unique and useful protecting group for silicon in synthesis. Using the new model compounds *rac*-**1**−*rac*-**4**, **5**, *rac*-**6**, *rac*-**7**, and **8**, we have been able to show that the TMOP group can be highly selectively removed under very mild conditions (1 mol equiv of hydrogen chloride in diethyl ether, 0 °C), in the presence of a wide range of other possible protecting groups for silicon to produce the corresponding synthetically useful chlorosilanes. Compared to the "traditional" hydrocarbon-based protecting groups for silicon tested, the TMOP group is by far the most readily removed by hydrogen chloride. As one expects, it is also much more easily cleaved than the DMOP and MOP groups, and thus offers the synthetic chemist a wide range of possibilities when used in conjunction with these other less labile protecting groups.

Additionally, this work has demonstrated that the (2,4,6-trimethoxyphenyl)silanes **9**−**11**, in the presence of catalytic amounts of an acid, may serve as very useful silylation reagents in synthesis under mild (0−35 °C) conditions, compared to "traditional" silylations done with chlorosilanes in the presence of a base or with other reagents such hexamethyldisilazane. Compounds **9**−**11** show a synthetically useful chemoselectivity for *O*-nucleophiles and against *N*- and *S*-nucleophiles. Additionally, the sterically hindered silanes **10** and **11** are able to differentiate between primary, secondary, and tertiary alcohols, giving good regioselective silylation of polyalcohols. Fine-tuning of this regioselectivity by modifying the substitution pattern of **9**−**11** (different combinations of the methyl, ethyl, and phenyl groups or introduction of other organyl groups, such as isopropyl or *tert*-butyl) should be possible. A convenient method of crystallization of the recyclable byproduct, 1,3,5-trimethoxybenzene, eased purification of the silylated products. Furthermore, as opposed to moisture sensitive chlorosilanes or disilazanes (e.g., hexamethyldisilazane), the silylation agents **9**−**11** can be easily handled as crystalline solids that are neither moisture nor air sensitive. In summary, (2,4,6-trimethoxyphenyl)silanes, such as **9**−**11**, can be regarded as a new class of silylation agents for organic alcohols and carboxylic acids, with a quite different set of properties. These novel reagents represent a synthetically useful addition to the commonly used "toolbox" of silylation agents.

Experimental Section

General Procedures. All syntheses (including the competitive silylations) were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR-51 apparatus was used for the bulb-to-bulb distillations. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed glass capillaries. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 22 °C on a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz), a Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz), or a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz). $CDCl_3$ or CD_2Cl_2 was used as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), $CHDCl_2$ (^{1}H, δ 5.32; CD_2Cl_2), CD_2Cl_2 (^{13}C, δ 53.8; CD_2Cl_2), or external TMS (^{29}Si, δ 0; $CDCl_3$, CD_2Cl_2). Analysis and assignment of the ^{1}H NMR data were supported by ^{1}H,^{1}H COSY, ^{13}C,^{1}H HMQC, ^{13}C,^{1}H HMBC, and ^{29}Si,^{1}H HMQC (optimized for $^{2}J_{SiH} = 7$ Hz) experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135, ^{13}C,^{1}H HMQC, and ^{13}C,^{1}H HMBC experiments. Gas chromatography (GC) was performed on a Shimadzu GC-14A or GC-14B gas chromatograph with a capillary column from Phenomenex of the type Zebron ZB-1 (length, 15 m; inside diameter, 0.32 mm). The other experimental parameters were as follows: flow rate, 0.67 mL/min; injector, split 30 mL/min, split ratio 1:10, 200 °C; detector, FID, 320 °C; carrier gas, N_2. The indicated retention times were obtained using the following temperature programs: program A, 40 °C (2 min) − 280 °C (10 min) with 20 °C/min; program B, 80 °C (2 min) − 280 °C (10 min) with 20 °C/min. Mass spectra were recorded on a coupled gas chromatograph−mass spectrometer (GC/EI-MS) with the following parameters: (a) gas chromatograph: Thermo MS-8060 with a capillary column from Phenomenex of the type Zebron ZB-1 (length, 15 m; inside diameter, 0.25 mm; flow rate, 1.00 mL/min; injector, split 36.6 mL/min, split ratio 1:25, 220 °C; carrier gas, He); temperature programs as above; (b) quadrupol mass spectrometer: Thermo TRIO-1000 with electron ionization (EI-MS, 70 eV). The *m*/*z* values of the molecular ions and the selected fragment ions are based on the atomic masses of the isotopes with the greatest natural abundance (^{1}H, ^{12}C, ^{35}Cl, ^{16}O, ^{28}Si).

Preparation of *rac*-Methyl(phenyl)(2,4,6-trimethoxyphenyl)-vinylsilane (*rac*-1). A 15 wt % solution of vinylmagnesium chloride (d = 0.97 g/mL; 41.5 mL, 69.6 mmol of Vi–MgCl) in THF was added dropwise at 20 °C within 30 min to a stirred solution of *rac*-**13** (19.5 g, 60.4 mmol) in THF (250 mL). After the addition was complete, the reaction mixture was heated under reflux for 1 h and subsequently stirred at 20 °C for 16 h, followed by the addition of water (2 mL). The solvent was removed under reduced pressure until the volume of the reaction mixture was ca. 50 mL. Diethyl ether (150 mL) and water (100 mL) were added, the organic layer was separated and washed with water (2 × 25 mL), and the combined aqueous layers were washed with diethyl ether (4 × 50 mL). The organic extracts were combined, dried over anhydrous sodium sulfate, and freed of solvents under reduced pressure. The residue was then dissolved in refluxing *n*-hexane (250 mL), and the resulting solution was stirred with activated charcoal for 5 min. The mixture was filtered hot through Celite 545 and the solvent removed under reduced pressure. The residue was redissolved in

refluxing *n*-hexane (200 mL), and the resulting solution was once again stirred for 5 min with activated charcoal and filtered hot through Celite 545. The filtrate was stored at −20 °C for 16 h and then separated by decantation from the oily film that had precipitated. The decanted solution was kept at −20 °C for 16 h, and the resulting precipitate was isolated by filtration and recrystallized twice from *n*-hexane at −20 °C to give *rac*-**1** in 63% yield as a colorless crystalline solid (12.0 g, 38.2 mmol); mp 68 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.62 (s, 3 H, SiCH_3), 3.61 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.80 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 5.71 (δ_A), 6.00 (δ_M), and 6.62 (δ_X) (3 H, CH_X=C$H_A H_M$, $^3J_{AX}$ = 20.5 Hz, $^2J_{AM}$ = 3.8 Hz, $^3J_{MX}$ = 14.5 Hz), 6.07 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 7.25−7.31 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.45−7.54 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ −1.7 (SiCH_3), 55.2 (*o*-OCH_3/*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.8 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 102.7 (*C*-1, $C_6H_2(OCH_3)_3$), 127.2 (*C*-3/*C*-5, C_6H_5), 128.2 (*C*-4, C_6H_5), 130.8 (CH=CH_2), 134.0 (*C*-2/*C*-6, C_6H_5), 139.3 (CH=CH_2), 139.7 (*C*-1, C_6H_5), 163.7 (*C*-4, $C_6H_2(OCH_3)_3$), 166.7 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ = −18.6. Anal. Calcd for $C_{18}H_{22}O_3Si$: C, 68.75; H, 7.05. Found: C, 68.3; H, 7.0.

Preparation of *rac*-Allyl(methyl)phenyl(2,4,6-trimethoxyphenyl)silane (*rac*-2). A solution of *rac*-**13** (21.5 g, 66.6 mmol) in diethyl ether (40 mL) was added dropwise at 20 °C within 30 min to a stirred solution of allylmagnesium chloride prepared from magnesium turnings (3.43 g, 141 mmol) and allyl chloride (10.2 g, 133 mmol) in diethyl ether (90 mL). After about half of the solution was added, the reaction mixture was diluted with diethyl ether (200 mL) to ease stirring. After the addition was complete, the reaction mixture was heated under reflux for 30 min, followed by the addition of water (100 mL). The aqueous layer was separated and washed with diethyl ether (4 × 100 mL), and the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The product crystallized from this residue and was redissolved in refluxing *n*-hexane (150 mL), and the resulting solution was filtered hot, diluted with *n*-hexane (50 mL), and once again heated to reflux. The product crystallized after slow cooling to −20 °C to give *rac*-**2** in 84% yield as a colorless crystalline solid (18.4 g, 56.0 mmol); mp 72 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.53 (s, 3 H, SiCH_3), 1.99−2.24 (m, 2 H, CH_2CH=CH_2), 3.63 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.80 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 4.75−4.89 (m, 2 H, CH_2CH=CH_2), 5.73−5.89 (m, 1 H, CH_2CH=CH_2), 6.06 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 7.22−7.30 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.45−7.53 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −2.2 (SiCH_3), 24.7 (CH_2CH=CH_2), 55.1 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.2 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.5 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 102.5 (*C*-1, $C_6H_2(OCH_3)_3$), 113.0 (CH_2CH=CH_2), 127.2 (*C*-3/*C*-5, C_6H_5), 128.2 (*C*-4, C_6H_5), 133.8 (*C*-2/*C*-6, C_6H_5), 136.1 (CH_2CH=CH_2), 139.9 (*C*-1, C_6H_5), 163.6 (*C*-4, $C_6H_2(OCH_3)_3$), 166.7 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −11.9. Anal. Calcd for $C_{19}H_{24}O_3Si$: C, 69.47; H, 7.36. Found: C, 69.2; H, 7.5.

Preparation of *rac*-Allyl(mesityl)methyl(2,4,6-trimethoxyphenyl)silane (*rac*-3). (a) Preparation of TMOP−Li. A 2.5 M solution of *n*-butyllithium in hexanes (37.0 mL, 92.5 mmol of *n*-BuLi) was added dropwise at 20 °C within 15 min to a stirred solution of 1,3,5-trimethoxybenzene (15.0 g, 89.2 mmol) in a mixture of 1,2-bis(dimethylamino)ethane (TMEDA; 10.6 g, 91.2 mmol) and *n*-hexane (60 mL), the resulting suspension of TMOP−Li was stirred at 20 °C for a further 16 h. **(b) Preparation of Mes–Li.** A 2.5 M solution of *n*-butyllithium in hexanes (75.0 mL, 188 mmol of *n*-BuLi) was added dropwise at −35 °C within 1 h to a stirred solution of 2-bromomesitylene (18.6 g, 93.4 mmol) in diethyl ether (150 mL). The reaction mixture was allowed to warm to −25 °C, stirred for 30 min at this temperature, and was then warmed to 20 °C within 1 h and stirred for a further 16 h (formation of a suspension of Mes–Li). **(c) Transformation of 14 into *rac*-3.** The suspension of TMOP−Li was added dropwise at 0 °C within 45 min to a stirred solution of **14** (13.3 g, 89.0 mmol) in diethyl ether (75 mL). The reaction mixture was stirred at 0 °C for 15 min, was allowed to warm to 20 °C, and was stirred for a further 30 min. The suspension of Mes–Li was then added dropwise at 0 °C within 45 min to the stirred reaction mixture, which was subsequently allowed to warm to 20 °C and stirred for 3 h. The precipitate was removed by filtration through a glass frit and washed with diethyl ether (3 × 50 mL), and the solvents were removed from the combined extracts under reduced pressure. The resulting residue was dissolved in a mixture of THF (100 mL) and *n*-hexane (150 mL), and the solution was added dropwise at 20 °C within 30 min to a stirred solution of allylmagnesium chloride prepared from magnesium turnings (5.61 g, 231 mmol) and allyl chloride (17.1 g, 223 mmol) in THF (120 mL). The reaction mixture was heated under reflux for 4 h, followed by the addition of water (100 mL). The organic layer was separated, the aqueous layer was diluted with water (150 mL) and washed with diethyl ether (5 × 100 mL), and the combined organic extracts were washed with water (50 mL), dried over anhydrous sodium sulfate, and freed of the solvents under reduced pressure. The oily residue was purified by bulb-to-bulb distillation (150−155 °C/0.01 mbar), and the solidified product was recrystallized from *n*-hexane (ca. 6 mL/1 g product) by slow cooling of a boiling solution to −20 °C to give *rac*-**3** in 36% yield (relative to **14**) as a colorless crystalline solid (11.9 g, 32.1 mmol); mp 110 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 0.60 (s, 3 H, SiCH_3), 2.13−2.26 (m, 5 H, CH_2CH=CH_2 and *p*-CH_3, $C_6H_2(CH_3)_3$), 2.29−2.31 (br. "s", 6 H, *o*-CH_3, $C_6H_2(CH_3)_3$), 3.58 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.78 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 4.72−4.84 (m, 2 H, CH_2CH=CH_2), 5.62−5.75 (m, 1 H, CH_2CH=CH_2), 6.03 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 6.69−6.72 (m, 2 H, *H*-3/*H*-5, $C_6H_2(CH_3)_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 2.6 (SiCH_3), 20.9 (*p*-CH_3, $C_6H_2(CH_3)_3$), 23.9 (*o*-CH_3, $C_6H_2(CH_3)_3$), 27.0 (CH_2CH=CH_2), 55.1 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 55.3 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 90.8 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 107.0 (*C*-1, $C_6H_2(OCH_3)_3$), 113.1 (CH_2-CH=CH_2), 128.6 (*C*-3/*C*-5, $C_6H_2(CH_3)_3$), 133.4 (*C*-1, $C_6H_2(CH_3)_3$), 136.6 (CH_2CH=CH_2) 137.4 (*C*-4, $C_6H_2(CH_3)_3$), 143.7 (*C*-2/*C*-6, $C_6H_2(CH_3)_3$), 163.0 (*C*-4, $C_6H_2(OCH_3)_3$), 165.6 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ −13.5. Anal. Calcd for $C_{22}H_{30}O_3Si$: C, 71.31; H, 8.16. Found: C, 71.2; H, 8.0.

Preparation of *rac*-Allyl(methyl)(1-naphthyl)(2,4,6-trimethoxyphenyl)silane (*rac*-4). (a) Preparation of TMOP−Li. A 2.5 M solution of *n*-butyllithium in hexanes (37.5 mL, 93.8 mmol of *n*-BuLi) was added dropwise at 20 °C within 20 min to a stirred solution of 1,3,5-trimethoxybenzene (15.0 g, 89.2 mmol) in a mixture of TMEDA (10.8 g, 92.9 mmol) and *n*-hexane (60 mL), and the resulting suspension of TMOP−Li was stirred at 20 °C for a further 16 h. **(b) Preparation of Np−Li**. A 2.5 M solution of *n*-butyllithium in hexanes (75.0 mL, 188 mmol of *n*-BuLi) was added dropwise at −50 °C within 30 min to a stirred solution of 1-bromonaphthalene (19.4 g, 93.7 mmol) in diethyl ether (150 mL). The reaction mixture was allowed to warm to −25 °C within 1 h, was then warmed to 0 °C within 30 min and stirred at this temperature for 30 min, and was finally warmed to 20 °C and stirred for a further 16 h (formation of a suspension of Np−Li). **(c) Transformation of 14 into *rac*-4.** The suspension of TMOP−Li was added dropwise at 0 °C within 45 min to a stirred solution of **14** (13.3 g, 89.0 mmol) in diethyl ether (100 mL). The reaction mixture was stirred at 0 °C for 15 min, was allowed to warm to 20 °C, and was stirred for a further 15 min. The suspension of Np−Li was then added dropwise at 0 °C within 30 min to the stirred reaction mixture, which was subsequently allowed to warm to 20 °C and stirred for 4.5 h. Finally, a solution of allylmagnesium chloride prepared from magnesium turnings (6.79 g, 279 mmol) and allyl chloride (20.5 g, 268 mmol) in THF (150 mL) was added dropwise at 20 °C within 10 min to the stirred reaction mixture, which was then heated under reflux for 1 h, followed by the addition

of water (200 mL). The organic layer was separated and washed with water (2 × 100 mL), the combined aqueous layers were diluted with water (400 mL) and washed with diethyl ether (2 × 100 mL), and the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting oily residue was purified three times by bulb-to-bulb distillation (first: 185−215 °C/0.01 mbar; second and third: 180−185 °C/0.01 mbar) to give *rac*-**4** in 52% yield as a colorless highly viscous liquid (17.4 g, 46.0 mmol). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.68 (s, 3 H, SiCH_3), 2.22−2.29 and 2.34−2.41 (m, 2 H, CH_2CH=CH_2), 3.53 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.78 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 4.72−4.87 (m, 2 H, CH_2CH=CH_2), 5.69−5.81 (m, 1 H, CH_2CH=CH_2), 6.05 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 7.30−7.35 (m, 1 H, *H*-6, $C_{10}H_7$), 7.36−7.40 (m, 1 H, *H*-7, $C_{10}H_7$), 7.41−7.45 (m, 1 H, *H*-3, $C_{10}H_7$), 7.70−7.74 (m, 1 H, *H*-2, $C_{10}H_7$), 7.78−7.81 (m, 2 H, *H*-4/*H*-8, $C_{10}H_7$), 8.08−8.11 (m, 1 H, *H*-5, $C_{10}H_7$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ −1.5 (SiCH_3), 24.8 (CH_2CH=CH_2), 55.09 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.11 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.7 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 103.8 (*C*-1, $C_6H_2(OCH_3)_3$), 113.1 (CH_2CH=CH_2), 124.8 (*C*-7, $C_{10}H_7$), 124.9 (*C*-3, $C_{10}H_7$), 125.0 (*C*-6, $C_{10}H_7$), 128.5 (*C*-5, $C_{10}H_7$), 128.6 (*C*-8, $C_{10}H_7$), 128.8 (*C*-4, $C_{10}H_7$), 132.9 (*C*-2, $C_{10}H_7$), 133.2 (*C*-4a, $C_{10}H_7$), 136.1 (CH_2CH=CH_2), 136.9 (*C*-8a, $C_{10}H_7$), 138.5 (*C*-1, $C_{10}H_7$), 163.5 (*C*-4, $C_6H_2(OCH_3)_3$), 166.3 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ −12.7. Anal. Calcd for $C_{23}H_{26}O_3Si$: C, 72.98; H, 6.92. Found: C, 73.1; H, 7.0.

Preparation of Dimethyl(2,4,6-trimethoxyphenyl)(trimethylsilyloxy)silane (5). A 2.5 M solution of *n*-butyllithium in hexanes (21.5 mL, 53.8 mmol of *n*-BuLi) was added dropwise at 20 °C within 20 min to a stirred solution of 1,3,5-trimethoxybenzene (8.75 g, 52.0 mmol) in a mixture of TMEDA (6.20 g, 53.4 mmol) and *n*-hexane (40 mL). The resulting suspension of TMOP−Li was stirred at 20 °C for a further 16 h and then added dropwise at 0 °C within 30 min to a stirred solution of **15** (6.71 g, 52.0 mmol) in *n*-hexane (50 mL). The reaction mixture was allowed to warm to 20 °C and stirred at this temperature for 45 min, a suspension of TMSO−Li (5.00 g, 52.0 mmol; Aldrich) in *n*-hexane (40 mL) was added dropwise at 20 °C within 20 min, and the mixture was stirred at 20 °C for 16 h. The precipitate was removed by filtration and washed with diethyl ether (2 × 50 mL), and the combined organic extracts were washed with water (3 × 50 mL), dried over anhydrous sodium sulfate, and freed of the solvents under reduced pressure. The product was purified twice by bulb-to-bulb distillation (120 °C/ 0.1 mbar), and it solidified thereafter immediately to give **5** in 73% yield as a colorless crystalline solid (12.0 g, 38.2 mmol); mp 33−34 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.01 (s, 9 H, Si-(CH_3)$_3$), 0.30 (s, 6 H, Si(CH_3)$_2$), 3.72 (s, 6 H, *o*-OCH_3, C_6H_2-$(OCH_3)_3$), 3.80 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 6.04 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 1.8 (Si(CH_3)$_3$), 3.9 (Si(CH_3)$_2$), 55.0 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.1 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.2 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 106.1 (*C*-1, $C_6H_2(OCH_3)_3$), 163.2 (*C*-4, $C_6H_2(OCH_3)_3$), 166.3 (*C*-2/*C*-6, C_6H_2-$(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −4.5 (Si(CH_3)$_2$), 6.4 (Si(CH_3)$_3$). Anal. Calcd for $C_{14}H_{26}O_4Si_2$: C, 53.46; H, 8.33. Found: C, 53.5; H, 8.3.

Preparation of *rac*-Allyl(mesityl)(1-naphthyl)phenylsilane (*rac*-6). (a) Preparation of Mes–Li. A 2.5 M solution of *n*-butyllithium in hexanes (128 mL, 320 mmol of *n*-BuLi) was added dropwise at −50 °C within 1 h to a stirred solution of 2-bromomesitylene (31.9 g, 160 mmol) in diethyl ether (240 mL). The reaction mixture was allowed to warm to −20 °C within 1 h, stirred for 30 min at this temperature, and was then warmed to 20 °C within 1 h and stirred for a further 16 h (formation of a suspension of Mes–Li). **(b) Preparation of Np−Li.** A 2.5 M solution of *n*-butyllithium in hexanes (128 mL, 320 mmol of *n*-BuLi) was added dropwise at −50 °C within 1 h to a stirred solution of 1-bromonaphthalene (33.1 g, 160 mmol) in diethyl ether (240 mL). The reaction mixture was allowed to warm to −20 °C within 1 h, stirred for 30 min at this temperature, and then allowed to warm to 20 °C within 1 h. The reaction mixture was diluted with diethyl ether (100 mL) and stirred at 20 °C for 16 h (formation of a suspension of Np−Li). **(c) Transformation of 16 into *rac*-6.** The suspension of Mes–Li was added dropwise at 0 °C within 1 h to a stirred solution of **16** (33.8 g, 160 mmol) in diethyl ether (150 mL), and the mixture was allowed to warm to 20 °C and stirred for 30 min. The suspension of Np−Li was then added dropwise at 0 °C within 1 h to the stirred reaction mixture, which was allowed to warm to 20 °C and stirred for 16 h. Finally, a solution of allylmagnesium chloride prepared from magnesium turnings (12.2 g, 502 mmol) and allyl chloride (36.7 g, 480 mmol) in THF (250 mL) was added dropwise at 20 °C within 30 min to the stirred reaction mixture, which was then heated under reflux for 1 h, followed by the addition of water (500 mL). The organic layer was separated and washed with water (2 × 100 mL), the combined aqueous layers were washed with diethyl ether (2 × 200 mL), and the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting oily residue was purified by bulb-to-bulb distillation (195−200 °C/0.01 mbar) to give a highly viscous liquid, which was crystallized from isopropanol (ca. 12 mL/1 g product) by cooling of a solution from 20 °C to −20 °C to give *rac*-**6** in 33% yield as a colorless crystalline solid (20.8 g, 53.0 mmol); mp 82−83 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.07−2.10 (br. "s", 6 H, *o*-CH_3, $C_6H_2(CH_3)_3$), 2.28−2.30 (br. "s", 3 H, *p*-CH_3, $C_6H_2(CH_3)_3$), 2.55−2.70 (m, 2 H, CH_2CH=CH_2), 4.64−4.73 and 4.82−4.93 (m, 2 H, CH_2CH=CH_2), 5.42−5.59 (m, 1 H, CH_2CH=CH_2), 6.80−6.85 (m, 2 H, *H*-3/*H*-5, $C_6H_2(CH_3)_3$), 7.28−7.47 (m, 6 H, *H*-3/*H*-4/*H*-5, C_6H_5, and *H*-3/*H*-6/*H*-7, $C_{10}H_7$), 7.53−7.58 (m, 1 H, *H*-2, $C_{10}H_7$), 7.61−7.68 (m, 2 H, *H*-2/*H*-6, C_6H_5), 7.81−7.88 (m, 2 H, *H*-4/*H*-8, $C_{10}H_7$), 7.92−7.99 (m, 1 H, *H*-5, $C_{10}H_7$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.0 (*p*-CH_3, $C_6H_2(CH_3)_3$), 25.2 (*o*-CH_3, $C_6H_2(CH_3)_3$), 25.6 (CH_2CH=CH_2), 114.7 (CH_2-CH=CH_2), 125.3 (*C*-7, $C_{10}H_7$), 125.5 (*C*-3, $C_{10}H_7$), 125.8 (*C*-6, $C_{10}H_7$), 127.9 (*C*-3/*C*-5, C_6H_5), 128.2 (*C*-8, $C_{10}H_7$), 128.9 (*C*-5, $C_{10}H_7$), 129.3 (*C*-4, C_6H_5), 129.4 (*C*-3/*C*-5, $C_6H_2(CH_3)_3$), 129.8 (*C*-4, $C_{10}H_7$), 133.3 (*C*-1, C_6H_5, and *C*-1, $C_6H_2(CH_3)_3$), 134.9 (*C*-2, $C_{10}H_7$), 135.5 (CH_2CH=CH_2), 135.7 (*C*-2/*C*-6, C_6H_5), 137.1 (*C*-4a, $C_{10}H_7$), 137.19 (*C*-8a, $C_{10}H_7$), 137.21 (*C*-1, $C_{10}H_7$), 139.3 (*C*-4, $C_6H_2(CH_3)_3$), 145.4 (*C*-2/*C*-6, $C_6H_2(CH_3)_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −14.5. Anal. Calcd for $C_{28}H_{28}Si$: C, 85.66; H, 7.19. Found: C, 85.3; H, 7.4.

Preparation of *rac*-(2,6-Dimethoxyphenyl)(4-methoxyphenyl)-phenyl(2,4,6-trimethoxyphenyl)silane (*rac*-7). A 2.5 M solution of *n*-butyllithium in hexanes (5.12 mL, 12.8 mmol of *n*-BuLi) was added dropwise at −75 °C within 5 min to a stirred solution of 1-bromo-4-methoxybenzene (2.23 g, 11.9 mmol) in THF (20 mL). After stirring the resulting mixture at −75 °C for a further 30 min, a solution of *rac*-**18** (4.08 g, 9.17 mmol) in THF (10 mL) was added within 10 min. After addition of THF (20 mL), the reaction mixture was allowed to warm to 20 °C and then stirred at 20 °C for 2 days. The solvent was removed under reduced pressure, and the residue was dried in vacuo (0.01 mbar, 20 °C, 2 h) and then dissolved in a refluxing mixture of diethyl ether (50 mL) and *n*-hexane (50 mL). The insoluble components were filtered off and washed sequentially with diethyl ether (2 × 10 mL) and a mixture of *n*-hexane and THF (1:1 (v/v)) (2 × 10 mL). The filtrate and wash solutions were combined, and the resulting solution was kept undisturbed at −20 °C for 2 days, and the resulting solid was isolated by filtration to give *rac*-**7** in 30% yield as a colorless solid (1.42 g, 2.75 mmol); mp 135−137 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 3.30 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.32 (s, 6 H, C_6H_3-$(OCH_3)_2$), 3.78 (s, 3 H, $C_6H_4OCH_3$), 3.80 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 6.07 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 6.49 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, *H*-3/*H*-5, $C_6H_3(OCH_3)_2$), 6.77−6.81 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.18−7.27 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.29

(t, $^3J_{HH}$ = 8.2 Hz, 1 H, *H*-4, $C_6H_3(OCH_3)_2$), 7.43−7.49 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$), 7.50−7.54 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 55.2 (*o*-O*C*H$_3$, $C_6H_2(OCH_3)_3$, and $C_6H_4OCH_3$), 55.3 ($C_6H_3(OCH_3)_2$), 55.5 (*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 91.2 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 104.5 (*C*-3/*C*-5, $C_6H_3(OCH_3)_2$), 105.9 (*C*-1, $C_6H_2(OCH_3)_3$), 112.4 (*C*-3/*C*-5, $C_6H_4OCH_3$), 114.9 (*C*-1, $C_6H_3(OCH_3)_2$), 126.6 (*C*-3/*C*-5, C_6H_5), 127.8 (*C*-4, $C_6H_3(OCH_3)_2$), 130.5 (*C*-1, $C_6H_4OCH_3$), 131.4 (*C*-4, C_6H_5), 136.4 (*C*-2/*C*-6, C_6H_5), 138.0 (*C*-2/*C*-6, $C_6H_4OCH_3$), 140.4 (*C*-1, C_6H_5), 159.9 (*C*-4, $C_6H_4OCH_3$), 163.5 (*C*-4, $C_6H_2(OCH_3)_3$), 165.5 (*C*-2/*C*-6, $C_6H_3(OCH_3)_2$), 166.4 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ −23.8. Anal. Calcd for $C_{30}H_{32}O_6Si$: C, 69.74; H 6.24. Found: C, 69.6; H, 6.3.

Preparation of (4-Methoxyphenyl)phenylbis(2,4,6-trimethoxyphenyl)silane (8). A 2.5 M solution of *n*-butyllithium in hexanes (4.00 mL, 10.0 mmol of *n*-BuLi) was added dropwise at −75 °C within 5 min to a stirred solution of 1-bromo-4-methoxybenzene (1.75 g, 9.36 mmol) in THF (30 mL). After stirring the resulting mixture at −75 °C for a further 30 min, a solution of **19** (3.29 g, 6.93 mmol) in THF (25 mL) was added within 10 min. The reaction mixture was allowed to warm to 20 °C and then stirred at 20 °C for 6 days. The solvent was removed under reduced pressure, and the residue was dried in vacuo (0.01 mbar, 20 °C, 1 h) and then dissolved in a refluxing mixture of diethyl ether (30 mL) and *n*-hexane (30 mL). The insoluble components were filtered off, washed with diethyl ether (2 × 10 mL), and discarded. The filtrate and wash solutions were combined, and the resulting solution was kept undisturbed at −20 °C for 2 days, and the resulting solid was isolated by filtration to give **8** in 51% yield as a colorless solid (1.94 g, 3.55 mmol); mp 146−149 °C. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ 3.31 (s, 12 H, *o*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 3.78 (s, 3 H, $C_6H_4OCH_3$), 3.81 (s, 6 H, *p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 6.08 (s, 4 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 6.78−6.81 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.20−7.25 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.44−7.47 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$), 7.50−7.53 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 55.2 (*o*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 55.3 (*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 55.5 ($C_6H_4OCH_3$), 91.3 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 106.1 (*C*-1, $C_6H_2(OCH_3)_3$), 112.4 (*C*-3/*C*-5, $C_6H_4OCH_3$), 126.6 (*C*-3/*C*-5, C_6H_5), 127.7 (*C*-4, C_6H_5), 130.9 (*C*-1, $C_6H_4OCH_3$), 136.3 (*C*-2/*C*-6, C_6H_5), 137.9 (*C*-2/*C*-6, $C_6H_4OCH_3$), 140.8 (*C*-1, C_6H_5), 159.8 (*C*-4, $C_6H_4OCH_3$), 163.5 (*C*-4, $C_6H_2(OCH_3)_3$), 166.5 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (99.4 MHz, CD_2Cl_2): δ −24.5. Anal. Calcd for $C_{31}H_{34}O_7Si$: C, 68.11; H, 6.27. Found: C, 68.1; H, 6.3.

General Procedure for the Synthesis of the Silylation Reagents 9−11. A suspension of one molar equivalent of (2,4,6-trimethoxyphenyl)lithium was prepared using *n*-buthyllithium (2.5 M in hexanes) and TMEDA as described above, and a solution of the respective chlorosilane in *n*-hexane (ca. 1 g/mL) was added dropwise within ca. 30 min. The resulting mixture was subsequently stirred at 20 °C or heated under reflux until the reaction was complete (GC control). The precipitate was removed by filtration, washed with diethyl ether, and discarded. The filtrate and wash solutions were combined, the solvents were removed under reduced pressure, and the residue was dried in vacuo (0.01 mbar, 20 °C, 1 h). The oily crude product was redissolved in refluxing *n*-hexane, the hot mixture was filtered, and the filtrate was allowed to cool slowly to −20 °C. The resulting solid was isolated by filtration and then further purified by recrystallization from *n*-hexane at −20 °C.

Preparation of Trimethyl(2,4,6-trimethoxyphenyl)silane (9). Treatment of a suspension of (2,4,6-trimethoxyphenyl)lithium made from a 2.5 M solution of *n*-butyllithium in hexanes (76.0 mL, 190 mmol of *n*-BuLi), TMEDA (22.1 g, 190 mmol), and 1,3,5-trimethoxybenzene (31.0 g, 184 mmol) with **31** (20.0 g, 184 mmol) gave **9** in 74% yield as a colorless crystalline solid (32.7 g, 136 mmol); mp 82 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.24 (s, 9 H, Si*CH*$_3$), 3.72 (s, 6 H, *o*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 3.80 (s, 3 H, *p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 6.06 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 1.4 (Si*C*H$_3$), 55.1 (*o*-O*C*H$_3$/*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 90.4 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 105.8 (*C*-1, $C_6H_2(OCH_3)_3$), 163.0 (*C*-4, $C_6H_2(OCH_3)_3$), 166.3 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −6.6. GC/EI-MS: t_R, 7.1 min (B); *m*/*z* (%), 240 (23) [M$^+$], 165 (100). Anal. Calcd for $C_{12}H_{20}O_3Si$: C, 59.96; H, 8.39. Found: C, 59.9; H 8.1.

Preparation of Methyldiphenyl(2,4,6-trimethoxyphenyl)silane (10). Treatment of a suspension of (2,4,6-trimethoxyphenyl)lithium made from a 2.5 M solution of *n*-butyllithium in hexanes (53.2 mL, 133 mmol of *n*-BuLi), TMEDA (15.5 g, 133 mmol), and 1,3,5-trimethoxybenzene (21.7 g, 129 mmol) with **32** (30.0 g, 129 mmol) gave **10** in 78% yield as a colorless crystalline solid (36.9 g, 101 mmol); mp 109 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.80 (s, 3 H, Si*CH*$_3$), 3.46 (s, 6 H, *o*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 3.81 (s, 3 H, *p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 6.07 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 7.23−7.35 (m, 6 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.47−7.56 (m, 4 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 0.5 (Si*C*H$_3$), 55.0 (*o*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 55.2 (*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 90.8 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 102.3 (*C*-1, $C_6H_2(OCH_3)_3$), 127.2 (*C*-3/*C*-5, C_6H_5), 128.2 (*C*-4, C_6H_5), 134.7 (*C*-2/*C*-6, C_6H_5), 139.5 (*C*-1, C_6H_5), 163.9 (*C*-4, $C_6H_2(OCH_3)_3$), 166.9 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −14.4. GC/EI-MS: t_R, 11.9 min (B); *m*/*z* (%), 364 (36) [M$^+$], 349 (100). Anal. Calcd for $C_{22}H_{24}O_3Si$: C, 72.49; H, 6.64. Found: C, 72.4; H, 6.7.

Preparation of Triethyl(2,4,6-trimethoxyphenyl)silane (11). Treatment of a suspension of (2,4,6-trimethoxyphenyl)lithium made from a 2.5 M solution of *n*-butyllithium in hexanes (13.5 mL, 33.8 mmol of *n*-BuLi), TMEDA (3.94 g, 33.9 mmol), and 1,3,5-trimethoxybenzene (5.58 g, 33.2 mmol) with **33** (5.01 g, 33.2 mmol) gave **11** in 72% yield as a colorless crystalline solid (6.77 g, 24.0 mmol); mp 45 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.72−0.82 (m, 6 H, C*H*$_2$CH$_3$), 0.85−0.94 (m, 9 H, CH$_2$C*H*$_3$), 3.71 (s, 6 H, *o*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 3.80 (s, 3 H, *p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 6.05 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 5.3 (*C*H$_2$CH$_3$), 7.9 (CH$_2$*C*H$_3$), 55.0 (*o*-O*C*H$_3$/*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 90.2 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 103.3 (*C*-1, $C_6H_2(OCH_3)_3$), 162.9 (*C*-4, $C_6H_2(OCH_3)_3$), 166.8 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 2.5. GC/EI-MS: t_R, 8.5 min (B); *m*/*z* (%), 282 (45) [M$^+$], 253 (100). Anal. Calcd for $C_{15}H_{26}O_3Si$: C, 63.79; H, 9.28. Found: C, 63.9; H 9.1.

Dichloro(methyl)phenylsilane (12). This compound was commercially available.

Preparation of *rac*-Chloro(methyl)phenyl(2,4,6-trimethoxyphenyl)silane (*rac*-13). A 2.5 M solution of *n*-butyllithium in hexanes (46.0 mL, 115 mmol of *n*-BuLi) was added dropwise at 20 °C within 10 min to a stirred solution of 1,3,5-trimethoxybenzene (18.6 g, 111 mmol) in a mixture of TMEDA (13.3 g, 114 mmol) and *n*-hexane (70 mL). The resulting suspension of TMOP−Li was stirred at 20 °C for a further 16 h and then added dropwise at 0 °C within 30 min to a stirred solution of **12** (22.0 g, 115 mmol) in *n*-hexane (100 mL). The reaction mixture was diluted with *n*-hexane (100 mL) and stirred at 0 °C for 30 min and then at 20 °C for a further 16 h. The precipitate was removed by filtration through a glass frit and washed with diethyl ether (2 × 20 mL), and the filtrate and wash solutions were combined and concentrated under reduced pressure. The resulting residue was dried in vacuo (0.01 mbar, 20 °C, 1 h) and then dissolved in refluxing *n*-hexane (150 mL). The insoluble components were removed by filtration of the hot solution, and the filtrate was diluted with *n*-hexane (200 mL). The product crystallized from the resulting solution after it was kept at −20 °C for 7 days and was isolated by filtration, washed with cold (0 °C) *n*-hexane, and dried in vacuo (0.01 mbar, 20 °C, 1 h) to give *rac*-**13** in 73% yield as a colorless crystalline solid (26.3 g, 81.5 mmol); mp 55−56 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 0.91 (s, 3 H, Si*CH*$_3$), 3.65 (s, 6 H, *o*-OC*H*$_3$, $C_6H_2(OCH_3)_3$),

3.82 (s, 3 H, *p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 6.10 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 7.31−7.39 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.60−7.66 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 5.8 (Si*C*H$_3$), 55.6 (*o*-OC*H*$_3$/*p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 91.1 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 101.0 (*C*-1, $C_6H_2(OCH_3)_3$), 127.8 (*C*-3/*C*-5, C_6H_5), 129.6 (*C*-4, C_6H_5), 133.6 (*C*-2/*C*-6, C_6H_5), 138.7 (*C*-1, C_6H_5), 165.4 (*C*-4, $C_6H_2(OCH_3)_3$), 167.1 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ 7.2. Anal. Calcd for $C_{16}H_{19}ClO_3Si$: C, 59.52; H, 5.93. Found: C, 59.4; H, 5.9.

Trichloro(methyl)silane (14). This compound was commercially available.

Dichlorodimethylsilane (15). This compound was commercially available.

Trichloro(phenyl)silane (16). This compound was commercially available.

Preparation of Trichloro(phenyl)silane (16). Trifluoromethanesulfonic acid (2.33 g, 15.5 mmol) was added in a single portion at 0 °C to a stirred solution of **28** (4.00 g, 14.1 mmol) in *n*-hexane (30 mL). After the reaction mixture was stirred at 0 °C for 2.5 h (complete and selective cleavage of the MOP group (by GC control)), triethylammonium chloride (2.33 g, 16.9 mmol) was added in a single portion, and the mixture was stirred at 0 °C for 1 h and then kept undisturbed at −20 °C for 17 h. The upper layer of the resulting two-phase sytem was separated from the lower layer (triethylammonium trifluoromethanesulfonate) by means of a syringe, and the solvent was removed by distillation at atmospheric pressure. The resulting residue was purified twice by fractional distillation in vacuo to give **16** in 52% yield as a colorless liquid (1.54 g, 7.28 mmol); bp 65−66 °C/7 mbar. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 7.51−7.56 (m, 2 H, *H*-3/*H*-5), 7.59−7.65 (m, 1 H, *H*-4), 7.82−7.85 (m, 2 H, *H*-2/*H*-6). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 129.0 (*C*-3/*C*-5), 131.7 (*C*-1), 133.3 (*C*-4), 133.5 (*C*-2/*C*-6). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ 0.6. These NMR data were identical to those of a commercially available sample.

Preparation of Dichloro(phenyl)(2,4,6-trimethoxyphenyl)-silane (17). A 2.5 M solution of *n*-butyllithium in hexanes (12.2 mL, 30.5 mmol of *n*-BuLi) was added dropwise at 20 °C within 10 min to a stirred solution of 1,3,5-trimethoxybenzene (4.89 g, 29.1 mmol) in a mixture of TMEDA (3.56 g, 30.6 mmol) and *n*-hexane (30 mL). The resulting suspension of TMOP−Li was stirred at 20 °C for a further 20 h and then added to a stirred solution of **16** (6.16 g, 29.1 mmol) in *n*-hexane (20 mL) at 0 °C within 10 min. The mixture was stirred at 0 °C for 2 h and then at 20 °C for a further 21 h. The precipitate was filtered off and washed with diethyl ether (2 × 20 mL), the filtrate and wash solutions were combined, and the solvents were removed under reduced pressure. The oily residue was purified by fractional distillation in vacuo to give 5.92 g of a yellowish oil (bp 145−149 °C/0.02 mbar), which was dissolved in refluxing *n*-hexane (60 mL). The insoluble components were filtered off and discarded, and the filtrate was kept at −20 °C for 7 days. The resulting solid was isolated by filtration, washed with cold (0 °C) *n*-hexane, and dried in vacuo (0.01 mbar, 20 °C, 1 h) to give **17** in 48% yield as a colorless crystalline solid (4.76 g, 13.9 mmol); mp 41−43 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 3.62 (s, 6 H, *o*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 3.83 (s, 3 H, *p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 6.10 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 7.38−7.49 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.73−7.77 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 55.7 (*o*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 55.8 (*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 91.4 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 99.0 (*C*-1, $C_6H_2(OCH_3)_3$), 128.0 (*C*-3/*C*-5, C_6H_5), 130.7 (*C*-4, C_6H_5), 133.4 (*C*-2/*C*-6, C_6H_5), 137.1 (*C*-1, C_6H_5), 166.4 (*C*-4, $C_6H_2(OCH_3)_3$), 167.0 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ 0.9. Anal. Calcd for $C_{15}H_{16}Cl_2O_3Si$: C, 52.48; H, 4.70. Found: C, 52.6; H, 4.7.

Preparation of *rac*-Chloro(2,6-dimethoxyphenyl)phenyl(2,4,6-trimethoxyphenyl)silane (*rac*-18). A 2.5 M solution of *n*-butyllithium in hexanes (7.16 mL, 17.9 mmol of *n*-BuLi) was added dropwise at 0 °C within 15 min to a stirred solution of 1,3-dimethoxybenzene (2.48 g, 17.9 mmol) in a mixture of TMEDA (2.10 g, 18.1 mmol) and *n*-hexane (40 mL). The resulting suspension of DMOP−Li was stirred at 20 °C for a further 17 h and subsequently added to a stirred solution of **17** (6.16 g, 17.9 mmol) in diethyl ether (20 mL) at 0 °C within 10 min. After addition of diethyl ether (60 mL) and *n*-hexane (20 mL), the reaction mixture was heated under reflux for 2.5 h. The precipitate was filtered off and washed with diethyl ether (2 × 20 mL), and the filtrate and wash solutions were combined and concentrated under reduced pressure. The residue was dried in vacuo (0.01 mbar, 50 °C, 4 h) and then dissolved in a refluxing mixture of *n*-hexane (100 mL) and diethyl ether (100 mL). After removing insoluble components by filtration, the filtrate was kept at −20 °C for 7 days. The resulting solid was isolated by filtration, washed with *n*-hexane (2 × 10 mL), and recrystallized from diethyl ether (70 mL) by slow cooling of a boiling solution to −20 °C to give *rac*-**18** in 25% yield as a colorless crystalline solid (2.01 g, 4.52 mmol); mp 79−80 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 3.45 (s, 6 H, *o*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 3.48 (s, 6 H, $C_6H_3(OCH_3)_2$), 3.82 (s, 3 H, *p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 6.10 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 6.52 (d, $^3J_{HH}$ = 8.3 Hz, 2 H, *H*-3/*H*-5, $C_6H_3(OCH_3)_2$), 7.27−7.36 (m, 4 H, *H*-3/*H*-4/*H*-5, C_6H_5, and *H*-4, $C_6H_3(OCH_3)_2$), 7.61−7.68 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 55.6 (*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 55.6 (*o*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 55.7 ($C_6H_3(OCH_3)_2$), 91.4 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 104.2 (*C*-1, $C_6H_2(OCH_3)_3$), 104.7 (*C*-3/*C*-5, $C_6H_3(OCH_3)_2$), 113.2 (*C*-1, $C_6H_3(OCH_3)_2$), 127.1 (*C*-3/*C*-5, C_6H_5), 128.9 (*C*-4, C_6H_5), 132.6 (*C*-4, $C_6H_3(OCH_3)_2$), 134.4 (*C*-2/*C*-6, C_6H_5), 139.9 (*C*-1, C_6H_5), 164.4 (*C*-4, $C_6H_2(OCH_3)_3$), 165.3 (*C*-2/*C*-6, $C_6H_3(OCH_3)_2$), 166.4 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ −8.7. Anal. Calcd for $C_{23}H_{25}ClO_5Si$: C, 62.08; H, 5.66. Found: C, 62.4; H, 5.8.

Preparation of Chloro(phenyl)bis(2,4,6-trimethoxyphenyl)-silane (19). A 2.5 M solution of *n*-butyllithium in hexanes (17.6 mL, 44.0 mmol of *n*-BuLi) was added dropwise at 20 °C within 15 min to a stirred solution of 1,3,5-trimethoxybenzene (7.06 g, 42.0 mmol) in a mixture of TMEDA (4.88 g, 42.0 mmol) and *n*-hexane (50 mL). The resulting suspension of TMOP−Li was stirred at 20 °C for a further 16 h and subsequently added to a stirred solution of **16** (4.45 g, 21.0 mmol) in a mixture of *n*-hexane (50 mL) and THF (50 mL) at 0 °C within 20 min. After addition of *n*-hexane (60 mL), the reaction mixture was heated under reflux for 1 h. The precipitate was filtered off and washed with *n*-hexane (2 × 10 mL), and the filtrate and wash solutions were combined and concentrated under reduced pressure. The oily residue was dried in vacuo (0.01 mbar, 50 °C, 2 h) and then dissolved in a refluxing mixture of *n*-hexane (70 mL) and THF (50 mL). After removing insoluble components by filtration, the filtrate was kept undisturbed at −20 °C for 3 days. The resulting solid was isolated by filtration and then further purified by recrystallization from a mixture of *n*-hexane (10 mL) and THF (10 mL) by slow cooling of a boiling solution to −20 °C to give **19** in 33% yield as a colorless crystalline solid (3.28 g, 6.91 mmol); mp 129−132 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 3.46 (s, 12 H, *o*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 3.81 (s, 6 H, *p*-OC*H*$_3$, $C_6H_2(OCH_3)_3$), 6.08 (s, 4 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 7.28−7.33 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.60−7.64 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 55.6 (*o*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 55.7 (*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 91.4 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 104.5 (*C*-1, $C_6H_2(OCH_3)_3$), 127.0 (*C*-3/*C*-5, C_6H_5), 128.7 (*C*-4, C_6H_5), 134.3 (*C*-2/*C*-6, C_6H_5), 140.3 (*C*-1, C_6H_5), 164.3 (*C*-4, $C_6H_2(OCH_3)_3$), 166.4 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ −8.9. Anal. Calcd for $C_{24}H_{27}ClO_6Si$: C, 60.69; H, 5.73. Found: C, 60.3; H 5.7.

General Procedure for the Selective Cleavage of the 2,4,6-Trimethoxyphenyl Group with Hydrogen Chloride. A stoichiometric amount of a 2.0 M hydrogen chloride solution in diethyl ether was added to a stirred solution or suspension of the respective

(2,4,6-trimethoxyphenyl)silane in diethyl ether (ca. 0.5 M) in a single portion at 0 °C. The resulting mixture was stirred for an appropriate period of time, during which the reaction progress was monitored by GC. (In the case of *rac*-**1**−*rac*-**4** (→ formation of *rac*-**20**−*rac*-**23**), no significant amounts of undesired byproducts could be observed, and the reactions were essentially quantitative by GC control.) After the reaction was complete, the solvent was removed under reduced pressure, and the resulting residue was dissolved in *n*-pentane or *n*-hexane (ca. 1.5 mL/1 g crude product). The solution was kept at −20 °C for 2 h to crystallize the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was then separated with a syringe, and the solid was recrystallized a second time with a fresh portion of *n*-pentane or *n*-hexane. (Although the 1,3,5-trimethoxybenzene was discarded, in principle it is possible to recrystallize and reisolate it at this stage for reuse; see ref 8 for related reactions in which this step was performed.) The combined solutions were freed of the solvent under reduced pressure, and the chlorosilane product was purified by fractional distillation in vacuo. (The yields given for compounds *rac*-**20**−*rac*-**23** (see below) are those of the pure products. The conversion (by GC control) was in all cases complete. In some cases, the low yields result from difficult distillations due to the similar boiling points of 1,3,5-trimethoxybenzene and the chlorosilane product. Should the complete removal of the 1,3,5-trimethoxybenze be impossible, it is conceivable that a small impurity would not hinder further synthetic steps undertaken with the chlorosilane product, as the 1,3,5-trimethoxybenzene is likely relatively inert except in the presence of very strong bases or very strong electrophiles.)

Preparation of *rac*-Chloro(methyl)phenyl(vinyl)silane (*rac*-20). Treatment of *rac*-**1** (6.68 g, 21.2 mmol) with a 2.0 M solution of hydrogen chloride in diethyl ether (11.0 mL, 22.0 mmol of HCl) gave *rac*-**20** in 61% yield as a colorless liquid (2.38 g, 13.0 mmol); bp 62 °C/6 mbar. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.74 (s, 3 H, SiCH_3), 5.96 (δ_A), 6.20 (δ_M), and 6.33 (δ_X) (3 H, CH_X=C$H_A H_M$, $^3J_{AX}$ = 19.5 Hz, $^2J_{AM}$ = 3.8 Hz, $^3J_{MX}$ = 14.5 Hz), 7.35−7.49 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.59−7.67 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 0.3 (Si*C*H$_3$), 128.1 (*C*-3/*C*-5, C_6H_5), 130.5 (*C*-4, C_6H_5), 133.7 (*C*-2/*C*-6, C_6H_5), 134.2 (*C*H=CH$_2$), 134.4 (*C*-1, C_6H_5), 136.0 (CH=*C*H$_2$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = 8.1. Anal. Calcd for $C_9H_{11}ClSi$: C, 59.16; H, 6.07. Found: C, 59.1; H, 6.0.

Preparation of *rac*-Allyl(chloro)methyl(phenyl)silane (*rac*-21). Treatment of *rac*-**2** (6.00 g, 18.3 mmol) with a 2.0 M solution of hydrogen chloride in diethyl ether (10.0 mL, 20.0 mmol of HCl) gave *rac*-**21** in 23% yield as a colorless liquid (824 mg, 4.19 mmol); bp 79−80 °C/6 mbar. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.66 (s, 3 H, SiCH_3), 2.00−2.10 (m, 2 H, CH_2CH=CH$_2$), 4.92−5.02 (m, 2 H, CH$_2$CH=CH_2), 5.69−5.87 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.34−7.48 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.58−7.64 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −0.4 (Si*C*H$_3$), 25.6 (*C*H$_2$CH=CH$_2$), 115.9 (CH$_2$CH=*C*H$_2$), 128.1 (*C*-3/*C*-5, C_6H_5), 130.5 (*C*-4, C_6H_5), 131.7 (CH$_2$*C*H=CH$_2$), 133.4 (*C*-2/*C*-6, C_6H_5), 134.7 (*C*-1, C_6H_5). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 17.0. Anal. Calcd for $C_{10}H_{13}ClSi$: C, 61.05; H, 6.66. Found: C, 61.2; H, 6.8.

Preparation of *rac*-Allyl(chloro)mesityl(methyl)silane (*rac*-22). Treatment of *rac*-**3** (8.00 g, 21.6 mmol) with a 2.0 M solution of hydrogen chloride in diethyl ether (10.8 mL, 21.6 mmol of HCl) gave *rac*-**22** in 52% yield as a colorless liquid (2.71 g, 11.3 mmol); bp 75−76 °C/0.1 mbar. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.82 (s, 3 H, SiCH_3), 2.11−2.19 (m, 2 H, CH_2CH=CH$_2$), 2.24−2.26 (br. "s", 3 H, *p*-CH_3, $C_6H_2(CH_3)_3$), 2.48−2.50 (br. "s", 6 H, *o*-CH_3, $C_6H_2(CH_3)_3$), 4.92−5.02 (m, 2 H, CH$_2$CH=CH_2), 5.70−5.86 (m, 1 H, CH$_2$C*H*=CH$_2$), 6.82−6.85 (m, 2 H, *H*-3/*H*-5, $C_6H_2(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 6.1 (Si*C*H$_3$), 21.0 (*p*-*C*H$_3$, $C_6H_2(CH_3)_3$), 24.7 (*o*-*C*H$_3$, $C_6H_2(CH_3)_3$), 28.4 (*C*H$_2$CH=CH$_2$), 115.9 (CH$_2$CH=*C*H$_2$), 128.2 (*C*-1, $C_6H_2(CH_3)_3$), 129.6 (*C*-3/*C*-5, $C_6H_2(CH_3)_3$), 132.4 (CH$_2$*C*H=CH$_2$), 140.4 (*C*-4, $C_6H_2(CH_3)_3$), 144.5 (*C*-2/*C*-6, $C_6H_2(CH_3)_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 16.5. Anal. Calcd for $C_{13}H_{19}ClSi$: C, 65.38; H, 8.02. Found: C, 65.1; H, 7.9.

Preparation of *rac*-Allyl(chloro)methyl(1-naphthyl)silane (*rac*-23). Treatment of *rac*-**4** (10.5 g, 27.7 mmol) with a 2.0 M solution of hydrogen chloride in diethyl ether (14.0 mL, 28.0 mmol of HCl) gave *rac*-**23** in 60% yield as a colorless liquid (4.07 g, 16.5 mmol); bp 109−110 °C/0.01 mbar. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.86 (s, 3 H, SiCH_3), 2.21−2.36 (m, 2 H, CH_2CH=CH$_2$), 4.94−5.05 (m, 2 H, CH$_2$CH=CH_2), 5.73−5.90 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.44−7.61 (m, 3 H, *H*-3/*H*-6/*H*-7, $C_{10}H_7$), 7.81−7.86 (m, 1 H, *H*-2, $C_{10}H_7$), 7.86−7.91 (m, 1 H, *H*-4, $C_{10}H_7$), 7.92−7.98 (m, 1 H, *H*-8, $C_{10}H_7$), 8.20−8.27 (m, 1 H, *H*-5, $C_{10}H_7$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 1.1 (Si*C*H$_3$), 26.3 (*C*H$_2$CH=CH$_2$), 116.0 (CH$_2$CH=*C*H$_2$), 124.9 (*C*-6, $C_{10}H_7$), 125.8 (*C*-7, $C_{10}H_7$), 126.4 (*C*-3, $C_{10}H_7$), 127.6 (*C*-5, $C_{10}H_7$), 129.2 (*C*-4, $C_{10}H_7$), 131.6 (*C*-8, $C_{10}H_7$), 131.9 (CH$_2$*C*H=CH$_2$), 132.1 (*C*-4a, $C_{10}H_7$), 133.5 (*C*-8a, $C_{10}H_7$), 134.3 (*C*-2, $C_{10}H_7$), 136.0 (*C*-1, $C_{10}H_7$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 17.9. Anal. Calcd for $C_{14}H_{15}ClSi$: C, 68.13; H, 6.13. Found: C, 67.6; H, 6.3.

Preparation of *rac*-Chloro(2,6-dimethoxyphenyl)(4-methoxyphenyl)phenylsilane (*rac*-26). A 2.0 M solution of hydrogen chloride in diethyl ether (3.60 mL, 7.20 mmol of HCl) was added at 0 °C in a single portion to a solution of *rac*-**7** (3.70 g, 7.16 mmol) in THF (25 mL). After the reaction mixture was stirred at 0 °C for 1 h (complete and selective cleavage of the TMOP group (by GC control)), the solvent was removed under reduced pressure. The 1,3,5-trimethoxybenzene was removed by distillation (bp 53−57 °C, 0.003 mbar), the residue was dissolved in a refluxing mixture of diethyl ether (20 mL) and *n*-hexane (10 mL), and the insoluble components were removed by filtration. The filtrate was kept undisturbed at −20 °C for 5 days, and the resulting solid was isolated by filtration to give *rac*-**26** in 80% yield as a colorless crystalline solid (2.21 g, 5.74 mmol); mp 104−106 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 3.48 (s, 6 H, $C_6H_3(OCH_3)_2$), 3.83 (s, 3 H, $C_6H_4OCH_3$), 6.57 (d, $^3J_{HH}$ = 8.3 Hz, 2 H, *H*-3/*H*-5, $C_6H_3(OCH_3)_2$), 6.92−6.96 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.34−7.42 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5) 7.44 (t, $^3J_{HH}$ = 8.3 Hz, 1 H, *H*-4, $C_6H_3(OCH_3)_2$), 7.55−7.60 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$), 7.61−7.65 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 55.4 ($C_6H_4OCH_3$), 55.6 ($C_6H_3(OCH_3)_2$), 104.8 (*C*-3/*C*-5, $C_6H_3(OCH_3)_2$), 108.4 (*C*-1, $C_6H_3(OCH_3)_2$), 113.6 (*C*-3/*C*-5, $C_6H_4OCH_3$), 127.4 (*C*-1, $C_6H_4OCH_3$), 127.8 (*C*-3/*C*-5, C_6H_5), 129.8 (*C*-4, C_6H_5), 134.4 (*C*-4, $C_6H_3(OCH_3)_2$), 134.6 (*C*-2/*C*-6, C_6H_5), 136.5 (*C*-2/*C*-6, $C_6H_4OCH_3$), 137.5 (*C*-1, C_6H_5), 161.4 (*C*-4, $C_6H_4OCH_3$), 166.2 (*C*-4, $C_6H_3(OCH_3)_2$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ −2.8. (For another synthetic method, see the Supporting Information.)

Preparation of *rac*-Chloro(4-methoxyphenyl)phenyl(2,4,6-trimethoxyphenyl)silane (*rac*-27). A 2.0 M solution of hydrogen chloride in diethyl ether (3.79 mL, 7.58 mmol of HCl) was added at 0 °C within 30 min to a solution of **8** (4.14 g, 7.58 mmol) in THF (25 mL). After the reaction mixture was stirred at 0 °C for 1.5 h (complete and selective cleavage of one of the TMOP groups (by GC control)), the solvent was removed under reduced pressure. The 1,3,5-trimethoxybenzene was removed by distillation (bp 53−57 °C, 0.003 mbar), and the resulting residue was dissolved in a refluxing mixture of diethyl ether (20 mL) and *n*-hexane (10 mL). After the insoluble components were removed by filtration, the filtrate was kept undisturbed at −20 °C for 9 days. The resulting solid was isolated by filtration to give *rac*-**27** in 39% yield as a colorless crystalline solid (1.23 g, 2.96 mmol); mp 94−96 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 3.46 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.82 (s, 3 H, $C_6H_4OCH_3$), 3.84 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 6.12 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 6.90−6.95 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.33−7.43 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.53−7.58 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$), 7.59−7.63 (m, 2 H,

H-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 55.4 ($C_6H_4OCH_3$), 55.6 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.7 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 91.6 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 100.0 (*C*-1, $C_6H_2(OCH_3)_3$), 113.6 (*C*-3/*C*-5, $C_6H_4OCH_3$), 127.75 (*C*-3/*C*-5, C_6H_5), 127.82 (*C*-1, $C_6H_4OCH_3$), 129.7 (*C*-4, C_6H_5), 134.6 (*C*-2/*C*-6, C_6H_5), 136.5 (*C*-2/*C*-6, $C_6H_4OCH_3$), 137.9 (*C*-1, C_6H_5), 161.4 (*C*-4, $C_6H_4OCH_3$), 165.7 (*C*-4, $C_6H_2(OCH_3)_3$), 167.4 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ −3.0. (For another synthetic method, see the Supporting Information.)

Preparation of Dichloro(4-methoxyphenyl)phenylsilane (28). Method A. A 2.0 M solution of hydrogen chloride in diethyl ether (5.70 mL, 11.4 mmol of HCl) was added at 20 °C in a single portion to a stirred solution of *rac*-**26** (2.17 g, 5.64 mmol) in THF (15 mL). After the reaction mixture was stirred at 20 °C for 8 days (complete and selective cleavage of the DMOP group (by GC control)), the solvent was removed under reduced pressure. The 1,3-dimethoxybenzene was removed by distillation (bp 32−35 °C, 0.004 mbar), and the residue was purified by fractional distillation in vacuo to give **28** in 47% yield as a colorless liquid (753 mg, 2.66 mmol); bp 133−136 °C/0.003 mbar. ^1H NMR (300.1 MHz, CD_2Cl_2): δ 3.85 (s, 3 H, $C_6H_4OCH_3$), 7.00−7.05 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.46−7.60 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.69−7.74 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$), 7.76−7.81 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 55.6 ($C_6H_4OCH_3$), 114.5 (*C*-3/*C*-5, $C_6H_4OCH_3$), 123.0 (*C*-1, $C_6H_4OCH_3$), 128.8 (*C*-3/*C*-5, C_6H_5), 132.2 (*C*-4, C_6H_5), 132.7 (*C*-1, C_6H_5), 134.4 (*C*-2/*C*-6, C_6H_5), 136.3 (*C*-2/*C*-6, $C_6H_4OCH_3$), 163.1 (*C*-4, $C_6H_4OCH_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ 6.3.

Method B. A 2.0 M solution of hydrogen chloride in diethyl ether (1.85 mL, 3.70 mmol of HCl) was added in a single portion at 20 °C to a solution of *rac*-**27** (1.50 g, 3.61 mmol) in THF (10 mL). After the reaction mixture was stirred at 20 °C for 3.5 h (complete and selective cleavage of the TMOP group (by GC control)), the solvent was removed under reduced pressure. The 1,3,5-trimethoxybenzene was removed by distillation (bp 53−57 °C, 0.003 mbar), and the residue was purified by fractional distillation in vacuo to give **28** in 34% yield as a colorless liquid (349 mg, 1.23 mmol); bp 133−136 °C/0.003 mbar. The NMR data of the product were identical to those of the product obtained by Method A. (For a third synthetic method, see the Supporting Information.)

General Procedure for the Selective Cleavage of the 2,4,6-Trimethoxyphenyl Group by Acid Catalysis. An excess amount of methanol and ca. 7 mol % trifluoroacetic acid were added sequentially at 20 °C (water bath cooling) in single portions to a stirred solution or suspension of the respective (2,4,6-trimethoxyphenyl)silane in diethyl ether (ca. 1.5 M). The reaction mixture was stirred for an appropriate period of time, during which the reaction progress was monitored by GC control. (No significant amounts of undesired byproducts could be observed, and the reactions were essentially quantitative by GC control.) The workup procedure to remove most of the 1,3,5-trimethoxybenzene was analogous to that for the cleavages with hydrogen chloride. (The 1,3,5-trimethoxybenzene may also be recrystallized and recycled as part of these reactions.)

Preparation of *rac*-Methoxy(methyl)phenyl(vinyl)silane (*rac*-29). Treatment of *rac*-**1** (9.00 g, 28.6 mmol) with methanol (4.59 g, 143 mmol) and trifluoroacetic acid (228 mg, 2.00 mmol) gave *rac*-**29** in 51% yield as a colorless liquid (2.60 g, 14.6 mmol); bp 85−86 °C/13 mbar. ^1H NMR (400.1 MHz, $CDCl_3$): δ 0.44 (s, 3 H, $SiCH_3$), 3.48 (s, 3 H, $SiOCH_3$), 5.87 (δ_A), 6.16 (δ_M), and 6.28 (δ_X) (3 H, $CH_X{=}CH_AH_M$, $^3J_{AX}$ = 20.1 Hz, $^2J_{AM}$ = 4.1 Hz, $^3J_{MX}$ = 14.9 Hz), 7.34−7.44 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.55−7.61 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −4.0 ($SiCH_3$), 51.0 ($SiOCH_3$), 127.9 (*C*-3/*C*-5, C_6H_5), 129.8 (*C*-4, C_6H_5), 134.0 (*C*-2/*C*-6, C_6H_5), 134.9 ($CH{=}CH_2$), 135.3 ($CH{=}CH_2$), 135.7 (*C*-1, C_6H_5). ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ −2.5. Anal. Calcd for $C_{10}H_{14}OSi$: C, 67.36; H, 7.91. Found: C, 67.4; H, 7.9.

Preparation of *rac*-Allyl(methoxy)methyl(phenyl)silane (*rac*-30). Treatment of *rac*-**2** (6.00 g, 18.3 mmol) with methanol (882 mg, 27.5 mmol) and trifluoroacetic acid (134 mg, 1.18 mmol) gave *rac*-**30** in 40% yield as a colorless liquid (1.42 g, 7.38 mmol); bp 75 °C/6 mbar. Due to the similarity in boiling points for *rac*-**30** and 1,3,5-trimethoxybenzene, the product was determined by NMR analysis to contain a 3 mol % impurity and therefore no elemental analysis was performed. ^1H NMR (300.1 MHz, $CDCl_3$): δ 0.38 (s, 3 H, $SiCH_3$), 1.79−1.97 (m, 2 H, $CH_2CH{=}CH_2$), 3.47 (s, 3 H, $SiOCH_3$), 4.86−4.98 (m, 2 H, $CH_2CH{=}CH_2$), 5.72−5.89 (m, 1 H, $CH_2CH{=}CH_2$), 7.32−7.44 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.51−7.61 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −4.7 ($SiCH_3$), 22.7 ($CH_2CH{=}CH_2$), 51.0 ($SiOCH_3$), 114.5 ($CH_2CH{=}CH_2$), 127.9 (*C*-3/*C*-5, C_6H_5), 129.8 (*C*-4, C_6H_5), 133.3 ($CH_2CH{=}CH_2$), 133.7 (*C*-2/*C*-6, C_6H_5), 136.0 (*C*-1, C_6H_5). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 5.6.

Chlorotrimethylsilane (31). This compound was commercially available.

Chloro(methyl)diphenylsilane (32). This compound was commercially available.

Chlorotriethylsilane (33). This compound was commercially available.

General Procedure for the Silylation of *O*-Nucleophiles Using the Silylation Reagents 9−11 with the Reisolation of 1,3,5-Trimethoxybenzene. A stoichiometric amount of the respective alcohol, phenol, or carboxylic acid to be silylated and 5−9 mol % trifluoroacetic acid were added sequentially at 20 °C (water bath cooling) in single portions to a stirred solution or suspension of the respective (2,4,6-trimethoxyphenyl)silane in diethyl ether or *n*-pentane (ca. 2.5 M). (In the case of phenols and carboxylic acids, the reaction may proceed slowly without catalytic amounts of trifluoroacetic acid, as observed in the syntheses of **37**, **38**, **42**, and **46**; however, more efficient silylations are achieved with the use of small amounts of a strong acid. Silylations of primary alcohols with **9** should be cooled with a water bath, as these reactions may proceed exothermally enough to cause the solvent to reflux.) The reaction mixture was allowed to stir at 20 °C or heated under reflux for an appropriate period of time, during which the reaction progress was followed by GC control. All reactions for which a product was isolated gave no significant byproducts and showed ≥95% conversion by GC to the desired silylated product. After completed reaction, in case a precipitate was formed, the mixture was heated gently to dissolve all solids, and then cooled to −20 °C to crystallize the byproduct, 1,3,5-trimethoxybenzene. (In the case of silylations performed in diethyl ether, the solvent was first removed and the residue dissolved in *n*-pentane before cooling to −20 °C to improve the removal of 1,3,5-trimethoxybenzene, which is more soluble in diethyl ether.) The mother liquor was removed from the crystalline byproduct, 1,3,5-trimethoxybenzene, at −20 °C with a syringe, and the 1,3,5-trimethoxybenzene was redissolved in *n*-pentane and recrystallized at −20 °C. The mother liquors were combined, and the product was purified by distillation (isolated yields up to 80%). The byproduct was recrystallized from *n*-hexane to give analytically pure crystalline 1,3,5-trimethoxybenzene in 75−85% yield, which can be reused to synthesize the silylation reagents **9**−**11**. In some instances, the complete removal of the solvent (in the case of the volatile silylated alcohols) or 1,3,5-trimethoxybenzene (due to coincidentally similar boiling points of product and byproduct) was impossible. However, all silylations performed gave products with ≥93% purity by GC control. Therefore, the identities of all isolated silylated products were confirmed by comparison of their NMR spectra with those of samples of commercial origin or with those of samples synthesized similarly to established procedures using the respective alcohol, phenol, or hydroxycarboxylic acid and the respective chlorotriorganylsilane in the presence of triethylamine.

The identification of the products was further confirmed by GC/EI-MS analysis. Complete synthetic details for compounds **34**−**46**, as well as for experiments with *N*- and *S*-nucleophiles (compounds **47** and **48**), are given in the Supporting Information.

Competitive Silylation of a Mixture of Primary, Secondary, and Tertiary Alcohols with 10. Trifluoroacetic acid (71.0 mg, 623 μmol) was added at 20 °C in a single portion to a stirred mixture of **10** (3.03 g, 8.31 mmol), ethanol (128 mg, 2.78 mmol), isopropanol (168 mg, 2.80 mmol), and *tert*-butanol (206 mg, 2.78 mmol) in diethyl ether (10 mL). The resulting mixture was stirred at 20 °C for the duration of the experiment. The relative concentrations of the three possible products, **39**−**41**, were determined in intervals of 2 h by GC analysis. The data were plotted with the program Microsoft Excel, using the slope of the linear regression best-fit line as an approximate measure of the speed of each possible reaction. The results are given in Figure 1. Reagent **10** silylates a primary alcohol in a mixture approximately 3.4 times more quickly than a comparable secondary alcohol. The silylation of the tertiary alcohol was not observable until almost 8 h after the start of the experiment.

Competitive Silylation of a Mixture of Primary, Secondary, and Tertiary Alcohols with 11. Trifluoroacetic acid (113 mg, 991 μmol) was added at 20 °C in a single portion to a stirred mixture of **11** (4.01 g, 14.2 mmol), ethanol (218 mg, 4.73 mmol), isopropanol (284 mg, 4.73 mmol), and *tert*-butanol (351 mg, 4.74 mmol) in diethyl ether (17 mL). The resulting mixture was stirred at 20 °C for the duration of the experiment. The relative concentrations of the three possible products, **43**−**45**, were determined in intervals of 2 h by GC analysis. The data were plotted with the program Microsoft Excel, using the slope of the linear regression best-fit line as an approximate measure of the speed of each possible reaction. The results are given in Figure 1. Reagent **11** silylates a primary alcohol in a mixture approximately 5.3 times more quickly than a comparable secondary alcohol. The silylation of the tertiary alcohol was not observed during the course of the experiment.

Regioselective Silylation with 10: Preparation of an Isomeric Mixture of *rac*-1-(Methyldiphenylsilyloxy)-3-(trimethylsilyloxy)-butane (*rac*-49) and *rac*-1-(Trimethylsilyloxy)-3-(methyldiphenylsilyloxy)butane (*rac*-50). A solution of **10** (4.00 g, 11.0 mmol) in dichloromethane (30 mL) was added at 0 °C within 2.5 h to a stirred solution of butane-1,3-diol (990 mg, 11.0 mmol) and trifluoroacetic acid (63.0 mg, 553 μmol) in dichloromethane (15 mL). The resulting mixture was stirred at 0 °C for an additional 4 h, and then triethylamine (1.22 g, 12.1 mmol) and **31** (1.32 g, 12.1 mmol) were added sequentially, each in a single portion at 0 °C. The mixture was stirred at 0 °C for 30 min and then allowed to warm to 20 °C. The solvents were removed under reduced pressure, and the residue was treated with *n*-pentane (10 mL) and warmed gently to ca. 30 °C. The resulting mixture was then cooled to −20 °C for 2 h, and the mother liquor was separated from the precipitate (1,3,5-trimethoxybenzene and triethylammonium chloride) with a syringe. The precipitate was treated with a fresh portion of *n*-pentane (10 mL), warmed gently to ca. 30 °C, cooled to −20 °C for 2 h, and the mother liquor was separated from the precipitate with a syringe. The mother liquors were combined, and the isomeric mixture was purified by distillation to give *rac*-**49**/*rac*-**50** in 46% yield as a colorless liquid (1.80 g, 5.02 mmol); bp 126−127 °C/0.07 mbar. Based upon the following NMR data, the ratio *rac*-**49**:*rac*-**50** was ca. 82:18. ^{1}H NMR (500.1 MHz, CD_2Cl_2; data for two isomers, the major isomer marked with an asterisk): δ 0.06 (s, 1.6 H, $CH_2OSi(CH_3)_3$), 0.07* (s, 7.4 H, $CHOSi(CH_3)_3$), 0.64* (s, 2.5 H, $CH_2OSi(C_6H_5)_2CH_3$), 0.66 (s, 0.5 H, $CHOSi(C_6H_5)_2CH_3$), 1.11* (d, $^3J_{HH}$ = 6.2 Hz, 2.5 H, $CH_3CHOSi(CH_3)_3$), 1.15 (d, $^3J_{HH}$ = 6.2 Hz, 0.5 H, $CH_3CHOSi(C_6H_5)_2CH_3$), 1.59−1.85 (m, 2 H, $CH_3CHCH_2CH_2O$), 3.59−3.81 (m, 2 H, $CH_3CHCH_2CH_2O$), 3.95−4.13 (m, 1 H, $CH_3CHCH_2CH_2O$), 7.33−7.45 (m, 6 H, *H*-3/*H*-4/*H*-5, $Si(C_6H_5)_2CH_3$), 7.55−7.62 (m, 4 H, *H*-2/*H*-6, $Si(C_6H_5)_2CH_3$). ^{13}C NMR (125.8 MHz, CD_2Cl_2; data for two isomers, as well as for diastereotopic phenyl groups; the major isomer marked with an asterisk): δ −3.1* ($CH_2OSi(C_6H_5)_2CH_3$), −2.4 ($CHOSi(C_6H_5)_2CH_3$), −0.5 ($CH_2OSi(CH_3)_3$), 0.2* ($CHOSi(CH_3)_3$), 24.0 ($CH_3CHOSi(C_6H_5)_2CH_3$), 24.2* ($CH_3CHOSi(CH_3)_3$), 42.7* ($CH_3CHCH_2CH_2OSi(C_6H_5)_2CH_3$), 42.8 ($CH_3CHCH_2CH_2OSi(CH_3)_3$), 59.7 ($CH_2OSi(CH_3)_3$), 60.7* ($CH_2OSi(C_6H_5)_2CH_3$), 65.6* ($CHOSi(CH_3)_3$), 67.0 ($CHOSi(C_6H_5)_2CH_3$), 128.09 and 128.10 (*C*-3/*C*-5, $CHOSi(C_6H_5)_2CH_3$), 128.17* and 128.18* (*C*-3/*C*-5, $CH_2OSi(C_6H_5)_2CH_3$), 129.98 and 129.99 (*C*-4, $CHOSi(C_6H_5)_2CH_3$), 130.09* and 130.10* (*C*-4, $CH_2OSi(C_6H_5)_2CH_3$), 134.61* and 134.62* (*C*-2/*C*-6, $CH_2OSi(C_6H_5)_2CH_3$), 134.67 (*C*-2/*C*-6, $CHOSi(C_6H_5)_2CH_3$), 136.82* and 136.87* (*C*-1, $CH_2OSi(C_6H_5)_2CH_3$), 137.4 and 137.5 (*C*-1, $CHOSi(C_6H_5)_2CH_3$). ^{29}Si NMR (99.4 MHz, CD_2Cl_2; data for two isomers, the major isomer marked with an asterisk): δ −5.8 ($CHOSi(C_6H_5)_2CH_3$), −3.6* ($CH_2OSi(C_6H_5)_2CH_3$), 14.7* ($CHOSi(CH_3)_3$), 16.7 ($CH_2OSi(CH_3)_3$). Anal. Calcd for $C_{20}H_{30}O_2Si_2$: C, 66.98; H, 8.43. Found: C, 66.9; H 8.3.

Regioselective Silylation with 11: Preparation of an Isomeric Mixture of *rac*-1-(Triethysilyloxy)-3-(trimethylsilyloxy)butane (*rac*-51) and *rac*-1-(Trimethylsilyloxy)-3-(triethylsilyloxy)butane (*rac*-52). A solution of **11** (4.14 g, 14.7 mmol) in dichloromethane (20 mL) was added at 0 °C within 10 min to a stirred solution of butane-1,3-diol (1.32 g, 14.6 mmol) and trifluoroacetic acid (84.0 mg, 737 μmol) in dichloromethane (10 mL). The resulting mixture was stirred at 0 °C for an additional 1.5 h, and then triethylamine (1.71 g, 16.9 mmol) and **31** (1.75 g, 16.1 mmol) were added sequentially, each in a single portion at 0 °C. The mixture was diluted with dichloromethane (10 mL), stirred at 0 °C for 30 min, and then allowed to warm to 20 °C. The precipitate (1,3,5-trimethoxybenzene and triethylammonium chloride) was removed by filtration and washed with *n*-pentane (2 × 10 mL). The filtrate and wash solutions were combined, and the solvents were removed under reduced pressure. The residue was treated with *n*-pentane (15 mL) and warmed gently to ca. 30 °C. The resulting mixture was then cooled to −20 °C for 2 h, and the mother liquor was separated from the precipitate with a syringe. The precipitate was treated with a fresh portion of *n*-pentane (15 mL), warmed gently to ca. 30 °C, cooled to −20 °C for 2 h, and the mother liquor was separated from the precipitate with a syringe. The mother liquors were combined, and the isomeric mixture was purified by distillation to give *rac*-**51**/*rac*-**52** in 18% yield as a colorless liquid (742 mg, 2.68 mmol); bp 52−54 °C/0.03 mbar. Due to the similar boiling points of the product mixture and 1,3,5-trimethoxybenzene, the product was determined to contain a 3 mol % impurity by NMR analysis and therefore no elemental analysis was performed. Based upon the following NMR data, the ratio *rac*-**51**:*rac*-**52** was ca. 90:10. ^{1}H NMR (500.1 MHz, CD_2Cl_2; data for two isomers, the major isomer marked with an asterisk): δ 0.086 (s, 1 H, $CH_2OSi(CH_3)_3$), 0.092* (s, 8 H, $CHOSi(CH_3)_3$), 0.54−0.66 (m, 6 H, $CH_2OSi(CH_2CH_3)_3$ and $CHOSi(CH_2CH_3)_3$), 0.89−1.02 (m, 9 H, $CH_2OSi(CH_2CH_3)_3$ and $CHOSi(CH_2CH_3)_3$), 1.13* (d, $^3J_{HH}$ = 6.2 Hz, 2.7 H, $CH_3CHOSi(CH_3)_3$), 1.14 (d, $^3J_{HH}$ = 6.2 Hz, 0.3 H, $CH_3CHOSi(CH_2CH_3)_3$), 1.53−1.68 (m, 2 H, $CH_3CHCH_2CH_2O$), 3.58−3.71 (m, 2 H, $CH_3CHCH_2CH_2O$), 3.90−4.00 (m, 1 H, $CH_3CHCH_2CH_2O$). ^{13}C NMR (125.8 MHz, CD_2Cl_2; data for two isomers, the major isomer marked with an asterisk): δ −0.5 ($CH_2OSi(CH_3)_3$), 0.3* ($CHOSi(CH_3)_3$), 4.8* ($CH_2OSi(CH_2CH_3)_3$), 5.3 ($CHOSi(CH_2CH_3)_3$), 6.96* ($CH_2OSi(CH_2CH_3)_3$), 7.03 ($CHOSi(CH_2CH_3)_3$), 24.3 ($CH_3CHCH_2CH_2O$), 43.1 ($CH_3CHCH_2CH_2O$), 59.8 ($CH_2OSi(CH_3)_3$), 60.0* ($CH_2OSi(CH_2CH_3)_3$), 65.7* ($CHOSi(CH_3)_3$), and 65.8 ($CHOSi(CH_2CH_3)_3$). ^{29}Si NMR (99.4 MHz, CD_2Cl_2; data for two isomers, the major isomer marked with an asterisk): δ 14.6* ($CHOSi(CH_3)_3$), 16.4 ($CH_2OSi(CH_3)_3$), 16.6 ($CHOSi(CH_2CH_3)_3$), 18.1* ($CH_2OSi(CH_2CH_3)_3$).

Crystal Structure Analyses. Suitable single crystals of *rac*-**1**−*rac*-**3**, *rac*-**6**, **9**−**11**, *rac*-**18,** and *rac*-**26** were obtained by crystal-

lization at −20 °C from *n*-hexane/diethyl ether (*rac*-**1**, **9**, *rac*-**26**), at −20 °C from *n*-hexane (*rac*-**2**, **11**), at 20 °C from *n*-hexane (*rac*-**3**), at −20 °C from dichloromethane/*n*-hexane (*rac*-**6**), at −20 °C from *n*-pentane/diethyl ether (**10**), or at −20 °C from diethyl ether (*rac*-**18**). The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (*rac*-**1**−*rac*-**3**, *rac*-**6, 9**−**11**, *rac*-**18**: Stoe IPDS, graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å); *rac*-**26**: Bruker-Nonius Kappa-APEX2 CCD system with Göbel mirror, Mo Kα radiation ($\lambda = 0.71073$ Å)). The structures were solved by direct methods.[9] All non-hydrogen atoms were refined anisotropically.[10] A riding model was employed in the refinement of the hydrogen atoms. For the results of these studies, see the Supporting Information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC−657316 (*rac*-**1**), CCDC−657317 (*rac*-**2**), CCDC−657318 (*rac*-**3**), CCDC−657319 (*rac*-**6**), CCDC−657320 (**9**), CCDC−657321 (**10**), CCDC−657322 (**11**), CCDC−657323 (*rac*-**18**), and CCDC−657324 (*rac*-**26**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, (+44)1223/336033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Synthetic and analytical details for the attempted syntheses of **24** and *rac*-**25**, for the syntheses of *rac*-**26**, *rac*-**27**, and **28** (starting from **16**), and for the syntheses of **34**−**46** and the attempted syntheses of **47** and **48** (silylations carried out with **9**−**11**) are provided. Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for *rac*-**1**−*rac*-**3**, *rac*-**6**, **9**−**11**, *rac*-**18**, and *rac*-**26** are provided in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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