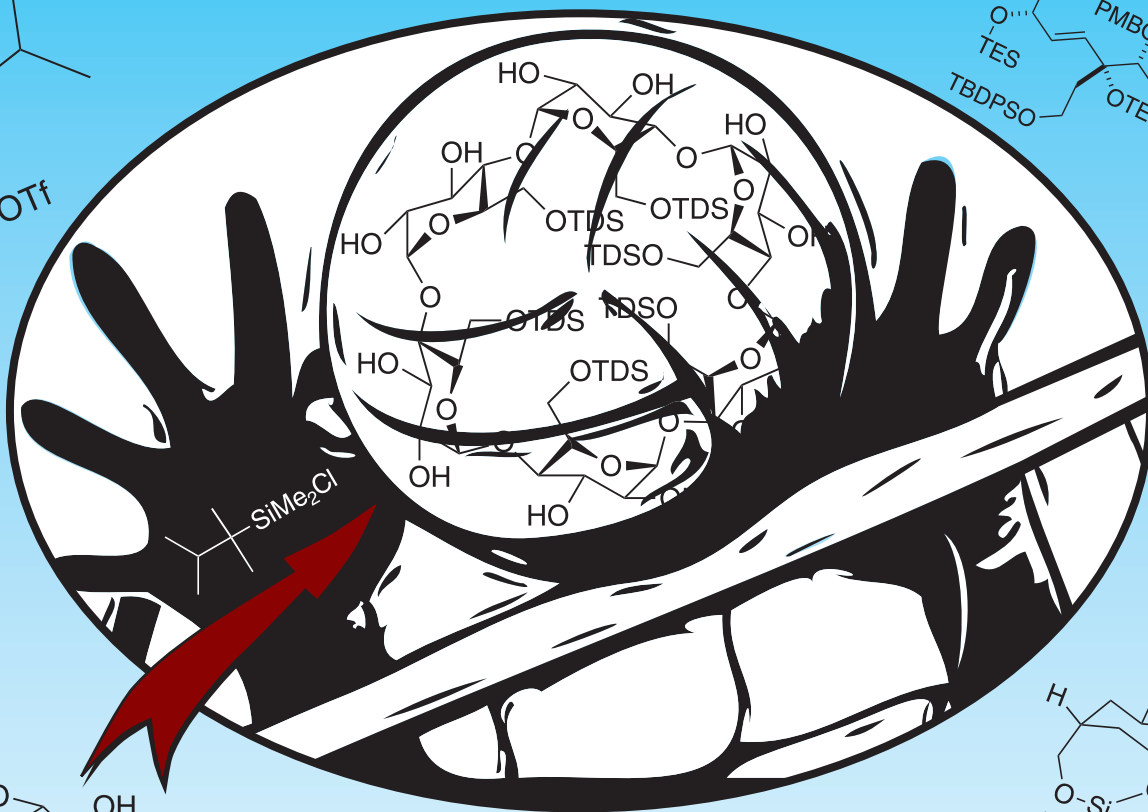


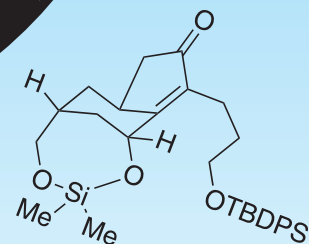
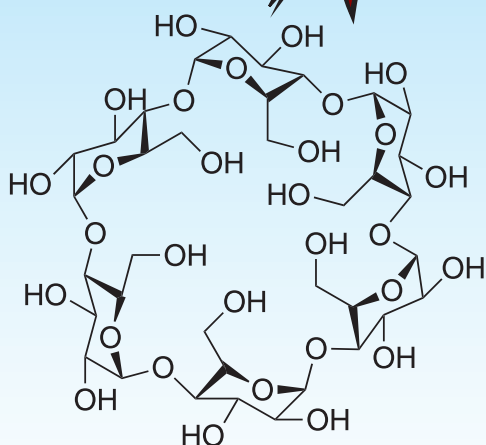
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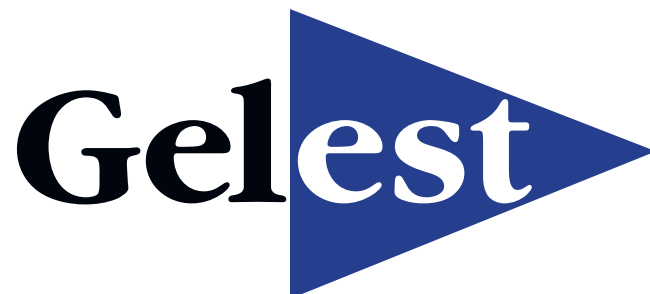
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Silicon-Based Blocking Agents



By Gerald L Larson, Ph.D.
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Silicon-Based Protecting Agents

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General Considerations

The synthesis of organic molecules frequently involves the manipulation of several functional groups, thus resulting in the conversion of one functional group in the presence of one or more other functional groups. This can lead to concerns regarding competing reaction pathways taking place with a negative effect on yield and purification of the desired product. The accommodation of an effective preparation of a synthetic target can often require the protection of certain groups in order to limit their reactivity. Functional groups that commonly require protection are those containing a reactive hydrogen as encountered with alcohols, amines, thiols, and carboxylic acids. In addition, the protection of these groups must be reversible such that the original functionality can be regenerated after the desired chemical transformations elsewhere in the molecule have been carried out. Organosilanes have shown to be particularly effective in the protection of the reactive hydrogen functionalities and have been successfully employed in the protection of these groups for many years. Organosilanes are an excellent fit for this application as they are hydrogen-like, can be introduced in high yield, and can be removed under selective conditions. A number of representative examples of the application of organosilane protection of various functional groups are to be found in this brochure.

The ideal protecting group for an active hydrogen moiety such as an alcohol or amine would be one that would mimic the hydrogen atom itself, but have more flexibility in its reactivity. It would be readily introduced in high yield onto the substrate to be protected, be stable over a wide range of reaction conditions and, at the same time, could be selectively removed in high yield in the presence of other functional groups including other protecting groups, both silyl and non-silyl. While no single silyl group can fulfill all of these requirements in all cases, the available range of silicon-based blocking agents offers the synthetic chemist viable answers for nearly every protection–reaction(s)-deprotection challenge. The ability to vary the organic groups on silicon introduces the highly-useful potential to alter the organosilyl groups in terms of steric demand and electronic nature, thus allowing one to select the appropriate organosilyl protecting group to fit a particular set of synthetic needs.

The commonly used tri-substituted organosilane blocking agents, along with their common acronyms, are shown in **Figure 1**.

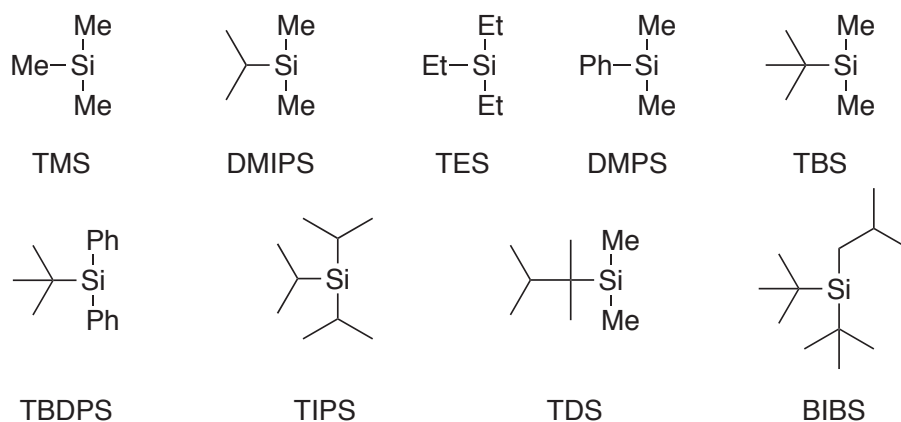


Figure 1

The use of silicon-based blocking agents has been reviewed with regards to reaction/deprotection,¹⁻⁸ oxidation of silyl ethers,⁹ and selective deprotection.¹⁰⁻¹²

Introduction of the Silyl Group

In general, smaller organosilyl groups make the silyl group easier to introduce, easier to remove and, at the same time, less stable to a wider variety of reaction conditions. A general reactivity scale based on steric factors is that shown in **Figure 2**.

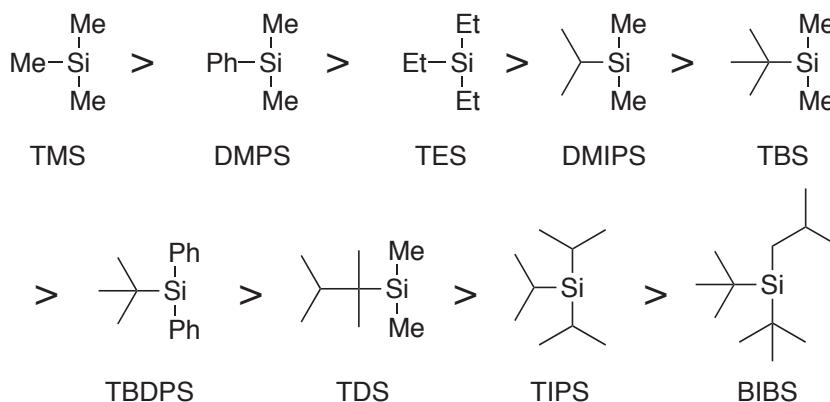


Figure 2

The leaving group on silicon also plays a significant role in the reactivity of the organosilane. The general relative reactivity of $\text{R}_3\text{Si-X}$ as a function of the leaving group X as shown in **Figure 3** is:



Figure 3

Other organosilane derivatives, such as trimethylsilylperchlorate and bis(trimethylsilyl)sulfate, though very reactive, have not proven practical. The reactivity trends shown in **Figure 3** will not apply to all sets of reaction conditions and substrates, but serve to present a useful and practical working guide.

Consideration of By-products

The introduction of a silyl group onto an active hydrogen substrate results in the formation of the corresponding protonated leaving group from silicon. This protonated by-product can be acidic, basic or neutral as shown by some examples in **Figure 4**. In terms of the leaving group, various considerations need to be addressed when evaluating a potential silicon-based blocking agent including safety, potential effect of the by-product on the molecule and final product purification issues.

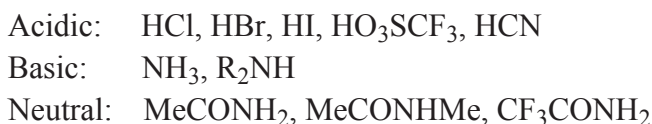


Figure 4

Stability of Silyl-Protected Functional Groups

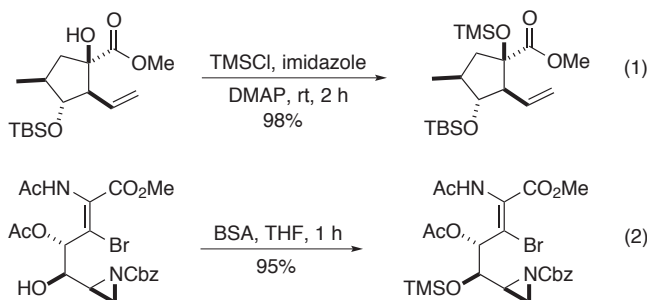
The relative stabilities of the silyl-protected functional groups, for example alcohols as silyl ethers, parallels their relative rates and ease of introduction, that is to say that, in general, “the easier to introduce the easier to remove”. The reader is reminded, however, that although the stability of the system does depend strongly on the nature of the silyl group, its surrounding environment and reaction conditions, in particular pH, play a significant role on the stability as well. For instance, phenyl-substituted silyl ethers are equal to or even more reactive than their less encumbered trimethylsilyl counterparts under basic conditions, but can be more stable under acid conditions. The reader is referred to three excellent compilations of numerous protocols for the selective deprotection of one silyl group in the presence of other silyl protecting groups and to **Tables 7 through 20** of this brochure.¹⁰⁻¹² A general study of the relative stabilities of silyl-protected alcohols to a variety of reaction conditions is summarized in **Table 1**.

Table 1
Resistance of Silylated Alcohols to Chemical Transformations
 $t^{1/2}$ for Si-OR bond scission at room temperature

Blocking group	Substrate	HCl -THF	KF methanol	CH ₃ MgBr/ ether	n-Butyl lithium	LAH -THF	Pyridinium Chlorochromate
(CH ₃) ₃ Si-	n-butanol	<15 min	2 min	48 hr	2 hr	30 min	<30 min
	cyclohexanol	<15 min	2 min	>48 hr	3 hr	1 hr	<30 min
	t-butanol	<15 min	24 hr	>48 hr	50 hr	24 hr	<30 min
(C ₂ H ₅) ₃ Si-	n-butanol	<15 min	2 hr	no reaction	24 hr	1 hr	<30 min
	cyclohexanol	<15 min	20 hr	no reaction	>48 hr	2 hr	<30 min
	t-butanol	<15 min	no reaction	no reaction	no reaction	no reaction	1 hr
cyclohexylMe ₂ Si-	cyclohexanol	< 15 min	10 hr	no reaction	36 hr	2 hr	<30 min
ⁱ Pr(CH ₃) ₂ Si-	cyclohexanol	10-30 min	24-30 hr	no reaction	>60 hr	3 hr	<30 min
^t BuMe ₂ Si-	n-butanol	>3 hr	no reaction	no reaction	no reaction	25 hr	10 hr
	cyclohexanol	>3 hr	no reaction	no reaction	no reaction	>50 hr	>20 hr
	t-butanol	no reaction	no reaction	no reaction	no reaction	no reaction	>20 hr
^h HexylMe ₂ Si-	n-butanol	16 hr	no reaction	no reaction	no reaction	>30 hr	22 hr
	cyclohexanol	30 hr	no reaction	no reaction	no reaction	no reaction	50 hr
	t-butanol	no reaction	no reaction	no reaction	no reaction	no reaction	no reaction
ⁱ Pr ₃ Si-	cyclohexanol	no reaction	no reaction	no reaction	no reaction	no reaction	>72 hr
^t BuPh ₂ Si-	n-butanol	no reaction	100 hr	no reaction	no reaction	no reaction	no reaction
	cyclohexanol	no reaction	no reaction	no reaction	no reaction	no reaction	no reaction
	t-butanol	no reaction	no reaction	no reaction	no reaction	no reaction	no reaction

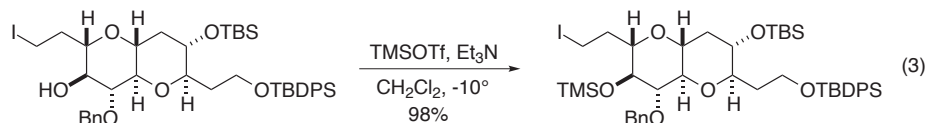
The Trimethylsilyl, TMS, Group

The trimethylsilyl protecting group has been in use for many years. It is typically introduced *via* two common, commercially available reagents, namely, hexamethyldisilazane (HMDS) and chlorotrimethylsilane (TMS-Cl). When chlorotrimethylsilane is employed the resulting HCl by-product must be handled by off gassing or by trapping. Trapping is commonly done *via* the addition of triethylamine or pyridine. The reaction with HMDS liberates ammonia as the by-product and this must be off-gassed or trapped in some way. It is normally off-gassed to a scrubber system. The reaction of HMDS is oftentimes quite slow, but can be catalyzed by the addition of one of several catalysts including TMS-Cl, ammonium chloride, or lithium chloride. Dimethylaminopyridine and imidazole have also been successfully employed as catalysts (Eq. 1).¹³ In addition to these very common and high-use reagents, the TMS group can be introduced with bis(trimethylsilyl)acetamide, BSA, or bis(trimethylsilyl)trifluoroacetamide, BSTFA, both of which give off a neutral by-product, acetamide and trifluoroacetamide, respectively (Eq. 2).¹⁴



If greater reactivity and a more benign by-product are desired, one can turn to dimethylaminotrimethylsilane or N-trimethylsilylimidazole. Due to their excellent reactivity these reagents are commonly used to trimethylsilylate remaining non-silylated hydroxyls on the silica in the preparation of chromatography columns.

Trimethylsilyltriflate (TMS-OTf) is a very reactive silylating agent able to silylate most alcohols in high yield. The triflic acid by-product is typically trapped with a tertiary amine (**Eq. 3**).¹⁵



The various reagents available for the introduction of the TMS group are listed in Table 2. Deprotection of TMS ethers can be readily effected with dilute aqueous or methanolic HCl. TMS-protected alcohols have been selectively deprotected in the presence of a TES-protected alcohol.^{16,17}

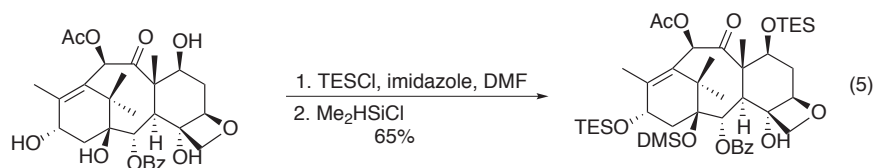
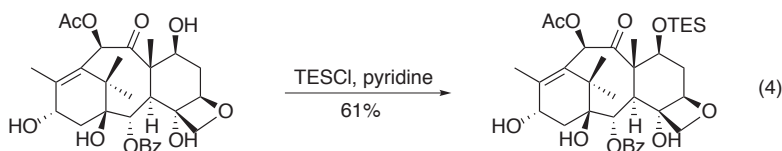
Nafion SAC-13 has been shown to be a recyclable catalyst for the trimethylsilylation of primary, secondary and tertiary alcohols in excellent yields and short reaction times.¹⁸

The Triethylsilyl, TES, Group

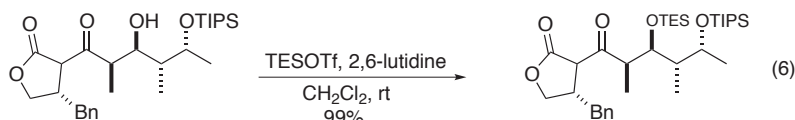
The triethylsilyl protecting group is primarily used for the protection of alcohols, although other groups including amines and carboxylic acids have been protected as their TES derivatives. A key consideration in the use of the TES protecting group is based on the generalization that its ease of removal falls between that of the more reactive TMS and the less reactive TBS groups. This presents various options for selective deprotection, which are often required in multi-step synthetic sequences.

The main reagent used for the preparation of triethylsilyl ethers is chlorotriethylsilane, TES-Cl. Since the triethylsilyl group is considerably more sterically hindered than the TMS group the usual protocol for its introduction is to employ a promoter such as imidazole, DMAP, or 2,6-lutidine to enhance the rate of silylation. Tertiary alcohols react very poorly with TES-Cl. Pyridine can also be used as a promoter. Alternatively, the triethylsilyltriflate TES-OTf can be used to introduce the triethylsilyl group. TES ethers can be selectively removed in the presence of TBS ethers.¹⁹

The combination of TES-Cl and pyridine selectively silylates a more hindered secondary alcohol over that of another secondary alcohol as shown in **Eq. 4**. This was employed in an efficient approach to a key intermediate for the synthesis of taxol derivatives. On the other hand, replacing the pyridine with imidazole results in the silylation of both secondary alcohols (**Eq. 5**).²⁰

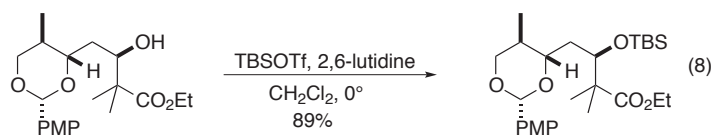
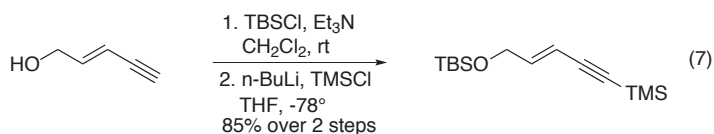


The direct triethylsilylation of alcohols in the presence of 2,6-lutidine as a promoter is accomplished with the use of TES-OTf in dichloromethane (**Eq. 6**).²¹



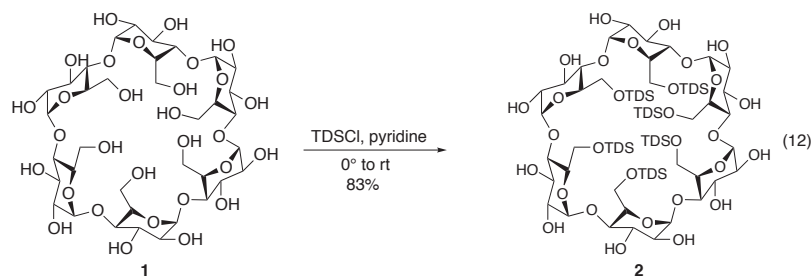
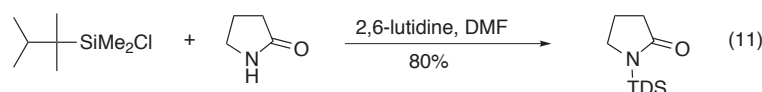
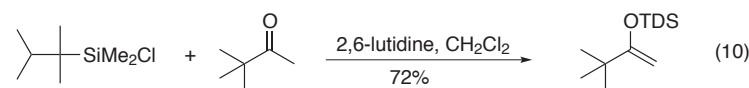
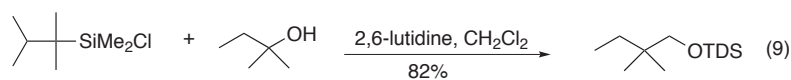
The Tert-Butyldimethylsilyl, TBS, Group

The TBS group is used for the protection of alcohols, amines, thiols, lactams, and carboxyl acids.^{22,23} The TBS group is typically introduced *via* the tert-butyldimethylchlorosilane, TBS-Cl, using imidazole, 2,6-lutidine or DMAP as promoters, though triethylamine can also be used (Eq. 7).²² The high stability of TBS-protected groups, in particular alcohols, to a variety of reaction conditions, its clean NMR characteristics and its facile removal with fluoride ion sources make it a popular choice among the silicon-based blocking agents. TBS ethers can be removed in the presence of TIPS and TBDPS ethers.^{24,25} Stork and Hudrlik initially illustrated the ability of the TBS group to form stable silyl enol ethers of ketones.²⁶ An example of the use of TBS-Cl is shown in Eq. 7 and of TBS-OTf in Eq. 8.^{27,28}



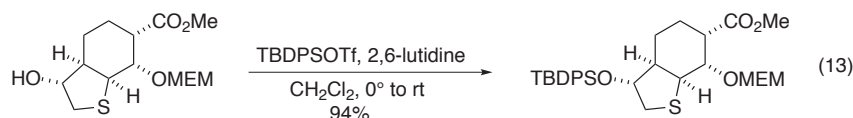
The Thexyldimethylsilyl, TDS, Group

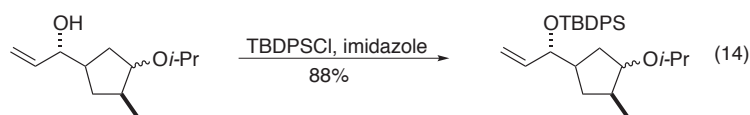
The thexyldimethylsilyl moiety was originally reported in 1985 for the highly stable protection of alcohols, amines, amides, mercaptans and acids.²⁹ It can be introduced *via* reaction of the thexyldimethylchlorosilane, TDS-Cl, with promotion from triethylamine or imidazole in DMF, dichloromethane, or diethyl ether. Some examples, including one of a ketone to a TDS enol ether, are shown in Eqs. 9 - 11. The cyclodextrin **1** was selectively thexyldimethylsilylated at the C-6 alcohols to provide **2** in good yield (Eq. 12).³⁰ Deprotection was accomplished with DIBAL-H.



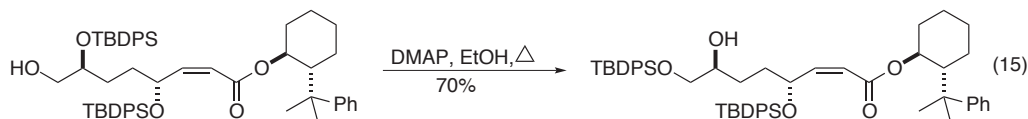
The Tert-butyl diphenylsilyl, TBDPS, Group

The tert-butyl diphenylsilyl, TBDPS, group was first reported by Hanessian and Lavallee as a sterically hindered silylating agent with enhanced stability under acidic conditions.³¹ It is best introduced *via* the triflate (Eq. 13), but can also be introduced *via* the chloride (Eq. 14).³² Tert-butyl diphenylsilylated alcohols, indeed, show excellent stability under acidic conditions.



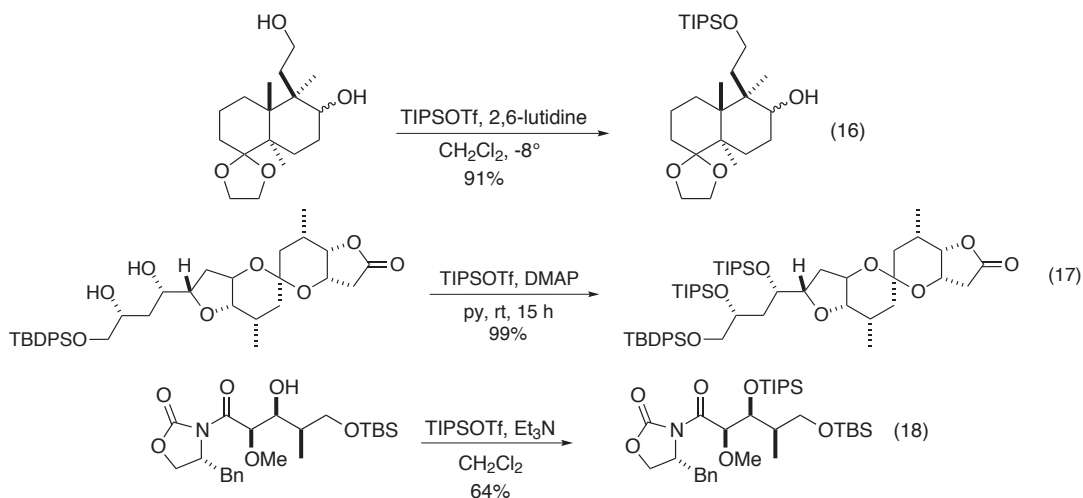


As with other silyl protecting groups the TBDPS group can be induced to migrate to a lesser sterically demanding position (Eq. 15).³³



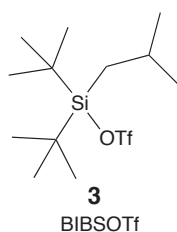
The Triisopropylsilyl Group

The triisopropylsilyl, TIPS, group is more sterically demanding than the TBS and TBDPS groups and can survive deprotection protocols that will remove these groups in its presence. It is a useful group for the protection of primary and secondary alcohols, although it reacts with secondary alcohols only under forcing conditions.³⁴ It is essentially unreactive with tertiary alcohols and is typically introduced *via* the reaction of triisopropylchlorosilane, TIPS-Cl, or triisopropylsilyltriflate, TIPS-OTf, in the presence of a promoter such as imidazole or 2,6-lutidine (Eq. 16).³⁵ Promotion with DMAP in pyridine appears to be a reactive combination, providing TIPS-protected secondary alcohols in good yields (Eqs. 17 & 18).³⁶ Due to the bulky nature of the TIPS group it demonstrates excellent selectivity in the silylation of compounds with more than one hydroxyl group. TIPS-protected alcohols show excellent stability under basic conditions including *n*-butyllithium reactions.

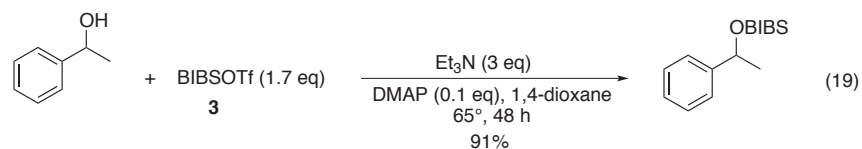


A Novel Highly Sterically-Hindered Organosilane Blocking Agent

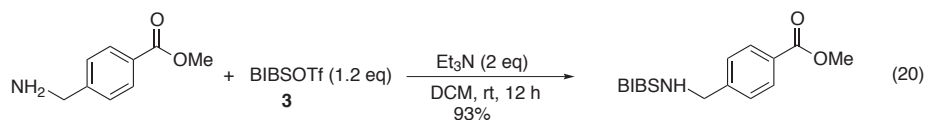
Although the *tert*-butyldiphenylsilyl and triisopropylsilyl protecting groups offer excellent stability in terms of their resistance to an extensive variety of reaction conditions, there remains a need for an even more robust silicon-based protecting group in particular for groups other than the hydroxyl group. This would especially be true for the protection of amines and carboxylic acids. Professor E. J. Corey and coworkers have developed and studied a readily synthesized, very sterically demanding and stable organosilane blocking agent, namely, di-*tert*-butylisobutylsilyl trifluoromethanesulfonate **3**, BIBSOTf.³⁷



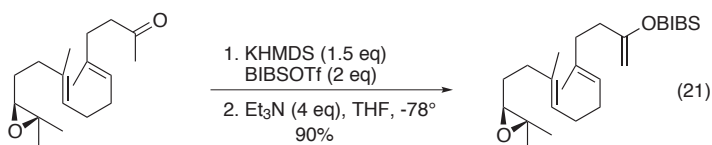
In order to obtain good conversions of the substrates to the silylated derivatives with this severely sterically crowded organosilane the more reactive triflate form, **3**, is required. In the silylation of alcohols typical reaction conditions are 65° in 1,4-dioxane in the presence of triethylamine and DMAP for several hours (Eq. 19). The reactivity depends strongly on the alcohol as well, with p-nitrophenol silylating nicely and phenol requiring the reaction of potassium phenoxide with **3** to get the phenoxysilane.



The silylation of primary amines with **3** proceeds well and in high yield, but secondary amines react very poorly and are best protected as the corresponding carbamates (Eq. 20).



The potassium enolate of ketones reacts with **3** to give the highly protected silyl enol ether again in high yield (Eq. 21).



The silylating reagent **3** shows some intriguing chemoselectivities as illustrated by the products prepared below in Figure 5. For example, the selective protection of a primary amine over that of a primary aniline, a primary amine over that of a primary alcohol, a carboxylic acid over a primary alcohol, and the formation of a silyl enol ether over the silylation of a phenol are all possible as illustrated with the examples in Figure 5.

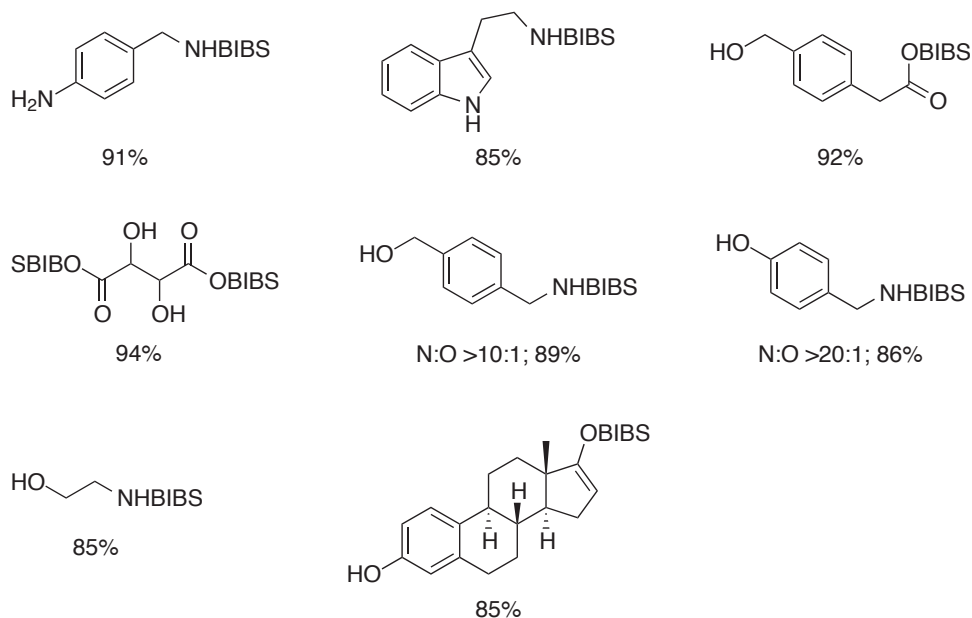
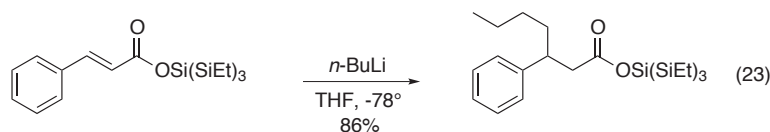
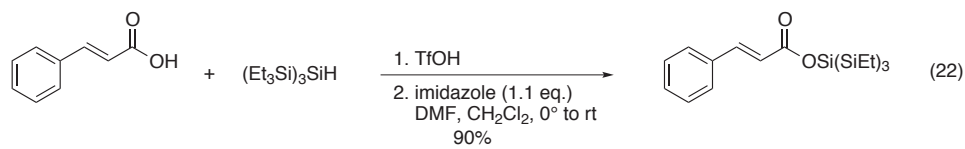


Figure 5

More recently a supersilyl group, tris(triethylsilyl)silyl, has been reported to provide highly stable silylated carboxylic acids (Eqs. 22 & 23). The supersilyl-silylated acids were shown to be stable to Grignard and organolithium reagents in addition to DIBAL-H and LiHMDS, however, they were not stable to methyllithium.^{38,39}



Bridged Organosilyl Protecting Groups

The use of various silylene units such as the dimethyl-, DMS,⁴⁰ diethyl-, DES,⁴¹ diisopropyl-, DIPS,⁴² di-tert-butyl-, DTBS,^{42,43} and diphenylsilylene, DPS,⁴⁴ groups have been employed for the protection of diols, hydroxyacids, diamines, and similar difunctional systems. Here again, as expected, the more hindered the silicon center the more stable the silylated species becomes. Thus, the DTBS ethers of diols are hydrolytically stable between pH 4 and pH 10. The 6- and 7-membered ring systems from the silylene derivatives of 1,3- and 1,4-diols are more stable than the 5-membered rings resulting from the bridged silylation of 1,2-diols. The disilylethane derivative, tetramethyldisilylethane, STABASE, is used for the protection of primary amines, including those of esters of aminoacids.⁴⁵ The tetraisopropylidisiloxanyl unit (from TIPDS) is highly useful for the protection of the 3',5'-dihydroxyl moieties of nucleosides.⁴⁶ The benzostabbase, BSB, group can be used to protect primary aliphatic and aromatic amines.^{47,48}

The commonly utilized silicon-based agents for the protection of diols and related functionalities such as diamines and hydroxy acids are shown in Figure 6.

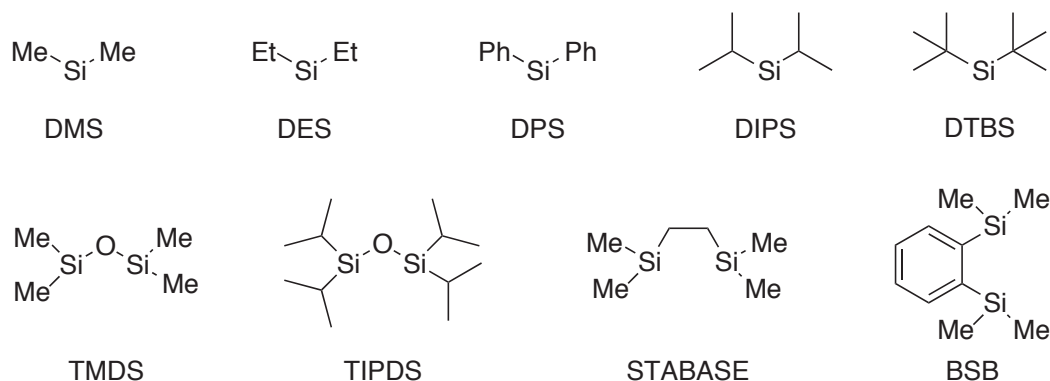
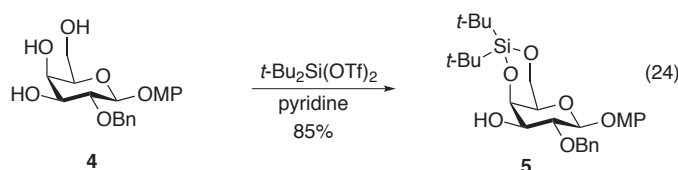
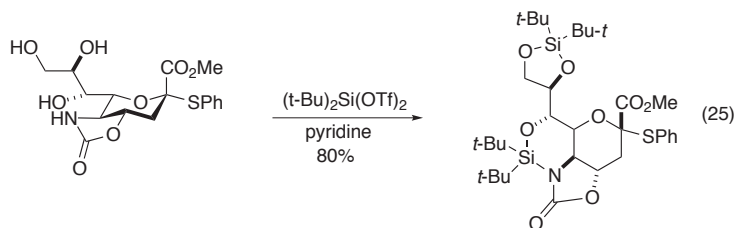


Figure 6

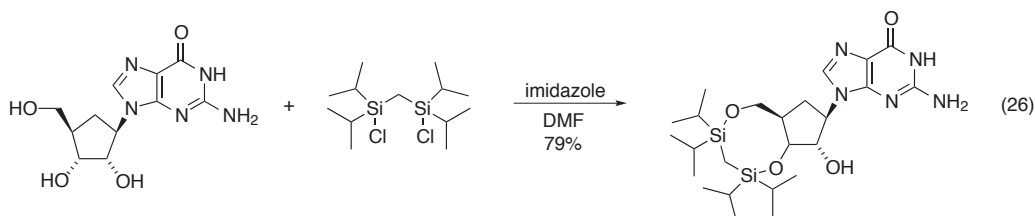
The direct silylation of the triol **4** with di-tert-butylsilylbis(trifluoromethanesulfonate) results in the exclusive silylation of the C-4 and C-6 alcohols to form **5** (Eq. 24).⁴⁹



Di-tert-butylsilylbis(triflate) was used in the synthesis of a double-protected sialic acid building block. This key building block was used to provide the sialylation of primary and secondary hydroxyl groups on galactosides (**Eq. 25**).⁵⁰



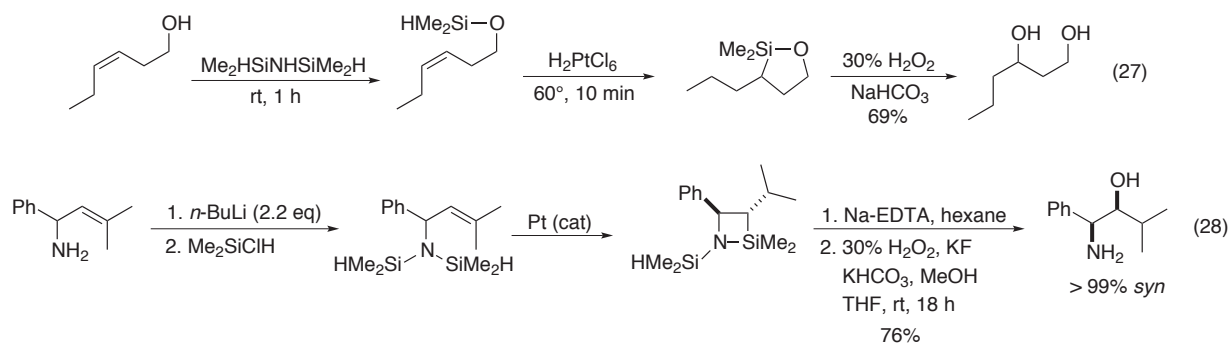
In order to overcome the lability of the tetraisopropylsilyloxanyl-3',5'-protected oligonucleotides, a bridging protecting group for this application, wherein the oxygen is replaced with a methylene group, was developed. This silyl protecting group proved to be equally selective in its reaction and much less labile under strong basic conditions required for the alkylation of the 2-hydroxyl group (**Eq. 26**).⁵¹



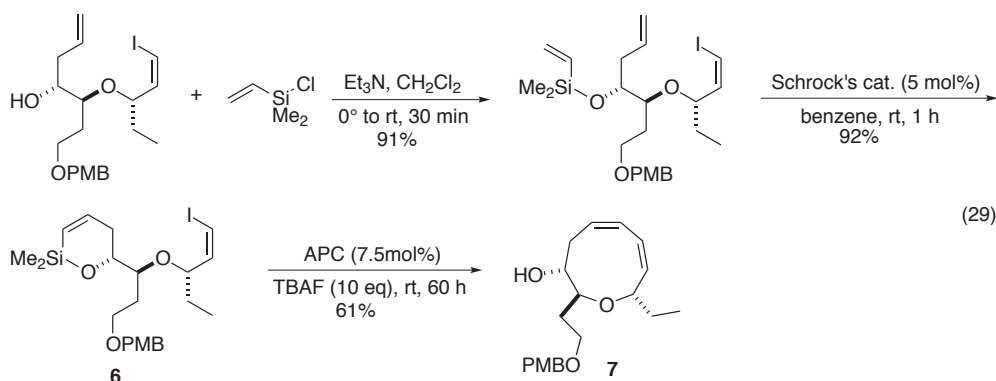
Silylation of Alcohols Employed in Templating Protocols

In addition to the ability to moderate the reactivity of the organosilane groups both sterically and electronically, another distinct advantage of the organosilanes is the ability to take advantage of the tetravalent nature of the silicon atom to employ multiple reactivities in the same reagent. This has successfully been used in a templating fashion wherein the silyl group is attached to an alcohol substituent and then the silyl group is intramolecularly reacted with a second functional group in the molecule.

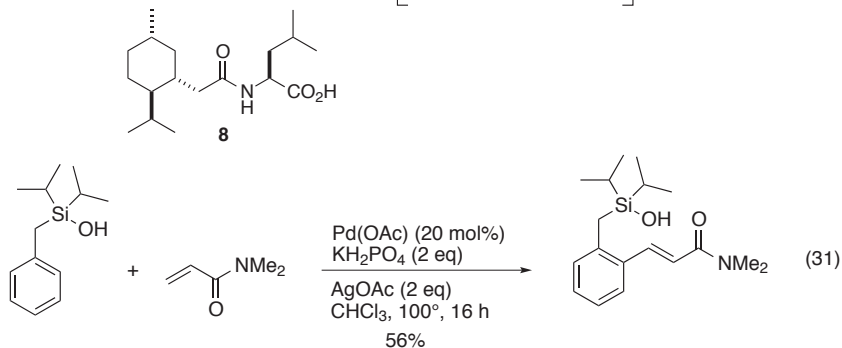
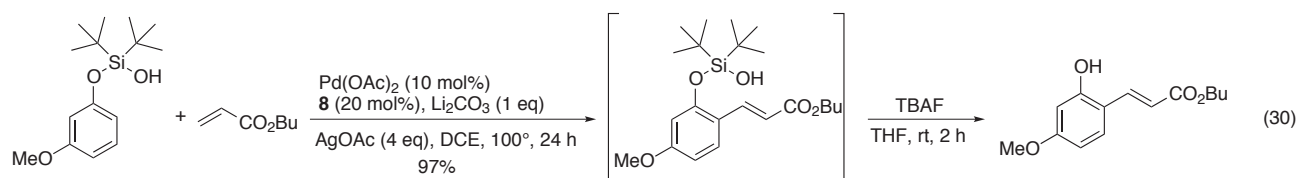
The sequential silylation/hydrosilylation of suitably unsaturated alcohols can lead to oxa-silaheterocycles, which can, in turn, be converted to various organic systems *via* functionalization of the resulting silicon-carbon bond. The silylation-hydrosilylation-oxidation sequence shown in **Eq. 27** is a good example.⁵² A similar sequence was conducted in an enantioselective manner.⁵³ In the case of allyl amines intramolecular ring closure occurs to give the four-membered ring structure oxidation of which provides the β -aminoethanol derivative.⁵⁴ The stereoselectivity can be impressive (**Eq. 28**).



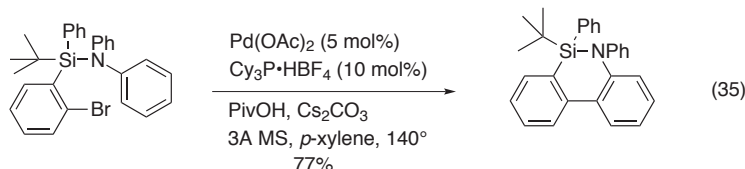
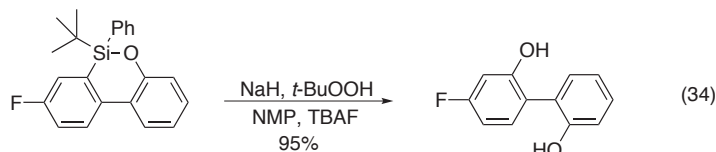
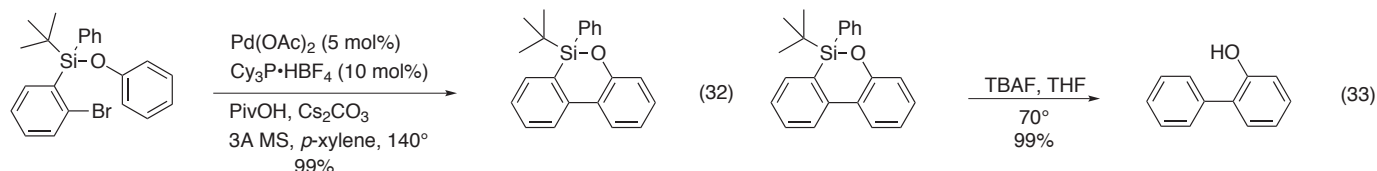
Denmark and Yang established a vinylsilane butenyl ether geometry to carry out a ring-closing-metathesis reaction that set up the alkoxy silane **6** for an intramolecular cross-coupling step to prepare **7** in a synthesis of (+)-brasilenyne (**Eq. 29**).⁵⁵



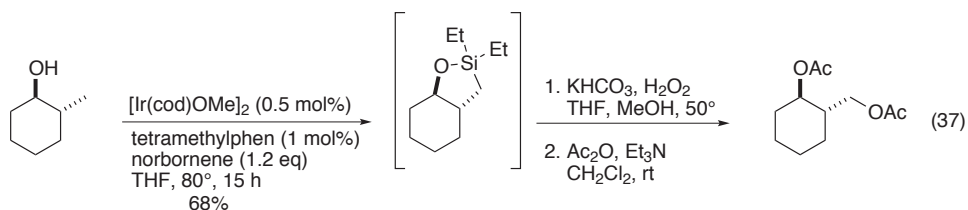
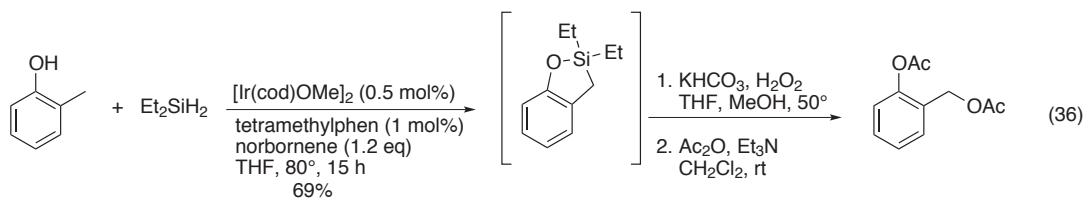
In a somewhat different use of a silyl protecting group for the introduction of organic functionality aryloxydi-tert-butylsilanols were shown to direct the ortho-vinylation of the aryl group *via* a C-H vinylation process. This provides a combination of phenol protection, directing effect and cross-coupling as shown in **Eq. 30**. In addition other silanol directing chemistries are demonstrated in this work, as, for example, that shown in **Eq. 31**.⁵⁶



In a clever application of a silicon-directed cross-coupling aryloxy-substituted *o*-bromoarylsilanes are intramolecularly cross-coupled to form an oxa-silabiphenyl ring system, which can be further modified including desilylation and oxidation (**Eqs. 32 - 34**). The conversion works well with aminofunctional system to form the aza-silabiphenyl ring system (**Eq. 35**).⁵⁷



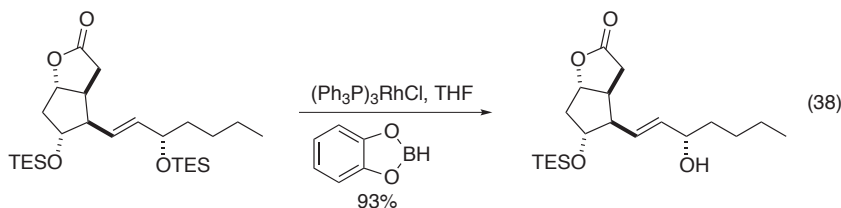
Simmons and Hartwig have utilized an iridium-catalyzed dehydrogenative silylation-C-H activation sequence to prepare oxasilacyclopentanes, which can be oxidized to 1,3-diols. The C-H activation occurs at the γ -position from the siloxy group (Eqs. 36 & 37).⁵⁸



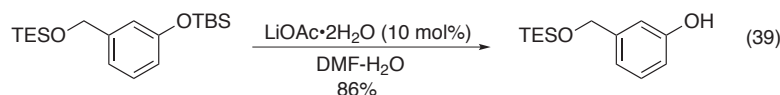
Deprotection of Silyl Ethers

The clean deprotection or desilylation of a silyl-protected functional group is essential to its utility. The relative stability correlation of trisubstituted silyl ethers towards hydrolysis under acid conditions is: TMS \approx DMPS \approx MDPS < TES \approx DMIPS < TPS < TBS < TDS < TIPS << TBDPS < DTBMS.⁵⁹ The relative stabilities towards hydrolysis in alkaline medium is: TMS \approx DMPS \approx MDPS < DMIPS \approx TES < TBDPS \approx TBS < TDS < TIPS < DTBMS.⁵⁹ Denmark and coworkers have looked at the steric and electronic effects influencing the desilylation of silyl ethers under both acid and base conditions.⁶⁰ In addition the long-range structural effects on the desilylation of silyl ethers has been investigated.⁶¹ Typical deprotection protocols for the removal of silyl ethers are acidic aqueous THF, or acidic methanol, alkaline aqueous solutions and sources of fluoride ion, most commonly tetra-*n*-butylammonium fluoride, TBAF, in various solvents. The TBAF reagent has been used in the deprotection of all silyl ethers though the conditions will change depending on the nature of the silyl ether and its surrounding environment. A selection of some interesting and potentially useful examples of selective removal of one silyl ether in the presence of another are shown here.

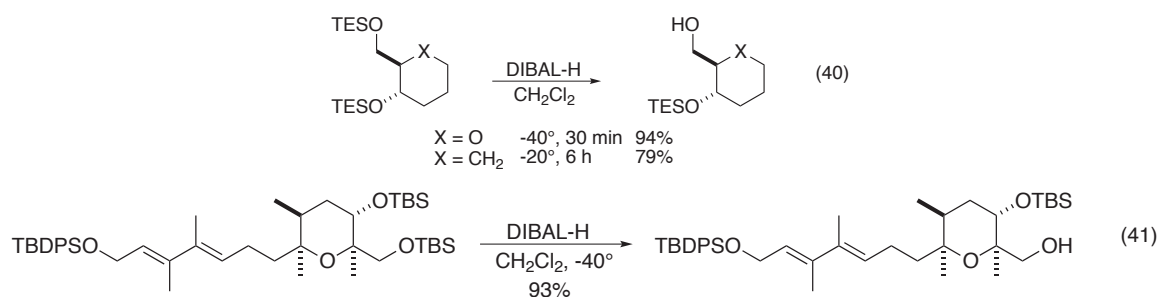
Catecholborane in the presence of Wilkinson's catalyst selectively deprotects TES ethers in the presence of other TES ethers, as well as TBS and TIPS ethers (Eq. 38).⁶² An excess of the catecholborane is required for good yields. Esters and olefins were shown to be stable to the reaction conditions.



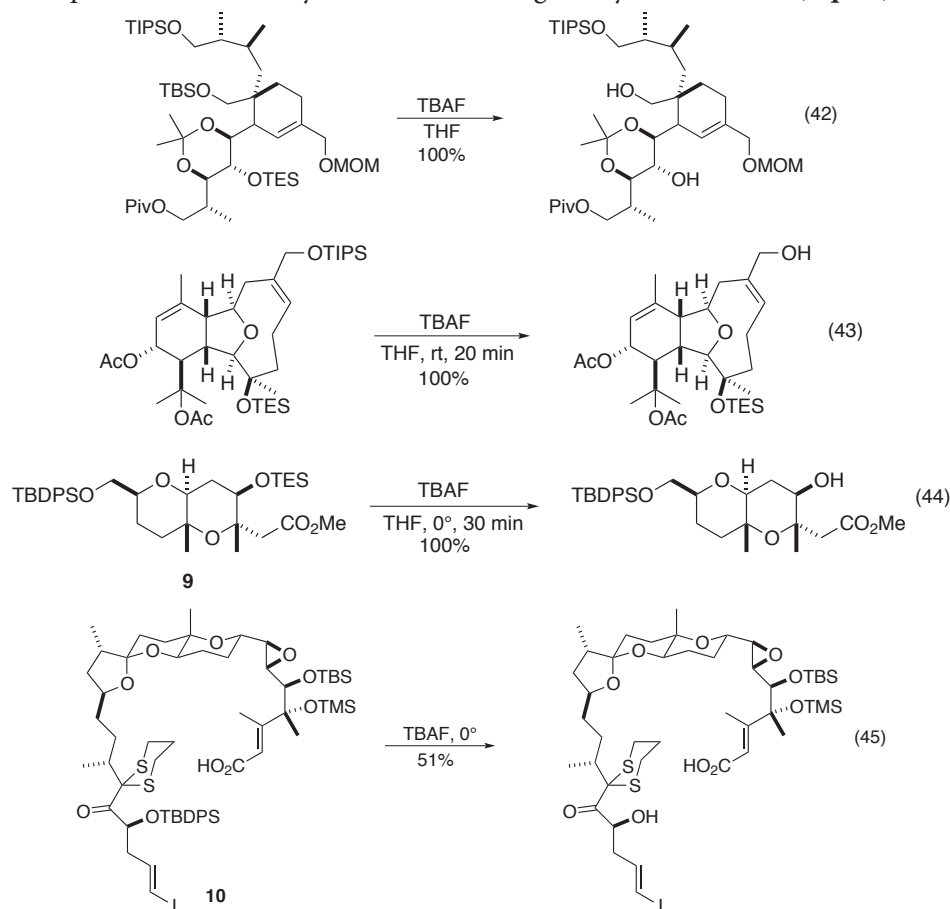
A highly selective deprotection of silyl phenol ethers employs catalytic lithium acetate in moist DMF (Eq. 39).⁶³ The procedure is tolerant of aliphatic silyl ethers, epoxides, and acetates.



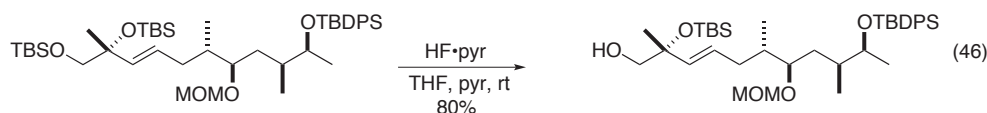
Diisobutylalane, DIBAL-H, has been employed in the selective deprotection of primary TES ethers in the presence of secondary TES ethers (Eq. 40).⁶⁴ The selective removal of TES ethers in the presence of TBS and TBDPS ethers as well as a primary TBS ether in the presence of a secondary TBS ether was also shown to be possible with this reagent (Eq. 41).

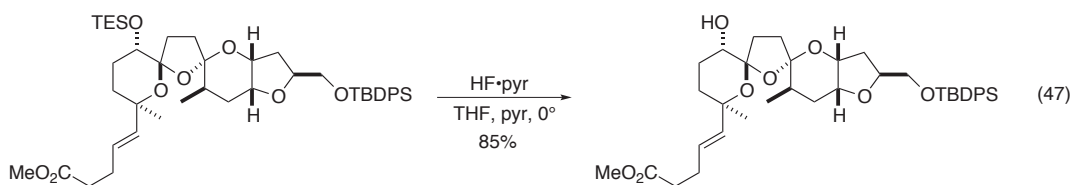


Even though the use of TBAF in THF is a common method for the deprotection of nearly all silyl ethers it can also be selective as shown in Eq. 42 where a primary TIPS ether is untouched by the reagent under the conditions employed.⁶⁵ The strong influence of the environment around a silyl ether is shown in Eq. 43 where a primary TIPS ether is selectively removed in the presence of a tertiary TES ether with the TBAF/THF reagent.⁶⁶ On the other hand the secondary TES ether in **9** is selectively reacted in the presence of the primary TBDPS ether in quantitative yield (Eq. 44).⁶⁷ In an extraordinary example of the influence of the surrounding environment is the selectivity shown in the TBAF deprotection of the secondary TBDPS ether of **10** in the presence of a tertiary TMS ether, although the yield is modest (Eq. 45).⁶⁸

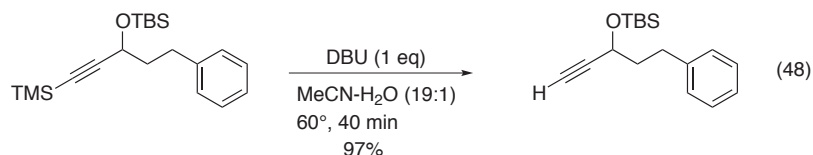


Pyridinium fluoride, HF•pyr has been commonly used for the selective deprotection of silyl ethers in the presence of other silyl ethers as illustrated in Eqs. 46 & 47).^{69,70}





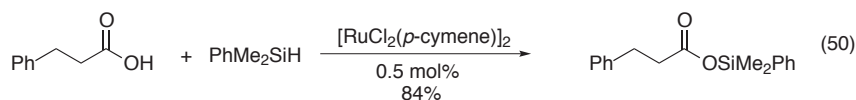
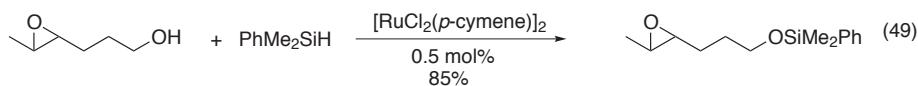
The selective removal of an ethynyl trimethylsilyl group in the presence of silyl ethers was demonstrated with DBU either in stoichiometric or catalytic amounts. When carried out catalytically the required time for complete reaction was increased (Eq. 48).⁷¹



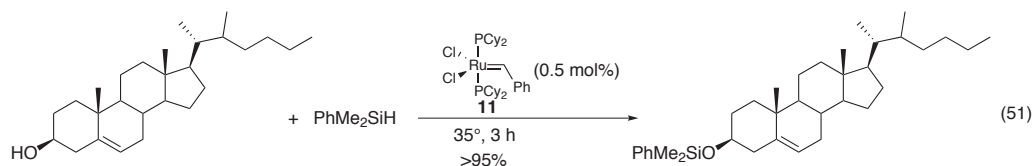
Dehydrogenative Silylation of Alcohols and Other Functionalities

In addition to the more common approaches to the silylation of organic functional groups with chloro, amino, and related silanes, it is possible to react the Si-H bond with alcohols accompanied by the loss of dihydrogen in a process known as dehydrogenative silylation.⁷² The dehydrogenative silylation requires catalysis beyond the normal acid or base. The dehydrogenative silylation approach can offer advantages particularly in cases of the more hindered organosilane protecting groups such as the TES and TBS groups. In the case of the extremely popular and useful TBS protecting group the standard TBS-Cl used for the protection of alcohols is an air-sensitive solid with a melting point of 91° and a boiling point of 120° making it difficult to handle.²² In the case of the TES group, triethylsilane is readily available as a highly useful reducing agent used in organic synthesis and is the most common precursor to the TES-Cl.⁷³

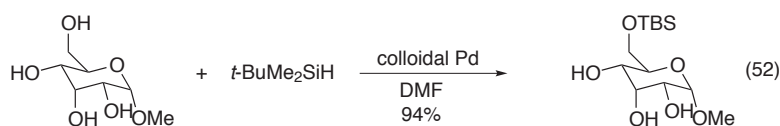
The silylation of alcohols and carboxylic acids with triethylsilane or phenyldimethylsilane was accomplished under the influence of (*p*-cymene)ruthenium dichloride catalysis (Eqs. 49 & 50).⁷⁴ Other dinuclear ruthenium catalysts were also shown to be effective in the dehydrogenative silylation of carboxylic acids albeit at a slower reaction rate.



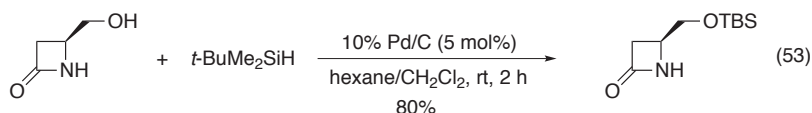
The Grubbs catalyst **11** effects the dehydrogenative silylation of alcohols of all types. In this approach phenyldimethylsilane and diphenylmethylsilane proved to be more reactive than either triethylsilane or tert-butyldimethylsilane (Eq. 51). The release of dihydrogen during the reaction was shown to cause some hydrogenation of olefinic functional groups, but no evidence of cross metathesis was found.⁷⁵



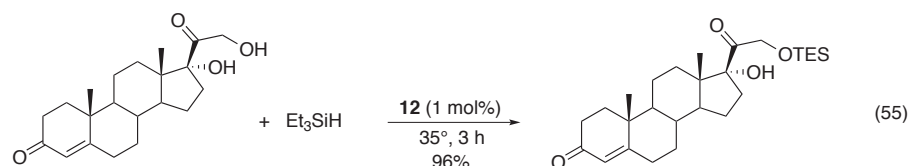
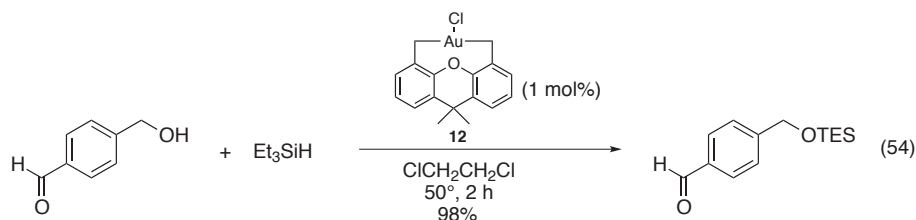
Tert-butyldimethylsilane was shown to very selectively silylate the primary alcohol of methyl glycosides when catalyzed by Pd(0) in the form of a colloidal solution of palladium in DMF (Eq. 52).⁷⁶ The method complements that of other approaches in many instances.



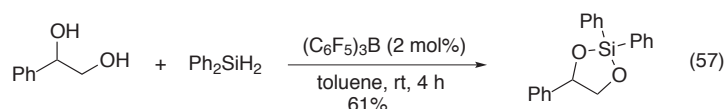
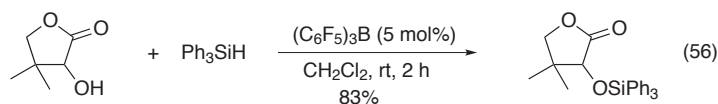
The dehydrogenative silylation of alcohols, amines and carboxylic acids was shown to be possible with only a 5 mol% loading of 10% Pd on charcoal (**Eq. 53**).⁷⁷ It could be assumed that olefins would not be tolerated under these conditions unless the dihydrogen by-product were to be effectively removed.



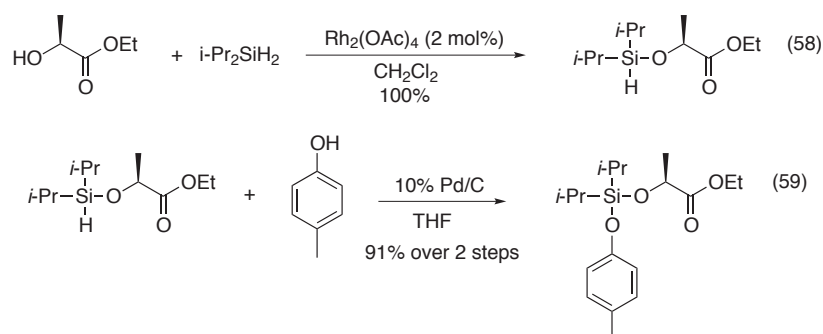
The gold xantphos complex **12** can effect the dehydrogenative triethylsilylation of alcohols with a strong preference for primary alcohols. It was also shown to triethylsilylate an alcohol in the presence of an aldehyde and ketone without reduction of the aldehyde or ketone groups, respectively (**Eqs. 54 & 55**).⁷⁸



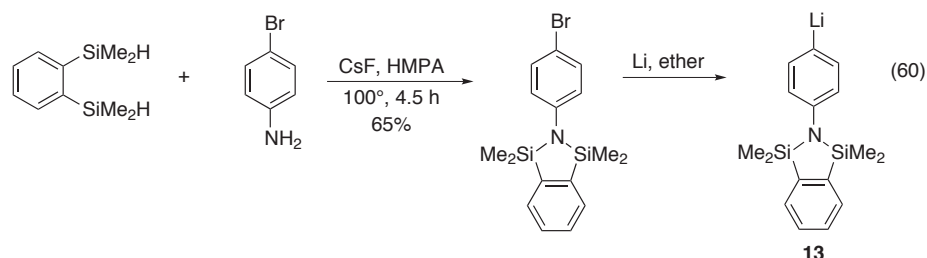
The strong Lewis acid, tris(pentafluorophenyl)boron, was shown to catalyze the dehydrogenative silylation of primary, secondary, tertiary, and phenolic alcohols, including some very highly hindered ones (**Eq. 56**).⁷⁹ The catalyst has been shown to function by activation of the Si-H bond by bonding to the hydridic hydrogen making the silyl group highly electrophilic. The study emphasizes the use of triphenylsilane as the silylating agent, but demonstrates the use of triethylsilane, tert-butyl dimethylsilane and phenyldimethylsilane as well. However, the more highly hindered tribenzylsilane and triisopropylsilane failed to react. Diols can be protected in cyclic form *via* dehydrogenative silylation with diphenylsilane (**Eq. 57**).⁷⁹



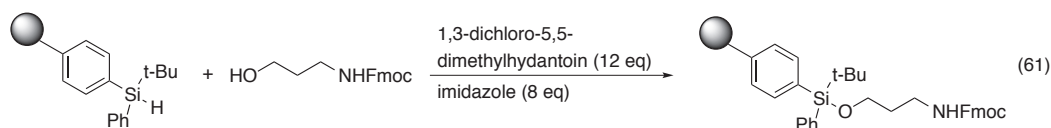
The sequential dehydrogenative silylation of dialkylsilanes can result in the formation of mixed dialkyldialkoxysilanes. This was shown with dirhodium tetraacetate or Pd/C catalysis (**Eqs. 58 & 59**).⁸⁰ A similar approach was employed to prepare phenylalkoxysilanes, Ph(RO)SiH₂, with the preferred catalyst being bis(hexafluoroacetylacetonato)copper (II). In some cases the dialkoxysilane was formed in these reactions.^{81,82}



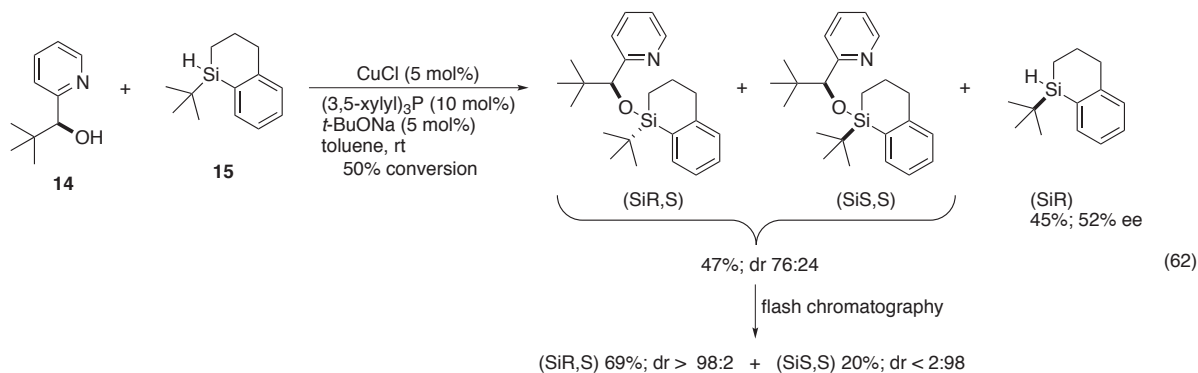
A benzostabbase protection of an aniline based on 1,2-bis(dimethylsilyl)benzene was prepared by dehydrogenative coupling and successfully used in the preparation of the amine-protected 4-lithioaniline, **13** (Eq. 60).^{47,48}



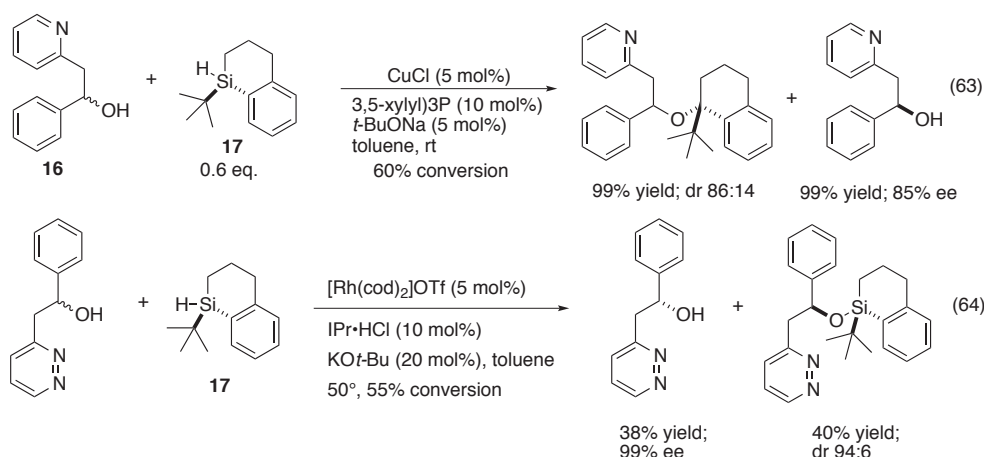
A solid-phase tert-butyldiarylsilyl, TBDAS, protecting group was developed for the purpose of solid-phase synthetic applications. The group, similar in many respects to the TBDPS group was found to be quite robust (Eq. 61).⁸³ Fluoride ion in the form of TBAF or TAS-F in THF was found to cleave the protected alcohol in high yield.



A dehydrogenative silylation approach was used in a classical resolution of the two enantiomers of cyclic silane **15**. Thus, (-)-menthol was reacted with racemic **14** and the resulting diastereomers separated by flash chromatography. The purified diastereomers could be cleanly reduced with DIBAL-H with complete retention at silicon (Eq. 62).⁸⁴



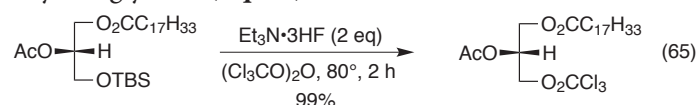
The enantiomerically highly enriched silane **17** was used in a dehydrogenative silylation for the kinetic resolution of racemic secondary alcohols containing a donor group. A series of 2-pyridylethyl alcohols was subjected to dehydrogenative silylation conditions to provide the diastereomeric mixture of silylated alcohols and the enantiomerically enriched alcohol as illustrated by the conversion of **16** (Eq. 63).⁸⁵⁻⁸⁷ A similar investigation was undertaken in the kinetic resolution of b-donor functionalized benzyl alcohols (Eq. 64).⁸⁸ Finally, a similar approach was applied to the kinetic desymmetrization of racemic diols.⁸⁹



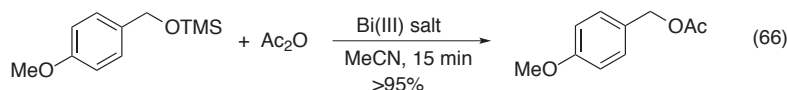
Direct Conversion of Silyl Ethers to Organic Functionality

The direct conversion of a silyl-protected group to a subsequent organic functionality without prior deprotection would be useful. A few selected examples of such direct conversions of silyl ethers are presented herein.

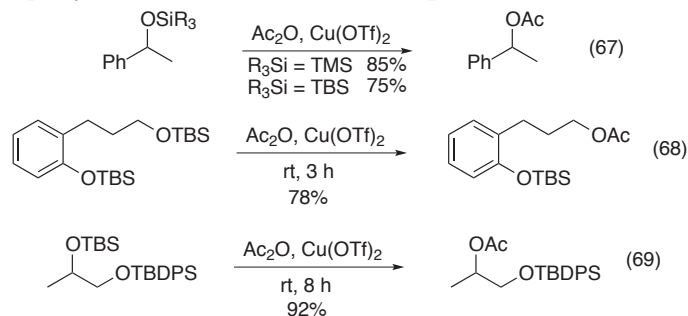
The conversion of a TBS ether directly to the corresponding trichloroacetate ester has been reported. This is illustrated by the synthesis of 1-oleoyl-2-acetyl-*sn*-glycerol (**Eq. 65**).⁹⁰



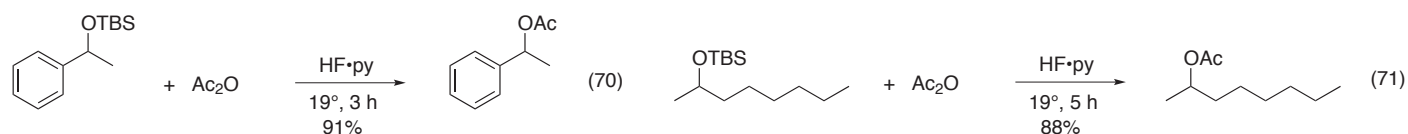
In one of several published methods to convert a silyl ether to the corresponding acetate this conversion was shown to occur with acetic anhydride under the influence of bismuth(III) catalysis (**Eq. 66**).⁹¹ THP ethers were also shown to undergo the corresponding conversion. Bismuth (III) chloride, triflate and trifluoroacetate all produced similar high yields of the acetates. A similar reaction takes place to form benzoates with benzoic anhydride.



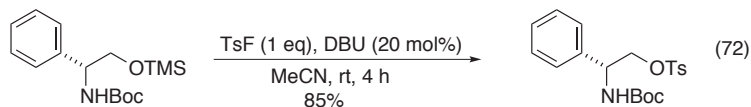
This same conversion can be accomplished with some selectivity employing Cu(II) triflate as the catalyst. Under these conditions it was shown that secondary silyl ethers react well, TBS ethers react only slightly more sluggishly than TMS ethers, but considerably more rapidly than TBDPS ethers and that phenolic TBS ethers react very poorly (**Eqs. 67 - 69**).⁹²



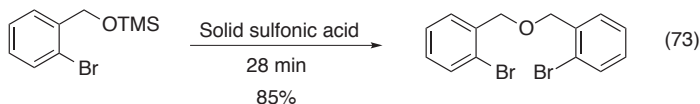
The direct transformation of primary and secondary TBS ethers to their acetates is possible with acetic anhydride and HF•pyr (**Eqs. 70 & 71**).⁹³



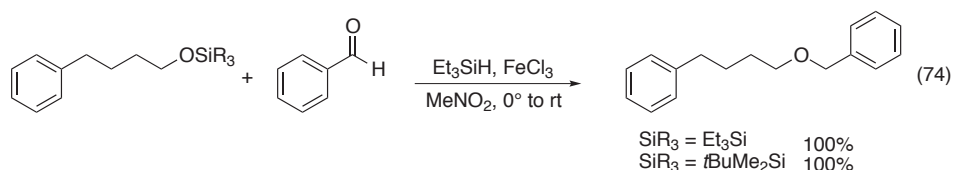
A high-yielding, one-step conversion of silyl ethers to the corresponding tosylate is accomplished by the reaction of the silyl ether with tosyl fluoride in the presence of DBU as a catalyst (**Eq. 72**).⁹⁴ This direct methodology was demonstrated to be useful with TMS, TES, and TBS ethers in high yields as well. The presence of the fluoride aids in the promotion of the reaction as the use of tosyl chloride gave poor conversions to the tosylate.



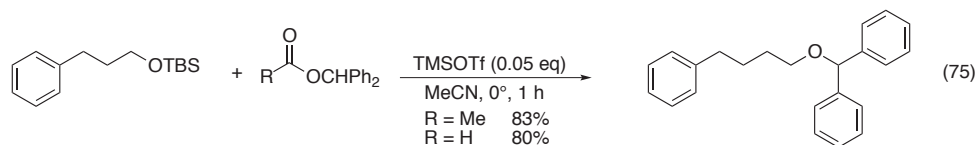
A carbon-based solid acid was used as an alternative to the more common sulfuric acid for the conversion of trimethylsilyl ethers to their corresponding symmetrical ethers under mild conditions (**Eq. 73**).⁹⁵



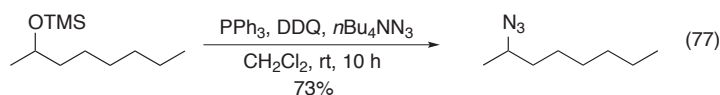
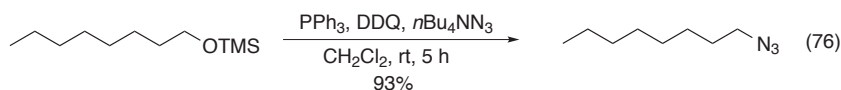
Iron(III) chloride was shown to catalyze the direct conversion of TES or TBS ethers to benzyl ethers with benzaldehyde employing triethylsilane as a reducing agent for the reduction of the benzaldehyde (**Eq. 74**).⁹⁶ Aldehydes other than benzaldehyde such as propionaldehyde and n-pentanal provided the corresponding unsymmetrical dialkyl ethers.



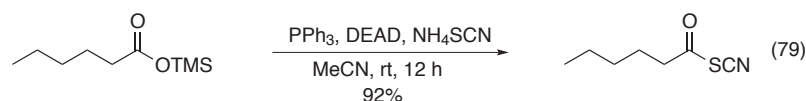
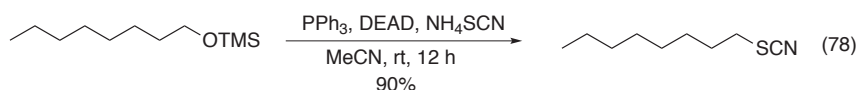
The direct conversion of silyl ethers into their respective diphenylmethyl (DPM) ethers is readily brought about by the reaction with diphenylmethyl formate or acetate in the presence of a catalytic amount of TMSOTf (**Eq. 75**).⁹⁷



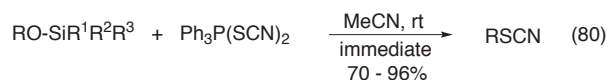
Trimethylsilyl ethers are directly converted to alkyl azides in a rather straightforward manner. Primary silyl ethers are more reactive than secondary or tertiary silyl ethers in this transformation (**Eqs. 76 & 77**).⁹⁸



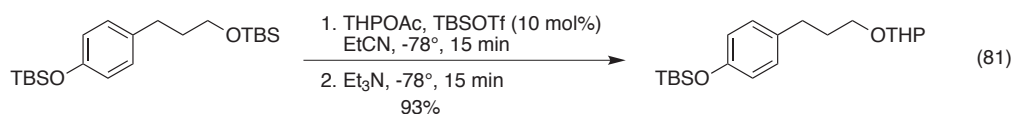
In a similar fashion it was found that trimethylsilyl ethers can be directly converted to thiocyanates as shown in **Eq. 78**.⁹⁹ Interestingly, the corresponding transformation of trimethylsilylcarboxylic acids serves to provide the acyl thiocyanate (**Eq. 79**).



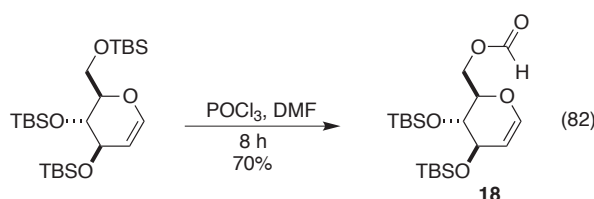
In a slightly different approach triphenyldithiocyanatophosphorus, generated in-situ, directly converts silyl ethers to the thiocyanates in good yields (**Eq. 80**).¹⁰⁰



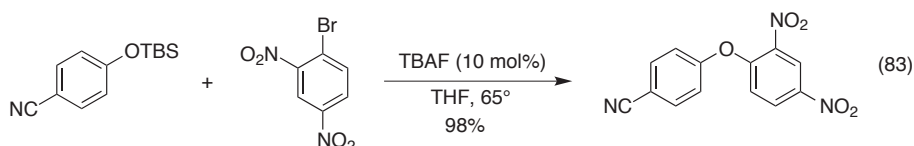
The formation of a THP ether directly from a TBS ether is possible from inexpensive reagents. Catalysis by TBSOTf or TfOH provided the THP ethers in high yields (**Eq. 81**).¹⁰¹ The highly sterically crowded TIPS ethers are also converted to THP ethers under these conditions.



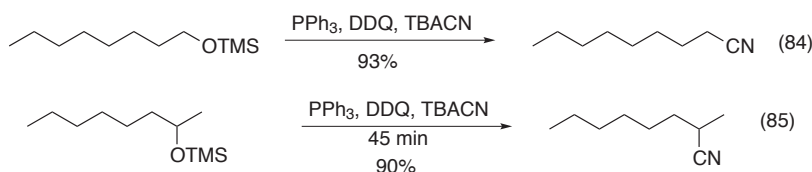
Under Vilsmeier-Haack conditions the trisilyl-protected D-glucal is selectively converted to the C-6 formate **18** (**Eq. 82**).¹⁰²



TBS phenolic ethers can provide the starting point for the formation of aryl-alkyl and diaryl ethers in a fluoride-catalyzed substitution reaction (**Eq. 83**).¹⁰³

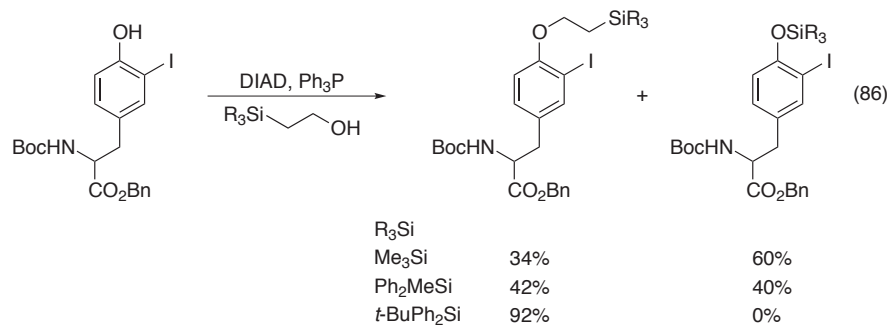


The combination of triphenylphosphine, DDQ, and tetra-n-butylammonium cyanide serves to convert TMS ethers to the nitrile (**Eqs. 84 & 85**).¹⁰⁴

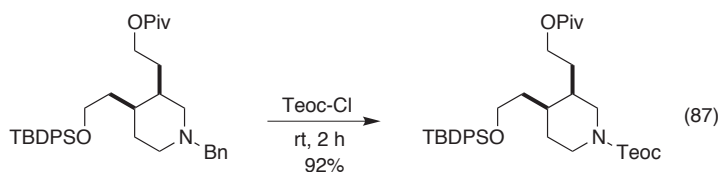


Other

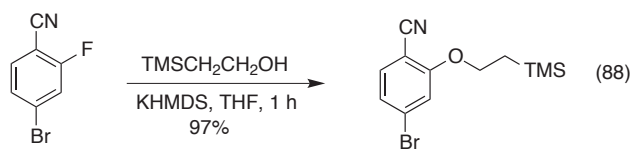
The 2-(tert-butyldiphenylsilyl)ethyl, TBDPSE, group has been shown to be an excellent protecting group for phenols. The protection of several phenols was carried out in excellent yields with none of the direct O-Si derivative being formed, as is the case with other silylethanol protecting groups (**Eq. 86**).¹⁰⁵ The group has been shown to be stable to a variety of reaction conditions. Strong acid or fluoride serves for the deprotection step.



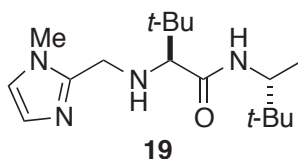
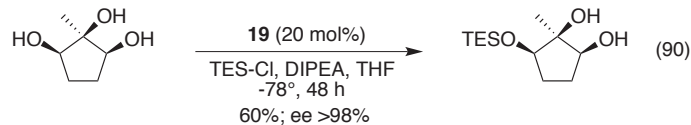
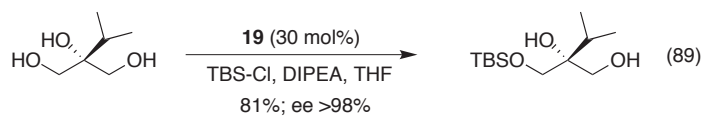
Trimethylsilylethanol was reacted with triphosgene to generate trimethylsilylethylchloroformate (Teoc-Cl) 'in-situ' and this was used to convert N-benzylpiperidines to N-Teoc protected piperidines (**Eq. 87**).¹⁰⁶



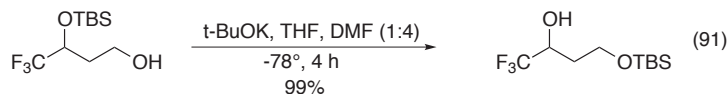
The direct conversion of aryl fluorides to aryloxyethylsilyl ethers using trimethylsilylethanol has been reported. This interesting formation of a silyl-protected alcohol results in the conversion of an aryl fluoride to a phenol (**Eq. 88**).¹⁰⁷ The conversion occurs in modest to excellent yield with only electronic deficient aryl fluorides able to undergo the reaction. The aromatic rings must be electron poor for a successful conversion. It is interesting to note that the substitution reaction occurs in favor of the Peterson elimination to form trimethylsilanol and ethylene.



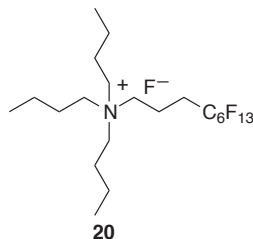
The catalyst **19** was employed in the enantioselective protection of one of the two prochiral hydroxyl groups. The presence of the 2-hydroxyl group proved necessary for success. This was used in an enantioselective synthesis of cleroidincin F 2 and cleroidincin C 3 (**Eqs. 89 & 90**).¹⁰⁸



Reminiscent of a Brook rearrangement the observation of an oxygen to oxygen silyl migration under the proper conditions is noted. An example of the migration of a TBS group from a secondary oxygen to a primary oxygen is shown in **Eq. 91**.¹⁰⁹

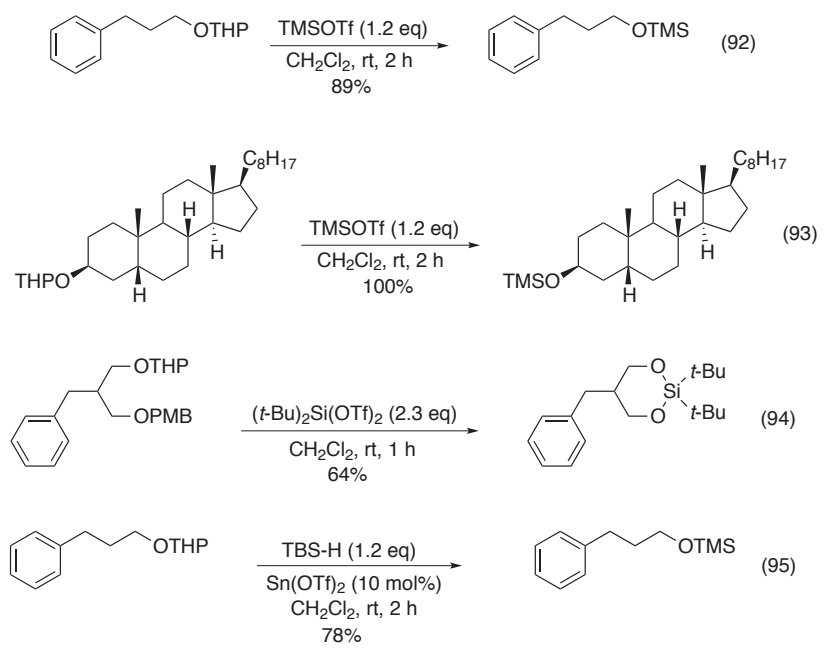


A fluorinated version of TBAF, **20**, has been reported. This presents a potential solution to the issue of removing the TBAF after a deprotection step has been carried out. It has been shown to be selective in the removal of TES ethers in the presence of TBS ethers.¹¹⁰

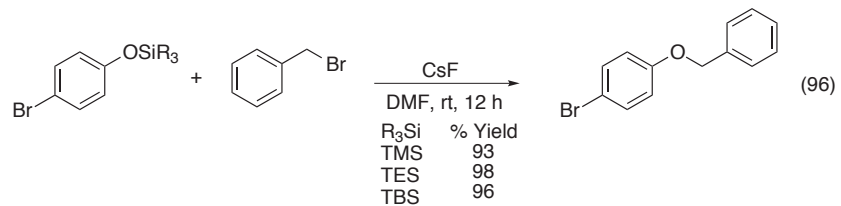


Silver fluoride has been found to selectively desilylate ethynyltriisopropylsilanes in the presence of several other functional moieties.¹¹¹

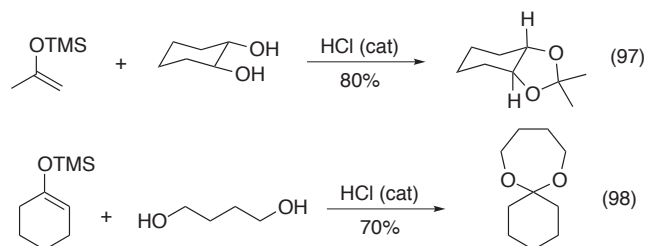
The direct conversion of THP ethers to silyl ethers is possible *via* the reaction with the silyl triflate (**Eqs. 92 & 93**).¹¹² This is possible with protected 1,3-diols derivatives and with PMB-protected alcohols as well (**Eq. 94**). The conversion of PMB ethers to silyl ethers has also been accomplished with the silyl triflate and triethylamine (**Eq. 95**).¹¹³



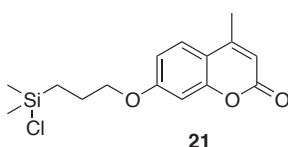
Silyl ethers were converted to arylalkyl ethers *via* fluoride ion desilylation substitution. The alkyl halide must be a reactive one. Direct esterification of the silyl ether is also possible under similar conditions (**Eq. 96**).¹¹⁴



In an interesting twist on the use of an organosilane for protection of diols, Larson and Hernández found that the enol trimethylsilyl ether of acetone very effectively provided acetonides from diols. As an extension of this it was found that enol trimethylsilyl ethers are excellent reagents for the formation of the corresponding even the acetonide of trans-1,2-cyclohexanediol (Eq. 97 & 98).¹¹⁵ The corresponding reactions were also shown to occur with 2-mercaptoethanol and enol trimethylsilyl ethers.



The fluorescent organosilane **21** represents a silicon-based protecting group that has the capability of serving as a fluorescent tag as well.¹¹⁶



The organosilanes **22**, **23**, and **24** represent potential chiral silicon-based protecting groups. The intriguing pentafluorophenylsilane **25**, known as the flophemesyl chloride, is used as a derivatizing agent for electron-capture detection and photoionization detection.^{117,118}

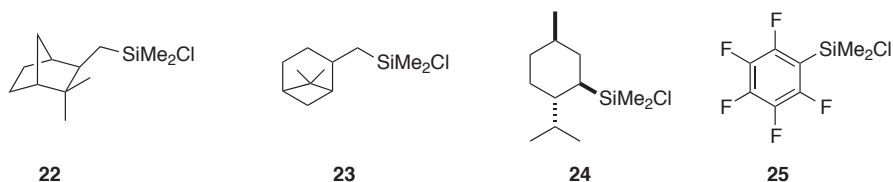


Table 2
Trimethylsilyl Blocking Agents

Product	Structure	Comments	Pricing
SIT8510.0 Trimethylchlorosilane, TMCS [75-77-4]		Reacts in presence of HCl acceptor. ⁶ Will silylate strong acids with expulsion of HCl. ¹¹⁹ High purity grade available, SIT8510.1. Protects hindered alcohols w/ Mg/DME. ¹²⁰	25g \$12.00 750g \$48.00 3kg \$180.00 15kg \$291.00
SIT8430.0 Trimethylbromosilane, TMBS [2857-97-8]		More reactive than SIT8510.0 Less reactive, but more photolytically stable than SIT8564.0. ¹²¹	25g \$36.00 2.5kg \$700.00
SIT8564.0 Trimethyliodosilane, TMIS [16029-98-4]		Extremely reactive silylating agent. ¹²¹ Used with HMDS for hindered alcohols. ¹²² Forms enol silyl ethers with ketones and SIT8620.0. ¹²³	25g \$54.00 100g \$176.00 2.5kg \$1,056.00

Table 2 (continued)

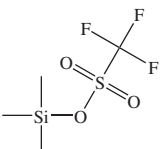
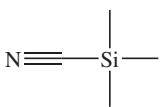
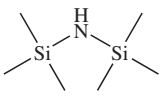
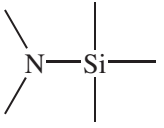
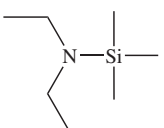
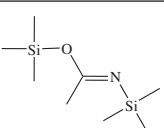
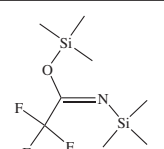
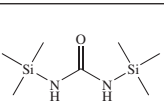
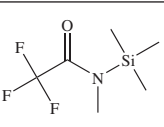
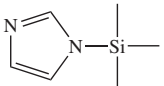
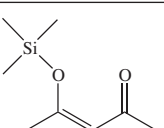
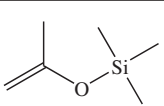
Product	Structure	Comments	Pricing
SIT8620.0 Trimethylsilyltrifluoromethanesulfonate TMSOTf [27607-77-8]		Strong silylating agent for C- or O-silylations. ^{123,124} Reacts w/ nitroalkanes to give N, N-bis (trimethylsiloxy) enamines. ^{125,126} These are useful reagents. ¹²⁷	25g \$36.00 100g \$117.00 2.5kg \$1,095.00
SIT8585.0 Trimethylsilyl Cyanide TMSCN [7677-24-9]		Releases toxic HCN upon reaction. Extremely reactive silylating agent for acids and alcohols. Amines and thiols react more slowly than acids and alcohols. Does not react with amides, ureas or carbonates. ¹²⁸ Silylates amino acids. ¹²⁹ *includes liquid dispensing cylinder	25g \$60.00* 1.5kg \$840.00*
SIH6110.0 Hexamethyldisilazane, HMDS [999-97-3]		Releases ammonia upon reaction. Both trimethylsilyl groups used. Silylations catalyzed by SIT8510.0 and other reagents. ⁶	25g \$10.00 1.5kg \$60.00 14kg \$315.00
SID3605.0 Dimethylaminotrimethylsilane, TMSDMA [2083-91-2]		Similar to SID6110.0 and SID3398.0 Liberates Me ₂ NH upon reaction. Liberates Me ₂ NH upon reaction. Silylates urea-formaldehyde polycondensates. ¹³⁰ Silylates phosphorous acids. ¹³¹	25g \$38.00 100g \$123.00 2kg \$920.00
SID3398.0 Diethylaminotrimethylsilane, TMSDMEA [996-50-9]		Releases diethylamine upon reaction. Moderately strong silylating agent. Selectively silylates equatorial over axial hydroxyls. ¹³²	25g \$28.00 100g \$90.00 2kg \$920.00
SIB1846.0 Bis(Trimethylsilyl)acetamide, BSA [10416-59-8]		More reactive than SIH6110.0. Releases neutral acetamide upon re-action. Both silyl groups used. Used for silylation in analytical applications. ¹³³ Reactions catalyzed by acid. Forms enol silyl ethers in ionic liquids. ¹³⁴	25g \$18.00 100g \$58.00 2kg \$560.00
SIB1876.0 Bis(Trimethylsilyl)trifluoroacetamide, BSTFA [25561-30-2]		More reactive than BSA (SIB1846.0). Commonly used for analytical purposes. Reacts very well in DMF or acetonitrile. ^{14,133}	25g \$58.00 100g \$188.00 2kg \$1,360.00
SIB1878.0 Bis(Trimethylsilyl)urea, BSU [18297-63-7]		By-product is urea. Used for alcohols and acids. ¹³⁵ Used in synthesis of penicillins and cephalosporins. ¹³⁶	50g \$16.00 250g \$60.00 10kg \$780.00
SIM6576.0 N-Methyl-N-Trimethylsilyltrifluoroacetamide MSTFA [24589-78-4]		Silylation reagent similar to SIB1846.0, but with liquid, volatile byproduct.	25g \$64.00 100g \$224.00
SIT8590.0 Trimethylsilylimidazole, TMSIM [7449-74-3]		Powerful silylating agent for alcohols. Does not react with aliphatic amines. ⁶	25g \$26.00 100g \$84.00 2kg \$620.00
SIT8572.0 2-Trimethylsiloxy-pent-2-en-4-one [13257-81-3]		Reacts with 1°, 2° and 3° alcohols. ¹³⁷	25g \$68.00
SII6460.0 Isopropenoxytrimethylsilane, IPOTMS [1833-53-0]		By-product is acetone. Good for alcohols and acids. ¹³⁸ Provides acetanides with diols. ¹¹⁵	5g \$68.00

Table 2 (continued)

Product	Structure	Comments	Pricing
SIM6496.0 1-Methoxy-1-trimethylsiloxy- 2-methyl-1-propene [31469-15-5]		Used for silylation of acids, alcohols, thiols, amides and ketones. ^{139,140}	25g \$94.00 100g \$306.00
SIM6571.5 Methyl Trimethylsilylacetate [2916-76-9]		Used for 3° alcohols and enolizable ketones. ^{141,142}	10g \$90.00
SIE4901.6 Ethyl Trimethylsilylacetate [4071-88-9]		Silylation of ketones, alcohols, acetylenes, thiols under the influence of fluoride ion. ^{143-145d}	5g \$40.00
SIA0555.0 Allyltrimethylsilane [762-72-1]		Neutral propylene by-product. Acid-catalyzed silylations. Used for acids ¹⁴⁶ and thiols. ¹⁴⁷ Employed in the synthesis of N-trimethylsilylpyridinium triflate an active trimethylsilylating agent. ¹⁴⁸	25g \$39.00 100g \$126.00 1.5kg \$780.00
SIT8588.5 2-(Trimethylsilyl)ethoxymethyl- chloride, 95%, SEM-Cl [76513-69-4]		Hydroxyl group protecting unit. Deprotected with fluoride ion. ¹⁴⁹ Used to protect carboxylic acids. ^{150,151} Protects anomeric center of pyranosides. ¹⁵² Used for the introduction of hydroxymethyl group. ¹⁵³	5g \$92.00 25g \$368.00
SIT8580.0 Trimethylsilyl Azide [4648-54-8]			10g \$34.00 50g \$136.00

Table 3
Trialkylsilyl Blocking Agents

Product	Structure	Comments	Pricing
SIT8250.0 Triethylchlorosilane [994-30-9]		Stability of ethers intermediate between TMS and TBS ethers. ¹⁵⁴ Good for 1°, 2°, 3° alcohols. Can be cleaved in presence of TBS, TIPS and TBDPS ethers. ¹⁰	10g \$18.00 50g \$72.00 2kg \$750.00
SID3603.0 N,N-Dimethylaminotriethylsilane [3550-35-4]		Very reactive triethylsilyl protecting group. Dimethylamine by-product produced.	50g \$145.00
SIB1937.0 n-Butyldimethyl(dimethylamino) silane [181231-67-4]		Reactive aminofunctional organosilane.	10g \$45.00 50g \$190.00
SIT8335.0 Triethylsilyl-trifluoromethanesul- fonate [79271-56-0]		More reactive than SIT8250.0. Useful for more hindered alcohols. ¹⁵⁵	10g \$44.00 50g \$144.00 2kg \$2,120.00

Table 3 (continued)

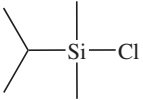
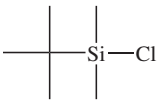
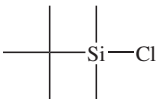
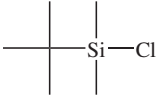
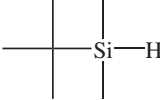
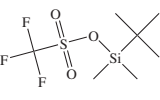
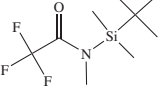
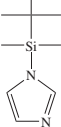
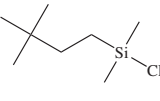
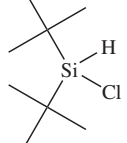
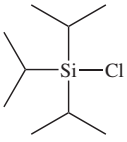
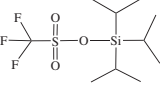
Product	Structure	Comments	Pricing
SII6462.0 Isopropylchlorosilane [3634-56-8]		Ethers comparable in stability to those of TES-protected ethers. ¹⁵⁶	25g \$64.00 100g \$208.00 2kg \$1,880.00
SIB1935.0 and SIB1935.2 tert-Butyldimethylchlorosilane [18162-48-6]		Excellent for 1° and 2° alcohols. Silylation catalyzed by imidazole. Stable to many reagents. ²² Can be selectively cleaved in presence of acetate, THP and benzyl ethers ¹⁵⁷ among others. ¹⁵⁸	25g \$40.00 100g \$130.00 750g \$351.00 2kg \$720.00
SIB1935.4 tert-Butyldimethylchlorosilane, 3M in THF [18162-48-6]			100g \$60.00 2kg \$344.00
SIB1935.5 tert-Butyldimethylchlorosilane, 2.85M in toluene [18162-48-6]			100g \$60.00 2kg \$344.00 750g \$158.00
SIB1938.0 tert-butyltrimethylsilane [29681-57-0]		Sterically hindered organosilane capable of dehydrogenative coupling. ⁷⁶	5g \$38.00 25g \$152.00
SIB1967.0 tert-Butyldimethylsilyltrifluoro- methanesulfonate [69739-34-0]		More reactive than SIB1935.0 ¹⁵⁹ Converts acetates to TBS ethers. ¹⁶⁰	10g \$58.00 50g \$232.00 2kg \$980.00
SIB1966.0 N-(tert-Butyldimethylsilyl)- N-trifluoroacetamide [77377-52-7]		Employed in silylations for analytical purposes. ^{161,162}	5g \$88.00
SIB1964.0 tert-butyltrimethylsilylimidazole		Reactive sterically hindered organosilane.	1g \$64.00
SID4065.0 3,3-Dimethylbutyldimethyl- chlorosilane [56310-20-4]		Sterically hindered neohexylchlorosilane protecting group.	10g \$82.00
SID3120.0 Di-tert-butylchlorosilane [56310-18-0]		Used in selective silylation of internal alcohols or diols. ¹⁶³ Employed in the <i>o</i> -vinylation of phenols <i>via</i> silylation/direction sequence. ¹⁶⁴	
SIT8384.0 Triisopropylchlorosilane [13154-24-0]		TIPS ethers more stable than TBS ethers. ²⁴ Protects carboxylic acids. ¹⁶⁵ Used in synthesis of free-4-hydroxyhexopyranoses. ¹⁶⁶	25g \$48.00 100g \$156.00 2kg \$1,480.00
SIT8387.0 Triisopropylsilyltrifluoromethane- sulfonate [80522-42-5]		More reactive than SIT8384.0. ¹⁶⁷ Used to make Tsoc, (triisopropylsilyloxycarbonyl) protecting groups for amines. ¹⁶⁸	10g \$49.00 50g \$196.00 2kg \$1,720.00

Table 3 (continued)

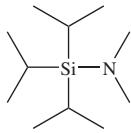
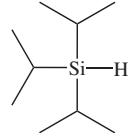
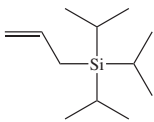
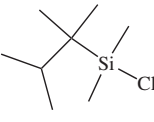
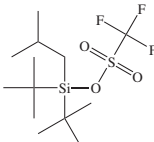
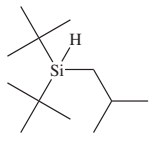
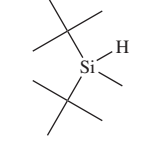
Product	Structure	Comments	Pricing
SIT8384.5 Triisopropyl(dimethylamino)silane [181231-66-3]		Reactive sterically hindered organosilane.	10g \$92.00
SIT8385.0 Triisopropylsilane [6485-79-6]		Silylates strong acids with loss of hydrogen. ¹⁶⁷ Silylates 1° alcohols selectively. ²⁵	25g \$26.00 100g \$84.00 1.5kg \$1,005.00
SIA0535.0 Allyltriisopropylsilane [24400-84-8]		Reaction w/ triflic acid and then pyridine gives the active triisopropylsilylating agent, triisopropylsilylpyridinium triflate. ¹⁴⁸	5.0g \$124.00
SIT7906.0 Thexyldimethylchlorosilane [67373-56-2]		Ethers show stability similar to or greater than the TBS ethers. Used for 1° and 2° amines. ^{29,169} Selective for 1° alcohols. ¹⁶⁹	25g \$52.00 100g \$169.00 750g \$860.00
SID3226.0 Di-tert-butylisobutylsilyltrifluoromethanesulfonate, BIBS [1314639-86-5]		Highly sterically-hindered blocking agent useful for protection of alcohols, amines, acids, enol silyl ethers. ³⁷	10g \$165.00
SID3224.0 Di-tert-butylisobutylsilane BIBS-H [1314639-86-4]		Highly sterically-hindered silane for potential dehydrogenative silylation. ^{37,76}	10g \$180.00
SID3258.0 Di-tert-butylmethylsilane [56310-20-4]		Highly sterically-hindered silane for potential dehydrogenative silylation.	10g \$82.00

Table 4
Phenyl-Containing Blocking Agents

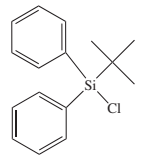
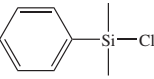
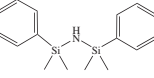
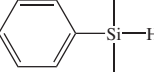
Product	Structure	Comments	Pricing
SIB1968.0 tert-Butyldiphenylchlorosilane [58479-61-1]		Forms more stable ethers than TBS ethers. ³¹ Used to protect phenols, ¹⁷⁰ amines, ¹⁷¹ carboxylic acids, and amides. ^{172,173}	10g \$26.00 50g \$104.00 2kg \$1,520.00
SIP6728.0 Phenyldimethylchlorosilane [768-33-2]		Used in analytical procedures. ¹⁷⁵	25g \$26.00 100g \$84.00 2kg \$760.00
SID4586.0 Diphenyltetramethyldisilazane [3449-26-1]		Similar to SIP6728.0. Emits ammonia upon reaction. Used for silylation of capillary columns. ¹⁷⁶	5g \$36.00 25g \$144.00 2kg \$1,720.00
SIP6729.0 Phenyldimethylsilane [766-77-8]		Reacts with alcohols in presence of Wilkinson's catalyst. ¹⁷⁷	25g \$42.00 100g \$136.00 2kg \$1,080.00

Table 4 (continued)

Product	Structure	Comments	Pricing
SID4552.0 Diphenylmethylchlorosilane [144-79-6]		Stability versus other silyl ethers studied. ⁶⁰	25g \$32.00 100g \$84.00 2.5kg \$580.00
SIT8645.0 Triphenylchlorosilane [76-86-8]		Ethers hydrolyze comparably to TMS ethers in base and 4 times slower in acid. ¹⁷⁸ Can lead to solid products. ¹⁷⁹	25g \$56.00 100g \$176.00
SIA0575.0 Allyltriphenylsilane [18752-21-1]		Reaction w/triflic acid and then pyridine gives triphenylsilylpyridinium triflate, an active triphenylsilylating agent. ¹⁴⁸	2.5g \$52.00
SID4552.5 Diphenylmethyl(dimethylamino)-silane [68733-63-1]		More reactive than SID4552.0. Liberates dimethylamine upon reaction.	25g \$48.00
SIB1026.4 1,3-Bis(4-biphenyl)-1,1,3,3-tetramethyldisilazane		Reactivity and stability similar to that of SID4586.0	10g \$154.00

Table 5
Specialty Silicon-Based Blocking Agents

Product	Structure	Comments	Pricing
SIP6716.1 Pentafluorophenyldimethylchlorosilane FLOPHMESYL CHLORIDE [20082-71-7]		Ethers detectable at femtogram level by ECD. Forms excellent derivatives for mass spectral analysis. ^{117,118,180,181}	5g \$162.00
SIT8589.2 Trimethylsilylethanol [2916-68-9]		Used for protection of acids. ^{182,183}	10g \$94.00 50g \$376.00
SIC2285.0 Chloromethyldimethylchlorosilane [1719-57-9]		Can form cyclic products with appropriate 1,2-difunctional substrates. ¹⁸⁴ Used in analytical applications for greater ECD detectability. ¹⁸⁵	25g \$16.00 750g \$160.00 2kg \$310.00
SIB1890.0 Bromomethyldimethylchlorosilane [16532-02-8]		Has been applied to the synthesis of diols and β -methyl alcohols. ^{186,187}	25g \$64.00 100g \$208.00
SID3535.0 Diisopropylchlorosilane [2227-29-4]		Silylates and reduces β -hydroxy ketones selectively. ¹⁸⁸ Photochemically removable. ¹⁸⁹	5g \$40.00 25g \$160.00

Table 5 (continued)

Product	Structure	Comments	Pricing
SIH5840.4 (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)-dimethylchlorosilane [74612-30-9]		Potential blocking agent for fluorous phase synthesis. ¹⁹⁰	5g \$44.00 25g \$176.00
SIB1815.5 Bis(tridecafluoro-1,1,2,2-tetrahydrooctyldimethylsiloxy)-methylchlorosilane		Potential blocking agent for fluorous phase synthesis. ¹⁹⁰	5g \$175.00
SIB1837.0 Bis(trimethylsiloxy)dichlorosilane [2750-44-9]		Sterically-hindered for the protection of diols	25g \$96.00
SIC2266.8 7-[3-(Chlorodimethylsilyl)propoxy]-4-methylcoumarin [129119-77-3]		Flourescent tag silicon-based protecting group. ¹¹⁶	10g \$80.00
SIC2056.2 (-)-Camphanyldimethylchlorosilane [684284-12-6]		Chiral silicon-based protecting group.	10g \$88.00
SID4074.0 (Dimethylchlorosilyl)methyl-7,7-dimethylnorpinane [72269-53-5]		Chiral silicon-based blocking agent.	10g \$37.00
SIM6472.7 (-)-Menthyl dimethylsilane		Chiral silicon-based protecting group <i>via</i> dehydrogenative silylation. ⁷⁶	5g \$170.00

Table 6
Bridging Silicon-Based Blocking Agents

Product	Structure	Comments	Pricing
SID4120.0 and SID4120.1 Dimethyldichlorosilane [75-78-5]		Reacts with alcohols, ¹⁹¹ diols, ⁹²⁵ and hydroxy carboxylic acids. ¹⁹³ Employed as a protecting group/template in C-glycoside synthesis. ¹⁹⁴	500g \$29.00 2kg \$68.00
SIB1072.0 Bis(Dimethylamino)dimethylsilane [3768-58-9]		More reactive than SIB4120.0. Reacted with diols, ¹⁹⁵ diamines, ¹⁹⁶ and treatment for glass. ¹⁹⁷	25g \$32.00 100g \$104.00 2kg \$620.00
SIB1068.0 Bis(Diethylamino)dimethylsilane [4669-59-4]		Similar to SIB1072.0.	50g \$136.00 2kg \$820.00
SIH6102.0 Hexamethylcyclotrisilazane [1009-93-4]		Silylates diols with loss of ammonia. Similar in reactivity to HMDS. ^{198,199}	25g \$26.00 100g \$84.00 2kg \$640.00

Table 6 (continued)

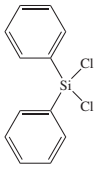
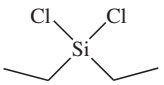
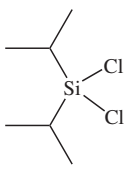
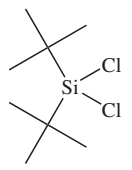
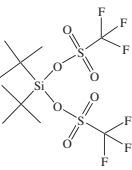
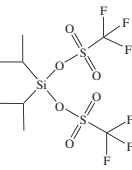
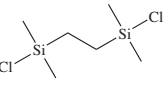
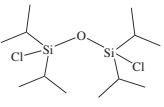
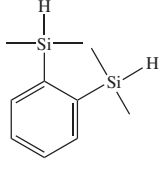
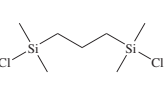
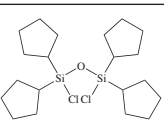
Product	Structure	Comments	Pricing
SID4510.1 Diphenyldichlorosilane [80-10-4]		Reacts with alcohols, ²⁰⁰ diols, ¹⁹⁵ 2-hydroxybenzoic acids. ²⁰¹	25g \$14.00 100g \$46.00 2kg \$390.00
SID3402.0 Diethyldichlorosilane [996-50-9]		Similar to, but more stable derivatives than dimethylsilylenes.	25g \$32.00 100g \$104.00 1kg \$660.00
SID3537.0 Diisopropyldichlorosilane [7751-38-4]		Forms tethered silyl ethers from diols. ^{42,202,203} Protects 3',5' hydroxyls of nucleosides, but less effectively than SIT7273.0. ²⁰⁴	10g \$21.00 50g \$84.00 1kg \$880.00
SID3205.0 Di-tert-butyl-dichlorosilane [18395-90-9]		Used to protect 1,2-diols, ⁴³ and 1,3- diols. ²⁰⁵ Forms 4,6-cyclic di-tert-butylsilylenediyl ethers w/glycopyranosides. ²⁰⁶	5g \$104.00 25g \$416.00
SID3345.0 Di-tert-butylsilylbis(trifluoromethanesulfonate) [85272-31-7]		More reactive than SID3205.0. ⁴² Converts 1,3-diols to cyclic protected 1,3-diols. ²⁰⁷ Reacts w/1,3-diols in preference to 1,2-diols. ²⁰⁸	5g \$52.00 25g \$208.00
SID3534.0 Di-isopropylbis(trifluoromethanesulfonyl)silane [85272-30-6]		More reactive than SID3345.0. Protects diols ²⁰⁹	5g \$114.00
SIB1042.0 Bis(dimethylchlorosilyl)ethane [13528-93-3]		Protection for 1° amines, ^{210,211} including amino acid esters. ²¹²	25g \$22.00 100g \$72.00 2kg \$930.00
SIT7273.0 Tetraisopropyldichlorodisiloxane [69304-37-6]		Highly useful for protection of 3',5'- dihydroxynucleosides. ⁴⁶ Protects 1,2-diequatorial diols. ²¹³	5g \$72.00 25g \$312.00 2kg \$2,520.00
SIB1084.0 1,2-Bis(dimethylsilyl)benzene [17985-72-7]		Used to protect anilines, ⁴⁸ amines, ¹⁸⁸ and amino acids. ²¹⁴	2.5g \$142.00
SIB1048.2 1,3-Bis(chlorodimethylsilyl)-propane [2295-06-9]		Potentially useful silylating agent for diols and related systems.	5g \$104.00
SIT7087.0 1,1,3,3-Tetracyclopentyl-dichloro-disiloxane		Used in the protection of 3',5'-dihydroxynucleosides.	5g \$65.00 25g \$260.00

Table 7
Deprotection Of 1° Silyl Ethers In The Presence Of Other 1° Silyl Ethers

Deprotection of:	In the Presence of:				
	1° TMS	1° TES	1° TIPS	1° TBS	1° TBDPS
1° TMS	[bmim]Cl ²¹⁵ , allylPPh ₃ S ₂ O ₈ ²¹⁶	NaHCO ₃ ²¹⁷ , Br ₂ /PVPP ²¹⁸	NaOH/EtOH ²¹⁹ , MCM-41 ²²⁰	NaOH/EtOH ²¹⁹ , Cu(NO ₃) ₂ ²²¹ , Ce(NO ₃) ₃ ²²¹ , [Bu ₂ (NCS)Sn] ₂ O ²²² BiCl ₃ ²²⁵ , Bi(O ₂ CCF ₃) ₃ ²²³ , K ₂ CO ₃ ²²⁴ , MCM-41 ²²⁰ , Br ₂ /PVPP ²¹⁸ , K ₂ CO ₃ ²²⁵ , Mn ^{III} -Schiff-base/H ₂ O ₂ ²²⁶	NaOH/EtOH ²¹⁹ , Cu(NO ₃) ₂ ²²¹ , Ce(NO ₃) ₃ ¹³³ , HCl ^{219,227} , K ₂ CO ₃ ²²⁸ , Swern ²²⁹
1° TES			TFA ²³⁰ , H ₂ /Pd-C ^{231,232} , MCM-41 ²²⁰ , HOAc/uw ²³³ , MeCHClO ₂ CCl ²³⁴ , flourous TBAF ¹¹⁰ , FeCl ₃ ²¹⁶ , 2-hydroxymethylphenol/hv ²³⁵ , TMS-Br/MeOH ²³⁶ , catecholborane/(PPh ₃) ₃ RhCl ⁶² , FeCl ₃ /Et ₃ SiH/ArCHO ²³⁷	HF/pyr ²³⁸ , TCNQ/MeCN/H ₂ O ²³⁹ , DDQ/MeCN/H ₂ O ^{239,240} , CSA ^{241,242} , IBX/DMSO ²⁴³ , MCM-41 ²²⁰ , H ₂ /Pd-C ²³¹ , HCO ₂ H ²⁴⁴ , MeCHClO ₂ CCl ²³⁴ , flourous TBAF ¹¹⁰ , FeCl ₃ ²¹⁶ , 2-hydroxymethylphenol/hv ²³⁵ , catecholborane/(PPh ₃) ₃ RhCl ⁶² , Swern ²⁴⁵	SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , DDQ/MeCN/H ₂ O ^{239,240} , MCM-41/MeOH ²²⁰ , CSA ^{247,248} , H ₂ /Pd-C ^{231,232,249} , TMSOTf/HCO ₂ DPM/SiO ₂ ⁹⁷ , ZnBr ₂ /H ₂ O ²⁵⁰ , HCl ^{251,252} , PPTS ²⁵³⁻²⁵⁵ , CSA ^{256,257} , HOAc/uw ²³³ , MeCHClO ₂ CCl ²³⁴ , FeCl ₃ ²¹⁶ , Fe(OTs) ₃ ²⁵⁸ , 2-hydroxymethylphenol/hv ²³⁵ , TMS-Br/MeOH ²³⁶ , FeCl ₃ /Et ₃ SiH/ArCHO ²³⁷ , Swern ²⁵⁹
1° TIPS					
1° TBS			HCl/EtOH ^{219,260,261} , H ₂ SiF ₆ /tBuOH ²⁶²⁻²⁶⁴ , NaOH/EtOH ²⁴ , Cyclohexene/PdO ²⁶⁵ , Alumina ²⁶⁶ , H ₂ SO ₄ ²⁶⁷ , CSA ^{268,269} , PPTS ²⁷⁰ , H ₂ /Pd-C ^{231,249} , TMS-OTf/Et ₃ N/MeOH ²⁷¹ , CeCl ₃ •7H ₂ O/NaI ¹⁵⁷ , Decaborane ²⁷² , AcCl/MeOH, HOAc/uw ²³³ , MeCHClO ₂ CCl ²³⁴ , HF•pyr ²⁷⁴ , FeCl ₃ ²¹⁶ , TMS-Br/MeOH ²³⁶ , H ₂ /Pd-C ²³² , TBAF ⁶⁵ , pyridinium tribromide ²⁷⁵ , FeCl ₃ /Et ₃ SiH/ArCHO ²³⁷	TsOH/THF/H ₂ O ²⁵ , Cl ₂ CHCO ₂ H ^{276,277} , TBAF ²⁷⁸⁻²⁸⁰ , TBSOTf ²⁸¹ , HOAc ²⁸² , PPTS ^{279,283} , DDQ ²⁸⁴ , MnO ₂ /AlCl ₃ ²⁸⁵ , DMSO/H ₂ O ²⁸⁶ , H ₂ /Pd-C ²³¹ , CrO ₃ /H ₅ IO ₆ ²⁸⁷	HCl ^{219,288-291} , HOAc ^{31,292-296} , CSA ^{242,297-311} , PPTS ^{287,312-327} , TsOH ³²⁸⁻³³⁰ , MeOH/CCl ₄ ³³¹ , Cu(NO ₃) ₂ ²²¹ , Ce(NO ₃) ₃ ²²¹ , Cyclohexene/PdO ²⁶⁵ , Alumina ²⁵ , SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , DDQ/MeCN/H ₂ O ^{239,240} , AcBr/CH ₂ Cl ₂ ³³² , TMSOTf ³³³ , HF-pyr/THF ³³⁴ , H ₂ SO ₄ ³³⁵ , TFA ^{284,336,337} , TsOH ^{338,339} , LL-ALPS-SO ₃ H ³⁴⁰ , AcCl/MeOH ³⁴¹ , Zn(BF ₄) ₂ ³⁴² , Cu(OTf) ₂ /Ac ₂ O ³⁴³ , InCl ₃ ³⁴⁴ , CeCl ₃ •7H ₂ O/NaI ^{157,345} , H ₂ O/NaI ¹⁵⁷ , Ce(OTf) ₄ /THF/H ₂ O ³⁴⁶ , PdCl ₂ (MeCN) ₂ ³⁴⁷ , I ₂ /MeOH ³⁴⁸ , Br ₂ /MeOH ³⁴⁹ , IBr ³⁵⁰ , LiCl/DMF ³⁵¹ , CCl ₄ /MeOH ³⁵² , ZnBr ₂ /H ₂ O ²⁵⁰ , ZrCl ₄ /Ac ₂ O ³⁵³ , HF-pyr ^{274,354,355} , I ₂ /KOH ³¹⁵ , H ₂ /Pd-C ^{231,232,249} , Bu ₄ NOH/MeOH ³⁵⁶ , TBAF ³⁵⁷ , TMSOTf/HCO ₂ DPM/SiO ₂ ⁹⁷ , Decaborane ²⁷² , pyridinium tribromide ²⁷⁵ , MeCHClO ₂ CCl ²³⁴ , 2-hydroxymethylphenol/hv ²³⁵ , FeCl ₃ ²¹⁶ , CrO ₃ /H ₅ IO ₆ ²⁸⁷ , FeCl ₃ /Et ₃ SiH/ArCHO ²³⁷ , TMS-Cl/KF•2H ₂ O ³⁵⁸ , Cl ₃ CO ₂ H ³⁵⁹ , BF ₃ •OEt ₂ ^{225,300} , TMS-Cl ³⁶⁰ , TMS-Br/MeOH ²³⁶ , (MeCN) ₂ PdCl ₂ ³⁶¹ , SbCl ₃ ³⁶² , Fe(OTs) ₃ ²⁵⁸ , NiCl ₂ •6H ₂ O HSCH ₂ CH ₂ SH ³⁶³ , CuBr ₂ ³⁶⁴ , LiCl/H ₂ O/DMF ³⁶⁵ , sulfated SnO ₂ ³⁶⁶ , Bi(OTf) ₃ ³⁶⁷ , Sc(OTf) ₃ ³⁶⁷ , SnCl ₂ •2H ₂ O ³⁶⁸ , TBPA•SbCl ₆ ³⁶⁹ , CCl ₄ /MeOH ³⁷⁰ , MeCOPPh ₃ Br ³⁷¹
1° TBDPS			KOH ^{372,373} , TBAF/HOAc ^{353,374}	TBAF/HOAc ^{253,254,375-378} , TBATB/MeOH ³⁵⁶ , NaOH ^{376,379-381} , Bu ₄ NOH ³⁷⁵ , KOH/DMPU ³⁸²	LiAlH ₄ ³⁸³ , HF-pyr ³⁸⁴ , TBAF ²⁸⁰

Table 8
Deprotection Of 1° Silyl Ethers In The Presence Of 2° Silyl Ethers

Deprotection of:	In the Presence of:				
	2° TMS	2° TES	2° TIPS	2° TBS	2° TBDPS
1° TMS	Rexyn 101 ³⁸⁵ , K ₂ CO ₃ /MeOH ³⁸⁶ , Alumina ²⁶⁶ , HOAc ³⁸⁷ /HOAc/ Ac ₂ O ³⁸⁸ , [bmim]Cl ²¹⁵ , NaHCO ₃ ³⁸⁹ , K ₂ CO ₃ ³⁹⁰ , Swern ^{391,392}	NaHCO ₃ ²¹⁷ , Swern ³⁹¹	K ₂ CO ₃ ³⁹³	BF ₃ OEt ₂ ³⁹⁴ , HF•pyr ³⁹⁵	
1° TES	Swern ³⁹¹	HOAc ^{16,396-398} , CSA ²⁶⁴ , PPTS ^{253,254,256, 399-402} , HBr/PPh ₃ ⁴⁰³ /HF•pyr ²¹⁷ , TBAF ⁴⁰⁴⁻⁴¹¹ , KF ⁴¹² , LiOH ²¹⁷ , Swern ^{13,391,400, 413-420} , CrO ₃ •2pyr ⁴²¹ , HF•pyr ²⁴¹ , K ₂ CO ₃ ⁴²² , DIBAL-H ⁶⁴ , DDQ ⁴²³	HOAc ¹⁶ , TMSOTf/i-Pr ₂ NEt ⁴²⁴ , HF•pyr ^{217,425} , LiOH ²¹⁷ /TMS-Br/ MeOH ²³⁶ , HOAc/uw ²³³ , PPTS ⁴²⁶	HOAc/H ₂ O/THF ^{16,427} , RMgX ⁴²⁸ , HCl ⁴²⁹ , HBr/PPh ₃ ⁴⁰³ /CSA ^{241,264,430,431} , PPTS ⁴³² , TFA ⁴³³⁻⁴³⁵ , HF•pyr ⁴³⁶⁻⁴³⁸ , HF ⁴¹² , TMSOTf/i-Pr ₂ EtN ⁴²⁴ , TBAF ^{264,404} , KF ⁴¹² , Swern ^{418,419,439-441} , HCO ₂ H ²⁴⁴ , NaClO ₂ ⁴³⁸ , DIBAL-H ⁶⁴ , DDQ ⁴⁴¹	SiF ₄ /CH ₂ Cl ₂ ⁴⁴² , DDQ ^{239,240} , TsOH ⁴¹³ , citric acid ⁴⁴³ , TMSOTf/i-Pr ₂ NEt ⁴²⁴ , TMSOTf/Et ₃ N ²⁷¹ , HCl ³⁹⁸ , PPTS ⁴⁴⁴ , TBAF ⁴⁴⁵ , DIBAL-H ⁶⁴
1° TIPS			TBAF ^{425,446} , CSA ⁴⁴⁸ , SiF ₄ ⁴⁴⁹ , POCl ₃ -DMF ^{102,442} (TfO) ₂ O-DMF ^{102,442} , CBr ₄ /MeOH ⁴⁵⁰ , CAN/SiO ₂ ⁴⁵¹ , TFA ⁴⁵² , HF•pyr ⁴⁵³	TFA/H ₂ O/THF ⁴⁵⁴ , TBAF ^{447,455,456}	TFA/H ₂ O/THF ⁴⁵⁸ , CSA ⁴⁵⁹
1° TBS		HF•pyr ²⁴¹ , HOAc ⁴⁶⁰ , pyridinium, tribromide ²⁷⁵	HCl ^{24,261,462,463} , HOAc ^{31,166,168,169,370,464-472} , TsOH/PPTS ^{473,474} , HF•pyr ⁴⁷⁵⁻⁴⁸⁵ /NaOH ²⁴ , Cyclohexene/PdO ²⁶⁵ , TsOH ⁴⁸⁶⁻⁴⁸⁹ , H ₂ SO ₄ ⁴⁹⁰ , CSA ^{268-270,304,462,481,482,491-495} , PPTS ^{478,496} , NH ₄ Cl/MeOH ⁴⁹⁷ , TBAF ^{264,498} , polymeric DCKA ⁴⁹⁹ , HOAc/uw ²³³ , Cl ₃ CO ₂ H ³⁵⁹ , (HF) ₃ •xNEt ₃ ⁵⁰⁰ , TMS-Br/TBAB/Ac ₂ O ⁵⁰¹ , (CF ₃ CO) ₂ O/MeOH ⁵⁰¹ , PCC/Celite ³⁴	HCl ^{291,488,502-504} , HOAc ^{16,505-515} , TFA/H ₂ O/THF ⁵¹⁶⁻⁵¹⁸ , CSA ^{242,268-270,298,306,316,307, 481,482,519-545} , PPTS ^{279,283,316,546-587} , Acid Amberlite ⁵⁸⁸ , NH ₄ F ^{273,549,589-5917} , HF ⁵⁹⁸⁻⁶⁰² , H ₂ SiF ₆ /tBuOH ²⁶³ , HF•pyr ^{381,382,477-479,481-485,498,505,506,532,536-538, 541-545,560-587,603-648} , H ₂ /wet Pd ⁶⁴⁹ , H ₂ /Pd-C ²³¹ , NBS/DMSO ⁶⁵⁰ , TBAF ^{424,651-665} , MeOH/CCl ₄ ³³¹ , NaOH ²⁴ , TFA ^{337,615-619} , TsOH ^{330,338,339,613,666-672} , TsOH/Bu ₄ NHSO ₄ ⁶¹⁴ , Alumina ^{262,663,673,674} , (CF ₃ SO ₂) ₂ /DMF ¹⁰² , AgOAc ⁶⁷⁵ , CAN/PrOH ⁴⁵¹ , acidic CHCl ₃ ⁶²⁰ , Cu(OTf) ₂ /Ac ₂ O ⁹² , BCl ₃ ⁶²¹ , Cyclohexene/PdO ⁶⁷⁶ , H ₂ SiF ₆ ⁶⁷⁷ , TAS-F ⁶⁷⁸ , CBr ₄ -hv ^{679,680} , Jones ⁵⁶⁶ , LiBr/18-C-6 ⁶⁸¹ , CAN/i-PrOH ⁶⁸² , POCl ₃ -DMF ^{102,684} , (TfO) ₂ O-DMF ^{102,684} , QFC ⁶⁸⁵ , Bu ₄ NBr ₃ /MeOH ³⁵⁶ , MnO ₂ /AlCl ₃ ²⁸⁵ , Oxone ⁶⁸⁶ , CAN/SiO ₂ ⁴⁵¹ , TMS-Cl/KF/MeOH ³⁵⁸ , pyridinium tribromide ²⁷⁵ , CBr ₄ /hv ⁶⁸⁷ , ZnBr ₂ ⁶⁸⁸ , SnCl ₂ ⁶⁸⁸ , Bi(OTf) ₃ ³⁶⁷ , CeCl ₃ •7H ₂ O/NaI ⁶⁸⁸ , SbCl ₃ ³⁶² , flourous TBAF ¹¹⁰ , LiAlH ₄ ⁶⁸⁹ , DIBAL-H ⁶⁴ , NaIO ₄ ^{690,691} , I ₂ /MeOH ⁶⁹² , HClO ₄ /SiO ₂ ⁴³⁸ , (HF) ₃ •xNEt ₃ ⁶²⁸	HOAc ^{512,693-696} , TsOH ⁶⁹⁷⁻⁷⁰⁴ , TBAF ^{705,706} , PPTS ^{313,327,702,707-711} , HF•pyr ^{32,69,197,712,714} , HF ^{459,715-718} , HCl ^{461,719} , NaOH ⁷²⁰ , H ₂ SiF ₆ ⁷²¹ , CSA ^{309-311,722-729} , BF ₃ •OEt ₂ ⁷³⁰ , NBS/DMSO ^{452,731} , CrO ₃ /H ₅ IO ₆ ²⁸⁷ , TBPA•SbCl ₆ ³⁶⁸ , TMSOTf/Et ₃ N ²⁷¹ , Cu(OTf) ₂ /Ac ₂ O ³⁴² , Zn(OTf) ₂ ³⁴¹ , K ₂ CO ₃ ^{102,683} , TBTU ⁷³² , QFC poly DCKA ⁷³³ , InCl ₃ ³⁴³ , IBr/DCM ¹⁵⁸

Table 8 (continued)

Deprotection of:	In the Presence of:				
	2° TMS	2° TES	2° TIPS	2° TBS	2° TBDPS
1° TBDPS		TBAF/HOAc ^{377,734,735} , NaOH/DMPU ⁷³⁶ , Hf•pyr ²⁷ , TMSCN/Sc(OTf) ₃ ⁷³⁷ DIBAL-H ⁶⁴	NaH/HMPA ⁷³⁸ , Hf•pyr ^{358,739-740} , KOH/18-C-6 ⁷⁴¹ , KOH ^{273,742} , NaOH ^{319,470} , TASF ⁶³⁹	TBAF ^{566,571,650,743-746} , TBAF/HOAc ^{242,253,254,304,324,374,376,377,561,568,734,735,739,747-758} , KOH ⁷⁵⁹⁻⁷⁶¹ , KOH/18-C-6 ⁷⁴¹ NaOH ^{380,762,763} , NaOH/DMPU ⁷³⁶ , NH ₄ F ^{594,597,764-772} , NH ₄ F/HFIP ⁷⁷³ , TAS-F ^{418,774,775} , NaH/propargyl alcohol ²⁸⁹ , NaH/HMPA ⁷⁵⁹ , TMSCN/Sc(OTf) ₃ ⁷³⁷ , HF•pyr ²⁷	Hf•pyr ^{383,725,776-779} , NH ₄ F ^{764,766} , TBAF ^{458,208,780} , CSA ⁷⁸¹ , alumina ^{33,266,782} , POCl ₃ -DMF ^{102,683} , (TfO) ₂ O-DMF ^{102,683}

Table 9

Deprotection Of 1° Silyl Ethers In The Presence Of 3° Silyl Ethers

Deprotection of:	In the Presence of:				
	3° TMS	3° TES	3° TIPS	3° TBS	3° TBDPS
1° TMS	PPTS ⁷⁸³ , Swern ²²⁹				
1° TES	PPTS ⁷⁸⁴	Hf•pyr ^{480,567,575,785,786} , CSA ^{248,787} , PPTS ^{253,254,398} , KF/glycol ⁷⁸⁸ Swern ²⁵⁹		Amberlyst-15 ⁷⁸⁹ , TBAF/HOAc ⁴⁰⁴ , PPTS ²⁴²	HOAc ⁷⁹⁰
1° TIPS		TBAF ^{66,791}		TBAF ⁷⁸⁵ , SiF ₄ ⁷⁸³	
1° TBS		CSA ^{248,787,794} , Hf•pyr ^{479,480,567, 575,640,786,795,796} , Sc(OTf) ₃ ³⁶⁶ , TBAF/HOAc ⁵⁵⁵		TBAF ^{445,585,627,797,798} , CSA ^{242,303,308, 309,743,799,800} , Hf•pyr ^{69,586} , H ₂ SiF ₆ ³³⁰ , SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , MeOH/CCl ₄ ⁴⁴¹ , NH ₄ F ^{128,801} , oxone ⁶⁸⁵ , BF ₃ •OEt ₂ ⁸⁰² , DDQ ⁸⁰³	
1° TBDPS		TBAF/HOAc ⁷³⁵ , HF•pyr ²⁷		TAS-F ⁸⁰⁴ , TBAF/HOAc ^{242, 253,254,750}	

Table 10

Deprotection Of 2° Silyl Ethers In The Presence Of 1° Silyl Ethers

Deprotection of:	In the Presence of:				
	1° TMS	1° TES	1° TIPS	1° TBS	1° TBDPS
2° TMS	Amberlyst 15 ³⁸⁴ , [bmim]Cl ²¹⁵		TBAF ^{65,447} , PPTS ⁸⁰⁵ , NH ₄ F ⁸⁰⁶	HCl ⁸⁰⁷ , K ₂ CO ₃ /MeOH ^{378,808} , TsOH ⁸⁰⁹ , citric acid ⁶⁷⁶ , PPTS ³⁸⁸ , IBX/4-methoxy-pyridine-oxide ⁶⁷ , H ₂ SiF ₆ ³⁸⁸ , NaOH ⁴⁶²	HCl ^{810,811} , TsOH ^{809,812-815} , Acetone/Me ₂ C(OMe) ₂ /CSA ⁸¹⁶ , PhSeCl/K ₂ CO ₃ ⁷⁸⁵ , TBAF ⁸¹⁷ , PPTS ^{818,819} , Alumina ²⁶⁶ , K ₂ CO ₃ /MeOH ⁸²⁰ , HOAc ⁸²¹ , CSA ^{822,823} , HF•pyr ⁸²⁴ , BF ₃ •OEt ₂ ⁸²¹ , TMS-OTf ^{573,825}
2° TES		Hf•pyr ¹⁷	TFA ^{453,826} , H ₂ SiF ₆ /HF/H ₂ O ⁸²⁷ , HCl ⁸⁰⁷ , HOAc ^{458,713} , CSA ^{241,267,828,829} , PPTS ^{446,740,830-833} , HF•pyr ^{217,264, 424,446} , Ph ₃ P-HBr ²⁶⁷ , HF-Et ₃ N ⁸³⁴ , TBAF ^{352,372} , H ₂ SO ₄ ²⁶⁷ , TsOH ⁸³⁵ , FeCl ₃ ²¹⁶ , Zn(OTf) ₂ /EtSH ⁸³⁶	DDQ/MeCN/H ₂ O ²⁴⁰ , HCl/py ⁸³⁷ , NH ₄ Cl ^{838,839} , TBAF/THF ⁸³⁸ Hf•pyr ²²⁴ , I ₂ /Ag ₂ CO ₃ ^{840,841} , Pd/C, MeOH ⁸⁴² , Pd/C, H ₂ ²³¹ , H ₂ SiF ₆ ⁶⁷⁶ , NaOH ⁴⁸⁹ , HCO ₂ H ²⁴⁴ , PPTS ⁸⁴³ , TiCl ₄ ⁸⁴⁴ , MCPBA/NaHCO ₃ ⁵⁵⁶	HCl ^{227,253,254,562,571,816,845-847} , HOAc ^{289,848} , Cl ₃ CCO ₂ H ⁴⁴¹ , TsOH ^{269,414,444,813,845,846,849-855} , HF/MeCN ^{785,857} , Et ₃ N-HF ⁸⁵⁸ , Hf•pyr ^{19,228,859,860} , TBAF ^{297,352,841,861,862} , SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , CSA ^{242,299,303,813,863-866} , PPTS ^{298,318,784,831,850,867-870} , TFA ^{400,871,872} , H ₂ SO ₄ ⁸⁶¹ , BF ₃ •OEt ₂ ^{269,850} , BF ₃ •OEt ₂ /Et ₃ SiH ₇₄₂ ⁷⁴² , DDQ ^{240,873} , tetrabromocyclohexadienone/PPh ₃ ⁸⁷⁴ , H ₂ Pd/C ⁸⁷⁵ , HOAc ⁸⁷⁶⁻⁸⁷⁸ , TMS-Br/MeOH ²³⁶ , TMS-OTf ^{860,879-881} , TES-OTf ⁸⁸² , FeCl ₃ ²¹⁶ , Zn(OTf) ₂ /EtSH ^{253,254,836,865} , PhSeCl/K ₂ CO ₃ ⁷⁸⁵ , ZnBr ₂ /H ₂ O ²⁵⁰
2° TIPS			TBAF/HOAc ³⁹²		
2° TBS			H ₂ SiF ₆ /HF/H ₂ O ⁶⁹⁷ , CSA ⁸³⁰ , TMS-OTf ⁸⁸³ , 2-mercapto-benzothiazole/Ph ₃ P/DIAD ⁸³³	DIBAL-H ⁸⁸⁴ , MnO ₂ /AlCl ₃ ²⁸⁵ , LiAlH ₄ ⁸⁸⁵	HCl ^{24,886} , HOAc ⁸⁸⁷⁻⁸⁸⁹ , TsOH ⁸⁹⁰⁻⁸⁹³ , PPTS ^{304,312,383,894-896} , BF ₃ •OEt ₂ ⁸⁹⁷ , TMS-OTf ^{771,332,383,725,852,879,880,898} , HF/MeCN ⁵¹⁵ , TBAF ^{296,773,899,900} , SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , CSA/MeOH ²⁹⁸ , H ₂ SiF ₆ ⁷⁴¹ , Cu(OTf) ₂ /Ac ₂ O ⁹² , InCl ₃ ³⁴³ , LiAlH ₄ ^{901,902} , IBr ⁹⁰³ , P ₂ O ₅ /(MeO) ₂ CH ₂ ³³⁸ , LiCl/DMF ³⁵⁰ , polymeric DCKA ⁷³³ , ZnBr ₂ /H ₂ O ²⁵⁰ , Zn(BF ₄) ₂ ³⁴¹ , Amberlyst-15 ⁶³⁹ , AcCl/MeOH ⁹⁰⁴ , SnCl ₄ ⁹⁰⁵ , [PdCl ₂ (MeCN) ₂] ⁹⁰⁶ , CrO ₃ /H ₂ IO ₆ ²⁸⁷ , DDQ ^{907,908} , NaIO ₄ ⁶⁸⁹ , TBPA•SbCl ₆ ³⁶⁸
2° TBDPS				NaH/HMPA ⁹⁰⁹ , TBATB/MeOH ³⁵⁵	

Table 11
Deprotection Of 2° Silyl Ethers In The Presence Of 1° Silyl Ethers

Deprotection of:	In the Presence of:				
	2° TMS	2° TES	2° TIPS	2° TBS	2° TBDPS
2° TMS	TBAF ⁹¹⁰ , SiO ₂ -Cl/ NaI ⁹¹¹ , [bmim]Cl ²¹⁵ , KF/polyether-diol ⁹¹²	Hf•pyr ^{575,913} , TBAF ⁴¹⁰ , KF ⁷³⁶ , citric acid ⁹¹⁴ , PhCOF ⁹¹⁵	Citric Acid ⁹¹⁶ , TBAF/HOAc ^{917,918} , FeCl ₃ ⁹¹⁹ , TBAF ⁴⁴⁷ , KF ⁴¹¹ , NaOH ⁴⁶² , H ₂ SiF ₆ ⁶⁷⁶ , HF•pyr ⁴²⁵	HCl ⁹²⁰ , TsOH ^{813,815,921,922} , HOAc ^{479,923,924} , PPTS ^{925,926} , HF/Et ₃ N ⁹²⁷ , Citric Acid/MeOH ^{928,929} , Cu(NO ₃) ₂ ²²¹ , Ce(NO ₃) ₃ ²²¹ , DDQ/wet EtOAc ⁹³⁰ , K ₂ CO ₃ ^{479,820,931-934} , HOAc ^{935,936} , CSA ⁹³⁷ , Hf•pyr ^{425,575,913} , HF/Et ₃ N ⁹³⁸ , BF ₃ -OEt ₂ ^{939,940} , KF ^{411,736} , TBAF ⁹⁴¹ , TFA ^{942,943} , SnCl ₄ ⁹⁴⁴	TBAF ⁹⁴⁵ , Cu(NO ₃) ₂ ²²¹ , Ce(NO ₃) ₃ ²²¹ , K ₂ CO ₃ ^{479,931,933,934} , NaIO ₄ ⁹⁴⁶ , HOAc ⁴⁷⁹ , K ₂ CO ₃ ^{479,931}
2° TES		HOAc ⁹⁴⁷⁻⁹⁵⁰ , TBAF ^{402,403,540,951-953} , TsOH ⁹⁵⁴ , TFA ^{955,956} , Hf•pyr ^{575,779} , (NH ₄)HF ₂ ⁹⁵⁷ , KF ⁴¹¹ , NaOH/DMPU ⁷³⁶ , CSA ⁵³² , PPTS ⁴⁷⁷ , catecholborane/ (Ph ₃) ₃ RhCl ⁶²	TFA ^{453,958,959} , HOAc ^{233,949,950,960-962} , PPTS ^{16,425,477,480,740,963} , MoO ₅ /HMPA ^{929,964} , WO ₅ /HMPA ^{964,965} , Hf•pyr ^{21,217,966} , H ₂ SO ₄ ²⁶⁷ , TFA ⁹⁶⁷ , Zn(OTf) ₂ /EtSH ^{968,969} , NH ₄ F ⁹⁶⁷ , Amberlyst-15 ⁹⁷⁰ , CSA ^{303,829,971} , TMS-Br/MeOH ²³⁶ , (HF) ₃ •xNEt ₃ ⁴⁹⁹ , BF ₃ •OEt ₂ /Et ₃ SiH ⁷⁴²	HOAc ^{514,741,878,949,959,972,97} , TFA ^{434,453,955,956,958,959,976} , PPTS ^{13,16,242,438,446,546,641,784,831-833} , 868,885,895,937,977-989, HF ^{990,991} , Hf•pyr ^{27,264,395,399,428,575,859,913,990,992-1001,1046} , HF-Et ₃ N ^{398,949,1002} , TBAF ^{289,402,403,540,952,953,1003-1009} , HCl ^{1010,1011} , PTSA/MeOH ⁴³⁶ , CSA ^{241,242,534,830,971} , TsOH ^{436,813,835,853,1046} , DDQ ^{240,1012} , MCM-41/MeOH ²²⁰ , TfOH/H ₂ O-THF ¹⁰¹³ , WO ₅ /HMPA ^{964,965} , MoO ₅ /HMPA ^{964,065} , Zn(OTf) ₂ /EtSH ⁹⁶⁸ , TiCl ₃ (O-iPr) ⁹⁹⁵ , KF ⁴¹¹ , NaOH/DMPU ⁷³⁶ , MCM-41 ²²⁰ , PdCl ₂ /CuCl/H ₂ O ¹⁰¹⁴ , HCO ₂ H ²⁴⁴ , TES-OTf ⁸⁸² , TAS-F ¹⁰⁴⁶ , PdCl ₂ /CuCl ₂ /O ₂ ¹⁰¹⁵ , (NH ₄) ₆ Mo ₇ O ₂₄ /H ₂ O ¹⁰¹⁶ , Et ₃ BOMe/NaBH ₄ ¹⁰¹⁷ , EtSH/Zn(OTf) ₂ ⁹⁶⁹ , Cp ₂ ZrHCl ¹⁰¹⁸	HCl ^{414,1019} , HOAc ^{58,713,1020-1022} , CSA ¹⁰²³⁻¹⁰²⁵ , PPTS ^{843,987} , HF ^{533,990,995,1026,1027} , Hf•pyr ²⁸⁶ , TBAF ^{296,444,1028-1030} , K ₂ CO ₃ ^{1031,1032} , SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , DDQ/MeCN/H ₂ O ²⁴⁰ , NaIO ₄ ⁹⁴⁶ , BF ₃ •OEt ₂ ¹⁰³³
2° TIPS			HF ^{578,1034} , PPTS ¹⁰³⁵	TBAF ¹⁰³⁶⁻¹⁰⁴⁰ , PTSA/MeOH ⁴⁸² , TsOH ⁴⁸¹ , HF/Et ₃ N ²¹ , LiAlH ₄ ¹⁰⁴¹	NaIO ₄ ⁹⁴⁶
2° TBS	HCl ¹⁰⁴²	TBAF ⁹⁹⁵	HCl ^{24,1043-1045} , H ₂ SiF ₆ (aq) ²⁶⁵ , HOAc ^{13,233,961,962} , HF ^{515,578,1034} , TBAF ^{270,918,1046-1048} , CSA ^{480,1049,1050} , Et ₃ N-3HF ¹⁰⁵¹ , H ₂ SiF ₆ /Et ₃ N ¹⁰⁵² , PPTS ^{469,1053} , TsOH ⁴⁸⁸	HCl ²⁴ , CSA ^{403,1054-1056} , TsOH ¹⁰⁵⁷ , HF ^{515,1058-1061} , LiAlH ₄ ³⁸² , KF/H ₂ O ¹⁰⁶² , TBAF ^{28,541,576,577,659,902,945,980,981,985,1063-1075} , H ₂ SO ₄ ¹⁰⁷⁶ , Hf•pyr ^{477,640,1075,1077-1080} , HF/Et ₃ N ⁹⁴⁹ , HOAc ⁹⁵⁰ , P ₂ O ₅ /(MeO) ₂ CH ₂ ³³⁸ , MnO ₂ /AlCl ₃ ²⁸⁵ , TMS-OTf ⁵² , BF ₃ •OEt ₂ ¹⁰⁸¹ , PPTS ^{896,1082} , SnCl ₄ ⁹⁰⁵ , TAS-F ¹⁰⁷⁹ , NaOH ³⁸⁰ , NaIO ₄ ⁶⁸⁹ , salen-Mn(III)/PhIO ¹⁰⁸³ , 2-mercaptobenzothiazine/Ph ₃ P/DIAD ⁸³³	TsOH ¹⁰⁸⁴⁻¹⁰⁸⁶ , HCO ₂ H/THF/H ₂ O ¹⁰⁸⁷ , CSA ^{726,1056,1088,1089} , PPTS ¹⁰⁹⁰⁻¹⁰⁹³ , HF/MeCN ¹⁰⁹⁴ , TBAF ^{651,899,1095,1096} , SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , Cu(NO ₃) ₂ ²²¹ , Ce(NO ₃) ₃ ²²¹ , DDQ/MeCN/H ₂ O ²⁴⁰ , HCl ^{1097,1098} , HOAc ^{889,1099-1101} , Hf•pyr ^{712,713,1102} , TMS-OTf ^{383,725,898} , BF ₃ •OEt ₂ ¹¹⁰³ , Sc(OTf) ₃ ¹¹⁰⁴ , NaIO ₄ ⁹⁴⁶ , HCl ^{1105,1106} , TiCl ₄ ¹¹⁰⁷ , NaIO ₄ ⁶⁸⁹ , CrO ₃ /H ₂ IO ₆ ⁷³¹ , NaBH ₄ ³³
2° TBDPS			TBAF/THF ⁴⁶⁰	HF•pyr ⁴⁷⁹ , TBAF ³² , TAS-F ¹¹⁰⁸	NaBH ₄ ³³

Table 12
Deprotection Of 2° Silyl Ethers In The Presence Of 3° Silyl Ethers

Deprotection of:	In the Presence of:			
	3° TMS	3° TES	3° TIPS	3° TBS
2° TMS	TsOH ^{922,1109}	HOAc ⁹²³ , CSA ¹¹¹⁰ , KP ^{411,736} , TBAF ⁶⁵ HF•pyr ^{575,913}		HOAc/HCl ¹¹¹¹
2° TES		TsOH ¹¹¹² , HF•pyr ^{27,264,573,575,779,9913,96} , HCl ^{1010,1011} , PPTS ^{784,885,1113,1114} , TBAF ^{65,402,952,1115,1116}		HOAc ¹¹¹⁷ , CSA ^{242,303,650,829,865} , HCl ⁴⁰⁴ , TfOH ¹⁰¹³ , Zn(OTf) ₂ /EtSH ^{253,254,865} , Cp ₂ ZrHCl ¹⁰¹⁸
2° TIPS				
2° TBS			H ₂ SiF ₆ / ^t BuOH/H ₂ O ²⁶³	HOAc ¹¹¹⁸ , CSA ^{1119,1120} , TBAF ^{1121,1122} , TfOH ¹⁰¹³ , HF ¹¹²³
2° TBDPS	TBAF ³²			

Table 13
Deprotection Of 3° Silyl Ethers In The Presence Of 1° Silyl Ethers

Deprotection of:	In the Presence of:				
	1° TMS	1° TES	1° TIPS	1° TBS	1° TBDPS
3° TMS			PPTS/MeOH ⁸³⁴ , PPTS ¹¹²⁴ , HCl ⁸²⁸	ClCH ₂ CO ₂ H/MeOH ²⁷⁶ , HCl ¹¹²⁶ , BH ₃ -SMe ₂ ¹¹²⁷	HCl ³³⁶ , HOAc ⁷⁹⁰ , BF ₃ -OEt ₂ ¹¹²⁸⁻¹¹³⁰ , PPTS ¹¹³¹ , K ₂ CO ₃ ^{256,1132}
3° TES			HF-Et ₃ N ⁸³⁴ , TBAF ¹¹³³ , PPTS ¹¹²⁵	SiO ₂ ¹¹³⁴ , TBAF/ NH ₄ Cl ¹¹³³ , LiHMDS/CeCl ₃ ⁵⁵⁵	TBAF ¹¹³³ , HCl ⁸⁴⁷ , CSA ¹¹³⁵
3° TIPS					
3° TBS					LiAlH ₄ ^{1119,1136}
3° TBDPS					

Table 14
Deprotection Of 3° Silyl Ethers In The Presence Of 2° Silyl Ethers

Deprotection of:	In the Presence of:				
	2° TMS	2° TES	2° TIPS	2° TBS	2° TBDPS
3° TMS	TBAF/HOAc ¹¹³⁷ , K ₂ CO ₃ ¹¹³⁷	TBAF ^{13,1018}	TBAF/HOAc ^{918,1138}	HCl ^{336,1126,1139} , LiAlH ₄ ¹¹⁴⁰ , TBAF ^{13,1018,1138,1141} , FeCl ₃ ¹¹³² , HF ¹⁰⁶¹ , HF•pyr ¹¹⁴² , K ₂ CO ₃ ¹¹³² , HOAc ¹¹⁴² , PPTS ²²⁹ , H ₂ /Pd(OH) ₂ -C ¹¹⁴³ , BH ₃ •THF ¹¹⁴⁴	HCl ⁷⁸³ , H ₂ SiF ₆ ^{720,1145} , K ₂ CO ₃ ⁴⁶⁰ , TBAF ¹¹⁴⁶
3° TES		LiAlH ₄ ⁹⁹⁶	TBAF/HOAc ¹¹³⁸	Et ₃ NHF ^{1147,1148} , HF-Et ₃ N ^{398,1002} , TBAF/HOAc ¹¹³⁸ , TBAF ¹¹⁴⁹ , LiHMDS/CeCl ₃ ⁵⁵⁵	TBAF ¹¹⁴⁶
3° TIPS					
3° TBS			TBAF/HOAc ¹¹³⁸	TBAF ¹¹¹⁷	TBAF ⁶⁹
3° TBDPS					

Table 15
Deprotection Of 3° Silyl Ethers In The Presence Of 3° Silyl Ethers

Deprotection of:	In the Presence of:				
	3° TMS	3° TES	3° TIPS	3° TBS	3° TBDPS
3° TMS			HCl/THF ¹¹⁵⁰		
3° TES	LiHMDS/CeCl ₃ ⁵⁵⁵	TBAF ¹¹¹⁶			
3° TIPS					
3° TBS				CSA ¹¹⁵¹	
3° TBDPS					

Table 16
Deprotection Of Aryl Silyl Ethers In The Presence Of Alkyl Silyl Ethers

Deprotection of:	In the Presence of:				
	1° TMS	1° TES	1° TIPS	1° TBS	1° TBDPS
ArOTMS	Dowex 1-X8 (HO ⁻ form) ¹¹⁵²			TBAF ^{1153,1154} , BiCl ₃ ⁹⁰⁵ , Bi(O ₂ CCF ₃) ₃ ⁹⁰⁵ , Bi(OTf) ₃ ⁹⁰⁵ , PIFA-MK10 ¹¹⁵⁵	
ArOTES		DBU ¹¹⁵⁶	NaOH ²¹⁹	NaOH ²¹⁹	
ArOTBS		LiOAc ⁶³		NaOH ²¹⁹ , K ₂ CO ₃ ^{1157,1158} , TBAF ^{375,1155,1159-1163} , KF/18-crown-6 ¹¹⁶³ , KF/Al ₂ O ₃ /MeCN ¹¹⁶⁴ , KF-Al ₂ O ₃ ¹¹⁶⁵ , CsF/RX/DMF ¹¹⁶⁶ , CsCO ₃ ¹¹⁶⁷ , Et ₃ NO ¹¹⁶⁸ , LiOH ¹¹⁶⁹ , NaOH/TBAH ¹¹⁶⁶ , KOH ¹¹⁷⁰ , LiOH/RX/DMF ¹¹⁷¹ , TMG ¹¹⁷² , PIFA-MK10 ¹¹⁵⁵ , DMSO/H ₂ O ²⁸⁶ , KF/glycol ⁷⁸⁸ , SelectFluor ¹¹⁷³ , DBU ^{1156,1174,1175} , CuBr ⁸⁷⁹ , LiOAc ⁶³	TBATB/MeOH ³⁵⁵ , Zn(BH ₄) ₂ ³⁴¹ , TBAF ^{1176,1177} , NaOH/TBAH ¹¹⁶⁶ , LiOAc ⁶³
ArOTIPS		PIFA-MK10 ¹¹⁵⁵	PIFA-MK10 ¹¹⁵⁵ , KF/glycol ⁷⁸⁸	PIFA-MK10 ¹¹⁵⁵ , KOAc ⁶³	NaOH ¹¹⁷⁸ , KF/glycol ⁷⁸⁸ , LiOAc ⁶³
ArOTBDPS		NaOH ²¹⁹ , PIFA-MK10 ¹¹⁵⁵	NaOH ²¹⁹ , PIFA-MK10 ¹¹⁵⁵	NaOH ²¹⁹ , PIFA-MK10 ¹¹⁵⁵	TMG ¹¹⁷²

Table 17
Deprotection Of Aryl Silyl Ethers In The Presence Of 2° and 3° Alkyl Silyl Ethers

Deprotection of:	In the Presence of:			
	2° TMS	2° TBS	2° TBDPS	3° TBS
ArOTMS				
ArOTES		CsF ¹¹⁷⁹		
ArOTBS	TBAF ²⁹⁹ , Triton-B ^{982,983}	TBAF ^{518,691,1180,1181} , Triton-B ^{982,983} , LiOAc ⁶³		10% HCl ¹¹⁸²
ArOTIPS	KOAc ⁶³	TBAF ²⁸ , NaOMe ^{1183,1184}	NaOMe ^{1183,1184}	TBAF ¹¹⁸⁵ , NaOH ¹¹⁷⁸
ArOTBDPS		NaOH ²¹⁹ , PIFA-MK10 ¹¹⁵⁵		TMG ¹¹⁷²

Table 18
Deprotection Of Alkyl Silyl Ethers In The Presence Of Phenolic Silyl Ethers

Deprotection of:	In the Presence of:				
	ArOTMS	ArOTES	ArOTBS	ArOTIPS	ArOTBDPS
1° TMS	Dowex CCR-2 (H ⁺ form) ¹¹⁵² , Br ₂ /PVPP ²¹⁸		HCl ²¹⁹	HCl ²¹⁹ , Amberlite IR-120 (H ⁺ form) ¹¹⁸⁶	HCl ²¹⁹
2° TMS				Amberlite IR-120 (H ⁺ form) ¹¹⁸⁶	
1° TES		FeCl ₃ ²¹⁶ , Pd/C/MeOH ⁸⁴² , MeCClO ₂ CCl ²³⁴	ZnBr ₂ /H ₂ O ²⁵⁰ , FeCl ₃ /Et ₃ SiH/ArCHO ⁹⁶	ZnBr ₂ /H ₂ O ²⁵⁰ , HOAc ¹¹⁸⁷	ZnBr ₂ /H ₂ O ²⁵⁰
2° TES			PPTS ¹¹⁸⁸ , BiBr ₃ /Et ₃ SiH ¹¹⁸⁹ , ZnBr ₂ /H ₂ O ²⁵⁰ , NaHSO ₄ -SiO ₂ ¹¹⁹⁰ HOAc ¹¹⁸⁷	ZnBr ₂ /H ₂ O ²⁵⁰ , HOAc ¹¹⁸⁷	ZnBr ₂ /H ₂ O ²⁵⁰

Table 18 (continued)

Deprotection of:	In the Presence of:				
	ArOTMS	ArOTES	ArOTBS	ArOTIPS	ArOTBDPS
1° TBS		FeCl ₃ ²¹⁶	HCl ^{219,1191} , TFA ¹¹⁹² , PPTS ^{1157,1193} , HF/MeCN ^{1157,1194,1195} , BF ₃ •OEt ₂ ^{1157,1196} , SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , MeOH/CCl ₄ ³³⁰ , TMS-Cl/H ₂ O/CH ₃ CN ¹¹⁹⁷ , Oxone/MeOH ⁶⁸⁵ , Nafion-H/NaI ¹¹⁹⁸ , LL-ALPS-SO ₃ H ³³⁹ , AcCl/MeOH ³⁴⁰ , TMS-Cl/H ₂ O ¹¹⁹⁷ , TMS-Cl/NaI/H ₂ O ¹¹⁹⁷ , Me ₂ SBr ₂ ¹¹⁹⁸ , TBSOTf/THPOAc ¹⁰¹ , BiBr ₃ /H ₂ O/MeCN ¹¹⁹⁹ , BiCl ₃ /NaI ¹²⁰⁰ , CeCl ₃ •7H ₂ O ¹¹⁶⁹ , CuOTf/Ac ₂ O ⁹² , Sc(OTf) ₃ /H ₂ O ¹¹⁰⁴ , MeCHClO ₂ CCl ₂ ²³⁴ , FeCl ₃ /Et ₃ SiH/ArCHO ⁹⁶ , ZnBr ₂ /H ₂ O ²⁵⁰ , InCl ₃ ³⁴³ , ZrCl ₄ /Ac ₂ O ¹²⁰¹ , decaborane ²⁷² , Ce(OTf) ₄ /THF/H ₂ O ³⁴⁵ , CBr ₄ /MeOH ⁴⁴⁹ , I ₂ /MeOH ¹²⁰² , CAN/SiO ₂ ⁴⁵⁰ , H ₂ /Pd-C ¹²⁰³ , HCO ₂ H ^{1204,1205} , HClO ₄ -SiO ₂ ¹²⁰⁶ , KHSO ₄ ¹²⁰⁷ , NaHSO ₄ -SiO ₂ ¹⁹⁰ , TMS-Br ²³⁶ , pyridinium tribromide ²⁷⁵ , TMS-Cl/KF/MeOH ³⁵⁷ , FeCl ₃ /Ac ₂ O ¹²⁰⁸ , Fe(OTs) ₃ •6H ₂ O ²⁵⁸ , CeCl ₃ •7H ₂ O ¹²⁰⁹ , Ce(OTf) ₃ •xH ₂ O ¹²¹⁰ , sulfated SnO ₂ ³⁶⁵ , SnCl ₂ •2H ₂ O ³⁶⁷ , Bi(OTf) ₃ ³⁶⁶ , NHPI/Co(O ₂ CPh) ₂ /O ₂ ¹²¹¹ , NIS/MeOH ¹²¹² , I ₂ /MeOH ^{691,1213,1214} , SelectFluor/MeCN ¹¹⁷³ , MeCOPPh ₃ Br ³⁷⁰ , TBPA•SbCl ₆ ³⁶⁸	HCl ²¹⁹ , Amberlite IR-120 (H ⁺ form) ¹¹⁸⁶ , HF•pyr ¹²¹⁵ , BF ₃ •OEt ₂ ¹²¹⁶ , ZnBr ₂ /H ₂ O ²⁵⁰ , ZrCl ₄ /Ac ₂ O ¹²⁰¹	HCl ^{219,468} , ZnBr ₂ /H ₂ O ²⁵⁰ , InCl ₃ ³⁴³ , BiOClO ₄ ¹²¹⁷ TsOH ³⁶⁹
2° TBS			TFA ^{1218,1219} , BF ₃ •OEt ₂ ^{1157,1196} , HF/MeCN ¹¹⁵⁹ , PPTS ¹¹⁵⁷ , SiF ₄ /CH ₂ Cl ₂ ²⁴⁶ , Nafion-H/NaI ¹¹⁹⁸ , BiBr ₃ /H ₂ O/ MeCN ¹¹⁹⁹ , BiCl ₃ /NaI ¹²⁰⁰ , CeCl ₃ •7H ₂ O ¹¹⁶⁹ , ZnBr ₂ /H ₂ O ²⁵⁰ , InCl ₃ ³⁴³ , Me ₂ SBr ₂ ¹¹⁹⁸ , MeCOPPh ₃ Br ³⁷⁰ , (PhO) ₂ PON ₃ ¹²²⁰	TFA ¹²¹⁹ , ZnBr ₂ /H ₂ O ²⁵⁰	ZnBr ₂ /H ₂ O ²⁵⁰
1° TIPS				HCl ²¹⁹ , CBr ₄ /MeOH ⁴⁴⁹ , I ₂ /MeOH ¹²⁰² , TMS-Br ²³⁶ , SelectFluor/MeCN ¹¹⁷³	HCl ²¹⁹ , Sc(OTf) ₃ /H ₂ O ⁷¹² , CBr ₄ /MeOH ⁴⁴⁹ , I ₂ /MeOH ¹²⁰²
1° TBDPS				HCl ²¹⁹	HCl ²¹⁹ , Sc(OTf) ₃ /H ₂ O ⁷¹² , CBr ₄ /MeOH ⁴⁴⁹ , I ₂ /MeOH ¹²⁰² , HClO ₄ -SiO ₂ ¹²⁰⁶ , TMS-Br ²³⁶ , MeCHClO ₂ CCl ₂ ²³⁴ , SelectFluor/MeCN ¹¹⁷³

Table 19
Deprotection Of Silylene- And Disiloxane-Protected Diols
In The Presence Of 2° Alkyl Silyl Ethers

Deprotection of:	In the Presence of:				
	2° TMS	2° TES	2° TIPS	2° TBS	2° TBDPS
DTBS silylene				HF•pyr ^{43,205,1221,1222} , KF/MeOH ^{1062,1223,1224}	
TIPDS siloxane					HF/MeCN ¹²²⁵

Table 20
Deprotection Of Aryl Silyl Ethers In The Presence Of Another Aryl Silyl Ether

Deprotection of:	In the Presence of:				
	ArOTMS	ArOTES	ArOTBS	ArOTIPS	ArOTBDPS
ArOTMS					
ArOTES					
ArOTBS			SbCl ₃ ¹¹⁷⁸ , KF-Al ₂ O ₃ ¹²²⁶ , CCl ₄ /MeOH ¹²²⁷ , NaClO ₂ /NaH ₂ PO ₄ /py ¹²²⁸ KF/HBr/ HOAc ¹²²⁹		HCl ¹¹⁷⁸ , HClO ₄ •SiO ₂ ¹²⁰⁶ , LiOAc ⁶³
ArOTIPS				NaOMe ^{1183,1184}	KOAc ¹²³⁰
ArOTBDPS					

GENERAL SILYLATION PROCEDURES

1. Hexamethyldisilazane, SIH6110.0, SIH6110.1, in trimethylsilylation of alcohols.

One equivalent of the alcohol to be silylated is mixed with 0.5 equivalents of HMDS, SIH6110.0, in an inert solvent or without solvent. Warming the reaction to 40 – 50 °C or adding a drop of TMSCl, SIT8510.0, can significantly accelerate the rate of reaction. The reaction is allowed to continue until no further evidence of the evolution of ammonia is observed. For primary and secondary alcohols the reaction is rapid and nearly quantitative. For tertiary alcohols the reaction will be slower.

2. Trimethylchlorosilane, SIT8510.0, SIT8510.1, in trimethylsilylation of alcohols.

One equivalent of the alcohol, 1.1 equivalents of pyridine or triethylamine are mixed in an inert solvent and one equivalent of trimethylchlorosilane, SIT8510.0 or SIT8510.1, is added. The amine can also be used as the reaction solvent. The reaction can be followed any of the standard techniques including thin layer and gas chromatography. The reaction is quite fast with primary and secondary alcohols and slower with tertiary alcohols. The trimethylsilylation of amides and amines can be accomplished by a modification of this procedure wherein the reaction mixture is heated to reflux for 16 h.

3. Trimethylbromosilane, SIT8430.0, or Trimethyliodosilane, SIT8564.0 in the trimethylsilylation of alcohols.

One equivalent of the alcohol, 1.1 equivalents of a suitable amine base are mixed in an inert solvent and 1 equivalent of the trimethylbromosilane, SIT8430.0, or trimethyliodosilane, SIT8564.0, is added. Both of these reagents are more reactive than the corresponding trimethylchlorosilane.

4. Trimethyliodosilane, SIT8564.0, and Hexamethyldisilazane, SIH6110.0, combination in the trimethylsilylation of hindered alcohols.

One equivalent of the alcohol and 2.2 equivalents of trimethyliodosilane, SIT8564.0, along with 1.1 equivalents of hexamethyldisilazane, SIH6110.0, are mixed in pyridine and the reaction stirred at room temperature.

5. Trimethylsilyltrifluoromethanesulfonate, SIT8620.0, or Trimethylsilyl Cyanide, SIT8585.1 in the trimethylsilylation of alcohols.

Trimethylsilylation with these very reactive organosilanes is carried out by the simple mixing of the alcohol and the silane in an inert solvent and allowing the reaction to occur, usually at room temperature. **CAUTION:** the reagent trimethylsilyl cyanide generates hydrogen cyanide as a by-product.

6. Allyltrimethylsilane, SIA0555.0, in the trimethylsilylation of carboxylic acids.

One equivalent of the acid is dissolved in carbon tetrachloride (other solvents such as dichloromethane can probably be used as well) and 1.1 equivalents of allyltrimethylsilane, SIA0555.0, are added. To this reaction mixture is added about three drops of triflic acid. The reaction is very fast being complete when the evolution of propylene gas ceases.

7. **Triethylchlorosilane, SIT8250.0, tert-butyldimethylchlorosilane, SIB1935.0, tert-butyldiphenylchlorosilane, SIB1968.0, Triisopropylchlorosilane, SIT8384.0, or Thexyldimethylchlorosilane, SIT7906.0 in the silylation of alcohols.**
One equivalent of the alcohol is dissolved in DMF along with 1.1 equivalents of the chlorosilane and 2.2 equivalents of imidazole or 2,6-lutidine are added. The reaction is normally heated to about 40°C for 10 to 20 h.
8. **Tert-butyldimethylsilylation of an alcohol in dichloromethane.**
The tert-butyldimethylsilylation of an alcohol has been carried out by treating 0.89 equivalents of tert-butyldimethylchlorosilane, SIB1935.0, in dichloromethane with 0.91 equivalents of the alcohol, 1.19 equivalents of triethylamine, and 0.036 equivalents of 4-dimethylaminopyridine at room temperature for several hours.
9. **Triisopropylsilyltrifluoromethanesulfonate, SIT8620.0, in the TIPS silylation of alcohols.**
One equivalent of the alcohol is reacted with 1.1 equivalents of triisopropylsilyltrifluoromethanesulfonate, SIT8620.0, in dichloromethane with 2.2 equivalents of 2,6-lutidine as catalyst. The reaction can be carried out as low as -78°C in less than 5 h depending on the structure of the alcohol.
10. **Tert-butyldimethylsilyltrifluoromethanesulfonate, SIB1967.0, in the TBS silylation of alcohols.**
One equivalent of the alcohol is treated with tert-butyldimethylsilyltrifluoromethanesulfonate, SIB1967.0, as a 1M solution in 50:50 mixture by volume of dichloromethane and pyridine. Additional SIB1967.0 may have to be added to finish the reaction for the lower reactive alcohols.
11. **Di-tert-butylysilylbis(trifluoromethanesulfonate), SID3345.0, in the silylation of diols.**
One equivalent of the diol is reacted at room temperature with 1.2 equivalents of di-tert-butylysilylbis(trifluoromethanesulfonate), SID3345.0, and 3 equivalents of 2,6-lutidine in chloroform. 1,3-Diols and 1,4-diols are, in general, more reactive than 1,2-diols.
12. **Tert-butyldiphenylchlorosilane, SIB1968.0, in the TBDPS silylation of primary amines.**
One equivalent of the primary amine is reacted with tert-butyldiphenylchlorosilane, SID1968.0, and 1.5 equivalents of triethylamine in acetonitrile at room temperature for 1 to 3 h. Secondary amines do not silylate under these conditions.
13. **1,2-Bis(chlorodimethylsilyl)ethane, SIB1042.0, in the silylation of primary amines.**
One equivalent of the primary amine is reacted with 1 equivalent of the 1,2-bis(chlorodimethylsilyl)ethane, SIB1042.0, and 2 equivalents of triethylamine in dichloromethane at room temperature for 2 to 3 h. A convenient way to isolate the product is to filter, concentrate, add pentane, filter again and concentrate to provide the product in high purity without further purification.
14. **1,1,3,3-Tetraisopropyl-1,3-dichlorodisiloxane, SIT7273.0, in the silylation of nucleosides.**
One equivalent of the nucleoside is reacted with the silane, SIT7273.0, and 4.4 equivalents of imidazole in DMF at room temperature. The yields are typically 80 percent.
15. **1,2-Bis(dimethylsilyl)benzene, SIB1084.0, in the silylation of primary amines.**
One equivalent of the amine is reacted with SIB1084.0 and a catalytic amount of Wilkinson's catalyst, tris(triphenylphosphine)rhodium (I) chloride, in toluene.
16. **Trimethylsilylethanol, SIT8589.2, in the protection of carboxylic acids.**
One equivalent of the acid is reacted with trimethylsilylethanol, SIT8589.2, one equivalent of dicyclohexylcarbodiimide, in ethyl acetate with a catalytic amount of DMAP added. A typical reaction time is about 12 h at room temperature.
17. **Triisopropylchlorosilane, SIT8384.0, in the trimethylsilylation of alcohols.**
One equivalent of the acid is reacted with triisopropylchlorosilane, SIT8384.0, and 1.4 equivalents of triethylamine in dichloromethane for 1 h at -35°C and then 15 h at room temperature.

18. Triisopropylsilyltrifluoromethanesulfonate, SIT8387.0, as precursor to triisopropylsilylcarbamate, Tsoc, protecting group.

The amine is reacted with carbon dioxide in the presence of triethylamine at -78°C for 30 to 60 minutes. This mixture is then treated with triisopropylsilyltrifluoromethanesulfonate, SIT8387.0, at room temperature. The reaction mixture can be washed with water without hydrolysis of the protecting group.

19. Formation of acetonides of diols with Isopropenoxytrimethylsilane, SII6460.0.

One equivalent of the diol is mixed with isopropoxytrimethylsilane, SII6460.0, in an inert solvent (THF, ether, toluene) and 1 to 2 drops of concentrated HCl or trimethylchlorosilane are added. The reaction is complete in less than 30 minutes.

20. Dimethylaminotrimethylsilane or diethylaminotrimethylsilane in the trimethylsilylation of alcohols.

One equivalent of the alcohol or amine is reacted with the aminotrimethylsilane and dimethylamine (or diethylamine) is removed by distillation as the reaction proceeds. These reagents are particularly useful in the silylation of amines. HMDS, SIH6110.0, is preferred for the trimethylsilylation of alcohols.

21. Trimethylsilylimidazole, TMSI, SIT8590.0, in the silylation of alcohols.

Trimethylsilylimidazole, SIT8590.0, is a very reactive silylating agent, especially for alcohols. It is typically reacted with an equivalent amount of the alcohol in the presence or absence of an acid catalyst.

22. N,O-Bis(trimethylsilyl)acetamide, SIB1846.0, trimethylsilylation of alcohols.

One equivalent of the alcohol is reacted with 0.5 equivalents of N,O-bis(trimethylsilyl)acetamide, SIB1846.0, in an inert solvent. The reaction proceeds faster with a small amount of trimethylchlorosilane, SIT8510.0, as catalyst.

23. N,O-Bis(trimethylsilyl)trifluoroacetamide, SIB1876.0, trimethylsilylation of alcohols.

One equivalent of the alcohol is reacted with 0.5 equivalents of N,O-bis(trimethylsilyl)trifluoroacetamide, BSTFA, SIB1876.0, in an inert solvent with or without trimethylchlorosilane, SIT8510.0, catalysis. This has the advantage of producing the liquid byproduct, trifluoroacetamide, which is oftentimes easier to remove than the solid acetamide from SIB1846.0 or the diphenylurea from SIB1878.0.

24. N,N-Bis(trimethylsilyl)urea, BSU, SIB1878.0, in the trimethylsilylation of alcohols.

Two equivalents of the solid trimethylsilylating agent are reacted with one equivalent of the alcohol in an inert solvent. The solid, insoluble diphenylurea produced is readily removed by filtration and the product purified.

DEPROTECTION OF SILYL ETHERS

1. Acid-catalyzed cleavage of trimethylsilyl ethers

The silylated alcohol (0.4 mmol) in dichloromethane (4 mL) is treated with a drop of 1N HCl and the reaction mixture is stirred for 30 min.

In a transesterification approach a 0.5 M solution of trimethylsilylated alcohol in methanol is treated with pyridinium p-toluenesulfonate (PPTS) at room temperature for 30 min. The lower boiling trimethylmethoxysilane is removed by distillation.

2. Base-catalyzed cleavage of trimethylsilyl ethers.

The mildest conditions for the base-catalyzed deprotection of trimethylsilyl ethers is the treatment of a methanol solution of the silylated alcohol with an excess of potassium carbonate for 1 to 2 h.

3. Selective cleavage of a triethylsilyl ether with hydrogen fluoride-pyridine – representative procedure for the cleavage of silyl ethers with HF•pyr.

Treatment of 180 mmol of the silylated alcohol with 4 mL of the stock solution of HF•pyr (2 mL of HF•pyr, 4 mL pyridine, 16 mL THF) for 2 to 3 h results in the cleavage of the triethylsilyl ether.

4. Acid-catalyzed cleavage of triethylsilyl ethers.

A methanol solution of the silyl ether held at 0 °C is treated with p-toluenesulfonic acid (0.33 eq.) for 1 to 2 h. Alternatively, a THF solution of the triethylsilyl ether is treated with an aqueous solution of trifluoromethanesulfonic acid.

5. Cleavage of a tert-butyldimethylsilyl ether with tetra-n-butylammonium fluoride - representative procedure for the deprotection of silyl ethers with TBAF.

A solution of the silyl ether in THF (approximately 4 M) is treated with 3 equivalents of 1 M TBAF in THF at room temperature until the silyl ether is converted. This depends on the environment of the TBS ether, but usually requires from 2 to 16 h.

6. Cleavage of a tert-butyldimethylsilyl ether with tris(dimethylamino)sulfur(trimethylsilyl)difluoride - representative procedure for the deprotections of silyl ethers with TAS-F.

A 0.4 M solution of the silylated alcohol in THF is added to the TAS-F, SIT8715.0, at room temperature and the resulting solution stirred for 1 to 2 h.

7. Cleavage of a tert-butyldimethylsilyl ether with HF – representative procedure for the deprotection of silyl ethers with HF.

Hydrofluoric acid (49% aqueous solution, excess) is added to the silyl ether in acetonitrile at 0°. After stirring for a short time (typically 10 to 30 min) the reaction mixture is carefully quenched by the addition of saturated aqueous sodium hydrogen carbonate (CAUTION: STRONG EVOLUTION OF CARBON DIOXIDE).

8. Cleavage of a tert-butyldiphenylsilyl ether with TBAF in acetic acid.

A stock solution of TBAF in acetic acid is prepared (0.15 mL of HOAc per 1.0 mL of 1M TBAF in THF). The silyl ether is dissolved in THF and reacted with an excess of the stock solution for several h.

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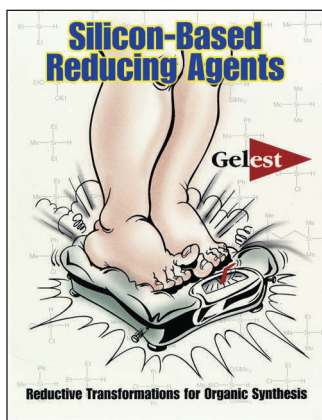
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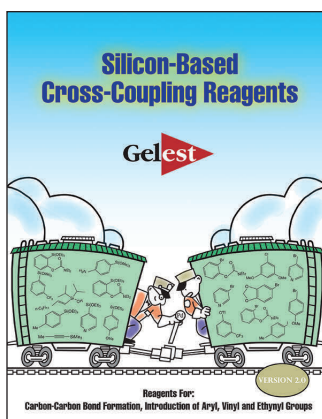
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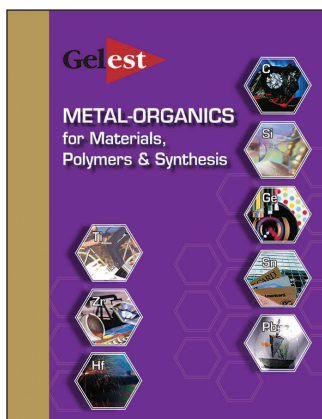
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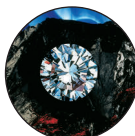
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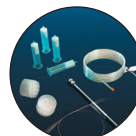
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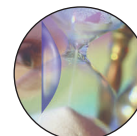
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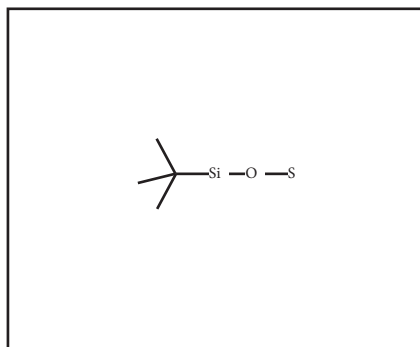


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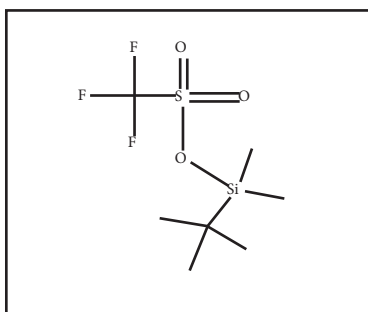


Figure 3

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HMIS	3-3-1-X HMIS Key	Refractive Index	1.3848 /
M. W.	264.33	Flash Point	36° C (98° F)
BP °C/mm Hg	65 / 10		
Specific Gravity	1.151 /		
Purity			
Reactivity/Apps			
Addition Properties			
Fieser			
Reference	review: G. Simchen. Adv. Silicon Chem., 1, 189, 1991 JAI Press		
Application	powerful silylation reagent and Lewis acid		

Figure 4

No.	Structure	Name	Catnum	CAS	Formula
1		t-BUTYLDIMETHYLSILYLTRIFLUOROMETHANESULFONATE	SIB1967.0	69739-34-0	C7H15F3O3SSi
2		DI-t-BUTYLSILYLBIS(TRIFLUOROMETHANESULFONATE)	SID3345.0	85272-31-7	C10H18F6O6S2Si



For additional information on Gelest's products and services or to inquire on how we may assist in *Enabling Your Technology*, please contact:

11 East Steel Rd.
Morrisville, PA 19067 USA
Phone (USA): 215-547-1015
Fax (USA): 215-547-2484
Phone (UK): 44(0)1622 741115
info@gelest.com



Stroofstrasse 27 Geb. 2901
65933 Frankfurt am Main,
Germany
Phone (DE): 49(0)69-3800-2150
Fax (DE): 49(0)69-3800-2300
info@gelestde.com