4.4.33 Product Subclass 33: Arylsilanes

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General Introduction

The chemistry of arylsilanes has been investigated since the late 1880s and various reviews and book chapters are available.[1–13] Arylsilanes have captured the interest of many chemists due to their ease of preparation, their conversion into other functional groups by the ipso-substitution reaction, and the ease with which the silyl group can be removed from the aromatic ring and replaced with a hydrogen atom. Arylsilanes have been used as blocking groups, as traceless linkers for solid-phase synthesis, and as fluorous labels for fluorous synthesis. The preparation of arylsilanes and their applications will be overviewed in this section.

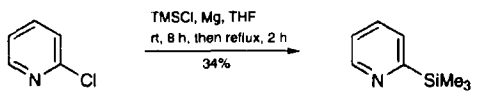
Synthesis of Product Subclass 33

4.4.33.1 Method 1: Via the Würtz–Fittig Reaction

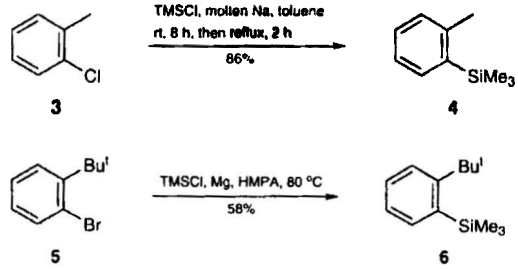
The Würtz–Fittig-type coupling[14,15] between an aryl halide, chlorosilane, and metal (Li, Na, or Mg) was the first method reported for the preparation of arylsilanes. In 1885, tetraphenylsilane was prepared by mixing chlorobenzene (4 mol), tetrachlorosilane (1 mol), and sodium metal (8 mol).[16] This in situ procedure reduces the amount of isomerization and decomposition that can accompany methods in which the organometallic reagent is prepared separately. Both aryl chlorides and bromides are used extensively in this reaction and the most commonly employed metal is magnesium; however, successful examples with sodium have also appeared. For example, 2-chloropyridine (**1**) is converted into 2-(trimethylsilyl)pyridine (**2**) by stirring a mixture of **1**, chlorotrimethylsilane, and magnesium turnings in tetrahydrofuran for eight hours at room temperature and then two hours under reflux (Scheme 1);[17] 2-(trimethylsilyl)pyridine (**2**) is formed in 34% yield. In a similar manner, trimethyl(2-tolyl)silane (**4**) is prepared in 86% yield from 2-chlorotoluene (**3**), chlorotrimethylsilane, and molten sodium.[18]

A useful variant of this method is to perform the reaction with magnesium metal using hexamethylphosphoric triamide as the solvent.[19,20] This reaction has been studied in detail and is found to be very general. Aryl chlorides, bromides, and iodides can be used along with heteroaromatic systems, such as pyridines and thiophenes. In addition, hindered systems, which do not form Grignard reagents in high yields, react well under these conditions. For example, 1-bromo-2-*tert*-butylbenzene (**5**) gives (2-*tert*-butylphenyl)trimethylsilane (**6**) in 58% yield (Scheme 1).

Scheme 1 Arylsilanes via a Würtz–Fittig-Type Coupling[17,18,20]



for references see p 709



(2-*tert*-Butylphenyl)trimethylsilane (6):[20]

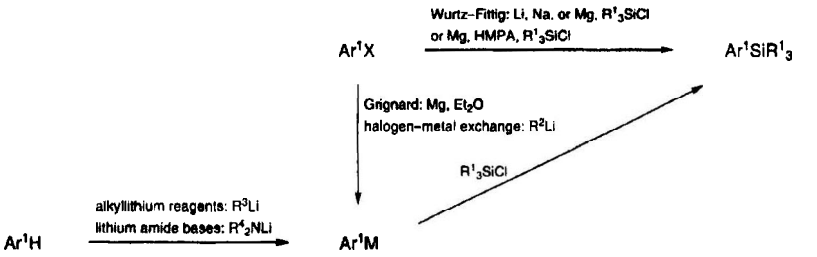
CAUTION: *Hexamethylphosphoric triamide (HMPA) is a substance suspected of carcinogenic potential in man. Appropriate safety precautions and procedures should be adopted when handling this reagent.*

A few drops of 2-bromo-1-*tert*-butylbenzene (**5**; 9.50 g, 0.044 mol) were added to a stirred mixture of Mg (1.46 g, 0.06 mol) and TMSCl (8.62 g, 0.08 mol) in HMPA (8.8 mL). The mixture was warmed until foaming started and 1,2-dibromoethane (a few drops) was added to initiate the reaction. Once the reaction had started, the remaining aryl halide in HMPA (volume not given) was added over 5 h at 80 °C. After stirring for an additional 45 h at 80 °C, the mixture was cooled and added to ice-cold aq $NaHCO_3$ (5 g·L^{-1}). The mixture was then filtered and the filtrate extracted with Et_2O. The Et_2O extracts were washed with H_2O, dried, and the Et_2O removed under reduced pressure to leave an oil that was purified by distillation to give **6**; yield: 5.33 g (58%); bp 120 °C/13 Torr.

4.4.33.2 Method 2: Silylation of Aryl-Substituted Metals

The use of aryl-substituted metals for the introduction of silyl groups onto aryl and heteroaryl systems remains the most common method for the construction of arylsilanes. This is mainly because the methods developed for forming aryl-substituted metals have evolved significantly since the 1970s and trisubstituted chlorosilanes are readily available from commercial sources. There are five main variations of the formation of arylsilanes via aryl-substituted metals (Scheme 2). The oldest is the Würtz–Fittig-type coupling in which an aryl halide, chlorosilane, and a metal are mixed and allowed to react in situ (see Section 4.4.33.1). Two other methods that use aryl halides as starting materials are the preparation of a Grignard reagent with magnesium and halogen–lithium exchange reactions with alkyllithium reagents. Finally, aryl systems containing *ortho*-lithiation directors or entities that render aryl hydrogens more acidic than normal can be directly metalated using alkyllithium reagents or lithium amide bases. These latter methods avoid the need for an aryl halide starting material.

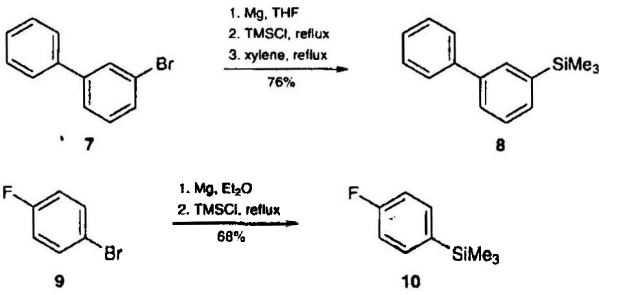
Scheme 2 Formation of Arylsilanes from Aryl-Substituted Metals



4.4.33.2.1 Variation 1: Via Grignard Reagents

Many arylsilanes have been prepared by the stepwise preparation of a Grignard reagent from an appropriate aryl halide followed by the addition of a chlorosilane.[5] In this manner, 3-bromobiphenyl (**7**) is converted into (biphenyl-3-yl)trimethylsilane (**8**) in 76% yield (Scheme 3).[21] Cyanotrimethylsilane or ethoxytrimethylsilane have also been used instead of chlorotrimethylsilane.[22] The Grignard method is not efficient for hindered halides, thus, *ortho*-substituted arylsilanes can be difficult to prepare. Functional groups that react with Grignard reagents must either be protected (e.g., carbonyl groups, alcohols, etc.) or cannot be present in the starting material (e.g., nitriles, esters, etc.). Aryl chlorides, bromides, and iodides have been employed using this procedure and the relative reactivity of different halides with magnesium has been used to selectively convert certain halides into trimethylsilyl groups. For example, 1-bromo-4-fluorobenzene (**9**) is selectively converted into (4-fluorophenyl)trimethylsilane (**10**) in 68% yield (Scheme 3).[23] The entrainment method has also been successful for the conversion of some halides, which are unreactive toward magnesium, into arylsilanes.[24] This method involves the continuous addition of an alkyl bromide throughout the reaction time so that the surface of the magnesium remains active.

Scheme 3 Arylsilanes via Preformed Grignard Reagents[21,23]



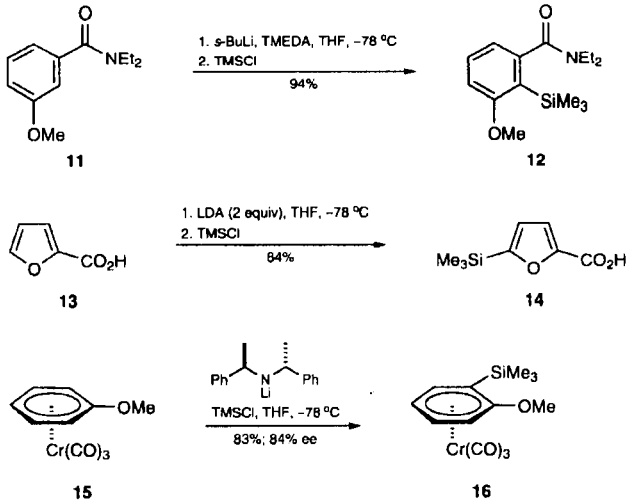
(Biphenyl-3-yl)trimethylsilane (8):[21]
A Grignard soln was prepared from Mg (0.04 g-atom) and 3-bromobiphenyl (**7**; 9.32 g, 0.04 mol) in THF (150 mL). To this mixture was gradually added a soln of TMSCl (3.81 mL, 0.03 mol) in THF and the soln refluxed for 1 h. The solvent was removed under reduced pressure, xylene (150 mL) added, and the mixture was heated at reflux overnight. A standard workup provided **8**; yield: 6.8 g (76%); bp 78–82 °C/0.03 Torr.

for references see p 709

4.4.33.2.2 Variation 2: Via Organolithium Reagents

It is well known that aromatic rings with appropriate heteroatom-containing substituents can be *ortho*-metalated using organolithium reagents.[25–32] The resulting anion(s) can be treated with electrophiles, of which a variety of trisubstituted chlorosilanes have been reported. A vast array of groups can be used to direct *ortho*-metalation (e.g., amides, ethers, sulfides, sulfones, acetals, carbamates, urethanes, some alcohols and acids, and imines to mention a few), thus this method is probably the most versatile for the preparation of silyl-substituted aromatic systems.[25,27,32] For example, treatment of *N,N*-diethyl-3-methoxybenzamide (**11**) with *sec*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine at −78 °C followed by the addition of chlorotrimethylsilane gives *N,N*-diethyl-3-methoxy-2-(trimethylsilyl)benzamide (**12**) in 94% yield (Scheme 4).[33] Some heteroaromatic systems, such as furans, thiophenes, pyrroles, indoles, pyrazoles, and imidazoles, can be directly lithiated at the α-position without the need of an adjacent directing group. Treatment of these anions with chlorosilanes provides an expedient route to silyl-substituted heteroaromatic systems.[34] 5-(Trimethylsilyl)-2-furoic acid (**14**) is prepared in high yield by treatment of 2-furoic acid (**13**) with two equivalents of lithium diisopropylamide followed by chlorotrimethylsilane (Scheme 4).[35] A vast array of other heteroaromatic systems have been directly lithiated with and without the aid of directing groups.[25] Interestingly, the tricarbonylchromium complexes of 1-methyl-1*H*-indole have been silylated at the α-position.[36] In other cases, lithium amide bases have been used to directly lithiate an aromatic system.[37] A particularly noteworthy example is the treatment of tricarbonyl(η^6-anisole)chromium(0) (**15**) with lithium bis[(*R*)-1-phenylethyl]amide, in the presence of chlorotrimethylsilane to form **16** in 83% yield with 84% ee (Scheme 4).[38]

Scheme 4 Arylsilanes from Directed Metalation Reactions[33,35,38]



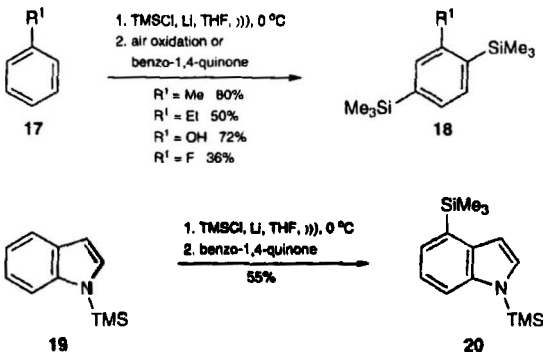
N,N-Diethyl-3-methoxy-2-(trimethylsilyl)benzamide (12):[33]
A soln of benzamide **11** (3.25 g, 15.7 mmol) in anhyd THF (5 mL) was added dropwise to a stirred soln of a 1.1 M *s*-BuLi in cyclohexane (15.7 mL, 17.3 mmol)–TMEDA (1:1, 2.6 mL, 17.3 mmol) complex in anhyd THF at −78 °C under argon. After 1 h, TMSCl (6.1 mL, 47.1 mmol) was added. The resultant soln was warmed to rt overnight, after which sat. aq NH_4Cl (20 mL) was added and the THF removed under reduced pressure. The mixture was extracted with CH_2Cl_2 and the combined extracts washed with brine. The CH_2Cl_2 lay-

er was dried (Na_2SO_4) and the solvent removed to leave an oil that was purified by MPLC to give **12** as a colorless solid that was recrystallized (hexane); yield: 4.12 g (94%); mp 54–55 °C.

4.4.33.2.3 Variation 3: Via Reductive Silylation Followed by Oxidation

A variety of 1,4-bis(trimethylsilyl)-2-substituted benzene rings **18** can be prepared via a silyl Birch reduction of a monosubstituted benzene ring **17** followed by either an air oxidation or by stirring the formed cyclohexa-1,4-diene in the presence of benzo-1,4-quinone (Scheme 5).[39–42] Some heterocyclic aromatic systems behave in a similar manner. 1-(Trimethylsilyl)-1*H*-indole (**19**) can be treated in a similar manner to provide 1,4-bis(trimethylsilyl)-1*H*-indole (**20**) in 55% yield after an oxidative workup with benzo-1,4-quinone.

Scheme 5 Arylsilanes via Reductive Silylation Followed by Oxidation[39–42]



2,5-Bis(trimethylsilyl)phenol (18, R^1 = OH); Typical Procedure:[41]
To phenol (**17**, R^1 = OH; 0.94 g, 10 mmol) at 0 °C in dry THF (30 mL) under argon was added TMSCl (5.43 g, 50 mmol) followed by Li (0.35 g, 50 mmol) cut into ca. 20 pieces. The mixture was agitated in an ultrasonic bath at 0–5 °C for 3 h and then at 40 °C for 12 h. The THF was evaporated under reduced pressure and the residue was triturated with hexane (4 × 40 mL). The combined extracts were filtered through Celite and refluxed in air for 72 h. The solvent was evaporated under reduced pressure and the residue purified by column chromatography (silica gel, hexane) to give **18** (R^1 = OH); yield: 1.72 g (72%).

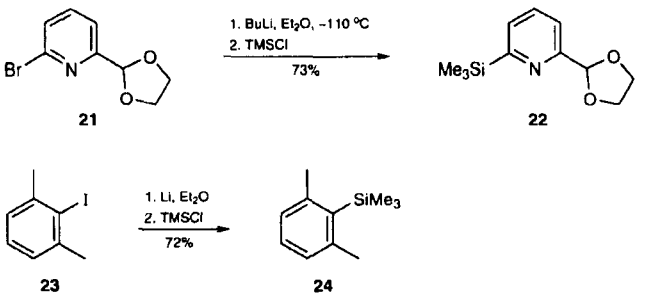
4.4.33.2.4 Variation 4: Via Halogen–Metal Exchange

An alternative method for forming arylsilanes from aryl halides is to treat the aryl halide with either lithium metal[43] or an organolithium reagent. The halide then undergoes a halogen–metal exchange reaction and the resulting anion is treated with a chlorosilane to provide the arylsilane. This method has become fairly popular among chemists because organolithium reagents are commercially available. The reactivity of aryl halides toward lithium metal or organolithium reagents follows the order I>Br>Cl>F. Thus, most of the reactions in this section start with aryl iodides or bromides. Most chlorides react very slowly (if at all) with lithium and most fluorides are inert. This relative reactivity allows selective exchange with compounds containing polyhalogenated aromatic systems. The use of lithium metal with an aryl halide is very closely related to a Grignard reaction and has been applied to a large range of aryl and heteroaryl systems containing halides;[5] e.g. halogen–metal exchange of 2-bromo-6-(1,3-dioxolan-2-yl)pyridine (**21**) with

for references see p 709

butyllithium at −110 °C followed by the addition of chlorotrimethylsilane provides 2-(1,3-dioxolan-2-yl)-6-(trimethylsilyl)pyridine (**22**) in 73% yield (Scheme 6).[44] Lithium metal can also be used in place of an organolithium reagent, e.g. 2-iodo-1,3-dimethylbenzene (**23**) is converted into (2,6-dimethylphenyl)trimethylsilane (**24**) in 72% yield using metallic lithium (Scheme 6).[43]

Scheme 6 Arylsilanes from Aryl Halides Using Lithium Metal or Organolithium Reagents[43,44]

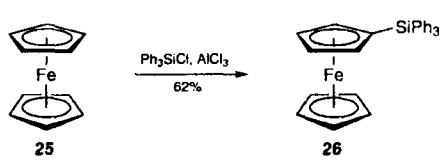


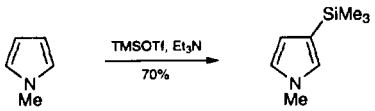
2-(1,3-Dioxolan-2-yl)-6-(trimethylsilyl)pyridine (22):[44]
A soln of 2-bromo-6-(1,3-dioxolan-2-yl)pyridine (**21**; 3.1 g, 13.5 mmol) in Et_2O (20 mL) was added to BuLi (9.6 mL, 13.5 mmol) at −110 °C under N_2 over 10 min. The mixture was warmed to −78 °C and maintained at this temperature for 30 min, then cooled to −100 °C, and TMSCl (1.47 g, 13.5 mmol) added. The mixture was stirred for 1 h after which it was warmed to 20 °C and stirred for an additional 24 h. The mixture was filtered through Celite, the solvent evaporated, and the residue distilled to give **22**; yield: 2.2 g (73%); bp 104 °C/0.1 Torr.

4.4.33.3 Method 3: Electrophilic Aromatic Substitutions

The preparation of arylsilanes via an electrophilic aromatic substitution reaction has been limited to highly activated nonbenzenoid systems. This may be due, in part, to the instability of silylenium ions [R_3Si^+].[45,46] Ferrocene (**25**) has been silylated using chloro- and aminosilanes under Friedel–Crafts conditions ($AlCl_3$) providing silylated ferrocene derivatives **26** in good yields (Scheme 7).[47] In addition, 1-methyl-1*H*-pyrrole (**27**) can be silylated selectively in the 3-position using trimethylsilyl triflate in the presence of a hindered base to give **28**.[48] It is also reported that benzene and toluene can be silylated in the presence of aluminum trichloride and *N,N*-diisopropylethylamine (Hünig's base); however, the product yield is 1.6% or less.[49]

Scheme 7 Arylsilanes from Electrophilic Aromatic Substitutions[47,48]





27 28

1-Methyl-3-(trimethylsilyl)-1*H*-pyrrole (28):[48]
1-Methyl-1*H*-pyrrole (**27**; 2 g, 24 mmol) was dissolved in Et_3N (15 mL) and TMSOTf (4.63 mL, 24 mmol) was added and stirring continued overnight. The lower phase was separated, washed with abs Et_2O, mixed with solid NaOH for 30 min, filtered, concentrated, and distilled to give **28**; yield: 2.6 g (70%); bp 65–67 °C/12 Torr.

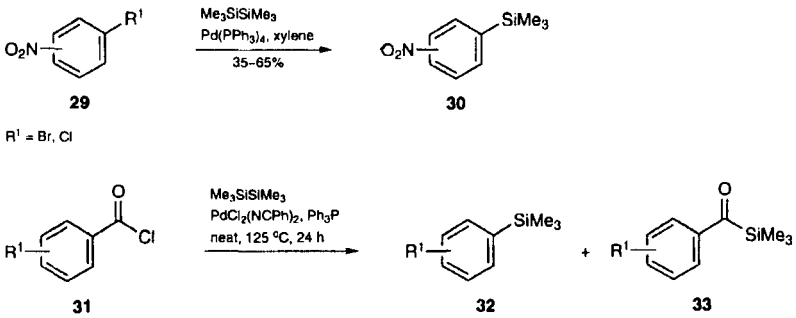
4.4.33.4 Method 4: From Transition-Metal-Catalyzed Reactions

Arylsilanes have been made from various aryl halides via transition-metal-catalyzed reactions. The most common transition metal employed is palladium; however, successful reactions with nickel or rhodium are also reported.

4.4.33.4.1 Variation 1: From Palladium Reagents

Nitro-substituted arylsilanes **30** can be prepared by heating a mixture of nitro-substituted aryl bromides (or chlorides) **29** and hexamethyldisilane in the presence of tetrakis(triphenylphosphine)palladium(0). Yields range from 35 to 65% depending on the placement of the nitro group present on the starting aryl halide (Scheme 8).[50,51] Other variations of this reaction have also been reported, including a review on the activation of Si—Si bonds by transition metals;[52–56] e.g. 1,1,2,2-tetraethoxy-1,2-dimethyldisilane can be used.[57] A variation of the above reaction has also been developed. While the reaction of an aryl acid chloride **31** with hexamethyldisilane in the presence of bis(benzonitrile)dichloropalladium gives a mixture of **32** and **33**, the use of a disilane containing chlorine atoms provides only the substituted arylsilane **34** via a silyl decarbonylation reaction. This reaction shows good scope giving yields ranging from 25 to 89%.[58,59] An alternative to using a disilane, is to treat an aryl iodide **35** with triethoxysilane in the presence of a palladium(0) catalyst to give the triethoxysilylaryl system **36** with yields ranging from 20 to 84%.[60] Finally, 2-(trimethylsilyl)-1*H*-indoles **37** can be prepared by treating 2-iodoaniline with a 1-(trimethylsilyl)alkyne in the presence of palladium(II) acetate.[61]

Scheme 8 Arylsilanes from Palladium-Catalyzed Reactions[50,51,58–61]



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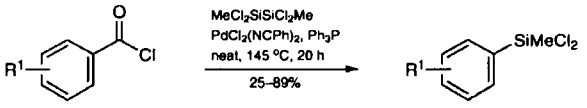
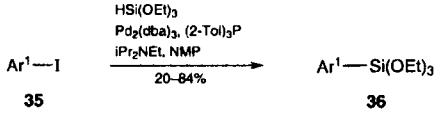


31 34

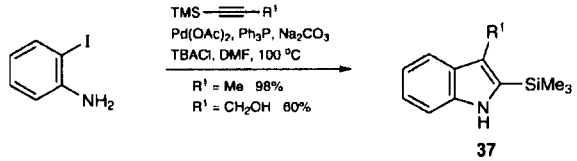
R^1	Yield (%) of **34**	Ref	R^1	Yield (%) of **34**	Ref
H	89	[58]	4-OMe	52	[58]
2-Me	13	[58]	3-NO_2	74	[58]
3-Me	47	[58]	4-NO_2	72	[58]
4-Me	58	[58]	4-CN	77	[58]
2-Cl	25	[58]	2-COCl[a]	19[c]	[58]
3-Cl	73	[58]	3-COCl[a]	61	[58]
4-Cl	86	[58]	4-COCl[a]	83	[58]
2-OMe	32	[58]	3-COCl[b]	66	[58]
3-OMe	71	[58]	4-COCl[b]	64	[58]

[a] 1 equivalent of disilane.
[b] 2 equivalents of disilane.
[c] GC yield.



35 36

R^1	Reaction Time (h)	Yield (%) of **36**	Ref
Ph	1	83	[60]
4-$Me_2NC_6H_4$	1	81	[60]
4-$AcHNC_6H_4$	1	72	[60]
4-$AcOC_6H_4$	1	77	[60]
4-Tol	1	82	[60]
4-ClC_6H_4	4	72	[60]
4-$EtO_2CC_6H_4$	16	23	[60]
4-NCC_6H_4	16	20	[60]
2-thienyl	1	84	[60]
3-pyridyl	1	56	[60]



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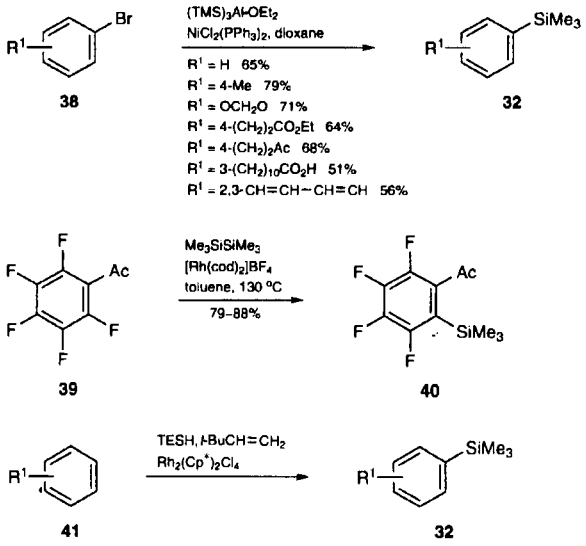
Trimethyl(2-nitrophenyl)silane (30, nitroaryl = 2-$O_2NC_6H_4$):[51]
A mixture of 1-chloro-2-nitrobenzene (4.72 g, 30 mmol), $Me_3SiSiMe_3$ (8.8 g, 60 mmol), $Pd(PPh_3)_4$ (0.35 g, 0.30 mmol), and xylene (15 mL) was placed into a Pyrex tube containing a Teflon-covered stir bar. The tube was cooled in liq N_2, evacuated to 0.3 Torr, sealed, and heated at 150 °C for 40 h with stirring. The tube was cooled to rt and opened. GC analysis indicated that the 1-chloro-2-nitrobenzene had been completely consumed. The mixture was diluted with petroleum ether (45 mL) and the dark precipitate was removed by filtration. Evaporation of the filtrate and distillation of the residue gave **30** as a yellow liquid; yield: 3.8 g (65%); bp 115–117 °C.

4.4.33.4.2 Variation 2: From Nickel and Rhodium Reagents

Other transition metals, such as nickel and rhodium, have been used for the preparation of arylsilanes. Aryl bromides **38** can be converted into arylsilanes **32** when they are treated with a mixture of tris(trimethylsilyl)aluminum–diethyl ether complex and dichlorobis(triphenylphosphine)nickel(II), yields range from 51 to 79% (Scheme 9).[62] Usually when aryl halides are employed in a transition metal reaction, the halide is restricted to iodine, bromine, or chlorine. However, when a C–F bond is *ortho* to a ketone as in **39**, the fluorine atom can be exchanged for a silyl moiety to give **40** when treated with triethylsilane and bis(cycloocta-1,5-diene)rhodium tetrafluoroborate {$[Rh(cod)_2]BF_4$}.[63] This reaction followed a paper in which a rhodium-catalyzed H–F exchange reaction between hexafluorobenzene and hydrosilanes was described.[64,65] Various monosubstituted benzene rings have been transformed into arylsilanes by a dehydrogenative transfer–coupling reaction. When arenes **41** are treated with triethylsilane in the presence of di-μ-chlorobis[chloro(η^5-pentamethylcyclopentadienyl)rhodium and 3,3-dimethylbut-1-ene, mixtures of *ortho*, *meta*, and *para* isomers of **32** are obtained.[66]

Scheme 9 Arylsilanes from Nickel- and Rhodium-Catalyzed Reactions[62,63,66]



for references see p 709

(2-Acetyl-3,4,5-6-tetrafluorophenyl)trimethylsilane (40):[63]
A mixture of 1-acetyl-2,3,4,5,6-pentafluorobenzene (**39**; 210 mg, 1 mmol), $Me_3SiSiMe_3$ (1.46 g, 10 mmol), and $[Rh(cod)_2]BF_4$ (40.9 mg, 0.1 mmol) in toluene (1 mL) was heated at 130 °C in an oil bath for 20 h in a 50-mL screw-capped pressure vial to give **40** as a colorless oil; yield: 210 mg (79%).

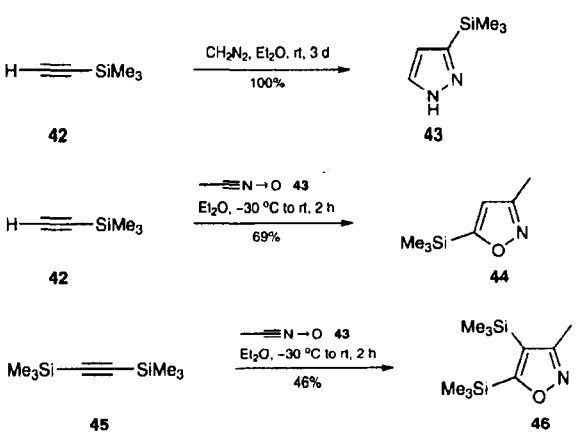
4.4.33.5 Method 5: From Cycloaddition Reactions

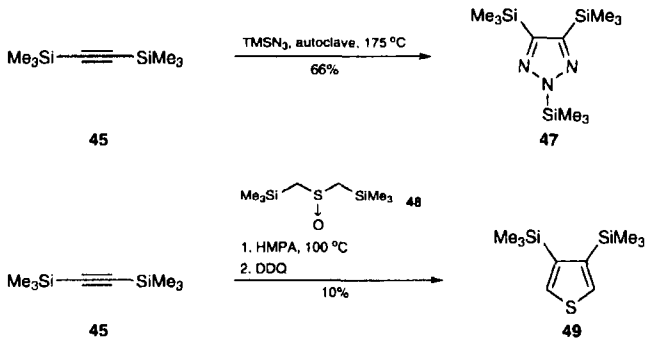
The preparation of arylsilanes via various cycloaddition reactions is the next most commonly used method for the preparation of this class of compounds. Of the various cycloaddition reactions possible, the most common are the use of the cobalt-mediated co-oligomerization of diynes with substituted acetylenes and Diels–Alder/retro-Diels–Alder sequences.

4.4.33.5.1 Variation 1: Via [2+3]-Dipolar Cycloadditions

Silyl-substituted heterocycles have been prepared via [2+3] dipolar cycloadditions. For example, 3-(trimethylsilyl)-1*H*-pyrazole (**43**) is prepared quantitatively by mixing diazomethane with (trimethylsilyl)acetylene (**42**) in diethyl ether at room temperature for three days (Scheme 10).[67,68] A variety of silyl-substituted 1*H*-pyrazoles have been synthesized via this dipolar cycloaddition strategy.[67,68] 3-Methyl-5-(trimethylsilyl)isoxazole (**44**) can be prepared by a similar reaction between alkyne **42** and nitrile oxide **43**.[69] The reaction between chlorobis(trimethylsilyl)methylenephosphine and a nitrile oxide to provide a silylated 1,2,4-oxazaphosphole has also been reported.[70] 3-Methyl-4,5-bis(trimethylsilyl)isoxazole (**46**) is also available via the reaction of nitrile oxide **43** with alkyne **45**. Triazole **47** is prepared in 66% yield by the dipolar addition of azidotrimethysilane and alkyne **45**.[71] Other silyl-substituted triazoles are possible using various azide starting materials.[71] Finally, 3,4-bis(trimethylsilyl)thiophene (**49**) can be prepared, albeit in 10% yield, by the dipolar addition of bis[(trimethylsilyl)methyl]sulfoxide (**48**) and bis(trimethylsilyl)acetylene (**45**), followed by 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone oxidation of the dihydrothiophene intermediate.[79]

Scheme 10 Arylsilanes from [2+3] Dipolar Cycloaddition[67–69,71,79]





3-(Trimethylsilyl)-1*H*-pyrazole (43):[67,68]

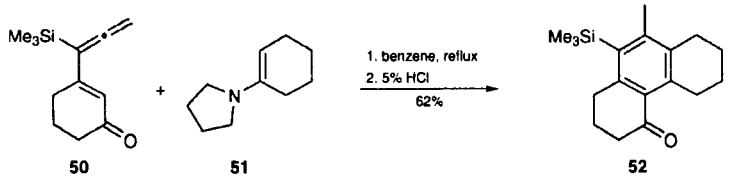
> **CAUTION:** *Diazomethane is highly toxic and irritating. It is also a detonator and appropriate safety precautions should be taken when using this reagent (e.g., special glassware, use of a blast shield, etc.).*

(Trimethylsilyl)acetylene (**42**, 4.91 g, 50 mmol) and diazomethane (2.94 g, 70 mmol) in dry Et_2O (100 mL) were stored in the dark for 3 d at rt. After destroying the excess diazomethane by short boiling, the mixture was filtered and the solvent removed under reduced pressure to give **43**; yield: 7.01 g (100%); mp 79–80 °C.

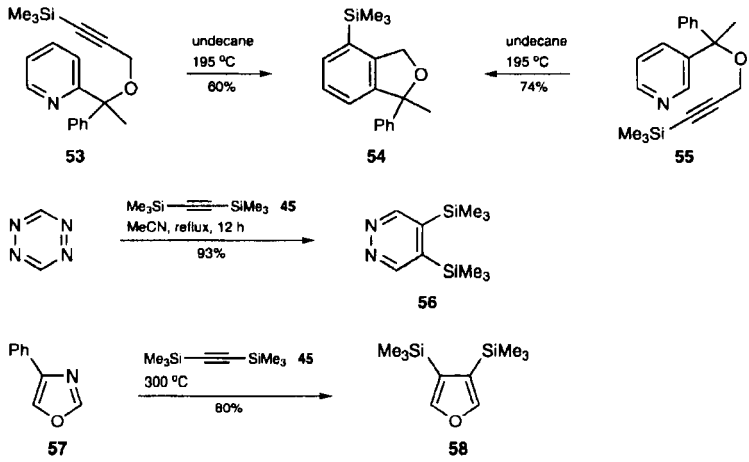
4.4.33.5.2 Variation 2: Via [4+2] Cycloadditions

A variety of aryl and heteroarylsilanes have been synthesized using either a Diels–Alder [4+2] cycloaddition followed by aromatization of the resulting cyclohexene ring, or by using a Diels–Alder/retro-Diels–Alder sequence. Only a few selected examples are provided here (Scheme 11). When silylallene **50** is heated with enamine **51** and the product from the [4+2] cycloaddition treated with 5% hydrochloric acid, arylsilane **52** is formed in 62% yield (Scheme 11).[72] Other examples of this reaction sequence with yields ranging from 51 to 92% are also reported (Scheme 11). There are many examples in the literature that employ a tandem Diels–Alder/retro-Diels–Alder sequence to produce arylsilanes. Pyridines **53** and **55** form arylsilane **54** in 60 and 74% yield, respectively, when heated at 195 °C in undecane.[73] A variety of silyl-substituted pyridazines have been synthesized using this strategy.[74–76] For example, treatment of tetrazine with bis(trimethylsilyl)acetylene (**45**) gives 4,5-bis(trimethylsilyl)pyridazine (**56**) in 93% yield.[76] 3,4-Bis(trimethylsilyl)furan (**58**) is synthesized in 80% yield via a similar sequence starting from 4-phenyloxazole (**57**).[34,77,78] The same authors prepared 3,4-bis(trimethylsilyl)thiophene in 92% yield using a thiazole as the starting heterocycle.[79] In addition to these examples, various α-pyrones[80,81] and tetraphenylcyclopentadienone[82] have been used as starting materials to prepare arylsilanes via a tandem Diels–Alder/retro-Diels–Alder sequence.

Scheme 11 Arylsilanes from [4+2]-Cycloaddition Reactions[72,73,76,77]



for references see p 709

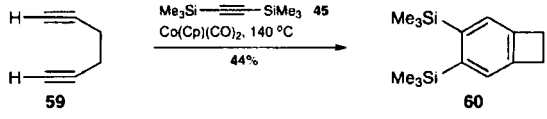


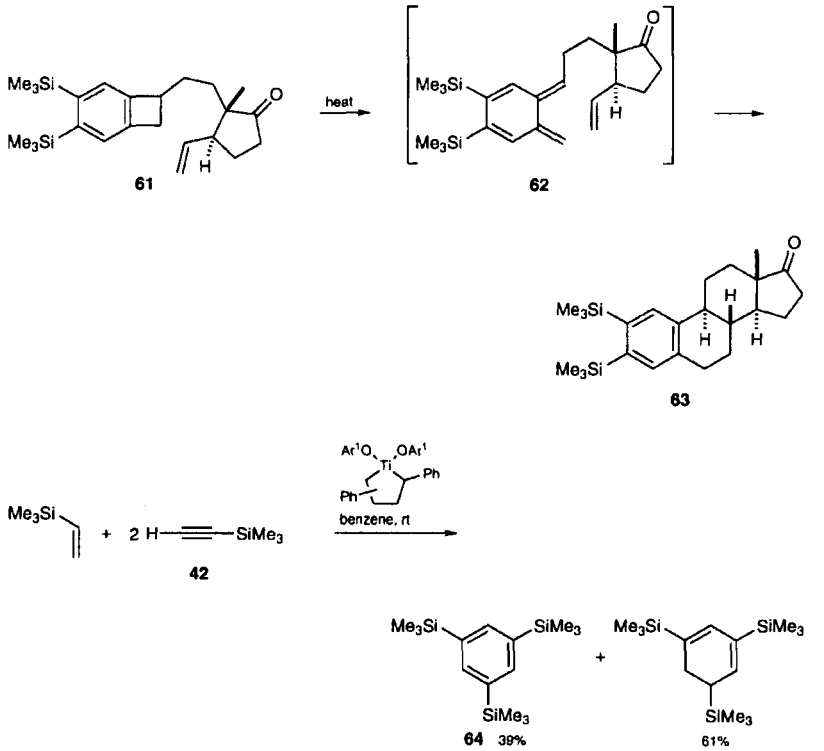
4,5-Bis(trimethylsilyl)pyridazine (56):[76]
The red soln of tetrazine (175 mg, 2.13 mmol) and bis(trimethylsilyl)acetylene (**45**; 375 mg, 2.2 mmol) in dry MeCN (5 mL) was refluxed overnight. After 12 h, the bright yellow soln was concentrated under reduced pressure and the residue was recrystallized [petroleum ether (bp 40–60 °C)] to give **56** as colorless needles; yield: 445 mg (93%); mp 94–95 °C.

4.4.33.5.3 Variation 3: Via [2+2+2] Cycloadditions

The cobalt-mediated co-oligomerization of diynes **59** with substituted acetylenes **45** is a very useful method for the preparation of a variety of arylsilanes **60** (Scheme 12). This reaction was initally reported in 1975[83–86] and is still being used at the time of writing. The reaction is easy to perform, tolerates a variety of functional groups and has led to the formation of silyl-substituted benzocyclobutenes, indanes, tetralins, naphthalenes, and has also been employed in a synthesis of angular [4]- and [5]-phenylene.[87] Interestingly, the co-oligomerization reaction to form silyl-substituted bicyclo[4.2.0]octatrienyl silanes **61** has been used in tandem with an intramolecular Diels–Alder reaction of the intermediate *o*-quinodimethane **62** that results when the four-membered ring opens and is trapped by a dienophile.[88–91] This reaction sequence is used to prepare silyl-substituted aromatic-containing steroid skeletons **63** (Scheme 12). Some other examples include more steroids,[92,93] isoquinolines,[94] the basic skeleton of phyllocladane-type diterpenes,[95] and the aphidicolan and stemodan skeletons.[96] Also, a titanium-based catalyst is used in a termolecular cyclization to prepare 1,3,5-tris(trimethylsilyl)benzene (**64**) in 39% yield.[97]

Scheme 12 Arylsilanes from [2+2+2]-Cycloaddition Reactions[83–85,92,93,97]





3,4-Bis(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene (60):[83–85]
Bis(trimethylsilyl)acetylene (**45**; 25 mL, 110 mmol) containing $CoCp(CO)_2$ (30 µL) was refluxed under N_2 at 140 °C on an oil bath. To this was added hexa-1,5-diyne (**59**; 1 g, 12.8 mmol) in bis(trimethylsilyl)acetylene (**45**; 5 mL, 22.1 mmol) containing $CoCp(CO)_2$ (20 µL) via a syringe pump with magnetic stirring over 72 h. The reaction flask was cooled, connected to a vacuum line, and the low-boiling substances vacuum transferred off to give recovered bis(trimethylsilyl)acetylene. The dark oily residue was chromatographed [silica (100 g), pentane (200-mL fractions)]. Fractions 2 and 3 gave **60** as a light yellow oil, which was crystallized ($MeOH/Et_2O$, −20 °C); yield: 1.39 g (44%); mp 43–44 °C.

4.4.33.6 Method 6: Via Silyl Migrations

The formation of arylsilanes via the migration of a silicon moiety from oxygen to carbon has been known since the 1970s. Both [1,3] O→C and [1,4] O→C silyl migrations have been reported in the synthesis of arylsilanes and they will be treated in different sections.

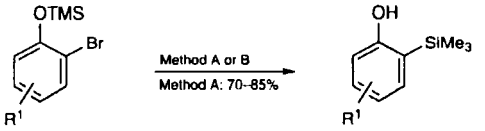
4.4.33.6.1 Variation 1: Via [1,3] Oxygen-to-Carbon Silyl Migrations

It was reported in 1975 that a variety of 2-bromo-*O*-(trimethylsilyl)phenols **65** undergo a [1,3] O→C silyl migration when treated with magnesium metal in tetrahydrofuran to give 2-(trimethylsilyl)phenols **66** (Scheme 13).[98,99] The reaction is high yielding (70–85%) and essentially complete after one hour. Similar migrations are reported[100] when phenols such as **65** are treated with *tert*-butyllithium. These migrations have been shown to be in-

for references see p 709

tramolecular.[5] Since the first report of this migration, other groups[101–103] have employed this migration with a variety of substrates.

Scheme 13 Arylsilanes from [1,3] O→C Silyl Migrations[98,100]



R^1	R^2	Method[a]	Yield (%)	Ref
H	H	A	80	[98]
H	H	B	76	[100]
H	Me	B	93	[100]
H	*t*-Bu	A	80	[98]
t-Bu	*t*-Bu	A	85	[98]
TMS	H	A	84	[98]
TMS	*t*-Bu	A	70	[98]

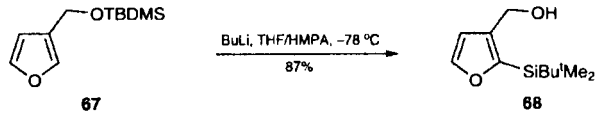
[a] Method A: Mg, THF, 1h, 65 °C; B: *t*-BuLi, THF, −78 °C.

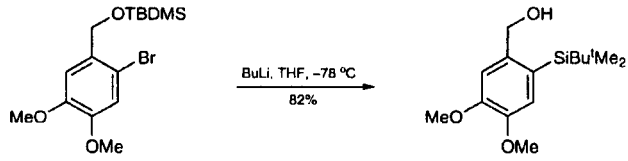
2-(Trimethylsilyl)phenol (66, R^1 = H); Typical Procedure:[98]
To Mg (2.4 g, 0.1 mol) in THF (50 mL) was added dropwise (2-bromophenoxy)trimethylsilane (**65**; 23.0 g, 0.09 mol) dissolved in THF (20 mL). The mixture was maintained at 65 °C for 1 h and then quenched with aq NH_4Cl. The organic products were extracted with Et_2O, dried ($MgSO_4$), and the solvent removed under reduced pressure to leave the product; yield: 12.8 g (82%); bp 109–110 °C/25 Torr.

4.4.33.6.2 Variation 2: Via [1,4] Oxygen-to-Carbon Silyl Migrations

It has been reported that 2-silyl-(3-hydroxymethyl)furans and -thiophenes can be synthesized via a [1,4] O→C silyl migration.[104,105] For example, 3-(*tert*-butyldimethylsiloxy)furan (**67**), when treated with butyllithium in tetrahydrofuran with hexamethylphosphoric triamide gives 2-(*tert*-butyldimethylsilyl)furan-3-methanol (**68**) in 87% yield (Scheme 14). A variety of substituted silanes undergo the migration, and thiophenes can also be employed. In addition, silyl esters can be used as starting materials, these migrate to form 2-silylated-3-furoic acids and 2-silylated-thiophene-3-carboxylic acids.[105,106] A similar migration is possible starting with silylated alcohol **69**. Treatment of **69** with butyllithium at −78 °C in tetrahydrofuran gives the migrated product **70** in 82% yield.[107]

Scheme 14 Arylsilanes from [1,4] O→C Silyl Migrations[105,107]





69 70

2-(*tert*-Butyldimethylsilyl)furan-3-methanol (68):[105]

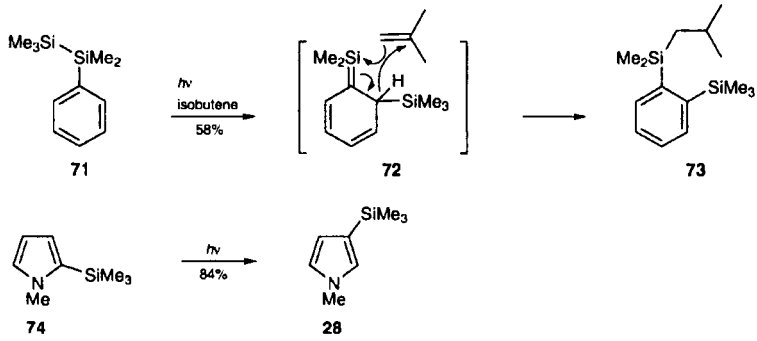
> **CAUTION:** *Hexamethylphosphoric triamide (HMPA) is a substance suspected of carcinogenic potential in man. Appropriate safety precautions and procedures should be adopted when handling this reagent.*

A soln of freshly distilled silylated alcohol **67** (0.7 g, 3.3 mmol) and HMPA (0.62 mL, 3.6 mmol) in dry THF (10 mL) was cooled to −78 °C under argon and treated with 2.5 M BuLi in hexanes (1.44 mL, 3.6 mmol). The soln was allowed to warm to rt over 6 h and stirred at rt overnight. Sat. aq NH_4Cl was added and the soln extracted with Et_2O. The organic layer was washed with sat. aq $CuSO_4$ (3 ×) and dried (Na_2SO_4). The solvent was removed to afford **68**; yield: 0.61 g (87%); bp 75–78 °C/0.02 Torr.

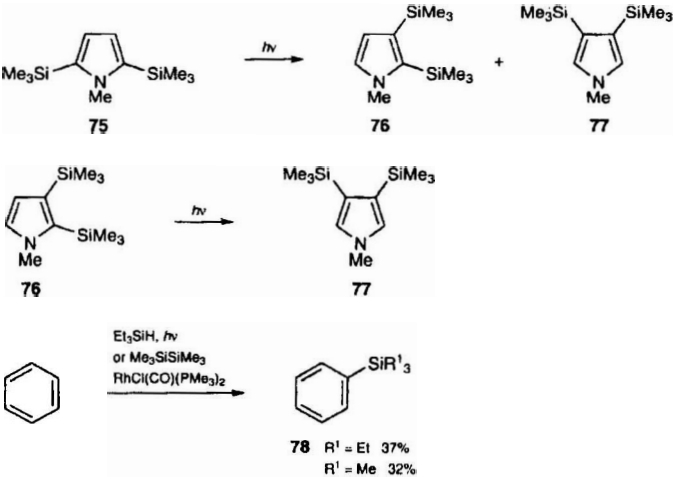
4.4.33.7 Method 7: Via Photochemical Reactions

In 1975 it was reported that the 1,2-disilyl-substituted benzene ring **73** could be prepared in 59% yield by the photolysis of 1,1,1,2,2-pentamethyl-2-phenyldisilane (**71**) in the presence of isobutene (Scheme 15).[108–110] The reaction is believed to proceed via the unstable intermediate **72** that has a C=Si bond. This intermediate adds to isobutene to give product **73**. A variety of substituted benzene and naphthalene[111] rings undergo this reaction. An interesting photochemical rearrangement of 1-methyl-2-(trimethylsilyl)-1*H*-pyrrole (**74**) has been reported.[112] When 1*H*-pyrrole **74** is photolyzed, 1-methyl-3-(trimethylsilyl)-1*H*-pyrrole (**28**) is formed in 84% yield. In a similar reaction, 1-methyl-2,5-bis(trimethylsilyl)-1*H*-pyrrole (**75**) provides a mixture of trisubstituted 1*H*-pyrroles **76** and **77** in 39 and 41% yields, respectively. However, when 1-methyl-2,3-(trimethylsilyl)-1*H*-pyrrole (**76**) is photolyzed for one hour the 3,4-disilyl-substituted 1*H*-pyrrole **77** is formed in 50% yield. No other products are detected in the mixture. Similarly, triethyl(phenyl)silane (**78**; R^1 = Et) and trimethyl(phenyl)silane (**78**; R^1 = Me) can be prepared by photolyzing a mixture of benzene with either triethylsilane or hexamethyldisilane in the presence of carbonylchlorobis(trimethylphosphine)rhodium [RhCl(CO)(PMe_3)$_2$] at room temperature for 16.5 hours.[113] A small amount of biphenyl is also formed.

Scheme 15 Arylsilanes from Photochemical Reactions[108–110,112,113]



for references see p 709



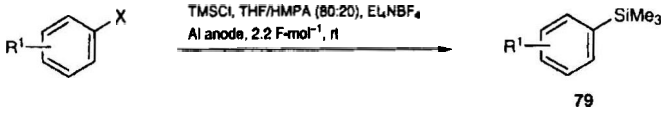
1-Methyl-3-(trimethylsilyl)-1*H*-pyrrole (28):[112]

1-Methyl-2-(trimethylsilyl)-1*H*-pyrrole (**74**; 1.39 g, 9.1 mmol) in degassed pentane (150 mL) was irradiated for 50 min with a 450-W Hanovia lamp. ^{1}H NMR and GC analysis of the yellow photolysate revealed trace amounts of unreacted **74** and clean formation of only 1*H*-pyrrole **28**. 1*H*-Pyrrole **28** was isolated by preparative GC (10-ft 15% SE-30); yield: 1.17 g (84%).

4.4.33.8 Method 8: Via Electrochemical Reactions

Trimethysilylated benzene rings can be prepared by an electrochemical reductive trimethylsilylation (Scheme 16).[114] A mixture of bromobenzene, chlorotrimethylsilane, and tetrahydrofuran/hexamethylphosphoric triamide (80:20) is electrolyzed by using an aluminum anode (or magnesium anode with magnesium chloride) and passing 2.2 F·mol^{-1} of electricity; trimethyl(phenyl)silane (**79**, R^1 = H) is formed in 76% yield. This reaction has good scope, providing arylsilanes in yields ranging from 50–76%.

Scheme 16 Arylsilanes from Electrochemical Reactions[114]



R^1	X	Yield (%)	Ref
H	Br	76	[114]
H	Br	50[a]	[114]
H	Cl	70	[114]
2-Me	Br	63	[114]
2-Me	Cl	65	[114]
3-Me	Cl	76	[114]
4-Me	Cl	65	[114]

[a] Mg anode, DMF, $MgCl_2$, rt.

Trimethyl(phenyl)silane (79, R^1 = H); Typical Procedure:[114]

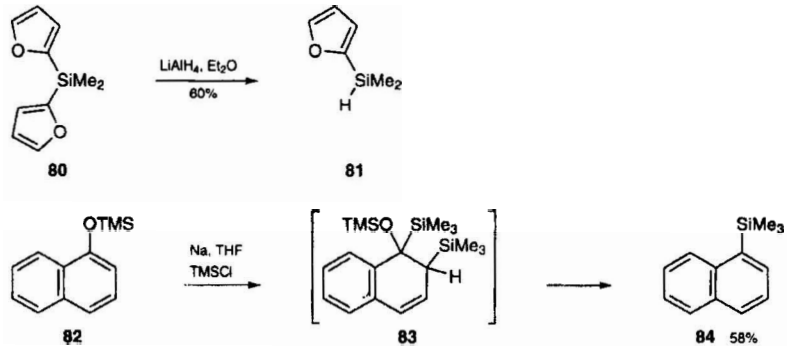
CAUTION: *Hexamethylphosphoric triamide (HMPA) is a substance suspected of carcinogenic potential in man. Appropriate safety precautions should be adopted when handling this reagent.*

The supporting electrolyte [(Et_4NBF_4) an amount just sufficient to permit passage of an electrical current, i.e., enough to make a 0.02 M soln] and the solvent (THF/HMPA 80:20, 50 mL) were introduced into a cell with an Al anode. The soln was deaerated by bubbling argon through it for 20 min during which time the soln was irradiated with ultrasound. A large excess of TMSCl (six to nine times the theoretically required amount) was then added. Any HCl produced by the reaction of TMSCl with H_2O was removed by electrolyzing the soln (I = 100 mA). The other hydrolysis product $(TMS)_2O$ is electrochemically inert. When evolution of H_2 had ceased, the bromobenzene (2.2 g, 14 mmol) was introduced using a syringe. Electrolysis (I = 50 mA) was then initiated and was continued until the theoretically required quantity of electricity had been passed. H_2O was then added to the mixture, and the whole was extracted with Et_2O (3 × 50 mL). The Et_2O was dried (Na_2SO_4) and concentrated. Distillation gave **79**; yield: 1.59 g (76%); bp 168–170 °C.

4.4.33.9 Methods 9: Additional Methods

Lithium aluminum hydride will cleave the C–Si bond in di(2-furyl)dimethylsilane (**80**) providing 2-furyl(dimethyl)silane (**81**) in 60% yield (Scheme 17).[115] Cleavage of Si–C sp^2 bonds occurs more readily than that of Si–C sp^3 bonds. In an interesting reaction, trimethylsilyl-protected 1-naphthol **82**, when treated with sodium metal (in THF) in the presence of chlorotrimethylsilane provides trimethyl(1-naphthyl)silane (**84**) in 58% yield.[116] This reaction initially appears to be just a reductive deoxygenation, but is rationalized by the addition of two trimethylsilyl groups to the naphthalene ring to form **83**, followed by an elimination of hexamethyldisilanol to give **84**.

Scheme 17 Arylsilanes via Other Reactions[115,116]



Applications of Product Subclass 33 in Organic Synthesis

4.4.33.10 Method 10: Ipso-Substitution Reactions

The replacement of a silyl group on an aromatic ring by electrophiles is referred to as an ipso substitution when the incoming electrophile attaches to the same carbon atom that the silyl group leaves. For most electrophiles, ipso substitution of a silyl group is faster than replacement of a hydrogen atom.[117,118] This is probably due to the stabilization of

for references see p 709

the cation intermediate by the silyl leaving group.[119,120] The trimethylsilyl group is most commonly used for ipso substitutions due to its relatively small size when compared to other silyl moieties. A variety of electrophiles have been employed in this reaction and Table 1 shows some reagents that have been used along with the functional group that replaces the silyl group.

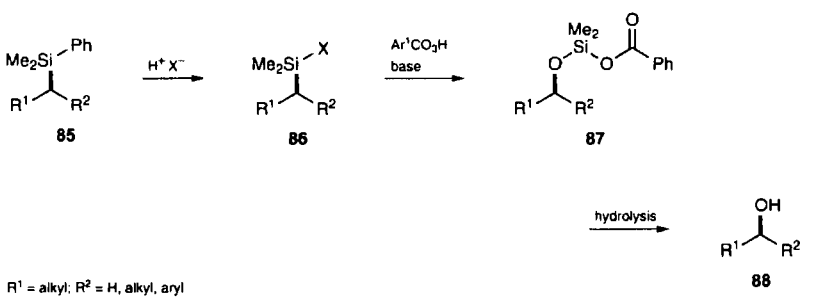
Table 1 Various Reagents Used for Ipso Substitutions of Arylsilanes[92,93,127–137]

Electrophilic Reagents	E	Ref	Electrophilic Reagents	E	Ref
H_2SO_4	H	[121]	SO_3	SO_3H	[122]
$R^1SO_2Cl/AlCl_3$	SO_2R^1	[123]	NO_2 (N_2O_4)	NO_2	[124]
$^{18}F_2/CFCl_3$ or $CH_3CO_2{}^{18}F$/AcOH	^{18}F	[125]	$Pb(OAc)_4/BF_3{\bullet}OEt_2$	F	[126]
Cl_2/AcOH	Cl	[127]	Br_2/AcOH	Br	[127]
$NH_4{}^{82}Br$/NCS/HOAc	^{82}Br	[128]	$Na^{77}Br$/*t*-BuOOH/AcOH	^{77}Br	[128,129]
I_2	I	[130]	$Na^{131}I$/NCS/HOAc	^{131}I	[128,129]
ICl	I	[131]	$R^1COCl/AlCl_3$	COR^1	[132]
$PhCH_2Br/AlCl_3$	CH_2Ph	[132]	$Hg(OAc)_2$	HgOAc	[133]
1. $Hg(OAc)_2$, AcOH 2. $BH_3{\bullet}THF$ 3. $NaOH/H_2O_2$	OH	[134]	PCl_3	PCl_2	[135]
$Pb(OCOCF_3)_4$	OH	[92,93]	$[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-cyclohexadienyl})]BF_4^-$	$C_6H_7Fe(CO)_3$	[136]
1. BBr_3 2. 5% HCl	$B(OH)_2$	[137]			

4.4.33.11 Method 11: Oxidation of the C–Si Bond

In 1984 it was shown that a dimethylphenylsilyl group could undergo a two-step reaction to convert the C–Si bond into a C–O bond with retention of stereochemistry (Scheme 18).[138] Since then, the procedure has been simplified to a one-pot sequence. The two-step procedure involves an initial ipso substitution of the aryl–silicon bond (**85**→**86**) with a halide (usually F or Br) followed by an oxidation step (**86**→**87**) with a peracid in the presence of base. Hydrolysis during workup provides the alcohol **88**. Further information on this reaction can be found in Section 4.4.18 on silyl peroxides and in a review.[139] Although the dimethylphenylsilyl group is the most commonly used, other arylsilanes have been used for this oxidation.

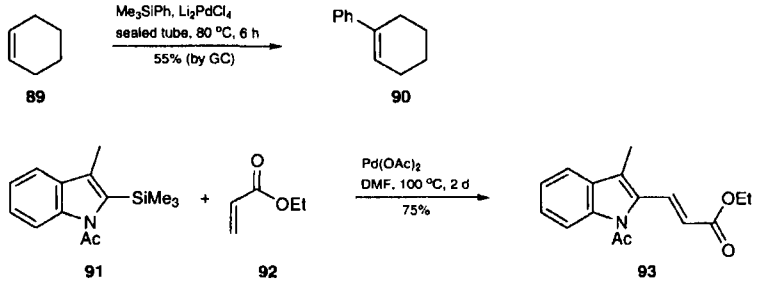
Scheme 18 Oxidation of Aryl–Silicon Bonds[138–153]



4.4.33.12 Method 12: Cross-Coupling Reactions

Arylsilanes have been used in Heck and cross-coupling reactions to provide 1-arylalkenes and aryl–aryl systems respectively. The first example of a Heck reaction with an arylsilane was reported in 1974 where trimethyl(phenyl)silane was treated with cyclohex-1-ene (**89**) in the presence of lithium tetrachloropalladate(II) (Li_2PdCl_4) to form 1-phenylcyclohex-1-ene (**90**) in 55% yield (Scheme 19).[154] Indole **91** has also been shown to react with ethyl acrylate (**92**) or but-1-en-3-one and one equivalent of palladium(II) acetate to provide **93** in 75% yield.[155]

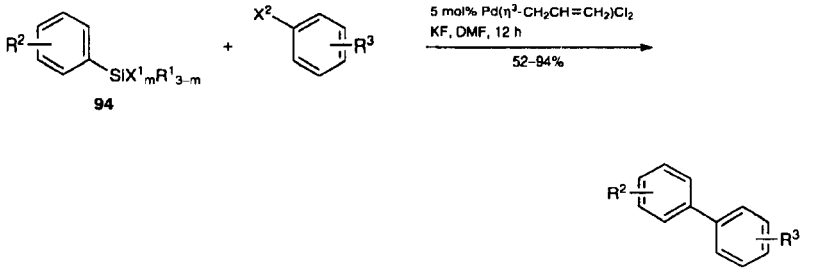
Scheme 19 Use of Arylsilanes in Heck Reactions[154,155]



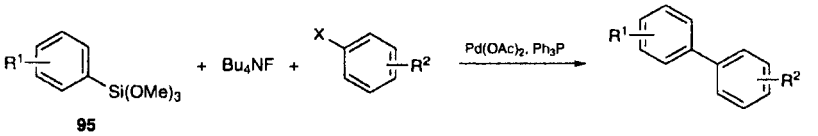
It is well known that cross-coupling reactions proceed between aryl halides or triflates and arylstannanes (Stille)[156] or arylboronic acids (Suzuki).[157] Arylsilanes have also found complementary use in cross-coupling reactions as the "organometallic" component.[158–160] The advantages are that silicon compounds are less toxic than stannanes; unlike boronic acid derivatives, silicon reagents are easily prepared and are stable to a wide variety of reaction conditions in organic synthesis; and the silicon activating group can be carried through a synthesis prior to its activation for the cross-coupling reaction. Scheme 20 illustrates that aryl—$Si(X^1)_mR_{3-m}$ **94**,[161–163] aryl—$Si(OMe)_3$ **95**,[164,165] and aryl—$Si(OH)Me_2$ **96**[166] have been used as the "organometallic" component in cross-coupling reactions with aryl halides in the presence of palladium catalysts. In addition, aryl—$SiMe_n(OMe)_{3-n}$ **97**[167] undergoes a cross-coupling reaction with aryl iodides in the presence of copper(I) iodide without the need for the addition of fluoride ion. This method minimizes the desilylation side reactions reported when fluoride ion is added to faciliate other cross-coupling reactions. Finally, diaryl ketones are prepared by performing cross-coupling reactions between aryl—$Si(R)F_2$ **98** and an aryl iodide under an atmosphere of carbon monoxide.[168]

for references see p 709

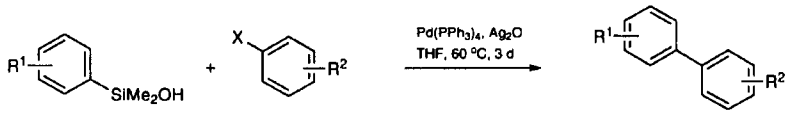
Scheme 20 Use of Arylsilanes in Cross-Coupling Reactions[161-168]



R^1	X^1	m	R^2	R^3	X^2	Yield (%)	Ref
Me	Cl	1	4-OMe	4-CN	Cl	93	[163]
Et	F	2	H	4-OEt	I	81	[161]
Et	F	2	4-Me	3-CH_2OH	I	86	[161]
Et	F	2	4-Me	4-CN	I	67	[161]
Et	Cl	2	4-OMe	3-Ac	Cl	62	[163]
Pr	F	2	3-OMe	3-CHO	I	83	[161]
Pr	F	2	3-OMe	4-CO_2Me	I	76	[161]
Pr	F	2	4-CF_3	4-OAc	I	47	[161]
Ph	F	1	H	4-Ac	I	98	[162]

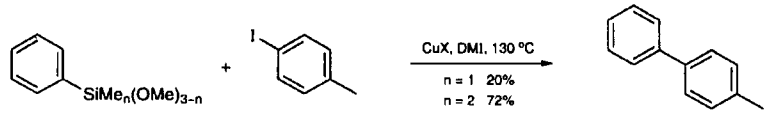


R^1	R^2	X	Yield (%)	Ref
H	4-Me	I	90	[165]
H	4-OMe	I	54	[165]
H	4-Ac	Br	56	[165]
4-$(CH_2)_4Me$	4-Ac	Br	84	[164]
4-$(CH_2)_3CH(Et)_2$	4-CO_2Et	Br	84	[164]
4-$(CH_2)_3CHEt(CH_2)_4Me$	4-NO_2	Br	74	[164]
4-$(CH_2)_3CHEtCH_2OH$	3,4-F	Br	82	[164]

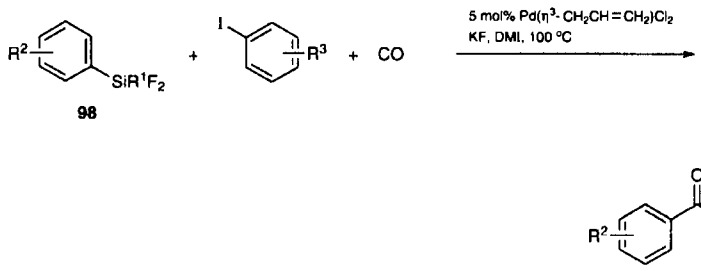


96

R^1	R^2	X	Yield (%)	Ref
2-Me	4-OMe	I	30	[166]
4-OMe	H	Br	2	[166]
4-OMe	H	I	80	[166]
4-OMe	4-CF_3	I	54	[166]
4-OMe	4-NO_2	I	45	[166]
4-CF_3	4-OMe	I	84	[166]



97



98

R^1	R^2	R^3	Yield (%)	Ref
Me	H	4-CO_2Me	61	[168]
Me	H	4-CN	60	[168]
Me	4-Me	4-Ac	91	[168]
Et	4-Me	4-OEt	69	[168]
Et	3-OMe	3-CHO	80	[168]

4.4.33.13 Method 13: Protection of Hydroxy Groups

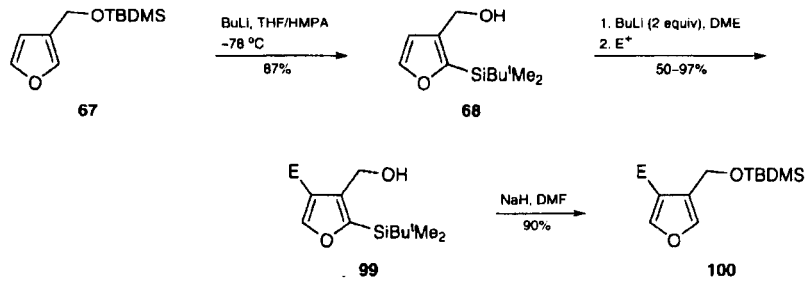
Arylsilanes have been used extensively as protecting groups in organic synthesis. Readers are referred to the section on silyl ethers (Section 4.4.17) and to a book on this topic.[169]

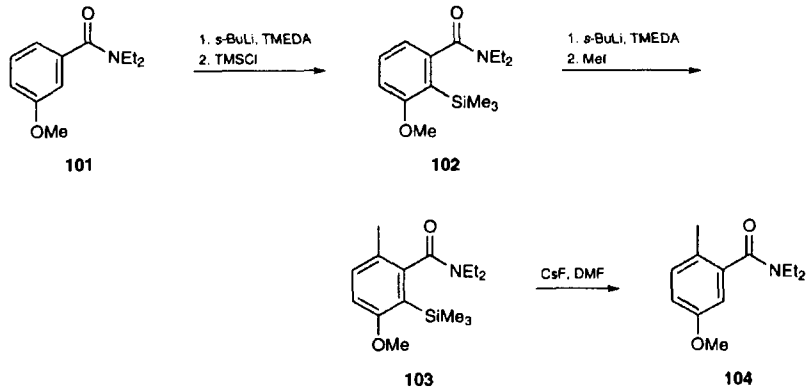
for references see p 709

4.4.33.14 Method 14: Use as a Blocking Group

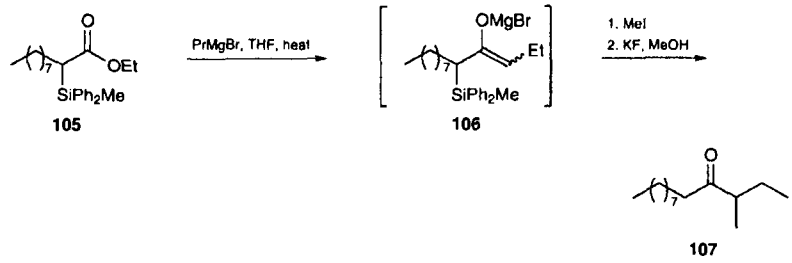
As outlined in Section 4.4.33.2.2, silyl groups can be introduced onto aromatic and heteroaromatic rings via an *ortho*-metalation reaction. The aromatic ring is initially substituted with an *ortho*-lithiation director. Treatment with an organolithium reagent results in the formation of an aryl anion that is trapped with a chlorosilane to provide the arylsilane. In some cases, the two sites *ortho* to the lithiation direction are regioisomeric and thus the initial site of lithiation sometimes is not where the new substituent is needed. Silyl groups have been used to block *ortho* sites in cases where a group is needed in the opposite *ortho* site to where lithiation initially takes place. For example, in an attempt to prepare 3,4-disubstituted furan rings **104** (Scheme 21), lithiation of 3-(*tert*-butyl)dimethylsiloxy)furan (**67**) results in the regioselective abstraction of the C2 hydrogen followed by the intramolecular migration of the silyl group into the C2 position to give **68** (Section 4.4.33.6.2).[105] With the C2 position blocked, treatment of **68** with 2.2 equivalents of butyllithium results in lithiation at the C4 position. Trapping this anion with electrophiles provides furan **99**.[170] Finally, migration of the C2 silyl group back to the hydroxy group gives **100**. Silyl groups have been used to block *ortho* sites on benzene rings (Scheme 21).[27] Treatment of **101** with *sec*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine and trapping the anion with chlorotrimethylsilane gives **102** in which the site between the two lithiation directors is now blocked.[171] A second lithiation followed by the addition of iodomethane gives **103**, which is desilylated with cesium fluoride in dimethylformamide to give **104**. The size of the methyldiphenylsilyl group can be used to great advantage when placed next to an ester or lactone (Scheme 22).[172] Ester lithium enolates can be directly C-silylated when treated with chloro(methyl)diphenylsilane.[173] The size of the silyl group will only allow the carbonyl group to be attacked once by a Grignard reagent, thereby providing ketones rather than tertiary alcohols. For example, treatment of **105** with propylmagnesium bromide gives enolate **106**, which is reacted with iodomethane. Removal of the silyl group with potassium fluoride/methanol gives ketone **107**.

Scheme 21 Use of Arylsilanes as Blocking Groups[170,171]





Scheme 22 Use of α-Arylsilyl Esters as Blocking Groups[172]

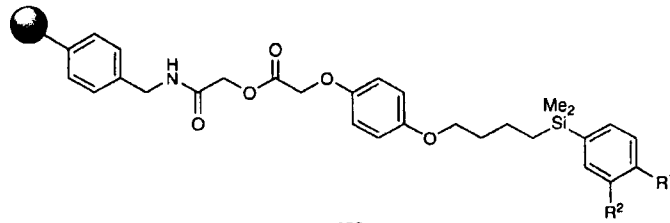


4.4.33.15 **Method 15:**
Use as Traceless Linkers in Solid-Phase Synthesis

A variety of trialkyl(aryl)silanes **108**,[174,175] dialkyl(phenyl)siloxy **109** (R^1 = iPr)[176] and **110**,[177] and triphenylsiloxy **109** (R^1 = Ph)[176] systems have been used as traceless linkers in solid-phase synthesis. A few examples are shown in Scheme 23. This topic will briefly be mentioned as there is already an excellent review on linkers for solid-phase organic synthesis.[178] The advantage of using a silyl group attached to an aromatic ring is that some aryl–silicon bonds can be cleaved easily by fluoride ion, trifluoroacetic acid, or hydrogen chloride with replacement of the silicon atom with a hydrogen atom. Thus, the library of compounds is removed from the solid support and does not contain the functional group to which the linker was originally attached. The silyl linker also remains attached to the solid support and in some cases can be reused. Occasionally, a silyl linker has been removed via an ipso substitution if a bromide or iodide was required on the library of compounds.[179,180]

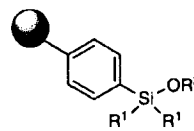
for references see p 709

Scheme 23 Arylsilanes as Linkers for Solid-Phase Synthesis[174–177]

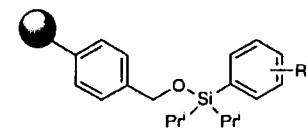


108

R^1 = NHBpoc; R^2 = H, $SnMe_3$, Bz



109 R^1 = iPr, Ph; R^2 = various oligosaccharides

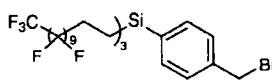


110

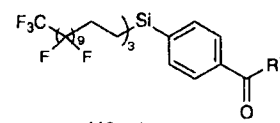
4.4.33.16 Method 16: Use as Fluorous Labels for Fluorous Synthesis

Arylsilanes have been used as fluorous labels for performing fluorous syntheses.[181–183] The main advantages for using an arylsilane are the ease with which the aryl–silicon bond can be cleaved and that three heavily fluorinated alkyl chains can be attached to the silicon atom. For example, a fluorous arylsilane benzyl protecting group **111** has been developed for alcohols and used in the fluorous synthesis of a disaccharide (Scheme 24).[184] In addition, fluorous arylsilanes **112** (R^1 = OH) and **112** (R^1 = Br)[185] have been used in an Ugi[186] and Biginelli[187] reaction, respectively. The aryl–silicon bond in the products from the Ugi and Biginelli reactions is cleaved using tetrabutylammonium fluoride in tetrahydrofuran. Surprisingly, the aryl–silicon bond was stable to lithium hydroxide in a tetrahydrofuran/water mixture, hydrogen fluoride in pyridine, cesium fluoride in tetrahydrofuran, and trifluoroacetic acid in dichloromethane.

Scheme 24 Fluorous Arylsilanes Used in Fluorous Synthesis[184,185]



111



112 R^1 = OH, Br

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