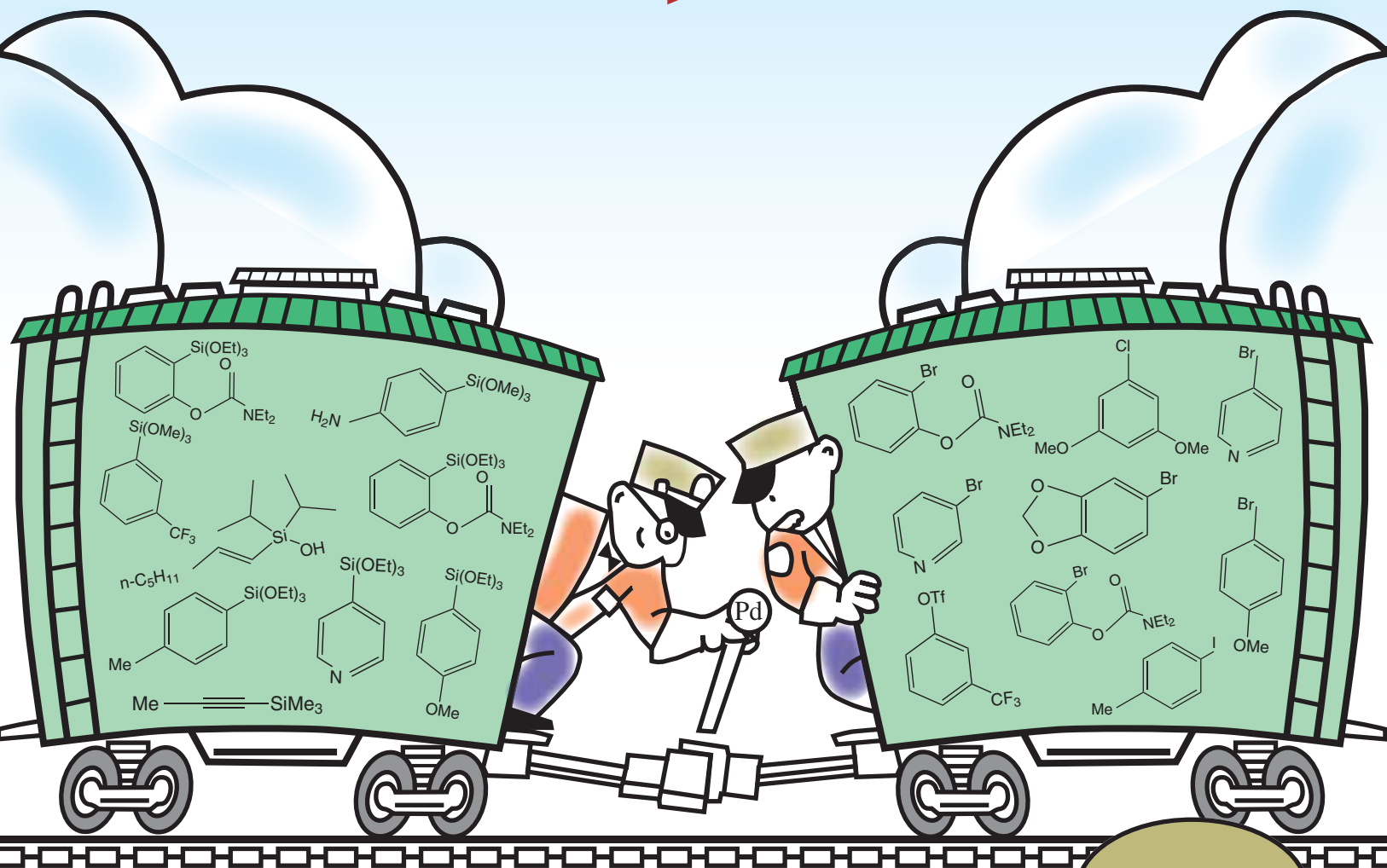


# Silicon-Based Cross-Coupling Reagents



VERSION 2.0

Reagents For:  
Carbon-Carbon Bond Formation, Introduction of Aryl, Vinyl and Ethynyl Groups



## Gelest, Inc.

Telephone: General 215-547-1015  
Order Entry 888-734-8344  
Technical Service: 215-547-1016  
215-547-2484  
FAX: 215-547-2484  
Internet: www.gelest.com  
e-mail: sales@gelest.com  
Correspondence: 11 East Steel Rd.  
Morrisville, PA 19067  
USA

**For further information consult our web site at: [www.gelest.com](http://www.gelest.com)**

### **In Europe:**

For commercial and  
bulk quantities contact:

#### **Gelest Ltd.**

46 Pickering Street  
Maidstone  
Kent ME15 9RR  
United Kingdom  
Tel: +44(0)-1622-741115  
Fax: +44(0)-8701-308421  
e-mail: europe@gelest.com

### **In India:**

For commercial and  
research quantities contact:

#### **Gautavik International**

301, A Wing Chandan Co-op Hsg Soc.  
Dadabhai Cross Road North  
Vile Parle West, Mumbai 400056  
India  
Tel: 91-22-26703175  
Fax: 91-9619190510  
Email: vasantiyadav@yahoo.co.in

### **In Japan:**

For commercial and  
research quantities contact:

#### **AZmax Co. Ltd. Tokyo Office**

Matsuda Yaesudori, Bldg F8  
1-10-7 Hatchoubori, Chou-Ku  
Tokyo 104-0032  
Tel: 81-3-5543-1630  
Fax: 81-3-5543-0312  
e-mail: sales@azmax.co.jp  
on-line catalog: www.azmax.co.jp

For research quantities in Europe:

#### **Gelest Inc.**

Stroofstrasse 27 Geb.2901  
65933 Frankfurt am Main,  
Germany  
Tel: +49-(0)-69-3800-2150  
Fax: +49-(0)-69-3800-2300  
e-mail: info@gelestde.com  
Internet: www.gelestde.com

### **In South-East Asia:**

For commercial and  
research quantities contact:

#### **Gulf Chemical**

39 Jalan Pemimpin  
Tai Lee Industrial Building #04-03  
Singapore 577182  
Tel: 65-6358-3185  
Fax: 65-6353-2542  
e-mail: support@gulfchem.com.sg

# Silicon-Based Cross-Coupling Reactions



Gerald L. Larson, Ph.D.  
*Vice President, Research and Development*

Materials for the Synthesis of:

Biaryls  
Styrenes  
Dienes  
Trienes  
Aryl Acetylenes  
Diaryl Acetylenes  
Pyridines  
Enynes

Supplement to the Gelest Catalog, "Silicon Compounds: Silanes and Silicones"  
which is available upon request

## SILICON-BASED CROSS-COUPLING REACTIONS

### Introduction

The advent of the cross-coupling reaction introduced a new and highly useful methodology for the formation of carbon-carbon bonds.<sup>1,2</sup> This general class of reactions involves two partners, with one typically being a suitable organometallic reagent - the nucleophile - and the other a suitable organic substrate, normally an unsaturated halide, tosylate or similar - the electrophile.

Numerous examples of the coupling of aryl and vinyl halides with olefins in the Heck reaction,<sup>1a</sup> with organotin reagents in the Stille reaction,<sup>3,4</sup> with boronic acids in the Suzuki-Miyaura coupling,<sup>5,6</sup> and the coupling of aryl and vinyl halides with acetylenes in the Sonogashira reaction<sup>7,8</sup> have been reviewed. The vinylation of aryl halides has been recently reviewed.<sup>9</sup> An excellent perspective on the development and mechanistic understanding of the silicon-based cross-coupling methods has appeared.<sup>10</sup> A review on the practical aspects of the silicon-based cross-coupling chemistry provides a useful view of the potential utility and advantages and disadvantages of the various protocols available.<sup>11</sup> A general review of alkyl, alkenyl, and alkynyl cross-coupling reactions compares those of silicon with other available methods.<sup>12</sup> A review emphasizing the mechanistic aspects of the activation of organosilanes in the silicon-based cross-coupling reactions has appeared.<sup>13</sup> In addition, the use of Pd-catalyzed cross-coupling reactions in total synthesis has been reviewed.<sup>14</sup> Hiyama and coworkers have reviewed the use of internal activation of the organosilane in silicon-based cross-coupling reactions.<sup>15</sup> All of these reactions have demonstrated the ability to generate biaryls, 1,3-dienes, and styrene derivatives in excellent yields principally from aryl or vinyl iodides and bromides, although the less expensive corresponding chlorides can also be used in certain circumstances. These reactions are in large part promoted by a palladium catalyst. Differences come in the choice of the palladium catalyst and, equally importantly, the choice of ligands to complex the palladium during the reaction.

The early work of Hiyama<sup>16-18</sup> showed that arylsilanes and vinylsilanes with fluorine ligands are capable of undergoing cross-coupling reactions with aryl and vinyl iodides in a manner similar to the reactions of the organostannanes and boronic acids. This work has been greatly expanded upon by others, most notably Denmark, with significant input by DeShong, Nájera, and Wolf, among others, in addition to the continuing excellent work of the Hiyama group. These authors have illustrated numerous methods of utilizing organosilanes in a variety of cross-coupling applications.

Table I summarizes a comparison of the various cross-coupling approaches.

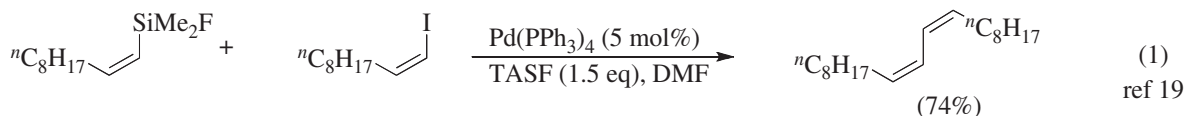
**Table 1. A Comparison of Cross-Coupling Methods**

Reaction	Metal	Catalyst	Advantages	Disadvantages
Stille	Tin	Palladium	good yields	tin toxicity Bu <sub>3</sub> Sn is large
Suzuki Miyaura	Boron	Palladium	good yields varied syntheses of boronic acids boronic acids commercially available	organoboranes air sensitive cost of boronic acids
Sonogashira		Palladium Copper Silicon	good yields acetylenes available	
Hiyama	Silicon	Palladium	good yields aqueous solvent possible silanes are air stable silanes easily handled silanes readily synthesized	can require 1-3 eq of fluoride few commercial sources of organsilanes
Negishi	Zinc	Copper Nickel Palladium Various transition metals	made from inexpensive zinc functional group tolerant strong for sp <sup>3</sup> cross-couplings excellent selectivity many commercially available	typically need organoiodides for both partners

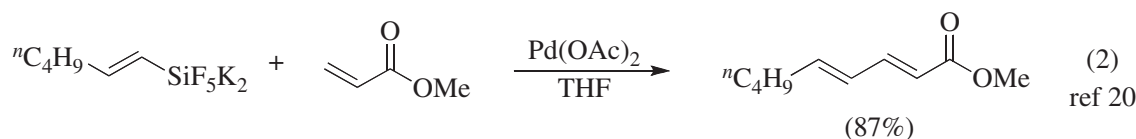
### Silicon-Based Cross-Coupling Reactions with fluorosilanes

The goal of the early work in the use of organosilanes as the organometallic component in the cross-coupling reactions was to take advantage of the polarizing and activating effect of fluorine ligands on the silicon atom. Thus, phenyltrifluorosilane couples with aryl bromides in modest to good yield.

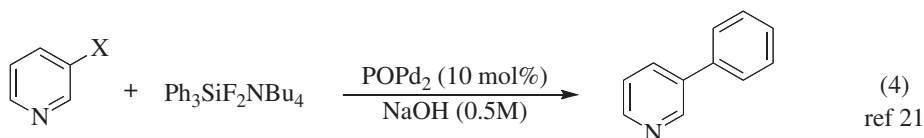
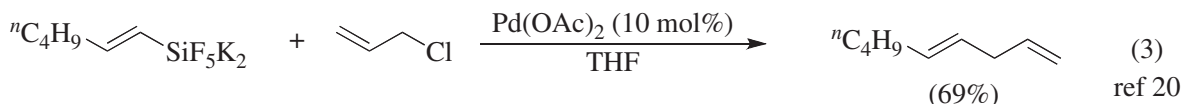
The presence of a fluorine ligand on silicon aids in the coupling of the silane in various cross-coupling applications. For instance, (Z)-1-(fluorodimethylsilyl)-1-decene is coupled with (Z)-1-iodo-1-decene in good yield to form the corresponding Z,Z-diene (Eq. 1).<sup>19</sup>



Vinylpentafluorosilicates undergo Heck coupling reactions (Eq. 2).<sup>20</sup> This system also couples well with allyl chloride (Eq. 3).<sup>20</sup> The tetrabutylammonium triphenyldifluorosilicate cross-coupling with aryl bromides or chlorides is also possible, with bromides being the more reactive electrophilic component (Eq. 4).<sup>21</sup>

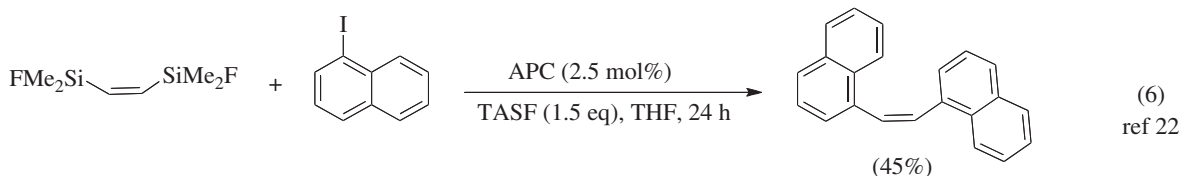
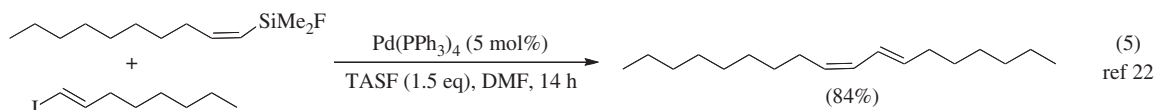


12 Related examples:  
(20 - 69%)

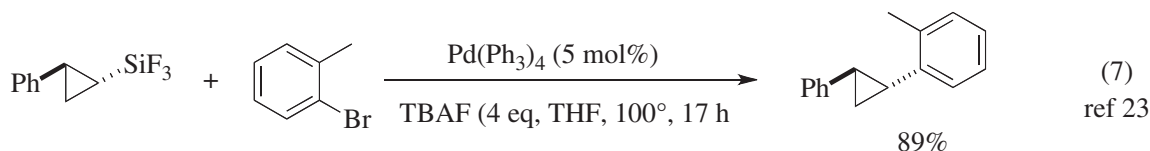


X = Br (92%); X = Cl (56%)

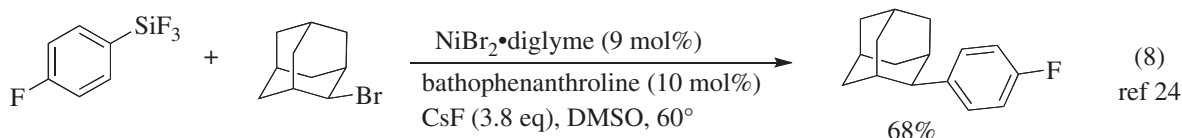
Alkenyldimethylfluorosilanes, readily prepared from the corresponding esters, cross-couple with vinyl and aryl iodides under the influence of fluoride ion promotion (Eqs. 5, 6).<sup>22</sup>



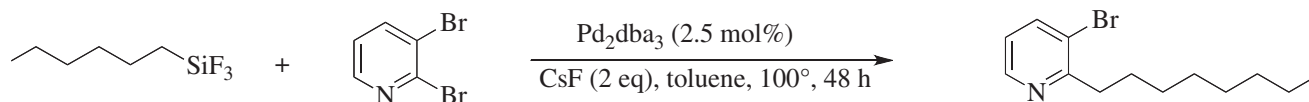
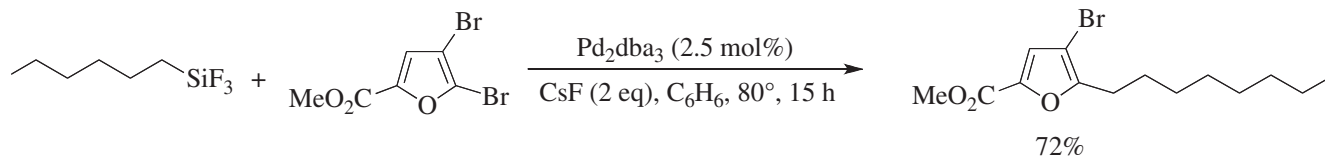
Cyclopropyltrifluorosilanes can be prepared by cyclopropanation of a vinyltrichlorosilane, in turn available via hydrosilylation of an acetylene. These cyclopropyltrifluorosilanes were shown to cross-couple with aryl bromides to give the arylcyclopropane in good yields (Eq. 7).<sup>23</sup> This is a good example of an  $sp^3$  organosilane cross-coupling.



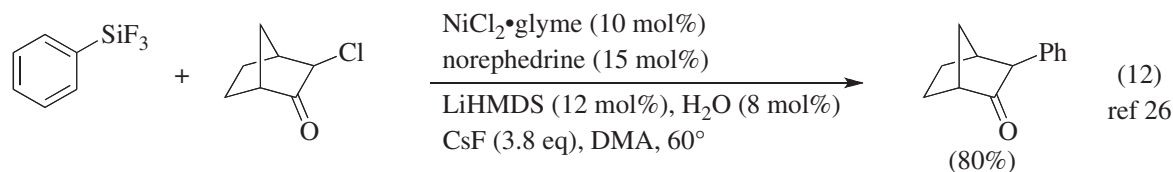
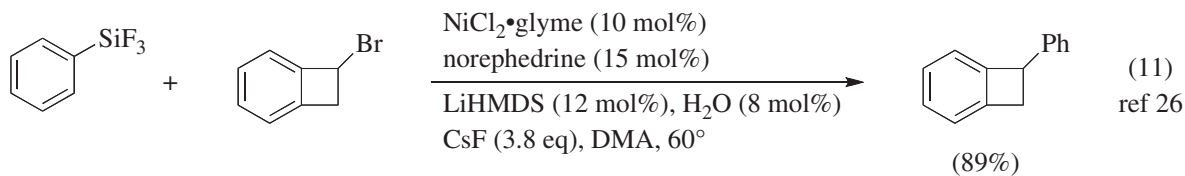
Cross-coupling of aryltrifluorosilanes with secondary alkyl bromides and iodides occurs in good yields (Eq. 8).<sup>24</sup>



The coupling of an alkyltrifluorosilane with aryl bromides gives good yields of the alkylated aromatic ring.<sup>25</sup> The reaction was shown to be regioselective with 2,3-dibromofurans and 2,3-dibromopyridine (Eqs. 9, 10).

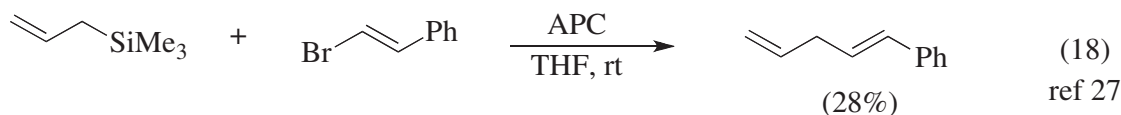
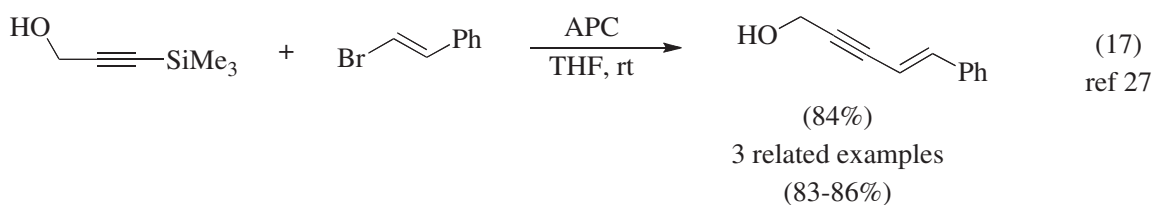
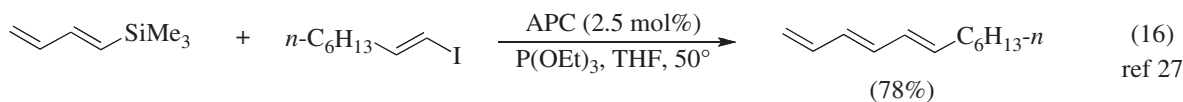
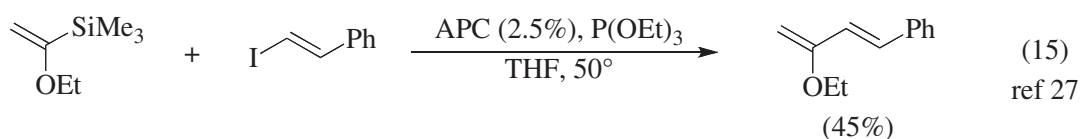
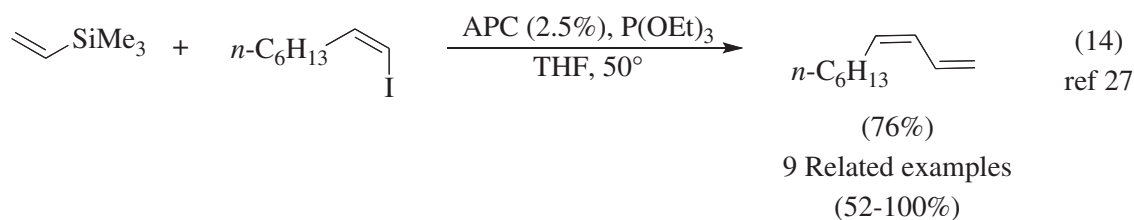
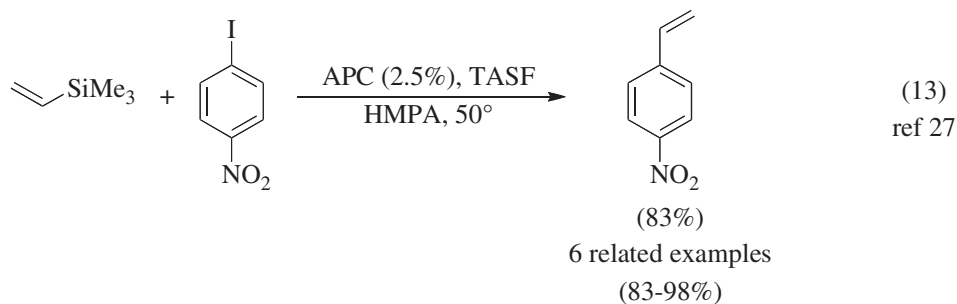


Nickel in combination with an amino alcohol ligand, for example norephedrine, was found to provide the most versatile and efficient catalyst for Hiyama cross-coupling reactions of alkyl electrophiles with aryltrifluorosilanes that has been described to date. Unprecedented Hiyama reactions of activated secondary alkyl bromides were achieved, as were the first Hiyama couplings of activated alkyl chlorides (Eqs. 11, 12).<sup>26</sup>

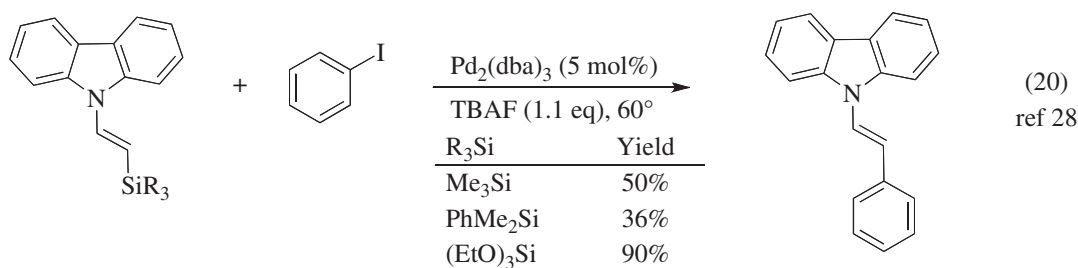


### Silicon-Based Cross-Coupling Reactions with Trialkylsilyl Groups

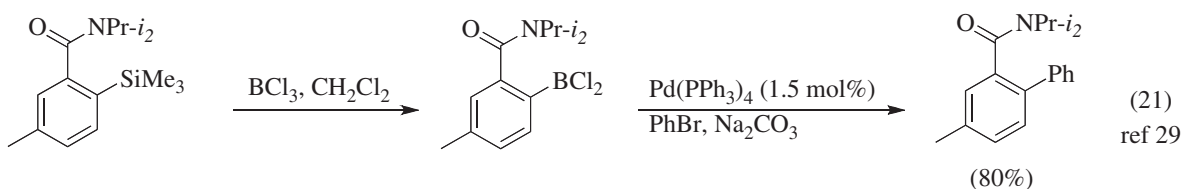
Trimethylvinylsilanes can be used to directly vinylate aryl and vinyl iodides in moderate to excellent yields as shown in Eqs. 13 to 16.<sup>27</sup> The allylpalladium chloride dimer, APC, is an excellent catalyst for these reactions. Ethynyltrimethylsilanes undergo Sonogashira-type cross-coupling reactions to form enynes (Eq. 17) and allyltrimethylsilane can lead to 1,4-dienes (Eq. 18) or 1,5-dienes (Eq. 19) when cross-coupled with vinyl halides or allyl halides, respectively.<sup>27</sup>



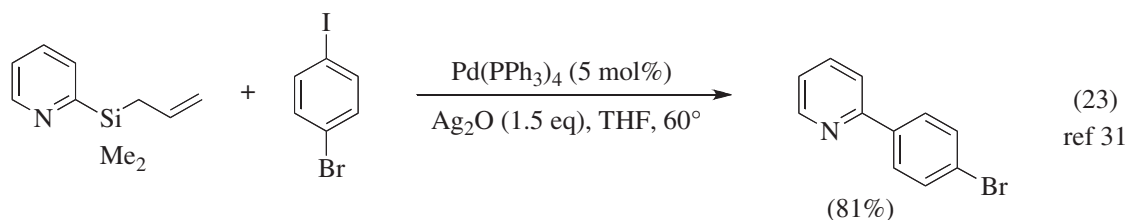
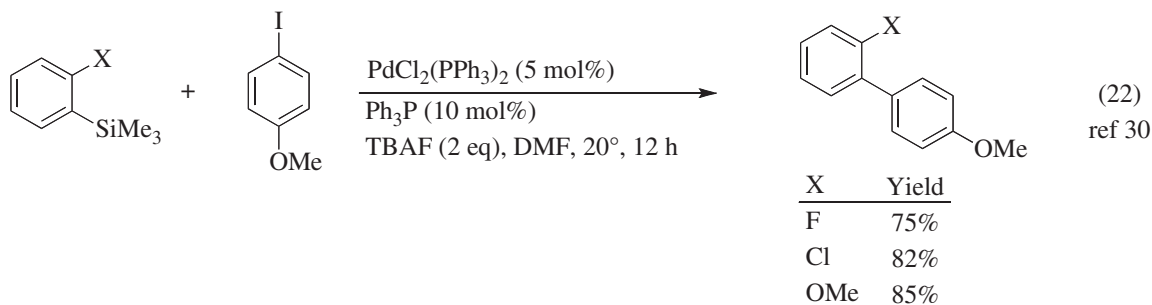
A study of the reactivities of  $\beta$ -silyl ethylcarbazole showed that the triethoxysilyl group is more effective in the cross-coupling with aryl iodobenzene than either the phenyldimethylsilyl or trimethylsilyl derivatives (Eq. 20).<sup>28</sup>



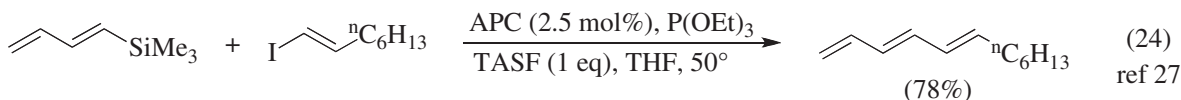
Aryltrimethylsilanes can be cross-coupled with aryl bromides after first being converted to the dichloroborane (Eq. 21).<sup>29</sup> This approach, which really uses the boronic acid Suzuki methodology, provides a clean, in-situ route to the arylboronic acid derivative.



*o*-Fluoro-, chloro- or methoxyphenyltrimethylsilanes undergo efficient cross-coupling reactions with aryl iodides transferring the *o*-aryl substituent (Eq. 22).<sup>30</sup> 2-Allyldimethylsilylpyridine cross-couples the 2-pyridyl group with aryl iodides (Eq. 23).<sup>31</sup> In this reaction the allyl group serves as a source of the silanol functionality, the reactive silyl intermediate in the cross-coupling step.

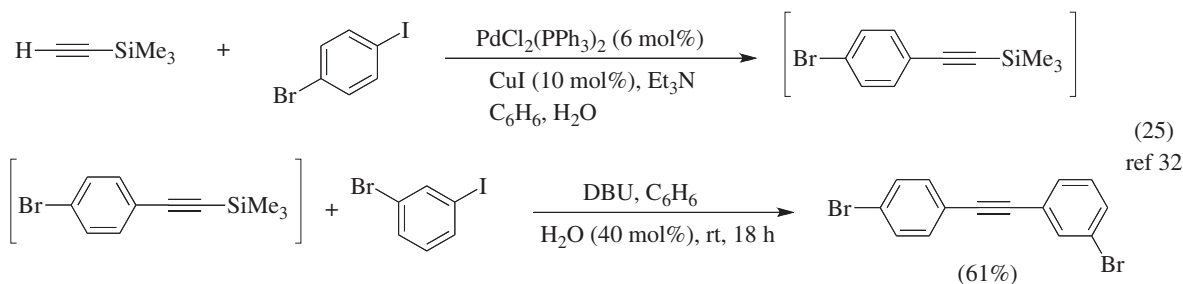


The cross-coupling of alkenyl-, alkynyl-, and allyltrimethylsilanes with vinyl and aryl iodides occur in good yields (Eq. 24).<sup>27</sup> The reactions require fluoride promotion for favorable results.

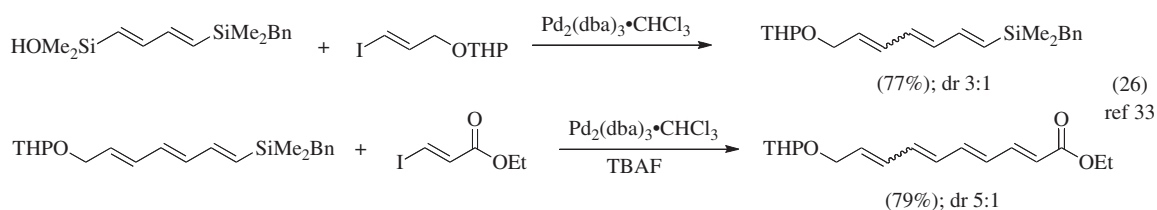




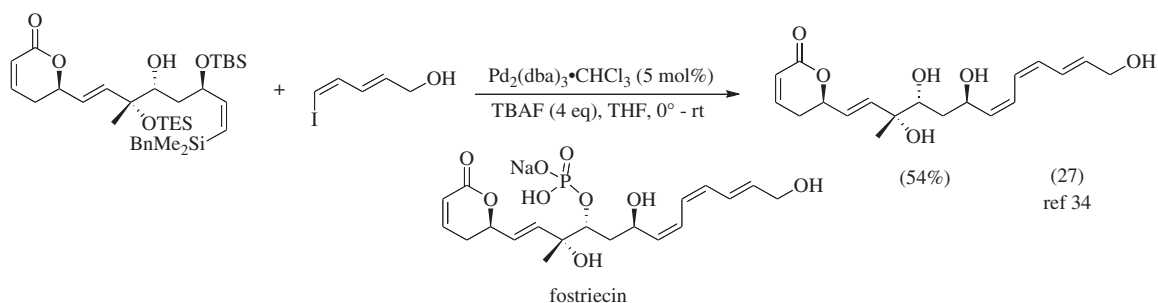
The significant difference in the reactivity of the C-H bond versus the C-Si bond in the cross-coupling reactions of ethynyltrimethylsilane allows for the facile stepwise preparation of unsymmetrical diarylacetylenes (Eq. 25).<sup>32</sup>



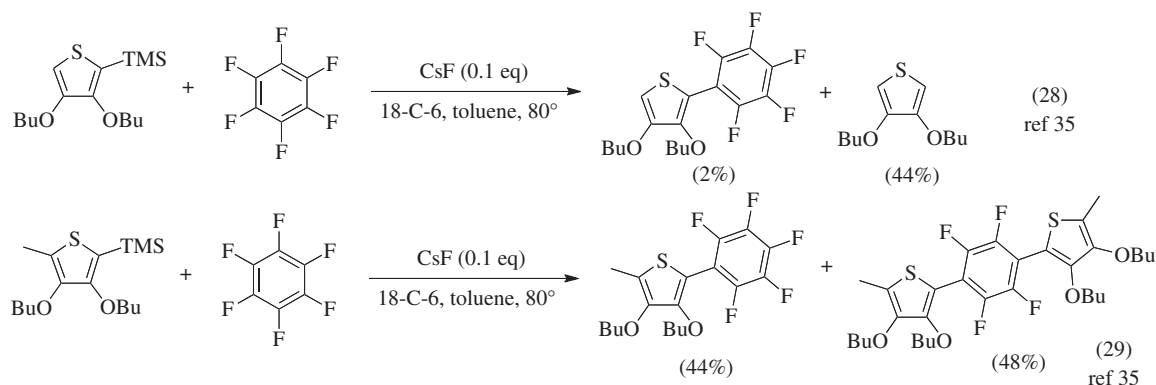
The synthesis of a key intermediate conjugated tetraene in the total synthesis of RK-397, a polyene macrocycle, was accomplished taking advantage of the sequential, selective silicon-based cross-coupling steps to prepare a key difunctional conjugated tetraene. Thus, the dimethylsilanol moiety cross-couples in the absence of fluoride promotion whereas the benzyldimethylsilyl unit requires fluoride activation (Eq. 26).<sup>33</sup>



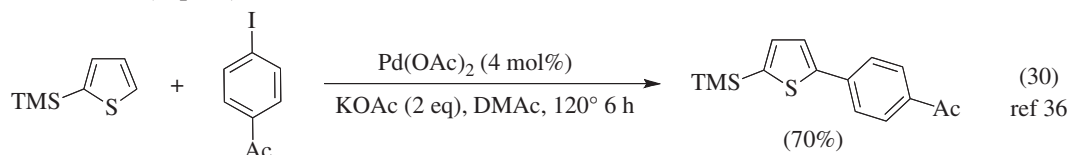
Advantage was taken of the excellent stability of the benzyldimethylsilyl group in a cross-coupling step in the synthesis of fostriecin, a cytotoxic phosphate ester (Eq. 27).<sup>34</sup> The reaction conditions required demonstrate the potential drawback of the protocols that require fluoride promotion in that the silyl protecting groups are removed under the reaction conditions.



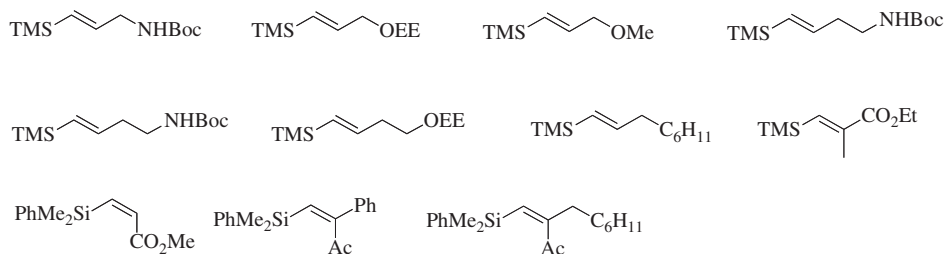
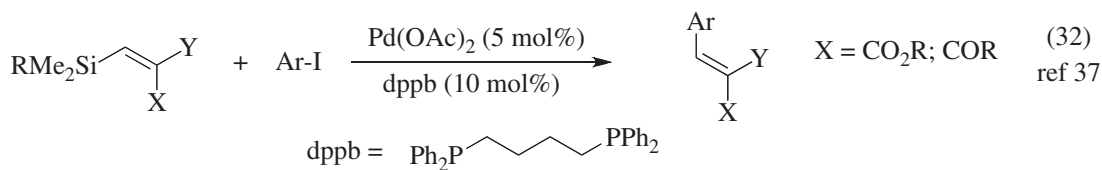
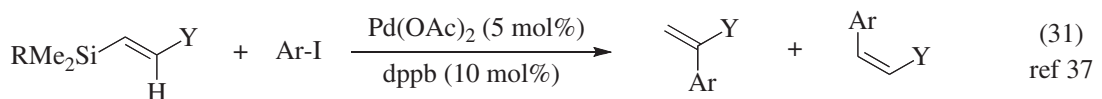
The cesium fluoride-catalyzed direct pentafluorophenylation of a 2-trimethylsilylthiophene proved possible (Eqs. 28, 29).<sup>35</sup> It is advantageous to block the 5-position of the thiophene to avoid a side reduction reaction.



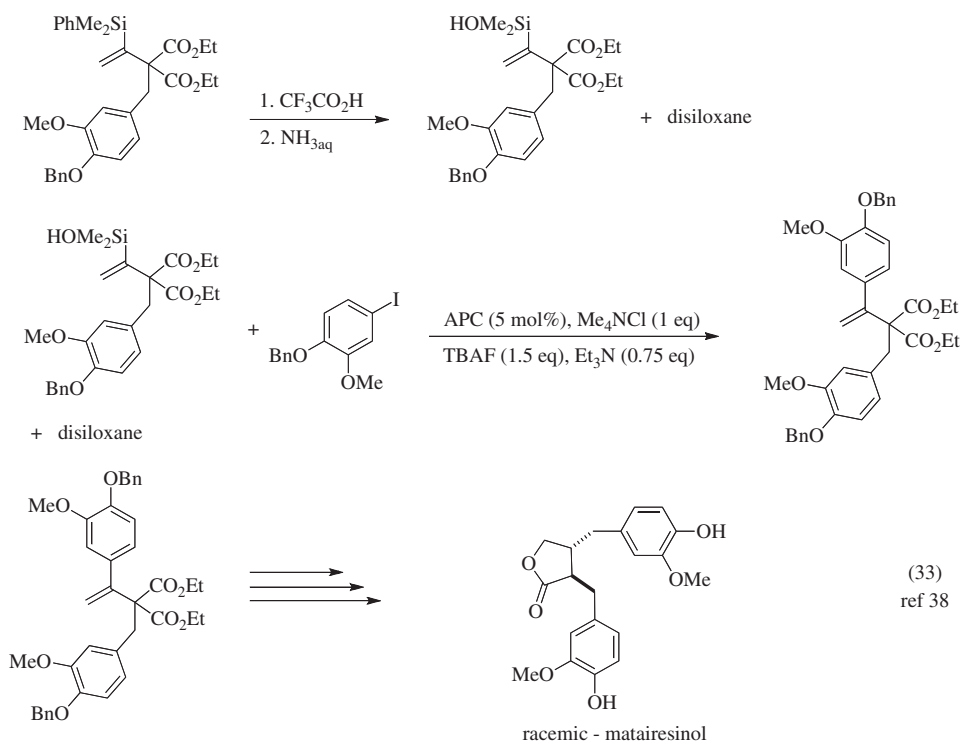
Various trimethylsilylated thiophenes cross-couple at the 5-C-H site rather than the C-Si site under conditions in which fluoride ion is not involved (Eq. 30).<sup>36</sup>



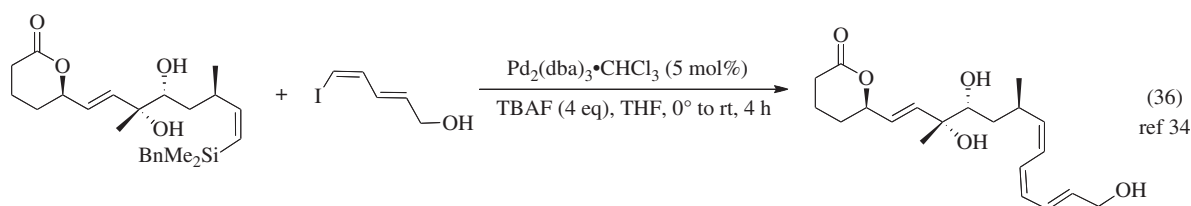
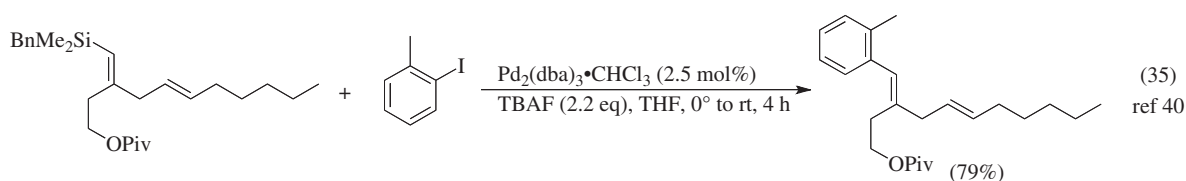
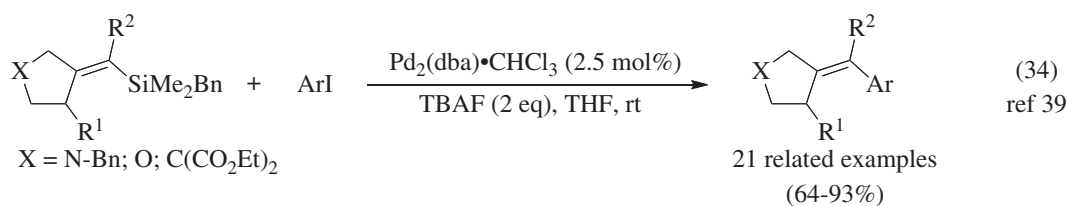
Esters, ketones, mono-protected primary amines, and ethers are tolerated in the cross-coupling of alkenylsilanes with aryl iodides (Eqs. 31, 32).<sup>37</sup> Several of the vinylsilane systems employed in the study are shown below. The nature of the functional group influences the regiochemistry of the coupling step.



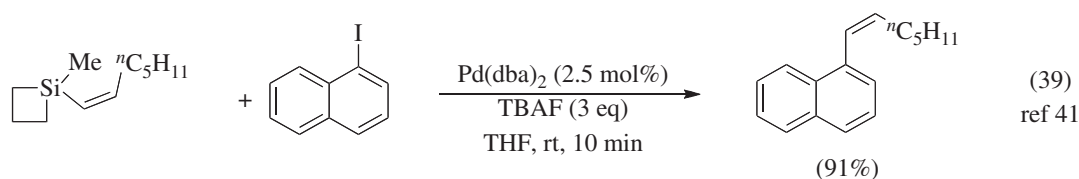
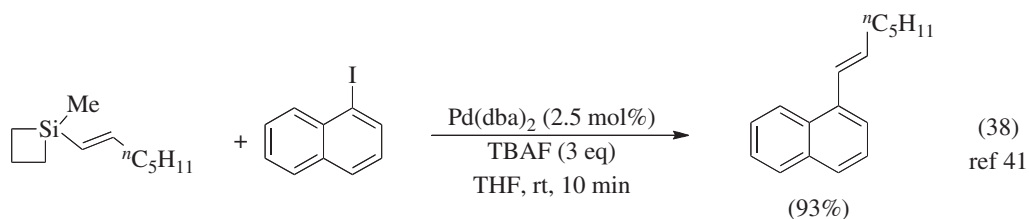
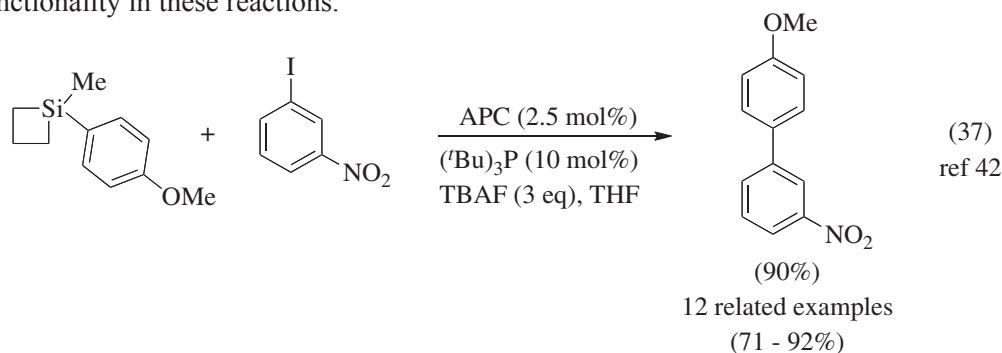
The phenyldimethylsilyl group can be utilized in cross-coupling reactions, but first the phenyl group must be converted to a silanol derivative, which then undergoes the cross-coupling reaction (Eq. 33).<sup>38</sup> The reaction sequence was applied to the synthesis of matairesinol.



Advantage can be taken of the facile fluorodebenzylation of benzylsilanes to use benzyldimethylsilyl groups in cross-coupling reactions utilizing organosilanes.<sup>39-40</sup> Examples of this approach are shown in Eqs. 34, 35, 36. In these reactions the active silane species is the fluorosilane.

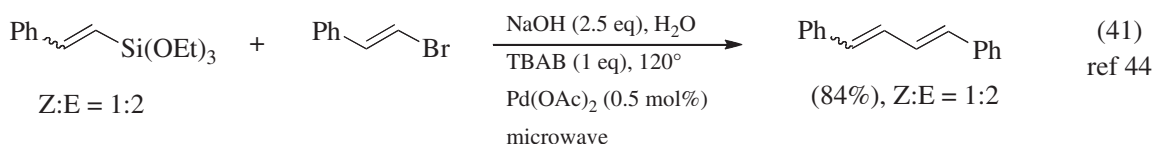
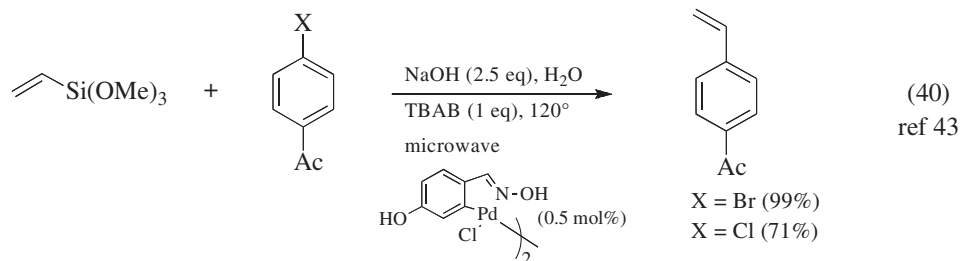


In a similar manner the aryl or vinyl silacyclobutanes under the influence of fluoride ion cross-couple well with aryl iodides (Eqs. 37, 38, 39).<sup>42,43</sup> It has been shown that due to the ring strain the silacyclobutane unit is a precursor to the reactive silanol functionality in these reactions.

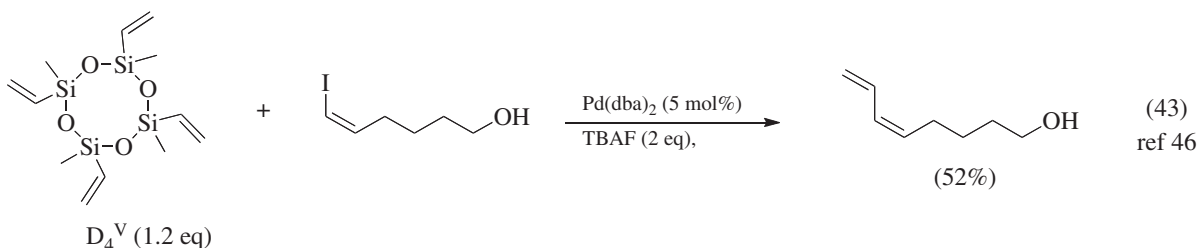
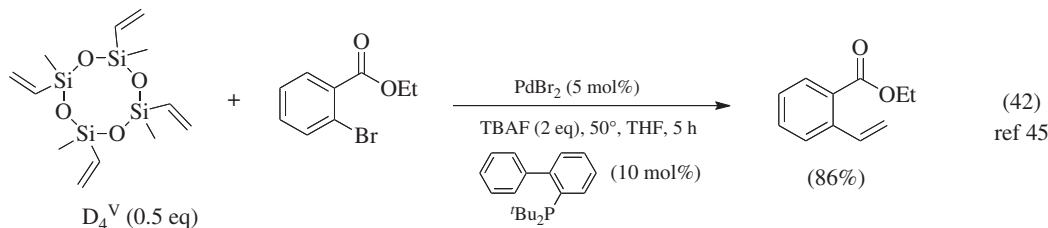


### Silicon-Based Vinylation of Aryl and Vinyl Halides

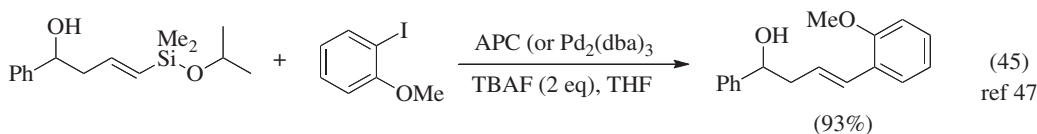
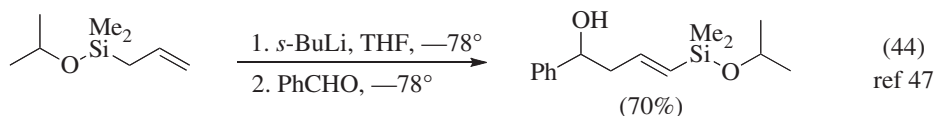
The direct vinylation of aryl halides leading to styrene derivatives and of vinyl halides leading to conjugated dienes represent important transformations in organic synthesis. The cross-coupling of the commercially available vinyltrimethoxysilane or vinyltriethoxysilane with aryl bromides and chlorides brings about the vinylation leading to the corresponding styrene in good yields. Best results are obtained when microwave stimulation is applied (Eq. 40).<sup>43,44</sup> The reaction also works well with vinyl bromides. (Eq. 41).



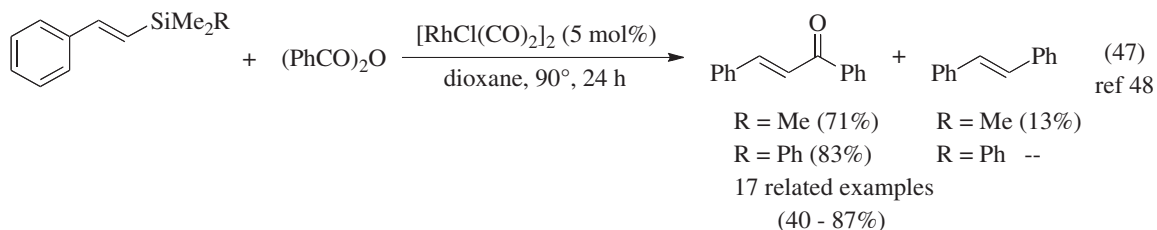
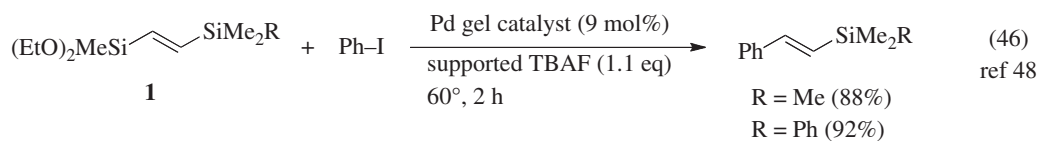
The readily available vinylsilane, tetravinyltetramethylcyclotetrasiloxane, ( $D_4^V$ ) can be used to vinylate aryl and vinyl iodides and bromides in good yields (Eqs. 42 and 43).<sup>46,47</sup>



4-Silyl homoallylic alcohols, prepared by lithiation of allyldimethyl(isopropoxy)silane and reaction of the resulting lithium reagent with aldehydes can then be cross-coupled with aryl or vinyl iodides (Eqs. 44, 45).<sup>48</sup>

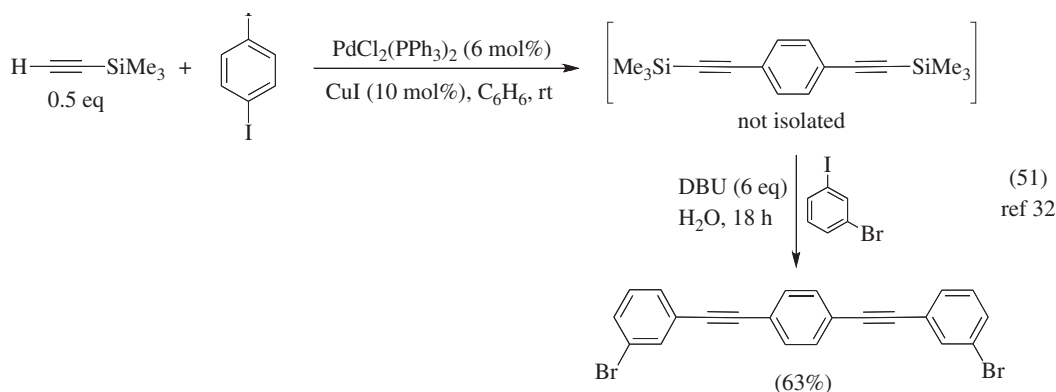
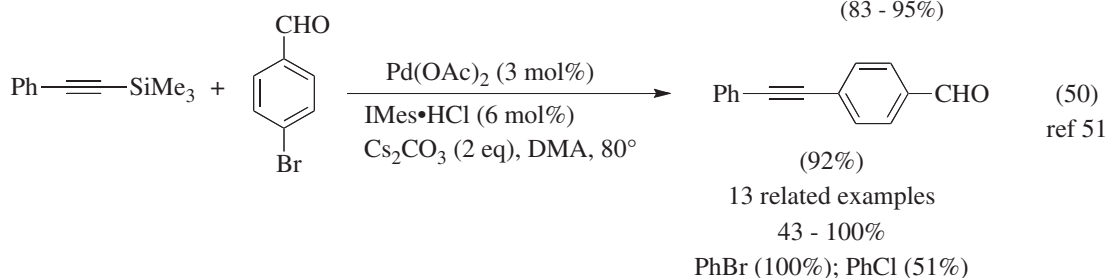
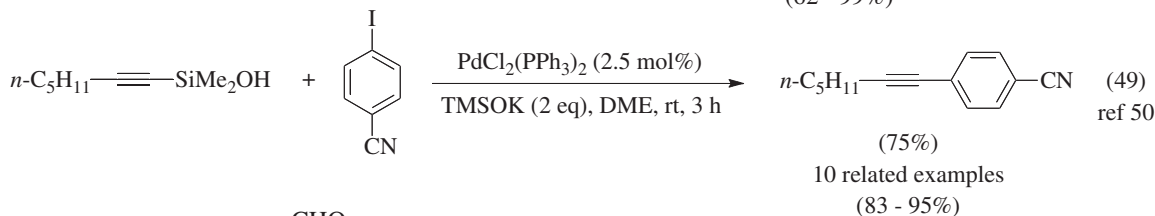
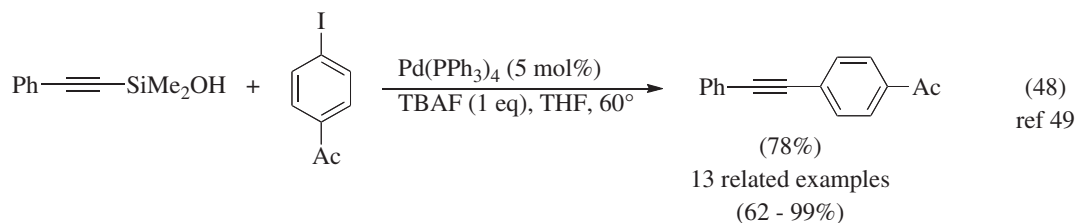


The bis(silyl)ethylene, **1**, was employed for the stereoselective introduction of an aryl group via the more reactive diethoxymethylsilyl moiety followed by electrophilic desilylation of the phenyldimethylsilyl or trimethylsilyl group (Eq. 46). This leads to  $\alpha,\beta$ -unsaturated ketones (Eq. 47).<sup>48</sup>



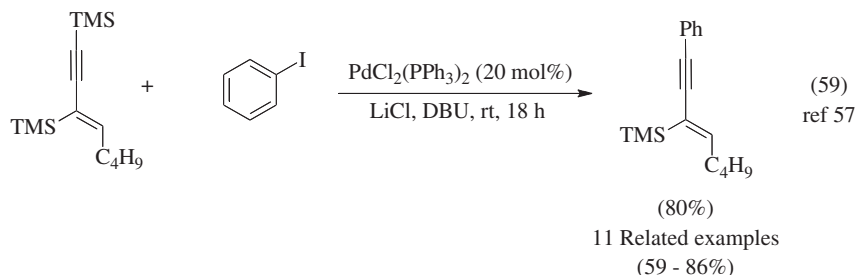
### Silicon-Based Alkynyl Cross-Couplings

Alkynyldimethylsilanols react with aryl iodides to give arylacetylenes in good yields (Eqs. 48, 49).<sup>49,50</sup> Aryl bromides work as well, but aryl chlorides are poorer substrates under these conditions. (Eq. 50).<sup>51</sup> The difference in the reactivity between the  $sp$ -carbon and a hydrogen and the  $sp$ -carbon and a trimethylsilyl group was shown in the synthesis of 1,4-bis(3-bromophenylethynyl)benzene (Eq. 51).<sup>32</sup>

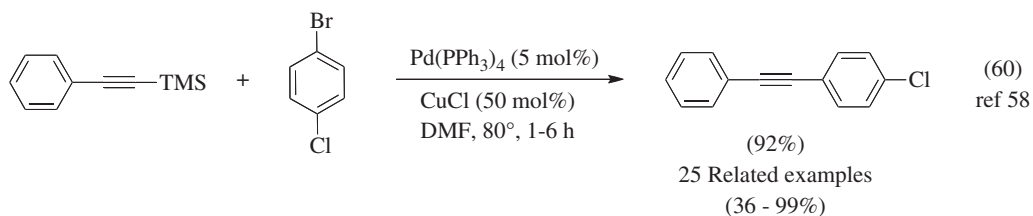




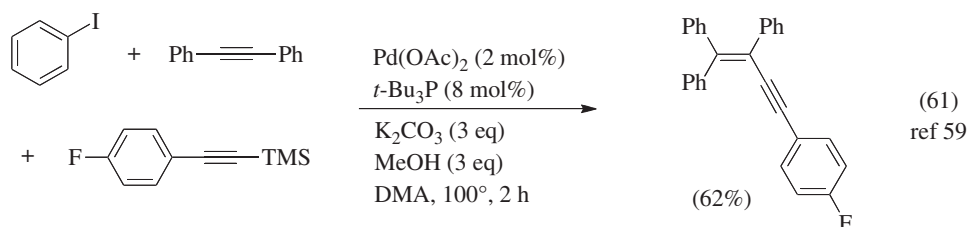
The silicon-Sonogashira cross-coupling occurs over that of the silicon-based vinylation reaction as shown in Eq. 59.<sup>57</sup>



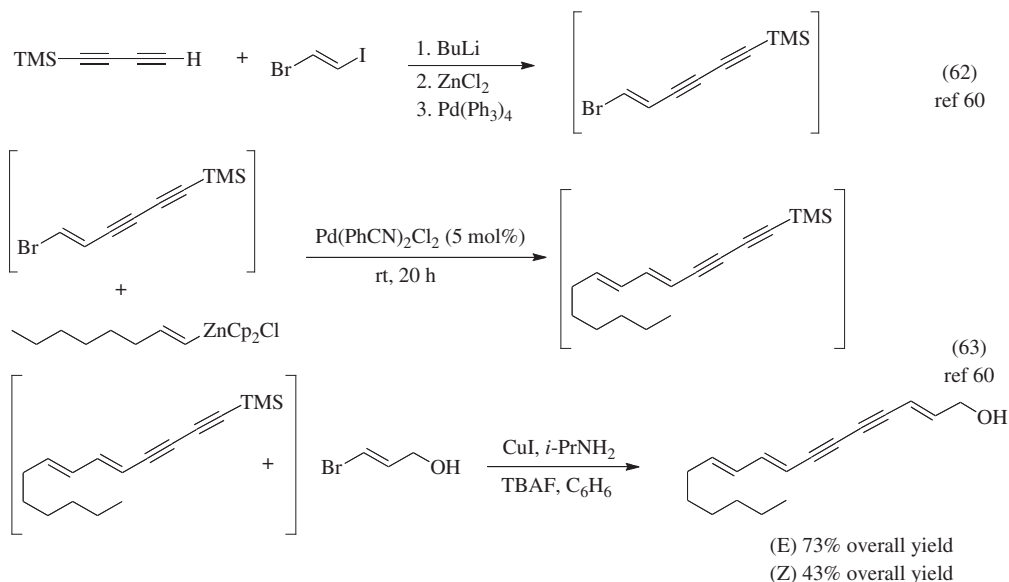
Non-basic, Cu(I)-catalyzed cross-coupling of alkynylsilanes with aryl iodides have been reported and provides a route to unsymmetrical diaryl acetylenes in good to excellent yields (Eq. 60).<sup>58</sup> A typical problem with these is the homo-coupling to 1,3-dialkynes (Glaser-type product). The use of bis(trimethylsilyl)acetylene allows the generation of unsymmetrical diaryl acetylenes in a one-pot procedure.



The use of a 1-trimethylsilylalkyne rather than the terminal acetylene permits the three-component coupling of an internal acetylene, an aryl iodide and the alkynyltrimethylsilane (Eq. 61).<sup>60</sup> Use of the terminal acetylene gives a high yield of the direct Sonogashira coupling product without incorporation of the internal acetylene.

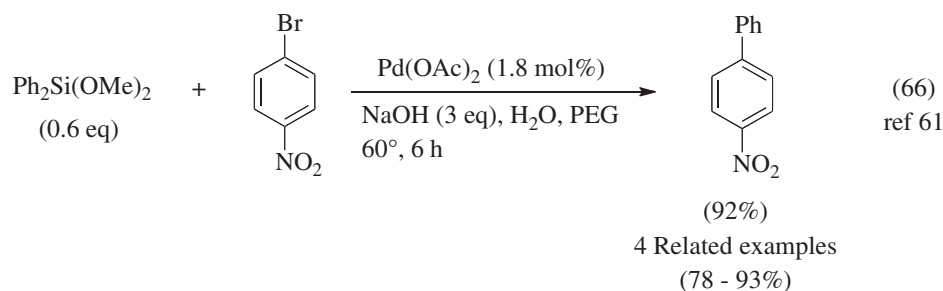
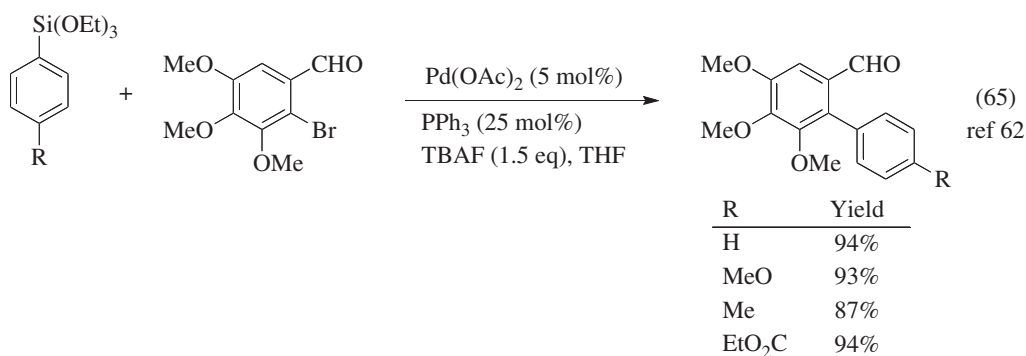
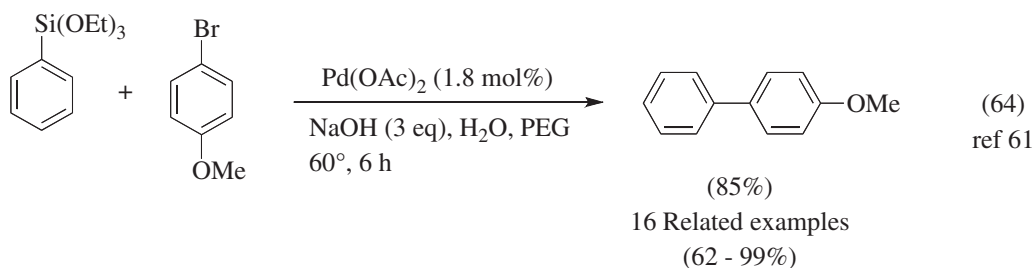


Trimethylsilylbutadiyne was subjected to a zinc-mediated cross-coupling with 2-bromoiodoethylene and the product of this similarly cross-coupled with a 1-octenylzinc reagent to form a conjugated diyne-diene. This was in turn used in a trimethylsilylethynyl cross-coupling with (E)-1-bromopropargyl alcohol (eqns 62 and 63).<sup>60</sup>

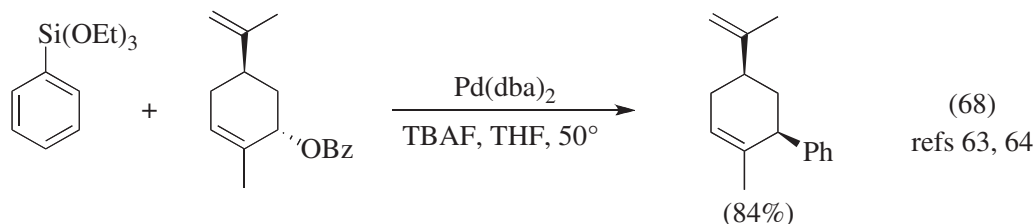
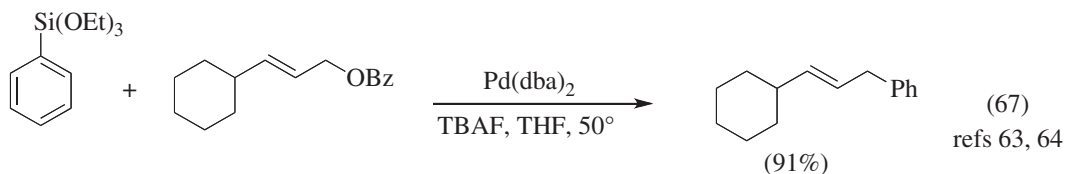


### Silicon-Based Cross-Coupling Reactions with Organosilyl Esters

The study of various aryltrialkoxysilanes, principally trimethoxy and triethoxy derivatives, in cross-coupling applications indicates the wide potential for such systems in the synthesis of biaryls and styrene derivatives. A large number of examples are known a few of which are shown herein. Thus, the commercially available phenyltriethoxysilane can be coupled with aryl bromides to give the corresponding biaryl in good to excellent yields (Eq. 62).<sup>61</sup> Sterically hindered aryl bromides couple well with the aryltriethoxysilanes (Eq. 63).<sup>62</sup> Diphenyldimethoxysilane provides the phenyl group in the cross-coupling with aryl bromides (Eq. 64).<sup>61</sup> Both phenyl groups can be incorporated.

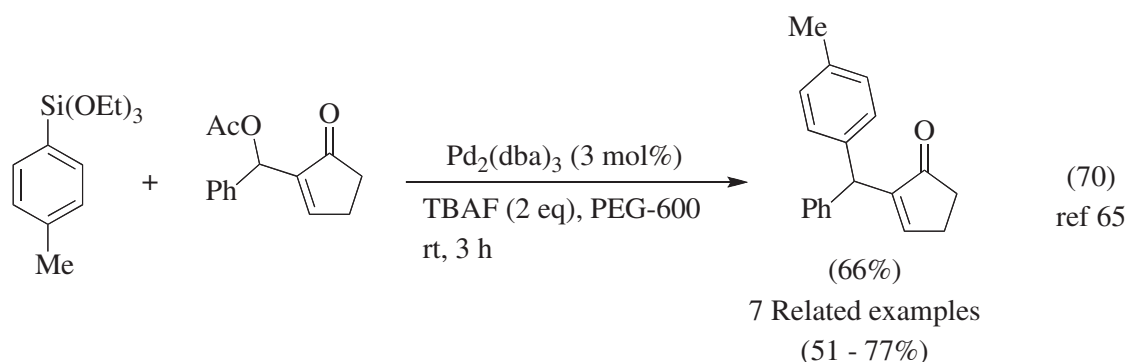
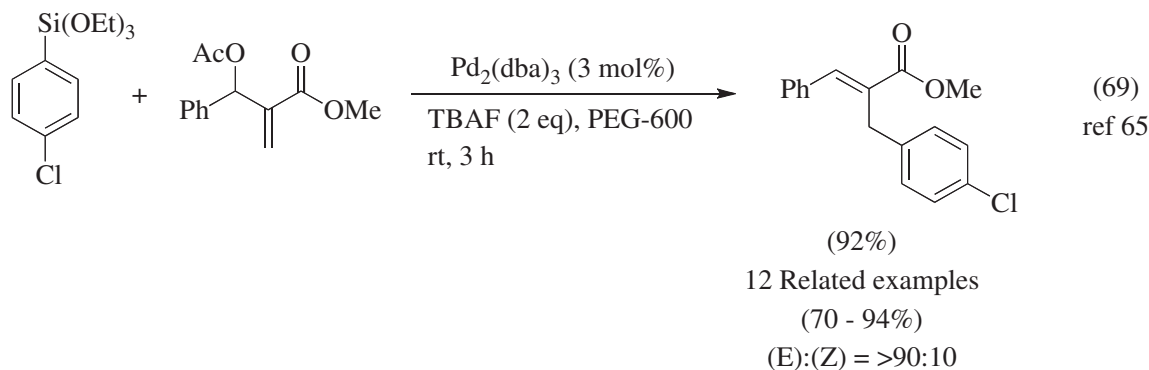


Allyl benzoates react with aryl triethoxysilanes under cross-coupling conditions providing the allylbenzene derivative (Eqs. 67, 68).<sup>63,64</sup>

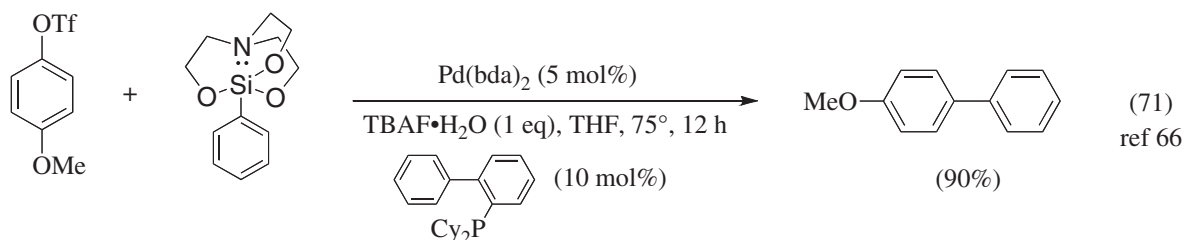




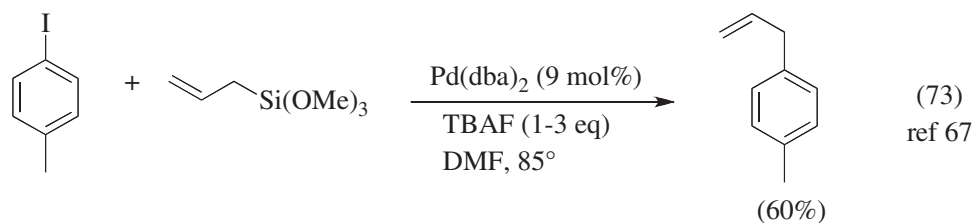
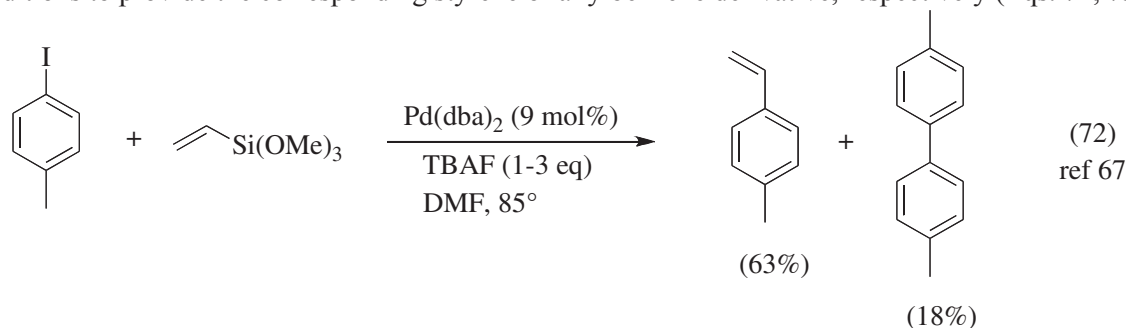
A similar reaction is possible with the Bayless-Hillman allyl acetates to form  $\alpha$ -benzylated  $\alpha,\beta$ -unsaturated esters. (Eqs. 69, 70).<sup>65</sup>



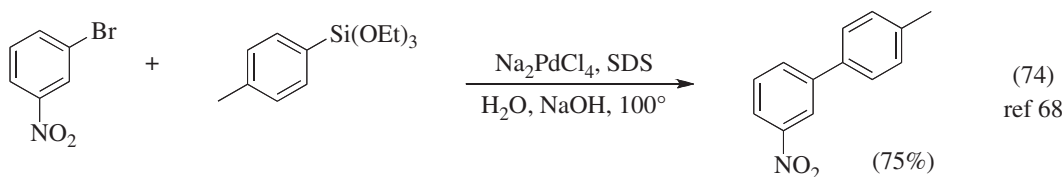
In addition to the standard trimethoxysilyl or triethoxysilyl reagents, the silatranes are also viable reagents for cross-coupling reactions (Eq. 71).<sup>66</sup> It should be noted that some silatranes show high levels of toxicity.



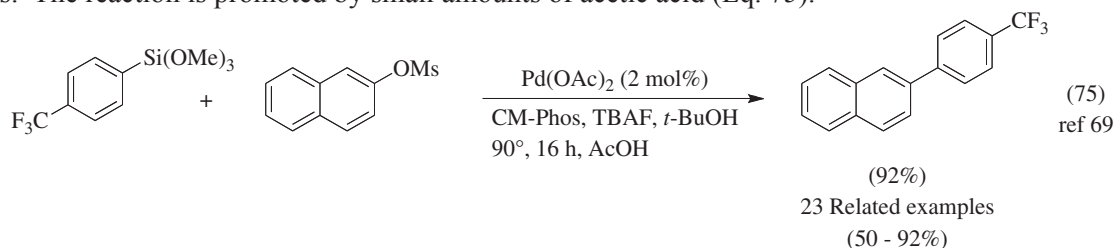
Vinyltrimethoxysilane and allyltrimethoxysilane, both commercially available, will react with aryl iodides under cross-coupling conditions to provide the corresponding styrene or allylbenzene derivative, respectively (Eqs. 72, 73).<sup>67</sup>



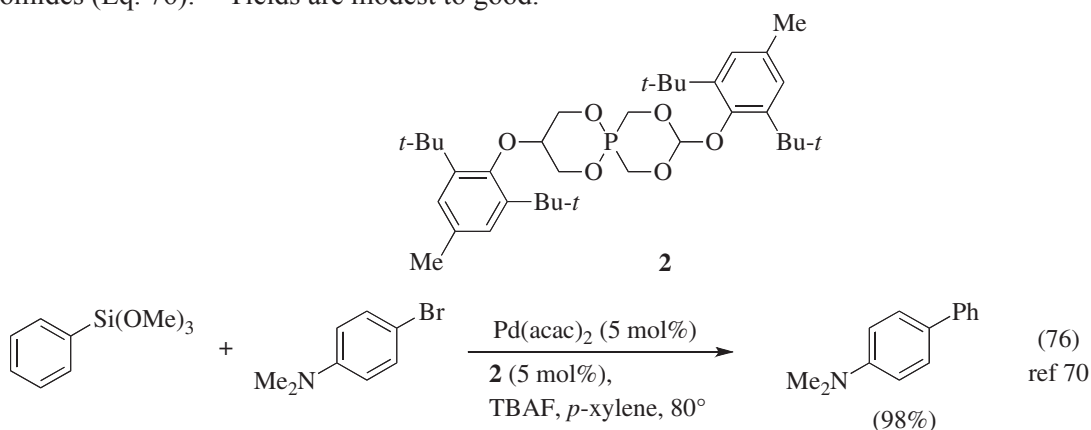
A fluoride-free, aqueous-based cross-coupling of aryl bromides and iodides with arylsilyl esters using an inexpensive Pd catalyst and a surfactant, SDS, provides a practical approach to silicon-based cross-couplings (Eq. 74).<sup>68</sup> This very fast reaction is proposed to go through 'in-situ'-generated palladium particles. Moreover, the reaction can be performed in air.



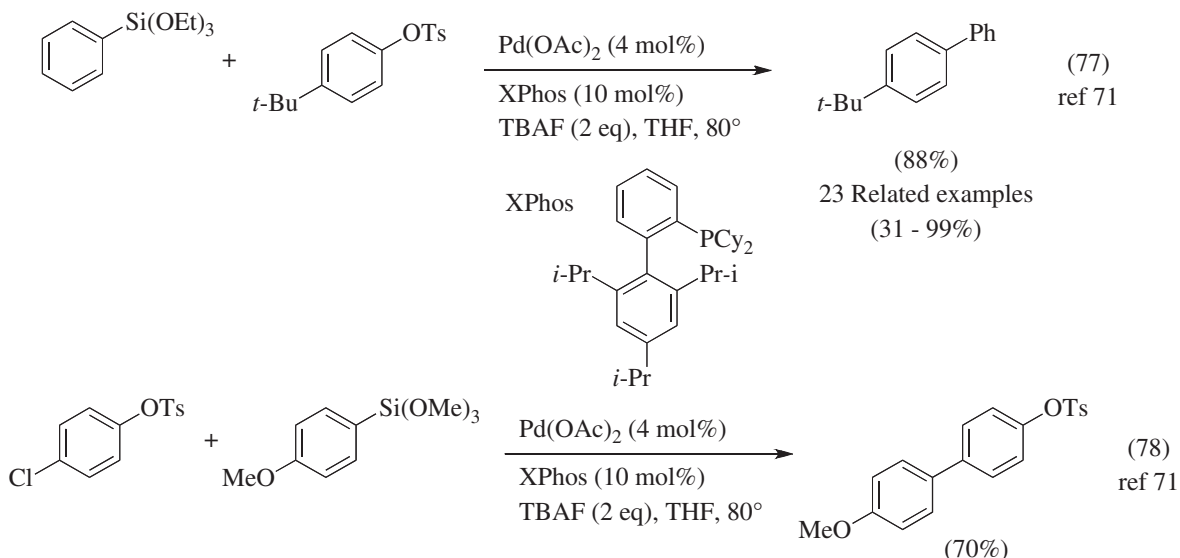
A 2-(2-dicyclohexylphosphino)phenylindol ligand (CM-Phos) and Pd(OAc)<sub>2</sub> allows the coupling of arylsilyl esters with aryl mesylates. The reaction is promoted by small amounts of acetic acid (Eq. 75).<sup>69</sup>



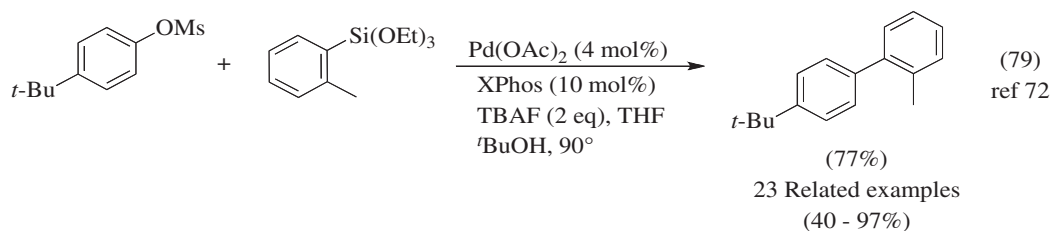
The spiroarylphosphite, **2**, with Pd(acac)<sub>2</sub> and TBAF bring about the cross-coupling of phenyltrimethoxysilane with various aryl bromides (Eq. 76).<sup>70</sup> Yields are modest to good.



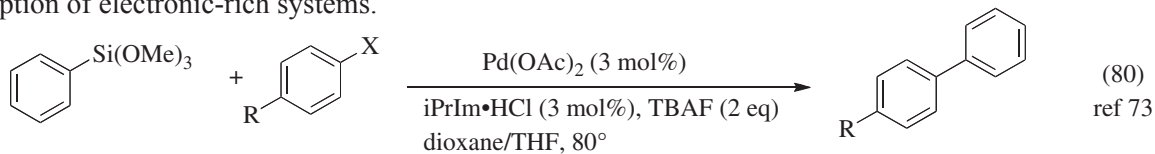
The cross-coupling of arylsilyl esters with aromatic tosylates and related esters has been reported (Eq. 77).<sup>71</sup> The XPhos ligand proved to provide the best yields. An aryl chloride reacts better than the corresponding tosylate (Eq. 78).



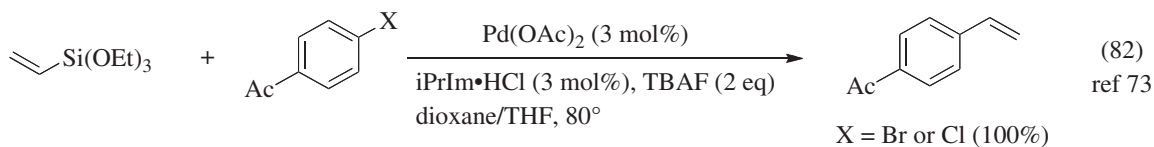
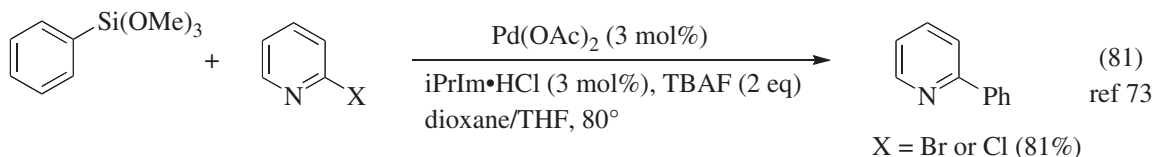
The cross-coupling of arylsilyl esters with aryl mesylates is carried out with TBAF and Pd(OAc)<sub>2</sub> in excellent yields (Eq. 79).<sup>72</sup> The ligand XPhos provides the better yields.



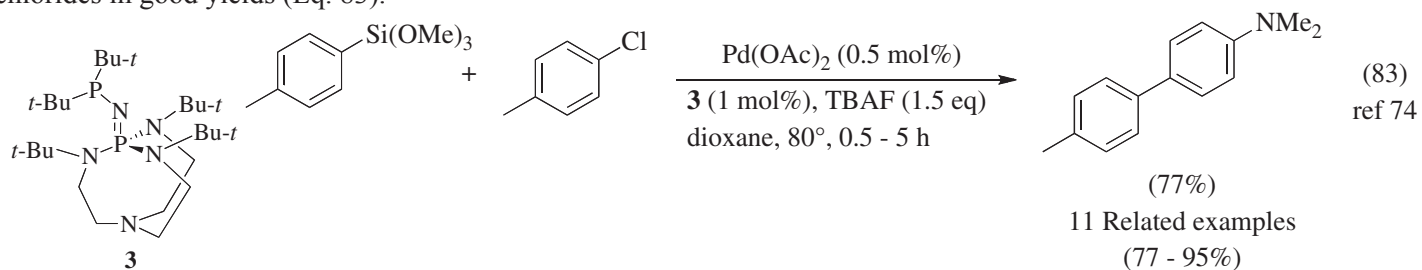
The combination of an imidazolium salt with palladium acetate cross-couples vinyl- and aryltrialkoxysilanes with aryl bromides and chlorides (Eqs. 80, 81, 82).<sup>73</sup> Although the chlorides react more slowly they give comparable yields with the exception of electronic-rich systems.



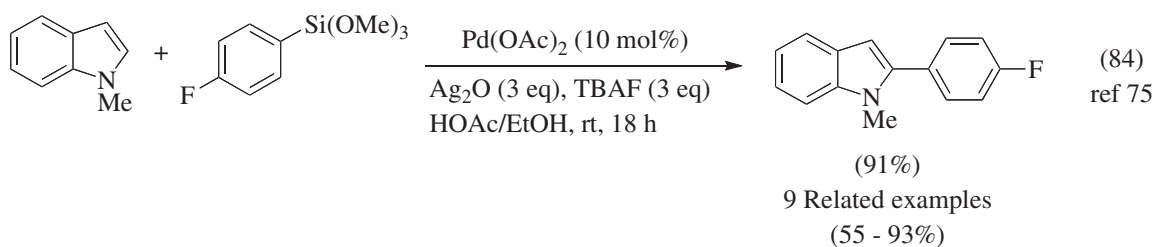
X	R	Yield
Br	H	100%
Br	Me	93%
Br	Ac	100%
Cl	OMe	19%
Cl	Me	29%
Cl	Ac	100%
Cl	CN	100%



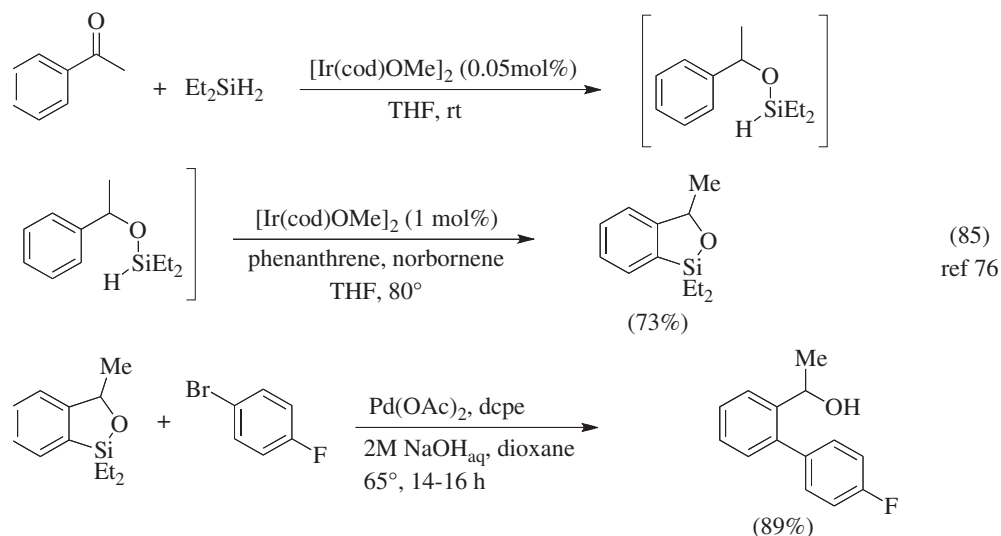
The ligand **3**, was found to bring about the palladium-catalyzed cross-coupling of aryltrimethoxysilanes with aryl chlorides in good yields (Eq. 83).<sup>74</sup>



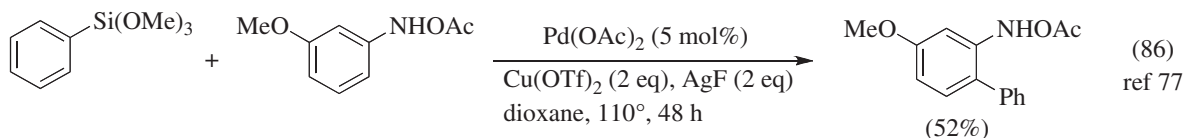
The direct cross-coupling of an arylsilyl ester with indoles provides a convenient route to 1-aryl indoles (Eq. 84).<sup>75</sup>



In an interesting approach to ortho-functional biaryl systems the silylation of acetophenone derivatives or the corresponding benzyl alcohol was used to prepare oxasiloles. The synthetic utility of the oxasiloles was demonstrated by a Tamao oxidation to the *o*-substituted phenols, and in the Hiyama cross-coupling for the formation of the *o*-functional biphenyl (Eq. 85).<sup>76</sup>

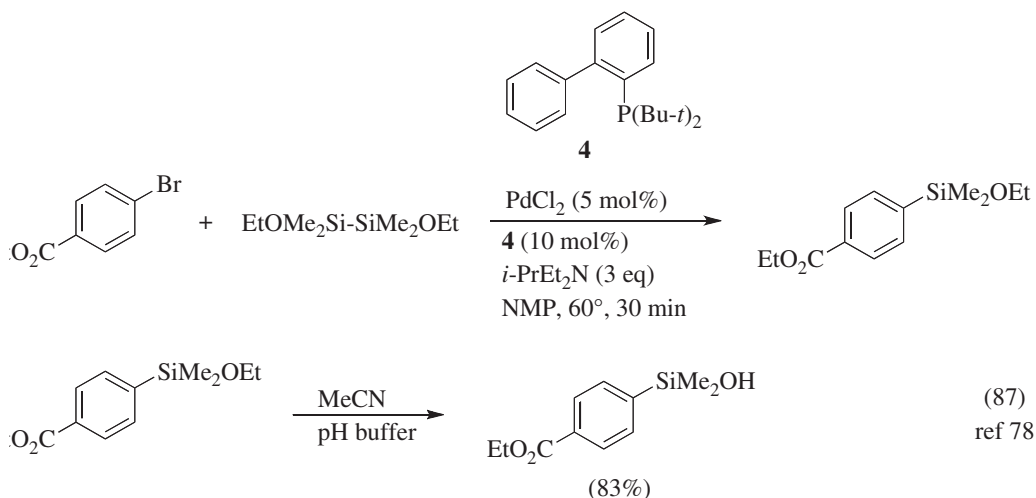


The direct ortho-arylation of acetanilides is possible with a variety of aryltriethoxysilanes. In the case of a 3-substituted acetanilide the arylation occurs at the least hindered 6-position (Eq. 86).<sup>77</sup>

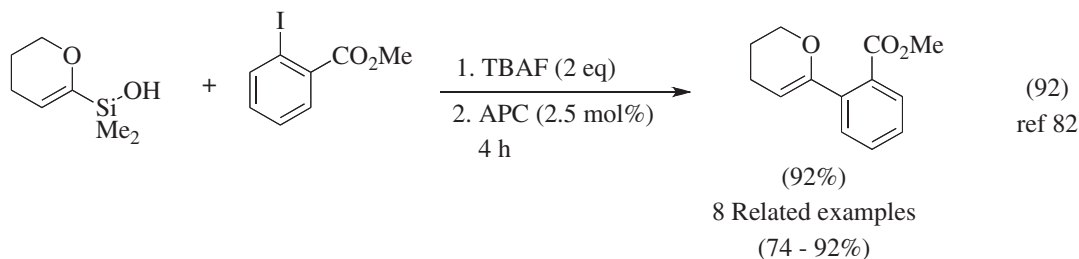
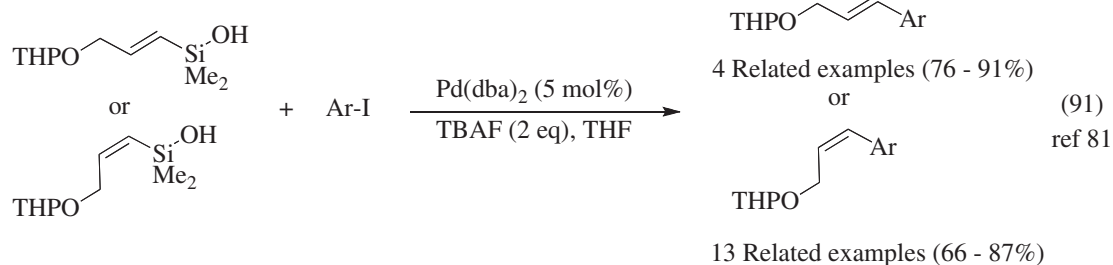
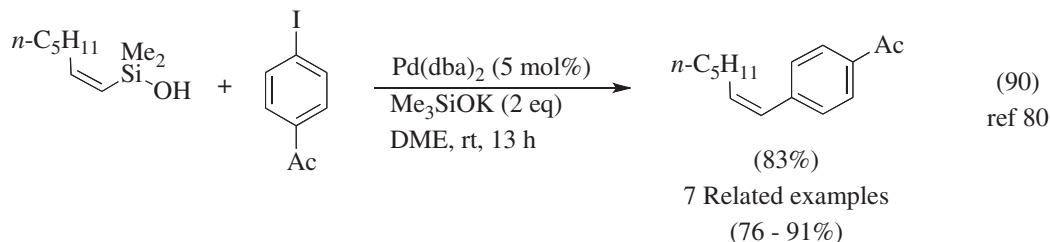
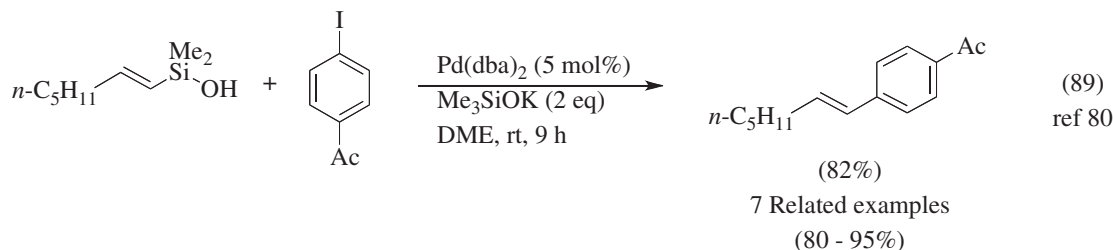
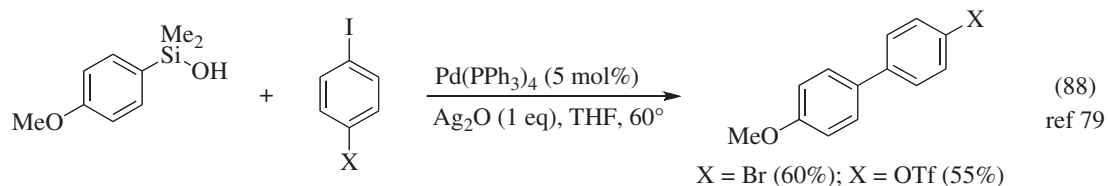


### Silicon-Based Cross-Coupling Reactions with Silanols

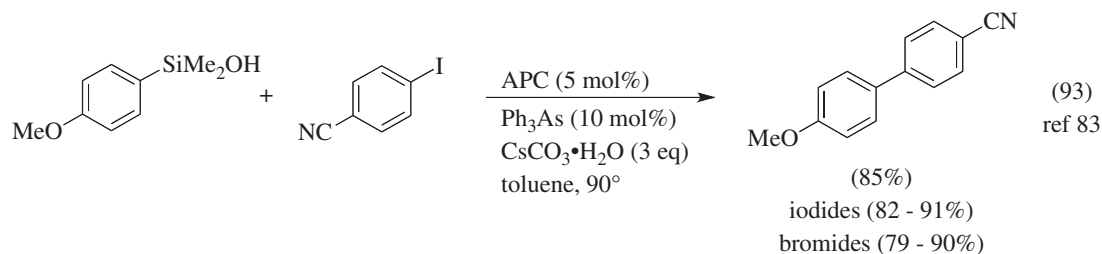
Silanols can be prepared in a number of ways; most commonly by way of careful hydrolysis of chloro-, amino- or alkoxy silanes. The requisite aryl- or vinylsilane is oftentimes prepared by the reaction of a Grignard or organolithium reagent on the chloro- or alkoxy silane. The insertion of an ethoxydimethylsilyl group into an aryl iodide or bromide followed by hydrolysis of the ethoxy group to the silanol provides a direct route to aryl dimethylsilanols without the need for and drawbacks of, a Grignard or organolithium reaction to prepare the aryl silane (Eq. 87).<sup>78</sup>



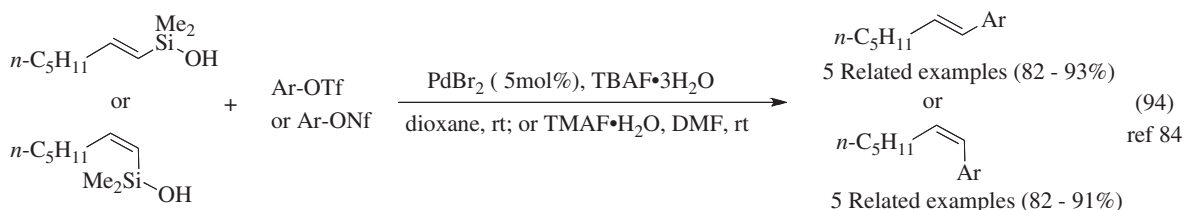
In a fashion similar to the cross-coupling of boronic acids with aryl and vinyl halides, aryl<sup>79</sup> and vinylsilanols<sup>80</sup> are useful in cross-coupling approaches to styrenes (Eqs. 88, 89) and conjugated dienes. These reactions are typically carried out in the presence of a base and are, in fact, reactions of the in-situ-generated silanolate. In the case of vinylsilanes the reactions are stereospecific with respect to the geometry of the starting alkenylsilane (Eqs. 90, 91).<sup>79,81</sup> The  $\alpha$ -dimethylsilanol of an enol ether can be employed as well (Eq. 92).<sup>82</sup>



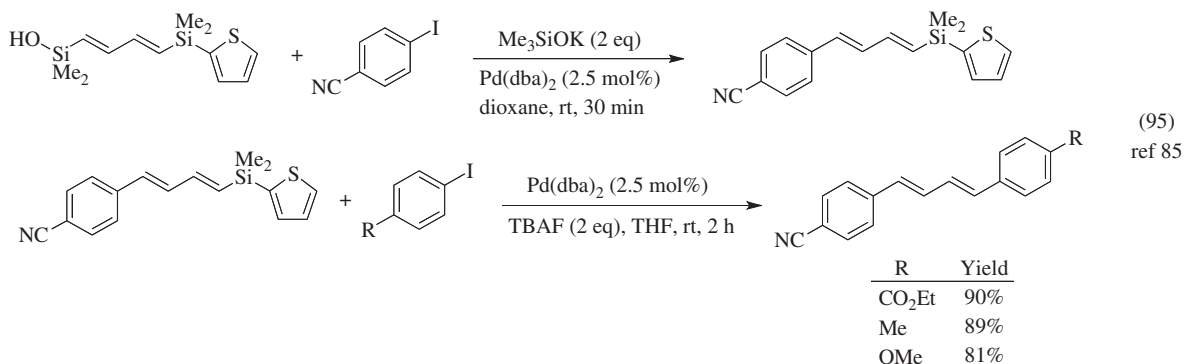
2-Arylindoles have been prepared in excellent yields by the cross-coupling of the 2-dimethylhydroxysilylindole with aryl bromides or iodides (Eq. 93).<sup>83</sup>



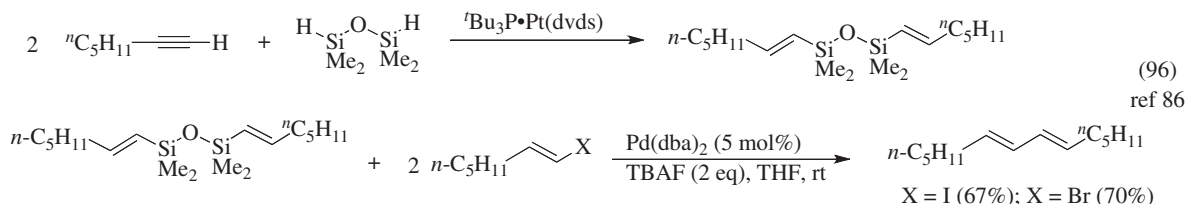
The reaction of vinylsilanols with aryltriflates or nonafluorosulfonates gives the corresponding styrene in good yields (Eq. 94).<sup>84</sup>



An example of the selective cross-coupling of a vinylsilanol in the presence of a 2-thienyldimethylsilyl group is known. This allows for the sequential cross-coupling of two sites on a molecule (Eq. 95).<sup>85</sup>



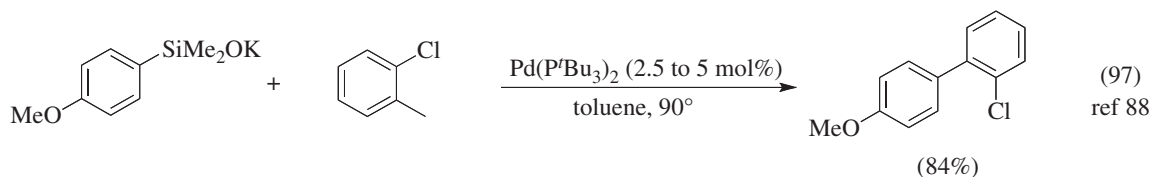
The readily prepared and easily handled disiloxanes under fluoride ion promotion undergo cross-coupling reactions (Eq. 96).<sup>86</sup>



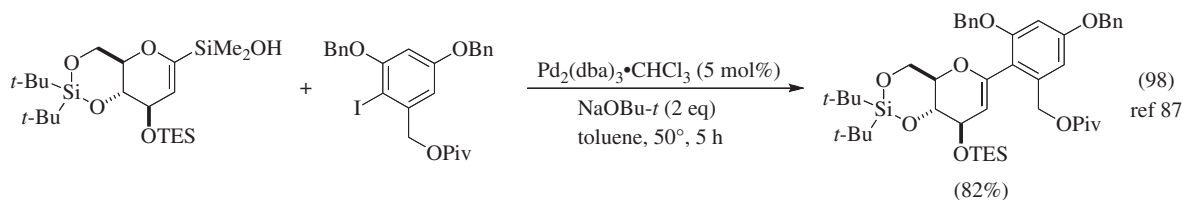
### Silicon-Based Cross-Coupling Reactions with Silanolates

An emphasis on the use of sodium or potassium silanolates in silicon-based cross-coupling reactions has surfaced recently. This has been in conjunction with and a result of thorough mechanistic studies that show that many of the protocols used in the cross-coupling of organosilanes proceed through a silanol or the corresponding silanolate. An excellent discussion of the history of the silicon-based cross-coupling reactions and the mechanism has been published.<sup>87</sup> In many ways this finding points the way to practical approaches using organosilanes as the nucleophilic partner in cross-coupling reactions as the silanolates are readily prepared and, though moisture sensitive, are otherwise very stable and easily handled. They also show good solubility in organic solvents and can be stored as solutions. The reactions do not require the use of fluoride promotion.

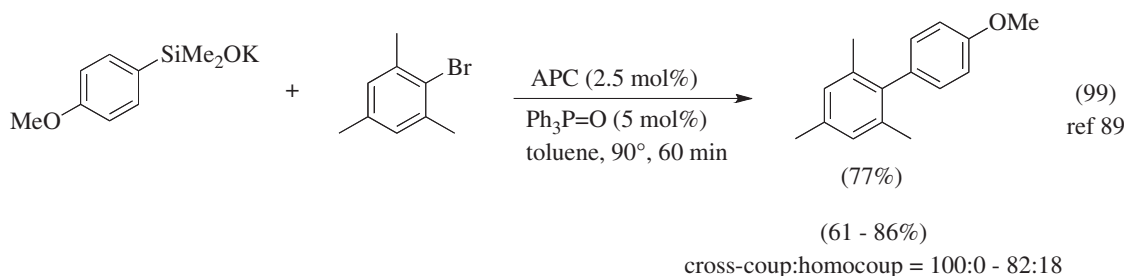
Bis(tert-butyl)phosphine palladium (0) is the key in the successful cross-coupling of aryl- and heteroarylsilanolates with aryl- and heteroaryl halides. A very thorough study of the range and applications of the methodology has been published (Eq. 97).<sup>88</sup>



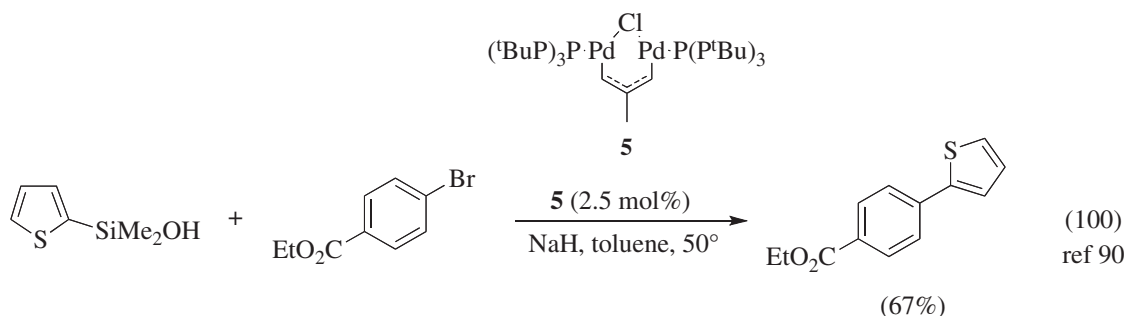
An excellent review that looks into the history of the silicon-based cross-coupling methodology and the arrival at the true mechanisms of the reactions has been published. The importance of silanols and silanolates in these important transformations is well documented therein (Eq. 98).<sup>87</sup>



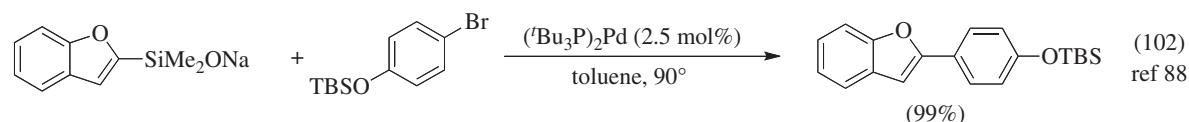
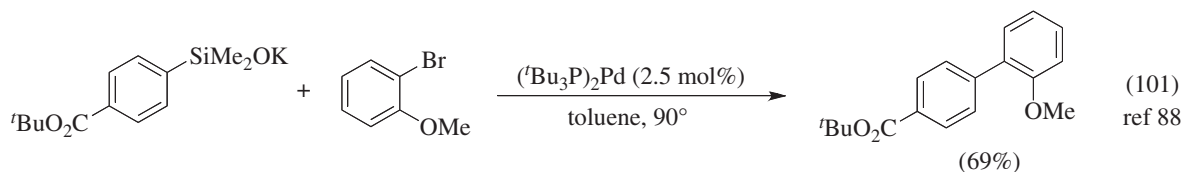
Based on a thorough study of the mechanism of the silicon-based cross-coupling reaction it was discovered that phosphine oxides, such as triphenylphosphine oxide, are excellent and inexpensive ligands for the transformations. The combination of allylpalladium chloride dimer, APC, and triphenylphosphine oxide proves to be an excellent one for the cross-coupling of potassium silanolates with aryl bromides (Eq. 99).<sup>89</sup>



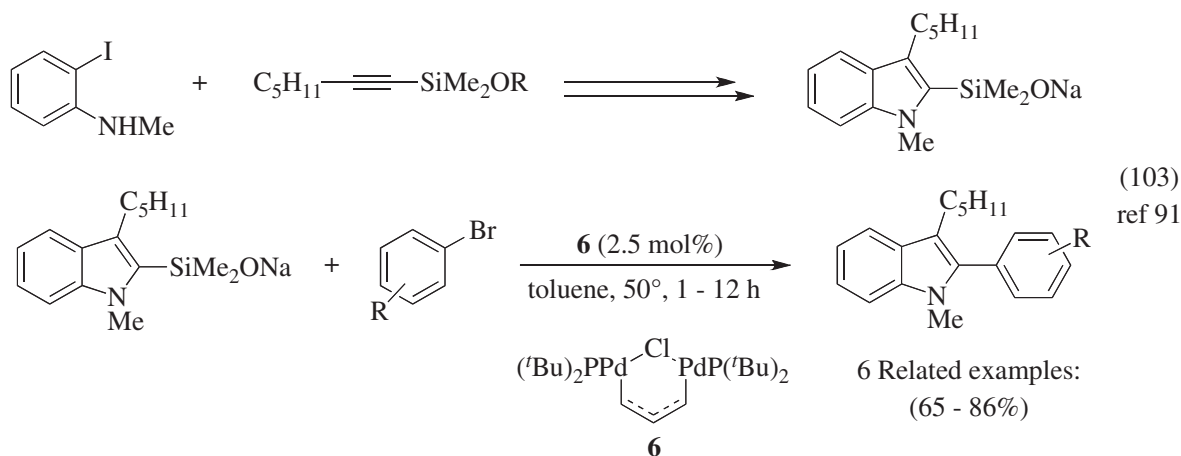
The reaction of heterocyclic sodium silanolates, generated 'in-situ', with aryl iodides and bromides gives good yields of the biaryls (Eq. 100).<sup>90</sup> A special Pd(I) catalyst, **5**, is required for best results.



A major paper covering the use of potassium and sodium silanolates in the cross-coupling of arylsilanes with aryl and vinyl halides has appeared (Eqs. 101, 102).<sup>88</sup> This work demonstrates the practicality and strong potential for the use of arylsilanolates in silicon-based cross-coupling protocols. Good yields obtained with both electron poor and electron rich as well as sterically hindered electrophilic partners. The key to the success of these cross-coupling reactions is the use of (*t*-Bu<sub>3</sub>P)<sub>2</sub>Pd (0) catalyst of choice. Importantly, no other special ligands or fluoride are required.



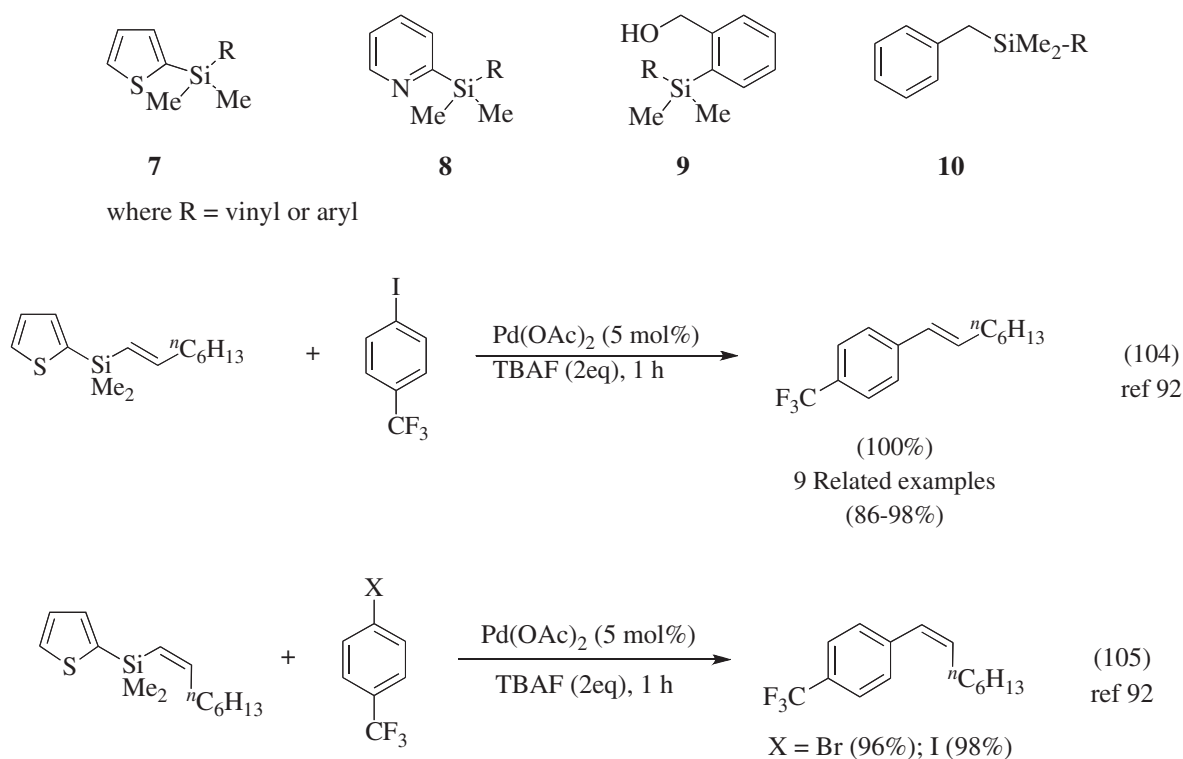
A combination of Larock heteroannulation and silicon-based cross-coupling leads to 2,3-disubstituted indoles (Eq. 103).<sup>91</sup> Silanols as well as silanolates can be the nucleophilic reagents employed in the cross-coupling. The silyl group employed both to direct the regioselectivity of the heteroannulation and bring about the cross-coupling.



### Silicon-Based Cross-Coupling Reactions with Special Ligands on Silicon

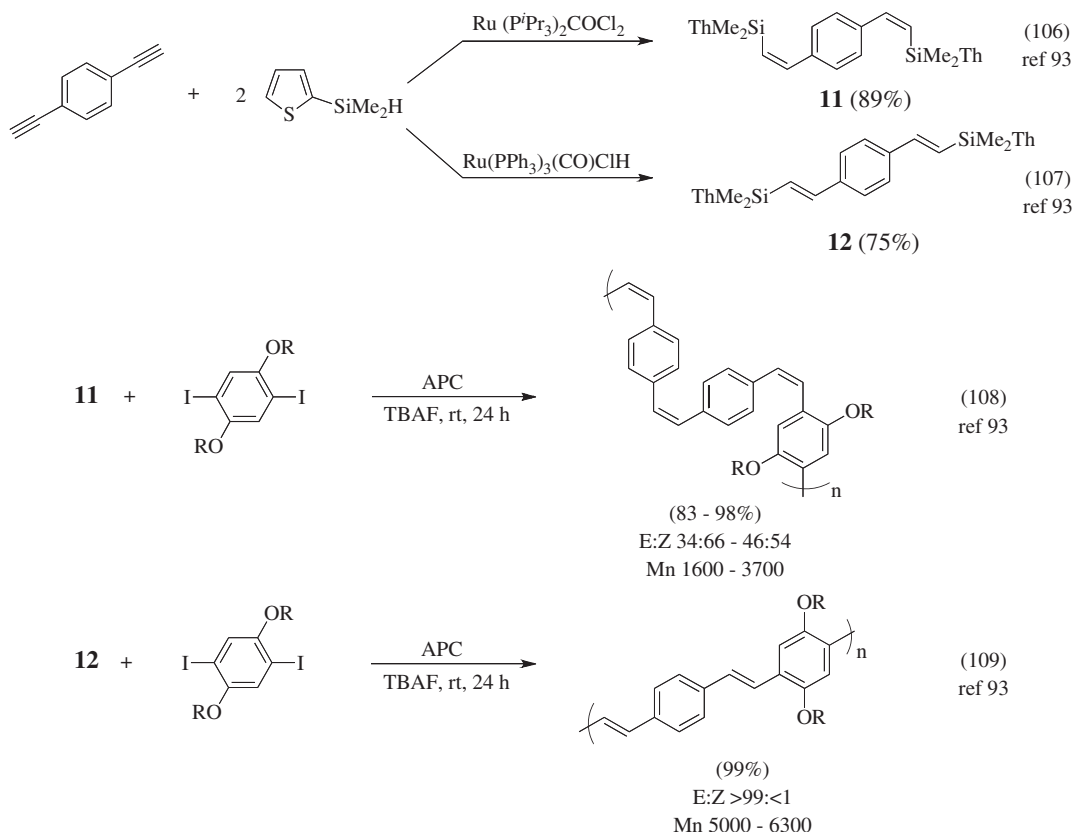
Advances in the technology applied to the silicon-based cross-coupling reactions have led to the employment of special ligands attached to silicon through Si-C bonds. The purpose of this approach is to avoid the need for the fluoride ion promotion of the reactions and to add to the stability and ease of handling of the organosilanes. A key requirement of the special ligand approach is that the activating ligand on the silicon atom is not involved in the cross-coupling itself. Among such useful systems employed are the 2-thiophenylsilanes **7**, the 2-pyridylsilanes **8**, benzyltrimethylsilanes, **9**, and the *o*-hydroxymethylphenylsilanes **10**. These ligands activate the silane for the cross-coupling reaction without themselves being transferred.

The 2-thiophenylsilane derivatives **7** have been employed in the tag strategy for the separation, recovery and recycling of the precursor to the reactive intermediates themselves. Many of these reagents still require the promotional effect of fluoride ion in their reactions (Eqs. 104, 105).<sup>92</sup>

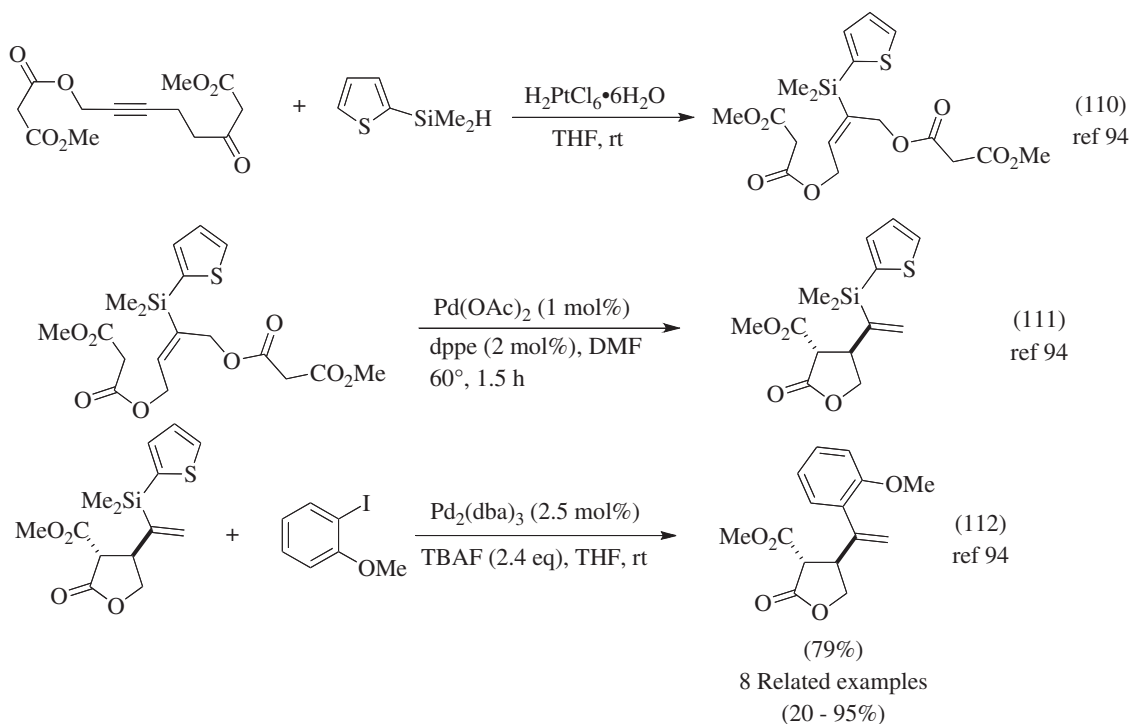




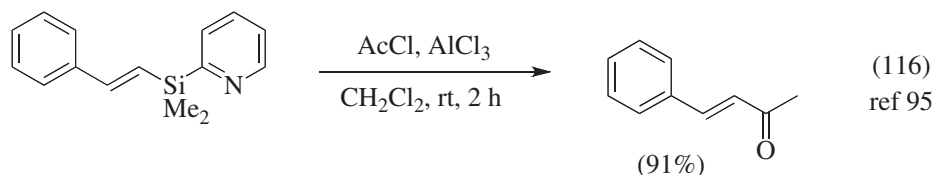
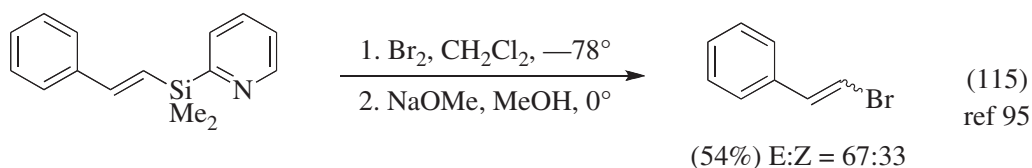
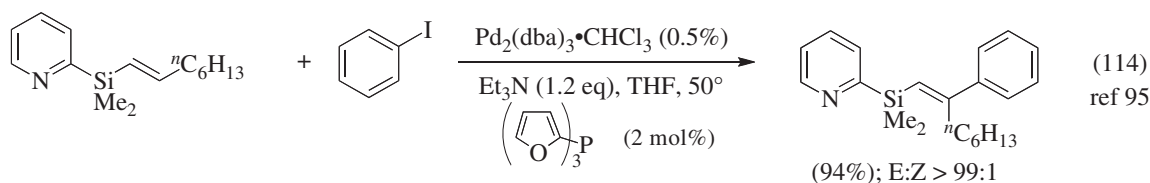
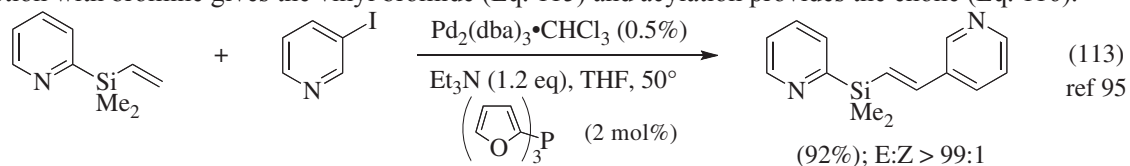
Advantage was taken of the 2-thienyl ligand, Th, on silicon to prepare stereodefined (E) and (Z)-poly(*p*-phenylenevinylene)s via the hydrosilylation of *p*-diethynylbenzene with 2-thienyldimethylsilane and then cross-coupling with diiodobenzene derivatives (Eqs. 106, 107, 108, 109).<sup>93</sup>



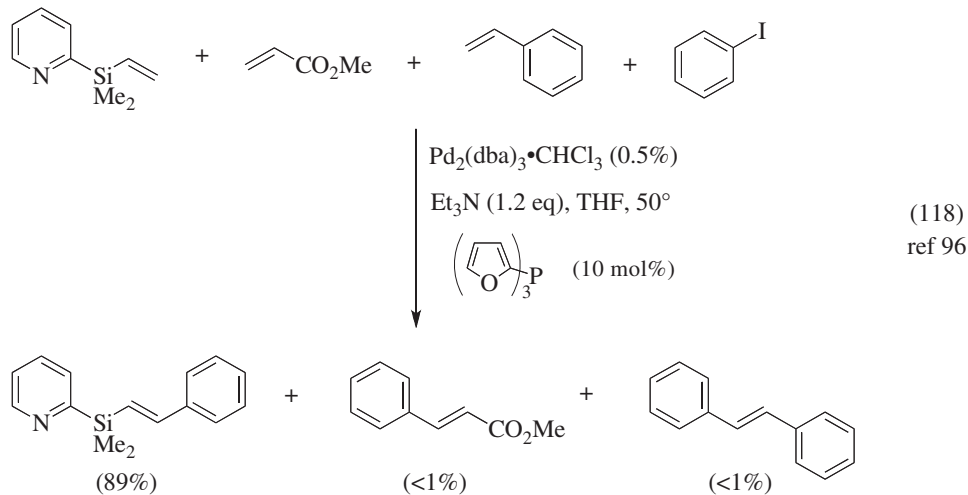
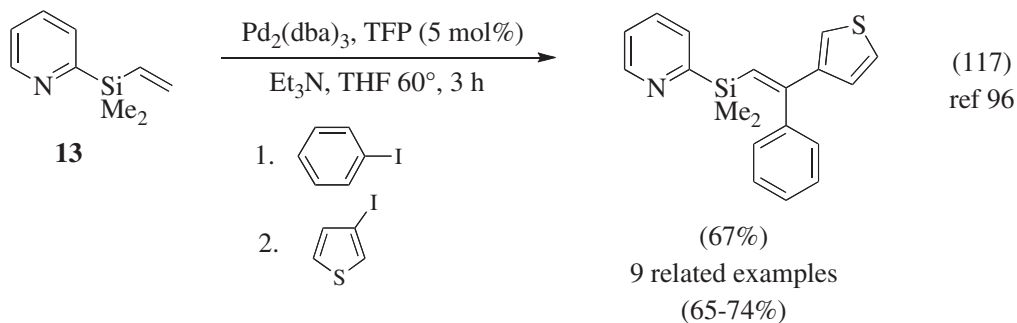
The combined use of the 2-thienyl ligand in the silicon-based cross-coupling and of the silyl group to dictate the regioselectivity of the intramolecular allylic alkylation prior to the cross-coupling step was employed in the synthesis of model systems for podophyllotoxin and picropodophyllin natural products (Eqs. 110, 111, 112).<sup>94</sup>



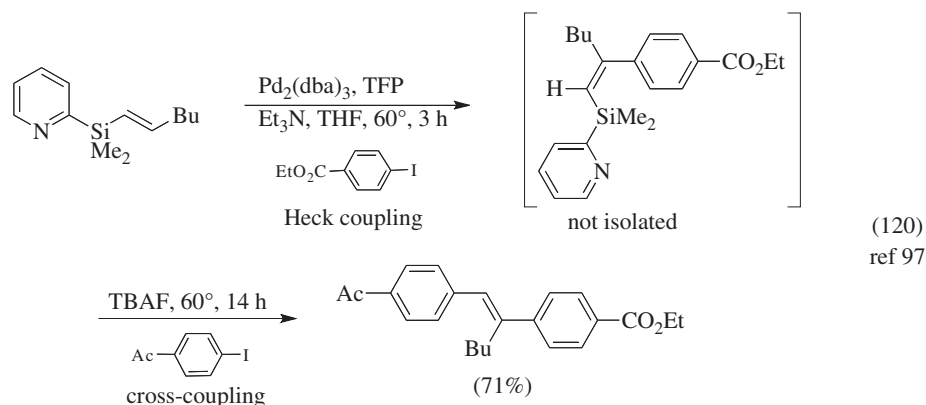
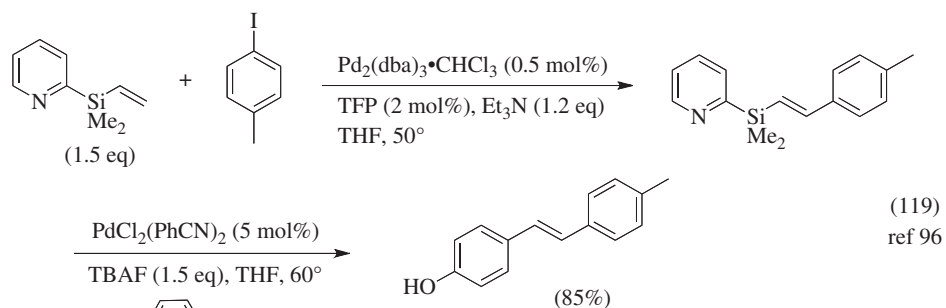
A second approach has been to employ the 2-pyridylsilane derivatives. Thus, vinyl(2-pyridyl)dimethylsilane, a totally thermally and hydrolytically stable system, undergoes a Heck coupling with aryl iodides (Eq. 113).<sup>95</sup> With substituted vinylsilanes of this type the stereochemistry of the olefin is maintained (Eq. 114).<sup>95</sup> The resulting vinylsilanes can then be further converted; for example, reaction with bromine gives the vinyl bromide (Eq. 115) and acylation provides the enone (Eq. 116).<sup>95</sup>



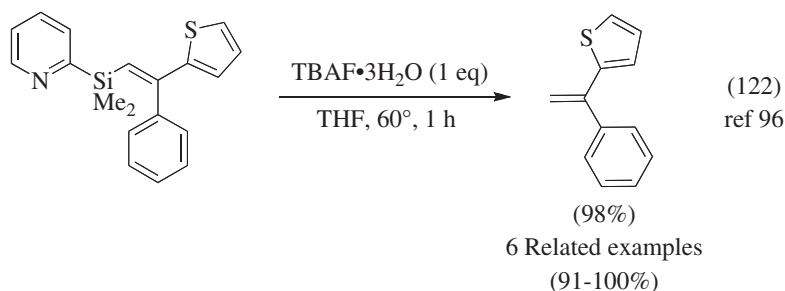
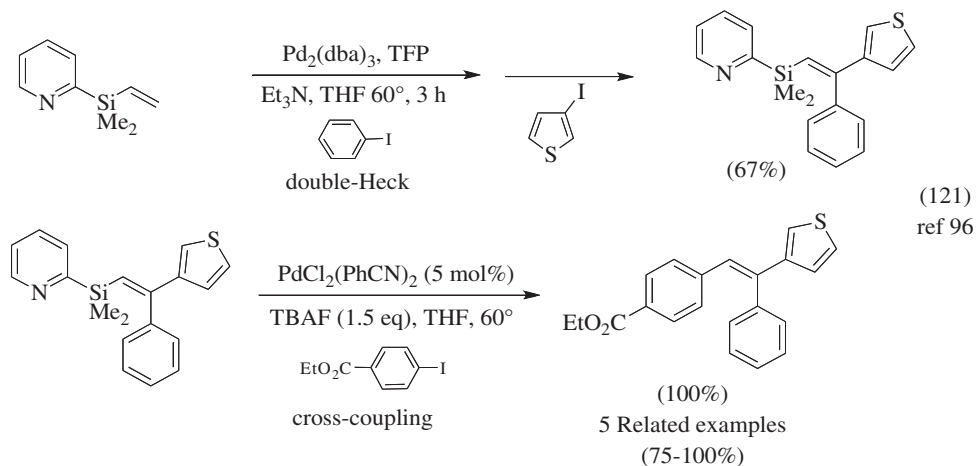
A one-pot, double-Heck coupling is possible as shown in Eq. 117.<sup>96</sup> The sequential approach gives higher overall yields, however. The high reactivity of the 2-pyridylvinylsilane **13** towards the Heck reaction is illustrated in the competitive reaction experiment, wherein the selectivity for the Heck reaction of **13** with iodobenzene over that between iodobenzene and methyl acrylate or between iodobenzene and styrene is clearly shown (Eq. 118).<sup>96</sup>



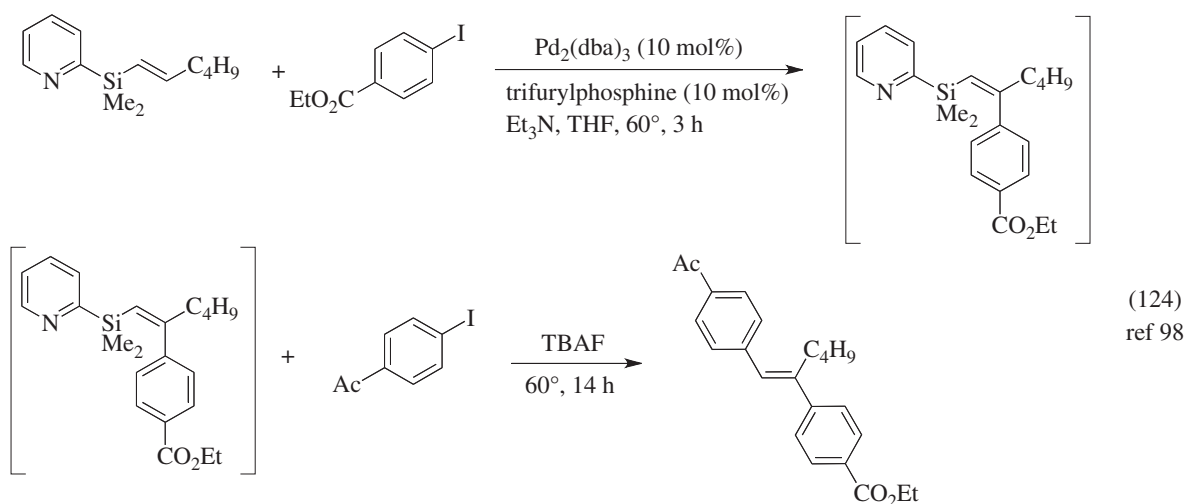
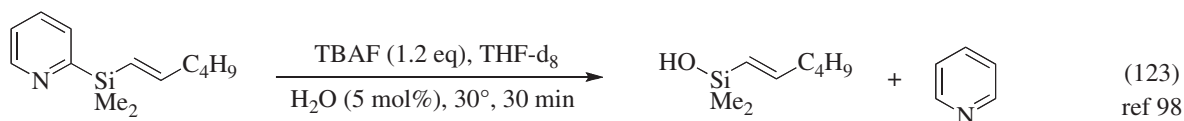
A combination of a Heck reaction followed by a silicon-based cross-coupling reaction can be used to stereoselectively prepare (E)-1,2-diarylethylenes (Eq. 119).<sup>96,97</sup> A one-pot version of this sequence is also possible (Eq. 120).<sup>97</sup>



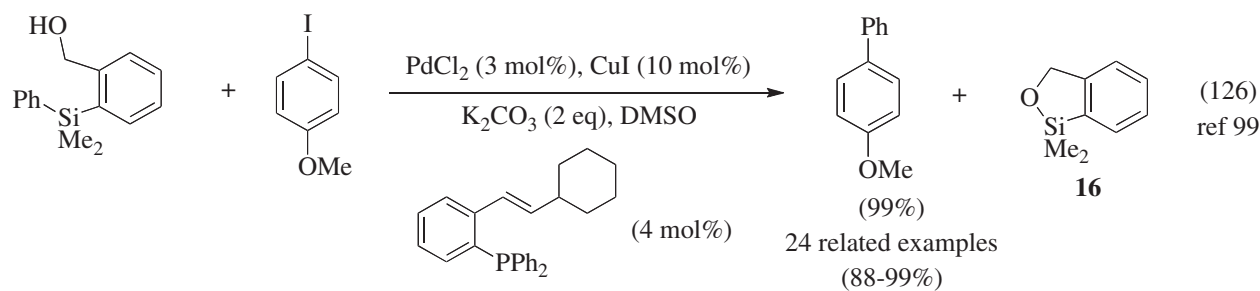
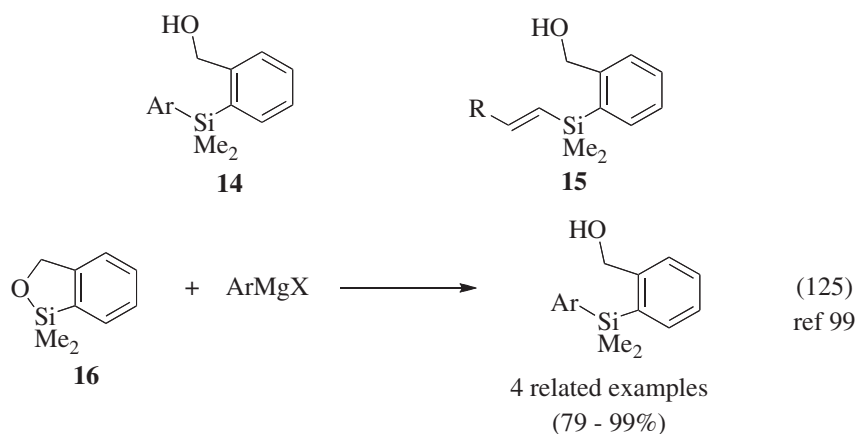
The double-Heck-Hiyama cross-coupling sequence provides 1,2,3-triaryl ethylenes with the opportunity to introduce three different aryl groups (Eq. 121).<sup>96</sup> Furthermore, the protodesilylation of the resulting vinylsilanes from the double Heck sequence leads to 1,1-diarylethylenes. (Eq. 122).<sup>96</sup>



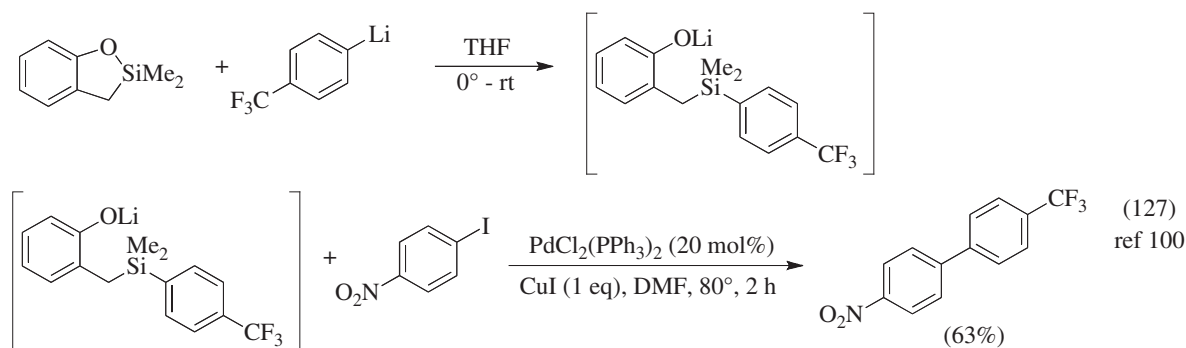
The presence of the 2-pyridyl ligand on alkenyldimethylsilanes allows for the cross-coupling of the alkenyl group with aryl iodides (Eq. 124). The 2-pyridyl group is a precursor to the reactive silanol (Eq. 123).<sup>98</sup>



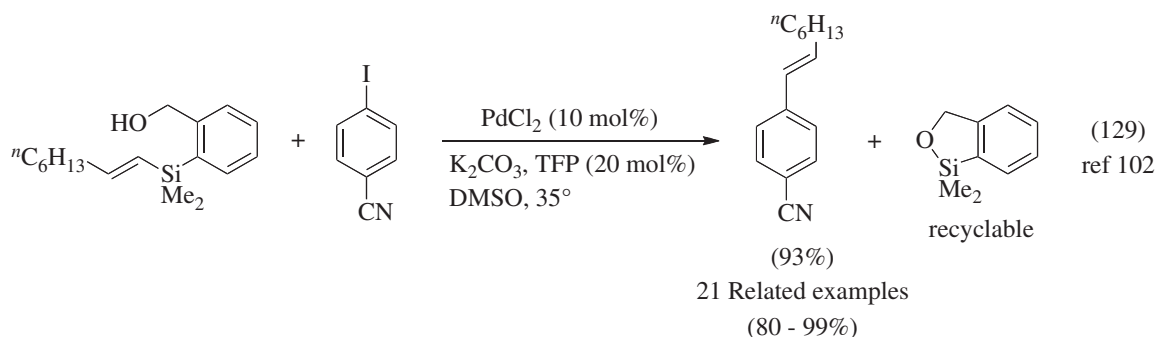
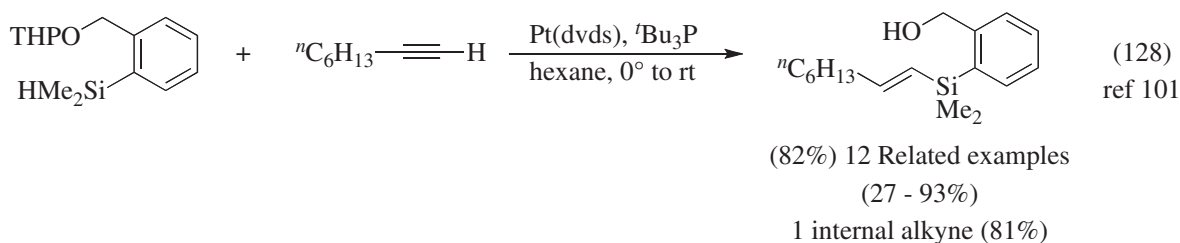
The (2-hydroxymethylphenyl)silane-derived silacycle **16** can be reacted with aryl or vinyl Grignard reagents or their organolithium counterparts to give the corresponding vinyl(2-hydroxymethylphenyl)silane or the aryl(2-hydroxymethylphenyl)silane, for example **14** or **15** (Eq. 125). The *o*-hydroxymethyl group provides an activating effect for the effective cross-coupling of the aryl group with aryl or vinyl halides (Eq. 126).<sup>99</sup> A potentially significant aspect of this approach is that the silabenzofuran is regenerated during the cross-coupling reaction and can be recycled.



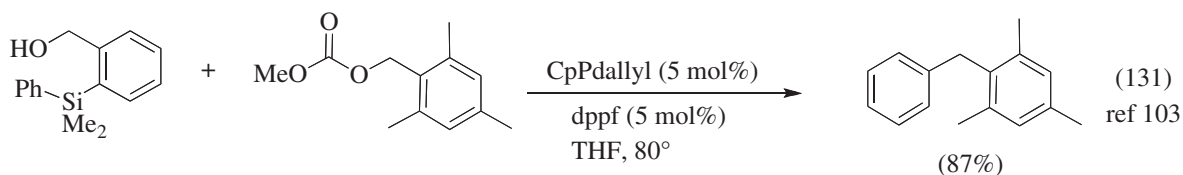
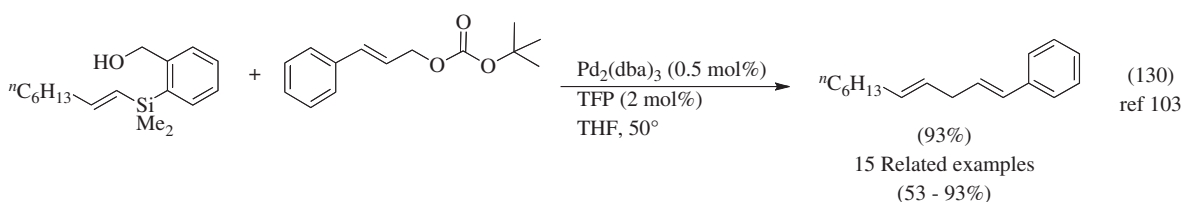
This recycling aspect was put to use illustrating where the silabenzofuran can be employed for the essential cross-coupling of aryllithiums to aryl halides. Thus, the silabenzofuran operates as a carrier for the organolithium reagent allowing its reaction with an aryl halide, a reaction the aryllithium reagent itself is not capable of in good yield (Eq. 127).<sup>100</sup>



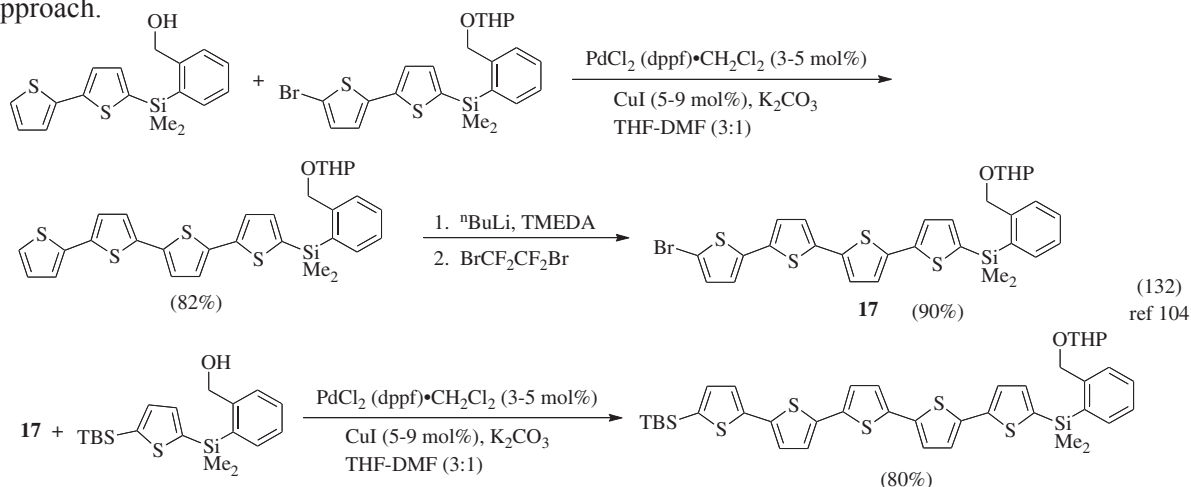
The hydrosilylation of terminal acetylenes under Karstedt, bis-divinyltetramethyldisiloxanyl platinum(0), catalysis (Gelest SIP6831.2) gives the (E)-vinylsilane carrying the *o*-hydroxymethylphenyl promoter group. Cross-coupling of the (E)-vinylsilane with aryl iodides gives 2-aryl olefins in excellent yields (Eqs. 128, 129).<sup>101,102</sup>



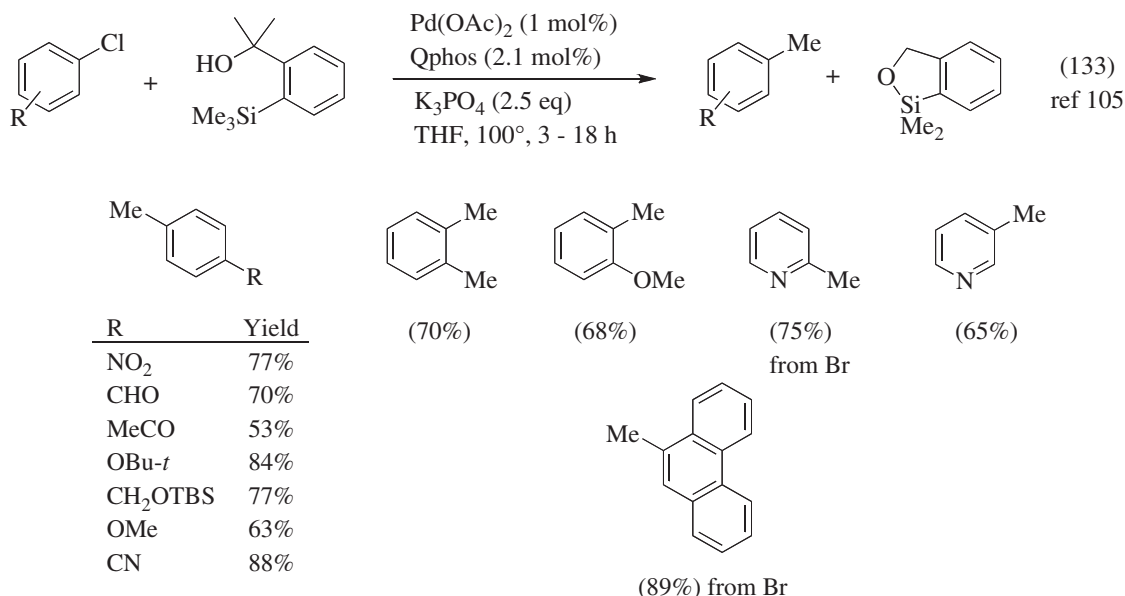
The arylated systems with the *o*-hydroxymethylphenyl promotion also couple with allyl and benzyl carbonates (Eqs. 130, 131).<sup>103</sup> Related chemistry presents advantages for the cross-coupling with electron poor electrophilic partners.



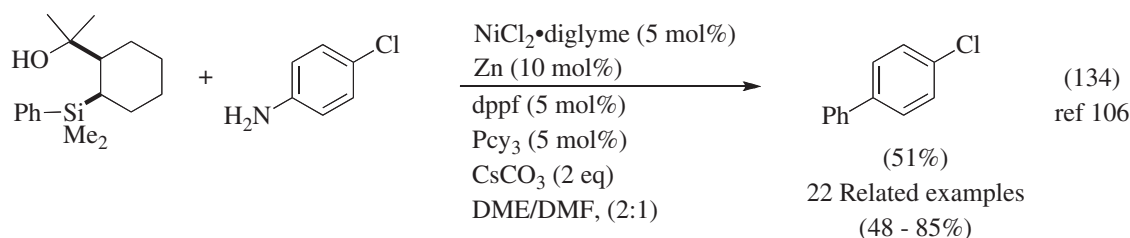
Taking advantage of the strong reactivity of the (2-hydroxymethylphenyl)dimethylarylsilanes and the non-reactivity of the OH protected (THP or Ac) derivative it has proven possible to iteratively construct oligomeric systems in good yields and with total specificity (Eq. 132).<sup>104</sup> The iterative synthesis of polythiophenes is an excellent example of this activation-deactivation approach.



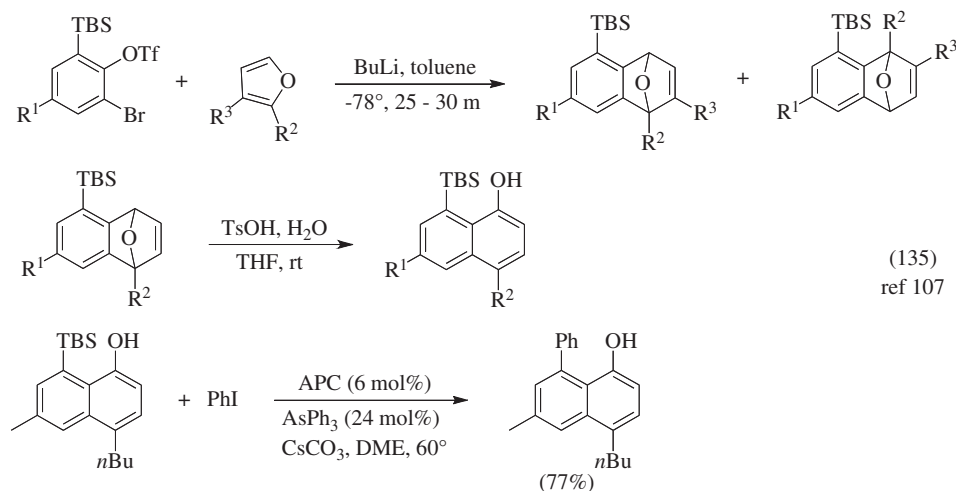
Hiyama and coworkers have employed the (2-hydroxymethyl)phenylsilane system to transfer an alkyl group from silicon to aryl halides, including aryl chlorides. They have used a 2-hydroxypropyl system, leading to the gem-dimethylbenzosilafuran by-product, to significant advantage in these reactions (Eq. 133).<sup>105</sup> No reaction of the phenyl-Si bond is seen under these conditions. With the simple hydroxymethyl analog only the benzaldehyde and reduction of the aryl chloride are observed.



In work that mimics that of the 2-hydroxymethylphenylsilane cross-couplings the specialty ligand prepared from *cis*-2-(2-hydroxypropyl)cyclohexyldimethylarylsilanes can be used in nickel-catalyzed cross-coupling reactions with aryl chlorides and tosylates (Eq. 134).<sup>106</sup> Recycling of the parent silicon reagent is again possible.

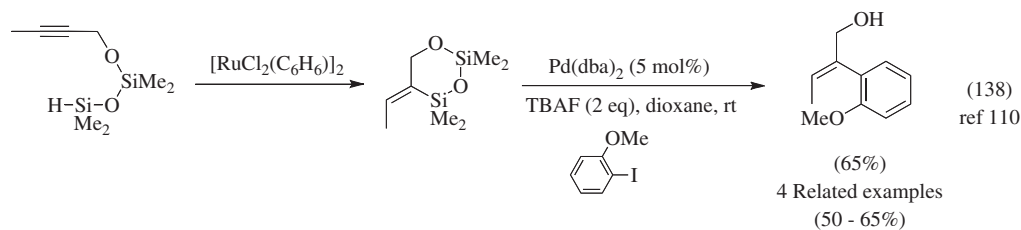
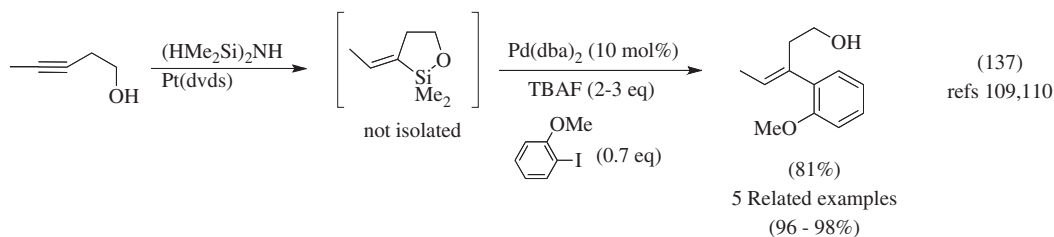
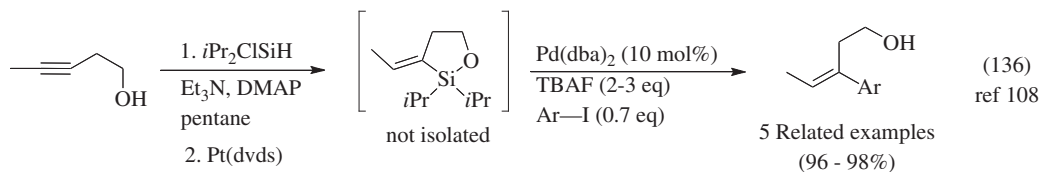


Another example of intramolecular activation of an arylsilane for cross-coupling is shown in the example of 8-*tert*-butyldimethylsilyl-1-naphthols, prepared via a Diels-Alder approach, and their cross-coupling with aryl iodides (Eq. 135).<sup>107</sup>

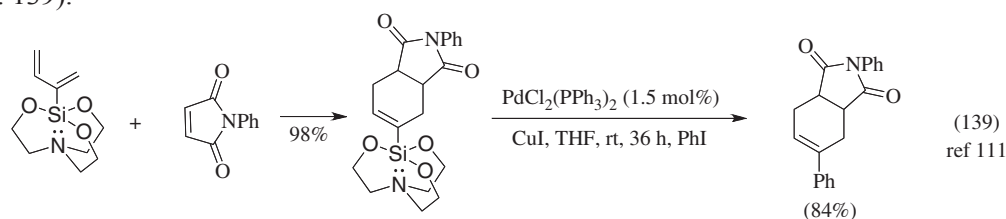


### Silicon-Based Template and Related Cross-Coupling Sequences

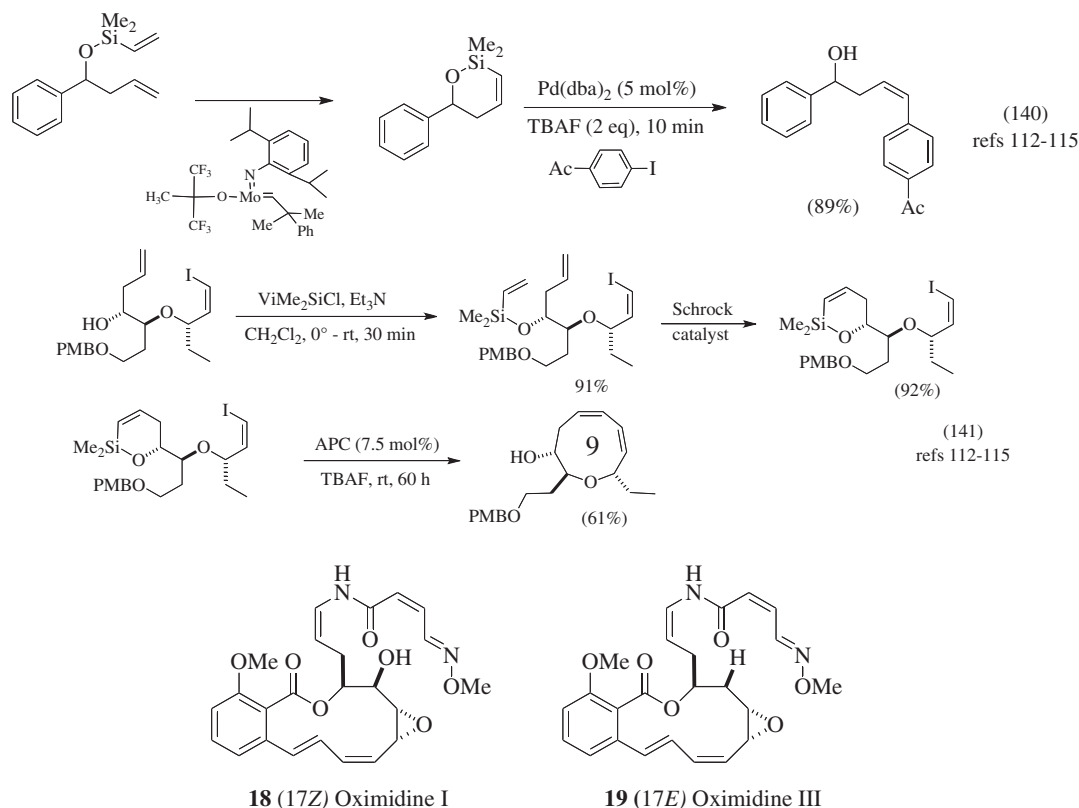
The ability of available organosilanes to both silylate alcohols and hydrosilylate alkynes can be used to generate interesting stereo-defined, organofunctionalized olefins. For example, the O-silylation of a hydroxyalkyl acetylene with *sym*-tetramethyldisilazane followed by intramolecular hydrosilylation of the acetylene provides an intermediate vinylsilane, which also has the requisite alkoxy substituent for cross-coupling. The stereochemical outcome of the reaction is determined by the *cis* hydrosilylation resulting from the intramolecular hydrosilylation step (Eqs. 136, 137).<sup>108,109</sup> Tetramethyldisiloxane is useful in this type of templated cross-coupling approach as well (Eq. 138).<sup>110</sup>



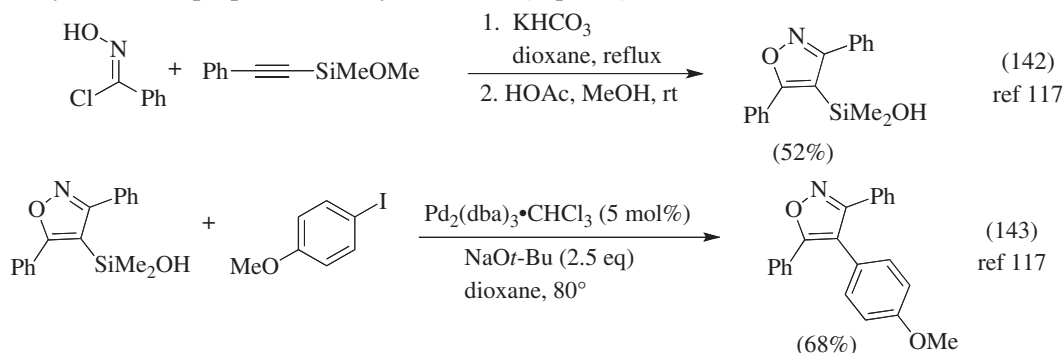
The use of 2-(1,3-butadienyl)silatrane in a Diels-Alder-cross-coupling sequence provides an entry into 1-arylated cyclohexenes (Eq. 139).<sup>111</sup>



An O-silylation, cross-metathesis, cross-coupling sequence can be employed in the generation of interesting species via inter- or intramolecular processes (Eqs. 140, 141).<sup>112-115</sup> This general approach was used in a synthesis of (17Z) oximidine I, **18**, and (17E) oximidine III, **19**.<sup>116</sup>

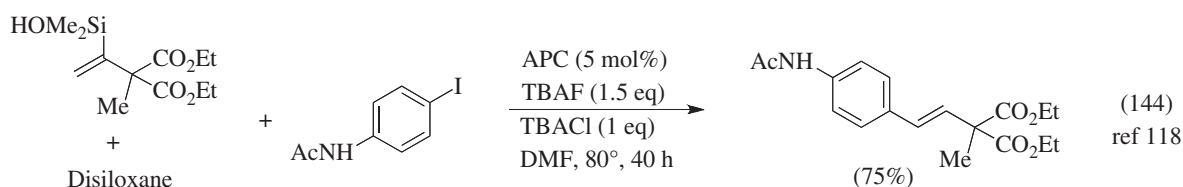


Starting with a silylalkyne the silyl group can be used to direct the regioselective cycloaddition with an in-situ-generated nitrile oxide to generate the 4-silylisoxazole (Eq. 142).<sup>117</sup> The regioselectivity is only about 4:1, but any undesired 5-silyl isomer is hydrolyzed under acid conditions leaving only the desired isomer. This heteroarylsilane can then be cross-coupled with an aryl iodide to prepare the 4-arylisoxazole (Eq. 143).<sup>117</sup>



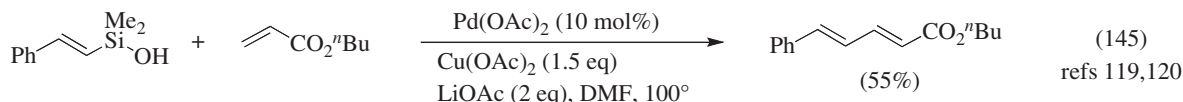
### Silicon-Based Heck Coupling Reactions

A highly regio- and stereoselective Heck coupling to vinylsilanols is accomplished with APC (Eq. 144).<sup>118</sup> Placement of the aryl group is beta to the silicon atom and the silicon group can be removed with fluoride treatment.

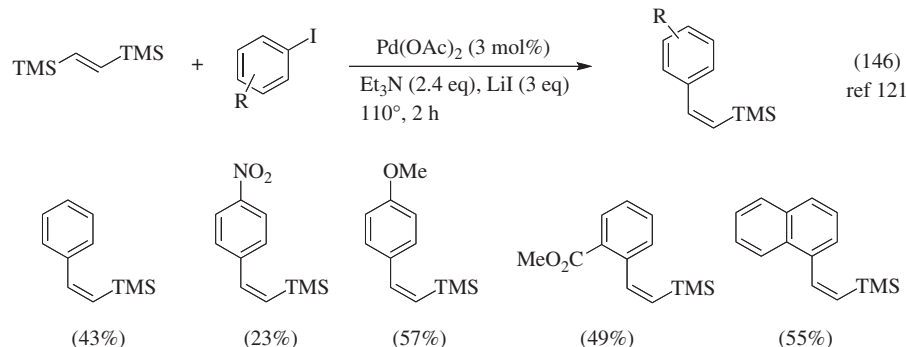




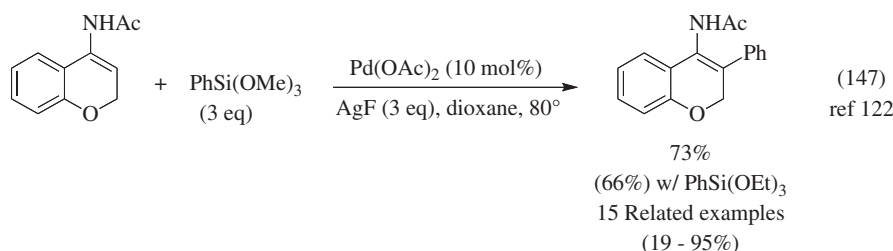
Vinylsilanols are shown to undergo Heck coupling (Eq. 145).<sup>119,120</sup>



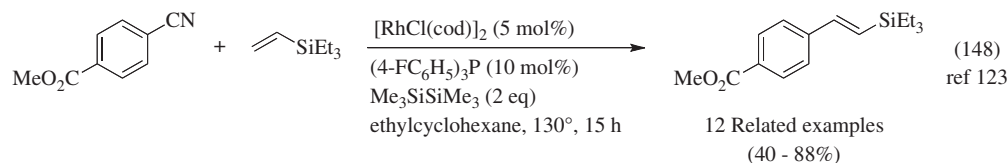
A stereospecific arylation of (E)-1,2-bis(trimethylsilyl)ethylene is possible producing (Z)-2-aryl-1-trimethylsilyl ethylenes (Eq. 146).<sup>121</sup>



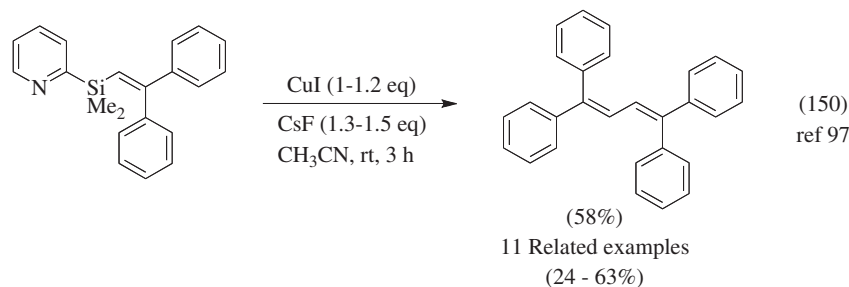
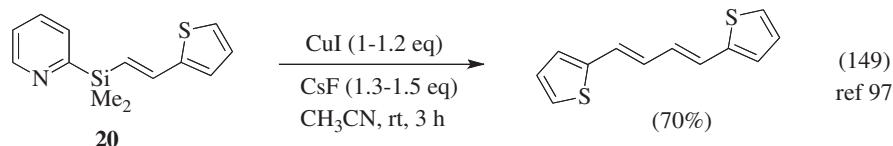
C-H activation was employed in the direct silicon-based arylation of enamides with modest to good yields (Eq. 147).<sup>122</sup> The reactions are catalyzed with Pd(OAc)<sub>2</sub> and promoted with AgF.



Displacement of the cyano group on aryl- or alkenyl cyanides is possible via a Heck coupling with vinylsilanes and rhodium catalysis (Eq. 148).<sup>123</sup> The vinyl silane can be used for further reactions.

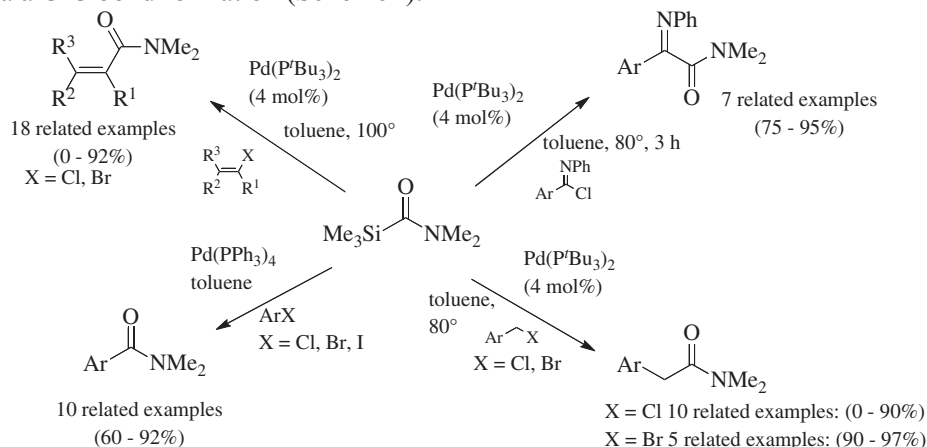


A sequence of a Heck coupling to give **20** and a homocoupling provides an excellent entry into 1,4-diaryl-1,3-butadienes and 1,1,4,4-tetraaryl-1,3-butadienes. This was successfully employed in the preparation of various arylated 1,3-butadienes with interesting photophysical properties (Eqs. 149, 150).<sup>97</sup>



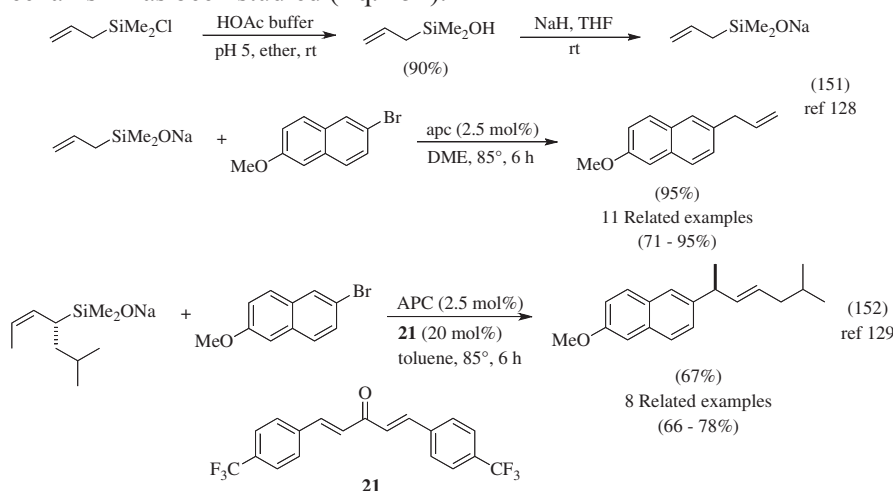
### Miscellaneous Coupling Reactions

In a nice series of papers the cross-coupling of *N,N*-dimethylcarbamoyltrimethylsilane with vinyl halides, aryl halides, benzyl halides and imidoyl chlorides was demonstrated as shown below. The result is the facile introduction of the dimethylamido group via a C-C bond formation (Scheme I).<sup>124-127</sup>

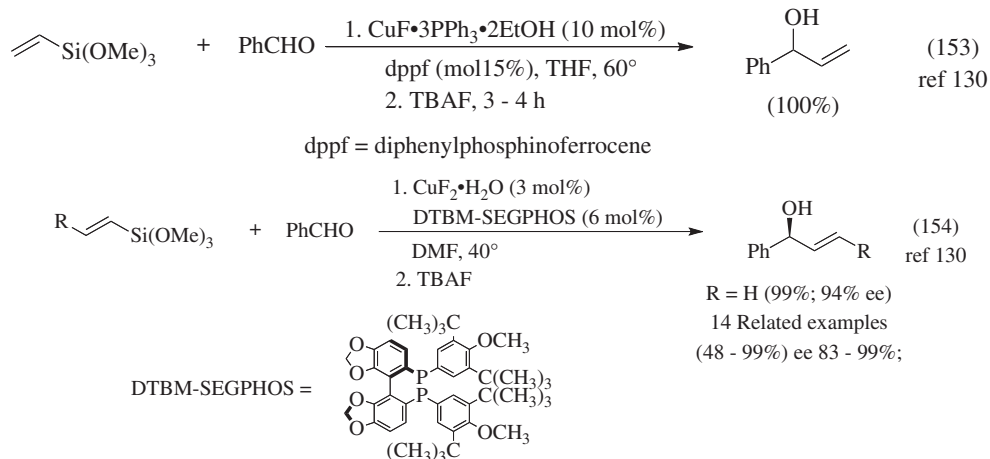


Scheme 1 refs 124-127

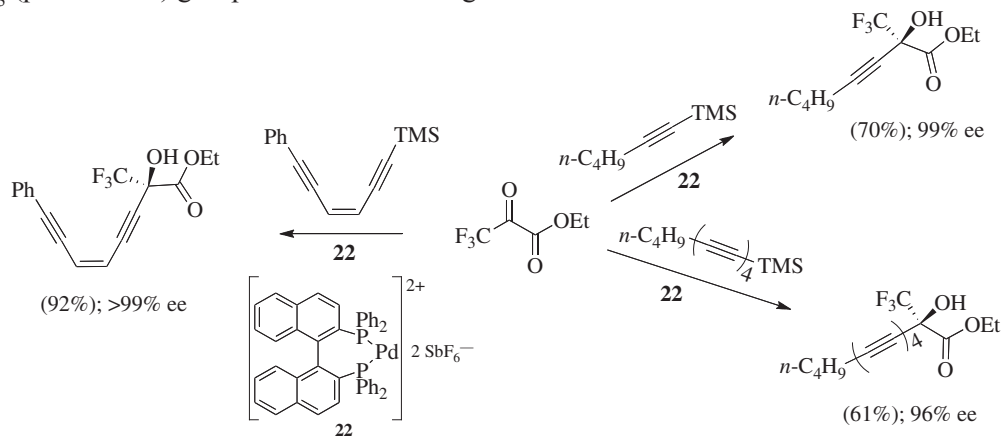
The sodium salts of allyldimethylsilanol and related allylsilanes are readily coupled with a variety of aryl bromides in good yields (Eq. 151).<sup>128</sup> A combination of allylpalladium chloride dimer, APC, and triphenylphosphine oxide is best for the sterically unencumbered substrates whereas for the more sterically challenged systems the benzylidene acetone ligand, **21**, proved best. The mechanism has been studied (Eq. 152).<sup>129</sup>



Vinylalkoxysilanes undergo a Grignard-type coupling with aldehydes to form enones (Eq. 153).<sup>130</sup> A change in the conditions with the utilization of the chiral ligand, DTBM-SEGPHOS, results in enantioselective addition to the carbonyl (Eq. 154).<sup>130</sup> The yields and ee values are very good.

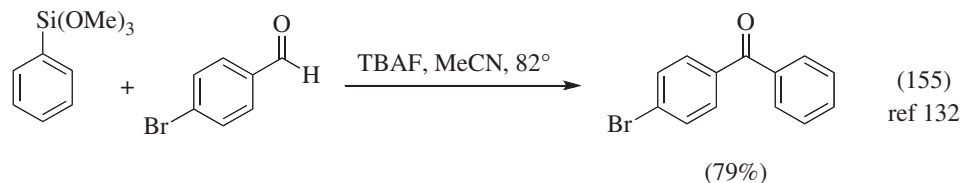


A highly enantioselective alkynylation catalyzed by the dicationic (*S*)-BINAP-Pd complex with a variety of alkynylsilanes and trifluoropyruvate is described (Scheme 2).<sup>131</sup> The catalytic reaction is applicable to highly enantioselective addition of polyynes to trifluoropyruvate to construct  $\alpha$ -trifluoromethyl-substituted tertiary alcohols. A highly enantioselective alkynylation catalyzed by the dicationic (*S*)-BINAP-Pd complex with a variety of alkynylsilanes and trifluoropyruvate is described. The catalytic reaction is applicable to highly enantioselective addition of the polyynes to trifluoropyruvate to construct  $\alpha$ -trifluoromethyl-substituted tertiary alcohols trifluoromethyl group. The SiMe<sub>2</sub>Ph, SiMe<sub>2</sub>Bu-*t*, (low yield and ee) and Si(OEt)<sub>3</sub> (poor results) groups were also investigated.

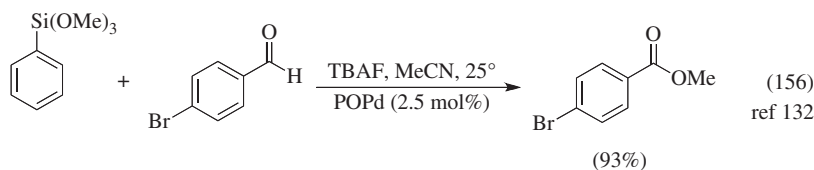


Scheme 2 ref 131

Phenyltrimethoxysilane reacts with aromatic aldehydes under the influence of TBAF to give benzophenones (Eq. 155)<sup>132</sup> and under essentially the same conditions, but with the addition of a palladium catalyst, provides the corresponding methyl benzoate (Eq. 156).<sup>132</sup>

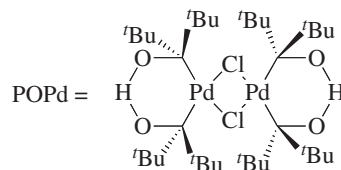
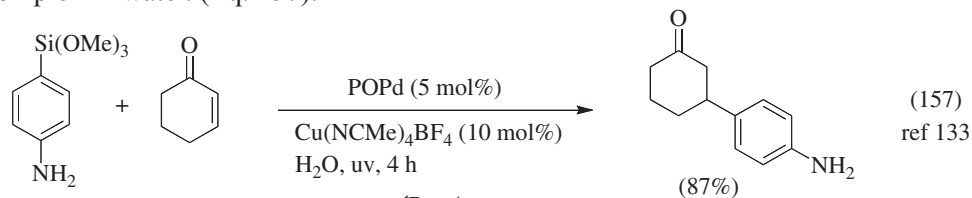


(79%)  
10 Related examples  
(73 - 99%)

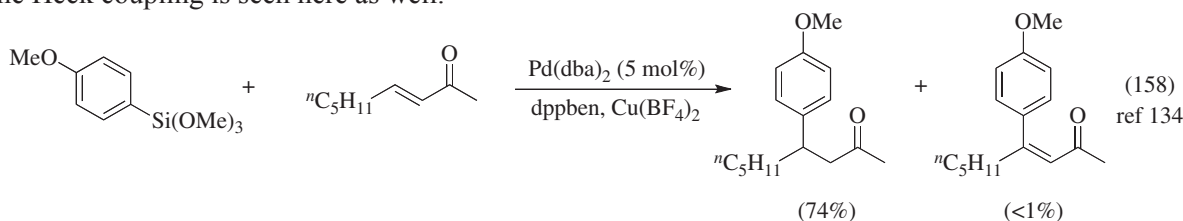


(93%)  
10 Related examples  
(78 - 97%)

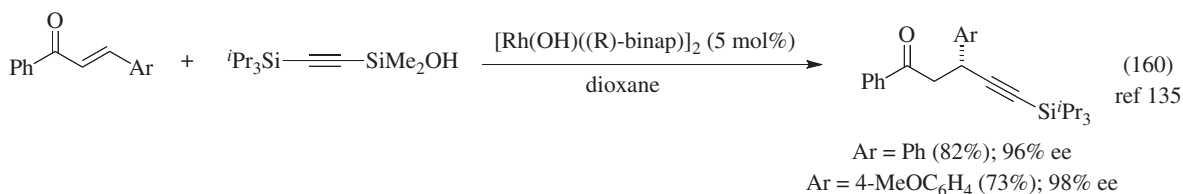
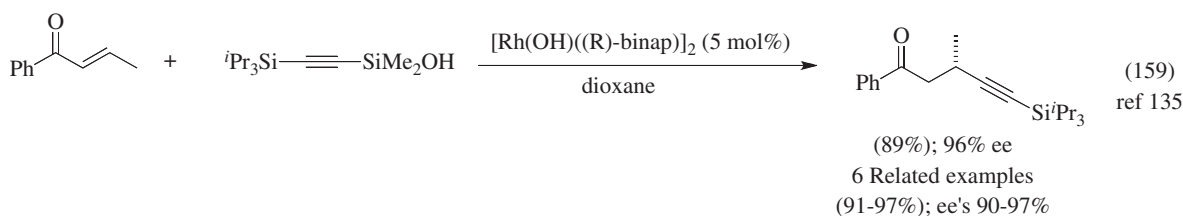
A number of Michael additions of aryl, vinyl and ethynyl silanes to  $\alpha,\beta$ -unsaturated carbonyl systems have been reported. The coupling of organosilyl esters with enones to form  $\beta$ -aryl ketones is possible when catalyzed by a palladium phosphinous acid complex in water. (Eq. 157).<sup>133</sup>



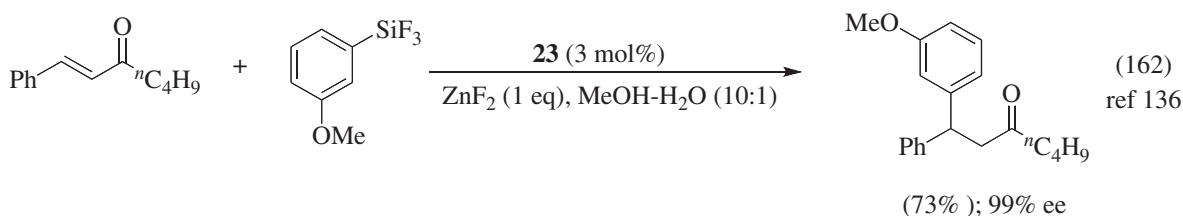
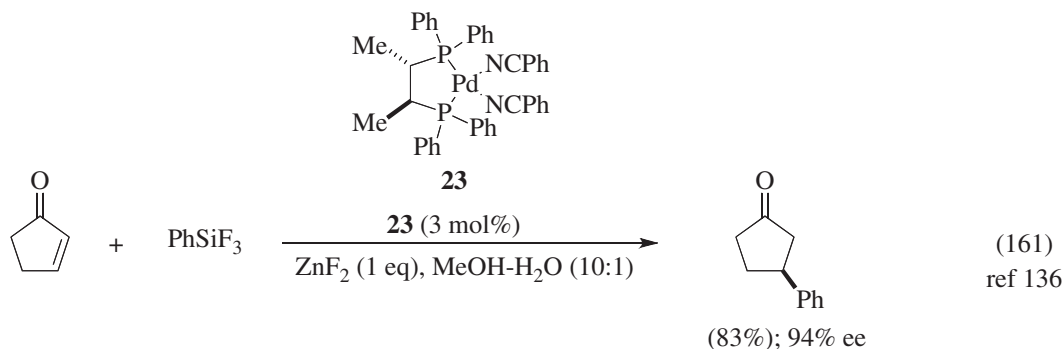
Catalytic 1,4-addition of arylsiloxanes to enones was carried out at 75°C in the presence of a dicationic palladium(II) catalyst in aqueous 1,4-dioxane (Eq. 158).<sup>134</sup> A nitrile-free complex generated in situ from Pd(dba)<sub>2</sub> and Cu(BF<sub>4</sub>)<sub>2</sub> in the presence of dppe or dppben was recognized to be the best catalyst to achieve high yields for the representative enones and enals. Some Heck coupling is seen here as well.



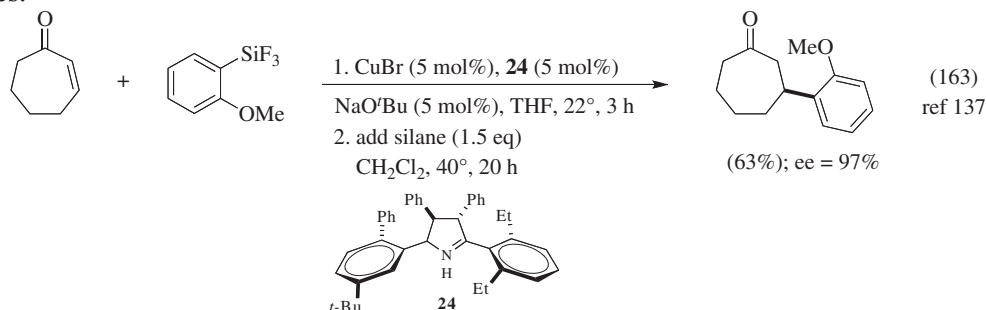
Use of triisopropylsilylethynylsilanols gives selective ethynylation with retention of the triisopropylsilyl moiety (Eq. 159).<sup>135</sup> A sephos ligand is used to impart the enantioselectivity in prior work that was limited in that  $\beta$ -aryl enones reacted very poorly resulting in higher yields of the 1,3-diyne formation. A way to circumvent this is via the use of ethynylsilanols (Eq. 160).<sup>135</sup>



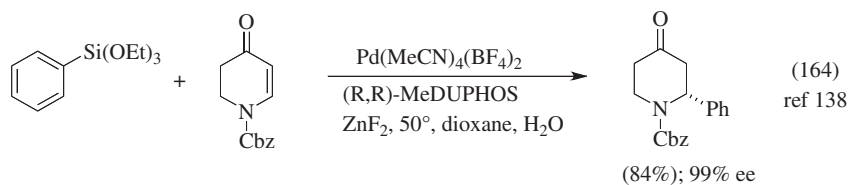
Aryltrifluorosilanes were cross-coupled in an enantioselective, 1,4-addition manner to enones. Best yields were obtained with Ph<sub>3</sub>Bi and PhBF<sub>3</sub>K. Phenyltrifluorosilane gave good yields and good to excellent enantiomeric ratios. Zinc fluoride was a good promoter for the silane reactions (Eqs. 161, 162).<sup>136</sup>



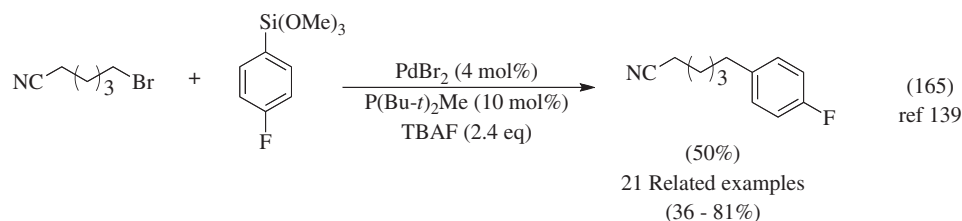
The cross-coupling of aryl- and alkenyltrifluorosilanes with enones to form  $\beta$ -aryl- or  $\beta$ -alkenylketones has proven possible in an enantioselective manner when catalyzed by a chiral, non-C<sub>2</sub>-symmetric, copper-based NHC (N-heterocyclic carbene). The reaction is proposed to proceed via an alkenyl- or aryl copper NHC N-heterocyclic intermediate generated via an in-situ-generated alkenyl- or aryltetrafluorosilicate (Eq. 163).<sup>137</sup> The reaction requires a 50 percent excess of the silyl reagent and 1.5 equivalents of TASF for activation. The yields of the reaction are good to excellent with enantiomeric ratios ranging from 47 to 97 percent. The approach complements that of the 1,4-reduction of unsaturated  $\beta$ -substituted enones.



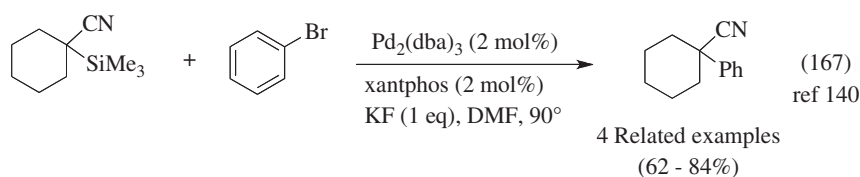
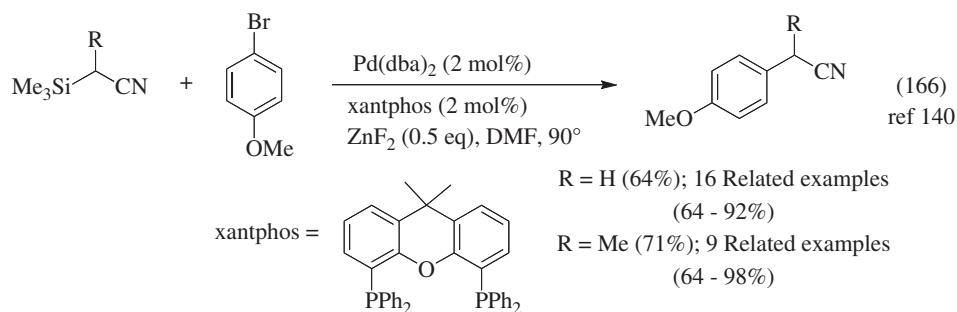
The complex formed from  $\text{Pd}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$  and (*R,R*)-MeDUPHOS is a highly enantioselective catalyst for the asymmetric conjugate addition of aryltriethylsiloxanes to a variety of unsaturated ketones, lactones and lactams (Eq. 164).<sup>138</sup> Yields are good and ee values are excellent.



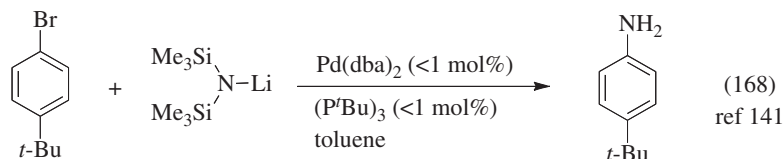
Aryltrimethoxysilanes couple well with primary alkyl bromides. Several examples are reported (Eq. 165).<sup>139</sup>



$\alpha$ -Cyanoalkyltrimethylsilanes are coupled to aryl bromides to give the  $\alpha$ -aryl nitrile (Eqs. 166, 167).<sup>140</sup>

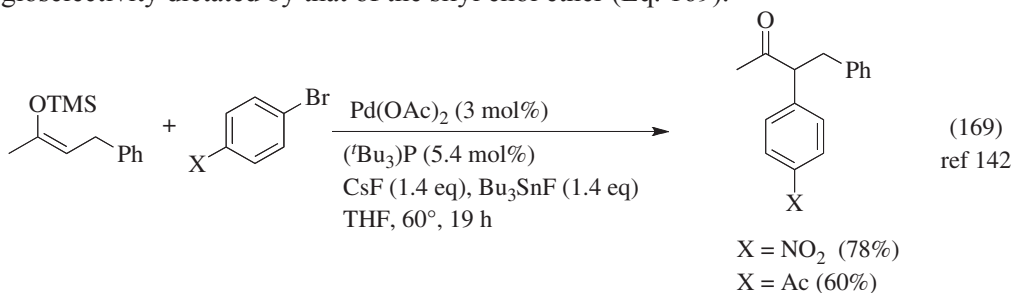


Lithium bis(trimethylsilylamide) provides the amine group in a cross-coupling amination of aryl bromides to form primary anilines (Eq. 168).<sup>141</sup>

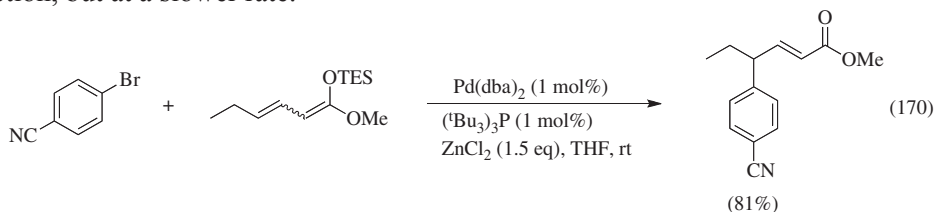


ArBr (92%) 23 Related examples  
(65 - 99%)  
ArCl (89%) 9 Related examples  
(62 - 99%)

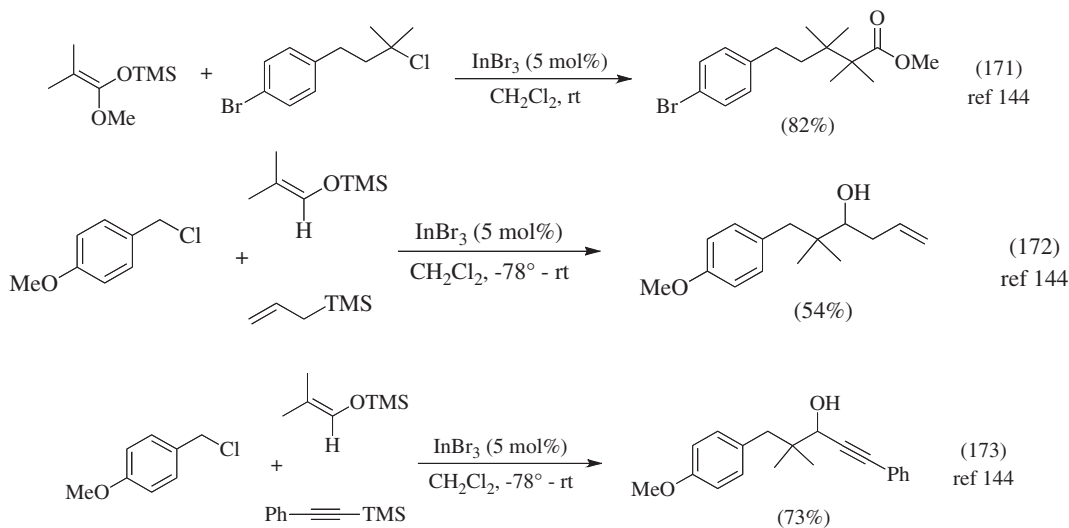
The cross-coupling of a silyl enol ether with aryl bromides results in the  $\alpha$ -arylation of the carbonyl system. Thus, the reaction of the trimethylsilyl enol ether of a ketone with an aryl bromide under palladium catalysis provides the  $\alpha$ -arylated ketone with the regioselectivity dictated by that of the silyl enol ether (Eq. 169).<sup>142</sup>



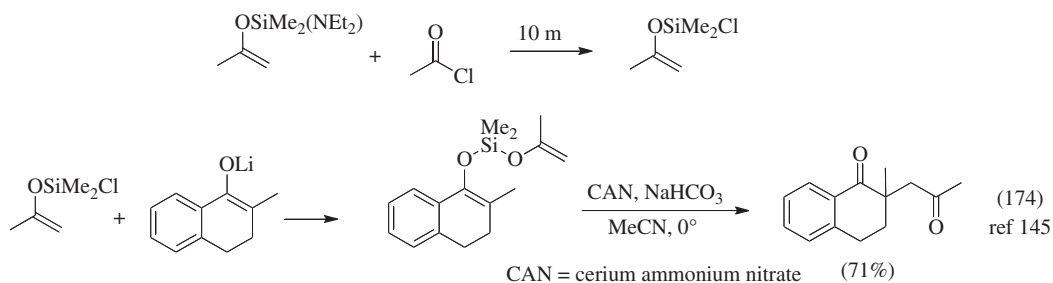
The palladium-catalyzed  $\gamma$ -arylation of the silyl ketene acetals of  $\alpha,\beta$ -unsaturated esters is reported (Eq. 170).<sup>143</sup> The reaction works best with ZnCl<sub>2</sub> activation and Pd(dba)<sub>2</sub>. TES enol ethers are better than trimethylsilyl enol ethers for this transformation. The aryl chlorides and iodides did not work as well as the bromides. Methyltrioctylammonium chloride also catalyzes the reaction, but at a slower rate.



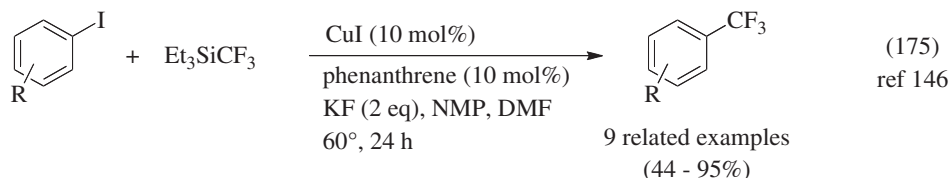
Indium trichloride or indium tribromide will catalyze the alkyl chloride alkylation of silyl enolates of aldehydes, ketones, esters, amides, thioesters (Eq. 171).<sup>144</sup> A three-component, single-pot alkylation/allylations or alkylation/alkynylations combinations are also possible with InBr<sub>3</sub> as the catalyst (Eqs. 172, 173).<sup>144</sup> Alkylations occur with alkyl chlorides capable of forming a strong carbocations. The yields are excellent.



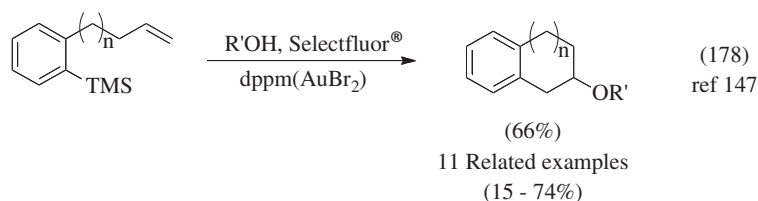
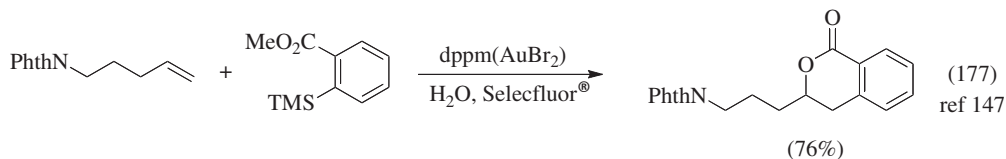
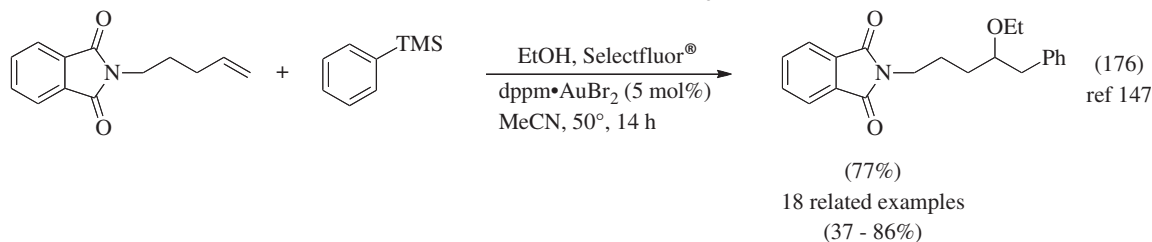
The formation of 1,4-dicarbonyl systems results from the formation of a C-C bond from a silyl bis-enol ether system (Eq. 174).<sup>145</sup> The overall connection of two  $\alpha$ -carbons is the net result of such a transformation.



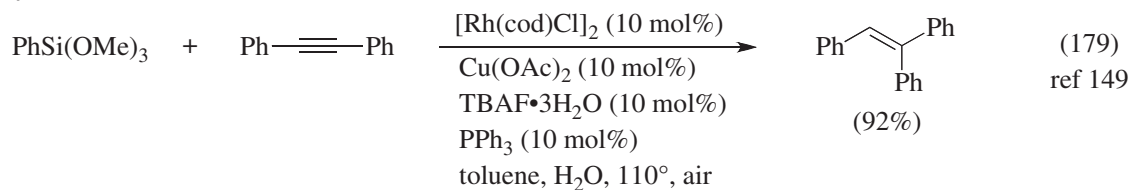
Triethyltrifluoromethylsilane can be employed to introduce the trifluoromethyl group onto aromatic rings in good yields under favorable conditions (Eq. 175).<sup>146</sup>



The alkoxyarylation of olefins can be accomplished via the reaction of the olefin with an alcohol and an aryltrimethylsilane in the presence of Selectfluor<sup>®</sup> and a gold catalyst (Eq. 176).<sup>147</sup> The use of the aryltrimethylsilane gives less homocoupling as compared with the results using an arylboronic acid. Intramolecular coupling works as well (Eqs. 177, 178). An extension of the intramolecular version of this transformation can also be done with Ph<sub>3</sub>AuCl under similar conditions.<sup>148</sup>

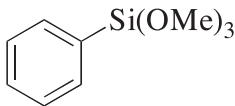
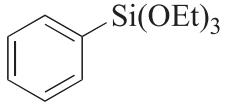
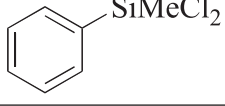
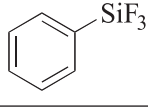
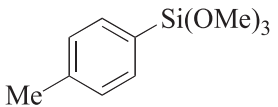
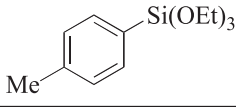
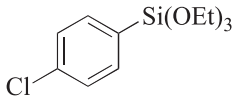
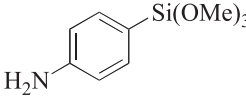
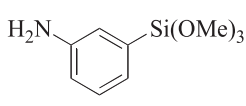


Under catalysis of the combination of Cu(OAc)<sub>2</sub>, [Rh(cod)Cl]<sub>2</sub> and promotion with TBAF the direct hydroarylation of acetylenes with arylsilyl esters results in the formation of a new C-C bond (Eq. 179).<sup>149</sup> The addition of the aryl and H groups is predominantly syn (cis). When carried out in the presence of D<sub>2</sub>O the addition of the aryl moiety and deuterium occurs across the triple bond. Unfortunately, only symmetrical acetylenes were investigated so that the question of regioselectivity has not been addressed.

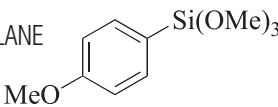
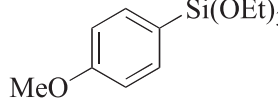
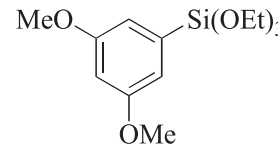
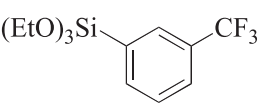
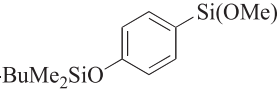
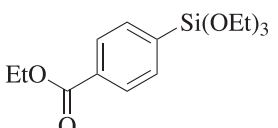
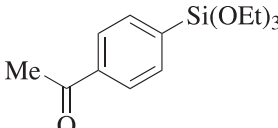
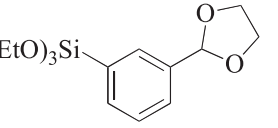
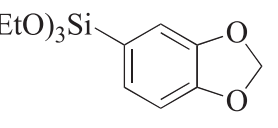
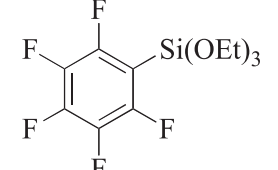
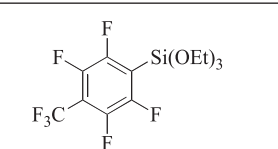


## TABLE 2 ORGANOSILANE CROSS-COUPLING AGENTS

### ARYLSILANE CROSS-COUPLING AGENTS

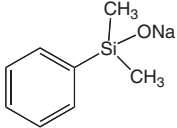
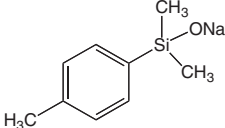
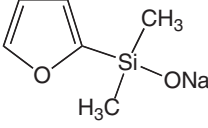
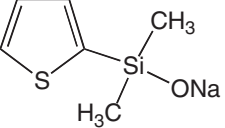
ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIP6822.0 PHENYLTRIMETHOXYSILANE [2996-92-1]		Cross-couples w/ aryl bromides w/o fluoride and w/ NaOH. <sup>61,191,152</sup> High yields w/ Pd and carbene ligands. <sup>73</sup> Cross-coupled in presence of aryl aldehyde. <sup>132</sup> Cross-coupled w/ alkynyl bromides and iodides. <sup>139</sup> N-arylates nitrogen heterocycles. <sup>152</sup> Reacts with 2° amines to give anilines. <sup>153</sup> Undergoes 1,4-addition to enones. <sup>82</sup> 1,2- and 1,4-addition to aldehydes. <sup>154</sup> Undergoes coupling <sup>26</sup> and asymmetric coupling w/ $\alpha$ -bromoesters. <sup>155</sup>	100g \$11.00 2kg \$98.00 18kg \$562.00
SIP6821.0 PHENYLTRIETHOXYSILANE [780-69-8]		Cross-couples w/ aryl bromides w/o amine or phosphine ligands. <sup>156</sup> Phenylates allyl acetates. <sup>65</sup> $\beta$ -phenylates enones under aqueous base conditions. <sup>157</sup>	100g \$11.00 2kg \$112.00 17kg \$510.00
SIP6738.0 PHENYLMETHYLDICHLOROSILANE [149-74-6]		Reacts well under the influence of NaOH versus fluoride activation w/ aryl chlorides, bromides, and iodides. <sup>158</sup>	25g \$12.00 500g \$64.00 18kg \$1224.00
SIP6821.5 PHENYLTRIFLUOROSILANE [368-47-8]		Cross-couples w/ aryl and vinyl triflates. <sup>159</sup> Couples w/ aryl bromides in presence of fluoride. <sup>160,161</sup> Couples with 2° alkyl bromides and iodides. <sup>26</sup>	50g \$108.00
SIT8042.0 <i>p</i> -TOLYLTRIMETHOXYSILANE [17873-01-7]		Example of aryltrimethoxysilane for cross-coupling application. Reacts w/ $\alpha$ -bromo esters to give $\alpha$ - <i>p</i> -tolyl esters. <sup>26</sup> Couples w/o fluoride in aqueous medium. <sup>162</sup> Michael adds to enones in aqueous medium. <sup>133</sup> Undergoes asymmetric coupling w/ $\alpha$ -bromoesters. <sup>155</sup>	10g \$38.00 50g \$152.00
SIT8041.0 <i>p</i> -TOLYLTRIETHOXYSILANE [79349-33-0]		Undergoes conjugate addition to enones. <sup>155</sup>	5g \$62.00
SIC2332.3 4-CHLOROPHENYLTRIETHOXYSILANE [21700-74-3]		Undergoes conjugate addition to enones. <sup>155</sup>	10g \$139.00
SIA0599.1 4-AMINOPHENYLTRIMETHOXYSILANE [33976-43-1]		Couples w/o fluoride in aqueous medium. <sup>162</sup>	5g \$110.00 100g \$1680.00
SIA0599.0 3-AMINOPHENYLTRIMETHOXYSILANE [70411-42-6]		Potential for introduction of <i>m</i> -anilino group.	5g \$94.00 100g \$1476.00






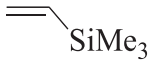

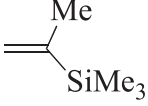
ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIM6492.55 <i>p</i> -METHOXYPHENYLTRIMETHOXSILANE [21130-91-6]		Undergoes asymmetric coupling w/ $\alpha$ -bromoesters. <sup>155</sup> Couples w/ heterocyclic amines. <sup>152</sup>	5g \$52.00
SIM6492.53 <i>p</i> -METHOXYPHENYLTRIETHOXSILANE [53392-03-3]		Undergoes conjugate addition to enones. <sup>157</sup>	5g \$65.00
SID3544.0 3,5-DIMETHOXYPHENYL- TRIETHOXSILANE		Reacts w/ aryl bromides and iodides.	5g \$175.00
SIT8343.0 3-TRIFLUOROMETHYL- PHENYLTRIMETHOXSILANE [53883-59-3]		Useful for introduction of <i>m</i> -trifluoromethylphenyl group.	2.5g \$210.00
SIB1939.65 4- <i>tert</i> -BUTYLDIMETHYL- SILOXYPHENYLTRIMETHOXSILANE		Useful for introduction of <i>p</i> -TBS-protected phenol group.	2.5g \$180.00
SIE4901.3 ETHYL 4-TRIETHOXSILYL- BENZOATE [197662-64-9]		Useful for preparation of derivatized benzoic acid esters.	2.5g \$260.00
SIT8177.0 4-TRIETHOXSILYL- ACETOPHENONE [438569-05-2]		Useful for preparation of acetophenone derivatives.	2.5g \$220.00
SIT8185.9 2-(3-TRIETHOXSILYL- PHENYL)-1,3-DIOXOLANE		Useful for the preparation of benzaldehyde derivatives.	5g \$175.00
SIM6509.0 3,4-METHYLENEDIOXY- PHENYLTRIETHOXSILANE [376353-50-3]		Used in the coupling to allyl carbonates and allyl benzoates. <sup>63,64</sup>	2.5g \$210.00
SIP6716.7 PENTAFLUOROPHENYL- TRIETHOXSILANE [20083-34-5]		Useful for the preparation of pentafluorophenyl derivatives.	5g \$82.00 25g \$328.00
SIT8345.0 4-TRIFLUOROMETHYLTETRA- FLUOROPHENYLTRIETHOXSILANE [561069-04-3]		Example of fluorinated arylsilane for cross-coupling.	5g \$102.00 25g \$408.00

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIN6596.8 1-NAPHTHYLTRIETHOXSILANE [18052-76-1]		Undergoes asymmetric coupling w/ $\alpha$ -bromoesters. <sup>155</sup>	5g \$180.00
SIN6597.0 1-NAPHTHYLTRIMETHOXSILANE [18052-76-1]		Undergoes asymmetric coupling w/ $\alpha$ -bromoesters. <sup>155</sup>	5g \$180.00
SID4535.0 DIPHENYLDIMETHOXSILANE [6843-66-9]		Alternative to phenyltrimethoxysilane for the cross-coupling of a phenyl group.	100g \$16.00 2kg \$190.00 18kg \$1152.00
SID4525.0 DIPHENYLDIETHOXSILANE [2553-19-7]		Alternative to phenyltriethoxysilane for the cross-coupling of a phenyl group.	25g \$18.00 100g \$58.00 2kg \$265.00 18kg \$1440.00
SID4599.0 DI(4-TOLYL)DIMETHOXSILANE [92779-72-1]		Alternative to <i>p</i> -tolyltrimethoxysilane.	25g \$158.00
SIP6934.0 3-PYRIDYLTRIETHOXSILANE [129663-08-7]		For preparation of 3-substituted pyridines.	5g \$190.00
SIP6932.0 2-PYRIDYLTRIETHOXSILANE, 95% [213602-91-6]		For preparation of 2-substituted pyridines.	5g \$135.00
SIP6936.0 4-PYRIDYLTRIETHOXSILANE [166262-04-0]		For preparation of 4-substituted pyridines.	5g \$190.00
SIP6923.0 (2-PYRIDYL)ALLYLDIMETHYLSILANE [118722-54-6]		Water and air-stable arylsilane for formation of 2-aryl pyridines. <sup>31</sup> Allylates aldehydes, ketones and imines. <sup>163</sup>	5g \$184.00
SIP6823.0 PHENYLTRIMETHYLSILANE [768-32-1]		Alternative to phenyltriethoxysilane or phenyltrimethoxysilane for the cross-coupling of a phenyl group.	25g \$36.00
SIC2334.0 4-CHLOROPHENYLTRIMETHYLSILANE [10557-71-8]		Introduction of the <i>p</i> -chlorophenyl group. Potential for formation of triaryls.	25g \$84.00
SIM6492.3 1-(4-METHOXYPHENYL)-1-CHLORO-1-SILACYCLOBUTANE [251453-07-3]		Example of aryl-substituted silacyclobutane useful for the transfer of an aryl group in cross-coupling applications. <sup>43</sup>	2.5g \$136.00
SIA6977.0 SODIUM ALLYLDIMETHYLSILANOLATE, 2M in THF			10g \$180.00

PLEASE INQUIRE ABOUT CUSTOM SYNTHESIS

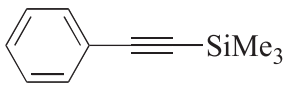
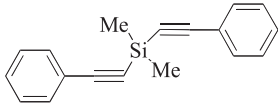
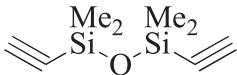
ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIS6986.1 SODIUM PHENYLDIMETHYLSILANOLATE, 2M in THF			10g \$90.00
SIS6983.0 SODIUM (4-METHYLPHENYL)- DIMETHYLSILANOLATE, 2M in THF			10g \$120.00
SIS6980.6 SODIUM (2-FURYL)DIMETHYLSILANOLATE, 2M in THF			10g \$175.00
SIS6987.0 SODIUM (2-THIENYL)DIMETHYLSILANOLATE, 2M in THF			10g \$175.00

**TABLE 3 ALKENYLSILANE CROSS-COUPLING AGENTS**

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIV9220.0 VINYLTRIMETHOXSILANE [2768-02-7]		For vinylations. Reacts w/ $\alpha$ -bromo esters to give $\alpha$ -vinyl esters in high ee. <sup>26</sup> Alkenyltrialkoxysilanes react w/ aryl bromides and iodides to form styrenes under fluoride- and ligand-free and aqueous conditions. <sup>45</sup> Reacts also in presence of fluoride. <sup>44</sup>	25g \$10.00 2kg \$96.00 16kg \$352.00
SIV9112.0 VINYLTRIETHOXSILANE [78-08-0]		For vinylations. Reacts with enamines to give (E)- $\beta$ -silylenamines, which cross-couple w/ aryl iodides to give $\beta$ -aryl enamines. <sup>28</sup>	25g \$10.00 2kg \$110.00 16kg \$472.00
SIV9072.0 VINYLDIMETHYLETHOXSILANE [5356-83-2]		Vinylates aryl halides. <sup>164</sup>	10g \$24.00 50g \$96.00
SIV9250.0 VINYLTRIMETHYLSILANE [754-05-2]		Undergoes Heck coupling to (E)- $\beta$ -substituted vinyltrimethylsilanes, which can then be cross-coupled further. <sup>165</sup>	10g \$16.00 100g \$114.00 1.5kg \$930.00
SIV9084.0 VINYL METHYLDICHLOROSILANE [124-70-9]		Reacts to vinylate aryl halides under NaOH-moderated conditions. <sup>158</sup>	25g \$11.00 2.5kg \$162.50 18kg \$621.00
SIP6905.0 2-PROPENYLTRIMETHYLSILANE [18163-07-0]		For introduction of the 2-propenyl moiety.	5g \$148.00

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIT7900.0 1,3,5,7-TETRAVINYL-1,3,5,7-TETRAMETHYL- CYCLOTETRASIOXANE [2554-06-5]		Excellent and inexpensive reagent for vinylations in cross-coupling reactions for the formation of styrenes and dienes. <sup>46,47,166</sup>	25g \$18.00 100g \$58.00 2kg \$390.00 17kg \$1356.00
SIT8737.0 1,3,5-TRIVINYL-1,3,5-TRIMETHYL- CYCLOTETRISIOXANE [3901-77-7]		Excellent reagent for vinylations in cross-coupling reactions for the formation of styrenes and dienes. <sup>47,164</sup>	5g \$31.00 25g \$124.00 2kg \$2800.00
SID4613.0 1,3-DIVINYLTETRAMETHYLDISILOXANE [2627-95-4]		Potential vinyl donor in cross-coupling reactions.	50g \$20.00 500g \$152.00 2kg \$380.00 15kg \$1800.00
SID4606.0 DIVINYLDIMETHYLSILANE [10519-87-6]		Potential vinyl donor in cross-coupling reactions.	5g \$28.00 25g \$112.00 1.5kg \$2730.00
SID4614.0 1,4-DIVINYLTETRAMETHYLDISILETHANE [84677-98-5]		Potential vinyl donor in cross-coupling reactions.	10g \$45.00 50g \$190.00
SIT7546.0 1,1,3,3-TETRAMETHYLDISILOXANE [3277-26-7]		Hydrosilylates terminal alkynes to form alkenylsilanes capable of cross-coupling w/ aryl and vinyl halides. <sup>86</sup>	25g \$15.00 250g \$105.00 1.5kg \$279.00
SIH5844.5 (E)-HEPTENYLDIISOPROPYLSILANOL [261717-41-3]		Stable silanol for cross-coupling of olefinic group. <sup>80,81,166</sup> Vinylsilanols couple w/ aryl triflates and nonflates. <sup>84</sup> Potassium salts are also reactive and do not require fluoride. <sup>167</sup>	2.5g \$275.00
SIB1910.0 1-BROMOVINYLTRIMETHYLSILANE [13683-41-5]		Useful for cross-coupling to 1-substituted vinylsilanes	5g \$116.00
SIB1910.1 2-BROMOVINYLTRIMETHYLSILANE [41309-43-7]		Useful for cross-coupling to 2-substituted vinylsilanes.	5g \$68.00
SIB1857.9 1,2-BIS(TRIMETHYLSILYL)ETHYLENE [1473-61-6]		Reacts w/ aryl iodides to form (E)-β-trimethylsilylstyrenes. <sup>121</sup>	10g \$176.00
SIB1941.0 4-(tert-BUTYLDIMETHYLSILOXY)STYRENE [84494-81-5]		Useful for Heck cross-coupling to substituted protected-hydroxy functional styrenes.	10g \$148.00

**TABLE 4 ALKYNYSILANE CROSS-COUPLING AGENTS**

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIE4904.0 ETHYNYLTRIMETHYLSILANE [1066-54-2]	$\text{H}-\text{C}\equiv\text{C}-\text{SiMe}_3$	Useful in Sonogashira reactions with differentiated reactivity at each terminus leading to unsymmetrical diaryl acetylenes. <sup>32</sup> Reacts w/ aryl aldehydes to give diethynylmethanes (1,4-diyne). <sup>53</sup>	5g \$29.00 25g \$116.00 1.5kg \$710.00 13kg \$3770.00
SIE4902.0 ETHYNYLTRIETHYLSILANE [1777-03-3]	$\text{H}-\text{C}\equiv\text{C}-\text{SiEt}_3$	More stable protected acetylene useful in Sonogashira reactions.	5g \$75.00 1.5kg \$4170.00
SIB1850.0 BIS(TRIMETHYLSILYL)ACETYLENE [14630-40-1]	$\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$	Useful in Sonogashira reactions.	10g \$32.00 50g \$126.00 1.5kg \$1275.00 13kg \$5655.00
SIT8606.5 1-TRIMETHYLSILYLPROPYLENE [6224-91-5]	$\text{Me}-\text{C}\equiv\text{C}-\text{SiMe}_3$	Useful in Sonogashira reactions.	5g \$24.00 25g \$96.00 1.5kg \$1200.00 13kg \$6175.00
SIP6736.0 PHENYLETHYNYLTRIMETHYLSILANE [2170-06-1]		Useful in trimethylsilyl-mediated Sonogashira reactions. <sup>52,56</sup> Arylethynylsilanes react w/ propargyl chlorides to form 1,2-diene-4-yne. <sup>54</sup> Ethynylsilanes react w/ propargyl halides to form 1,4-diyne. <sup>55</sup>	5g \$24.00 25g \$96.00
SIH5848.0 1-HEPTYNYLTRIMETHYLSILANE [15719-56-9]	$n\text{-C}_5\text{H}_{11}-\text{C}\equiv\text{C}-\text{SiMe}_3$	Useful in Sonogashira reactions. See SIP6736.0	10g \$102.00
SIB1760.0 BIS(PHENYLETHYNYL)DIMETHYLSILANE [2170-08-3]		Useful in Sonogashira reactions. See SIP6736.0	5g \$106.00
SID3425.0 1,3-BIS(ETHYNYL)TETRAMETHYL-DISILOXANE 18204-93-8]		Useful in Sonogashira reactions.	10g \$210.00
SIT8604.0 1-TRIMETHYLSILYLPROPARGYL ALCOHOL [5272-36-6]	$\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$	Useful in Sonogashira reactions to give substituted propargyl alcohols.	5g \$64.00 25g \$256.00 2kg \$3800.00
SIT8583.0 1-TRIMETHYLSILYLBUT-1-YNE-3-OL [6999-19-5]	$\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{Me})\text{H}$	Useful in Sonogashira reactions to give substituted propargyl alcohols.	10g \$41.00

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIT8606.3 3-TRIMETHYLSILYLPROPYNAL [2975-46-4]	$\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{CHO}$	Potential for the formation of alkynyl aldehydes.	25g \$134.00
SIT8623.0 TRIMETHYLSILYL(TRIMETHYL- SILYL)PROPYNOATE [97927-35-0]	$\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{CO}_2\text{SiMe}_3$	Potential for the formation of propiolic acid derivatives.	2.5g \$164.00
SIP6903.0 PROPARGYLOXYTRIMETHYLSILANE [5582-62-7]	$\text{H}-\text{C}\equiv\text{C}-\text{CH}_2\text{OSiMe}_3$	Useful in Sonogashira reactions to give substituted trimethylsilyl-protected propargyl alcohols.	25g \$64.00 2kg \$1840.00
SIB1939.5 4-(tert-BUTYLDIMETHYLSILOXY)- BUTYNE [78592-82-2]	$\text{H}-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{Bu-}t$	Potential for the formation of TBS-protected butynols.	10g \$70.00
SIT8606.6 3-TRIMETHYLSILYLPROPIONIC ACID [5683-31-8]	$\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$	Potential for the formation of propiolic acid derivatives.	5g \$124.00

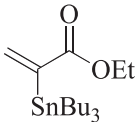
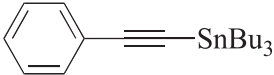
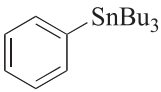
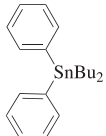
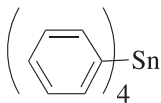
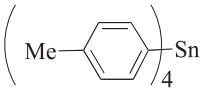
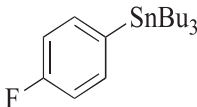
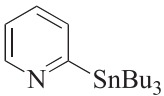
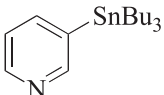
**TABLE 5 MISCELLANEOUS SILANE CROSS-COUPLING AGENTS**

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIC2568.0 CYCLOTRIMETHYLENEDICHLOROSILANE [2351-33-9]		Precursor for aryl-substituted silacyclobutanes useful for aryl cross-coupling reactions. <sup>43</sup>	10g \$54.00 50g \$216.00
SIC2572.0 CYCLOTRIMETHYLENE- METHYLCHLOROSILANE [2351-34-0]		Precursor for aryl- and vinyl-substituted silacyclobutanes useful for aryl cross-coupling reactions. <sup>42,43,168</sup>	5g \$102.00
SIB0971.0 BENZYLTRIETHOXSILANE [2549-99-7]		Transfer of benzyl group possible.	10g \$42.00 50g \$168.00
SIB0962.0 BENZYLDIMETHYLCHLOROSILANE [1833-31-4]		Useful for the preparation of benzyldimethylsilyl derivatives wherein the benzyl group is a latent reactive group on silicon. <sup>29,40</sup>	10g \$46.00 50g \$184.00
SIB0964.0 BENZYLDIMETHYLSILANE [1631-70-5]		Useful for the preparation of benzyldimethylsilyl derivatives wherein the benzyl group is a latent reactive group on silicon. <sup>39</sup>	10g \$38.00 50g \$152.00
SIA0555.0 ALLYLTRIMETHYLSILANE [762-72-1]		Reacts w/ vinyl bromides to give 1,4-dienes and w/ allyl bromides to give 1,5-dienes. <sup>27</sup>	25g \$32.00 100g \$104.00 1.5kg \$720.00

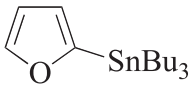
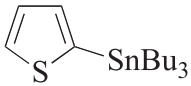

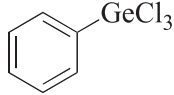
ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIA0540.0 ALLYLTRIMETHOXYSILANE [2551-83-9]		Allylates aryl iodides. <sup>67</sup>	10g \$24.00 50g \$96.00 2kg \$840.00
SIH6110.0 HEXAMETHYLDISILAZANE [999-97-3]		Lithium reagent reacts w/ aryl chlorides or bromides to provide anilines. <sup>141</sup>	25g \$10.00 1.5kg \$60.00 14kg \$305.00
SIL6467.0 LITHIUM HEXAMETHYLDISILAZIDE [4039-32-1]		Reacts w/ aryl chlorides or bromides to give anilines. <sup>141</sup>	25g \$16.00 100g \$52.00 2kg \$832.00
SIT8579.0 TRIMETHYLSILYLACETONITRILE [18293-53-3]	$\text{Me}_3\text{Si}-\text{CH}_2\text{CN}$	Cyanomethylates aryl bromides. <sup>140</sup>	5g \$52.00 25g \$208.00
SIP6901.0 POTASSIUM TRIMETHYLSILANOLATE [10519-96-7]	$\text{Me}_3\text{Si}-\text{O}-\text{K}$	Catalyst for the cross-coupling of aryl and vinylsilanes. <sup>165</sup>	25g \$21.00 100g \$68.00 2kg \$1160.00
SIP6899.0 POTASSIUM TRIETHYLSILANOLATE	$\text{Et}_3\text{Si}-\text{O}-\text{K}$	Catalyst for the cross-coupling of aryl and vinylsilanes. <sup>165</sup>	10g \$60.00 50g \$240.00
SID3395.2 1,2-DIETHOXYTETRAMETHYLDISILANE	$\text{EtOMe}_2\text{Si}-\text{SiMe}_2\text{OEt}$	Useful for the preparation of aryl- and vinylsilanols.	

**TABLE 6 ORGANOTIN CROSS-COUPLING AGENTS**

ORGANOTIN	STRUCTURE	COMMENTS	PRICING
SNE4620 1-ETHOXYVINYLTRI- <i>n</i> -BUTYL TIN [99674-02-7]		Transfer of acyl group equivalent in Stille Coupling	5g \$72.00 25g \$288.00 2kg \$4800.00
SNV9100 VINYLTRI- <i>n</i> -BUTYL TIN [7486-35-3]		Stille Coupling vinylation reagent	5g \$56.00 25g \$224.00 2kg \$4800.00
SND4600 DIVINYLDIMETHYL TIN [7330-43-0]		Stille Coupling vinylation reagent	5g \$42.00
SNT7906 TETRAVINYL TIN [1112-56-7]		Stille Coupling vinylation reagent	5g \$56.00 25g \$224.00
SNB1794 (E)-1,2-BIS(TRI- <i>n</i> -BUTYL-STANNYL)ETHYLENE [14275-61-7]		$\beta$ -Tri- <i>n</i> -butylstannylvinyl group or reagent for the formation of stilbenes	5g \$260.00

ORGANOTIN	STRUCTURE	COMMENTS	PRICING
SNE4900.3 ETHYL 2-(TRI- <i>n</i> -BUTYL TIN)- PROPENOATE [128266-87-5]		Transfer of ethyl 1-acrylate group for formation of $\alpha$ -substituted acrylates	2.5g \$92.00
SNE4900 ETHYNYLTRI- <i>n</i> -BUTYL TIN [994-89-8]	$\text{H}-\equiv-\text{SnBu}_3$	Transfer of ethynyl group.	2.5g \$57.00 10g \$186.00
SNP6925 PROPYNYLTRI- <i>n</i> -BUTYL TIN [64099-82-7]	$\text{H}_3\text{C}-\equiv-\text{SnBu}_3$	Transfer of propynyl group.	5g \$146.00
SIT8588.8 TRIMETHYLSILYLETHYNYLTRI- <i>n</i> - BUTYL TIN [81353-38-0]	$\text{Me}_3\text{Si}-\equiv-\text{SnBu}_3$	Transfer of trimethylsilylethynyl group.	10g \$92.00
SNP6734 PHENYLETHYNYLTRI- <i>n</i> -BUTYL TIN [3757-88-8]		Transfer of phenylethynyl group.	10g \$36.00
SNP6740 PHENYLTRI- <i>n</i> -BUTYL TIN [960-16-7]		Stille Coupling phenylation reagent.	10g \$58.00 50g \$232.00
SND4505 DIPHENYLDI- <i>n</i> -BUTYL TIN [6452-61-5]		Stille Coupling phenylation reagent.	25g \$40.00 100g \$130.00
SNT7760 TETRAPHENYL TIN [595-90-4]		Stille Coupling phenylation reagent.	100g \$39.00 500g \$156.00
SNT7894 TETRA( <i>p</i> -TOLYL) TIN [6746-22-1]		Stille Coupling <i>p</i> -tolylation reagent.	10g \$48.00 50g \$192.00
SNF4915 4-FLUOROPHENYLTRI- <i>n</i> -BUTYL TIN [17151-47-2]		Stille Coupling <i>p</i> -fluorophenyl transfer reagent.	5g \$196.00
SNP6935 2-PYRIDYLTRI- <i>n</i> -BUTYL TIN [17997-47-6]		Stille Coupling for formation of 2-pyridyl derivatives.	5g \$72.00
SNP6936 3-PYRIDYLTRI- <i>n</i> -BUTYL TIN [59020-10-9]		Stille Coupling for formation of 3-pyridyl derivatives.	2.5g \$124.00



ORGANOTIN	STRUCTURE	COMMENTS	PRICING
SNT8125 2-TRI- <i>n</i> -BUTYLSTANNYL FURAN [118486-94-5]		Stille Coupling for formation of 2-furanyl derivatives.	10g \$48.00
SNT7909 2-TRI- <i>n</i> -BUTYLSTANNYLTHIOPHENE [54663-78-4]		Stille Coupling for formation of 2-thienyl derivatives.	10g \$32.00
SNT8585 TRIMETHYLSILYLTRI- <i>n</i> -BUTYL TIN [17995-46-3]	$\text{Me}_3\text{Si}-\text{SnBu}_3$	Undergoes addition to olefins.	2.5g \$36.00 10g \$117.00
GEV9200 VINYLTRIETHYLGERMANE [6207-41-0]		Vinylation reagent.	2.5g \$116.00
GEP6800 PHENYLTRICHLOROGERMANE [1074-29-9]		Phenylation reagent.	2.5g \$70.00 10g \$228.00

## Summary and Conclusions

The expanding applications of cross-coupling reactions in organic syntheses have placed these reactions in the sphere of providing short and efficient routes to starting materials for sophisticated syntheses. Moreover, they provide excellent protocols for the preparation of intermediates and final active pharmaceutical ingredients. Their applications have spread to the syntheses of complicated multiaryl systems of importance in several electronic fields. As illustrated with the examples presented in this brochure the organosilane approach is viable for a range of cross-coupling combinations. Due in part to their earlier discovery as well as their excellent results, the metal components needed in the cross-coupling methodologies have been dominated by boron, zinc and tin systems. Based on the wide-ranging examples presented in this brochure, the author feels that the advantages of ease of handling, templating potential, and non-toxicity of the organosilanes will serve to promote the organosilane approaches to the carbon-carbon bond formation via cross-coupling and as viable alternatives to these more-established systems.

## References

1. a. de Meijere, A.; Diederich, F. Eds. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, 2004. b. Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem. Int. Ed.* **1990**, *29*, 977. c. Negishi, E. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley-Interscience: New York, 2002. d. Pd-catalyzed cross-coupling: Littke, A. F.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 4176.
2. Silicon-based cross-coupling: a. Denmark, S. E.; Sweis, R. F. *Chem. Pharm. Bull.* **2002**, *50*, 1531. b. Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F. Stang, P. J. Eds. Wiley-VCH: Weinheim, 1998; Chapter 10. c. Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471. d. Hatanaka, Y.; Hiyama, T. *Synlett.* **1991**, 845. e. Denmark, S. E.; Sweis, R. F. *Acct. Chem. Res.* **2002**, *35*, 835.
3. Mitchell, T. N. In *Metal-Catalyzed Cross-coupling Reactions*; Diederich, F.; Stang, P. J. Eds. Wiley-VCH: Weinheim, Germany, 1998; Chapter 4.
4. Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1.
5. Miyaoura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
6. Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213.
7. Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 2632.
8. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975** *16*, 4467.
9. Denmark, S. E.; Butler, C. R. *Chem. Commun.* **2009**, 20.
10. Denmark, S. E. *J. Org. Chem.* **2009**, *74*, 2915.
11. Slagt, V. F.; de Vries, A. H. M.; de Vries, J. G.; Kellogg, R. M. *Org. Proc. Res. Dev.* **2010**, *14*, 30.
12. Stefani, H. A.; Guarezemini, A. S.; Rodrigo Cella, R. *Tetrahedron* **2010**, *66*, 7871.
13. Rauf, W.; Hazari, A.; Gouverneur, V.; Brown, J. M. *Pure Appl. Chem.* **2010**, *82*, 1415.
14. a. Palladium-Catalyzed. Cross-Coupling Reactions in Total Synthesis: Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem. Int. Ed.* **2005**, *44*, 4442. b. Denmark, S. E.; Liu, J. H-C. *Angew. Chem. Int. Ed.* **2010**, *49*, 2978.
15. Chen, J.; Tanaka, M.; Sahoo, A. K.; Takeda, M.; Yada, A.; Nakao, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 554.
16. Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 58.
17. Hiyama, T.; Hatanaka, Y. *Pure & Appl. Chem.* **1994**, *66*, 1471.
18. Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 58.
19. Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1989**, *54*, 268.
20. Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, *1*, 542.
21. Lerebours, R.; Wolf, C. *Synthesis* **2005**, 2287.
22. Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1989**, *54*, 268.
23. Beaulieu, L.-P. B.; Delvos, L. B.; Charette, A. B. *Org. Lett.* **2010**, *12*, 1348.
24. Powell, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 7788.
25. Schweizer, S. A.; Bach, T. *Synlett* **2010**, 81.
26. Strotman, N. A.; Sommer, S.; Fu, G. C. *Angew. Chem. Int. Ed.* **2007**, *46*, 3556.
27. Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.
28. Marciniak, B.; Majchrzak, M.; Prukala, W.; Kubicki, M.; Chadyniak, D. *J. Org. Chem.* **2005**, *70*, 8550.
29. Zhao, Z.; Snieckus, V. *Org. Lett.* **2005**, *7*, 2523.
30. Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett.* **2005**, *7*, 697.
31. Nokami, T.; Tomida, Y.; Kamei, T.; Itami, K.; Yoshida, J. *Org. Lett.* **2006**, *8*, 729.
32. Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199.
33. Denmark, S. E.; Fujimori, S. *J. Am. Chem. Soc.* **2005**, *127*, 8971.

34. Trost, B. M.; Frederiksen, M. U.; Papillon, J. P. N.; Harrington, P. E.; Shin, S.; Shireman, B. T. *J. Am. Chem. Soc.* **2005**, *127*, 3666.
35. Wang, Y.; Watson, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 2536.
36. Chen, L.; Roger, J.; Bruneau, C.; Dixneuf, P. H.; Doucet, H. *Chem. Commun.* **2011**, 1872.
37. Alvisi, D.; Blart, E.; Bonini, B. F.; Mazzanti, G.; Ricci, A.; Zani, P. *J. Org. Chem.* **1996**, *61*, 7139.
38. Singh, R.; Singh, G. C.; Ghosh, S.K. *Eur. J. Org. Chem.* **2007**, 5376.
39. Denmark, S. E.; Liu, J. H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 3737.
40. Trost, B. M.; Machacek, M. R.; Ball, Z. T. *Org. Lett.* **2003**, *5*, 1895.
41. Trost, B. M.; Frederiksen, M. U.; Papillon, J. P. N.; Harrington, P. E.; Shin, S.; Shireman, B. T. *J. Am. Chem. Soc.* **2005**, *127*, 3666.
42. Denmark, S. E.; Choi, J. Y. *J. Am. Chem. Soc.* **1999**, *121*, 5821.
43. Denmark, S. E.; Wu, Z. *Org. Lett.* **1999**, *1*, 1495.
44. Alacid, E.; Nájera, C. *Adv. Synth. Catal.* **2006**, *348*, 2085.
45. Alacid, E.; Nájera, C. *J. Org. Chem.* **2008**, *73*, 2315.
46. Denmark, S. E.; Butler, C. R. *Org. Lett.* **2006**, *8*, 63.
47. Denmark, S. E.; Wang, Z. *J. Organomet. Chem.* **2001**, *624*, 372.
48. Li, L.; Navasero, N. *Org. Lett.* **2004**, *6*, 3091.
49. Thiot, C.; Mioskowski, C.; Wagner, A. *Eur. J. Org. Chem.* **2009**, 3219.
50. Chang, S.; Yang, S. H.; Lee, P. H. *Tetrahedron Lett.* **2001**, *42*, 4833.
51. Denmark, S. E.; Tymonko, S. A. *J. Org. Chem.* **2003**, *68*, 9151.
52. Yang, C.; Nolan, S. P. *Organometallics* **2002**, *21*, 1020.
53. Girard, D.; Broussous, S.; Provot, O.; Brion, J.-D.; Alami, M. *Tetrahedron Lett.* **2007**, *48*, 6022.
54. Montel, F.; Beaudegnies, R.; Kessabi, J.; Martin, B.; Muller, E.; Wendeborn, S.; Jung, P. M. *Org. Lett.* **2006**, *8*, 1905.
55. Kuninobu, Y.; Ishii, E.; Takai, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 3296.
56. Nishihara, Y.; Ikegashira, K.; Hirabayashi, K.; Ando, J.; Mori, A.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 1780.
57. Horita, A.; Tsurugi, H.; Funayama, A.; Satoh, T.; Miura, M. *Org. Lett.* **2007**, *9*, 2231.
58. Hoshi, M.; Iizawa, T.; Okimoto, M.; Shirakawa, K. *Synthesis* **2008**, 3591.
59. Nishihara, Y.; Inoue, E.; Ogawa, D.; Okada, Y.; Noyori, S.; Takagi, K. *Tetrahedron Lett.* **2009**, *50*, 4643.
60. Ghasemi, H.; Antunes, L. M.; Organ, M. G. *Org. Lett.* **2004**, *6*, 2913.
61. Shi, S.; Zhang, Y. *J. Org. Chem.* **2007**, *72*, 5927.
62. Seganish, W. M.; DeShong, P. *Org. Lett.* **2006**, *8*, 3951.
63. Correia, R.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7159.
64. Shukla, K. H.; Boehmier, D. J.; Bogacyzk, S.; Duvall, B. R.; Peterson, W. A.; McElroy, W. T.; DeShong, P. *Org. Lett.* **2006**, *8*, 4183.
65. Kabalka, G. W.; Dong, G.; Venkataiah, B.; Chen, C. *J. Org. Chem.* **2005**, *70*, 9207.
66. Riggelman, S.; DeShong, P. *J. Org. Chem.* **2003**, *68*, 8106.
67. Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 1684.
68. Ranu, B. C.; Dey, R.; Chattopadhyay, K. *Tetrahedron Lett.* **2008**, *49*, 3430.
69. So, C. M.; Lee, H. W.; Lau, C. P.; Kwong, F. Y. *Org. Lett.* **2009**, *11*, 317.
70. Ju, J.; Nam, H.; Jung, H. M.; Lee, S. *Tetrahedron Lett.* **2006**, *47*, 8673.
71. Zhang, L.; Wu, J. *J. Am. Chem. Soc.* **2008**, *130*, 12250.
72. Zhang, L.; Qing, J.; Yang, P.; Wu, J. *Org. Lett.* **2008**, *10*, 4971.
73. Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053.
74. Raders, S. M.; Kingston, J. V.; Verkade, J. G. *J. Org. Chem.* **2010**, *75*, 1744.
75. Liang, Z.; Yao, B.; Zhang, Y. *Org. Lett.* **2010**, *12*, 3185.
76. Simmons E. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 17092.
77. Yang, S.; Li, B.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 6066.
78. Denmark, S. E.; Kallemeyn, J. M. *Org. Lett.* **2003**, *5*, 3483.
79. Hirabayashi, K.; Mori, A.; Kawashima, J.; Suguro, M.; Nishihara, Y.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 5342.
80. Denmark, S. E.; Sweis, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 6439.
81. Denmark, S. E.; Pan, W. *J. Organomet. Chem.* **2002**, *653*, 98.
82. Denmark, S. E. Neuville, L. *Org. Lett.* **2000**, *2*, 3221.
83. Denmark, S. E.; Ober, M. H. *Org. Lett.* **2003**, *5*, 1357.
84. Denmark, S. E.; Sweis, R. F. *Org. Lett.* **2002**, *4*, 3771.

85. Denmark, S. E.; Tymonko, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 8004.
86. Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073.
87. Denmark, S. E.; Baird, J. D. *Chem. Eur. J.* **2006**, *12*, 4954.
88. Denmark, S. E.; Smith, R. C.; Chang, W-T. T.; Muhuhi, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 3104.
89. Denmark, S. E.; Smith, R. C.; Tymonko, S. A. *Tetrahedron* **2007**, *63*, 5730.
90. Denmark, S. E.; Baird, J. D. *Org. Lett.* **2006**, *8*, 793.
91. Denmark, S. E.; Baird, J. D. *Tetrahedron* **2009**, *65*, 3120.
92. Hosoi, K.; Nozaki, K.; Hiyama, T. *Chem. Lett.* **2002**, 138.
93. Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49.
94. Vitale, M.; Prestat, G.; Lopes, D.; Madec, D.; Kammerer, C.; Poli, G.; Girnita, L. *J. Org. Chem.* **2008**, *73*, 5795.
95. Itami, K.; Mitsudo, K.; Kamei, T.; Koike, T.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122*, 12013.
96. Itami, K.; Nokami, T.; Ishimura, Y.; Mitsudo, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 11577.
97. Itami, K.; Ushioji, Y.; Nokami, T.; Ohashi, Y.; Yoshida, J. *Org. Lett.* **2004**, *6*, 3695.
98. Itami, K.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 5600.
99. Nakao, Y.; Sahoo, A. K.; Yada, A.; Chen, J.; Hiyama, T. *Sci. Tech. Adv. Mat.* **2006**, *7*, 536.
100. Son, E.-C.; Tsuji, H.; Saeki, T.; Tamao, K. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 492.
101. Nakao, Y.; Imanaka, H.; Chen, J.; Yada, A.; Hiyama, T. *J. Organomet. Chem.* **2007**, *692*, 585.
102. Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, *127*, 6952.
103. Nakao, Y.; Ebata, S.; Chen, J.; Imanaka, H.; Hiyama, T. *Chem. Lett.* **2007**, 606.
104. Nakao, Y.; Chen, J.; Tanaka, M.; Hiyama, T. *J. Am. Chem. Soc.* **2007**, *129*, 11694.
105. Nakao, Y.; Takeda, M.; Matsumoto, T.; Hiyama, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 4447.
106. Tang, S.; Takeda, M.; Nakao, Y.; Hiyama, T. *Chem. Commun.* **2011**, 307.
107. Akai, S.; Ikawa, T.; Takayanagi, S.; Morikawa, Y.; Mohri, S.; Tsubakiyama, M.; Egi, M.; Wada, Y.; Kita, Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 7673.
108. Denmark, S. E.; Pan, W. *Org. Lett.* **2001**, *3*, 61.
109. Denmark, S. E.; Pan, W. *Org. Lett.* **2002**, *4*, 4163.
110. Denmark, S. E.; Pan, W. *Org. Lett.* **2003**, *5*, 1119.
111. Pidaparathi, R. R.; Welker, M. E.; Day, C. S.; Wright, M. W. *Org. Lett.* **2007**, *9*, 1623.
112. Denmark, S. E.; Yang, S.-M. *Org. Lett.* **2001**, *3*, 1749.
113. Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 15196.
114. Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 2102.
115. Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2004**, *126*, 12432.
116. Denmark, S. E.; Muhuhi, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 11768.
117. Denmark, S. E.; Kallemeyn, J. M. *J. Org. Chem.* **2005**, *70*, 2839.
118. Singh, R.; Singh, G. C.; Ghosh, S. K. *Tetrahedron Lett.* **2005**, *46*, 4719.
119. Hirabayashi, K.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Org. Lett.* **1999**, *1*, 299.
120. Hirabayashi, K.; Nishihara, Y.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 7893.
121. Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1773.
122. Zhou, H.; Xu, Y.-H.; Chung, W.-J.; Loh, T.-P. *Angew. Chem. Int. Ed.* **2009**, *48*, 5355.
123. Kita, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2010**, *12*, 1864.
124. Cunico, R. F.; Pandey, R. K. *J. Org. Chem.* **2005**, *70*, 5344.
125. Cunico, R. F.; Pandey, R. K. *J. Org. Chem.* **2005**, *70*, 9048.
126. Cunico, R. F.; Maity, B. C. *Org. Lett.* **2002**, *4*, 4357.
127. Cunico, R. F.; Maity, B. C. *Org. Lett.* **2003**, *5*, 4947.
128. Denmark, S. E.; Werner, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 16382.
129. Denmark, S. E.; Werner, N. S. *J. Am. Chem. Soc.* **2010**, *132*, 3612.
130. Tomita, D.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2005**, *127*, 4138.
131. Aikawa, K.; Hioki, Y.; Mikami, K. *Org. Lett.* **2010**, *12*, 5716.
132. Lerebours, R.; Wolf, C. *J. Am. Chem. Soc.* **2006**, *128*, 13052.
133. Lerebours, R.; Wolf, C. *Org. Lett.* **2007**, *9*, 2737.
134. Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Chem. Lett.* **2003**, 752.
135. Nishimura, T.; Tokuji, S.; Sawano, T.; Hayashi, T. *Org. Lett.* **2009**, *11*, 3222.
136. Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N. *Organometallics* **2005**, *24*, 5025.
137. Lee, K.; Hoveyda, A. H. *J. Org. Chem.* **2009**, *74*, 4455.

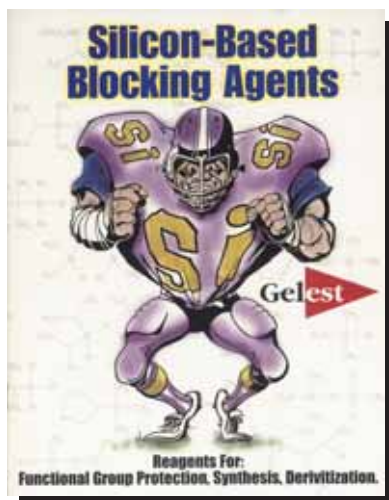
138. Gini, F.; Hessen, B.; Feringa, B. L.; Minnaard, A. J. *Chem. Commun.* **2007**, 710.
139. Lee, J.-Y.; Fu, G. C. *J. Am. Chem. Soc.*, **2003**, *125*, 5616.
140. Wu, L.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 15824.
141. Lee, S.; Jorgensen, M.; Hartwig, J. F. *Org. Lett.* **2001**, *3*, 2729.
142. Su, W.; Raders, S.; Verkade, J. G.; Liao, X.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2006**, *45*, 5852.
143. Huang, D. S.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 5757.
144. Nishimoto, Y.; Yasuda, M.; Baba, A. *Org. Lett.* **2007**, *9*, 4931.
145. Cliff, M. D.; Taylor, C. N.; Thomson, R. J. *Org. Lett.* **2007**, *9*, 4667.
146. Oishi, M.; Kondo, H.; Amii, H. *Chem. Commun.* **2009**, 1909.
147. Brenzovich, Jr., W. E.; Brazeau, J.-F.; Toste, F. D. *Org. Lett.* **2010**, *12*, 4728.
148. Ball, L. T.; Green, M.; Lloyd-Jones, G. C.; Russell, C. A. *Org. Lett.* **2010**, *12*, 4724.
149. Lin, B.; Liu, M.; Ye, Z.; Zhang, Q.; Cheng, J. *Tetrahedron Lett.* **2009**, *50*, 1714.
150. Alacid, E.; Nájera, C. *Adv. Synth. Catal.* **2006**, *348*, 945.
151. Gordillo, A.; de Jesus, E.; Lopez-Mardomino, C. *Org. Lett.* **2006**, *8*, 3517.
152. Song, R.-J.; Deng, C.-L.; Xie, Y.;-X.; Li, J.-H. *Tetrahedron Lett.* **2007**, *48*, 7845.
153. Lam, P. Y. S.; Deudon, S.; Averill, K. M.; Ming, R. L.; DeShong, P.; Clark, C. G. *J. Am. Chem. Soc.* **2000**, *122*, 7600.
154. Murata, M.; Shimazaki, R.; Ishikura, M.; Watanabe, S.; Masuda, Y. *Synthesis*, 2002, 717.
155. Dai, X.; Strotman, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 3302.
156. Mino, T.; Shirae, Y.; Saito, T.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2006**, *71*, 9499.
157. Denmark, S. E.; Amishiro, N. *J. Org. Chem.* **2003**, *68*, 6997.
158. Hagiwara, E.; Gouda, K.; Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 439.
159. Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1990**, *31*, 2719.
160. Matsubashi, H.; Kuroboshi, M.; Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 6507.
161. Matsubashi, H.; Asai, S.; Hirabayashi, K.; Hatanaka, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 437.
162. Wolf, C.; Lerebours, R. *Org. Lett.* **2004**, *6*, 1147.
163. Kamel, T.; Fujita, K.; Itami, K.; Yoshida, J. *Org. Lett.* **2005**, *7*, 4725.
164. Denmark, S. E.; Butler, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 3690.
165. Jeffery, T. *Tetrahedron Lett.* **1999**, *40*, 1673.
166. Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565.
167. Denmark, S. E.; Kallemeyn, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 15958.
168. Denmark, S. E.; Wang, Z. *Synthesis* **2000**, 999.



# Gelest Synthetic Chemistry Product Literature

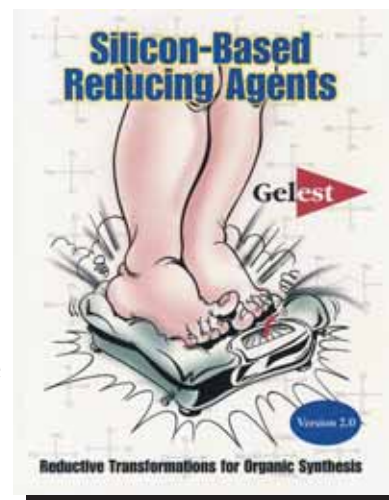
## *Silicon-Based Blocking Agents*

These silicon reagents are used for functional group protection, synthesis and derivatization. The 32 page brochure presents detailed application information on silylation reagent for pharmaceutical synthesis and analysis. Detailed descriptions are presented on selectivity for reactions, resistance to chemical transformations and selective deblocking conditions. Over 780- references are provided.



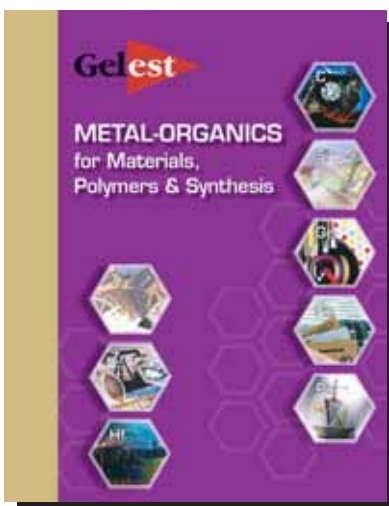
## *Silicon-Based Reducing Agents*

These silicon-based reagents are employed in the reduction of various organic and inorganic systems. The 32 page brochure presents information complete with literature references for a variety of reductions using organosilanes.



## *Metal-Organics for Material & Polymer Technology*

The latest Gelest catalog provides many new compounds with applications on optical, microelectronic, diagnostic and materials applications. Highly referenced listings and device applications are presented.



## *Silicon Compounds Silanes & Silicones*

Detailed chemical properties and reference articles for over 1500 compounds. The 592 page catalog of silane and silicone chemistry includes scholarly reviews as well as detailed application information.



