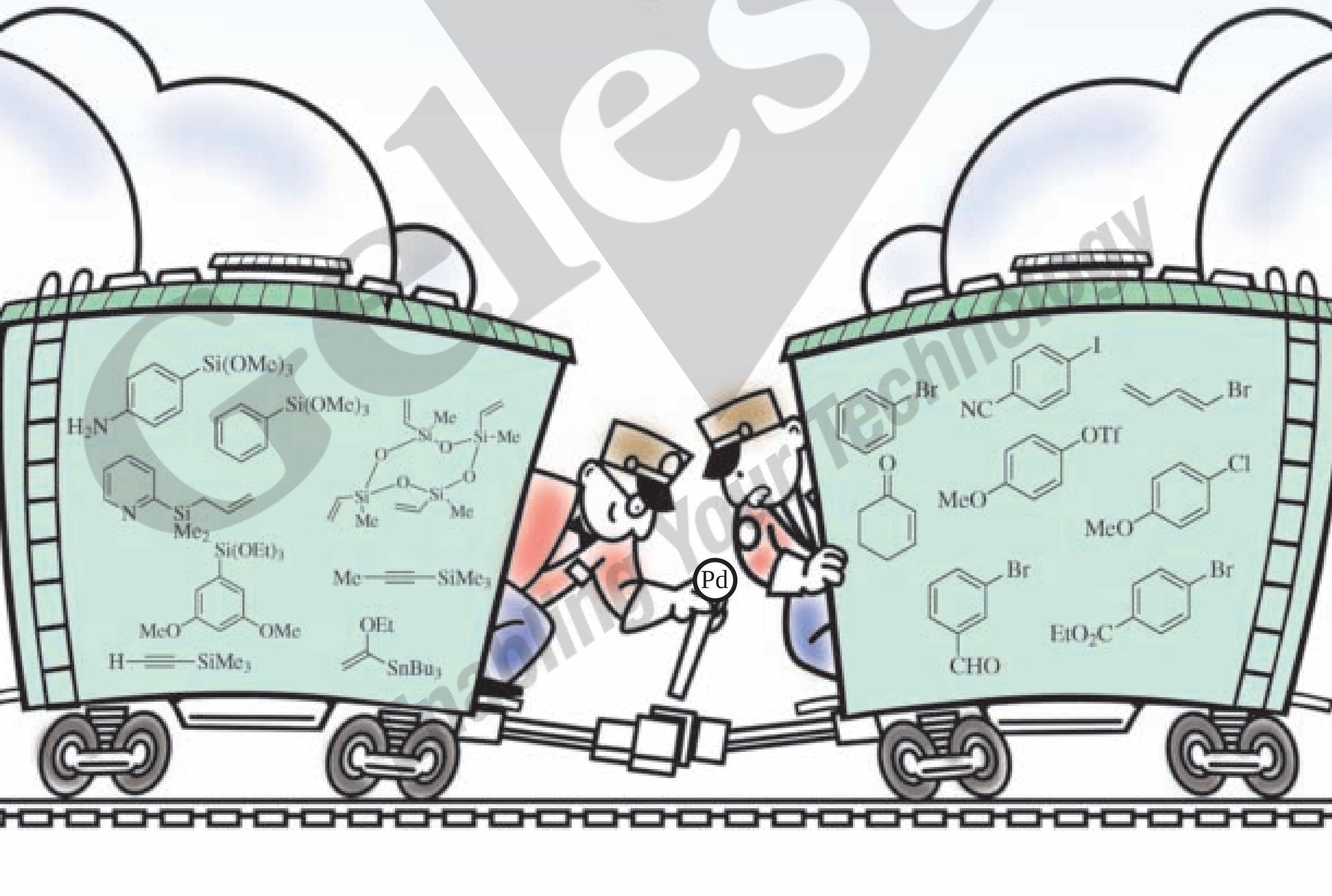
Silicon-Based Cross-Coupling Reagents

Gelest



Reagents For:

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

Gelest, Inc.

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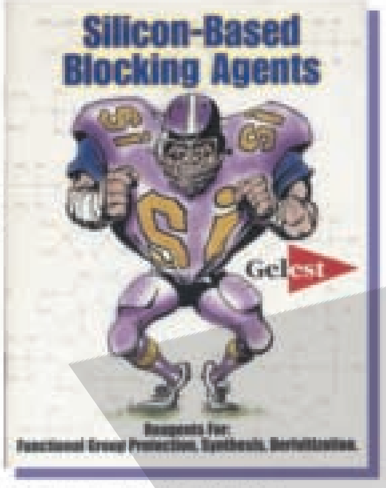
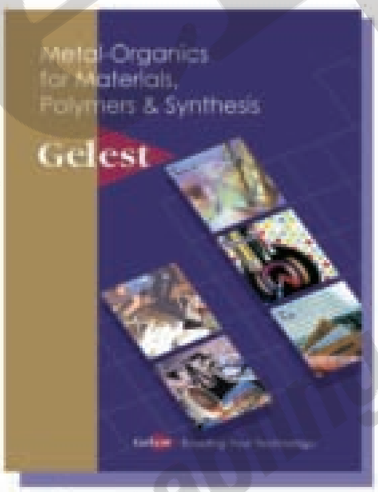


Silicon-Based Blocking Agents

These silicon reagents are used for functional group protection, synthesis and derivatization. The 32 page brochure presents detailed application information on silylation reagents 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.



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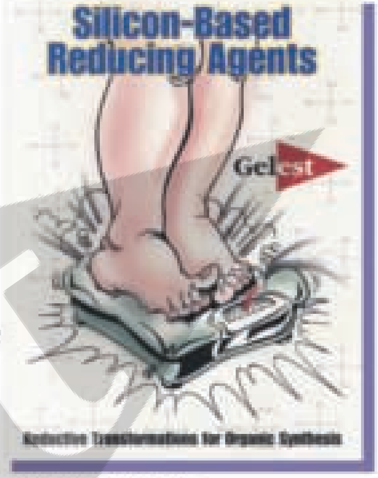
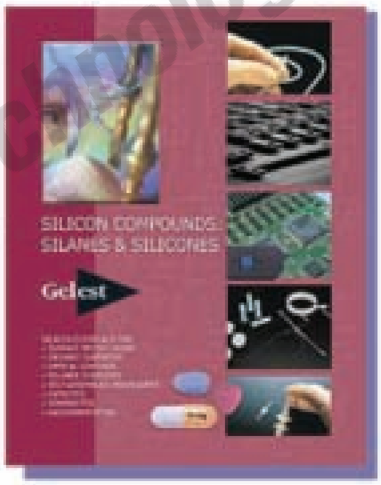


Silicon Based Reducing Agents

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.



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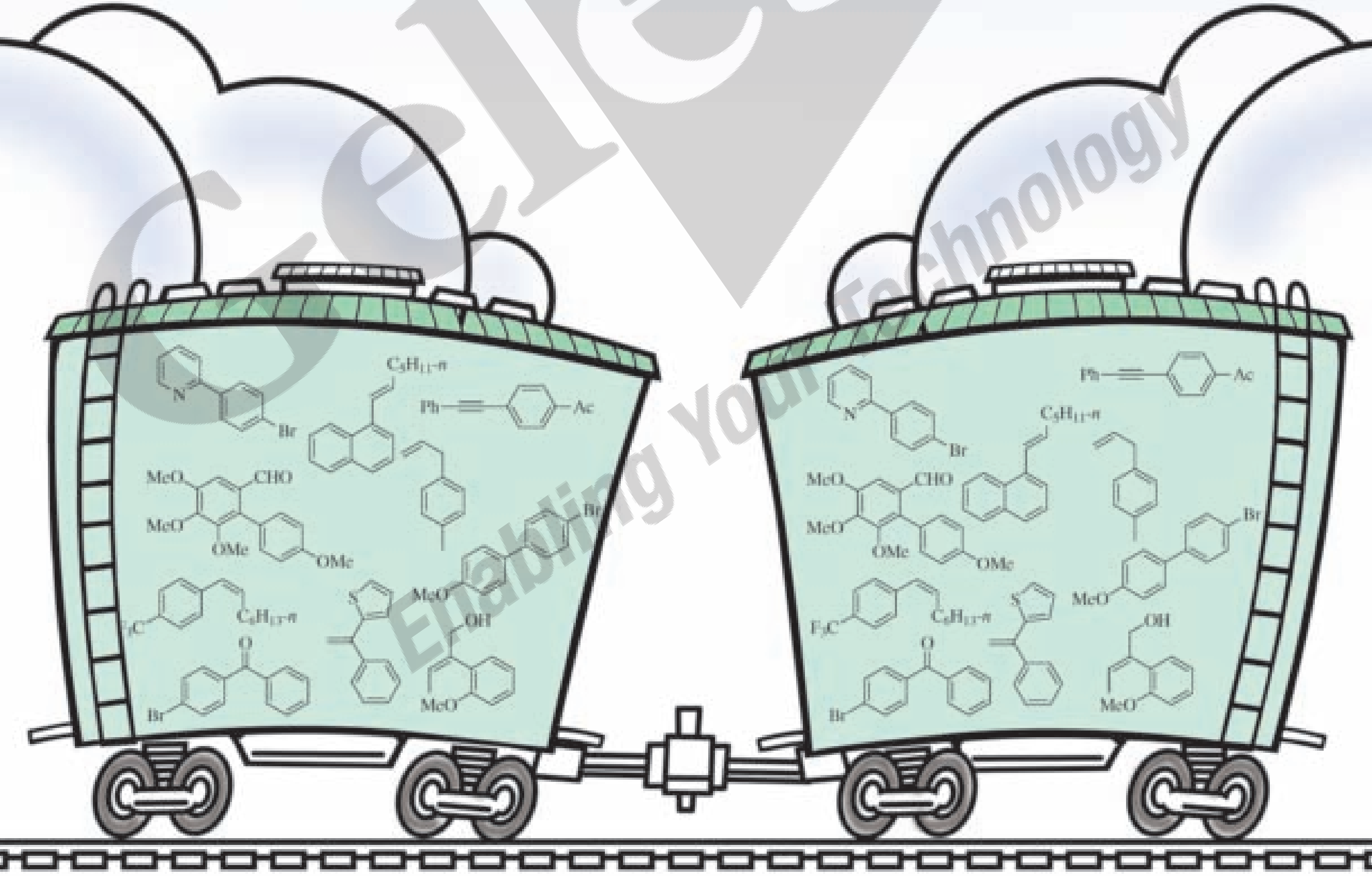

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Silicon-Based Cross-Coupling Reactions

Gelest

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

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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.[1,2] This general class of reactions involves two partners, with one typically being a suitable organometallic reagent and the other a suitable organic substrate.

Numerous examples of the coupling of aryl and vinyl halides with olefins in the Heck reaction,[1a] with organotin reagents in the Stille reaction,[3,4] with boronic acids in the Suzuki-Miyaura coupling,[5,6] and the coupling of aryl and vinyl halides with acetylenes in the Sonogashira reaction[7,8] have been reviewed. In addition, the use of Pd-catalyzed cross-coupling reactions in total synthesis has been reviewed.[9] All of these reactions have shown 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 important, the choice of ligands to complex the palladium during the reaction.

The early work of Hiyama[10-12] showed that arylsilanes and vinylsilanes with fluorine ligands could undergo 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, DeShong, and Wolf in addition to the continuing work of the Hiyama group. These authors have illustrated numerous methods of utilizing organosilanes in a variety of cross-coupling applications.

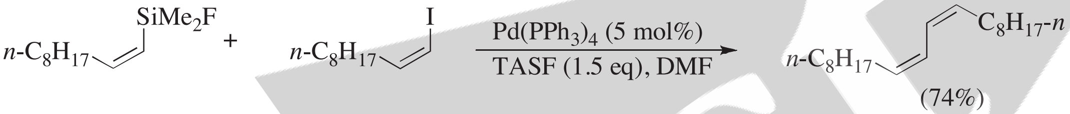
Table 1. A comparison of Cross-Coupling Methods

Reaction	Metal	Catalyst	Advantages	Disadvantages
Stille	Tin	Palladium	good yields reagents available	tin toxicity Bu_3Sn moiety is large
Suzuki-Miyaura	Boron	Palladium	good yields varied syntheses 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 air stable Silanes easily handled, Silanes readily synthesized	can require 1-3 eq of flouride few commercial sources of organosilanes

Cross-Coupling Reactions with Aryl-, Vinylfluoro- and chlorosilanes

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 Z,Z-diene (Eq. 1).[13]

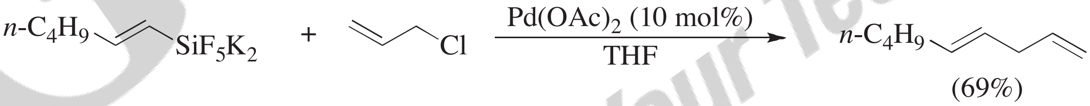


(1)
ref 13

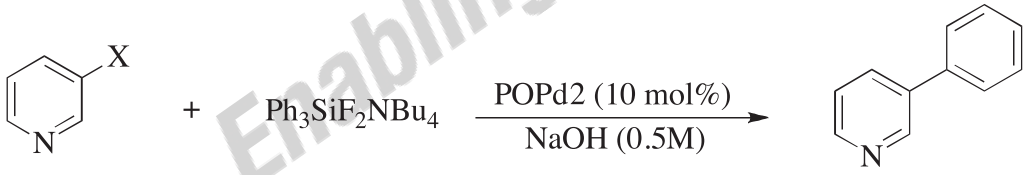
Vinylpentafluorosilicates undergo Heck coupling reactions (Eq. 2).[14] This system also couples well with allyl chloride (Eq. 3).[14] The cross-coupling with aryl bromides or chlorides with the Wolf palladium phosphite complex is also possible, with bromides being the more reactive (Eq. 4).[15]

(2)
ref 14

(87%) 12 examples
with related examples:
(20 - 69%)



(3)
ref 14

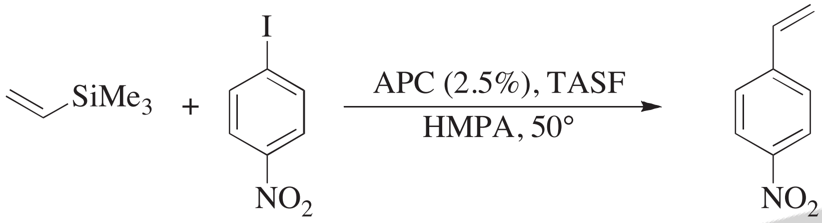


(4)
ref 15

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

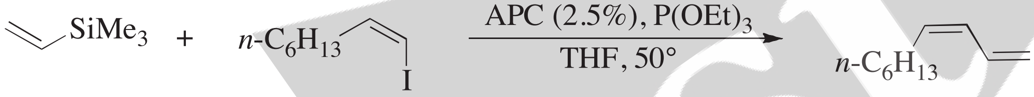
Trialkylsilyl Groups

Trimethylvinylsilanes can be used to directly vinylate aryl and vinyl iodides in moderate to excellent yields as shown in Eqs. 5 to 8.[16] The allylpalladium chloride dimer, APC, is an excellelnt catalyst for these reactions. Ethynyltrimethylsilanes undergo Sonogashira-type cross-coupling reactions to form enynes (Eq. 9) and allyltrimethylsilane provides 1,4-dienes (Eq. 10) or 1,5-dienes (Eq. 11) when cross-coupled with vinyl halides or allyl halides, respectively.[16]



(83%), 6 examples: (83-98%)

(5)
ref 16



(76%), 9 examples (52-100%)

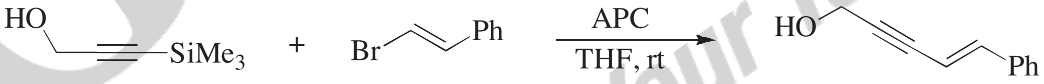
(6)
ref 16

(45%)

(7)
ref 16

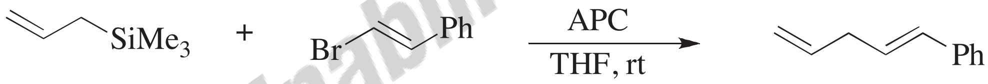
(78%)

(8)
ref 16



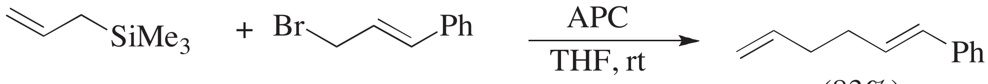
(84%) 3 examples: (83-86%)

(9)
ref 16



(28%)

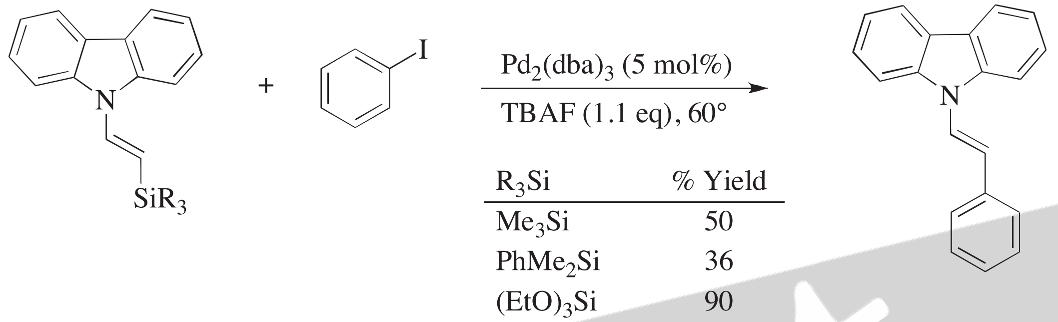
(10)
ref 16



(83%)

(11)
ref 16

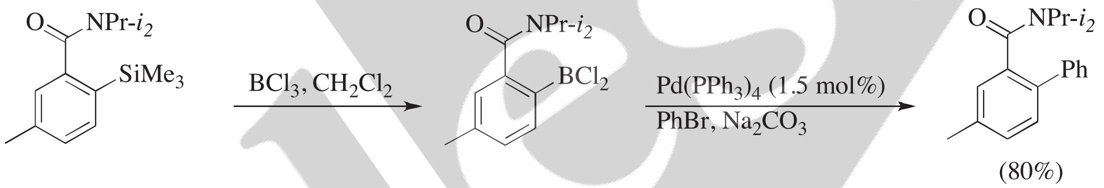
A study of the reactivities of β-silylethylcarbazole showed that the triethoxysilyl group is more effective in the cross-coupling with aryl iodobenzene than either the phenyldimethylsilyl or trimethylsilyl derivatives (Eq. 12).[17]



R_3Si	% Yield
Me_3Si	50
$PhMe_2Si$	36
$(EtO)_3Si$	90

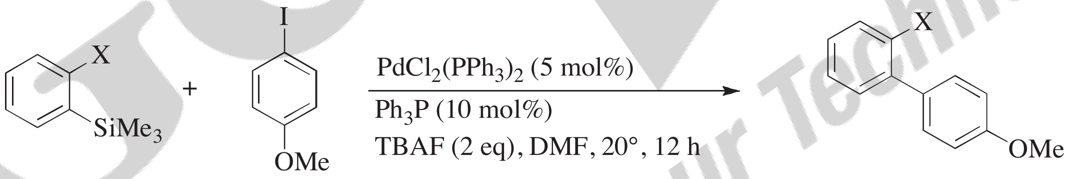
(12)
ref 17

Aryltrimethylsilanes can be cross-coupled with aryl bromides after first being converted to the dichloroborane (Eq. 13).[18] This approach, which really uses the boronic acid Suzuki methodology, provides a clean in-situ route to the arylboronic acid derivative.



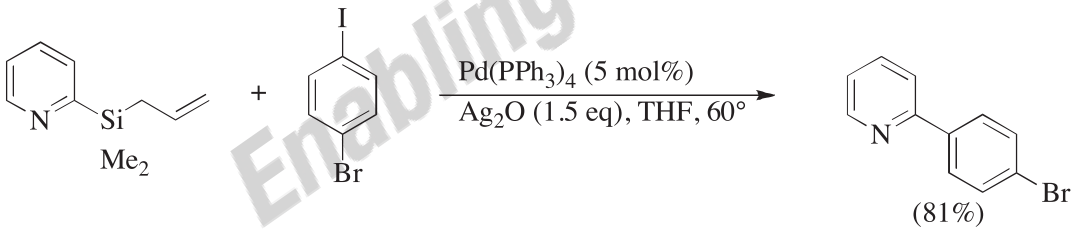
(13)
ref 18

o-Fluoro-, chloro- or methoxyphenyltrimethylsilanes undergo efficient cross-coupling reactions with aryl iodides transferring the *o*-aryl substituent (Eq. 14).[19] 2-Allyldimethylsilylpyridine cross-couples the 2-pyridyl group with aryl iodides (Eq. 15).[20]



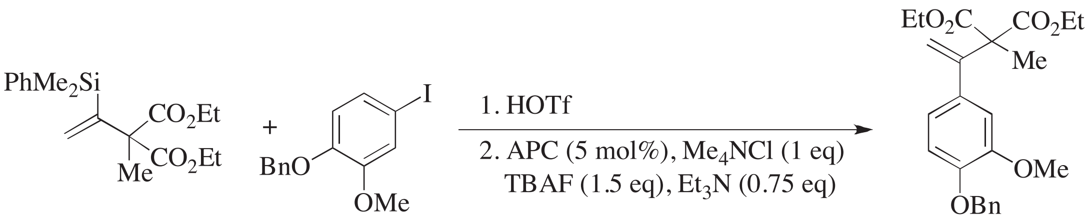
(14)
ref 19

X = F (75%); X = Cl (82%); X = OMe (85%)



(15)
ref 20

The phenyldimethylsilyl group can be utilized in cross-coupling reactions, but first the phenyl group is converted to a silanol derivative, which then undergoes the cross-coupling reaction (Eq. 16).[21]



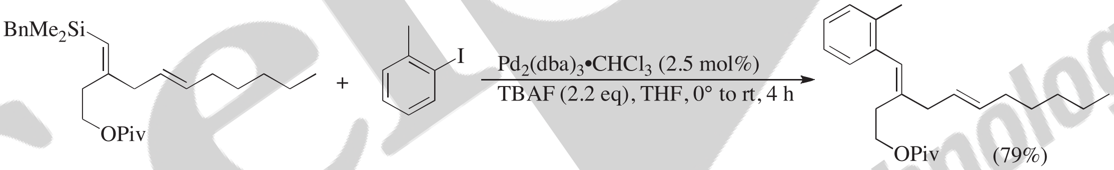
(16)
ref 21

Advantage can be taken of the facile fluorodebenzylation of benzylsilanes to use benzyldimethylsilyl groups in cross-coupling reactions with organosilanes.[22-24] Examples of this approach are shown in Eqs. 17 to 19. In these reactions the active silane species is the fluorosilane.

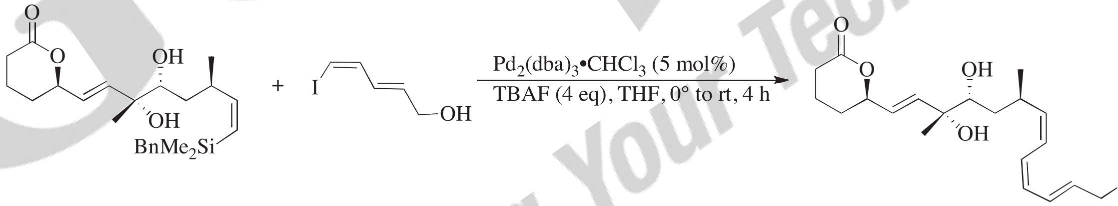
X = N-Bn; O; C(CO$_2$Et)$_2$

21 examples: (64-93%)

(17)
ref 22

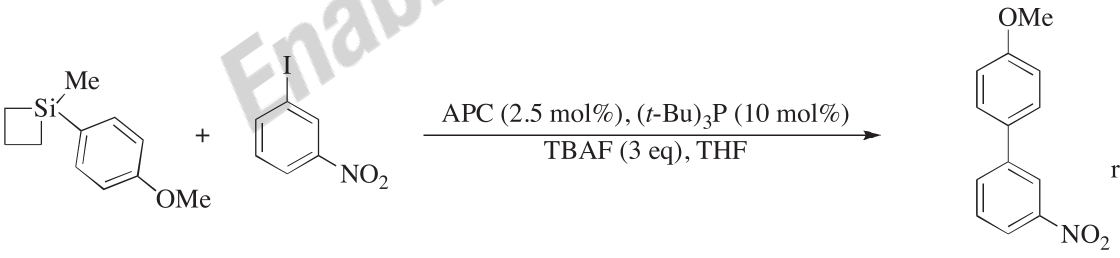


(18)
ref 23

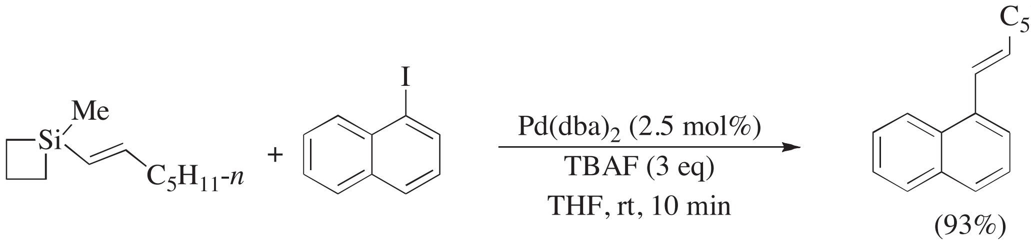


(19)
ref 24

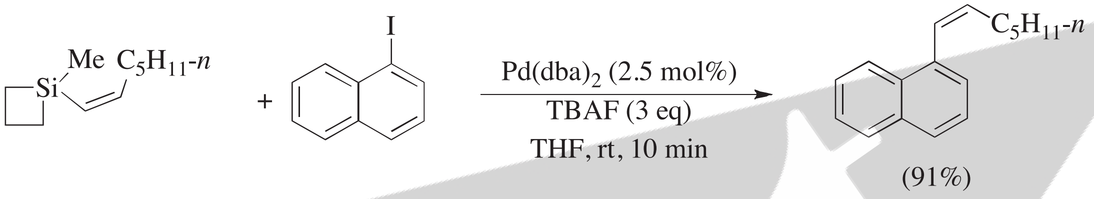
In a similar manner the aryl or vinyl silacyclobutanes under the influence of fluoride ion cross-couple well with aryl iodides (Eqs. 20 to 22).[25,26]



(20)
ref 26



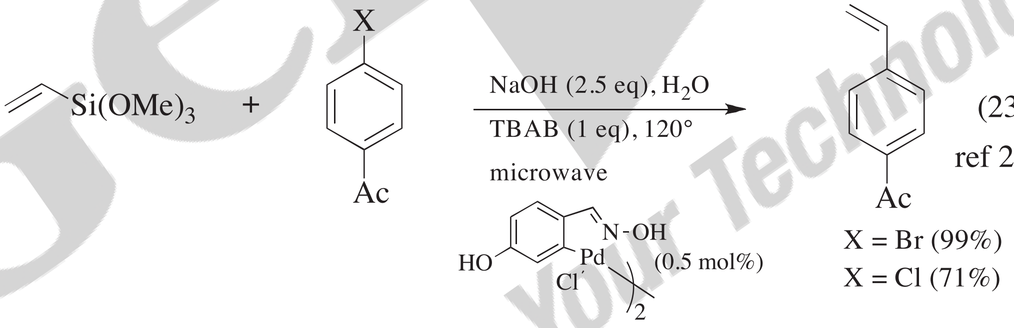
(21)
ref 25



(22)
ref 25

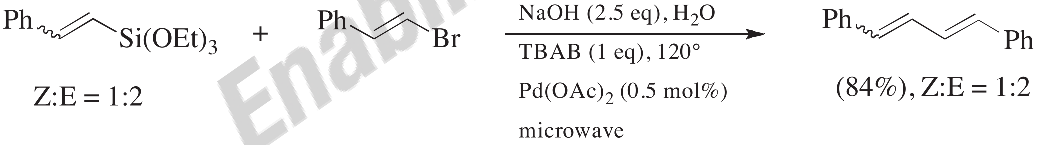
Vinylation of Aryl and Vinyl Halides

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. 23).[27,28] The reaction also works well with vinyl bromides. (Eq. 24).



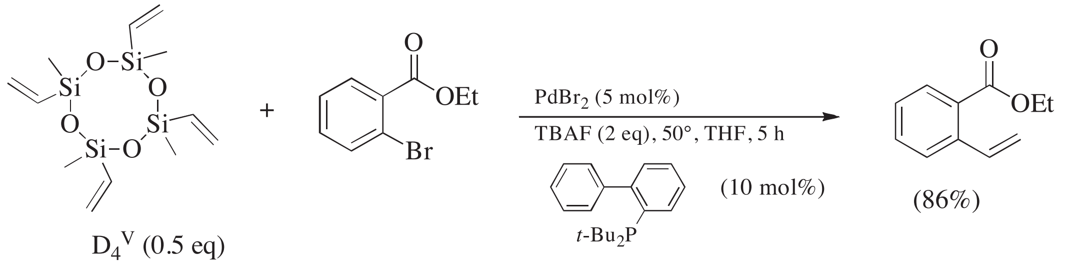
(23)
ref 27

X = Br (99%)
X = Cl (71%)

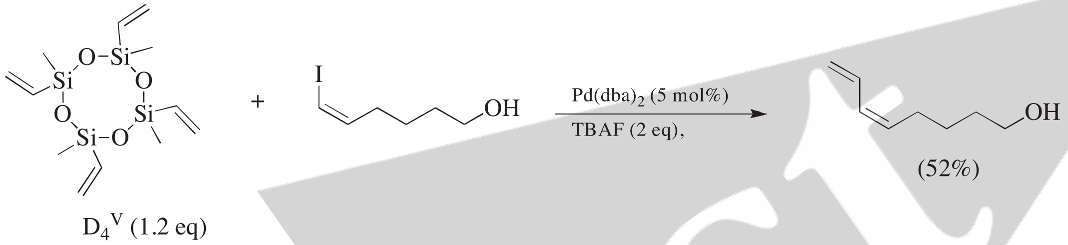


(24)
ref 28

The readily available vinylsilane, tetravinyltetramethylcyclotetrasiloxane, (D_4^V) can be used to vinylate aryl and vinyl iodides and bromides in good yields (Eqs. 25 and 26).[29,30]



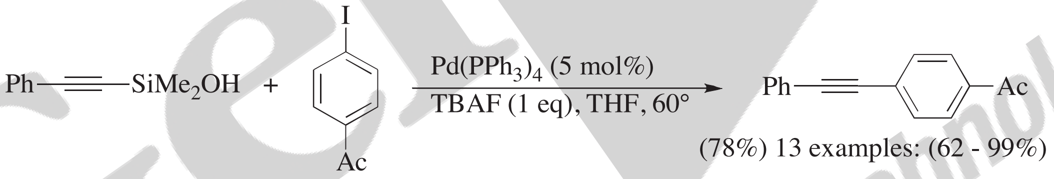
(25)
ref 29



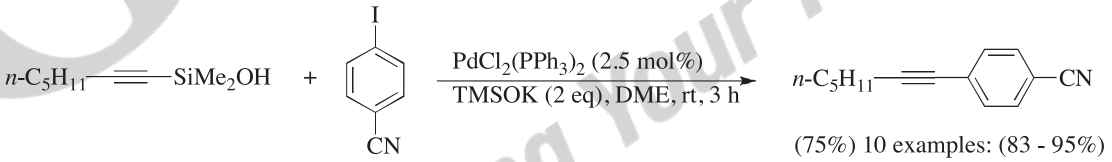
(26)
ref 30

Alkynyl Cross-Couplings

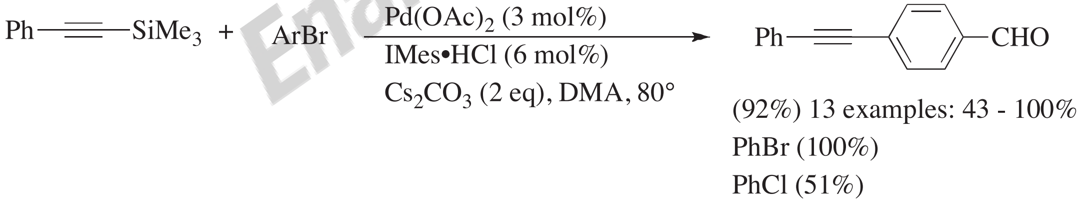
Alkynyldimethylsilanols react with aryl iodides to give arylacetylenes in good yields (Eqs. 27 and 28).[31,32] aryl bromides (Eq. 29).[33] The yields are generally very good. The difference in the reactivity between the sp-carbon and a hydrogen and the sp-carbon and a trimethylsilyl group was shown in the synthesis of 1,4-bis(3-bromophenylethynyl)benzene (Eq. 30).[34]



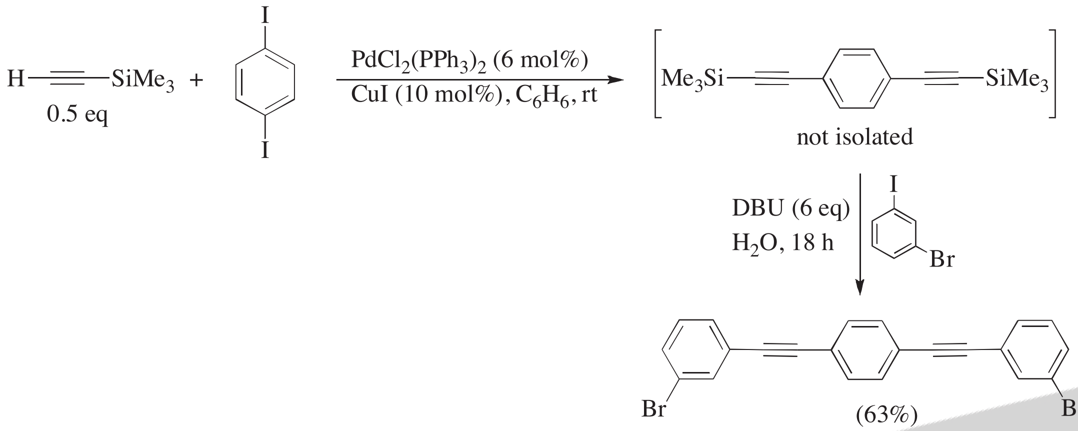
(27)
ref 31



(28)
ref 32



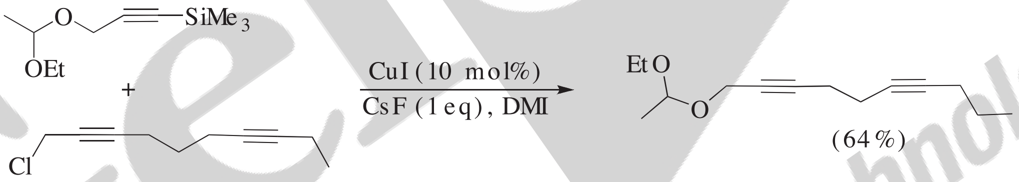
(29)
ref 33



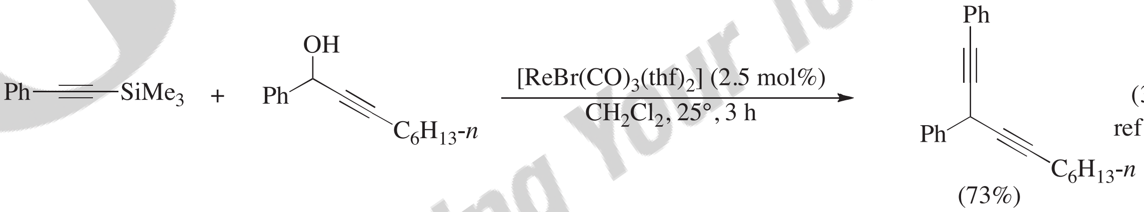
(30)
ref 34

Alkynyltrimethylsilanes can be cross-coupled with propargyl chlorides as shown in Eqs. 31 and 32.[35,36] A similar reaction occurs with propargyl alcohols (Eq. 33).[37] In one case an aldehyde is converted to the di-alkynyl derivative via a propargyl alcohol intermediate formed by the addition of the first alkynyl group to the aldehyde (Eq. 34).[37]

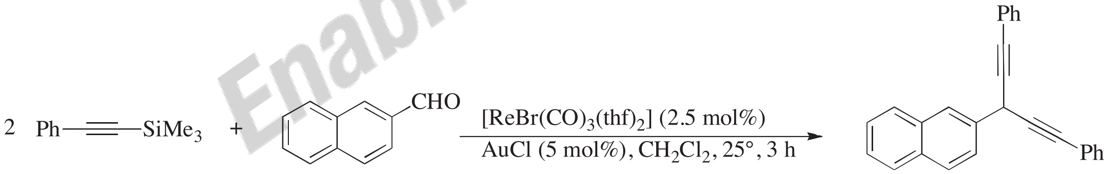
(31)
ref 36



(32)
ref 35



(33)
ref 37



(34)
ref 36

(55%) 7 examples: (33 - 80%)

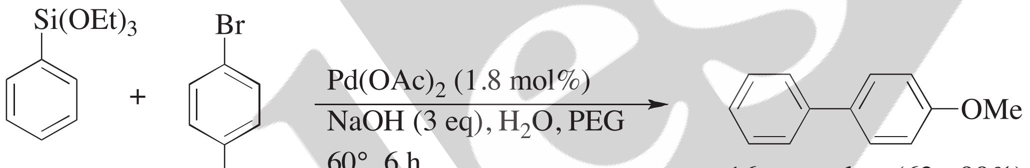
Homocoupling of alkynylsilanes can produce 1,3-butadiynes (Eq. 35) The yields are good to excellent.[38]

5 examples: (70 - 99%)

(35)
ref 38

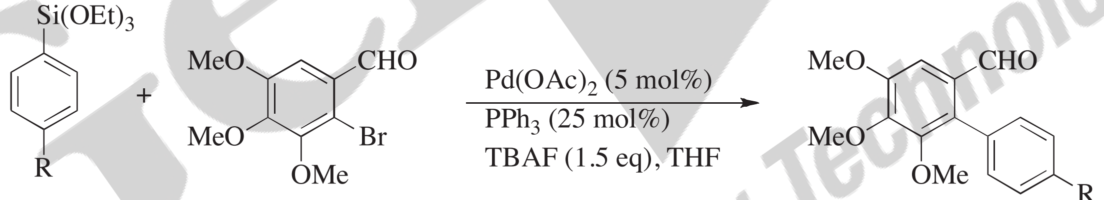
Alkoxysilanes in Cross-Coupling Reactions

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 number of examples are known a few of which are shown herein. Thus, the commercially available phenyltriethoxysilane is nicely coupled with aryl bromides to give the corresponding biaryl in good to excellent yields (Eq. 36).[39] Sterically hindered aryl bromides couple well with the aryltriethoxysilanes (Eq. 37).[40] Diphenyldimethoxysilanes provides the phenyl group in the cross-coupling with aryl bromides (Eq. 38).[39] Both phenyl groups can be used.



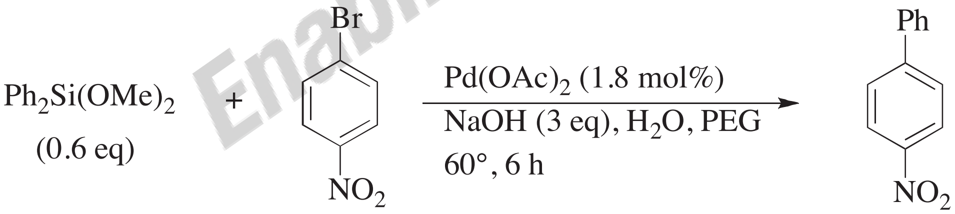
16 examples: (62 - 99%)

(36)
ref 39



(37)
ref 40

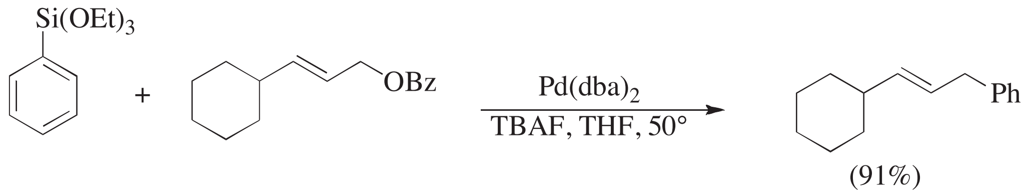
R	% Yield
H	94
MeO	93
Me	87
EtO_2C	94



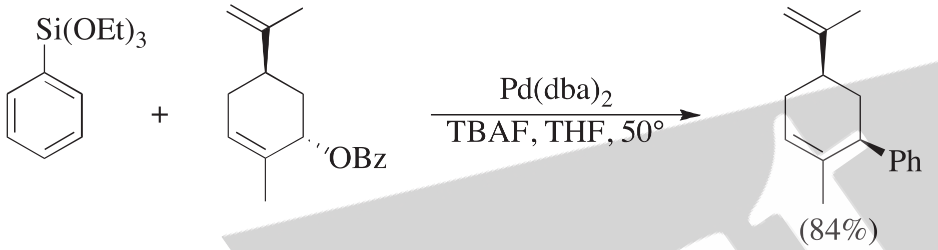
4 examples: (78 - 93%)

(38)
ref 39

Allyl benzoates react with aryl triethoxysilanes under cross-coupling conditions providing the allylbenzene derivative (Eqs. 39 and 40).[41,42]

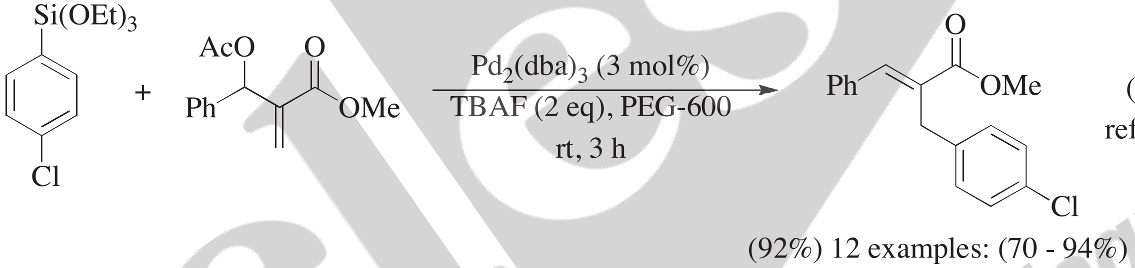


(39)
refs 41,42

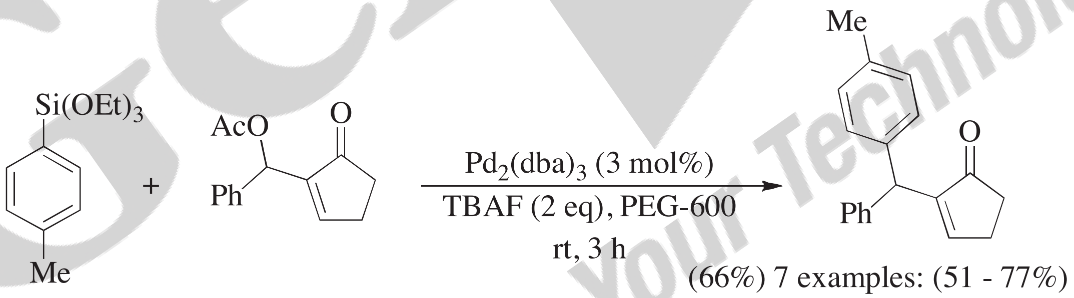


(40)
refs 41,42

A similar reaction is possible with allyl acetates as well (Eqs. 41 and 42).[43]

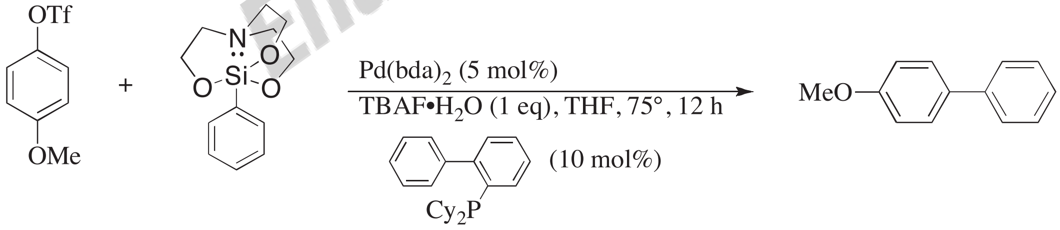


(41)
ref 43



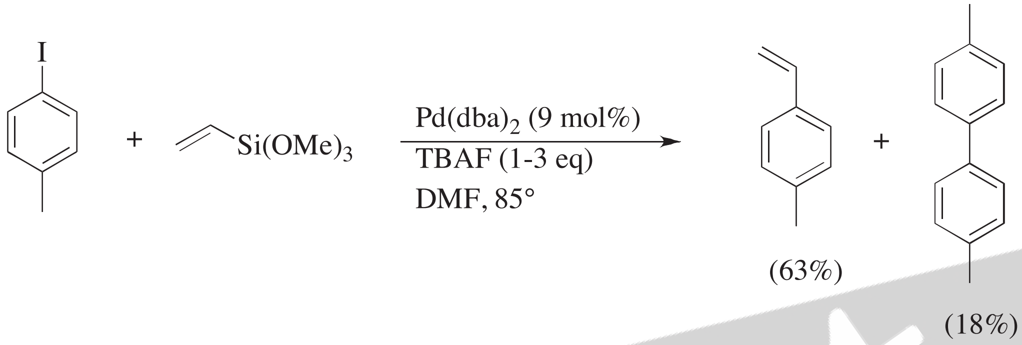
(42)
ref 43

In addition to the standard trimethoxysilyl or triethoxysilyl reagents, the silatranes are also viable reagents for cross-coupling reactions (Eq. 43).[44] It should be noted that some silatranes show high levels of toxicity.

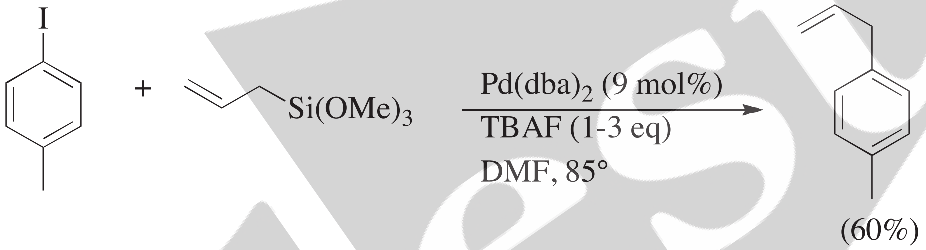


(43)
ref 44

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. 44 and 45).[45]



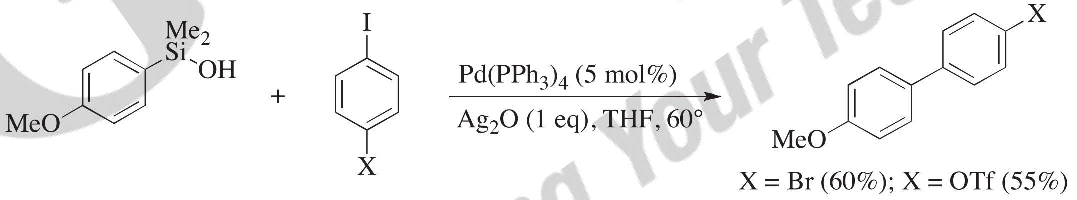
(44)
ref 45



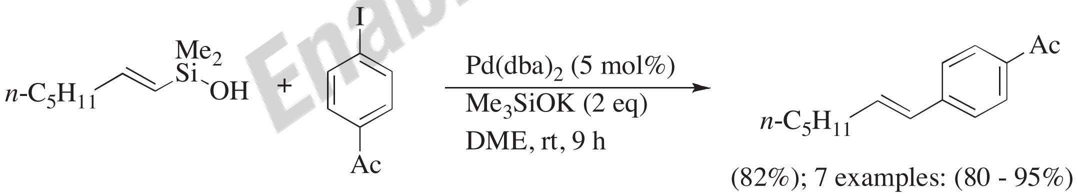
(45)
ref 45

Silanol-Based Cross-Coupling Reactions

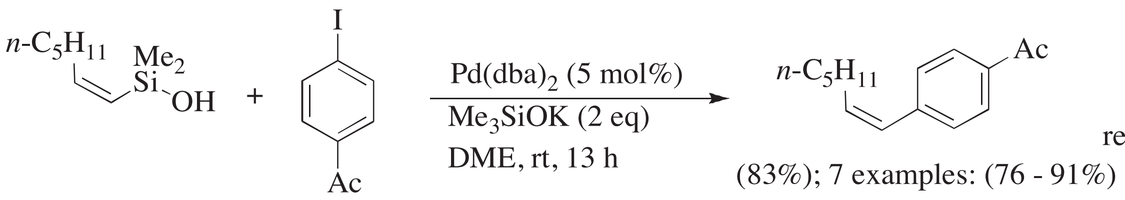
In a fashion similar to the cross-coupling of boronic acids with aryl and vinyl halides, aryl[46] and vinylsilanols[47] are useful in cross-coupling approaches to styrenes (Eqs. 46 and 47) and conjugated dienes. In the case of vinylsilanes the reactions are stereospecific with respect to the geometry of the starting vinylsilane (Eqs. 48 and 49).[47,48] The α-dimethylsilanol of an enol ether can be employed as well (Eq. 50).[49]



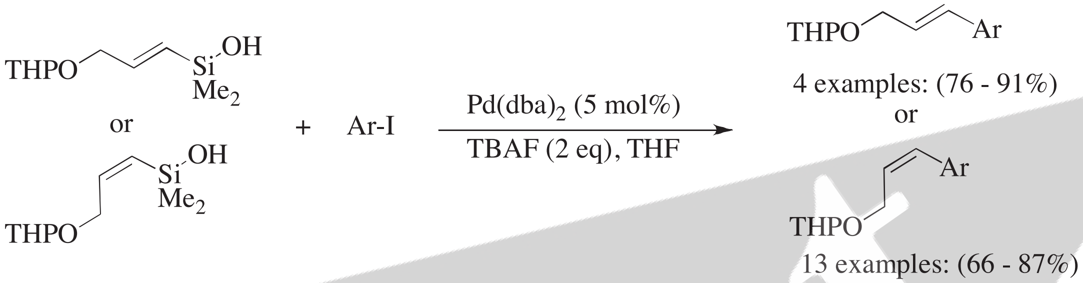
(46)
ref 46



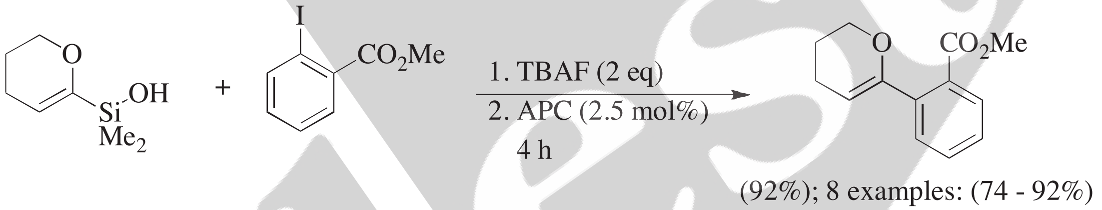
(47)
ref 47



(48)
ref 47

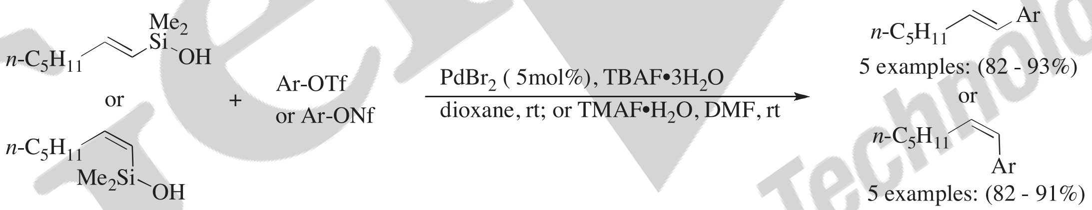


(49)
ref 48



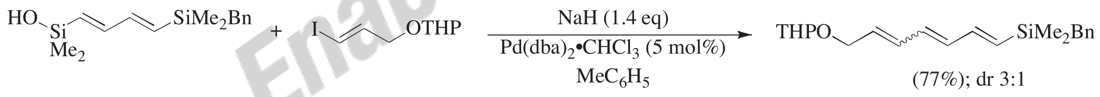
(50)
ref 49

The reaction of vinylsilanols with aryltriflates or nonafluorosulfonates gives the corresponding styrene in good yields (Eq. 51)[50]

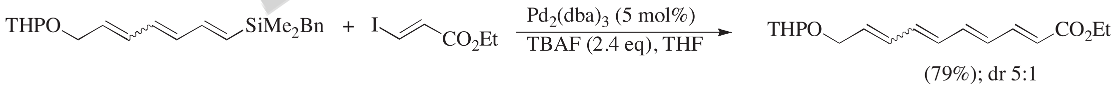


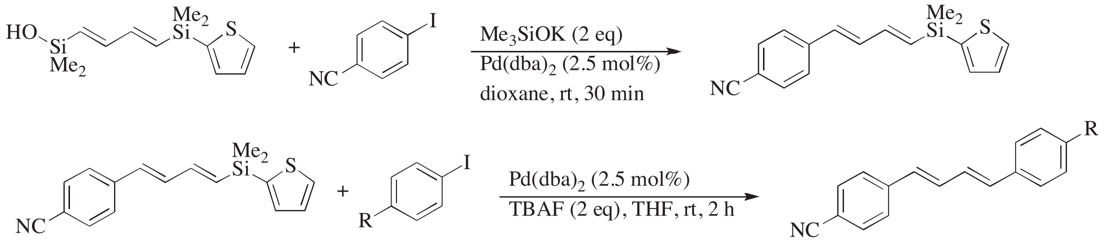
(51)
ref 50

An example of the selective cross-coupling of a vinylsilanol in the presence of a vinyldimethylbenzylsilane is known. This allows for the sequential cross-coupling of two sites on a molecule (Eq. 52).[51] A similar sequence is possible by employing the silanol for the initial cross-coupling and the 2-thienyldimethylsilyl group for the second (Eq. 53).[52]



(52)
ref 51

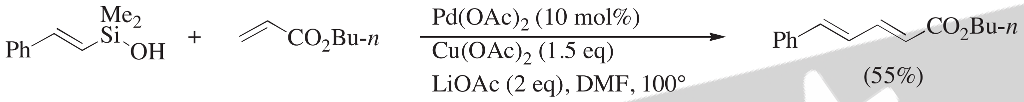




(53)
ref 52

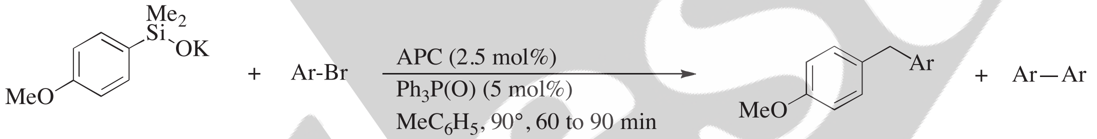
R = CO_2Et (90%); Me (89%); OMe (81%)

Vinylsilanols are shown to undergo Heck coupling (Eq. 54).[53,54]



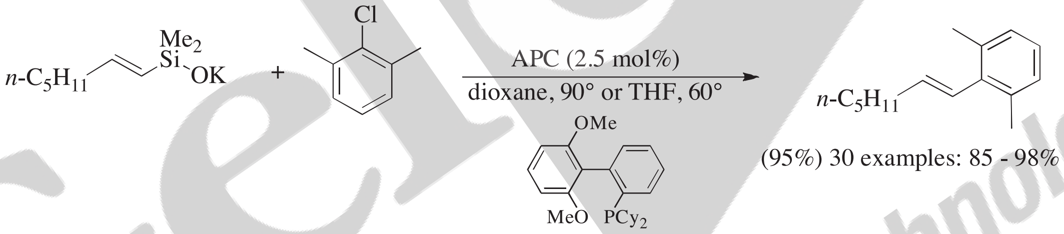
(54)
refs 53, 54

The pre-formed potassium salts of aryl or vinylsilanols undergo cross-coupling reactions in excellent yields and avoid the need of a fluoride ion source (Eqs. 55 and 56).[55,56]



14 examples: (61 - 86%)

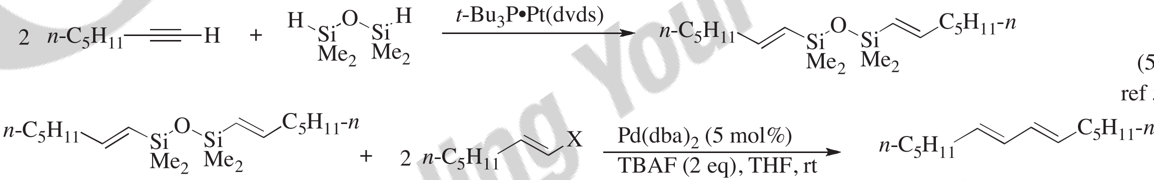
(55)
ref 55



(95%) 30 examples: 85 - 98%

(56)
ref 56

The readily prepared and easily handled disiloxanes under fluoride ion promotion undergo cross-coupling reactions (Eq. 57).[57]



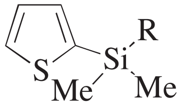
(57)
ref 57

X = I (67%); X = Br (70%)

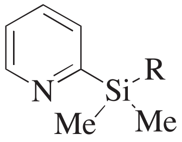
Special Ligands

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 handling of the organosilanes involved. A key necessity of the special ligand approach is that the activating ligand on the silicon atom not be involved in the cross-coupling itself. Among such useful systems employed in this regard are the 2-thiophenyl silanes **1**, the 2-

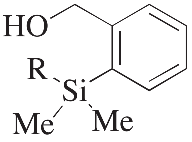
pyridylsilanes **2**, and the *o*-hydroxymethylphenylsilanes **3**. These ligands activate the silane for the cross-coupling reaction without themselves being transferred. The 2-silylthiophene derivatives **1** have been employed in the tag strategy for the separation, recovery and recycling of the precursor to the reactive intermediates themselves. Many of these reagents still require the promotional effect of fluoride ion in their reactions (Eqs. 58 and 59).[58]



1

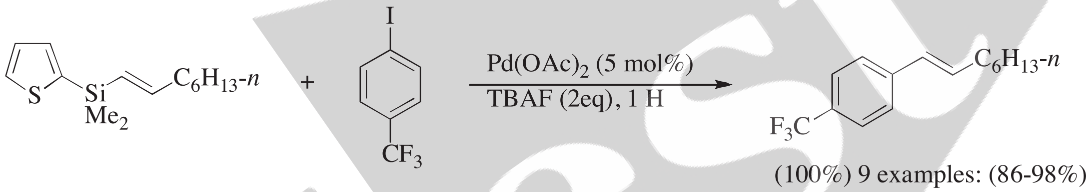


2



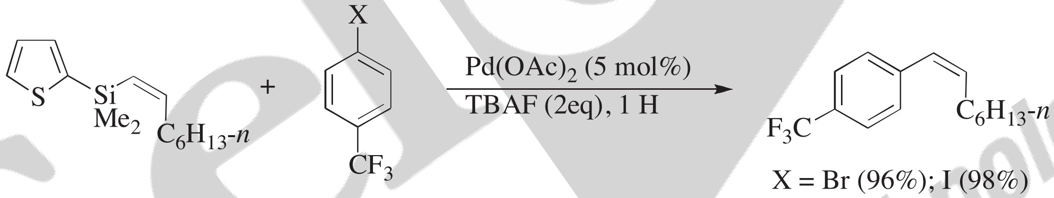
3

where R = vinyl or aryl



(100%) 9 examples: (86-98%)

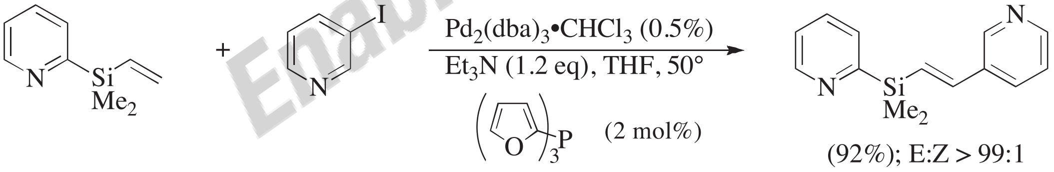
(58)
ref 58



X = Br (96%); I (98%)

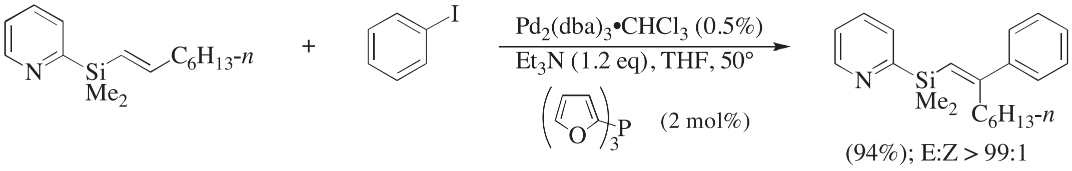
(59)
ref 58

A second approach has been to employ the 2-pyridylsilane derivatives **2**. Thus, vinyl(2-pyridyl)dimethylsilane, a totally thermally and hydrolytically stable system, undergoes a Heck coupling with aryl iodides (Eq. 60).[59] With substituted vinylsilanes of this type the stereochemistry of the olefin is maintained (Eq. 61).[59] The resulting vinylsilanes can then be further converted; for example, reaction with bromine gives the vinyl bromide (Eq. 62) and acylation provides the enone (Eq. 63).[59]

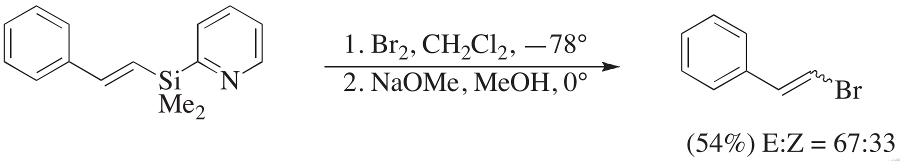


(92%); E:Z > 99:1

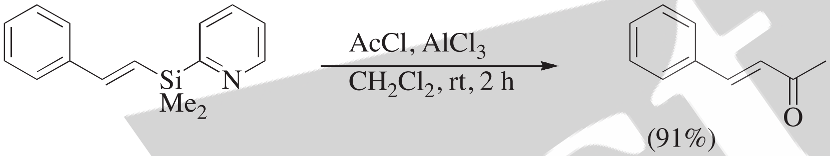
(60)
ref 59



(61)
ref 59

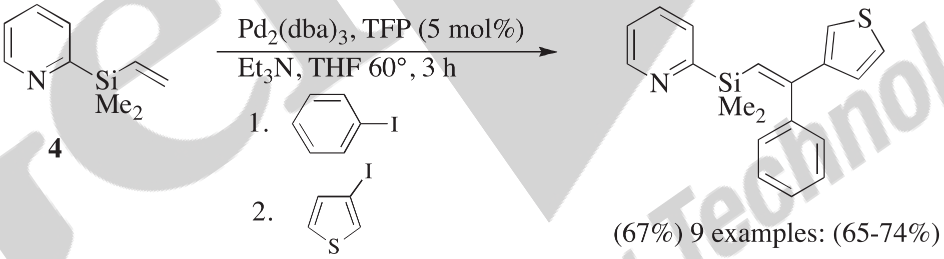


(62)
ref 59

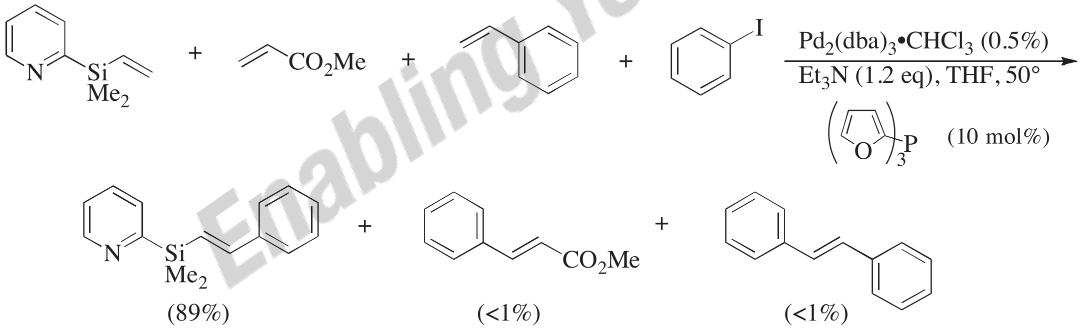


(63)
ref 59

A one-pot, double-Heck coupling is possible as shown in Eq. 64.[60] The sequential approach gives higher overall yields, however.[60] The high reactivity of the 2-pyridylvinylsilane **4** towards the Heck reaction is illustrated in the competitive reaction experiment, wherein the selectivity for the Heck reaction of **4** with iodobenzene over that between iodobenzene and methyl acrylate or between iodobenzene and styrene is clearly shown (Eq. 65).[60]

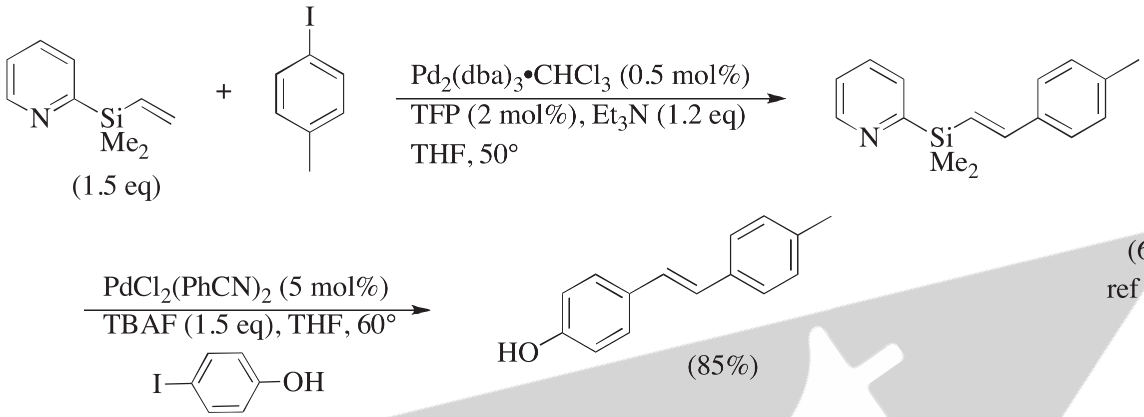


(64)
ref 60

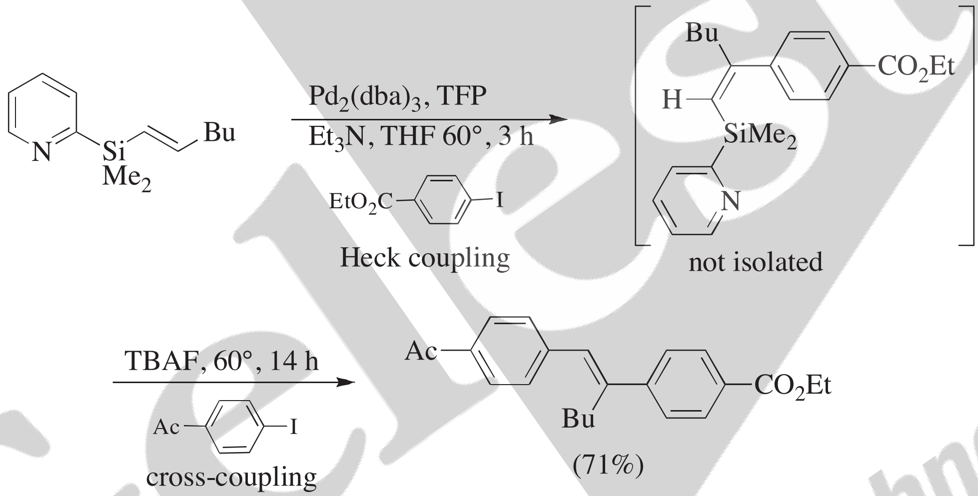


(65)
ref 60

The sequence of a Heck reaction followed by a silicon-based cross-coupling reaction can be used to stereoselectively prepare (E)-1,2-diarylethylenes (Eq. 66).[60,61] A one-pot version of this sequence is also possible (Eq. 67).[61]

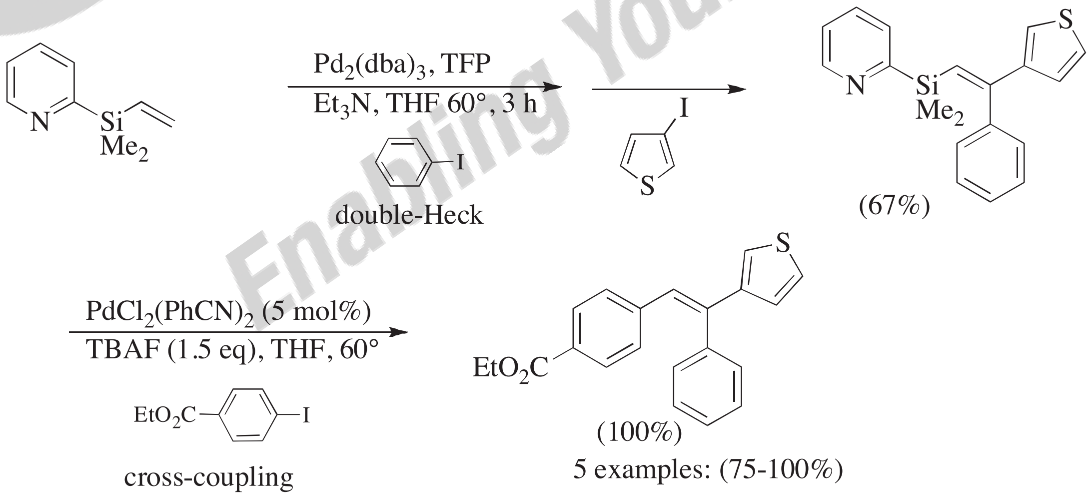


(66)
ref 60

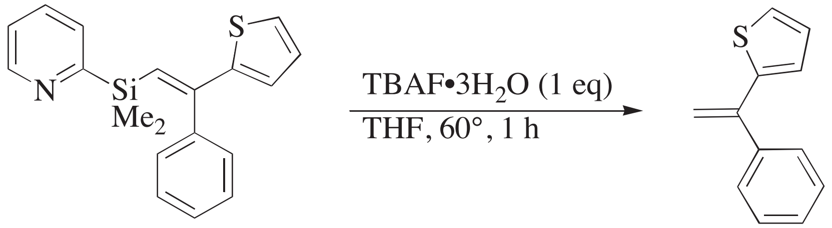


(67)
ref 61

The double-Heck-Hiyama cross-coupling sequence provides 1,2,3-triarylated ethylenes with the opportunity to introduce three different aryl groups (Eq. 68).[60] Furthermore, the protodesilylation of the resulting vinylsilanes from the Heck/Hiyama sequences leads to 1,1-diarylethylenes and 1,1,2-triarylethylenes (Eq. 69).[60]



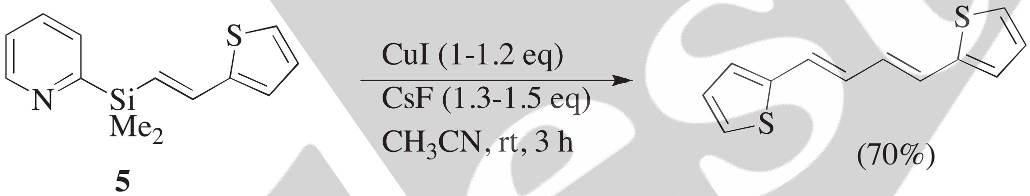
(68)
ref 60



(69)
ref 60

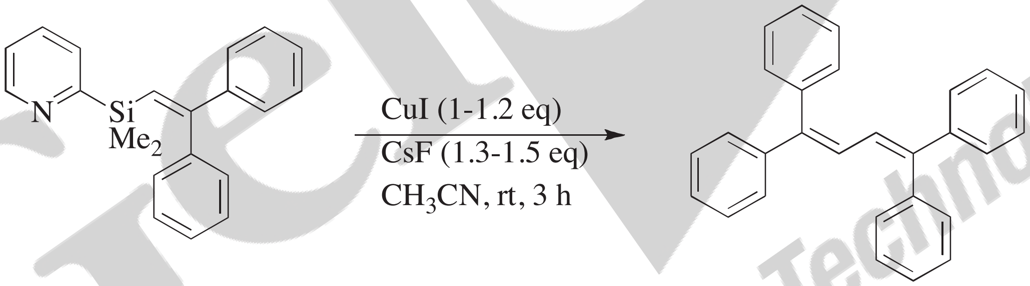
98% 6 examples: (91-100%)

A sequence of a Heck coupling to give **5** and a homocoupling provides an excellent entry into 1,4-diaryl-1,3-butadienes and 1,1,4,4-tetraaryl-1,3-butadienes and was successfully employed in the preparation of various arylated 1,3-butadienes with interesting photophysical properties (Eqs. 70 and 71).[61]



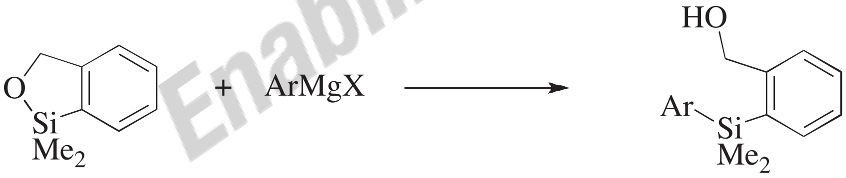
5

(70)
ref 61



(71)
ref 61

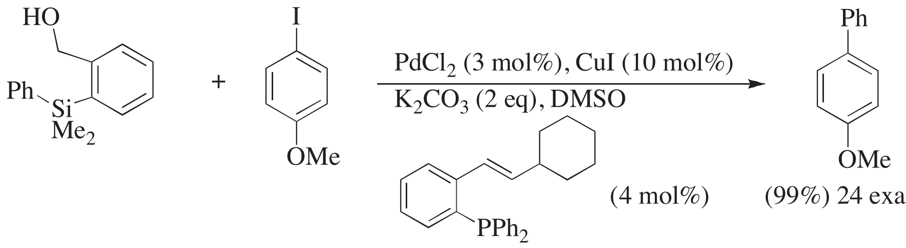
The (2-hydroxymethylphenyl)silane-derived silacycle **6** can be reacted with aryl Grignard reagents to give the corresponding vinyl(2-hydroxymethylphenyl)silane or the aryl(2-hydroxymethylphenyl)silane (Eq. 72). The *o*-hydroxymethyl group provides an activating effect for the effective cross-coupling of the aryl group with aryl and vinyl halides (Eq. 73).[62] An iterative metallation, silylation, cross-coupling sequence is reported wherein oligoarenes are synthesized (Eq. 74).[63]



6

(72)
ref 62

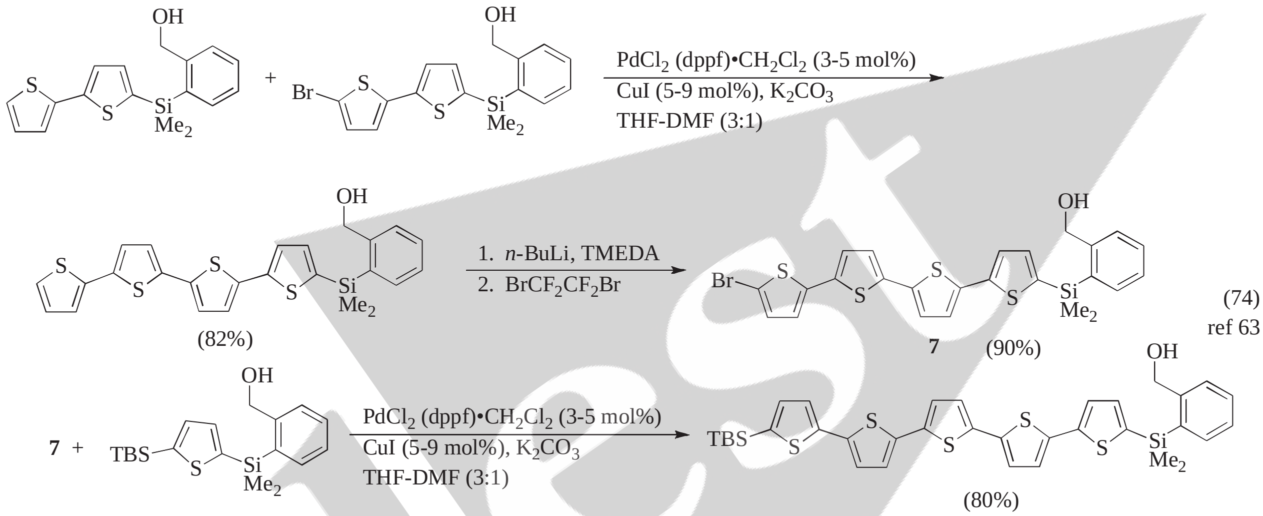
4 examples: (79-99%)



(4 mol%)

(99%) 24 examples: (88-99%)

(73)
ref 62



(82%)

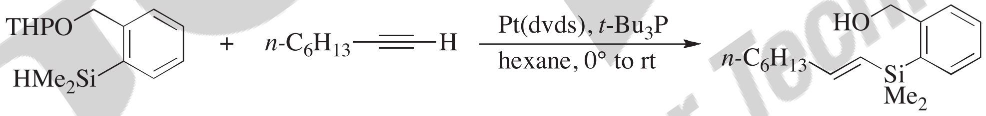
7 (90%)

(74)
ref 63

7 +

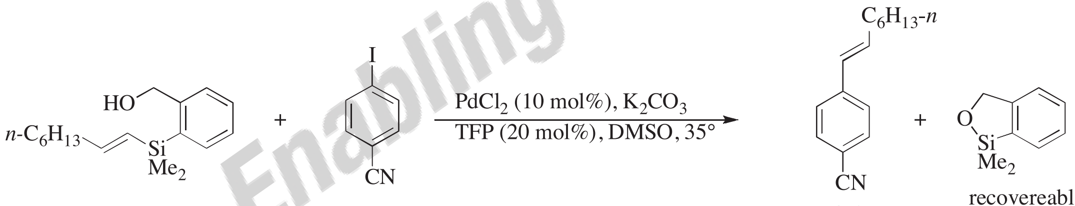
(80%)

The hydrosilylation of terminal acetylenes under Karstedt catalysis gives the (E)-vinylsilane carrying the promotional *o*-hydroxymethylphenyl group. Cross-coupling of the (E)-vinylsilane with aryl iodides gives 2-aryl olefins in excellent yields (Eqs. 75 and 76).[64,65]



(75)
ref 64

(82%) 12 examples (27-93%)
1 internal alkyne (81%)

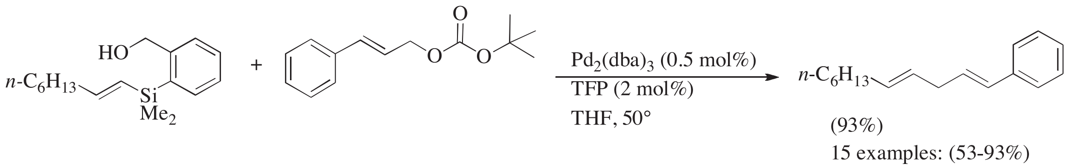


(76)
ref 65

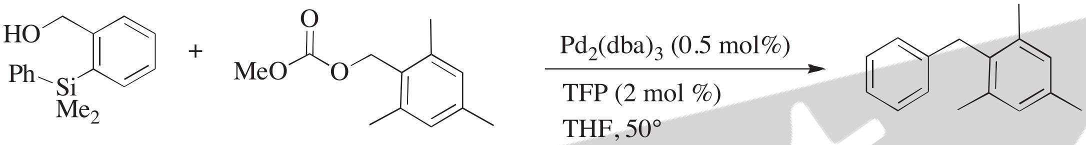
recovereable for re-use

(93%)
21 examples: (80-99%)

The arylated systems with the *o*-hydroxymethylphenyl promotion also couple with allyl and benzyl carbonates (Eqs. 77 and 78).[66]



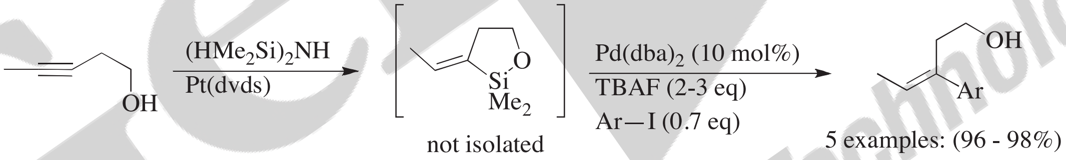
(77)
ref 66



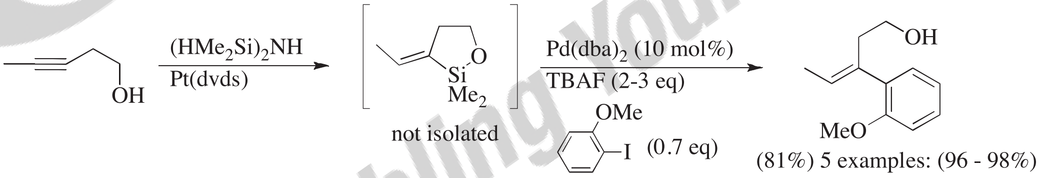
(78)
ref 66

Silicon-Based Template-Cross-Coupling Sequences

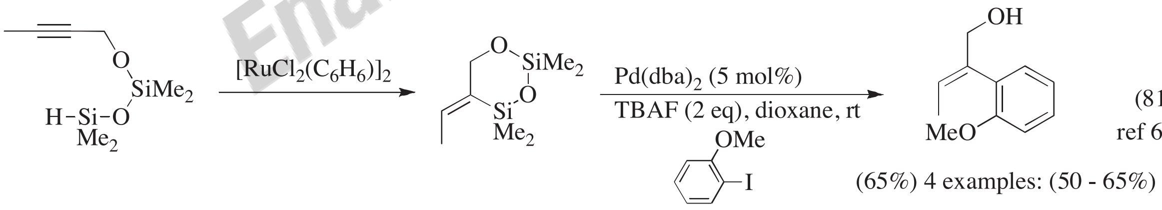
The ability of available organosilanes to both silylate alcohols and hydrosilylate alkynes can be used to generate interesting stereo-defined, organofunctionalized olefins. For example, the O-silylation of a hydroxyalkyl acetylene with *sym*-tetramethyldisilazane followed by intramolecular hydrosilylation 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. 79 and 80).[67,68] Tetramethyldisiloxane is useful in this type of templated cross-coupling approach as well (Eq. 81).[69]



(79)
refs 67,68

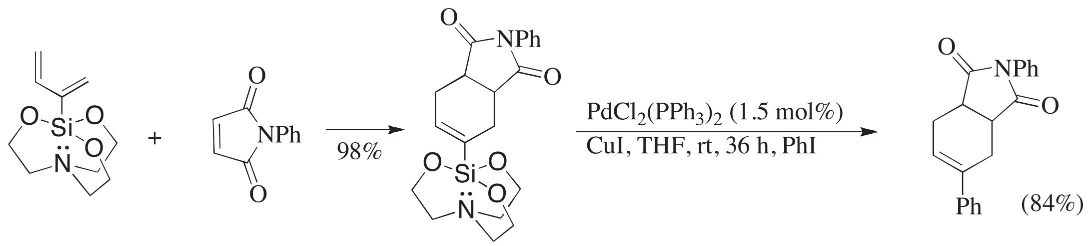


(80)
refs 67,68



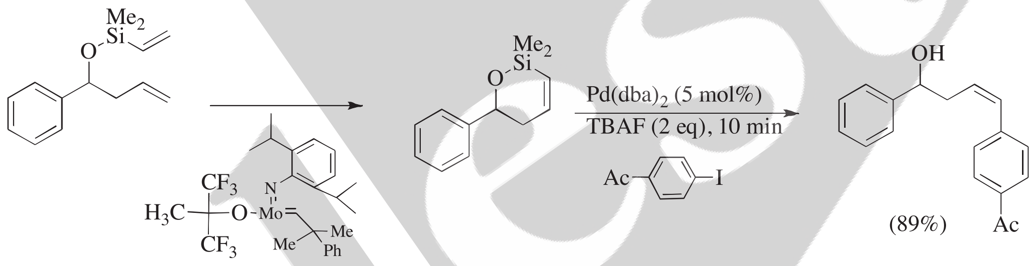
(81)
ref 69

The use of 2-(1,3-butadienyl)silatrane in a Diels-Alder-cross-coupling sequence provides an entry into 1-arylated cyclohexenes (Eq. 82).[70]

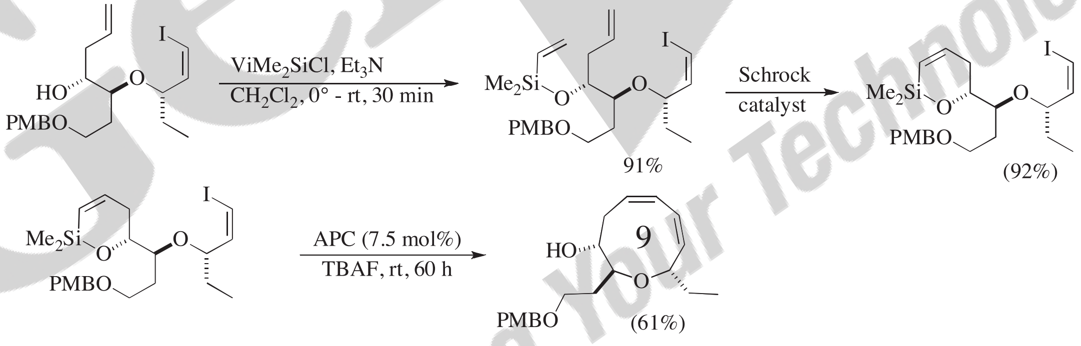


(82)
ref 70

An O-silylation, cross-metathesis, cross-coupling sequence can be employed in the generation of interesting species via inter- or intramolecular processes (Eqs. 83 and 84).[71-74]



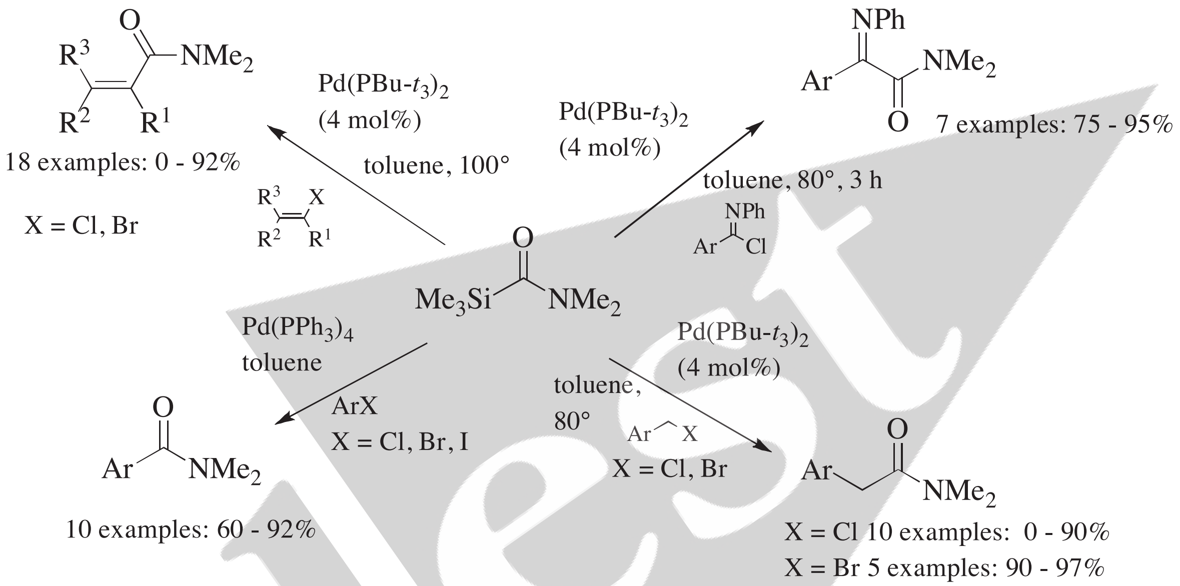
(83)
refs 71-74



(84)
refs 71-74

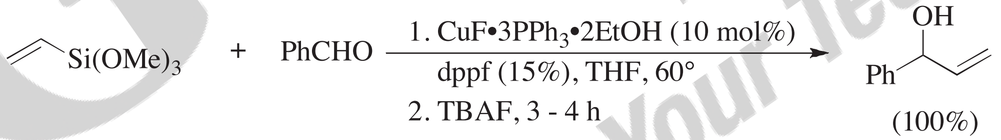
Miscellaneous Coupling Reactions

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).[75-78]

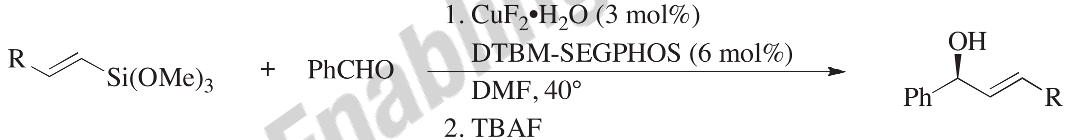


Scheme I refs 75-78

Vinylalkoxysilanes undergo a Grignard-type coupling with aldehydes to form enones (Eq. 85).[79] A change in the conditions with the utilization of the chiral ligand, DTBM-SEGPHOS, results in enantioselective addition to the carbonyl (Eq. 86).[79] The yields and ee values are very good.



(85)
ref 79



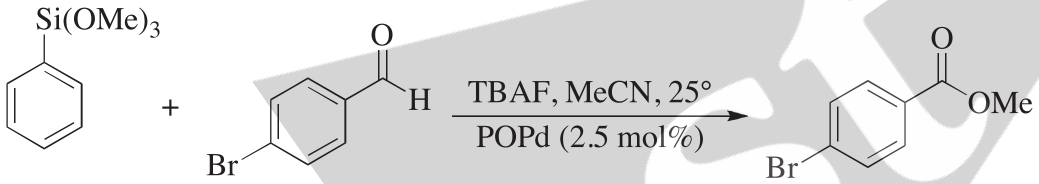
(86)
ref 79

R = H (99%; 94% ee) 14 examples:
yields (48 - 99%) ee = 83 - 99%;
w/ one at 52% ee

Phenyltrimethoxysilane reacts with aromatic aldehydes under the influence of TBAF to give acetophenones (Eq. 87)[80] and under essentially the same conditions, but with the addition of a palladium catalyst provides the corresponding methyl benzoate (Eq. 88).[80]

(87)
ref 80

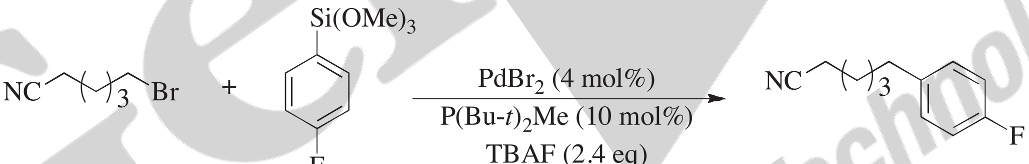
(79%) 10 examples: (73 - 99%)



(88)
ref 80

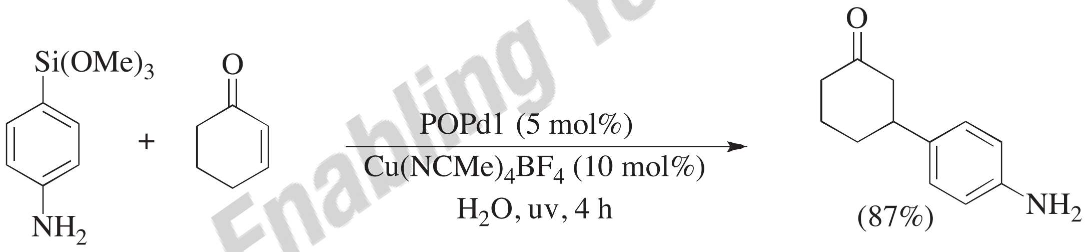
(93%) 10 examples: (78 - 97%)

Aryltrimethoxysilanes couple well with primary alkyl bromides. Several examples are reported (Eq. 89).[81] The coupling of these systems with enones to form β-aryl ketones is also possible when catalyzed by a palladium phosphinous acid complex in water. (Eq. 90).[82]



(89)
ref 81

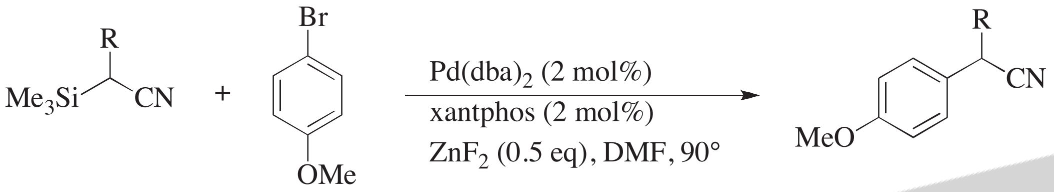
(50%) 21 examples: (36 - 81%)



(87%)

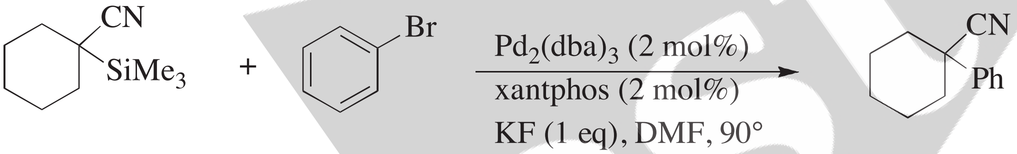
(90)
ref 82

α-Cyanoalkyltrimethylsilanes are coupled to aryl bromides to give the α-aryl nitrile (Eqs. 91 and 92).[83]



(91)
ref 83

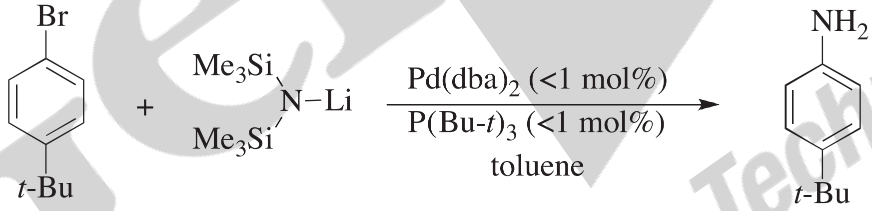
R = H (64%); 16 examples: (64 - 92%)
R = Me (71%); 9 examples: (64 - 98%)



(92)
ref 83

4 examples: (62 - 84%)

Lithium bis(trimethylsilylamide) provides the amine group in a cross-coupling with aryl bromides to form primary anilines (Eq. 93).[84]

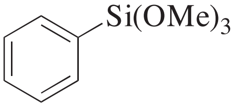
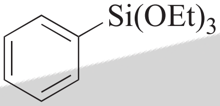
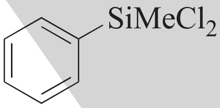
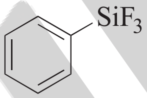
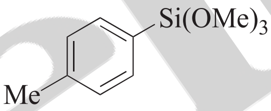
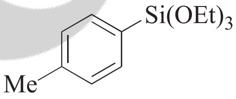
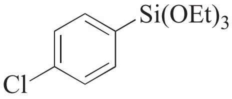
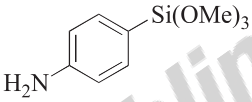


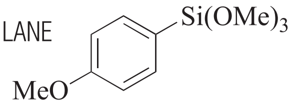
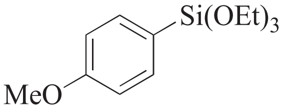
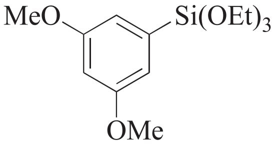
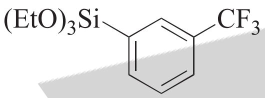
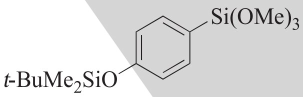
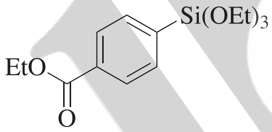
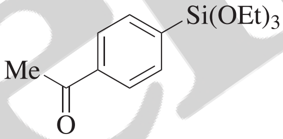
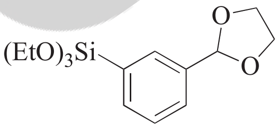
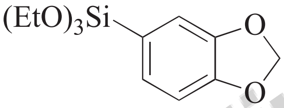
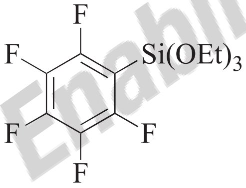
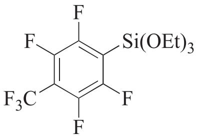
(93)
ref 84

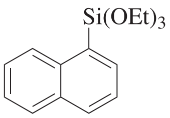
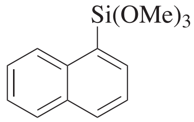
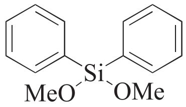
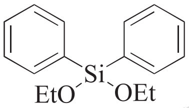
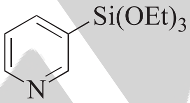
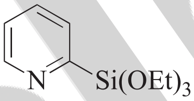
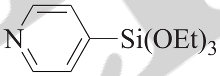
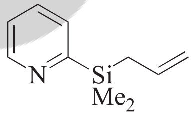
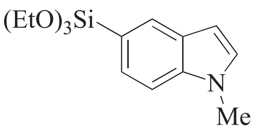
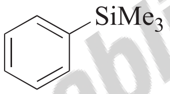
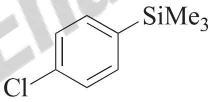
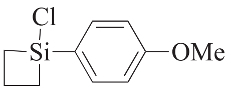
ArBr (92%) 23 examples: (65 - 99%)
ArCl (89%) 9 examples: (62 - 99%)

TABLE 2 ORGANOSILANE CROSS-COUPLING AGENTS

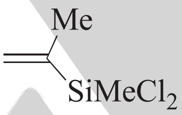
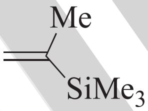
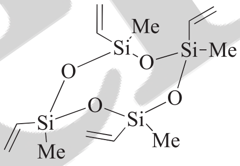
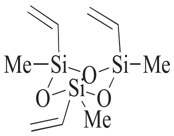
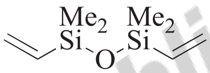
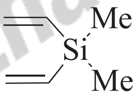
ARYLSILANE CROSS-COUPLING AGENTS

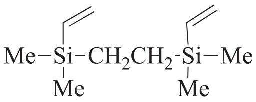
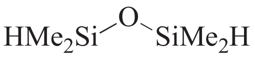
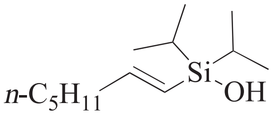
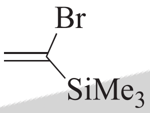
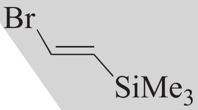
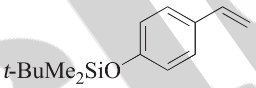
ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIP6822.0 PHENYLTRIMETHOXYSILANE [2996-92-1]		Cross-couples w/ aryl bromides w/o fluoride and w/ NaOH.[39,85,86,39] High yields w/ Pd and carbene ligands.[87] Cross-coupled in presence of aryl aldehyde.[80] Cross-coupled w/ alkynyl bromides and iodides.[81] N-arylates nitrogen heterocycles.[88] Reacts with 2° amines to give anilines.[89] Undergoes 1,4-addition to enones.82 1,2- and 1,4-addition to aldehydes.[90] Undergoes coupling[91] and asymmetric coupling w/ α-bromoesters.[92]	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.[93] Phenylates allyl acetates.[43] β-phenylates enones under aqueous base conditions.[94]	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.[95]	25g $12.00 500g $64.00 18kg $1224.00
SIP6821.5 PHENYLTRIFLUOROSILANE [368-47-8]		Cross-couples w/ aryl and vinyl triflates.[96] Couples w/ aryl bromides in presence of fluoride.[97,98] Couples with 2° alkyl bromides and iodides.[91]	50g $108.00
SIT8042.0 *p*-TOLYLTRIMETHOXYSILANE [17873-01-7]		Example of aryltrimethoxysilane for cross-coupling application. Reacts w/ α-bromo esters to give α-*p*-tolyl esters.[91] Couples w/o fluoride in aqueous medium.[99] Michael adds to enones in aqueous medium.[82] Undergoes asymmetric coupling w/ α-bromoesters.[92]	10g $38.00 50g $152.00
SIT8041.0 *p*-TOLYLTRIETHOXYSILANE [79349-33-0]		Undergoes conjugate addition to enones.[92]	5g $62.00
SIC2332.3 4-CHLOROPHENYLTRIETHOXYSILANE [21700-74-3]		Undergoes conjugate addition to enones.[92]	10g $139.00
SIA0599.1 4-AMINOPHENYLTRIMETHOXYSILANE [33976-43-1]		Couples w/o fluoride in aqueous medium.[99]	5g $94.00 100g $1476.00
SIA0599.0 3-AMINOPHENYLTRIMETHOXYSILANE [70411-42-6]		Potential for introduction of *m*-anilino group.	5g $82.00 100g $1476.0

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIM6492.55 *p*-METHOXYPHENYLTRIMETHOXYSILANE [21130-91-6]		Undergoes asymmetric coupling w/ α-bromoesters.[92] Couples w/ heterocyclic amines.[88]	5g $52.00
SIM6492.53 *p*-METHOXYPHENYLTRIETHOXYSILANE [53392-03-3]		Undergoes conjugate addition to enones.[94]	5g $65.00
SID3544.0 3,5-DIMETHOXYPHENYL-TRIETHOXYSILANE		Reacts w/ aryl bromides and iodides.	5g $175.00
SIT8343.0 3-TRIFLUOROMETHYL-PHENYLTRIMETHOXYSILANE [53883-59-3]		Useful for introduction of *m*-trifluoromethylphenyl group.	2.5g $210.00
SIB1939.65 4-TERT-BUTYLDIMETHYL-SILOXYPHENYLTRIMETHOXYSILANE		Useful for introduction of *p*-TBS-protected phenol group.	2.5g $180.00
SIE4901.3 ETHYL 4-TRIETHOXYSILYLBENZOATE [197662-64-9]		Useful for preparation of derivatized benzoic acid esters.	2.5g $220.00
SIT8177.0 4-TRIETHOXYSILYLACETOPHENONE [438569-05-2]		Useful for preparation of acetophenone derivatives.	2.5g $220.00
SIT8185.9 2-(3-TRIETHOXYSILYL-PHENYL)-1,3-DIOXOLANE		Useful for the preparation of benzaldehyde derivatives.	5g $175.00
SIM6509.0 3,4-METHYLENEDIOXY-PHENYLTRIETHOXYSILANE [376353-50-3]		Used in the coupling to allyl carbonates and allyl benzoates.[41,42]	2.5g $210.00
SIP6716.7 PENTAFLUOROPHENYL-TRIETHOXYSILANE [20083-34-5]		Useful for the preparation of pentafluorophenyl derivatives.	5g $82.00 25g $328.00
SIT8345.0 4-TRIFLUOROMETHYLTETRA-FLUOROPHENYLTRIETHOXYSILANE [561069-04-3]		Example of fluorinated arylsilane for cross-coupling.	5g $102.00 25g $408.00

ORGANOSILANE	**STRUCTURE**	**COMMENTS**	**PRICING**
SIN6596.8 1-NAPHTHYLTRIETHOXYSILANE [18052-76-1]		Undergoes asymmetric coupling w/ α-bromoesters.[92]	5g $180.00
SIN6597.0 1-NAPHTHYLTRIMETHOXYSILANE [18052-76-1]		Undergoes asymmetric coupling w/ α-bromoesters.[92]	5g $180.00
SID4535.0 DIPHENYLDIMETHOXYSILANE [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 DIPHENYLDIETHOXYSILANE [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)DIMETHOXYSILANE [92779-72-1]		Alternative to *p*-tolyltrimethoxysilane.	25g $158.00
SIP6934.0 3-PYRIDYLTRIETHOXYSILANE [129663-08-7]		For preparation of 3-substituted pyridines.	5g $190.00
SIP6932.0 2-PYRIDYLTRIETHOXYSILANE, 95% [213602-91-6]		For preparation of 2-substituted pyridines.	5g $135.00
SIP6936.0 4-PYRIDYLTRIETHOXYSILANE [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.[20] Allylates aldehydes, ketones and imines.[100]	5g $184.00
SIT8185.85 5-(TRIETHOXYSILYL)-1-METHYLINDOLE [808770-01-6]		For preparation of 5-substituted indoles.	2.5g $190.00
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 *p*-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.[26]	2.5g $136.00

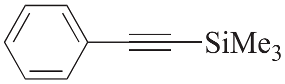
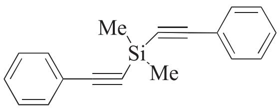
VINYLSILANES FOR CROSS-COUPLING

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIV9220.0 VINYLTRIMETHOXYSILANE [2768-02-7]		For vinylations. Reacts w/ α-bromo esters to give α-vinyl esters in high ee.[91] Alkenyltrialkoxysilanes react w/ aryl bromides and iodides to form styrenes under fluoride- and ligand-free and aqeous conditions.[28] Reacts also in presence of fluoride.[27]	25g $10.00 2kg $96.00 16kg $352.00
SIV9112.0 VINYLTRIETHOXYSILANE [78-08-0]		For vinylations. Reacts with enamines to give (E)-β-silylenamines, which cross-couple w/ aryl iodides to give β-aryl enamines.[17]	25g $10.00 2kg $110.00 16kg $472.0
SIV9072.0 VINYLDIMETHYLETHOXYSILANE [5356-83-2]		Vinylates aryl halides.[102]	10g $24.00 50g $96.00
SIV9250.0 VINYLTRIMETHYLSILANE [754-05-2]		Undergoes Heck coupling to (E)- β-substituted vinyltrimethylsilanes, which can then be cross-coupled further.[103]	10g $16.00 100g $114.00 1.5kg $930.00
SIV9084.0 VINYLMETHYLDICHLOROSILANE [124-70-9]		Reacts to vinylate aryl halides under NaOH-moderated conditions.[95]	25g $11.00 2.5kg $130.00 18kg $621.00
SIP6905.0 2-PROPENYLTRIMETHYLSILANE [18163-07-0]		For introduction of the 2-propenyl moiety.	5g $148.00
SIT7900.0 1,3,5,7-TETRAVINYL-1,3,5,7-TETRAMETHYL-CYCLOTETRASILOXANE [2554-06-5]		Excellent and inexpensive reagent for vinylations in cross-coupling reactions for the formation of styrenes and dienes.[29,30,104]	25g $18.00 100g $58.00 2kg $390.00 17kg $1356.00
SIT8737.0 1,3,5-TRIVINYL-1,3,5-TRIMETHYL-CYCLOTRISILOXANE [3901-77-7]		Excellent reagent for vinylations in cross-coupling reactions for the formation of styrenes and dienes.[30,102]	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 $2400.00

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SID4614.0 1,4-DIVINYLTETRAMETHYLDISILYLETHANE [84677-98-5]	 $Me-Si(CH=CH_2)(Me)-CH_2CH_2-Si(CH=CH_2)(Me)-Me$	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.[57]	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.[47,48,104] Vinylsilanols couple w/ aryl triflates and nonflates.[50] Potassium salts are also reactive and do not require fluoride.[56]	2.5g $275.00
SIB1910.0 1-BROMOVINYLTRIMETHYLSILANE [13683-41-5]		Useful for cross-coupling to 1-substituted vinylsilanes	5g $64.00 25g $256.00
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 for (E)-β-trimethylsilylstyrenes.[105]	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

ETHYNYLSILANES FOR CROSS-COUPLING

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIE4904.0 ETHYNYLTRIMETHYLSILANE [1066-54-2]	$H-\equiv-SiMe_3$	Useful in Sonogashira reactions with differentiated reactivity at each terminus leading to unsymmetrical diaryl acetylenes.[34] Reacts w/ aryl aldehydes to give diethynylmethanes (1,4-diynes).[35]	5g $29.00 25g $116.00 1.5kg $1065.00 13kg $5460.00
SIE4902.0 ETHYNYLTRIETHYLSILANE [1777-03-3]	$H-\equiv-SiEt_3$	More stable protected acetylene useful in Sonogashira reactions.	5g $75.00 1.5kg $3300.00
SIB1850.0 BIS(TRIMETHYLSILYL)ACETYLENE [14630-40-1]	$Me_3Si-\equiv-SiMe_3$	Useful in Sonogashira reactions.	10g $32.00 50g $126.00 1.5kg $1275.00 13kg $6318.00
SIT8606.5 1-TRIMETHYLSILYLPROPYNE [6224-91-5]	$Me-\equiv-SiMe_3$	Useful in Sonogashira reactions.	5g $24.00 25g $96.00 1.5kg $1800.00 13kg $11,375.00

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIP6736.0 PHENYLETHYNYLTRIMETHYLSILANE [2170-06-1]		Useful in trimethylsilyl-mediated Sonogashira reactions.[33,38] Arylethynylsilanes react w/ propargyl chlorides to form 1,2-diene-4-ynes.[36] Ethynylsilanes react w/ propargyl halides to form 1,4-diynes.[37]	5g $24.00 25g $96.00
SIH5848.0 1-HEPTYNYLTRIMETHYLSILANE [15719-56-9]	$n\text{-}C_5H_{11}-\equiv-SiMe_3$	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]	$Me_3Si-\equiv-CH_2OH$	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]	 $Me_3Si-\equiv-\overset{OH}{\underset{H}{C}}-Me$	Useful in Sonogashira reactions to give substituted propargyl alcohols.	10g $41.00
SIT8606.3 3-TRIMETHYLSILYLPROPYNAL [2975-46-4]	$Me_3Si-\equiv-CHO$	Potential for the formation of alkynyl aldehydes.	2.5g $134.00
SIT8623.0 TRIMETHYLSILYL(TRIMETHYL-SILYL)PROPYNOATE [97927-35-0]	$Me_3Si-\equiv-CO_2SiMe_3$	Potential for the formation of propiolic acid derivatives.	2.5g $164.00
SIP6903.0 PROPARGYLOXYTRIMETHYLSILANE [5582-62-7]	$H-\equiv-CH_2OSiMe_3$	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]	$H-\equiv-CH_2CH_2OSiMe_2Bu\text{-}t$	Potential for the formation of TBS-protected butynols.	10g $70.00
SIT8606.6 3-TRIMETHYLSILYLPROPIONIC ACID [5683-31-8]	$Me_3Si-\equiv-CO_2H$	Potential for the formation of propiolic acid derivatives.	5g $124.00

MISCELLANEOUS SILANES FOR CROSS-COUPLING

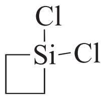
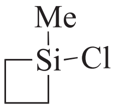
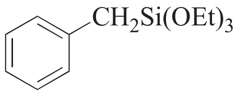
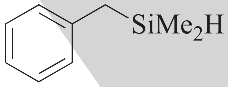
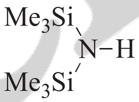
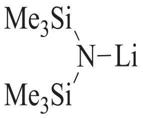
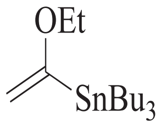
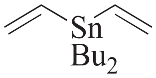
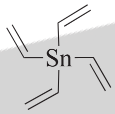
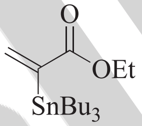
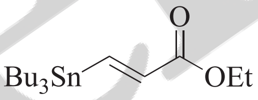
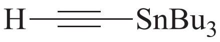
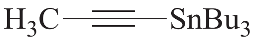
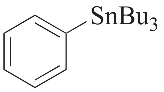
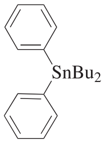
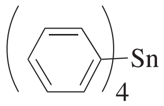
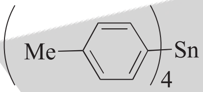
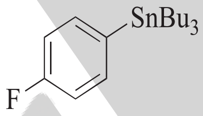
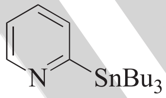
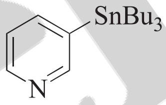
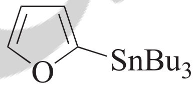
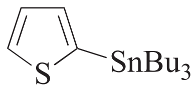
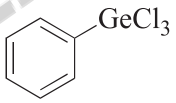
ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SIC2568.0 CYCLOTRIMETHYLENEDICHLOROSILANE [2351-33-9]		Precursor for aryl-substituted silacyclobutanes useful for aryl cross-coupling reactions.[26]	10g $54.00 50g $216.00
SIC2572.0 CYCLOTRIMETHYLENE-METHYLCHLOROSILANE [2351-34-0]		Precursor for aryl- and vinyl-substituted silacyclobutanes useful for aryl cross-coupling reactions.[26,25,101]	5g $102.00
SIB0971.0 BENZYLTRIETHOXYSILANE [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.[18,23]	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.[22]	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.[16]	25g $32.00 100g $104.00 1.5kg $720.00
SIA0540.0 ALLYLTRIMETHOXYSILANE [2551-83-9]		Allylates aryl iodides.[45]	10g $24.00 50g $96.00 2kg $720.00
SIH6110.0 HEXAMETHYLDISILAZANE [999-97-3]		Lithium reagent reacts w/ aryl chlorides or bromides to provide anilines.[84]	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.[84]	25g $16.00 100g $52.00 2kg $832.00
SIT8579.0 TRIMETHYLSILYLACETONITRILE [18293-53-3]	$Me_3Si{-}CH_2CN$	Cyanomethylates aryl bromides.[83]	5g $52.00 25g $208.00
SIP6901.0 POTASSIUM TRIMETHYLSILANOLATE [10519-96-7]	$Me_3Si{-}O\text{-}K$	Catalyst for the cross-coupling of aryl and vinylsilanes.[103]	25g $21.00 100g $68.00 2kg $1160.00
SIP6899.0 POTASSIUM TRIETHYLSILANOLATE	$Et_3Si{-}O\text{-}K$	Catalyst for the cross-coupling of aryl and vinylsilanes.[103]	10g $60.00 50g $240.00

TABLE 3 ORGANOTIN CROSS-COUPLING AGENTS

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SNE4620 1-ETHOXYVINYLTRI-*n*-BUTYLTIN [99674-02-7]		Transfer of acyl group equivalent in Stille Coupling	5g $72.00 25g $288.00 2kg $8200.00
SNV9100 VINYLTRI-*n*-BUTYLTIN [7486-35-3]		Stille Coupling vinylation reagent	5g $56.00 25g $224.00 2kg $6200.00
SND4600 DIVINYLDIMETHYLTIN [7330-43-0]		Stille Coupling vinylation reagent	5g $42.00
SNT7906 TETRAVINYLTIN [1112-56-7]		Stille Coupling vinylation reagent	5g $48.00 25g $192.00
SNB1794 (E)-1,2-BIS(TRI-*n*-BUTYL-STANNYL)ETHYLENE [14275-61-7]		β-Tri-*n*-butylstannylvinyl group or reagent for the formation of stilbenes	5g $260.00
SNE4900.3 ETHYL 2-(TRI-*n*-BUTYLTIN)-PROPENOATE [128266-87-5]		Transfer of ethyl 1-acrylate group for formation of α-substituted acrylates	2.5g $92.00
SNE4900.3 ETHYL 3-(TRI-*n*-BUTYLTIN)-PROPENOATE		Transfer of ethyl 2-acrylate group for formation of β-substituted acrylates.	2.5g $92.00
SNE4900 ETHYNYLTRI-*n*-BUTYLTIN [994-89-8]		Transfer of ethynyl group.	2.5g $57.00 10g $186.00
SNP6925 PROPYNYLTRI-*n*-BUTYLTIN [64099-82-7]		Transfer of propynyl group.	5g $146.00
SIT8588.8 TRIMETHYLSILYLETHYNYLTRI-*n*-BUTYLTIN [81353-38-0]		Transfer of trimethylsilylethynyl group.	10g $92.00
SNP6734 PHENYLETHYNYLTRI-*n*-BUTYLTIN [3757-88-8]		Transfer of phenylethynyl group.	10g $28.00

ORGANOSILANE	STRUCTURE	COMMENTS	PRICING
SNP6740 PHENYLTRI-*n*-BUTYLTIN [960-16-7]		Stille Coupling phenylation reagent.	10g $58.00 50g $232.00
SND4505 DIPHENYLDI-*n*-BUTYLTIN [6452-61-5]		Stille Coupling phenylation reagent.	25g $40.00 100g $130.00
SNT7760 TETRAPHENYLTIN [595-90-4]		Stille Coupling phenylation reagent.	100g $29.00 500g $116.00
SNT7894 TETRA(*p*-TOLYL)TIN [6746-22-1]		Stille Couppling *p*-tolylation reagent.	10g $48.00 50g $192.00
SNF4915 4-FLUOROPHENYLTRI-*n*-BUTYLTIN [17151-47-2]		Stille Coupling *p*-fluorophenyl transfer reagent.	5g $180.00
SNP6935 2-PYRIDYLTRI-*n*-BUTYLTIN [17997-47-6]		Stille Coupling for formation of 2-pyridiyl derivatives.	5g $72.00
SNP6936 3-PYRIDYLTRI-*n*-BUTYLTIN [59020-10-9]		Stille Coupling for formation of 3-pyridiyl derivatives.	5g $124.00
SNT8125 2-TRI-*n*-BUTYLSTANNYLFURAN [118486-94-5]		Stille Coupling for formation of 2-furanyl derivatives.	10g $48.00
SNT7909 2-TRI-*n*-BUTYLSTANNYLTHIOPHENE [54663-78-4]		Stille Coupling for formation of 2-thienyl derivatives.	10g $32.00
SNT8585 TRIMETHYLSILYLTRI-*n*-BUTYLTIN [17995-46-3]	$Me_3Si-SnBu_3$	Undergoes addition to olefins.	2.5g $34.00 10g $110.00
GEV9200 VINYLTRIETHYLGERMANE [6207-41-0]		Vinylation reagent.	2.5g $88.00 10g $286.00
GEP6800 PHENYLTRICHLOROGERMANE [1074-29-9]		Phenylation reagent.	2.5g $42.00 10g $134.00

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