

III.2.13.2 Other α -Hetero-Substituted Organometals in Palladium-Catalyzed Cross-Coupling

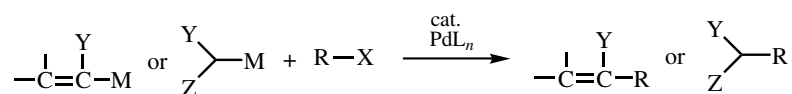
FEN-TAIR LUO

A. INTRODUCTION

The cross-coupling reaction of α -hetero-substituted organometals with organic halides and related electrophiles represents one of the most straightforward methods for making carbon–carbon bonds especially in the formation of various heterocyclic derivatives. This section will emphasize on the Pd-catalyzed cross-coupling reactions via some α -hetero-substituted organometals except metal cyanides, which are described in **Sect. III.2.13.1**. These heteroatoms, incorporated in positions that are α to the metals, include halogens (F, Cl, Br, I) and other electronegative elements, such as O, S, Se, N, and P, as well as some metals, such as B, Al, Zn, Si, and Sn (**Scheme 1**). It is important from the synthetic viewpoint to develop procedures for coupling various α -hetero-substituted alkenylmetals or α,α -disubstituted alkylmetals, the carbonylanion equivalents, with electrophiles.^[1] This section is subdivided according to the use of different metals, such as Al, B, Cu, Li, Mg, Hg, Sn, and Zn, in the α -hetero-substituted organometals.

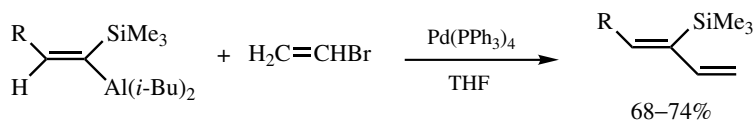
B. ORGANOALUMINUM COMPOUNDS

Relatively few reactions on the Pd-catalyzed cross-coupling reaction of organoaluminum with electrophiles have been reported in the literature. However, Negishi and Luo have reported the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross coupling reaction of α -trialkylsilyl-, α -alkoxy-, or α -alkylthio-substituted alkenylaluminum and alkenylzinc compounds with vinyl or aryl halides to form hetero-substituted arylated alkenes or conjugated dienes suitable for the Diels–Alder reaction, respectively; the stereospecificity of the reactions is $\geq 98\%$ (**Scheme 2**).^[2] Saulnier and co-workers have reported the chemoselective synthesis of allyltrimethylsilanes by the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of vinyl triflates with tris[(trimethylsilyl)methyl]aluminum (**Scheme 3**).^[3]

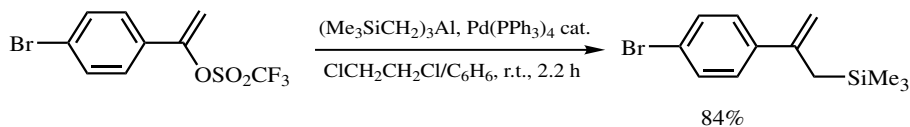


(Z may or may not be the same as Y)

Scheme 1



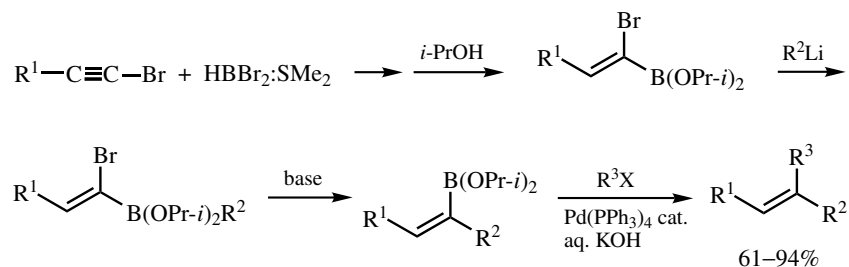
Scheme 2



Scheme 3

C. ORGANOBORON COMPOUNDS

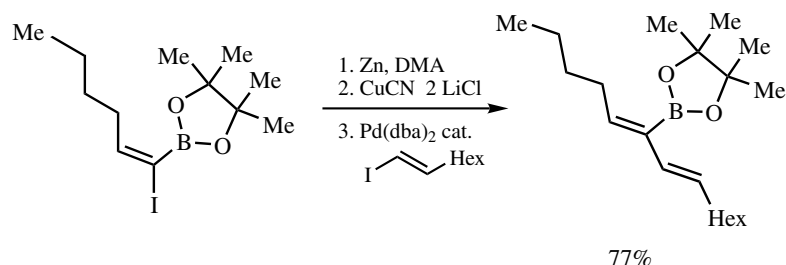
Suzuki and co-workers have reported the reaction of diisopropyl α -bromoalkenylboronates, readily obtained from hydroboration of 1-bromoalkynes and followed by the addition of organolithium, with base to give 1-organo-1-alkenylboronates. The $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction with organic halides proceeds smoothly in the presence of base to form highly stereo- and regiospecific trisubstituted alkenes (**Scheme 4**).^{[4],[5]} Likewise, Waas and co-workers have reported the conversion of α -iodoalkenylboronates, readily prepared by the hydroboration of 1-iodoalkynes, to 1,1-bimetallics of boron and zinc or copper, which react with a wide range of electrophiles to afford polyfunctional boronic esters. After hydrogen peroxide oxidation, polyfunctional ketones were produced in good to excellent yields (**Scheme 5**).^[6] Note that α -iodoalkenylboronates may undergo cross-coupling with organozinc compounds in the



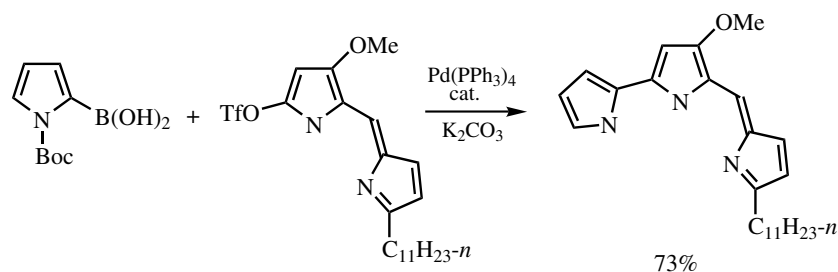
Scheme 4

presence of Pd catalyst to give 1-organo-1-alkenylboronic esters or α -organoalkenylboronates.^[7]

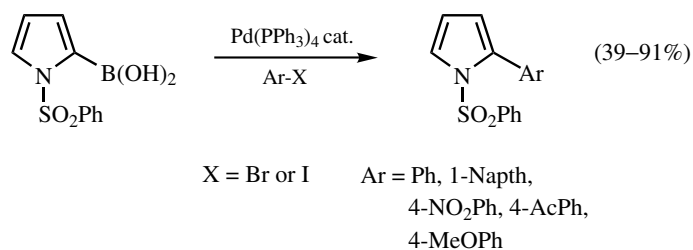
The Suzuki coupling methodology has widely been used in the preparation of pyrrole derivatives. Thus, the immunosuppressive agent undecylprodigiosine can be prepared by the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of two pyrrole rings (**Scheme 6**).^[8] The preparation of 2-aryl-1-(phenylsulfonyl)pyrroles can also be realized by cross-coupling of 1-(phenylsulfonyl)pyrrole-2-boronic acid and aryl bromides or iodides (**Scheme 7**).^[9] Similarly, Suzuki coupling of 2-thienylboronic acid with either aryl halides or triflate could give the corresponding thienyl derivatives.^{[10]–[18]} Likewise, 2-furanylboronic acid could cross-coupling with either aryl or vinyl halides or triflate via the Suzuki reaction to give the corresponding furanyl derivatives.^{[11], [19]–[25]} Triethyl(1-methylindol-2-yl)borate has been used for the Pd-catalyzed tandem cyclization and cross-coupling reaction with acetylenic or vinylic aryl halides to form ellipticine analogs (**Scheme 8**).^{[26], [27]}



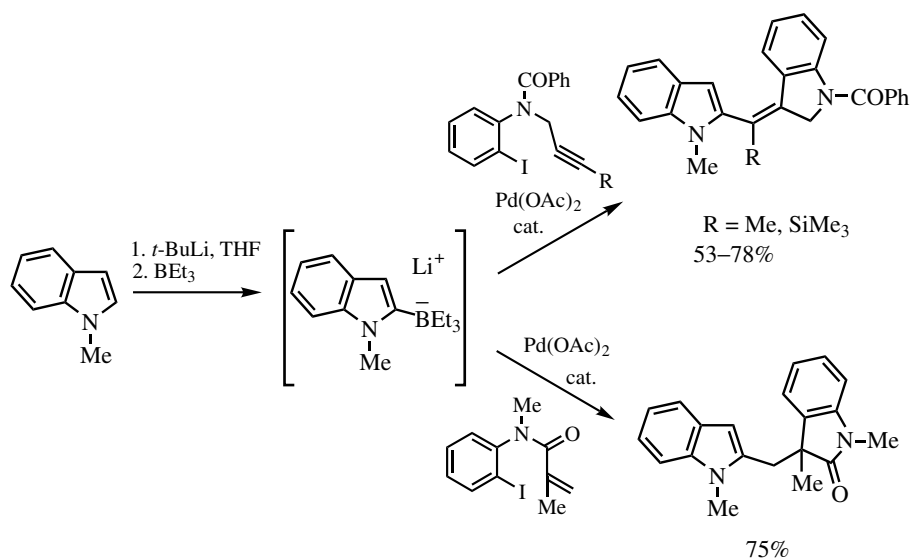
Scheme 5



Scheme 6

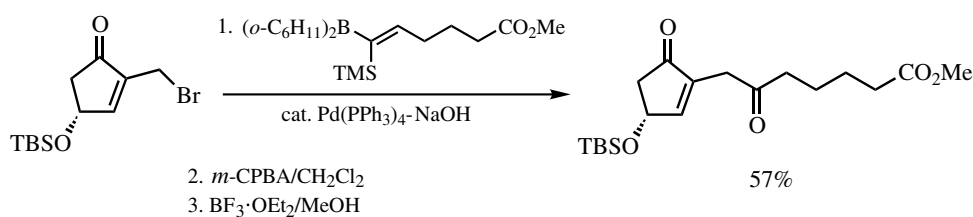


Scheme 7



Scheme 8

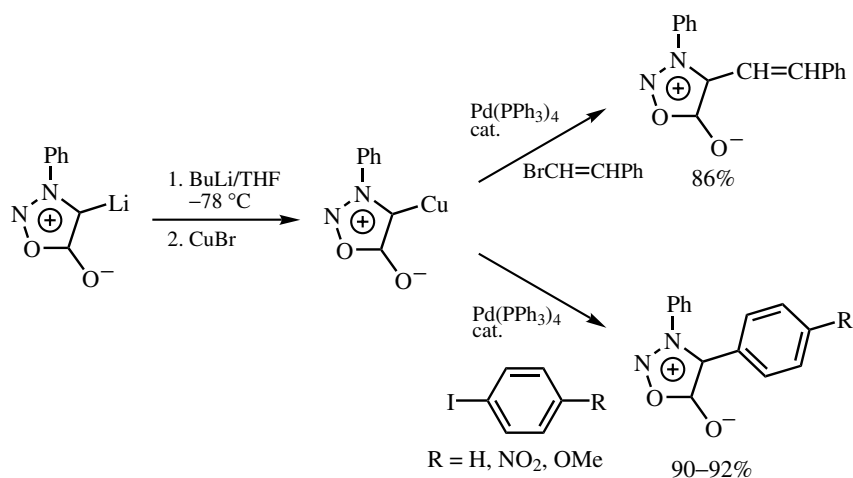
The $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of α -silylalkenylborane with 2-bromomethyl-4-siloxycyclopent-2-enone followed by the conversion to an epoxy and keto group could form a key component for the preparation of 6-keto-prostaglandins (Scheme 9).^[28] Suzuki coupling of aryl or vinyl bromides with α -silylalkenylborane under basic conditions or α -silylalkenylborate could provide the corresponding silylated styrenes and 1,3-dienes with highly stereoselectivity ($>98\%$).^{[2], [29]} Soderquist and co-workers have reported that allyl, benzyl, and propargyl silanes can be prepared via Suzuki reaction of vinyl, alkynyl, and aryl bromides with the air-stable organoborane, 10-trimethylsilylmethyl-9-oxa-10-borabicyclo[3.3.2]decane, in excellent yields.^[30]



Scheme 9

D. ORGANOCOPPER COMPOUNDS

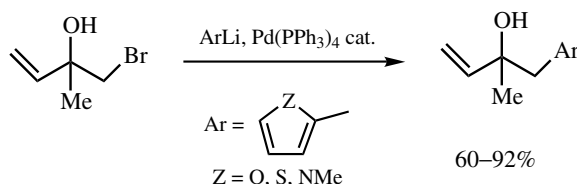
Kalinin and Min have reported the synthesis of aryl- and vinyl-sydnone from the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of 4-copper-3-phenylsydnone with aryl and vinyl halides (Scheme 10).^[31]



Scheme 10

E. ORGANOLITHIUM COMPOUNDS

Araki and co-workers have reported the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of isoprene bromohydrin with heteroaromatic organolithium reagents in good yields without rearrangement (**Scheme 11**).^[32] Pelter and co-workers have reported that the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reactions of 2-lithiofuran with allyl or benzyl bromides work well, but fail with aryl bromide.^[33]

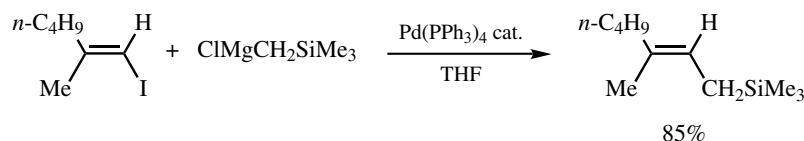


Scheme 11

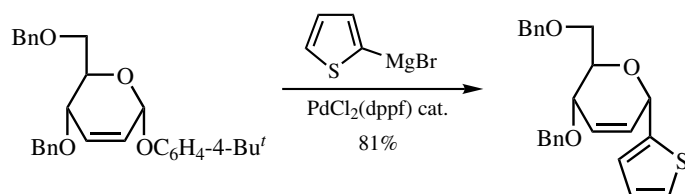
F. ORGANOMAGNESIUM COMPOUNDS

Negishi and co-workers have reported the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of trimethylsilylmethylmagnesium chloride with alkenyl iodides to form allylsilanes in excellent yields and in a highly stereo- and regioselective manner (**Scheme 12**).^{[34],[35]} Sugihara and Ogasawara have reported the $[\text{PdCl}_2(\text{PPh}_3)_2]$ -catalyzed cross-coupling reaction of optically active 2-chlorovinylcarbinols with trimethylsilylmethylmagnesium chloride to form certain optically active allyl alcohols.^[36] Alternatively, Hevesi and co-workers have reported the $[\text{PdCl}_2(\text{PPh}_3)_2]$ -catalyzed cross-coupling reaction of vinyl selenides with trimethylsilylmethylmagnesium chloride to form allylsilanes.^[37] Minato and co-workers have reported the $[\text{PdCl}_2(\text{dppb})]$ - or $[\text{PdCl}_2(\text{dppf})]$ -catalyzed cross-coupling reaction of 1-methyl-2-pyrrolylmagnesium bromide with aryl and heteroaryl halides to

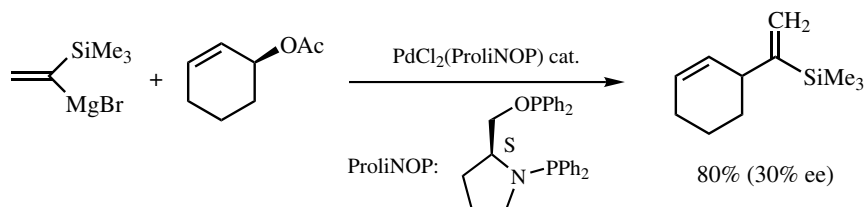
give the corresponding 2-substituted pyrroles in good to excellent yields.^{[38],[39]} Likewise, 2-thienylmagnesium bromide could be coupled with *p*-*tert*-butylphenyl α -*O*- Δ^2 -glycopyranoside to form *C*- α -aryl- Δ^2 -glycopyranosides in the presence of PdCl₂(dppf) catalyst (**Scheme 13**).^{[39],[40]} The [PdCl₂(dppb)]-catalyzed cross-coupling reactions of α -silylvinylmagnesium bromide with heteroaryl bromides have also been reported.^[7] Buono and co-workers have reported the use of PdCl₂(MeCN)₂ catalyst and chiral AMPP (aminophosphine phosphinite) ligands^[41] in the allylation of 1-trimethylsilylvinylmagnesium bromide with 3-cyclohexenyl acetate to give a versatile synthon, 3-(1-trimethylsilylvinyl)cyclohexene, in high yields and with ee up to 33% (**Scheme 14**).^[42]



Scheme 12



Scheme 13



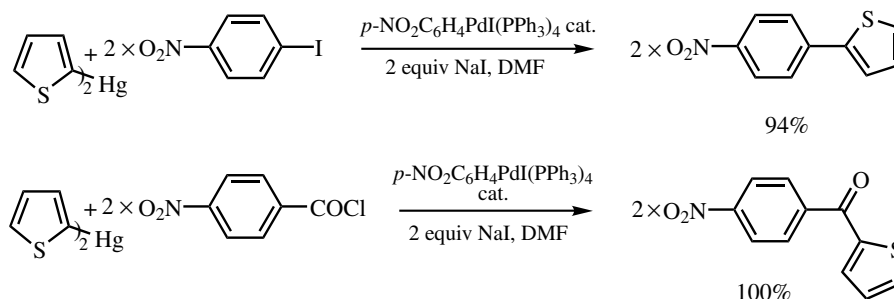
Scheme 14

G. ORGANOMERCURY COMPOUNDS

Bumagin and co-workers have reported the $\text{ArPdI}(\text{PPh}_3)_2$ -catalyzed cross-coupling of 2-furanyl or 2-thienylmercurials with aromatic halides in the presence of iodide ion to give coupling products in high yields. In the case of acyl halides, unsymmetrical diaryl ketones could be obtained in good yields (**Scheme 15**).^{[43],[44]}

H. ORGANOTIN COMPOUNDS

α -Hetero-substituted organotin compounds (**Scheme 16**) have been used extensively in the Pd-catalyzed cross-coupling reaction with various electrophiles, since the tin



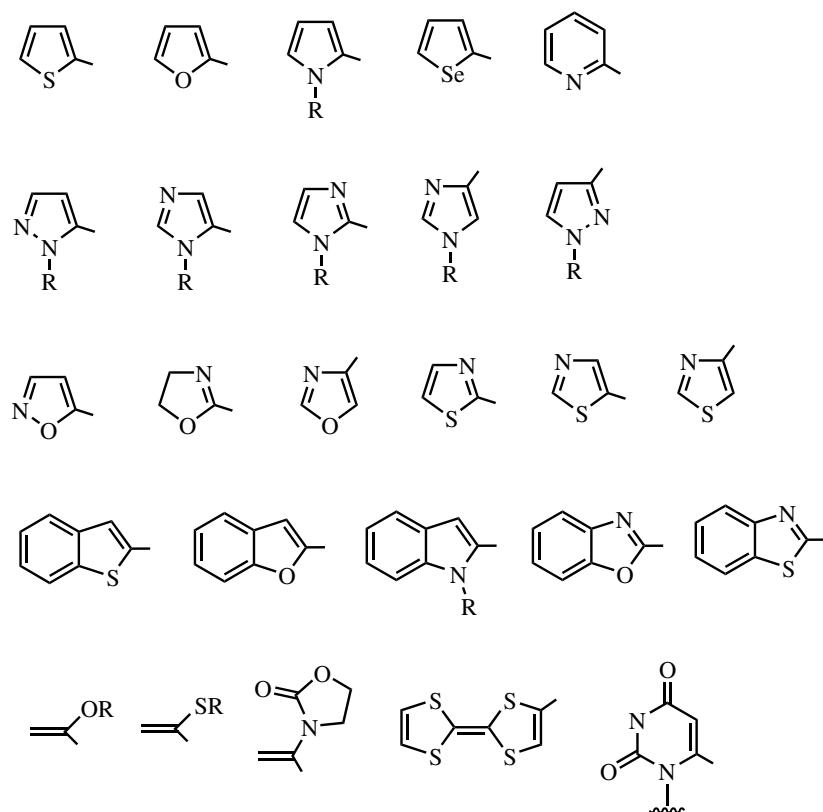
Scheme 15

derivatives may tolerate a variety of functional groups both in the organometallic reagent and in heterocyclic halides. Matthews and co-workers have reported the use of (1-fluorovinyl) tributyltin as a synthetic equivalent for the 1-fluoroethene anion in the Pd-catalyzed cross-coupling with aryl iodide, aryl triflate, or acid chloride to form the corresponding alkenyl fluoride derivatives.^{[45],[46]} Shi and co-workers have reported the addition of copper(I) iodide as a cocatalyst in the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of (1-fluorovinyl)tributyltin reagent to give better yields.^[47] The cross-coupling of hexabutyldistannane with (4-bromophenyl)methylsulfone in the presence of both $\text{Pd}(\text{OAc})_2$ and $\text{Pd}(\text{PPh}_3)_4$ catalysts could give methyl[4-(tributylstannyl)phenyl]sulfone.^[21] Likewise, hexamethyldistannane can couple with triflated oxazole by the aid of Pd catalyst to give 4-trimethylstannyloxazole.^[48]

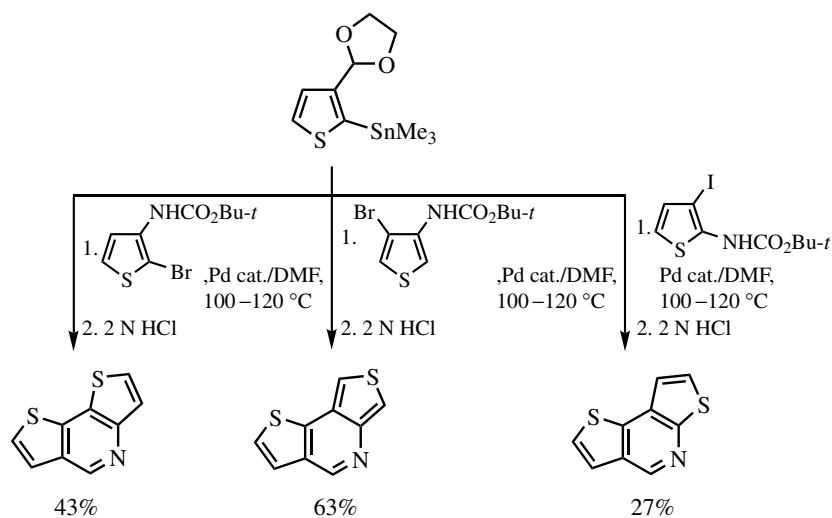
The Pd-catalyzed cross-coupling of 2-thienyl-, 2-pyrrolyl-, 2-furyl-, and 2-pyridyltin reagents with various organic halides or triflates, such as aryl, heteroaryl, allyl, and alkenyl halides, have been extensively studied and reported in the literature.^{[49]–[98]} The intact functional groups include aldehyde,^{[49],[50]} ester,^{[49],[50]} alcohol,^[49] amide,^{[50],[51]} amino,^{[52],[53]} nitro group,^[54] and uracil moiety.^{[55],[56]} Gronowitz and co-workers have reported the synthesis of dithienopyridines and other fused heterocycles through Pd-catalyzed cross-coupling of 2-thienyltin reagent with *N*-(halo-heteroaryl)carbamates (Scheme 17).^{[57]–[61]} Kang and co-workers have reported the Pd-catalyzed cross-coupling of 2-thienyl and 2-furyltin compounds with iodanes^[74] or hypervalent iodonium salts^[75] (Scheme 18). Liebeskind and Wang have reported the construction of substituted benzo- and dibenzofurans or thiophenes by the Pd-catalyzed cross-coupling of 2-furyl- or 2-thienyltin reagent with 4-chloro-2,3-disubstituted-2-cyclobutenones and followed by thermolysis at 100 °C (Scheme 19).^[80] Under the same conditions, both 2-(tri-*n*-butylstannyl)benzofuran and 2-(tri-*n*-butylstannyl)thiophene react with 4-chloro-2,3-disubstituted-2-cyclobutenones to form dibenzoheteroaryls.^[80] Similarly, 2-benzofuranyl-, 2-benzothiophenyl-, or 2-indolyltin reagents may couple with aryl, heteroaryl, alkenyl, alkynyl, or alkyl halides in the presence of Pd catalyst to give the corresponding coupled products in good yields and in a stereoselective manner.^{[80],[81],[84],[99]–[105]} Intramolecular cyclization based on the Pd-catalyzed cross-coupling reaction of 2-indolyltin and vinyl or benzyl bromide could give high yields of the corresponding seven- and nine-membered ring (Scheme 20).^[103] 2-Selenienyltin compound also has been used in the Pd-catalyzed cross-coupling reaction with iodopyrimidine.^[83] Alkenyltin containing α -alkylthio or α -alkyloxy substituents reacts readily with chloropurines and aryl halides in the

presence of Pd catalyst to produce alkenylated purines and benzenes, respectively.^{[86]–[88],[92],[106]} Liebeskind and Wang have reported the synthesis of substituted 2-pyrones by carbonylative cross-coupling and thermolysis of 4-halocyclobutenones with 2-ethoxyvinyl-, 2-furyl-, and 2-thienyltin reagents (**Scheme 21**).^[89] Optically active ene carbamates were α -lithiated by lithium tetramethylpiperidide in the presence of trialkylstannyl chlorides to produce α -stannylated compounds.^[107] These stannylated compounds underwent facile Pd-catalyzed cross-coupling with acid chlorides to produce α -keto ene carbamates in good yields (**Scheme 22**). The Pd-catalyzed cross-coupling of stannylated 2- and 4-oxazole,^{[48],[108]} 5-isoxazole,^{[93],[98]} 2-benzoxazole,^[109] 2-, 4-, and 5-thiazole,^{[82],[85],[93],[110]} 2-benzothiazole,^{[91],[109]} 2-, 4-, and 5-imidazole,^{[85],[90],[93],[111]–[113]} 3-pyrazole,^{[114]–[116]} 2-oxazoline,^{[117],[118]} and 6-uridine^[119] with various organic electrophiles have been reported in the literature to give the corresponding regio- and stereoselective products. Iyoda and co-workers have reported the Pd-catalyzed cross-coupling of (trialkylstannyl)tetrathiafulvalene with aryl, naphthyl, or 1,6-methano[10]annulene halides to give the corresponding tetrathiafulvalene-substituted aryl, naphthalene, and 1,6-methano[10]annulene derivatives.^{[120],[121]}

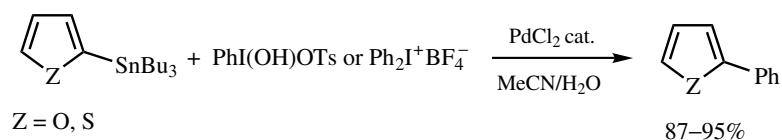
α -Hetero-substituted organotin compounds



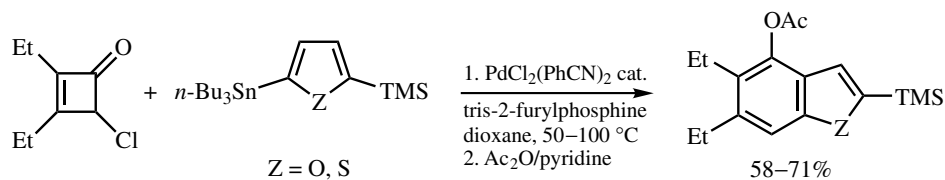
Scheme 16



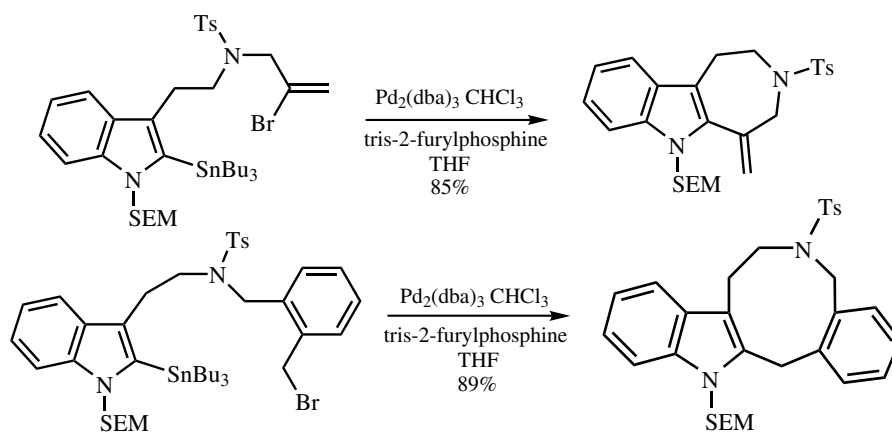
Scheme 17



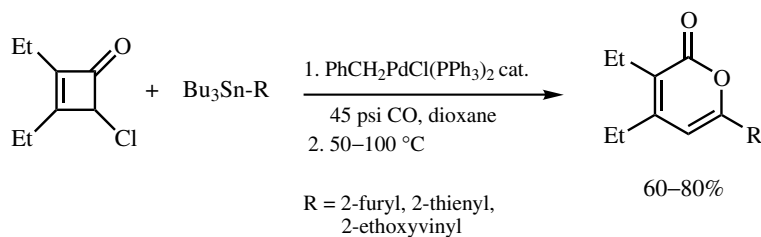
Scheme 18



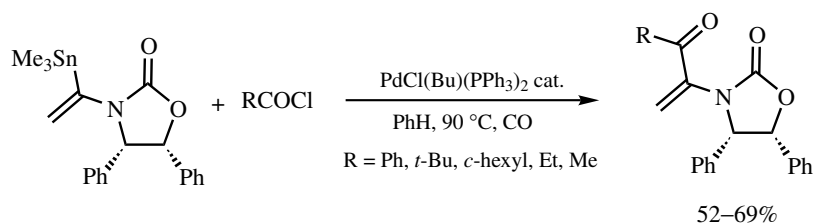
Scheme 19



Scheme 20



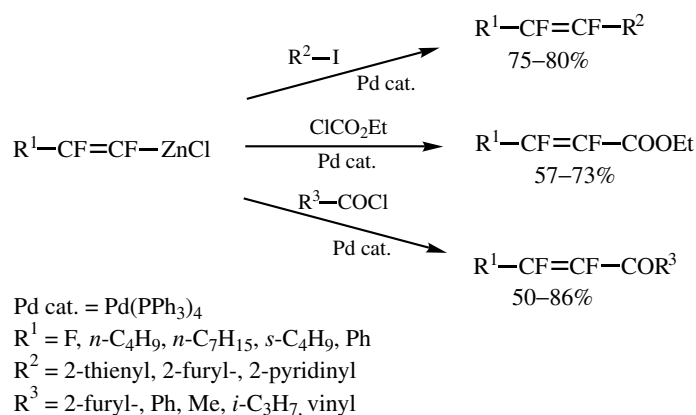
Scheme 21



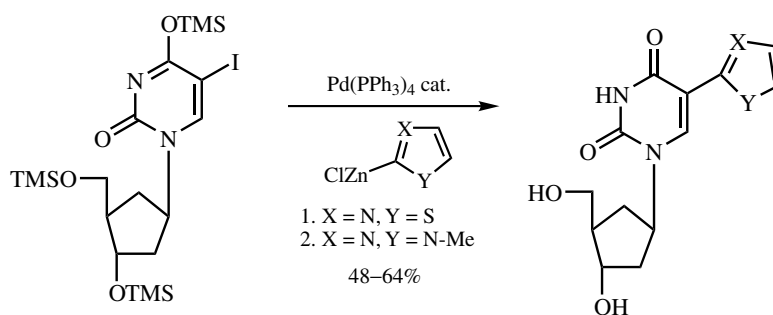
Scheme 22

I. ORGANOZINC COMPOUNDS

Burton, Davis, and Heinze have reported the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of aromatic iodides with (*E*)-1,2-difluoroethenylzinc chloride in DMF to form α,β -difluorostyrenes in good yields and in a stereoselective manner.^{[122],[123]} Gillet and co-workers have reported the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of fluorovinylzinc reagents with acid chlorides, ethyl chloroacetate, or alkenyl iodides to form fluorovinyl ketones, esters, and heterocycles in good yields (**Scheme 23**).^[124] A general method for the preparation of 2-(2-pyridyl)indoles based on the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of 1-(benzenesulfonyl)-2-indolylzinc chloride with 2-halopyridines has been reported.^[125] This method has been used in the preparation of the indolo[2,3-*a*]quinolizidine ring system of a large number of indole alkaloids.^[126] 2'-Deoxyuridines with a five-membered heterocyclic substituent at the 5-position were synthesized by $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed coupling reactions of 5-iodo-2'-deoxyuridines with activated heteroaromatics (**Scheme 24**).^[55] Alkenylzinc containing α -alkoxy or α -alkylthio substituents react readily with aryl or alkenyl halides in the presence of a Pd catalyst to produce arylated alkenes or conjugated dienes, respectively, with high ($\geq 98\%$) stereoselectivities.^{[2],[127]–[130]} 2-Furylzinc chloride could couple with alkenyl triflates in the presence of $\text{Pd}(\text{PPh}_3)_4$ catalyst to form 2-vinylfurans.^[131] Hyuga and co-workers have reported a one-pot synthesis of prostaglandin B₁ methyl ester by a stepwise Pd-catalyzed cross-coupling reaction of (*E*)-(2-bromoethenyl)diisopropoxyborane with α -methoxy-alkenylzinc chloride followed by addition and elimination of 3-bromocyclopentenone derivatives.^[132] Luo and co-workers have reported a one-pot conversion of terminal alkynes into *gem*-disubstituted alkenes via the addition of *in situ* generated hydrogen iodide and Pd-catalyzed cross-coupling with organozinc reagents including 2-furyl- and 2-thienylzinc chloride.^{[133],[134]} Luo, Wang, and Chov have reported the tandem cyclization and cross-coupling reaction of acetylenic aryl iodides with 2-heteroarylzinc chloride to

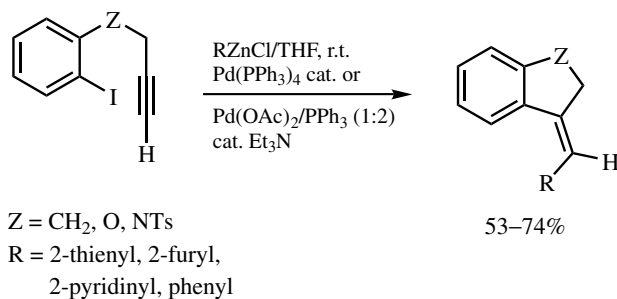


Scheme 23

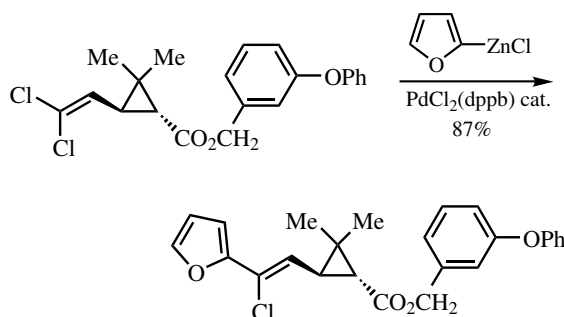


Scheme 24

form 1-indanylidene, (*Z*)-2,3-dihydro-3-(arylmethylene)benzofurans, or (*Z*)-3-methylene-2,3-dihydroindole derivatives (Scheme 25).^{[135]–[138]} It is noted that both 2-furyl and 2-thienylzinc chloride can undergo cross-coupling reaction with dichloroethenyl cyclopropanecarboxylates in the presence of PdCl₂(dppb) catalyst to form pyrethroids (Scheme 26).^[139] The Pd-catalyzed cross-coupling reaction of 2-thienylzinc chloride with other aromatic halides to form thiophene compounds have been extensively applied to new materials with second order optical nonlinearities.^[140] Kalinin and co-workers have reported the [Pd(PPh₃)₄]-catalyzed cross-coupling reaction of 4-bromo-2-pyrone with 2-thienylzinc chloride to form 4-substituted 2*H*-pyran-2-one.^[141] Bellina and co-workers have reported a highly regioselective [Pd(PPh₃)₄]-catalyzed cross-coupling reaction of 2-thienylzinc chloride with easily available (*Z*)- and (*E*)-alkyl 2,3-dibromopropenoates to form stereoisomerically pure (*Z*)- and (*E*)-alkyl 2-bromo-3-(2-thienyl)propenoates in good yields.^[142] Takahashi and co-workers have reported the synthesis of novel *p*-terphenylquinone analogs involving a central dihydrothiophenediylidene structure by the [Pd(PPh₃)₄]-catalyzed cross-coupling reaction of 4-alkoxyaryl halides and thienylzinc chloride.^[143] Goldfinger and co-workers have reported the use of [Pd(PPh₃)₄]-catalyzed cross-coupling reaction of thienylzinc chloride and *p*-dibromobenzene for the synthesis of rigid and fused polycyclic aromatics useful for a number of advanced materials applied in nonlinear optical, photoluminescent, electroluminescent, and molecular-based sensory

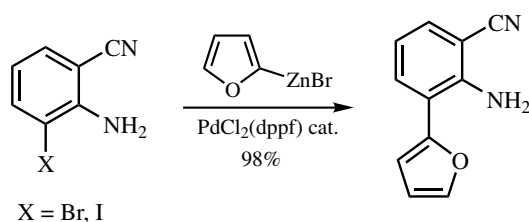


Scheme 25

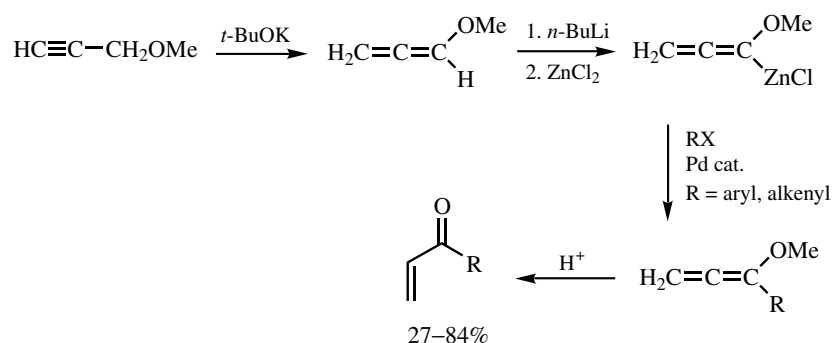


Scheme 26

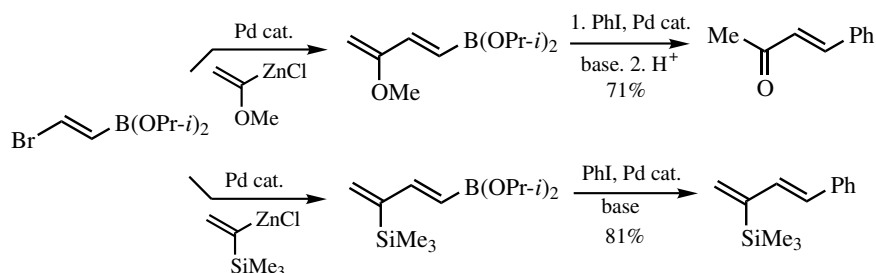
devices.^[144] The efficient Pd-catalyzed synthesis of unsymmetrical donor–acceptor biaryls, polyaryls, or heteroaryls from the cross-coupling of substituted aromatic zinc reagent and aryl halides have been reported.^{[33],[145],[146]} Keenan and Kruse have reported the cross-coupling of 2-furylzinc chloride with 2-methoxy-5-[(trifluoromethyl)sulfonyl]oxy}tropone in the presence of $\text{Pd}(\text{PPh}_3)_4$ catalyst to give 5-(2-thienyl)tropone in good yield.^[147] Roth and Fuller have reported the mild $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of aryl fluorosulfonates with 2-furylzinc chloride in a regioselective manner.^[148] Brandão and co-workers have reported a general combined metallation by the aid of an amide group and Pd-catalyzed cross-coupling methodology involving 2-furylzinc or 2-thienylzinc chloride to form the regiospecific hetero-ring-fused *o*-naphthoquinones.^[11] Campbell and co-workers have reported a convenient synthesis of 3-substituted anthranilonitriles by the $[\text{PdCl}_2(\text{dppf})]$ -catalyzed cross-coupling reaction of 2-furylzinc bromide with 3-iodoanthranilonitrile (**Scheme 27**).^[149] Russell and Hegedus have reported the cross-coupling of zinc salts of allenic ethers with aryl and alkenyl halides by using Pd catalyst to give α,β -unsaturated ketones, the allenic ether serving as a source of the acryloyl group (**Scheme 28**).^[128] Suzuki and co-workers and Mazal and Vaultier have reported a stepwise cross-coupling reaction of (*E*)-(2-bromoethenyl)diisopropoxyborane with α -methoxyalkenylzinc chloride or α -trimethylsilylvinylylzinc chloride and organic halides by using $\text{PdCl}_2(\text{PPh}_3)_2$ as the catalyst to form α,β -unsaturated ketones or (*E*)-olefins in good yields with high (*E*)-stereoselectivities (**Scheme 29**).^{[150]–[152]} Tius and co-workers have shown that the chlorozinc derivative of sugar could give much better results in the cross-coupling reaction with iodoanthracene by the aid of an active Pd catalyst, generated *in situ* by the reduction of $\text{PdCl}_2(\text{PPh}_3)_2$ with diisobutylaluminum hydride in THF



Scheme 27

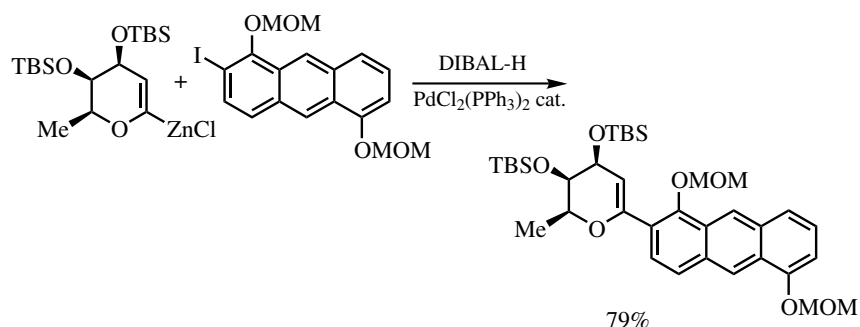


Scheme 28

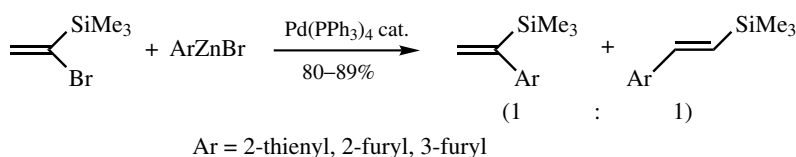


Scheme 29

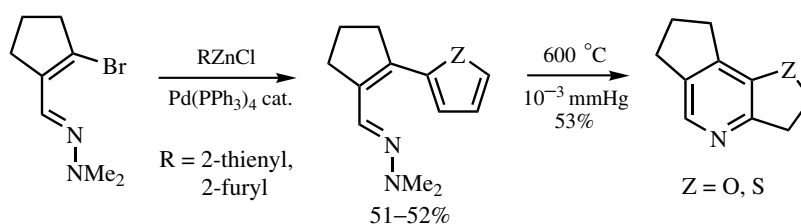
(**Scheme 30**).^[153] Friesen and co-workers have also reported the $[\text{PdCl}_2(\text{PPh}_3)_2]$ -catalyzed cross-coupling of 2-furylzinc chloride or 2-furyldimethoxyborane with iodo-glucal to form C-furyl glucals in good yields.^{[154],[155]} Anderson and co-workers have demonstrated the use of oxazol-2-ylzinc chloride has great advantage over the use of the corresponding tin reagent in the Pd-catalyzed cross-coupling of iodoindole derivatives in both yield and toxicity aspects.^[156] Ennis and Gilchrist have reported that the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of (1-bromovinyl)trimethylsilane with 2-thienyl-, 2-furyl-, or 3-furylzinc bromide may give both 1- and 2-substituted vinylsilanes in about 1:1 ratio (**Scheme 31**).^[157] Gilchrist, Kemmitt, and Germain have reported that the $[\text{Pd}(\text{PPh}_3)_4]$ -catalyzed cross-coupling reaction of 2-bromocyclopentene-1-carboxaldehyde *N,N*-dimethylhydrazone with 2-furyl- and 2-thienylzinc chlorides provides a route to the corresponding 2-heteroaryl-cyclopentene-1-carboxaldehyde dimethylhydrazones. These compounds could be cyclized under flash vacuum pyrolysis at 600 °C and 10^{-3} mmHg to give 6,7-dihydro-5*H*-2-pyrindines (**Scheme 32**).^[158] The



Scheme 30

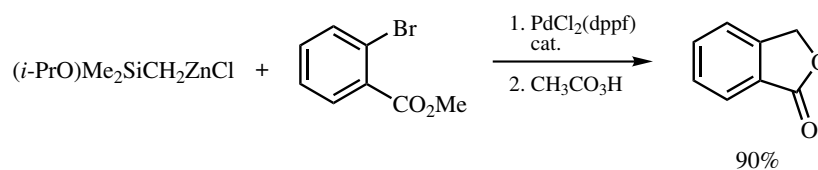


Scheme 31



Scheme 32

cross-coupling product from 2-bromocyclopentene-1-carboxaldehyde *N,N*-dimethylhydrazone with α -trimethylsilylvinylzinc chloride may undergo cyclization at or below 60°C with a loss of dimethylamine.^{[158]–[160]} Normally, α -trimethylsilylvinylzinc chloride may couple with aryl, 2- or 3-heteroaryl, and alkenyl halides in the presence of a pertinent Pd catalyst to form regio- and stereoselective products.^{[39],[161]} It is noted that trimethylsilylmethylzinc chloride may couple with (*Z*)-2-bromo-1-alkenylboranes, prepared from the bromoboration of 1-alkynes with tribromoborane, in the presence of Pd catalyst to give 2,2-disubstituted alkenylboranes, which in turn can be used for further Pd-catalyzed cross-coupling to form the trisubstituted alkenes directly.^[162] Treatment of the allylsilane, obtained from the first step in the previous reaction, with acid could give 2-methyl-1-alkenes in good yields.^{[7],[162]} Chatani and co-workers have reported the use of $(\text{Me}_3\text{SiCH}_2)_2\text{Zn}$, Me_3SiI , and phenyl acetylene to form (*E*)-2-phenyl-1,3-bis(trimethylsilyl)-2-phenylprop-1-ene in 66% yield.^[163] Kercher and Livinghouse also have reported the $[\text{PdCl}_2(\text{PPh}_3)_2]$ -catalyzed cross-coupling of $(\text{Me}_3\text{SiCH}_2)_2\text{Zn}$ with 1,1-dibromoalkenes to form 1,1-bis(trimethylsilylmethyl)-alkenes.^[164] Tamao and co-workers have reported that the cross-coupling of (diisopropoxymethylsilyl)-methylzinc chloride with aryl bromides followed by oxidation could give benzyl alcohols in fair



Scheme 33

to good yields.^[165] Here, (diisopropoxymethylsilyl)methylzinc chloride reagent serves as a nucleophilic hydroxymethylating agent of aryl halide via Pd-catalyzed cross-coupling and subsequent oxidative cleavage of the silicon–carbon bond (**Scheme 33**).

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