Transition metal-catalyzed three-component coupling of allenes and the related allylation reactions

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The feature article surveys the transition metal-catalyzed three-component coupling of allenes and the related allylation reactions. Most of the reactions shown in the article mechanistically proceed *via* oxidative addition of organic electrophiles to metals, followed by carbometallation of allene and then transmetalation by main group metals or reagents and organometallic reagents. These reactions provide an efficient route for the synthesis of various substituted allyl and vinyl metal reagents and complex organic molecules in highly regio-, stereo- and chemoselective manner in one pot. The metal reagents or π-allyl–metal intermediates obtained from the reaction are utilized for the allylation of aldehydes, ketones and imines, producing various homoallylic alcohols and amines in a highly regio- and stereoselective manner.

Introduction

The transition metal-catalyzed three-component coupling involving the oxidative addition of an organic electrophile to a metal, followed by insertion of a carbon–carbon multiple bond and then termination by a nucleophile is an efficient method in organic synthesis for the construction of two new chemical bonds from three different components (Scheme 1).[1] In the design of these three-component coupling reactions, the control of both regio- and stereoselectivity and suppression of the reactivity of competitive reactions such as direct coupling of electrophile and nucleophile, β-hydride elimination and polymerization of the carbon–carbon multiple bonds are important considerations.

While alkynes,[2] alkenes,[3] conjugated dienes[4] and allenes[5] are widely employed as unsaturated π-components in the metal-catalyzed addition reactions.[1] Until recently, allenes have gained less attention than the other three classes of π-components. This is likely due to the lower availability and the complicated selectivity problems of allenes. While regio- and stereoselectivity are all encountered for metal-catalyzed addition reactions involving alkynes, alkenes, conjugated dienes and allenes, an additional regioselectivity problem, at each of the two orthogonal double bonds is encountered for allenes.[6]

Despite the complicated regio- and stereoselectivity, allenes are suitable π-components for transition metal-catalyzed three-component coupling reactions due to their easy coordination to metal centers and insertion into a metal–carbon bond to form a π-allyl–metal intermediate that is relatively stable to β-hydride elimination and polymerization, but is readily attacked by mild nucleophiles.[5–8] In 1984, Shimizu and Tsuji observed the three-component reaction of allenes with aromatic or alkenyl halides and secondary amines in the presence of phosphine palladium catalysts to provide 2-aromatic or alkenyl allylic amines.[9] In the same year, Cazes's group observed the three-component reaction of allenes with vinyl halides or vinyl triflates and the anion of a malonic type

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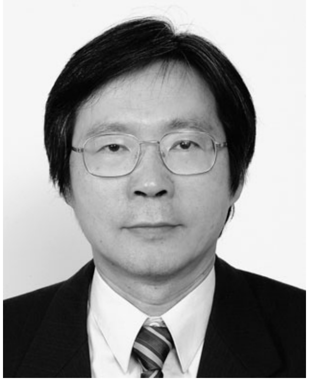

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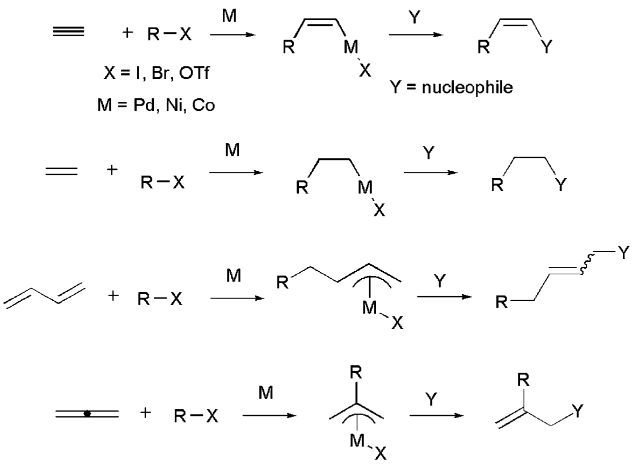
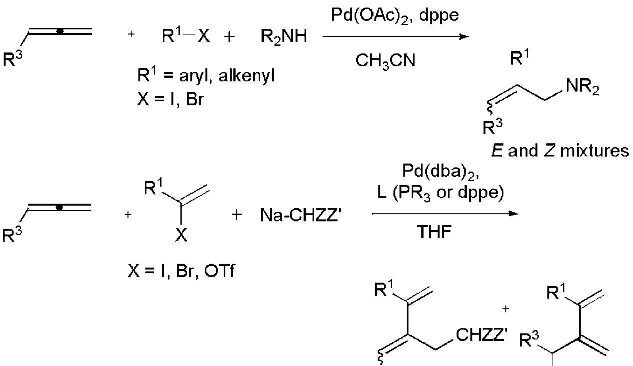


Scheme 1

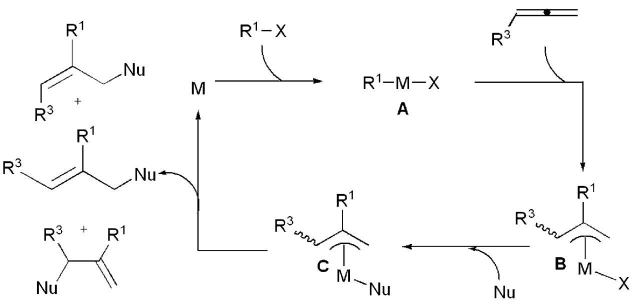
pronucleophiles in the presence of phosphine palladium catalyst to give functionalized dienes.[10] However, these phosphine palladium-catalyzed reactions suffer from the drawback of low regio- and stereoselectivity (Scheme 2).

In the three-component coupling reaction, the organic moiety attached to the oxidative adduct **A** likely acts as a mild nucleophile adding mostly to the electron deficient carbon, that is, to the sp carbon of allene giving a π-allyl metal complex **B** (Scheme 3). Thus, these three-component coupling reactions of allenes are generally highly regioselective. The facial selectivity of the coordination of double bonds of allenes to the oxidative adduct of a metal center decides the stereochemistry of the product. The additional regioselectivity is due to the possibility of attack of nucleophile at the two active centers of the π-allyl palladium complex **C**. The regioselectivity can be easily overcome, but the stereo- and additional regioselectivity are generally key problems of three-component coupling reactions.[5–8]

The three-component coupling reactions of allenes were successfully applied to the synthesis of various carbocyclic and heterocyclic compounds as well as allyl and alkenyl metal reagents.[5–8] Allyl metal reagents are highly valuable intermediates that have been used in the construction of various homoallylic alcohols and amines in a highly regio- and stereoselective manner.[11] In addition, alkenyl metal reagents are versatile precursors in coupling reactions.[12]



Scheme 2



Scheme 3

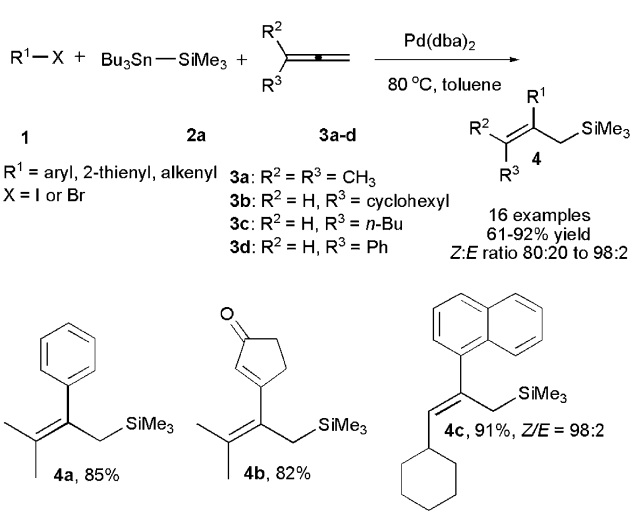
In this feature article, we wish to summarize various regio- and stereoselective three-component coupling reactions of allenes using dimetal reagents or organometallic reagents as nucleophiles and the application of the metal reagents or π-allyl–metal intermediates produced from the reaction for the regio- and stereoselective allylation of aldehydes, ketones and imines. We should point out that three-component coupling reactions of allenes with electrophiles and pronucleophiles are not included in the present feature article. This subject[7] and other allene chemistry were covered in previous reviews.[7,8]

I Three-component coupling of allenes

I.1 Carbometallation of allenes

I.1a Palladium-catalyzed carbosilylation of allenes with organic halides and $Bu_3SnSiMe_3$. In 1999, we reported the carbosilylation of allenes catalyzed by the palladium complex $Pd(dba)_2$ involving a three-component coupling of organic halide **1**, allene **3** and trimethyl(tributylstannane)silane (**2a**) to give allylic silane **4** (Scheme 4).[13] Thus, when iodobenzene was treated with $Bu_3SnSiMe_3$ (**2a**) and 1,1-dimethylallene (**3a**) in the presence of $Pd(dba)_2$ (5 mol%) in toluene at 80 °C for 7 h, allylic silane **4a** was obtained in 85% yield. The catalytic reaction was completely regioselective, in which the aryl and silyl groups were added to the middle and terminal carbon of allene, respectively.

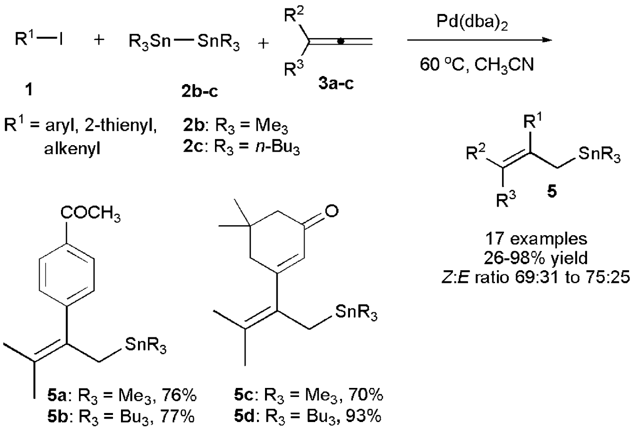
Under similar reaction conditions, various aryl halides, 2-iodothiophene and alkenyl halides underwent three-



Scheme 4

component coupling reaction with $Bu_3SnSiMe_3$ (**2a**) and 1,1-dimethylallene (**3a**) giving the corresponding allylic silanes **4** in 61–92% yields. In addition to **3a**, monosubstituted allenes **3b–d** also efficiently reacted with iodobenzene and $Bu_3SnSiMe_3$, giving allylic silanes **4** in 80–91% yields in a highly stereoselective manner ($Z:E$ ratios of 80 : 20 to 98 : 2). Bulkier organic halides and allenes gave allylic silanes in higher $E:Z$ ratios. For example, the reaction of 1-iodonapthalene and $Bu_3SnSiMe_3$ (**2a**) with cyclohexyl allene (**3b**), afforded allylic silane **4c** in 91% yield with a $Z:E$ ratio of 98 : 2 (Scheme 4). The structures of products **4a–c** and the corresponding yields are shown in Scheme 4.

I.1b Palladium-catalyzed carbostannation of allenes with organic iodides and distannanes. Palladium complex $Pd(dba)_2$ also catalyzed the carbostannation of allenes (Scheme 5), but slow addition of the distannane reagent to the reaction solution was required to obtain high product yield.[14] Treatment of *p*-iodoacetophenone with $Me_3SnSnMe_3$ (**2b**) and 1,1-dimethylallene (**3a**) in the presence of $Pd(dba)_2$ in CH_3CN at 60 °C provided a trace amount of allylstannane **5a** (Scheme 5). The major product observed was the direct coupling of *p*-iodoacetophenone with $Me_3SnSnMe_3$ giving *p*-acetylphenyltrimethylstannane (*p*-$COCH_3$–C_6H_4–$SnMe_3$). The high reactivity of **2b** towards the oxidative adduct of organic halide and Pd(0) giving little chance for the insertion of allene into the palladium–carbon bond of the oxidative adduct likely accounts for the high yield of two-component coupling product, arylstannane.

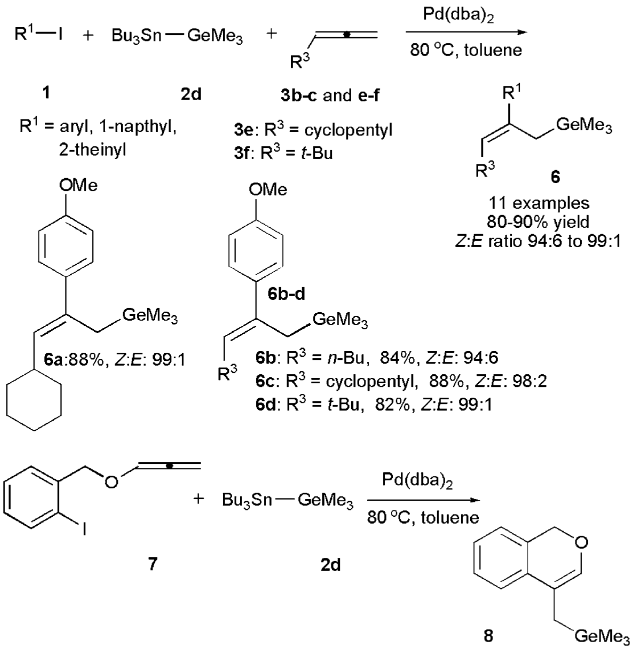


Scheme 5

Fortunately, the competing direct coupling product *p*-acetylphenyltrimethylstannane (*p*-$COCH_3$–C_6H_4–$SnMe_3$) was effectively suppressed by a slow addition of $Me_3SnSnMe_3$ over a period of 2 h to the reaction mixture of *p*-iodoacetophenone and 1,1-dimethylallene. The corresponding reaction afforded a three-component coupling product allylstannation **5a** in 76% yield. Similarly, *p*-iodoacetophenone reacted with 1,1-dimethylallene and (n-$Bu_3Sn)_2$ (**2c**) in the presence of $Pd(dba)_2$ providing allylstannane **5b** in 77% yield. Under similar reaction conditions, monosubstituted allenes **3b–c** also underwent carbostannation with aryl iodides and $Me_3SnSnMe_3$ or (n-$Bu_3Sn)_2$, producing allylstannanes **5** with moderate stereoselectivity ($Z:E$ ratios of 69 : 31 to 75 : 25).

In the reaction, hexa-*n*-butylditin (**2c**) generally gave higher yield of the allylstannane product **5b** and **5d** than hexamethylditin (**2b**) (**5a** and **5c**). This is probably due to the lower reactivity of **2c** towards the oxidative adduct of organic halide and Pd(0) providing longer time for the insertion of allene into the palladium–carbon bond of the oxidative adduct to give a higher yield of allylstannane product, particularly when the concentration of **2c** in the solution is kept low by slow addition *via* a syringe pump.

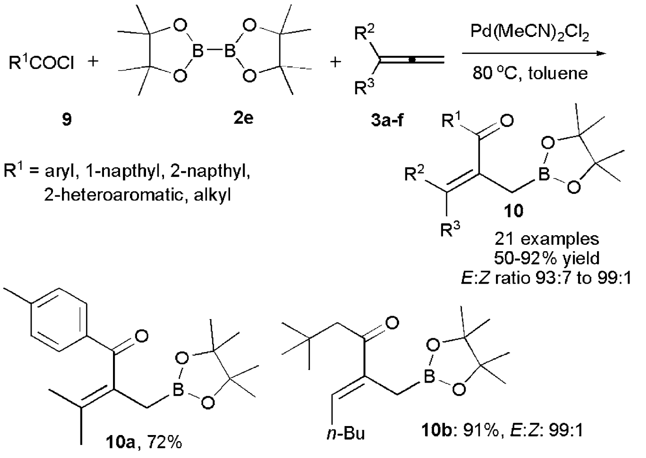
I.1c Palladium-catalyzed carbogermanylation of allenes with organic iodides and $Bu_3SnGeMe_3$. When, the reaction of 4-iodoanisole, $Bu_3SnGeMe_3$ (**2d**) and cyclohexylallene (**3b**) was carried out in the presence of $Pd(dba)_2$ (5 mol%) in toluene at 80 °C for 8 h, allyl germane **6a** was obtained in 88% yield (Scheme 6).[15] The catalytic reaction was highly regio-, stereo- and chemoselective; the aryl and the germyl groups were added to the middle and terminal carbons of the allene moiety; the *Z*-stereoselectivity of product **6a** was greater than 99%. Several aromatic iodides and allenes were successfully employed in the carbogermanylation reaction with $Bu_3SnGeMe_3$ (**2d**). In all cases, the *Z*-stereoisomers of allylgermane products were obtained exclusively or predominantly.



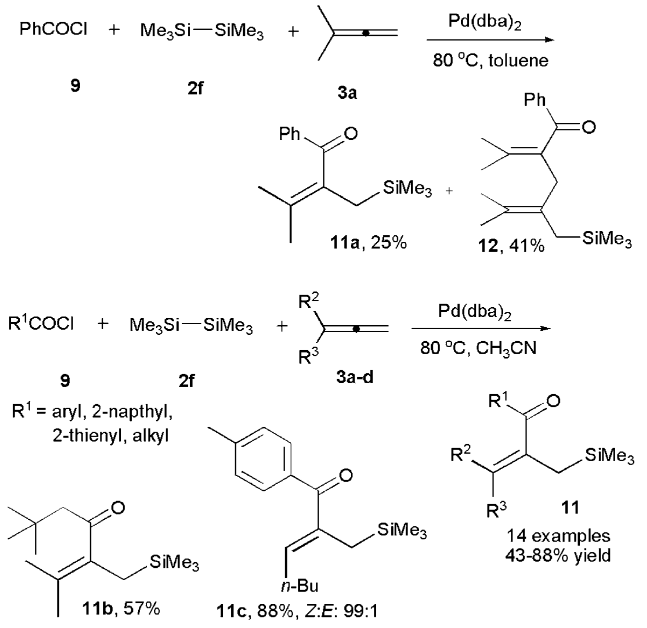
Scheme 6

The present carbogermanylation reaction can be successfully extended to a partially intermolecular version (Scheme 6). Thus, treatment of 2-iodobenzyloxy allene (**7**) with $Bu_3SnGeMe_3$ (**2d**) in the presence of $Pd(dba)_2$ afforded isochromene derivative **8** in 78% yield.

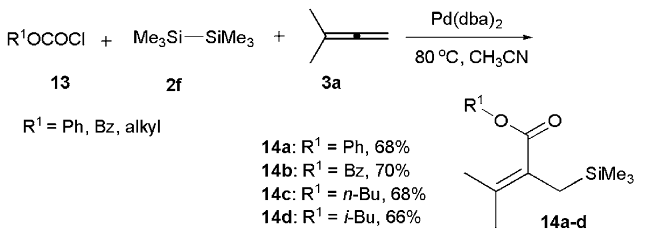
I.1d Palladium-catalyzed acylboration of allenes with acyl halides and diboron reagents. In addition to aromatic and vinyl halides, aroyl and alkanoyl halides also successfully employed as electrophiles for the three-component coupling reaction (Schemes 7–10).[16] When 4-methylbenzoyl chloride was treated



Scheme 7



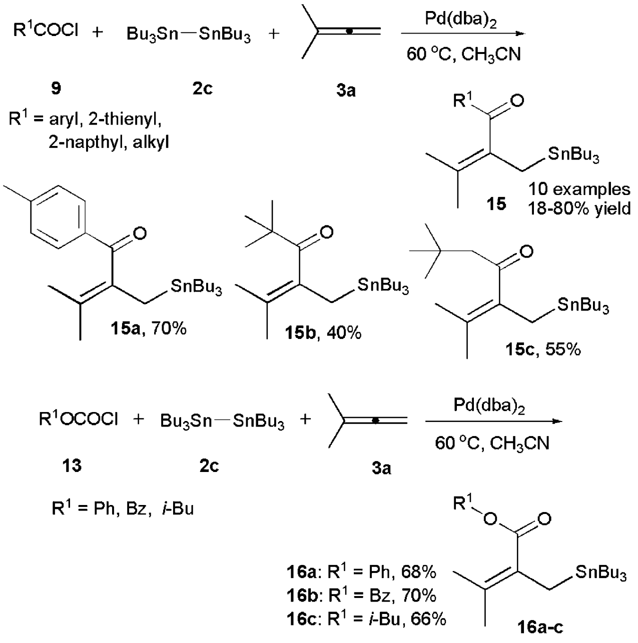
Scheme 8



Scheme 9

with bis(pinacolato)diboron (**2e**) and 1,1-dimethylallene (**3a**) in the presence of $PdCl_2(MeCN)_2$ in toluene at 80 °C for 10 h, 2-acylallylboronate **10a** was observed in 72% yield (Scheme 7).[16a]

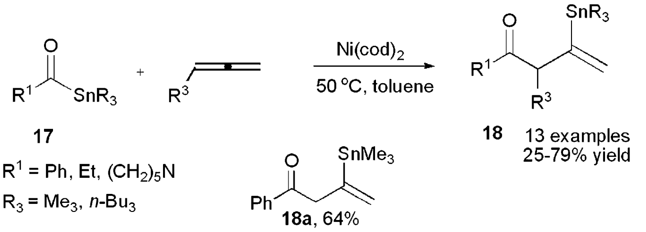
The catalytic reaction also worked well with various aroyl, heterocyclic carbonyl and alkanoyl chlorides, affording the corresponding allylboronates **10** in 50–92% yields. Surprisingly, alkanoyl chloride reacted with allene much faster than aroyl chloride under the standard reaction conditions. The reaction was extended smoothly to various monosubstituted allenes **3b–f**. In all cases, the *E* isomers of acylboration products **10** were obtained predominantly.



Scheme 10

I.1e Palladium-catalyzed acylsilation of allenes with acyl halides and $Me_3SiSiMe_3$. The observed acylboration of allenes prompted us to examine the feasibility of acylsilation and acylstannation of allenes (Schemes 8 and 10).[16b] The reaction of benzoyl chloride with hexamethyldisilane (**2f**) and 1,1-dimethylallene (**3a**) in the presence of $Pd(dba)_2$ in toluene at 80 °C for 5 h gave a mixture of products 2-acylallylsilane **11a** and **12** in 25 and 41% yields, respectively (Scheme 8). Compound **12** was a double-allene insertion product consisting of two molecules of allene, an acyl, and a silyl group. In order to increase the selectivity of the formation of 2-acylallylsilane, the effect of solvents were investigated. The results revealed that CH_3CN gave only 2-acylallylsilane product **11a** in 80% yield with no double-allene insertion product **12**. The exclusive formation of acylsilation product in CH_3CN is probably due to the coordination of CH_3CN molecules to the palladium intermediate from carbopalladation of allene. The coordinating ability and the high concentration of these solvent molecules prevent further bonding of a second allene molecule to the palladium intermediate and completely inhibit the double-allene insertion process.

Under similar reaction conditions, a series of acyl chlorides underwent three-component coupling reaction with hexamethyldisilane (**2f**) and allene **3a** in the presence of $Pd(dba)_2$ in CH_3CN affording the corresponding 2-acylallylsilanes **11** in 43–88% yields. The catalytic reaction was also successfully applied to monosubstituted allenes **3b–d**. Thus, cyclohexyl and *n*-butyl allenes **3b–c** afforded the *Z*-allyl silanes **11** as the sole products, while phenyl allene gave the corresponding 2-acylallylsilane with an *E* : *Z* ratio of 30 : 70.



Scheme 11

I.1f Palladium-catalyzed silyl esterification of allenes with chloroformates and $Me_3SiSiMe_3$.

Chloroformates **13** can also be successfully employed as electrophile in the present carbosilation reaction (Scheme 9).[16b] Accordingly, treatment of phenyl chloroformate with hexamethyldisilane (**2f**) and 1,1-dimethylallene (**3a**) in the presence of $Pd(dba)_2$ in CH_3CN afforded 2-((trimethylsilyl)methyl)acrylate **14a** in 68% yield. Various chloroformates **13** including benzyl and aliphatic chloroformates were compatible for the present silylesterification reaction of allenes and afforded the corresponding 2-((trimethylsilyl)methyl)acrylates **14b–d** in 66–70% yields.

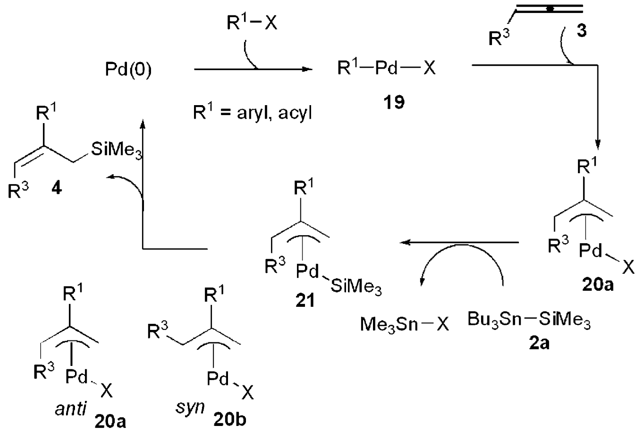
I.1g Palladium-catalyzed acylstannylation of allenes with organic halides and distannanes.

Slow addition of hexabutylditin (**2c**) to a mixture of 4-methylbenzoyl chloride and 1,1-dimethylallene (**3a**) over a period of 2 h in the presence of $Pd(dba)_2$ (5 mol%) in CH_3CN at 60 °C afforded the three-component coupling product, 2-acylallylstannane **15a** in 70% yield (Scheme 10).[16b] Several aroyl chlorides and chloroformates were successfully used for the catalytic three-component reaction with allene **3a** and distannane **2c**. The reaction was not compatible with monosubstituted allenes and did not give the desired 2-acylallylstannanes.

Previously, Hiyama *et al.* demonstrated two-component acylstannation of allenes catalyzed by a nickel complex.[17] Propane-1,2-diene undergoes acylstannation with trimethyl(benzoyl)tin (**17a**) in the presence of $Ni(cod)_2$ in toluene at 50 °C to give acylstannation product **18a** in 64% yield (Scheme 11). In the reaction, the acyl group of acylstannane **17** adds to the highly substituted carbon and the tin group to the center carbon of allene. In our reaction, the acyl group predominantly adds to the middle carbon and the tin group to the terminal carbon of the allene moiety (Scheme 10).

I.1h Mechanism of palladium-catalyzed carbometallation of allenes.

A possible reaction mechanism of carbosilylation of allenes is shown in Scheme 12. The catalytic reaction is likely initiated by the oxidative addition of organic halide to Pd(0) affording arylpalladium(II) intermediate **19**. The terminal double bond of allene is then coordinated favorably to the palladium center of **19** at the face opposite to the substituent R^3 to avoid steric congestion. Carbopalladation of the coordinated double bond of the allene affords π-allyl palladium complex **20a** with the R^3 group *anti* to the R^1 group of the π-allyl moiety. Transmetalation of **20a** with $Bu_3SnSiMe_3$ (**2a**) furnishes intermediate **21**. Subsequent reductive elimination of **21** affords the final product and regenerates the active palladium catalyst. The *anti* form of **20a** is responsible for the stereoselectivity of the present catalytic reactions (*vide infra*) (Scheme 18). Similar mechanisms are also expected for the other carbometallations of allenes.[13–16]



Scheme 12

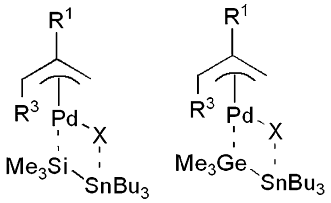


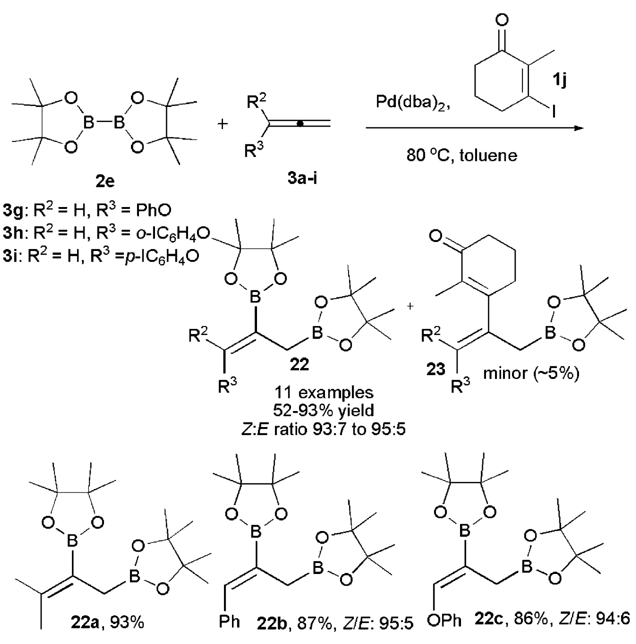
Fig. 1

The observation of only allylsilane[13] and allylgermane[15] with no formation of allylstannane[14] in the carbosilylation (Scheme 4) and carbogermanylation (Scheme 6) of allene using $Bu_3SnSiMe_3$ (**2a**) and $Bu_3SnGeMe_3$ (**2d**) as the organometallic reagents, respectively, can be rationalized by the high chemoselective transmetalation of **20** with silylstannane **2a** or stannylgermane **2d** to form intermediate **21**. It is likely that a cyclic S_E2 pathway is involved in the transmetalation step (Fig. 1). While the exact reason for the high chemoselective transmetalation is not clear, the great affinity of the $-SnBu_3$ moiety for halide is probably the driving force for the chemoselectivity.

It is noteworthy that, all 2-aryl-, acylallylmetalation reactions were highly regio-, stereo- and chemoselective, with the aryl or acyl group being added predominantly to the middle carbon of allene and the metal group to the terminal carbon of the allene moiety. Moreover, in all the cases acyl group was added to the allene moiety without decarbonylation indicating that the acylpalladation of allene is faster than the decarbonylation of the acyl–palladium intermediate.[16]

I.1i Palladium-catalyzed diboration of allenes initiated by carboboration.

In 2001, we reported the phosphine-free palladium-catalyzed addition of diboron with allenes using organic halide as the initiator (Scheme 13).[18a] At the time this result was published, there was no palladium complex-catalyzed diboration of alkenes or alkynes, whereas platinum complexes were known to readily catalyze the addition of diboron reagents to unsaturated carbon–carbon bonds to provide diboronic compounds.[19] The difference in the reactivity of Pt and Pd lies in the ability to undergo oxidative addition of the B–B bond to these metal(0) species. While stable oxidative



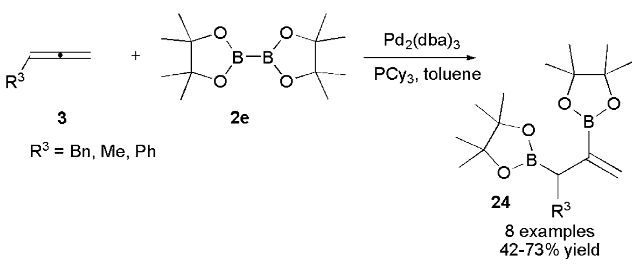
Scheme 13

adducts of diboron to Pt species are reported, no oxidative addition of diboron to Pd are known.[20] In addition, the theoretical calculation also demonstrated that the oxidative addition product of diboron compound to Pd is generally not stable.[20]

The reaction of diboron **2e** with alkenyl iodide **1j** and 1,1-dimethylallene (**3a**) in the presence of Pd(dba)$_2$ (5 mol%) in toluene at 80 °C surprisingly gave diboration product **22a** in 93% yield bearing both vinylic and allylic boron moieties (Scheme 13). In addition, the catalytic reaction also produced carboboration product **23** in *ca.* 5% yield. It is noteworthy that the yield of **23** did not vary significantly with the amount of alkenyl iodide **1j** used. Optimization studies revealed that no diboration occured in the absence of the alkenyl iodide **1j**. The amount of carboboration product **23** was approximately equal to that of the Pd catalyst used (5 mol%). Further studies showed that the diboration reaction can be initiated by a small amount of alkenyl iodide **1j** ($\sim$5 mol%). Other organic iodides such as aromatic and vinyl iodides and I_2 were also effective for the present diboration reaction.

In addition to **3a**, monosubstituted allenes **3b–i** also efficiently reacted with **2e** to give the corresponding diboration products **22** in 52–93% yields. These reactions were highly regio- and stereoselective. In all cases, only the diboronic products with one boryl group adding to the middle carbon and the other to the non-substituted terminal carbon of the allene moiety, with *Z*-stereoselectivity greater than 93–95% were observed.

Later, Morken and co-workers demonstrated phosphine palladium complex catalyzed addition of diboropinacolate with allene (Scheme 14).[21] The reaction of allene **3** with diboropinocolate **2e** in the presence of Pd$_2$(dba)$_3$ and PCy$_3$ furnished diboration product **24** in good yield. It is surprising that, in our diboration reaction of allenes, boron in the allylic group is attached to the less substituted carbon, that is, terminal carbon of allene **22** (Scheme 13). In contrast, in the present reaction, boron is attached to the substituted carbon, that is, internal carbon of allene **24** (Scheme 14).



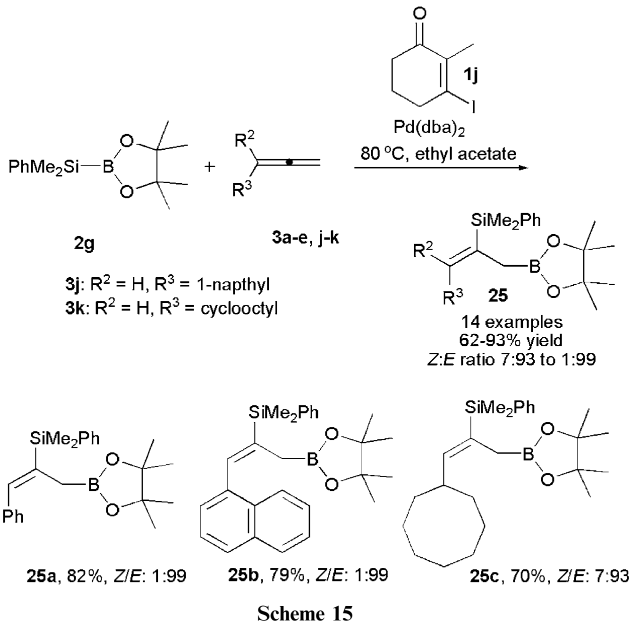
Scheme 14

I.1j Palladium-catalyzed silaboration of allenes initiated by carboboration.

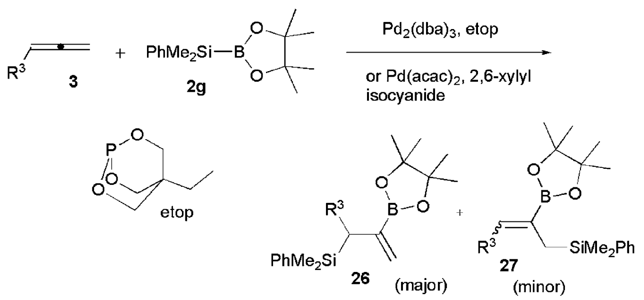
Very recently, we reported the addition of borylsilane to allenes using an organic iodide as an initiator and Pd(dba)$_2$ as catalyst (Scheme 15).[18b] When phenylallene (**3d**) was treated with borylsilane **2g** in the presence of a catalytic amount of Pd(dba)$_2$ and alkenyl iodide **1j** in ethyl acetate at 80 °C, 82% of (*E*)-2-silylallylboronate **25a** was observed as a sole product. In addition to **25**, $\sim$5% of carboboration product **23** was also observed (Scheme 13). The silaboration was totally regioselective with the silyl group of borylsilane **2g** adding to the central carbon and the boryl group to the unsubstituted terminal carbon of allene.

Under similar reaction conditions, various monosubstituted allenes efficiently underwent silaboration with **2g** to give the corresponding 2-silylallylboronates **25** in 62–93% yields. The reactions showed very high *E*-stereoselectivity with the *E* : *Z* ratios lying in the range from 93 : 7 to 99 : 1.

Previously, Ito's group observed silaboration of allenes in the presence of palladium catalysts.[22,23] The addition of silylborane **2g** to allene **3** in the presence of Pd$_2$(dba)$_3$ and etop (4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane)[23a] or Pd(acac)$_2$ and 2,6-xylyl isocyanide[23b] gave two regioisomers **26** and **27**, both having the boryl group attached to the central carbon of the allene moiety (Scheme 16). It is noteworthy that



Scheme 15

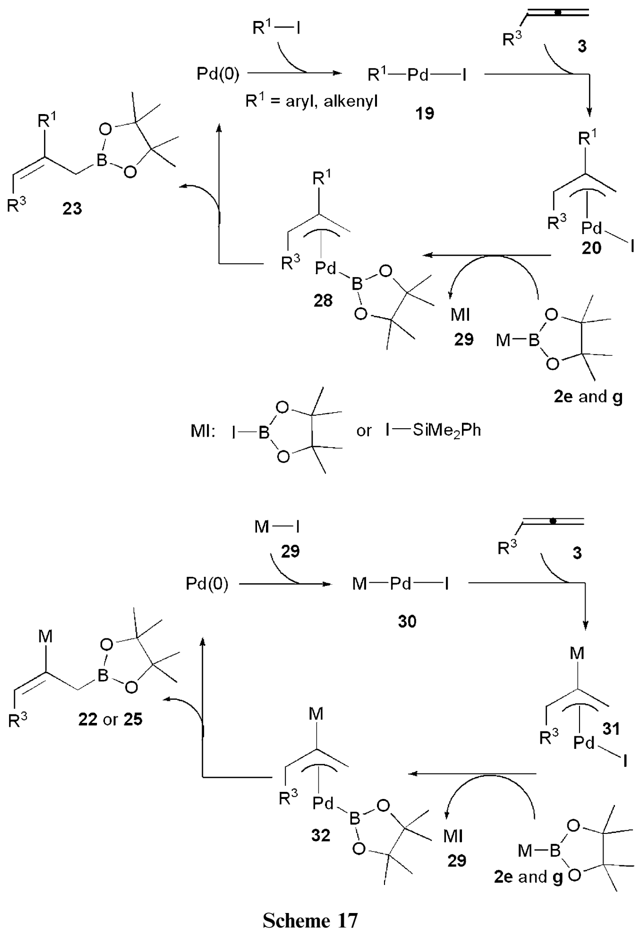


Scheme 16

in our silaboration of allenes, the silyl and boron group added to the center and less hindered carbon of allene **25**, respectively (Scheme 15).

I.1k Proposed mechanism for diboration and silaboration of allenes initiated by carboboration. The requirement of a small amount of an organic halide is crucial for the understanding of the mechanism of diboration and silaboration of allenes (Scheme 17). The organic iodide likely acts as an initiator undergoing oxidative addition with Pd(0) to give a palladium(II) intermediate **19** that reacts with allene **3** and diborane **2e** to afford **28** and boryl iodide **29**. Subsequent reductive elimination of **28** affords **23** and regenerates the palladium catalyst.

Boryl iodide **29** then reacts with Pd(0) to begin the catalytic reaction (Scheme 17). Oxidative addition of **29** to Pd(0) species affords Pd(II) intermediate **30**. The terminal double bond rather than the internal double bond of the allene is then coordinated favorably to the palladium center of **30** at the face opposite to the substituent R^3 to avoid steric congestion. Subsequent insertion of the coordinated double bond of allene affords π-allyl palladium complex **31** with the R^3 group *anti* to the boryl group. Transmetalation of **31** with diborane **2e** affords π-allyl palladium species **32**. Reductive elimination of **32** yields the final product **22** and regenerates the Pd(0) catalyst. A similar reaction mechanism is also expected for the silaboration of allenes.

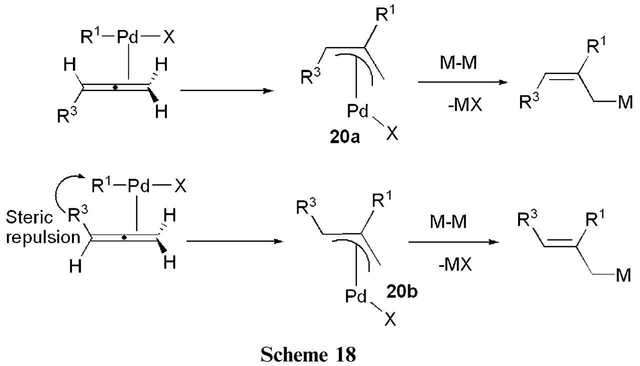


Scheme 17

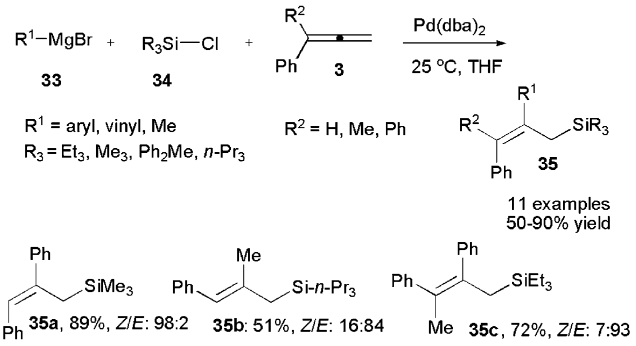
I.1l Rationale for the observed high stereoselectivity of carbometallation, diboration and silaboration of allenes. The observation of high stereoselectivity in carbometallation, diboration and silaboration with monosubstituted allenes is an interesting feature of these Pd(dba)$_2$-catalyzed reactions. In order to explain the high stereoselectivity, a mechanism involving face-selective coordination of allenes to the palladium center of oxidative adduct is proposed (Scheme 18). When the terminal double bond of allene is coordinated to the palladium center at the face opposite to the substituent R^3, the steric congestion of R^3 and R^1 can be avoided, so giving *anti* π-allyl palladium complex **20a**. On the other hand, coordination of the terminal double bond of allene to the palladium center at the other face with R^3 *syn* to the palladium center or coordination of the internal double bond of allene to the palladium center will lead to an increase of steric repulsion and so is less likely to afford *syn* π-allyl palladium complex **20b**. The *anti* form **20a** is responsible for the high stereoselectivity.

The use of a phosphine-free palladium complex as a catalyst also key for the observation of high stereoselectivity. In the reported phosphine–palladium-catalyzed three-component reaction of allenes (Scheme 2),[5,6] the observed three-component product was generally obtained with low stereoselectivity. This is probably due to an *anti* and *syn* rearrangement of the allyl group on the palladium complex *via* a σ- and π-allyl exchange induced by PPh$_3$.[24] Our results also clearly revealed that in the carbometallation of monosubstituted allenes with organic halides and dimetal reagents in the presence of phosphine palladium complex, the three-component products were obtained with low stereoselectivity.[13–17]

I.1m Carbosilylation of allenes with Grignard reagents and chlorosilanes. Very recently, Terao and coworkers observed a palladium-catalyzed carbosilylation of allenes with Grignard reagents and chlorosilanes. (Scheme 19).[25] The reaction of



Scheme 18

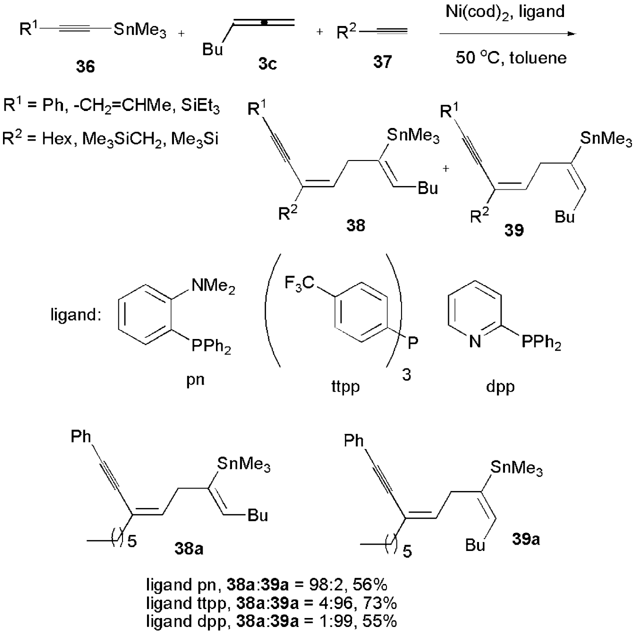


Scheme 19

PhMgBr (**33**), Et_3SiCl (**34**) with phenylallene (**3d**) in THF in the presence of $Pd(dba)_2$ at room temperature for 1 h afforded carbosilylated product **35a** bearing a phenyl group at the central carbon and triethylsilyl group at the terminal carbon in 92% yield with a 98 : 2 *Z* : *E* ratio. Under similar reaction conditions, various aryl allenes **3** and Grignard reagents **33** including aromatic, vinyl and methyl magnesium bromides were successfully involved in the reaction with Et_3SiCl to give the corresponding carbosilylation product **35** in 38–80% yields. In addition to Et_3SiCl, other chlorosilanes such as Me_3SiCl, $Ph_2MeSiCl$ and *n*-Pr_3SiCl were also used.

I.1n Nickel-catalyzed tandem alkynylstannation of allenes and alkynes. The nickel-catalyzed tandem alkynylstannation of allenes and alkynes with alkynylstannane was observed by Hiyama and co-workers.[26] Trimethyl(phenylethynyl)stannane (**36a**) reacted with *n*-butylallene (**3c**) and oct-1-yne (**37a**) in the presence of $Ni(cod)_2$ and ligand pn to give a mixture of tandem alkynylstannylation products **38a** and **39a** in 56% combined yield with a 98 : 2 ratio (Scheme 20). The ligand plays a crucial role to determine the product in the present reaction. When ligand pn was used in the reaction, product **38** was observed in major amount. Whereas, when ligand ttpp or dpp (Scheme 20) was used in the reaction, product **39** was observed as the major product. Internal alkynes also efficiently participated in the present tandem carbostannation reaction. The same group also studied two-component alkynylstannation and alkynylcyanation of allenes in the presence of nickel complex.[27]

The catalytic reaction proceeds *via* oxidative addition of an alkynylstannane with a nickel complex giving alkynylnickel(II) intermediate **40** (Scheme 21). Coordination of the terminal double bond of an allene into alkynylnickel(II) intermediate **40** followed by insertion to Ni–Sn in a direction that avoids steric repulsion of the Bu substitutent gives π-allyl nickel complex **41**. This π-allyl nickel complex is in *anti–syn* isomerization forms **41a** and **41b**. This isomerization is highly ligand dependent. If ttpp or dpp is used as ligand, *anti* form **41a** is predominant. If pn is used, *syn* form **41b** is predominant. Alkyne then inserts into the bond between the nickel atom and the non-substituted allyl carbon of **41a** or the corresponding *syn*-isomer **41b** affording intermediate **42**. Subsequent reductive elimination of intermediate **42** affords alkynylstannation product **38** or **39**. Intermediate **41a** accounts for product **39**, and intermediate **41b** accounts for product **38**, respectively.



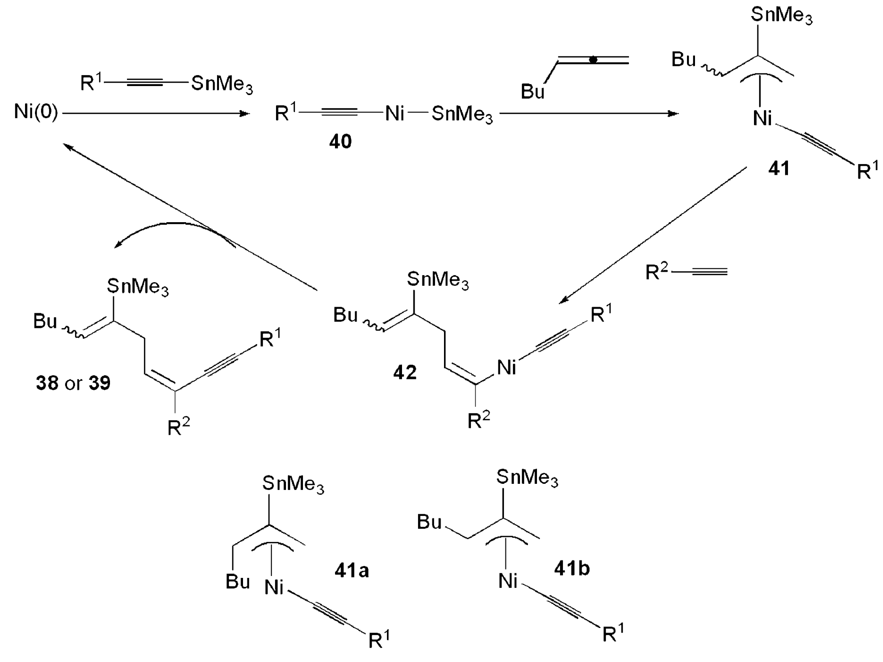
Scheme 20

I.2 Coupling of allenes with organic halides and organometallic reagents

I.2a Palladium-catalyzed partially intermolecular coupling of halo-substituted allenes with Suzuki reagents. In 1997, Grigg *et al.* showed a palladium-catalyzed partially intermolecular coupling of 2-iodophenoxyallene with organoboron reagents (Scheme 22).[28] The reaction of 2-iodophenoxyallene (**43a**) and phenylboronic acid (**44a**) was carried out in the presence of $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%) and Na_2CO_3 in a 2 : 1 mixture of toluene and water at 80 °C for 1 h, affording benzofuran derivatives **45a** in 61% yield and a trace of **46a**. The coupling reaction also worked with other organoboron reagents such as catechol boronate **44b** and sodium tetraphenylborate **44c**. In all cases benzofuran derivative **45a** was observed as the major product. A similar type of reaction was also successfully carried out with allene **43b** and organoboronic acids **44a**, **d–e**.

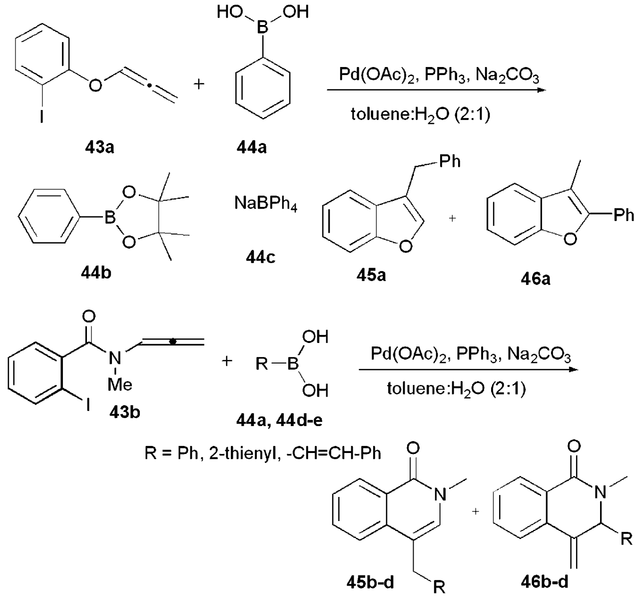
Zhu and Zhang reported a palladium-catalyzed cascade reaction of 1,2,7-triene with a Suzuki reagent which gave a cyclic product with high *cis* selectivity (Scheme 23).[29] Thus, treatment of 1,2,7-triene **47a** with phenylboronic acid (**44a**) in the presence of $Pd(PPh_3)_4$ and K_3PO_4 in toluene at 50 °C for 4 h gave a *cis* and *trans* mixture of five-membered ring products **48a** and **49a** in combined 95% yield with 85 : 15 ratio. Several aryl boronic acids and 1,2,7-trienes were also tested. In each case, the *cis* isomer was observed as the major product.

The catalytic reaction proceeds *via* oxidative addition of an allyl halide **47a** to Pd(0) generating palladium intermediate **50** (Scheme 23). Coordinative insertion of the internal double bond of allene forms a five-membered ring intermediate with a σ-vinyl palladium bond **51** instead of a common π-allyl palladium species. Transmetalation of aryl boronic acid with σ-vinyl palladium intermediate **51** followed by reductive elimination give the cyclized products **48a** and regenerates the Pd(0) catalyst.

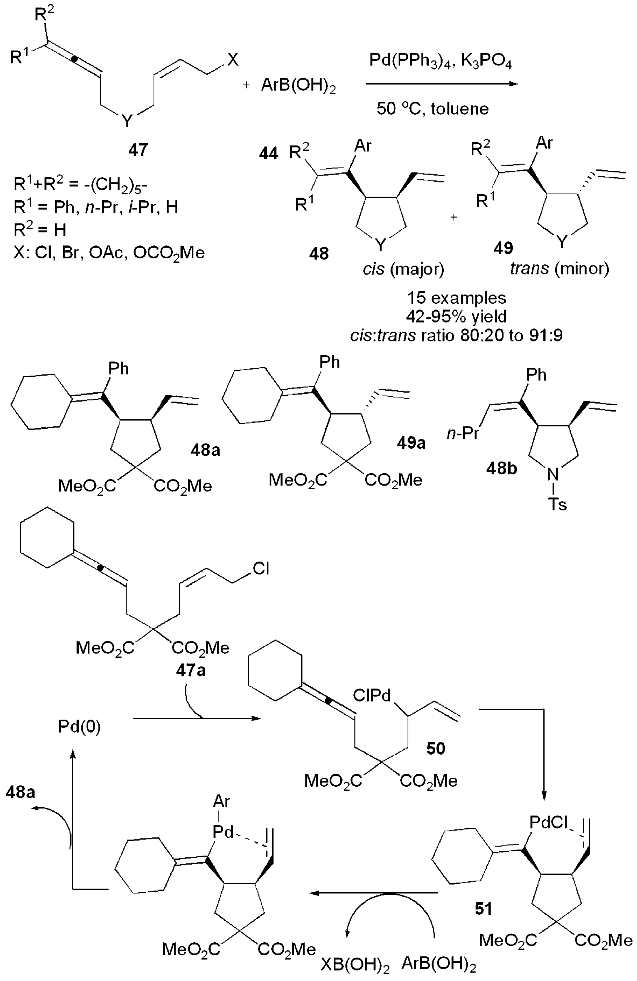


Scheme 21

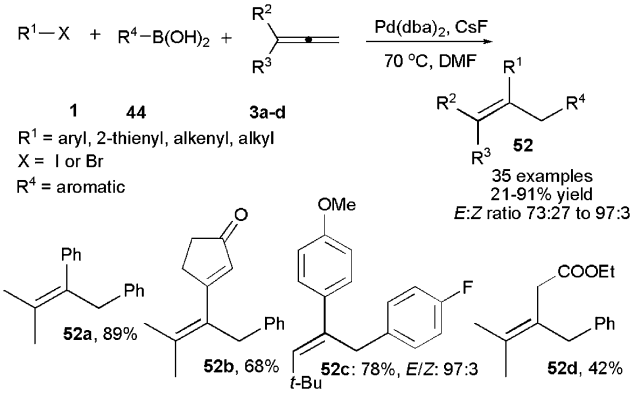
I.2b Palladium-catalyzed intermolecular coupling of allenes with organic halides and Suzuki reagents. We have reported a highly regio- and stereoselective palladium-catalyzed intermolecular three-component coupling of allenes, organic halides, and arylboronic acids (Scheme 24).[30a] When iodobenzene and phenylboronic acid was treated with 1,1-dimethylallene (**3a**) in the presence of $Pd(dba)_2$, CsF in DMF at 70 °C for 7 h, a three-component coupling product **52a** was observed in 89% isolated yield. The catalytic reaction was highly regioselective in which *p*-$MeOC_6H_4$ and C_6H_5 groups were added to the middle and unsubstituted terminal carbon of allene moiety, respectively.



Scheme 22



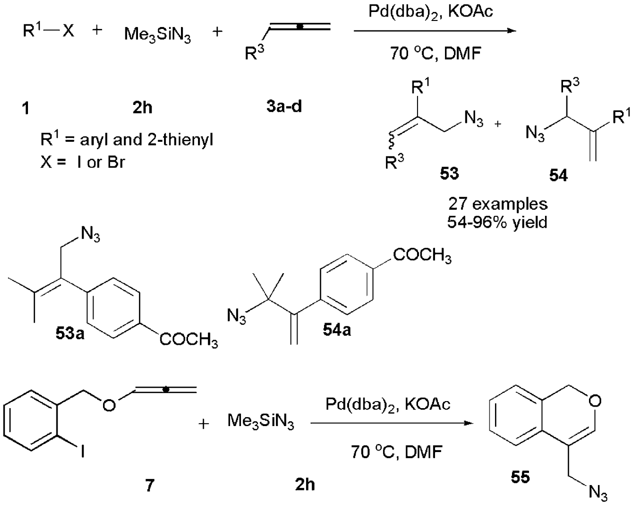
Scheme 23



Scheme 24

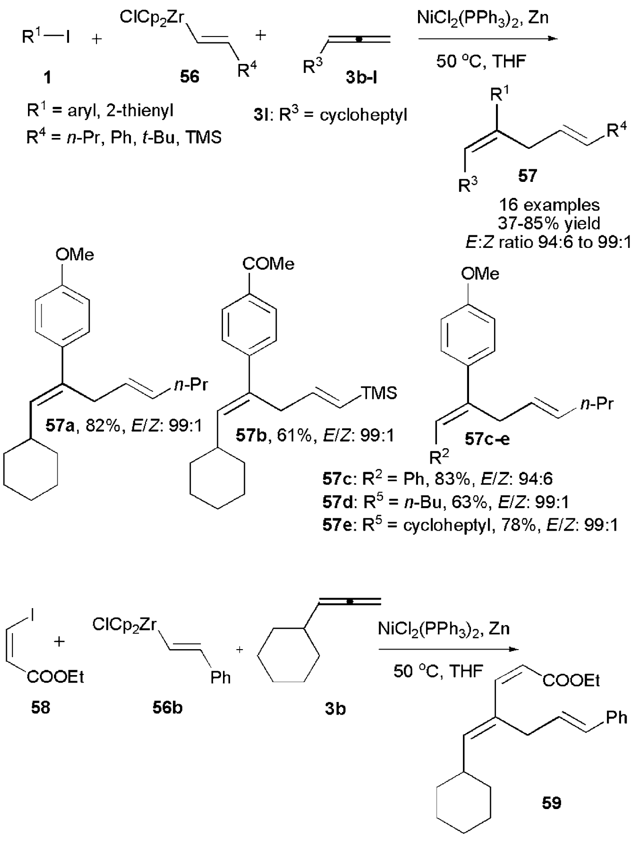
The selection of base was crucial for the success of the present three-component reaction. We observed that aryl halide reacted with allene in the presence of base K_2CO_3 to give substituted 1,3-butadienes.[30b] Optimization studies revealed that CsF was the best base for the present three-component reaction. In this case, 1,3-butadiene was not observed. A wide range of monosubstituted allenes, organic halides and arylboronic acid were successfully used for the present three-component reaction producing highly stereoselective allylic derivatives **52** in 69–85% yields. The stereoselectivity of these products depends on the bulkiness of allenes. In each case, an *E* stereoisomer was observed as the major product.

I.2c Palladium-catalyzed intermolecular coupling of allenes with organic halides and trimethylsilylazide. We also reported a palladium-catalyzed carboazidation of allenes with aryl iodides and trimethylsilyl azide (Scheme 25).[31a] Treatment of 4-iodoacetophenone and trimethylsilyl azide (**2h**) with 1,1-dimethylallene (**3a**) in the presence of Pd(dba)$_2$ and KOAc in DMF at 50 °C gave carboazidation products **53a** and **54a** in combined 92% yield with 84 : 16 ratio. Under similar reaction conditions, various aromatic halides reacted with **2h** and **3a** to give the corresponding carboazidation products **53** and **54** in good to excellent yields. In all cases, two regioisomeric carboazidation products were observed. The observation of two regioisomeric carboazidation products was due to the facile thermal 1,3-rearrangement of allyl azides. Experimental evidence supporting a rapid 1,3-azide shift of **53** to **54** was provided.[31a] The carboazidation reaction can be successfully extended into partially intermolecular version (Scheme 25). The reaction of 2-iodobenzyloxy allene (**7**) with trimethylsilyl azide (**2h**) in the presence of Pd(dba)$_2$ and KOAc in DMF at 50 °C gave **55** in 84% yield. Product **55** was previously prepared by Grigg *et al.* using 2-iodobenzyloxyallene and sodium azide, albeit in lower yield.[31b]



Scheme 25

I.2d Nickel-catalyzed intermolecular coupling reaction of allenes with organic halides and zirconium reagents. Recently, we demonstrated a nickel-catalyzed highly regio- and stereoselective three-component assembly of allenes, aryl halides and alkenylzirconium reagents (Scheme 26).[32] In most of the allene-involving three component reactions, palladium complexes were used as catalysts. This was the first report which describes allene-involving nickel-catalyzed three-component coupling reaction. The reaction of cyclohexyl allene (**3b**) with 4-iodoanisole and alkenylzirconium reagent *n*-Pr–CH═CH–ZrCp$_2$Cl (**56a**) in the presence of NiCl$_2$(PPh$_3$)$_2$ and zinc powder (reducing agent for Ni(II) to Ni(0)) in THF at 50 °C for 24 h gave a three-component coupling product **57a** in 82% yield (Scheme 26). The catalytic reaction is highly stereoselective, giving **57** with an *E*-stereoselectivity greater than 99%. It is interesting to note that the same reaction using the corresponding palladium phosphine complex as the



Scheme 26

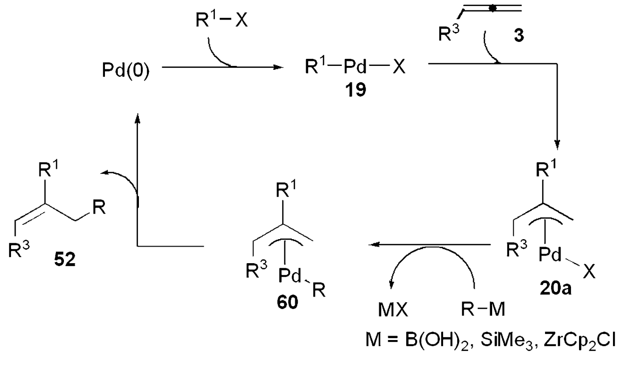
catalyst did not lead to the expected three-component product, but the direct coupling product 4-OMe–C_6H_4–CH=CH–*n*-Pr of 4-iodoanisole and **56a**.

Various aryl and 2-thienyl iodides, zirconium reagents and allenes were successfully employed in the present reaction giving 1,4-diene derivatives **57** in 37–85% yields. In all cases, an *E*-stereoisomer was observed as the major product. The reaction was successfully extended to vinyl iodide (Scheme 26). Thus, treatment of cyclohexylallene **3b** with ethyl (*Z*)-3-iodoacrylate (**58**) and styrylzirconium reagent **56b** in the presence of $NiCl_2(PPh_3)_2$ and zinc powder in THF afforded stereoselective triene **59** in 86% yield.

I.2e Mechanism for palladium- and nickel-catalyzed intermolecular three-component coupling of allenes. The catalytic reaction proceeds *via* oxidative addition of an organic halide to Pd(0) giving Pd(II) intermediate **19** (Scheme 27). The terminal double bond of the allene is coordinated to the palladium moiety at the face opposite to the substituent R^3 favorably to avoid steric congestion. Coordinative insertion of the allene to organopalladium species gives *anti* π-allyl palladium intermediate **20a**. Transmetalation of the organometallic reagent with intermediate **20a** affords intermediate **60**. Subsequent reductive elimination provides product **52** and regenerates the palladium(0) catalyst. The *anti* form of **20a** is responsible for the stereoselectivity of the present catalytic reactions (Scheme 18). Similar mechanisms are also expected for the other coupling of allenes (Schemes 25 and 26).

II Generation of allyl nucleophiles from allenes for allylation

The allyl group in a π-allyl palladium complex is generally electrophilic in nature and reacts readily with a nucleophile. However, the π-allyl group can become nucleophile if an electron donating ligand is present. In addition, the π-allyl palladium complex can be treated with main group metals or dimetal reagents to give allyl–metal reagents. In this section, we will review the use of π-allyl palladium complexes and allyl metal reagents generated from allenes as allylation reagents for aldehydes, ketones and imines.



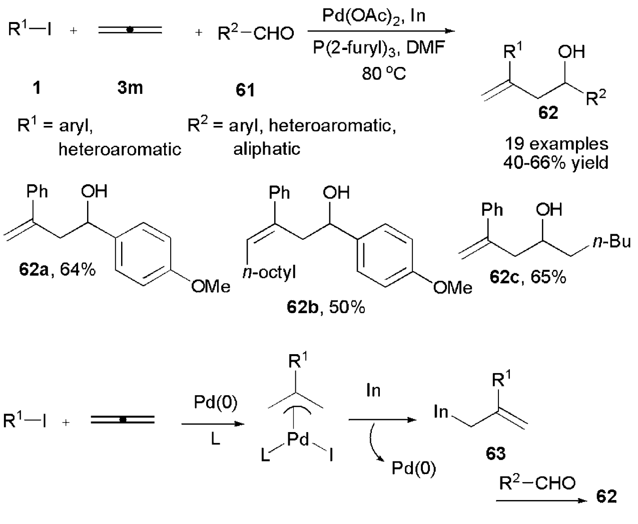
Scheme 27

II.1 Allylation of aldehydes, ketones or imines by reagents generated from palladium-catalyzed reaction of organic halides with allenes in the presence of In metal

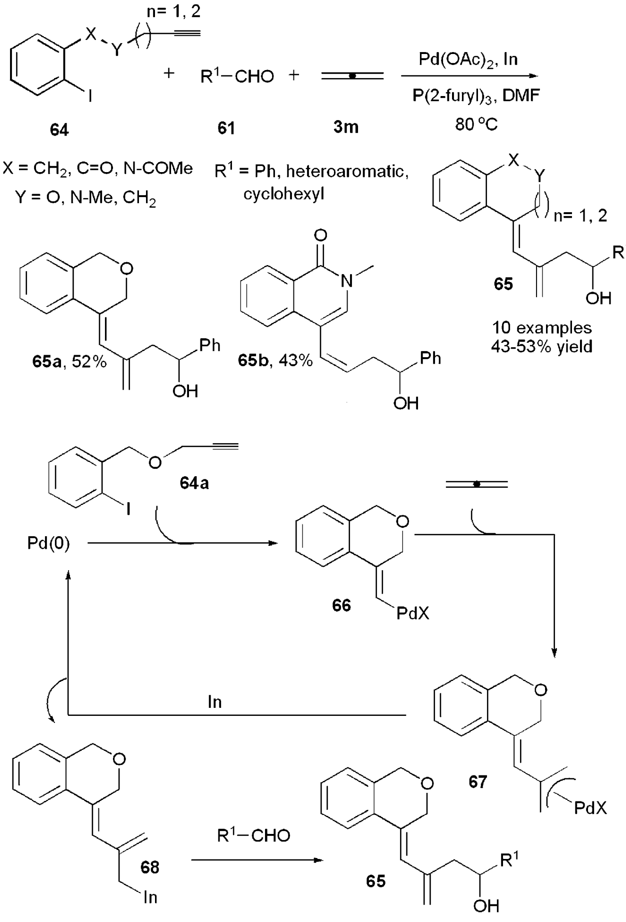
The three-components reactions of aryl halides, allenes and aldehydes or imines in the presence of indium metal were studied by Grigg *et al.* (Schemes 28, 29, 31 and 32).[33,34] Thus, iodobenzene reacts with allene **3m** and 4-methoxybenzaldehyde (**61a**) in the presence of $Pd(OAc)_2$, $P(2\text{-furyl})_3$ and indium at 80 °C for 18 h to give homoallylic alcohol **62a** in 64% yield (Scheme 28).[33] Various organic halides, aldehydes and octylallene were successfully used for the reaction. In this reaction, aromatic halide undergoes carbopalladation with the allene in the presence of palladium complex generating the π-allyl palladium complex. Transmetalation of indium with the electrophilic π-allyl palladium complex gives nucleophilic allylindium species **63** and regenerates the Pd(0) catalyst. Intermediate **63** then adds to aldehyde to give homoallylic alcohol **62**.

Grigg's group also demonstrated a palladium-catalyzed cascade addition of aryl halides onto proximate alkynes, allene and then aldehyde (Scheme 29).[34] 1-Iodo-2-((prop-2-ynyloxy)-methyl)benzene (**64a**) reacted with allene **3m** and benzaldehyde (**61a**) in the presence of $Pd(OAc)_2$, $P(2\text{-furyl})_3$ and indium at 80 °C to give allylation product **65a** in 52% yield. Various alkynes **64** and aldehydes **61** were successfully involved in the reaction with allene **3m** to give the corresponding allylation product **65** in 43–53% yields. The proposed mechanism is also shown in Scheme 29.

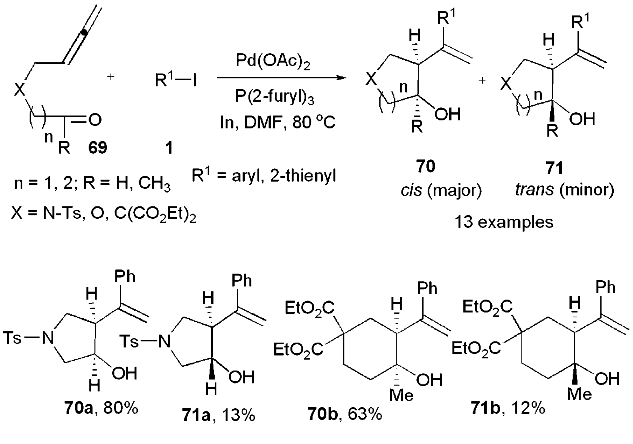
The partially intermolecular cyclization of aromatic iodides with allenyl–aldehydes and –ketones was observed by Kang *et al.* (Scheme 30).[35] Treatment of allenyl–aldehyde CH_2=C=$CHCH_2NTsCH_2CHO$ (**69a**) with iodobenzene in the presence of $Pd(OAc)_2$ (5 mol%), $P(2\text{-furyl})_3$ (10 mol%) and indium (1.2 equiv.) in DMF at 80 °C for 2 h gave a *cis* and *trans* mixture of cyclopentanols **70a** and **71a** in 80 and 13% yields, respectively. This Pd(0)/In-mediated arylative cyclization was successfully applied to synthesise various five- and six-membered ring cyclohexanol derivatives. In the reactions, the *cis* isomer was observed as the major product.



Scheme 28

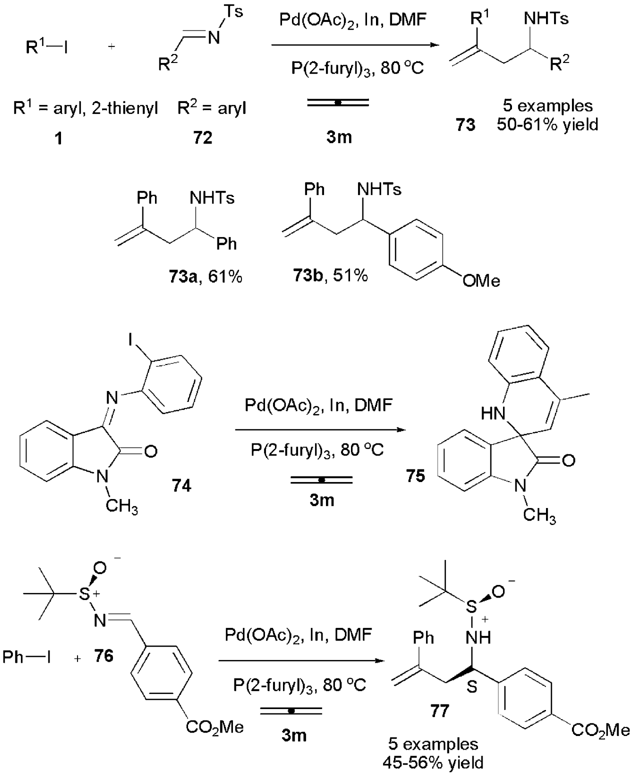


Scheme 29



Scheme 30

The allylation reaction also worked very well with imines (Scheme 31).[36] Thus, treatment of iodobenzene with allene **3m** and imine C_6H_5–CH=N–Ts in the presence of Pd(OAc)$_2$, P(2-furyl)$_3$ and indium at 80 °C for 18 h afforded allylic amine **73a** in 61% yield. Various aromatic halides **1** and imines **72** were successfully involved in the reaction with allene **3m** to give the corresponding homoallylic amines **73** in 50–61% yields. An intramolecular version of this allylation reaction was also tested giving **75**. Similarly, the allylation of enantiopure (*R*)-*N*-*tert*-butanesulfinyl imine **76** proceeded smoothly to afford a single diastereoisomer **77** in 56% yield. The absolute stereochemistry (*S*) of the new chiral centre of product **77** was determined by X-ray crystallography.



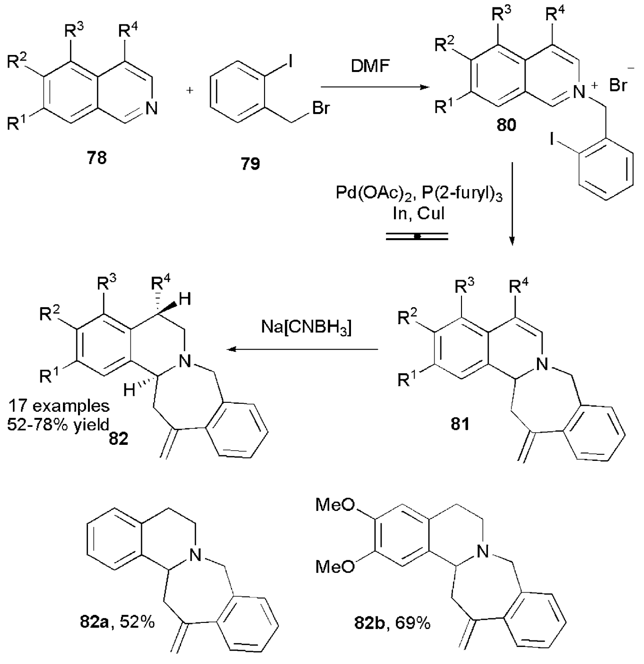
Scheme 31

Additives such as CuI or piperidine was found to decrease the reaction time from 18 to 2 h and increase the yield of the product significantly.[37]

This methodology was successfully applied to the synthesis of annulated benzazepines (Scheme 32).[38] Isoquinoline (**78**) reacts with 2-iodobenzyl bromide (**79**) in DMF to give iminium salt **80**. Addition of allene **3m** with iminium salt **80** followed by intramolecular allylation in the presence of palladium catalyst and indium gives enamine **81**. Reduction of enamine **81** with sodium cyanoborohydride affords benzazepine derivative **82** in 52–78% yields. Various benzazepines were prepared by employing different isoquinoline derivatives.

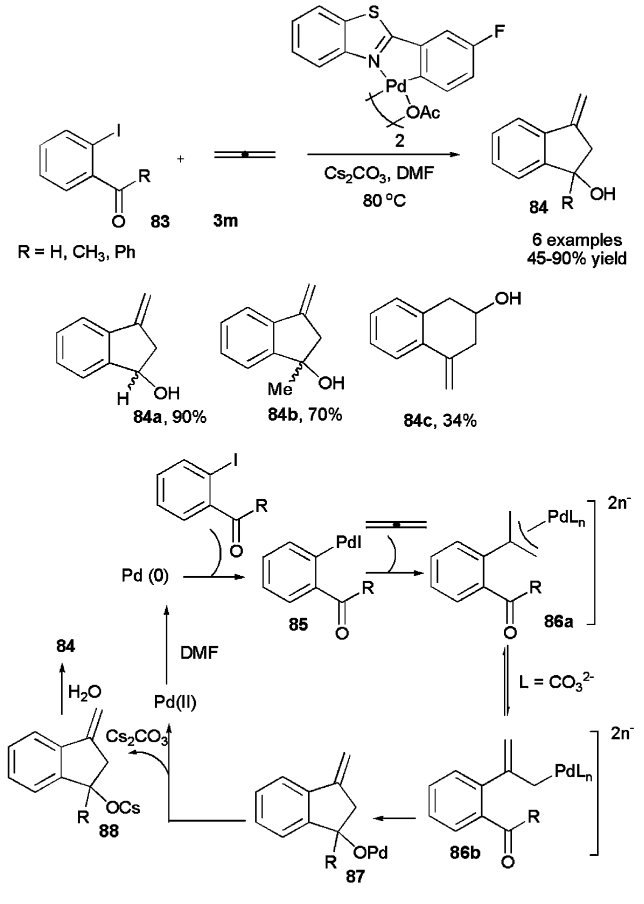
II.2 Catalytic direct addition of allylic palladium species to aldehydes, ketones and imines

Grigg's group observed an unusual reactivity of a π-allyl palladium complex with carbonyl compounds (Scheme 33).[39] Usually, a main group metal or electropositive metal is necessary to reverse the polarity of π-allyl palladium species. In the present reaction, the specially ligated π-allyl palladium complex itself acts as nucleophilic reagent. Thus, 2-iodobenzaldehyde **83a** reacts with allene **3m** in the presence of the specially ligated palladium complex in DMF and Cs$_2$CO$_3$ at 80 °C to afford cyclopentenol **84a** in 90% yield. In the reaction, 2-iodobenzaldehyde is more reactive than 2-bromobenzaldehyde and the formation of the five-membered ring product is more efficient than that of six-membered ring product. Cs$_2$CO$_3$ plays a crucial role in the present reaction. The proposed



Scheme 32

mechanism of the catalytic reaction is shown in Scheme 33. Oxidative addition of 2-iodobenzaldehyde **83a** with Pd(0) gives oxidative adduct **85**. Carbopalladation of allene with intermediate **85** affords η^3-species **86a** and η^1-species **86b**. Intramolecular nucleophilic addition of η^1-allyl species to the carbonyl group affords the five-membered ring palladium species **87**. Hydrolysis of intermediate **87** with the assistance of base gives **84** and a Pd(II) species. The latter is then reduced to Pd(0) likely by the solvent to restart the catalytic reaction.

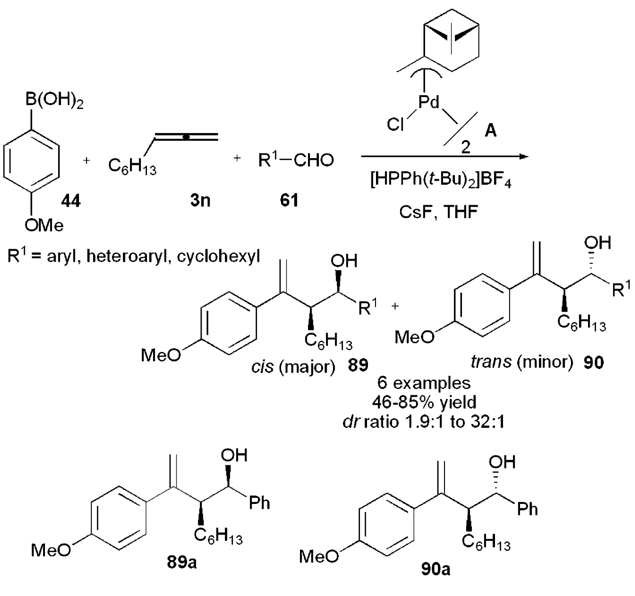


Scheme 33

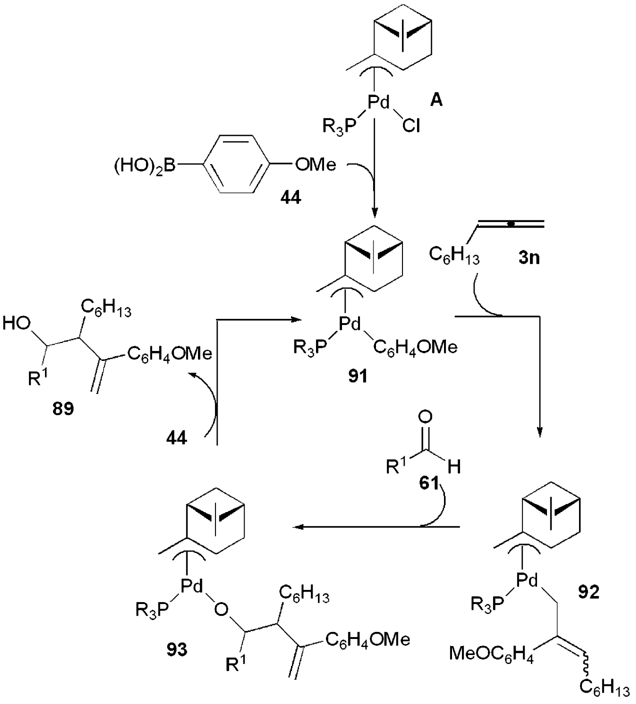
A palladium-catalyzed three-component coupling of arylboronic acids, allenes and aldehydes was reported by Hopkins and Malinakova (Scheme 34).[40] Treatment of 4-methoxyphenylboronic acid with 1,2-nonadiene (**3n**) and benzaldehyde (**61a**) in the presence of palladium complex **A**, [HPPh(t-Bu)$_2$]BF$_4$ and CsF in THF at room temperature for 24 h afforded *cis*-homoallylic alcohol **89a** in 64% yield. In addition to **89a**, an another diastereomer *trans*-homoallylic alcohol **90a** was observed in 12% yield. Under similar reaction conditions, various aldehydes were examined. In the reactions, homoallylic alcohols **89** and **90** were observed in combined 46–85% yields. In all cases, product **89** was observed in major amount.

The catalytic reaction proceeds *via* transmetalation of phenylboronic acid **44** with π-allyl palladium complex **A** giving intermediate **91** (Scheme 35). Migratory insertion of allene **3n** with intermediate **91** provides intermediate **92**. The σ-bonded allyl group in **92** is likely transferred to aldehyde **61** *via* an open transition state to give intermediate **93**. Transmetalation of phenylboronic acid **44** with intermediate **93** followed by protonation gives product **89** and regenerates intermediate **91**.

Very interestingly, a similar reaction using allenyl ester **3o** as the allene substrate instead of **3n** gave cyclic lactone **94a** in 75% yield (Scheme 36).[41] In the previous reaction (Scheme 34), allylation of aldehyde occured at the sterically hindered carbon of allene, while in the present reaction allylation of aldehyde occurred at the allene carbon away from the ester group. Various aromatic, heteroaromatic and vinylic boronic acids also efficiently participated in the reaction affording the corresponding lactones **94** in 32–78% yields. The allylation reaction of aldehydes **61** also proceeded with boronic acid **44** and substituted allenyl esters **3p–q** furnishing cyclic lactones **95** and (Z)-alcohols **96** in 47–65% combined yields.

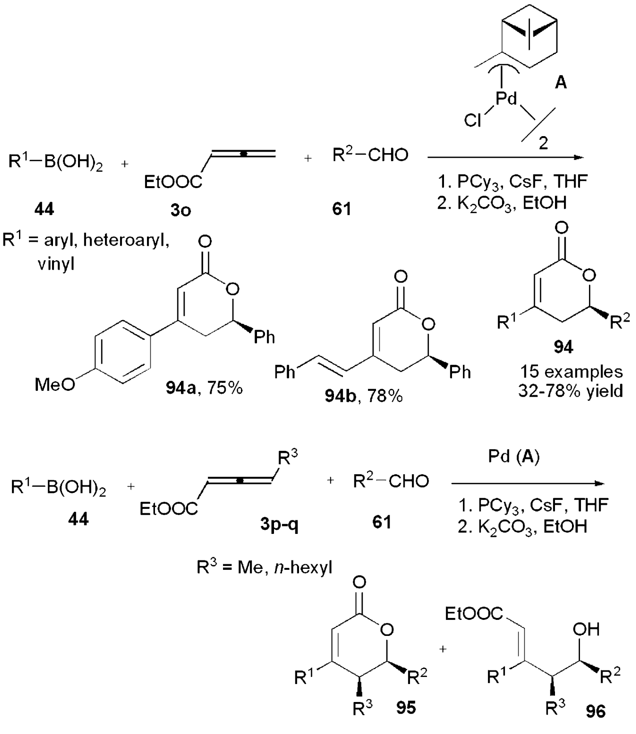


Scheme 34

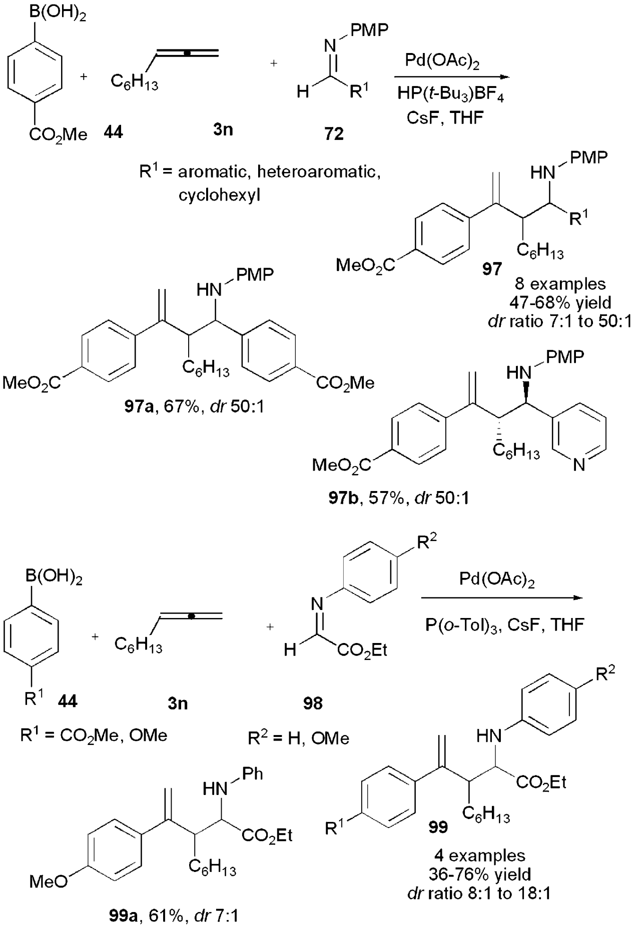


Scheme 35

The direct allylation reaction was successfully extended to imines and activated ethyl iminoacetates (Scheme 37).[42] Thus, treatment of 4-(methoxycarbonyl)phenylboronic acid with 1,2-nonadiene (**3n**) and imine 4-CO_2CH_3–C_6H_4–CH=N–PMP (**72a**) in the presence of $Pd(OAc)_2$, $HP(t\text{-}Bu_3)BF_4$ and CsF in THF at room temperature for 24 h afforded allylic amine **97a** in 67% yield with a *dr* ratio 50 : 1. Under similar reaction conditions, various aromatic and heteroaromatic imines **72** efficiently participated in the reaction with **44** and **3n** giving allylic amines **97** in 47–68% yields. In all cases, an *anti* stereoisomer was observed as the major product (diastereoisomeric ratios of 7 : 1 to 50 : 1). The allylation reaction also worked with activated ethyl iminoacetates **98**. The reaction of 4-methoxyphenylboronic acid with 1,2-nonadiene (**3n**) and ethyl iminoacetate CO_2Et–CH=N–Ph (**98a**) in the presence of $Pd(OAc)_2$, $P(o\text{-}Tol)_3$ and CsF in THF gave amine **99a** in 61% yield with a 7 : 1 diastereoisomeric ratio. Under similar reaction conditions, other phenylboronic acids and iminoacetate were also examined with **3n**.

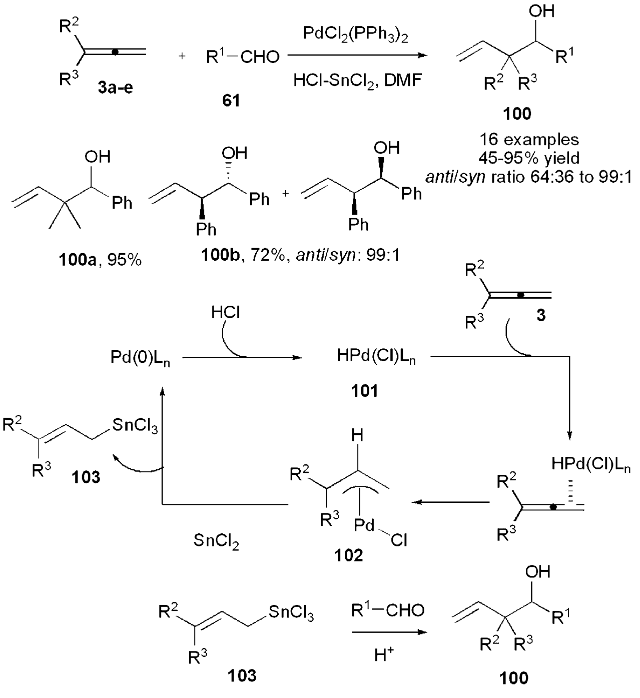


Scheme 36



Scheme 37

II.3a Allylation of aldehydes by allylic stannanes generated from HCl, allenes and $SnCl_2$. We found a palladium-catalyzed highly regio- and stereoselective allylation of aldehydes by *in situ* generated allylstannane species (Scheme 38).[43] Treatment of 1,1-dimethylallene (**3a**) with $SnCl_2$ and benzaldehyde (**61a**) in the presence of $PdCl_2(PPh_3)_2$, HCl in DMF at room temperature gave allylation product **100a** in 95% yield. Under similar reaction conditions, various monosubstituted allenes **3b–e** undergo allylation with benzaldehyde (**61a**) to give the corresponding allylation products **100** in 72–95% yields with highly regio- and stereoselective manner. In all cases, allylation of aldehyde occurs exclusively at the substituted carbon of allene, and an *anti* stereoisomer was observed as the major



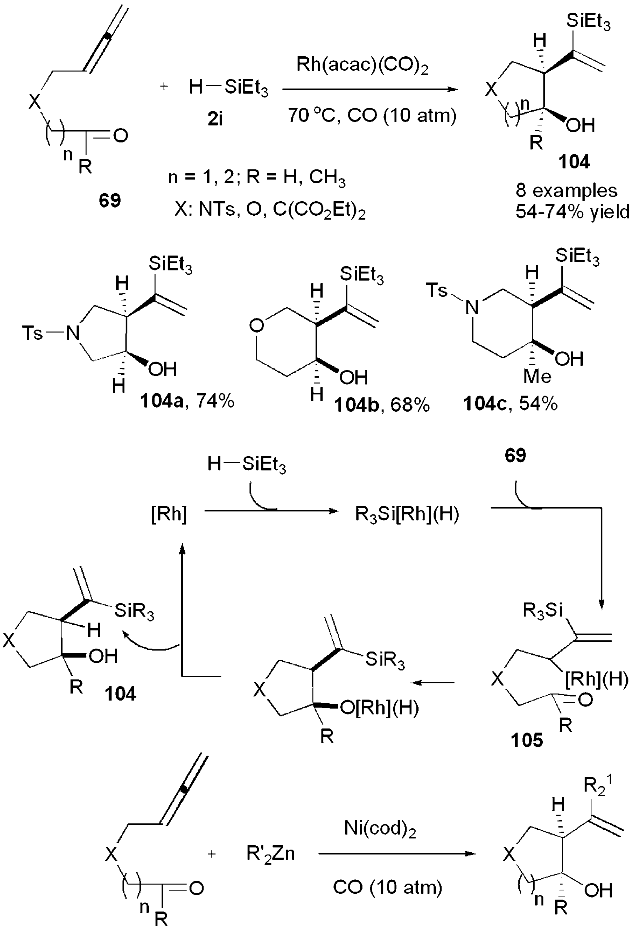
Scheme 38

product. In addition to benzaldehyde, other aromatic aldehydes also work very well.

The possible reaction mechanism of the present allylation of aldehydes is proposed in Scheme 38. The catalytic reaction proceeds in two stages. First, the reaction is likely initiated by reduction of the palladium(II) complex to a palladium(0) species by tin(II). Oxidative addition of HCl with palladium(0) gives oxidative adduct **101**. Coordinative insertion of allene with Pd(II)–H species leads to π-allyl palladium species **102**. Nucleophilic attack of $SnCl_2$ with π-allyl palladium species **102** gives the hydrostannylation product **103** and regenerates the palladium(0) species. Second, allylation of benzaldehyde by the *in situ* generated allyltin species **103** *via* a chair form six-membered ring transition state gives the final homoallylic alcohol **100** and completes the reaction.

II.3b Silylative carbocyclization of allenyl–aldehyde or –ketone with Et_3SiH. A rhodium-catalyzed silylative carbocyclization of allenyl–aldehyde and –ketone with Et_3SiH was demonstrated by Yu and co-workers (Scheme 39).[44a] Treatment of allenyl–aldehyde $CH_2{=}C{=}CHCH_2NTsCH_2CHO$ (**69a**) with Et_3SiH (**2i**) in the presence of $Rh(acac)(CO)_2$ and CO (10 atm) at 80 °C gave highly stereoselective *cis*-silylative carbocyclization product **104a** in 74% yield. The catalytic reaction proceeds *via* addition of $Et_3Si[Rh](H)$ generated from [Rh] with Et_3SiH to the internal double bond of the allene moiety **69** forming thermodynamically favorable allylic rhodium intermediate **105**. Subsequent cyclization of **105** followed by reductive elimination affords the cyclopentanol **104** and regenerates the Rh complex.

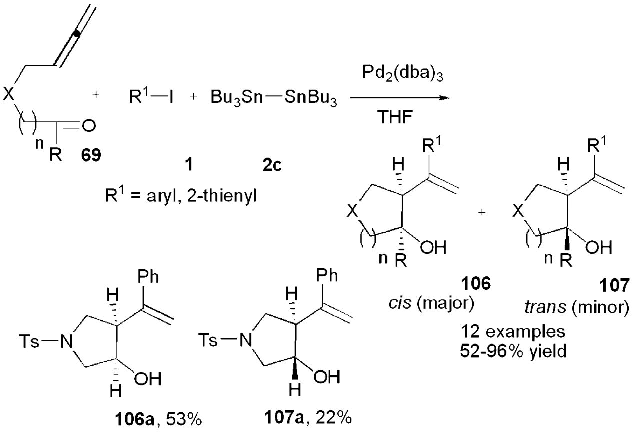
In a mechanistically different pathway, similar types of *cis*-cyclic alcohols have been synthesized by a nickel-catalyzed addition of organozinc to allenyl–aldehydes or –ketones (Scheme 39).[44b]



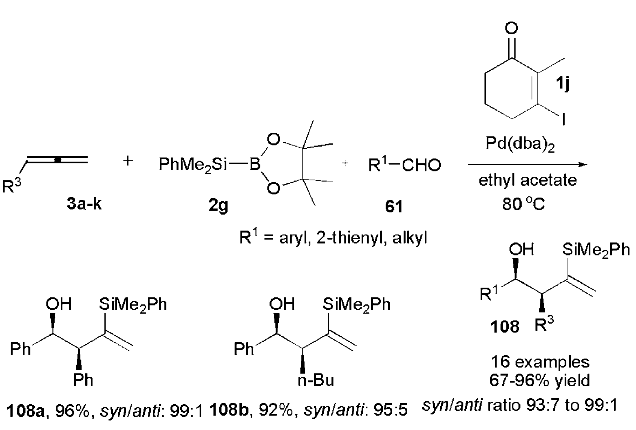
Scheme 39

II.4a Allylation of aldehydes or ketones by allylic stannanes generated from organic halides, allenes and distannanes. Ha and Kang reported a palladium-catalyzed carbostannation and allylation of allenyl–aldehydes or –ketones with aryl iodides and distannanes (Scheme 40).[45] When iodobenzene **1** was treated with allenyl–aldehyde $CH_2{=}C{=}CHCH_2NTsCH_2CHO$ (**69a**) and $Bu_3SnSnBu_3$ (**2c**) in the presence of $Pd_2(dba)_3$ in THF at room temperature for 12 h, *cis* and *trans* cyclopentanols **106a** and **107a** in 53 and 22% yields were observed. Under similar reaction conditions, various allenyl–aldehydes, allenyl–ketones and organic halides were successfully used. By employing this method, various cyclopentanols and cyclohexanols were prepared in 52–96% yields.

II.4b Allylation of aldehydes by allylic boranes generated from allenes and B–Si using organic halide as an initiator. We reported a palladium-catalyzed silaboration of allenes and allylation with aldehydes using organic iodides as initiators (Scheme 41).[18b] This reaction is an application of silaboration of allenes reported previously (see Scheme 15). Thus, treatment of phenylallene (**3d**) with borylsilane **2g** and benzaldehyde (**61a**) in the presence of $Pd(dba)_2$ (5 mol%) and alkenyl iodide **1j** (10 mol%) at 80 °C in ethyl acetate for 5 h afforded homoallylic alcohol **108a** in 96% yield with an excellent *syn* selectivity (>99%). Under similar reaction conditions, various allenes, aromatic, heteroaromatic and aliphatic aldehydes



Scheme 40



Scheme 41

were successfully employed. In the reactions, homoallylic alcohols **108** were observed in 67–96% yields with *syn* : *anti* ratios of 93 : 7 to 99 : 1.

Conclusions

In this feature article, we have presented transition metal-catalyzed three-component coupling reactions of allenes and their application in allylation reactions. Although the reactions of allenes show different kinds of selectivities, the selectivities can generally be tuned by changing the environment of the catalysts and reaction temperature. Most of the presented three-component coupling reactions are highly regio-, stereo- and chemoselective. They are convenient methods for the preparation of various allyl and alkenyl metal reagents and for use *in situ* for the allylation of aldehydes, ketones and imines to synthesize various complex allylic alcohols, allylic amines in one pot.

Acknowledgements

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