Making and Breaking of Sn−C and In−C Bonds in Situ: The Cases of Allyltins and Allylindiums

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1. Introduction

"On the seashore of endless worlds, children meet...
...they know not how to swim,
they know not how to cast nets.
Pearl fishers dive for pearls;
merchants sail in their ships,
while children gather pebbles
and scatter them again.
They seek not for hidden treasures,
they know not how to cast nests."
Rabindranath Tagore [Gitanjali]

In the area of the generation of an allylmetal and exploitation of its metal−carbon bond reactivity, chemists have come a long way from "gathering pebbles and scattering them again", to "how to cast nests".[1] A mild indulgence into the 100+ years of the database of allylmetals will provide the reader with the following generalized observations:[1−5] (a) main group metal (hereafter Mgm) allyls have come first, transition metal (hereafter Tm) allyls followed through, (b) among the allyl-Mgms, those of magnesium and lithium have fetched many initial glories in the field, but *the rest* were not far behind, (c) *allyl-Mgms of tin and indium*, chosen for deliberation in this review, show many similarlities in their chemistry that appeal to organic, organometallic, and inorganic chemists alike—the contrast that exists between the two is that while the former is mature and still-growing, the latter is young and fast-growing.

In terms of nucleophilic organic reactivity, allyltin and allylindium have gained distinct significance and are widely used to introduce allyl functionality to an electrophilic carbon or heteroatom center. Out of these, reactions leading to a new carbon−carbon bond having desired regio- and stereoselectivity gained immense importance in the synthesis of various important natural and pseudonatural products. The utility of allylstannanes is further indicated by the commercial availability of many of them, which are synthesized using standard Grignard and Grignard-like protocols. Even though allylindiums are not yet commercially available, in recent times they have made a distinct presence in laboratory and pilot scale reactions.

An organic chemist utilizing a functionalized allyltin or allylindium may recourse to the reaction of a functionalized allyl electrophile and corresponding metal precursor; thereafter, the ex situ generated allylmetal is coupled with an

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Ujjal Kanti Roy received B.Sc. (Honors) in Chemistry in 1999 and his M.Sc. in pure chemistry (majoring in organic chemistry) in 2001, both from Calcutta University, with a brilliant academic record. He then joined the research group of Prof. Sujit Roy to pursue doctoral studies in the area of organic and organometallic reactivity of tin−transition metal dual reagent systems. Following graduation, he continued his association in the Roy group as a Post-Doctoral Research Associate (January 2008 to January 2009, Department of Science and Technology, India). Dr. Roy is now working on Organic Electronic Materials as a Post-Doctoral Fellow in the Department of Organic Chemistry at the Weizmann Institute of Science, Israel. Dr. Roy is a member of the Chemical Research Society of India. His current research interests include the development of new synthetic methods using inorganic and organometallic compounds as homogeneous catalysts, asymmetric synthesis, and synthesis and characterization of organic electronic materials.

Sujit Roy was born at Darjeeling, the tea-N-tourism famed tiny Himalayan town, completed his B.Sc. (Honors) and M.Sc. in Chemistry, and climbed down the hill. After successive stints at IIT Kanpur (1981−87, Ph.D. under Prof. B.D. Gupta), UWO London (1987−90, postdoctoral fellow with Prof. R. J. Puddephatt, FRS), IICT Hyderabad (1991−99, Scientist), and CRC Sapporo (1998, JICA participant in the group of Prof. Tamotsu Takahashi), he joined IIT-Kharagpur in 1999 and has been a full-professor since 2004. In June 2009, Prof. Roy moved to IIT-Bhubaneswar as the founding Head of the School of Basic Sciences and Dean (Faculty, Planning and Administration). The research theme of the Roy-group is to delve into the organometallic arena, work within the landscape of catalysis for fine-chemicals, and address the issues of atom-economy, selectivity, and eco-econo-enantiosustenance. On-going research efforts are on the development of novel organic-activation pathways within the portals of dual/bimetallic catalysis, and the multicomponent coupling approach. In tandem, the group also works on the diagnosis of intermediates, and mechanistic elucidation. Prof. Roy has been elected as a Fellow of the Indian Academy of Sciences (2008), and he is the recipient of the Chemical Research Society of India Bronze Medal (2005), the CSIR Young Scientist Award (1994), and a University Gold Medal (1980). When not busy, he joins his daughter Ipsita in listening to music, in reading poems, or in nature-watching.

organic partner. In recent years, yet another strategy has emerged as a powerful tool, which involves the generation

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

○ Used for *in situ* generation of allyltin
△ Used for *in situ* generation of allylindium

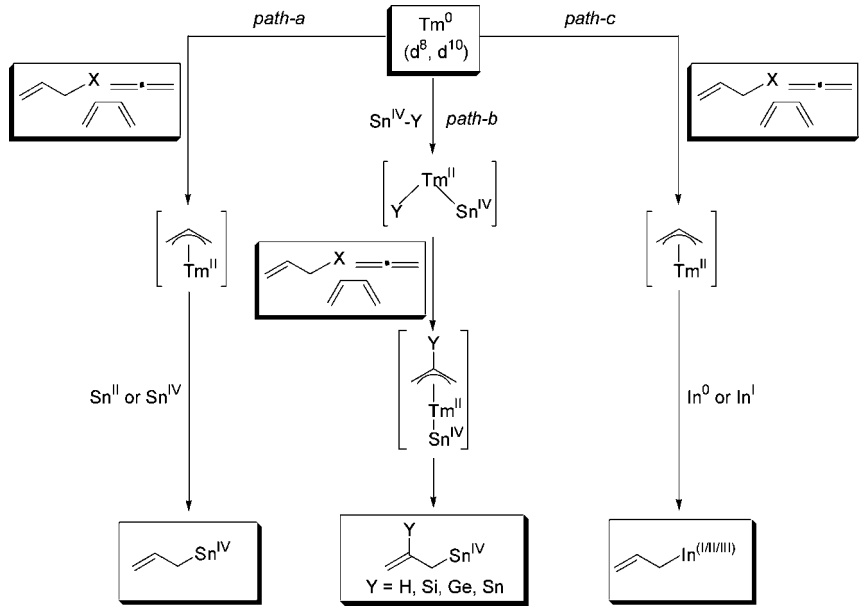
Figure 1. Transition metal catalysts used for the in situ generation of allyltin and allylindium.

of allyltin/allylindium in situ under the aegis of a transition metal catalyst or an additive and coupling the same with an organic partner in tandem. Homogeneous catalysts used in the in situ generation of allyltin or allylindium are mostly of d^8 or d^{10} transition metal salts or complexes; only a limited application is observed with titanium(III) [d^1], cobalt(II) [d^7], and molybdenum(0) [d^5] systems (Figure 1). Conceptually, development in this field relies *on the ability of the transition metal to activate either the electrophile or the metal precursor* in the initial stage (Scheme 1). The present article primarily aims to look into the trials and tribunals of organic as well as organometallic chemists in employing *these two strategies* over the past decade. Additionally, we have briefly touched upon newer developments in the direct activation of allyl electrophiles without Tm-assistance and transmetallative activation of other allyl-Mgms to allyltin/indium. While looking into the synthetic efficacy of the above strategies, the mechanistic developments have also been analyzed. However, we have excluded from this review the details on the application of in situ generated allyltin and allylindium toward the synthesis of natural products.

There are few elegant review articles related to allyltins and allylindiums in organic synthesis.[1,3−5] An early review on both the in situ and ex situ generation and reactivity of allylmetals including allyltins and allylindiums is by Yamamoto.[1e] Thomas, Marshall, and Denmark accounted the stereo- and enantioaspects of the generation and reactivity of allyltins and allylindiums.[1b−d,3b,d] The articles by Fleming and Barbero focus on the generation of allyltins via stannylcupration of C−C multiple bonds.[3c,f] Marshall and Masuyama have reviewed many aspects of the in situ generation and reactivity of allyltins up to 2000.[1c,d,3e] The recent personal research account by Marshall on the reactivity of organotins would additionally enlighten the interested reader.[3a] The generation and reactivity of allylindiums were reviewed up to 2004 by Araki and Nair.[4d,e] Both these articles have enlisted previous accounts and reviews which are of importance to an organic chemist.[4] There are also a few reviews and minireviews in recent time on the in situ generation and reactivity of allylindiums.[4a−c] For a specific discussion on in situ generation and reactivity of allyltins and allylindiums in an aqueous medium, the reader is referred to the reviews by Li and Chan.[5] In the present review, we have aimed to be concise in our presentation for the period that overlaps with the above-mentioned articles. Even though we have tried our best to cover the published literature with due care, major omissions (if any) are purely inadvertent, and the senior author apologizes for the same.

For our ease, we have divided this review into two major parts: (a) in situ generation and reactivity of allyltin, and (b) in situ generation and reactivity of allylindium. The reader may also note that all through this review a compound

Scheme 1



labeled with a lower case indicates a reagent, a product, or an isolable species. On the other hand, a species labeled with an upper case indicates a transient intermediate or a proposed transition state. For example, compare **37a** and **37b** versus **37A** and **37B** in Scheme 100.

2. Allyltin

Keeping in line with the introductory remarks, as well as Scheme 1 (path-a and path-b), this section is divided into five major categories, in accordance with the in situ generation of allyltin via (i) initial strong activation of an organic precursor at Tm, (ii) initial weak activation of an organic precursor at Tm, (iii) initial activation of a tin precursor at Tm, (iv) direct activation of an allyl electrophile at the Sn^0/Sn^{II}/Sn^{IV} center without the participation of a transition metal, and (v) transmetallative activation of a group-4 allylic organometallic precursor. As the journey proceeds, it may be seen that besides the dominance of palladium(0), other d^8/d^{10}−Tm catalysts have been making exciting entries in this field.

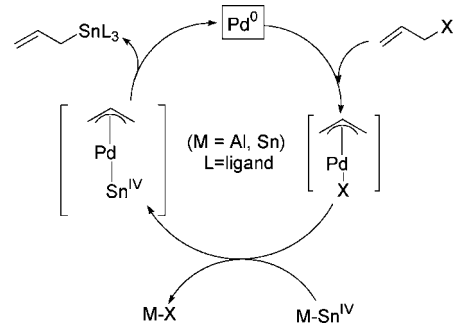
2.1. Allyltin via Strong Activation of an Organic Precursor at the Transition Metal Center

Allyl halides and surrogates, allenes, and dienes are easily activated across a low-valent electron rich transition metal center, and they ultimately result in an π-allylmetal (Scheme 1, path-a). Allyl transfer from the latter to a tin(IV) or tin(II) precursor generates a σ-allylstannane. This unique strategy remained the backbone of several synthetic exploitations. In order to closely look into these strategies individually, this section has been further divided into subcategories depending on the organic precursor and Sn(II/IV) source.

2.1.1. Allyltin from an Allyl Electrophile and a Tin(IV) Precursor

The ability of palladium(0) to activate allylic esters and halides has been exploited in a meaningful way by several groups for the in situ generation of functionalized allylstannanes. In the catalytic cycle, the first step involves the formation of π-allylpalladium(II) starting from allyl halide

Scheme 2



or its surrogate. Follow up transmetalation with a tin(IV) precursor provides an allyl−Pd−Sn^{IV} intermediate, from which reductive elimination leads to the desired allyltin(IV) species, regenerating the palladium(0) catalyst (Scheme 2).

The earliest example of this category involves the synthesis of allylstannane from allyl acetate and (tributylstannyl)diethylaluminum ($Et_2AlSnBu_3$) in the presence of catalytic $Pd(PPh_3)_4$ (Scheme 3).[6] The reaction is highly chemoselective toward allyl acetate, without affecting enone, ester, and ketone functionalities (entries 3, 5, and 6). Expectedly, the tributylstannyl group is introduced at the less substituted carbon atom (entries 2, 3, 4, and 6).

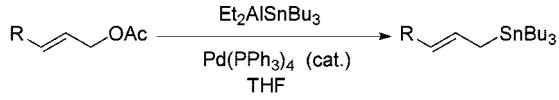
The mechanism of the reaction (Scheme 4) indicates inversion of configuration of the carbon atom attached to the acetate group, during the formation of the π-allylpalladium intermediate, which is followed by stereoirregular intramolecular attack of the -$SnBu_3$ group to generate the desired allylstannane.

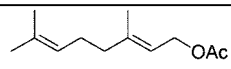
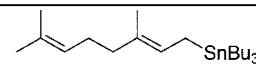
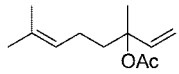
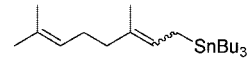
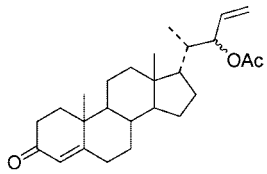
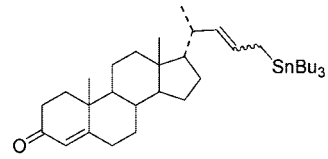
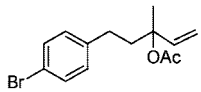
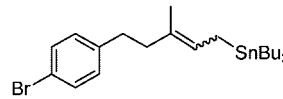
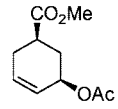
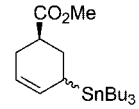
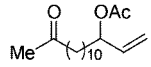
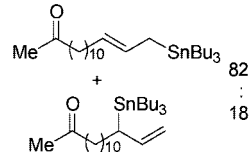
Allylstannane generated using the above strategy is amenable to further reaction with carbonyl compounds in the presence of Lewis acids through an S_E2' pathway (Scheme 5).

The oxidative−addition/transmetalation strategy is further extended to reductive cyclization of aryl or vinyl bromides such as **1a** using palladium(0) catalyst (Scheme 6).[7] The noteworthy mechanistic feature of this reaction is the activation of both aryl and allyl centers by palladium(0).

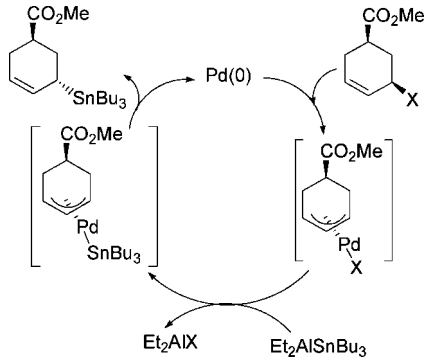
The *cis*-geometry at the ring junction is expected when formation of palladacycle **1A** is involved in the ring closing

Scheme 3

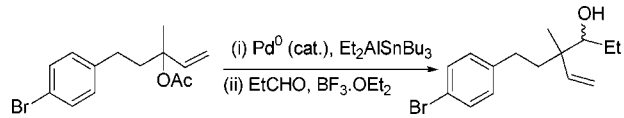


#	Allyl acetate	Temp (°C)/ Time (h)	Product	Yield (%)	*trans:cis*
1		35/6		68	100:0
2		25/20		74	50:50
3		25/20		70	90:10
4		25/20		61	60:40
5		25/20		73	70:30
6		25/20		71	-

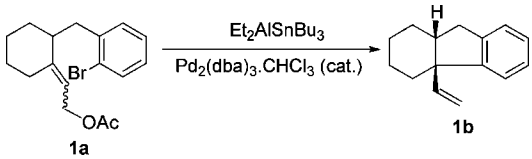
Scheme 4



Scheme 5



Scheme 6



step (Scheme 7). Two pathways may be suggested. The first one (path-a) involves initial activation of an allylic appendage as in Scheme 4. Another route (path-b) may involve initial activation of a vinylic (or aryl) appendage across Pd(0). However, the latter route seems less likely, since allyl electrophiles are preferentially activated by Pd(0) when compared with vinyl/aryl electrophiles.

That the entire catalytic sequence can be operated on a single substrate having both an allyl electrophile and a carbonyl functionality is demonstrated in precursor **2a** (Scheme 8). Formation of allylstannane **2b** and tandem intermolecular carbonyl allylation leads to a mixture of (1*R**,2*S**,5*R**)-2-acetyl-1,2-dimethyl-5-vinylcyclohexanol (**2c**) and (1*R**,2*S**,5*S**)-2-acetyl-1,2-dimethyl-5-vinylcyclohexanol (**2d**).[8]

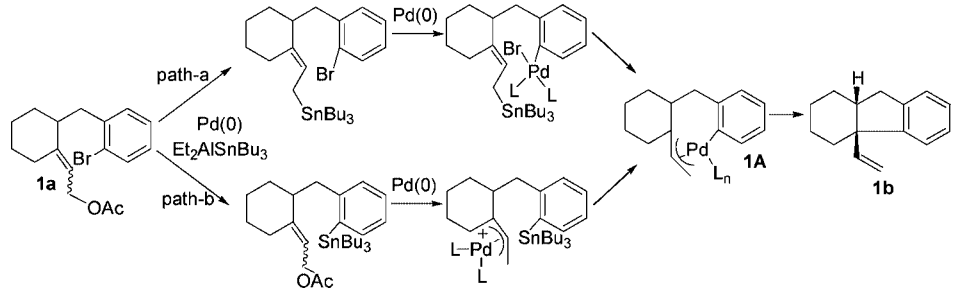
Allylstannane can also be synthesized from allylic phosphate using $Et_2AlSnBu_3$ or $Et_2AlSnClF_2$ in the presence of catalytic $Pd(PPh_3)_4$ (Scheme 9).[9] The in situ generated allyltin is further utilized for carbonyl allylation. From the yields of homoallylic alcohols, the $Et_2AlSnClF_2$ reagent is judged as superior to $Et_2AlSnBu_3$.

It may be noted that *cis*-phosphates give predominantly *trans*-product (Scheme 10). This is indicative of a mechanism similar to the one shown in Scheme 4. The formation of deuterated regioisomers in a 1:1 ratio is also a good indicator of the participation of a symmetrical π-allylpalladium intermediate.

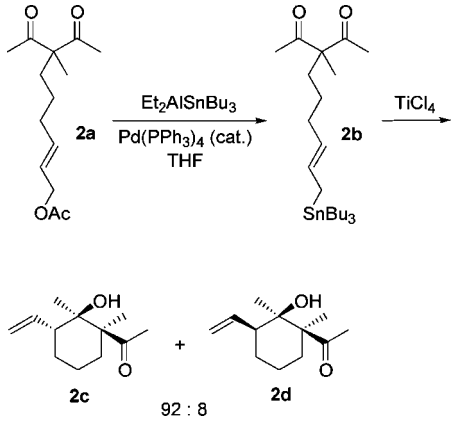
In a similar approach, allylstannanes can be prepared from $Me_3Sn-SnMe_3$ and allylic acetates or halides (Scheme 11).[10] The driving force of the reaction is the formation of Me_3SnX (X = Cl, Br, I, OAc) as the thermodynamically more stable species.

The above strategy was followed for the formation of substituted 1-vinyl-1,2-dihydronaphthalene (**3b**) from α,ω-

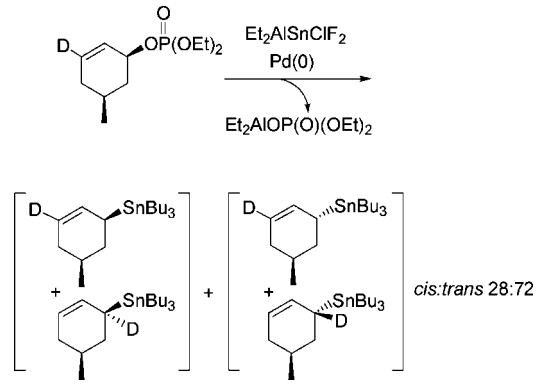
Scheme 7



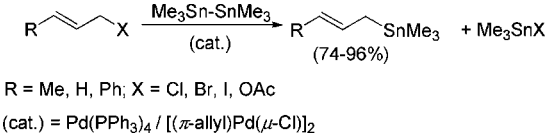
Scheme 8



Scheme 10



Scheme 11



bis(allyl acetate) (**3a**) (Scheme 12).[11] Note that the solvent system comprises a mixture of 1-hexene and THF; the former helps in generating an active Pd(0) catalyst via an in situ Wacker reaction.

Inanaga and co-workers synthesized allylstannane in a different way.[12] Electrophilic Bu_3SnCl reacts with an allyl samarium intermediate, which, in turn, is produced from a transient π-allylpalladium species and SmI_2. These transmetalations exhibit similar regio- and stereochemical features to those of the direct nucleophilic substitutions involving $Et_2AlSnBu_3$ (Scheme 13).

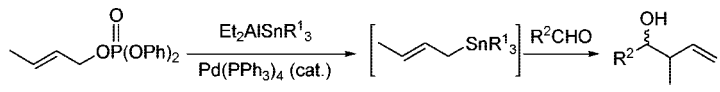
Polymer supported allyltin reagents can be synthesized using Zn/Sn transmetalation (Scheme 14). These reusable tin(IV) reagents react with aldehydes in the presence of cerium(III) or indium(III) salts to afford high yields of homoallylic alcohols, practically uncontaminated with organotin residues (less than 5 ppm).[13]

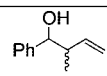
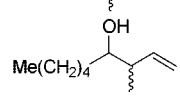
2.1.2. Allyltin from Allene and Tin(IV) Precursor

Allenes serve as alternate sources to allyl halides and acetates, for the in situ generation of allylstannanes from hexaalkylditin reagent under the aegis of a palladium(0) catalyst. The strategy is useful for the synthesis of aryl and alkenyl substituted allylstannanes from aryl/alkenyl halide and allene as organic precursors. In the catalytic cycle, the first step involves the oxidative addition of R^1-X (R^1 = H, aryl, vinyl; X = halide) to palladium(0) to form $R^1-Pd^{II}-X$ (Scheme 15). The electrophilic palladium(II) then forms a coordinated complex with one of the double bonds of an allene (*an important step in the mechanism*), followed by insertion of an allene into the "R^1-Pd" bond to give a π-allylpalladium(II) species. The subsequent Pd/Sn transmetalation step leads to the desired allyltin(IV) species (Scheme 15).

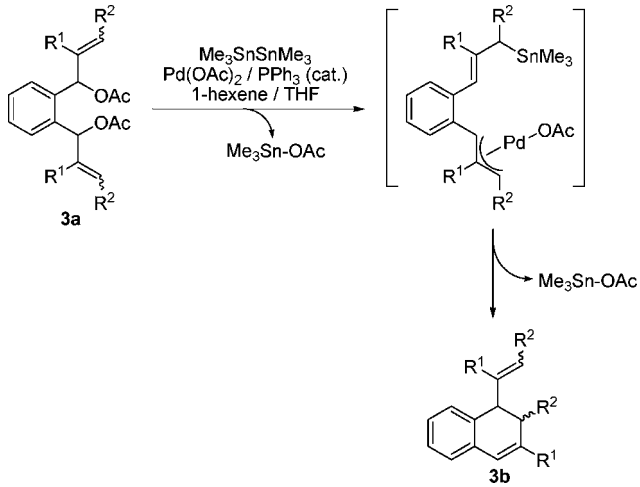
An example of this category includes $Pd(dba)_2$ assisted reaction of aryl/alkenyl iodides with allenes and hexaalkylditins, giving rise to substituted allylstannanes (Scheme 16).[14] The reaction proceeds well with aryl, heteroaryl, and alkenyl iodides having electron-withdrawing groups.

Scheme 9

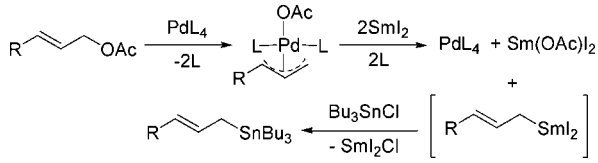


R^2CHO	Product	Product Yield (%) using $Et_2AlSnBu_3$	Product Yield (%) using $Et_2AlSnClF_2$
PhCHO		70 *syn*:*anti* 41:59	96 *syn*:*anti* 33:67
$Me(CH_2)_4CHO$		65 *syn*:*anti* 47:53	80 *syn*:*anti* 50:50

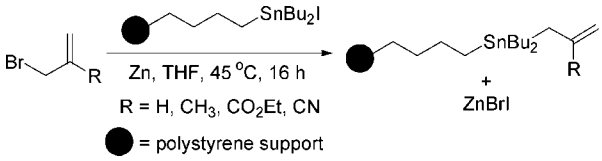
Scheme 12



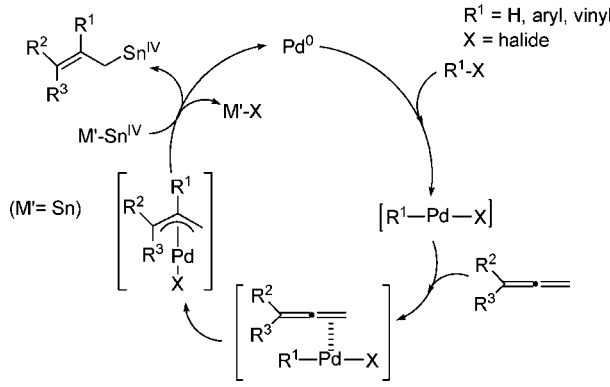
Scheme 13



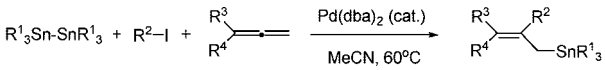
Scheme 14



Scheme 15



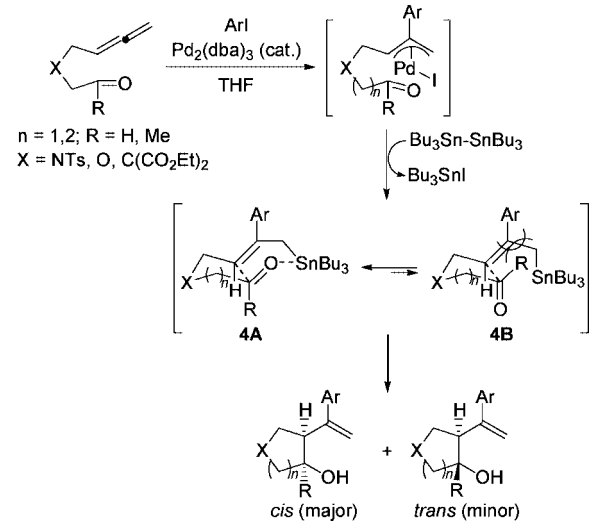
Scheme 16



#	R^1	R^2	R^3	R^4	Yield (%)
1	Me	$EtO_2CCH{=}CH$-	Me	Me	40
2	^{n}Bu	$EtO_2CCH{=}CH$-	Me	Me	81
3	^{n}Bu	$EtO_2CCH{=}CH$-	H	^{n}Bu	98
4	Me	4-$NO_2C_6H_4$-	H	cyclo-C_6H_{11}	73
5	Me	4-$EtO_2CC_6H_4$-	Me	Me	69

The generation of allylstannane from an allene using Bu_6Sn_2/Pd^0 reagent and its tandem reaction with an organic electrophile in one pot is possible when the starting allene is suitably tailored. Thus, δ- and ε-allenyl aldehydes and ketones fulfill such a requirement and undergo arylative cyclization in the presence of aryl iodides (Scheme 17).[15] The preferential formation of a *cis*-isomer over a *trans*-isomer can be explained from the comparative higher stability of intermediate **4A** with respect to **4B**. The relative instability of intermediate **4B** may be due to steric reasons, since bulky Ar-groups such as thiophene give exclusively *cis*-isomer.

Scheme 17



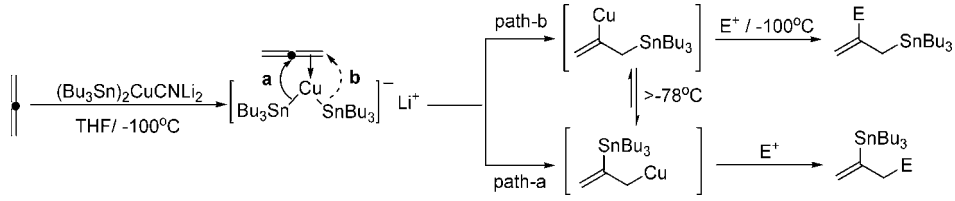
The stannylcupration of allene easily affords allylstannanes, the regiochemistry of which is greatly influenced by the temperature of the reaction.[16] It is expected that preactivation of an allenic π-system across the copper center of stannylcuprate would be the initial activation step (Scheme 18). The stannylcupration of allenes is a reversible process, whose final outcome strongly depends on temperature. Thus, the higher order cuprate $(Bu_3Sn)_2Cu(CN)Li_2$ reacts with allene at −100 °C to form allylstannane (the kinetic product), whereas similar reaction at 0 °C gives vinylstannane (the thermodynamic product). The in situ generated allylstannane−vinylcuprate is reactive toward various electrophiles (E^+). However, since at higher temperature the kinetic intermediate (allylstannane−vinylcuprate) starts to interconvert to the thermodynamic intermediate (vinylstannane−allylcuprate), there is a very limited range of electrophiles that can react with the kinetic product. Being free from the above limitation, the thermodynamic intermediate reacts with a range of carbon electrophiles (Scheme 18).[16b−d]

Interestingly, in the case of the lower order cuprate $(Bu_3Sn)CuCNLi$, the stannylcupration of allenes is regioselective toward allylstannane even up to −40 °C. Above −40 °C allylstannane is the major product with a minor amount of vinylstannane. The temperature advantage provides the opportunity to capture various electrophiles, leading to selective formation of substituted allylstannanes (Scheme 19).[16d]

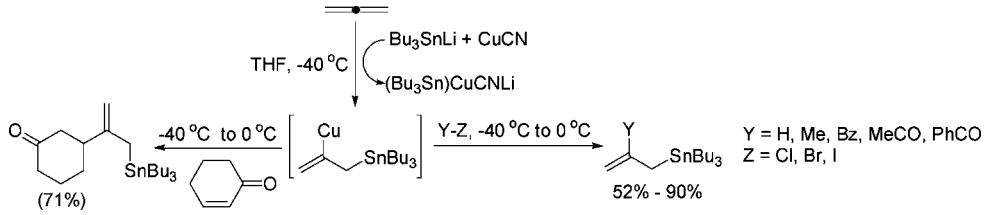
2.1.3. Allyltin from Allyl Electrophile and Tin(II) Precursor

The strategy discussed so far toward the synthesis of allylstannane majorly relies on the initial formation of an allyl−Pd^{II}−SnR_3 intermediate from allyl−Pd^{II}−X via transmetalation by a tin(IV) reagent. In this context, the dynamic behavior of η^3-allyl palladium(II) and platinum(II) complexes containing $SnCl_3$ ligand in solution is noteworthy (Scheme 20).[17] A *syn*−*syn* and *anti*−*anti* exchange of allylic protons

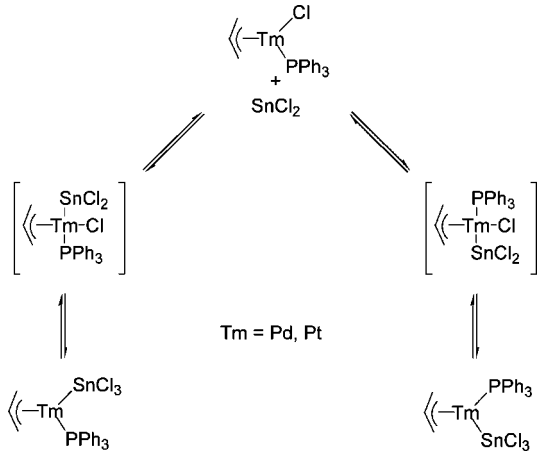
Scheme 18



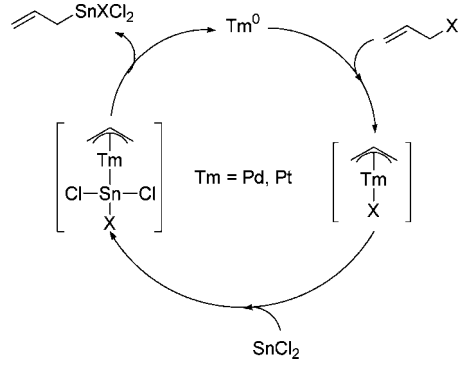
Scheme 19



Scheme 20



Scheme 21



is observed in these complexes during successive insertion and dissociation of $SnCl_2$ into a Tm−Cl bond.

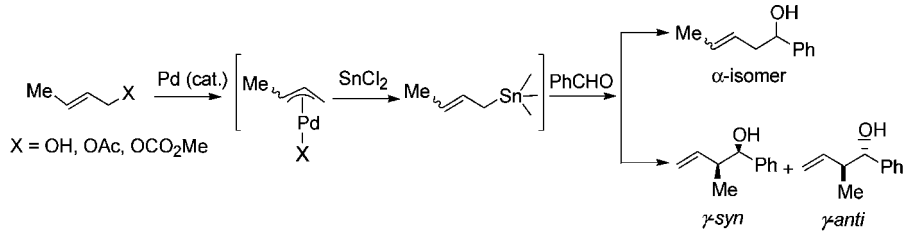
The reactive precursor allyl−Tm^{II}−SnX_3 offers a unique opportunity to test for a tandem insertion/reductive elimination sequence to generate allylstannane in situ from allyl halide or surrogates, tin(II) halide, and palladium/platinum catalyst. While this new catalytic cycle (Scheme 21) has some resemblance to Scheme 2, use of $SnCl_2$ instead of tin(IV) precursor adds to its novelty and operational simplicity.

Among the Tm−Sn^{II} systems, $PdCl_2(PhCN)_2$−$SnCl_2$ is an effective and well-studied reagent for the generation of allylstannane using allylic acetates, alcohols, or carbonates.[18] In situ reaction with a carbonyl compound leads to the formation of a corresponding homoallylic alcohol (Scheme 22). Chemo-, regio-, and diastereoselectivity aspects are extensively studied under varying reaction conditions. The reaction is kinetically faster with aldehyde than ketone, and in most cases, it is γ-regioselective.[18a−d] Under ambient conditions, reactions in DMSO and ethylene glycol (EG) as solvents show *syn*-diastereoselectivity, whereas DMF, DMI, and THF offer *anti*-selectivity. The presence of H_2O also enhances the *anti*-selectivity. It is suggested that *syn*-selectivity arises via an acyclic transition state **5B**, whereas the formation of a six-membered cyclic transition state **5A** favors *anti*-selectivity (Scheme 23). In order to rationalize the solvent effect, the authors suggested that a solvent which remains strongly coordinated to the tin(IV) center will disfavor the formation of a six-membered cyclic transition state and hence would be *syn*-selective. Therefore, DMSO should be better coordinating compared to THF, DMI, or DMF. In the case of DMI as solvent, the diastereoselectivity is found to be dependent on the allylic substrate and temperature (Scheme 22).[18e] For example, the reaction of *E*-crotyl carbonate at 10 °C exhibits *anti*-selectivity, whereas that of *E*-crotyl acetate at 60 °C shows *syn*-selectivity. Interestingly, reaction in diethylether under ultrasonication favors the formation of the α-adduct.[18f,g]

Allylation reactions using the above strategy via $PdCl_2(PhCN)_2$−$SnCl_2$ can accommodate a number of functionalized allyl alcohols. Furthermore, with respect to carbonyl efficiency, the reaction is very general (Scheme 24). Thus, allylation of α-hydroxy ketones is efficiently mediated in THF to afford the corresponding diols with high regio- and diastereoselectivity (Scheme 24(i)).[19] Diastereoselective diallylation of 1,2-diketone affords 1,2-diol as the major product (Scheme 24(ii)).[20] Diol formation can be attributed to the coordination of a carbonyl group to Sn^{IV} in a monoallylatedtin(IV) alkoxide intermediate. It is suggested that, in the case of a less bulky group (R^6-), carbonyl attack occurs along *path-a*, leading to formation of the *syn*-product, whereas, in the case of a bulky group (such as Ph-), attack along *path-b* is preferred. The Pd^{II}−Sn^{II} reagent can also facilitate the allylation of aldehyde from 2-methylenepropane-1,3-diol (Scheme 24(iii)).[21] Yet, in another variation, the reagent has been used for the allylation of resin-bound aldehydes, which could have potential application in combinatorial chemistry (Scheme 24(iv)).[22]

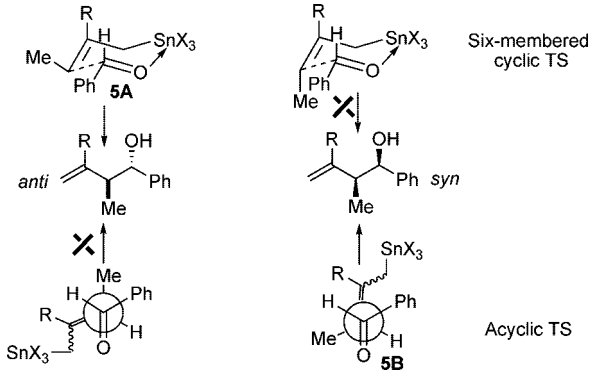
The Pd^{II}/Sn^{II} reagent is also useful for the formation of α-methylene-γ-butyrolactone from 2-(hydroxymethyl)acrylates in DMI−H_2O (Scheme 25).[23] It has been suggested that

Scheme 22



X	Solvent	Temp (°C)	Time (h)	Yield (%)	γ-*syn*:γ-*anti*:α	Ref
OCOMe	DMI	50	20	69	61:39:0	18a, 18e
OCO_2Me	DMI	10	84	95	31:69:0	18e
OH	DMI	25	36	63	29:71:0	18b
OH	DMF	25	63	89	30:70:0	18c
OH	DMSO	25	136	34	65:35:0	18d
OH	DMSO-H_2O (28 mM)	25	77	65	49:51:0	18d
OH	DMSO-H_2O (169 mM)	25	70	70	16:84:0	18d
OH	EG	25	37	78	58:42:0	18d
OH	EG-H_2O (56 mM)	25	17	99	17:83:0	18d
OH	THF	-10	139	81	9:91:0	18d
OH	THF-H_2O (25 mM)	25	13	70	17:83:0	18d
OH	Et_2O, ultrasound	25	4	76	25 (γ):75(α)	18f, 18g

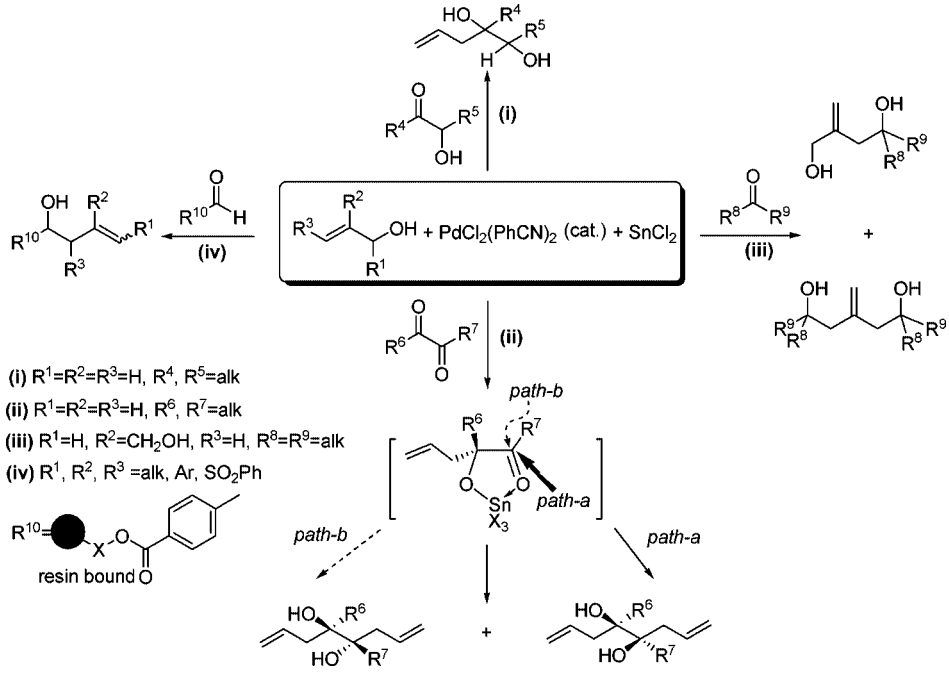
Scheme 23



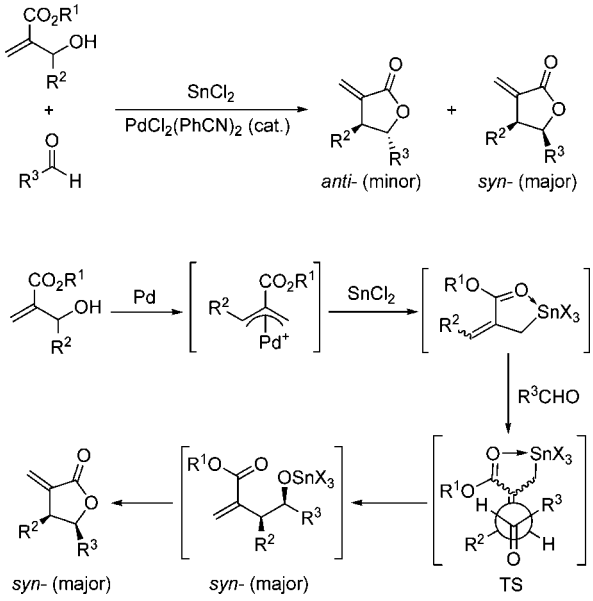
chelation of an oxygen atom of the ester group to tin in the allyltin(IV) intermediate prevents the formation of six-membered cyclic-TS; instead the acyclic antiperiplanar-TS controls the observed *syn*- regioselectivity.

$PdCl_2(PhCN)_2$-catalyzed carbonyl allylations by a mixture of (*E*)- and (*Z*)-1,3-dichloropropene with $SnCl_2$ or SnI_2/Bu_4NI (equivalent to $Bu_4N^+SnI_3^-$) reagent produce a *syn*-rich π-allyl-Pd^{II} intermediate which gives rise to (*E*)-rich allylstannane (Scheme 26).[24] Interestingly, the softness at the tin-center in the allylstannane intermediate controls the diastereoselectivity of carbonyl addition. Thus, for $SnCl_2$ and $Bu_4N^+SnI_3^-$ reagents, the diastereoselection in the resulting 1-substituted-2-chlorobut-3-en-1-ol is found to be *anti*- and *syn*-, respectively (Scheme 26). Such diastereoselectivity is

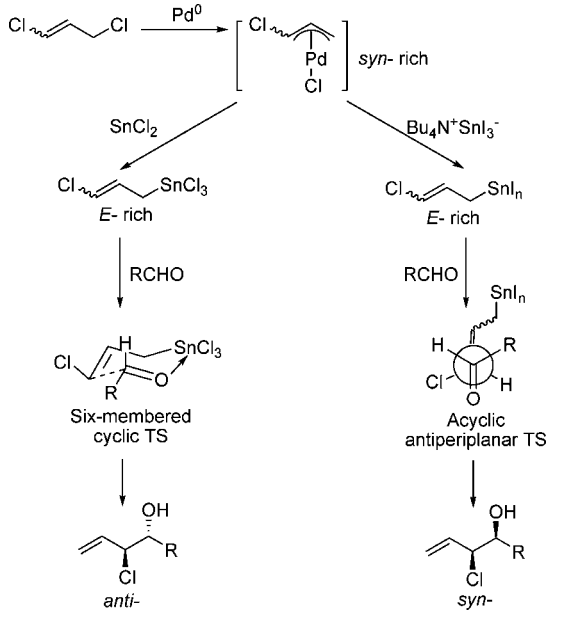
Scheme 24



Scheme 25



Scheme 26

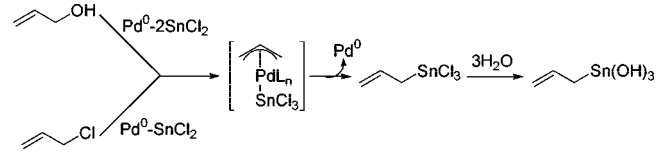


reminiscent of the transition states discussed earlier (vide Scheme 23).

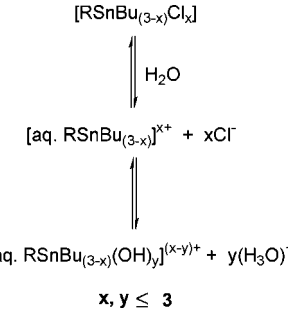
Carbonyl allylation via $Pd^{II}-Sn^{II}$ reagent has been the subject of various spectroscopic diagnoses including ^{1}H, ^{13}C, and ^{119}Sn NMR studies. While the catalytic cycle as in Scheme 21 is generally accepted, the exact nature of the in situ generated allyltin(IV) intermediate is often debated. In the case of an allyl halide, it has been suggested that an allyltrihalostannane intermediate is first formed which in the presence of water forms more nucleophilic allylating agent. Since two equivalents of $SnCl_2$ is required for allyl alcohol activation, the authors speculated that the allyl alcohol is first converted to allyl chloride; the latter then enters into the catalytic cycle (Scheme 27).[18d]

Tagliavini and co-workers studied the role of water in carbonyl allylation reactions.[25] They have ascribed the formation of either allylhydroxytin or cationic hydrated allyltin intermediates (Scheme 28).

Scheme 27



Scheme 28



It is now well-accepted that a $Tm-Sn^{II}$ combination can efficiently mediate the Barbier allylation reaction in fully aqueous or aqueous−organic biphasic media.[26,27] These reactions are popularly included under the green-Barbier regime. Catalytic $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$ is efficient for the allylation of aldehydes in an aqueous−organic biphasic system (Scheme 29).[26a] In contrast, hydrophobic catalyst $PdCl_2[P(p\text{-}C_6H_4CH_3)_3]_2$ exhibits poor reactivity. It is also noteworthy that the $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2-SnCl_2$ reagent system promotes the carbonylation of allyl chloride in dilute alcoholic−aqueous NaOH/toluene medium in the presence of carbon monoxide, affording butenoic acid in 92% yield (Scheme 29).[26b]

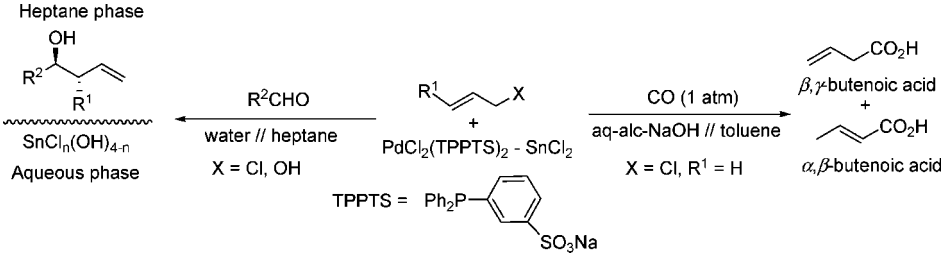
Guo and co-workers carried out an elaborate study to reexamine the effect of metal chlorides as additives (10−100%) in $SnCl_2$ promoted all-aqueous carbonyl allylation reactions (Scheme 30).[27a−d] The additives can be classified under three distinct categories based on the yield of homoallylic alcohol: *group-A*—most efficient (>95%); *group-B*—low to moderately active (∼6−40%); and *group-C*—very poorly active (<5%). It is further found that *aqueous $SnCl_2$ alone at a very high concentration* is also effective, while dilution with water drastically retards the yield of the product (Figure 2).

Roy et al. have also shown the effect of controlled addition of water in the $Pd^0/SnCl_2$ mediated allylation of arylepoxides, which affords the corresponding homoallyl alcohols with a two carbon extension and 100% γ-regioselectivity (Scheme 31, Figure 3).[28] It has been proposed that controlled addition of water generates a reactive allyltin(IV) species **6B** from **6A** (Scheme 32) and also minimizes the hydrolytic decomposition of aryl epoxides. The end-organic product arises from simultaneous rearrangement of arylepoxide to the corresponding benzylic aldehyde followed by carbonyl allylation.

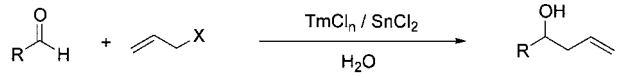
The reactivity of allyltrihalostannane toward arylepoxides can also be tuned by the addition of stoichiometric LiOH in anhydrous dichloromethane as solvent (Scheme 33).[29] In hindsight, it appears that *LiOH in DCM* plays a similar role as that of *water in DMSO* toward the formation of reactive allylhalohydroxystannane (vide **6B** in Scheme 32).

Development of reusable catalyst is an important criterion in green-chemistry. Keeping this principle in view, Cai et al. achieved Pd^0-SnCl_2 mediated allylation of aldehydes

Scheme 29



Scheme 30



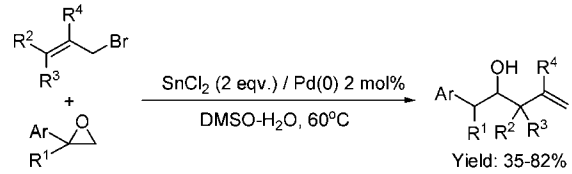
Group-A/most efficient:$TiCl_3$, $CuCl_2$, and $PdCl_2$
Group-B/low to moderately active: $LaCl_3$, $CrCl_3$, $MnCl_2$, $FeCl_2$, $CoCl_2$, and $NiCl_2$
Group-C/very poorly active: $MgCl_2$, $ZnCl_2$, $CdCl_2$, $InCl_3$, $PbCl_2$, and $BiCl_3$

using a silica-supported palladium(0) complex (Scheme 34).[30] The poly-γ-diphenylarsinopropylsiloxane palladium(0) complex has been prepared from γ-chloropropyltriethoxysilane via immobilization on fumed silica, followed by reaction with potassium diphenylarsenide and palladium chloride and finally by reduction with hydrazine hydrate. This polymeric palladium complex could be successfully reused. After a second recycle, it was found that the yield of homoallylic alcohol decreased by only 2% and 3% after each recycle, respectively.

In an interesting development toward the heterogeneous-Barbier reaction, tetragonal blue-black tin(II) oxide (β-SnO) has been used for the allylation of various aldehydes in the presence of catalytic platinum(II) and palladium(0) complexes to generate homoallylic alcohols with 100% γ-regioselectivity (Scheme 35).[31]

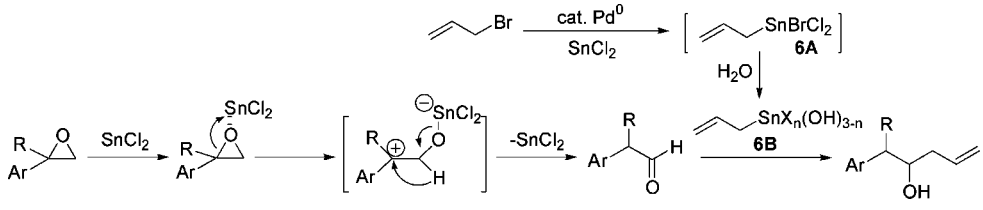
This work demonstrates the success of the redox-transmetalation strategy to promote allyl transfer from allyl-Pd and allyl-Pt to β-SnO, and utilization of the in situ generated allylstannane toward carbonyl allylation. Water has a pronounced effect in the reaction, since the use of dry THF as solvent yields <15% of the product. The formation of an σ-allyltin species via a π-allylpalladium intermediate is suggested from ^{1}H NMR and EIMS studies. An S_E2' allylation pathway has been proposed to explain the observed regioselectivity (Scheme 36).

Scheme 31

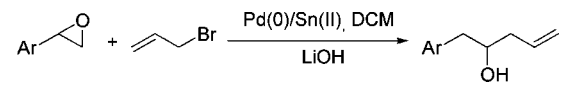


Ar = Ph, anthryl
R^1 = Me, H
R^2, R^3, R^4 = a combination of H, Me, ^{n}Pr

Scheme 32



Scheme 33



Formylferrocenes are also amenable to Barbier allylation in the presence of Tm/β-SnO (Tm = Pd^0, Pt^{II}) reagent in aqueous−organic medium (Schemes 37).[32] One may note that while 3,3-disubstituted allyl halides afford the expected homoallylic alcohols, other allyl halides lead to the unexpected formation of 1,3-dienes via elimination of water. Moreover, in the case of 1,1′-bisformylferrocenes, only one carbonyl group could be allylated.

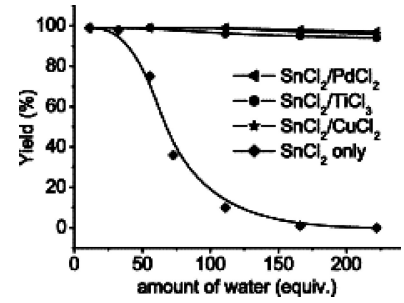


Figure 2. Effect of water on the allylation of aldehydes. Reproduced with permission from ref 27a.

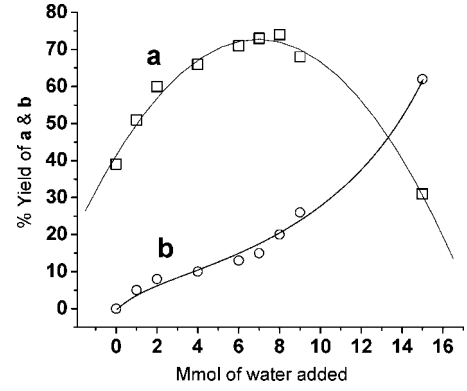
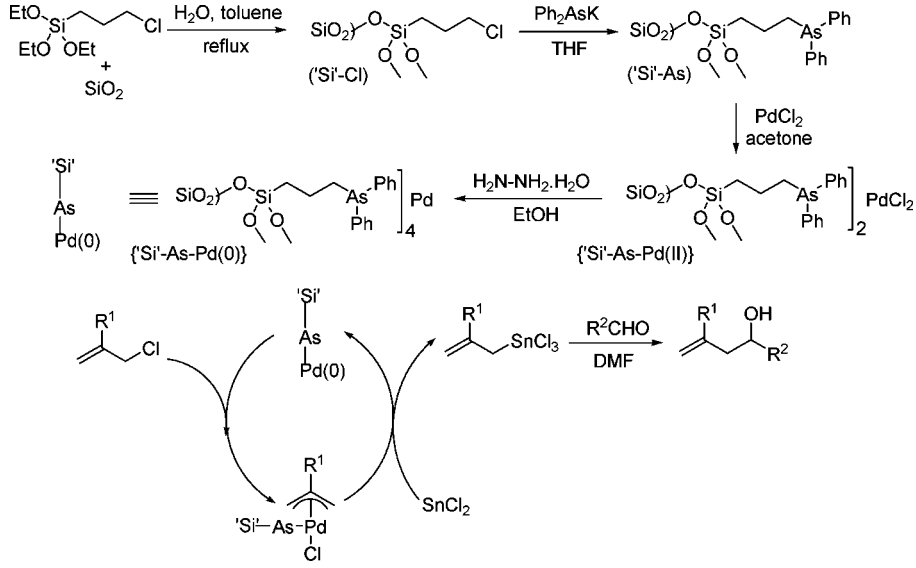
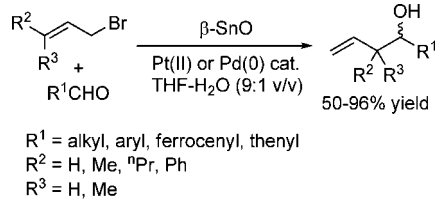


Figure 3. Effect of water on the allylation of styrene oxide [Reproduced with permission from ref 28a]: (a) 1-phenylpent-4-en-2-ol; (b) 1-phenylethane-1,2-diol. Conditions: styrene oxide, 1 mmol; $SnCl_2$, 2 mmol; allyl bromide, 3 mmol; $Pd_2(dba)_3 \cdot CHCl_3$, 2 mol %; DMSO, 3 mL; 60 °C; 11 h.

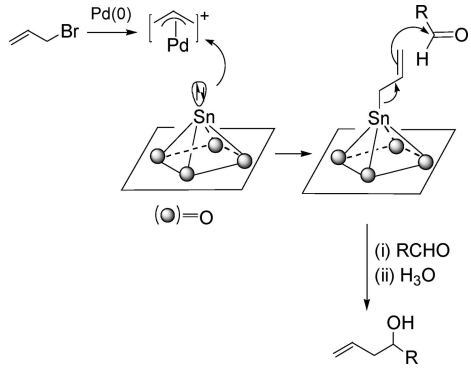
Scheme 34



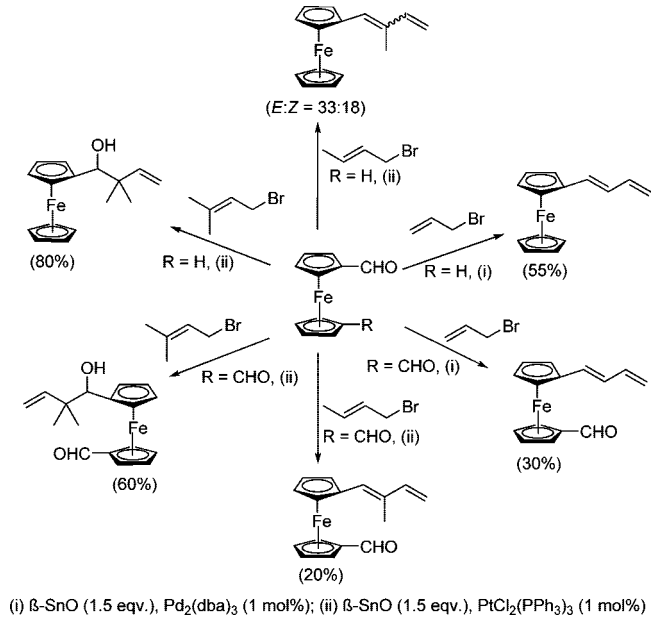
Scheme 35



Scheme 36



Scheme 37

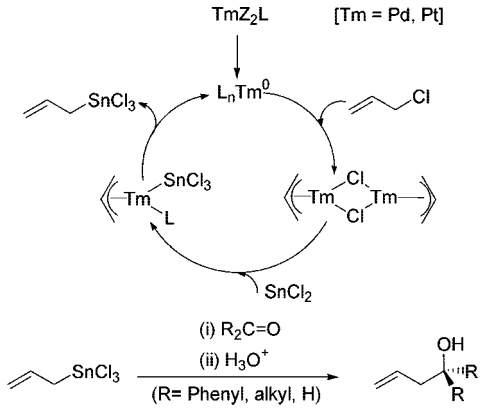


At this juncture, we would like to draw the attention of the reader back to Scheme 21, which shows the Tm/Sn^{II}-assisted generation of allyltrihalostannane as the active organometallic product in the catalytic cycle. From this, one may conclude that allyltrihalostannane can be potentially employed in many nucleophilic addition reactions, including carbonyl allylation in an absolutely anhydrous medium. However, in most of the carbonyl allylation reactions presented so far in this section,[18−28,31,32] an aqueous or aqueous−organic medium has been used. The influence of water has been often attributed to the generation of a more nucleophilic allyltin species such as [allyl-$Sn(OH)_nX_{3-n}$] or [allyl-$Sn(H_2O)_mX_n]^{(3-n)+}$. Presented below are those allylation reactions which have been executed based in Scheme 21, *but in absolute anhydrous medium.*

Thoonen et al. showed that halo or methyl platinum and palladium complexes of the type TmZ_2L (where Tm = Pt, Pd; Z = Me, Cl; L = 2,2′-bipyridine, 1,10-phenanthroline, or dppe) efficiently catalyze the reaction of allyl halides (3-chloropropene, 3-bromopropene, 3-chloro-2-methylpropene, 1-chloro-2-butene) with SnX_2 (X = Cl, Br) to generate the corresponding allyltrihalostannane under absolute anhydrous conditions (Scheme 38).[33] Among the catalysts, $PdMe_2$(phen) was adjudged the best for the generation of allyltrichlorostannane from allyl chloride and $SnCl_2$. The catalytic efficiency decreases in the order $PdCl_2$(phen), $PdCl_2$(bipy) > $PdMe_2$(bipy) > $PtCl_2$(phen) > $PtMe_2$(bipy) > $PtMe_2$(phen) > $PtCl_2$(bipy). On the other hand, $PdCl_2(PhCN)_2$ and $Pd(PPh_3)_4$ showed no activity. In a few cases, the authors have used the in situ generated allyltrihalostannanes for carbonyl allylation.

Roy et al. have exploited the reactivity of in situ generated allyltrihalostannanes toward aldehydes to generate the corresponding homoallyloxytin(IV) intermediate **7A** in anhydrous medium (Scheme 39).[28a,34] The presence of two reactive sites in **7A** (nucleophilic terminal alkene and electrophilic carbon in C−OSn) makes it a potential candidate for further reaction with a suitable third partner. In effect then, the strategy culminates into a three-component cascade coupling (3-C^3) reaction, with the third partner being an

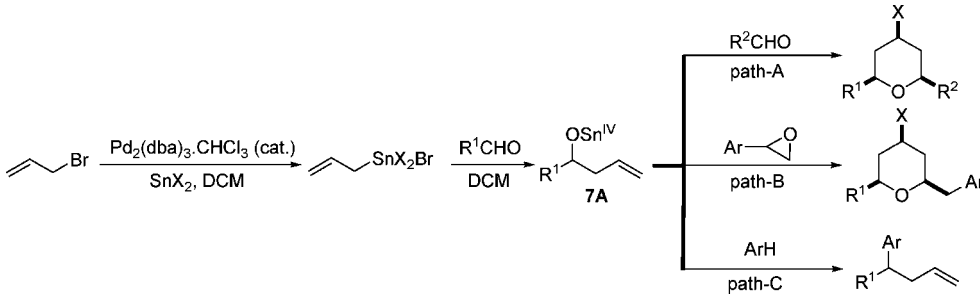
Scheme 38



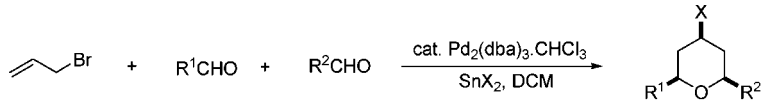
aldehyde (Scheme 39, path-A), an aryl epoxide (Scheme 39, path-B), or an arene (Scheme 39, path-C). The corresponding end-organic products are tetrahydropyrans, benzyl tetrahydropyrans, and 4,4-diarylbut-1-enes, respectively. For the generation of **7A**, $Pd_2(dba)_3 \cdot CHCl_3$ is found to be the best catalyst compared to $Pd(PPh_3)_4$, $Cu(acac)_2$, and $CuCl(SMe_2)$. It may be noted that tetrahydropyrans are important building blocks in natural product synthesis, and 4-arylbut-1-enes are potential substrates for further structural elaboration.

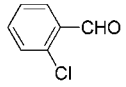
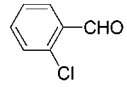
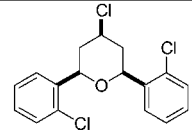
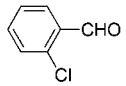
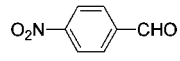
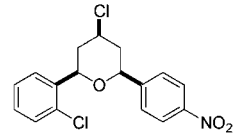
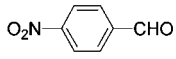
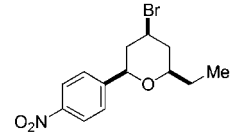
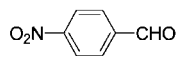
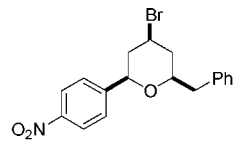
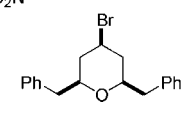
The important aspects of the first 3-C^3 strategy (Scheme 39 path-A, and Scheme 40) are as follows: (i) the reaction can accommodate both aromatic and aliphatic aldehydes, (ii) in all cases the substituents at the 2,4,6-positions in the tetrahydropyran ring maintain an *all-cis* relationship, (iii) reactions with $SnBr_2$ in place of $SnCl_2$ afford the corresponding bromo derivatives, and (iv) the substituents at the 2- and 6- positions in the tetrahydropyran ring can be varied by employing two different aldehydes, with proper tuning of reaction conditions. The second 3-C^3 strategy (Scheme 39 path-B, and Scheme 40) is conceptually similar to the first one. The formation of the benzyl tetrahydropyran derivatives is attributed to prior rearrangement of arylepoxides to the corresponding benzylic aldehydes under Pd(0)/Sn(II) assistance (Scheme 32).[28] This assumption gains additional ground from the fact that 3-C^3-coupling involving allyl halide-epoxide-epoxide results in the formation of symmetrical dibenzyl-substituted tetrahydropyran (Scheme 40, entry 5). The coupling between homoallyloxytin(IV) and

Scheme 39

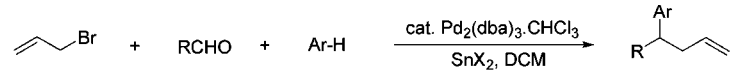


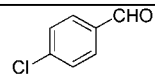
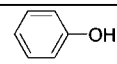
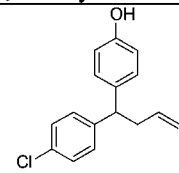
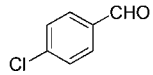
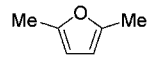
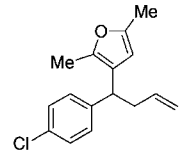
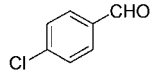
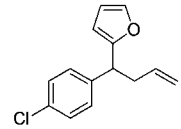
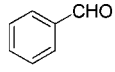
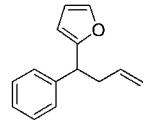
Scheme 40



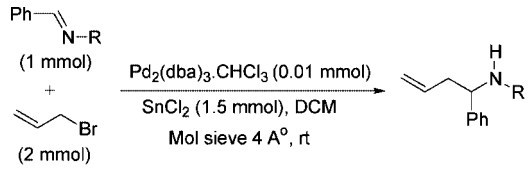
#	R^1CHO	R^2CHO	SnX_2	Tetrahydropyran	Yield (%)
1			$SnCl_2$		81
2			$SnCl_2$		77
3		$MeCH_2CHO$	$SnBr_2$		89
4			$SnBr_2$		63
5			$SnBr_2$		57

Scheme 41



#	RCHO	Ar-H	4,4-diarylbut-1-ene	Yield (%)
1				90
2				90
3				88
4				62

Scheme 42



R	Yield (%)
CH_2Ph	11
Ph	33
C_6H_4-*p*-NO_2	39
COPh	81
SO_2-*p*-tol	89

the aldehyde or benzylic aldehyde is assumed to follow a Prins-like mechanism.

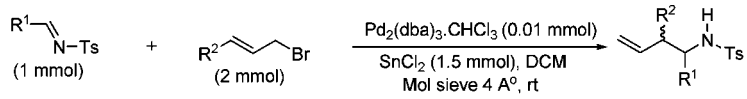
The third 3-C^3 strategy (Scheme 39, path-C) can be equated to a consecutive Barbier allylation and Friedel−Crafts alkylation reaction. It has been found that activated arenes as well as heteroarenes are reasonably effective, while ring deactivated aromatic aldehydes and ring activated arenes are better (Scheme 41).

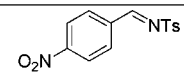
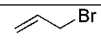
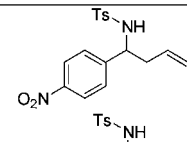
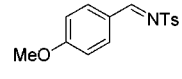
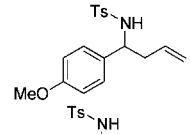
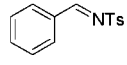
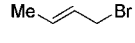
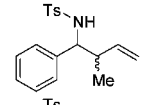
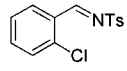
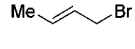
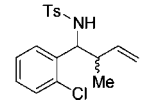
Under strictly anhydrous conditions, in situ generated allyltrihalostannanes also show facile reactivity toward conjugatively stabilized *N*-substituted imines, in general, and sulfonimines, in particular, resulting in the formation of the corresponding homoallylamine derivatives in a one-pot Barbier fashion (Scheme 42).[35]

The strategy has been extended toward the reaction of allyl and crotyl bromides with sulfonimines (Scheme 43). A salient observation in the case of crotyl bromide is the formation of the corresponding homoallylamines with 100% γ-regioselectivity.

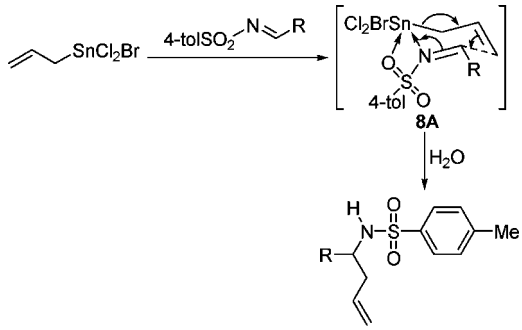
The plausible reaction pathway in the above reaction involves the activation of allyltrihalostannane by sulfonimine

Scheme 43

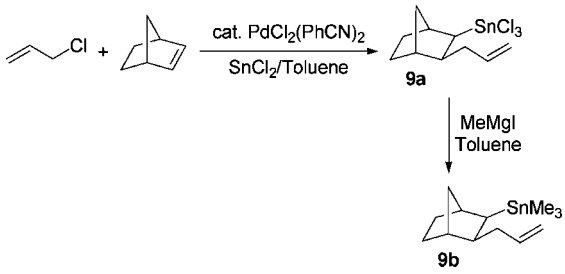


Sulfonimine	Bromides	Products	Yield (%)
			88
			80
			76
			65

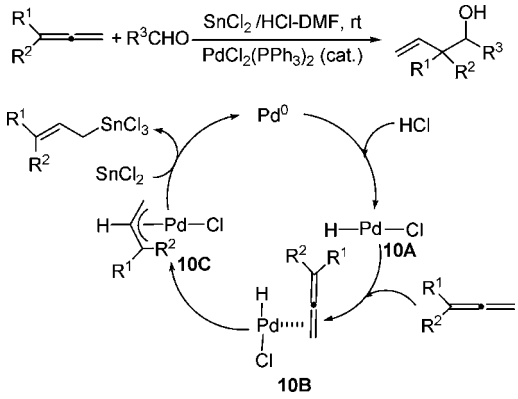
Scheme 44



Scheme 45



Scheme 46



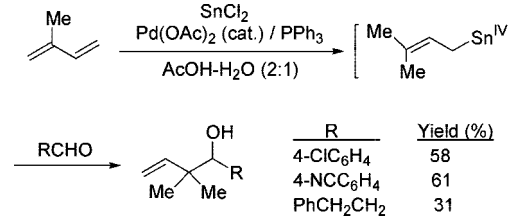
via N- and O-coordination as in six-membered transition state 8A—concomitant S_E2' attack followed by hydrolysis furnishes the end organic product (Scheme 44).

Allyltrihalostannanes generated in situ using $Pd^{II}/SnCl_2$ reagent also mediate the carbostannylation of alkenes in one-pot.[36] For example, norbornene reacts with allyl chloride in toluene in the presence of catalytic $PdCl_2(PhCN)_2$ and $SnCl_2$ to give allyl(trihalostannyl)norbornane **9a** in 97% yield (Scheme 45). The halogen atoms on tin are easily functionalized by subsequent treatment with Grignard reagent.

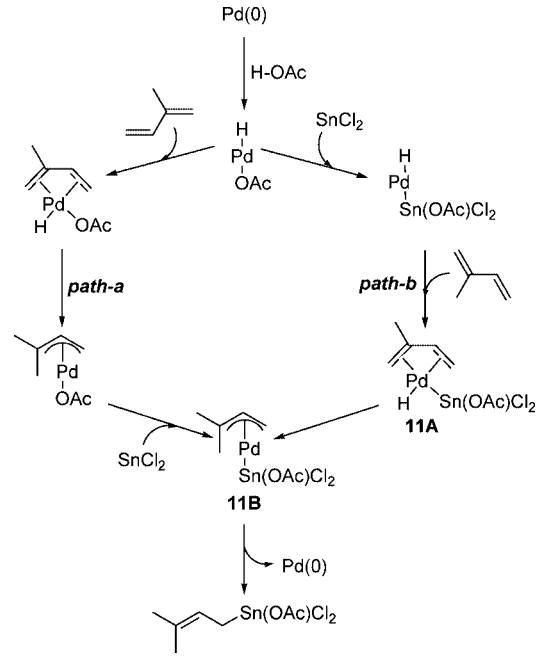
2.1.4. Allyltin from Allene or Diene and a Tin(II) Precursor

Tin(II) precursors also facilitate the generation of allylstannane from allenes. Thus, in the presence of $SnCl_2$, catalytic palladium(II) complex, and a Brönsted acid, allenes are converted to allylstannanes in DMF as solvent. The in situ generated allylstannane is further reacted with aldehyde to give homoallylic alcohol in good yield and high *γ-anti*-selectivity (Scheme 46).[37] The mechanism involves a palladium(0) promoted cycle. Oxidative addition of H−Cl across the palladium(0) forms reactive $H-Pd^{II}-Cl$ intermediate **10A**. The latter acts as a key intermediate for subsequent coordination with allene **10B** and formation of

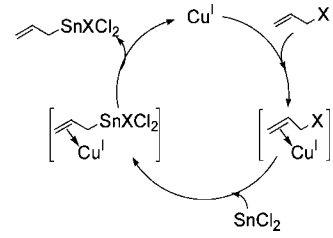
Scheme 47



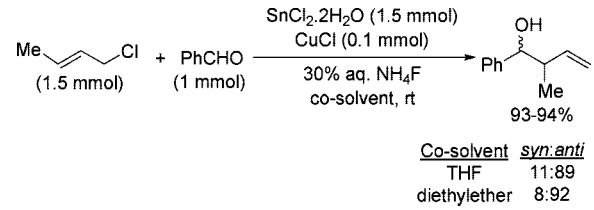
Scheme 48



Scheme 49



Scheme 50

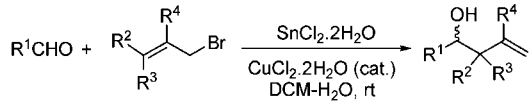


π-allyl-Pd(II) intermediate **10C**. Insertion of $SnCl_2$ and reductive elimination of Pd(0) gives rise to the desired allylstannane.

The above strategy is applicable to 1,3-dienes as well. For example, isoprene is conveniently converted to allylstannane using $Pd(OAc)_2/SnCl_2$ in the presence of acetic acid. The allylstannane is further reacted in one-pot with aldehyde to furnish the respective homoallyl alcohol (Scheme 47).[38]

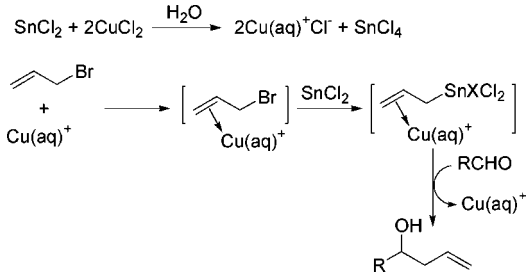
The mechanism is expected to be similar to that of allene. However, one may consider two plausible pathways for the generation of the bimetallic π-allyl−Pd−Sn intermediate **11B**

Scheme 51



R^1	R^2	R^3	R^4	Yield (%)	*syn*:*anti*
4-ClC_6H_4	H	H	H	88	-
4-ClC_6H_4	Me	H	H	91	30:70
4-ClC_6H_4	Ph	H	H	72	0:100

Scheme 52

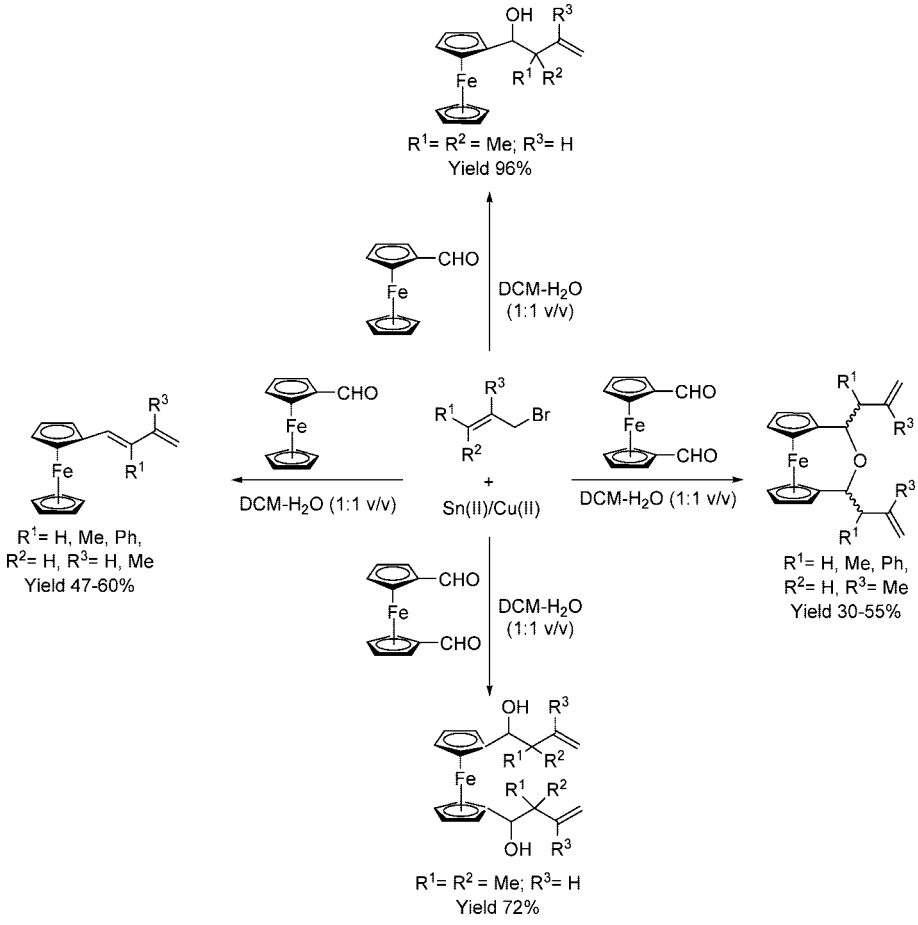


(Scheme 48, *path-a* and *path-b*). *Path-a* is conceptually identical to Scheme 46. *Path-b* invokes an early insertion of $SnCl_2$ across H−Pd−OAc and coordination of the bimetallic Pd−Sn intermediate to the diene to give **11A**. Finally, hydride migration from **11A** will afford the π-allyl−Pd−Sn intermediate **11B**.

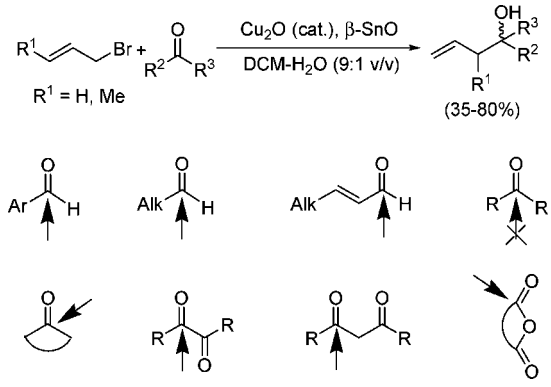
2.2. Allyltin via Weak Activation of an Organic Precursor at the Transition Metal Center

Generation of allylstannane by the weak activation of an organic precursor across transition metal salts/complexes has been exploited in a few cases; the metal which is most pronounced in this category is copper. As elaborated below, a successful Barbier allylation protocol has been developed using the dual reagent combination of Cu^0/Sn^{II}, Cu^I/Sn^{II}, Cu^{II}/Sn^{II}, and even Cu_2O/SnO. Copper(I), being in the d^{10} configuration, is expected to react in a similar manner to its d^{10}-equivalent palladium(0). However, unlike palladium(0), which activates an allyl electrophile by oxidative-addition, copper(I) weakly activates an allyl halide toward the formation of an alkene−copper(I) complex, and the bonding is favored by a formidable $d\pi-p\pi^*$ interaction.[39] The alkene−copper(I) intermediate promotes oxidative addition of a *now-activated* carbon−halogen bond to tin(II) to generate the allyltin(IV) species (Scheme 49).

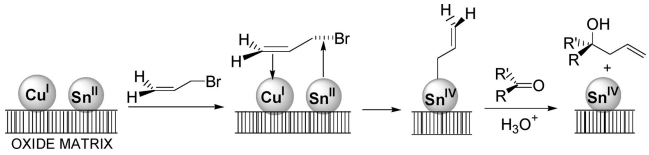
Scheme 53



Scheme 54



Scheme 55



An early report in this category is the allylation of aldehydes from allyl halides/sulfonates in the presence of $SnCl_2 \cdot 2H_2O$ and catalytic copper(I) salts to afford homoallyl alcohols with solvent-dependent diastereoselectivity.[40] For example, the reaction of crotyl chloride with benzaldehyde in the presence of $SnCl_2/CuCl/NH_4F$ in THF−H_2O shows *γ-anti* selectivity (Scheme 50). In sharp contrast, a similar reaction in Et_2O−H_2O leads to *γ-syn* selection.

Roy and co-workers have emphasized the role of water in the reaction and the ability of copper(II) to act as a precatalyst (Scheme 51).[41] The reaction is chemoselective toward aldehydes and shows exclusive γ-regioselectivity along with high *anti*-diastereoselectivity (Scheme 51).[41]

Reaction monitored by ^1H NMR, CV, and EIMS indicates (a) prior activation of allyl halide via alkene−copper(I) interaction, (b) preferential oxidative interaction of allyl halide across Sn(II), and (c) formation of allyltrihalostannane as the initial reactive intermediate (Scheme 52).

The $Cu^{II}/SnCl_2$ dual reagent also mediates the γ-regioselective allylation of formylferrocene with allyl bromides in DCM−H_2O (1:1) to afford the corresponding ferrocenyl dienes (Scheme 53).[42] On the other hand, similar reactions of 1,1′-bisformylferrocene yield oxa-bridged [3]-ferrocenophanes having allyl pendants. The latter appear to result from the dehydration of intermediate homoallylic alcohols. This proposal is supported by the isolation of homoallylic alcohols from the reactions of formylferrocene and 1,1′-bisformylferrocene with 1-bromo-3-methylbut-2-ene.

The Barbier allylation is also applicable to *an all-oxide reagent* comprising β-SnO/catalytic-Cu_2O, affording the corresponding homoallylic alcohols with exclusive γ-regioselectivity but poor diastereoselectivity (Scheme 54).[43] The oxide-reagent accommodates various aldehydes, including heteroaromatic aldehydes. It also shows facile reactivity toward 1,2- and 1,3-diketones, cyclic monoketones, and anhydrides. In these cases, only the corresponding monoallylated products are formed. Interestingly, acyclic monoketones such as acetophenone remain unaffected.

The interaction of allyl halide with β-SnO in the presence or absence of Cu_2O has been studied by XPS and XRD, indicating that the reagent combination activates allyl halides preferentially via two kinds of interaction. The first one is characterized as an alkene−copper(I) interaction at the copper site, and the second is an interaction of a surface organometallic species at the tin site in which tin is in the +IV oxidation state (Scheme 55).

Guo and co-workers have presented the synthesis of homoallylic alcohol in water alone using $SnCl_2 \cdot 2H_2O$ and catalytic copper metal as the reagent (Scheme 56).[44]

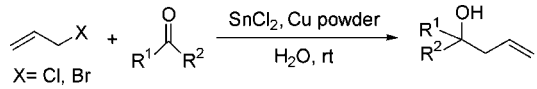
Synthesis of a chiral allyltin(IV) reagent is achieved from tin(II)-catecholate [$Sn(O_2C_6H_4)$], allyl halide, chiral dialkyl tartrate, and DBU (Scheme 57).[45] This reagent reacts with aldehyde in the presence of catalytic copper(I) or copper(II) salts to form homoallylic alcohol in high enantioselectivity. (+)-Di-*tert*-butyl tartrate is found to be the most efficient chiral auxiliary.

Allylstannane (in situ generated from Sn(II) hetereocycle **12a**, allyl bromide, and catalytic CuCl) reacts with aldehyde in the presence of Ti(IV)/BINOL to afford the corresponding homoallylic alcohol **12b** with poor enantioselectivity (Scheme 58).[46]

2.3. Allyltin via Initial Activation of a Tin(IV) Precursor at the Transition Metal Center

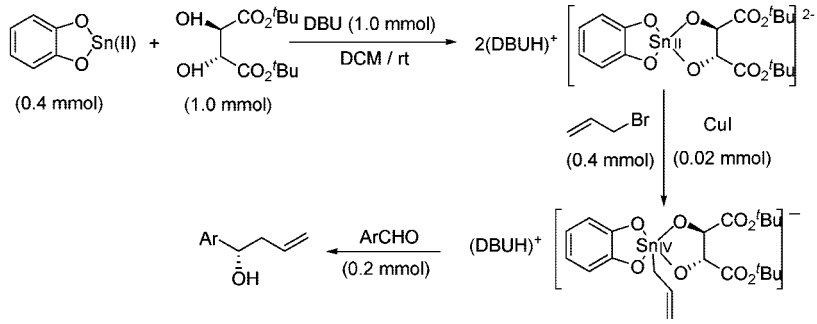
Allylstannane generation under this category is again dictated by palladium(0) catalysis, with fewer reactions promoted by Ni^0 and Pt^0—the d^{10} congeners. Depending upon the nature of the substrate and the tin(IV) precursor, allylstannane generation can be further divided into several subclasses.

Scheme 56



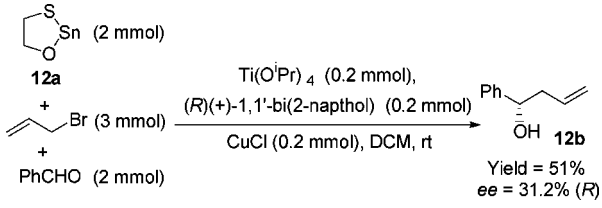
R^1	R^2	X	Time (h)	Yield (%)
CH_2=CH	H	Br	4	94
CCl_3	H	Cl	3	95
		Br	3	96
Ph	H	Cl	8	100
		Br	8	100
Me	Et	Cl	3	92
		Br	3	95

Scheme 57



Homoallylic alcohols		
Ar	Yield %	*ee* %
Ph	98	91
4-Cl-Ph	99	89
4-CH_3-Ph	96	92
2-CH_3-Ph	99	94
1-naphthyl	97	91

Scheme 58



2.3.1. Allyltin via Monostannylation of Allyl Electrophiles

Palladium pincer complex **13a** catalyzes the stannylation of allyl chloride, allyl phosphonate, and vinyl epoxide with hexaalkylditin reagent under mild conditions (Scheme 59).[47]

Most notably, the reaction proceeds via palladium(II) intermediates without the involvement of any allyl-Pd species (Scheme 60). Thus, hexamethylditin reacts with **13a** to afford a stannyl-Pd(II) complex. Thereafter, a direct transfer of the trimethylstannyl group to the allylic substrate provides the desired allylstannane.

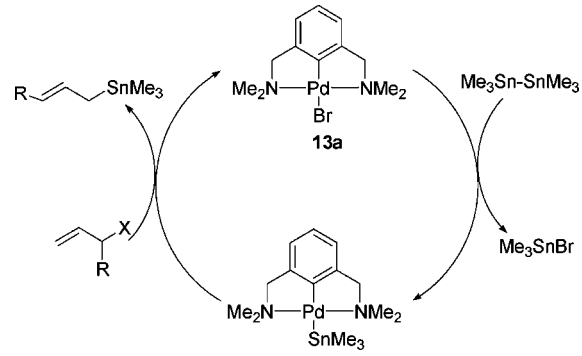
A combined catalytic system (**13a** + **13b**) is shown to be effective for the allylation of aldehydes and imines. Each of the catalysts serves distinct roles, as shown in Scheme 61. The reaction affords the corresponding homoallylic derivatives with high regioselectivity but poor stereoselectivity.

2.3.2. Allyltin via Dimetalation of Allene

Allylstannanes can be generated in a facile manner from allenes and bimetallic tin(IV) reagents such as Me_3M-SnR_3 (M = Si, Sn, Ge; R = alkyl), as shown in Scheme 62.[48−51]

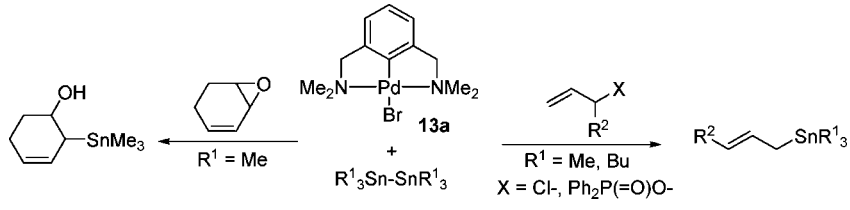
The reactions are of distinct mechanistic importance. Keeping this in view, a general catalytic cycle is discussed first. The cycle relies on the unique ability of palladium(0) to activate the bimetallic

Scheme 60

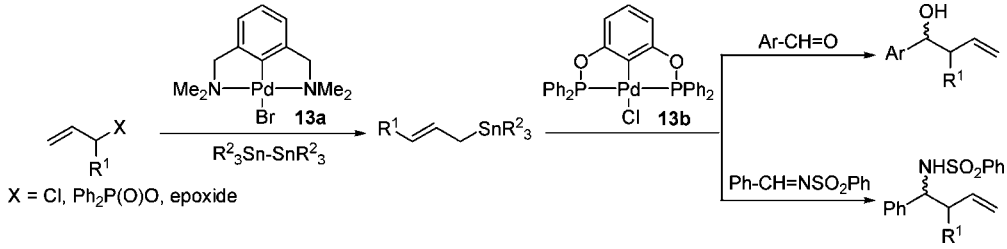


$M-Sn^{IV}$ precursor (Scheme 63). Thus, oxidative addition of $R^2_3M-SnR^3_3$ across palladium(0) leads to intermediate $R^2_3M-Pd^{II}-SnR^3_3$ (**14A**) (Scheme 63). This step is well-supported by the isolation and characterization of Pd−Sn bimetallic complexes such as $Pd(PMe_3)_2(SnMe_3)_2$, $Pd(PMePh_2)_2(SnMe_3)_2$, and $Pd[\eta^2\text{-}(SiMe_2CH_2CH_2PPh_2)][\eta^2\text{-}(SnMe_2CH_2CH_2PPh_2)]$.[52,53] It may be noted that due to the presence of a positive dipole in the Si−Sn bond compared to the Sn−Sn bond, the oxidative addition of $R^2_3Si-SnR^3_3$ across Pd(0) will be more facile than that of $R^2_3Sn-SnR^3_3$. The bond dissociation energy of M−Sn in the corresponding hexaalkyl derivatives is generally in the order Sn−Sn < Si−Sn < Ge−Sn.[51] Therefore, it is also expected that the Ge−Sn moiety will be the least reactive during oxidative addition across Pd(0). The next step of the catalytic cycle involves the coordination of allene to Pd^{II} (Scheme 63). Variation in the mode of coordination of allene will lead to intermediates **14B** and/or **14C**. In the following step, the migration of R^3_3Sn or R^2_3M to the central carbon of the allene can give rise to two

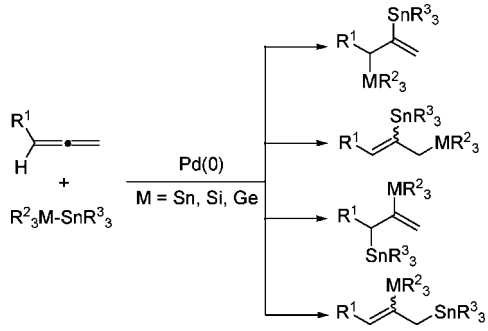
Scheme 59



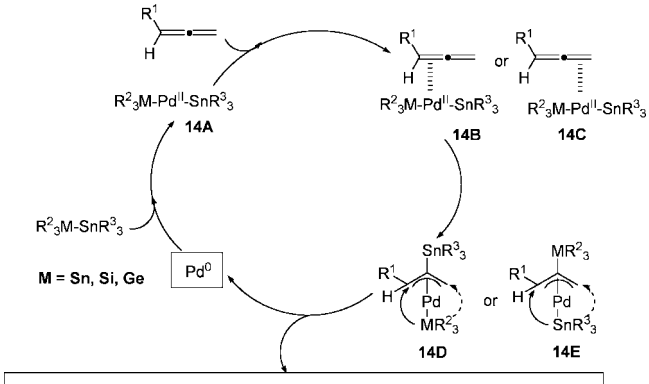
Scheme 61



Scheme 62



Scheme 63



different π-allyl-Pd(II) intermediates, **14D** and/or **14E**. The final step involves reductive elimination of Pd(0) from **14D** and/or **14E**, leading to the products **15**, **16**, and **17** as various isomers.

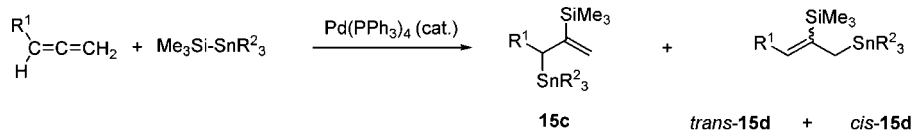
Note that the above catalytic sequence may in principle generate three different vinyl stannanes and three different allylstannanes for each M (Si or Sn or Ge). For example, in silastannylation (M = Si), the vinylstannanes would be **15a**, *cis*-**15b**, and *trans*-**15b**, while the allylstannanes would be **15c**, *cis*-**15d**, and *trans*-**15d**. It is therefore a formidable challenge to overcome the complexity and tune the reaction toward a desired allylstannane. As will be shown below, such a control can be achieved by judicious choice of allene, $R^2_3M-SnR^3_3$, and reaction conditions.

For example, the reaction of $Me_3Si-SnR^2_3$ with various allenes affords the corresponding allylstannanes **15c**, *cis*-**15d**, and *trans*-**15d** in varying ratios (Scheme 64).[48] The ratio varies depending upon the substitutent in the allene (R^1-) and Si−Sn precursor (R^2-). For R^1 = ^{n}Bu, R^2 = ^{n}Bu (entry 1), and R^1 = ^{n}Bu, R^2 = Me (entry 2), the reaction leads to the major formation of *trans*-**15d** along with other isomers. Allylstannane **15c** predominates for R^1 = ^{t}Bu, cyclohexyl and R^2 = Me (chiefly entries 3 and 4).

Cheng and co-workers have shown that reaction of silylstannylation of allenes can also be catalyzed by phosphine-free palladium(0) complexes. Thus, in the presence of catalytic $Pd_2(dba)_3$ in toluene, allylstannane *trans*-**15d** (vide Scheme 63) is obtained in good to excellent yields.[49] For example, silylstannylation of allene PhCH=C=CH_2 with Me_3Si-$SnBu_3$ gives (*E*)-$Bu_3SnCH_2C(SiMe_3)$=CHPh in 91% isolated yield.

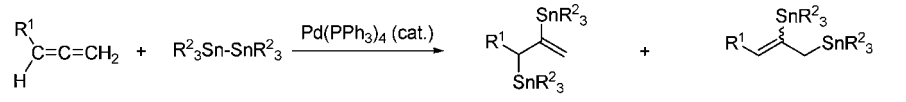
The reactivities of hexaalkylditin reagents toward allenes under the aegies of catalytic palladium(0) are similar to those of their Si−Sn analogues (Scheme 65).[48b,50] It may be noted that, for R^1 = Me-, R^2 = Me- (entry 1), R^1 = Et-, R^2 = ^{n}Bu- (entry 2), and R^1 = ^{n}Bu-, R^2 = ^{t}Bu- (entry 4) allylstannane, *trans*-**16b** is the major product. It can be seen that in general the yields do not decrease on going from R^2 = Me- to ^{t}Bu-, though the latter may require longer reaction time. The allylstannanes synthesized using the above protocol have been successfully utilized for carbonyl allylation. They

Scheme 64



#	R^1	R^2	Temp (^{o}C)	Time (h)	Yield (%)	Isomer ratio		
						15c	*trans*-**15d**	*cis*-**15d**
1	^{n}Bu	^{n}Bu	85	20	67	-	73	27
2	^{n}Bu	Me	85	1.5	70	41	54	5
3	^{t}Bu	Me	85	36	38	95	5	
4	c-hexyl	Me	85	1.5	70	90	10	-

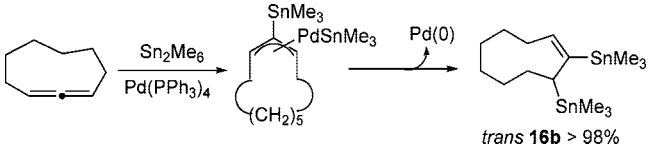
Scheme 65



16a trans-16b cis-16b

#	R^1	R^2	Temp (°C)	Time (h)	Yield (%)	Isomer ratio		
						16a	*trans*-**16b**	*cis*-**16b**
1	Me	Me	85	48	39	12	59	29
2	Et	Bu	85	17	92	-	76	24
3	Me	^{t}Bu	85	48	51	93	6	1
4	Bu	^{t}Bu	85	144	80	-	100	-

Scheme 66



trans **16b** > 98%

are also useful for lithio-destannylation followed by the addition of various electrophiles.[50]

An interesting extension of dimetalation of allene is the conversion of cyclic allenes (C_9−C_{13}) into synthetically promising 2,3-bis(trimethylstannyl)cycloalk-1-enes by the palladium(0)-catalyzed addition of hexaalkyldistannanes.[50c] For example, the reaction of 1,2-cyclononadiene with Sn_2Me_6 yields distannane *trans*-**16b** as the major isomer (Scheme 66).

In the reaction of $R^1{}_3Si$−$SnR^2{}_3$ with allenes, we have previously shown that the -$SiR^1{}_3$ group always attacks the central carbon atom of the allene. In sharp contrast, in the case of $R^1{}_3Ge$−$SnR^2{}_3$, the regioselectivity varies, depending upon the substitutent on the allene (Scheme 67). For R = MeO- (entry 1), vinylstannane **17a** is obtained exclusively by initial attack of Bu_3Sn- to the central carbon atom of the allene. However, for bulky substitutents on the allene, a mixture of allylstannanes **17c** and **17d** is obtained (entries 2 and 3).[51]

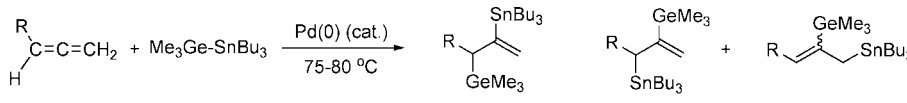
Rajanbabu and co-workers have delineated an interesting palladium(0) catalyzed silastannylation−cyclization reaction of allenynes having terminal acetylenes.[54] This useful cyclization can accommodate a number of functional groups and various Si−Sn precursors. As delineated in Scheme 68, the reaction of **18a** with Ph_3Sn−$SiMe_2{}^t$Bu in the presence of catalytic $Pd_2(dba)_3$·$CHCl_3$/$P(C_6F_5)_3$ at ambient temperature gives rise to the cyclized product **18b**. The reactivity of $Pd(0)/P(C_6F_5)_3$ is found to be in the order $PdCl_2(PhCN)_2$ > Pd(π-allyl)(OTf) ≈ $Pd_2(dba)_3$·$CHCl_3$ ≫ $PdCl_2(Ph_3P)_2$ ≈ $Pd(PPh_3)_4$. Interestingly, similar reaction of **18a** in the presence of Bu_3Sn−$SiMe_3$ leads to the formation of 81% uncyclized product **18c**, the rest being the cyclized product **18d**. Moreover, upon heating at 45 °C for 48 h, the uncyclized allylstannane **18c** is quantitatively converted into the cyclized product **18d**. It may be deduced, therefore, that for the reaction of Ph_3Sn−$SiMe_2Bu^t$ with **18a** the uncyclized intermediate **18A** is highly reactive toward cyclization, thereby preventing its isolation.

The proposed mechanism involves initial oxidative addition of a Si−Sn precursor across Pd(0) followed by bidentate coordination of allene and acetylene on Si−Pd^{II}−Sn to generate intermediate **18B**. Internal silyl transfer from **18B** leads to stable π-allyl-Pd^{II}−Sn intermediate **18C**, which on reductive elimination gives allylstannane **18A** or **18c**, with the regeneration of catalyst (Scheme 69). A parallel cycle operates in tandem from intermediate **18C**, involving cyclization, leading to intermediate **18D**. Concomitant reductive elimination from the latter yields the exocyclic vinyl stannane **18b** or **18d**, regenerating the Pd(0). The conversion of allylstannane **18A** or **18c** to exocyclic vinyl stannane **18b** or **18d**, respectively, can be rationalized by the formation of intermediate **18C** from **18A** or **18c** and palladium(0) (Scheme 69, dotted arrow). Intermediate **18C** would take part in the usual manner to give **18b** or **18d**.

The chemo- and regiocontrols are mostly dictated by the stereoelectronic factors around the allene unit. For example, the *Z*-geometry of the exocyclic vinylstannane **18b** or **18d** is a consequence of *syn*-carbometalation and subsequent reductive elimination from bimetallic Pd−Sn intermediate **18D** with retention of configuration at the vinyl carbon. The cyclization appears to be limited to allene-ynes with terminal acetylenes.

A closely similar palladium(0) assisted tandem silastannylation followed by allyl addition to a carbonyl group is achieved using Me_3Si−$SnBu_3$ and δ- and ε-allenyl aldehydes and ketones **19a** (Scheme 70).[55] Among the catalysts, [(π-allyl)Pd(μ-Cl)]$_2$ is superior to $Pd(PPh_3)_4$, $Pd_2(dba)_3$·$CHCl_3$,

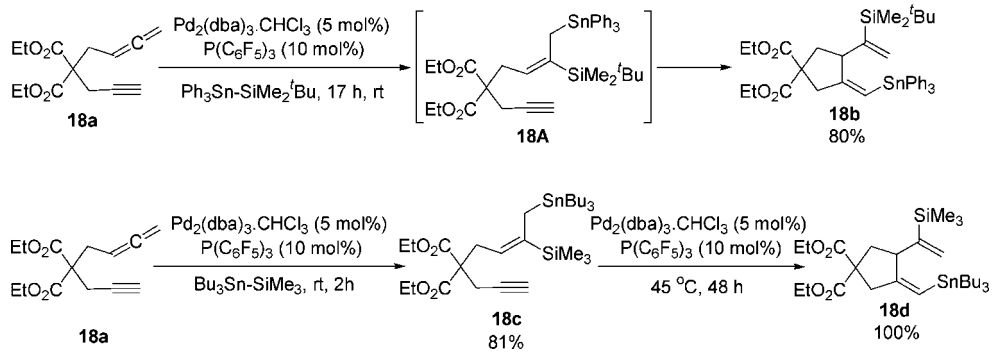
Scheme 67



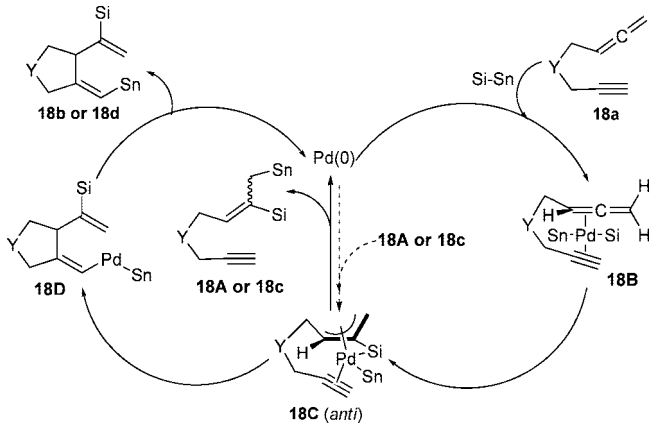
17a 17c 17d

#	R	Time (h)	GC yield (%)		
			17a	**17c**	**17d**
1	MeO	3.5	93	-	-
2	c-hexylidene	24	-	25	75
3	^{t}Bu	26	-	84	10

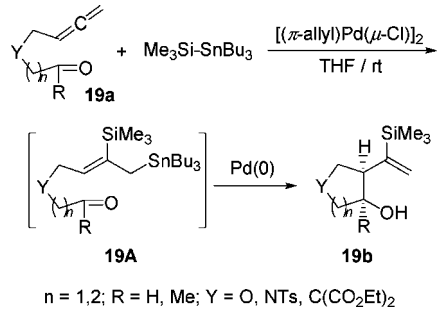
Scheme 68



Scheme 69



Scheme 70



$Pd_2(dba)_3$, $PdCl_2(PPh_3)_2$, $PtCl_2(PPh_3)_2$, and $PdCl_2$. The reaction is highly regioselective, with the migration of a $SiMe_3$ group exclusively to the central carbon atom of the allene, with the cyclized product **19b** arising via the intermediate **19A**.

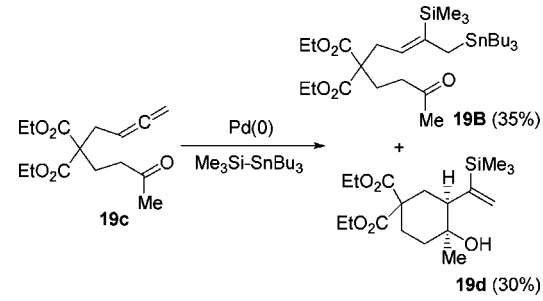
Indeed, in a specific case of silastannylation of ε-allenyl ketone **19c**, the mechanistically viable allylstannane intermediate **19B** has been isolated from the reaction mixture along with the desired cyclized product **19d** (Scheme 71).

The reaction of 1,2,4,5-tetrastannacyclohexanes and 1,1-dimethylallene in the presence of catalytic palladium(0) affords 4-methylene-1,3-distannacyclopentanes (Scheme 72).[56]

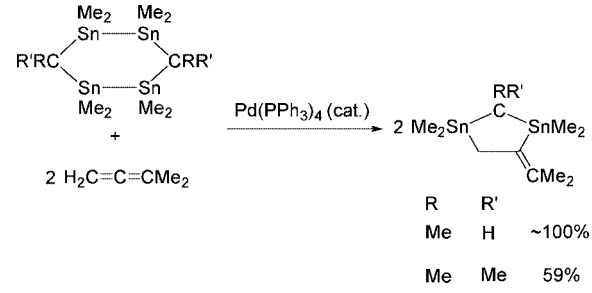
2.3.3. Allyltin via Mono- and Dimetalation of Diene

Like its allene counterpart, activation of diene by a Tm(0)/Sn(IV) combination is a synthetically useful strategy to generate allylstannane. Thus, 1,4-silastannylation of 1,3-diene with Si−Sn reagent in the presence of $Pt(CO)_2(PPh_3)_2$ catalyst results in the formation of *trans*-product with

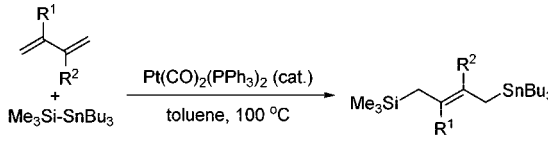
Scheme 71



Scheme 72

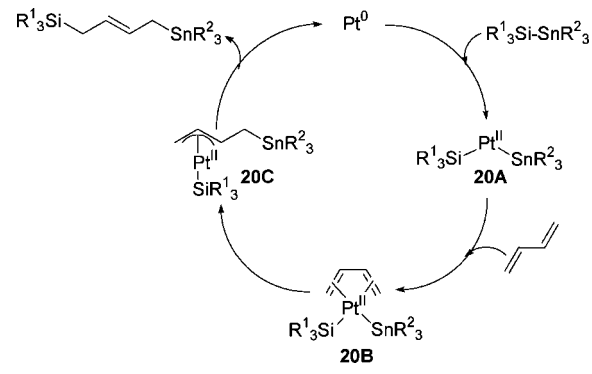


Scheme 73

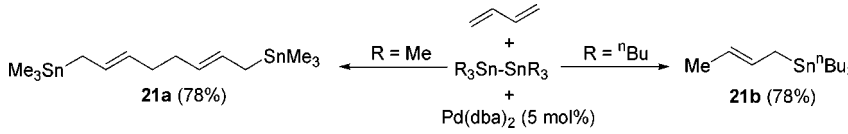


R^1	R^2	Yield (%)
H	H	84
H	Me	84
H	Ph	85

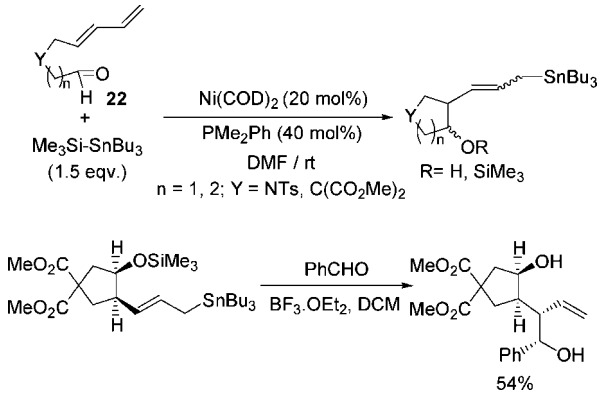
Scheme 74



Scheme 75



Scheme 76

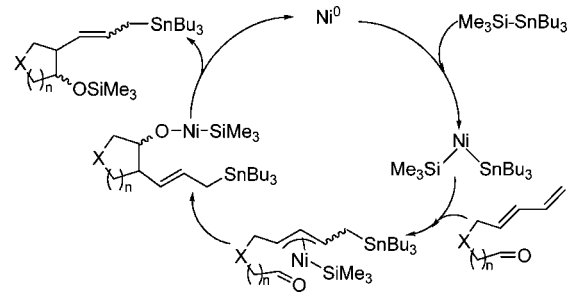


exclusive regioselectivity (Scheme 73).[57] Catalysts such as $Pd(PPh_3)_4$, $Pd(CO)(PPh_3)_3$, $Pt(PPh_3)_4$, $Pt(C_2H_4)(PPh_3)_2$, $PtCl_2(PPh_3)_2$, and $Pd(dba)_2$ are less effective as compared to $Pt(CO)_2(PPh_3)_2$. The ex situ generated allylstannane has been used in a subsequent Stille coupling reaction with aromatic halides and triflates.[57]

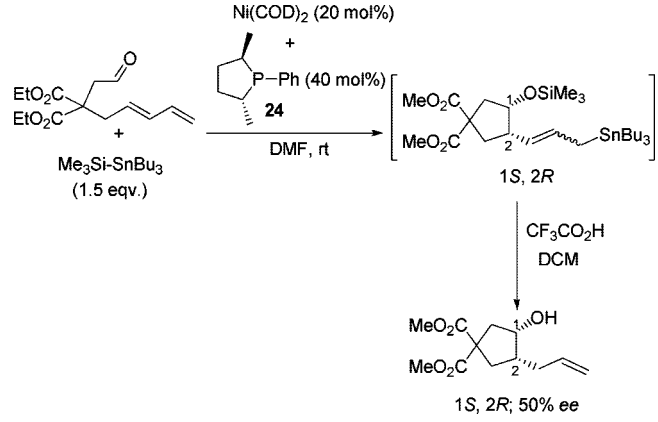
The proposed mechanism for the generation of allylstannane involves initial activation of $R^1{}_3Si-SnR^2{}_3$ across platinum(0) to give the bimetallic intermediate **20A**. Coordination of the diene to the latter gives intermediate **20B**. Migration of $SnR^2{}_3$ to the terminal carbon atom of diene in **20B** leads to the formation of a bimetallic π-allyl-$Pt^{II}-Si$ intermediate **20C**, from which reductive elimination provides the desired allyl stannane with the regeneration of the catalyst (Scheme 74).

Allylstannanes have also been obtained via palladium(0) catalyzed distannation of 1,3-dienes. An interesting example in this category is the reaction of $Me_3Sn-SnMe_3$ with 2 equiv of 1,3-butadiene in the presence of catalytic $Pd(dba)_2$, leading to the corresponding allylstannanes **21a** via a dimerization−doublestannation reaction (Scheme 75).[58] It may be noted that similar reaction but with hexaalkyldistannanes having ^{n}Bu- as the bulky alkyl substituents does not lead to dimerization−double stannation; instead formal hydrostannation occurs, giving rise to allylstannanes **21b**. 1,3-Diene is the possible hydrogen source for hydrostannation.

Scheme 78



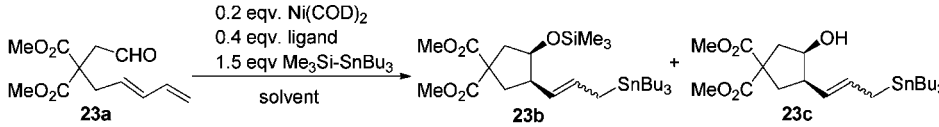
Scheme 79



Silastannylation of 1,3-diene of the type **22** is also possible in the presence of catalytic Ni(0)/PMe_2Ph, leading to the corresponding allylstannane (Scheme 76).[59] The latter is amenable to further carbonyl allylation with an aldehyde in the presence of Lewis acid catalyst.[59]

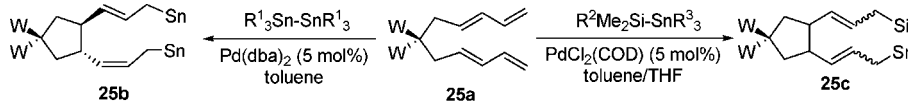
Control studies with **23a** indicate the profound role of solvent and ligand toward cyclization (Scheme 77).[59] For example, in toluene as the solvent, the bismetallative silastannyl cyclization is completely inhibited in the absence of any phosphine ligand or even in the presence of PPh_3,

Scheme 77



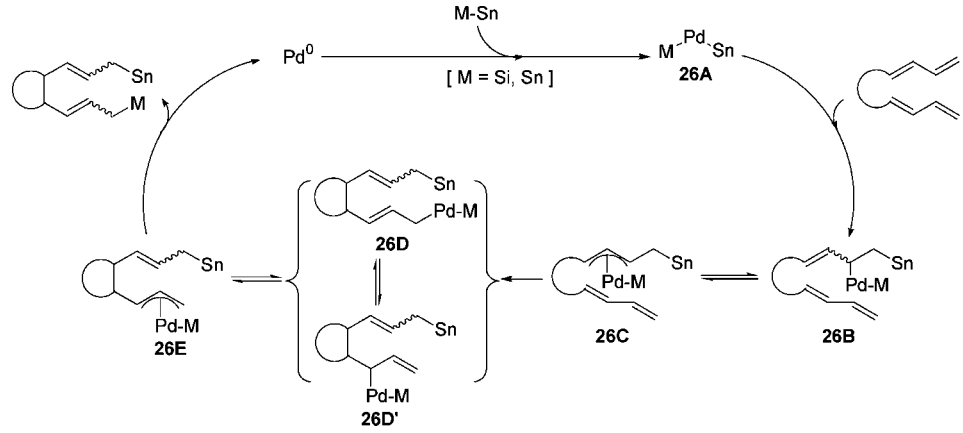
Ligand	Solvent	Temp (°C)	Time (h)	Yield (%)	**23b**/**23c**	*E*/*Z* ratio **23b**	**23c**
PCy3	toluene	50	13	0	-	-	-
PMe_2Ph	toluene	rt	24	23	**23c** only	-	100:0
Nil	DMF	rt	2	55	**23b** only	100:0	-
PMe_2Ph	DMF	rt	2	66	1.5/1	3.6/1	3.4/1
PMe_2Ph	MeCN	rt	4	46	2.5/1	3.8/1	2.5/1
PMe_2Ph	THF	rt	18	43	1/21	*not determined*	7.61

Scheme 80

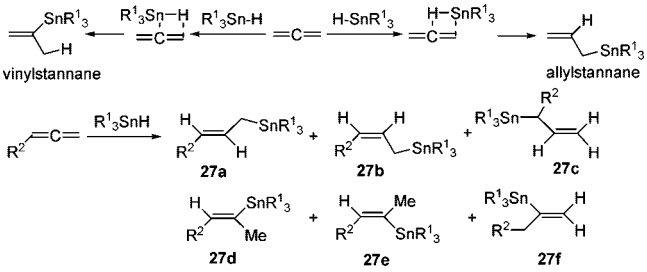


(W= -CO_2Et, -CO_2^{i}Pr, -$SO_2C_6H_4$Me-*p*), (R^1= Me, ^{n}Bu), (R^2= Ph, R^3= Me), (R^2= ^{t}Bu, R^3= Me), (R^2= Me, R^3= Ph), (R^2= Me, R^3= ^{n}Bu)

Scheme 81



Scheme 82

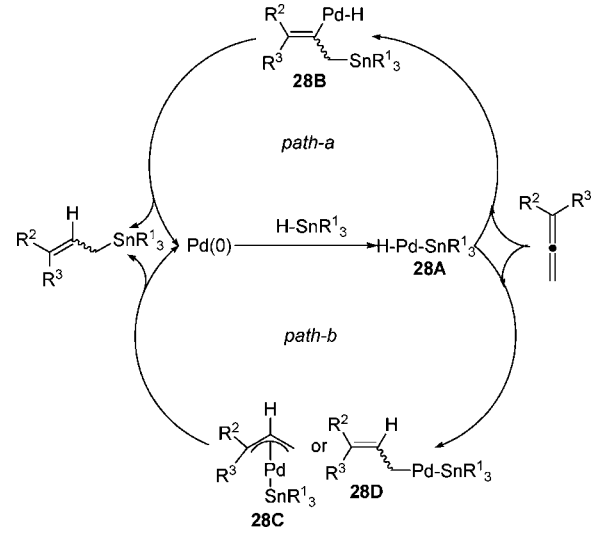


$P(OEt)_3$, and PCy_3. However, under similar conditions, PMe_2Ph shows some reactivity. In contrast, polar solvents such as DMF promote cyclization even without the addition of phosphine ligand. A combination of $Ni(COD)_2$/PMe_2Ph in DMF is judged as the best.

The mechanism involves initial activation of $Me_3Si-SnBu_3$ across Ni(0) to afford the "Si−Ni^{II}−Sn" intermediate, with subsequent activation of diene to afford the π-allyl-Ni^{II} intermediate. Concomittant cyclization and reductive elimination affords the end-organic product (Scheme 78).

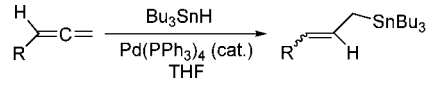
When the silastannylative cyclization is carried out in the presence of a chiral monodentate phosphine ligand **24**, the cyclized product is obtained with modest enantiomeric excess (Scheme 79).

Scheme 84



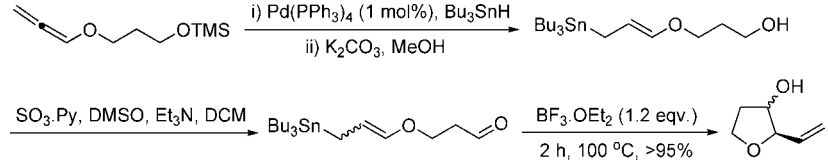
Distannation or silastannylation of bisdiene also constitutes a good pathway for the synthesis of allylstannane (Scheme 80).[60] Thus, the reaction of bisdiene **25a** (W = CO_2R) with hexaalkylditin in the presence of catalytic palladium(0) leads to the formation of product **25b** as exclusive *trans*-(*E*)(*Z*) isomer. When W = -SO_2Tol, the major product is *trans*-(*E*)(*E*), and the minor products are *trans*-(*E*)(*Z*) and *cis*-

Scheme 83

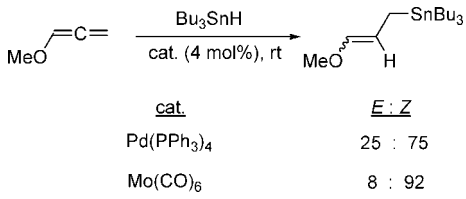


R	Yield (%)	*E*:*Z*
C_8H_{17}	78	33:67
$PhCH_2$	66	38:62
MeO	69	19:81
Ph	60	95:5
4-$MeOC_6H_4$	75	95:5

Scheme 85



Scheme 86



(*E*)(*E*). In contrast to distannanation, analogous silastannylation shows the formation of **25c** as a complicated mixture containing various stereoisomers (vide ^{1}H and ^{13}C NMR).

The catalytic cycle in the above distannation/silastannylation of bisdienes is similar to those discussed earlier for allenes and 1,3-dienes (chiefly Schemes 63, 69, 74, and 78). Expectedly, the cycle begins with prior oxidative addition of an M−Sn bond (M = Si, Sn) across Pd(0) to afford the bimetallic Pd−Sn intermediate **26A** (Scheme 81). The ususal sequence of events involving intermediates **26B** to **26E** leads to the end-organic product, regenerating the catalyst.

2.3.4. Allyltin via Hydrostannation of Allene and a Diene

Synthesis of allylstannane from allene is also possible via hydrostannation using organotin(IV) hydrides. In principle, reaction of allene with trialkyltin hydride (R^1_3SnH) can give rise to six different products (**27a**−**27f**) depending on the mode of addition of an H−Sn bond across the double bond of allene (Scheme 82).[61]

However, by proper choice of substrate and catalyst, it is possible to regulate both regio- and stereoselectivity. A case in point is the $Pd(PPh_3)_4$ catalyzed reaction of allene with Bu_3SnH (Scheme 83).[61,62] For aliphatic, benzylic, and alkoxy allenes, the reactions afford corresponding allylstannanes with good regioselectivity but varying stereoselectivity (*E:Z* ratio). Interestingly, allenes having aromatic substituents show excellent stereoselectivity toward (*E*)-allylstannane.[62]

The proposed catalytic cycle (Scheme 84) involves an oxidative addition of R^1_3Sn-H across Pd(0) to generate $R^1_3Sn-Pd^{II}-H$ intermediate **28A**. Pallada-stannylation of allene can give a vinylpalladium species **28B** (path-a). Alternately, the interaction of **28A** with allene followed by hydropalladation would lead to π-allyl-$Pd^{II}-SnR^1_3$ intermediate **28C** or **28D** (path-b). Either of the two intermediates is capable of undergoing reductive elimination to furnish allylstannane. It is noteworthy that bimetallic Pd−Sn complexes such as *cis*-$(R_2PC_2H_4PR_2)PdH(SnR'_3)$ [R = ^{i}Pr, ^{t}Bu; R′ = Me, ^{n}Bu] and *trans*-$(PPh_3)_2PtH(SnMe_3)$ are well-known.[63,64]

Palladium(0) assisted hydrostannation of allenic ethers gives rise to the corresponding allylstannanes. Yamamoto and co-workers have utilized this approach for the synthesis of β-hydroxy cyclic ethers (Scheme 85).[65a,b] Construction of such units is considered to be key steps toward the synthesis of polyether natural products.[65c]

Even though the dominance of palladium(0) is observed in the hydrostannation of allenes, other catalysts have been tried out as well. Catalysis via molybdenum(0) is noteworthy due to interesting stereoselectivity aspects. This is exemplified in the hydrostannation of methoxyallene with Bu_3SnH, which leads to the corresponding allylstannane as a mixture of *E*- and *Z*-isomers. As shown in Scheme 86, catalytic $Mo(CO)_6$ favors the *Z*-isomer, whereas $Pd(PPh_3)_4$ favors the *E*-isomer.[66]

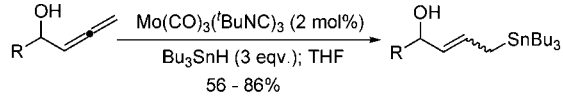
Allenyl carbinols also undergo *Z*-selective hydrostannation in the presence of catalytic $Mo(CO)_3(^{t}BuNC)_3$, giving rise to corresponding allyl stannanes (Scheme 87).[67]

The formation of allylstannanes can be explained by the catalytic cycle shown in Scheme 88. The cycle begins by ligand dissociation to generate active Mo(0) **29A**, which upon oxidative addition of Sn−H gives intermediate **29B**. The interaction of the latter with allene followed by hydrometalation would afford the bimetallic allyl-$Mo^{II}-SnBu_3$ intermediate **29D**. Subsequent reductive elimination provides the desired allyl stannane, regenerating the active catalyst.

Generation of allylstannane by hydrostannation of δ- and ω-allenyl aryl halide and subsequent cyclization at the proximal carbon provides a good methodology for the synthesis of small and large ring compounds (Scheme 89).[68]

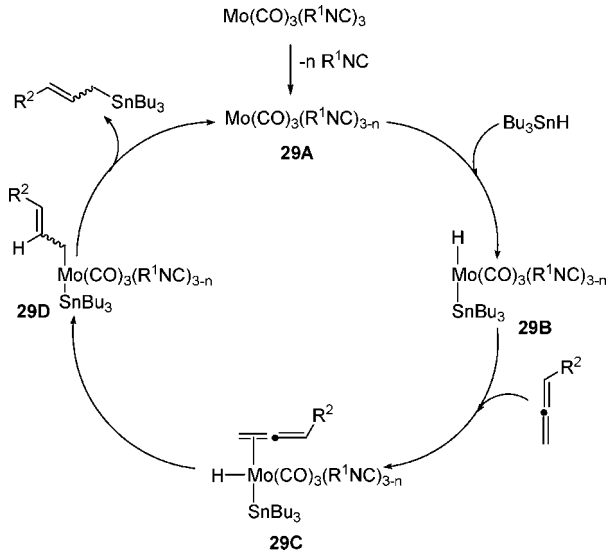
Palladium catalyzed domino coupling has been achieved using allenyl substrates such as **30a**, leading to spiro derivatives **30b** via intermediate allylstannane **30A** (Scheme 90).[68] The reaction involves a number of interesting sequential steps such as hydrostannation, cyclization, and anion capture.

Scheme 87

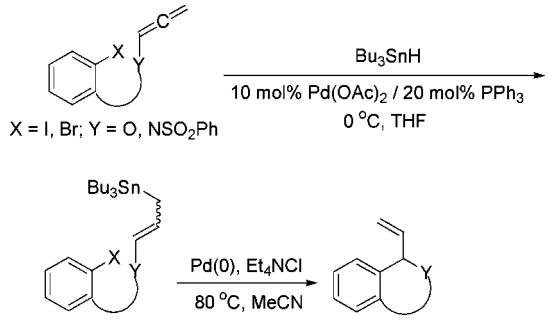


R	Time (h)	Temp (^{o}C)	Ratio *E* : *Z*
$PhCH_2$	18	rt	1 : 2
Me_2CHCH_2	18	rt	3 : 5
2-$NO_2C_6H_4$	4	55	1 : 1
4-ClC_6H_4	4	55	1 : 1
2,6-$Cl_2C_6H_3$	4	55	1 : 2

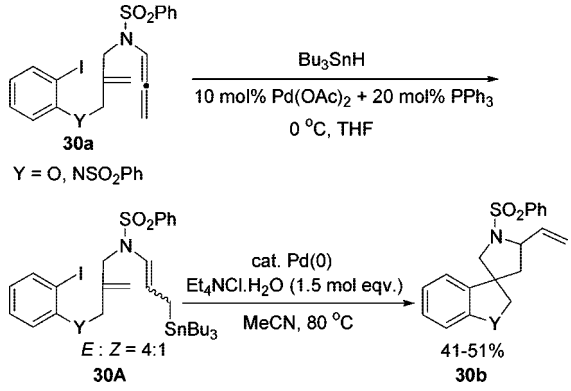
Scheme 88



Scheme 89

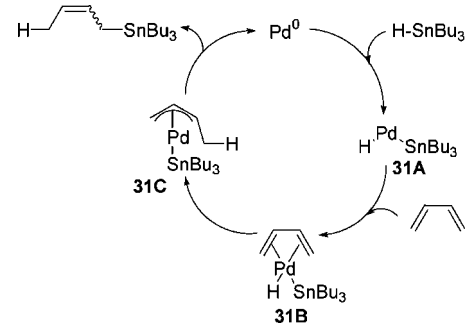


Scheme 90

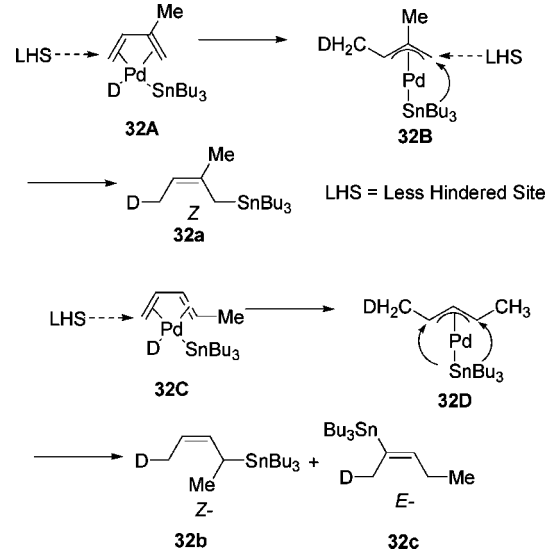


Palladium(0) catalyzed hydrostannation of dienes affords the corresponding allylstannanes with interesting stereocontrol, depending upon the substituents at the 1- and 2-positions of the diene (Scheme 91).[69] One may note that even minor stereoelectronic perturbation in the diene can majorly influence the stereochemistry of the end-product (entry 2 vs 3).

Scheme 92



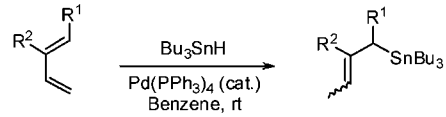
Scheme 93



The mechanistic steps of the hydrostannation of diene presented in Scheme 94 are similar to those discussed earlier (chiefly Scheme 84). Thus, oxidative addition of Bu_3Sn-H across Pd^0 gives $Bu_3Sn-Pd^{II}-H$ intermediate **31A** (Scheme 92). The interaction of the latter with diene followed by hydrostannantion would afford the bimetallic π-allyl-$Pd^{II}-SnR_3$ intermediate **31C**. The cycle completes with subsequent reductive elimination, providing the desired allylstannane.

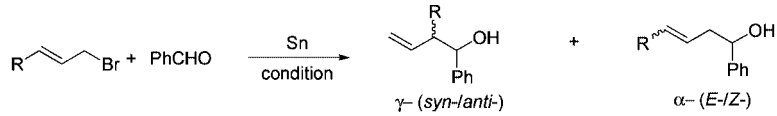
Mechanistic studies with Bu_3Sn-D and isoprene/1-methylbutadiene indicate the following (Scheme 93): (i) the hydride always migrates to the least hindered site of the (diene)$-Pd^{II}-Sn^{IV}$ intermediate (as in **32A** and **32C**), (ii) the stereoselectivity of the allylstannane product depends on

Scheme 91



entry	R^1	R^2	Yield (%)	*E*:*Z* ratio
1	H	H	91	0:100
2	H	Me	61	0:100
3	H	AcO	72	100:0
4	Me	H	45	36:64

Scheme 94



#	R	Nature of Sn(0)	Condition	Yield (%)	γ(*syn*/*anti*): α(*E*/*Z*)	Ref
1	H	commercial[a]	THF, rt, 12 h	82	-	73
2	H	150 mesh	H_2O, 60-80 °C to rt, 12 h	95	-	74
3	H	150 mesh	H_2O, HBr, rt	95	-	74
4	H	commercial-powder	»», neat, 12 h	98	-	75
5	H	commercial-powder	bmim,[b] rt, overnight	100	-	76
6	H	150 mesh	H_2O, HBr or heat	95	-	74
7	CO_2Et	powder	H_2O, rt	71	100(68/32):0	77
8	CO_2Et	powder	CTAB,[c] H_2O, rt	81	100(95/5):0	77
9	CO_2Et	powder	$n$$Bu_4NBr$, H_2O, rt	73	100(70/30):0	77
10	CO_2Et	powder	PEG,[d] H_2O, rt	71	100(91/9):0	77
11	CO_2Et	powder	Silica gel, H_2O, rt	74	100(64/36):0	77
12	CO_2Et	20 nm	H_2O, rt, 12 h	61	100(94:6):0	70
13	Me	commercial[a]	THF, rt, 12 h	76	100(59/41):0	73
14	Me	powder	DCM-H_2O, rt, 48 h	83	45(50/50): 55(75/25)	72
15	Me	325 mesh (99.8%)	H_2O, aq. HCl,[e] rt, 5 min	90	100(70/30):0	78
16	Me	commercial-powder	bmim,[b] rt, overnight	75	100(43/57):0	76
17	Me	commercial-powder	emim,[f] rt, overnight	75	100(42/58):0	76
18	Me	20 nm	H_2O, rt, 24 h	85	61(67/33): 39(26/74)	70
19	Me	powder	H_2O, $NaBF_4$, rt, 10 h	73	0:100(62/38)	71
20	Me	200 mesh Sn-powder Al	Cat HBr, Et_2O-H_2O (2:1), 9 h	87	(60/40):0	79
21	Ph	powder	H_2O, rt, 3 day	80	1:99(100/0)	72

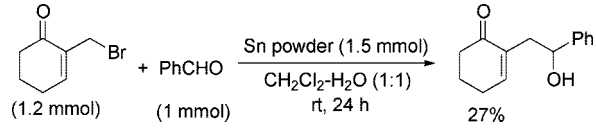
[a]Washed with 10% NaOH, water and methanol; different condition; [b]1-Butyl-3-methylimidazolium tetrafluoroborate; [c]Cetyltrimethylammonium bromide; [d]polyethylene glycol; [e]1.0 mol L^{-1} HCl (2.0 mL); [f]1-Ethyl-3-methylimidazolium tetrafluoroborate

the mode of reductive elimination from the π-allyl-Pd^{II}−Sn^{IV} intermediate (as in **32B** and **32D**)—the Bu_3Sn-group always prefers the less hindered site of the allyl appendage. Thus, in the case of isoprene, the *Z*-allylstannane **32a** is obtained exclusively. On the contrary, in the case of 1-methylbutadiene, due to comparable steric perturbation for the migration of the Bu_3Sn-group at the arrowed sites, a mixture of *E*- and *Z*-allylstannanes **32b** and **32c** is obtained.

2.4. Allyltin via Direct Activation of an Organic Precursor at the Tin Metal Center

Allylstannane can be generated in situ by direct activation of allyl halides and surrogates at a tin metal center with or without the help of a nontransition metal additive. In order to closely look into these strategies, this section has been further divided into subcategories depending on the tin(0)/tin(II)/tin(IV) source.

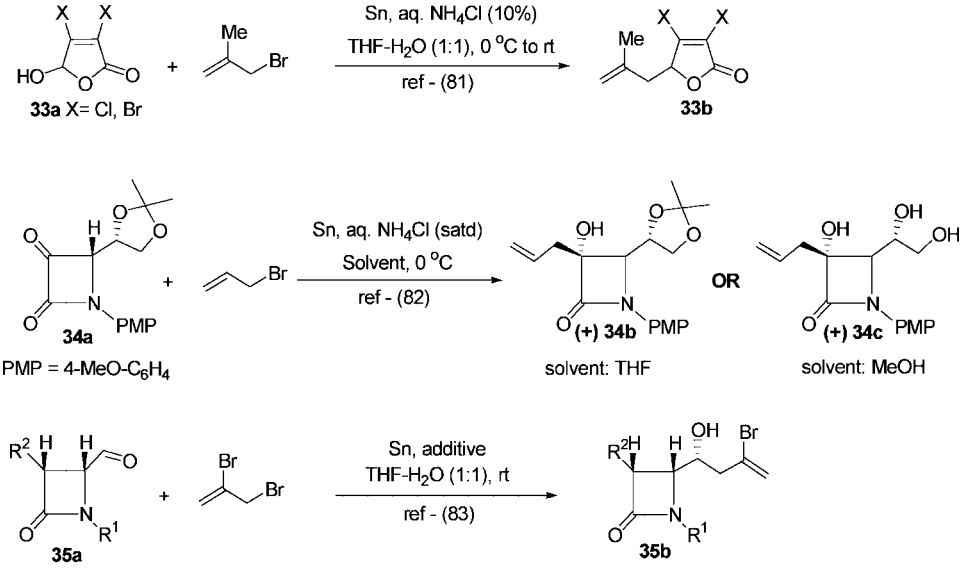
Scheme 95



2.4.1. Allyltin via Direct Activation of Allyl Electrophiles at the Tin(0) Center

Oxidative addition of allyl electrophiles across elemental tin easily affords reactive allyltin(II/IV) reagents which are amenable to reaction with carbonyls, imines, lactones, lactams, and other electrophiles in one-pot. Due to the ease of operation, the utility of the end-organic product(s), and interesting mechanistic features, these Barbier-type reactions have been studied under various conditions.[70−85] We have presented below the product profile and reaction conditions. Thereafter, the present understanding on the mechanistic features of these reactions is highlighted.

Scheme 96



R^1 = *p*-MeO-C_6H_4, H_2C=CH-CH_2, H_2C=CH-CH_2-CH_2, HC≡C−CH_2, HC≡C−CH_2-CH_2

R^2 = OMe, OPh, OCH_2CH=CH_2, OCH=CHCOOMe, H_2C=CH, H_2C=C-CH_3, HC≡C−CH_2O, H_2C=CH-CH_2, HC≡C−CH_2

additive = NH_4Cl, $InCl_3$, $In(OTf)_3$, $HfCl_4$, $BiCl_3$, HCl, HBr

(a) Tin(0) promoted carbonyl allylation is applicable to both aldehydes and ketones. Reaction conditions markedly affect the yields and isomer ratio in the resulting homoallylic alcohols. In order to highlight the variance, we have showcased a few selected examples of the reaction of benzaldehyde with 3-substituted allyl bromides in Scheme 94, from which one may note that (i) in the majority of the cases the reactions are highly γ-regioselective, although diastereoselectivity (*syn*/*anti*) varies from case to case and (ii) under three-distinct reaction conditions, namely nano-Sn/H_2O,[70] Sn/H_2O/$NaBF_4$,[71] and Sn-powder/H_2O[72] under ambient conditions, considerable α-regioselectivity has been obtained.

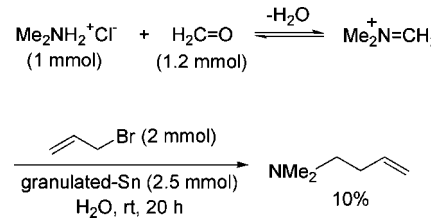
(b) Reaction of metallic tin with allylstannane derived from halides such as 2-bromomethylcyclohexenone also undergoes α-regioselective carbonyl allylation with a range of aldehydes (Scheme 95).[80]

(c) Tin-mediated Barbier-allylation proved to be quite useful in the case of cyclic derivates containing a carbonyl functionality. Few of the notable examples include mucohalic acids (3,4-dihalo-5-hydroxy-5*H*-furan-2-one) **33a**,[81] azetidine-2,3-diones **34a**,[82] and 4-oxoazetidine-2-carbaldehydes **35a**.[83] In all cases, allylation proceeds smoothly under the reaction conditions shown in Scheme 96.

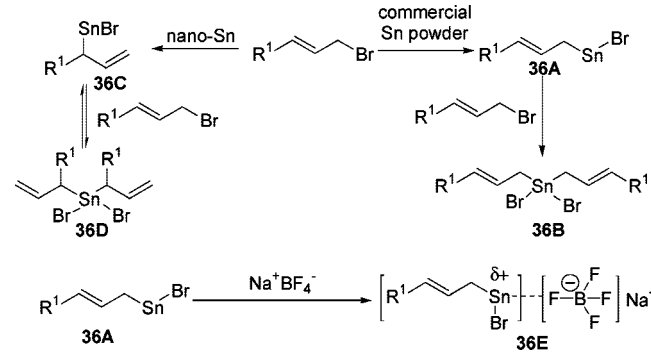
(d) One-pot Barbier allylation of iminium ions, generated from secondary amines and formaldehyde, proceeds in the presence of allyl bromide and metallic tin in water at acidic pH (Scheme 97).[84] Further studies indicate that the reaction is better suited with Zn metal in comparison to metallic tin.

The mechanism of activation of allyl halide across elemental tin has been of interest to organometallic chemists for the past three decades. Major inquisitions are centered on the role of polar solvents (in particular water) and additives to (i) generate reactive allyltins and (ii) to control the regio- and stereoselectivity in the end-organic product. The mechanistic tools utilized include in situ NMR studies and theoretical studies. It has been observed that, irrespective of the size of the elemental tin particle, the stepwise

Scheme 97



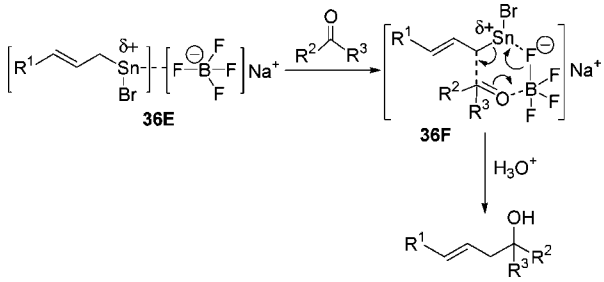
Scheme 98



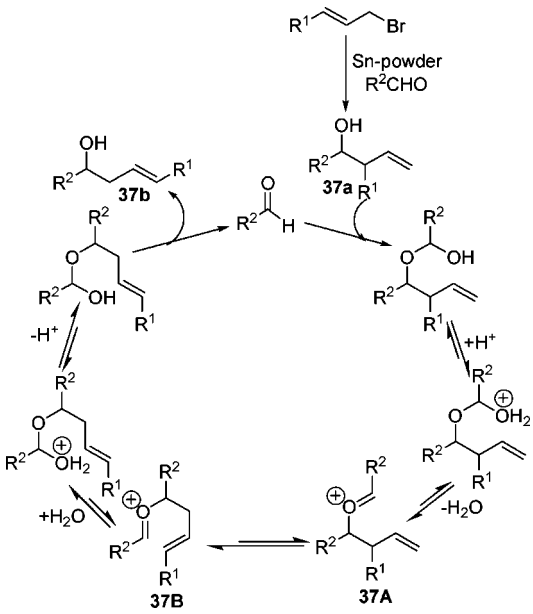
oxidative-addition of allyl halide across Sn(0) leads to the formation of monoallyltin(II) and diallyltin(IV) species **36A**−**D** (Scheme 98). Note that the regioselectivity in the allylstannanes alters with the size of the tin particle. On the other hand, when $NaBF_4$ is used as an additive, yet another monoallyltin(II) species, **36E**, is formed, in which BF_4^- coordinates to the tin(II) center via a strong Sn···F interaction.

Formation of γ-homoallylic alcohol would require the assistance of (i) an S_E2' pathway involving intermediate **36A** and **36B** and (ii) an S_E2 pathway involving intermediate **36C** and **36D**. The reverse would be the case for the formation of an α-homoallylic alcohol. The stereoselectivity in γ-ho-

Scheme 99



Scheme 100



moallylic alcohols may be explained via transition states similar to those discussed earlier (chiefly Scheme 23).

The observed α-regioselective carbonyl allylation in water in the case of tin metal/$NaBF_4$ reagent has been invoking the intermediacy of **36E** (Scheme 99).[71] Quantum calculation indicates that Sn···F interaction in **36E** enhances the electron density (hence nucleophilicity) at the α-carbon in comparison to the γ-carbon atom of allylstannane. Coordination to aldehyde results in the formation of transition state **36F**, from which the α-homoallylic alcohol is obtained after hydrolysis.

Loh and co-workers have carried out extensive in situ ^1H NMR studies, crossover experiments, and stereochemical studies to explain the mechanism of α-regioselection in carbonyl allylation using tin-powder/allyl bromide/aldehyde in aqueous−organic medium or in fully aqueous medium.[72] These studies clearly point out that the initially formed γ-homoallylic alcohol **37a** undergoes a retroene reaction in the presence of aldehyde, giving rise to intermediate **37A** (Scheme 100). 2-Oxonia[3,3]sigmatropic rearrangement of **37A** affords the intermediate **37B**. The α-isomer **37b** is obtained from intermediate **37B** via usual hydration and deprotonation steps.

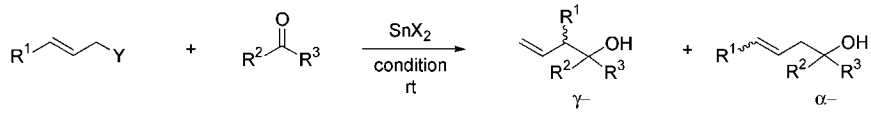
Metallic tin has been used recently for enantioselective allylation of aldehyde using easily accessible carbohydrate saccharose as chiral promoter. For example, in the case of furnishing homoallylic alcohol from benzaldehyde and allyl bromide using 1.2 equiv of saccharose, 71% *ee* is observed at room temperature. But, when the temperature is reduced to 0 °C, keeping all the parameters the same, 81% *ee* is observed.[85]

2.4.2. Allyltin via Direct Activation of Allyl Electrophiles at the Tin(II) Center

In specific cases, allyl halides and alcohols can be activated directly by certain tin(II) salts with or without the help of additives. This is in contrast to the more general allylic activation using "Sn(II)/catalytic Tm" discussed earlier (sections 2.1.3 and 2.2). In this section, we will discuss the modes of generation of allylstannanes either in the absence of an additive or in the presence of a nontransition metal additive.

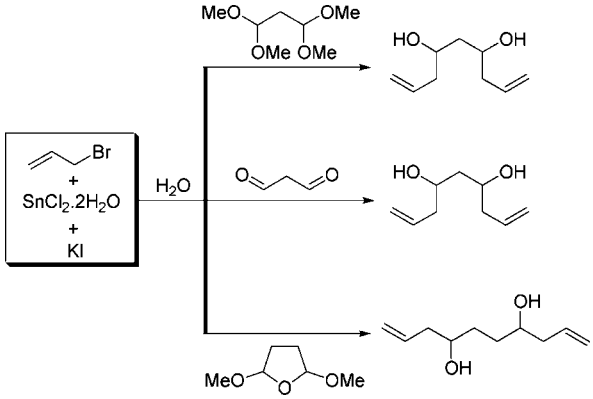
An early demonstration by Mukaiyama et al. shows that the reaction of allyl iodide and tin(II) fluoride in organic solvent generates reactive allylhalostannane in the absence

Scheme 101

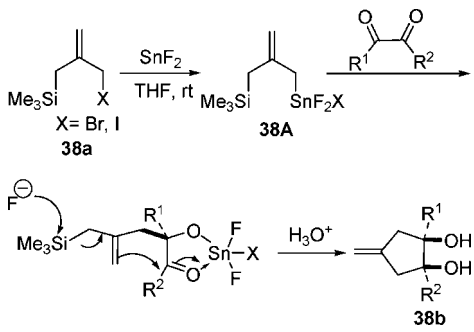


#	R^1	Y	carbonyl	SnX_2, condition	Yield (%)	γ(*syn*:*anti*) :α(*E*:*Z*)	*Ref*
1	H	I	PhCHO	SnF_2, DMI, 1 h	88	-	86
2	^{n}Pr	OH	^{n}PrCHO	SnI_2, Me_3SiCl, NaI, MeCN-H_2O	64	3: 97(32/68)	87
3	H	Br	PhCHO	aq. $SnCl_2$ (2-5M)	98	-	27
4	H	Br	PhCHO	aq. $SnCl_2$ (2M), >>>, 2 h	90	-	88
5	Me	Br	PhCHO	$SnCl_2.2H_2O$, [bmim]BF_4, H_2O, 24 h	96	90(22/78): 10	89
6	H	Br	PhCOMe	$SnCl_2.2H_2O$, [bmim]BF_4, H_2O, 24 h	73	-	89
7	Me	Cl	PhCHO	$SnCl_2.2H_2O$, KI, H_2O	79	65(62/38): 35(43:57)	90
8	Ph	Cl	PhCHO	$SnCl_2.2H_2O$, KI, H_2O	80	57(1/99): 43	90
9	H	Br	$PhCH(OMe)_2$	$SnCl_2.2H_2O$, KI, H_2O	89	-	90

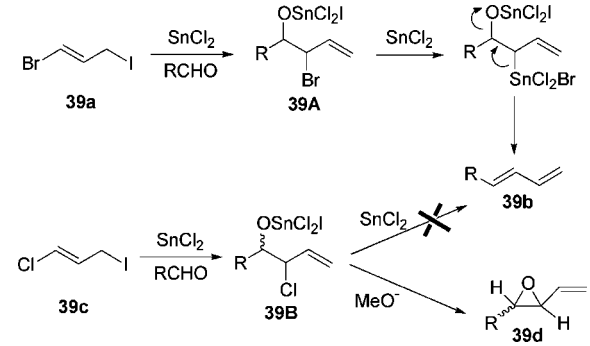
Scheme 102



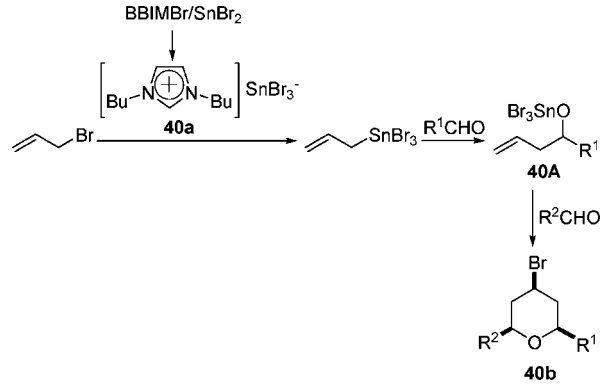
Scheme 103



Scheme 104



Scheme 105



of any additive (Scheme 101, entry 1).[86] The latter mediates facile allylation of aldehyde. Allyl iodide can also be generated in situ from allyl alcohol using TMSCl/NaI; the corresponding carbonyl allylation leads to α-homoallylic alcohol (entry 2).[87] As mentioned earlier (vide Figure 2), aqueous tin(II) chloride (2−5 M) mediates facile carbonyl allylation of aldehyde using allyl bromide (entry 3).[27] Ultrasonication also facilitates the reaction (entry 4).[88] Both [bmim][BF_4] and KI have been proved to be efficient additives in aqueous carbonyl allylation using $SnCl_2$ and allyl halide (entry 5−9).[89,90] Pereyre and co-workers showed that LiBr is equally effective.[91]

The reagent combination of $SnCl_2$/KI mediates facile allylation of dialdehydes or their acetals in water to afford the corresponding diols (Scheme 102).[90]

In situ generated allyldifluorohalostannane **38a**, having a trimethylsilyl-pendant, reacts with 1,2-diketone, triggering a highly stereoselective double-allylation and concomitant annulation to provide the corresponding 1,2-diol **38b** (Scheme 103).[92]

The reactivity of the homoallyloxytin(IV) intermediate, generated from an allyl halide/tin(II)/aldehyde, has also been tested in reactions other than the usual carbonyl allylation. For example, intermediate **39A**, generated from 1-bromo-3-iodoprop-l-ene, undergoes further stannylation followed by Peterson-like elimination, providing the corresponding diene **39b** (Scheme 104).[93a] However, such a reaction fails in the case of 1-chloro-3-iodoprop-l-ene, probably due to the inability of **39B** to undergo a second stannylation reaction. Interestingly, **39B** is proved to be a good candidate for the synthesis of vinyloxiranes (Scheme 104).[93b]

Homoallyloxytin(IV) intermediate **40A** (generated from allyl bromide, room temperature ionic liquid **40a**, and an aldehyde) undergoes a Prins-like cyclization with a second aldehyde to afford the corresponding tetrahydropyran derivative **40b** in a highly stereoselective fashion (Scheme 105).[94]

It has been observed that, irrespective of the nature of aldehyde, the substituents at the 2,4,6-positions in the tetrahydropyran ring in **40b** always maintain an *all-cis* relationship.

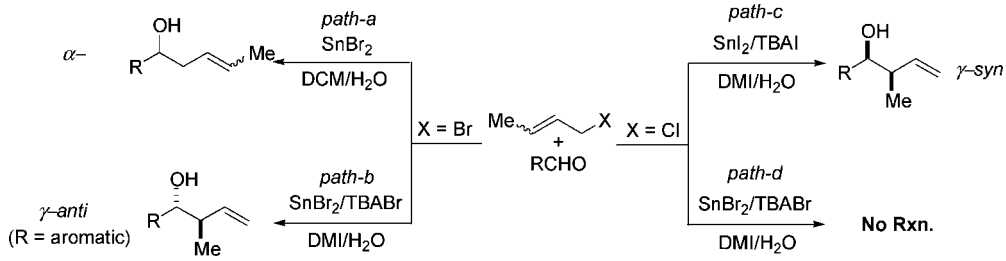
Masuyama and co-workers investigated the stereoselectivity aspects in great detail in the tin(II) halide promoted reaction of allyl halide and aldehyde in the presence of tetraalkylammonium halides as additive in biphasic medium.[95a−d] Reactions of substituted allyl halides in the presence or absence of these salts show interesting regio- and stereoselection (Scheme 106). For example, in the case of 1-bromobut-2-ene, α-regioselective allylation is observed by employing only $SnBr_2$ as the reagent in DCM−water (*path-a*). However, addition of tetrabutylammonium bromide (TBABr) to the above causes *γ-anti* selective allylation (*path-b*). Yet, in the case of 1-chlorobut-2-ene, a combination of tin(II) iodide and tetrabutylammonium iodide (TBAI) in 1,3-dimethylimidazolidin-2-one/water facilitates *γ-syn* selective allylation (*path-c*). In contrast, 1-chlorobut-2-ene remains unreactive toward aldehyde in the presence of $SnBr_2$/TBABr (*path-d*).

The authors suggested the formation of six-membered transition states **41A** and **41B** to explain the observed α- and *γ*-regioselectivity (Scheme 107). It may be noted that in TS **41A** the carbonyl oxygen coordinates to the Sn(II) center instead of the available Sn(IV) center, which is a bit surprising.

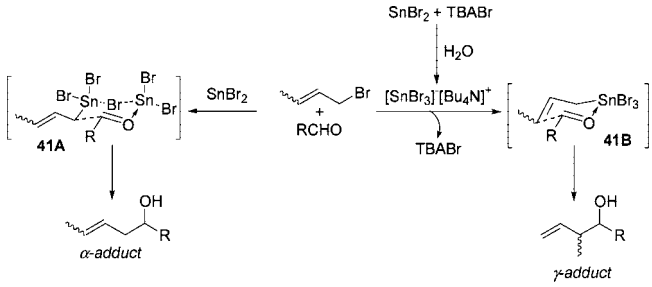
The *γ-syn*-selection in the cases of SnI_2 and SnI_2/TBAI can be easily rationalized, invoking acyclic antiperiplanar transition states **42C** and **42D**, respectively (Scheme 108). In these cases, the formation of six-membered cyclic transition states is disfavored due to the weak Lewis acidity of the Sn(IV) center in allylstannanes **42A** and **42B**, respectively.

Chiral Sn(IV)−diethyl tartrate mediated enantioselective carbonyl allylation is also noteworthy in this context (Scheme

Scheme 106



Scheme 107



109).[96] Chiral allylstannanes such as complex **43a** can be easily prepared by treatment of $SnCl_2$ with 2 equiv of disodium diethyl tartrate followed by addition of an allyl bromide. The reaction of **43a** with aldehydes affords optically active homoallylic alcohols in 50−80% yield with low enantiomeric excess (Scheme 109).

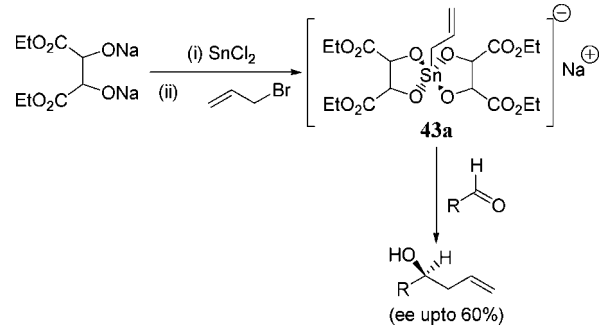
2.4.3. Allyltin via Direct Activation of Allyl Electrophiles at the Tin(IV) Center

Allylstannane can be generated directly from an allyl electrophile and tin(IV) halide in the presence of alkali metal or quaternary ammonium salts as additive. For example, reaction of allyl halide or mesylate with $SnCl_4/Bu_4NI$ in dichloromethane generates reactive allyltin(IV). The latter promotes facile allylation of aldehydes in one pot to afford the corresponding homoallylic alcohols (Scheme 110).[97]

A similar reaction has also been carried out using either (i) SnI_4/Bu_4NI in dichloromethane or (ii) SnI_4/NaI in 1,3-dimethylimidazolidin-2-one (DMI) (Scheme 111).[98]

The suggested mechanism involves prior reduction of Sn(IV) salt **44A** to the corresponding Sn(II) salt **44B**; the latter then participates in the formation of allyltin(IV) halide in an usual way (Scheme 112).

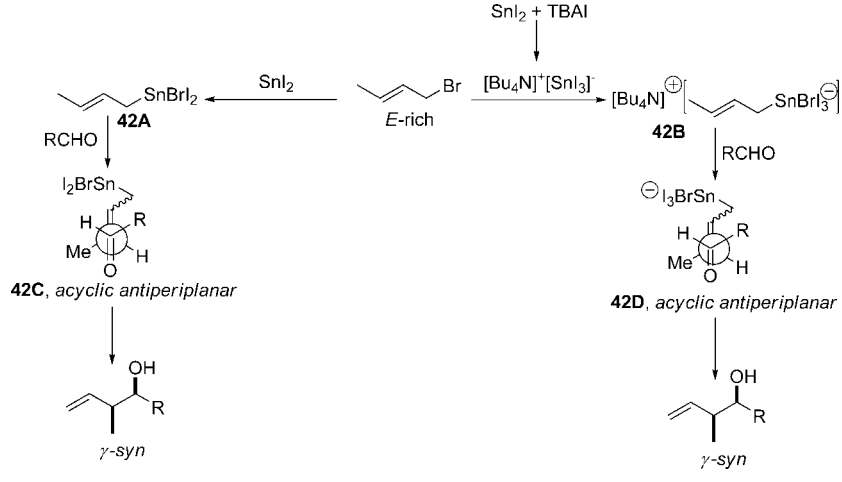
Scheme 109



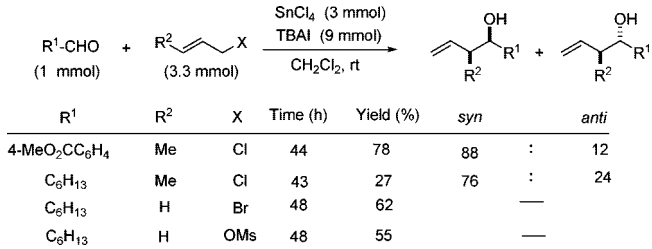
2.5. Allyltin via Direct Transmetallative Activation of Group-14 Allylmetals

Group-14 allylmetals **45a** (M = Si, Ge, Sn), having remote heteroatom functionality, undergo facile transmetalation with tin(IV) halide to generate reactive allylhalostannanes **45A** via an S_N2' pathway; the latter undergo nucleophilic addition reactions with carbonyls or imines in a S_E2' fashion, leading to the corresponding homoallylic alcohols or amines **45b** (Scheme 113). Note that the second stage of the reaction involves the formation of intermediate **45C** via the well-known six-membered transition state **45B**. The major utility of such a one-pot/two-stage strategy is to bring about a high degree of stereocontrol in the end-organic product. The stereocontrol arises due to chelation-assisted stabilization of **45A** and **45B**, the nature of the substituents, and the ring size. It is noteworthy that to date stabilization of 4-, 5-, 6-, and 7-membered rings in cyclic chelated allylstannane **45A** has been achieved. Interestingly, due to the trigonal bipyramidal geometry of tin(IV) in **45B**, the side-chain in the α-carbon "$(Q)_n$" prefers to orient toward the axial position. This is one important reason for the generally observed (*Z*)-

Scheme 108

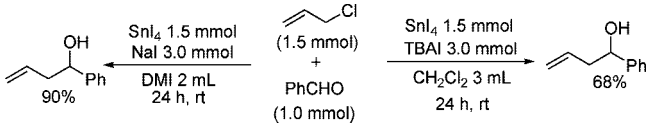


Scheme 110

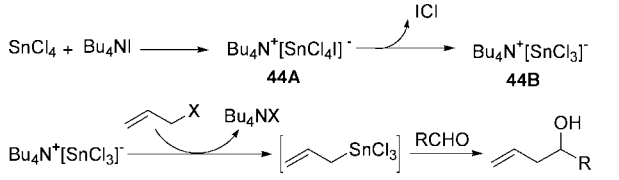


R^1	R^2	X	Time (h)	Yield (%)	*syn*		*anti*
4-$MeO_2CC_6H_4$	Me	Cl	44	78	88	:	12
C_6H_{13}	Me	Cl	43	27	76	:	24
C_6H_{13}	H	Br	48	62		—	
C_6H_{13}	H	OMs	48	55		—	

Scheme 111



Scheme 112

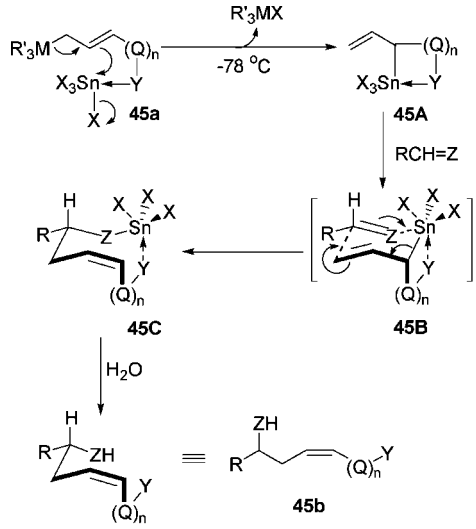


selectivity of the double bond in the end-product **45b**. Thomas and co-workers have richly exploited these strategies for the synthesis of many natural products and intermediates.[3b,d,99] We will briefly present below the stereochemical aspects of the reactions based on the initial group-14 allylic precursors (Si, Ge, Sn), taking selected examples, wherever possible.

2.5.1. Allyltin from Allylsilane via Transmetalation

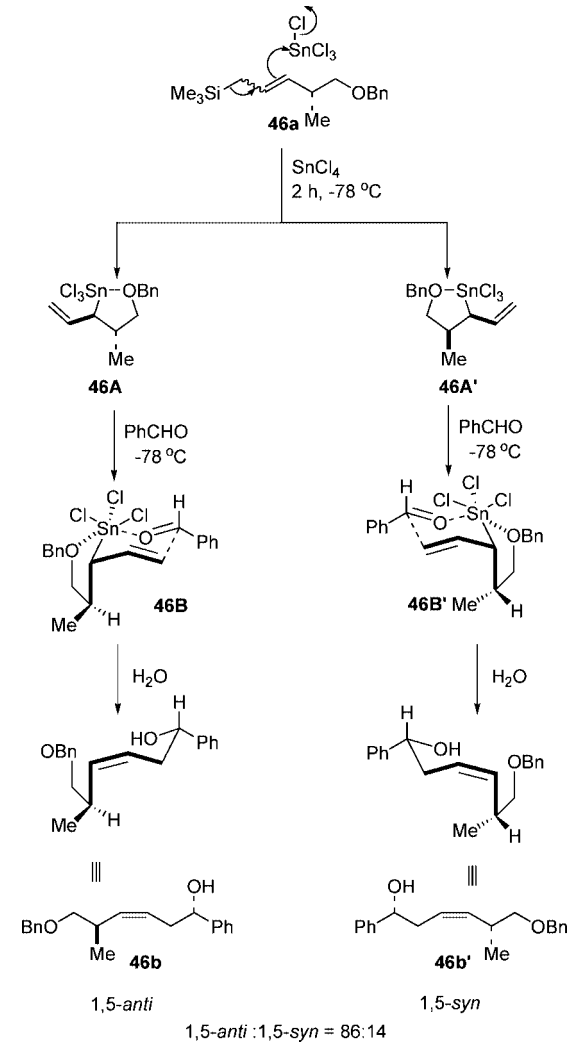
Via Five-Membered Cyclic Chelated Allylstannane Intermediate. Allyltrimethylsilane **46a** reacts with tin(IV) chloride at −78 °C, leading to 5-membered allylstannane intermediates **46A** and **46A′**. Follow up carbonyl allylation gives rise to the corresponding homoallylic alcohol as a mixture of diastereomers 1,5-*anti*-**46b** and 1,5-*syn*-**46b′** (Scheme 114).[100]

Scheme 113



M = Si, Ge, Sn; Q = homo or hetero atom chain
X = halogen; Y = coordinating hetero atom functionality
Z = O or NR''; R, R', R'' = Ar/alk; n = 1-3

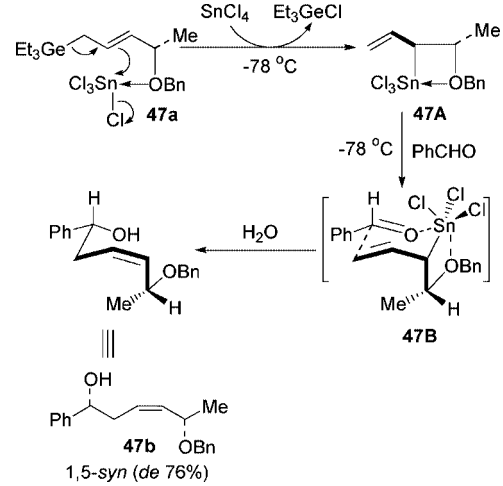
Scheme 114



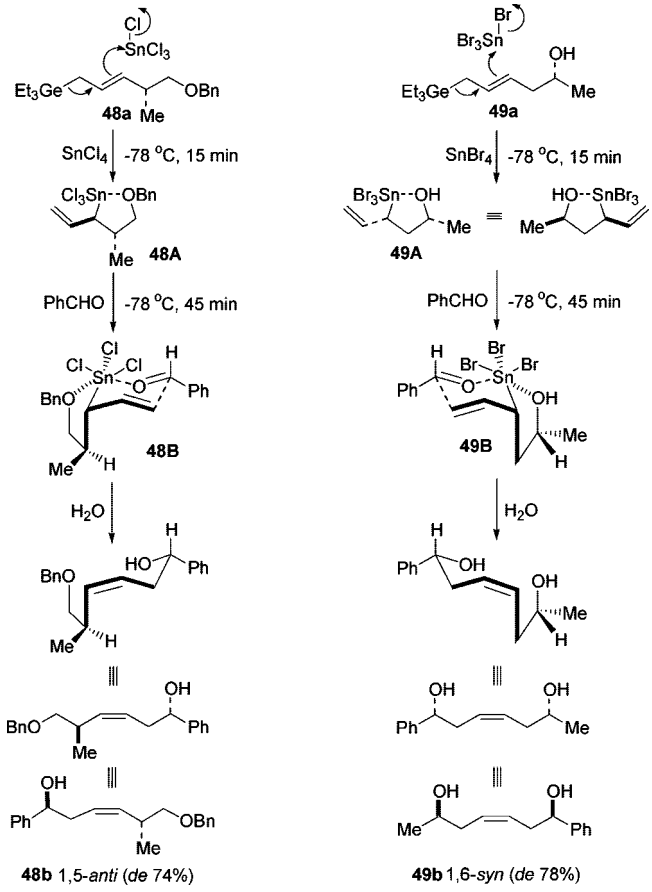
2.5.2. Allyltin from Allylgermane via Transmetalation

Via Four-Membered Cyclic Chelated Allylstannane Intermediate. Stabilization of 4-membered allyltrichlorostannane **47A** and **47A′** has been observed in the reaction of tin(IV) chloride with allyltriethylgermane **47a**, which further reacts with aldehydes, leading to alcohol **47b** with 1,5-*syn* selectivity (Scheme 115).[101]

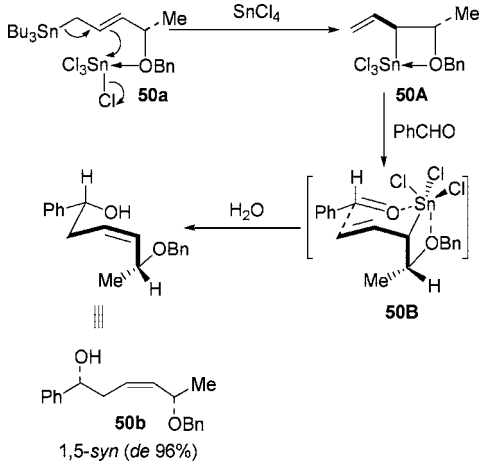
Scheme 115



Scheme 116

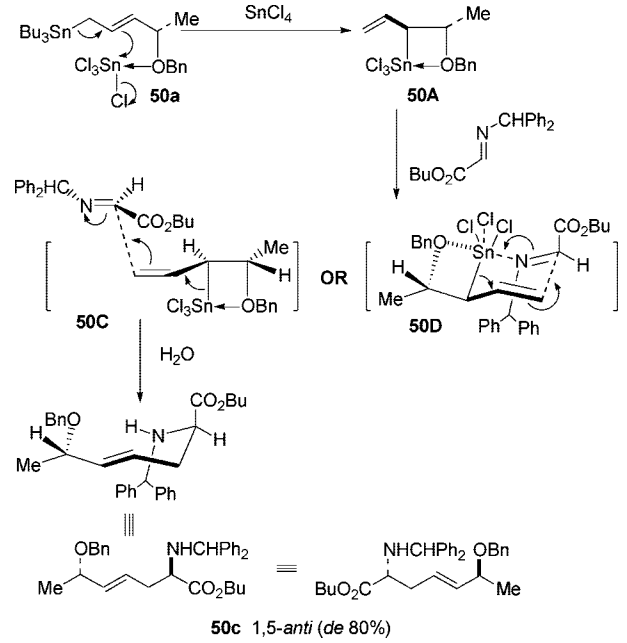


Scheme 117

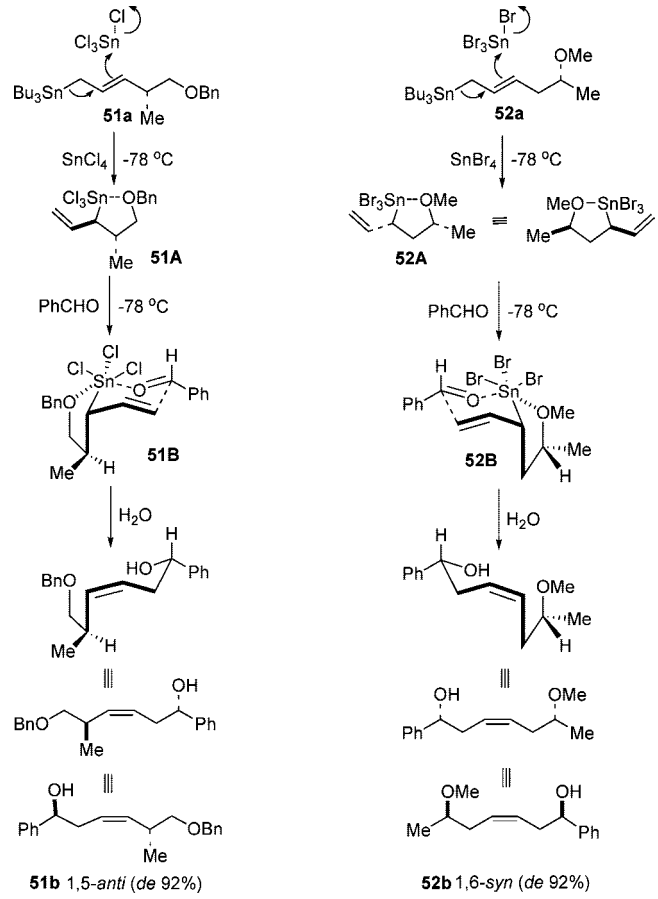


Via Five-Membered Cyclic Chelated Allylstannane Intermediate. When reacted with tin(IV) halide followed by a carbonyl, allyltrialkylgermanes produce a diastereomeric mixture of homoallylic alcohols with appreciable 1,5- or 1,6-stereocontrol.[101,102] The stereocontrol depends on the substitutents on the allyl chain of the germane precursor. As shown in Scheme 116, the reaction sequence starting from **48a** leads to alcohol **48b** with a useful level of 1,5-stereocontrol via 5-membered intermediates **48A**. Under similar reaction conditions, **49a** gives alcohol **49b** with 1,6-stereocontrol via intermediates **49A**.

Scheme 118



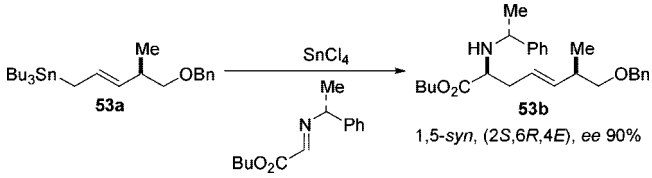
Scheme 119



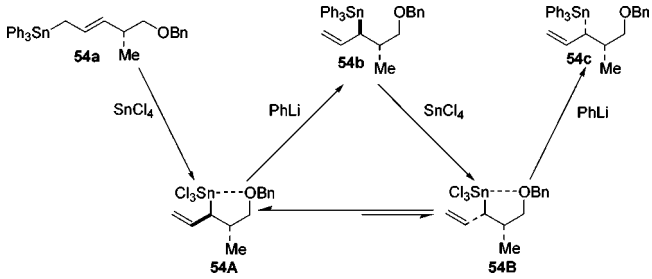
2.5.3. Allyltin from Allylstannane via Transmetalation

Transmetalation of allylstannanes having remote heteroatom substituents at the 4-, 5-, and 6- positions, with tin(IV) halide, leads to chelated allylhalostannanes which react with aldehydes and imines with a useful level of 1,5-, 1,6-, and 1,7-stereocontrol.

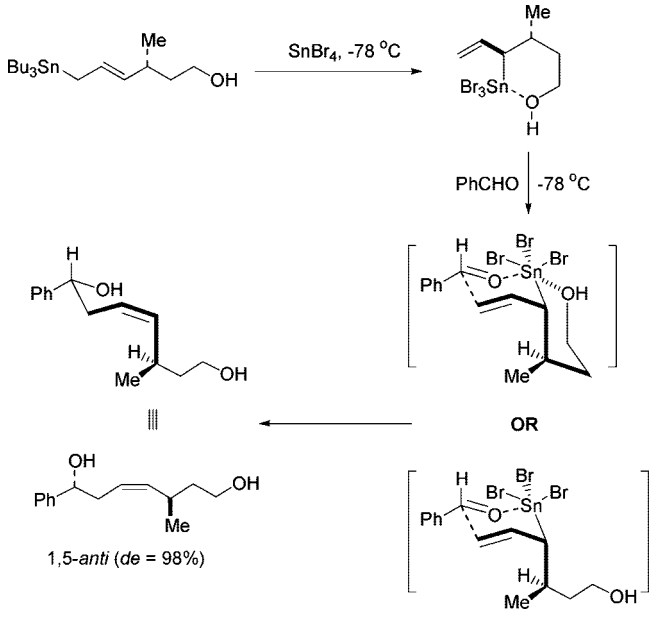
Scheme 120



Scheme 121



Scheme 122



Via Four-Membered Cyclic Chelated Allylstannane Intermediate. Transmetalation from allylstannanes, which proceeds via a 4-membered chelated intermediate, shows a useful level of 1,5-stereocontrol under carbonyl and imine allylation reaction conditions.[3d,103,104] An interesting difference between the two reactions is the (*Z*)- versus (*E*)-geometry of the double bond in the products **50b** and **50c** (Scheme 117 and 118). Note that both the reactions involve the common allyltrichlorostannane intermediate **50A**. It has been suggested that while carbonyl allylation proceeds via the expected cyclic transition state **50B** (Scheme 117), allylation of imine could involve the open-chain transition state **50C** or the cyclic transition state **50D** (Scheme 118).

Via Five-Membered Cyclic Chelated Allylstannane Intermediate. Transmetalation from allylstannanes proceeding via a 5-membered chelated intermediate also shows a useful level of 1,5- and 1,6-stereocontrol under nucleophilic addition reactions.[105,106] Two examples of allylation are shown in Scheme 119 which involve transmetalation of allyltributylstannanes **51a** and **52a** with $SnCl_4$ to generate reactive allyltrihalostannane intermediates **51A** and **52A**, respectively. Subsequent carbonyl allylation with benzaldehyde results in highly diastereoselective formation of the corresponding alcohols **51b** and **52b**.

Using a similar strategy as above, Hallet et al. could achieve effective 1,5-asymmetric induction for the allylation of chiral imines, as exemplified for the formation of **53b** from **53a** (Scheme 120).[107] The observed (*E*)-geometry of the double bond in **53b** distinguishes it from the carbonyl allylation.

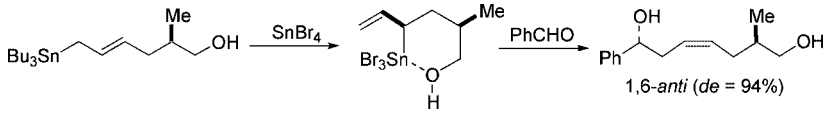
Tin-to-tin transmetalation of allylstannane **54a** with tin(IV) chloride generates the expected 5-membered chelated intermediate **54A**, which on phenylation at the Sn-center gives the organotin product **54b** with 100% *anti*-selectivity (Scheme 121).[108] A repeat sequence of transmetalation−phenylation with **54b** provides the organotin product **54c** with exclusive *syn*-selectivity via the intermediate **54B**. From the sequence of reactions it has been established that **54A** is more stable than **54B** (Scheme 121).

Via Six-Membered Cyclic Chelated Allylstannane Intermediate. Allylstannanes with a remote heteroatom substituent (1,6-) react with aldehydes in the presence of tin(IV) halide with efficient 1,5-, 1,6-, and 1,7-asymmetric induction. The three examples shown in Schemes 122−124 demonstrate the utility of such asymmetric induction in the case of allyltin precursors having a hydroxyl pendant as chelating group.[109]

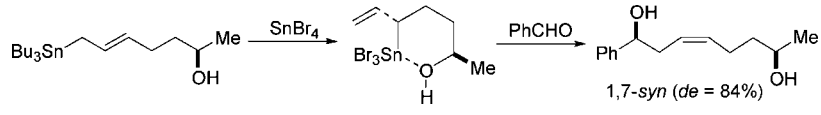
Via Seven-Membered Cyclic Chelated Allylstannane Intermediate. Upon transmetalation with tin(IV) chloride, allyltin precursor **55a**, having a terminal carbamate functionality, provided the corresponding 7-membered cyclic intermediate **55A** via chelation through a carbonyl oxygen (Scheme 125).[110] Follow-up carbonyl allylation lead to the corresponding alcohol **55b** with high 1,4-stereocontrol via the bicyclic transition state **55B**.

Allyltin intermediate **56A**, having a terminal ester group, also shows chelation via carbonyl oxygen (Scheme 126).[99,111] Upon reaction with aldehyde, a one-bond fused 6,7-bicyclic transition state **56B** is obtained from which the product homoallyl alcohol **56b** emerges with a moderate level of 1,5-stereocontrol.

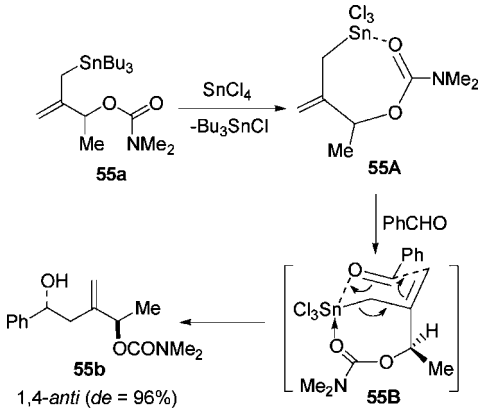
Scheme 123



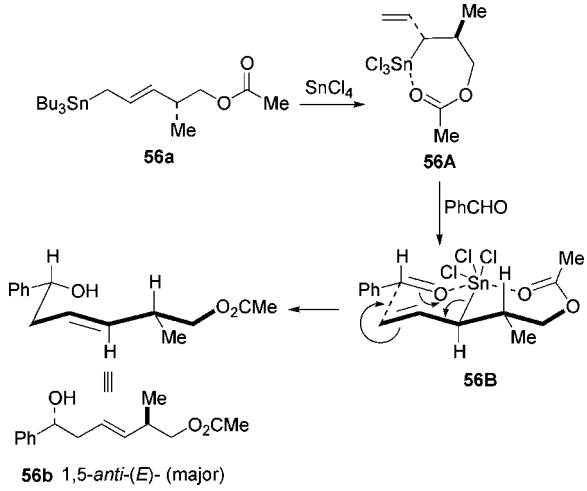
Scheme 124



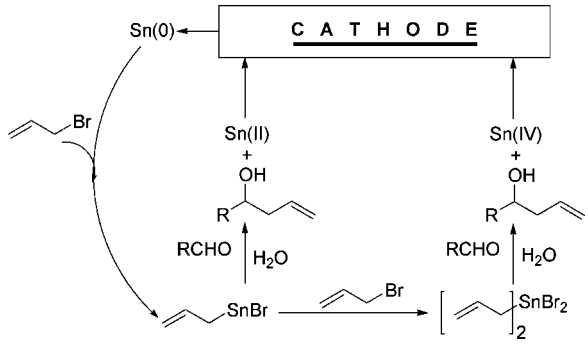
Scheme 125



Scheme 126



Scheme 127

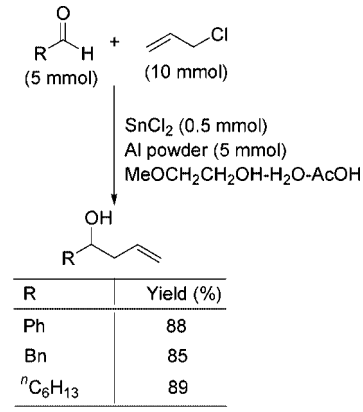


2.6. Allyltin via Miscellaneous Routes

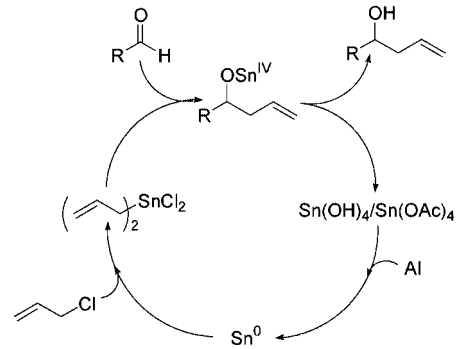
Routes to in situ generated allylstannanes and their organic applications which could not be incorporated in the previous sections are presented below.

A novel tin-mediated aqueous carbonyl allylation via electrochemical reduction at constant potential using tin(II) chloride as the initial feed has been recently reported by Miao, Wang, and co-workers (Scheme 127).[112] In this process, Sn(II) and Sn(IV) (byproduct after carbonyl allylation) are reduced at the graphite cathode to Sn(0). Oxidative addition of allyl bromide across Sn^0 possibly generates both allyltin(II) and allyltin(IV) intermediates in sequence. Subsequent carbonyl allylation followed by hydrolysis leads to the desired homoallylic alcohol and Br^-. The latter is

Scheme 128



R	Yield (%)
Ph	88
Bn	85
$^nC_6H_{13}$	89



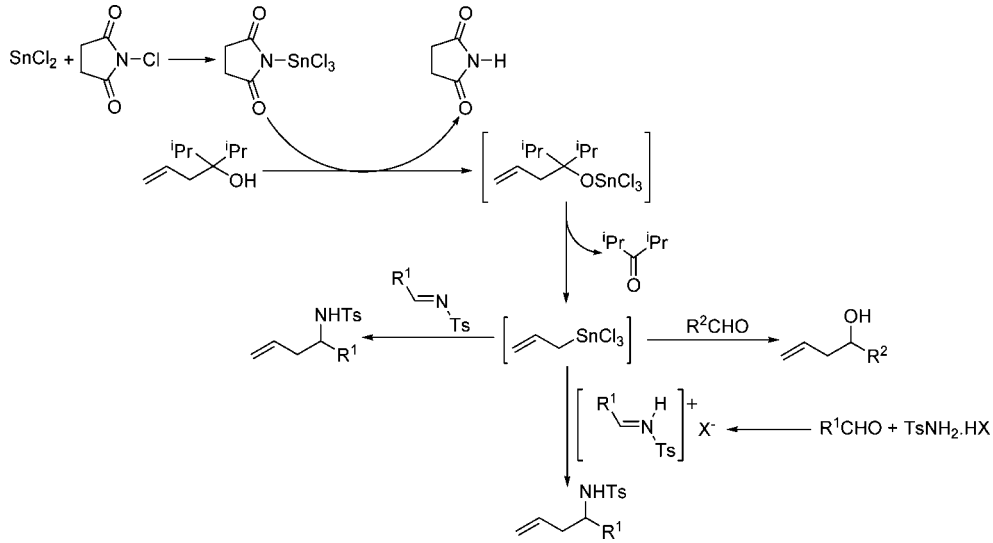
oxidized at the anode to generate Br_2 that is hydrolyzed in water. Using a single feed of tin(II) chloride (10 mmol), the carbonyl allylation has been successfully operated up to five cycles with an overall feed of 25 mmol of benzaldehyde.

Note that Torri and co-workers demonstrated in 1984 a conceptually similar electrochemical allylation using allyl bromide, aldehyde, and catalytic Sn(0) as initial feed via the electroreductive regeneration of allyltin in AcOH−methanol.[113] Interestingly, the same group has also demonstrated that electrochemical reduction can be substituted by chemical reduction with aluminum metal with little change in turnover number (Scheme 128).[114]

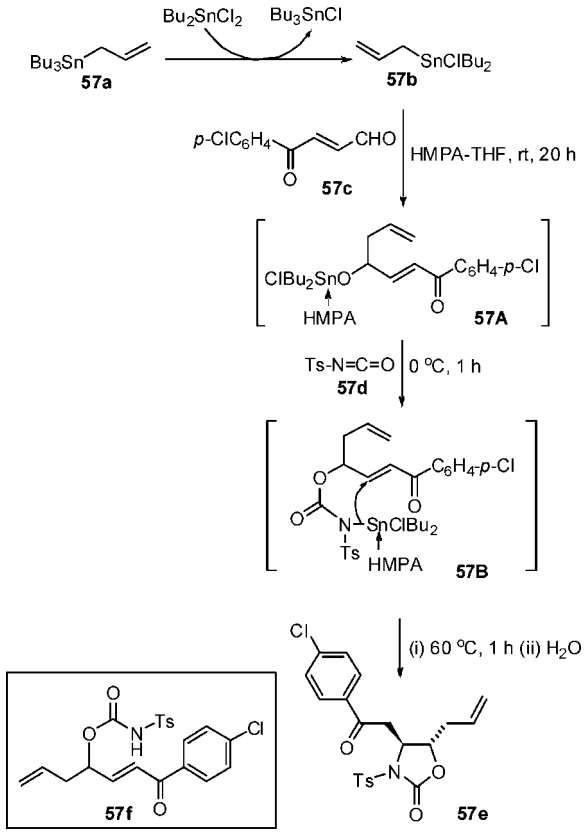
1,1-Diisopropylhomoallylic alcohol reacts with tin(II) chloride and *N*-chlorosuccinimide in dichloromethane at low temperature, providing allyltrichlorostannane, with the elimination of diisopropyl ketone (Scheme 129). The in situ generated allylstannane reacts with aldehydes, imines, or iminium salts to afford the corresponding allylation products (Scheme 129).[115,116]

Baba and co-workers demonstrated an interesting one-pot sequential coupling strategy involving allyltributylstannane **57a**, dibutyltindichloride, bifunctional carbonyl compound **57c**, substituted isocyanate **57d**, and HMPA in the presence of THF as solvent, leading to the formation of 2-oxazolidinones **57e** with a high degree of regio- and diastereoselectivity.[117] It may be noted that, in the carbonyl allylation stage, the reactive allylating species is allyldibutylchlorostannane **57b**, which is generated in situ by the redistribution reaction between **57a** and Bu_2SnCl_2. That allyltributylstannane **57a** alone does not undergo any reaction indicates the important role of the chloro substitutent at the tin center of allylstannane **57b**. Moreover, the allylation reaction is highly chemoselective to the formyl group leaving the enone moiety intact. Subsequent to the carbonyl allylation, the generated Sn−O bond in **57A** reacts with **57d**, giving rise to adduct **57e**

Scheme 129



Scheme 130



through the intermediate **57B**. The "Sn−N" bond in **57B** triggers the ring-closure step. It is observed that HMPA has a special role in the cyclization step. It is proposed that coordination of HMPA to the tin center enhances the nucleophilicity of the pentacoordinate tin amide species **57B**, facilitating the intramolecular conjugate addition. Indeed, in the absence of HMPA, the ring-closing is disfavored and only the linear adduct **57f** is obtained (Scheme 130).[117]

One may note that in the 2-oxazolidinone derivative **57e** the 4,5-*trans*-disubstituted isomer predomates. Such selectivity has been explained in terms of the 1,3-allylic strain in the intramolecular addition (Scheme 131).

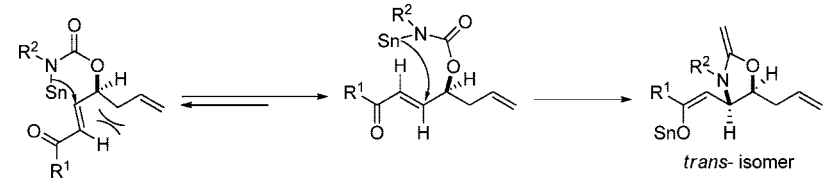
Sugar allyltins are useful starting materials for the preparation of highly oxygenated carbocyclic derivatives. Jarosz and co-workers have contributed significantly in this area, and the reader is referred to recent reviews.[118] It is noteworthy that there are a limited number of stereoselective routes to primary sugar allyltins. One of the conventional methods utilizes the conversion of an allylic alcohol into a xanthate followed by thermal [3,3] rearrangement to the corresponding thiocarbonate (Scheme 132). The latter reacts with tributyltin hydride, providing the desired allylstannane via a radical S_R2' process (Scheme 132).[118,119]

A more recent method involves the reaction of tri-*n*-butylstannylcuprate with sugar allyl bromides.[119b,120,121] The reaction proceeds with complete retention of the configuration of the double bond (Scheme 133). However, a minor pathway involves the formation of secondary isomer arising from an S_N2' pathway.

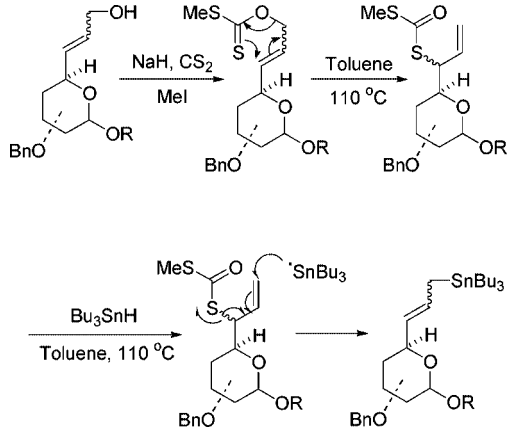
Schrock et al. has recently demonstrated the homologation of vinylstannane to allylstannane using ethylene in the presence of a catalytic molybdenum(IV) complex Mo(=NAr)(CH_2=CH_2)[biphen] (Scheme 134).[122] An isotopic labeling experiment indicates that both methylene groups of ethylene are transferred in this homologation reaction.

The authors have proposed the possible mechanisms for the catalytic conversion of vinyltributylstannane to allyltributylstannane. The sequence of steps of the catalytic reaction has been depicted in Scheme 135.

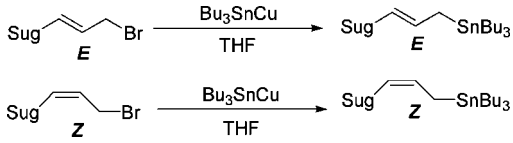
Scheme 131



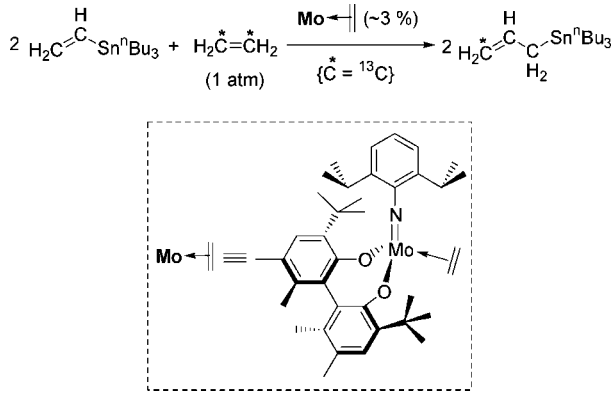
Scheme 132



Scheme 133



Scheme 134

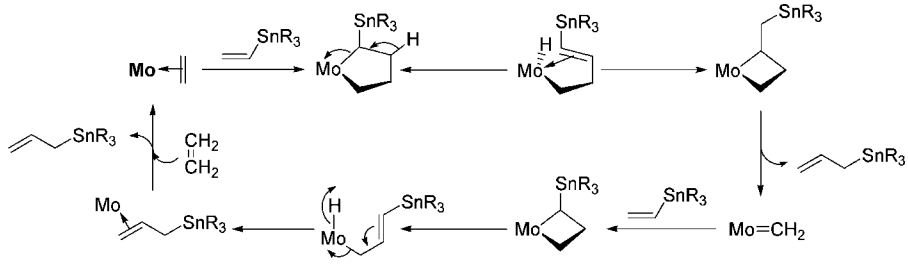


Sato and co-workers demonstrated interesting titanium(II) mediated reductive conversion of chiral propargyl stannane **58a** to chiral allylstannane **58b** with *Z*-selectivity (Scheme 136). The reaction involves initial formation of bimetallic intermediate **58A**, which upon hydrolysis gives the desired allylstannane.[123]

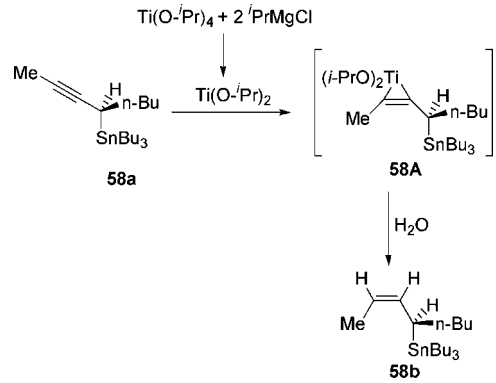
An interesting Ni(0) catalyzed conversion of acylstannane to allylstannane is shown by Shirakawa et al. The reaction may be equated to a formal 1,4-acylstannation of 1,3-diene (Scheme 137).[124]

The catalytic cycle involves initial oxidative addition of acyl-Sn(IV) across Ni(0) to give a bimetallic Ni−Sn intermediate **59A** (Scheme 138). Coordination of diene to

Scheme 135



Scheme 136



the latter gives intermediate **58B**. Migration of SnR^2_3 to the terminal carbon of diene in **59B** leads to the formation of π-allyl-Ni^{II} intermediate **59C**, from which reductive elimination provides the desired allyl stannane with the regeneration of the catalyst.

3. Allylindium

It may be recalled from the general introduction (chiefly Scheme 1, path-C, and Figure 1) that in situ generation of allylindiums is the primary choice in hand to an organic chemist. This can be achieved starting from indium metal, indium(I) halide, or indium(III) halide. The primary modes of activation of organic/organometallic precursors across In(0/I/III) provide interesting insight (Scheme 139). Important observations that emerge from this depiction are as follows.

(a) Metallic indium can directly activate allyl halide in both organic and aqueous medium, giving rise to reactive allylindium(III) and allylindium(I), respectively.

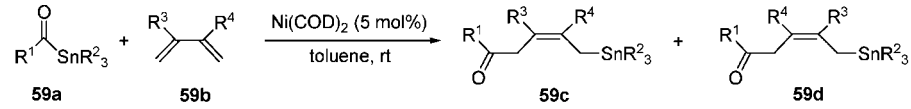
(b) Allyl transfer from in situ generated π-allylmetals (Tm = Pd, Ni) to In(0) also shows dependency on solvent. For example, reaction in aqueous and organic solvent provides allylindium(I) and allylindium(II), respectively.

(c) In few cases, allyl transfer has been accomplished from π-allylmetals (Tm = Pd, Ni) to indium(I) halide, resulting in the formation of allylindium(III).

(d) Transmetallative activation of allyl organometallics of magnesium, mercury, and tin with indium(III) halide leads to the facile generation of allylindium(III).

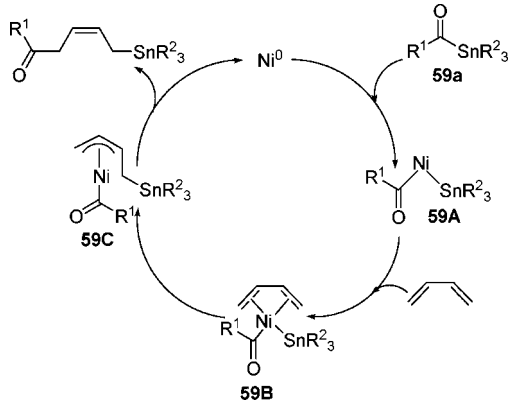
We have attempted to concisely present below the above developments, minimizing overlap with previous reviews on the subject. As pointed out earlier, due to their emerging importance, organic reactivity of allylindiums is well covered in recent reviews.[4,5] Additionally, the account by Pardoe and Downs on the chemistry of indium in formal 0, +1, and +2 oxidation states provides interesting mechanistic and structural insights.[125]

Scheme 137

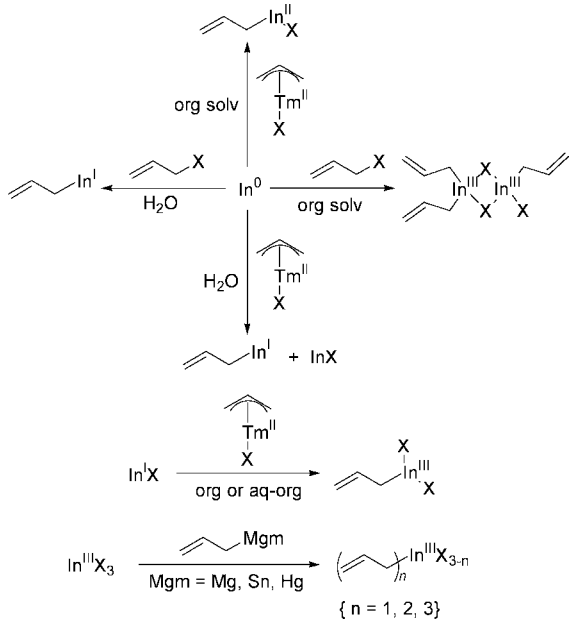


#	R^1	R^2	R^3	R^4	Time (h)	Yield (%)	**59c:59d**
1	Ph	Me	Me	H	2	74	33:67
2	Ph	Me	Ph	H	2	68	47:53
3	Ph	Me	$SiMe_3$	H	2	84	44:56
4	Ph	Me	CH_2SiMe_3	H	2	86	39:61
5	Et	Bu	Me	Me	24	56	**59c** only

Scheme 138

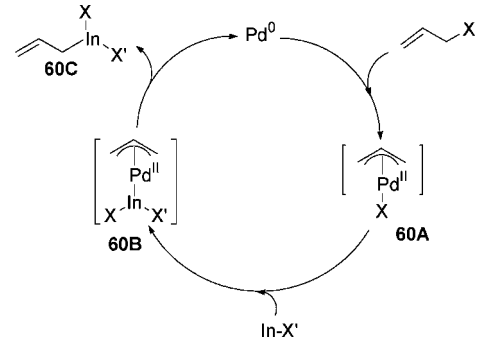


Scheme 139



Keeping in line with the discussion on allylstannanes (section 2), the present section is also divided into three major parts in accordance with the generation of allylindium via (i) initial activation of allyl, allene, or diene as electrophiles at the transition metal center (Tm), (ii) direct activation of allyl electrophile across metallic indium without the participation of a transition metal, and (iii) transmetallative activation of allyl magnesium, mercury, and tin with indium trihalide.

Scheme 140



3.1. Allylindium via Initial Activation of Organic Precursor at the Transition Metal Center

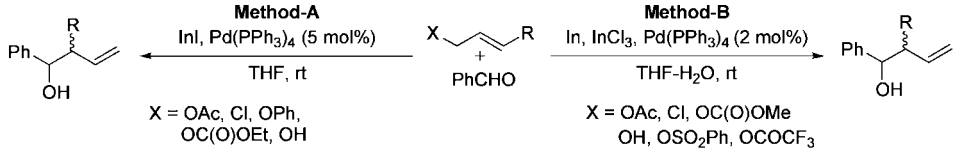
Allyl halides and their surrogates, as well as allenes and dienes, are easily activated across a reactive Tm(0) catalyst (Tm = Pd, Ni) to give rise to the corresponding π-allyl-Tm(II) intermediate. Allyl transfer from the latter to indium(I) or indium(0) generates reactive allylindium, which is utilized in situ for subsequent C−C bond forming reactions. Accordingly, this section has been further divided into two subcategories depending on the organic electrophile and indium precursor.

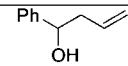
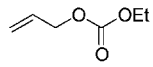
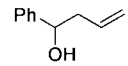
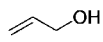
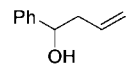
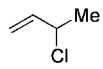
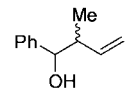
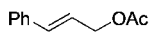
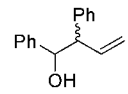
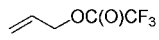
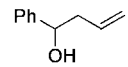
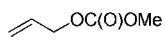
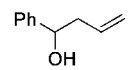
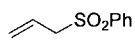
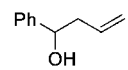
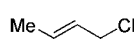
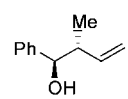
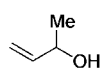
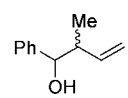
3.1.1. Allylindium from Allyl Electrophiles, Dienes, and an Indium(I) Precursor

The oxidative addition of allyl halides, esters, carbonates, ethers, cyclic amines, and alcohols across palladium(0) leads to well-known π-allylpalladium(II) intermediate **60A** (Scheme 140). Subsequent insertion of indium(I) halide provides the corresponding π-allyl-Pd^{II}−In^{III} intermediate **60B**. Follow-up reductive elimination affords allylindium(III) **60C**. The overall reaction may be viewed as a redox transmetalation and is analogous to the catalytic cycle involving an allyl electrophile, tin(II) halide, and catalytic Pd(0) (chiefly Scheme 21). It may also be noted that indium(I) halide (In-X′) may be used directly or generated in situ by mixing indium metal and indium trihalide.

Araki et al. have successfully used the above strategy for the Barbier allylation of aldehydes using InI and catalytic $Pd(PPh_3)_4$ in organic solvent, leading to the formation of homoallylic alcohols with high regioselectivity and varying diastereoselectivity (Scheme 141, method A).[126] Kim and coworkers have extended the strategy for the regioselective allylation of aldehydes in aqueous−organic medium using in situ generated InCl (Scheme 141, method B).[127]

Scheme 141



#	allyl precursor	product[a]	method	time (h)	yield (%)	*syn*/*anti*
1			A	1.5	89	-
2			A	1.5	76	-
3			A	13	76	-
4			A	1.5	92	58:42
5			A	1.5	100	14:86
6			B	24	80	-
7			B	5	96	-
8			B	40	54	-
9			B	20	93	50:50
10			B	20	95	36/64

Araki and co-workers have also delineated a facile carbonyl allylation from allyl alcohols using indium(I) iodide and in situ generated Ni(0) as the active catalyst (Scheme 142).[128] Like its palladium(0) counterpart, the reaction involves a redox-transmetalation sequence to generate allylindium(III) from π-allylnickel(II). The former reacts with aldehyde or ketone to provide the corresponding γ-homoallylic alcohols with a useful level of stereoselectivity.

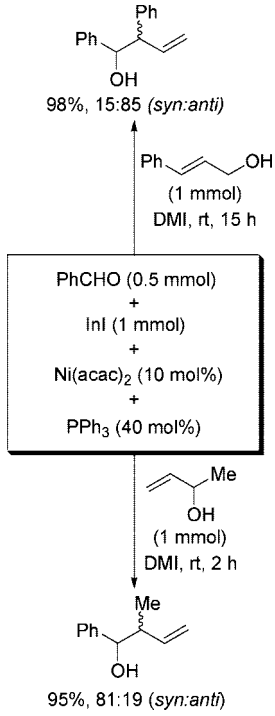
Allylic esters or carbonates built on a carbohydrate framework react with aldehydes in the presence of Pd(0)/In(I) reagent to provide the corresponding homoallylic derivatives with varying regio- and diastereoselectivity (Scheme 143).[129]

Applications of Pd(0)/In(I) assisted Barbier allylation in the construction of highly functionalized carbocyclic scaffolds have been demonstrated by Miller and co-workers.[130] For example, the reaction of bicyclic *N*-oxide **61a** as the allyl precursor with benzyloxyacetaldehyde leads to the formation of three isomers **61b**−**d** in varying ratios depending upon the conditions (Scheme 144).[130a] Reaction in THF−H_2O leads to the best selectivity, in favor of 1,4-*syn* adduct **61b** (entries 2 and 3). In contrast, the 1,2-adduct **61d** predominates in THF−phosphate buffer medium (entry 5). Addition of tetraalkylammonium salts leads to a mixture of all three isomers.

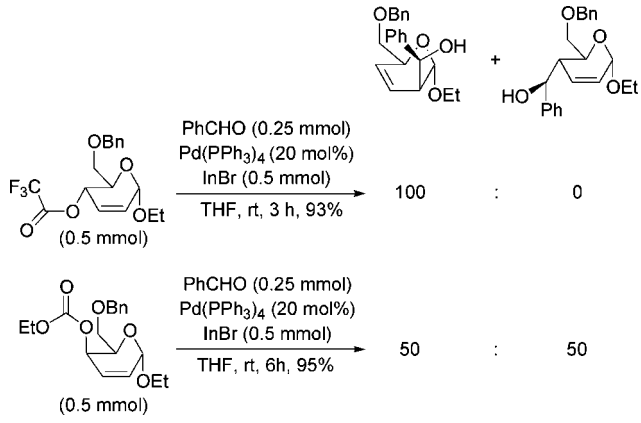
The formation of the major isomer **61b** can be explained involving chelation assisted allylation of benzyloxyacetaldehyde in a S_E2' sequence (Scheme 145). In brief, the mechanism involves prior activation of the C−O bond in **61a** to form cyclic π-allylpalladium(II) intermediate **61A**. Insertion of In(I) across Pd−O, followed by reductive elimination gives cyclic allylindium(III) intermediate **61C** as the major isomer. Nucleophilic addition of **61C** to an aldehyde affords the 1,4-*syn* adducts **61b** via six-membered transition states **61D** and **61D′**.

The Pd(0)-InI reagent also facilitates the in situ generation of allylindium(III) from vinyloxirane as allyl precursor. Barbier-like carbonyl allylation provides the corresponding 1,3-diol and/or 1,5-diol as the end organic product under organic or organic−aqueous conditions.[126a,131] In most of the

Scheme 142

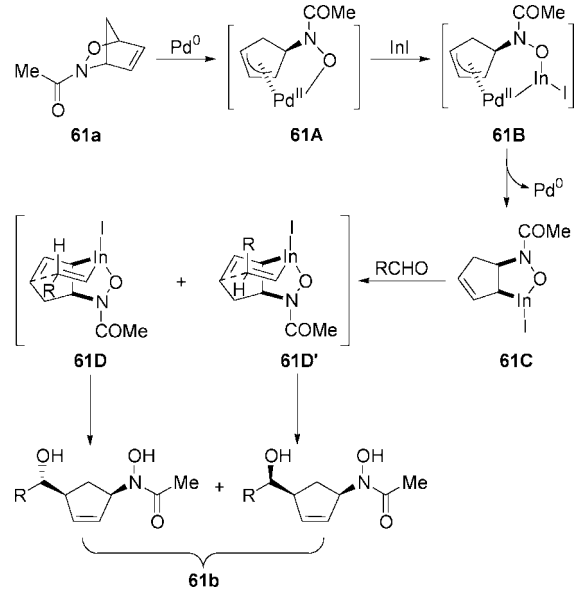


Scheme 143

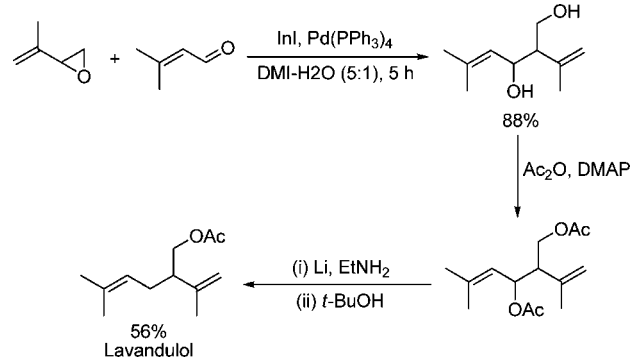


cases, the 1,3-diol product predominates. Using this approach, Lavandulol has been successfully synthesized starting with 2-(2-methyl)vinyloxirane and 3,3-dimethylacrylaldehyde (Prenal) (Scheme 146).[131b]

Scheme 145

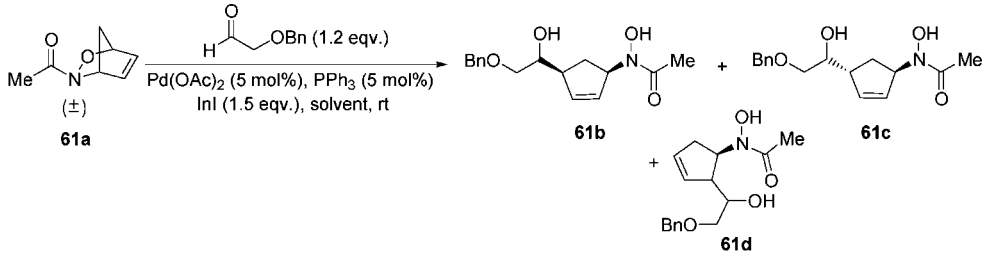


Scheme 146



The generation of allylindium(III) from vinyloxirane and Pd(0)−In(I) also involves a redox-transmetalation step akin to Scheme 140. As outlined in Scheme 147, the sequence of steps involves (i) oxidative addition of an allylic C−O bond of oxirane to generate π-allylpalladium(II) intermediates **62A** and **62A′**, (ii) insertion of InI across a Pd−O bond to provide

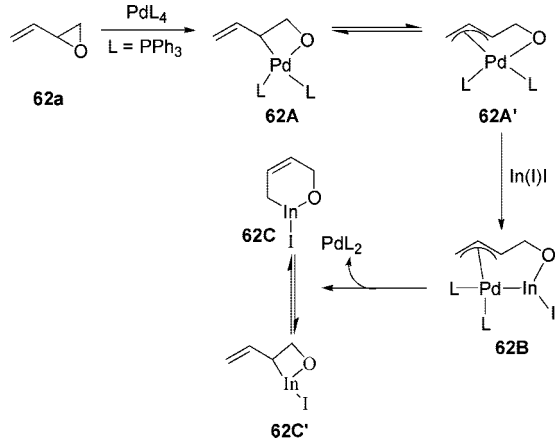
Scheme 144



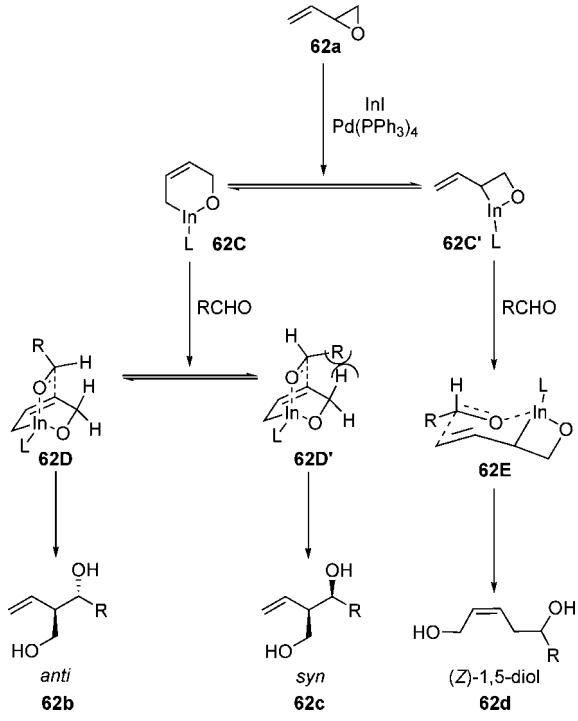
entry	solvent system	yield (%)	product ratio[a]
1	THF	75	4.8:4.5:1
2	THF-H_2O (1:1)	62	10:1:trace
3	THF-H_2O (3:1)	62	14:1:1
4	THF-H_2O (3:1); Bu_4NI or Bu_4NBr	55	8.8:4:1
5	THF/pH 7.5, 1 M phosphate buffer (3:1)	51	trace:1:1.4

[a]determined by ^{1}H-NMR integration

Scheme 147



Scheme 148



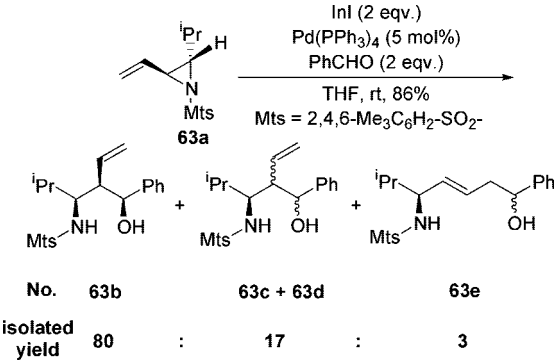
bimetallic $Pd^{II}-In^{III}$ intermediate **62B**, and (iii) reductive elimination of Pd(0) to give chelated allylindium(III) alkoxides **62C** and **62C′**.

The formation of diastereomeric 1,3-diols **62b** and **62c** can be easily rationalized involving allyl transfer from allylindium **62C** to aldehyde in a S_E2' sequence via bicyclic transition states **62D** and **62D′** (Scheme 148). An analogous sequence from allylindium **62C′** will lead to the 1,5-diol **62d** via transition state **62E**.

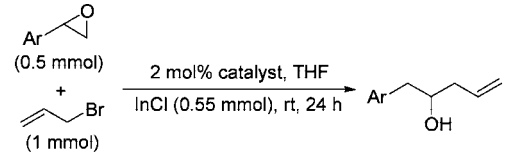
As exemplified in Scheme 149, vinylaziridines also react with aldehydes in the presence of Pd(0)/InI reagent to afford the corresponding 1,3-amino alcohols **63b**, **63c**, and **63d** as the major product and the 1,5-amino alcohols **63e** as the minor product.[132]

Like its tin(II) counterpart (chiefly Schemes 31 and 33), the Pd(0)/In(I) reagent is also effective in promoting simultaneous rearrangement of arylepoxide to the corresponding benzylic aldehyde followed by carbonyl allylation (Scheme 150).[133] Of particular interest is the fact that allylation can be promoted by a homogeneous palladium(0) catalyst such as $Pd(PPh_3)_4$ (entry 1), as well as heterogeneous

Scheme 149



Scheme 150



#	Ar	Catalyst	TOF (d^{-1})
1	Ph	$Pd(PPh_3)_4$	41.0
2	Ph	NanoPd-6	37.0 (1st cycle)
			34.5 (2nd cycle)
			34.0 (3rd cycle)
3	Ph	NanoPd-2.6	14.5
4	*p*-BrC_6H_4	NanoPd-6	31.0
5	*m*-ClC_6H_4	NanoPd-6	34.5

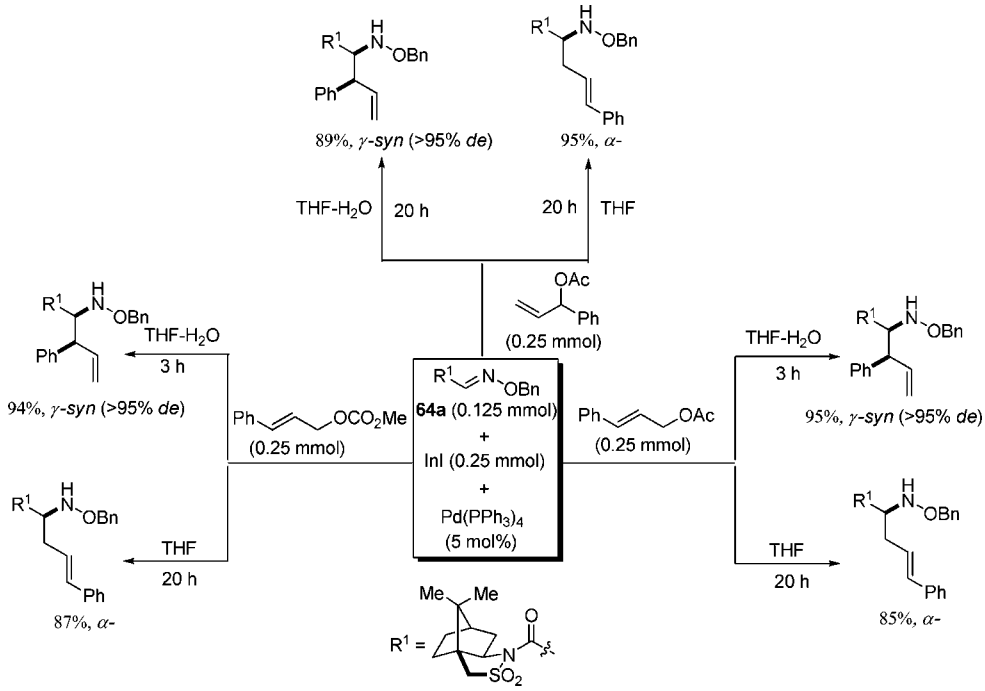
mesoporous silica supported palladium(0) catalysts, namely NanoPd-2.6 (pore diameter 2.6 nm) and NanoPd-6 (pore diameter 6 nm) (entries 2−6). Most importantly, the catalytic activity of NanoPd-6 remains undeterred even after three cycles without significant loss of TOF (entry 2).

Pd(0)−In(I) mediated Barbier-like allylation of conjugatively stabilized imines shows interesting substrate and solvent dependent regio- and diastereoselectivity.[134] For example, allylation of glyoxylic oxime ether **64a** in dry THF leads to the exclusive formation of the corresponding α-adduct, while in THF−H_2O the *γ-syn*-adduct is formed in >95% diastereomeric excess (Scheme 151).

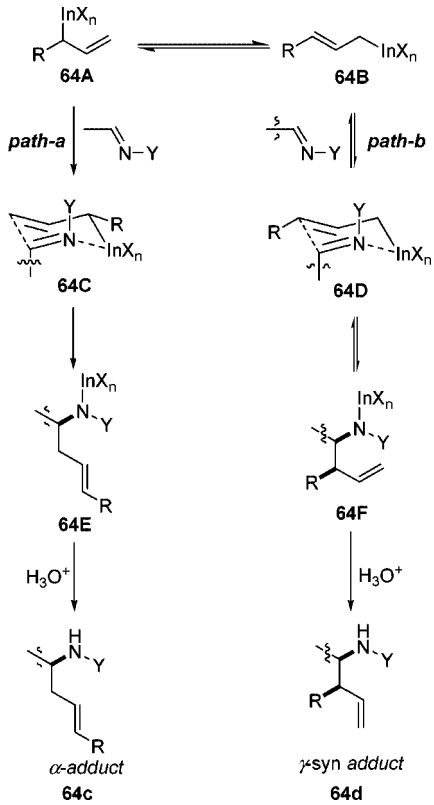
In order to explain the above observation, we would recall Scheme 140, which shows Pd(0)/In(I) assisted in situ generation of allylindium(III). It is well-known that allylmetals often exist in two regioisomers (such as **64A** and **64B** in Scheme 152) due to metallotropic rearrangement. The extent of rearrangement dictates the isomer ratio in the end-organic product, depending upon the metal, substitutents on the allyl moiety, and the reaction conditions. In the present case, nucleophilic addition of allylindium **64A** to imine under anhydrous reaction conditions will afford the thermodynamically stable α-adduct **64E** due to the reversibility of the reaction following an S_E2' pathway via six-membered transition state **64C** (Scheme 152, path-a). In contrast, the presence of water suppresses the reversibility between the adduct **64F** and allylindium **64B** by quick trapping of the kinetic *γ*-adduct **64F** (Scheme 152, path-b).

On the other hand, allylation of *N*-sulfonylimine **64b** gives always the *γ*-adduct, which indicates that this is not a reversible process, probably due to the extra stabilization of the indium-bonding adduct **64F** by an electron withdrawing *N*-sulfonyl group (Scheme 153).[134]

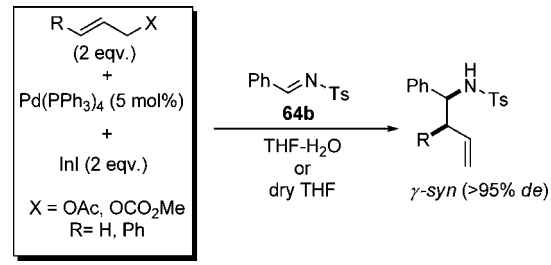
Scheme 151



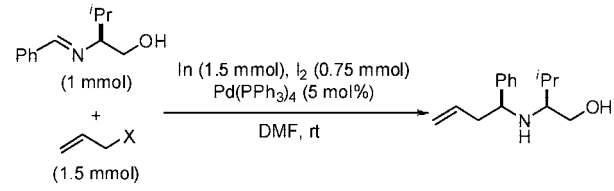
Scheme 152



Scheme 153



Scheme 154



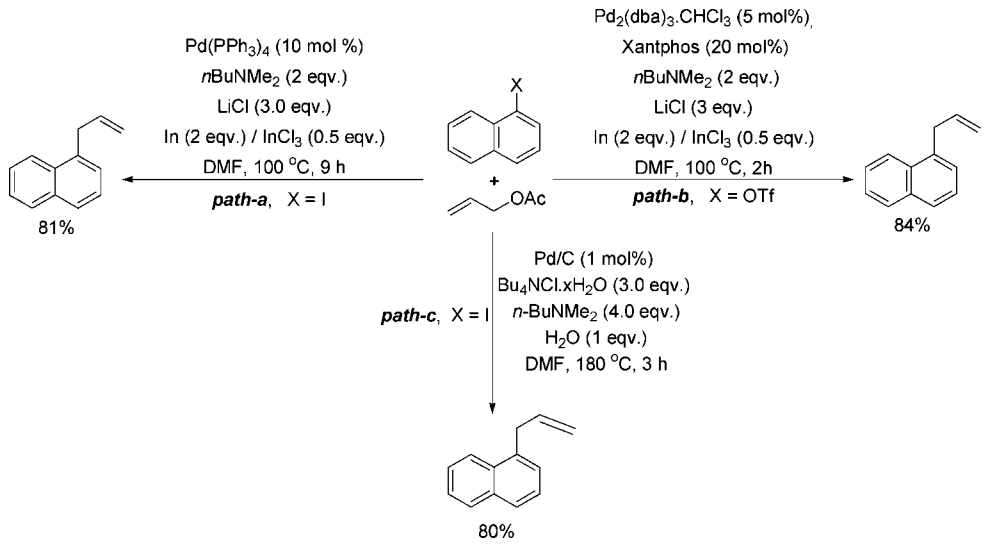
#	X	time (h)	yield (%)	*de* (%)
1	OAc	3	95	>99
2	OCO_2Et	3	92	>99
3[a]	OPh	15	81	>99
4[a]	Cl	15	52	90
5[a]	OH	24	24	78

[a] In (2 mmol), iodine (2 mmol)

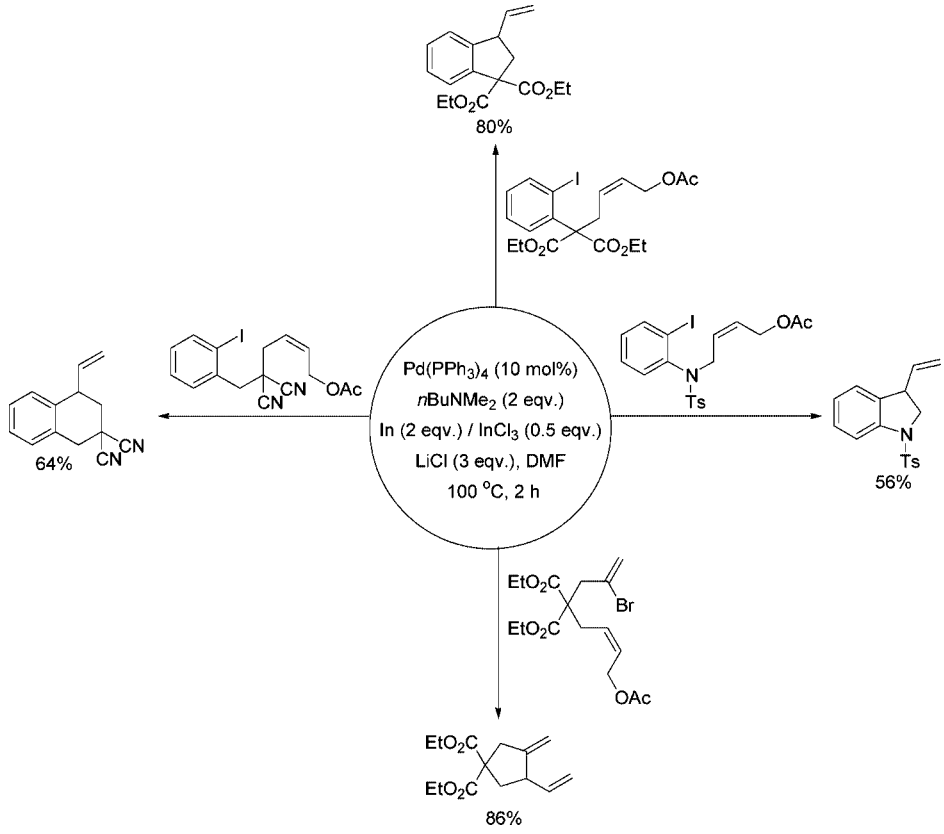
Yanada et al. have reported an analogus allylation process using optically active aldimines, catalytic palladium(0), and in situ generated indium(I) iodide (Scheme 154).[135] It may be considered that the allylindium species are generated in situ via the reaction of a π-allylpalladium(II) complex with In and I_2. The process is economical, since the otherwise expensive indium(I) iodide reagent is generated in situ simply by mixing commercial grade indium powder and iodine in DMF.

Intermolecular aryl−allyl cross-coupling using aryl iodide and allyl acetate can be effectively mediated by Pd(0)/In(I) reagent under the reaction conditions shown in Scheme 155 (path-a).[136] Note that for the facile activation of aryl bromide or triflate, one needs to simply vary the phosphine ligand to Xantphos (path-b).[137] It may be noted that under slightly varying reaction conditions, *but in the absence of indium reagent*, a Heck-type coupling can be executed from aryl iodide and allyl acetate (path-c).[138]

Scheme 155



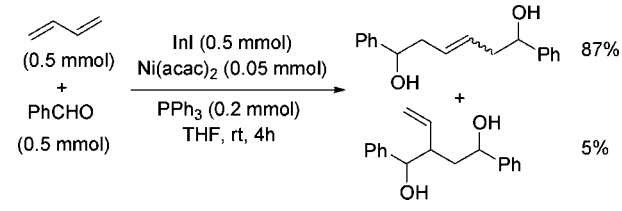
Scheme 156



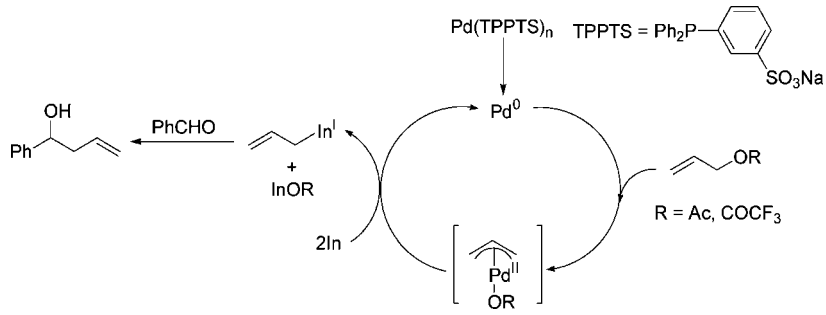
Intramolecular versions of the Pd(0)/In(I) assisted aryl−allyl and vinyl−allyl cross-coupling reactions have been achieved toward the synthesis of cyclopentanes, cyclohexanes, tetrahydronaphthalenes, and indane derivatives as well as their homologues or heteroanalogues, as exemplified in Scheme 156.

An unusual Ni(0)/In(I) promoted bis(carbonyl allylation) reaction has been reported by Hirashita et al. involving 1,3-diene and an aldehyde toward the formation of the corresponding 1,6-diol as the major product (Scheme 157).[139] The authors speculate a two-step allylation mechanism involving the initial addition of a Ni−diene complex to aldehyde, giving rise to a π-allyl−Ni^{II} intermediate, and subsequent redox-transmetalation with InI to generate a σ-allyl−In^{III} species. In the second step, the σ-allyl−In^{III} species adds to another aldehyde, furnishing the end-organic products.

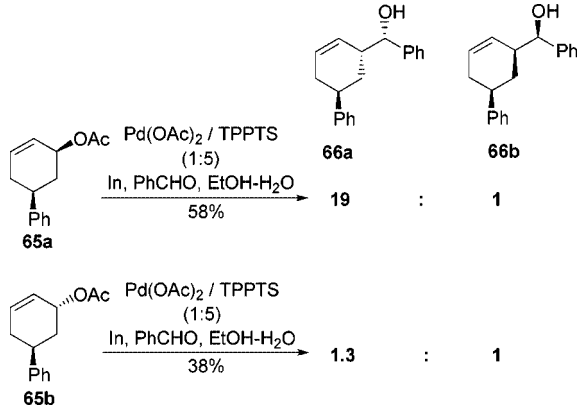
Scheme 157



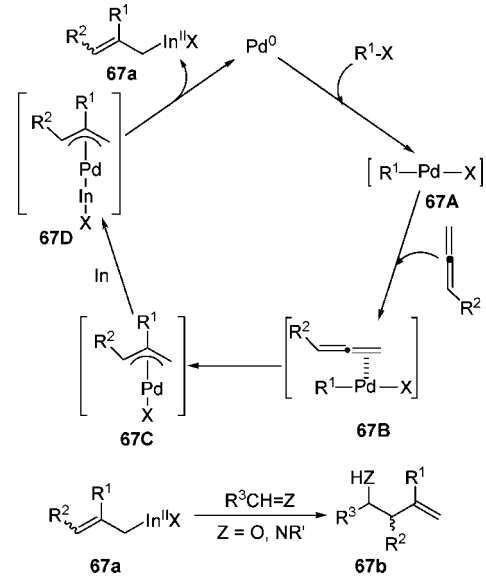
Scheme 158



Scheme 159



Scheme 160



3.1.2. Allylindium from an Allyl Electrophile, an Allene or Diene, and Metallic Indium

As stated in the beginning of section 3, metallic indium can directly activate allyl halide in both organic and aqueous medium, giving rise to allylindium derivatives. Another less explored route involves allyl transfer from π-allylpalladium(II) to metallic indium to generate a reactive allylindium derivative. For example, a π-allylpalladium(II) intermediate, generated via oxidative addition of allylacetate or allyltrifluoroacetate undergoes facile redox-transmetalation with 2 equiv of indium(0) to give allylindium(I) along with indium(I) hydroxide/ester in water (Scheme 158).[140] The in situ generated allylindium(I) species undergoes smooth carbonyl allylation in water, affording the corresponding homoallyl alcohols in excellent yield. The $Pd^0(TPPTS)_n$ catalyst can be reused in up to two cycles with minimal reduction in TOF.

The stereochemical outcome for the reaction of benzaldehyde with cyclohexenyl acetate **65a** and **65b** shows an interesting 1,2-*syn* selectivity (Scheme 159). Note that both the allylic precursors lead to the formation of a mixture of homoallylic alcohols **66a** and **66b**, with the former being the major isomer.

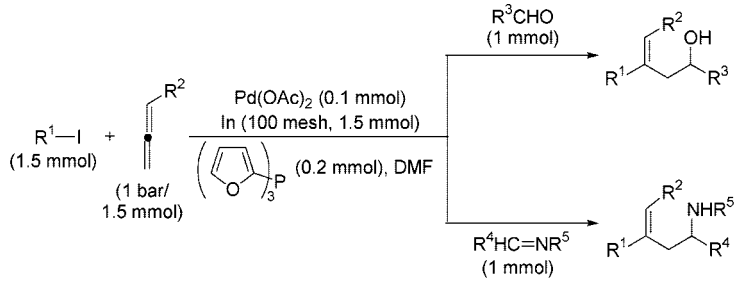
The reaction of allenes with aryl halide (R^1X), indium(0), and catalytic palladium(0) lead to the in situ formation of the corresponding allylindium(II) intermediate (Scheme 160).[141−144] The latter promotes facile one-pot allylation of carbonyls and imines. These reactions have synthetic and mechanistic resemblance to the activation of allene by Pd(0)/Sn(IV) and Pd(0)/Sn(II) reagents discussed earlier (chiefly Schemes 15, 16, 46, 62, and 63).

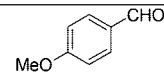
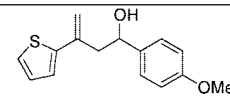
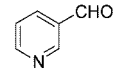
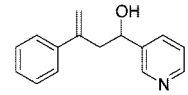
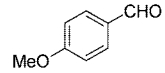
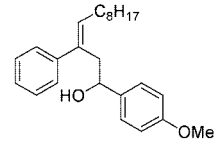
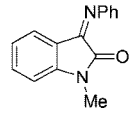
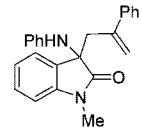
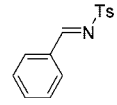
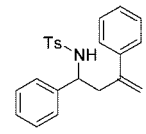
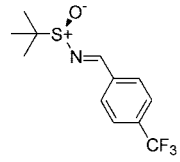
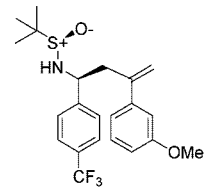
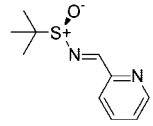
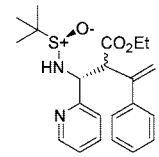
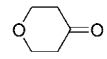
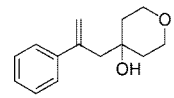
As detailed in Scheme 160, the catalytic cycle involves prior oxidative addition of R^1X to palladium(0) to form $R^1-Pd^{II}-X$ **67A**, which coordinates to allene. Migration of an aryl group (R^1-) to the central carbon of the coordinated allene gives the π-allyl-Pd^{II} intermediate **67C**. A redox-transmetalation sequence involving **67C** and indium(0) leads to the formation of reactive allylindium(II) **67a** via the intermediacy of **67D**, having an unusual bimetallic $Pd^{II}-In^{II}$ motif. The entire sequence can be viewed/executed in a manner to deliver the one-pot three-component coupling product **67b** from the reaction of aryl halide (R^1X), an allene, and an aldehyde/imine (Scheme 160).

Grigg and co-workers have successfully exploited the above one-pot three-component C−C coupling strategy within intermolecular as well as intramolecular regimes.[141] Only a few selected examples are accrued in Scheme 161 to demonstrate the generality of the concept. Recently the same group has also shown that additives, such as amines, CuI, or ascorbic acid, have beneficial effects in promoting cascade-coupling in the case of less reactive electrophilic carbonyls and iminies (Scheme 161, entries 7 and 8).[141f,g]

In the intramolecular regime, the coupling strategy has been extended to cyclization reactions involving two components, one of which incorporates two functionalities in the same molecule (Scheme 162). The three variations thus

Scheme 161



#	R^1	R^2	carbonyl/ imine	product	yield (%)
1	2-thienyl	H			66
2	Ph-	H			65
3	Ph-	C_8H_{17}			50
4	Ph-	H			61
5	Ph-	H			61
6	3-$MeOC_6H_4$-	H			54
7[a]	Ph-	CO_2Et			60
8[b]	Ph-	H			81

[a] CuI (20 mol %) and ascorbic acid (40 mol %) are needed. [b] CuI (40 mol %) is needed

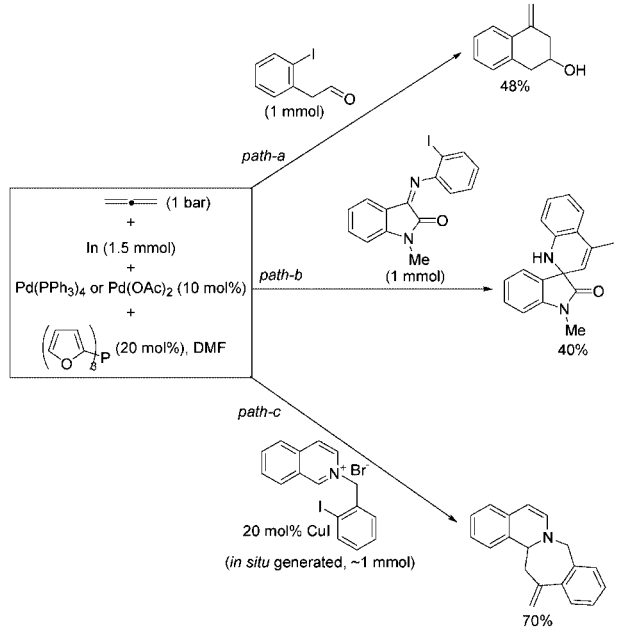
obtained are as follows: (i) coupling between an allene and a substrate having suitably disposed aryl iodide and a carbonyl/imine group (Type-I),[141a,b,142] (ii) coupling between an aryl iodide and a substrate having suitably disposed allene and a carbonyl/imine group (Type-II),[143] and (iii) coupling between an aldehyde and a substrate having suitably disposed aryl iodide and an allene group (Type-III).[141a]

Yet another coupling strategy involves a three-component cascade featuring an allene, an aldehyde, and an aryl iodide having a proximate alkyne to afford heterocyclic and carbocyclic dienes (Scheme 163).[144] It is worthy to note that, in specific cases, cyclization reactions, apparently similar to Type-I in Scheme 162, have been achieved in the absence of metallic indium (Scheme 164, path-a vs path-b).[141a,145]

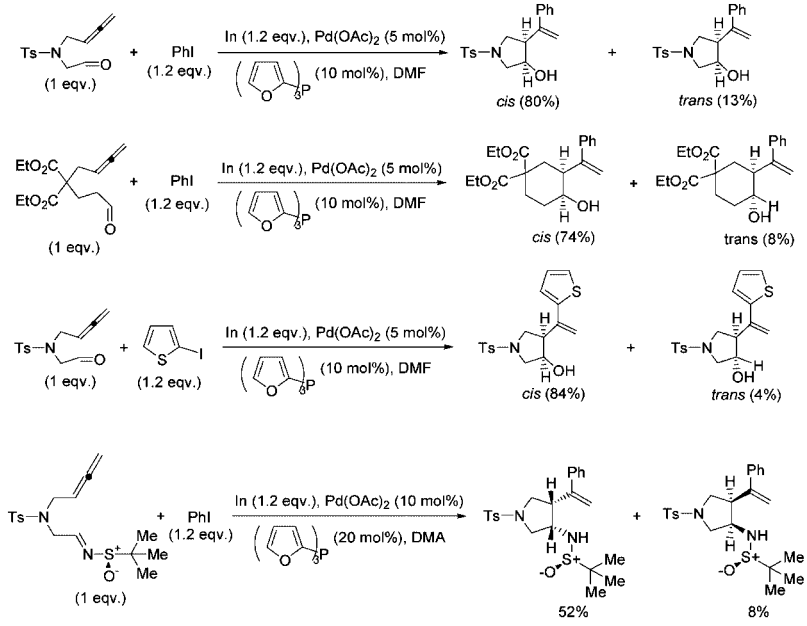
Palladium(0) catalyzed cyclization involving an aryl iodide and a 1,3-diene is also possible via the redox-transmetalation/carbonyl allylation sequence enumerated in Scheme 165.[146] The sequence begins with the generation of π-allylpalladium(II) intermediate **68A** from the precursor **68a**. In situ transmetalation of **68A** with indium(0) generates allylindium intermediate **68B**, which upon Barbier-type carbonyl allylation affords the heterocyclic homoallylic alcohol **68b**.

Scheme 162

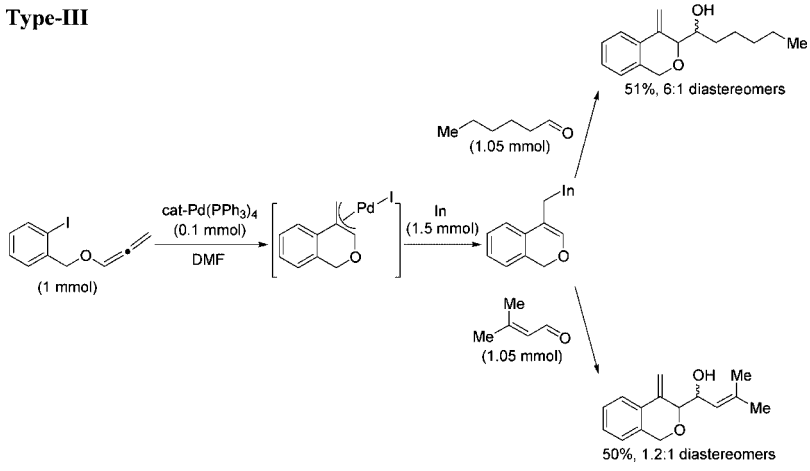
Type-I



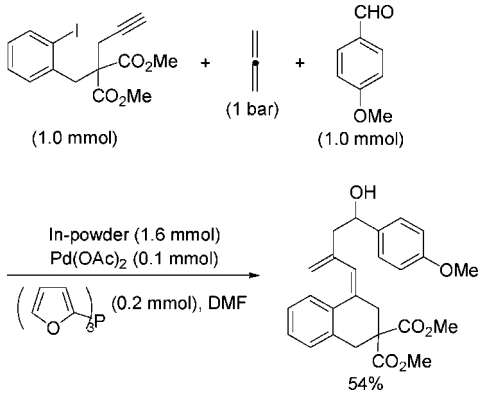
Type-II



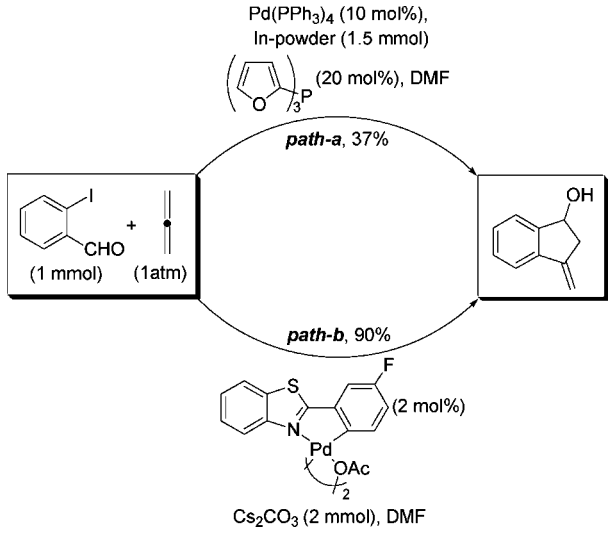
Type-III



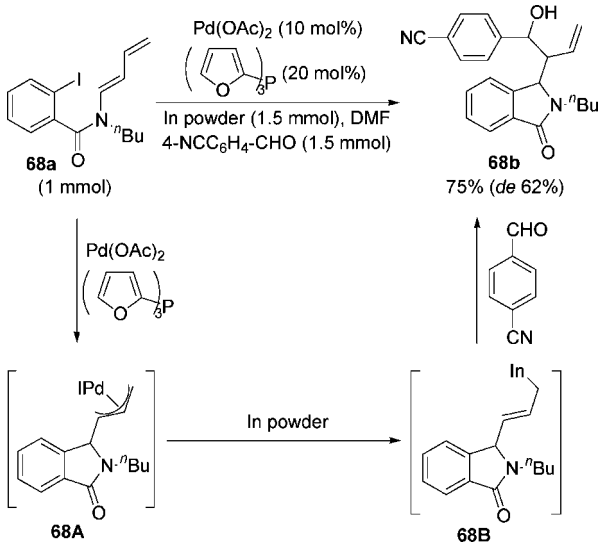
Scheme 163



Scheme 164



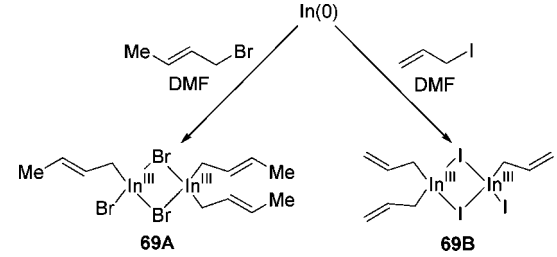
Scheme 165



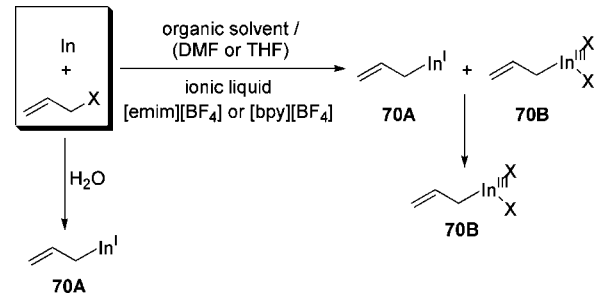
3.2. Allylindium via Direct Activation of an Organic Precursor at the Indium Metal Center

Allylindium can be generated in situ by direct activation of allyl halides and surrogates at the indium metal center without the help of a transition metal catalyst/additive. Such reactions are often carried out in a polar medium (organic, aqueous, aqueous−organic, or ionic liquid). When the reaction was first discovered, it was proposed that indium metal mediated allylation in aqueous medium proceeds on the metal surface with a single electron transfer (SET) from the metal to the allyl bromide to generate a reactive radical anion species.[147] Subsequent studies led to the general acceptance that (i) the allylindium intermediate is involved in the reactions and (ii) the reactivity of the allyl halide varies as *iodide* ≈ *bromide* ≫ *chloride*, with allyl fluoride being inactive.

Scheme 166



Scheme 167

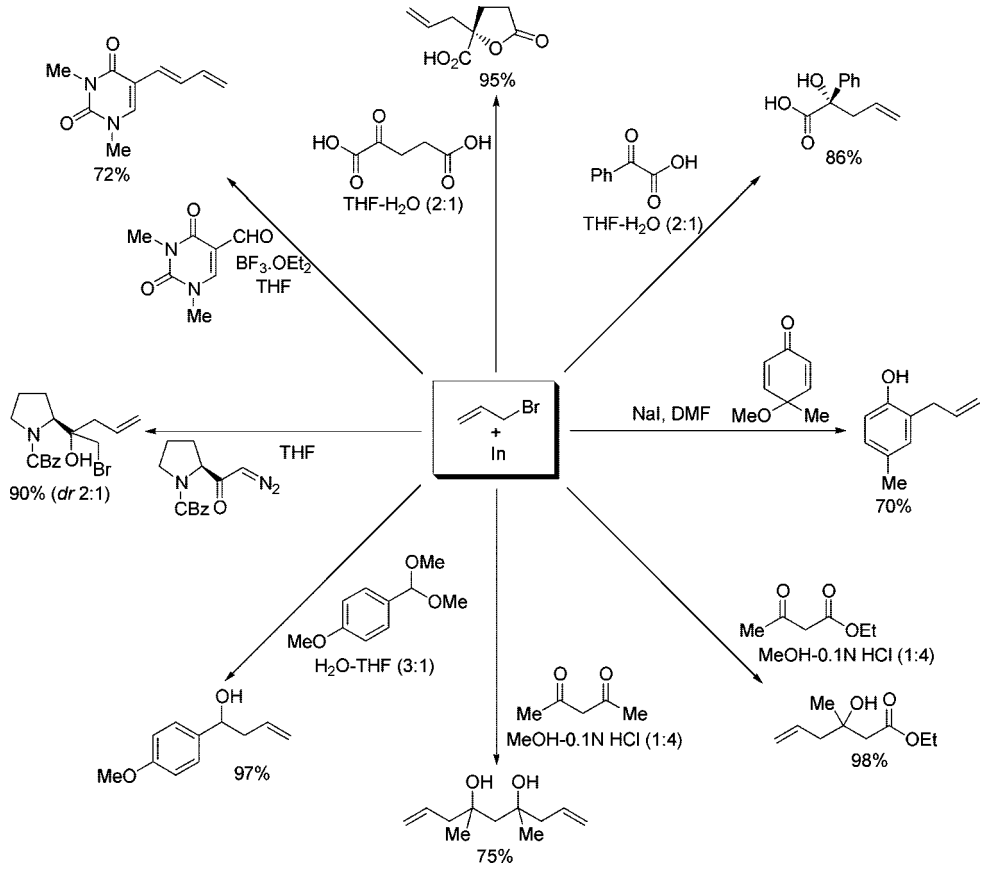


Araki et al. proposed the formation of allylindium sesquihalide $allyl_3In_2X_3$ in polar organic solvents such as THF or DMF (Scheme 166).[148]

Later studies by Chan et al. indicate that the reaction of allyl bromide with metallic indium (in polar organic solvent or in ionic liquid) produces a mixture of two allylindium species, namely allyl-In^{I} (**70A**) and allyl-$In^{III}X_2$ (**70B**) at the initial stage (Scheme 167).[149] Allylindium dihalide (allyl-InX_2, **70B)** predominates as the reaction proceeds. In the case of water as solvent, allyl-In^{I} **70A** alone is formed as a transient but discrete intermediate.[149a] The formation of indium(I) instead of indium(III) intermediate is consistent with the observation that indium has a relatively low first ionization potential but relatively high second or third ionization potentials.[150] As discussed later (section 3.4, Schemes 227), only strong reducing agents are capable of overcoming the In(III→0) potential.[151]

The reader may note that there are numerous reports on the organic reactivity of allylindiums generated vide Schemes 166 and 167.[4,5] Among these, recent reports are more focused on the application of these strategies in the syntheses of complex organic molecules. It may also be noted that the utility of these strategies is covered in a few previous reviews.[4,5] Keeping this in view, we have attempted to present below only the major reactivity patterns of allylindiums toward nucleophilic addition to a C−Y multiple bond (Y = O, N, C) and related organometallic coupling reactions.

Scheme 168



Addition to C═O Bonds

Carbonyl allylation reactions with indium metal can be conveniently carried out under organic, organic−aqueous, aqueous medium, ionic liquid, and even solventless conditions.[148,152] Various kinds of metallic indium sources are also used, including the cheaper form of granular indium. Moreover, a variety of functional groups can be crafted in the allyl and carbonyl motifs. The list includes aldehydes, ketones, protected aldehydes, protected ketones, diketones, α-diazoketones, cyclic ketones, sugars, lactams, lactones, α,β-unsaturated carbonyls, esters, anhydrides, quinines, formyl-quinolones, and many others (Scheme 168).[148,152]

Metallic indium mediated allylation has also been applied to various cyclization reactions.[153] For example, the reaction of 2-(bromomethyl)acrylic acid (**71a**) with carbonyl compound **71b** affords the corresponding α-methylene-γ-butyrolactones **71c** (Scheme 169).[153a,b] Sequential nucleophilic and electrophilic alkylations of 1,3-dicarbonyl compound **72a** with a trimethylenemethane zwitterion equivalent **72b** lead to a novel [3 + 2] annulation.[153c] Indium mediated one-pot intramolecular allylation of **73a** followed by carbocyclization provides the *cis*-fused α-methylene-γ-butyrolactones **73b**.[153d] Li et al. have been successful in promoting an interesting intramolecular carbonyl allylation of **74a** and subsequent two-carbon ring expansion, leading to cycloheptanone derivative **74b**.[153e,f] *S*-Proline catalyzes the asymmetric Mannich-type reactions in aqueous media to provide γ-allyl substituted α-amino acid derivative **75c** with excellent diastereoselectivity and high enantioselectivity.[153g]

An allylation−lactonization sequence has been achieved at room temperature from the aldehydes **76a** and **76b** using In(0)/allyl bromide in DMF (Scheme 170).[154] The corresponding 7-membered lactones **76c** are **76d** are obtained as the single diastereomers in near quantitative yield.

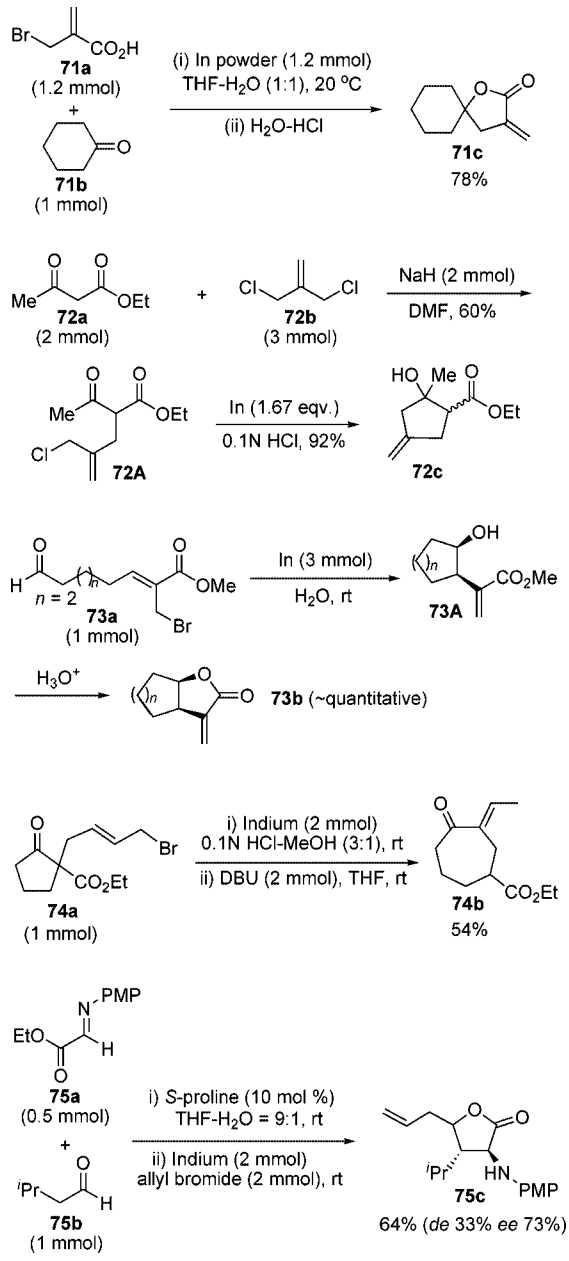
The indium mediated carbonyl allylation reaction is equally efficient for cyclic ketones and anhydrides (Scheme 171).[155] Complex motifs such as α-keto-β-lactams **77a** and **78a** undergo monoallylation under mild reaction conditions to give the α-allyl-β-lactams **77b** and **78b**, respectively.[155a−c] 2,3-Indolinedione (isatin) **79a** also undergoes regioselective allylation to give the corresponding monoallylated product **79b**.[155d,e] On the contrary to the above cases, the allylation of pthalic anhydride **80a** by 3,3-dimethylallyl bromide and allyl iodide gives rise to the mono- and diallylation products **80b** and **80c**, respectively.[155f]

Shin et al. have demonstrated an easy-to-execute allylation−epoxidation sequence for the synthesis of epoxides from α-chlorocarbonyl precursors (Scheme 172).[156] It is noteworthy that the efficiency of the reaction depends on the substituents at the carbon bearing chlorine and the allyl halide.

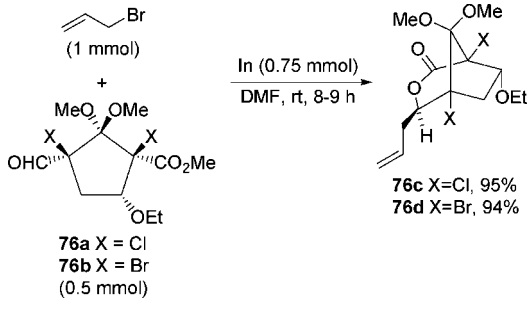
Carbonyl compounds bearing a heterocyclic appendage show interesting substrate dependent reactivity. A case in point is the allylation of *N*-acylimidazoles versus that of *N*-acylpyrazoles (Scheme 173).[157] Under identical reaction conditions the former gives the diallylated alcohol **81a** as the major product, whereas the latter provides allyl phenyl ketone **81b** (Scheme 173).[157]

Indole-3-carboxaldehyde is a fine example of a heterocyclic aldehyde which undergoes an interesting one-pot three-component coupling reaction with allyl halide and pyrazole as the other partners (Scheme 174).[158] This reaction is rather

Scheme 169



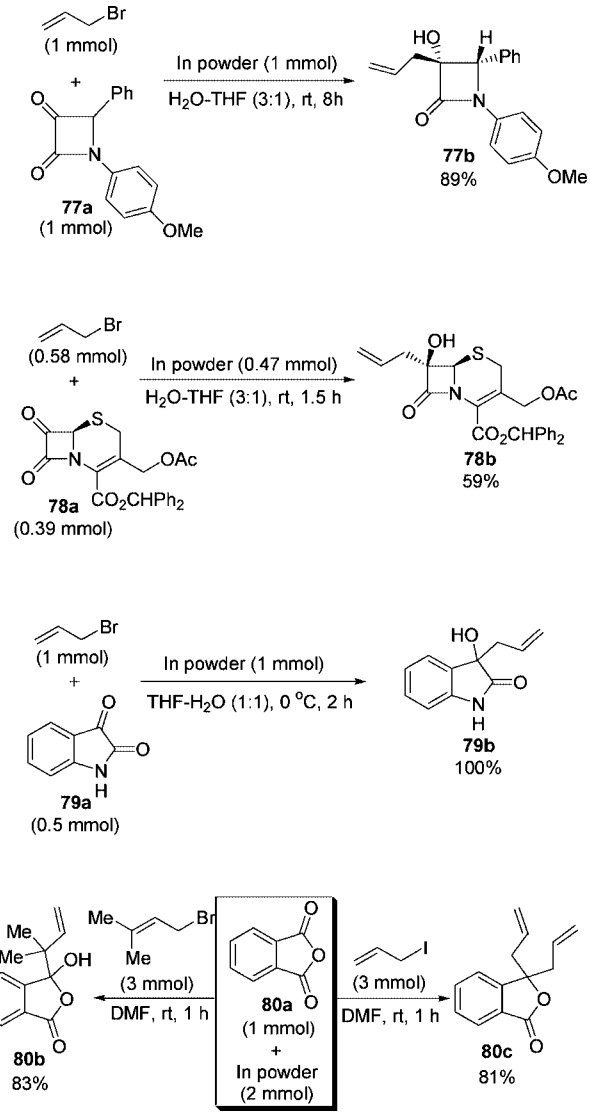
Scheme 170



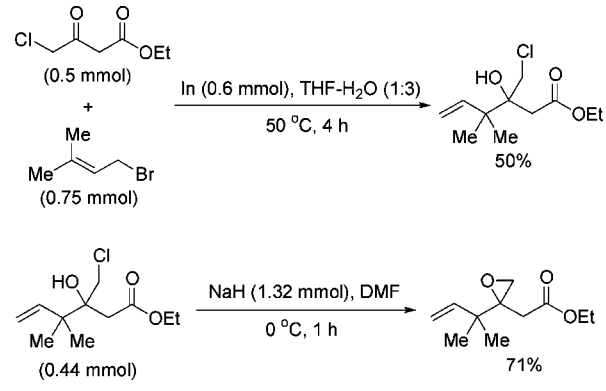
general with respect to substituents at the N-1 and C-2 positions of the aldehyde precursor.

Indium mediated allylation of aldehydes using 4-bromo-2-eno-pyranoside in aqueous media provides the unsaturated analogues of *C*-branched sugars which can be elaborated to the branched sugars (Scheme 175).[159]

Scheme 171



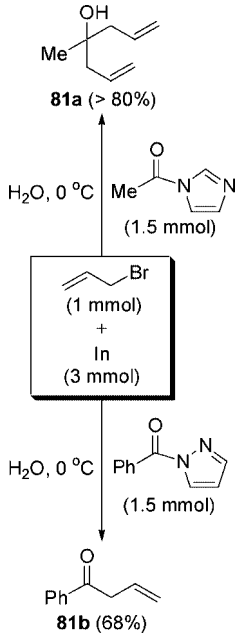
Scheme 172



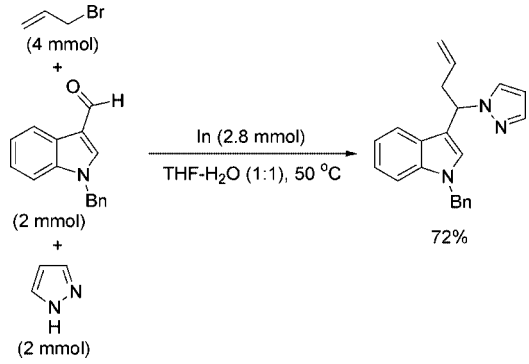
The reaction of an allylindium sesquihalide with epoxide leads to the corresponding homoallylic alcohol as the exclusive product (Scheme 176).[160] The latter arises via attack of allyl nucleophile to epoxide-rearranged aldehyde. The epoxide rearrangement is believed to be due to the Lewis acidity (LA) of the allylindium sesquihalide.

The novel diindium reagent **82A**, prepared from 3-bromo-1-iodopropene **82a**, undergoes a Pd(0)-assisted sequential one-pot three-component coupling with aldehyde/ketone,

Scheme 173



Scheme 174



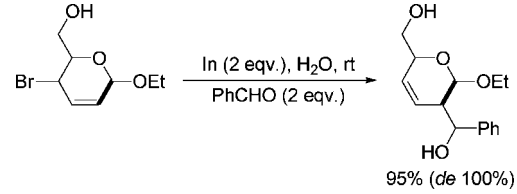
followed by aryl/alkenyl/allyl halide providing the linear homoallylic alcohol **82b** as the end organic product (Scheme 177).[161]

When α,β-unsaturated ketones are allylated by in situ generated allylindium, unexpected rearrangement results to give vinylcyclopropane derivatives (Scheme 178).[162]

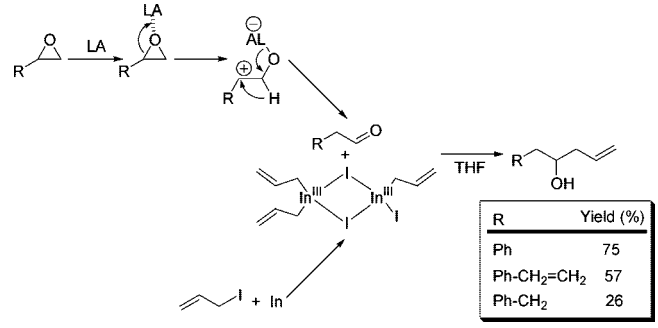
In most cases, indium metal mediated carbonyl allylation reactions are highly chemo- and regioselective; some general features have been highlighted in Scheme 179 and briefly pointed out here.[163] Even though both aldehyde and ketone can be allylated, the reaction is kinetically faster with aldehyde. Competition between 1,2-addition and 1,4-addition occurs in the indium(0) mediated allylation reaction of α,β-enones. In the absence of a Lewis acid, the 1,2-addition is favored,[163a] while in some cases, Lewis acids promote the formation of a 1,4-addition product.[163b,c] Facile allylation of 1,2-dicarbonyl compounds is promoted by In(0)/NaI to give the corresponding α-hydroxyketones.[163d,e] Both the α-ketophosphonates and β-ketophosphonates are allylated by in situ generated allylindium species under mild conditions.[163f,g]

High α-regioselectivity can be maintained for a carbonyl allylation reaction using 3-bromo-3,3-difluoro-1-propenyl

Scheme 175



Scheme 176



R	Yield (%)
Ph	75
Ph-CH_2=CH_2	57
Ph-CH_2	26

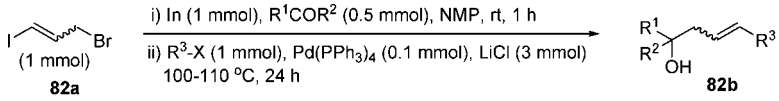
compounds (Scheme 180).[164] The α-regioselectivity is explained on the basis of a single allylindium intermediate in which the negative charge resides at the α-carbon (CF_2 site), thereby preventing an allyl transfer via the otherwise common S_E2' pathway.

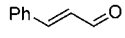
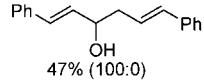
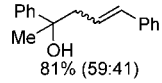
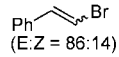
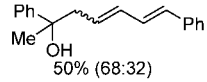
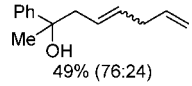
Loh et al. have shown that solvents can also guide the regioselectivity in an allylation reaction. For example, the reaction of crotyl bromide with cyclohexanal in 10(M) ethanol gives rise to the corresponding homoallylic alcohol with 100% γ-regioselectivity (Scheme 181).[165] In contrast, reaction in 10(M) water as the solvent provides the α-regioisomer as the major product.

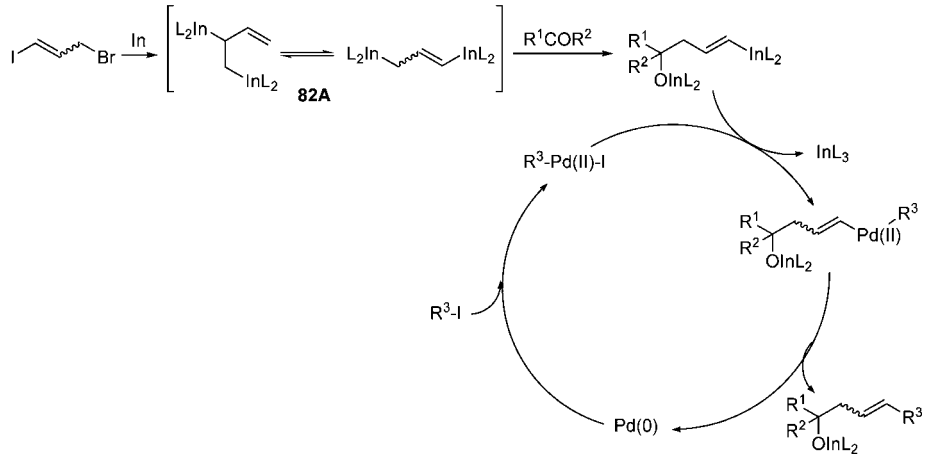
As pointed out earlier, another attractive feature of the indium metal mediated carbonyl allylation reaction is the ability to achieve a high degree of diastereoselection.[166−178] The latter depends upon the substituent(s) on the carbonyl and the allyl halide. For a succinct introduction of this aspect of the chemistry, the reader is referred to the review by Li and Chan.[5b] We would summarize here some of the key features of carbonyl allylation, restricting to those which follow an S_E2' pathway. For clarity of presentation, the carbonyl compound chosen is often an aldehyde. Such a pathway would provide a γ-regioselective homoallylic alcohol as the end-organic product. As shown in Scheme 182, the stereochemical feature in the product can be quite complex for reactions between a 3-substituted allyl halide (FG′ ≠ H) and an α-substituted aldehyde (FG ≠ H) (Scheme 182, *path-a*). On the other hand, 1,2-diastereomers would result when one of the substitutents, FG or FG′, is a hydrogen atom (Scheme 182, *path-b* or *path-c*).

Commonly the formation of a γ-*anti*-homoallylic alcohol is ascribed due to the presence of a sterically bulky substituent, FG or FG′′ (Scheme 183).[166] Chan and co-workers have explained the diastereoselection by involving a Zimmerman type transition state with the allylindium species.[5b,166] It is also well-established that the geometry around the allylic C=C bond (*E*/*Z*) in the precursor allyl halide does not contribute significantly toward *syn*−*anti* diastereoselectivity.

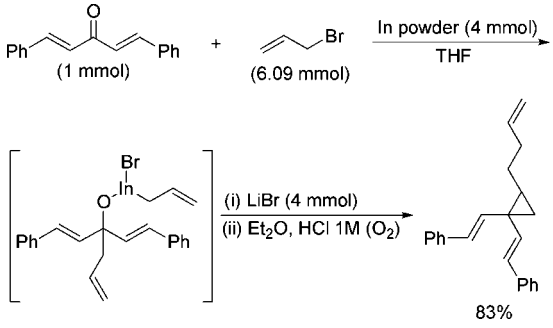
Scheme 177



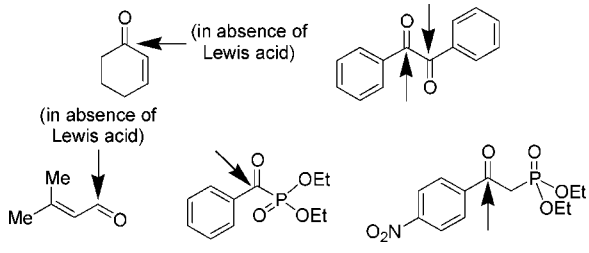
R^1COR^2	R^3X	**82b** (*E*:*Z*)
	PhI	 47% (100:0)
PhCOMe	PhI	 81% (59:41)
PhCOMe	 (E:Z = 86:14)	 50% (68:32)
PhCOMe		 49% (76:24)



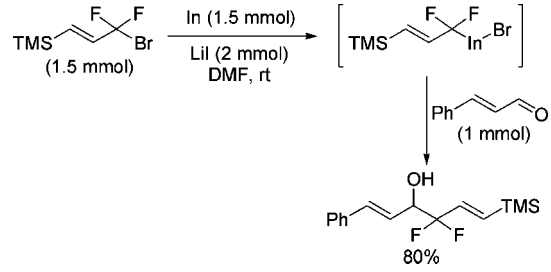
Scheme 178



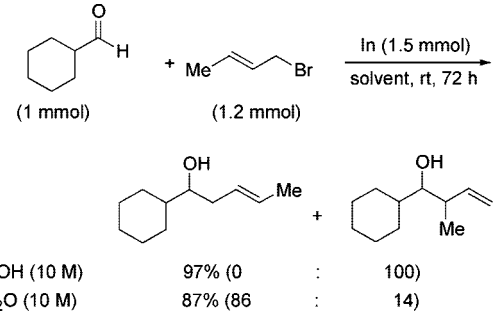
Scheme 179



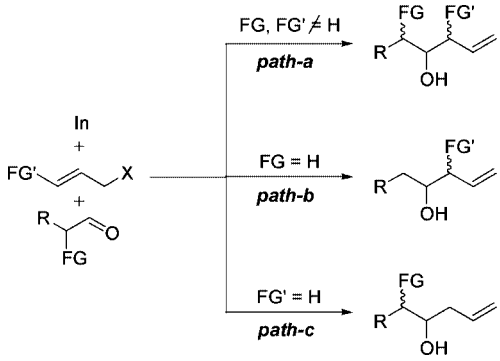
Scheme 180



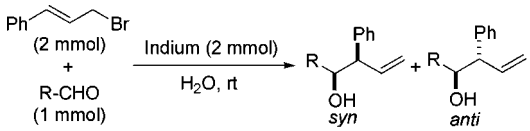
Scheme 181



Scheme 182

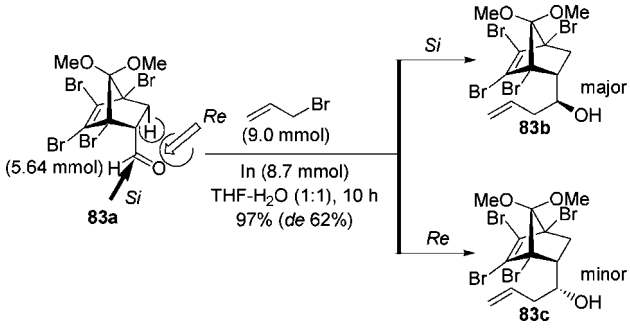


Scheme 183



R	yield (%)	syn : anti
Ph	88	4 : 96
Me_2CH	88	4 : 96
c-C_6H_{11}	75	10 : 90
n-C_8H_{17}	80	31 : 69

Scheme 184

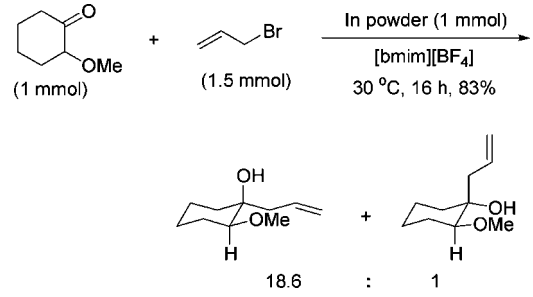


In(0)-mediated allylation of tetrabromo norbornyl derivative **83a** leads to the formation of **83b** as the major diastereomer (Scheme 184).[167] The observation is explained by the preferential attack of allylindium from the less hindered *Si*-face of **83a**. It may be noted that the product homoallyl derivatives are potential building blocks for the synthesis of steroidal and related bioactive molecules.

As elaborated later, when FG or FG' is a heteroatom donor, the major product is generally the γ-*syn*-homoallylic alcohol (Scheme 182, *path-b*).[5b] The importance of chelation-assisted diastereocontrol in In(0)-mediated carbonyl allylation has been well demonstrated by Paquette and co-workers.[168,169] Chelation-assisted high diastereoselectivity can be explained by the chelation-Cram model and Felkin's model.[5b]

α-Hydroxyaldehydes in general and carbohydrates in particular show *syn*-diastereoselectivity in In(0) mediated allylation reactions. A representative example is shown in Scheme 185 for the aqueous carbonyl allylation of **84a**, which gives the corresponding homoallylic alcohol with *syn*-preference (*de* 71%).[171] Such selectivity can be explained by either the chelation-Cram model or the Felkin's model. Similar reactions of α-alkoxyaldehydes show interesting behavior depending upon the solvent.[172] It is generally agreed that in organic medium the alkoxy group serves as a moderately strong donor, thereby ensuring chelation, while in aqueous medium the alkoxy group often behaves as a poor donor, thereby preventing the chelation.[169a,170]

Scheme 186



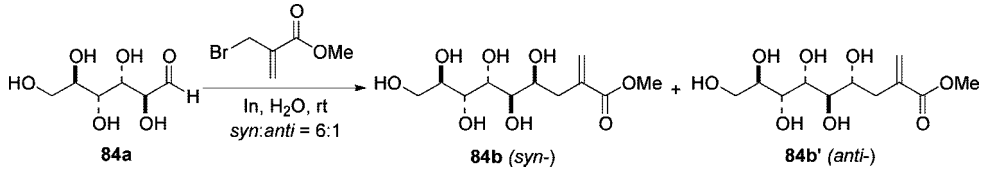
Ionic liquids as solvent also control the stereochemical outcome in carbonyl allylation. For example, allylation of 2-methoxycyclohexanone in [bmim][BF_4] shows a higher selectivity than that in conventional solvents such as water and THF, thereby further augmenting the chelation-assisted mechanism (Scheme 186).[173]

Indium mediated allylation of benzoins and their derivatives in THF−H_2O provides a range of homoallylic alcohols with high diastereoselectivity via chelation control (Scheme 187).[174] In these reactions, the formation of *syn*-products can be visualized on the basis of the classic Cram's chelation model (Scheme 187).

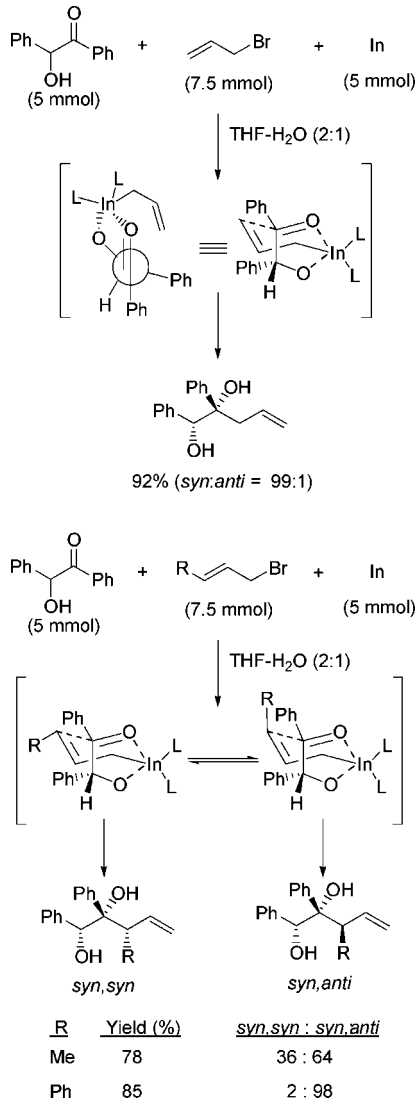
Khan et al. demonstrated an indium mediated regio- and diastereoselective allylation of norbornyl α-diketone **85**.[175] In the case of 5-*endo* substituted derivatives **85**, it has been shown that the diastereoselection is chelation-controlled (Scheme 188). Thus, nonchelating groups (such as 5-*endo* phenyl) direct the addition from the sterically less congested exoface, diagonal to the substituent. On the contrary, chelating substituents (such as 5-*endo* ethoxy) lead to a selectivity reversal.

Trombini and co-workers achieved a novel chelation-assisted diastereoselective allylation from the reaction of 3-halopropenyl carboxylates with indium metal and an aldehyde.[176,177] The end-organic product is isolated after hydrolysis in basic medium, leading to the alk-1-ene-3,4-diols (Scheme 189). It is interesting to note that the diastereoselectivity depends mainly upon the nature of the carbonyl compound. For example, conjugated aldehydes such as benzaldehyde, acrolein, (*E*)-cinnamaldehyde, 2-furfural, *etc.* afford the *syn*-adducts, while unconjugated aldehydes such as cyclohexanal, decanal, *etc.* provide the *anti*-adducts (Scheme 189).

Scheme 185



Scheme 187



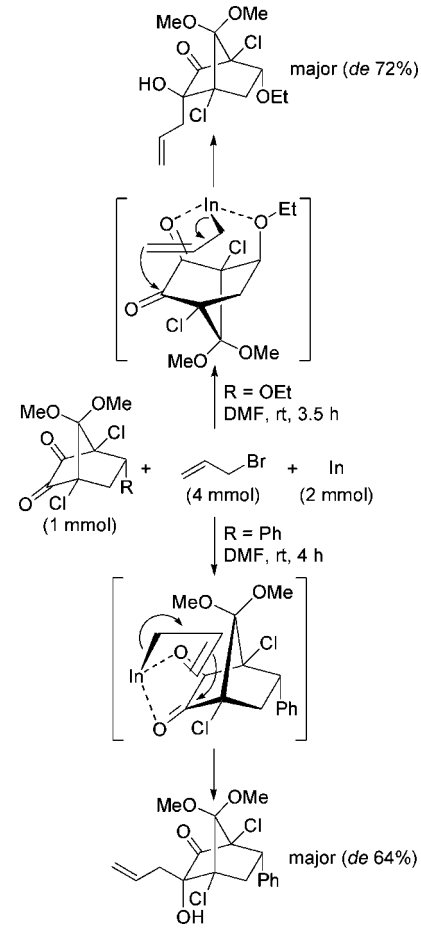
R	Yield (%)	syn,syn : syn,anti
Me	78	36 : 64
Ph	85	2 : 98

Finally, we would like to highlight an interesting case of γ-adduct to α-adduct conversion in the In(0)-promoted carbonyl allylation reaction of ethyl 4-bromocrotonate **85a** with unactivated ketones, as demonstrated by Baba and coworkers (Scheme 190).[178] For example, the reaction of **85a** with 4-chloroacetophenone in THF after 0.5 h gives exclusively the γ-adduct **85b**. Curiously, the same reaction after 17 h provides the α-adduct **85c** as the sole product. The reaction has been successfully extended to several carbonyl compounds. It has been revealed that while the γ-adduct is a kinetic product, the α-adduct is a thermodynamic product.

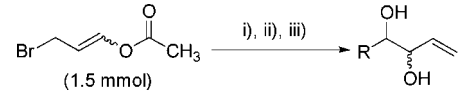
From mechanistic investigations, the authors have suggested a plausible pathway as shown in Scheme 191. The suggestion includes (a) prior formation of allylindium(III) species **85A**, (b) metallotropic rearrangement involving **85A** and **85B**, and (c) reaction of **85A** or **85B** with the ketone by route-a or route-b via S_E2'-pathways to afford the γ- or α-adducts, respectively. The presence of equilibrium between various transition states/transient intermediates has been speculated to rationalize the γ- to α-conversion.

The catalytic asymmetric carbonyl allylation reaction using metallic indium is of more recent origin and can be done by the employment of chiral ligands as an external source of chiral auxiliary via complexation. The suitable chiral promoters (ligands) which have been used for the asymmetric

Scheme 188



Scheme 189



R	yield (%)	syn : anti
Ph	91%	85 : 15
cyclohexyl	70%	10 : 90

i) In (1 mmol), THF, 0 °C to rt, 4 h
ii) RCHO (1 mmol), -78 °C, 4 h
iii) K_2CO_3 (3 mmol), MeOH-H_2O (9:1), rt, 12 h

indium-mediated carbonyl allylation reactions to give homoallylic alcohols in moderate to good *ee*'s and yields are as follows (Figure 4):[179]

Before concluding this subsection, it may be mentioned that metallic indium mediated chemo-, regio-, diastereo-, and enantioselective allylation reactions have been applied successfully to a wide range of complex organic transformations and natural product syntheses.[180]

Addition to a C−N Multiple Bond

Like their carbonyl counterparts, *N*-substituted imines, azirines, enamines, and nitriles are easily allylated using allyl halide and metallic indium.[181] Perhaps the first example in the field is by Mosset et al.[181a] A few chosen examples are shown in Scheme 192. It may be noted that the allylation reaction can be conducted in organic−aqueous, aqueous, or ionic liquid medium as well as under solvent-free conditions. Quinolines, isoquinolines, and cyclic iminium cations are also allylated in this way.

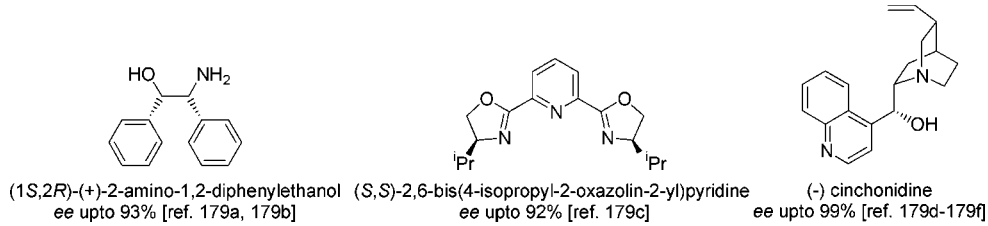
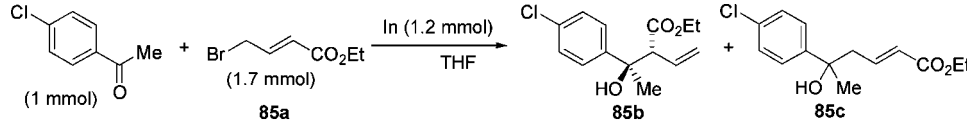


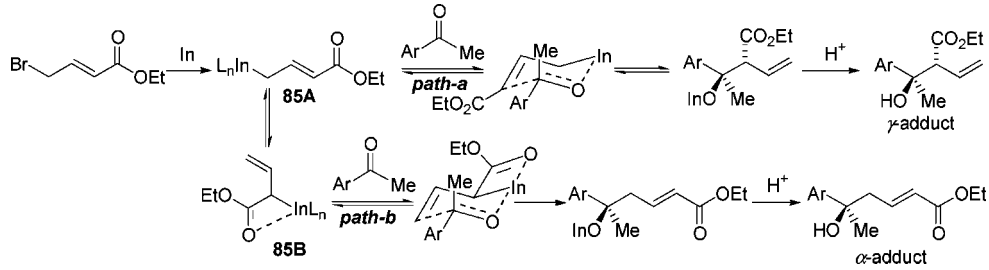
Figure 4. Representative Chiral Promoters in In(0)-Mediated Carbonyl Allylation

Scheme 190

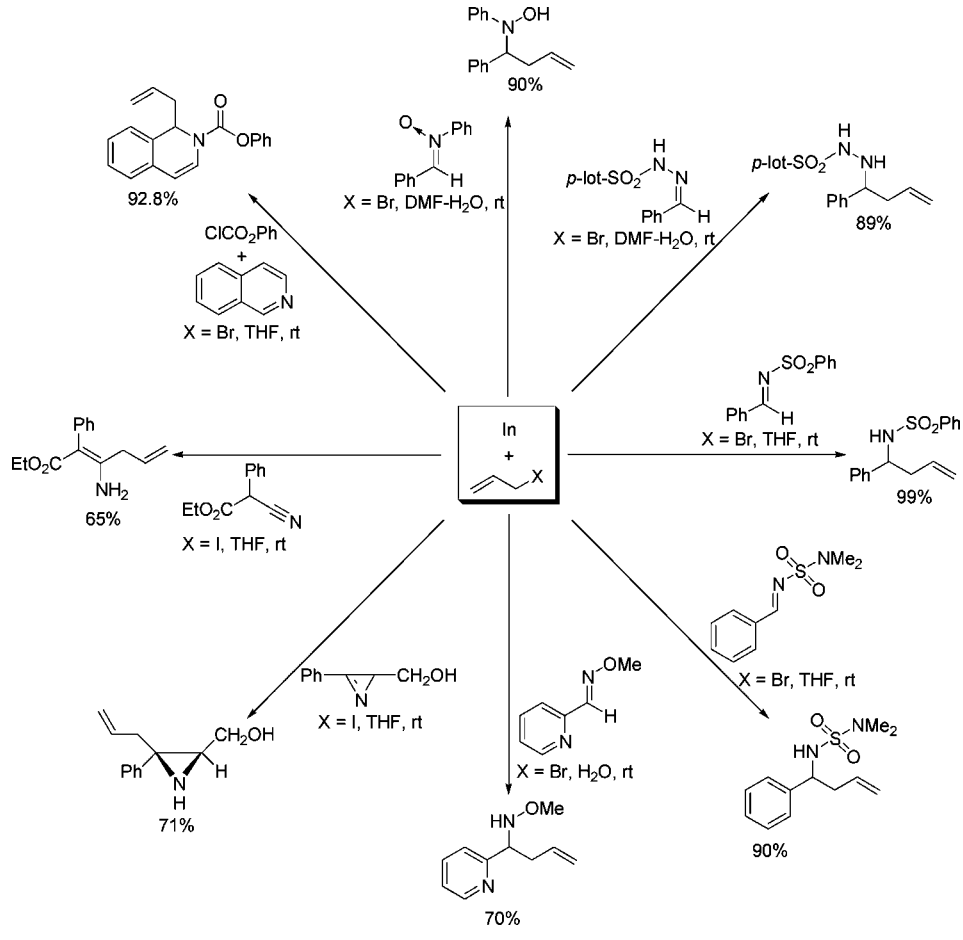


time (h)	85b yield (%)	85c yield (%)
0.5	50	0
17	0	>95

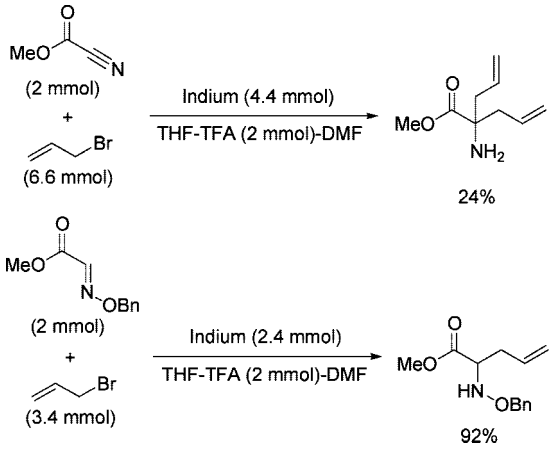
Scheme 191



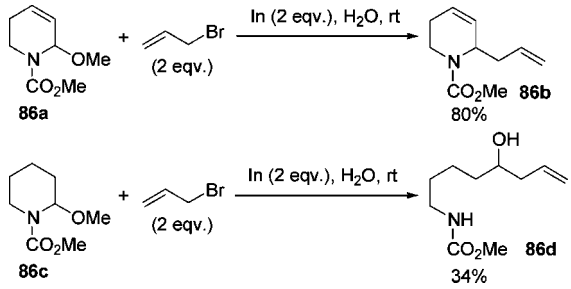
Scheme 192



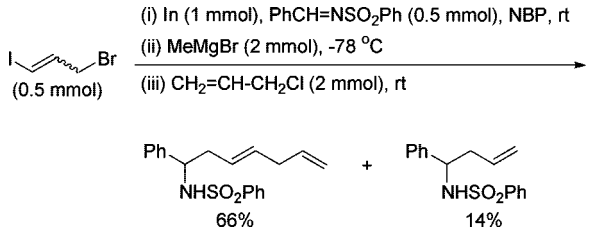
Scheme 193



Scheme 194



Scheme 195



In situ generated allylindium reacts with an activated nitrile or *O*-functionalized oxime, providing the corresponding free (or protected) homoallyl amine in a one pot-process (Scheme 193).[182]

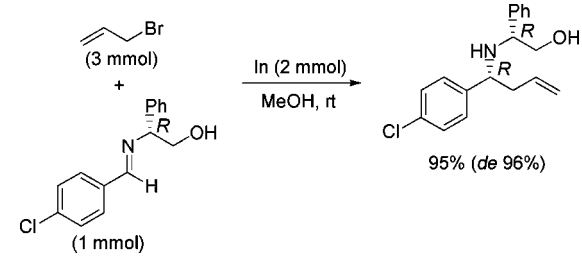
Water as a solvent accelerates the In(0)-mediated allylation of β,γ-unsaturated piperidinium ion which is generated from β,γ-unsaturated-α-methoxy-*N*-methoxycarbonylpiperidine (**86a**) (Scheme 194).[183] Interestingly, a similar reaction with β,γ-saturated-α-methoxy-*N*-methoxycarbonylpiperidine (**86c**) leads to the ring opened product **86d**.

3-Component cascade coupling of 1,3-dihalopropene with sulfonimine and allyl chloride as the other partners can be accomplished using an in situ generated indium ate-complex (Scheme 195).[184]

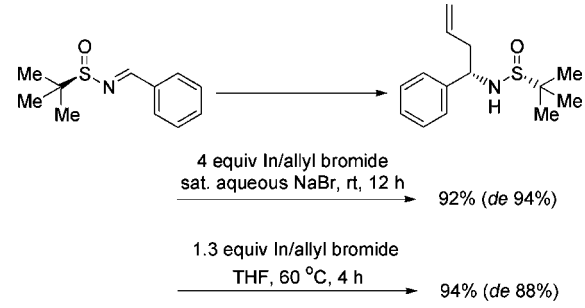
Like its carbonyl counterpart, it is always challenging to achieve highly diastereoselective allylation of imines using In(0) and an allyl electrophile under mild reaction conditions. We have chosen a few recent examples to highlight the success toward this goal. For example, chiral aldimines derived from phenylglycinol can be allylated with allyl bromide in alcoholic solvents to achieve excellent 1,2-diastereoselectivity (Scheme 196).[185]

N-tert-Butylsulfinyl aldimines are also amenable to highly diastereoselective allylation with allyl bromide and In(0), providing the corresponding *N-tert*-butylsulfinylamines

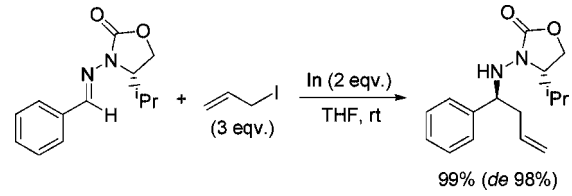
Scheme 196



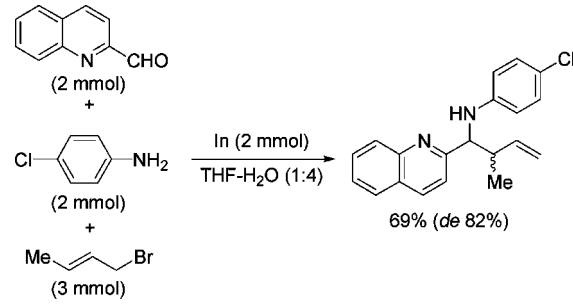
Scheme 197



Scheme 198



Scheme 199



(Scheme 197).[186] The reaction can be conducted either in THF or in saturated aqueous sodium bromide medium.

In situ generated allylindium reacts with chiral hydrazones (derived from both aromatic and aliphatic aldehydes) to provide the corresponding homoallyl amine derivatives with high diastereoselectivity (Scheme 198).[187]

Diastereoselective allylation is also achieved using imines generated in situ from an aryl amine and 2-pyridinecarboxaldehyde or 2-quinolinecarboxaldehyde in aqueous media (Scheme 199).[188]

Metallic indium mediated catalytic asymmetric allylation of imines is of significance recently. Enantioselective addition of an allyl-metal to the imine C═N bond can be grouped into two categories: (i) by the introduction of intrinsic chiral substituents into the substrate imine molecule or (ii) by employing a chiral ligand as an external source of a chiral auxiliary which will bind to the indium center. Most of the stereoselective manipulations of imine with allylindium fall under the first category; however, the difficulty to find proper chiral substituents limits its application. Catalytic Lewis acid

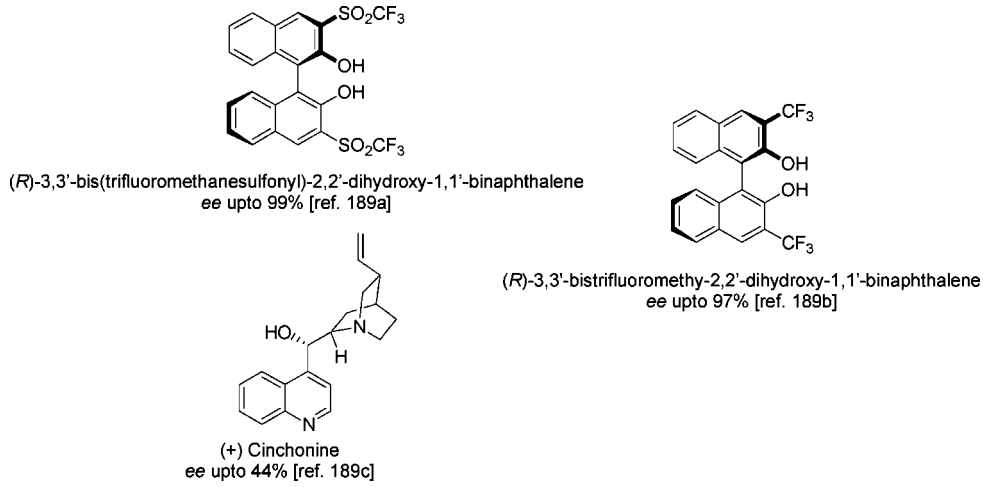
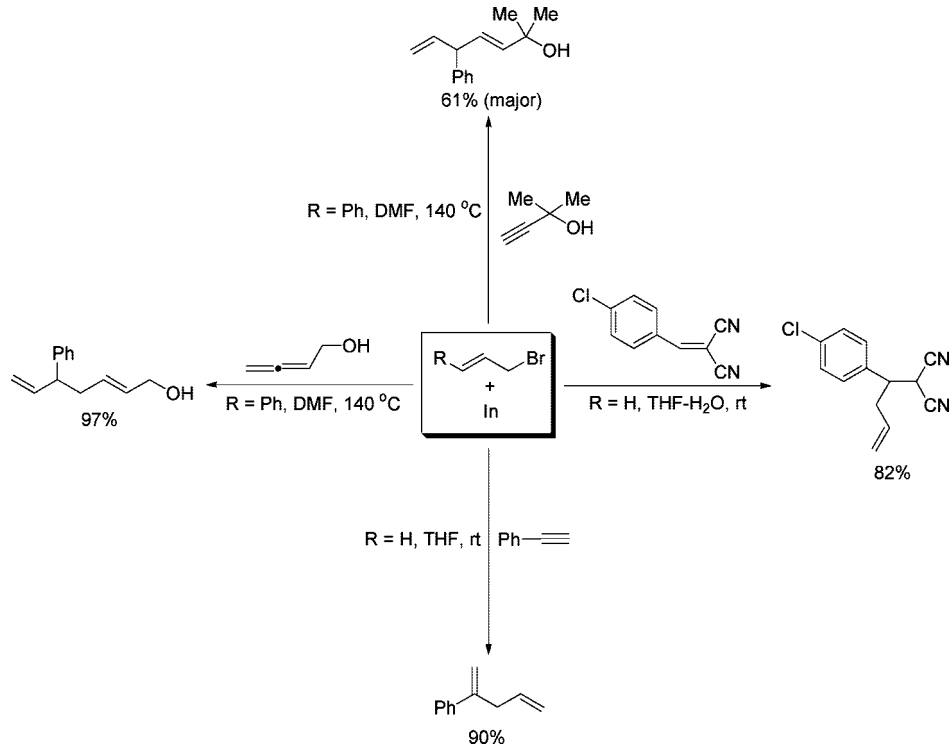


Figure 5. Representative chiral promoters in In(0)-mediated imine allylation.

Scheme 200



promoters are able to enhance the reactivity in some cases, but they also generate the undesirable reverse reaction of converting the imine back to carbonyl and amine functionality. So the second approach seems of more general appeal. However, there is an increasing need to design suitable chiral promoters (ligands) to achieve the same. In Figure 5, we have listed those chiral ligands which constitute successful examples.[189]

Addition to C−C Multiple Bonds

The reaction of in situ generated allylindium with a C−C multiple bond can be categorized into the following classes: carboindation in Markovnikov or anti-Markovnikov fashion, Michael type 1,4-addition, and other S_N2'-like reactions (Scheme 200).[190] The regioselectivity and stereoselectivity aspects of these C−C bond forming reactions are also very important.

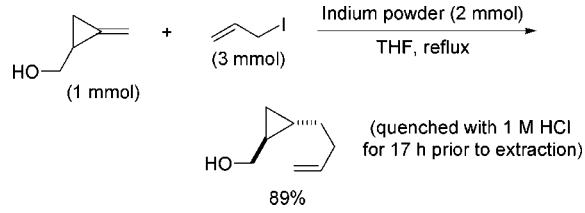
Methylenecyclopropanes with hydroxymethyl pendant at the ring undergo stereoselective allylindation with in situ generated allylindium sesquiiodide to afford the corresponding allylated products, in which the allyl group is attached at the external sp^2 carbon (Scheme 201).[191]

In(0)-mediated intramolecular cyclization of tethered allyl halides onto terminal alkynes proceeds smoothly to give unsaturated carbocycles and heterocycles in good yields (Scheme 202).[192]

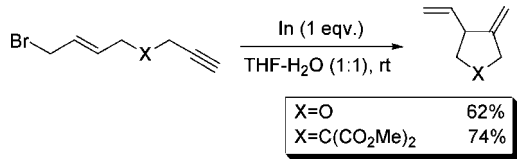
As shown in Scheme 203, addition of allylindium to functionalized allenynes such as **87a** proceeds regioselectively through anti-Markovnikov addition to produce the corresponding dienyne **87b**.[193]

Araki and co-workers recently demonstrated a double allylation protocol from cyclopropenes using in situ generated allylindium sesquiiodide, giving the corresponding *cis*-diallylcyclopropanes in high yields (Scheme 204).[194] The reactions are carried out in a one-pot three-stage fashion. The sequential stages are as follows: (a) *cis*-addition of allyl-In, (b) deprotonation of vinylic-H of the cyclopropene ring by an organometallic reagent (EtMgBr, $Me_2CuCNLi_2$, Et_2Zn,

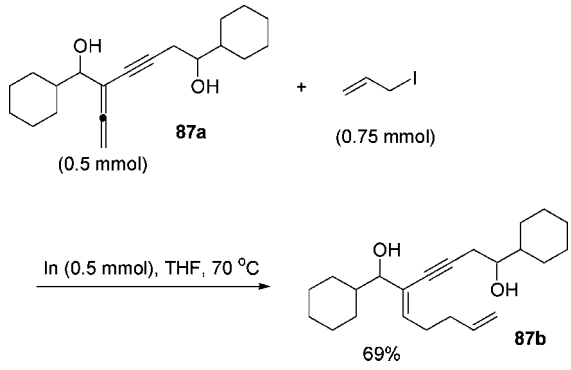
Scheme 201



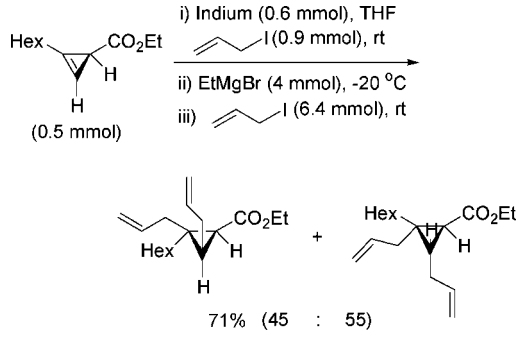
Scheme 202



Scheme 203



Scheme 204



or Et_3Al), and (c) reaction of the resulting intermediate with allyl iodide (Scheme 204).

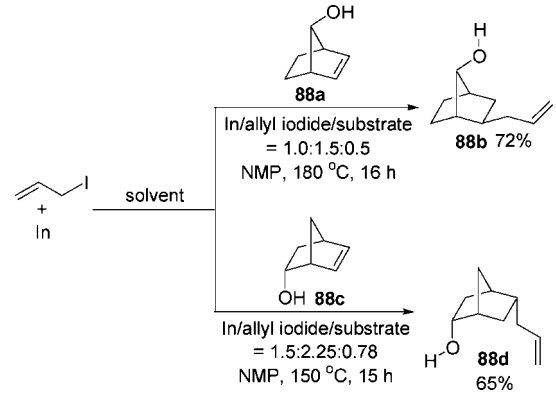
The indium-mediated allylation of nonactivated carbon−carbon double bonds of norborneols **88a** or **88c** proceeds with high regio- and stereoselectivity to afford the corresponding C-allylated derivatives **88b** or **88d** (Scheme 205).[195] Note that the regio- and stereochemistry of the allylindium addition is highly regulated via chelation with the neighboring hydroxyl group.

3-*tert*-Butyldimethylsilyloxyalk-2-enylsulfonium salts, in situ generated from the reaction of α,β-enones with dimethyl sulfide in the presence of TBSOTf, undergo a novel nucleophilic substitution with allylindium(III), providing silyl enol ethers of δ,ε-alkenyl ketones (Scheme 206).[196] The reaction may be viewed as a formal equivalent to Michael addition.

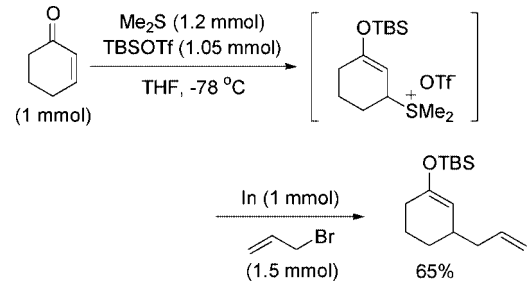
Other Allylative Coupling Reactions

Lee and co-workers have developed a formal indium-equivalent of Stille coupling. This bench-friendly protocol

Scheme 205



Scheme 206



utilizes in situ generated allylindium as the allylating partner.[197] Under the catalytic influence of palladium(0), facile cross-coupling reactions take place between the allylindium reagent and organic electrophiles such as allyl carbonate, aryl/vinyl triflates, vinyl halides, dibromo olefins, and alkynyl iodides (Scheme 207). In most cases, lithium chloride is used as an additive, and the resulting allyl derivatives are obtained in good to excellent yields.

In situ generated allylindium and methallylindium reagents react with a variety of tertiary propargyl alcohols to afford the corresponding tri- and tetra-substituted allenes (Scheme 208).[198] The reaction assumes importance in view of the mild protocol and the absence of other additives.

Apparent *ipso*-subsitution of a hydroxyl group by an allyl functionality is demonstrated in the reaction of 3-hydroxylphthalide with allyl bromides in the presence of In/AcOH in THF as solvent, affording the corresponding allylphthalides (Scheme 209).[199]

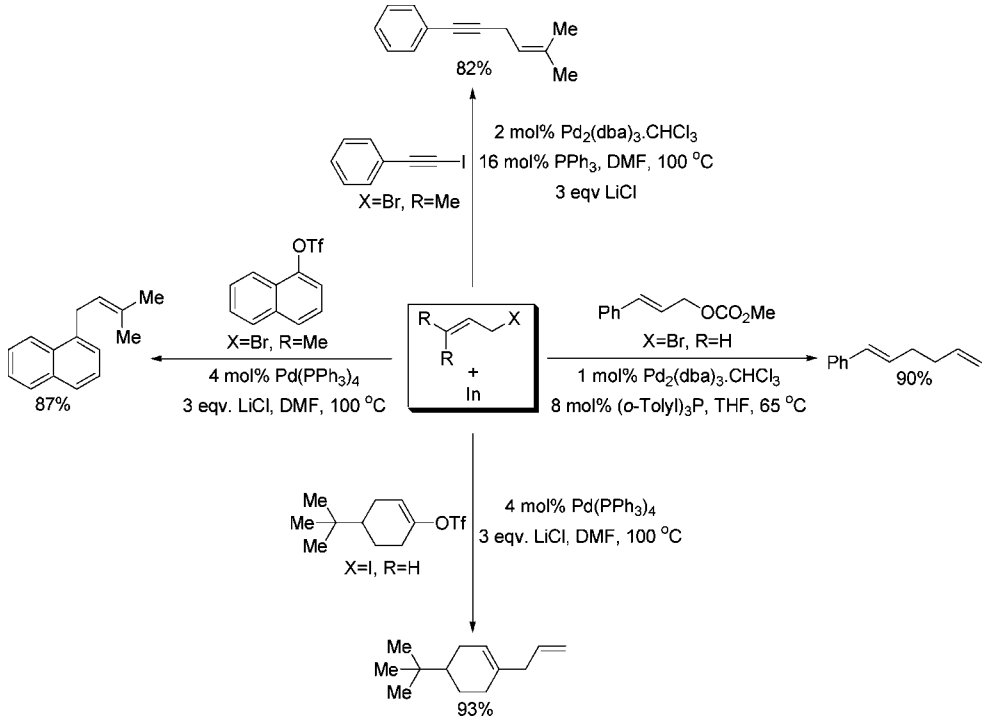
Allylindium reagents, generated in situ from allyl electrophiles and metallic indium, couple efficiently with a number of halides/esters, leading to C−C bond formation.[200−202] Scheme 210 illustrates a few examples where the coupling partner is an acid chloride, a benzyl halide, azetidinones, or a difluoroacylsilane. Note that, in the case of fluorinated acylsilanes, allylation occurs without Brook rearrangement.

In situ generated allylindium halides having remote alkene functionality undergo 5-*exo*-trig cyclization under photochemical or radical reaction conditions (Scheme 211).[203]

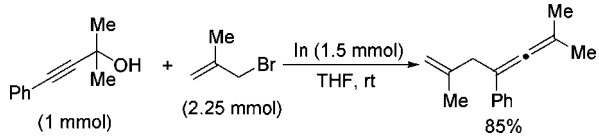
Azabicyclic olefins undergo facile palladium-catalyzed ring-opening with in situ generated allylindium reagents to afford *trans*-3,4-disubstituted hydrazinocyclopentenes in good to excellent yields (Scheme 212).[204]

5-Methylisoxazolines are obtained in good yields through a highly selective nucleophilic addition of allylindium reagent to benzonitrile oxides with concomitant C−O heterocyclization (Scheme 213).[205]

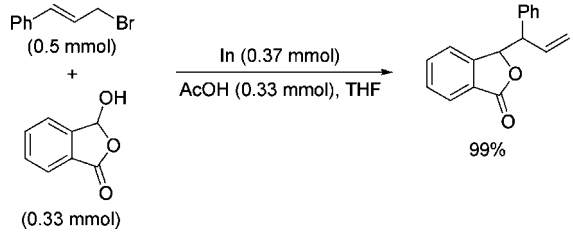
Scheme 207



Scheme 208



Scheme 209

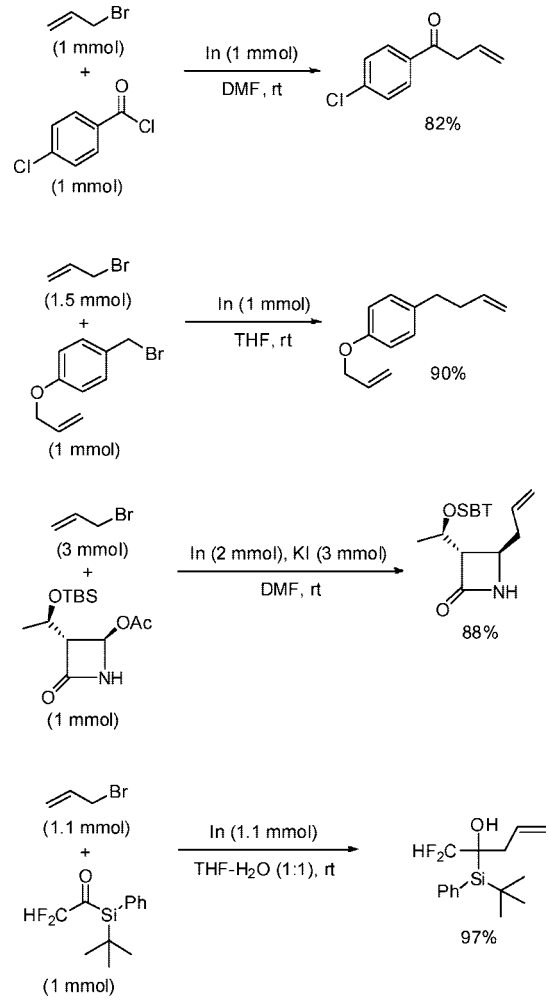


Regio- and stereoselective allylation of pyridinium and quinolinium salts by the addition of in situ generated allylindium reagents toward intermediary cation−π complexes affords a 1,2-adduct preferentially, whereas the addition of a prenylindium reagent gives a 1,4-adduct as the major product with good regio- and stereoselectivities (Scheme 214).[206]

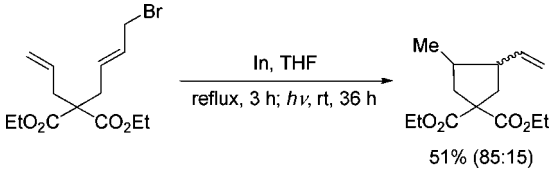
3.3. Allylindium via Direct Transmetallative Activation of Allyl-Sn(IV), Hg(II), and Mg(II)

Allylmetal precursors **89a** (M = Sn, Hg, Mg) undergo transmetalation (with InX/InX_3) or redox-transmetalation (with metallic indium) to generate reactive allylindium(I) or allylindium(III) derivatives (Scheme 215). It may be noted that the transmetallative route for the generation of allylindium derivatives is less explored compared to their allylstannane counterpart (please see section 2.5).

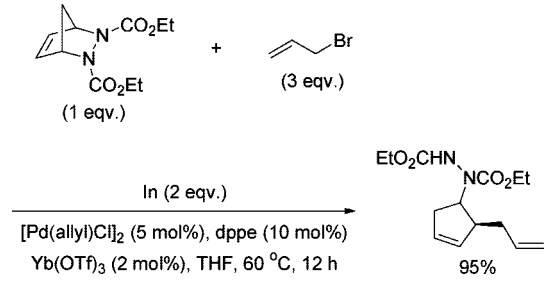
Scheme 210



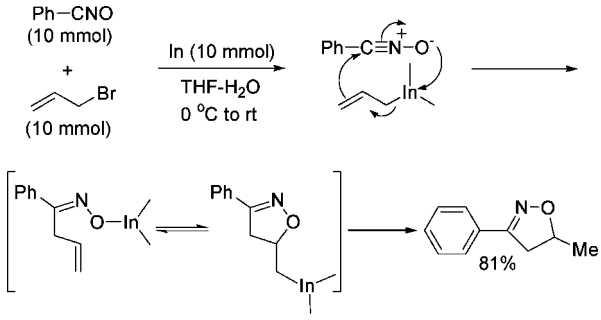
Scheme 211



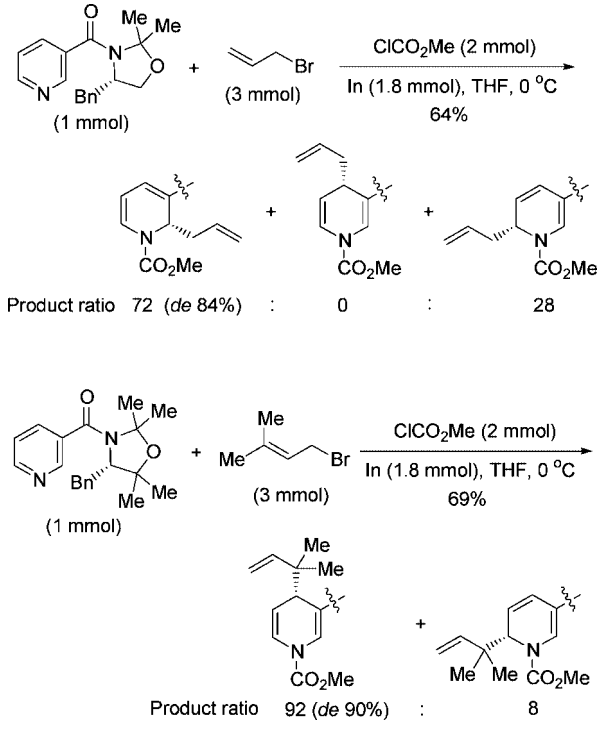
Scheme 212



Scheme 213

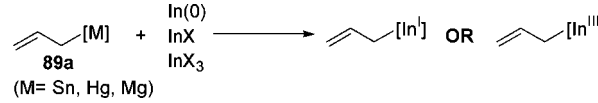


Scheme 214

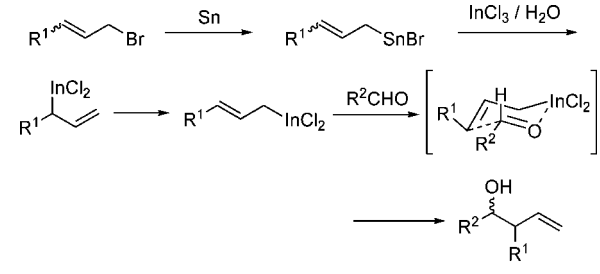


Allylstannanes undergo facile transmetalation via the above strategy to generate allylindium(III) derivatives.[207] The reaction follows an S_E2' pathway and can be carried out in either organic or aqueous medium (Scheme 216). Concomitant one-pot carbonyl allylation provides the corresponding homoallylic alcohols with high regio- and diastereoselectivity.

Scheme 215



Scheme 216



R^1	R^2	yield%	anti/syn
CO_2Et	C_6H_{11}	65%	99:1
Me	Ph	80%	50:50

Baba and co-workers have recently isolated allylindium(III) dihalide via transmetalation between allyltributylstannane and indium trihalide (Scheme 217).[208a] Marshall and co-workers developed an elegant route to chiral monoprotected *anti*-1,2-diols via tin-to-indium transmetalation and carbonyl allylation (Scheme 218).[208b] The high degree of stereoselectivity achieved is due to chelation-assistance similar to the ones discussed earlier (see section 2.5).

Useful levels of remote 1,5-stereocontrol can also be achieved via similar chelation-assisted transmetallative activation/carbonyl allylation (Scheme 219).[209]

Diallylmercury undergoes transmetalation with indium(I) iodide to generate allylindium(I) **70A** in a fully aqueous medium (Scheme 220).[210] It is noteworthy that allylindium **70A** can also be obtained via a novel redox-transmetalation pathway involving diallylmercury and metallic indium. The reactivity of **70A** has been tested by reacting with 2-methylcyclohexanone.

Facile transmetalation involving allylmagnesium halide and indium trihalide generates reactive allylindium(III) intermediates in situ, with the latter being utilized in a follow-up allylation reaction.[172,191,211] For example, allylindium-dichloride **90A** mediates the allylation of unprotected carbohydrates such as ribose **90a** in aqueous ethanol, providing the corresponding allylated derivate **90b** with high diastereoselectivity (Scheme 221).[172]

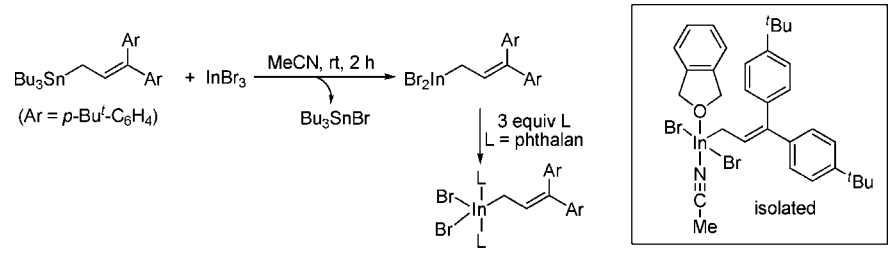
Triallylindium(III), generated via magnesium-to-indium transmetalation, reacts with α,β-unsaturated nitrile and carbonyl compounds to give the corresponding 1,4-addition products (Scheme 222).[212]

3.4. Allylindium via Miscellaneous Routes

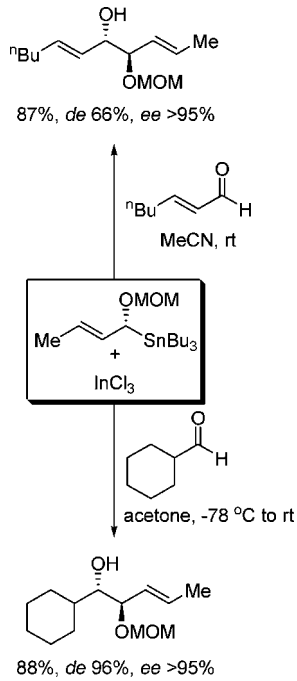
Few examples for the generation of allylindiums that are conceptually distinct from those described so far are included in this section.

Indium(I) iodide is found to mediate the Barbier allylation in the absence of any additive to give homoallylic alcohols (Scheme 223).[213] It appears that such a reaction involves the prior generation of an allylindium(III) intermediate via oxidative addition of allyl halide across indium(I) iodide.

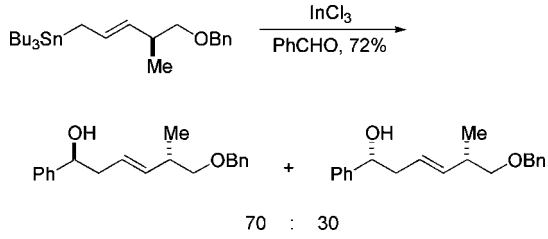
Scheme 217



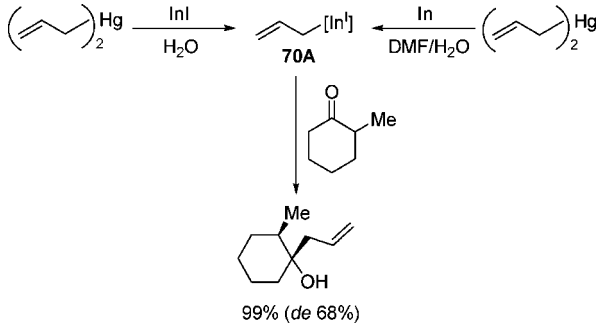
Scheme 218



Scheme 219



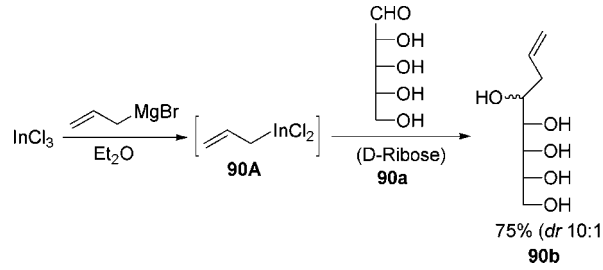
Scheme 220



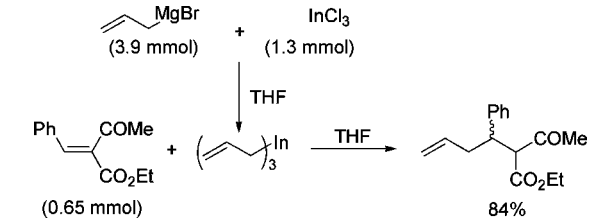
Ranu et al. have reported an unusual indium(I) iodide catalyzed allylation of α,β-unsaturated nitriles leading to the corresponding α,β-unsaturated imines (Scheme 224).[214]

Allylation of various acylhydrazones using a dual combination of catalytic indium(I) and stoichiometric allylbo-

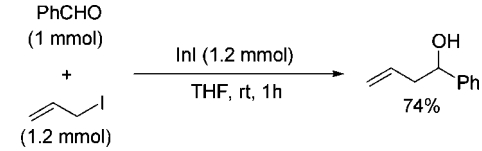
Scheme 221



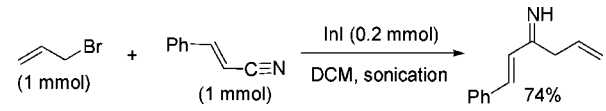
Scheme 222



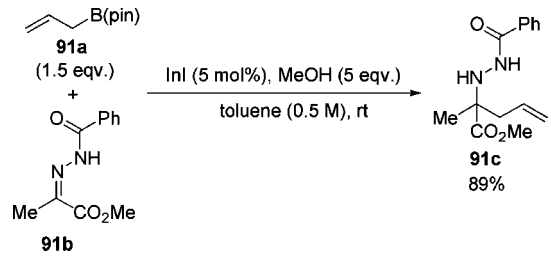
Scheme 223



Scheme 224

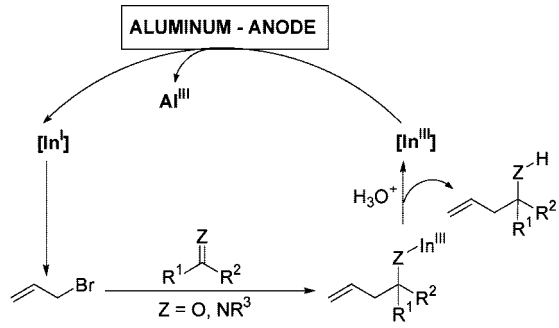


Scheme 225



ron(III) reagent such as **91a** has been developed by Kobayashi and co-workers (Scheme 225).[215] This operationally simple carbon−carbon bond forming reaction displays remarkable substrate scope and functional group tolerance. The strategy is also applied to the allylation of ketones in toluene−methanol medium. While mechanistic investigations are underway, the authors have speculated that the reaction involves a boron-to-indium transmetalation stage.

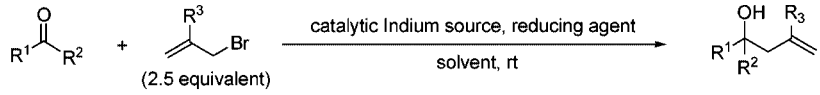
Scheme 226

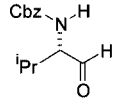
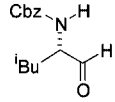
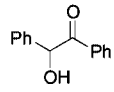


#	R^1	R^2	Z	Product yield (%)
1	C_6H_5	H	O	89
	C_6H_5	Me	O	96
1	C_6H_5	H	NPh	86
2	4-ClC_6H_4	H	NPh	95
4	4-$MeOC_6H_4$	Me	NPh	25[a]

[a] reduced secondary amine is the major product

Scheme 227



#	R^1R^2C=O	R^3	reagent	yield (%)	*de* (%)
1	PhCHO	H	0.1 eqv. In, 5 eqv. Mn and TMS-Cl, THF	88	-
2	$C_6H_{11}CHO$	H		83	-
3	Ph_2C=O	H		98	-
4	PhMeC=O	H		80	-
5		CO_2Me	0.15 eqv. $InCl_3$, 1.3 eqv. Al, THF-H_2O (1:1)	79	60
6		CO_2Me		64	50
7		H	0.1 eqv. In, 5 eqv. Mn and TMS-Cl, THF	81	60

Hilt et al. demonstrated the electroreductive regeneration of low-valent indium(I) reagents for the allylative addition across C=O and C=N double bonds.[216] The protocol has been successful in the case of aldehydes and ketones, as well as for aldimines derived from anilines (Scheme 226). The corresponding homoallylic alcohols or homoallylic amines have been obtained in good yields. However, for ketimines and electron-poor aldimines, direct electrochemical or chemical reduction becomes a competing side reaction. Note that hydrazones and sulfonimines give mostly the reduced products with only minor amounts of the allylated products.[216b]

Interestingly, the electroreductive regeneration of low-valent indium can be substituted by chemical reductants such as aluminum metal or a Mn/TMSCl reagent.[151,176,177a] Use of catalytic indium in these reactions is noteworthy. A few examples are shown in Scheme 227.[151] The proposed catalytic cycle is analogous to the allylation using aluminum metal and catalytic tin(II) chloride (vide Scheme 128).

4. Conclusions

"Tell me, is the rose naked
Or is that her only dress?
Why do trees conceal
The splendor of their roots?"
Pablo Neruda [The Book of Questions]

We hope that the deliberations in this account have enlightened the reader on *the core organometallic concepts* which constitute the *roots* to "making and breaking of an allyl−Sn or an allyl−In bond in situ".

In a nut-shell, the in situ generation of Sn−C/In-C may be viewed under two major classes: (i) a redox-transmetalation pathway involving allyl transfer from "allyl-[Tm]" to Sn(II)/In(I), ensuring catalytic regeneration of the [Tm] reagent, and (ii) oxidative−addition of allyl halide and surrogates across Sn(0)/In(0) without assistance of a Tm-partner. The reader might have also noticed that the "allyl-

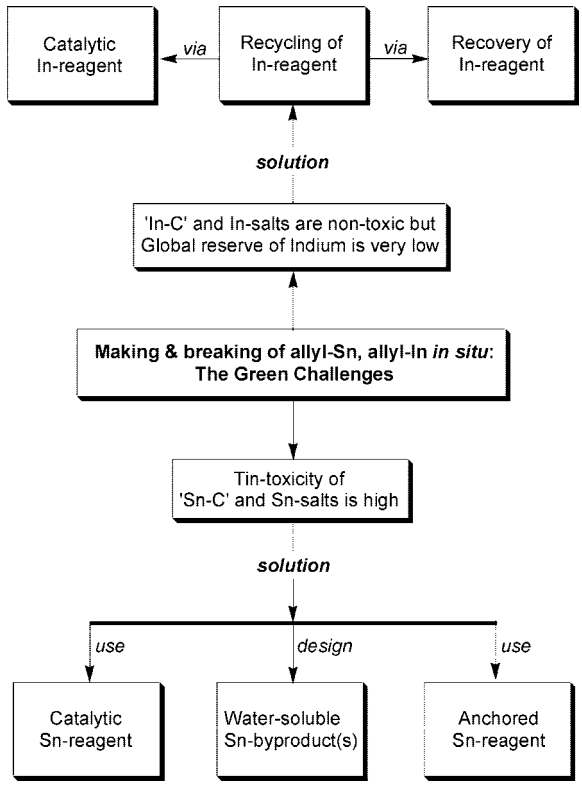


Figure 6.

Sn/In" generated via the above routes further serves as a source of an allyl-nucleophile in the follow up C−C bond formation.

A process chemist is expected to appreciate the splendor of the above concepts due to the usefulness of the in situ and one-pot strategies in generating a diverse range of end "organic structural motifs" with tunable-selectivity. On the other hand, someone interested in mechanistic aspects may like to raise questions on the explicit relationship(s) between various selectivities and the catalytic intermediates.

What is the future scope of explorations in the area of "*in situ/one-pot* Barbier-like chemistry of allyl-Sn and allyl-In reagents"? Instead of posing long-distance objectives and scopes, we would like to emphasize a few key areas which need immediate exploration to strengthen the roots and enrich the overall beauty of the chemistry. In our view, these areas are (i) broadening the scope of the redox-transmetalation strategy by incorporating a Tm/Sn(0) and Tm/In(0) partnership, (ii) enhancing the synthetic utility from a small building-block to a complex architectural design invoking multistep strategies and chiral executions, (iii) probing the mechanistic details further to better our understanding of the origin of various selectivity issues vis-à-vis the nature of "allyl-Sn/In" intermediates, and finally (iv) accepting the green challenges. In the green-frontier, one may note that in the case of Sn-reagents, tin-toxicity is a major concern.[2a,217] While In-reagents are apparently nontoxic, the estimated global reserve of indium is very low.[218] Therefore, multiprong synthetic strategies are required (Figure 6) to take care of the above issues and thereby greening the related chemistry.

5. Acknowledgments

S.R. extends his thanks to the colleagues of *the tin-group* (including the current and former members), in particular to those whose names appear in the reference section. He expresses his warm gratitude to Professors Ranajit De, B. D. Gupta, and R. J. Puddephatt for their intellectual influence in his formative years and to Prof. S. Chandrasekaran for much help and inspiration. He is also indebted to his wife Indira and daughter Ipsita for their constant encouragement and support. Generous research funding from DST, CSIR, and GAIL is duly acknowledged. U.K.R. thanks UGC, CSIR, and DST for fellowships.

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