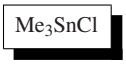
Chlorotrimethylstannane



[1066-45-1] C_3H_9ClSn (MW 199.25)
InChI = 1/3CH3.ClH.Sn/h3*1H3;1H;/q;;;;+1/p-1/f3CH3.Cl.Sn/h;;;1h;/q;;;-1;m/rC3H9ClSn/c1-5(2,3)4/h1-3H3
InChIKey = KWTSZCJMWHGPOS-CEHDEUOCCS

(starting material for the synthesis of alkyl-, allyl-, alkenyl-, and alkynyltrimethylstannanes and trimethyltin enolates; palladium-catalyzed coupling reactions[14])

Alternate Name: trimethyltin chloride.
Physical Data: mp 37–39 °C; bp 153–156 °C.
Solubility: sol ether, THF, hexane, CH_2Cl_2.
Form Supplied in: white solid; widely available.
Handling, Storage, and Precautions: is air stable, but is decomposed by moisture. Commercially available trimethyltin chloride may be used as received. The reagent is very toxic and corrosive, and should be handed with gloves in a fume hood.

Original Commentary

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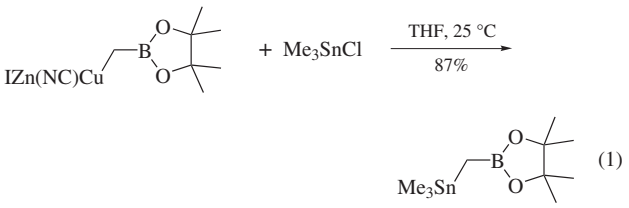
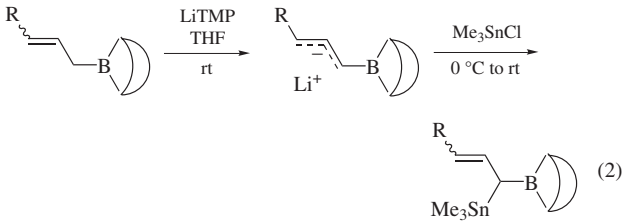
Introduction. Trimethyltin hydride, cyanide, methoxide, azide, and lithium are prepared from trimethyltin chloride by the procedures similar to those given in ***Tributylchlorostannane***. Similarly, hexamethylditin, bis(trimethyltin) oxide, and diethylaminotrimethyltin are prepared from trimethyltin chloride.

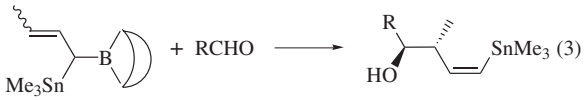
Organotrimethyltins via Transmetalation. Lithiated 1,3-dithianes react with trialkyltin or triphenyltin chlorides to form the corresponding 1,3-dithian-2-yltin compounds.[1] The organocopper compound, derived from (α-(dialkoxyboryl)alkyl)zinc iodide and CuCN·2LiCl, reacts with trimethyltin chloride to afford the α-boron substituted organotin in 87% yield (eq 1).[2] Accordingly, sulfur- and boron-stabilized anions are readily converted to the corresponding trimethyltin derivatives.



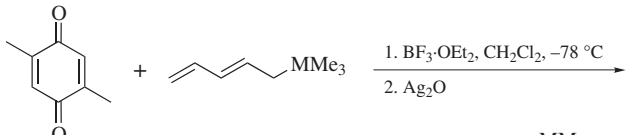
Allyl anions are also transformed to the corresponding allyltrimethyltin derivatives in high yields. Allyl anions substituted by 9-BBN, generated from ***B-Allyl-9-borabicyclo[3.3.1]nonane*** by treatment with ***Lithium 2,2,6,6-Tetramethylpiperidide*** (LTMP) react with trimethyltin chloride to afford the α-trimethyltin-substituted allyl-9-BBN in good yields (eq 2).[3] Trimethyltin bromide may also be used in this procedure. The resulting allylic borane reacts with aldehydes in the presence of pyridine to produce the *anti*-homoallyl alcohols with a (*Z*)-alkenyltrimethylstannyl group (eq 3)[4] (see also ***9-[1-(Trimethylsilyl)-2(E)-butenyl]-9-borabicyclo[3.3.1]nonane***). γ-Chloro-substituted allyltrimethyltins are prepared by the reaction of trimethyltin chloride with chloro-substituted allyllithiums, which are generated from allyl chlorides and LTMP.[5] 2,4-Pentadienyltrimethylstannane, prepared by the reaction of pentadienyllithium with trimethyltin chloride, reacts with *p*-quinones in the presence of $BF_3{\cdot}OEt_2$ to afford the corresponding pentadienylated conjugate adducts in fair to good yields without formation of the Diels–Alder adduct (eq 4).[6] On the other hand, the use of 2,4-pentadienyltrimethylsilane produces the Diels–Alder adduct exclusively. The tin reagent produces the conjugate adducts with *p*-quinones, regardless of the substituents and their substitution pattern. With α,β-unsaturated aldehydes, the pentadienyl tin reagent gives the 1,2-adducts (pentadienyl carbinols), whereas the 1,4-adduct is obtained with chalcone.[6] Here also, the reaction of pentadienyltrimethylsilane with crotonaldehyde affords the corresponding Diels–Alder adduct.[7]



R = Bu, 70%; Me, 72%

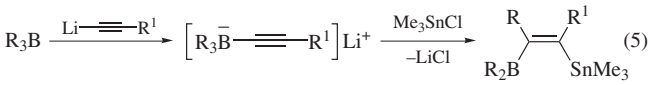


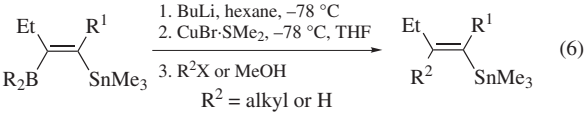
R = Ph, 70%; Bu, 70%



M = Sn	86%	0%
M = Si	0%	91%

The intramolecular transfer reaction of lithium 1-alkynyltrialkylborates, prepared in situ from lithium acetylides and trialkylboranes, induced by trimethyltin chloride is highly stereoselective, with the resultant dialkylboryl-substituted alkenylstannanes having the migrating alkyl group *trans* to the trialkyltin group (eq 5).[8] Conversion of the resulting dialkylboryl group (R = Et) to the alkenylcopper followed by treatment with methanol or alkyl halides produces di- or trisubstituted alkenyltrimethylstannanes, respectively (eq 6).[9] By starting from conjugated terminal enynes, 2-(trimethylstannyl)-1,3-butadienes are similarly synthesized.

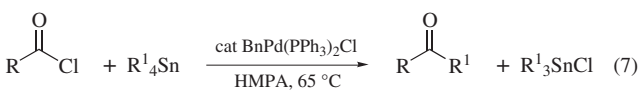




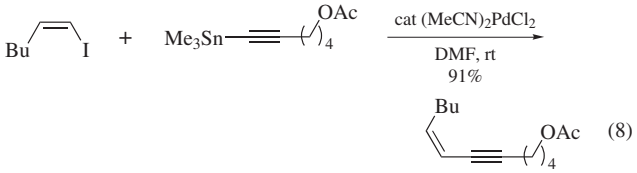
Alkenylstannanes have been utilized for a variety of synthetic applications. The palladium-catalyzed coupling reaction of vinyl triflates and vinyl halides with alkenylstannanes affords 1,3-dienes.[10] The facile transmetalation reaction between alkenylstannanes and alkyllithiums remains as one of the most direct routes to certain alkenyllithium reagents. Treatment of alkenylstannanes with iodine affords the corresponding vinyl iodides with retention of configuration of the vinyl group.

Although the hydrostannylation reaction of alkynes provides a simple route to alkenylstannanes, it is generally not stereoselective. The addition reaction of (trialkylstannyl)copper and related reagents to 1-alkynes and α,β-alkynic esters and amides exhibits high regio- and stereoselectivity.[11] Vinyl triflates and vinyl iodides have also been converted to alkenylstannanes by the reaction with $Me_3SnMgMe$ in the presence of ***Copper(I) Cyanide*** catalyst.[11b] The hydroalumination of alkynes with ***Diisobutylaluminum Hydride*** followed by treatment with ***Methyllithium*** yields alanates, which are converted to alkenyltrimethylstannanes by addition of trimethyltin chloride (see also ***Tri-butylchlorostannane***).[12] Generally, conversion of vinylalanes to alanates (ate complexes) is needed to enhance the reactivity toward electrophiles such as Me_3SnCl. The direct transmetalation of vinylalanes to vinylstannanes is accomplished by carrying out the reaction with Me_3SnCl in the presence of LiX (X = Cl, Br, I) in DME.[13]

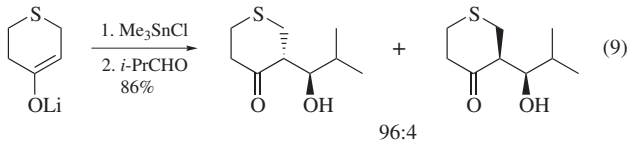
Palladium-catalyzed Reactions. ***Benzylchlorobis(triphenylphosphine)palladium(II)*** catalyzes the reaction of acid chlorides with tetraorganotin compounds (Me_4Sn, Ph_4Sn, Ph_3SnMe, Me_3SnCH_2Ph, $(PhCH_2)_4Sn$, Bu_4Sn, $Bu_3SnCH{=}CH_2$, Me_3SnCl) to give ketones in quantitative yields (eq 7).[14] Trimethyltin chloride (1 equiv) also reacts with benzoyl chloride to give acetophenone in quantitative yield, although the reaction takes five times longer to reach completion than the reaction using ***Tetramethylstannane***. By using a trimethyl- or tributylorganotin reagent, the group other than the methyl or butyl groups transfers exclusively in the following order: RC≡C > RCH=CH > aryl > RCH=$CHCH_2$ ≈ arylCH_2 > $MeOCH_2$.



The palladium-catalyzed coupling of alkenyl iodides with alkynyltrimethylstannanes takes place under mild conditions, stereospecifically and chemoselectively, to give high yields of conjugated enynes (eq 8).[15] Organic groups on tin undergo selective transmetalation with palladium, as shown above, and the alkynic group has the fastest transfer rate of all the organic substituents.



Trimethyltin Enolates. Trimethyltin enolates, prepared in situ from lithium enolates and trimethyltin chloride, undergo a rapid aldol condensation with aldehydes to give nearly a 1:1 mixture of the *syn* and *anti* aldols in high yields.[16] However, the trimethyltin enolate generated in situ from the lithium enolate of 4-thianone gives the *anti* aldol with very high diastereoselectivity upon treatment with 2-methylpropanal (eq 9).[17] The lithium enolate itself also provides high *anti* diastereoselectivity (95:5) in this case.



First Update

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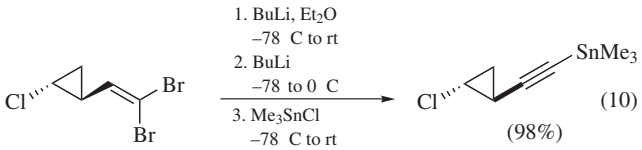
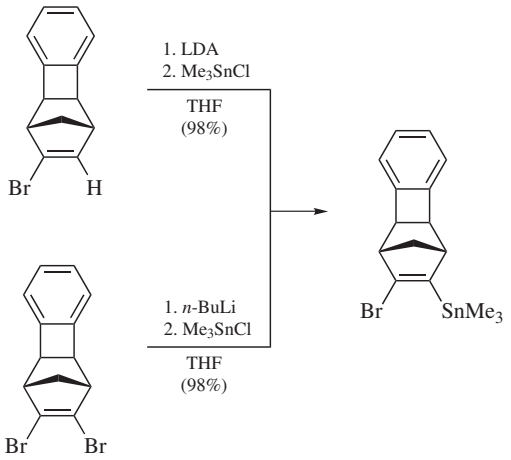
Organotrimethyltins via Transmetalation.

Preparation of sp, sp^2, and sp^3 Organostananes. Lithium–tin exchange is a well-established method for making organostannanes. Recent applications of chlorotrimethylstannane in such exchanges include the treatment of dibromoalkenes (eq 10)[18] or bromoalkynes[19] with butyllithium followed by addition of Me_3SnCl to provide the corresponding alkynylstannanes in good yields.

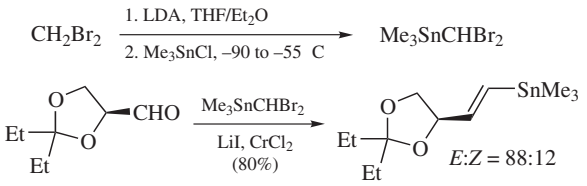


Trimethyltin substituted arylstannanes have been prepared from chlorotrimethylstannane and aryllithiums, which themselves can arise from hydroxy[20] or amine group-directed orthometalation reactions. Vinyltrimethylstannanes can be similarly generated. For example, irrespective of its method of generation, a vinyllithium can be trapped with Me_3SnCl to provide for an efficient synthesis of a bromosubstituted vinylstannane (eq 11).[21]



(11)

An alternative approach to trimethylvinylstannanes involves the chromium-mediated reaction of $Me_3SnCHBr_2$ with aldehydes (eq 12).[22] Here, the trimethyldibromomethylstannane reagent is prepared by the reaction of LDA and methylene bromide followed by treatment with chlorotrimethylstannane. As with many reactions of Me_3SnCl, the same process can also be carried out with Bu_3SnCl; however, in this chemistry, $Bu_3SnCHBr_2$ gave much lower yields of the corresponding vinylstannanes, albeit with improvements in the *E/Z* product ratios.



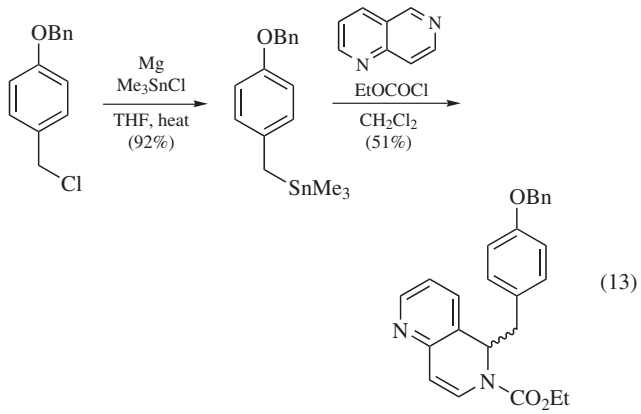
(12)

Vinyltrimethyltins can also be efficiently prepared by Pd-catalyzed hydrostannations of alkynes with trimethyltin hydride generated in situ from the reduction of chlorotrimethylstannane by polylmethylhydrosiloxane (PMHS)[23] or Red-Sil[24] that have been made hypercoordinate with KF(aq).[25]

Allyltrimethylstannanes can also be prepared via lithium/tin exchange.[26] Likewise, benzyltrimethylstannanes can be prepared under Barbier conditions by reacting the corresponding benzyl chlorides with Mg(0) and then chlorotrimethylstannane. Such a process has been used in the facile syntheses of benzyl-substituted dihydroisoquinolines and dihydronaphthyridines. For example, a benzylstannane prepared in this manner participated in the nucleophilc alkylation of 1,6-naphthyridine in the presence of ethyl chloroformate (eq 13).[27]

Unactivated organolithiums can also transmetalate with chlorotrimethylstannane. An interesting example of such a reaction is shown in eq 14. In this case, Me_3SnCl was trapped by an organolithium species that was generated during the cyclization of an α-amino carbanion, which itself came about from the tin–lithium exchange of a tributyltin moiety.[28]

Preparation and Application of Chiral Organostannanes. Transmetalations involving chlorotrimethylstannane have figured prominently in asymmetric syntheses. Chlorotrimethylstannane reacts with asymmetric carbanions to afford enantioenriched stannanes. For example, deprotonation of **1** with *n*-BuLi/(–)-sparteine proceeds smoothly and the resultant lithium compound can be trapped with Me_3SnCl to afford stannane **2** with full retention of stereochemistry (eq 15).[29] Optically active allyltrimethylstannanes can also be made in this way.[30]



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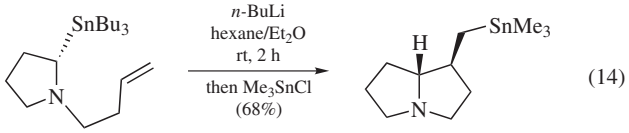

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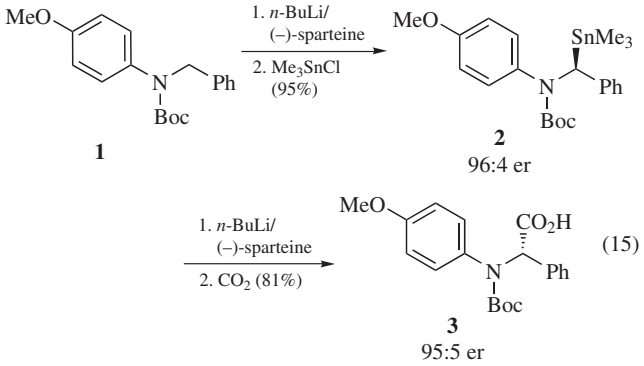


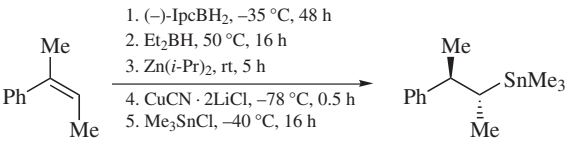
(15)

Stereochemically pure organostannanes may also be transmetalated with organolithiums. The stereochemical course of such tin–lithium exchanges depends on the conditions and substrates employed, with either retention[31] or inversion[32] of configuration possible. In the case of optically active stannane **2** (eq 15), reaction with *n*-BuLi/(–)-sparteine and then CO_2 produces the stereoinverted enantioenriched amino acid **3**.[33]

Another approach to chiral organostannanes involves the stereospecific asymmetric hydroboration of *E*- or *Z*-trisubstituted alkenes, followed by a series of transmetalations (B–Zn–Cu–Sn) that culminate in the reaction of chlorotrimethylstannane with an organocopper species. Such sequences furnish optically active organostannanes with excellent control of absolute and relative stereochemistry (eq 16).[34]

An optically active propargyl trimethylstannane has been prepared with chirality transfer from a chiral allenyltitanium reacting with chlorotrimethylstannane. The chiral allenyltitanium is generated in situ by the reaction of enantioenriched propargyl phosphates and Ti(O-*i*-Pr)$_4$/*i*-PrMgCl.[35] Resubjecting the optically active propargyl trimethylstannane to Ti(O-*i*-Pr)$_4$/*i*-PrMgCl and then water, allows for the stereoselective formation of the

Z-allylic trimethylstannane with conservation of the stereogenic center (eq 17).



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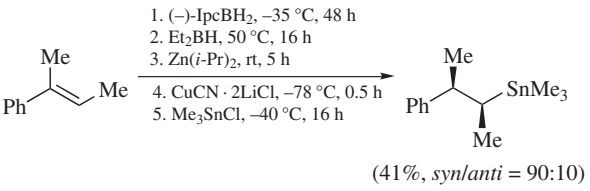
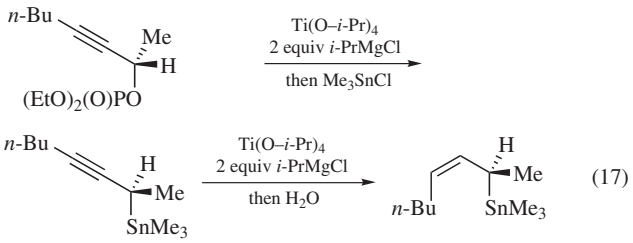
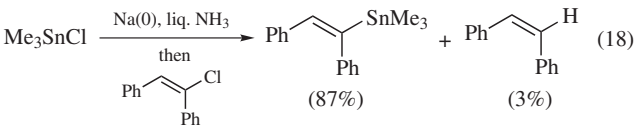




(17)

Finally, the stereospecific transmetalation of cyclopropylmagnesium reagents with chlorotrimethylstannane has also been reported for the preparation of cyclopropylstannanes.[36]

Generation and Reaction of Trimethylstannyl Nucleophiles. Trimethylstannyl anions can be easily prepared by treatment of chlorotrimethylstannane with Na or Li metal. Such anions are strong nucleophiles, which readily participate in the formation of tin–carbon bonds through a variety of pathways including S_N2 reactions,[37] $S_{RN}1$ reactions (eq 18),[38] and halogen–metal exchanges.[39]



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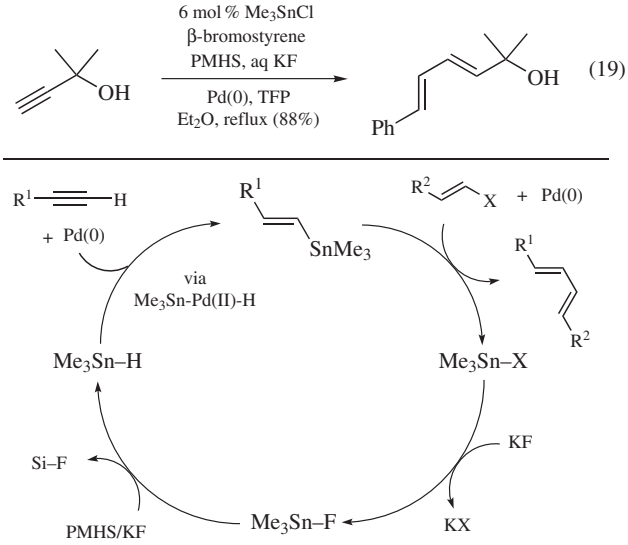
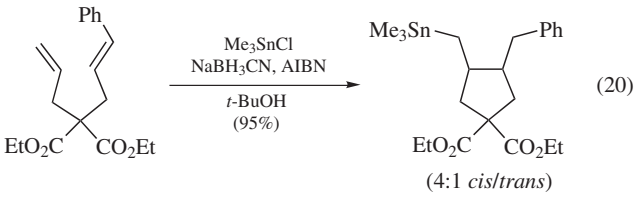
In Situ Generation and Reaction of Trimethyltin Hydride.

Stille Reactions Catalytic in Tin. As previously discussed, it has been reported that vinyltrimethyltins can be efficiently prepared by Pd-catalyzed hydrostannations with trimethyltin hydride that is generated in situ from chlorotrimethylstannane.[25] It has also been shown that vinyltrimethyltins, so formed, can be used in a one-pot hydrostannation/Stille sequence. Moreover, the trimethyltin halide by-product of the Stille reaction can be recycled back to trimethyltin hydride, thereby rendering the entire process catalytic in tin (eq 19).[40,41] It is important to note that Me_3SnCl is superior to Bu_3SnCl in this chemistry, as vinyltributylstannanes react too slowly to maintain good catalyst turnover numbers.



(19)

Radical-mediated Carbocyclizations. Trimethyltin hydride can also be prepared by the $NaBH_3CN$ reduction of chlorotrimethylstannane. This combination can be joined with catalytic AIBN to create conditions that will affect radical-mediated carbocyclizations. In this way unactivated dienes or trienes can be transformed to a variety of carbocycles, including tetrahydrofurans, pyrrolidines, etc. (eq 20).[42]



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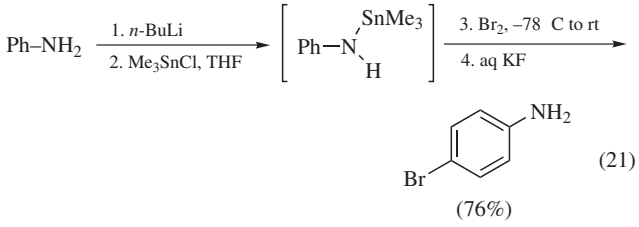
In Situ Generation and Reaction of Trimethyltin Amides and Ethers.

Trimethyltin Amides and the Regioselective Bromination of Aromatic Amines. Chlorotrimethylstannane also reacts efficiently with lithium amides to afford trimethyltin amides. This reaction has been employed elegantly in the selective one-pot bromination of amino-substituted arenes and heteroarenes.[43] Here, the trimethyltin amide can be made by the treatment of an aromatic amine with *n*-BuLi, followed by the addition of Me_3SnCl (eq 21). The in situ generated *N*-trimethyltin substituted aromatic amine is then treated with bromine. The trimethyltin moiety appears to create a steric block to orthobromination. As a result, the reactions tend to be highly regioselective in favor of the *para*-brominated compounds (an exception to this rule is 2-aminonaphthalene, which gave 1-bromo-2-amino naphthalene in 91% yield). At the end of this sequence the reaction mixture is exposed to aq KF, which cleaves the trimethyltin amide to afford the *para*-brominated arene.

Trimethyltin Ether-mediated Cyclizations. During their synthesis of amphidinolide K, Williams and Meyer found that stereoselective formation of a 2,5-cis-tetrahydrofuran benefited from the addition of chlorotrimethylstannane to the reaction.[44] The role

of this additive is to generate the trimethyltin ether, which maintained the nucleophilicity of the oxygen, thus accelerating the Pd-mediated cyclization and suppressing unwanted intramolecular acyl transfer (eq 22).



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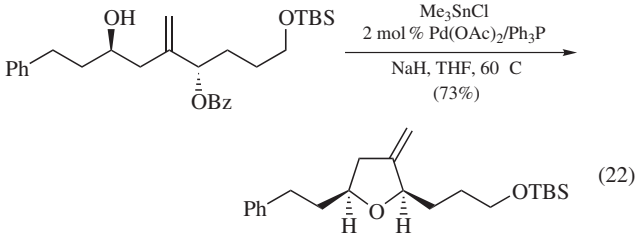
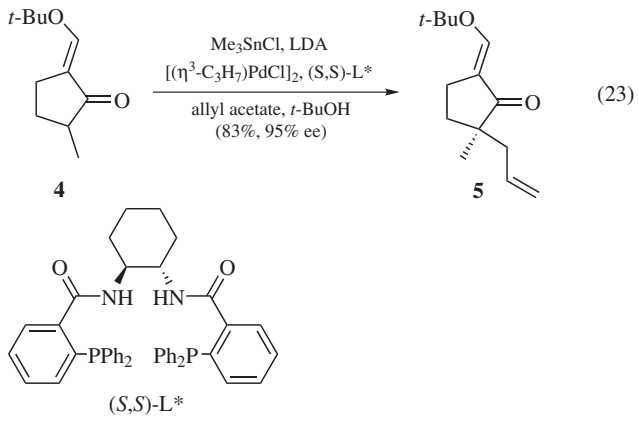


(22)

Chlorotrimethylstannane as a Lewis Acid in Asymmetric Allylic Alkylations. Chlorotrimethylstannane can serve as a Lewis acid in the asymmetric alkylation of ketone enolates to generate quaternary carbon centers. For example, reaction of ketone **4** with LDA in the presence of a catalytic amount of a chiral palladium complex, allyl acetate, and Me_3SnCl affords allylated product **5** in 83% yield and with 95% ee (eq 23).[45] Such reactions have proven useful in the total syntheses of hamigeran B[46] and allocyathin B_2.[47] It is also worth noting that, while Bu_3SnCl, can be used in place of Me_3SnCl, the reaction yields and enantiomeric excesses tend to be slightly better when Me_3SnCl serves as the Lewis acid.



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