

Fluorination

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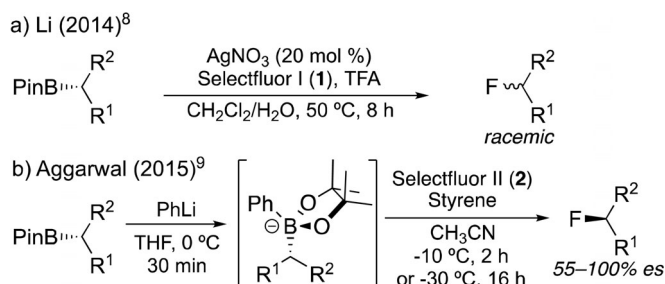
Stereospecific Electrophilic Fluorination of Alkylcarbostannatrane Reagents

Xinghua Ma, Mohamed Diane, Glenn Ralph, Christine Chen, and Mark R. Biscoe*

Abstract: We report the use of isolable primary and secondary alkylcarbostannatrane nucleophiles in site-specific fluorination reactions. These reactions occur without the need for transition metal catalysis or in situ activation of the nucleophile. In the absence of the carbostannatrane backbone, alkyltin nucleophiles exhibit no activity towards fluorination. When enantioenriched alkylcarbostannatranes are employed, fluorination occurs predominately via a stereoinvertive mechanism to generate highly enantioenriched alkyl fluoride compounds. These conditions can also be extended to stereospecific chlorination, bromination, and iodination reactions.

Incorporation of carbon–fluorine bonds into drug candidates has been shown to improve pharmacological properties such as metabolic stability, bioavailability, and solubility compared to their non-fluorinated analogs.^[1] Rapid, late-stage incorporation of ¹⁸F into organic molecules also enables the preparation of new radiochemical probes for positron emission tomography (PET) imaging.^[2] Therefore, efficient methods by which to install C–F bonds rapidly and reliably are of great synthetic importance.

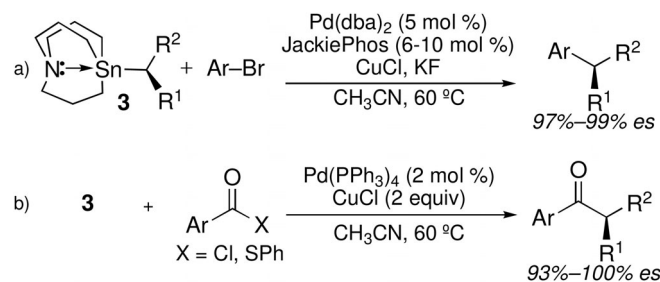
Over the past few years, significant advances have been made in the preparation of aryl fluorides using electrophilic and nucleophilic fluorine sources.^[3] However, fewer methods have been reported that enable the incorporation of fluorine into aliphatic units with high regiochemical and stereochemical control. Recently, Ritter^[4] and Doyle^[5] have separately developed powerful methods to effect the stereoinvertive deoxyfluorination of alcohols. These deoxyfluorination reactions, as well as earlier processes using DAST and Deoxyfluor,^[6] directly employ enantioenriched alcohols as the source of stereochemistry. Gandelman^[7] and Li^[8] (Scheme 1 a) have reported transition-metal-catalyzed approaches towards the preparation of alkyl fluorides. These processes proceed through radical intermediates, and therefore the stereochemistry of the resulting alkyl fluoride is difficult to control in a general manner. Stereospecific electrophilic fluorination of configurationally stable organometallic nucleophiles constitutes an alternative route towards the preparation of enantiomerically enriched alkyl fluoride compounds,



Scheme 1. Electrophilic fluorination of enantioenriched secondary alkylboron reagents.

which could enable direct, late-stage access to fluorinated compounds that are inaccessible using the aforementioned processes. Because chiral secondary alkylboron and alkyltin compounds exhibit high configurational stability, enantioenriched alkylboron and alkyltin compounds are ideal candidates for use in stereospecific fluorination reactions. Aggarwal has nicely demonstrated the power of this approach using phenyl lithium-activated, enantioenriched alkylboronate nucleophiles in stereospecific electrophilic substitution reactions with Selectfluor II (2) (Scheme 1 b).^[9,10] The use of alkyltin reagents has not been previously reported in this capacity, yet may offer important synthetic advantages over other methods.

Our research group has recently begun to investigate the use of alkylcarbostannatranes in organic synthesis. We have demonstrated that secondary alkylcarbostannatrane reagents (3) can be employed in stereospecific Pd-catalyzed cross-coupling reactions with aryl (Scheme 2 a) and acyl (Scheme 2 b) electrophiles.^[11,12] The transannular N–Sn interaction in the carbostannatrane backbone selectively activates its apical substituent, which facilitates the transfer of alkyl groups that are otherwise unactivated towards transmetalation.^[13,14] Enantioenriched alkylcarbostannatranes can also be stored indefinitely under ambient conditions without erosion



Scheme 2. Use of enantioenriched alkylcarbostannatranes in stereospecific Pd-catalyzed cross-coupling reactions.

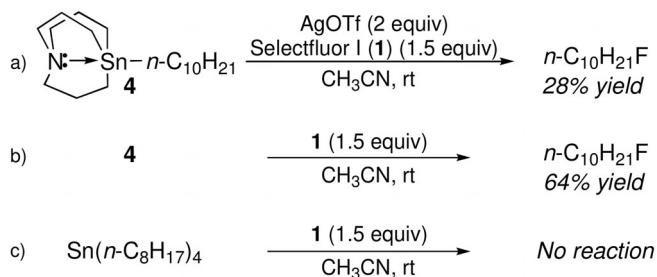
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of enantiopurity. During product isolation, tin byproducts from carbastannatranes are easily removed by standard column chromatography. Thus, alkylcarbastannatranes reagents have tremendous potential for broad application as isolable sources of stereodefined alkyl nucleophiles in organic synthesis. Herein, we report the use of isolable primary and secondary alkylcarbastannatranes nucleophiles in site-specific fluorination reactions. These reactions occur without the need for transition metal catalysis or in situ activation. When enantioenriched alkylcarbastannatranes are employed, fluorination occurs predominately via a stereoinvertive mechanism to generate highly enantioenriched alkyl fluoride compounds. These conditions can also be extended to stereospecific chlorination, bromination, and iodination reactions. Thus, isolable, enantioenriched alkylcarbastannatranes can serve as general building blocks for broad use in the preparation of enantiomerically enriched alkyl halides.

Electrophilic fluorination reactions constitute a standard strategy through which organofluorine compounds are prepared.^[3] Using Selectfluor I (**1**) as the electrophilic source of fluorine, Ritter has developed methods for the silver-mediated and silver-catalyzed fluorination of aryltributylstannanes.^[15] However, this method has not been applied to the fluorination of alkylstannanes. Because the carbastannatranes backbone selectively labilizes its apical substituent, we felt that alkylcarbastannatranes might undergo selective alkyl fluorination using the fluorination method developed by Ritter. When primary alkylcarbastannatranes **4** was subjected to silver-mediated fluorination conditions, *n*-decyl fluoride was generated at room temperature, though only in 28% yield (Scheme 3a). In control reactions where the silver additive

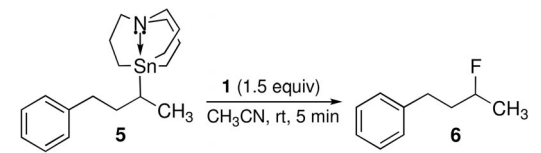


Scheme 3. Electrophilic fluorination of primary alkylstannanes with and without silver.

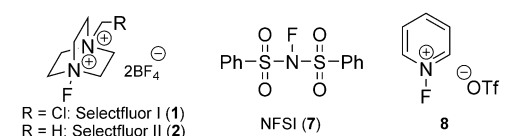
was omitted, we were surprised to observe that **4** underwent electrophilic fluorination much more efficiently, with an improved yield of 64% (Scheme 3b). When tetraoctylstannane was subjected to identical conditions, no formation of the corresponding alkylfluoride resulted (Scheme 3c). Thus, the carbastannatranes backbone facilitates direct alkyl fluorination via reaction with **1** in the absence of transition metal catalysis or exogenous activation. This again demonstrates the unique ability of the carbastannatranes backbone to facilitate the selective transfer of alkyl groups that are otherwise unactivated towards transfer. In this case, however, alkyl transfer does not occur via a transmetalation reaction, but by direct reaction with a non-metal electrophile.

Having established the ability of alkylcarbastannatranes to undergo direct fluorination reactions with **1**, we investigated the effect of variations in the reaction conditions. Because the transfer of secondary alkyl groups from tin is more challenging than the transfer of primary alkyl groups, we chose to employ secondary alkylcarbastannatranes **5** to optimize the reaction conditions (Table 1). Using **1** in aceto-

Table 1: Optimization of the catalyst-free electrophilic fluorination of **5**.



Entry	Variations from above	Yield [%] ^[a]
1	none	62
2	0 °C instead of rt; 2 h instead of 5 min	50
3	Selectfluor II (2) instead of 1	50
4	NSFI (7) instead of 1	31
5	8 instead of 1	0
6	DMSO instead of CH ₃ CN; 2 h instead of 5 min	0
7	DMF instead of CH ₃ CN; 2 h instead of 5 min	45
8	methanol instead of CH ₃ CN; 2 h instead of 5 min	39
9	Cy ₄ Sn instead of 5 ; 2 h instead of 5 min	0 ^[b]

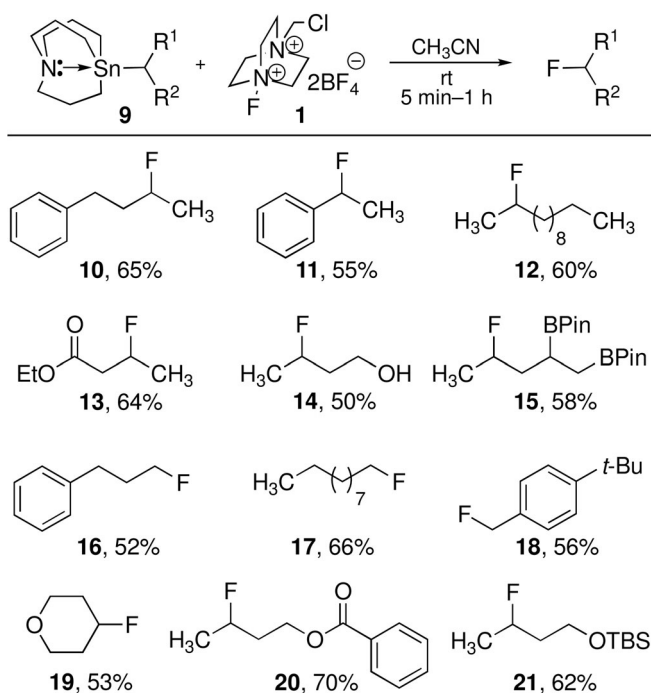


R = Cl: Selectfluor I (**1**)
R = H: Selectfluor II (**2**)
NSFI (**7**)
8

[a] Yields determined by GC analysis. [b] Yield of fluorocyclohexane.

nitrile, we found that the fluorination of **5** was complete in five minutes at room temperature. Use of other electrophilic fluorinating reagents and solvents resulted in lower yields. The fluorinated product (**6**) formed exclusively, without evidence of protodestannylation (see the Supporting Information for gas chromatograph data). As was observed using tetraoctylstannane (primary alkyl groups) in place of **4** (Scheme 3), Cy₄Sn (secondary alkyl groups) was inert towards the fluorination conditions used for carbastannatranes **5**.

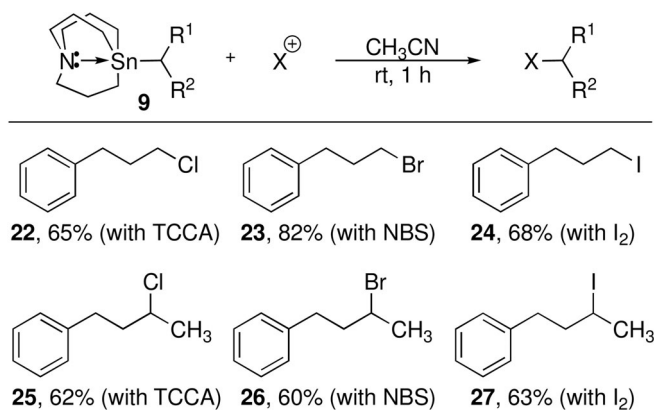
Using the optimized conditions, we explored the substrate scope of this fluorination reaction. We found that primary alkyl, secondary alkyl, and benzylic carbastannatranes derivatives could be successfully fluorinated (Scheme 4) under these conditions. Yields generally fall within the range of 50–70% with no concurrent formation of protodestannylated byproducts in any reaction. Due to the mild conditions of this reaction, sensitive functional groups such as alcohols (**14**), esters (**13** and **20**), boronate esters (**15**), and silyl ethers (**21**) are well tolerated. Fluorination of an oxygen-containing heterocycle (**19**) also proceeded smoothly. Secondary alkylcarbastannatranes derivatives consistently undergo fluorination reactions within minutes at RT, while primary derivatives tend to require slightly longer reaction times (ca. 1 h) in the absence of heating. Because the C–Sn bond of **9** tolerates even the harshest reduction conditions, remote functional groups



can be readily modified without disturbing the carbostannatranane fragment.^[16] Thus, our fluorination process should enable late-stage access to potentially important fluorinated molecules that would be particularly difficult, if not impossible, to prepare using existing methods of direct fluorine incorporation. The speed and simplicity of these reactions, combined with the unique stability/reactivity properties of alkylcarbostannatranes, suggests that this work could be extended to the use of electrophilic ¹⁸F sources for the preparation of radiolabeled compounds for applications in PET imaging.^[2,17]

To explore the scope of this transformation with respect to electrophilic halogenation reactions, we employed the standard fluorination conditions in chlorination, bromination, and iodination reactions. Using primary and secondary alkylcarbostannatranane nucleophiles, the corresponding chlorinated, brominated, and iodinated products were cleanly produced in good yield (Scheme 5) through reactions with trichloroisocyanuric acid (TCCA), *N*-bromosuccinimide (NBS), and iodine, respectively. Thus, alkylcarbostannatranes can be broadly utilized in electrophilic halogenation reactions with one set of reaction conditions.

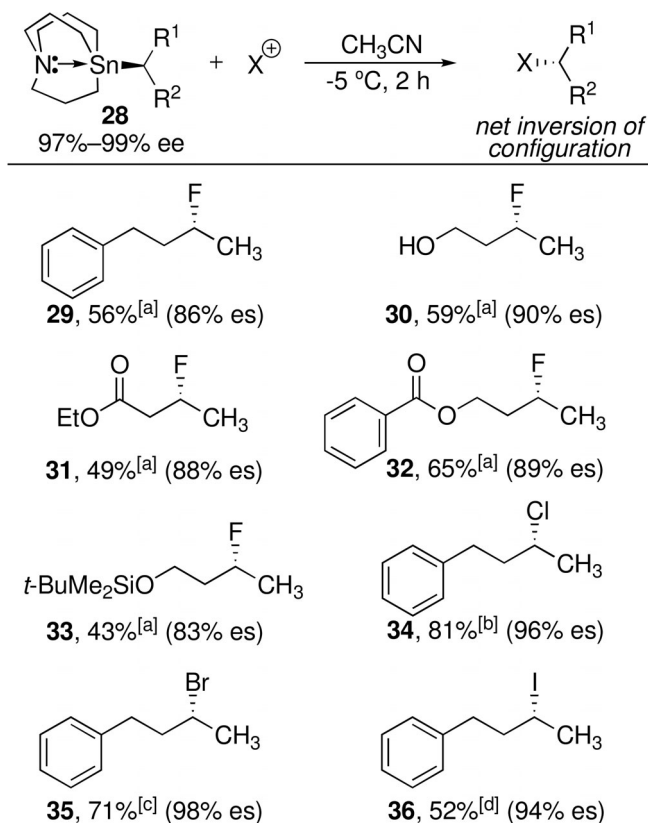
To probe the stereochemical course of this process, we subjected enantioenriched secondary alkylcarbostannatranes (**28**) to the fluorination conditions of Scheme 4. These reactions generated optically active alkyl fluorides with net inversion of absolute configuration. Aggarwal has previously demonstrated that styrene is effective as a radical inhibitor in electrophilic fluorination reactions of alkylboronates.^[9] Consistent with these results, we observed enhanced stereospecificity when styrene was included in fluorination reactions using enantioenriched **28**. When the fluorination reactions are conducted at -5°C in the presence of styrene, enantio-



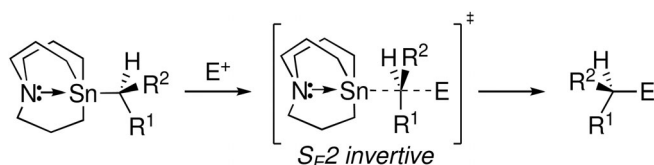
enriched alkyl fluoride products form with % es values^[18] ranging from 83–90%. In the absence of styrene, fluorinated products are obtained with depressed enantiospecificities (% es values approximately 15–20% lower). This is the first example of an enantiospecific fluorination reaction involving an enantioenriched alkylstannane, and also the first system that enables stereospecific electrophilic fluorination without the requirement for exogenous activation of the organometallic nucleophile.^[9] The juxtaposition of ambient stability and high reactivity through a stereospecific pathway is a particularly special feature of this system. In contrast, enantioenriched alkylboron nucleophiles require in situ activation with phenyl lithium to generate highly nucleophilic alkylboronate intermediates, which potentially limits the intrinsic functional group compatibility of the system. When an enantioenriched benzylcarbostannatranane was employed in this fluorination reaction, low stereospecificity was observed.^[19] This is consistent with the increased propensity of benzylic nucleophiles to react via radical pathways when in the presence of strongly oxidizing reagents such as Selectfluor I (**1**).

Previous use of enantioenriched tetraalkylstannanes in electrophilic chlorination, bromination, and iodination reactions resulted in highly variable enantiospecificities for halogen transfer, which depended intimately upon the steric properties of the spectator alkyl groups.^[10c–i] Using our standard conditions with TCCA, NBS, and NIS, stereospecific halogenation of enantioenriched alkylcarbostannatranes can be achieved with only nominal loss of enantiopurity. Like the analogous fluorination process, these halogenation reactions occur with net inversion of configuration. Thus, stereospecific fluorination, chlorination, bromination, and iodination of enantioenriched alkylcarbostannatranes can be achieved using the reaction conditions of Scheme 6.

The mechanism of these reactions is consistent with a stereoinvertive S_E2 polar mechanism (Scheme 7).^[10] Aggarwal^[9] and Jensen^[10g] have previously demonstrated that the use of polar solvents such as acetonitrile and methanol support a stereoinvertive S_E2 mechanism in which charge separation is expected to occur in the transition state. Consistent with Aggarwal's observation that electrophilic reactions of secondary alkylboronates result in net stereo-



Scheme 6. Stereospecific electrophilic halogenations of enantio-enriched alkylcarbastannatranes. [a] **1** (1.5 equiv), styrene (1 equiv), pyridine (0.5 equiv); [b] TCCA (1.5 equiv); [c] NBS (1.5 equiv); [d] NIS (1.5 equiv).



Scheme 7. Proposed mechanism of electrophilic substitution.

inversion, we have previously observed that transmetalation of unactivated secondary alkylboron nucleophiles to palladium predominately occurs through a stereoinvertive pathway.^[20] However, our observation that alkylcarbastannatranes undergo predominately stereoinvertive transfer in reactions with electrophilic halogenating reagents contrasts with the preferred stereoretentive transmetalation pathway observed when enantioenriched alkylcarbastannatranes are employed in Pd-catalyzed cross-coupling reactions (see Scheme 2).^[11,21] This cautions against inferring the stereochemical pathway of alkyl transfer from related, but non-identical systems, and underscores the potential sensitivity of the stereochemical outcome to changes in reaction conditions.

In summary, we have demonstrated that the carbastannatrane backbone activates primary and secondary alkyl groups towards electrophilic fluorination reactions. These reactions occur without the need for transition metal catalysis or in situ

activation of the nucleophile. Using one set of reaction conditions, we have successfully fluorinated primary alkyl, secondary alkyl, and benzylic carbastannatrane derivatives. When an enantioenriched alkylcarbastannatrane reagent is employed, the reactions proceed primarily through a stereoinvertive mechanism. This enables the direct preparation of optically active alkyl fluorides from enantioenriched alkylcarbastannatranes. These reaction conditions can also be extended to stereospecific chlorination, bromination, and iodination reactions. This reaction constitutes an exceedingly rare example of the direct, stereospecific functionalization of configurationally stable, isolable, main group organometallic nucleophiles. Because secondary alkyl transfer from tetraalkyltin compounds was not readily achievable prior to the use of carbastannatranes, few methods are available through which to prepare enantioenriched alkylstannanes.^[16] This constitutes the current bottleneck to wider adoption of stereospecific alkylcarbastannatrane chemistry, which we are actively addressing. We are also currently investigating extensions of this chemistry to stereospecific carbon–carbon bond-forming reactions, as well the use of other isolable metallatrane-based nucleophiles to improve the yields and enantiospecificity of halogenation reactions. Details of this work will be reported in due course.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbastannatrane · fluorination · halogenation · Selectfluor · stereospecificity

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- [16] Alkylcarbastannatranes can be prepared using an alkylmetal nucleophile with carbastannatrane chloride, or via the umpolung process using an alkyl mesylate with lithium carbastannatrane. If sensitive functional groups are present, alkylzinc nucleophiles or zincated carbastannatrane can be employed (see the Supporting Information).
- [17] ^{18}F conditions are typically very different to standard batch scale conditions. To better mimic ^{18}F conditions, we employed 50-fold and 100-fold excesses of **9** under dilute conditions (0.02 M Selectfluor I). After only 10 min and without further reaction optimization, GC yields (product **10**) of 30% and 25% were cleanly obtained, respectively.
- [18] Enantiospecificity (es) = $(ee_{\text{product}}/ee_{\text{starting material}}) \times 100\%$.
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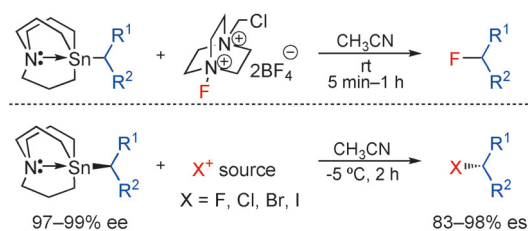
Communications



Fluorination

X. Ma, M. Diane, G. Ralph, C. Chen,
M. R. Biscoe* ————— ■■■■-■■■■

Stereospecific Electrophilic Fluorination
of Alkylcarbostannatrane Reagents



Speed matters: Site-specific fluorination reactions of isolable primary and secondary alkylcarbostannatrane nucleophiles occur fast, without the need for transition metal catalysis, or in situ activation of the

nucleophile. The reaction conditions can also be extended to stereospecific chlorination, bromination, and iodination reactions.