Synthesis, Characterization, and Reactivity of Tricarbastannatranes

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The synthesis of a series of tricarbastannatrane complexes is described, and the structure of ionic triptych complexes $[N(CH_2CH_2CH_2)_3Sn](BF_4)$, $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$, $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$, $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$ $[[N(CH_2CH_2CH_2)_3Sn]_2Cl_{0.2}F_{0.8}][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$, and $[(N(CH_2CH_2CH_2)_3Sn][allyl(B(C_6F_5)_3]$ is established by NMR spectroscopy and X-ray crystallography.

After demonstrating the Lewis acidity of tricarbastannatrane complexes toward various Lewis bases by NMR studies, the reactivity of tricarbastannatranes in conjugate addition to electrophilic alkenes was studied. Using alkyl-tricarbastannatranes as nucleophiles, the first $B(C_6F_5)_3$-promoted conjugate addition to benzylidene Meldrum's acids was carried out under mild conditions. The mechanism of the addition has been investigated by deuterium labeling experiments. It was shown that unsaturated carbonyl compounds can be efficiently activated by the Lewis acidic tricarbastannatrane. Furthermore, the structure of the reaction intermediates was determined by NMR and mass spectroscopy.

The reactivity of tricarbastannatranes was further investigated by the addition of *i*Pr-tricarbastannatrane to activated double bonds. In the presence of catalytic amounts of $B(C_6F_5)_3$, *i*Pr-tricarbastannatrane acts as a hydride source to generate $[HB(C_6F_5)_3]^-$, and reduces olefins, namely benzylidene 1,3-dimethylbarbituric acids. Detailed mechanistic studies on the reduction reaction were performed by NMR spectroscopy and mass spectrometry. Conjugate additions of isopropyl group to the benzylidene 1,3-dimethylbarbituric acids along with the reduced products were observed.

To expand the applications of tricarbastannatranes in carbon–carbon bond formation reactions, allyl-tricarbastannatrane was added to carbon–carbon double bonds that bear strongly electron-withdrawing substituents under mild reaction conditions. The tin enolate species, which is generated by the addition of allyl-tricarbastannatrane to benzylidene 1,3-dimethylbarbituric acid, is characterized by multinuclear NMR spectroscopy.

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Thank you
Azadeh Kavoosi
June 2016

To Mom, Dad, Alaleh, and Ali

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List of Schemes

List of Abbreviations

Ac	acetyl
acac	acetylacetonate
Ar	aryl
atm	atmosphere
Bn	benzyl
Boc	tert-butyloxycarbonyl
br	broad
Bpin	Boron pinacol ester (pinacolate boron)
Bu	butyl
calcd	calculated
COD	Cycloocta-1,5-diene
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
DMF	dimethylformamide
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone
Dipp	2,6-Diisopropylphenyl
DPP	diphenylphosphinate
dppf	1,1′-bis(diphenylphosphino)ferrocene
dr	Diastereomeric ratio
ee	enantiomeric excess
Et	ethyl
EtOAc	ethyl acetate
equiv	equivalent
er	enantiomeric ratio

ESI	electrospray ionization
EWG	Electron withdrawing group
h	hour
hal	halogen
HFIP	Hexafluoroisopropanol
HMPA	hexamethylphosphoramide
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
Hz	hertz
^{i}Pr	*iso*-propyl
J	spin coupling constant
m	multiplet
m	meta
M	Metal or molarity (moles/litre)
Me	methyl
MeCN	acetonitrile
Meldrum's acid	2,2-dimehtyl-1,3-dioxane-4,6-dione
Mes	mesityl
MOM	methoxymethyl ether
NA	not available or not applicable
n.d.	not determined
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser enhancement
NR	no reaction
Nu	nucleophile
o	ortho

OTf	triflate (trifluoromethanesulfonate)
p	para
PET	Positron Emission Tomography
Ph	phenyl
ppm	Parts per million
q	quartet
quant	quantitative
quint	quintet
rt	room temperature
s	singlet
SEM	2-(trimethylsilyl)ethoxy]methyl acetal
SM	starting material
t	triplet
^{t}Bu	*tert*-butyl
TBAF	tetra-*n*-butylammonium fluoride
TC	2-thiophenecarboxylate
temp	temperature
TES	triethylsilyl
THF	tetrahydofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Tr	triphenylmethyl (trityl)
UV	ultraviolet

Chapter 1
Introduction

1.1 Tricarbastannatranes

Tricarbastannatranes belong to a class of tricyclic compounds called atranes. Since the 1960s the term "atrane" has been used to refer to a tricyclic molecule with three five-membered rings (Structure **1.1**, Figure 1.1).[1] These compounds are designated as triptych derivatives, and exhibit trigonal bipyramidal structure with strong interamolecular 1,5-interactions.[2] Several atranes, such as silatranes (M = Si), stannatranes (M = Sn), germatranes (M = Ge), etc., have been synthesized to date. Silatranes, wherein M = Si, E = O, and R is an organic substituent, were the first bicyclo[3.3.3]skeleton containing compounds to be investigated.[3] As demonstrated in the equilibrium in Figure 1.1, depending on the E and R substituents, the transannular coordinate bond of pentacoordinated atranes (**1.1**) can be stretched and even be absent to generate pro-atranes (**1.2**). In addition to the significant biological activity exhibited by some derivatives of the compounds with [3.3.3]skeleton, their salient features also include the racemization of their chiral molecular skeleton, and their transannular interaction.[4]

Tin containing atranes (i.e., M = Sn) are categorized into stannatranes (E = O), carbastanntranes ($E = CR_2$), azastannatranes (E = NR) and thiastannatranes (E = S). Among stannatranes, tricarbastannatranes have an environment around tin atom similar to organotin compounds and have been used in Stille cross-coupling reactions. In this chapter, the preparation of tricarbstannatranes (M = Sn, $E = CH_2$), and their applications in Stille cross-coupling reactions will be introduced.

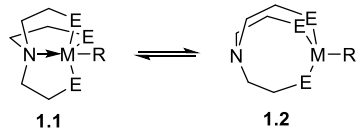


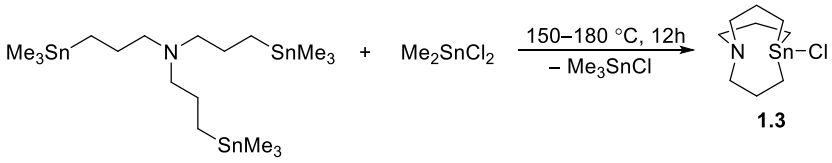
Figure 1.1. Metallatrane structures

1.1.1 Synthesis of Tricarbastannatranes

1-Aza-5-stanna-5-chlorotricyclo[3.3.3.$0^{1,5}$]undecane, referred to as chloro-tricarbastannatrane, is a valuable reagent as a precursor to other tricarbastannatrane derivatives. This reagent was first synthesized in 1984 by transmetalation of $N(CH_2CH_2CH_2MgCl)_3$ with $SnCl_4$ in 12% yield.[5] Alternatively, thermal redistribution of $N(CH_2CH_2CH_2SnMe_3)_3$ with dimethyltin dichloride yielded

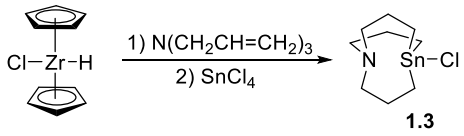
40% of chloro-tricarbastannatrane, and Me_3SnCl—which is the reaction's byproduct—was removed by vacuum distillation (Scheme 1.1).[6,7] In this procedure, $N(CH_2CH_2CH_2SnMe_3)_3$ was prepared from the reaction of $N(CH_2CH_2CH_2Cl)_3$ with $NaSnMe_3$ in liquid ammonia at –78 °C. The drawbacks to this procedure include harsh reaction conditions, handling of methyltin derivatives and a low yield, which would make this method difficult to scale up.

Scheme 1.1. Synthesis of chloro-tricarbastannatrane from $N(CH_2CH_2CH_2SnMe_3)_3$



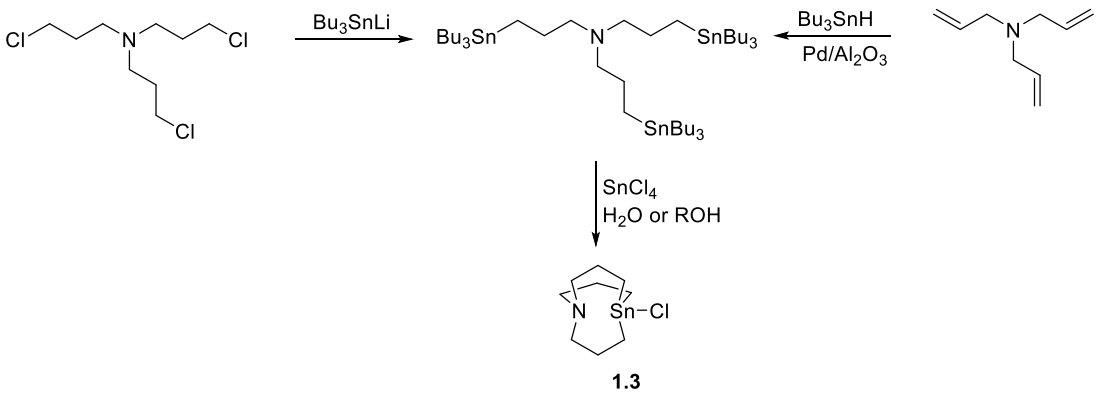
Another method to prepare chloro-tricarbastannatrane (**1.3**) includes hydrozirconation of triallylamine with Cp_2ZrHCl (Schwartz's reagent), followed by transmetalation with Sn(IV) chloride to furnish chloro-tricarbastannatrane in 50% yield (Scheme 1.2).[8] Due to the high dilution required for this reaction, it is difficult to scale up. [9]

Scheme 1.2. Synthesis of chloro-tricarbastanntrane using Schwartz's reagent



A method for making **1.3** using a thermal distribution approach on large scale was reported in 2000.[9] In this procedure, less toxic $N(CH_2CH_2CH_2SnBu_3)_3$ was applied instead of its trimethyl analogue. $N(CH_2CH_2CH_2SnBu_3)_3$ was generated in 78% yield from the reaction of $N(CH_2CH_2CH_2Cl)_3$ with Bu_3SnLi. $N(CH_2CH_2CH_2SnBu_3)_3$ was also prepared by hydrostannylation of triallylamine using Bu_3SnH under Pd/Al_2O_3 catalyzed condition in 66% yield (Scheme 1.3). Tricarbastannatrane **1.3** was obtained in 50–55% yield by thermal distribution of $N(CH_2CH_2CH_2SnBu_3)_3$ and Sn(IV) chloride at 70–100 °C in the presence of a small amount of water or an alcohol.

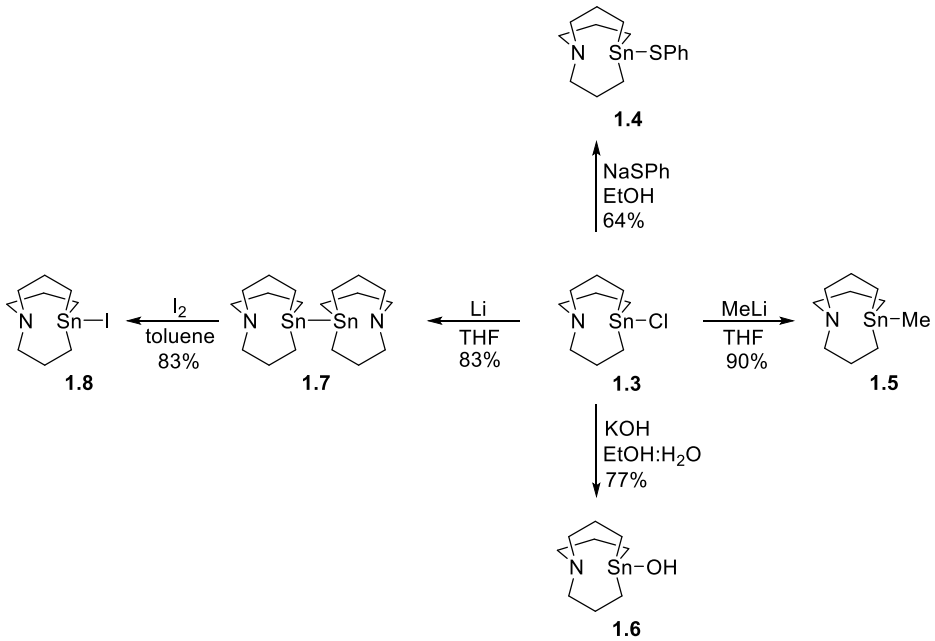
Scheme 1.3. Synthesis of chloro-tricarbastannatrane from $N(CH_2CH_2CH_2SnBu_3)_3$



1.3

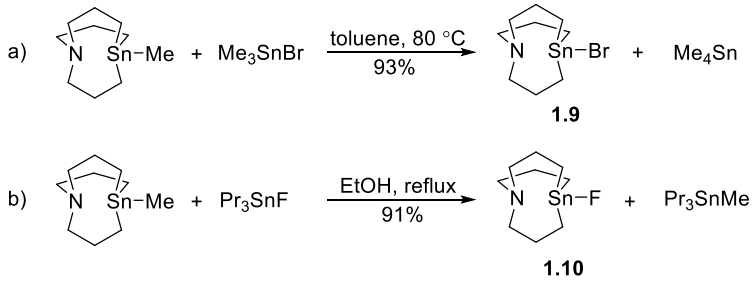
Other tricarbastannatranes such as alkyl, halo, hydroxyl, and phenylthio-tricarbastannatranes were generated from chloro-tricarbastannatrane.[10] Refluxing $N(CH_2CH_2CH_2)_3SnCl$ (**1.3**) with KOH in EtOH:H_2O (1:2) after 3 hours, afforded $N(CH_2CH_2CH_2)_3SnOH$ in 77% yield. $N(CH_2CH_2CH_2)_3SnSPh$ was obtained in 64% yield by refluxing **1.3** and PhSNa in EtOH. Furthermore, bis-tricarbastannatrane $[N(CH_2CH_2CH_2)_3Sn]_2$ was generated by the addition of lithium to **1.3** in THF in 83% yield. The addition of iodine to bis-tricarbastannatrane (**1.7**) in toluene yielded 83% of iodo-tricarbastannatrane (**1.8**) (Scheme 1.4).

Scheme 1.4. Synthesis of different tricarbastannatranes from chloro-tricarbastannatrane



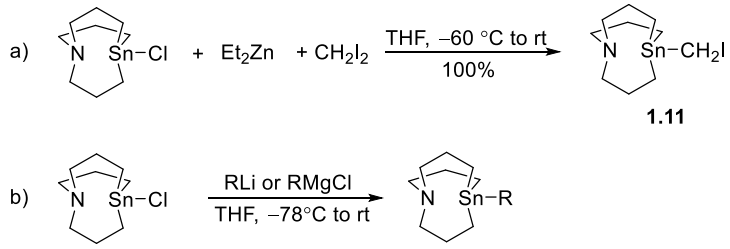
Methyl-tricarbastannatrane (**1.5**) is the first alkyl-tricarbastannatrane, which was synthesized from **1.3** by the addition of excess amount of methyllithium to $N(CH_2CH_2CH_2)_3SnCl$ in Et_2O or THF (Scheme 1.4).[2,11] Bromo-tricarbastannatrane (**1.9**) and fluoro-tricarbastannatrane (**1.10**) were synthesized by the addition of trialkyltin halide to methyl-tricarbastannatrane. As shown in Scheme 1.5a, addition of trimethyltin bromide to **1.5** in toluene afforded **1.9** in 93% yield. In the same manner, transmetallation of triisopropyltin fluoride with **1.5** in EtOH furnished tricarbastannatrane **1.10** in 91% yield (Scheme 1.5b).[12]

Scheme 1.5. Synthesis of bromo-tricarbastannatrane and fluoro-tricarbastannatrane from $N(CH_2CH_2CH_2)_3SnMe$



Transmetalation of chloro-tricarbastannatrane with organolithium,[8] Grignard,[13] and organozinc[14] reagents provided facile access to other primary and secondary organotricarbastannatranes (Scheme 1.6).

Scheme 1.6. Synthesis of primary and secondary organotricarbastannatranes



1.1.2 NMR Studies on Tricarbastannatranes

^{1}H NMR studies on tricarbastannatranes **1.3**–**1.9** were reported in 1988.[10] At room temperature, all of the stannatranes had identical patterns with different chemical shifts depending on the substituent

R. The CH_2 protons appeared as a quintet, and $SnCH_2$ and NCH_2 protons provided well resolved triplets at room temperature. Broadened spectra were observed for NCH_2 and CH_2 in halo-tricarbastannatranes and methyl-tricarbastannatrane at –70 °C. However, $SnCH_2$ triplets remained well resolved with no change. ^{1}H NMR at –105 °C showed that the protons within the methylene groups became chemically inequivalent. There are two possible mechanisms for making the protons of each methylene group equivalent. As demonstrated in Figure 1.2, the racemization of the chiral skeleton can proceed either through all-planar transition state (pathway a) or by stepwise ring inversions (pathway b) (Figure 1.1).

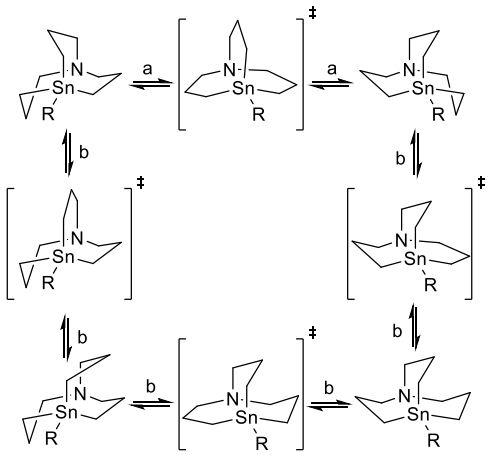


Figure 1.2. Proposed pathways for racemization

^{119}Sn and ^{13}C NMR data for tricarbastannatranes **1.3**–**1.9** are summarized and compared in Table 1.1. The ^{119}Sn NMR high field shifts confirmed the intramolecular tin–nitrogen interaction.

Table 1.1. ^{119}Sn and ^{13}C NMR data of $N(CH_2CH_2CH_2)_3SnR$

Compound	R	Solvent	T(°C)	Chemical shift δ (ppm)			
				Sn	CH_2Sn	CH_2	CH_2N
1.3	Cl	$CDCl_3$	30	19.5	13.9	23.2	54.8
1.4	SPh	$CDCl_3$	30	–5.4	11.4	23.4	54.9
1.5	Me	C_6D_6	30	–14.4	8.2	23.8	54.9
1.6	OH	$CDCl_3$	30	–16.9	10.3	23.2	55.0
1.7	$Sn(CH_2CH_2CH_2)_3N$	C_7D_8	30	–77.4	9.4	24.2	55.4
1.8	I	$CDCl_3$	30	–43.0	16.6	23.8	55.2
1.9	Br	$CDCl_3$	30	1.2	14.8	23.6	55.1

1.1.3 Tricarbastannatranes in Stille Cross-coupling Reactions

The Stille reaction is a versatile carbon–carbon bond forming reaction, which involves the cross-coupling of an organostannane reagent with an organohalide or pseudohalide in the presence of a palladium catalyst.[15] Trialkyltin reagents, such as trimethyl or tributyltin derivatives have been used as coupling partners in Stille couplings. The low polarity and strength of tin–carbon bond in alkyltins, as well as enhanced migratory aptitude of sp and sp^2 carbons over sp^3 carbons make aryl, alkenyl or alkynyl groups the transferable groups in the presence of alkyl ligands. Tributyltins are preferred over trimethyltin reagents due to lower toxicity. However, trimethyltin were chosen over their butyl analogues in some cases because trimethyltin halide can easily be removed as a byproduct from the reaction mixture.

There are some drawbacks to using conventional alkylstannane reagents in Stille coupling reactions. As mentioned above, alkylstannanes do not transfer easily, and few examples of primary alkyl groups transfer in Stille couplings have been reported.[16] In addition, in a coupling reaction of secondary alkylstannane reagents with electrophiles, β-hydride elimination is a competing reaction. Furthermore, although aryl and alkenylstannanes couple readily with different electrophiles under palladium-catalyzed conditions, some attempts at using stannane reagents in Stille couplings failed due to their low reactivity.

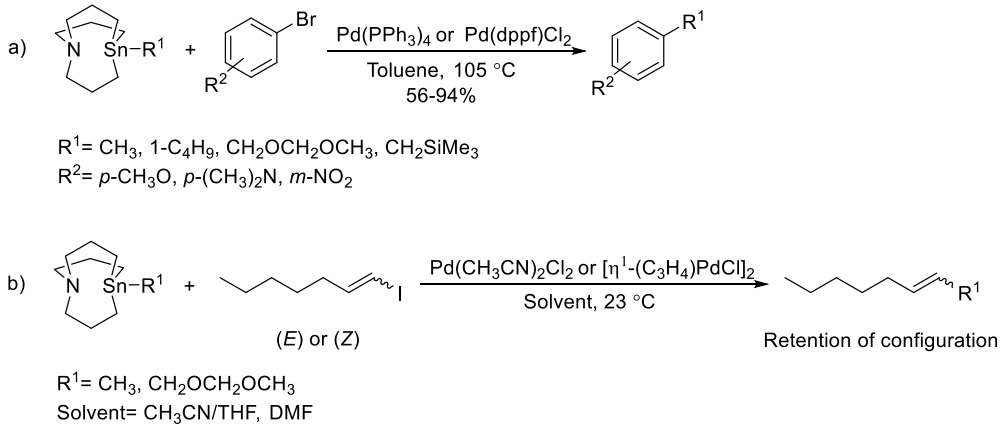
Tircarbastannatranes were applied to address the above problems. Tricarbastannatrane's unique structural features make them efficient nucleophiles in Stille reactions for the selective transfer of

alkyl groups. Due to the intramolecular tin–nitrogen interaction, the pentacoordinated tin center is less electrophilic and tin–carbon bond is more polarized and on average 0.1 Å longer than a typical alkylstannane.[8] As a result, enhanced reactivity of tricarbastannatranes in the transmetalation step of coupling reactions is observed. The stable tricyclic[3.3.3]skeleton in tricarbastannatranes consists of two axial and three equatorial groups. Thus, pentacoordianted tetraorganotricarbastannatranes possess only one labile group, and can transfer the reactive apical group selectively in their transformations.

The first example of using alkyl-tricarbastannatranes as coupling reagents in Stille coupling reactions was reported by Vedejs and coworkers.[8] Different primary alkyl-tricarbastannatranes coupled with phenyl bromide derivatives (Scheme 1.7a). The tricarbastannatranes were very efficient in transferring the alkyl groups even to electron-rich electrophiles, such as 4-bromo-*N*,*N*-dimethylaniline. Attempts to couple this substrate with the conventional vinyl tributyltin had previously failed. Alkyl-tricarbastannatranes demonstrated higher reactivity compared to R_4Sn reagents. While less than 5% conversion was obtained using tetramethyltin in the reaction with *p*-bromoanisole, **1.5** furnished *p*-methoxytoluene in 67% yield. In addition, the CH_2OR group transfer with tributylstannane derivatives was not efficient due to the competing reactions between the transfer of butyl groups and the desired CH_2OR group. However, $CH_2OCH_2OCH_3$ group was transferred selectively to bromobenzene derivatives using the corresponding tricarbastannatrane reagent, and the products were obtained in high yields.

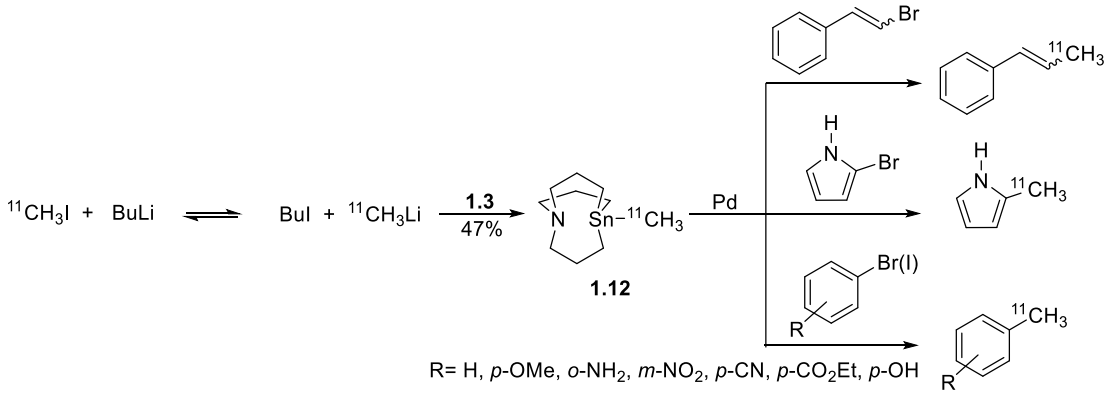
Rearrangement of *sec*-butyl-tricarbastannatrane through β-hydride elimination under palladium-catalyzed conditions led to the formation of the *n*-butyl cross-coupled product.[8] Therefore, these reaction conditions were not effective for secondary alkyl group transfer. Stereospecific coupling of alkyl-tricarbastannatrane with *(E)*- or *(Z)*-1-iodo-1-heptene in the presence of a catalytic amounts of palladium catalyst, yielded the *(E)*- or the *(Z)*-alkene products with >98% retention of geometry (Scheme 1.7b).

Scheme 1.7. Alkyl-tricarbastannatranes as coupling mediators



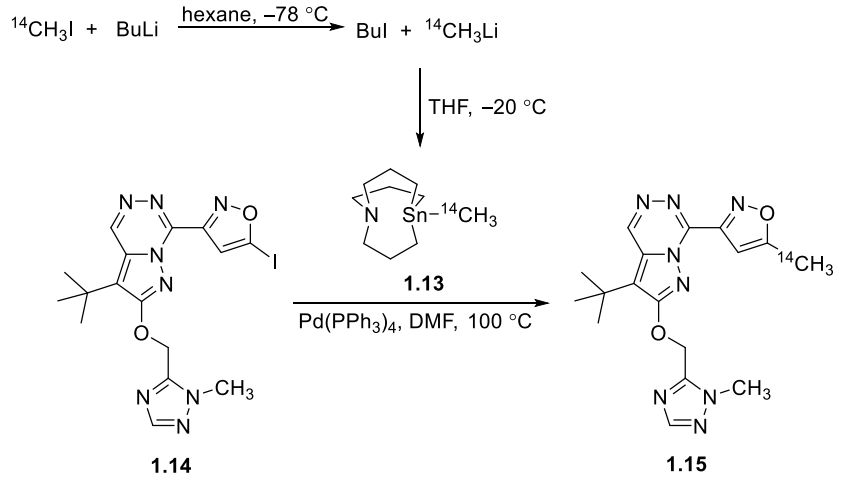
Tricarbastannatranes have also been used in the synthesis of radiopharmaceuticals for the Positron Emission Tomography (PET) technique.[17] Because of the short half-lives of radionuclides applied in PET and radiation safety issues, the synthetic method to make the target molecules should be quick and efficient. Stille coupling reactions of organostannanes with iodo[^{11}C]methane to form the coupled products with a [^{11}C]carbon–carbon bond were applied in the production of PET tracers. [^{11}C]-methylcarbastannatrane (**1.12**) was used to rapidly and selectively transfer of the [^{11}C]-methyl group to aryl- and vinyl halides in Stille reactions. Tricarbastannatrane **1.12** was obtained from the reaction of [^{11}C]-methyllithium and tricarbastanntrane **1.3** in average yields of 47% (20–90% yields). [^{11}C]-methyllithium was obtained by an exchange reaction between iodo[^{11}C]-methane and butyl lithium at low temperatures (Scheme 1.8).

Scheme 1.8. Synthesis and Stille coupling reactions of [^{11}C]methyl-tricarbastannatrane



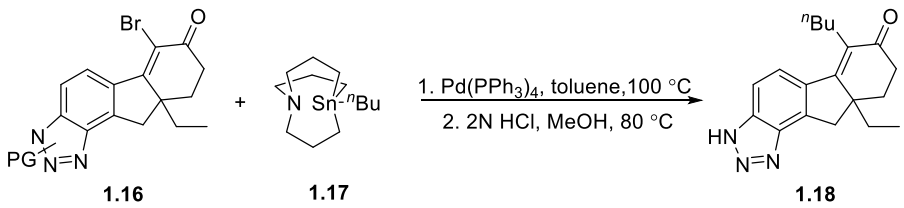
Another application of a labeled methyl-tricarbastannatrane in a Stille cross-coupling reaction was reported in the synthesis of radiolabeled triazine **1.15**.[18] [^{14}C]-Isotope was introduced at the C-5 position of the isoxazole by a palladium-catalyzed cross-coupling reaction of [^{14}C]-methyl-tricarbastannatrane (**1.13**) and iodoisoxazole **1.14** in dimethyformamide (DMF) at 100 °C. Similar to tricarbastannatrane **1.12**, radiolabeled compound **1.13** was prepared from [^{14}C]-methyllithium (Scheme 1.9).

Scheme 1.9. Applying labeled [^{14}C]-methyl-tricarbastannatrane in the synthesis of a triazine



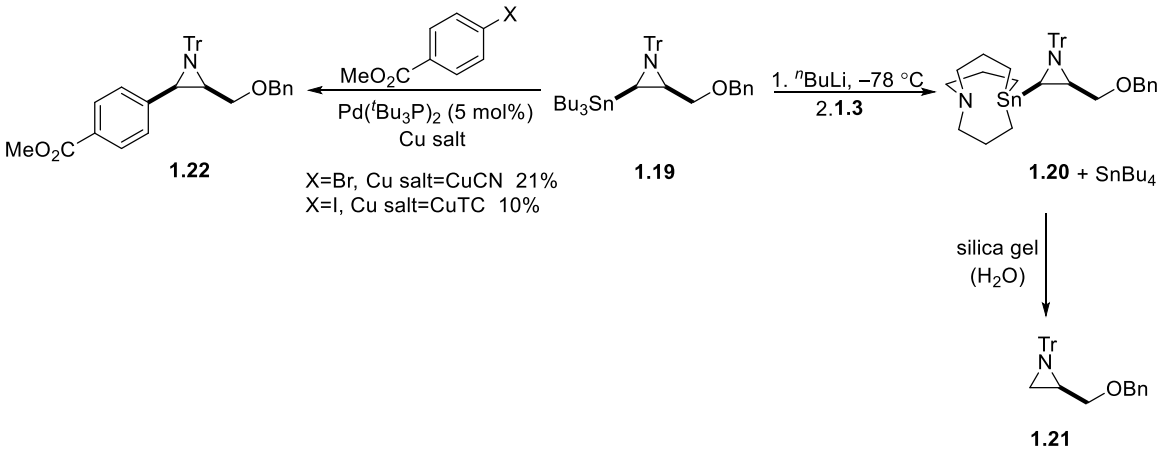
n-Butyl-tricarbastannatrane was used to prepare triazolo-tetrahydrofluorenone **1.18**, which is a selective estrogen receptor beta agonist.[19] The $Pd(PPh_3)_4$-catalyzed cross-coupling reaction of protected triazole **1.16** with tricarbastannatrane **1.17** in toluene at 100 °C was followed by the treatment of the mixture with hydrochloric acid (2N) at 80 °C, and afforded deprotected triazole **1.18** (PG = MOM or SEM) (Scheme 1.10).

Scheme 1.10. Reaction of *n*-butyl-tricarbastannatrane with a triazolo-tetrahydrofluorenone derivative



Vedejs and coworkers reported the generation of substituted aziridines using an aziridinyltricarbastannatrane **1.20** and halo ester derivatives in the presence of $(^tBu_3P)_2Pd$ and $CuOP(O)Ph_2$ (CuDPP).[20] Tricarbastannatrane **1.20** was prepared by tin–lithium exchange from tributyl tin **1.19**, followed by the reaction with **1.3**. Attempts to purify of **1.20** failed because it protodestannylated on silica gel, and generated aziridine **1.21** (Scheme 1.11). Such behavior was not observed for tricarbastannatranes with an exocyclic sp^3 hybridized tin–carbon bond.[8] It was postulated that protonation of **1.20** on silica gel stems from the strained ring and the increased s-character of tin–carbon bond because of the electron pair on nitrogen atom. Crude **1.20** was stable in refluxing toluene for more than two days under an inert atmosphere, and no decomposition was observed.

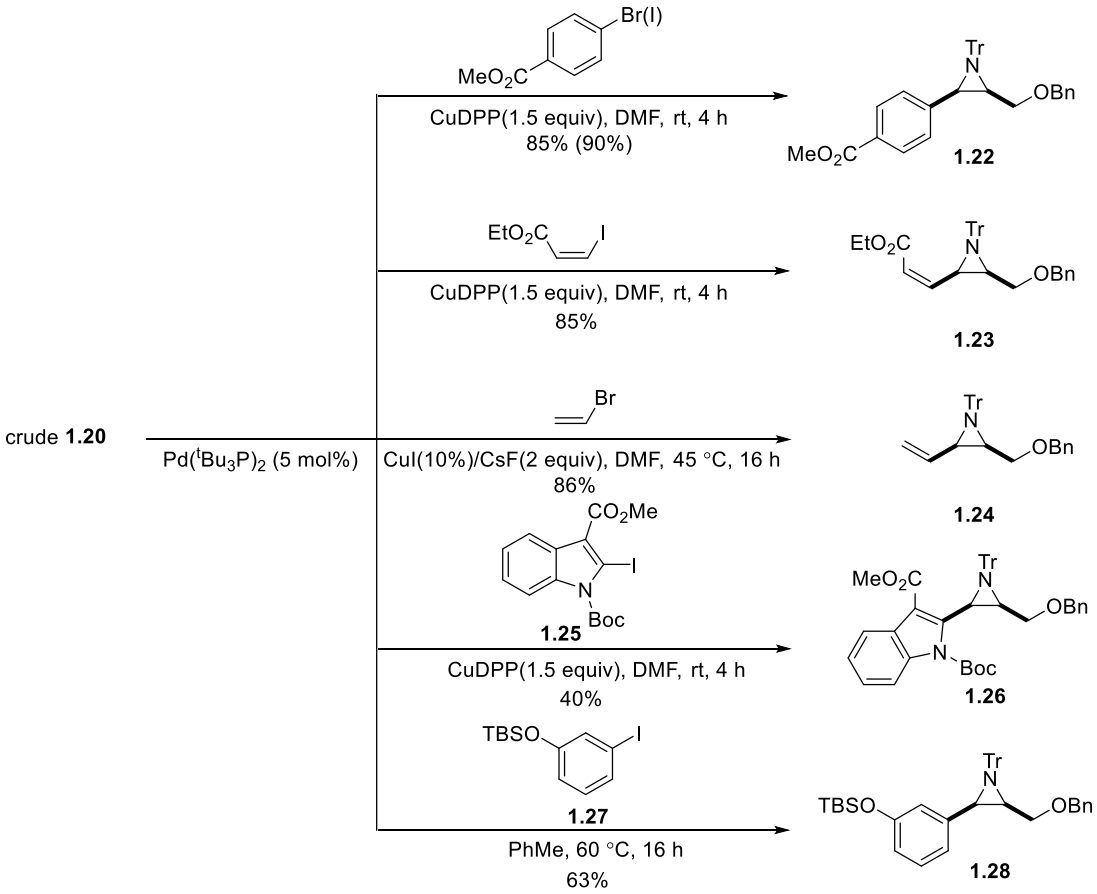
Scheme 1.11. Synthesis of an aziridinyltricarbastannatrane derivative from chloro-tricarbastannatrane



$Pd(^tBu_3P)_2$-catalyzed coupling reaction of stannane **1.19** with halobenzenes in the presence of copper salts provided the coupled product **1.22** in low yields (Scheme 1.11). In order to modify the result, crude **1.20** was used as a coupling reagent. It was expected that because of the transannular nitrogen–tin bond, **1.20** would exhibit faster transmetalation than Bu_4Sn, which is the by-product of the tin–lithium exchange reaction. Reaction of **1.20** with methyl 4-iodobenzoate in DMF with 5 mol% of $Pd(PPh_3)_2Cl_2$ furnished **1.22** in 40% yield after 16 h at 100 °C. It was found that using CuDPP as an additive could improve the reaction yield, and 90% of **1.22** was obtained with 5 mol% of $Pd(^tBu_3P)_2$ and 1.5 equivalent of CuDPP. The coupled product was obtained under the same condition with methyl 4-bromobenzoate in 85% yield. More functionalized substrates were coupled under these modified conditions. Aziridine **1.23** was obtained in 85% yield with *Z*-iodoacrylate. However, applying the same condition to vinylbromide afforded the desired adduct **1.24** in only 40% yield as

well as 50% of a side product from dimerization of the aziridine subunit. The yield of **1.24** was improved to 86% by using CuI/CsF as an alternative copper source. The reaction of iodoindole substrate **1.25** with crude **1.20** gave the coupled product **1.26** in 40% yield. The reaction of electron-rich substrate **1.27** under copper-free condition furnished 63% yield of the desired product **1.28** (Scheme 1.12).

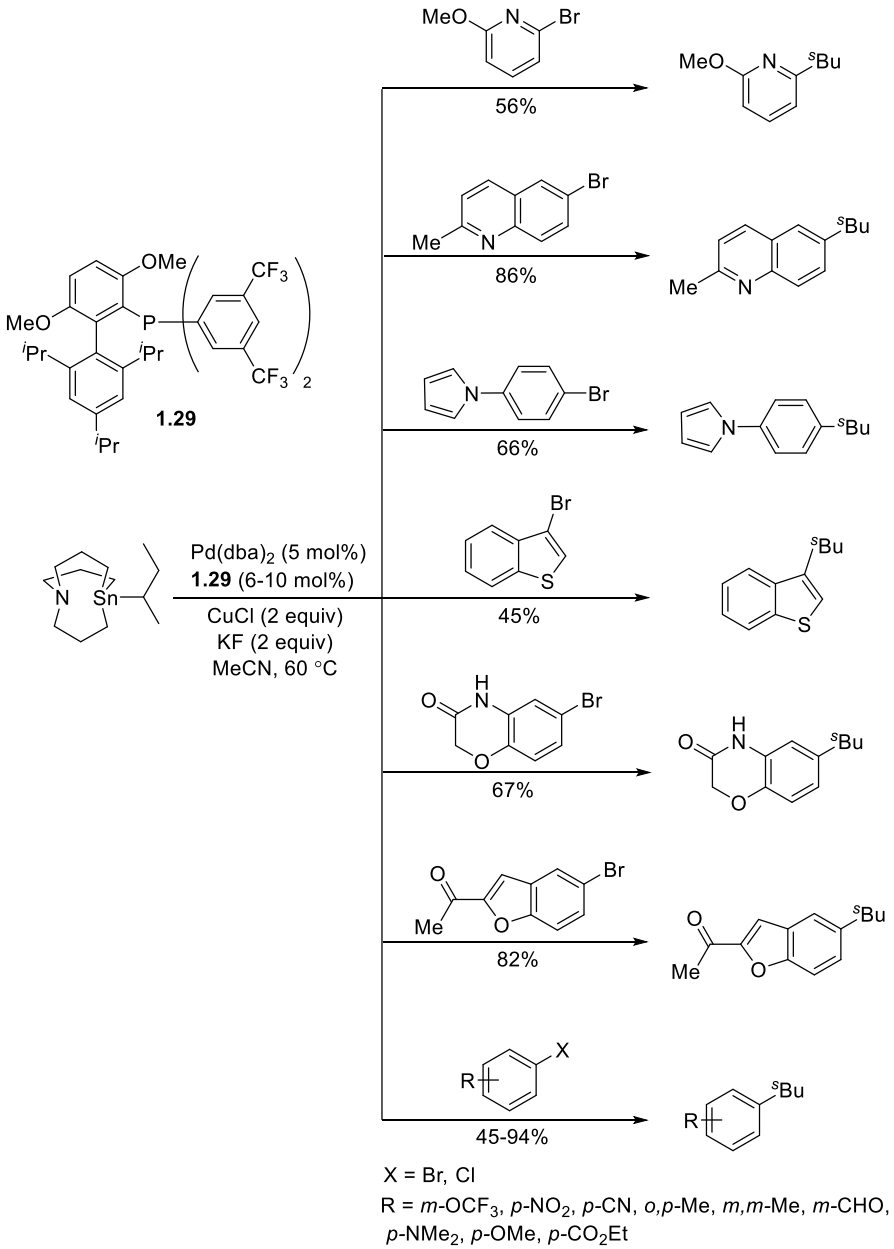
Scheme 1.12. Stille couplings of aziridinyl tricarbastannatrane with functionalized substrates



Recently, Biscoe and coworkers reported the Stille cross-coupling reactions of secondary alkyl-tricarbastannatranes with aryl halides.[13] As discussed earlier, Vedejs and colleagues reported the first selective transfer of alkyl group in Stille reactions by using alkyl-tricarbastannatranes.[8] However, this original work was limited to transfer of primary alkyl groups, and secondary alkyl group trasfer led to the linear product via β-hydride elimination. It was shown that JackiePhos Ligand **1.29** could facilitate the transfer of *sec*-butyl group from the corresponding tricarbastannatrane to aryl bromides

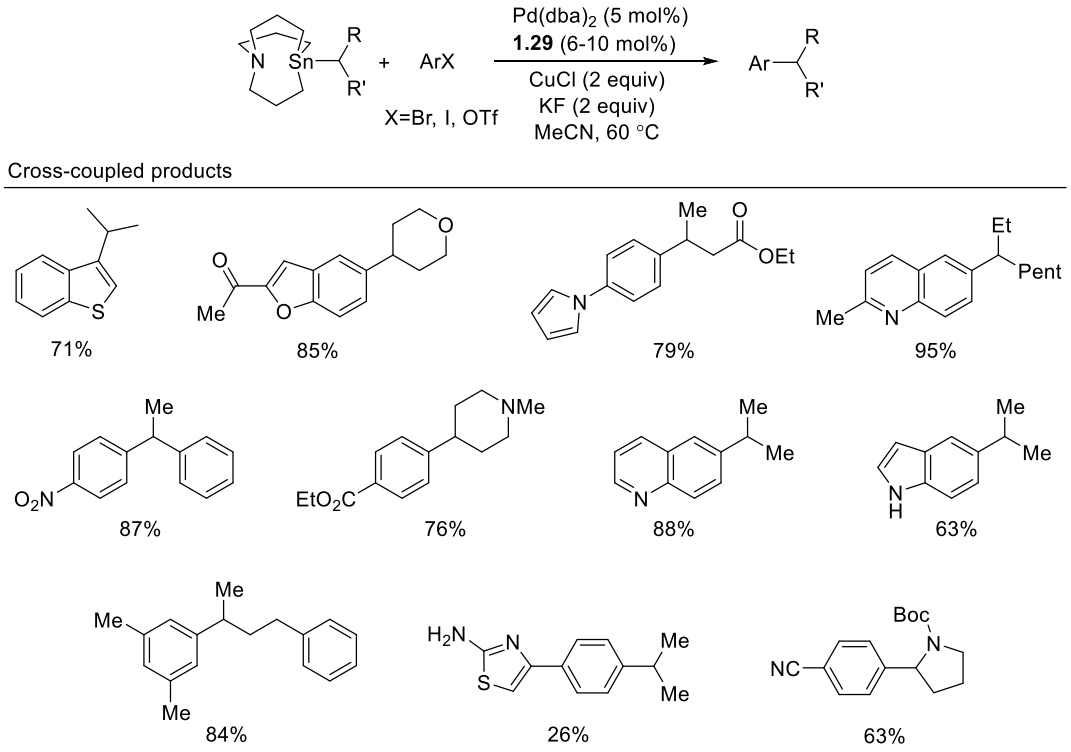
in the presence of $Pd(dba)_2$ catalyst. High yields of the coupled products were provided by electron-deficient, electron-neutral and electron-poor aryl bromides. In addition to aryl bromide, the Stille coupling did proceed with electron-deficient aryl chlorides (Scheme 1.13).

Scheme 1.13. Stille couplings of *sec*-butyltricarbastannatrane with aryl bromides



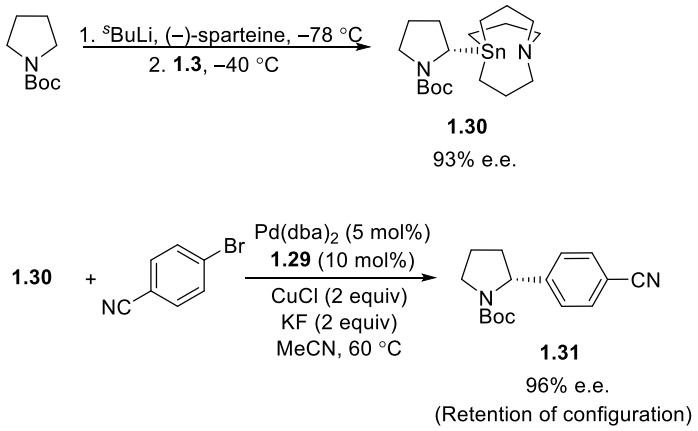
Different secondary alkyl-tricarbastannatranes were applied under the palladium-catalyzed condition to aryl bromides, aryl iodides and aryl triflates. As depicted in Scheme 1.14, the secondary alkyl groups containing ethers, esters, amines, and amides formed the cross-coupled products (26–95% yields).

Scheme 1.14. Stille couplings of different secondary alkyl-tricarbastannatranes with aryl bromides, chlorides and triflates



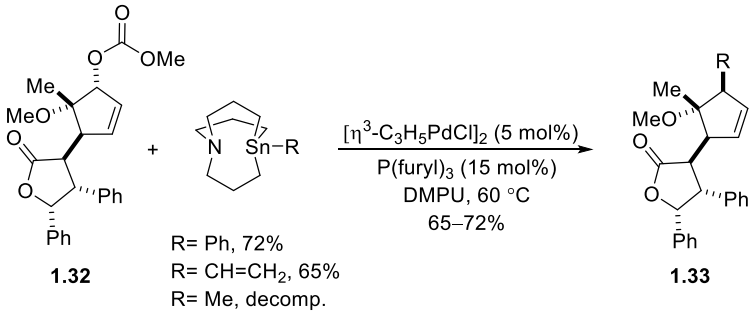
Optically active alkyl-tricarbastannatrane **1.30** was generated from *N*-Boc-pyrrolidine, *sec*-butyllithium, and (–)-sparteine. Compound **1.30** was isolated in 93% ee, and underwent a cross-coupling reaction with 4-bromobenzonitrile. Retention of configuration was observed, and cross-coupled product **1.31** was isolated in 96% ee (Scheme 1.15).

Scheme 1.15. Stille cross-coupling of optically active secondary alkyl-tricarbastannatrane with 4-bromo benzonitrile



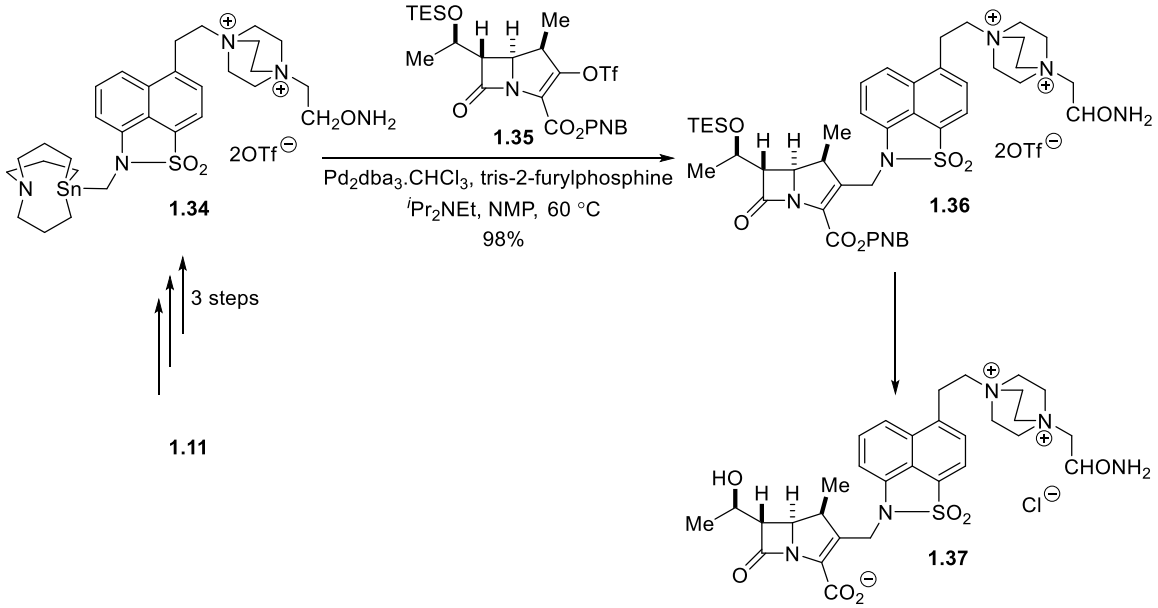
Palladium-catalyzed allylic substitution reactions of sterically demanding methylcarbonate **1.32** were studied by Hegedus and coworkers.[11] Alkylation of allylic carbonates via transmetalation is more challenging and less common than direct nucleophilic additions of soft nucleophiles. Allylic carbonates are generally less reactive than allylic halides toward oxidative addition. Therefore, more nucleophilic ligands are required for facile transmetalation with palladium (II) intermediates. Furthermore, in this reaction, the presence of two bulky groups on palladium in a π-allyl intermediate could sterically hinder transmetalation. Consequently, transmetalation of **1.32** with different palladium catalysts, such as $Pd(PPh_3)_4$, $Pd(acac)_2/PPh_3$, $[\eta^3\text{-}C_3H_5PdCl]_2/PPh_3$, etc., and organometallic nucleophiles ranging from $NaBH_4$, BnZnBr, PhZnCl, (vinyl)$SnBu_3$, $PhSnMe_3$, to (*p*-MeOPh)$SnBu_3$ led to the starting material recovery or dienes formation. In such a challenging transmetalation, vinyl- and phenyl-tricarbastannatranes afforded the desired products **1.33** in good yields with inversion of configuration. However, decomposition was observed with methyl-tricarbastannatrane (Scheme 1.16).

Scheme 1.16. Allylic alkylation via transmetalation of tricarbastannatranes



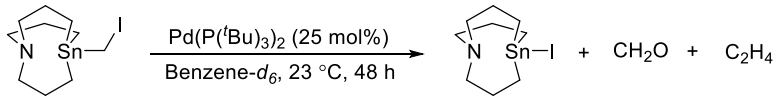
β-lactam **1.37** is applied for the treatment of bacterial infections. One of the most convergent synthetic routes is the connection of carbapenem core **1.35** with M-CH_2NRR' chain.[14] Although the cross-coupling of the carbapenem with Bu_3SnCH_2OH was facile,[21] Suzuki or Stille coupling of **1.35** with any CH_2NRR' failed. It was proposed that the transmetalation step in the catalytic cycle might be the problem. Therefore, tricarbastannatrane **1.34** was synthesized from **1.11** in three steps, and used in Stille coupling reaction with carbapenem **1.35** to furnish β-lactam **1.36** in 98% yield (Scheme 1.17).

Scheme 1.17. Applying a tricarbastannatrane derivative in a carbapenem synthesis



The Kikukawa[22] and the Busacca-Farina[23,24] mechanisms are two different pathways in *cine*-substitution mechanism in the Stille coupling reactions. These pathways were studied by Fillion and coworkers using iodomethyl-tricarbastannatrane.[25] When tricarbastannatrane **1.11** reacted with $Pd(P(^tBu)_3)_2$, the decomposition of **1.11** at room temperature after 36–48 hours led to the formation of ethylene gas through dimerization of carbenes. Monitoring the reaction by ^1H, and ^{119}Sn NMR experiments in a sealed NMR tube showed that, in addition to ethylene, a quantitative amount of **1.8** and less than 1% of formaldehyde were formed with the residual O_2 present in solution (Scheme 1.18).

Scheme 1.18. Decomposition of iodomethyl-tricarbastannatrane in the presence of $Pd(P(^tBu)_3)_2$



1.11 **1.8**

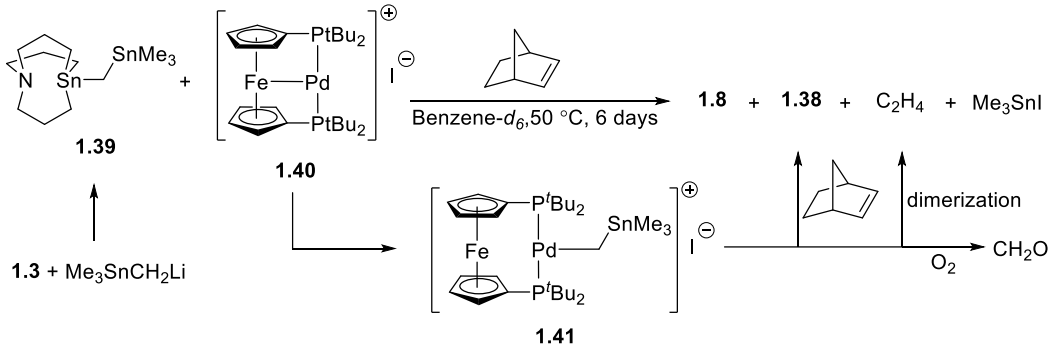
Decomposition of **1.11** in the presence of 25% mol of $Pd(P(^tBu)_3)_2$, and a 5-fold excess norbornene afforded exo-tricyclo[3.2.1.$0^{2,4}$]octane (**1.38**) after 48 hours at room temperature in 64% yield (Scheme 1.19). In addition to **1.38**, ethylene, formaldehyde, and tricarbastannatrane **1.8** were generated in the reaction. These observations supported the existence of methylene carbenoid as the reaction intermediate (Scheme 1.20). Tricarbastannatrane **1.11** showed to be more reactive than Bu_3SnCH_2I and Me_3SnCH_2I, as $Pd(P(^tBu)_3)_2$-catalyzed cyclopropanation of 9-fold excess of norbornene by Bu_3SnCH_2I furnished compound **1.38** in 71% yield after 15 days (based on 33% conversion). $MeSnBu_3$, $CH_2(SnBu_3)_2$, ethylene and formaldehyde were formed in this transformation as well.

Scheme 1.19. Decomposition of iodomethyl-tricarbastannatrane in the presence of norbornene and $Pd(P(^tBu)_3)_2$

1.38

It was postulated that sp^3-*gem*-dimetallic Pd-stannylalkane intermediate **1.41** was generated via transmetalation of tricarbastannatrane **1.39** with cationic Pd(II) catalyst **1.40** (Scheme 1.20). This intermediate could not be detected by NMR spectroscopy. This intermediate displayed carbenoid reactivity and led to the formation of ethylene, and generated tricycle **1.38** by cyclopropanation of norbornene. In addition, **1.41** can also react with the trace of oxygen in solution to furnish formaldehyde. The preparation of the sp^3-*gem*-dimetallic halo-Pd(II)/trialkylstannylalkane species, which led to a palladium-stabilized carbene, supported the Busacca-Farine *cine*-substitution mechanism.

Scheme 1.20. sp^3-Gem-dimetallic intermediate formation



As mentioned in the above section, within the stannatranes family, only tricarbastannatranes have carbons attached to the tin atom. Therefore, the environment around the tin atom of tricarbastannatrane derivatives is similar to that of organotin compounds. Therefore, they are the only derivatives in the stannatrane family that have been used in organic synthesis as nucleophiles. However, the applications of tricarbastannatrane derivatives are limited to Stille cross-coupling reactions, and no example of direct addition of the apical alkyl group in alkyl-tricarbastannatranes has been reported.[16] Moreover, the axial Sn−C bond in alkyl-tricarbastannatranes, is highly reactive.[8] As a result, it was postulated that alkyl-tricarbastannatranes are capable of transferring alkyl groups to activated electrophiles, such as α,β-unsaturated carbonyl compounds, to form carbon−carbon bonds under mild reaction conditions.

In addition to the use of alkyl-tricarbastannatranes in carbon−carbon bond formation reactions, the intramolecularly stabilized organotin cation can be studied by removing the apical group from tricarbastannatranes. To the best of our knowledge, the characteristic and stability of cationic stannatrane species have not been studied to date. It was proposed that the cationic tin center in the

tricarbastannatrane skeleton should be stabilized by the electron pair of the nitrogen atom; thus, this skeleton should show the shortest tin−nitrogen interaction among tricarbastannatranes.[26] Tricoordinated tin cations, such as tributyltin, degrade in the absence of a stabilizing reagent or a Lewis basic solvent.[27] However, the tetracoordinated tin cation is expected to be more stable and less Lewis acidic than its trialkyltin analogs. In addition, cationic tricarbastannatrane complexes should be able to act as a weak Lewis acid to activated electron-deficient electrophiles in non-coordinating solvents.

Based on the above discussion, applying pentacoordinated alkyl-tricarbastannatrane in conjugate addition reactions has several advantages over other alkyltin reagents. First, the apical alkyl group can be selectively transferred from tin to α,β-unsaturated carbonyl compounds. Second, the stable Lewis acidic tricarbastannatrane cation can activate the electrophile by coordintion to the carbonyl group of α,β-unsaturated carbonyl compounds. Thrid, the stable tetracoordinated cation can be recovered as a crystalline chloro-tricarbastannatrane[8,9] with dilute HCl solution in the reaction workup.

1.2 Research Objectives

The major focus of this thesis is the development of new methods for carbon–carbon bond formation, and alkene reduction using organotricarbastannatranes. As mentioned above, tricarbastannatranes could transfer their apical alkyl group selectively in the presence of a palladium catalyst in carbon–carbon bond forming process. The objective is to transfer the apical group of tricarbastannatranes directly to an activated electrophile to form a carbon–carbon or carbon–hydrogen bond. It was postulated that after transferring of the apical alkyl group, a cationic tricarbastannatrane species was formed as a side product. Therefore, to gain insight into the mechanism of the reaction, cationic complexes of tricarbastannatrane were synthesized and characterized as well.

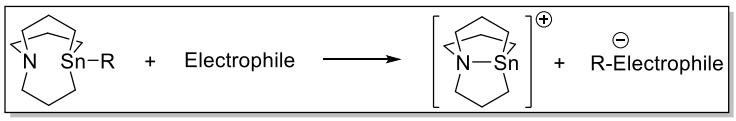


Figure 1.3. Transfer of the apical group of organotricarbastannatranes to an electrophile

1.3 Dissertation Outline

This dissertation is divided into two main parts: the next chapter, which concentrates on the synthesis and characterization of ionic tricarbastannatrane complexes, and the subsequent three

chapters, which focus on tricarbastannatrane reactions to form carbon–carbon as well as carbon–hydrogen bonds. These chapters are organized as follows.

Chapter 2

This chapter investigates the synthesis and structural studies of tricarbastannatrane complexes. The structure of complexes $[N(CH_2CH_2CH_2)_3Sn](BF_4)$, $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$, $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$, and $[[N(CH_2CH_2CH_2)_3Sn]_2Cl_{0.2}F_{0.8}][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ are determined by X-ray crystallography.

Chapter 3

In this chapter the $B(C_6F_5)_3$-promoted conjugate additions of alkyl-tricarbastannatranes to benzylidene Meldrum's acid derivatives under mild conditions are studied. The mechanism of the addition is investigated, and NMR spectroscopy and mass spectrometry techniques are used to determine the structure of the reaction intermediate. Furthermore, complex $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$ is characterized by X-ray diffraction analysis.

Chapter 4

Insitu hydride abstraction from isopropyl-tricarbastannatrane by tris(pentafluoropheynl)borane, $B(C_6F_5)_3$ is demonstrated in this chapter. The hydride abstraction yielded $[HB(C_6F_5)_3]^-$, the cationic tricarbastannatrane species, and propene gas. This process is followed by the reduction of benzylidene barbituric acids via hydride transfer from the generated borohydride to the electrophilic benzylic carbon under catalytic conditions.

Chapter 5

This chapter describes the carbon–carbon bond formation by the conjugate addition of allyl-tricarbastanntrane to benzylidene derivatives of Meldrum's acid and 1,3-dimethyl barbituric acid under mild reaction conditions. It is demonstrated that functionalized all-carbon quaternary stereocentres can be generated by this process as well.

Chapter 6

The last chapter concludes the dissertation, highlights its contributions, and suggests topics for future research.

Chapter 2

Synthesis and Characterization of Tricarbastannatrane Complexes

The synthesis and characterization of a series of tin ionic triptych complexes in solid state and solution are described in this chapter. Complexes $[N(CH_2CH_2CH_2)_3Sn](BF_4)$, $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$, $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$ *and* $[[N(CH_2CH_2CH_2)_3Sn]_2Cl_{0.2}F_{0.8}][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ *were characterized by X-ray diffraction analyses, multinuclear NMR spectroscopy, and mass spectrometry.*

2.1 Introduction

Hypervalent triorganotin compounds with the substituent pattern XC_3SnY are excellent models for tetrahedron–trigonal bipyramid path. Along this path, lengthening of Sn–Y bond and change of the C–Sn–C angles from 109.5° (tetrahedron) to 120° (trigonal bipyramid) happens due to the donor atom X approach to the tin atom. In an ideal trigonal bipyramidal molecular geometry, the difference of equatorial and axial angles is 90° [(3 × 120) – (3 × 90)] (Figure 2.1).

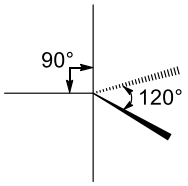


Figure 2.1. Ideal trigonal bipyramidal molecular geometry

Some representative structures of mono, di, and tricyclic pentacoordinated tin compounds are illustrated in Figure 2.2.[28] The stability of the pentacoordinate structure is determined by the electronegativity of the atoms attached to the tin atom.

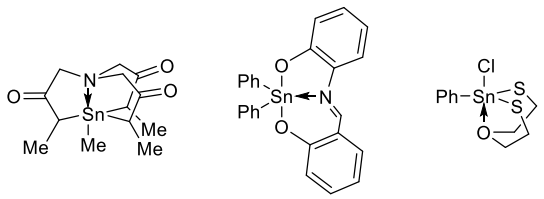


Figure 2.2. Representative structures of pentacoordinated tin compounds

Tricarbastannatranes are characterized by their cage structure, and display pentacoordinated tin centre resulting from intramolecular donor–acceptor interactions. This interaction is the result of the atrane frame and the Lewis acidity of the tin atom. As a result of N→Sn coordination, the tin atom shows a distorted trigonal bipyramidal configuration with the nitrogen and the apical group occupying the axial positions. The strength of the transannular Sn–N bonds depends on the nature of substituents on the tin atom. Tricarbastannatranes have been known for a long time,[5] but only a few examples have been synthesized, and fewer have been structurally characterized by single crystal X-ray diffraction analysis.

As discussed in Chapter 1, chloro-tricarbastannatrane (**2.1**) was first synthesized in 1984.[5] The structure was determined by X-ray crystallography by Jurkschat and coworkers in 1985.[29] That study had reported a 2.613(7) Å Sn–Cl bond. However, it was later found that the actual Sn–Cl in **2.1** is 2.52(1) Å, and the sample which was used in the initial study was contaminated with some impurities.[12] To obtain more information about the structure of tricarbastannatrane **2.1**, the X-ray structure of **2.1** was reinvestigated by our group. In the initial studies, crystals suitable for X-ray analysis were obtained in toluene.[26] However, we obtained single crystals of chloro-tricarbastannatrane from 1,2-dichloromethane/pentane solution. Our data was close to the values reported by Jurkschat and coworkers.[12]

The X-ray structure is illustrated in Figure 2.3. Compound **2.1** crystallizes in the space group $P6_3$ with parameters $\alpha = b = 8.3691(2)$ Å, $c = 9.1053(2)$ Å, and V = 552.309 Å^3. The structure was refined to a final R value of 0.001. The molecule is symmetric with the chlorine, tin and nitrogen atoms lying on a crystallographic three-fold axis. The structure has a trigonal bipyramidal molecular geometry around the tin atom, and the nitrogen and chlorine atoms occupy apical positions. The compound displays C_3 symmetry as a result of uniform envelope conformations of three five-member rings. As a result of this conformation, the molecule is chiral.

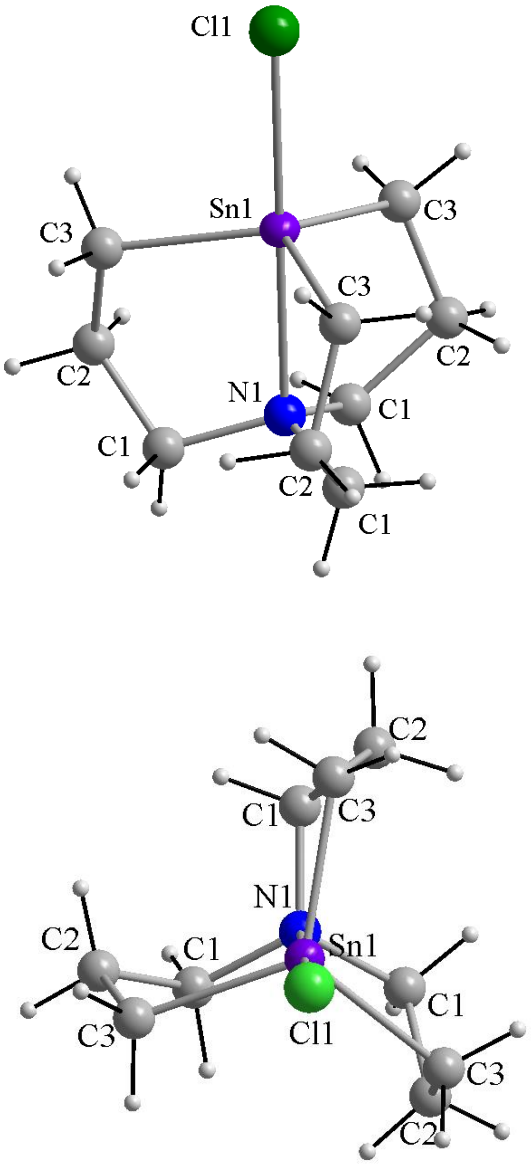


Figure 2.3. X-ray structure of chloro-tricarbastannatrane

Selected bond distances and bond angles are summarized in Table 2.1. The nitrogen–tin bond in **2.1** is 2.364 Å, which is shorter than the intra- and intermolecular Sn–N interactions in other triorganotin halide complexes such as $Me_2NCH_2C_6H_4SnPh_2Br$ (Sn–N bond of 2.630(2) Å)[30] and 2-[l-(*S*)-$Me_2NCH(Me)$]$C_6H_4SnMePhBr$ (Sn–N bond of 2.476(7) Å).[31] The lengthening of Sn–Cl bond was observed as a result of the transannular Sn–N bond. This Sn–Cl bond is longer than those in many

pentacoordinated triorganotin chlorides,[27] such as $Ph_3SnCl(Ph_2POCH)_2$ (Sn–Cl bond of 2.489(3) Å) (Figure 2.4).[32]

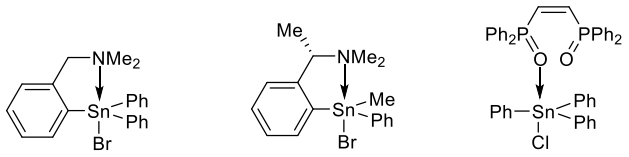


Figure 2.4. Sn–N and Sn–Cl bonds in some pentacoordinated tin compounds

Table 2.1. Bond distances and bond angles in chloro-tricarbastannatrane

	Bond length (Å)
Sn(1)–Cl(1)	2.523
Sn(1)–N(1)	2.364
Sn(1)–C(3)	2.151
N(1)–C(1)	1.484
C(1)–C(2)	1.525(3)
C(2)–C(3)	1.531(4)
	Bond angles (°)
N(1)–Sn(1)–Cl(1)	180.0
C(3)–Sn(1)–Cl(1)	99.7
C(3)–Sn(1)–N(1)	80.3
C(3)–Sn(1)–C(3)	117.2
C(1)–N(1)–Sn(1)	105.7
C(2)–C(3)–Sn(1)	108.0
C(1)–C(2)–C(3)	110.8(3)
C(2)–C(1)–N(1)	110.2
C(1)–N(1)–C(1)	113.0

As depicted in Table 2.1, C(3)–Sn(1)–C(3) bond angle is 117.2°, which deviates slightly from the ideal trigonal bipyramidal 120° angle. Therefore, the tin atom has a distorted trigonal bipyramidal geometry in **2.1**, and it lies 0.36 Å below the plane containing the three equivalent C3 atoms. The angles around the nitrogen atom deviate from the tetrahedral geometry due to the nitrogen–tin interaction, and the nitrogen atom is situated 0.395 Å below the plane occupied by three C1 atoms.

As previously discussed in section 1.1.1, $N(CH_2CH_2CH_2)_3SnF$ (**2.2**) can be formed from $N(CH_2CH_2CH_2)_3SnMe$ and Pr_3SnF in EtOH.[12] Attempts at obtaining crystals of **2.2** failed under inert conditions, and crystalline **2.2** was obtained only as its water adduct $N(CH_2CH_2CH_2)_3SnF{\cdot}H_2O$ (**2.3**).

The molecular structure of **2.3** is shown in Figure 2.5. In compound **2.3**, two molecules of **2.2** are held together by the intermolecular Sn(1)•••F(2) interaction. In addition, strong hydrogen bridges F(1)•••H•••O(1)•••H•••F(2) link the two tricarbastannatrane molecules. This dimer is attached to a second dimer by a second molecule of water O(2). The geometrical pattern around Sn(1) and Sn(2) can be described as monocapped trigonal bipyramid.

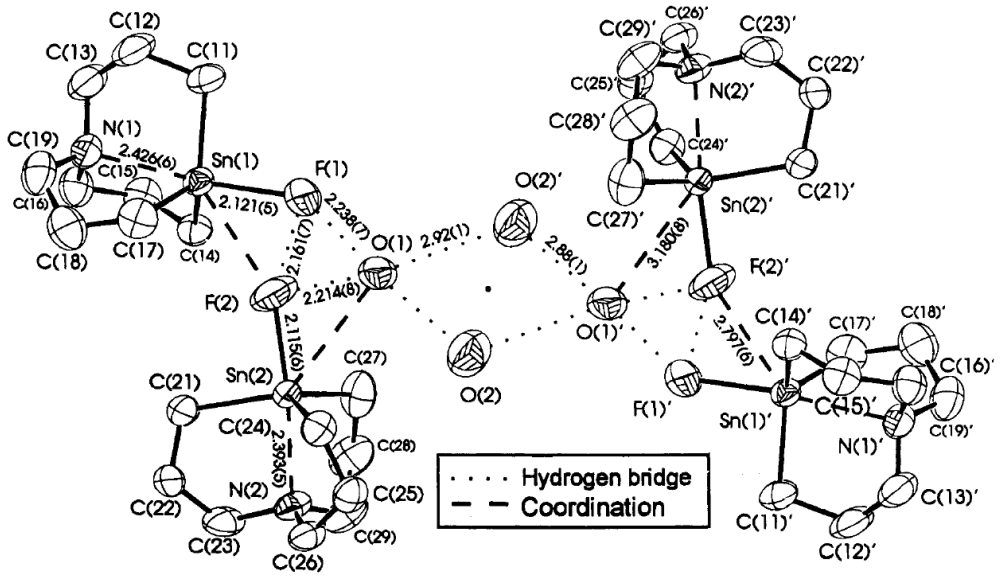


Figure 2.5. X-ray structure of $N(CH_2CH_2CH_2)_3SnF{\bullet}H_2O$.[12] (with permission from ACS publications)

Some bond lengths and bond angles of **2.3** are summarized in Table 2.2. Intermolecular Sn(1)•••F(2) and Sn(2)•••O(1) interactions are 2.797(6) Å and 3.180(8) Å, respectively. These strong Sn–F and weak Sn–O interactions led to slight distortion of the ideal atrane frame. 7.3° and 6° deviation from the ideal value of 180° was observed in N(1)–Sn(1)–F(1) and N(2)–Sn(2)–F(2) angles, respectively. Sn(1)–F(1) and Sn(2)–F(2) bonds of 2.121(5) Å and 2.115(6) Å are longer than an Sn–F single bond of 1.96 Å due to the transannular Sn–N interaction.[12,33]

Table 2.2. Bond distances and bond angles in $N(CH_2CH_2CH_2)_3SnF{\bullet}H_2O$

	Bond length (Å)
Sn(1)–N(1)	2.426(6)
Sn(1)–C(11)	2.146(7)
Sn(1)–C(14)	2.132(9)
Sn(1)–C(17)	2.145(9)
Sn(1)–F(1)	2.121(5)
Sn(2)–N(2)	2.393(5)
Sn(2)–C(21)	2.145(8)
Sn(2)–C(24)	2.135(8)
Sn(2)–C(27)	2.126(7)
Sn(2)–O(1)	3180(8)
Sn(2)–F(2)	2.115(6)
	Bond angles (°)
N(1)–Sn(1)–F(1)	172.7(2)
F(1)–Sn(1)–C(11)	102.3(2)
F(1)–Sn(1)–C(14)	94.1(3)
F(1)–Sn(1)–C(17)	106.9(3)
C(11)–Sn(1)–C(14)	119.5(3)
C(14)–Sn(1)–C(17)	112.8(4)
C(11)–Sn(1)–C(17)	116.8(3)
N(2)–Sn(2)–F(2)	174.0(2)
F(2)–Sn(2)–C(21)	102.4(3)
F(2)–Sn(2)–C(24)	93.6(3)
F(2)–Sn(2)–C(27)	104.4(3)
C(21)–Sn(2)–C(24)	117.6(3)
C(24)–Sn(2)–C(27)	115.0(3)
C(21)–Sn(2)–C(27)	118.1(3)

The X-ray structures of $N(CH_2CH_2CH_2)_3SnI$ and $N(CH_2CH_2CH_2)_3SnBr$ were obtained as well. These structures are almost identical, and illustrated in Figure 2.6 by the representative structure of bromo-tricarbastannatrane. The tin atoms in these structures show a distorted trigonal bipyramidal configuration in which three methylene carbons are in equatorial positions, and nitrogen and halogen are in axial positions.

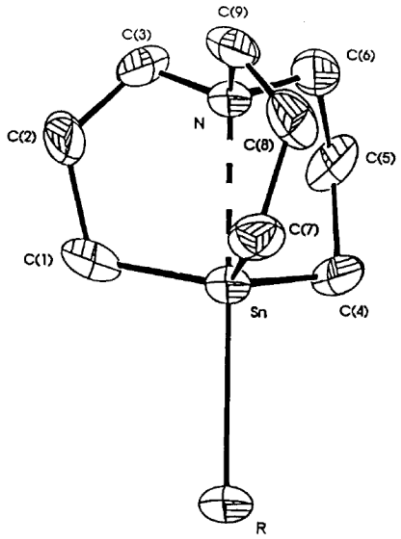


Figure 2.6. ORTEP drawing of $N(CH_2CH_2CH_2)_3SnBr$.[12] (with permission from ACS publications)

A few bond angles and bond lengths are listed in Table 2.3. The shortest Sn–N interaction corresponds to bromo-tricarbastannatrane.

Table 2.3. Bond distances and bond angles in $N(CH_2CH_2CH_2)_3SnBr$ and $N(CH_2CH_2CH_2)_3SnI$

	$N(CH_2CH_2CH_2)_3SnBr$	$N(CH_2CH_2CH_2)_3SnI$
		Bond length (Å)
Sn–N	2.28(2)	2.375(6)
Sn–X	2.693(2)	2.896(1)
Sn–C	2.20(1)	2.152(8)
		Bond angles (°)
N–Sn–R	180	179.6(1)
N–Sn–C	81.2(3)	80.5(3)
R–Sn–C	98.8(3)	99.5(2)
C–Sn–C	117.7(6)	117.3(3)

It was earlier mentioned in section 1.1.1 that the treatment of **2.1** with methyllithium yields methyl-tricarbastannatrane.[2] A concentrated solution of methyl-tricarbastannatrane in diethyl ether provided crystals suitable for X-ray analysis.[26] X-ray crystallographic studies revealed that the overall geometry of this tetraorganotin is similar to that of **2.1** and other halotricarbastannatranes. However, the Sn–N bond of 2.624(8) Å is much longer than those in halo-tricarbastannatranes. Thus, due to the

absence of any electronegative atom attached to the tin atom, the longest transannular Sn–N interaction was observed in this tricarbastannatrane. Because of the weak Sn–N bond, the configuration of the tin atom is regarded as a monocapped tetrahedron and is distorted from the ideal trigonal bipyramidal.

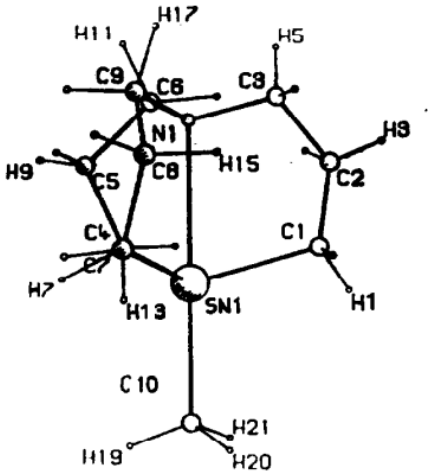


Figure 2.7. Molecular structure of $N(CH_2CH_2CH_2)_3SnMe$.[32] (with permission from Elsevier)

The equatorial angles of 113.4° for C(1)–Sn(1)–C(4), C(1)–Sn(1)–C(7), and C(4)–Sn(1)–C(7) are closer to a tetrahedral angle (≈109.5°) than to trigonal bipyramidal angle (120°). In addition, the apical angles of 105.2° for C(10)–Sn(1)–C(1), C(10)–Sn(1)–C(4), and C(10)–Sn(1)–C(7) are close to a tetrahedral angle. The deviation of the tin atom from the plane comprised of the carbon atoms C(1), C(4), and C(7) is 0.569 Å. However, the nitrogen atom deviation from the plane defined by C(3), C(6), and C(9) is 0.375 Å. Due to interamolecular Sn–N interaction, the Sn(1)–C(10) bond of 2.214 Å shows the anticipated lengthening.[32]

Table 2.4. Bond distances and bond angles in methyl-tricarbastannatrane

	Bond length (Å)
Sn(1)–C(10)	2.214(11)
Sn(1)–N(1)	2.624(8)
Sn(1)–C(1)	2.151(8)
N(1)–C(3)	1.449(11)
C(1)–C(2)	1.504(13)
C(2)–C(3)	1.524(11)
	Bond angles (°)
N(1)–Sn(1)–C(10)	179.6
C(4)–Sn(1)–C(1)	113.1(4)
C(7)–Sn(1)–C(1)	113.7(4)
C(7)–Sn(1)–C(4)	113.3(4)
C(10)–Sn(1)–C(1)	105.3(4)
C(10)–Sn(1)–C(4)	105.0(4)
C(10)–Sn(1)–C(7)	105.4(4)

2.2 Proposal

In context with our ongoing studies on the development of new methods for carbon–carbon bond formation, we proposed that the alkyl group in alkyl-tricarbastannatranes could be transferred to an electrophile. It was postulated that after transferring the apical alkyl group, a cationic tricarbastannatrane would be generated. It was expected that the cationic tricarbastannatrane should exhibit a weak Lewis acidity as well as a stronger Sn–N interaction in comparison to those in halo-tricarbastannatranes. However, to the best of our knowledge prior to embarking on this project, there has been no systematic study on the Lewis acidity and the stability, as well as the intramolecular interaction of ionic tricarbastannatranes. In this regard, the objective was to synthesize and characterize cationic complexes of carbastannatranes. It was proposed that cationic tricarbastannatranes could be generated from chloro-tricarabastannatrane and the corresponding silver salts. The structure and Lewis acidity of tricarbastannatrane complexes were established using NMR spectroscopy, mass spectrometry, and X-ray crystallography techniques.

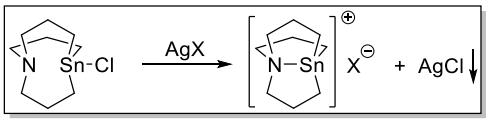
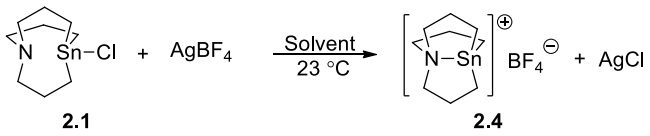


Figure 2.8. Proposal for the synthesis tricarbastannatrane complexes

2.3 Result and discussion

As mentioned earlier, the formation of tricarbastannatrane complex $[N(CH_2CH_2CH_2)_3Sn](BF_4)$ (**2.4**) in THF was reported by Tzschach and Jurkschat, which showed a deshielded ^{119}Sn NMR shift (Scheme 2.1) at δ = 103 ppm.[2] We suspected that the chemical shift might not be indicative of free $[N(CH_2CH_2CH_2)_3Sn]^+$ (**2.5**) in solution, as Lewis acid **2.5** could potentially interact with THF. Organ and coworkers reported the formation of $[n\text{Bu}_3\text{Sn}\cdot\text{THF}]^+[HB(C_6F_5)_3]^-$ by the reaction of $n\text{Bu}_3\text{SnH}$ and $B(C_6F_5)_3$ in THF; THF could stabilize the stannyl cation $[n\text{Bu}_3\text{Sn}]^+$.[26] Therefore, the formation of complex **2.4** was reinvestigated in the absence of a Lewis basic solvent through the addition of $AgBF_4$ to a solution of chloro-tristannatrane in 1,2-dichloroethane (Scheme 2.1).[34] A ^{119}Sn chemical shift of δ = 145.8 ppm corresponding to $[N(CH_2CH_2CH_2)_3Sn]^+$ (**2.5**) in complex **2.4** was observed (Table 2.5, entry 2). NMR experiments also revealed that complex **2.4** was stable at room temperature in solution for more than one week and remained unchanged for more than 2 hours at 70 °C.

Scheme 2.1. Reaction of chloro-tricarbastannatrane and silver tetrafluoroborate



2.1 **2.4**

Crystallization of **2.4** in a pentane/1,2-dichloroethane mixture yielded crystals that were analyzed by X-ray crystallography. This compound recrystallizes in the orthorhombic space group Pnma with *a* = 12.0477(10) **Å**, *b* = 8.3632(7) **Å**, and *c* = 12.7309(10) **Å**. As depicted in Figure 2.9, the salient feature of this structure is its exceptionally short Sn–N bond [2.219(9) Å]. In addition, the counter ion $[BF_4]^-$ interacts with the positively charged tricarbastannatrane **2.5** [Sn–F bond is 2.374(11) Å]. The geometry around the pentacoordinated tin(IV) ion is distorted trigonal bipyramidal. In addition, HRMS (ESI) supported the formation of complex **2.4** showing an ion peak at *m/z* 260.04512 corresponding to **2.5**, and an ion peak at *m/z* 87.00237 is attributed to BF_4.

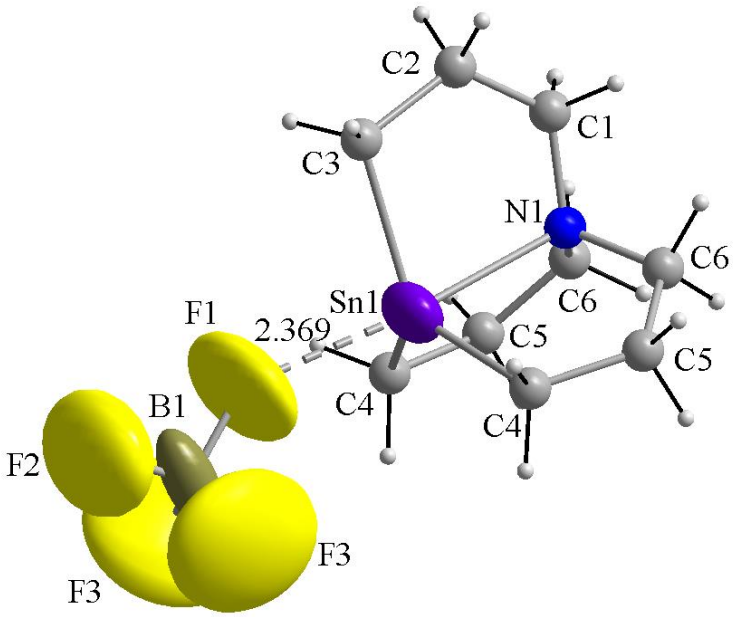


Figure 2.9. X-ray Structure of $[N(CH_2CH_2CH_2)_3Sn](BF_4)$

Additional information about the structure of ionic triptych complexes was obtained by preparing $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$ (**2.6a**) through the reaction of $AgSbF_6$ with **2.1** (Figure 2.10). The formation of ionic triptych in solution was supported by a deshielded ^{119}Sn NMR signal at δ = 197.8 ppm (Table 2.5, entry 3). This compound was recrystallized in the monoclinic space group $P2_1/c$ with α = 14.5513(3) **Å**, b = 13.9626(3) **Å**, and c = 15.0103(3) **Å**. The tin atom adopts a trigonal bipyramidal geometry with the carbons of the alkyl groups in equatorial positions. C–Sn–C angles [120.2(4), 119.0(4), 118.5(4)] deviate from the ideal angle of 120°. In this complex, a longer Sn–F interaction (Sn–F 2.48 Å and 2.52 Å) and a more deshielded tin center depicts looser interaction between **2.5** and $[SbF_6]^-$ compared to its interaction with $[BF_4]^-$ in complex **2.4**. In addition, the Sn–N bond length is 2.213(5) Å, suggesting a stronger transannular Lewis acid–base interaction than in **2.4**. Of note, complex **2.6a** was stable for more than a week in 1,2-dichloroethane at room temperature.

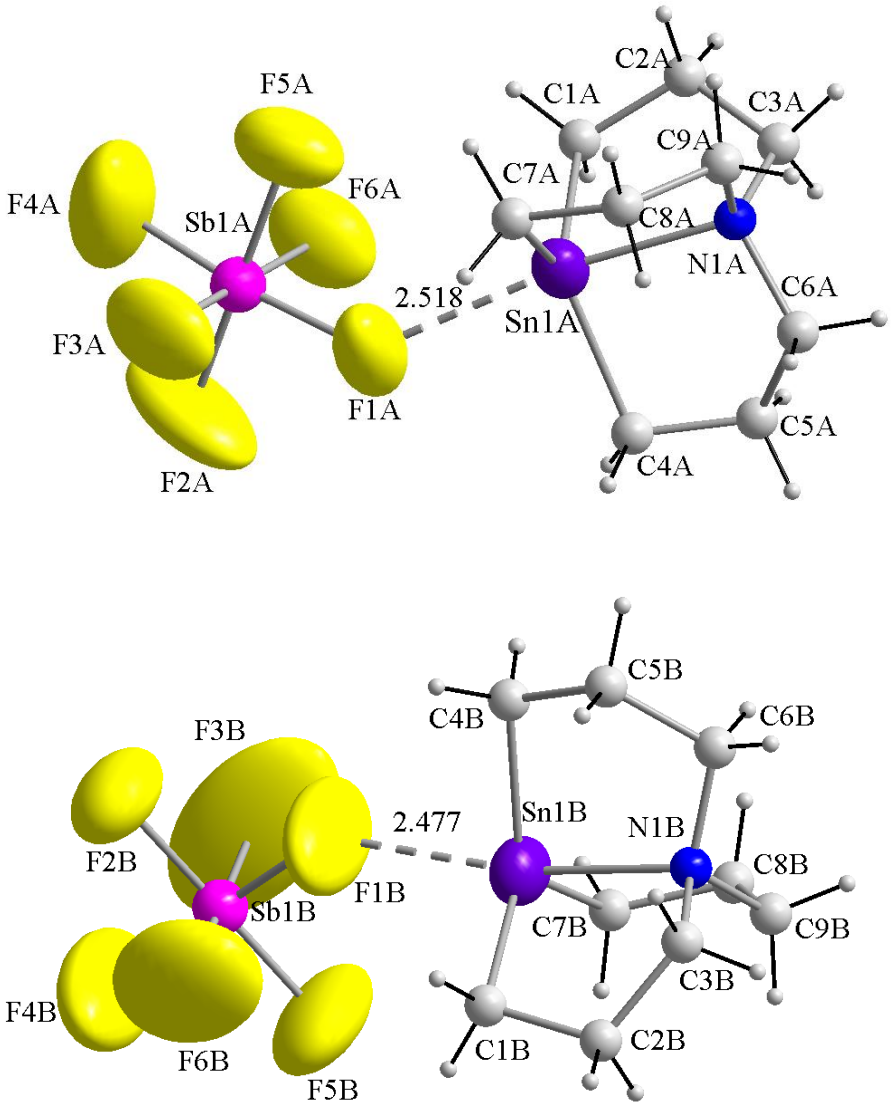


Figure 2.10. X-ray structure of $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$

A solution of complex **2.6a** containing traces of chloride ion crystallized to yield $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$ (**2.6b**). The crystal lattice of this complex is defined by the space group I23, in which one chlorine atom is surrounded by four ionic triptychs and the $[SbF_6]^-$ counter ions are shared along the edge of the unit cell (Figure 2.11). The Sn–N bond length in **2.6b** is 2.223(3) Å and the distance between chlorine and tin atoms is 2.921 Å, which is significantly longer than the Sn–Cl bond of 2.52 Å in **2.1**. According to the X-ray structure, there is no interaction

between the chlorine and tin atoms in **2.6b,** establishing the formation and stability of free ionic triptych **2.5**.

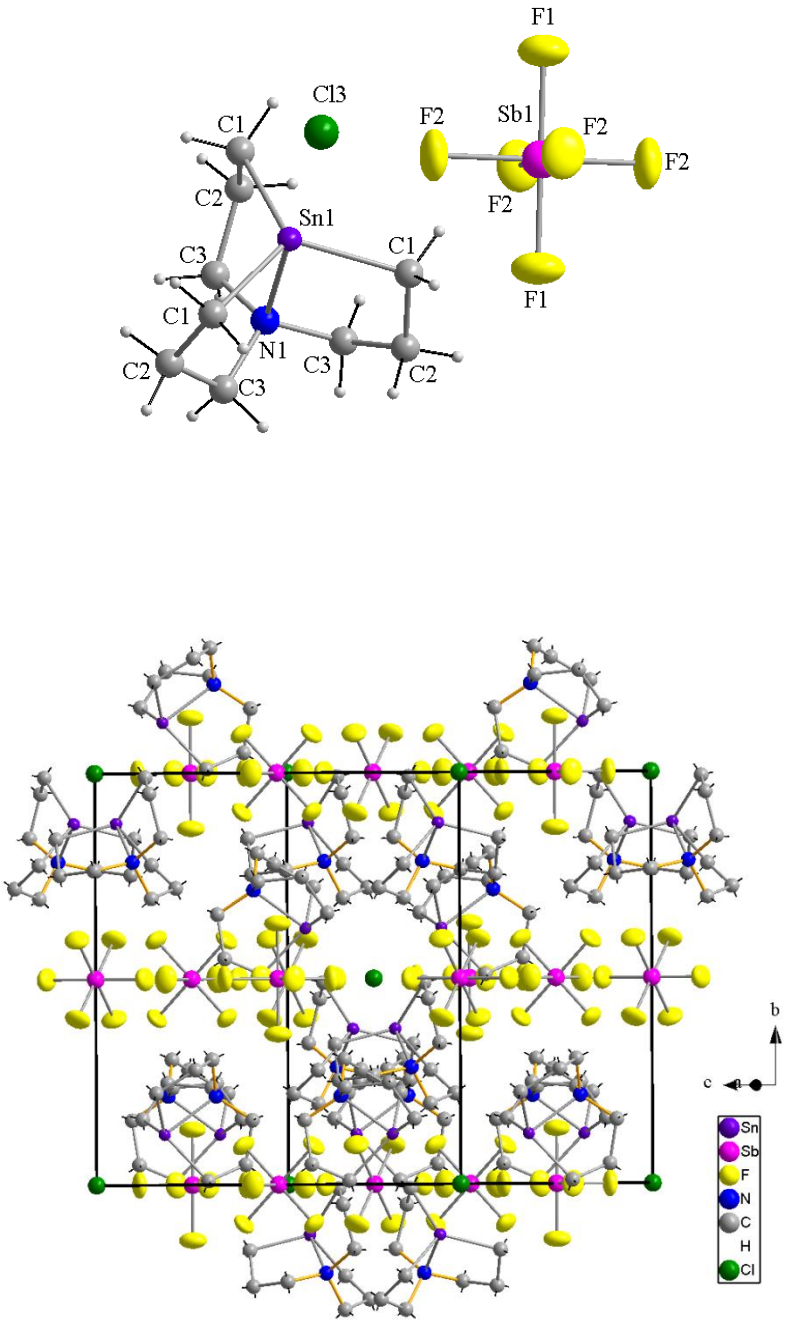


Figure 2.11. X-ray Structure of $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$

Then, complex $[N(CH_2CH_2CH_2)_3Sn][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ (**2.7**), that contains the bulky and non-coordinating counter ion $[B[3,5\text{-}(CF_3)_2C_6H_3]_4]$[35] was synthesized from $Ag[B[3,5\text{-}(CF_3)_2C_6H_3]_4]$. A deshielded ^{119}Sn signal was observed at δ = 198.1 (Table 2.5, entry 4). Crystallization of **2.7** in pentane/1,2-dicholorethane solution revealed the formation of complex **2.8** with the general formula $[[N(CH_2CH_2CH_2)_3Sn]_2Cl_{0.2}F_{0.8}][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$, in which fluorine and chlorine atoms bond to two cationic carbastannatranes **2.5** with 1:4 ratio, respectively (Figure 2.12). The Sn–N distance of 2.366(3) Å and 2.345(3) Å are significanly longer than the Sn–N distance in other cationic tricarbastannatrane complexes. Sn(1)–Cl(1) distance of 2.542(6) Å and Sn(2)–Cl(1) distance of 2.589(6) Å are slightly longer than Sn–Cl bond in **2.1**. Interaction between fluorine and two tin atoms are evidenced by the close F–Sn(1) and F–Sn(2) approach (2.189(3) Å, 2.203(3) Å). The source of fluorine atom in this complex is likely MgBrF. It is a byproduct of the reaction between $[3,5\text{-}(CF_3)_2C_6H_3]MgBr$ and $NaBF_4$, which is the step prior to the exchange reaction between $Na[B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ and $AgNO_3$ in the preparation of $Ag[B[3,5\text{-}(CF_3)_2C_6H_3]_4]$. The source of chlorine atom may be from the trace of silver chloride (Figure 2.8). Of note, as depicted in Figure 2.12, fluorine atoms in one of the CF_3 groups in $[B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ are disordered.

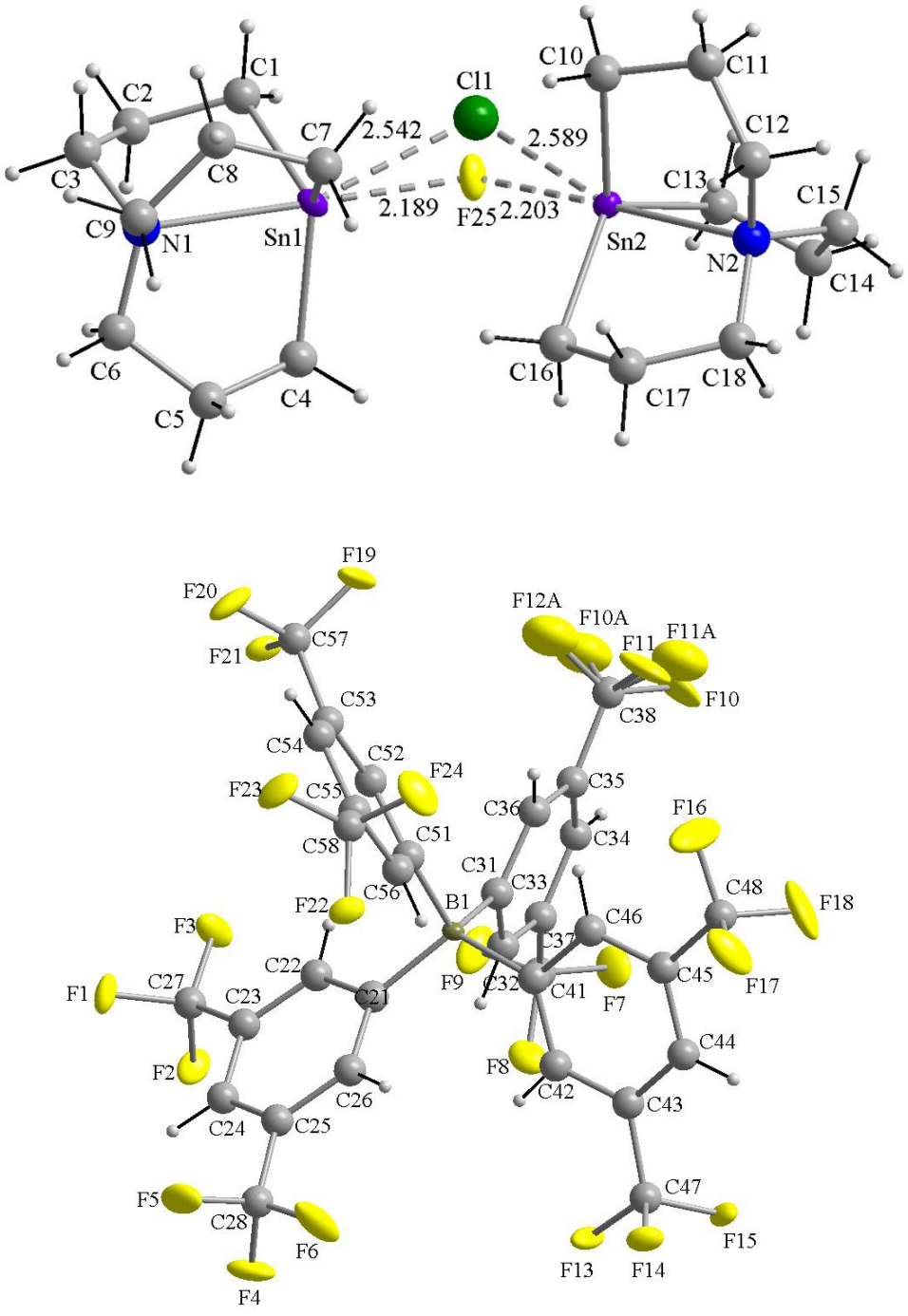
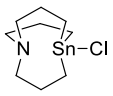
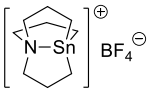
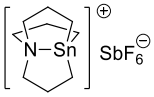
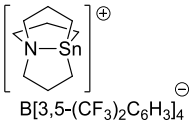
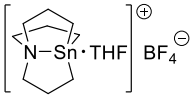
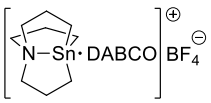
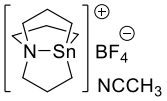


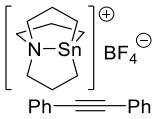
Figure 2.12. X-ray Structure of $[[N(CH_2CH_2CH_2)_3Sn]_2Cl_{0.2}F_{0.8}][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$

All of the efforts to make complex $[N(CH_2CH_2CH_2)_3Sn][B(C_6F_5)_4]$ from $Ag[B(C_6F_5)_4]$ failed due to its decomposition in 1,2-dichloroethane. This reactivity has been previously reported.[36]

The coordination of various Lewis bases to complex **2.4** was then studied (Table 2.5, entry 5-8). While the addition of one equivalent of DABCO showed a significant change of the ^{119}Sn chemical shift from δ = 145.8 ppm to δ = 61.4 ppm (Δ ppm = 84.4), adding one equivalent of CH_3CN (Δppm = 3.3) or diphenylacetylene (Δppm = 1.6) showed negligible changes. A ^{119}Sn chemical shift of 131.8 ppm was observed after one equivalent of THF was added to **2.4** (Δppm = 14.0), indicating its moderate coordinating ability toward **2.5**. This result reflects the exceptional stability and moderate Lewis acidity of **2.5**.

Table 2.5. NMR studies on tricarbastannatrane complexes.[34]

Entry	Carbastannatrane	NMR chemical shifts (ppm)			
		^{1}H	^{13}C	^{119}Sn	^{11}B
1		1.13(t) 1.78 (m) 2.42(t)	13.0 22.9 54.3	17.6	NA
2		1.47(t) 1.96 (m) 2.57(t)	12.6 23.6 55.0	145.8	–2.1
3		1.61(t) 2.04 (m) 2.64(t)	14.2 24.4 55.4	197.8	NA
4		1.64(t) 2.04 (m) 2.63(t)	16.5 24.7 55.5	198.1	–7.2
5		1.37 (t) 1.94 (m) 2.56 (t)[a]	11.5 23.3 54.7[b]	131.8	–1.6
6		Broad	13.0 22.8 54.3 [c]	61.4	–1.7
7		1.45 (t) 1.95 (m) 2.57 (t)[d]	12.5 23.6 54.9 [d]	142.5	–1.6

8		1.46 (t, 6H) 1.95 (m, 6H) 2.56 (t, 6H)[e]	12.5 23.6 54.9 [f]	144.2	–1.6

[a] One broad signal observed for THF at 1.82 ppm and the other THF signal overlaps with 1,2-dichloroethane signal. [b] Two signals at 25.01, 68.12 ppm belong to THF. Free THF carbon chemical shifts in 1,2-dichloethane are 25.2, 66.9 ppm. [c] Two signals at 44.6, 46.9 ppm belong to DABCO. Free DABCO chemical shift in 1,2-dichloroethane is 47.09 ppm. [d] CH_3CN signals in proton and ^{13}C NMR were 2.2 and 1.5 ppm respectively. [e] Diphenylacetylene proton chemical shifts are 7.4 and 7.5 ppm. [f] ^{13}C NMR chemical shifts of diphenyl acetylene are 88.5, 122.3, 127.9, 127.9, 131.0 ppm.

2.4 Summary

The structure of a number of intramolecularly stabilized cage-type organotin cations in solution and in the solid state has been determined. The formation of stable cationic tricarbastannatrane **2.5** and its weak Lewis acidity was confirmed by ^{119}Sn NMR. Furthermore, a lot of characteristic knowledge about ionic tricarbastannatrans were extracted. In addition, the structures of complexes $[N(CH_2CH_2CH_2)_3Sn](BF_4)$, $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$, $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$ and $[[N(CH_2CH_2CH_2)_3Sn]_2Cl_{0.2}F_{0.8}][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ were determined by X-ray crystallography. Important features of these ionic triptych complexes are their stability as well as their short transannular Sn–N bond.

2.5 Experimental

2.5.1 General Considerations

All reactions were carried out in oven or flame-dried glassware under dry nitrogen atmosphere using standard Schlenk techniques or in a glove box. 1,2-Dichloroethane was distilled over CaH_2. THF was distilled over sodium/benzophenone ketyl before use. Acetonitrile was dried by distillation from CaH_2. Pentane was dried over $LiAlH_4$ and distilled prior to use. $CDCl_3$ was distilled over P_2O_5, and stored on 4 Å Linde molecular sieves. All solvents were degassed via three freeze-pump-thaw cycles following distillation. DABCO was sublimed (60–90 °C at 0.1 mm Hg) in a Kugelrohr distillation apparatus by cooling the collecting flask with dry ice. Reactions were monitored by thin-layer chromatography on commercially prepared plates with a particle size of 60 Å. Developed plates

were visualized under a UV lamp (254 nm), or stained with ceric ammonium molybdate. Flash chromatography was performed using 230-400 mesh silica gel.

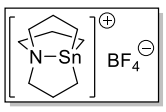
2.5.2 Characterization

Unless otherwise noted, ^{1}H and ^{13}C NMR spectra for all adduct products were obtained in $CDCl_3$ at 300 and 75 MHz, respectively. Chemical shifts are reported in parts per million (ppm, δ) relative to tetramethylsilane (TMS) as an external standard. Proton and carbon spectra were calibrated against the solvent residual peak [$CHCl_3$ (7.24 ppm) and $CDCl_3$ (77.0 ppm)] and in case of 1,2-dichlorethane against known solvent resonance [^{1}H (3.72 ppm) and ^{13}C (43.6 ppm)]. ^{11}B and ^{119}Sn NMR spectra of tricarbastannatranes were recorded on Bruker Avance-300 (^{11}B: 96 MHz, ^{119}Sn: 112 MHz) with ^{1}H decoupling in 1,2-dichloroethane calibrated against external BF_3•OEt_2 and Me_4Sn, respectively. The spectral references (sr) which were obtained from the external standards were used to calibrate all ^{119}Sn NMR and ^{11}B NMR chemical shifts. Spectral reference values of –171.61 Hz and –5.13 Hz were used to calibrate ^{119}Sn and ^{11}B chemical shifts in 1,2-dichloroethane, respectively. Abbreviations used to define NMR spectral mutiplicities are as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High resolution mass spectra (ESI) were run at the University of Waterloo Mass Spectrometry facility. Fragment signals are given in mass per charge number (m/z).

The following compounds were prepared according to literature procedures: 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (**2.1**),[8] $Ag[B[3,5\text{-}(CF_3)_2C_6H_3]_4]$.[37] Other reagents were purchased from commercial suppliers and used without further purification.

Crystals of **2.4**, **2.6a**, **2.6b**, and **2.8** for X-ray analyses were obtained after recrystallization in anhydrous 1,2-dichloroethane at room temperature, followed by the drop-wise addition of dry pentane to reach a cloudy point. Then 1,2-dichloroethane was added drop-wise until the solutions became clear again and then were allowed to stand under nitrogen at the mentioned temperature to form single crystals. Complex **4b** was formed from the solution of **4a** in the presence a small trace of chloride ion.

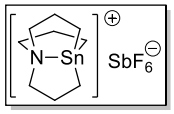
$[N(CH_2CH_2CH_2)_3Sn](BF_4)$ (2.4).



To a solution of **2.1** (15 mg, 0.051 mmol) in 1,2-dichloroethane (0.5 ml), was added $AgBF_4$ (9.9 mg, 0.051 mmol). After filtration of AgCl through a fritted Schlenk filter, the solution was transferred to a J. Young NMR tube. The product was characterized by NMR techniques. Single crystals of **2** were obtained upon recrystallization using

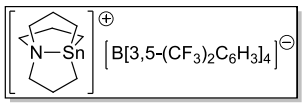
pentane/1,2-dichloroethane at 23 °C. ^{1}H NMR ($Cl(CH_2)_2Cl$, 300 MHz) δ 2.57 (t, 6H, NCH_2), 1.96 (m, 6H, CH_2), 1.47 (t, 6H, SnCH_2); ^{13}C NMR ($Cl(CH_2)_2Cl$, 75 MHz) δ 55.0 (NCH_2), 23.6 (CH_2),12.6 (SnCH_2); ^{119}Sn NMR ($Cl(CH_2)_2Cl$, 112 MHz) δ 146.8; ^{11}B NMR ($Cl(CH_2)_2Cl$, 96 MHz) δ –2.1. HRMS (–ESI) *m/z* calcd. for BF_4 (M^-): 87.00237. Found: 87.00264; HRMS (+ESI) *m/z* calcd. for $C_9H_{18}NSn$ (M^+): 260.04557. Found: 260.04512.

[N(CH$_2$CH$_2$CH$_2$)$_3$Sn](SbF$_6$) (2.6a).



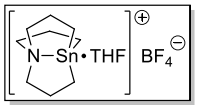
To a solution of **1** (15.0 mg, 0.0510 mmol) in 1,2-dichloroethane (0.5 ml), was added $AgSbF_6$ (17.5 mg, 0.0510 mmol). After filtration of AgCl through a fritted Schlenk filter, the solution was transferred to a J. Young NMR tube. Single crystals of **2.6a** were obtained upon recrystallization in pentane/1,2-dichloroethane at –16 °C. When the filtration was carried out through a filtering pipet, which was prepared by insertion of a small piece of cotton wool into a Pasteur pipet, complex **2.6b** was formed in the presence of a small trace of silver salt in the solution; ^{1}H NMR ($Cl(CH_2)_2Cl$, 300 MHz) δ 2.64 (t, 6H, NCH_2), 2.04 (m, 6H, CH_2), 1.61 (t, 6H, SnCH_2); ^{13}C NMR ($Cl(CH_2)_2Cl$, 75 MHz) δ 55.4 (NCH_2), 24.4 (CH_2),14.2 (SnCH_2); ^{119}Sn NMR ($Cl(CH_2)_2Cl$, 112 MHz) δ 197.8. HRMS (–ESI) *m/z* calcd. for SbF_6 (M^-): 234.89479. Found: 234.89380; HRMS (+ESI) *m/z* calcd. for $C_9H_{18}NSn$ (M^+): 260.04557. Found: 260.04462.

[N(CH$_2$CH$_2$CH$_2$)$_3$Sn][B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$] (2.7).



To a solution of **2.1** (15.0 mg, 0.0510 mmol) in 1,2-dichloroethane (0.5 ml), was added Ag[B[3,5-$(CF_3)_2C_6H_3]_4$] (49.6 mg, 0.0510 mmol). After filtration of AgCl through a fritted Schlenk filter, the solution was transferred to a J. Young NMR tube. ^{1}H NMR ($Cl(CH_2)_2Cl$, 300 MHz) δ 2.63 (t, 6H, NCH_2), 2.04 (m, 6H, CH_2), 1.64 (t, 6H, SnCH_2); ^{13}C NMR ($Cl(CH_2)_2Cl$, 75 MHz) δ 55.5 (NCH_2), 24.7 (CH_2), 16.5 (SnCH_2); ^{119}Sn NMR ($Cl(CH_2)_2Cl$, 112 MHz) δ 198.1; ^{11}B NMR ($Cl(CH_2)_2Cl$, 96 MHz) δ –7.2.

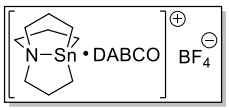
[N(CH$_2$CH$_2$CH$_2$)$_3$Sn]•THF (BF$_4$).



To a solution of **2.4** (17.6 mg, 0.0510 mmol) in 1,2-dichloroethane (0.5 ml) in a J. Young NMR tube, was added THF (4.0 µL, 0.051 mmol). ^{1}H NMR ($Cl(CH_2)_2Cl$, 300 MHz) δ 2.56 (t, 6H, NCH_2), 1.94 (m, 6H, CH_2), 1.82 (br, 4H, CH_2),1.37 (br,

6H, SnCH_2); ^{13}C NMR (Cl(CH_2)$_2$Cl, 75 MHz) δ 68.1 (OCH_2), 54.7 (N*C*H2), 25.0 (CH_2), 23.3 (CH_2), 11.5 (SnCH_2); ^{119}Sn NMR (Cl(CH_2)$_2$Cl, 112 MHz) δ 131.8; ^{11}B NMR (Cl(CH_2)$_2$Cl, 96 MHz) δ –1.61.

[N($CH_2CH_2CH_2$)$_3$Sn]•DABCO (BF_4).



To a solution of **2.4** (17.6 mg, 0.0510 mmol) in 1,2-dichloroethane (0.5 ml) in a J. Young NMR tube, was added dry DABCO (5.8 mg, 0.051 mmol). ^{13}C NMR (Cl(CH_2)$_2$Cl, 75 MHz) δ 54.3 (NCH_2), 46.9 (NCH_2), 44.6 (NCH_2), 22.8 (CH_2), 13.0 (SnCH_2); ^{119}Sn NMR (Cl(CH_2)$_2$Cl, 112 MHz) δ 61.4; ^{11}B NMR (Cl(CH_2)$_2$Cl, 96 MHz) δ –1.7.

Chapter 3

$B(C_6F_5)_3$-Promoted Conjugate Alkylation of Benzylidene Meldrum's Acids Using Alkyl-tricarbastannatranes

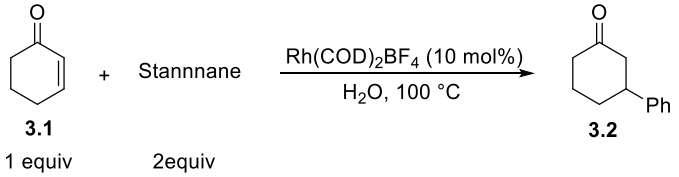
The ability of methyl-tricarbastannatrane to transfer the apical methyl group to $B(C_6F_5)_3$ is studied. In addition, the structure of $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$ is determined by X-ray crystallography. Furthermore, the $B(C_6F_5)_3$-promoted conjugate addition of alkyl-tricarbastannatranes to benzylidene Meldrum's acids under mild conditions is presented. The mechanism of the addition has been investigated, and NMR and mass spectroscopy techniques have been used to determine the structure of the reaction intermediates.

3.1 Introduction

The conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds is an important method for the construction of carbon–carbon bonds. Conjugate additions of different organometallic reagents, such as organocopper, organolithium, and organoboron with or without catalysts have been reported.[38] Among organometallic compounds, a variety of organostannanes have been employed due to their availability, air and moisture stability, and their functional group tolerance.[39] Reactions of stannane reagents, such as aryl- and alkenylstannanes have been typically promoted by a rhodium or palladium catalyst.

Reactivity of organotin reagents in the conjugate addition to 1-cyclohexen-2-one (**3.1**) was investigated by Li and coworkers.[40] Various phenylstannanes and phenyltin chloride derivatives were added to **3.1** in the presence of $Rh(COD)_2BF_4$ in water (Scheme 3.1). Product **3.2** was obtained in 85% yield with trimethyl(phenyl)tin. The electronic effect of substituents on phenyltin reagents was studied. Tin reagents Ph_3SnR with electron donating groups (R = Bu, OH, OMe) provided moderate yields of the product. However, the reaction was strongly inhibited by an electron withdrawing group (R = Cl). Most notably, the yield of the addition of the phenyl group using $PhSnCl_3$ reagent was increased to 92% by the addition of potassium hydroxide, due to halogen–hydroxyl exchange.

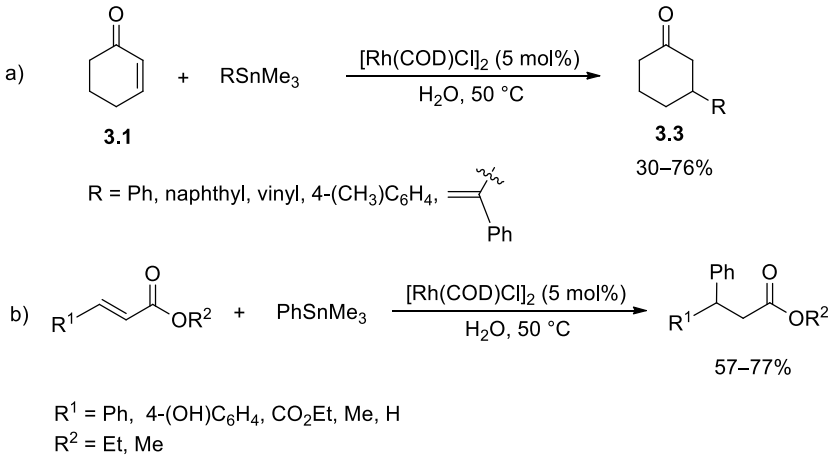
Scheme 3.1. Electronic effects of tin substituents



Stannane	Yield
$PhSnMe_3$	85
Ph_4Sn	11
Ph_3SnBu	62
Ph_3SnOH	52
Ph_3SnOMe	53
Ph_3SnCl	trace
$PhSnCl_3$/KOH	92

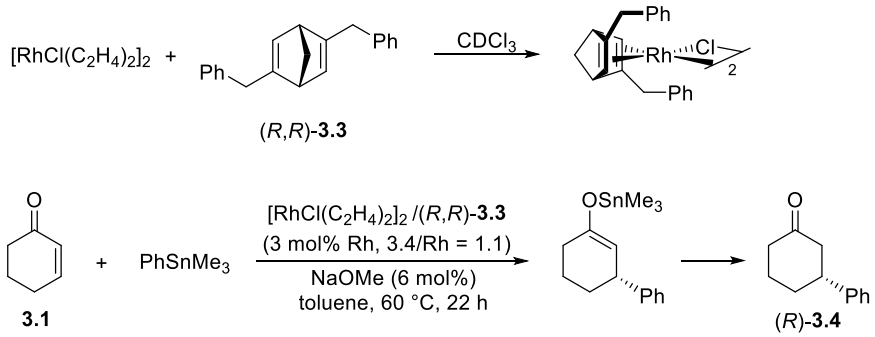
Similarly, conjugate additions of trialkyl(aryl)- and trialkyl(vinyl)tin reagents to 1-cyclohexen-2-one was reported using 5 mol% of $[Rh(COD)Cl]_2$ in water at 50 °C (Scheme 3.2a).[41] Tributyl(vinyl)tin provided only 30% of the product, and the highest yield of the product (76%) was obtained using trimethyl(phenyl)tin. Addition of $PhSnMe_3$ to conjugated carbonyl compounds, such as acrylates or maleates, under these reaction conditions furnished the products in 57–77% yields (Scheme 3.2b).

Scheme 3.2. Conjugated addition of trimethyl(aryl)- and trimethyl(vinyl)tin derivatives



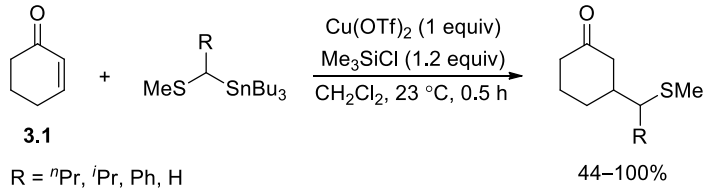
Later, rhodium-catalyzed asymmetric conjugate addition of trimethyl(phenyl)tin to **3.1** was reported by Hayashi and coworkers.[42] NMR studies showed that addition of 1.1 equivalent (to rhodium) of (*R*,*R*)-**3.3** to a solution of $[RhCl(C_2H_4)_2]_2$ in $CDCl_3$ could form chelating diene complex [RhCl-((*R*,*R*)-**3.3**)]$_2$ at room temperature in 1 hour. This complex was generated in-situ in the reaction of $PhSnMe_3$ with **3.1** in toluene, and furnished (*R*)-**3.4** in 80% yield, and 95% *ee* on hydrolysis (Scheme 3.3).

Scheme 3.3. Asymmetric conjugate addition of trimethylphenyl tin to 1-cyclohexen-2-one



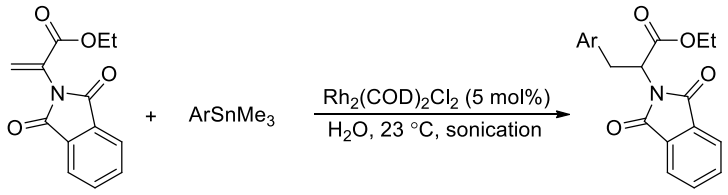
Recently, copper-mediated conjugate addition of different α-sulfur substituted organostannanes to **3.1** was reported.[43] α-Sulfur-substituted alkyl groups were added at the β position of **3.1** in the presence of copper(II) triflate and trimethylsilyl chloride to form the *γ*-sulfur-substituted ketones in 44–100% yields (Scheme 3.4). These conjugate additions were not diastereoselective, and a mixture of two diastereomers was obtained in all cases.

Scheme 3.4. Conjugate addition of α-sulfur substituted organostannanes to 1-cyclohexen-2-one



Under rhodium catalysis, synthesis of α-amino acid derivatives was demonstrated.[44] Aryltin reagents were applied to α-phthalimidoacrylate in the presence of $[Rh(COD)Cl]_2$ in water. The reaction mixtures were sonicated at room temperature, and the desired products were obtained in 32–82% yields (Scheme 3.5).

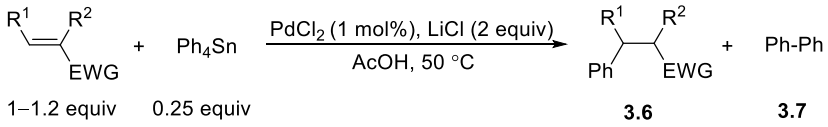
Scheme 3.5. Conjugate addition of trimethyl(aryl)tin derivatives to ethyl α-phthalimidoacrylate

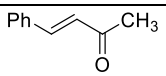
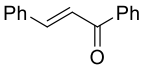
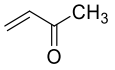
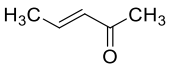
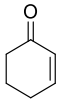
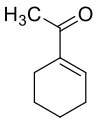
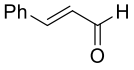


Ar = Ph, *p*-ClPh, *p*-MePh, *m*-MePh, *p*-MeO, *t*-BuPh

Tetraphenyltin addition to α,β-unsaturated aldehyde and ketones under palladium-catalyzed conditions in the presence of a metal chloride salt was reported by Uemura and coworkers.[45] In their studies, different solvents and palladium catalysts were examined, and $PdCl_2$/LiCl/AcOH system was found to be an effective system to generate products **3.6**. As shown in Table 3.1, different Michael acceptors have been reacted under this condition, and products **3.6a**–**h** were obtained in modest to good yields. It was revealed that slightly fewer than four phenyl groups of tetraphenyltin were transferred in these transformations. In addition, the formation of the biphenyl side product was observed with all substrates, and with substrates **3.5f**–**h** biphenyl was the major product (Table 3.1, entries 6–8). No reaction was observed with methyl cinnamate and cinnamonitrile.

Table 3.1. Addition of tetraphenyltin using $PdCl_2$/LiCl/AcOH system

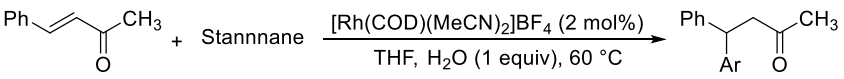


Entry	Substrate	Yield (%)	
		3.6	**3.7**
1[a]	 **3.5a**	81	3
2	 **3.5b**	56	35
3	 **3.5c**	81	10
4	 **3.5d**	69	18
5	 **3.5e**	63	28
6	 **3.5f**	26	55
7	 **3.5g**	4	66
8	 **3.5h**	28	55

[a] Reaction was performed at 25 °C

Further developement of conjugate addition of organotins to **3.5a** was reported by Oi and coworkers.[46] These reactions were carried out under cationic rhodium catalysis in THF, and in the presence of one equivalent of water as a protic additive to prevent a further reaction of the stannyl enol ether intermediate with starting material **3.5a**. Addition of an equimolar amount of protic species, such as water or methanol, could improve the reaction yield through immediate conversion of the silyl enol ether to ketone. Under this condition, tetraphenyltin yielded only 11% of product **3.6a**. Higher yields of the product was obtained with trimethyl(phenyl)tin and tributyl(phenyl)tin. Furthermore, 4-fluorophenyl and 4-methoxypheny groups were added at the β position of **3.5a** to furnish the adducts in good yields. However, no reactivity was observed with styryltrimethyl stannane (Table 3.2).

Table 3.2. Conjugate addition of organostannanes to benzylideneacetone

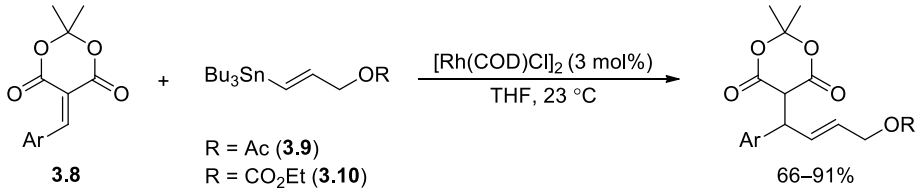


Entry	Stannatrane	Yield
1	Ph_4Sn	11
2	$PhSnMe_3$	98
3	$PhSnBu_3$	70
4	*p*-$FC_6H_4SnMe_3$	68
5	*p*-$MeOC_6H_4SnMe_3$	74
6	$PhCH{=}CHSnMe_3$	NR

The Fillion group described the addition of alkenylstannanes to benzylidene Meldrum's acids in the presence of a rhodium catalyst under mild reaction conditions (Scheme 3.6).[47] (*E*/*Z*)-3-(tributylstannyl)allyl acetate (**3.9**) and ethyl carbonate (**3.10**) are ambiphilic reagents wherein allylic acetate or carbonate acts as an electrophile under palladium-catalyzed conditions, and the tin–carbon bond acts as a nucleophile.[48] Stannanes **3.9** and **3.10** were added in the presence of $[Rh(COD)Cl]_2$ to benzylidene Meldrum's acids with a range of aromatic substitutions, and high yields of the products were obtained. Employing these alkenylstannanes under $[Rh(COD)(MeCN)_2]BF_4$ catalysis afforded

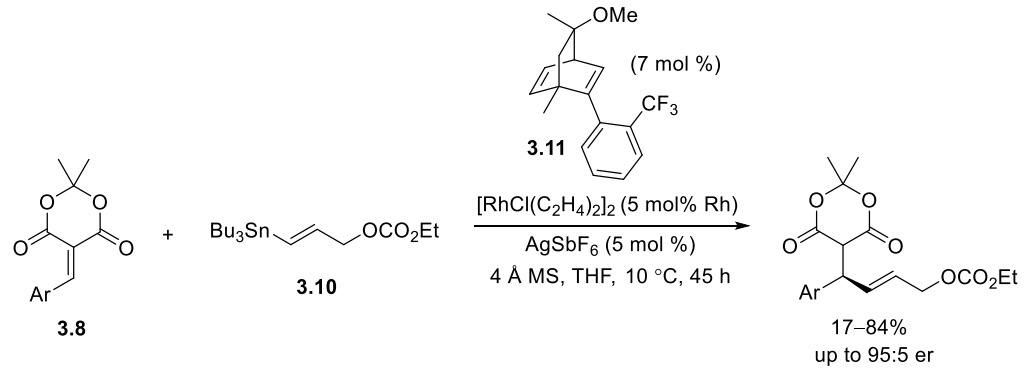
comparable yields. The increased reactivity of **3.9** and **3.10** compared to the previously described alkenylstannanes[46] is plausibly due to the facile rhodium–tin transmetalation, which is attributed to the more polarized tin–carbon bond.

Scheme 3.6. Conjugate addition of alkenylstannanes to benzylidene Meldrum's acid



Enantioselective conjugate addition of **3.10** to benzylidenes **3.8** employing a cationic Rh(I)-diene complex as catalyst was reported by the Fillion group.[49] (R)-Carvone derived ligand **3.11** with a large group at the *ortho* position of the arene group, provided the desired products with high enantiomeric ratio (er) (Scheme 3.7). In addition, $AgSbF_6$ was found to be effective in increasing er by forming the cationic Rh(I) complex. Furthermore, higher yields were obtained by preventing hydrolysis of the benzylidenes; powdered molecular sieves were introduced to the reaction mixtures. Regardless of substituents on the phenyl ring, high enantioselectivity was observed in this method.

Scheme 3.7. Enantioselective addition of alkenylstannanes to benzylidene Meldrum's acids



As mentioned above, carbon–carbon bond formation reactions using conjugate additions of stannane reagents were limited to trimethyl, triphenyl and tributylstannane derivatives. In recent years, utilizing less volatile organotin compounds has been preferred due to general environmental concerns about the toxicity and disposal of organostannanes.

3.2 Proposal

The objective was to develop a protocol for addition of a more stable, reactive, and versatile alkylstannane reagent to an electrophile in a conjugate fashion under mild reaction conditions. It was postulated that exceptionally long tin–carbon bond in methyl-tricarbastannatrane would allow the efficient addition of the apical methyl group to an electrophile. Meanwhile, it was proposed that a quantitative recovery of the tricarbastannatrane cation would be simply achieved as chloro-tricarbastannatrane by treatment of the reaction mixture with a dilute HCl solution.

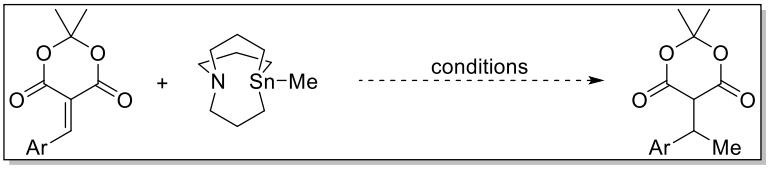
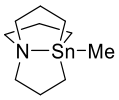
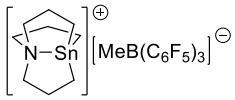
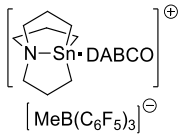


Figure 3.1. Proposal for conjugate addition of methyl-tricarbastannatrane to electrophilic alkenes

3.3 Results and discussion

The ability of methyl-tricarabstannatrane (**3.12**) to transfer the apical methyl group was examined. The methyl transfer study was carried out using $B(C_6F_5)_3$.[50] Complex $[N(CH_2CH_2CH_2)_3Sn][MeB(C_6F_5)_3]$ (**3.13**) formed by the addition of $B(C_6F_5)_3$ to a solution of **3.12** in 1,2-dichloroethane.[34] The generation of complex **3.13** in a sealed NMR tube was monitored by ^{119}Sn NMR. A remarkable change in ^{119}Sn chemical shift from δ –16.3 to δ 252.9 (Δppm = 269.2 ppm) diagnosed the quantitative generation of complex **3.13** (Table 3.3, entry 2). Furthermore, ^{11}B chemical shift was changed from δ 57.3 to δ –16.3, which confirmed the formation of $[MeB(C_6F_5)_3]^-$. $[MeB(C_6F_5)_3]^-$ was detected by HRMS (ESI) showing an ion peak at *m/z* 527.00751. Addition of DABCO to complex **3.13** was later examined. After the addition of one equivalent of DABCO to **3.13** in 1,2-dichloroethane, the ^{119}Sn chemical change from δ 252.9 to δ 61.9 (Δppm = 191.0 ppm) suggested the formation of strong Lewis base/Lewis acid complex $[N(CH_2CH_2CH_2)_3Sn]$•DABCO (Table 3.3, entry 3). The generation of DABCO•$[N(CH_2CH_2CH_2)_3Sn]$ was earlier discussed in Chapter 2 by the addition of DABCO to $[N(CH_2CH_2CH_2)_3Sn][BF_4]$ (Table 2.5, entry 6). In addition, this complex was detected by HRMS (ESI), which showed an ion peak at *m/z* 372.14609.

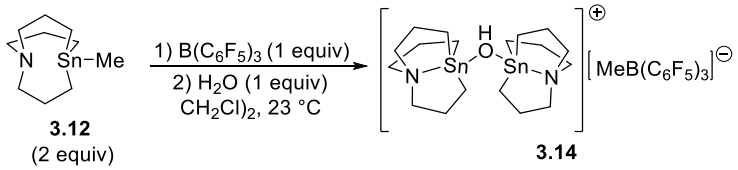
Table 3.3. NMR studies on complex $[N(CH_2CH_2CH_2)_3Sn][MeB(C_6F_5)_3]$

entry	stannatrane	NMR chemical shifts (ppm)			
		^{1}H	^{13}C	^{119}Sn	^{11}B[a]
1		– 0.39 (s) 0.59 (t) 1.59 (m) 2.33 (t)	– 5.3 7.5 22.9 54.2	– 16.3	NA
2	 **3.13**	0.43 (brs) 1.76 (m) 2.12 (m) 2.71 (t)	17.6 25.3 55.9[b]	252.9	– 15.5
3		0.42 (brs) 1.20 (t) 1.87 (m) 2.48 (t)	7.5 22.5 45.1 45.9 53.9[c]	61.9	– 15.5

[a] ^{11}B NMR chemical shift of $B(C_6F_5)_3$ in 1,2-dichloroethane is 57.3 ppm. [b] No signal for methyl group bonded to boron is observed due to quadrupolar relaxation of the boron. [c] Two peaks at 45.1, 45.9 ppm belong to DABCO.

Complex **3.13** was stable at room temperature for more than 24 hours. However, it decomposed to unidentified products upon warming the solution to 35 °C in a sealed NMR tube. Complex **3.13** is an oil, and could not be characterized by X-ray crystallography. However, complex $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$ (**3.14**) was obtained as colourless crystals upon the reaction of one equivalent of water, two equivalents of methyl-tricarbastannatrane, and one equivalent of $B(C_6F_5)_3$ in 1,2-dichloroethane (Scheme 3.8). This complex was stable under air at room temperature for more than 24 hours.

Scheme 3.8. Synthesis of complex $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$



Crystals suitable for X-ray analysis were obtained by recrystallization of **3.14** from 1,2-dichloroethane/pentane. The X-ray structure is illustrated in Figure 3.2. Compound **3.14** crystallizes in the space group $P2_1/c$ with parameters α = 13.9005(6) Å, b = 12.6463(5) Å, and c = 26.1186(9) Å, V = 4012.7(3) Å^3. In this structure, the pentacoordinated tin is linked to tetracoordinated nitrogen atom in each tricarbastannatrane unit. Sn(1)–N(1) and Sn(2)–N(2) bond lengths are 2.372(3) Å and 2.366(3) Å, respectively. These Sn–N distances are very similar to those in chloro-tricarbastannatrane (2.364 Å) and iodo-tricarbastannatrane (2.375 Å)[12] (Tables 2.1 and 2.3).

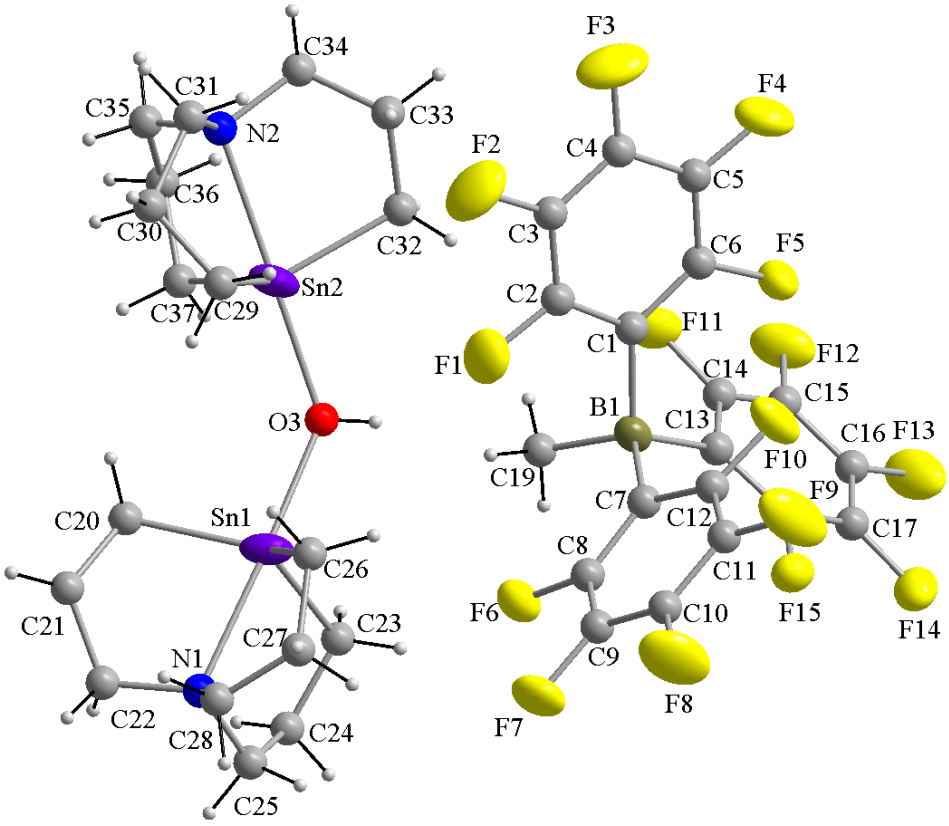


Figure 3.2. X-ray structure of compound $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$

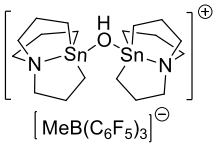
As demonstrated in Table 3.4, bond angles around two tin atoms have average values between those of tetrahedral and trigonal bipyramidal geometries. Therefore, the structure of compound **3.14** has a distorted trigonal bipyramidal molecular geometry around the tin atoms, and the nitrogen and oxygen atoms occupy the axial positions.

Table 3.4. Selected bond angles in $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$

	Bond angles (°)
C(20)-Sn(1)-C(23)	118.6(2)
C(20)-Sn(1)-C(26)	117.7(2)
C(23)-Sn(1)-C(26)	115.92(19)
C(29)-Sn(2)-C(32)	117.62(19)
C(29)-Sn(2)-C(37)	118.1(2)
C(32)-Sn(2)-C(37)	116.18(18)
O(3)-Sn(1)-N(1)	177.44(13)
O(3)-Sn(2)-N(2)	179.16(12)

NMR studies on complex **3.14** showed a ^{11}B signal at $\delta = -14.9$ ppm, and a ^{119}Sn signal at δ 43.1 in $CDCl_3$. A broad singlet at δ 0.50 in ^{1}H NMR is attributed to the methyl group attached to the boron atom. No signal for methyl group bonded to boron is observed in ^{13}C NMR due to quadrupolar relaxation of the boron. In addition to its X-ray structure and NMR data (Table 3.5), HRMS (ESI) supported the formation of complex **3.14**. An ion peak at *m/z* 527.09664 was attributed to $[(N(CH_2CH_2CH_2)_3{}^{115}Sn)_2OH]^+$.

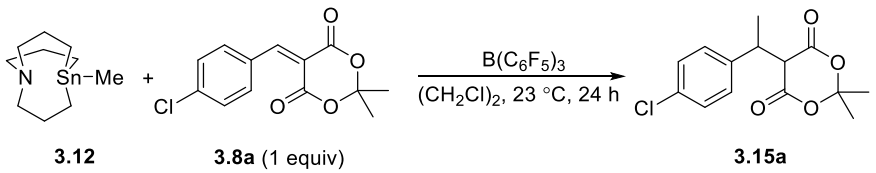
Table 3.5. NMR studies on complex $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$

stannatrane	NMR chemical shifts (ppm) [a]			
	^{1}H	^{13}C	^{119}Sn	^{11}B
	0.50 (bs) 1.05 (m) 1.84 (m) 2.46 (t)	11.3 23.2 54.7	43.1	– 14.9

[a] NMR studies on complex **3.14** were carried out in $CDCl_3$.

The reactivity of tricarbastannatrane **3.12** in the conjugate addition reaction with electrophilic alkenes, was then investigated. Benzylidene Meldrum's acids (**3.8**), which were previously studied by the Fillion group, seemed like an ideal starting point in this study. It was postulated that the superior electrophilicity of **3.8** would allow the efficient conjugate addition of the methyl group under mild reaction conditions. Unexpectedly, in the presence of one equivalent of **3.12** and one equivalent of $B(C_6F_5)_3$, no reactivity was observed (Table 3.6, entry 1) at room temperature. However, full conversion to product **3.15a** was observed when two equivalents of methyl-tricarbastannatrane and one equivalent of $B(C_6F_5)_3$ reacted with **3.8a**. (Table 3.6, entry 4). Less than 20% conversion to product **3.15a** was obtained using 0.2 equivalent of $B(C_6F_5)_3$ (Table 3.6, entry 5).

Table 3.6. $B(C_6F_5)_3$-promoted reaction of methyl-tricarbastannatrane with 4-chloro-benzylidene Meldrum's acid

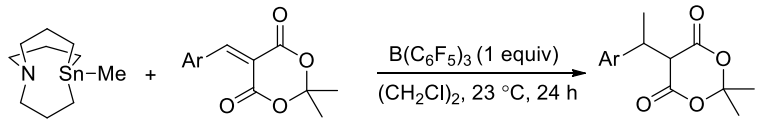


3.12 **3.8a** (1 equiv) **3.15a**

Entry	Equiv of **3.12**	Equiv of $B(C_6F_5)_3$	Conversion	Yield [%]
1	1	1	0	0
2	1.2	1	<20	n.d.
3	2	0	0	0
4	2	1	>95	92
5	2	0.2	<20	n.d.

Gratifyingly, the addition of methyl-tricarbastannatrane to benzylidene Meldrum's acids was general, regardless of the nature of substituent on the phenyl ring (Table 3.7). Different functional groups, such as boronic esters, nitro, and halides, at meta- and para positions of the phenyl ring were tolerated, and methylated products **3.15a**–**l** were obtained in good to excellent yields (78–92%). The yields were consistent with different electron-withdrawing substituents. In addition to the desired products, unreacted starting materials were recovered from the reaction mixtures.

Table 3.7. $B(C_6F_5)_3$-promoted reaction of methyl-tricarbastannatrane with benzylidene Meldrum's acids

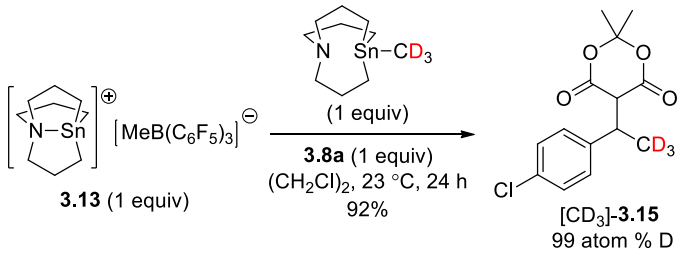


(2 equiv) **3.8** (1 equiv) **3.15**

Entry	Ar	product	Yield [%]
1	4-ClC_6H_4 (**3.8a**)	**3.15a**	92
2	3-$(MeO)C_6H_4$ (**3.8b**)	**3.15b**	90
3	2-Naphthyl (**3.8c**)	**3.15c**	78
4	4-$(CN)C_6H_4$ (**3.8d**)	**3.15d**	83
5	4-BrC_6H_4 (**3.8e**)	**3.15e**	88
6	3-$[B(O_2C_6H_{12})]C_6H_4$ (**3.8f**)	**3.15f**	91
7	4-$[B(O_2C_6H_{12})]C_6H_4$ (**3.8g**)	**3.15g**	81
8	3-FC_6H_4 (**3.8h**)	**3.15h**	92
9	3-BrC_6H_4 (**3.8i**)	**3.15i**	90
10	4-$(CO_2CH_3)C_6H_4$ (**3.8j**)	**3.15j**	82
11	4-FC_6H_4 (**3.8k**)	**3.15k**	85
12	4-$(NO_2)C_6H_4$ (**3.8l**)	**3.15l**	79

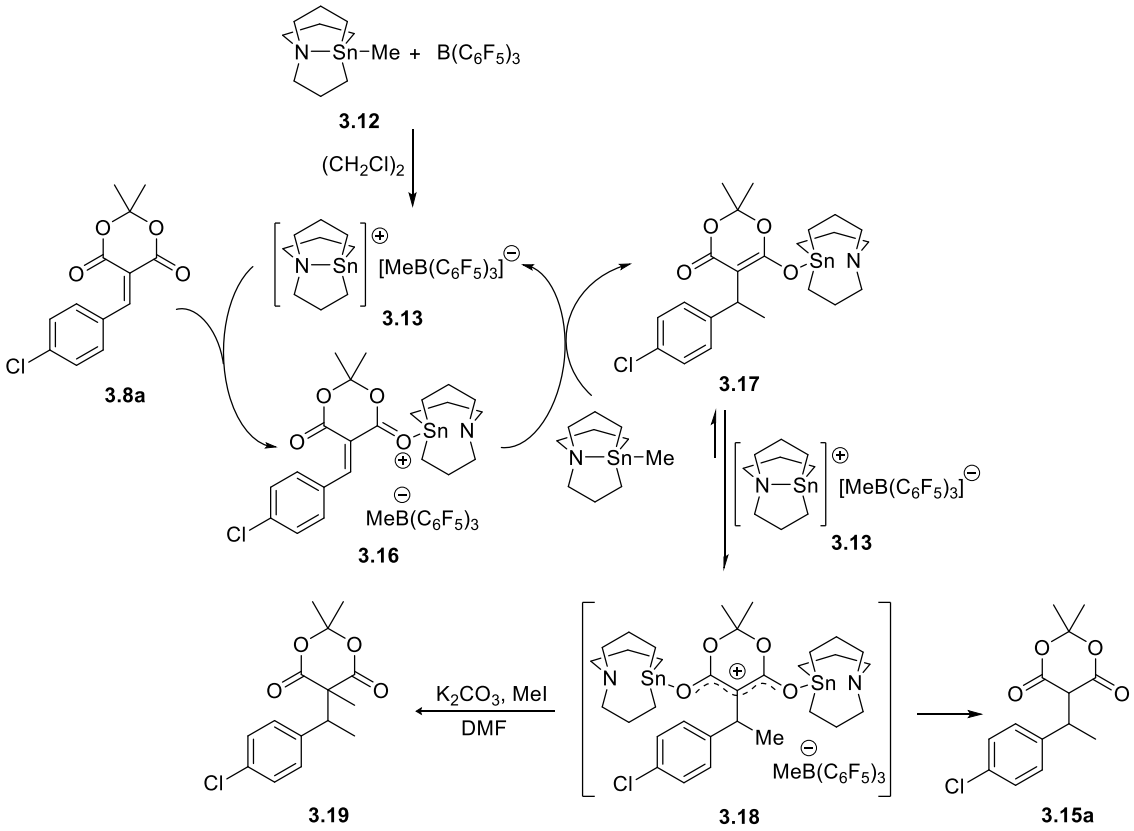
To gain additional insights into the mechanism by which the methyl group is delivered from **3.12** to benzylidene **3.8a**, a deuterium-labeling experiment was carried out. As illustrated in Scheme 3.9, $[CD_3]$-methy-tricarbastannatrane (**$[CD_3]$-3.12**) and **3.8a** were added to complex **3.13** in 1,2-dichloroethane at room temperature. Only deuterated methyl was added to **3.8a**, and **$[CD_3]$-3.15a** was obtained in 92% yield. This finding and the results in Table 3.6 indicates that complex $[N(CH_2CH_2CH_2)_3Sn][MeB(C_6F_5)_3]$ (**3.13**) is inert in this transformation. Compound **3.12** is the sole methyl donor in this reaction, and $[MeB(C_6F_5)_3]^-$ is only a bystander counter ion. This observation justifies the need for two equivalents of the methyl-tricarbastannatrane in this methodology, and $[(N(CH_2CH_2CH_2)_3Sn]^+$ likely acts as a Lewis acid to activate the electrophile by binding to **3.8a**.

Scheme 3.9. Reaction of [CD_3]-methy-tricarbastannatrane with 4-chloro-benzylidene Meldrum's acid



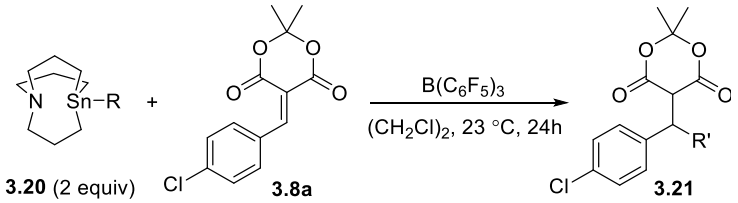
Based on the formation of [CD_3]-**3.15**, it was proposed that the first step in the $B(C_6F_5)_3$-promoted conjugate reaction is the ion pair **3.13** by the addition of the methyl group from **3.12** to $B(C_6F_5)_3$. Then, complex **3.16** is formed through the coordination of one of the carbonyl groups of **3.8a** to Lewis acidic $[(N(CH_2CH_2CH_2)_3Sn]^+$ (Scheme 3.10). Complex **3.16** was detected by a ^{119}Sn signal at δ = 129.6 ppm. Subsequently, mono-stannatrane enolate **3.17** is generated by the methyl delivery from the second equivalent of **3.12**. In addition to compound **3.17**, complex **3.13** is reformed in this step. $[(N(CH_2CH_2CH_2)_3Sn]^+$ is then scavenged by Lewis basic enolate **3.17** to yield bis-stannatrane **3.18**. The formation of this intermediate rationalizes the lack of turnover and the need for two equivalents of methyl-tricarbastannatrane for this reaction to proceed. The reaction progress was monitored by NMR. A single ^{119}Sn signal at δ = 47.7 ppm was observed upon consuming the starting material, which is consistent with symmetrical intermediate **3.18**. Furthermore, the formation of this intermediate was confirmed by HRMS (ESI), showing an ion peak at *m/z* 801.15004 with an isotope distribution pattern attributed to the ion $[C_{32}H_{50}O_4N_2ClSn_2]^+$. Monitoring the reaction mixture by NMR in a sealed NMR tube confirmed that intermediate **3.18** was stable in 1,2-dichloroethane for about one week at room temperature. An acidic workup with dilute HCl solution provided product **3.15a** as well as chloro-tricarbastannatrane. Complex **3.18** was also trapped in situ with iodomethane to form methylated product **3.19** (Scheme 3.10).

Scheme 3.10. Proposed mechanism of the $B(C_6F_5)_3$-promoted reaction



The generality of the addition was further investigated with a series of organotricarbastannatranes to **3.8a** (Table 3.8). The apical group transfer was achieved selectively with *n*-butyl-tricarbastannatrane (**3.20a**), and allyl-tricarbastannatrane (**3.20c**) to furnish products **3.21a** and **3.21c** in excellent yields. In addition, 86% yield of product **3.21f** was obtained with but-2-yn-1-yl-tricarbastannatrane (**3.20f**). Furthermore, moderate yields were observed with benzyl- and vinyl-tricarbastannatranes **3.20d** and **3.20e** (Table 3.8, entries 4–5).

Table 3.8. $B(C_6F_5)_3$-promoted reaction of organotricarbastannatranes

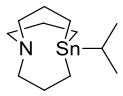
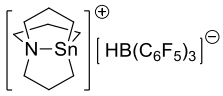


3.20 (2 equiv) **3.8a** **3.21**

Entry	R	R′	Product	Yield [%]
1	^{n}Bu (**3.20a**)	^{n}Bu	**3.21a**	89
2	^{i}Pr (**3.20b**)	H[a]	**3.21b**	74
3	Allyl (**3.20c**)	Allyl	**3.21c**	96
4	Benzyl (**3.20d**)	Benzyl	**3.21d**	49
5	Vinyl (**3.20e**)	Vinyl	**3.21e**	34
6	$CH_2C{\equiv}CMe$ (**3.20f**)	$H_2C{=}C{=}CMe$	**3.21f**	86

Interestingly, addition of ^{i}Pr-tricarbastannatrane (**3.20b**) led to the generation of reduced product **3.21b** (Table 3.7, entry 2). The presence of propene gas[51] was observed, when the reaction was monitored by ^{1}H NMR in a sealed NMR tube (Figure 3.3). NMR studies on **3.20b** were carried out in dry $CDCl_3$, and the results are summarized in Table 3.9. While **3.20b** showed a ^{119}Sn signal at δ = –5.9 ppm, reaction of one equivalent of $B(C_6F_5)_3$ with **3.20b** yielded a tricarbastannatrane complex with a ^{119}Sn signal at δ = 140.9 ppm. Characterization of this complex supported the formation of $[N(CH_2CH_2CH_2)_3Sn][HB(C_6F_5)_3]$ (**3.22**). In addition, $[HB(C_6F_5)_3]^-$ was detected by mass spectrometry showing an ion peak at *m/z* 512.99267 (negative mode). More studies on using ^{i}Pr-tricarbastannatrane as hydride source in the reduction of activated olefins will be discussed in Chapter 4.

Table 3.9. NMR studies on complex $[N(CH_2CH_2CH_2)_3Sn][HB(C_6F_5)_3]$

Entry	Substrate	NMR chemical shifts (ppm)			
		^{1}H	^{13}C	^{119}Sn	^{11}B
1		0.60 (t) 0.70 (m) 1.05 (d) 1.63 (m) 2.33 (t)	4.41 17.44 21.40 23.38 54.69	– 5.88	NA
2		1.41 (t) 2.02 (t) 2.66 (t) [a]	14.70 24.69 56.11 [b]	140.86	– 16.93

[a] Peaks at 1.70, 4.89–5.03 and 5.74–5.89 ppm belong to propene. [b] Three peaks at 19.27, 115.54 and 133.74 ppm belong to propene.

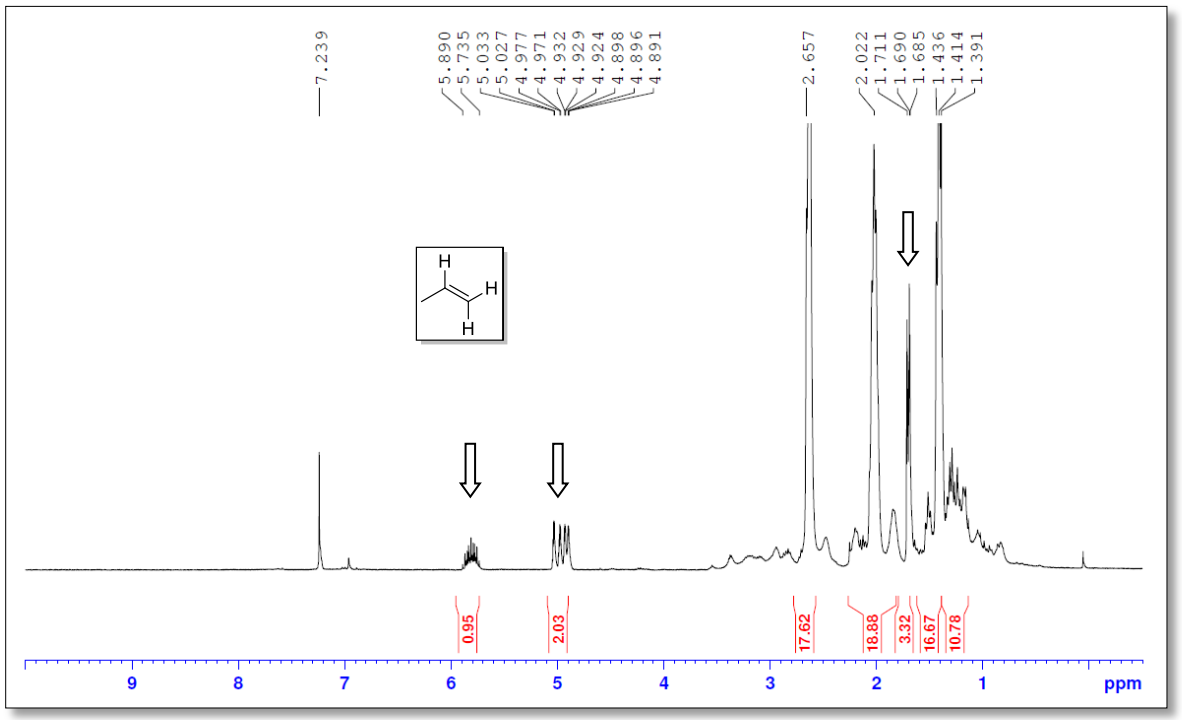
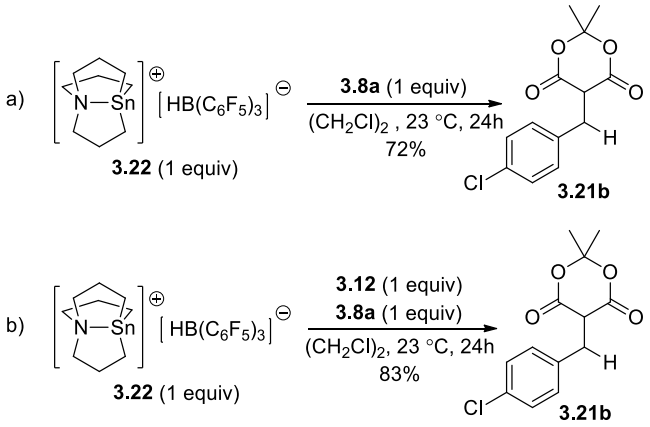


Figure 3.3. ^{1}H NMR Spectrum of the reaction between ^{i}Pr-tricarbastannatrane and $B(C_6F_5)_3$ in $CDCl_3$

When **3.8a** was added to a solution of one equivalent **3.20a** and one equivalent $B(C_6F_5)_3$, product **3.21b** was obtained in 72% yield (Scheme 3.11a). This observation suggests that $[HB(C_6F_5)_3]^-$ is likely the hydride source in this transformation. A competition experiment was carried out in the presence of methyl-tricarbastannatrane (Scheme 3.11b). In this experiment one equivalent of **3.8a** was added to equimolar mixture of **3.12** and complex **3.22**. Product **3.21b** was obtained in 83% yield as the only product in the reaction.

Scheme 3.11. Reaction of $[N(CH_2CH_2CH_2)_3Sn][HB(C_6F_5)_3]$ with 4-chloro-benzylidene Meldrum's acid



3.4 Summary

In summary, the advancement of alkyl-tricarbastannatrane chemistry was demontrated. The transfer of the apical methyl group of methyl-tricarbastannatrane to $B(C_6F_5)_3$ was studied in solution. The structure of $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$ was determined by X-ray crystallography analysis. Moreover, conjugate addition of organotricarbastannatranes to benzylidene Meldrum's acids has been carried out in the presence of $B(C_6F_5)_3$ under mild conditions to provide the products in good yields. The combination of alkyl-tricarbastannatranes and $B(C_6F_5)_3$ enabled the direct alkyl group transfer to electrophilic alkenes. The recovery of the tricarbastannatrane cation was achieved as chloro-tricarbastannatrane by treatment of the reaction mixture with a dilute HCl solution. The mechanism of the addition has been investigated, and NMR spectrometry and mass spectroscopy have been used to determine the structure of the symmetrical bis-stannatrane intermediate.

3.5 Experimental

3.5.1 General Considerations

All reactions were carried out in oven or flame-dried glassware under dry nitrogen atmosphere using standard Schlenk techniques or in a glove box. All solvents were degassed via 3 freeze-pump-thaw cycles following distillation. 1,2-Dichloroethane was distilled over CaH_2, THF was distilled over sodium/benzophenone ketyl, Acetonitrile was dried by distillation from CaH_2, Pentane was dried over $LiAlH_4$ and distilled prior to use, $CDCl_3$ was distilled from P_2O_5, and stored on 4 Å Linde molecular sieves. Reactions were monitored by thin-layer chromatography on commercially prepared plates with a particle size of 60 Å. Developed plates were visualized under a UV lamp (254 nm), or stained with ceric ammonium molybdate. Flash chromatography was performed using 230-400 mesh silica gel.

3.5.2 Characterization

Unless otherwise noted, ^{1}H and ^{13}C NMR spectra for all adduct products were obtained in $CDCl_3$ at 300 and 75 MHz, respectively. Chemical shifts are reported in parts per million (ppm, δ) relative to tetramethylsilane (TMS) as an external standard. Proton and carbon spectra were calibrated against the solvent residual peak [$CHCl_3$ (7.24 ppm) and $CDCl_3$ (77.0 ppm)] and in case of 1,2-dichlorethane against known solvent resonance [^{1}H (3.72 ppm) and ^{13}C (43.6 ppm)]. ^{11}B and ^{119}Sn NMR spectra of tricarbastannatranes were recorded on Bruker Avance-300 (^{11}B: 96 MHz, ^{119}Sn: 112 MHz) with ^{1}H decoupling in 1,2-dichloroethane calibrated against external BF_3•OEt_2 and Me_4Sn, respectively. The spectral references (sr) which were obtained from the external standards, were used to calibrate all ^{119}Sn NMR and ^{11}B NMR chemical shifts. Spectral reference values of –171.61 Hz and –5.13 Hz were used to calibrate ^{119}Sn and ^{11}B chemical shifts in 1,2-dichloroethane, respectively. Abbreviations used to define NMR spectral mutiplicities are as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High resolution mass spectra (ESI) were run at the University of Waterloo Mass Spectrometry facility. Fragment signals are given in mass per charge number (m/z).

The following compounds were prepared according to literature procedures: 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane,[8] 5-methyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.12**),[5] 5-(benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8a-l**),[52] 5-butyl-1-aza-5-stannabicyclo[3.3.3] undecane (**3.20a**),[8] 5-(*iso*-propyl)-1-aza-5-stannabicyclo[3.3.3]undecane (**3.20b**),[13] 5-vinyl-1-aza-5-

stannabicyclo[3.3.3]undecane (**3.20e**),[11] Ag[B[3,5-$(CF_3)_2C_6H_3]_4$].[53] Other reagents were purchased from commercial suppliers and used without further purification.

X-ray quality crystals of **3.14** were obtained after recrystallization in anhydrous 1,2-dichloroethane at room temperature, followed by the drop-wise addition of dry pentane to reach a cloudy point. Then 1,2-dichloroethane was added drop-wise until the solutions became clear again and then were allowed to stand under nitrogen at the mentioned temperature to form single crystals.

General Experimental Procedure A - Synthesis of Alkyl-tricarbastannatranes

Appropriate Grignard reagents (2 equiv.) were added dropwise to a suspension of 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (1 equiv.) in anhydrous THF at -78°C. The resulting mixture was stirred at -78 °C for 3 h, allowed to warm to room temperature, and stirred overnight. The reaction mixture was poured into a separatory funnel containing a mixture of Et_2O and water. The layers were partitioned, and the organic layer was washed with brine, dried over $MgSO_4$, and filtered. Solvent was removed under reduced pressure to provide the crude product. The crude tricarbastannatrane reagents were used without further purification.

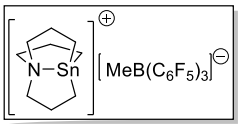
General Experimental Procedure B - Synthesis of Compounds 3.15a-l

Benzylidene Meldrum's acid (0.100 mmol) was added to a solution of 5-methyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.12**) (54.8 mg, 0.200 mmol) and tris(pentafluorophenyl)borane (51.1 mg, 0.100 mmol) in 1 mL of 1,2-dichloroethane and the mixture was stirred for 24 h at 23 °C. All volatiles were evaporated under vacuum and the product was purified by flash chromatography (EtOAc:hexanes) on silica gel.

General Experimental Procedure C - Synthesis of Compounds 3.21a-f

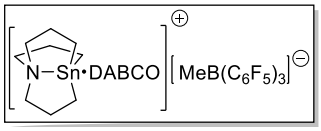
5-(4-Chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8a**) (26.7 mg, 0.100 mmol) was added to a solution of alkyl-tricarbastannatrane (0.200 mmol) and tris(pentafluorophenyl)borane (**7**) (51.1 mg, 0.100 mmol) in 1 mL of 1,2-dichloroethane and the mixture was stirred for 24 h at 23 °C. All volatiles were evaporated under vacuum and the product was purified by flash chromatography (EtOAc:hexanes) on silica gel.

[N(CH$_2$CH$_2$CH$_2$)$_3$Sn][MeB(C$_6$F$_5$)$_3$] (3.13).



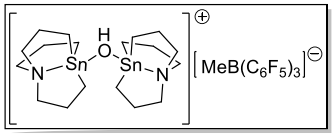
To a solution of 5-methyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.12**) (14.0 mg, 0.0510 mmol) in 1,2-dichloroethane (0.5 ml) in a J. Young NMR tube, was added tris(pentafluorophenyl)borane (26.1 mg, 0.0510 mmol). ^{1}H NMR (Cl(CH$_2$)$_2$Cl, 300 MHz) δ 2.71 (t, 6H, NC*H*2), 2.12 (m, 6H, C*H*$_2$), 1.76 (m, 6H, SnC*H*$_2$), 0.43 (brs, 3H, BC*H*3); ^{13}C NMR (Cl(CH$_2$)$_2$Cl, 75 MHz) δ 55.9 (N*C*H$_2$), 25.3 (*C*H$_2$), 17.5 (Sn*C*H$_2$); ^{119}Sn NMR (Cl(CH$_2$)$_2$Cl, 112 MHz) δ 253.0; ^{11}B NMR (Cl(CH$_2$)$_2$Cl, 96 MHz) δ –15.5. HRMS (–ESI) *m/z* calcd. for C$_{19}$H$_3$BF$_{15}$ (M$^-$): 527.00828. Found: 527.00751; HRMS (+ESI) *m/z* calcd. for C$_9$H$_{18}$NSn (M$^+$): 260.04557. Found: 260.04546.

[[N(CH$_2$CH$_2$CH$_2$)$_3$Sn]•DABCO][MeB(C$_6$F$_5$)$_3$].



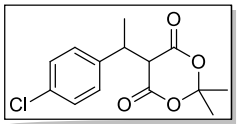
To a solution of **3.13** (40.1 mg, 0.0510 mmol) in 1,2-dichloroethane (0.5 ml) in a J. Young NMR tube, was added DABCO (5.8 mg, 0.051 mmol). ^{1}H NMR (Cl(CH$_2$)$_2$Cl, 300 MHz) δ 2.84 (brm, NC*H*2), 2.61 (brm, NC*H*2), 2.48 (t, 6H, NC*H*2), 1.87 (m, 6H, C*H*2), 1.20 (t, 6H, SnC*H*2), 0.42 (brs, 3H, BC*H*3); ^{13}C NMR (Cl(CH$_2$)$_2$Cl, 75 MHz) δ 53.9 (N*C*H2), 45.9 (N*C*H2), 45.1 (N*C*H2), 22.5 (*C*H2), 7.5 (Sn*C*H2); ^{119}Sn NMR (Cl(CH$_2$)$_2$Cl, 112 MHz) δ 61.9; ^{11}B NMR (Cl(CH$_2$)$_2$Cl, 96 MHz) δ –15.5. HRMS (–ESI) *m/z* calcd. for C$_{19}$H$_3$BF$_{15}$ (M$^-$): 527.00828. Found: 527.00876; HRMS (+ESI) *m/z* calcd. for C$_{15}$H$_{30}$N$_3$Sn (M$^+$): 372.14562. Found: 372.14609.

[(N(CH$_2$CH$_2$CH$_2$)$_3$Sn)$_2$OH][MeB(C$_6$F$_5$)$_3$] (3.14).



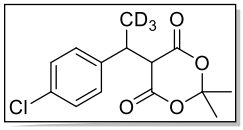
To a solution of 5-methyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.12**) (54.8 mg, 0.200 mmol) in 1,2-dichloroethane (1 ml) in a vial, was added tris(pentafluorophenyl)borane (51.1 mg, 0.100 mmol) and deionized water (1.8 µL). After 5 minutes, all volatiles were evaporated under vacuum, yielding **9** as colorless solid. Single crystals of **9** were obtained upon recrystallization in pentane/1,2-dichloroethane at rt. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.46 (t, 12H, NC*H*$_2$), 1.84 (m, 12H, C*H*$_2$), 1.05 (t, 12H, SnC*H*$_2$), 0.50 (brs, 3H, BC*H*$_3$); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 54.7 (N*C*H$_2$), 23.2 (*C*H$_2$), 11.3 (Sn*C*H$_2$); ^{119}Sn NMR (CDCl$_3$, 112 MHz) δ 43.1; ^{11}B NMR (CDCl$_3$, 96 MHz) δ –14.9. HRMS (+ESI) *m/z* calcd. for C$_{18}$H$_{37}$N$_2$O^{115}Sn$_2$ (M$^+$): 527.09673. Found: 527.09664.

5-(1-(4-Chlorophenyl)ethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.15a).



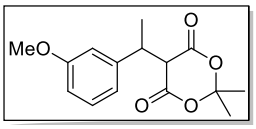
Prepared according to the General Procedure B from 5-(4-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8a**) (26.7 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:5) and isolated as a white solid (26.1 mg, 92% yield). M.p. 118-120°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.24 (m, 4H), 3.97 (m, 1H), 3.65 (d, J = 3.0 Hz, 1H), 1.67 (s, 3H), 1.60 (d, J = 7.5 Hz, 3H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.7, 164.5, 139.6, 133.2, 129.9, 128.6, 105.1, 52.4, 38.5, 28.2, 27.8, 17.6. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_4Cl$ $(M+H)^+$: 283.07316. Found: 283.07314.

5-(1-(4-Chlorophenyl)ethyl-2,2,2-*d*$_3$)-2,2-dimethyl-1,3-dioxane-4,6-dione ([CD$_3$]-3.15a).



To a solution of **3.13** (78.6 mg, 0.100 mmol) in 1,2-dichloroethane (1 ml) was added 5-(4-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8a**) (26.7 mg, 0.100 mmol) and 5-(methyl-d_3)-1-aza-5-stannabicyclo[3.3.3]undecane ([CD_3]-**3.12**) (99 atom % D, 27.7 mg, 0.100 mmol) and the mixture was stirred for 24 h at ambient temperature. All volatiles were evaporated under vacuum and the product was purified by flash chromatography on silica gel eluting with EtOAc:hexanes (1:5) and isolated as a white solid (99 atom % D, 26.1 mg, 92% yield). M.p. 118-120°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.24 (m, 4H), 3.95 (brs, 1H), 3.64 (d, J = 2.4 Hz, 1H), 1.67 (s, 3H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.7, 164.5, 139.6, 133.2, 129.9, 128.6, 105.1, 52.4, 38.3, 28.2, 27.8; ^{2}H NMR ($CHCl_3$, 46 MHz) δ 1.58. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}{}^{2}H_3O_4Cl$ $(M+H)^+$: 286.09199. Found: 286.09193.

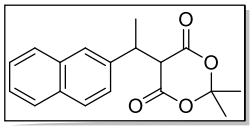
5-(1-(3-Methoxyphenyl)ethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.15b).



Prepared according to the General Procedure B from 5-(3-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8b**) (26.2 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:7) and isolated as a colorless oil (25.1 mg, 90% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21 (t, J = 7.8 Hz,1H), 6.93-6.90 (m, 2H), 6.78 (d, J = 8.1 Hz, 1H), 3.99-3.93 (m, 1H), 3.78 (s, 1H), 3.67 (d, J = 2.7 Hz, 1H), 1.66 (s, 3H), 1.63 (d, J = 7.5 Hz, 3H),1.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 164.7, 159.6, 142.7, 129.5, 120.5, 114.0,

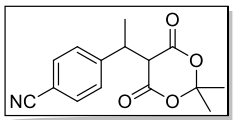
112.8, 105.2, 55.2, 52.4, 39.4, 28.1, 27.9, 17.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}O_5$ $(M+H)^+$: 279.12270; Found: 279.12275.

2,2-Dimethyl-5-(1-(naphthalen-2-yl)ethyl)-1,3-dioxane-4,6-dione (3.15c).



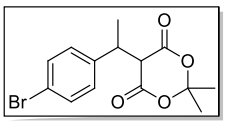
Prepared according to the General Procedure B from 2,2-dimethyl-5-(naphthalen-2-ylmethylene)-1,3-dioxane-4,6-dione (**3.8c**) (28.2 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:7) and isolated as a pale yellow solid (23.5 mg, 79% yield). M.p. 122-123 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.93-7.62 (m, 4H), 7.49-7.43 (m, 3H), 4.19-4.13 (m, 1H), 3.77 (d, J = 3.0 Hz, 1H), 1.73 (d, J = 7.2 Hz, 1H), 1.65 (s, 3H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 164.8, 138.6, 133.2, 132.6, 128.1, 128.0, 127.5, 127.3, 126.3, 126.1, 125.9, 105.1, 52.5, 39.4, 28.1, 27.8, 17.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{19}O_4$ $(M+H)^+$: 299.12779; Found: 299.12762.

4-(1-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-yl)ethyl)benzonitrile (3.15d).



Prepared according to the General Procedure B from 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl)benzonitrile (**3.8d**) (25.7 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:7 to 1:4) and isolated as a white solid (22.6 mg, 83% yield). M.p. 127-128 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59 (d, J = 8.1 Hz,1H), 7.50 (d, J = 8.4 Hz, 1H), 4.09-4.01 (m, 1H), 3.70 (d, J = 3.0 Hz, 1H), 1.71 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H), 1.59 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.2, 164.1, 146.7, 132.2, 129.4, 118.7, 111.1, 105.2, 52.2, 38.3, 28.1, 27.5, 16.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}O_4N$ $(M+H)^+$: 274.10738; Found: 274.10730.

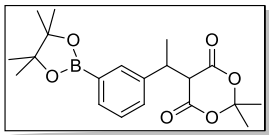
5-(1-(4-Bromophenyl)ethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.15e).



Prepared according to the General Procedure B from 5-(4-bromobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8e**) (31.1 mg, 0.100 mmol); the reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:7) and isolated as a white solid (28.7 mg, 88% yield). M.p. 112-114°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.41 (d, J = 8.4 Hz,1H), 7.23 (d, J = 8.4 Hz, 1H), 4.00-3.91 (m, 1H), 3.65 (d, J = 3.0 Hz, 1H), 1.68 (s, 3H), 1.60 (d, J = 7.2 Hz, 3H),1.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ

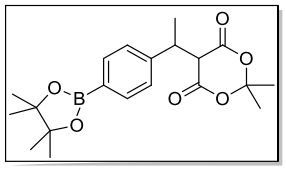
164.6, 164.5, 140.1, 131.5, 130.2, 121.3, 105.1, 52.4, 38.5, 28.2, 27.8, 17.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_4Br$ $(M+H)^+$: 327.02265; Found: 327.02234.

2,2-Dimethyl-5-(1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)-1,3-dioxane-4,6-dione (3.15f).



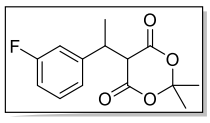
Prepared according to the General Procedure B from 2,2-dimethyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)- 1,3-dioxane-4,6-dione (**3.8f**) (35.8 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:7) and isolated as a colorless oil (34.0 mg, 91% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72-7.66 (m, 2H),7.52 (d, J = 7.8 Hz,1H), 7.32 (t, J = 7.5 Hz, 1H), 4.04-3.96 (m, 1H), 3.72 (d, J = 3.0 Hz, 1H), 1.67 (s, 3H), 1.58 (d, J = 7.2 Hz, 3H),1.42 (s, 3H) ,1.32 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 164.5, 140.7, 134.6, 133.8, 131.1, 127.9, 105.1, 83.8, 52.7, 39.0, 28.2, 27.8, 24.9, 24.8, 16.8. HRMS (ESI) *m/z* calcd for $C_{20}H_{28}O_6B$ $(M+H)^+$: 375.19735. Found: 375.19720.

2,2-Dimethyl-5-(1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)-1,3-dioxane-4,6-dione (3.15g).



Prepared according to the General Procedure B from 2,2-dimethyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)- 1,3-dioxane-4,6-dione (**3.8g**) (35.8 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:7) and isolated as a colorless oil (30.3 mg, 81% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 4.02-3.95 (m, 1H), 3.69 (d, J = 3.0 Hz, 1H), 1.65 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H),1.38 (s, 3H) ,1.31 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.7, 164.7, 144.4, 135.0, 128.0, 105.1, 83.8, 52.5, 39.3, 28.2, 27.8, 24.8, 17.3. HRMS (ESI) *m/z* calcd for $C_{20}H_{28}O_6B$ $(M+H)^+$: 375.19735. Found: 375.19723.

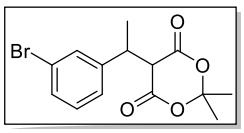
5-(1-(3-Fluorophenyl)ethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.15h).



Prepared according to the General Procedure B from 5-(3-fluorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8h**) (25.0 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:5) and isolated as a colorless oil (24.5 mg, 92% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ

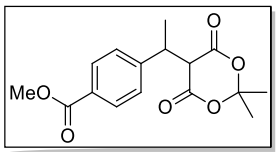
7.27-7.22 (m, 1H), 7.14-7.08 (m, 2H), 6.95 (t, J = 6.6 Hz, 2H), 4.04-3.96 (m, 1H), 3.68 (d, J = 3.0 Hz, 1H), 1.69 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H),1.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.6, 164.5, 162.8 (d, $J_{C\text{-}F}$ = 244.4 Hz), 143.7 (d, $J_{C\text{-}F}$ = 7.1 Hz), 129.9 (d, $J_{C\text{-}F}$ = 8.2 Hz), 124.0 (d, $J_{C\text{-}F}$ = 2.6 Hz), 115.6, 115.3, 114.4, 114.1, 105.2, 52.4, 38.7, 28.2, 27.7, 17.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_4F$ $(M+H)^+$: 267.10271; Found: 267.10266.

5-(1-(3-Bromophenyl)ethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.15i).



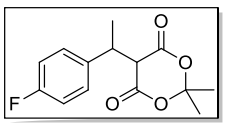
Prepared according to the General Procedure B from 5-(3-bromobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8i**) (31.1 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:5) and isolated as a colorless oil (29.4 mg, 90% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51 (t, J = 1.5 Hz,1H), 7.38-7.29 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 4.00-3.92 (m, 1H), 3.67 (d, J = 2.7 Hz, 1H), 1.69 (s, 3H), 1.59 (d, J = 7.2 Hz, 3H),1.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.5, 164.4, 143.6, 131.5, 130.4, 130.0, 127.1, 122.5, 105.2, 52.3, 38.5, 28.2, 27.7, 17.1. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_4Br$ $(M+H)^+$: 327.02265; Found: 327.02260.

Methyl 4-(1-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)ethyl)benzoate (3.15j).



Prepared according to the General Procedure B from methyl 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl)benzoate (**3.8j**) (29.0 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:7) and isolated as a white solid (27.1 mg, 92% yield). M.p. 119-122°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96 (d, J = 8.1 Hz,1H), 7.42 (d, J = 8.4 Hz, 1H), 4.08-4.01 (m, 1H), 3.88 (s, 1H), 3.71 (d, J = 3.0 Hz, 1H), 1.68 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H),1.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.7, 164.5, 164.4, 146.4, 129.7, 129.1, 128.4, 105.1, 52.3, 52.0, 38.7, 28.1, 27.6, 17.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}O_6$ $(M+H)^+$: 307.11761; Found: 307.11766.

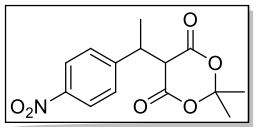
5-(1-(4-Fluorophenyl)ethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.15k).



Prepared according to the General Procedure B from 5-(4-fluorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8k**) (25.0 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:5) and isolated as a white solid (22.6 mg, 85% yield). M.p. 137-138°C; ^{1}H NMR

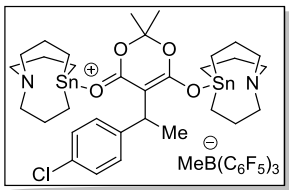
($CDCl_3$, 300 MHz) δ 7.34-7.29 (m, 2H), 7.00-6.94 (m, 2H), 4.00-3.95 (m, 1H), 3.63 (d, J = 2.7 Hz, 1H), 1.66 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H),1.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 164.6, 162.0 (d, $J_{C\text{-}F}$ = 244.4 Hz), 136.7 (d, $J_{C\text{-}F}$ = 3.1 Hz), 130.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.0 Hz), 105.1, 52.5, 38.6, 28.1, 27.8, 17.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_4F$ $(M+H)^+$: 267.10271; Found: 267.10265.

2,2-Dimethyl-5-(1-(4-nitrophenyl)ethyl)-1,3-dioxane-4,6-dione (3.15l).



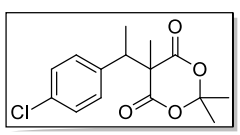
Prepared according to the General Procedure B from 5-(4-nitrobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8l**) (27.7 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:6) and isolated as a white solid (23.7 mg, 85% yield). M.p. 154-156°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.15 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 4.15-4.07 (m, 1H), 3.73 (d, J = 2.7 Hz, 1H), 1.72 (s, 3H), 1.63 (d, J = 7.2 Hz, 3H),1.59 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.2, 164.0, 148.8, 147.1, 129.6, 123.5, 105.2, 52.2, 38.0, 28.2, 27.4, 16.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_6N$ $(M+H)^+$: 294.09721; Found: 294.09709.

Bis-tricarbastannatrane intermediate 3.18.



In a J-Young NMR tube, 5-(4-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**10a**) (26.7 mg, 0.100 mmol) was added to a solution of 5-methyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.12**) (54.8 mg, 0.200 mmol) and tris(pentafluorophenyl)borane (**7**) (51 mg, 0.10 mmol) in 1 mL of dry $CDCl_3$ and the mixture was stirred for 24 h at ambient temperature; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.19 (m, 4H), 3.96 (m, 1H), 2.56 (brs, 12H), 1.93 (brs, 12H), 1.65 (brs, 9H), 1.47 (d, J = 7.2 Hz, 3H), 1.23 (brs, 12H) , 0.59 (brs, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.9, 144.4, 130.9, 128.5, 127.6, 104.6, 84.0, 54.8, 32.6, 24.7, 23.1, 17.3, 11.5; ^{119}Sn NMR ($Cl(CH_2)_2Cl$, 112 MHz) δ 47.6; ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ 44.9; HRMS (+ESI) *m/z* calcd for $C_{32}H_{50}O_4N_2ClSn_2$ (M^+): 801.14976; Found: 801.15004. HRMS (–ESI) *m/z* calcd. for $C_{19}H_3BF_{15}$ (M^-): 527.00828. Found: 527.00791.

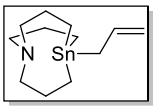
5-(1-(4-Chlorophenyl)ethyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (3.19).



5-(4-Chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8a**) (26.7 mg, 0.100 mmol) was added to a solution of 5-methyl-1-aza-5-

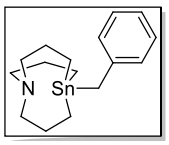
stannabicyclo[3.3.3]undecane (**6**) (54.8 mg, 0.20 mmol) and tris(pentafluorophenyl)borane (51.1 mg, 0.100 mmol) in 1 mL of 1,2-dichloroethane and the solution was stirred for 24 h at ambient temperature. Then, K_2CO_3 (27.6 mg, 0.200 mmol), DMF (0.5 ml) and iodomethane (0.05 ml, 0.80 mmol) were added to the reaction mixture which was stirred for 22 h at room temperature. The workup consisted of adding water and extracting with CH_2Cl_2 (3X), and then the combined organic layers that were washed with sat. brine solution (1X), dried over $MgSO_4$, filtered and concentrated; reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:5) and isolated as a white solid (24.6 mg, 83% yield). M.p. 114-116°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25 (d, J = 8.7 Hz, 2H), δ 7.09 (d, J = 8.7 Hz, 2H), 3.51-3.44 (m, 1H), 1.63 (s, 3H), 1.57 (s, 3H), 1.52 (d, J = 7.2 Hz, 3H), 1.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.2, 168.6, 138.7, 133.6, 129.9, 128.6, 104.9, 54.1, 48.0, 30.2, 27.5, 22.0, 15.2. HRMS (DART) *m/z* calcd for $C_{15}H_{21}NO_4Cl$ $(M + NH_4)^+$: 314.11536. Found: 314.11528.

5-Allyl-1-aza-5-stannabicyclo[3.3.3]undecane (3.20c).



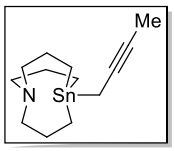
The General Procedure A was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (235 mg, 0.798 mmol) in THF (3.2 mL), and allylmagnesium chloride (2.0 M in THF, 0.78 mL, 1.56 mmol). A pale yellow oil (227 mg, 97 % yield) was isolated. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.99-5.84 (m, 1H), 4.56 (dt, J = 16.5, 1.2 Hz, 1H), 4.41 (dd, J = 9.8, 2.4 Hz, 1H), 2.34 (t, J = 5.4 Hz, 6H), 1.63 (m, 6H), 1.42 (d, J = 8.7 Hz, 2H), 0.66 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.7, 105.2, 54.7, 24.5, 23.2, 6.3. HRMS (ESI) *m/z* calcd for $C_{12}H_{24}N^{116}Sn$ $(M+H)^+$: 298.09207. Found: 298.09194.

5-Benzyl-1-aza-5-stannabicyclo[3.3.3]undecane (3.20d).



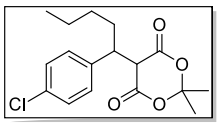
The General Procedure A was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (103 mg, 0.350 mmol) in THF (1.5 mL), and benzylmagnesium chloride (2.0 M in THF, 0.34 mL, 0.68 mmol). A colorless oil (108 mg, 91% yield) was isolated. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.09 (t, J = 7.8 Hz, 2H), 6.86 (d, J = 7.5 Hz, 3H), 2.31 (t, J = 5.7 Hz, 6H), 1.94 (s, 2H), 1.60 (m, 6H), 0.62 (t, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.5, 128.4, 126.2, 121.2, 54.5, 26.7, 23.2, 6.4. HRMS (ESI) *m/z* calcd for $C_{16}H_{26}N^{116}Sn$ $(M+H)^+$: 348.10772. Found: 348.10751.

5-(But-2-yn-1-yl)-1-aza-5-stannabicyclo[3.3.3]undecane (3.20f).



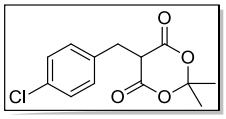
The General Procedure A was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (201 mg, 0.683 mmol) in THF (2.5 mL), and but-2-yn-1-ylmagnesium bromide[54] (0.3 M in Et_2O, 5.00 mL, 1.50 mmol). A yellow oil was obtained. The crude stannatryl reagent was used without further purification, as chromatography on silica gel led to decomposition of the product. Octa-2,6-diyne was obtained as the major byproduct from the homocoupling of the Grignard reagent.[55] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.38 (m, 8H), 1.78-1.67 (m, 12H), 1.06 (m, 2H), 0.78 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.0, 71.6, 54.6, 23.2, 6.9, 3.9, 2.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{24}N^{116}Sn$ $(M+H)^+$: 314.09252. Found: 314.09221.

5-(1-(4-Chlorophenyl)pentyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.21a).



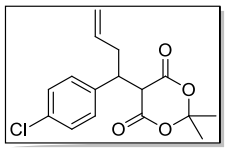
Prepared according to the General Procedure C from 5-butyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.20a**) (63.2 mg, 0.200 mmol); reaction was purified eluting with EtOAc:hexanes (1:7) and isolated as a colorless oil (28.9 mg, 89% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25 (s, 4H), 3.78-3.69 (m, 1H), 3.64 (d, J = 3.0 Hz, 1H), 2.29-2.16 (m, 1H), 2.00-1.89 (m, 1H), 1.64 (s, 3H), 1.37-1.19 (m, 7H), 0.85 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.4, 164.6, 138.2, 133.4, 130.6, 128.7, 105.3, 51.3, 45.1, 32.1, 30.1, 28.1, 28.1, 22.4, 13.9. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}O_4Cl$ $(M+H)^+$: 325.12011. Found: 325.12006.

5-(4-Chlorobenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.21b).[56]



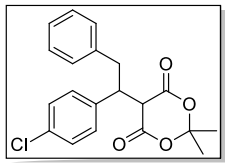
Prepared according to the General Procedure C from 5-(*iso*-propyl)-1-aza-5-stannabicyclo[3.3.3]undecane (**3.20b**) (60.4 mg, 0.200 mmol) or by the reaction of **3.20b** (30.2 mg, 0.100 mmol), tris(pentafluorophenyl)borane (51.1 mg, 0.100 mmol), and 5-(4-Chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3.8a**) (26.7 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:5) and isolated as a white solid (19.8 mg, 74% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25 (s, 4H), 3.71 (t, J = 4.8 Hz, 1H), 3.43 (d, J = 4.8 Hz, 2H), 1.73 (s, 3H), 1.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.0, 135.5, 131.3, 128.7, 105.2, 48.0, 31.3, 28.4, 27.2. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_4Cl$ $(M+H)^+$: 269.05751. Found: 269.05748.

5-(1-(4-Chlorophenyl)but-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.21c).[57]



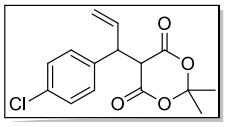
Prepared according to the General Procedure C from 5-allyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.20c**) (60.0 mg, 0.200 mmol); reaction was purified eluting with EtOAc:hexanes (1:7) and isolated as a white solid (29.7 mg, 96% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30-7.22 (m, 4H), 5.83-5.69 (m, 1H), 5.21 (d, J = 17.0 Hz, 1H), 5.13 (d, J = 10.0 Hz, 1H), 3.88-3.82 (m, 1H), 3.76 (d, J = 2.8 Hz, 1H), 3.06-2.95 (m, 1H), 2.77-2.69 (m, 1H), 1.64 (s, 3H), 1.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) 165.6, 164.4, 138.0, 135.5, 133.5, 130.5, 128.7, 118.8, 105.2, 49.4, 44.0, 36.4, 28.1, 27.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_4Cl$ $(M+H)^+$: 309.08881. Found: 309.08871.

5-(1-(4-Chlorophenyl)but-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.21d).



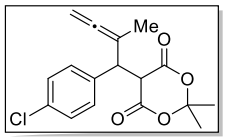
Prepared according to the General Procedure C from 5-benzyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.20d**) (70.0 mg, 0.200 mmol); reaction was purified eluting with EtOAc:hexanes (1:9 to 1:6) and isolated as a white solid (17.6 mg, 49% yield). M.p. 138-139°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33-7.24 (m, 9H), 4.08-4.01 (m, 1H), 3.67-3.59 (m, 1H), 3.52 (d, J = 2.7 Hz, 1H), 3.24-3.18 (m, 1H), 1.54 (s, 3H), 1.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.7, 164.4, 138.8, 137.9, 133.6, 130.6, 129.2, 128.8, 128.8, 127.0, 105.2, 48.5, 46.5, 38.2, 28.1, 27.8. HRMS (ESI) *m/z* calcd for $C_{20}H_{20}O_4Cl$ $(M+H)^+$: 359.10446. Found: 359.10454.

5-(1-(4-Chlorophenyl)but-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.21e).[58]



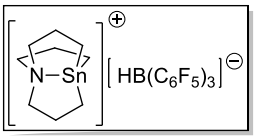
Prepared according to the General Procedure C from 5-vinyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.20e**) (57.2 mg, 0.200 mmol); reaction was purified eluting with EtOAc:hexanes (1:9 to 1:6) and isolated as a white solid (9.9 mg, 34% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.24 (m, 1H), 6.50-6.38 (m, 1H), 5.28 (d, J = 3.9, 1H), 5.23 (s, 1H), 4.52 (dd, J = 6.3, 2.1 Hz, 1H), 3.83 (d, J = 2.8 Hz, 1H), 1.55 (s, 3H), 1.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.3, 164.2, 137.9, 136.2, 133.3, 130.1, 128.7, 105.2, 52.1, 47.3, 28.2, 27.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}O_4Cl$ $(M+H)^+$: 295.07316. Found: 295.07318.

5-(1-(4-Chlorophenyl)-2-methylbuta-2,3-dien-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3.21f).



Prepared according to the General Procedure C from 5-(but-2-yn-1-yl)-1-aza-5-stannabicyclo[3.3.3]undecane (80.0 mg of crude **3.20f**); reaction was purified eluting with EtOAc:hexanes (1:6) and isolated as a white solid (27.6 mg, 86% yield). M.p. 161-162°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40 (d, J = 8.4, 2H), 7.28 (d, J = 8.4, 2H), 4.84 (brs, 2H), 4.39 (m, 1H), 3.82 (d, J = 3.0, 1H), 1.69 (s, 3H), 1.63 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 206.1, 164.0, 136.0, 133.3, 131.9, 128.3, 104.7, 97.6, 79.1, 51.0, 46.2, 28.3, 27.1, 18.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}O_4Cl$ $(M+H)^+$: 321.08881. Found: 321.08884.

[N(CH$_2$CH$_2$CH$_2$)$_3$Sn] [HB(C$_6$F$_5$)$_3$] (3.22).



To a solution of 5-isopropyl-1-aza-5-stannabicyclo[3.3.3]undecane (**3.20b**) (30.2 mg, 0.100 mmol) in $CDCl_3$ (1 ml) in a vial, was added tris(pentafluorophenyl)borane (51.1 mg, 0.100 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.66 (m, 6H, NC*H*2), 2.02 (m, 6H, C*H*2), 1.41 (t, J = 6.6, 6H, SnC*H*2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 56.1 (N*C*H2), 24.7 (*C*H2), 14.7 (Sn*C*H2); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ 140.9; ^{119}Sn NMR ($Cl(CH_2)_2Cl$, 112 MHz) δ 157.5; ^{11}B NMR ($CDCl_3$, 96 MHz) δ –16.9. HRMS (–ESI) *m/z* calcd. for $C_{18}HBF_{15}$ (M^-): 512.99263. Found: 512.99267; (+ESI) *m/z* calcd. for $C_9H_{18}NSn$ (M^+): 260.04557. Found: 260.04546.

Chapter 4

$B(C_6F_5)_3$-Catalyzed Conjugate Reduction of Olefins Using ^{i}Pr-tricarbastannatrane as a Hydride Source

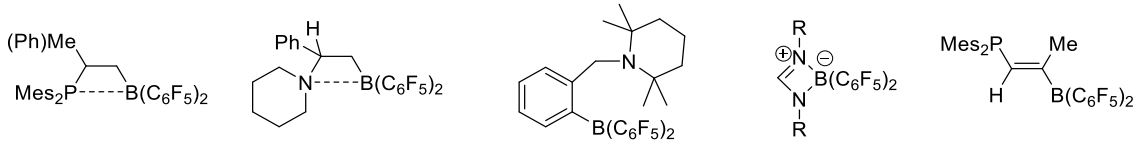
This chapter shows that tris(pentafluoropheynl)borane, $B(C_6F_5)_3$, is an effective catalyst to abstract a hydride from ^{i}Pr-tricarbastannatrane in-situ to yield $[N(CH_2CH_2CH_2)_3Sn]^+[HB(C_6F_5)_3]^-$ along with propene gas. This process is followed by reduction of benzylidene barbituric acids by transfer of the hydride from the generated borohydride to the electrophilic olefin, under catalytic conditions. In addition, detailed mechanistic studies are presented.

4.1 Introduction

The reduction of olefins is one of the most important and common transformations in organic synthesis. Although the use of H_2 activation by transition metal catalysts or main-group hydride source reagents, such as $NaBH_4$ and $LiAlH_4$,[59] is very common, these reagents are not very efficient in large scale reduction processes due to cost and waste disposal concerns. Therefore, employing a strong organometallic Lewis acid, e. g., $B(C_6F_5)_3$ as a catalyst could tackle the waste and cost issues related to the main group hydrides, as well as product toxicity and environmental concerns connected with precious metal catalysts.

Lewis acids (LA) and Lewis bases (LB) usually form adducts in solution. However, nitrogen and phosphorus Lewis bases with bulky substituents and boron Lewis acids with strongly electron-withdrawing bulky pentafluorophenyl substituents can generate intramolecular Frustrated Lewis pairs (FLP). These frustrated pairs can activate dihydrogen to yield phosphonium (or ammonium)/hydridoborate zwitterions.[60] Other small molecules, such as carbonyl compounds, dienes, diynes, and nitric oxide can also be activated by Frustrated Lewis pairs (FLP). Some examples of intramolecular FLPs are depicted in Scheme 4.1.

Scheme 4.1. Some examples of intramolecular Frustrated Lewis Pairs (FLP)

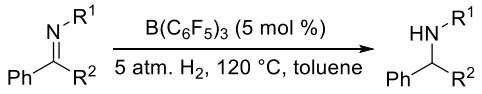


Alternatively, in an intermolecular manner, the strong bulky Lewis acid $B(C_6F_5)_3$ abstracts a hydride by the heterolytic cleavage of H–H, H–Si and H–C(sp^3) bonds to form $[HB(C_6F_5)_3]^-$ in the presence of sterically encumbered Lewis bases. The reactive borohydride promotes in several transformations, such as hydrosilylation[61] and reduction of imines, aziridines, silyl enol ethers, nitrogen-based heterocycles, etc.[62] The following is a survey of the literature with regard to methodologies on $B(C_6F_5)_3$–catalyzed reduction of a variety of unsaturated substrates.

An early approach to imines reduction promoted by Lewis acid–base complexes was reported by Stephan and co-workers in 2007.[63] It was demonstrated that their reduction with hydrogen occurs only under favorable electronic and more importantly steric conditions of Lewis pairs. Not only are sufficient steric demands required to preclude the formation of classical Lewis acid–Lewis base adducts, but the frustrated Lewis pair must be strong enough to activate H_2.

It was later shown independently by Stephan's[64] and Klankermayer's[65] groups that the $B(C_6F_5)_3$-catalyzed hydrogenation of basic sterically-hindered imines could be accomplished in the absences of a Lewis base (Scheme 4.2). It was also shown that the addition of a catalytic amount of $P(C_6H_2Me_3)_3$ (5 mol%) accelerated the hydrogenation of electron-deficient imines by increasing the ability of phosphine/borane pair to split hydrogen heterolytically.

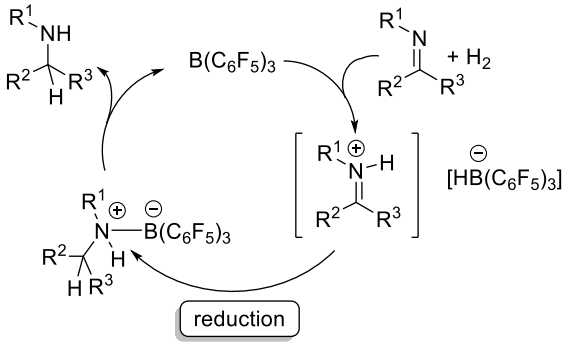
Scheme 4.2. Hydrogenation of imines



R^1 = ^{t}Bu, $CHPh_2$, SO_2Ph, Dipp
R^2 = H, Ph, Me

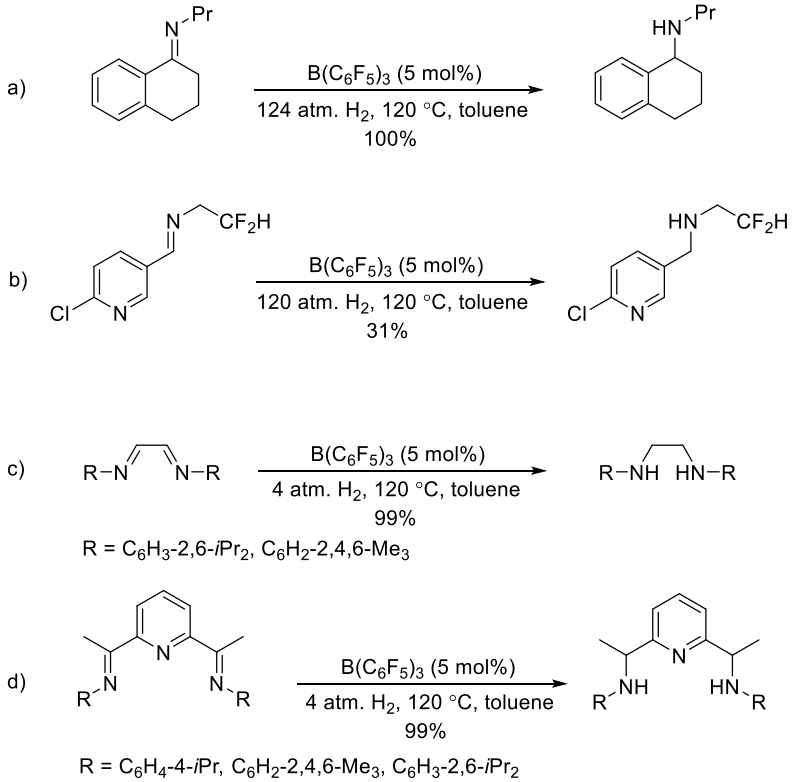
Experimental mechanistic studies suggested the heterolytic hydrogen splitting by imine–borane FLP. This cleavage yields an ion pair consisting of iminium and hydridoborate ions (Scheme 4.3). Hydride transfer from the borohydride to the protonated imine regenerates the free boron and leads to the formation of the amine-boron dative adduct, which is dissociated thermally to release the amine. The regenerated free borane can re-enter the catalytic cycle.

Scheme 4.3. Proposed mechanism for imines reduction



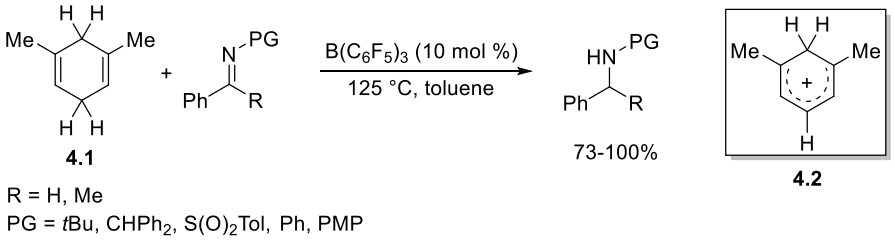
Some commercially relevant imine and diimine substrates,[66] which were hydrogenated by $B(C_6F_5)_3$, are shown in Scheme 4.4. Reduction of all substrates was carried out in toluene at 120 °C with 5 mol % the catalyst. In the case of the substrate with pyridine fragment, a 31% yield was obtained at 120 bar of H_2 pressure after 20 hours (Scheme 4.4b). Applying $B(C_6F_5)_3$ reduced different diimines to the corresponding diamines quantitatively under catalytic conditions.

Scheme 4.4. Reduction of commercially relevant imines and diimines



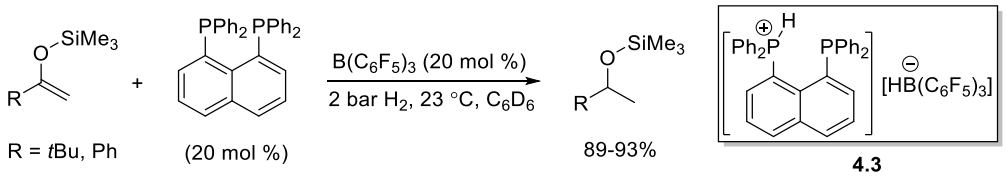
It has been shown that $B(C_6F_5)_3$ is a strong enough Lewis acid to release dihydrogen from 1,5-dimethylcyclohexa-1,4-diene **4.1** to yield *m*-xylene as a byproduct through Wheland complex **4.2**.[67] It was found that high reaction temperature was crucial for the hydride abstraction. However, cyclohexa-1,4-diene did not show any reactivity even at 125 °C. Oestreich and Chatterjee proposed that the hyperconjugation ability of the methyl groups stabilized the phenonium ion intermediate. Using this hydrogen source, different aldimines and ketimines were reduced with 10 mol % of $B(C_6F_5)_3$ (Scheme 4.5).

Scheme 4.5. Hydrogenation of imines using 1,5-dimethylcyclohexa-1,4-diene



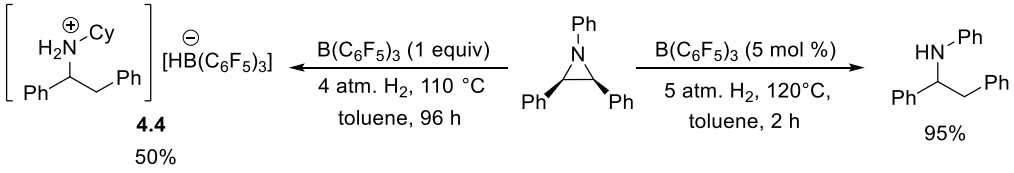
Erker and coworkers reported the reduction of silyl enol ethers applying $B(C_6F_5)_3$ and $C_{10}H_6(PPh_2)_2$ as a FLP catalyst.[68] Salt $[C_{10}H_6(PPh_2)_2H][HB(C_6F_5)_3]$ (**4.3**) was generated under hydrogen at ambient temperature. By heating the solution of **4.3** in d_6-benzene at 60 °C, $B(C_6F_5)_3$ and the bis-phosphine Lewis base were formed quantitatively by releasing H_2 gas, indicating the reversibility of this process. Appling 20 mol % of $B(C_6F_5)_3/C_{10}H_6(PPh_2)_2$ under 2 bar H_2 with silyl enol ethers afforded the reduced products in 85–93% yield (Scheme 4.6). For less hindered substrate (R = Me), forcing condition was required and full conversion to the reduced product was obtained with 60 bar H_2 pressure.

Scheme 4.6. Hydrogenation of silyl enol ethers



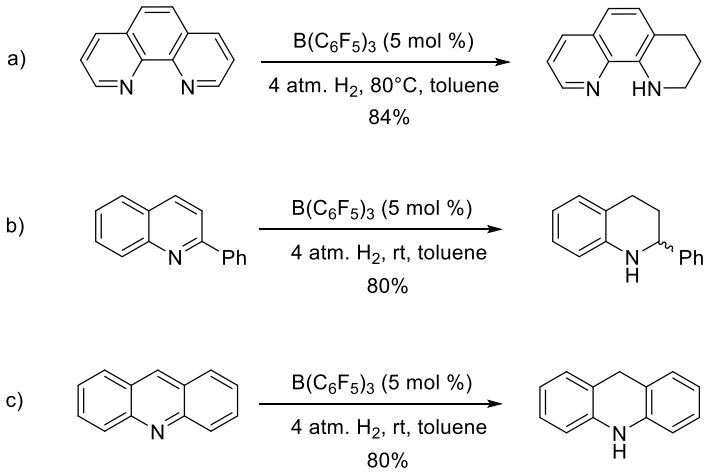
In addition to imines, *cis*-triphenylaziridine was shown to undergo reductive ring opening with catalytic amount of $B(C_6F_5)_3$ to yield 95% of racemic *N*-(1,2-diphenylethyl)aniline.[66] However, treatment of the aziridine with one equivalent of $B(C_6F_5)_3$ for 96 h at 110 °C reduced the *N*-bound phenyl ring to afforded $[CyNH_2CHPhCH_2Ph][HB(C_6F_5)_3]$ (**4.4**).[69]

Scheme 4.7. Reduction of *cis*-triphenylaziridine



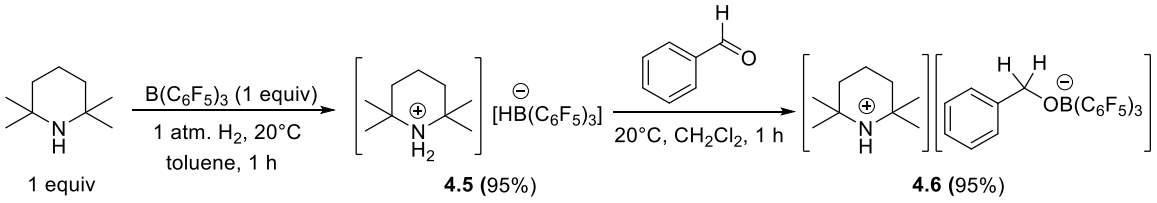
To expand the scope of substrates, Stephan group employed $B(C_6F_5)_3$ as a catalyst to reduce nitrogen-based heterocycles.[70] One of the nitrogen-containing rings in 1,10-phenanthroline was reduced in 3 hours at 110 °C (Scheme 4.8a). In addition to phenanthroline, the *N*-containing ring in 2-phenylquinoline was also reduced under mild condition to afford 1,2,3,4-tetrahydro-2-phenylquinoline in 80% yield (Scheme 4.8b). It should be noted that two equivalents of hydrogen were applied for the above reductions. Furthermore, applying 4 atm of hydrogen at room temperature to acridine in the presence of 5 mol % of the catalyst led to hydrogenation of the central ring, and the reduced product was isolated in 80% yield.

Scheme 4.8. Reduction of nitrogen-based heterocycles



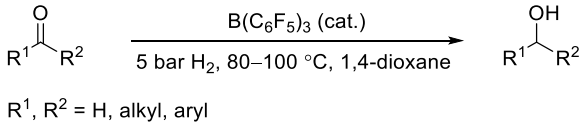
While all the above-mentioned substrates such as imines, aziridines and silyl enol ethers are reduced in a catalytic manner, reduction of aldehydes was initially carried out with stoichiometric amount of the catalyst.[71] Sumerin and coworkers reported the reduction of benzaldehyde under mild condition using one equivalent of salt **4.5**. It was proposed that hydrogen cleavage by $B(C_6F_5)_3$ and the amine could be carried out in a concerted pathway. Reduced product **4.6** was obtained in 95% yield.

Scheme 4.9. Reduction of benzaldehyde



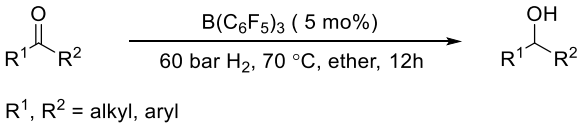
Recently, Ashley and coworkers reported the hydrogenation of a variety of aliphatic and aromatic aldehydes and ketones under $B(C_6F_5)_3$-catalyzed conditions.[72] The role of solvent is crucial in this protocol, as the solvent and $B(C_6F_5)_3$ behave as a frustrated Lewis pair to activate hydrogen. Replacing THF with 1,4-dioxane significantly improved the reactivity of $B(C_6F_5)_3$. Low extent of H_2 activation was observed in THF due to the presence of very small amounts of uncoordinated $B(C_6F_5)_3$ in the reaction mixture. However, more free $B(C_6F_5)_3$ in 1,4-dioxane led to higher yields of hydrogenation reactions (Scheme 4.10).

Scheme 4.10. Hydrogenation of aliphatic and aromatic aldehydes and ketones



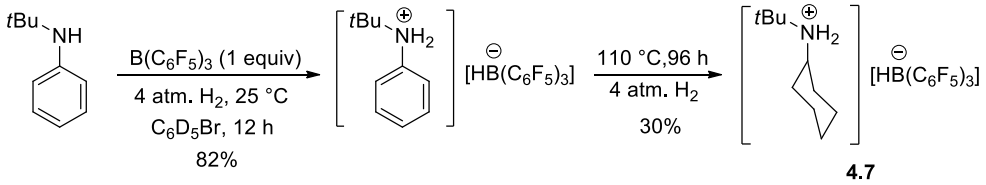
Another method on the $B(C_6F_5)_3$-catalyzed reduction of ketones in an ethereal solvent was reported by Stephan and coworkers.[73] In this method hydrogenation of aryl and alkyl ketones to alcohols was carried out in $^{i}Pr_2O$ or Et_2O.

Scheme 4.11. Hydrogenation of aryl and alkyl ketones



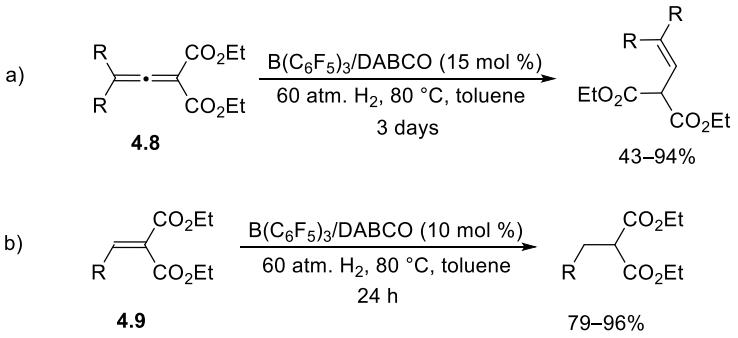
The reduction of an aromatic ring in sterically hindered anilines with stoichiometric amount of $B(C_6F_5)_3$ was recently reported by Stephan and coworkers.[71] As mentioned above, using a stoichiometric amount of the boron Lewis acid in the reduction of *cis*-triphenylaziridine led to the hydrogenation of *N*-bound phenyl ring. This reduction was also accomplished with a variety of anilines. As an example, reduction of *t*-butylaniline has been demonstrated in Scheme 4.12. The phenyl ring was hydrogenated under H_2 after 96 h at 110 °C to afford salt **4.7**.

Scheme 4.12. Hydrogenation of *t*-butylaniline

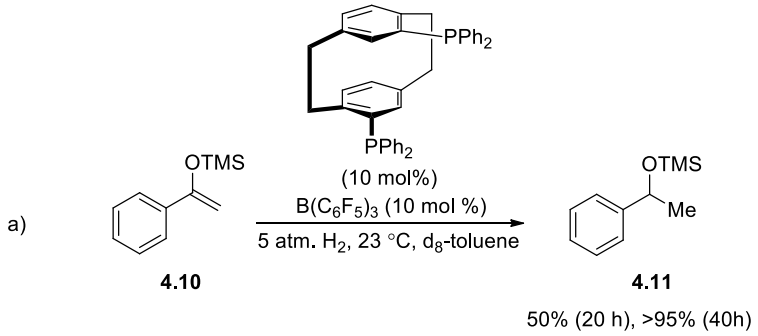


Alcarazo and co-workers extended $B(C_6F_5)_3$-catalyzed reductions to allenic esters and olefins.[74] Different bases such as $^tBu_3P$, Mes_3P, 2,6-lutidine, and DABCO were screened, and DABCO was found to be the most suitable base for this transformation. Allenes **4.8** were reduced with 15 mol % of the catalytic mixture of DABCO and $B(C_6F_5)_3$ after 3 days with 60 atm of hydrogen in toluene at 80 °C (Scheme 4.13a). Under similar reaction conditions alkylidene malonates **4.9** could also be hydrogenated to provide the reduced products in high yields (Scheme 4.13b). Similarly, the combination of [2,2]-bis(phosphine)paracyclophane and $B(C_6F_5)_3$ can reduce silyl enol ether **4.10** to yield more than 95% of the reduced product **4.11** after 40 hours (Scheme 4.14).[75]

Scheme 4.13. Reduction of olefins and allene–esters



Scheme 4.14. Reduction of silyl enol ether



4.2 Proposal

We recently discovered that $B(C_6F_5)_3$ is capable of insitu hydride abstraction from ^{i}Pr-tricarbastannatrane and formation of propene gas. The transfer of the hydride from the borohydride to 4-chlorobenzylidene Meldrum's acid was then accomplished to reduce the activated double bond under stoichiometric condition (Chapter 3). The purpose of this chapter is to develop conditions to apply ^{i}Pr-tricarbastannatrane as a reducing reagent for the reduction of activated electrophiles in a catalytic manner. In this regard, we propose that highly electrophilic olefins may be reduced under Lewis acid catalysis.

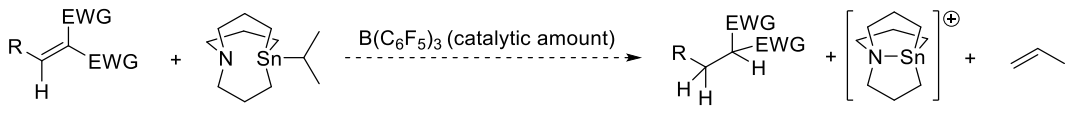
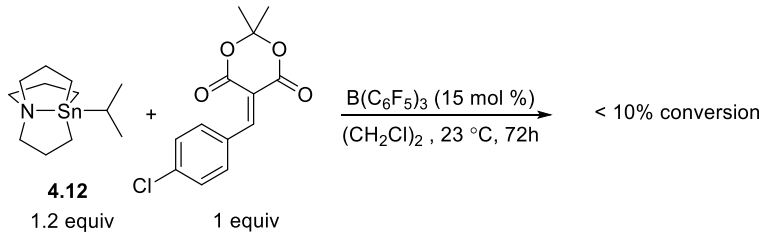


Figure 4.1. Proposal for the reduction of activated olefins

4.3 Results and Discussion

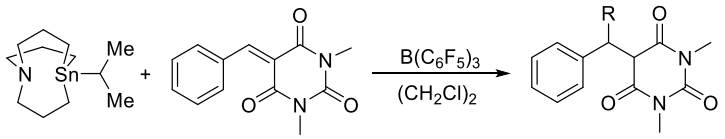
As mentioned in Chapter 3, in our previous effort on $B(C_6F_5)_3$-promoted conjugate alkylation of benzylidene derivatives of Meldrum's acid, applying ^{i}Pr-carbstannatrane (**4.12**) as an alkylating agent, furnished the reduced product. However, using 15 mol% $B(C_6F_5)_3$ in the reaction of 1.2 equivalent of ^{i}Pr-carbstannatrane with 4-chlorobenzylidene Meldrum's acid at 23 °C, led to less than 10% conversion (Scheme 4.15). Increasing the reaction temperature to 95 °C led to the decomposition of the reaction intermediate. Solvents, such as toluene and trifluorotoluene at 120 °C did not improve the result.

Scheme 4.15. $B(C_6F_5)_3$-catalyzed reduction of 4-chlorobenzylidene Meldrum's acid



However, we found that the reduction of benzylidene 1,3-dimethylbarbituric acids **4.13a** could be carried out in a catalytic manner using **4.12** as a reducing agent. Herein, we present $B(C_6F_5)_3$-catalyzed conjugate reduction of benzylidene derivatives of 1,3-dimethyl barbituric acid. In our initial efforts to reduce an activated olefin with catalytic amount of $B(C_6F_5)_3$, the reaction of one equivalent of **4.13a** with 1.2 equivalent of **4.12** was performed. Although the reaction was sluggish with 10 mol % of $B(C_6F_5)_3$ (Table 4.1, entry 2), or at room temperature (Table 4.1, entry 3), full conversion was observed at 95 °C after 36 h with 15 mol % of the catalyst in a sealed NMR tube. Besides, only 14% of **4.14a** was obtained in the absence of the catalyst. In addition to the reduced product **4.14a** as a major product, **4.15a** was isolated in 8% yield (Table 4.1, entry 4).

Table 4.1. $B(C_6F_5)_3$-catalyzed conjugate addition of ^{i}Pr-tricarbastannatrane to benzylidene 1,3-dimethylbarbituric acid



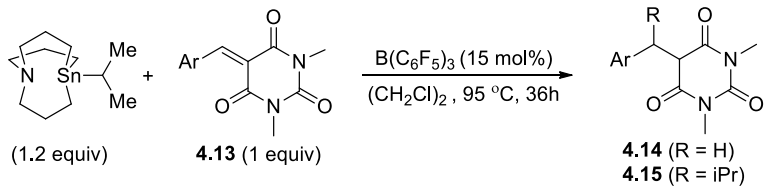
4.12 (1.2 equiv) **4.13a** (1 equiv) **4.14a** (R = H) **4.15a** (R = ^{i}Pr)

Entry	Equiv of $B(C_6F_5)_3$	T[°C] / t [h]	Yield of **4.14a**. [%][a]	Yield of **4.15a**[%][a]
1	0	95/72	14	n.d.
2	0.10	95/72	78	n.d.
3	0.15	25/72	43	n.d.
4	0.15	95/36	91	8

[a] Yield of isolated product.

The scope of the electrophile was then investigated under the optimized condition. As shown in Table 4.2, reduced products **4.14a**–**4.14m** were obtained in good to excellent yield (72–94%). Crude NMR of the reaction mixtures showed the presence of the alkylated adducts from the conjugate addition of isopropyl group to substrates **4.13a-4.13m**. The ratio of **4.14**:**4.15** was obtained by analysis the crude ^{1}H NMR spectra of the reactions mixtures. The alkylated byproducts **4.15a**–**4.15l** were isolated in 5–23% yield. Substrate **4.13m** was the exception, which yielded 73% of alkylated product **4.15m** as the major product, and **4.14** was obtained in 24% yield (Table 4.1, entry 13).

Table 4.2. $B(C_6F_5)_3$-Catalyzed conjugate addition of ^{i}Pr-tricarbastannatrane to benzylidene barbituric acids



(1.2 equiv) **4.13** (1 equiv)

4.14 (R = H)
4.15 (R = iPr)

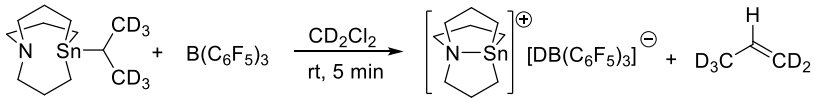
Entry	Ar	Ratio **4.14**:**4.15** [a]	Yield of **4.14** [%][b]	Yield of **4.15** [%][b]
1	C_6H_5 (**4.13a**)	92:8	91	8
2	4-(MeO)C_6H_4 (**4.13b**)	78:22	72	21
3	4-ClC_6H_4 (**4.13c**)	86:14	83	14
4	3-FC_6H_4 (**4.13d**)	82:18	81	17
5	2-Naphthyl (**4.13e**)	88:12	86	11
6	4-(CN)C_6H_4 (**4.13f**)	88:12	84	14
7	3-[B($O_2C_6H_{12}$)]C_6H_4 (**4.13g**)	86:14	85	13
8	3-BrC_6H_4 (**4.13h**)	80:20	79	20
9	4-[B($O_2C_6H_{12}$)]C_6H_4 (**4.13i**)	82:18	82	14
10	4-BrC_6H_4 (**4.13j**)	77:23	74	23
11	3-(MeO)C_6H_4 (**4.13k**)	94:6	94	5
12	4-FC_6H_4 (**4.13l**)	89:11	88	10
13	4-(NO_2)C_6H_4 (**4.13m**)	23:77	24	73

[a] Determined by analysis of the ^{1}H NMR spectra of the crude reaction mixtures. [b] Yield of isolated product.

In an effort to gain mechanistic insight, equimolar mixtures of $B(C_6F_5)_3$ and ^{i}Pr-tricarbastannatrane-d_6 (**4.12-d$_6$**) in CD_2Cl_2 were studied by ^{1}H, ^{2}D, ^{11}B and ^{119}Sn NMR spectroscopy

at room temperature in a sealed NMR tube. The formation of D_2CCHCD_3 gas was confirmed by a broad singlet signal at δ = 5.82 ppm in ^{1}H NMR as well as two signals, one doublet at δ = 1.68 ppm and another multiplet at δ = 5.08–4.94, in the ^{2}HNMR. The complex $[N(CH_2CH_2CH_2)_3Sn][DB(C_6F_5)_3]$ (**4.16**) was detected by ^{119}Sn and ^{11}B NMR spectra showing signals at δ = 151.4 ppm and δ = –18.1 ppm, respectively (Scheme 4.16). In addition to NMR data, the formation of complex **4.16** was supported by HRMS (ESI) analysis, and the ion peak at m/z 513.99935 was attributed to $[DB(C_6F_5)_3]^-$.

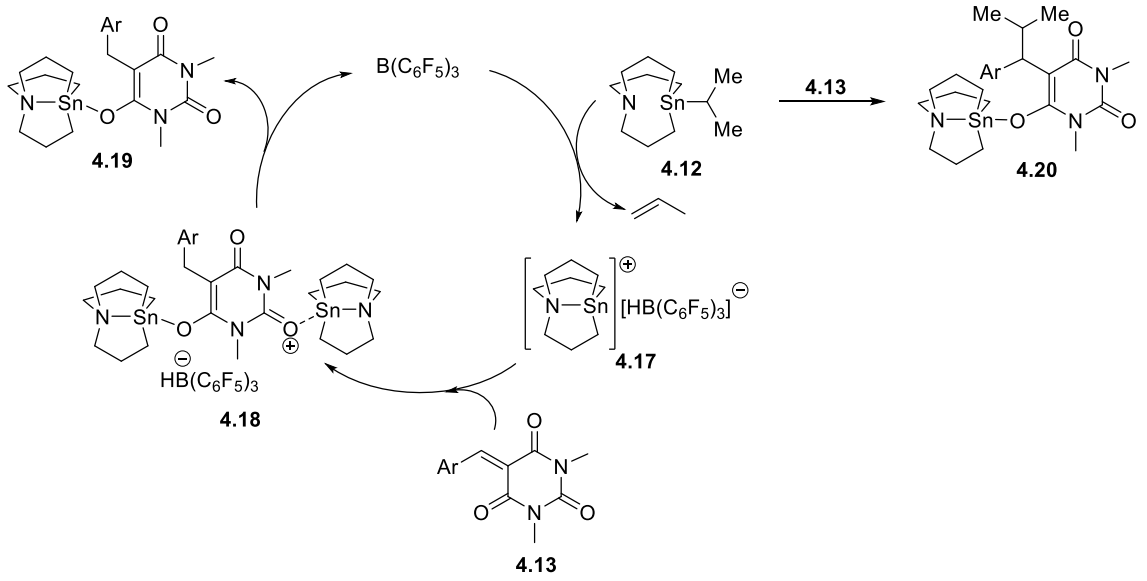
Scheme 4.16. Formation of $[N(CH_2CH_2CH_2)_3Sn][DB(C_6F_5)_3]$



4.12-d$_6$ **4.16**

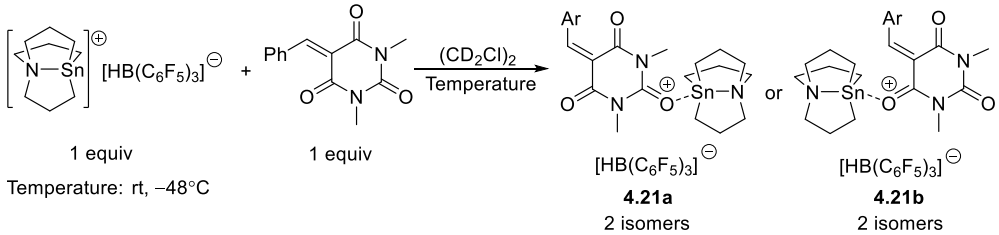
The reaction of one equivalent of complex **4.16** with one equivalent of benzylidene 1,3-dimethylbarbituric acid furnished the product **[D]-4.14a** in 88% yield. Therefore, $[DB(C_6F_5)_3]^-$ is likely the hydride source in this transformation. Based on the above result, we propose that the first step of the reduction is the formation of complex $[N(CH_2CH_2CH_2)_3Sn][HB(C_6F_5)_3]$ (**4.17**). Then, **4.13** is activated by coordination of its carbonyl groups to tricarbastannatrane cation to generate activated bis-stannatrane complexe **4.18**. The formation of this complex was confirmed by HRMS (ESI) spectra that showed an ion peak at m/z 765.18713 (Ar = Ph). Subsequently, hydride transfer from $[HB(C_6F_5)_3]^-$ reduces the benzylidene barbituric acid to regenerate $B(C_6F_5)_3$ and forms enolate **4.19** which can be protonated to generate the reduced product **4.14** (Scheme 4.17). Enolate **4.19** was detected by HRMS (ESI) analysis which showed an ion peak at *m/z* 506.14844 (Ar = Ph). Conjugated alkylated product **4.15** was proposed to be produced by protonation of enolate **4.20** which generated by direct isopropyl group addition from **4.12**. The formation of enolate **4.20** (A r = 4-ClC_6H_4) was supported by HRMS (ESI), showing an ion peak at *m/z* 579.14496 attributed to $C_{25}H_{36}N_3O_3Cl^{118}Sn$.

Scheme 4.17. Proposed mechanism



It was proposed that in addition to intermediate **4.18**, mono-stannatrane intermediates **4.21a** and **4.21b** could be reaction intermediates in the above transformations (Scheme 4.18). Therefore, ^{13}C NMR of 1:1 mixture of complex **4.17** and **4.13a** was carried out at room temperature and at –48 °C in CD_2Cl_2. The ^{13}C NMR spectrum of the mixture was compared with ^{13}C NMR spectrum of **4.13a**, and no change in chemical shift of **4.13a** was observed. HRMS (ESI) experiment was also carried out on the reaction mixture. None of these experiments supported the presence of mono-stannatrane intermediates in the reaction mixture.

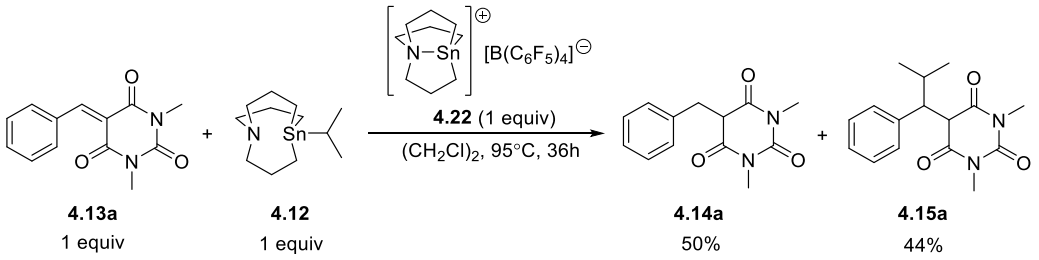
Scheme 4.18. NMR studies on mono-stannatrane intermediates



The role of Lewis acidic $[N(CH_2CH_2CH_2)_3Sn]^+$ in the activation of the benzylidene substrate was examined by the addition of complex $[N(CH_2CH_2CH_2)_3Sn][B(C_6F_5)_4]$ (**4.22**) to equimolar mixture of

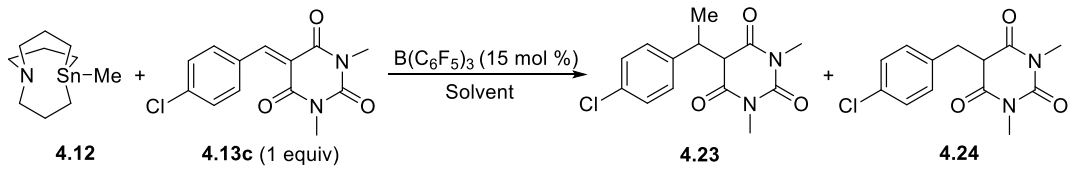
4.12 and **4.13a**. Compound **4.22** was generated by mixing one equivalent of trityl tetrakis(pentafluorophenyl)borate and methyl-tricarbastannatrane in 1,2-dicholoethane. The formation of complex **4.22** was supported by ^{119}Sn NMR spectra showing a signal at δ = 251.1 ppm. As demonstrated in Scheme 4.19, 50% of the reduced product **4.14a**, and 44% of product **4.15a** were obtained in the presence of complex **4.22**, with 5% of starting material **4.13a** was recovered in this transformation. This reaction showed that $[N(CH_2CH_2CH_2)_3Sn]^+$ catalyzed both reactions in more than 90% conversion. However, the selectivity of the reaction is rather poor with respect to the formation of reduced product **4.14a**. On the other hand, although $[N(CH_2CH_2CH_2)_3Sn]^+$ could activate the electrophile, in the absence of $B(C_6F_5)_3$, hydride was transferred from **4.12** directly to the olefin, applying $B(C_6F_5)_3$ as a Lewis acid improved the yield of **4.14a** (Table 4.2, entry 1). The ability of **4.12** to deliver either a hydride or isopropyl is unselective. As previously mentioned, the reaction between $B(C_6F_5)_3$ and **4.12** generates Lewis acidic $[N(CH_2CH_2CH_2)_3Sn]^+$ and hydride source $[HB(C_6F_5)_3]^-$ simultaneously, thus increasing the selectivity of the conjugate addition towards the formation of the desired product.

Scheme 4.19. $[N(CH_2CH_2CH_2)_3Sn]^+$ as a Lewis acid



Moreover, an effort was made to expand the nucleophile scope to the synthesis of methylated adducts using methyl-tricarbastannatrane. Initial attempt with 4-chlorobenzylidene 1,3-dimethylbarbituric acid (**4.13c**) in 1,2-dichloroethane yielded a low conversion, and 26% of the methylated adducts was obtained (Table 4.3, entry 1). Trying different solvents, such as trifluorotoluene, toluene and chlorobenzene, did not improve the yield significantly (Table 4.3, entries 2–4). Increasing the amount of methyl-tricarbastannatrane as well as the reaction concentration did not improve the yield considerably, and 43% of product **4.23** was obtained (Table 4.3, entry 5).

Table 4.3. $B(C_6F_5)_3$-catalyzed conjugate addition of methyl-tricarbastannatrane to 4-chlorobenzylidene 1,3-dimethylbarbituric acid



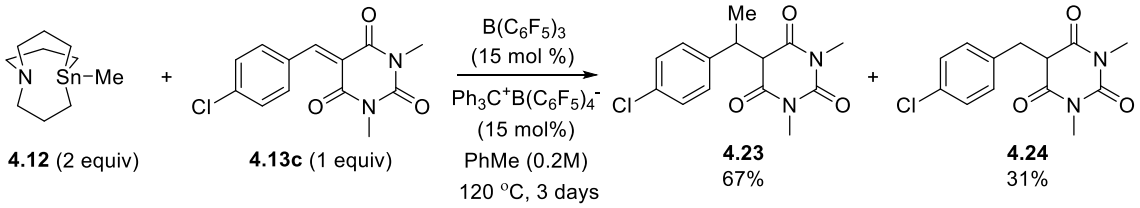
4.12 **4.13c** (1 equiv) **4.23** **4.24**

Entry	Equiv of Me-tricarabastannatrane	T[°C] /t [h]	Solvent	Yield of **4.23** [%][a]	Yield of **4.24** [%][b]
1	1.2	95/72	$(CH_2Cl)_2$	26	48
2	1.2	120/72	PhMe	27	29
3	1.2	120/72	$PhCF_3$	30	34
4	1.2	120/72	PhCl	17	49
5	2.0	120/72	PhMe	43	54

[a] Yield of isolated product. [b] Reactions were run at 0.1 M of **4.13c** exept entry 5, run at 0.2 M.

At this stage, it was postulated that the reaction might be best improved by increasing the loading of $[N(CH_2CH_2CH_2)_3Sn]^+$ to further activate electrophile **4.13c**. Thus, 15 mol % of salt **4.22** was added to the reaction as an extra source of Lewis acidic tricarbastannatrane cation. The yield of **4.23** increased to 67% as a result of applying this additive (Scheme 4.20). Of note, increasing the amount of **4.22** to 25% furnished **4.23** in 71% yield, and did not improve the result significantly.

Scheme 4.20. Methylation of 4-chlorobenzylidene 1,3-dimethylbarbituric acid



4.12 (2 equiv) **4.13c** (1 equiv) **4.23** 67% **4.24** 31%

4.4 Summary

In summary, we have developed the first $B(C_6F_5)_3$-catalyzed conjugate reduction of benzylidene derivatives of 1,3-dimethylbarbituric acid, using readily available ^{i}Pr-tricarbastannatrane. This new method distiguishes itself form the previous works in that ^{i}Pr-tricarbastannatrane serves as an in situ hydride source. The combination of ^{i}Pr-tricarbastannatrane and $B(C_6F_5)_3$ resulted in the formation of the intramolecularly stabilized organotin cation, $[HB(C_6F_5)_3]^-$, and propene gas, and the reduced adducts were obtained in good to excellent yield. In addition, isopropyl group transfer from ^{i}Pr-tricarbastannatrane furnished alkylated products as by-products. The mechanism of the reduction was investigated by NMR and HRMS techniques, and a bis-stannatrane intermediate was detected by HRMS (ESI). Deuterium-labeling experiments starting from ^{i}Pr-tricarbastannatrane-d_6 demonstrated that β-hydride transfer to $B(C_6F_5)_3$ generated $[DB(C_6F_5)_3]^-$ which could reduce the electrophile. Furthermore, methyl addition from methyl-tricarbastannatrane to 4-chlorobenzylidene 1,3-dimethylbarbituric acid under $B(C_6F_5)_3$-catalyzed condition yielded moderate amounts of the methylated adduct.

4.5 Experimental

4.5.1 General Considerations

All reactions were carried out in oven or flame-dried glassware under dry nitrogen atmosphere using standard Schlenk techniques or in a glove box. 1,2-Dichloroethane and CD_2Cl_2 were distilled over CaH_2 and then degassed via 3 freeze-pump-thaw cycles following distillation. Reactions were monitored by thin-layer chromatography on commercially prepared plates with a particle size of 60 Å. Developed plates were visualized under a UV lamp (254 nm), or stained with ceric ammonium molybdate. Flash chromatography was performed using 230-400 mesh silica gel.

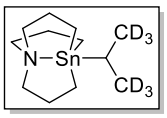
4.5.2 Characterization

Unless otherwise noted, ^{1}H and ^{13}C NMR spectra for all adduct products were obtained in $CDCl_3$ at 300 and 75 MHz, respectively. Chemical shifts are reported in parts per million (ppm, δ) relative to tetramethylsilane (TMS) as an external standard. Proton and carbon spectra were calibrated against the solvent residual peak [$CHCl_3$ (7.24 ppm) and $CDCl_3$ (77.0 ppm)], [CH_2Cl_2 (5.32 ppm) and CD_2Cl_2 (53.8 ppm)], and in case of 1,2-dichlorethane against known solvent resonance [^{1}H (3.72 ppm) and ^{13}C (43.6 ppm)]. ^{11}B and ^{119}Sn NMR spectra of tricarbastannatranes were recorded on Bruker Avance-

300 (^{11}B: 96 MHz, ^{119}Sn: 112 MHz) with ^{1}H decoupling in 1,2-dichloroethane calibrated against external BF_3•OEt_2 and Me_4Sn, respectively. The spectral references (sr) which were obtained from the external standards, were used to calibrate all ^{119}Sn NMR and ^{11}B NMR chemical shifts. Spectral reference values of –171.61 Hz and –5.13 Hz were used to calibrate ^{119}Sn and ^{11}B chemical shifts in 1,2-dichloroethane, respectively. Abbreviations used to define NMR spectral mutiplicities are as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High resolution mass spectra (ESI) were run at the University of Waterloo Mass Spectrometry facility. Fragment signals are given in mass per charge number (m/z).

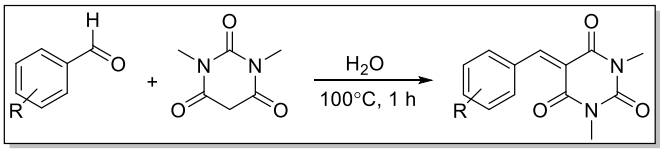
The following compounds were prepared according to literature procedures: 5-(*iso*-propyl)-1-aza-5-stannabicyclo[3.3.3]undecane,[13] 5-benzylidene-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**4.13a**),[76] 5-(4-methoxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**4.13b**),[77] 5-(4-chlorobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**4.13c**),[13] 1,3-dimethyl-5-(4-nitrobenzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**4.13m**),[78] 5-methyl-1-aza-5-stannabicyclo[3.3.3]undecane,[5] Other reagents were purchased from commercial suppliers and used without further purification.

5-(propan-2-yl-1,1,1,3,3,3-d_6)-1-aza-5-stannabicyclo[3.3.3]undecane (d_6-4.12)



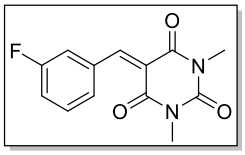
(Propan-2-yl-1,1,1,3,3,3-d_6)magnesium bromide reagent[79] (2 equiv.) was added dropwise to a suspension of 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (235 mg, 0.798 mmol) in anhydrous THF at -78°C. The resulting mixture was stirred at -78 °C for 3 h, allowed to warm to room temperature, and stirred overnight. The reaction mixture was poured into a separatory funnel containing a mixture of Et_2O and water. The layers were partitioned, and the organic layer was washed with brine, dried over $MgSO_4$, and filtered. Solvent was removed under reduced pressure to provide the crude product. A yellow oil (259 mg, 84 % yield) was isolated and was used without further purification; ^{1}H NMR ($CDCl_3$,300 MHz) δ 2.33 (t, J = 5.4 Hz, 6H), 1.62 (m, 6H), 1.45 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 54.7, 23.4, 16.8, 4.4; ^{2}H NMR ($CHCl_3$, 46 MHz) δ 1.00 (brd, J = 0.1 Hz). HRMS (+ESI) *m/z* calcd. for $C_{12}H_{19}{}^{2}H_6NSn$ $(M)^+$: 309.13801. Found: 309.15384.

General Experimental Procedure A - Synthesis of benzylidene 1,3-dimethylbarbituric acids (4.13d–4.13l)



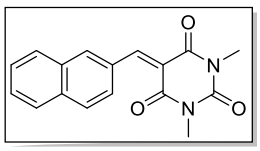
To a stirred solution of the 1,3-dimethylbarbituric acid (1.56 g, 10.0 mmol) in water (40 ml) was added the corresponding benzaldehyde (10.0 mmol) rapidly and all at once at ambient temperature. After refluxing for an hour, the solid produced was isolated by simple filtration and dried. The solid product **4.13b-4.13l** was used without further purification unless otherwise noted.

5-(3-Fluorobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.13d).



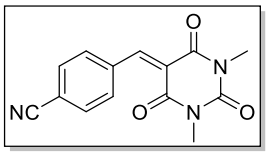
Prepared according to General Procedure A from 4-fluorobenzaldehyde (1.24 g, 10.0 mmol); reaction was purified by recrystallization from MeOH and isolated as a white solid (2.12 g, 81% yield); M.p. 143-145 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.49 (s, 1H), 7.89 (d, J = 10.2 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.41 (q, J = 5.7 Hz, 1H), 7.21 (td, J = 8.3, 2.7 Hz, 1H), 3.41 (s, 3H), 3.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.1, 162.0 (d, $J_{C\text{-}F}$ = 245.0 Hz), 160.0, 157.1 (d, $J_{C\text{-}F}$ = 2.3 Hz), 151.0, 134.5 (d, $J_{C\text{-}F}$ = 8.5 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 119.4 (d, $J_{C\text{-}F}$ = 5.7 Hz),) 119.3 (d, $J_{C\text{-}F}$ = 50.2 Hz), 118.6, 29.0, 28.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}O_3N_2F$ $(M+H)^+$: 263.08320; Found: 263.08249.

1,3-Dimethyl-5-(naphthalen-2-ylmethylene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.13e).



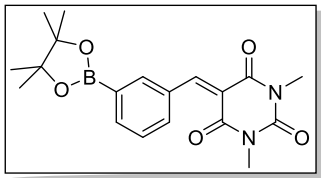
Prepared according to General Procedure A from 2-naphthaldehyde (1.56 g, 10.0 mmol); isolated as a pale yellow solid (2.56 g, 87% yield); M.p. 206-207 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.69 (s, 1H), 8.57 (s, 1H), 8.13 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.7 Hz, 2H), 3.41 (s, 3H), 3.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.6, 160.4, 159.2, 151.3, 136.4, 135.3, 132.5, 130.3, 129.6, 129.0, 128.7, 127.7, 127.6, 126.7, 117.2, 29.1, 28.4. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}N_2O_3$ $(M+H)^+$: 295.10827; Found: 295.10764.

4-((1,3-Dimethyl-2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene)methyl)benzonitrile (4.13f).



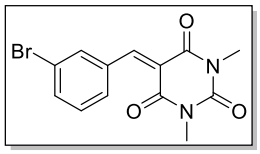
Prepared according to General Procedure A from 4-formylbenzonitrile (1.31 g, 10.0 mmol); isolated as a white solid (2.40 g, 89% yield). M.p. 185-186 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.50 (s, 1H), 7.91 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 3.41 (s, 3H), 3.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.5, 159.8, 155.8, 150.9, 137.1, 132.0, 131.7, 120.3, 118.1, 114.8, 29.2, 28.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{11}O_3N_3$ $(M+H)^+$: 270.08787; Found: 270.08701.

1,3-Dimethyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.13g).



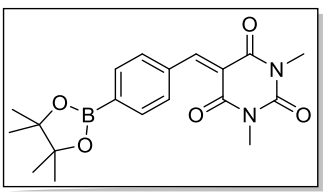
Prepared according to General Procedure A from 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2.32 g, 10.0 mmol); isolated as a white solid (2.36 g, 64% yield); M.p. 189-190 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.59 (s, 1H), 8.34 (d, J = 8.1 Hz,1H), 8.19 (s, 1H), 7.92 (d, J = 7.2 Hz,1H), 7.45 (t, J = 7.8 Hz, 1H), 3.39 (s, 3H), 3.34 (s, 3H) ,1.33 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.4, 160.3, 159.5, 151.3, 140.5, 139.1, 135.0, 132.2, 127.6, 117.5, 84.1, 29.0, 28.4, 24.9. HRMS (ESI) *m/z* calcd for $C_{19}H_{24}O_5N_2B$ $(M+H)^+$: 371.17783. Found: 371.17722.

5-(3-Bromobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.13h).



Prepared according to General Procedure A from 3-bromobenzaldehyde (1.85 g, 10.0 mmol); Recrystallized from MeOH and isolated as a white solid (2.77 g, 86% yield); M.p. 151-153 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.44 (s, 1H), 8.16 (s, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 3.40 (s, 3H), 3.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.0, 160.0, 157.0, 151.0, 135.2, 135.2, 134.5, 131.4, 129.6, 122.2, 118.8, 29.1, 28.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}O_3N_2Br$ $(M+H)^+$: 323.00313; Found: 323.00320.

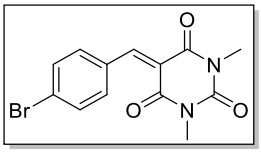
1,3-Dimethyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.13i).



Prepared according to General Procedure A from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2.32 g, 10.0

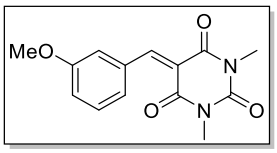
mmol); Isolated as a white solid (1.96 g, 53% yield); M.p. 195-197 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.55 (s, 1H), 7.92 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 3.40 (s, 3H), 3.34 (s, 3H), 1.33 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 160.1, 159.1, 151.2, 135.1, 134.3, 131.7, 118.2, 84.1, 29.0, 28.4, 24.8. HRMS (ESI) *m/z* calcd for $C_{19}H_{24}O_5N_2B$ $(M+H)^+$: 371.17783. Found: 371.17685.

5-(4-Bromobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.13j).



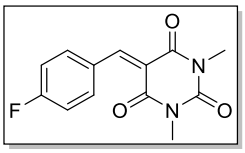
Prepared according to General Procedure A from 4-bromobenzaldehyde (1.85 g, 10.0 mmol); Isolated as a white solid (2.77 g, 86% yield); M.p. 175-176 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.43 (s, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 3.38 (s, 3H), 3.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.2, 160.3, 157.5, 151.1, 134.8, 131.6, 131.4, 128.0, 117.9, 29.1, 28.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}O_3N_2Br$ $(M+H)^+$: 323.00313; Found: 323.00311.

5-(3-Methoxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.13k).



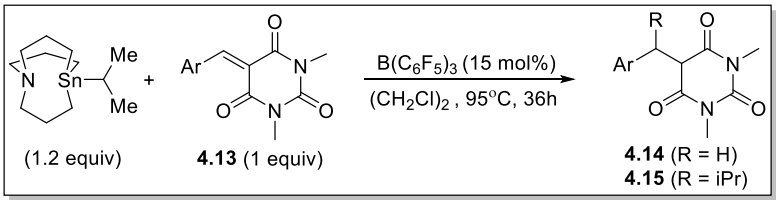
Prepared according to General Procedure A from 3-methoxybenzaldehdye (1.36 mg, 10.0 mmol); isolated as a yellow solid (2.47 g, 90% yield); M.p. 139-141 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.52 (s, 1H), 7.76 (s, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.06 (dd, J = 8.3, 2.7 Hz, 1H), 3.84 (s, 3H), 3.40 (s, 3H), 3.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.5, 160.3, 159.2, 159.1, 151.2, 133.8, 129.2, 126.6, 119.4, 117.7, 117.6, 55.4, 29.1, 28.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{15}O_4N_2$ $(M+H)^+$: 275.10318; Found: 275.10260.

5-(4-Fluorobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.13l).



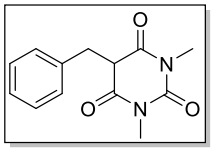
Prepared according to General Procedure A from 4-fluorobenzaldehyde (1.24 g, 10.0 mmol); isolated as a pale yellow solid (2.04 g, 78% yield). M.p. 169-171°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.50 (s, 1H), 8.20-8.15 (m, 2H), 7.16-7.09 (m, 2H), 3.40 (s, 3H), 3.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.3 (d, $J_{C\text{-}F}$ = 256.0 Hz), 162.4, 160.4, 157.7, 151.1, 136.7 (d, $J_{C\text{-}F}$ = 9.3 Hz), 128.8 (d, $J_{C\text{-}F}$ = 3.1 Hz), 116.9, 115.5 (d, $J_{C\text{-}F}$ = 21.6 Hz), 29.0, 28.3. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}O_3N_2F$ $(M+H)^+$: 263.08320; Found: 263.08237.

General Experimental Procedure B - Synthesis of Compounds 4.14 and 4.15



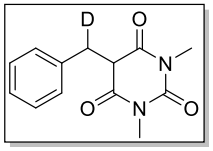
In a J. Young NMR tube, benzylidene 1,3-dimethylbarbituric acid (0.100 mmol) was added to a solution of 5-isopropyl-1-aza-5-stannabicyclo[3.3.3]undecane (36.2 mg, 0.120 mmol) and tris(pentafluorophenyl)borane (8.0 mg, 0.015 mmol) in 1 mL of 1,2-dichloroethane and the mixture was put in a preheated oil bath at 95°C for 36 h. All volatiles were evaporated under vacuum and the product was purified by flash chromatography (EtOAc:pentane) on silica gel. In these reactions, compounds **4.15a-l** were isolated as byproducts.

5-Benzylidene-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14a).



Prepared according to General Procedure B from **4.13a** (24.4 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:5 to 1:4) and isolated as a white solid (22.4 mg, 91% yield); M.p. 115-116 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23-7.21 (m, 3H), 7.03-6.99 (m, 2H), 3.75 (t, J = 4.8 Hz, 1H), 3.45 (d, J = 4.5 Hz, 2H), 3.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.3, 151.0, 135.1, 128.8, 128.6, 127.8, 50.7, 37.9, 28.2. HRMS (ESI) *m/z* calcd for $C_{13}H_{15}O_3N_2$ $(M+H)^+$: 247.10827; Found: 247.10773; 1,3-Dimethyl-5-(2-methyl-1-phenylpropyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15a)**: Isolated as a white solid (2.3 mg, 8% yield); M.p. 88-89 °C; ^{1}H NMR (CDCl3, 300 MHz) δ 7.22-7.19 (m, 3H), 6.91-6.88 (m, 2H), 3.91 (d, J = 3.6 Hz, 1H), 3.06 (s, 3H), 3.00 (dd, J = 11.3, 3.6 Hz, 2H), 2.94 (s, 3H), 2.53-2.41 (m, 1H), 1.31 (d, J = 6.6 Hz, 3H), 0.72 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.5, 167.3, 150.9, 138.0, 128.4, 128.1, 127.6, 59.3, 52.0, 28.6, 28.0, 27.8, 21.5, 21.3. HRMS (ESI) *m/z* calcd for $C_{16}H_{21}O_3N_2$ $(M+H)^+$: 289.15522; Found: 289.15463.

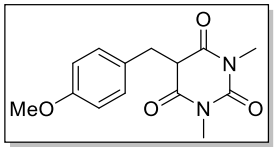
1,3-Dimethyl-5-(phenylmethyl-*d*)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione ([D]-4.14a).



In a vial, **4.13a** (24.4 mg, 0.100 mmol) was added to a solution of 5-(propan-2-yl-1,1,1,3,3,3-d_6)-1-aza-5-stannabicyclo[3.3.3]undecane (30.1 mg, 0.100 mmol)

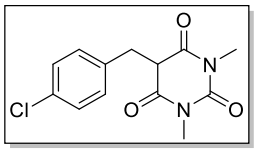
and tris(pentafluorophenyl)borane (51.1 mg, 0.100 mmol) in 1,2-dichloroethane (1 ml). After stirring for 24 h at room temperature, all volatiles were removed and the reaction was purified eluting with EtOAc:pentane (1:4) and the product was isolated as a white solid (21.8 mg, 88% yield); M.p. 115-116 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23-7.20 (m, 3H), 7.02-6.99 (m, 2H), 3.75 (m, 1H), 3.44 (d, J = 4.5 Hz, 1H), 3.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.3, 151.0, 135.1, 135.1, 128.8, 128.6, 127.8, 50.7, 50.6, 37.9, 28.2. ^{2}H NMR ($CHCl_3$, 46 MHz) δ 3.45. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}{}^{2}HO_3N_2$ $(M+H)^+$: 248.11400; Found: 248.11369.

5-(4-Methoxybenzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14b).



Prepared according to General Procedure B from **4.13b** (27.4 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a white solid (19.9 mg, 72% yield); M.p. 88-89 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.93 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 3.74-3.70 (m, 4H), 3.39 (d, J = 4.5 Hz, 2H), 3.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.4, 159.1, 151.0, 130.0, 127.0, 113.9, 55.2, 50.9, 37.1, 28.2. HRMS (ESI) *m/z* calcd for $C_{14}H_{17}O_4N_2$ $(M+H)^+$: 277.11883; Found: 277.11841; 5-(1-(4-Methoxyphenyl)-2-methylpropyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15b)**: Isolated as a colorless oil (6.7 mg, 21% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.82 (dt, J = 8.7, 2.7 Hz, 2H), 6.73 (dt, J = 9.0, 2.7 Hz, 2H), 3.88 (d, J = 3.6 Hz, 2H), 3.74 (s, 3H), 3.07 (s, 3H), 2.99-2.94 (m, 4H), 2.48-2.35 (m, 1H), 1.29 (d, J = 6.3 Hz, 3H), 0.70 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.7, 167.4, 159.2, 150.9, 129.9, 128.6, 113.8, 58.4, 55.2, 52.0, 28.8, 28.0, 27.9, 21.5, 21.4. HRMS (ESI) *m/z* calcd for $C_{17}H_{23}O_4N_2$ $(M+H)^+$: 319.16578; Found: 319.16525.

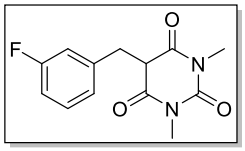
5-(4-Chlorobenzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14c).[80]



Prepared according to General Procedure B from **4.13c** (27.9 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a white solid (23.3 mg, 83% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 3.74 (t, J = 4.8 Hz, 1H), 3.44 (d, J = 4.8 Hz, 2H), 3.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8, 150.9, 134.0, 133.7, 130.4, 128.8, 50.4, 36.0, 28.3; 5-(1-(4-Chlorophenyl)-2-methylpropyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15c)**: Isolated as a colorless oil (4.5 mg, 14% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19 (d, J = 8.1 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.89 (d, J = 3.6 Hz, 1H), 3.08-2.99 (m,

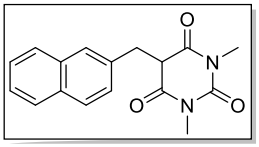
4H), 2.51-2.38 (m, 1H), 1.28 (d, J = 6.3 Hz, 3H), 0.69 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.2, 167.0, 150.7, 136.8, 133.8, 129.0, 128.7, 58.0, 51.6, 28.8, 28.1, 27.9, 21.4, 21.3. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}O_3N_2Cl$ $(M+H)^+$: 323.11625; Found: 323.11572.

5-(3-Fluorobenzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14d).



Prepared according to General Procedure B from **4.13d** (26.2 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a white solid (21.4 mg, 81% yield); M.p. 100-102 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.17 (q, J = 6.6 Hz, 1H), 6.89 (t, J = 8.4 Hz, 1H), 6.82-6.74 (m, 2H), 3.74 (t, J = 4.5 Hz, 1H), 3.43 (d, J = 4.8 Hz, 2H), 3.13 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8, 162.6 (d, $J_{C\text{-}F}$ = 245.4 Hz), 150.9, 137.9 (d, $J_{C\text{-}F}$ = 7.4 Hz), 130.1 (d, $J_{C\text{-}F}$ = 8.3 Hz), 124.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.5 Hz), 114.6 (d, $J_{C\text{-}F}$ = 20.8 Hz), 50.3, 36.5, 36.4, 28.2. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_3N_2F$ $(M+H)^+$: 265.09885; Found: 265.09818; 5-(1-(3-Fluorophenyl)-2-methylpropyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15d)**: Isolated as a white solid (5.2 mg, 17% yield); M.p. 68-70 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19 (q, J = 6.0 Hz, 1H), 6.92 (td, J = 8.4, 2.4 Hz, 1H), 6.72-6.64 (m, 2H), 3.89 (d, J = 3.6 Hz, 3H), 3.10-2.99 (m, 4H), 2.51-2.38 (m, 1H), 1.30 (d, J = 6.3 Hz, 3H), 0.73 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.1(d, $J_{C\text{-}F}$ = 163.6 Hz), 162.8 (d, $J_{C\text{-}F}$ = 245.9 Hz), 150.8, 140.9 (d, $J_{C\text{-}F}$ = 6.8 Hz), 130.0 (d, $J_{C\text{-}F}$ = 8.3 Hz), 123.4 (d, $J_{C\text{-}F}$ = 2.7 Hz), 115.1, 114.9, 114.5 (d, $J_{C\text{-}F}$ = 21.5 Hz), 58.5, 51.6, 28.7, 28.1, 27.9, 21.4, 21.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}O_3N_2F$ $(M+H)^+$: 307.14580; Found: 307.14545.

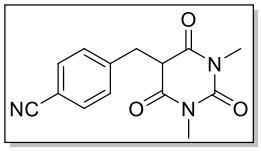
1,3-Dimethyl-5-(naphthalen-2-ylmethyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14e).



Prepared according to General Procedure B from **4.13e** (29.4 g, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:pentane (1:5) and isolated as a yellow solid (25.5 mg, 86% yield); M.p. 126-128 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78-7.69 (m, 3H), 7.52 (s, 1H), 7.45-7.42 (m, 2H), 7.13 (d, J = 8.4 Hz, 1H), 3.83 (t, J = 4.8 Hz, 1H), 3.62 (d, J = 4.8 Hz, 1H), 3.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.2, 150.5, 133.3, 132.7, 132.6, 128.3, 127.9, 127.7, 127.5, 126.7, 126.4, 126.1, 50.7, 37.6, 28.2. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}O_3N_2$ $(M+H)^+$: 279.12392; Found: 279.12296; 1,3-Dimethyl-5-(2-methyl-1-(naphthalen-2-yl)propyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15e)**: Isolated as a yellow oil (3.7 mg, 11% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.77-7.69 (m, 3H), 7.45-7.40 (m, 3H), 7.02 (d, J = 8.4 Hz, 1H), 3.98 (d, J = 3.6 Hz, 1H),

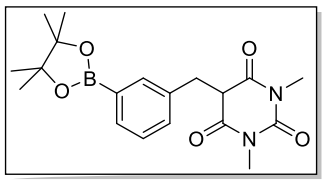
3.20 (dd, J = 11.1, 3.6 Hz, 1H), 3.05 (s, 3H), 2.85 (s, 3H), 2.67-2.55 (m, 1H), 1.36 (d, J = 6.3 Hz, 3H), 0.74 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.5, 167.3, 150.7, 135.5, 133.2, 132.8, 128.2, 127.7, 127.5, 127.1, 126.5, 126.2, 124.8, 59.2, 52.0, 28.7, 28.0, 27.9, 21.6, 21.4. HRMS (ESI) *m/z* calcd for $C_{20}H_{23}O_3N_2$ $(M+H)^+$: 339.17087; Found: 339.17111.

4-((1,3-Dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)methyl)benzonitrile (4.14f).[81]



Prepared according to General Procedure B from **4.13f** (26.9 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a colorless oil (22.8 mg, 84% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 3.79 (t, J = 4.8 Hz, 1H), 3.52 (d, J = 4.8 Hz, 2H), 3.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.3, 150.8, 141.6, 132.3, 130.1, 118.4, 111.6, 50.1, 35.3, 28.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{14}O_3N_3$ $(M+H)^+$: 272.10297; Found: 272.10278; 4-(1-(1,3-Dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)-2-Methylpropyl)benzonitrile **(4.15f)**: Isolated as a colorless oil (4.4 mg, 14% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 3.92 (d, J = 3.6 Hz, 1H), 3.17-3.10 (m, 4H), 3.00 (s, 3H), 2.59-2.45 (m, 1H), 1.29 (d, J = 6.6 Hz, 2H), 0.69 (d, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.6, 166.6, 150.5, 144.2, 132.3, 128.7, 118.2, 112.1, 58.0, 51.3, 28.7, 28.2, 28.0, 21.4, 21.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{20}O_3N_3$ $(M+H)^+$: 314.15047; Found: 314.15012.

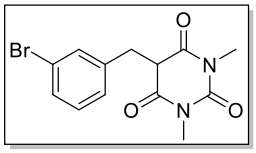
1,3-Dimethyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14g).



Prepared according to General Procedure B from **4.13g** (37.0 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a white solid (31.6 mg, 85% yield); M.p. 142-144 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) 7.65 (d, J = 7.2 Hz, 1H), 7.43 (s, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 3.75 (t, J = 4.5 Hz, 1H), 3.43 (d, J = 4.5 Hz, 1H), 3.08 (s, 6H), 1.30 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.4, 150.9, 134.8, 134.2, 131.7, 127.9, 83.9, 50.8, 38.5, 28.5, 24.8. HRMS (ESI) *m/z* calcd for $C_{19}H_{26}O_5N_2B$ $(M+H)^+$: 373.19348. Found: 373.19266; 1,3-Dimethyl-5-(2-methyl-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15g)**: Isolated as a white solid (5.4 mg, 13% yield); M.p. 161-163 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) 7.64 (d, J = 7.5 Hz, 1H), 7.32 (s, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 3.90 (d, J = 3.6 Hz, 1H), 3.06 (s, 3H),

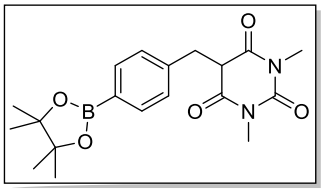
3.01 (dd, J = 19.1, 3.9 Hz, 1H), 2.89 (s, 3H), 2.54-2.41 (m, 1H), 1.33-1.30 (m, 15H), 0.72 (d, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.6, 167.3, 150.8, 137.1, 134.5, 133.5, 130.9, 127.7, 83.9, 59.5, 52.1, 28.5, 27.9, 27.8, 24.9, 24.8, 21.7, 21.3. HRMS (ESI) *m/z* calcd for $C_{22}H_{32}O_5N_2B$ $(M+H)^+$: 415.24043. Found: 415.24023.

5-(3-Bromobenzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14h).



Prepared according to General Procedure B from **4.13h** (32.3 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a white solid (25.7 mg, 79% yield); M.p. 84-86 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36 (d, J = 7.8 Hz, 1H), 7.22 (s, 1H), 7.09 (t, J = 7.8 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 3.74 (t, J = 4.8 Hz, 1H), 3.41 (d, J = 4.8 Hz, 2H), 3.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8, 150.9, 137.7, 132.0, 130.9, 127.6, 122.6, 50.4, 36.6, 28.3. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_3N_2Br$ $(M+H)^+$: 325.01878; Found: 325.01837; 5-(1-(3-Bromophenyl)-2-methylpropyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15h)**: Isolated as a white solid (7.3 mg, 20% yield); M.p. 121-124 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36 (d, J = 8.7 Hz, 1H), 7.12-7.07 (m, 2H), 6.85 (d, J = 7.8 Hz, 1H), 3.90 (d, J = 3.9 Hz, 1H), 3.11 (s, 3H), 3.01-2.96 (m, 4H), 2.50-2.38 (m, 1H), 1.30 (d, J = 6.3 Hz, 3H), 0.73 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.2, 167.0, 150.8, 140.6, 131.2, 130.7, 130.0, 126.4, 122.7, 58.6, 51.7, 28.6, 28.1, 27.9, 21.5, 21.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}O_3N_2Br$ $(M+H)^+$: 367.06573; Found: 367.06549.

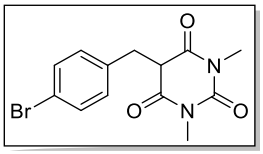
1,3-Dimethyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14i).



Prepared according to General Procedure B from **4.13i** (37.0 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:6 to 1:4) and isolated as a white solid (30.5 mg, 82% yield); M.p. 131-133 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 3.76 (t, J = 4.8 Hz, 1H), 3.46 (d, J = 4.8 Hz, 2H), 3.12 (s, 6H), 1.32 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.2, 150.9, 138.3, 135.1, 128.3, 83.9, 50.5, 37.7, 28.2, 24.9. HRMS (ESI) *m/z* calcd for $C_{19}H_{26}O_5N_2B$ $(M+H)^+$: 373.19348. Found: 373.19247; 1,3-Dimethyl-5-(2-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl) pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15i)**: Isolated as a colorless oil (5.8 mg, 14% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.5 Hz, 2H), 3.91 (d, J = 3.6 Hz, 1H), 3.08-2.96 (m,

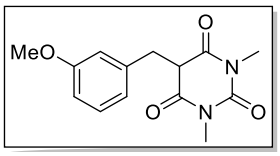
7H), 2.55-2.43 (m, 1H), 1.32-1.29 (m, 15H), 0.67 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.4, 167.3, 150.8, 141.3, 135.0, 127.1, 83.9, 59.1, 51.7, 28.7, 28.1, 27.9, 24.9, 21.5, 21.3. HRMS (ESI) *m/z* calcd for $C_{22}H_{32}O_5N_2B$ $(M+H)^+$: 415.24043. Found: 415.23969.

5-(4-bromobenzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14j).



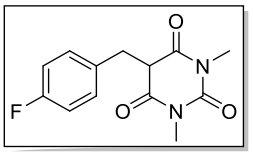
Prepared according to General Procedure B from **4.13j** (32.3 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a white solid (24.1 mg, 74% yield); M.p. 85-87 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.1 Hz, 2H), 3.74 (t, J = 4.8 Hz, 1H), 3.42 (d, J = 4.5 Hz, 2H), 3.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8, 150.9, 134.6, 131.8, 130.8, 121.8, 50.3, 36.0, 28.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_3N_2Br$ $(M+H)^+$: 325.01878. Found: 325.01831; 5-(1-(4-Bromophenyl)-2-methylpropyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15j)**: Isolated as a colorless oil (8.4 mg, 23% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.1 Hz, 2H), 3.89 (d, J = 3.6 Hz, 2H), 3.09 (s, 3H), 3.04-3.00 (m, 4H), 2.51-2.39 (m, 1H), 1.28 (d, J = 6.3 Hz, 3H), 0.69 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.1, 167.0, 150.7, 137.4, 131.7, 129.4, 121.9, 58.0, 51.5, 28.8, 28.1, 27.9, 21.4, 21.3. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}O_3N_2Br$ $(M+H)^+$: 367.06573. Found: 367.06542.

5-(3-Methoxybenzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14k).



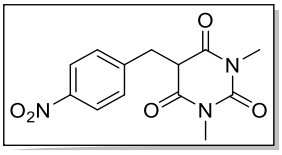
Prepared according to General Procedure B from **4.13k** (27.4 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a pale yellow solid (26.0 mg, 94% yield); M.p. 64-66 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13 (t, J = 7.8 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 6.60-6.56 (m, 2H), 3.76-3.72 (m, 4H), 3.42 (d, J = 4.8 Hz, 2H), 3.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.2, 159.7, 151.0, 136.6, 129.6, 121.1, 114.4, 113.3, 55.1, 50.6, 37.7, 28.2. HRMS (ESI) *m/z* calcd for $C_{14}H_{17}O_4N_2$ $(M+H)^+$: 277.11883. Found: 277.11789; 5-(1-(3-Methoxyphenyl)-2-methylpropyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15k)**: Isolated as a white solid (1.6 mg, 5% yield); M.p. 100-102 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12 (t, J = 7.8 Hz, 1H), 6.74 (dd, J = 8.4, 2.4 Hz, 1H), 6.50-6.47 (m, 2H), 3.89 (d, J = 3.6 Hz, 2H), 3.72 (s, 3H), 3.08 (s, 3H), 3.00-3.95 (m, 4H), 2.50-2.38 (m, 1H), 1.30 (d, J = 6.3 Hz, 3H), 0.74 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.5, 167.3, 159.8, 139.6, 129.4, 119.8, 113.7, 113.0, 59.1, 55.2, 51.9, 28.6, 28.0, 27.9, 21.5, 21.3. HRMS (ESI) *m/z* calcd for $C_{17}H_{23}O_4N_2$ $(M+H)^+$: 319.16578. Found: 319.16437.

5-(4-Fluorobenzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14l).



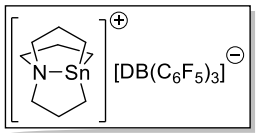
Prepared according to General Procedure B from **4.13l** (26.2 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a white solid (23.3 mg, 88% yield); M.p. 59-61 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.03-6.87 (m, 4H), 3.73 (t, J = 4.8 Hz, 1H), 3.43 (d, J = 4.8 Hz, 2H), 3.13 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.0, 162.6 (d, $J_{C\text{-}F}$ = 245.3 Hz), 150.9, 131.1, 130.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.2 Hz), 50.6, 36.3, 28.3. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_3N_2F$ $(M+H)^+$: 265.09885. Found: 265.09769; 5-(1-(4-Fluorophenyl)-2-methylpropyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15l)**: Isolated as a colorless oil (3.1 mg, 10% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.95-6.86 (m, 4H), 3.90 (d, J = 3.6 Hz, 1H), 3.09 (s, 3H), 3.05-2.99 (m, 4H), 2.50-2.38 (m, 1H), 1.30 (d, J = 6.3 Hz, 3H), 0.70 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.3, 167.1, 162.2 (d, $J_{C\text{-}F}$ = 246.0 Hz), 150.8, 133.9 (d, $J_{C\text{-}F}$ = 3.8 Hz), 129.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.1 Hz), 58.1, 51.8, 28.9, 28.1, 27.9, 21.4, 21.3. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}O_3N_2F$ $(M+H)^+$: 307.14580. Found: 307.14517.

1,3-Dimethyl-5-(4-nitrobenzyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4.14m).[82]



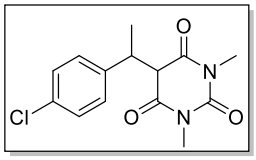
Prepared according to General Procedure B from **4.13m** (28.9 mg, 0.100 mmol); reaction was purified eluting with EtOAc:pentane (1:4) and isolated as a white solid (7.0 mg, 24% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 3.82 (t, J = 4.8 Hz, 1H), 3.58 (d, J = 5.1 Hz, 2H), 3.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.2, 150.5, 147.4, 143.9, 130.3, 123.7, 50.0, 34.7, 28.5. 1,3-Dimethyl-5-(2-methyl-1-(4-nitrophenyl)propyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(4.15m)**: Isolated as a pale yellow oil (24.3 mg, 76% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 3.94 (d, J = 3.3 Hz, 1H), 3.25 (d, J = 3.3 Hz, 1H), 3.21 (d, J = 3.3 Hz, 1H), 3.12 (s, 3H), 3.02 (s, 3H), 2.51 (m, 1H), 1.30 (d, J = 6.3 Hz, 3H), 0.70 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.5, 166.6, 150.5, 147.5, 146.4, 128.9, 123.7, 57.6, 51.2, 28.9, 28.3, 28.1, 21.4, 21.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}O_5N_3$ $(M+H)^+$: 334.13975. Found: 334.13864.

$[N(CH_2CH_2CH_2)_3Sn][DB(C_6F_5)_3]$ (4.16).



To a solution of 5-(propan-2-yl-1,1,1,3,3,3-d_6)-1-aza-5-stannabicyclo[3.3.3]undecane (30.1 mg, 0.100 mmol) in CD_2Cl_2 (1 ml) in a vial, was added tris(pentafluorophenyl)borane (51.1 mg, 0.100 mmol). After stirring for 2 min, the solution was transferred to a J. Young NMR tube; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 2.66 (m, 6H, NC*H*2), 2.04 (m, 6H, C*H*2), 1.45 (t, J = 6.6, 6H, SnC*H*2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 56.5 (N*C*H2), 25.2 (*C*H2), 15.4 (Sn*C*H2); ^{119}Sn NMR (CD_2Cl_2, 112 MHz) δ 151.4; ^{11}B NMR ($CDCl_3$, 96 MHz) δ –18.1. HRMS (–ESI) *m/z* calcd. for $C_{18}{}^2HBF_{15}$ (M^-): 512.99891. Found: 513.99935; (+ESI) *m/z* calcd. for $C_9H_{18}NSn$ (M^+): 260.04557. Found: 260.04538.

5-(1-(4-Chlorophenyl)ethyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3H,5*H*)-trione (4.23).



5-(4-chlorobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (27.9 mg, 0.100 mmol) was added to a solution of 5-methyl-1-aza-5-stannabicyclo[3.3.3]undecane (54.8 mg, 0.200 mmol), tris(pentafluorophenyl)borane (8.0 mg, 0.015 mmol) and trityl tetrakis(pentafluorophenyl)borate (13.8 mg, 0.015 mmol) in 0.5 mL of toluene and the mixture was put in a preheated oil bath at 120 °C for 72 h. All volatiles were evaporated under vacuum and the product was purified by flash chromatography using EtOAc:pentane (1:4) on silica gel; the product was isolated as a colorless oil (19.7 mg, 67% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 3.74-3.65 (m, 1H), 3.56 (d, J = 3.9 Hz, 1H), 3.07 (s, 3H), 3.05 (s, 3H), 1.58 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.6, 166.9, 150.9, 137.9, 133.9, 128.6, 128.3, 55.8, 44.1, 28.1, 28.0, 18.4. HRMS (+ESI) *m/z* calcd. for $C_{14}H_{16}O_3N_2Cl$ $(M+H)^+$: 295.08440. Found: 295.08481.

Chapter 5

Conjugate Allylation of Activated Olefins Using Allyl-tricarbastannatrane

Conjugate allylations of α,β-unsaturated carbonyl compounds can generate products containing synthetically useful olefin and carbonyl functional groups. The electrophilicity of benzylidene Meldrum's acids and benzylidene 1,3-dimethyl barbituric acids was combined with the high reactivity of allyl-tricarbastannatrane for development of a mild conjugate allylation reaction. This chapter describes the carbon–carbon bond formation by the conjugate addition of apical allyl group of allyl-tricarbastanntrane to activated olefins to provide the allylated products in excellent yields. It is also shown that functionalized all-carbon quaternary stereocentres can be generated by this process.

5.1 Nucleophilic allylation

The mild and efficient construction of carbon–carbon σ bond via conjugate addition reactions presents an ongoing challenge in organic synthesis. Of all the organic groups that can be introduced into a molecule, the allyl group is one of the most versatile. The double bond of the allyl group can participate in a number of synthetically useful transformations, such as epoxidation, hydroboration, ozonolysis, olefin methathesis, etc. (Figure 5.1).

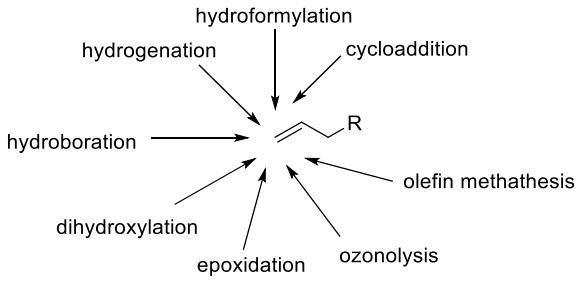
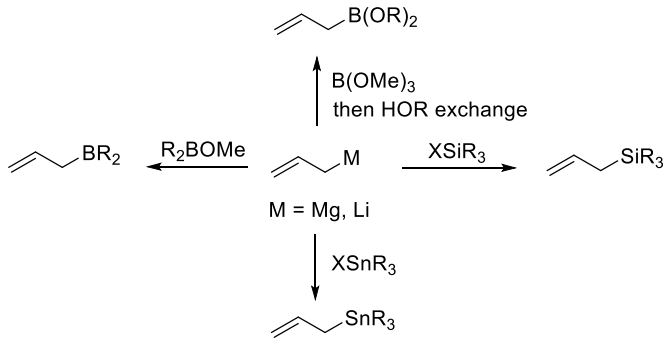


Figure 5.1. Transformation of the allyl group

A major challenge in conjugate allylations is the competition between 1,2-addition and 1,4-addition. The outcome of the reaction often depends on the combination of a nucleophile and an electrophile. To form the desired 1,4-addition products, organomagnesium, organocopper and organozinc reagents were previously utilized in conjugate additions. Although these reagents are

useful, they are often too basic and reactive to be used in a selective manner. The reactivity of these conventional reagents can be reduced by changing the metal to silicon, boron and tin (Scheme 5.1).[83]

Scheme 5.1. Formation of allylsilane, allylborane and allylstannane reagents

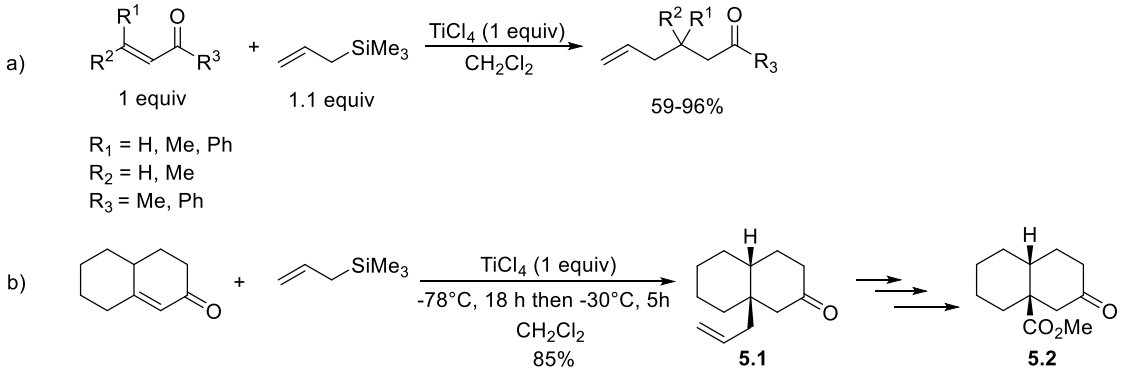


The conjugate allylation of α,β-enones is a fundamentally important transformation, since it generates a new carbon–carbon bond. Moreover, the allylated product contains synthetically useful olefin and carbonyl functional groups. Nevertheless, such reactions with nucleophilic allyl reagents have remained relatively underdeveloped, and a few examples of conjugate addition of allyl metal reagents have been reported. These additions can be done selectively to α,β-unsaturated carbonyl compounds using stoichiometric amount of organometallic reagents such as allylsilanes, allylboranes, and allylstannanes under Lewis acid-activated or transition metal-catalyzed conditions. On this basis, the following sections review the conjugate addition of allylsilanes to different Michael acceptors under $TiCl_4$-prompted or fluoride-catalyzed conditions. Then, the conjugate allylation of allylB(pin) to activated double bonds under nickel- or palladium-catalyzed condition will be discussed. Lastly, conjugate additions of allylstannae reagents to α,β-unsaturated carbonyl compounds will be presented.

5.1.1 Conjugate addition reactions of allylsilane reagents

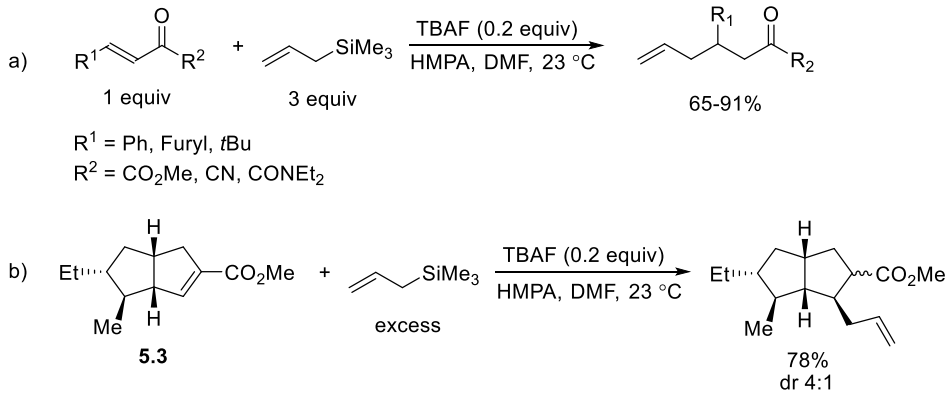
The first example of Lewis acid-promoted addition of allylsilanes to α,β-unsaturated ketones was reported by Hosomi and Sukurai.[84] It was shown that the allylation to α,β-enones could be applied in the presence of one equivalent of $TiCl_4$ to form δ,ε-enones (1,4-adducts) (Scheme 5.2a). Additionally, the allylation of fused cyclic α,β-enones with allyltrimethylsilane was demonstrated. As a result, a stereoselective conjugate addition of the allyl group to the electrophile was observed, and product **5.1** was obtained in 85% yield, which was converted to ketoester **5.2** in four steps (Scheme 5.2b).

Scheme 5.2. Conjugated allylation of α,β-enones with allyltrimethylsilane



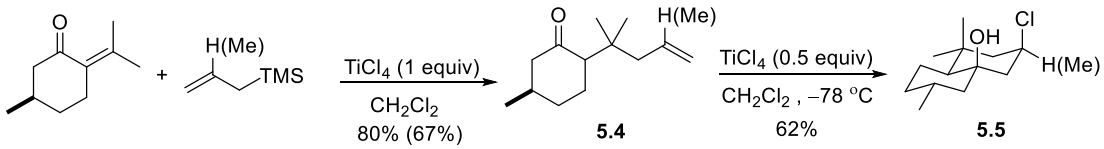
In 1978, Hosomi and coworkers reported that an allylic nucleopilic species can be generated in the presence of tetra-*n*-butylammonium fluoride (TBAF) by cleaving the allyl–silicon bond in trimethylallylsilane to form $[n\text{-}Bu_4N]^+[CH_2{=}CHCH_2]^-$ and Me_3SiF. In their studies, it was shown that the selectivity of the reaction for yielding 1,4-adducts was low, and 1,2-adducts were formed as major products in the reaction condition applied (TBAF in refluxing THF).[85] Majetich and coworkers showed that the solvent role is crucial in this transformation, as using a more polar solvent, such as DMF with added hexamethylphosphoramide (HMPA), led to good yields of the conjugate addition products.[86] As shown in Scheme 5.3, only 1,4-conjugate additions were observed under the fluoride catalysis condition for monoactivated α,β-unsaturated esters, nitriles, and amides. It was suggested that the pentacoordinate silicon intermediate was the active species in this transformation. This method has recently been applied towards the total synthesis of aburatubolactam from ester **5.3** (Scheme 5.3b).[87]

Scheme 5.3. Conjugated allylation of α,β-enones using allylsilane, TBAF, and HMPA



Another example of conjugate addition of allylsilane reagents to α,β-unsaturated carbonyl compounds was reported in 2007 by Coates and coworkers.[88] They demonstrated the conjugate addition of allyl- and methallyltrimethylsilane to pulegone to form ketone **5.4** as the major diastereomer. The double bond of the allyl group participated in an intramolecular halo-Prins cyclization of the product with 0.5 equivalent $TiCl_4$ at –78 °C to afford cis chlorohydrins **5.5** (Scheme 5.4). It should be mentioned that ketone **5.4** was initially protected as a titanium-enolate, and the Prins cyclization reaction could not occur. Therefore, the Ti-enolate was first protonated, and Prins cyclization of the ketone furnished the product afterwards.

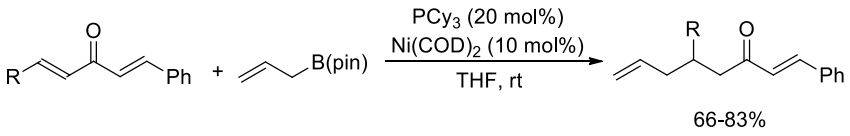
Scheme 5.4. Sakurai reaction of pulegone



5.1.2 Conjugate addition reactions of allylborane reagents

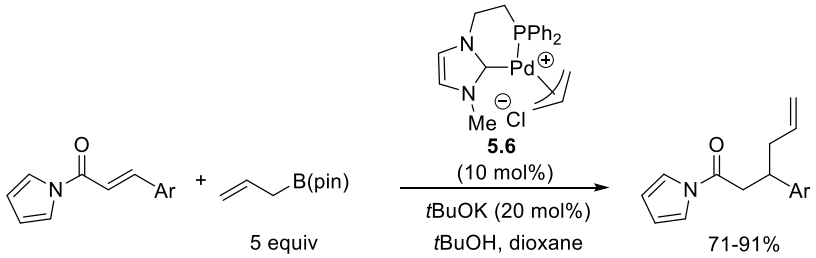
In addition to allyl silanes for nucleophilic addition of the allyl group, nucleophilic allyl boranes have emerged as useful allylating reagents for allytion of α,β-unsaturated carbonyl compounds in the last decade. Nickel-catalyzed conjugate addition of allylB(pin) to nonsymmetric ketones was reported in 2007 by Morken and coworkers.[89] Combination of electron-rich phosphine ligands, such as PCy_3 with $Ni(COD)_2$, led to the addition of the allyl group from allylB(pin) to the alkylidene site of the ketone. A good selectivity (>61:39) was observed, and adducts were isolated in 66–83% yields under mild reaction conditions. A unique mechanism was proposed for this reaction, in which the styryl unit serves as an auxiliary unit to activate the enone and facilitate the oxidative addition of the Ni complex. The allyl group is transferred from boron to nickel, followed by its transfer to β position of the boron enolate. Then, the catalyst along with the styryl group is regenerated in the reductive elimination step (Scheme 5.5).

Scheme 5.5. Conjugated allylation of α,β-enones with allylborane



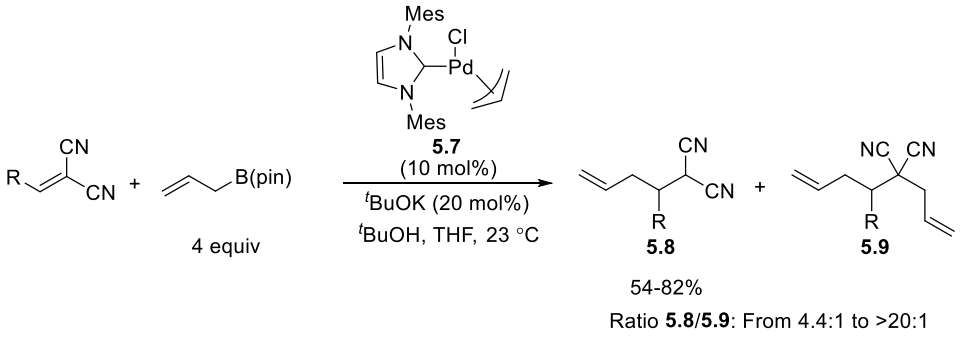
Palladium-catalyzed conjugate addition of an allylboronic ester to α,β-unsaturated N-acylpyrroles was presented by Jarvo and coworkers.[90] The palladium catalyst **5.6**, which was ligated by a bidentate N-heterocyclic carbene (NHC) ligand, afforded the desired 1,4-adducts (Scheme 5.6). It was found that the highest yield of allylation products was obtained with the combination of dioxane and *tert*-amyl alcohol. The use of *tert*-amyl alcohol minimized the formation of ester byproducts by preventing the alkoxide attack on the *N*-acylpyrroles. Moreover, the addition of potassium *tert*-butoxide as a base improved the yields, resulting in the formation of the products in 71–91%.

Scheme 5.6. Conjugate allylation of α,β-unsaturated N-acylpyrroles



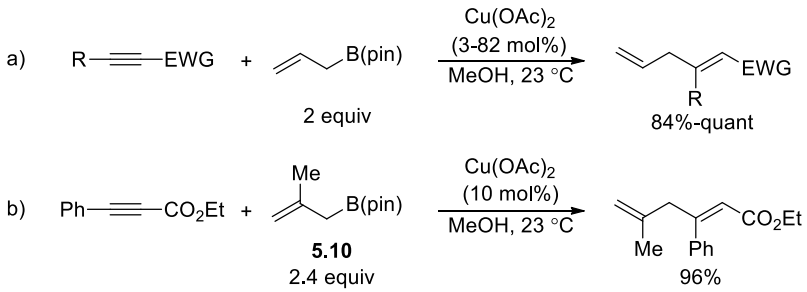
Jarvo and coworkers presented another NHC-ligated palladium-catalyzed conjugate allylation to malononitriles in 2009.[91] Alkylidene malonates were shown to be susceptible to bis-allylation reactions. It was found that the catalyst affected the selectivity of the reaction. For example, 2.8:1 ratio of **5.8** to **5.9** was obtained when complex **5.6** was used with (4-methoxybenzylidene)malononitrile (R = 4-(OMe)C_6H_4). Different NHC-ligated complexes were examined, and **5.7** favoured the formation of monoallylated adduct, and was the most selective catalyst for this transformation (Scheme 5.7).

Scheme 5.7. Conjugate allylation of malononitrile derivatives



Recently, Yamamoto and coworkers investigated copper-catalyzed conjugate allylation of electron-deficient alkynes with allylB(pin) (Scheme 5.8a).[92] Different functionalized alkynes bearing electron-withdrawing groups, such as amides, nitriles, esters, and sulfones, were reacted to obtain the allylated products in high regio- and stereoselectivity at room temperature. To broaden the nucleophile scope, the reaction of methallylboronate **5.10** with ethyl phenylpropiolate was also tried, which proceeded sluggishly with 5 mol% of the catalyst. However, as shown in Scheme 5.8b, full conversion was observed by increasing the catalyst load to 10% and using 2.4 equivalents of **5.10**.

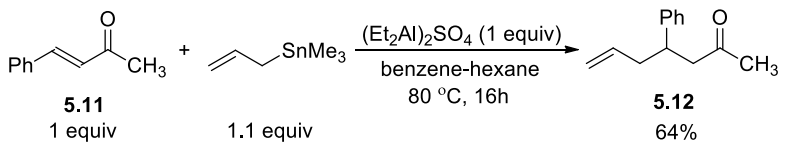
Scheme 5.8. Copper-catalyzed conjugate allylation of activated alkynes



5.1.3 Conjugate addition reactions of allylstannane reagents

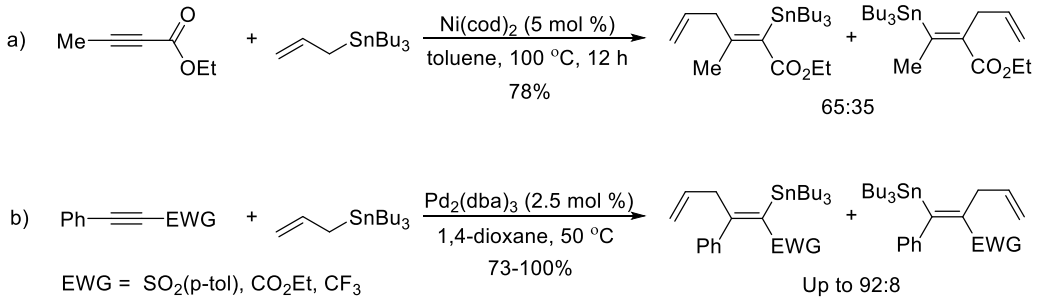
The double bond of the allyl group in allylstannanes is more nucleophilic than that in allylsilane[93], because the first ionization potential of allylstannanes is lower than that of the corresponding allylsilane.[94] In 1979, Hosomi and coworkers reported the first execution of conjugate addition of allylstannanes to α,β-enones promoted by bis(diethylaluminum)sulfate.[95] It was shown that α,β-enone **5.11** could be activated by $(Et_2Al)_2SO_4$ to give allylated product **5.12** in 64% yield (Scheme 5.9).

Scheme 5.9. Pioneering Lewis acid promoted conjugate allyaltion of α,β-enones using allylstannane



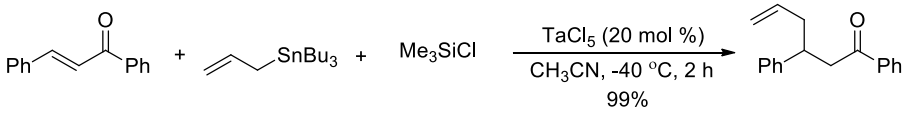
Shirakawa and coworkers reported the allylstannylation of internal alkynes in the presence of nickel(0) catalyst.[96] The reaction was stereoselevtive, resulting in the syn addition alkenylstannane product (Scheme 5.10a). Configuration of the allylstannylation products were determined by NMR studies (NOE and coupling constant). In addition, the ratio of the products was obtained by ^{119}Sn NMR. The palladium-catalyzed allylstannylation of activated alkynes was also demonstrated.[97] Higher setero- and regioselectivity as well as higher catalytic activity were observed under Pd(0)-catalyzed condition (Scheme 5.10b). These reactions proceeded at lower temperatures compared with those under the nickel-catalyzed condition.[95]

Scheme 5.10. Ni(0)- and Pd(0)-catalyzed allylstannylations of internal alkynes



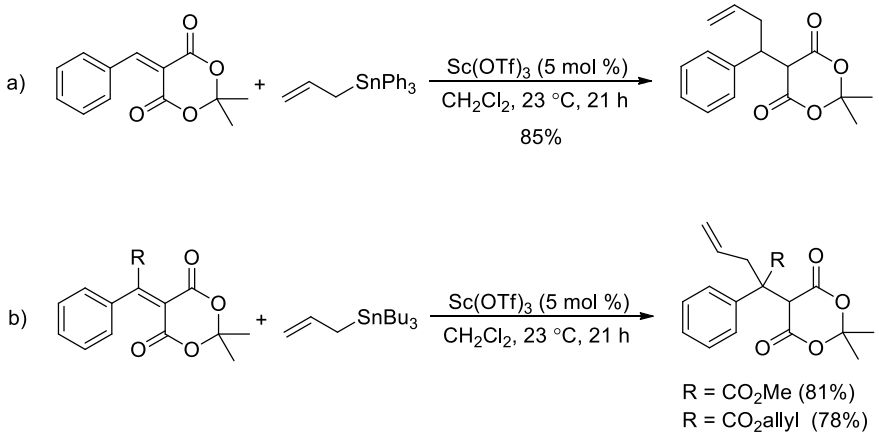
Shibata and coworkers published conjugate allylation of enones using allylstannane and tantalum (V) chloride in 2002.[98] The tantalum reagent was formed by transmetalation with the tin reagent. It was found that the addition of an equimolar amount of trimethylsilyl chloride to the reaction mixture could regenerate the $TaCl_5$ catalyst by trapping the tantalum enolate, thus forming a silyl enolate (Scheme 5.11). The transmetalation of tin with tantalum was confirmed by adding one equivalent of $TaCl_5$ to allyltri-*n*-butyl tin, and so nBu$_3$SnCl was formed after 30 min in CH_3CN quantitatively. It was also found that the combination of $TiCl_4$ and the allyl reagent afforded no product. Therefore, unlike allylstannane-titanium combination, the allylstannane-tantalum combination has been confirmed to be an efficient system for this transformation.

Scheme 5.11. Conjugate addition of allyltantalum to chalcone



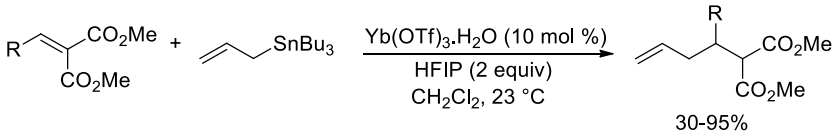
In 2009, the Fillion group reported the $Sc(OTf)_3$-catalyzed conjugate allylations of alkylidene Meldrum's acids using allyltriphenylstannane reagents.[99] While 92% of benzylidene Meldrum's acid was recovered in the absence of $Sc(OTf)_3$, 74% of the allylated product was obtained with 10 mol% of the scandium catalyst after 1.5 hours at room temperature. Reducing the catalyst amount to 5 mol% and increasing the reaction time to 21 hours furnished the product in 85% yield (Scheme 5.12a). It was demonstrated that the reaction was compatible with different functional groups on the phenyl ring. Furthermore, more nucleophilic allylation reagent $allylSnBu_3$ was used for accessing all-carbon quaternary stereocenters from tetrasubstituted alkylidenes (Scheme 5.12b).

Scheme 5.12. Conjugate addition of allylstannane reagents to benzylidene Meldrum's acids



One of the recent examples of allylation of activated olefins was reported by Lam and coworkers, wherein $Yb(OTf)_3$-catalyzed allylstannylation of alkylidene malonates was demonstrated (Scheme 5.13).[100] In these reactions, 1,4-addition of allyltributylstannane in the presence of a catalytic amount of $Yb(OTf)_3$, produced 30–95% of the desired products. Hexafluoroisopropanol (HFIP) was found to be an efficient additive by assisting the catalytic turnover through the protonation of the intermediate. Furthermore, it was found that *t*BuOH also could also be used as an economical alternative for HFIP.

Scheme 5.13. Conjugate addition of allyltributylstannane to alkylidene malonates



5.2 Proposal

The $B(C_6F_5)_3$-promoted conjugate allylation of benzylidene Meldrum's acid has been earlier reported in this thesis (Table 3.7). The objective of this chapter is to develop a method for conjugate allylation of activated olefins using the bench-top stable allyl-tricarbastannatrane under catalytic conditions. Benzylidene barbituric acid derivatives seem like an ideal starting point, because they were successfully employed as conjugate addition acceptors under $B(C_6F_5)_3$-catalyzed conditions (Chapter 4). It was postulated that the superior electrophilicity of benzylidene 1,3-dimethylbarbituric acids would allow the efficient addition of allyl-tricarbastannatrane under catalytic conditions.

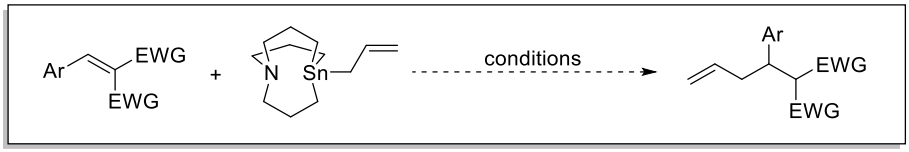
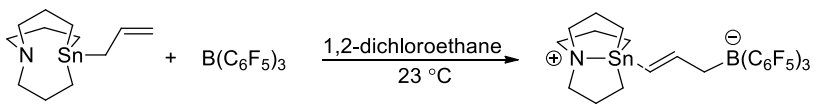


Figure 5.2. Proposal for the conjugate addition of allyl-tricarbastannatrane to activated olefins

5.3 Result and discussion

The ability of the allyl-tricarbastannatrane (**5.13**) to deliver the allyl group to tris(pentafluorophenyl)borane was first examined. As shown in Scheme 5.14, one equivalent of $B(C_6F_5)_3$ was added to one equivalent of **5.13** in 1,2-dichloroethane at room temperature to form complex $[(N(CH_2CH_2CH_2)_3Sn][allyl(B(C_6F_5)_3]$ (**5.14**). The reaction was studied in a sealed NMR tube and monitored by NMR spectroscopy. A remarkable change in a ^{119}Sn NMR chemical shift form δ –32.1 to δ 125.3 (Δppm = 157.4) was observed which implies that the tin atom possesses cationic character. The tin chemical shift at δ 125.3 indicates an interaction between $B(C_6F_5)_3$ and the tin atom of the Lewis acidic $[(N(CH_2CH_2CH_2)_3Sn]^+$. In addition to ^{119}Sn chemical shift, ^{11}B NMR chemical shift at δ = –14.2 ppm supported the formation of the complex. As previously reported in Chapter 3, the ^{11}B NMR chemical shift of free $B(C_6F_5)_3$ in 1,2-dichloroethane is δ = 57.3 ppm.

Scheme 5.14. Formation of complex $[(N(CH_2CH_2CH_2)_3Sn][allyl(B(C_6F_5)_3]$



5.13 **5.14**

NMR studies on **5.14** in CD_2Cl_2 were first carried out at room temperature. As the temperature was cooled to –70 °C, no significant change was observed in the chemical shifts of ^{11}B, ^{119}Sn, and ^{1}H NMR spectra (Table 5.1). At room temperature $SnCH_2$ and NCH_2 protons gave well resolved triplets and the CH_2 protons appear as a quintet. In addition, the double bond protons of the allyl group appear at δ = 4.50 ppm as a broad signal. At 500 Hz and –70 °C a strong broadening of the CH_2, NCH_2, and $SnCH_2$ peaks was observed. However, the double bond protons gave two well resolved doublets at δ = 4.53 ppm and δ = 4.32 ppm, and CH protons appeared at δ = 6.78–6.62 ppm as multiplet. This proton is more deshielded than CH proton of allyl group in allyl-tricarbastannatrane (Table 5.1).

Table 5.1. NMR studies on $[(N(CH_2CH_2CH_2)_3Sn][allyl(B(C_6F_5)_3]$ in CD_2Cl_2

	^{11}B NMR	^{119}Sn NMR	^{1}H NMR
rt	– 13.4	105.3[a]	6.78–6.62 (m)[b] 5.00 (br) 2.65 (t) 2.05 (t) 1.58 (t)
– 70 °C	– 13.8	99.2	6.78–6.72 (m) 4.53 (d) 4.32 (d) 2.59 (br) 1.96 (br) 1.49 (br)

[a] Allyl-tricarbastannatrane tin chemical shift in CD_2Cl_2 is –34.1 ppm. [b] Allyl-tricarbastannatrane proton chemical shifts in CD_2Cl_2 is 6.01–5.84 (m), 4.71 (d), 4.39 (d), 2.37 (t), 1.70–1.62 (m), 1.41 (d), 0.71 (t).

Crystallization of **5.14** from a *n*-pentane/1,2-dichloroethane mixture yielded crystals that were analyzed by X-ray crystallography (Figure 5.3). Compound **5.14** was recrystallized in the monoclinic space group $P2_1/c$ with a = 15.1636(5) Å, b = 13.1838(4) Å, and c = 16.3184(5) Å. The molecular geometry around the tin atom is a distorted trigonal bipyramidal with the nitrogen and carbon atoms in axial positions. The interaction between cationic tricarbastannatrane and the alkene of the allyl group attached to boron was confirmed by X-ray crystallography. As illustrated in Figure 5.3, the Sn–

C distance in this structure is 2.74 Å and Sn–N bond is 2.29 Å. Furthermore, the presence of [allylB(C_6F_5)$_3$] was detected by HRMS (ESI), thus showing an ion peak at *m/z* 553.02417.

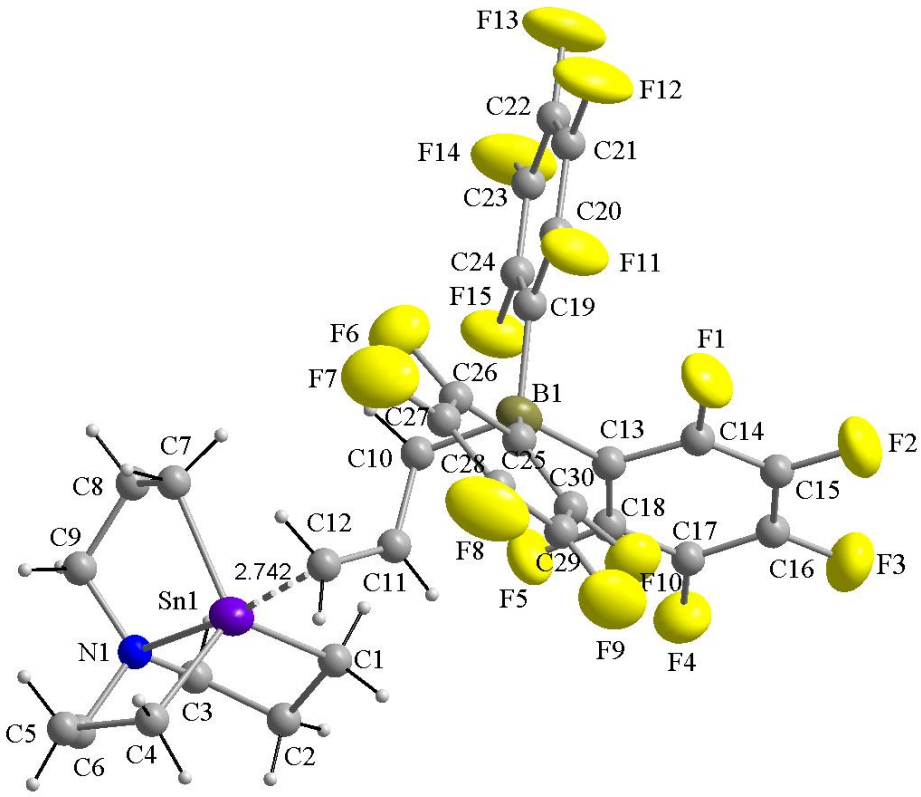
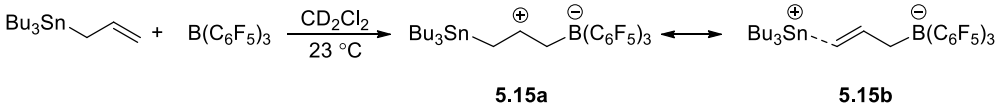


Figure 5.3. X-ray structure of [(N($CH_2CH_2CH_2$)$_3$Sn][allyl(B(C_6F_5)$_3$]

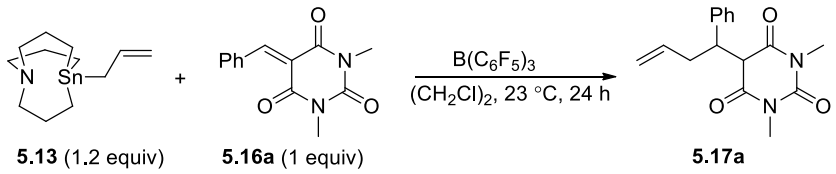
Piers and coworkers previously reported the interaction between B(C_6F_5)$_3$ and allyltributylstannane.[101] In their studies multinuclear NMR data supported the formation of adduct **5.15a/5.15b** (Scheme 5.15) with a ^{119}Sn NMR signal at δ = 181.3 ppm and ^{11}B NMR peak at δ = –13.9 ppm in CD_2Cl_2. However, X-ray structures of adducts were not reported.

Scheme 5.15. Interaction between B(C_6F_5)$_3$ and allyltributylstannane



In consideration of potential substrates for conjugate allylation using tricarbastannatrane **5.13**, we were drawn to benzylidene 1,3-dimethylbarbituric acids as electrophiles. Benzylidene 1,3-dimethylbarbituric acid (**5.16a**) was added to a mixture of $B(C_6F_5)_3$ and **5.13** in 1,2-dichloroethane, and more than 95% conversion was obtained with 10 mol% and 5 mol% of the Lewis acid (Table 5.2, entries 1–2). To our surprise, the allyl-tricarbastannatrane reagent was shown to be very reactive toward electrophile **5.16a**, and allylated product **5.17a** was obtained in 92% yield in the absence of $B(C_6F_5)_3$ at room temperature. (Table 5.2, entry 3).

Table 5.2. Reaction of allyl-tricarbastannatrane with benzylidene 1,3-dimethylbarbituric acid

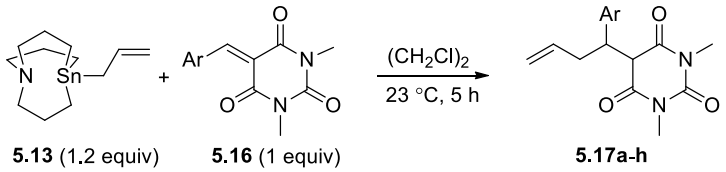


5.13 (1.2 equiv) **5.16a** (1 equiv) **5.17a**

Entry	$B(C_6F_5)_3$ (mol %)	Conversion	Yield [%]
1	10	>95	91
2	5	>95	90
3	0	>95	92

Monitoring the reaction by TLC revealed the fully consumption of **5.16a** after 5 hours (Table 5.3, entry 1). With these conditions in hand, the scope of the reaction on benzylidene barbituric acid derivatives was then studied. All reactions proceeded in excellent yields over an array of substitution pattern (Table 5.3).

Table 5.3. Conjugate addition of allyl-tricarbastannatrane to benzylidene 1,3-dimethylbarbituric acids

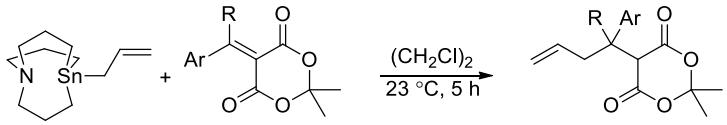


Entry	Ar	Product	Yield [%][a]
1	C_6H_5 (**5.16a**)	**5.17a**	92
2	3-(MeO)C_6H_4 (**5.16b**)	**5.17b**	95
3	4-ClC_6H_4 (**5.16c**)	**5.17c**	quant
4	3-FC_6H_4 (**5.16d**)	**5.17d**	97
5	2-Naphthyl (**5.16e**)	**5.17e**	quant
6	4-(CN)C_6H_4 (**5.16f**)	**5.17f**	99
7	3-[B($O_2C_6H_{12}$)]C_6H_4 (**5.16g**)	**5.17g**	94
8	3-BrC_6H_4 (**5.16h**)	**5.17h**	92

[a] Yield of isolated product

Extension of the allylation reaction condition to other related electrophiles such as benzylidene Medrum's acids was met with great success (Table 5.4, entreis 1-7), as allylated products **5.19a**–**5.19g** were obtained in excellent yields. The scope of the conjugate allylation reaction on tetrasubstituted olefins to form all-carbon quaternary centers was next explored (Table 5.4, entries 8–12). The reactions were found to proceed in full conversions, and furnished products **5.19h**–**l** in almost quantitative yields. Allyl-tricarbastannatrane is an air and moisture stable reagent, thus all the allyl addition reactions were carried out in the absence of an inert atmosphere.

Table 5.4. Conjugate addition of allyl-tricarbastannatrane to benzylidene Meldrum's acids



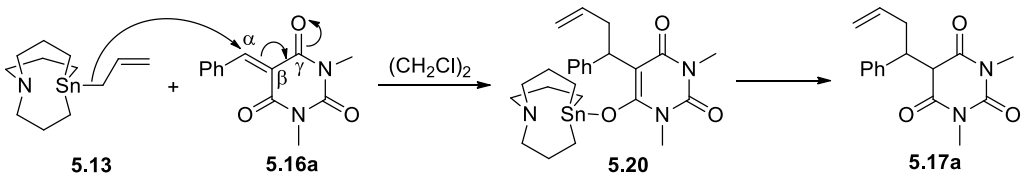
5.13 (1.2 equiv) **5.18** (1 equiv) **5.19a-l**

Entry	Ar	R	Substrate	Product	Yield [%][a]
1	C_6H_5	H	**5.18a**	**5.19a**	91
2	3-(MeO)C_6H_4	H	**5.18b**	**5.19b**	quant
3	4-ClC_6H_4	H	**5.18c**	**5.19c**	quant
4	3-FC_6H_4	H	**5.18d**	**5.19d**	96
5	4-(NO_2)C_6H_4	H	**5.18e**	**5.19e**	quant
6	4-(CN)C_6H_4	H	**5.18f**	**5.19f**	94
7	3-[B($O_2C_6H_{12}$)]C_6H_4	H	**5.18g**	**5.19g**	98
8	4-BrC_6H_4	CO_2Me	**5.18h**	**5.19h**	93
9	3-ClC_6H_4	CO_2Me	**5.18i**	**5.19i**	96
10	3-(MeO)C_6H_4	CO_2Me	**5.18j**	**5.19j**	quant
11	4-ClC_6H_4	CO_2Me	**5.18k**	**5.19k**	97
12	2-Naphthyl	CO_2Me	**5.18l**	**5.19l**	quant

[a] Yield of isolated product

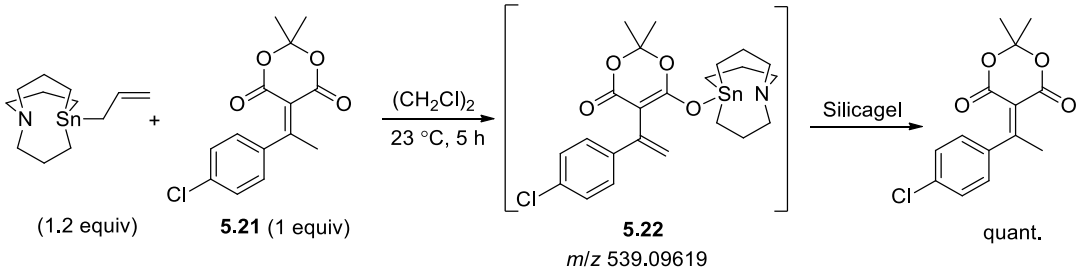
A plausible mechanism of the reaction to account for these observations is given in Scheme 5.16. Nucleophilic attack by allyl-tricarbastannatrane to the α position of the benzylidene 1,3-dimethyl barbituric acid gives enolate **5.20** (Scheme 5.16). This enolate was characterized by ^{119}Sn, ^{13}C and ^{1}H NMR experiments, and showed a ^{119}Sn chemical shift at δ = 27.3 ppm. Protonation of **5.20** on silica gel furnishes product **5.17a**.

Scheme 5.16. Proposed mechanism



Applying tetrasubstituted alkene **5.21** to the above mentioned reaction condition was unproductive even at 95 °C. The benzylidene **5.21** was completely recovered after performing a Flash chromatography. However, intermediate **5.22** was observed by HRMS (ESI), thus showing an ion peak at *m/z* 539.09619. In addition to mass spectroscopy, the formation of **5.22** was ascertained by NMR. Deprotonation of the methyl group by the allyl anion furnished intermediate **5.22** which was subsequently protonated on silica gel to regenerate the starting material (Scheme 5.17).

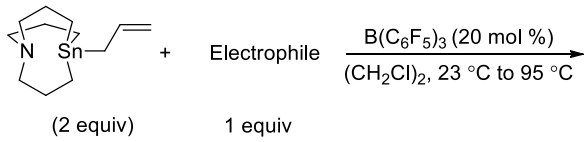
Scheme 5.17. Conjugate addition of allyl-tricarbastannatrane to 5-(1-(4-chlorophenyl)ethylidene) Meldrum's acid

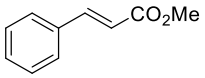
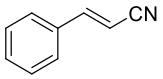
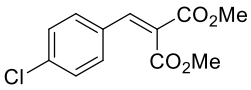
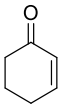
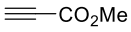
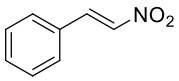
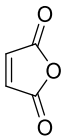


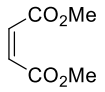
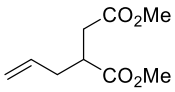
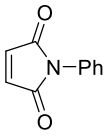
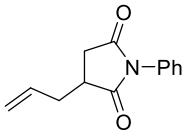
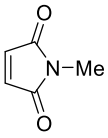
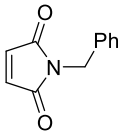
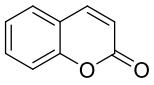
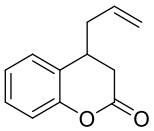
An extension of this methodology to other Michael acceptors under catalytic conditions was also investigated. Table 5.5 have demonstrated different electrophiles that have been examined with excess amounts of allyl-tricarbastannatrane and 20 mol% of $B(C_6F_5)_3$. Unexpectedly, no reactivity was observed with methyl cinnamate (**5.23**), cinnamonitrile (**5.24**), dimethyl benzylidenemalonate (**5.25**), 2-cyclohexenone (**5.26**), and methyl propiolate (**5.27**) after 48 hours at elevated temperature. Furthermore, reactions of β-nitorstyrene (**5.28**), 2,5-furandione (**5.29**), and *N*-benzylmaleimide (**5.33**) under this condition led to the decomposition of starting materials. In addition, applying dimethylmaleate (**5.30**), *N*-phenylmaleimide (**5.32**), and *N*-methylmaleimide (**5.34**) resulted in the formation of insoluble brown precipitates, and small amounts of allylated products were isolated in

the case of **5.30** and **5.32**. Moreover, low conversion was observed with coumarin (**5.36**) at ambient temperature. Increasing the temperature did not improve the result, and decomposition of the starting material and reaction intermediate(s) happened at elevated temperature (Table 5.5, entry 12).

Table 5.5. Exploring the reactivity of different Michael acceptors

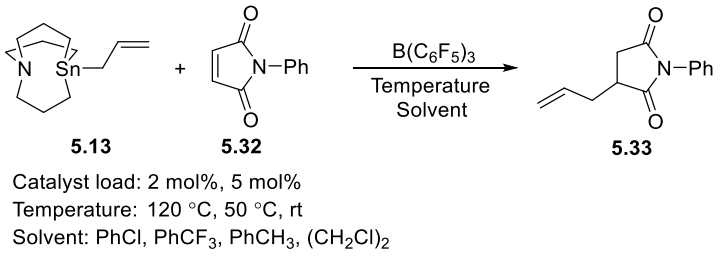


Entry	Ar	Result	Product
1	 **5.23**	no reaction	NA
2	 **5.24**	no reaction	NA
3	 **5.25**	no reaction	NA
4	 **5.26**	no reaction	NA
5	 **5.27**	no reaction	NA
6	 **5.28**	decomposition	NA
7	 **5.29**	decomposition	NA

8	 **5.30**	insoluble solid	 **5.31** 21%
9	 **5.32**	insoluble solid	 **5.33** 25%
10	 **5.34**	insoluble solid	NA
11	 **5.35**	decomposition	NA
12	 **5.36**	low conversion (rt) decomposition (95 °C)	 **5.37** 17%

Efforts were also made to improve the yield of product **5.33**. To avoid polymerization of the maleimide, catalytic load was decreased to 5 mol% (Scheme 5.18), and lower temperatures were examined. Furthermore, different solvents, such as toluene, α,α,α-trifluorotoluene, chlorobenzene and 1,2-dichloroethane were screened, and the highest yield (33%) was obtained in toluene. No further drastic improvement was noticed when the amount of the catalyst was decreased to 2 mol%.

Scheme 5.18. Screening different conditions



5.4 Summary

In summary, we have developed a conjugate allylation method by using bench-top stable allyl-tricarbastannatrane. It has been found that allyl-tricarbastannatrane readily reacted with electron-defiecient olefins under mild reaction conditions to provide conjugate allylation products in excellent yields. Benzylidene derivatives of Meldrum's acid and 1,3-dimethyl barbituric acid have been shown to be excellent acceptors for the conjugate allylation. In contrast to other methods, the presented procedure could be carried out without any catalyst, and in air. The simplicity of this procedure makes this an interesting method for obtaining a variety of δ,ε-unsaturated carbonyl compounds, including those bearing the all-carbon quaternary center. The intermediate of the reaction was characterized by NMR. Furthermore, the structure of $[(N(CH_2CH_2CH_2)_3Sn][allyl(B(C_6F_5)_3]$ was determined by X-ray crystallography. The X-ray analysis on $[(N(CH_2CH_2CH_2)_3Sn][allyl(B(C_6F_5)_3]$ showed a weak coordination of the allyl group to the tin atom of the tricarbastannatrane.

5.5 Experimental

5.5.1 General Considerations

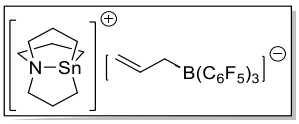
1,2-Dichloroethane was distilled over CaH_2. CD_2Cl_2 was distilled from CaH_2 and then degassed via three freeze-pump-thaw cycles following distillation. Toluene was distilled over sodium/benzophenone. Chlorobenzene and trifluorotoluene were distilled over CaH_2. Reactions were monitored by thin-layer chromatography on commercially prepared plates with a particle size of 60 Å. Developed plates were visualized under a UV lamp (254 nm), or stained with ceric ammonium molybdate. Flash chromatography was performed using 230-400 mesh silica gel.

5.5.2 Characterization

Unless otherwise noted, ^{1}H and ^{13}C NMR spectra for all adduct products were obtained in $CDCl_3$ at 300 and 75 MHz, respectively. Chemical shifts are reported in parts per million (ppm, δ) relative to tetramethylsilane (TMS) as an external standard. Proton and carbon spectra were calibrated against the solvent residual peak [$CHCl_3$ (7.24 ppm) and $CDCl_3$ (77.0 ppm)], [CH_2Cl_2 (5.32 ppm) and CD_2Cl_2 (53.8 ppm)], and in case of 1,2-dichlorethane against known solvent resonance [^{1}H (3.72 ppm) and ^{13}C (43.6 ppm)]. ^{11}B and ^{119}Sn NMR spectra of tricarbastannatranes were recorded on Bruker Avance-300 (^{11}B: 96 MHz, ^{119}Sn: 112 MHz) with ^{1}H decoupling in 1,2-dichloroethane calibrated against external BF_3•OEt_2 and Me_4Sn, respectively. The spectral references (sr) which were obtained from the external standards, were used to calibrate all ^{119}Sn NMR and ^{11}B NMR chemical shifts. Spectral reference values of –171.61 Hz and –5.13 Hz were used to calibrate ^{119}Sn and ^{11}B chemical shifts in 1,2-dichloroethane, respectively. Abbreviations used to define NMR spectral mutiplicities are as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High resolution mass spectra (ESI) were run at the University of Waterloo Mass Spectrometry facility. Fragment signals are given in mass per charge number (m/z).

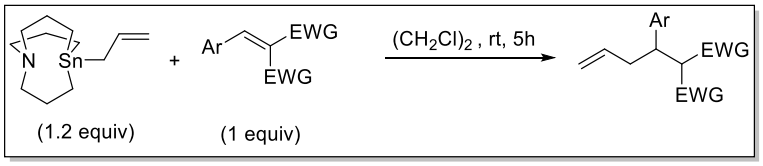
The following compounds were prepared according to literature procedures: 5-allyl-1-aza-5-stannabicyclo[3.3.3]undecane (**5.13**),[34] 5-(benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione derivatives (**5.18a-g**),[102] methyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-2-phenylpent-4-enoate (**5.18h-l**),[103] 5-(1-(4-chlorophenyl)ethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**5.21**),[104] and Other reagents were purchased from commercial suppliers and used without further purification.

$N(CH_2CH_2CH_2)_3Sn][allylB(C_6F_5)_3]$ (5.14).



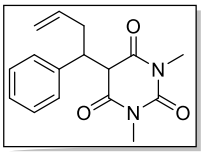
To a solution of 5-allyl-1-aza-5-stannabicyclo[3.3.3]undecane (**5.13**) (15.0 mg, 0.0510 mmol) in 1,2-dichloroethane (0.5 ml) in a J. Young NMR tube, was added tris(pentafluorophenyl)borane (26.1 mg, 0.0510 mmol). ^{1}H NMR ($Cl(CH_2)_2Cl$, 300 MHz) δ 6.70 (m), 4.55 (brd), 4.43 (brd), 2.59 (brm), 2.32 (brm), 1.99 (brm), 1.54 (brm); ^{13}C NMR ($Cl(CH_2)_2Cl$, 75 MHz) δ 163.5, 71.2, 55.1, 24.0, 15.2; ^{119}Sn NMR ($Cl(CH_2)_2Cl$, 112 MHz) δ 125.3; ^{11}B NMR ($Cl(CH_2)_2Cl$, 96 MHz) δ –14.2. HRMS (–ESI) *m/z* calcd. for $C_{21}H_5BF_{15}$ (M^-): 553.02393. Found: 553.02417; HRMS (+ESI) *m/z* calcd. for $C_9H_{18}NSn$ (M^+): 260.04557. Found: 260.04553.

General Experimental Procedure - Synthesis of Compounds 5.17 and 5.19



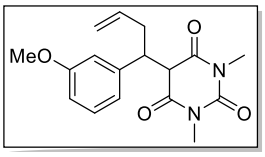
Benzylidene 1,3-dimethylbarbituric acids (**5.16**) (0.100 mmol) or benzylidene Meldrum's acids (**5.18**) (0.100 mmol) was added to a solution of 5-allyl-1-aza-5-stannabicyclo[3.3.3]undecane (**5.13**) (36.0 mg, 0.120 mmol) in 1 mL of 1,2-dichloroethane and the mixture was stirred at ambient temperature for 5 h. All volatiles were evaporated under vacuum and the product was purified by flash chromatography (EtOAc:pentane) on silica gel.

1,3-Dimethyl-5-(1-phenylbut-3-en-1-yl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (5.17a).



Prepared according to the general procedure from 5-benzylidene-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5.16a**) (24.4 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:pentane (1:4 to 1:3) and isolated as a white solid (26.3 mg, 92% yield). M.p. 86-87°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25-7.24 (m, 3H), 6.98-6.98 (m, 2H), 5.86-5.72 (m, 1H), 5.25 (d, J = 17.1 Hz, 1H), 5.13 (d, J = 10.2 Hz, 1H), 3.74 (d, J = 3.0 Hz, 1H), 3.60-3.54 (m, 1H), 3.05 (s, 3H), 3.02 (s, 3H), 3.00-2.92 (m, 1H), 2.74-2.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.2, 167.1, 150.9, 137.7, 135.2, 128.5, 128.3, 127.3, 118.6, 53.3, 50.3, 35.9, 28.1, 27.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}O_3N_2$ $(M+H)^+$: 287.13902; Found: 287.13828.

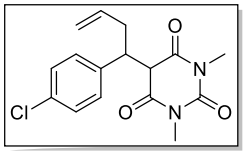
5-(1-(3-Methoxyphenyl)but-3-en-1-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (5.17b).



Prepared according to the general procedure from 5-(3-methoxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5.16b**) (27.4 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:4) and isolated as a white solid (30.0 mg, 95% yield). M.p. 62-64°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.14 (t, J = 8.1 Hz, 1H), 6.76 (dd, J = 8.4, 2.4 Hz, 1H), 6.55-6.51 (m, 2H), 5.85-5.71 (m, 1H), 5.25 (dd, J = 17.1, 1.2 Hz, 1H), 5.12 (d, J = 10.2 Hz, 1H), 3.72 (s, 4H), 3.55-3.49 (m, 1H), 3.05 (s, 3H), 3.02 (s, 3H), 2.96-2.85

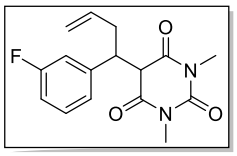
(m, 1H), 2.71-2.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.1, 167.1, 159.8, 151.0, 139.4, 135.2, 129.5, 119.5, 118.6, 113.3, 55.2, 53.2, 50.2, 36.0, 28.1, 28.0. HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_4N_2$ $(M+H)^+$: 317.14958; Found: 317.14993.

5-(1-(4-Chlorophenyl)but-3-en-1-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (5.17c).



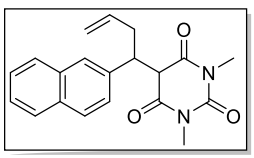
Prepared according to the general procedure from 5-(4-chlorobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5.16c**) (27.9 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:5) and isolated as a colorless oil (32.1 mg, quantitative yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 8.1 Hz, 1H), 5.81-5.67 (m, 1H), 5.21 (d, J = 17.1 Hz, 1H), 5.11 (d, J = 10.2 Hz, 1H), 3.72 (d, J = 3.0 Hz, 1H), 3.62-3.57 (m, 1H), 3.08 (s, 3H), 3.05 (s, 3H), 2.97-2.86 (m, 1H), 2.69-2.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.8, 166.9, 150.8, 136.6, 134.9, 134.1, 128.8, 128.7, 118.8, 52.9, 49.1, 36.1, 28.2, 28.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_3N_2Cl$ $(M+H)^+$: 321.10005; Found: 321.09915.

5-(1-(3-Fluorophenyl)but-3-en-1-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (5.17d).



Prepared according to the general procedure from 5-(3-fluorobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5.16d**) (26.2 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:4) and isolated as a colorless oil (29.5 mg, 97% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22-7.17 (m, 1H), 6.96-6.90 (m, 2H), 6.77-6.69 (m, 2H), 5.77-5.71 (m, 1H), 5.23 (d, J = 17.1, 1.5 Hz, 1H), 5.12 (d, J = 10.2 Hz, 1H), 3.72 (d, J = 3.3 Hz, 1H), 3.62-3.55 (m, 1H), 3.07 (s, 3H), 3.05 (s, 3H), 2.96-2.86 (m, 1H), 2.70-2.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.8, 166.9, 162.8 (d, $J_{C\text{-}F}$ = 245.9 Hz), 150.9, 140.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 134.8, 130.1(d, $J_{C\text{-}F}$ = 8.3 Hz), 123.2 (d, $J_{C\text{-}F}$ = 2.9 Hz), 118.8, 115.1 (d, $J_{C\text{-}F}$ = 20.9 Hz), 114.42 (d, $J_{C\text{-}F}$ = 21.7 Hz), 52.9, 49.5, 49.4, 35.9, 28.1, 27.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_3N_2F$ $(M+H)^+$: 305.12960; Found: 305.13068.

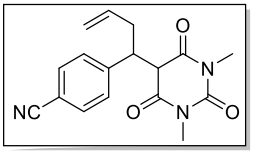
1,3-Dimethyl-5-(1-(naphthalen-2-yl)but-3-en-1-yl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (5.17e).



Prepared according to the general procedure from 1,3-dimethyl-5-(naphthalen-2-ylmethylene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5.16e**) (29.4 mg, 0.100 mmol); reaction was purified by flash chromatography on silica

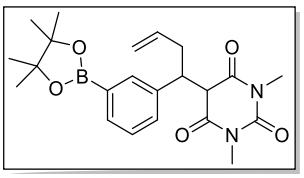
gel with EtOAc:hexanes (1:5) and isolated as a colorless oil (33.6 mg, quantitative yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.77-7.70 (m, 3H), 7.46-7.43 (m, 3H), 7.07 (d, J = 8.7, 1.5 Hz, 1H),5.88-5.74 (m, 1H), 5.26 (d, J = 15.6 Hz, 1H), 5.12 (d, J = 10.2 Hz, 1H), 3.81-3.72 (m, 2H), 3.09-2.97 (m, 7H), 2.84-2.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.1, 167.2, 150.7, 135.2, 135.2, 133.2, 132.9, 128.2, 127.7, 127.5, 126.6, 126.5, 126.3, 124.8, 118.6, 53.3, 50.3, 36.2, 28.1, 27.9. HRMS (ESI) *m/z* calcd for $C_{20}H_{21}O_3N_2$ $(M+H)^+$: 337.15467; Found: 337.15408.

4-(1-(1,3-Dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)but-3-en-1-yl)benzonitrile (5.17f).



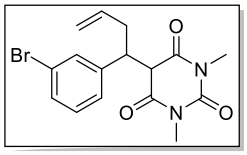
Prepared according to the general procedure from 4-((1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5(2*H*)-ylidene)methyl)benzonitrile (**5.16f**) (26.9 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:6) and isolated as a colorless oil (30.8 mg, 99% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 5.78-5.65 (m, 1H), 5.20 (dd, J = 17.1, 1.2 Hz, 1H), 5.11 (d, J = 9.9 Hz, 1H), 3.76-3.70 (m, 2H), 3.10 (s, 3H), 3.07 (s, 3H), 2.96-2.89 (m, 1H), 2.72-2.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.1, 166.6, 150.6, 144.0, 134.5, 132.3, 128.6, 119.1, 118.2, 112.1, 52.5, 48.7, 35.8, 28.3, 28.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}N_3O_3$ $(M+H)^+$: 312.13427; Found: 312.13391.

1,3-Dimethyl-5-(1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-1-yl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (5.17g).



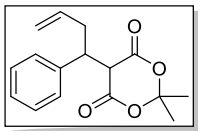
Prepared according to the general procedure from 1,3-dimethyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5.16g**) (37.0 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:6) and isolated as a colorless oil (38.7 mg, 94% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 (d, J = 7.2 Hz, 1H), 7.37 (s, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 7.5 Hz, 1H), 5.85-5.71 (m, 1H), 5.24 (d, J = 17.1 Hz, 1H), 5.11 (d, J = 10.2 Hz, 1H), 3.72 (d, J = 3.0 Hz, 1H), 3.57-3.52 (m, 1H), 3.00-2.88 (m, 7H), 2.72-2.63 (m, 1H), 1.30 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.2, 167.1, 150.8, 136.8, 135.2, 134.7, 133.5, 130.1, 127.8, 118.5, 83.9, 53.4, 50.6, 35.8, 28.0, 27.8, 24.8. HRMS (ESI) *m/z* calcd for $C_{22}H_{30}BN_2O_5$ $(M+H)^+$: 413.22423; Found: 413.22412.

5-(1-(3-Bromophenyl)but-3-en-1-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (5.17h).



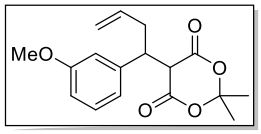
Prepared according to the general procedure from 5-(3-bromobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5.16h**) (32.3 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:6) and isolated as a white solid (33.6 mg, 92% yield). M.p. 97-99°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.37 (d, J = 7.8, 0.6 Hz, 1H), 7.16 (s, 1H), 7.11 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 5.82-5.68 (m, 1H), 5.23 (d, J = 17.0, 0.9 Hz, 1H), 5.13 (d, J = 10.2 Hz, 1H), 3.72 (d, J = 3.3 Hz, 1H), 3.58-3.51 (m, 1H), 3.08 (s, 3H), 3.06 (s, 3H), 2.96-2.85 (m, 1H), 2.68-2.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.8, 166.9, 150.8, 140.3, 134.7, 131.4, 130.6, 130.0, 126.0, 122.7, 118.9, 53.0, 49.6, 35.8, 28.2, 27.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_3N_2Br$ $(M+H)^+$: 365.04953; Found: 365.05008.

2,2-Dimethyl-5-(1-phenylbut-3-en-1-yl)-1,3-dioxane-4,6-dione (5.19a).[24]



Prepared according to the general procedure from 5-benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**5.18a**) (23.2 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:5) and isolated as a colorless oil (24.9 mg, 91% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23-7.22 (m, 3H), 6.96-6.94 (m, 2H), 5.85-5.71 (m, 1H), 5.23 (dd, J = 17.1, 1.2 Hz, 1H), 5.12 (d, J = 10.2, 1H), 3.72 (d, J = 3.3, 1H), 3.59-3.53 (m, 1H), 3.03 (s, 3H), 3.00 (s, 3H), 2.98-2.88 (m, 1H), 2.72-2.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.2, 167.1, 150.9, 137.8, 135.2, 128.5, 128.3, 127.3, 118.6, 53.3, 50.3, 35.9, 28.1, 27.9.

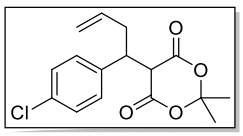
5-(1-(3-Methoxyphenyl)but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (5.19b).



Prepared according to the general procedure from 5-(3-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**5.18b**) (26.2 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:4) and isolated as a colorless oil (30.3 mg, quantitative yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.18 (t, J = 7.8 Hz,1H), 6.90-6.86 (m, 2H), 6.76 (dd, J = 8.3, 1.8 Hz, 1H), 5.86-5.72 (m, 1H), 5.22 (d, J = 17.1 Hz,1H), 5.12 (d, J = 9.9 Hz,1H), 3.87-3.80 (m, 1H), 3.76 (s, 3H), 3.09-3.01 (m, 1H), 2.79-2.71 (m, 1H), 1.61 (s, 3H), 1.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.9, 164.6, 159.7, 141.2, 135.7, 129.6, 121.1, 118.6, 114.4, 113.4, 105.3,

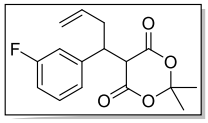
55.2, 49.3, 45.2, 36.5, 28.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_5$ $(M+H)^+$: 305.13835; Found: 305.13818.

5-(1-(4-Chlorophenyl)but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (5.19c).[103]



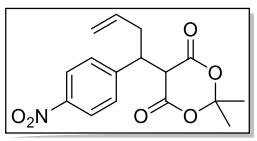
Prepared according to the general procedure from 5-(4-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**5.18c**) (26.7 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:5) and isolated as a white solid (30.9 mg, quantitative yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29-7.22 (m, 4H), 5.83-5.69 (m, 1H), 5.23-5.10 (m, 2H), 3.89-3.82 (m, 1H), 3.76 (d, J = 3.0 Hz, 1H), 3.06-2.95 (m, 1H), 2.78-2.69 (m, 1H), 1.64 (s, 3H), 1.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.6, 164.4, 138.0, 135.5, 133.5, 130.5, 128.7, 118.8, 105.2, 49.4, 44.0, 36.4, 28.1, 27.9.

5-(1-(3-Fluorophenyl)but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (5.19d).



Prepared according to the general procedure from 5-(3-fluorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**5.18d**) (25.0 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:5) and isolated as a white solid (28.0 mg, 96% yield). M.p. 60-61°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28-7.12 (m, 1H), 7.09-7.05 (m, 2H), 6.96-6.89 (m, 1H), 5.79-5.73 (m, 1H), 5.22 (d, J = 17.1, 1.2 Hz, 1H), 5.13 (d, J = 9.9 Hz, 1H), 3.91-3.85 (m, 1H), 3.77 (d, J = 2.7 Hz, 1H), 3.06-3.96 (m, 1H), 2.79-2.73 (m, 1H), 1.64 (s, 3H), 1.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.0 (d, $J_{C\text{-}F}$ = 85.3 Hz), 162.8 (d, $J_{C\text{-}F}$ = 241.9 Hz) , 142.2 (d, $J_{C\text{-}F}$ = 7.1 Hz), 135.4, 130.0 (d, $J_{C\text{-}F}$ = 8.2 Hz), 124.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 118.9, 116.0 (d, $J_{C\text{-}F}$ = 21.7 Hz), 114.7, 114.4, 105.3, 49.3, 44.3, 44.3, 36.3, 281.7, 27.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_4F$ $(M+H)^+$: 293.11836; Found: 293.11890.

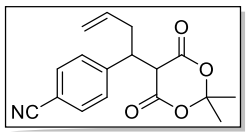
2,2-Dimethyl-5-(1-(4-nitrophenyl)but-3-en-1-yl)-1,3-dioxane-4,6-dione (5.19e).[23]



Prepared according to the general procedure from 5-(4-nitrobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**5.18e**) (27.7 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:4) and isolated as a colorless oil (31.8 mg, quantitative yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.12 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 5.82-5.68 (m, 1H), 5.23-5.12 (m, 2H), 4.05-3.99 (m, 1H), 3.83 (d, J = 2.7 Hz, 1H), 3.07-2.97 (m, 1H), 2.84-2.75 (m, 1H), 1.69 (s,

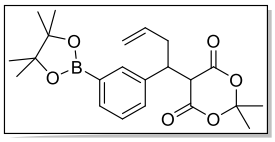
3H), 1.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 164.0, 147.2, 147.1, 135.0, 130.3, 123.5, 119.3, 105.2, 49.3, 43.4, 36.0, 28.1, 27.5.

4-(1-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-yl)but-3-en-1-yl)benzonitrile (5.19f).[23]



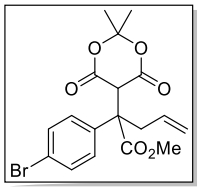
Prepared according to the general procedure from 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl)benzonitrile (**5.18f**) (25.7 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:5 to 1:3) and isolated as a white solid (28.1 mg, 94% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 5.82-5.68 (m, 1H), 5.23-5.12 (m, 2H), 3.98-3.92 (m, 1H), 3.80 (d, J = 2.7 Hz, 3H), 3.06-2.96 (m, 1H), 2.8-2.72 (m, 1H), 1.67 (s, 3H), 1.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.0, 164.1, 162.8, 145.1, 135.0, 132.2, 130.1, 119.2, 118.6, 111.5, 105.2, 49.2, 43.8, 36.1, 36.0, 28.1, 27.6, 27.6.

2,2-Dimethyl-5-(1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-1-yl)-1,3-dioxane-4,6-dione (5.19g).



Prepared according to the general procedure from 2,2-dimethyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)-1,3-dioxane-4,6-dione (**5.18g**) (35.8 mg, 0.100 mmol); reaction was purified by flash chromatography on silica gel with EtOAc:hexanes (1:5) and isolated as a colorless oil (39.3 mg, 98% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70-7.65 (m, 2H),7.47 (d, J = 8.1 Hz,1H), 7.29 (t, J = 7.5 Hz, 1H), 5.85-5.71 (m, 1H), 5.20 (d, J = 18.3 Hz, 1H), 5.10 (d, J = 10.2 Hz, 1H), 3.94-3.88 (m, 1H), 3.77 (d, J = 2.7 Hz, 1H), 3.07-2.96 (m, 1H), 2.77-2.70 (m, 1H),1.61 (s, 3H), 1.31 (s, 12H), 1.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.6, 164.7, 139.2, 135.9, 135.3, 134.1, 131.5, 128.1, 118.5, 105.2, 83.2, 49.5, 44.8, 36.2, 28.1, 28.00, 24.9, 24.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{30}O_6B$ $(M+H)^+$: 401.21300. Found: 401.21347.

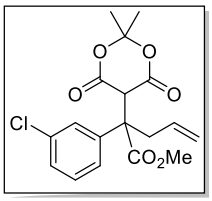
Methyl 2-(4-bromophenyl)-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)pent-4-enoate (5.19h).[23]



Prepared according to the general procedure from methyl 2-(4-bromophenyl)-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)acetate (**5.18h**) (36.9 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:5) and isolated as a white solid (38.2 mg, 93% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 5.86-5.72 (m, 1H), 5.12-5.07 (m, 2H), 4.62 (s,

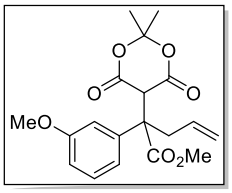
1H), 3.71 (s, 3H), 3.46-3.39 (m, 1H), 3.15-3.08 (m, 1H), 1.82 (s, 3H), 1.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.3, 163.0, 162.8, 136.8, 133.7, 131.3, 129.6, 121.8, 119.7, 104.8, 54.2, 52.9, 51.6, 39.0, 28.5, 26.4.

Methyl 2-(3-chlorophenyl)-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)pent-4-enoate (5.19i).



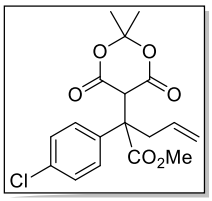
Prepared according to the general procedure from methyl 2-(3-chlorophenyl)-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)acetate (**5.18i**) (32.5 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:5) and isolated as a white solid (35.2 mg, 96% yield). M.p. 111-113°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45 (s, 1H), 7.34-7.23 (m, 3H), 5.87-5.73 (m, 1H), 5.11-5.06 (m, 2H), 4.64 (s, 1H), 3.71 (s, 3H), 3.44-3.37 (m, 1H), 3.15-3.07 (m, 1H), 1.83 (s, 3H), 1.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.2, 163.0, 162.6, 140.1, 134.2, 133.8, 129.3, 127.9, 127.7, 125.7, 119.8, 104.8, 54.2, 53.0, 51.4, 38.8, 28.5, 26.5. HRMS (ESI) *m/z* calcd for $C_{18}H_{20}O_6Cl$ $(M+H)^+$: 367.09429; Found: 367.09500.

Methyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-2-(3-methoxyphenyl)pent-4-enoate (5.19j).



Prepared according to the general procedure from methyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-2-(3-methoxyphenyl)acetate (**5.18j**) (32.0 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:4) and isolated as a white solid (36.2 mg, quantitative yield). M.p. 105-107°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27 (d, J = 8.4 Hz, 1H), 7.04-7.02 (m, 2H), 6.83 (d, J = 8.1, 1.2 Hz, 1H), 5.95-5.81 (m, 1H), 5.12-5.07 (m, 2H), 4.71 (s, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.50-3.43 (m, 1H), 3.18-3.10 (m, 1H), 1.85 (s, 3H), 1.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.6, 163.3, 162.7, 159.4, 139.8, 134.5, 129.1, 119.4, 119.4, 114.2, 112.0, 104.6, 55.2, 54.3, 52.8, 51.3, 38.7, 28.5, 26.5. HRMS (ESI) *m/z* calcd for $C_{19}H_{23}O_7$ $(M+H)^+$: 363.14383; Found: 363.14423.

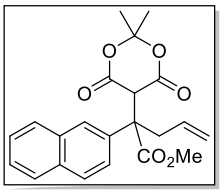
Methyl 2-(4-chlorophenyl)-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)pent-4-enoate (5.19k).



Prepared according to the General Procedure B from methyl 2-(4-chlorophenyl)-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)acetate (**5.18k**) (32.5 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:5) and isolated as a white solid (38.2 mg, 93% yield). M.p. 140-141°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 5.86-5.72 (m, 1H), 5.12-5.06 (m, 2H), 4.63 (s, 1H), 3.71 (s, 3H), 3.46-3.39 (m, 1H), 3.16-3.08 (m, 1H), 1.82 (s, 3H), 1.65

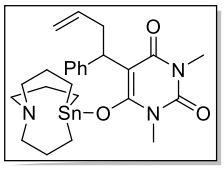
(s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.4, 163.0, 162.8, 136.2, 133.7, 129.2, 128.3, 119.7, 104.8, 54.1, 52.9, 51.6, 39.0, 28.5, 26.5. HRMS (ESI) *m/z* calcd for $C_{18}H_{20}O_6Cl$ $(M+H)^+$: 367.09429; Found: 367.09436.

Methyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-2-(naphthalen-2-yl)pent-4-enoate (5.19l).[23]



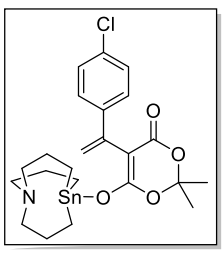
Prepared according to the General Procedure B from methyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-2-(naphthalen-2-yl)acetate (**5.18l**) (34.0 mg, 0.100 mmol); reaction was purified eluting with EtOAc:hexanes (1:4) and isolated as a white solid (38.0 mg, quantitative yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91 (s, 1H), 7.83-7.78 (m, 3H),7.59 (d, J = 9.0, 1.8 Hz, 1H), 7.48-7.43 (m, 2H), 5.99-5.85 (m, 1H), 5.16-5.08 (m, 2H), 4.83 (s, 1H), 3.71 (s, 3H), 3.63-3.56 (m, 1H), 3.32-3.25 (m, 1H), 1.85 (s, 3H), 1.64 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.7, 163.4, 162.8, 135.5, 134.4, 133.0, 132.4, 128.4, 127.7, 127.3, 126.7, 126.4, 126.1, 125.1, 119.5, 104.7, 54.6, 52.9, 51.4, 38.8, 28.5, 26.5.

6-((1-Aza-5-stannabicyclo[3.3.3]undecan-5-yl)oxy)-1,3-dimethyl-5-(1-phenylbut-3-en-1-yl)pyrimidine-2,4(1*H*,3*H*)-dione (5.20).



Prepared according to the general procedure from 5-benzylidene-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5.16a**) (24.4 mg, 0.100 mmol); the solvent was removed after 5 h by rotary evaporation and the crude compound was dried on vacuum. It was characterized without further purification; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42 (d, J = 7.2 Hz, 2H), 7.19 (t, J = 7.8 Hz, 2H), 7.09-7.04 (m, 1H), 5.85-5.71 (m, 1H), 4.95 (d, J = 13.8 Hz, 1H), 4.86 (d, J = 9.9 Hz, 1H), 4.03 (brs, 1H), 3.23 (s, 6H), 3.11-2.91 (m, 2H), 2.43 (brt, 6H), 1.80 (brt, 6H), 1.13 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.7, 161.6, 152.8, 145.6, 139.3, 128.1, 127.8, 125.3, 114.6, 94.6, 55.0, 41.4, 36.9, 23.3, 11.3; ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ 27.3.

6-((1-Aza-5-stannabicyclo[3.3.3]undecan-5-yl)oxy)-5-(1-(4-chlorophenyl)vinyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (5.22).



Prepared according to the general procedure from 5-(1-(4-chlorophenyl)ethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (**5.21**) (28.2 mg, 0.100 mmol); the reaction solvent was removed after 5 h by rotary evaporation and the crude compound

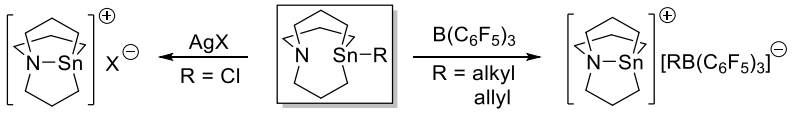
was dried on vacuum. It was characterized without further purification; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33-7.16 (m, 4H), 5.52 (d, J = 12.9 Hz, 2H), 2.46 (t, J = 5.4 Hz, 6H), 1.85-1.80 (m, 6H), 1.77 (s, 6H), 1.00 (t, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.8, 161.2, 142.3, 131.7, 128.8, 127.9, 127.7, 117.0, 102.5, 101.0, 55.0, 25.8, 23.2, 11.0; ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ 21.9. HRMS (ESI) *m/z* calcd for $C_{23}H_{31}O_4NClSn$ $(M+H)^+$: 539.09692; Found: 539.09619.

Chapter 6
Conclusions and Future Work

6.1 Conclusions

Syntheses of tricarbastannatrane complexes from the reaction of chloro-tricarbastannatrane and silver salts have been described. In addition, it was demonstrated that cationic tricarbastannatranes could be generated through the reaction between alkyl-tricarbastannatrane and $B(C_6F_5)_3$. The structure of a number of tricarbastannatrane complexes in solution and solid state has been established, namely $[N(CH_2CH_2CH_2)_3Sn][BF_4]$, $[N(CH_2CH_2CH_2)_3Sn][SbF_6]$, $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$, $[[N(CH_2CH_2CH_2)_3Sn]_2Cl_{0.2}F_{0.8}][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$, $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$, and $[(N(CH_2CH_2CH_2)_3Sn][allyl(B(C_6F_5)_3]$. The structures were characterized by X-ray diffraction analyses, multinuclear NMR spectroscopy, and mass spectrometry. Due to the intramolecular nitrogen–tin interaction in the atrane frame, the pentacoordinated tin atom in these complexes has a distorted trigonal bipyramidal molecular geometry. Stability and a weak Lewis acidity are important features of $[N(CH_2CH_2CH_2)_3Sn]^+$ moiety in these complexes (Scheme 6.1).

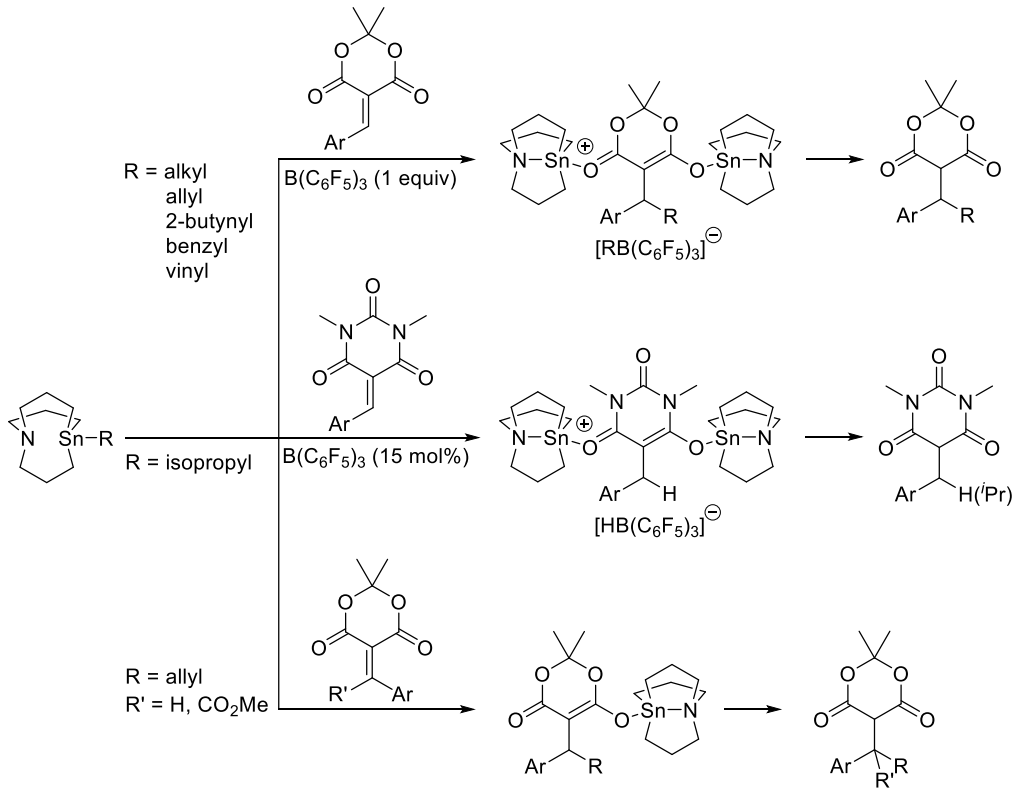
Scheme 6.1. Syntheses of tricarbastannatrane complexes



Furthermore, the construction of carbon–carbon and carbon–hydrogen bonds using tricarbastannatranes was described in this thesis. The $B(C_6F_5)_3$–promoted conjugate alkylation of benzylidene Meldrum's acids using tricarbastannatranes was carried out under mild conditions. The structure of the reaction's symmetrical bis-stannatrane intermediate was determined by NMR spectroscopy and mass spectrometry. Moreover, the $B(C_6F_5)_3$–catalyzed conjugate reduction of benzylidene 1,3-dimethylbarbituric acids was presented by applying readily available ^{i}Pr-tricarbastannatrane as an in-situ hydride source. The reduced adducts were obtained in good to excellent yield. In addition, isopropyl group transfer from ^{i}Pr-tricarbastannatrane furnished alkylated products as byproducts under the reaction conditions. The reduction mechanism was investigated by NMR and mass spectrometry techniques. In addition, conjugate allylations of activated olefins using

bench-top stable allyl-tricarbastannatrane were explored, and the allylation products were obtained in excellent yields. The tin enolate intermediate of the reaction was characterized by NMR spectroscopy (Scheme 6.2).

Scheme 6.2. Reactivity of tricarbastannatranes

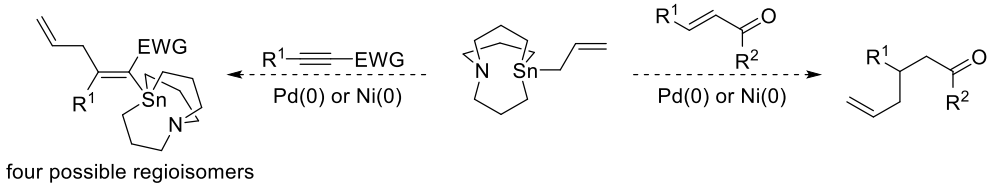


6.2 Future work

A catalytic method for conjugate addition of methyl- and allyl-tricarbastannatranes to carbon–carbon double or triple bonds that bear strongly electron-withdrawing substituents remains a desirable process. Future work on this methodology should focus on screening and developing alternate catalysts for additions of organotricarbastannatranes to unsaturated carbon–carbon bonds. In this regard, $Pd_2(dba)_3$[99] and $Ni(cod)_2$[98] have been observed to be efficient catalysts in allylstannylation of alkynes (Section 5.1.3). Therefore, conjugate addition of allyl-tricarbastannatrane to activated olefins can be examined in the presence of various Pd(0) or Ni(0) catalyst. Furthermore, addition of allyl-tricarbastannatrane to alkynes can be investigated under these sets of conditions. Different

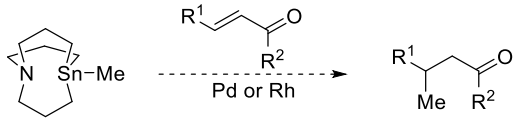
regioisomers can be formed after allylcarbastannatration of an alkyne (Scheme 6.3). These adducts can be applied in further transformations, such as Stille cross-coupling reactions.

Scheme 6.3. Proposed future work: Addition of allyl-tricarbastannatrane to alkenes and alkynes in the presence of Ni(0) or Pd(0) catalyst.



Transmetalation of organostannanes with palladium [46] and rhodium [47] catalysts have been reported. Intramolecular coordination of the nitrogen atom to the tin atom in tricarbastannatrane backbone selectively activates the apical alkyl group towards transmetalation.[13] Conjugate addition of alkyl-tricarbastannatrane to α,β-unsaturated carbonyl compounds can be studied in the presence of palladium or rhodium catalyst.

Scheme 6.4. Proposed future work: Conjugate addition of alkyl-tricarbastannatrane to α,β-unsaturated carbonyl compounds in the presence of palladium or rhodium catalysts



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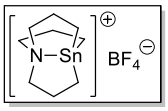
Appendix

Crystallographic Data

X-Ray Data for Complex **2.4**
From pentane/1,2-dichloroethane



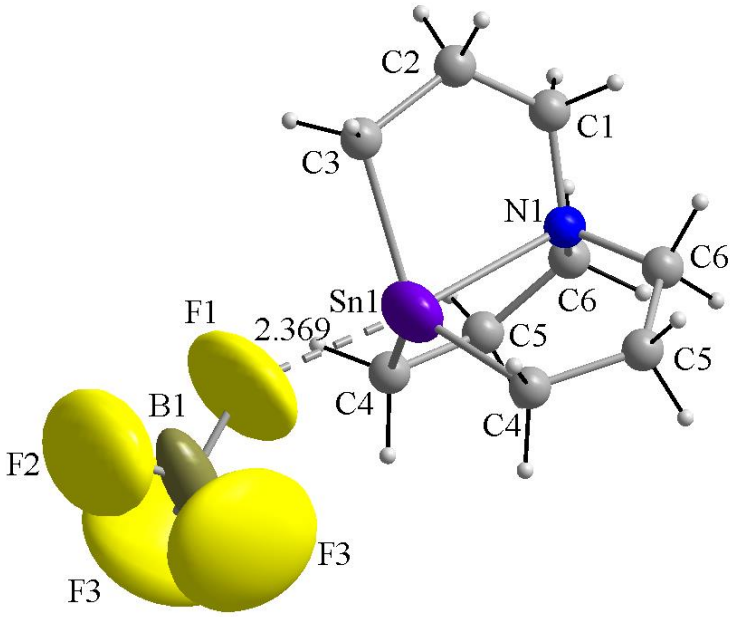


Table 1. Crystal data and structure refinement for Complex **2**

Identification code	AK245a_0ma_a
Empirical formula	C9 H18 B F4 N Sn
Formula weight	345.74
Temperature	273(2) K
Wavelength	0.71073 Å

Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 12.0744(14) Å	α = 90°.
	b = 8.3741(10) Å	β = 90°.
	c = 12.7457(15) Å	γ = 90°.
Volume	1288.7(3) $Å^3$	
Z	4	
Density (calculated)	1.782 Mg/m^3	
Absorption coefficient	2.004 mm^{-1}	
F(000)	680	
Crystal size	0.200 x 0.060 x 0.020 mm^3	
Theta range for data collection	3.197 to 25.993°.	
Index ranges	-14<=h<=14, -9<=k<=10, -15<=l<=15	
Reflections collected	9916	
Independent reflections	1355 [R(int) = 0.0455]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.6615	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1355 / 32 / 86	
Goodness-of-fit on F^2	1.145	
Final R indices [I>2sigma(I)]	R1 = 0.0694, wR2 = 0.1284	
R indices (all data)	R1 = 0.0950, wR2 = 0.1430	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.650 and -1.442 e.$Å^{-3}$	

Table 2. Atomic ccordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AK245a_0ma_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	1548(1)	2500	5102(1)	68(1)

N(1)	2937(8)	2500	3961(7)	55(2)
C(1)	2248(12)	4680(20)	5579(12)	152(6)
C(2)	3225(12)	4950(15)	4969(11)	114(4)
C(3)	3570(11)	3930(18)	4136(14)	168(7)
C(4)	560(12)	2500	3696(12)	88(4)
C(5)	1346(14)	2500	2817(11)	94(5)
C(6)	2459(16)	2500	2969(12)	193(12)
B(1)	-350(20)	2500	7144(19)	101(6)
F(1)	-51(12)	2500	6186(11)	246(8)
F(2)	-1393(13)	2500	7152(15)	287(11)
F(3)	-46(15)	3648(16)	7619(13)	310(8)
H(1A)	1724	5538	5472	182
H(1B)	2435	4633	6318	182
H(2A)	3152	6010	4671	137
H(2B)	3838	4998	5461	137
H(3A)	4331	3621	4268	201
H(3B)	3563	4547	3493	201
H(4A)	93	1559	3671	106
H(4B)	93	3441	3671	106
H(5A)	1176	1571	2392	112
H(5B)	1176	3429	2392	112
H(6A)	2747	3429	2605	231
H(6B)	2747	1571	2605	231

Table 3. Bond lengths [Å] and angles [°] for AK245a_0ma_a.

Sn(1)-C(1)	2.098(14)
Sn(1)-C(1)#1	2.098(14)
Sn(1)-C(4)	2.152(13)
Sn(1)-N(1)	2.219(9)
Sn(1)-F(1)	2.374(11)

N(1)-C(6)	1.390(19)
N(1)-C(3)#1	1.438(13)
N(1)-C(3)	1.438(13)
C(1)-C(2)	1.431(17)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.424(17)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.47(2)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.36(2)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
B(1)-F(3)#1	1.195(19)
B(1)-F(3)	1.195(19)
B(1)-F(2)	1.26(3)
B(1)-F(1)	1.27(2)

C(1)-Sn(1)-C(1)#1	120.5(9)
C(1)-Sn(1)-C(4)	117.7(5)
C(1)#1-Sn(1)-C(4)	117.7(5)
C(1)-Sn(1)-N(1)	83.4(4)
C(1)#1-Sn(1)-N(1)	83.4(4)
C(4)-Sn(1)-N(1)	82.7(5)
C(1)-Sn(1)-F(1)	99.2(4)
C(1)#1-Sn(1)-F(1)	99.2(4)
C(4)-Sn(1)-F(1)	91.9(6)

N(1)-Sn(1)-F(1)	174.6(5)
C(6)-N(1)-C(3)#1	111.2(10)
C(6)-N(1)-C(3)	111.2(10)
C(3)#1-N(1)-C(3)	112.8(16)
C(6)-N(1)-Sn(1)	106.4(10)
C(3)#1-N(1)-Sn(1)	107.5(7)
C(3)-N(1)-Sn(1)	107.5(7)
C(2)-C(1)-Sn(1)	108.3(8)
C(2)-C(1)-H(1A)	110.0
Sn(1)-C(1)-H(1A)	110.0
C(2)-C(1)-H(1B)	110.0
Sn(1)-C(1)-H(1B)	110.0
H(1A)-C(1)-H(1B)	108.4
C(3)-C(2)-C(1)	123.3(11)
C(3)-C(2)-H(2A)	106.5
C(1)-C(2)-H(2A)	106.5
C(3)-C(2)-H(2B)	106.5
C(1)-C(2)-H(2B)	106.5
H(2A)-C(2)-H(2B)	106.5
C(2)-C(3)-N(1)	117.4(10)
C(2)-C(3)-H(3A)	108.0
N(1)-C(3)-H(3A)	108.0
C(2)-C(3)-H(3B)	108.0
N(1)-C(3)-H(3B)	108.0
H(3A)-C(3)-H(3B)	107.2
C(5)-C(4)-Sn(1)	106.1(9)
C(5)-C(4)-H(4A)	110.5
Sn(1)-C(4)-H(4A)	110.5
C(5)-C(4)-H(4B)	110.5
Sn(1)-C(4)-H(4B)	110.5
H(4A)-C(4)-H(4B)	108.7
C(6)-C(5)-C(4)	122.0(13)
C(6)-C(5)-H(5A)	106.8

C(4)-C(5)-H(5A)	106.8
C(6)-C(5)-H(5B)	106.8
C(4)-C(5)-H(5B)	106.8
H(5A)-C(5)-H(5B)	106.7
C(5)-C(6)-N(1)	122.7(15)
C(5)-C(6)-H(6A)	106.6
N(1)-C(6)-H(6A)	106.6
C(5)-C(6)-H(6B)	106.6
N(1)-C(6)-H(6B)	106.6
H(6A)-C(6)-H(6B)	106.6
F(3)#1-B(1)-F(3)	107(3)
F(3)#1-B(1)-F(2)	107.8(14)
F(3)-B(1)-F(2)	107.8(14)
F(3)#1-B(1)-F(1)	113.4(13)
F(3)-B(1)-F(1)	113.4(13)
F(2)-B(1)-F(1)	107(3)
B(1)-F(1)-Sn(1)	142.1(17)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for AK245a_0ma_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	57(1)	97(1)	48(1)	0	15(1)	0
N(1)	55(5)	56(5)	53(5)	0	10(4)	0
C(1)	117(10)	175(13)	163(13)	-129(12)	-12(7)	12(8)
C(2)	136(10)	71(7)	134(10)	-23(7)	-39(7)	-28(7)
C(3)	123(10)	111(11)	271(17)	-70(11)	105(10)	-71(9)
C(4)	59(7)	115(13)	91(7)	0	-27(5)	0
C(5)	116(10)	113(13)	52(6)	0	-26(6)	0

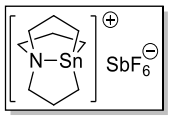
C(6)	100(9)	430(40)	46(6)	0	10(6)	0
B(1)	118(11)	58(10)	127(13)	0	84(12)	0
F(1)	156(11)	450(30)	133(8)	0	90(9)	0
F(2)	126(10)	520(40)	219(18)	0	65(10)	0
F(3)	429(18)	188(12)	313(14)	-106(12)	-22(16)	-99(13)

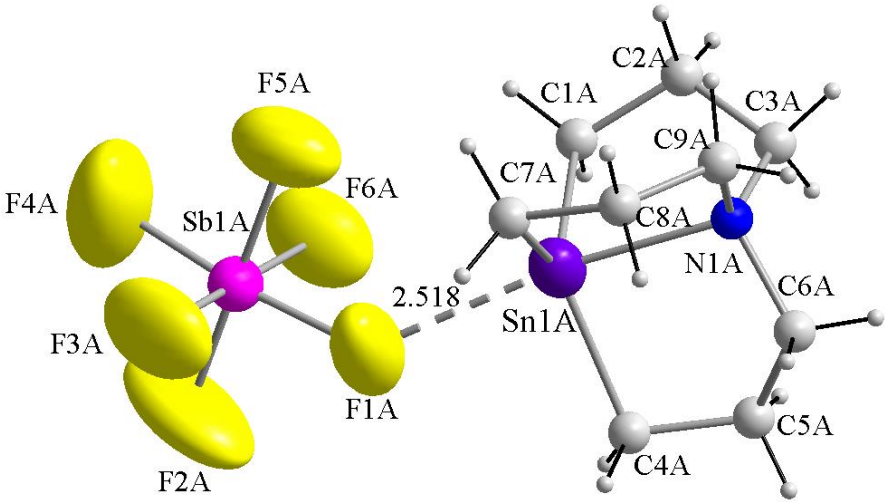
Table 5. Hydrogen coordinates (x 10^4) and displacement parameters ($Å^2$ x 10^3) for AK245a_0ma_a.

	x	y	z	U(eq)
H(1A)	1724	5538	5472	182
H(1B)	2435	4633	6318	182
H(2A)	3152	6010	4671	137
H(2B)	3838	4998	5461	137
H(3A)	4331	3621	4268	201
H(3B)	3563	4547	3493	201
H(4A)	93	1559	3671	106
H(4B)	93	3441	3671	106
H(5A)	1176	1571	2392	112
H(5B)	1176	3429	2392	112
H(6A)	2747	3429	2605	231
H(6B)	2747	1571	2605	231

X-Ray Data for Complex **2.6a**

From pentane/1,2-dichloroethane





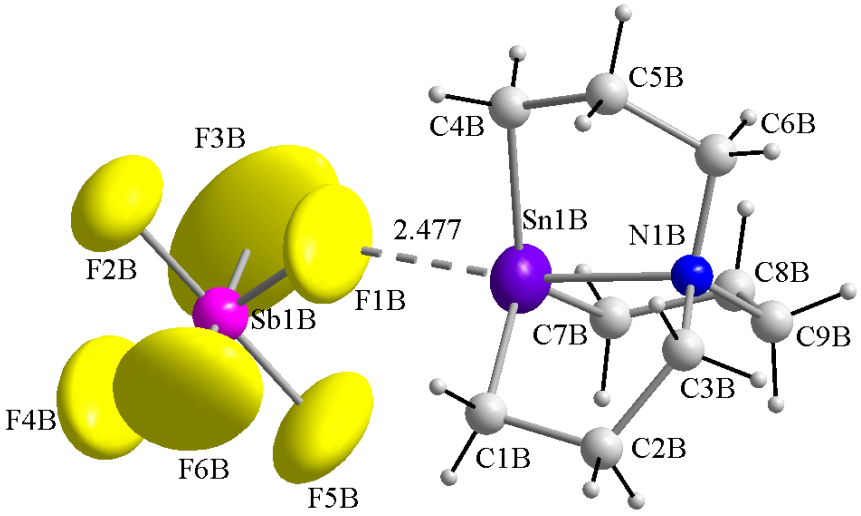


Table 1. Crystal data and structure refinement for complex **4a**

Identification code	AK-SbF6_0m	
Empirical formula	C18 H36 F12 N2 Sb2 Sn2	
Formula weight	989.37	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.5513(3) Å	α= 90°.
	b = 13.9626(3) Å	β= 93.7219(9)°.
	c = 15.0103(3) Å	γ = 90°.
Volume	3043.27(11) $Å^3$	
Z	4	
Density (calculated)	2.159 Mg/m^3	
Absorption coefficient	3.463 mm^{-1}	
F(000)	1872	
Crystal size	0.340 x 0.260 x 0.060 mm^3	
Theta range for data collection	1.402 to 27.994°.	
Index ranges	-19<=h<=19, -18<=k<=18, -19<=l<=19	
Reflections collected	31318	
Independent reflections	7352 [R(int) = 0.0250]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.5509	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7352 / 0 / 325	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1241	
R indices (all data)	R1 = 0.0627, wR2 = 0.1379	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.715 and -1.097 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for AK-SbF6_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1A)	3822(1)	1320(1)	1285(1)	53(1)
N(1A)	4541(4)	2411(4)	2142(4)	62(1)
C(1A)	4635(6)	1847(6)	267(5)	76(2)
C(2A)	5075(6)	2738(7)	625(5)	86(2)
C(3A)	5315(7)	2757(8)	1609(6)	102(3)
C(4A)	4389(7)	327(6)	2242(6)	90(3)
C(5A)	5097(7)	849(8)	2788(6)	101(3)
C(6A)	4873(7)	1857(8)	2966(6)	97(3)
C(7A)	2603(5)	2076(7)	1574(6)	83(2)
C(8A)	2896(6)	2734(7)	2320(8)	98(3)
C(9A)	3839(6)	3132(6)	2326(7)	91(3)
Sb(1A)	2590(1)	-231(1)	-690(1)	67(1)
F(1A)	3057(6)	-69(6)	465(4)	145(3)
F(2A)	2714(6)	-1500(5)	-665(9)	205(5)
F(3A)	1430(4)	-364(5)	-313(6)	150(3)
F(4A)	2104(9)	-235(10)	-1845(6)	236(6)
F(5A)	2477(5)	1128(5)	-728(6)	137(2)
F(6A)	3782(4)	-57(5)	-1043(5)	130(2)
Sn(1B)	8922(1)	3277(1)	-971(1)	62(1)
N(1B)	9610(4)	2251(4)	-1831(3)	59(1)
C(1B)	9619(7)	4340(6)	-1688(6)	88(2)
C(2B)	9947(7)	3826(7)	-2487(6)	95(3)
C(3B)	10296(6)	2818(7)	-2299(5)	83(2)
C(4B)	9675(6)	2557(6)	87(4)	79(2)
C(5B)	10383(6)	1963(7)	-353(5)	87(2)
C(6B)	10031(7)	1516(6)	-1235(5)	84(2)
C(7B)	7691(6)	2694(8)	-1559(7)	100(3)
C(8B)	7979(6)	1782(8)	-2006(7)	99(3)

C(9B)	8866(6)	1848(7)	-2450(5)	85(2)
Sb(1B)	7475(1)	5205(1)	366(1)	67(1)
F(1B)	8299(7)	4256(7)	226(6)	209(5)
F(2B)	7942(6)	5363(6)	1525(4)	149(3)
F(3B)	6703(11)	4420(14)	762(10)	373(13)
F(4B)	6806(12)	6278(10)	453(8)	291(9)
F(5B)	7059(8)	5066(8)	-796(5)	198(5)
F(6B)	8426(11)	5969(10)	-2(9)	273(7)

Table 3. Bond length [Å] and angles [°] for AK-SbF6_0m.

Sn(1A)-C(1A)	2.123(7)
Sn(1A)-C(4A)	2.124(8)
Sn(1A)-C(7A)	2.133(8)
Sn(1A)-N(1A)	2.213(5)
Sn(1A)-F(1A)	2.518(6)
N(1A)-C(9A)	1.473(10)
N(1A)-C(3A)	1.504(10)
N(1A)-C(6A)	1.512(11)
C(1A)-C(2A)	1.485(11)
C(1A)-H(1AA)	0.9700
C(1A)-H(1AB)	0.9700
C(2A)-C(3A)	1.496(12)
C(2A)-H(2AA)	0.9700
C(2A)-H(2AB)	0.9700
C(3A)-H(3AA)	0.9700
C(3A)-H(3AB)	0.9700
C(4A)-C(5A)	1.468(14)
C(4A)-H(4AA)	0.9700
C(4A)-H(4AB)	0.9700
C(5A)-C(6A)	1.473(14)

C(5A)-H(5AA)	0.9700
C(5A)-H(5AB)	0.9700
C(6A)-H(6AA)	0.9700
C(6A)-H(6AB)	0.9700
C(7A)-C(8A)	1.489(13)
C(7A)-H(7AA)	0.9700
C(7A)-H(7AB)	0.9700
C(8A)-C(9A)	1.479(12)
C(8A)-H(8AA)	0.9700
C(8A)-H(8AB)	0.9700
C(9A)-H(9AA)	0.9700
C(9A)-H(9AB)	0.9700
Sb(1A)-F(2A)	1.781(7)
Sb(1A)-F(3A)	1.825(6)
Sb(1A)-F(4A)	1.829(8)
Sb(1A)-F(1A)	1.835(6)
Sb(1A)-F(6A)	1.862(6)
Sb(1A)-F(5A)	1.905(7)
Sn(1B)-C(7B)	2.108(9)
Sn(1B)-C(4B)	2.123(8)
Sn(1B)-C(1B)	2.129(9)
Sn(1B)-N(1B)	2.210(5)
Sn(1B)-F(1B)	2.477(7)
N(1B)-C(6B)	1.469(9)
N(1B)-C(3B)	1.486(10)
N(1B)-C(9B)	1.491(9)
C(1B)-C(2B)	1.502(13)
C(1B)-H(1BA)	0.9700
C(1B)-H(1BB)	0.9700
C(2B)-C(3B)	1.517(13)
C(2B)-H(2BA)	0.9700
C(2B)-H(2BB)	0.9700
C(3B)-H(3BA)	0.9700

C(3B)-H(3BB)	0.9700
C(4B)-C(5B)	1.507(12)
C(4B)-H(4BA)	0.9700
C(4B)-H(4BB)	0.9700
C(5B)-C(6B)	1.522(11)
C(5B)-H(5BA)	0.9700
C(5B)-H(5BB)	0.9700
C(6B)-H(6BA)	0.9700
C(6B)-H(6BB)	0.9700
C(7B)-C(8B)	1.511(14)
C(7B)-H(7BA)	0.9700
C(7B)-H(7BB)	0.9700
C(8B)-C(9B)	1.494(12)
C(8B)-H(8BA)	0.9700
C(8B)-H(8BB)	0.9700
C(9B)-H(9BA)	0.9700
C(9B)-H(9BB)	0.9700
Sb(1B)-F(3B)	1.703(9)
Sb(1B)-F(4B)	1.796(9)
Sb(1B)-F(1B)	1.808(7)
Sb(1B)-F(5B)	1.818(7)
Sb(1B)-F(2B)	1.840(6)
Sb(1B)-F(6B)	1.859(10)

C(1A)-Sn(1A)-C(4A)	120.2(4)
C(1A)-Sn(1A)-C(7A)	119.0(4)
C(4A)-Sn(1A)-C(7A)	118.5(4)
C(1A)-Sn(1A)-N(1A)	85.2(2)
C(4A)-Sn(1A)-N(1A)	84.7(3)
C(7A)-Sn(1A)-N(1A)	84.8(3)
C(1A)-Sn(1A)-F(1A)	99.5(3)
C(4A)-Sn(1A)-F(1A)	88.2(3)
C(7A)-Sn(1A)-F(1A)	97.6(3)

N(1A)-Sn(1A)-F(1A)	172.8(2)
C(9A)-N(1A)-C(3A)	115.7(7)
C(9A)-N(1A)-C(6A)	112.7(6)
C(3A)-N(1A)-C(6A)	112.8(7)
C(9A)-N(1A)-Sn(1A)	105.8(4)
C(3A)-N(1A)-Sn(1A)	104.7(4)
C(6A)-N(1A)-Sn(1A)	103.7(5)
C(2A)-C(1A)-Sn(1A)	106.1(5)
C(2A)-C(1A)-H(1AA)	110.5
Sn(1A)-C(1A)-H(1AA)	110.5
C(2A)-C(1A)-H(1AB)	110.5
Sn(1A)-C(1A)-H(1AB)	110.5
H(1AA)-C(1A)-H(1AB)	108.7
C(1A)-C(2A)-C(3A)	116.1(7)
C(1A)-C(2A)-H(2AA)	108.3
C(3A)-C(2A)-H(2AA)	108.3
C(1A)-C(2A)-H(2AB)	108.3
C(3A)-C(2A)-H(2AB)	108.3
H(2AA)-C(2A)-H(2AB)	107.4
C(2A)-C(3A)-N(1A)	112.6(7)
C(2A)-C(3A)-H(3AA)	109.1
N(1A)-C(3A)-H(3AA)	109.1
C(2A)-C(3A)-H(3AB)	109.1
N(1A)-C(3A)-H(3AB)	109.1
H(3AA)-C(3A)-H(3AB)	107.8
C(5A)-C(4A)-Sn(1A)	106.3(6)
C(5A)-C(4A)-H(4AA)	110.5
Sn(1A)-C(4A)-H(4AA)	110.5
C(5A)-C(4A)-H(4AB)	110.5
Sn(1A)-C(4A)-H(4AB)	110.5
H(4AA)-C(4A)-H(4AB)	108.7
C(4A)-C(5A)-C(6A)	114.8(8)
C(4A)-C(5A)-H(5AA)	108.6

C(6A)-C(5A)-H(5AA)	108.6
C(4A)-C(5A)-H(5AB)	108.6
C(6A)-C(5A)-H(5AB)	108.6
H(5AA)-C(5A)-H(5AB)	107.5
C(5A)-C(6A)-N(1A)	113.8(7)
C(5A)-C(6A)-H(6AA)	108.8
N(1A)-C(6A)-H(6AA)	108.8
C(5A)-C(6A)-H(6AB)	108.8
N(1A)-C(6A)-H(6AB)	108.8
H(6AA)-C(6A)-H(6AB)	107.7
C(8A)-C(7A)-Sn(1A)	104.9(5)
C(8A)-C(7A)-H(7AA)	110.8
Sn(1A)-C(7A)-H(7AA)	110.8
C(8A)-C(7A)-H(7AB)	110.8
Sn(1A)-C(7A)-H(7AB)	110.8
H(7AA)-C(7A)-H(7AB)	108.9
C(9A)-C(8A)-C(7A)	117.2(7)
C(9A)-C(8A)-H(8AA)	108.0
C(7A)-C(8A)-H(8AA)	108.0
C(9A)-C(8A)-H(8AB)	108.0
C(7A)-C(8A)-H(8AB)	108.0
H(8AA)-C(8A)-H(8AB)	107.2
N(1A)-C(9A)-C(8A)	113.3(7)
N(1A)-C(9A)-H(9AA)	108.9
C(8A)-C(9A)-H(9AA)	108.9
N(1A)-C(9A)-H(9AB)	108.9
C(8A)-C(9A)-H(9AB)	108.9
H(9AA)-C(9A)-H(9AB)	107.7
F(2A)-Sb(1A)-F(3A)	89.2(4)
F(2A)-Sb(1A)-F(4A)	92.9(6)
F(3A)-Sb(1A)-F(4A)	89.1(5)
F(2A)-Sb(1A)-F(1A)	94.1(5)
F(3A)-Sb(1A)-F(1A)	90.7(4)

F(4A)-Sb(1A)-F(1A)	173.0(5)
F(2A)-Sb(1A)-F(6A)	92.4(4)
F(3A)-Sb(1A)-F(6A)	177.8(4)
F(4A)-Sb(1A)-F(6A)	92.4(5)
F(1A)-Sb(1A)-F(6A)	87.6(4)
F(2A)-Sb(1A)-F(5A)	179.0(4)
F(3A)-Sb(1A)-F(5A)	91.8(3)
F(4A)-Sb(1A)-F(5A)	87.0(5)
F(1A)-Sb(1A)-F(5A)	86.0(4)
F(6A)-Sb(1A)-F(5A)	86.6(3)
Sb(1A)-F(1A)-Sn(1A)	133.0(3)
C(7B)-Sn(1B)-C(4B)	120.9(4)
C(7B)-Sn(1B)-C(1B)	118.5(4)
C(4B)-Sn(1B)-C(1B)	117.9(3)
C(7B)-Sn(1B)-N(1B)	84.9(3)
C(4B)-Sn(1B)-N(1B)	84.2(3)
C(1B)-Sn(1B)-N(1B)	84.7(3)
C(7B)-Sn(1B)-F(1B)	100.1(4)
C(4B)-Sn(1B)-F(1B)	85.1(3)
C(1B)-Sn(1B)-F(1B)	101.0(4)
N(1B)-Sn(1B)-F(1B)	169.2(2)
C(6B)-N(1B)-C(3B)	113.1(6)
C(6B)-N(1B)-C(9B)	111.9(7)
C(3B)-N(1B)-C(9B)	112.9(6)
C(6B)-N(1B)-Sn(1B)	106.5(4)
C(3B)-N(1B)-Sn(1B)	105.9(4)
C(9B)-N(1B)-Sn(1B)	105.7(4)
C(2B)-C(1B)-Sn(1B)	104.8(6)
C(2B)-C(1B)-H(1BA)	110.8
Sn(1B)-C(1B)-H(1BA)	110.8
C(2B)-C(1B)-H(1BB)	110.8
Sn(1B)-C(1B)-H(1BB)	110.8
H(1BA)-C(1B)-H(1BB)	108.9

C(1B)-C(2B)-C(3B)	114.5(7)
C(1B)-C(2B)-H(2BA)	108.6
C(3B)-C(2B)-H(2BA)	108.6
C(1B)-C(2B)-H(2BB)	108.6
C(3B)-C(2B)-H(2BB)	108.6
H(2BA)-C(2B)-H(2BB)	107.6
N(1B)-C(3B)-C(2B)	110.8(7)
N(1B)-C(3B)-H(3BA)	109.5
C(2B)-C(3B)-H(3BA)	109.5
N(1B)-C(3B)-H(3BB)	109.5
C(2B)-C(3B)-H(3BB)	109.5
H(3BA)-C(3B)-H(3BB)	108.1
C(5B)-C(4B)-Sn(1B)	105.5(5)
C(5B)-C(4B)-H(4BA)	110.6
Sn(1B)-C(4B)-H(4BA)	110.6
C(5B)-C(4B)-H(4BB)	110.6
Sn(1B)-C(4B)-H(4BB)	110.6
H(4BA)-C(4B)-H(4BB)	108.8
C(4B)-C(5B)-C(6B)	113.9(7)
C(4B)-C(5B)-H(5BA)	108.8
C(6B)-C(5B)-H(5BA)	108.8
C(4B)-C(5B)-H(5BB)	108.8
C(6B)-C(5B)-H(5BB)	108.8
H(5BA)-C(5B)-H(5BB)	107.7
N(1B)-C(6B)-C(5B)	110.3(6)
N(1B)-C(6B)-H(6BA)	109.6
C(5B)-C(6B)-H(6BA)	109.6
N(1B)-C(6B)-H(6BB)	109.6
C(5B)-C(6B)-H(6BB)	109.6
H(6BA)-C(6B)-H(6BB)	108.1
C(8B)-C(7B)-Sn(1B)	105.0(5)
C(8B)-C(7B)-H(7BA)	110.8
Sn(1B)-C(7B)-H(7BA)	110.8

C(8B)-C(7B)-H(7BB)	110.8
Sn(1B)-C(7B)-H(7BB)	110.8
H(7BA)-C(7B)-H(7BB)	108.8
C(9B)-C(8B)-C(7B)	114.8(8)
C(9B)-C(8B)-H(8BA)	108.6
C(7B)-C(8B)-H(8BA)	108.6
C(9B)-C(8B)-H(8BB)	108.6
C(7B)-C(8B)-H(8BB)	108.6
H(8BA)-C(8B)-H(8BB)	107.5
N(1B)-C(9B)-C(8B)	111.0(6)
N(1B)-C(9B)-H(9BA)	109.4
C(8B)-C(9B)-H(9BA)	109.4
N(1B)-C(9B)-H(9BB)	109.4
C(8B)-C(9B)-H(9BB)	109.4
H(9BA)-C(9B)-H(9BB)	108.0
F(3B)-Sb(1B)-F(4B)	97.9(10)
F(3B)-Sb(1B)-F(1B)	91.5(9)
F(4B)-Sb(1B)-F(1B)	170.5(8)
F(3B)-Sb(1B)-F(5B)	94.6(6)
F(4B)-Sb(1B)-F(5B)	90.6(5)
F(1B)-Sb(1B)-F(5B)	89.6(4)
F(3B)-Sb(1B)-F(2B)	87.7(6)
F(4B)-Sb(1B)-F(2B)	90.0(4)
F(1B)-Sb(1B)-F(2B)	89.4(4)
F(5B)-Sb(1B)-F(2B)	177.6(5)
F(3B)-Sb(1B)-F(6B)	173.2(9)
F(4B)-Sb(1B)-F(6B)	87.7(8)
F(1B)-Sb(1B)-F(6B)	82.8(7)
F(5B)-Sb(1B)-F(6B)	89.1(6)
F(2B)-Sb(1B)-F(6B)	88.6(5)
Sb(1B)-F(1B)-Sn(1B)	139.9(5)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for AK-SbF6_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1A)	56(1)	54(1)	49(1)	-2(1)	6(1)	-9(1)
N(1A)	57(3)	68(3)	62(3)	-17(3)	9(2)	-11(3)
C(1A)	77(5)	100(6)	52(4)	1(3)	10(3)	-19(4)
C(2A)	82(5)	97(6)	81(5)	12(4)	16(4)	-33(5)
C(3A)	84(6)	118(8)	104(7)	-34(6)	18(5)	-47(6)
C(4A)	117(7)	66(5)	88(6)	24(4)	29(5)	27(5)
C(5A)	112(7)	116(8)	74(5)	24(5)	-5(5)	28(6)
C(6A)	88(6)	137(9)	64(4)	-26(5)	-13(4)	21(6)
C(7A)	50(4)	93(6)	105(6)	1(5)	4(4)	-3(4)
C(8A)	69(5)	82(6)	145(8)	-30(6)	32(5)	7(4)
C(9A)	88(6)	67(5)	119(7)	-32(5)	8(5)	7(4)
Sb(1A)	57(1)	74(1)	70(1)	-20(1)	4(1)	-12(1)
F(1A)	190(7)	158(6)	82(4)	4(4)	-16(4)	-87(5)
F(2A)	148(7)	64(4)	409(16)	-28(6)	58(9)	8(4)
F(3A)	69(3)	145(6)	241(9)	24(6)	46(4)	-15(4)
F(4A)	255(12)	326(15)	120(6)	16(8)	-54(7)	-120(11)
F(5A)	114(5)	96(4)	205(7)	33(4)	30(5)	3(3)
F(6A)	91(4)	129(5)	179(6)	-9(4)	66(4)	0(3)
Sn(1B)	56(1)	71(1)	61(1)	-9(1)	6(1)	12(1)
N(1B)	50(3)	74(4)	54(3)	-11(2)	2(2)	6(2)
C(1B)	93(6)	72(5)	98(6)	11(4)	-5(5)	-3(4)
C(2B)	95(6)	109(7)	81(5)	33(5)	5(4)	-9(5)
C(3B)	70(5)	111(7)	69(4)	-5(4)	24(4)	-2(4)
C(4B)	101(6)	91(5)	45(3)	-2(3)	-4(3)	-14(5)
C(5B)	87(6)	97(6)	75(5)	11(4)	-22(4)	16(5)
C(6B)	94(6)	76(5)	80(5)	-5(4)	-2(4)	28(4)
C(7B)	51(4)	142(9)	105(6)	-12(6)	0(4)	-2(5)
C(8B)	75(6)	123(8)	96(6)	-14(6)	-15(5)	-33(5)

C(9B)	81(5)	103(6)	71(5)	-30(4)	-6(4)	-11(5)
Sb(1B)	64(1)	69(1)	70(1)	-10(1)	5(1)	15(1)
F(1B)	247(11)	220(9)	159(7)	-63(7)	1(7)	159(9)
F(2B)	169(7)	185(7)	90(4)	-22(4)	-18(4)	31(6)
F(3B)	342(19)	520(30)	268(15)	-19(16)	84(13)	-340(20)
F(4B)	410(20)	259(13)	198(10)	-64(9)	-52(11)	237(14)
F(5B)	227(10)	257(11)	101(5)	-49(6)	-59(6)	51(8)
F(6B)	320(16)	233(13)	267(13)	66(10)	22(12)	-154(12)

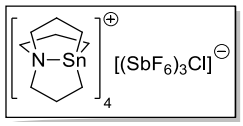
Table 5. Hydrogen coordinates (x 10^{4}) and isotropic displacement parameters ($Å^2$x 10^{3}) for AK-SbF6_0m.

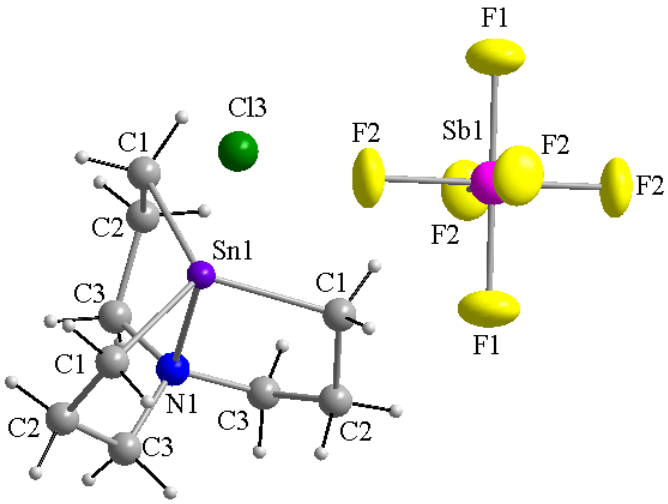
	x	y	z	U(eq)
H(1AA)	5099	1381	128	91
H(1AB)	4252	1981	-272	91
H(2AA)	4663	3270	478	103
H(2AB)	5633	2845	320	103
H(3AA)	5476	3406	1788	122
H(3AB)	5852	2356	1742	122
H(4AA)	3915	91	2612	108
H(4AB)	4659	-213	1948	108
H(5AA)	5668	828	2488	121
H(5AB)	5202	519	3354	121
H(6AA)	5417	2170	3237	117
H(6AB)	4401	1877	3393	117
H(7AA)	2361	2433	1057	99
H(7AB)	2133	1636	1754	99
H(8AA)	2467	3266	2311	118
H(8AB)	2840	2394	2877	118

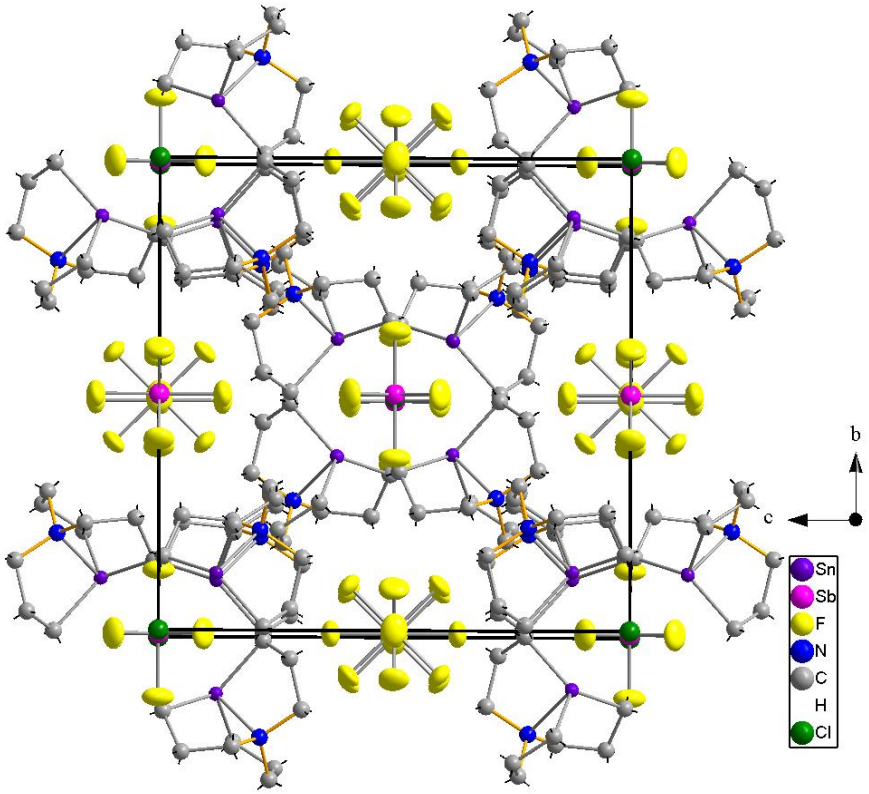
H(9AA)	3849	3636	1882	110
H(9AB)	3995	3418	2905	110
H(1BA)	9205	4858	-1871	106
H(1BB)	10135	4601	-1325	106
H(2BA)	10437	4197	-2727	114
H(2BB)	9443	3795	-2943	114
H(3BA)	10417	2505	-2857	99
H(3BB)	10870	2846	-1933	99
H(4BA)	9971	3013	499	95
H(4BB)	9271	2151	412	95
H(5BA)	10592	1456	53	105
H(5BB)	10909	2365	-456	105
H(6BA)	10538	1216	-1517	100
H(6BB)	9580	1026	-1126	100
H(7BA)	7260	2558	-1108	119
H(7BB)	7404	3133	-1993	119
H(8BA)	8033	1278	-1561	118
H(8BB)	7496	1598	-2448	118
H(9BA)	9044	1215	-2643	103
H(9BB)	8783	2252	-2975	103

X-Ray Data for Complex **2.6b**

From pentane/1,2-dichloroethane







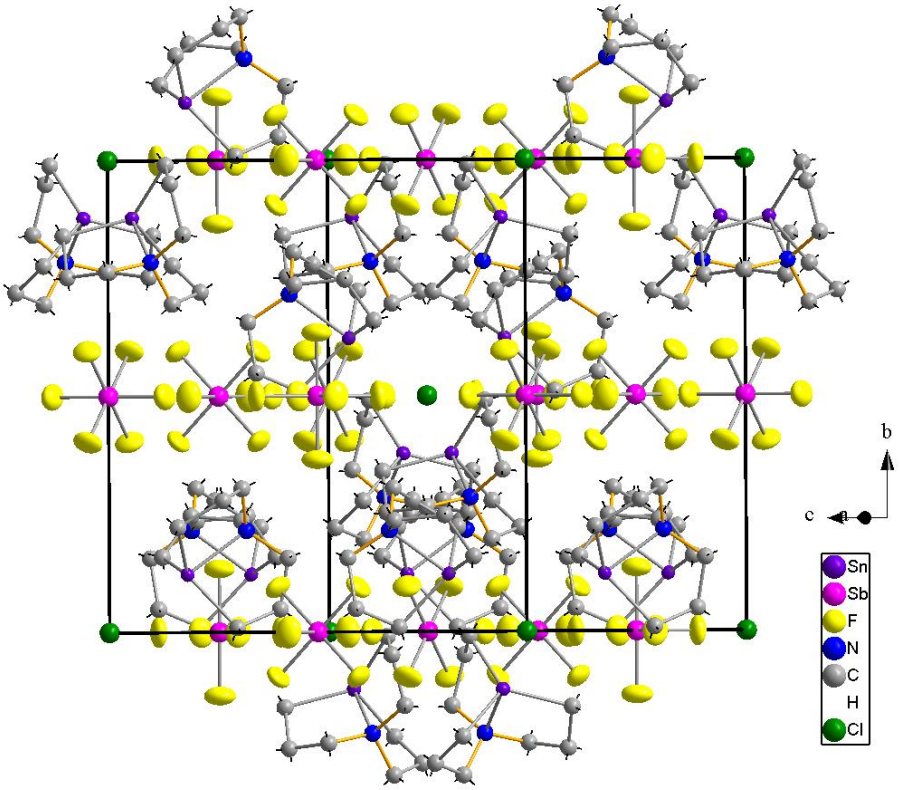


Table 1. Crystal data and structure refinement for complex **4b**

Identification code	AK_236_0m	
Empirical formula	C36 H72 Cl F18 N4 Sb3 Sn4	
Formula weight	1778.43	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	I23	
Unit cell dimensions	a = 13.78560(10) Å	α= 90°.
	b = 13.78560(10) Å	β= 90°.
	c = 13.78560(10) Å	γ = 90°.
Volume	2619.85(6) $Å^3$	
Z	2	
Density (calculated)	2.254 Mg/m^3	
Absorption coefficient	3.545 mm^{-1}	

F(000)	1696
Crystal size	0.220 x 0.120 x 0.040 mm^3
Theta range for data collection	2.089 to 26.328°.
Index ranges	-17<=h<=17, -17<=k<=17, -17<=l<=17
Reflections collected	19515
Independent reflections	906 [R(int) = 0.0134]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.6684
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	906 / 13 / 52
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)]	R1 = 0.0080, wR2 = 0.0210
R indices (all data)	R1 = 0.0080, wR2 = 0.0210
Absolute structure parameter	0.005(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.286 and -0.176 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for AK_236_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	8777(1)	1223(1)	8777(1)	18(1)
Sb(1)	5000	0	10000	26(1)
F(1)	5000	-1346(2)	10000	64(1)
F(2)	5963(1)	-2(2)	9047(1)	57(1)
N(1)	7846(1)	2154(1)	7846(1)	21(1)
C(1)	8404(2)	98(2)	7776(1)	26(1)
C(2)	7530(2)	491(2)	7209(2)	27(1)
C(3)	7641(2)	1568(1)	6958(1)	25(1)
Cl(3)	10000	0	10000	18(1)

Table 3. Bond lengths [Å] and angles [°] for AK_236_0m.

Sn(1)-C(1)#1	2.139(2)
Sn(1)-C(1)#2	2.139(2)
Sn(1)-C(1)	2.139(2)
Sn(1)-N(1)	2.223(3)
Sb(1)-F(1)#3	1.855(3)
Sb(1)-F(1)	1.855(3)
Sb(1)-F(2)#4	1.8674(14)
Sb(1)-F(2)#3	1.8674(14)
Sb(1)-F(2)#5	1.8674(14)
Sb(1)-F(2)	1.8674(14)
N(1)-C(3)	1.493(2)
N(1)-C(3)#2	1.493(2)
N(1)-C(3)#1	1.493(2)
C(1)-C(2)	1.536(3)
C(1)-H(1B)	0.9900
C(1)-H(1C)	0.9900
C(2)-C(3)	1.531(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(1)#1-Sn(1)-C(1)#2	119.164(17)
C(1)#1-Sn(1)-C(1)	119.163(17)
C(1)#2-Sn(1)-C(1)	119.164(17)
C(1)#1-Sn(1)-N(1)	84.72(5)
C(1)#2-Sn(1)-N(1)	84.72(5)
C(1)-Sn(1)-N(1)	84.72(5)
F(1)#3-Sb(1)-F(1)	180.0
F(1)#3-Sb(1)-F(2)#4	89.93(8)
F(1)-Sb(1)-F(2)#4	90.07(8)

F(1)#3-Sb(1)-F(2)#3	89.93(8)
F(1)-Sb(1)-F(2)#3	90.07(8)
F(2)#4-Sb(1)-F(2)#3	179.86(16)
F(1)#3-Sb(1)-F(2)#5	90.07(8)
F(1)-Sb(1)-F(2)#5	89.93(8)
F(2)#4-Sb(1)-F(2)#5	90.61(9)
F(2)#3-Sb(1)-F(2)#5	89.39(9)
F(1)#3-Sb(1)-F(2)	90.07(8)
F(1)-Sb(1)-F(2)	89.93(8)
F(2)#4-Sb(1)-F(2)	89.39(9)
F(2)#3-Sb(1)-F(2)	90.61(9)
F(2)#5-Sb(1)-F(2)	179.87(16)
C(3)-N(1)-C(3)#2	113.03(11)
C(3)-N(1)-C(3)#1	113.03(11)
C(3)#2-N(1)-C(3)#1	113.03(11)
C(3)-N(1)-Sn(1)	105.62(14)
C(3)#2-N(1)-Sn(1)	105.62(14)
C(3)#1-N(1)-Sn(1)	105.62(14)
C(2)-C(1)-Sn(1)	105.08(13)
C(2)-C(1)-H(1B)	110.7
Sn(1)-C(1)-H(1B)	110.7
C(2)-C(1)-H(1C)	110.7
Sn(1)-C(1)-H(1C)	110.7
H(1B)-C(1)-H(1C)	108.8
C(3)-C(2)-C(1)	112.26(18)
C(3)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2A)	109.2
C(3)-C(2)-H(2B)	109.2
C(1)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
N(1)-C(3)-C(2)	111.04(17)
N(1)-C(3)-H(3A)	109.4
C(2)-C(3)-H(3A)	109.4

N(1)-C(3)-H(3B)	109.4
C(2)-C(3)-H(3B)	109.4
H(3A)-C(3)-H(3B)	108.0

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,-z+1,x #2 z,-x+1,-y+1 #3 -x+1,-y,z

#4 x,-y,-z+2 #5 -x+1,y,-z+2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for AK_236_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	18(1)	18(1)	18(1)	1(1)	-1(1)	1(1)
Sb(1)	22(1)	31(1)	24(1)	0	0	0
F(1)	66(1)	32(1)	96(2)	0	5(2)	0
F(2)	42(1)	85(1)	43(1)	-2(1)	20(1)	-4(1)
N(1)	21(1)	21(1)	21(1)	1(1)	-1(1)	1(1)
C(1)	34(1)	19(1)	24(1)	0(1)	0(1)	1(1)
C(2)	32(1)	26(1)	22(1)	-1(1)	-3(1)	-5(1)
C(3)	29(1)	26(1)	18(1)	1(1)	-4(1)	-1(1)
Cl(3)	18(1)	18(1)	18(1)	0	0	0

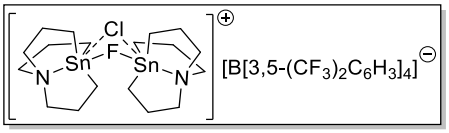
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 x\ 10^3$) for AK_236_0m.

	x	y	z	U(eq)
H(1B)	8953	-41	7333	31

H(1C)	8230	-505	8125	31
H(2A)	7454	115	6602	32
H(2B)	6935	401	7601	32
H(3A)	8178	1649	6489	30
H(3B)	7037	1804	6650	30

X-Ray Data for Complex **2.8**

From pentane/1,2-dichloroethane



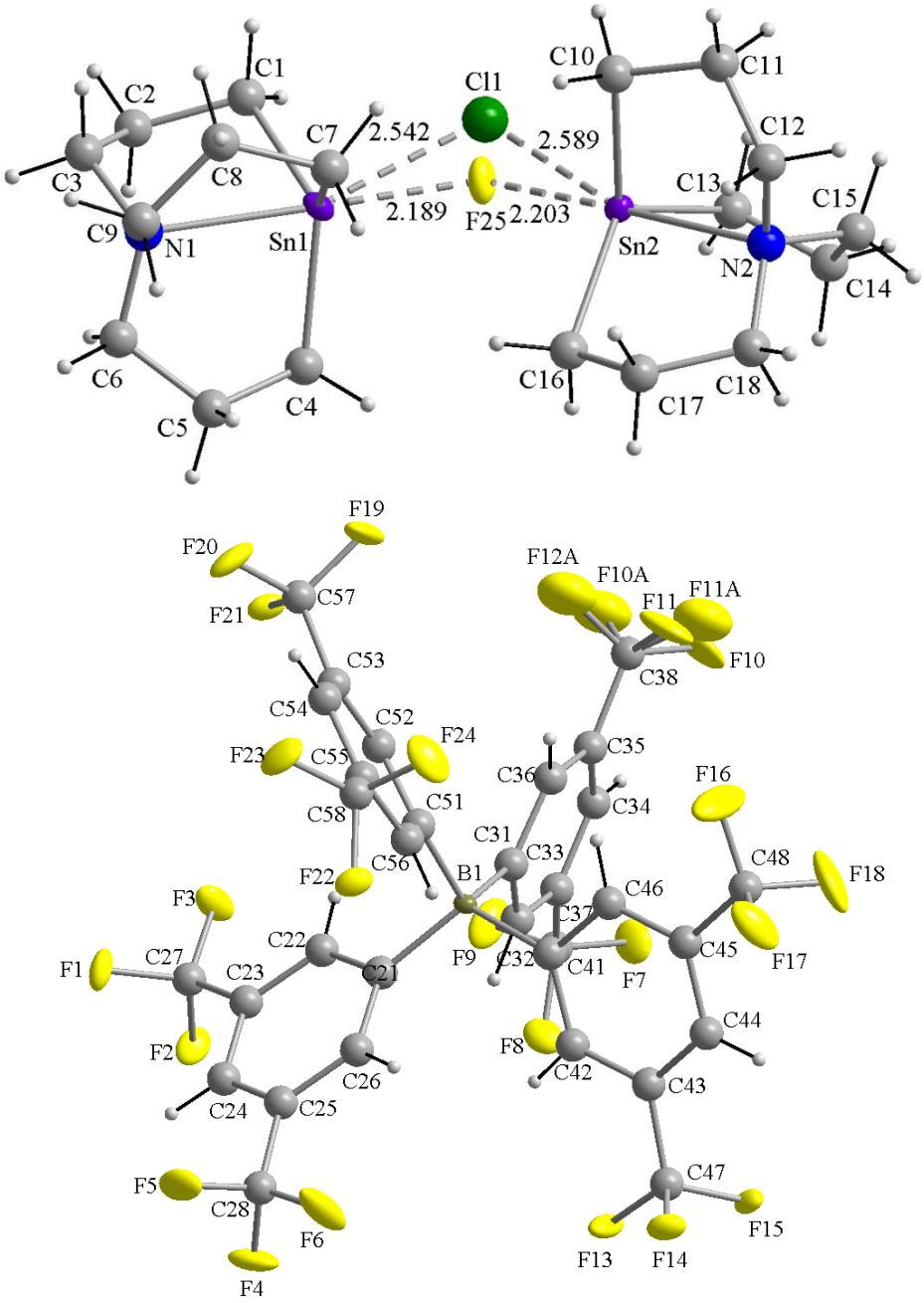


Table 1. Crystal data and structure refinement for d14106.

Identification code	d14106	
Empirical formula	C50 H48 B Cl0.20 F24.81 N2 Sn2	
Formula weight	1403.30	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 25.5057(8) Å	α= 90°.
	b = 14.6814(4) Å	β= 109.3070(10)°.
	c = 30.0172(9) Å	γ = 90°.
Volume	10608.1(5) $Å^3$	
Z	8	
Density (calculated)	1.757 Mg/m^3	
Absorption coefficient	1.077 mm^{-1}	
F(000)	5548	
Crystal size	0.360 x 0.220 x 0.200 mm^3	
Theta range for data collection	1.438 to 27.574°.	
Index ranges	-32<=h<=33, -18<=k<=19, -39<=l<=38	
Reflections collected	40571	
Independent reflections	12234 [R(int) = 0.0258]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6804	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12234 / 46 / 747	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.0909	
R indices (all data)	R1 = 0.0517, wR2 = 0.0978	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.532 and -2.054 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d14106. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	6607(1)	3744(1)	7355(1)	16(1)
Sn(2)	5037(1)	3761(1)	6514(1)	14(1)
F(25)	5732(1)	3346(2)	7142(2)	25(1)
Cl(1)	5637(2)	3431(4)	7380(2)	27(2)
N(1)	7537(1)	4256(2)	7567(1)	19(1)
N(2)	4299(1)	4162(2)	5836(1)	17(1)
C(1)	6854(2)	3553(4)	8101(2)	42(1)
C(2)	7485(2)	3504(3)	8285(1)	40(1)
C(3)	7751(2)	4271(4)	8084(1)	40(1)
C(4)	6908(2)	2774(3)	6969(1)	28(1)
C(5)	7433(2)	3176(3)	6911(1)	29(1)
C(6)	7820(2)	3589(3)	7357(2)	29(1)
C(7)	6462(2)	5110(3)	7084(2)	29(1)
C(8)	6984(2)	5665(3)	7337(2)	28(1)
C(9)	7511(2)	5173(3)	7347(2)	28(1)
C(10)	4855(2)	5075(3)	6737(2)	36(1)
C(11)	4284(2)	5350(3)	6417(2)	32(1)
C(12)	4168(2)	5126(3)	5907(2)	37(1)
C(13)	4477(2)	2683(3)	6519(2)	31(1)
C(14)	4038(2)	2632(3)	6031(1)	28(1)
C(15)	3834(2)	3549(3)	5822(2)	35(1)
C(16)	5476(2)	3760(3)	6017(1)	27(1)
C(17)	5121(2)	4241(3)	5576(1)	32(1)
C(18)	4509(2)	4054(3)	5439(1)	34(1)
F(1)	2955(1)	6668(2)	4278(1)	24(1)
F(2)	3667(1)	5911(2)	4691(1)	26(1)
F(3)	3755(1)	7305(2)	4513(1)	29(1)
F(4)	2734(1)	5251(2)	5899(1)	35(1)

F(5)	2040(1)	6112(2)	5603(1)	36(1)
F(6)	2583(1)	6352(2)	6304(1)	56(1)
F(7)	6185(1)	7517(2)	6149(1)	33(1)
F(8)	5460(1)	6715(2)	6087(1)	29(1)
F(9)	5587(1)	7254(2)	5467(1)	40(1)
F(10)	6059(1)	10833(2)	6059(2)	50(1)
F(11)	5359(2)	11462(2)	6126(2)	45(1)
F(12)	5354(3)	11085(4)	5427(2)	81(2)
F(10A)	5732(7)	10797(10)	5521(5)	74(3)
F(11A)	5701(8)	11456(8)	6188(4)	74(3)
F(12A)	5113(5)	11321(10)	5542(5)	74(3)
F(13)	4237(1)	6568(1)	7392(1)	28(1)
F(14)	3955(1)	7256(2)	7902(1)	24(1)
F(15)	4821(1)	7231(2)	7988(1)	25(1)
F(16)	4123(2)	11391(2)	7343(1)	63(1)
F(17)	3933(1)	10698(2)	7893(1)	42(1)
F(18)	4760(1)	10828(2)	7919(1)	52(1)
F(19)	3455(1)	12072(2)	4882(1)	43(1)
F(20)	2627(1)	11701(2)	4465(1)	32(1)
F(21)	3313(1)	10844(1)	4469(1)	23(1)
F(22)	1995(1)	10176(1)	6138(1)	22(1)
F(23)	1680(1)	11145(2)	5582(1)	32(1)
F(24)	2301(1)	11539(2)	6234(1)	37(1)
C(21)	3559(1)	8010(2)	5784(1)	10(1)
C(22)	3608(1)	7760(2)	5347(1)	11(1)
C(23)	3330(1)	7021(2)	5091(1)	11(1)
C(24)	2978(1)	6491(2)	5255(1)	12(1)
C(25)	2925(1)	6722(2)	5686(1)	12(1)
C(26)	3204(1)	7470(2)	5940(1)	11(1)
C(27)	3427(1)	6739(2)	4644(1)	15(1)
C(28)	2572(1)	6124(2)	5874(1)	18(1)
C(31)	4485(1)	9029(2)	5989(1)	12(1)
C(32)	4805(1)	8251(2)	5992(1)	13(1)

C(33)	5330(1)	8298(2)	5949(1)	18(1)
C(34)	5564(1)	9135(3)	5909(1)	24(1)
C(35)	5264(2)	9913(3)	5918(2)	26(1)
C(36)	4735(1)	9861(2)	5959(1)	19(1)
C(37)	5638(1)	7450(3)	5916(1)	21(1)
C(38)	5501(1)	10817(3)	5867(1)	42(1)
C(41)	3993(1)	8948(2)	6622(1)	10(1)
C(42)	4096(1)	8156(2)	6897(1)	11(1)
C(43)	4246(1)	8177(2)	7386(1)	12(1)
C(44)	4306(1)	8997(2)	7628(1)	14(1)
C(45)	4206(1)	9790(2)	7363(1)	14(1)
C(46)	4052(1)	9769(2)	6873(1)	12(1)
C(47)	4316(1)	7310(2)	7661(1)	13(1)
C(48)	4248(1)	10676(2)	7621(1)	18(1)
C(51)	3440(1)	9755(2)	5793(1)	10(1)
C(52)	3451(1)	10202(2)	5385(1)	13(1)
C(53)	3056(1)	10847(2)	5158(1)	14(1)
C(54)	2624(1)	11070(2)	5323(1)	14(1)
C(55)	2596(1)	10619(2)	5721(1)	13(1)
C(56)	2994(1)	9978(2)	5949(1)	12(1)
C(57)	3115(2)	11358(2)	4746(1)	20(1)
C(58)	2144(1)	10871(2)	5917(1)	18(1)
B(1)	3869(1)	8936(2)	6049(1)	11(1)

Table 3. Bond lengths [Å] and angles [°] for d14106.

Sn(1)-C(4)	2.133(4)
Sn(1)-C(1)	2.135(4)
Sn(1)-C(7)	2.148(4)
Sn(1)-F(25)	2.189(3)
Sn(1)-N(1)	2.366(3)
Sn(1)-Cl(1)	2.542(6)
Sn(2)-C(13)	2.136(4)
Sn(2)-C(10)	2.141(4)
Sn(2)-C(16)	2.143(4)
Sn(2)-F(25)	2.203(3)
Sn(2)-N(2)	2.345(3)
Sn(2)-Cl(1)	2.589(6)
N(1)-C(3)	1.465(5)
N(1)-C(6)	1.475(5)
N(1)-C(9)	1.491(5)
N(2)-C(18)	1.469(5)
N(2)-C(15)	1.478(5)
N(2)-C(12)	1.486(5)
C(1)-C(2)	1.522(7)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.536(7)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.524(5)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.504(6)
C(5)-H(5A)	0.9900

C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.533(5)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.517(5)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.512(6)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.497(6)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.522(5)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.503(6)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.510(5)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.502(6)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900

C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
F(1)-C(27)	1.338(4)
F(2)-C(27)	1.347(4)
F(3)-C(27)	1.328(4)
F(4)-C(28)	1.341(4)
F(5)-C(28)	1.331(4)
F(6)-C(28)	1.324(4)
F(7)-C(37)	1.341(4)
F(8)-C(37)	1.338(4)
F(9)-C(37)	1.343(4)
F(10)-C(38)	1.347(4)
F(11)-C(38)	1.350(4)
F(12)-C(38)	1.309(4)
F(10A)-C(38)	1.353(5)
F(10A)-F(12A)	1.78(2)
F(11A)-C(38)	1.321(5)
F(12A)-C(38)	1.358(5)
F(13)-C(47)	1.331(4)
F(14)-C(47)	1.348(4)
F(15)-C(47)	1.341(3)
F(16)-C(48)	1.314(4)
F(17)-C(48)	1.324(4)
F(18)-C(48)	1.335(4)
F(19)-C(57)	1.337(4)
F(20)-C(57)	1.348(4)
F(21)-C(57)	1.338(4)
F(22)-C(58)	1.339(4)
F(23)-C(58)	1.338(4)
F(24)-C(58)	1.332(4)
C(21)-C(26)	1.396(4)
C(21)-C(22)	1.408(4)
C(21)-B(1)	1.640(4)

C(22)-C(23)	1.382(4)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.393(4)
C(23)-C(27)	1.502(4)
C(24)-C(25)	1.386(4)
C(24)-H(24A)	0.9500
C(25)-C(26)	1.392(4)
C(25)-C(28)	1.497(4)
C(26)-H(26A)	0.9500
C(31)-C(36)	1.394(5)
C(31)-C(32)	1.403(4)
C(31)-B(1)	1.645(4)
C(32)-C(33)	1.388(4)
C(32)-H(32A)	0.9500
C(33)-C(34)	1.387(5)
C(33)-C(37)	1.493(5)
C(34)-C(35)	1.381(5)
C(34)-H(34A)	0.9500
C(35)-C(36)	1.397(5)
C(35)-C(38)	1.487(6)
C(36)-H(36A)	0.9500
C(41)-C(42)	1.398(4)
C(41)-C(46)	1.401(4)
C(41)-B(1)	1.644(4)
C(42)-C(43)	1.391(4)
C(42)-H(42A)	0.9500
C(43)-C(44)	1.388(4)
C(43)-C(47)	1.496(4)
C(44)-C(45)	1.384(5)
C(44)-H(44A)	0.9500
C(45)-C(46)	1.392(4)
C(45)-C(48)	1.498(4)
C(46)-H(46A)	0.9500

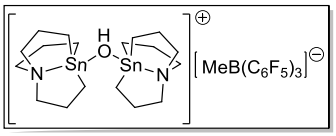
C(51)-C(52)	1.399(4)
C(51)-C(56)	1.404(4)
C(51)-B(1)	1.637(4)
C(52)-C(53)	1.386(4)
C(52)-H(52A)	0.9500
C(53)-C(54)	1.387(5)
C(53)-C(57)	1.497(4)
C(54)-C(55)	1.389(4)
C(54)-H(54A)	0.9500
C(55)-C(56)	1.388(4)
C(55)-C(58)	1.502(4)
C(56)-H(56A)	0.9500

C(4)-Sn(1)-C(1)	116.57(18)
C(4)-Sn(1)-C(7)	117.79(17)
C(1)-Sn(1)-C(7)	118.24(19)
C(4)-Sn(1)-F(25)	100.29(16)
C(1)-Sn(1)-F(25)	100.93(18)
C(7)-Sn(1)-F(25)	96.17(12)
C(4)-Sn(1)-N(1)	81.30(13)
C(1)-Sn(1)-N(1)	80.65(15)
C(7)-Sn(1)-N(1)	80.68(12)
F(25)-Sn(1)-N(1)	176.85(10)
C(4)-Sn(1)-Cl(1)	115.13(18)
C(1)-Sn(1)-Cl(1)	84.08(19)
C(7)-Sn(1)-Cl(1)	97.59(16)
N(1)-Sn(1)-Cl(1)	161.49(17)
C(13)-Sn(2)-C(10)	116.82(19)
C(13)-Sn(2)-C(16)	120.57(17)
C(10)-Sn(2)-C(16)	115.82(18)
C(13)-Sn(2)-F(25)	98.07(13)
C(10)-Sn(2)-F(25)	100.30(15)
C(16)-Sn(2)-F(25)	97.88(16)

C(13)-Sn(2)-N(2)	81.06(13)
C(10)-Sn(2)-N(2)	81.44(13)
C(16)-Sn(2)-N(2)	81.33(12)
F(25)-Sn(2)-N(2)	178.27(12)
C(13)-Sn(2)-Cl(1)	91.72(16)
C(10)-Sn(2)-Cl(1)	88.41(18)
C(16)-Sn(2)-Cl(1)	115.31(18)
N(2)-Sn(2)-Cl(1)	163.16(17)
Sn(1)-F(25)-Sn(2)	129.07(18)
Sn(1)-Cl(1)-Sn(2)	101.2(2)
C(3)-N(1)-C(6)	113.5(3)
C(3)-N(1)-C(9)	113.7(3)
C(6)-N(1)-C(9)	111.5(3)
C(3)-N(1)-Sn(1)	106.2(2)
C(6)-N(1)-Sn(1)	105.3(2)
C(9)-N(1)-Sn(1)	105.8(2)
C(18)-N(2)-C(15)	114.5(3)
C(18)-N(2)-C(12)	112.2(3)
C(15)-N(2)-C(12)	111.6(3)
C(18)-N(2)-Sn(2)	106.0(2)
C(15)-N(2)-Sn(2)	106.1(2)
C(12)-N(2)-Sn(2)	105.6(2)
C(2)-C(1)-Sn(1)	107.3(3)
C(2)-C(1)-H(1A)	110.2
Sn(1)-C(1)-H(1A)	110.2
C(2)-C(1)-H(1B)	110.2
Sn(1)-C(1)-H(1B)	110.2
H(1A)-C(1)-H(1B)	108.5
C(1)-C(2)-C(3)	111.9(4)
C(1)-C(2)-H(2A)	109.2
C(3)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2B)	109.2
C(3)-C(2)-H(2B)	109.2

H(2A)-C(2)-H(2B)	107.9
N(1)-C(3)-C(2)	110.4(3)
N(1)-C(3)-H(3A)	109.6
C(2)-C(3)-H(3A)	109.6
N(1)-C(3)-H(3B)	109.6
C(2)-C(3)-H(3B)	109.6
H(3A)-C(3)-H(3B)	108.1
C(5)-C(4)-Sn(1)	106.9(2)
C(5)-C(4)-H(4A)	110.3
Sn(1)-C(4)-H(4A)	110.3
C(5)-C(4)-H(4B)	110.3
Sn(1)-C(4)-H(4B)	110.3
H(4A)-C(4)-H(4B)	108.6
C(6)-C(5)-C(4)	113.4(3)
C(6)-C(5)-H(5A)	108.9
C(4)-C(5)-H(5A)	108.9
C(6)-C(5)-H(5B)	108.9
C(4)-C(5)-H(5B)	108.9
H(5A)-C(5)-H(5B)	107.7
N(1)-C(6)-C(5)	112.2(3)
N(1)-C(6)-H(6A)	109.2
C(5)-C(6)-H(6A)	109.2
N(1)-C(6)-H(6B)	109.2
C(5)-C(6)-H(6B)	109.2
H(6A)-C(6)-H(6B)	107.9

X-Ray Data for Complex **3.14**
From pentane/1,2-dichloroethane



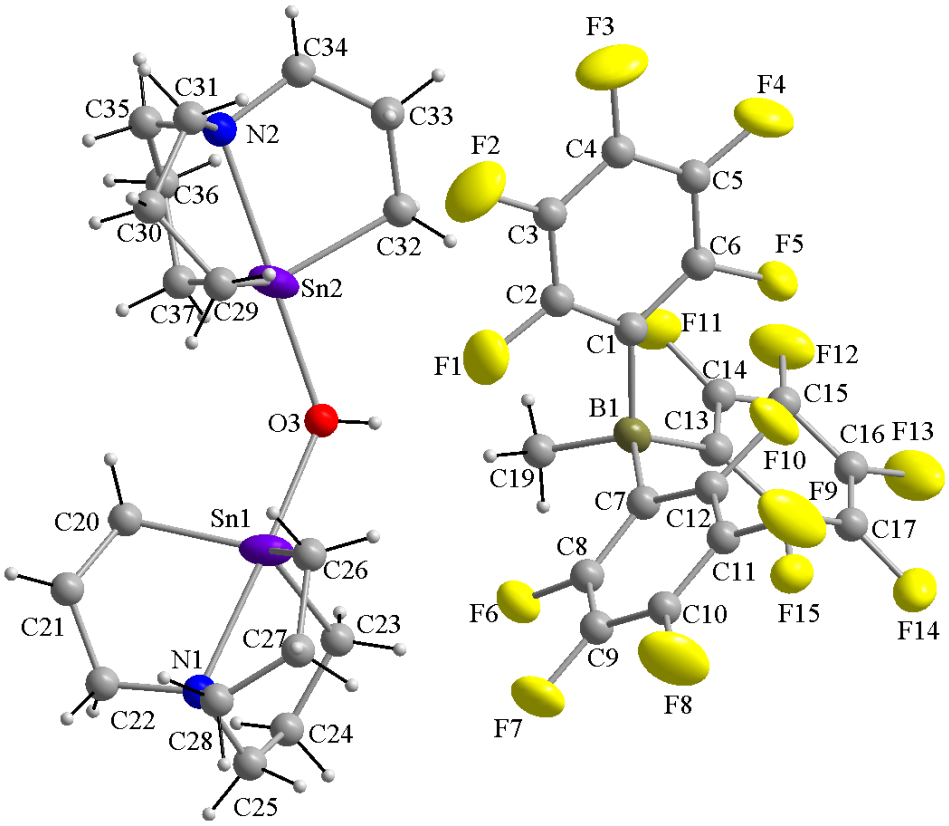


Table 1. Crystal data and structure refinement for complex **3.14**

Identification code	Azadeh112_0m
Empirical formula	C37 H39 B F15 N2 O Sn2
Formula weight	1060.89
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$

Unit cell dimensions	a = 13.9005(6) Å	α= 90°.
	b = 12.6463(5) Å	β= 119.077(2)°.
	c = 26.1186(9) Å	γ = 90°.
Volume	4012.7(3) $Å^3$	
Z	4	
Density (calculated)	1.756 Mg/m^3	
Absorption coefficient	1.348 mm^{-1}	
F(000)	2092	
Crystal size	0.12 x 0.08 x 0.02 mm^3	
Theta range for data collection	1.841 to 30.082°.	
Index ranges	-19<=h<=19, -17<=k<=17, -36<=l<=36	
Reflections collected	74979	
Independent reflections	11755 [R(int) = 0.0660]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9736 and 0.8551	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11755 / 0 / 524	
Goodness-of-fit on F^2	1.182	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.0819	
R indices (all data)	R1 = 0.0937, wR2 = 0.0991	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.161 and -1.376 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Azadeh112_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	908(2)	-3190(2)	-384(1)	56(1)
F(2)	-1214(2)	-3509(2)	-1095(1)	76(1)
F(3)	-2351(2)	-2328(3)	-2080(1)	75(1)

F(4)	-1279(2)	-755(2)	-2314(1)	55(1)
F(5)	828(2)	-413(2)	-1625(1)	39(1)
F(6)	3674(2)	-2412(2)	775(1)	44(1)
F(7)	3558(2)	-1628(2)	1677(1)	53(1)
F(8)	2286(3)	74(3)	1556(1)	78(1)
F(9)	1094(3)	986(3)	478(1)	83(1)
F(10)	1193(2)	214(2)	-441(1)	55(1)
F(11)	2436(2)	-2024(2)	-1569(1)	46(1)
F(12)	3425(2)	-880(2)	-2032(1)	60(1)
F(13)	4518(2)	911(2)	-1500(1)	69(1)
F(14)	4636(2)	1521(2)	-467(1)	53(1)
F(15)	3651(2)	423(2)	-1(1)	42(1)
C(1)	1017(3)	-1805(3)	-970(2)	31(1)
C(2)	416(3)	-2567(3)	-866(2)	40(1)
C(3)	-692(4)	-2748(4)	-1228(2)	49(1)
C(4)	-1269(3)	-2158(4)	-1722(2)	49(1)
C(5)	-727(3)	-1379(3)	-1842(2)	40(1)
C(6)	387(3)	-1222(3)	-1468(2)	32(1)
C(7)	2399(3)	-1167(3)	102(2)	31(1)
C(8)	2997(3)	-1575(3)	665(2)	32(1)
C(9)	2964(3)	-1172(3)	1146(2)	38(1)
C(10)	2323(4)	-322(4)	1085(2)	50(1)
C(11)	1718(4)	133(4)	544(2)	50(1)
C(12)	1776(3)	-297(3)	75(2)	42(1)
C(13)	2965(3)	-870(3)	-759(2)	30(1)
C(14)	2973(3)	-1141(3)	-1274(2)	36(1)
C(15)	3475(3)	-560(4)	-1523(2)	43(1)
C(16)	4027(3)	345(4)	-1257(2)	45(1)
C(17)	4073(3)	649(3)	-744(2)	39(1)
C(18)	3546(3)	43(3)	-512(2)	33(1)
C(19)	2930(3)	-2776(3)	-395(2)	31(1)
B(1)	2360(3)	-1655(3)	-498(2)	31(1)
Sn(1)	3809(1)	-5499(1)	714(1)	42(1)

Sn(2)	1377(1)	-6091(1)	-875(1)	39(1)
N(1)	4943(3)	-5823(3)	1730(1)	45(1)
N(2)	-167(2)	-7006(3)	-1604(1)	39(1)
O(3)	2794(2)	-5278(3)	-215(1)	57(1)
C(20)	3766(5)	-7193(4)	709(2)	80(2)
C(21)	4177(5)	-7579(5)	1314(2)	87(2)
C(22)	5080(5)	-6973(4)	1786(2)	75(2)
C(23)	5287(3)	-4724(5)	843(2)	67(2)
C(24)	6218(4)	-5092(5)	1419(2)	75(2)
C(25)	5979(4)	-5224(5)	1904(2)	80(2)
C(26)	2875(3)	-4682(3)	1042(2)	44(1)
C(27)	3589(4)	-4516(5)	1685(2)	80(2)
C(28)	4345(4)	-5380(4)	2012(2)	65(1)
C(29)	495(4)	-6359(4)	-408(2)	60(1)
C(30)	-279(4)	-7298(4)	-699(2)	59(1)
C(31)	-922(4)	-7137(4)	-1359(2)	57(1)
C(32)	754(4)	-4903(3)	-1549(2)	49(1)
C(33)	-459(4)	-5163(4)	-1958(2)	54(1)
C(34)	-634(4)	-6316(4)	-2127(2)	51(1)
C(35)	260(4)	-8000(4)	-1695(2)	51(1)
C(36)	1417(3)	-7873(4)	-1611(2)	47(1)
C(37)	2185(3)	-7394(4)	-1011(2)	52(1)

Table 3. Bond lengths [Å] and angles [°] for Azadeh112_0m.

F(1)-C(2)	1.356(5)
F(2)-C(3)	1.349(5)
F(3)-C(4)	1.348(4)
F(4)-C(5)	1.346(5)
F(5)-C(6)	1.355(4)

F(6)-C(8)	1.351(4)
F(7)-C(9)	1.350(4)
F(8)-C(10)	1.350(4)
F(9)-C(11)	1.342(5)
F(10)-C(12)	1.353(4)
F(11)-C(14)	1.356(4)
F(12)-C(15)	1.361(4)
F(13)-C(16)	1.344(4)
F(14)-C(17)	1.343(5)
F(15)-C(18)	1.359(4)
C(1)-C(6)	1.377(5)
C(1)-C(2)	1.385(5)
C(1)-B(1)	1.675(5)
C(2)-C(3)	1.379(6)
C(3)-C(4)	1.364(6)
C(4)-C(5)	1.365(6)
C(5)-C(6)	1.385(5)
C(7)-C(12)	1.381(5)
C(7)-C(8)	1.389(5)
C(7)-B(1)	1.662(5)
C(8)-C(9)	1.377(5)
C(9)-C(10)	1.356(6)
C(10)-C(11)	1.372(6)
C(11)-C(12)	1.376(5)
C(13)-C(18)	1.377(5)
C(13)-C(14)	1.394(5)
C(13)-B(1)	1.647(5)
C(14)-C(15)	1.374(5)
C(15)-C(16)	1.364(6)
C(16)-C(17)	1.364(6)
C(17)-C(18)	1.385(5)
C(19)-B(1)	1.582(5)
C(19)-H(19A)	0.9600

C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
Sn(1)-C(26)	2.139(4)
Sn(1)-C(20)	2.142(6)
Sn(1)-C(23)	2.149(4)
Sn(1)-O(3)	2.152(3)
Sn(1)-N(1)	2.372(3)
Sn(2)-C(37)	2.119(4)
Sn(2)-C(29)	2.136(4)
Sn(2)-O(3)	2.146(3)
Sn(2)-C(32)	2.151(4)
Sn(2)-N(2)	2.366(3)
N(1)-C(28)	1.463(5)
N(1)-C(22)	1.465(6)
N(1)-C(25)	1.490(6)
N(2)-C(35)	1.459(5)
N(2)-C(34)	1.478(5)
N(2)-C(31)	1.480(5)
O(3)-H(3X)	0.8200
C(20)-C(21)	1.479(7)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(22)	1.475(7)
C(21)-H(21A)	0.9300
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-C(24)	1.504(7)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-C(25)	1.465(7)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-H(25A)	0.9700

C(25)-H(25B)	0.9700
C(26)-C(27)	1.492(6)
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
C(27)-C(28)	1.468(7)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-C(30)	1.533(7)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-C(31)	1.522(6)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-C(33)	1.529(6)
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-C(34)	1.507(6)
C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700
C(34)-H(34A)	0.9700
C(34)-H(34B)	0.9700
C(35)-C(36)	1.522(6)
C(35)-H(35A)	0.9700
C(35)-H(35B)	0.9700
C(36)-C(37)	1.530(6)
C(36)-H(36A)	0.9700
C(36)-H(36B)	0.9700
C(37)-H(37A)	0.9700
C(37)-H(37B)	0.9700

C(6)-C(1)-C(2)	113.0(3)
C(6)-C(1)-B(1)	127.2(3)
C(2)-C(1)-B(1)	119.8(3)
F(1)-C(2)-C(3)	115.5(4)
F(1)-C(2)-C(1)	120.4(4)
C(3)-C(2)-C(1)	124.1(4)
F(2)-C(3)-C(4)	119.5(4)
F(2)-C(3)-C(2)	120.2(4)
C(4)-C(3)-C(2)	120.3(4)
F(3)-C(4)-C(3)	120.9(4)
F(3)-C(4)-C(5)	120.7(4)
C(3)-C(4)-C(5)	118.4(4)
F(4)-C(5)-C(4)	120.0(4)
F(4)-C(5)-C(6)	120.4(4)
C(4)-C(5)-C(6)	119.6(4)
F(5)-C(6)-C(1)	121.1(3)
F(5)-C(6)-C(5)	114.3(3)
C(1)-C(6)-C(5)	124.6(4)
C(12)-C(7)-C(8)	112.9(3)
C(12)-C(7)-B(1)	121.0(3)
C(8)-C(7)-B(1)	126.1(3)
F(6)-C(8)-C(9)	115.1(3)
F(6)-C(8)-C(7)	120.9(3)
C(9)-C(8)-C(7)	124.0(3)
F(7)-C(9)-C(10)	119.9(4)
F(7)-C(9)-C(8)	120.3(4)
C(10)-C(9)-C(8)	119.9(4)
F(8)-C(10)-C(9)	120.0(4)
F(8)-C(10)-C(11)	120.5(4)
C(9)-C(10)-C(11)	119.5(4)
F(9)-C(11)-C(10)	120.2(4)
F(9)-C(11)-C(12)	121.1(4)

C(10)-C(11)-C(12)	118.7(4)
F(10)-C(12)-C(11)	115.6(4)
F(10)-C(12)-C(7)	119.2(3)
C(11)-C(12)-C(7)	125.1(4)
C(18)-C(13)-C(14)	112.3(3)
C(18)-C(13)-B(1)	127.9(3)
C(14)-C(13)-B(1)	119.8(3)
F(11)-C(14)-C(15)	116.0(3)
F(11)-C(14)-C(13)	119.3(3)
C(15)-C(14)-C(13)	124.7(4)
F(12)-C(15)-C(16)	119.8(4)
F(12)-C(15)-C(14)	120.5(4)
C(16)-C(15)-C(14)	119.8(4)
F(13)-C(16)-C(17)	121.5(4)
F(13)-C(16)-C(15)	119.6(4)
C(17)-C(16)-C(15)	118.9(4)
F(14)-C(17)-C(16)	119.9(4)
F(14)-C(17)-C(18)	120.7(4)
C(16)-C(17)-C(18)	119.4(4)
F(15)-C(18)-C(13)	120.9(3)
F(15)-C(18)-C(17)	114.1(3)
C(13)-C(18)-C(17)	125.0(4)
B(1)-C(19)-H(19A)	109.5
B(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
B(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(19)-B(1)-C(13)	107.3(3)
C(19)-B(1)-C(7)	112.8(3)
C(13)-B(1)-C(7)	112.2(3)
C(19)-B(1)-C(1)	108.1(3)
C(13)-B(1)-C(1)	112.0(3)

C(7)-B(1)-C(1)	104.5(3)
C(26)-Sn(1)-C(20)	117.7(2)
C(26)-Sn(1)-C(23)	115.92(19)
C(20)-Sn(1)-C(23)	118.6(2)
C(26)-Sn(1)-O(3)	101.28(14)
C(20)-Sn(1)-O(3)	97.02(17)
C(23)-Sn(1)-O(3)	99.85(15)
C(26)-Sn(1)-N(1)	80.64(14)
C(20)-Sn(1)-N(1)	80.55(17)
C(23)-Sn(1)-N(1)	80.71(15)
O(3)-Sn(1)-N(1)	177.44(13)
C(37)-Sn(2)-C(29)	118.1(2)
C(37)-Sn(2)-O(3)	98.81(15)
C(29)-Sn(2)-O(3)	100.05(15)
C(37)-Sn(2)-C(32)	116.18(18)
C(29)-Sn(2)-C(32)	117.62(19)
O(3)-Sn(2)-C(32)	99.80(15)
C(37)-Sn(2)-N(2)	80.36(14)
C(29)-Sn(2)-N(2)	80.44(15)
O(3)-Sn(2)-N(2)	179.16(12)
C(32)-Sn(2)-N(2)	80.53(14)
C(28)-N(1)-C(22)	114.1(4)
C(28)-N(1)-C(25)	110.7(4)
C(22)-N(1)-C(25)	114.5(4)
C(28)-N(1)-Sn(1)	105.5(3)
C(22)-N(1)-Sn(1)	105.4(3)
C(25)-N(1)-Sn(1)	105.7(3)
C(35)-N(2)-C(34)	112.9(3)
C(35)-N(2)-C(31)	113.9(4)
C(34)-N(2)-C(31)	112.3(3)
C(35)-N(2)-Sn(2)	105.7(2)
C(34)-N(2)-Sn(2)	105.9(2)
C(31)-N(2)-Sn(2)	105.3(2)

Sn(2)-O(3)-Sn(1)	133.34(16)
Sn(2)-O(3)-H(3X)	109.5
Sn(1)-O(3)-H(3X)	109.9
C(21)-C(20)-Sn(1)	109.2(4)
C(21)-C(20)-H(20A)	109.8
Sn(1)-C(20)-H(20A)	109.8
C(21)-C(20)-H(20B)	109.8
Sn(1)-C(20)-H(20B)	109.8
H(20A)-C(20)-H(20B)	108.3
C(22)-C(21)-C(20)	116.8(5)
C(22)-C(21)-H(21A)	121.6
C(20)-C(21)-H(21A)	121.6
N(1)-C(22)-C(21)	114.5(4)
N(1)-C(22)-H(22A)	108.6
C(21)-C(22)-H(22A)	108.6
N(1)-C(22)-H(22B)	108.6
C(21)-C(22)-H(22B)	108.6
H(22A)-C(22)-H(22B)	107.6
C(24)-C(23)-Sn(1)	108.0(3)
C(24)-C(23)-H(23A)	110.1
Sn(1)-C(23)-H(23A)	110.1
C(24)-C(23)-H(23B)	110.1
Sn(1)-C(23)-H(23B)	110.1
H(23A)-C(23)-H(23B)	108.4
C(25)-C(24)-C(23)	116.9(4)
C(25)-C(24)-H(24A)	108.1
C(23)-C(24)-H(24A)	108.1
C(25)-C(24)-H(24B)	108.1
C(23)-C(24)-H(24B)	108.1
H(24A)-C(24)-H(24B)	107.3
C(24)-C(25)-N(1)	112.7(4)
C(24)-C(25)-H(25A)	109.0
N(1)-C(25)-H(25A)	109.0

C(24)-C(25)-H(25B)	109.0
N(1)-C(25)-H(25B)	109.0
H(25A)-C(25)-H(25B)	107.8
C(27)-C(26)-Sn(1)	108.5(3)
C(27)-C(26)-H(26A)	110.0
Sn(1)-C(26)-H(26A)	110.0
C(27)-C(26)-H(26B)	110.0
Sn(1)-C(26)-H(26B)	110.0
H(26A)-C(26)-H(26B)	108.4
C(28)-C(27)-C(26)	116.6(5)
C(28)-C(27)-H(27A)	108.1
C(26)-C(27)-H(27A)	108.1
C(28)-C(27)-H(27B)	108.1
C(26)-C(27)-H(27B)	108.1
H(27A)-C(27)-H(27B)	107.3
N(1)-C(28)-C(27)	114.3(4)
N(1)-C(28)-H(28A)	108.7
C(27)-C(28)-H(28A)	108.7
N(1)-C(28)-H(28B)	108.7
C(27)-C(28)-H(28B)	108.7
H(28A)-C(28)-H(28B)	107.6
C(30)-C(29)-Sn(2)	107.4(3)
C(30)-C(29)-H(29A)	110.2
Sn(2)-C(29)-H(29A)	110.2
C(30)-C(29)-H(29B)	110.2
Sn(2)-C(29)-H(29B)	110.2
H(29A)-C(29)-H(29B)	108.5
C(31)-C(30)-C(29)	110.0(4)
C(31)-C(30)-H(30A)	109.7
C(29)-C(30)-H(30A)	109.7
C(31)-C(30)-H(30B)	109.7
C(29)-C(30)-H(30B)	109.7
H(30A)-C(30)-H(30B)	108.2

N(2)-C(31)-C(30)	110.8(3)
N(2)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31A)	109.5
N(2)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	108.1
C(33)-C(32)-Sn(2)	106.9(3)
C(33)-C(32)-H(32A)	110.4
Sn(2)-C(32)-H(32A)	110.4
C(33)-C(32)-H(32B)	110.4
Sn(2)-C(32)-H(32B)	110.4
H(32A)-C(32)-H(32B)	108.6
C(34)-C(33)-C(32)	112.2(3)
C(34)-C(33)-H(33A)	109.2
C(32)-C(33)-H(33A)	109.2
C(34)-C(33)-H(33B)	109.2
C(32)-C(33)-H(33B)	109.2
H(33A)-C(33)-H(33B)	107.9
N(2)-C(34)-C(33)	111.4(3)
N(2)-C(34)-H(34A)	109.4
C(33)-C(34)-H(34A)	109.4
N(2)-C(34)-H(34B)	109.4
C(33)-C(34)-H(34B)	109.4
H(34A)-C(34)-H(34B)	108.0
N(2)-C(35)-C(36)	111.8(4)
N(2)-C(35)-H(35A)	109.3
C(36)-C(35)-H(35A)	109.3
N(2)-C(35)-H(35B)	109.3
C(36)-C(35)-H(35B)	109.3
H(35A)-C(35)-H(35B)	107.9
C(35)-C(36)-C(37)	110.6(3)
C(35)-C(36)-H(36A)	109.5
C(37)-C(36)-H(36A)	109.5

C(35)-C(36)-H(36B)	109.5
C(37)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	108.1
C(36)-C(37)-Sn(2)	108.5(3)
C(36)-C(37)-H(37A)	110.0
Sn(2)-C(37)-H(37A)	110.0
C(36)-C(37)-H(37B)	110.0
Sn(2)-C(37)-H(37B)	110.0
H(37A)-C(37)-H(37B)	108.4

Table 4. Atomic displacement parameters ($Å^2 x\ 10^3$) for Azadeh112_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	76(2)	56(2)	52(2)	7(1)	43(1)	-11(1)
F(2)	79(2)	82(2)	91(2)	-18(2)	61(2)	-41(2)
F(3)	36(1)	111(2)	77(2)	-27(2)	26(1)	-25(2)
F(4)	33(1)	84(2)	41(1)	1(1)	12(1)	9(1)
F(5)	34(1)	43(1)	36(1)	8(1)	16(1)	2(1)
F(6)	46(1)	49(1)	35(1)	8(1)	18(1)	5(1)
F(7)	56(2)	74(2)	24(1)	8(1)	15(1)	1(1)
F(8)	92(2)	112(2)	35(2)	-9(2)	36(2)	27(2)
F(9)	102(2)	95(2)	47(2)	-6(2)	32(2)	55(2)
F(10)	74(2)	53(2)	29(1)	4(1)	18(1)	32(1)
F(11)	48(1)	60(2)	33(1)	-12(1)	22(1)	-5(1)
F(12)	47(1)	105(2)	36(1)	2(1)	27(1)	-1(1)
F(13)	47(2)	105(2)	60(2)	20(2)	30(1)	-18(2)
F(14)	38(1)	48(1)	62(2)	6(1)	16(1)	-9(1)
F(15)	43(1)	40(1)	37(1)	-6(1)	16(1)	-2(1)
C(1)	38(2)	35(2)	30(2)	-8(2)	23(2)	-4(2)
C(2)	49(2)	42(2)	38(2)	-8(2)	28(2)	-6(2)
C(3)	56(3)	53(3)	59(3)	-19(2)	44(2)	-23(2)

C(4)	33(2)	70(3)	50(3)	-22(2)	25(2)	-15(2)
C(5)	31(2)	57(3)	34(2)	-8(2)	18(2)	2(2)
C(6)	34(2)	37(2)	33(2)	-7(2)	21(2)	-4(2)
C(7)	36(2)	31(2)	26(2)	-2(2)	16(2)	-1(2)
C(8)	32(2)	32(2)	32(2)	2(2)	17(2)	-2(2)
C(9)	37(2)	52(3)	22(2)	2(2)	12(2)	-4(2)
C(10)	53(3)	72(3)	31(2)	-12(2)	24(2)	2(2)
C(11)	54(3)	61(3)	36(2)	-3(2)	22(2)	20(2)
C(12)	48(2)	48(3)	25(2)	3(2)	15(2)	10(2)
C(13)	24(2)	37(2)	25(2)	2(2)	9(1)	3(1)
C(14)	28(2)	51(2)	28(2)	-1(2)	12(2)	0(2)
C(15)	29(2)	74(3)	28(2)	7(2)	14(2)	8(2)
C(16)	25(2)	65(3)	41(2)	16(2)	14(2)	1(2)
C(17)	23(2)	43(2)	43(2)	6(2)	9(2)	2(2)
C(18)	28(2)	39(2)	27(2)	4(2)	10(2)	5(2)
C(19)	44(2)	22(2)	25(2)	-1(1)	16(2)	2(2)
B(1)	35(2)	33(2)	25(2)	1(2)	15(2)	4(2)
Sn(1)	29(1)	65(1)	26(1)	-8(1)	8(1)	-1(1)
Sn(2)	30(1)	61(1)	21(1)	1(1)	8(1)	8(1)
N(1)	35(2)	66(3)	30(2)	-2(2)	11(2)	7(2)
N(2)	32(2)	54(2)	28(2)	-2(2)	12(1)	4(2)
O(3)	45(2)	82(2)	27(2)	-2(2)	3(1)	-9(2)
C(20)	84(4)	74(4)	58(3)	-19(3)	15(3)	7(3)
C(21)	102(5)	70(4)	57(4)	6(3)	13(3)	-19(3)
C(22)	81(4)	68(4)	51(3)	7(3)	12(3)	27(3)
C(23)	35(2)	126(5)	44(3)	0(3)	21(2)	-6(3)
C(24)	38(3)	132(5)	48(3)	-15(3)	15(2)	-14(3)
C(25)	42(3)	134(6)	43(3)	-5(3)	5(2)	-8(3)
C(26)	35(2)	50(3)	53(3)	11(2)	26(2)	2(2)
C(27)	67(3)	122(5)	54(3)	-7(3)	33(3)	35(3)
C(28)	83(4)	81(4)	39(3)	8(2)	35(3)	26(3)
C(29)	56(3)	91(4)	37(2)	-5(2)	27(2)	1(3)
C(30)	55(3)	88(4)	46(3)	0(3)	35(2)	-1(3)

C(31)	39(2)	74(3)	57(3)	-7(3)	24(2)	-1(2)
C(32)	55(3)	44(2)	40(2)	-1(2)	17(2)	10(2)
C(33)	50(3)	62(3)	34(2)	6(2)	8(2)	23(2)
C(34)	42(2)	68(3)	29(2)	-3(2)	6(2)	10(2)
C(35)	51(3)	49(3)	50(3)	-8(2)	21(2)	2(2)
C(36)	51(2)	48(3)	48(3)	4(2)	29(2)	13(2)
C(37)	38(2)	58(3)	58(3)	7(2)	21(2)	16(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Azadeh112_0m.

	x	y	z	U(eq)
H(19A)	3715	-2691	-188	46
H(19B)	2711	-3109	-766	46
H(19C)	2710	-3210	-168	46
H(3X)	2745	-4646	-295	86
H(20A)	3018	-7437	462	96
H(20B)	4222	-7468	553	96
H(21A)	3880	-8175	1394	105
H(22A)	5145	-7186	2158	90
H(22B)	5764	-7157	1793	90
H(23A)	5436	-4902	527	80
H(23B)	5204	-3963	848	80
H(24A)	6479	-5764	1355	90
H(24B)	6817	-4589	1541	90
H(25A)	5920	-4532	2047	96
H(25B)	6586	-5594	2222	96
H(26A)	2627	-4006	846	53
H(26B)	2232	-5095	970	53
H(27A)	4022	-3882	1741	95

H(27B)	3117	-4386	1855	95
H(28A)	4875	-5121	2397	78
H(28B)	3928	-5941	2067	78
H(29A)	1002	-6516	0	71
H(29B)	74	-5735	-425	71
H(30A)	147	-7945	-611	70
H(30B)	-785	-7363	-545	70
H(31A)	-1396	-7742	-1541	68
H(31B)	-1384	-6515	-1447	68
H(32A)	825	-4207	-1379	59
H(32B)	1160	-4914	-1764	59
H(33A)	-882	-4982	-1765	65
H(33B)	-728	-4736	-2309	65
H(34A)	-1417	-6454	-2361	62
H(34B)	-289	-6478	-2363	62
H(35A)	-226	-8254	-2089	62
H(35B)	270	-8524	-1422	62
H(36A)	1395	-7419	-1916	56
H(36B)	1697	-8558	-1644	56
H(37A)	2863	-7162	-996	63
H(37B)	2365	-7919	-707	63

Table 6. Torsion angles [°] for Azadeh112_0m.

C(6)-C(1)-C(2)-F(1)	-178.2(3)
B(1)-C(1)-C(2)-F(1)	0.3(5)
C(6)-C(1)-C(2)-C(3)	1.4(5)
B(1)-C(1)-C(2)-C(3)	179.9(4)
F(1)-C(2)-C(3)-F(2)	-0.5(6)
C(1)-C(2)-C(3)-F(2)	179.9(4)
F(1)-C(2)-C(3)-C(4)	179.3(4)

C(1)-C(2)-C(3)-C(4)	-0.4(6)
F(2)-C(3)-C(4)-F(3)	-0.4(6)
C(2)-C(3)-C(4)-F(3)	179.9(4)
F(2)-C(3)-C(4)-C(5)	178.8(4)
C(2)-C(3)-C(4)-C(5)	-0.9(6)
F(3)-C(4)-C(5)-F(4)	1.6(6)
C(3)-C(4)-C(5)-F(4)	-177.6(4)
F(3)-C(4)-C(5)-C(6)	-179.8(4)
C(3)-C(4)-C(5)-C(6)	1.0(6)
C(2)-C(1)-C(6)-F(5)	177.3(3)
B(1)-C(1)-C(6)-F(5)	-1.0(5)
C(2)-C(1)-C(6)-C(5)	-1.3(5)
B(1)-C(1)-C(6)-C(5)	-179.6(3)
F(4)-C(5)-C(6)-F(5)	0.0(5)
C(4)-C(5)-C(6)-F(5)	-178.6(3)
F(4)-C(5)-C(6)-C(1)	178.7(3)
C(4)-C(5)-C(6)-C(1)	0.1(6)
C(12)-C(7)-C(8)-F(6)	-178.3(3)
B(1)-C(7)-C(8)-F(6)	3.9(5)
C(12)-C(7)-C(8)-C(9)	1.0(5)
B(1)-C(7)-C(8)-C(9)	-176.9(4)
F(6)-C(8)-C(9)-F(7)	-1.8(5)
C(7)-C(8)-C(9)-F(7)	178.9(3)
F(6)-C(8)-C(9)-C(10)	179.0(4)
C(7)-C(8)-C(9)-C(10)	-0.3(6)
F(7)-C(9)-C(10)-F(8)	0.6(6)
C(8)-C(9)-C(10)-F(8)	179.8(4)
F(7)-C(9)-C(10)-C(11)	-179.7(4)
C(8)-C(9)-C(10)-C(11)	-0.5(7)
F(8)-C(10)-C(11)-F(9)	0.8(7)
C(9)-C(10)-C(11)-F(9)	-178.9(4)
F(8)-C(10)-C(11)-C(12)	-179.8(4)
C(9)-C(10)-C(11)-C(12)	0.5(7)

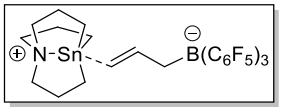
F(9)-C(11)-C(12)-F(10)	1.8(7)
C(10)-C(11)-C(12)-F(10)	-177.6(4)
F(9)-C(11)-C(12)-C(7)	179.6(4)
C(10)-C(11)-C(12)-C(7)	0.3(7)
C(8)-C(7)-C(12)-F(10)	176.8(3)
B(1)-C(7)-C(12)-F(10)	-5.2(6)
C(8)-C(7)-C(12)-C(11)	-1.0(6)
B(1)-C(7)-C(12)-C(11)	177.0(4)
C(18)-C(13)-C(14)-F(11)	179.9(3)
B(1)-C(13)-C(14)-F(11)	3.1(5)
C(18)-C(13)-C(14)-C(15)	-1.6(5)
B(1)-C(13)-C(14)-C(15)	-178.3(3)
F(11)-C(14)-C(15)-F(12)	-0.4(5)
C(13)-C(14)-C(15)-F(12)	-179.0(3)
F(11)-C(14)-C(15)-C(16)	179.5(3)
C(13)-C(14)-C(15)-C(16)	0.9(6)
F(12)-C(15)-C(16)-F(13)	-0.2(6)
C(14)-C(15)-C(16)-F(13)	179.9(3)
F(12)-C(15)-C(16)-C(17)	-179.6(3)
C(14)-C(15)-C(16)-C(17)	0.5(6)
F(13)-C(16)-C(17)-F(14)	-1.2(6)
C(15)-C(16)-C(17)-F(14)	178.3(3)
F(13)-C(16)-C(17)-C(18)	179.5(3)
C(15)-C(16)-C(17)-C(18)	-1.0(6)
C(14)-C(13)-C(18)-F(15)	-178.7(3)
B(1)-C(13)-C(18)-F(15)	-2.2(5)
C(14)-C(13)-C(18)-C(17)	0.9(5)
B(1)-C(13)-C(18)-C(17)	177.4(3)
F(14)-C(17)-C(18)-F(15)	0.6(5)
C(16)-C(17)-C(18)-F(15)	179.9(3)
F(14)-C(17)-C(18)-C(13)	-179.0(3)
C(16)-C(17)-C(18)-C(13)	0.3(6)
C(18)-C(13)-B(1)-C(19)	-118.4(4)

C(14)-C(13)-B(1)-C(19)	57.8(4)
C(18)-C(13)-B(1)-C(7)	6.1(5)
C(14)-C(13)-B(1)-C(7)	-177.7(3)
C(18)-C(13)-B(1)-C(1)	123.2(4)
C(14)-C(13)-B(1)-C(1)	-60.6(4)
C(12)-C(7)-B(1)-C(19)	-168.0(3)
C(8)-C(7)-B(1)-C(19)	9.6(5)
C(12)-C(7)-B(1)-C(13)	70.6(4)
C(8)-C(7)-B(1)-C(13)	-111.7(4)
C(12)-C(7)-B(1)-C(1)	-50.9(4)
C(8)-C(7)-B(1)-C(1)	126.8(4)
C(6)-C(1)-B(1)-C(19)	-130.2(4)
C(2)-C(1)-B(1)-C(19)	51.6(4)
C(6)-C(1)-B(1)-C(13)	-12.2(5)
C(2)-C(1)-B(1)-C(13)	169.6(3)
C(6)-C(1)-B(1)-C(7)	109.4(4)
C(2)-C(1)-B(1)-C(7)	-68.8(4)
Sn(1)-C(20)-C(21)-C(22)	-36.0(7)
C(28)-N(1)-C(22)-C(21)	89.2(6)
C(25)-N(1)-C(22)-C(21)	-141.8(5)
Sn(1)-N(1)-C(22)-C(21)	-26.0(6)
C(20)-C(21)-C(22)-N(1)	43.9(8)
Sn(1)-C(23)-C(24)-C(25)	-39.3(7)
C(23)-C(24)-C(25)-N(1)	47.3(8)
C(28)-N(1)-C(25)-C(24)	-141.7(5)
C(22)-N(1)-C(25)-C(24)	87.6(6)
Sn(1)-N(1)-C(25)-C(24)	-28.0(6)
Sn(1)-C(26)-C(27)-C(28)	-37.8(6)
C(22)-N(1)-C(28)-C(27)	-141.4(5)
C(25)-N(1)-C(28)-C(27)	87.7(6)
Sn(1)-N(1)-C(28)-C(27)	-26.2(6)
C(26)-C(27)-C(28)-N(1)	45.2(7)
Sn(2)-C(29)-C(30)-C(31)	-49.2(4)

C(35)-N(2)-C(31)-C(30)	80.9(5)
C(34)-N(2)-C(31)-C(30)	-149.2(4)
Sn(2)-N(2)-C(31)-C(30)	-34.4(4)
C(29)-C(30)-C(31)-N(2)	57.8(5)
Sn(2)-C(32)-C(33)-C(34)	-47.2(4)
C(35)-N(2)-C(34)-C(33)	-146.9(4)
C(31)-N(2)-C(34)-C(33)	82.8(5)
Sn(2)-N(2)-C(34)-C(33)	-31.7(4)
C(32)-C(33)-C(34)-N(2)	54.9(5)
C(34)-N(2)-C(35)-C(36)	82.3(4)
C(31)-N(2)-C(35)-C(36)	-148.1(4)
Sn(2)-N(2)-C(35)-C(36)	-33.0(4)
N(2)-C(35)-C(36)-C(37)	54.6(5)
C(35)-C(36)-C(37)-Sn(2)	-46.2(4)

5.6. X-Ray Data for Complex 5.14

From pentane/1,2-dichloroethane



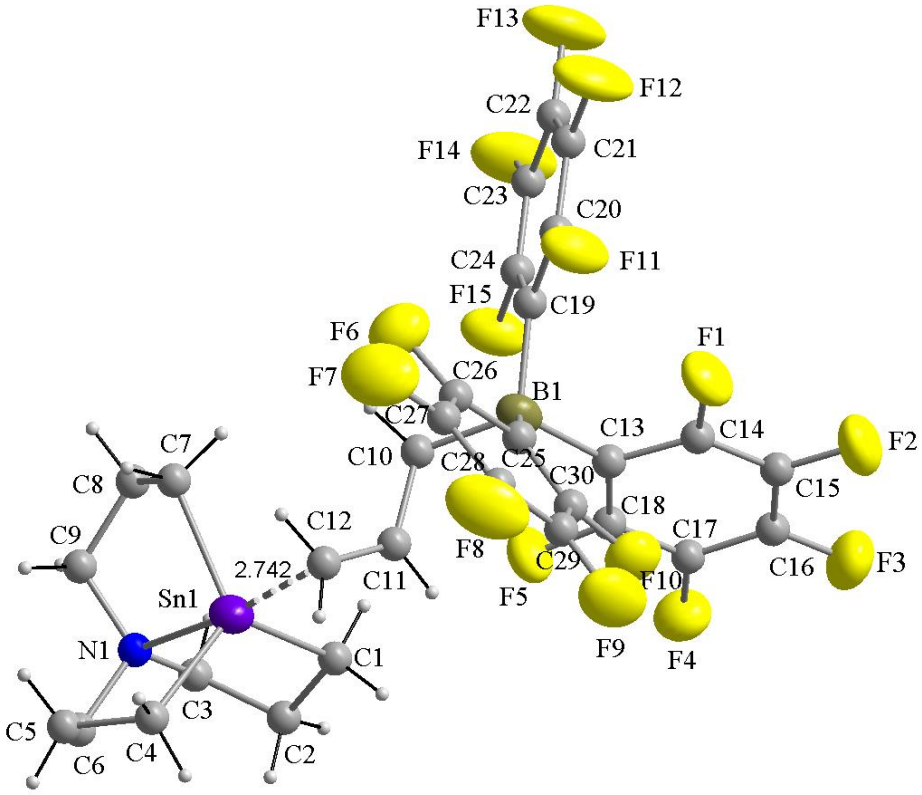


Table 1. Crystallographic data of $C_{30}H_{23}BF_{15}NSn$

Empirical formula	$C_{30}H_{23}BF_{15}NSn$	
Formula weight	811.99	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$\boldsymbol{P}2_1/c$	
Unit cell dimensions	a = 15.1636(5) Å	α = 90°.
	b = 13.1838(4) Å	β = 108.7157(15)°.
	c = 16.3184(5) Å	γ = 90°.

Volume	3089.77(17) $Å^3$
Z	4
Density (calculated)	1.746 g/cm^3
Absorption coefficient	0.941 mm^{-1}
F(000)	1600
Crystal size	0.400 x 0.200 x 0.100 mm^3
Theta range for data collection	1.418 to 27.998°.
Index ranges	-18<=h<=20, -17<=k<=17, -21<=l<=19
Reflections collected	46572
Independent reflections	7461 [R(int) = 0.0149]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.6809
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7461 / 0 / 439
Goodness-of-fit on F^2	1.052
Final R indices [I>2 σ(I)]	R1 = 0.0281, wR2 = 0.0762
R indices (all data)	R1 = 0.0370, wR2 = 0.0886
Largest diff. peak and hole	0.555 and -0.270 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $C_{30}H_{23}BF_{15}NSn$

	x	y	z	U(eq)
Sn(1)	2430(1)	9316(1)	1623(1)	39(1)
N(1)	2005(2)	7826(2)	2113(1)	52(1)
B(1)	-2505(2)	8657(2)	1158(2)	40(1)
F(1)	-3317(1)	7810(1)	2360(1)	67(1)
F(2)	-4587(1)	8604(2)	2980(1)	80(1)
F(3)	-5254(1)	10501(2)	2509(1)	85(1)
F(4)	-4694(1)	11538(1)	1327(1)	69(1)
F(5)	-3476(1)	10753(1)	666(1)	58(1)

F(6)	-1365(1)	7140(1)	693(1)	68(1)
F(7)	-1916(2)	5434(2)	-187(2)	95(1)
F(8)	-3728(2)	4864(1)	-688(1)	96(1)
F(9)	-4995(1)	6086(2)	-316(1)	85(1)
F(10)	-4489(1)	7777(1)	542(1)	64(1)
F(11)	-1641(1)	6794(1)	2290(1)	66(1)
F(12)	-231(1)	6830(1)	3724(1)	90(1)
F(13)	634(1)	8595(2)	4372(1)	96(1)
F(14)	25(2)	10354(1)	3505(1)	92(1)
F(15)	-1398(1)	10360(1)	2060(1)	64(1)
C(1)	3213(2)	8324(2)	1084(2)	59(1)
C(2)	3313(3)	7344(2)	1605(2)	74(1)
C(3)	2416(2)	7008(2)	1731(2)	66(1)
C(4)	2965(2)	9650(2)	2979(2)	54(1)
C(5)	2469(2)	8934(3)	3405(2)	72(1)
C(6)	2413(3)	7865(2)	3071(2)	71(1)
C(7)	967(2)	9425(2)	975(2)	65(1)
C(8)	597(2)	8362(3)	969(2)	81(1)
C(9)	979(2)	7820(2)	1805(2)	73(1)
C(10)	-2196(2)	9300(2)	413(1)	40(1)
C(11)	-2897(2)	9206(2)	-459(1)	41(1)
C(12)	-2762(2)	8765(2)	-1144(2)	55(1)
C(13)	-3308(2)	9232(2)	1485(1)	40(1)
C(14)	-3635(2)	8748(2)	2091(2)	49(1)
C(15)	-4278(2)	9145(2)	2424(2)	57(1)
C(16)	-4636(2)	10093(2)	2176(2)	57(1)
C(17)	-4350(2)	10611(2)	1580(2)	50(1)
C(18)	-3705(2)	10179(2)	1251(1)	43(1)
C(19)	-1597(2)	8574(2)	2055(1)	42(1)
C(20)	-1254(2)	7711(2)	2541(2)	49(1)
C(21)	-523(2)	7707(2)	3304(2)	58(1)
C(22)	-83(2)	8594(2)	3632(2)	62(1)
C(23)	-389(2)	9477(2)	3198(2)	58(1)

C(24)	-1125(2)	9445(2)	2435(2)	48(1)
C(25)	-2879(2)	7548(2)	704(1)	43(1)
C(26)	-2280(2)	6905(2)	474(2)	52(1)
C(27)	-2541(2)	6015(2)	15(2)	63(1)
C(28)	-3457(3)	5733(2)	-234(2)	65(1)
C(29)	-4091(2)	6334(2)	-46(2)	58(1)
C(30)	-3802(2)	7223(2)	410(1)	49(1)
H(1A)	2886	8200	476	70
H(1B)	3819	8611	1142	70
H(2A)	3533	6811	1310	89
H(2B)	3778	7443	2167	89
H(3A)	1977	6811	1178	79
H(3B)	2534	6421	2109	79
H(4A)	3632	9539	3197	64
H(4B)	2837	10349	3088	64
H(5A)	2792	8930	4023	86
H(5B)	1843	9183	3312	86
H(6A)	3033	7573	3244	85
H(6B)	2035	7462	3327	85
H(7A)	680	9882	1281	78
H(7B)	843	9673	389	78
H(8A)	-76	8392	818	98
H(8B)	741	7974	522	98
H(9A)	753	8141	2235	88
H(9B)	760	7124	1737	88
H(10A)	-2119	10010	576	48
H(10B)	-1602	9047	396	48
H(11A)	-3483	9481	-536	49
H(12A)	-2150(20)	8500(20)	-1098(19)	66
H(12B)	-3230(20)	8630(20)	-1620(20)	66

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Bond lengths [Å] and angles [°] for $C_{30}H_{23}BF_{15}NSn$

Sn(1)-C(7)	2.134(3)
Sn(1)-C(1)	2.137(3)
Sn(1)-C(4)	2.143(2)
Sn(1)-N(1)	2.290(2)
N(1)-C(9)	1.473(4)
N(1)-C(3)	1.480(3)
N(1)-C(6)	1.486(4)
B(1)-C(25)	1.655(3)
B(1)-C(13)	1.661(4)
B(1)-C(19)	1.661(3)
B(1)-C(10)	1.666(3)
F(1)-C(14)	1.348(3)
F(2)-C(15)	1.350(3)
F(3)-C(16)	1.338(3)
F(4)-C(17)	1.341(3)
F(5)-C(18)	1.347(3)
F(6)-C(26)	1.353(3)
F(7)-C(27)	1.340(4)
F(8)-C(28)	1.354(3)
F(9)-C(29)	1.339(3)
F(10)-C(30)	1.344(3)
F(11)-C(20)	1.349(3)
F(12)-C(21)	1.344(3)
F(13)-C(22)	1.340(3)
F(14)-C(23)	1.335(3)
F(15)-C(24)	1.355(3)
C(1)-C(2)	1.527(4)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.506(5)
C(2)-H(2A)	0.9700

C(2)-H(2B)	0.9700
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.508(4)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.502(5)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.509(4)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.484(5)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.484(3)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.333(3)
C(11)-H(11A)	0.9300
C(12)-H(12A)	0.97(3)
C(12)-H(12B)	0.88(3)
C(13)-C(18)	1.385(3)
C(13)-C(14)	1.395(3)
C(14)-C(15)	1.365(4)
C(15)-C(16)	1.371(4)
C(16)-C(17)	1.368(4)
C(17)-C(18)	1.382(4)
C(19)-C(20)	1.389(3)

C(19)-C(24)	1.390(3)
C(20)-C(21)	1.376(3)
C(21)-C(22)	1.367(4)
C(22)-C(23)	1.365(4)
C(23)-C(24)	1.381(3)
C(25)-C(26)	1.379(4)
C(25)-C(30)	1.394(3)
C(26)-C(27)	1.380(4)
C(27)-C(28)	1.367(5)
C(28)-C(29)	1.355(5)
C(29)-C(30)	1.382(3)

C(7)-Sn(1)-C(1)	117.62(13)
C(7)-Sn(1)-C(4)	119.14(13)
C(1)-Sn(1)-C(4)	118.31(11)
C(7)-Sn(1)-N(1)	82.34(10)
C(1)-Sn(1)-N(1)	82.77(9)
C(4)-Sn(1)-N(1)	82.61(9)
C(9)-N(1)-C(3)	113.2(2)
C(9)-N(1)-C(6)	113.4(3)
C(3)-N(1)-C(6)	112.2(2)
C(9)-N(1)-Sn(1)	105.69(16)
C(3)-N(1)-Sn(1)	105.93(16)
C(6)-N(1)-Sn(1)	105.59(16)
C(25)-B(1)-C(13)	111.43(18)
C(25)-B(1)-C(19)	113.81(18)
C(13)-B(1)-C(19)	103.49(17)
C(25)-B(1)-C(10)	105.02(17)
C(13)-B(1)-C(10)	114.15(18)
C(19)-B(1)-C(10)	109.18(18)
C(2)-C(1)-Sn(1)	104.93(19)
C(2)-C(1)-H(1A)	110.8
Sn(1)-C(1)-H(1A)	110.8

C(2)-C(1)-H(1B)	110.8
Sn(1)-C(1)-H(1B)	110.8
H(1A)-C(1)-H(1B)	108.8
C(3)-C(2)-C(1)	113.1(3)
C(3)-C(2)-H(2A)	109.0
C(1)-C(2)-H(2A)	109.0
C(3)-C(2)-H(2B)	109.0
C(1)-C(2)-H(2B)	109.0
H(2A)-C(2)-H(2B)	107.8
N(1)-C(3)-C(2)	111.4(2)
N(1)-C(3)-H(3A)	109.4
C(2)-C(3)-H(3A)	109.4
N(1)-C(3)-H(3B)	109.4
C(2)-C(3)-H(3B)	109.4
H(3A)-C(3)-H(3B)	108.0
C(5)-C(4)-Sn(1)	105.52(18)
C(5)-C(4)-H(4A)	110.6
Sn(1)-C(4)-H(4A)	110.6
C(5)-C(4)-H(4B)	110.6
Sn(1)-C(4)-H(4B)	110.6
H(4A)-C(4)-H(4B)	108.8
C(6)-C(5)-C(4)	113.5(3)
C(6)-C(5)-H(5A)	108.9
C(4)-C(5)-H(5A)	108.9
C(6)-C(5)-H(5B)	108.9
C(4)-C(5)-H(5B)	108.9
H(5A)-C(5)-H(5B)	107.7
N(1)-C(6)-C(5)	111.7(2)
N(1)-C(6)-H(6A)	109.3
C(5)-C(6)-H(6A)	109.3
N(1)-C(6)-H(6B)	109.3
C(5)-C(6)-H(6B)	109.3
H(6A)-C(6)-H(6B)	107.9

C(8)-C(7)-Sn(1)	105.41(18)
C(8)-C(7)-H(7A)	110.7
Sn(1)-C(7)-H(7A)	110.7
C(8)-C(7)-H(7B)	110.7
Sn(1)-C(7)-H(7B)	110.7
H(7A)-C(7)-H(7B)	108.8
C(9)-C(8)-C(7)	114.0(3)
C(9)-C(8)-H(8A)	108.8
C(7)-C(8)-H(8A)	108.8
C(9)-C(8)-H(8B)	108.8
C(7)-C(8)-H(8B)	108.8
H(8A)-C(8)-H(8B)	107.7
N(1)-C(9)-C(8)	111.6(3)
N(1)-C(9)-H(9A)	109.3
C(8)-C(9)-H(9A)	109.3
N(1)-C(9)-H(9B)	109.3
C(8)-C(9)-H(9B)	109.3
H(9A)-C(9)-H(9B)	108.0
C(11)-C(10)-B(1)	112.04(18)
C(11)-C(10)-H(10A)	109.2
B(1)-C(10)-H(10A)	109.2
C(11)-C(10)-H(10B)	109.2
B(1)-C(10)-H(10B)	109.2
H(10A)-C(10)-H(10B)	107.9
C(12)-C(11)-C(10)	125.9(2)
C(12)-C(11)-H(11A)	117.1
C(10)-C(11)-H(11A)	117.1
C(11)-C(12)-H(12A)	119.5(18)
C(11)-C(12)-H(12B)	122(2)
H(12A)-C(12)-H(12B)	118(3)
C(18)-C(13)-C(14)	112.7(2)
C(18)-C(13)-B(1)	128.4(2)
C(14)-C(13)-B(1)	118.9(2)

F(1)-C(14)-C(15)	116.7(2)
F(1)-C(14)-C(13)	118.6(2)
C(15)-C(14)-C(13)	124.7(2)
F(2)-C(15)-C(14)	120.7(3)
F(2)-C(15)-C(16)	119.4(3)
C(14)-C(15)-C(16)	119.9(2)
F(3)-C(16)-C(17)	120.7(3)
F(3)-C(16)-C(15)	120.6(3)
C(17)-C(16)-C(15)	118.7(2)
F(4)-C(17)-C(16)	119.6(2)
F(4)-C(17)-C(18)	120.6(2)
C(16)-C(17)-C(18)	119.7(2)
F(5)-C(18)-C(17)	114.8(2)
F(5)-C(18)-C(13)	120.9(2)
C(17)-C(18)-C(13)	124.3(2)
C(20)-C(19)-C(24)	112.2(2)
C(20)-C(19)-B(1)	127.66(19)
C(24)-C(19)-B(1)	120.05(19)
F(11)-C(20)-C(21)	114.7(2)
F(11)-C(20)-C(19)	120.9(2)
C(21)-C(20)-C(19)	124.4(2)
F(12)-C(21)-C(22)	119.8(2)
F(12)-C(21)-C(20)	120.1(2)
C(22)-C(21)-C(20)	120.1(2)
F(13)-C(22)-C(23)	120.6(2)
F(13)-C(22)-C(21)	120.4(2)
C(23)-C(22)-C(21)	119.0(2)
F(14)-C(23)-C(22)	120.2(2)
F(14)-C(23)-C(24)	120.8(2)
C(22)-C(23)-C(24)	119.0(2)
F(15)-C(24)-C(23)	114.9(2)
F(15)-C(24)-C(19)	119.7(2)
C(23)-C(24)-C(19)	125.4(2)

C(26)-C(25)-C(30)	113.2(2)
C(26)-C(25)-B(1)	120.2(2)
C(30)-C(25)-B(1)	126.0(2)
F(6)-C(26)-C(25)	119.8(2)
F(6)-C(26)-C(27)	115.4(3)
C(25)-C(26)-C(27)	124.8(3)
F(7)-C(27)-C(28)	120.2(3)
F(7)-C(27)-C(26)	121.1(3)
C(28)-C(27)-C(26)	118.7(3)
F(8)-C(28)-C(29)	120.3(3)
F(8)-C(28)-C(27)	119.7(3)
C(29)-C(28)-C(27)	120.0(2)
F(9)-C(29)-C(28)	120.6(2)
F(9)-C(29)-C(30)	119.9(3)
C(28)-C(29)-C(30)	119.5(3)
F(10)-C(30)-C(29)	114.8(2)
F(10)-C(30)-C(25)	121.4(2)
C(29)-C(30)-C(25)	123.8(3)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_{30}H_{23}BF_{15}NSn$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	42(1)	35(1)	38(1)	3(1)	8(1)	4(1)
N(1)	62(1)	40(1)	52(1)	6(1)	17(1)	1(1)
B(1)	46(1)	33(1)	35(1)	1(1)	6(1)	-6(1)
F(1)	85(1)	59(1)	60(1)	23(1)	26(1)	-4(1)
F(2)	79(1)	110(2)	60(1)	13(1)	35(1)	-20(1)
F(3)	61(1)	124(2)	82(1)	-1(1)	39(1)	10(1)
F(4)	65(1)	64(1)	76(1)	2(1)	21(1)	17(1)

F(5)	80(1)	43(1)	61(1)	14(1)	36(1)	7(1)
F(6)	58(1)	58(1)	86(1)	-11(1)	18(1)	4(1)
F(7)	113(2)	63(1)	98(2)	-24(1)	18(1)	23(1)
F(8)	139(2)	44(1)	80(1)	-21(1)	-1(1)	-16(1)
F(9)	79(1)	80(1)	79(1)	-10(1)	3(1)	-42(1)
F(10)	49(1)	70(1)	67(1)	-12(1)	10(1)	-13(1)
F(11)	79(1)	40(1)	60(1)	11(1)	-6(1)	-17(1)
F(12)	102(1)	60(1)	73(1)	29(1)	-20(1)	-9(1)
F(13)	96(1)	85(1)	64(1)	13(1)	-33(1)	-21(1)
F(14)	105(2)	55(1)	78(1)	-9(1)	-25(1)	-24(1)
F(15)	82(1)	34(1)	58(1)	-2(1)	-4(1)	-3(1)
C(1)	75(2)	50(1)	57(2)	0(1)	30(1)	10(1)
C(2)	97(2)	49(2)	83(2)	5(1)	39(2)	24(2)
C(3)	94(2)	33(1)	70(2)	2(1)	25(2)	4(1)
C(4)	63(2)	53(1)	40(1)	-3(1)	9(1)	2(1)
C(5)	95(2)	74(2)	48(2)	0(1)	26(2)	-9(2)
C(6)	105(2)	60(2)	53(2)	16(1)	32(2)	3(2)
C(7)	44(1)	62(2)	76(2)	15(1)	1(1)	6(1)
C(8)	50(2)	79(2)	99(3)	6(2)	0(2)	-12(2)
C(9)	62(2)	58(2)	102(2)	7(2)	29(2)	-14(1)
C(10)	44(1)	38(1)	38(1)	2(1)	12(1)	-2(1)
C(11)	48(1)	37(1)	38(1)	5(1)	12(1)	-2(1)
C(12)	79(2)	41(1)	43(1)	-2(1)	16(1)	0(1)
C(13)	44(1)	40(1)	32(1)	0(1)	7(1)	-7(1)
C(14)	54(1)	51(1)	38(1)	5(1)	10(1)	-10(1)
C(15)	52(1)	80(2)	37(1)	4(1)	13(1)	-17(1)
C(16)	39(1)	83(2)	47(1)	-7(1)	12(1)	-6(1)
C(17)	43(1)	57(1)	44(1)	-4(1)	7(1)	-1(1)
C(18)	46(1)	44(1)	36(1)	0(1)	10(1)	-7(1)
C(19)	46(1)	38(1)	38(1)	3(1)	8(1)	-6(1)
C(20)	54(1)	40(1)	44(1)	5(1)	5(1)	-11(1)
C(21)	64(2)	49(1)	49(1)	15(1)	1(1)	-6(1)
C(22)	61(2)	64(2)	43(1)	5(1)	-7(1)	-12(1)

C(23)	63(2)	47(1)	51(1)	-6(1)	0(1)	-14(1)
C(24)	56(1)	38(1)	41(1)	2(1)	6(1)	-3(1)
C(25)	52(1)	33(1)	36(1)	3(1)	5(1)	-7(1)
C(26)	61(2)	39(1)	48(1)	1(1)	7(1)	-4(1)
C(27)	85(2)	39(1)	55(2)	-2(1)	10(1)	10(1)
C(28)	98(2)	35(1)	45(1)	-4(1)	0(1)	-12(1)
C(29)	72(2)	47(1)	44(1)	2(1)	2(1)	-22(1)
C(30)	58(1)	42(1)	37(1)	3(1)	4(1)	-12(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

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