Stereoselective allylboration using (*B*)-γ-alkoxyallyldiisopinocampheylboranes: highly selective reactions for organic synthesis

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Dedicated to the memory of Professor Herbert C. Brown

Abstract
This review describes the synthesis of novel alkoxyallylborane reagents derived from α-pinene and their applications in stereoselective total synthesis of natural products. These reagents can be conveniently prepared and react readily with a wide variety of aldehydes and imines to provide the corresponding α-alkoxy substituted homoallylic alcohols/amines respectively. The (*Z*)-γ-alkoxyallylborane reagents provide 1,2-*syn* α-alkoxy homoallylic alcohols/amines while the corresponding (*E*)-γ-alkoxyallylborane reagents furnish 1,2-*anti* products exclusively in very high enantioselectivities.

Keywords: Allylboration, alkoxyallylboration, α-pinene, diisopinocampheylborane, homoallylic alcohol, α-alkoxy-homoallylic alcohols, 1,2-*syn* diols, protecting groups

Contents

Introduction

Allylboration is an important C-C bond forming reaction in organic chemistry.[1] Reaction of "allyl"boranes **1** with aldehydes **2** is advantageous over many "allyl"metalations in terms of stereoselectivity because allylboration proceeds via a rigid six-membered boracyclic transition state **3** (Figure 1). Unlike several other metals that produce toxic metal byproducts, boron eventually gets converted to boric acid salts that are non-toxic and less cumbersome to dispose. There are theoretically five different points of substitution on the "allyl" borane **2** thereby making this reaction highly versatile in terms of obtaining a wide variety of complex products.

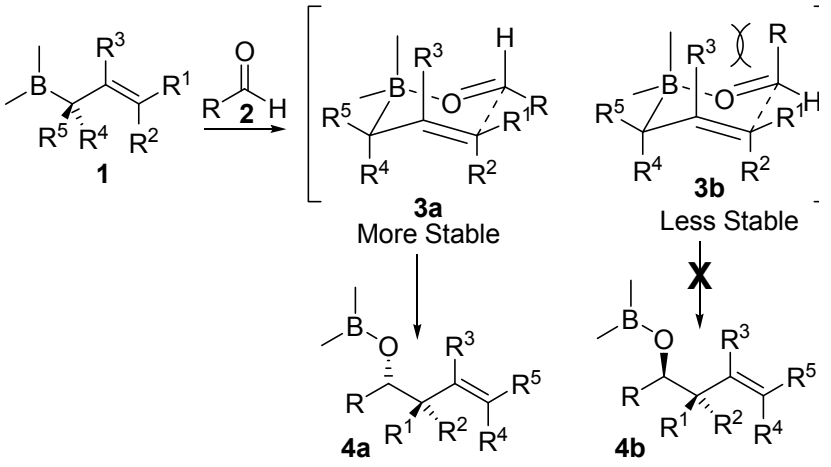


Figure 1. The scope of "allyl"boration.

Several chiral auxiliaries have been examined for the asymmetric allylboration of aldehydes/imines to prepare the optically pure homoallylic alcohols/amines in high ee and de.[2] Hoffmann, Brown, Yamamoto, Roush, and others have made significant contributions in this area. Hoffmann pioneered the first asymmetric allyl and crotylborations utilizing a camphor-derived auxiliary[3] for both single and double diastereoselective asymmetric synthesis.[4] Yamamoto and coworkers introduced tartrate esters as chiral auxiliaries for propargylboration and allenylboration of aldehydes to produce homoallenyl and homopropargylic alcohols respectively in very high ee.[5] They demonstrated that the ee's of the alcohols depend on the sterics of the alkyl group in the tartrate ester. Ethyl and isopropyl tartrates lead to lower ee's, while sterically bulky groups such as cyclododecyl and 2,4-dimethylpentyl tartrates lead to higher ee's.[6] Roush extended the use of isopropyl tartrate as a chiral auxiliary for allyl and crotylborations.[7] Several other "allyl"boranes derived from chiral 1,2-diols **5-8**,[8] oxazaborolane **9**,[9] and diazaborolane **10**,[10] *etc.* have also been developed for the asymmetric allylboration of aldehydes/imines (Figure 2).

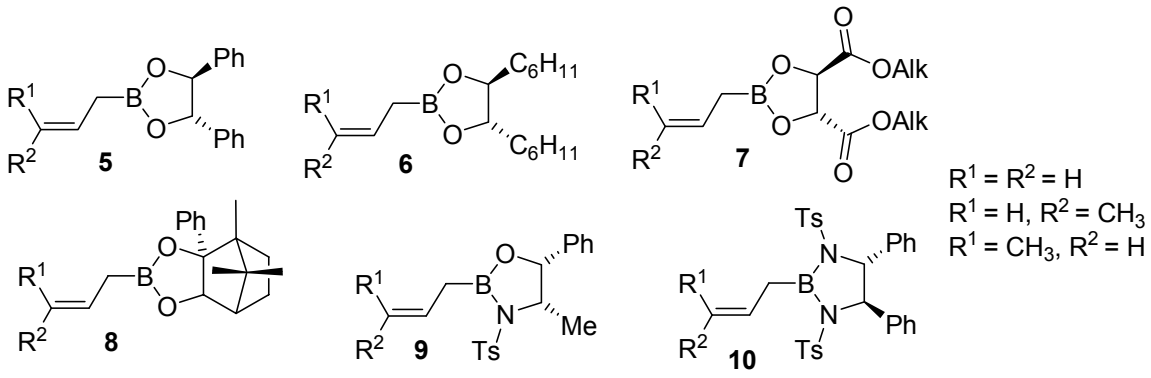
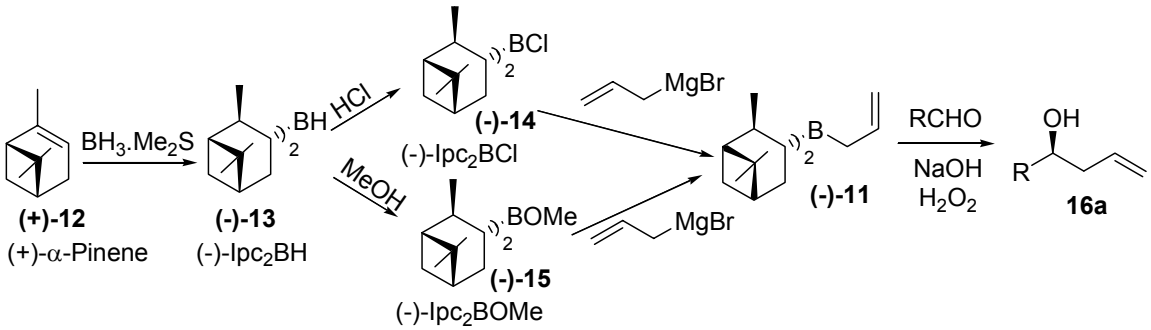


Figure 2. Various chiral auxiliary-based "allyl"boranes.

However, till date, the chiral allylborane derived from α-pinene (*B*-allyldiisopinocampheylborane **11)**,[11] has proven to be the most effective in terms of high optical purity observed for a wide range of achiral and chiral aldehydes (Scheme 1).[2a,b] Several higher order "allyl"boranes derived from α-pinene have been readily prepared either *in situ* or as isolable reagents.[2a,b] All these reagents provide very good yields of the corresponding homoallylic alcohols/amines upon reaction with aldehydes/imines in excellent enantio- and diastereoselectivities.

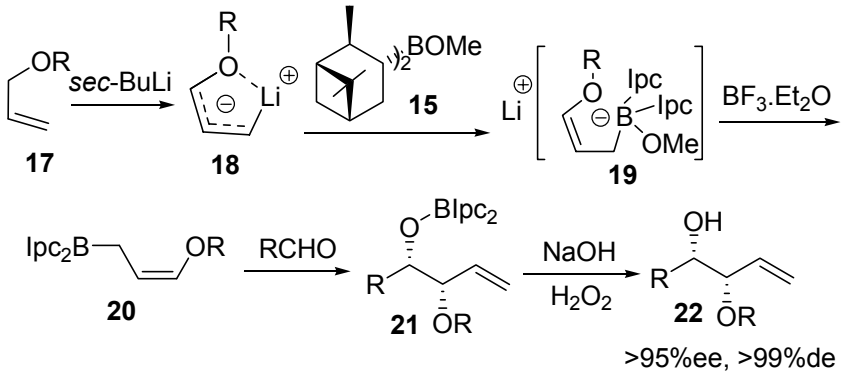


Scheme 1. Preparation and reactivity of *B*-allyldiisopinocampheylborane.

1. Preparation of (*B*)-(*Z*)-γ-[alkoxyallyl]diisopinocampheylborane

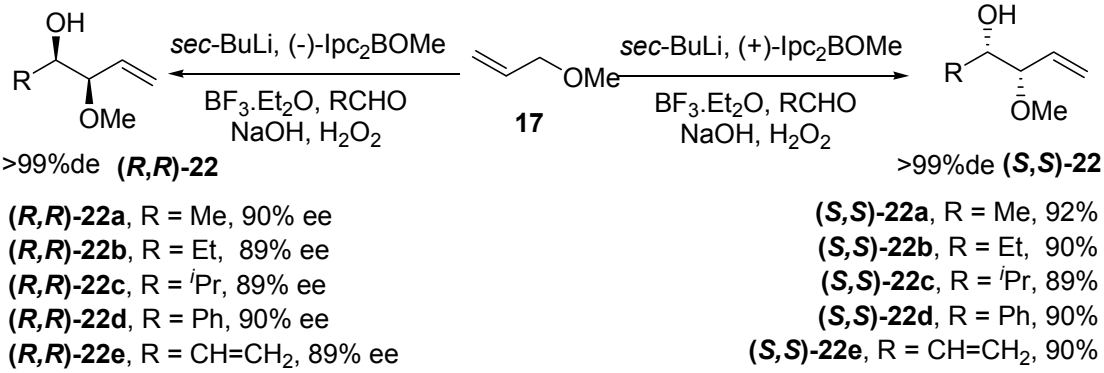
One of the several higher order allylboranes developed by Brown *et. al.* is (*B*)-(*Z*)-γ-alkoxyallyldiisopinocampheylborane **20**. This reagent is typically prepared and used *in situ*. Thus, the treatment of allylic ether **17** with a strong base such as *sec*-BuLi results in the formation of a (*Z*)-allylic anion **18**. The exclusive *Z*-stereochemistry of the double bond is explained based on the coordination of lithium and oxygen resulting in a five membered cyclic transition state.[12] Reaction of this anion **18** with Ipc_2BOMe provides an "ate" complex **19**, with a

(*Z*) geometric conformation of the olefin. Addition of a strong Lewis acid to the "ate" complex **19**, releases the allylborane reagent (*B*)-(*Z*)-(γ)-alkoxyallyldiisopinocampheylborane **20**. Reaction of aldehyde with **20** followed by oxidative workup using alkaline hydroperoxide yields the 1,2-*syn* α-alkoxy homoallylic alcohol **22** in very high de and ee (Scheme 2).



Scheme 2. Mechanism of alkoxyallylboration.

The reaction is highly reagent controlled and the enantiomer of the homoallylic alcohol is strictly governed by the antipode of Ipc_2BOMe used. e.g. the reagent obtained from (+)-Ipc_2BOMe always furnishes homoallylic alcohols with α-configuration while the analogous reagent obtained from (-)-Ipc_2BOMe provides alcohols with β-configuration (Scheme 3).[13] Thus the reaction of allylmethyl ether **17** with *sec*-butyl lithium followed by (+)-Ipc_2BOMe, $BF_3.Et_2O$, and acetaldehyde provided (*S*,*S*)-**22a** in 92% ee. Similarly, acetaldehyde provided 90% ee of (*R*,*R*)-**22a** upon reaction with the alkoxyallylborane derived from (-)-Ipc_2BOMe. A variety of aldehydes such as propionaldehyde, isobutyraldehyde, benzaldehyde, and acrolein afforded the corresponding (*R*,*R*)- or (*S*,*S*)- alcohols in 89-92% ee depending on the antipode of the reagent used (Scheme 3).[13]



Scheme 3. Reagent controlled alkoxyallylboration.

Although the alkoxyallylboration using allyl methyl ether is highly useful, the methoxy group in the product homoallylic alcohols requires strong reaction conditions and reagents for deprotection. This sometimes limits the application of the reagent especially in a molecule with sensitive functional/protecting groups. Accordingly, following the initial reports by Brown, several groups have modified the protecting groups on the reagent to obtain a variety of alkoxyallylborane reagents **20a-f** (Figure 3). For example, the allylborane obtained by replacing the methoxy group (**20a**) with methoxymethyl (MOM) group (**20b)** results in the formation of α-MOM substituted homoallylic alcohols, which could be further deprotected under mild reaction conditions to afford the 1,2-*syn* diols. The utility of several of these substituted reagents will be discussed in detail in the following sections.

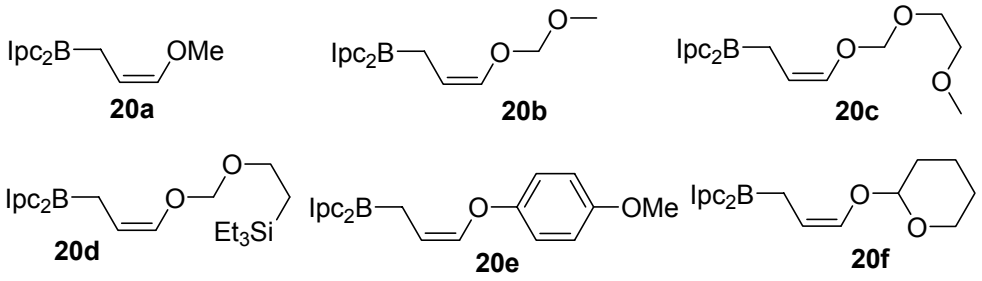
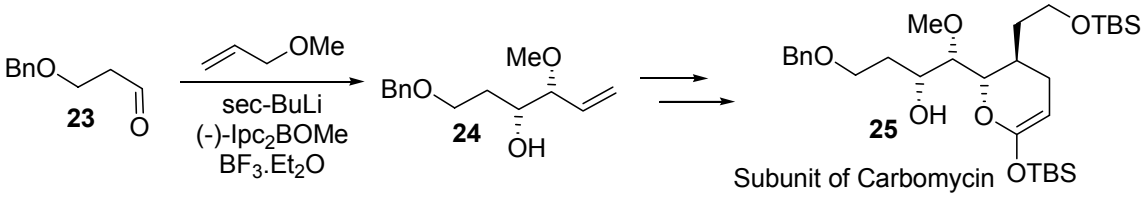


Figure 3. Various (*B*)-*γ*-alkoxyallyldiisopinocampheylboranes.

2. Applications of (*B*)-(*Z*)-γ-[methoxyallyl]diisopinocampheylborane, 20a

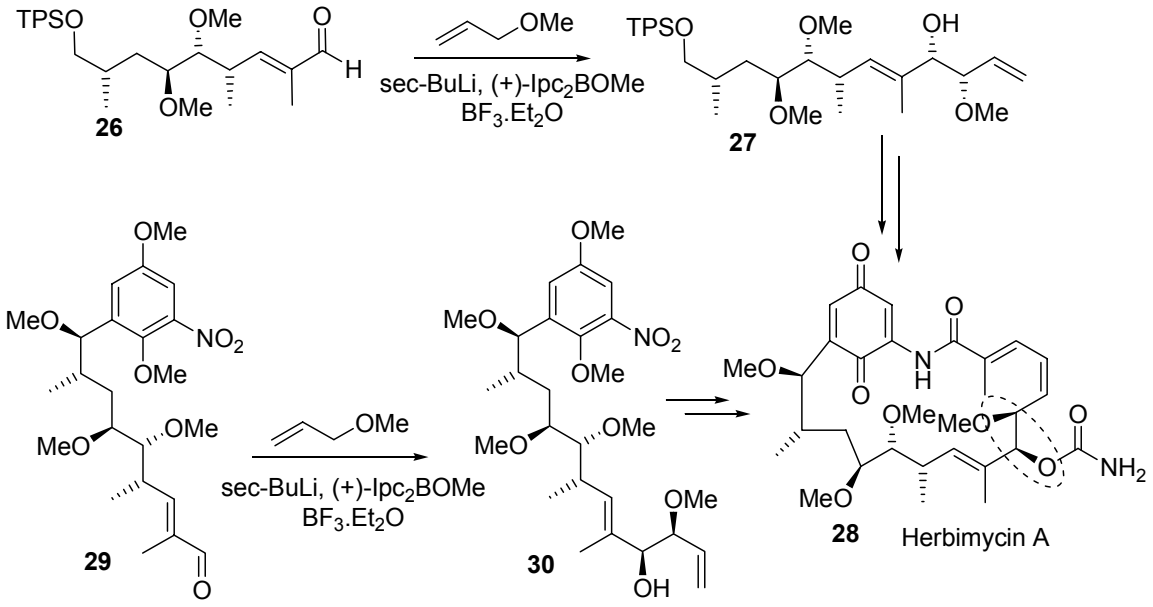
A formal synthesis of Carbomycin, a macrolide antibiotic, was achieved by Wuts and coworkers by utilizing the stereoselective alkoxyallylboration with **20a** (Scheme 4).[14] Thus the reaction of 3-benzyloxypropionaldehyde **23** with **20a** afforded the homoallylic alcohol **24** in >99% diastereoselectivity and 90% ee. Further transformations on **24** provided the subunit **25**, which was earlier synthesized by Nicolaou during the synthesis of Carbomycin.[15]



Scheme 4. Synthesis of a subunit of Carbomycin.

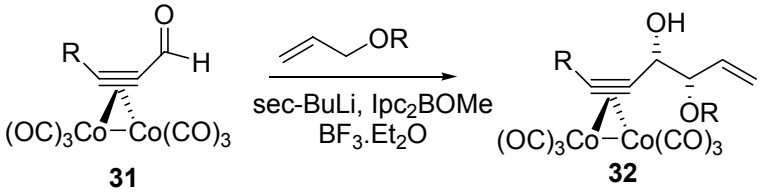
Several research groups have employed alkoxyallylboration as a key step in the synthesis of Herbimycin A, a potent antibiotic belonging to the class benzoquinoid ansamycin.[16] Tatsuta reported the alkoxyallylboration of an α-β-unsaturated aldehyde **26** with allylborane **20a**

providing the homoallylic alcohol **27**, which was further converted to Herbimycin A **28** in several steps.[16a] Very recently, a similar type of aldehyde was also utilized by Cossy towards the synthesis of Herbimycin.[16c] Panek and Carter utilized alkoxyallylboration of a highly advanced intermediate **29** to ascertain the C_6-C_7 stereochemistry in Herbimycin A (Scheme 5).[16b]



Scheme 5. Synthesis of Herbimycin.

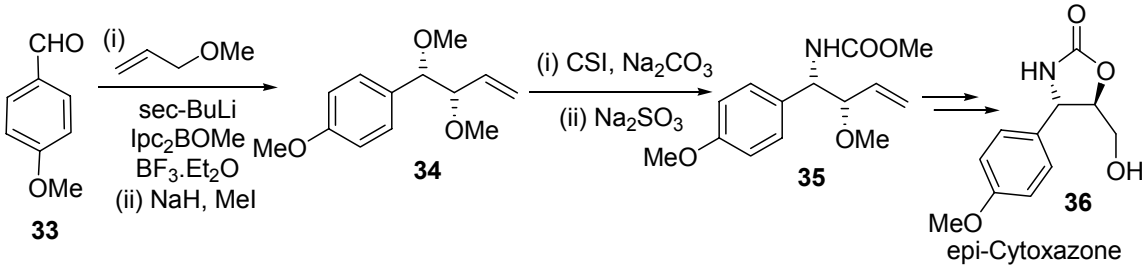
Ganesh and Nicholas demonstrated that the cobalt carbonyl complexes of the acetylenic aldehydes **31** react with γ-methoxyallyldiisopinocampheylborane **20a** to provide the homoallylic alcohols **32** in high yield and stereoselectivity (Scheme 6).[17] It is important to note that the corresponding uncomplexed acetylenic aldehydes react under the same conditions and provide a very low yield of the product alcohols. It is relatively straight forward to carry out the deprotection of the cobalt carbonyl complexes using ceric ammonium nitrate to obtain the free homoallylic alcohols.



Scheme 6. Alkoxyallylboration of $CO_2(CO)_6$ complexes of acetylenic aldehydes.

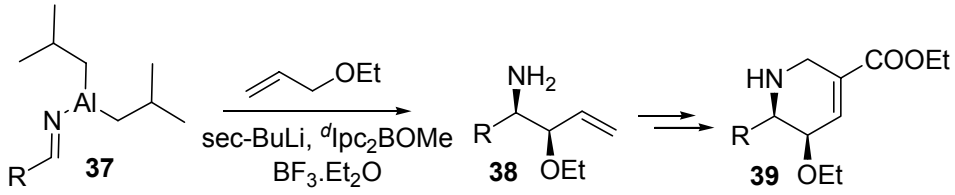
Jung and coworkers developed a novel regio- and diastereoselective amination of allylic ethers using chlorosulfonyl isocyanate CSI.[18] A wide variety of allylic ethers (e.g. **34**) undergo

this amination providing the corresponding acetamides **35**. They were further able to extend this protocol for the synthesis of novel cytokine modulators namely cytoxazone and *epi*-cytoxazone **36** starting from the alkoxyallylboration of *p*-anisaldehyde **33** (Scheme 7).[19]



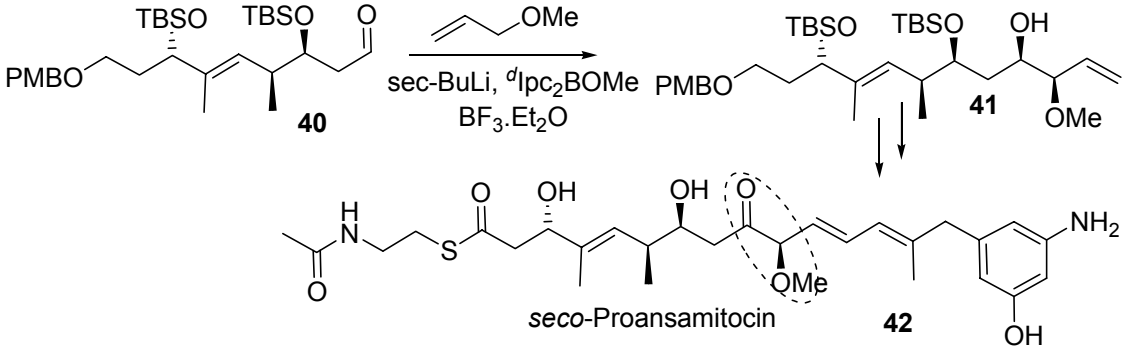
Scheme 7. Synthesis of epi-Cytoxazone.

There are very few reports of "allyl"boration of imines in the literature and recently Ramachandran *et al.* performed the alkoxyallylboration of imines as a key step for the synthesis of functionalized tetrahydropyridines. Partial reduction of nitriles with DiBAL-H provided the *N*-aluminoimines **37**, which underwent alkoxyallylboration to afford the homoallylic amines **38** which were converted to the tetrahydropyridines **39** utilizing ring closing metathesis as a key step (Scheme 8).[20]



Scheme 8. Alkoxyallylboration of imines.

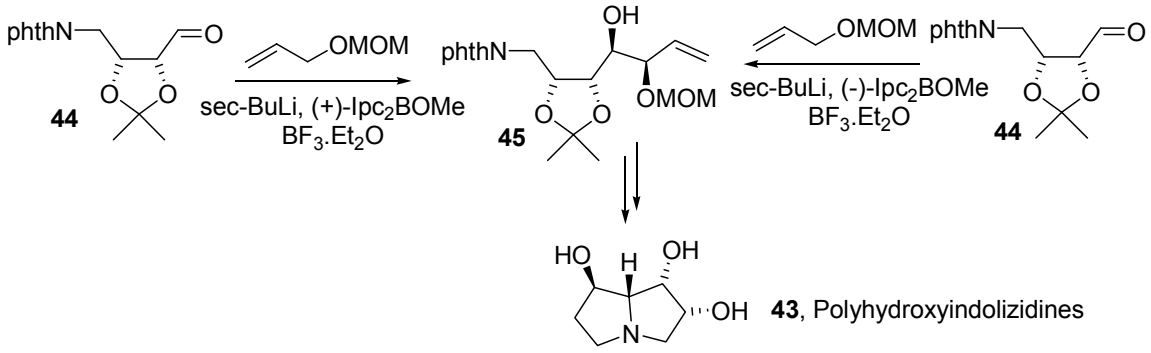
Kirschning and coworkers described the synthesis of proansamitocin **42**, a key biosynthetic intermediate of a highly potent anti-tumor agent ansamitocin, utilizing the alkoxyallylboration of chiral aldehyde **40** with allylborane **20a** as a key step (Scheme 9).[21]



Scheme 9. Synthesis of *seco*-Proansamitocin.

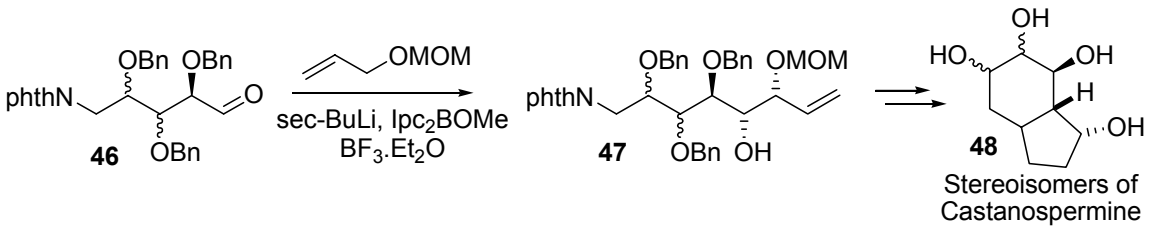
3. Applications of (*B*)-(*Z*)-γ-[(methoxymethoxy)allyl]diisopinocampheyl borane, 20b

Burgess and Henderson developed a novel approach for the synthesis of polyhydroxylated indolizidines **43** utilizing the homoallylic alcohols obtained from the alkoxyallylboration of aldehydes in four steps. They observed that the allylboranes obtained from both (+)- and (-)-Ipc_2BOMe react with the aldehyde **44** to provide the same enantiomer of the homoallylic alcohol **45** (Scheme 10).[22] This is an interesting observation, as in most cases, α-pinene based allyl reagents undergo reagent controlled additions to aldehydes, and incipient chirality of the substrate has no enantiocontrol over the product formation.



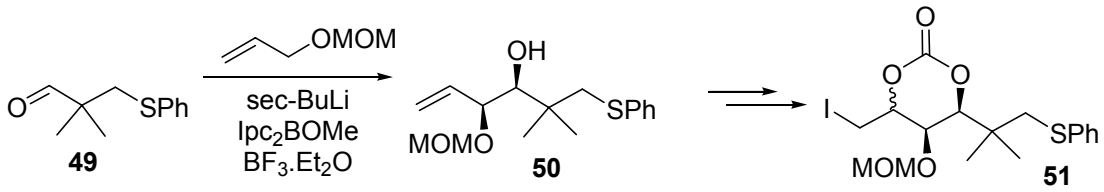
Scheme 10. Substrate controlled alkoxyallylboration.

Burgess and coworkers further synthesized several stereoisomers of castanospermine **48** utilizing alkoxyallylboration of aldehyde **46** as one of the key steps (Scheme 11).[23]



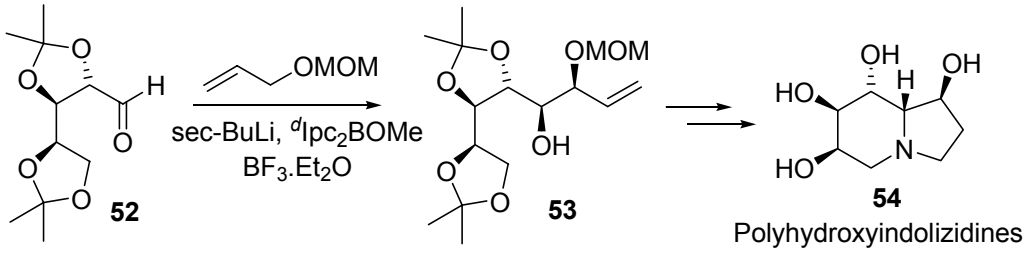
Scheme 11. Synthesis of Castanospermine stereoisomers.

Smith and Duan developed an IBr mediated diastereoselective electrophilic cyclization of carbonates derived from homoallylic alcohols **50** to afford α-iodocarbonate **51** (Scheme 12).[24] The product iodocarbonates are highly versatile intermediates in organic synthesis and can be utilized for the synthesis of epoxy alcohols, iodohydrins, diols, triols, cyclic carbonates etc. [25]



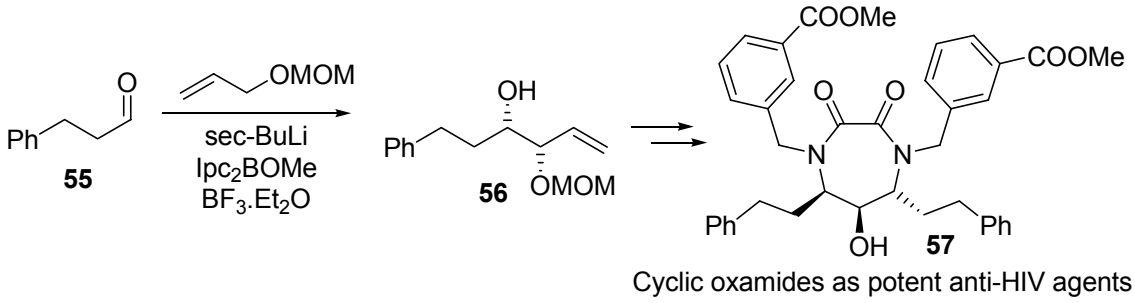
Scheme 12. Iodolactonization of homoallylic alcohols.

Alkoxyallylboration of an aldehyde **52** derived from arabinose, with γ-methoxymethoxyallyldiisopinocampheylborane **20b** provided the homoallylic alcohol **53** in 80% yield and >99% diastereoselectivity (Scheme 13).[26] Jadhav *et*. *al*. were able to convert the octose derivative **53** into the polyhydroxyindolizidine **54** in seven further transformations. Several of these indolizidines such as castanospermine, swainsonine etc. exhibit potent anti-cancer, anti-viral, and anti-AIDS activities.[27]



Scheme 13. Synthesis of polyhydroxyindolizidines.

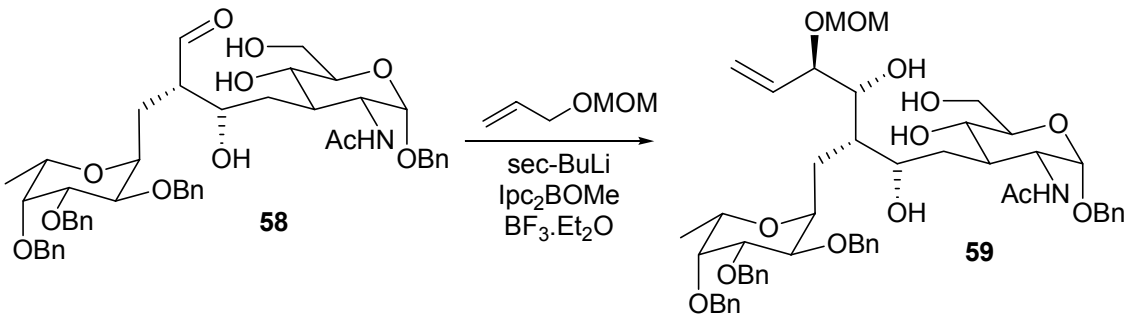
Jadhav and coworkers were successful in synthesizing cyclic oxamides **57** as potent anti-HIV agents starting from the alkoxyallylboration of 3-phenylpropionaldehyde **55** with **20b** (Scheme 14).[28]



Scheme 14. Synthesis of cyclic oxamides

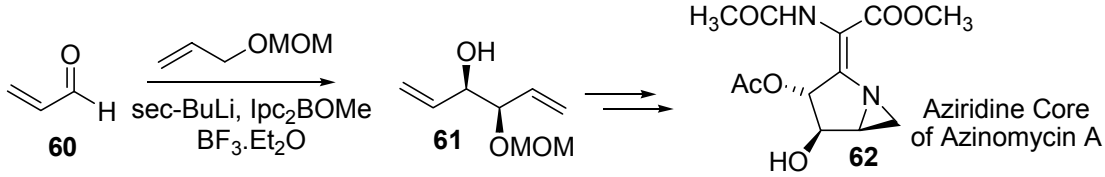
Sutherland and Armstrong prepared a diverse set of C-trisaccharides as potential inhibitors for the cell surface proteins of the bacterium Helicobactor *pylori* utilizing alkoxyallylboration of

a disachcharide aldehyde **58** with **20b** yielding the homoallylic alcohol **59** which was further transformed into the C-trisaccharide in several steps (Scheme 15).[29]



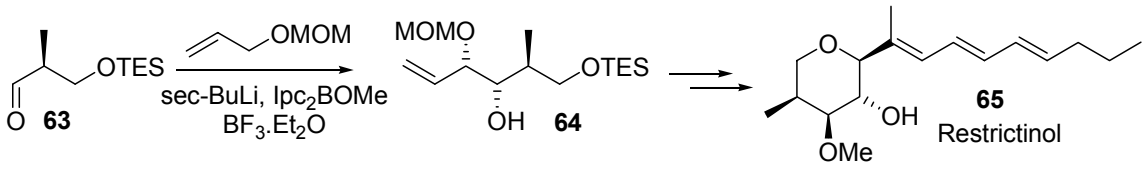
Scheme 15. Synthesis of C-trisaccharides.

Coleman and coworkers demonstrated the synthesis of a potent anti-tumor agent Azinomycin A starting with alkoxyallylboration of acrolein with allylborane reagent **20b** (Scheme 16).[30] The homoallylic alcohol **61**, thus obtained was conveniently transformed into the fully functionalized aziridine core **62**, of Azinomycin A.



Scheme 16. Synthesis of Azinomycin A.

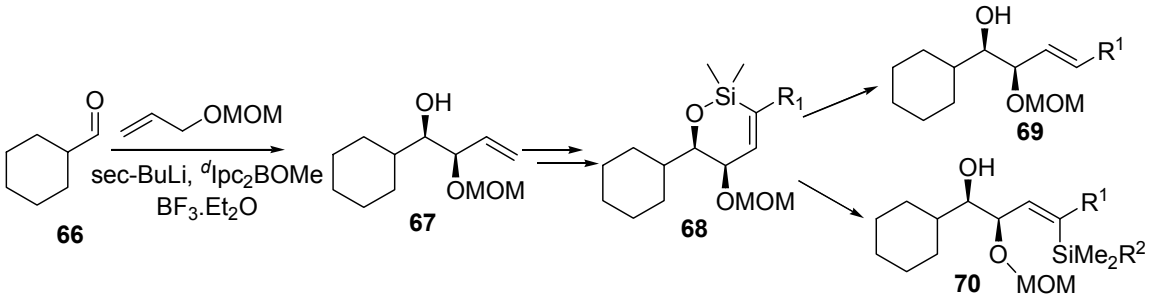
Barrett and coworkers synthesized restrictinol, the hydrolysis product of the anti-fungal natural product restricticin, utilizing the alkoxyallylboration of the α-chiral aldehyde **63** derived from Roche's ester (Scheme 17).[31] The homoallylic alcohol **64** thus obtained was further transformed into restrictinol.



Scheme 17. Synthesis of Restrictinol.

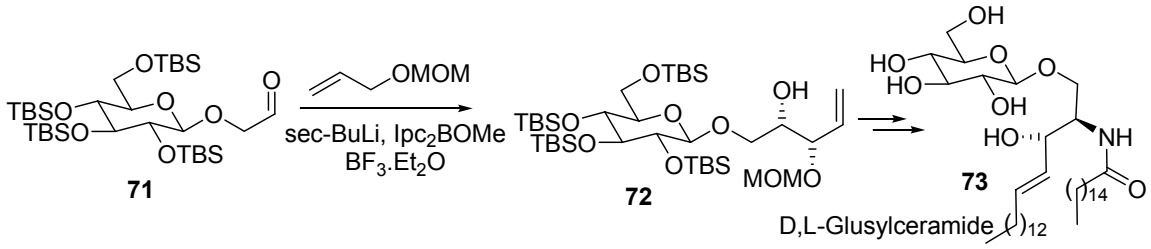
Barrett's group also developed an efficient method for the formation of 1,2-oxasilines **68** starting from the homoallylic alcohols **67**. Protection of alcohols **67** as vinylsilyl ethers,

followed by ring closing metathesis afforded the oxasilines **68**, which undergo fluoride mediated deprotection to provide the δ-substituted homoallylic alcohols **69**. Alkyl metals also react with the oxasilines **68** to afford the δ-alkyl-δ-silyl disubstituted homoallylic alcohols **70** (Scheme 18).[32]



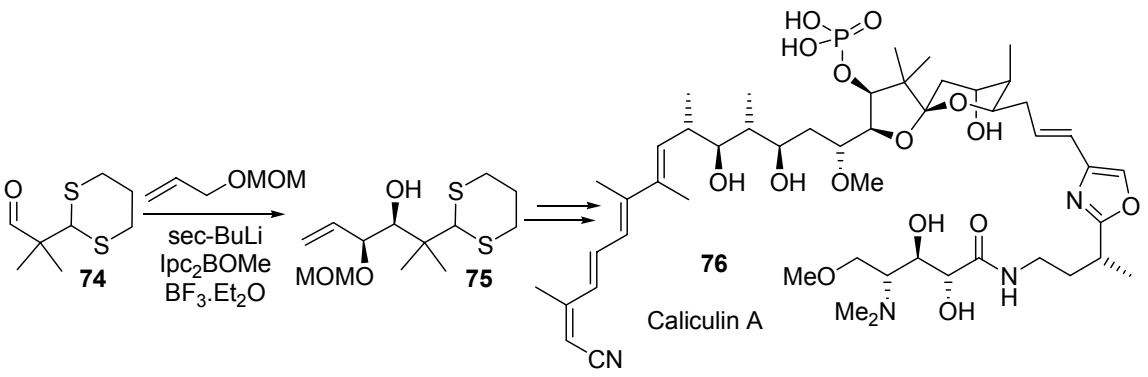
Scheme 18. Synthesis and applications of 1,2-oxasilines.

Barrett's group expanded the scope of the above protocol for the synthesis of glycosphingolipids as depicted in Scheme 19.[33] Thus the alkoxyallylboration of the aldehyde **71** with allylborane **20b** afforded the homoallylic alcohol **72** that upon silyl protection followed by ring closing metathesis afforded the oxasilines that were eventually transformed into the D, L-Glucosylceramide **73** (Scheme 19).

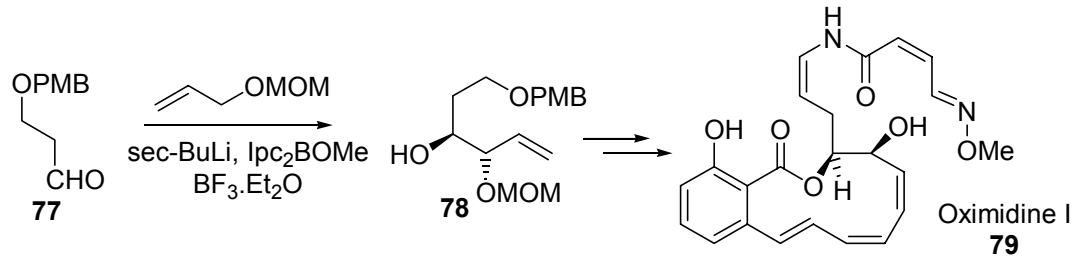


Scheme 19. Synthesis of glycosphingolipids.

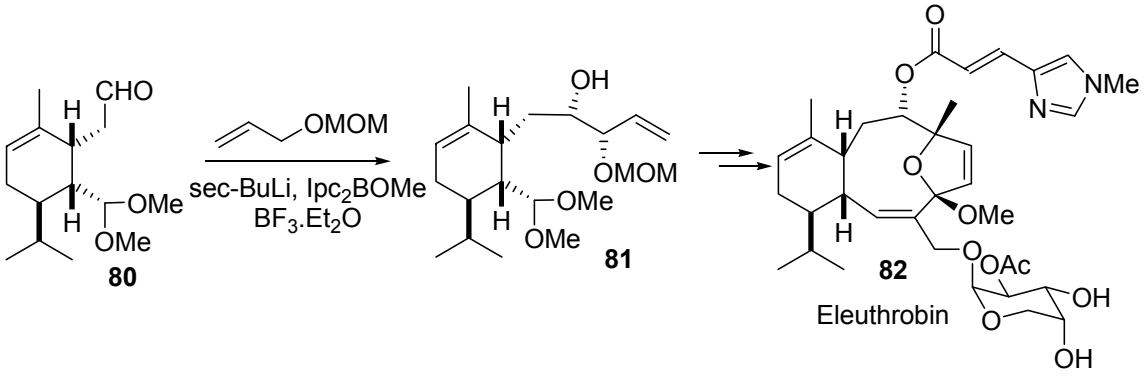
Several others including Smith (Calyculin A, Scheme 20),[34] Porco (Oximidines, Scheme 21),[35] Gennari (Eleuthrobin, Scheme 22),[36] DeBrabander (Peloruside, Scheme 23),[37] Zhou (C_1-C_{16} subunit of Peloruside, Scheme 24),[38] and Negishi (C_1-C_{16} side chain of Mycolactone, Scheme 25)[39] have employed alkoxyallylboration using reagent **20b** en route to their stereoselective syntheses of several biologically important molecules.



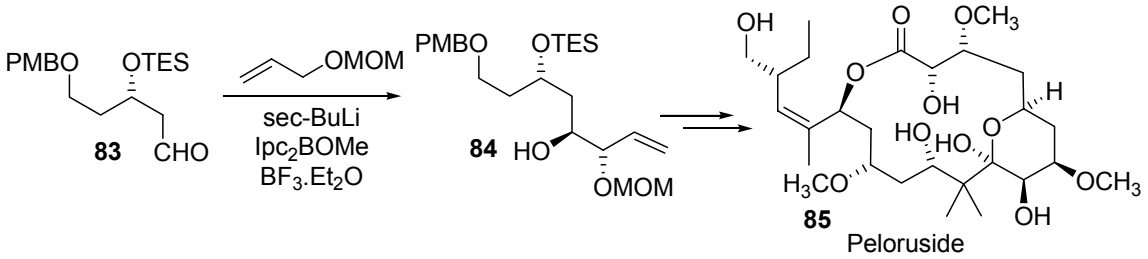
Scheme 20. Synthesis of Calyculin A.



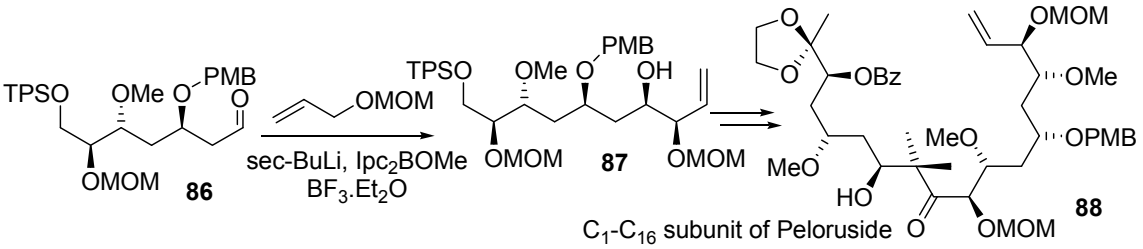
Scheme 21. Synthesis of Oximidine.



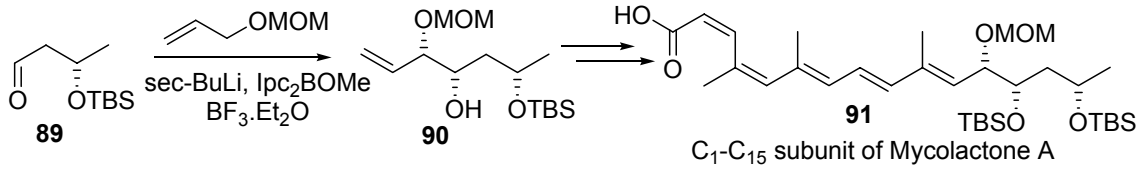
Scheme 22. Synthesis of Eleuthrobin.



Scheme 23. Synthesis of Peloruside.



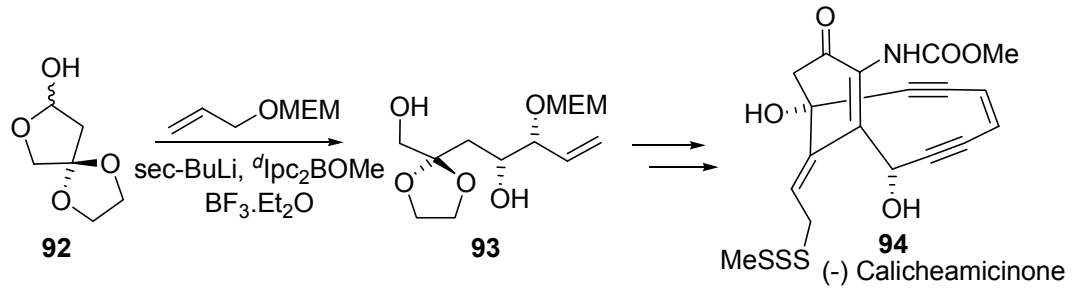
Scheme 24. Synthesis of C_1-C_{16} subunit of Peloruside.



Scheme 25. Synthesis of C_1-C_{15} side chain of Mycolactone A.

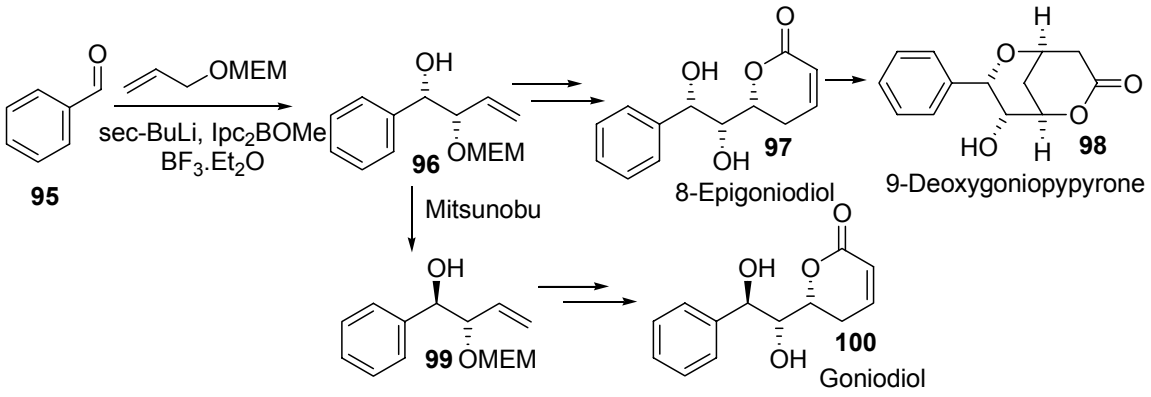
4. Applications of (*B*)-(*Z*)-γ-[(2-methoxyethoxymethoxy)allyl]diisopino-campheylborane, 20c

Nicolaou described the total synthesis of Calicheamicinone **94** involving the alkoxyallylboration of a γ-lactol **92** with *B*-γ-methoxyethoxymethoxyallyldiisopino campheylborane **21c** as a key step (Scheme 26).[40]



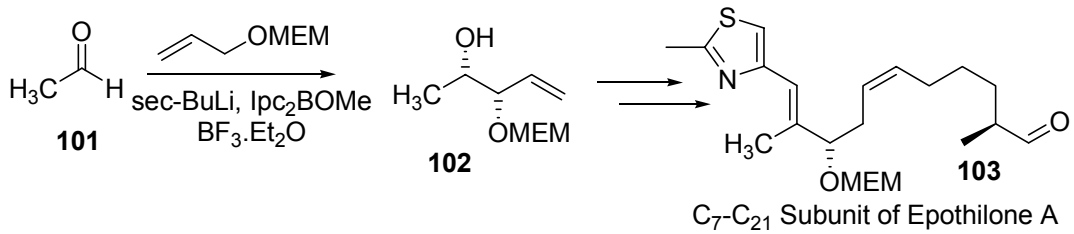
Scheme 26. Synthesis of (-)-Calicheamicinone.

Ramachandran *et al.* have demonstrated the utility of alkoxyallylboration with *B*-γ-alkoxyallyldiisopinocampheylborane as the key step for the synthesis of several anti-tumor styryllactones such as goniodiol, epigoniodiol, and deoxygoniopypyrone.[41] The alkoxyallylboration of benzaldehyde with **20c**, provided (*S*, *S*)-α-alkoxyhomoallylic alcohol **96**. The target lactones **97-100** were prepared in 6-7 steps starting from the homoallylic alcohol **96** via tandem allylboration and ring closing metathesis protocol (Scheme 27).



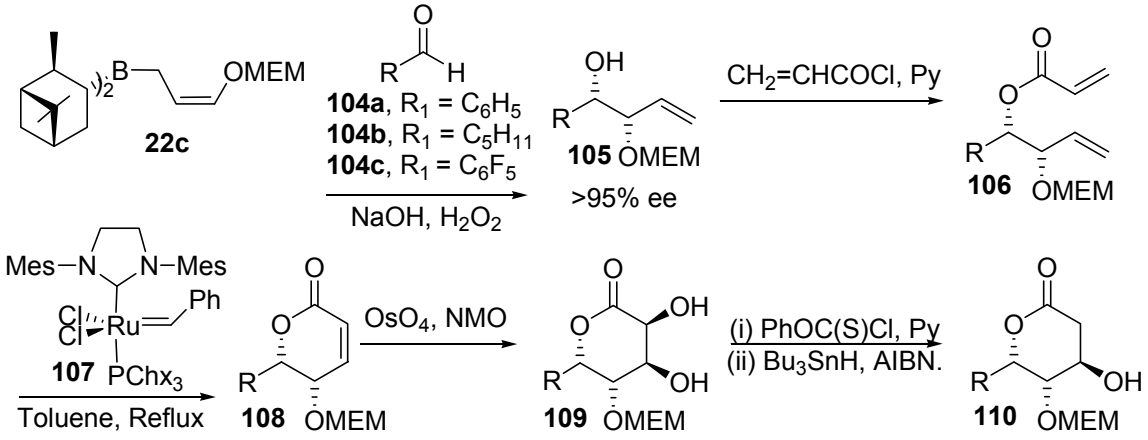
Scheme 27. Stereoselective synthesis of styryllactones.

The same group also achieved the stereoselective synthesis of C_7-C_{21} subunit of potent anti-cancer agent Epothilone A, **103** starting from the (*S*,*S*) α-alkoxyhomoallylic alcohol **102** derived from the alkoxyallylboration of acetaldehyde (Scheme 28).[42]



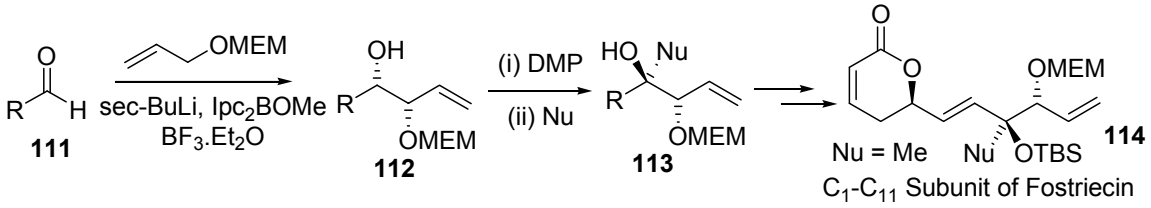
Scheme 28. Synthesis of C_7-C_{21} subunit of Epothilone.

They were further able to demonstrate the applicability of the α-alkoxy homoallylic alcohols for the synthesis of β-hydroxy-δ-lactones.[43] The reaction of homoallylic alcohols **105** with acryloyl chloride followed by ring closing metathesis with Grubbs's II Generation catalyst **107** afforded α-pyrones **108**. Diastereoselective dihydroxylation of the double bond in **108** provided the 1,2-*cis* diol **109** that upon reaction with phenyl chlorothionoformate and Bu_3SnH and AIBN yielded the α-hydroxy-δ-lactone **110** regioselectively (Scheme 29). This protocol was applied for the synthesis of C_1-C_8 and C_{15}-C_{21} subunits of a potent anti-cancer agent Discodermolide.[43]



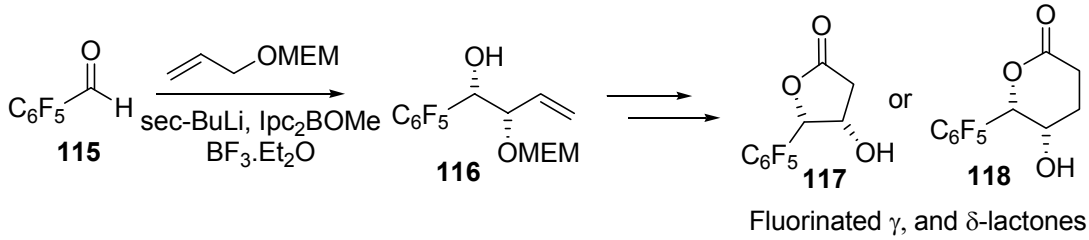
Scheme 29. Diastereoselective dihydroxylation and regioselective deoxygenation.

Oxidation of the α-alkoxy alcohols **112** derived from alkoxyallylboration of aldehydes, afforded the α-alkoxyketones that underwent diastereoselective chelation controlled nucleophilic addition with a variety of nucleophiles affording the homoallylic chiral tertiary alcohols **113**. Further transformations on alcohol **113** yielded the C_1-C_{11} subunit of Fostriecin (Scheme 30).[44]

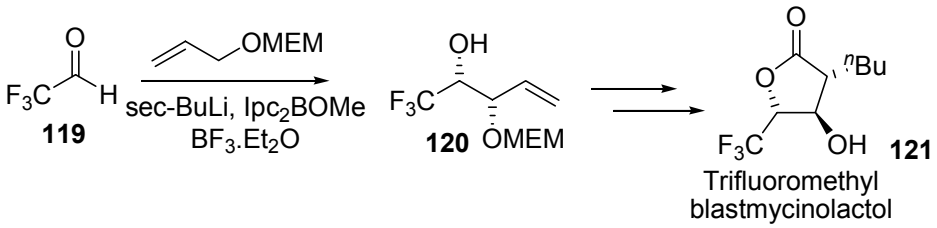


Scheme 30. Synthesis of C_1-C_{11} subunit of Fostriecin.

Extension of alkoxyallylboration to perfluoroaldehydes, provided the fluoro-homoallylic alcohols **116** which were eventually converted to the fluorinated γ-lactones **117** and δ-lactones **118** in 2-3 steps (Scheme 31).[45] A trifluoromethyl analog of blastmycinolactol **121** was also synthesized starting the homoallylic alcohol **120** derived from alkoxyallylboration of trifluoroacetaldehyde **119** (Scheme 32).[46]

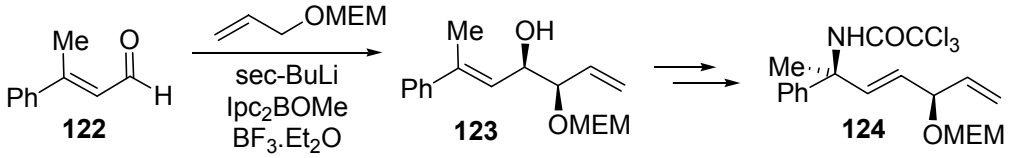


Scheme 31. Synthesis of fluorinated γ-and δ-lactones.



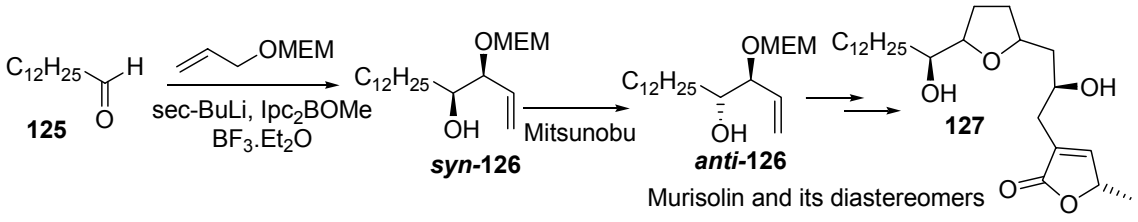
Scheme 32. Synthesis of fluorinated blastmycinolactol.

The same group utilized the homoallylic alcohols obtained by the alkoxyallylboration of α,β-unsaturated aldehyde **122**, for the synthesis of acetamides **124** via a [3,3]-sigmatropic Overman rearrangement[47] (Scheme 33).[48]



Scheme 33. Overman rearrangement of homoallylic alcohols.

Recently, Curran and coworkers utilized the alkoxyallylboration of *n*-tridecanal with both antipodes of *B*-γ-alkoxyallyldiisopinocampheylborane for the synthesis of (*S*, *S*) and (*R*, *R*) 1,2-*syn* α-alkoxy homoallylic alcohols ***syn*-126**.[49] Mitsunobu inversion of the corresponding alcohols afforded two anti alcohols ***anti*-126**. All these four diastereomers were later tagged to a fluorous PMB-bromide[50] and were converted to (+)-Murisolin and fifteen other diastereomers in several steps (**Scheme 34**).

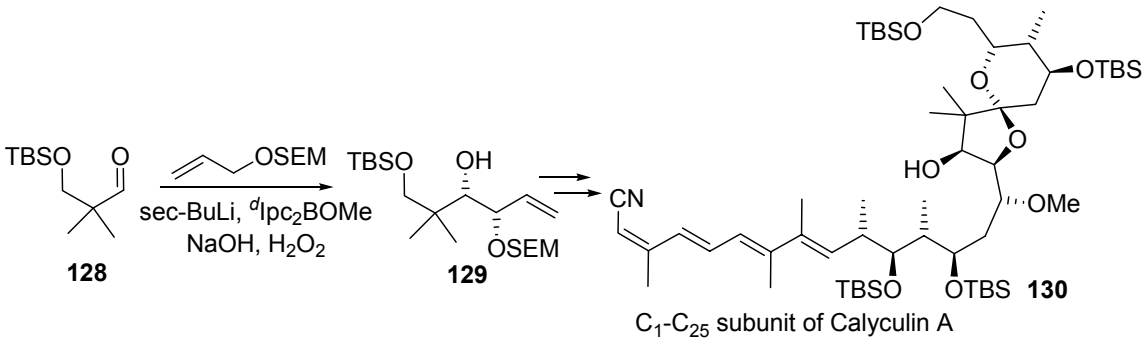


Scheme 34. Synthesis of Murisolin and its stereoisomer libraries.

5. Applications of (*B*)-(*Z*)-γ-[(2-trimethylsilylethoxymethoxy)allyl] diisopinocampheylborane, 20d

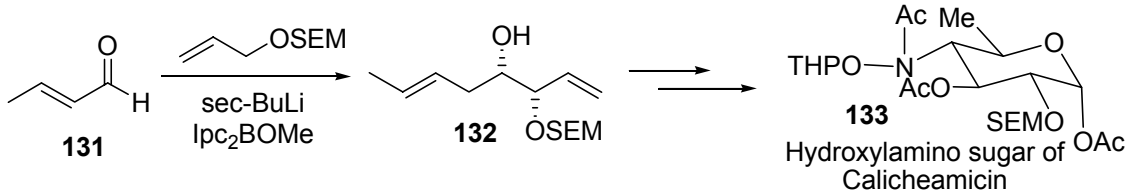
Barrett and coworkers demonstrated for the first time that silyl protecting groups could also be utilized for the alkoxyallylboration of aldehydes (Scheme 35).[51] As is apparent, the SEM ether is

sensitive to the Lewis acid ($BF_3.Et_2O$), and hence they carried out the allylboration without the use of $BF_3.Et_2O$. The "ate" complex of the reagent **20d** was equally reactive like the free "allyl"borane to provide the alcohol **129** that upon further transformations provided the C_1-C_{25} subunit **130** of Calyculin A (Scheme 35).

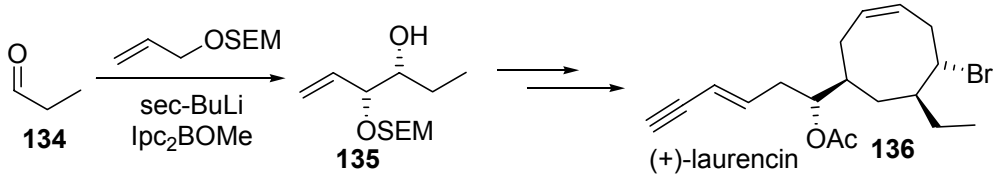


Scheme 35. Synthesis of C_1-C_{25} subunit of Calyculin A.

Similarly, Roush (hydroxylamino sugar of Calicheamycin, Scheme 36),[52] and Overman (Laurencin, Scheme 37)[53] also utilized the alkoxyallylboration of the corresponding aldehydes **131** and **134** with *B*-*γ*-trimethylsilylethoxymethoxyallyldiisopinocampheyl-borane **20d** as the main steps in their respective syntheses.



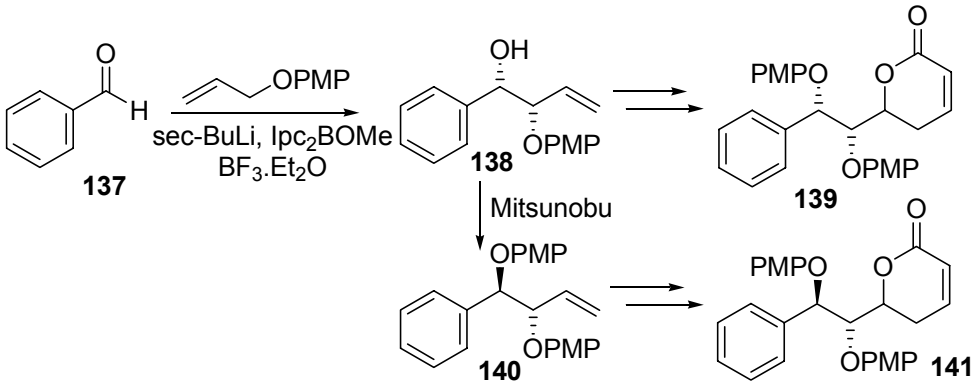
Scheme 36. Synthesis of hydroxylamino sugar of Calicheamicin.



Scheme 37. Synthesis of Laurencin.

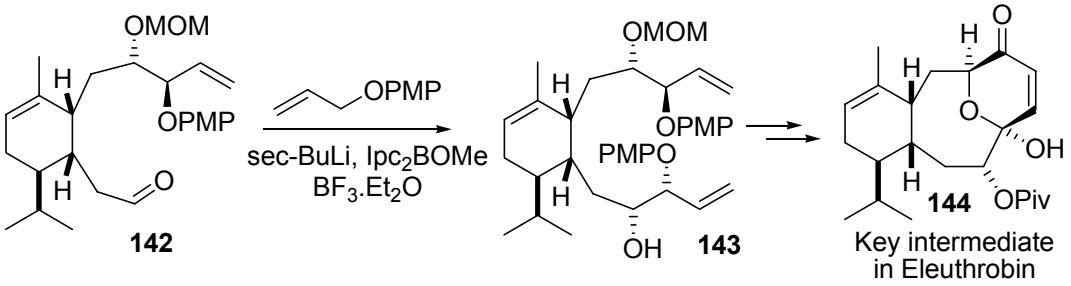
6. Applications of (*B*)-(*Z*)-γ-[(4-methoxyphenoxy)allyl]diisopino-campheylborane (20e)

Incorporation of an aryl moiety as the protecting group in the alkoxyallylborane, was achieved en route to the synthesis of styryllactones epigoniodiol **139** and goniodiol **141**. As is evident, the two structures possess *syn*- and *anti*- 1,2-diol moieties respectively. The initial alkoxyallylboration of benzaldehyde with allylborane **20e** led to the formation of the homoallylic alcohol **138**. The judicious choice of PMP protecting group in the allylborane 20e was made, so as to utilize *p*-methoxyphenol as a nucleophile in the next step (Mitsunobu inversion) of alcohol **138** to bis aryl ether **140** (Scheme 38).[41]



Scheme 38. Synthesis of styryllactones.

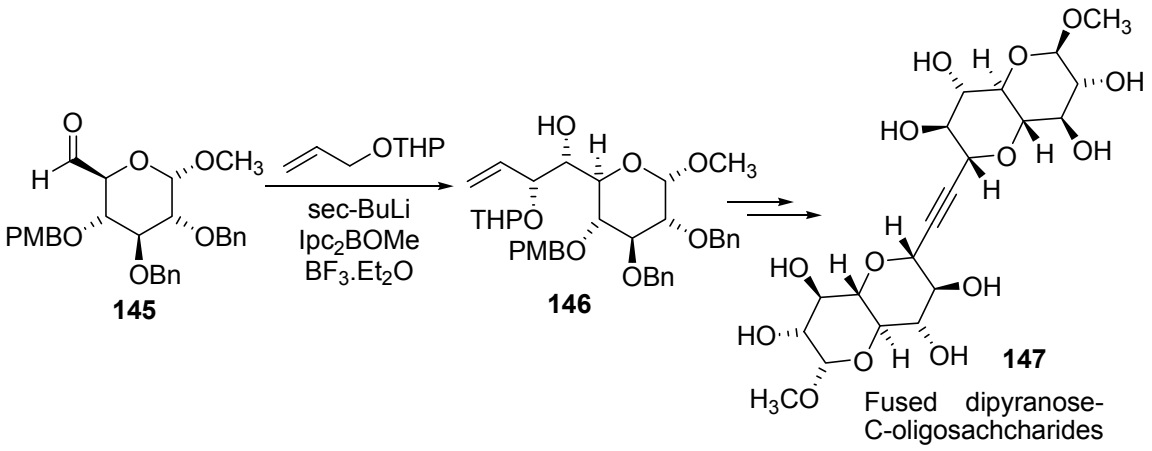
Gennari and workers utilized the reagent **20e** for alkoxyallylboration of **142** en route to the synthesis of a key intermediate of eleuthrobin **144** (Scheme 39).[36c, 54]



Scheme 39. Synthesis of the core of Eleuthrobin.

7. Applications of (*B*)-(*Z*)-γ-[(2-tetrahydropyranyloxy)allyl]diisopino-campheylborane (20f)

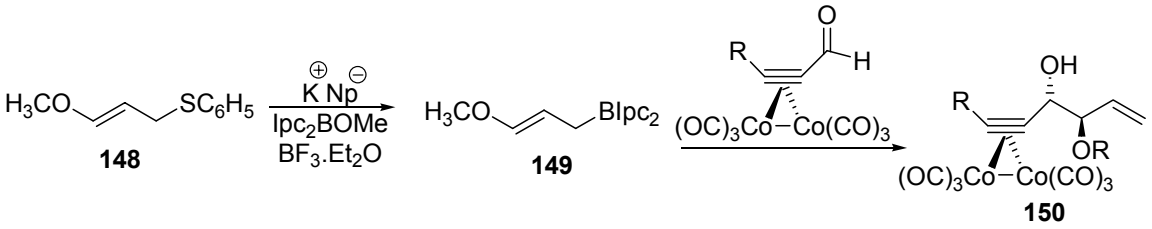
Armstrong and Sutherlin demonstrated the use of tetrahydropyranyloxyallyldiisopino campheylborane **20f** with a sugar based aldehyde **145** to obtain the alcohol **146** which was eventually converted to fused dihydropyranose oligosachcharides **147** (Scheme 40).[55]



Scheme 40. Synthesis of *C*-oligosachcharides.

8. Preparation and Applications of (*B*)-(*E*)-γ-Methoxyallyldiisopino campheylborane (149)

Ganesh and Nicholas were successful in the synthesis of *anti*-β-alkoxyhomoallylic alcohols **150** via the alkoxyallylboration of cobalt complexed acetylenic aldehydes with the *E*-methoxyallyldiisopinocampheylborane (Scheme 41).[56] The (*E*)- alkoxyallylborane **149** was prepared utilizing a procedure by Hoffmann and coworkers involving the reduction of methoxy-3-(phenylthio)propene **148** with potassium naphthalenide and subsequent treatment with Ipc_2BOMe (Scheme 41).[57]



Scheme 41. Synthesis of (E)-γ-alkoxyallyldiisopinocampheylborane.

Conclusions

In conclusion, this review describes novel alkoxyallylboranes derived from α-pinene and their applications in stereoselective total synthesis of natural products. These reagents upon reaction with a wide variety of aldehydes provide very high diastereo- and enantioselectivities for the product β-alkoxy-homoallylic alcohols. This account presents the convenient preparation and synthetic utility of these highly selective reagents for total synthesis of complex natural products. We believe that this review demonstrates the potential and robustness of the α-pinene based alkoxyallylborane reagents and provides an impetus towards enhancing the applications of these highly selective reagents for organic synthesis.

Acknowledgements

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