4,5-Diisopropyl-*B*-[(*E*)-[(3′-menthofuryl)dimethylsilyl]allyl]-1,3,2-dioxaborolane, an Improved Chiral Reagent for the Anti α-Hydroxyallylation of Aldehydes: Application to the Enantioselective Synthesis of (−)-Swainsonine

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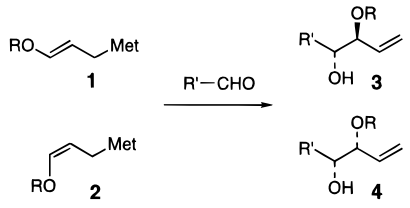
Diisopropyl tartrate-modified (*E*)-[γ-(furyldimethylsilyl)allyl]boronates **10** and **11** were designed for the enantioselective synthesis of substituted *anti*-3,4-dihydroxy-1-butenes **9** via the *anti*-α-hydroxyallylation of aldehydes. The reactions of aldehydes with **10** and **11** provided furyldimethylsilyl-substituted *anti*-1,2-silanols **12** and **13** with good enantioselectivity (74−82% ee), and the silanols were oxidized to the corresponding *anti*-1,2-diols **9** by a modified Fleming−Tamao oxidation protocol. The high reactivity of the (menthofuryl)silane unit toward electrophilic substitution allowed complete protodesilylation of menthofuryl-substituted silanols **13** and subsequent oxidation to diols **9** in a one-pot operation without competing protodesilylation of the allylsilane unit. However, a two-step protocol was required for the protodesilylation−oxidation of the less reactive 2-(5-methyl)-furyl-substituted silanols **12**. Reagents **10** and **11** exhibited similar diastereoselectivity in double asymmetric reactions with three chiral aldehydes **23**−**25** (80 to >92% de, with the exception of the mismatched reactions with aldehyde **25**, which were essentially unselective). However, [[[2-(5-methylfuryl)]dimethylsilyl]allyl]boronate **10** could only be synthesized in ≤15% yield, and oxidations of the 2-(5-methylfuryl)-substituted silanols **12** were lower-yielding than oxidations of the corresponding menthofuryl-substituted silanols **13**. Thus, diisopropyl tartrate-modified (*E*)-[γ-[(menthofuryl)dimethylsilyl]allyl]boronate **11** proved to be the more useful of the two reagents. As a demonstration of the utility of **11** in the synthesis of polyhydroxylated natural products, this new reagent was used in a brief and highly stereoselective synthesis of the naturally occurring alkaloid (−)-swainsonine (**42**).

The stereoselective synthesis of carbohydrates and other polyoxygenated natural products from acyclic precursors remains a topic of considerable interest. The challenge of creating intermediates with multiple contiguous oxygenated stereogenic centers has received substantial attention from organic chemists, and a variety of strategies for meeting this challenge have been described.[1−6] The α-hydroxyallylation of aldehydes with (γ-alkoxyallyl)metal reagents (such as **1** or **2**) is a particularly attractive strategy, as these α-hydroxyallylation reactions generate *syn*- or *anti*-1,2-diols in concert with the formation of a carbon−carbon bond.[7−9]

Brown,[10] Marshall,[9] Yamamoto,[11,12] and we[13] have developed highly enantioselective procedures for the synthesis of syn diol monoethers **4** via the reactions of aldehydes with (*Z*)-(γ-alkoxyallyl)boranes[10] or (*Z*)-(γ-alkoxyallyl)stannanes.[9,11−13] However, efforts to synthesize substituted *anti*-3,4-dihydroxy-1-butenes **3** from (*E*)-(γ-alkoxyallyl)metal reagents have not met with as much success. (*E*)-(γ-Alkoxyallyl)boron reagents have proved difficult to synthesize because of the configurational instability of the (*E*)-γ-alkoxyally anion precursors.[14,15] Takai's (γ-alkoxyallyl)chromium reagent, generated *in situ* by the reduction of an acrolein acetal with $CrCl_2$, offers direct and often high-yielding access to *anti*-1,2-diol monoethers **3**, but this reagent suffers from poor diastereoselectivity in a number of cases.[16] Recently, Marshall has circumvented some of these difficulties by transmetalating enantioenriched α-alkoxyallylic stannanes with $InCl_3$, presumably giving rise to allylindium reagents, which react with aldehydes enantioselectively to provide *anti*-1,2-diol monoethers **3** as the major products.[17,18]



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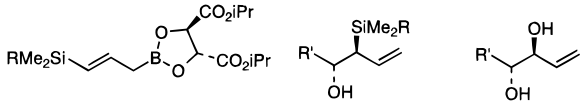
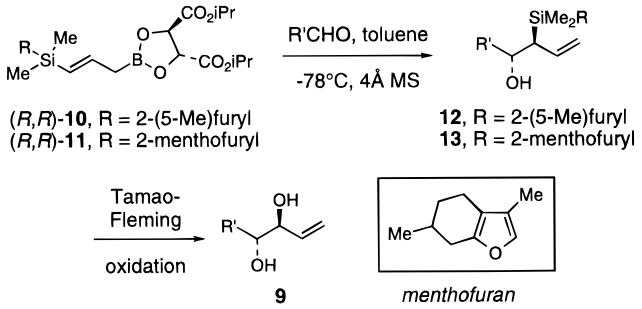
The initial difficulties associated with the stereoselective synthesis of (*E*)-γ-alkoxyallyl metal reagents[14,15] prompted the development of indirect methods for synthesis of substituted *anti*-3,4-dihydroxy-1-butenes. The (*E*)-[γ-[(dialkylamino)silyl]allyl]zinc reagent developed by Tamao and Ito reacts diastereoselectively with aldehydes to give *anti*-silanol intermediates that are then oxidized with retention of C-Si stereochemistry to the corresponding *anti*-3,4-diols **3** (R = H).[19] We[20−22] and, subsequently, Barrett[23] extended the Tamao strategy to the asymmetric synthesis of *anti*-1,2-diols with the use of (*E*)-γ-silyl-substituted allylboron reagents containing, respectively, diisopropyl tartrate and B-diisopinocampheyl[24] chiral auxiliaries. Brown has recently developed a related strategy for the indirect α-hydroxyallylation of aldehydes via reactions with an (*E*)-γ-boryl-substituted allyldiisopinocampheylborane.[25]



(*R,R*)-**5**, R = OC_6H_{11} **7**, R = OC_6H_{11} **9**
(*R,R*)-**6**, R = C_6H_5 **8**, R = C_6H_5

We previously developed the diisopropyl tartrate−modified (*E*)-γ-silyl-substituted allylboronate reagents **5** and **6** for the synthesis of *anti*-1,2-diols **9**.[20−22] (Cyclohexyloxy)dimethylsilyl-substituted allylboronate **5** reacts with achiral aldehydes (R′CHO) to provide *anti*-1,2-silanols **7** in good yield, though with only moderate enantioselectivity (64−72% ee);[20,22] silanols **7** were then oxidized to *anti*-1,2-diols **9** via the Tamao procedure.[26,27] Unfortunately, although the phenyldimethylsilyl-substituted allylboronate **6** proved to be more enantioselective than **5** (81−87% ee), the resulting *anti*-1,2-silanols **8** could not be oxidized to the corresponding diols **9**.[21,22]

Fleming and co-workers have shown that the phenyldimethylsilyl group can be converted to a hydroxyl with retention of stereochemistry via electrophilic substitution of the phenyl group to provide a heteroatom-substituted silane, which can then be oxidized to the corresponding alcohol.[26,28,29] However, electrophilic substitution reactions of the allylsilane unit are faster than those of the phenylsilane group; thus, the Fleming procedure cannot be used to convert a phenyldimethylsilyl unit to a hydroxyl group in the presence of an allylsilane.[30] Consequently, allylboronate **6** did not prove to be a useful reagent for the synthesis of *anti*-1,2-diols **9**.



(*R,R*)-**10**, R = 2-(5-Me)furyl **12**, R = 2-(5-Me)furyl
(*R,R*)-**11**, R = 2-menthofuryl **13**, R = 2-menthofuryl

9

Because furans undergo a variety of electrophilic substitution reactions, including protodesilylation, much faster than do correspondingly substituted phenyl groups,[31] we anticipated that replacement of the phenyldimethylsilyl group in silanols **8** with a furyldimethylsilyl group would allow us to convert the resulting silanols **12** or **13** to diols **9** via a modified Tamao−Fleming oxidation. Stork had previously demonstrated that furylsilanes can function as hydroxyl surrogates, via cleavage to fluorosilanes (which are suitable substrates for the Tamao oxidation), upon treatment with *n*-Bu_4NF in THF.[32] Also, subsequent to the initiation of our work, Kocienski demonstrated that allylic furyldimethylsilanes can be converted to allylic alcohols by a sequence involving photooxidation of the furylsilane unit prior to the Tamao-Fleming oxidation.[33]

We report herein the synthesis of the furyldimethylsilyl-substituted allylboronates **10** and **11** and the development of mild protodesilylation−oxidation conditions suitable for elaboration of allylic silanes **12** and **13** to diols **9** in good to excellent yields. As a demonstration of the utility of these new reagents in the synthesis of polyhydroxylated natural products, we also describe the use of reagent **11** in a brief and highly stereoselective synthesis of the naturally occurring alkaloid (−)-swainsonine. A preliminary account of these investigations has been reported.[34]

Diisopropyl Tartrate-Modified (*E*)-[γ-[[2-(5-Methylfuryl)]dimethylsilyl]allyl boronate. The protodesilylation of aryltrimethylsilanes has been thoroughly studied by Earborn and co-workers.[31,35,36] Various substituted phenyltrimethylsilanes [*e.g.*, anisyltrimethylsilane (k_{rel} = 1500) and mesityltrimethylsilane (k_{rel} = 53 600)] and heteroaryltrimethylsilanes [*e.g.*, 2-(phenylthio)trimethylsilane (k_{rel} = 4800) and 2-furyltrimethylsilane (k_{rel} = 17 200)] undergo protodesilylation much more readily than does phenyltrimethylsilane.[15a,16] The very large difference (>10^4) in the rate of protodesilylation of furyltrimethylsilane compared to phenyltrimethylsilane suggested that it might be possible to protodesilylate a furylsilane in the presence of an allylsilane. We initially chose to use the 5-methylfuryl-substituted allylsilane **15** rather than one containing a simpler (unsubstituted) furan because the 5-methyl group would prevent metalation at the C(5) position during the synthesis of allylboronate **10**.

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(30) Fleming has recently reported the use of the (2-methylbut-2-enyl)diphenylsilyl group as a hydroxyl surrogate and has shown that this new unit can be converted to a hydroxyl in the presence of a 1,2-disubstituted allylsilane (Fleming, I.; Winter, S. B. D. *Tetrahedron Lett.* **1993**, *45*, 7287). However, we suspect that this new silyl group cannot be used in the synthesis of allylboronates like **6**, **10**, or **11** because the 2-methylbut-2-enyl moiety might be metalated competitively with the allyl unit under the reaction conditions.
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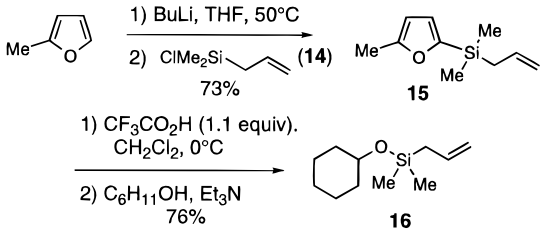
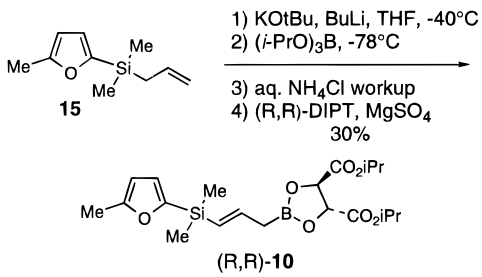
(36) Deans, F. B.; Earborn, C. *J. Chem. Soc.* **1959**, 2299.

Allylsilane **15** was prepared from 2-methylfuran by metalation with *n*-BuLi in THF and subsequent silylation with allyldimethylchlorosilane (**14**).[37] As a test of our hypothesis that protodesilylation of the furylsilane would be faster than the allylsilane, a solution of **15** in CH_2Cl_2 at 0 °C was treated with 1.1 equiv of trifluoroacetic acid. Although we were not able to isolate the intermediate product, presumably the trifluoroacetate-substituted dimethylallylsilane, addition of cyclohexanol and triethylamine to the crude product provided (cyclohexyloxy)-dimethylallylsilane (**16**) in 76% yield.

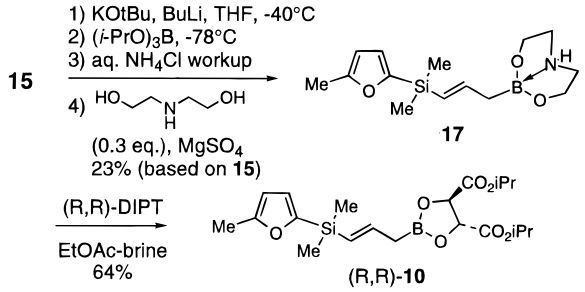


Allylboronate **10** was prepared from allylsilane **15** using the procedure previously employed for the synthesis of γ-silyl-substituted allylboronates **5** and **6**.[22,38] Thus, a solution of **15** in THF was treated with potassium *tert*-butoxide and *n*-butyllithium (1.0 equiv each) at −40 °C for 15−20 min and then cooled to −78 °C and treated with triisopropyl borate (1.0 equiv) for 15 min. The mixture was poured into aqueous NH_4Cl, extracted with Et_2O, treated with either (*R*,*R*)- or (*S*,*S*)-diisopropyl tartrate (1.0 equiv), and then dried over $MgSO_4$ and concentrated *in vacuo*.

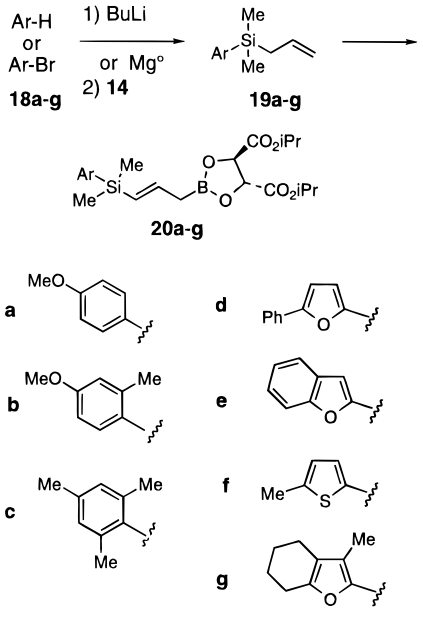


Both the yield and the purity of reagent **10** were low, and our attempts to purify **10** were unsuccessful. Reactions of crude **10** with various aldehydes were low yielding, presumably because of the impurity of the reagent. We attempted to improve the yield and purity of **10** by varying the reaction temperature and duration, and by experimenting with different bases (including *n*-BuLi, *n*-BuLi with TMEDA, *s*-BuLi, and *s*-BuLi with TMEDA), but the yield (< 30%) and the purity remained low.

To improve the purity of the reagent, we turned to a two-step procedure that proceeds by way of the crystalline diethanolamine complex **17**.[38] Treatment of the crude allylboronic acid with 0.3 equiv of diethanolamine provided crude **17** that was purified by recrystallization (23% yield from **15**). The amount of diethanolamine used in this experiment was dictated by the amount of allylboronic acid estimated to be present in the product of the metalation procedure; use of larger amounts of diethanolamine gave an oily product from which crystallization of **17** was exceedingly difficult. Hydrolysis of **17** in a two-phase mixture of EtOAc and brine and immediate esterification of the allylboronic acid with either (*R*,*R*)- or (*S*,*S*)-diisopropyl tartrate provided reagent **10** that was contaminated with *ca.* 20% of DIPT; the yield was generally 50−65%. Reagent **10** was stored over 4 Å molecular sieves at −20 °C as a 0.5 M solution in toluene. Although the reagent was sufficiently pure to use in the α-hydroxyallylation of a variety of aldehydes, the yield of **10** synthesized by this two-step procedure was very low (≤15% from **15**).



We examined the possibility of replacing the 5-methylfuryl unit in **10** with other aryl groups, in the hope of improving the yield of the allylboronate synthesis. We found that allylsilanes **19a** and **19b** derived from anisole (**18a**) and *m*-methylanisole (**18b**) were readily converted to the corresponding allylboronate reagents **20a** and **20b** under the conditions described for the synthesis of reagent **10**, but the β-hydroxyallylsilanes resulting from addition of these reagents to a simple aldehyde could not be protodesilylated with CF_3CO_2H. Mesityldimethylallylsilane (**19c**) was compatible with CF_3CO_2H protodesilylation, but we had difficulty synthesizing this allylsilane in acceptable yield or purity.



We also studied the metalation of several furyl-substituted allylsilanes (**15**, **19d**, and **19e**) and one phenylthio-substituted allylsilane (**19f**). We subjected these allylsilanes to the metalation conditions for the synthesis of boronate reagent **10** and then quenched the (*E*)-γ-silyl allyl anions with deuterated methanol instead of triisopropyl borate. With allylsilane **15**, we suspected that the furan C(5)-methyl group might be metalated under the reaction conditions, but when only 1 equiv each of *n*-BuLi and KO-*t*-Bu were used, ^{2}H NMR analysis of

(37) Häbich, D.; Effenberger, F. *Synthesis* **1979**, 841.
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Table 1. α-Hydroxyallylation of Achiral Aldehydes

				allylation step[a]		oxidation step[b,c]		
entry	R′CHO	reagent	R	product	yield[d] (%)	product	yield[d] (%)	% ee[e]
1	*c*-C_6H_{11}CHO	(*S,S*)-**10**	5-methylfuryl-	**12a**	83	(*R,S*)-**9a**	61	82
2		(*S,S*)-**11**	menthofuryl-	**13a**	87	(*R,S*)-**9a**	79	81
3[f]		(*R,R*)-**5**	$C_6H_{11}O$-	**7a**	95	(*S,R*)-**9a**	95	72
4[f]		(*R,R*)-**6**	Ph-	**8a**	88			87[g]
5	*n*-C_5H_{11}CHO	(*S,S*)-**10**	5-methylfuryl-	**12b**	77	(*R,S*)-**9b**	43	74
6		(*S,S*)-**11**	menthofuryl-	**13b**	86	(*R,S*)-**9b**	82	74
7[f]		(*R,R*)-**5**	$C_6H_{11}O$-	**7b**	86	(*S,R*)-**9b**	95	64
8[f]		(*R,R*)-**6**	Ph-	**8b**	95			81[g]

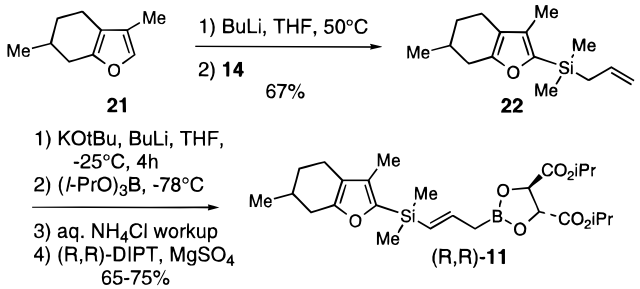
[a] The allylboration reactions of **10** and **11** were performed by treatment of a 0.5 M solution of aldehyde in toluene with a 0.5 M solution of each allylboronate reagent in toluene. The reactions were run at −78 °C, in the presence of activated, crushed 4 Å molecular sieves. The reactions with **10** were quenched after 4 h by filtration through a plug of silica gel, whereas the reactions with **11** were quenched after four hours by addition of a −78 °C, 1 M solution of $NaBH_4$ in EtOH. [b] A two-step protodesilylation/oxidation sequence was used for silanols **12a** and **12b**: the silanols were treated with CH_3CO_2H in CH_2Cl_2 at 0 °C for 15 min, then solvent was removed *in vacuo*, the residue was dissolved in 1:1 THF-MeOH, and H_2O_2 (20 equiv), $KHCO_3$ (2 equiv), and KF (2 equiv) were added at ambient temperature. [c] A one-pot protodesilylation/oxidation sequence was used for silanols **13a** and **13b**: these silanols were treated with CH_3CO_2H in THF at −0 °C to room temperature (ca. 1 h), then MeOH (cosolvent), H_2O_2 (20 equiv), $KHCO_3$ (2 equiv), and KF (2 equiv) were added. [d] Yield of product isolated chromatographically. [e] Determined by NMR analysis of the bis-MTPA esters prepared from **9a** and **9b**, unless indicated otherwise. [f] The data summarized in entries 3, 4, 7, and 8 are reproduced from ref 20. [g] % Ee's for the vinylogous oxidation products of **8a** and **8b** determined as described in ref 22.

the recovered allylsilane showed that no metalation had occurred at that site. However, the mass balance of the reaction was low, indicating that decomposition of the allylsilane was occurring under the reaction conditions. Similar metalation studies with heteroaryl-substituted allylsilanes **19d**−**f** and a variety of bases (*n*-BuLi−KO-*t*-Bu, *n*-BuLi, and *s*-BuLi) also resulted in extensive decomposition of the starting materials.

We concluded that deprotonation at C(3) of the furan or thiophene nucleus and subsequent eliminative ring-opening[39] was most likely responsible for the decomposition of furyl- and phenylthio-substituted allylsilanes **15** and **19d**−**f** during the metalation reactions, especially as it is known that a C(2)-silyl substituent favors this type of ring-opening reaction.[40,41] Accordingly, we synthesized allylsilane **19g**, which bears a methyl at the furan C(3) and thus cannot be metalated at that site. This allylsilane was efficiently metalated and converted to the corresponding allylboronate **20g**, and it was compatible with CF_3CO_2H protodesilylation. However, 2,3,4-alkyl-substituted furans such as **18g**, the precursor for allylsilane **19g**, are not readily available from simple starting materials; in this case, **18g** was prepared in five steps from cyclohexene-1-acetonitrile.[42] Because the furan moiety of allylboronate **20g** is destined to be discarded immediately after the allylation reaction, we decided that the synthesis of furan **18g** was, for our purposes, prohibitively long.

Fortunately, at this point we made the serendipitous discovery that the 2,3,4-alkyl-substituted furan **21** is commercially available from the Flavors and Fragrances Division of Aldrich for less than $1 per gram. Known as menthofuran, **21** is a natural product, one of the fragrant components of peppermint oil.

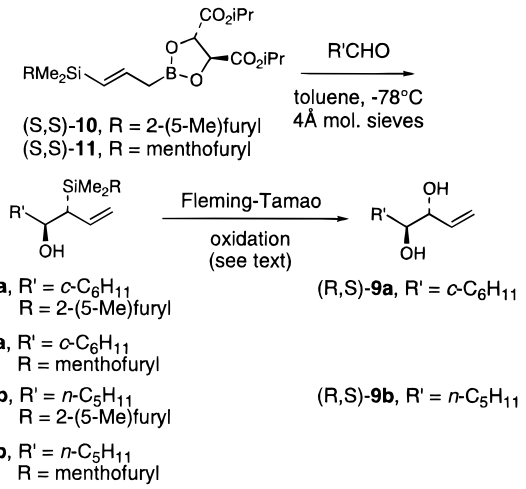
Diisopropyl Tartrate-Modified (*E*)-[γ-[(Menthofuryl)dimethylsilyl]allyl]boronate 11. [(Menthofuryl)dimethylallyl]silane **22** was prepared from menthofuran **21** by metalation and subsequent silylation with allyldimethylchlorosilane (**14**).[37] (*E*)-(γ-Silylallyl)boronate **11** was then prepared from allylsilane **22** following the general outline of our synthesis of reagent **10** (see Experimental Section for complete details). The crude product, consisting primarily of reagent **11**, DIPT, and residual **22**, was analyzed by ^1H NMR spectroscopy to determine the weight percentage of **11** in the mixture; the yield of **11** was generally 65−75%. Reagent **11** was stored over 4 Å molecular sieves at −20 °C as a 0.5 M solution in toluene.[43]



Anti α-Hydroxyallylation of Achiral Aldehydes. The enantioselectivity of the new reagents **10** and **11** was assessed by the allylation of two representative achiral aldehydes, cyclohexanecarboxaldehyde and hexanal (see Table 1). Following our standard procedure for the allylation of aldehydes with diisopropyl tartrate-modified allylboronates,[38,44] we treated a 0.5 M solution of each aldehyde in toluene with a 0.5 M solution of each allylboronate reagent in toluene. The reactions were run at −78 °C, in the presence of activated, crushed 4 Å molecular sieves. The reactions with reagent **10** were quenched after four hours by filtration through a plug of silica gel, whereas the reactions with reagent **11** were quenched after 4 h by addition of a −78 °C, 1 M solution of $NaBH_4$ in EtOH.[44] The 3,4-*anti*-silanols **12a**,**b** and **13a**,**b** were the only products observed in all cases.

(39) Gilchrist, T. L. *Adv. Heterocycl. Chem.* **1987**, *41*, 41.
(40) Karlsson, J. O.; Gronowitz, S.; Frejd, T. *J. Org. Chem.* **1982**, *47*, 374.
(41) Gronowitz, S.; Frejd, T.; Karlsson, J. O.; Lawitz, K.; Pedaja, P.; Pettersson, K. *Chem. Scr.* **1981**, *18*, 192.
(42) Grieco, P. A.; Pogonowski, C. S.; Burke, S. *J. Org. Chem.* **1975**, *40*, 542.
(43) Owing to the stereocenter in the menthofuryl residue, (*R,R*)- and (*S,S*)-**11** are in fact diastereomers, and not enantiomers. However, because this stereocenter is so far removed from the site of developing stereochemistry in the allylboration transition state, we assume that it has an insignificant influence on the allylboration stereoselectivity and feel safe in treating (*R,R*)-**11** and (*S,S*)-**11** as "pseudoenantiomers." The enantiomeric purity of the menthofuran used in the preparation of (*R,R*)-**11** and (*S,S*)-**11** was not determined.
(44) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 4109.

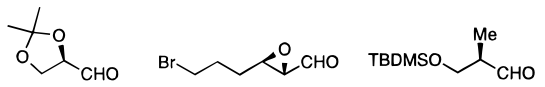
The silanols **12a**,**b** and **13a**,**b** were oxidized to the corresponding *anti*-1,2-diols **9a** and **9b** by a modified Fleming−Tamao oxidation.[19,26−29] The 5-methylfuryl-substituted silanols **12a** and **12b** were dissolved in CH_2Cl_2 and cooled to 0 °C. Addition of CF_3CO_2H resulted in rapid (>15 min) protodesilylation of the furyl nucleus, and each of the subsequent oxidations was effected by removal of the solvent *in vacuo*, dissolution of the residue in 1:1 THF−MeOH, and addition of H_2O_2 (20 equiv), $KHCO_3$ (2 equiv), and KF (2 equiv).



Protodesilylation of the menthofuryl-substituted silanols **13a** and **13b** with CF_3CO_2H in CH_2Cl_2 was nearly instantaneous even at −40 °C. This very rapid protodesilylation of the menthofuran group, as compared to the 5-methylfuran group, is no doubt due to steric and hyperconjugative effects.[31] Because of this increased rate, we were able to perform the protodesilylation reactions of the menthofuryl-substituted silanols in THF, which made the protodesilylation−oxidation sequence a very simple one-pot procedure.[45] Once the protodesilylation reactions were complete (*ca.* 1 h at 0 °C to room temperature), the oxidation reactions were performed *in situ* by addition of H_2O_2 (20 equiv), $KHCO_3$ (2 equiv), KF (2 equiv), and MeOH (cosolvent). The protodesilylation-oxidation sequence is clearly more efficient with the menthofuryl-substituted silanols **13a** and **13b** than with the corresponding 2-(5-methylfuryl)-substituted silanols **12a** and **12b** (see Table 1), most likely because of the milder protodesilylation conditions.

We were unable to determine the ee's of silanols **12** and **13** directly by Mosher ester analysis[46] because the esterification reactions were not efficient (presumably due to steric hindrance by the neighboring trialkylsilyl groups). However, the diols **9a** and **9b** were readily converted into the bis-MTPA esters, and these diesters were used to determine the enantioselectivity of the α-hydroxyallylation for each aldehyde. For comparison, data for the analogous reactions with boronate reagents **5** and **6** are also presented in Table 1 (entries 3, 4, 7, and 8).[22]

Anti α-Hydroxyallylation of Chiral Aldehydes. Double asymmetric reactions of α-hydroxyallylation reagents **10** and **11** with three representative chiral aldehydes, glyceraldehyde acetonide **23**, (2*S*,3*R*)-6-bromo-2,3-epoxyhexanal (**24**), and (2*R*)-3-[(*tert*-butyldimethylsilyl)-oxy]-2-methylpropanal (**25**), were also examined in order to more fully document the stereoselectivity of these new reagents.[47] Results of these experiments are summarized in Table 2, along with comparative data for the reactions of **23**, **24**, and **25** with the first-generation allylboronate reagent **5**.[22]



23 **24** **25**

The reactions of glyceraldehyde acetonide (**23**) with both enantiomers of reagents **10** and **11**[43] (Table 2, entries 1−4) proceeded with excellent diastereoselectivity. This is perhaps not surprising, since **23** is an excellent (high selectivity) substrate for the tartrate ester-modified allylborating reagents.[48] The matched double asymmetric reactions of **23** with (*S*,*S*)-**10** and (*S*,*S*)-**11**, like the previously reported reaction with (*S*,*S*)-**5**,[22] provided ≥95:5 selectivity for diastereomer **26**, while the mismatched double asymmetric reactions with (*R*,*R*)-**10** and (*R*,*R*)-**11** showed selectivity of 92−94:8−6 favoring diastereomer **27**.[49] This is a considerable improvement over the 85:15 selectivity obtained in the mismatched reaction of **23** with (*R*,*R*)-**5** (Table 2, entry 6).[22]

Like **23**, the double asymmetric reactions of epoxy aldehyde **24** gave consistently excellent results with both enantiomers of **10** and **11**[43] (Table 2, entries 7−10).[50] This is in striking contrast to the mismatched reaction with (*S*,*S*)-**5**, which provided only a 2:1 mixture of diastereomers **28c**:**29c** (Table 2, entry 11). However, the enantiomeric purity of **24** (92% ee; determined by Mosher ester analysis of the corresponding epoxy alcohol) puts an upper limit on the diastereoselectivity that can be achieved in these reactions. Assuming that enantiomerically pure **24** had been used, it can be calculated that the diastereoselectivity of the reactions with (*S*,*S*)-**10** (Table 2, entry 7), (*R*,*R*)-**10** (Table 2, entry 8), and (*S*,*S*)-**11** (Table 2, entry 9) would have been 93:7, 7:93, and 93:7, respectively, whereas the matched double asymmetric reaction of **24** and (*R*,*R*)-**11** would have provided a 1:99

(45) The Lewis basicity of THF significantly attenuates the reactivity of the CF_3CO_2H, and thus, THF is not a suitable solvent for the protodesilylation of the less reactive [[2-(5-methylfuryl)]allyl]silanes, which were protodesilylated in CH_2Cl_2. However, the subsequent Tamao oxidation is not efficient in either neat CH_2Cl_2 or CH_2Cl_2−MeOH mixtures, so the CH_2Cl_2 was removed in vacuo and replaced with THF−MeOH for the oxidation. With the very reactive (menthofuryl)allylsilanes, we were able to perform the protodesilylation in THF and simply add the MeOH cosolvent at the start of the Tamao oxidation.

(46) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(47) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

(48) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Straub, J. A.; Palkowitz, A. D. *J. Org. Chem.* **1990**, *55*, 4117.

(49) The intrinsic diastereofacial selectivity of **23** was assessed via reaction with pinacol (*E*)-[γ-(dimethylphenylsilyl)allyl]boronate (see ref 22), which provided a 58:42 mixture of diastereomers **26d**:**27d** (R = Ph). Therefore, diastereomer **26** is the product of matched double asymmetric reactions with the chiral allylboronates **10** and **11**.

(50) We did not determine the instrinsic face selectivity of epoxy aldehyde **24**. However, it is reasonable to expect that diastereofacial selectivity of **24** will be similar to the structurally related aldehyde (2*R*,3*S*)-4-(benzyloxy)-2,3-epoxybutanal, for which the facial selectivity has been determined [60:40 favoring the diastereomer corresponding to **29d** (R = Ph) in reaction with pinacol (*E*)-[γ-(dimethylphenylsilyl)-allyl]boronate; see ref 22]. On this basis, diastereomer **29** should be the product of the matched reactions of **24** with (*R*,*R*)-**10** and (*R*,*R*)-**11**.

Table 2. Double Asymmetric α-Hydroxyallylation of Chiral Aldehydes

				allylation step[a]			oxidation step[b,c,d]	
entry	aldehyde	reagent	R	products	ratio[e]	yield[f]	product	yield[f]
1	23	(*S*,*S*)-**10**	5-methylfuryl-	**26a**:**27a**	95:5	93	**32**[c]	65
2		(*R*,*R*)-**10**	5-methylfuryl-	**26a**:**27a**	6:94	90	**33**[c]	65
3		(*S*,*S*)-**11**	menthofuryl-	**26b**:**27b**	>96:4	79	**32**[d]	77
4		(*R*,*R*)-**11**	menthofuryl-	**26b**:**27b**	8:92	85	**33**[d]	82
5[g]		(*S*,*S*)-**5**	$C_6H_{11}O$-	**26c**:**27c**	>95:5	82	**32**[g]	92
6[g]		(*R*,*R*)-**5**	$C_6H_{11}O$-	**26c**:**27c**	15:85	88	**33**[g]	95
7	**24**[h]	(*S*,*S*)-**10**	5-methylfuryl-	**28a**:**29a**	90:10[i]	69	**34**[c]	57
8	[h]	(*R*,*R*)-**10**	5-methylfuryl-	**28a**:**29a**	10:90[i]	68		
9	[h]	(*S*,*S*)-**11**	menthofuryl-	**28b**:**29b**	90:10[j]	81	**34**[d]	85
10	[h]	(*R*,*R*)-**11**	menthofuryl-	**28b**:**29b**	4:96[j]	82	**35**[d]	79
11	[h]	(*S*,*S*)-**5**	$C_6H_{11}O$-	**28c**:**29c**	67:33	78	**34**[k]	44
12	25	(*S*,*S*)-**10**	5-methylfuryl-	**30a**:**31a**	>96:4	67	**36**[c]	56
13		(*R*,*R*)-**10**	5-methylfuryl-	**30a**:**31a**	33:67	58	**37**[c]	53
14		(*S*,*S*)-**11**	menthofuryl-	**30b**:**31b**	94:6	82	**36**[d]	82
15		(*R*,*R*)-**11**	menthofuryl-	**30b**:**31b**	45:55	80	**37**[d]	76
16[g]		(*S*,*S*)-**5**	$C_6H_{11}O$-	**30c**:**31c**	>95:5	76	**36**[g]	88
17[g]		(*R*,*R*)-**5**	$C_6H_{11}O$-	**30c**:**31c**	36:64	70	**37**[g]	86

[a] The allylboration reactions with reagents **10** and **11** were performed by treatment of a 0.5 M solution of aldehyde in toluene with a 0.5 M solution of each allylboronate reagent in toluene. The reactions were run at −78 °C, in the presence of activated, crushed 4 Å molecular sieves. The reactions with **10** were quenched after 4 h by filtration through a plug of silica gel, whereas the reactions with **11** were quenched after 4 h by addition of a −78 °C, 1 M solution of $NaBH_4$ in EtOH. [b] All modified Tamao oxidations were performed on the purified, major product of the allylboration experiments summarized in each entry. [c] The two-step protodesilylation/oxidation sequence described in footnote (b) of Table 1 was used for silanols **26a**, **27a**, **28a**, **30a** and **31a** (*i.e.*, products of allylboration experiments with 5-methylfuryl-substituted reagent **10**). [d] The one-pot protodesilylation/oxidation sequence described in footnote (c) of Table 1 was used for silanols **26b**, **27b**, **28b**, **29b**, **30b** and **31b** (*i.e.*, products of allylboration experiments with menthofuryl-substituted reagent **11**). [e] Product ratios determined by ^{1}H NMR analysis of the crude allylboration reaction mixture after filtration through a short plug of silica gel, with care taken not to separate the reaction diastereomers. [f] Yield of product(s) isolated chromatographically. [g] The data in entries 5, 6, 16, and 17 are reproduced from ref 22. [h] The enantiomeric purity of epoxyalcohol **24** used in these experiments was 92% ee. [i] If enantiomerically pure epoxyaldehyde **24** had been used in this experiment (see footnote (*g*)), the ratio of **28a**:**29a** would have been 93:7 and 7:93 in the double asymmetric reactions with (*S*,*S*)- and (*R*,*R*)-**10**, respectively (see text for discussion). [j] If enantiomerically pure epoxyaldehyde **24** had been used in this experiment (see footnote (*g*)), the ratio of **28b**:**29b** would have been 93:7 and 1:>99 in the double asymmetric reactions with (*S*,*S*)- and (*R*,*R*)-**11**, respectively (see text for discussion). [k] The Tamao oxidation of **28c** was performed under standard conditions (2 equiv of $KF{\cdot}2H_2O$, 2 equiv of $KHCO_3$ and 20 equiv of 30% H_2O_2 in 1:1 THF−MeOH).

mixture favoring diastereomer **29b** (Table 2, entry 10).[51] Consistent with this analysis is the fact that the enantiomeric purity of the minor product (i.e., **29b**) from the reaction of **24** with (*S*,*S*)-**11** (Table 2, entry 9) was only 58% ee,[52] which corresponds well with the % ee we expected (≤60% ee) for this minor product on the basis of diastereoselectivities calculated for the reactions with the enantiomerically pure epoxy aldehyde.

The matched double asymmetric reactions of α-methyl-*β*-alkoxy aldehyde **25** with (*S*,*S*)-**10** and (*S*,*S*)-**11** proceeded with excellent stereoselectivity (≥94:6; Table 2, entries 12 and 14), but the mismatched reaction with (*R*,*R*)-**10** and (*R*,*R*)-**11** did not display any significant diastereoselectivity (Table 2, entries 13 and 15).[53] These results track the stereoselectivity pattern previously documented for the reactions of **25** with both enantiomers of **5** (Table 2, entries 16 and 17).[22]

The modified Fleming-Tamao oxidations of the 2-(5-methyl)furyl-substituted silanols **26a**, **27a**, **28a**, **30a,** Table 2, and **31a** (Table 2, entries 1, 2, 7, 12 and 13) were performed as described for the achiral aldehydes. The yields of the protodesilylation−oxidation reactions of these silanols were moderate in all cases (53−65%). The oxidation of silanol **29a** (Table 2, entry 8) was not performed, though the corresponding diol **35** was subsequently obtained by the oxidation of menthofuryl-substituted silanol **29b**.

The menthofuryl-substituted silanols **26b**, **27b**, **28b**, **29b**, **30b**, and **31b** (Table 2, entries 3, 4, 9, 10, 14, and 15) proved to be excellent substrates for the one-pot protodesilylation-oxidation sequence described previously for achiral aldehydes **13a** and **13b**, and in this way diols **32**−**37** were obtained in 76−85% yield. Here, as with the achiral aldehydes, the protodesilylation−oxidation sequence is more efficient with the menthofuryl-substituted silanols than with the corresponding 2-(5-methylfuryl)-substituted silanols, most likely because of the milder protodesilylation conditions.[45]

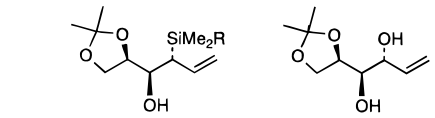
In summary, the data summarized in Table 2 demonstrate that reagents **10** and **11** are both more enantioselective than the first-generation [(alkoxysilyl)allyl]boronate **5**, as clearly demonstrated in the mismatched double asymmetric reactions with glyceraldehyde acetonide **23** (Table 2, entries 2, 4, and 6), and especially in reactions with epoxyaldehyde **25** (Table 2, entries 7, 9, and 11). Although reagents **10** and **11** display comparable selectivity in most of the reactions examined, the greater ease of preparation of **11** and the considerably higher yields of diols obtained in the one-pot protodesilylation-oxidation sequence for the menthofuryl-substituted silanols clearly define **11** as the superior reagent for these applications.

Enantioselective Synthesis of Swainsonine. As a demonstration of the utility of our new *anti*-α-hydroxyallylation reagents in the synthesis of polyhydroxylated natural products, we used reagent **11** in a brief and highly stereoselective total synthesis of the trihydroxy-

(51) For a discussion of this point, and other examples, see: Roush, W. R.; Straub, J. A.; VanNieuwenhze, M. S. *J. Org. Chem.* **1991**, *56*, 1636.

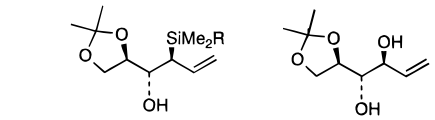
(52) The enantiomeric purity of **29** was determined by Mosher ester analysis of the derived diol **35**.

(53) The intrinsic diastereofacial selectivity of **25** was assessed via reaction with pinacol (*E*)-[*γ*-(dimethylphenylsilyl)allyl]boronate (see ref 22), which provided a 73:27 mixture of diastereomers **30d**:**31d** (R = Ph). Therefore, diastereomer **30** is the product of matched double asymmetric reactions with the chiral allylboronates **10** and **11**.



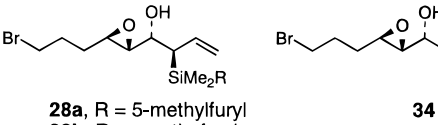
26a, R = 5-methylfuryl
26b, R = menthofuryl
26c, R = -OC_6H_{11}

32



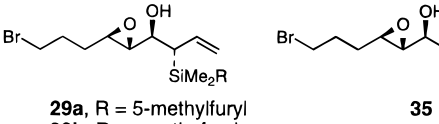
27a, R = 5-methylfuryl
27b, R = menthofuryl
27c, R = -OC_6H_{11}

33



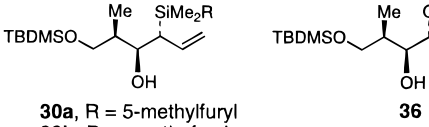
28a, R = 5-methylfuryl
28b, R = menthofuryl
28c, R = -OC_6H_{11}

34



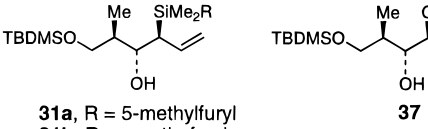
29a, R = 5-methylfuryl
29b, R = menthofuryl
29c, R = -OC_6H_{11}

35



30a, R = 5-methylfuryl
30b, R = menthofuryl
30c, R = -OC_6H_{11}

36



31a, R = 5-methylfuryl
31b, R = menthofuryl
31c, R = -OC_6H_{11}

37

indolizidine alkaloid (−)-swainsonine (**42**). Since its initial isolation from fungal cultures more than two decades ago,[54] swainsonine has attracted considerable attention because of its potent biological activity as an inhibitor of glycoprotein-processing α-mannosidases and because of its possible therapeutic value.[55−57] Swainsonine, its epimers, and its analogs, are widely used in the study of glycosidases and glycoprotein processing; additionally, the natural product reached phase I clinical trials as a potential anticancer drug, and various 2-*O*- and 8-*O*-esters of are being examined as drug candidates with improved pharmacokinetics and reduced side effects.[55]

Swainsonine's combination of significant biological properties and moderate structural complexity make it an attractive synthetic target. More than a dozen syntheses of swainsonine, its epimers, and its analogs have been published in the past several years,[58−63] and many more syntheses of this family of compounds have been reported in the past decade.[55,58] Most of the approaches to swainsonine originate from carbohydrate precursors, with many or all of the four chiral centers required in the product already present in the starting material; other approaches begin with *R*-glutamic acid, D-tartaric acid, D-malic acid, and D-isoascorbic acid as the chiral precursors.[55,58] The first synthesis of swainsonine from achiral precursors was published by Sharpless in 1985, but this route is fairly lengthy (20 steps).[63] To our knowledge, Zhou and co-workers' formal synthesis of swainsonine is the only other synthesis that begins from achiral precursors. This synthesis provided 8-*O*-benzyl-1,2-di-*O*-isopropylidene swainsonine in nine steps and 8% overall yield from an achiral α-furfuryl sulfonamide (which, in turn, was synthesized in two steps from *p*-toluenesulfonamide and 2-furaldehyde dialkyl acetal).[59]

Our synthesis of swainsonine began with 4-bromobutanal (**38**), which is available in two steps from THF (Scheme 1).[64,65] The Horner−Wadsworth−Emmons reaction of **38** with triethyl phosphonoacetate provided exclusively the *trans* α,β-unsaturated ester, and DIBAL reduction of this ester gave the known allylic alcohol **39**.[64] Sharpless asymmetric epoxidation[66] of **39** provided epoxy alcohol **40** with an enantiomeric purity of 92% ee (as determined by Mosher ester analysis),[46] and oxidation of **40** with SO_3−pyridine in DMSO provided epoxy aldehyde **24**.[67] The α-hydroxyallylation of **24** with (*S,S*)-**11**, as previously described, proceeded with 90:10 diastereoselectivity; the major product, silanol **28b**, was obtained in 73% yield simply by recrystallization of the mixture of diastereomers from hexanes (the minor diastereomer **29b** is an oil). Silanol **28b** was then subjected to our one-pot protodesilylation−oxidation protocol to give diol **34** in 85% yield, thus completing the α-hydroxyallylation of aldehyde **24**.

Protection of diol **34** as an acetonide and ozonolysis of the terminal alkene provided aldehyde **41**. Reductive amination[68,69] of this aldehyde was accompanied by spontaneous ring closure to form the indolizidine nucleus of swainsonine acetonide, which was deprotected by acidic hydrolysis to provide (−)-swainsonine (**42**) [mp 137−140 °C; $[\alpha]^{26}_D = -85.5°$ (*c* 0.42, CH_3OH) [lit.[54] mp 144−145 °C; $[\alpha]^{25}_D = -87.2°$ (*c* 2.1, CH_3OH); lit.[58] mp 141−143 °C; $[\alpha]^{26}_D = -82.6°$ (*c* 1.03, CH_3OH); lit.[62] mp 138−140 °C; $[\alpha]^{27}_D = -85.2°$ (*c* 0.5, CH_3OH)]] in 10 steps and 16% overall yield from 4-bromobutanal **38**.

Summary. We have developed the diisopropyl tartrate-modified (*E*)-[γ-[(menthofuryl)dimethylsilyl]allyl]-boronate **11** as an improved chiral reagent for the *anti*-α-hydroxyallylation of aldehydes. Reactions of **11** with two achiral aldehydes provided the corresponding *anti*-

(54) Guengerich, F. P.; DiMari, S. J.; Broquist, H. P. *J. Am. Chem. Soc.* **1973**, *95*, 2055.
(55) Michael, J. P. *Nat. Prod. Rep.* **1995**, 535 and literature cited therein.
(56) Elbein, A. D. *FASEB J.* **1991**, *5*, 3055 and references therein.
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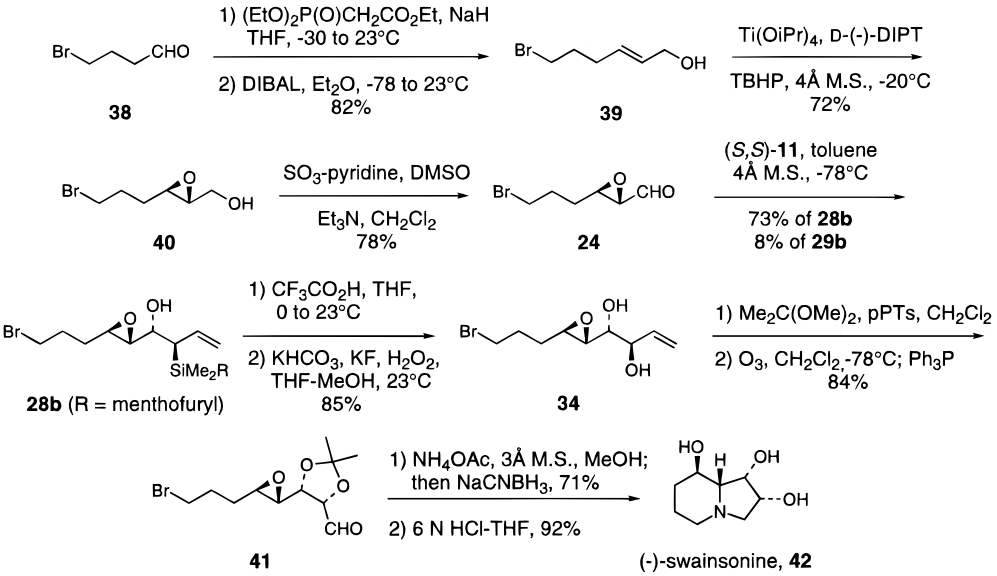
Scheme 1



1,2-diols **9a** and **9b** in good yields (64−70% over two steps) and with respectable enantioselectivities (74−81% ee). Double asymmetric reactions of both enantiomers of reagent **11** with each of three chiral aldehydes (**23**−**25**) provided the corresponding *anti*-1,2-diols **32**−**37** in good yields (60−79% over two steps) and with respectable diastereoselectivities (80−90% de, with the exception of the mismatched reaction of **25** with (*R*,*R*)-**11**, which was essentially unselective). Reagent **11** is thus a clear improvement over the two *anti*-α-hydroxyallylation reagents developed previously in our laboratory: reagent **5**, which showed poor enantioselectivity, and reagent **6**, which was incompatible with the protodesilylation−oxidation sequence.[20−22]

We have also synthesized a related *anti*-α-hydroxyallylation reagent, tartrate ester-modified (*E*)-[γ-[2-(5-methylfuryl)dimethylsilyl]allyl]boronate **10**. This reagent was slightly more stereoselective than reagent **11** in some, though not all, of the double asymmetric reactions examined in this study (see Table 2). However, we were unable to synthesize this reagent in good yield (≤15%), and the overall yields for the two-step α-hydroxyallylation sequence were consistently lower with reagent **10** than were the analogous reactions with reagent **11**, owing to the more vigorous conditions required to promote the protodesilylation of the 2-(5-methylfuryl)silane unit.[45] On this basis we concluded that reagent **11** is the more efficient of our two new reagents for the *anti*-α-hydroxyallylation of aldehydes. As a demonstration of the application of reagent **11** to the synthesis of polyhydroxylated natural products from achiral precursors, we used our new reagent in a brief, enantioselective synthesis of the trihydroxyindolizidine alkaloid (−)-swainsonine (**42**).

Experimental Section[70]

Allyldimethyl[2-(5-methylfuryl)]silane (15). 2-Methylfuran (3.05 g, 37.1 mmol) was added dropwise to BuLi (14.8 mL of a 2.5 M solution in hexanes, 37.1 mmol) in 15 mL of THF. The mixture was heated to 50 °C for 1 h and then cooled to 0 °C. Allylchlorodimethylsilane (**14**) (5.4 mL, 37.1 mmol) was added to the cooled solution dropwise, and the mixture was warmed to room temperature and stirred overnight (20 h) and then filtered through Celite and concentrated to a dark red oil. This crude product was filtered through a plug of silica gel (eluting with hexanes) and then distilled under vacuum (5 mmHg, bp 45 °C) to yield 4.91 g (73%) of **15** as a colorless liquid: R_f = 0.82 (5:1 hexanes−CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (d, *J* = 3.0 Hz, 1 H), 5.96 (dq, *J* = 0.8, 3.0 Hz, 1 H), 5.78 (ddd, *J* = 8.1, 10.2, 16.1 Hz, 1 H), 4.91−4.84 (m, 2 H), 2.33 (d, 0.6 Hz, 3 H), 1.75 (dt, *J* = 1.2, 8.1 Hz, 2 H), 0.25 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 134.3, 121.4, 113.5, 105.7, 26.4, 23.1, 13.7, 0.1, −3.7; IR (neat) 3060, 2955, 2920, 1625, 1590, 1490 cm^{-1}; HRMS calcd for $C_{10}H_{16}OSi$ 180.0960, found 180.0971.

(*E*)-[γ-[[2′-(5′-Methylfuryl)]dimethylsilyl]allyl]boronate−Diethanolamine Complex (17). A 1.0 M solution of KO-*t*-Bu in THF (16.6 mL, 16.6 mmol) was cooled to −78 °C, and allylsilane **15** (3.0 g, 16.6 mmol) in 5 mL of THF was added. *n*-BuLi (6.6 mL of a 2.5 M solution, 16.6 mmol) was added dropwise to this mixture at a rate such that the internal temperature of the solution did not rise above −40 °C. The mixture was allowed to warm to −40 °C, stirred at this temperature for 15 min, and then cooled to −78 °C. Triisopropyl borate (3.8 mL, 16.6 mmol) was added dropwise, and the mixture was stirred for 15 min at −78 °C and then poured into a separatory funnel containing 20 mL of a saturated NH_4Cl solution. The phases were separated and the aqueous phase was extracted with 4 × 10 mL of Et_2O. The combined organics were treated with $MgSO_4$, and a 3 M solution of diethanolamine (0.52 g, 5.0 mmol)[71] in *i*-PrOH was added. The mixture was stirred overnight and then filtered and concentrated to a dark yellow oil, which was dissolved in toluene and concentrated to a dark yellow solid. This solid was dissolved in hot benzene and filtered and then recrystallized from benzene−hexanes to yield 1.11 g of **17** (23% based on **15**) as a pale yellow solid: mp 130−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (dt, *J* = 7.8, 18.5 Hz, 1 H), 6.63 (d, *J* = 3.0 Hz, 1 H), 5.90 (dd, *J* = 3.0, 0.8 Hz, 1 H), 5.74 (dt, *J* = 1.1, 17.5 Hz, 1 H), 4.66 (br s, 1 H), 3.67 (m, 2 H) 3.58 (m, 2 H), 2.55 (m, 2 H), 2.07 (d, *J* = 0.5 Hz, 3 H), 1.95 (d, *J* = 7.8 Hz, 2 H), 1.84 (m, 2 H), 0.41 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 156.3, 155.2, 121.7, 106.4, 62.8, 51.3, 13.7, −2.2; IR (CH_2Cl_2) 3320−3280, 3160−3100, 3040, 2960, 2860, 2920, 2860, 1600 cm^{-1}; HRMS calcd for $C_{14}H_{25}{}^{10}BO_3Si$ 293.1726, found 293.1732.

(70) For general experimental details, see: Roush, W. R.; Hunt, J. A. *J. Org. Chem.* **1995**, *60*, 798. Unless otherwise noted, all compounds purified by chromatography are sufficiently pure (>95% by ^{1}H NMR analysis) for use in subsequent reactions

(71) Diethanolamine complex **17** would not crystallize if larger quantities of diethanolamine were used. The stoichiometry (0.3 equiv of diethanolamine) here is consistent with the efficiency of the preparation of allylboronate **10** directly from allylsilane **15**.

Diisopropyl Tartrate-Modified (*E*)-[γ-[[2′-(5′-Methylfuryl)]dimethylsilyl]allyl]boronate [(*R,R*)-10 and (*S,S*)-10]. A two-phase mixture of diethanolamine complex **17** (1.0 g, 3.41 mmol) and L-(*R,R*)-DIPT (0.73 mL, 3.41 mmol) in 20 mL of brine and 10 mL of EtOAc was stirred vigorously for 1 h. The mixture was poured into a separatory funnel containing 20 mL of EtOAc, 20 mL of brine, and 2 mL of 1 M $NaHSO_4$ and shaken well. The phases were separated, and the aqueous phase was extracted with 4 × 20 mL of EtOAc. The combined organics were stirred over $MgSO_4$ overnight (20 h), filtered, concentrated, and then pumped to a constant weight to yield 1.25 g of a light yellow oil. This crude product consisted of (*R,R*)-**10** contaminated with *ca.* 20% of DIPT, as determined by ^{1}H NMR analysis; the yield of *(R,R)*-**10** was calculated to be 64%. Crude (*R,R*)-**10** was dissolved in toluene (*ca.* 0.5 M) and stored at −20 °C over crushed 4 Å molecular sieves: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, *J* = 3.5, 1 H), 6.21 (dt, *J* = 7.3, 18.3 Hz, 1 H), 5.94 (m, 1 H), 5.76 (dt, *J* = 1.6, 18.3 Hz, 1 H), 5.20−5.08 (m, 2.5 H), 4.78 (s, 2 H), 2.32 (d, *J* = 0.8, 3 H), 2.08 (dd, *J* = 1.6, 7.3 Hz, 2 H), 1.32−1.28 (m, 13 H), 0.30 (s, 6 H).

The same procedure was followed for the synthesis of (*S,S*)-**10** from diethanolamine complex **16** and D-(*S,S*)-DIPT.

Allyldimethyl[2-(4,5,6,7-tetrahydro-3,6-dimethylbenzofuryl)]silane (22). 2-4,5,6,7-Tetrahydro-3,6-dimethylbenzofuran [**21** (menthofuran), 10.0 g, 66.6 mmol] in 10 mL of THF was added dropwise to a solution of *n*-BuLi (34 mL of a 1.96 M solution in hexanes, 66.6 mmol) in 30 mL of THF. The mixture was heated to 50 °C for 1 h then cooled to 0 °C. Allylchlorodimethylsilane (**14**) (4.9 mL, 4.5 mmol) was added to the cooled solution dropwise, and the mixture was warmed to room temperature and stirred overnight (20 h) and then filtered through Celite and concentrated to a dark yellow oil. This oil was filtered through a plug of silica gel (eluting with hexanes) and then distilled under vacuum (5 mmHg, bp 136−139 °C) to yield 11.0 g (67%) of **22** as a colorless oil: R_f = 0.90 (100% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (m, 1 H), 4.82 (m, 2 H), 2.67 (br dd, *J* = 5.4, 16.4 Hz, 1 H), 2.41−2.25 (m, 2 H), 2.18 (qt, *J* = 2.2, 9.4 Hz, 1 H), 1.99 (s, 3 H), 1.95−1.74 (m, 4 H), 1.40−1.28 (m, 2 H), 1.07 (d, *J* = 6.8 Hz, 3 H), 0.27 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 150.4, 134.7, 130.8, 117.9, 31.9, 31.4, 29.6, 23.6, 21.5, 20.0, 9.3, −3.2; IR (neat) 3070, 2950, 2920, 2840, 1630 cm^{-1}; HRMS calcd for $C_{15}H_{25}OSi$ (M + 1) 249.1668, found 249.1667.

Diisopropyl Tartrate-Modified (*E*)-[γ-[[2′-(4′,5′,6′,7′-Tetrahydro-3′,6′-dimethylbenzofuryl)]dimethylsilyl]allyl]-boronate [(*S,S*)-11 and (*R,R*)-11]. KO-*t*-Bu (2.26 g, 20.1 mmol) was weighed out under an atmosphere of dry N_2 and dissolved in 30 mL of THF; the solution was then cooled to −78 °C. Allylsilane **22** (5.00 g, 20.1 mmol) in 10 mL of THF was added dropwise. *n*-BuLi (10.7 mL of a 1.88 M solution in hexanes, 20.1 mmol) was added dropwise to this mixture at a rate such that the internal temperature of the solution did not rise above −25 °C. The mixture was transferred to −25 °C bath, stirred at this temperature for 4 h, and then recooled to −78 °C. Triisopropyl borate (4.6 mL, 20.1 mmol) was added dropwise, and the mixture was stirred for 15 min at −78 °C and then poured into a separatory funnel containing 30 mL of a saturated NH_4Cl solution and D-(*S,S*)-DIPT (4.3 mL, 20.1 mmol) in 10 mL of Et_2O. The phases were separated, and the aqueous phase was extracted with 4 × 15 mL of Et_2O. The combined organics were stirred over $MgSO_4$ overnight (20 h), filtered, and concentrated *in vacuo* to a constant weight of 9.30 g of a colorless oil. This crude product consisted of (*S,S*)-**11** contaminated with ca. 20% of DIPT and *ca.* 10% of allylsilane **22**, as determined by ^{1}H NMR analysis; the yield of (*S,S*)-**11** was calculated to be 67%. Crude (*S,S*)-**11** was dissolved in toluene (ca. 0.5 M) and stored at −20 °C over crushed 4 Å molecular sieves: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (dt, *J* = 7.0, 18.3 Hz, 1 H), 5.79 (dt, *J* = 1.6, 18.3 Hz, 1 H), 5.11 (m, 2 H), 4.78 (s, 2 H), 2.67 (br dd, *J* = 4.3, 15.3 Hz, 1 H), 2.40−2.12 (m, 3 H), 2.05 (dd, *J* = 1.4, 7.3 Hz, 1 H), 1.99−1.76 (m, 6 H), 1.30 (d, *J* = 6.4 Hz, 12 H), 1.06 (d, *J* = 6.4 Hz, 3 H), 0.31 (s, 6 H).

The same procedure was followed for the synthesis of (*R,R*)-**11** from allylsilane **22**, triisopropyl borate, and L-(*R,R*)-DIPT.

Representative Procedure for Reactions of Reagent 10 and Aldehydes: 1-Cyclohexyl-2-[2′-(5′-methylfuryl)]-dimethylsilyl]but-3-en-1-ol (12a). A solution of freshly distilled cyclohexanecarboxaldehyde (63 μL, 0.52 mmol) in 0.5 mL of toluene was stirred over crushed 4 Å molecular sieves for 15 min and then cooled to −78 °C and added dropwise over 5 min to a −78 °C solution of (*S,S*)-10 in toluene (1.25 mL of a 0.5 M solution, 0.62 mmol). The resulting mixture was stirred at −78 °C for 4 h, at which point TLC analysis showed that no starting material remained. The reaction mixture was added directly to a silica gel column and eluted with 9:1 hexanes−Et_2O to yield 126 mg (83%) of **12a** as a colorless oil: R_f = 0.51 (6:1 hexanes−Et_2O); $[\alpha]^{23}_D$ = 15.5° (*c* 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (d, *J* = 3.2 Hz, 1 H), 5.97 (dq, *J* = 1.1, 2.9 Hz, 1 H), 5.85 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.03 (dd, *J* = 2.2, 10.2 Hz, 1 H), 4.89 (ddd, *J* = 0.8, 2.2, 17.2 Hz, 1 H), 3.43 (dt, *J* = 4.0, 7.8 Hz, 1 H), 2.33 (d, *J* = 1.1 Hz, 3 H), 2.12 (dd, *J* = 4.0, 10.5, 1 H), 1.91−1.84 (m, 1 H), 1.78 (d, *J* = 4.3 Hz, 1 H), 1.74−1.58 (m, 3 H), 1.42−0.82 (m, 7 H), 0.29 (s, 3 H), 0.28 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 156.4, 134.8, 122.2, 115.1, 105.9, 75.8, 41.9, 39.0, 29.2, 28.6, 26.4, 26.2, 25.9, 13.7, −3.8, −4.2; IR (neat) 3600−3450, 3060, 2920, 2830, 1625, 1590 cm^{-1}; HRMS calcd for $C_{17}H_{27}OSi$ (M − OH) 275.1824, found 275.1818. Anal. Calcd for $C_{17}H_{28}O_2Si$: C, 69.81; H, 9.65. Found: C, 69.71; H, 9.86.

3-[[2′-(5′-Methylfuryl)]dimethylsilyl]non-1-en-4-ol (12b). **12b** was prepared in 77% yield from freshly distilled hexanal and (*S,S*)-**10**: R_f = 0.50 (5:1 hexanes−Et_2O); $[\alpha]^{23}_D$ = 4.8° (*c* 0.49, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 6.61 (d, *J* = 3.2 Hz, 1 H), 5.96 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.87 (dq, *J* = 0.8, 3.0 Hz, 1 H), 5.02 (dd, *J* = 2.4, 10.5 Hz, 1 H), 4.91 (ddd *J* = 0.8, 2.4, 17.2 Hz, 1 H), 3.78 (m, 1 H), 2.07 (s, 3 H), 1.94 (dd, *J* = 3.5, 10.5, 1 H), 1.46−1.16 (m, 9 H), 0.86 (m, 3 H), 0.41 (s, 3 H), 0.38 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 158.8, 135.4, 122.7, 115.3, 106.4, 71.5, 41.9, 37.5, 32.2, 25.9, 23.0, 14.3, 13.6, −3.4, −3.8; IR (neat) 3550−3400, 2960, 2920, 2850, 1625, 1590 cm^{-1}; HRMS calcd for $C_{16}H_{27}OSi$ (M − OH), 263.1824, found 263.1823. Anal. Calcd for $C_{16}H_{28}O_2Si$: C, 68.51; H, 10.19. Found: C, 68.53; H, 10.19.

(3*R*,4*S*,5*R*)-5,6-O-Isopropylidene-3-[[2′-(5′-methylfuryl)]-dimethylsilyl]hex-1-en-4-ol (26a). 26a was prepared in 93% yield (86% major diastereomer **26a**, 7% minor diastereomer **27a**) from freshly distilled glyceraldehyde acetonide **23** and (*S,S*)-**10**. The reaction stereoselectivity was determined to be 95:5 by ^{1}H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 5:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **26a** follow: R_f = 0.25 (3:1 hexanes−Et_2O); $[\alpha]^{26}_D$ = 1.5° (*c* 1.81, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 6.65 (d, *J* = 3.0 Hz, 1 H), 6.12 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.87 (dq, *J* = 0.8, 3.0 Hz, 1 H), 4.91 (dd, *J* = 1.9, 10.2 Hz, 1 H), 4.75 (dd, *J* = 2.2, 17.2 Hz, 1 H), 4.12 (dt, *J* = 6.4, 8.1 Hz, 1 H), 3.78−3.73 (m, 2 H), 3.36 (dd, *J* = 6.7, 8.1 Hz, 1 H), 2.36 (t, *J* = 2.2 Hz, 1 H), 2.08 (d, *J* = 0.8 Hz, 3 H), 1.79 (dt, *J* = 2.2, 10.8 Hz, 1 H), 1.29 (s, 3 H), 1.22 (s, 3 H), 0.49 (s, 3 H), 0.43 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 156.6, 156.5, 134.6, 128.5, 122.8, 114.8, 109.5, 106.4, 79.7, 73.8, 65.9, 38.2, 27.0, 25.7, 13.6, −3.7; IR (neat) 3520−3460, 1625, 1595 cm^{-1}; HRMS calcd for $C_{16}H_{26}O_4Si$ 310.1593, found 310.1607. Anal. Calcd for $C_{16}H_{26}O_4Si$: C, 61.90; H, 8.44. Found: C, 61.82; H, 8.44.

(3*S*,4*R*,5*R*)-5,6-O-Isopropylidene-3-[[2′-(5′-methylfuryl)]-dimethylsilyl]hex-1-en-4-ol (27a). 27a was prepared in 90% yield (83% major diastereomer **27a**, 7% minor diastereomer **26a**) from freshly distilled glyceraldehyde acetonide **23** and (*R,R*)-**10**. The reaction stereoselectivity was determined to be 94:6 by ^{1}H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 5:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **27a** follow: R_f = 0.13 (3:1 hexanes−Et_2O); $[\alpha]^{25}_D$ = 5.7° (*c* 1.08, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 6.58 (d, *J* = 3.0 Hz, 1 H), 5.96 (ddd, *J* = 10.5, 10.5, 16.9 Hz, 1 H), 5.84 (dq, *J* = 0.8, 3.0 Hz, 1 H), 4.98−4.89 (m, 2 H), 4.03 (m, 1 H), 3.95−3.85 (m, 3 H), 2.17 (dd, *J* = 2.0, 10.8 Hz, 1 H), 2.04 (d, *J* = 0.8 Hz, 3 H), 1.80 (d, *J* = 3.6 Hz, 1 H), 1.33 (s, 3 H), 1.27 (s, 3 H), 0.37 (s, 3 H), 0.33 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 157.0, 156.3, 134.6, 128.5, 122.9, 115.8, 108.3, 106.4, 78.9, 71.8, 66.0,

38.4, 26.9, 25.6, 13.5, −3.8, −4.1; IR (neat) 3550−3450, 1625, 1595 cm^{-1}; HRMS calcd for $C_{15}H_{23}O_4Si$ (M − CH_3) 295.1343, found 295.1354. Anal. Calcd for $C_{16}H_{26}O_4Si$: C, 61.90; H, 8.44. Found: C, 61.73; H, 8.50.

(3*R*,4*S*,5*S*,6*R*)-9-bromo-3-[[2′-(5′-methylfuryl)]dimethylsilyl]-5,6-epoxynon-1-en-4-ol (28a). **28a** was prepared in 69% yield (62% major diastereomer **28a**, 7% minor diastereomer **29a**) from epoxy aldehyde **24** and (*S*,*S*)-**10**. The reaction stereoselectivity was determined to be 90:10 by ^1H NMR and HPLC analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 5:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **28a** follow: HPLC t_R 9.70 min (10 mm column, 4 mL/min, 20% hexanes−EtOAc); R_f = 0.39 (1:1 hexanes−Et_2O); $[\alpha]^{26}_D$ = −5.5° (*c* 0.65, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.59 (d, *J* = 3.0 Hz, 1 H), 5.97 (dq, *J* = 3.0, 0.8 Hz, 1 H), 5.87 (ddd, *J* = 10.2, 10.2, 17.2 Hz, 1 H), 5.02 (dd, *J* = 2.14, 10.2 Hz, 1 H), 4.96 (ddd, *J* = 0.8, 2.2, 17.2 Hz, 1 H), 3.99 (dd, *J* = 3.2, 5.9 Hz, 1 H), 3.43 (m, 2 H) 3.03 (ddd, *J* = 2.4, 5.1, 7.0 Hz, 1 H), 2.72 (t, *J* = 2.4 Hz, 1 H), 2.33 (d, *J* = 1.0 Hz, 3 H), 2.07 (dd, *J* = 3.5, 10.5, 1 H), 2.02−1.92 (m, 3 H), 1.76−1.68 (m, 1 H), 1.62−1.52 (m, 2 H) 0.30 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 155.7, 134.2, 122.5, 115.4, 105.9, 68.4, 60.8, 54.6, 38.8, 33.2, 30.2, 29.1, 13.7, −4.0, −4.4; IR (neat) 3540−3380, 1620, 1590 cm^{-1}; HRMS calcd for $C_{16}H_{26}O_3Si^{81}Br$ (M + 1) 375.0807, found 375.0826. Anal. Calcd for $C_{16}H_{25}O_3SiBr$: C, 51.47; H, 6.75. Found: C, 51.71; H, 7.00.

(3*S*,4*R*,5*S*,6*R*)-9-bromo-3-[[2′-(5′-methylfuryl)]dimethylsilyl]-5,6-epoxynon-1-en-4-ol (**29a**). **29a** was prepared in 68% yield (63% major diastereomer **29a**, 5% minor diastereomer **28a**) from epoxy aldehyde **24** and (*R*,*R*)-**10**. The reaction stereoselectivity was determined to be 90:10 by ^1H NMR and HPLC analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 5:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **29a** follow: HPLC t_R 12.21 min (10 mm column, 4 mL/min, 20% hexanes−EtOAc); R_f = 0.30 (1:1 hexanes−Et_2O); $[\alpha]^{26}_D$ = 21.1° (*c* 1.39, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.58 (d, *J* = 3.2 Hz, 1 H), 6.00−5.90 (m, 2 H), 5.07 (dd, *J* = 2.2, 10.5 Hz, 1 H), 4.97 (dd, *J* = 1.9, 16.9 Hz, 1 H), 3.61 (dd, *J* = 4.8, 9.4 Hz, 1 H), 3.42 (m, 2 H), 2.83 (m, 2 H), 2.32 (d, *J* = 0.5 Hz, 3 H), 2.09−1.88 (m, 4 H), 1.61−1.51 (m, 1 H), 0.35 (s, 3 H), 0.30 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 155.6, 134.2, 122.5, 115.7, 106.0, 71.4, 61.4, 55.9, 40.5, 33.0, 30.1, 29.1, 13.7, −3.8, −4.2; IR (neat) 3500−3300, 2960, 2860, 2820 cm^{-1}; HRMS calcd for $C_{16}H_{26}O_3Si^{81}Br$ (M + 1) 375.0807, found 375.0826. Anal. Calcd for $C_{16}H_{25}O_3SiBr$: C, 51.47; H, 6.75. Found: C, 51.74; H, 6.68.

(3*R*,4*S*,5*R*)-6-[(*tert*-Butyldimethylsilyl)oxy]-3-[[2′-(5′-methylfuryl)]dimethyl silyl]-5-methylhex-1-en-4-ol (**30a**). **30a** was prepared in 67% yield (64% major diastereomer **30a**, 3% minor diastereomer **31a**) from **25** and (*S*,*S*)-**10**. The reaction stereoselectivity was determined to be >96:4 by ^1H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 19:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **30a** follow: R_f = 0.36 (9:1 hexanes−Et_2O); $[\alpha]^{25}_D$ = −4.7° (*c* 0.36, C_6H_6); ^1H NMR (400 MHz, C_6D_6) δ 6.62 (d, *J* = 3.0 Hz, 1 H), 5.96 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.86 (dq, *J* = 0.8, 3.0 Hz, 1 H), 4.99 (dd, *J* = 2.2, 10.5 Hz, 1 H), 4.92 (ddd, *J* = 0.8, 2.2, 17.2 Hz, 1 H), 4.01 (ddd, *J* = 4.3, 4.6, 3.8 Hz, 1 H), 3.52 (dq, *J* = 5.1, 9.9 Hz, 2 H), 2.21 (dd, *J* = 4.8, 10.5 Hz, 1 H), 2.08 (s, 3 H), 1.97 (d, *J* = 4.3 Hz, 1 H), 1.86−1.77 (m, 1 H), 0.98 (d, *J* = 7.0 Hz, 3 H), 0.95 (s, 9 H), 0.43 (s, 3 H), 0.39 (s, 3 H), 0.03 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 156.1, 136.4, 122.2, 114.7, 105.8, 73.0, 67.1, 40.0, 39.4, 25.9, 18.2, 13.7, 11.2, −3.5, −4.4, −5.6; IR (neat) 3600−3480, 1650, 1590 cm^{-1}; HRMS calcd for $C_{19}H_{35}O_3Si_2$ (M − CH_3), 367.2115, found 367.2141. Anal. Calcd for $C_{20}H_{38}O_3Si_2$: C, 62.77; H, 10.01. Found: C, 63.24; H, 10.26.

(3*S*,4*R*,5*R*)-6-[(*tert*-Butyldimethylsilyl)oxy]-3-[2′-(5′-methylfuryl)]dimethyl silyl]-5-methylhex-1-en-4-ol (**31a**). **31a** was prepared in 58% yield (40% major diastereomer **31a**, 18% minor diastereomer **30a**) from **25** and (*R*,*R*)-**10**. The reaction stereoselectivity was determined to be 67:33 by ^1H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 20:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **31a** follow: R_f = 0.55 (9:1 hexanes−Et_2O); $[\alpha]^{26}_D$ = −21.9° (*c* 1.24, C_6H_6); ^1H NMR (400 MHz, C_6D_6) δ 6.73 (d, *J* = 3.2 Hz, 1 H), 6.30 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.91 (dq, *J* = 0.8, 3.0 Hz, 1 H), 5.07 (dd, *J* = 2.4, 10.5 Hz, 1 H), 4.96 (dd, *J* = 2.4, 17.5 Hz, 1 H), 4.12 (t, *J* = 1.9 Hz, 1 H), 3.86 (br d, *J* = 9.1 Hz, 2 H), 3.56 (dd, *J* = 4.0, 9.9 Hz, 1 H), 3.38 (t, *J* = 9.1 Hz, 1 H), 2.21 (dt, *J* = 2.2, 10.5 Hz, 1 H), 2.10 (s, 3 H), 1.98−1.87 (m, 1 H), 0.87 (s, 9 H), 0.61 (s, 3 H), 0.58 (d, *J* = 7.2 Hz, 3 H), 0.54 (s, 3 H), 0.05 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 156.3, 134.9, 121.8, 114.2, 105.7, 69.3, 39.1, 38.9, 25.9, 18.2, 13.7, 12.8, −3.9, −5.5, −5.6; IR (neat) 3500 (br), 1625, 1595 cm^{-1}; HRMS calcd for $C_{20}H_{37}O_2Si_2$ (M − OH), 365.2322, found 365.2343. Anal. Calcd for $C_{20}H_{38}O_3Si_2$: C, 62.77; H, 10.01. Found: C, 62.50; H, 10.22.

Representative Procedure for Reactions of Reagent 11 and Aldehydes: (3*R*,4*S*,5*S*,6*R*)-9-Bromo-3-[[2′-(4′,5′,6′,7′-tetrahydro-3′,6′-dimethylbenzofuryl)]dimethylsilyl]-5,6-epoxynon-1-en-4-ol (**28b**). Aldehyde **24** (350 mg, 1.81 mmol) was dissolved in 2 mL of toluene, stirred over 100 mg of crushed 4 Å molecular sieves for 15 min at room temperature, and then cooled to −78 °C. A 0.78 M solution of allylboronate (*S*,*S*)-**11** in toluene (3.5 mL, 2.72 mmol) was stirred over 200 mg of crushed 4 Å molecular sieves for 15 min at room temperature and then cooled to −78 °C. The aldehyde solution was added to the solution of reagent **11** dropwise via cannula, and the resulting mixture was stirred at −78 °C for 4 h, at which point TLC analysis showed that no starting material remained. A 1 M solution of $NaBH_4$ in EtOH (3 mL) was cooled to −78 °C and added dropwise via cannula to the reaction mixture. The mixture was allowed to warm to room temperature and then partitioned between 30 mL of Et_2O and 10 mL of pH 7 buffer saturated with NaCl. The aqueous phase was extracted with 3 × 15 mL of Et_2O, and the combined organics were dried over $MgSO_4$, filtered, and concentrated to a colorless oil. The reaction stereoselectivity was determined to be 90:10 (**28b**:**29b**) by ^1H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 5:1 hexanes−Et_2O. The major diastereomer **28b** was separated from the minor isomer **29b** by recrystallization from hexanes to yield 583 mg (73%) of **28b** as a white solid; concentration of the mother liquor provided 65 mg (8%) of **29b** as a colorless oil (81% total). Data for **28b** follow: R_f = 0.69 (1:1 hexanes−Et_2O); mp 114−116 °C; $[\alpha]^{26}_D$ = 31.9° (*c* 0.26, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.03 (dd, *J* = 1.9, 10.2 Hz, 1 H), 4.98 (dd, *J* = 1.3, 17.2 Hz, 1 H), 3.97 (dd, *J* = 3.2, 5.6 Hz, 1 H), 3.43 (m, 2 H), 3.02 (ddd, *J* = 2.2, 4.6, 7.0 Hz, 1 H), 2.71−2.64 (m, 2 H), 2.41−1.65 (m, 13 H), 1.58−1.48 (m, 1 H), 1.40−1.28 (m, 1 H), 1.07 (d, *J* = 6.4 Hz, 3 H), 0.36 (s, 3 H), 0.32 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 155.0, 150.0, 135.1, 131.9, 118.3, 115.0, 68.8, 60.9, 54.4, 39.0, 33.2, 32.2, 31.6, 30.4, 29.8, 29.4, 21.4, 20.2, 9.6, −3.1, −3.3; IR ($CHCl_3$) 2980, 2925, 2900, 1615 cm^{-1}; HRMS calcd for $C_{21}H_{33}O_3Si^{79}Br$ 440.1373, found 440.1362. Anal. Calcd for $C_{21}H_{33}O_3SiBr$: C, 57.13; H, 7.53. Found: C, 56.46; H, 7.67.

(3*S*,4*R*,5*S*,6*R*)-9-Bromo-3-[[2′-(4′,5′,6′,7′-tetrahydro-3′,6′-dimethyl benzofuryl)]dimethylsilyl]-5,6-epoxynon-1-en-4-ol (29b). **29b** was prepared in 82% yield (79% major diastereomer **29b**, 5% minor diastereomer **28b**) from epoxy aldehyde **24** and (*R*,*R*)-**11**. The reaction stereoselectivity was determined to be 96:4 by ^1H NMR analysis of the crude reaction mixture after filtration of the mixture through a silica gel plug, eluting with 5:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **29b** follow: R_f = 0.63 (1:1 hexanes−Et_2O); $[\alpha]^{27}_D$ = 50.3° (*c* 0.61, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.96 (ddd, *J* = 10.2, 10.2, 17.2 Hz, 1 H), 5.07 (dd, *J* = 1.9, 10.2 Hz, 1 H), 4.99 (ddd, *J* = 0.5, 1.9, 17.4 Hz, 1 H), 3.60 (dd, *J* = 4.6, 9.7 Hz, 1 H), 3.42 (m, 2 H), 2.82 (m, 2 H), 2.65 (br dd, *J* = 5.1, 16.1 Hz, 1 H), 2.40−1.69 (m, 13 H), 1.60−1.48 (m, 1 H), 1.39−1.27 (m, 1 H), 1.07 (d, *J* = 6.8 Hz, 3 H), 0.35 (s, 3 H), 0.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 149.0, 134.6, 132.0, 118.2, 115.5, 71.6, 61.5, 56.0, 40.8, 33.0, 31.9, 31.3, 30.0, 29.6, 29.1, 21.5, 19.9, 9.4, −3.1, −3.7; IR (neat) 3580−3300, 2960, 2920, 1660 cm^{-1}; HRMS calcd for

$C_{21}H_{33}O_3Si^{81}Br$ 42.1373, found 442.1367. Anal. Calcd for $C_{21}H_{33}O_3SiBr$: C, 57.13; H, 7.53. Found: C, 56.37; H, 7.73.

1-Cyclohexyl-2-[[2′-(4′,5′,6′,7′-tetrahydro-3′,6′-dimethylbenzofuryl)] dimethylsilyl]but-3-en-1-ol (**13a**). **13a** was prepared in 87% yield from freshly distilled cyclohexanecarboxaldehyde and (*S,S*)-**11**: R_f = 0.50 (5:1 hexanes−Et_2O); $[\alpha]^{27}_D$ = 0.8° (*c* 1.03, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 6.05 (ddd, *J* = 10.2, 10.2, 17.2 Hz, 1 H), 5.04 (dd, *J* = 2.2, 10.2 Hz, 1 H), 4.95 (dd, *J* = 2.2, 17.2 Hz, 1 H), 3.52 (m, 1 H), 2.30−1.84 (m, 7 H), 1.22−1.00 (m, 4 H), 0.92−0.80 (m, 5 H), 0.52 (s, 3 H), 0.48 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 154.9, 150.4, 135.8, 131.5, 118.3, 114.8, 76.0, 42.5, 39.7, 32.2, 31.6, 29.8, 29.4, 29.1, 26.8, 26.6, 26.3, 21.4, 20.2, 9.6, −2.8, −3.3; IR (neat) 3600−3500, 2930, 2860, 1660 cm^{-1}; HRMS calcd for $C_{22}H_{36}O_2Si$ 360.2475, found 360.2468.

3-[2′-(4′,5′,6′,7′-Tetrahydro-3′,6′-dimethylbenzofuryl)-dimethyl]silylnon-1-ene-4-ol (**13b**). Prepared in 80% yield from freshly distilled hexanal and (*S,S*)-**11**: R_f = 0.60 (9:1 hexanes−Et_2O); $[\alpha]^{25}_D$ = 41.6° (*c* 1.00, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 6.04 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.06 (dd, *J* = 2.2, 10.5 Hz, 1 H), 4.97 (m, 1 H), 3.88 (m, 1 H), 2.61 (br dd, *J* = 5.4, 16.1 Hz, 1 H), 2.28−1.98 (m, 7 H), 1.68−1.09 (m, 12 H), 0.86 (t, *J* = 6.4 Hz, 3 H), 0.82 (d, *J* = 6.8 Hz, 3 H), 0.51 (s, 3 H), 0.47 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 155.0, 150.3, 135.9, 131.6, 128.5, 118.3, 115.2, 71.5, 42.5, 37.5, 32.2, 32.1, 31.6, 29.8, 25.9, 23.0, 21.4, 20.2, 14.3, 9.6, −2.7, −3.2; IR (neat) 3600−3450, 2960, 2930, 2870, 1625 cm^{-1}; HRMS calcd for $C_{21}H_{36}O_2Si$ 348.2475, found 348.2481.

(3*R*,4*S*,5*R*)-5,6-O-Isopropylidene-3-[2′-(4′,5′,6′,7′-tetrahydro-3′,6′-dimethylbenzofuryl)]dimethylsilyl]hex-1-en-4-ol (**26b**). **26b** was prepared in 79% yield (77% of major diastereomer **26b**, 2% of minor diastereomer **27b**) from freshly distilled glyceraldehyde acetonide **23** and (*S,S*)-**11**. The reaction stereoselectivity was determined to be >96:4 by ^{1}H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 5:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **26b** follow: R_f = 0.60 (2:1 hexanes−Et_2O); $[\alpha]^{28}_D$ = 31.1° (*c* 1.15, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 6.19 (ddd, *J* = 10.2, 10.2, 17.2 Hz, 1 H), 4.94 (dd, *J* = 2.4, 10.2 Hz, 1 H), 4.82 (dd, *J* = 2.2, 17.2 Hz, 1 H) 4.15 (m, 1 H) 3.83 (dt, *J* = 2.4, 8.3 Hz, 1 H), 3.80 (dd, *J* = 6.4, 8.3 Hz, 1 H), 3.43 (dd, *J* = 7.0, 8.0 Hz, 1 H), 2.63 (br dd, *J* = 5.1, 15.6 Hz, 1 H), 2.16 (t, *J* = 2.2 Hz, 1 H), 2.28−2.08 (m, 3 H), 2.01 (s, 3 H), 1.91 (dt, *J* = 2.2, 10.7 Hz, 1 H), 1.72−1.52 (m, 2 H), 1.27 (s, 3 H), 1.22 (s, 3 H), 1.18−1.08 (m, 1 H), 0.82 (d, *J* = 6.8 Hz, 3 H), 0.59 (s, 3 H), 0.50 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 154.8, 150.1, 135.0, 131.7, 118.2, 114.8, 109.5, 79.6, 73.9, 66.0, 38.5, 32.2, 31.6, 29.8, 25.7, 21.4, 20.2, 9.6, −2.9, −3.2; IR (neat) 3600−3420, 2970, 2920, 1625 cm^{-1}; HRMS calcd for $C_{21}H_{34}O_4Si$ 378.2217, found 378.2239. Anal. Calcd for $C_{21}H_{34}O_4Si$: C, 66.63; H, 9.05. Found: C, 66.60; H, 9.25.

(3*S*,4*R*,5*R*)-5,6-O-Isopropylidene-3-[[2′-(4′,5′,6′,7′-tetrahydro-3′,6′-dimethylbenzofuryl)]dimethylsilyl]hex-1-ene-4-ol (**27b**). Prepared in 85% yield (78% of major diastereomer **27b**, 7% of minor diastereomer **26b**) from freshly distilled glyceraldehyde acetonide **23** and (*R,R*)-**11**. The reaction stereoselectivity was determined to be 92:8 by ^{1}H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 5:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **27b** follow: R_f = 0.50 (2:1 hexanes−Et_2O); $[\alpha]^{28}_D$ = 25.3° (*c* 1.19, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 6.06 (m, 1 H), 5.01 (m, 2 H), 4.11 (m, 1 H) 4.02−3.88 (m, 3 H), 2.58 (br dd, *J* = 5.2, 16.4 Hz, 1 H), 2.29 (dd, *J* = 2.0, 10.8 Hz, 1 H), 2.26−1.96 (m, 7 H), 1.66−1.50 (m, 2 H), 1.36 (s, 3 H), 1.28 (s, 3 H), 1.20−1.06 (m, 1 H), 0.47 (s, 3 H), 0.42 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 155.1, 149.9, 134.9, 132.1, 118.4, 115.6, 108.3, 78.8, 72.1, 66.2, 38.9, 32.1, 31.5, 29.7, 27.0, 25.6, 21.3, 20.1, 9.5, −3.1, −3.4; IR (neat) 3550−3400, 2960, 2920, 1620 cm^{-1}; HRMS calcd for $C_{21}H_{34}O_4Si$ (M^+) 378.2217, found 378.2213. Anal. Calcd for $C_{21}H_{34}O_4Si$: C, 66.63; H, 9.05. Found: C, 66.84; H, 9.30.

(3*R*,4*S*,5*R*)-6-[(*tert*-Butyldimethylsilyl)oxy]-3-[[2′-(4′,5′,6′,7′-tetrahydro-3′,6′-dimethylbenzofuryl)]dimethylsilyl]-5-methylhex-1-en-4-ol (**30b**). Prepared in 82% yield (75% of major diastereomer **30b**, 7% of minor diastereomer **31b**) from **25** and (*S,S*)-**11**. The reaction stereoselectivity was determined to be 94:6 by ^{1}H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 9:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **30b** follow: R_f = 0.75 (9:1 hexanes−Et_2O); $[\alpha]^{26}_D$ = 28.2° (*c* 1.19, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 6.10 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.02 (dd, *J* = 2.2, 10.2 Hz, 1 H), 4.98 (dd, *J* = 2.2, 17.2 Hz, 1 H), 4.07 (dd, *J* = 4.8, 9.1 Hz, 1 H), 3.57 (m, 2 H), 2.62 (br dd, *J* = 5.2, 16.0 Hz, 1 H), 2.32−2.06 (m, 5 H), 2.03 (s, 3 H), 1.85 (m, 1 H), 1.72−1.53 (m, 2 H), 1.20−1.08 (m, 1 H), 1.01 (d, *J* = 6.4 Hz, 3 H), 0.96 (s, 9 H), 0.83 (d, *J* = 6.4 Hz, 3 H), 0.53 (s, 3 H), 0.49 (s, 3 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, C_6D_6) δ 154.9, 150.2, 137.0, 131.6, 118.2, 114.5, 72.3, 66.6, 41.0, 40.8, 32.2, 31.6, 29.8, 26.1, 21.4, 20.2, 18.4, 12.3, 9.6, −2.7, −3.4, −5.4; IR (neat) 3600−3480, 2960, 2930, 2860, 1625 cm^{-1}; HRMS calcd for $C_{25}H_{47}O_3Si_2$ (M + 1), 451.3051, found 451.3052. Anal. Calcd for $C_{25}H_{46}O_3Si_2$: C, 66.60; H, 10.29. Found: C, 66.76; H, 10.43.

(3*S*,4*R*,5*R*)-6-[(*tert*-Butyldimethylsilyl)oxy]-3-[[2′-(4′,5′,6′,7′-tetrahydro-3′,6′-dimethylbenzofuryl)]dimethylsilyl]-5-methylhex-1-en-4-ol (**31b**). Prepared in 80% yield (44% of major diastereomer **31b**, 36% minor diastereomer **30b**) from **25** and (*R,R*)-**11**. The reaction stereoselectivity was determined to be 55:45 by ^{1}H NMR analysis of the reaction mixture after filtration of the mixture through a silica gel plug, eluting with 9:1 hexanes−Et_2O, to remove excess allylboronate reagent. Data for **31b** follow: R_f = 0.60 (9:1 hexanes−Et_2O); $[\alpha]^{28}_D$ = 15.8° (*c* 0.19, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 6.35 (ddd, *J* = 10.5, 10.5, 17.2 Hz, 1 H), 5.09 (dd, *J* = 2.2, 10.2 Hz, 1 H), 5.02 (dd, *J* = 2.4, 17.5 Hz, 1 H), 4.03 (t, *J* = 1.6 Hz, 1 H), 3.89 (br d, *J* = 9.1 Hz, 1 H), 3.56 (dd, *J* = 4.0, 9.9 Hz, 1 H), 3.38 (dd, *J* = 8.6, 9.7 Hz, 1 H), 2.64 (br dd, *J* = 5.2, 15.6 Hz, 1 H), 2.32−2.10 (m, 6 H), 2.00−1.88 (m, 1 H), 1.70−1.52 (m, 2 H), 1.40−1.08 (m, 3 H), 0.88 (s, 9 H), 0.82 (d, *J* = 6.8 Hz, 3 H), 0.70 (s, 3 H), 0.62 (d, *J* = 6.4 Hz, 3 H), 0.61 (s, 3 H), 0.06 (s, 6 H); ^{13}C NMR (100 MHz, C_6D_6) δ 154.6, 150.9, 135.8, 131.5, 118.2, 114.3, 77.3, 69.7, 40.0, 39.4, 32.3, 31.7, 29.8, 26.0, 21.5, 20.3, 18.3, 12.7, 9.7, −2.8, −5.6, −5.7; IR (neat) 3520−3480, 2960, 2930, 2860, 1625 cm^{-1}; HRMS calcd for $C_{25}H_{46}O_3Si_2$ 450.2973, found 450.2967. Anal. Calcd for $C_{25}H_{46}O_3Si_2$: C, 66.60; H, 10.29. Found: C, 66.53; H, 10.46.

Representative Procedure for Protodesilylation−Oxidation of 2-(5-Methylfuryl)-Substituted Silanols: (*R,S*)-1-Cyclohexylbut-3-ene-1,2-diol (**9a**). Silanol **12a** (40 mg, 0.14 mmol) was dissolved in 1 mL of CH_2Cl_2, and the solution was cooled to 0 °C. CF_3CO_2H (11.6 μL, 0.15 mmol) was added dropwise via syringe, and the mixture was stirred for 10 min at 0 °C, at which point no starting material remained by TLC analysis. The mixture was concentrated, and to the residue was added 1 mL of THF−CH_3OH (1:1), $KHCO_3$ (28 mg, 0.28 mmol), $KF\cdot 2H_2O$ (28 mg, 0.28 mmol), and 30% H_2O_2 (290 μL, 2.8 mmol). The mixture was stirred overnight (*ca.* 16 h) at room temperature; the reaction was then quenched by addition of $Na_2S_2O_3$ (670 mg, 4.2 mmol). The mixture was stirred for 30 min with the $Na_2S_2O_3$, and then the solids were filtered and rinsed well with EtOAc. The filtrate was concentrated and the crude product purified by flash chromatography, eluting with 1:1 hexanes−EtOAc, to yield 14 mg (61%) of known[22] diol *(R,S)*-**9a** as a white solid (82% ee, as determined by Mosher ester analysis[46]): mp 62−64 °C; $[\alpha]^{24}_D$ = 16.3° (*c* 0.27, $CHCl_3$) [lit.[22] $[\alpha]^{23}_D$ = 12.3 (*c* 2.3, $CHCl_3$)].

Diol **9a** was also prepared in 79% yield and 81% ee (as determined by Mosher ester analysis)[46] from silanol **13a** by using the procedure subsequently described for preparation of **34**: mp 63−64 °C; $[\alpha]^{24}_D$ = 14.3° (*c* 0.60, $CHCl_3$).

(*R,S*)-Non-1-ene-3,4-diol (**9b**). The known[22] diol **9b** was prepared in 43% yield and 74% ee (as determined by Mosher ester analysis[46]) from silanol **12b**: mp 35−38 °C; $[\alpha]^{27}_D$ = 8.4° (*c* 0.62, $CHCl_3$). Diol **9b** was also prepared in 82% yield and 74% ee (as determined by Mosher ester analysis[36]) from silanol **13b** by using the procedure subsequently described for preparation of **34**: mp 37−39 °C; $[\alpha]^{29}_D$ = 8.3° (*c* 0.45, $CHCl_3$).

(3*R*,4*R*,5*R*)-5,6-*O*-Isopropylidenehex-1-ene-3,4-diol (**32**). The known[22] diol **32** was prepared in 65% yield from silanol **26a**. Diol **32** was also prepared in 77% yield from silanol **26b** by using the procedure subsequently described for preparation of **34**.

(3*S*,4*S*,5*R*)-5,6-*O*-Isopropylidenehex-1-ene-3,4-diol (**33**). The known[22] diol **33** was prepared in 65% yield from silanol **27a**. Diol **33** was also prepared in 82% yield from silanol **27b** by using the procedure subsequently described for preparation of **34**.

(3*R*,4*S*,5*R*)-6-[(tert-Butyldimethylsilyl)oxy]-5-methylhex-1-ene-3,4-diol (**36**). The known[22] diol **36** was prepared in 56% yield from silanol **30a**. Diol **36** was also prepared in 82% yield from silanol **30b** by using the procedure subsequently described for preparation of **34**.

(3*R*,4*S*,5*R*)-6-[(*tert*-Butyldimethylsilyl)oxy]-5-methylhex-1-ene-3,4-diol (**37**). The known[22] diol **37** was prepared in 53% yield from silanol **31a**. Diol **37** was also prepared in 76% yield from silanol **31b** by using the procedure subsequently described for preparation of **34**.

Representative Procedure for Protodesilylation−Oxidation of Menthofuryl-Substituted Silanols: (3*R*,4*S*,-5*S*,6*R*)-9-Bromo-5,6-epoxynon-1-ene-3,4-diol (**34**). Silanol **28b** (363 mg, 0.82 mmol) was dissolved in 1.5 mL of THF, and the solution was cooled to 0 °C. CF_3CO_2H (70 μL, 0.90 mmol) in 0.5 mL of THF was added dropwise via syringe, and the mixture was warmed to room temperature and stirred for 2.5 h, at which point no starting material remained by TLC analysis. To the solution was added 2 mL of CH_3OH, $KHCO_3$ (160 mg, 1.60 mmol), $KF{\cdot}2H_2O$ (160 mg, 1.60 mmol), and 30% H_2O_2 (1.6 mL, 16.0 mmol). The mixture was stirred for 24 h; then the reaction was quenched by addition of $Na_2S_2O_3$ (3.8 g, 24.0 mmol). The mixture was stirred over $Na_2S_2O_3$ for 30 min, Na_2SO_4 was added, and the solids were filtered and rinsed well with EtOAc. The filtrate was concentrated and the crude product was purified by flash chromatography, eluting with a gradient system of 1:1 hexanes−Et_2O to 100% Et_2O, to yield 176 mg (85%) of diol **34**: R_f = 0.16 (2:1 Et_2O−hexanes); $[\alpha]^{23}_D$ = 11.2° (*c* 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (ddd, *J* = 6.2, 10.5, 17.2 Hz, 1 H), 5.32 (dt, *J* = 1.3, 17.2 Hz, 1 H), 5.42 (dt, *J* = 1.3, 10.7 Hz, 1 H), 4.35 (m, 1 H), 3.82 (t, *J* = 4.0 Hz, 1 H), 3.47 (m, 2 H), 3.05 (ddd, *J* = 2.2, 5.1, 6.7 Hz, 1 H), 2.91 (dd, *J* = 2.2, 4.0 Hz, 1 H), 2.28−2.12 (br s, 1 H), 2.10−1.98 (m, 2 H), 1.82−1.52 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 117.7, 74.0, 71.4, 57.3, 54.6, 33.0, 30.0, 29.1; IR (neat) 3500−3300, 2930 cm^{-1}; HRMS calcd for $C_9H_{15}O_3{}^{81}Br$, 252.0180, found 252.0196. Anal. Calcd for $C_9H_{15}O_3Br$: C, 43.04; H, 6.02. Found: C, 42.89; H, 6.03.

Diol **34** was also prepared in 57% yield from silanol **28a** by using the procedure described for preparation of **9a**.

(3*S*,4*R*,5*S*,6*R*)-9-Bromo-5,6-epoxynon-1-ene-3,4-diol (**35**). Diol **35** was prepared in 79% yield from silanol **29b**: R_f = 0.15 (2:1 Et_2O−hexanes); mp 58−59 °C; $[\alpha]^{26}_D$ = 18.7° (*c* 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (ddd, *J* = 5.6, 10.7, 17.2 Hz, 1 H), 5.43 (dt, *J* = 1.6, 17.3 Hz, 1 H), 5.32 (dt, *J* = 1.6, 10.8 Hz, 1 H), 4.30 (br s, 1 H), 3.61 (m, 1 H) 3.50 (m, 2 H), 2.95 (m, 2 H), 2.37−2.25 (m, 2 H), 2.10 (m, 2 H), 1.88−1.78 (m, 1 H), 1.70−1.58 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 117.4, 74.6, 72.2, 57.7, 55.1, 32.9, 30.0, 29.1; IR ($CHCl_3$) 3600−3500, 3010, 2920 cm^{-1}; HRMS calcd for $C_9H_{16}O_3{}^{81}Br$ (M + 1) 253.0258, found 253.0267. Anal. Calcd for $C_9H_{15}O_3Br$: C, 43.04; H, 6.02. Found: C, 43.10; H, 6.11.

6-Bromohex-2-enol (**39**). To a 1 L flask equipped with an overhead mechanical stirrer was added 3.6 g (88.9 mmol) of a 60% dispersion of NaH in oil. The dispersion was rinsed with dry THF to remove oil; 260 mL of THF was then added. Triethyl phosphonoacetate (16.6 g, 74.1 mmol) in 10 mL of THF was added, and after gas evolution ceased, the mixture was cooled to −50 °C in a dry ice−*i*-PrOH bath. To the cold mixture was added 4-bromobutanal (**38**)[64,65] (12.3 g, 81.5 mmol) in 10 mL of THF. The resulting mixture was allowed to warm slowly to room temperature and stirred for 2.5 h. The mixture was recooled to 0 °C and quenched by addition of H_2O (150 mL). The phases were separated, and the aqueous phase was extracted with 3 × 100 mL of Et_2O. The combined organics were washed with brine (150 mL), dried over $MgSO_4$, filtered, and concentrated to a yellow oil that was purified by vacuum distillation (5 mmHg, bp 95−100 °C) to yield 13.9 g (85%) of the known[64,65] ethyl 6-bromohex-2-enoate as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (dt, *J* = 7.0, 15.6 Hz, 1 H), 5.88 (dt, *J* = 1.6, 15.6 Hz, 2 H), 4.19 (q, *J* = 7.3 Hz, 2 H) 3.41 (t, *J* = 6.7 Hz, 2 H) 2.39 (dq, *J* = 1.6, 7.0 Hz, 2 H), 2.02 (p, *J* = 6.7, 2 H), 1.29 (t, *J* = 7.3 Hz, 3 H).

To a 0 °C solution of ethyl 6-bromohex-2-enoate (11.3 g, 51.1 mmol) in 50 mL of Et_2O was added 150 mL of a 1.0 M solution of DIBAL in hexanes. The mixture was allowed to warm to room temperature, stirred for 2 h at this temperature, and then recooled to 0 °C and quenched by addition of 200 mL of 1 N HCl. The phases were separated, and the aqueous layer was extracted with 3 × 100 mL of Et_2O. The combined organics were dried over $MgSO_4$ filtered, and concentrated to a colorless oil. The crude product was purified by vacuum distillation (5 mmHg, bp 95−100 °C) to yield 7.92 g (87%) of the known[64,65] allylic alcohol **39**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (m, 2 H), 4.10 (d, *J* = 4.6 Hz, 2 H) 3.41 (t, *J* = 6.7 Hz, 2 H) 2.22 (dd, *J* = 5.9, 7.0 Hz, 2 H), 1.95 (quintet, *J* = 6.7 Hz, 2 H).

(2*S*,3*R*)-6-Bromo-2,3-epoxyhexanol (**40**). CH_2Cl_2 (100 mL) was stirred over crushed 4 Å molecular sieves for 15 min; $Ti(OiPr)_4$ (1.7 mL, 5.8 mmol) was then added, and the solution was cooled to −30 °C in a H_2O−ethylene glycol bath. D-DIPT (1.6 mL, 7.7 mmol) was added, and the solution was stirred for 5 min at −30 °C; allylic alcohol **39** (6.9 g, 38.5 mmol) in 10 mL of CH_2Cl_2 was then added, and the solution was stirred for 20 min at −30 °C. *tert*-Butyl hydroperoxide (13.6 mL of a 4.27 M solution in toluene) was added, and the reaction mixture was stored at −20 °C for 2 d, filtered through Celite, and concentrated to a yellow oil. The crude product was purified by flash chromatography, eluting with 1:1 hexanes−EtOAc, to yield 5.48 g (73%) of epoxy alcohol **40**: R_f = 0.17 (1:1 hexanes−EtOAc); $[\alpha]^{23}_D$ = 8.4° (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (ddd, *J* = 2.7, 2.4, 12.6 Hz, 1 H), 3.66 (ddd, *J* = 4.0, 7.3, 12.6 Hz, 1 H), 3.46 (m, 2 H), 3.00 (ddd, *J* = 2.4, 4.6, 7.0 Hz, 1 H), 2.96 (dt, *J* = 2.4, 4.0 Hz, 1 H), 2.12−1.95 (m, 2 H), 1.90−1.81 (m, 1 H), 1.72−1.60 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.4, 58.2, 54.8. 33.0, 30.0, 29.2; IR (neat) 3500−3300, 2920, 2860 cm^{-1}; HRMS calcd for $C_6H_{12}O_2{}^{81}Br$ (M + 1) 196.9997, found 196.9980; calcd for $C_6H_{12}O_2{}^{79}Br$ (M + 1) 195.0017, found 195.0013.

Enantiomeric Purity Analysis of 40. Mosher ester analysis of **40** followed the standard literature procedure.[46] **(*S*)-MTPA ester**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.66 (m, 2 H), 7.08−6.90 (m, 3 H), 3.95 (dd, *J* = 3.8, 11.8 Hz, 1 H) 3.71 (dd, *J* = 6.5, 12.1 Hz, 1 H) 3.38 (s, 3 H) 2.82−2.70 (m, 2 H), 2.32 (ddd, *J* = 2.2, 3.2, 5.6 Hz, 1 H), 2.12 (ddd, *J* = 2.2, 4.6, 6.7 Hz, 1 H), 1.43−1.24 (m, 2 H). 1.18−1.24 (m, 1 H), 1.03−0.93 (m, 1 H). **(*R*)-MTPA ester**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.57 (m, 2 H), 7.45−7.36 (m, 3 H), 4.12 (dd, *J* = 3.2, 12.0 Hz, 1 H), 3.67 (dd, *J* = 5.6, 12.0 Hz, 1 H), 3.42 (s, 3 H), 2.85−2.75 (m, 2 H), 2.39 (ddd, *J* = 2.2, 3.2, 5.6 Hz, 1 H), 2.25 (ddd, *J* = 2.2, 5.6, 6.7 Hz, 1 H), 1.45−1.25 (m, 2 H). 1.21−1.09 (m, 1 H), 1.05−0.97 (m, 1 H).

(2*R*,3*R*)-6-Bromo-2,3-epoxyhexanal (**24**). To a 0 °C solution of alcohol **40** (0.5 g, 2.6 mmol) in 4 mL of CH_2Cl_2 was added 5 mL of dry DMSO, Et_3N (1.8 mL, 12.8 mmol), and SO_3−pyridine (2.04 g, 12.8 mmol). The cooling bath was removed, and the mixture was stirred for 20 min at room temperature, at which point TLC analysis showed that no starting material remained. The mixture was diluted with 35 mL of Et_2O and washed with 20 mL of saturated aqueous $NaHCO_3$ and 20 mL of brine. The aqueous washes were extracted with 4 × 10 mL of EtOAc, and the combined organics were dried over $MgSO_4$, filtered, and concentrated to a yellow oil. The crude product was purified by flash chromatography, eluting with 2:1 hexanes−EtOAc, to yield 392 mg (80%) of epoxy aldehyde **24**: R_f = 0.50 (1:1 hexanes−EtOAc); $[\alpha]^{26}_D$ = −24.8° (*c* 0.21, C_6H_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 6.2 Hz, 1 H), 3.47 (m, 2 H), 3.28 (ddd, *J* = 1.9, 4.3, 6.2 Hz, 1 H), 3.19 (dd, *J* = 1.9, 6.2 Hz, 1 H), 2.20−1.90 (m, 3 H), 1.80−1.70 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 58.9, 55.8. 32.4, 29.8, 28.9; IR (neat) 2960, 2920, 2860, 1725 cm^{-1}; HRMS for $C_6H_{10}O_2{}^{81}$-Br (M + 1) 193.9763, found 193.9853.

(3*R*,4*S*,5*S*,6*R*)-9-Bromo-5,6-epoxy-3,4-*O*-dihydroxynonan-1-al 3,4-Acetonide (**41**). Diol **34** (99 mg, 0.39 mmol), *p*-PTS (5 mg, 0.02 mmol), and 2,2-dimethoxypropane (0.5 mL, 44 mmol) were dissoved in 1 mL of CH_2Cl_2. The solution was heated to reflux for 2 h, at which point no starting material

remained by TLC analysis. The solution was cooled to room temperature, diluted with 10 mL of of Et_2O, and washed with 5 mL of saturated aqueous $NaHCO_3$ solution The aqueous phase was extracted with 3 × 5 mL of Et_2O, and the combined organics were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography, eluting with 9:1 hexanes−Et_2O, to yield 107 mg of (3*R*,4*S*,5*S*,6*R*)-9-bromo-5,6-epoxy-3,4-dihydroxynon-1-ene 3,4-acetonide (95%) as a colorless oil: R_f = 0.72 (2:1 Et_2O−hexanes); $[\alpha]^{25}_D$ = 3.9° (*c* 1.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (ddd, *J* = 7.0, 10.5, 17.2 Hz, 1 H), 5.48 (dt, *J* = 1.3, 17.2 Hz, 1 H), 5.36 (dt, *J* = 1.3, 10.5 Hz, 1 H), 4.72 (t, *J* = 6.7 Hz, 1 H), 3.80 (t, *J* = 6.5 Hz, 1 H), 3.46 (m, 2 H), 2.90 (ddd, *J* = 2.2, 4.8, 7.0 Hz, 1 H), 2.77 (dd, *J* = 2.2, 7.5 Hz, 1 H), 2.10−1.97 (m, 2 H), 1.88−1.80 (m, 1 H), 1.68−1.59 (m, 1 H), 1.52 (s, 3 H), 1.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4, 118.8, 109.3, 78.6, 78.5, 56.5, 55.8, 32.9, 29.9, 29.2, 27.7, 25.1; IR ($CHCl_3$) 2980, 2930, 1450, 1430 cm^{-1}; HRMS calcd for $C_{11}H_{16}O_3{}^{79}Br$ (M − CH_3), 275.0278, found 275.0291. Anal. Calcd for $C_{12}H_{19}O_3Br$: C, 49.50; H, 6.58. Found: C, 49.69; H, 6.46.

(3*R*,4*S*,5*S*,6*R*)-9-Bromo-5,6-epoxy-3,4-dihydroxynon-1-ene 3,4-acetonide from the preceding experiment (105 mg, 0.36 mmol) was dissolved in 6 mL of CH_2Cl_2, and the solution was cooled to −78 °C. A stream of O_3 in O_2 was bubbled through this solution until the solution turned blue and TLC analysis of the reaction mixture showed no starting material; the solution was then flushed with O_2 for 5 min, and Ph_3P was added. The mixture was allowed to warm to room temperature stirred for 1 h at this temperature, and then concentrated *in vacuo*. The crude product was purified by flash chromatography, eluting with 1:1 hexanes−EtOAc, to yield 92 mg (88%) of aldehyde **41**: R_f = 0.26 (1:1 hexanes−EtOAc); $[\alpha]^{25}_D$ = 27.6° (*c* 0.21, C_6H_6); ^{1}H NMR (400 MHz, C_6D_6) δ 9.56 (d, *J* = 2.4 Hz, 1 H), 4.00 (dd, *J* = 2.4, 7.0 Hz, 1 H), 3.71 (dd, *J* = 5.9, 7.0 Hz, 1 H), 2.84 (m, 2 H), 2.58 (dd, *J* = 2.4, 5.9 Hz, 1 H), 2.45 (ddd, *J* = 1.9, 4.6, 6.7 Hz, 1 H), 1.50−1.38 (m, 5 H), 1.30−1.20 (m, 1 H), 1.14−1.02 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 111.7, 81.6, 77.5, 56.6, 55.3, 32.8. 29.7, 29.0, 27.2, 25.2; IR ($CHCl_3$) 2985, 2930, 1735, 1450, 1435 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_4{}^{79}Br$ (M − CH_3) 277.0071, found 277.0067. Anal. Calcd for $C_{11}H_{17}O_4Br$: C, 45.07; H, 5.85. Found: C, 44.95; H, 5.98.

(1*S*,2*R*,8*R*,8a*R*)-8-Hydroxy-1,2-(isopropylidenedioxy)-indolizine (Swainsonine Acetonide). A mixture of aldehyde **41** (30 mg, 0.10 mmol), NH_4OAc (10 mg, 0.15 mmol), and 25 mg of 3 Å molecular sieves in 1 mL of CH_3OH was heated to reflux for 6 h. The mixture was cooled to room temperature, and $NaBH_3CN$ (13 mg, 0.20 mmol) was added.[68] The mixture was stirred for 12 h at room temperature; 1 mL of saturated aqueous $NaHCO_3$ was then added, and the CH_3OH was removed in vacuo. The remaining suspension was extracted with 4 × 10 mL of EtOAc, and the combined extracts were concentrated to a pale yellow oil. The crude product was purified by flash chromatography, eluting with a gradient system of 1:1 hexanes−EtOAc to 100% EtOAc to yield 15 mg (71%) of swainsonine acetonide[54,61] as an off-white solid: R_f = 0.10 (1:1 hexanes−EtOAc); mp 102−103 °C (lit.[54] mp 105−107 °C; lit.[61] mp 100−103 °C); $[\alpha]^{26}_D$ = −84.6° (*c* 1.53, CH_3OH) [lit.[54] $[\alpha]^{24}_D$ = −75.1° (*c* 1.54, CH_3OH); lit.[61] $[\alpha]^{25}_D$ = −72.7° (*c* 0.43, CH_3OH)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (dd, *J* = 4.6, 6.2 Hz, 1 H), 4.61 (dd, *J* = 4.3, 6.5 Hz, 1 H), 3.83 (m, 1 H), 3.15 (d, *J* = 10.5 Hz, 1 H), 2.99 (dt, *J* = 3.2, 10.5 Hz, 1 H), 2.13 (dd, *J* = 4.3, 10.8 Hz, 1 H), 2.05 (m, 2 H), 1.85 (m, 1 H), 1.71−1.60 (m, 3 H), 1.50 (s, 3 H), 1.33 (s, 3 H), 1.30−1.17 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.5, 79.3, 78.3, 73.7, 67.6, 60.0, 51.6, 33.0, 26.0, 25.0, 24.1; HRMS calcd for $C_{11}H_{19}NO_3$ 213.1360, found 213.1358.

(1*S*,2*R*,8*R*,8a*R*)-1,2,8-Trihydroxyindolizine (42) [(−)-Swainsonine]. Swainsonine acetonide (15 mg, 0.07 mmol) was dissolved in 1 mL of THF, and 1 mL of 6 N HCl was added. The mixture was stirred vigorously for 20 h at ambient temperature and then concentrated *in vacuo*. The crude product was purified by ion-exchange chromatography with Amberlite IRA-400(OH), eluting with distilled H_2O, to yield 11 mg (92%) of (−)-swainsonine (**42**) as a white crystalline solid: R_f = 0.35 (4:4:4:1 *n*-BuOH−$CHCl_3$−CH_3OH−concd NH_4OH); mp 137−140 °C (lit.[54] mp 144−145 °C; lit.[58] mp 141−143 °C; lit.[62] mp 138−140 °C); $[\alpha]^{26}_D$ = −85.5° (*c* 0.42 CH_3OH); [lit.[54] $[\alpha]^{25}_D$ = −87.2° (*c* 2.1, CH_3OH); lit.[58] $[\alpha]^{26}_D$ = −82.6° (*c* 1.03, CH_3OH); lit.[62] $[\alpha]^{27}_D$ = −85.2° (*c* 0.5, CH_3OH)]; ^{1}H NMR (400 MHz, D_2O) δ 4.33 (ddd, *J* = 2.4, 6.2, 8.0 Hz, 1 H), 4.24 (dd, *J* = 3.8, 5.9 Hz, 1 H), 3.78 (ddd, *J* = 4.6, 9.7, 10.7 Hz, 1 H), 2.89 (br d, overlapping with dd δ 2.86, 1 H), 2.86 (dd, overlapping with br d δ 2.89, *J* = 2.1, 11.0 Hz, 1 H), 2.05 (m, 1 H), 1.93 (dt, overlapping with dd δ 1.89, *J* = 3.0, 12.4 Hz, 1 H), 1.89 (dd, overlapping with dt δ 1.93, *J* = 3.5, 9.4 Hz, 1 H), 1.71 (m, 1 H), 1.50 (qt, *J* = 4.0, 13.4 Hz, 1 H), 1.22 (qd, *J* = 4.6, 12.4 Hz, 1 H); ^{13}C NMR (100 MHz, D_2O) δ 73.1, 70.0, 69.4, 66.7, 61.0, 52.0, 32.8, 23.6; HRMS calcd for $C_8H_{16}NO_3$ (M + 1) 174.1126, found 174.1133.

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Supporting Information Available: ^{1}H NMR spectra of (*R*,*R*)-**10**, (*R*,*R*)-**11**, **13a**,**b**, **15**, **17**, **22**, **24**, **40**, and **42** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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