Studies in the Transmetalation of Cyclopropyl, Vinyl, and Epoxy Stannanes

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Diastereomerically pure cyclopropyl, vinyl, and epoxy stannanes have been converted to the corresponding organolithium species and trapped with a variety of electrophiles. The stereochemistry of the products was retained throughout the transmetalation–trapping sequence. The stereochemistry of the tributyltin moiety and the carbinol side chain was shown to have a dramatic influence on the rate of transmetalation. 1,4-Silyl migrations were observed for silicon groups of varying steric bulk, and crossover experiments showed the migration was an intramolecular process. Access to silanes which are difficult to prepare was achieved.

Introduction

Organolithium reagents have found widespread use in organic synthesis in C–C bond-forming reactions.[2–5] Most organolithium reagents are prepared via one of the following routes: (i) the reaction of lithium metal with an organic halide, (ii) the halogen–metal exchange between a simple organolithium reagent and an organic halide,[5] iii) the hydrogen–metal exchange between an organolithium reagent and a suitable hydrocarbon,[6–8] or (iv) the metal–metal exchange between an organolithium and another less electropositive organometallic species (eq 1).[9–19]

$$RM + R'Li \longrightarrow RLi + R'M \qquad (1)$$

Exchange reactions of this type have been reported between organic derivatives of antimony, selenium, tellurium, boron, silicon, lead, mercury, and tin. Among these, the reaction between an organotin compound and a simple organolithium species has attracted the most attention and has found many applications in organic synthesis. The reaction is formally an equilibrium and proceeds in the direction of placing the more electropositive lithium on the more electronegative carbon atom (eq 2).

$$R^1_3SnR^2 + R^3Li \rightleftharpoons R^2Li + R^1_3SnR^3 \qquad (2)$$

The driving force is the relative difference in base strengths of the organolithium species. From a synthetic point of view, this means that a complete tin–lithium exchange can be obtained when R^1 and R^3 are alkyl or aryl and R^2 equals an allyl, benzyl, vinyl, cyclopropyl, α-heterosubstituted alkyl, or an epoxy moiety. The mild and clean generation of a carbanion is achieved with only the relatively inert tetraalkylstannane formed as a byproduct.

The selectivity of the tin–lithium transmetalation is also an attractive feature. Chemoselective transmetalation reactions in the presence of other functional groups are often possible.[20–22] Competition between deprotonation and transmetalation depends on the organotin precursor used and on the experimental conditions. The

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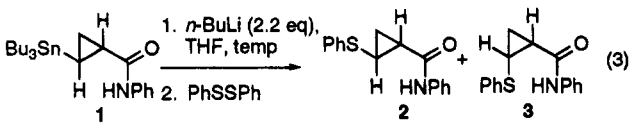
general trend is that tin–lithium exchange occurs with alkyllithiums, whereas deprotonation is favored with lithium amides.[20,22]

α-Alkoxy, α-amino, and other α-heteroatom organolithium chemistry has expanded considerably over the last few years.[23,24] Carbanions bearing an α-oxygen,[25] -nitrogen,[8b,26] -sulfur,[20b,27] -selenium,[28] and -silicon[29] substituent have all been prepared via tin–lithium exchange.

A variety of α-heterosubstituted and functionalized stannylcyclopropanes have been successfully converted to the corresponding cyclopropyllithium anion upon treatment with an organolithium.[30] Since the first report of the tin–lithium exchange reaction of a stannylcyclopropane by Seyferth and Cohen,[31] only scattered accounts have appeared on this topic[32] and utilization in synthesis has been scarce.[33] This is somewhat surprising, since the chemoselectivity of this reaction is high. For example, selective C–Sn over C–Br bond cleavage is possible,[32a,b] and other functional groups are also tolerated during the transmetalation procedure.[31,32]

Moreover, the tin–lithium transmetalation proceeds with clean retention of configuration for the stereocontrolled formation of cyclopropyl organolithiums.[33] Information on the configurational stability of the resulting cyclopropyllithium in polar solvents is also available.[34]

For example, unsubstituted and 1-alkyl-substituted cyclopropyllithiums are usually found to be configurationally stable, even at elevated temperature.[33–35] However, in some cases where chelation of the cyclopropyllithium with a nearby group is possible in only one of the isomeric forms, a more complex situation was found. The (*E*)-(tributylstannyl)cyclopropylamide **1** reacts smoothly with *n*-BuLi at −78 °C to afford **2** exclusively after trapping of the anion with diphenyl disulfide (eq 3).[32c] However, when the reaction is performed at 0 °C, epimerization of the initially formed (*E*)-cyclopropyllithium to the thermodynamically more stable, chelated *cis*-lithio intermediate occurs, resulting in a mixture of (*E*)- and (*Z*)-cyclopropane sulfides **2** and **3**.



-78 °C	100	:	0	44%
0 °C	35	:	65	66%

Cyclopropanes substituted with an α-functional group are able to delocalize the cyclopropyl anion and generally do not maintain their stereointegrity.[32,36–40] Phenylsulfonyl-,[36] cyano-,[37] isocyano-,[38] and acetylenyl-[39] substituted cyclopropyl carbanions, and α-bromo-,[32a,b] α-silyl-,[32c] α-sulfur-,[40a] and sulfur ylide-substituted cyclopropyllithiums[40b] all epimerize at ambient or in some cases even at low temperatures.

During the course of our transmetalation studies, we encountered an interesting example of a silyl migration reaction.[41] Several types of silyl migration reactions have been discovered, of which the 1,2 carbon-to-oxygen rearrangement (Brook rearrangement) is probably the most well documented.[42,43] The reverse Brook rearrangement, the migration of silicon from oxygen to carbon has also been reported, and higher order reactions (1,*n* where *n* = 3, 4, or 5) are also known,[44–46] although they are generally considered to be less facile (eq 4). The relative

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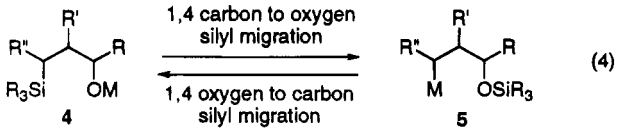
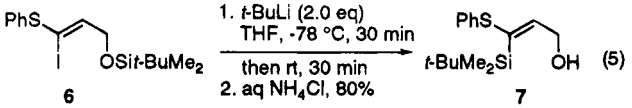


(4)

The first example of an oxygen-to-carbon 1,4-rearrangement appears to be that reported by Speier[48] and was followed by other accounts.[49,50] Evans showed, during a study of homoenolate equivalents, that the steric bulk of the migrating group was extremely important.[49b] The migration could be suppressed by substituting the trimethylsilyl group by a triethylsilyl group. Others showed that the reaction is quite general with respect to silicon in that triethylsilyl, triisopropylsilyl, and *tert*-butyldimethylsilyl groups can all undergo the migration.[49,50]

Since these reactions are formerly equilibrium processes, carbon-to-oxygen (Brook type) 1,4-silyl rearrangements have also been observed.[51] The two most important factors controlling the direction of the equilibrium are the basicity of the carbanion and the alkoxide counterion. In general, if the carbanion which is formed upon cleavage of the carbon–silicon bond bears electron acceptors, the equilibrium is shifted toward the carbon-to-oxygen migration.[52] Also, lithium alkoxides favor oxygen-to-carbon migration,[49,50] while potassium and sodium alkoxides shift the equilibrium toward the formation of the silyl ether.[51f,h] Negishi showed that a 1,4 O-to-C-migration of a *tert*-butyldimethylsilyl group *did not compete* with alkylation if the electrophile was part of the same molecule, i.e., an intramolecular cyclization.[53]

Magriotis and Kim reported the silyl migration of (*Z*)-iodoallylic silyl ethers occurs smoothly upon treatment with *t*-BuLi to provide a variety of (*Z*)-silyl-substituted primary allylic alcohols (eq 5).[50e]

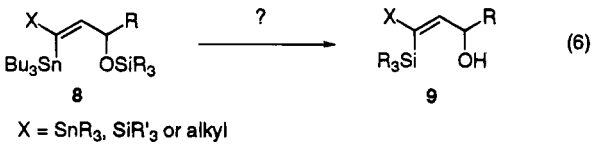


(5)

Objectives

Our discovery of a simple route to a variety of diasteromerically pure stannylalkyl and stannylsilyl cyclopropylcarbinols made a study of the tin–lithium reaction of these substrates possible. Our goal was to develop a strategy that would allow the synthesis of a multitude of highly substituted cyclopropanes.

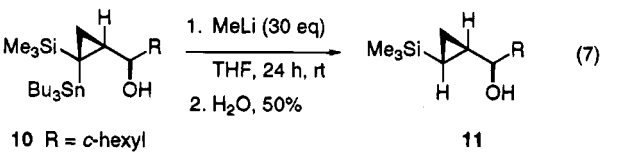
The generality of the 1,4 oxygen-to-carbon migration reaction was also evaluated to see whether this strategy could be expanded beyond the formation of cyclopropylsilanes. It was considered that a 1,4-silyl migration of a (*Z*)-stannylallylic silyl ether would provide a simple solution for the synthesis of those (*Z*)-silylalkenes which are difficult to prepare by existing methodology (eq 6).[54,55]



(6)

Results and Discussion

The tin–lithium exchange of the bimetallic cyclopropanecarbinol **10** was investigated. It was found that the transmetalation was best performed using MeLi in THF (eq 7). However, even after treatment of **10** for 24 h, with up to 30 equiv of MeLi, only partial transmetalation had occurred, and **11** was isolated in 50% yield.[56]



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(51) For C-to-O 1,4-silyl migrations, see: (a) Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1978**, *43*, 1947. (b) Matsuda, I.; Murata, S.; Ishii, Y. *J. Chem. Soc., Perkin Trans. I* **1979**, 26. (c) Isobe, M.; Kitamura, M.; Goto, T. *Tetrahedron Lett.* **1979**, 3465. (d) Fleming, I ; Floyd, C. D. *J. Chem. Soc., Perkin Trans. I* **1981**, 969. (e) Takeda, T.; Naito, S.; Ando, K.; Fujiwara, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 967. (f) Brook, A. G.; Chrusciel, J. J. *Organometallics* **1984**, *3*, 1317. (g) Isobe, M.; Ichikawa, Y.; Funabashi, Y.; Mio, S. Goto, T. *Tetrahedron* **1986**, *42*, 2863. (h) Spinazzé, P. G.; Keay, B. A. *Tetrahedron Lett.* **1989**, *30*, 1765. (i) Tietze, L. F.; Geissler, H.; Gewert, J. A.; Jakobi, U. *Synlett* **1994**, 511.

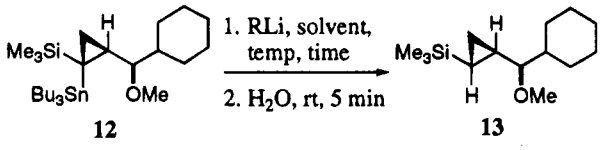
(52) For a case where O-to-C silyl migration does not take place, as a result of stabilization of the carbanion by a phenyl sulfone group, see: (a) Ashwell, M.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. I* **1989**, 835. (b) Dunn, S. F. C.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. I* **1992**, 2863.

(53) Negishi, E.; Zhang, Y.; Bagheri, V. *Tetrahedron Lett.* **1987**, *28*, 5793.

(54) For an approach to (*Z*)-silylalkenes via silylmetalation of an acetylene, see: Fugami, K.; Hibino, J.; Nakatsukasa, S.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1988**, *44*, 4277.

(55) For different approaches to (*Z*)-silylalkenes via hydrometalation of an acetylene, see the following. Hydromagnesiation: (a) Sato, F.; Kobayashi, Y. *Org. Synth.* **1990**, *69*, 106 and references therein. Hydroboration: (b) Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2941. (c) Uchida, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1977**, *33*, 2987. (d) Zweifel, G.; Backlund, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184. (e) Soderquist, J. A.; Colberg, J. C.; Del Valle, L. *J. Am. Chem. Soc.* **1989**, *111*, 4873. (f) Soderquist, J. A.; Colberg, J. C. *Synlett* **1989**, 25. Hydroalumination: (g) Baba, S.; Van Horn, D. E.; Negishi, E. *Tetrahedron Lett.* **1976**, 1927. (h) Eisch, J. J.; Damasevitz, G. A.; *J. Org. Chem.* **1976**, *41*, 2214. (i) Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2215. (j) Marshall, J. A.; Shearer, B. G.; Crooks, S. L. *J. Org. Chem.* **1987**, *52*, 1236. (k) Ziegler, F. E.; Mikami, K. *Tetrahedron Lett.* **1984**, *25*, 131.

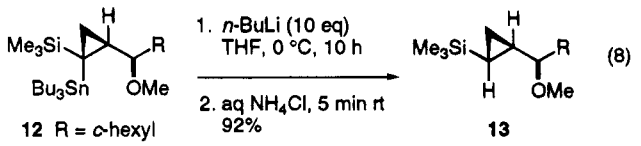
Table 1. Effect of the Solvent and RLi on the Tin–Lithium Transmetalation of 12



entry	RLi (equiv)	solvent	temp, time	yield (%)[a]
1	BuLi (30)	THF	0 °C, 10 h	92
2	BuLi (30)	DME	0 °C, 15 h	20[b]
3	BuLi (30)	Et_2O	0 °C, 3 h; rt, 12 h	<5[b]
4	BuLi (30)	hexane	0 °C, 3 h; rt, 12 h	<5[b]
5	MeLi (1.05)	THF	0 °C, 5 min; rt, 20 min	93
6	MeLi (1.1)	DME	0 °C, 5 min; rt, 35 min	91
7	MeLi (30)	Et_2O	0 °C, 3 h; rt, 12 h	<5[b]
8	MeLi (30)	hexane	0 °C, 3 h; rt, 12 h	<5[b]

[a] Isolated yields are reported unless noted otherwise. [b] Conversion was determined by ^1H NMR on the crude mixture.

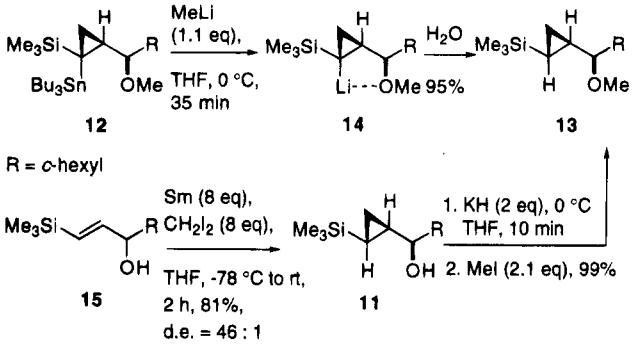
Since we were concerned that the presence of the lithium alkoxide was preventing a smooth tin–lithium exchange, we prepared the corresponding methyl ether **12** (KH (2 equiv), THF, 0 °C; MeI (2.1 equiv), quantitative yield). Indeed, treatment of the methyl ether **12** with a large excess of *n*-BuLi in THF for 10 h at 0 °C, followed by protonation, resulted in 92% of the silylcyclopropane **13** (eq 8 and Table 1, entry 1).



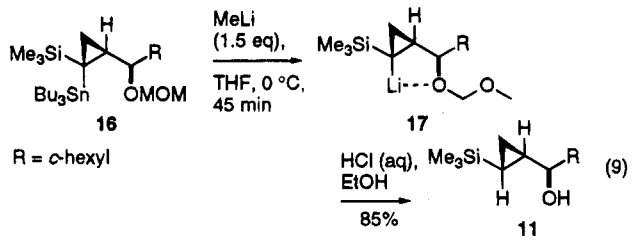
An examination of the effect of solvents on the transmetalation rate revealed that, while the reaction was nearly complete after 10 h in THF, transmetalation was considerably slower in dimethoxyethane and did not proceed in diethyl ether and hexane (see Table 1, entries 1–4). Encouraged by the enhanced transmetalation rate of the methyl ether **12** over the alcohol **10** in THF, the effect of the organolithium on the transmetalation rate was investigated. It was found that an extremely efficient reaction occurred upon treatment of **12** using only a slight excess of MeLi (see Table 1, entry 5). The silylcyclopropane **13** was obtained in high yield after protonation. THF clearly is the best solvent, but complete transmetalation in dimethoxyethane did occur (entry 6). Diethyl ether and hexane were found to be completely ineffective solvent systems, since less than 5% of the tin–lithium exchange had occurred, even after prolonged reaction times (entries 7 and 8).

To confirm that the transmetalation/protonation sequence had occurred with overall retention of configuration at the cyclopropyl carbon, the following study was executed. Transmetalation of **12** forms the α-silylcyclopropyl anion **14** (Scheme 1). These silyl-substituted anions have been shown to be configurationally labile species and epimerization can occur readily. However, we suspected that the *cis*-lithio chelated intermediate **14** would be thermodynamically more stable than the epimerized *trans*-lithiocyclopropane.[57] Protonation of the intermediate **14** would then lead to the product **13** with overall retention of configuration. This was confirmed by preparation of the product **13** via an independent route (Scheme 1). Methylation of the *trans*-silylcyclopropane **11**, obtained from cyclopropanation of the (*E*)-silylallylic alcohol **15**,[58] gave the methyl ether **13**. Comparison of the ^1H and ^{13}C NMR data showed that cyclopropanes prepared via the two different routes were identical.

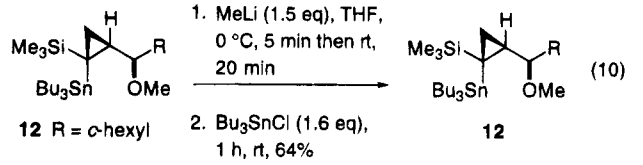
Scheme 1



The methoxymethyl-protected substrate **16** could also be transmetalated. After treatment with 1.5 equiv of MeLi and trapping of the carbanion **17**, the protecting group was removed with 20% aqueous hydrochloric acid to provide **11** in 85% yield which was identical to the product formed above (eq 9).



When **14** was treated with tributyltin chloride, stannylation occurred to provide **12** in 64% yield (eq 10). Comparison of the ^{13}C and ^{119}Sn NMR spectra of the restannylated product with those of the starting material **12** showed that these two compounds were identical. Thus, the transmetalation and restannylation of **12** had occurred with overall retention of configuration.



The synthetic utility of the bimetallic cyclopropane **12** was investigated by trapping the anion with a variety of electrophiles to provide highly functionalized cyclopropanes in good yields. Surprisingly, trimethylsilyl chloride did not react under the reaction conditions (see entry 2, Table 2).

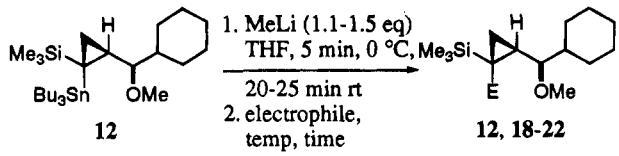
The tin–lithium exchange investigation was extended to the (*E*)- and (*Z*)-stannylalkyl cyclopropanes. Transmetalation for the (*Z*)-stannylalkylcyclopropane **23** was best achieved with MeLi in THF to give **25** in high yield (eq 11). Comparison of the entries 2 and 4 in Table 3 shows that, while complete transmetalation of **23** was

(56) For a successful hydroxyl-directed tin–lithium exchange process, see, for example: Newman-Evans, R. H.; Carpenter, B. K. *Tetrahedron Lett.* **1985**, *26*, 1141.

(57) In a comparison of the thermodynamic stability of 5-membered and 6-membered chelated organolithiums, it was shown that the 5-membered chelate was favored. See: Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1987**, *322*, 141.

(58) Lautens, M.; Delanghe, P. H. M. *J. Org. Chem.* **1992**, *57*, 798.

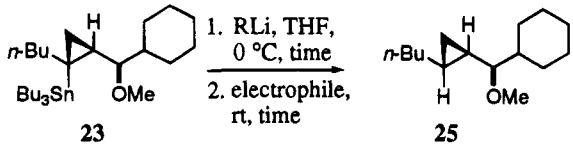
Table 2. Tin–Lithium Transmetalation/Electrophilic Trapping of 12



entry	electrophile	temp, time	product	E	yield (%)[a]
1	Bu_3SnCl	1 h, rt	**12**	Bu_3Sn	64
2	Me_3SiCl	1 h, rt	**18**	Me_3Si	0
3	CO_2 (g)	30 min, rt	**19**	HOOC	75
4	PhSSPh	1 h, −78 °C to rt	**20**	PhS	84[b]
5	PhSSPh, then MCPBA	1 h, −78 °C to rt	**21**	$PhSO_2$	79[c]
6	$(CHO)_n$	0 °C, 1 h	**22**	$HOCH_2$	89

[a] Isolated yields are reported unless noted otherwise. [b] The product was contaminated with some of the protonated product **13**. Careful chromatography on silica gel provided a pure sample. [c] The crude product was immediately converted to the corresponding sulfone; the reported number is the overall yield for two steps.

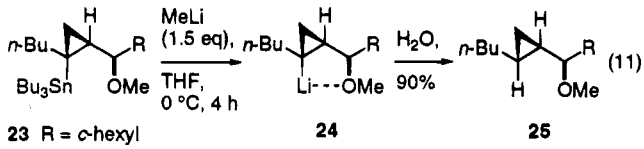
Table 3. Effect of RLi on the Tin-Lithium Transmetalation of 23



entry	RLi (equiv)	time	electrophile	time	yield (%)[a]
1	MeLi (10)	3 h	H_2O	5 min	90
2	MeLi (1.5)	4 h	H_2O	5 min	90
3	BuLi (5)	7 h	H_2O	5 min	30[b]
4	BuLi (30)	4 h	H_2O	5 min	95
5	MeLi (3)	4 h	Bu_3SnCl	1 h	72[c]

[a] Isolated yields are reported unless noted otherwise. [b] The percent conversion was determined from the ^1H NMR of the crude mixture. [c] The product formed was **23**.

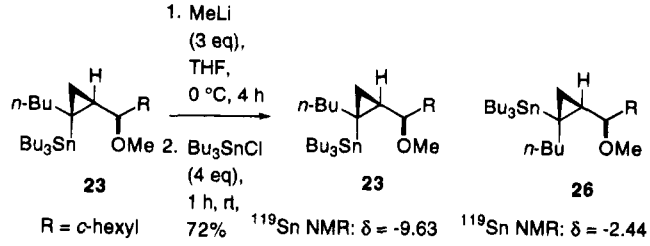
obtained using only 1.5 equiv of MeLi for 4 h at 0 °C, a large excess of *n*-BuLi was required to achieve the same percent conversion.



The replacement of a silyl moiety for an alkyl group has a measurable effect on the transmetalation reaction rate. Tin–lithium exchange of **23** required 4 h at 0 °C, while the bimetallic stannylsilylcyclopropane **12** was complete in 25 min (compare Table 1, entry 5 and Table 3, entry 2). The ability of silyl groups to stabilize an α-carbanion seems to be responsible for the change, since the steric bulk of a Me_3Si group (*A* value of 2.5)[59] is larger than that of a *n*-butyl moiety (*A* value of 1.9).[60,61]

Following transmetalation of **23** with 3 equiv of MeLi, the cyclopropyllithium was treated with tributyltin chloride and stannylation occurred, providing **23** in 72% yield

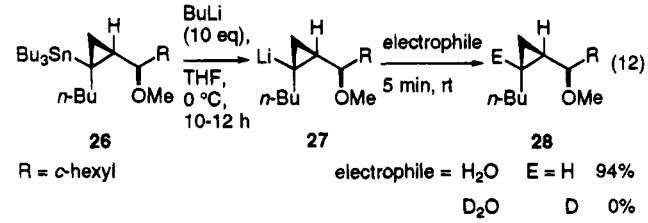
Scheme 2



(Scheme 2). Comparison of the ^{13}C and ^{119}Sn NMR spectra obtained from transmetalation/restannylation with the starting material **23** and its isomer **26** clearly showed that **23** was produced. Thus, the transmetalation and restannylation of the alkylstannylcyclopropane **23** also proceeds with overall retention of configuration.

^{119}Sn NMR is a very useful tool for the assignment of geometric isomers of stannyl-substituted cyclopropanes. In several cases, we have observed that the ^{119}Sn shift is very sensitive to the geometric relationship of the cyclopropane. It was noticed that the resonance for (*Z*)-stannylcyclopropanes is always 7 to 10 ppm more upfield compared to the (*E*)-isomer (Scheme 2).[62] An analogy to the steric compression effect for geometric isomers in ^{13}C NMR can be seen.[63]

In contrast to the smooth transmetalation of (*Z*)-stannylalkylcyclopropane **23** with MeLi, the isomeric (*E*)-stannylalkylcyclopropane **26** did not undergo the tin–lithium exchange, even with a large excess of MeLi (see Table 4, entry 1). In addition, attempts using an excess of *i*-PrLi or *s*-BuLi did not result in any significant extent of reaction (see Table 4, entries 2 and 3). However, complete transmetalation was achieved with 10 equiv of *n*-BuLi in THF to yield the *cis*-substituted cyclopropane **28** in 94% yield (see eq 12 and Table 4, entry 4).

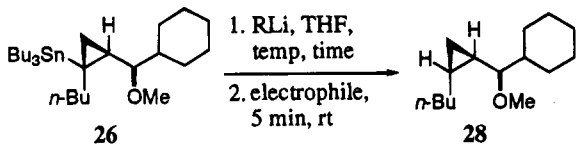


Treatment of **27** with D_2O did not produce any of the deuterated cyclopropane but rather the protonated cyclopropane **28**.[30] The reactivity of the cyclopropyllithium **27** in THF at 0 °C is sufficiently high to elude trapping but transmetalation at lower temperatures was found to be extremely slow, (see Table 4, entry 6). After 3 days at −40 °C, only 40% of tin–lithium exchange had occurred.

Reaction of the (*E*)-trimethylstannylcyclopropane **29** was examined to determine whether the less sterically hindered trimethylstannyl moiety would lead to a more efficient transmetalation reaction. As in the tributylstannyl analog **26**, treatment of **29** with excess MeLi at

(59) Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* **1982**, *47*, 5153.
(60) Hirsch, J. A. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley Interscience: 1967; Vol. 1, p 199.
(61) Adcock, W.; Aldous, G. L.; Kitching, W. *Tetrahedron Lett.* **1978**, 3387.
(62) A similar effect in the ^{119}Sn NMR has been observed for *cis*- and *trans*-substituted vinylstannanes. See: (a) Quintard, J.-P.; Degueil-Castaing, M.; Dumartin, G.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1982**, *234*, 27. (b) Rossi, R.; Carpita, A.; Bellina, F.; De Santis, M.; Veracini, C. A. *Gazz. Chim. Ital.* **1990**, *120*, 457. (c) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868.
(63) (a) Levy, G. C.; Nelson, G. L. in *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley: New York, 1972, p 24. (b) Grutzner, J. B. *J. Chem. Soc., Chem. Commun.* **1974**, 64.

Table 4. Effect of RLi on the Tin–Lithium Transmetalation of 26

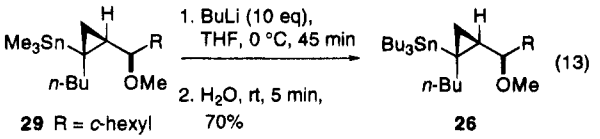


26 28

entry	RLi (equiv)	temp, time	electrophile	yield (%)[a]
1	MeLi (30)	0 °C, 18 h	H_2O	<10[b]
2	*i*-PrLi (10)	−23 to 0 °C, 18 h	H_2O	<5[b]
3	*s*-BuLi (10)	−23 to 0 °C, 18 h	H_2O	<10[b]
4	BuLi (10)	0 °C, 10 h	H_2O	94
5	BuLi (10)	0 °C, 12 h	D_2O	0[c]
6	BuLi (10)	−40 °C, 3 days	H_2O	40[b]

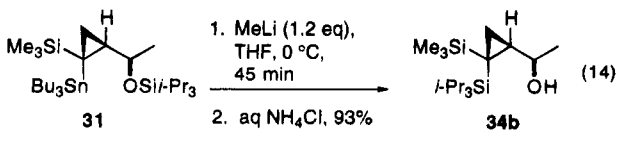
[a] Isolated yields are reported unless noted otherwise. [b] Conversion was determined by ^1H NMR on the crude mixture. [c] The protonated product **28** was obtained in 94% yield.

0 °C did not result in any significant transmetalation. *n*-BuLi was also ineffective at cleaving the cyclopropyl carbon–Sn bond. Instead, after treatment of **29** with 5–10 equiv of *n*-BuLi for 45 min at 0 °C, another stannyl-containing product formed as the major product. Its ^1H and ^{119}Sn NMR spectra were identical to those of **26**, which indicates that the methyl substituents on the trimethyltin moiety were exchanged for *n*-butyl groups (eq 13). The basicity of the (*E*)-lithio-*n*-butylcyclopropane **27** is obviously greater than that of MeLi. The previously noted instability of **27** in THF is in accord with this observation.



29 R = *c*-hexyl **26** (13)

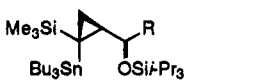
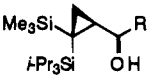
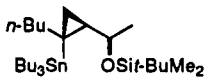
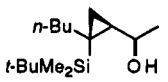
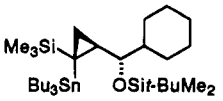
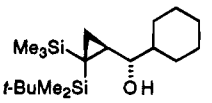
Tin–Lithium Exchange with Silyl Ethers. The scope of the transmetalation reaction was further explored using a silyl ether as a protecting group for the hydroxyl moiety.[64] Since silyl ethers are readily cleaved by treatment with fluoride-containing reagents, we would be able to perform the transmetalation/electrophilic trapping sequence, followed by liberation of the hydroxyl group. The free hydroxyl moiety could then be used as a handle for further chemical manipulations. However, treatment of the cyclopropylstannane **31** with 1.2 equiv of MeLi in THF gave the disilylcyclopropanecarbinol **34b** in excellent yield (eq 14).



31 **34b** (14)

The formation of the product can be explained by a reaction sequence in which the tin–lithium transmetalation of the cyclopropylstannane **31** is followed by a 1,4 oxygen-to-carbon silyl migration. The migration can proceed in one step or via a pentavalent silicon intermediate. Protonation of the lithium alkoxide then provides the final product **34b**.

Table 5. 1,4 Oxygen-to-Carbon Silyl Migration of Stannylcyclopropanes

entry	substrate[a]	eq MeLi, temp, time[b]	product[c]	yield(%)[d]
1	 **30** R = *n*-Pr	1.2, 0 °C, 30 min	 **34a**	91
2	**31** Me	1.2, 0 °C, 45 min	**34b**	75
3	 **32**	5.0, 0 °C to rt, 20 h	 **35**	90
4	 **33**	1.1, 0 °C, 2 h	 **36**	92

[a] All silyl ethers were prepared by standard etherification procedures; see ref 64. [b] All reactions were performed in THF. [c] Only one diastereomer was observed. [d] Isolated yields of analytically pure product.

Other examples of the silyl transfer reaction of cyclopropylstannanes were found (Table 5). The reaction is considerably faster for α-silylstannyl cyclopropanes than for α-alkylstannylcyclopropanes (compare entries 1 and 2 with 3). This is most likely a reflection of the ease of transmetalation for these substrates, indicating that transmetalation is the rate-determining step under these conditions.

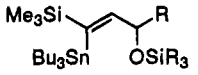
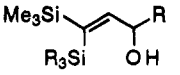
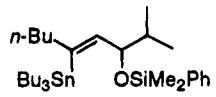
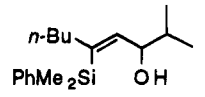
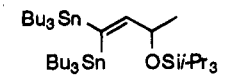
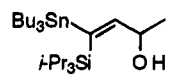
The scope of the silyl migration was studied on allylic, epoxy, cyclopropyl, and aliphatic carbinol silyl ethers. The data in Table 6 show that migration is general for the preparation of primary as well as secondary (*Z*)-silylallylic alcohols. The reactions can be performed at 0 °C or at −40 °C and were often done within 15 min at 0 °C, while somewhat longer reaction times were required at lower temperatures. Silicon groups of varying size are transferred equally well, and isolated yields of the vinylsilanes were nearly quantitative for most cases. Migration of a trimethylsilyl group is accompanied by some products resulting from competing C–Si cleavage (Table 6, entry 9).[65] Migration of a phenyldimethylsilyl group was particularly important in light of the synthetic utility of this group as a precursor to a hydroxyl moiety with retention of stereochemistry (entry 10).[66] Retention of configuration at the carbon-bearing tin was observed for vinyl substrates. Moreover, no contamination by the protonated allylic alcohols or isomeric vinylsilanes was observed. These observations indicate that, once the *cis*-vinyllithium intermediate is formed, it undergoes a rapid silyl migration. Transmetalation of the distannylalkene **41** is a particularly interesting example from a mechanistic and synthetic perspective (entry 11). Migration of the silicon provides a novel route to *(E)*-stannyl-*(Z)*-silyl olefins which are unavailable by other routes, including our modification of the Sato reaction. Whereas the *(Z)*-lithio species can undergo simple migration,[67] isomerization of the *(E)*- to the *(Z)*-lithio species must precede migration. Very recently, another report on the silyl

(64) (a) Ogilvie, K. K.; Sadana, K. L.; Thompson, E. A.; Quilliam, M. A.; Westmore, J. B. *Tetrahedron Lett.* **1974**, 2861. (b) Ogilvie, K. K.; Thompson, E. A.; Quilliam, M. A.; Westmore, J. B. *Tetrahedron Lett.* **1974**, 2865. (c) Cunico, R. F.; Bedell, L. *J. Org. Chem.* **1980**, *45*, 4797.

(65) Cleavage of the C–Si bond was a competing side reaction, as 37% of the (*Z*)-stannylsilylallylic alcohol was also isolated. Johnson, M. Undergraduate research project, April 1993, University of Toronto.

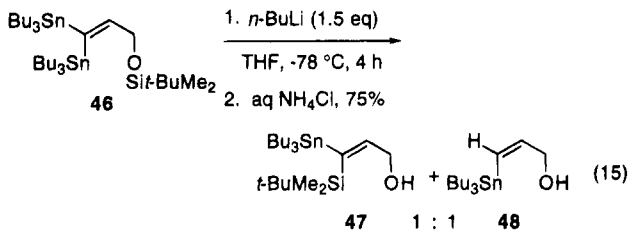
(66) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229.

Table 6. 1,4 Oxygen-to-Carbon Silyl Migration of Vinylstannanes

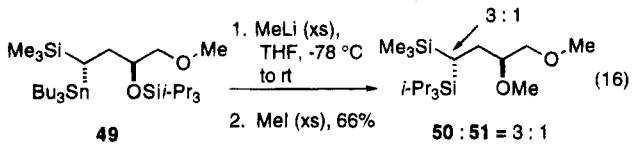
entry	substrate[a]	equiv MeLi, temp, time[b]	product	yield (%)[c]
				
	R R$_3$Si			
1	**37a** *i*-Pr *i*-Pr$_3$Si	1.5, 0 °C, 10 min	**42a**	86
2	**37b** *n*-Pr *i*-Pr$_3$Si	5.0, 0 °C, 1 h	**42b**	94
3	**37c** Me *i*-Pr$_3$Si	1.2, -40 °C, 2 h	**42c**	88
4	**37c** Me *i*-Pr$_3$Si	1.2, 0 °C, 30 min	**42c**	97
5	**37d** H *i*-Pr$_3$Si	1.2, 0 °C, 15 min	**42d**	98
6	**38a** H *t*-BuMe$_2$Si	1.2, 0 °C, 15 min	**43a**	97
7	**38b** Me *t*-BuMe$_2$Si	1.2, -40 °C, 30 min	**43b**	92
8	**38c** *i*-Pr *t*-BuMe$_2$Si	1.5, 0 °C, 10 min	**43c**	91
9	**39** Me Me$_3$Si	1.2, -78 °C, 2 h	**43d**	58[d]
10	 **40**	1.5, -40 °C, 1.5 h	 **44**	79
11	 **41**	3.4, 0 °C, 2.5 h, rt 1 h	 **45**	40[e]

[a] All silyl ethers were prepared by standard etherification procedures; see ref 64. [b] All reactions were performed in THF. [c] Isolated yields of analytically pure product. [d] Cleavage of the Si–O bond was also observed. [e] Some destannylated product was also observed.

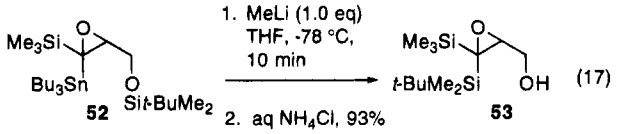
migration of a 1,1-distannylallylic silyl ether appeared (eq 15).[68] Treatment of the *t*-BuMe$_2$Si ether **46** with 1.5 equiv of *n*-BuLi at −78 °C for 4 h resulted in the isolation of a 1:1 mixture of the alcohol **47** and the (*Z*)-vinylstannane **48** in 75% yield.



Silyl transfer to an aliphatic carbon was also found to be an efficient process (eq 16). Upon treatment of **49** with MeLi in THF, followed by addition of methyl iodide, **50** and **51** were isolated as a 3:1 mixture in 66% yield. The major product arose from a 1,4-migration of the *i*-Pr$_3$Si moiety with partial retention of stereochemistry.



Moreover, the transmetalation/silyl migration can be extended to stannyl epoxides (eq 17). Tin–lithium transmetalation reactions of stannyl epoxides have previously been reported, and the corresponding lithio epoxides are stable species at low temperatures.[69-71] At −78 °C, transmetalation/silyl migration of **52** is rapid and gives the disilyl epoxy carbinol **53** in 93% yield. However, at 0 °C and using 1 equiv of MeLi, quantitative desilylation occurred, providing the stannylsilylepoxycarbinol. It is interesting to realize that, at this temperature, desilylation of the *t*-BuMe$_2$Si is faster than either transmetalation or reaction with the epoxide.



Mechanistic Investigation of the Silyl Migration Process. Although these migrations are formally reversible, no starting material was recovered after workup. Under these conditions, the equilibrium clearly lies completely on the side of the lithium alkoxide. The driving force for this reaction is presumably the formation of a covalent O–Li bond (hard–hard), rather than a C–Li bond (soft–hard). Replacement of lithium by sodium or potassium should cause reversal of the migration, a process that is well documented.[51,72]

(67) (a) Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1985**, *281*, 163. (b) Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1987**, *322*, 141.

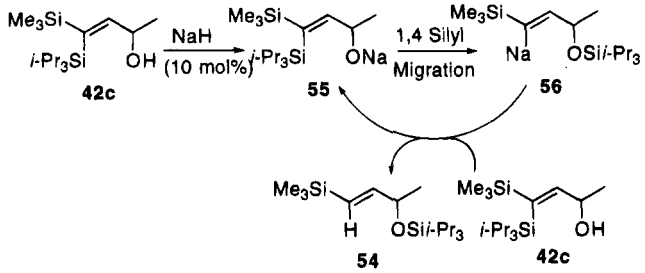
(68) Zhao, Y.; Quayle, P.; Kuo, E. A. *Tetrahedron Lett.* **1994**, *35*, 3797.

(69) (a) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1988**, *341*, 293. (b) Molander, G. A.; Mautner, K. *J. Org. Chem.* **1989**, *54*, 4042. (c) Lohse, P.; Loner, H.; Acklin, P.; Sternfeld, F.; Pfaltz, A. *Tetrahedron Lett.* **1991**, *32*, 615. (d) Soderquist, J. A.; Lopez, C. *Tetrahedron Lett.* **1991**, *32*, 6305.

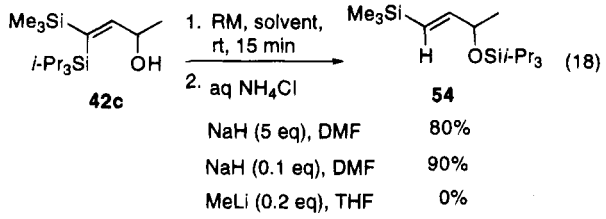
(70) For the preparation of an α-silyl oxiranyllithium anion via deprotonation of an silyl epoxide, see: (a) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4646. (b) See also refs 69a and 69b.

(71) See refs 69 and 70 and the following: (a) Cope, A. C.; Trumbull, P. A.; Trumbull, E. R. *J. Am. Chem. Soc.* **1958**, *80*, 2844. (b) Crandall, J. K.; Lin, L.-H. C. *J. Am. Chem. Soc.* **1967**, *89*, 4526. (c) *Ibid.* **1967**, *89*, 4527. (d) Crandall, J. K.; Apparu, M. *Org. React.* **1983**, *29*, 345. (e) Florio, S.; Ingrosso, G.; Troisi, L.; Lucchini, V. *Tetrahedron Lett.* **1993**, *34*, 1363.

Scheme 3

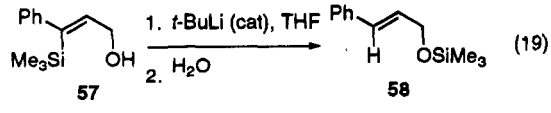


Indeed, we found that treatment of **42c** with 5 equiv of NaH in DMF led to a carbon-to-oxygen migration to give **54** in 80% yield. No starting material was observed. Moreover, this conversion can also be achieved using only a catalytic amount of NaH. Thus, treatment of **42c** with only 10% of NaH also provided **54** in excellent yield (eq 18).



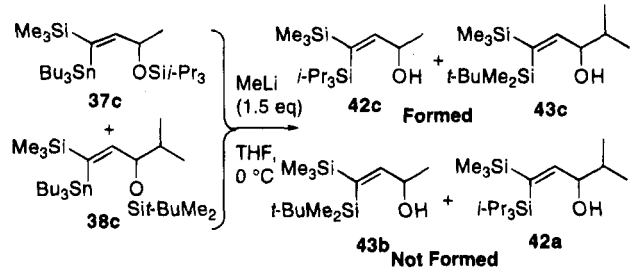
The mechanism of the catalytic process is shown in Scheme 3. Formation of a small amount of the sodium alkoxide **55** is followed by carbon-to-oxygen silyl migration (1,4-Brook rearrangement) to yield **56**, which contains a basic vinyl carbanion. Proton transfer from the hydroxyl of the starting alcohol **42d** to the vinylsodium anion regenerates the sodium alkoxide **55** and forms the final product **54**. While the catalytic process is theoretically also possible when a catalytic amount of MeLi is employed (although it should proceed at a slower rate), treatment of **42d** with 20 mol % of MeLi in THF did not result in any detectable amount of silyl ether **54** after prolonged reaction times (eq 18).

This result is in contrast to a recent observation by Magriotis *et al.* who achieved a carbon-to-oxygen silyl migration of **57**, using a catalytic amount of *t*-BuLi (eq 19).[50e] It is very likely that, in this system, the phenyl moiety in **57** is responsible for shifting the equilibrium toward the silyl ether by stabilizing the lithium anion, thereby generating enough vinyllithium to initiate the catalytic cycle.



A crossover experiment was conducted to demonstrate the intramolecularity of the migration process.[49d,50a,e] Upon treatment of a mixture of **37c** and **38c** with 1.5 equiv of MeLi in THF at 0 °C for 45 min, only two products were isolated (Scheme 4). Examination of the ^{13}C NMR spectrum (100 MHz) of the mixture and comparison to authentic samples of all four possible products showed that only **42c** and **43c** were formed. No crossover products could be observed.

Scheme 4



Conclusions

In conclusion, we have shown that (*Z*)-stannylsilyl- and (*Z*)-stannylalkylcyclopropanes have potential as building blocks in organic chemistry. They can be transmetalated and trapped with various electrophiles. Transmetalation of silyl ethers of stereochemically defined vinyl, epoxy, and cyclopropyl stannanes undergo 1,4-silyl migrations to generate a variety of (*Z*)-vinyl, epoxy, and cyclopropyl silanes, and hetero- and homobimetallic compounds which are not readily prepared using existing methodology.

Experimental Section

General Information. Unless stated otherwise, commercial reagents were used without purification. Tetrahydrofuran and diethyl ether were distilled immediately prior to use from sodium wire/benzophenone. *tert*-Butyldimethylsilyl triflate was prepared according to a literature procedure from triflic acid and *tert*-butyldimethylsilyl chloride.[73] Imidazole was recrystallized from diethyl ether. Paraformaldehyde was dried on a vacuum pump before use.

General Procedure A for the Methyl Ether Synthesis. To a flame-dried flask equipped with a stirbar and capped with a rubber septum was added KH (2–2.5 equiv, 35 wt % in mineral oil). The KH was washed three times with dry pentane. The flask was cooled to 0 °C, and 18-crown-6 ether (one crystal) was added for more hindered alcohols. A precooled solution of the alcohol (1 equiv) in THF was added to the KH. The reaction mixture was stirred for 15 min, followed by addition of MeI (2.1–3.0 equiv). After stirring at 0 °C for 5–15 min, the mixture was warmed to rt and stirred for an additional 30–60 min. Aqueous workup and purification by flash chromatography on silica gel, eluting with hexanes: diethyl ether 20:1, afforded the desired ether.

General Procedure B for the Transmetalation/Electrophilic Trapping of Stannylcyclopropanes. To a flame-dried flask equipped with a stirbar and capped with a rubber septum was added MeLi (1.2–3.0 equiv, solution in diethyl ether). The diethyl ether was removed with a stream of nitrogen (or with a vacuum pump in the case of larger volumes of ether). THF (1/2 of the total volume) was added, and the flask was cooled to 0 °C. A precooled (0 °C) solution of the substrate in the remaining THF was added, and the reaction mixture was stirred for 5 min at 0 °C followed by 20–25 min at rt. The electrophile (1.5–4.0 equiv) was added at the desired temperature, and the reaction mixture was stirred. Aqueous saturated NH_4Cl was added, and the mixture was extracted three times with diethyl ether. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 20 to 10:1, afforded the product.

General Procedure C for the Silylation, Using a Silyl Chloride.[64] A dry round-bottom flask, equipped with a stirbar and capped with a rubber septum, was flame-dried under a stream of nitrogen. The silyl chloride, alcohol, and imidazole were added to the flask and dissolved in DMF (1 M solution).

(72) For 1,3 C-to-O silyl migrations, see: Yamamoto, K.; Kimura, T.; Tomo, Y. *Tetrahedron Lett.* **1985**, *26*, 4505.

(73) Corey, E. J.; Cho, H.; Rücker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.

The reaction mixture was stirred under nitrogen at rt for 24 to 48 h and monitored by TLC. When the reaction was complete, the reaction mixture was diluted with hexane:CH_2Cl_2 10:1, washed three times with brine, dried over $MgSO_4$, and filtered. After concentration *in vacuo*, the crude product was purified by flash chromatography on silica gel.

General Procedure D for the Silylation, Using a Silyl Triflate.[73] A dry round-bottom flask, equipped with a stirbar and capped with a rubber septum, was flame-dried under a stream of nitrogen. The alcohol (1 equiv) and 2,6-lutidine (2 equiv) were dissolved in CH_2Cl_2, and the mixture was cooled to the desired temperature. The silyl triflate (1.2–1.5 equiv) was added dropwise, and the reaction mixture was stirred for 15 min. Aqueous saturated K_2CO_3 was added, and the mixture was extracted with diethyl ether. The combined organic layer was washed three times with brine, dried over $MgSO_4$, and filtered. After concentration *in vacuo*, the crude product was purified by flash chromatography on silica gel.

General Procedure E for the Transmetalation of the Stannyl-Substituted Cyclopropanes; Procedure for the 1,4 Oxygen-to-Carbon Silyl Migration. A round-bottom flask, equipped with a stirbar and capped with a rubber septum, was flame-dried while being flushed with nitrogen. Methyllithium (solution in diethyl ether) was added to the flask. The diethyl ether was removed with a vacuum pump or a stream of nitrogen, and dry THF was added to the white powder. To a round-bottom flask equipped with a stirbar, capped with a rubber septum, and flame-dried under a nitrogen atmosphere was added 1 equiv of the cyclopropane. Both flasks were cooled to the desired temperature. The cyclopropane in THF was transferred via cannula to the methyllithium solution. The reaction mixture was stirred, and the reaction was followed by TLC. After the transmetalation was complete, the electrophile was added at the desired temperature. The reaction was quenched with saturated aqueous NH_4Cl solution, and the solution was extracted with diethyl ether. The combined organic layers were washed three times with brine, dried over anhydrous $MgSO_4$, and filtered. After concentration *in vacuo*, the crude product was purified by flash chromatography on silica gel.

Note: To induce the silyl migration, exchange of the diethyl ether solvent for THF was not necessary, and for convenience, methyllithium in diethyl ether was often added directly to the cyclopropane.

(*R)-[(1*S**,2*S**)-2-(Tributylstannyl)-2-(trimethylsilyl)-cyclopropyl]cyclohexylmethyl Methyl Ether (12).** According to the general procedure A, a solution of **10** (500 mg, 0.97 mmol) in 10 mL of THF was added to a mixture of washed KH (222 mg, 35 wt % in mineral oil, 1.94 mmol) and 18-crown-6 (one crystal). MeI (0.13 mL, 2.04 mmol) was added, and the reaction was stirred for 5 min at 0 °C followed by 1 h at rt. After aqueous workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 513 mg (100%) of **12** was isolated as a colorless oil: IR (cm^{-1}, neat) 3022 (w), 2959 (s), 2931 (s), 2854 (s), 1455 (m), 1244 (m), 1110 (m), 1089 (m), 857 (m), 829 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.38 (3H, s), 2.39 (2H, dd, J = 9.1, 2.2 Hz), 1.82–1.61 (5H, m), 1.52–1.14 (24H, m), 1.05 (1H, ddd, J = 9.1, 7.7, 4.3 Hz), 0.97 (1H, dd, J = 7.2, 3.4 Hz), 0.89 (9H, t, J = 7.3 Hz), 0.88–0.80 (9H, m), 0.76 (1H, dd, J = 4.3, 3.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.22 (J_{Sn-C} = 29.0 Hz), 57.74, 43.07, 30.68, 29.27 (J_{Sn-C} = 18.9 Hz), 27.67 (J = 62.8 Hz), 26.69, 26.67, 26.65, 26.06, 21.66, 14.23, 13.64, 11.62 (J_{Sn-C} = 319.5 Hz), −0.00, −1.22, −4.50; ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −3.83; HRMS calcd for $C_{25}H_{51}OSiSn$ (M − CH_3)$^+$ 515.2731, found 515.2739; HRMS calcd for $C_{22}H_{45}OSiSn$ (M − C_4H_9)$^+$ 473.2262, found 473.2262.

The product **12** was prepared also using the following procedure. According to the general procedure B, a solution of **12** (40 mg, 0.075 mmol) in 1 mL of THF was added to a solution of MeLi (0.08 mL, 1.5 M solution in diethyl ether, 0.11 mmol) in 1 mL of THF, and the mixture was stirred for 25 min at rt. Bu_3SnCl (33 μL, 0.12 mmol) was added, and the mixture was stirred for 1 h at rt. After regular workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 30 mg (64%) of **12** was obtained as a colorless oil accompanied by some of the inseparable **13**. Spectroscopic data: *vide supra*.

(*R)-[(1*S**,2*R**)-2-(Trimethylsilyl)cyclopropyl]cyclohexylmethyl Methyl Ether (13).** According to the general procedure A, a solution of the alcohol **11** (150 mg, 0.66 mmol) in 4 mL of THF was added to a mixture of washed KH (91 mg, 35 wt % in mineral oil, 0.79 mmol) and 18-crown-6 ether (16 mg, 0.06 mmol). MeI (62 μL, 0.99 mmol) was added, and the reaction was stirred for 30 min at 0 °C. After aqueous workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 157 mg (99%) of **13** was isolated as a colorless oil: IR (cm^{-1}, neat) 3058 (w), 2931 (s), 2854 (s), 2819 (m), 1448 (m), 1251 (s), 1110 (s), 1089 (s), 836 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.38 (3H, s), 2.19 (1H, dd, J = 8.7, 3.9 Hz), 1.82–1.63 (4H, m), 1.53–1.41 (1H, m), 1.28–1.10 (6H, m), 0.71 (1H, dddd, J = 8.7, 7.2, 7.0, 4.5 Hz), 0.55 (1H, ddd, J = 10.1, 4.5, 3.8 Hz), 0.50 (1H, ddd, J = 7.2, 6.9, 3.8 Hz), −0.06 (9H, s), −0.66 (1H, ddd, J = 10.1, 7.0, 6.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 91.07, 57.53, 43.43, 29.65, 28.30, 26.84, 26.78, 26.72, 16.50, 8.59, 0.00, −2.15; HRMS calcd for $C_8H_{17}OSi$ (M − C_6H_{11})$^+$ 157.1049, found 157.1057.

The product **13** was prepared also using the following procedure. According to the general procedure B, a solution of **12** (80 mg, 0.15 mmol) in 1 mL of THF was added to a solution of MeLi (0.11 mL, 1.5 M solution in diethyl ether, 0.16 mmol) in 1 mL of THF, and the mixture was stirred for 5 min at 0 °C followed by 20 min at rt. Aqueous saturated NH_4Cl was added, and the mixture was stirred for 5 min at rt. After regular workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 33.5 mg (93%) of **13** was obtained as a colorless oil. Spectroscopic data: *vide supra*.

(*R)-[(1*S**,2*S**)-2-(Tributylstannyl)-2-(trimethylsilyl)-cyclopropyl]cyclohexylmethyl Methoxymethyl Ether (16).** According to the general procedure A, a solution of **10** (500 mg, 0.97 mmol) in 5 mL of THF was added to a mixture of washed KH (222 mg, 35 wt % in mineral oil, 1.94 mmol) and 18-crown-6 ether (one crystal). MOMCl (0.16 mL, 2.04 mmol) was added, and the reaction was stirred for 30 min at 0 °C followed by 15 min at rt. After aqueous workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 521 mg (96%) of **16** was isolated as a colorless oil: IR (cm^{-1}, neat) 2931 (s), 1452 (m), 1247 (m), 1045 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 4.93 (1H, d, J = 6.4 Hz), 4.50 (1H, d, J = 6.4 Hz), 3.32 (3H, s), 2.81 (1H, dd, J = 9.5, 1.5 Hz), 1.88–1.12 (23H, m), 1.07 (1H, ddd, J = 9.5, 7.4, 4.4 Hz), 0.94 (1H, dd, J = 7.4, 3.7 Hz), 0.88 (9H, t, J = 7.3 Hz), 0.84 (6H, m), 0.76 (1H, dd, J = 4.4, 3.7 Hz), −0.08 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 94.29, 83.40, 55.01, 43.05, 30.95, 29.22, 27.67, 26.70, 26.64, 25.84, 21.52, 14.39, 13.62, 11.52, −1.26, −3.75.

[1α,2β(*S)]-2-(Cyclohexylmethoxymethyl)-1-(trimethylsilyl)cyclopropanecarboxylic Acid (19).** According to the general procedure B, a solution of **12** (40 mg, 0.075 mmol) in 1 mL of THF was added to a solution of MeLi (0.08 mL, 1.5 M solution in diethyl ether, 0.11 mmol) in 1 mL of THF, and the mixture was stirred for 5 min at 0 °C followed by 20 min at rt. Carbon dioxide was bubbled through the solution for 30 min at rt. After acidification with 10% aqueous HCl, regular workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20 to 5:1, afforded 16 mg (75%) of **19** as a white solid: IR (cm^{-1}, neat) 3184 (br, s), 2931 (s), 284 (s), 1680 (s), 1448 (m), 1300 (m), 1251 (m), 1110 (m), 1089 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 12.5 (1H, br s), 3.38 (3H, s), 2.96 (1H, dd, J = 8.7, 3.4 Hz), 1.96–1.51 (4H, m), 1.50 (1H, dd, J = 6.7, 4.1 Hz), 1.41 (1H, m), 1.28 (1H, m), 1.25–1.06 (6H, m), 1.04 (1H, dd, J = 7.0, 4.1 Hz), 0.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.43, 83.81, 57.84, 42.70, 29.52, 27.07, 26.56, 26.49, 26.44, 26.26, 16.08, 15.19, −2.55; HRMS calcd for $C_{15}H_{28}O_3Si$ (M)$^+$ 284.1808, found 284.1824.

(*R)-[(1*S**,2*S**)-2-(Phenylthio)-2-(trimethylsilyl)cyclopropyl]cyclohexylmethyl Methyl Ether (20).** According to the general procedure B, a solution of **12** (80 mg, 0.15 mmol) in 1 mL of THF was added to a solution of MeLi (0.11 mL, 1.5 M solution in diethyl ether, 0.16 mmol) in 1 mL of THF, and the mixture was stirred for 5 min at 0 °C followed by 20 min at rt. The reaction mixture was cooled to −78 °C, and PhSSPh

(34.9 mg, 0.16 mmol) was added. The mixture was allowed to warm to rt and stirred for another 1 h at rt. After regular workup and careful purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 11 mg (21%) of **20** was obtained as a colorless oil. A fraction contaminated with the protonated product **13** was also isolated (combined yield of pure and impure **20** was 84%). **20**: IR (cm^{-1}, neat) 3058 (w), 2931 (s), 2854 (s), 1581 (w), 1476 (m), 1448 (m), 1251 (m), 1110 (m), 1089 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (2H, m), 7.22 (2H, m), 7.07 (1H, m), 3.36 (3H, s), 3.13 (1H, dd, J = 9.2, 3.0 Hz), 1.82–1.44 (5H, m), 1.55 (1H, dd, J = 8.0, 4.6 Hz), 1.38–1.16 (7H, m), 1.14 (1H, dd, J = 6.4, 4.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.73, 128.40 (2), 127.32 (2), 124.72, 86.46, 58.09, 43.06, 29.96, 26.68, 26.66, 26.59, 26.51, 24.40, 20.48, 12.83, −2.53; HRMS calcd for $C_{20}H_{32}O_3SSi$ $(M)^+$ 380.1841, found 380.1842.

(*R)-[(1*S**,2*S**)-2-(Phenylsulfonyl)-2-(trimethylsilyl)cyclopropyl]cyclohexylmethyl Methyl Ether (21).** According to the general procedure B, a solution of **12** (40 mg, 0.08 mmol) in 0.5 mL of THF was added to a solution of MeLi (0.06 mL, 1.37 M solution in diethyl ether, 0.08 mmol) in 0.5 mL of THF and stirred for 5 min at 0 °C followed by 20 min at rt. The reaction mixture was cooled to −78 °C, and PhSSPh (18.1 mg, 0.084 mmol) was added. The mixture was allowed to warm to rt and stirred for another 1 h at rt. After regular workup and concentration in vacuo, the crude reaction mixture was dissolved in 2 mL of CH_2Cl_2 and cooled to 0 °C. *m*-Chloroperbenzoic acid (31 mg, 90% in *m*-chlorobenzoic acid, 0.16 mmol) was added, and the reaction mixture was stirred for 1 h at 0 °C. After regular aqueous workup, the crude mixture was purified by flash chromatography, eluting with hexanes:diethyl ether 10:1 to 3:1. **21** (22.8 mg, 79%) was isolated as a colorless oil which solidified on standing: mp = 97–98 °C; IR (cm^{-1}, neat) 3445 (br, m), 3065 (w), 2973 (w), 2931 (s), 2854 (m), 1448 (m), 1293 (s), 1159 (s), 1145 (s), 1110 (s), 1089 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (2H, m), 7.57 (1H, m), 7.50 (2H, m), 3.87 (1H, dd, J = 10.0, 2.7 Hz), 3.47 (3H, s), 2.00 (1H, dd, J = 7.2, 4.6 Hz), 1.90–1.56 (7H, m), 1.42–1.10 (6H, m), −0.20 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.26, 132.91, 128.81 (2), 127.66 (2), 82.86, 58.75, 42.85, 33.52, 30.25, 28.96, 26.72, 26.61, 26.56, 26.42, 17.83, −1.87; HRMS calcd for $C_{20}H_{32}O_3SSi$ $(M)^+$ 380.1841, found 380.1842.

([1α,2β(*S)]-2-(Cyclohexylmethoxymethyl)-1-(trimethylsilyl)cyclopropyl)methanol (22).** According to the general procedure B, a solution of **12** (200 mg, 0.38 mmol) in 5 mL of THF was added to a solution of MeLi (0.41 mL, 1.4 M solution in diethyl ether, 0.58 mmol) in 5 mL of THF, and the solution was stirred for 5 min at 0 °C followed by 20 min at rt. The reaction mixture was cooled to 0 °C, and solid paraformaldehyde (30 mg, 1.0 mmol) was added. The mixture was allowed to warm to rt and stirred for another 1 h at rt. After regular workup and concentration in vacuo, the crude reaction mixture was purified by flash chromatography, eluting with hexanes:diethyl ether 10:1. **22** (91 mg, 89%) was isolated as a colorless oil.

(*R)-[(1*S**,2*S**)-2-Butyl-2-(tributylstannnyl)cyclopropyl]-cyclohexylmethyl Methyl Ether (23).** According to the general procedure A, a solution of the alcohol (57 mg, 0.11 mmol) in 1 mL of THF was added to a mixture of washed KH (26 mg, 35 wt % in mineral oil, 0.23 mmol) and 18-crown-6 ether (2 mg). MeI (15 μL, 0.24 mmol) was added, and the reaction mixture was stirred for 1 h at rt. After aqueous workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 59 mg (100%) of **23** was isolated as a colorless oil: IR (cm^{-1}, neat) 2959 (s), 2924 (s), 2854 (s), 1462 (m), 1377 (w), 1110 (w), 1096 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 3.33 (3H, s), 2.35 (1H, dd, J = 8.6, 2.4 Hz), 1.77–1.15 (29H, m), 0.92–0.78 (9H, m), 0.88 (9H, t, J = 7.2 Hz), 0.68 (1H, ddd, J = 8.6, 8.3, 4.8 Hz), 0.59 (1H, dd, J = 4.8, 3.9 Hz), 0.54 (1H, dd, J = 8.3, 3.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 88.36, 57.50, 42.53, 42.22 (J_{Sn-C} = 18.6 Hz), 32.76 (J_{Sn-C} = 8.7 Hz), 30.43, 29.31 (J_{Sn-C} = 19.1 Hz), 27.63 (J_{Sn-C} = 58.5 Hz), 26.75 (2), 26.63, 25.52, 23.00, 17.01, 14.09, 13.65, 13.32, 10.27 (J_{Sn-C} = 307.5 Hz), one carbon missing; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −9.63; HRMS calcd for $C_{23}H_{45}OSn$ $(M - C_4H_9)^+$ 457.2492, found 457.2488.

The product **23** was also obtained using the following procedure. According to the general procedure B, a solution of **23** (40 mg, 0.075 mmol) in 1 mL of THF was added to a solution of MeLi (0.15 mL, 1.5 M solution in diethyl ether, 0.23 mmol) in 1 mL of THF, and the mixture was stirred for 4 h at 0 °C. Bu_3SnCl (83 μL, 0.31 mmol) was added, and the mixture was stirred for 1 h at rt. After regular workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 29 mg (72%) of **23** was obtained as a colorless oil. Spectroscopic data: *vide supra*.

(*R)-[(1*S**,2*R**)-2-Butylcyclopropylcyclohexylmethyl Methyl Ether (25).** According to the general procedure A, a solution of the alcohol (10 mg, 0.05 mmol) in 1 mL of THF was added to a mixture of washed KH (11 mg, 35 wt % in mineral oil, 0.10 mmol) and 18-crown-6 ether (1 mg). MeI (6 μL, 0.10 mmol) was added, and the reaction mixture was stirred for 1 h at rt. After aqueous workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 11 mg (99%) of **25** was isolated as a colorless oil: IR (cm^{-1}, neat) 3065 (w), 2924 (s), 2854 (s), 1736 (w), 1448 (m), 1110 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 3.34 (3H, s), 2.25 (1H, dd, J = 8.6, 5.0 Hz), 1.79–1.62 (5H, m), 1.38–1.15 (12H, m), 0.87 (3H, t, J = 7.1 Hz), 0.51 (1H, m), 0.45 (2H, m), 0.33 (1H, ddd, J = 7.7, 4.2, 3.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.31, 57.32, 43.01, 33.51, 31.64, 29.14, 28.81, 26.75, 26.58 (2), 22.62, 19.84, 15.41, 14.13, 11.13; HRMS calcd for $C_{15}H_{27}O$ $(M - H)^+$ 223.2062, found 223.2061.

The product **25** was also obtained via the following procedure. According to the general procedure B, a solution of **23** (20 mg, 0.04 mmol) in 0.5 mL of THF was added to a solution of MeLi (0.04 mL, 1.5 M solution in diethyl ether, 0.058 mmol) in 0.5 mL of THF, and the mixture was stirred for 4 h at 0 °C. Aqueous saturated NH_4Cl was added, and the mixture was stirred for 5 min at rt. After regular workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 7.9 mg (90%) of **25** was obtained as a colorless oil. Spectroscopic data: *vide supra*.

(*R)-[(1*S**,2*R**)-2-Butyl-2-(tributylstannnyl)cyclopropyl]cyclohexylmethyl Methyl Ether (26).** According to the general procedure A, a solution of the alcohol (220 mg, 0.44 mmol) in 5 mL of THF was added to a mixture of washed KH (101 mg, 35 wt % in mineral oil, 1.94 mmol) and 18-crown-6 ether (11 mg, 0.04 mmol). MeI (0.13 mL, 2.04 mmol) was added and, the reaction mixture was stirred for 10 min at 0 °C followed by 30 min at rt. After aqueous workup and purification by flash chromatography, eluting with hexanes: diethyl ether 20:1, 220 mg (97%) of **26** was isolated as a colorless oil: IR (cm^{-1}, neat) 3030 (w), 2959 (s), 2924 (s), 2854 (s), 1462 (m), 1448 (m), 1377 (w), 1110 (m), 1089 (m); ^1H NMR (200 MHz, $CDCl_3$) δ 3.36 (3H, s), 2.72 (1H, ddd, J = 9.2, 4.2, 2.4 Hz), 1.75–1.14 (29H, m), 0.87 (9H, t, J = 7.1 Hz), 0.81–0.70 (11H, m), 0.38 (1H, dd, J = 2.3, 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 85.68, 57.24, 43.26, 35.30, 33.72, 29.65, 29.21 (J = 19.2 Hz), 27.87, 27.61 (J_{Sn-C} = 55.8 Hz), 26.71 (2), 26.61, 23.11, 22.36, 15.75, 14.21, 13.68, 13.11, 9.03 (J_{Sn-C} = 303.3 Hz); ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −2.44; HRMS calcd for $C_{23}H_{45}OSn$ $(M - C_4H_9)^+$ 457.2492, found 457.2486. Anal. Calcd for $C_{27}H_{54}OSn$: C, 63.16; H, 10.6. Found: C, 63.31; H, 10.10.

The product **26** was also obtained via the following procedure. According to the general procedure B, a solution of **29** (40 mg, 0.10 mmol) in 1 mL of THF was added to a solution of *n*-BuLi (0.46 mL, 2.5 M solution in hexane, 1.0 mmol) in 1 mL of THF, and the mixture was stirred for 45 min at 0 °C. Aqueous saturated NH_4Cl was added, and the mixture was stirred for 5 min at rt. After regular workup and purification by flash chromatography, eluting with hexanes:diethyl ether 20:1, 36 mg (70%) of **26** was obtained as a colorless oil. Spectroscopic data: *vide supra*.

(*R)-[(1*S**,2*S**)-2-Butylcyclopropyl]cyclohexylmethyl Methyl Ether (28).** According to the general procedure B, a solution of **26** (30 mg, 0.06 mmol) in 0.5 mL of THF was added to a solution of BuLi (0.23 mL, 2.5 M solution in hexane, 0.58 mmol) in 0.5 mL of THF, and the mixture was stirred for 10 h at 0 °C. Aqueous saturated NH_4Cl was added, and the mixture was stirred for 5 min at rt. After regular workup and

purification by flash chromatography, eluting with hexanes: diethyl ether 10:1, 12.3 mg (94%) of **28** was obtained as a colorless oil: IR (cm^{-1}, neat) 3065 (w), 2924 (s), 284 (s), 2818 (m), 1448 (m), 1110 (m), 1089 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 3.34 (3H, s), 2.58 (1H, dd, J = 9.0, 4.8 Hz), 1.84–1.03 (16H, m), 0.88 (3H, t, J = 7.0 Hz), 0.79 (2H, m), 0.71 (1H, m), 0.10 (1H, ddd, J = 5.2, 3.9, 3.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 85.40, 56.90, 42.88, 32.41, 29.31, 29.27, 27.95, 26.66 (2), 26.55, 22.58, 17.67, 15.09, 14.15, 10.38; HRMS calcd for $C_{15}H_{27}O$ (M − H)$^+$ 223.2062, found 223.2062; HRMS calcd for $C_{14}H_{25}$ (M − OCH_3)$^+$ 193.1956, found 193.1948.

(*R)-[(1*S**,2*R**)-2-Butyl-2-(trimethylstannyl)cyclopropyl]cyclohexylmethyl Methyl Ether (29).** According to the general procedure A, a solution of the alcohol (200 mg, 0.54 mmol) in 5 mL of THF was added to a mixture of washed KH (92 mg, 35 wt % in mineral oil, 0.80 mmol) and 18-crown-6 ether (14 mg, 0.05 mmol). MeI (0.054 mL, 0.86 mmol) was added, and the reaction mixture was stirred for 15 min at 0 °C followed by 30 min at rt. After aqueous workup and purification by flash chromatography, eluting with hexanes: diethyl ether 20:1, 201 mg (97%) of **29** was isolated as a colorless oil: IR (cm^{-1}, neat) 3037 (w), 2924 (s), 2854 (s), 2819 (m), 1448 (s), 1188 (m), 1110 (s), 1089 (s), 941 (m), 766 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.36 (3H, s), 2.72 (1H, dd, J = 9.0, 4.6 Hz), 1.81–1.44 (5H, m), 1.34–1.00 (12H, m), 0.87 (3H, t, J = 7.0 Hz), 0.78 (2H, m), 0.41 (1H, m), −0.01 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 85.35 (J_{Sn-C} = 10.5 Hz), 57.04, 43.17, 34.75 (J_{Sn-C} = 19.6 Hz), 33.51 (J_{Sn-C} = 13.8 Hz), 29.37, 28.01, 26.70, 26.67, 26.60, 22.99, 22.36, 15.32, 14.18, 12.55, −10.44 (J_{Sn-C} = 325.6, 311.1 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ 20.07; HRMS calcd for $C_{17}H_{33}OSn$ (M − CH_3)$^+$ 373.1553, found 373.1561.

(*R)-[(1*S**,2*S**)-2-(Tributylstannyl)-2-(trimethylsilyl)cyclopropyl]butyl Triisopropylsilyl Ether (30).** According to the general procedure C, triisopropylsilyl chloride (49 mg, 0.25 mmol), the cyclopropyl alcohol (80 mg, 0.17 mmol), and imidazole (29 mg, 0.42 mmol) were dissolved in 0.15 mL of DMF. The reaction mixture was stirred at rt for 48 h and diluted with hexanes:CH_2Cl_2 9:1, washed, and dried. Purification by flash chromatography on silica gel, eluting with hexanes, gave 75 mg (71%) of **30** as a pure colorless oil. Further elution with hexanes:diethyl ether 5:1 yielded 23 mg of starting material. **30**: IR (cm^{-1}, neat) 3023 (w), 2966 (s), 2938 (s), 2868 (s), 1462 (s), 1377 (m), 1251 (s), 1103 (s), 1012 (s), 885 (s), 836 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.12 (1H, dq, J = 5.7, 3.5 Hz), 1.58–1.37 (10H, m), 1.30 (6H, m), 1.05 (21H, m), 0.91–0.84 (3H, m), 0.88 (9H, t, J = 7.3 Hz), 0.84–0.72 (8H, m), 0.79 (1H, dd, J = 3.7, 3.3 Hz), −0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 77.45 (J_{Sn-C} = 29.0 Hz), 40.96, 29.22 (J_{Sn-C} = 18.8 Hz), 27.65 (J_{Sn-C} = 62.2 Hz), 27.46, 18.40, 18.31, 18.04, 15.49, 14.61, 13.59, 12.96, 11.40 (J_{Sn-C} = 305.1 Hz), −1.34, −1.87; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −3.79; HRMS calcd for $C_{27}H_{59}OSi_2Sn$ (M − C_4H_9)$^+$ 575.3126, found 575.3112.

(*R)[(1*S**,2*S**)-2-(Tributylstannyl)-2-(trimethylsilyl)cyclopropyl]ethyl Triisopropylsilyl Ether (31).** According to the general procedure C, triisopropylsilyl chloride (65 mg, 0.34 mmol), the cyclopropyl alcohol (100 mg, 0.22 mmol), and imidazole (37 mg, 0.55 mmol) were dissolved in 0.2 mL of DMF. The reaction mixture was stirred at rt for 30 h, diluted with hexanes:CH_2Cl_2 9:1, washed, and dried. Purification by flash chromatography on silica gel, eluting with hexanes, gave 109 mg (83%) of **31** as a colorless oil: IR (cm^{-1}, neat) 3030 (w), 2955 (s), 2924 (s), 2868 (s), 1462 (s), 1370 (m), 1250 (s), 1110 (s), 990 (s), 836 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.19 (1H, dq, J = 8.7, 6.0 Hz), 1.43 (6H, m), 1.30 (6H, m), 1.24 (3H, d, J = 6.0 Hz), 1.08–0.98 (3H, m), 1.05 (18H, s), 0.88 (9H, t, J = 7.3 Hz), 0.85–0.70 (8H, m), 0.61 (1H, dd, J = 4.0, 3.9 Hz), −0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.06 (J_{Sn-C} = 32.2 Hz), 29.44, 29.22 (J_{Sn-C} = 18.9 Hz), 27.65 (J_{Sn-C} = 63.6 Hz), 25.06, 18.23, 18.18, 14.95, 13.61, 12.66 (J_{Sn-C} = 58.2 Hz), 11.34 (J_{Sn-C} = 304.5 Hz), −1.37, −1.98; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −3.84; HRMS calcd for $C_{25}H_{55}OSi_2Sn$ (M − C_4H_9)$^+$ 547.2813, found 547.2793.

(*R)-[(1*S**,2*S**)-2-Butyl-2-(tributylstannyl)cyclopropyl]ethyl *tert*-Butyldimethylsilyl Ether (32).** According to the general procedure D, the alcohol (50 mg, 0.116 mmol) was dissolved in 1 mL of CH_2Cl_2, followed by addition of 2,6-lutidine (0.04 mL, 0.174 mmol), and was then cooled to −78 °C. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.034 mL, 0.290 mmol) was added, and the reaction mixture was stirred for 30 min at −78 °C. Regular workup, followed by flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1, gave 57 mg (90%) of **32** as a colorless oil: IR (cm^{-1}, neat) 3044 (w), 2959 (s), 2924 (s), 2875 (s), 2854 (s), 1462 (m), 1377 (m), 1251 (m), 1096 (s), 1082 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 2.91 (1H, dq, J = 9.3, 6.1 Hz), 1.82–1.10 (18H, m), 1.24 (3H, d, J = 6.1 Hz), 0.91–0.75 (27 H, m), 0.73–0.36 (3H, m), 0.01 (3H, s), 0.00 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 74.35, 42.16, 33.22, 29.38 (J_{Sn-C} = 19.1 Hz), 27.73 (J_{Sn-C} = 59.4 Hz), 26.05, 24.73, 23.07, 18.28, 17.39, 16.25, 14.23, 13.79, 10.03 (J_{Sn-C} = 160.1 Hz), −4.01, −4.09; HRMS calcd for $C_{23}H_{49}OSiSn$ (M − C_4H_9)$^+$ 489.2575, found 489.2598.

(*R)-[(1*S**,2*S**)-2-(Triisopropylsilyl)-2-(trimethylsilyl)cyclopropyl]-1-butanol (34a).** According to the general procedure E, MeLi (0.21 mL, 1.5 M in Et_2O, 0.32 mmol) was added to the reaction flask. The diethyl ether was replaced with 0.5 mL of THF, and the flask was cooled to 0 °C. Silyl ether **30** (40 mg, 0.063 mmol) was added in 0.5 mL of THF to the cooled reaction flask, and the mixture was stirred for 1 h at 0 °C. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, gave 19.7 mg (91%) of **34a** as a white solid: R_f = 0.39 on silica gel (hexanes:diethyl ether 2:1); IR (cm^{-1}, neat) 3325 (br, m), 2959 (s), 2868 (s), 1469 (m), 1251 (m), 1068 (m), 1012 (m), 948 (m), 885 (m), 836 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.44 (1H, m), 1.75 (1H, m), 1.54 (2H, m), 1.37 (2H, m), 1.13 (21H, m), 0.99–0.89 (3H, m), 0.92 (3H, t, J = 7.2 Hz), −0.03 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 73.39, 39.96, 30.17, 20.58, 20.07, 19.16, 15.28, 14.31, −0.16, −0.82; HRMS calcd for $C_{18}H_{39}OSi_2$ (M − CH_3)$^+$ 327.2539, found 327.2540; HRMS calcd for $C_{16}H_{35}OSi_2$ (M − C_3H_7)$^+$ 299.2226, found 299.2214.

(*R)-[(1*S**,2*S**)-2-(Triisopropylsilyl)-2-(trimethylsilyl)cyclopropyl]-1-ethanol (34b).** According to the general procedure E, MeLi (0.18 mL, 1.5 M in diethyl ether, 0.25 mmol) was added to the reaction flask. The diethyl ether was replaced with 0.5 mL of THF, and the flask was cooled to 0 °C. Silyl ether **31** (30 mg, 0.051 mmol) was added in 0.5 mL of THF to the cooled reaction flask, and the mixture was stirred for 1 h at 0 °C. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 7:1, gave 11.6 mg (75%) of **34b** as a white solid: IR (cm^{-1}, neat) 3310 (br, s), 2973 (s), 2945 (s), 2868 (s), 1469 (m), 1251 (m), 1096 (m), 1075 (m), 1018 (m), 941 (m), 836 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.60 (1H, dt, J = 6.2, 6.0 Hz), 1.48 (1H, m), 1.37 (3H, d, J = 6.0 Hz), 1.14–1.05 (3H, m), 1.13 (18H, s), 0.97–0.90 (3H, m), −0.03 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.99, 31,39, 23.46, 20.47, 19.96, 15.22 (J_{Si-C} = 7.6 Hz), 14.37, −0.37 (J_{Si-C} = 52.3 Hz), −0.95 (J_{Si-C} = 52.2 Hz); HRMS calcd for $C_{16}H_{35}OSi_2$ (M − CH_3)$^+$ 299.2226, found 299.2226.

(*R)-[(1*S**,2*S**)-2-Butyl-2-(*tert*-butyldimethylsilyl)cyclopropyl]-1-ethanol (35).** According to the general procedure E, MeLi (0.07 mL, 1.4 M in Et_2O, 0.25 mmol) was added to the reaction flask. The diethyl ether was replaced with 0.5 mL of THF, and the flask was cooled to 0 °C. Silyl ether **32** (27 mg, 0.049 mmol) was added in 0.5 mL of THF to the cooled reaction flask. The reaction was allowed to warm up to rt over 20 h. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1), gave 11.3 mg (90%) of **35** as a colorless oil: IR (cm^{-1}, neat) 3367 (br, m), 2959 (s), 2924 (s), 2860 (s), 1469 (m), 1251 (s), 1096 (m), 822 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.46 (1H, dq, J = 9.9, 6.0 Hz), 1.95 (1H, m), 1.40 (1H, br s), 1.36 (1H, m), 1.33 (3H, d, J = 6.0 Hz), 1.27–1.15 (4H, m), 0.94 (9H, s), 0.85 (3H, t, J = 7.2 Hz), 0.67 (1H, ddd, J = 9.9, 8.2, 5.6 Hz), 0.57 (1H, dd, J = 5.6, 4.0 Hz), 0.48 (1H, dd, J = 8.2, 4.0 Hz), 0.05 (3H, s), −0.11 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.83, 40.60, 34.55, 31.36, 27.73, 23.74, 23.18, 18.69, 16.90, 14.03, 12.15, −2.93, −3.48; HRMS calcd for $C_{11}H_{23}OSi$ (M − C_4H_9)$^+$ 199.1518, found 199.1502.

(*S)-[(1*S**,2*S**)-2-(*tert*-Butyldimethylsilyl)-2-(trimethylsilyl)cyclopropyl]cyclohexylmethanol (36).** According to the general procedure E, the silyl ether **33** (100 mg, 0.16 mmol) was dissolved in 2 mL of THF, and the reaction flask

was cooled to 0 °C. MeLi (0.12 mL, 1.4 M in Et_2O, 0.17 mmol) was added to the reaction flask. The reaction mixture was stirred at 0 °C for 2 h. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, gave 76.6 mg (92%) of **36** as a colorless oil: ^1H NMR (200 MHz, $CDCl_3$) δ 3.03 (1H, ddd, J = 9.2, 5.9, 3.0 Hz), 1.89 (1H, dm, J = 12.5 Hz), 1.80−1.68 (3H, m), 1.64 (1H, m), 1.42 (1H, m), 1.30 (1H d, J = 3.3 Hz), 1.28−1.00 (6H, m), 0.96 (9H, s), 0.88 (1H, dd, J = 7.7, 3.7 Hz), 0.73 (1H, dd, J = 5.1, 3.7 Hz), 0.05 (3H, s), 0.03 (3H, s), −0.01 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.90, 45.07, 29.32, 28.86, 28.59, 28.41, 26.59, 26.36, 26.21, 18.76, 13.79, −0.18, −1.50, −1.99, −4.14

(*Z*)-1-(Tributylstannyl)-1-(trimethylsilyl)-4-methyl-1-penten-3-yl Triisopropylsilyl Ether (37a). According to the general procedure C, triisopropylsilyl chloride (0.14 mL, 0.66 mmol), the alcohol (202 mg, 0.44 mmol), and imidazole (75 mg, 1.10 mmol) were dissolved in 0.4 mL of DMF, and the mixture was stirred at rt for 48 h. The reaction mixture was diluted with hexanes:CH_2Cl_2 9:1, washed, and dried. Purification by flash chromatography on silica gel, eluting with hexanes, gave 73.4 mg (27%) of **37a** as a colorless oil. Further elution with hexanes:ethyl acetate 10:1 resulted in the recovery of 140 mg of starting material. **37a:** IR (cm^{-1}, neat) 2959 (m), 2868 (w), 1462 (w), 1377 (w), 1243 (m), 1054 (m), 885 (m), 836 (m); ^1H NMR (200 MHz, $CDCl_3$) δ 6.80 (1H, d, J = 7.2 Hz) (J_{Sn-H} = 172.2 Hz), 3.94 (1H, m), 1.59 (1H, m), 1.48−1.16 (12H, m), 1.03 (21H, s), 0.96 (6H, d, J = 6.6 Hz), 0.91−0.84 (15H, m) 0.06 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.86, 141.34, 81.62, 36.89, 29.67, 27.97, 20.23, 18.59, 16.06, 13.92, 12.96, 11.87, 0.40; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −56.52; HRMS calcd for $C_{26}H_{57}OSi_2$ (M − C_4H_9)$^+$ 561.2970, found 561.2973.

(*Z*)-1-(Tributylstannyl)-1-(trimethylsilyl)-1-hexen-3-yl Triisopropylsilyl Ether (37b). According to the general procedure C, triisopropylsilyl chloride (49 mg, 0.25 mmol), the allylic alcohol (80 mg, 0.17 mmol), and imidazole (29 mg, 0.42 mmol) were dissolved in 0.15 mL of DMF. The reaction mixture was stirred at rt for 48 h, diluted with hexanes:CH_2Cl_2 9:1, washed, and dried. Purification by flash chromatography on silica gel, eluting with hexanes, gave 75 mg (70%) of **37b** as a colorless oil. Further elution with hexanes:diethyl ether 5:1 resulted in the recovery of 22 mg of starting material. **37b:** IR (cm^{-1}, neat) 2959 (s), 2924 (s), 2868 (s), 1567 (w), 1462 (m), 1244 (m), 1096 (s), 871 (s), 836 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (1H, d, J = 7.0 Hz) (J_{Sn-H} = 174.5 Hz), 4.06 (1H, dt, J = 7.0, 3.6 Hz), 1.52−1.23 (16H, m), 1.02 (21H, m), 0.92−0.87 (9H, m), 0.88 (9H, t, J = 7.2 Hz), 0.03 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.43 (J_{Sn-C} = 31.0 Hz), 139.32 (J_{Sn-C} = 237.5 Hz), 77.48, 41.66, 29.26, 27.61 (J_{Sn-C} = 63.0 Hz), 18.33, 18.16, 14.63, 13.62, 12.46 (J_{Sn-C} = 59.2 Hz), 11.37 (J_{Sn-C} = 305.8 Hz), 0.02; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −56.54; HRMS calcd for $C_{26}H_{57}OSi_2Sn$ (M − C_4H_9)$^+$ 561.2970, found 561.2965.

(*Z*)-4-(Tributylstannyl)-4-(trimethylsilyl)-3-buten-2-yl Triisopropylsilyl Ether (37c). According to the general procedure C, triisopropylsilyl chloride (0.19 mL, 0.87 mmol), the allylic alcohol (0.25 g, 0.58 mmol), 4-(dimethylamino)-pyridine (7 mg, 0.06 mmol), and imidazole (99 mg, 1.45 mmol) were dissolved in 0.4 mL of dry DMF. The reaction mixture was stirred at rt for 24 h, diluted with hexanes:CH_2Cl_2 9:1, washed, and dried. Purification by flash chromatography on silica gel, eluting with hexanes, gave 0.281 g (88%) of **37c** as a pure colorless oil: IR (cm^{-1}, neat) 2959 (s), 2938 (s), 2868 (s), 1574 (w), 1461 (m), 1244 (m), 1089 (m), 1068 (m), 1005 (w), 871 (m), 836 (m); ^1H NMR (200 MHz, $CDCl_3$) δ 6.74 (1H, d, J = 6.6 Hz) (J_{Sn-H} = 173.0 Hz), 4.17 (1H, dq, J = 6.6, 6.3 Hz), 1.58−1.20 (12H, m), 1.19 (3H, d, J = 6.3 Hz), 1.02 (21H, m), 0.95−0.80 (15H, m), 0.04 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 161.78, 138.62, 73.82, 29.25, 27.58, 25.19, 18.08 (2), 13.56, 12.42, 11.42, 0.03; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −55.34; HRMS calcd for $C_{24}H_{53}OSi_2Sn$ (M − C_4H_9)$^+$ 533.2657, found 533.2647.

(*Z*)-3-(Tributylstannyl)-3-(trimethylsilyl)-2-propen-1-yl Triisopropylsilyl Ether (37d). According to the general procedure C, triisopropylsilyl chloride (2.1 mL, 9.7 mmol), the allylic alcohol (3.4 g, 8.1 mmol), imidazole (1.38 g, 20.3 mmol), and DMAP (50 mg, 0.41 mmol) were dissolved in 7 mL of DMF. The reaction mixture was stirred at rt for 45 min and then diluted with hexanes:CH_2Cl_2 9:1, washed with water, and brine, and dried over $MgSO_4$. Purification by flash chromatography on silica gel, eluting with hexanes to hexanes:diethyl ether 20:1, gave 4.51 g (97%) of **37d** as a colorless oil: IR (cm^{-1}, neat) 2945 (s), 2868 (s), 1574 (m), 1465 (s), 1378 (m), 1358 (m), 1259 (s), 1246 (s), 1107 (s), 1067 (s), 1014 (m), 883 (s), 834 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (1H, t, J = 4.8 Hz) (J_{Sn-H} = 177.3, 169.2 Hz), 4.24 (2H, d, J = 4.8 Hz), 1.44 (6H, m), 1.29 (6H, m), 1.10 (3H, m), 1.07 (18H, s), 0.85−0.93 (15H, m), 0.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.90 (J_{Sn-C} = 21.2 Hz), 141.94, 68.25 (J_{Sn-C} = 65.2 Hz), 29.25 (J_{Sn-C} = 19.1 Hz), 27.51 (J_{Sn-C} = 33.7 Hz), 18.04, 13.68, 12.07, 11.16, −0.27; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −52.50.

(*Z*)-3-(Tributylstannyl)-3-(trimethylsilyl)-2-propen-1-yl *tert*-Butyldimethylsilyl Ether (38a). According to the general procedure C, *tert*-butyldimethylsilyl chloride (171 mg, 1.14 mmol), the allylic alcohol (400 mg, 0.95 mmol), imidazole (129 mg, 1.90 mmol), and DMAP (12.4 mg, 0.1 mmol) were dissolved in 0.8 mL of DMF. The reaction mixture was stirred at rt for 3 h, diluted with hexanes:CH_2Cl_2 9:1, washed with brine, and dried. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1, gave 485 mg (95%) of **38a** as a colorless oil: IR (cm^{-1}, neat) 2957 (s), 2924 (s), 2875 (s), 1462 (w), 1247 (m), 1102 (m), 836 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 6.77 (1H, t, J = 5.0 Hz) (J_{Sn-H} = 175.1, 168.1 Hz), 4.16 (2H, d, J = 5.0 Hz), 1.43 (6H, m), 1.29 (6H, sext, J = 7.3 Hz), 0.89 (6H, m), 0.90 (9H, s), 0.87 (9H, t, J = 7.3 Hz), 0.07 (6H, s), 0.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.33 (J_{Sn-C} = 22.0 Hz), 142.62, 68.18 (J_{Sn-C} = 38.9 Hz), 29.22 (J_{Sn-C} = 19.0 Hz), 27.45 (J_{Sn-C} = 59.3 Hz), 26.03, 18.45, 13.66, 11.24 (J_{Sn-C} = 321.5, 306.8 Hz), −0.29, −5.00; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −52.27.

(*Z*)-4-(Tributylstannyl)-4-(trimethylsilyl)-3-buten-2-yl *tert*-Butyldimethylsilyl Ether (38b). According to the general procedure C, the allylic alcohol (250 mg, 0.577 mmol) was dissolved in 4 mL of CH_2Cl_2 and cooled to −78 °C. 2,6-Lutidine (0.167 mL, 1.44 mmol) was added, followed by *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.199 mL, 0.865 mmol), and the reaction mixture was stirred for 30 min at −78 °C. Regular workup (saturated aqueous NH_4Cl, diethyl ether, brine, $MgSO_4$), followed by flash chromatography on silica gel, eluting with hexanes, gave 295 mg (93%) of **38b** as a colorless oil: IR (cm^{-1}, neat) 2959 (s), 2931 (s), 2854 (s), 1574 (w), 1462 (m), 1251 (s), 1138 (w), 1082 (s), 1005 (m), 878 (m), 836 (s), 773 (m); ^1H NMR (200 MHz, $CDCl_3$) δ 6.67 (1H, d, J = 7.2 Hz) (J_{Sn-H} = 169.8 Hz), 4.11 (1H, dq, J = 7.2, 6.2 Hz), 1.58−1.18 (12H, m), 1.15 (3H, d, J = 6.2 Hz), 0.95−0.76 (24H, m), 0.04 (9H, s), 0.02 (6H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 160.67 (J_{Sn-C} = 20.2 Hz), 139.62, 74.44 (J_{Sn-C} = 61.4 Hz), 29.36 (J_{Sn-C} = 19.1 Hz), 27.66 (J_{Sn-C} = 61.5 Hz), 26.00, 25.03, 18.28, 13.76, 11.57 (J_{Sn-C} = 307.2 Hz), 0.07 (J_{Sn-C} = 52.2 Hz), −4.25 ; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −54.32; HRMS calcd for $C_{21}H_{47}OSi_2Sn$ (M − C_4H_9)$^+$ 491.2187, found 491.2154; HRMS calcd for $C_{24}H_{53}OSi_2Sn$ (M − CH_3)$^+$ 533.2670, found 533.2659.

(*Z*)-1-(Tributylstannyl)-1-(trimethylsilyl)-4-methyl-1-penten-3-yl *tert*-Butyldimethylsilyl Ether (38c). According to the general procedure C, *tert*-butyldimethylsilyl chloride (130 mg, 0.86 mmol), the allylic alcohol (200 mg, 0.43 mmol), and imidazole (88 mg, 0.129 mmol) were dissolved in 0.4 mL of DMF. The reaction mixture was stirred at rt for 24 h, diluted with hexanes:CH_2Cl_2 9:1, washed, and dried. Purification by flash chromatography on silica gel, eluting with hexanes:ethyl acetate 20:1, gave 212 mg (86%) of **38c** as a colorless oil: IR (cm^{-1}, neat) 2952 (s), 2931 (s), 2854 (m), 1567 (w), 1461 (m), 1377 (w), 1363 (w), 1250 (m), 1053 (m), 885 (m), 836 (s), ^1H NMR (200 MHz, $CDCl_3$) δ 6.72 (1H, d, J = 7.6 Hz) (J_{Sn-H} = 169.8 Hz), 3.71 (1H, m), 1.60 (1H, m), 1.54−1.21 (12H, m), 0.94−0.84 (30H, m) 0.05 (9H, s), −0.11 (3H, s), −0.04 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.93, 142.03, 82.05, 36.03, 29.73, 28.00, 26.34, 20.33, 16.33, 14.03, 12.07, 0.53, −3.08, −3.94; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −55.63; HRMS calcd for $C_{23}H_{51}OSi_2Sn$ (M − C_4H_9)$^+$ 519.2500, found 519.2495.

(*Z*)-2-Methyl-5-(tributylstannyl)-4-nonen-3-yl Dimethylphenylsilyl Ether (40). MeLi (0.15 mL, 1.5 M in diethyl ether, 0.22 mmol) was added to a solution of the alcohol (100

mg, 0.22 mmol) in 2 mL of THF at 0 °C, and the mixture was stirred for 5 min. Dimethylphenylsilyl chloride (0.04 mL, 0.22 mmol) was added. The reaction mixture was warmed to rt and stirred for 5 h. Saturated aqueous NH_4Cl was added, the mixture was extracted with diethyl ether, and the combined organic layer was washed with brine. Purification by flash chromatography on silica gel, eluting with hexanes, gave 87.4 mg (67%) of **40** as a colorless oil. Further elution with hexanes:diethyl ether 10:1 resulted in the recovery of 20 mg of starting material. **40:** IR (cm^{-1}, neat) 3072 (w), 3051 (w), 2959 (s), 2924 (s), 2875 (s), 2861 (s), 1462 (m), 1251 (m), 1117 (s), 1054 (s), 829 (s), 786 (m), 702 (m); ^1H NMR (200 MHz, $CDCl_3$) δ 7.58 (2H, m), 7.36 (2H, m), 6.06 (1H, d, J = 8.7 Hz) (J_{Sn-H} = 143.1 Hz), 3.81 (1H, dd, J = 8.7, 3.9 Hz), 2.16 (2H, m), 1.62 (1H, m), 1.55−1.20 (14H, m), 1.01−0.70 (21H, m), 0.34 (6H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.40, 143.61 (J_{Sn-C} = 28.0 Hz), 139.30, 133.59 (2), 129.19, 127.59 (2), 80.11, 40.37, 35.84, 32.39, 29.27 (J_{Sn-C} = 19.1 Hz), 27.50 (J_{Sn-C} = 60.4 Hz), 22.50, 19.37, 17.05, 13.98, 13.62, 10.48 (J_{Sn-C} = 327.0 Hz), 0.05, −0.14; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −57.24; HRMS calcd for $C_{26}H_{47}OSiSn$ (M − C_4H_9)$^+$ 523.2418, found 523.2440.

4,4-Bis(tributylstannyl)-3-buten-2-yl Triisopropylsilyl Ether (41). According to the general procedure C, triisopropylsilyl chloride (90 mg, 0.47 mmol), the allylic alcohol (171 mg, 0.26 mmol), and imidazole (60 mg, 0.88 mmol) were dissolved in 1 mL of DMF, and the solution was stirred at rt for 48 h. The reaction mixture was then diluted with ether, washed, and dried. Purification by flash chromatography on silica gel, eluting with hexanes:ethyl acetate 10:1, gave 205 mg (98%) of **41** as a colorless oil: IR (cm^{-1}, neat) 2958 (s), 2926 (s), 28.68 (s), 1463 (m), 1376 (m), 1087 (m); ^1H NMR (200 MHz, $CDCl_3$) δ 6.70 (1H, d, J = 6.8 Hz) (J_{Sn-H} = 189.4 Hz, 103.3 Hz), 4.08 (1H, m), 1.56−0.74 (78H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.43, 138.29, 74.88, 29.20, 29.04, 27.52, 27.35, 25.47, 17.91, 13.50, 13.43, 12.21, 11.17, 10.25.

(*Z*)-1-(Triisopropylsilyl)-1-(trimethylsilyl)-4-methyl-1-penten-3-ol (42a). According to the general procedure E, MeLi (0.1 mL, 1.365 M in Et_2O, 0.137 mmol) was added to a solution of silyl ether **37a** (54.7 mg, 0.088 mmol) in 1 mL of THF at −78 °C. After 2 h of being stirred at −78 °C, the mixture was warmed to 0 °C for 10 min. Regular workup, followed by purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, gave 24.9 mg (86%) of **42a** as a colorless oil: IR (cm^{-1}, neat) 3486 (br, m), 2952 (s), 2868 (s), 1553 (m), 1469 (m), 1384 (m), 1363 (m), 1251 (s), 1012 (m), 871 (s), 836 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 6.76 (1H, d, J = 9.4 Hz), 3.93 (1H, m), 2.78 (1H, m), 1.25 (1H, m), 1.10−1.09 (18H, m), 1.07−1.05 (3H, d, J = 3.0 Hz), 0.97 (3H, d, J = 6.6 Hz), 0.89 (3H, d, J = 7.0 Hz), 0.13 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.12, 141.37, 77.32, 34.17, 19.50, 19.42, 17.04, 13.89, 2.02; HRMS calcd for $C_{17}H_{37}OSi_2$ (M − CH_3)$^+$ 313.2383, found 313.2386; HRMS calcd for $C_{15}H_{33}OSi_2$ (M − C_3H_7)$^+$ 285.2070, found 285.2084.

(*Z*)-1-(Triisopropylsilyl)-1-(trimethylsilyl)-1-hexen-3-ol (42b). According to the general procedure E, MeLi (0.22 mL, 1.4 M in diethyl ether, 0.32 mmol) was added to the reaction flask. The ether was replaced with 0.5 mL of THF, and the flask was cooled to 0 °C. Silyl ether **37b** (40 mg, 0.065 mmol) was dissolved in 0.5 mL of THF, and the solution was transferred to the cooled reaction flask and stirred at 0 °C for 1 h. Purification by flash chromatography on silica gel (hexanes:diethyl ether 10:1) gave 20 mg (94%) of **42b** as a pure colorless oil: R_f = 0.53 on silica gel (hexanes:diethyl ether 2:1); IR (cm^{-1}, neat) 3431 (br, m), 2959 (s), 2868 (s), 1553 (w), 1469 (m), 1251 (s), 1019 (m), 871 (s), 836 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 6.67 (1H, d, J = 9.2 Hz), 4.19 (1H, m), 1.57−1.31 (5H, m), 1.30−1.17 (3H, m), 1.09−1.05 (18H, 3 times s), 0.92 (3H, t, J = 7.0 Hz), 0.13 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.22, 138.95, 72.74, 38.99, 19.47, 18.54, 14.16, 13.78, 1.97; HRMS calcd for $C_{17}H_{37}OSi_2$ (M − CH_3)$^+$ 313.2383, found 313.2396; HRMS calcd for $C_{15}H_{33}OSi_2$ (M − C_3H_7)$^+$ 285.2070, found 285.2070.

(*Z*)-4-(Triisopropylsilyl)-4-(trimethylsilyl)-3-buten-2-ol (42c). According to the general procedure E, silyl ether **37c** (492 mg, 0.83 mmol) was dissolved in 7 mL of dry THF, and the reaction flask was cooled to 0 °C. MeLi (0.73 mL, 1.37 M solution in diethyl ether, 1.0 mmol) was slowly added to the reaction flask. The reaction mixture was stirred at 0 °C for 30 min. Purification by flash chromatography on silica gel (hexanes:diethyl ether 20:1 to 2:1) gave 243 mg (97%) of **42c** as a colorless oil: IR (cm^{-1}, neat) 3423 (br, m), 2959 (s), 2924 (s), 2875 (s), 2853 (s), 1574 (w), 1461 (m), 1377 (w), 1243 (s), 1075 (w), 1046 (w); ^1H NMR (200 MHz, $CDCl_3$) δ 6.65 (1H, d, J = 9.2 Hz), 4.38 (1H, ddq, J = 9.2, 6.1, 3.3 Hz), 1.35 (1H, d, J = 3.3 Hz), 1.31−1.07 (3H, d, J = 6.1 Hz), 1.05 (18H, m), 0.13 (9H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.16, 138.41, 69.39, 22.51, 19.27, 13.53, 1.69; HRMS calcd for $C_{15}H_{33}OSi_2$ (M − CH_3)$^+$ 285.2084, found 285.2070; HRMS calcd for $C_{13}H_{29}OSi_2$ (M − C_3H_7)$^+$ 257.1755 found 257.1757.

(*Z*)-1-(Triisopropylsilyl)-1-(trimethylsilyl)-1-propen-3-ol (42d). According to the general procedure E, silyl ether **37d** (3.5 g, 6.08 mmol) was dissolved in 30 mL of THF, and the reaction mixture was cooled to 0 °C. MeLi (5.2 mL, 1.4 M solution in Et_2O, 7.3 mmol) was slowly added, and the reaction mixture was stirred at 0 °C for 10 min. Purification by flash chromatography on silica gel, eluting with hexanes to hexanes:diethyl ether 10:1, gave 1.71 g (98%) of **42d** as a white solid: IR (cm^{-1}, Nujol) 3334 (br, m), 2955 (s), 2922 (s), 2858 (s), 1562 (m), 1470 (m), 1024 (m), 873 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 6.90 (1H, t, J = 5.9 Hz), 4.23 (2H, br s), 1.48 (1H, br s), 1.21 (3H, sept, J = 7.3 Hz), 1.05 (18H, d, J = 7.3 Hz), 0.13 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.91, 139.34, 65.57, 19.31, 13.50, 1.85. Anal. Calcd for $C_{15}H_{34}OSi_2$: C, 62.86; H, 11.96. Found: C, 62.45; H, 11.76.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-(trimethylsilyl)-1-propen-3-ol (43a). According to the general procedure E, MeLi (0.58 mL, 1.37 M solution in Et_2O, 0.79 mmol) was added to the reaction flask. The diethyl ether was replaced with 3 mL of THF, and the flask was cooled to 0 °C. Silyl ether **38a** (350 mg, 0.66 mmol) was added in 3 mL of THF to the cooled reaction flask, and the mixture was stirred for 15 min at 0 °C. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, gave 155.4 mg (97%) of **43a** as a white solid: IR (cm^{-1}, neat) 3325 (br, m), 2956 (s), 2897 (s), 2858 (s), 1462 (m), 1250 (s), 938 (s), 881 (s), 836 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (1H, t, J = 5.9 Hz), 4.23 (2H, t, J = 5.9 Hz), 1.36 (1H, d, J = 5.9 Hz), 0.87 (9H, s), 0.14 (6H, s), 0.11 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.08, 141.06, 65.68, 27.56, 18.14, 1.07, −1.42.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-(trimethylsilyl)-1-buten-3-ol (43b). According to the general procedure E, MeLi (0.29 mL, 1.5 M in diethyl ether, 0.44 mmol) was added to the reaction flask. The ether was replaced with 2.5 mL of THF, and the flask was cooled to −40 °C. Silyl ether **38b** (200 mg, 0.37 mmol) was dissolved in 2.5 mL of THF and transferred to the cooled reaction flask, and the mixture was stirred for 30 min at −40 °C. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to hexanes:diethyl ether 8:1, gave 87 mg (92%) of **43b** as a colorless oil: IR (cm^{-1}, neat) 3353 (br, s), 2959 (s), 2931 (s), 2896 (s), 2861 (s), 1567 (m), 1476 (m), 1462 (m), 1363 (m), 1251 (s), 1054 (s), 906 (s), 857 (s), 836 (s), 801 (s), 681 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 6.56 (1H, d, J = 9.1 Hz), 4.42 (1H, ddq, J = 9.1, 6.1, 3.1 Hz), 1.46 (1H, d, J = 3.1 Hz), 1.20 (3H, d, J = 6.1 Hz), 0.88 (9H, s), 0.16 (3H, s), 0.12 (3H, s), 0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.72, 139.14, 69.93, 27.56, 22.57, 17.70, 1.08, −0.73, −1.28; HRMS calcd for $C_{12}H_{27}OSi_2$ (M − CH_3)$^+$ 243.1600, found 243.1590; HRMS calcd for $C_9H_{21}OSi_2$ (M − C_4H_9)$^+$ 201.1131, found 201.1133.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-(trimethylsilyl)-4-methyl-1-penten-3-ol (43c). According to the general procedure E, MeLi (1.19 mL, 1.365 M in Et_2O, 1.6 mmol) was added to a solution of silyl ether **38c** (187 mg, 0.32 mmol) in 3 mL of THF at −78 °C. After being stirred for 1.5 h at −78 °C, the mixture was stirred at 0 °C for 1 h. Regular workup, followed by purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, gave 83.3 mg (91%) of **43c** as a colorless oil: IR (cm^{-1}, neat) 3430 (br, w), 2959 (s), 2924 (s), 2854 (m), 1567 (w), 1462 (m), 1377 (w), 1363 (w), 1251 (m), 1068 (w), 1004 (w), 878 (m), 835 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 6.69 (1H, d, J = 9.4 Hz), 3.94 (1H, m), 1.66 (1H, m), 1.31 (1H, d, J = 3.4 Hz), 0.96 (3H, d, J = 6.6 Hz), 0.89 (3H, s), 0.88

(9H, s), 0.12 (3H, s), 0.11 (3H, s), 0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.30, 141.27, 77.65, 34.02, 27.60, 19.35, 17.21, 1.25, −0.21, −1.27; HRMS calcd for $C_{13}H_{27}OSi_2(M - C_2H_7)^+$ 255.1600, found 255.1598; HRMS calcd for $C_{11}H_{25}OSi_2$ $(M - C_4H_9)^+$ 229.1444, found 229.1430; HRMS calcd for $C_{10}H_{21}OSi_2$ $(M - C_5H_{13})^+$ 213.1131, found 213.1144.

(*Z*)-2-Methyl-5-(dimethylphenylsilyl)-4-nonen-3-ol (44). According to the general procedure E, MeLi (0.09 mL, 1.5 M solution in Et_2O, 0.062 mmol) was added to the reaction flask. The diethyl ether was replaced with 0.25 mL of THF, and the flask was cooled to −40 °C. Silyl ether **40** (24 mg, 0.041 mmol) was added in 0.25 mL of THF to the cooled reaction flask, and the mixture was stirred at −40 °C for 1.5 h. Purification by flash chromatography on silica gel, eluting with hexanes to hexanes:diethyl ether 20:1, gave 9.5 mg (79%) of **44** as a colorless oil: IR (cm^{-1}, neat) 3431 (br, m), 3071 (w), 3051 (w), 2959 (s), 2924 (s), 2875 (s), 1469 (m), 1427 (m), 1251 (s), 1110 (s), 1005 (m), 836 (s), 814 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, m), 7.35 (3H, m), 5.99 (1H, d, J = 9.8 Hz), 3.72 (1H, ddd, J = 9.8, 6.8, 3.1 Hz), 2.12 (2H, m), 1.49 (1H, m), 1.32 (4H, m), 0.95 (1H, d, J = 3.1 Hz), 0.86 (3H, t, J = 7.0 Hz), 0.80 (3H, d, J = 6.6 Hz), 0.68 (3H, d, J = 6.9 Hz), 0.42 (3H, s), 0.40 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.48, 142.57, 139.96, 133.61 (2), 129.07, 127.97 (2), 75.49, 38.19, 33.73, 32.80, 22.51, 18.57, 18.08, 13.95, −0.68, −0.75; HRMS calcd for $C_{17}H_{27}OSi$ $(M - CH_3)^+$ 275.1831, found 275.1834.

(*E*)-1-(Tributylstannyl)-1-(triisopropylsilyl)-1-buten-3-ol (45). According to the general procedure E, MeLi (2.4 mL, 1.4 M in diethyl ether, 3.4 mmol) was added to a solution of silyl ether **41** (190 mg, 0.24 mmol) in 2.5 mL of THF at 0 °C. After stirring for 2.5 h at 0 °C, the mixture was warmed to rt for 1.5 h. Regular workup, followed by purification by flash chromatography on silica gel, eluting with hexanes:ethyl acetate 10:1, gave 49 mg (40%) of **45** as a colorless oil: IR (cm^{-1}, neat) 3405 (br, m), 2955 (s), 2925 (s), 2867 (s), 1463 (m), 1376 (m), 1071 (m), 881 (m); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.53 (1H, d, J = 8.9 Hz, J_{Sn-H} = 109.4 Hz), 4.24 (1H, m), 1.23 (3H, d, J = 6.1 Hz), 1.54−0.79 (49H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.47, 141.47, 70.49, 28.90, 27.25, , 22.66, 18.98, 13.77, 13.45, 11.73; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −20.08; HRMS calcd for $C_{25}H_{54}OSiSn$ $(M)^+$ 518.2949, found 518.2966.

(2*S,4*S**)-4-(Tributylstannyl)-4-(trimethylsilyl)-2-(triisopropylsiloxy)-1-methoxybutane (49).** According to the general procedure C, triisopropylsilyl chloride (77 mg, 0.40 mmol), the alcohol (154 mg, 0.33 mmol), and imidazole (60 mg, 0.35 mmol) were dissolved in 1 mL of dry DMF. The reaction mixture was stirred at rt for 48 h, diluted with diethyl ether, washed, and dried. Purification by flash chromatography on silica gel, eluting with hexanes:ethyl acetate 10:1, gave 117 mg (86%) of **49** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.95−3.67 (1H, m), 3.35−3.31 (2H, m), 3.31 (3H, s), 1.82−0.78 (50H), 0.42 (1H, dd, J = 8.7, 6.0 Hz), −0.01 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 76.95, 73.81, 58.95, 33.73, 29.17, 27.50, 13.49, 9.84, 18.05, 12.58, 6.68, −0.27.

(2*S,4*S**)-4-(Triisopropylsilyl)-4-(trimethylsilyl)-1,2-dimethoxybutane (50).** According to the general procedure E, MeLi (1.0 mL, 1.4 M in diethyl ether, 1.4 mmol) was added to a solution of substrate **49** (62 mg, 0.10 mmol) in 1 mL of THF at −78 °C. After 2.5 h of being stirred at −78 °C, the mixture was warmed to rt for 15 min and was then recooled to −78 °C. After addition of 1 mL of MeI, the mixture was slowly warmed to rt and stirred overnight. Regular aqueous workup, followed by purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, afforded 17 mg (49%) of **50** and 5 mg (14.5%) of **51**, both as a colorless oil: **50:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (1H, dd, J = 9.8, 7.3 Hz), 3.40−3.30 (2H, m, overlapping), 3.40, 3.34 (6H, s), 1.82−1.70 (2H, m), 1.10−1.03 (21H, m), 0.19 (1H, dd, J = 8.3, 5.5 Hz), −0.02 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.45, 73.76, 59.17, 57.47, 28.38, 19.67, 19.38, 12.68, 4.86, 1.83.

(2*S,4*R**)-4-(Triisopropylsilyl)-4-(trimethylsilyl)-1,2-dimethoxybutane (51):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.41 (3H, s), 3.33 (3H, s), 3.34−3.21 (3H, m), 1.82−1.50 (2H, m), 1.08−1.01 (21H, m), 0.51 (1H, dd, J = 9.8, 6.4 Hz), −0.03 (9H, s).

(2*S,3*R**)-3-(Tributylstannyl)-3-(trimethylsilyl)-2,3-epoxypropyl *tert*-Butyldimethylsilyl Ether (52).** According to the general procedure D, the epoxy alcohol (310 mg, 0.71 mmol) was dissolved in 5 mL of CH_2Cl_2, followed by addition of 2,6-lutidine (0.17 mL, 1.42 mmol), and cooled to 0 °C. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.18 mL, 0.78 mmol) was added, and the reaction mixture was stirred for 30 min at 0 °C. Regular workup, followed by flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1, gave 370 mg (95%) of **52** as a colorless oil: IR (cm^{-1}, neat) 2958 (s), 2928 (s), 2857 (s), 1461 (m), 1250 (s), 1115 (m), 1070 (m), 833 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (1H, dd, J = 11.4, 2.6 Hz), 3.41 (1H, dd, J = 11.4, 7.0 Hz), 3.15 (1H, dd, J = 7.0, 2.6 Hz), 1.45 (6H, m), 1.29 (6H, m), 0.90 (6H, m), 0.89 (9H, s), 0.87 (9H, t, J = 7.3 Hz), 0.08 (3H, s), 0.07 (3H, s), −0.00 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.66, 61.13, 55.46, 29.04 (J_{Sn-C} = 19.0 Hz), 27.43 (J_{Sn-C} = 60.0 Hz), 25.90, 18.32, 13.55, 10.74 (J_{Sn-C} = 316.0, 301.4 Hz), −2.83, −5.06, −5.33; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −27.55.

(2*S,3*R**)-3-(Triisopropylsilyl)-3-(trimethylsilyl)-2,3-epoxypropan-1-ol (53).** According to the general procedure E, silyl ether **52** (105 mg, 0.19 mmol) was dissolved in 2 mL of THF, and the reaction flask was cooled to −78 °C. MeLi (0.14 mL, 1.4 M solution in Et_2O, 0.19 mmol) was slowly added, and the reaction mixture was stirred at −78 °C for 10 min. Purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, gave 46.2 mg (93%) of **53** as a colorless oil: IR (cm^{-1}, neat) 3381 (br, m), 2952 (s), 2929 (s), 2860 (s), 1462 (m), 1251 (s), 1033 (s), 885 (m), 836 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (1H, ddd, J = 11.9, 8.8 (disappears with D_2O), 2.8 Hz), 3.62 (1H, ddd, J = 11.9, 8.2, 4.0 (disappears with D_2O) Hz), 3.19 (1H, dd, J = 8.2, 2.8 Hz), 1.87 (1H, dd, J = 8.8, 4.0 (disappears with D_2O) Hz), 0.93 (9H, s), 0.11 (3H, s), 0.06 (3H, s), 0.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 65.15, 62.13, 51.42, 27.62, 18.03, −1.59, −2.23, −2.43.

(*E*)-4-(Trimethylsilyl)-3-buten-2-yl Triisopropylsilyl Ether (54). A dry round-bottom flask, equipped with a stirbar and capped with a rubber septum, was flame-dried under a stream of nitrogen. NaH (0.4 mg, 60% in mineral oil, 0.01 mmol) was added quickly, and the solution was washed twice with 0.5 mL of dry pentane. In another flask, alcohol **42d** (30 mg, 0.10 mmol) was dissolved in 0.5 mL of dry DMF and transferred via cannula to the reaction flask. The reaction mixture was stirred at room temperature and monitored by TLC. After 15 min, saturated aqueous NH_4Cl was added, and the product was extracted with diethyl ether. The combined organic layer was washed three times with brine, dried over $MgSO_4$, and filtered. After concentration *in vacuo*, the crude product was purified by flash chromatography on silica gel, eluting with hexanes to hexanes:diethyl ether 20:1, affording 27 mg (90%) of **54** as a colorless oil: IR (cm^{-1}, neat) 2952 (s), 2868 (s), 1623 (w), 1462 (m), 1251 (m), 1138 (m), 1096 (s), 984 (m), 871 (s), 836 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.00 (1H, dd, J = 18.7, 5.3 Hz), 5.73 (1H, dd, J = 18.7, 1.2 Hz), 4.32 (1H, ddq, J = 6.3, 5.3, 1.2 Hz), 1.21 (3H, d, J = 6.3 Hz), 1.03 (21 H, m), 0.03 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.69, 126.93, 71.49, 24.38, 18.06, 18.04, 12.28, −1.33; HRMS calcd for $C_{15}H_{33}OSi_2$ $(M - CH_3)^+$ 285.2070, found 285.2062; HRMS calcd for $C_{16}H_{36}OSi_2$ $(M)^+$ 300.2305, found 300.2321.

Crossover Experiment of 37c and 38c. A dry round-bottom flask, equipped with a stirbar and capped with a rubber septum, was flame-dried under a stream of nitrogen. MeLi (0.077 mL, 1.5 M solution in diethyl ether, 0.11 mmol) was added to the flask. The diethyl ether was removed with a stream of nitrogen, and the flask was cooled to 0 °C. In another flask, a mixture of the substrates **37c** (19 mg, 0.032 mmol) and **38c** (26 mg, 0.045 mmol) was dissolved in 0.5 mL of THF. The latter solution was transferred via cannula to the cooled flask. The reaction was stirred at 0 °C for 45 min. Saturated aqueous NH_4Cl solution was added, and the product was extracted with diethyl ether. The combined organic layers were washed three times with brine, dried over $MgSO_4$, and filtered. After concentration *in vacuo*, the methyltributyltin was removed from the crude reaction mixture by flash chromatography on silica gel, eluting with hexanes. As soon as all the methyltributyltin was collected, elution was con-

tinued with hexanes:diethyl ether 1:1, and these next fractions were combined. Concentration *in vacuo* gave 20 mg (88%) of a colorless oil. Comparison of the ^{13}C NMR (100 MHz, $CDCl_3$) of the mixture, with the four possible pure, authentic products, **42a**, **42c**, **43b**, and **43c** showed only peaks corresponding with compounds **42c** and **43c**, arising from an intramolecular reaction, with no crossover products **43b** and **42a** observed.

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Supplementary Material Available: ^{13}C NMR spectra (35 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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