Diastereoselectivity in the Cyclopropanation of 3,3-Bimetallic Allylic Alcohols. Preparation of Diastereomeric Cyclopropyl Carbinols via a Simple Oxidation–Reduction Sequence

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A highly diastereoselective cyclopropanation of allylic alcohols, containing a silyl and/or stannyl group using samarium/dihalomethane, provides a variety of bimetallic cyclopropane carbinols in good yield. A comparison with the more traditional Simmons–Smith conditions and its variants is made. The diastereoselectivity varies from 1:10 to >50:1 and depends on the substituents on the carbinol side chain (R-group) and on the substituents on the alkene portion of the allylic alcohol. Excellent diastereoselectivity (>50:1) was always obtained whenever a *cis*-substituent was present. Moreover, the minor diastereomer from the cyclopropanation can easily be obtained via a simple oxidation of the major cyclopropyl carbinol, followed by a selective reduction of the corresponding cyclopropyl ketone. Using $LiAlH_4$ at 0 °C, facial selectivities of 15 to 20:1 are obtained for this reduction, while slightly higher selectivities up to (29:1) can be obtained using DIBAL-H. The combination of the cyclopropanation and oxidation/selective reduction sequence provides access to both diastereomeric bimetallic cyclopropanes.

Introduction

The cyclopropane unit is found as a structural element in a wide range of naturally occurring compounds isolated from plants and microorganisms.[2] Recently, the physiological importance of various substituted cyclopropyl amino acids as biologically active mimics of oligopeptides has initiated several new research programs.[3] Moreover, the use of cyclopropanes in mechanistic studies[4] and their utility as building blocks in organic synthesis[5] warrants the interest in these three-membered carbocycles from various fields in organic chemistry. Despite the many existing strategies for the efficient construction of cyclopropanes,[6] new or improved methodologies toward functionalized cyclopropanes are still sought. A myriad of investigations for the design and development of new, efficient methods for the selective synthesis of substituted cyclopropanes are ongoing.[7] In addition, procedures for the asymmetric synthesis of cyclopropanes have in the last ten years received significant attention.[6c,d,8–10]

Central to all these synthetic efforts is the ability to control the regio-, stereo-, and enantioselectivity of the

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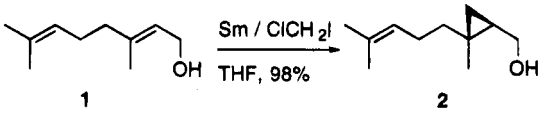
reaction. Heteroatom-directed reactions have proven to be an invaluable tool in aiding this goal.[11] Many reactions can be steered toward a specific site by taking advantage of a nearby, heteroatom-containing, functional group.[11b] Examples include the directed epoxidation,[12,13] dihydroxylation,[14] hydrogenation,[15] and many different directed carbo- and hydrometalation reactions,[16] which are extremely useful methods for the construction of multiple adjacent stereocenters. Directed cyclopropanation reactions are also well known and are of current interest.[17-23] Interactions between the heteroatom functionality and the reagent usually precedes the ensuing chemical transformation. A variety of functional groups can be used to deliver the reagent to its reaction site in a selective fashion.[11b] Due to its abundance in many natural and non-natural products and as a result of its high directing ability, the hydroxyl moiety is the most popular and most frequently used.

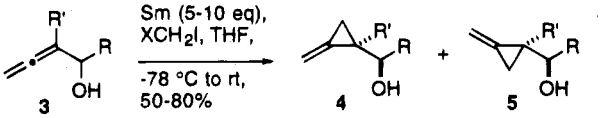
In 1958, Simmons and Smith reported that treatment of simple alkenes with a mixture of methylene iodide and zinc–copper couple results in the formation of cyclopropanes.[24] The reaction is not only high yielding, but also stereospecific with regard to the geometry of the olefin.[25,26] Since the early discovery of Simmons and Smith, several modifications for the cyclopropanation process emerged, using more activated and reliable zinc catalysts,[27] or a zinc–silver couple.[28] Diethylzinc has also proven to be advantageous in many cases[29] and has been the reagent of choice in recent reports on the asymmetric cyclopropanation.[10] Metals other than zinc have also successfully been used in the cyclopropanation. Both trialkylaluminum[30] and samarium[21] have been shown to cyclopropanate olefins in the presence of diiodomethane.

The directing potential of the hydroxyl moiety in these methylenation reactions is also well established.[17] Winstein and co-workers first noticed that cyclopropanation of 3-cyclopenten-1-ol with methylene iodide in the presence of a zinc–copper couple resulted in the *syn*-cyclopropyl carbinol as a single stereoisomer in 75% yield.[17a] Molander reported that a nearby hydroxyl moiety was necessary for the efficient cyclopropanation of allylic alcohols using samarium.[21] That is, in the cyclopropanation of geraniol (**1**), reaction of the olefin adjacent to the hydroxyl group occurs with > 95% selectivity (eq 1).



1 2 (1)

We later showed that, by taking advantage of the hydroxyl dependence of the reaction, a highly regioselective cyclopropanation of α-allenic alcohols is feasible (eq 2).[31]



3 4 5 (2)

R = alkyl, R' = H, Me, OMe 1 - 50 : 1

Furthermore, it was shown by Molander that the samarium-mediated cyclopropanation can be highly diastereoselective. The results of these studies may be summarized as follows: (*Z*)-olefins undergo diastereoselective cyclopropanation with diastereoselectivities >100:1 (eq 3). (*E*)-Olefins also undergo cyclopropanation with selectivities which increase as the steric size of R and R′ increases (eq 4). Excellent selectivities are obtained when R is large; however, when R is small, the facial selectivity is reversed and modest selectivities are ob-

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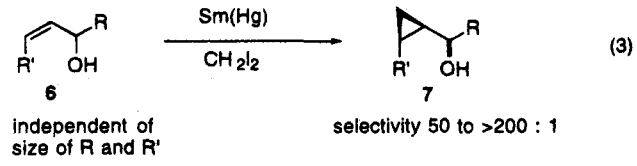
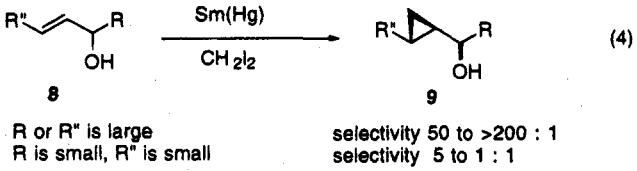
tained (approximately 1:4–6).





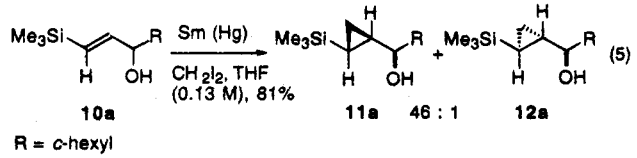
Objectives and Choice of Cyclopropanating Agent

In light of the demonstrated utility of silylated[32] and stannylated[33] cyclopropane and our interest in 1,1-dimetalated compounds bearing tin and/or silicon,[34] a study to evaluate the reactivity and diastereoselectivity of metalated olefins under the cyclopropanation reaction conditions was initiated.

While considering suitable procedures for the cyclopropanation of the tributyltin and/or trimethylsilyl substituted allylic alcohols, we were concerned about two potential problems. It has been reported that silyl-substituted olefins are less reactive under Simmons–Smith type cyclopropanation conditions than alkyl substituted alkenes,[32,35] and thus forcing conditions might be necessary with a *silicon and a tin* in the molecule. Secondly, the relatively weak carbon–tin bond might lead to destannylation under the reaction conditions (e.g. heating at reflux in the presence of zinc metal). After a brief comparison of the reported methods for cyclopropanation of allylic alcohols, we concluded that the samarium-derived carbenoids were suitable as an effective, relatively mild cyclopropanation. The samarium-mediated reaction occurs between −60 and −50 °C, in contrast to the diethylzinc and the zinc–copper procedures which are usually done between 0 °C and rt, and refluxing diethyl ether, respectively.

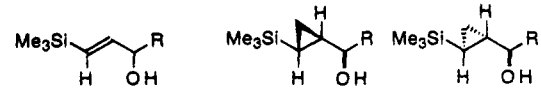
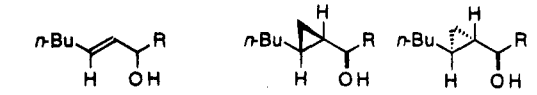
Results and Discussion

The optimum conditions for cyclopropanation were established using (*E*)-vinylsilane **10a** (eq 5). Under the conditions described by Molander (4 equiv of the samarium and the CH_2I_2 reagent), a low yield of the desired cyclopropane was obtained. By increasing to 10 equiv of the samarium reagent and running the reaction at a higher concentration (0.13 M), the yield improved to 81% and the diastereoselectivity was excellent, as **11a** and **12a** were obtained in a 46:1 ratio (see also Table 1, entry 1).

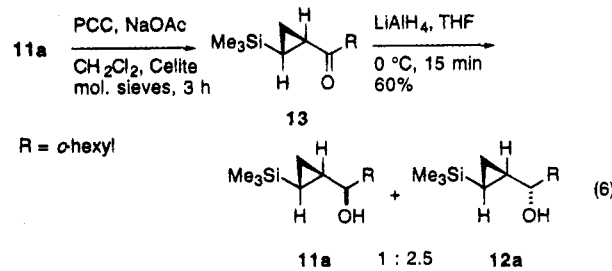


Since the cyclopropanation was highly diastereoselective, the minor product was obtained via an oxidation/nonselective reduction sequence (eq 6). Thus, PCC/NaOAc oxidation of the cyclopropyl alcohol **11a** to the ketone **13**, followed by nonselective reduction with $LiAlH_4$, generated authentic mixtures of diastereomers. Purification of the two alcohols **11a** and **12a**, which were well separated by flash chromatography, and comparison of their NMR spectra and GC retention times allowed us to determine the level of diastereoselection in the directed cyclopropanation of allylic alcohol **10a**.

Table 1. Directed Cyclopropanation of Disubstituted Allylic Alcohols

entry	substrate	products[a] diastereoselectivity			yield (%)[b]
					
		11		**12**	
1	**10a** R = *c*-hexyl	46	:	1	81
2	**c** *n*-Pr	1	:	1.3	84
3	**d** Me	1	:	10	76
					
		15		**16**	
4	**14a** R = *c*-hexyl	18	:	1	73
5	**b** *i*-Pr	5.5	:	1	85
6	**c** *n*-Pr	1.5	:	1	94
					
		18		**19**	
7	**17c** R = *n*-Pr	>100	:	1	67
8	**d** Me	>100	:	1	67

[a] The diastereoselectivity was measured by capillary GC (Carbowax HP 20M) on the crude mixture. [b] Isolated yields of pure product are reported.



Encouraged by the efficient and smooth cyclopropanation of **10a**, we investigated the effect of the R-group on the diastereoselectivity (Table 1, entries 1–3). Decreasing the steric bulk of the R-group from cyclohexyl to *n*-propyl to methyl affected the sense and level of diastereoselection. The diastereoselectivity *decreased and then reversed in this series*.

A similar trend, although less dramatic, was found for the (*E*)-alkyl-substituted alkenes **14a–c**. With the relatively bulky cyclohexyl group, a synthetically useful 18:1

(32) Paquette, L. A. *Chem. Rev.* **1986**, *86*, 733 and references therein.
(33) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1984**, *25*, 2415.
(34) (a) Lautens, M.; Huboux, A. H. *Tetrahedron Lett.* **1990**, *31*, 3105. (b) Lautens, M.; Huboux, A. H.; Chin, B.; Downer, J. *Tetrahedron Lett.* **1990**, *31*, 5829.
(35) Seyferth, D.; Burlitch, J. M.; Minasz, R. J.; Mui, J. Y.-P.; Simmons, H. D., Jr.; Treiber, A. J. H.; Dowd, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 4259.

mixture of **15a** and **16a** was obtained (Table 1, entry 4). However, a significant drop in selectivity, to a nearly equimolar mixture, was obtained using sterically less hindered R-groups (entries 5 and 6). The difference in selectivity observed upon changing from an *(E)*-Si to an alkyl substituent is noteworthy.

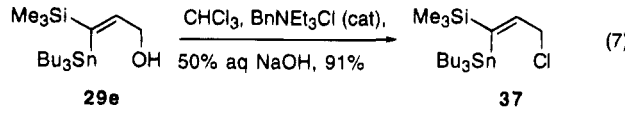
Substrates with a (*Z*)-substituent react to give the cyclopropanes in much higher selectivity than those with only an (*E*)-substituent, and the selectivity is not dependent on the size of the R-group. Thus, vinylsilanes **17c,d** were converted into **18c,d** with diastereoselectivities of >100:1 (Table 1, entries 7 and 8).

Trisubstituted olefins, bearing a trialkyltin and alkyl group, react smoothly with the cyclopropanating agent to yield a single diastereomer in good yield (Table 2, entries 1–6). While tributyl was usually used as the tin substituent, cyclopropanation of the analogous (*E*)-trimethyltin olefin **23a** was also successful (Table 2, entry 3). Both geometric isomers **20** and **26** undergo smooth cyclopropanation equally well. While the (*E*)-tributylstannyl allylic alcohols **20** react cleanly, destannylation was sometimes a problem with (*Z*)-tributylstannyl substrates **26** (entries 4–7).

The factors influencing the destannylation were investigated. The amount of destannylation varied somewhat depending on the batch of samarium. In one instance, treatment of **26a** gave 27% of the desired product **27a**, along with 58% of **15a**. Typically **27a** (63% yield) predominates with less than 5% of the destannylated product **15a**. Moreover, when destannylation was observed, the amount of undesired product depended on the size of the R-group. For example, using the same batch of samarium, the amount of destannylation diminished with decreasing size of R-group; 58% for R = cyclohexyl, 8% for R = *i*-Pr, 0% for R = *n*-Pr, Me. The destannylation of these (*Z*)-stannyl allylic alcohols and a similar dependence on the R-group was also observed in the rhodium-catalyzed hydrogenation.[36] The origin of this problem is not clear, but differences in activity between the source of Zn and Sm has been noted previously.[21,27c]

Other 1,1-bimetallic olefins including **29a–e**, **32a**, **32e** and **35** were examined (Table 2, entries 8, 12–14, 18, 20, and 21). The allylic alcohols **29**, bearing a tin and a silicon group and the distannyl substrates **32**, react smoothly with the samarium carbenoid. Single diastereomers were obtained in all cases in good yield and destannylation was never a problem. Cyclopropanation of the disilyl alkene **35**, however, was very sluggish and only 14% of the product **36** could be isolated, together with 41% of the unreacted **35** (entry 21). This result is not surprising, since it is our experience that the samarium-mediated cyclopropanations are sensitive to steric hindrance. The substrate **35** bears a bulky (*i*-Pr)$_3$Si-group which interferes with the incoming carbenoid. Decomposition of the samarium carbenoid becomes the major pathway and is believed to occur either via insertion into the O–H bond or via dimerization of two samarium carbenoids to form ethylene.[21b]

For a few substrates, a comparison with other cyclopropanating procedures was made (Table 2). When allylic alcohol **29a** was reacted with zinc–copper couple in refluxing diethyl ether, destannylation occurred predominantly (Table 2, entry 9). Also, reaction with samarium diiodide and chloroiodomethane did not result in any of the desired cyclopropane and only starting material was recovered (entry 10). In contrast, the primary allylic alcohol **29e** reacted smoothly under the same conditions (entry 15). Apparently, the SmI_2-mediated cyclopropanation conditions are much more sensitive to steric effects than when metallic samarium is used. Attempted dichlorocyclopropanation of **29e**, using dichlorocarbene, generated from $CHCl_3$, NaOH, and the phase transfer agent $BnNEt_3Cl$,[23] did not give any of the cyclopropanated product and instead the bimetallic allyl chloride **37** was isolated (eq 7).



29e **37** (7)

The reluctance of this type of alkene to undergo cyclopropanation can be ascribed to the silyl and perhaps also the stannyl substituent. While alkyl-substituted alkenes are smoothly converted to the dichlorocyclopropane,[23] a monosilyl-substituted olefin did not react under these conditions.[37]

A successful cyclopropanation was also obtained using Denmark's improved diethyl zinc conditions.[29d] Treatment of **29a** with premixed diethylzinc and chloroiodomethane in 1,2-dichloroethane at 0 °C afforded the bimetallic cyclopropane **30a** in 80% yield, along with 9% of the destannylated product **11** (entry 11). Analysis of the crude reaction mixture by ^{1}H NMR showed that the diastereoselection exceeded 50:1. Other bimetallic stannyl-silyl and distannyl substrates reacted with good chemo- and stereoselectivity (entries 16 and 19).

Transition state structures with the hydroxyl group pointing "outside" can be used as a working model to explain the observed diastereoselectivities (Scheme 1). Pereyre, and later Molander, used this model to explain the diastereoselection for the zinc- and samarium-catalyzed cyclopropanations of allylic alcohols, respectively.[21a,b,22] *Ab initio* calculations by Houk supported these models and they are now often referred to as "the outside Houk model".[38] In this model the hydroxyl moiety, which delivers the carbenoid, and the olefin are at an angle of approximately 150°. The observed diastereoselectivity for the (*Z*)-isomer can then be rationalized as follows. Minimization of steric interactions between the R group and the *cis* substituent, coupled with complexation between the hydroxyl group and the incoming carbenoid, differentiates the two possible transition structures **38** and **39**. Thus, the (*Z*)-alkyl or (*Z*)-tributyltin group controls the diastereoselectivity by minimizing the allylic strain in the reactive rotamer.[39]

For the (*E*)-allylic alcohols, little diastereoselectivity was observed for substrates in which both R and R″ are relatively small groups (Table 1, entries 2 and 6). For these cases the allylic interaction between the R-group and the substituent on the olefin is minimal. However,

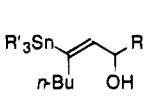
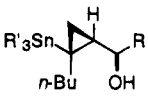
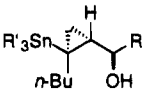
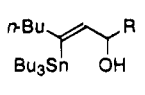
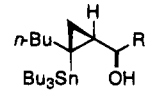
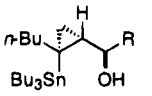
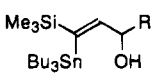
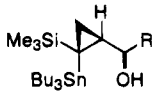
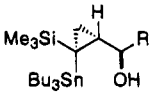
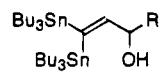
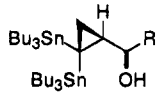
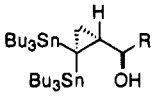
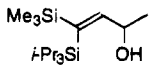
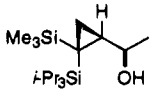
(36) (a) Lautens, M.; Zhang, C. H.; Crudden, C. M. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 232. (b) Lautens, M.; Zhang, C. H.; Crudden, C. M.; Goh, B. J.; Johnson, M. J. A. *J. Org. Chem.* **1994**, *59*, 6208.

(37) Trost, B. M.; Tour, J. M. *J. Org. Chem.* **1989**, *54*, 484.

(38) (a) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162. (b) Houk, K. N.; Rondan, N. G.; Wu, Y.-D.; Metz, J. T.; Paddon-Row, M. N. *Tetrahedron* **1984**, *40*, 2257. (c) Mareda, J.; Rondan, N. G.; Houk, K. N.; Clark, T.; R von Schleyer, P. *J. Am. Chem. Soc.* **1983**, *105*, 6997.

(39) For a recent review on allylic strain, see: Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841.

Table 2. Directed Cyclopropanation of Trisubstituted Allylic Alcohols

entry	substrate	conditions	products/diastereoselectivity[a]			yield(%)[b]
						
			21 (R' = *n*-Bu)		**22**	
			24 (R' = Me)		**25**	
1	**20a** R = *c*-hexyl, R' = *n*-Bu	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	75
2	**d** Me *n*-Bu	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	76
3	**23a** *c*-hexyl Me	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	70
						
			27		**28**	
4	**26a** R = *c*-hexyl	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	63 (27)[c]
5	**b** *i*-Pr	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	89
6	**c** *n*-Pr	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	77
7	**d** Me	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	81
						
			30		**31**	
8	**29a** R = *c*-hexyl	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	80
9	**a**	Zn(Cu), CH_2I_2, Et_2O, 35 °C		--		--[d]
10	**a**	SmI_2, $ClCH_2I$, THF, -78 °C to rt		--		0
11	**a**	Et_2Zn, $ClCH_2I$, 1,2-DCE, 0 °C	>50	:	1	80[e]
12	**c** *n*-Pr	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	67
13	**d** Me	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	85
14	**e** H	Sm(Hg), CH_2I_2, THF, -78 °C to rt		--		90
15	**e**	SmI_2, $ClCH_2I$, THF, -78 °C to rt		--		81
16	**e**	Et_2Zn, $ClCH_2I$, 1,2-DCE, 0 °C		--		65
17	**e**	$CHCl_3$, 50 % NaOH, $BnNEt_3Cl$	The allylic chloride was obtained, see text			0
						
			33		**34**	
18	**32a** R = *c*-hexyl	Sm(Hg), CH_2I_2, THF, -78 °C to rt	>50	:	1	71
19	**a**	Et_2Zn, CH_2I_2, CH_2Cl_2, 0 °C	>50	:	1	92
20	**e** H	Sm(Hg), CH_2I_2, THF, -78 °C to rt		--		77
						
21	**35**	Sm(Hg), CH_2I_2, THF, -78 °C to rt	**36**			14[f]

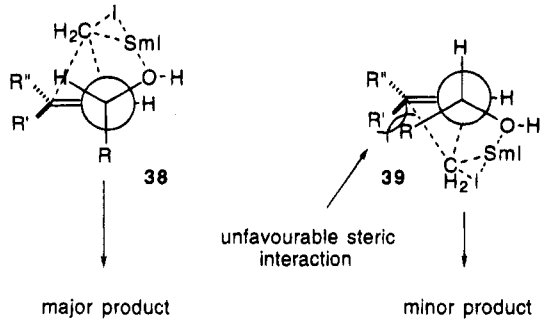
[a] The diastereoselectivity was measured by ^1H NMR (400 MHz) on the crude mixture; no minor product could be observed. [b] Isolated yields of pure product are reported. [c] Using one batch of samarium only 27% of **27** was obtained, together with 58% of destannylated product **15a**. [d] Only destannylated product was observed. [e] 9% of the destannylated product **11a** was also obtained. [f] 41% of starting material was also recovered.

as the R-group was increased in size to cyclohexyl, good selectivities were again obtained. It can be argued that the bulky cyclohexyl group prefers to occupy the position perpendicular to the alkene compared to an inside position. This would certainly avoid steric interactions with the incoming carbenoid and perhaps also with the olefin. This increase of the energy difference between conformations **38** and **39** then leads to the formation of the major isomer. It is not yet clear why there is a more pronounced diastereoselectivity for the cyclopropanation ofthe (*E*)-silyl alkene **10a** (46:1) over the (*E*)-*n*-butyl alkene **14a** (18:1) (Table 1, compare entries 1 and 4). Unfortunately, the reversal of selectivity in the case where R = Me (Table 1, entry 3) cannot be readily explained by this model and is not entirely understood.

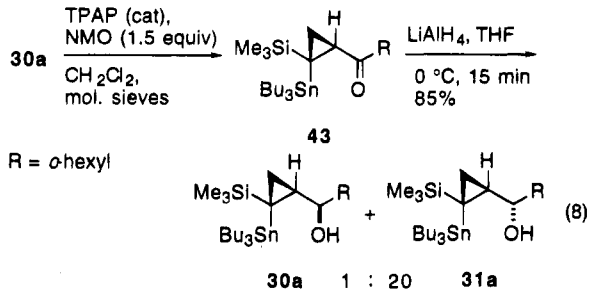
A sufficiently large body of data is now available so that the "outside Houk model" can be used as a reliable tool to predict diastereoselection in the Zn(Cu)-, Et_2Zn-, and Sm(Hg)-promoted cyclopropanations for all (*Z*)-substituted and many (*E*)-substituted allylic alcohols.

Diastereoselective Reduction of Cyclopropyl Ketones. As was discussed earlier, in many of the highly

Scheme 1



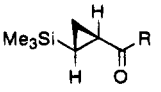
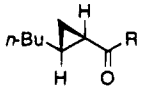
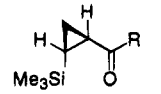
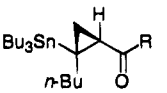
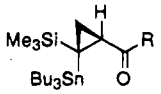
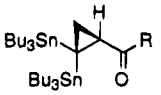
stereoselective cyclopropanations, the minor product was obtained via an oxidation/nonselective reduction sequence. However, attempted NaOAc-buffered PCC oxidation of the stannyl-substituted cyclopropyl alcohols **27**, **30**, and **33** to the corresponding ketones was not efficient and led to destruction of the molecule under the reaction conditions.[40] Fortunately, the tetrapropylammonium perruthenate (TPAP)/4-methylmorpholine *N*-oxide (NMO) oxidation procedure was mild enough to obtain the desired ketones (eq 8).[41] A nonselective $LiAlH_4$ reduction was anticipated which would give access to the minor diastereomer after flash chromatography.



When the stannyl cyclopropyl ketone **43** was treated with $LiAlH_4$ in THF at 0 °C, a smooth reduction of the ketone occurred, without any detectable destannylation. However, analysis of the crude product mixture by ^1H NMR (400 MHz) revealed that the hydride addition had occurred with high diastereoselectivity! *Importantly, the major product produced from the $LiAlH_4$ reduction is the minor product resulting from the highly selective cyclopropanation.* Thus, both diastereomeric cyclopropyl ketones **30a** and **31a** are now readily available.

A study was executed to provide insight on the factors governing this selectivity (Table 3).[42] While reduction of the disubstituted (*E*)-trimethylsilyl and (*E*)-butylcyclopropyl ketones **13** and **40a,b** was virtually nonselective (entries 1–3), treatment of the (*Z*)-silyl cyclopropyl ketone **41** gave a 15:1 mixture of **19c** and **18c** (entry 4). Hydride delivery to the trisubstituted cyclopropyl ketones **42–44** afforded both cyclopropyl alcohols in 15–20:1 selectivity in nearly quantitative yield (entries 5–7). For all cases examined, the diastereomeric alcohols were easily separated by flash chromatography on silica gel. Comparison of the ^1H and ^{13}C NMR spectra of these cyclopropyl carbinols with the crude spectra obtained after cyclopropanation, allowed us to determine the level of diastereoselection in the directed cyclopropanation of these tin-substituted allylic alcohols.

Table 3. Diastereoselective Reduction of Cyclopropyl Ketones

entry	substrate	conditions[a]	products	de[b]	yield (%)[c]
			**11a** : **12a**		
1	**13** R = *c*-hexyl	$LiAlH_4$, 0 °C	1 :	2.5	60
			**15a** : **16a**		
2	**40a** R = *c*-hexyl	$LiAlH_4$, 0 °C	1 :	1	92
3	**b** *i*-Pr	$LiAlH_4$, 0 °C	1 :	1	62
			**18c** : **19c**		
4	**41** R = *n*-Pr	$LiAlH_4$, 0 °C	1 :	15	48
			**21a** : **22a**		
5	**42** R = *c*-hexyl	$LiAlH_4$, 0 °C	1 :	15	88
			**30a** : **31a**		
6	**43** R = *c*-hexyl	$LiAlH_4$, 0 °C	1 :	20	85
			**33a** : **34a**		
7	**44** R = *c*-hexyl	$LiAlH_4$, 0 °C	1 :	17	88

[a] All reaction were performed in THF. [b] The diastereoselectivity was measured by ^1H NMR (400 MHz) on the crude mixture. [c] Isolated yields of pure product are reported.

Stereocontrol in the reduction of acyclic ketones is governed by nearby stereocenters and the facial preference can often be predicted on the basis of an analysis of the reactive conformation in the transition state.[42] For the 1,2-addition of nucleophiles to ketones flanked by an adjacent stereocenter, several models have been formulated to predict the stereochemical outcome of the reaction. The Felkin–Ahn model **45**[43] is used when the α-stereocenter contains nonpolar or nonchelating groups, while for α-heteroatom-substituted carbonyl compounds Cram's cyclic (or chelate) model **46**[44] is usually applicable (Figure 1).

(40) The presence of a substituent appears to be responsible for these side reactions, see: Piers, E.; Jean, M.; Marrs, P. S. *Tetrahedron Lett.* **1987**, *28*, 5075.

(41) (a) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1625. (b) Griffith, W. P.; Ley, S. V. *Aldrichim. Acta* **1990**, *23*, 13.

(42) For reviews and recent accounts on chelated and nonchelated nucleophilic additions to unsymmetrical carbonyls, see: (a) Oishi, T.; Nakata, T. *Acc. Chem. Res.* **1984**, *17*, 338. (b) Reetz, M. T. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 556. (c) Málek, J. *Org. React.* **1985**, *34*, 1. For some recent leading references, see: (d) Reetz, M. T.; Hüllmann, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1600. (e) Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 908. (f) Marshall, J. A.; Tang, Y. *J. Org. Chem.* **1993**, *58*, 3233.

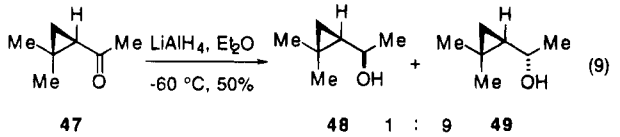
(43) (a) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. (b) Cherest, M.; Prudent, N. *Tetrahedron* **1980**, *36*, 1599. (c) Anh, N. T.; Eisenstein, O. *Nouv. J. Chem.* **1977**, 61. (d) Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145.

(44) Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748.

Figure 1. Models used to predict the stereochemical outcome in the reduction of ketones bearing an α-stereocenter.

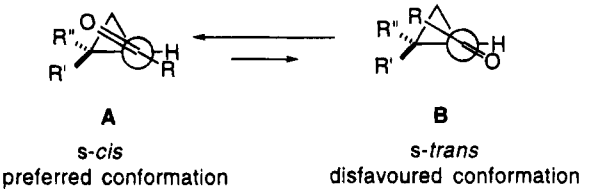
The diastereoselectivity in the nucleophilic reduction of ketones α-substituted by a small ring have also been studied. α,β-Epoxy-[45] and α,β-aziridine[46] substituted ketones and aldehydes are special cases of the α-heteroatom-substituted carbonyl compounds. Consequently, under chelation controlled conditions, 1,2-addition reactions to α,β-epoxy- and α,β-aziridine carbonyls proceed with good stereoselectivity. However, a survey of the literature revealed that only two groups have briefly reported on the selective reduction of cyclopropyl ketones.[21c,47,48]

In an isolated example, a French group reported that, treatment of the trisubstituted cyclopropyl ketone **47** with $LiAlH_4$, resulted in a 9:1 diastereomeric mixture of the cyclopropyl carbinols **48** and **49** (eq 9).[47] Later, Kitazume reported that trifluoromethyl cyclopropyl ketones can be reduced with good diastereoselectivities, using L-selectride. However, no specific selectivities were mentioned and the major cyclopropyl carbinols were obtained in only 37−46% yield.[21c]

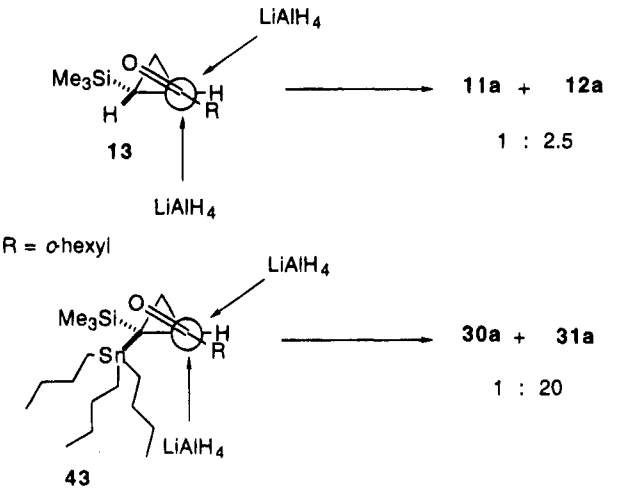


If the conformation of the transition state of reduction is similar to that of the substrate, then an understanding of the factors which control the conformation can be helpful in order to explain the observed selectivity in the reduction. The ability of the cyclopropyl group to conjugate with the carbonyl π-system has been proposed.[49] Delocalization of electrons is possible via overlap between the cyclopropyl C−C bonds and the carbonyl π-orbitals. The degree of conjugative interaction in cyclopropyl ketones is dependent on the relative orientations of the carbonyl and the cyclopropyl group. Interaction between the cyclopropyl C−C bonds and the carbonyl π-orbitals is maximized when the cyclopropane and the carbonyl are oriented orthogonally. Both the *s*-(*cis*)-conformation **A** and *s*-(*trans*)-conformation **B** in **50** are able to provide maximum stabilization (Scheme 2).[50]

Scheme 2



Scheme 3



Computational studies indicate that the *s*-(*cis*)-conformation **A** is favored by 1.6−3.0 kcal mol^{-1} over the *s*-(*trans*)-conformation **B**, depending on the substitution pattern on the cyclopropane.[50b] For unsubstituted and (*trans*)-substituted cyclopropyl ketones the energy difference was found to approximately 1.6 kcal mol^{-1}, while in the (*cis*)-substituted cyclopropyl ketones an energy difference of 3.0 kcal mol^{-1} was reported in favor of the *s*-(*cis*)-conformer (Scheme 2). However, these studies conclude that conjugative overlap is not a significant factor. Further studies in our lab may provide information on this issue.

The *s*-(*cis*)-conformer can be used as a model for the reduction of the cyclopropyl ketones (Scheme 3). It can be seen that in the case of the (*E*)-cyclopropyl ketone **13**, no facial preference for reduction of the ketone is expected. That is, the nucleophilic hydride experiences nearly similar steric hindrance on both sides of the cyclopropyl ketone and a modest 2.5:1 selectivity toward **12** is obtained. This is in contrast to the (*Z*)-substituted cyclopropyl ketone **43**, where a steric interaction between the (*Z*)-tributylstannyl substituent and the incoming hydride disfavors attack from one face of the ketone. Consequently, hydride attack will preferentially come from the less hindered side to form the diastereomer **31a**. Just as in the cyclopropanation of the bimetallic allylic alcohols, it is the (*Z*)-tributylstannyl group which controls the diastereoselectivity in these cyclopropyl ketone reductions. Thus either diastereomeric cyclopropylcarbinol can now easily be obtained via a cyclopropanation, or an oxidation/reduction sequence if the other diastereomer is desired.

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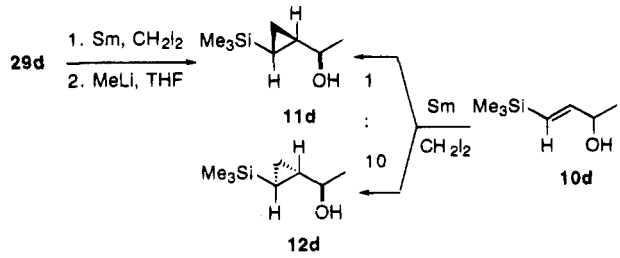
(47) Rocquet, F.; Sevin, A.; Chodkiewicz, W. *C. R. Seances Acad. Sci. Ser. C* **1970**, *270*, 848.

(48) For a diastereoselective reduction of methylenecyclopropane ketones, see: Audo, D.; Vincens, M.; Dumont, C.; Vidal, M. *Can. J. Chem.* **1981**, *59*, 2199.

(49) (a) Schaffner, K.; Snatzke, G. *Helv. Chim. Acta* **1965**, 347. (b) Djerassi, C.; Klyne, W.; Norin, T.; Ohloff, G.; Klein, E. *Tetrahedron* **1965**, *21*, 163. (c) Monti, S. A. *J. Org. Chem.* **1970**, *35*, 380.

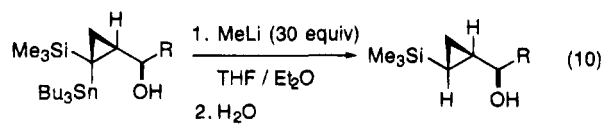
(50) (a) Pelissier, M.; Serafini, A.; Devanneaux, J.; Labarre, J.-F.; Tocanne, J.-F. *Tetrahedron* **1971**, *27*, 3271. (b) Tocanne, J.-F. *Tetrahedron* **1972**, *28*, 389. (c) Aroney, M. J.; Calderbank, K. E.; Stootman, H. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1365. (d) Andrieu, C. G.; Lemarié, B.; Paquer, D. *Org. Magn. Reson.* **1974**, *6*, 479. (e) Fournier, C.; Lemarié, B.; Braillon, B.; Paquer, D.; Vazeux, M. *Bull. Soc. Chim. Fr.* **1980** (II), 463.

Scheme 4



Determination of the Relative Stereochemistry. It is clear that for the allylic alcohols bearing a substituent *syn* to the hydroxy alkyl moiety, the major product of the cyclopropanation can easily be predicted from an analysis of the transition state models for the cyclopropanation (Scheme 1). This method can be confidently used irrespective of the size of the alkyl groups and is well precedented.[21a,b,22,38] However, for the (*E*)-substituted allylic alcohols, the factors which control the diastereoselectivity in the cyclopropanation procedure are not obvious. Furthermore the selectivity is highly dependent on the size of the R- and R″-substituents. A tentative assignment was made for the major and minor diastereomers **11** and **12** (Table 1), based on R_f values and CGC retention times. An unequivocal confirmation of these proposed structures was obtained via independent syntheses of **11a** and **11d**, from the stereochemically defined cyclopropyl stannanes **30a** and **30d** which was used to confirm the relative stereochemistry.

Treatment of **30a** with excess methyllithium, led to very slow tin−lithium exchange (eq 10). Quenching of the dianion with water gave **11a** in 50% yield, rather than **12a** as demonstrated by comparison of the ^{1}H NMR spectra and CGC retention times. Similarly, when **30d** was exposed to the transmetalation/protonation sequence, **11d** was obtained in 40% yield. This confirmed the tentative assignment of the major and minor diastereomer and proved that there was indeed a reversal in the major diastereomeric product with decreasing R-group (Table 1, entries 1−3).



30a R = *c*-hexyl **11a** 50%
d Me **d** 40%

In addition to its value in determining the relative stereochemistry of some reactions, the transmetalation−protonation sequence offers further benefits. Comparison of the selectivity in the cyclopropanation of **10d** and **29d** (compare Table 1, entry 3 and Table 2, entry 13) demonstrates that replacement of a hydrogen by a tin moiety completely reverses the sense of diastereoselection. Access to **11d**, the diastereomer which is not available from a direct cyclopropanation, is feasible by removal of the tin moiety following cyclopropanation of **29d** (Scheme 4). Thus, the tin moiety acts as a removable diastereoselectivity controller group.

A detailed investigation of the factors influencing the transmetalation and its synthetic utility will be described shortly.

Summary

Metalated allylic alcohols, bearing a tin and/or silicon group, can be cyclopropanated in very good yields, providing functionalized metallic- and bimetallic cyclopropanes. (*Z*)-substituted allylic alcohols provide excellent levels of diastereoselectivity independent of the size of the R-group, while (*E*)-substituted alkenes afford very good diastereomeric excesses for R = cyclohexyl, moderate diastereoselectivities are obtained when R = *n*-Pr or Me. The minor products from the cyclopropanation of (*Z*)-substituted olefins can be obtained via a simple oxidation-reduction sequence.

Experimental Section

General Information. Unless stated otherwise commercial reagents were used without purification. Tetrahydrofuran was distilled immediately prior to use from sodium wire/benzophenone. Diiodomethane was distilled from copper powder at reduced pressure. Samarium metal (<40 mesh) was purchased from Rhône-Poulenc, Shelton, CT. The (*E*)-alkyl allylic alcohols **14a−c** were prepared according to a literature procedure.[51] The (*E*)-silyl allylic alcohols **10a−d** were prepared using a literature procedure, developed by Sato *et al.*[52] The (*E*)-stannyl-alkyl- and 1,1-bimetallic substrates **20a,d**, **23d**, **29a,c−e**, and **32a,e** were prepared using a modification of this reaction.[34a] The (*Z*)-stannyl allylic alcohol **26a−d** were prepared by the palladium-catalyzed hydrostannation of the ynone,[53] followed by reduction of the enone to the allylic alcohols.[54] Vinylsilanes **17c,d** were prepared by partial cis-hydrogenation of the silyl acetylenes.[55]

General Spectroscopic Information. Diastereomeric ratios were determined with a Hewlett Packard 5890A gas chromatograph, equipped with a Carbowax HP-20M or a Silicone HP-5 column and connected with a Hewlett Packard 3396A integrator, for the non-tin-containing compounds. All runs were executed isothermally, with the oven temperature between 75−150 °C. Ratios were determined on the crude reaction mixture prior to chromatography, and retention times were compared with the separated pure diastereomers. For the tin-containing compounds, the diastereomeric ratios were determined by integration of the carbinol hydrogen in the ^{1}H NMR-spectrum (400 MHz) of the crude reaction mixture, prior to chromatography.

General Procedure A for the Cyclopropanation with Samarium/Diiodomethane. To a dry round bottom flask, equipped with a stirbar and capped with a rubber septum, was added samarium metal. The flask containing the samarium was flame-dried, while flushing with nitrogen. After the flask was allowed to cool to room temperature, mercuric chloride (10 mol % based on samarium) was added quickly, followed by half of the total volume of THF. The grey suspension was stirred for 10 min. The allylic alcohol was dissolved in an equal volume of THF and transferred via cannula to the flask. The flask was cooled to −78 °C, and diiodomethane was added dropwise. The mixture was allowed to warm to room temperature over 2 h and stirred for an additional 2−4 h. The viscous dark blue reaction mixture was quenched with a saturated aqueous K_2CO_3 solution and extracted two times with diethyl ether. The combined organic layer was washed three times with brine, dried over anhydrous $MgSO_4$, and filtered. Concentration of the crude product was done *in vacuo* or by short path distillation for volatile substrates. Purification was executed by flash chromatography on silica gel, followed by kugelrohr distillation for volatile substrates.

General Procedure B for the Cyclopropanation with Samarium Diiodide/Chloroiodomethane. To a dry round bottom flask, equipped with a stirbar and capped with a rubber septum, was added samarium metal (10 equiv). The flask

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(53) Piers, E.; Tillyer, R. D. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2124.
(54) Gemal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.
(55) Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553.

containing samarium was flame-dried, while flushing with nitrogen. After the flask was allowed to cool to room temperature, diiodoethane (10 equiv) was added in dry THF. The mixture was stirred at 0 °C for 1 h and after the solution had turned dark blue, for another 2–5 h at rt. The allylic alcohol was dissolved in THF and transferred via cannula to the flask and stirred for 30 min at rt. The flask was cooled to −78 °C, and chloroiodomethane was added dropwise. The mixture was allowed to warm to room temperature over 2 h, and stirred for an additional 2–4 h. Regular aqueous work up as in procedure A and purification by flash chromatography afforded the pure product.

General Procedure C for the Cyclopropanation with Diethylzinc/Dihalomethane.[29d] To a dry round bottom flask, equipped with a stirbar and capped with a rubber septum, was added dichloroethane. The flask was cooled to 0 °C and diethylzinc (2 equiv) was added, followed by dropwise addition of dihalomethane (4 equiv). The mixture was stirred at 0 °C for 5–10 min. The allylic alcohol was dissolved in dichloroethane and added via cannula to the flask and stirred for 15 min at 0 °C. Saturated aqueous NH_4Cl was added, and the mixture was extracted two times with diethyl ether. The combined organic layer was washed three times with brine, dried over anhydrous $MgSO_4$, and filtered. After concentration of the crude product *in vacuo*, purification by flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1, afforded the pure product.

General Procedure D for the PCC Oxidation. A round bottom flask, equipped with a stirbar and capped with a rubber septum was flame-dried under a stream of nitrogen. The cyclopropyl alcohol (1 equiv) was dissolved in dry CH_2Cl_2 and NaOAc (1.5–2.5 equiv), Celite (5 times wt % of PCC), and 4 Å molecular sieves (0.5 wt % of PCC) were added consecutively. The reaction mixture was cooled to 0 °C and pyridinium chlorochromate (PCC, 2–3 equiv) was added quickly. The reaction was stirred for 15 min at 0 °C and allowed to warm to room temperature for 2–6 h. The reaction was followed by TLC and when finished, the dark brown, crude reaction mixture was filtered through a short column of silica gel, eluting with CH_2Cl_2. The resulting colorless solution was concentrated *in vacuo*, and the crude mixture was purified by flash chromatography on silica gel.

General Procedure E for the TPAP/NMO Oxidation.[41] A round bottom flask, equipped with a stirbar and capped with a rubber septum, was flame-dried under a stream of nitrogen. The cyclopropyl alcohol (1 equiv) was dissolved in dry CH_2Cl_2 and 4-methylmorpholine *N*-oxide (NMO), and 4 Å molecular sieves (100 wt % of cyclopropyl carbinol) were added consecutively. The reaction mixture was stirred for 10 min and a catalytic amount of tetrapropylammonium perruthenate (TPAP) was added quickly. The reaction was followed by TLC and was usually finished in 3–4 h. The crude reaction mixture was filtered through a short column of silica gel, eluting with CH_2Cl_2 and concentrated *in vacuo*.

General Procedure F for the $LiAlH_4$ Reduction. The ketone was dissolved in dry THF in a round bottom flask, equipped with a stirbar. The solution was cooled to 0 °C, and $LiAlH_4$ was added in one portion. The suspension was stirred for 10 min at 0 °C and then saturated aqueous NH_4Cl was added. The mixture was extracted three times with diethyl ether, and the combined ethereal layers were washed with aqueous saturated Rochelle's salt and brine. After drying over $MgSO_4$, filtration and concentration *in vacuo*, the crude product was obtained. ^1H NMR (400 MHz) on the crude mixture was used to determine the diastereomeric excess. Flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1, afforded the pure product.

General Procedure G for the Tin–Lithium Exchange Followed by Protonation. A schlenk flask, capped with a rubber septum, was flame-dried while flushing with nitrogen. Methyllithium (30 equiv) was added in diethyl ether to the schlenk flask. The diethyl ether was removed with a vacuum pump, 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 nitrogen atmosphere, was added the stannylcyclopropane (1 equiv). Methyllithium in THF was transferred via cannula to the cyclopropane. The reaction mixture was stirred for 24 h at rt, quenched with saturated aqueous NH_4Cl solution, and 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.

Cyclopropanation of (*E*)-1-Cyclohexyl-3-(trimethylsilyl)-2-propen-1-ol (10a). According to the general procedure A, allylic alcohol **10a** (0.45 g, 2.1 mmol) was reacted with samarium (3.2 g, 21.2 mmol) and CH_2I_2 (1.6 mL, 20.0 mmol) in 15 mL of THF. After workup, 0.39 g (81%) of a colorless oil was obtained as a 46:1 mixture of **11a** and **12a**, as determined by GC-analysis. Flash chromatography on silica gel, eluting with 15:1 hexanes:diethyl ether, afforded the pure major diastereomer **11a**.

(*R)-[(1*S**,2*R**)-2-(Trimethylsilyl)cyclopropyl]cyclohexylmethanol (11a):** R_f = 0.39 on silica gel (4:1 hexanes:diethyl ether); GC retention time = 11.6 min (150 °C); IR (cm^{-1}, neat) 3379 (br, m), 3058 (w), 2994 (m), 2952 (s), 2925 (s), 2853 (s), 1450 (m), 1248 (s), 1045 (m), 849 (s), 835 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 2.59 (1H, ddd, J = 8.8, 5.0, 2.9 Hz (disappears with D_2O)), 1.82–1.63 (4H, m), 1.53–1.41 (1H, m), 1.44 (1H, d, J = 2.9 Hz (disappears with D_2O)), 1.25–1.07 (6H, m), 0.83 (1H, dddd, J = 8.8, 7.2, 6.5, 4.4 Hz), 0.43 (1H, ddd, J = 10.1, 4.4, 3.8 Hz), 0.38 (1H, ddd, J = 7.2, 6.9, 3.8 Hz), −0.06 (9H, s), −0.45 (1H, ddd, J = 10.1, 6.9, 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 82.48, 44.15, 29.12, 28.19, 26.47, 26.18 (2), 19.64, 6.15, 2.57, −2.60; HRMS calcd for $C_{13}H_{25}OSi$ (M − H)$^+$ 225.1675, found 225.1667. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.79; H, 11.67.

(*S)-[(1*S**,2*R**)-2-(Trimethylsilyl)cyclopropyl]cyclohexylmethanol (12a).** According to procedure D, **37a** (20 mg, 0.09 mmol) was dissolved in 2.5 mL of CH_2Cl_2. Celite (290 mg), molecular sieves (29 mg), and NaOAc (18 mg, 0.23 mmol) were added consecutively. To the cooled suspension was added PCC (58 mg, 0.27 mmol), and the mixture was stirred for 2 h at rt. The mixture was filtered through silica gel and concentrated to yield **13**, which was used immediately in the next step. According to procedure F, the ketone **13** was dissolved in 2.5 mL of dry THF. $LiAlH_4$ (12 mg, 0.32 mmol) was added at 0 °C, and the mixture was stirred for 10 min. After regular aqueous workup, **12a** and **11a** were obtained as a 2.5:1 mixture. Flash chromatography on silica gel, eluting with hexanes:diethyl ether 7:1, afforded 7 mg (35%) of pure **12a**. R_f = 0.64 on silica gel (4:1 hexanes:diethyl ether); GC retention time = 10.2 min (150 °C); IR (cm^{-1}, neat) 3395 (br, m), 2995 (w), 2924 (s), 2854 (s), 1448 (w), 1251 (m), 836 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.58, (1H, ddd, J = 8.3, 6.7, 2.7 Hz (disappears with D_2O)), 1.92–1.62 (5H, m), 1.51–1.42 (1H, m), 1.28–0.99 (6H, m), 0.80 (1H, dddd, J = 8.3, 7.5, 6.5, 4.5 Hz), 0.50 (1H, ddd, J = 10.1, 4.5, 4.0 Hz), 0.46 (1H, ddd, J = 7.5, 6.8, 4.0 Hz), −0.06 (9H, s), −0.52 (1H, ddd, J = 10.1, 6.8, 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 81.90, 44.39, 29.03 (2), 26.47, 26.16, 26.03, 20.43, 7.71, 1.04, −2.63.

The product **11a** was also prepared using the following procedure: According to the general procedure G, alcohol **30a** (50 mg, 0.09 mmol) was treated with MeLi (1.9 mL, 1.4 M solution in Et_2O, 2.7 mmol) in 1.0 mL of THF. The reaction mixture was stirred for 24 h, followed by regular aqueous workup. Cyclopropyl carbinol **11a** (10 mg, 50%) was obtained as a colorless liquid following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1. Spectroscopic data: *vide supra*.

Cyclopropanation of (*E*)-1-(Trimethylsilyl)-1-hexen-3-ol (10c). According to the general procedure A, allylic alcohol **10c** (100 mg, 0.58 mmol) was treated with samarium (870 mg, 5.8 mmol) and CH_2I_2 (0.44 mL, 5.5 mmol) in 4 mL of THF. After workup, 91 mg (84%) of a colorless oil was obtained as a 1.3:1 mixture of two diastereomers, as determined by GC-analysis. Flash chromatography on silica gel, eluting with 7:1 hexanes:diethyl ether, provided each of the pure diastereomers.

(*S)-[(1*S**,2*R**)-2-(Trimethylsilyl)cyclopropyl]-1-butanol (11c):** R_f = 0.28 on silica gel (4:1 hexanes:diethyl ether); GC retention time = 15.3 min (75 °C); IR (cm^{-1}, neat) 3366

(br, m), 3062 (w), 2991 (m), 2958 (s), 2930 (s), 2874 (m), 1465 (m), 1249 (s), 1016 (m), 978 (m), 836 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.81 (1H, dt, J = 8.3, 5.9 Hz), 1.59–1.37 (4H, m), 1.22 (1H, s), 0.89 (3H, t, J = 7.0 Hz), 0.76 (1H, dddd, J = 8.3, 7.4, 6.8, 4.5 Hz), 0.45 (1H, ddd, J = 10.3, 4.5, 3.8 Hz), 0.40 (1H, ddd, J = 7.4, 6.8, 3.8 Hz), −0.09 (9H, s), −0.52 (1H, ddd, J = 10.3, 6.8, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 77.84, 39.39, 22.40, 18.84, 14.13, 6.88, 2.21, −2.46; HRMS calcd for $C_{10}H_{21}OSi$ $(M - H)^+$ 185.1362, found 185.1346.

(*R)-[(1*S**,2*R**)-2-(Trimethylsilyl)cyclopropyl]-1-butanol (12c):** R_f = 0.44 on silica gel (4:1 hexanes:diethyl ether); GC retention time = 12.2 min (75 °C); IR (cm^{-1}, neat) 3367 (br, m), 3058 (w), 2959 (s), 2938 (s), 2875 (m), 1469 (m), 1413 (m), 1251 (s), 976 (m), 941 (m), 836 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.90 (1H, dt, J = 7.7, 6.0 Hz), 1.56–1.34 (5H, m), 0.90 (3H, t, J = 7.1 Hz), 0.76 (1H, dddd, J = 7.7, 7.7, 6.3, 4.6 Hz), 0.45 (1H, ddd, J = 10.1, 4.6, 4.0 Hz), 0.41 (1H, ddd, J = 7.7, 6.7, 4.0 Hz), −0.07 (9H, s), −0.48 (1H, ddd, J = 10.1, 6.7, 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 77.05, 39.32, 22.49, 18.83, 13.98, 6.66, 1.59, −2.66; HRMS calcd for $C_{10}H_{21}OSi$ $(M - H)^+$ 185.1362, found 185.1367.

Cyclopropanation of (*E*)-4-(Trimethylsilyl)-3-buten-2-ol (10d). According to the general procedure A, allylic alcohol **10d** (300 mg, 2.1 mmol) was reacted with samarium (3.1 g, 21 mmol) and CH_2I_2 (1.5 mL, 19 mmol) in 15 mL of THF. After workup, 260 mg (76%) of a colorless liquid was obtained, as a 10:1 mixture of two diastereomers, as determined by GC-analysis. Both diastereomers were obtained using flash chromatography on silica gel, eluting with 10:1 pentane–diethyl ether, followed by removal of the solvent via short path distillation, and kugelrohr distillation (45 min at 40 °C at 760 mmHg). Kugelrohr distillation (70–80 °C at 760 mmHg) yielded pure product.

(*R)-[(1*S**,2*R**)-2-(Trimethylsilyl)cyclopropyl]-1-ethanol (11d):** R_f = 0.37 on silica gel (1.4:1 hexanes:diethyl ether); GC retention time = 7.4 min (100 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02 (1H, dq, J = 8.3, 6.2 Hz), 1.65 (1H, br s), 1.23 (3H, d, J = 6.2 Hz), 0.76 (1H, dddd, J = 8.3, 7.2, 6.5, 4.4 Hz), 0.50 (1H, ddd, J = 10.2, 4.4, 4.0 Hz), 0.41 (1H, ddd, J = 7.2, 6.8, 4.0 Hz), −0.08 (9H, s), −0.56 (1H, ddd, J = 10.2, 6.8, 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.12, 23.62, 22.54, 7.50, 1.88, −2.49.

(*S)-[(1*S**,2*R**)-2-(Trimethylsilyl)cyclopropyl]-1-ethanol (12d):** R_f = 0.46 on silica gel (1.4:1 hexanes:diethyl ether); GC retention time = 6.5 min (100 °C); IR (cm^{-1}, neat) 3384 (br, s), 3057 (w), 2955 (s), 2897 (s) 1248 (s), 1103 (m), 969 (m), 917 (m), 849 (s), 835 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10 (1H, dq, J = 7.7, 6.2 Hz), 1.35 (1H, br s), 1.26 (3H, d, J = 6.2 Hz), 0.79 (1H, dddd, J = 7.7, 7.7, 6.5, 4.6 Hz), 0.43 (1H, ddd, J = 10.1, 4.6, 4.0 Hz), 0.40 (1H, ddd, J = 7.7, 6.8, 4.0 Hz), −0.06 (9H, s), −0.44 (1H, ddd, J = 10.1, 6.8, 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.47, 23.90, 22.44, 6.43, 2.62, −2.42; HRMS calcd for $C_8H_{17}OSi$ $(M - H)^+$ 157.1049, found 157.1051.

The product **11d** was also obtained using the following procedure: According to the general procedure G, alcohol **30d** (40 mg, 0.08 mmol) was treated with MeLi (1.9 mL, 1.4 M solution in Et_2O, 2.7 mmol) in 1.0 mL of THF. The reaction mixture was stirred for 24 h, followed by regular aqueous workup. Cyclopropyl carbinol **30d** (8 mg, 40%) was obtained as a colorless liquid following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1. Spectroscopic data: *vide supra*.

Cyclopropanation of (*E*)-1-Cyclohexyl-2-hepten-1-ol (14a). According to the general procedure A, allylic alcohol **14a** (100 mg, 0.51 mmol) was reacted with samarium (610 mg, 4.1 mmol) and CH_2I_2 (0.31 mL, 3.8 mmol) in 4.5 mL of THF. After workup, the colorless oil was obtained as a 18:1 mixture of two diastereomers, as determined by GC-analysis. Flash chromatography on silica gel, eluting with 10:1 hexanes:diethyl ether, afforded 75 mg (70%) of the pure major diastereomer **15a** as a colorless oil.

(*R)-[(1*S**,2*R**)-1,2-Methanohexyl]cyclohexylmethanol (15a):** R_f = 0.33 (hexanes:diethyl ether 2:1); IR (cm^{-1}, neat) 3388 (br, m), 3065 (w), 2995 (m), 2959 (s), 2924 (s), 2854 (s), 1448 (m), 1082 (m), 1026 (m), 892 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (1H, dd, J = 8.8, 5.9 Hz), 1.90–1.62 (6H, m), 1.50–1.05 (12H, m), 0.87 (3H, t, J = 7.2 Hz), 0.64 (1H, m), 0.59 (1H, m), 0.36 (1H, ddd, J = 8.8, 4.6, 4.4 Hz), 0.22 (1H, ddd, J = 8.1, 4.9, 4.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.83, 44.39, 33.33, 31.54, 29.11, 28.78, 26.65, 26.38, 26.26, 23.54, 22.56, 17.72, 14.08, 9.36; HRMS calcd for $C_{14}H_{26}O$ (M^+) 210.1984, found 210.1982.

In the cyclopropanation toward the stannylated cyclopropane **27a**, 14 mg (58%) of the destannylated cyclopropane **15a** was also obtained as a colorless oil.

(*S)-[(1*S**,2*R**)-1,2-Methanohexyl]cyclohexylmethanol (16a).** According to procedure D, **15a** (47 mg, 0.22 mmol) was dissolved in 5 mL of CH_2Cl_2. Celite (720 mg), molecular sieves (72 mg), and NaOAc (45 mg, 0.55 mmol) were added consecutively. To the cooled suspension was added PCC (144 mg, 0.27 mmol), and the mixture was stirred at 0 °C for 15 min and for 1 h at rt. The mixture was filtered through silica gel and concentrated to yield **40a**, which was used immediately in the next step.

According to procedure F, the ketone **40a** was dissolved in 5 mL of dry THF. $LiAlH_4$ (29 mg, 0.77 mmol) was added at 0 °C, and the mixture was stirred for 15 min. After regular aqueous workup, **15a** and **16a** were obtained as a 1:1 mixture. Flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, afforded 21 mg (45%) of pure **16a** as a white solid. R_f = 0.56 (hexanes:diethyl ether 2:1); IR (cm^{-1}, neat) 3374 (br, m), 3058(w), 2995 (m), 2959 (s), 2917 (s), 2854 (s), 1469 (m), 1448 (m), 1033 (m), 1012 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (1H, ddd, J = 7.3, 7.3 Hz), 1.87–1.60 (5H, m), 1.47–0.97 (13H, m), 0.86 (3H, t, J = 7.0 Hz), 0.60 (2H, m), 0.37 (1H, ddd, J = 8.3, 4.8, 4.5 Hz), 0.32 (1H, ddd, J = 8.3, 5.1, 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.81, 44.40, 33.45, 31.94, 29.16, 28.82, 26.63, 26.35, 26.24, 23.39, 22.54, 16.19, 14.08, 11.02; HRMS calcd for $C_{14}H_{26}O$ $(M)^+$ 210.1984, found 210.1990. Further elution provided 22 mg (47%) of **16a** as a colorless oil.

Cyclopropanation of (*E*)-2-Methyl-4-nonen-3-ol (14b). According to the general procedure A, allylic alcohol **14b** (88 mg, 0.56 mmol) was treated with samarium (842 mg, 5.6 mmol) and CH_2I_2 (0.43 mL, 5.3 mmol) in 4 mL of THF. After workup, the crude mixture was obtained as a 5.5:1 mixture of **15b** and **16b**, as determined by GC-analysis. Flash chromatography on silica gel, eluting with 20:1 hexanes:diethyl ether, provided each of the pure diastereomers in a combined yield of 85% as colorless oils.

(*R)-2-Methyl-(4*S**,5*R**)-4,5-methano-3-nonanol (15b):**[21b] R_f = 0.23 on silica gel (2:1 hexanes:diethyl ether); GC retention time = 10.4 min (Carbowax HP20M, 75 °C isothermal); IR (cm^{-1}, neat) 3381 (br, m), 3064 (w), 2959 (s), 2924 (s), 2875 (m), 1469 (m), 1377 (m), 1258 (w), 1026 (m), 998 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (1H, ddd, J = 8.8, 5.6, 3.3 Hz (disappears with D_2O)), 1.78 (1H, dqq, J = 6.9, 6.8, 5.6 Hz), 1.40–1.23 (5H, m), 1.35 (1H, d, J = 3.3 Hz (disappears with D_2O)), 1.07 (1H, m), 0.97 (3H, d, J = 6.8 Hz), 0.96 (3H, d, J = 6.9 Hz), 0.87 (3H, t, J = 7.2 Hz), 0.67–0.57 (2H, m), 0.39 (1H, ddd, J = 8.5, 4.8, 4.5 Hz), 0.24 (1H, ddd, J = 8.6, 5.2, 4.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.40, 34.23, 33.34, 31.54, 23.42, 22.57, 18.74, 18.12, 17.84, 14.07, 9.37; HRMS calcd for $C_{11}H_{22}O$ $(M)^+$ 170.1671, found 170.1660; calcd for $C_8H_{15}O$ $(M - C_3H_7)^+$ 127.1123, found 127.1123.

(*S)-2-Methyl-(4*S**,5*R**)-4,5-methano-3-nonanol (16b).**[21b] The product was also obtained via the oxidation/reduction sequence. According to procedure D, **15b** (49 mg, 0.29 mmol) was dissolved in 4 mL of CH_2Cl_2. Celite (927 mg), molecular sieves (93 mg), and NaOAc (59 mg, 0.72 mmol) were added consecutively. To the cooled suspension was added PCC (185 mg, 0.86 mmol), and the mixture was stirred at 0 °C for 15 min and for 2 h at rt. The mixture was filtered through silica gel and concentrated to yield **40b**, which was used immediately in the next step.

According to procedure F, the ketone **40b** was dissolved in 5 mL of dry THF. $LiAlH_4$ (33 mg, 0.87 mmol) was added at 0 °C, and the mixture was stirred for 10 min. After regular aqueous workup, **15b** and **16b** were obtained as a 1:1 mixture. Flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, afforded 13 mg (27%) of pure **16b** as a volatile liquid. R_f = 0.39 on silica gel (4:1 hexanes:diethyl

ether); GC retention time = 8.8 min (Carbowax HP20M, 75 °C isothermal); IR (cm^{-1}, neat) 3388 (br, s), 2959 (s), 2924 (s), 2875 (s), 1645 (w), 1469 (m), 1384 (m), 1257 (w), 1026 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.60, (1H, ddd, J = 8.6, 5.7, 3.3 Hz), 1.76 (1H, d sept, J = 6.7, 5.7 Hz), 1.41–1.15 (6H, m), 1.32 (1H, d, J = 3.3 Hz), 0.95 (6H, d, J = 6.7 Hz), 0.87 (3H, t, J = 7.1 Hz), 0.65–0.55 (2H, m), 0.38 (1H, ddd, J = 8.4, 5.1, 4.8 Hz), 0.32 (1H, ddd, J = 8.6, 5.3, 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.41, 34.27, 33.45, 31.95, 23.27, 22.55, 18.77, 18.21, 16.22, 14.10, 11.01. Further elution provided 15 mg (31%) of **15b** as a colorless liquid.

Cyclopropanation of (*E*)-5-Decen-4-ol (14c). According to the general procedure A, allylic alcohol **39b** (200 mg, 1.27 mmol) was treated with samarium (1.90 g, 12.8 mmol) and CH_2I_2 (0.97 mL, 12.1 mmol) in 13 mL of THF. After workup, the crude mixture was obtained as a 1.5:1 mixture of **15c** and **16c**, as determined by GC-analysis. Flash chromatography on silica gel, eluting with 20:1 hexanes:diethyl ether, provided each of the pure diastereomers in a combined yield of 94% as colorless oils.

(*R)-(5*S**,6*R**)-5,6-methano-4-decanol (15c):** IR (cm^{-1}, neat) 3360 (br, s), 3065 (w), 2959 (s), 2924 (s), 2875 (s), 2861 (s), 1462 (m), 1377 (m), 1117 (m), 1068 (m), 1026 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.83 (1H, dt, J = 8.1, 6.2 Hz), 1.60–1.15 (11H, m), 0.89 (3H, t, J = 7.3 Hz), 0.85 (3H, t, J = 7.2 Hz), 0.56 (2H, m), 0.38 (1H, ddd, J = 8.5, 4.7, 4.7 Hz), 0.21 (1H, ddd, J = 8.1, 4.9, 4.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.09, 39.43, 33.36, 31.61, 25.78, 22.49, 18.89, 16.98, 14.14, 14.03, 9.81; HRMS calcd for $C_{11}H_{22}O$ $(M)^+$ 170.1671, found 170.1664.

S*-(5S*,6R*)-5,6-methano-4-decanol (16c): IR (cm^{-1}, neat) 3367 (m, br), 3058 (w), 2959 (s), 2924 (s), 2875 (s), 2854 (m), 1462 (m), 1377 (w), 1117 (w), 1068 (w), 1026 (m) ^1H NMR (400 MHz, $CDCl_3$) δ 2.87 (1H, dt, J = 7.7, 6.2 Hz), 1.53–1.12 (11H, m), 0.88 (3H, t, J = 7.2 Hz), 0.85 (3H, t, J = 7.2 Hz), 0.59 (2H, m), 0.32 (1H, ddd, J = 8.1, 5.1, 4.7 Hz), 0.25 (1H, ddd, J = 8.6, 5.2, 4.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.02, 39.23, 33.41, 31.90, 25.59, 22.50, 18.90, 16.63, 14.15, 14.05, 9.91.

Cyclopropanation of (*Z*)-1-(Trimethylsilyl)-1-hexen-3-ol (17c). According to the general procedure A, allylic alcohol **42c** (100 mg, 0.58 mmol) was reacted with samarium (872 mg, 5.80 mmol) and CH_2I_2 (0.44 mL, 5.4 mmol) in 6 mL of THF. The crude reaction mixture was obtained as a >100:1 mixture of **18c** and **19c**, as determined by GC-analysis. After flash chromatography on silica gel, eluting with 8:1 pentane:diethyl ether, the pure major diastereomer **18c** (72 mg, 67%) was obtained as a colorless oil.

(*R)-[(1*S**,2*S**)-2-(Trimethylsilyl)cyclopropyl]-1-butanol (18c):** R_f = 0.36 on silica gel (2.3:1 hexanes:diethyl ether); GC retention time = 11.6 min (75 °C); IR (cm^{-1}, neat) 3374 (br, m), 3065 (w), 2995 (m), 2959 (s), 2931 (s), 2875 (m), 1462 (w), 1251 (s), 963 (m), 941, (m), 836 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 3.00 (1H, dt, J = 9.5, 3.0 Hz), 1.66–1.33 (5H, m), 1.16 (1H, dddd, J = 9.6, 9.5, 7.7, 5.0 Hz), 0.91 (3H, t, J = 7.0 Hz), 0.78 (1H, ddd, J = 9.8, 7.7, 3.6 Hz), 0.23 (1H, ddd, J = 7.8, 5.0, 3.6 Hz), 0.00 (9H, s), −0.26 (1H, ddd, J = 9.8, 9.6, 7.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 74.45, 39.98, 25.01, 19.13, 14.29, 7.02, 3.40, −0.05 (J_{Si-C} = 51.9 Hz); HRMS calcd for $C_9H_{19}OSi$ $(M - CH_3)^+$ 171.1205, found, 171.1204.

(*S)-[(1*S**,2*S**)-2-(Trimethylsilyl)cyclopropyl]-1-butanol (19c).** According to procedure D, **43c** (20 mg, 0.11 mmol) was dissolved in 2.5 mL of CH_2Cl_2. Celite (350 mg), molecular sieves (35 mg), and NaOAc (22 mg, 0.27 mmol) were added consecutively. To the cooled suspension was added PCC (69 mg, 0.32 mmol), and the mixture was stirred at 0 °C for 15 min and for 3 h at rt. The mixture was filtered through silica gel and concentrated to yield **41**, which was used immediately in the next step.

According to procedure F, the ketone **41** was dissolved in 2.5 mL of dry THF. $LiAlH_4$ (15 mg, 0.39 mmol) was added at 0 °C, and the mixture was stirred for 15 min. After regular aqueous workup, **19c** and **18c** were obtained as a 15:1 mixture. Flash chromatography on silica gel, eluting with hexanes: diethyl ether 10:1, afforded 9 mg (45%) of pure **19c** as a volatile liquid. R_f = 0.67 on silica gel (2.3:1 hexanes:diethyl ether); GC retention time = 8.0 min (75 °C); ^1H NMR (200 MHz, $CDCl_3$) δ 2.92 (1H, dt, J = 9.7, 5.3 Hz), 1.65–1.23 (5H, m,), 1.12 (1H, dddd, J = 9.7, 9.1, 8.1, 5.0 Hz), 0.90 (3H, t, J = 6.9 Hz), 0.82 (1H, ddd, J = 10.0, 8.1, 3.8 Hz), 0.16 (1H, ddd, J = 7.7, 5.0, 3.8 Hz), 0.06 (9H, s), −0.33 (1H, ddd, J = 10.0, 9.1, 7.7 Hz). Further elution afforded 0.5 mg (3%) of **18c** as a colorless oil.

Cyclopropanation of (*Z*)-4-(Trimethylsilyl)-3-buten-2-ol (17d). According to the general procedure A, allylic alcohol **17d** (120 mg, 0.83 mmol) was treated with samarium (1.05 g, 7.0 mmol) and CH_2I_2 (0.53 mL, 6.6 mmol) in 6 mL of THF. The crude mixture was obtained as a >100:1 mixture of **18d** and **19d**, as determined by GC-analysis. After flash chromatography on silica gel, eluting with 7:1 pentane:diethyl ether, the pure major diastereomer **18d** (88 mg, 67%) was obtained as a colorless oil. Removal of the solvent by short path distillation, followed by kugelrohr distillation (40 °C at 760 mmHg) gave the cyclopropane.

(*R)-[(1*S**,2*S**)-2-(Trimethylsilyl)cyclopropyl]-1-ethanol (18d):** R_f = 0.27 on silica gel (2.6:1 hexanes:diethyl ether); GC retention time 17.2 min (100 °C, Silicone HP-5 column); IR (cm^{-1}, neat) 3367 (br m), 3065 (w), 2959 (s), 2903 (w), 1244 (s), 948 (s), 836 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.17 (1H, dq, J = 9.6, 6.1 Hz), 1.47 (1H, br s), 1.31 (3H, d, J = 6.1 Hz), 1.15 (1H, dddd, J = 9.7, 9.6, 7.7, 5.0 Hz), 0.80 (1H, ddd, J = 9.9, 7.7, 3.7 Hz), 0.24 (1H, ddd, J = 7.7, 5.0, 3.7 Hz), −0.02 (9H, s), −0.24 (1H, ddd, J = 9.9, 9.7, 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.05, 26.13, 23.43, 7.14, 3.20, −0.17 (J_{Si-C} = 52.0 Hz); HRMS calcd for $C_7H_{15}OSi$ $(M - H)^+$ 143.0892, found 143.0892.

Cyclopropanation of (*E*)-1-Cyclohexyl-3-(tributylstannyl)-2-hexen-1-ol (20a). According to the general procedure A, allylic alcohol **20a** (100 mg, 0.2 mmol) was treated with samarium (360 mg, 2.4 mmol) and CH_2I_2 (0.17 mL, 2.2 mmol) in 2.5 mL of THF. Cyclopropyl carbinol **21a** (69 mg, 67%) was obtained as a viscous colorless oil following flash chromatography on silica gel, eluting with 10:1 pentane:diethyl ether.

(*R)-[(1*S**,2*R**)-2-Butyl-2-(tributylstannyl)cyclopropyl]-cyclohexylmethanol (21a):** IR (cm^{-1}, neat) 3344 (br, m), 3031 (w), 2957 (s), 2925 (s), 2870 (s), 2852 (s), 1463 (s), 1450 (s), 1417 (m), 1376 (m), 1070 (m), 1024 (m); ^1H NMR (200 MHz, $CDCl_3$) δ 3.09 (1H, dd, J = 8.8, 5.2 Hz), 1.95–1.00 (30H, m), 0.87 (9H, t, J = 7.1 Hz), 0.80–0.60 (11H, m), 0.23 (1H, dd, J = 4.7, 4.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.14, 44.85, 35.37 (J_{Sn-C} = 16.5 Hz), 33.56 (J_{Sn-C} = 11.0 Hz), 29.58, 29.18 (J_{Sn-C} = 19.2 Hz), 28.10, 27.59 (J_{Sn-C} = 55.8 Hz), 26.64, 26.51, 26.31, 26.13, 23.06, 16.13, 14.16, 14.13, 13.68, 9.01 (J_{Sn-C} = 318.5, 304.4 Hz); ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −3.65. Anal. Calcd for $C_{26}H_{52}OSn$: C, 62.53; H, 10.50. Found: C, 62.82; H, 10.52.

(*S)-[(1*S**,2*R**)-2-Butyl-2-(tributylstannyl)cyclopropyl]-cyclohexylmethanol (22a).** According to procedure F, the ketone **42** (18 mg, 0.04 mmol) was dissolved in 0.5 mL of dry THF. $LiAlH_4$ (1.5 mg, 0.04 mmol) was added at 0 °C, and the mixture was stirred for 15 min. After regular aqueous workup, **22a** and **21a** were obtained as a 15:1 mixture. Flash chromatography on silica gel, eluting with hexanes:diethyl ether 10:1, afforded **22a** (15.1 mg, 83%) as a colorless oil: R_f = 0.54 on silica gel (2.6:1 hexanes:diethyl ether); GC retention time = 14.4 min (100 °C, Silicone HP-5 column); IR (cm^{-1}, neat) 3508 (br, w), 3037 (w), 2952 (s), 2931 (s), 2854 (s), 1462 (s), 1377 (m), 1075 (m), 1012 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 3.07 (1H, ddd, J = 9.6, 6.3, 3.2 Hz (disappears with D_2O)), 1.91 (1H, m), 1.82–1.60 (5H, m), 1.52–1.00 (26H, m), 0.87 (12H, t, J = 7.2 Hz), 0.77 (6H, m), 0.22 (1H, dd, J = 4.8, 4.8 Hz)(J_{Sn-H} = 36.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 77.23, 45.01, 34.32 (J_{Sn-C} = 17.4 Hz), 33.66 (J_{Sn-C} = 10.8 Hz), 29.42, 29.17 (J_{Sn-C} = 19.3 Hz), 28.97, 27.53 (J_{Sn-C} = 54.9 Hz), 26.64, 26.39, 26.24, 25.83 (J_{Sn-C} = 9.9 Hz), 23.13, 15.91, 14.13, 13.69, 12.58, 8.95 (J_{Sn-C} = 319.0, 304.9 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −3.16. Further elution afforded **46a** (1.0 mg, 6%) as a colorless oil.

Cyclopropanation of (*E*)-4-(Tributylstannyl)-3-octen-2-ol (20d). According to the general procedure A, allylic alcohol **20d** (300 mg, 0.72 mmol) was treated with samarium (1.08 g, 7.2 mmol) and CH_2I_2 (0.52 mL, 6.48 mmol) in 10 mL of THF. Cyclopropyl carbinol **21d** (239 mg, 80%) was obtained

as a colorless viscous oil following flash chromatography on silica gel, eluting with 7:1 hexanes:diethyl ether.

(*R)-[(1*S**,2*R**)-2-Butyl-2-(tributylstannyl)cyclopropyl]-1-ethanol (21d):** IR (cm^{-1}, neat) 3344 (br, m), 3057 (w), 2958 (s), 2925 (s), 2871 (s), 2854 (s), 1464 (m), 1376 (m), 1105 (m), 1089 (m), 1073 (m); ^1H NMR (200 MHz, $CDCl_3$) δ 3.49 (1H, ddq, J = 8.8, 6.1, 3.0 Hz (disappears with D_2O)), 1.49–1.21 (19H, m), 1.30 (3H, d, J = 6.1 Hz), 0.87 (12H, t, J = 7.0 Hz), 0.80–0.65 (8H, m), 0.27 (1H, dd, J = 4.4, 4.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 69.10, 34.75, 33.38, 29.15, 29.00, 27.40, 23.66, 22.90, 14.73, 14.42, 13.90, 13.49, 8.77; ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −3.31. Anal. Calcd for $C_{21}H_{44}OSn$: C, 58.49; H, 10.28. Found: C, 58.86; H, 10.14.

Cyclopropanation of (*E*)-1-Cyclohexyl-3-(trimethylstannyl)-2-hexen-1-ol (23a). According to the general procedure A, allylic alcohol **23a** (1.0 g, 2.8 mmol) was treated with samarium (4.2 g, 27.8 mmol) and CH_2I_2 (2.13 mL, 26.4 mmol) in 25 mL of THF. Cyclopropyl carbinol **24a** (711 mg, 70%) was obtained as a viscous colorless oil following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1.

(*R)-[(1*S**,2*R**)-2-Butyl-2-(trimethylstannyl)cyclopropyl]cyclohexylmethanol (24a):** IR (cm^{-1}, neat) 3353 (br, m), 3037 (w), 2959 (s), 2924 (s), 2854 (s), 1448 (m), 1026 (m), 766 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.09 (1H, ddd, J = 9.4, 5.8, 3.6 Hz), 1.89 (1H, m), 1.78–1.60 (4H, m), 1.45–0.98 (13H, m), 1.35 (1H, d, J = 3.6 Hz), 0.86 (3H, m), 0.66 (1H, ddd, J = 7.7, 5.2, 4.5 Hz)(J_{Sn-H} = 60.8 Hz), 0.26 (1H, dd, J = 4.9, 4.5 Hz)(J_{Sn-H} = 38.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.94, 44.93, 34.83 (J_{Sn-C} = 19.1 Hz), 33.36 (J_{Sn-C} = 14.0 Hz), 29.28, 28.42, 26.63, 26.48, 26.28, 26.14, 22.95, 15.57, 14.13 (J_{Sn-C} = 12.2 Hz), −10.45 (J_{Sn-C} = 327.0, 312.5 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ 18.96; HRMS calcd for $C_{16}H_{31}OSn$ $(M - CH_3)^+$ 359.1397, found 359.1376.

Cyclopropanation of (*Z*)-1-Cyclohexyl-3-(tributylstannyl)-2-hexen-1-ol (26a). According to the general procedure A, allylic alcohol **26a** (85 mg, 0.18 mmol) was treated with samarium (264 mg, 1.76 mmol) and CH_2I_2 (0.13 mL, 1.67 mmol) in 1.5 mL of THF. Cyclopropyl carbinol **27a** (55 mg, 63%) was obtained as a viscous colorless oil following flash chromatography on silica gel, eluting with 20:1 hexanes:diethyl ether.

(*R)-[(1*S**,2*S**)-2-Butyl-2-(tributylstannnyl)cyclopropyl]-cyclohexylmethanol (27a):** IR (cm^{-1}, neat) 3452 (br, m), 3044 (w), 2959 (s), 2924 (s), 2854 (s), 1469 (m), 1448 (m), 1377 (m), 1082 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.79 (1H, ddd, J = 7.7, 4.0, 3.7 Hz), 1.87–1.15 (30H, m), 0.88 (9H, t, J = 7.2 Hz), 0.85–0.74 (10H, m,), 0.44–0.38 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.41 (J_{Sn-C} = 20.5 Hz), 43.72, 42.01 (J_{Sn-C} = 18.3 Hz), 32.77, 30.63, 29.28 (J_{Sn-C} = 18.8 Hz), 28.51, 27.61 (J_{Sn-C} = 59.2 Hz), 26.62 (2), 26.41, 26.32, 22.92, 15.91, 14.55, 14.09, 13.66, 10.19 (J_{Sn-C} = 310.0 Hz); ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −8.39; HRMS calcd for $C_{22}H_{43}OSn$ $(M - C_4H_9)^+$ 443.2336, found 443.2330.

Cyclopropanation of (*Z*)-2-Methyl-5-(tributylstannyl)-4-nonen-3-ol (26b). According to the general procedure A, allylic alcohol **26b** (75 mg, 0.17 mmol) was treated with samarium (252 mg, 1.68 mmol) and CH_2I_2 (0.13 mL, 1.60 mmol) in 2.0 mL of THF. Cyclopropyl carbinol **27b** (69 mg, 89%) was obtained as a viscous colorless oil following flash chromatography on silica gel, eluting with hexanes to 20:1 hexanes:diethyl ether.

(*R)-2-Methyl-(4*S**,5*S**)-4,5-methano-5-(tributylstannyl)-3-nonanol (27b):** R_f = 0.45 on silica gel (5:1 hexanes:diethyl ether); IR (cm^{-1}, neat) 3438 (br, m), 3044 (w), 2959 (s), 2924 (s), 2875 (s), 2854 (s), 1462 (m), 1377 (m), 991 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.82 (1H, ddd, J = 7.8, 4.1, 3.7 Hz), 1.76 (2H, m), 1.50–1.20 (18H, m), 1.14 (1H, d, J = 4.1 Hz), 0.98 (3H, d, J = 7.0 Hz), 0.97 (3H, d, J = 6.8 Hz), 0.90–0.78 (18H, m), 0.42 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.55, 42.06, 33.41, 32.83, 29.24 (J_{Sn-C} = 18.8 Hz), 28.80, 27.58 (J_{Sn-C} = 59.3 Hz), 22.94, 20.09, 16.06, 15.68, 14.47, 14.10, 13.66, 10.08 (J_{Sn-C} = 324.6, 310.3 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −8.28; HRMS calcd for $C_{19}H_{39}OSn$ $(M - C_4H_9)^+$ 403.2032, found 403.2010.

Cyclopropanation of (*Z*)-6-(Tributylstannyl)-5-decen-4-ol (26c). According to the general procedure A, allylic alcohol **26c** (75 mg, 0.17 mmol) was treated with samarium (252 mg, 1.68 mmol) and CH_2I_2 (0.13 mL, 1.60 mmol) in 2.0 mL of THF. Cyclopropyl carbinol **27c** (59 mg, 77%) was obtained as a viscous colorless oil following flash chromatography on silica gel, eluting with hexanes to 20:1 hexanes:diethyl ether.

R*-(5*S,6*S**)-5,6-Methano-6-(tributylstannyl)-4-decanol (27c):** R_f = 0.43 (hexanes:diethyl ether 5:1); IR (cm^{-1}, neat) 3402 (br, m), 2959 (s), 2924 (s), 2882 (s), 2854 (s), 1461 (m), 1377 (m), 1068 (m), 1025 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.85 (1H, ddt, J = 8.8, 8.8, 2.8 Hz), 1.76 (2H, m), 1.62–1.20 (21H, m), 0.95–0.78 (22H, m), 0.63 (1H, m), 0.42 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.23, 41.88, 39.67, 32.88, 31.57, 29.23 (J_{Sn-C} = 18.8 Hz), 27.59 (J_{Sn-C} = 58.8 Hz), 22.92, 19.34, 16.17, 14.72, 14.23, 14.09, 13.66, 9.98 (J_{Sn-C} = 323.9, 309.7 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −7.80; HRMS calcd for $C_{18}H_{39}OSi_2$ $(M-CH_3)^+$ 327.2539, found 327.2540; calcd for $C_{19}H_{39}OSn$ $(M-C_4H_9)^+$ 403.2023, found 403.2017.

Cyclopropanation of (*Z*)-4-(Tributylstannyl)-3-octen-2-ol (26d). According to the general procedure A, allylic alcohol **26d** (50 mg, 0.12 mmol) was treated with samarium (180 mg, 1.20 mmol) and CH_2I_2 (0.09 mL, 1.14 mmol) in 1.5 mL of THF. Cyclopropyl carbinol **27d** (42 mg, 81%) was obtained as a viscous colorless oil following flash chromatography on silica gel, eluting with hexanes to hexanes:diethyl ether 20:1.

R*-(3*S,4*S**)-3,4-Methano-4-(tributylstannyl)octan-2-ol (27d):** R_f = 0.4 (hexanes:diethyl ether 2:1); IR (cm^{-1}, neat) 3360 (br, m), 2966 (s), 2924 (s), 2875 (s), 2854 (s), 1462 (m), 1377 (m), 1096 (m), 1068 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 3.03 (1H, ddd, J = 8.8, 6.0, 2.6 Hz), 1.76 (1H, m), 1.49–1.38 (7H, m), 1.30 (3H, d, J = 6.0 Hz), 1.33–1.22 (12H, m), 0.88 (9H, t, J = 7.3 Hz), 0.87–0.79 (9H, m), 0.62 (1H, m), 0.42 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.78 (J_{Sn-C} = 25.3 Hz), 41.80, 32.94, 32.81, 29.20 (J_{Sn-C} = 18.9 Hz), 27.56 (J_{Sn-C} = 59.6 Hz), 23.20, 22.89, 16.27, 14.89, 14.09, 13.66, 9.92 (J_{Sn-C} = 309.8 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −7.62; HRMS calcd for $C_{17}H_{35}OSn$ $(M - C_4H_9)^+$ 375.1710, found 375.1705.

Cyclopropanation of (*Z*)-1-Cyclohexyl-3-(tributylstannyl)-3-(trimethylsilyl)-2-propen-1-ol (29a). According to the general procedure A, allylic alcohol **29a** (1.0 g, 1.99 mmol) was treated with samarium (3.0 g, 19.9 mmol) and CH_2I_2 (1.5 mL, 18.9 mmol) in 17 mL of THF. Cyclopropyl carbinol **30a** (825 mg, 80%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with 15:1 hexanes:diethyl ether.

The product was also obtained following the general procedure D, starting from allylic alcohol **31a** (200 mg, 0.40 mmol) and using Et_2Zn (81 μL, 0.80 mmol) and $ClCH_2I$ (117 μL, 1.60 mmol) in 3 mL of 1,2-dichloroethane. Cyclopropyl carbinol **30a** (165 mg, 80%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1. Further elution afforded 8 mg (9%) of the destannylated cyclopropane **11a**.

Attempted cyclopropanation following the general procedure B did not result in any reaction, and only starting material was isolated.

(*R)-[(1*S**,2*S**)-2-(Tributylstannyl)-2-(trimethylsilyl)-cyclopropyl]cyclohexylmethanol (30a):** IR (cm^{-1}, neat) 3392 (br, m), 3028 (w), 2956 (s), 2919 (s), 2870 (s), 2853 (s), 1463 (s), 1450 (s), 1258 (s), 1247 (s), 1016 (s), 959 (s), 851 (s), 832 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 2.83 (1H, ddd, J = 8.8, 3.3 (disappears with D_2O), 2.8 Hz), 1.78–1.12 (24H, m), 0.88 (9H, t, J = 7.1 Hz), 0.86–0.77 (8H, m), 0.59 (1H, dd, J = 4.3, 3.6 Hz), −0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.39 (J_{Sn-C} = 30.3 Hz), 43.78, 30.66, 29.36 (J_{Sn-C} = 18.6 Hz), 27.74 (J_{Sn-C} = 62.2 Hz), 26.74, 26.72, 26.55, 26.26, 24.32 (J_{Sn-C} = 21.2 Hz), 13.77, 11.79, 11.61 (J_{Sn-C} = 320.9, 306.7 Hz), −0.80, −1.10; ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −3.38; HRMS calcd for $C_{24}H_{49}OSiSn$ $(M - CH_3)^+$ 501.2575, found 501.2585; calcd for $C_{21}H_{43}OSiSn$ $(M - C_4H_9)^+$ 459.2105, found 459.2125. Anal. Calcd for $C_{25}H_{52}OSiSn$: C, 58.25; H, 10.17. Found: C, 58.26; H, 10.31.

(S*)-[(1S*,2S*)-2-(Tributylstannyl)-2-(trimethylsilyl)-cyclopropyl]cyclohexylmethanol (31a). According to procedure E, **30a** (50 mg, 0.10 mmol) was dissolved in 2 mL of CH_2Cl_2. NMO (17 mg, 0.15 mmol) and molecular sieves were added, followed by TPAP (1 mg), and the mixture was stirred for 4 h at rt. The mixture was filtered through silica gel and concentrated to yield **43** which was used immediately in the next step.

According to procedure F, the ketone **43** was dissolved in 2.0 mL of dry THF. $LiAlH_4$ (4 mg, 0.10 mmol) was added at 0 °C and the mixture was stirred for 5 min. After regular aqueous workup, **31a** and **30a** were obtained as a 20:1 mixture. Flash chromatography on silica gel, eluting with hexanes: diethyl ether 20:1, afforded 40 mg (80%) of pure **31a**: IR (cm^{-1}, neat) 3611 (m), 3496 (br, m), 3029 (m), 2954 (s), 2925 (s), 2854 (s), 1452 (m), 1375 (m), 1250 (s), 1021 (m), 937 (m), 833 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.57 (1H, ddd, J = 9.2, 6.6, 3.3 Hz (disappears with D_2O)), 1.93−1.60 (5H, m), 1.45 (6H, m), 1.30 (6H, m), 1.34−1.00 (8H, m), 1.18 (1H, d, J = 3.3 Hz), 0.88 (9H, t, J = 7.1 Hz), 0.85 (6H, m), 0.61 (1H, dd, J = 4.0, 3.7 Hz), −0.08 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.04 (J_{Sn-C} = 33.0 Hz), 44.82, 29.31, 29.23, 29.16, 27.63 (J_{Sn-C} = 63.0, 60.1 Hz), 26.64, 26.29, 26.15, 25.70, 13.67, 13.43, 11.24 (J_{Sn-C} = 320.8, 306.8 Hz), −1.30, −2.15; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −4.84.

Cyclopropanation of (Z)-1-(Tributylstannyl)-1-(trimethylsilyl)-1-hexen-3-ol (29c). According to the general procedure A, allylic alcohol **29c** (200 mg, 0.43 mmol) was treated with samarium (650 mg, 4.3 mmol) and CH_2I_2 (0.32 mL, 4.0 mmol) in 3.5 mL of THF. Cyclopropyl carbinol **30c** (137 mg, 67%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with 10:1 pentane: diethyl ether.

(R*)-[(1S*,2S*)-2-(Tributylstannyl)-2-(trimethylsilyl)-cyclopropyl]-1-butanol (30c): IR (cm^{-1}, neat) 3365 (br, m), 3029 (w), 2957 (s), 2929 (s), 2872 (s), 2857 (s), 1464 (m), 1376 (w), 1248 (s), 833 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 2.95 (1H, m), 1.59−1.20 (17H, m), 1.04−0.77 (11H, m), 0.87 (9H, t, J = 7.1 Hz), 0.60 (1H, dd, J = 4.3, 3.5 Hz), −0.10 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 77.08, 39.77, 29.20 (J_{Sn-C} = 18.7 Hz), 27.73, 27.61 (J_{Sn-C} = 61.6 Hz), 19.18, 14.30, 13.62, 11.65, 11.26 (J_{Sn-C} = 321.6, 307.4 Hz), −0.97, −1.36; ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −2.55; HRMS calcd for $C_{21}H_{45}OSiSn$ $(M - CH_3)^+$ 461.2262, found 461.2272; calcd for $C_{18}H_{39}OSiSn$ $(M - C_4H_9)^+$ 419.1792, found 419.1758. Anal. Calcd for $C_{22}H_{48}OSiSn$: C, 55.58; H, 10.18. Found: C, 55.84; H, 10.27.

Cyclopropanation of (Z)-4-(Tributylstannyl)-4-(trimethylsilyl)-3-buten-2-ol (29d). According to the general procedure A, allylic alcohol **29d** (300 mg, 0.69 mmol) was treated with samarium (1.0 g, 6.9 mmol) and CH_2I_2 (0.56 mL, 6.9 mmol) in 8.0 mL of THF. Cyclopropyl carbinol **30d** (263 mg, 85%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1.

(R*)-[(1S*,2S*)-2-(Tributylstannyl)-2-(trimethylsilyl)-cyclopropyl]-1-ethanol (30d): IR (cm^{-1}, neat) 3345 (br, m), 3035 (w), 2957 (s), 2925 (s), 2871 (s), 2854 (s), 1463 (m), 1259 (m), 1247 (s), 1099 (m), 1070 (m), 957 (m), 940 (m), 833 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 3.12 (1H, ddd, J = 8.8, 6.1, 2.9 Hz (disappears with D_2O)), 1.51−1.20 (13H, m), 1.27 (3H, d, J = 6.1 Hz), 0.98 (1H, ddd, J = 8.8, 7.2, 4.2 Hz), 0.87 (9H, t, J = 7.1 Hz), 0.86−0.78 (7H, m), 0.60 (1H, dd, J = 4.2, 3.6 Hz), −0.10 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.54, 29.15 (J_{Sn-C} = 18.8 Hz), 28.93 (J_{Sn-C} = 20.8 Hz), 27.56 (J_{Sn-C} = 62.8 Hz), 23.27, 13.60, 11.91 (J_{Sn-C} = 21.0 Hz), 11.21 (J_{Sn-C} = 322.0, 307.8 Hz), −0.95, −1.43; ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −2.20; HRMS calcd for $C_{19}H_{41}OSiSn$ $(M - CH_3)^+$ 433.1949, found 433.1928; calcd for $C_{16}H_{35}OSiSn$ $(M - C_4H_9)^+$ 391.1479, found 391.1468.

Cyclopropanation of (Z)-3-(Tributylstannyl)-3-(trimethylsilyl)-2-propen-1-ol (29e). According to the general procedure A, allylic alcohol **29e** (3.0 g, 7.15 mmol) was treated with samarium (5.4 g, 35.8 mmol) and CH_2I_2 (2.6 mL, 32.2 mmol) in 8.0 mL of THF. Cyclopropyl carbinol **30e** (2.80 g, 90%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1.

The product was also obtained following the general procedure B, starting from allylic alcohol **29e** (125 mg, 0.48 mmol) and using samarium (451 mg, 3.0 mmol), 1,2 diiodoethane (845 mg, 3.0 mmol) and $ClCH_2I$ (0.22 mL, 3.0 mmol) in 3 mL of dry THF. Cyclopropyl carbinol **30e** (105 mg, 81%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1.

The product was also obtained following the general procedure D, starting from allylic alcohol **29e** (200 mg, 0.48 mmol) and using Et_2Zn (97 μL, 0.95 mmol) and $ClCH_2I$ (139 μL, 1.91 mmol) in 3 mL of 1,2-dichloroethane. Cyclopropyl carbinol **30e** (134 mg, 65%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes: diethyl ether 20:1 to 10:1.

[2-(Tributylstannyl)-2-(trimethylsilyl)cyclopropyl]-1-methanol (30e): IR (cm^{-1}, neat) 3325 (br, m), 3032 (w), 2960 (s), 2929 (s), 2875 (s), 2861 (s), 1464 (m), 1247 (s), 1032 (s), 851 (s), 835 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 3.64 (1H, dd, J = 10.6, 5.9 Hz), 3.29 (1H, dd, J = 10.6, 8.1 Hz), 1.49−1.38 (7H, m), 1.29 (6H, sext, J = 7.3 Hz), 0.87 (9H, t, J = 7.3 Hz), 0.81 (8H, m), 0.54 (1H, dd, J = 4.0, 3.7 Hz), −0.10 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.20 (J_{Sn-C} = 18.9 Hz), 29.13 (J_{Sn-C} = 19.0 Hz), 27.56 (J_{Sn-C} = 62.2, 59.3 Hz), 22.61, 13.62, 11.92 (J_{Sn-C} = 21.2 Hz), 11.08 (J_{Sn-C} = 321.5, 306.8 Hz), −1.74, −1.46; ^{119}Sn NMR (75 MHz, $CDCl_3$) δ −1.06.

Cyclopropanation of (Z)-1-Cyclohexyl-3,3-bis(tributylstannyl)-2-propen-1-ol (32a). According to the general procedure A, allylic alcohol **32a** (100 mg, 0.14 mmol) was treated with samarium (210 mg, 1.40 mmol) and CH_2I_2 (0.11 mL, 1.40 mmol) in 2 mL of THF. Cyclopropyl carbinol **33a** (72 mg, 71%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes: diethyl ether 15:1.

The product was also obtained following the general procedure D, starting from allylic alcohol **32a** (100 mg, 0.14 mmol) and using Et_2Zn (40 μL, 0.42 mmol) and CH_2I_2 (34 μL, 0.42 mmol) in 2 mL of CH_2Cl_2. Cyclopropyl carbinol **33a** (94 mg, 92%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1.

(R*)-[(1S*,2S*)-2,2-Bis(tributylstannyl)cyclopropyl]-cyclohexylmethanol (33a): IR (cm^{-1}, neat) 3430 (m), 2957 (s), 2925 (s), 2872 (s), 2856 (s), 1463 (m), 1377 (m), 1071 (m), 959 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.71 (1H, ddd, J = 8.4, 3.3, 3.3 Hz), 1.86−1.56 (5H, m), 1.50−1.14 (31H, m), 0.93 (1H, dd, J = 7.4, 3.6 Hz), 0.88 (9H, t, J = 7.3 Hz), 0.87 (9H, t, J = 7.3 Hz), 0.84−0.73 (13H, m), 0.67 (1H, dd, J = 4.0, 3.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.93 (J_{Sn-C} = 33.6, 25.6 Hz), 43.72, 30.75, 29.37 (J_{Sn-C} = 19.0 Hz), 29.30 (J_{Sn-C} = 19.0 Hz), 27.73 (J_{Sn-C} = 61.5 Hz), 27.70 (J_{Sn-C} = 57.1 Hz), 26.66 (2), 26.47, 26.32, 25.02 (J_{Sn-C} = 23.4, 17.6 Hz), 13.69 (2), 12.14 (J_{Sn-C} = 26.4, 22.7 Hz), 11.36 (J_{Sn-C} = 318.5, 303.9 Hz), 9.55 (J_{Sn-C} = 314.1, 300.2 Hz), −4.21; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ 17.44, 4.06.

(S*)-[(1S*,2S*)-2,2-Bis(tributylstannyl)cyclopropyl]-cyclohexylmethanol (34a). According to procedure E, **33a** (65 mg, 0.09 mmol) was dissolved in 2 mL of CH_2Cl_2. NMO (17 mg, 0.15 mmol) and molecular sieves were added, followed by TPAP (1 mg), and the mixture was stirred for 4 h at rt. The mixture was filtered through silica gel and concentrated to yield **44** which was used immediately in the next step.

According to procedure F, the ketone **44** was dissolved in 1.5 mL of dry THF. $LiAlH_4$ (4 mg, 0.10 mmol) was added at 0 °C, and the mixture was stirred for 5 min. After regular aqueous workup, **34a** and **33a** were obtained as a 17:1 mixture. Flash chromatography on silica gel, eluting with hexanes: diethyl ether 20:1, afforded 53 mg (82%) of pure **34a**: IR (cm^{-1}, neat) 3613 (w), 3495 (br, w), 2938 (s), 2854 (s), 1459 (s), 1418 (m), 1378 (s), 1342 (m), 1071 (m), 1009 (m), 924 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (1H, ddd, J = 9.2, 6.2, 2.9 Hz), 1.91−1.60 (5H, m), 1.52−1.03 (31H, m), 1.01 (1H, dd, J = 7.0, 4.0 Hz), 0.88 (9H, t, J = 7.3 Hz), 0.87 (9H, t, J = 7.3 Hz), 0.85−0.74 (13H, m), 0.69 (1H, dd, J = 4.1, 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.63, 44.76, 29.33 (2) (J_{Sn-C} = 19.1 Hz), 29.30

(J_{Sn-C} = 19.0 Hz), 29.15, 27.69 (J_{Sn-C} = 59.3 Hz), 27.64 (J_{Sn-C} = 56.4 Hz), 26.68, 26.36, 26.22, 25.68 (J_{Sn-C} = 22.1, 19.1 Hz), 13.93 (J_{Sn-C} = 24.9 Hz), 13.69 (2), 11.13 (J_{Sn-C} = 317.8, 303.2 Hz), 9.54 (J_{Sn-C} = 315.0, 301.8 Hz), −5.70; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ 15.79, 3.02.

Cyclopropanation of (*Z*)-3,3-Bis(tributylstannyl)prop-2-en-1-ol (32e). According to the general procedure A, allylic alcohol **32e** (140 mg, 0.22 mmol) was treated with samarium (331 mg, 2.2 mmol) and CH_2I_2 (0.17 mL, 2.1 mmol) in 2.5 mL of THF. Cyclopropyl carbinol **33e** (110 mg, 77%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1.

2,2-Bis(tributylstannyl)cyclopropyl-1-methanol (33e): IR (cm^{-1}, neat) 3334 (br, w), 2955 (s), 2927 (s), 2874 (s), 2853 (s), 1462 (s), 1377 (w), 1068 (w), 1026 (s), 864 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (1H, ddd, *J* = 11.4 Hz (disappears with D_2O)), 11.0, 5.9 Hz), 3.22 (1H, ddd, *J* = 11.0, 8.1, 5.1 (disappears with D_2O), 1.50−1.23 (25H, m), 0.95 (1H, dd, *J* = 6.6, 4.0 Hz), 0.88 (9H, t, *J* = 7.0 Hz), 0.87 (9H, t, *J* = 7.0 Hz), 0.81−0.67 (12H, m), 0.63 (1H, dd, *J* = 4.0, 3.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.63 (J_{Sn-C} = 41.7, 24.2 Hz), 29.27 (J_{Sn-C} = 18.3 Hz), 27.64 (J_{Sn-C} = 60.0 Hz), 27.62 (J_{Sn-C} = 54.2 Hz), 13.68, 13.66, 12.80 (J_{Sn-C} = 24.2 Hz), 11.09 (J_{Sn-C} = 317.8, 303.2 Hz), 9.59 (J_{Sn-C} = 316.4, 303.2 Hz), −5.84 (J_{Sn-C} = 264.2 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ 17.14, 7.51.

Cyclopropanation of (*Z*)-4-(Triisopropylsilyl)-4-(trimethylsilyl)-3-buten-2-ol (35). According to the general procedure A, allylic alcohol **35** (35 mg, 0.12 mmol) was treated with samarium (150 mg, 1.0 mmol) and CH_2I_2 (76 μL, 0.95 mmol) in 0.8 mL of THF. Cyclopropyl carbinol **36** (5.1 mg, 14%) was obtained as a colorless viscous oil following flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1, along with 23 mg (41%) of starting material.

(*R)-[(1*S**,2*S**)-2-(Triisopropylsilyl)-2-(trimethylsilyl)-cyclopropyl]-1-ethanol (36):** 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); ^{1}H 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 $C_{16}H_{36}OSi_2$ $(M - CH_3)^+$ 299.2226, found 299.2226.

(*Z*)-3-Chloro-1-(tributylstannyl)-1-(trimethylsilyl)propene (37). Allylic alcohol **29e** (2.0 g, 4.77 mmol) was dissolved in 20 mL of chloroform. Benzyltriethylammonium chloride (40 mg) was added, and the solution was cooled to 0 °C. NaOH (10 mL, 50 wt % in H_2O) was added dropwise. The mixture was stirred at 0 °C for 3 h and extracted three times with diethyl ether. The combined ethereal layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography, eluting with hexanes, afforded 1.90 g (91%) of the allylic chloride **37** as a colorless oil: IR (cm^{-1}, neat) 2959 (s), 2924 (s), 2875 (m), 2854 (m),1466 (w), 1247 (s), 937 (w), 883 (s), 834 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (1H, t, *J* = 7.0 Hz)(J_{Sn-H} = 157.8, 150.5 Hz), 3.98 (2H, d, *J* = 7.0 Hz), 1.48−1.26 (12H, m), 0.95−0.85 (15H, m), 0.06 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.35, 148.40 (J_{Sn-C} = 23.5 Hz) , 48.13 (J_{Sn-C} = 41.0 Hz), 29.13 (J_{Sn-C} = 19.0 Hz), 27.36 (J_{Sn-C} = 60.1 Hz), 13.64, 11.42 (J_{Sn-C} = 325.1, 310.5 Hz), −0.47; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −52.27.

(1*S,2*R**)-2-Butyl-2-(tributylstannyl)cyclopropyl Cyclohexyl Ketone (42).** According to procedure D, **21a** (30 mg, 0.06 mmol) was dissolved in 3 mL of CH_2Cl_2. Celite (194 mg), molecular sieves (19 mg), and NaOAc (12 mg, 0.15 mmol) were added consecutively. To the cooled suspension was added PCC (39 mg, 0.18 mmol), and the mixture was stirred at 0 °C for 15 min and for 3 h at rt. The mixture was purified by flash chromatography on silica gel, eluting with hexanes:diethyl ether 20:1 to 10:1. Concentration *in vacuo* afforded **42a** (19.4 mg, 65%) as a colorless oil: IR (cm^{-1}, neat) 2959 (s), 2931 (s), 2854 (s), 1694 (m), 1462 (w), 1377 (w), 1258 (w), 1068 (m), 836 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (1H, m), 1.97 (1H, dd, *J* = 6.7, 4.9 Hz), 1.89−1.62 (6H, m), 1.52−1.14 (24H, m), 0.93−0.80 (18H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.82, 52.55, 33.28, 31.92, 29.14 (J_{Sn-C} = 19.4 Hz), 28.88, 28.80, 28.70, 27.54 (J_{Sn-C} = 56.5 Hz), 25.97, 25.91, 25.89, 25.81, 22.82, 19.60, 14.12, 13.69, 9.25 (J_{Sn-C} = 322.8, 308.2 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −0.00; HRMS calcd for $C_{22}H_{41}OSn$ $(M - C_4H_9)^+$ 441.2179, found 441.2149.

(1*S,2*S**)-2-(Tributylstannyl)-2-(trimethylsilyl)cyclopropyl Cyclohexyl Ketone (43).** According to the general procedure E, alcohol **30a** (250 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (10 mL), followed by addition of NMO (85 mg, 0.75 mmol) and TPAP (catalytic amount). After regular aqueous workup, flash chromatography purification and concentration *in vacuo*, **43** (244 mg, 95%) was obtained as a colorless oil: IR (cm^{-1}, neat) 2956 (s), 2928 (s), 2853 (s), 1687 (s), 1453 (m), 1248 (s), 847 (s), 836 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (1H, m), 2.00 (1H, dd, *J* = 6.9, 3.5 Hz), 1.95−1.65 (5H, m), 1.50−1.10 (18H, m), 1.08 (1H, dd, *J* = 6.9, 2.2 Hz), 1.05 (1H, *J* = 3.5, 2.2 Hz), −0.07 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.46, 51.88, 29.30 (J_{Sn-C} = 15.3 Hz), 28.82, 28.69, 27.69 (J_{Sn-C} = 63.7 Hz), 26.51 (J_{Sn-C} = 18.3 Hz), 26.02, 25.91, 25.85, 20.27, 13.78, 11.85 (J_{Sn-C} = 343.5, 328.8 Hz), −1.56; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −14.20. Anal. Calcd for $C_{25}H_{50}OSiSn$: C, 58.48; H, 9.82. Found: C, 58.51; H, 9.93.

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Supplementary Material Available: ^{1}H or ^{13}C spectra of many of the compounds reported are provided (24 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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