Triethylborane-Induced Radical Cyclization of 1-Allyloxy-2-halosilacyclopentane. Stereoselective Synthesis of 1,3,6-Triols Starting from Silacyclobutane

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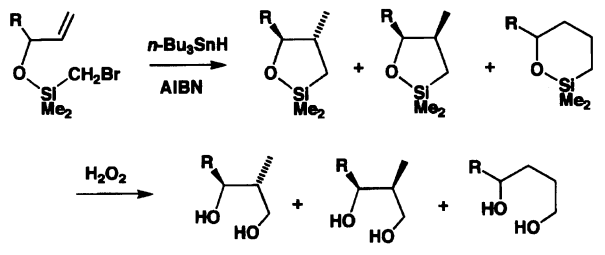
1-Allyloxy-2-bromo-1-phenylsilacyclopentane was synthesized by a ring-enlargement reaction of 1-allyloxy-1-phenylsilacyclobutane with $LiCHBr_2$. The treatment of 1-allyloxy-2-bromo-1-phenylsilacyclopentane with *n*-Bu_3SnH in the presence of a catalytic amount of Et_3B provided 2-oxa-1-silabicyclo[3.3.0]octane, which was converted into 1,3,6-triol by an oxidative cleavage of silicon–carbon bonds with H_2O_2. An intermolecular radical addition of 2-iodosilacyclopentane to acetylenic compounds afforded the corresponding iodoalkenes.

Radical cyclization reactions developed during the last several years represent a breakthrough for synthetic radical chemistry.[1] These reactions exhibit interesting regioselectivities and stereoselectivities, and can be carried out with a variety of functional groups. Silylmethyl radical cyclizations have been widely used as an indirect method for acyclic stereocontrol.[2] The (bromomethyl)dimethylsilyl group is currently being used as a hydroxymethyl radical equivalent. For instance, 1,3-diols or 1,4-diols were stereoselectively synthesized starting from (bromomethyl)dimethylsilyl allylic ethers via intramolecular radical cyclization followed by the H_2O_2 oxidation of the silicon–carbon bonds (Scheme 1).[3]

We have recently reported that the addition of lithium carbenoids, such as $LiCHX_2$ (X=Br, I), to 1,1-dimethylsilacyclobutane provided the corresponding 2-halosilacyclopentanes.[4] Here, we wish to describe (1) the preparation of 1-allyloxy-2-halosilacyclopentanes, (2) the stereoselective cyclization of 2-silacyclopentyl radicals derived from 1-allyloxy-2-halosilacyclopentanes and its application to the synthesis of 1,3,6-triols, and (3) the intermolecular addition of 2-iodosilacyclopentane to acetylenes.[5]

(1) Preparation of 1-Allyloxy-2-halosilacyclopentanes. It occurred to us that, if a carbon radical could be effectively generated at the 2-position on the 1-allyloxy-2-halosilacyclopentane, a cyclization reaction would readily proceed to provide a bicyclic compound, which would be transformed into 1,3,6-triol by an oxidative cleavage of the carbon–silicon bonds. We have, indeed, found that these steps proceed well, as indicated by the results shown in Section (2).

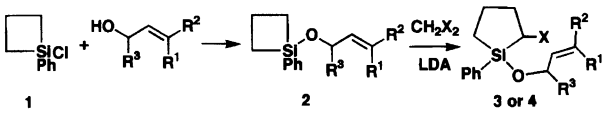


Scheme 1.

The starting materials, 1-allyloxy-2-halo-silacyclopentanes, were prepared as follows. The treatment of 3-chloropropyldichlorophenylsilane with magnesium gave 1-chloro-1-phenylsilacyclobutane (**1**) following the reported procedure.[6] The addition of allylic alcohols to a benzene solution of **1** in the presence of pyridine afforded 1-allyloxysilacyclobutanes **2**. The treatment of **2** with lithium carbenoid, such as $LiCHBr_2$ or $LiCHI_2$, which was prepared form dibromomethane or diiodomethane with lithium diisopropylamide (LDA), provided the corresponding 1-allyloxy-2-halosilacyclopentanes, **3a**—**e** and **4a**—**c**, in good yields[6] (Table 1).

(2) Radical Cyclization of 1-Allyloxy-2-halosilacyclopentane and Its Application to Stereoselective Synthesis of 1,3,6-Triol. The intramolecular cyclization of 1-allyloxy-2-halosilacyclopentane **3a** with *n*-Bu_3SnH in the presence of a catalytic amount of triethylborane[8] afforded cyclized products **5a** and **6a**. Compounds **5a** and **6a** were not sufficiently stable to be purified by silica-gel column chromatography, and were converted into triacetates **9a** and **10a** (**9a**:**10a**=86:14) by direct oxidation[9] followed by acetylation in 32% overall yield from **3a** (method **A**). The treatment of **3b** or **3c** with *n*-Bu_3SnH–Et_3B and subsequent oxidation with H_2O_2, KF, $KHCO_3$ also gave an isomeric mixture of the corresponding triacetate **9b** and

Table 1.



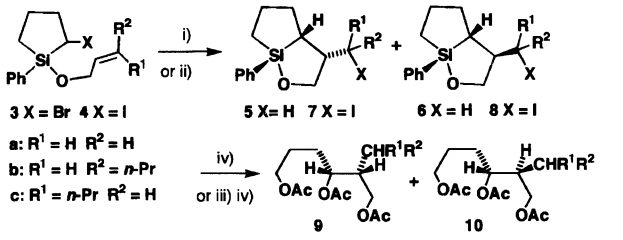
	R^1	R^2	R^3	Yield of **2**	Yield of **3** (X=Br)	Yield of **4** (X=I)
a:	H	H	H	73%	44%	47%
b:	H	*n*-Pr	H	82%	66%	58%
c:	*n*-Pr	H	H	77%	41%	73%
d:	H	H	*t*-Bu	48%	74%	
e:	H	Me	*t*-Bu	66%	76%	

10b (**9b** : **10b**=82 : 18) or **9c** and **10c** (**9c** : **10c**=64 : 36) in 60 or 72% overall yield, respectively. An atom transfer cyclization[10] reaction of **4a**, **4b**, or **4c** with a catalytic amount of Et_3B gave cyclized products **7a** and **8a**, **7b** and **8b**, or **7c** and **8c**, which were transformed into the same isomeric mixture of triacetates **9a** : **10a**= 88 : 12, **9b** : **10b**=88 : 12, **9c** : **10c**=70 : 30 by successive treatments with *n*-Bu_3SnH, H_2O_2–KF–$KHCO_3$, and Ac_2O–pyridine in 37, 35, or 22% overall yield, based on the starting silacyclopentane (method **B**) (Table 2). No 6-*endo* cyclization product was obtained at all under both reaction conditions i) and ii).

The preferential formation of the *endo* bicyclic product **5** or **7** to an *exo* bicyclic product, **6** or **8**, might be explained in a similar fashion as being the preferential formation of *endo*-2-methylbicyclo[3.3.0]octane in the reaction of 1-bromo-2-(3-butenyl)cyclopentane with *n*-Bu_3SnH in the presence of AIBN.[11]

The assignment of the stereochemistry of triacetates **9a** and **10a** was performed by a comparison with an authentic sample prepared as follows. The treatment of *cis* epoxy alcohol **11** with Me_2CuLi gave mono(2-tetrahydropyranyl) ether of *erythro*-2-methyl-1,3,6-hexanetriol under a regioselective ring opening.[12] Removal of the hydroxy protective group and acetylation provided *erythro* triacetate **12**, which was identical with a major product **9a** (Scheme 2). Following the same procedure, *threo* triacetate **10a** was prepared starting from the corresponding *trans* epoxy alcohol, and was identified by a comparison with a sample generated from **3a**.

Table 2.



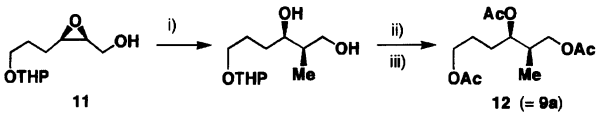
	R^1	R^2	X	Method	Yield of **9**+**10**	Ratio of **9** : **10**
3a:	H	H	Br	**A**	32%	86 : 14
3b:	H	*n*-Pr	Br	**A**	60%	82 : 18
3c:	*n*-Pr	H	Br	**A**	72%	64 : 36
4a:	H	H	I	**B**	37%	88 : 12
4b:	H	*n*-Pr	I	**B**	35%	88 : 12
4c:	*n*-Pr	H	I	**B**	22%	70 : 30

Method **A**: i) *n*-Bu_3SnH–Et_3B, iv) H_2O_2–KF–$KHCO_3$, then Ac_2O–pyridine. Method **B**: ii) Et_3B, iii) *n*-Bu_3SnH–Et_3B, iv) H_2O_2–KF–$KHCO_3$, then Ac_2O–pyridine.

The cyclization of 1-allyloxy-2-bromosilacyclopentanes prepared from secondary allylic alcohols was proved to proceed with high stereospecificity. The addition of $LiCHBr_2$ to 1-allyloxysilacyclobutane **2d** provided a mixture of two diastereomers, **3d-1** and **3d-2**, in a 1 : 1 ratio, which were separated from each other by silica-gel column chromatography. The treatment of **3d-1** with *n*-Bu_3SnH–Et_3B in benzene at 25 °C gave 2-oxa-1-silabicyclo[3.3.0]octane **13d-1** and 2-oxa-1-silabicyclo[4.3.0]nonane **14d-1** in 41 and 9% yields, along with a reduction product **15** in 16% yield. In contrast, the diastereomer **3d-2** provided **13d-2** (65%), **14d-2** (9%), and **15** (15%) upon a treatment with *n*-Bu_3SnH–Et_3B. In these reactions of **3d-1** and **3d-2**, although the 5-*exo* mode cyclization predominated, the 6-*endo* mode could also be observed. However, cyclization reaction of **3e-1** or **3e-2** gave only a 5-*exo* mode product, **13e-1** or **13e-2** (Scheme 3).

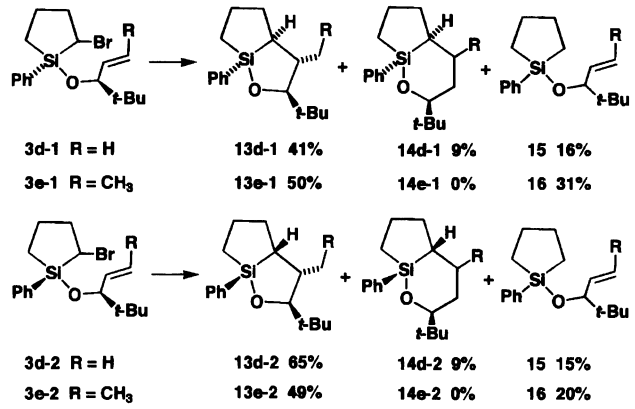
It is worth noting that the product **13d-1**, **13d-2**, **13e-1**, or **13e-2** was obtained as a single stereoisomer without any contamination by other diastereomers. This high stereoselectivity may be due to the great steric repulsion between bulky *t*-butyl and ethenyl or propenyl groups in a transition state of cyclization.

The oxidative cleavage of the carbon–silicon bonds of **13d-1** with H_2O_2–KF–$KHCO_3$ provided (4*S**,5*S**, 6*S**)-1,4,6-triacetoxy-5,7,7-trimethyloctane **17**, and oxidation of **13d-2** afforded a stereoisomeric (4*R**,5*S**, 6*S**)-triacetate **18**. Bicyclo compounds **13e-1** and **13e-2** could also be transformed to triacetates **19** and **20**,



i) Me_2CuLi ii) *p*-TsOH / MeOH iii) Ac_2O / pyridine

Scheme 2.



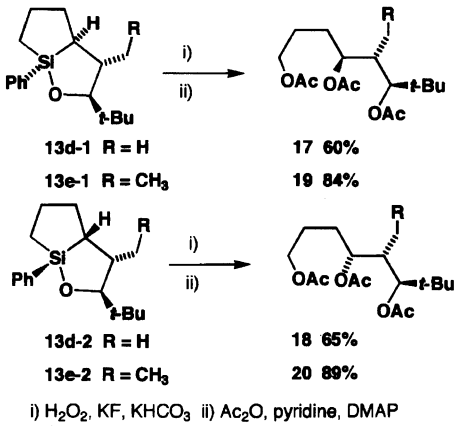
Scheme 3.

respectively (Scheme 4).

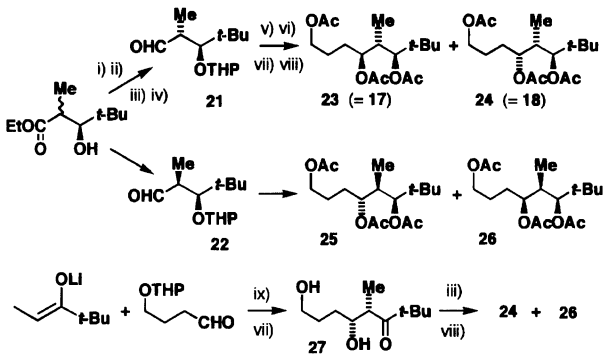
Stereochemical assignments of **17** and **18** were performed by comparisons with authentic samples of four possible diastereomers: **23** ($4S^*,5S^*,6S^*$), **24** ($4R^*,5S^*,6S^*$), **25** ($4R^*,5R^*,6S^*$), and **26** ($4S^*,5R^*,6S^*$), prepared as shown below (Scheme 5). An aldol reaction of 4-(2-tetrahydropyranyloxy)butanal with lithium enolate derived from *t*-butyl ethyl ketone provided an *erythro* adduct **27**[13] after deprotection of THP ether. Reduction followed by acetylation afforded a diastereomeric mixture of **24** and **26**. The triacetate **24** was identical with one of the diastereomers generated from **21**; the other isomer **26** showed identical spectral data as a diastereomer derived from the other isomer **22**.

Assignments of the stereochemistry of triacetates **19** and **20** were also performed by comparisons with authentic samples of four possible diastereomers prepared by the same route as shown above.

(3) Intermolecular Radical Addition of 2-Halosilacyclopentane to Carbon–Carbon Multiple Bond. Compared with intramolecular radical cyclization, there have been few reports concerning intermolecular silylmethyl radical addition to a carbon–carbon multiple bond. We previously reported that alkyl iodides, such as *t*-butyl iodide or isopropyl iodide, added to nonactivated alkynes as well as activated alkynes in



Scheme 4.



Scheme 5.

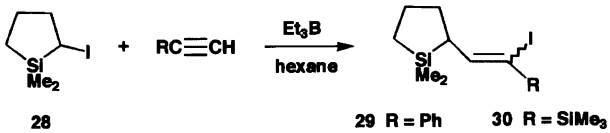
the presence of a catalytic amount of Et_3B.[14] Here, we examined the intermolecular reaction of 2-iodo-1,1-dimethylsilacyclopentane (**28**) with alkynes and alkenes. The addition of Et_3B to a hexane solution of **28** and phenylacetylene or trimethylsilylacetylene at room temperature provided iodoalkene **29** ($E:Z=24:76$) or **30** ($E:Z=<1:99$) in 41 or 55% yield (Scheme 6).

In contrast, an aliphatic terminal alkyne or alkene can not be used as a radical acceptor. For example, the reaction of 2-iodo-1,1-dimethylsilacyclopentane with 1-dodecyne or 1-dodecene resulted in a recovery of the starting 1-dodecyne or 1-dodecene along with reduced 1,1-dimethylsilacyclopentane. The reaction of **28** with electron-deficient olefins, such as methyl acrylate, also resulted in the formation of 1,1-dimethylsilacyclopentane.

Experimental

A distillation of the products was performed by the use of Kugelrohr (Büchi); the boiling points are indicated by the air-bath temperature values without any correction. The melting points were obtained on a Yanako MP-50929 melting-point apparatus and are uncorrected. The NMR spectra (^1H and ^{13}C) were recorded on a Varian Gemini 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University. TLC was carried out on silica-gel (Kieselgel 60 F254). Silica-gel column chromatography was performed on a Wakogel C-200.

Preparation of 1-Allyloxysilacyclobutane 2a, 2b, 2c, 2d, and 2e. The reaction of 1-chloro-1-phenylsilacyclobutane with 2-propen-1-ol is representative. 2-Propen-1-ol (0.54 ml, 8.0 mmol) was added to a solution of pyridine (0.71 ml, 8.8 mmol) and 1-chloro-1-phenylsilacyclo-



Scheme 6.

butane (1.46 g, 8.0 mmol), which was prepared according to the reported procedure,[6] in benzene (16 ml) at room temperature under an argon atmosphere. After being stirred for 2 h, the resulting precipitate was filtered through a glass filter. The filtrate was concentrated in vacuo. Distillation of the residual oil using Kugelrohr afforded 1-allyloxy-1-phenylsilacyclobutane (**2a**, 1.20 g, 5.9 mmol) in 73% yield: Bp 51—52 °C (bath temp, 1.0 Torr, 1 Torr=133.322 Pa); IR (neat) 3066, 2966, 2920, 2854, 1429, 1123, 1073, 1034, 918, 853, 738, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.38—1.63 (m, 4H), 1.63—1.90 (m, 1H), 2.01—2.26 (m, 1H), 4.36 (ddd, J=4.8, 1.7, 1.7 Hz, 2H), 5.21 (ddt, J=10.4, 1.7, 1.7 Hz, 1H), 5.39 (ddt, J=17.1, 1.7, 1.7 Hz, 1H), 6.08 (ddt, J=17.1, 10.4, 4.8 Hz, 1H), 7.46—7.60 (m, 3H), 7.75—7.88 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.73, 17.86, 64.50, 114.96, 127.98, 130.17, 133.57, 136.62. Found: C, 70.62; H, 8.04%. Calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89%.

1-((*E*)-2-Hexenyloxy)-1-phenylsilacyclobutane (2b): Bp 74—75 °C (bath temp, 0.5 Torr); IR (neat) 2958, 2926, 2866, 1420, 1117, 1054, 969, 853, 738, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, J=7.3 Hz, 3H), 1.25—1.88 (m, 7H), 1.93—2.25 (m, 3H), 4.30 (d, J=4.2 Hz, 2H), 5.60 (dt, J=15.4, 4.7 Hz, 1H), 5.70 (dt, J=15.4, 5.8 Hz, 1H), 7.35—7.65 (m, 3H), 7.63—7.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.71, 13.77, 17.94, 22.25, 34.28, 65.54, 127.93, 128.07, 128.37, 130.07, 132.71, 133.58. Found: C, 73.32; H, 9.17%. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00%.

1-((*Z*)-2-Hexenyloxy)-1-phenylsilacyclobutane (2c): Bp 74—75 °C (bath temp, 0.5 Torr); IR (neat) 3010, 2956, 2924, 2868, 1458, 1430, 1123, 1075, 853 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, J=7.3 Hz, 3H), 1.37 (tq, J=7.3, 7.3 Hz, 2H), 1.39—1.60 (m, 4H), 1.61—1.81 (m, 1H), 2.00 (dt, J=7.3, 7.3 Hz, 2H), 2.00—2.20 (m, 1H), 4.39 (dd, J=1.4, 6.5 Hz, 2H), 5.49 (dtt, J=10.8, 1.4, 7.3 Hz, 1H), 5.62 (dtt, J=10.8, 1.4, 6.5 Hz, 1H), 7.38—7.48 (m, 3H), 7.65—7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.71, 13.80, 17.87, 22.66, 29.51, 59.62, 127.95, 128.06, 128.45, 130.09, 131.97, 133.58. Found: C, 72.84; H, 9.13%. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00%.

1-(1-*t*-Butylallyloxy)-1-phenylsilacyclobutane (2d): Bp 77—78 °C (bath temp, 0.5 Torr); IR (neat) 2954, 2866, 1479, 1429, 1392, 1363, 1124, 1065, 1031, 995, 921, 854, 738, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (s, 9H), 1.35—1.78 (m, 5H), 2.00—2.16 (m, 1H), 3.96 (dt, J=6.8, 1.2 Hz, 1H), 5.13 (dt, J=10.5, 1.2 Hz, 1H), 5.17 (dt, J=17.1, 1.2 Hz, 1H), 5.92 (ddd, J=6.8, 10.5, 17.1 Hz, 1H), 7.36—7.48 (m, 3H), 7.66—7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.66, 18.35, 18.95, 25.84, 35.28, 82.70, 116.13, 127.83, 127.88, 133.62, 137.95. Found: C, 73.54; H, 9.39%. Calcd for $C_{16}H_{24}OSi$: C, 73.78; H, 9.29%.

1-((*E*)-1-*t*-Butyl-2-butenyloxy)-1-phenylsilacyclobutane (2e): Bp 78—79 °C (bath temp, 0.5 Torr); IR (neat) 2952, 2864, 1478, 1429, 1391, 1362, 1123, 1089, 1046, 970, 917, 857, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (s, 9H), 1.33—1.85 (m, 5H), 1.68 (d, J=4.4 Hz, 3H), 1.98—2.23 (m, 1H), 3.90 (d, J=4.4 Hz, 1H), 5.45—5.70 (m, 2H), 7.38—7.58 (m, 3H), 7.68—7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.75, 17.74, 18.40, 19.05, 25.90, 35.36, 82.70, 127.57, 127.78, 127.96, 129.77, 130.99, 133.62. Found: C, 74.51; H, 9.83%. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55%.

Preparation of 1-Allyloxy-2-halosilacyclopentane 3a—3c, and 4a—4c. The reaction of 1-allyloxy-1-phenylsilacyclobutane (**2a**) with (dibromomethyl)lithium is representative. Butyllithium (1.5 M hexane solution (1 M=1 mol dm^{-3}), 4.2 ml, 6.3 mmol) was added to a solution of diisopropylamine (0.96 ml, 6.9 mmol) in THF (7 ml) at 0 °C. The resulting solution of lithium diisopropylamide was added dropwise to a solution of **2a** (1.17 g, 5.7 mmol) and dibromomethane (0.44 ml, 6.3 mmol) in THF (12 ml) over a period of 30 min by a syringe pump at −78 °C under an argon atmosphere. The resulting mixture was stirred at −78 °C for another 30 min after completion of the addition. Then, the cooled bath was removed and the reaction mixture was allowed to come to room temperature. The reaction mixture was poured into saturated aqueous NH_4Cl and extracted with ethyl acetate (25 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Distillation of the residual oil using Kugelrohr provided 1-allyloxy-2-bromo-1-phenylsilacyclopentane (**3a**, 749 mg, 2.5 mmol) in 44% yield as a 9:1 stereoisomeric mixture. Separation of the isomers by silica-gel column chromatography (hexane/AcOEt=40/1) caused a selective decomposition of the minor product: major product: Bp 116—117 °C (bath temp, 0.5 Torr); IR (neat) 2934, 2860, 1429, 1119, 1070, 1035, 919, 818, 737, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (ddd, J=8.3, 8.3, 10.3 Hz, 1H), 1.18 (ddd, J=6.0, 8.0, 10.3 Hz, 1H), 1.88—2.10 (m, 2H), 2.10—2.38 (m, 2H), 3.67 (dd, J=4.8, 4.8 Hz, 1H), 4.23 (dt, J=4.8, 1.7 Hz, 2H), 5.15 (ddt, J=1.6, 10.4, 1.7 Hz, 1H), 5.28 (ddt, J=1.6, 17.1, 1.7 Hz, 1H), 5.93 (ddt, J=10.4, 17.1, 4.8 Hz, 1H), 7.35—7.58 (m, 3H), 7.63—7.83 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.44, 22.54, 35.88, 37.61, 64.82, 115.20, 127.73, 127.81, 130.50, 134.98, 136.23. Found: C, 52.27; H, 5.86%. Calcd for $C_{13}H_{17}BrOSi$: C, 52.52; H, 5.77%.

1-Allyloxy-2-iodo-1-phenylsilacyclopentane (4a): Bp 106—107 °C (bath temp, 1.0 Torr); IR (neat) 3066, 2932, 2856, 1429, 1117, 1084, 1047, 919, 823, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (t, J=7.6 Hz, 2H), 1.58—1.75 (m, 1H), 1.90—2.25 (m, 3H), 3.34 (dd, J=6.8, 7.0 Hz, 1H), 4.40 (dt, J=4.7, 1.8 Hz, 1H), 4.41 (dt, J=4.7, 1.8 Hz, 1H), 5.14 (ddt, J=10.4, 1.8, 1.8 Hz, 1H), 5.34 (ddt, J=17.1, 1.8, 1.8 Hz, 1H), 5.98 (ddt, J=10.4, 17.1, 4.7 Hz, 1H), 7.38—7.55 (m, 3H), 7.63—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.37, 8.72, 24.49, 38.60, 65.38, 115.05, 128.15, 128.23, 130.41, 133.91, 136.27. Found: C, 45.25; H, 5.05%. Calcd for $C_{13}H_{17}IOSi$: C, 45.35; H, 4.98%.

2-Bromo-1-((*E*)-2-hexenyloxy)-1-phenylsilacyclopentane (3b): Bp 121—122 °C (bath temp, 0.5 Torr); IR (neat) 2928, 2862, 1429, 1117, 1057, 969, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=7.4 Hz, 3H), 0.98—1.20 (m, 2H), 1.41 (tq, J=7.4, 7.4 Hz, 2H), 1.63—1.85 (m, 1H), 1.93—2.23 (m, 5H), 3.61 (dd, J=5.8, 5.8 Hz, 1H), 4.32 (dd, J=4.0, 12.5 Hz, 1H), 4.37 (dd, J=5.0, 12.5 Hz, 1H), 5.63 (dt, J=15.2, 4.0 Hz, 1H), 5.73 (dt, J=15.2, 5.0 Hz, 1H), 7.40—7.58 (m, 3H), 7.60—7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.83, 13.71, 22.24, 22.57, 34.27, 35.85, 37.42, 65.55, 127.68, 128.11, 130.34, 132.82, 133.95, 135.00. Found: C, 56.77; H, 6.93%. Calcd for $C_{16}H_{23}BrOSi$: C, 56.63; H, 6.83%.

1-((*E*)-2-Hexenyloxy)-2-iodo-1-phenylsilacyclopentane (4b): Bp 130—131 °C (bath temp, 0.5 Torr); IR (neat) 2926, 2858, 1429, 1117, 1057, 969, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=7.4 Hz, 3H), 0.92—1.05 (m, 2H), 1.38 (tq, J=7.4, 7.4 Hz, 2H), 1.60—1.78 (m, 1H), 1.92—2.21 (m, 5H), 3.34 (dd, J=6.6, 6.6 Hz, 1H), 4.31 (dd,

J=4.3, 19.5 Hz, 1H), 4.36 (dd, J=5.0, 19.5 Hz, 1H), 5.61 (dt, J=15.2, 4.3 Hz, 1H), 5.66 (dt, J=15.2, 5.0 Hz, 1H), 7.35—7.48 (m, 3H), 7.56—7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.55, 8.88, 13.72, 22.26, 24.45, 34.27, 38.55, 65.47, 128.07, 130.22, 130.30, 132.76, 133.79, 133.93. Found: C, 49.87; H, 5.94%. Calcd for $C_{16}H_{23}IOSi$: C, 49.74; H, 6.00%.

2-Bromo-1-((*Z*)-2-hexenyloxy)-1-phenylsilacyclopentane (3c): Bp 122—123 °C (0.5 Torr, bath temp); IR (neat) 2930, 2864, 1429, 1117, 1078, 755, 737, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86 (t, J=7.3 Hz, 3H), 0.88—0.98 (m, 1H), 0.98—1.12 (m, 1H), 1.34 (tq, J=7.3, 7.3 Hz, 2H), 1.66—1.80 (m, 1H), 1.94 (dt, J=7.3, 7.4 Hz, 2H), 1.98—2.19 (m, 3H), 3.58 (dd, J=5.8, 5.8 Hz, 1H), 4.45 (dd, J=6.2, 19.5 Hz, 1H), 4.49 (dd, J=6.2, 19.5 Hz, 1H), 5.47 (ttt, J=1.3, 7.3, 10.9 Hz, 1H), 5.62 (ttt, J=1.3, 6.2, 10.9 Hz, 1H), 7.34—7.48 (m, 3H), 7.56—7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.81, 13.71, 22.56, 22.67, 29.54, 35.84, 37.43, 60.69, 128.12, 128.35, 130.35, 131.91, 133.84, 133.94. Found: C, 56.84; H, 6.91%. Calcd for $C_{16}H_{23}OSiBr$: C, 56.63; H, 6.83%.

1-((*Z*)-2-Hexenyloxy)-2-iodo-1-phenylsilacyclopentane (4c): Bp 128—130 °C (bath temp, 0.3 Torr); IR (neat) 2928, 2860, 1429, 1117, 1081, 755, 737, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.84 (t, J=7.4 Hz, 3H), 0.90—1.09 (m, 2H), 1.34 (tq, J=7.4, 7.4 Hz, 2H), 1.58—1.80 (m, 1H), 1.92—2.22 (m, 5H), 3.35 (dd, J=6.6, 6.6 Hz, 1H), 4.42 (dd, J=6.5, 21.0 Hz, 1H), 4.48 (dd, J=6.0, 21.0 Hz, 1H), 5.47 (dt, J=11.0, 6.5 Hz, 1H), 5.63 (dt, J=11.0, 6.0 Hz, 1H), 7.33—7.48 (m, 3H), 7.58—7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.58, 8.86, 13.73, 22.68, 24.43, 29.59, 38.58, 60.67, 128.10, 128.29, 130.30, 131.86, 133.72, 133.94. Found: C, 50.04; H, 5.97%. Calcd for $C_{16}H_{23}IOSi$: C, 49.74; H, 6.00%.

Preparation of 2-Bromo-1-(*t*-butyl-2-alkenyloxy)-silacyclopentane 3d-1, 3d-2, 3e-1, and 3e-2. Diastereomeric mixtures **3d-1** and **3d-2**, or **3e-1** and **3e-2**, prepared by the same procedure as described for the preparation of **3a**, were separated by silica-gel column chromatography (hexane). Faster moving band: (1*R**)-2-Bromo-1-((1*S**)-1-*t*-butyl-2-allyloxy)-1-phenylsilacyclopentane (**3d-1**); R_f=0.60 (hexane); Bp 119—121 °C (bath temp, 0.5 Torr); IR (neat) 3066, 2950, 2864, 1429, 1364, 1116, 1077, 1033, 997, 928, 856, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.85—1.10 (m, 2H), 0.93 (s, 9H), 1.63—1.85 (m, 1H), 1.94—2.19 (m, 3H), 3.49 (dd, J=5.4, 5.4 Hz, 1H), 4.05 (d, J=7.8 Hz, 1H), 5.06 (d, J=16.7 Hz, 1H), 5.08 (d, J=10.8 Hz, 1H), 5.85 (ddd, J=7.8, 10.8, 16.7 Hz, 1H), 7.38—7.53 (m, 3H), 7.58—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.42, 22.25, 25.93, 35.54, 36.77, 36.91, 84.22, 117.08, 127.90, 130.00, 133.96, 135.23, 137.98. Found: C, 57.83; H, 7.22%. Calcd for $C_{17}H_{25}BrOSi$: C, 57.78; H, 7.13%.

Slower moving band: (1*S**)-2-Bromo-1-((1*S**)-1-*t*-butyl-2-propen-1-oxy)-1-phenylsilacyclopentane (**3d-2**); R_f=0.58 (hexane); Bp 120—121 °C (bath temp, 0.5 Torr); IR (neat) 2950, 2864, 1479, 1460, 1429, 1363, 1117, 1075, 1033, 996, 931, 856, 738, 712, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (s, 9H), 0.91—1.07 (m, 2H), 1.55—1.83 (m, 1H), 1.95—2.20 (m, 3H), 3.46 (dd, J=5.8, 5.8 Hz, 1H), 3.80 (d, J=7.9 Hz, 1H), 5.02 (dd, J=1.7, 17.1 Hz, 1H), 5.10 (dd, J=1.7, 10.4 Hz, 1H), 5.88 (ddd, J=7.9, 10.4, 17.1 Hz, 1H), 7.38—7.55 (m, 3H), 7.60—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.74, 22.58, 25.82, 35.59, 35.90, 36.53, 83.93, 117.07, 127.90, 127.98, 130.14, 134.14, 137.93. Found: C, 57.83; H, 7.07%. Calcd for $C_{17}H_{25}BrOSi$: C, 57.78; H, 7.13%.

(1*R)-2-Bromo-1-((*E*)-(1*S**)-1-*t*-butyl-2-butenyloxy)-1-phenylsilacyclopentane (3e-1):** Faster moving band; R_f=0.60 (hexane); Bp 115—116 °C (bath temp, 0.5 Torr); IR (neat) 2948, 2862, 1478, 1459, 1449, 1429, 1362, 1115, 1093, 1056, 971, 860, 737, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.78—1.15 (m, 2H), 0.91 (s, 9H), 1.60 (d, J=4.8 Hz, 3H), 1.63—1.85 (m, 1H), 1.88—2.20 (m, 3H), 3.48 (dd, J=5.2, 5.2 Hz, 1H), 4.00 (d, J=7.1 Hz, 1H), 5.43 (dq, J=15.4, 4.8 Hz, 1H), 5.53 (dd, J=7.1, 15.4 Hz, 1H), 7.38—7.55 (m, 3H), 7.58—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.19, 17.18, 21.86, 25.53, 35.15, 36.46, 36.55, 83.58, 127.39, 128.10, 129.43, 130.61, 133.51, 135.28. Found: C, 58.85; H, 7.47%. Calcd for $C_{18}H_{27}BrOSi$: C, 58.84; H, 7.41%.

(1*S)-2-Bromo-1-((*E*)-(1*S**)-1-*t*-butyl-2-butenyloxy)-1-phenylsilacyclopentane (3e-2):** Slower moving band; R_f=0.58 (hexane); Bp 115—116 °C (bath temp, 0.5 Torr); IR (neat) 2950, 2862, 1654, 1459, 1449, 1429, 1363, 1115, 1093, 1056, 970, 737, 711, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.80—1.05 (m, 2H), 0.88 (s, 9H), 1.50—1.75 (m, 1H), 1.63 (d, J=5.0 Hz, 3H), 1.93—2.20 (m, 3H), 3.34 (dd, J=5.9, 5.9 Hz, 1H), 3.78 (d, J=7.9 Hz, 1H), 5.37 (dq, J=15.4, 5.0 Hz, 1H), 5.51 (dd, J=15.4, 7.9 Hz, 1H), 7.35—7.53 (m, 3H), 7.55—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.97, 17.66, 22.66, 25.87, 35.49, 36.00, 36.58, 83.66, 127.93, 128.71, 129.99, 130.97, 134.05, 135.11. Found: C, 58.90; H, 7.52%. Calcd for $C_{18}H_{27}BrOSi$: C, 58.84; H, 7.41%.

Et_3B-*n*-Bu_3SnH Induced Radical Cyclization of 1-Allyloxy-2-halosilacyclopentane and Successive Transformation to 1,3,6-Triacetoxyalkane (Method A). The reaction of 1-allyloxy-2-bromo-1-phenylsilacyclopentane (**3a**) is representative. A triethylborane (0.96 M hexane solution, 0.17 ml, 0.16 mmol) was added to a solution of **3a** (240 mg, 0.81 mmol) and *n*-Bu_3SnH (260 mg, 0.89 mmol) in benzene (40 ml) at 25 °C under an argon atmosphere. After being stirred for 3 h at room temperature, the resulting reaction mixture was concentrated. The crude reaction mixture was diluted with THF (8 ml) and MeOH (8 ml). Potassium fluoride (188 mg, 3.24 mmol), $KHCO_3$ (810 mg, 8.1 mmol), and H_2O_2 (30%, 920 mg, 8.1 mmol) were added, and the whole was stirred for 10 h at room temperature. The resulting precipitate was filtered through Celite, and the filtrate was concentrated in vacuo. To the crude reaction mixture were added acetic anhydride (2 ml) and pyridine (1 ml). After being stirred for 12 h at room temperature, the reaction mixture was poured into 1 M HCl and extracted with ethyl acetate (25 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography (hexane/AcOEt=3/1) to give an 84:16 mixture of *erythro*-1,3,6-triacetoxy-2-methylhexane (**9a**) and *threo*-1,3,6-triacetoxy-2-methylhexane (**10a**) in 32% overall yield. Separation of **9a** and **10a** was performed by preparative TLC (hexane/AcOEt=5/1).

9a: Bp 77—78 °C (bath temp, 0.5 Torr); IR (neat) 2960, 1738, 1369, 1235, 1038, 966 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.96 (d, J=7.0, 3H), 1.53—1.77 (m, 5H), 2.06 (s, 3H), 2.07 (s, 6H), 3.89 (dd, J=6.4, 11.0 Hz, 1H), 4.00 (dd, J=7.1, 11.0 Hz, 1H), 4.07 (t, J=6.2 Hz, 2H), 4.90—5.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=11.33, 20.82, 20.87, 20.92, 24.89, 27.93, 35.74, 63.91, 65.70, 73.10, 170.58, 170.97. Found: C, 56.72; H, 8.12%. Calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.09%.

10a: Bp 77—78 °C (bath temp, 0.5 Torr); IR (neat) 2960,

1738, 1369, 1235, 1038, 966 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (d, J=7.0 Hz, 3H), 1.52—1.73 (m, 5H), 2.06 (s, 3H), 2.07 (s, 6H), 3.95—4.10 (m, 4H), 4.90—4.98 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=13.46, 20.82, 20.92, 24.53, 27.66, 35.96, 64.02, 65.55, 74.27, 170.58, 171.12. Found: C, 56.40; H, 7.92%. Calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.09%.

***erythro*-1,3,6-Triacetoxy-2-butylhexane (9b):** Bp 97—98 °C (bath temp, 0.5 Torr); IR (neat) 2954, 2868, 1740, 1459, 1368, 1236, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (t, J=7.5 Hz, 3H), 1.25—1.58 (m, 5H), 1.58—2.00 (m, 6H), 2.05 (s, 9H), 4.05—4.25 (m, 4H), 4.95—5.18 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=13.82, 20.83, 20.96, 22.84, 22.73, 25.00, 26.47, 27.33, 29.40, 40.66, 63.50, 63.78, 73.36, 170.61, 170.71, 171.00. Found: C, 60.48; H, 9.06%. Calcd for $C_{16}H_{28}O_6$: C, 60.74; H, 8.92%.

***threo*-1,3,6-Triacetoxy-2-butylhexane (10b):** Bp 97—98 °C (bath temp, 0.5 Torr); IR (neat) 2954, 2864, 1740, 1466, 1459, 1368, 1237, 1043 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (t, J=7.6 Hz, 3H), 1.18—1.58 (m, 5H), 1.60—2.02 (m, 6H), 2.05 (s, 9H), 4.03—4.27 (m, 4H), 5.00—5.15 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=13.50, 17.48, 24.76, 25.16, 26.15, 27.44, 27.97, 29.06, 40.79, 63.47, 64.04, 73.32, 170.57, 170.96. Found: C, 60.57; H, 8.86%. Calcd for $C_{16}H_{28}O_6$: C, 60.74; H, 8.92%.

Atom Transfer Cyclization of 1-Allyloxy-2-iodosilacyclopentane and Successive Transformation to 1,3,6-Triacetoxyalkane (Method B). The reaction of 1-allyloxy-2-iodo-1-phenylsilacyclopentane (**4a**) is representative. Triethylborane (0.96 M hexane solution, 0.52 ml, 0.50 mmol) was added to a solution of **4a** (344 mg, 1.0 mmol) in hexane (10 ml) at 25 °C under an argon atmosphere. After being stirred for 24 h, n-Bu_3SnH (320 mg, 1.1 mmol) and Et_3B (0.1 ml, 0.96 mmol) were added to the reaction mixture, and the whole was stirred for 3 h at room temperature. The resulting mixture was concentrated. The crude reaction mixture was diluted with THF (10 ml) and MeOH (10 ml). Potassium fluoride (230 mg, 4 mmol), $KHCO_3$ (1.0 g, 10 mmol), and H_2O_2 (30%, 1.1 g, 10 mmol) were added, and the resulting mixture was stirred for 10 h at room temperature. The precipitate was filtered through Celite, and the filtrate was concentrated in vacuo. To the crude reaction mixture were added acetic anhydride (2 ml) and pyridine (1 ml). After being stirred for 12 h at room temperature, the reaction mixture was poured into 1 M HCl and extracted with ethyl acetate (25 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/AcOEt=3/1) gave an 88:12 mixture of *erythro*-1,3,6-triacetoxy-2-methylhexane (**9a**) and *threo*-1,3,6-triacetoxy-2-methylhexane (**10a**) in a 32% overall yield.

Preparation of *cis*-6-(2-Tetrahydropyranyloxy)-2,3-epoxyhexan-1-ol (11). A solution of 6-(2-tetrahydropyranyloxy)-2-hexyn-1-ol (2.72 g, 13 mmol) in EtOH (5 ml) was added to a suspension of $Ni(OAc)_2 \cdot 4H_2O$ (870 mg, 3.5 mmol) and $NaBH_4$ (170 mg, 4.5 mmol) in EtOH (13 ml) at room temperature under a hydrogen atmosphere. After being stirred for 1.5 h, the resulting precipitate was filtered through a Celite–Na_2SO_4 column; the filtrate was concentrated in vacuo. The crude reaction mixture was diluted with CH_2Cl_2 (30 ml). Sodium acetate (2.3 g, 28 mmol) and *m*CPBA (2.4 g, 13 mmol) were added, and the whole was stirred for 2 h at room temperature. The resulting reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (30 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography (hexane/AcOEt=2/1) to give the title compound (1.28 g, 5.9 mmol) in 46% overall yield: Bp 105—107 °C (bath temp, 0.3 Torr); IR (neat) 3432 (broad), 2938, 2866, 1455, 1442, 1353, 1200, 1136, 1119, 1074, 1033, 985, 904, 867, 812 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.45—2.00 (m, 10H), 2.20—2.95 (bs, 1H, OH), 3.00—3.10 (m, 1H), 3.12—3.22 (m, 1H), 3.42—3.58 (m, 2H), 3.71—3.93 (m, 4H), 4.52—4.61 (m, 1H); ^{13}C NMR ($CDCl_3$) δ sets of 1:1 peaks (19.74, 20.05), (23.82, 24.64), (25.25, 25.30), (26.29, 26.65), (30.65, 30.76), 56.74, (57.00, 57.10), (59.88, 60.44), (62.70, 63.21), (66.29, 66.86), (99.10, 99.29). Found: C, 60.83; H, 9.38%. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32%.

Conversion of 11 into 12. Methyllithium (1.15 M, diethyl ether solution, 11.3 ml, 13 mmol) was added to a suspension of CuI (1.19 g, 6.25 mmol) in ether (19 ml) at −45 °C under an argon atmosphere, and the mixture was stirred for 20 min. A solution of epoxy alcohol **11** (216 mg, 1.0 mmol) in ether (5 ml) was successively added, and the whole was stirred for 30 min at −45 °C and for another 30 min at 0 °C. The reaction mixture was diluted with ethyl acetate (25 ml). Water (1.2 ml) was added and stirring was continued for 5 min. Then, saturated aqueous NH_4Cl (0.6 ml) was added. The supernatant was taken by decantation and poured into saturated aqueous $NaHCO_3$. Extraction with ethyl acetate (20 ml×3) followed by concentration gave a residual oil, which was submitted to silica-gel column chromatography (AcOEt) to give *erythro*-2-methyl-6-(2-tetrahydropyranyloxy)-1,3-hexanediol (126 mg, 0.54 mmol) in 54% yield: Bp 103—104 °C (bath temp, 0.3 Torr); IR (neat) 3366 (broad), 2940, 2870, 1453, 1353, 1200, 1120, 1075, 1024, 972 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85—0.96 (m, 3H), 1.12—1.38 (m, 1H), 1.48—1.90 (m, 10H), 2.30—3.30 (bs, 2H, OH), 3.35—3.94 (m, 7H), 4.53—4.64 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=10.38, 14.57, 19.56, 19.78, 25.28, 26.75, 27.13, 29.41, 30.53, 31.23, 35.39, 39.17, 62.45, 62.64, 64.88, 66.97, 67.62, 67.76, 74.38, 74.52, 75.33. An analytically pure sample was obtained after deprotection and acetylation. The compound was diluted with MeOH (5 ml) followed by the addition of *p*-TsOH (30 mg). The mixture was stirred for 10 h at room temperature. The resulting mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (10 ml×5) and $CHCl_3$/EtOH (3/1) (10 ml×5). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Acetic anhydride (2 ml) and pyridine (1 ml) were added to the residual oil, and the whole was stirred for 12 h. An extractive workup followed by purification by silica-gel column chromatography (hexane/AcOEt=3/1) provided triacetate **12** (164 mg, 0.52 mmol), whose spectral data were identical with those of **9a**.

Radical Cyclization of 3d-1, 3d-2, 3e-1, and 3e-2. The reaction of (1R^*)-2-Bromo-1-((1S^*)-1-*t*-butylallyloxy)-1-phenylsilacyclopentane (**3d-1**) with n-Bu_3SnH and Et_3B is representative. Triethylborane (0.96 M hexane solution, 0.17 ml, 0.16 mmol) was added to a solution of **3d-1** (282 mg, 0.80 mmol) and n-Bu_3SnH (0.24 ml, 0.88 mmol) in benzene (40 ml) at 25 °C under an argon atmosphere. After being stirred for 2 h at room temperature, the reaction mix-

ture was diluted with CH_2Cl_2 (40 ml). Potassium fluoride (400 mg) and saturated aqueous KF (0.8 ml) were added, and the whole was stirred for another 4 h. The resulting precipitate was filtered through Celite 545, and the filtrate was concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography (hexane/AcOEt=40/1) to give (1*S**,3*S**,4*R**,5*S**)-3-*t*-butyl-4-methyl-1-phenyl-2-oxa-1-silabicyclo[3.3.0]octane (**13d-1**, 90 mg, 0.33 mmol), (1*S**,3*S**,6*S**)-3-*t*-butyl-1-phenyl-2-oxa-1-silabicyclo[4.3.0]-nonane (**14d-1**, 25 mg, 0.09 mmol), and 1-(1-*t*-butylallyl-oxy)-1-phenylsilacyclopentane (**15**, 32 mg, 0.12 mmol).

13d-1: Bp 84—86 °C (bath temp, 0.5 Torr); IR (neat) 2948, 2862, 1430, 1361, 1119, 1005, 870, 840, 732, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.66 (ddd, J=8.2, 10.4, 15.7 Hz, 1H), 0.96 (s, 9H), 1.14 (d, J=6.6 Hz, 3H), 1.25—1.52 (m, 2H), 1.52—1.88 (m, 4H), 1.90—2.07 (m, 1H), 3.43 (d, J=3.5 Hz, 1H), 7.38—7.50 (m, 3H), 7.63—7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.66, 17.27, 22.86, 23.73, 26.64, 32.99, 33.61, 41.26, 94.35, 127.90, 130.02, 134.22. Found: C, 74.16; H, 9.77%. Calcd for $C_{17}H_{26}OSi$: C, 74.35; H, 9.54%.

14d-1: Bp 73—75 °C (bath temp, 0.5 Torr); IR (neat) 2944, 2922, 2844, 1429, 1363, 1117, 1053, 1024, 946, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.72—0.88 (m, 1H), 0.93 (s, 9H), 1.09—1.18 (m, 1H), 1.40—1.62 (m, 5H), 1.78—1.98 (m, 3H), 1.98—2.10 (m, 1H), 3.47 (dd, J=2.3, 10.1 Hz, 1H), 7.35—7.42 (m, 3H), 7.56—7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14.34, 20.35, 25.07, 25.77, 26.02, 28.13, 32.16, 35.48, 83.75, 127.83, 129.51, 133.55, 137.28. Found: C, 74.56; H, 9.69%. Calcd for $C_{17}H_{26}OSi$: C, 74.35; H, 9.54%.

15: Bp 73—75 °C (bath temp, 0.5 Torr); IR (neat) 2948, 2862, 1429, 1362, 1117, 1075, 1026, 996, 922, 854, 844, 790, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.65—1.03 (m, 4H), 0.89 (s, 9H), 1.50—1.85 (m, 4H), 3.77 (d, J=7.0 Hz, 1H), 5.03—5.15 (m, 2H), 5.86 (ddd, J=7.0, 9.7, 17.9 Hz, 1H), 7.35—7.50 (m, 3H), 7.60—7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.66, 11.91, 25.86, 26.39, 26.52, 35.37, 82.66, 116.12, 127.66, 129.36, 133.91, 137.54, 138.24. Found: C, 74.31; H, 9.63%. Calcd for $C_{17}H_{26}OSi$: C, 74.35; H, 9.54%.

(1*R,3*S**,4*R**,5*R**)-3-*t*-Butyl-4-methyl-1-phenyl-2-oxa-1-silabicyclo[3.3.0]octane (13d-2):** Bp 84—86 °C (0.5 Torr, bath temp); IR (neat) 2946, 2862, 1430, 1361, 1119, 1005, 870, 840, 733, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.75—1.04 (m, 1H), 0.97 (s, 9H), 1.11 (d, J=6.7 Hz, 3H), 1.25—1.53 (m, 2H), 1.53—1.88 (m, 4H), 2.08—2.25 (m, 1H), 3.39 (d, J=8.7 Hz, 1H), 7.39—7.50 (m, 3H), 7.64—7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.19, 17.27, 26.30, 26.78, 27.07, 27.35, 28.26, 29.44, 36.88, 91.89, 127.84, 130.07, 134.30, 134.58. Found: C, 74.06; H, 9.51%. Calcd for $C_{17}H_{26}OSi$: C, 74.35; H, 9.54%.

(1*R,3*S**,6*R**)-3-*t*-Butyl-1-phenyl-2-oxa-1-silabicyclo[4.3.0]nonane (14d-2):** Bp 73—75 °C (bath temp, 0.5 Torr); IR (neat) 2944, 2918, 2844, 1429, 1363, 1117, 1055, 1026, 947, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.70 (ddd, J=9.0, 10.3, 15.5 Hz, 1H), 0.96 (s, 9H), 1.08—2.05 (m, 9H), 2.07—2.25 (m, 1H), 3.45 (dd, J=1.9, 10.5 Hz, 1H), 7.33—7.42 (m, 3H), 7.56—7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.54, 20.72, 22.93, 25.59, 26.88, 28.59, 33.03, 84.15, 127.66, 129.41, 133.85, 137.71. Found: C, 74.21; H, 9.76%. Calcd for $C_{17}H_{26}OSi$: C, 74.35; H, 9.54%.

(1*S,3*S**,4*R**,5*S**)-3-*t*-Butyl-4-ethyl-1-phenyl-2-oxa-1-silabicyclo[3.3.0]octane (13e-1):** Bp 81—82 °C (bath temp, 0.5 Torr); IR (neat) 2950, 2926, 2864, 1118, 1046, 1018, 856, 732, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.70 (ddd, J=7.8, 10.8, 16.2 Hz, 1H), 0.96 (s, 9H), 0.97—1.15 (m, 1H), 0.98 (t, J=7.0 Hz, 3H), 1.15—1.40 (m, 2H), 1.45—2.05 (m, 6H), 3.53 (d, J=7.8 Hz, 1H), 7.37—7.55 (m, 3H), 7.63—7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.74, 12.09, 24.10, 26.54, 30.15, 31.02, 35.07, 36.34, 48.78, 93.41, 127.90, 130.01, 134.21, 135.37. Found: C, 74.69; H, 10.02%. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78%.

(1*R,3*S**,4*R**,5*R**)-3-*t*-Butyl-4-ethyl-1-phenyl-2-oxa-1-silabicyclo[3.3.0]octane (13e-2):** Bp 81—82 °C (bath temp, 0.5 Torr); IR (neat) 2948, 2868, 1430, 1361, 1119, 1037, 1017, 986, 860, 733, 709, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (t, J=7.2 Hz, 3H), 0.96 (s, 9H), 1.25—1.48 (m, 2H), 1.53—2.02 (m, 8H), 3.42 (d, J=9.1 Hz, 1H), 7.38—7.52 (m, 3H), 7.65—7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=12.90, 13.33, 22.81, 24.88, 26.28, 27.01, 27.26, 36.00, 44.99, 90.41, 127.84, 130.13, 134.26, 134.81. Found: C, 74.65; H, 9.94%. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78%.

1-((*E*)-1-*t*-Butyl-2-butenyloxy)-1-phenylsilacyclopentane (16): Bp 73—74 °C (bath temp, 0.5 Torr); IR (neat) 2930, 2854, 1654, 1450, 1429, 1362, 1116, 1090, 1074, 1051, 1024, 970, 859, 786, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.65—0.98 (m, 4H), 0.87 (s, 9H), 1.50—1.85 (m, 4H), 1.64 (d, J=4.6 Hz, 3H), 3.71 (dd, J=2.2, 5.6 Hz, 1H), 5.35—5.65 (m, 2H), 7.35—7.48 (m, 3H), 7.60—7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.64, 12.01, 17.68, 25.92, 26.32, 26.49, 35.45, 82.58, 127.44, 127.60, 129.25, 121.28, 133.92, 137.92. Found: C, 74.66; H, 10.06%. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78%.

Conversion of 13d-1, 13d-2, 13e-1, and 13e-2 into the Corresponding Triacetate 17, 18, 19, 20. Reaction of **13d-1** is representative. Potassium fluoride (35 mg, 0.60 mmol), $KHCO_3$ (120 mg, 1.2 mmol), and H_2O_2 (30%, 210 mg, 1.8 mmol) were added to a solution of **13d-1** (82 mg, 0.30 mmol) in THF (3 ml) and MeOH (3 ml) at 25 °C. After being stirred for 24 h at room temperature, the resulting reaction mixture was poured into aqueous $NaHSO_3$ and extracted with ethyl acetate (15 ml×4) and ether (15 ml×4). The combined organic layers were concentrated. The residual oil was submitted to silica-gel column chromatography (AcOEt) to give (4*S**,5*S**,6*S**)-5,7,7-trimethyl-1,4,6-octanetriol (37 mg, 0.18 mmol). Acetic anhydride (2 ml), pyridine (1 ml), and 4-(*N*,*N*-dimethylamino)pyridine (10 mg) were added to the triol. After being stirred for 12 h, the resulting reaction mixture was poured into 1 M HCl and extracted with ethyl acetate (15 ml×3). The combined organic layers were concentrated in vacuo. Purification by silica-gel column chromatography (hexane/AcOEt=3/1) provided (4*S**,5*S**,6*S**)-1,4,6-triacetoxy-5,7,7-trimethyloctane (**17**, 60 mg, 0.18 mmol) in 60% overall yield: Bp 92—94 °C (bath temp, 0.3 Torr); IR (neat) 2960, 2874, 1734, 1467, 1370, 1235, 1089, 1021, 967 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (s, 9H), 0.99 (d, J=7.2 Hz, 3H), 1.49—1.68 (m, 4H), 2.04 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 2.08—2.20 (m, 1H), 4.03 (t, J=5.7 Hz, 2H), 4.58 (d, J=5.2 Hz, 1H), 4.91—4.98 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=15.61, 20.97, 21.24, 21.29, 25.04, 26.30, 27.04, 35.54, 36.72, 64.20, 74.31, 82.78, 170.62, 170.96, 171.11. Found: C, 61.72; H, 9.37%. Calcd for $C_{17}H_{30}O_6$: C, 61.76; H, 9.15%.

(4*R,5*S**,6*S**)-1,4,6-Triacetoxy-5,7,7-trimethyloctane (18):** Bp 92—94 °C (bath temp, 0.3 Torr); IR (neat) 2958, 2872, 1734, 1466, 1372, 1246, 1045, 1024, 965

cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (s, 9H), 1.09 (d, J=7.0 Hz, 3H), 1.48—1.72 (m, 4H), 1.90—2.05 (m, 1H), 2.00 (s, 3H), 2.02 (s, 3H), 2.06 (s, 3H), 4.06 (t, J=6.0 Hz, 2H), 4.59 (d, J=5.9 Hz, 1H), 5.11 (ddd, J=1.8, 7.0, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.76, 20.92, 21.19, 25.09, 26.37, 29.42, 35.48, 35.60, 64.05, 72.30, 81.29, 170.61, 170.65, 171.08. Found: C, 61.86; H, 9.45%. Calcd for $C_{17}H_{30}O_6$: C, 61.79; H, 9.15%.

(4*S,5*S**,6*S**)-1,4,6-Triacetoxy-5-ethyl-7,7-dimethyloctane (19):** Bp 94—96 °C (bath temp, 0.3 Torr); IR (neat) 2958, 2874, 1740, 1467, 1371, 1235, 1087, 1021 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (t, J=7.4 Hz, 3H), 0.96 (s, 9H), 1.22—1.38 (m, 1H), 1.42—1.60 (m, 5H), 1.82—1.92 (m, 1H), 2.04 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 4.00—4.10 (m, 2H), 4.77 (d, J=3.3 Hz, 1H), 5.11—5.19 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=11.84, 20.96, 21.20, 22.56, 25.35, 26.16, 28.01, 35.60, 43.37, 64.24, 73.62, 80.08, 170.62, 170.68, 171.06. Found: C, 62.98; H, 9.59%. Calcd for $C_{18}H_{32}O_6$: C, 62.76; H, 9.37%.

(4*R,5*S**,6*S**)-1,4,6-Triacetoxy-5-ethyl-7,7-dimethyloctane (20):** Bp 94—96 °C (bath temp, 0.3 Torr); IR (neat) 2960, 2872, 1739, 1466, 1374, 1243, 1099, 1022, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (s, 9H), 1.00 (t, J=7.4 Hz, 3H), 1.34—1.51 (m, 1H), 1.53—1.78 (m, 6H), 1.99 (s, 3H), 2.00 (s, 3H), 2.05 (s, 3H), 4.07 (t, J=6.1 Hz, 2H), 4.76 (d, J=1.8 Hz, 1H), 5.27—5.33 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=12.96, 20.78, 20.97, 21.24, 21.29, 25.21, 26.37, 30.80, 35.51, 42.63, 64.00, 71.95, 79.29, 170.10, 170.73, 171.03. Found: C, 63.03; H, 9.56%. Calcd for $C_{18}H_{32}O_6$: C, 62.76; H, 9.37%.

Preparation of Ethyl 3-Hydroxy-2,4,4-trimethylpentanoate and Methyl 2-Ethyl-3-hydroxy-4,4-dimethylpentanate. The title compounds were prepared from ethyl 2-bromopropanoate (or methyl 2-bromobutanoate) and 2,2-dimethylpropanal. Diethylaluminium chloride (1.0 M hexane solution, 2.0 ml, 2.0 mmol) was added to a mixture of ethyl 2-bromopropanoate (2.0 g, 11 mmol), 2,2-dimethylpropanal (860 mg, 10 mmol), and zinc dust (1.0 g, 15 mmol) in THF (20 ml) at room temperature under an argon atmosphere. After being stirred for 2 h, the reaction mixture was poured into 1 M HCl and extracted with ether (30 ml×3). The combined organic layers were concentrated. The residual oil was submitted to silica-gel column chromatography (hexane/AcOEt=5/1) to give ethyl *threo*-3-hydroxy-2,4,4-trimethylpentanoate (580 mg, 3.1 mmol) and ethyl *erythro*-3-hydroxy-2,4,4-trimethylpentanoate (550 mg, 2.9 mmol) in 60% yield:

Ethyl *threo*-3-hydroxy-2,4,4-trimethylpentanoate: Faster moving band; R_f=0.5 (hexane/AcOEt=5/1); Bp 93—94 °C (bath temp, 25 Torr); IR (neat) 3488 (broad), 2956, 2872, 1736, 1711, 1460, 1378, 1180, 1121, 1057, 1025, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (s, 9H), 1.29 (t, J=7.1 Hz, 3H), 1.36 (d, J=7.2 Hz, 3H), 2.73 (dq, J=2.0, 7.2 Hz, 1H), 3.17 (d, J=2.0 Hz, 1H), 3.60—3.87 (bs, 1H, OH), 4.15 (q, J=7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.96, 18.15, 26.15, 36.01, 38.22, 60.69, 82.66, 177.66. Found: C, 63.61; H, 10.89%. Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71%.

Ethyl *erythro*-3-hydroxy-2,4,4-trimethylpentanoate: Slower moving band; R_f=0.3 (hexane/AcOEt=5/1); Bp 93—94 °C (bath temp, 25 Torr); IR (neat) 3490 (broad), 2954, 2872, 1717, 1459, 1374, 1179, 1047, 1007 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (s, 9H), 1.23 (d, J=7.2 Hz, 3H), 1.27 (t, J=7.1 Hz, 3H), 2.10—2.28 (bs, 1H, OH), 2.69 (dq, J=4.4, 7.2 Hz, 1H), 3.64 (d, J=4.4 Hz, 1H), 4.14 (q, J=7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=12.93, 14.07, 26.48, 35.50, 41.06, 60.55, 78.06, 177.19. Found: C, 63.52; H, 10.91%. Calcd for $C_{10}H_{20}O_3$: C, 63.76; H, 10.71%.

Methyl *threo*-2-Ethyl-3-hydroxy-4,4-dimethylpentanoate: Bp 94—96 °C (bath temp, 25 Torr); IR (neat) 3496 (broad), 2956, 2872, 1712, 1459, 1437, 1368, 1270, 1194, 1165, 1116, 1069, 992, 974, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (s, 9H), 0.94 (t, J=7.5 Hz, 3H), 1.70 (ddq, J=6.1, 13.7, 7.5 Hz, 1H), 1.91 (ddq, J=9.0, 13.7, 7.5 Hz, 1H), 2.54 (ddd, J=1.8, 6.1, 9.0 Hz, 1H), 3.27 (d, J=1.8 Hz, 1H), 3.40—3.90 (bs, 1H, OH), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=11.99, 25.82, 26.09, 35.88, 45.79, 51.62, 80.77, 177.53. Found: C, 63.65; H, 10.91%. Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71%.

Methyl *erythro*-2-Ethyl-3-hydroxy-4,4-dimethylpentanoate: Bp 94—96 °C (bath temp, 25 Torr); IR (neat) 3412 (broad), 2956, 2874, 1717, 1637, 1459, 1364, 1265, 1195, 1164, 1052, 993, 909, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=7.5 Hz, 3H), 0.93 (s, 9H), 1.57—1.73 (m, 1H), 1.74—1.93 (m, 1H), 2.06—2.20 (bs, 1H, OH), 2.50 (ddd, J=4.0, 6.2, 10.4 Hz, 1H), 3.56 (d, J=5.5 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=11.85, 21.90, 26.16, 35.79, 48.97, 51.42, 78.68, 176.67. Found: C, 63.71; H, 10.99%. Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71%.

Conversion of Ethyl 3-Hydroxy-2,4,4-trimethylpentanoate and Methyl 2-Ethyl-3-hydroxy-4,4-dimethylpentanoate into the Corresponding Triacetate. Preparation of **23** and **24** from ethyl *threo*-3-hydroxy-2,4,4-trimethylpentanoate is representative. 3,4-Dihydro-2*H*-pyran (430 mg, 5.0 mmol) and *p*-TsOH (20 mg) were added to a solution of ethyl *threo*-3-hydroxy-2,4,4-trimethylpentanoate (580 mg, 3.1 mmol) in ether (15 ml). The mixture was stirred for 1 h at room temperature, and poured into saturated aqueous $NaHCO_3$. Extraction and concentration followed by purification by silica-gel column chromatography (hexane/AcOEt=10/1) gave ethyl 3-(2-tetrahydropyranyloxy)pentanoate (600 mg, 2.2 mmol) in 71% yield. The THP ether was added to a suspension of lithium aluminium hydride (80 mg, 2.1 mmol) in THF (10 ml) at 0 °C under an argon atmosphere, and the mixture was stirred for 1 h. Then H_2O (0.1 ml) was added, and 3 M NaOH (0.1 ml) was successively added, and the whole was stirred for another 1 h. The resulting precipitate was filtered through Na_2SO_4 column and washed with ether. The filtrate was concentrated. The residual oil was submitted to silica-gel column chromatography (hexane/AcOEt=3/1) to give 2,4,4-trimethyl-3-(2-tetrahydropyranyloxy)pentan-1-ol. A solution of DMSO (0.42 ml, 6.0 mmol) in CH_2Cl_2 (4 ml) was added to a CH_2Cl_2 (4 ml) solution of oxalyl chloride (0.26 ml, 3.0 mmol) at −78 °C under argon atmosphere. The mixture was stirred for 20 min at −78 °C. A solution of 2,4,4-trimethyl-3-(2-tetrahydropyranyloxy)pentan-1-ol in CH_2Cl_2 (4 ml) was added and the whole was stirred for 30 min. Triethylamine (1.67 ml, 12 mmol) was added with stirring. The reaction mixture was allowed to warm to room temperature and was stirred then for another 30 min. Work-up and purification by silica-gel column chromatography (hexane/AcOEt=5/1) gave 3-(2-tetrahydropyranyloxy)-2,4,4-trimethylpentanal (**21**, 350 mg, 1.5 mmol) in 69% yield. Butyllithium (1.6 M hexane solution, 0.75 ml, 1.2 mmol) was added to a solution of 3-(2-tetrahydropyran-

yloxy)propyne (168 mg, 1.2 mmol) in THF (1.2 ml) at −78 °C, and the reaction mixture was stirred for 30 min. A solution of 3-hydroxy-2,4,4-trimethylpentanal tetrahydropyranyl ether (233 mg, 1.0 mmol) in THF (1.0 ml) was added. After being stirred for 30 min, the reaction mixture was allowed to warm to room temperature, poured into water, and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude reaction mixture was diluted with ethyl acetate (2.5 ml). A catalytic amount of PtO_2 was added and the mixture was stirred for 10 h under an hydrogen atmosphere. The precipitate was filtered through a Na_2SO_4 column, and the filtrate was concentrated in vacuo. Methanol (3 ml) and *p*-TsOH (10 mg) were added to the crude reaction mixture. After being stirred for 5 h, the resulting mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (15 ml×4) and ether (15 ml×2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography (AcOEt) to provide 5,7,7-trimethyl-1,4,6-octanetriol (168 mg, 0.82 mmol). Acetic anhydride (2.0 ml), pyridine (1.0 ml), and 4-(*N*,*N*-dimethylamino)pyridine (10 mg) were added to the triol, and the mixture was stirred for 10 h. A work-up and purification by silica-gel column chromatography (hexane/AcOEt=3/1) gave ($4S^*$,$5S^*$,$6S^*$)-1,4,6-triacetoxy-5,7,7-trimethyloctane (**23**) and ($4R^*$,$5S^*$,$6S^*$)-1,4,6-triacetoxy-5,7,7-trimethyloctane (**24**) (267 mg, 0.81 mmol) as 4:6 diastereomeric mixture. The spectral data of **23** were identical with **17**, and those of **24** were identical with **18**.

($4R^*$,$5R^*$,$6S^*$)-1,4,6-Triacetoxy-5,7,7-trimethyloctane (25): Bp 92—94 °C (bath temp, 0.3 Torr), IR (neat) 2958, 2872, 1738, 1467, 1370, 1247, 1024, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (s, 9H), 0.93 (d, J=7.1 Hz, 3H), 1.48—1.72 (m, 4H), 2.04 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 2.10—2.20 (m, 1H), 3.97—4.12 (m, 2H), 4.75 (d, J=1.8 Hz, 1H), 4.80 (ddd, J=4.2, 4.2, 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=10.90, 20.92, 21.22, 25.19, 25.96, 26.59, 35.83, 35.94, 63.97, 76.78, 77.91, 170.30, 170.98, 171.15. Found: C, 61.58; H, 9.29%. Calcd for $C_{17}H_{30}O_6$: C, 61.79; H, 9.15%.

($4S^*$,$5R^*$,$6S^*$)-1,4,6-Triacetoxy-5,7,7-trimethyloctane (26): Bp 92—94 °C (bath temp, 0.3 Torr); IR (neat) 2958, 2874, 1739, 1482, 1466, 1437, 1371, 1241, 1023, 968 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (d, J=7.3 Hz, 3H), 0.92 (s, 9H), 1.50—1.82 (m, 4H), 2.00—2.18 (m, 1H), 2.05 (s, 6H), 2.06 (s, 3H), 4.05 (t, J=5.9 Hz, 2H), 4.75 (d, J=1.8 Hz, 1H), 4.75—4.83 (m, 1H), ^{13}C NMR ($CDCl_3$) δ=11.46, 20.93, 21.11, 24.55, 26.27, 27.03, 35.64, 35.82, 35.95, 64.08, 76.78, 77.53, 170.44, 170.67, 171.15. Found: C, 61.96; H, 9.45%. Calcd for $C_{17}H_{30}O_6$: C, 61.79; H, 9.15%.

($4R^*$,$5R^*$,$6S^*$)-1,4,6-Triacetoxy-5-ethyl-7,7-dimethyloctane: Bp 94—96 °C (bath temp, 0.3 Torr); IR (neat) 2958, 2874, 1741, 1467, 1372, 1244, 1075, 1021, 976 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (s, 9H), 0.96 (t, J=7.4 Hz, 3H), 1.10—1.27 (m, 1H), 1.48—1.74 (m, 6H), 2.00 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 3.99—4.14 (m, 2H), 4.89 (d, J=1.8 Hz, 1H), 4.92—4.97 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=12.91, 19.45, 20.97, 25.22, 26.28, 28.11, 35.66, 43.29, 63.95, 74.32, 77.00, 169.95, 170.79, 171.14. Found: C, 63.05; H, 9.59%. Calcd for $C_{18}H_{32}O_6$: C, 62.76; H, 9.37%.

($4S^*$,$5R^*$,$6S^*$)-1,4,6-Triacetoxy-5-ethyl-7,7-dimethyloctane: Bp 94—96 °C (bath temp, 0.3 Torr); IR (neat) 2960, 2874, 1736, 1467, 1370, 1241, 1045, 1020, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (s, 9H), 1.00 (t, J=7.4 Hz, 3H), 1.12—1.30 (m, 1H), 1.40—1.88 (m, 5H), 1.89—1.98 (m, 1H), 2.04 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 4.01 (dt, J=10.8, 5.5 Hz, 1H), 4.10 (dt, J=10.8, 6.6 Hz, 1H), 4.88 (d, J=1.3 Hz, 1H), 4.97 (ddd, J=2.6, 3.5, 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=12.66, 19.44, 20.95, 21.24, 24.82, 25.38, 25.90, 35.92, 43.01, 63.89, 74.46, 77.03, 170.24, 170.80, 171.13. Found: C, 62.52; H, 9.26%. Calcd for $C_{18}H_{32}O_6$: C, 62.76; H, 9.37%.

Preparation of *erythro*-5,8-Dihydroxy-2,2,4-trimethyl-3-octanone (27) and *erythro*-4-Ethyl-5,8-dihydroxy-2,2-dimethyl-3-octanone. The preparation of **27** is representative. A solution of *t*-butyl ethyl ketone (342 mg, 3.0 mmol) in THF (3 ml) was added to a solution of lithium diisopropylamide (3.0 mmol) which was prepared from diisopropylamine (0.46 ml, 3.3 mmol) and butyllithium (1.5 M hexane solution, 2.0 ml, 3.0 mmol) in THF (3 ml), at −78 °C under an argon atmosphere. After being stirred for 30 min at −78 °C, a solution of 4-(2-tetrahydropyranyloxy)-butanal (541 mg, 3.0 mmol) was added and the whole was stirred for 1 h at −78 °C. The resulting mixture was poured into water and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude reaction mixture was diluted with MeOH (15 ml) and *p*-TsOH (10 mg) was added, and the mixture was stirred for 3 h. Extractive work up and purification by silica-gel column chromatography (hexane/AcOEt=1/2) gave *erythro*-5,8-dihydroxy-2,2,4-trimethyl-3-octanone (**27**, 444 mg, 2.2 mmol) in 73% yield: Bp 85—86 °C (bath temp, 0.3 Torr); IR (neat) 3338 (broad), 2938, 2870, 1696, 1479, 1458, 1395, 1368, 1055, 984 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.11 (d, J=6.9 Hz, 3H), 1.17 (s, 9H), 1.38—1.77 (m, 4H), 3.03 (dq, J=3.1, 6.9 Hz, 1H), 3.09—3.60 (bs, 2H, OH), 3.59—3.77 (m, 3H); ^{13}C NMR ($CDCl_3$) δ=11.53, 25.96, 29.74, 31.62, 43.50, 44.97, 62.61, 71.81, 222.29. Found: C, 65.39; H, 11.04%. Calcd for $C_{11}H_{22}O_3$: C, 65.31; H, 10.96%.

***erythro*-4-Ethyl-5,8-dihydroxy-2,2-dimethyl-3-octanone:** Bp 103—104 °C (bath temp, 0.3 Torr), IR (neat) 3240 (broad), 2930, 2872, 1686, 1480, 1460, 1367, 1055, 1000, 861 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, J=7.6 Hz, 3H), 1.17 (s, 9H), 1.46—1.83 (m, 6H), 2.70—3.30 (bs, 2H, OH), 3.00 (ddd, J=2.9, 4.4, 8.3 Hz, 1H), 3.59—3.75 (m, 3H); ^{13}C NMR ($CDCl_3$) δ=12.76, 19.35, 26.19, 29.93, 32.04, 44.85, 51.13, 62.62, 71.65, 221.29. Found: C, 66.23; H, 11.41%. Calcd for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18%.

Conversion of *erythro*-5,8-Dihydroxy-2,2,4-trimethyl-3-octanone (27) and *erythro*-4-Ethyl-5,8-dihydroxy-2,2-dimethyl-3-octanone into the Corresponding Triacetate. The conversion of **27** into **24** and **26** is representative. To a suspension of $LiAlH_4$ (38 mg, 0.9 mmol) in THF (2 ml), was added a solution of **27** (61 mg, 0.3 mmol) in THF (1 ml) at 0 °C under an argon atmosphere. After being stirred for 1 h, water (0.5 ml) was slowly added with stirring; the resulting mixture was poured into 1 M HCl, and extracted with ethyl acetate (15 ml×4) and ether (15 ml×2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. To the crude reaction mixture, were added Ac_2O (2 ml), pyridine (1 ml), and 4-(*N*,*N*-dimethylamino)pyridine (10 mg), and the whole was stirred for 10 h. A work-up and purification by silica-

gel column chromatography (hexane/AcOEt=3/1) provided ($4R^*$,$5S^*$,$6S^*$)-1,4,6-triacetoxy-5,7,7-trimethyloctane (**24**) and ($4S^*$,$5R^*$,$6S^*$)-1,4,6-triacetoxy-5,7,7-trimethyloctane (**26**) (83 mg, 0.24 mmol) as 35:65 diastereomeric mixture in 80% yield.

Intermolecular Radical Addition of 2-Iodo-1,1-dimethylsilacyclopentane (28) to Acetylenes. The typical procedure is as follows. Triethyl borane (1.0 M hexane solution, 1.0 ml, 1.0 mmol) was added to a solution of **28** (240 mg, 1.0 mmol) and phenylacetylene (0.33 ml, 3.0 mmol) in hexane (6 ml) under an argon atmosphere at 25 °C. After being stirred for 20 h, the resulting mixture was concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography (hexane) to give 2-(2-iodo-2-phenylethenyl)-1,1-dimethylsilacyclopentane (**29**, E/Z= 24/76, 140 mg, 0.41 mmol) in 41% yield: Bp 94—95 °C (bath temp, 0.3 Torr); IR (neat) 2926, 2848, 1608, 1488, 1443, 1248, 1226, 1125, 1069, 1044, 839, 816, 781, 756, 712, 693 cm^{-1};

Major product: ^1H NMR ($CDCl_3$) δ=0.10 (s, 3H), 0.35 (s, 3H), 0.50—0.82 (m, 2H), 1.50—1.68 (m, 2H), 1.72—1.94 (m, 1H), 1.96—2.10 (m, 1H), 2.17—2.24 (m, 1H), 5.87 (d, J=9.2 Hz, 1H), 7.17—7.36 (m, 3H), 7.40—7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.15, −0.31, 13.60, 25.48, 34.04, 39.72, 99.04, 127.44, 128.16, 128.44, 128.96, 143.46.

Minor product: ^1H NMR ($CDCl_3$) δ=−0.05 (s, 3H), 0.15 (s, 3H), 1.50—1.68 (m, 2H), 1.72—1.94 (m, 1H), 1.96—2.10 (m, 1H), 2.17—2.24 (m, 1H), 6.37 (d, J=11.0 Hz, 1H), 7.17—7.36 (m, 3H), 7.40—7.48 (m, 2H). Found: C, 49.20; H, 5.74%. Calcd for $C_{14}H_{19}ISi$: C, 49.12; H, 5.59%.

(*Z*)-2-(2-Iodo-2-trimethylsilylethenyl)-1,1-dimethylsilacyclopentane (30): Bp 95—96 °C (bath temp, 25 Torr); IR (neat) 2950, 2930, 2850, 1582, 1449, 1406, 1248, 1123, 1066, 1042, 1018, 897, 837, 780, 751, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.01 (s, 3H), 0.17 (s, 9H), 0.31 (s, 3H), 0.50—0.63 (m, 1H), 0.66—0.77 (m, 1H), 1.48—1.62 (m, 2H), 1.75—1.89 (m, 1H), 1.90—2.01 (m, 1H), 2.18—2.31 (m, 1H), 6.03 (d, J=8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−3.51, −1.15, −0.24, 13.62, 25.48, 33.72, 40.89, 106.47, 152.08. Found: C, 38.80; H, 6.86%. Calcd for $C_{11}H_{23}ISi_2$: C, 39.04; H, 6.85%.

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