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The Novel Skeletal Rearrangement of Cyclopentanones into Hydroazulenones via a Radical Process and its Application to the Formal Synthesis of Damsinic Acid

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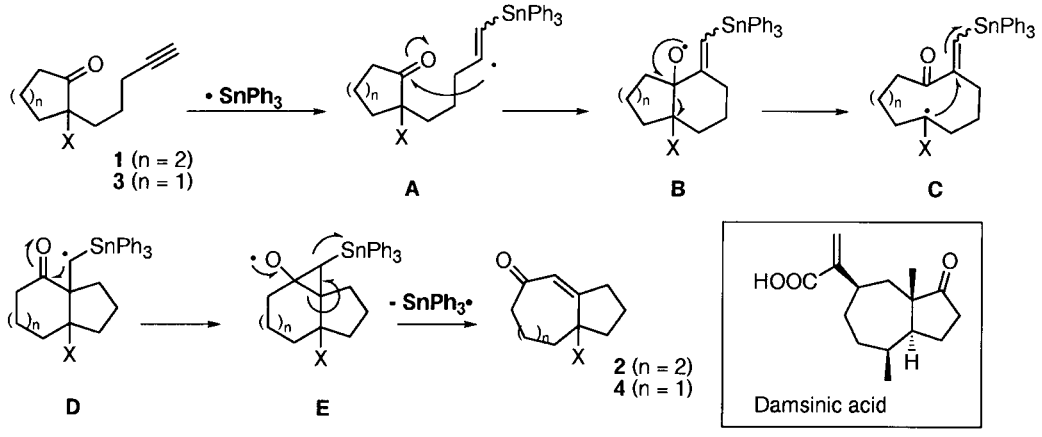
Abstract—A new skeletal rearrangement of cyclopentanones with pentynyl side chains into hydroazulene compounds via a radical process was developed. The presence of a triethylsilyloxy group at the α-position of the cyclopentanone was found to increase the reactivity. Except for this, there was no limitation of the reaction. The reaction was also applied to synthetic studies of damsinic acid, which was isolated from *Ambrosia ambrosioides* (Cav.) Payne along with damsin.

Introduction

A radical process has been recognized as being a useful method for the construction of a carbon–carbon bond. An extension of this reaction to an intramolecular mode increased its potency in organic synthesis. One of the most important advantages is that a highly hindered carbon–carbon bond and quaternary stereogenic center can be easily constructed through a radical cyclization.[1] A skeletal rearrangement including ring expansion via a radical process would be a more attractive method because of its potential for the synthesis of medium and large rings.[2] We previously reported that treatment of cyclohexanones **1** with triphenyltin hydride and azobisisobutyronitrile (AIBN) in refluxing benzene gave bicyclo[6.3.0]undecanones **2** in fairly good yield[3] as shown in Scheme 1. In this transformation, the stannylvinyl radical **A** derived from **1** attacked the carbonyl group on the proximate ring. The resulting oxy radical **B** was then converted into a tertiary carbon-centered radical **C** through a ring opening. The radical **C** was added



Scheme 1.

Keywords: radical skeletal rearrangement; cyclopentanone derivatives; hydroazulene compound; damsinic acid.
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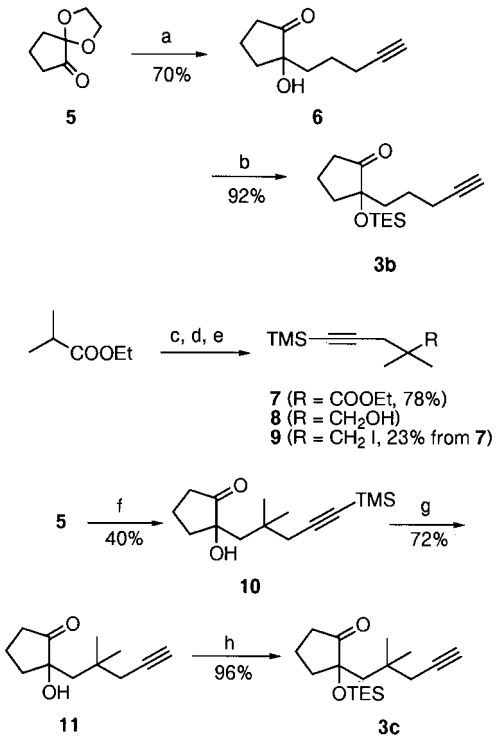


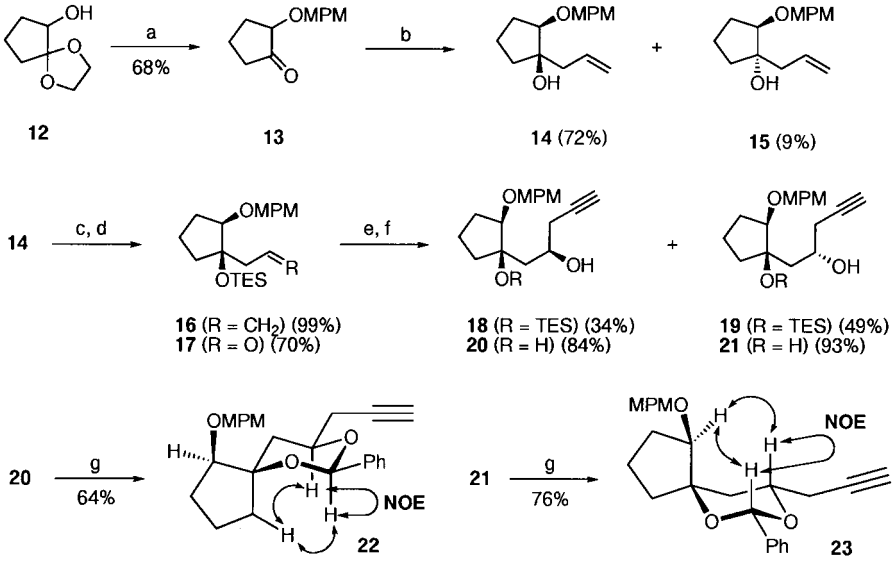
Scheme 2. *Reagents:* (a) (i) 5-iodo-1-trimethylsilyl-1-pentyne, *tert*-BuLi, Et_2O, −70°C; (ii) TBAF, THF, 0°C; (iii) dil. H_2SO_4, AcOH, H_2O, THF 70°C; (b) 2,6-di-*tert*-butylpyridine, TESOTf, CH_2Cl_2, −68°C; (c) LDA, 3-bromo-1-trimethylsilyl-1-propyne, THF, −78°C; (d) $LiAlH_4$, Et_2O, 0°C; (e) (i) TsCl, DMAP, pyridine, 0°C; (ii) NaI, DMF, 110°C; (f) (i) **9**, *tert*-BuLi, Et_2O, −78°C; (ii) dil. H_2SO_4, AcOH, H_2O, THF, 70°C; (g) TBAF, THF, 0°C; (h) 2,6-di-*tert*-butylpyridine, TESOTF, CH_2Cl_2, −78°C.

to the proximate stannylvinyl group, generating a secondary carbon-centered radical **D**. Finally, the addition of the radical to the carbonyl group followed by ring-opening afforded **2**. In the last step, $Ph_3Sn\cdot$ should be regenerated. This facile ring transformation was considered to be applicable to the construction of a hydroazulene skeleton, which is presented in a wide variety of natural sources. We report here the radical skeletal rearrangement of cyclopentanones **3** to hydroazulenone compounds **4**.[4] Furthermore, the formal synthesis of damsinic acid based on the newly developed method is also described.

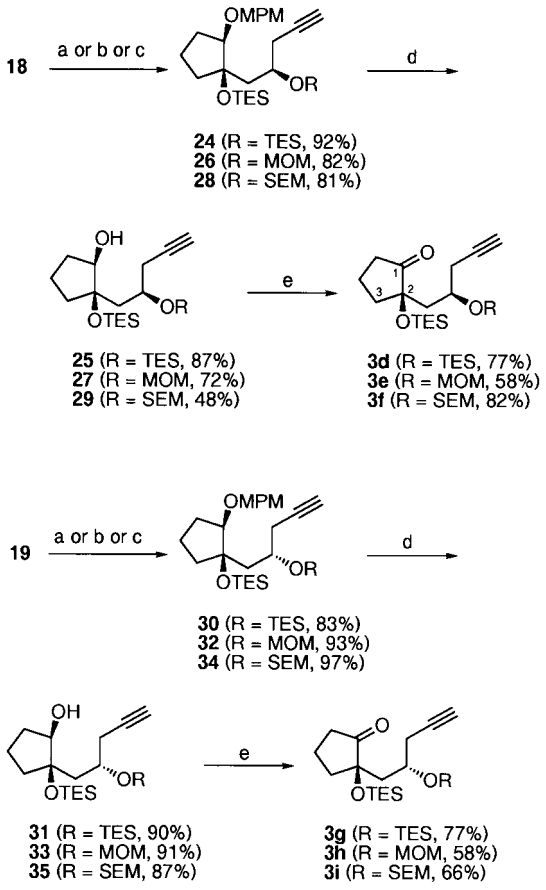
Synthesis of substrates 3a–i (Scheme 2)

Cyclopentanones **3a–i** were selected as substrates of the radical skeletal rearrangement. Compound **3a** (Scheme 5) was prepared by the reported method[5]. Compound **3b** was prepared from cyclopentanone **5**.[6] Treatment of **5** with 5-trimethyl-4-pentynyllithium, derived from 5-iodo-1-trimethylsilyl-1-pentyne[7] and *tert*-BuLi, followed by desilylation with tetrabutylammonium fluoride (TBAF) and deacetalization gave **6** in 70% yield. Silylation of **6** with triethylsilyl trifluoromethanesulfonate (TESOTf) in the presence of 2,6-di-*tert*-butylpyridine afforded **3b** in 92% yield. Compound **3c** was synthesized on the basis of the coupling of **5** and a side chain moiety **9**, which was derived from ethyl 2-methylpropionate. Alkylation of 2-methylpropionate with trimethylsilylpropargyl bromide gave **7** in 78% yield. Reduction of **7** with $LiAlH_4$, followed by the sequence of tosylation and iodination afforded **9**. Coupling of **5** with an alkyllithium reagent, derived from **9**, followed by deacetalization gave **10**, which was converted into **11** on treatment with TBAF. Silylation of **11** with TESOTf afforded **3c** in 96% yield (Scheme 3).

Next, we prepared ketones **3d–i** (Scheme 4), which were expected to be converted into hydroazulenone **4d–i** with a hydroxy group on the cyclopentane ring (Tables 1 and 2). This hydroxy group in **4d–i** would be important for the synthesis of natural products. At first, alcohols **18** and **19**, which were common intermediates of **3d–i**, were prepared from hydroxy ketal **12**.[6] Protection of **12** by the methoxyphenylmethyl (MPM) group followed by deacetalization afforded the ketone **13**. Treatment of **13** with an allyl grignard reagent gave two isomeric alcohols, **14** and **15**.



Scheme 3. *Reagents:* (a) (i) MPMCl, NaH, DMSO, THF, rt; (ii) dil. H_2SO_4, AcOH, H_2O, THF, 70°C; (b) allyl bromide, Mg, 0°C; (c) 2,6-di-*tert*-butylpyridine, TESOTf, CH_2Cl_2, −68°C; (d) OsO_4, $NaIO_4$, *tert*-BuOH, H_2O, rt; (e) propargyl bromide, Mg, $HgCl_2$, Et_2O, 0°C; (f) TBAF, THF, 0°C; (g) benzaldehyde, PPTS, benzene, 45°C.



Scheme 4. *Reagents:* (a) TESOTf, 2,6-lutidine, CH_2Cl_2, −78°C; (b) MOMCl, $(i\text{-Pr})_2$NEt, DMAP, rt; (c) SEMCl, $(i\text{-Pr})_2$NEt, CH_2Cl_2, rt; (d) DDQ, H_2O, CH_2Cl_2, rt; (e) TPAP, NMO, MS4 Å, CH_2Cl_2, rt.

After being separated, the major isomer **14** was converted into aldehyde **17** by the sequence of silylation and oxidative cleavage of olefin. Treatment of **17** with a propargyl grignard reagent provided two isomeric alcohols **18** and **19**, which were separated by column chromatography on silca gel. To determine the stereochemistry of these compounds, **18** and **19** were converted into acetals, **22** and **23**, respectively. These compounds exhibited NOE correlations as shown in Scheme 3.

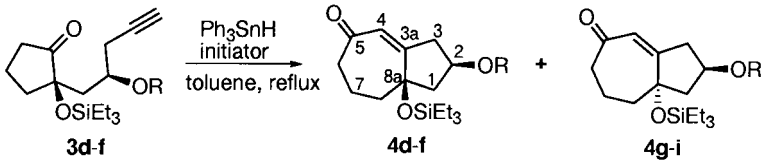
Compound **18** was converted into **3d**, **3e** and **3f** in good yields by the sequence of protection of the hydroxy group (TES, methoxymethyl (MOM) or silyloxyethoxymethyl (SEM) group), deprotection of the MPM group, and oxidation with tetrapropylammonium perruthenate (TPAP). Alcohol **19** was also converted into **3g–i** by the same procedure.

Radical skeletal rearrangement

Radical skeletal rearrangement of **3** was carried out by treatment with Ph_3SnH (1.5–2 equiv.)[8] and AIBN (1.1–1.5 equiv.). The general procedure was that a toluene solution of Ph_3SnH and AIBN was added to a refluxing solution of **3** in toluene using a syringe pump. Contrary to our expectation, treatment of **3a** under radical conditions gave a complex mixture, while **3b** with a silyloxy group at the C-2 position was converted into hydroazulenone compound **4b** (39%) and vinyl stannane **36** (43%). An electron-donating substituent such as a silyloxy group at the C-2 position might be essential for smooth conversion of the skeletal rearrangement.[4] This group should stabilize the radical intermediate **C** and facilitate the attack of the radical on the *exo* olefin. The substituents at the side chain in substrates were also crucial for reactivity. Conversion of **3c** proceeded smoothly under the standard conditions to give **4c** in 79% yield. This result might be explained by considering that geminal dimethyl substituents increased the ground state strain energy of the radical intermediate **A** (Scheme 5).[9]

The effect of substituents at the side chain was further examined by using **3d–i** (Tables 1 and 2). Compounds **3d** and **3g**, having a TESO group at the side chain, were successfully converted into the rearranged products in good yield using either AIBN or azobis(cyclohexane)carbonitrile (ACN)[10] as an initiator. Except for **3e**, the substrates **3f**, **3h** and **3i**, which have acetal groups at the side chain, were less reactive under the radical conditions using AIBN. The acetal group may not be bulky enough to lower the activation energy for the first cyclization step. It is worth mentioning that the rearrangements of **3f**, **3h** and **3i** were improved by using ACN instead of AIBN. Since compared to AIBN, the more thermally stable compound ACN can generate a sufficient concentration of $Ph_3Sn\cdot$ continuously at 110°C and move the equilibrium point of this reaction toward cyclization.

Table 1. Radical cyclization of **3d–f**

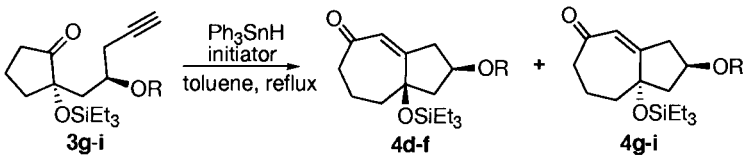


3d-f 4d-f 4g-i

Run	Substrate	R	Initiator	Yield of **4** (%)	Recovery of **3** (%)	Ratio of isomers[a]
1	**3d**	$SiEt_3$	AIBN	60	8	**4d**:**4g**=2.3:1
2	**3d**	$SiEt_3$	ACN	68	–	**4d**:**4g**=2.2:1
3	**3e**	MOM	AIBN	51	24	**4e**:**4h**=1.8:1
4	**3e**	MOM	ACN	74	–	**4e**:**4h**=1.2:1
5	**3f**	SEM	AIBN	19	61	**4f**:**4i**=1.2:1
6	**3f**	SEM	ACN	55	14	**4f**:**4i**=2.1:1

[a] Ratio was determined with ^{1}H NMR.

Table 2. Radical cyclization of **3g–i**

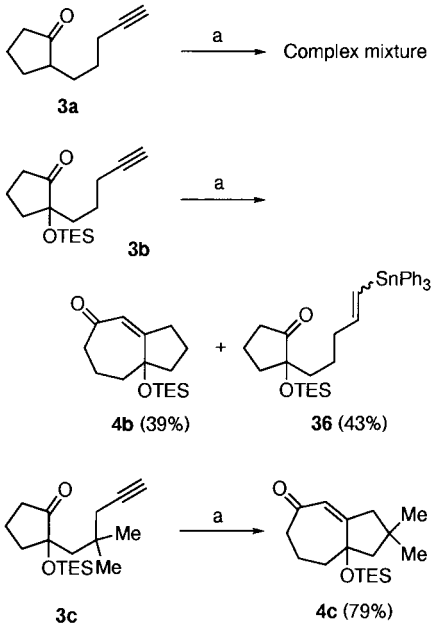


Run	Substrate	R	Initiator	Yield of **4** (%)	Recovery of **3** (%)	Ratio of isomers[a]
1	**3g**	$SiEt_3$	AIBN	64	–	**4d**:**4g**=1:3.4
2	**3h**	MOM	AIBN	11	66	**4e**:**4h**=1:3.5
3	**3h**	MOM	ACN	57	–	**4e**:**4h**=1:6.2
4	**3i**	SEM	AIBN	13	55	**4f**:**4i**=1:3
5	**3i**	SEM	ACN	45	27	**4f**:**4i**=1:2.8

[a] Ratio was determined with ^{1}H NMR.

It should be noted that the reaction of **3d–i** was concomitant with partial epimerization to give two isomeric hydroazulene compounds. The stereochemistries of **4d–f** (*cis*-isomers) and **4g–i** (*trans*-isomers) were assigned on the basis of ^{1}H NMR. The C-2 proton peak of **4d–f** appeared at a higher magnetic field (ca. 0.4 ppm) than that of **4g–i**. The relative configuration of **4h** was unequivocally determined by X-ray analysis of **37**, which was prepared from **4h** by 3 steps (Scheme 6).

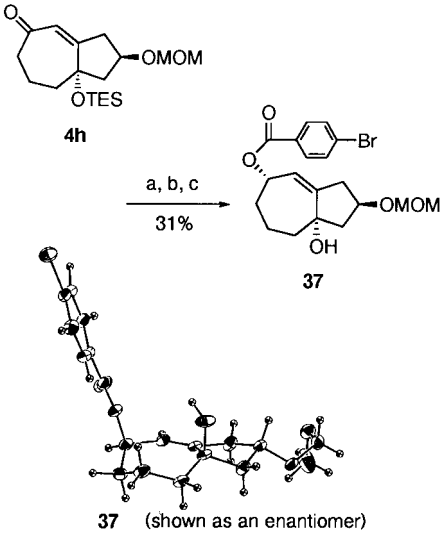
The epimerization might be due to the interconversion between conformation **C-1** and **C-2** in the 9-membered radical intermediate, as shown in Scheme 7. The ratio of isomeric products was dependent on the substrate structure. That is, when **3d–f** was subjected to radical conditions, *cis*-isomers, **4d–f**, were major products. On the other hand, **3g–i** afforded **4g–i** as major products under the same conditions. These findings suggested that the cyclization of radical **C** followed by subsequent processes proceeds to give hydroazulenic products before the equilibration between **C-1** and **C-2** is established.



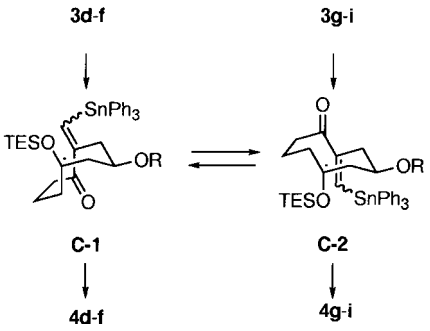
Scheme 5. *Reagents:* (a) Ph_3SnH, AIBN, toluene, reflux.

Synthetic studies of damsinic acid

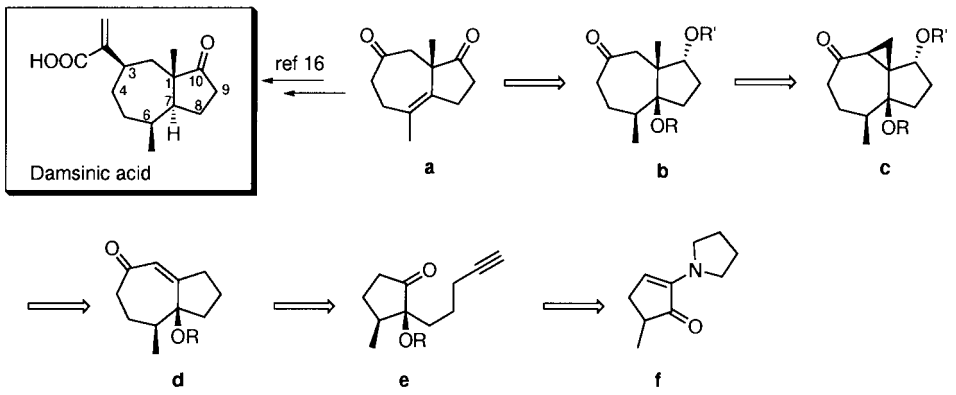
We then applied this reaction to the synthesis of pseudoguaianolides,[11] a group of non-isoprenoid hydroazulenic sesquiterpenes.[12] These compounds are different from other hydroazulenic natural products in that they possess an angular methyl group at the C-1 position. This means that 1,2-methyl migration from C-10 to C-1 proceeds at some stage in their biosynthesis.[13] It has also been shown that various members exhibit significant antitumor or co-carcinogenic activity.[14] Damsinic acid,[15] which was



Scheme 6. *Reagents:* (a) DIBAH, toluene, −78°C; (b) *p*-bromobenzoyl chloride, DMAP, Pyr, rt; (c) TBAF, THF, 0°C.



Scheme 7.



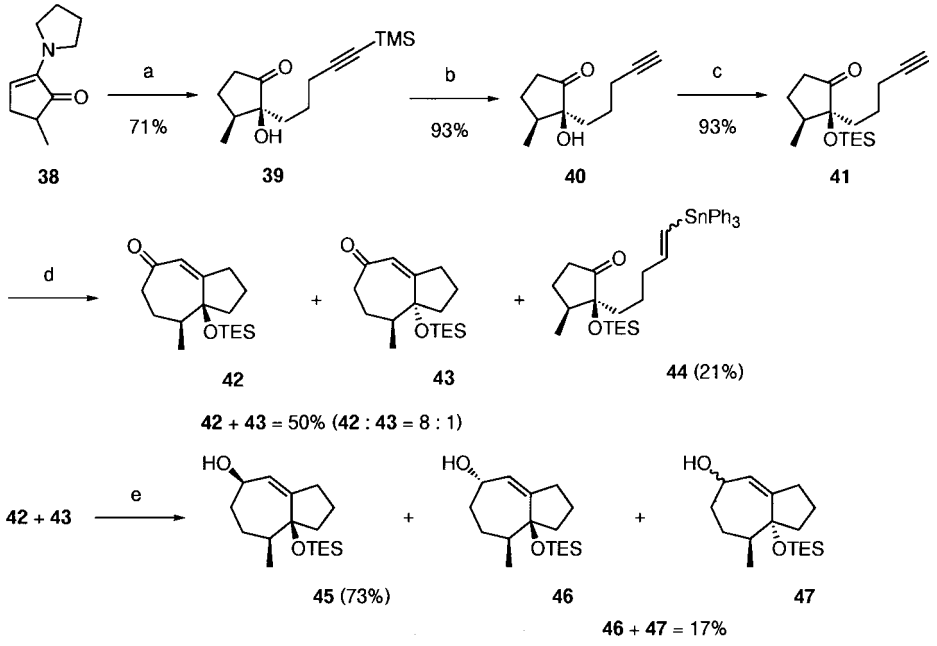
Scheme 8.

isolated from *Ambrosia ambrosioides* (Cav.) Payne along with damsin, has the same relative configuration as other pseudoguaianolides at C-1, 3, 6 and 10. We describe here synthetic studies of damsinic acid based on a newly developed radical skeletal rearrangement.

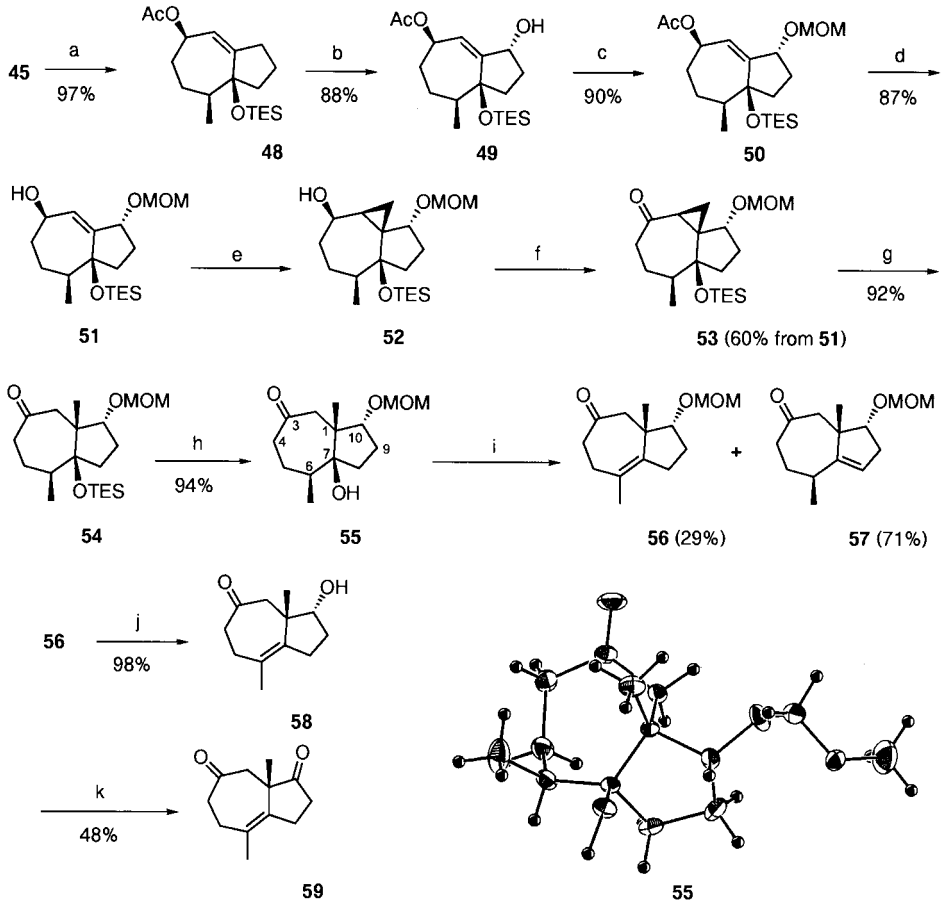
Our retrosynthetic strategy is shown in Scheme 8. Damsinic acid has already been prepared from diketone **a** by Lansbury's group.[16] The diketone **a** was expected to be easily prepared from **b**, which might be obtained by carrying out cyclopropanation and hydroxylation at the C-10 position of the enone **d**. The enone **d** could be prepared by the radical skeletal rearrangement of the cyclopentanone derivative **e**. Furthermore, the installation of a pentynyl side chain to enamine **f** followed by hydrolysis was expected to give **e**.

Coupling of enamine **38**[17] with 5-trimethylsilyloxy-4-pentynyl lithium followed by the sequence of removal of the trimethylsilyl (TMS) group and silylation of the tertiary alcohol group gave ketone **41** in good yield. The radical skeletal rearrangement of **41** by using ACN afforded an inseparable mixture of **42** and **43** (50%, **42**:**43**=8:1) and vinyl stannane **44** (21%). Fortunately, reduction of the mixture with diisobutylaluminum hydride (DIBAH) followed by column chromatography with silica gel gave the desired alcohol **45** (73%) as a single compound and a mixture of **46** and **47** (17%) (Scheme 9).

The alcohol **45** was further acetylated to give **48** in 97% yield. Hydroxylation of **48** at the C-10 position has been achieved by SeO_2 oxidation, and the desired allyl alcohol **49** was obtained in 88% yield. In this oxidation reaction, the presence of pyridine was essential for obtaining an excellent yield.[18] The hydroxy group was stereoselectively introduced from the α-side, which was later proved by X-ray analysis. After protection of the hydroxy gruop in **49** by the MOM group, the acetyl group of **50** was hydrolyzed with potassium carbonate to give **51**. Stereoselective cyclopropanation of **51** by Simmons–Smith's method[19] followed by oxidation with TPAP afforded **53** in 60% yield (2 steps).



Scheme 9. *Reagents:* (a) 4-iodo-1-trimethylsilyl-1-pentyne, *tert*-BuLi, Et_2O, −70°C; (b) TBAF, THF, 0°C; (c) 2,6-di-*tert*-butylpyridine, TESOTf, CH_2Cl_2, −75°C; (d) Ph_3SnH, ACN, toluene, reflux; (e) DIBAH, toluene, 75°C.



Scheme 10. *Reagents:* (a) Ac_2O, DMAP, pyridin, rt; (b) SeO_2, pyr, toluene, reflux; (c) MOMCl, $(i\text{-Pr})_2NEt$, CH_2Cl_2, rt; (d) K_2CO_3, MeOH, rt; (e) Zn–Cu, CH_2I_2, DME, Et_2O, reflux; (f) TPAP, NMO, CH_2Cl_2, rt; (g) H_2, $Pd(OH)_2$–C, EtOH, rt; (h) TBAF, THF, 0°C; (i) MsCl, Et_3N, CH_2C_2, rt; (j) HCl, THF, rt; (k) TPAP, NMO, CH_2Cl_2, rt.

Catalytic hydrogenation of **53** led to the cyclopropane ring-opening to give **54** in 92% yield. When **54** was desilylated on treatment with TBAF, crystal alcohol **55** was obtained in 94% yield. The relative configuration of **55** was unequivocally determined to be (1β, 6β, 7β, 10α) by X-ray crystallography. Treatment of **55** with methanesulfonyl chloride (MsCl) in the presence of triethyamine caused dehydration, giving the desired product **56** and its olefinic isomer **57** in the ratio of 1:2.3. These were separated by column chromatography on silica gel. A number of attempts at isomerization from **57** to **56** were made,[20] but the reaction did not proceed. Finally, compound **56** was treated with HCl in THF to afford the secondary alcohol **58**, which was successfully converted into diketone **59** by oxidation with TPAP. Spectroscopic data of **59** were in agreement with those of **59**, which was prepared by our group using Lansbury's method (Scheme 10).

Conclusions

We developed a new method for the construction of a hydroazulene ring by a radical skeletal rearrangement. The triethylsilyloxy group at the C-2 position in substrates was found to increase the yield of this reaction. Substituents at other positions did not disturb the skeletal rearrangement. We also achieved the formal total synthesis of damsinic acid based on the radical skeletal rearrangement of cycloalkanone **41**. This novel reaction is expected to be applicable to other pseudoguaianolides.

Experimental

Melting points were measured using a Yanaco micro point apparatus and are uncorrected.[1]H NMR spectra were recorded on a JEOL JNM-GX270 (270 MHz) spectrometer in $CDCl_3$ unless otherwise specified, and chemical shift values are expressed in δ (ppm) with tetramethylsilane as an internal standard. ^{13}C NMR spectra (68 MHz) were also recorded in $CDCl_3$ unless otherwise specified, and chemical shift values are expressed in δ(ppm) with $CDCl_3$ as an internal standard. Coupling constants (*J*) are expressed in hertz (Hz). Abbreviations are as follows: s=singlet, d=doublet, t=triplet, q=qualted, quint. =quinted, m=multiplet, and br=broad. The secondary ion mass spectra (SI-MS) and electron impact mass spectra (EI-MS) were measured using a Hitachi-M-2000 mass spectrometer, and IR spectra were measured using a JASCO FT-IR7000. Reactions were followed by thin-layer chromatography (TLC) on Silica gel 60 F_{254}-precoated TLC plates. Solvents were dried according to the established procedure by distillation under an argon atmosphere from the appropriate drying agent. Column chromatography was carried out

using silica gel (Silica gel 60, Merck, 70–230 or 230–400 mesh).

2-Hydroxy-2-pent-4-ynylcyclopentan-1-one (6). To a solution of 5-iodo-1-trimethylsilyl-1-pentyne (1.56 g, 7.1 mmol) in ether (30 ml) was added dropwisely *tert*-BuLi (1.57 M in *n*-pentane solution, 8.0 ml, 12.6 mmol) under an argon atmosphere, and the reaction mixture was stirred at −70°C for 35 min. At the same temperature, a solution of **5** (625 mg, 4.4 mmol) in ether (20 ml) was added. After being stirred for 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (5/1) as an eluent to give alcohol material (2.32 g). This obtained alcohol was dissolved in THF (40 ml), and TBAF (1.0 M in THF, 10.0 ml, 10.0 mmol) was added at 0°C. After being stirred for 40 min, the reaction mixture was quenched with saturated aqueous NH_4Cl, extracted with ether. Combined extracts were washed with brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (3/1) as an eluent to give desilylated compound (1.69 g). To a solution of the desilylated compound in AcOH (11 ml), H_2O (11 ml) and THF (11 ml) was added conc. H_2SO_4 (0.45 ml) at room temperature. After being stirred for 2 h at 70°C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (5/2) as an eluent to give **6** (1.27 g, 70% from **5**) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.63 (1H, s), 2.35–2.27 (2H, m), 2.24–2.15 (2H, m), 2.09–1.73 (4H, m), 1.93 (1H, t, J=2.7 Hz), 1.67–1.50 (4H, m). ^{13}C NMR ($CDCl_3$) δ: 219.6, 83.7, 78.7, 68.8, 34.6, 34.5, 34.2, 22.0, 18.5, 17.0. IR (neat) cm^{-1}: 3450, 3300, 2110, 1740. EI-MS *m/z*: 166 (M^+), 149, 138, 127, 110. HIMS *m/z*: 166.0965 (Calcd for $C_{10}H_{14}O_2$: 166.0993).

2-(1,1-Diethyl-1-silapropoxy)-2-pent-4-ynylcyclopentan-1-one (3b). To a solution of **6** (176.7 mg, 1.1 mmol) and 2,6-di-*tert*-butylpyridine (0.74 ml, 3.3 mmol) in CH_2Cl_2 (5 ml) was added TESOTf (0.38 ml, 1.7 mmol) at −68°C under an argon atmosphere. After being stirred for 5 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (20/1) as an eluent to give **3b** (274.5 mg, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.33–2.15 (4H, m), 2.05–1.48 (9H, m), 0.92 (9H, t, J=7.8 Hz), 0.59 (6H, q, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 217.8, 84.0, 80.6, 68.6, 36.7, 35.2, 34.8, 22.4, 18.7, 17.5, 6.9, 6.2. IR (neat) cm^{-1}: 3300, 2110, 1740. EI-MS *m/z*: 251 ($M^+-C_2H_5$), 224, 213, 195. HIMS *m/z*: 251.1483 (Calcd for $C_{14}H_{23}O_2Si$: 251.1467).

Ethyl 2,2,6,6-tetramethyl-6-silahept-4-ynoate (7). LDA was prepared from diisopropylamine (3.1 ml, 22.1 mmol) and *n*-BuLi (1.68 M in hexane, 13 ml, 21.8 mmol) in THF (20 ml) under an argon atmosphere at −78°C. A solution of ethyl 2-methylpropanate (2.0 g, 17.2 mmol) in THF (7.5 ml) was added to the LDA solution. After being stirred for 35 min, a solution of 3-bromo-1-trimethylsilyl-1-propyne (3.2 ml, 22 mmol) in THF (6.5 ml) was added to the reaction mixture. After being stirred for an additional 1.5 h at −78°C, the reaction mixture was quenched with saturated aqueous NH_4Cl at 0°C and extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (20/1) as an eluent to give **7** (3.04 g, 13.5 mmol, 78%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.14 (2H, q, J=7.1 Hz), 2.46 (2H, s), 1.23 (3H, t, J=7.1 Hz), 1.23 (6H, s), 0.14 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 103.7, 87.3, 60.5, 42.1, 30.9, 24.4, 14.1, 0.1. IR (neat) cm^{-1}: 2180, 1730. EI-MS *m/z*: 226 (M^+), 212, 153, 84. HIMS *m/z*: 226.1404 (Calcd for $C_{12}H_{22}O_2Si$: 226.1388).

7-Iodo-2,2,6,6-tetramethyl-2-silahept-3-yne (9). Under an argon atmosphere, to an ice-cooling suspension of $LiAlH_4$ (779 mg, 20.5 mmol) in ether (200 ml) was added dropwisely a solution of **7** (3.04 g, 13.4 mmol) in ether (22 ml) for 45 min. After 15 min, the mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was quenched with 4% NaOH (2.7 ml), diluted with ether and filtered through a Celite pad. The filtrate was evaporated under reduced pressure to give a crude alcohol **8** (2.22 g). To a solution of **8** in pyridine (10 ml) were added DMAP (146 mg, 1.2 mmol) and *p*-toluenesulfonyl chloride (3.12 g, 16.4 mmol) at 0°C. After 5 min, the mixture was warmed to room temperature and stirred for 18 h. Then the reaction mixture was partitioned between ether (10 ml) and H_2O (10 ml). The separated aqueous layer was extracted with ether. Combined organic layers were washed with cold 1% HCl, saturated aqueous $NaHCO_3$ and brine. The dried ($MgSO_4$) solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (10/1) as an eluent to give a crude *p*-toluenesulfonate (1.73 g). A mixture of NaI (1.56 g, 10 mmol) and the crude *p*-toluenesulfonate in DMF (7 ml) was heated at 110°C for 18 h. Then the mixture was partitioned between *n*-pentane and H_2O. The separated aqueous layer was extracted with *n*-pentane. Combined organic layers were washed with 5% $Na_2S_2O_3$, H_2O and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by distillation under reduced pressure (50°C / 0.5 mmHg) to give **9** (1.0 g, 23% from **7**) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 3.26 (3H, s), 2.28 (2H, s), 1.13 (6H, s), 0.16 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 103.9, 34.0, 32.4, 26.4, 24.6, 22.3, 0.1. IR (neat) cm^{-1}: 2902, 2178. EI-MS *m/z*: 294 (M^+), 238, 209, 167, 78. HIMS *m/z*: 294.0302 (Calcd for $C_{10}H_{19}ISi$: 294.0300).

2-Hydroxy-2-(2,2,6,6-tetramethyl-6-silahept-4-ynyl)cyclopentan-1-one (10). To a solution of **9** (1.43 g, 4.9 mol) in ether (30 ml) was added *tert*-BuLi (1.7 M in *n*-pentane, 6.0 ml, 10.2 mmol) under an argon atmosphere at −78°C, and the reaction mixture was stirred for 2.5 h. At the same temperature, a solution of **5** (666 mg, 4.7 mmol) in ether (15 ml) was added. After being stirred for 1.5 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and

extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a crude material (435 mg). In a similar manner as the preparation of **6**, the crude material was converted into **10** (311.0 mg, 40% from **5**) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.31 (1H, d, J=16.9 Hz), 2.40–1.88 (7H, m), 2.17 (1H, d, J=16.9 Hz), 1.91 (1H, d, J=15.3 Hz), 1.51 (1H, d, J=15.3 Hz), 1.09 (3H, s), 1.08 (3H, s), 0.16 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 210.9, 103.1, 79.5, 44.4, 37.0, 34.4, 34.0, 33.7, 29.2, 28.3, 17.3, 0.1. IR (neat) cm^{-1}: 3460, 2170, 1745. EI-MS *m/z*: 266 (M^+), 265, 251, 238, 223, 137, 119, 86. HIMS *m/z*: 266.1673 (Calcd for $C_{15}H_{26}O_2Si$: 266.1701).

2-(2,2-Dimethyl-4-ynyl)-2-hydroxycyclopentan-1-one (11). To a solution of **10** (311 mg, 1.2 mmol) in THF (3 ml) was added TBAF (1.0 M in THF, 1.5 ml, 1.5 mmol) at 0°C. After being stirred for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (5/1) as an eluent to give **11** (163 mg, 72%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.38–1.88 (8H, m), 2.04 (1H, t, J=2.6 Hz), 1.88 (1H, d, J=15.2 Hz), 1.55 (1H, brs), 1.54 (1H, d, J=15.2 Hz), 1.10 (3H, s), 1.09 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 215.3, 83.2, 80.1, 71.4, 45.0, 37.5, 34.8, 33.3, 29.5, 29.0, 18.1. IR (neat) cm^{-1}: 3450, 3300, 2110, 1740. EI-MS *m/z*: 194 (M^+), 179, 151, 61. HIMS *m/z*: 194.1307 (Calcd for $C_{12}H_{18}O_2$: 194.1306).

2-(1,1-Diethyl-1-silapropoxy)-2-(2,2-dimethyl-4-ynyl)cyclopentan-1-one (3c). In the similar manner as the preparation of **3b**, **11** (163 mg, 0.84 mmol) was converted into **3c** (248 mg, 96%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.29–1.82 (8H, m), 1.98 (1H, t, J=2.7 Hz), 1.77 (1H, d, J=14.8 Hz), 1.57 (1H, d, J=14.8 Hz), 1.08 (3H, s), 1.07 (3H, s), 0.93 (9H, t, J=7.8 Hz), 0.58 (6H, q, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 218.3, 82.8, 81.7, 70.2, 45.2, 38.1, 34.6, 34.2, 33.0, 28.3, 28.3, 17.5, 7.03, 6.30. IR (neat) cm^{-1}: 3300, 2110, 1750. EI-MS *m/z*: 308 (M^+), 279, 269, 252, 118, 82. HIMS *m/z*: 308.2182 (Calcd for $C_{18}H_{32}O_2Si$: 308.2170).

2-[(4-Methoxyphenyl)methoxy]-cyclopentan-1-one (13). Under a nitrogen atmosphere, to a mixture of NaH (60% dispersion in mineral oil, 9.5 g, 237.5 mmol) and DMSO (200 ml) was added dropwisely a solution of **12** (19 g, 131.8 mmol) in THF (100 ml). Then the mixture was treated with a solution of 4-methoxybenzyl chloride (25 g, ca 159.7 mmol) in THF (100 ml), and the whole mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with Et_2NH (10 ml). To the ice-cooling mixture was added saturated aqueous NH_4Cl. The resulting mixture was extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a crude material (32.7 g). In a similar manner as the preparation of **6**, the crude material was converted into **13** (19.5 g, 68% from **12**) as a colorless oil after column chromatography with hexane–AcOEt (3/1) as an eluent. ^{1}H NMR ($CDCl_3$) δ: 7.30 (2H, d, J=8.7 Hz), 6.88 (2H, d, J=8.7 Hz), 4.76 (1H, d, J=11.6 Hz), 4.62 (1H, d, J=11.6 Hz), 3.80 (3H, s), 3.78 (1H, m), 2.28–1.97 (4H, m), 1.89–1.65 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 216.4, 159.3, 129.7, 129.6, 113.8, 79.7, 71.6, 55.2, 35.4, 29.6, 17.3. IR (neat) cm^{-1}: 1740. EI-MS *m/z*: 220 (M^+), 181, 137, 122, 77. HIMS *m/z*: 220.1109 (Calcd for $C_{13}H_{16}O_3$: 220.1099).

(1*R,2*R**)-2-[(4-Methoxyphenyl)methoxy]-1-prop-2-enylcyclopentan-1-ol (14), (1*R**,2*S**)-2-[(4-methoxyphenyl)-methoxy]-1-prop-2-enylcyclopentan-1-ol (15).** Under a nitrogen atmosphere, to a suspension of Mg (turnings, 188.2 mg, 7.7 mmol) in ether (0.6 ml) was added dropwisely a solution of allylbromide (0.7 ml, 8.1 mmol) in ether (7.5 ml) at room temperature. To the reaction mixture, a solution of **13** (238.8 mg, 1.09 mmol) in ether (2.8 ml) was added at 0°C. After being stirred for 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. Combined extracts were washed with brine (3 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (10/1) as an eluent to give **14** (203.8 mg, 72%) as a colorless oil and **15** (26.9 mg, 9%) as a colorless oil. **14**: ^{1}H NMR ($CDCl_3$) δ: 7.26 (2H, d, J=8.8 Hz), 6.89 (2H, d, J=8.8 Hz), 5.88 (1H, m), 5.09–5.01 (2H, m), 4.57 (1H, d, J=11.4 Hz), 4.43 (1H, d, J=11.4 Hz), 3.81 (3H, s), 3.54 (1H, t, J=5.8 Hz), 2.72 (1H, s), 2.33 (1H, ddt, J=14.0, 7.0, 1.3 Hz), 2.21 (1H, ddt, J=14.0, 7.7, 1.3 Hz), 1.96–1.40 (6H, m). ^{13}C NMR ($CDCl_3$) δ: 159.3, 134.5, 130.3, 129.3, 117.4, 113.8, 82.8, 79.8, 71.4, 55.3, 43.7, 35.2, 28.7, 19.5. IR (neat) cm^{-1}: 3550, 3060, 1640. EI-MS *m/z*: 262 (M^+), 235, 141, 122, 99. HIMS *m/z*: 262.1542 (Calcd for $C_{16}H_{22}O_3$: 262.1568). **15**: ^{1}H NMR ($CDCl_3$) δ: 7.25 (2H, d, J=8.5 Hz), 6.89 (2H, d, J=8.5 Hz), 5.86 (1H, m), 5.22–5.13 (2H, m), 4.52 (1H, d, J=11.6 Hz), 4.35 (1H, d, J=11.6 Hz), 3.80 (3H, s), 3.58 (1H, m), 2.56 (1H, dd, J=13.8, 7.0 Hz), 2.36 (1H, dd, J=13.8, 7.9 Hz), 1.82–1.59 (7H, m). ^{13}C NMR ($CDCl_3$) δ: 159.1, 134.5, 130.9, 129.1, 119.0, 113.7, 85.8, 82.4, 70.6, 55.3, 40.1, 36.1, 28.6, 20.3. IR (neat) cm^{-1}: 3460, 3076, 1640, 1610. EI-MS *m/z*: 262 (M^+), 181, 148, 121, 99. HIMS *m/z*: 262.1545 (Calcd for $C_{16}H_{22}O_3$: 262.1568).

(1*R,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)methoxy]-1-prop-2-enylcyclopentane (16).** In a similar manner as the preparation of **3b**, **14** (524.2 mg, 2.0 mmol) was converted into **16** (747.1 mg, 99%) as a colorless oil after column chromatography with hexane–AcOEt (50/1) as an eluent. ^{1}H NMR ($CDCl_3$) δ: 7.62 (2H, d, J=8.8 Hz), 6.86 (2H, d, J=8.8 Hz), 5.84 (1H, m), 5.06–4.95 (2H, m), 4.53 (1H, d, J=11.9 Hz), 4.47 (1H, d, J=11.9 Hz), 3.81 (3H, s), 3.44 (1H, t, J=6.2 Hz), 2.35–2.20 (2H, m), 1.85–1.34 (6H, m), 0.93 (9H, t, J=7.8 Hz), 0.61 (6H, q, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 165.2, 136.2, 134.9, 129.1, 117.0, 113.5, 83.6, 82.4, 71.2, 55.3, 43.3, 35.5, 27.8, 19.0, 7.2, 6.9. IR (neat) cm^{-1}: 1640, 1610. EI-MS *m/z*: 376 (M^+), 347, 255, 171, 122, 87. HIMS *m/z*: 376.2449 (Calcd for $C_{22}H_{36}O_3Si$: 376.2449).

2-[(1*R,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)methoxy]-cyclopentyl]ethanal (17).** A mixture of **16** (9.5 g, 25.3 mmol) in ether (70 ml) and H_2O (70 ml) was treated with OsO_4 (3.9 mg/ml in *tert*-BuOH, 70 ml,

1.4 mmol) and $NaIO_4$ (16 g, 76 mmol) at room temperature. After being stirred for 1 h, the reaction mixture was extracted with ether. Combined extracts were washed with saturated aqueous $NaHCO_3$ and brine (5 ml). The dried (Na_2SO_4) solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (8/1) as an eluent to give **17** (6.7 g, 70%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 9.87 (1H, t, J=3.2 Hz), 7.24 (2H, d, J=8.6 Hz), 6.86 (2H, d, J=8.6 Hz), 4.55 (1H, d, J=11.7 Hz), 4.43 (1H, d, J=11.7 Hz), 3.80 (3H, s), 3.50 (1H, t, J=3.0 Hz), 2.56 (1H, dd, J=15.2, 3.2 Hz), 2.43 (1H, dd, J=15.2, 3.2 Hz), 1.98–1.40 (6H, m), 0.92 (9H, t, J=7.9 Hz), 0.62 (6H, q, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 203.0, 134.7, 130.8, 129.3, 113.7, 83.6, 82.0, 71.3, 55.3, 52.5, 36.4, 27.0, 19.0, 7.12, 6.74. IR (neat) cm^{-1}: 2860, 1725. EI-MS *m/z*: 378 (M^+), 377, 363, 331, 258, 125. HIMS *m/z*: 378.2220 (Calcd for $C_{21}H_{34}O_4Si$: 378.2225).

(2*R)-1-{(1*R**,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)methoxy]cyclopentyl}pent-4-yn-2-ol (18), (2*S**)-1-{(1*R**,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)methoxy]cyclopentyl}pent-4-yn-2-ol (19).** Under a nitrogen atmosphere, to a mixture of Mg (turnings, 56.1 mg, 2.3 mmol) in ether (0.5 ml) was added a solution of propargyl bromide (0.05 ml) in ether (5 ml) and $HgCl_2$ (1 mg) at room temperature. Additional propargyl bromide (total 0.2 ml, 2.2 mmol) was added again to the reaction mixture, and the mixture was stirred until the reaction started. The whole mixture was then cooled to 0°C. A solution of **17** (172.4 mg, 0.46 mmol) in ether (2 ml) was added to the reaction mixture. After being stirred for 10 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. Combined extracts were washed with brine (3 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (8/1) as an eluent to give more-polar **18** (65.7 mg, 34%) as a colorless oil and less-polar **19** (94.1 mg, 49%) as a colorless oil. **18**: ^{1}H NMR ($CDCl_3$) δ: 7.25 (2H, d, J=8.7 Hz), 6.84 (2H, d, J=8.7 Hz), 4.68 (1H, d, J=1.2 Hz), 4.56 (1H, d, J=11.0 Hz), 4.40 (1H, d, J=11.0 Hz), 4.09 (1H, m), 3.80 (3H, s), 3.56 (1H, dd, J=7.8, 6.8 Hz), 2.43 (1H, ddd, J=16.6, 5.3, 2.6 Hz), 2.30 (1H, ddd, J=16.6, 7.4, 2.6 Hz), 2.00 (1H, t, J=2.6 Hz), 1.97–1.40 (8H, m), 0.95 (9H, t, J=7.8 Hz), 0.64 (6H, q, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 159.2, 129.9, 129.4, 113.7, 84.9, 82.8, 81.6, 70.7, 70.0, 66.4, 55.2, 46.2, 37.2, 27.5, 27.0, 18.4, 7.14, 6.68. IR (neat) cm^{-1}: 3400, 2122. EI-MS *m/z*: 418 (M^+), 403, 379, 297, 199. HIMS *m/z*: 418.2560 (Calcd for $C_{24}H_{38}O_4Si$: 418.2537). **19**: ^{1}H NMR ($CDCl_3$) δ: 7.27 (2H, d, J=8.7 Hz), 6.87 (2H, d, J=8.7 Hz), 4.60 (1H, d, J=11.2 Hz), 4.43 (1H, d, J=11.2 Hz), 4.13–4.05 (2H, m), 3.80 (3H, s), 3.65 (1H, t, J=5.1 Hz), 2.40 (1H, ddd, J=16.7, 5.4, 2.6 Hz), 2.27 (1H, ddd, J=16.7, 7.1, 2.6 Hz), 2.00 (1H, t, J=2.6 Hz), 2.04–1.42 (8H, m), 0.94 (9H, t, J=7.8 Hz), 0.64 (6H, q, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 159.0, 130.9, 129.1, 113.6, 84.9, 82.5, 81.2, 71.3, 70.1, 67.7, 55.2, 44.8, 37.6, 28.1, 27.5, 19.2, 7.09, 6.72. IR (neat) cm^{-1}: 3475, 2110. EI-MS *m/z*: 418 (M^+), 359, 297, 267, 199. HIMS *m/z*: 418.2542 (Calcd for $C_{24}H_{38}O_4Si$: 418.2537).

(1*R,2*R**)-1-((2*R**)-2-Hydroxypent-4-ynyl)-2-[(4-methoxyphenyl)methoxy]-cyclopentan-1-ol (20).** In the similar manner as the preparation of **11**, **18** (180 mg, 0.43 mmol) was converted into **20** (110.1 mg, 84%). Recrystallization from toluene–hexane (1/5) afforded **20** as a colorless cubic, mp 61°C. ^{1}H NMR ($CDCl_3$) δ: 7.25 (2H, d, J=8.7 Hz), 6.89 (2H, d, J=8.7 Hz), 4.60 (1H, d, J=11.4 Hz), 4.45 (1H, d, J=11.4 Hz), 4.10 (1H, m), 3.81 (3H, s), 3.55 (1H, t, J=5.2 Hz), 2.44 (1H, ddd, J=16.5, 5.3, 2.6 Hz), 2.31 (1H, ddd, J=16.5, 7.3, 2.6 Hz), 2.02 (1H, t, J=2.6 Hz), 1.99–1.48 (8H, m). ^{13}C NMR ($CDCl_3$) δ: 159.4, 129.7, 129.5, 113.9, 84.3, 81.4, 81.3, 71.5, 70.1, 68.2, 55.3, 43.8, 35.0, 28.4, 27.3, 19.4. IR (neat) cm^{-1}: 3446, 2120. EI-MS *m/z*: 304 (M^+), 286, 218, 165, 93. HIMS *m/z*: 304.1701 (Calcd for $C_{18}H_{24}O_4$: 304.1673).

(1*R,5*R**,7*S**,9*R**)-1-[(4-Methoxyphenyl)methoxy]-6,8-dioxa-7-phenyl-9-prop-2-ynylspiro[4.5]decane (22).** A mixture of **20** (38.7 mg, 0.13 mmol), benzaldehyde (0.04 ml, 0.57 mmol) and pyridinium *p*-toluenesulfonate (3 mg, 0.01 mmol) in benzene (1 ml) was stirred at 40–45°C for 2 days. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (10/1) as an eluent to give **22** (32.1 mg, 64%) as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6) δ: 7.68 (2H, brd, J=6.8 Hz), 7.26 (2H, dd, J=8.6, 1.9 Hz), 7.21–7.17 (2H, m), 7.12 (1H, t, J=7.3 Hz), 6.77 (2H, d, J=8.4 Hz), 5.58 (1H, s), 4.65 (1H, dd, J=11.8, 1.7 Hz), 4.56 (1H, d, J=11.8 Hz), 3.78 (1H, m), 3.33 (1H, t, J=5.7 Hz), 3.32 (3H, s), 2.47 (1H, ddd, J=16.6, 5.5, 2.8 Hz), 2.25 (1H, ddd, J=16.6, 7.6, 2.8 Hz), 2.00 (1H, m), 1.85–1.72 (4H, m), 1.65 (1H, m), 1.41 (1H, ddd, J=13.7, 9.2, 4.7 Hz), 1.34–1.24 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 159.0, 138.9, 131.2, 129.2, 128.5, 128.1, 126.3, 113.6, 96.2, 84.9, 83.1, 80.0, 72.2, 71.9, 70.4, 55.3, 36.9, 29.7, 27.8, 25.9, 19.1. IR (neat) cm^{-1}: 3294, 2124. EI-MS *m/z*: 392 (M^+), 271, 121, 99. HIMS *m/z*: 392.1963 (Calcd for $C_{25}H_{28}O_4$: 392.1986).

(1*R,2*R**)-1-((2*S**)-2-Hydroxypent-4-ynyl)-2-[(4-methoxyphenyl)methoxy]-cyclopentan-1-ol (21).** In the similar manner as preparation of **11**, **19** (90 mg, 0.21 mmol) was converted into **21** (61.1 mg, 93%). Recrystallization from toluene–hexane (1/5) afforded **21** as colorless needles, mp 65°C. ^{1}H NMR ($CDCl_3$) δ: 7.26 (2H, d, J=8.4 Hz), 6.89 (2H, d, J=8.4 Hz), 4.60 (1H, d, J=11.4 Hz), 4.43 (1H, d, J=11.4 Hz), 4.05 (1H, m), 3.81 (3H, s), 3.73 (1H, brs), 3.65 (1H, t, J=5.2 Hz), 3.29 (1H, brs), 2.41 (1H, ddd, J=17.0, 5.9, 2.6 Hz), 2.34 (1H, ddd, J=17.0, 6.8, 2.6 Hz), 2.02 (1H, t, J=2.6 Hz), 1.89–1.45 (8H, m). ^{13}C NMR ($CDCl_3$) δ: 159.6, 130.1, 129.6, 114.1, 83.1, 81.4, 81.2, 71.6, 70.5, 68.1, 55.5, 43.8, 38.6, 28.7, 27.8, 20.0. IR (neat) cm^{-1}: 3440, 2110. EI-MS *m/z*: 304 (M^+), 286, 265, 218, 78. HIMS *m/z*: 304.1702 (Calcd for $C_{18}H_{24}O_4$: 304.1673).

(1*R,5*R**,7*R**,9*R**)-1-[(4-Methoxyphenyl)methoxy]-6,8-dioxa-7-phenyl-9-prop-2-ynylspiro[4.5]decane (23).** In the same manner as the preparation of **22**, **21** (68.7 mg, 0.23 mmol) was converted into **23** (67.0 mg, 76%) as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6) δ: 7.76 (2H, d, J=8.0 Hz), 7.22–7.18 (4H, m), 7.11 (1H, t, J=7.2 Hz), 6.79 (2H, d, J=8.6 Hz), 6.25 (1H, s), 4.45 (1H, d,

J=11.5 Hz), 4.26 (1H, m), 4.14 (1H, d, J=11.5 Hz), 3.68 (1H, t, J=5.8 Hz), 3.30 (3H, s), 2.49 (1H, ddd, J=16.5, 5.0, 2.7 Hz), 2.26 (1H, ddd, J=16.5, 7.6, 2.7 Hz), 2.04 (1H, ddd, J=13.2, 9.4, 5.8 Hz), 1.89 (1H, m), 1.82 (1H, t, J=2.7 Hz), 1.76 (1H, m), 1.66–1.60 (2H, m), 1.55 (1H, dd, J=13.3, 2.5 Hz), 1.40 (1H, ddd, J=13.2, 9.4, 5.6 Hz), 1.25 (1H, m). ^{13}C NMR ($CDCl_3$) δ: 159.2, 139.1, 130.4, 129.4, 128.5, 128.1, 126.3, 113.8, 97.4, 82.2, 81.7, 80.1, 71.9, 70.6, 70.5, 55.3, 38.4, 38.2, 28.3, 26.0, 18.3. IR (neat) cm^{-1}: 3294, 2124. EI-MS m/z: 392 (M^+), 271, 121, 99. HIMS m/z: 392.1975 (Calcd for $C_{25}H_{28}O_4$: 392.1986).

1-[(1*R)-1-({(1*R**,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)-methoxy]cyclopentyl}methyl)but-3-ynyloxy]-1,1-diethyl-1-silapropane (24).** To a solution of **18** (315.6 mg, 0.75 mmol) and 2,6-lutidine (0.5 ml, 2.2 mmol) in CH_2Cl_2 (7 ml) was added TESOTf (0.25 ml, 1.1 mmol) at −78°C. After being stirred for 2 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ether. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (10/1) as an eluent to give **24** (371.0 mg, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 7.27 (2H, d, J=8.7 Hz), 6.86 (2H, d, J=8.7 Hz), 4.56 (1H, d, J=12.0 Hz), 4.49 (1H, d, J=12.0 Hz), 4.06 (1H, m), 3.80 (3H, s), 3.66 (1H, t, J=4.8 Hz), 2.44 (1H, ddd, J=16.4, 6.0, 2.7 Hz), 2.35 (1H, ddd, J=16.4, 5.0, 2.7 Hz), 1.98 (1H, t, J=2.7 Hz), 1.93–1.44 (6H, m), 1.88 (1H, dd, J=14.3, 5.0 Hz), 1.74 (1H, dd, J=14.3, 5.0 Hz), 0.99–0.85 (18H, m), 0.67–0.55 (12H, m). ^{13}C NMR ($CDCl_3$) δ: 158.9, 131.5, 128.9, 113.5, 83.5, 82.2, 81.7, 71.0, 70.2, 67.8, 55.2, 45.9, 36.8, 28.6, 27.3, 19.2, 7.3, 6.9, 6.9, 5.2. IR (neat) cm^{-1}: 3314, 2124. EI-MS m/z: 532 (M^+), 494, 381, 235, 132, 115. HIMS m/z: 532.3426 (Calcd for $C_{30}H_{52}O_4Si$: 532.3401).

(1*R,2*R**)-2-[(2*R**)-2-(1,1-Diethyl-1-silapropoxy)pent-4-ynyl]-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-ol (25).** To a mixture of **24** (328.0 mg, 0.62 mmol) and H_2O (0.34 ml) in CH_2Cl_2 (6 ml) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (192.5 mg, 0.85 mmol) at room temperature. After 15 min, saturated aqueous $NaHCO_3$ was added. The reaction mixture was extracted with CH_2Cl_2. Combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (30/1) as an eluent to give **25** (220.7 mg, 0.53 mmol, 87%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.13 (1H, m), 4.00 (1H, q, J=5.0 Hz), 2.54 (1H, d, J=5.0 Hz), 2.40–2.37 (2H, m), 2.01 (1H, t, J=2.7 Hz), 2.05–1.42 (7H, m), 1.73 (1H, dd, J=14.7, 7.8 Hz), 0.98 (9H, t, J=7.9 Hz), 0.97 (9H, t, J=7.9 Hz), 0.69–0.59 (12H, m). ^{13}C NMR ($CDCl_3$) δ: 83.6, 81.2, 75.2, 70.5, 67.5, 45.4, 37.2, 30.7, 28.9, 19.6, 7.1, 6.9, 6.6, 5.2. IR (neat) cm^{-1}: 3550, 2120. EI-MS m/z: 412 (M^+), 383, 280, 251, 115. HIMS m/z: 412.2848 (Calcd for $C_{22}H_{44}O_3Si$: 412.2827).

(2*R)-2-[(2*R**)-2-(1,1-Diethyl-1-silapropoxy)pent-4-ynyl]-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-one (3d).** To a mixture of **25** (220.7 mg, 0.53 mmol) and molecular sieves 4 Å (145.5 mg) in CH_2Cl_2 (3 ml) was added *N*-methylmorpholine-*N*-oxide (NMO, 146.4 mg, 1.2 mmol) and TPAP (15.5 mg, 0.04 mmol). After being stirred for 1.5 h at room temperature, the reaction mixture was diluted with ether. The mixture was filtered through florisil. The filtrate was evaporated in vacuo. The residue was purified by column chromatography with hexane–AcOEt (20/1) as an eluent to give **3d** (168.5 mg, 77%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.04 (1H, quint., J=5.4 Hz), 2.45–2.42 (2H, m), 2.29–2.19 (2H, m), 2.07–1.80 (7H, m), 0.97–0.90 (18H, m), 0.68–0.53 (12H, m). ^{13}C NMR ($CDCl_3$) δ: 216.9, 81.4, 80.2, 70.2, 66.8, 43.5, 37.6, 34.2, 28.4, 16.9, 7.0, 6.9, 6.3, 4.9. IR (neat) cm^{-1}: 3316, 2124, 1752. EI-MS m/z: 410 (M^+), 381, 343, 299, 249, 155, 115, 87. HIMS m/z: 410.2688 (Calcd for $C_{22}H_{42}O_3Si_2$: 410.2670).

(1*R)-1-({(1*R**,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)-methoxy]cyclopentyl}methyl)-1-(methoxymethoxy)but-3-yne (26).** Under an argon atmosphere, a mixture of **18** (1.01 g, 2.4 mmol), (i-Pr)$_2$NEt (10 ml, 57.4 mmol), methoxymethyl chloride (3 ml, 39.5 mmol) and *N*,*N*-dimethylaminopyridine (66.7 mg, 0.55 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 19 h. The reaction mixture was quenched with 10 ml of saturated aqueous $NaHCO_3$ and extracted with ether. Combined extracts were washed with H_2O and brine, and dried ($MgSO_4$). The solvent was removed in vacuo. The residue was purified by column chromatography with hexane–AcOEt (7/1) as an eluent to give **26** (922.0 mg, 82%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 7.26 (2H, d, J=8.7 Hz), 6.86 (2H, d, J=8.7 Hz), 4.62 (1H, d, J=6.9 Hz), 4.56 (1H, d, J=6.9 Hz), 4.55 (1H, d, J=12.0 Hz), 4.48 (1H, d, J=12.0 Hz), 3.91 (1H, m), 3.80 (3H, s), 3.65 (1H, dd, J=5.8, 4.1 Hz), 3.34 (3H, s), 2.60 (1H, ddd, J=16.8, 5.8, 2.6 Hz), 2.43 (1H, ddd, J=16.8, 4.3, 2.6 Hz), 1.98 (1H, t, J=2.6 Hz), 1.88 (1H, dd, J=14.8, 6.7 Hz), 1.78 (1H, dd, J=14.8, 4.9 Hz), 2.00–1.42 (6H, m), 0.97–0.90 (9H, m), 0.67–0.58 (6H, m). ^{13}C NMR ($CDCl_3$) δ: 158.9, 131.3, 129.1, 113.6, 96.4, 83.3, 82.1, 81.2, 73.6, 71.1, 70.0, 55.7, 55.2, 43.5, 37.1, 27.5, 26.0, 19.2, 7.3, 6.9. IR (neat) cm^{-1}: 3300, 2110, 1610. EI-MS m/z: 462 (M^+), 423, 341, 279, 122. HIMS m/z: 462.2775 (Calcd for $C_{26}H_{42}O_5Si$: 462.2799).

(1*R,2*R**)-2-[(2*R**)-2-(Methoxymethoxy)pent-4-ynyl]-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-ol (27).** In the similar manner as the preparation of **25**, **26** (1.0 mg, 2.17 mmol) was converted into **27** (534.4 mg, 72%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.72 (1H, d, J=7.1 Hz), 4.69 (1H, d, J=7.1 Hz), 3.98–3.89 (2H, m), 3.41 (3H, s), 2.60 (1H, ddd, J=16.8, 6.3, 2.6 Hz), 2.45 (1H, ddd, J=16.8, 4.0, 2.8 Hz), 2.01 (1H, t, J=2.7 Hz), 2.02–1.40 (7H, m), 1.96 (1H, dd, J=14.9, 3.4 Hz), 1.86 (1H, dd, J=14.9, 7.8 Hz), 1.02–0.96 (9H, m), 0.72–0.63 (6H, m). ^{13}C NMR ($CDCl_3$) δ: 96.7, 83.0, 80.9, 75.6, 73.2, 70.3, 55.9, 43.8, 37.7, 31.3, 26.0, 19.6, 7.1, 6.6. IR (neat) cm^{-1}: 3540, 2110. EI-MS m/z: 343 (M^+), 304, 284, 229, 115. HIMS m/z: 342.2249 (Calcd for $C_{18}H_{34}O_4Si$: 342.2225).

(2*R)-2-[(2*R**)-2-(Methoxymethoxy)pent-4-ynyl]-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-one (3e).** In the similar manner as the preparation of **3d**, **27** (144.5 mg, 0.42 mmol) was converted into **3e** (85 mg, 58%) as a

colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.61 (1H, d, J=7.1 Hz), 4.48 (1H, d, J=7.1 Hz), 3.86 (1H, m), 3.36 (3H, s), 2.60 (1H, ddd, J=16.8, 6.3, 2.6 Hz), 2.48 (1H, ddd, J=16.8, 4.0, 2.8 Hz), 2.36 (1H, m), 2.23–1.80 (5H, m), 2.11 (1H, dd, J=14.8, 7.6 Hz), 2.00 (1H, t, J=2.6 Hz), 1.88 (1H, dd, J=14.8, 3.3 Hz), 0.96–0.91 (9H, m), 0.63–0.53 (6H, m). ^{13}C NMR ($CDCl_3$) δ: 216.9, 97.5, 80.9, 80.3, 73.3, 70.1, 55.7, 42.6, 37.6, 33.8, 26.3, 16.5, 7.0, 6.3. IR (neat) cm^{-1}: 2110, 1750. EI-MS *m/z*: 340 (M^+), 279, 249, 222. HIMS *m/z*: 340.2093 (Calcd for $C_{18}H_{32}O_4Si$: 340.2067).

(1*R)-1-({(1*R**,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)-methoxy]cyclopentyl}methyl)-1-[(3,3-dimethyl-3-silabutoxy)methoxy]but-3-yne (28).** Under an argon atmosphere, a mixture of **18** (470.5 mg, 1.12 mmol), (i-Pr)$_2$NEt (1.0 ml, 5.7 mmol), and 2-(trimethylsilyl)ethoxymethyl chloride (0.6 ml, 3.4 mmol) in CH_2Cl_2 (0.6 ml) was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (3 ml) and extracted with ether. Combined extracts were washed with H_2O and brine, and dried ($MgSO_4$). The solvent was evaporated in vacuo. The residue was purified by column chromatography with hexane–AcOEt (10/1) as an eluent to give **28** (497.1 mg, 81%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 7.25 (2H, d, J=8.1 Hz), 6.85 (2H, d, J=8.1 Hz), 4.98–4.44 (4H, m), 3.89 (1H, m), 3.80 (3H, s), 3.80–3.44 (3H, m), 2.63 (1H, m), 2.47–2.32 (2H, m), 2.17–1.43 (8H, m), 0.98–0.86 (11H, m), 0.66–0.56 (6H, m), 0.01 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 129.1, 113.6, 94.8, 83.4, 82.2, 81.5, 73.7, 71.2, 70.0, 65.4, 55.3, 43.5, 37.1, 27.6, 26.1, 19.3, 18.2, 7.3, 6.9, −1.4. IR (neat) cm^{-1}: 3314, 2122, 1613. EI-MS *m/z*: 548 (M^+), 509, 451, 281, 149, 122. HIMS *m/z*: 548.3353 (Calcd for $C_{30}H_{52}O_5Si_2$: 548.3351).

(1*R,2*R**)-2-{(2*R**)-2-[(3,3-Dimethyl-3-silabutoxy)methyl]-pent-4-ynyl}-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-ol (29).** In a similar manner as the preparation of **25**, **28** (497.1 mg, 0.9 mmol) was converted into **29** (186.7 mg, 48%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.79–4.65 (2H, m), 3.98–3.88 (2H, m), 3.76 (1H, m), 3.55 (1H, m), 2.63 (1H, m), 2.45 (1H, m), 2.01–1.40 (10H, m), 1.01–0.91 (11H, m), 0.72–0.63 (6H, m), 0.02 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 95.0, 83.1, 81.0, 75.6, 73.2, 70.3, 65.7, 43.9, 37.7, 31.4, 25.2, 19.7, 18.2, 7.2, 6.4, −1.4. IR (neat) cm^{-1}: 3350, 2120. Positive SI-MS *m/z*: 429 $(M+H)^+$, 311, 279, 251, 185, 103. HIMS *m/z*: 429.2852 (Calcd for $C_{22}H_{45}O_4Si_2$: 429.2854).

(2*R)-2-{(2*R**)-2-[(3,3-Dimethyl-3-silabutoxy)methyl]-pent-4-ynyl}-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-one (3f).** In a similar manner as the preparation of **3d**, **29** (394.5 mg, 0.92 mmol) was converted into **3f** (321.2 mg, 82%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.61 (1H, d, J=7.3 Hz), 4.56 (1H, d, J=7.3 Hz), 3.84 (1H, m), 3.76 (1H, m), 3.44 (1H, m), 2.62 (1H, ddd, J=16.8, 6.3, 2.6 Hz), 2.47 (1H, ddd, J=16.8, 3.7, 2.6 Hz), 2.35 (1H, m), 2.23–1.82 (5H, m), 2.11 (1H, dd, J=14.8, 7.7 Hz), 1.99 (1H, t, J=2.6 Hz), 1.87 (1H, dd, J=14.8, 3.2 Hz), 0.98–0.85 (11H, m), 0.63–0.54 (6H, m), 0.01 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 216.9, 95.8, 80.9, 80.3, 73.2, 70.1, 65.4, 42.7, 37.6, 33.8, 26.3, 18.1, 16.5, 7.0, 6.3, −1.5. IR (neat) cm^{-1}: 3316, 2122, 1754. Positive SI-MS *m/z*: 427 $(M+H)^+$, 409, 351, 279, 199, 115. HIMS *m/z*: 427.2690 (Calcd for $C_{22}H_{43}O_4Si_2$: 427.2697).

1-[(1*S)-1-({(1*R**,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)-methoxy]cyclopentyl}methyl)but-3-ynyloxy]-1,1-diethyl-1-silapropane (30).** In the similar manner as the preparation of **24**, **19** (176.7 mg, 1.1 mmol) was converted into **30** (312.4 mg, 83%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 7.26 (2H, d, J=8.7 Hz), 6.86 (2H, d, J=8.7 Hz), 4.53 (1H, d, J=11.6 Hz), 4.40 (1H, d, J=11.6 Hz), 4.12 (1H, m), 3.81 (3H, s), 3.46 (1H, t, J=7.0 Hz), 2.46 (1H, ddd, J=16.8, 6.0, 2.6 Hz), 2.35 (1H, ddd, J=16.8, 4.6, 2.6 Hz), 2.02 (1H, m), 1.99 (1H, t, J=2.6 Hz), 1.84–1.42 (7H, m), 0.99–0.85 (18H, m), 0.67–0.55 (12H, m). ^{13}C NMR ($CDCl_3$) δ: 159.0, 131.0, 129.4, 113.5, 84.7, 83.0, 81.7, 71.0, 70.2, 68.1, 55.2, 45.6, 36.2, 28.7, 27.0, 19.2, 7.34, 7.01, 6.94, 5.23. IR (neat) cm^{-1}: 3314, 2124, 1615. EI-MS *m/z*: 532 (M^+), 493, 381, 235, 115. HIMS *m/z*: 532.3384 (Calcd for $C_{30}H_{52}O_4Si$: 532.3401).

(1*R,2*R**)-2-[(2*S**)-2-(1,1-Diethyl-1-silapropoxy)pent-4-ynyl]-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-ol (31).** In the similar manner as the preparation of **25**, **30** (310 mg, 0.58 mmol) was converted into **31** (218.7 mg, 90%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 3.98 (1H, tt, J=6.5, 4.9 Hz), 3.89 (1H, q, J=8.1 Hz), 2.52–2.34 (3H, m), 2.01 (1H, t, J=2.6 Hz), 1.98–1.89 (3H, m), 1.81–1.68 (2H, m), 1.64–1.40 (3H, m), 1.01–0.94 (18H, m), 0.71–0.58 (12H, m). ^{13}C NMR ($CDCl_3$) δ: 83.0, 81.2, 76.6, 70.6, 68.5, 44.3, 35.7, 31.5, 28.4, 19.3, 7.1, 6.8, 6.6, 5.2. IR (neat) cm^{-1}: 3550, 3300, 2120. EI-MS *m/z*: 412 (M^+), 383, 280, 185, 118. HIMS *m/z*: 412.2843 (Calcd for $C_{22}H_{44}O_3Si$: 412.2827).

(2*R)-2-[(2*S**)-2-(1,1-Diethyl-1-silapropoxy)pent-4-ynyl]-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-one (3g).** In a similar manner as the preparation of **3d**, **31** (213.3 mg, 0.52 mmol) was converted into **3g** (163.5 mg, 0.40 mmol, 77%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.19 (1H, m), 2.44 (1H, ddd, J=16.7, 6.4, 2.7 Hz), 2.36 (1H, ddd, J=16.7, 5.0, 2.7 Hz), 2.29–2.16 (3H, m), 2.00–1.80 (4H, m), 1.98 (1H, t, J=2.7 Hz), 1.65 (1H, dd, J=14.4, 7.3 Hz), 1.01–0.90 (18H, m), 0.69–0.54 (12H, m). ^{13}C NMR ($CDCl_3$) δ: 218.1, 81.1, 80.0, 70.4, 67.3, 42.1, 36.9, 35.1, 28.5, 17.6, 7.0, 6.9, 6.2, 5.2. IR (neat) cm^{-1}: 3300, 2110, 1745. EI-MS *m/z*: 410 (M^+), 383, 353, 250, 115. HIMS *m/z*: 410.2678 (Calcd for $C_{22}H_{42}O_3Si_2$: 410.2670).

(1*S)-1-({(1*R**,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)-methoxy]cyclopentyl}methyl)-1-(methoxymethoxy)but-3-yne (32).** In the similar manner as the preparation of **26**, **19** (930.9 mg, 2.2 mmol) was converted into **32** (958.3 mg, 93%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 7.26 (2H, d, J=8.7 Hz), 6.86 (2H, d, J=8.7 Hz), 4.73 (1H, d, J=6.9 Hz), 4.67 (1H, d, J=6.9 Hz), 4.54 (1H, d, J=11.6 Hz), 4.40 (1H, d, J=11.6 Hz), 3.92 (1H, m), 3.81 (3H, s), 3.44 (1H, t, J=7.4 Hz), 3.39 (3H, s), 2.63 (1H, ddd, J=16.8, 5.9, 2.7 Hz), 2.43 (1H, ddd, J=16.8, 4.1, 2.7 Hz), 2.00 (1H, t, J=2.7 Hz), 1.99 (1H, dd, J=14.7, 3.5 Hz), 1.88–1.43 (6H, m), 1.67 (1H, dd, J=14.7, 8.1 Hz), 0.92–0.86 (9H, m), 0.65–0.54 (6H, m). ^{13}C NMR ($CDCl_3$) δ: 159.0, 130.8, 129.4, 113.5, 96.6, 84.5, 82.8, 81.2, 73.8,

71.2, 70.0, 55.7, 55.2, 43.3, 36.5, 26.9, 26.2, 19.2, 7.29, 6.96. IR (neat) cm^{-1}: 3300, 2110, 1610. EI-MS *m/z*: 462 (M^+), 423, 341, 279, 121. HIMS *m/z*: 462.2771 (Calcd for $C_{26}H_{42}O_5Si$: 462.2799).

(1*R,2*R**)-2-[(2*S**)-2-(Methoxymethoxy)pent-4-ynyl]-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-ol (33).** In the similar manner as the preparation of **25**, **32** (958.3 mg, 2.1 mmol) was converted into **33** (645.3 mg, 91%) as a colorless oil. ^1H NMR ($CDCl_3$) δ: 4.70 (2H, s), 3.86–3.76 (2H, m), 3.40 (3H, s), 2.66–2.48 (2H, m), 2.50 (1H, d, *J*=7.9 Hz), 2.07–1.88 (4H, m), 1.86–1.68 (3H, m), 1.66–1.40 (2H, m), 0.98–0.95 (9H, m), 0.72–0.63 (6H, m). ^{13}C NMR ($CDCl_3$) δ: 96.1, 82.7, 80.9, 76.6, 73.5, 70.3, 55.8, 42.9, 36.3, 31.7, 25.7, 19.3, 7.1, 6.6. IR (neat) cm^{-1}: 3496, 3314, 2122. EI-MS *m/z*: 343, 342 (M^+), 304, 229, 211, 131, 115. HIMS *m/z*: 342.2244 (Calcd for $C_{18}H_{34}O_4Si$: 342.2225).

(2*R)-2-[(2*S**)-2-(Methoxymethoxy)pent-4-ynyl]-2-(1,1-diethyl-1-silapropoxy)-cyclopentan-1-one (3h).** In the similar manner as the preparation of **3d**, **33** (603.2 mg, 1.76 mmol) was converted into **3h** (346.7 mg, 58%) as a colorless oil. ^1H NMR ($CDCl_3$) δ: 4.73 (1H, d, *J*=6.8 Hz), 4.70 (1H, d, *J*=6.8 Hz), 4.00 (1H, ddt, *J*=7.8, 5.9, 4.2 Hz), 3.40 (3H, s), 2.61 (1H, ddd, *J*=16.8, 5.9, 2.6 Hz), 2.45 (1H, ddd, *J*=16.8, 4.2, 2.6 Hz), 2.30–2.15 (3H, m), 2.00 (1H, t, *J*=2.6 Hz), 1.91 (1H, dd, *J*=14.7, 4.2 Hz), 1.78 (1H, dd, *J*=14.7, 7.8 Hz), 2.02–1.78 (3H, m), 0.96–0.90 (9H, m), 0.63–0.54 (6H, m). ^{13}C NMR ($CDCl_3$) δ: 218.1, 96.4, 80.8, 79.7, 73.0, 70.3, 55.9, 39.7, 36.9, 35.3, 25.9, 17.8, 7.0, 6.2. IR (neat) cm^{-1}: 3300, 2100, 1745. EI-MS *m/z*: 340 (M^+), 273, 222, 185, 119. HIMS *m/z*: 340.2319 (Calcd for $C_{18}H_{32}O_4Si$: 340.2067).

(1*S)-1-{[1-({(1*R**,2*R**)-1-(1,1-Diethyl-1-silapropoxy)-2-[(4-methoxyphenyl)-methoxy]cyclopentyl}methyl)-but-3-ynyloxy]methoxy}-3,3-dimethyl-3-silabutane (34).** In the similar manner as the preparation of **28**, **19** (657.7 mg, 1.57 mmol) was converted into **34** (836.3 mg, 97%) as a colorless oil. ^1H NMR ($CDCl_3$) δ: 7.26 (2H, d, *J*=8.6 Hz), 6.86 (2H, d, *J*=8.6 Hz), 4.74 (2H, s), 4.53 (1H, d, *J*=11.6 Hz), 4.41 (1H, d, *J*=11.6 Hz), 3.92 (1H, m), 3.81 (3H, s), 3.84–3.41 (3H, m), 2.66 (1H, ddd, *J*=16.9, 5.4, 2.7 Hz), 2.42 (1H, ddd, *J*=16.9, 4.1, 2.7 Hz), 1.99 (1H, t, *J*=2.7 Hz), 1.97 (1H, m), 1.85–1.40 (7H, m), 0.92–0.86 (11H, m), 0.68–0.54 (6H, m), 0.01 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 132.3, 130.9, 115.0, 96.3, 86.1, 84.4, 82.8, 75.2, 72.6, 71.4, 66.9, 56.7, 44.8, 37.9, 28.4, 27.7, 20.7, 19.6, 8.8, 8.5, 0.0. IR (neat) cm^{-1}: 2878, 1613. EI-MS *m/z*: 548 (M^+), 509, 451, 122. HIMS *m/z*: 548.3321 (Calcd for $C_{30}H_{52}O_5Si_2$: 548.3351).

(1*R,2*R**)-2-{(2*S**)-2-[(3,3-Dimethyl-3-silabutoxy)methyl]-pent-4-ynyl}-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-ol (35).** In the similar manner as the preparation of **25**, **34** (826.3 mg, 1.5 mmol) was converted into **35** (568.8 mg, 87%) as a colorless oil. ^1H NMR ($CDCl_3$) δ: 4.76 (1H, d, *J*=7.3 Hz), 4.71 (1H, d, *J*=7.3 Hz), 3.84–3.51 (4H, m), 2.58–2.48 (3H, m), 1.99 (1H, t, *J*=2.6 Hz), 2.06–1.90 (3H, m), 1.83–1.72 (2H, m), 1.62–1.46 (3H, m), 1.01–0.90 (11H, m), 0.70–0.62 (6H, m), 0.02 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 94.3, 82.7, 81.0, 76.7, 73.5, 70.3, 65.6, 43.4, 36.2, 31.7, 25.7, 19.3, 18.1, 7.1, 6.6, −1.5. IR (neat) cm^{-1}: 3350, 3300, 2120. Positive SI-MS *m/z*: 429 $(M+H)^+$, 311, 281, 199, 185, 103. HIMS *m/z*: 429.2832 (Calcd for $C_{22}H_{45}O_4Si_2$: 429.2854).

(2*R)-2-{(2*S**)-2-[(3,3-Dimethyl-3-silabutoxy)methyl]-pent-4-ynyl}-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-one (3i).** In the similar manner as the preparation of **3d**, **35** (568.8 mg, 1.3 mmol) was converted into **3i** (371.5 mg, 66%) as a colorless oil. ^1H NMR ($CDCl_3$) δ: 4.77 (1H, d, *J*=7.1 Hz), 4.73 (1H, d, *J*=7.1 Hz), 4.00 (1H, ddt, *J*=7.8, 5.9, 4.0 Hz), 3.77 (1H, m), 3.54 (1H, m), 2.63 (1H, ddd, *J*=16.8, 5.9, 2.6 Hz), 2.45 (1H, ddd, *J*=16.8, 4.1, 2.6 Hz), 2.30–2.15 (3H, m), 2.00–1.74 (3H, m), 1.98 (1H, t, *J*=2.6 Hz), 1.88 (1H, dd, *J*=14.8, 4.0 Hz), 1.78 (1H, dd, *J*=14.8, 7.8 Hz), 0.97–0.88 (11H, m), 0.63–0.54 (6H, m), 0.02 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 218.0, 94.7, 80.8, 79.7, 72.9, 70.2, 65.5, 39.6, 36.8, 35.2, 25.9, 18.1, 17.7, 7.0, 6.2, −1.5. IR (neat) cm^{-1}: 3316, 2110, 1750. Positive SI-MS *m/z*: 427 $(M+H)^+$, 409, 351, 279, 199, 115. HIMS *m/z*: 427.2700 (Calcd for $C_{22}H_{43}O_4Si_2$: 427.2697).

General procedure for radical skeletal rearrangement

Under an argon atmosphere, a solution of Ph_3SnH (113.9 mg, 0.32 mmol, 2.0 equiv.) and AIBN (41.3 mg, 0.25 mmol, 1.6 equiv.) or ACN (1,1′-azobis cyclohexanecarbonitrile, 61.1 mg, 0.25 mmol, 1.6 equiv.) in toluene (4 ml) was added to a refluxing solution of substrate **3** (0.16 mmol) in toluene (4 ml, 40 mM) using a syringe pump. The reaction mixture was stirred for 5 min to 7.5 h. The reaction mixture was cooled to room temperature and the solvent was evaporated in vacuo. The residue was purified by flash column chromatography with benzene–AcOEt (30/1) as an eluent. In the case of using **3d–i**, hydroazulenones were obtained as a diastereo mixture. The ratio of these diastereomers of enones was determined by ^1H NMR spectra, respectively. These diastereomers were partially separated by repeated flash column chromatography. Reaction conditions and yields are summarized in Scheme 5 and Tables 1 and 2.

8a-(1,1-Diethyl-1-silapropoxy)-1,2,3,6,7,8,8a-heptahydroazulen-5-one (4b). Colorless oil, ^1H NMR ($CDCl_3$) δ: 5.88 (1H, dd, *J*=3.9, 1.7 Hz), 3.02 (1H, ddd, *J*=15.6, 10.5, 3.7 Hz), 2.77–2.63 (1H, m), 2.52–2.36 (2H,m), 2.21–1.54 (8H, m), 0.93 (9H, t, *J*=8.0 Hz), 0.60 (6H, q, *J*=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 204.8, 164.8, 125.2, 82.6, 43.6, 42.0, 38.0, 34.2, 22.2, 19.6, 7.0, 6.5. IR (neat) cm^{-1}: 1665. EI-MS *m/z*: 280 (M^+), 251, 131, 103. HIMS *m/z*: 280.1879 (Calcd for $C_{16}H_{28}O_2Si$: 280.1858).

2-(4*EZ*)-6,6,6-Triphenyl-6-stannahex-4-enyl)-2-(1,1-diethyl-1-silapropoxy)cyclopentan-1-one (36). Colorless oil, ^1H NMR ($CDCl_3$) δ: 7.66–7.32 (15H, m), 6.80–6.03 (2H, m), 2.35–1.30 (12H, m), 0.92 (9H, t, *J*=8.0 Hz), 0.57 (6H, q, *J*=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 217.1, 152.8, 138.6, 137.3, 137.0, 136.9, 128.9, 128.5, 123.9, 81.5, 38.9, 38.1, 35.5, 32.8, 26.2, 23.4, 12.5, 7.0, 6.3. IR (neat) cm^{-1}: 1740. EI-MS *m/z*: 604 ($M^+-C_2H_4$), 555, 499, 423, 351, 253, 86. HIMS *m/z*: 604.1844 (Calcd for $C_{32}H_{40}O_2SiSn$: 604.1818).

8a-(1,1-Diethyl-1-silapropoxy)-2,2-dimethyl-1,2,3,6,7,8,8a-heptahydroazulen-5-one (4c). Colorless oil, ^{1}H NMR ($CDCl_3$) δ: 5.88 (1H, dd, J=2.6, 1.3 Hz), 3.00 (1H, ddd, J=14.9, 10.9, 4.0 Hz), 2.71 (1H, dd, J=15.7, 2.6 Hz), 2.43 (1H, dddd, J=14.9, 6.4, 3.9, 2.0 Hz), 2.22–1.65 (7H, m), 1.15 (3H, s), 0.93 (3H, s), 0.93 (9H, t, J=7.9 Hz), 0.60 (6H, q, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 204.5, 165.3, 126.2, 82.4, 58.3, 50.2, 41.6, 41.0, 35.9, 29.7, 28.2, 19.5, 7.0, 6.6. IR (neat) cm^{-1}: 1660. EI-MS m/z: 308 (M^+), 279, 252, 177, 138. HIMS m/z: 308.2194 (Calcd for $C_{18}H_{32}O_2Si$: 308.2170).

(2*R,8a*R**)-2,8a-bis(1,1-Diethyl-1-silapropoxy)-1,2,3,6,7,8,8a-heptahydroazulen-5-one (4d).** Colorless oil, ^{1}H NMR ($CDCl_3$) δ: 5.85 (1H, m), 4.00 (1H, tt, J=9.3, 6.8 Hz), 3.05 (1H, ddd, J=16.9, 11.5, 2.9 Hz), 2.81–2.65 (2H, m), 2.42–2.32 (1H, m), 2.20–2.01 (3H, m), 1.91 (1H, m), 1.76–1.61 (2H, m), 0.99–0.90 (18H, m), 0.65–0.55 (12H, m). ^{13}C NMR ($CDCl_3$) δ: 205.8, 161.5, 126.0, 80.0, 69.0, 52.1, 44.1, 40.5, 39.1, 19.5, 7.0, 6.7, 6.4, 4.7. IR (neat) cm^{-1}: 1670. EI-MS m/z: 410 (M^+), 381, 354, 278, 249, 148. HIMS m/z: 410.2684 (Calcd for $C_{22}H_{42}O_3Si_2$: 410.2670).

(2*R,8a*R**)-8a-(1,1-Diethyl-1-silapropoxy)-2-(methoxymethoxy)-1,2,3,6,7,8,8a-heptahydroazulen-5-one (4e).** Colorless oil, ^{1}H NMR ($CDCl_3$) δ: 5.88 (1H, brs), 4.65 (2H, s), 3.93 (1H, tt, J=9.5, 6.6 Hz), 3.38 (3H, s), 3.04 (1H, ddd, J=16.7, 12.0, 3.0 Hz), 2.84 (1H, m), 2.78 (1H, ddd, J=16.4, 9.5, 3.0 Hz), 2.38 (1H, ddt, J=16.7, 6.4, 2.1 Hz), 2.30 (1H, ddd, J=12.7, 6.6, 1.6 Hz), 2.11 (1H, dd, J=12.8, 9.5 Hz), 2.10 (1H, m), 1.93 (1H, m), 1.73–1.64 (2H, m), 0.93 (9H, t, J=7.9 Hz), 0.61 (6H, q, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 206.4, 160.9, 126.5, 96.2, 80.3, 74.2, 55.8, 49.6, 41.6, 40.9, 39.2, 19.8, 7.3, 6.7. IR (neat) cm^{-1}: 1670. EI-MS m/z: 340 (M^+), 311, 281, 249, 222, 147. HIMS m/z: 340.2052 (Calcd for $C_{18}H_{32}O_4Si$: 340.2067).

(2*R,8a*R**)-8a-(1,1-Diethyl-1-silapropoxy)-2-[(3,3-dimethyl-3-silabutoxy)methoxy]-1,2,3,6,7,8,8a-heptahydroazulen-5-one (4f).** Colorless oil, ^{1}H NMR ($CDCl_3$) δ: 5.87 (1H, brs), 4.70 (2H, s), 3.93 (1H, tt, J=9.5, 6.7 Hz), 3.66–3.58 (2H, m), 3.04 (1H, ddd, J=16.7, 11.9, 3.1 Hz), 2.83 (1H, m), 2.78 (1H, m), 2.42–2.27 (2H, m), 2.17–1.82 (3H, m), 1.78–1.60 (2H, m), 0.97–0.90 (11H, m), 0.65–0.56 (6H, m), 0.03 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 207.7, 160.7, 126.2, 94.3, 80.1, 73.9, 65.4, 49.5, 41.4, 40.6, 39.0, 19.5, 18.2, 7.0, 6.4, −1.5. IR (neat) cm^{-1}: 1671. EI-MS m/z: 426 (M^+), 369, 278, 249, 219. HIMS m/z: 426.2608 (Calcd for $C_{22}H_{42}O_4Si_2$: 426.2619).

(2*S,8a*R**)-2,8a-Bis(1,1-diethyl-1-silapropoxy)-1,2,3,6,7,8,8a-heptahydroazulen-5-one (4g).** Colorless oil, ^{1}H NMR ($CDCl_3$) δ: 5.87 (1H, m), 4.45 (1H, m), 3.04–2.91 (2H, m), 2.49–2.38 (2H, m), 2.24–1.67 (5H, m), 1.90 (1H, ddd, J=13.7, 5.6, 1.7 Hz), 0.98–0.90 (18H, m), 0.63–0.54 (12H, m). ^{13}C NMR ($CDCl_3$) δ: 204.6, 162.7, 126.3, 82.0, 69.9, 52.7, 44.2, 42.1, 39.3, 19.4, 7.0, 6.7, 6.5, 4.7. IR (neat) cm^{-1}: 1660. EI-MS m/z: 410 (M^+), 381, 354, 278, 250, 147. HIMS m/z: 410.2684 (Calcd for $C_{22}H_{42}O_3Si_2$: 410.2670).

(2*S,8a*R**)-8a-(1,1-Diethyl-1-silapropoxy)-2-(methoxymethoxy)-1,2,3,6,7,8,8a-heptahydroazulen-5-one (4h).** Colorless oil, ^{1}H NMR ($CDCl_3$) δ: 5.90 (1H, s), 4.62 (2H, s), 4.33 (1H, tt, J=5.9, 4.5 Hz), 3.35 (3H, s), 3.04–2.99 (1H, m), 2.98 (1H, ddd, J=15.4, 10.3, 4.2 Hz), 2.58 (1H, m), 2.44 (1H, ddd, J=15.4, 7.4, 3.8 Hz), 2.30 (1H, dd, J=13.8, 5.9 Hz), 2.15 (1H, m), 2.04–1.93 (3H, m), 1.75 (1H, m), 0.94 (9H, t, J=7.9 Hz), 0.61 (6H, q, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 204.1, 161.8, 127.4, 95.4, 81.7, 74.4, 55.4, 49.8, 42.3, 41.1, 39.0, 19.3, 7.0, 6.4. IR (neat) cm^{-1}: 1665. EI-MS m/z: 340 (M^+), 311, 249, 222. HIMS m/z: 340.2061 (Calcd for $C_{18}H_{32}O_4Si$: 340.2067).

(2*S,8a*R**)-8a-(1,1-Diethyl-1-silapropoxy)-2-[(3,3-dimethyl-3-silabutoxy)methoxy]-1,2,3,6,7,8,8a-heptahydroazulen-5-one (4i).** Colorless oil, ^{1}H NMR ($CDCl_3$) δ: 5.90 (1H, brs), 4.66 (2H, s), 4.35 (1H, tt, J=5.6, 4.4 Hz), 3.62–3.56 (2H, m), 3.02 (1H, m), 2.98 (1H, m), 2.57 (1H, m), 2.44 (1H, m), 2.29 (1H, m), 2.15 (1H, m), 2.07–1.89 (3H, m), 1.76 (1H, m), 0.96–0.90 (11H, m), 0.65–0.56 (6H, m), 0.02 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 204.2, 161.9, 126.5, 93.7, 81.7, 74.4, 65.3, 49.8, 42.3, 41.1, 39.0, 19.4, 18.1, 7.1, 6.5, −1.4. IR (neat) cm^{-1}: 1673. EI-MS m/z: 426 (M^+), 397, 339, 249, 147. HIMS m/z: 426.2618 (Calcd for $C_{22}H_{42}O_4Si_2$: 426.2619).

(3*R,7*R**,9*S**)-7-Hydroxy-9-(methoxymethoxy)bicyclo-[5.3.0]dec-1-en-3-yl 4-bromobenzoate (37).** To a solution of **4h** (43.6 mg, 0.13 mmol) in toluene (0.5 ml) was added DIBAH (1.02 M in toluene, 0.2 ml, 0.2 mmol) at −78°C under an argon atmosphere. After being stirred for 35 min, saturated aqueous NH_4Cl (0.5 ml) was added. The reaction mixture was allowed to warm up to room temperature and was then diluted with ether. Anhydrous magnesium sulfate was then added to the reaction mixture. After 1 h, the mixture was filtered through a Celite pad and the pad was washed with ether. The filtrate and washings were evaporated under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (4/1) as an eluent to give alcohol (25.3 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 6.02 (1H, dt, J=7.3, 2.2 Hz), 4.63 (2H, s), 4.19 (1H, quint., J=6.4 Hz), 4.11–3.95 (2H,m), 3.36 (3H, s), 2.78 (1H, ddt, J=16.2, 5.9, 1.7 Hz), 2.41–2.28 (3H, m), 2.01–1.93 (2H, m), 1.83 (1H, dd, J=13.8, 7.2 Hz), 1.72 (1H, dd, J=13.8, 2.8 Hz), 1.64–1.57 (2H, m), 1.02–0.90 (9H, m), 0.74–0.58 (6H, m). IR (neat) cm^{-1}: 3475.

To a solution of alcohol (25.3 mg) in pyridine (1 ml) was added *p*-bromobenzoyl chloride (125 mg, 0.57 mmol) and DMAP (2.4 mg, 0.02 mmol) at 0°C under an argon atmosphere. After being stirred for 13 h at room temperature, the reaction mixture was partitioned between ether and H_2O. The product was extracted with ether. The combined organic layers were washed with brine and dried ($MgSO_4$). The solvent was evaporated in vacuo. The residue was purified by column chromatography with hexane–AcOEt (10/1) as an eluent to give the ester (36.5 mg) as a light-yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.92 (2H, d, J=8.7 Hz), 7.56 (2H, d, J=8.7 Hz), 5.64 (1H, brs), 5.51 (1H, m), 4.62 (2H, s), 4.34 (1H, m), 3.35 (3H, s), 3.00 (1H, m), 2.47–1.55 (9H, m), 0.95 (9H, t, J=7.4 Hz), 0.64 (6H, q, J=7.4 Hz). IR (neat) cm^{-1}: 2858, 1712.

To a solution of ester (36.5 mg) in THF (0.5 ml), TBAF

(1.0 M in THF, 0.1 ml, 0.1 mmol) was added at 0°C. After being stirred for 30 min, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with AcOEt. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (5/1) as an eluent to give **37** (27.2 mg, 53% from **4h**) as a light-yellow crystal. Recrystallization from EtOH afforded **37** as a colorless prism, mp 95°C. ^{1}H NMR ($CDCl_3$) δ: 7.85 (2H, d, J=8.7 Hz), 7.59 (2H, d, J=8.7 Hz), 5.93 (1H, dt, J=7.4, 2.1 Hz), 5.55 (1H, t, J=7.2 Hz), 4.65 (1H, d, J=6.8 Hz), 4.63 (1H, d, J=6.8 Hz), 4.29 (1H, tt, J=8.1, 6.2 Hz), 3.35 (3H, s), 2.89 (1H, ddt, J=16.4, 6.4, 1.8 Hz), 2.67 (1H, d, J=1.2 Hz), 2.46 (1H, ddd, J=16.4, 7.9, 2.6 Hz), 2.34–2.04 (4H, m), 1.82–1.67 (4H, m). ^{13}C NMR ($CDCl_3$) δ: 228.4, 203.6, 164.6, 154.6, 132.0, 130.9, 122.1, 95.8, 78.5, 75.1, 71.3, 55.3, 49.0, 41.3, 38.6, 31.8, 19.0. IR ($CHCl_3$) cm^{-1}: 3568, 1717. EI-MS m/z: 412 (M^+), 411, 351, 350, 330, 185, 157, 148. HIMS m/z: 410.0750, 412.0698 (Calcd for $C_{19}H_{23}O_5Br$: 410.0728, 412.0708). Crystal data for **37**: $C_{19}H_{23}O_5Br$, M=411.29; 47.7<2θ<49.4; monoclinic; $P2_1/n$; a=10.118 (4) Å, b=6.402 (4) Å, c=28.461 (3) Å, β=90.54 (2)°; V=1844 (1) Å^3; Z=4; D_{calc}=1.482 g/cm^3: μ(CuKα)= 32.67 cm^{-1}; F(000)=848; full-matrix least-squares refinement was based on 2,708 observed reflections (I>3.00σ(I)) and 298 variable parameters, R=0.067, Rw=0.073.

(2S^*,3S^*)-2-(6,6-Dimethyl-6-silahept-4-ynyl)-2-hydroxy-3-methylcyclopentane-1-one (39). To a solution of 4-iodo-1-trimethylsilyl-1-pentyne (1.89 g, 7.1 mol) in ether (30 ml) was added *tert*-butyllithium (1.57 M in *n*-pentane, 9.8 ml, 15.4 mmol) dropwisely under an argon atmosphere at −70°C, and the reaction mixture was stirred for 35 min. At the same temperature, a solution of **38** (778 mg, 4.7 mmol) in ether (5 ml) was added to the reaction mixture. After being stirred for 15 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (5/1) as an eluent to give **39** (848 mg, 71%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.34–2.01 (6H, m), 1.72–1.44 (6H, m), 0.96 (3H, d, J=7.1 Hz), 0.14 (9H, s). ^{13}C NMR ($CDCl_3$) δ: 219.4, 106.6, 84.9, 80.6, 38.0, 34.4, 32.5, 25.1, 22.5, 19.9, 13.8, 0.04. IR (neat) cm^{-1}: 3470, 1740. EI-MS m/z: 252 (M^+), 237, 196, 181, 167, 73. HIMS m/z: 252.1565 (Calcd for $C_{14}H_{24}O_2Si$: 252.1544).

(2S^*,3S^*)-2-Hydroxy-3-methyl-2-pent-4-ynylcyclopentan-1-one (40). To a solution of **39** (682 mg, 2.7 mmol) in THF (6 ml) was added TBAF (1.0 M in THF, 4.0 ml, 4.0 mmol) at 0°C. After being stirred for 40 min, the reaction was quenched with saturated aqueous NH_4Cl, and extracted with AcOEt. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (5/1) as an eluent to give **40** (451 mg, 93%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.35–2.02 (7H, m), 1.96 (1H, t, J=2.6 Hz), 1.76–1.46 (5H, m), 0.96 (3H, d, J=6.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 219.5, 83.8, 80.6, 68.8, 38.1, 34.6, 32.5, 25.1, 22.3, 18.6, 13.9. IR (neat) cm^{-1}: 3550, 3300, 2100, 1740. EI-MS m/z: 180 (M^+), 165, 137, 124, 113, 95. HIMS m/z: 180.1137 (Calcd for $C_{11}H_{16}O_2$: 180.1149).

(2S^*,3S^*)-2-(1,1-Diethyl-1-silapropoxy)-3-methyl-2-pent-4-ynylcyclopentan-1-one (41). To a solution of **40** (288 mg, 1.6 mmol) and 2,6-di-*tert*-butylpyridine (0.7 ml, 3.1 mmol) in CH_2Cl_2 (3 ml) was added TESOTf (0.56 ml, 2.5 mmol) at −75°C. After being stirred for 3.3 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with AcOEt. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (30/1) as an eluent to give **41** (440 mg, 93%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.39 (1H, ddd, J=19.0, 8.5, 2.1 Hz), 2.19 (2H, m), 2.08 (1H, dd, J=19.0, 9.2 Hz), 1.99–1.63 (5H, m), 1.96 (1H, t, J=2.7 Hz), 1.51–1.23 (2H, m), 1.02 (3H, d, J=6.4 Hz), 0.92 (9H, t, J=7.9 Hz), 0.59 (6H, q, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 216.9, 83.7, 81.2, 68.6, 39.1, 35.2, 32.7, 26.1, 23.4, 18.9, 12.6, 6.9, 6.2. IR (neat) cm^{-1}: 3300, 2120, 1745. EI-MS m/z: 265 ($M^+-C_2H_5$), 238, 227, 209. HIMS m/z: 265.1653 (Calcd for $C_{15}H_{25}O_2Si$: 265.1623).

(8S^*,8aS^*)-8a-(1,1-Diethyl-1-silapropoxy)-8-methyl-1,2,3,6,7,8,8a-hepta-hydroazulen-5-one (42). Radical skeletal rearrangement of **41** (1.01 g, 3.4 mmol), according to the general procedure, gave a mixture of **42** and **43** (401 mg, 50%, **42**:**43**=8:1) as a colorless oil and **44** (441 mg, 21%) as a colorless oil. **42**: ^{1}H NMR ($CDCl_3$) δ: 5.86 (1H, dd, J=2.0, 1.5 Hz), 3.03 (1H, dd, J=16.3, 10.9 Hz), 2.74–2.29 (3H, m), 1.92–1.50 (7H, m), 1.08 (3H, d, J=6.4 Hz), 0.92 (9H, t, J=7.9 Hz), 0.57 (6H, q, J=7.9 Hz). **42**: ^{13}C NMR ($CDCl_3$) δ: 205.6, 165.8, 125.3, 84.6, 41.6, 39.7, 39.0, 34.4, 28.4, 22.4, 16.5, 7.1, 6.5. IR (neat) cm^{-1}: 2950, 1665. EI-MS m/z: 294 (M^+), 279, 265, 251, 209. HIMS m/z: 294.2018 (Calcd for $C_{17}H_{30}O_2Si$: 294.2014). **43** was presented from: ^{1}H NMR ($CDCl_3$) δ: 5.92 (brs), 3.04 (dd, J=15.4, 10.9 Hz), 2.83 (m). ^{13}C NMR ($CDCl_3$) δ: 40.5, 40.1, 34.9, 29.7, 27.9, 22.2, 17.2.

(2S^*,3S^*)-2-(4ZE)-6,6,6-Triphenyl-6-stannahex-4-enyl)-2-(1,1-diethyl-1-sila-propoxy)-3-methylcyclopentan-1-one (44). Colorless oil, ^{1}H NMR ($CDCl_3$) δ: 7.59–7.53 (6H, m), 7.40–7.33 (9H, m), 6.22–6.18 (2H, m), 2.39 (1H, ddd, J=19.3, 8.8, 2.2 Hz), 2.11–1.51 (10H, m), 1.37–1.12 (2H, m), 1.00 (1H, d, J=6.4 Hz), 0.89 (9H, t, J=8.2 Hz), 0.56 (6H, q, J=8.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 217.1, 152.8, 138.6, 137.3, 137.0, 136.9, 128.9, 128.5, 123.9, 81.5, 38.9, 38.1, 35.5, 32.8, 26.2, 23.4, 12.5, 7.0, 6.3. IR (neat) cm^{-1}: 1745. EI-MS m/z: 618 ($M^+-C_2H_4$), 569, 437, 351, 267, 86. HIMS m/z: 618.1975 (Calcd for $C_{33}H_{42}O_2Si^{120}Sn$: 618.1974).

(3R^*,6S^*,7S^*)-7-(1,1-Diethyl-1-silapropoxy)-6-methyl-bicyclo[5.3.0]dec-1-en-3-ol (45). Under an argon atmosphere, to a solution of the mixture of **42** and **43** (845 mg, 2.87 mmol) in toluene (30 ml) was added DIBAH (1.01 M in toluene, 4.3 ml, 4.3 mmol) at −75°C. After being stirred for 1.5 h, the reaction was quenched with saturated aqueous NH_4Cl (1.2 ml) and diluted with ether, and then anhydrous $MgSO_4$ was added. After 1 h, the mixture was filtered through a Celite pad and the pad was

washed with ether. The filtrate and washings were evaporated under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (20/1) as an eluent to give **45** (631 mg, 73%) and a mixture of **46** and **47** (149 mg) as a colorless oil. **45**: ^{1}H NMR ($CDCl_3$) δ: 6.00 (1H, dt, J=7.3, 2.2 Hz), 4.02 (1H, m), 3.60 (1H, d, J=11.0 Hz), 2.48 (1H, m), 2.34–2.14 (2H, m), 2.05–1.90 (2H, m), 1.80–1.31 (6H, m), 0.99 (9H, t, J=7.8 Hz), 0.96 (3H, d, J=6.6 Hz), 0.70 (6H, q, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 152.4, 127.3, 86.0, 66.5, 42.2, 41.8, 34.9, 34.6, 28.2, 22.9, 18.5, 7.1, 6.9. IR ($CHCl_3$) cm^{-1}: 3422, 2960. EI-MS m/z: 296 (M^+), 278, 267, 251, 225, 211, 83. HIMS m/z: 296.2144 (Calcd for $C_{17}H_{32}O_2Si$: 269.2170). mixture of **46** and **47**: ^{1}H NMR ($CDCl_3$) δ: 5.60 (1H, brs), 4.58 (1H, brd, J=11.2 Hz), 2.46–1.16 (10H, m), 0.96 (9H, t, J=7.8 Hz), 0.89 (3H, d, J=6.6 Hz), 0.60 (6H, q, J=7.8 Hz).

(3*R,6*S**,7*S**)-7-(1,1-Diethyl-1-silapropoxy)-6-methylbicyclo[5.3.0]dec-1-en-3-yl acetate (48).** A mixture of **45** (2.11 g, 7.13 mmol), Ac_2O (1 ml, 10.6 mmol), pyridine (25 ml) and DMAP (90 mg, 0.73 mmol) was stirred at room temperature for 15.5 h. The reaction mixture was diluted with ether and water. The organic layer was extracted with ether. Combined extracts were washed with ice-cooled 1% HCl (5 ml×8) and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (15/1) as an eluent to give **48** (2.28 g, 97%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 5.53 (2H, dt, J=3.7, 1.5 Hz), 5.26 (1H, dddd, J=9.5, 3.7, 2.2, 1.5 Hz), 2.25 (1H, m), 2.35 (1H, m), 2.18 (1H, m), 2.04 (3H, s), 1.92–1.43 (7H, m), 0.96 (9H, t, J=7.9 Hz), 0.96 (3H, d, J=6.4 Hz), 0.62 (6H, q, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 170.6, 151.1, 124.4, 84.2, 71.7, 42.2, 41.2, 33.6, 31.9, 28.8, 21.6, 21.4, 17.9, 7.3, 6.8. IR ($CHCl_3$) cm^{-1}: 1738. EI-MS m/z: 338 (M^+), 309, 278, 145, 131, 155, 86. HIMS m/z: 338.2274 (Calcd for $C_{19}H_{34}O_3Si$: 338.2275).

(3*R,6*S**,7*S**,10*R**)-7-(1,1-Diethyl-1-silapropoxy)-10-hydroxy-6-methyl-bicyclo[5.3.0]dec-1-en-3-yl acetate (49).** A solution of **48** (168 mg, 0.5 mmol), pyridine (0.08 ml) and SeO_2 (55 mg, 0.52 mmol) in toluene (5 ml) was refluxed for 3 h. The mixture was diluted with AcOEt and filtered through a Celite pad, and then the pad was washed with AcOEt. The filtrate and washings were concentrated under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (4/1) as an eluent to give **49** (156 mg, 0.44 mmol, 88%) as a light-yellow oil. ^{1}H NMR ($CDCl_3$) δ: 5.90 (1H, dt, J=3.9, 1.2 Hz), 5.31 (1H, m), 4.60 (1H, m), 2.30–1.88 (2H, m), 2.06 (3H, s), 1.84–1.49 (7H, m), 1.37 (1H, d, J=4.9 Hz), 0.99 (3H, d, J=6.4 Hz), 0.95 (9H, t, J=7.9 Hz), 0.60 (6H, q, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 170.5, 155.2, 127.8, 83.7, 75.5, 71.3, 41.9, 38.1, 31.9, 31.4, 28.5, 21.3, 17.7, 7.2, 6.8. IR (neat) cm^{-1}: 3424, 1738. EI-MS m/z: 354 (M^+), 294, 279, 251, 237, 223. HIMS m/z: 354.2201 (Calcd for $C_{19}H_{34}O_4Si$: 354.2225).

(3*R,6*S**,7*S**,10*R**)-7-(1,1-Diethyl-1-silapropoxy)-10-(methoxymethoxy)-6-methylbicyclo[5.3.0]dec-1-en-3-yl acetate (50).** Under an argon atmosphere, a mixture of **49** (3.27 g, 9.24 mmol), (i-Pr)$_2$NEt (3.3 ml, 18.5 mmol) and MOMCl (1.4 ml, 18.5 mmol) in CH_2Cl_2 (95 ml) was stirred at room temperature for 11 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 ml) and extracted with CH_2Cl_2. Combined extracts were washed with H_2O and brine, and dried ($MgSO_4$). The solvent was evaporated in vacuo. The residue was purified by column chromatography with hexane–AcOEt (15/1) as an eluent to give **50** (3.31 g, 90%) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ: 5.89 (1H, dt, J=4.2, 1.2 Hz), 5.34 (1H, m), 4.72 (1H, d, J=7.0 Hz), 4.66 (1H, d, J=7.0 Hz), 4.50 (1H, m), 3.39 (3H, s), 2.15 (1H, m), 2.05 (3H, s), 1.51–2.04 (8H, m), 0.97 (3H, d, J=5.9 Hz), 0.95 (9H, t, J=7.9 Hz), 0.60 (6H, q, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 170.8, 152.0, 129.2, 95.6, 84.0, 80.3, 71.7, 55.9, 42.0, 38.9, 31.8, 29.6, 29.0, 21.8, 18.1, 7.7, 7.3. IR (neat) cm^{-1}: 1738. EI-MS m/z: 398 (M^+), 366, 353, 337, 293. HIMS m/z: 398.2456 (Calcd for $C_{21}H_{38}O_5Si$: 398.2486).

(3*R,6*S**,7*S**,10*R**)-7-(1,1-Diethyl-1-silapropoxy)-10-(methoxymethoxy)-6-methylbicyclo[5.3.0]dec-1-en-3-ol (51).** A solution of **50** (3.43 g, 8.62 mmol) in MeOH (40 ml) was treated with K_2CO_3 (2.83 g 17.2 mmol) at room temperature. After 1.8 h, the orange solution was diluted with 20 ml of water and then evaporated in vacuo. The aqueous layer was extracted with AcOEt. Combined extracts were washed with H_2O and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (10/1) as an eluent to give **51** (2.68 g, 87%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 6.27 (1H, dd, J=8.1, 1.2 Hz), 4.69 (1H, d, J=6.8 Hz), 4.60 (1H, d, J=6.8 Hz), 4.37 (1H, brs), 4.14 (1H, m), 3.82 (1H, d, J=11.2 Hz), 3.36 (3H, s), 2.23 (1H, m), 2.07–1.42 (8H, m), 0.98 (9H, t, J=7.8 Hz), 0.96 (3H, d, J=7.3 Hz), 0.67 (6H, q, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 151.3, 133.0, 93.6, 85.2, 79.1, 66.2, 55.2, 42.2, 37.5, 34.4, 30.0, 28.1, 18.2, 7.0, 6.8. IR (neat) cm^{-1}: 3440. EI-MS m/z: 356 (M^+), 339, 295, 266, 224. HIMS m/z: 356.2354 (Calcd for $C_{19}H_{36}O_4Si$: 356.2381).

(1*R,3*S**,7*S**,8*S**,11*R**)-8-(1,1-Diethyl-1-silapropoxy)-11-(methoxymethoxy)-7-methyltricyclo[6.3.0⟨1,3⟩]undecan-4-one (53).** In a 100-ml two-necked flask, to a green solution of $Cu(OAc)_2$ (184 mg, 1.01 mmol) in acetic acid (8 ml) was added Zn powder (2.2 g, 33.7 mmol) at 110°C. After 5 min, a dark reddish-gray precipitate was formed, and the precipitate was then cooled to room temperature. The precipitate was washed with one portion of acetic acid (2 ml) followed by three portions of ether (5 ml×3). Under an argon atmosphere, to a dispersion of this amalgam in ether (20 ml), with heating to reflux, was added dropwisely a solution of **51** (600 mg, 1.69 mmol), CH_2I_2 (1.4 ml, 16.9 mmol) and 1,2-dimethoxyethane (1.76 ml, 16.9 mmol) in ether (35 ml) for 15 min. After being refluxed for 1 h, the reaction mixture was cooled in an ice bath and then quenched by addition of saturated aqueous NH_4Cl and ether. The mixture was stirred for 30 min at room temperature. The resultant brown and gray precipitates were removed by filtration through a Celite pad, and the pad was washed with ether. The combined filtrate and washings were concentrated in vacuo. The yellow residue was diluted with ether, and the separated aqueous layer was extracted with ether. Combined extracts were washed with H_2O, saturated aqueous $NaHCO_3$ and brine. The dried (Na_2SO_4)

solvent was evaporated in vacuo. The residue was purified by column chromatography using florisil with hexane–AcOEt (5/1) as an eluent to give an impure **52** (1.11 g) as a colorless oil. This compound was used in the next step without further purification. ^{1}H NMR ($CDCl_3$) δ: 4.60 (1H, d, J=6.6 Hz), 4.50 (1H, d, J=6.6 Hz), 4.21 (1H, quint., J=5.9 Hz), 3.49 (1H, dd, J=7.2, 4.5 Hz), 3.32 (3H, s), 2.24–1.46 (11H, m), 1.00 (9H, t, J=7.9 Hz), 0.89 (3H, d, J=6.8 Hz), 0.71 (6H, q, J=7.9 Hz), 0.47 (1H, dd, J=9.5, 4.6 Hz). IR (neat) cm^{-1}: 3364. To an ice-cooling solution of **52** (1.11 g) in CH_2Cl_2 (15 ml) was added NMO (317 mg, 2.7 mmol) and TPAP (23.7 mg, 0.07 mmol). The mixture was stirred at room temperature for 1.25 h and then diluted with ether. The mixture was filtered through florisil, and the florisil pad was washed with ether. The combined filtrate was evaporated in vacuo to give a residue, which was purified by column chromatography with hexane–AcOEt (5/1) as an eluent to afford **53** (375.5 mg, 60%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.60 (1H, d, J=7.1 Hz), 4.50 (1H, d, J=7.1 Hz), 3.42 (1H, brt, J=3.9 Hz), 3.35 (3H, s), 2.62 (1H, dt, J=11.1, 7.8 Hz), 2.39 (1H, ddd, J=9.5, 8.8, 6.3 Hz), 2.25 (1H, ddd, J=9.0, 6.4, 1.3 Hz), 2.13–1.44 (8H, m), 1.18 (1H, dd, J=9.0, 5.0 Hz), 1.00 (3H, d, J=6.6 Hz), 1.02–0.93 (9H, m), 0.72–0.63 (6H, m). ^{13}C NMR ($CDCl_3$) δ: 210.5, 95.2, 85.7, 83.6, 55.5, 45.9, 40.7, 37.6, 35.6, 35.2, 29.7, 29.1, 21.7, 17.1, 7.3, 6.8. IR (neat) cm^{-1}: 1675. EI-MS *m*/*z*: 368 (M^+), 323, 307, 236, 133. HIMS *m*/*z*: 368.2401 (Calcd for $C_{20}H_{36}O_4Si$: 368.2408).

(1*R,6*S**,7*S**,10*R**)-7-(1,1-Diethyl-1-silapropoxy)-10-(methoxymethoxy)-1,6-dimethylbicyclo[5.3.0]undecan-3-one (54).** A solution of **53** (12 mg, 0.033mmol) in EtOH (0.4 ml) was stirred at room temperature in the presence of 20% $Pd(OH)_2$ on carbon (10 mg) under a hydrogen atmosphere. When hydrogen consumption ceased, the catalyst was filtered off. The filtrate was evaporated in vacuo. The residue was purified by column chromatography with hexane–AcOEt (5/1) as an eluent to give **54** (11.1 mg, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.63 (1H, d, J=6.6 Hz), 4.56 (1H, d, J=6.6 Hz), 3.93 (1H, t, J=8.1 Hz), 3.34 (3H, s), 2.61–2.29 (4H, m), 2.14–2.02 (3H, m), 1.79–1.53 (4H, m), 1.01 (3H, s), 1.01 (3H, d, J=7.3 Hz), 0.98 (9H, t, J=7.7 Hz), 0.66 (6H, q, J=7.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 214.3, 96.6, 87.2, 85.6, 55.3, 50.5, 43.9, 40.9, 39.5, 34.5, 26.6, 25.3, 19.1, 14.5, 7.3, 6.6. IR (neat) cm^{-1}: 1696. EI-MS *m*/*z*: 370 (M^+), 341, 309, 239, 131, 90. HIMS *m*/*z*: 370.2532 (Calcd for $C_{20}H_{38}O_4Si$: 370.2537).

(1*R,6*S**,7*S**,10*R**)-7-Hydroxy-10-(methoxymethoxy)-1,6-dimethylbicyclo-[5.3.0]undecan-3-one (55).** To a solution of **54** (278 mg, 0.75 mmol) in THF (1 ml) was added TBAF (1.0 M in THF, 2.3 ml, 2.3 mmol) at 0 °C. After being stirred for 10 h, the reaction mixture was quenched with saturated aqueous potassium sodium (+)-tartrate, extracted with AcOEt. Combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (1/1) as an eluent to give **55** (180.2 mg, 94%) as a colorless crystal. Recrystallization from toluene afforded **55** as a colorless prism. mp. 81°C. ^{1}H NMR ($CDCl_3$) δ: 4.63 (1H, d, J=6.7 Hz), 4.56 (1H, d, J=6.7 Hz), 3.90 (1H, t, J=7.1 Hz), 3.34 (3H, s), 2.55–2.10 (6H, m), 1.89–1.40 (6H, m), 1.06 (3H, d, J=7.1 Hz), 1.06 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 213.5, 96.1, 85.8, 83.3, 55.4, 49.5, 44.8, 41.5, 41.5, 36.8, 26.7, 25.6, 20.1, 15.7. IR ($CHCl_3$) cm^{-1}: 3417, 1678. EI-MS *m*/*z*: 256 (M^+), 238, 225, 194, 166. HIMS *m*/*z*: 256.1695 (Calcd for $C_{14}H_{24}O_4$: 256.1673). Crystal data for **55**: $C_{14}H_{24}O_4$, M=256.34; $20.5<2\theta<29.6$;monoclinic; $P2_1/c$; a=8.382 (5) Å, b=7.446 (3) Å, c=22.899 (4) Å, β=100.01 (3)°; V=1407 (1) Å^3; Z=4; D_{calc}=1.210 g/cm^3; μ(CuKα)=6.72 cm^{-1}; F(000)=560; full-matrix least-squares refinement was based on 1,852 observed reflections ($I>5.00\sigma(I)$) and 163 variable parameters, R=0.062, Rw=0.079.

(3a*S,3*R**)-3-(Methoxymethoxy)-8,3a-dimethyl-1,2,3,4,6,7,3a-hepta-hydroazulen-5-one (56) and (3a*S**,3*R**,8*S**)-3-(methoxymethoxy)-8,3a-dimethyl-2,3,4,6a,7,8,3a-hepta-hydroazulen-5-one (57).** To a solution of **55** (27.7 mg, 0.11 mmol) in CH_2Cl_2 (0.7 ml) was added MsCl (0.2 ml, 1.2 mmol) and Et_3N (0.2 ml, 1.4 mmol) at room temperature, and a light-yellow precipitate was formed. After 3 h, to the ice-cooled mixture was added additional MsCl (0.2 ml, 1.2 mmol) and Et_3N (0.2 ml, 1.4 mmol). After being stirred for 50 min, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with AcOEt. The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (10/1) as an eluent to give **56** (7.6 mg, 0.032 mmol, 29%) as a colorless oil and **57** (18.4 mg, 71%) as a colorless oil. **56**: ^{1}H NMR ($CDCl_3$) δ: 4.67 (1H, d, J=6.8 Hz), 4.56 (1H, d, J=6.8 Hz), 3.64 (1H, m), 3.37 (3H, s), 3.10 (1H, d, J=13.2 Hz), 2.61–2.34 (6H, m), 2.36 (1H, d, J=13.2 Hz), 1.99–1.77 (2H, m), 1.73 (3H, s), 1.04 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 214.0, 140.9, 127.6, 95.0, 88.0, 55.7, 50.3, 47.4, 43.0, 30.3, 29.0, 27.4, 24.3, 23.2. IR (neat) cm^{-1}: 1705. EI-MS *m*/*z*: 238 (M^+), 206, 193, 175, 86. HIMS *m*/*z*: 238.1557 (Calcd for $C_{14}H_{22}O_3$: 238.1568). **57**: ^{1}H NMR ($CDCl_3$) δ: 5.45 (1H, t, J=2.4 Hz), 4.67 (1H, d, J=6.7 Hz), 4.59 (1H, d, J=6.7 Hz), 3.85 (1H, t, J=6.0 Hz), 3.37 (3H, s), 2.86 (1H, m), 2.78 (1H, d, J=12.4 Hz), 2.55 (1H, ddd, J=16.1, 6.0, 2.4 Hz), 2.43 (1H, d, J=12.4 Hz), 2.43–2.38 (2H, m), 2.22 (1H, ddd, J=16.1, 6.0, 2.4 Hz), 1.98 (1H, m), 1.65 (1H, m), 1.18 (3H, s), 1.14 (3H, d, J=7.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 213.3, 152.0, 124.0, 95.8, 87.0, 55.5, 49.22, 49.17, 41.8, 36.8, 35.2, 29.4, 24.9, 22.2. IR (neat) cm^{-1}: 1700. EI-MS *m*/*z*: 238 (M^+), 223, 206, 176, 83. HIMS *m*/*z*: 238.1542 (Calcd for $C_{14}H_{22}O_3$: 238.1568).

(3a*S,3*R**)-3-hydroxy-8,3a-dimethyl-1,2,3,4,6,7,3a-hepta-hydroazulen-5-one (58).** To an ice-cooled solution of **56** (12.1 mg, 0.051 mmol) in THF (0.9 ml), conc. HCl (0.04 ml) was added. The solution was stirred at room temperature for 2.5 h, and then conc. HCl (0.02 ml) was added again at 0°C. After being stirred at room temperature for 14 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with AcOEt. Combined extracts were washed with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane–AcOEt (2/1) as an eluent to give **58** (9.7 mg, 98%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 3.77 (1H, brd, J=3.7 Hz), 2.92 (1H, d, J=12.8 Hz), 2.57 (1H, d, J=12.8 Hz), 2.56–2.24 (6H, m),

2.09–1.95 (2H, m), 1.72 (3H, s), 1.05 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 213.9, 140.1, 128.5, 83.7, 49.5, 48.5, 43.4, 30.6, 29.5, 28.3, 24.8, 22.8. IR ($CHCl_3$) cm^{-1}: 3622, 1698. EI-MS *m/z*: 194 (M^+), 166, 149, 138, 84. HIMS *m/z*: 194.1331 (Calcd for $C_{12}H_{18}O_2$: 194.1306). mp: 68–70°C. NOE correlation (10%) between C_3–H and C_{3a}-methyl–H was observed.

(8a*S)-4,8-Dimethyl-2,3,5,6,8,8a-heptahydroazulene-1,7-dione (59).** To an ice-cooled solution of **58** (5 mg, 0.026 mmol) in CH_2Cl_2 (0.3 ml) was added NMO (5.4 mg, 0.05 mmol) and TPAP (1 mg, 0.03 mmol). The mixture was stirred at room temperature for 5 min and then diluted with ether. The reaction mixture was filtered through florisil, and the florisil column was washed with ether. The solvent was then evaporated in vacuo. The residue was purified by column chromatography with hexane–AcOEt (2/1) as an eluent to give **59** (2.4 mg, 48%) as a light-yellow oil. ^1H NMR ($CDCl_3$) δ: 2.83–2.26 (10H, m), 1.81 (3H, s), 1.14 (3H, s). These ^1H NMR data correspond to Lansbury's synthetic intermediate **59**. ^{13}C NMR ($CDCl_3$) δ: 218.4, 210.3, 137.2, 131.0, 70.8, 48.7, 43.5, 35.5, 30.1, 24.2, 22.9, 21.9. IR (neat) cm^{-1}: 1744, 1707. EI-MS *m/z*: 192 (M^+), 177, 164, 149, 121. HIMS *m/z*: 192.1138 (Calcd for $C_{12}H_{16}O_2$: 192.1149).

X-Ray crystallography

Data for the crystal structure determinations were collected on a Rigaku AFC5s diffractometer. The structure was solved with MITHRIL and refined by the DIRDIF program.

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