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Synthesis of eleven-membered carbocycles via a homo-Cope type of five-carbon ring expansion reaction utilized β-(hydroxymethyl)allylsilane

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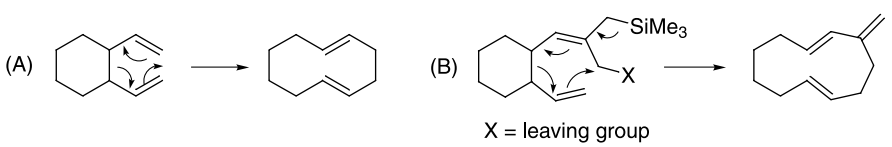
Abstract—Eleven-membered carbocycles were synthesized from six-membered compounds fitted with a β-(hydroxymethyl)allylsilane unit via the title reaction. Namely, *trans*- and *cis*-(*E*)-2-(trimethylsilylmethyl)-3-(2-vinylcyclohex-1-yl)prop-2-en-1-ol were treated with Tf_2O in CH_2Cl_2 in the presence of 2,6-lutidine to afford (1*E*)-3-methylenecycloundeca-1,6-diene in good yield. The geometry of the product was shown to depend upon the *trans*- and *cis*-substitution pattern on the cyclohexane ring of the substrates; i.e. *trans*-isomer afforded (6*E*)-product exclusively and *cis*-isomer afforded the mixture of (6*E*)- and (6*Z*)-product in 1:2 ratio. The (*Z*)-substrate with respect to allylsilane moiety afforded the same ring expansion product, however, the yield was lower than the reaction with the (*E*)-substrate. The substrates bearing *t*-butyl or benzyloxy substituents on the cyclohexane ring also afforded the product analogously, indicating that the reaction depends upon the conformation of the substrate. On the other hand, the substrate bearing isopropenyl group instead of a simple vinyl group did not afford the ring expansion product but produced bicyclo[5.4.0]undecane via the ene reaction.

1. Introduction

Eleven-membered carbocycles are grouped as medium-sized rings and are basic carbocyclic systems in natural terpenes, such as humulanes in sesquiterpenes and lathyrols or dollabelanes in diterpenes.[1,2] Particularly, many natural dollabelanes[3] have been found in the last two decades and have been the focus of attention as interesting synthetic targets by several chemists.[4] For the synthesis of medium-sized ring compounds,[5,6] the ring expansion method is one of the most important method, among which the Cope rearrangement is widely utilized as the four-carbon ring expansion reaction.[7] Various germacrane type of compounds were synthesized by this method,[8] since the direct cyclization to prepare ten-membered rings is not easy. One-, two-, three-, and four-carbon ring expansion reactions have been established as common synthetic methods fitted with a high level of quality and availability,[9] whereas, to our knowledge, only one example of a five-carbon ring expansion reaction is reported by Takayanagi et al. based on the rearrangement of silyl group.[10]

β-(Hydroxymethyl)allylsilane is a versatile three-carbon unit in organic synthesis, which can be used for the synthesis of odd-membered ring compounds.[11,12] For example, Giguere et al. reported the synthesis of hydroazulene derivatives via intramolecular homo-Diels–Alder reaction utilizing this unit as the dienophile.[13] As the related carbon 1,3-dipole, we have developed various synthetic methods utilizing β-carbonylallylsilanes.[11] For examples, self-cyclization of 2-(trimethylsilylmethyl)pentadienal[14] and intramolecular cyclization of (2-functionalized allyl)-trimethylsilane with acid chloride[15] were established as new synthetic methods to spiro[4.5]decanes and α-methylene-γ-lactones, respectively. On the course of our continuous study, we planned a new five-carbon ring expansion method via the homo-Cope reaction. Namely, as depicted in Scheme 1, the homo-Cope type of reaction (reaction B) is



Scheme 1.

Keywords: silicon and compounds; ring transformation; ene-reaction.

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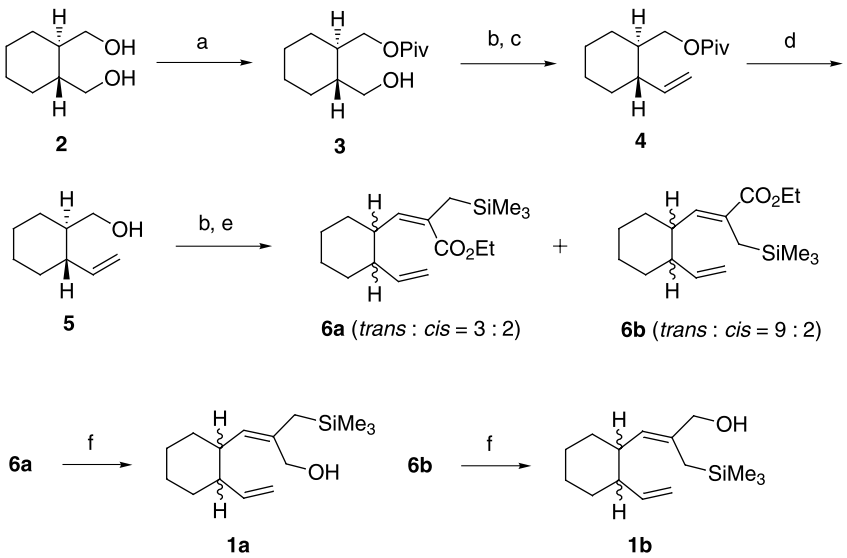


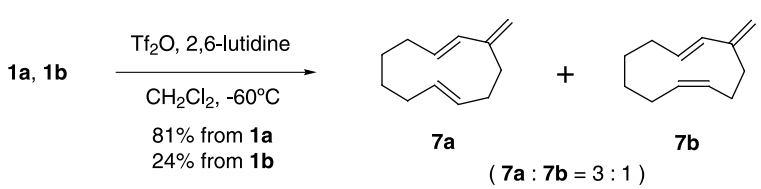
Scheme 2. *Reagents*: (a) PivCl, pyridine, $CHCl_3$; (b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (c) $[Ph_3PCH_3]^+Br^-$, *n*-BuLi, THF; (d) $LiAlH_4$, THF; (e) $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME; (f) DIBAL-H, CH_2Cl_2.

expected to proceed by replacing one of the two C=C double bonds in the Cope rearrangement (reaction A) with a β-(hydroxymethyl)allylsilane unit. A formal homo-Cope rearrangement of 1,6-heptadiene was reported by Hoshstrate et al.[16] but the reaction of 7-substituted-1,5-heptadiene is not known. Here we report the synthesis of eleven-membered carbocycles from a cyclohexane ring having β-(hydroxymethyl)allylsilane moiety via a new homo-Cope type of ring expansion reaction.[17]

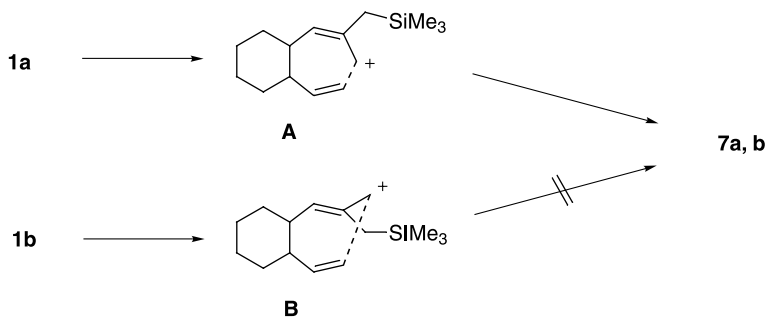
2. Results and discussion

On the above basis, we first studied the ring expansion reaction using the most simple substrates **1a** and **1b** which have a β-(hydroxymethyl)allylsilane unit and a vinyl group on the cyclohexane ring. The substrates **1a**,**b** were prepared as shown in Scheme 2. Namely, *trans*-1,2-cyclohexanedimethanol **2**, prepared from *trans*-1,2-cyclohexanedicarboxylic acid by esterification and $LiAlH_4$ reduction, was first monoprotected with a pivaloyl group to give alcohol **3** (93%), which was oxidized to the aldehyde followed by the Wittig methylenation to afford alkene **4** (83% in two steps). Reductive deprotection of the pivaloyl group in **4** gave alcohol **5** (98%), to which, after oxidation to the aldehyde, a β-(ethoxycarbonyl)allylsilane unit was introduced using $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$ as the Horner–Wadsworth–Emmons (HWE) reagent[18] giving **6a**,**b** in 60% from **5**. The NMR experiment showed that the products **6a**,**b** consists of four-isomers, among which (*E*)-allylsilane (**6a**) and (*Z*)-allylsilane (**6b**) could be separated by repetitive column chromatography, however, unfortunately, the isomers with respect to the cyclohexane ring could not be separated. The ratio of **6a** to **6b** was 6:5, and each consisted of *trans*- and *cis*-substituted cyclohexanes in 3:2 and 9:2 ratios, respectively. The geometry of the double bond was determined from the chemical shifts of the conjugated olefinic protons; i.e. δ 5.41 for *E*-isomer (**6a**) and δ 6.40 for *Z*-isomer (**6b**).[19] Preparation of *cis*-**6a** and *cis*-**6b** from *cis*-1,4-cyclohexanedimethanol was also tried according to the same reaction scheme, and resulted in obtaining the same mixture of four diastereomers of **6a** and **6b**, which is the result of the isomerization during the HWE reaction. Each **6a** and **6b** was reduced by DIBAL-H to afford the substrates **1a** and **1b**, respectively (**1a**: 95%, **1b**: 93%).

The ring expansion reaction was performed following the homo-Diels–Alder reaction reported by Giguere et al.[13a] Thus, the substrate **1a** was treated with Tf_2O in the presence of 2,6-lutidine in dry CH_2Cl_2 solvent at −60°C affording the desired eleven-membered hydrocarbons **7a** and **7b** in a short reaction time (within 30 min) in a 81% yield (Scheme 3). The ^1H NMR spectrum of the product showed that the two compounds **7a** and **7b** (**7a**/**7b**=3:1) were the isomers with respect to the non-conjugated double bond and the geometry was determined from their *J*-values (*J*=15.5 Hz for **7a**, *J*=10.6 Hz for **7b**), whereas the conjugated double bond in both compounds were of the *E*-form (*J*=15.8 Hz for both **7a** and **7b**). In contrast, the reaction of **1b** resulted in the formation of the same mixture of **7a** and **7b** (**7a**/**7b**=3:1) in low yield (24%). Such contrastive results indicate that the isomerization from **1b** to **1a** prior to the ring expansion reaction is a favorable pathway. As shown in Scheme 4, the



Scheme 3.



Scheme 4.

direct cyclization of **1b** seemed to be of considerable disadvantage compared with that of **1a**, since the seven-membered transition state **B**, generated from **1b**, is included in the highly strained *trans*-substituted double bond. On the other hand, **1a** leads more favorable transition state **A** which includes a *cis*-substituted double bond. A related *E*/*Z* isomerization of a functionalized allylsilane moiety was observed previously for β-formylallylsilane[14] and β-(ethoxycarbonyl)allylsilane.[19]

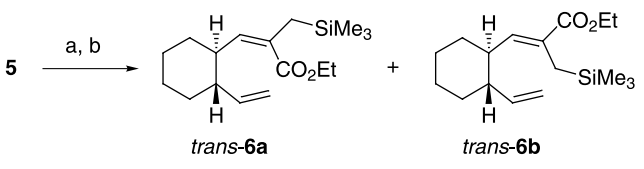
To explore the stereochemistry of the reaction, we next prepared three mixtures of **1a** with different *trans*/*cis* ratios by repetitive column chromatography, however, the complete separation of the two isomers was impossible. Each diastereomer mixtures were exposed to the same reaction conditions, respectively, and the results are shown in Table 1. The extraporation of these data showed that *trans*-**1a** affords **7a** selectively, whereas *cis*-**1a** affords **7a** and **7b** in a 1:2 ratio.

Table 1.

Entry	Isomer ratio in **1a** (*trans*/*cis*)	Ratio of **7a** and **7b**
1	88:12	93:7
2	68:32	78:22
3	60:40[a]	75:25
4	44:56	63:37

[a] Original ratio.

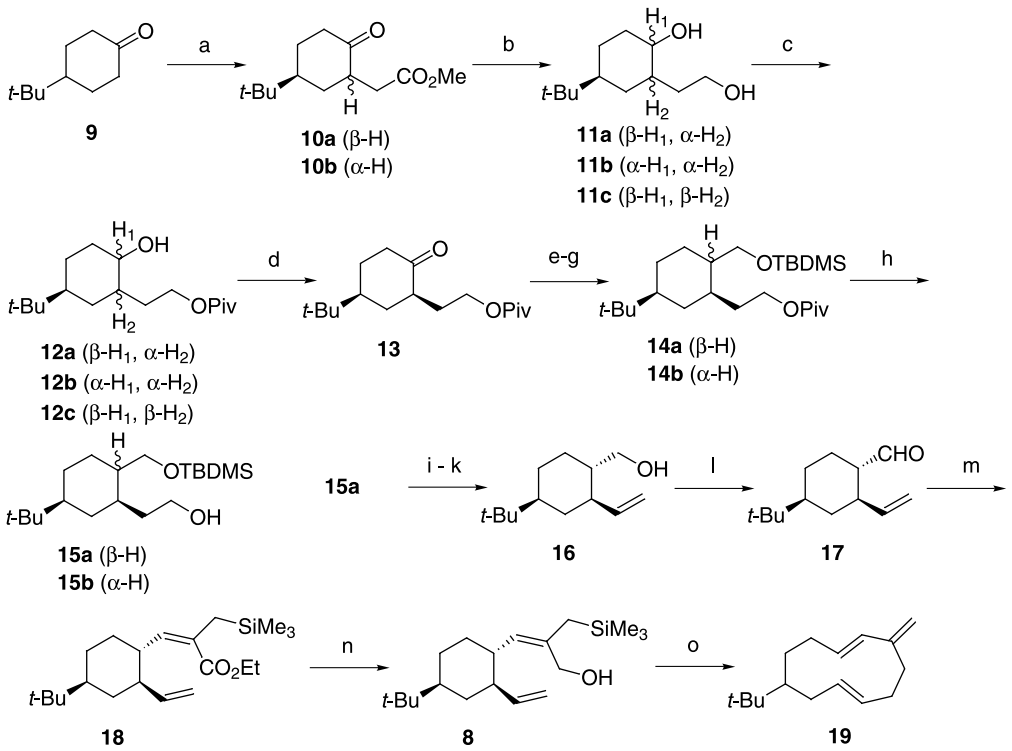
We recently developed an (*E*)-selective synthesis of β-(ethoxycarbonyl)allylsilane utilizing $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$[20] prepared from Ando-phosphonate[21] as the HWE reagent. From the above study, it is obvious that the (*E*)-allylsilane is more suitable than the (*Z*)-allylsilane as the substrate for this five-carbon ring expansion reaction. Therefore, we applied this (*E*)-selective synthesis to obtain intermediate **6a**. When the aldehyde prepared from alcohol **5** was treated with the above phosphonate, allylsilane **6a** was obtained preferentially in an excellent yield (90%; **6a**/**6b**=94:6). Moreover, to



Scheme 5. *Reagents*: (a) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (b) $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, THF.

our surprise, the reaction proceeded without isomerization at the α-carbon giving only *trans*-**6a** exclusively (Scheme 5). We carried out the ring expansion reaction using a pure *trans*-**1a** in hand after the reduction. As expected, the product **7a** was obtained as the sole product in a 95% yield, and thus we could display the evidence that *trans*-**1a** affords **7a** as the only product. Also, the overall yield of the synthesis from diol **2** to eleven-membered carbocycle (**7a** and/or **7b**) was much increased (50%) compared with our first attempt (23%).

Since the homo-Cope reaction of the basic substrate **1a** was successful, we next studied the substituent effect on cyclohexane ring with the substrates bearing a bulky substituent (*t*-Bu) **8** or the oxygen functionality (BnO) **20**, expecting to obtain the stereochemical informations of this reaction. The substrate **8** was first synthesized by the route shown in Scheme 6. Ethoxycarbonylmethylation[22] of commercially available 4-*t*-butylcyclohexanone (**9**) followed by the reduction of **10** afforded diol **11** (79% in two steps). Though compound **11** was obtained as the mixture of three diastereomers, monoprotection with a pivaloyl group (**12**) and oxidation afforded cyclohexanone **13** (82% in two steps) as the single diastereomer. It was found that the diastereomer of **13** was also produced in these reactions, however, isomerization occurred quickly during work-up of the oxidation reaction to afford the thermodynamically more stable product, **13**. Ketone **13** was next methylenated via the Wittig reaction followed by hydroboration using 9-BBN to the alcohol, which was masked by a TBDMS group to obtain **14** (92% in three steps). Deprotection of the pivaloyl group by $LiAlH_4$ afforded a mixture of **15a** and **15b** (94%) in a 2:1 ratio, which could easily be separated by the usual column chromatography. The stereochemistry of **15a**,**b** was determined from the chemical shifts and their half-band widths of the methyne protons on the cyclohexane ring bonding *t*-butyldimethylsilyloxymethyl group (δ 1.12, $W_{1/2}$=22 Hz for **15a** and δ 1.89, $W_{1/2}$=14 Hz for **15b**). The major isomer, **15a**, was nitrophenylselenylated,[23] and exposed to the conditions of oxidative elimination followed by the removal of the TBDMS group to afford alcohol **16** (78% in three steps). The alcohol was oxidized to the aldehyde **17** (100%), followed by the (*E*)-selective introduction of a silyl group with the Ando-HWE reagent[20] giving (*E*)-β-(ethoxycarbonyl)allylsilane **18** (81%). Compound **15b** also afforded the same allylsilane **18** by the same operations, which is the result of the isomerization from *cis*-isomer to *trans*-isomer during oxidation (**16** to **17**) as well as the HWE reaction (**17** to **18**). The unsaturated ester **18** was finally reduced to obtain substrate **8** (100%).



Scheme 6. *Reagents*: (a) LDA, $BrCH_2CO_2Me$, HMPA, THF; (b) $LiAlH_4$, THF; (c) PivCl, pyridine, $CHCl_3$; (d) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (e) $[Ph_3PCH_3]^+Br^-$, *t*-BuOK, PhMe; (f) 9-BBN, NaOH, H_2O_2, THF; (g) TBDMSCl, DMAP, Et_3N, CH_2Cl_2; (h) $LiAlH_4$, THF; (i) *o*-$NO_2C_6H_4SeCN$, *n*-Bu_3P, THF; (j) H_2O_2, THF; (k) TBAF, THF; (l) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (m) $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, THF; (n) DIBAL-H, CH_2Cl_2; (o) Tf_2O, 2,6-lutidine, CH_2Cl_2.

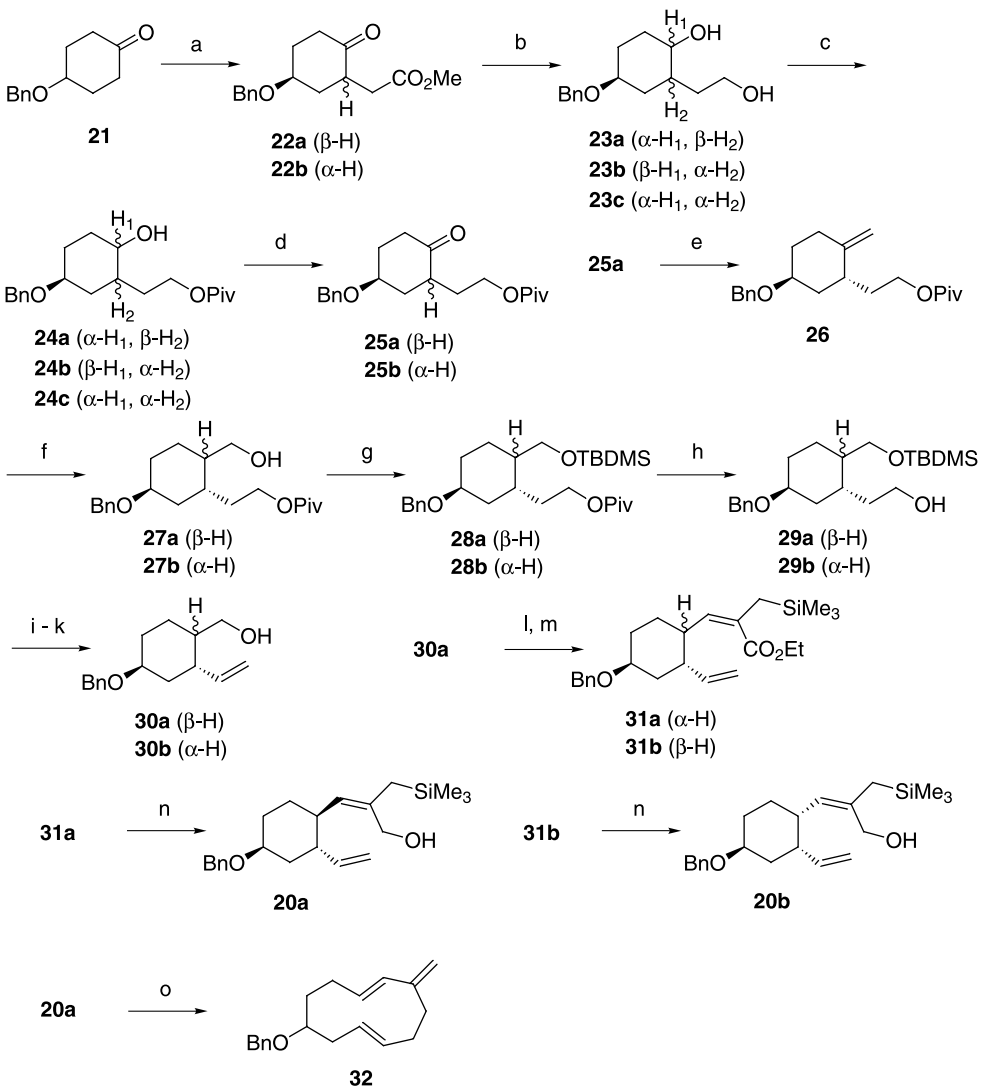
The substrate **8**, in which all three side chains are fixed in equatorial orientations on cyclohexane ring, was exposed to the condition of the ring expansion reaction as described for **1a**, giving the desired eleven-membered ring compound **19** in a 75% yield. As expected, product **19** was obtained as a single diastereomer having *E*-form with respect to both the conjugated and non-conjugated double bonds, which was confirmed by *J*-value of its olefinic proton on ^1H NMR (see Section 3).

The substrates **20a** and **20b**, having benzyloxy substituent, were prepared by a similar route (Scheme 7). 4-Benzyloxycyclohexanone **21**, which was easily prepared from commercially available 1,2-cyclohexanediol by monobenzylation and oxidation, was first converted to the diol **23** (69% in two steps) via **22**. After monoprotection of **23** with a pivaloyl group (**24**), the ketone **25** (**25a/25b**=3:1) was prepared by a Swern oxidation (86% in two steps). When the major isomer **25a** was exposed to the condition of Wittig olefination, the epimerization at the α-position of the carbonyl group occurred to give an inseparable mixture of **26** and its diastereomer in a 3:1 ratio. This undesired result was improved by the usage of the Nozaki–Lombardo procedure[24] to give the alkene **26** (88%) as a single isomer. Then, the same reaction sequence described for the substrate having a *t*-butyl group afforded a mixture of **31a** and **31b** (**31a/31b**=1:2) after an Ando-HWE reaction. When the introduction of allylsilane was carried out under weak-base conditions (DBU/NaI),[25] **31a** (74%) was obtained as the single isomer. These compounds, **31a** and **31b**, were then reduced to obtain the substrates **20a** and **20b**, respectively (**20a**: 96%, **20b**: 100%).

The ring expansion reaction of the substrates **20a** and **20b** were carried out under the same reaction conditions as described for both **1a** and **8**. The reaction of **20a** proceeded smoothly to afford the expected eleven-membered ring compound **32** in an 88% yield. The product **32** was also obtained as the single diastereomer with an *E*-form with respect to both the conjugated and non-conjugated double bonds. On the other hand, the ring expansion product was not obtained from **20b** in spite of the disappearance of **20b** on TLC. The detection of products from the complex reaction mixture was unsuccessful.

As a further study of the substituent effect, we next designed substrate **33** with an isopropenyl group instead of a simple vinyl group. Substrate **33** was synthesized from commercially available 2-cyclohexene-1-carbaldehyde (**34**) as shown in Scheme 8. Namely, **34** was exposed to the condition reported by Kuwajima et al.[26] to give the 1,4-adduct (48%) as *trans*/*cis* mixture of 7:3 ratio, which was easily isomerized to **35** (92%) by the treatment with DBU. The (*E*)-selective introduction of β-(ethoxycarbonyl)allylsilane afforded **36** in a 51% yield. The substrate **33** (97%) was obtained by a reduction using DIBAL-H.

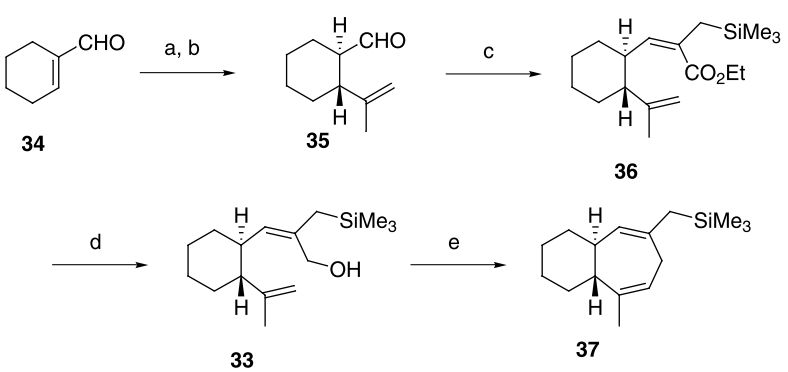
When **33** was exposed to the reaction condition described above, bicyclo[5.4.0]undecane **37** was afforded as the sole product in a 62% yield, and the structure of which was confirmed by the ^1H and ^{13}C NMR spectra including COSY experiments. Compound **37** is obviously the product of an ene reaction, which indicates that the cleavage of the C–C single bond to give the eleven-membered ring did not take place but deprotonation occurred from the seven-membered



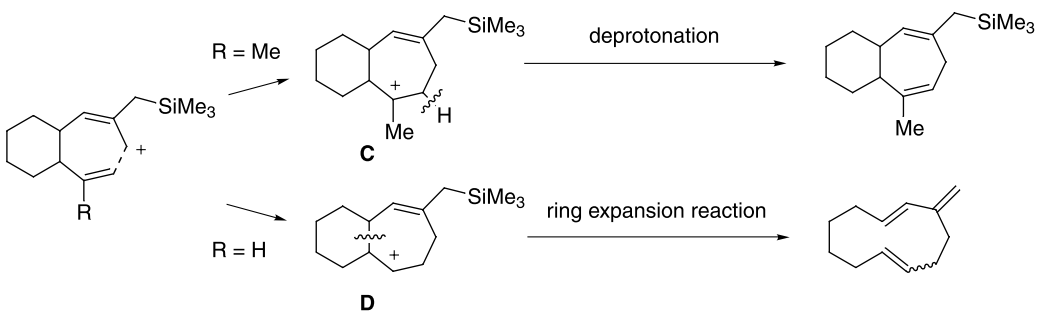
Scheme 7. *Reagents*: (a) LDA, $BrCH_2CO_2Me$, HMPA, THF; (b) $LiAlH_4$, THF; (c) PivCl, pyridine, $CHCl_3$; (d) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (e) CH_2Br_2, Zn, $TiCl_4$, CH_2Cl_2, THF; (f) 9-BBN, NaOH, H_2O_2, THF; (g) TBDMSCl, DMAP, Et_3N, CH_2Cl_2; (h) $LiAlH_4$, THF; (i) *o*-$NO_2C_6H_4SeCN$, *n*-Bu_3P, THF; (j) H_2O_2, THF; (k) TBAF, THF; (l) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (m) $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH (or DBU/NaI), THF; (n) DIBAL-H, CH_2Cl_2; (o) Tf_2O, 2,6-lutidine, CH_2Cl_2.

intermediate carbocation **C** (Scheme 9). From this result, it is estimated that the pathway of five-carbon ring expansion reaction is stepwise via the cation **D** as the intermediate, however, the concerted mechanism for vinyl substituted compounds such as **1** cannot be ruled out. This ene reaction is expected to be a novel synthetic method to form seven-membered ring compounds.

The explanations of the stereochemical outcome of the homo-Cope reaction are as follows. As shown in

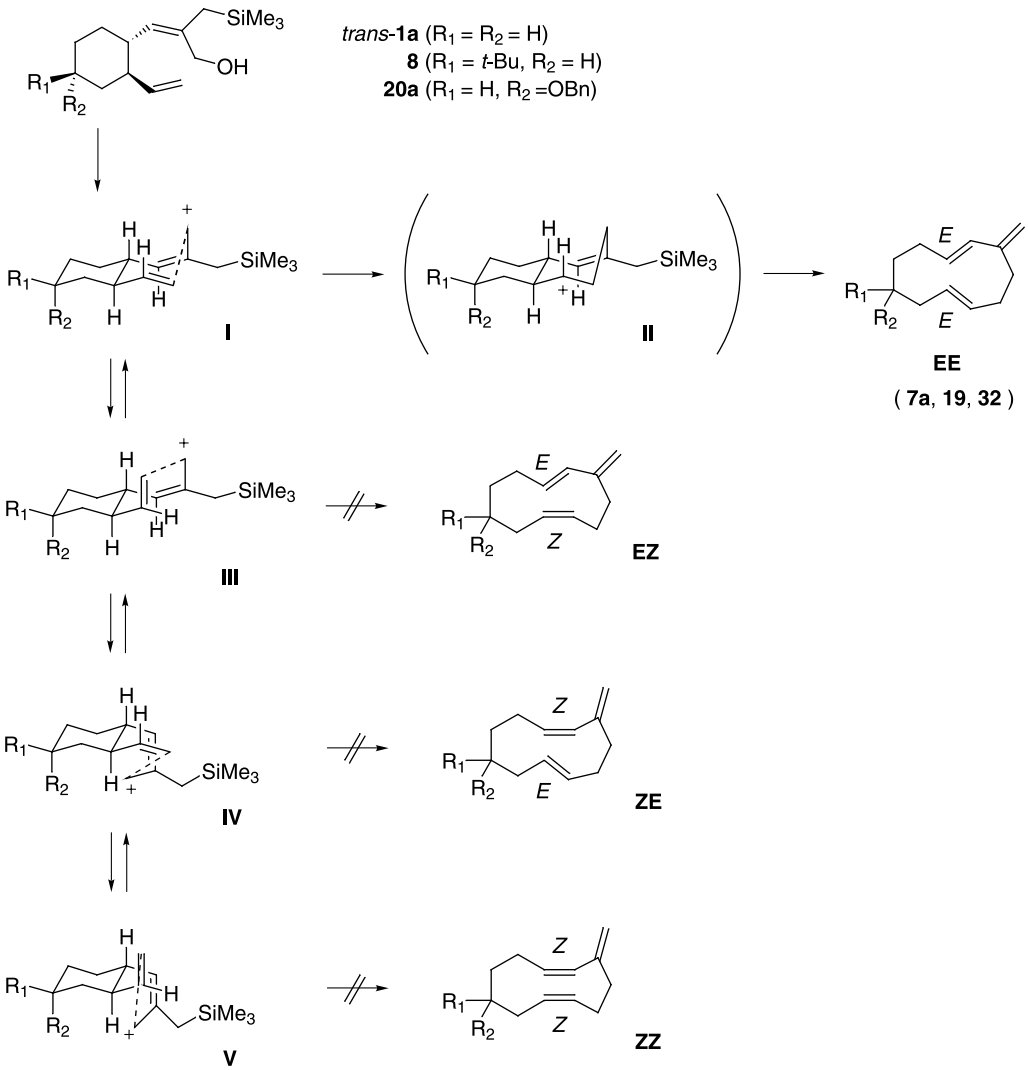


Scheme 8. *Reagents*: (a) $H_2C{=}CMeMgBr$, $CuBrSMe_2$, TMSCl, HMPA, HCl, THF; (b) DBU, CH_2Cl_2; (c) $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, THF; (d) DIBAL-H, CH_2Cl_2; (e) Tf_2O, 2,6-lutidine, CH_2Cl_2.

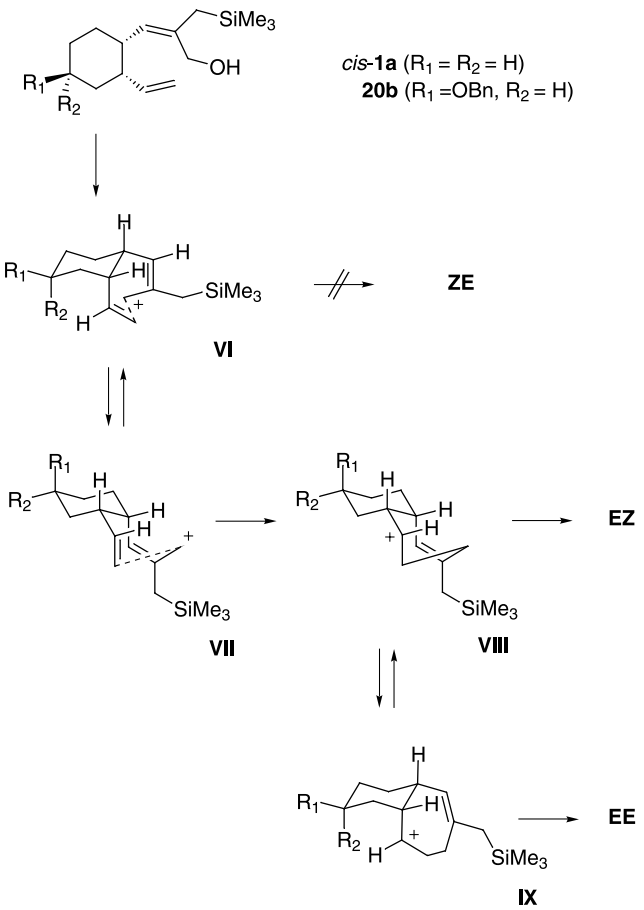


Scheme 9.

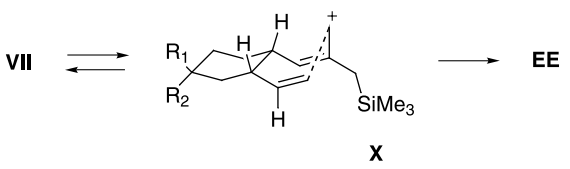
Scheme 10, the stereoselective formation of the *EE*-product (**EE**) from *trans*-**1a**, **8**, and **20a** can be rationalized by the intermediate **I** (and **II** for stepwise mechanism) in which two side chains, the vinyl group and the allylsilane group, take equatorial orientations on the chair conformation of the cyclohexane ring. Three related conformations **III**–**V** are possible by the rotation of two C(sp^3)–C(sp^2) single bonds, which lead **EZ**, **ZE**, and **ZZ**, respectively. However, among four conformers, only **I** is suitable for the reaction, since the reaction sites of the other three conformers are too distant to react (indicated in dotted line). Following the stepwise mechanism, the reaction from *cis*-**1a** is interpreted in accordance with Scheme 11. Two conformers **VI** and **VII** can be considered as the intermediates based on the assumption that the distance of the two reaction sites is the same for conformer **I** but not for **III**–**V**. The expected products from **VI** and **VII** are **ZE** and **EZ**, respectively, however, **EZ** and **EE** were the products from *cis*-**1a**. This means that the major product **EZ** can be rationalized by the conformers **VII** and **VIII**. The minor product **EE** must be formed via **IX**, which is the flipped conformer of **VIII**. The disadvantage of **VI** is understood by the sterical hinderance



Scheme 10.



Scheme 11.



Scheme 12.

of the reacting carbon (indicated as carbocation) which comes over the cyclohexane ring together with a large trifluoromethanesulfonyloxy group. If the reaction is not stepwise but concerted, the formation of **EE** must be explained by **X**, which has a boat like (or twist chair) conformation for the cyclohexane ring (Scheme 12). The fact that no reaction proceeded from **20b** is considered to be the conformational disadvantage of both **VII** and **X** as well as **VI**, namely, that the benzyloxy substituent takes axial orientation in both **VII** and **X**.

In conclusion, eleven-membered carbocycles were synthesized from six-membered carbocycle through a homo-Cope type of new five-carbon ring expansion reaction using β-(hydroxymethyl)allylsilane unit in place of C=C double bond of Cope rearrangement. The ring expansion product was obtained more efficiently when (*E*)-allylsilane was used as the substrate than (*Z*)-allylsilane. It was found that the geometry of double-bond in the product was determined by the *cis*/*trans* substitution pattern of the two reaction units on the cyclohexane ring. Namely, the reaction product has the triene system with only *E*-configuration with respect to the conjugated double bond, whereas the *trans*-substrate produces the product having an *E*-configuration with respect to the non-conjugated double bond, and the *cis*-substrate produces the product having a *Z*-double bond as the major component along with the minor *E*-product. On the other hand, the substrate having an isopropenyl group did not afford an eleven-membered ring compound but the bicyclo[5.4.0]undecene derivative was obtained via the ene reaction. The establishment of such a ring expansion reaction from the present study enables the ring-size control, i.e. the production of different sized compounds from the same sized ring substrate, and thus offers a new strategy in organic synthesis.

3. Experimental

3.1. General procedure

Melting points were measured on a Laboratory Devises Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Jasco FT/IR-230 spectrometer. Both ^{1}H and ^{13}C NMR spectra were measured on a Jeol GSX-400 (400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. Chemical shifts were reported on the δ scale (ppm) with solvent ($CHCl_3$=7.26) as an internal standard. The signal of the solvent ($CDCl_3$=77.00) was used as a standard for ^{13}C NMR spectra. Both low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were obtained on a Jeol SX-102A, JMS-DX303, Shimadzu GCMS-QP5050, or JMS-GCMATE II mass spectrometer with the CI method unless otherwise noted. Analytical TLC was done on precoated TLC plates (Kieselgel 60 F254, layer thickness 0.2 mm). Wakogel C-200 was used for column chromatography. Anhydrous Na_2SO_4 or $MgSO_4$ was used for drying of extracted organic layers. For dry solvents, tetrahydrofuran (THF), Et_2O, and 1,2-dimethoxyethane (DME) were distilled from $LiAlH_4$; $CHCl_3$ and CH_2Cl_2 were distilled from CaH_2 before use.

3.2. Synthesis and homo-Cope reaction of 1a

3.2.1. [(1*RS*,2*RS*)-2-(Hydroxymethyl)cyclohex-1-yl]methyl pivalate (3). In a 200 cm^3 round bottomed flask attached to a $CaCl_2$ drying tube was placed a solution of **2** (3.173 g, 22.00 mmol) in dry pyridine (8.9 cm^3, 110 mmol; distilled from CaH_2) and dry $CHCl_3$ (150 cm^3). After being cooled to −60°C, pivaloyl chloride (3.3 cm^3, 26.8 mmol) was added dropwise, and the mixture was allowed to warm slowly to room temperature over 8 h. The reaction was quenched by addition of a small amount of water. 2 M HCl (60 cm^3) was added, and the mixture was extracted with $CHCl_3$ followed by drying and concentration. The residue was purified by silica gel (150 g) column chromatography using hexane/AcOEt (70:30) as eluent to give **3** (4.659 g, 93%) as an oil; IR (neat) 1728 (C=O) and 3447 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.09–1.29 (4H, m), 1.21 (9H, s), 1.30–1.40 (1H, m), 1.51–1.62 (1H, m), 1.70–1.83 (5H, m), 3.64 (2H, d, *J*=4.5 Hz), 4.00 (1H, dd, *J*=6.0, 11.0 Hz), and 4.12 (1H, dd, *J*=4.5, 11.0 Hz); ^{13}C NMR ($CDCl_3$) δ=25.77, 25.83, 27.19 (3C), 29.49, 29.93, 38.54, 38.85, 42.15, 65.68, 67.56, and 178.67; LRMS (EI) *m*/*z* 228 (M^+; 6%), 198 (100), 171 (93), 141 (86), 104 (90), 78 (95),

66 (99), 65 (96), and 59 (84); HRMS [Found: *m/z* 228.1736 (M^+). Calcd for $C_{13}H_{24}O_3$: *M*, 228.1726].

3.2.2. [(1*RS*,2*SR*)-2-Vinylcyclohex-1-yl]methyl pivalate (4). *Swern oxidation*. To a stirred solution of $(COCl)_2$ (3.9 cm^3, 44.7 mmol) in dry CH_2Cl_2 (80 cm^3) was added dropwise DMSO (4.3 cm^3, 60.6 mmol) at −60°C under Ar atmosphere. After being stirred for 5 min, a solution of **3** (3.421 g, 14.98 mmol) in dry CH_2Cl_2 (15 cm^3) was added dropwise to this solution. The solution was stirred for 1.5 h at the same temperature, Et_3N (12.6 cm^3, 89.7 mmol) was added, and the reaction mixture was allowed to warm to room temperature. The stirring was continued for 1 h, and the reaction was quenched by the addition of water. Extraction with CH_2Cl_2 followed by drying and concentration gave an oily residue (5.054 g), which was not purified.

Wittig reaction. To a stirred suspension of methyltriphenylphosphonium bromide (10.71 g, 29.97 mmol) in dry THF (60 cm^3) was added *n*-BuLi (19.0 cm^3, 28.5 mmol; 1.50 M solution in hexane) dropwise at 0°C under Ar atmosphere. After being stirred at room temperature for 4 h, the clear yellow solution was recooled to 0°C and a solution of the above residue (5.054 g) in dry THF (15 cm^3) was added dropwise. The mixture was stirred for 20 h at room temperature, and to this was added a saturated aqueous solution of NH_4Cl (100 cm^3). This was extracted with Et_2O and dried. Evaporation of the solvent followed by silica gel (100 g) column chromatography using hexane/AcOEt (95:5) as eluent afforded **4** (2.835 g, 83%) as an oil; IR (neat) 1640 (C=C) and 1731 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.06–1.29 (4H, m), 1.20 (9H, s), 1.39–1.49 (1H, m), 1.63–1.91 (5H, m), 3.84 (1H, dd, *J*=6.5, 11.0 Hz), 4.06 (1H, dd, *J*=3.5, 11.0 Hz), 4.92–5.01 (2H, m), and 5.63 (1H, ddd, *J*=9.3, 10.1, 17.1 Hz); ^{13}C NMR ($CDCl_3$) δ=25.75, 25.79, 27.23 (3C), 29.40, 33.31, 38.84, 41.11, 45.02, 67.60, 114.42, 142.38, and 178.55; LRMS *m/z* 225 (M^++H; 100%), 223 (2), 167 (2), 143 (4), 123 (71), 122 (48), 85 (22), 81 (15), and 67 (6); HRMS [Found: *m/z* 225.1841 (M^++H). Calcd for $C_{14}H_{25}O_2$: *M*, 225.1856].

3.2.3. (1*RS*,2*SR*)-2-Vinylcyclohexanemethanol (5). In a 200 cm^3 round bottomed flask attached to a $CaCl_2$ drying tube was placed a suspension of $LiAlH_4$ (554.8 mg, 14.62 mmol) in dry Et_2O (40 cm^3). After being cooled to 0°C, a solution of **4** (2.699 g, 12.03 mmol) in dry Et_2O (20 cm^3) was added, and the mixture was stirred at room temperature for 20 h. The reaction was quenched by the addition of a small amount of moistured Et_2O. 2 M HCl (70 cm^3) was added to clear solution, and the mixture was extracted with Et_2O and dried. Evaporation of the solvent followed by silica gel (80 g) column chromatography using pentane/Et_2O (80:20 to 60:40) as eluent gave **5** (1.658 g, 98%) as an oil; IR (neat) 1639 (C=C) and 3338 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00–1.36 (5H, m), 1.62–1.87 (6H, m), 3.44 (1H, dd, *J*=5.8, 11.0 Hz), 3.62 (1H, dd, *J*=4.7, 11.0 Hz), 4.96 (1H, dd, *J*=2.1, 10.0 Hz), 5.05 (1H, ddd, *J*=0.8, 2.1, 17.0 Hz), and 5.72 (1H, ddd, *J*=9.1, 10.0, 17.0 Hz); ^{13}C NMR ($CDCl_3$) δ=25.73, 25.77, 29.07, 33.41, 44.26, 45.97, 67.15, 114.05, and 143.77; LRMS (EI) *m/z* 122 (M^+-H_2O; 93%), 110 (86), 94 (97), 91 (97), 65 (100), and 52 (99); HRMS [Found: *m/z* 122.1094 (M^+-H_2O). Calcd for C_9H_{14}: *M*, 122.1096].

3.2.4. Ethyl (*E*)-2-(trimethylsilylmethyl)-3-(2-vinylcyclohex-1-yl)prop-2-enoate (6a) and ethyl (*Z*)-2-(trimethylsilylmethyl)-3-(2-vinylcyclohex-1-yl)prop-2-enoate (6b). *Swern oxidation*. According to the same procedure shown in the synthesis of **4**, compound **5** (1.625 g, 11.59 mmol) was oxidized. The resultant crude aldehyde (2.488 g) was used for the next reaction without purification.

HWE reaction. To a stirred suspension of NaH (1.069 g, 24.50 mmol; 55% in mineral oil which was removed by washing with dry hexane) in dry DME (90 cm^3) was added $(EtO)_2P(O)CH_2CO_2Et$ (4.6 cm^3, 23.0 mmol) dropwise at 0°C under Ar atmosphere. After being stirred at 0°C for 4 h, (iodomethyl)trimethylsilane (3.85 cm^3, 25.7 mmol) was added and the mixture was heated to 70°C for 3 h. This was recooled to 0°C, and a second portion of NaH (691.0 mg, 15.84 mmol; mineral oil was not removed) was added. After the mixture had been warmed slowly to room temperature, the stirring was continued for 1 h. This was cooled to 0°C again, a solution of the above aldehyde (2.488 g) in dry DME (10 cm^3) was added dropwise, and the mixture was stirred at room temperature for 14 h. A saturated NH_4Cl aq. (100 cm^3) was added, the mixture was extracted with Et_2O, and dried. Evaporation of the solvent followed by silica gel (100 g) column chromatography using hexane/Et_2O (99:1) as eluent afforded a mixture of **6a** and **6b** (2.045 g, 60%), which could be separated by the repetition of the chromatography.

Compound **6a**. An oil; IR (neat) 1673 (C=C) and 1714 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) for *trans*-**6a** δ=−0.03 (9H, s), 1.01–1.11 (1H, m), 1.14–1.30 (3H, m), 1.30 (3H, t, *J*=7.0 Hz), 1.70 (2H, AB), 1.67–1.78 (5H, m), 2.78 (1H, ddt, *J*=3.6, 11.2, 10.0 Hz), 4.16 (2H, q, *J*=7.0 Hz), 4.85 (1H, dd, *J*=2.0, 10.0 Hz), 4.92 (1H, dd, *J*=2.0, 17.2 Hz), 5.41 (1H, d, *J*=10.0 Hz), and 5.64 (1H, ddd, *J*=7.8, 10.0, 17.2 Hz); for *cis*-**6a** δ=−0.03 (9H, s), 1.14–1.30 (3H, m), 1.30 (3H, t, *J*=7.0 Hz), 1.36–1.45 (1H, m), 1.51–1.64 (4H, m), 1.72 (2H, br s), 2.31–2.39 (1H, m), 3.15 (1H, br dq, *J*=10.0, 4.6 Hz), 4.17 (2H, q, *J*=7.0 Hz), 4.97 (1H, ddd, *J*=1.2, 2.1, 17.0 Hz), 4.99 (1H, ddd, *J*=1.1, 2.1, 10.3 Hz), 5.68 (1H, d, *J*=10.0 Hz), and 5.92 (1H, ddd, *J*=7.8, 10.3, 17.0 Hz); ^{13}C NMR ($CDCl_3$) for *trans*-**6a** δ=−1.62 (3C), 14.22, 23.97, 25.63, 25.83, 32.59, 32.90, 42.67, 48.16, 59.93, 113.19, 127.99, 143.45, 144.08, and 168.44; LRMS (EI) *m/z* 294 (M^+; 99%), 279 (95), 212 (92), 211 (91), 147 (86), 94 (100), 75 (98), and 73 (95); HRMS [Found: *m/z* 294.1973 (M^+). Calcd for $C_{17}H_{30}O_2Si$: *M*, 294.1996].

Compound **6b**. An oil; IR (neat) 1637 (C=C) and 1709 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) for *trans*-**6b** δ=0.00 (9H, s), 1.11–1.33 (4H, m), 1.28 (3H, t, *J*=7.1 Hz), 1.56–1.67 (2H, m), 1.72 (1H, d, *J*=13.0 Hz), 1.71–1.82 (2H, m), 1.78 (1H, d, *J*=13.0 Hz), 1.82–1.90 (1H, m), 2.00 (1H, dq, *J*=3.2, 10.2 Hz), 4.16 (2H, q, *J*=7.1 Hz), 4.87 (1H, ddd, *J*=0.8, 1.9, 10.3 Hz), 4.94 (1H, ddd, *J*=1.3, 1.9, 17.2 Hz), 5.63 (1H, ddd, *J*=7.3, 10.3, 17.2 Hz), and 6.40 (1H, d, *J*=10.2 Hz); ^{13}C NMR ($CDCl_3$) for *trans*-**6b** δ=−0.86 (3C), 14.27, 17.29, 25.52, 25.63, 31.66, 31.88, 42.83, 46.83, 60.34, 113.48, 129.15, 142.32, 142.54, and 168.62; LRMS (EI) *m/z* 294 (M^+; 91%), 280 (100), 249 (100), 213 (94), 185 (98), 175 (93), 119 (99), 93 (98), 74 (94), and 67 (92);

HRMS [Found: *m/z* 294.1992 (M^+). Calcd for $C_{17}H_{30}O_2Si$; *M*, 294.1996].

3.2.5. (*E*)-2-(Trimethylsilylmethyl)-3-(2-vinylcyclohex-1-yl)prop-2-en-1-ol (1a). To a stirred solution of DIBAL-H (3.8 cm^3, 3.80 mmol; 1.0 M solution in cyclohexane) in dry CH_2Cl_2 (10 cm^3) was added a solution of **6a** (366.0 mg, 1.24 mmol) in dry CH_2Cl_2 (5 cm^3) at −60°C under Ar atmosphere. After the mixture had been stirred for 1 h at −60°C, MeOH (1 cm^3) was added, and the mixture was further stirred for 30 min at room temperature. The resultant gel was filtrated and washed with CH_2Cl_2. Evaporation of the solvent followed by silica gel (15 g) column chromatography using hexane/Et_2O (97:3 to 85:15) as eluent afforded **1a** (297.1 mg, 95%); an oil; IR (neat) 1639 (C=C) and 3334 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) for *trans*-**1a** δ=−0.01 (9H, s), 1.06–1.29 (5H, m), 1.56 (2H, AB), 1.57–1.64 (1H, m), 1.66–1.77 (4H, m), 2.05 (1H, dq, *J*=3.7, 10.1 Hz), 3.93 (1H, br d, *J*=11.4 Hz), 4.04 (1H, br d, *J*=11.4 Hz), 4.87 (1H, d, *J*=10.1 Hz), 4.88–4.94 (2H, m), and 5.64 (1H, ddd, *J*=7.6, 10.3, 17.2 Hz); for *cis*-**1a** δ=0.01 (9H, s), 1.06–1.77 (9H, m), 1.60 (2H, br s), 2.22 (1H, tt, *J*=4.8, 8.0 Hz), 2.65 (1H, dq, *J*=10.1, 4.8 Hz), 3.99 (1H, br d, *J*=11.5 Hz), 4.05 (1H, br d, *J*=11.5 Hz), 4.93–4.99 (2H, m), 5.28 (1H, d, *J*=10.1 Hz), and 5.76–5.85 (1H, m); ^{13}C NMR ($CDCl_3$) for *trans*-**1a** δ=−1.22 (3C), 24.71, 25.80, 25.85, 32.16, 34.22, 42.01, 47.39, 62.07, 113.41, 131.88, 134.94, and 143.65; for *cis*-**1a** δ=−1.22 (3C), 22.58, 24.27, 25.03, 28.51, 31.78, 37.91, 44.89, 61.71, 113.91, 127.22, 135.92, and 142.01; LRMS *m/z* 235 (M^+−OH; 37%), 162 (24), 161 (33), 147 (10), 133 (14), 121 (20), 107 (22), 81 (31), and 73 (100); HRMS [Found: *m/z* 235.1832 (M^+−OH). Calcd for $C_{15}H_{27}Si$: *M*, 235.1863].

3.2.6. (*Z*)-2-(Trimethylsilylmethyl)-3-(2-vinylcyclohex-1-yl)prop-2-en-1-ol (1b). According to the same procedure, compound **6b** (467.2 mg, 1.59 mmol) was reduced to give **1b** (373.4 mg, 93%); an oil; IR (neat) 1639 (C=C) and 3334 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) for *trans*-**1b** δ=0.03 (9H, s), 1.02–1.13 (1H, m), 1.13–1.30 (3H, m), 1.40 (1H, br s), 1.47 (1H, br d, *J*=13.8 Hz), 1.60 (1H, dd, *J*=1.0, 13.8 Hz), 1.50–1.79 (5H, m), 1.83–1.93 (1H, m), 3.92 (2H, br s), 4.85 (1H, ddd, *J*=0.8, 2.2, 10.3 Hz), 4.90 (1H, ddd, *J*=1.1, 2.2, 17.2 Hz), 5.07 (1H, br d, *J*=9.8 Hz), and 5.67 (1H, ddd, *J*=7.3, 10.3, 17.2 Hz); ^{13}C NMR ($CDCl_3$) for *trans*-**1b** δ=−0.59 (3C), 19.08, 25.81, 25.86, 32.05, 32.99, 41.47, 47.58, 68.83, 112.84, 128.56, 136.16, and 143.25; LRMS *m/z* 235 (M^+−OH; 43%), 162 (44), 161 (40), 147 (16), 134 (16), 133 (20), 121 (23), 107 (23), 81 (24), and 73 (100); HRMS [Found: *m/z* 235.1824 (M^+−OH). Calcd for $C_{15}H_{27}Si$: *M*, 235.1863].

3.2.7. (1*E*,6*E*)-3-Methylenecycloundeca-1,6-diene (7a) and (1*E*,6*Z*)-3-methylenecycloundeca-1,6-diene (7b)—homo-Cope reaction of 1a. To a stirred solution of **1a** (76.3 mg, 0.30 mmol) in dry CH_2Cl_2 (5 cm^3) were added 2,6-lutidine (0.085 cm^3, 0.73 mmol) and Tf_2O (0.075 cm^3, 0.45 mmol) at −60°C under Ar atmosphere, and the stirring was continued for 30 min. The reaction was quenched by addition of a saturated Na_2CO_3 aq. (40 cm^3), and the mixture was extracted with CH_2Cl_2. The organic layer was washed successively with saturated Na_2CO_3 aq. and 2 M HCl, and dried. Evaporation of the solvent followed by silica gel (4 g) column chromatography using hexane as eluent afforded a mixture of **7a** and **7b** (39.8 mg, 81%) as an oil; IR (neat) 1603 (C=C) and 1655 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) for **7a** δ=1.44–1.51 (2H, m), 1.58–1.63 (2H, m), 1.93–2.00 (2H, m), 2.01–2.08 (2H, m), 2.12–2.19 (2H, m), 2.31–2.37 (2H, m), 4.81 (1H, d, *J*=2.0 Hz), 4.85 (1H, d, *J*=2.0 Hz), 5.11 (1H, dt, *J*=15.5, 7.7 Hz), 5.34 (1H, dt, *J*=15.5, 7.6 Hz), 5.40 (1H, dt, *J*=15.8, 7.3 Hz), and 5.91 (1H, br d, *J*=15.8 Hz); for **7b** δ=1.44–2.37 (12H, m), 4.73 (2H, br s), 5.24–5.32 (1H, m), 5.49 (1H, dtt, *J*=10.6, 8.6, 1.7 Hz), 5.88 (1H, dt, *J*=15.8, 6.8 Hz), and 6.03 (1H, br d, *J*=15.8 Hz); ^{13}C NMR ($CDCl_3$) for **7a** δ=27.55, 29.88, 32.27, 33.98, 34.76, 34.88, 112.64, 130.82, 130.92, 134.45, 137.83, and 148.78; for **7b** δ=25.56, 26.64, 26.80, 28.64, 29.69, 32.85, 111.21, 129.52, 130.18 (2C), 135.66, and 149.65; LRMS (EI) *m/z* 162 (M^+; 66%), 160 (23), 133 (35), 119 (51), 105 (56), 91 (83), 73 (100), 58 (91), and 57 (26); HRMS [Found: *m/z* 162.1389 (M^+). Calcd for $C_{12}H_{18}$: *M*, 162.1409]. The ratio of **7a** and **7b** was determined from the integral values of each olefinic protons (e.g. **7a**: δ 5.91, **7b**: δ 6.03).

3.3. Synthesis and homo-Cope reaction of 8

3.3.1. Methyl 2-[(1*SR*,5*SR*)-5-*t*-butyl-2-oxocyclohex-1-yl]acetate (10a) and methyl 2-[(1*RS*,5*SR*)-5-*t*-butyl-2-oxocyclohex-1-yl]acetate (10b). To a stirred solution of *i*-Pr_2NH (3.4 cm^3, 24.2 mmol) in dry THF (30 cm^3) was added *n*-BuLi (15.5 cm^3, 24.2 mmol; 1.56 M solution in hexane) at −60°C under Ar atmosphere. After being stirred for 20 min, a solution of **9** (3.088 g, 20.02 mmol) in dry THF (15 cm^3) was added dropwise to this solution. The solution was stirred for 30 min at the same temperature, then HMPA (4.2 cm^3, 24.1 mmol) and $BrCH_2CO_2Et$ (3.7 cm^3, 40.2 mmol) were added subsequently. After the reaction mixture had been stirred for 20 min, a saturated NH_4Cl aq. (50 cm^3) was added, and the mixture was extracted with AcOEt and dried. Evaporation of the solvent followed by silica gel (120 g) column chromatography using hexane/AcOEt (97:3 to 90:10) as eluent afforded **10** (4.016 g, 89%) as a diastereomer mixture. The following spectral data were obtained after partial separation into *cis*- and *trans*-isomers by silica gel column chromatography.

Compound **10a**. An oil; IR (neat) 1714 (C=O) and 1738 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (9H, s), 1.44–1.53 (1H, m), 1.55–1.72 (3H, m), 1.83–1.95 (2H, m), 2.31 (1H, dd, *J*=7.0, 15.6 Hz), 2.40–2.49 (1H, m), 2.72 (1H, dd, *J*=7.0, 15.6 Hz), 2.94 (1H, quint, *J*=7.3 Hz), and 3.68 (3H, s); ^{13}C NMR ($CDCl_3$) δ=23.74, 27.08 (3C), 29.35, 32.93, 34.59, 38.57, 42.34, 43.50, 51.71, 172.39, and 213.42; LRMS *m/z* 227 (M^++H; 11%), 196 (13), 195 (100), 194 (5), 179 (6), 169 (8), 138 (6), 137 (7), 57 (15), and 55 (6); HRMS [Found: *m/z* 227.1662 (M^++H). Calcd for $C_{13}H_{23}O_3$: *M*, 227.1648].

Compound **10b**. An oil; IR (neat) 1716 (C=O) and 1739 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (9H, s), 1.23 (1H, dt, *J*=12.1, 12.5 Hz), 1.43 (1H, ddt, *J*=5.6, 12.1, 12.5 Hz), 1.65 (1H, tt, *J*=2.9, 12.1 Hz), 2.08–2.15 (2H, m), 2.15 (1H, dd, *J*=5.8, 16.4 Hz), 2.33–2.46 (2H, m), 2.78 (1H, dd, *J*=7.2, 16.4 Hz), 2.84–2.93 (1H, m), and 3.68 (3H, s); ^{13}C NMR ($CDCl_3$) δ=27.53 (3C), 28.42, 32.33, 34.20, 34.76,

41.02, 46.19, 46.85, 51.59, 172.98, and 211.32; LRMS *m/z* 227 (M^++H; 94%), 226 (7), 196 (13), 195 (100), 181 (6), 179 (5), 169 (11), 138 (5), 137 (9), and 57 (9); HRMS [Found: *m/z* 227.1662 (M^++H). Calcd for $C_{13}H_{23}O_3$: *M*, 227.1648].

3.3.2. (1*SR*,2*RS*,4*SR*)-4-*t*-Butyl-2-(2-hydroxyethyl)cyclohexan-1-ol (11a), (1*RS*,2*RS*,4*SR*)-4-*t*-butyl-2-(2-hydroxyethyl)cyclohexan-1-ol (11b), and (1*SR*,2*SR*,4*SR*)-4-*t*-butyl-2-(2-hydroxyethyl)cyclohexan-1-ol (11c). According to the same procedure described for the synthesis of **5**, the above γ-ketoester (4.280 g, 18.91 mmol) was reduced by $LiAlH_4$. The crude product was purified by silica gel (100 g) column chromatography using hexane/AcOEt (70:30 to 80:20) as eluent to give diol **11** (3.369 g, 89%) as a diastereomer mixture. The following spectral data were obtained after partial purification.

Compound **11a**. Mp. 72–75°C; IR (CH_2Cl_2) 3336 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.76–0.89 (1H, m), 0.83 (9H, s), 0.94–1.09 (2H, m), 1.18–1.37 (2H, m), 1.48–1.56 (1H, m), 1.64–1.76 (3H, m), 1.96–2.03 (1H, m), 3.16 (1H, dt, *J*=4.3, 10.5 Hz), 3.59 (1H, ddd, *J*=3.4, 10.0, 10.5 Hz), 3.75 (1H, dt, *J*=10.5, 4.3 Hz), and 4.46 (2H, br s); ^{13}C NMR ($CDCl_3$) δ=25.57, 27.56 (3C), 32.19, 33.82, 35.47, 38.46, 44.42, 47.20, 61.47, and 75.06; LRMS *m/z* 201 (M^++H; 36%), 183 (72), 165 (52), 149 (12), 139 (36), 125 (24), 109 (100), 101 (15), 95 (59), 83 (33), and 57 (87); HRMS [Found: *m/z* 201.1791 (M^++H). Calcd for $C_{12}H_{25}O_2$: *M*, 201.1856].

Compound **11b**. Mp. 87–90°C; IR (CH_2Cl_2) 3365 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (9H, s), 1.05 (1H, tt, *J*=2.8, 12.0 Hz), 1.16 (1H, q, *J*=12.0 Hz), 1.23–1.72 (7H, m), 1.87–1.94 (1H, m), 2.48 (1H, br s), 2.55 (1H, br s), 3.65–3.78 (2H, m), and 3.91 (1H, br q-like, *J*=3 Hz); ^{13}C NMR ($CDCl_3$) δ=20.67, 27.20, 27.58 (3C), 32.54, 33.75, 36.17, 39.69, 48.00, 60.26, and 68.01; LRMS *m/z* 201 (M^++H; 58%), 183 (100), 165 (31), 139 (22), 125 (19), 109 (59), 95 (35), 81 (16), and 57 (42); HRMS [Found: *m/z* 201.1768 (M^++H). Calcd for $C_{12}H_{25}O_2$: *M*, 201.1856].

Compound **11c**. Mp. 103–106°C; IR (CH_2Cl_2) 3267 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.82 (9H, s), 0.97–1.09 (1H, m), 1.10 (1H, tt, *J*=3.0, 12.1 Hz), 1.25 (1H, dt, *J*=3.6, 12.4 Hz), 1.42–1.55 (2H, m), 1.67 (1H, dq, *J*=13.0, 3.0 Hz), 1.69–1.79 (2H, m), 1.90–2.01 (1H, m), 2.07–2.14 (1H, m), 3.47 (2H, br s), 3.57 (1H, dt, *J*=3.6, 10.4 Hz), 3.72 (1H, dt, *J*=11.8, 4.0 Hz), and 3.78 (1H, dt, *J*=10.4, 4.7 Hz); ^{13}C NMR ($CDCl_3$) δ=25.85, 27.58 (3C), 30.32, 30.83, 32.05, 32.30, 39.20, 40.85, 62.66, and 72.38; LRMS *m/z* 201 (M^++H; 8%), 183 (36), 165 (30), 139 (27), 125 (20), 109 (85), 95 (57), 83 (27), and 57 (100); HRMS [Found: *m/z* 201.1924 (M^++H). Calcd for $C_{12}H_{25}O_2$: *M*, 201.1856].

3.3.3. 2-[(1*RS*,2*SR*,5*SR*)-5-*t*-Butyl-2-hydroxycyclohex-1-yl]ethyl pivalate (12a), 2-[(1*RS*,2*RS*,5*SR*)-5-*t*-butyl-2-hydroxycyclohex-1-yl]ethyl pivalate (12b), and 2-[(1*SR*,2*SR*,5*SR*)-5-*t*-butyl-2-hydroxycyclohex-1-yl]ethyl pivalate (12c). According to the same procedure described for the synthesis of **3**, compound **11** (2.615 g, 13.05 mmol) was monopivalated. The crude product was purified by silica gel (50 g) column chromatography using hexane/AcOEt (97:3 to 70:30) as eluent to give **12** (3.474 g, 94%) as a diastereomer mixture. The following spectral data were collected after partial purification.

Compound **12a**. Mp. 66–68°C; IR (CH_2Cl_2) 1726 (C=O) and 3427 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.71–0.85 (1H, m), 0.80 (9H, s), 0.94–1.02 (2H, m), 1.14 (9H, s), 1.17–1.33 (2H, m), 1.45 (1H, dq, *J*=13.8, 6.8 Hz), 1.68–1.79 (2H, m), 1.93–2.01 (1H, m), 2.04 (1H, ddt, *J*=4.2, 13.8, 6.8 Hz), 2.32 (1H, br s), 3.13 (1H, dt, *J*=4.4, 10.8 Hz), and 4.12 (2H, br t, *J*=6.8 Hz); ^{13}C NMR ($CDCl_3$) δ=25.66, 27.16 (3C), 27.57 (3C), 31.81, 31.85, 32.24, 35.93, 38.62, 42.67, 47.27, 63.12, 74.61, and 178.49; LRMS *m/z* 285 (M^++H; 96%), 267 (90), 183 (65), 165 (99), 149 (21), 109 (72), 95 (65), and 57 (100); HRMS [Found: *m/z* 285.2398 (M^++H). Calcd for $C_{17}H_{33}O_3$: *M*, 285.2430].

Compound **12b**. An oil; IR (neat) 1730 (C=O) and 3477 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.78–0.88 (1H, m), 0.84 (9H, s), 0.97–1.35 (3H, m), 1.18 (9H, s), 1.41–1.55 (4H, m), 1.59 (1H, dq, *J*=13.8, 6.8 Hz), 1.74 (1H, dq, *J*=13.8, 6.8 Hz), 1.86–1.93 (1H, m), 3.85 (1H, br q-like, *J*=2.5 Hz), and 4.12 (2H, br t, *J*=6.8 Hz); ^{13}C NMR ($CDCl_3$) δ=20.55, 27.22 (3C), 27.39, 27.54 (3C), 31.89, 32.51, 33.85, 38.74, 39.13, 47.85, 62.75, 67.73, and 178.50; LRMS *m/z* 285 (M^++H; 6%), 267 (11), 183 (27), 165 (48), 109 (63), 95 (56), and 57 (100); HRMS [Found: *m/z* 285.2394 (M^++H). Calcd for $C_{17}H_{33}O_3$: *M*, 285.2430].

Compound **12c**. Mp. 41–44°C; IR (CH_2Cl_2) 1726 (C=O) and 3438 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84 (9H, s), 0.99–1.28 (2H, m), 1.20 (9H, s), 1.38–1.80 (7H, m), 1.90–2.07 (2H, m), 3.73 (1H, dt, *J*=12.0, 4.5 Hz), 4.08 (1H, dt, *J*=10.8, 7.1 Hz), and 4.13–4.21 (1H, m); ^{13}C NMR ($CDCl_3$) δ=24.71, 25.67, 27.28 (3C), 27.62 (3C), 29.56, 30.08, 32.10, 36.90, 38.77, 40.46, 63.91, 72.76, and 178.62; LRMS *m/z* 285 (M^++H; 7%), 267 (9), 183 (25), 165 (24), 109 (33), 95 (28), and 57 (100); HRMS [Found: *m/z* 285.2336 (M^++H). Calcd for $C_{17}H_{33}O_3$: *M*, 285.2430].

3.3.4. 2-[(1*RS*,5*SR*)-5-*t*-Butyl-2-oxocyclohex-1-yl]ethyl pivalate (13). According to the same procedure shown in the synthesis of **4**, compound **12** was oxidized by the Swern method. The crude ketone was purified by silica gel (100 g) column chromatography using hexane/AcOEt (98:2 to 90:10) as eluent to give **13** (2.989 g, 87%) as an oil; IR (neat) 1727 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (9H, s), 1.13–1.24 (1H, m), 1.18 (9H, s), 1.44 (1H, dq, *J*=4.7, 12.6 Hz), 1.49 (1H, dq, *J*=13.8, 6.4 Hz), 1.59 (1H, tt, *J*=3.0, 12.2 Hz), 2.07–2.14 (1H, m), 2.14 (1H, dt, *J*=13.8, 3.3 Hz), 2.17 (1H, dq, *J*=13.8, 6.4 Hz), 2.28–2.44 (3H, m), 4.07 (1H, dt, *J*=10.8, 6.4 Hz), and 4.13 (1H, dt, *J*=10.8, 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ=27.18 (3C), 27.62 (3C), 28.37, 28.67, 32.43, 35.14, 38.69, 41.54, 46.63, 47.17, 62.57, 178.51, and 212.48; LRMS *m/z* 283 (M^++H; 5%), 221 (5), 181 (100), 180 (25), 154 (20), 139 (6), 89 (79), and 61 (7); HRMS [Found: *m/z* 283.2258 (M^++H). Calcd for $C_{17}H_{31}O_3$: *M*, 283.2274].

3.3.5. 2-[(1*RS*,2*SR*,5*SR*)-5-*t*-Butyl-2-(*t*-butyldimethylsilyloxymethyl)cyclohex-1-yl]ethyl pivalate (14a) and 2-[(1*RS*,2*RS*,5*SR*)-5-*t*-butyl-2-(*t*-butyldimethylsilyloxymethyl)cyclohex-1-yl]ethyl pivalate (14b). *Wittig*

reaction. To a stirred suspension of methyltriphenylphosphonium bromide (10.64 g, 29.78 mmol) in toluene (60 cm^3) were added *t*-BuOK (3.311 mg, 29.51 mmol) and the mixture was refluxed for 3 h under Ar atmosphere. After being cooled to room temperature, the mixture was filtrated, and the filtrate was added to a solution of **13** (2.098 g, 7.43 mmol) in toluene (20 cm^3). The reaction mixture was stirred at room temperature for 1 h, and then water (100 cm^3) was added. Extraction with AcOEt followed by drying and evaporation of the solvent afforded an oily residue, from which the polar by-product was removed by silica gel (80 g) column chromatography using hexane/Et_2O (199:1 to 97:3) as eluent. The resultant crude oily product (2.055 g) was used in the next hydroboration reaction without purification.

Hydroboration. The above oil (2.055 g) was dissolved in dry THF (10 cm^3) and to this was added 9-BBN with stirring (30.0 cm^3, 15.0 mmol; 0.5 M solution in THF) at 0°C under Ar atmosphere. The stirring was continued for 24 h at room temperature. The reaction mixture was cooled to 0°C, and water (1 cm^3), 6 M NaOH (1.5 cm^3), and 35% H_2O_2 (2.6 cm^3) were added carefully. After the stirring had been continued for 1 h at room temperature, 2 M HCl (5 cm^3) and a saturated aqueous solution of NH_4Cl (20 cm^3) were added. The mixture was extracted with AcOEt, dried, and the solvent was evaporated. The polar by-product was removed by silica gel (60 g) column chromatography using hexane/AcOEt (97:3 to 70:30) as eluent to give crude product of alcohol (3.013 g), however to obtain pure compound was not possible. This was used in the next step without characterization.

t-Butyldimethylsilylation. To a stirred solution of the above residue (3.013 g) in CH_2Cl_2 (20 cm^3) was added Et_3N (3.00 cm^3, 21.3 mmol), DMAP (87.5 mg, 0.716 mmol), and TBDMSCl (3.282 g, 21.78 mmol) at room temperature. After stirring for 19 h, the reaction mixture was diluted with Et_2O (150 cm^3), washed with saturated $NaHCO_3$ aq. and NH_4Cl aq., and dried. Evaporation of the solvent followed by silica gel (50 g) column chromatography using hexane/AcOEt (99:1) as eluent afforded **14** (2.811 g, 92% in three steps from **13**). The following spectral data were collected after partial purification.

Compound **14a**. An oil; IR (neat) 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.03 (6H, s), 0.74 (1H, q, *J*=11.8 Hz), 0.83 (9H, s), 0.88 (9H, s), 0.90–1.01 (2H, m), 1.05–1.17 (2H, m), 1.19 (9H, s), 1.24–1.36 (1H, m), 1.38–1.48 (1H, m), 1.74–1.85 (3H, m), 1.92 (1H, ddt, *J*=3.2, 13.6, 7.6 Hz), 3.50 (1H, dd, *J*=4.8, 10.0 Hz), 3.60 (1H, dd, *J*=2.8, 10.0 Hz), and 4.06–4.13 (2H, m); ^{13}C NMR ($CDCl_3$) δ=−5.37, −5.35, 18.35, 25.99 (3C), 26.93, 27.26 (3C), 27.60 (3C), 30.68, 32.31, 32.46, 33.09, 36.52, 38.71, 44.41, 47.88, 62.82, 65.75, and 178.51; LRMS *m/z* 413 (M^++H; 40%), 355 (25), 311 (100), 179 (33), 159 (33), 123 (41), 109 (35), 95 (14), and 57 (41); HRMS [Found: *m/z* 413.3412 (M^++H). Calcd for $C_{24}H_{49}O_3Si$: *M*, 413.3451].

Compound **14b**. An oil; IR (neat) 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.04 (6H, br s), 0.85–0.92 (1H, m), 0.83 (9H, s), 0.89 (9H, s), 1.00–1.07 (2H, m), 1.19 (9H, s), 1.22–1.32 (1H, m), 1.47–1.56 (3H, m), 1.58–1.76 (2H, m), 1.78–1.85 (1H, m), 1.99 (1H, dq-like, *J*=13, 2.5 Hz), 3.53 (1H, dd, *J*=8.4, 10.0 Hz), 3.66 (1H, dd, *J*=6.0, 10.0 Hz), and 4.06–4.16 (2H, m); ^{13}C NMR ($CDCl_3$) δ=−5.33, −5.26, 18.32, 21.55, 26.01 (3C), 27.27 (3C), 27.55 (3C), 28.59, 29.02, 32.55, 33.25, 37.09, 38.60, 38.75, 48.25, 60.65, 63.26, and 178.51; LRMS *m/z* 413 (M^++H; 48%), 355 (38), 311 (100), 179 (61), 159 (69), 123 (86), 109 (70), 95 (30), and 57 (86); HRMS [Found: *m/z* 413.3535 (M^++H). Calcd for $C_{24}H_{49}O_3Si$: *M*, 413.3451].

3.3.6. 2-[(1*RS*,2*SR*,5*SR*)-5-*t*-Butyl-2-(*t*-butyldimethylsilyloxymethyl)cyclohex-1-yl]ethanol (15a) and 2-[(1*RS*,2*RS*,5*SR*)-5-*t*-butyl-2-(*t*-butyldimethylsilyloxymethyl)-cyclohex-1-yl]ethanol (15b). According to the same procedure described for the synthesis of **5**, compound **14** (2.529 g, 12.03 mmol) was deprotected to **15**. The crude alcohol was purified by silica gel (50 g) column chromatography using hexane/AcOEt (95:5 to 80:20) as eluent. Purification by silica gel column chromatography was repeated until **15a** (1.243 g, 62%) and **15b** (649.2 mg, 32%) were obtained.

Compound **15a**. An oil; IR (neat) 3327 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.04 (6H, s), 0.73–0.86 (1H, m), 0.83 (9H, s), 0.89 (9H, s), 0.92–1.03 (2H, m), 1.06–1.18 (2H, m, $W_{1/2}$=22 Hz), 1.25–1.35 (1H, m), 1.40–1.49 (1H, m), 1.73–1.84 (4H, m), 1.87 (1H, br s), 3.59 (2H, br s), and 3.61–3.76 (2H, m); ^{13}C NMR ($CDCl_3$) δ=−5.41, −5.37, 18.30, 21.62, 25.95 (3C), 27.47 (3C), 28.86, 29.32, 32.47, 37.12, 37.39, 38.57, 48.19, 61.10, and 61.63; LRMS *m/z* 329 (M^++H; 10%), 311 (2), 271 (3), 197 (2), 179 (3), 109 (4), 89 (100), and 61 (10); HRMS [Found: *m/z* 329.2874 (M^++H). Calcd for $C_{19}H_{41}O_2Si$: *M*, 329.2857].

Compound **15b**. An oil; IR (neat) 3328 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.05 (6H, s), 0.83 (9H, s), 0.89 (9H, s), 0.98–1.10 (2H, m), 1.31 (1H, tt, *J*=3.6, 13.3 Hz), 1.40–1.53 (3H, m), 1.61–1.73 (3H, m), 1.74 (1H, br s), 1.85–1.93 (1H, m, $W_{1/2}$=14 Hz), 1.96 (1H, dq, *J*=13.3, 3.0 Hz), 3.53 (1H, dd, *J*=7.6, 10.0 Hz), and 3.65–3.77 (3H, m); ^{13}C NMR ($CDCl_3$) δ=−5.45, −5.43, 18.33, 25.93 (3C), 26.88, 27.53 (3C), 30.80, 32.39, 33.76, 36.40, 36.81, 44.42, 47.80, 61.18, and 66.11; LRMS *m/z* 329 (M^++H; 16%), 311 (1), 271 (2), 197 (3), 179 (9), 123 (8), 109 (7), 89 (100), and 61 (9); HRMS [Found: *m/z* 329.2869 (M^++H). Calcd for $C_{19}H_{41}O_2Si$: *M*, 329.2857].

3.3.7. (1*SR*,2*RS*,4*SR*)-4-*t*-Butyl-2-vinylcyclohexanemethanol (16). To a stirred mixture of **15a** (390.6 mg, 1.189 mmol) and 2-nitrophenylselenocyanate (324.4 mg, 1.427 mmol) in THF (4 cm^3) was added dropwise *n*-Bu_3P (0.35 cm^3, 1.419 mmol) at room temperature under Ar atmosphere and the stirring was continued for 2 h. After evaporation of the solvent, the residue was roughly purified by silica gel (20 g) column chromatography using hexane/Et_2O (100:0 to 97:3) as eluent to give a yellow oil (522.9 mg) containing the nitrophenylselenylated compound as the major component, which was dissolved in THF (10 cm^3) with stirring. To this was added 35% H_2O_2 (3 cm^3) at 0°C and the stirring was continued for 17 h at room temperature. Water (50 cm^3) was added and the mixture was extracted with hexane, and dried. Evaporation of the solvent afforded a residue which contains **16** and its silylated compound. In order to complete the desilylation,

this mixture was dissolved in THF (10 cm^3) to which was added TBAF (801.2 mg, 3.06 mmol) at the room temperature with stirring. After stirring for 3.5 h, the reaction was quenched by the addition of a saturated NH_4Cl aq. followed by extraction with Et_2O and drying. Evaporation of the solvent followed by silica gel (15 g) column chromatography using pentane/Et_2O (95:5 to 60:40) as eluent gave **16** (181.0 mg, 78%) as an oil; IR (neat) 1638 (C=C) and 3337 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85 (9H, s), 0.87–1.12 (4H, m), 1.19–1.31 (1H, m), 1.46 (1H, br s), 1.68 (1H, dq-like, J=3, 13 Hz), 1.77–1.90 (3H, m), 3.43 (1H, dd, J=5.8, 11.0 Hz), 3.62 (1H, dd, J=4.8, 11.0 Hz), 4.97 (1H, dd, J=2.2, 10.2 Hz), 5.05 (1H, dd, J=2.2, 17.2 Hz), and 5.72 (1H, ddd, J=9.5, 10.2, 17.2 Hz); ^{13}C NMR ($CDCl_3$) δ=26.58, 27.49 (3C), 29.46, 32.34, 34.50, 44.19, 46.43, 47.21, 67.14, 114.05, and 143.99; LRMS m/z 197 (M^++H; 77%), 179 (100), 139 (44), 123 (77), 109 (69), 95 (27), 81 (24), and 67 (11); HRMS [Found: m/z 197.1888 (M^++H). Calcd for $C_{13}H_{25}O$: M, 197.1907].

3.3.8. (1*SR*,2*RS*,4*SR*)-4-*t*-Butyl-2-vinylcyclohexane-1-carbaldehyde (17). According to the same procedure described for the synthesis of **4**, compound **16** (102.0 mg, 0.520 mmol) was oxidized by the Swern method. The crude product was purified by silica gel (5 g) column chromatography using hexane/Et_2O (99:1) as eluent to give **17** (100.6 mg, 100%) as an oil; IR (neat) 1651 (C=C), 1728 (C=O), and 2711 (CHO) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (9H, s), 0.89–1.05 (2H, m), 1.09 (1H, tt, J=2.7, 12.0 Hz), 1.27–1.38 (1H, m), 1.79–1.92 (3H, m), 2.05 (1H, tt, J=3.7, 11.8 Hz), 2.24 (1H, ddt, J=3.7, 8.0, 11.8 Hz), 5.00 (1H, dd, J=1.7, 10.1 Hz), 5.03 (1H, br d, J=17.0 Hz), 5.71 (1H, ddd, J=8.0, 10.1, 17.0 Hz), and 9.55 (1H, d, J=3.7 Hz); ^{13}C NMR ($CDCl_3$) δ=25.52, 26.28, 27.41 (3C), 32.38, 33.28, 42.93, 46.88, 54.36, 114.91, 141.28, and 205.35; LRMS (EI) m/z 194 (M^+; 3%), 179 (4), 167 (8), 149 (22), 138 (25), 137 (16), 109 (27), 91 (16), 81 (15), 67 (20), 57 (100), and 55 (18); HRMS [Found: m/z 194.1680 (M^+). Calcd for $C_{13}H_{22}O$; M, 194.1672]; Analysis as semicarbazone (Mp 185–187°C) [Found: C, 67.00; H, 9.80; N, 16.61%. Calcd for $C_{14}H_{25}N_3O$: C, 66.89; H, 10.02; N, 16.72%].

3.3.9. Ethyl (*E*)-3-[(1*SR*,2*RS*,4*SR*)-4-*t*-butyl-2-vinylcyclohex-1-yl]-2-(trimethylsilylmethyl)prop-2-enoate (18). To a stirred suspension of NaH (26.7 mg, 0.612 mmol; 55% in mineral oil which was not removed) in THF (2 cm^3) was added dropwise at 0°C a solution of $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$[20] (293.2 mg, 0.721 mmol) in THF (2 cm^3), and the stirring was continued at 0°C for 30 min. The solution was cooled to −60°C, and to this was added dropwise a solution of **17** (85.0 mg, 0.437 mmol) in THF (2 cm^3). After stirring for 30 min at −60°C, the reaction mixture was allowed to warm slowly to room temperature over 17 h. The reaction was quenched by the addition of a saturated NH_4Cl aq. (20 cm^3), and the mixture was extracted with AcOEt. The combined extract was washed with water and brine, and then dried. Evaporation of the solvent followed by silica gel (8 g) column chromatography using hexane/Et_2O (199:1) as eluent gave **18** (123.5 mg, 81%) as an oil; IR (neat) 1637 (C=C) and 1714 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.04 (9H, s), 0.80–1.13 (5H, m), 0.84 (9H, s), 1.29 (3H, t, J=6.8 Hz), 1.69 (2H, br s), 1.68–1.85 (3H, m), 2.73 (1H, br dq-like, J=4, 10 Hz), 4.15 (2H, q, J=6.8 Hz), 4.86 (1H, dd, J=2.0, 10.4 Hz), 4.92 (1H, dd, J=2.0, 17.2 Hz), 5.40 (1H, d, J=10.0 Hz), and 5.64 (1H, ddd, J=8.2, 10.4, 17.2 Hz); ^{13}C NMR ($CDCl_3$) δ=−1.61 (3C), 14.24, 23.96, 26.46, 27.49 (3C), 32.38, 33.19, 33.68, 42.57, 47.31, 48.64, 59.91, 113.17, 128.15, 143.61, 144.27, and 168.39; LRMS m/z 351 (M^++H; 100%), 335 (32), 305 (6), 293 (3), 212 (25), 211 (13), 185 (5), 147 (3), 94 (6), and 73 (10); HRMS [Found: m/z 351.2710 (M^++H). Calcd for $C_{21}H_{39}O_2Si$: M, 351.2701].

3.3.10. (*E*)-3-[(1*SR*,2*RS*,4*SR*)-4-*t*-Butyl-2-vinylcyclohex-1-yl]-2-(trimethylsilylmethyl)prop-2-en-1-ol (8). According to the same procedure shown in the synthesis of **1a** and **1b**, compound **18** (73.0 mg, 0.208 mmol) was reduced to afford **8** (64.0 mg, 100%); an oil; IR (neat) 1637 (C=C) and 3336 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.01 (9H, s), 0.80–1.27 (5H, m), 0.85 (9H, s), 1.56 (2H, AB), 1.65–1.79 (4H, m), 1.99 (1H, ddt, J=3.8, 11.3, 10.0 Hz), 3.93 (1H, d, J=11.5 Hz), 4.03 (1H, d, J=11.5 Hz), 4.84 (1H, d, J=9.8 Hz), 4.89–4.95 (2H, m), and 5.62 (1H, ddd, J=7.8, 10.2, 17.3 Hz); ^{13}C NMR ($CDCl_3$) δ=−1.33 (3C), 24.69, 26.59, 27.49 (3C), 32.37, 33.23, 34.47, 41.85, 47.18, 47.86, 62.07, 113.48, 131.86, 135.23, and 143.91; LRMS m/z 308 (M^+; 2%), 218 (14), 217 (4), 161 (17), 119 (5), 105 (4), 89 (100), 73 (11), and 61 (10); HRMS [Found: m/z 308.2520 (M^+). Calcd for $C_{19}H_{36}OSi$: M, 308.2517].

3.3.11. (1*E*,6*E*)-9-*t*-Butyl-3-methylenecycloundeca-1,6-diene (19)—homo-Cope reaction of 8. According to the same procedure shown in the synthesis of **7a** and **7b**, compound **8** (14.9 mg, 0.048 mmol) was converted to the eleven-membered carbocycle. The purification of the product was performed by silica gel (1 g) column chromatography using pentane as eluent to afford **19** (7.9 mg, 75%) as an oil; IR (neat) 1603 and 1651 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87–0.95 (1H, m), 0.87 (9H, s), 1.04 (1H, ddt, J=12.1, 14.3, 3.0 Hz), 1.46 (1H, dt, J=12.1, 9.8 Hz), 1.69 (1H, ddt, J=2.5, 9.5, 12.1 Hz), 1.95 (1H, ddt, J=5.5, 14.3, 3.0 Hz), 2.01–2.12 (1H, m), 2.19–2.34 (4H, m), 2.38–2.46 (1H, m), 4.84 (1H, br s), 4.85 (1H, br s), 5.14 (1H, ddd, J=5.5, 9.8, 15.2 Hz), 5.25–5.35 (1H, m), 5.48 (1H, ddd, J=6.5, 9.5, 15.8 Hz), and 5.89 (1H, br d, J=15.8 Hz); ^{13}C NMR ($CDCl_3$) δ=27.21 (3C), 32.25, 32.53, 33.92, 34.36, 34.87, 35.25, 49.22, 112.64, 131.12, 131.20, 132.89, 137.28, and 148.70; LRMS (EI) m/z 218 (M^+; 5%), 175 (2), 161 (7), 147 (4), 133 (7), 119 (17), 105 (22), 91 (33), 80 (39), 57 (97), and 41 (100); HRMS [Found: m/z 218.2026 (M^+). Calcd for $C_{16}H_{26}$: M, 218.2036].

3.4. Synthesis and homo-Cope reaction of 20a

3.4.1. Methyl 2-[(1*SR*,5*SR*)-5-benzyloxy-2-oxocyclohex-1-yl]acetate (22a) and methyl 2-[(1*RS*,5*SR*)-5-benzyloxy-2-oxocyclohex-1-yl]acetate (22b). According to the same procedure described for the synthesis of **10**, compound **21** (4.663 g, 22.83 mmol) was converted to **22** (4.952 g, 78%), which was obtained as a diastereomer mixture. The following spectral data were obtained after partial separation into **22a** and **22b**.

Compound **22a**. An oil; IR (neat) 1712 (C=O) and 1738 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.61 (1H, dt, J=2.3, 13.4 Hz), 1.80 (1H, ddt, J=2.3, 4.4, 13.7 Hz), 2.21 (1H, dd,

J=6.4, 16.8 Hz), 2.26–2.45 (3H, m), 2.74 (1H, dd, *J*=6.8, 16.8 Hz), 2.81 (1H, dt, *J*=6.4, 13.7 Hz), 3.33 (1H, dq, *J*=13.2, 6.4 Hz), 3.68 (3H, s), 3.87 (1H, quint-like, *J*=2.5 Hz), 4.60 (1H, d, *J*=12.0 Hz), 4.67 (1H, d, *J*=12.0 Hz), 7.28–7.33 (1H, m), and 7.34–7.41 (4H, m); ^{13}C NMR ($CDCl_3$) δ=31.08, 33.68, 36.54, 36.84, 41.40, 51.62, 70.17, 71.35, 127.46 (2C), 127.62, 128.41 (2C), 138.36, 172.75, and 210.80; LRMS *m/z* 277 (M^++H; 26%), 245 (18), 227 (17), 197 (9), 181 (14), 169 (20), 155 (13), 137 (20), 119 (7), and 91 (100); HRMS [Found: *m/z* 277.1494 (M^++H). Calcd for $C_{16}H_{21}O_4$: *M*, 277.1440].

Compound **22b**. An oil; IR (neat) 1716 (C=O) and 1738 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.55 (1H, dt, *J*=11.2, 12.8 Hz), 1.69–1.81 (1H, m), 2.19 (1H, dd, *J*=6.0, 16.4 Hz), 2.35–2.44 (4H, m), 2.80 (1H, dd, *J*=7.0, 16.4 Hz), 2.90 (1H, dq, *J*=12.8, 6.6 Hz), 3.68 (3H, s), 3.90 (1H, tt, *J*=4.2, 12.8 Hz), 4.60 (2H, br s), and 7.27–7.39 (5H, m); ^{13}C NMR ($CDCl_3$) δ=31.80, 33.93, 37.78, 38.01, 43.47, 51.72, 70.65, 74.59, 127.50 (2C), 127.69, 128.44 (2C), 138.23, 172.67, and 209.22; LRMS *m/z* 277 (M^++H; 7%), 245 (5), 181 (10), 170 (6), 169 (6), 155 (6), 137 (8), and 91 (100); HRMS [Found: *m/z* 277.1441 (M^++H). Calcd for $C_{16}H_{21}O_4$: *M*, 277.1440].

3.4.2. (1*RS*,2*RS*,4*SR*)-4-Benzyloxy-2-(2-hydroxyethyl)-cyclohexan-1-ol (23a), (1*SR*,2*SR*,4*SR*)-4-benzyloxy-2-(2-hydroxyethyl)cyclohexan-1-ol (23b), and (1*RS*,2*SR*,4*SR*)-4-benzyloxy-2-(2-hydroxyethyl)cyclohexan-1-ol (23c). According to the same procedure described for the synthesis of **11**, compound **22** (3.784 g, 18.91 mmol) was reduced to the diol **23** (3.044 g, 89%). Although the mixture of diastereomer was used in the next reaction, partial purification was made to obtain **23a**–**c**.

Compound **23a**. An oil; IR (CH_2Cl_2) 3330 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20 (1H, ddd, *J*=2.4, 12.4, 14.4 Hz), 1.39 (1H, ddt, *J*=2.4, 4.8, 13.8 Hz), 1.49–1.57 (1H, m), 1.65–1.83 (4H, m), 1.95 (1H, dq, *J*=14.0, 3.2 Hz), 1.99–2.06 (1H, m), 2.76 (2H, br s), 3.29 (1H, dt, *J*=4.8, 10.4 Hz), 3.60–3.67 (2H, m), 3.75 (1H, ddd, *J*=4.1, 5.1, 10.8 Hz), 4.46 (1H, d, *J*=12.0 Hz), 4.52 (1H, d, *J*=12.0 Hz), 7.24–7.29 (1H, m), and 7.31–7.36 (4H, m); ^{13}C NMR ($CDCl_3$) δ=27.91, 29.31, 36.23, 37.69, 38.42, 61.17, 69.67, 72.21, 74.31, 127.25, 127.32 (2C), 128.17 (2C), and 138.75; LRMS *m/z* 251 (M^++H; 36%), 233 (37), 215 (31), 197 (25), 185 (11), 141 (14), 125 (29), 107 (22), and 91 (100); HRMS [Found: *m/z* 251.1634 (M^++H). Calcd for $C_{15}H_{23}O_3$: *M*, 251.1648].

Compound **23b**. Mp. 121.5–124.5°C; IR (CH_2Cl_2) 3261 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.18 (1H, dt, *J*=10.8, 12.8 Hz), 1.26–1.38 (2H, m), 1.39–1.49 (1H, m), 1.55–1.62 (1H, m), 1.70–1.79 (1H, m), 1.98–2.07 (2H, m), 2.08–2.14 (1H, m), 3.30 (1H, dt, *J*=4.2, 9.7 Hz), 3.38 (1H, tt, *J*=4.0, 10.4 Hz), 3.63 (1H, dt, *J*=3.3, 10.4 Hz), 3.69 (2H, br s), 3.80 (1H, ddd, *J*=4.3, 5.0, 10.5 Hz), 4.54 (2H, AB), 7.25–7.30 (1H, m), and 7.31–7.37 (4H, m); ^{13}C NMR ($CDCl_3$) δ=30.26, 32.90, 37.70, 38.05, 42.25, 61.46, 70.24, 74.22, 76.41, 127.43, 127.45 (2C), 128.31 (2C), and 138.63; LRMS *m/z* 251 (M^++H; 9%), 233 (17), 140 (14), 126 (12), 125 (48), 107 (27), and 91 (100); HRMS [Found: *m/z* 251.1551 (M^++H). Calcd for $C_{15}H_{23}O_3$: *M*, 251.1648].

Compound **23c**. An oil; IR (CH_2Cl_2) 3363 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.36–1.80 (7H, m), 1.85–1.94 (2H, m), 3.05 (2H, br s), 3.38 (1H, tt, *J*=4.4, 10.6 Hz), 3.57–3.76 (2H, m), 3.86 (1H, br q-like, *J*=2.5 Hz), 4.57 (2H, AB), and 7.25–7.37 (5H, m); ^{13}C NMR ($CDCl_3$) δ=25.90, 31.10, 32.03, 35.35, 38.00, 59.85, 67.37, 69.75, 77.08, 127.34, 127.46 (2C), 128.26 (2C), and 138.79; LRMS *m/z* 251 (M^++H; 8%), 197 (13), 126 (12), 125 (57), 119 (10), 108 (12), 107 (45), and 91 (100); HRMS [Found: *m/z* 251.1642 (M^++H). Calcd for $C_{15}H_{23}O_3$: *M*, 251.1648].

3.4.3. 2-[(1*RS*,2*RS*,5*SR*)-5-Benzyloxy-2-hydroxycyclohex-1-yl]ethyl pivalate (24a), 2-[(1*SR*,2*SR*,5*SR*)-5-benzyloxy-2-hydroxycyclohex-1-yl]ethyl pivalate (24b), and 2-[(1*SR*,2*RS*,5*SR*)-5-benzyloxy-2-hydroxycyclohex-1-yl]ethyl pivalate (24c). According to the same procedure described for the synthesis of **12**, compound **23** (3.752 g, 13.05 mmol) was pivaloylated to afford **24** (4.722 g, 94%) as the diastereomer mixture. The following spectral data were obtained after partial purification.

Compound **24a**. An oil; IR (neat) 1726 (C=O) and 3440 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.13–1.22 (1H, m), 1.19 (9H, s), 1.39–1.54 (2H, m), 1.59 (1H, br s), 1.66–1.88 (3H, m), 1.97–2.10 (3H, m), 3.31 (1H, dt, *J*=4.8, 10.0 Hz), 3.64 (1H, quint, *J*=3.0 Hz), 4.10–4.21 (2H, m), 4.49 (2H, AB), 7.24–7.30 (1H, m), and 7.31–7.36 (4H, m); ^{13}C NMR ($CDCl_3$) δ=27.13 (3C), 28.17, 29.86, 31.37, 34.13, 36.66, 38.63, 62.79, 69.61, 71.96, 74.08, 127.21 (2C), 127.27, 128.22 (2C), 138.95, and 178.65; LRMS *m/z* 335 (M^++H; 100%), 317 (44), 233 (62), 231 (13), 215 (18), 197 (45), 141 (17), 125 (21), 107 (32), and 91 (31); HRMS [Found: *m/z* 335.2287 (M^++H). Calcd for $C_{20}H_{31}O_4$: *M*, 335.2223].

Compound **24b**. An oil; IR (neat) 1726 (C=O) and 3442 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.04–1.17 (1H, m), 1.20 (9H, s), 1.25–1.45 (3H, m), 1.49–1.60 (1H, m), 1.76 (1H, br s), 1.98–2.19 (4H, m), 3.30 (1H, dt, *J*=4.3, 10.0 Hz), 3.36 (1H, tt, *J*=4.1, 10.8 Hz), 4.13 (1H, dt, *J*=10.8, 7.0 Hz), 4.18 (1H, ddd, *J*=6.2, 7.2, 10.8 Hz), 4.54 (2H, s), 7.25–7.30 (1H, m), and 7.31–7.36 (4H, m); ^{13}C NMR ($CDCl_3$) δ=27.23 (3C), 30.39, 31.55, 33.29, 36.22, 38.72, 40.47, 62.71, 70.19, 73.89, 76.34, 127.40 (3C), 128.29 (2C), 138.62, and 178.50; LRMS *m/z* 335 (M^++H; 12%), 317 (30), 233 (36), 231 (29), 215 (19), 197 (48), 141 (27), 125 (60), 114 (14), 107 (55), and 91 (100); HRMS [Found: *m/z* 335.2207 (M^++H). Calcd for $C_{20}H_{31}O_4$: *M*, 335.2223].

Compound **24c**. An oil; IR (neat) 1726 (C=O) and 3481 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.19 (9H, s), 1.10–1.25 (1H, m), 1.40–1.54 (3H, m), 1.58–1.94 (6H, m), 3.35 (1H, tt, *J*=4.1, 10.8 Hz), 3.83 (1H, br q-like, *J*=2.5 Hz), 4.11–4.15 (2H, m), 4.57 (2H, s), 7.25–7.29 (1H, m), and 7.31–7.36 (4H, m); ^{13}C NMR ($CDCl_3$) δ=25.85, 27.21 (3C), 31.26, 31.34, 32.36, 37.36, 38.74, 62.50, 66.93, 69.71, 76.72, 127.31, 127.39 (2C), 128.24 (2C), 138.81, and 178.45; LRMS *m/z* 335 (M^++H; 37%), 317 (20), 233 (42), 231 (29), 215 (27), 197 (58), 152 (22), 141 (34), 125 (73), 119 (35), 107 (100), and 91 (87); HRMS [Found: *m/z* 335.2147 (M^++H). Calcd for $C_{20}H_{31}O_4$: *M*, 335.2223].

3.4.4. 2-[(1*RS*,5*SR*)-5-Benzyloxy-2-oxocyclohex-1-yl]ethyl pivalate (25a) and 2-[(1*SR*,5*SR*)-5-benzyloxy-2-oxocyclohex-1-yl]ethyl pivalate (25b). According to the same procedure described for the synthesis of **13**, the diastereomer mixture of **24** (4.722 g, 14.12 mmol) was oxidized to a mixture of **25a** and **25b**. The crude product was purified by the repetition of silica gel (100, 40, 20, and 5 g) column chromatography using hexane/AcOEt (95:5 to 80:20) as eluent to give **25a** (3.244 g, 69%) and **25b** (1.037 g, 22%).

Compound **25a**. An oil; IR (neat) 1712 (C=O) and 1726 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.16 (9H, s), 1.48 (1H, dq, *J*=13.5, 7.2 Hz), 1.54 (1H, dt, *J*=2.4, 13.2 Hz), 1.79 (1H, ddt, *J*=2.6, 4.8, 13.8 Hz), 2.18 (1H, dq, *J*=13.5, 7.2 Hz), 2.27 (1H, ddd, *J*=2.5, 4.6, 13.5 Hz), 2.30–2.44 (2H, m), 2.75 (1H, dt, *J*=6.0, 13.5 Hz), 2.91 (1H, dq, *J*=13.0, 6.8 Hz), 3.86 (1H, quint-like, *J*=2.5 Hz), 4.07 (1H, dt, *J*=10.6, 7.0 Hz), 4.13 (1H, dt, *J*=10.6, 7.0 Hz), 4.60 (2H, AB), and 7.27–7.38 (5H, m); ^{13}C NMR ($CDCl_3$) δ=27.14 (3C), 27.92, 31.20, 37.00, 37.45, 38.67, 41.47, 62.25, 70.18, 71.59, 127.28 (2C), 127.58, 128.39 (2C), 138.44, 178.46, and 211.93; LRMS *m*/*z* 333 (M^++H; 9%), 231 (100), 204 (7), 183 (2), 139 (10), 124 (22), 89 (32), and 61 (3); HRMS [Found: *m*/*z* 333.2061 (M^++H). Calcd for $C_{20}H_{29}O_4$: *M*, 333.2067].

Compound **25b**. An oil; IR (neat) 1714 (C=O) and 1722 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (9H, s), 1.48–1.59 (2H, m), 1.70–1.83 (1H, m), 2.19 (1H, dq, *J*=14.0, 6.8 Hz), 2.29–2.49 (5H, m), 3.84 (1H, tt, *J*=4.0, 10.8 Hz), 4.07 (1H, dt, *J*=11.5, 6.8 Hz), 4.12 (1H, dt, *J*=11.5, 6.8 Hz), 4.60 (2H, s), and 7.27–7.38 (5H, m); ^{13}C NMR ($CDCl_3$) δ=27.16 (3C), 28.38, 31.90, 37.92, 38.26, 38.68, 43.88, 62.23, 70.58, 74.67, 127.48 (2C), 127.70, 128.46 (2C), 138.29, 178.43, and 210.39; LRMS (EI) *m*/*z* 230 (M^+−PivOH; 26%), 204 (11), 139 (24), 124 (88), 122 (16), 91 (100), 85 (17), 65 (9), 57 (51), and 55 (10); HRMS [Found: *m*/*z* 230.1307 (M^+−PivOH). Calcd for $C_{15}H_{18}O_2$:*M*, 230.1307].

3.4.5. 2-[(1*RS*,5*SR*)-5-Benzyloxy-2-methylenecyclohex-1-yl]ethyl pivalate (26). To a stirred suspension of Zn powder (2.879 g, 44.04 mmol) and CH_2Br_2 (1.00 cm^3, 14.4 mmol) in THF (25 cm^3) was added dropwise $TiCl_4$ (10.0 cm^3, 10.0 mmol; 1.0 M solution in CH_2Cl_2) over 10 min at −60°C under Ar atmosphere. The mixture was allowed to warm to 5°C, and the stirring was continued for 72 h. The resulting slurry was quickly poured into a solution of **25a** (1.437 g, 4.32 mmol) in CH_2Cl_2 (20 cm^3) at room temperature, and the stirring was continued for 1 h. The reaction was quenched by careful addition of a saturated Na_2CO_3 aq. (50 cm^3), and diluted by water (100 cm^3) and Et_2O (200 cm^3). The mixture was extracted with Et_2O and dried. Evaporation of the solvent followed by silica gel (30 g) column chromatography using hexane/AcOEt (98:2 to 97:3) as eluent gave **26** (1.254 g, 88%) as an oil; IR (neat) 1647 (C=C) and 1728 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.19 (9H, s), 1.58–1.67 (2H, m), 1.68–1.75 (1H, m), 1.79–1.94 (3H, m), 2.12–2.19 (1H, m), 2.29–2.39 (1H, m), 2.55 (1H, br quint-like, *J*=7 Hz), 3.71 (1H, tt, *J*=3.6, 7.2 Hz), 4.02 (1H, dt, *J*=10.8, 6.8 Hz), 4.10 (1H, dt, *J*=10.8, 6.8 Hz), 4.55 (2H, AB), 4.64 (1H, br s), 4.74 (1H, br s), and 7.25–7.36 (5H, m); ^{13}C NMR ($CDCl_3$) δ=27.22 (3C), 30.25, 31.13, 32.87, 36.67, 38.01, 38.71, 62.63, 69.92, 73.07, 107.31, 127.27 (2C), 127.28, 128.22 (2C), 138.87, 149.93, and 178.42; LRMS *m*/*z* 331 (M^++H; 12%), 253 (2), 211 (10), 210 (45), 163 (13), 121 (100), 120 (63), 91 (47), and 79 (5); HRMS [Found: *m*/*z* 331.2278 (M^++H). Calcd for $C_{21}H_{31}O_3$: *M*, 331.2274].

3.4.6. 2-[(1*RS*,2*SR*,5*SR*)-5-Benzyloxy-2-(hydroxymethyl)cyclohex-1-yl]ethyl pivalate (27a) and 2-[(1*RS*,2*RS*,5*SR*)-5-benzyloxy-2-(hydroxymethyl)cyclohex-1-yl]ethyl pivalate (27b). According to the same procedure described for the synthesis of **14**, compound **26** (1.254 g, 3.795 mmol) was treated with 9-BBN. The crude product was purified by silica gel (40 g) column chromatography using hexane/AcOEt (90:10 to 50:50) as eluent to afford **27** (1.203 g, 91%) as the diastereomer mixture. The following spectral data were obtained after partial separation into **27a** and **27b**.

Compound **27a**. An oil; IR (neat) 1726 (C=O) and 3388 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.19 (9H, s), 1.24–1.35 (1H, m), 1.38–1.52 (3H, m), 1.62 (1H, ddt, *J*=5.1, 12.3, 7.4 Hz), 1.68 (1H, ddt, *J*=5.6, 13.2, 3.6 Hz), 1.74–1.82 (1H, m), 1.85–1.93 (1H, m), 1.95–2.02 (1H, m), 2.10–2.19 (1H, m), 3.50–3.59 (3H, m), 4.08 (1H, br), 4.04–4.15 (2H, m), 4.51 (1H, d, *J*=12.0 Hz), 4.57 (1H, d, *J*=12.0 Hz), and 7.24–7.35 (5H, m); ^{13}C NMR ($CDCl_3$) δ=22.45, 27.04, 27.19 (3C), 29.95, 30.97, 34.45, 38.74, 41.60, 63.18, 63.45, 69.96, 73.30, 127.32, 127.39 (2C), 128.22 (2C), 138.72, and 178.73; LRMS *m*/*z* 349 (M^++H; 15%), 241 (32), 229 (11), 155 (15), 139 (100), 121 (77), 103 (23), 91 (94), and 57 (32); HRMS [Found: *m*/*z* 349.2383 (M^++H). Calcd for $C_{21}H_{33}O_4$: *M*, 349.2380].

Compound **27b**. An oil; IR (neat) 1720 (C=O) and 3438 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.19 (9H, s), 1.20–1.30 (1H, m), 1.30–1.38 (1H, m), 1.42–1.52 (2H, m), 1.55–1.69 (2H, m), 1.69 (1H, br s), 1.78–2.03 (4H, m), 3.58 (1H, dd, *J*=6.4, 10.8 Hz), 3.67–3.71 (1H, m), 3.72 (1H, dd, *J*=4.0, 10.8 Hz), 4.06 (1H, dt, *J*=7.2, 11.2 Hz), 4.14 (1H, ddd, *J*=6.4, 7.2, 11.0 Hz), 4.50 (2H, AB), and 7.24–7.35 (5H, m); ^{13}C NMR ($CDCl_3$) δ=23.48, 27.14 (3C), 28.95, 30.11, 31.80, 34.86, 38.65, 43.30, 62.36, 65.37, 69.62, 72.71, 127.26 (3C), 128.23 (2C), 139.08, and 178.70; LRMS *m*/*z* 349 (M^++H; 8%), 247 (9), 229 (8), 211 (9), 155 (11), 140 (12), 139 (52), 121 (76), 91 (100), and 57 (24); HRMS [Found: *m*/*z* 349.2318 (M^++H). Calcd for $C_{21}H_{33}O_4$: *M*, 349.2380].

3.4.7. 2-[(1*RS*,2*SR*,5*SR*)-5-Benzyloxy-2-(*t*-butyldimethylsilyloxymethyl)cyclohex-1-yl]ethyl pivalate (28a) and 2-[(1*RS*,2*RS*,5*SR*)-5-benzyloxy-2-(*t*-butyldimethylsilyloxymethyl)cyclohex-1-yl]ethyl pivalate (28b). According to the same procedure described for the synthesis of **14**, the above alcohol (1.203 g, 3.45 mmol) was converted to **28** (1.530 g, 96%), which was obtained as the diastereomer mixture. The following spectral data were obtained after partial separation into **28a** and **28b**.

Compound **28a**. An oil; IR (neat) 1728 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.03 (6H, s), 0.88 (9H, s), 1.19 (9H, s), 1.23–1.32 (1H, m), 1.35–1.50 (3H, m), 1.56–1.68 (2H, m), 1.70–1.79 (1H, m), 1.85–2.02 (2H, m), 2.11–2.18 (1H, m),

3.47–3.55 (3H, m), 4.05 (1H, dt, *J*=10.8, 7.2 Hz), 4.11 (1H, ddd, *J*=6.0, 7.2, 10.8 Hz), 4.51 (1H, d, *J*=12.0 Hz), 4.54 (1H, d, *J*=12.0 Hz), 7.25–7.28 (1H, m), and 7.30–7.35 (4H, m); ^{13}C NMR ($CDCl_3$) δ=−5.36, −5.34, 18.29, 22.60, 25.95 (3C), 26.91, 27.24 (3C), 30.27, 31.15, 34.50, 38.72, 41.54, 63.24, 63.93, 69.93, 73.46, 127.26, 127.37 (2C), 128.22 (2C), 138.93, and 178.43; LRMS *m/z* 405 (M^+-t-Bu; 7%), 355 (16), 253 (28), 159 (20), 121 (100), 91 (63), and 57 (18); HRMS [Found: *m/z* 405.2378 (M^+-t-Bu). Calcd for $C_{23}H_{37}O_4Si$: *M*, 405.2442].

Compound **28b**. An oil; IR (neat) 1728 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.04 (6H, br s), 0.89 (9H, s), 1.17 (9H, s), 1.20–1.61 (6H, m), 1.78–1.99 (4H, m), 3.51 (1H, dd, *J*=6.4, 10.0 Hz), 3.65 (1H, dd, *J*=4.4, 10.0 Hz), 3.65–3.69 (1H, m), 4.02–4.13 (2H, m), 4.49 (2H, AB), 7.23–7.28 (1H, m), and 7.29–7.35 (4H, m); ^{13}C NMR ($CDCl_3$) δ=−5.45, −5.44, 18.26, 23.65, 25.91 (3C), 27.17 (3C), 29.05, 30.45, 31.90, 34.76, 38.64, 43.35, 62.55, 65.58, 69.52, 72.91, 127.18, 127.23 (2C), 128.21 (2C), 139.25, and 178.62; LRMS *m/z* 405 (M^+-t-Bu; 9%), 361 (14), 355 (10), 331 (12), 253 (14), 211 (11), 159 (16), 121 (100), 91 (96), and 75 (13); HRMS [Found: *m/z* 405.2456 (M^+-t-Bu). Calcd for $C_{23}H_{37}O_4Si$: *M*, 405.2442].

3.4.8. 2-[(1*RS*,2*SR*,5*SR*)-5-Benzyloxy-2-(*t*-butyldimethylsilyloxymethyl)cyclohex-1-yl]ethanol (29a) and 2-[(1*RS*,2*RS*,5*SR*)-5-benzyloxy-2-(*t*-butyldimethylsilyloxymethyl)cyclohex-1-yl]ethanol (29b). According to the same procedure described for the synthesis of **5**, compound **28** (654.6 mg, 1.415 mmol) was deprotected to afford **29** (503.6 mg, 94%) as the diastereomer mixture. The following spectral data were obtained after partial separation into **29a** and **29b**.

Compound **29a**. An oil; IR (neat) 3421 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.05 (6H, br s), 0.89 (9H, s), 1.15–1.49 (4H, m), 1.52–1.62 (2H, m), 1.68–2.03 (4H, m), 2.10–2.18 (1H, m), 3.47–3.73 (5H, m), 4.51 (1H, d, *J*=12.4 Hz), 4.55 (1H, d, *J*=12.4 Hz), and 7.24–7.37 (5H, m); ^{13}C NMR ($CDCl_3$) δ=−5.46, −5.37, 18.23, 22.59, 25.87 (3C), 30.37, 31.14 (2C), 35.61, 41.66, 62.00, 64.18, 69.92, 73.69, 127.37, 127.47 (2C), 128.31 (2C), and 139.00; LRMS *m/z* 379 (M^++H; 17%), 271 (21), 213 (11), 139 (67), 121 (100), and 91 (96); HRMS [Found: *m/z* 379.2682 (M^++H). Calcd for $C_{22}H_{39}O_3Si$: *M*, 379.2650].

Compound **29b**. An oil; IR (neat) 3446 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.06 (6H, s), 0.91 (9H, s), 1.25–1.39 (2H, m), 1.41–1.52 (2H, m), 1.53–1.60 (2H, m), 1.71–1.86 (2H, m), 1.87–1.95 (3H, m), 3.56 (1H, dd, *J*=6.0, 10.0 Hz), 3.59–3.71 (4H, m), 4.47 (1H, d, *J*=12.0 Hz), 4.53 (1H, d, *J*=12.0 Hz), and 7.24–7.39 (5H, m); ^{13}C NMR ($CDCl_3$) δ=−5.43 (2C), 18.30, 23.85, 25.91 (3C), 28.96, 30.53, 35.39, 36.07, 43.36, 60.85, 65.96, 69.64, 73.15, 127.27, 127.36 (2C), 128.27 (2C), and 139.22; LRMS *m/z* 379 (M^++H; 14%), 271 (11), 213 (19), 139 (45), 121 (89), and 91 (100); HRMS [Found: *m/z* 379.2626 (M^++H). Calcd for $C_{22}H_{39}O_3Si$: *M*, 379.2650].

3.4.9. (1*SR*,2*SR*,4*SR*)-4-Benzyloxy-2-vinylcyclohexanemethanol (30a) and (1*RS*,2*SR*,4*SR*)-4-benzyloxy-2-vinylcyclohexanemethanol (30b). According to the same procedure described for the synthesis of **16**, compound **29** (509.1 mg, 1.485 mmol) was converted to **30a** and **30b** (273.6 mg, 83% in three steps from **29**). Two products, **30a** and **30b**, were separated by the repetition of column chromatography.

Compound **30a**. An oil; IR (neat) 1635 (C=C) and 3421 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.23–1.34 (1H, m), 1.41 (1H, ddt, *J*=3.4, 10.0, 12.6 Hz), 1.47 (1H, br s), 1.62 (1H, ddd, *J*=4.3, 10.5, 12.8 Hz), 1.66–1.80 (2H, m), 2.04 (1H, ddt, *J*=2.2, 12.6, 4.1 Hz), 2.07–2.14 (1H, m), 2.74 (1H, dq, *J*=8.8, 4.0 Hz), 3.45 (1H, dd, *J*=6.5, 10.8 Hz), 3.50 (1H, dd, *J*=7.2, 10.8 Hz), 3.62 (1H, tt, *J*=4.0, 10.3 Hz), 4.54 (2H, s), 5.06 (1H, dd, *J*=2.2, 10.3 Hz), 5.12 (1H, ddd, *J*=1.1, 2.2, 16.9 Hz), 5.91 (1H, ddd, *J*=8.8, 10.3, 16.9 Hz), and 7.24–7.36 (5H, m); ^{13}C NMR ($CDCl_3$) δ=22.92, 31.11, 37.06, 40.17, 41.98, 65.16, 69.99, 73.59, 116.14, 127.38, 127.49 (2C), 128.32 (2C), 138.19, and 138.96; LRMS *m/z* 247 (M^++H; 11%), 229 (12), 211 (22), 199 (9), 173 (22), 155 (20), 139 (64), 121 (47), and 91 (100); HRMS [Found: *m/z* 247.1701 (M^++H). Calcd for $C_{16}H_{23}O_2$: *M*, 247.1699].

Compound **30b**. An oil; IR (neat) 1637 (C=C) and 3392 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31–1.58 (4H, m), 1.63 (1H, dq, *J*=12.4, 3.5 Hz), 1.65 (1H, br s), 1.92 (1H, ddt, *J*=2.6, 13.8, 3.4 Hz), 2.03 (1H, d quint, *J*=13.5, 3.0 Hz), 2.29 (1H, ddt, *J*=3.8, 12.6, 9.5 Hz), 3.45 (1H, dd, *J*=5.9, 11.0 Hz), 3.67 (1H, dd, *J*=5.1, 11.0 Hz), 3.72 (1H, quint, *J*=3.0 Hz), 4.51 (2H, AB), 4.99 (1H, dd, *J*=1.8, 10.3 Hz), 5.08 (1H, ddd, *J*=0.7, 1.8, 17.2 Hz), 5.70 (1H, ddd, *J*=9.2, 10.3, 17.2 Hz), and 7.25–7.38 (5H, m); ^{13}C NMR ($CDCl_3$) δ=23.01, 28.94, 36.58, 39.96, 43.92, 66.97, 69.71, 72.36, 114.64, 127.30, 127.34 (2C), 128.28 (2C), 139.14, and 143.15; LRMS *m/z* 247 (M^++H; 65%), 229 (34), 211 (63), 199 (36), 155 (75), 121 (69), 91 (100), and 81 (13); HRMS [Found: *m/z* 247.1693 (M^++H). Calcd for $C_{16}H_{23}O_2$: *M*, 247.1699].

3.4.10. Ethyl (*E*)-3-[(1*RS*,2*SR*,4*SR*)-4-benzyloxy-2-vinylcyclohex-1-yl]-2-(trimethylsilylmethyl)prop-2-enoate (31a) and ethyl (*E*)-3-[(1*SR*,2*SR*,4*SR*)-4-benzyloxy-2-vinylcyclohex-1-yl]-2-(trimethylsilylmethyl)prop-2-enoate (31b). According to the same procedure described for the synthesis of **4**, compound **30a** (119.5 mg, 0.485 mmol) was oxidized by the Swern method. Then, this mixture was converted to the silylated compounds **31a** and **31b** in accordance with the synthesis of **18**. The crude product was purified by the repetition of silica gel (10 g) column chromatography using hexane/Et_2O (100:0 to 97:3) as eluent to give **31a** (58.8 mg, 30%) and **31b** (113.9 mg, 59%).

Compound **31a**. An oil; IR (neat) 1637 (C=C) and 1712 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.03 (9H, s), 1.30 (3H, t, *J*=7.0 Hz), 1.25–1.37 (1H, m), 1.40–1.51 (1H, m), 1.52–1.59 (2H, m), 1.71 (2H, AB), 1.95–2.03 (2H, m), 2.24 (1H, ddt, *J*=3.4, 8.2, 11.8 Hz), 2.80–2.90 (1H, m), 3.73 (1H, quint, *J*=2.6 Hz), 4.16 (2H, q, *J*=7.0 Hz), 4.52 (2H, AB), 4.89 (1H, dd, *J*=1.8, 10.2 Hz), 4.95 (1H, ddd, *J*=0.8, 1.8, 17.1 Hz), 5.49 (1H, d, *J*=10.0 Hz), 5.64 (1H, ddd, *J*=8.2, 10.2, 17.1 Hz), and 7.25–7.39 (5H, m); ^{13}C NMR ($CDCl_3$) δ=−1.62 (3C), 14.20, 23.94, 26.63, 28.84, 35.77, 41.78, 42.19, 59.92, 69.70, 72.46, 113.66, 127.28, 127.33

(2C), 128.15, 128.27 (2C), 139.18, 142.89, 143.85, and 168.36; LRMS *m/z* 401 (M^++H; 100%), 385 (30), 355 (8), 309 (30), 293 (35), 212 (39), 174 (7), 145 (6), 91 (22), and 73 (12); HRMS [Found: *m/z* 401.2491 (M^++H). Calcd for $C_{24}H_{37}O_3Si$: *M*, 401.2493].

Compound **31b**. An oil; IR (neat) 1635 (C=C) and 1712 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.03 (9H, s), 1.30 (3H, t, *J*=7.2 Hz), 1.39–1.56 (2H, m), 1.66–1.79 (2H, m), 1.72 (2H, AB), 1.92–2.00 (2H, m), 2.69 (1H, br dq, *J*=8.2, 5.0 Hz), 3.11 (1H, tt, *J*=5.0, 10.0 Hz), 3.66 (1H, tt, *J*=3.7, 8.7 Hz), 4.18 (2H, q, *J*=7.2 Hz), 4.53 (2H, s), 4.99–5.06 (2H, m), 5.59 (1H, d, *J*=10.0 Hz), 5.88 (1H, ddd, *J*=8.2, 10.5, 17.0 Hz), and 7.24–7.36 (5H, m); ^{13}C NMR ($CDCl_3$) δ=−1.68 (3C), 14.21, 24.30, 26.83, 30.09, 35.62, 39.37, 41.93, 60.14, 69.87, 72.95, 115.72, 127.34, 127.46 (2C), 128.31 (2C), 129.34, 139.07, 139.11, 140.08, and 168.39; LRMS *m/z* 401 (M^++H; 100%), 385 (30), 355 (10), 309 (55), 293 (94), 277 (9), 212 (39), 211 (13), 191 (8), 145 (7), 133 (5), 91 (28), and 73 (15); HRMS [Found: *m/z* 401.2494 (M^++H). Calcd for $C_{24}H_{37}O_3Si$: *M*, 401.2493].

3.4.11. (*E*)-3-[(1*RS*,2*SR*,4*SR*)-4-Benzyloxy-2-vinylcyclohex-1-yl]-2-(trimethylsilylmethyl)prop-2-en-1-ol (20a). According to the same procedure described for the synthesis of **1a** and **1b**, compound **31a** (53.3 mg, 0.133 mmol) was reduced to **20a** (45.8 mg, 96%); an oil; IR (neat) 1637 (C=C) and 3392 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.00 (9H, s), 1.18 (1H, br s), 1.25–1.47 (3H, m), 1.58 (2H, AB), 1.57–1.67 (1H, m), 1.95–2.06 (2H, m), 2.06–2.16 (1H, m), 2.22 (1H, ddt, *J*=3.5, 8.0, 11.5 Hz), 3.75 (1H, quint-like, *J*=3 Hz), 3.95 (1H, d, *J*=11.2 Hz), 4.05 (1H, d, *J*=11.2 Hz), 4.51 (2H, AB), 4.91–4.98 (3H, m), 5.65 (1H, ddd, *J*=8.0, 10.4, 17.2 Hz), and 7.25–7.38 (5H, m); ^{13}C NMR ($CDCl_3$) δ=−1.32 (3C), 24.71, 27.89, 28.94, 35.28, 41.08, 41.59, 62.06, 69.70, 72.37, 113.86, 127.30, 127.34 (2C), 128.28 (2C), 131.55, 135.23, 139.16, and 143.21; LRMS *m/z* 341 (M^+−OH; 11%), 251 (12), 235 (23), 233 (27), 177 (16), 161 (42), 159 (35), 133 (15), 119 (20), 91 (100), and 73 (45); HRMS [Found: *m/z* 341.2262 (M^+−OH). Calcd for $C_{22}H_{33}OSi$: *M*, 341.2282].

3.4.12. (*E*)-3-[(1*SR*,2*SR*,4*SR*)-4-Benzyloxy-2-vinylcyclohex-1-yl]-2-(trimethylsilylmethyl)prop-2-en-1-ol (20b). Similarly, **31b** (38.8 mg, 0.097 mmol) was reduced to **20b** (34.6 mg, 100%); an oil; IR (neat) 1637 (C=C) and 3421 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.01 (9H, s), 1.16 (1H, br s), 1.34–1.43 (1H, m), 1.54–1.64 (1H, m), 1.60 (2H, br s), 1.73 (1H, ddt, *J*=4.0, 7.4, 13.0 Hz), 1.78–1.91 (3H, m), 2.56–2.67 (2H, m), 3.68 (1H, tt, *J*=3.4, 7.2 Hz), 4.04 (2H, br s), 4.53 (2H, s), 4.97–5.03 (2H, m), 5.19 (1H, d, *J*=9.7 Hz), 5.75–5.85 (1H, m), and 7.24–7.37 (5H, m); ^{13}C NMR ($CDCl_3$) δ=−1.32 (3C), 24.89, 27.40, 28.35, 34.20, 37.68, 41.56, 61.72, 69.85, 72.89, 115.02, 127.09, 127.34, 127.43 (2C), 128.31 (2C), 136.49, 139.09, and 140.56; LRMS *m/z* 358 (M^+; 7%), 341 (30), 323 (5), 249 (24), 214 (10), 177 (17), 159 (48), 133 (20), 131 (17), 91 (100), and 73 (44); HRMS [Found: *m/z* 358.2320 (M^+). Calcd for $C_{22}H_{34}O_2Si$: *M*, 358.2309].

3.4.13. (1*E*,6*E*)-9-Benzyloxy-3-methylenecycloundeca-1,6-diene (32)—homo-Cope reaction of 20a. According to the same procedure described for the synthesis of **7**, **20a** (28.0 mg, 0.078 mmol) was treated with trifluoromethanesulfonic anhydride and 2,6-lutidine in CH_2Cl_2. The crude product was purified by silica gel (1 g) column chromatography using pentane/Et_2O (98:2) as eluent to afford **32** (18.5 mg, 88%) as an oil; IR (neat) 1603 (C=C) and 1650 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.68–1.77 (1H, m), 1.94 (1H, ddt, *J*=2.6, 9.9, 12.8 Hz), 2.00–2.18 (3H, m), 2.25–2.34 (2H, m), 2.34–2.46 (2H, m), 2.54 (1H, br dd, *J*=5.5, 12.5 Hz), 3.22 (1H, br t-like, *J*=8 Hz), 4.52 (2H, s), 4.84 (2H, AB), 5.12 (1H, ddd, *J*=5.5, 9.5, 15.6 Hz), 5.35 (1H, ddd, *J*=5.1, 9.9, 16.1 Hz), 5.36–5.46 (1H, m), 5.84 (1H, br d, *J*=16.1 Hz), and 7.25–7.38 (5H, m); ^{13}C NMR ($CDCl_3$) δ=31.52, 32.21, 34.70, 37.19, 39.90, 70.35, 80.40, 113.07, 127.42, 127.49 (2C), 128.35 (2C), 128.65, 131.01, 133.84, 137.07, 138.79, and 148.30; LRMS (EI) *m/z* 177 (M^+−CH_2Ph; 20%), 160 (58), 159 (49), 133 (63), 131 (42), 105 (51), 91 (100), 79 (56), 65 (37), and 55 (19); HRMS [Found: *m/z* 177.1236 (M^+−CH_2Ph). Calcd for $C_{12}H_{17}O$: *M*, 177.1280].

3.5. Synthesis and ene-reaction of 33

3.5.1. (1*RS*,2*RS*)-2-Isopropenylcyclohexane-1-carbaldehyde (35). To a vigorously stirred mixture of Mg (483.1 mg, 20.13 mmol) and dry THF (2 cm^3) was added dropwise 2-bromoprop-2-ene (1.80 cm^3, 21.3 mmol) at 0°C under Ar atmosphere. After the beginning of the formation of the Grignard reagent, the mixture was diluted with THF (18 cm^3), and the stirring was continued for 30 min at room temperature. To a stirred suspension of $CuBrMe_2S$ (754.1 mg, 3.668 mmol) in dry THF (20 cm^3) was added the above Grignard reagent by a syringe at −50°C under Ar atmosphere, and HMPA (7.0 cm^3, 40.2 mmol) was also added. Then to this mixture was added dropwise at the same temperature a solution of **34** (1.475 g, 13.39 mml) in dry THF (10 cm^3) containing TMSCl (3.40 cm^3, 26.8 mmol), and the stirring was continued for 1 h. The mixture was treated with 1 M HCl (40 cm^3) at −50°C, and was allowed to warm to room temperature. This was extracted with Et_2O, the combined organic layer was washed with water, and dried. Evaporation of the solvent followed by silica gel (20 g) column chromatography using pentane/Et_2O (100:0 to 199:1) as eluent afforded *trans*- and *cis*-**35** (984.6 mg, 48%) as an inseparable mixture (*trans*-**35**:*cis*-**35**=3:7). This resultant oil was dissolved in CH_2Cl_2 and to this was added DBU (1.0 cm^3, 6.70 mmol) at room temperature with stirring which was continued for 24 h. Evaporation of the solvent followed by silica gel (20 g) column chromatography using pentane/Et_2O (199:1 to 99:1) as eluent afforded **35** (902.9 mg, 92%) as an oil; IR (neat) 1643 (C=C), 1726 (C=O), and 2710 (CHO) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22–1.39 (4H, m), 1.70 (3H, dd, *J*=0.8, 1.2 Hz), 1.73–1.84 (4H, m), 2.16–2.25 (1H, m), 2.29 (1H, tt, *J*=3.6, 11.2 Hz), 4.72 (1H, br s), 4.74 (1H, quint, *J*=1.2 Hz), and 9.45 (1H, d, *J*=3.6 Hz); ^{13}C NMR ($CDCl_3$) δ=19.97, 24.69, 25.69, 26.22, 31.35, 46.25, 52.74, 111.43, 147.33, and 204.84; LRMS (EI) *m/z* 123 (M^+−CHO; 100%), 109 (54), 95 (34), 81 (85), 67 (63), 55 (42), and 53 (18); HRMS [Found: *m/z* 123.1136 (M^+−CHO). Calcd for C_9H_{15}: *M*, 123.1175]; Analysis as semicarbazone (Mp 161–163°C) [Found: C, 62.91; H, 9.07; N, 19.86%. Calcd for $C_{14}H_{25}N_3O$: C, 63.13; H, 9.15; N, 20.08%].

3.5.2. Ethyl (*E*)-3-[(1*RS*,2*RS*)-2-isopropenylcyclohex-1-yl]-2-(trimethylsilylmethyl)prop-2-enoate (36). According to the same procedure described for the synthesis of **18**, compound **35** (161.0 mg, 1.058 mmol) was converted to the silylated compound **36** (165.1 mg, 51%); an oil; IR (neat) 1643 (C=C) and 1712 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.05 (9H, s), 1.07 (1H, ddt, *J*=3.0, 9.6, 12.1 Hz), 1.19–1.37 (3H, m), 1.30 (3H, t, *J*=7.2 Hz), 1.58 (3H, br s), 1.58–1.83 (5H, m), 1.67 (2H, br s), 2.98 (1H, ddt, *J*=3.6, 10.8, 9.8 Hz), 4.17 (2H, q, *J*=7.2 Hz), 4.60 (1H, br s), 4.65 (1H, d, *J*=2.0 Hz), and 5.39 (1H, d, *J*=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ=−1.68 (3C), 14.24, 18.82, 23.95, 25.87, 26.29, 31.87, 33.09, 40.74, 52.62, 59.89, 110.49, 127.54, 144.03, 149.28, and 168.42; LRMS *m/z* 309 (M^++H; 100%), 293 (80), 263 (11), 226 (57), 225 (5), 190 (6), 161 (6), 135 (3), 108 (10), and 73 (14); HRMS [Found: *m/z* 309.2231 (M^++H). Calcd for $C_{18}H_{33}O_2Si$: *M*, 309.2231].

3.5.3. (*E*)-3-[(1*RS*,2*RS*)-2-Isopropenylcyclohex-1-yl]-2-(trimethylsilylmethyl)prop-2-en-1-ol (33). According to the same procedure described for the synthesis of **1a** and **1b**, compound **36** (161.0 mg, 0.522 mmol) was reduced to **33** (134.2 mg, 97%); an oil; IR (neat) 1643 (C=C) and 3344 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.02 (9H, s), 1.06–1.18 (1H, m), 1.21–1.34 (3H, m), 1.54 (2H, br s), 1.61 (3H, br s), 1.57–1.79 (6H, m), 2.22 (1H, ddt, *J*=3.6, 10.0, 10.4 Hz), 3.96 (1H, d, *J*=11.3 Hz), 4.05 (1H, d, *J*=11.3 Hz), 4.65–4.68 (2H, m), and 4.85 (1H, d, *J*=10.0 Hz); ^{13}C NMR ($CDCl_3$) δ=−1.37 (3C), 20.31, 24.51, 25.98, 26.27, 32.15, 34.67, 40.48, 51.92, 61.99, 110.12, 131.94, 134.48, and 150.10; LRMS *m/z* 267 (M^++H; 6%), 249 (100), 248 (10), 176 (21), 161 (23), 133 (15), 93 (12), and 73 (32); HRMS [Found: *m/z* 267.2130 (M^++H). Calcd for $C_{16}H_{31}OSi$: *M*, 267.2125].

3.5.4. (2*Z*,5*E*)-2-Methyl-5-(trimethylsilylmethyl)bicyclo[5.4.0]nona-2,5-diene (37). Compound **33** (29.6 mg, 0.111 mmol) was treated with trifluoromethanesulfonic anhydride and 2,6-lutidine in CH_2Cl_2 as the case of the synthesis of **7a** and **7b**. The crude product was purified by silica gel (5 g) column chromatography using pentane as eluent to afford **37** (17.0 mg, 62%); an oil; IR (neat) 1641 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.00 (9H, s), 1.04–1.33 (3H, m), 1.46 (1H, d, *J*=13.3 Hz), 1.51 (1H, d, *J*=13.3 Hz), 1.63 (3H, br s), 1.68–1.78 (4H, m), 1.91–2.01 (2H, m), 2.12–2.22 (1H, m), 2.38 (1H, dd, *J*=7.4, 16.0 Hz), 2.77 (1H, br d, *J*=16.0 Hz), 4.85 (1H, dd, *J*=1.0, 4.8 Hz), and 5.54 (1H, m); ^{13}C NMR ($CDCl_3$) δ=−1.42, 22.89, 26.38, 26.69, 30.36, 30.82, 32.22, 34.60, 40.46, 44.82, 122.97, 127.21, 139.57, and 140.30; LRMS *m/z* 248 (M^+; 34%), 233 (17), 174 (7), 161 (9), 147 (9), 134 (5), 105 (7), 91 (7), 74 (10), and 73 (100); HRMS [Found: *m/z* 248.1875 (M^+). Calcd for $C_{16}H_{28}Si$: *M*, 248.1941].

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