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Synthesis of spiro[4.5]decane and bicyclo[4.3.0]nonane ring systems by self-cyclization of (*Z*)- and (*E*)-2-(trimethylsilylmethyl)pentadienal derivative

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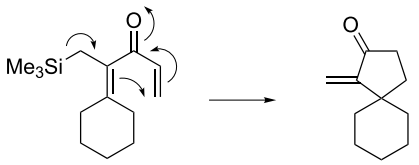
Abstract—The two title carbon frameworks were synthesized utilizing a new type of iron-induced cyclization reaction of 2-(trimethylsilylmethyl)pentadienal. 2-Methylspiro[4.5]dec-2-en-1-one was obtained from (*Z*)- and (*E*)-4-cyclohexylidene-2-(trimethylsilylmethyl)but-2-enal. It was found that the (*Z*)-substrate isomerized to (*E*)-intermediate followed by cyclization to afford the initial product, 2-methylenespiro[4.5]dec-3-en-1-ol, which was isomerized to the above product. The cyclization of 4-(4-alkyl)cyclohexylidene-2-(trimethylsilylmethyl)but-2-enal proceeded stereoselectively. While, (*E*)-3-(cyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-en-1-al cyclized immediately affording 8-methylenebicyclo[4.3.0]non-9-en-7-ol. The corresponding (*Z*)-isomer gave several cyclization products as a complex mixture.

1. Introduction

α-(Trialkylsilylmethyl)-α,β-unsaturated carbonyl is a unique building block in organic synthesis since the β-carbon reacts as an allylsilane[1] but not as an unsaturated carbonyl, and therefore, this moiety acts as a carbon 1,3-dipole based on the nucleophilicity of the β-carbon and the electrophilicity of the carbonyl carbon.[2] By using this unit, various five-membered compounds were synthesized.[3,4] For example, we obtained γ-lactones by the reaction with aldehyde[5] or ketone.[6] Cyclopentane ring was also synthesized by the reaction with an enone.[7] Nishitani et al. prepared γ- and δ-lactones by the reaction with either an aldehyde[8] or an epoxide,[9] respectively.

Further conjugation of C=C double bond to this moiety enables self-cyclization to form a five-membered ring compound, and therefore, the reaction is not expected to be a simple extension. There are two ways for further conjugation, namely on the C=C side or on the carbonyl side, leading to β-(trialkylmethyl)-α,β,γ,δ-unsaturated carbonyl or α-(trialkylmethyl)divinyl ketone, respectively. We previously reported the synthesis of spiro[4.5]decane **2** by Lewis acid promoted Nazarov cyclization of α-(trimethylsilylmethyl)divinyl ketone **1**,[10] in which the reaction was activated by an allylic trimethylsilyl group. The formal reaction mechanism from **1** to **2** is illustrated in Scheme 1. Related silicon directed Nazarov cyclization is well documented by Denmark et al.[11]



1 **2**

Scheme 1.

In contrast to the classic Nazarov cyclization of cross-conjugated divinyl ketone, linearly conjugated α,β,γ,δ-unsaturated carbonyl compounds, such as penta-2,4-dienal, are not suitable substrates for the Nazarov or related type of self-cyclization, since the δ-carbon is too electron deficient to react with the carbonyl group. We envisioned that the α,β,γ,δ-unsaturated carbonyl can also cyclize with itself if this moiety is substituted by a trimethylsilylmethyl group at β-position. Namely, by the presence of this substituent, the δ-carbon of **3** becomes nucleophilic, as a part of allylsilane, which is expected to react with the carbonyl to form the five-membered ring compound **4** (Scheme 2, Eq. A). However, in our previous study, ethyl 2-(trimethylsilylmethyl)penta-2,4-dienoate **5** or -dienoic acid **6** (R^1=R^2=CH_3, R^1,R^2=$(CH_2)_4$) did not cyclize in this way but produced

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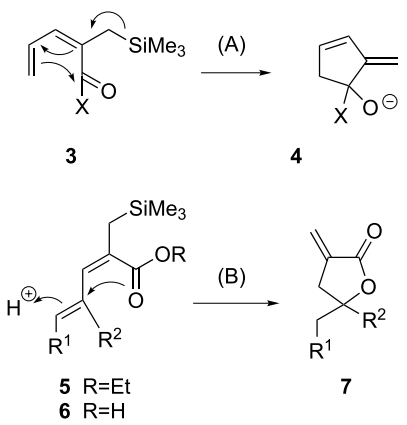


Scheme 2.

γ-lactone **7** via a protonic acid treatment (Eq. B).[12] This is probably due to the low reactivity of the ester group. Thus, we planned to use an aldehyde instead of an ester in order to obtain a five-membered carbocycle via the reaction mode shown in Eq. A.

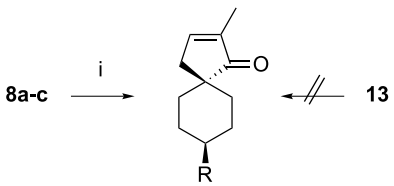
To compare this new type of cyclization with the Nazarov cyclization of our previous report, we first chose the spiro[4.5]decane ring as the synthetic target. Spiro[4.5]-decane is one of the basic ring systems in natural sesquiterpenes such as acoranes or vetispiranes.[13,14] Here we report the synthesis of the spiro[4.5]decane ring system by a new spiro-cyclopentannulation using the cyclization of linearly conjugated pentadienal.[15] Synthesis of bicyclo[4.3.0]nonane ring system by the same method is also described.

2. Results and discussion

2.1. Synthesis of spiro[4.5]decane ring system

As the initial study, compound **8a** was designed as the cyclization precursor. The substrate was synthesized as shown in Scheme 3. Namely, to 2-cyclohexylideneacetaldehyde (**9a**), prepared from cyclohexanone by Horner–Emmons reaction followed by DIBAL-H reduction and MnO_2 oxidation, a β-(ethoxycarbonyl)allylsilane unit was introduced by using Hoffman's reagent[4] $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$ giving **10a** in a 51% yield. The geometry of the double bond in **10a** was determined to be *Z* based on the chemical shift of the olefinic proton (see Section 4). The DIBAL-H reduction of **10a** afforded **11a** in a 92% yield, which was subsequently oxidized by MnO_2 giving substrate **8a** (89%).

The cyclization of **8a** was carried out by the same procedure reported for the Nazarov cyclization.[10] Namely, **8a** was treated with ca. 2 equiv. of $FeCl_3$ in CH_2Cl_2 at −60 °C followed by slow warming to room temperature over 7 h. As a result, a spiro[4.5]decane compound was obtained but this was not the expected dienol but enone **12a** (78% yield, Scheme 4). Some other Lewis acids, such as $AlCl_3$, Et_2AlCl and BF_3OEt_2 were also used but without success.



Scheme 4. *Reagents and conditions*: (i) $FeCl_3$, CH_2Cl_2, −60 °C to rt.

The stereochemistry of the cyclization reaction was then studied using the substrates **8b** and **8c**, which were prepared analogously from 4-*t*-butyl- and 4-methylclohexanone, respectively, in accordance to Scheme 3. When **8b** was treated under the same reaction conditions, spiro[4.5]decanone **12b** was obtained as a single diastereomer in 80% yield (Scheme 4). The stereostructure of **12b** was determined from the NOE signal observed between allylic methylene and the axial protons on the cyclohexane ring as shown in Figure 1. Similarly, **8c** afforded **12c** in a 70% yield, which was again obtained as a single diastereomer, and its structure was determined independently in the same way (Fig. 1).

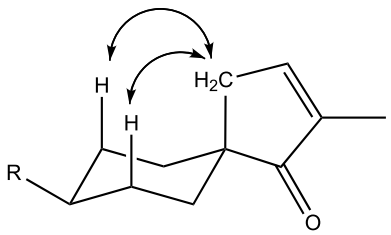
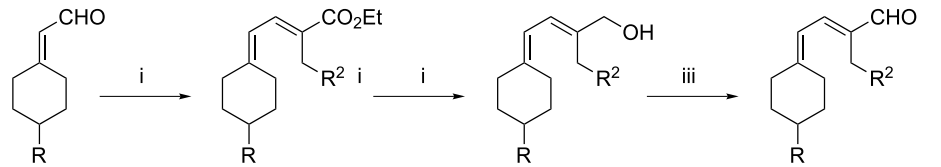
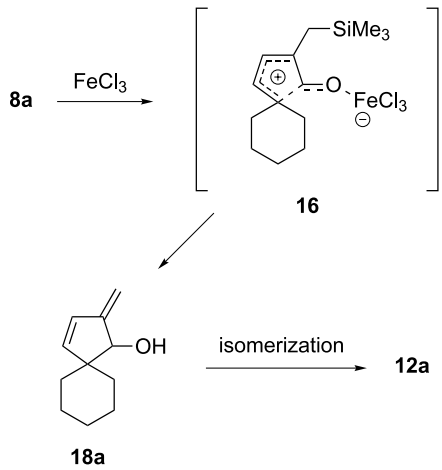


Figure 1.



Scheme 3. *Reagents and conditions*: (i) for **10a–c**: $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME, rt; for **14**: $(EtO)_2P(O)CH(CO_2Et)CH_3$, NaH, DME, rt; (ii) DIBAL-H, CH_2Cl_2, −60 °C; (iii) MnO_2, CH_2Cl_2, rt.

To demonstrate whether the reaction proceeds via a silicon-stabilized carbocation as the intermediate, the desilylated substrate **13** was prepared (Scheme 3). Under the same reaction conditions described above, **13** did not afford any cyclization product, as expected, but was recovered without reaction (Scheme 4). From this result, it is obvious that the cyclization from **8a** to **12a** proceeds via the silicon-stabilized carbocation **16** as the intermediate (Scheme 5). Since the two reaction sites in **8a** are too far apart to react (cf. two sites are close for its (*E*)-isomer **17a**), it is easily expected that **8a** could cyclize after isomerization to (*E*)-intermediate (vide infra) by the aid of Lewis acid. The related isomerization from (*Z*)-β-carbonylallylsilane to its (*E*)-isomer was also observed previously in the reaction of α-(trimethylsilylmethyl)-α,β,γ,δ-unsaturated carboxylic acid.[12] From **16**, the initial cyclization product via the expected mode should be dienol **18a** (see also Scheme 1). Although, the reaction mechanism cannot be specified at this stage, isomerization from **18a** to the enone **12a** is considered to be a plausible pathway.



Scheme 5.

Recently, we established a new method to prepare (*E*)-β-(ethoxycarbonyl)allylsilanes from aldehydes via the Ando-HWE (Horner–Wadsworth–Emmons) reaction.[16] In order to clarify the above reaction mechanism, we prepared the (*E*)-substrate **17a** by this method (Scheme 6). Namely, **19a** was synthesized from **9a** by using $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$ giving a mixture of both the (*E*)-isomer **19a** and the (*Z*)-isomer **10a** in an 89% yield (**19a/10a**=9:1). DIBAL-H reduction (**20a**, 86%) followed by MnO_2 oxidation afforded **17a** in a 71% yield after separation from its (*Z*)-isomer.

The result of the cyclization reaction of **17a** is listed in Table 1 and Scheme 7. As expected, the reaction was much faster than in the case of **8a**. When **17a** was treated with $FeCl_3$ in CH_2Cl_2 at 0 °C, the reaction proceeded within 20 min and β,γ-unsaturated enone **21a** was afforded instead of the conjugated compound **12a** (Entries 1,2) Interestingly, when the reaction was carried out at −60 °C, the originally expected dienol **18a** was obtained in good yield (Entry 4).

Table 1. Cyclization of **17a**[a]

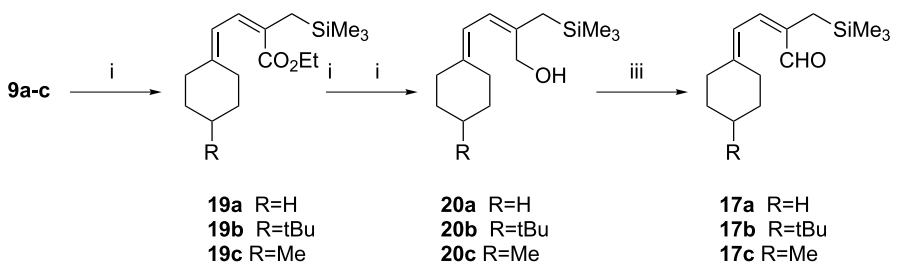
Entry	$FeCl_3$ (equiv.)	Temp (°C)	Product	Yield (%)
1	1	0	**21a**	41
2	Excess[b]	0	**21a**	83
3	1	−60	**18a**	34
4	Excess[b]	−60	**18a**	78

[a] All reactions were carried out in CH_2Cl_2 for 20 min under Ar atmosphere.
[b] About 10 equiv.

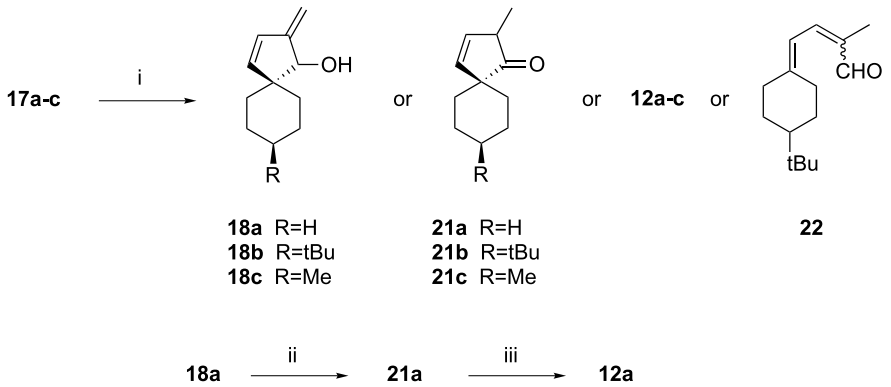
From these results, it could be considered that the initial cyclization product from **17a** or **8a** is **18a**, the originally expected product. Also, it is very likely that **21a** is the isomerization product at higher temperature, and in addition, that **12a** is the final isomerization product with a longer reaction time. To demonstrate this, **18a** was treated with the same reagent except that the reaction was carried out at 0 °C for 20 min to afford **21a** in 97% yield. Similarly, when **21a** was treated under the same reaction condition as for **8a** (−60 °C to room temperature, 2 days), **12a** was obtained in an 87% yield. These results clearly indicate that the cyclization of **8a** or **17a** proceeded via the intermediates **18a** and **21a**.

Cyclization of the substituted compounds **17b** and **17c** were also studied and the results are shown in Table 2. From **17b**, the initial cyclization product **18b** could not be isolated when the reaction was carried out at −60 °C. Under this condition, the desilylated product **22** (a mixture of *E*- and *Z*-isomers) was detected together with **21b** (Entry 3). The isomerization reaction of **21b** was also carried out under the same reaction conditions as Entry 4 affording **12b** in a 71% yield. The results of the cyclization of **17c** (Entries 5–7) were almost consistent with those of **17b**, except that **18c** was obtained in a low yield at −60 °C and a lack of experimental reproducibility (Entry 6). These results indicate that dienols **18b**,**c** are not stable enough for handling.

The stereoselectivity of the cyclization reaction from **17b** or **17c** (so as **8b** and **8c**) can be rationalized by a preferential equatorial attack to the exocyclic double bond (Scheme 8).[17]



Scheme 6. *Reagents and conditions*: (i) $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, THF, rt; (ii) DIBAL-H, CH_2Cl_2, −60 °C; (iii) MnO_2, CH_2Cl_2, rt.



Scheme 7. *Reagents and conditions*: (i) see Table 1; (ii) $FeCl_3$, CH_2Cl_2, 0 °C; (iii) $FeCl_3$, CH_2Cl_2, −60 °C to rt.

Table 2. Cyclization of **17b** and **17c**[a]

Entry	Substrate	Temp (°C)	Time	Product	Yield (%)
1	**17b**	0	20 min	**21b**	93
2	**17b**	−15	20 min	**21b**	89
3	**17b**	−60	20 min	**21b**, **22**	Not determined
4	**17b**	−60 to rt	2 days	**12b**	81
5	**17c**	0	20 min	**21c**	74
6	**17c**	−60	20 min	**18c**	18[b]
7	**17c**	−60 to rt	2 days	**12c**	64

[a] All reactions were carried out in CH_2Cl_2 under Ar atmosphere with about 4 equiv. of $FeCl_3$.
[b] The result was not reproducible.

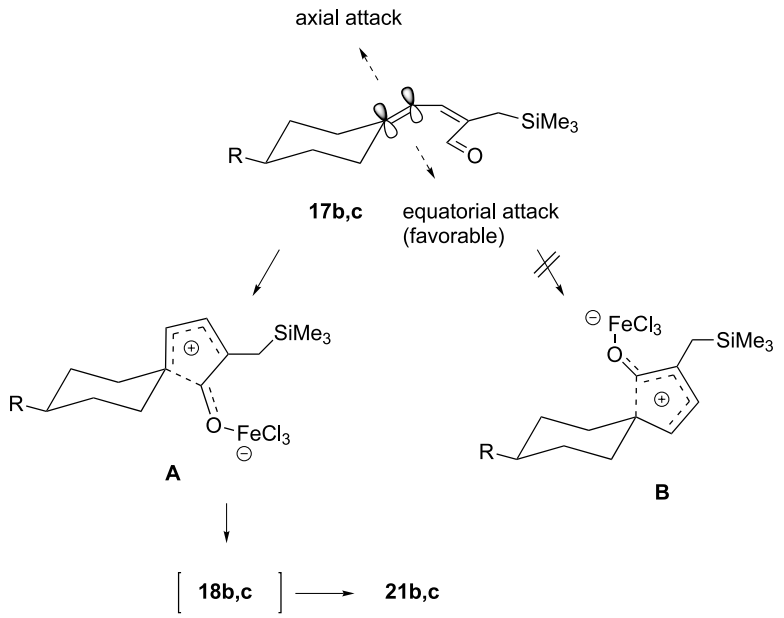
Namely, transition state **B** is less favorable than **A** since the carbonyl oxygen, together with bulky Lewis acid, comes over the cyclohexane ring. From the transition state **A**, **21b**,**c** is considered to be obtained via **18b**,**c**. It is interesting that this stereoselectivity was much higher than the related Nazarov cyclization.[10]

2.2. Synthesis of bicyclo[4.3.0]nonane ring system

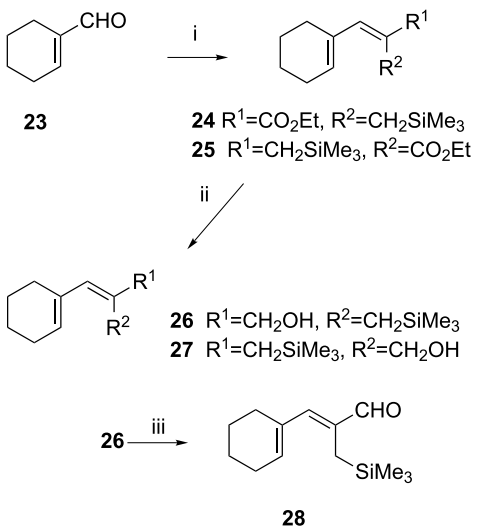
Following the success of the synthesis of the spiro[4.5]-decane carbon skeleton, we next focused on the use of this method to synthesize the hydrindane, or bicyclo[4.3.0]-nonane, carbon framework from cyclohexane derivatives. Hydrindane is one of the key structures in various terpenoid,[13,14] which also appears as the CD rings of steroids.

The cyclization of both (*Z*)- and (*E*)-allylsilanes were studied. The substrates were synthesized in accordance to Scheme 9. Namely, to the α,β-unsaturated aldehyde **23** was introduced the β-(ethoxycarbonyl)allylsilane moiety by treatment with $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$/NaH in DME to afford **24** and **25** in a 61% yield (**24**/**25**=6:1). Reduction of the ester group with DIBAL-H yielded alcohols **26** and **27** after separation by column chromatography. The (*Z*)-isomer **26** was oxidized by MnO_2 to afford **28** in a 92% yield. When $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$ was used as the Horner–Wadsworth–Emmons reagent, **25** was obtained preferentially (*E*/*Z*=97:3, 95% yield). The alcohol **27** was then obtained by DIBAL-H reduction followed by purification.

In contrast to the oxidation of **26**, when **27** was subjected to



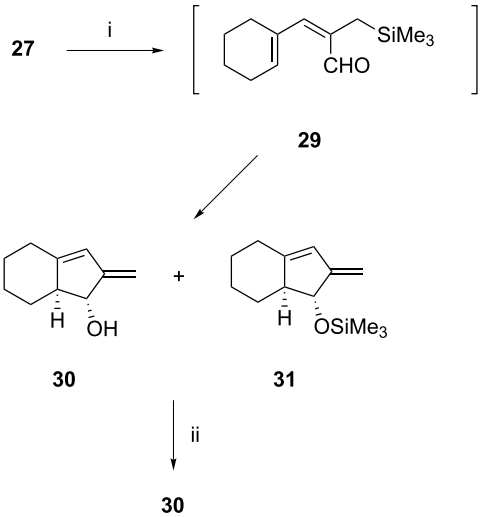
Scheme 8.



Scheme 9. *Reagents and conditions*: (i) for **24**: $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME, rt; for **25**: $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, THF, rt; (ii) DIBAL-H, CH_2Cl_2, −60 °C; (iii) MnO_2, CH_2Cl_2, rt.

MnO_2 oxidation, the corresponding aldehyde **29** was not obtained but the cyclization product **30** (20%) was afforded together with its trimethylsilyl ether **31** (63%) (Scheme 10). However, the yields of the two products varied, and in some case, only **30** was afforded in good yield (93%). Since **31** was too volatile to isolate, the reaction mixture was treated with Bu_4NF giving **30** effectively without being accompanied by **31**. The formation of the aldehyde **29** could not be detected on a TLC, which indicates that the oxidation product was immediately cyclized. The stereochemistry of **30** was determined from the ^1H NMR spectrum including NOE which was observed between the proton attached to the hydroxy-bearing carbon (7-H) and one of the axial protons on the cyclohexane ring (5-H) as shown in Figure 2.

The stereoselective formation of **30** can easily be explained by the *s-trans* conformation of the enone moiety in the precursor enal **29** (Scheme 11). Although both the *s-trans* conformer **C** and the *s-cis* conformer **D** are possible with



Scheme 10. *Reagents and conditions*: (i) MnO_2, CH_2Cl_2, rt, (ii) Bu_4NF, Et_2O, rt.

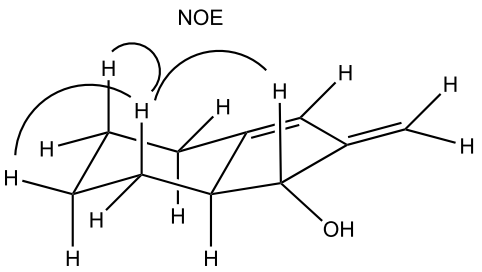
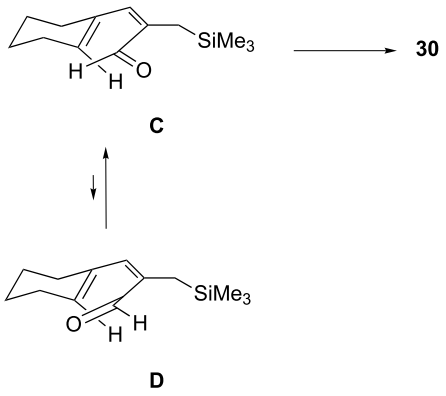


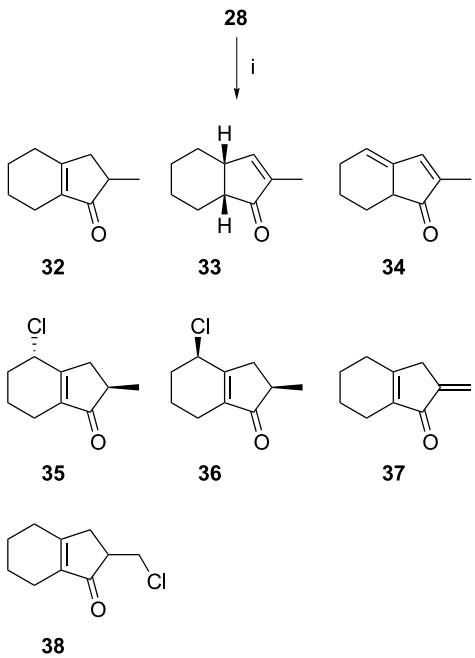
Figure 2.



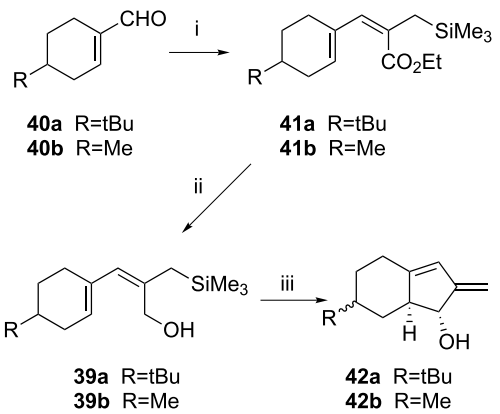
Scheme 11.

respect to the enone moiety, conformer **C** is favorable over **D**, since the carbonyl oxygen takes on a congested position in **D**.

The cyclization of **28** was also studied by the treatment with ca. 1.5 equiv. of $FeCl_3$ in CH_2Cl_2 at room temperature. The reaction proceeded slowly, and after for 4 days, many products were detected on a TLC. This complex mixture of the products was roughly separated by silica-gel column chromatography, and five compounds **32**–**36** could be



Scheme 12. *Reagents and conditions*: (i) $FeCl_3$, CH_2Cl_2, rt.



Scheme 13. *Reagents and conditions*: (i) $(PhO)_2P(O)CH(CO_2Et)CH_2$-$SiMe_3$, NaH, THF, rt; (ii) DIBAL-H, CH_2Cl_2, −60 °C; (iii) (a) MnO_2, CH_2Cl_2, rt; (b) SiO_2, Et_2O, rt; (c) Bu_4NF, Et_2O, rt.

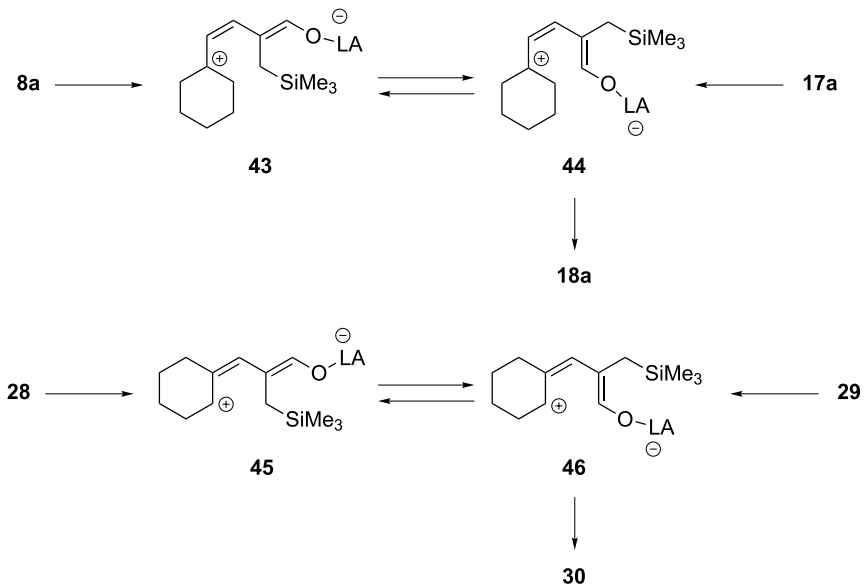
identified from the ^1H NMR and mass spectra (Scheme 12), among which **32** was found to be the major product (ca. 36% yield). The other compounds include isomeric enone **33**, dienone **34**, and two chlorides **35** and **36**. The structure of these products was determined by ^1H and ^{13}C NMR and mass spectra. The stereochemistry of two chlorides **35** and **36** were established by NOE experiment. Namely, NOE was observed between C*H*Cl (2-H) and 9β-H for **35**; between C*H*Cl and 9α-H for **36**. The *cis*-fused structure for **33** was deduced from *J*-value of methine proton (6-H). Compound **34** is considered to be formed from **33** by further oxidation caused by $FeCl_3$.[11b] Two chlorides must be chlorination products from **32**. When the reaction was carried out with ca. 4 equiv. of $FeCl_3$, the two oxidized products **37** and **38** were also found in the mixture. Some other Lewis acids such as Et_2AlCl, $AlCl_3$, and $TiCl_4$ were tested instead of $FeCl_3$ but none of them gave us satisfactory results.

The substituent effect for the cyclization of (*E*)-isomer was examined. The cyclization precursor, alcohols **39a** and **39b**, were prepared in same way (Scheme 13). The MnO_2 promoted cyclization of **39a** and **39b** proceeded slower than the case of **27**, and the reaction completed after stirring with silica gel to afford **42a** (94%) and **42b** (94%), respectively, after treatment with Bu_4NF. In contrast to the synthesis of spiro[4.5]decane ring, no stereoselectivity was observed. Namely, both dienols **42a** and **42b** were obtained in 1:1 mixture of diastereomers.

As mentioned above, a remarkable difference in reactivity based on the geometry of 2-(trimethylsilylmethyl)pentadienal was observed for the case of (*Z*)-isomer **28** and (*E*)-isomer **29**. While in contrast, the same spiro[4.5]decane ring compounds **12a**–**c** were obtained from both (*Z*)-isomers **8a**–**c** and (*E*)-isomers **17a**–**c**. This difference can be rationalized by an easier isomerization from **8** to (*E*)-intermediate (i.e., **43**–**44**) than from **28** (i.e., **45**–**46**) in the presence of Lewis acid (Scheme 14). Namely, the intermediate carbocation is tertiary for **43** (and **44**) and secondary for **45** (and **46**). Since **18** and **21**, the products from **17** at lower temperature, were not obtained from **8**, it can be predicted that *Z*/*E* isomerization requires more energy than the cyclization.

3. Conclusion

A new cyclization reaction of linearly conjugated pentadienal assisted by allylic trimethylsilyl group was established. Both spiro[4.5]decane and bicyclo[4.3.0]nonane carbon frameworks were synthesized by this method. In the synthesis of spiro[4.5]decane, it was found that (1) both (*Z*)- and (*E*)-precursors afford the same product enone in good yields under appropriate conditions, (2) the reaction proceeds via a silicon-stabilized carbocation as the intermediate to afford the initial product dienol, (3) isomerization reaction occurs from dienol to conjugated enone, and (4) the cyclization reaction is stereoselective. While, a remarkable difference in reactivity based on (*Z*)- or (*E*)-precursor was observed for the synthesis of bicyclo[4.3.0]-nonane. Therefore, (*E*)-precursor is required for the



Scheme 14. LA=Lewis acid.

cyclization of 4,5-disubstituted-2-(trimethylsilylmethyl)-pentadienal, while geometry of the functionalized allylsilane is not an important factor for the cyclization reaction of 5,5-disubstituted derivative.

4. Experimental

4.1. General procedure

Melting points were measured on a Laboratory Devices Mel-Temp apparatus. 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, unless otherwise noted. The signal of the solvent ($CDCl_3$=77.0) was used as a standard for all ^{13}C NMR spectra. Both low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a Jeol SX-102A, JMS-DX303, CMATE II, or Shimadzu GCMS-QP5050 mass spectrometer with the EI method unless otherwise noted. Analytical TLC was done on precoated TLC plates (Kieselgel 60 F254, layer thickness 0.2 mm). Wakogel C-200 or C-300 was used for column chromatography. Anhydrous Na_2SO_4 or $MgSO_4$ was used for drying the extracted organic layers.

4.2. (*Z*)-Selective HWE reaction

To a stirred suspension of NaH (1018 mg, 23.3 mmol; 55% in mineral oil which was removed by washing with dry hexane) in dry DME (80 cm^3; distilled from CaH_2) was added $(EtO)_2P(O)CH_2CO_2Et$ (4.2 cm^3, 21.2 mmol) dropwise at 0 °C under Ar. After being stirred for 40 min, iodomethyltrimethylsilane (3.6 cm^3, 24.3 mmol) was added, and the mixture was heated to 70 °C for 4 h. The flask was cooled to 0 °C again, and a second portion of NaH (960 mg, 22.0 mmol; mineral oil was not removed) was added. After being stirred at 0 °C for 2 h, a solution of 2-cyclohexylideneacetaldehyde (1.648 g, 13.3 mmol) in DME (28 cm^3) was added, and the mixture was stirred at room temperature for 14 h. An aqueous solution of NH_4Cl was added, and the resulting aqueous mixture was extracted with Et_2O, and dried. Evaporation of the solvent followed by silica gel (80 g) column chromatography using hexane/AcOEt (99.5:0.5) as eluent afforded **10a** (1.891 g, 51%). Similarly, **10b** and **10c** were obtained in 35 and 58% yields, respectively. For the preparation of **14**, methyl iodide was used instead of iodomethyltrimethylsilane (32% yield). See Ref. [12] for the synthesis and the spectral data of **24**.

4.2.1. (*Z*)-Ethyl 4-cyclohexylidene-2-(trimethylsilylmethyl)but-2-enoate (10a). An oil; IR (neat) 1702 (C=O), 1630, 1258, 851, and 754 cm^{-1}; ^{1}H NMR δ=−0.01 (9H, s, $SiMe_3$), 1.30 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.54–1.62 (6H, m, $(CH_2)_3$), 1.93 (2H, br s, CH_2SiMe_3), 2.19–2.24 (2H, m, C=CCH_2), 2.36–2.41 (2H, m, C=CCH_2), 4.19 (2H, q, *J*=7.1 Hz, OCH_2CH_3), 5.94 (1H, br d, *J*=11.9 Hz, C_{ring}=CH), and 7.40 (1H, d, *J*=11.9 Hz, C*H*=CCO_2Et); ^{13}C NMR δ=−1.06 (3C), 14.36, 17.32, 26.70, 27.99, 28.80, 29.72, 38.19, 60.39, 118.68, 127.54, 130.33, 150.66, and 169.06; MS *m*/*z* 280 (M^+, 34%), 265 (18), 235 (11), 162 (32), 133 (40), 91 (54), and 73 (100); HRMS [Found: *m*/*z* 280.1907 (M^+). Calcd for $C_{16}H_{28}O_2Si$: M, 280.1859].

4.2.2. (*Z*)-Ethyl 4-(4-*t*-butylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-enoate (10b). An oil; IR (neat) 1704 (C=O), 1633, 1365, 1250, 852, and 755 cm^{-1}; ^{1}H NMR δ=0.00 (9H, s, $SiMe_3$), 0.85 (9H, s, *t*Bu), 0.99–1.28 (3H, m), 1.30 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.80–1.98 (3H, m), 1.93 (2H, br s, CH_2SiMe_3), 2.12–2.21 (1H, m), 2.31–2.38 (1H, m), 2.96–3.01 (1H, m), 4.19 (2H, q, *J*=7.1 Hz, OCH_2CH_3), 5.93 (1H, br d, *J*=10.8 Hz, C_{ring}=CH), and 7.40 (1H, d, *J*=10.8 Hz, C*H*=CCO_2Et); ^{13}C NMR δ=−1.05 (3C), 14.36, 17.32, 27.59 (3C), 28.63, 29.43, 29.48, 32.46, 38.01, 48.27, 60.38, 118.33, 127.52, 130.42, 150.67, and 169.05; MS *m*/*z* 336 (M^+, 100%), 205 (7), 189 (89), and 107 (15); HRMS [Found: *m*/*z* 336.2438 (M^+). Calcd for $C_{20}H_{36}O_2Si$: M, 336.2486].

4.2.3. (*Z*)-Ethyl 4-(4-methylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-enoate (10c). An oil; IR (neat) 1704 (C=O), 1632, 1260, and 852 cm^{-1}; ^{1}H NMR δ=−0.01 (9H, s, $SiMe_3$), 0.91 (3H, d, *J*=6.5 Hz, Me), 0.95–1.11 (2H, m), 1.30 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.54–1.66 (1H, m), 1.77–1.97 (3H, m), 1.93 (2H, br s, CH_2SiMe_3), 2.14–2.33 (2H, m), 2.85–2.92 (1H, m), 4.19 (2H, q, *J*=7.1 Hz, OCH_2CH_3), 5.95 (1H, br d, *J*=10.8 Hz, C_{ring}=CH), and 7.40 (1H, d, *J*=10.8 Hz, C*H*=CCO_2Et); ^{13}C NMR δ=−1.06 (3C), 14.36, 17.32, 21.81, 28.92, 32.70, 35.99, 36.81, 37.48, 60.38, 118.77, 127.58, 130.41, 150.24, and 169.05; MS *m*/*z* 294 (M^+, 100%), 279 (7), 237 (7), 147 (97), 143 (91), and 75 (98); HRMS [Found: *m*/*z* 294.1990 (M^+). Calcd for $C_{17}H_{30}O_2Si$: M, 294.2016].

4.2.4. (*E*)-Ethyl 4-cyclohexylidene-2-methylbut-2-enoate (14). An oil; IR (neat) 1704 (C=O), 1635, 1447, 1256, 1112, and 752 cm^{-1}; ^{1}H NMR (Me_4Si=0.00) δ=1.31 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.55–1.68 (6H, m, $(CH_2)_3$), 1.93 (3H, d, *J*=2.1 Hz, C=CCH_3), 2.20–2.27 (2H, m, C=CCH_2), 2.37–2.43 (2H, m, C=CCH_2), 4.21 (2H, q, *J*=7.1 Hz, OCH_2CH_3), 6.07 (1H, br d, *J*=11.8 Hz, C_{ring}=CH), and 7.51 (1H, dq, *J*=11.8, 1.3 Hz, C*H*=CCO_2Et); ^{13}C NMR δ=12.31, 14.37, 26.64, 27.93, 28.67, 29.72, 38.16, 60.38, 117.97, 124.67, 133.59, 152.39, and 169.07; MS *m*/*z* 208 (M^+, 88%), 196 (100), 182 (93), 150 (90), 137 (100), 96 (99), and 68 (99); HRMS [Found: *m*/*z* 208.1427 (M^+). Calcd for $C_{13}H_{20}O_2$: M, 208.1464].

4.3. (*E*)-Selective HWE reaction

To a stirred suspension of NaH (242 mg, 5.57 mmol; 55% in mineral oil) in dry THF (20 cm^3; distilled from $LiAlH_4$) was added a solution of $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$ (1.98 g, 4.87 mmol) in THF (15 cm^3) dropwise at 0 °C under Ar. After being stirred for 30 min, the mixture was cooled to −60 °C, and a solution of 2-cyclohexylideneacetaldehyde (446.1 mg, 3.59 mmol) in THF (20 cm^3) was added. The stirring was continued at −60 °C for 4 h, then the mixture was allowed to warm to room temperature followed by stirring at room temperature for 12 h. An aqueous solution of NH_4Cl was added, and the resulting aqueous mixture was extracted with AcOEt, and dried. Evaporation of the solvent followed by silica gel (40 g)

column chromatography using hexane/AcOEt (97:3) as eluent afforded a mixture of **19a** and **10a** (1007.6 mg, 51%, **19a/10a**=9:1). Similarly, **19b**, **19c**, **41a**, and **41b** were obtained in 62, 88, 97, and 96% yields, respectively. These compounds were obtained together with a small amount of corresponding (*Z*)-isomer (ca. 1–10%) which were removed at later stage. See Ref. 16 for the synthesis of **25**.

4.3.1. (*E*)-Ethyl 4-cyclohexylidene-2-(trimethylsilylmethyl)but-2-enoate (19a). An oil; IR (neat) 1703 (C=O), 1630, 1198, 1159, and 852 cm^{-1}; ^1H NMR δ=0.00 (9H, s, $SiMe_3$), 1.32 (3H, t, *J*=7.2 Hz, OCH_2CH_3), 1.54–1.62 (6H, m, $(CH_2)_3$), 1.82 (2H, s, CH_2SiMe_3), 2.18–2.23 (2H, m, $C{=}CCH_2$), 2.29–2.34 (2H, m, $C{=}CCH_2$), 4.20 (2H, q, *J*=7.2 Hz, OCH_2CH_3), 6.51 (1H, d, *J*=12.0 Hz, $CH{=}CCO_2Et$), and 6.77 (1H, br d, *J*=12.0 Hz, $C_{ring}{=}CH$); ^{13}C NMR δ=−1.61 (3C), 14.30, 24.66, 26.77, 27.82, 28.51, 28.91, 37.97, 60.09, 119.28, 126.30, 132.29, 148.42, and 168.30; MS *m*/*z* 280 (M^+, 36%), 265 (16), 235 (16), 162 (51), 133 (55), 91 (68), and 73 (100); HRMS [Found: *m*/*z* 280.1948 (M^+). Calcd for $C_{16}H_{28}O_2Si$: M, 280.1859].

4.3.2. (*E*)-Ethyl 4-(4-*t*-butylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-enoate (19b). An oil; IR (neat) 1703 (C=O), 1631, 1365, 1178, 852, and 756 cm^{-1}; ^1H NMR δ=0.01 (9H, s, $SiMe_3$), 0.85 (9H, s, *t*Bu), 0.98–1.34 (3H, m), 1.32 (3H, t, *J*=7.2 Hz, OCH_2CH_3), 1.75–1.94 (5H, m), 2.09–2.18 (1H, m), 2.32–2.39 (1H, m), 2.85–2.92 (1H, m), 4.20 (2H, q, *J*=7.2 Hz, OCH_2CH_3), 6.51 (1H, d, *J*=11.6 Hz, $CH{=}CCO_2Et$), and 6.77 (1H, br d, *J*=11.6 Hz, $C_{ring}{=}CH$); ^{13}C NMR δ=−1.60 (3C), 14.31, 24.65, 27.59 (3C), 28.45, 28.69, 29.10, 32.47, 37.79, 48.32, 60.10, 118.96, 126.32, 132.38, 148.40, and 168.29; MS *m*/*z* 336 (M^+, 33%), 321 (15), 237 (21), 169 (29), 119 (45), and 73 (100); HRMS [Found: *m*/*z* 336.2441 (M^+). Calcd for $C_{20}H_{36}O_2Si$: M, 336.2486].

4.3.3. (*E*)-Ethyl 4-(4-methylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-enoate (19c). An oil; IR (neat) 1693 (C=O), 1628, 1190, and 852 cm^{-1}; ^1H NMR δ=0.00 (9H, s, $SiMe_3$), 0.90 (3H, d, *J*=6.5 Hz, Me), 0.95–1.14 (2H, m), 1.32 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.50–1.94 (6H, m), 2.11–2.21 (1H, m), 2.26–2.33 (1H, m), 2.75–2.83 (1H, m), 4.20 (2H, q, *J*=7.1 Hz, OCH_2CH_3), 6.51 (1H, d, *J*=10.8 Hz, $CH{=}CCO_2Et$), and 6.78 (1H, br d, *J*=10.8 Hz, $C_{ring}{=}CH$); ^{13}C NMR δ=−1.61 (3C), 14.11, 24.68, 28.14, 31.58, 32.77, 35.90, 36.59, 37.27, 60.08, 119.42, 126.41, 132.36, 147.93, and 168.29; MS *m*/*z* 294 (M^+, 3%), 279 (1), 237 (3), 176 (9), 147 (12), 119 (18), and 73 (100); HRMS [Found: *m*/*z* 294.2011 (M^+). Calcd for $C_{17}H_{30}O_2Si$: M, 294.2016].

4.3.4. (*E*)-Ethyl 3-(cyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-enoate (25). An oil; IR (neat) 1722 (C=O), 1626, 1373, 1219, and 850 cm^{-1}; ^1H NMR δ=0.02 (9H, s, $SiMe_3$), 1.28 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.51–1.62 (4H, m), 1.72 (2H, br s, CH_2SiMe_3), 2.01–2.11 (4H, m), 4.15 (2H, q, *J*=7.1 Hz, OCH_2CH_3), 5.60–5.64 (1H, m, $C{=}CHCH_2$), and 5.82 (1H, br s, $CH{=}CCO_2Et$); ^{13}C NMR δ=−1.60 (3C), 14.08, 21.98, 22.68, 25.65, 25.76, 26.89, 60.33, 128.50, 128.62, 133.61, 135.23, and 171.00; MS *m*/*z* 266 (M^+, 2%), 251 (1), 237 (2), 221 (3), 148 (18), 119 (17), 91 (19), and 73 (100); HRMS (CI) [Found: *m*/*z* 267.1758 (M^++H). Calcd for $C_{15}H_{27}O_2Si$: M, 267.1780].

4.3.5. (*E*)-Ethyl 3-(4-*t*-butylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-enoate (41a). An oil; IR (neat) 1722 (C=O), 1632, 1365, 1248, 1088, and 854 cm^{-1}; ^1H NMR δ=0.03 (9H, s, $SiMe_3$), 0.85 (9H, s, *t*-Bu), 1.05–1.17 (1H, m), 1.22–1.32 (1H, m), 1.29 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.69 (1H, d, *J*=13.8 Hz, $CHHSiMe_3$), 1.76 (1H, d, *J*=13.8 Hz, $CHHSiMe_3$), 1.77–1.92 (2H, m), 2.02–2.17 (3H, m), 4.14 (1H, dq, *J*=11.0, 7.1 Hz, $OCHHCH_3$), 4.19 (1H, dq, *J*=11.0, 7.1 Hz, $OCHHCH_3$), 5.63–5.68 (1H, m, $C{=}CHCH_2$), and 5.85 (1H, br s, $CH{=}CCO_2Et$); ^{13}C NMR δ=−1.56 (3C), 14.12, 24.10, 25.73, 27.11 (3C), 27.49, 28.19, 32.15, 43.67, 60.37, 128.48, 129.42, 133.23, 135.05, and 171.00; MS *m*/*z* 322 (M^+, 3%), 307 (1), 277 (2), 204 (16), 175 (9), 147 (12), 119 (15), and 73 (100); HRMS (CI) [Found: *m*/*z* 323.2341 (M^++H). Calcd for $C_{19}H_{35}O_2Si$: M, 323.2406].

4.3.6. (*E*)-Ethyl 3-(4-methylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-enoate (41b). An oil; IR (neat) 1720 (C=O), 1624, 1248, 1219, and 852 cm^{-1}; ^1H NMR δ=0.03 (9H, s, $SiMe_3$), 0.94 (3H, d, *J*=6.3 Hz, Me), 1.18 (1H, ddt, *J*=5.2, 12.4, 10.8 Hz), 1.28 (3H, t, *J*=7.2 Hz, OCH_2CH_3), 1.58–1.74 (3H, m), 1.70 (1H, d, *J*=13.6 Hz, $CHHSiMe_3$), 1.74 (1H, d, *J*=13.6 Hz, $CHHSiMe_3$), 1.99–2.20 (3H, m), 4.13 (1H, dq, *J*=10.7, 7.2 Hz, $OCHHCH_3$), 4.16 (1H, dq, *J*=10.7, 7.2 Hz, $OCHHCH_3$), 5.57–5.61 (1H, m, $C{=}CHCH_2$), and 5.83 (1H, br s, $CH{=}CCO_2Et$); ^{13}C NMR δ=−1.57 (3C), 14.11, 21.75, 25.68, 26.88, 28.01, 30.99, 34.39, 60.34, 128.17, 128.75, 133.31, 134.86, and 171.01; MS *m*/*z* 280 (M^+, 2%), 235 (2), 162 (14), 133 (18), 91 (18), and 73 (100); HRMS (CI) [Found: *m*/*z* 281.1985 (M^++H). Calcd for $C_{16}H_{29}O_2Si$: M, 281.1937].

4.4. DIBAL-H reduction

In a 50 cm^3 two-necked flask was placed a solution of **10a** (152.6 mg, 554.1 mmol) in dry CH_2Cl_2 (12 cm^3; distilled from CaH_2) with stirring under Ar. To this was added DIBAL-H (1.63 cm^3, 1.63 mmol; 1 M solution in hexane) at −60 °C, and the stirring was continued for 30 min at the same temperature. MeOH (2 cm^3) was added, and the flask was quickly warmed to room temperature. After being stirred for 30 min, a saturated aqueous solution of Rochelle salt (30 cm^3) was added, and the mixture was extracted with CH_2Cl_2 and dried. Evaporation of the solvent followed by silica gel (1 g) column chromatography using hexane/AcOEt (96:4) as eluent afforded **11a** (120.1 mg, 93%). Similarly, **10b**, **10c**, **14**, **19a**, **24**, **25**, **41a**, and **41b** afforded **11b**, **11c**, **15**, **20a**, **26**, **27**, **39a**, and **39b** in 96, 91, 74, 86, 91, 98, 82, and 81% yields, respectively.

Compounds **19b** and **19c** were reduced by $LiAlH_4$ in Et_2O giving **20b** and **20c** in 99 and 92% yields, respectively.

4.4.1. (*Z*)-4-Cyclohexylidene-2-(trimethylsilylmethyl)-but-2-en-1-ol (11a). An oil; IR (neat) 3320 (OH), 1608, 1447, 1248, 852, and 691 cm^{-1}; ^1H NMR δ=0.04 (9H, s, $SiMe_3$), 1.49–1.58 (7H, m, $(CH_2)_3$ and OH), 1.71 (2H, br s, CH_2SiMe_3), 2.13–2.18 (2H, m, $C{=}CCH_2$), 2.24–2.30 (2H, m, $C{=}CCH_2$), 4.03 (2H, br s, CH_2OH), 5.83 (1H, br d,

J=11.2 Hz, C_{ring}=CH), and 6.20 (1H, br d, J=11.2 Hz, C*H*=CCH_2OH); ^{13}C NMR δ=−0.71 (3C), 19.40, 26.87, 27.80, 28.79, 29.15, 37.77, 68.95, 118.01, 118.17, 137.25, and 142.24; MS m/z 238 (M^+, 9%), 193 (4), 148 (34), 133 (22), 105 (83), and 73 (199); HRMS [Found: m/z 238.1791 (M^+). Calcd for $C_{14}H_{26}OSi$: M, 238.1754].

4.4.2. (*Z*)-4-(4-*t*-Butylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-en-1-ol (11b). An oil; IR (neat) 3310 (OH), 1609, 1364, 1248, and 839 cm^{-1}; ^1H NMR δ=0.04 (9H, s, $SiMe_3$), 0.85 (9H, s, *t*Bu), 0.95–1.91 (7H, m), 1.71 (2H, br s, CH_2SiMe_3), 2.05–2.15 (1H, m), 2.24–2.31 (1H, m), 2.82–2.88 (1H, m), 4.03 (2H, br s, CH_2OH), 5.83 (1H, br d, J=11.2 Hz, C_{ring}=CH), and 6.20 (1H, br d, J=11.2 Hz, C*H*=CCH_2OH); ^{13}C NMR δ=−0.70 (3C), 19.40, 27.62 (3C), 28.43, 28.93, 29.39, 32.46, 37.60, 48.42, 68.95, 117.82, 118.09, 137.28, and 142.25; MS m/z 294 (M^+, 42%), 275 (66), 247 (100), 213 (98), 198 (75), 116 (61), and 86 (80); HRMS [Found: m/z 294.2338 (M^+). Calcd for $C_{18}H_{34}OSi$: M, 294.2380].

4.4.3. (*Z*)-4-(4-Methylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-en-1-ol (11c). An oil; IR (neat) 3310 (OH), 1608, 1456, 1248, and 839 cm^{-1}; ^1H NMR δ=0.03 (9H, s, $SiMe_3$), 0.99 (3H, d, J=6.5 Hz, Me), 0.82–1.88 (7H, m), 1.70 (2H, br s, CH_2SiMe_3), 2.07–2.26 (2H, m), 2.70–2.79 (1H, m), 4.02 (2H, br s, CH_2OH), 5.84 (1H, br d, J=11.2 Hz, C_{ring}=CH), and 6.20 (1H, br d, J=11.2 Hz, C*H*=CCH_2-OH); ^{13}C NMR δ=−0.71 (3C), 19.40, 22.00, 28.37, 32.84, 35.91, 36.90, 37.06, 68.93, 118.09, 118.29, 137.33, and 141.78; MS m/z 252 (M^+, 86%), 193 (84), 147 (96), 135 (87), 121 (100), and 77 (97); HRMS [Found: m/z 252.1893 (M^+). Calcd for $C_{15}H_{28}OSi$: M, 252.1910].

4.4.4. (*E*)-4-Cyclohexylidene-2-methylbut-2-en-1-ol (15). Mp 38.5–40.5 °C; IR (Nujol) 3340 (OH), 1008, and 861 cm^{-1}; ^1H NMR (Me_4Si=0.00) δ=1.00–1.75 (7H, m, $(CH_2)_3$ and OH), 1.79 (3H, s, C=CCH_3), 2.15–2.21 (2H, m, C=CCH_2), 2.26–2.32 (2H, m, C=CCH_2), 4.08 (2H, s, CH_2OH), 5.97 (1H, br d, J=11.4 Hz, C_{ring}=CH), and 6.30 (1H, d sext, J=11.4, 1.2 Hz, C*H*=CCH_2OH); ^{13}C NMR δ=13.96, 26.81, 27.77, 28.68, 29.13, 37.71, 69.22, 117.29, 120.78, 134.51, and 143.93; MS m/z 166 (M^+, 6%), 165 (M^+−H, 44), 148 (73), 121 (13), 105 (35), and 43 (100); HRMS [Found: m/z 166.1322 (M^+). Calcd for $C_{11}H_{18}O$: M, 166.1358].

4.4.5. (*E*)-4-Cyclohexylidene-2-(trimethylsilylmethyl)-but-2-en-1-ol (20a). An oil; IR (neat) 3390 (OH), 1624, 1448, 1248, and 852 cm^{-1}; ^1H NMR δ=0.03 (9H, s, $SiMe_3$), 1.50–1.58 (7H, m, $(CH_2)_3$ and OH), 1.68 (2H, s, CH_2SiMe_3), 2.11–2.17 (2H, m, C=CCH_2), 2.23–2.28 (2H, m, C=CCH_2), 4.19 (2H, br s, CH_2OH), and 6.01 (2H, br s, C=CH–CH=C); ^{13}C NMR δ=−1.32 (3C), 26.00, 26.83, 27.68, 28.56, 28.88, 37.60, 61.85, 116.95, 121.67, 136.46, and 141.68; MS m/z 238 (M^+, 4%), 148 (27), 133 (23), 105 (92), and 73 (199); HRMS [Found: m/z 238.1715 (M^+). Calcd for $C_{14}H_{26}OSi$: M, 238.1754].

4.4.6. (*E*)-4-(4-*t*-Butylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-en-1-ol (20b). An oil; IR (neat) 3360 (OH), 1604, 1365, 1248, and 850 cm^{-1}; ^1H NMR δ=0.03 (9H, s, $SiMe_3$), 0.85 (9H, s, *t*Bu), 0.97–1.92 (7H, m), 1.69 (2H, br s, CH_2SiMe_3), 2.05–2.15 (1H, m), 2.24–2.31 (1H, m), 2.78–2.85 (1H, m), 4.18 (1H, d, J=12.0 Hz, C*H*OH), 4.21 (1H, d, J=12.0 Hz, CH*H*OH), and 6.01 (2H, s, CH=CH); ^{13}C NMR δ=−1.31 (3C), 26.04, 27.61 (3C), 28.32, 28.69, 29.14, 32.48, 37.45, 48.40, 61.91, 116.62, 121.78, 136.48, and 141.69; MS m/z 294 (M^+, 4%), 276 (20), 204 (21), 105 (42), 73 (100), and 57 (100); HRMS [Found: m/z 294.2336 (M^+). Calcd for $C_{18}H_{34}OSi$: M, 294.2380].

4.4.7. (*E*)-4-(4-Methylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-en-1-ol (20c). An oil; IR (neat) 3320 (OH), 1604, 1454, 1246, 1011, and 849 cm^{-1}; ^1H NMR δ=0.03 (9H, s, $SiMe_3$), 0.85–1.88 (7H, m), 0.90 (3H, d, J=6.6 Hz, Me), 1.68 (2H, br s, CH_2SiMe_3), 2.06–2.26 (2H, m), 2.68–2.77 (1H, m), 4.18 (1H, d, J=11.9 Hz, C*H*OH), 4.20 (1H, d, J=11.9 Hz, CH*H*OH), and 6.01 (2H, s, CH=CH); ^{13}C NMR δ=−1.32 (3C), 21.99, 26.04, 28.13, 32.81, 35.81, 36.68, 36.92, 61.90, 117.06, 121.79, 136.53, and 141.26; MS m/z 252 (M^+, 2%), 162 (23), 147 (14), 105 (94), 91 (53), and 57 (100); HRMS [Found: m/z 252.1918 (M^+). Calcd for $C_{15}H_{28}OSi$: M, 252.1910].

4.4.8. (*Z*)-3-(Cyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-en-1-ol (26). An oil; IR (neat) 3320 (OH), 1689, 1643, 1437, 1248, 1028, and 852 cm^{-1}; ^1H NMR δ=0.04 (9H, s, $SiMe_3$), 1.53–1.68 (5H, m), 1.84 (2H, br s, CH_2SiMe_3), 2.05–2.13 (4H, m), 3.98 (2H, br s, CH_2OH), 5.60–5.64 (1H, m, C=C*H*CH_2), and 5.71 (1H, br s, C*H*=CCH_2OH); ^{13}C NMR δ=−0.57 (3C), 19.76, 22.20, 22.96, 25.58, 29.37, 69.49, 125.44, 126.09, 128.97, and 135.13; MS m/z 224 (M^+, 1%), 134 (12), 119 (44), 105 (57), 91 (100), and 73 (100); HRMS [Found: m/z 224.1590 (M^+). Calcd for $C_{13}H_{24}OSi$: M, 224.1597].

4.4.9. (*E*)-3-(Cyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-en-1-ol (27). An oil; IR (neat) 3325 (OH), 1637, 1437, 1246, 1016, and 850 cm^{-1}; ^1H NMR δ=0.01 (9H, s, $SiMe_3$), 1.51–1.64 (4H, m), 1.63 (2H, br s, CH_2SiMe_3), 1.77 (1H, br, OH), 1.95–2.01 (2H, m), 2.03–2.10 (2H, m), 4.16 (2H, s, CH_2OH), 5.40–5.44 (1H, m, C=C*H*CH_2), and 5.50 (1H, br s, C*H*=CCH_2OH); ^{13}C NMR δ=1.27 (3C), 22.12, 22.81, 25.04, 25.48, 29.42, 62.89, 125.41, 128.96, 135.08, and 136.97; MS m/z 224 (M^+, 1%), 134 (10), 119 (40), 105 (52), 91 (94), and 73 (100); HRMS (CI) [Found: m/z 225.1576 (M^++H). Calcd for $C_{13}H_{25}OSi$: M, 225.1675].

4.4.10. (*E*)-3-(*t*-Butylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-en-1-ol (39a). An oil; IR (neat) 3390 (OH), 1637, 1467, 1365, 1245, and 854 cm^{-1}; ^1H NMR δ=0.03 (9H, s, $SiMe_3$), 0.87 (9H, s, *t*-Bu), 1.10–1.30 (2H, m), 1.45 (1H, br, OH), 1.63 (1H, d, J=13.5 Hz, C*H*H$SiMe_3$), 1.67 (1H, d, J=13.5 Hz, CH*H*$SiMe_3$), 1.78–1.92 (2H, m), 2.05–2.16 (3H, m), 4.12 (1H, d, J=12.0 Hz, OC*H*HOH), 4.24 (1H, d, J=12.0 Hz, OCH*H*OH), 5.44–5.48 (1H, m, C=C*H*CH_2), and 5.55 (1H, br s, C*H*=CCH_2-OH); ^{13}C NMR δ=−1.26 (3C), 24.19, 25.14, 27.14, 27.18 (3C), 30.94, 32.19, 43.81, 62.70, 125.85, 128.54, 134.93, and 137.01; MS m/z 280 (M^+, 1%), 251 (1), 190 (4), 175 (5), 133 (26), 106 (34), 91 (52), 73 (89), and 57 (100); HRMS (CI) [Found: m/z 281.2343 (M^++H). Calcd for $C_{17}H_{33}OSi$: M, 281.2301].

4.4.11. (*E*)-3-(Methylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-en-1-ol (39b). An oil; IR (neat) 3330 (OH), 1637, 1458, 1248, 1012, and 856 cm^{-1}; ^1H NMR δ=0.03 (9H, s, $SiMe_3$), 0.95 (3H, d, J=6.6 Hz, Me), 1.16–1.27 (1H, m), 1.56–1.74 (6H, m), 1.97–2.19 (3H, m), 4.13 (1H, d, J=12.2 Hz, OC*H*HOH), 4.21 (1H, d, J=12.2 Hz, OCH*H*OH), 5.38–5.42 (1H, m, C=C*H*CH_2), and 5.53 (1H, br s, C*H*=CCH_2OH); ^{13}C NMR δ=−1.29 (3C), 21.76, 24.98, 28.08, 29.47, 31.05, 34.07, 62.61, 125.00, 128.62, 134.67, and 136.99; MS *m*/*z* 238 (M^+, 1%), 223 (1), 148 (12), 133 (23), 106 (64), 91 (86), and 73 (100); HRMS [Found: *m*/*z* 238.1738 (M^+). Calcd for $C_{14}H_{26}OSi$: M, 238.1753].

4.5. MnO_2 oxidation

In a 50 cm^3 round-bottomed flask fitted with $CaCl_2$ drying tube was placed a solution of **11a** (104.3 mg, 473.4 mmol) in dry CH_2Cl_2 (15 cm^3; distilled from CaH_2) at room temperature, and to this was added a suspension of MnO_2 (2.1 g) in CH_2Cl_2 (3 cm^3) with vigorous stirring. After this had been stirred for 15 h, the mixture was filtered through Celite, and the filtrate was concentrated. The resultant crude oil was chromatographed on silica gel (1 g) using hexane/AcOEt (99:1) as eluent to afford **8a** (91.7 mg, 89%). Similarly, **11b**, **11c**, **15**, **20a**, **20b**, **20c**, and **26** afforded **8b**, **8c**, **13**, **17a**, **17b**, **17c**, and **28** in 88, 81, 51, 71, 64, 75, and 85% yields, respectively. These compounds were purified free from their geometrical isomers at this stage.

4.5.1. (*Z*)-4-Cyclohexylidene-2-(trimethylsilylmethyl)but-2-enal (8a). An oil; IR (neat) 2705 (CHO), 1675 (C=O), 1627, 1447, 1249, and 854 cm^{-1}; ^1H NMR δ=−0.02 (9H, s, $SiMe_3$), 1.60–1.67 (6H, m, $(CH_2)_3$), 1.85 (2H, br s, C*H*$_2SiMe_3$), 2.25–2.30 (2H, m, C=CCH_2), 2.40–2.46 (2H, m, C=CCH_2), 6.16 (1H, d quint, J=11.6, 0.9 Hz, C_{ring}=CH), 7.02 (1H, d, J=11.6 Hz, C*H*=CCHO), and 9.39 (1H, s, CHO); ^{13}C NMR δ=−1.05 (3C), 14.74, 26.58, 28.05, 28.80, 29.87, 38.39, 118.81, 138.90, 141.62, 153.97, and 194.96; MS *m*/*z* 236 (M^+, 30%), 221 (26), 193 (38), 180 (15), 91 (17), and 73 (100); HRMS [Found: *m*/*z* 236.1565 (M^+). Calcd for $C_{14}H_{24}OSi$: M, 236.1597].

4.5.2. (*Z*)-4-(4-*t*-Butylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-enal (8b). An oil; IR (neat) 2707 (CHO), 1677 (C=O), 1628, 1365, 1248, 1226, and 855 cm^{-1}; ^1H NMR δ=−0.02 (9H, s, $SiMe_3$), 0.87 (9H, s, *t*Bu), 1.02–1.32 (3H, m), 1.85 (2H, br s, C*H*$_2SiMe_3$), 1.88–2.02 (3H, m), 2.17–2.27 (1H, m), 2.38–2.44 (1H, m), 2.96–3.03 (1H, m), 6.15 (1H, br d, J=11.5 Hz, C_{ring}=CH), 7.01 (1H, d, J=11.5 Hz, C*H*=CCHO), and 9.39 (1H, s, CHO); ^{13}C NMR δ=−1.04 (3C), 14.74, 27.58 (3C), 28.70, 29.44, 29.63, 32.48, 38.20, 48.18, 118.48, 138.88, 141.72, 153.97, and 194.94; MS *m*/*z* 292 (M^+, 91%), 277 (87), 194 (98), 180 (86), and 73 (100); HRMS [Found: *m*/*z* 292.2202 (M^+). Calcd for $C_{18}H_{32}OSi$: M, 292.2224].

4.5.3. (*Z*)-4-(4-Methylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-enal (8c). An oil; IR (neat) 2707 (CHO), 1676 (C=O), 1626, 1248, 1223, and 855 cm^{-1}; ^1H NMR δ=−0.02 (9H, s, $SiMe_3$), 0.93 (3H, d, J=6.5 Hz, Me), 0.99–1.15 (2H, m), 1.55–1.73 (1H, m), 1.82–2.04 (3H, m), 1.85 (2H, br s, C*H*$_2SiMe_3$), 2.19–2.39 (2H, m), 2.86–2.93 (1H, m), 6.17 (1H, br d, J=11.6 Hz, C_{ring}=CH), 7.01 (1H, d, J=11.6 Hz, C*H*=CCHO), and 9.38 (1H, s, CHO); ^{13}C NMR δ=1.05 (3C), 14.74, 21.70, 29.08, 32.62, 36.00, 36.76, 37.67, 118.90, 138.94, 141.69, 153.56, and 194.95; MS *m*/*z* 250 (M^+, 100%), 235 (99), 193 (94), 180 (6), 147 (5), and 75 (94); HRMS [Found: *m*/*z* 250.1725 (M^+). Calcd for $C_{15}H_{26}OSi$: M, 250.1754].

4.5.4. (*E*)-4-Cyclohexylidene-2-methylbut-2-enal (13). An oil; IR (neat) 2708 (CHO), 1681 (C=O), 1629, 1447, 1234, 1223, 1187, and 1011 cm^{-1}; ^1H NMR (Me_4Si=0.00) δ=1.13–1.91 (6H, m, $(CH_2)_3$), 1.84 (3H, d, J=1.0 Hz, C=CCH_3), 2.28–2.33 (2H, m, C=CCH_2), 2.42–2.48 (2H, m, C=CCH_2), 6.28 (1H, br d, J=11.8 Hz, C_{ring}=CH), 7.17 (1H, dq, J=11.8, 1.1 Hz, C*H*=CCHO), and 9.45 (1H, s, CHO); ^{13}C NMR δ=9.19, 26.50, 27.99, 28.66, 29.89, 38.37, 118.09, 135.71, 144.46, 155.85, and 195.35; MS *m*/*z* 164 (M^+, 97%), 149 (3), 135 (3), and 121 (100); HRMS [Found: *m*/*z* 164.1161 (M^+). Calcd for $C_{11}H_{16}O$: M, 164.1202].

4.5.5. (*E*)-4-Cyclohexylidene-2-(trimethylsilylmethyl)but-2-enal (17a). An oil; IR (neat) 1660 (C=O), 1626, 1248, 856, and 739 cm^{-1}; ^1H NMR δ=−0.02 (9H, s, $SiMe_3$), 1.57–1.66 (6H, m, $(CH_2)_3$), 1.72 (2H, s, C*H*$_2$-$SiMe_3$), 2.22–2.27 (2H, m, C=CCH_2), 2.33–2.38 (2H, m, C=CCH_2), 6.77 (1H, br d, J=12.4 Hz, C_{ring}=CH), 7.07 (1H, d, J=12.4 Hz, C*H*=CCHO), and 10.03 (1H, s, CHO); ^{13}C NMR δ=−1.60 (3C), 19.93, 26.62, 27.87, 28.56, 28.94, 38.18, 114.99, 134.89, 138.48, 151.04, and 190.11; MS *m*/*z* 236 (M^+, 7%), 221 (8), 193 (19), 180 (7), 91 (12), 73 (100), and 45 (37); HRMS [Found: *m*/*z* 236.1585 (M^+). Calcd for $C_{14}H_{24}OSi$: M, 236.1597].

4.5.6. (*E*)-4-(4-*t*-Butylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-enal (17b). An oil; IR (neat) 1662 (C=O), 1630, 1365, 1248, and 856 cm^{-1}; ^1H NMR δ=−0.02 (9H, s, $SiMe_3$), 0.87 (9H, s, *t*Bu), 1.00–1.30 (3H, m), 1.69 (1H, d, J=13.0 Hz, C*H*$HSiMe_3$), 1.74 (1H, d, J=13.0 Hz, CH*H*$SiMe_3$), 1.79–2.00 (3H, m), 2.14–2.24 (1H, m), 2.36–2.41 (1H, m), 2.89–2.95 (1H, m), 6.77 (1H, br d, J=12.6 Hz, C_{ring}=CH), 7.07 (1H, d, J=12.6 Hz, C*H*=CCHO), and 10.30 (1H, s, CHO); ^{13}C NMR δ=−1.60 (3C), 19.90, 27.57 (3C), 28.52, 28.71, 29.16, 32.48, 38.00, 48.21, 114.67, 134.86, 138.61, 151.03, and 190.12; MS *m*/*z* 292 (M^+, 3%), 277 (4), 193 (32), and 73 (100); HRMS [Found: *m*/*z* 292.2223 (M^+). Calcd for $C_{18}H_{32}OSi$: M, 292.2224].

4.5.7. (*E*)-4-(4-Methylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-enal (17c). An oil; IR (neat) 1660 (C=O), 1626, 1248, 1146, and 856 cm^{-1}; ^1H NMR δ=−0.02 (9H, s, $SiMe_3$), 0.93 (3H, d, J=6.5 Hz, Me), 0.98–1.16 (2H, m), 1.70 (1H, d, J=12.8 Hz, C*H*$HSiMe_3$), 1.73 (1H, d, J=12.8 Hz, CH*H*$SiMe_3$), 1.58–1.96 (4H, m), 2.17–2.36 (2H, m), 2.79–2.86 (1H, m), 6.78 (1H, br d, J=12.4 Hz, C_{ring}=CH), 7.06 (1H, d, J=12.4 Hz, C*H*=CCHO), and 10.29 (1H, s, CHO); ^{13}C NMR δ=−1.59 (3C), 19.97, 21.74, 28.18, 32.68, 35.88, 36.58, 37.48, 115.10, 134.98, 138.54, 150.61, and 190.11; MS *m*/*z* 250 (M^+, 4%), 235 (5), 193 (25), 103 (16), and 73 (100); HRMS [Found: *m*/*z* 250.1758 (M^+). Calcd for $C_{15}H_{26}OSi$: M, 250.1754].

4.5.8. (*Z*)-3-(Cyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-enal (28). An oil; IR (neat) 1680 (C=O), 1615, 1249, and 856 cm^{-1}; ^1H NMR δ=−0.01 (9H, s, $SiMe_3$), 1.58–1.74 (4H, m), 2.02 (2H, br s, CH_2SiMe_3), 2.20–2.26 (2H, m), 2.31–2.37 (2H, m), 6.12–6.17 (1H, m, C=C*H*CH_2), 6.53 (1H, br s, C*H*=CCHO), and 9.31 (1H, s, CHO); ^{13}C NMR δ=−0.94 (3C), 15.53, 21.63, 22.59, 26.41, 28.33, 135.80, 136.61, 138.15, 150.66, and 196.19; MS *m/z* 221 (M^+− H, 3%), 207 (3), 180 (6), 131 (7), 117 (9), 104 (10), 91 (18), and 73 (100); HRMS [Found: *m/z* 222.1428 (M^+). Calcd for $C_{13}H_{22}OSi$: M, 222.1441].

4.6. Cyclization of 27

By the same procedure described above, compound **27** (25.6 mg, 0.114 mmol) was treated with MnO_2 (260 mg) in dry CH_2Cl_2 (10 cm^3) at room temperature for 75 min. After filtration through Celite, the filtrate was concentrated and chromatographed on silica gel (1 g) using pentane/Et_2O (99:1) as eluent to afford **30** (5.1 mg, 20%) and **31** (10.7 mg, 63%).

4.6.1. 8-Methylenebicyclo[4.3.0]non-9-en-7-ol (30). An oil; IR (neat) 3350 (OH), 1639, 1446, 1036, 868, and 739 cm^{-1}; ^1H NMR δ=1.04 (1H, dq, *J*=3.3, 12.5 Hz, 5β-H), 1.17–1.44 (2H, m, 3β-H and 4α-H), 1.68 (1H, br d, *J*=6 Hz, OH), 1.77–1.89 (2H, m, 3α-H and 4β-H), 2.06 (1H, br dt, *J*=5, 13 Hz, 2α-H), 2.14–2.22 (1H, m, 5α-H), 2.34–2.41 (1H, m, 6-H), 2.49 (1H, ddt, *J*=4.0, 13.9, 2.2 Hz, 2β-H), 4.26 (1H, br s, 7-H), 4.88 (1H, br s, C=C*H*H), 4.91 (1H, d, *J*=1.5 Hz, C=CH*H*), and 5.79 (1H, br s, 9-H); ^{13}C NMR δ=25.57, 26.91, 29.47, 29.69, 32.75, 79.65, 102.55, 123.05, 153.61, and 156.61; MS *m/z* 150 (M^+, 74%), 135 (17), 121 (81), 108 (81), 91 (79), and 79 (100); HRMS [Found: *m/z* 150.1040 (M^+). Calcd for $C_{10}H_{14}O$: M, 150.1045].

4.6.2. 8-Methylene-7-(trimethylsilyloxy)bicyclo[4.3.0]non-9-ene (31). An oil; IR (CH_2Cl_2) 1458, 1097, 1030, and 802 cm^{-1}; ^1H NMR δ=0.18 (9H, s, $SiMe_3$), 1.03 (1H, dq, *J*=3.3, 12.5 Hz), 1.16–1.44 (2H, m), 1.76–1.88 (2H, m), 1.98–2.19 (2H, m), 2.35–2.50 (2H, m), 4.31 (1H, dt, *J*=3.4, 2.2 Hz, C*H*OSiMe$_3$), 4.75 (1H, br s, C=C*H*H), 4.86 (1H, d, *J*=1.6 Hz, C=CH*H*), and 5.78 (1H, br s, CH=C); ^{13}C NMR δ=0.43 (3C), 25.61, 26.72, 29.47, 32.65, 53.56, 80.15, 102.17, 123.43, 152.43, and 155.70; MS *m/z* 222 (M^+, 31%), 207 (10), 180 (18), 117 (23), 104 (27), 91 (32), and 73 (100); HRMS [Found: *m/z* 222.1438 (M^+). Calcd for $C_{13}H_{22}OSi$: M, 222.1441].

4.7. Cyclization of 39a,b

By the same procedure, compound **39a** (34.2 mg, 0.122 mmol) was treated with MnO_2 (450 mg) at room temperature for 5 min. After the mixture had been filtered through Celite, the solvent was evaporated off. The resultant oily residue was dissolved in Et_2O (5 cm^3), silica gel (ca. 100 mg) was added, and the mixture was stirred for 3 days. The silica gel was filtered off, washed with Et_2O, and the solvent was partly evaporated. Et_2O was added to a volume of ca. 5 cm^3 again, and Bu_4NF (31 mg) was added. After the mixture had been stirred at room temperature for 4 h, an aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O and dried. Evaporation of the solvent followed by florisil (2 g) column chromatography using hexane/Et_2O (99:1) as eluent afforded **42a** (23.2 mg, 94%). Similarly, **39b** (20.5 mg, 0.086 mmol) afforded **42b** (13.3 mg, 94%).

4.7.1. 4-*t*-Butyl-8-methylenebicyclo[4.3.0]non-9-en-7-ol (42a). An oil; IR (neat) 3390 (OH), 1639, 1365, 1265, 1072, 866, and 737 cm^{-1}; ^1H NMR δ=0.87 (9H of one isomer, s, *t*-Bu), 0.87 (9H of one isomer, s, *t*-Bu), 0.79–2.69 (9H, m), 4.24–4.32 (1H, m, C*H*OH), 4.84–4.90 (2H, m, C=CH_2), 5.77 (1H of one isomer, s, C=C*H*C=CH_2), and 5.82 (1H of one isomer, s, C=C*H*C=CH_2); ^{13}C NMR δ=23.51, 25.92, 27.56 (3C), 27.64 (3C), 27.77, 29.21, 29.66, 32.49, 32.98, 33.72, 43.10, 43.31, 50.59, 54.60, 79.88, 81.24, 101.58, 102.36, 122.67, 123.68, 153.09, 153.60, 156.81, and 157.02; MS *m/z* 206 (M^+, 1%), 188 (31), 173 (9), 131 (48), 104 (32), 57 (39), and 43 (100); HRMS (CI) [Found: *m/z* 207.1652 (M^++H). Calcd for $C_{14}H_{23}O$: M, 207.1749].

4.7.2. 4-Methyl-8-methylenebicyclo[4.3.0]non-9-en-7-ol (42b). An oil; IR (neat) 3370 (OH), 1639, 1265, 1049, 868, and 739 cm^{-1}; ^1H NMR δ=0.71–2.63 (9H, m), 0.93 (3H of one isomer, d, *J*=6.5 Hz, Me), 1.08 (3H of one isomer, d, *J*=7.1 Hz, Me), 4.25 (1H, br s, C*H*OH), 4.87–4.92 (2H, m, C=CH_2), and 5.79 (1H, s, C=C*H*C=CH_2); ^{13}C NMR δ=16.88, 22.14, 24.24, 27.75, 28.93, 31.99, 32.06, 35.25, 38.07, 41.04, 48.98, 54.22, 79.63, 80.01, 102.54 (for both isomers), 122.84, 123.12, 153.24, 153.86, 156.58, and 156.83; MS *m/z* 164 (M^+, 48%), 149 (33), 131 (44), 122 (61), 91 (61), and 79 (100); HRMS (CI) [Found: *m/z* 165.1274 (M^++H). Calcd for $C_{11}H_{17}O$: M, 165.1279].

4.8. Cyclization of 8a–c and 17a–c

To a stirred solution of $FeCl_3$ (63.4 mg, 391 mmol) in dry CH_2Cl_2 (6 cm^3; distilled from CaH_2) was added a solution of **8a** (42.8 mg, 181 mmol) in CH_2Cl_2 (10 cm^3) dropwise at −60 °C under Ar. Monitoring on TLC, the mixture was slowly warmed to room temperature over 7 h. A saturated aqueous solution of $NaHCO_3$ was added, and the mixture was extracted with CH_2Cl_2 and dried. Evaporation of the solvent followed by silica gel (15 g) column chromatography using hexane/AcOEt (98:2) afforded **12a** (23.3 mg, 78%). Similarly, **8b** and **8c** gave **12b** and **12c** in 80 and 70% yields, respectively. See Tables 1 and 2 for the modified reaction conditions of the cyclization of **17a–c**.

4.8.1. 2-Methylspiro[4.5]dec-2-en-1-one (12a). An oil; UV (EtOH) λ_{max} 227.4 nm (ε 1.0×10^{-4}); IR (neat) 1702 (C=O), 1640, 1261, 1098, 1021, and 804 cm^{-1}; ^1H NMR δ=1.20–1.40 (6H, m), 1.52–1.77 (4H, m), 1.77 (3H, dt, *J*=1.3, 2.3 Hz, Me), 2.42 (2H, quint, *J*=2.3 Hz, C=CCH_2), and 7.23 (1H, tq, *J*=2.3, 1.3 Hz, C=CH); ^{13}C NMR δ=10.39, 23.05 (2C), 25.25, 33.40 (2C), 39.97, 48.08, 139.65, 155.74, and 214.42; MS *m/z* 164 (M^+, 16%), 149 (7), 121 (16), 109 (100), 96 (28), 79 (16), and 41 (31); HRMS [Found: *m/z* 164.1216 (M^+). Calcd for $C_{11}H_{16}O$: M, 164.1202].

4.8.2. 8-*t*-Butyl-2-methylspiro[4.5]dec-2-en-1-one (12b). An oil; IR (neat) 1706 (C=O), 1637, and 1009 cm^{-1}; ^1H

NMR δ=0.85 (9H, s, *t*Bu), 1.00–1.11 (3H, m), 1.24–1.35 (2H, m), 1.53–1.66 (2H, m), 1.73–1.80 (2H, m), 1.77 (3H, dt, J=1.4, 2.2 Hz, Me), 2.39 (2H, quint, J=2.2 Hz, C=CCH_2), and 7.23 (1H, tq, J=2.2, 1.4 Hz, C=C*H*); ^{1}H NMR (C_6D_6=7.15) δ=0.79 (9H, s, *t*Bu), 0.76–0.96 (3H, m, 7_{ax}-H, 8-H, and 9_{ax}-H), 1.15–1.21 (2H, m, 6_{eq}-H and 10_{eq}-H), 1.52–1.59 (2H, m, 7_{eq}-H and 9_{eq}-H), 1.70 (3H, dt, J=1.4, 2.2 Hz, Me), 1.74 (2H, br dt, J=3.5, 13 Hz, 6_{ax}-H and 10_{ax}-H), 1.91 (2H, quint, J=2.2 Hz, C=CCH_2), and 6.57 (1H, tq, J=2.2, 1.4 Hz, C=C*H*); ^{13}C NMR δ=10.39 (CH_3), 24.04 ($2CH_2$), 27.43 ($3CH_3$), 32.40 (C), 34.07 ($2CH_2$), 39.90 (CH_2), 46.93 (CH), 48.08 (C), 139.84 (C), 155.82 (CH), and 214.66 (CO); MS *m*/*z* 220 (M^+, 7%), 205 (3), 163 (100), 109 (97), and 57 (98); HRMS [Found: *m*/*z* 220.1783 (M^+). Calcd for $C_{15}H_{24}O$: M, 220.1828].

4.8.3. 2,8-Dimethylspiro[4.5]dec-2-en-1-one (12c). An oil; UV (EtOH) λ_{max} 227.8 nm (ε 1.0×10^{-4}); IR (neat) 1703 (C=O), 1641, 1452, 1072, and 1021 cm^{-1}; ^{1}H NMR δ=0.90 (3H, d, J=6.5 Hz, Me), 0.93–1.05 (2H, m, 7_{ax}-H and 9_{ax}-H), 1.21–1.28 (2H, m, 6_{eq}-H and 10_{eq}-H), 1.36–1.49 (1H, m, 8-H), 1.61 (2H, br dt, J=3.5, 13 Hz, 6_{ax}-H and 10_{ax}-H), 1.66–1.72 (2H, m, 7_{eq}-H and 9_{eq}-H), 1.77 (3H, dt, J=1.4, 2.3 Hz, Me), 2.39 (2H, quint, J=2.3 Hz, C=CCH_2), and 7.23 (1H, tq, J=2.3, 1.4 Hz, C=C*H*); ^{13}C NMR δ=10.40, 22.64, 31.55, 31.87 (2C), 33.53 (2C), 39.84, 47.81, 139.80, 155.85, and 214.69; MS *m*/*z* 178 (M^+, 18%), 121 (16), 109 (98), and 96 (100); HRMS [Found: *m*/*z* 179.1402 (M^+-H). Calcd for $C_{12}H_{19}O$: M, 179.1437].

4.8.4. 2-Methylenespiro[4.5]dec-3-en-1-ol (18a). An oil; IR (neat) 3390 (OH), 1643, 1450, 1101, 1947, 870, 800, and 735 cm^{-1}; ^{1}H NMR δ=1.24–1.68 (11H, m), 4.18 (1H, br s, C*H*OH), 5.02–5.05 (2H, m, C=CH_2), 6.12 (1H, d, J=6.4 Hz, C*H*=CH–C=C), and 6.21 (1H, br d, J=6.4 Hz, CH=C*H*–C=C); ^{13}C NMR δ=22.93, 23.37, 26.00, 31.05, 36.04, 51.18, 80.80, 105.61, 129.40, 144.67, and 155.81; MS *m*/*z* 164 (M^+, 5%), 149 (14), 135 (23), 121 (100), 108 (54), 91 (60), 79 (59), 67 (51), and 41 (82); HRMS [Found: *m*/*z* 164.1297 (M^+). Calcd for $C_{11}H_{16}O$: M, 164.1202].

4.8.5. 2-Methylspiro[4.5]dec-3-en-1-one (21a). An oil; IR (neat) 1738 (C=O), 1676, 1624, 1452, and 1161 cm^{-1}; ^{1}H NMR δ=1.15 (3H, d, J=7.5 Hz, Me), 1.20–1.78 (10H, m), 2.96 (1H, tq, J=2.2, 7.5 Hz, C*H*Me), 6.03 (1H, dd, J=2.2, 7.2 Hz, C*H*=CH), and 6.30 (1H, dd, J=2.2, 7.2 Hz, CH=C*H*); ^{13}C NMR δ=15.96, 22.18, 22.34, 25.68, 33.48, 33.59, 46.51, 54.01, 132.15, 135.87, and 195.70; MS *m*/*z* 164 (M^+, 5%), 136 (100), 121 (21), 107 (68), 94 (34), 79 (92), and 41 (68); HRMS [Found: *m*/*z* 164.1169 (M^+). Calcd for $C_{11}H_{16}O$: M, 164.1202].

4.8.6. 8-*t*-Butyl-2-methylspiro[4.5]dec-3-en-1-one (21b). Mp 43–45 °C; IR (neat) 1739 (C=O), 1676, 1630, 1450, 1365, and 856 cm^{-1}; ^{1}H NMR δ=0.87 (9H, s, *t*Bu), 1.11–1.77 (9H, m), 1.15 (3H, d, J=7.6 Hz, Me), 2.96 (1H, tq, J=2.1, 7.6 Hz, C*H*Me), 6.05 (1H, dd, J=2.0, 7.2 Hz, C*H*=CH), and 6.37 (1H, dd, J=2.2, 7.2 Hz, CH=C*H*); ^{13}C NMR (C_6D_6=128.00) δ=15.96, 23.54, 23.71, 27.46 (3C), 32.36, 34.40, 34.54, 46.44, 47.51, 54.31, 132.65, 135.32, and 221.13; MS *m*/*z* 220 (M^+, 4%), 192 (43), 149 (11), 135 (28), 121 (28), 93 (38), 79 (57), and 57 (100); HRMS [Found: *m*/*z* 220.1818 (M^+). Calcd for $C_{15}H_{24}O$: M, 220.1828].

4.8.7. 2,8-Dimethylspiro[4.5]dec-3-en-1-one (21c). An oil; IR (CH_2Cl_2) 1738 (C=O), 1450, 1377, 955, and 883 cm^{-1}; ^{1}H NMR δ=0.91 (3H, d, J=6.5 Hz, Me), 1.00–1.69 (9H, m), 1.13 (3H, d, J=7.5 Hz, Me), 2.94 (1H, tq, J=2.1, 7.5 Hz, COC*H*Me), 6.03 (1H, dd, J=2.1, 7.1 Hz, C*H*=CH), and 6.36 (1H, dd, J=2.1, 7.1 Hz, CH=C*H*); ^{13}C NMR (C_6D_6=128.00) δ=15.95, 22.65, 31.28, 31.42, 32.30, 33.97, 34.03, 46.90, 54.03, 132.63, 135.28, and 221.24; MS *m*/*z* 178 (M^+, 4%), 150 (95), 135 (20), 121 (45), 93 (67), 79 (87), and 41 (100); HRMS [Found: *m*/*z* 178.1366 (M^+-H). Calcd for $C_{12}H_{18}O$: M, 178.1358].

4.9. The cyclization products obtained from 28

The following compounds were detected from ^{1}H and ^{13}C NMR spectra and GC–MS after partial separation into several groups, however, it was difficult to isolate each compounds.

4.9.1. 8-Methylbicyclo[4.3.0]non-1(6)-en-7-one (32). ^{1}H NMR δ=1.17 (3H, d, J=7.3 Hz, Me), 1.61–1.76 (4H, m, 3-H_2 and 4-H_2), 2.03–2.15 (3H, m, 2-H_2 and 9-H), 2.26–2.32 (2H, m, 5-H_2), 2.38 (1H, d quint, J=2.0, 7.3 Hz, 8-H), and 2.72 (1H, dm, J=ca. 18 Hz, 9-H); ^{13}C NMR δ=16.58, 20.09, 21.71, 22.18, 28.43, 39.16, 39.81, 137.43, 171.82, and 211.59; GC–MS *m*/*z* 150 (M^+, 43%), 135 (91), 122 (23), 107 (45), 91 (30), and 79 (100).

4.9.2. *cis*-8-Methylbicyclo[4.3.0]non-8-en-7-one (33). ^{1}H NMR δ=1.06–2.02 (8H, m), 1.78 (3H, t, J=1.5 Hz, Me), 2.41 (1H, q, J=6.4 Hz, 6-H), 2.80–2.88 (1H, m, 1-H), and 7.23 (1H, sextet, J=1.5 Hz, 9-H); ^{13}C NMR δ=10.26, 21.09, 21.27, 22.84, 28.09, 38.64, 45.50, 139.83, 161.31, and 211.96; GC–MS *m*/*z* 150 (M^+, 54%), 135 (12), 121 (39), 107 (29), 93 (28), 79 (80), 69 (94), and 41 (100).

4.9.3. 8-Methylbicyclo[4.3.0]nona-1,8-dien-7-one (34). ^{1}H NMR δ=1.06–2.02 (3H, m), 1.85 (3H, br s, Me), 2.08–2.19 (1H, m, 3-H), 2.25 (1H, ddt, J=4.5, 12.7, 3.5 Hz, 5-H), 2.37 (1H, dm, J=ca. 18 Hz, 3-H), 2.69 (1H, dd-like, J=4.9, 12.0 Hz, 6-H), 5.77 (1H, br t, J=3 Hz, 2-H), and 7.37 (1H, br s, 9-H); ^{13}C NMR δ=10.29, 22.13, 22.58, 25.73, 46.95, 121.83, 139.00, 140.90, 150.85, and 207.61; GC–MS *m*/*z* 148 (M^+, 63%), 133 (26), 120 (25), 105 (95), 91 (100), 77 (47), and 51 (47).

4.9.4. *trans*-2-Chloro-8-methylbicyclo[4.3.0]non-1(6)-en-7-one (35). ^{1}H NMR δ=1.19 (3H, d, J=7.3 Hz, Me), 1.69–1.94 (2H, m, 4-H_2), 2.03 (1H, dm, J=ca. 18 Hz, 9β-H), 2.04–2.18 (3H, m, 3-H_2 and 5-H), 2.27 (1H, dm, J=ca. 18 Hz, 5-H), 2.46 (1H, d quint, J=2.2, 7.3 Hz, 8α-H), 3.13 (1H, ddt, J=6.7, 18.2, 2.2 Hz, 9α-H), and 4.69 (1H, br t, J=4.5 Hz, 2β-H); ^{13}C NMR δ=16.38, 18.27, 19.99, 32.80, 36.38, 40.03, 54.94, 139.74, 165.89, and 211.54; GC–MS *m*/*z* 186 (M^+ for ^{37}Cl, 14%), 184 (M^+ for ^{35}Cl, 39), 169 (44), 149 (30), 121 (65), 91 (90), and 79 (100).

4.9.5. *cis*-2-Chloro-8-methylbicyclo[4.3.0]non-1(6)-en-7-one (36). ^{1}H NMR δ=1.21 (3H, d, J=7.4 Hz, Me), 1.70–1.94 (2H, m, 4-H_2), 2.03–2.17 (3H, m, 3-H_2 and 5-H), 2.26

(1H, dm, J=ca. 18 Hz, 5-H), 2.42–2.50 (2H, m, 8α-H, 9α-H), 2.69 (1H, m, 9β-H), and 4.70 (1H, br t, J=4.5 Hz, 2α-H); ^{13}C NMR δ=16.22, 18.30, 19.96, 32.79, 36.45, 40.16, 54.91, 139.80, 166.09, and 211.33; GC–MS m/z 186 (M^+ for ^{37}Cl, 17%), 184 (M^+ for ^{35}Cl, 44), 169 (45), 149 (29), 121 (69), 91 (96), and 79 (100).

4.9.6. 8-Methenebicyclo[4.3.0]non-1(6)-en-7-one (37). ^{1}H NMR δ=1.62–1.79 (4H, m, 3-H_2 and 4-H_2), 2.19–2.25 (2H, m, 2-H_2 or 5-H_2), 2.34–2.40 (2H, m, 5-H_2 or 2-H_2), 3.07 (2H, sept, J=1.3 Hz, 9-H_2), 5.34 (1H, q, J=1.3 Hz, C=C*H*H), and 6.05 (1H, q, J=1.3 Hz, C=CH*H*); ^{13}C NMR δ=20.29, 21.64, 22.12, 28.05, 35.49, 115.20, 140.73, 142.05, 167.84, and 195.40; GC–MS m/z 148 (M^+, 73%), 133 (11), 120 (26), 105 (51), and 91 (100).

4.9.7. 8-(Chloromethyl)bicyclo[4.3.0]non-1(6)-en-7-one (38). ^{1}H NMR δ=1.62–1.79 (4H, m, 3-H_2 and 4-H_2), 2.10–2.17 (2H, m, 2-H_2 or 5-H_2), 2.32–2.38 (2H, m, 5-H_2 or 2-H_2), 2.51 (1H, dm, J=18 Hz, 9-H), 2.65–2.79 (2H, m, 8-H and 9-H), 3.73 (1H, dd, J=6.6, 10.8 Hz, C*H*HCl), and 3.82 (1H, dd, J=3.7, 10.8 Hz, CH*H*Cl); ^{13}C NMR δ=19.99, 21.54, 22.03, 28.48, 34.88, 44.75, 46.82, 138.54, 173.36, and 206.15; GC–MS m/z 186 (M^+ for ^{37}Cl, 7%), 184 (M^+ for ^{35}Cl, 21), 149 (35), 107 (100), and 79 (71).

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References and notes

1. For the reaction of allylsilanes, see: (a) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375–1408. (b) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063–2192. (c) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207–2293. (d) Majetich, G. *Organic Synthesis: Theory and Application*; Hudlicky, T., Ed.; JAI: Greenwich, 1989; Vol. 1, pp 173–240.
2. (a) Kuroda, C.; Suzuki, H. *Curr. Org. Chem.* **2003**, *7*, 115–131. (b) Kuroda, C. *Recent Res. Dev. Pure Appl. Chem.* **1998**, *2*, 189–198.
3. For the synthesis of ring compounds: (a) Ho, T.-L. *Carbocycle Construction in Terpene Synthesis*; VCH: New York, 1988. (b) Thebtaranonth, C.; Thebtaranonth, Y. *Cyclization Reactions*; CRC: Boca Raton, 1994.
4. For related work on the reaction of functionalized allylsilane reported recently from our laboratory: (a) Suzuki, H.; Monda, A.; Kuroda, C. *Tetrahedron Lett.* **2001**, *42*, 1915–1917. (b) Suzuki, H.; Kuroda, C. *Tetrahedron* **2003**, *59*, 3157–3174. (c) Kuroda, C.; Kasahara, T.; Akiyama, K.; Amemiya, T.; Kunishima, T.; Kimura, Y. *Tetrahedron* **2002**, *58*, 4493–4504. (d) Kuroda, C.; Anzai, S. *Chem. Lett.* **1998**, 875–876. (e) Kuroda, C.; Tang, C. Y.; Tanabe, M.; Funakoshi, M. *Bull. Chem. Soc. Jpn* **1999**, *72*, 1583–1587.
5. Kuroda, C.; Kobayashi, K.; Koito, A.; Anzai, S. *Bull. Chem. Soc. Jpn* **2001**, *74*, 1947–1961, and references cited therein.
6. Kuroda, C.; Ito, K. *Bull. Chem. Soc. Jpn* **1996**, *69*, 2297–2303.
7. Kuroda, C.; Nogami, H.; Ohnishi, Y.; Kimura, Y.; Satoh, J. Y. *Tetrahedron* **1997**, *53*, 839–858.
8. Nishitani, K.; Nakamura, Y.; Orii, R.; Arai, C.; Yamakawa, K. *Chem. Pharm. Bull.* **1993**, *41*, 822–831.
9. Nishitani, K.; Harada, Y.; Nakamura, Y.; Yokoo, K.; Yamakawa, K. *Tetrahedron Lett.* **1994**, *35*, 7809–7812.
10. Kuroda, C.; Koshio, H.; Koito, A.; Sumiya, H.; Murase, A.; Hirono, Y. *Tetrahedron* **2000**, *56*, 6441–6455.
11. (a) Denmark, S. E. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, pp 751–784. (b) Denmark, S. E.; Klix, R. C. *Tetrahedron* **1988**, *44*, 4043–4060. (c) Denmark, S. E.; Wallace, M. A.; Walker, C. B., Jr. *J. Org. Chem.* **1990**, *55*, 5543–5545.
12. Kuroda, C.; Mitsumata, N.; Tang, C. Y. *Bull. Chem. Soc. Jpn* **1996**, *69*, 1409–1416.
13. Devon, T. K.; Scott, A. I. *Handbook of Naturally Occurring Compounds*; Academic: New York, 1972; Vol. II.
14. Fraga, B. M. *Nat. Prod. Rep.* **1999**, *16*, 21–38, **1999**, *16*, 711–730; **2000**, *17*, 483–504; **2001**, *18*, 650–673; **2002**, *19*, 650–672.
15. Preliminary communications: Kuroda, C.; Koshio, H. *Chem. Lett.* **2000**, 962–963.
16. Suzuki, H.; Kuroda, C. *J. Chem. Res.* **2003**, 310–312.
17. Caine, D. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 3, pp 1–63.