 Bull. Chem. Soc. Jpn., 74, 1947–1961 (2001)

Intramolecular Cyclization of (2-Functionalized Allyl)trimethylsilane with Acid Chloride. Synthesis of Two Guaianolide-Type α-Methylene γ-Lactones

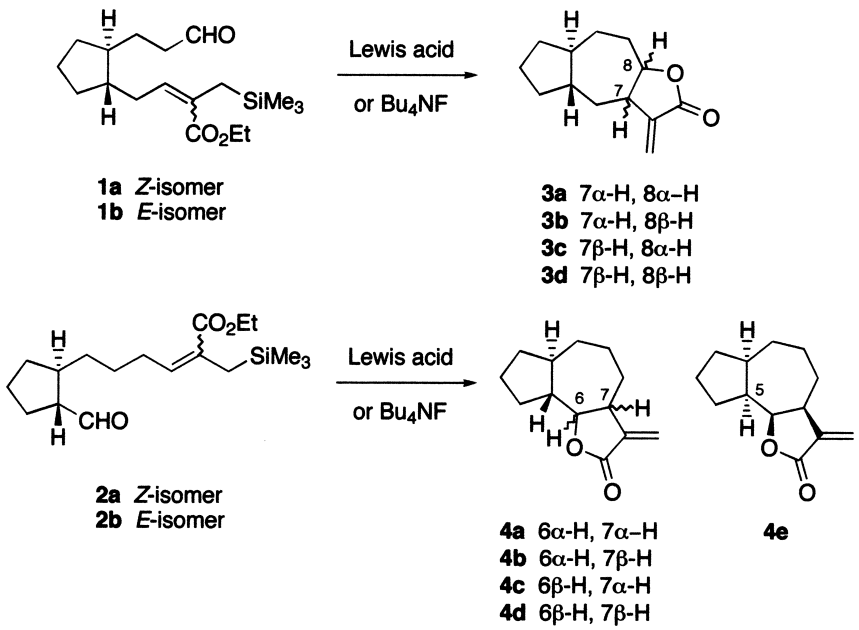
Chiaki Kuroda,* Kenichi Kobayashi, Akira Koito, and Shuzo Anzai

Department of Chemistry, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501

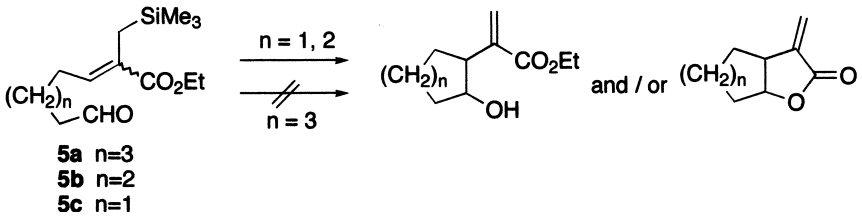
(Received April 23, 2001)

α-Methylene *γ*-lactone fused to seven-membered carbocycle was synthesized by intramolecular cyclization of (2-ethoxycarbonylallyl)trimethylsilane or (2-acetoxymethylallyl)trimethylsilane with acid chloride. The former was found to be a better way for seven-membered carbocyclization, while the latter method was applicable to the synthesis of *α*-methylene *γ*-lactones fused to eight- and fourteen-membered carbocycles. Both guaian-8,12- and 6,12-olide type of compounds were synthesized by this method, in which the cyclization reaction proceeded stereoselectively. It was also found that both (*Z*)- and (*E*)-allylsilanes afford the same stereoisomer as the major product.

α-Methylene *γ*-lactone unit is an important structure in terpenes because of its biological activity,[1] and various carbon skeletons of natural sesqui- and diterpenes are found to have this common structure.[2] A number of synthetic efforts have been made to form this structure;[3,4] however most of them include carbocyclization, lactonization, and *α*-methylenation independently, except some cyclizations of allylmetals.[5] We reported[6–8] that intramolecular Hosomi-Sakurai reaction[9] of (2-ethoxycarbonylallyl)trimethylsilane is an excellent method, since the above three synthetic stages are included in a single concept. However, a problem remains about the yields when this method is applied to the synthesis of seven-membered carbocycle,[7] which is one of the major class of sesquiterpenes such as guaianolides and pseudoguaianolides.[2a] Thus the cyclization of **1a**,**b** and **2a**,**b** afforded guaianolide-type of compounds **3a**–**d** and **4a**–**e**, respectively, in only 10–30% yields (Scheme 1).[7] Epimerization at C(5) also occurred when **2b** was treated with $TiCl_4$ to give **4e**.[7b] In contrast, syntheses of eudesmanolide- or cadinanolide-type of compounds, which include six-membered ring formation reaction, were performed in good yields.[8] Nishitani et al.[10] also reported a similar reaction, in which seven-membered carbocyclization does not proceed at all from acyclic compound **5a**, while formation of five- and six-membered ring occurs in high yields from **5b** and **5c**,



Scheme 1.

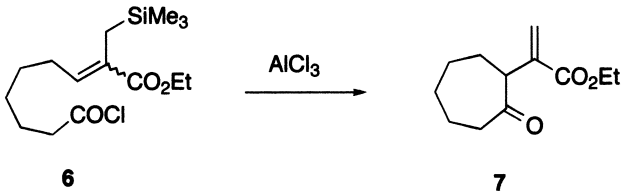


5a n=3
5b n=2
5c n=1

Scheme 2.

respectively (Scheme 2). We supposed that the major reason of this low reactivity towards seven-membered carbocyclization is due to the reduced nucleophilicity of the allylsilane by conjugation with ethoxycarbonyl group, since Majetich et al.[11] obtained a seven-membered ring in good yields by intramolecular cyclization of *non-functionalized* allylsilane with unsaturated carbonyl.

On the basis of such information, we planned to use more reactive acid chloride as an electron acceptor, instead of aldehyde, in the seven-membered ring formation reaction. Reaction of allylsilane with acid chloride is developed as a simple acylation method.[12] Recently, Kang et al.[13] reported the reaction of (2-substituted allyl)trimethylsilanes, such as (2-silyl- and 2-stannylallyl)trimethylsilane, with acid chloride. However, the reaction of (2-ethoxycarbonylallyl)trimethylsilane, deactivated by conjugation with carbonyl group, has not yet been investigated in our knowledge. In a preliminary communication,[14] we reported that cyclization of compound **6** proceeds in good yield, giving ketone **7** (Scheme 3). We also reported that



6 **7**

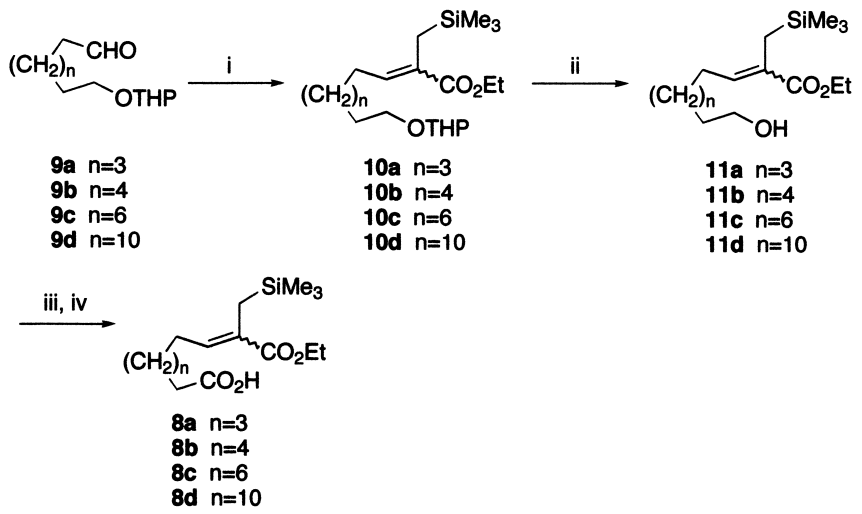
Scheme 3.

α-methylene γ-lactones fused to eight- and fourteen-membered carbocycles can be synthesized by intramolecular cyclization of (2-acetoxymethylallyl)trimethylsilane with acid chloride. Here we report the details of these reactions as well as its application to the synthesis of two types of guaianolides, **3** and **4**, which were obtained in better yields than with the previous method.[7]

Results and Discussion

Synthesis of Fused Methylene Lactone from Conjugated Allylsilane. As the basis, cyclization of ethyl 2-(trimethylsilylmethyl)-8-chlorocarbonyloct-2-enoate (**6**) was first studied. The precursor, carboxylic acid **8a**, was prepared as shown in Scheme 4. Thus to the aldehyde **9a**, obtained according to Nishitani's report,[10b] was introduced 2-(trimethylsilylmethyl)acrylate moiety[7,8] giving **10a** (58%). The *Z*/*E* ratio of the acrylate moiety was determined to be ca. 2:1, judging from the chemical shift of the olefinic protons (see experimental). The tetrahydropyran-2-yl group was then hydrolyzed to afford **11a** in 86% yield. Swern oxidation followed by chlorite oxidation afforded **8a** in 88% yield from **11a**.

With the acid **8a** in hand, acid chloride **6** was prepared by treatment with oxalyl chloride, and its Lewis acid-promoted cyclization reaction was examined (Scheme 5 and Table 1). The formation of acid chloride was confirmed by low-field shift of the signal of CH_2COCl in the ^{1}H-NMR spectrum (δ 2.89 for *Z*-isomer and δ 2.88 for *E*-isomer, each t, J = 7.3 Hz)



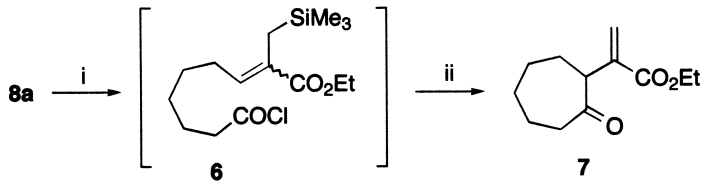
9a n=3
9b n=4
9c n=6
9d n=10

10a n=3
10b n=4
10c n=6
10d n=10

11a n=3
11b n=4
11c n=6
11d n=10

8a n=3
8b n=4
8c n=6
8d n=10

Scheme 4. Reagents and conditions: i) $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME, r.t.; ii) 5% HCl aq, THF, r.t.; iii) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -55 °C to r.t.; iv) $NaClO_2$, NaH_2PO_4, 2-methyl-2-butene, *t*-BuOH aq, r.t.



Scheme 5. Reagents and conditions: i) $(COCl)_2$, CH_2Cl_2, 50 °C; ii) $AlCl_3$, CH_2Cl_2, reflux.

Table 1. Cyclization of **6** to **7**[a)]

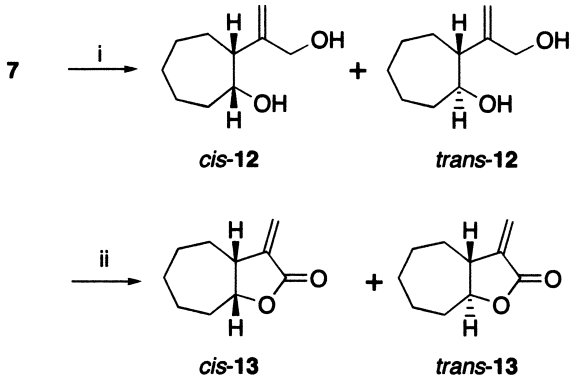
Entry	Lewis acid (molar amount)	Temp.	Time/h	Yield/%[b)]
1	$AlCl_3$ (3)	r.t.	19	39[c)]
2	$AlCl_3$ (3)	reflux	2.5	70
3	$TiCl_4$ (5)	reflux	5	21
4	FeF_3 (5)	r.t	45	0[d)]
5	BF_3OEt_2 (3)	r.t.	67	6[e)]
6	$EtAlCl_2$ (3)	reflux	3	0[d)]

a) All reactions were carried out in CH_2Cl_2. b) From **8a**. c) 20% of **8a** was recovered. d) No reaction proceeded. e) 77% of **8a** was recovered.

and the absorption of C=O in the IR spectrum (1806 cm^{-1}), however **6** was not isolated. Although simple acylation of allylsilane was performed at lower temperature in the literature,[12,13] higher temperature was required for **6** because of conjugation with ethoxycarbonyl group. First, the reaction was carried out with an excess amount of $AlCl_3$ as the Lewis acid in CH_2Cl_2 at room temperature to afford the expected product **7** in 39% yield from **8a** (Entry 1). Compound **7** was obtained in 70% yield when the reaction temperature was elevated to reflux for 2.5 h (Entry 2). Some other Lewis acids, such as $TiCl_4$, FeF_3, BF_3OEt_2, and $EtAlCl_2$, were also used but none of them were better than $AlCl_3$ (Entries 3–6).

We then tried to convert the product **7** into lactones by reduction and oxidation sequence. However, reduction of **7** was not easy. For example, when **7** was treated with $NaBH_4$ or $LiAlH_4$, several products were detected on TLC,# among which the expected diol **12** was not obtained at all. L-Selectride® was also used but was unsuccessful. The expected diol **12** was afforded in 73% yield as a mixture of *cis*-**12** and *trans*-**12** (ratio 6:1) when **7** was reduced with DIBAL-H (Scheme 6). The lactone **13** (*cis*:*trans* = 6:1) was then obtained in 80% yield by oxidation with MnO_2.[15] The spectral data of both *cis*-**13** and *trans*-**13** were consistent with those in the literature;[16] however, the stereochemistry of the lactone was confirmed by NOE experiment, observed between two methyne protons for the *cis*-isomer.

Succeeding the seven-membered ring formation reaction, cyclizations towards eight-, ten-, and fourteen-membered rings were next examined by the same way, since these substructures are also found in natural sesquiterpenes. The α-methylene γ-lactones fused to ten- and fourteen-membered carbocycles are the major structure of natural germacranolides[2a] or cembranolides,[2b] respectively. The α-methylene γ-lactones fused to eight-membered carbocycle are also found as natural products,[17] though not a major skeleton. The acids **8b–d** were prepared from **9b–d**, respectively, by the parallel route shown in Scheme 4. However, **8b–d** were recovered without cyclization when these compounds were exposed to the same reaction conditions, i.e., with $AlCl_3$ in refluxing CH_2Cl_2, after conversion into acid chloride.

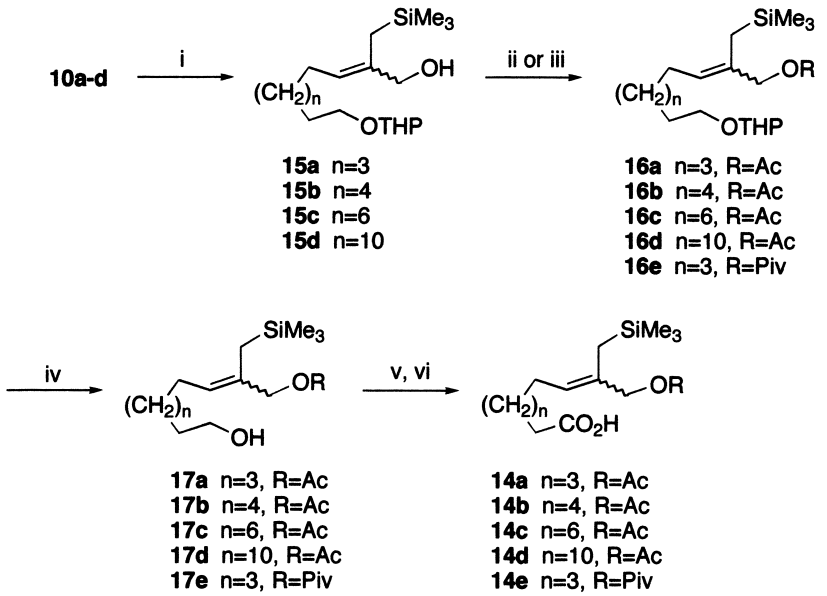


Scheme 6. Reagents and conditions: i) DIBAL-H, Et_2O, −60 °C; ii) MnO_2, CH_2Cl_2, r.t.

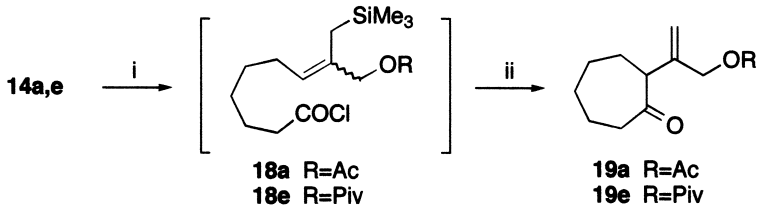
Synthesis of Fused Methylene Lactone from Nonconjugated Allylsilane. There are two problems about the above method. One is the limitation of the reducing agents (**7** to **12**) and the other is the failure of the cyclization towards larger-sized rings. The latter problem is probably caused by the presence of a conjugating ethoxycarbonyl group, which reduces the nucleophilicity of allylsilane in the cyclization reaction. Then, we explored another route involving reduction of ethoxycarbonyl group prior to the cyclization, which would result in the cyclization of protected (2-hydroxymethylallyl)trimethylsilane.

First, cyclization towards seven-membered ring was studied. The acetate **14a** and pivalate **14e** were used as the substrates, which were prepared from **10a** according to Scheme 7. Thus after reduction of ethoxycarbonyl group with DIBAL-H (**15a**, 91%), the resultant hydroxy group was esterified to give acetate **16a** (94%) or pivalate **16e** (92%). Hydrolysis of THP

Although the each products were not identified, judging from the ^1H NMR spectrum, it was suggested that the reduction of C=C double bond occurred to yield saturated product.



Scheme 7. Reagents and conditions: i) DIBAL-H, CH_2Cl_2, −60 °C; ii) Ac_2O, pyridine, r.t.; iii) PivCl, pyridine, r.t.; iv–vi) see Scheme 4.



Scheme 8. Reagents and conditions: i) $(COCl)_2$, CH_2Cl_2, 50 °C; ii) $AlCl_3$, CH_2Cl_2, r.t.

Table 2. Cyclization of **18a** and **18e**[a)]

Entry	Substrate	Product	Solvent	Temp.	Time/h	Yield/%[b)]
1	**18a**	**19a**	CH_2Cl_2	reflux	1	35
2	**18a**	**19a**	CH_2Cl_2	r.t.	18	50
3	**18a**	**19a**	CH_3NO_2	0 °C	2	16
4	**18e**	**19e**	CH_2Cl_2	reflux	2	37

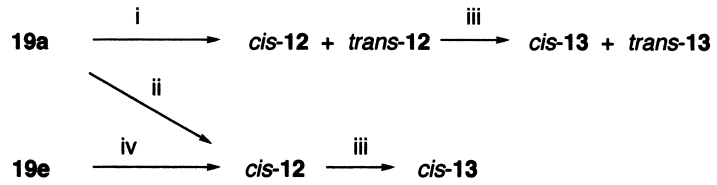
a) All reactions were carried out with excess amount of $AlCl_3$. b) From **14a** or **14e**.

group afforded **17a** (90%) and **17e** (96%), which were subjected to two-step oxidation, as described above, giving carboxylic acids **14a** and **14e** in 91% and 90% yields, respectively.

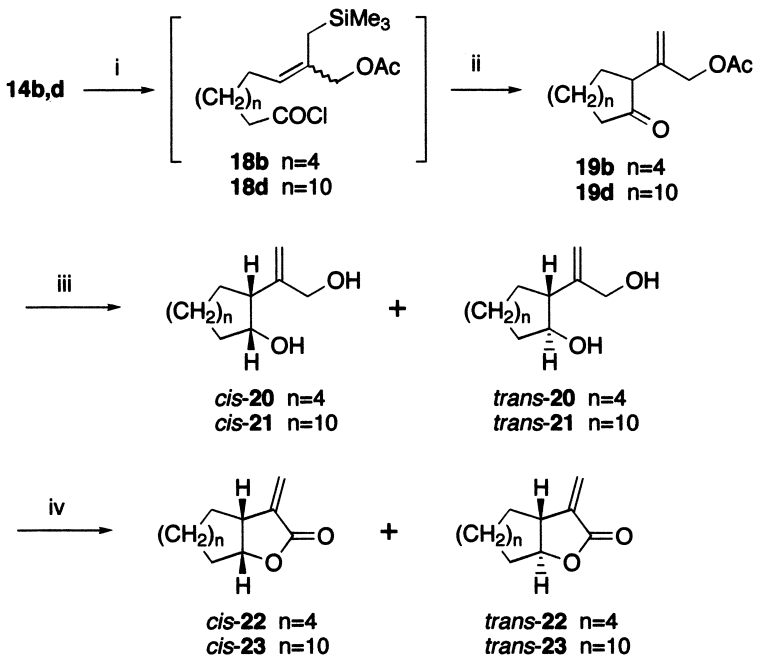
The cyclization reaction of **14a** and **14e** was then studied after conversion into acid chlorides **18a** and **18e**, respectively (Scheme 8). The results are summarized in Table 2. First, the reaction was carried out following the case of **8a**, i.e., with an excess amount of $AlCl_3$ in refluxing CH_2Cl_2, giving the expected seven-membered carbocycle **19a** in 35% yield from **14a** (Entry 1). The yield of **19a** was improved to 50% by treatment at room temperature (Entry 2). The reaction proceeded faster in nitromethane as the solvent but the result was less satisfactory (Entry 3). In all cases, formation of many by-products was detected on TLC, which made the yield lower than the reaction of **8a**. By a similar way, **18e** afforded the cyclization product **19e** (Entry 4), but again, by-products were detected on TLC. No improvement was obtained when **18e** was treated at room temperature.

Reduction of the cyclization product **19a** with DIBAL-H gave the same mixture of diols *cis*-**12** and *trans*-**12** (ratio 6:1; 90% yield), as the reduction of **7**. However, in this case, L-Selectride® was also useful as the reducing agent to afford only *cis*-**12** in 76% yield, which could be converted to *cis*-**13** (Scheme 9). From **19e**, $LiAlH_4$ was added successively after addition of L-Selectride, giving *cis*-**12** in 97% yield.

Carbocyclization towards eight-, ten-, and fourteen-membered rings was then examined using acetates **14b–d** as the substrates; these compounds were prepared from **10b–d** by following the same way as described in Scheme 7. On treatment with $AlCl_3$ in CH_2Cl_2 at room temperature, the acid chloride **18b** afforded eight-membered ring **19b** (34% yield from **14b**), and **18d** afforded fourteen-membered ring **19d** (15%



Scheme 9. Reagents and conditions: i) DIBAL-H, CH_2Cl_2, −60 °C; ii) L-Selectride, Et_2O, −60 °C; iii) MnO_2, CH_2Cl_2, r.t.; iv) L-Selectride, THF, $LiAlH_4$, 0 °C.



Scheme 10. Reagents and conditions: i) $(COCl)_2$, CH_2Cl_2, 50 °C; ii) $AlCl_3$, CH_2Cl_2, r.t.; iii) L-Selectride, Et_2O, −60 °C; iv) MnO_2, CH_2Cl_2, r.t.

yield from **14d**) (Scheme 10). However, ten-membered carbocyclization reaction did not occur from **14c**. Reduction of **19b** and **19d** with L-Selectride® produced **20** (56%; *cis*:*trans* = 3:1[##]) and **21** (98%; *cis*:*trans* = 3:2), respectively, which were converted to fused α-methylene γ-lactones **22** (82%; *cis*:*trans* = 3:1) and **23** (90%; *cis*:*trans* = 3:2). The stereochemistry of these lactones were determined from NOE experiment as described for **13**, i.e., NOEs were observed between two methyne protons for both *cis*-**22**[###] and *cis*-**23**.

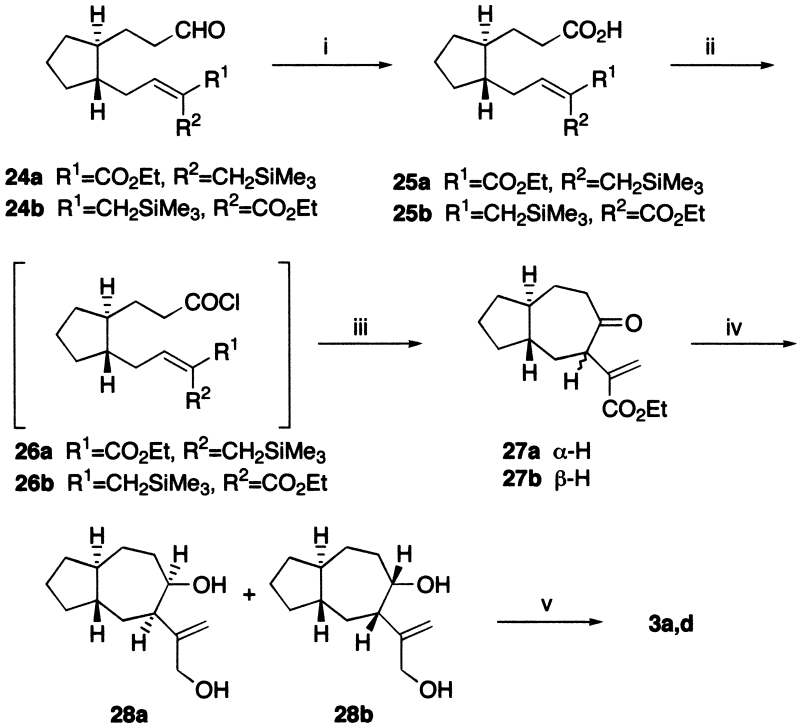
Synthesis of Guaianolide-Type of Fused Ring System. Since the present method, cyclization of functionalized allylsilane with acid chloride, was established as an excellent method to synthesize α-methylene γ-lactone fused to seven-membered carbocycle, synthesis of two types of model compounds of guaianolides, i.e., guaian-8,12-olide and -6,12-olide was then studied as an application. Compounds **3** and **4** were chosen as the synthetic targets, since they were obtained in poor yields by the previous method.[7] Another purpose of the synthesis of **3** and **4** is to find out the stereochemistry of the cyclization reaction. Although we could obtain seven-membered carbocycle by the above study, no information was obtained about the stereochemistry of the cyclization reaction, since both (*Z*)-**6** and (*E*)-**6** produce the same product **7**, and both (*Z*)-**18** and (*E*)-**18** give the same product **19**.

The synthesis of **3** was performed using ester-conjugated compounds **25a** and **25b** as the substrates, since the seven-membered carbocyclization from **8a** took place in better yield than from **14a**. The substrates **25a** and **25b** were prepared by chlorite oxidation of **24a** and **24b**, respectively (**25a**:78%, **25b**:75%), which were synthesized according to the previous report[7a] (Scheme 11). When the acid chloride **26a**, obtained from **25a**, was treated with $AlCl_3$, **27** was afforded as a mixture of stereoisomers (**27a**:**27b** = 1:5) in 61% yield, while **25b** afforded mostly **27b** (**27a**:**27b** = 1:22) in 92% yield through acid chloride **26b**. The stereochemistry of the product was determined by conversion into known lactones. Namely, the isomer mixture of **27** (**27a**:**27b** = 1:22) was reduced stereoselectively by DIBAL-H to diol **28** (63%, **28a**:**28b** = 1:22), which was treated with MnO_2 to afford lactones **3a**,**d** (91%, **3a**:**3d** = 1:22). From this result, it was established that the major cyclization product **27b** has 7β-H configuration.

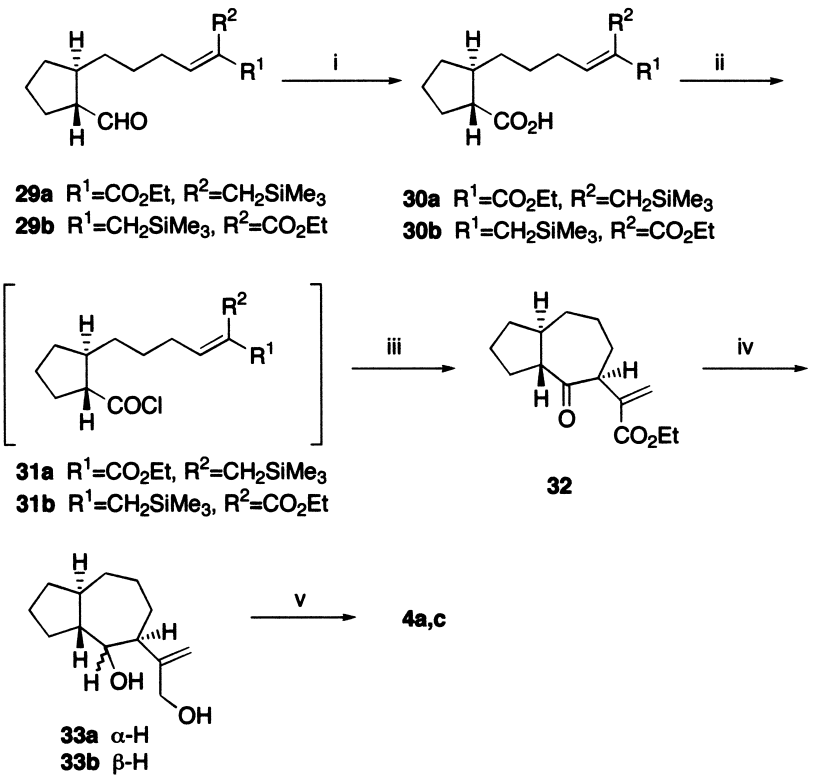
The present method was also applied to the synthesis of **4**,

The description in the preliminary communication (ref. 14) must be alterd.

Nishitani *et al*. synthesized **22** but the stereochemistry was not determined (ref. 10b). The spectral data obtained here clearly indicates that their product is *cis*-**22**.

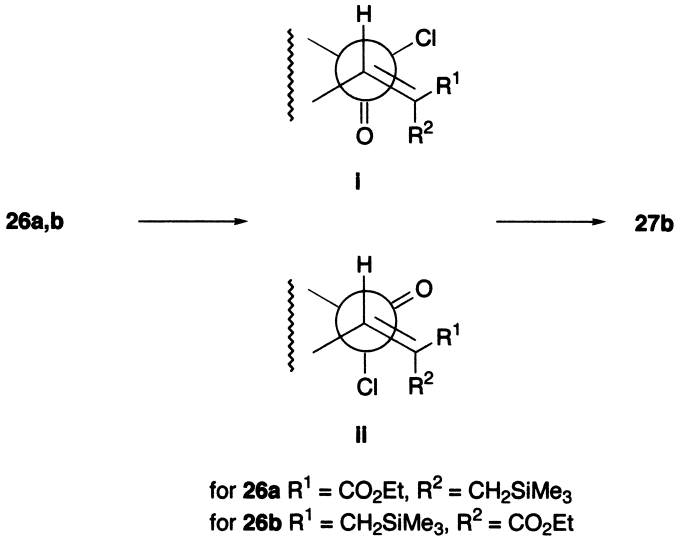


Scheme 11. Reagents and conditions: i) $NaClO_2$, NaH_2PO_4, 2-methylbut-2-ene, *t*-BuOH aq, r.t.; ii) $(COCl)_2$, CH_2Cl_2, 50 °C; iii) $AlCl_3$, CH_2Cl_2, reflux; iv) DIBAL-H, Et_2O, −60 to −30 °C; v) MnO_2, CH_2Cl_2, r.t.



Scheme 12. See Scheme 11 for the reagents and conditions.

expecting that epimerization at C(5) would not occur. Compounds **29a** and **29b** were first prepared by following the previous route,[7b] and then oxidized to afford **30a** and **30b** in 93% and 94% yields, respectively (Scheme 12). When the acid chloride **31b**, obtained from **30b**, was treated with $AlCl_3$, cyclization product **32** was obtained as a single diastereomer in 86% yield. The cyclization of *Z*-isomer **31a** proceeded very slowly giving the same product **32** in 17% yield together with



Scheme 13.

71% of recovered **30a** (thus the yield of **32** based on consumed material is 60%). Reduction of **32** with DIBAL-H afforded **33** (83%) as a mixture of stereoisomers (**33a**:**33b** = 5:1). This was then oxidized to yield lactone **4** in 71% yield, which was found to consist of **4a** and **4c** in 5:1 ratio. Accordingly, the stereochemistry of **32** was established to have 7α-H.

Stereochemistry of the Cyclization Reaction. In the synthesis of 8-olide **3**, both **26a** and **26b** afforded **27b** predominantly over **27a**, although the selectivity from **26b** was much higher than that from **26a**. This stereoselectivity (7β-H selectivity) was roughly the same as the cyclization of the corresponding aldehyde **1a** and **1b**, from which **3c** and/or **3d** were obtained as the major products.[7a] Therefore we conclude that both aldehyde (**1a**,**b**) and acid chloride (**26a**,**b**) take similar conformations in the transition state. Considering the fact that both (*Z*)- and (*E*)-precursors gave the same product, we assume that the major product **27b** was obtained through **i** or **ii** in which the large substituent [C=C(CO_2Et)CH_2SiMe_3] takes an equatorial-like orientation against forming a seven-membered ring (Scheme 13). As to the direction of acid chloride moiety, no information was obtained from the present study since both **i** and **ii** afford the same product **27b**. Although we originally explained the stereoselectivity by means of sterical interaction,[7] recent research developements,[18] including our related work,[19] implies that secondary orbital overlap between carbonyl oxygen and silicon-bearing carbon will rationalize the stereoselectivity. Assuming this effect, the favorable isomer is **i** for **26a** and **ii** for **26b**.

The stereoselective formation of **32** from both **31a** and **31b** in the synthesis of 6-olide can also be explained by taking the equatorial-like orientation of the large group [C=C(CO_2Et)-CH_2SiMe_3]. However, it is not easy to discuss the stereochemistry in detail, since Lewis acid dependence was observed for the cyclization of **2a**,**b**.[7b]

It was found that the yield from *E*-isomer (**26b**, **31b**) is better than that from *Z*-isomer (**26a**, **31a**); the difference between **31a** and **31b** was especially remarkable. However, the reason of this difference in reactivity between *E*- and *Z*-isomers is not clear yet, since such a difference is not distinct in the six-membered carbocyclization reaction.[8a] Also, the cyclization of **26b** and **31b** proceeded in much better yield than that of the acyclic compound **6**. This can be rationalized by conformational effect due to the fused cyclopentane ring, which makes two reaction sites, double bond and acid chloride, easier to approach. The same effect of fused cyclopentane ring is already observed when the cyclization of **1a**,**b** and **2a**,**b** was compared with **5a**.[7,10]

Conclusion

α-Methylene γ-lactones fused to seven-membered carbocycle were obtained through intramolecular cyclization of both (2-ethoxycarbonyl- and 2-acetoxymethylallyl)trimethylsilane with acid chloride. The former is suitable for seven-membered carbocyclization, but the latter has an advantage on both lactonization-step and the synthesis of eight- and fourteen-membered carbocycles.

Synthesis of guaian-8,12-olide and -6,12-olide were also successfully performed by the intramolecular cyclization of (2-ethoxycarbonylallyl)trimethylsilane with acid chloride. By comparison with the cyclization with aldehyde previously reported,[7] although the synthetic steps are longer, the overall efficiency of this method was established. It was also found that the cyclization reaction proceeded stereoselectively but not stereospecifically to give the same stereoisomer predominantly from both (*Z*)- and (*E*)-allylsilanes.

Experimental

General Procedures. IR spectra were taken on a Hitachi 270-30 or 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 are reported on the δ scale (ppm) with the solvent chloroform ($CHCl_3$ = 7.26 for ^{1}H; $CDCl_3$ = 77.00 for ^{13}C) as internal standard, unless otherwise noted. Both low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a Jeol SX-102A mass spectrometer with the EI method. Analytical TLC was done on coated TLC plates (Kieselgel 60 F_{254}, layer thickness 0.2 mm). Wakogel C-200 or C-300 were used for column chromatography.

Anhydrous Na_2SO_4 or $MgSO_4$ were used for drying of extracted organic layers. For reactions requiring dry solvents, tetrahydrofuran (THF), Et_2O, 1,2-dimethoxyethane (DME), and CH_2Cl_2 were distilled from CaH_2; dimethyl sulfoxide (DMSO) and pyridine were distilled from 4A molecular sieve.

Wittig Reaction. To a stirred suspension of NaH (1.82 g, 45.5 mmol; 60% in mineral oil which was removed by washing with dry hexane) in dry DME (150 cm^3) was added $(EtO)_2P(O)CH_2CO_2Et$ (7.96 cm^3, 40.1 mmol) dropwise at 0 °C under Ar. After being stirred at room temperature for 30 min, ICH_2SiMe_3 (7.14 cm^3, 48.1 mmol) was added and the mixture was heated to 70 °C for 4 h. This was cooled to 0 °C again, and a second portion of NaH (1.50 g, 37.4 mmol; mineral oil was not removed) was added. After this was stirred at 0 °C for 1.5 h, a solution of **9a** (26.7 mmol, prepared from 5.78 g of 7-(tetrahydropyran-2-yloxy)heptan-1-ol by Swern oxidation and not purified) in DME (50 cm^3) was added, and the mixture was stirred at room temperature for 17 h. An aqueous solution of NH_4Cl was added, the mixture was extracted with Et_2O, and dried. Evaporation of the solvent followed by silica gel (40 g) column chromatography using hexane–AcOEt (99.5:0.5 to 97.5:2.5) as eluent afforded **10a** (5.90 g, 60%). Compounds **10b–d** were prepared according to the same procedure in 58, 80, and 61% yields from the corresponding ω-(tetrahydropyran-2-yloxy)alkan-1-ols.

Ethyl 9-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)non-2-enoate (10a). An oil; IR (neat) 1711 (C=O), 1635 (C=C), 1248, 1175, 1035, and 853 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.0 Hz, OCH_2CH_3), 1.26–1.88 (14H, m), 1.80 (2H, br s, CH_2SiMe_3), 2.08 (2H, br q, J = 7 Hz, CH_2CH=C), 3.38 (1H, dt, J = 9.5, 6.5 Hz), 3.50 (1H, m), 3.73 (1H, dt, J = 9.5, 6.8 Hz), 3.87 (1H, m), 4.17 (2H, q, J = 7.0 Hz, OCH_2CH_3), 4.57 (1H, m), and 6.60 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.02 (9H, s, $SiMe_3$), 1.30 (3H, t, J = 7.0 Hz, OCH_2CH_3), 1.26–1.88 (14H, m), 1.72 (2H, br s, CH_2SiMe_3), 2.39 (2H, br q, J = 7 Hz, CH_2CH=C), 3.38 (1H, dt, J = 9.5, 6.7 Hz), 3.50 (1H, m), 3.72 (1H, dt, J = 9.5, 6.7 Hz), 3.87 (1H, m), 4.17 (2H, q, J = 7.0 Hz, OCH_2CH_3), 4.57 (1H, m), and 5.65 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.06 (3C), 14.29, 17.26, 19.69, 25.50, 26.14, 28.78, 29.03, 29.32, 29.67, 30.77, 60.37, 62.34, 67.57, 98.85, 130.01, 138.51, and 168.43; MS *m/z* (rel intensity) 370 (M^+, 17), 355 (48), 286 (64), 271 (59), 241 (45), 225 (46), 200 (58), 156 (80), and 75 (100); HRMS [Found: *m/z* 370.2527 (M^+). Calcd for $C_{20}H_{38}O_4Si$: M, 370.2540].

Ethyl 10-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)dec-2-enoate (10b). An oil; IR (neat) 1711 (C=O), 1637 (C=C), 1248, 1174, 1036, and 852 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.28 (3H, t, J = 7.0 Hz, OCH_2CH_3), 1.28–1.86 (16H, m), 1.79 (2H, br s, CH_2SiMe_3), 2.06 (2H, br q, J = 7 Hz, CH_2CH=C), 3.37 (1H, dt, J = 9.4, 6.6 Hz), 3.49 (1H, m), 3.72 (1H, dt, J = 9.4, 6.9 Hz), 3.86 (1H, m), 4.16 (2H, q, J = 7.0 Hz, OCH_2CH_3), 4.57 (1H, m), and 6.59 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.03 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.0 Hz, OCH_2CH_3), 1.28–1.86 (16H, m), 1.71 (2H, br s, CH_2SiMe_3), 2.38 (2H, br q, J = 7 Hz, CH_2CH=C), 3.37 (1H, dt, J = ca. 9, 7 Hz), 3.49 (1H, m), 3.72 (1H, dt, J = 9.0, 7.0 Hz), 3.86 (1H, m), 4.16 (2H, q, J = 7.0 Hz, OCH_2CH_3), 4.57 (1H, m), and 5.65 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.07 (3C), 14.27, 17.23, 19.68, 25.48, 26.16, 28.76, 29.07, 29.33, 29.41, 29.71, 30.76, 60.35, 62.34, 67.61, 98.84, 129.94, 138.57, and 168.42; MS *m/z* (rel intensity) 384 (M^+, 34), 369 (82), 300 (72), 294 (88), 239 (83), 200 (94), and 157 (100); HRMS [Found: *m/z* 384.2689 (M^+). Calcd for $C_{21}H_{40}O_4Si$: M, 384.2697].

Ethyl 12-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)dodec-2-enoate (10c). An oil; IR (neat) 1710 (C=O), 1636 (C=C), 1248, 1174, 1035, and 852 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ −0.03 (9H, s, $SiMe_3$), 1.27 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.24–1.84 (20H, m), 1.77 (2H, br s, CH_2SiMe_3), 2.05 (2H, br q, J = 7 Hz, CH_2CH=C), 3.35 (1H, dt, J = 9.5, 6.6 Hz), 3.48 (1H, m), 3.70 (1H, dt, J = 9.5, 6.8 Hz), 3.84 (1H, m), 4.14 (2H, q, J = 7.1 Hz, OCH_2CH_3), 4.55 (1H, m), and 6.58 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.04 (9H, s, $SiMe_3$), 1.28 (3H, t, J = 7.0 Hz, OCH_2CH_3), 1.24–1.84 (20H, m), 1.70 (2H, br s, CH_2SiMe_3), 2.36 (2H, br q, J = 7 Hz, CH_2CH=C), 3.35 (1H, dt, J = ca. 9, 7 Hz), 3.48 (1H, m), 3.70 (1H, dt, J = ca. 9, 7 Hz), 3.84 (1H, m), 4.14 (2H, q, J = 7.0 Hz, OCH_2CH_3), 4.55 (1H, m), and 5.63 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.12 (3C), 14.23, 17.16, 19.64, 25.44, 26.17, 28.76, 29.38 (2C), 29.41 (2C), 29.43, 29.68, 30.72, 60.28, 62.25, 67.60, 98.74, 129.85, 139.15, and 168.36; MS *m/z* (rel intensity) 412 (M^+, 5), 397 (5), 328 (14), 322 (13), 313 (15), 279 (13), 267 (14), 224 (18), 185 (56), 156 (59), 85 (100), and 73 (68); HRMS [Found: *m/z* 412.3056 (M^+). Calcd for $C_{23}H_{44}O_4Si$: M, 412.3010].

Ethyl 12-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)hexadec-2-enoate (10d). An oil; IR (neat) 1710 (C=O), 1636 (C=C), 1249, 1173, 1035, and 852 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.24–1.87 (28H, m), 1.80 (2H, br s, CH_2SiMe_3), 2.06 (2H, br q, J = 7 Hz, CH_2CH=C), 3.38 (1H, dt, J = 9.5, 6.6 Hz), 3.50 (1H, m), 3.72 (1H, dt, J = 9.5, 6.8 Hz), 3.87 (1H, m), 4.17 (2H, q, J = 7.1 Hz, OCH_2CH_3), 4.55–4.59 (1H, m), and 6.60 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.02 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.0 Hz, OCH_2CH_3), 1.24–1.87 (28H, m), 1.71 (2H, br s, CH_2SiMe_3), 2.38 (2H, br q, J = 7 Hz, CH_2CH=C), 3.38 (1H, dt, J = 9.5, 6.6 Hz), 3.50 (1H, m), 3.72 (1H, dt, J = 9.5, 6.8 Hz), 3.87 (1H, m), 4.17 (2H, q, J = 7.0 Hz, OCH_2CH_3), 4.57 (1H, m), and 5.66 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.07 (3C), 14.28, 17.21, 19.69, 25.49, 26.23, 28.81, 29.11, 29.49 (3C), 29.55, 29.59 (2C), 29.63 (2C), 29.74, 30.77, 60.34, 62.33, 67.69, 98.83, 129.87, 138.70, and 168.45; MS *m/z* (rel intensity) 469 (M^++H, 87), 468 (M^+, 23), 455 (93), 440 (92), 387 (100), 311 (89), 297 (83), 268 (82), 220 (83), 175 (80), and 119 (76); HRMS [Found: *m/z* 469.3758 (M^++H). Calcd for $C_{27}H_{53}O_4Si$: M, 469.3715].

Reduction. To a stirred solution of **10a** (1075.4 mg, 2.902 mmol) in CH_2Cl_2 (100 cm^3) was added a solution of DIBAL-H (11.6 cm^3, 11.6 mmol; 1.0 mol dm^{-3} solution in cyclohexane) at −60 °C under Ar, and the mixture was stirred at that temperature for 2 h. After this was warmed to room temperature, MeOH and a saturated aqueous solution of Rochelle salt was added with vigorous stirring. Extraction with CH_2Cl_2 followed by drying and evaporation of the solvent gave an oily residue, which was chromatographed on silica gel (20 g) using hexane-AcOEt (98:2 to 75:25) as eluent to yield **15a** (880.9 mg, 91%). Compounds **15b–d** were prepared by the same procedure in 93, 78, and 78% yields, respectively.

9-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)non-2-en-1-ol (15a). An oil; IR (neat) 3440 (OH), 1655 (C=C), 1248, 1024, and 852 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ 0.02 (9H, s, $SiMe_3$), 1.30–2.08 (19H, m), 3.38 (1H, dt, J = 9.3, 6.6 Hz), 3.49 (1H, m), 3.73 (1H, dt, J = 9.3, 6.8 Hz), 3.86 (1H, m), 3.94 (2H, br s, CH_2OH), 4.57 (1H, m), and 5.28 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.30–2.08 (19H, m), 3.38 (1H, dt, J = ca. 9, 7 Hz), 3.49 (1H, m), 3.72 (1H,

dt, J = ca. 9, 7 Hz), 3.86 (1H, m), 4.06 (2H, br s, CH_2OH), 4.57 (1H, m), and 5.12 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.69 (3C), 18.85, 19.68, 25.49, 26.17, 28.05, 29.26, 29.63, 29.69, 30.77, 62.34, 67.61, 68.67, 98.84, 123.53, and 136.77; MS *m/z* (rel intensity) 328 (M^+, 2), 298 (2), 262 (3), 228 (3), 219 (4), 152 (8), 101 (16), 85 (100), and 75 (74); HRMS [Found: *m/z* 328.2455 (M^+). Calcd for $C_{18}H_{36}O_3Si$: M, 328.2435]; Analysis [Found: C, 65.51; H, 10.75%. Calcd for $C_{18}H_{36}O_3Si$: C, 65.80; H, 11.04%].

10-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)dec-2-en-1-ol (15b). An oil; IR (neat) 3450 (OH), 1655 (C=C), 1247, 1025, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.24–2.08 (21H, m), 3.38 (1H, dt, J = 9.5, 6.6 Hz), 3.50 (1H, m), 3.72 (1H, dt, J = 9.5, 6.8 Hz), 3.87 (1H, m), 3.95 (2H, d, J = 1.1 Hz, CH_2OH), 4.57 (1H, m), and 5.29 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.01 (9H, s, $SiMe_3$), 1.24–2.08 (21H, m), 3.38 (1H, dt, J = ca. 9, 7 Hz), 3.50 (1H, m), 3.72 (1H, dt, J = ca. 9, 7 Hz), 3.87 (1H, m), 4.06 (2H, br s, CH_2OH), 4.57 (1H, m), and 5.12 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.69 (3C), 18.85, 19.69, 25.50, 26.19, 28.10, 29.38, 29.40, 29.64, 29.72, 30.78, 62.34, 67.66, 68.68, 98.84, 123.59, and 136.72; MS *m/z* (rel intensity) 343 (M^++H, 27), 325 (6), 309 (4), 259 (100), 143 (80), 93 (89), and 75 (93); HRMS [Found: *m/z* 343.2648 (M^++H). Calcd for $C_{19}H_{39}O_3Si$: M, 343.2670].

12-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)dodec-2-en-1-ol (15c). An oil; IR (neat) 3450 (OH), 1655 (C=C), 1248, 1032, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.25–2.08 (25H, m), 3.38 (1H, dt, J = 9.5, 6.7 Hz), 3.50 (1H, m), 3.73 (1H, dt, J = 9.5, 6.9 Hz), 3.87 (1H, m), 3.95 (2H, d, J = 1.0 Hz, CH_2OH), 4.57 (1H, m), and 5.29 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.01 (9H, s, $SiMe_3$), 1.25–2.08 (25H, m), 3.38 (1H, dt, J = ca. 9, 7 Hz), 3.50 (1H, m), 3.73 (1H, dt, J = ca. 9, 7 Hz), 3.87 (1H, m), 4.06 (2H, br s, CH_2OH), 4.57 (1H, m), and 5.13 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.69 (3C), 18.84, 19.69, 25.50, 26.22, 28.12, 29.45 (2C), 29.51, 29.53, 29.70, 29.74, 30.78, 62.34, 67.69, 68.69, 98.84, 123.66, and 136.67; MS *m/z* (rel intensity) 371 (M^++H, 100), 370 (M^+, 17), 353 (9), 288 (96), 270 (73), 254 (26), 197 (34), 159 (79), 141 (75), and 59 (70); HRMS [Found: *m/z* 370.2878 (M^+). Calcd for $C_{21}H_{42}O_3Si$: M, 370.2905].

16-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)hexadec-2-en-1-ol (15d). An oil; IR (neat) 3450 (OH), 1655 (C=C), 1248, 1025, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.24–2.08 (33H, m), 3.38 (1H, dt, J = 9.5, 6.7 Hz), 3.50 (1H, m), 3.73 (1H, dt, J = 9.5, 6.9 Hz), 3.87 (1H, m), 3.95 (2H, d, J = 1.1 Hz, CH_2OH), 4.57 (1H, m), and 5.29 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.01 (9H, s, $SiMe_3$), 1.24–2.08 (33H, m), 3.38 (1H, dt, J = ca. 9, 7 Hz), 3.50 (1H, m), 3.73 (1H, dt, J = ca. 9, 7 Hz), 3.87 (1H, m), 4.06 (2H, br s, CH_2OH), 4.57 (1H, m), and 5.13 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.69 (3C), 18.85, 19.69, 25.51, 26.23, 28.14, 29.49 (2C), 29.60 (2C), 29.62 (2C), 29.64 (2C), 29.72, 29.76, 30.79, 62.33, 67.70, 68.70, 98.84, 123.71, and 136.65; MS *m/z* (rel intensity) 427 (M^++H, 100), 409 (15), 344 (98), 326 (85), 253 (63), 159 (79), 108 (76), and 59 (60); HRMS [Found: *m/z* 427.3582 (M^++H). Calcd for $C_{25}H_{51}O_3Si$: M, 427.3609].

Acetylation/Pivaloylation. To a stirred solution of **15a** (880.9 mg, 2.681 mmol) in dry pyridine (5.0 cm^3) was added acetic anhydride (0.30 cm^3, 3.22 mmol) at 0 °C. A silica-gel drying tube was attached to the flask, and the mixture was stirred at room temperature for 20 h. AcOEt and HCl aq (ca. 1 mol dm^{-3}) were added, and the resultant two layers were separated. The organic layer was washed successively with HCl aq and brine, and then dried. Evaporation of the solvent followed by silica gel (11 g) column chromatography using hexane–AcOEt (98:2 to 97:3) as eluent afforded **16a** (938.0 mg, 94%). Similarly, **16b–d** were obtained in 98, 90, and 88% yields, respectively. For the synthesis of **16e** (92% yield), pivaloyl chloride was used instead of acetic anhydride.

9-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)non-2-enyl Acetate (16a). An oil; IR (neat) 1739 (C=O), 1655 (C=C), 1249, 1025, and 849 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.30–2.10 (18H, m), 2.07 (3H, s, Ac), 3.38 (1H, dt, J = 9.5, 6.6 Hz), 3.49 (1H, m), 3.72 (1H, dt, J = 9.5, 6.8 Hz), 3.86 (1H, m), 4.40 (2H, br s, CH_2OAc), 4.57 (1H, m), and 5.32 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.30–2.10 (18H, m), 2.06 (3H, s, Ac), 3.37 (1H, dt, J = 9.4, 6.5 Hz), 3.49 (1H, m), 3.72 (1H, dt, J = 9.4, 6.8 Hz), 3.86 (1H, m), 4.51 (2H, br s, CH_2OAc), 4.57 (1H, m), and 5.23 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.72 (3C), 19.17, 19.67, 21.07, 25.48, 26.15, 28.18, 29.28, 29.41, 29.69, 30.76, 62.31, 67.60, 70.18, 98.82, 127.13, 131.71, and 170.97; MS *m/z* (rel intensity) 370 (M^+, 7), 311 (100), 280 (25), 227 (89), 173 (91), 129 (93), 118 (91), and 77 (93); HRMS [Found: *m/z* 370.2537 (M^+). Calcd for $C_{20}H_{38}O_4Si$: M, 370.2540].

10-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)dec-2-enyl Acetate (16b). An oil; IR (neat) 1740 (C=O), 1655 (C=C), 1248, 1033, and 847 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.28−2.09 (20H, m), 2.07 (3H, s, Ac), 3.37 (1H, dt, J = 9.5, 6.5 Hz), 3.50 (1H, m), 3.73 (1H, dt, J = 9.5, 6.8 Hz), 3.87 (1H, m), 4.40 (2H, br s, CH_2OAc), 4.57 (1H, m), and 5.32 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.28–2.09 (20H, m), 2.06 (3H, s, Ac), 3.37 (1H, dt, J = ca. 9, 7 Hz), 3.50 (1H, m), 3.72 (1H, dt, J = ca. 9, 7 Hz), 3.87 (1H, m), 4.51 (2H, br s, CH_2OAc), 4.57 (1H, m), and 5.23 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.71 (3C), 19.17, 19.70, 21.09, 25.49, 26.19, 28.24, 29.39 (2C), 29.43, 29.72, 30.77, 62.35, 67.66, 70.21, 98.85, 127.21, 131.67, and 170.99; MS *m/z* (rel intensity) 384 (M^+, 4), 369 (2), 325 (66), 295 (24), 259 (25), 241 (100), 173 (77), 150 (99), and 86 (92); HRMS [Found: *m/z* 384.2663 (M^+). Calcd for $C_{21}H_{40}O_4Si$: M, 384.2697].

12-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)dodec-2-enyl Acetate (16c). An oil; IR (neat) 1741 (C=O), 1655 (C=C), 1248, 1033, and 846 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.23–2.09 (24H, m), 2.07 (3H, s, Ac), 3.38 (1H, dt, J = 9.5, 6.6 Hz), 3.50 (1H, m), 3.72 (1H, dt, J = 9.5, 6.9 Hz), 3.87 (1H, m), 4.40 (2H, br s, CH_2OAc), 4.57 (1H, m), and 5.32 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.23–2.09 (24H, m), 2.06 (3H, s, Ac), 3.38 (1H, dt, J = ca. 9, 7 Hz), 3.50 (1H, m), 3.72 (1H, dt, J = ca. 9, 7 Hz), 3.87 (1H, m), 4.51 (2H, br s, CH_2OAc), 4.57 (1H, m), and 5.24 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.72 (3C), 19.16, 19.69, 21.08, 25.49, 26.23, 28.27, 29.46 (2C), 29.47 (2C), 29.52, 29.74, 30.78, 62.34, 67.68, 70.22, 98.84, 127.27, 131.62, and 170.98; MS *m/z* (rel intensity) 412 (M^+, 39), 386 (28), 366 (24), 354 (95), 330 (99), 271 (100), 252 (93), 180 (90), and 87 (88); HRMS [Found: *m/z* 412.3026 (M^+). Calcd for $C_{23}H_{44}O_4Si$: M, 412.3010].

16-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)hexadec-2-enyl Acetate (16d). An oil; IR (neat) 1741 (C=O), 1655 (C=C), 1248, 1034, and 848 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.24–2.09 (32H, m), 2.07 (3H, s, Ac), 3.38 (1H, dt, J = 9.5, 6.7 Hz), 3.50 (1H, m), 3.73 (1H, dt, J = 9.5,

6.9 Hz), 3.87 (1H, m), 4.40 (2H, br s, CH_2OAc), 4.57 (1H, m), and 5.34 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.01 (9H, s, $SiMe_3$), 1.24–2.09 (32H, m), 2.07 (3H, s, Ac), 3.38 (1H, dt, J = ca. 9, 7 Hz), 3.50 (1H, m), 3.73 (1H, dt, J = ca. 9, 7 Hz), 3.87 (1H, m), 4.52 (2H, br s, CH_2OAc), 4.57 (1H, m), and 5.24 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.71 (3C), 19.17, 19.69, 21.08, 25.50, 26.23, 28.28, 29.48 (3C), 29.56, 29.60 (3C), 29.64 (2C), 29.75, 30.78, 62.34, 67.70, 70.23, 98.84, 127.32, 131.61, and 170.98; MS *m/z* (rel intensity) 468 (M^+, 14), 410 (66), 379 (57), 326 (65), 237 (56), 185 (100), 177 (74), and 102 (62); HRMS [Found: *m/z* 468.3662 (M^+). Calcd for $C_{27}H_{52}O_4Si$: M, 468.3637].

9-(Tetrahydropyran-2-yloxy)-2-(trimethylsilylmethyl)non-2-enyl Pivalate (16e). An oil; IR (neat) 1730 (C=O), 1655 (C=C), 1151, 1034, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.02 (9H, s, $SiMe_3$), 1.20 (9H, s, Piv), 1.29–2.07 (16H, m), 1.53 (2H, br s, C$H_2$$SiMe_3$), 3.37 (1H, dt, J = 9.5, 6.5 Hz), 3.49 (1H, m), 3.72 (1H, dt, J = 9.5, 6.9 Hz), 3.85 (1H, m), 4.38 (2H, br s, CH_2OPiv), 4.56 (1H, m), and 5.28 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.20 (9H, s, Piv), 1.29–2.07 (16H, m), 1.53 (2H, br s, C$H_2$$SiMe_3$), 3.36 (1H, dt, J = ca. 9, 7 Hz), 3.49 (1H, m), 3.72 (1H, dt, J = 9.5, 6.9 Hz), 3.85 (1H, m), 4.49 (2H, br s, CH_2OPiv), 4.56 (1H, m), and 5.20 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.79 (3C), 18.86, 19.67, 25.47, 26.15, 27.24 (3C), 28.01, 29.23, 29.47, 29.70, 30.75, 38.81, 62.30, 67.60, 69.35, 98.80, 125.77, 131.98, and 178.27; MS *m/z* (rel intensity) 412 (M^+, 3), 322 (9), 310 (100), 226 (92), 175 (74), 159 (75), 121 (90), 93 (97), and 79 (97); HRMS [Found: *m/z* 412.3034 (M^+). Calcd for $C_{23}H_{44}O_4Si$: M, 412.3010].

Hydrolysis. Compound **10a** (2.446 g, 6.600 mmol) was dissolved in THF (40 cm^3), and to this was added 5% HCl aq (10 cm^3). After this mixture was stirred at room temperature for 14 h, $NaHCO_3$ was added, and the new mixture was extracted with Et_2O and dried. Evaporation of the solvent followed by silica gel (50 g) column chromatography using hexane–AcOEt (99:1 to 90:10) as eluent afforded **11a** (1.629 g, 86%). Compounds **11b–d** and **17a–e** were prepared by the same procedure in 91, 80, 82, 90, 87, 76, 70, and 96% yields, respectively.

Ethyl 9-Hydroxy-2-(trimethylsilylmethyl)non-2-enoate (11a). An oil; IR (neat) 3400 (OH), 1714 (C=O), 1638 (C=C), 1252, 1176, and 856 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.28 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.30–1.60 (8H, m), 1.68 (1H, br, OH), 1.79 (2H, br s, C$H_2$$SiMe_3$), 2.08 (2H, br q, J = 7 Hz, CH_2CH=C), 3.63 (2H, t, J = 6.4 Hz, CH_2OH), 4.16 (2H, q, J = 7.1 Hz, OC$H_2$$CH_3$), and 6.59 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.03 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.30–1.60 (8H, m), 1.68 (1H, br, OH), 1.72 (2H, br s, C$H_2$$SiMe_3$), 2.39 (2H, br q, J = 7 Hz, CH_2CH=C), 3.62 (2H, t, J = 6.4 Hz, CH_2OH), 4.16 (2H, q, J = 7.1 Hz, OC$H_2$$CH_3$), and 5.64 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.09 (3C), 14.26, 17.23, 25.60, 28.76, 28.99, 29.24, 32.65, 60.38, 62.91, 130.02, 138.41, and 168.42; MS *m/z* (rel intensity) 286 (M^+, 43), 271 (65), 241 (51), 200 (44), 185 (100), and 73 (99); HRMS [Found: *m/z* 286.1947 (M^+). Calcd for $C_{15}H_{30}O_3Si$: M, 286.1965]; Analysis [Found: C, 62.75; H, 10.31%. Calcd for $C_{15}H_{30}O_3Si$: C, 62.89; H, 10.55%].

Ethyl 10-Hydroxy-2-(trimethylsilylmethyl)dec-2-enoate (11b). An oil; IR (neat) 3360 (OH), 1709 (C=O), 1635 (C=C), 1248, 1174, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ −0.02 (9H, s, $SiMe_3$), 1.28 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.29–1.60 (11H, m), 1.79 (2H, br s, C$H_2$$SiMe_3$), 2.07 (2H, br q, J = 7 Hz, CH_2CH=C), 3.63 (2H, t, J = 6.5 Hz, CH_2OH), 4.16 (2H, q, J = 7.1 Hz, OC$H_2$$CH_3$), and 6.59 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.03 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.29–1.60 (11H, m), 1.72 (2H, br s, C$H_2$$SiMe_3$), 2.38 (2H, br q, J = 7 Hz, CH_2CH=C), 3.63 (2H, t, J = 6.5 Hz, CH_2OH), 4.16 (2H, q, J = 7.1 Hz, OC$H_2$$CH_3$), and 5.65 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.08 (3C), 14.26, 17.22, 25.62, 28.72, 29.04, 29.24, 29.40, 32.71, 60.36, 62.96, 129.97, 138.52, and 168.43; MS *m/z* (rel intensity) 300 (M^+, 17), 285 (24), 226 (24), 185 (85), and 73 (100); HRMS [Found: *m/z* 300.2072 (M^+). Calcd for $C_{16}H_{32}O_3Si$: M, 300.2122].

Ethyl 12-Hydroxy-2-(trimethylsilylmethyl)dodec-2-enoate (11c). An oil; IR (neat) 3400 (OH), 1710 (C=O), 1635 (C=C), 1248, 1175, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.0 Hz, OCH_2CH_3), 1.27–1.60 (15H, m), 1.79 (2H, br s, C$H_2$$SiMe_3$), 2.07 (2H, br q, J = 7 Hz, CH_2CH=C), 3.63 (2H, t, J = 6.5 Hz, CH_2OH), 4.16 (2H, q, J = 7.0 Hz, OC$H_2$$CH_3$), and 6.59 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.02 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.0 Hz, OCH_2CH_3), 1.27–1.60 (15H, m), 1.72 (2H, br s, C$H_2$$SiMe_3$), 2.38 (2H, br q, J = 7 Hz, CH_2CH=C), 3.63 (2H, t, J = 6.5 Hz, CH_2OH), 4.16 (2H, q, J = 7.0 Hz, OC$H_2$$CH_3$), and 5.65 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.19 (3C), 14.14, 17.09, 25.63, 28.67, 28.97, 29.28 (2C), 29.32, 29.37, 32.62, 60.26, 62.71, 129.79, 138.56, and 168.36; MS *m/z* (rel intensity) 328 (M^+, 21), 313 (37), 283 (22), 267 (19), 224 (17), 200 (19), 185 (100), and 73 (93); HRMS [Found: *m/z* 328.2474 (M^+). Calcd for $C_{18}H_{36}O_3Si$: M, 328.2435].

Ethyl 12-Hydroxy-2-(trimethylsilylmethyl)hexadec-2-enoate (11d). An oil; IR (neat) 3370 (OH), 1710 (C=O), 1636 (C=C), 1248, 1175, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.24–1.60 (23H, m), 1.79 (2H, br s, C$H_2$$SiMe_3$), 2.07 (2H, br q, J = 7 Hz, CH_2CH=C), 3.63 (2H, t, J = 6.6 Hz, CH_2OH), 4.16 (2H, q, J = 7.1 Hz, OC$H_2$$CH_3$), and 6.60 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ −0.02 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.24–1.60 (23H, m), 1.72 (2H, br s, C$H_2$$SiMe_3$), 2.38 (2H, br q, J = 7 Hz, CH_2CH=C), 3.63 (2H, t, J = 6.6 Hz, CH_2OH), 4.16 (2H, q, J = 7.1 Hz, OC$H_2$$CH_3$), and 5.65 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.07 (3C), 14.27, 17.22, 25.72, 28.81, 29.10, 29.41 (2C), 29.47 (2C), 29.53, 29.56, 29.60 (2C), 32.79, 60.36, 63.07, 129.88, 138.71, and 168.48; MS *m/z* (rel intensity) 385 (M^++H, 25), 370 (100), 340 (51), 342 (67), 281 (30), 200 (42), 185 (56), 97 (78), and 83 (77); HRMS [Found: *m/z* 385.3151 (M^++H). Calcd for $C_{22}H_{45}O_3Si$: M, 385.3140].

9-Hydroxy-2-(trimethylsilylmethyl)non-2-enyl Acetate (17a). An oil; IR (neat) 3410 (OH), 1739 (C=O), 1655 (C=C), 1249, 1025, and 849 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.29–1.60 (11H, m), 1.96 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 3.63 (2H, t, J = 6.6 Hz, CH_2OH), 4.40 (2H, br s, CH_2OAc), and 5.32 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.29–1.60 (11H, m), 2.06 (3H, s, Ac), 2.07 (2H, br q, J = 7 Hz, CH_2CH=C), 3.63 (2H, t, J = 6.6 Hz, CH_2OH), 4.51 (2H, br s, CH_2OAc), and 5.23 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.72 (3C), 19.17, 21.07, 25.63, 28.15, 29.19, 29.41, 32.70, 62.96, 70.17, 127.04, 131.77, and 171.00; MS *m/z* (rel intensity) 226 (M^+−AcOH, 39), 133 (92), 117 (68), 81 (100), 75 (96), and 43 (96); HRMS [Found: *m/z* 226.1747 (M^+−AcOH). Calcd for $C_{13}H_{26}OSi$: M, 226.1754].

10-Hydroxy-2-(trimethylsilylmethyl)dec-2-enyl Acetate

(17b). An oil; IR (neat) 3410 (OH), 1739 (C=O), 1655 (C=C), 1249, 1024, 848, and 757 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.27–1.60 (13H, m), 1.95 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 3.64 (2H, t, J = 6.6 Hz, CH_2OH), 4.40 (2H, br s, CH_2OAc), and 5.32 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.27–1.60 (13H, m), 2.05 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 3.64 (2H, t, J = 6.6 Hz, CH_2OH), 4.52 (2H, br s, CH_2OAc), and 5.23 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.72 (3C), 19.18, 21.07, 25.65, 28.21, 29.29, 29.35, 29.38, 32.74, 63.03, 70.18, 127.13, 131.73, and 171.00; MS *m/z* (rel intensity) 301 (M^++H, 6), 259 (16), 241 (94), 226 (7), 199 (8), 184 (20), 168 (24), 134 (100), and 118 (96); HRMS [Found: *m/z* 301.2246 (M^++H). Calcd for $C_{16}H_{33}O_3Si$: M, 301.2200].

12-Hydroxy-2-(trimethylsilylmethyl)dodec-2-enyl Acetate (17c). An oil; IR (neat) 3400 (OH), 1740 (C=O), 1656 (C=C), 1249, 1024, and 848 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.25–1.60 (17H, m), 1.95 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 3.63 (2H, t, J = 6.6 Hz, CH_2OH), 4.40 (2H, br s, CH_2OAc), and 5.32 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.25–1.60 (17H, m), 2.04 (2H, br q, J = 7 Hz, CH_2CH=C), 2.06 (3H, s, Ac), 3.63 (2H, t, J = 6.6 Hz, CH_2OH), 4.51 (2H, br s, CH_2OAc), and 5.23 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.72 (3C), 19.17, 21.08, 25.71, 28.24, 29.38, 29.41, 29.45 (2C), 29.51, 32.78, 63.05, 70.22, 127.24, 131.64, and 171.00; MS *m/z* (rel intensity) 329 (M^++H, 80), 287 (73), 270 (77), 197 (88), 110 (99), 76 (94), and 53 (100); HRMS [Found: *m/z* 329.2533 (M^++H). Calcd for $C_{18}H_{37}O_3Si$: M, 329.2513].

16-Hydroxy-2-(trimethylsilylmethyl)hexadec-2-enyl Acetate (17d). An oil; IR (neat) 3370 (OH), 1741 (C=O), 1655 (C=C), 1249, 1024, and 848 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.24–1.60 (25H, m), 1.95 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 3.64 (2H, t, J = 6.6 Hz, CH_2OH), 4.40 (2H, br s, CH_2OAc), and 5.33 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.24–1.60 (25H, m), 2.04 (2H, br q, J = 7 Hz, CH_2CH=C), 2.06 (3H, s, Ac), 3.64 (2H, t, J = 6.6 Hz, CH_2OH), 4.52 (2H, br s, CH_2OAc), and 5.24 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.71 (3C), 19.17, 21.08, 25.73, 28.27, 29.41, 29.46, 29.47 (2C), 29.54, 29.59 (2C), 29.63 (2C), 32.80, 63.07, 70.24, 127.32, 131.61, and 171.00; MS *m/z* (rel intensity) 384 (M^+, 1), 342 (1), 252 (1), 133 (59), 117 (69), 95 (67), 81 (86), and 73 (100); HRMS [Found: *m/z* 384.3019 (M^+). Calcd for $C_{22}H_{44}O_3Si$: M, 384.3061].

9-Hydroxy-2-(trimethylsilylmethyl)non-2-enyl Pivalate (17e). An oil; IR (neat) 3370 (OH), 1728 (C=O), 1655 (C=C), 1284, 1248, 1155, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.21 (9H, s, Piv), 1.30–1.60 (9H, m), 1.54 (2H, br s, CH_2SiMe_3), 1.96 (2H, m, CH_2CH=C), 3.64 (2H, t, J = 6.5 Hz, CH_2OH), 4.39 (2H, d, J = 0.8 Hz, CH_2OPiv), and 5.28 (1H, br t, J = 7 Hz, CH=C); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.21 (9H, s, Piv), 1.30–1.60 (9H, m), 1.54 (2H, br s, CH_2SiMe_3), 2.05 (2H, m, CH_2CH=C), 3.63 (2H, t, J = 6.5 Hz, CH_2OH), 4.50 (2H, br s, CH_2OPiv), and 5.21 (1H, br t, J = 7 Hz, CH=C); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.79 (3C), 18.87, 25.63, 27.22 (3C), 27.97, 29.13, 29.47, 32.70, 38.81, 62.95, 69.35, 125.69, 132.05, and 178.33; MS *m/z* (rel intensity) 329 (M^++H, 3), 328 (M^+, 3), 315 (5), 298 (8), 241 (11), 228 (57), 211 (29), 177 (74), 161 (74), 139 (100), 98 (97), and 82 (92); HRMS [Found: *m/z* 328.2424 (M^+). Calcd for $C_{18}H_{36}O_3Si$: M, 328.2435].

Oxidation. A solution of oxalyl chloride (0.91 cm^3, 10.5 mmol) and DMSO (1.49 cm^3, 20.9 mmol) in CH_2Cl_2 (20 cm^3) was stirred at −55 °C for 10 min under Ar, and to this was added a solution of **11a** (999.7 mg, 3.490 mmol) in CH_2Cl_2 (10 cm^3). After this was stirred for 1 h, Et_3N was added, and the flask was warmed to room temperature with continuous stirring for 30 min. Water was added, and the mixture was extracted with CH_2Cl_2. Without drying, the solvent was evaporated off, and the residue was dissolved in *t*-BuOH (55 cm^3) and 2-methylbut-2-ene (30 cm^3). A solution of $NaClO_2$ (1.26 g, 14.0 mmol) and NaH_2PO_4•$2H_2O$ (1.09 g, 6.98 mmol) in water (30 cm^3) was added slowly with vigorous stirring, and the resultant yellow solution was stirred at room temperature until it become clear solution (about 15 min). An aqueous solution of HCl (ca. 1 mol dm^{-3}) was added, and the mixture was extracted with CH_2Cl_2 and dried. Evaporation of the solvent followed by silica gel (12 g) column chromatography using hexane–AcOEt (95:5 to 80:20) as eluent afforded **8a** (917.3 mg, 88%). By the same procedure, **8b–d** and **14a–e** were obtained in 80, 86, 93, 91, 82, 88, 96, and 90% yields, respectively.

8-Ethoxycarbonyl-9-(trimethylsilyl)non-7-enoic Acid (8a). An oil; IR (neat) 2800–3500 (OH), 1712 (C=O), 1635 (C=C), 1248, 1175, and 852 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.28 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.33–1.69 (6H, m), 1.79 (2H, br s, CH_2SiMe_3), 2.09 (2H, br q, J = 7 Hz, CH_2CH=C), 2.35 (2H, t, J = 7.4 Hz, CH_2CO_2H), 4.16 (2H, q, J = 7.1 Hz, OCH_2CH_3), 6.58 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ −0.03 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.33–1.69 (6H, m), 1.72 (2H, br s, CH_2SiMe_3), 2.34 (2H, t, J = 7.4 Hz, CH_2CO_2H), 2.39 (2H, br q, J = 7 Hz, CH_2CH=C), 4.16 (2H, q, J = 7.1 Hz, OCH_2CH_3), 5.64 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.22 (3C), 14.11, 17.13, 24.38, 28.31, 28.72, 29.21, 33.82, 60.33, 130.07, 138.04, 168.32, and 179.59; MS *m/z* (rel intensity) 283 (M^+−OH, 30), 269 (47), 227 (17), 211 (55), 195 (47), 153 (22), 129 (19), 107 (19), 73 (100), and 45 (88); HRMS [Found: *m/z* 283.1740 (M^+−OH). Calcd for $C_{15}H_{27}O_3Si$: M, 283.1730]; Analysis [Found: C, 59.67; H, 9.10%. Calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39%].

9-Ethoxycarbonyl-10-(trimethylsilyl)dec-8-enoic Acid (8b). An oil; IR (neat) 2800–3500 (OH), 1711 (C=O), 1635 (C=C), 1248, 1174, and 852 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ −0.02 (9H, s, $SiMe_3$), 1.28 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.32–1.68 (8H, m), 1.79 (2H, br s, CH_2SiMe_3), 2.08 (2H, br q, J = 7 Hz, CH_2CH=C), 2.34 (2H, t, J = 7.4 Hz, CH_2CO_2H), 4.16 (2H, q, J = 7.1 Hz, OCH_2CH_3), 6.58 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ −0.03 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.32–1.68 (8H, m), 1.72 (2H, br s, CH_2SiMe_3), 2.34 (2H, t, J = 7.4 Hz, CH_2CO_2H), 2.38 (2H, br q, J = 7 Hz, CH_2CH=C), 4.16 (2H, q, J = 7.1 Hz, OCH_2CH_3), 5.64 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.09 (3C), 14.25, 17.24, 24.53, 28.56, 28.87, 28.97, 29.03, 33.94, 60.41, 130.08, 138.34, 168.44, and 179.85; MS *m/z* (rel intensity) 314 (M^+, 7), 299 (26), 285 (7), 269 (17), 256 (16), 226 (100), 176 (37), 160 (39), 121 (39), and 85 (88); HRMS [Found: *m/z* 314.1878 (M^+). Calcd for $C_{16}H_{30}O_4Si$: M, 314.1914].

11-Ethoxycarbonyl-12-(trimethylsilyl)dodec-10-enoic Acid (8c). An oil; IR (neat) 2800–3400 (OH), 1710 (C=O), 1636 (C=C), 1248, 1174, and 852 cm^{-1}; ^1H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.28–1.67 (12H, m), 1.79 (2H, br s, CH_2SiMe_3), 2.07 (2H, br q, J = 7 Hz, CH_2CH=C), 2.34 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.16 (2H, q, J = 7.1 Hz, OCH_2CH_3), 6.59 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ −0.02 (9H, s,

$SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.28–1.67 (12H, m), 1.72 (2H, br s, CH_2SiMe_3), 2.34 (2H, t, J = 7.5 Hz, CH_2CO_2H), 2.38 (2H, br q, J = 7 Hz, CH_2CH=C), 4.16 (2H, q, J = 7.1 Hz, OCH_2CH_3), 5.65 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.07 (3C), 14.27, 17.22, 24.62, 28.75, 28.96, 29.06, 29.09, 29.22, 29.35, 33.95, 60.39, 129.94, 138.62, 168.49, and 179.65; MS *m/z* (rel intensity) 342 (M^+, 3), 328 (46), 298 (23), 254 (27), 207 (46), 186 (100), 179 (31), 149 (32), 95 (49), 81 (77), and 75 (75); HRMS [Found: *m/z* 342.2180 (M^+). Calcd for $C_{18}H_{34}O_4Si$: M, 342.2227].

15-Ethoxycarbonyl-16-(trimethylsilyl)hexadec-7-enoic Acid (8d). An oil; IR (neat) 2800–3400 (OH), 1710 (C=O), 1636 (C=C), 1248, 1174, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ −0.01 (9H, s, $SiMe_3$), 1.29 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.24–1.67 (20H, m), 1.80 (2H, br s, CH_2SiMe_3), 2.07 (2H, br q, J = 7 Hz, CH_2CH=C), 2.36 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.17 (2H, q, J = 7.1 Hz, OCH_2CH_3), 6.60 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ −0.02 (9H, s, $SiMe_3$), 1.30 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.24–1.67 (20H, m), 1.72 (2H, br s, CH_2SiMe_3), 2.36 (2H, t, J = 7.5 Hz, CH_2CO_2H), 2.38 (2H, br q, J = 7 Hz, CH_2CH=C), 4.17 (2H, q, J = 7.1 Hz, OCH_2CH_3), 5.66 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −1.07 (3C), 14.28, 17.22, 24.67, 28.81, 29.03, 29.11, 29.21, 29.39, 29.47 (2C), 29.51, 29.54, 29.56, 33.81, 60.38, 129.88, 138.73, 168.49, and 178.79; MS *m/z* (rel intensity) 399 (M^++H, 9), 385 (72), 354 (100), 338 (34), 324 (36), 310 (55), 264 (89), 235 (82), 200 (64), 169 (75), and 157 (77); HRMS [Found: *m/z* 399.2911 (M^++H). Calcd for $C_{22}H_{43}O_4Si$: M, 399.2932].

9-Acetoxy-8-(trimethylsilylmethyl)non-7-enoic Acid (14a). An oil; IR (neat) 2800–3500 (OH), 1739 (C=O), 1711 (C=O), 1248, 1024, and 847 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.31–1.69 (6H, m), 1.53 (2H, br s, CH_2SiMe_3), 1.96 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 2.35 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.40 (2H, br s, CH_2OAc), 5.31 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.31–1.69 (6H, m), 1.53 (2H, br s, CH_2SiMe_3), 2.06 (2H, br q, J = 7 Hz, CH_2CH=C), 2.06 (3H, s, Ac), 2.34 (2H, t, J = 7.4 Hz, CH_2CO_2H), 4.51 (2H, br s, CH_2OAc), 5.22 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.74 (3C), 19.20, 21.06, 24.56, 28.00, 28.81, 29.06, 33.94, 70.10, 126.67, 131.99, 171.05, and 179.81; MS *m/z* (rel intensity) 241 (M^+−OAc, 31), 226 (14), 159 (21), 151 (39), 129 (56), 69 (100), and 57 (61); HRMS [Found: *m/z* 241.1609 (M^+−OAc). Calcd for $C_{13}H_{25}O_2Si$: M, 241.1624].

10-Acetoxy-9-(trimethylsilylmethyl)dec-8-enoic Acid (14b). An oil; IR (neat) 2800–3500 (OH), 1739 (C=O), 1710 (C=O), 1249, 1024, and 849 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.30–1.69 (8H, m), 1.54 (2H, br s, CH_2SiMe_3), 1.95 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 2.35 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.40 (2H, br s, CH_2OAc), 5.31 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.30–1.69 (8H, m), 1.54 (2H, br s, CH_2SiMe_3), 2.05 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 2.34 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.51 (2H, br s, CH_2OAc), 5.22 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.73 (3C), 19.18, 21.07, 24.57, 28.12, 28.92, 28.98, 29.22, 33.94, 70.17, 126.95, 131.82, 171.07, and 179.74; MS *m/z* (rel intensity) 314 (M^+, 1), 313 (M^+−H, 2), 285 (27), 257 (47), 239 (100), 213 (34), 185 (40), 169 (38), 98 (43), and 70 (54); HRMS [Found: *m/z* 314.1901 (M^+). Calcd for $C_{16}H_{30}O_4Si$: M, 314.1914].

12-Acetoxy-11-(trimethylsilylmethyl)dodec-10-enoic Acid (14c). An oil; IR (neat) 2800–3500 (OH), 1740 (C=O), 1711 (C=O), 1249, 1024, and 849 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.25–1.67 (12H, m), 1.54 (2H, br s, CH_2SiMe_3), 1.95 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 2.34 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.40 (2H, br s, CH_2OAc), 5.32 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.25–1.67 (12H, m), 1.54 (2H, br s, CH_2SiMe_3), 2.04 (2H, br q, J = 7 Hz, CH_2CH=C), 2.06 (3H, s, Ac), 2.34 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.51 (2H, br s, CH_2OAc), 5.23 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.72 (3C), 19.18, 21.09, 24.66, 28.23, 29.00, 29.15, 29.29, 29.35, 29.42, 33.92, 70.23, 127.21, 131.67, 171.07, and 179.40; MS *m/z* (rel intensity) 342 (M^+, 1), 301 (8), 268 (15), 211 (17), 192 (18), 149 (29), 136 (61), 107 (92), 80 (89), 59 (100), and 54 (99); HRMS [Found: *m/z* 342.2182 (M^+). Calcd for $C_{18}H_{34}O_4Si$: M, 342.2227].

16-Acetoxy-15-(trimethylsilylmethyl)hexadec-14-enoic Acid (14d). An oil; IR (neat) 2800-3500 (OH), 1740 (C=O), 1711 (C=O), 1249, 1024, and 847 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.23–1.67 (20H, m), 1.55 (2H, br s, CH_2SiMe_3), 1.95 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 2.34 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.40 (2H, br s, CH_2OAc), 5.33 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ 0.01 (9H, s, $SiMe_3$), 1.23–1.67 (20H, m), 1.54 (2H, br s, CH_2SiMe_3), 2.05 (2H, br q, J = 7 Hz, CH_2CH=C), 2.07 (3H, s, Ac), 2.34 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.52 (2H, br s, CH_2OAc), 5.24 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.71 (3C), 19.16, 21.09, 24.67, 28.27, 29.04, 29.22, 29.41, 29.47 (2C), 29.54, 29.57 (2C), 29.59, 33.88, 70.26, 127.34, 131.60, 171.06, and 179.09; MS *m/z* (rel intensity) 339 (M^+−OAc, 100), 324 (90), 267 (83), 249 (87), 193 (38), 151 (68), 134 (76), 93 (86), and 74 (95); HRMS [Found: *m/z* 339.2696 (M^+−OAc). Calcd for $C_{20}H_{39}O_2Si$: M, 339.2721].

9-Pivaloyloxy-8-(trimethylsilylmethyl)non-7-enoic Acid (14e). An oil; IR (neat) 2800–3400 (OH), 1728 (C=O), 1711 (C=O), 1282, 1248, 1153, and 849 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *Z*-isomer: δ 0.03 (9H, s, $SiMe_3$), 1.21 (9H, s, Piv), 1.30–1.68 (6H, m), 1.53 (2H, br s, CH_2SiMe_3), 1.96 (2H, m, CH_2CH=C), 2.35 (2H, t, J = 7.5 Hz, CH_2CO_2H), 4.39 (2H, br s, CH_2OPiv), 5.27 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); for *E*-isomer: δ 0.00 (9H, s, $SiMe_3$), 1.20 (9H, s, Piv), 1.30–1.68 (6H, m), 1.53 (2H, br s, CH_2SiMe_3), 2.06 (2H, m, CH_2CH=C), 2.34 (2H, t, J = 7.4 Hz, CH_2CO_2H), 4.49 (2H, br s, CH_2OPiv), 5.20 (1H, br t, J = 7 Hz, CH=C), and 9–11 (1H, very br, CO_2H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer: δ −0.78 (3C), 18.92, 24.57, 27.24 (3C), 27.84, 28.79, 29.14, 33.96, 38.82, 69.30, 125.35, 132.28, 178.34, and 179.85; MS *m/z* (rel intensity) 342 (M^+, 6), 312 (40), 256 (38), 240 (100), 225 (36), 168 (49), and 117 (33); HRMS [Found: *m/z* 342.2271 (M^+). Calcd for $C_{18}H_{34}O_4Si$: M, 342.2227].

Cyclization. To a stirred solution of **8a** (237.0 mg, 0.789 mmol) in CH_2Cl_2 (1.5 cm^3) was added oxalyl chloride (0.21 cm^3, 2.37 mmol) under a $CaCl_2$ drying tube. This was heated to 50 °C for 2 h, and then the mixture was evaporated to dryness. The resultant acid chloride was dissolved in CH_2Cl_2 (10 cm^3), which was then added to a stirred solution of $AlCl_3$ (315.5 mg, 2.366 mmol) in CH_2Cl_2 (70 cm^3) under Ar. After the contents were heated to reflux for 2.5 h, the flask was cooled to room temperature, and HCl aq (ca. 1 mol dm^{-3}) was added. Extraction with CH_2Cl_2, drying,

followed by evaporation of the solvent afforded an oily residue, which was chromatographed on silica gel (20 g) using pentane–Et_2O (95:5 to 80:20) as eluent to give **7** (116.6 mg, 70%). See text for the cyclization of related compounds.

Ethyl 2-(2-Oxocycloheptyl)acrylate (7). An oil; IR (neat) 1709 (C=O), 1634 (C=C), and 1174 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.24–2.03 (8H, m), 2.56 (1H, ddd, J = 4.0, 11.4, 15.4 Hz, C*H*HCO), 2.72 (1H, ddt, J = 0.8, 15.4, 4.5 Hz, CH*H*CO), 3.68 (1H, br dd, J = 2, 11 Hz, COCHC=C), 4.16 (1H, dq, J = 10.7, 7.1 Hz, OC*H*HCH$_3$), 4.16 (1H, dq, J = 10.7, 7.1 Hz, OCH*H*CH$_3$), 5.63 (1H, br s, C=C*H*H), and 6.35 (1H, br s, C=CH*H*); ^{13}C NMR ($CDCl_3$) δ 14.08 (CH_3), 23.57 (CH_2), 28.81 (CH_2), 29.66 (CH_2), 29.90 (CH_2), 43.62 (CH_2), 53.44 (CH), 60.88 (CH_2), 125.79 (CH_2), 140.84 (C), 166.52 (CO), and 212.85 (CO); MS *m/z* (rel intensity) 210 (M^+, 25), 194 (46), 182 (26), 165 (67), 136 (41), 121 (43), 91 (53), 79 (57), and 57 (100); HRMS [Found: *m/z* 210.1263 (M^+). Calcd for $C_{12}H_{18}O_3$: M, 210.1256].

2-(2-Oxocycloheptyl)allyl Acetate (19a). An oil; IR (neat) 1741 (C=O), 1702 (C=O), 1648 (C=C), 1230, and 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32–2.03 (8H, m), 2.06 (3H, s, Ac), 2.48 (1H, m, C*H*HC=O), 2.59 (1H, ddd, J = 3.5, 11.9, 13.5 Hz, CH*H*C=O), 3.20 (1H, br dd, J = 3, 12 Hz, COCHC=C), 4.55 (2H, br s, CH_2OAc), 5.07 (1H, br s, C=C*H*H), and 5.23 (1H, br s, C=CH*H*); ^{13}C NMR ($CDCl_3$) δ 20.91 (CH_3), 24.93 (CH_2), 28.59 (CH_2), 29.65 (CH_2), 29.69 (CH_2), 42.48 (CH_2), 56.19 (CH), 66.25 (CH_2), 114.59 (CH_2), 142.84 (C), 170.53 (CO), and 212.81 (CO); MS *m/z* (rel intensity) 167 (M^+-Ac, 26), 149 (68), 137 (28), 81 (52), and 69 (100); HRMS [Found: *m/z* 167.1071 (M^+-Ac). Calcd for $C_{10}H_{15}O_2$: M, 167.1073].

2-(2-Oxocyclooctyl)allyl Acetate (19b). An oil; IR (neat) 1743 (C=O), 1699 (C=O), 1648 (C=C), 1233, and 1029 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29–2.13 (10H, m), 2.07 (3H, s, Ac), 2.29 (1H, ddd, J = 3.5, 5.4, 13.0 Hz, C*H*HC=O), 2.60 (1H, ddd, J = 4.9, 11.2, 13.0 Hz, CH*H*C=O), 3.24 (1H, br dd, J = 2, 12 Hz, COCHC=C), 4.61 (2H, br s, CH_2OAc), 5.20 (1H, br s, C=C*H*H), and 5.23 (1H, br s, C=CH*H*); ^{13}C NMR ($CDCl_3$) δ 20.91 (CH_3), 24.59 (CH_2), 26.32 (CH_2), 26.34 (CH_2), 26.88 (CH_2), 30.20 (CH_2), 40.27 (CH_2), 54.57 (CH), 66.43 (CH_2), 114.66 (CH_2), 142.08 (C), 170.47 (CO), and 215.75 (CO); MS *m/z* (rel intensity) 224 (M^+, 33), 206 (19), 183 (86), 167 (79), 153 (100), 127 (96), 117 (94), 99 (96), and 72 (99); HRMS [Found: *m/z* 224.1395 (M^+). Calcd for $C_{13}H_{20}O_3$: M, 224.1413].

2-(2-Oxocyclotetradecyl)allyl Acetate (19d). An oil; IR (neat) 1746 (C=O), 1712 (C=O), 1647 (C=C), 1227, and 1032 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15–2.12 (22H, m), 2.08 (3H, s, Ac), 2.42 (1H, ddd, J = 5.0, 7.6, 16.6 Hz, C*H*HC=O), 2.56 (1H, ddd, J = 5.0, 8.1, 16.6 Hz, CH*H*C=O), 3.29 (1H, br dd, J = 4, 10 Hz, COCHC=C), 4.52 (2H, br s, CH_2OAc), 5.12 (1H, br s, C=C*H*H), and 5.19 (1H, br s, C=CH*H*); ^{13}C NMR ($CDCl_3$) δ 20.85 (CH_3), 22.68 (CH_2), 24.23 (CH_2), 25.16 (CH_2 ×2), 25.29 (CH_2), 25.32 (CH_2), 25.47 (CH_2), 25.63 (CH_2), 25.93 (CH_2), 26.06 (CH_2), 29.83 (CH_2), 39.24 (CH_2), 54.68 (CH), 66.02 (CH_2), 115.38 (CH_2), 142.13 (C), 170.50 (CO), and 210.73 (CO); MS *m/z* (rel intensity) 266 (M^+-CH_2CO, 4), 248 (29), 205 (6), 149 (9), 135 (16), 121 (20), 109 (26), 95 (46), 81 (55), 55 (67), and 43 (100); HRMS [Found: *m/z* 266.2269 (M^+-CH_2CO). Calcd for $C_{17}H_{30}O_2$: M, 266.2247].

2-(2-Oxocycloheptyl)allyl Pivalate (19e). An oil; IR (neat) 1732 (C=O), 1703 (C=O), 1647 (C=C), 1282, and 1151 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (9H, s, Piv), 1.30–2.03 (8H, m), 2.44–2.63 (2H, m, CH_2C=O), 3.19 (1H, br dd, J = 3, 12 Hz, COCHC=C), 4.53 (2H, br s, CH_2OPiv), 5.04 (1H, br s, C=C*H*H), and 5.21 (1H, br s, C=CH*H*); ^{13}C NMR ($CDCl_3$) δ 24.94, 27.16 (3C), 28.63, 29.71, 29.78, 38.76, 42.54, 56.14, 66.03, 113.82, 143.13, 177.97, and 212.75; MS *m/z* (rel intensity) 167 (M^+-Piv, 6), 150 (M^+-PivOH, 71), 79 (32), 57 (84), and 41 (100); MS (CI) *m/z* (rel intensity) 253 (M^++H, 21) and 151 (M^+-OPiv, 100); HRMS [Found: *m/z* 167.1050 (M^+-Piv). Calcd for $C_{10}H_{15}O_2$: M, 167.1073].

Reduction. 1) by DIBAL-H. Compound **7** (83.8 mg, 0.400 mmol) was treated with DIBAL-H (0.086 cm^3, 0.98 mmol; 1.0 mol dm^{-3} in hexane) as described for the synthesis of **15a**, except that Et_2O (10 cm^3) was used as the solvent. Silica gel (ca. 1 g) column chromatography using hexane–AcOEt (100:0 to 25:75) as eluent afforded **12** (49.4 mg, 73%; 6:1 mixture of *cis*-**12** and *trans*-**12**). Similarly DIBAL-H reduction of **19a** afforded **12** in 90% yield (*cis*:*trans* = 6:1).

2) by L-Selectride. To a stirred solution of L-Selectride (0.39 cm^3, 0.39 mmol; 1.0 mol dm^{-3} solution in THF) under Ar was added a solution of **19a** (16.3 mg, 0.078 mmol) in dry Et_2O (4 cm^3) at −60 °C. The mixture was slowly warmed to room temperature, and the stirring was continued for 14 h. HCl aq (ca. 1 mol dm^{-3} solution) was added, and the mixture was extracted with AcOEt and dried. Evaporation of the solvent followed by silica gel (0.5 g) chromatography using hexane-AcOEt (80:20 to 25:75) as eluent afforded *cis*-**12** (10.0 mg, 76%). By this method, **19b** afforded **20** (56%, *cis*:*trans* = 3:1); **19d** afforded **21** (98%, *cis*:*trans* = 3:2). For the reduction of pivalate, **19e** (46.8 mg, 0.186 mmol) in dry THF (5.0 cm^3) was first treated with L-Selectride (0.19 cm^3) as above, then after stirring at room temperature for 5 h, $LiAlH_4$ (46.8 mg, 0.186 mmol) was added at once. The mixture was stirred at room temperature for 14 h, and then worked up as described above to give *cis*-**12** (30.7 mg, 97%).

2-(2-Hydroxycycloheptyl)prop-2-en-1-ol (12). A viscous oil; IR (neat) 3320 (OH), 1639 (C=C), 1026, and 906 cm^{-1}; ^1H NMR ($CDCl_3$) for *cis*-isomer: δ 1.36–2.24 (12H, m), 2.37 (1H, dt, J = 11.0, 2.3 Hz, C*H*C=CH_2), 3.97 (1H, m, C*H*OH), 4.07 (1H, br d, J = 13 Hz, C*H*HOH), 4.15 (1H, dd, J = 1.0, 13.0 Hz, CH*H*OH), 4.98 (1H, br s, C=C*H*H), and 5.14 (1H, q, J = 1.4 Hz, C=CH*H*); for *trans*-isomer: δ 1.36–2.24 (13H, m), 4.09–4.17 (3H, m, CH_2OH and C*H*OH), 5.01 (1H, br s, C=C*H*H), and 5.15 (1H, q, J = 1.2 Hz, C=CH*H*); ^{13}C NMR ($CDCl_3$) for *cis*-isomer: δ 21.54 (CH_2), 25.94 (CH_2), 27.37 (CH_2), 28.08 (CH_2), 35.12 (CH_2), 49.56 (CH), 65.26 (CH_2), 71.33 (CH), 112.92 (CH_2), and 152.53 (C); MS *m/z* (rel intensity) 169 (M^+-H, 10), 152 (M^+-H_2O, 44), 137 (100), 123 (96), 119 (90), 97 (87), 91 (84), 84 (81), 69 (80), and 57 (70); HRMS [Found: *m/z* 169.1185 (M^+-H). Calcd for $C_{10}H_{17}O_2$: M, 169.1229].

2-(2-Hydroxycyclooctyl)prop-2-en-1-ol (20). A viscous oil; IR (neat) 3340 (OH), 1638 (C=C), 1040, 897, and 737 cm^{-1}; ^1H NMR ($CDCl_3$) for *cis*-isomer: δ 1.23–2.54 (14H, m), 2.58 (1H, dt, J = 9.9, 2.2 Hz, C*H*C=CH_2), 3.83 (1H, ddd, J = 2.5, 5.3, 9.5 Hz, C*H*OH), 4.08 (1H, dd, J = 0.9, 13.0 Hz, C*H*HOH), 4.16 (1H, dd, J = 1.0, 13.0 Hz, CH*H*OH), 5.01 (1H, br s, C=C*H*H), and 5.17 (1H, q, J = 1.1 Hz, C=CH*H*); for *trans*-isomer: δ 1.23–2.54 (15H, m), 3.82 (1H, C*H*OH, coupling pattern was unreadable due to overlapping), 4.10 (1H, br d, J = 13 Hz, C*H*HOH), 4.14 (1H, br d, J = 13 Hz, CH*H*OH), 5.03 (1H, br s, C=C*H*H), and 5.19 (1H, q, J = 1.3 Hz, C=CH*H*); ^{13}C NMR ($CDCl_3$) for *cis*-isomer: δ 22.14, 25.49, 25.88, 27.17, 28.06, 32.40, 45.04, 65.65, 71.92, 113.26, and 152.64; MS *m/z* (rel intensity) 184 (M^+, 43), 152 (61), 137 (70), 124 (70), 92 (74), 65 (87), and 40 (100); HRMS [Found: *m/z* 184.1478 (M^+). Calcd for $C_{11}H_{20}O_2$: M, 184.1464].

2-(2-Hydroxycyclotetradecyl)prop-2-en-1-ol (21). A vis-

couse oil; IR (neat) 3220 (OH), 1647 (C=C), 1334, 1265, 1029, and 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–2.65 (27H, m) and 3.68–5.27 (5H, m, C*H*OH, CH_2OH, C=CH_2); FABMS *m/z* (rel intensity) 269 (M^++H, 13), 251 (63), 233 (93), 154 (65), 136 (100), and 109 (76).

Lactonization. To a stirred solution of **12** (56.7 mg, 0.333 mmol) in dry CH_2Cl_2 (2.0 cm^3) was added activated MnO_2 (ca. 170 mg) under a $CaCl_2$ drying tube, and the mixture was stirred at room temperature for 5 days. The solid was filtered off through Celite, and the filtrate was concentrated by rotary evaporator to give an oily residue, which was chromatographed on silica gel (0.5 g) using pentane-Et_2O (98:2 to 94:6) as eluent giving **13** (44.3 mg, 80%). By the same way, **20** and **21** afforded **22** (82%) and **23** (90%), respectively.

10-Methylene-8-oxabicyclo[5.3.0]decan-9-one (13).[4a,16] An oil; IR (neat) 1759 (C=O), 1658 (C=C), 1271, 1157, 1126, 997, and 754 cm^{-1}; ^1H NMR ($CDCl_3$; Me_4Si = 0.00 as the reference) for *cis*-isomer: δ 1.23-2.10 (10H, m), 3.23 (1H, dddt, *J* = 4.2, 8.2, 10.5, 2.9 Hz, C*H*C=CH_2), 4.71 (1H, ddd, *J* = 3.7, 8.6, 10.5 Hz, CHOCO), 5.55 (1H, d, *J* = 2.8 Hz, C=C*H*H), and 6.28 (1H, d, *J* = 3.0 Hz, C=CH*H*); for *trans*-isomer: δ 1.23–2.42 (10H, m), 2.76 (1H, dddt, *J* = 5.0, 9.0, 10.7, 3.3 Hz, C*H*C=CH_2), 4.14 (1H, ddd, *J* = 4.3, 9.2, 10.7 Hz, CHOCO), 5.45 (1H, d, *J* = 3.2 Hz, C=C*H*H), and 6.17 (1H, d, *J* = 3.4 Hz, C=CH*H*); NOE was observed between δ 4.71 and 3.23; The ratio of two isomers was determined from integration, see text; ^{13}C NMR ($CDCl_3$) for *cis*-isomer: δ 24.21 (CH_2), 27.39 (CH_2), 30.62 (CH_2), 31.20 (CH_2), 31.73 (CH_2), 43.03 (CH), 82.23 (CH), 121.97 (CH_2), 140.33 (C), and 170.34 (CO); for *trans*-isomer: δ 25.10, 25.28, 27.27, 27.95, 32.97, 45.61, 83.30, 119.55, 140.97, and 170.34; MS *m/z* (rel intensity) 166 (M^+, 100), 138 (71), 109 (43), 94 (57), 79 (55), and 67 (79); HRMS [Found: *m/z* 166.1006 (M^+). Calcd for $C_{10}H_{14}O_2$: M, 166.0994].

11-Methylene-9-oxabicyclo[6.3.0]undecan-10-one (22).[10b,16] An oil; IR (neat) 1763 (C=O), 1661 (C=C), 1274, 1142, and 983 cm^{-1}; ^1H NMR ($CDCl_3$) for *cis*-isomer: δ 1.16–1.95 (12H, m), 3.01 (1H, dtt, *J* = 5.1, 3.0, 7.9 Hz, C*H*C=CH_2), 4.72 (1H, ddd, *J* = 1.5, 7.9, 10.5 Hz, CHOCO), 5.55 (1H, d, *J* = 3.0 Hz, C=C*H*H), and 6.26 (1H, d, *J* = 3.0 Hz, C=CH*H*); for *trans*-isomer: δ 1.16–2.31 (12H, m), 2.88 (1H, m, C*H*C=CH_2), 4.43 (1H, ddd, *J* = 4.4, 7.5, 10.1 Hz, CHOCO), 5.51 (1H, d, *J* = 3.0 Hz, C=C*H*H), and 6.23 (1H, d, *J* = 3.4 Hz, C=CH*H*); NOE was observed between δ 4.72 and 3.01; ^{13}C NMR ($CDCl_3$) for *cis*-isomer: δ 25.06, 25.60, 27.02, 27.52, 28.59, 29.75, 43.36, 83.38, 121.60, 140.40, and 170.08; for *trans*-isomer: δ 26.67, 26.79, 29.69, 33.51, 35.21, 43.62, 83.86, and 120.91; MS *m/z* (rel intensity) 180 (M^+, 10), 151 (9), 124 (14), 110 (23), 96 (35), 81 (42), 67 (58), 54 (82), and 41 (100); HRMS [Found: *m/z* 180.1161 (M^+). Calcd for $C_{11}H_{16}O_2$: M, 180.1151].

17-Methylene-15-oxabicyclo[12.3.0]heptadecan-16-one (23).[10b] An oil; IR (neat) 1767 (C=O), 1663 (C=C), 1265, and 1116 cm^{-1}; ^1H NMR ($CDCl_3$) for *cis*-isomer: δ 1.14–1.78 (24H, m), 2.97 (1H, tq, *J* = 2.5, 7.1 Hz, C*H*C=CH_2), 4.51 (1H, dt, *J* = 5.2, 7.1 Hz, CHOCO), 5.48 (1H, d, *J* = 2.5 Hz, C=C*H*H), and 6.18 (1H, d, *J* = 2.7 Hz, C=CH*H*); for *trans*-isomer: δ 1.14–1.78 (24H, m), 2.71 (1H, dtt, *J* = 8.1, 2.5, 5.5 Hz, C*H*C=CH_2), 4.25 (1H, dt, *J* = 6.6, 5.5 Hz, CHOCO), 5.57 (1H, d, *J* = 2.4 Hz, C=C*H*H), and 6.24 (1H, d, *J* = 2.7 Hz, C=CH*H*); NOE was observed between δ 4.51 and 2.97; The ratio of two isomers was determined to be *cis*:*trans* = 3:2 from integration; MS *m/z* (rel intensity) 265 (M^++H, 79), 236 (53), 214 (18), 196 (20), 152 (4), 124 (5), 106 (3), and 47 (100); HRMS [Found: *m/z* 265.2119 (M^++H). Calcd for $C_{17}H_{29}O_2$: M, 265.2169].

Synthesis of Model Compounds of Guaianolides. See synthesis of **8a**, **7**, **12**, and **13** for the procedure of oxidation, cyclization, reduction, and lactonization procedures, respectively.

***trans*-2-[(*Z*)-3-Ethoxycarbonyl-4-(trimethylsilyl)but-2-en-1-yl]cyclopentanepropanoic Acid (25a).** An oil; IR (neat) 2800–3600 (OH), 1710 (C=O), 1249, and 852 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (9H, s, $SiMe_3$), 1.15–2.01 (10H, m), 1.29 (3H, t, *J* = 7.1 Hz, OCH_2CH_3), 1.81 (2H, br s, CH_2SiMe_3), 2.24–2.47 (4H, m, CH_2CH=C and CH_2CO_2H), 4.17 (2H, q, *J* = 7.1 Hz, OCH_2CH$_3$), and 6.62 (1H, t, *J* = 7.3 Hz, CH=C); ^{13}C NMR ($CDCl_3$) δ −1.01 (3C), 14.26, 17.36, 23.65, 29.78, 31.77, 32.06, 33.00, 33.94, 44.94, 45.31, 60.42, 130.53, 137.24, 168.40, and 179.55; MS *m/z* (rel intensity) 340 (M^+, 3), 325 (6), 278 (59), 228 (24), 200 (22), 149 (45), 73 (96), and 55 (100); HRMS [Found: *m/z* 340.2077 (M^+). Calcd for $C_{18}H_{32}O_4Si$: M, 340.2071].

***trans*-2-[(*E*)-3-Ethoxycarbonyl-4-(trimethylsilyl)but-2-en-1-yl]cyclopentanepropanoic Acid (25b).** An oil; IR (neat) 2800–3500 (OH), 1710 (C=O), 1248, and 851 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.03 (9H, s, $SiMe_3$), 1.10–1.93 (10H, m), 1.28 (3H, t, *J* = 7.1 Hz, OCH_2CH_3), 1.72 (2H, br s, CH_2SiMe_3), 2.22–2.61 (4H, m, CH_2CH=C and CH_2CO_2H), 4.16 (2H, q, *J* = 7.1 Hz, OCH_2CH$_3$), and 5.64 (1H, t, *J* = 7.6 Hz, CH=C); ^{13}C NMR ($CDCl_3$) δ −1.64 (3C), 14.27, 23.69, 24.18, 29.85, 31.75, 31.81, 33.10, 34.48, 44.89, 46.03, 60.08, 129.78, 137.63, 168.53, and 179.88; MS *m/z* (rel intensity) 341 (M^++H, 5), 328 (2), 256 (11), 149 (10), 137 (27), 81 (76), and 69 (100); HRMS [Found: *m/z* 341.2126 (M^++H). Calcd for $C_{18}H_{33}O_4Si$: M, 341.2149].

Ethyl 2-(4-Oxobicyclo[5.3.0]dec-3-yl)acrylate (27). An oil; IR (neat) 1710 (C=O), 1635 (C=C), 1259, 1173, and 805 cm^{-1}; ^1H NMR ($CDCl_3$; Me_4Si = 0.00 as the reference) for **27a**: δ 1.24–2.07 (12H, m), 1.29 (3H, t, *J* = 7.1 Hz, OCH_2CH_3), 2.50 (1H, dt, *J* = 11.2, 8.8 Hz, C*H*HCO), 2.79 (1H, m, CH*H*CO), 3.97 (1H, br t, *J* = 7 Hz, COCHC=C), 4.17 (2H, m, OCH_2CH$_3$), 5.65, (1H, br s, C=C*H*H), and 6.38 (1H, br s, C=CH*H*); for **27b**: δ 1.24–2.07 (12H, m), 1.28 (3H, t, *J* = 7.1 Hz, OCH_2CH_3), 2.59 (1H, ddd, *J* = 6.4, 11.2, 15.2 Hz, C*H*HCO), 2.82 (1H, ddd, *J* = 3.1, 6.0, 15.2 Hz, CH*H*CO), 3.77 (1H, br d, *J* = 12 Hz, COCHC=C), 4.17 (2H, m, OCH_2CH$_3$), 5.68 (1H, br s, C=C*H*H), and 6.39 (1H, br s, C=CH*H*); ^{13}C NMR ($CDCl_3$) for **27b**: δ 14.11, 21.74, 27.29, 33.55, 33.83, 34.74, 43.38, 46.97, 49.02, 52.33, 60.94, 125.80, 140.42, 166.62, and 213.01; MS *m/z* (rel intensity) 250 (M^+, 100), 232 (19), 222 (34), 204 (66), 176 (79), 154 (87), 95 (63), and 67 (92); HRMS [Found: *m/z* 250.1565 (M^+). Calcd for $C_{15}H_{22}O_3$: M, 250.1570].

2-(4-Hydroxybicyclo[5.3.0]dec-3-yl)prop-2-en-1-ol (28). An oil; IR (neat) 3300 (OH), 1637 (C=C), 1450, and 1027 cm^{-1}; ^1H NMR ($CDCl_3$; Me_4Si = 0.00 as the reference) for **28b**: δ 1.12–2.00 (14H, m), 2.45 (2H, br, OH ×2), 2.46 (1H, m, CHC=C), 4.03 (1H, dd, *J* = 3.0, 6.2 Hz, C*H*OH), 4.06 (1H, dd, *J* = 0.5, 12.8 Hz, C*H*HOH), 4.18 (1H, dd, *J* = 1.0, 12.8 Hz, CH*H*OH), 5.00 (1H, br s, C=C*H*H), and 5.09 (1H, q, *J* = 1.2 Hz, C=CH*H*); ^{13}C NMR ($CDCl_3$) for **28b**: δ 23.34, 29.28, 33.04, 34.38, 34.50, 35.20, 46.32, 47.13, 49.51, 65.39, 73.23, 113.18, and 152.44; MS *m/z* (rel intensity) 192 (M^+-H_2O, 68), 174 (34), 148 (50), 133 (59), 93 (75), 79 (97), and 67 (100); HRMS [Found: m/z 192.1486 (M^+-H_2O). Calcd for $C_{13}H_{20}O$: M, 192.1515].

***trans*-2-[(*Z*)-5-Ethoxycarbonyl-6-(trimethylsilyl)hex-4-en-1-yl]cyclopentanecarboxylic Acid (30a).** An oil; IR (neat) 2400–3600 (OH), 1704 (C=O), 1249, 1179, and 853 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.01 (9H, s, $SiMe_3$), 1.18–2.18 (13H, m), 1.29 (3H, t, *J* = 7.1 Hz, OCH_2CH_3), 1.80 (2H, br s, CH_2SiMe_3), 2.36 (1H, q, *J*

= 8.2 Hz, C*H*CO_2H), 4.16 (2H, q, J = 7.1 Hz, OC$H_2$$CH_3$), and 6.58 (1H, t, J = 7.3 Hz, CH=C); ^{13}C NMR ($CDCl_3$) δ −1.07 (3C), 14.28, 17.28, 24.87, 27.46, 29.25, 30.32, 32.59, 35.21, 44.27, 49.79, 60.42, 130.16, 138.18, 168.43, and 180.60; MS *m/z* (rel intensity) 340 (M^+, 90), 325 (98), 278 (97), 242 (99), and 147 (100); HRMS [Found: *m/z* 340.2079 (M^+). Calcd for $C_{18}H_{32}O_4Si$: M, 340.2071].

***trans*-2-[(*E*)-5-Ethoxycarbonyl-6-(trimethylsilyl)hex-4-en-1-yl]cyclopentanecarboxylic Acid (30b).** An oil; IR (neat) 2400–3600 (OH), 1704 (C=O), 1247, 1174, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.03 (9H, s, $SiMe_3$), 1.17–1.99 (9H, m), 1.29 (3H, t, J = 7.2 Hz, OCH_2CH_3), 1.72 (2H, br s, CH_2SiMe_3), 2.12 (1H, m), 2.37 (3H, m), 4.16 (2H, q, J = 7.2 Hz, OC$H_2$$CH_3$), and 5.64 (1H, t, J = 7.5 Hz, CH=C); ^{13}C NMR ($CDCl_3$) δ −1.68 (3C), 14.24, 24.05, 24.86, 28.40, 29.72, 30.26, 32.57, 35.01, 44.36, 50.17, 60.04, 129.44, 138.70, 168.45, and 182.83; MS *m/z* (rel intensity) 340 (M^+, 91), 297 (93), 278 (97), 250 (95), and 167 (100); HRMS [Found: *m/z* 340.2025 (M^+). Calcd for $C_{18}H_{32}O_4Si$: M, 340.2071].

Ethyl 2-(2-Oxobicyclo[5.3.0]dec-3-yl)acrylate (32). An oil; IR (neat) 1704 (C=O), 1629 (C=C), 1259, 1174, 1026, and 805 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25–2.25 (13H, m), 1.27 (3H, t, J = 7.1 Hz, OCH_2CH_3), 3.03 (1H, dt, J = 10.5, 8.2 Hz, CHCO), 3.21 (1H, dd, J = 2.6, 11.6 Hz, COCHC=C), 4.16 (2H, q, J = 7.1 Hz, OC$H_2$$CH_3$), 5.59 (1H, br s, C=C*H*H), and 6.20 (1H, d, J = 0.9 Hz, C=CH*H*); ^{13}C NMR ($CDCl_3$) δ 14.11, 24.12, 26.74, 29.75, 30.99, 35.71, 36.79, 44.96, 56.96, 57.71, 60.89, 126.41, 142.82, 166.13, and 212.48; MS *m/z* (rel intensity) 250 (M^+, 5), 222 (6), 204 (10), 176 (24), 148 (20), 95 (55), and 67 (100); HRMS [Found: *m/z* 250.1555 (M^+). Calcd for $C_{15}H_{22}O_3$: M, 250.1570].

2-(2-Hydroxybicyclo[5.3.0]dec-3-yl)prop-2-en-1-ol (33). An oil; IR (neat) 3340 (OH), 1638 (C=C), 1459, 1067, and 906 cm^{-1}; ^{1}H NMR ($CDCl_3$) for 33a: δ 1.12–2.22 (16H, m), 2.48 (1H, dd, J = 4.5, 9.8 Hz, CHC=C), 3.59 (1H, dd, J = 4.2, 7.5 Hz, C*H*OH), 4.09 (1H, d, J = 13.2 Hz, C*H*HOH), 4.14 (1H, d, J = 13.2 Hz, CH*H*OH), 4.98 (1H, br s, C=C*H*H), and 5.27 (1H, q, J = 1.2 Hz, C=CH*H*); ^{13}C NMR ($CDCl_3$) for 33a: δ 24.82, 26.15, 30.59, 33.88, 35.31, 36.91, 41.66, 49.49, 52.30, 65.57, 76.20, 113.29, and 152.09; MS *m/z* (rel intensity) 192 (M^+-H_2O, 1), 177 (3), 163 (3), 149 (29), 95 (30), 79 (46), 67 (50), and 41 (100); HRMS [Found: *m/z* 192.1487 (M^+-H_2O). Calcd for $C_{13}H_{20}O$: M, 192.1515].

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