Intramolecular Cyclization of 4-[3-(Trimethylsilyl)prop-1-en-1-yl]-cyclohexanecarbaldehyde with Loss of Formyl Carbon

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Treatment of *cis*- and *trans*-4-[3-(trimethylsilyl)prop-1-en-1-yl]cyclohexanecarbaldehyde (**2a** and **2b**) with tetrabutylammonium fluoride in dilute tetrahydrofuran afforded 7-vinylbicyclo[2.2.1]heptan-1-ol (**3**), the same product obtained from 4-[3-(trimethylsilyl)prop-1-en-1-yl]cyclohexanone (**1**). It was found that oxidative deformylation of **2a**, **b** to **1** takes place under basic conditions before the cyclization to **3**. It was also shown that cyclization of allylsilane with carbonyl does not proceed via an eclipsed conformation.

Allysilanes are versatile building blocks in organic syntheses as an allyl anion equivalent.[1] Intramolecular cyclization of allylsilane with a carbonyl group has been developed as a common method for the synthesis of cyclic compounds,[2,3] which is applied to the total synthesis of terpenoids.[4] We reported synthesis of α-methylene-γ-lactones, model compounds of biologically active sesquiterpenoids, via intramolecular cyclization of functionalized allylsilane with carbonyl,[5] and this was applied to the synthesis of carbobicyclic ring systems, such as bicyclo[4.3.0]-nonanes[6] and spiro[4.5]decanes.[7] To apply these reactions of allylsilane to the synthesis of more complex ring systems, we focused on the synthesis of bicyclo[2.2.1]heptane or bicyclo[2.2.2]octane ring systems. In this study, we chose simple allylsilanes **1** and **2a** as the substrates, which are expected to give bicyclo[2.2.1]heptane **3** and bicyclo[2.2.2]octane **4** (**4a** or **4b**), respectively (Scheme 1). Another purpose of this work is to analyze the stereochemistry of the cyclization reaction. It is reported, especially by Denmark's group,[8] that two double bonds, C=C of allylsilane and C=O, take a staggered (synclinal or antiperiplanar) conformation in the transition state.[9] Both Majetich et al.[10] and Denmark et al.[8] obtained bicyclo[2.2.2]octane ring compounds from substituted six-membered carbocycles, in which allylsilane and carbonyl can take a staggered conformation in the transition state. In our case, compound **1** can take the synclinal conformation **A**, while **2a** cannot take a staggered conformation and is obliged to take the eclipsed conformation **B** or **C** to produce the bicyclo[2.2.2]octane ring **4a** or **4b**, respectively. Here we report that the cyclization reaction does not proceed via an eclipsed conformation, but a new type of cyclization reaction including loss of formyl carbon takes place.

Results and Discussion

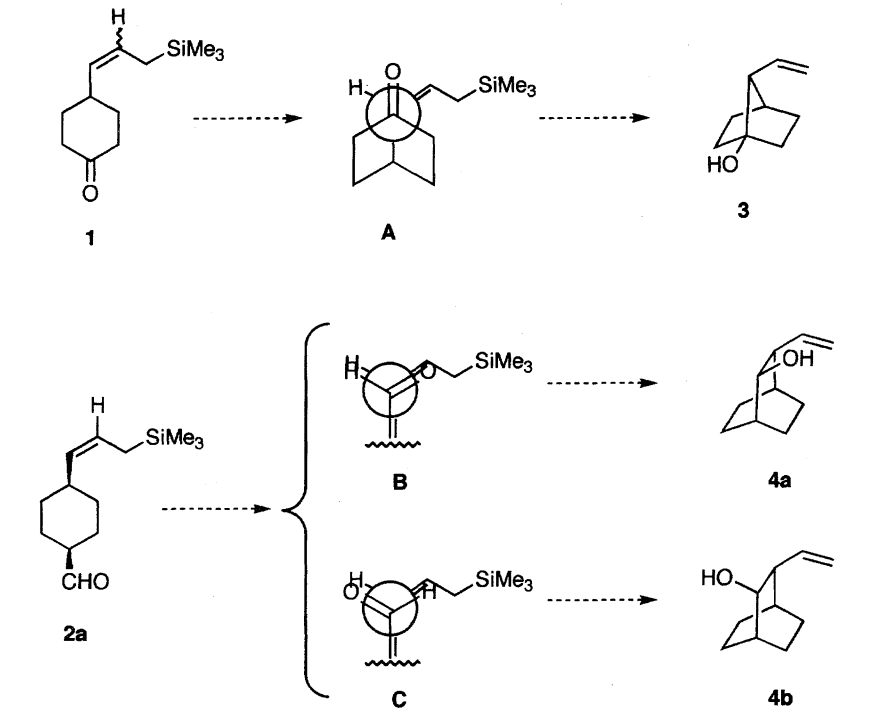
Compound **1** was prepared from cyclohexane-1,4-diol as shown in Scheme 2. Thus one of the hydroxy groups was first monoprotected with a tetrahydropyran-2-yl (THP) group giving **5**, and the other hydroxy group was oxidized to afford ketone **6**. One carbon homologation by the Wittig method gave **7**, which was converted to alcohol **8** by hydroboration.[5a] After Swern oxidation to **9**, an allylsilane moiety was introduced by Fleming's method[11] to give **10**. Removal of the THP group to **11** followed by oxidation afforded **1**, which was obtained as a mixture of *Z*- and *E*-allylsilanes (*Z*:*E* = 3:1). The geometry of the double bond was deduced from *J*-values between two olefinic protons; $J = 11$ Hz for the major isomer (*Z*-form) and $J = 15$ Hz for the minor isomer (*E*-form). Since the two isomers could not be separated from each other, this mixture was used in the following cyclization study.

Cyclization of **1** is summarized in Table 1. First, **1** was treated with some common Lewis acids. The expected cyclization product **3** was obtained by treatment with $TiCl_4$ (Run 3), while **3** was produced in lower yields on treatment with $SnCl_4$ or $BF_3 \cdot OEt_2$ (Runs 1 and 2). The same product was also produced by a tetrabutylammonium fluoride (TBAF)-promoted anionic reaction (Run 5). In all cases (Runs 1—5), several by-products were detected on TLC. Although the by-products could not be isolated, one of them is considered to be protiodesilylated compound **12**, judging from the presence of vinylic protons [$\delta = 5.01$—5.08 (2H,

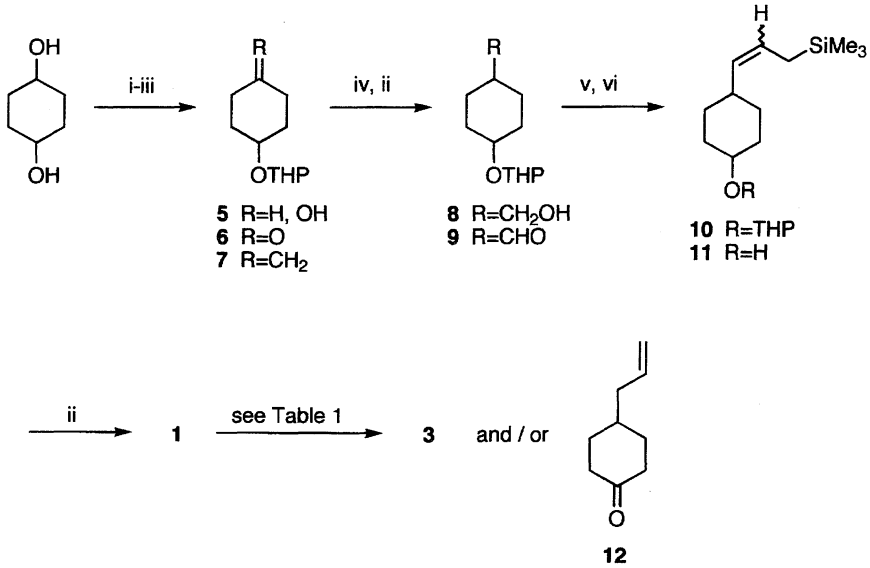
Table 1. Intramolecular Cyclization of **1**[a]

Run	Reagent	Solvent	Concn of **1** / mol dm^{-3}	Yield of **3** / %
1	$SnCl_4$	CH_2Cl_2	0.02	14
2	$BF_3 \cdot OEt_2$	CH_2Cl_2	0.02	10
3	$TiCl_4$	CH_2Cl_2	0.02	69
4	$TiCl_4$	THF	0.02	19[b]
5	TBAF	THF	0.02	53
6	TBAF	THF	0.0008	70[c]

a) All reactions were carried out at room temperature for 1 h with ca. 3 molar amounts of the reagent. b) Yield 28% after overnight reaction. c) Yield 95% based on consumed substrate.



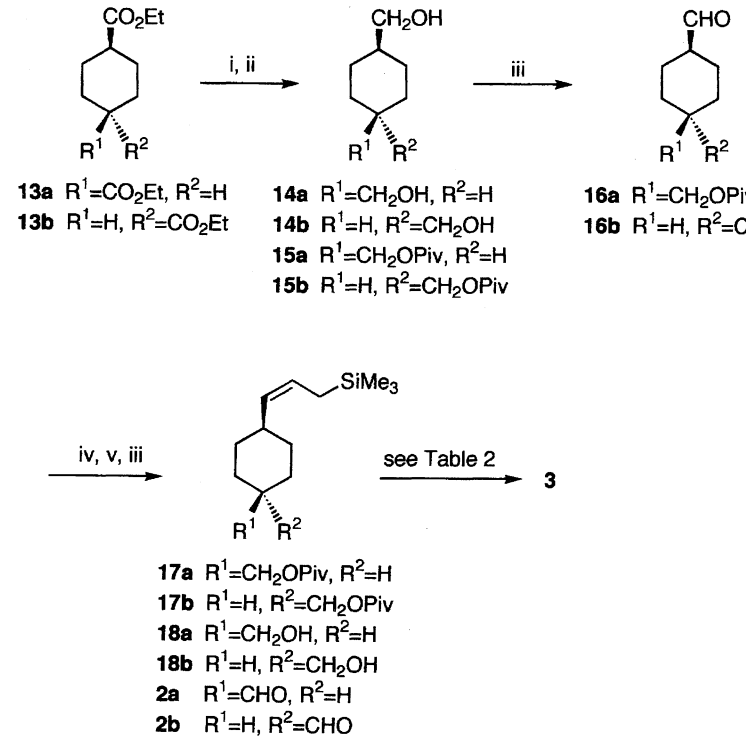
Scheme 1.



Scheme 2. Reagents and conditions: i, dihydropyrane, PPTS, $CHCl_3$, r.t.; ii, DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, -50 °C to r.t.; iii, $[Ph_3PCH_3]^+Br^-$, BuLi, Et_2O, r.t.; iv, (*i*PrMeCH)$_2$BH, diglyme, r.t., then H_2O_2 aq, NaOH aq, 40 °C; v, $[Ph_3P(CH_2)_2SiMe_3]^+Br^-$, BuLi, THF, r.t.; vi, 5% HCl, THF, r.t.

m, $CH_2CH{=}C\underline{H}_2$) and 5.75—5.87 (1H, m, $CH_2C\underline{H}{=}CH_2$); measured in $CDCl_3$ with tetramethylsilane as reference]. In contrast, when the cyclization with TBAF was done in diluted solution, **3** was obtained as the sole product (Run 6).

The other substrate, **2a**, was synthesized from diethyl *cis*-1,4-cyclohexanedicarboxylate **13a** according to Scheme 3. The ester **13a** was prepared by esterification of commercial carboxylic acid, which includes some *trans*-isomer (about 7%; measured by ^{1}H NMR after esterification to **13a/13b**), and therefore all compounds described in Scheme 3 are accompanied by *trans*-isomer to this extent. The ester **13a** was first reduced by $LiAlH_4$ to diol **14a**,[12] which was monoprotected with a 2,2-dimethylpropanoyl (pivaloyl = Piv) group giving **15a**. After Swern oxidation to **16a**, the allylsilane moiety was introduced by a Wittig reaction[11] affording **17a**, which consisted of mostly *Z*-isomer. Hydrolysis of the pivaloyl group to **18a** followed by Swern oxidation yielded **2a**. The *Z*-configuration of the double bond was identified at this stage from the *J*-value of the olefinic protons ($J = 11$ Hz). As described above, **2a** was accompanied by **2b** (**2a** : **2b** = ca. 7 : 1). Since these isomers were inseparable from each other at all stages in the scheme, the mixture of isomers was used



Scheme 3. Reagents and conditions: i, $LiAlH_4$, Et_2O, r.t.; ii, PivCl, pyridine, 0 °C; iii, DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, −50 °C to r.t.; iv, $[Ph_3P(CH_2)_2SiMe_3]^+Br^-$, BuLi, THF, r.t.; v, 7 mol dm^{-3} NaOH aq, EtOH, r.t. (for **18a**) or $LiAlH_4$, Et_2O, 0 °C (for **18b**).

in the following study without separation.

Lewis acid treatment of **2a** was studied using $TiCl_4$ and BF_3·OEt_2. In each cases, **2a** was mostly recovered without reaction, together with some undefined products detected on TLC. Fluoride-promoted cyclization of **2a** was done with 2.5 to 3 molar amounts of TBAF in dry THF at room temperature. The results are listed in Table 2. The reaction under the usual conditions (slightly diluted solution) afforded only a complex mixture (Run 1), while a cyclization product was obtained when the reaction was done in a highly diluted solution (Runs 2 and 3). It was found that the product was not the expected bicyclo[2.2.2]octane derivative **4** but bicyclo[2.2.1]heptane derivative **3**, which is the same product obtained from **1**. This result indicates that a one-carbon degradation occurred together with the cyclization reaction. Compound **3** was obtained as a sole product in 74% yield when the reaction atmosphere was set roughly where a small amount of molecular oxygen remained (Run 4). Since only a short reaction time was required by exposing the reaction mixture to air (Run 5), it was suggested that the deformylation reaction proceeds oxidatively by molecular oxygen under basic conditions.[13]

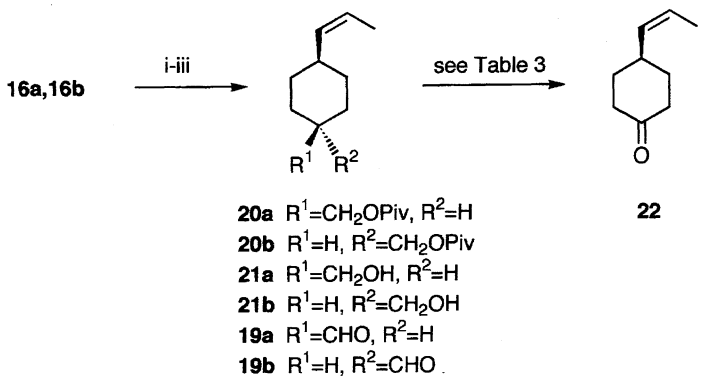
Table 2. Fluoride Promoted Cyclization of **2a** and **2b**[a]

Run	Substrate	Concn	Atmosphere[b]	Yield of **3**
		mol dm^{-3}		%
1	**2a**	0.008	Ar (A)	0
2	**2a**	0.0012	Ar (A)	19
3	**2a**	0.0006	Ar (A)	32
4	**2a**	0.0006	Ar (B)	74
5	**2a**	0.0008	Air	74[c]
6	**2b**	0.0005	Ar (A)	23
7	**2b**	0.0007	Ar (B)	65

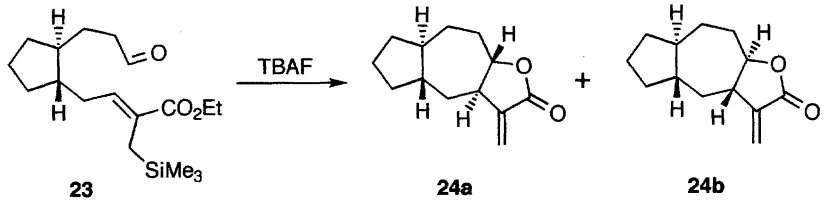
a) Reactions were carried out at room temperature for 15 to 20 h (except Run 5) with 2.5 to 3 molar amounts of TBAF. b) A: Ar atmosphere was set by vacuum replacement. B: Ar was flashed over the reaction mixture. c) The reaction completed after 1 h stirring.

From the results described above, it could be deduced that the cyclization of **2a** proceeds via **1**. To demonstrate this, our attention was next turned to the cyclization of *trans*-isomer **2b** under a hypothesis that the same product **3** must be obtained if the loss of formyl carbon takes place before the cyclization. Compound **2b** was prepared from *trans*-diester **13b** by the same route described for **2a** (Scheme 3). Treatment of **2b** with TBAF in diluted THF solution showed parallel results (Table 2; Runs 6 and 7). Thus **3** was obtained in 65% yield when the reaction atmosphere was set roughly. These results suggest that compound **1** is the intermediate in the reaction from both **2a** and **2b** to bicyclic product **3**, although **1** could not be isolated from the reaction mixture.

To establish that **1** is the intermediate, and to confirm the role of silicon atoms in this deformylation–cyclization sequence, the reaction of desilylized compound **19a** and **19b** was studied. The substrates **19a** and **19b** were prepared according to Scheme 4, where Fleming's Wittig reaction in the preparation of **2a,b** was replaced by $Ph_3P{=}CHCH_3$. Both **19a** and **19b** afforded the same deformylated ketone **22** upon treatment with TBAF in diluted THF (Table 3).



Scheme 4. Reagents and conditions: i, $[Ph_3PCH_2CH_3]^+Br^-$, BuLi, THF, r.t.; ii, $LiAlH_4$, Et_2O, r.t.; iii, DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, −50 °C to r.t.



Scheme 5.

Table 3. Reaction of **19a** and **19b** with TBAF[a)]

Run	Substrate	Atmosphere	Yield of **22**
			%
1	**19a**	Ar[b)]	21
2	**19a**	Air	58
3	**19b**	Ar[b)]	10
4	**19b**	Air	45

a) All reactions were carried out with ca. 3 molar amounts of TBAF in diluted THF solution. b) Method A of Table 2.

This indicates that oxidative deformylation occurs before the cyclization, and that the silicon atom acts in the cyclization step, not in deformylation. Since the yields were lower under Ar (Runs 1 and 3) and higher under air (Runs 2 and 4), it was confirmed again that the deformylation proceeds oxidatively by the aid of molecular oxygen, as reported by both Rheenen[13a)] and Sucrow.[13b)] The formation of **22** under the Ar atmosphere is to be explained by the presence of O_2 in the solvent, which indicates that only a small amount of O_2 is necessary in this oxidative deformylation reaction. Cyclohexanecarbaldehyde was also treated under the same reaction conditions (TBAF in dilute THF under air) giving cyclohexanone in 43% yield. However, in contrast to the case of **2a**, several by-products were detected on TLC.

In summary, the bicyclo[2.2.1]nonane ring system was synthesized from keto allylsilane **1**, as expected, while **2a** afforded deformylative product **3** instead of direct cyclization product **4**. It was shown that **3** was produced from both **2a** and **2b** via deformylated ketone **1**. As for the stereochemistry of the cyclization reaction, it is obvious that the formation of bicyclo[2.2.2]octane ring from **2a** depicted in Scheme 1 is prohibited, i.e., **2a** does not take the eclipsed conformation required for the formation of bicyclo[2.2.2]octane. We previously reported that fluoride-promoted cyclization of **23** was not affected by β-substituent in the formation of α-methylene-γ-lactone fused to seven-membered carbocycle **24a**, **b**, and that two double bonds approach with parallel orientation (Scheme 5).[5d,14)] The result obtained here strongly indicates that "parallel approach" does not mean an eclipsed transition state, although we cannot propose an exact conformation of the transition state from **23** to **24**. In contrast, **1** can take a synclinal transition state giving **3**, which is consistent with Denmark's study.[8)]

Another result obtained from this study is an oxidative deformylation reaction promoted by TBAF. It was found that the deformylation proceeds by molecular oxygen under basic conditions. Although the study of this deformylation was not detailed enough, it is interesting that the oxidation took place with a limited amount of air.

Experimental

General Procedures. UV spectra were measured on a JASCO Ubest-50 spectrometer. IR spectra were taken on a Hitachi 270-30 or JASCO FT/IR-230 spectrometer. Both ^1H and ^{13}C NMR spectra were measured on a JEOL GSX-400 (400 MHz for ^1H; 100 MHz for ^{13}C) spectrometer. Chemical shifts are reported on the δ scale (ppm) with tetramethylsilane ($Me_4Si = 0.00$) or chloroform ($CHCl_3 = 7.25$) as an internal standard. The signal of the solvent ($CDCl_3 = 77.0$) was used as a standard for ^{13}C NMR spectra 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 precoated 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 $MgSO_4$ was used for drying of extracted organic layers. For reactions requiring dry solvents, tetrahydrofuran (THF), Et_2O, diglyme, and CH_2Cl_2 were distilled from CaH_2; dimethyl sulfoxide (DMSO) was distilled from 4A molecular sieve.

4-(Tetrahydropyran-2-yloxy)cyclohexanol (5). In a 200 cm^3 round-bottomed flask was placed a solution of commercial cyclohexane-1,4-diol (5.101 g, 43.9 mmol; mixture of *cis*- and *trans*-isomers) in CH_2Cl_2/THF (120 cm^3; 2 : 1 ratio), and to this were added, 3,4-dihydro-2*H*-pyran (4.0 cm^3, 43.8 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (80 mg). After this was stirred at room temperature for 24 h, water was added, and the mixture was extracted with CH_2Cl_2. Evaporation of the solvent followed by silica-gel (100 g) column chromatography using hexane–AcOEt (4 : 1) as eluent afforded **5** (4.190 g, 48%) as an oil; IR (neat) 3420 cm^{-1} (OH); ^{1}H NMR (Me_4Si) δ = 1.20—2.07 (15H, m), 3.46—3.53 (1H, m, OCHH), 3.58—3.69 (1H, m, CHOH), 3.70—3.77 (1H, m, CHOTHP), 3.87—3.94 (1H, m, OCHH), and 4.68—4.72 (1H, m, OCHO); ^{13}C NMR (Me_4Si) for both isomers δ = 19.8 (CH_2), 19.9 (CH_2), 25.5 (CH_2), 25.6 (CH_2), 26.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 30.4 (CH_2), 30.8 (CH_2), 30.9 (CH_2), 31.2 (CH_2), 31.3 (CH_2), 32.8 (CH_2), 33.1 (CH_2), 62.6 (CH_2), 62.8 (CH_2), 68.2 (CH), 69.6 (CH), 71.0 (CH), 73.7 (CH), 96.5 (CH), and 97.0 (CH); MS *m/z* (rel intensity) 200 (M^+; 19), 182 ($M^+ - H_2O$; 41), 143 (28), 136 (30), 112 (100), and 102 (71); HRMS [Found: *m/z* 200.1393 (M^+). Calcd for $C_{11}H_{20}O_3$: M, 200.1413].

4-(Tetrahydropyran-2-yloxy)cyclohexanone (6). To a stirred solution of $(COCl)_2$ (1.8 cm^3, 21 mmol) in CH_2Cl_2 (30 cm^3) was added dry DMSO (2.5 cm^3, 35 mmol) at −60 °C under Ar. After being stirred for 3 min, a solution of **5** (991.0 mg, 4.95 mmol) in CH_2Cl_2 (10 cm^3) was added, and the mixture was further stirred for 1 h. Et_3N (7.0 cm^3, 50 mmol) was added, and the mixture was allowed to warm to room temperature. The reaction was quenched by the addition of aqueous NH_4Cl, and the resultant suspension was extracted with CH_2Cl_2. Evaporation of the solvent afforded a crude product **6**, which was used in the next step without purification. **6**: An oil; IR (neat) 1720 cm^{-1} (C=O); ^{1}H NMR (Me_4Si) δ = 1.51—2.16 (10H, m), 2.23—2.35 (2H, m, CHHCO ×2), 2.56 (1H, dddd, *J* = 1.5, 5.5, 10.0, 14.5 Hz, CHHCO), 2.65 (1H, dddd, *J* = 1.5, 6.0, 10.0, 14.5 Hz, CHHCO), 3.51—3.57 (1H, m, OCHH), 3.89—3.96 (1H, m, OCHH), 4.09 (1H, tt, *J* = 3.0, 6.0 Hz, CHOTHP), and 4.77 (1H, dd, *J* = 3.0, 4.5 Hz, OCHO); ^{13}C NMR δ = 19.7 (CH_2), 25.3 (CH_2), 30.0 (CH_2), 31.1 (CH_2), 32.2 (CH_2), 37.2 (CH_2), 37.5 (CH_2), 62.7 (CH_2), 69.8 (CH), 97.0 (CH), and 211.2 (CO); MS *m/z* (rel intensity) 198 (M^+; 1), 180 ($M^+ - H_2O$; 1), 119 (14), 117 (15), 97 (M^+ − OTHP; 44), and 85 (100); HRMS [Found: *m/z* 198.1263 (M^+). Calcd for $C_{11}H_{18}O_3$: M, 198.1256].

4-Methylene-1-(tetrahydropyran-2-yloxy)cyclohexane (7). To a stirred solution of $(Ph_3PCH_3)^+Br^-$ (2.17 g, 6.07 mmol) in dry Et_2O (60 cm^3) was added dropwise a solution of BuLi (3.5 cm^3, 6.0 mmol; 1.7 mol dm^{-3} in hexane) at 0 °C under Ar. After being stirred at room temperature for 4 h, the mixture was cooled to 0 °C again, and a solution of **6** (obtained above) in Et_2O (10 cm^3) was added. The mixture was stirred at room temperature for 16 h, then water was added. Extraction with Et_2O followed by evaporation of the solvent gave a crude product which was chromatographed on silica gel (30 g) using hexane–AcOEt (19 : 1) as eluent to afford **7** (830.2 mg, 85% from **5**) as an oil; IR (neat) 1655 cm^{-1} (C=C); ^{1}H NMR (Me_4Si) δ = 1.42—1.97 (10H, m), 2.00—2.13 (2H, m, CHHC=C ×2), 2.29—2.41 (2H, m, CHHC=C ×2), 3.47—3.53 (1H, m, OCHH), 3.80 (1H, tt, *J* = 3.5, 9.0 Hz, CHOTHP), 3.89—3.96 (1H, m, OCHH), 4.63 (2H, br s, C=CH_2), and 4.73 (1H, dd, *J* = 3.0, 4.5 Hz, OCHO); ^{13}C NMR δ = 19.9 (CH_2), 25.5 (CH_2), 31.2 (CH_2), 31.7 (CH_2), 31.9 (CH_2), 32.1 (CH_2), 34.2 (CH_2), 62.7 (CH_2), 73.0 (CH), 96.7 (CH), 107.4 (CH_2), and 148.2 (C); MS *m/z* (rel intensity) 196 (M^+; 7), 95 (50), and 85 (100); HRMS [Found: *m/z* 196.1454 (M^+). Calcd for $C_{12}H_{20}O_2$: M, 196.1464].

4-(Tetrahydropyran-2-yloxy)cyclohexanemethanol (8). To a stirred suspension of $NaBH_4$ (2.17 g, 57.4 mmol) in dry diglyme (60 cm^3) was added successively 2-methylbut-2-ene (22.4 cm^3, 211 mmol) and BF_3·OEt_2 (5.2 cm^3, 41 mmol) under Ar at 0 °C. After being stirred for 6 h, a solution of **7** (830.2 mg, 4.23 mmol) in diglyme (10 cm^3) was added, and the mixture was stirred at room temperature for 17 h. The flask was cooled to 0 °C again, then H_2O (23 cm^3), NaOH aq (23 cm^3; 3 mol dm^{-3} solution), and 35% H_2O_2 aq (29 cm^3) were added dropwise, successively. The mixture was stirred at 40 °C for 1.5 h, an aqueous solution of NaCl was added, and diglyme was partly removed by a rotary evaporator. Water was added, and the mixture was extracted with AcOEt and dried. Evaporation of the solvent followed by silica gel (25 g) column chromatography using hexane–AcOEt (2 : 1) as eluent afforded **8** (817.7 mg, 90%; 1 : 1 mixture of *cis*- and *trans*-disubstituted cyclohexanes) as an oil; IR (neat) 3470 cm^{-1} (OH); ^{1}H NMR (Me_4Si) δ = 0.92—2.10 (16H, m), 3.45 (2H ×1/2, d, *J* = 6.5 Hz, CH_2OH of *trans*-isomer), 3.50 (2H ×1/2, d, *J* = 6.5 Hz, CH_2OH of *cis*-isomer), 3.45—3.52 (1H, m, OCHHCH_2), 3.57 (1H ×1/2, tt, *J* = 4.5, 11.0 Hz, CHOTHP of *trans*-isomer), 3.87—3.95 (1H, m, OCHHCH_2, and 1H ×1/2, CHOTHP of *cis*-isomer), 4.66 (1H ×1/2, dd, *J* = 3.0, 4.5 Hz, OCHO of *cis*-isomer), and 4.73 (1H ×1/2, dd, *J* = 3.0, 4.5 Hz, OCHO of *trans*-isomer); ^{13}C NMR (Me_4Si) assigned for *trans*-isomer δ = 20.0 (CH_2), 25.6 (CH_2), 27.6 (CH_2), 27.9 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 33.1 (CH_2), 39.7 (CH), 62.8 (CH_2), 67.9 (CH_2), 75.2 (CH), and 96.8 (CH), assigned for *cis*-isomer δ = 19.9 (CH_2), 23.8 (CH_2), 24.1 (CH_2), 25.5 (CH_2), 28.4 (CH_2), 30.9 (CH_2), 31.3 (CH_2), 39.2 (CH), 62.8 (CH_2), 67.6 (CH_2), 70.9 (CH), and 96.8 (CH); MS *m/z* (rel intensity) 214 (M^+; 17), 196 ($M^+ - H_2O$; 13), 135 (14), 130 (19), 120 (31), 111 (61), 102 (88), 84 (100), and 60 (86); HRMS [Found: *m/z* 214.1548 (M^+). Calcd for $C_{12}H_{22}O_3$: M, 214.1570].

4-(Tetrahydropyran-2-yloxy)cyclohexanecarbaldehyde (9). Compound **8** (765.5 mg, 3.57 mmol) was oxidized by $(COCl)_2$ (1.5 cm^3, 17 mmol) and DMSO (2.0 cm^3, 28 mmol) by the procedure described for **6**. The crude product obtained after evaporation of the extracted solvent (CH_2Cl_2) was used in the following step without purification. **9** (1 : 1 mixture of *cis*- and *trans*-disubstituted cyclohexanes): An oil; IR (neat) 2720 (CHO) and 1730 cm^{-1} (C=O); ^{1}H NMR (Me_4Si) δ = 1.25—2.30 (15H, m), 3.46—3.94 (3H, m, OCH_2 and CHOTHP), 4.66—4.74 (1H, m, OCHO), 9.64 (1H ×1/2, d, *J* = 1.5 Hz, CHO of one isomer), and 9.65 (1H ×1/2, d, *J* = 1.0 Hz, CHO of the other isomer); ^{13}C NMR for both isomers δ = 19.7 (CH_2), 19.8 (CH_2), 21.1 (CH_2), 21.5 (CH_2), 23.8 (CH_2), 24.1 (CH_2), 25.4 (CH_2), 25.5 (CH_2), 28.2 (CH_2), 30.2 (CH_2), 30.5 (CH_2), 31.1 (CH_2), 31.1 (CH_2), 32.1 (CH_2), 48.3 (CH), 49.2 (CH), 62.6 (CH_2), 62.7 (CH_2), 70.8 (CH), 73.7 (CH), 96.6 (CH), 96.9 (CH), 204.1 (CHO), and 204.7 (CHO); MS *m/z* (rel intensity) 212 (M^+; 1.5), 194 (1.5), 149 (4), 128 (4), 111 (51), 93 (26), and 85 (100); HRMS [Found: *m/z* 212.1385 (M^+). Calcd for $C_{12}H_{20}O_3$: M, 212.1413].

1-[4-(Tetrahydropyran-2-yloxy)cyclohexan-1-yl]-3-(trimethylsilyl)prop-1-ene (10). To a stirred solution of $(Ph_3PCH_3)^+Br^-$ (2.56 g, 7.17 mmol) in dry THF (120 cm^3) was added a solution of BuLi (4.4 cm^3, 7.5 mmol; 1.7 mol dm^{-3} solution in hexane) at 0 °C under Ar. After being stirred for 1 h, iodomethyltrimethylsilane (1.45 cm^3, 9.77 mmol) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 1 h. This was cooled to −60 °C, and a second portion of BuLi (2.9 cm^3, 4.93 mmol) was added. The flask was slowly warmed to room temperature, and the stirring was continued for 1.5 h. This was cooled to −60 °C again, and a solution of **9** (obtained above) in THF (10 cm^3)

was added. After this was stirred at room temperature for 16 h, the reaction was quenched by addition of an aqueous solution of NH_4Cl. Extraction with Et_2O, drying, followed by silica gel (15 g) column chromatography using hexane–AcOEt (99 : 1) as eluent afforded **10** (715.3 mg, 68% from **8**; a mixture of four isomers, the ratio of which was not determined) as an oil; IR (neat) 1650 cm^{-1} (C=C); ^1H NMR ($CHCl_3$) $\delta = -0.05$ (9H $\times 1/13$, s, $SiMe_3$ of one of *E*-isomer), -0.04 (9H $\times 2/13$, s, $SiMe_3$ of one of *E*-isomer), -0.01 (9H $\times 10/13$, s, $SiMe_3$ of *Z*-isomer), 1.02—2.32 (17H, m), 3.43—3.94 (3H, m, OCH_2 and CHOTHP), 4.63—4.72 (1H, m, OCHO), and 5.00—5.43 (2H, m, CH=CH); MS *m/z* (rel intensity) 296 (M^+; 36), 212 (26), 150 (97), 85 (99), 73 (100), and 61 (99); HRMS [Found: *m/z* 296.2165 (M^+). Calcd for $C_{17}H_{32}O_2Si$: M, 296.2173].

4-[3-(Trimethylsilyl)prop-1-en-1-yl]cyclohexan-1-ol (11). Compound **10** (959.6 mg, 3.24 mmol) was dissolved in a mixture of THF (50 cm^3) and 5% aqueous HCl (13 cm^3). The resultant solution was stirred at room temperature for 32 h, and extracted with CH_2Cl_2. After drying and evaporation of the solvent, the crude product was chromatographed on silica gel (50 g) using hexane–AcOEt (19 : 1 and 17 : 3) as eluent to yield **11** (525.9 mg, 77%). ^1H and ^{13}C NMR data were collected after further separation into two groups, Group I ($R_f = 0.4$; hexane/AcOEt 4 : 1) and Group II ($R_f = 0.35$). **11**: An oil; IR (neat) 3370 (OH) and 1650 cm^{-1} (C=C); ^1H NMR ($CHCl_3$) Group I (*trans*-disubstituted cyclohexane; 6 : 1 mixture of *Z*- and *E*-allylsilanes) $\delta = -0.03$ (9H $\times 1/7$, s, $SiMe_3$ of *E*-isomer), -0.01 (9H $\times 6/7$, s, $SiMe_3$ of *Z*-isomer), 1.23—2.03 (9H plus 3H $\times 1/7$, m), 1.46 (2H $\times 6/7$, dd, $J = 1.0$, 8.5 Hz, CH_2SiMe_3 of *Z*-isomer), 2.27 (1H $\times 6/7$, tq, $J = 4.5$, 9.0 Hz, CHCH=CH of *Z*-isomer), 3.88—3.94 (1H $\times 1/7$, m, CHOH of *E*-isomer), 3.93 (1H $\times 6/7$, tt, $J = 3.0$, 5.0 Hz, CHOH of *Z*-isomer), and 5.19—5.42 (2H, m, CH=CH), Group II (*cis*-disubstituted cyclohexane; 5 : 1 mixture of *Z*- and *E*-allylsilanes) $\delta = -0.04$ (9H $\times 1/6$, s, $SiMe_3$ of *E*-isomer), -0.01 (9H $\times 5/6$, s, $SiMe_3$ of *Z*-isomer), 1.05—2.18 (10H plus 2H $\times 1/6$, m), 1.45 (2H, $\times 5/6$, dd, $J = 1.0$, 9.0 Hz, CH_2SiMe_3 of *Z*-isomer), 3.50—3.57 (1H $\times 1/6$, m, CHOH of *E*-isomer), 3.55 (1H $\times 5/6$, tt, $J = 4.5$, 11.0 Hz, CHOH of *Z*-isomer), and 4.09—5.42 (2H, m, CH=CH); ^{13}C NMR the major isomer of Group I $\delta = -1.8$ (3C), 18.5, 27.3 (2C), 32.0 (2C), 34.1, 66.8, 124.0, and 132.4, the major isomer of Group II $\delta = -1.9$ (3C), 18.5, 31.4 (2C), 35.0, 35.4 (2C), 70.6, 124.4, and 132.5; MS *m/z* (rel intensity) 212 (M^+; 19), 122 (12), 107 (18), 93 (23), and 73 (100); HRMS [Found: *m/z* 212.1595 (M^+). Calcd for $C_{12}H_{24}OSi$: M, 212.1597].

4-[3-(Trimethylsilyl)prop-1-en-1-yl]cyclohexanone (1). Swern oxidation of **11** (630.2 mg, 2.97 mmol) was done as described for the preparation of **6**, with $(COCl)_2$ (1.0 cm^3, 11 mmol), DMSO (1.5 cm^3, 21 mmol), and Et_3N (4.2 cm^3). Silica gel (30 g) column chromatography using hexane–AcOEt (19 : 1) as eluent afforded **1** (512.6 mg, 82%; 3 : 1 mixture of *Z*- and *E*-allylsilanes) as an oil; IR (neat) 1715 (C=O), 1655 cm^{-1} (C=C); ^1H NMR ($CHCl_3$) $\delta = -0.03$ (9H $\times 1/4$, s, $SiMe_3$ of *E*-isomer), 0.02 (9H $\times 3/4$, s, $SiMe_3$ of *Z*-isomer), 1.41 (2H $\times 1/4$, br d, $J = 7.5$ Hz, CH_2SiMe_3 of *E*-isomer), 1.52 (2H $\times 3/4$, dd, $J = 1.5$, 9.0 Hz, CH_2SiMe_3 of *Z*-isomer), 1.46—1.65 (2H, m), 1.89—2.04 (2H, m), 2.29—2.41 (4H plus 1H $\times 1/4$, m), 2.61—2.71 (1H $\times 3/4$, m, CHCH=CH of *Z*-isomer), 5.14 (1H $\times 3/4$, ddt, $J = 9.0$, 11.0, 1.5 Hz, CH=CHCH$_2$SiMe$_3$ of *Z*-isomer), 5.22 (1H $\times 1/4$, ddt, $J = 6.5$, 15.0, 1.0 Hz, CH=CHCH$_2$SiMe$_3$ of *E*-isomer), 5.39 (1H $\times 3/4$, ddt, $J = 1.0$, 11.0, 9.0 Hz, CH=CHCH$_2$SiMe$_3$ of *Z*-isomer), and 5.46 (1H $\times 1/4$, ddt, $J = 1.0$, 15.0, 8.0 Hz, CH=CHCH$_2$SiMe$_3$ of *E*-isomer); ^{13}C NMR assigned for *Z*-isomer $\delta = -1.9$ ($SiMe_3$), 18.8 (CH_2), 33.0 (CH_2 ×2), 34.2 (CH), 40.7 (CH_2 ×2), 125.7 (CH), 130.2 (CH), and 211.7 (CO), assigned for *E*-isomer $\delta = -2.1$ ($SiMe_3$), 22.7 (CH_2), 33.1 (CH_2 ×2), 38.9 (CH), 40.6 (CH_2 ×2), 125.8 (CH), 131.4 (CH), and 211.9 (CO); MS *m/z* (rel intensity) 210 (M^+; 15), 195 ($M^+ - Me$; 6), 181 (12), 168 (13), 142 (19), 127 (19), 83 (33), and 73 (100); HRMS [Found: *m/z* 210.1451 (M^+). Calcd for $C_{12}H_{22}OSi$: M, 210.1441]; Analysis [Found: C, 68.40; H, 10.34%. Calcd for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54%].

Cyclization of 1. To a stirred solution of TBAF (191 mg, 0.730 mmol) in dry THF (300 cm^3) was added dropwise a solution of **1** (51.3 mg, 0.244 mmol) in THF (10 cm^3) at -10 °C under Ar (Run 6 of Table 1). After this was stirred at room temperature for 1 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 silica gel (5 g) column chromatography using pentane–Et_2O (99 : 1) gave 7-vinylbicyclo[2.2.1]heptan-1-ol (**3**) (23.7 mg, 70%) as an oil; IR (neat) 3400 (OH) and 1640 cm^{-1} (C=C); ^1H NMR (C_6D_6; benzene = 7.15 as internal reference) $\delta = 1.09$—1.81 (10H, m), 2.02 (1H, dq, $J = 8.0$, 1.0 Hz, CHCH=CH$_2$), 5.09 (1H, ddd, $J = 1.0$, 2.5, 10.5 Hz, CH=CHH), 5.14 (1H, ddd, $J = 1.0$, 2.5, 17.0 Hz, CH=CHH), 5.76 (1H, ddd, $J = 8.0$, 10.5, 17.0 Hz, CH=CH$_2$); ^{13}C NMR (C_6D_6; $C_6D_6 = 128.0$ as internal reference) $\delta = 27.9$ (CH_2), 29.3 (CH_2), 32.9 (CH_2), 35.9 (CH_2), 38.8 (CH), 57.1 (CH), 83.4 (C), 117.4 (CH_2), and 136.0 (CH); MS *m/z* (rel intensity) 138 (M^+; 9), 123 (3), 109 (28), 96 (44), 85 (34), and 73 (100); HRMS [Found: *m/z* 138.1039 (M^+). Calcd for $C_9H_{14}O$: M, 138.1045].

***cis*-1,4-Cyclohexanedimethanol (14a).** To a stirred solution of **13a** (1.285 g, 5.63 mmol; contains about 7% of isomer **13b**, see text) in dry Et_2O (30 cm^3) was added $LiAlH_4$ (0.64 g, 16.9 mmol) at once, and by a $CaCl_2$ drying tube was attached to the flask. After the mixture was stirred at room temperature for 3 h, the reaction was quenched by addition of wet Et_2O and then H_2O. An aqueous solution of HCl (about 1 mol dm^{-3}) was added until the suspension become a clear solution. This was extracted with Et_2O and AcOEt, and then dried. Evaporation of the solvent followed by silica gel (40 g) column chromatography using $CHCl_3$–MeOH (19 : 1) as eluent afforded **14a** (797.0 mg, 98%) as an oil; IR (neat) 3350 cm^{-1} (OH); ^1H NMR (Me_4Si) $\delta = 1.37$—1.73 (12H, m) and 3.55 (4H, d, $J = 7.0$ Hz, CH_2OH ×2); ^{13}C NMR (Me_4Si) $\delta = 25.3$ (4C), 38.1 (2C), and 66.1 (2C); MS *m/z* (rel intensity) 144 (M^+; 38), 127 (77), 113 (100), and 84 (74); HRMS [Found: *m/z* 144.1140 (M^+). Calcd for $C_8H_{16}O_2$: M, 144.1151].

***trans*-1,4-Cyclohexanedimethanol (14b).** In a similar way, **13b** (4.882 g, 21.4 mmol) was treated with $LiAlH_4$ (2.44 g, 64.3 mmol) at room temperature to give **14b** (2.365 g, 77%); mp 61.5—62.5 °C; IR (Nujol) 3340 cm^{-1} (OH); ^1H NMR (Me_4Si) $\delta = 0.92$—1.04 (4H, m), 1.39—1.52 (2H, m), 1.56 (2H, br, OH ×2), 1.79—1.89 (4H, m), and 3.47 (4H, d, $J = 6.5$ Hz, CH_2OH ×2; ^{13}C NMR (Me_4Si) $\delta = 28.9$ (CH_2 ×4), 40.6 (CH ×2), and 68.6 (CH_2 ×2); MS *m/z* (rel intensity) 144 (M^+; 7), 126 (93), 113 (100), 109 (97), 96 (88), 94 (85), 82 (85), and 80 (84); HRMS [Found: *m/z* 144.1181 (M^+). Calcd for $C_8H_{16}O_2$: M, 144.1151]; Analysis [Found: C, 66.40; H, 11.10%. Calcd for $C_8H_{16}O_2$: C, 66.63: H, 11.18%].

***cis*-4-(Pivaloyloxymethyl)cyclohexanemethanol (15a).** A mixture of **14a** (1.992 g, 13.8 mmol) and pivaloyl chloride (2.04 cm^3, 16.6 mmol) in pyridine (70 cm^3) was kept at 0 °C for 2 h. A small amount of crashed ice (about 10 g) was added, and the mixture was stirred at room temperature for 1 h. After addition of dilute aqueous HCl, the mixture was extracted with AcOEt and dried. Evaporation of the solvent followed by silica gel (100 g) column chromatography using $CHCl_3$–MeOH (19 : 1) as eluent yielded **15a** (1.639 g, 52%) as an oil; IR (neat) 3470 (OH), 1735 (C=O), and 1170 cm^{-1} (C–O); ^1H NMR (Me_4Si) $\delta = 1.20$ (9H, s, $COCMe_3$), 1.38—1.92 (11H, m), 3.55 (2H, d, $J = 7.0$ Hz, CH_2OH), and 3.99

(2H, d, J = 7.0 Hz, C$\underline{H}_2$OPiv); ^{13}C NMR (Me_4Si) δ = 25.1 (2C), 25.4 (2C), 27.2 (3C), 34.6, 37.8, 38.9, 65.9, 67.1, and 178.8; MS m/z (rel intensity) 299 (M^++H; 35), 198 (55), 126 (97), 109 (92), 103 (97), 95 (98), and 79 (100); HRMS [Found: m/z 229.1787 (M^++H). Calcd for $C_{13}H_{25}O_3$: M, 229.1805].

***trans*-4-(Pivaloyloxymethyl)cyclohexanemethanol (15b).** By the same procedure, **14b** (1.82 g, 12.6 mmol) was treated with pivaloyl chloride (1.86 cm^3, 15.1 mmol) to afford **15b** (1.747 g, 61%) as an oil; IR (neat) 3460 (OH), 1735 (C=O), and 1170 cm^{-1} (C–O); ^{1}H NMR (Me_4Si) δ = 0.91—1.90 (11H, m), 1.20 (9H, s, COC$\underline{Me}_3$), 3.47 (2H, d, J = 6.5 Hz, C$\underline{H}_2$OH), and 3.89 (2H, d, J = 6.5 Hz, C$\underline{H}_2$OPiv); ^{13}C NMR (Me_4Si) δ = 27.2 (3C), 28.8 (2C), 29.0 (2C), 37.4, 38.9, 40.4, 68.5, 69.3, and 178.7; MS m/z (rel intensity) 229 (M^++H; 100), 211 (11), 127 (20), 110 (30), 107 (31), 94 (36), and 82 (31); HRMS [Found: m/z 229.1835 (M^++H). Calcd for $C_{13}H_{25}O_3$: M, 229.1805].

***cis*- 4- (Pivaloyloxymethyl)cyclohexanecarbaldehyde (16a).** Swern oxidation of **15a** (1.976 g, 8.65 mmol), according to the procedure described for the preparation of **6**, afforded a crude product **16a**, which was not purified. **16a**: An oil; IR (neat) 2720 (CHO), 1730 (C=O), and 1160 cm^{-1} (C–O); ^{1}H NMR (Me_4Si) δ = 1.08—1.17 (2H, m), 1.19 (9H, s, COC$\underline{Me}_3$), 1.56—1.78 (5H, m), 2.10—2.18 (2H, m), 2.44 (1H, quint, J = 4.5 Hz, C$\underline{H}$CHO), 3.87 (2H, d, J = 6.5 Hz, C$\underline{H}_2$OPiv), and 9.70 (1H, s, CHO); ^{13}C NMR δ = 23.6 (2C), 26.0 (2C), 27.2 (3C), 35.9, 38.8, 46.9, 68.1, 178.5, and 205.1; MS m/z (rel intensity) 226 (M^+; 3), 198 (3), 168 (22), 124 (98), 103 (79), 95 (86), and 57 (100); HRMS [Found: m/z 226.1548 (M^+). Calcd for $C_{13}H_{22}O_3$: M, 226.1570]; Analysis as semicarbazone (mp 135.0—137.5 °C) [Found: C, 59.37; H, 8.91; N, 14.74%. Calcd for $C_{14}H_{25}N_3O_3$: C, 59.34; H, 8.89; N, 14.83%].

***trans*-4-(Pivaloyloxymethyl)cyclohexanecarbaldehyde (16b).** Similarly, **15b** (600.4 mg, 2.63 mmol) gave a crude product containing **16b**: An oil; IR (neat) 2720 (CHO), 1730 (C=O), and 1165 cm^{-1} (C–O); ^{1}H NMR (Me_4Si) δ = 1.08 (2H, dq, J = 3.5, 12.0 Hz), 1.21 (9H, s, COC$\underline{Me}_3$), 1.29 (2H, dq, J = 3.5, 12.5 Hz), 1.65 (1H, ttt, J = 3.5, 6.5, 12.0 Hz, C$\underline{H}$CH$_2$OPiv), 1.87—1.93 (2H, m), 2.01—2.08 (2H, m), 2.20 (1H, dtt, J = 1.5, 3.5, 12.0 Hz, C$\underline{H}$CHO), 3.90 (2H, d, J = 6.5 Hz, C$\underline{H}_2$OPiv), and 9.63 (1H, d, J = 1.5 Hz, CHO); ^{13}C NMR (Me_4Si) δ = 25.3 (2C), 27.2 (3C), 28.3 (2C), 36.7, 38.9, 50.2, 68.8, 178.5, and 204.3; MS m/z (rel intensity) 227 (M^++H; 23), 134 (13), 125 (72), 124 (86), 119 (28), 95 (82), 86 (100), and 84 (91); HRMS [Found: m/z 227.1630 (M^++H). Calcd for $C_{13}H_{23}O_3$: M, 227.1648].

***cis*-4-[(*Z*)-3-(Trimethylsilyl)prop-1-en-1-yl]cyclohexylmethyl Pivaloate (17a).** According to the procedure described for the preparation of **10**, **16a** (prepared from 1.976 g of **15a**) was treated by the Wittig reaction giving **17a** (1.976 g, 74% from **15a**) as an oil; IR (neat) 1735 (C=O), 1660 (C=C), and 1155 cm^{-1} (C–O); ^{1}H NMR ($CHCl_3$) δ = −0.01 (9H, s, $SiMe_3$), 1.19 (9H, s, COC$\underline{Me}_3$), 1.38—1.85 (11H, m), 2.42—2.51 (1H, m, C$\underline{H}$CH=CH), 3.97 (2H, d, J = 7.0 Hz, C$\underline{H}_2$OPiv), and 5.27—5.40 (2H, m, CH=CH); ^{13}C NMR δ = −1.8 ($SiMe_3$), 18.5 (CH_2), 25.4 (CH_2 ×2), 27.2 (C$\underline{Me}_3$), 29.4 (CH_2 ×2), 32.6 (CH), 34.8 (CH), 38.8 (C), 67.5 (CH_2), 124.3 (CH), 131.1 (CH), and 178.6 (CO); MS m/z (rel intensity) 311 (M^++H; 10), 209 (6), 175 (38), 159 (58), and 73 (100); HRMS [Found: m/z 311.2383 (M^++H). Calcd for $C_{18}H_{35}O_2Si$: M, 311.2408].

***trans*- 4- [(*Z*)- 3- (Trimethylsilyl)prop- 1- en- 1- yl]cyclohexylmethyl Pivaloate (17b).** In the same way, **16b** (obtained above) gave **17b** (388.9 mg, 48% from **15b**) as an oil; IR (neat) 1735 (C=O), 1650 (C=C), and 1160 cm^{-1} (C–O); ^{1}H NMR ($CHCl_3$) δ = −0.02 (9H, s, $SiMe_3$), 0.95—1.78 (9H, m), 1.18 (9H, s, COC$\underline{Me}_3$), 1.44 (2H, dd, J = 1.5, 9.0 Hz, C$\underline{H}_2$SiMe$_3$), 2.06—2.17 (1H, m, C$\underline{H}$CH=CH), 3.85 (2H, d, J = 6.5 Hz, C$\underline{H}_2$OPiv), 5.05 (1H, ddt, J = 9.0, 10.5, 1.5 Hz, C$\underline{H}$=CHCH$_2$SiMe$_3$), and 5.26 (1H, ddt, J = 1.0, 10.5, 8.5 Hz, CH=C$\underline{H}$CH$_2$SiMe$_3$); ^{13}C NMR δ = −1.9 ($SiMe_3$), 18.5 (CH_2), 27.2 (C$\underline{Me}_3$), 29.3 (CH_2 ×2), 32.4 (CH_2 ×2), 35.9 (CH), 36.8 (CH), 38.8 (C), 69.5 (CH_2), 123.8 (CH), 133.3 (CH), and 178.6 (CO); MS m/z (rel intensity) 310 (M^+; 13), 208 (34), 175 (31), 159 (57), 129 (40), and 73 (100); HRMS [Found: m/z 310.2345 (M^+). Calcd for $C_{18}H_{34}O_2Si$: 310.2329].

***cis*-4-[(*Z*)-3-(Trimethylsilyl)prop-1-en-1-yl]cyclohexanemethanol (18a).** To a stirred solution of **17a** (669.8 mg, 2.16 mmol) in EtOH (100 cm^3) was added an aqueous solution of NaOH (60 cm^3; 7 mol dm^{-3} solution), and the mixture was stirred at room temperature for 92 h. After addition of saturated NH_4Cl aq, the pH of the solution was adjusted to about 6 by addition of dilute HCl. Extraction with $CHCl_3$ and AcOEt, followed by evaporation of the solvent gave an oily residue, which was chromatographed on silica gel (30 g) using hexane–AcOEt (19 : 1) as eluent to obtain **18a** (454.7 mg, 93%) as an oil; IR (neat) 3350 (OH) and 1645 cm^{-1} (C=C); ^{1}H NMR ($CHCl_3$) δ = −0.01 (9H, s, $SiMe_3$), 1.35—1.68 (12H, m), 2.42—2.51 (1H, m, C$\underline{H}$CH=CH), 3.54 (2H, d, J = 6.5 Hz, C$\underline{H}_2$OH), and 5.26—5.41 (2H, m, CH=CH); ^{13}C NMR δ = −1.8 (3C), 18.5, 25.3 (2C), 29.5 (2C), 32.8, 38.3, 66.6, 124.2, and 131.3; MS m/z (rel intensity) 227 (M^++H; 48), 152 (25), 121 (50), 107 (59), 94 (76), and 73 (100); HRMS [Found: m/z 227.1821 (M^++H). Calcd for $C_{13}H_{27}OSi$: M, 227.1832].

***trans*-4-[(*Z*)-3-(Trimethylsilyl)prop-1-en-1-yl]cyclohexanemethanol (18b).** To a stirred suspension of $LiAlH_4$ (51.3 mg, 1.35 mmol) in dry Et_2O (10 cm^3) was added dropwise a solution of **17b** (122.2 mg, 0.393 mmol) in Et_2O (12 cm^3) at 0 °C. After being stirred at 0 °C for 30 min under $CaCl_2$ drying tube, the reaction was quenched by the addition of wet Et_2O, H_2O, and dilute HCl, as described for **14a**. This was extracted with AcOEt and dried. Evaporation of the solvent followed by silica gel (6 g) column chromatography using hexane–AcOEt (9 : 1) as eluent afforded **18b** (76.0 mg, 85%) as an oil; IR (neat) 3360 (OH) and 1650 cm^{-1} (C=C); ^{1}H NMR ($CHCl_3$) δ = −0.01 (9H, s, $SiMe_3$), 0.92—1.81 (10H, m), 1.44 (2H, dd, J = 1.0, 9.0 Hz, C$\underline{H}_2$SiMe$_3$), 2.07—2.18 (1H, m, C$\underline{H}$CH=CH), 3.44 (2H, d, J = 6.0 Hz, C$\underline{H}_2$OH), 5.06 (1H, ddt, J = 9.0, 10.5, 1.5 Hz, C$\underline{H}$=CHCH$_2$SiMe$_3$), and 5.27 (1H, ddt, J = 1.0, 10.5, 9.0 Hz, CH=C$\underline{H}$CH$_2$SiMe$_3$); ^{13}C NMR δ = −1.9 (3C), 18.4, 29.1 (2C), 32.5 (2C), 36.0, 39.8, 68.4, 123.6, and 133.4; MS m/z (rel intensity) 227 (M^++H; 100), 226 (M^+; 95), 211 (20), 186 (14), 152 (96), 130 (98), 121 (92), 108 (94), and 91 (91); HRMS [Found: m/z 226.1757 (M^+). Calcd for $C_{13}H_{26}OSi$: M, 226.1754].

***cis*-4-[(*Z*)-3-(Trimethylsilyl)prop-1-en-1-yl]cyclohexanecarbaldehyde (2a).** Swern oxidation of **18a** (124.6 mg, 0.550 mmol) was done as described for **6** giving **2a** (111.9 mg, 91%) as an oil; IR (neat) 2710 (CHO), 1730 (C=O), and 1650 cm^{-1} (C=C); ^{1}H NMR ($CHCl_3$) δ = −0.03 (9H, s, $SiMe_3$), 1.10—1.65 (6H, m), 1.43 (2H, dd, J = 1.5, 8.5 Hz, C$\underline{H}_2$SiMe$_3$), 2.04 (2H, br dq, J = 13.0, 4.5 Hz), 2.27 (1H, br tq, J = 3.5, 9.5 Hz, C$\underline{H}$CH=CH), 2.35 (1H, br quint, J = 5.0 Hz, C$\underline{H}$CHO), 5.10 (1H, ddt, J = 9.0, 10.5, 1.5 Hz, C$\underline{H}$=CHCH$_2$SiMe$_3$), 5.28 (1H, ddt, J = 1.0, 10.5, 8.5 Hz, CH=C$\underline{H}$CH$_2$SiMe$_3$), and 9.67 (1H, br s, CHO); ^{13}C NMR δ = −1.9 (3C), 18.5, 23.7 (2C), 29.7 (2C), 34.1, 47.0, 124.2, 131.8, and 205.4; MS m/z (rel intensity) 224 (M^+; 39), 209 (9), 181 (76), 134 (20), 110 (59), 93 (81), and 73 (100); HRMS [Found: m/z 224.1595 (M^+). Calcd for $C_{13}H_{24}OSi$: M, 224.1597].

***trans*-4-[(*Z*)-3-(Trimethylsilyl)prop-1-en-1-yl]cyclohexanecarbaldehyde (2b).** Similarly, **18b** (54.6 mg, 0.241 mmol) afforded **2b** (48.5 mg, 90%) as an oil; IR (neat) 2710 (CHO), 1730 (C=O), and 1650 cm^{-1} (C=C); ^{1}H NMR ($CHCl_3$) δ = −0.01

(9H, s, $SiMe_3$), 1.03—1.35 (4H, m), 1.44 (2H, dd, J = 1.5, 9.0 Hz, $C\underline{H}_2SiMe_3$), 1.70—2.01 (4H, m), 2.09—2.21 (2H, m, $C\underline{H}CH{=}CH$ and $C\underline{H}CHO$), 5.05 (1H, ddt, J = 9.0, 10.5, 1.5 Hz, $C\underline{H}{=}CHCH_2SiMe_3$), 5.30 (1H, ddt, J = 1.0, 10.5, 8.5 Hz, $CH{=}C\underline{H}CH_2SiMe_3$), and 9.61 (1H, d, J = 1.5 Hz, CHO); ^{13}C NMR δ = −1.9 ($SiMe_3$), 18.5 (CH_2), 25.6 (CH_2 ×2), 31.8 (CH_2 ×2), 35.3 (CH), 49.8 (CH), 124.3 (CH), 132.5 (CH), and 204.5 (CO); MS *m/z* (rel intensity) 224 (M^+; 6), 181 (28), 134 (11), 119 (11), 106 (18), 91 (16), and 73 (100); HRMS [Found: *m/z* 224.1603 (M^+). Calcd for $C_{13}H_{24}OSi$: M, 224.1597]; Analysis as semicarbazone (mp 169.0—171.0 °C) [Found: C, 59.80; H, 9.53; N, 14.89%. Calcd for $C_{14}H_{27}N_3OSi$: C, 59.74; H, 9.67; N, 14.93%].

Cyclization of 2a and 2b. To a stirred solution of TBAF (66.9 mg, 0.256 mmol) in dry THF (150 cm^3) was added a solution of **2a** (22.0 mg, 0.0980 mmol) in THF (10 cm^3) at room temperature. The atmosphere was set by filling Ar over the reaction mixture and the stirring was continued for 18 h (Run 4 of Table 2). An aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O and dried. Evaporation of the solvent followed by silica gel (5 g) column chromatography using hexane–AcOEt (99 : 1) gave **3** (10.0 mg, 74%). Similarly, **2b** (46.0 mg, 0.205 mmol) produced **3** (18.4 mg, 65%) on treatment with TBAF (136 mg, 0.520 mmol) (Run 7 of Table 2).

***cis*-4-[(*Z*-Prop-1-en-1-yl]cyclohexylmethyl Pivaloate (20a).** To a stirred solution of $[Ph_3PCH_2CH_3]^+Br^-$ (3.152 g, 8.49 mmol) in dry THF (80 cm^3) was added BuLi (5.31 cm^3, 8.5 mmol; 1.6 mol dm^{-3} solution in hexane) at 0 °C under Ar. After being stirred at room temperature for 100 min, the mixture was cooled to 0 °C again, and a solution of **16a** (641 mg, 2.83 mmol) in THF (10 cm^3) was added. Stirring was continued at room temperature for 22 h, and to this was added a saturated aqueous solution of NH_4Cl. Extraction with Et_2O and subsequent evaporation of the solvent gave an oily residue, which was chromatographed on silica gel (80 g) using hexane–AcOEt (99 : 1) as eluent to yield **20a** (560 mg, 83%) as an oil; IR (neat) 1735 (C=O), 1655 (C=C), and 1160 cm^{-1} (C–O); ^{1}H NMR (Me_4Si) δ = 1.20 (9H, s, $COCMe_3$), 1.39—1.88 (9H, m), 1.62 (3H, dd, J = 1.5, 6.5 Hz, Me), 2.52—2.61 (1H, m, $C\underline{H}CH{=}CH$), 3.98 (2H, d, J = 7.0 Hz, $C\underline{H}_2OPiv$), 5.40 (1H, ddq, J = 1.0, 10.5, 6.5 Hz, $CH{=}C\underline{H}Me$), and 5.49 (1H, ddq, J = 9.0, 10.5, 1.5 Hz, $C\underline{H}{=}CHMe$); ^{13}C NMR δ = 12.9, 27.2 (3C), 29.2 (2C), 32.3 (2C), 35.8, 36.8, 38.8, 69.4, 122.4, 136.3, and 178.6; MS *m/z* (rel intensity) 238 (M^+; 12), 153 (7), 136 (100), 121 (34), 107 (78), 93 (34), and 57 (98); HRMS [Found: *m/z* 238.1946 (M^+). Calcd for $C_{15}H_{26}O_2$: M, 238.1934].

***trans*-4-[(*Z*)-Prop-1-en-1-yl]cyclohexylmethyl Pivaloate (20b).** By the same procedure, **16b** (1.752 g, 7.74 mmol) was converted to **20b** (1.713 g, 93%); an oil; IR (neat) 1730 (C=O), 1660 (C=C), and 1160 cm^{-1} (C–O); ^{1}H NMR (Me_4Si) δ = 1.00—1.80 (9H, m) 1.21 (9H, s, $COCMe_3$), 1.62 (3H, dd, J = 1.5, 6.5 Hz, Me), 2.18—2.29 (1H, m, $C\underline{H}CH{=}CH$), 3.88 (2H, d, J = 6.5 Hz, $C\underline{H}_2OPiv$), 5.19 (1H, ddq, J = 9.0, 10.5, 1.5 Hz, $C\underline{H}{=}CHMe$), and 5.36 (1H, ddq, J = 1.0, 10.5, 6.5 Hz, $CH{=}C\underline{H}Me$); ^{13}C NMR δ = 12.9, 27.2 (3C), 29.2 (2C), 32.3 (2C), 35.8, 36.7, 38.8, 69.4, 122.4, 136.3, and 178.6; MS *m/z* (rel intensity) 238 (M^+; 5), 153 (12), 136 (93), 121 (62), 107 (99), 93 (66), and 57 (100); HRMS [Found: *m/z* 238.1912 (M^+). Calcd for $C_{15}H_{26}O_2$: M, 238.1934].

***cis*-4-[(*Z*)-Prop-1-en-1-yl]cyclohexanemethanol (21a).** Compound **20a** (546 mg, 2.29 mmol) was reduced by $LiAlH_4$ (261 mg, 6.88 mmol) after the procedure described for **14a**. Silica gel (20 g) column chromatography using hexane–AcOEt (19 : 1 and 1 : 1) afforded **21a** (342.5 mg, 97%) as an oil; IR (neat) 3370 (OH) and 1660 cm^{-1} (C=C); ^{1}H NMR (Me_4Si) δ = 1.38—1.83 (10H, m), 1.62 (3H, dd, J = 1.5, 6.5 Hz, Me), 2.53—2.61 (1H, m, $C\underline{H}CH{=}CH$), 3.55 (2H, d, J = 6.5 Hz, $C\underline{H}_2OH$), 5.40 (1H, ddq, J = 1.0, 10.5, 6.5 Hz, $CH{=}C\underline{H}Me$), and 5.50 (1H, ddq, J = 9.0, 10.5, 1.5 Hz, $C\underline{H}{=}CHMe$); ^{13}C NMR δ = 12.9, 25.3 (2C), 29.3 (2C), 32.7, 38.2, 66.6, 122.7, and 134.5; MS *m/z* (rel intensity) 154 (M^+; 73),136 (90), 121 (90), 108 (86), 107 (85), 93 (92), 81 (94), 67 (94), 55 (96), and 41 (100); HRMS [Found: *m/z* 154.1395 (M^+). Calcd for $C_{10}H_{18}O$: M, 154.1358].

***trans*-4-[(*Z*)-Prop-1-en-1-yl]cyclohexanemethanol (21b).** In the same way, **20b** (1.7128 g, 7.19 mmol) gave **21b** (1.0985 g, 99%): An oil; IR (neat) 3370 (OH) and 1660 cm^{-1} (C=C); ^{1}H NMR (Me_4Si) δ = 0.95—1.84 (10H, m), 1.62 (3H, dd, J = 1.5, 6.5 Hz, Me), 2.19—2.30 (1H, m, $C\underline{H}CH{=}CH$), 3.46 (2H, d, J = 6.5 Hz, $C\underline{H}_2OH$), 5.20 (1H, ddq, J = 9.0, 10.5 1.5 Hz, $C\underline{H}{=}CHMe$), and 5.36 (1H, ddq, J = 1.0, 10.5, 6.5 Hz, $CH{=}C\underline{H}Me$); ^{13}C NMR (Me_4Si) δ = 12.9, 29.1 (2C), 32.4 (2C), 36.1, 40.0, 68.8, 122.3, and 136.5; MS *m/z* (rel intensity) 154 (M^+; 36), 136 (48), 121 (42), 107 (100), 93 (67), 81 (61), 79 (86), 67 (65), 55 (55), and 41 (64); HRMS [Found: *m/z* 154.1349 (M^+). Calcd for $C_{10}H_{18}O$: M, 154.1358].

***cis*-4-[(*Z*)-Prop-1-en-1-yl]cyclohexanecarbaldehyde (19a).** Swern oxidation of **21a** (257.3 mg, 1.67 mmol) with $(COCl)_2$ (0.44 cm^3), DMSO (0.71 cm^3), and Et_3N (2.53 cm^3) was done after the procedure described for **6**, giving **19a** (196.5 mg, 77%) after silica gel (20 g) chromatography using hexane–AcOEt (99 : 1) as eluent. **19a**: An oil; IR (neat) 2710 (CHO), 1725 (C=O), and 1660 cm^{-1} (C=C); ^{1}H NMR (Me_4Si) δ = 1.15—1.25 (2H, m), 1.52—1.70 (4H, m), 1.61 (3H, dd, J = 1.5, 6.5 Hz, Me), 2.07 (2H, br dq, J = 13.5, 4.5 Hz), 2.35—2.44 (2H, m, $C\underline{H}CHO$ and $C\underline{H}CH{=}CH$), 5.25 (1H, ddq, J = 9.0, 10.5, 1.5 Hz, $C\underline{H}{=}CHMe$), 5.37 (1H, ddq, J = 1.0, 10.5, 6.5 Hz, $CH{=}C\underline{H}Me$), and 9.71 (1H, br s, CHO); ^{13}C NMR δ = 12.9, 23.6 (2C), 29.5 (2C), 34.1, 47.1, 122.7, 135.0, and 205.4; MS *m/z* (rel intensity) 152 (M^+; 57), 134 (65), 121 (54), 119 (47), 109 (43), 93 (49), 81 (96), 79 (96), 67 (99), and 55 (100); HRMS [Found: *m/z* 152.1183 (M^+). Calcd for $C_{10}H_{16}O$: M, 152.1202]; Analysis as semicarbazone (mp 135.5—139.0 °C) [Found: C, 62.83; H, 8.98; N, 19.99%. Calcd for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08%].

***trans*-4-[(*Z*)-Prop-1-en-1-yl]cyclohexanecarbaldehyde (19b).** Similarly, **21b** (50.5 mg, 0.327 mmol) gave **19b** (32.2 mg, 65%); an oil; IR (neat) 2720 (CHO), 1730 (C=O), 1660 cm^{-1} (C=C); ^{1}H NMR (Me_4Si) δ = 1.13 (2H, dq, J = 3.5, 12.5 Hz), 1.33 (2H, dq, J = 3.5, 12.5 Hz), 1.62 (3H, dd, J = 2.0, 6.5 Hz, Me), 1.74—1.81 (2H, m), 1.97—2.04 (2H, m), 2.19 (1H, dtt, J = 1.5, 3.5, 12.0 Hz, $C\underline{H}CHO$), 2.26 (1H, br dtt, J = 9.0, 4.0, 11.5 Hz, $C\underline{H}CH{=}CH$), 5.20 (1H, ddq, J = 9.0, 10.5, 1.5 Hz, $C\underline{H}{=}CHMe$), 5.38 (1H, ddq, J = 1.0, 10.5, 6.5 Hz, $CH{=}C\underline{H}Me$), and 9.63 (1H, d, J = 1.5 Hz, CHO); ^{13}C NMR δ = 12.9, 25.6 (2C), 31.6 (2C), 35.3, 49.8, 122.9, 135.6, and 204.6; MS *m/z* (rel intensity) 152 (M^+; 93), 134 (93), 121 (95), 119 (94), 109 (99), 93 (98), 82 (97), 68 (98), and 53 (100); HRMS [Found: *m/z* 152.1157 (M^+). Calcd for $C_{10}H_{16}O$: M, 152.1202].

Cyclization of 19a and 19b. To a stirred solution of TBAF (341 mg, 1.30 mmol) in dry THF (140 cm^3) was added a solution of **19a** (79.6 mg, 0.523 mmol) in THF (10 cm^3) at 0 °C. A $CaCl_2$ drying tube was attached and the reaction mixture was stirred at room temperature for 22 h (Run 2 of Table 3). A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O. Evaporation of the solvent followed by silica gel (20 g) column chromatography using pentane–AcOEt (96 : 4) as eluent afforded **22** (41.9 mg, 58%). Similarly, **19b** (35.8 mg, 0.235 mmol) produced **22** (14.6 mg, 45%) on treatment with TBAF (153 mg, 0.585 mmol) (Run 4 of Table 3). (*Z*)-4-[Prop-1-en-1-yl]cyclohexanone (**22**): An oil; IR (neat) 1720 (C=O) and 1660 cm^{-1} (C=C); ^{1}H NMR (Me_4Si) δ = 1.52—1.64 (2H, m, $(C\underline{H}H)_2CHCH{=}CH$), 1.69 (3H, dd, J = 1.5,

6.5 Hz, Me), 1.94—2.02 (2H, m, (CHH)$_2$CHCH=CH), 2.37—2.43 (4H, m, $(CH_2)_2CO$), 2.72—2.83 (1H, m, CHCH=CH), 5.28 (1H, ddq, J = 9.0, 10.5, 1.5 Hz, CH=CHMe), and 5.48 (1H, ddq, J = 1.0, 10.5, 6.5 Hz, CH=CHMe); ^{13}C NMR δ = 13.1 (CH_3), 32.9 (CH_2 ×2), 34.1 (CH), 40.7 (CH_2 ×2), 124.2 (CH), 133.4 (CH), and 211.6 (CO); MS *m/z* (rel intensity) 138 (M^+; 52), 110 (15), 96 (18), 81 (32), 68 (100), 67 (79), and 39 (93); HRMS [Found: *m/z* 138.1022 (M^+). Calcd for $C_9H_{14}O$: M, 138.1045].

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