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Nazarov Cyclization of 4-Cycloalkylidene-5-(trimethylsilyl)pent-1-en-3-one Derivatives. Synthesis of Spiro[4.5]decane, Spiro[4.4]nonane, and Their Derivatives

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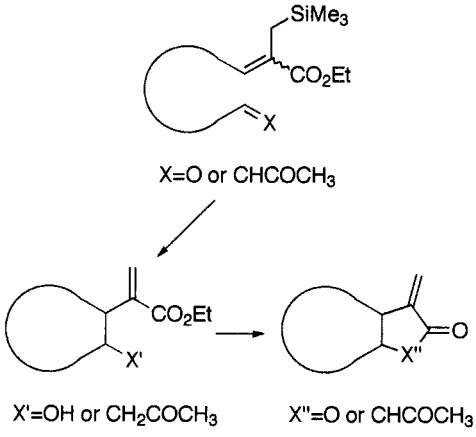
Abstract—Spiro[4.5]decane and spiro[4.4]nonane ring systems were synthesized by $FeCl_3$-induced Nazarov cyclization of α-(trimethylsilylmethyl)divinyl ketone derivatives. It was found that the double bond position of the product is controlled by the presence/absence of α′-substituent, while trimethylsilyl group is essential to obtain the products in good yields. Spiro[4.4]nonanes having *exo*-methylene group underwent rearrangement to bicyclo[4.3.0]nonanes. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Allylsilanes are versatile building blocks and the allylanion equivalent in organic synthesis,[1] while conjugated carbonyl groups are typical Michael acceptors. Therefore, conjugated allylsilane with a carbonyl group at the β-position (β-carbonylallylsilane), or its equivalent, is a unique block, since this moiety can react formally as both a nucleophile (allylsilane) and an electrophile (conjugated carbonyl) at the same carbon. This makes it easy to synthesize odd membered cyclic compounds.[2] We synthesized five-membered lactones[3,4] or carbocycles[5] related to sesquiterpenoids using intramolecular cyclization of β-(ethoxycarbonyl)allylsilane with carbonyl or conjugated carbonyl groups, respectively, as shown in the general Scheme 1.[6] The synthesis of five- and seven-membered rings was also developed from related β-(functionalizedmethyl)allylsilanes, such as β-(dialkoxymethyl)-,[7] β-(halomethyl)-,[8] and β-(hydroxymethyl)allylsilanes[9] including a silylated derivative[10] and Trost's trimethylenemethane.[11]

Compounds having further conjugated C=C double bond to the β-carbonylallylsilane moiety are not a simple variation, since extension of conjugated double bond itself enables five-membered ring formation. We reported that 2-(trimethylsilylmethyl)pentadienoic acid cyclizes itself to yield five-membered lactone.[12,13] Another type of further conjugated β-carbonylallylsilane is α-(trimethylsilylmethyl)divinyl ketone, which can easily be obtained from β-(ethoxycarbonyl)allylsilane. The α-(trimethylsilylmethyl)divinyl ketone moiety must be a good precursor for the Nazarov cyclization reaction, which would formally proceed as illustrated in Scheme 2, and thus the reaction is expected to proceed easily.

Nazarov cyclization is one of the classical methods to synthesize five-membered carbocycles.[14] Denmark et al. developed silicon-directed Nazarov cyclization reaction utilizing both vinyl-[15] and allyl-silane[16] derivatives, the latter of which represents remarkable rate enhancement. Moreover, although studies were made on limited ring



Scheme 1.

Keywords: Nazarov reactions; rearrangements; silicon and compounds; spiro compounds.

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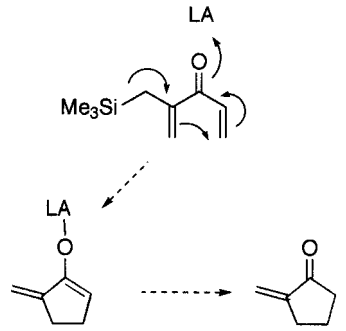
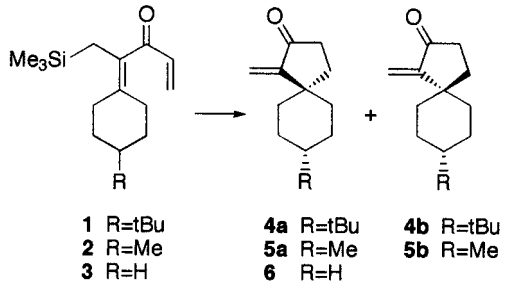


Scheme 2.



Scheme 3.

systems, the location of the double bond in the product is controlled by the position of the allylic silicon atom, as expected in Scheme 2.[16a] Kang et al.[17] reported the synthesis of various α-methylenecyclopentanones utilizing Nazarov cyclization of α′- and/or β′-substituted α-(trimethylsilylmethyl)divinyl ketones, however the reaction of β-substituted or β,β-disubstituted compounds were not studied. We reported the synthesis of the spiro[4.5]decane ring system,[18] one of the common structures in sesquiterpenes such as acoranes or vetispiranes,[19,20] using the Nazarov cyclization of β,β-disubstituted α-(trimethylsilylmethyl)divinyl ketones derived from β-(ethoxycarbonyl)allylsilane. We also reported that spiro[4.4]nonanes,[21] obtained by the same methodology, undergo skeletal rearrangement under the Nazarov condition to give bicyclo[4.3.0]nonanes.[22] Here we describe the full details of these reactions as well as the substituent effect on divinyl ketone moiety, which controls the double bond direction of the Nazarov cyclization.

Results and Discussion

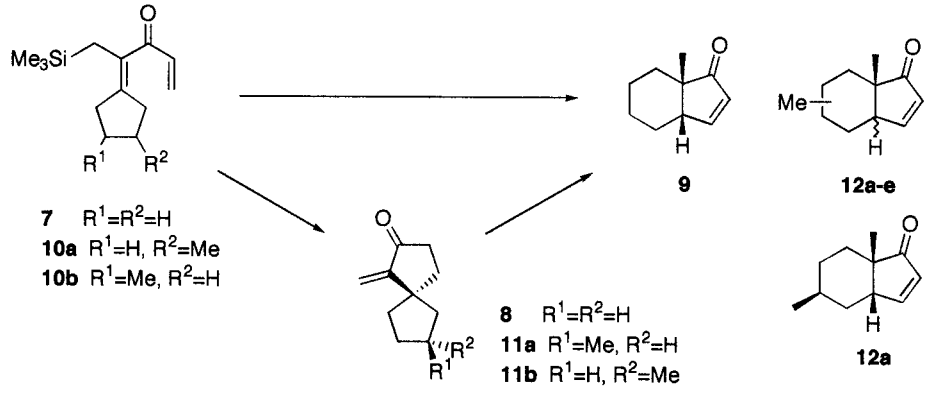
Initial study: synthesis of spiro[4.5]decanes[18]

We first studied the cyclization of **1**–**3** into spiro[4.5]-decanes. The Nazarov cyclization of **1** was carried out using $FeCl_3$ as a Lewis acid according to Kang's procedure[17] with a slight modification. Namely, 2.5 equiv. of $FeCl_3$ was added to a solution of **1** in CH_2Cl_2 at −60°C, and then the reaction mixture was slowly warmed to room temperature over a period of 7 h, giving a diastereomeric mixture of the spiro compounds, **4a** and **4b**, in 59% yield (Scheme 3). These two isomers could not be isolated from each other, and the ratio was determined to be **4a**:**4b**=5:1 from the ^1H NMR spectrum. The stereochemistry of the product was established from an NOE measurement, in which NOE was observed between the *t*-butyl group and one of the *exo*-methylenic protons for **4b**. The reaction at −60°C proceeded very slowly, while the reaction proceeded almost at once when $FeCl_3$ was added at 0°C, giving the products in lower yield (34%) together with many by-products as detected on TLC.

Compound **2** produced a mixture of **5a** and **5b** (61%, ratio 5:1) under the same reaction conditions (2.5 equiv. of $FeCl_3$, CH_2Cl_2, −60°C to room temperature). Similarly, **3** gave **6** in 67% yield. The structure of **5a** and **5b** was deduced from the chemical shifts of the olefinic protons compared with those of **4a** and **4b**. By TLC monitoring it was found that the reaction of **3** completed at −15°C (after 3.5 h warming from −60°C) giving the product **6** in 67% yield.

Tandem Nazarov cyclization—skeletal rearrangement[22]

Nazarov cyclization of the analogous compound **7**, divinyl ketone attached to five-membered ring, was studied next. When **7** was treated with $FeCl_3$ in CH_2Cl_2 at −30°C and then slowly warmed to 0°C for 4 h, the expected product spiro[4.4]nonane **8** was afforded in 56% yield. By TLC monitoring it was found that the reaction proceeds very slowly below −30°C. On the other hand, when **7** was treated at a higher temperature (i.e. when $FeCl_3$ was added at −10°C then stirred at room temperature for 24 h) compound **9**[23] was obtained as the sole product in 62% yield (Scheme 4). Treatment of **8** under the same reaction condition ($FeCl_3$, room temperature, 24 h) gave **9** in 60% yield.



Scheme 4.

Table 1. Tandem Nazarov cyclization–rearrangement of **10a** and **10b** (all reactions were carried out with 2.5 equiv. of $FeCl_3$ in CH_2Cl_2)

Entry	Substrate	Temperature	Time (h)	Yield (%)	Ratio (**12a**:**12b**:**12c**:**12d**:**12e**)
1	**10a**	rt[c]	25	64	72:12:5:3:8
2	**10b**	rt[c]	26	65	46:32:10:6:6
3	**11a**+**11b** (4:1)[a]	rt[c]	49	67	69:13:5:4:9
4	**11a**+**11b** (1:1)[b]	rt[c]	53	63	42:25:10:11:12
5	**10b**	rt[d]	25	67	13:13:9:26:39
6	**11a**+**11b** (4:1)[a]	rt[d]	18	69	9:0:0:22:69

[a] Obtained from **10a**; see text.
[b] Obtained from **10b**; see text.
[c] The reagents were added at −30°C and then the mixture was slowly warmed to room temperature over a period of 7 h, which is included in the reaction time.
[d] The reagents were added at −30°C and the cooling bath was immediately removed.

From these results, along with the observation of the behavior on TLC, it was suggested that **9** was formed from **7** via **8** as the intermediate.

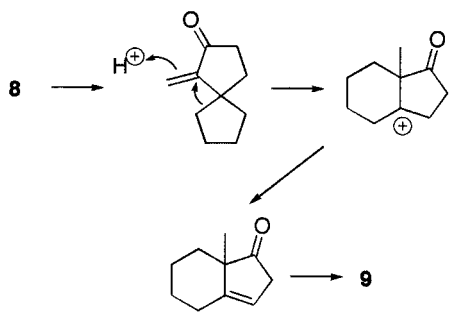
The stereochemistry of this tandem Nazarov cyclization—skeletal rearrangement was studied using methyl derivatives **10a** and **10b** as the substrates, which were prepared from 3-methylcyclopentanone as a 1:1 mixture and separated. First, **10a** and **10b** were treated with $FeCl_3$ at 0°C (reagents were mixed at −30°C, warmed to 0°C over 2.5 h, and then stirred at 0°C for 3.5 h) giving the two isomers spiro[4.4]-nonanes, **11a** and **11b** as an inseparable mixture (63% from **10a** and 66% from **10b**). The ratios of **11a**:**11b** were 4:1 from **10a**, and 1:1 from **10b**. The stereochemistry of **11a** and **11b** was determined from NOE experiments (see Experimental section).

The tandem Nazarov cyclization—rearrangement reaction was carried out at room temperature. The results are summarized in Table 1. In contrast to **9**, the rearranged product **12** consisted of five isomers (**12a**–**e**) as inseparable mixtures. The major isomer **12a** was shown to have the illustrated structure, which was determined by COSY and NOESY spectra (see Experimental section for detail). Although the exact structures of **12b**–**e** could not be determined, these compounds can be classified into two groups based on *J*-values of the olefinic protons, which suggests that **12b** (δ 5.88 and 6.65) and **12c** (δ 5.84 and 6.85) have a *cis*-fused hydrindane skeleton (dd, *J*=ca. 2, 6 Hz, for both olefinic protons); **12d** (δ 5.81 and 6.96) and **12e** (δ 5.80 and 6.95) have a *trans*-fused hydrindane moiety (br d, *J*=5.5 Hz, for both olefinic protons), by comparing their *J*-values with those of **9** and **12a**. It was confirmed here again that the bicyclo[4.3.0]nonane carbon framework is formed via spiro[4.4]nonane. Thus, both direct treatment of **10a** (entry 1) and treatment of the mixture of spiro compounds obtained from **10a** (entry 3) afforded mixtures of five isomers of **12** in similar ratios. The parallel result was also obtained from **10b** (entries 2 and 4). By comparison of the data of entries 3 and 4, it could be deduced that **12a** is formed from **11a** with about 90% selectivity, and **12b** is the major product from **11b**. Mixtures of isomers **12a**–**e** were obtained in different ratios when the reaction temperature was raised immediately after addition of the reagent (entries 5 and 6). The reaction mechanism of this rearrangement is not clear yet, however, formally, the reaction can be considered to proceed as shown in Scheme 5.[†]

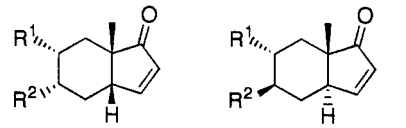
In order to find out whether this type of skeletal rearrangement also occurs from spiro[4.5]decanes, **4**–**6** were treated under the same reaction conditions. However, no reaction proceeded at all after the reaction temperature was elevated to 70°C. Accordingly, the rearrangement is considered to be limited to the strained spiro five–five membered ring system.

Substituent effect on divinyl ketone

The substituent effect on divinyl ketone moiety was then examined using β′-methyl derivatives **13a,b** and an α′-methyl derivative **14** as the substrates. The geometry of the double bond of **13a** and **13b** was determined from *J*-values of the olefinic protons. Both **13a** and **13b** afforded the same product **15**, as the case of **1**–**3**, but the yields were much higher, i.e. 93% from **13a** and 91% from **13b** (Scheme 6). It was found by monitoring on TLC that the reaction of **13b** was relatively faster than **13a**. Thus, the reaction of **13b** finished below −30°C while **13a** required a higher

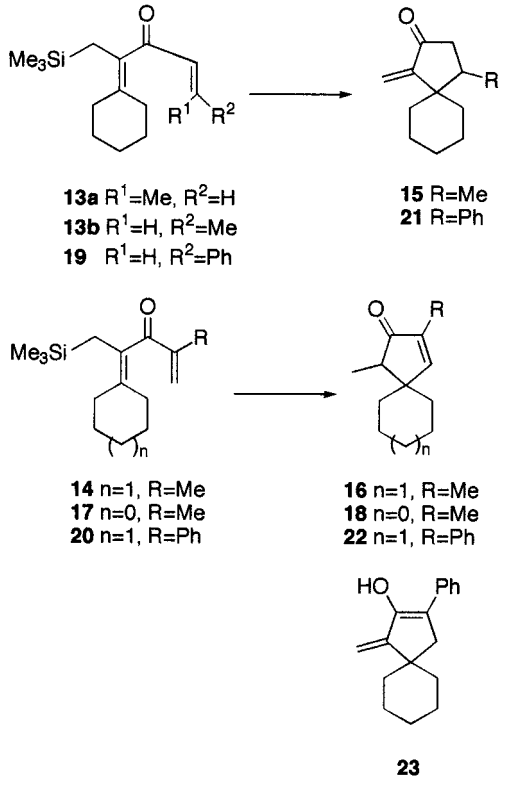


Scheme 5.



12b R^1=Me, R^2=H **12d** R^1=Me, R^2=H
12c R^1=H, R^2=Me **12e** R^1=H, R^2=Me

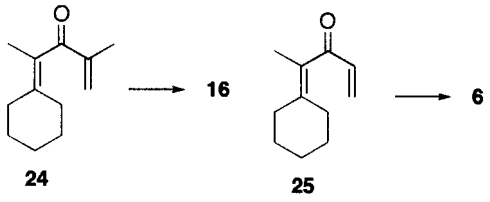
[†] Assuming Scheme 5, the structures of **12b**–**e** can be proposed as follows by considering stability of each compound, however, there is no experimental evidence to support these structures.



Scheme 6.

temperature. This can easily be explained by steric congestion between the methyl group and the cyclohexane ring. In contrast, **14** afforded a spiro[4.5]decane **16** having an endocyclic double bond in 55% yield, without being accompanied by a product having exocyclic double bond (Scheme 6). Similarly, the five-membered ring analog **17** afforded **18** in 46% yield. The reaction of **14** and **17** proceeded faster than **1** or **7**. Thus after addition of $FeCl_3$ at −60°C, the reaction was completed at −30°C (after 2 h for warming up from −60 to −30°C). No further reaction occurred when the flask was warmed to room temperature, while the reaction took place immediately with giving many by-products when $FeCl_3$ was added at −30°C. In contrast to **8** or **11a,b**, no rearrangement occurred with **18** after the reaction temperature was elevated to room temperature. From these results, it was suggested that the position of the double bond in the Nazarov product is determined by the presence/absence of the α′-substituent.

To confirm this, Nazarov cyclization of (*E*)-β′-phenyl derivative **19** and α′-phenyl derivative **20** was also studied. Compound **19** afforded *exo*-enone **21** in 80% yield, as the case of **13a,b**. While, **20** afforded an inseparable mixture of endo-enone **22** and enol form of *exo*-enone **23** (total yield 55%; ratio 2:1). The enol structure of **23** was determined from spectral data, including olefinic signals in ^{13}C NMR as well as the absence of C*H*Ph signal in the ^{1}H NMR. Although the results are not completely parallel with methyl-substituted compounds (**13a,b** and **14**), here again, the position of the double bond in the product was determined by the presence/absence of the α′-substituent. The reason why an α′-substituent determines the *exo/endo* double bond in the product is not clear yet.



Scheme 7.

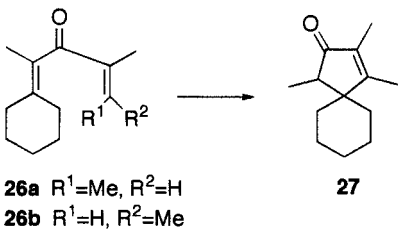
Effect of the silicon atom

The above result on the substituent effect is not consistent with our prediction that the double-bond location in the product is determined by silicon atom, as shown in Scheme 2. Then, to find out the role of the silicon atom, compounds **24** and **25**, desilylated substrate of **14** and **3**, respectively, were prepared. When **24** was treated under the same reaction condition as **14**, the same product **16** was obtained, however, the yield was decreased to 32% (Scheme 7). Compound **25** afforded **6**, the same product obtained from **3**, but again the yield was decreased to 39%. These results indicate that the trimethylsilyl group does not affect the position of the double bond in the product but is essential in its yield. This must be the result of the stabilization of the intermediate carbocation by silicon atom.[16,24] As mentioned above, the yields were also increased by the presence of β′-substituent (e.g. reaction of **13a,b**). This is probably also because of the stabilization of the intermediate.

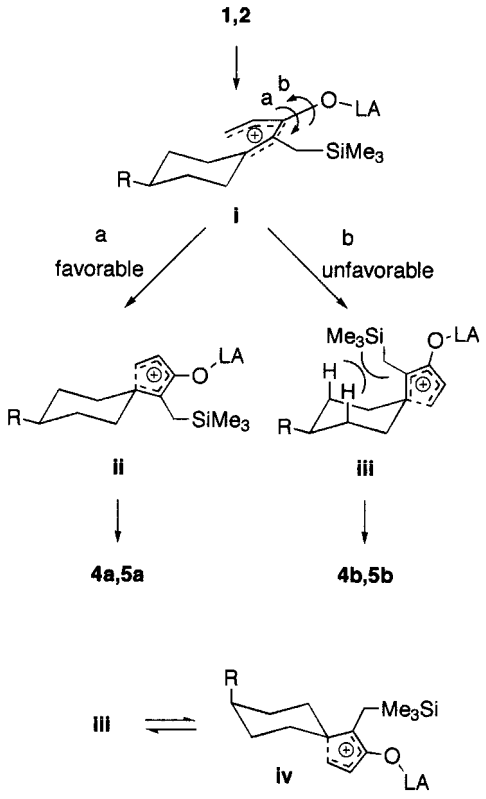
After the above results, compounds **26a,b** were designed based on the assumption that (1) the product would have endocyclic double bond because of the presence of α′-substituent and (2) the yield would not be low without the silicon atom because of the presence of β′-substituent. Compounds **26a** and **26b** were prepared as a 3:2 mixture and were separated by silica gel column chromatography. The *Z*- and *E*-geometries of **26a** and **26b**, respectively, were deduced by a comparison of the chemical shifts of the olefinic protons with those of **13a,b**. When **26a** and **26b** were treated with $FeCl_3$, the expected product **27** was afforded in 73 and 61% yields, respectively (Scheme 8). This result confirmed the above discussions.

Stereochemistry of the cyclization reaction

The stereoselectivity of the Nazarov cyclization can be rationalized by simple sterical congestion. The preferential formation of **4a** and **5a** over **4b** and **5b**, respectively, can be rationalized by steric interaction between cyclohexane ring and silicon-bearing carbon (not trimethylsilyl group[18]). Thus as depicted in Scheme 9, the silicon-bearing carbon

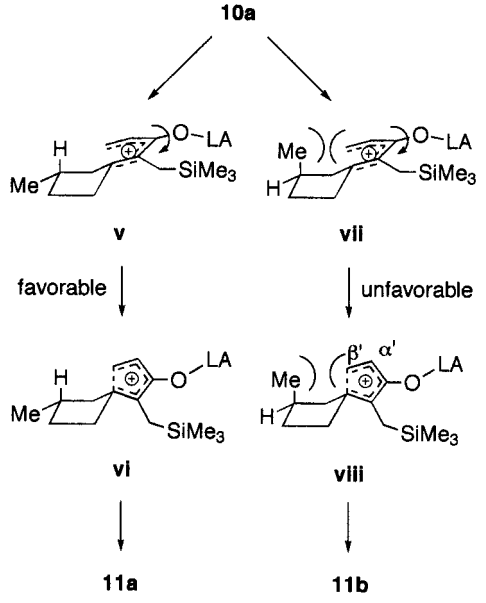


Scheme 8.



Scheme 9.

protrudes over the cyclohexane ring in **iii**, which makes this conformation unfavorable against **ii**. For the formation of **5b**, the conformation **iv** (R=Me) is also considerable since the divinyl ketone moiety is bigger than methyl group, however, this conformer is still less favorable than **ii** because of the presence of axial methyl group. Attacking direction to C(α)=C(β) double bond (exocyclic double bond) is not a major factor of the stereoselectivity, since an equatorial attack on the exocyclic double bond is normally favorable over an axial attack.[25]



Scheme 10.

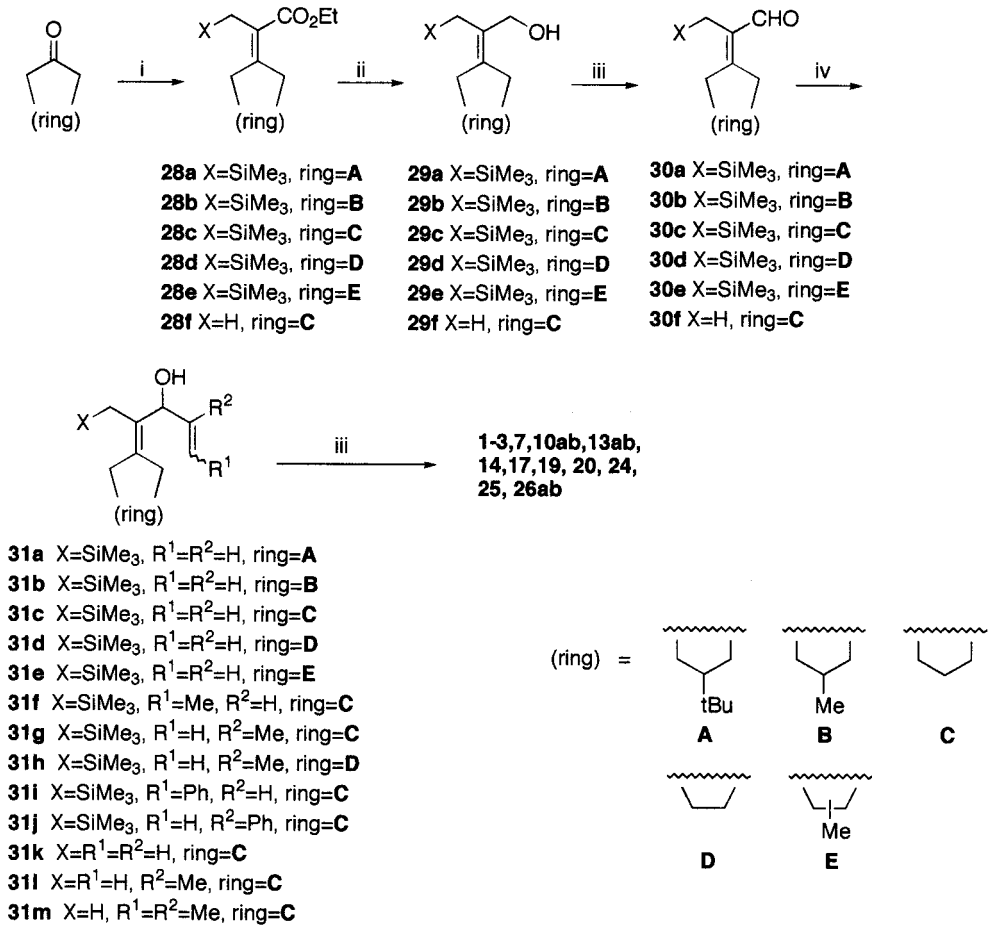
The preferential formation of **11a** over **11b** from **10a** can be explained by steric interaction between the methyl group and the C(α′)=C(β′) double bond as shown in Scheme 10, based on the assumption that the cyclopentane ring has envelope conformation with the biggest substituent (divinyl ketone moiety) equatorial-like orientation. Then, sterical congestion between methyl group and vinyl group appears in the cyclization reaction from **vii** to **viii**, and thus the reaction proceeded mainly through **v** to **vi** affording **11a**. The non-stereoselectivity observed for **10b** can be explained by the sufficient distance between methyl group and the C(α′)=C(β′) double bond in the transition state.

Synthesis of the substrates

The substrates used in this study were synthesized as described in Scheme 11. Starting from cycloalkanones, β-(ethoxycarbonyl)allylsilanes **28a–e** were first prepared by Hoffmann's method.[4,5,26] For the preparation of desilylated substrates, enone **28f** was prepared by Wittig–Horner reaction. The resulting ethoxycarbonyl group was then reduced by $LiAlH_4$ to the alcohols **29a–f**, which were then converted to the aldehydes **30a–f** by MnO_2 oxidation. To these compounds appropriate Grignard reagents were introduced giving the alcohols **31a–m**. Compounds **31a** and **31b** were obtained as a 1:1 mixture of the diastereomers, and **31e** contained four isomers, but these mixtures were not separated from each other. Finally, the alcohols **31a–m** were oxidized by MnO_2 to the substrates used in the present study. Compounds **10a** and **10b** were prepared as a mixture starting from 3-methylcyclopentanone and separated at the final stage, after the oxidation of **31e**. The double bond isomers **13a/13b** and **26a/26b** were also separated at the final stage.

Conclusion

First of all, we could show a new utility of β-(ethoxycarbonyl)allylsilane as an organic bifunctional unit. Synthesis of both spiro[4.5]decanes and spiro[4.4]nonanes through Nazarov cyclization of 4-cycloalkylidene-5-(trimethylsilyl)pent-1-en-3-one derivatives was established. Also, it was clarified that skeletal rearrangement occurs from spiro[4.4]nonanes to bicyclo[4.3.0]nonanes by elevation of the reaction temperature. This type of rearrangement is limited to strained five–five spiro ring system having exomethylene group. The synthesis of bicyclo[4.3.0]nonane ring system from a compound having five-membered carbocycles is one of the classical method.[2] However, this new entry to bicyclo[4.3.0]nonane from five-membered carbocycle is completely different from the classical method, since (1) the newly formed ring is still five-membered, and (2) the original five-membered ring enlarges to six-membered ring. This rare type of fused ring construction, "ring-expanding annulation", is also reported by Mock and Hartman utilizing an intramolecular reaction of the diazo ketone with cycloalkanone.[27] We have previously reported the synthesis of the bicyclo[4.3.0]nonane ring system from β-(ethoxycarbonyl)allylsilane.[5] The present synthetic method of bicyclo[4.3.0]nonane ring system via spiro[4.4]-nonanes is completely different from the previous strategy using similarly functionalized allylsilane.



Scheme 11. Reagents and conditions: (i) for **28a–e**, $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, DME, 70°C; (i) for **28f**, $(EtO)_2P(O)CH(CO_2Et)CH_3$, NaH, DME, 70°C; (ii) $LiAlH_4$, Et_2O, 0°C; (iii) MnO_2, CH_2Cl_2, rt; (iv) for **31a–e,k**, $BrMgCH{=}CH_2$, THF, rt; (iv) for **31f**, BrMgCH=CHMe, THF, rt; (iv) for **31g,h,l**, $BrMgCMe{=}CH_2$, THF, rt; (iv) for **31i**, BrMgCH=CHPh, THF, rt; (iv) for **31j**, $BrMgCPh{=}CH_2$, THF, rt; (iv) for **31m**, BrMgCMe=CHMe, THF, rt.

From the study on the substituent effect, the followings can be concluded. First, in spite of our prediction (Scheme 2), the double bond position in the product is controlled by the presence/absence of α′-substituent, not by the presence/absence of allylic silicon atom. Second, the allylic silicon atom is essential for obtaining the products in good yields, which must be the result of silicon-stabilization of the intermediate. Third, the β′-substituent also has an effect of increasing the yields. This implies that the alkyl substitution pattern is also important, as well as silyl group, in the Nazarov cyclization reaction.

Experimental

General procedures

Melting points were collected on a Laboratory Devices Mel-Temp apparatus. 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 were reported on the δ scale (ppm) with solvent ($CHCl_3$=7.25) as an internal standard, unless otherwise noted. 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, JMS-DX303, or Shimadzu GCMS-QP5050 mass spectrometer with the EI method unless otherwise noted. Analytical TLC was done on precoated TLC plates (Kieselgel 60 F254, layer thickness 0.2 mm). Wakogel C-200, C-300 or ICN Alumina N Act 1 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, 1,2-dimethoxyethane (DME), and CH_2Cl_2 were distilled from CaH_2.

Synthesis of 28 (Wittig reaction)

Typical Procedure. To a stirred suspension of NaH (613.3 mg, 15.33 mmol; 60% in mineral oil which was removed by washing with dry hexane) in dry DME (40 cm^3) was added $(EtO)_2P(O)CH_2CO_2Et$ (2.75 cm^3, 13.87 mmol) dropwise at 0°C under Ar. After being stirred for 40 min, ICH_2SiMe_3 (2.50 cm^3, 16.9 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 (505.5 mg, 12.64 mmol; mineral oil was not removed) was added. After being stirred at 0°C for 2 h, a solution of cyclohexanone (1.2 cm^3, 11.6 mmol) in DME (10 cm^3) was added, and the mixture was stirred at 70°C for 6 h, then at room temperature for 18 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 (30 g) column chromatography using pentane–Et_2O (99:1) as eluent afforded **28c** (1.5224 g, 52%). For the preparation of **28f**, methyl iodide was used instead of ICH_2SiMe_3.

Ethyl 2-(4-*t*-butylcyclohexylidene)-3-(trimethylsilyl)propanoate (28a). An oil; UV (pentane) λ_{max}=231 nm (ϵ 7.5×10^3; IR (neat) 1715 (C=O), 1640 (C=C), 1450, 1250, 1175, and 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) −0.01 (9H, s, $SiMe_3$), 0.83 (9H, s, *t*-Bu), 1.00–1.89 (7H, m), 1.29 (3H, t, *J*=7.2 Hz, OCH_2CH_3), 1.79 (2H, br s, CH_2SiMe_3), 2.55 (1H, br dq, *J*=14, 3 Hz, C=CC*H*H), 2.97 (1H, br dq, *J*=14, 3 Hz, C=CC*H*H), and 4.15 (2H, q, *J*=7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) −1.2 (3C), 14.2, 19.8, 27.5 (3C), 28.2, 28.8, 31.2, 32.1, 32.4, 48.0, 60.0, 122.3, 143.0, and 170.9; MS *m/z* 310 (M$^+$, 24%), 295 (26), 282 (31), 264 (24), 211 (29), 200 (33), and 149 (100); HRMS [Found: *m/z* 310.2301 (M$^+$). Calcd for $C_{18}H_{34}O_2Si$: M, 310.2329]; Analysis [Found: C, 69.40; H, 10.75%. Calcd for $C_{18}H_{34}O_2Si$: C, 69.62; H, 11.04%].

Ethyl 2-(4-methylcyclohexylidene)-3-(trimethylsilyl)propanoate (28b). An oil; UV (pentane) λ_{max}=230 nm (ϵ 6.1×10^3); IR (neat) 1720 (C=O), 1640 (C=C), 1460, 1250, 1190, and 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) −0.01 (9H, s, $SiMe_3$), 0.88 (3H, d, *J*=6.6 Hz, Me), 0.95–1.94 (7H, m), 1.28 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.78 (2H, s, CH_2SiMe_3), 2.47 (1H, m, C=CC*H*H), 2.86 (1H, br ddt, *J*=14, 2.5, 4 Hz, C=CC*H*H), and 4.15 (2H, q, *J*=7.1 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) −1.2 (3C), 14.2, 19.9, 21.8, 30.6, 31.7, 32.5, 35.7, 36.3, 60.1, 122.7, 142.3, and 171.0; MS *m/z* 268 (M$^+$, 15%), 253 (10), 220 (43), and 205 (100); HRMS [Found: *m/z* 268.1864 (M$^+$). Calcd for $C_{15}H_{28}O_2Si$: M, 268.1859]; Analysis [Found: C, 66.98; H, 10.23%. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51%].

Ethyl 2-cyclohexylidene-3-(trimethylsilyl)propanoate (28c). An oil; UV (pentane) λ_{max}=230 nm (ϵ 8.2×10^3); IR (neat) 1715 (C=O), 1645 (C=C), 1450, 1250, 1210, 1150, and 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) −0.01 (9H, s, $SiMe_3$), 1.28 (3H, t, *J*=7.2 Hz, OCH_2CH_3), 1.50–1.59 (6H, m, $(CH_2)_3$), 1.78 (2H, s, CH_2SiMe_3), 2.12 (2H, m, C=CCH_2), 2.36 (2H, m, C=CCH_2), and 4.15 (2H, q, *J*=7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) −1.2 (3C), 14.2, 19.8, 26.6, 27.6, 28.2, 31.3, 32.5, 60.1, 122.6, 142.7, and 171.0; MS *m/z* 254 (M$^+$, 18%), 239 (17), 226 (21), 211 (44), 136 (86), 108 (66), and 73 (100); HRMS [Found: *m/z* 254.1686 (M$^+$). Calcd for $C_{14}H_{26}O_2Si$: M, 254.1703].

Ethyl 2-cyclopentylidene-3-(trimethylsilyl)propanoate (28d). An oil; UV (pentane) λ_{max}=239 nm (ϵ 5.6×10^3); IR (neat) 1710 (C=O), 1635 (C=C), 1280, 1250, 1170, and 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) −0.03 (9H, s, $SiMe_3$), 1.27 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.58–1.70 (4H, m, CH_2CH_2), 1.76 (2H, br s, CH_2SiMe_3), 2.26 (2H, br t, *J*=7 Hz, C=CCH_2), 2.68 (2H, br t, *J*=7 Hz, C=CCH_2), and 4.13 (2H, q, *J*=7.1 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) −0.9 ($3CH_3$), 14.4 (CH_3), 20.6 (CH_2), 25.7 (CH_2), 27.2 (CH_2) 34.0 (CH_2), 34.3 (CH_2), 59.7 (CH_2), 121.2 (C), 155.6 (C), and 168.5 (CO); MS *m/z* 240 (M$^+$, 37%), 225 (46), 211 (17), 195 (27), 181 (20), 122 (88), and 73 (100); HRMS [Found: *m/z* 240.1514 (M$^+$). Calcd for $C_{13}H_{24}O_2Si$: M, 240.1546].

Ethyl 2-(3-methylcyclopentylidene)-3-(trimethylsilyl)-propanoate (28e). An oil; IR (neat) 1710 (C=O), 1635 (C=C), 1280, 1250, 1180, and 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) −0.02 (9H×1/2, s, $SiMe_3$), −0.02 (9H×1/2, s, $SiMe_3$), 1.00 (3H×1/2, d, *J*=6.5 Hz, $CHCH_3$), 1.00 (3H×1/2, d, *J*=6.5 Hz, $CHCH_3$), 1.27 (3H×1/2, t, *J*=7.1 Hz, OCH_2CH_3), 1.28 (3H×1/2, t, *J*=7.1 Hz, OCH_2CH_3), 1.14–3.00 (9H, m), 4.13 (2H×1/2, q, *J*=7.1 Hz, OCH_2CH_3), and 4.14 (2H×1/2, q, *J*=7.1 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) −0.8 (3C×2), 14.4 (×2), 19.7 (×2) 20.3, 20.5, 33.6 (×2), 33.7, 33.8, 35.1, 35.2, 42.5, 42.7, 59.7 (×2) 121.3, 121.3, 155.5, 155.6, 168.4, and 168.5 (for both isomers; assignment was not made); MS *m/z* 254 (M$^+$, 59%), 239 (M$^+$−Me, 71), 211 (28), 195 (42), 136 (68), and 73 (100); HRMS [Found: *m/z* 254.1707 (M$^+$). Calcd for $C_{14}H_{26}O_2Si$: M, 254.1703].

Ethyl 2-cyclohexylidenepropanoate (28f). An oil; IR (neat) 1715 (C=O), 1640 (C=C), 1450, 1205, and 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si=0.00) 1.30 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.55–1.64 (6H, m), 1.86 (3H, br s, C=CMe), 2.22 (2H, m, C=CCH_2), 2.43 (2H, m, C=CCH_2), and 4.19 (2H, q, *J*=7.1 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, Me_4Si=0.0) 14.3, 15.1, 26.6, 27.8, 28.2, 31.2, 32.4, 60.1, 119.9, 147.4, and 170.7; MS *m/z* 182 (M$^+$, 100%), 153 (48), 136 (91), 109 (78), and 55 (24); HRMS [Found: *m/z* 182.1312 (M$^+$). Calcd for $C_{11}H_{18}O_2$: M, 182.1307].

Synthesis of 29 ($LiAlH_4$ reduction)

Typical procedure. To a stirred suspension of $LiAlH_4$ (145 mg, 3.82 mmol) in dry Et_2O (35 cm^3) was added a solution of **28c** (322.5 mg, 1.268 mmol) in Et_2O (10 cm^3) at 0°C, and the mixture was stirred for 30 min under $CaCl_2$ drying tube. The reaction was quenched by successive addition of wet Et_2O and water. A dilute solution of HCl (ca. 1 mol dm^{-3}) was added and the resulted clear solution was extracted with CH_2Cl_2 and dried. Evaporation of the solvent followed by silica gel (20 g) column chromatography using pentane–Et_2O (98:2) as eluent afforded **29c** (254.9 mg, 95%).

2-(4-*t*-Butylcyclohexylidene)-3-trimethylsilyl-1-propanol (29a). An oil; IR (neat) 3340 (OH), 1650 (C=C), 1370, 1250, 990, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.00 (9H, s, $SiMe_3$), 0.83 (9H, s, *t*-Bu), 0.92–1.89 (9H, m), 2.53 (1H, br dq, *J*=14, 3 Hz, C=CC*H*H), 2.79 (1H, br dq, *J*=14, 3 Hz, C=CC*H*H), 4.02 (1H, br d, *J*=11 Hz, C*H*HOH), and 4.06 (1H, br d, *J*=11 Hz, CH*H*OH); ^{13}C NMR ($CDCl_3$) −0.8 (3C). 21.4, 27.6 (3C), 28.3, 29.3, 30.0, 31.0, 32.4, 48.3, 63.5, 126.6, and 135.1; MS *m/z* 268 (M$^+$, 11%), 253 (3), 237 (35), 178 (16), 163 (21), 123 (37), and 73 (100); HRMS [Found: *m/z* 268.2204 (M$^+$). Calcd for $C_{16}H_{32}OSi$: M, 268.2224].

2-(4-Methylcyclohexylidene)-3-trimethylsilyl-1-propanol (29b). An oil; IR (neat) 3340 (OH), 1650 (C=C), 1455, 1250, 1000, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) −0.01 (9H, s, $SiMe_3$), 0.83–1.84 (9H, m), 0.87 (3H, d, *J*=6.6 Hz, Me), 2.45 (1H, br dq, *J*=14, 3 Hz, C=CC*H*H), 2.69 (1H, br dq, *J*=14, 3 Hz, C=CC*H*H), and 4.03 (2H, br s, CH_2OH); ^{13}C NMR ($CDCl_3$) −0.8 (3C), 21.5, 22.0, 29.5, 30.5, 32.7, 36.0,

36.9, 63.5, 127.0, and 134.8; MS *m/z* 226 (M^+, 3%), 208 (5), 193 (5), 136 (33), 121 (59), 107 (49), 93 (94), and 73 (100); HRMS [Found: *m/z* 226.1764 (M^+). Calcd for $C_{13}H_{26}OSi$: M, 226.1754].

2-Cyclohexylidene-3-trimethylsilyl-1-propanol (29c). An oil; IR (neat) 3340 (OH), 1650 (C═C), 1450, 1250, 995, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) −0.01 (9H, s, $SiMe_3$), 1.46–1.57 (6H, m, $(CH_2)_3$), 1.65 (2H, s, CH_2SiMe$_3$), 2.07 (2H, m, C═CCH_2), 2.23 (2H, m, C═CCH_2), and 4.02 (2H, s, CH_2OH); ^{13}C NMR ($CDCl_3$) −0.8 (3C), 21.3, 26.8, 27.8, 28.7, 30.2, 31.2, 63.3, 126.9, and 135.2; MS *m/z* 212 (M^+, 14%), 197 (9), 167 (17), 149 (36), 122 (27), 107 (43), 93 (52), and 73 (100); HRMS [Found: *m/z* 212.1596 (M^+). Calcd for $C_{12}H_{24}OSi$: M, 212.1597].

2-Cyclopentylidene-3-trimethylsilyl-1-propanol (29d). An oil; IR (neat) 3350 (OH), 1670 (C═C), 1420, 1250, 1010, 980, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H, s, $SiMe_3$), 1.59 (2H, br s, CH_2SiMe$_3$), 1.56–1.67 (4H, m, CH_2CH_2), 2.12 (2H, m, C═CCH_2), 2.29 (2H, m, C═CCH_2), and 4.05 (2H, br s, CH_2OH); ^{13}C NMR ($CDCl_3$) −0.0 (3C), 21.7, 26.4, 27.0, 29.9, 31.5, 64.8, 127.1, and 138.2; MS *m/z* 198 (M^+, 15%), 181 (8), 165 (7), 108 (95), and 80 (100); HRMS [Found: *m/z* 198.1418 (M^+). Calcd for $C_{11}H_{22}OSi$: M, 198.1441].

2-(3-Methylcyclopentylidene)-3-trimethylsilyl-1-propanol (29e). An oil; IR (neat) 3340 (OH), 1670 (C═C), 1250, 990, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H×1/2, s, $SiMe_3$), 0.01 (9H×1/2, s, $SiMe_3$), 0.98 (3H×1/2, d, *J*=6.5 Hz, CHCH_3), 0.99 (3H×1/2, d, *J*=6.5 Hz, CHCH_3), 1.57 (2H, br s, CH_2SiMe$_3$), 1.13–2.56 (7H, m), and 4.03 (2H, br s, CH_2OH); ^{13}C NMR ($CDCl_3$) −0.6 (3C×2), 19.9 19.9, 21.5, 21.7, 29.5, 31.1, 34.4, 34.4, 34.9, 35.0, 38.5, 40.1, 64.5, 64.8, 127.2, 127.3, 138.1, and 138.1 (for both isomers; assignment was not made); MS *m/z* 212 (M^+, 8%), 122 (46), 107 (75), 93 (100), and 75 (99); HRMS [Found: *m/z* 212.1584 (M^+). Calcd for $C_{12}H_{24}OSi$: M, 212.1597].

2-Cyclohexylidene-1-propanol (29f). An oil; IR (neat) 3340 (OH), 1655 (C═C), 1445, and 1000 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si=0.00) 1.48–1.56 (6H, m), 1.77 (3H, s, C═CMe), 2.17 (2H, m, C═CCH_2), 2.24 (2H, m, C═CCH_2), and 4.13 (2H, s, CH_2OH); ^{13}C NMR ($CDCl_3$) 16.2, 26.8, 27.8, 28.5, 30.2, 30.8, 63.4, 124.2, and 137.9; MS *m/z* 140 (M^+, 13%), 122 (79), 107 (72), 93 (60), 79 (100), and 67 (89); HRMS [Found: *m/z* 140.1221 (M^+). Calcd for $C_9H_{16}O$: M, 140.1202].

Synthesis of 30 (MnO_2 oxidation)

Typical procedure. Compound **29c** (254.9 mg, 1.200 mmol) was dissolved in dry CH_2Cl_2 (50 cm^3) and to this was added an excess amount of MnO_2 (10.22 g). The resulting suspension was stirred at room temperature under a $CaCl_2$ drying tube for 4 days, and then filtered through Celite. The filtrate was evaporated under reduced pressure to give an oily residue, which was chromatographed on silica gel (20 g) using pentane–Et_2O (99:1) as eluent to afford **30c** (191.2 mg, 76%).

2-(4-*t*-Butylcyclohexylidene)-3-(trimethylsilyl)proponal (30a). An oil; IR (neat) 2770 (CHO), 1670 (C═O), 1615 (C═C), 1250, and 860 cm^{-1}; ^1H NMR ($CDCl_3$) −0.06 (9H, s, $SiMe_3$), 0.85 (9H, s, *t*-Bu), 1.08–2.03 (7H, m), 1.72 (1H, br d, *J*=13 Hz, C*H*HSiMe$_3$), 1.81 (1H, br d, *J*=13 Hz, CH*H*SiMe$_3$), 2.75 (1H, br dq, *J*=13, 2.5 Hz, C═CC*H*H), 3.52 (1H, br dq, *J*=13, 2.5 Hz, C═CC*H*H), and 10.15 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) −1.0 (3C), 15.0, 27.5 (3C), 28.4, 28.7, 29.4, 32.4, 33.5, 48.0, 132.0, 158.7, and 190.1; MS *m/z* 266 (M^+, 79%), 251 (84), 237 (36), 209 (68), 167 (43), 119 (40), and 73 (100); HRMS [Found: *m/z* 266.2096 (M^+). Calcd for $C_{16}H_{30}OSi$: M, 266.2067].

2-(4-Methylcyclohexylidene)-3-(trimethylsilyl)propanal (30b). An oil; IR (neat) 2770 (CHO), 1670 (C═O), 1615 (C═C), 1250, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) −0.06 (9H, s, $SiMe_3$), 0.91 (3H, d, *J*=6.6 Hz, Me), 1.03–2.12 (7H, m), 1.74 (1H, br d, *J*=13 Hz, C*H*HSiMe$_3$), 1.80 (1H, br d, *J*=13 Hz, CH*H*SiMe$_3$), 2.67 (1H, br dq, *J*=14, 2 Hz, C═CC*H*H), 3.41 (1H, br dq, *J*=14, 2 Hz, C═CC*H*H), and 10.15 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) −1.0 (3C), 15.1, 21.6, 28.3, 32.6, 33.0, 35.8, 36.8, 132.4, 158.5, and 190.2; MS *m/z* 224 (M^+, 34%), 209 (59), 195 (12), 181 (16), 167 (28), 119 (18), and 73 (100); HRMS [Found: *m/z* 224.1600 (M^+). Calcd for $C_{13}H_{24}OSi$: M, 224.1597].

2-Cyclohexylidene-3-(trimethylsilyl)propanal (30c). An oil; IR (neat) 2770 (CHO), 1670 (C═O), 1615 (C═C), 1250, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) −0.05 (9H, s, $SiMe_3$), 1.59–1.69 (6H, m, $(CH_2)_3$), 1.78 (2H, s, CH_2SiMe$_3$), 2.32 (2H, m, C═CCH_2), 2.73 (2H, m, C═CCH_2), and 10.17 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) −1.0 (3C), 14.9, 26.5, 27.9, 28.8, 29.1, 33.7, 132.2, 158.7, and 190.0; MS *m/z* 210 (M^+, 32%), 195 (48), 181 (12), 167 (17), and 73 (100); HRMS [Found: *m/z* 210.1405 (M^+). Calcd for $C_{12}H_{22}OSi$: M, 210.1441]; Analysis as semicarbazone (mp 187–188°C) [Found: C, 58.32; H, 9.17; N, 15.63%. Calcd for $C_{13}H_{25}N_3OSi$: C, 58.38; H, 9.42; N, 15.71%].

2-Cyclopentylidene-3-(trimethylsilyl)propanal (30d). An oil; IR (neat) 2760 (CHO), 1670 (C═O), 1630 (C═C), 1250, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) −0.05 (9H, s, $SiMe_3$), 1.66 (2H, br s, CH_2SiMe$_3$), 1.64–1.82 (4H, m, CH_2CH_2), 2.41 (2H, br t, *J*=7 Hz, C═CCH_2), 2.81 (2H, br t, *J*=7 Hz, C═CCH_2), and 9.94 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) 0.0 (3C), 16.8, 24.9, 27.0, 29.7, 34.2, 132.0, 164.2, and 191.5; MS *m/z* 196 (M^+, 62%), 181 (100), 113 (15), and 73 (95); HRMS [Found: *m/z* 196.1329 (M^+). Calcd for $C_{11}H_{20}OSi$: M, 196.1284]; Analysis as semicarbazone (mp 178–180°C) [Found: C, 56.84; H, 8.97; N, 16.64%. Calcd for $C_{12}H_{23}N_3OSi$: C, 56.88; H, 9.15; N, 16.58%].

2-(3-Methylcyclopentylidene)-3-(trimethylsilyl)propanal (30e). An oil; IR (neat) 2760 (CHO), 1670 (C═O), 1635 (C═C). 1250, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) −0.04 (9H×1/2, s, $SiMe_3$), −0.04 (9H×1/2, s, $SiMe_3$), 1.05 (3H×1/2, d, *J*=6.2 Hz, CHCH_3), 1.06 (3H×1/2, d, *J*=6.3 Hz, CHCH_3), 1.20–3.13 (7H, m), 1.65 (2H, br s, CH_2SiMe$_3$), 9.91 (1H×1/2, s, CHO), and 9.93 (1H×1/2, s, CHO); ^{13}C NMR ($CDCl_3$) −0.7 (3C×2), 16.6, 16.8, 19.6, 19.6, 29.3, 32.7, 33.1, 33.7, 34.7, 35.3, 38.1, 42.6, 100.2 (×2), 132.0 (×2), 191.5, and 191.5 (for both isomers; assignment was not made); MS *m/z* 210 (M^+, 30%), 195 (M^+−Me, 60), 181 (13), 113 (15), 105 (15), and 73 (100);

HRMS [Found: *m/z* 210.1405 (M^+). Calcd for $C_{12}H_{22}OSi$: M, 210.1441].

2-Cyclohexylidenepropanal (30f). An oil; IR (neat) 2770 (CHO), 1665 (C═O), 1625 (C═C), 1445, 1315, and 1285 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si=0.00) 1.63–1.73 (6H, m), 1.76 (3H, s, Me), 2.40 (2H, m, C═CCH_2), 2.74 (2H, m, C═CCH_2), and 10.19 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) 10.3, 26.4, 27.9, 28.7, 29.1, 33.3, 129.4, 162.6, and 190.5; MS *m/z* 138 (M^+, 100%), 123 (30), 109 (69), 95 (96), 81 (48), 67 (54), and 41 (84); HRMS [Found: *m/z* 138.1034 (M^+). Calcd for $C_9H_{14}O$: M, 138.1045]; Analysis as semicarbazone (mp 197–201°C) [Found: C, 61.25; H, 8.65; N, 21.44%. Calcd for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52%].

Synthesis of 31 (Grignard reaction)

Typical procedure. To a stirred solution of **30c** (83.1 mg, 0.39 mmol) in dry THF (20 cm^3) was added a solution of vinylmagnesium bromide (1.95 cm^3, 1.95 mmol; 1 mol dm^{-3} solution in THF) at 0°C under Ar. After being stirred for 1 h, an aqueous solution of NH_4Cl was added, and the mixture was extracted with AcOEt. Drying and evaporation of the solvent gave a crude product containing **31c**, which was not purified.

This type of dienols **31a–m** were not stable enough for purification on silica gel, and were used in the next MnO_2 oxidation without purification. The following spectral data were collected after careful purification by silica gel or alumina column chromatography, however it was not possible to obtain pure compound in some cases. For (*Z*)-**31f** and (*E*)-**31f**, separation from each other was made for only spectral purpose.

4-(4-*t*-Butylcyclohexylidene)-5-(trimethylsilyl)pent-1-en-3-ol (31a). An oil; IR (neat) 3450 (OH), 1645 (C═C), 1370, 1250, 1030, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H×1/2, s, $SiMe_3$), 0.01 (9H×1/2, s, $SiMe_3$), 0.82 (9H×1/2, s, *t*-Bu), 0.83 (9H×1/2, s, *t*-Bu), 0.9–1.9 (9H, m), 2.49 (1H, m, C═CC*H*H), 2.82 (1H, m, C═CC*H*H), 5.08 (2H, m, C═C*H*H and C*H*OH), 5.21 (1H×1/2, dt, *J*=17.2, 1.6 Hz, C═CH*H*), 5.23 (1H×1/2, dt, *J*=17.2, 1.6 Hz, C═CH*H*), 5.84 (1H×1/2, ddd, *J*=5.1, 10.6, 17.2 Hz, C*H*═CH_2), and 5.86 (1H×1/2, ddd, *J*=4.9, 10.5, 17.2 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) −0.1 (3C×2), 17.4, 17.5, 27.5 (3C×2), 28.2, 28.3, 28.8, 29.0, 30.0, 30.1, 31.6, 31.9, 32.4 (×2), 48.3, 48.4, 72.2, 72.5, 113.7, 113.7, 127.6, 127.9, 133.2, 133.5, 139.6, and 140.0 (for both isomers; assignment was not made); MS *m/z* 294 (M^+, 4%), 279 (5), 268 (3), 261 (3), 237 (62), 209 (19), 147 (18), 106 (67), and 73 (100); HRMS [Found: *m/z* 294.2373 (M^+). Calcd for $C_{18}H_{34}OSi$: M, 294.2380].

4-(4-Methylcyclohexylidene)-5-(trimethylsilyl)pent-1-en-3-ol (31b). An oil; IR (neat) 3430 (OH), 1645 (C═C), 1460, 1250, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H×1/2, s, $SiMe_3$), 0.01 (9H×1/2, s, $SiMe_3$), 0.8–1.9 (9H, m), 0.86 (3H×1/2, d, *J*=6.6 Hz, Me), 0.87 (3H×1/2, d, *J*=6.6 Hz, Me), 2.50 (1H, m, C═CC*H*H), 2.82 (1H, m, C═CC*H*H), 5.06 (2H, m, C═C*H*H and C*H*OH), 5.21 (1H×1/2, dt, *J*=17.2, 1.7 Hz, C═CH*H*), 5.23 (1H×1/2, dt, *J*=17.2, 1.7 Hz, C═CH*H*), 5.83 (1H×1/2, ddd, *J*=4.9, 10.4, 17.1 Hz, C*H*═CH_2), and 5.85 (1H×1/2, ddd, *J*=4.8, 10.4, 17.2 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) −0.2 (3C×2), 17.4, 17.7, 22.0, 22.1, 29.5, 29.6, 31.1, 31.4, 32.8, 32.9, 35.9, 36.0, 36.4, 36.6, 72.2, 72.6, 113.7, 113.8, 133.2 (×2), 139.6, 139.9, and 149.7 (×2) (for both isomers; assignment was not made); MS *m/z* 252 (M^+, 25%), 234 (55), 209 (100), 167 (39), and 136 (85); HRMS [Found: *m/z* 252.1868 (M^+). Calcd for $C_{15}H_{28}OSi$: M, 252.1910].

4-Cyclohexylidene-5-(trimethylsilyl)pent-1-en-3-ol (31c). An oil; IR (neat) 3420 (OH), 1640 (C═C), 1450, 1250, 1030, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H, s, $SiMe_3$), 1.4–1.6 (8H, m), 2.06 (2H, m, C═CCH_2), 2.24 (2H, m, C═CCH_2), 5.06 (1H, m, C*H*OH), 5.09 (1H, dt, *J*=10.4, 1.7 Hz, C═C*H*H), 5.22 (1H, dt, *J*=17.2, 1.7 Hz, C═CH*H*), and 5.85 (1H, ddd, *J*=4.9, 10.4, 17.2 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) −0.2 (3C), 17.4, 26.9, 27.7, 28.3, 30.3, 31.9, 72.2, 113.7, 128.0, 133.4, and 139.8; MS *m/z* 238 (M^+, 3%), 205 (9), 195 (10), 148 (30), 133 (43), 119 (47), 106 (100), and 80 (89); HRMS [Found: *m/z* 238.1752 (M^+). Calcd for $C_{14}H_{26}OSi$: M, 238.1754].

4-Cyclopentylidene-5-(trimethylsilyl)pent-1-en-3-ol (31d). An oil; IR (neat) 3420 (OH), 1645 (C═C), 1420, 1250, 995, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H, s, $SiMe_3$), 1.5–1.7 (6H, m), 2.0–2.4 (4H, m), 4.86 (1H, br d, *J*=5 Hz, C*H*OH), 5.08 (1H, dt, *J*=10.5, 1.6 Hz, C═C*H*H), 5.22 (1H, dt, *J*=17.2, 1.6 Hz, C═CH*H*), and 5.83 (1H, ddd, *J*=5.3, 10.5, 17.2 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) 0.0 ($3CH_3$), 18.8 (CH_2), 26.2 (CH_2), 27.0 (CH_2), 29.9 (CH_2), 32.0 (CH_2), 74.2 (CH), 113.9 (CH_2), 128.5 (C), 136.9 (C), and 139.0 (CH); MS *m/z* 224 (M^+, 11%), 209 (2), 191 (9), 134 (80), 119 (70), 106 (100), and 92 (80); HRMS [Found: *m/z* 224.1629 (M^+). Calcd for $C_{13}H_{24}OSi$: M, 224.1597].

4-(3-Methylcyclopentylidene)-5-(trimethylsilyl)pent-1-en-3-ol (31e). An oil; IR (neat) 3400 (OH), 1640 (C═C), 1245, 1020, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) 0.02 (9H×3/4, s, $SiMe_3$), 0.02 (9H×1/4, s, $SiMe_3$), 0.98 (3H×1/2, d, *J*=6.4 Hz, $CHCH_3$), 0.99 (3H×1/4, d, *J*=6.4 Hz, $CHCH_3$), 1.00 (3H×1/4, d, *J*=6.5 Hz, $CHCH_3$), 1.1–2.6 (9H, m), 4.85 (1H, br, C*H*OH), 5.09 (1H, m, C═C*H*H), 5.23 (1H, m, C═CH*H*), and 5.84 (1H, m, C*H*═CH_2); MS *m/z* 238 (M^+, 2%), 220 (28), 205 (36), 133 (47), 93 (66), and 73 (100); HRMS [Found: *m/z* 238.1799 (M^+). Calcd for $C_{14}H_{26}OSi$: M, 238.1754].

(*Z*)-2-Cyclohexylidene-1-(trimethylsilyl)hex-4-en-3-ol ((*Z*)-31f). An oil; IR (neat) 3460 (OH), 1655 (C═C), 1450, 1245, and 850 cm^{-1}; ^1H NMR (C_6D_6=7.15) 0.16 (9H, s, $SiMe_3$), 1.42–1.57 (6H, m), 1.52 (3H, dd, *J*=1.7, 6.9 Hz, CH_3), 1.67 (1H, br d, *J*=14 Hz, C*H*H$SiMe_3$), 1.71 (1H, br d, *J*=14 Hz, CH*H*$SiMe_3$), 2.07 (2H, m, C═CCH_2), 2.22 (2H, m, C═CCH_2), 5.32 (1H, br d, *J*=8 Hz, C*H*OH), 5.35 (1H, ddq, *J*=1.4, 10.7, 6.9 Hz, CH═C*H*CH_3), and 5.63 (1H, ddq, *J*=8.2, 10.7, 1.7 Hz, C*H*═C*H*CH_3); ^{13}C NMR (C_6D_6=128.0) 0.1 (3C), 13.3, 17.9, 27.3, 28.1, 28.6, 30.6, 32.1, 67.2, 124.7, 130.2, 131.9, and 133.6; MS *m/z* 252 (M^+, 3%), 234 (21), 219 (13), 205 (8), 160 (22), 147 (60), and 75 (100); HRMS [Found: *m/z* 252.1942 (M^+). Calcd for $C_{15}H_{28}OSi$: M, 252.1910].

(*E*)-2-Cyclohexylidene-1-(trimethylsilyl)hex-4-en-3-ol ((*E*)-31f). An oil; IR (neat) 3420 (OH), 1655 (C=C), 1450, 1245, and 850 cm^{-1}; ^1H NMR (C_6D_6=7.15) 0.15 (9H, s, $SiMe_3$), 1.40–1.52 (6H, m), 1.55 (3H, dd, *J*=1.0, 4.7 Hz, CH_3), 1.64 (1H, br d, *J*=14 Hz, C*H*HSiMe_3), 1.66 (1H, br d, *J*=14 Hz, CH*H*SiMe_3), 2.08 (2H, m, C=CCH_2), 2.19 (2H, m, C=CCH_2), 4.94 (1H, br d, *J*=3 Hz, C*H*OH), and 5.46–5.59 (2H, m, CH=CH); ^{13}C NMR (C_6D_6=128.0) 0.1 (3C), 17.6, 17.7, 27.3, 28.1, 28.7, 30.5, 32.2, 71.8, 124.6, 129.7, 131.7, and 133.9; MS *m/z* 252 (M^+, 3%), 251 (M^+-H, 6), 234 (56), 219 (52), 160 (15), 149 (24), and 73 (100); HRMS [Found: *m/z* 252.1914 (M^+). Calcd for $C_{15}H_{28}OSi$: M, 252.1910].

4-Cyclohexylidene-2-methyl-5-(trimethylsilyl)pent-1-en-3-ol (31g). An oil; IR (neat) 3480 (OH), 1655 (C=C), 1450, 1245, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H, s, $SiMe_3$), 1.38–1.60 (8H, m), 1.61 (3H, br s, CH_3), 1.98–2.34 (4H, m, C=CCH_2×2), 4.89 (1H, sext, *J*=1.5 Hz, C=C*H*H), 5.00 (1H, br s, C*H*OH), and 5.05 (1H, m, C=CH*H*); ^{13}C NMR ($CDCl_3$) −0.2 (3C), 16.4, 19.9, 26.9, 27.7, 28.2, 30.4, 32.1, 73.4, 109.3, 127.4, 133.8, and 146.5; MS *m/z* 234 (M^+-H_2O, 1%), 219 (1), 161 (4), 147 (26), 133 (15), 120 (28), 107 (71), and 73 (100); HRMS [Found: *m/z* 234.1779 (M^+-H_2O). Calcd for $C_{15}H_{26}Si$: M, 234.1805].

4-Cyclopentylidene-2-methyl-5-(trimethylsilyl)pent-1-en-3-ol (31h). An oil; IR (neat) 3480 (OH), 1655 (C=C), 1245, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) 0.02 (9H, s, $SiMe_3$), 1.39–1.68 (6H, m), 1.61 (3H, br s, Me), 2.11 (2H, m, C=CCH_2), 2.26 (1H, m, C=CC*H*H), 2.40 (1H, m, C=CCH*H*), 4.79 (1H, br s, C*H*OH), 4.89 (1H, sext, *J*=1.6 Hz, C=C*H*H), and 5.03 (1H, m, C=CH*H*); ^{13}C NMR ($CDCl_3$) 0.0 (3C), 18.2, 19.7, 26.3, 27.1, 30.3, 32.1, 76.0, 109.2, 127.9, 138.0, and 146.3; MS (CI method, isobutane) *m/z* 239 (M^++H, 2%), and 221 (M^+-OH, 100); HRMS [Found *m/z* 221.1723 (M^+-OH). Calcd for $C_{14}H_{25}Si$: M, 221.1727].

(*E*)-4-Cyclohexylidene-1-phenyl-5-(trimethylsilyl)pent-1-en-3-ol (31i). An oil; IR (neat) 3370 (OH), 1600 (C=C), 1450, 1245, 855, and 695 cm^{-1}; ^1H NMR (C_6D_6=7.15) 0.25 (9H, s, $SiMe_3$), 1.35–1.70 (12H, m), 4.24 (1H, m, C*H*OH), 6.19 (1H, dd, *J*=5.0, 16.0 Hz, C*H*=CHPh), 6.74 (1H, dd, *J*=1.6, 16.0 Hz, CH=C*H*Ph), and 7.00–7.31 (5H, m, Ph); MS *m/z* 314 (M^+, 89%), 299 (97), 279 (98), 229 (100), 192 (99), 160 (99), and 136 (99); HRMS [Found: *m/z* 314.2021 (M^+). Calcd for $C_{20}H_{30}OSi$: M, 314.2067].

4-Cyclohexylidene-2-phenyl-5-(trimethylsilyl)pent-1-en-3-ol (31j). An oil; IR (neat) 3470 (OH), 1630 (C=C), 1490, 1445, 1245, 853, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H, s, $SiMe_3$), 1.10–2.24 (12H, m), 5.33 (1H, t, *J*=1.5 Hz, C=C*H*H), 5.39 (1H, t, *J*=1.5 Hz, C=CH*H*), 5.60 (1H, br t, *J*=1.5 Hz, C*H*OH), and 7.23–7.33 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) −0.1 (3C), 17.1, 26.8, 27.6, 27.8, 30.6, 32.1, 72.1, 113.1, 127.0, 127.1 (2C), 127.3, 128.0 (2C), 134.6, 140.3, and 150.2; MS *m/z* 296 (M^+-H_2O, 10%), 278 (30), 224 (33), 209 (30), 195 (25), 169 (61), 91 (48), 73 (78), and 57 (100); HRMS [Found: *m/z* 296.1962 (M^+-H_2O). Calcd for $C_{20}H_{28}Si$: M, 296.1961].

4-Cyclohexylidenepent-1-en-3-ol (31k). An oil; IR (neat) 3410 (OH), 1640 (C=C), 1450, 1055, 990, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) 1.40–1.62 (6H, m), 1.58 (3H, s, Me), 2.03–2.24 (4H, m, C=CCH_2×2), 5.08 (1H, m, C=C*H*H), 5.20 (1H, m, C*H*OH), 5.22 (1H, m, C=CH*H*), and 5.84 (1H, m, C*H*=CH_2); ^{13}C NMR (C_6D_6=128.0) 11.8, 27.2, 28.1, 28.6, 30.3, 31.3, 71.0, 113.2, 126.0, 135.5, and 140.2; MS *m/z* 166 (M^+, 60%), 148 (100), 133 (97), 109 (84), 95 (84), and 83 (89); HRMS [Found: *m/z* 166.1308 (M^+). Calcd for $C_{11}H_{18}O$: M, 166.1358].

4-Cyclohexylidene-2-methylpent-1-en-3-ol (31l). An oil; IR (neat) 3380 (OH), 1655 (C=C), 1450, 1050, and 895 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si=0.00) 1.42–1.63 (6H, m), 1.51 (3H, br s, C_{ring}=CCH_3), 1.58 (3H, br s, CH_2=CC*H*$_3$), 2.05–2.37 (4H, m, C=CCH_2×2), 4.89 (1H, sext, *J*=1.6 Hz, C=C*H*H), and 5.07 (2H, m, C*H*OH and C=CH*H*); ^{13}C NMR ($CDCl_3$) 10.9, 19.8, 26.9, 27.9, 28.3, 30.3, 31.3, 72.7, 109.0, 124.0, 137.6, and 146.1; MS (CI method, isobutane) *m/z* 181 (M^++H, 7%) and 163 (M^+-OH, 100); HRMS [Found *m/z* 163.1487 (M^+-OH). Calcd for $C_{12}H_{19}$: M, 163.1488].

(*Z*)- and (*E*)-2-Cyclohexylidene-4-methylhex-4-en-3-ol (31m). An oil; IR (neat) 3360 (OH), 1655 (C=C), 1450, 1375, and 1000 cm^{-1}; ^1H NMR (C_6D_6=7.15) 1.35–1.51 (6H plus 3H×2/5, m), 1.57–1.61 (3H, m, C*H*$_3$CH=CC*H*$_3$), 1.61 (3H×2/5, br s, C_{ring}=CCH_3 of *E*-isomer), 1.76 (3H×3/5, br s, C_{ring}=CCH_3 of *Z*-isomer), 1.79 (3H×3/5, quint, *J*=1.4 Hz, CH_3CH=CC*H*$_3$ of *Z*-isomer), 2.01–2.22 (4H, m, C=CCH_2×2), 4.94 (1H×2/5, br s, C*H*OH of *E*-isomer), 5.23 (1H×3/5, q quint, *J*=6.9, 1.4 Hz, C=CH of *Z*-isomer), 5.36 (1H×3/5, br s, C*H*OH of *Z*-isomer), and 5.76 (1H×2/5, q quint, *J*=6.8, 1.5 Hz, C=CH of *E*-isomer); MS *m/z* 194 (M^+, 44%), 176 (100), 161 (87), and 137 (77); HRMS [Found: *m/z* 194.1681 (M^+). Calcd for $C_{13}H_{22}O$: M, 194.1672].

Synthesis of divinyl ketones (MnO_2 oxidation)

Typical procedure. The crude compound **31c**, obtained above, was subjected to the same procedure described for **29**. Purification of the product was carried out by silica gel (ca. 10 g) column chromatography using hexane–AcOEt (99.5:0.5) as eluent to yield **3** (47.8 mg, 51% from **30c**).

4-(4-*t*-Butylcyclohexylidene)-5-(trimethylsilyl)pent-1-en-3-one (1). An oil; IR (neat) 1670 (C=O), 1610 (C=C), 1250, 860, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) −0.03 (9H, s, $SiMe_3$), 0.83 (9H, s, *t*-Bu), 0.91–1.91 (7H, m), 1.70 (1H, br d, *J*=14 Hz, C*H*HSiMe_3), 1.76 (1H, br d, *J*=14 Hz, CH*H*SiMe_3), 2.49 (1H, m, C=CC*H*H), 2.58 (1H, br dq, *J*=14, 3 Hz, C=CC*H*H), 5.83 (1H, dd, *J*=1.6, 10.3 Hz, C=C*H*H), 6.19 (1H, dd, *J*=1.6, 17.5 Hz, C=CH*H*), and 6.42 (1H, dd, *J*=10.3, 17.5 Hz, C*H*=CH_2); ^{13}C NMR ($CDCl_3$) −0.9 ($3CH_3$), 20.4 (CH_2), 27.5 ($3CH_3$), 28.3 (CH_2), 28.7 (CH_2), 30.8 (CH_2), 32.4 (C), 32.7 (CH_2), 47.9 (CH), 128.9 (CH_2), 129.5 (C), 137.4 (CH), 138.7 (C), and 200.8 (CO); MS *m/z* 292 (M^+, 4%), 274 (11), 259 (4), 237 (13), 217 (34), 147 (22), 123 (32), 106 (64), and 73 (100); HRMS [Found: *m/z* 292.2216 (M^+). Calcd for $C_{18}H_{32}OSi$: M, 292.2224].

4-(4-Methylcyclohexylidene)-5-(trimethylsilyl)pent-1-en-3-one (2). An oil; IR (neat) 1670 (C=O), 1610 (C=C),

1265, and 800 cm^{-1}; ^1H NMR ($CDCl_3$) −0.02 (9H, s, $SiMe_3$), 0.89 (3H, d, J=6.6 Hz, Me), 0.87−1.90 (9H, m), 2.41 (1H, m, C═CC*H*H), 2.50 (1H, m, C═CC*H*H), 5.84 (1H, dd, J=1.7, 10.3 Hz, C═C*H*H), 6.19 (1H, dd, J=1:7, 17.6 Hz, C═CHH), and 6.41 (1H, dd, J=10.3, 17.6 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) −0.9 (3C), 20.5, 21.9, 30.2, 32.1, 32.4, 35.8, 36.2, 129.0, 129.9, 137.3, 138.1, and 200.9; MS *m/z* 250 (M^+, 24%), 235 (34), 208 (17), 193 (28), 182 (36), and 73 (100); HRMS [Found: *m/z* 250.1800 (M^+). Calcd for $C_{15}H_{26}OSi$: M, 250.1754].

4-Cyclohexylidene)-5-(trimethylsilyl)pent-1-en-3-one (3). An oil; IR (neat) 1670 (C═O), 1610 (C═C), 1260, 1030, and 805 cm^{-1}; ^1H NMR ($CDCl_3$) −0.02 (9H, s, $SiMe_3$), 1.43–1.61 (6H, m), 1.72 (2H, br s, C$H_2$$SiMe_3$), 2.13 (4H, m, C═C$CH_2$), 5.84 (1H, dd, J=1.8, 10.4 Hz, C═C*H*H), 6.19 (1H, dd, J=1.8, 17.4 Hz, C═CH*H*), and 6.41 (1H, dd, J=10.4, 17.4 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) −1.0 (3C), 20.3, 26.4, 27.7, 28.0, 30.8, 32.9, 128.9, 129.7, 137.4, 138.5, and 200.9; MS *m/z* 236 (M^+, 20%), 221 (28), 208 (7), 193 (19), 182 (20), and 73 (100); HRMS [Found: *m/z* 236.1580 (M^+). Calcd for $C_{14}H_{24}OSi$: M, 236.1597].

4-Cyclopentylidene-5-(trimethylsilyl)pent-1-en-3-one (7). An oil; IR (neat) 1660 (C═O), 1605 (C═C), 1405, 1250, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) −0.03 (9H, s, $SiMe_3$), 1.61–1.70 (4H, m, CH_2CH_2), 1.80 (2H, br s, C$H_2$$SiMe_3$), 2.28 (2H, m, C═C$CH_2$), 2.44 (2H, m, C═C$CH_2$), 5.69 (1H, dd, J=1.8, 10.3 Hz, C═C*H*H), 6.20 (1H, dd, J=1.8, 17.2 Hz, C═CH*H*), and 6.65 (1H, dd, J=10.3, 17.2 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) −0.90 (3C), 21.4, 25.4, 27.5, 33.3, 34.1, 127.5, 131.0, 136.2, 150.0, and 196.1; MS *m/z* 222 (M^+, 64%), 221 (55), 207 (43), 194 (23), and 71 (100); HRMS [Found: *m/z* 222.1442 (M^+). Calcd for $C_{13}H_{22}OSi$: M, 222.1441].

(*E*)-4-(3-Methylcyclopentylidene)-5-(trimethylsilyl)pent-1-en-3-one (10a). An oil; IR (neat) 1665 (C═O), 1605 (C═C), 1405, 1250, and 840 cm^{-1}; ^1H NMR ($CDCl_3$; detailed assignment was made by COSY spectrum) -0.04 (9H, s, $SiMe_3$), 0.99 (3H, d, J=6.2 Hz, 3′-Me), 1.23 (1H, m, 4′-H), 1.70 (1H, br d, J=14 Hz, C*H*H$SiMe_3$), 1.85 (1H, m, 4′-H), 1.86 (1H, br d, J=14 Hz, CH*H*$SiMe_3$), 1.96 (1H, m, 3′-H), 2.01 (1H, m, 2′-H), 2.26 (1H, br dt, J=18, 8 Hz, 5′-H), 2.39 (1H, br dd, J=8, 18 Hz, 5′-H), 2.64 (1H, br dd, J=5, 15 Hz, 2′-H), 5.69 (1H, dd, J=1.8, 10.3 Hz, C═C*H*H), 6.19 (1H, dd, J=1.8, 17.2 Hz, C═CH*H*), and 6.64 (1H, dd, J=10.3, 17.2 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) -0.9 (3C), 19.5, 21.1, 33.0, 33.4, 35.7, 42.6, 127.5, 131.3, 136.2, 149.9, and 196.0; MS *m/z* 236 (M^+, 31%), 221 (M^+−Me, 49), 181 (29), 91 (41), and 73 (100); HRMS Found: *m/z* 236.1559 (M^+). Calcd for $C_{14}H_{24}OSi$: M, 236.1597].

(*Z*)-4-(3-Methylcyclopentylidene)-5-(trimethylsilyl)pent-1-en-3-one (10b). An oil; IR (neat) 1660 (C═O), 1605 (C═C), 1400, 1250, 860, and 840 cm^{-1}; ^1H NMR ($CDCl_3$; detailed assignment was made by COSY spectrum) -0.04 (9H, s, $SiMe_3$), 1.02 (3H, d, J=6.5 Hz, 3′-Me), 1.22 (1H, m, 4′-H), 1.71 (1H, br d, J=14 Hz, C*H*H$SiMe_3$), 1.84 (2H, m, 2′-H and 4′-H), 1.86 (1H, br d, J=14 Hz, CH*H*$SiMe_3$), 2.00 (1H, m, 3′-H), 2.38 (1H, br dd, J=8, 17 Hz, 5′-H), 2.47 (1H, br dd, J=7, 17 Hz, 2′-H), 2.58 (1H, br dd, J=7, 17 Hz, 5′-H), 5.69 (1H, dd, J=1.9, 10.2 Hz, C═C*H*H), 6.19 (1H, dd, J=1.9, 17.2 Hz, C═CH*H*), and 6.64 (1H, dd, J=10.2, 17.2 Hz, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) −0.9 (3C), 19.8, 21.4, 33.6 (2C), 35.4, 41.9, 127.5, 131.1, 136.2, 150.0, and 196.1; MS *m/z* 236 (M^+, 7%), 220 (86), 205 (100), and 57 (32); HRMS [Found: *m/z* 236.1609 (M^+). Calcd for $C_{14}H_{24}OSi$: M, 236.1597].

(*Z*)-2-Cyclohexylidene-1-(trimethylsilyl)hex-4-en-3-one (13a). An oil; IR (neat) 1670 (C═O), 1610 (C═C), 1250, and 845 cm^{-1}; ^1H NMR ($CDCl_3$) −0.03 (9H, s, $SiMe_3$), 1.48–1.59 (6H, m), 1.74 (2H, br s, C$H_2$$SiMe_3$), 2.10 (2H, m, C═C$CH_2$), 2.11 (3H, d, J=5.5 Hz, Me), 2.22 (2H, m, C═CCH_2), and 6.13–6.23 (2H, m, CH═CH); ^{13}C NMR ($CDCl_3$) −1.0 ($3CH_3$), 15.8 (CH_3), 19.8 (CH_2), 26.6 (CH_2), 27.6 (CH_2), 28.2 (CH_2), 31.1 (CH_2), 32.4 (CH_2), 129.9 (CH), 132.9 (C), 138.1 (C), 141.9 (CH), and 200.5 (CO); MS *m/z* 250 (M^+, 5%), 235 (M^+−Me, 100), 207 (7), 193 (6), 167 (9), 145 (8), 117 (7), 83 (11), and 73 (62); HRMS [Found: *m/z* 250.1801 (M^+). Calcd for $C_{15}H_{26}OSi$: M, 250.1754].

(*E*)-2-Cyclohexylidene-1-(trimethylsilyl)hex-4-en-3-one (13b). An oil; IR (neat) 1655 (C═O), 1620 (C═C), 1445, 1245, and 845 cm^{-1}; ^1H NMR ($CDCl_3$) −0.03 (9H, s, $SiMe_3$), 1.41–1.60 (6H, m), 1.68 (2H, br s, C$H_2$$SiMe_3$), 1.89 (3H, dd, J=1.6, 6.9 Hz, Me), 2.05–2.14 (4H, m, C═CCH_2×2), 6.13 (1H, dq, J=15.5, 1.6 Hz, C*H*═C*H*CH_3), and 6.80 (1H, dq, J=15.5, 6.9 Hz, CH═C*H*CH_3); ^{13}C NMR ($CDCl_3$) -0.9 (3C), 18.3, 20.4, 26.5, 27.6, 28.0, 30.6, 32.7, 130.1, 132.9, 136.9, 144.1, and 201.0; MS *m/z* 250 (M^+, 8%), 235 (M^+−Me, 100), 205 (13), 193 (6), 167 (8), 145 (7), and 73 (51); HRMS [Found: *m/z* 250.1798 (M^+). Calcd for $C_{15}H_{26}OSi$: M, 250.1754].

4-Cyclohexylidene-2-methyl-5-(trimethylsilyl)pent-1-en-3-one (14). An oil; IR (neat) 1665 (C═O), 1630 (C═C), 1450, 1250, 860, and 840 cm^{-1}; ^1H NMR ($CDCl_3$), −0.04 (9H, s, $SiMe_3$), 1.37–1.57 (6H, m), 1.64 (2H, br s, C$H_2$$SiMe_3$), 1.86 (3H, t, J=1.1 Hz, Me), 1.94 (2H, m, C═CCH_2), 2.10 (2H, m, C═CCH_2), 5.79 (1H, quint, J=1.4 Hz, C═C*H*H), and 5.92 (1H, m, C═CH*H*); ^{13}C NMR ($CDCl_3$) −0.9 (3C), 16.8, 20.9, 26.5, 27.6, 27.7, 30.2, 32.9, 127.2, 128.7, 136.0, 144.4, and 203.7; MS *m/z* 250 (M^+, 6%), 235 (8), 226 (28), 175 (75), 159 (76), 73 (100), and 58 (83); HRMS [Found: *m/z* 250.1732 (M^+). Calcd for $C_{15}H_{26}OSi$: M, 250.1754].

4-Cyclopentylidene-2-methyl-5-(trimethylsilyl)pent-1-en-3-one (17). An oil; IR (neat) 1645 (C═O), 1630 (C═C), 1250, 860, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) −0.04 (9H, s, $SiMe_3$), 1.51–1.66 (4H, m, CH_2CH_2), 1.72 (2H, quint, J=1.0 Hz, C$H_2$$SiMe_3$), 1.88 (3H, dd, J=0.8, 1.5 Hz, Me), 2.13–2.24 (4H, m, C═CCH_2×2), 5.71 (1H, quint, J=1.5 Hz, C═C*H*H), and 5.76 (1H, dq, J=1.5, 0.8 Hz, C═CH*H*); ^{13}C NMR ($CDCl_3$) −1.0 (3C), 17.1, 22.7, 25.6, 27.2, 31.8, 33.3, 125.9, 129.4, 144.2, 144.4, and 202.3; MS *m/z* 236 (M^+, 42%), 221 (47), 205 (100), 195 (52), and 73 (62); HRMS [Found: *m/z* 236.1588 (M^+). Calcd for $C_{14}H_{24}OSi$: M, 236.1597].

(*E*)-4-Cyclohexylidene-1-phenyl-5-(trimethylsilyl)pent-1-en-3-one (19). An oil; IR (neat) 1640 (C═O), 1605 (C═C),

1575, 1450, 1250, 985, 840, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) 0.01 (9H, s, $SiMe_3$), 1.46–1.66 (6H, m), 1.79 (2H, br s, CH_2SiMe_3), 2.19 (4H, m, C=CCH_2×2), 6.77 (1H, d, J=16.0 Hz, C*H*=CHPh), and 7.37–7.56 (6H, m, Ph and CH=C*H*Ph); ^{13}C NMR ($CDCl_3$) −0.9 (3C), 20.5, 26.5, 27.7, 28.1, 30.8, 32.9, 127.5, 128.3 (2C), 128.9 (2C), 130.3, 130.5, 134.9, 137.9, 143.6, and 200.7; MS *m/z* 312 (M^+, 62%), 283 (62), 269 (58), 213 (88), 168 (85), 133 (100), 117 (99), and 78 (91); HRMS [Found: *m/z* 312.1902 (M^+). Calcd for $C_{20}H_{28}OSi$: M, 312.1910].

4-Cyclohexylidene-2-phenyl-5-(trimethylsilyl)pent-1-en-3-one (20). An oil; IR (neat) 1665 (C=O), 1445, 1245, 970, 840, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) 0.03 (9H, s, $SiMe_3$), 1.44–1.64 (6H, m), 1.74 (2H, br s, CH_2SiMe_3), 2.17 (4H, m, C=CCH_2×2), 6.07 (1H, d, J=1.2 Hz, C=C*H*H), 6.13 (1H, d, J=1.2 Hz, C=CH*H*), and 7.29–7.40 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) −0.8 (3C), 20.6, 26.5, 27.6, 27.8, 30.8, 32.8, 127.0, 128.1, 128.1 (2C), 128.3 (2C), 129.7, 136.9, 138.5, 149.0, and 202.1; MS *m/z* 312 (M^+, 93%), 256 (94), 242 (88), 228 (93), 205 (93), 171 (90), 143 (90), 98 (99), and 70 (100); HRMS [Found: *m/z* 312.1938 (M^+). Calcd for $C_{20}H_{28}OSi$: M, 312.1910].

4-Cyclohexylidene-2-methylpent-1-en-3-one (24). An oil; IR (neat) 1660 (C=O), 1630 (C=C), 1445, 1325, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si=0.00) 1.43–1.62 (6H, m), 1.77 (3H, br s, C_{ring}=CCH_3), 1.90 (3H, br s, CH_2=CCH_3), 1.96 (2H, m, C=CCH_2), 2.20 (2H, m, C=CCH_2), 5.87 (1H, quint, J=1.5 Hz, C=C*H*H), and 5.95 (1H, m, C=CH*H*); ^{13}C NMR ($CDCl_3$) 15.7, 16.6, 26.4, 27.6, 27.7, 29.6, 32.7, 126.1, 127.9, 138.7, 144.3, and 204.3; MS *m/z* 178 (M^+, 45%), 163 (58), 149 (14), 135 (97), 121 (65), 109 (24), 67 (47), and 41 (100); HRMS [Found: *m/z* 178.1389 (M^+). Calcd for $C_{12}H_{18}O$: M, 178.1358].

4-Cyclohexylidenepent-1-en-3-one (25). An oil; IR (neat) 1660 (C=O), 1605 (C=C), 1450, 1400, 1295, and 950 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si=0.00) 1.46–1.64 (6H, m), 1.79 (3H, br s, Me), 2.10 (2H, m, C=CCH_2), 2.22 (2H, m, C=CCH_2), 5.93 (1H, dd, J=1.7, 10.3 Hz, C=C*H*H), 6.19 (1H, dd, J=1.7, 17.3 Hz, C=CH*H*), and 6.40 (1H, dd, J=10.3, 17.3 Hz, C*H*=CH_2); ^{13}C NMR ($CDCl_3$) 15.2, 26.4, 27.7, 27.9, 30.1, 32.6, 126.2, 130.1, 137.1, 141.5, and 201.8; MS *m/z* 164 (M^+, 2%), 149 (3), 136 (3), 121 (12), 107 (4), 91 (4), 77 (4), 67 (7), 55 (15), and 43 (100); HRMS [Found: *m/z* 164.1171 (M^+). Calcd for $C_{11}H_{16}O$: M, 164.1202].

(*Z*)-2-Cyclohexylidene-4-methylhex-4-en-3-one (26a). An oil; IR (neat) 1640 (C=O), 1450, 1375, and 1000 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si=0.00) 1.48–1.62 (6H, m), 1.80 (3H, br s, C_{ring}=CCH_3), 1.83 (3H, dq, J=7.2, 1.4 Hz, CH_3CH=CCH_3), 1.87 (3H, quint, J=1.4 Hz, CH_3CH=CCH_3), 2.19 (4H, m, C=CCH_2×2), and 5.91 (1H, qq, J=1.4, 7.2 Hz, C=CH); ^{13}C NMR ($CDCl_3$) 14.6, 15.3, 20.5, 26.4, 27.3, 27.7, 30.6, 32.0, 129.2, 132.7, 137.3, 142.2, and 204.0; MS *m/z* 192 (M^+, 100%), 178 (23), 149 (60), 109 (30), and 55 (71); HRMS [Found: *m/z* 192.1492 (M^+). Calcd for $C_{13}H_{20}O$: M, 192.1515].

(*E*)-2-Cyclohexylidene-4-methylhex-4-en-3-one (26b). An oil; IR (neat) 1640 (C=O), 1445, 1285, 1230, and 1045 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si=0.00) 1.41–1.62 (6H, m), 1.75 (3H, br s, C_{ring}=CCH_3), 1.80 (3H, quint, J=1.0 Hz, CH_3CH=CCH_3), 1.87 (3H, dq, J=7.0, 1.0 Hz, CH_3CH=CCH_3), 1.92 (2H, br dd, J=5, 7 Hz, C=CCH_2), 2.19 (2H, br dd, J=5, 7 Hz, C=CCH_2), and 6.73 (1H, qq, J=1.2, 7.0 Hz, C=CH); ^{13}C NMR ($CDCl_3$) 10.3, 15.0, 15.9, 26.5, 27.6, 27.7, 29.6, 32.6, 126.3, 137.7, 137.9, 141.5, and 204.4; MS *m/z* 192 (M^+, 39%), 177 (100), 149 (32), 135 (82), 109 (13), and 55 (43); HRMS [Found: *m/z* 192.1516 (M^+). Calcd for $C_{13}H_{20}O$: M, 192.1515].

Nazarov cyclization

Typical procedure. To a stirred solution of dry $FeCl_3$ (69.5 mg, 0.429 mmol) in dry CH_2Cl_2 (10 cm^3) was added a solution of **3** (40.3 mg, 0.170 mmol) in CH_2Cl_2 (5 cm^3) at −60°C under Ar. The reaction temperature was slowly elevated to −15°C over a period of 3.5 h with stirring, and then an aqueous solution of NH_4Cl was added. The mixture was extracted with CH_2Cl_2 and dried. Evaporation of the solvent followed by silica gel (5 g) column chromatography using pentane–Et_2O (99:1) as eluent afforded **6** (18.7 mg, 67%).

For **10a** and **10b**, $FeCl_3$ and the substrate were mixed at −30°C, and the mixture was slowly warmed to 0°C over a period of 2.5 h. The stirring was continued at 0°C for 3.5 h followed by work up as described above. To obtain a rearranged product, the reaction temperature was elevated from −30°C to r.t. over a period of 7 h followed by stirring at room temperature as shown in Table 1.

8-*t*-Butyl-1-methylenespiro[4.5]decan-2-one (4a,b). An oil; UV (pentane) λ_{max}=228 nm (ϵ 6.5×10^3); IR (neat) 1730 (C=O), 1645 (C=C), 1265, 1100, and 735 cm^{-1}; ^1H NMR ($CDCl_3$) 1.00–1.72 (9H, m), 0.86 (9H×1/6, s, *t*-Bu of **4b**), 0.87 (9H×5/6, s, *t*-Bu of **4a**), 1.69 (2H×1/6, t, J=7.9 Hz, $COCH_2CH_2$ of **4b**), 1.83 (2H×5/6, t, J=7.9 Hz, $COCH_2CH_2$ of **4a**), 2.32 (2H×5/6, t, J=8.1 Hz, $COCH_2CH_2$ of **4a**), 2.34 (2H×1/6, t, J=8.1 Hz, $COCH_2CH_2$ of **4b**), 5.18 (1H×5/6, d, J=0.7 Hz, C=C*H*H of **4a**), 5.46 (1H×1/6, d, J=1.1 Hz, C=C*H*H of **4b**), 5.98 (1H×5/6, br s, C=CH*H* of **4a**), and 6.02 (1H×1/6, d, J=1.1 Hz, C=CH*H* of **4b**); NOE was observed between *t*-Bu (δ 0.86) and olefinic proton (δ 5.46) for **4b**; ^{13}C NMR (C_6D_6=128.0) assigned for **4a**: 23.3 ($2CH_2$), 27.6 ($3CH_3$), 28.5 (CH_2), 32.3 (C), 35.3 (CH_2), 37.6 ($2CH_2$), 43.2 (C), 47.6 (CH), 114.8 (CH_2), 155.4 (C), and 205.9 (CO); MS *m/z* 220 (M^+, 14%), 205 (4), 177 (5), 164 (25), 149 (11), 135 (22), 123 (23), 110 (74), and 57 (100); HRMS [Found: *m/z* 220.1869 (M^+). Calcd for $C_{15}H_{24}O$: M, 220.1828].

8-Methyl-1-methylenespiro[4.5]decan-2-one (5a,b). An oil; UV (pentane) λ_{max}=228 nm (ϵ 2.3×10^3); IR (neat) 1730 (C=O), 1640 (C=C), 1260, 1100, and 805 cm^{-1}; ^1H NMR ($CDCl_3$) 0.85–1.70 (9H, m), 0.93 (3H×5/6, d, J=6.2 Hz, Me of **5a**), 0.95 (3H×1/6, d, J=6.6 Hz, Me of **5b**), 1.74 (2H×1/6, t, J=8.1 Hz, $COCH_2CH_2$ of **5b**), 1.83 (2H×5/6, t, J=8.1 Hz, $COCH_2CH_2$ of **5a**), 2.32 (2H×5/6, t, J=8.1 Hz, $COCH_2CH_2$ of **5a**), 2.33 (2H×1/6, t, J=8.1 Hz, $COCH_2CH_2$ of **5b**), 5.18 (1H×5/6, d, J=0.7 Hz, C=C*H*H of **5a**), 5.41 (1H×1/6, d, J=0.7 Hz, C=C*H*H of **5b**), 5.98 (1H×5/6, br s, C=CH*H* of **5a**), and 6.00 (1H×1/6, d,

J=0.7 Hz, C=CH*H* of **5b**); ^{13}C NMR (C_6D_6=128.0) assigned for **5a**: 22.6 (CH_3), 28.6 (CH_2), 31.2 ($2CH_2$), 32.3 (CH), 35.2 (CH_2), 37.2 ($2CH_2$), 43.0 (C), 114.8 (CH_2), 155.4 (C), and 205.9 (CO); MS *m/z* 178 (M^+, 91%), 163 (7), 150 (23), 136 (54), 121 (100), 107 (50), 93 (57), and 79 (70); HRMS [Found: *m/z* 178.1346 (M^+). Calcd for $C_{12}H_{18}O$: M, 178.1358].

1-Methylenespiro[4.5]decan-2-one (6). An oil; UV (pentane) λ_{max}=226 nm (ϵ 4.8×10^3); IR (neat) 1730 (C=O), 1640 (C=C), 1265, 1100, and 805 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.20–1.72 (10H, m), 1.85 (2H, t, J=7.9 Hz, $COCH_2CH_2$), 2.32 (2H, t, J=7.9 Hz, $COCH_2CH_2$), 5.22 (1H, d, J=0.7 Hz, C=C*H*H), and 5.99 (1H, br s, C=CH*H*); ^{13}C NMR (C_6D_6=128.0) 22.5 (2C), 26.0, 29.4, 35.2, 37.1 (2C), 43.3, 115.1, 155.3, and 205.9; MS *m/z* 164 (M^+, 92%), 149 (12), 136 (21), 122 (100), 108 (35), 93 (55), and 79 (64); HRMS [Found: *m/z* 164.1237 (M^+). Calcd for $C_{11}H_{16}O$: M, 164.1202].

1-Methylenespiro[4.4]nonan-2-one (8). An oil; UV (pentane) λ_{max}=223 nm (ϵ 3.1×10^3); IR (neat) 1730 (C=O), 1645 (C=C), 1455, 1270, and 1100 cm^{-1}; ^{1}H NMR (C_6D_6=7.15) 1.20–1.50 (8H, m), 1.26 (2H, t, J=7.7 Hz, $COCH_2CH_2$), 1.99 (2H, t, J=7.7 Hz, $COCH_2CH_2$), 4.79 (1H, d, J=0.7 Hz, C=C*H*H), and 6.03 (1H, d, J=0.7 Hz, C=CH*H*); ^{13}C NMR (C_6D_6=128.0) 24.7 (2C), 30.2, 33.7, 36.5, 39.6 (2C), 113.8, 153.9, and 205.4; MS *m/z* 150 (M^+, 40%), 135 (6), 122 (12), 108 (86), 93 (37), 79 (41), and 72 (100); HRMS [Found: *m/z* 150.1047 (M^+). Calcd for $C_{10}H_{14}O$: M, 150.1045].

6-Methyl-1-methylenespiro[4.4]nonan-2-one (11a,b). The following data were obtained from 4:1 mixture. An oil; IR (neat) 1725 (C=O), 1635 (C=C), 1460, and 1095 cm^{-1}; ^{1}H NMR (C_6D_6=7.15) 0.86 (3H×1/5, d, J=6.6 Hz, Me of **11b**), 0.89 (3H×4/5, d, J=6.5 Hz, Me of **11a**), 1.27 (2H×4/5, m, $COCH_2CH_2$ of **11a**), 1.34 (2H×1/5, m, $COCH_2CH_2$ of **11b**), 0.96–1.87 (7H, m), 1.99 (2H×4/5, t, J=7.7 Hz, $COCH_2CH_2$ of **11a**), 2.00 (2H×1/5, t, J=7.7 Hz, $COCH_2CH_2$ of **11b**), 4.78 (1H×1/5, d, J=0.9 Hz, C=C*H*H of **11b**), 4.85 (1H×4/5, d, J=0.9 Hz, C=C*H*H of **11a**), 6.02 (1H×1/5, d, J=0.9 Hz, C=CH*H* of **11b**), and 6.05 (1H×4/5, d, J=0.9 Hz, C=CH*H* of **11a**); NOE signal was observed at olefinic proton (δ 4.85) for **11a** and methylenic protons (δ 1.34) for **11b**, respectively, on irradiation of methyl group (δ 0.89 for **11a** and 0.86 for **11b**); ^{13}C NMR (C_6D_6=128.0) assigned for **11a**: 20.5, 33.8, 33.9, 34.7, 36.3, 40.0, 49.0, 51.4, 113.8, 154.1, and 205.5; assigned for **11b**: 14.2, 20.8, 22.7, 35.4, 36.7, 39.5, 48.4, 51.6, 113.5, 155.0, and 205.3; MS *m/z* 164 (M^+, 66%), 122 (100), 107 (33), 96 (46), and 79 (59); HRMS [Found: *m/z* 164.1222 (M^+). Calcd for $C_{11}H_{16}O$: M, 164.1202].

4-Methyl-1-methylenespiro[4.5]decan-2-one (15). An oil; IR (neat) 1725 (C=O), 1635 (C=C), 1450, and 1150 cm^{-1}; ^{1}H NMR (C_6D_6=7.15) 0.56 (3H, d, J=7.0 Hz, Me), 0.84–1.40 (10H, m), 1.74 (1H, dd, J=2.7, 18.0 Hz, COC*H*H), 1.84 (1H, br d quint, J=2.5, 7 Hz, C*H*Me), 2.25 (1H, dd, J=6.7, 18.0 Hz, COCH*H*), 4.90 (1H, d, J=0.9 Hz, C=C*H*H), and 6.14 (1H, d, J=0.9 Hz, C=CH*H*); ^{13}C NMR (C_6D_6=128.0) 16.3, 22.2, 22.8, 26.0, 30.9, 33.1, 37.1, 43.7, 46.2, 115.9, 154.2, and 205.3; MS *m/z* 178 (M^+, 42%), 163 (14), 150 (27), 136 (64), 108 (100), 93 (78), and 79 (63); HRMS [Found: *m/z* 178.1369 (M^+). Calcd for $C_{12}H_{18}O$: M, 178.1358].

1,3-Dimethylspiro[4.5]dec-3-en-2-one (16). An oil; IR (neat) 1705 (C=O), 1635 (C=C), and 1450 cm^{-1}; ^{1}H NMR (C_6D_6=7.15) 0.90–1.44 (10H, m), 1.04 (3H, d, J=7.5 Hz, $CHCH_3$), 1.70 (3H, d, J=1.3 Hz, $C=CCH_3$), 1.84 (1H, q, J=7.5 Hz, $CHCH_3$), and 6.92 (1H, q, J=1.3 Hz, C=CH); ^{13}C NMR (C_6D_6=128.0) 10.4, 11.0, 22.9, 23.2, 26.0, 33.8, 37.7, 45.1, 52.5, 138.7, 161.7, and 209.4; MS *m/z* 178 (M^+, 4%), 163 (6), 150 (4), 135 (7), 122 (6), 79 (7), 57 (11), and 43 (100); HRMS [Found: *m/z* 178.1394 (M^+). Calcd for $C_{12}H_{18}O$: M, 178.1358].

1,3-Dimethylspiro[4.4]non-3-en-2-one (18). An oil; IR (neat) 1705 (C=O), 1640 (C=C), and 1450 cm^{-1}; ^{1}H NMR (C_6D_6=7.15) 1.02 (3H, d, J=7.5 Hz, $CHCH_3$), 1.14–1.47 (8H, m), 1.67 (3H, d, J=1.3 Hz, $C=CCH_3$), 1.95 (1H, q, J=7.5 Hz, $CHCH_3$), and 6.47 (1H, q, J=1.3 Hz, C=CH); ^{13}C NMR (C_6D_6=128.0) 10.2 (CH_3), 12.6 (CH_3), 24.3 (CH_2), 24.5 (CH_2), 33.0 (CH_2), 39.7 (CH_2), 50.2 (CH), 53.2 (C), 137.6 (C), 163.0 (CH), and 209.9 (CO); MS *m/z* 164 (M^+, 37%), 149 (M^+–Me, 90), 136 (63), 121 (38), 107 (65), 93 (52), and 79 (100); HRMS [Found: *m/z* 164.1159 (M^+). Calcd for $C_{11}H_{16}O$: M, 164.1202].

1-Methylene-4-phenylspiro[4.5]decan-2-one (21). An oil; IR (neat) 1725 (C=O), 1635 (C=C), 1450, 760, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si=0.00) 0.80–1.80 (10H, m), 2.52 (1H, dd, J=3.8, 18.9 Hz, COC*H*H), 2.87 (1H, dd, J=8.7, 18.9 Hz, COCH*H*), 3.36 (1H, dd, J=3.8, 8.7 Hz, C*H*Ph), 5.36 (1H, d, J=0.6 Hz, C=C*H*H), 6.16 (1H, br s, C=CH*H*), and 7.04–7.29 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) 21.7, 22.8, 25.5, 31.6, 38.0, 43.3, 46.9, 48.0, 117.2, 126.6, 128.2 (2C), 128.4 (2C), 141.9, 154.1, and 207.8; MS *m/z* 240 (M^+, 91%), 220 (97), 205 (89), 108 (96), 82 (100), and 55 (97); HRMS [Found: *m/z* 240.1494 (M^+). Calcd for $C_{17}H_{20}O$: M, 240.1515].

A mixture of 1-methyl-3-phenylspiro[4.5]dec-3-en-2-one (22) and 1-methylene-3-phenylspiro[4.5]dec-2-en-2-ol (23). An oil; IR (neat) 3240 (OH of **23**), 1700 (C=O of **22**), 1645 (C=C), 1450, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.17 (3H×2/3, d, J=7.5 Hz, CH_3 of **22**), 1.23–1.82 (10H×2/3 for **22** plus 12H×1/3(for **23**, m), 2.28 (1H×2/3, q, J=7.5 Hz, $CHCH_3$ of **22**), 5.46 (1H×1/3, br s, C=C*H*H of **23**), 6.15 (1H×1/3, br s, C=CH*H* of **23**), and 7.28–7.96 (5H plus 1H×2/3, m, Ph and CH=C of **22**); ^{13}C NMR ($CDCl_3$) assigned for **22**: 10.9, 22.8, 23.1, 25.8, 33.8, 37.5, 45.1, 53.9, 127.1 (2C), 128.3, 128.4 (2C), 131.8, 139.8, 163.7, and 209.1; assigned for **23**: 22.9 (2C), 25.7, 29.7, 36.5 (2C), 44.9, 115.8, 127.2 (2C), 128.4 (2C), 128.6, 141.8, 152.9, 159.3, and 194.5; MS *m/z* 240 (M^+, 92%), 197 (100), 184 (96), and 141 (88); HRMS [Found: *m/z* 240.1508 (M^+). Calcd for $C_{17}H_{20}O$: M, 240.1515].

1,3,4-Trimethylspiro[4.5]dec-3-en-2-one (27). An oil; IR (neat) 1700 (C=O), 1650 (C=C), 1450, and 1385 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si=0.00) 1.02–1.76 (10H, m), 1.17 (3H, d, J=7.4 Hz, $CHCH_3$), 1.66 (3H, q, J=0.7 Hz,

$CH_3C{=}C(CH_3)CO$), 1.92 (3H, q, J=0.7 Hz, $CH_3C{=}C(CH_3)CO$), and 2.28 (1H, q, J=7.4 Hz, $CHCH_3$); ^{13}C NMR ($CDCl_3$) 8.2, 12.6, 14.8, 23.1, 23.9, 25.2, 28.5, 38.0, 48.3, 49.3, 132.7, 176.3, and 212.2; MS m/z 192 (M^+, 77%), 177 (40), 149 (72), 136 (100), 121 (28), and 93 (24); HRMS [Found: m/z 192.1477 (M^+). Calcd for $C_{13}H_{20}O$: M, 192.1515].

Rearrangement

Typical procedure. Compound **8** (11.1 mg, 0.0738 mmol) was treated with $FeCl_3$ (30.5 mg) as described for the Nazarov cyclization, except that the reaction temperature was elevated to room temperature for 19 h. The crude product was chromatographed on silica gel (1 g) using pentane–Et_2O (98:2) as eluent to yield **9** (6.7 mg, 60%).

6-Methylbicyclo[4.3.0]non-8-en-7-one (9). An oil; UV (pentane) λ_{max}=217 nm (ϵ 4.4×10^3); IR (neat) 1715 (C=O), 1590 (C=C), 1465, 1265, 1075, and 810 cm^{-1}; ^1H NMR (C_6D_6=7.15) 0.98 (3H, s, Me), 0.96–1.40 (7H, m), 1.61 (1H, br ddd, J=6, 7, 14 Hz, 5-H), 2.06 (1H, ddt-like, J=5, 6, 2.5 Hz, 1-H), 5.91 (1H, dd, J=2.0, 5.7 Hz, COC*H*=CH), and 6.73 (1H, dd, J=2.6, 5.7 Hz, COCH=C*H*); NOE was observed between methyl group (δ 0.98) and methine proton (δ 2.06); ^{13}C NMR (C_6D_6=128.0) 19.5 (CH_2), 19.8 (CH_2), 23.2 (CH_3), 25.6 (CH_2), 30.9 (CH_2), 46.3 (C), 48.8 (CH), 131.8 (CH), 164.8 (CH), and 212.8 (CO); MS m/z 150 (M^+, 53%), 135 (M^+-Me, 100), 121 (26), 107 (26), 93 (41), and 79 (59); HRMS [Found: m/z 150.1045 (M^+). Calcd for $C_{10}H_{14}O$: M, 150.1045].

3(or 4),6-Dimethylbicyclo[4.3.0]non-8-en-7-one (12a–e). An oil; IR (neat) 1710 (C=O), 1585 (C=C), 1460, and 805 cm^{-1}; ^1H NMR (C_6D_6=7.15) assigned for **12a**: 0.68 (3H, d, J=6.1 Hz, Me), 0.69–0.78 (1H, br, 4β-H), 1.03 (3H, s, Me), 0.96–1.05 (2H, m, 2-H and 3-H), 1.19–1.32 (2H, m, 2-H and 4α-H), 1.32 (1H, ddd, J=4.0, 6.6, 13.6 Hz, 5β-H), 1.47 (1H, ddd, J=4.4, 10.0, 13.6 Hz, 5α-H), 2.18 (1H, dq-like, J=6, 2.5 Hz, 1-H), 5.90 (1H, dd, J=2.5, 5.7 Hz, 8-H), and 6.70 (1H, dd, J=2.2, 5.7 Hz, 9-H); NOESY signals were observed between δ 1.03–0.74, 1.03–0.68, 1.03–2.18, and 0.68–2.18; assigned for **12b**: 0.65 (3H, d, J=6.2 Hz, Me), 1.08 (4H, s, Me), 2.08 (1H, m, 1-H), 5.88 (1H, dd, J=2.5, 5.9 Hz, 8-H), and 6.65 (1H, dd, J=2.0, 5.9 Hz, 9-H); assigned for **12c**: 0.68 (3H, d, J=6.8 Hz, Me), 0.95 (3H, s, Me), 1.95 (1H, m, 1-H), 5.84 (1H, dd, J=1.5, 5.8 Hz, 8-H), and 6.85 (1H, dd, J=3.0, 5.8 Hz, 9-H); assigned for **12d**: 0.73 (3H, d, J=6.6 Hz, Me), 1.12 (3H, s, Me), 1.81 (1H, m, 1-H), 5.81 (1H, br d, J=5.5 Hz, 8-H) and 6.96 (1H, br d, J=5.5 Hz, 9-H); assigned for **12e**: 0.84 (3H, d, J=6.9 Hz, Me), 1.09 (3H, s, Me), 1.84 (1H, m, 1-H), 5.80 (1H, br d, J=5.5 Hz, 8-H) and 6.95 (1H, br d, J=5.5 Hz, 9-H); ^{13}C NMR (C_6D_6=128.0) assigned for **12a**: 21.0, 22.6, 26.8, 29.3, 32.0, 34.0, 46.2, 48.7, 131.6, 164.5, and 212.6; MS m/z 164 (M^+, 46%), 149 (M^+-Me, 100), 121 (27), 107 (28), 91 (34), 79 (38), and 57 (54); HRMS [Found: m/z 164.1228 (M^+). Calcd for $C_{11}H_{16}O$: M, 164, 1202].

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