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Preparation of Stereochemically Pure *E*- and *Z*-Alkenoic Acids and Their Methyl Esters from Bicyclo[*n*.1.0]alkan-1-ols. Application in the Synthesis of Insect Pheromones

D. M. Zubrytski[a], D. G. Kananovich[b],* and E. A. Matiushenkov[c]

[a] *Belarusian State University, Nezavisimosti av. 4, Minsk, 220030 Belarus*

[b] *Tallinn University of Technology, Akadeemia tee 15, Tallinn, 12618 Estonia*
**e-mail: dzmitry.kananovich@ttu.ee*

[c] *Olainfarm Joint Stock Company, Rupnicu str. 5, Olaine, 2114 Latvia*

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Abstract—Oxidative cleavage of *exo*- and *endo*-alkyl- and hydroxyalkyl-substituted bicyclo[*n*.1.0]alkan-1-ols with (diacetoxy-λ^3-iodanyl)benzene gave the corresponding methyl alkenoates exclusively with *E* or *Z* configuration of the double bond. This reaction was used as the key stage in the syntheses of stereoisomerically pure components of pest insect pheromones: (*E*)-dodec-9-en-1-yl acetate (European pine shoot moth *Rhyacionia buoliana*), (*Z*)-tetradec-11-en-1-yl acetate (European oak leafroller *Tortrix viridana*), and (3*E*,8*Z*,11*Z*)-tetradeca-3,8,11-trien-1-yl acetate (tomato leafminer *Tuta absoluta*).

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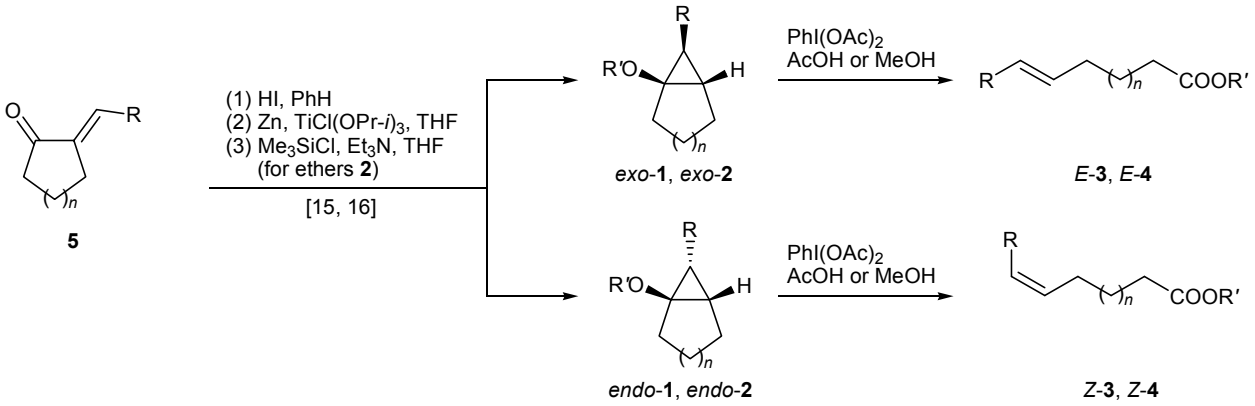
Synthetic pheromones are used in the monitoring of populations of pest insects and in pest control. Many insect sex pheromones contain unsaturated aliphatic alcohols or their esters with *E* or *Z* configuration of carbon–carbon double bonds [1–4], and contamination of synthetic pheromones even with insignificant impurities of stereoisomeric compounds may considerably reduce their attractive activity until its complete loss. For example, (*Z*)-dodec-9-en-1-yl acetate inhibits the attractive effect of its *E* isomer (the main component of the sex pheromone of the European pine shoot moth *Rhyacionia buoliana* [5]) so strongly that samples of (*E*)-dodec-9-en-1-yl acetate containing more than 2% of the *Z* isomer are completely inactive [6, 7]. Taking into account that separation of stereoisomers, especially separation of insignificant amounts of undesirable stereoisomer, is a very laborious process [8–10], methods ensuring highly stereoselective formation of C=C double bonds have acquired exceptional importance in the synthesis of components of insect pheromones.

An example of such transformations is oxidative cleavage of bicyclic hydroxy- and siloxycyclopropanes **1** and **2** by the action of lead tetraacetate [11] or nontoxic (diacetoxy-λ^3-iodanyl)benzene in acetic acid or methanol [12–16]. In this reaction, steric structure of the initial compound completely determines configuration of the double bond in the product, so that unsaturated acids **3** or their esters **4** are obtained exclusively with *E* or *Z* configuration of the double bond from the *exo* or *endo* isomers of **1** and **2**, respectively (Scheme 1).

Until recently, a significant limitation of this approach, which hampered its practical use, has been difficult accessibility of bicyclic hydroxy(trimethylsiloxy)cyclopropanes **1** and **2** substituted at the three-membered ring. Although compounds **1** and **2** can be synthesized by cyclopropanation of cyclic ketone enol ethers with carbenoid reagents [17] or by 1,3-cyclizations [18], there are some practical restrictions intrinsic to these reactions. For example, the Simmons–Smith cyclopropanation utilizes only 1,1-diiodoethane since zinc carbenoids generated from higher homologs are unstable, whereas a large excess of highly expensive 1,1-diiodoalkane is necessary to achieve high substrate conversion [19].

Relatively recently we have developed a procedure for the synthesis of alcohols **1** substituted at the cyclopropane ring by treatment of 2-alkylidenecycloalkan-1-ones **5** with hydrogen iodide and subsequent reaction

Scheme 1.



1, **3**, R′ = H; **2**, R′ = Me$_3$Si; **4**, R′ = Me; *n* = 1–4.

of β-iodo ketones thus formed with zinc in the presence of chloro(triisopropoxy)titanium in tetrahydrofuran (Scheme 1) [15]. This reaction gives mixtures of *endo* and thermodynamically more stable *exo* isomers **1** in good yields with the *exo* isomers prevailing. Oxidation of some *exo*-bicyclo[*n*.1.0]alkan-1-ols with PhI(OAc)$_2$ successfully afforded *E*-configured double bonds in the capsaicin [15] and (*R*)-(+)-recifeiolide (natural macrolide) molecules [16]. In the present work we used oxidative cleavage of the cyclopropane ring in substituted bicyclo[*n*.1.0]alkan-1-ols to accomplish stereoselective syntheses of insect pheromones, namely (*E*)-dodec-9-en-1-yl and (*Z*)-tetradec-11-en-1-yl acetates, pheromone components of the European pine shoot moth *Rhyacionia buoliana* and European oak leafroller *Tortrix viridana*, respectively, and (3*E*,8*Z*,11*Z*)-tetradeca-3,8,11-trien-1-yl acetate, pheromone of the tomato leafminer *Tuta absoluta*.

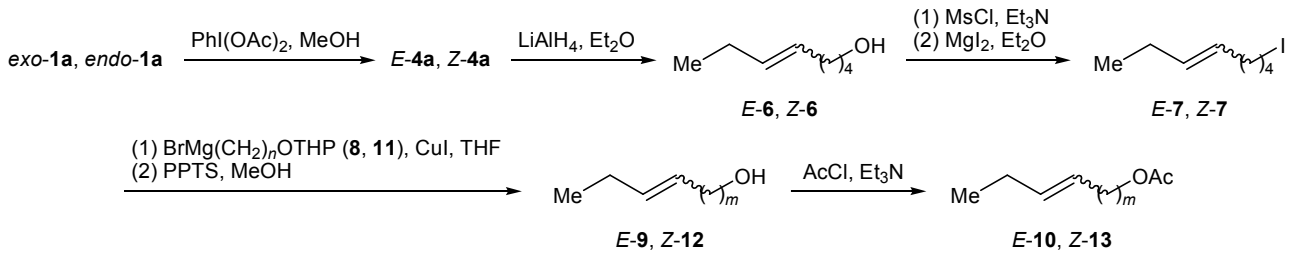
Initial *exo*- and *endo*-bicyclo[*n*.1.0]alkan-1-ols **1a** and **1d**–**1i** were synthesized according to [15, 16]. By

Oxidative cleavage of substituted bicyclo[*n*.1.0]alkan-1-ols **1** and their trimethylsilyl ethers **2** with (diacetoxy-λ^3-iodanyl)-benzene[a]

Substrate	*n*	R	R′	Product	Yield,[b] %
exo-**1a**	1	Et	H	*E*-**4a**	55
endo-**1a**	1	Et	H	*Z*-**4a**	60
exo-**2b**	1	Bu	Me$_3$Si	*E*-**3b**	69
endo-**2b**	1	Bu	Me$_3$Si	*Z*-**3b**	70
exo-**2c**	1	C_5H_{11}	Me$_3$Si	*E*-**3c**	76
endo-**2c**	1	C_5H_{11}	Me$_3$Si	*Z*-**3c**	70
exo-**1d**	2	Pr	H	*E*-**4d**	80
endo-**1d**	2	Pr	H	*Z*-**4d**	75
exo-**1e**	3	Pr	H	*E*-**4e**	71
endo-**1e**	3	Pr	H	*Z*-**4e**	78
exo-**1f**	3	C_6H_{13}	H	*E*-**4f**	81
endo-**1f**	3	C_6H_{13}	H	*Z*-**4f**	74
exo-**1g**	4	Pr	H	*E*-**4g**	83
endo-**1g**	4	Pr	H	*Z*-**4g**	74
exo-**1h**	2	$PhCH_2O(CH_2)_2$	H	*E*-**4h**	63
exo-**1i**	1	$HO(CH_2)_2$	H	*E*-**4i**	85

[a] Reagents: **1** (1 equiv), (AcO)$_2$IPh (1.1 equiv), MeOH (0.17–0.2 mM/mL); **2** (1 equiv), (AcO)$_2$IPh (1.1 equiv), AcOH (0.1 mM/mL).
[b] Pure compounds isolated by silica gel column chromatography.

Scheme 2.



8, $n = 4$; **11**, $n = 6$; **9**, **10**, $m = 8$; **12**, **13**, $m = 10$; PPTS is pyridinium *p*-toluenesulfonate, THP is tetrahydropyran-2-yl.

treatment of **1a** and **1d**–**1i** with (diacetoxy-λ^3-iodanyl)-benzene in methanol we obtained 55–85% of methyl alkenoates **4** with exclusive *E* or *Z* configuration (see table, Scheme 1). Cleavage of alcohols **1** with (diacetoxy-λ^3-iodanyl)benzene in acetic acid was reported [13] to produce unsaturated carboxylic acids **3** in ~50% yield; the yield was improved to 69–76% if the initial bicyclo[*n*.1.0]alkan-1-ols were preliminarily converted to trimethylsilyl ethers **2**.

The configuration of the double bond in **3** and **4** was confirmed by spectral data. In particular, the IR spectra of *E* isomers of **3** and **4** contained absorption bands in the region 960–970 cm^{-1} [11, 20], which are typical of *E*-alkenes; no such bands were present in the spectra of the corresponding *Z* isomers. Multiplet signals of olefinic protons in the ^1H NMR spectra were simplified to *AB* doublets with the aid of ^1H homodecoupling NMR experiments by selective irradiation of the allylic protons; we thus determined the coupling constants for the olefinic protons: $J \approx 11$ Hz for the *Z* isomers and $J \approx 15$ Hz for the *E* isomers [21].

Taking into account that the oxidative cleavage of cyclopropane derivatives **1** and **2** is stereospecific [11], the stereochemical purity of compounds **3** and **4** is determined only by efficiency of chromatographic separation of the *exo* and *endo* isomers of **1** at the stage of their preparation. This procedure usually involves no difficulties, whereas compounds *exo*-**1h** and *exo*-**1i** required no purification from the *endo* isomers since they were formed with 100% *exo*-diastereoselectivity, presumably due to chelation control at the stage of intramolecular cyclization of the corresponding β-metalloketone intermediate [16].

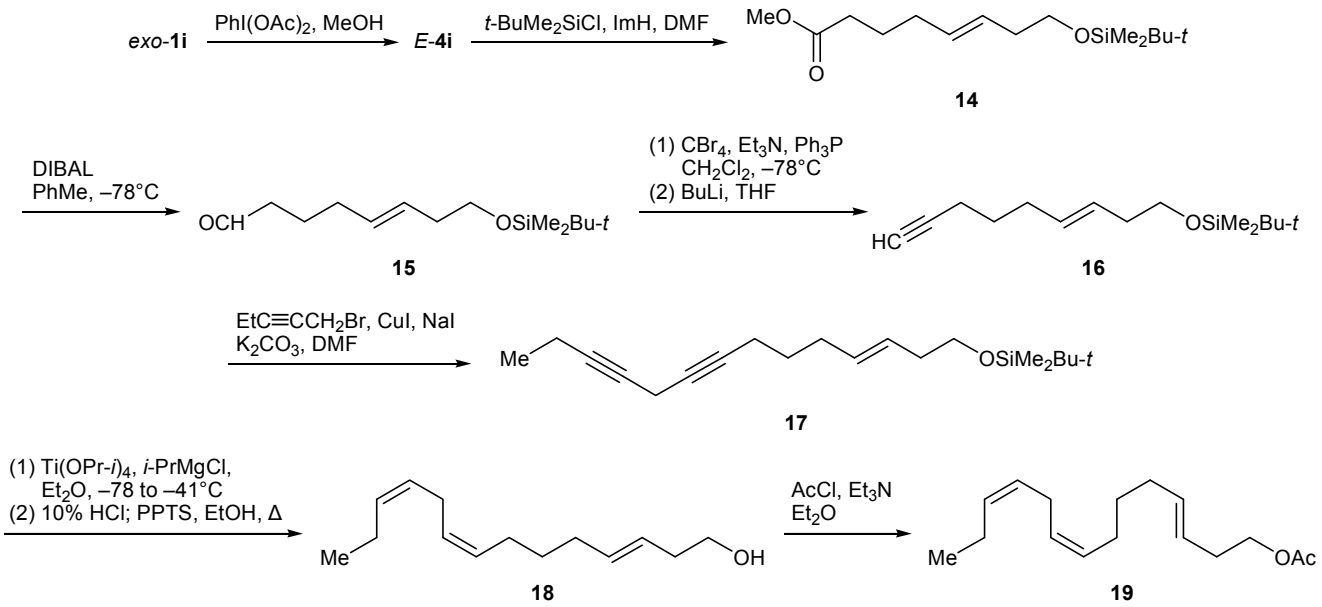
E- and *Z*-Alkenoic acids **3** and their esters **4** synthesized as described above can be used as building blocks in the preparation of stereoisomerically pure components of insect sex pheromones. We thus synthesized (*E*)-dodec-9-en-1-yl acetate (*E*-**10**) and (*Z*)-tetradec-11-en-1-yl acetate (*Z*-**13**) that are the major components of sex pheromones of the European pine shoot moth *Rhyacionia buoliana* [5] and European oak leafroller *Tortrix viridana* [22], respectively.

Compound *E*-**10** was synthesized from methyl (*E*)-oct-5-enoate (*E*-**4a**) which was obtained by oxidation of *exo*-6-ethylbicyclo[3.1.0]hexan-1-ol (*exo*-**1a**) (Scheme 2). The stereochemical purity of *E*-**4a** was estimated at ≥99% by ^1H NMR. Ester *E*-**4a** was reduced to unsaturated alcohol *E*-**6** with lithium tetrahydridoaluminate. The subsequent activation of the hydroxy group via transformation into methanesulfonate and nucleophilic substitution afforded unsaturated iodide *E*-**7**. Coupling of the latter with functionally substituted organomagnesium compound **8** in the presence of a catalytic amount (5–10 mol %) of copper(I) iodide. After removal of the tetrahydropyranyl protecting group, acylation of the resulting unsaturated alcohol *E*-**9** with acetyl chloride in the presence of triethylamine gave target acetate *E*-**10**. According to the GLC data, the product contained only 0.7% of the *Z* isomer.

Minor *endo*-6-ethylbicyclo[3.1.0]hexan-1-ol (*endo*-**1a**) obtained together with *exo*-**1a** was oxidized to methyl (*Z*)-oct-5-enoate *Z*-**4a** (*Z*/*E* ~98:2, according to the ^1H NMR data). Acetate *Z*-**13**, the major component of the sex pheromone of the European oak leafroller *Tortrix viridana*, was synthesized starting from ester *Z*-**4a** according to a scheme analogous to that described above (Scheme 2). The only difference was the use of homologous organomagnesium compound **11** in the coupling stage. The presence of more than 3% of the *E* isomer in the synthetic pheromone inhibited its attractive activity [22].

The described synthetic schemes utilized monofunctional building blocks with *E*- or *Z*-configured double bond of high stereochemical purity. Oxidative cleavage of the cyclopropane ring in bicyclo[*n*.1.0]-alkan-1-ols functionalized at the alkyl substituent, e.g., in hydroxyalkyl-substituted derivatives, gives rise to bifunctional building blocks.

Scheme 3.



DIBAL is diisobutylaluminum hydride, ImH is imidazole.

In this way, starting from 2-hydroxyethyl-substituted cyclopropanol *exo*-**1i** we synthesized (3*E*,8*Z*,11*Z*)-tetradeca-3,8,11-trien-1-yl acetate **19** which is the major component of the sex pheromone of the tomato leafminer *Tuta absoluta*, a very dangerous pest of growing tomatoes [23] (Scheme 3). The oxidative cleavage of *exo*-**1i** with (diacetoxy-λ^3-iodanyl)benzene in methanol gave 85% of ester *E*-**4i**. The hydroxy group in *E*-**4i** was protected by treatment with *tert*-butyl(chloro)dimethylsilane, and the ester group was reduced to aldehyde to obtain enal **15** in 76% yield over two stages. Aldehyde **15** was brought into the Corey–Fuchs reaction with carbon tetrabromide [24], followed by dehydrobromination of intermediate 1,1-dibromoalkene by the action of excess butyllithium. Enyne **16** was thus isolated in 84% yield over two stages. Cross-coupling of **16** with 1-bromopent-2-yne gave 85% of enediyne **17** [25, 26]. The two triple bonds in **17** were reduced with high *Z*-diastereoselectivity with alkoxytitanacyclopropane reagent generated *in situ* from tetraisopropoxytitanium and isopropylmagnesium chloride [27–30]. However, the yield of trienol **18** was fairly low (34%). The acetylation of **18** according to standard procedure gave target acetate **19**.

In summary, stereoselective oxidative cleavage of the cyclopropane ring in substituted bicyclo[*n*.1.0]-alkan-1-ols with (diacetoxy-λ^3-iodanyl)benzene in methanol or acetic acid gives unsaturated carboxylic acids or their methyl esters in 55–85% yield as highly stereochemically pure *E* or *Z* isomers. The synthetic utility of this reaction has been demonstrated by preparation of stereochemically pure components of insect sex pheromones, (*E*)-dodec-9-en-1-yl acetate, (*Z*)-tetradec-11-en-1-yl acetate, and (3*E*,8*Z*,11*Z*)-tetradeca-3,8,11-trien-1-yl acetate.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 500 (compound **17**; 500 and 126 MHz, respectively) and Bruker AC 400 (all other compounds; 400 and 100 MHz, respectively) spectrometers using $CDCl_3$ as solvent. The IR spectra were measured on a Bruker Vertex 70 spectrometer. The elemental analyses were obtained by the semi micro method. Compounds **1** were synthesized from ketones **5** as described in [15]. All solvents were dried and distilled prior to use. (Diacetoxy-λ^3-iodanyl)benzene was prepared from iodobenzene according to [31]. The progress of reactions was monitored by TLC on Sorbfil and Silufol UV-254 plates using petroleum ether–ethyl acetate mixtures at different ratios as eluent. The products were isolated by column chromatography on silica gel (Merck 60, 70–230 mesh) using petroleum ether–ethyl acetate mixtures at different ratios as eluent.

***exo*-6-Ethylbicyclo[3.1.0]hexan-1-ol (*exo*-1a).** Yield 60%. The spectral data were consistent with those reported in [15].

***endo*-6-Ethylbicyclo[3.1.0]hexan-1-ol (*endo*-1a).** Yield 24%. The spectral data were consistent with those reported in [15].

***exo*-7-Propylbicyclo[4.1.0]heptan-1-ol (*exo*-1d).** Yield 63%, colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 0.40 m (1H, cyclopropane), 0.65 d.d.d (1H, cyclopropane, J = 7.8, 6.0, 1.7 Hz), 0.79–0.95 m (1H), 0.90 t (3H, CH_3, J = 7.2 Hz), 0.98–1.12 m (1H), 1.15–1.24 m (2H), 1.31–1.50 m (5H), 1.86 d.d.d (1H, J = 13.1, 9.9, 5.6 Hz), 1.90–2.06 m (3H). ^{13}C NMR spectrum, δ_C, ppm: 14.1 (CH_3), 21.6 (CH_2), 22.0 (CH_2), 23.2 (CH_2), 24.6 (CH_2), 25.0 (CH), 29.1 (CH), 29.8 (CH_2), 32.9 (CH_2), 58.0 (COH). Found, %: C 77.81; H 11.78. $C_{10}H_{18}O$. Calculated, %: C 77.87; H 11.76.

***endo*-7-Propylbicyclo[4.1.0]heptan-1-ol (*endo*-1d).** Yield 20%, colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 0.81–0.96 m (2H), 0.93 t (3H, CH_3, J = 7.2 Hz), 1.11 d.d.d (1H, J = 11.0, 9.0, 2.3 Hz), 1.15–1.55 m (9H), 1.82–2.06 m (3H). ^{13}C NMR spectrum, δ_C, ppm: 14.2 (CH_3), 19.1 (CH_2), 21.6 (CH), 22.2 (CH_2), 22.6 (CH_2), 23.2 (CH_2), 25.8 (CH_2), 28.6 (CH), 29.1 (CH_2), 55.9 (COH). Found, %: C 77.80; H 11.77. $C_{10}H_{18}O$. Calculated, %: C 77.87; H 11.76.

***exo*-8-Propylbicyclo[5.1.0]octan-1-ol (*exo*-1e).** Yield 62%, colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 0.48–0.55 m (1H, cyclopropane), 0.57–0.65 m (1H, cyclopropane), 0.68–0.81 m (1H), 0.91 t (3H, CH_3, J = 6.9 Hz), 1.09–1.35 m (3H), 1.35–1.47 m (4H), 1.51 br.s (1H, OH), 1.59–1.75 m (3H), 1.78–1.88 m (1H), 2.10–2.26 m (2H). ^{13}C NMR spectrum, δ_C, ppm: 14.1 (CH_3), 23.3 (CH_2), 26.3 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 31.4 (2C, CH), 31.9 (CH_2), 32.4 (CH_2), 39.4 (CH_2), 62.9 (COH). Found, %: C 78.46; H 11.99. $C_{11}H_{20}O$. Calculated, %: C 78.51; H 11.98.

***endo*-8-Propylbicyclo[5.1.0]octan-1-ol (*endo*-1e).** Yield 12%, colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 0.75–0.90 m (1H), 0.91 t (3H, CH_3, J = 6.9 Hz), 0.99–1.44 m (9H), 1.58–1.96 m (6H), 1.97–2.07 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 14.2 (CH_3), 23.2 (CH_2), 25.4 (CH_2), 26.0 (CH_2), 26.7 (CH_2), 29.3 (CH), 29.6 (CH_2), 32.2 (CH), 32.6 (CH_2), 32.9 (CH_2), 62.1 (COH). Found, %: C 78.45; H 12.00. $C_{11}H_{20}O$. Calculated, %: C 78.51; H 11.98.

***exo*-8-Hexylbicyclo[5.1.0]octan-1-ol (*exo*-1f).** Yield 68%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3599 (OH, free), 3500 (OH, assoc.). ^{1}H NMR spectrum, δ, ppm: 0.47–0.55 m (1H, cyclopropane), 0.56–0.65 m (1H, cyclopropane), 0.68–0.81 m (1H), 0.88 t (3H, CH_3, J = 7.2 Hz), 1.08–1.50 m (14H), 1.58–1.76 m (3H), 1.76–1.89 m (1H), 2.08–2.28 m (2H). ^{13}C NMR spectrum, δ_C, ppm: 14.3 (CH_3), 22.8 (CH_2), 26.3 (CH_2), 27.7 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 30.3 (CH_2), 31.4 (CH), 31.9 (CH_2), 32.1 (CH_2), 32.4 (CH_2), 35.0 (CH), 39.4 (CH_2), 63.0 (COH). Found, %: C 79.88; H 12.48. $C_{14}H_{26}O$. Calculated, %: C 79.94; H 12.46.

***endo*-8-Hexylbicyclo[5.1.0]octan-1-ol (*endo*-1f).** Yield 15%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3599 (OH, free), 3500 (OH, assoc.). ^{1}H NMR spectrum, δ, ppm: 0.75–0.92 m (1H), 0.88 t (3H, CH_3, J = 6.9 Hz), 0.97–0.48 m (15H), 1.60–1.96 m (6H), 1.97–2.08 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 14.3 (CH_3), 22.8 (CH_2), 24.6 (CH_2), 25.4 (CH_2), 26.0 (CH_2), 29.4 (CH_2, CH), 29.6 (CH_2), 30.1 (CH_2), 32.0 (CH_2), 32.4 (CH), 32.6 (CH_2), 32.9 (CH_2), 62.1 (COH). Found, %: C 79.87; H 12.47. $C_{14}H_{26}O$. Calculated, %: C 79.94; H 12.46.

***exo*-9-Propylbicyclo[6.1.0]nonan-1-ol (*exo*-1g).** Yield 50%, colorless oily liquid. IR spectrum (CCl_4): ν 3593 cm^{-1} (OH, free). ^{1}H NMR spectrum, δ, ppm: 0.13–0.20 m (1H, cyclopropane), 0.34–0.42 m (1H, cyclopropane), 0.72–0.86 m (1H), 0.91 t (3H, CH_3, J = 6.9 Hz), 1.14–1.24 m (1H), 1.24–1.81 m (13H), 1.94–1.99 m (0.5H), 1.99–2.03 m (0.5H), 2.10 d.t (1H, J = 15.1, 3.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.1 (CH_3), 23.3 (CH_2), 25.3 (CH_2), 26.3 (CH_2), 26.6 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH), 30.7 (CH), 34.0 (CH_2), 60.2 (COH). Found, %: C 79.00; H 12.18. $C_{12}H_{22}O$. Calculated, %: C 79.06; H 12.16.

***endo*-9-Propylbicyclo[6.1.0]nonan-1-ol (*endo*-1g).** Yield 18%, colorless oily liquid. IR spectrum (CCl_4): ν 3600 cm^{-1} (OH, free). ^{1}H NMR spectrum, δ, ppm: 0.72–0.98 m (3H), 0.91 t (3H, CH_3, J = 7.4 Hz), 1.12–1.66 m (12H), 1.66–1.81 m (3H), 1.95 d.t (1H, J = 14.8, 3.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.26 (CH_3), 23.05 (CH_2), 23.38 (CH_2), 24.90 (CH_2), 26.22 (CH_2), 26.37 (CH_2), 26.64 (CH_2), 27.62 (CH), 28.05 (CH), 28.12 (CH_2), 28.99 (CH_2), 58.80 (COH). Found, %: C 79.01; H 12.17. $C_{12}H_{22}O$. Calculated, %: C 79.06; H 12.16.

***exo*-7-[2-(Benzyloxy)ethyl]bicyclo[4.1.0]heptan-1-ol (*exo*-1h).** Yield 80%. The spectral data were consistent with those reported in [16].

***exo*-6-(2-Hydroxyethyl)bicyclo[3.1.0]hexan-1-ol (*exo*-1i)** was synthesized as described in [16]. Yield 91%. The spectral data were consistent with those reported in [16].

Trimethylsilyl ethers **2b** and **2c** were synthesized according to the procedure described in [16].

***exo*-6-Butyl-1-(trimethylsiloxy)bicyclo[3.1.0]-hexane (*exo*-2b).** Yield 90%, colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 0.14 s (9H, $SiMe_3$), 0.59–0.67 m (1H, cyclopropane), 0.85–0.94 m (4H, CH_3, cyclopropane), 1.03–1.43 m (6H), 1.44–1.65 m (3H), 1.76–2.00 m (3H). ^{13}C NMR spectrum, δ_C, ppm: 1.2 (3C, CH_3), 14.3 (CH_3), 21.8 (CH_2), 22.8 (CH_2), 24.2 (CH), 27.0 (CH_2), 27.1 (CH_2), 29.4 (CH), 32.1 (CH_2), 34.7 (CH_2), 69.2 (COSi). Found, %: C 68.91; H 11.58. $C_{13}H_{26}OSi$. Calculated, %: C 68.96; H 11.57.

***endo*-6-Butyl-1-(trimethylsiloxy)bicyclo[3.1.0]-hexane (*endo*-2b).** Yield 91%, colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 0.12 s (9H, $SiMe_3$), 0.90 t (3H, CH_3, J = 6.9 Hz), 1.02–1.15 m (1H), 1.16–1.52 m (9H), 1.76–1.91 m (1H), 1.95–2.10 m (3H). ^{13}C NMR spectrum, δ_C, ppm: 1.1 (3C, CH_3), 14.3 (CH_3), 22.9 (CH_2), 23.2 (CH_2), 24.3 (CH_2), 25.1 (CH_2), 28.7 (CH), 29.8 (CH), 32.6 (CH_2), 32.7 (CH_2), 70.0 (COSi). Found, %: C 68.90; H 11.59. $C_{13}H_{26}OSi$. Calculated, %: C 68.96; H 11.57.

***exo*-6-Pentyl-1-(trimethylsiloxy)bicyclo[3.1.0]-hexane (*exo*-2c).** Yield 94%, colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 0.14 s (9H, $SiMe_3$), 0.58–0.68 m (1H, cyclopropane), 0.80–0.94 m (4H, CH_3, cyclopropane), 1.03–1.43 m (8H), 1.44–1.68 m (3H), 1.78–2.00 m (3H). ^{13}C NMR spectrum, δ_C, ppm: 1.3 (3C, CH_3), 14.3 (CH_3), 21.8 (CH_2), 22.9 (CH_2), 24.3 (CH), 27.0 (CH_2), 27.4 (CH_2), 29.4 (CH), 29.5 (CH_2), 32.1 (CH_2), 34.7 (CH_2), 69.2 (COSi). Found, %: C 69.87; H 11.75. $C_{14}H_{28}OSi$. Calculated, %: C 69.93; H 11.74.

***endo*-6-Pentyl-1-(trimethylsiloxy)bicyclo[3.1.0]-hexane (*endo*-2c).** Yield 95%, colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 0.12 s (9H, $SiMe_3$), 0.89 t (3H, CH_3, J = 6.9 Hz), 1.02–1.15 m (1H), 1.16–1.50 m (11H), 1.76–1.93 m (1H), 1.94–2.10 m (3H). ^{13}C NMR spectrum, δ_C, ppm: 1.12 (3C, CH_3), 14.24 (CH_3), 22.82 (CH_2), 23.46 (CH_2), 24.30 (CH_2), 25.08 (CH_2), 28.66 (CH), 29.88 (CH), 30.11 (CH_2), 32.05 (CH_2), 32.57 (CH_2), 69.97 (COSi). Found, %: C 69.88; H 11.76. $C_{14}H_{28}OSi$. Calculated, %: C 69.93; H 11.74.

Unsaturated esters 4 (*general procedure*). (Diacetoxy-λ^3-iodanyl)benzene, 1.77 g (5.5 mmol), was added with stirring to a solution of 5 mmol of bicyclic alcohol **1** in 25–30 mL of anhydrous methanol. The reaction was complete when the mixture became homogeneous (in less than 5 min). The solvent was evaporated under reduced pressure, the residue was dissolved in petroleum ether, and excess $PhI(OAc)_2$ was filtered off. The filtrate was evaporated, and ester **4** was separated from iodobenzene by silica gel column chromatography using first petroleum ether and then petroleum ether–ethyl acetate as eluent.

Methyl (*E*)-oct-5-enoate (*E*-4a). Yield 55%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3027 (=C–H), 1741 (C=O), 969 (*trans*-CH=CH). ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, J = 7.4 Hz), 1.68 quint (2H, C**H**$_2$CH$_2$CO, J = 7.4 Hz), 1.94–2.05 m (4H, C**H**$_2$CH=), 2.30 t (2H, CH_2CO, J = 7.4 Hz), 3.66 s (3H, OCH_3), 5.29–5.39 m and 5.41–5.51 m (1H each, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 14.0 (CH_3), 24.9 (CH_2), 25.7 (CH_2), 32.0 (CH_2), 33.5 (CH_2), 51.6 (OCH_3), 128.0 (CH), 133.3 (CH), 174.4 (C=O). Found, %: C 69.12; H 10.33. $C_9H_{16}O_2$. Calculated, %: C 69.19; H 10.32.

Methyl (*Z*)-oct-5-enoate (*Z*-4a). Yield 60%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3007 (=C–H), 1741 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, J = 7.4 Hz), 1.68 quint (2H, C**H**$_2$CH$_2$CO, J = 7.4 Hz), 1.96–2.11 m (4H, C**H**$_2$CH=), 2.31 t (2H, CH_2CO, J = 7.4 Hz), 3.66 s (3H, OCH_3), 5.24–5.33 m and 5.36–5.46 m (1H each, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 14.4 (CH_3), 20.6 (CH_2), 25.0 (CH_2), 26.5 (CH_2), 33.6 (CH_2), 51.6 (OCH_3), 127.9 (CH), 132.9 (CH), 174.3 (C=O). Found, %: C 69.13; H 10.33. $C_9H_{16}O_2$. Calculated, %: C 69.19; H 10.32.

Methyl (*E*)-undec-7-enoate (*E*-4e). Yield 71%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 1740 (C=O), 969 (*trans*-CH=CH). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, CH_3, J = 7.4 Hz), 1.24–1.41 m (6H, CH_2), 1.56–1.66 m (2H, C**H**$_2$CH$_2$CO), 1.90–2.01 m (4H, C**H**$_2$CH=), 2.30 t (2H, CH_2CO, J = 7.6 Hz), 3.66 s (3H, OCH_3), 5.33–5.40 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 13.8 (CH_3), 22.8 (CH_2), 25.0 (CH_2), 28.7 (CH_2), 29.3 (CH_2), 32.5 (CH_2), 34.2 (CH_2), 34.8 (CH_2), 51.6 (OCH_3), 130.3 (CH), 130.6 (CH), 174.5 (C=O). Found, %: C 72.62; H 11.19. $C_{12}H_{22}O_2$. Calculated, %: C 72.68; H 11.18.

Methyl (*Z*)-undec-7-enoate (*Z*-4e). Yield 78%, colorless oily liquid. IR spectrum (CCl_4): ν 1742 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 7.4 Hz), 1.27–1.43 m (6H, CH_2), 1.62 quint (2H, C**H**$_2$CH$_2$CO, J = 7.5 Hz), 1.94–2.06 m (4H, C**H**$_2$CH=), 2.30 t (2H, CH_2CO, J = 7.5 Hz), 3.66 s (3H, OCH_3), 5.29–5.40 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 14.0 (CH_3), 23.0 (CH_2), 25.0 (CH_2), 27.1 (CH_2), 28.9 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 34.2 (CH_2), 51.6 (OCH_3), 129.8 (CH), 130.1 (CH), 174.4 (C=O). Found, %: C 72.61; H 11.20. $C_{12}H_{22}O_2$. Calculated, %: C 72.68; H 11.18.

Methyl (*E*)-tetradec-7-enoate (*E*-4f). Yield 81%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 1741 (C=O), 966 (*trans*-CH=CH). ^1H NMR spectrum, δ, ppm: 0.87 t (3H, CH_3, J = 7.1 Hz), 1.18–1.41 m (12H, CH_2), 1.62 quint (2H, C**H**$_2$CH$_2$CO, J = 7.4 Hz), 1.90–2.03 m (4H, C**H**$_2$CH=), 2.30 t (2H, CH_2CO, J = 7.4 Hz), 3.66 s (3H, OCH_3), 5.29–5.45 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 14.3 (CH_3), 22.8 (CH_2), 25.0 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 32.5 (CH_2), 32.7 (CH_2), 34.2 (CH_2), 51.6 (OCH_3), 130.1 (CH), 130.8 (CH), 174.5 (CO). Found, %: C 74.88; H 11.76. $C_{15}H_{28}O_2$. Calculated, %: C 74.95; H 11.74.

Methyl (*Z*)-tetradec-7-enoate (*Z*-4f). Yield 74%, colorless oily liquid. IR spectrum (CCl_4): ν 1741 cm^{-1} (C=O). ^1H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 7.0 Hz), 1.19–1.42 m (12H, CH_2), 1.62 quint (2H, C**H**$_2$CH$_2$CO, J = 7.4 Hz), 1.93–2.07 m (4H, C**H**$_2$CH=), 2.30 t (2H, CH_2CO, J = 7.4 Hz), 3.66 s (3H, OCH_3), 5.26–5.42 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 14.3 (CH_3), 22.8 (CH_2), 25.0 (CH_2), 27.1 (CH_2), 27.4 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.5 (CH_2), 29.9 (CH_2), 31.9 (CH_2), 34.2 (CH_2), 51.6 (OCH_3), 129.6 (CH), 130.3 (CH), 174.4 (C=O). Found, %: C 74.89; H 11.75. $C_{15}H_{28}O_2$. Calculated, %: C 74.95; H 11.74.

Methyl (*E*)-9-(benzyloxy)non-6-enoate (*E*-4h). Yield 63%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3031 (C–H_{arom}), 1742 (C=O), 970 (*trans*-CH=CH). ^1H NMR spectrum, δ, ppm: 1.38 q (2H, J = 7.7 Hz), 1.62 q (2H, J = 7.9 Hz), 2.00 m (2H), 2.24–2.36 m (4H), 3.48 t (2H, J = 6.9 Hz), 3.66 s (3H, OCH_3), 4.51 s (2H, PhC**H**$_2$), 5.45 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 24.4 (CH_2), 28.8 (CH_2), 32.2 (CH_2), 33.0 (CH_2), 33.9 (CH_2), 51.4 (CH_2), 70.1 (CH_2), 72.8 (CH_2), 126.7 and 127.5 (CH=CH), 127.6 (CH_{arom}), 128.3 (2C, CH_{arom}), 131.8 (2C, CH_{arom}), 138.5 (C_{arom}), 174.2 (C=O). Found, %: C 73.81; H 8.77. $C_{17}H_{24}O_3$. Calculated, %: C 73.88; H 8.75.

Methyl (*E*)-8-hydroxyoct-5-enoate (*E*-4i). Yield 85%, colorless oily liquid. IR spectrum (film), ν, cm^{-1}: 3452 (OH), 1738 (C=O), 970 (*trans*-CH=CH). ^1H NMR spectrum, δ, ppm: 1.52 br.s (1H, OH), 1.66–1.76 quint (2H, 3-H, J = 7.4 Hz), 2.01–2.14 m (2H, 4-H), 2.22–2.35 m (4H, 2-H, 7-H), 3.63 t (2H, 8-H, J = 6.3 Hz), 3.67 s (3H, OCH_3), 5.36–5.46 m and 5.46–5.57 m (1H each, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 24.7 (C^3), 32.1 (C^4), 33.5 (C^2), 36.1 (C^7), 51.6 (OCH_3), 62.2 (C^8), 127.4 (C^6), 132.8 (C^5), 174.2 (C=O). Found, %: C 62.71; H 9.37. $C_9H_{16}O_3$. Calculated, %: C 62.77; H 9.36.

Unsaturated acids **3** were synthesized by oxidation of trimethylsilyl ethers **2b** and **2c** in acetic acid according to the procedure described in [13].

(*E*)-Dec-5-enoic acid (*E*-3b). Yield 69%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3537 (O–H), 3027 (=C–H), 1711 (C=O), 970 (*trans*-CH=CH). ^1H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 7.0 Hz), 1.20–1.40 m (4H, CH_2), 1.69 quint (2H, C**H**$_2$CH$_2$CO, J = 7.4 Hz), 1.91–2.00 m (2H, C**H**$_2$CH=), 2.03 q (2H, C**H**$_2$CH=, J = 6.9 Hz), 2.34 t (2H, CH_2CO, J = 7.4 Hz), 5.28–5.39 m and 5.39–5.49 m (1H each, CH=CH), 11.00 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 14.1 (CH_3), 22.3 (CH_2), 24.6 (CH_2), 31.8 (CH_2), 31.9 (CH_2), 32.4 (CH_2), 33.4 (CH_2), 128.8 (CH), 132.0 (CH), 180.2 (C=O). Found, %: C 70.48; H 10.67. $C_{10}H_{18}O_2$. Calculated, %: C 70.55; H 10.66.

(*Z*)-Dec-5-enoic acid (*Z*-3b). Yield 70%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3537 (O–H), 3009 (=C–H), 1711 (C=O). ^1H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 7.0 Hz), 1.20–1.40 m (4H, CH_2), 1.69 quint (2H, C**H**$_2$CH$_2$CO, J = 7.4 Hz), 1.96–2.06 m (2H, C**H**$_2$CH=), 2.09 q (2H, C**H**$_2$CH=, J = 6.9 Hz), 2.36 t (2H, CH_2CO, J = 7.4 Hz), 5.26–5.36 m and 5.37–5.47 m (1H each, CH=), 11.00 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 14.1 (CH_3), 22.5 (CH_2), 24.7 (CH_2), 26.5 (CH_2), 27.1 (CH_2), 32.0 (CH_2), 33.5 (CH_2), 128.3 (CH), 131.5 (CH), 180.0 (C=O). Found, %: C 70.47; H 10.68. $C_{10}H_{18}O_2$. Calculated, %: C 70.55; H 10.66.

(*E*)-Undec-5-enoic acid (*E*-3c). Yield 76%. The spectral data were in agreement with those reported in [32, 33].

(*Z*)-Undec-5-enoic acid (*Z*-3c). Yield 70%. The spectral data were in agreement with those reported in [32, 33].

(*E*)-Oct-5-en-1-ol (*E*-6). Yield 96%, colorless oily liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3638 (OH), 3020 (=C–H), 969 (*trans*-CH=CH). ^1H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, J = 7.4 Hz), 1.36 br.s (1H, OH), 1.36–1.47 m (2H, 3-H), 1.52–1.62 m (2H, 2-H), 1.93–2.06 m (4H, C**H**$_2$CH=), 3.64 t (2H, C**H**$_2$OH, J = 6.7 Hz), 5.32–5.51 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 14.1 (CH_3), 25.7 (CH_2), 25.8 (CH_2), 32.4 (2C, CH_2), 63.1 (CH_2OH), 128.9 (CH), 132.6 (CH). Found, %: C 74.87; H 12.60. $C_8H_{16}O$. Calculated, %: C 74.94; H 12.58.

(*Z*)-Oct-5-en-1-ol (*Z*-6). Yield 96%. The spectral data were consistent with those given in [34].

(*E*)-8-Iodooct-3-ene (*E*-7). Triethylamine, 1.0 mL (7.5 mmol), was added to a solution of 0.64 g

(5 mmol) of alcohol *E*-**6** in 10 mL of diethyl ether, the mixture was cooled to 0°C, and 0.46 mL (6 mmol) of methanesulfonyl chloride was added dropwise with stirring. When the reaction was complete, 10 mL of water was added, the mixture was stirred for 30 min, the organic layer was separated, the aqueous layer was extracted with diethyl ether (3×5 mL), and the combined organic extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain 0.95 g (4.6 mmol) of crude methanesulfonate which was dissolved in 10 mL of diethyl ether, the solution was cooled to 0°C, and a solution of magnesium iodide prepared from 0.23 g (9.2 mmol) of magnesium and 2.47 g (9.2 mmol) of methylene iodide in 10 mL of diethyl ether was added with vigorous stirring. The mixture was allowed to warm up to room temperature and stirred until the reaction was complete (~10 min, TLC). The mixture was then treated with slightly acidic water (HCl) on cooling to dissolve magnesium salts, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic extracts were washed with saturated aqueous solutions of $NaHCO_3$ and NaCl and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography. Yield 1.02 g (86%), reddish liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3027 (=C–H), 968 (*trans*-CH=CH). ^1H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, J = 7.4 Hz), 1.40–1.51 m (2H, 3-H), 1.77–1.87 m (2H, 2-H), 1.94–2.06 m (4H, C**H**$_2$CH=), 3.19 t (2H, CH_2I, J = 7.1 Hz), 5.29–5.41 m and 5.42–5.51 m (1H each, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 7.3 (CH_2I), 14.1 (CH_3), 25.7 (CH_2), 30.5 (CH_2), 31.6 (CH_2), 33.1 (CH_2), 128.4 (CH), 132.9 (CH). Found, %: C 40.28; H 6.37. $C_8H_{15}I$. Calculated, %: C 40.35; H 6.35.

(*Z*)-8-Iodooct-3-ene (*Z*-7) was synthesized in a similar way from 0.26 g (2 mmol) of alcohol *Z*-**6**. Yield 0.40 g (85%), reddish liquid. IR spectrum (CCl_4): ν 3007 cm^{-1} (=C–H). ^1H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, J = 7.4 Hz), 1.40–1.51 m (2H, 3-H), 1.78–1.88 m (2H, 2-H), 1.97–2.11 m (4H, C**H**$_2$CH=), 3.19 t (2H, CH_2I, J = 7.1 Hz), 5.25–5.34 m and 5.35–5.44 m (1H each, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 7.2 (CH_2I), 14.5 (CH_3), 20.7 (CH_2), 26.1 (CH_2), 30.7 (CH_2), 33.2 (CH_2), 128.4 (CH), 132.5 (CH). Found, %: C 40.29; H 6.36. $C_8H_{15}I$. Calculated, %: C 40.35; H 6.35.

(*E*)-Dodec-9-en-1-ol (*E*-9). Iodide *E*-**7**, 1.02 g (4.3 mmol), was dissolved in 7 mL of tetrahydrofuran, 0.05 g (0.26 mmol, 6 mol %) of copper(I) iodide was added, the mixture was cooled to –78°C, and 9.5 mL (7.6 mmol) of a 0.8 M solution of 4-(tetrahydro-2*H*-pyran-2-yloxy)butylmagnesium bromide (**8**) in tetrahydrofuran was added dropwise over a period of several minutes. The mixture was stirred for 30 min at –78°C, allowed to slowly warm up to room temperature (over a period of 1 h), stirred for 12 h at room temperature, and refluxed for 4 h. It was then cooled to room temperature and poured into a saturated aqueous solution of ammonium chloride adjusted to weakly alkaline reaction by adding aqueous ammonia. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, the residue was dissolved in 10 mL of methanol, a small amount of pyridinium *p*-toluenesulfonate was added, and the mixture was refluxed for 1 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether–ethyl acetate as eluent. Yield 0.63 g (80%), colorless liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3638 (O–H, free), 3500 (O–H, assoc.), 3022 (=C–H), 968 (*trans*-CH=CH). ^1H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, J = 7.4 Hz), 1.20–1.40 m (11H, CH_2, OH), 1.50–1.61 m (2H, 2-H), 1.91–2.04 m (4H, C**H**$_2$CH=), 3.63 t (2H, C**H**$_2$OH, J = 6.7 Hz), 5.32–5.49 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 14.2 (CH_3), 25.8 (CH_2), 25.9 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 32.7 (CH_2), 32.9 (CH_2), 63.2 (CH_2OH), 129.5 (CH), 132.0 (CH). Found, %: C 78.13; H 13.13. $C_{12}H_{24}O$. Calculated, %: C 78.20; H 13.12.

(*Z*)-Tetradec-11-en-1-ol (*Z*-12) was synthesized in a similar way by coupling of 0.40 g of (*Z*)-8-iodooct-3-ene (*Z*-**7**) with 6-(tetrahydro-2*H*-pyran-2-yloxy)hexylmagnesium bromide (**11**). Yield 0.29 g (80%), colorless liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3638 (O–H, free), 3500 (O–H, assoc.), 3006 (=C–H). ^1H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, J = 7.4 Hz), 1.20–1.40 m (14H, CH_2), 1.51–1.65 m (3H, 2-H, OH), 1.97–2.08 m (4H, C**H**$_2$CH=), 3.64 t (2H, C**H**$_2$OH, J = 6.7 Hz), 5.27–5.43 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 14.6 (CH_3), 20.7 (CH_2), 25.9 (CH_2), 27.2 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.67 (CH_2), 29.71 (CH_2), 29.75 (CH_2), 29.9 (CH_2), 33.0 (CH_2), 63.3 (CH_2OH), 129.5 (CH), 131.7 (CH). Found, %: C 79.11; H 13.31. $C_{14}H_{28}O$. Calculated, %: C 79.18; H 13.29.

(*E*)-Dodec-9-en-1-yl acetate (*E*-10). A solution of 0.63 g (3.4 mmol) of alcohol *E*-**9** in 8 mL of diethyl ether was cooled to 0°C, and 0.70 mL (5.1 mmol) of triethylamine and 0.29 mL (4.1 mmol) of acetyl chloride were added in succession. When the reaction was complete, 8 mL of water was added, the mixture was stirred for 15 min, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×5 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the product was purified by silica gel chromatography in a short column using petroleum ether–ethyl acetate as eluent. Yield 0.75 g (97%). The spectral data of *E*-**10** were consistent with those given in [7, 35].

(*Z*)-Tetradec-11-en-1-yl acetate (*Z*-13) was synthesized in a similar way. Yield 96%. The spectral data of *Z*-**13** were consistent with those given in [35].

Methyl (*E*)-8-[*tert*-butyl(dimethyl)silyloxy]oct-5-enoate (14). Imidazole, 1.04 g (15.3 mmol), was added in one portion with stirring to a solution of 1.76 g (10.2 mmol) of compound *E*-**4i** in 50 mL of freshly distilled dimethylformamide. When the mixture became homogeneous, it was cooled to 0°C, 1.85 g (12.3 mmol) of *tert*-butyl(chloro)dimethylsilane was added with stirring, and the mixture was allowed to warm up to room temperature. When the reaction was complete (TLC), the mixture was cooled to 0°C, and 40 mL of water and a mixture of 25 mL of petroleum ether and 5 mL of diethyl ether were added. The aqueous layer was separated and extracted with a 5:1 mixture of petroleum ether and diethyl ether (4×40 mL). The extracts were combined with the organic phase, washed with brine (2×10 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether–ethyl acetate (40:1 to 30:1) as eluent. Yield 2.78 g (95%), colorless liquid. IR spectrum (film), ν, cm^{-1}: 1742 (C=O), 1472 [$C(CH_3)_3$], 1463 [$C(CH_3)_3$], 1255 (Si–C), 969 (*trans*-CH=CH). ^{1}H NMR spectrum, δ, ppm: 0.04 s (6H, Me_2Si), 0.89 s (9H, *t*-BuSi), 1.69 quint (2H, 3-H, *J* = 7.6 Hz), 1.97–2.09 m (2H, 4-H), 2.15–2.25 m (2H, 7-H), 2.30 t (2H, 2-H, *J* = 7.6 Hz), 3.60 t (2H, 8-H, *J* = 6.9 Hz), 3.66 s (3H, OCH_3), 5.36–5.49 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: –5.1 (2C, Me_2Si), 18.5 (Si**C**Me_3), 24.8 (C^3), 26.1 [3C, C(**C**$H_3)_3$], 32.1 (C^4), 33.5 (C^2), 36.4 (C^7), 51.6 (OCH_3), 63.4 (C^8), 127.9 (C^6), 131.3 (C^5), 174.3 (C=O). Found, %: C 62.83; H 10.56. $C_{15}H_{30}O_3Si$. Calculated, %: C 62.89; H 10.55.

(*E*)-8-[*tert*-Butyl(dimethyl)silyloxy]oct-5-enal (15). A solution of 0.172 g (0.6 mmol) of ester **14** in 4 mL of anhydrous toluene was cooled to –78°C, and 0.68 mL (0.81 mmol) of a 1.2 M solution of hydrido-(diisobutyl)aluminum in anhydrous toluene was added dropwise with stirring in an inert atmosphere. The mixture was stirred for 1.5 h, 4 mL of anhydrous methanol was added, the mixture was allowed to warm up to room temperature, and an aqueous solution of potassium sodium tartrate was added to dissolve the precipitate. The aqueous layer was separated and extracted with diethyl ether (4×5 mL). The extracts were combined with the organic layer, washed with brine (2×5 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using petroleum ether–ethyl acetate (45:1) as eluent. Yield 0.123 g (80%), colorless liquid. IR spectrum (film), ν, cm^{-1}: 2820 [C(O)–H], 2714 [C(O)–H], 1729 (C=O), 1692 (C=C), 1472 [$C(CH_3)_3$], 1463 [$C(CH_3)_3$], 1256 (Si–C), 971 (*trans*-CH=CH). ^{1}H NMR spectrum, δ, ppm: 0.04 s (6H, Me_2Si), 0.88 s [9H, $SiC(CH_3)_3$], 1.69 quint (2H, 3-H, *J* = 7.3 Hz), 1.98–2.10 m (2H, 4-H), 2.15–2.26 m (2H, 7-H), 2.42 t.d (2H, 2-H, *J* = 7.3, 1.6 Hz), 3.60 t (2H, 8-H, *J* = 6.8 Hz), 5.35–5.50 m (2H, CH=CH), 9.76 t (1H, CHO, *J* = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: –5.11 (2C, Me_2Si), 18.5 [Si**C**$(CH_3)_3$], 21.9 (CH_2), 26.1 [3C, $SiC(\mathbf{C}H_3)_3$], 32.1 (CH_2), 36.4 (CH_2), 43.3 (CH_2), 63.3 (CH_2), 128.2 and 131.1 (CH=CH), 202.8 (C=O). Found, %: C 65.50; H 11.01. $C_{14}H_{28}O_2Si$. Calculated, %: C 65.57; H 11.00.

(*E*)-*tert*-Butyl(dimethyl)(non-3-en-8-yn-1-yloxy)-silane (16). A solution of 0.755 g (2.88 mmol) of triphenylphosphine in 3 mL of anhydrous methylene chloride was cooled to 0°C, and 0.480 g (1.44 mmol) of carbon tetrabromide was added in portions with stirring over a period of 15 min. The mixture was stirred for 30 min, and 0.8 mL (5.8 mmol) of triethylamine was added over a period of 15 min to the resulting dark orange solution. After 30 min, the red–violet solution was cooled to –78°C, and a solution of 0.123 g (0.48 mmol) of aldehyde **15** in 4 mL of methylene chloride was added dropwise. The mixture was stirred for 1 h at –78°C and allowed to warm up to 0°C, and 15 mL of petroleum ether was added to precipitate triphenylphosphine oxide. The precipitate was filtered off and thoroughly washed with a 10:1 mixture of petroleum ether and diethyl ether. The filtrate was evaporated to 1/3 of the initial volume under reduced pressure, and the precipitate was filtered off. The procedure was repeated until almost complete

removal of triphenylphosphine oxide. The solvent was removed under reduced pressure, and the residue containing intermediate 1,1-dibromoalkene was dissolved in 4 mL of anhydrous tetrahydrofuran, the solution of was cooled to –78°C, and 3 equiv of butyllithium was added. The mixture was stirred for 1 h, allowed to warm up to 0°C, and treated with 6 mL of water. The aqueous layer was separated and extracted with diethyl ether (3×5 mL). The extracts were combined with the organic phase and dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was purified by column chromatography using petroleum ether as eluent. Yield 0.102 g (84% over 2 stages), colorless liquid. IR spectrum (film), ν, cm^{-1}: 3314 (≡C–H), 2119 (C≡C), 1472 [$C(CH_3)_3$], 1463 [$C(CH_3)_3$], 1258 (Si–C), 970 (*trans*-CH=CH). ^{1}H NMR spectrum, δ, ppm: 0.05 s and 0.07 s (3H each, Me_2Si), 0.89 s [9H, $SiC(CH_3)_3$], 1.58 quint (2H, 6-H, *J* = 7.3 Hz), 1.94 t (1H, 9-H, *J* = 2.6 Hz), 2.06–2.14 m (2H, 5-H), 2.14–2.27 m (4H, 2-H, 7-H), 3.61 t (2H, 1-H, *J* = 6.9 Hz), 5.38–5.52 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: –5.1 and 1.2 (Me_2Si), 17.9 (C^7), 18.5 [Si**C**$(CH_3)_3$], 26.1 [3C, C(**C**$H_3)_3$], 28.3 (C^6), 31.7 (C^5), 36.4 (C^2), 63.4 (C^1), 68.4 (C^9), 84.6 (C^8), 127.8 (C^3), 131.3 (C^4). Found, %: C 71.30; H 11.17. $C_{15}H_{28}OSi$. Calculated, %: C 71.36; H 11.18.

(*E*)-*tert*-Butyl(dimethyl)(tetradec-3-ene-8,11-diyn-1-yloxy)silane (17). Alkyne **16**, 0.271 g (1.08 mmol), and 1-bromopent-2-yne, 0.174 g (1.18 mmol), were added with stirring to a mixture of 0.411 g (2.15 mmol) of anhydrous copper(I) iodide, 0.323 g (2.15 mmol) of anhydrous sodium iodide, and 0.223 g (1.61 mmol) of anhydrous potassium carbonate in 3 mL of anhydrous dimethylformamide. When the reaction was complete (TLC), the mixture was treated with 22 mL of a saturated aqueous solution of ammonium chloride, and the aqueous layer was separated and extracted with diethyl ether (4×10 mL). The extracts were combined with the organic phase, washed with brine (10 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using petroleum ether–ethyl acetate (200:1 to 70:1) as eluent. Yield 0.292 g (85%), colorless liquid. IR spectrum (film), ν, cm^{-1}: 2233 (C≡C), 2214 (C≡C), 1673 (C=C), 1472 [$C(CH_3)_3$], 1463 [$C(CH_3)_3$], 1257 (Si–C), 969 (*trans*-CH=CH). ^{1}H NMR spectrum, δ, ppm: 0.04 s (6H, Me_2Si), 0.88 s [9H, $SiC(CH_3)_3$], 1.11 t (3H, CH_3, *J* = 7.5 Hz), 1.54 quint (2H, 6-H, *J* = 7.3 Hz), 2.03–2.10 m (2H), 2.11–2.26 m (6H), 3.08–3.13 m (2H), 3.59 t (2H, 1-H, *J* = 6.9 Hz), 5.33–5.49 m (2H, CH=CH). ^{13}C NMR spectrum, δ_C, ppm: –5.1 (2C, Me_2Si), 1.2 (CH_2), 9.8 (CH_2), 12.5 (CH_2), 14.0 (CH_3), 18.3 [Si**C**$(CH_3)_3$], 26.1 [3C, SiC(**C**$H_3)_3$], 28.6 (CH_2), 31.9 (CH_2), 36.4 (CH_2), 63.4 (CH_2); 74.0, 74.8, 80.4, 81.9 (C≡C); 127.5 and 131.6 (CH=CH). Found, %: C 75.35; H 10.77. $C_{20}H_{34}OSi$. Calculated, %: C 75.40; H 10.76.

(3*E*,8*Z*,11*Z*)-Tetradeca-3,8,11-trien-1-ol (18). A solution of 0.258 g (0.81 mmol) of enediyne **17** and 1.20 mL (4.06 mmol) of tetraisopropoxytitanium in 18 mL of anhydrous diethyl ether was cooled to –78°C, and a solution of isopropylmagnesium chloride prepared from 1.2 mL (10.5 mmol) of 2-chloropropane and 0.340 g (14.2 mmol) of magnesium in 8 mL of diethyl ether was added over a period of 3 min. The mixture was allowed to warm up to –41°C over a period of 2.5 h, treated with 10% aqueous HCl, and allowed to warm up to room temperature. The aqueous phase was separated and extracted with diethyl ether (3×20 mL). The extracts were combined with the organic phase and washed with brine (15 mL), and the solvent was removed under reduced pressure. The residue containing TBDMS-protected alcohol **18** was dissolved in 3.5 mL of ethanol, 0.020 g of pyridinium *p*-toluenesulfonate was added, the mixture was refluxed for 15 min and cooled to room temperature, and 14 mL of water and 70 mL of petroleum ether were added. The aqueous phase was separated and extracted with diethyl ether (3×10 mL). The extracts were combined with the organic phase, washed with saturated aqueous solutions of sodium hydrogen carbonate (3 mL) and sodium chloride (15 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using petroleum ether–ethyl acetate (50:1 to 3:1) as eluent. Yield 0.058 g (34% over 2 stages), colorless liquid. IR spectrum (film), ν, cm^{-1}: 3339 (O–H), 1656 (C=C), 1650 (C=C), 969 (*trans*-CH=CH). ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, *J* = 7.5 Hz), 1.43 quint (2H, 6-H, *J* = 7.4 Hz), 1.57 br.s (1H, OH), 1.94–2.13 m (6H), 2.27 q (2H, 2-H, *J* = 6.4 Hz), 2.77 t (2H, 10-H, *J* = 5.7 Hz), 3.62 t (2H, 1-H, *J* = 6.4 Hz), 5.23–5.45 m (5H, CH=), 5.48–5.62 m (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 14.4 (CH_3), 20.7 (C^{13}), 25.7 (C^{10}), 26.8 (CH_2), 29.5 (CH_2), 32.3 (CH_2), 36.1 (C^2), 62.2 (C^1); 126.2, 127.4, 128.5, 129.8, 132.0, 134.0 (CH=CH). Found, %: C 80.65; H 11.60. $C_{14}H_{24}O$. Calculated, %: C 80.71; H 11.61.

(3*E*,8*Z*,11*Z*)-Tetradeca-3,8,11-trien-1-yl acetate (19) was synthesized by acylation of alcohol **18** with acetyl chloride in the presence of triethylamine. Yield

94%. The spectral data were consistent with those given in [27].

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