Preparation of Oxocanes by Electrophilic Cyclizations of Unsaturated Alcohols in the Presence of Bis(collidine)halonium(I) Hexafluorophosphates

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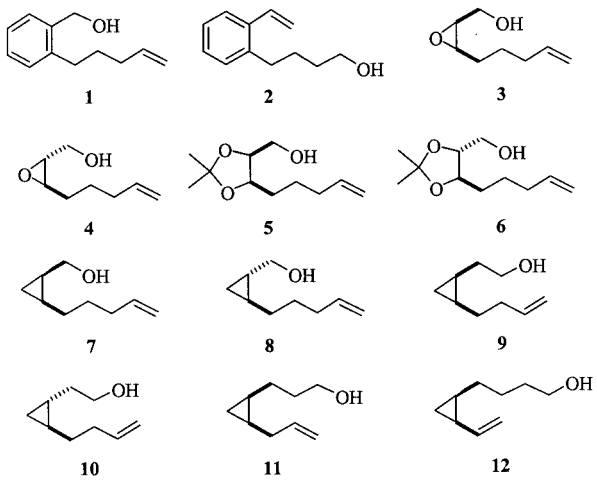
7-Octen-1-ols substituted in the sp^3–sp^3 carbon chain with carbocyclic (phenyl and cyclopropane) and heterocyclic (epoxide and dioxolane) moieties were prepared and their cyclizations in the presence of bis(collidine)iodonium(I) and -bromonium(I) hexafluorophosphates as electrophiles were studied. Oxocanes were obtained in modest to good yields when a rigid cyclic moiety (cyclopropane or phenyl) was present in the chain, while yields of cyclizations were lower if the cyclic component had a certain flexibility (dioxolane). Low yields were obtained with substrates bearing an epoxide substituent, probably because of stability problems due to the presence of collidine. With the vinylcyclopropane alcohol **12** we observed mainly the opening of the cyclopropane ring and the cyclization produced a tetrahydropyran derivative.

Introduction

The formation of oxocanes has been the subject of many studies during the last decade. The simplest method to obtain these compounds consists of the cyclization of linear substrates. The difficulty in this approach arises from the high activation enthalpy associated with the high activation entropy necessary for the formation of medium-sized ring compounds.[1] Many reactions have been examined, with greater or lesser degrees of success. Among the most promising we can cite the rhodium carbenoid cyclization of α-diazocarbonyl compounds[2] (reported yields were in the 40−73% range), the nucleophilic cyclization of iodides,[3] epoxides,[4] and esters[5] (60−87%), the cyclization of hexacarbonyldicobalt complexes[6] (43−84%), the cyclization of allylsilanes with methoxymethyl ethers[7] (53%), the cyclization of allyltin compounds with acetals[8] and of allylboranes with aldehydes[9] (30−35%), the cyclization of olefins with acetals[10] or thioacetals[11] induced by titanium salts or other Lewis acids (50−70%), radical cyclization with terminal double bonds[12] (40−50%), the reaction of alcohols with thioacetals[13] (55%), the palladium-induced cyclization of allyl carbonates[14] (74%), and the metathesis of dienes in the presence of ruthenium[15] and molybdenum[16] complexes (26−95%). We recently reported an efficient method for the preparation of oxepanes by electrophilic cyclization of 6-hepten-1-ols[17] in the presence of bis(collidine)iodonium(I) hexafluorophosphate as electrophile. Subsequently, we reported the preparation of medium-sized lactones with this reagent. However, the introduction of conformational constraint in the chain to be cyclized, which decreases the activation entropy of the reaction, is necessary to obtain satisfactory yields. We now wish to report our results concerning the formation of oxocanes by such an approach.

Results

We decided to study the influence of the introduction of a rigid (phenyl, epoxide, or cyclopropane) or a conforma-



Scheme 1

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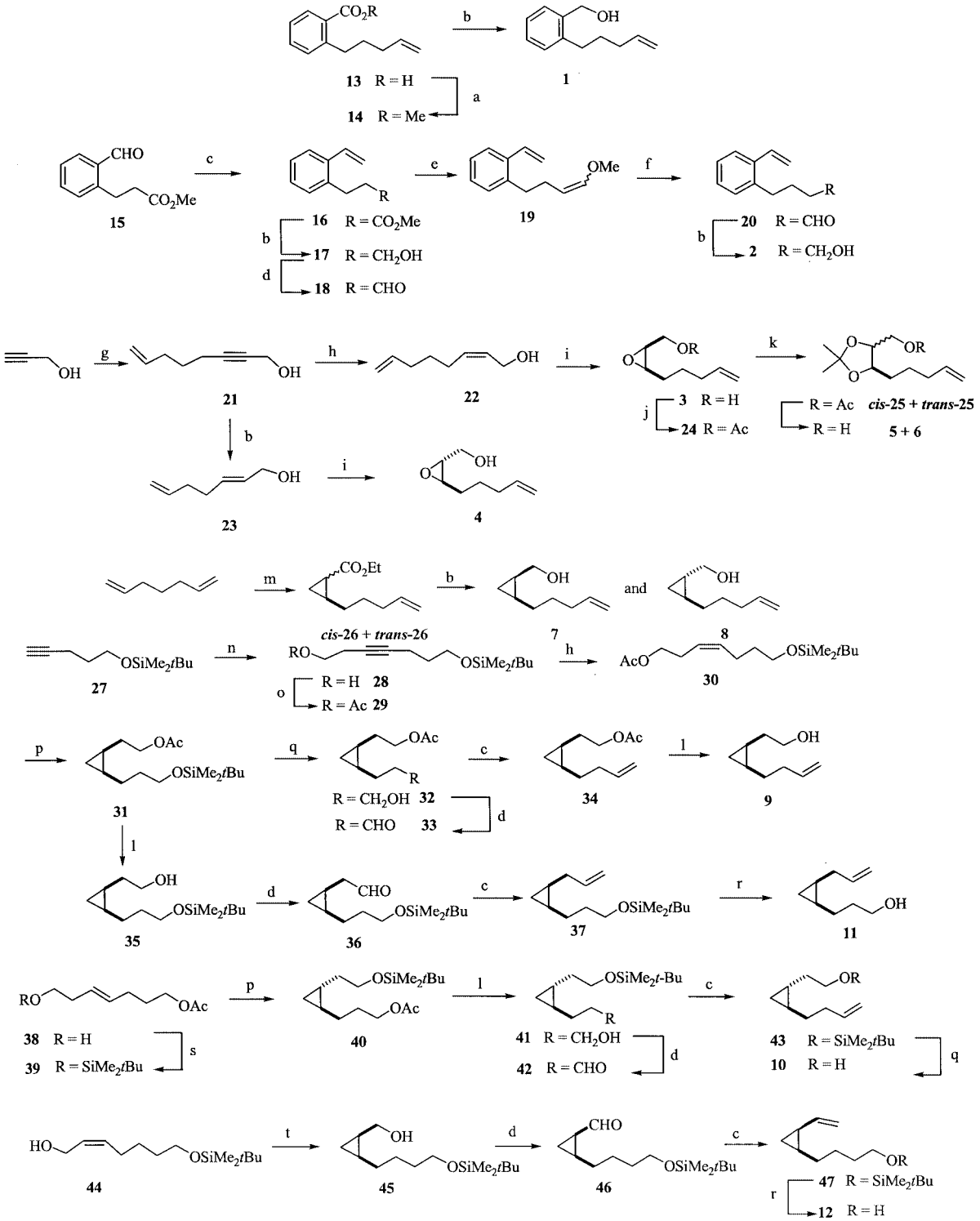


Scheme 2. a: MeOH/H^+ (75%); b: $LiAlH_4$, THF (**1**: 93%; **17**: 80%; **2**: 98%; **23**: 80%; **7**: 96%; **8**: 83%); c: $[Ph_3P^+CH_3]Br^-$, *n*BuLi, THF (**16**: 40%; **34**: 53%: **37**: 93%; **43**: 81%; **47**: 87%); d: $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2 (**18**: 90%; **33**: 70%; **36**: 83%; **42**: 73%; **46**: 87%); e: $[Ph_3P^+CH_2OMe]Cl^-$, *n*BuLi, THF (46%); f: $HClO_4$, THF (80%). g: 1-bromo-4-pentene, NH_3, $LiNH_2$ (97%); h: H_2 (1 atm), Lindlar catalyst (**22** in acetone: 90%; **30** in hexane: 95%); i: $VO(acac)_2$, *t*BuOOH, benzene (**3**: 72%; **4**: 75%); j: vinyl acetate, *t*BuOMe, PS lipase (95%); k: $BF_3{\cdot}Et_2O$, acetone (95%); l: K_2CO_3, MeOH (**5**, **6**: 95%; **9**: 70%; **35**: 95%; **41**: 99%); m: N_2CHCO_2Et, $Rh_2(OAc)_4$, benzene (60%); n: ethylene oxide, *n*BuLi, THF (82%); o: Ac_2O, DMAP, THF (77%); p: Et_2Zn, CH_2ICl, $(CH_2Cl)_2$ (**31**: 90%; **40**: 93%); q. $nBu_4N^+F^-$, THF (**32**: 100%; **10**: 82%); r: MeOH, cat. $ClSiMe_3$ (**11**: 86%; **12**: 93%); s: imidazole, THF, $ClSiMe_2tBu$ (94%); t: Et_2Zn, CH_2I_2, toluene, −40 °C (92%)

tionally more flexible (dioxolane) cyclic system into the carbon chains of 7-octenol-1-ols. The structures of the examined alcohols **1**−**12** are reported in Scheme 1. In all cases the carbon−carbon double bond was introduced in a terminal position to avoid the competitive formation of nine-membered cyclic ethers by *endo*-mode cyclizations.[18,19]

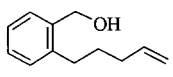
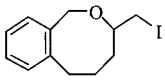
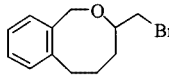
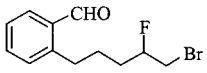
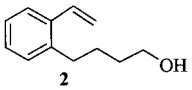
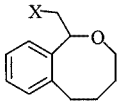
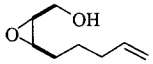
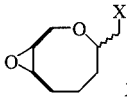
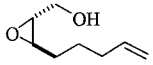
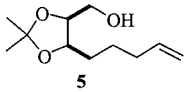
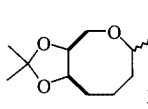
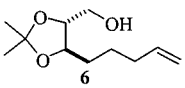
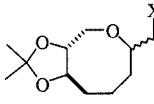
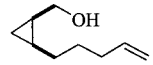
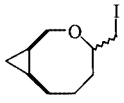
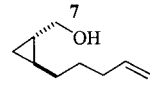
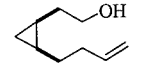
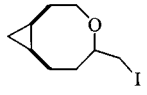
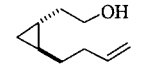
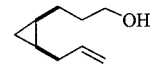
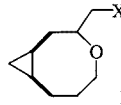
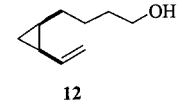
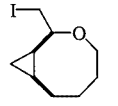
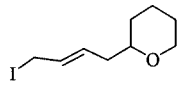
Preparation of Alcohols 1−12

The benzyl alcohol **1** was obtained in two steps from the benzoic acid **13**[19] by esterification (cat. $SOCl_2$ in MeOH) followed by lithium aluminum hydride reduction of the ester **14**. (Scheme 2). The styryl alcohol **2** was prepared in four steps, starting from the ester **15**.[20] Methylenation of the aldehyde function, followed by reduction of the ester function, gave the alcohol **17**, which was oxidized to the aldehyde **18**. This was homologated to the aldehyde **20** in two steps, and reduction of the aldehyde function furnished the desired alcohol **2** (Scheme 2). The *cis*-epoxide **3** was easily obtained in three steps from butynol. Coupling with 1-bromo-3-butene gave the required enyne **21**,[21] which was selectively reduced with hydrogen in the presence of Lindlar catalyst to give the dienol **22**. The double bond β to the alcohol function was then selectively oxidized in the presence of vanadyl acetylacetonate and *tert*-butyl hydroperoxide[22] to afford the *cis*-epoxide **3**. Lithium aluminum hydride reduction of the enyne **21** gave the (2*E*)-dienol **23**, which was transformed into the *trans*-epoxide **4** as reported for the preparation of compound **3** (Scheme 2). The acetate **24** was easily obtained by acetylation of alcohol **3** in the presence of *Pseudomonas cepacia* lipase (LP) in the presence of vinyl acetate (95%). The same acetate **24** was obtained in poorer yields (20%) by treatment of alcohol **3** with acetic anhydride and pyridine. In the presence of boron trifluoride−diethyl ether in acetone, this acetate was transformed into a *cis*/*trans* mixture (1:2) of dioxolanes **25**. After cleavage of the acetate function, the mixture of alcohols **5**/**6** was separated by flash chromatography. A *cis*/*trans* mixture of unsaturated esters **26** (40:60) was obtained by treatment of 1,6-heptadiene with ethyl diazoacetate.[23] After separation, the two esters were reduced with lithium aluminum hydride to give the alcohols *cis*-**7** and *trans*-**8**. Protection of 5-hexyn-1-ol as the *tert*-butyldimethylsilyl ether **27**, followed by treatment of the corresponding lithium acetylide with ethylene oxide, afforded the alcohol **28**, which was acetylated to give the compound **29**; *cis* hydrogenation of the carbon−carbon triple bond (Lindlar catalyst) provided compound **30**, which was treated with chloroiodomethane in the presence of diethylzinc to give the cyclopropane derivative **31** (Scheme 2). Selective cleavage of the silyl ether afforded the alcohol **32**, which was oxidized under Swern conditions to give the aldehyde **33**. Methylenation by a Wittig reaction at the aldehyde function, followed by cleavage of the acetate, gave the desired unsaturated alcohol **9**. Selective cleavage of the acetate function of the compound **31**, followed by the same reaction sequence as used for the preparation of the alcohol **9**, afforded the alcohol **11**. The *trans* diastereomer **10** was obtained from the bifunctional compound **38**[24] by treatment with chloroiodomethane in the presence of diethylzinc, followed by the sequence of reactions used for the preparation of the alcohol **9** (Scheme 2). The (2*Z*)-allylic alcohol **44**[25] was transformed into the cyclopropyl alcohol **45** in high yield. After oxidation of the alcohol function, Wittig reaction, and cleavage of the silyl ether, the resulting alcohol **12** was obtained in a satisfactory overall yield. All compounds **1**−**47** were fully characterized by analysis of their NMR and IR spectra.

Preparation of Oxocanes

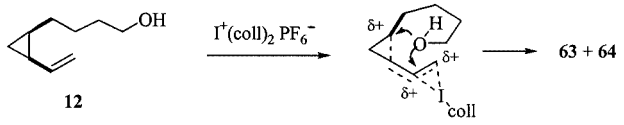
We then studied the haloetherification of alcohols **1**−**12** with bis(collidine)iodonium(I) and -bromonium(I) hexafluorophosphates[26] as electrophiles. The cyclizations were carried out in dichloromethane at room temperature. After completion of the reaction, the products were isolated by flash chromatography on silica gel and characterized by their NMR and IR spectra. Our results are reported in Table 1. Alcohol **1** reacted with bis(collidine)iodonium(I) hexafluorophosphate to produce the oxocane **48** in almost quantitative yield. (Table 1, Entry a). Use of the bromo reagent under the same reaction conditions gave the oxocane **49** in moderate yield (45%) in a mixture with the aldehyde **50** (10%) (Entry b). This aldehyde was formed by oxidation of the benzyl alcohol, followed by attack of the PF_6^- anion on the intermediate bromonium species. The oxidative nature of bis(collidine)bromonium(I) hexafluorophosphate had been reported previously.[27] With the styryl alcohols **2** (Entries c, d) the cyclizations appeared less efficient, although the iodooxocane **51** was obtained in a satisfactory yield. With the epoxides **3** and **4** (Entries e−g) the cyclizations were much less favorable. No product was isolated from the *trans* diastereomer **4**, while the oxocanes **53** and **54** were obtained only in low yields from the *cis* diastereomer **3**. These poor yields seem to be due to the low stability of the epoxides in the presence of collidine. No stability problems were observed with dioxolanes **5** and **6**. Surprisingly, both *cis* and *trans* diastereomers gave comparable results with the iodo reagent (Entries h and j), while with the bromo reagent only the *cis* diastereomer gave a satisfactory result (Entry j). Unlike the dioxolanes **5** and **6**, the *trans*-cyclopropyl alcohols **8** and **10** (Entries m and o) did not produce the desired oxocanes. As expected, oxocanes were obtained with satisfactory yields when starting from the *cis* compounds **7**, **9**, and **11** (Entries l, n, p, q). However, an exception was noted in the case of the alcohol **12** (Entry r), in which we observed mainly the ring-opening of the cyclopropane ring and the tetrahydropyran derivative **64** as the major product. Its formation can be explained by delocalization of the positive charge over carbon atoms 5, 7, and 8 of the intermediate iodonium species (Scheme 3). No oxocane was detected in the reaction mixture when the alcohol **12** was treated with the bromo reagent. Comparison of Entries a and c or l and n−p shows that the shorter the chain bearing the alcohol function, the higher is the yield in oxocane. When the cyclic system is conformationally rigid, the two chains to be cyclized must have a *cis* stereochemistry; however, if the cycle allows a certain mobility it makes no difference whether the two chains have *cis* or *trans* stereochemistry. In general, a 50:50 mixture of diastereomers was obtained during these cyclizations. This absence of diastereoselectivity is due to the long distance between the carbon−carbon double bond and the cycle. However, in two cases (Entries n and r), only one diastereomer was

Table 1. Haloetherification of alcohols **1**−**12**

Entry	Substrate	$X^+(coll)_2PF_6^-$	Product(s) (yield, %)
a	 **1**	X = I	 **48** (95)
b	**1**	X = Br	 **49** (45) +  **50** (10)
c	 **2**	X = I	 X = I **51** (65)
d		X = Br	X = Br **52** (32)
e	 **3**	X = I	 X = I **53** (25)[a]
f		X = Br	X = Br **54** (23)[a]
g	 **4**	X = I and Br	degradation
h	 **5**	X = I	 X = I **55** (43)[a]
i		X = Br	X = Br **56** (45)[a]
j	 **6**	X = I	 X = I **57** (41)[a]
k		X = Br	X = Br **58** (11)[a]
l	 **7**	X = I	 **59** (80)[a]
m	 **8**	X = I	N. R.
n	 **9**	X = I	 **60** (53)[b]
o	 **10**	X = I	N. R.
p	 **11**	X = I	 X = I **61** (63)[a]
q		X = Br	X = Br **62** (37)[a]
r	 **12**	X = I	 **63** (11)[b] +  **64** (55)

[a] 50:50 mixture of diastereomers. [b] Only one diastereomer was isolated.

isolated. While this result for the alcohol **12** is probably due to the presence of the cyclopropane ring α to the carbon−carbon double bond, the result obtained with alcohol **8** is much more surprising, and we do not for the moment have any explanation for it.



12

Scheme 3

In conclusion, we show in this publication that formation of oxocanes in satisfactory yields by electrophilic cyclization of unsaturated alcohols is possible if a cyclic substituent is introduced into the carbon−carbon chain of the alcohol to be cyclized. The results obtained with dioxolanes also show access to functionalized oxocanes. Applications of these results to the preparation of natural products is to be examined.

Experimental Section

General Remarks: All NMR spectra were measured in $CDCl_3$, and chemical shifts are expressed in ppm in relation to internal $CHCl_3$. All solvents were purified by known standard procedures; in particular, dichloromethane was distilled from CaH_2.

[2-(Pent-4-enyl)phenyl]methanol (1): This alcohol was obtained in two steps from 2-(pent-4-enyl)benzoic acid (**13**).[19] Thionyl chloride (1.0 mL) was added dropwise at 0 °C to 2-(pent-4-enyl)benzoic acid (2.500 g, 0.0131 mol) in solution in methanol (50 mL). After 12 h at room temp., the solvent was removed under vacuum. The residue was purified by chromatography on silica gel (diethyl ether/pentane, 30:70) to give 2.000 g (75%) of methyl 2-(pent-4-enyl)benzoate (**14**). ^{1}H NMR (250 MHz): δ = 7.90 (dd, J = 11 and 1 Hz, 11 H), 7.40 (m, 1 H), 7.22 (m, 2 H), 5.85 (m, 1 H), 5.00 (m, 2 H), 3.90 (s, 3 H), 2.96 (dd, J = 10 and 0.5 Hz), 2.15 (m, 2 H), 1.73 (m, 2 H) ppm. A solution of ester **14** (2.000 g, 9.8 mmol) in diethyl ether (5 mL) was added under argon at 0 °C and over 30 min to a suspension of lithium aluminum hydride (0.266 g, 7 mmol) in diethyl ether (50 mL). The mixture was stirred at reflux for 3 h. After conventional workup, the residue was purified by liquid chromatography on silica gel (diethyl ether/pentane, 50:50) to give 1.600 g (93%) of [2-(pent-4-enyl)phenyl]methanol (**1**). ^{1}H NMR (250 MHz): δ = 7.42−7.18 (m, 4 H), 5.89 (m, 1 H), 5.05 (m, 2 H), 4.73 (br. s, 2 H), 2.71 (dd, J = 10 and 0.5 Hz, 2 H), 2.15 (m, 2 H), 1.73 (m, 2 H) ppm. $C_{12}H_{16}O$ (176.3): calcd. C 81.77, H 9.15; found C 81.82, H 9.17.

Methyl 3-(2-Vinylphenyl)propanoate (16): *n*BuLi (1.6 M solution in hexane, 87.50 mL) was added at −20 °C under argon to a suspension of methyltriphenylphosphonium bromide (50.300 g, 0.14 mol) in THF (150 mL). After the mixture had been kept at this temperature for 30 min, methyl 3-(2-formylphenyl)propanoate[20] (**15**, 21.100 g, 0.11 mol) was added over 15 min. The mixture was allowed to warm to room temp., and after one night the solvents were removed. The residue was purified by chromatography on silica gel

(diethyl ether/pentane, 30:70) to give unsaturated ester **16** (8.400 g, 40%). ^{1}H NMR (250 MHz): δ = 7.50 (m, 1 H), 7.30−7.25 (m, 3 H), 7.00 (dd, *J* = 10.6, 15.9 Hz, 1 H), 5.65 (d, *J* = 10.0 Hz, 1 H), 5.30 (d, *J* = 10.0 Hz, 1 H), 3.67 (s, 3 H), 3.02 (t, *J* = 8 Hz, 2 H), 2.55 (m, 2 H) ppm.

3-(2-Vinylphenyl)propan-1-ol (17): This alcohol was prepared by treatment of the ester **16** with lithium aluminum hydride in THF by the procedure described for the preparation of the alcohol **1** (97%). ^{1}H NMR (250 MHz): δ = 7.52 (m, 1 H), 7.40−7.10 (m, 3 H), 7.02 (dd, *J* = 16 and 10 Hz, 1 H), 5.68 (dd, *J* = 0.5 and 16 Hz, 1 H), 5.32 (dd, *J* = 7 and 10 Hz, 1 H), 3.15 (t, *J* = 9 Hz, 2 H), 2.80 (m, 2 H), 1.88 (m, 3 H) ppm. ^{13}C NMR: δ = 139.1, 136.3, 134.4, 129.4, 127.6, 126.2, 125.6, 115.3, 61.9, 33.6, 29.3 ppm.

3-(2-Vinylphenyl)propionaldehyde (18): 3-(2-Vinylphenyl)propan-1-ol (**17**, 4.900 g, 0.03 mol) was added at −78 °C to a solution of oxalyl chloride (3.50 mL) in dichloromethane (20 mL). After the mixture had been kept at this temperature for 15 min, triethylamine (25.30 mL) was added. After the mixture had then been allowed to warm to room temp., water (30 mL) was added and the aqueous phase was extracted with diethyl ether (3 × 30 mL). The organic phase was dried ($MgSO_4$) and concentrated under vacuum to give the aldehyde **18** (4.750 g, 99%). The aldehyde was used without purification for the next step. ^{1}H NMR (250 MHz): δ = 9.80 (s, 1 H), 7.50 (m, 1 H), 7.30 (m, 3 H), 6.95 (dd, *J* = 17 and 10 Hz, 1 H), 5.65 (d, *J* = 17 Hz, 1 H), 5.30 (d, *J* = 10 Hz, 1 H), 3.00 (t, *J* = 7 Hz, 2 H), 2.70 (t, *J* = 7 Hz, 2 H) ppm. ^{13}C NMR: δ = 201.2, 137.4, 136.3, 133.9, 129.1, 127.8, 126.6, 125.9, 116.0, 44.5, 25.3 ppm.

1-[(3*Z*)- and (3*E*)-4-Methoxybut-3-enyl]-2-vinylbenzene (19): *tert*-Butyllithium (1.7 M solution in pentane (44 mL, 0.0747 mol) was added under argon at −78 °C to a suspension of (methoxymethyl)-triphenylphosphonium chloride (25.600 g, 0.0747 mol) in THF (175 mL). After 30 min, the aldehyde **18** (4.750 g, 0.0297 mol) was added. After the mixture had warmed to room temp., the solvents were removed under vacuum, and the residue was purified by chromatography on silica gel (pentane/diethyl ether, 92:8) to give an (*E*)/(*Z*) mixture (50:50) of the enol ethers **19** (2.500 g, 46%). ^{1}H NMR (250 MHz): δ = 7.55−6.92 (m, 5 H), 6.35 [d, *J* = 16 Hz, 1 H (first isomer)], 6.30 [d, *J* = 21 Hz, 1 H (second isomer)], 5.65 (d, *J* = 18 Hz, 1 H), 5.30 (d, *J* = 16 Hz, 1 H), 4.80 (m, 1 H), 3.50 [s, 3 H (first isomer)], 3.48 [s, 3 H (second isomer)], 2.95−2.60 (m, 4 H), 2.30−2.10 (m, 4 H) ppm.

4-(2-Vinylphenyl)butyraldehyde (20): Perchloric acid (70%, 20 mL) was added at 0 °C to a THF solution (40 mL) of enol ether **19** (2.300 g, 12.2 mmol). After the mixture had been kept at room temp. for 1 h, a 10% aqueous solution of sodium bicarbonate was added slowly until pH = 7 was reached. The aqueous phase was extracted with dichloromethane (3 × 50 mL), and the organic phase was dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by chromatography on silica gel (diethyl ether/pentane, 20:80) to give the aldehyde **20** (1.700 g, 80%). ^{1}H NMR (250 MHz): δ = 9.75 (br. s, 1 H), 7.52 (dd, *J* = 5 and 7 Hz, 1 H), 7.10 (m, 3 H), 7.04 (dd, *J* = 14 and 10 Hz, 1 H), 5.70 (dd, *J* = 20 and 0.5 Hz, 1 H), 5.35 (dd, *J* = 14 and 0.5 Hz, 1 H), 2.75 (t, *J* = 10 Hz, 2 H), 2.50 (t, *J* = 10 Hz, 2 H), 2.00 (m, 2 H) ppm. ^{13}C NMR: δ = 202.0, 138.5, 136.3, 134.2, 129.4, 128.4, 127.7, 125.7, 115.5, 43.0, 32.2, 23.1 ppm.

4-(2-Vinylphenyl)butan-1-ol (2): This alcohol was prepared by reduction of aldehyde **20** with lithium aluminum hydride in THF by the procedure described for the preparation of the alcohol **1** (98%). ^{1}H NMR (250 MHz): δ = 7.50 (m, 1 H), 7.10 (m, 3 H), 7.00 (dd, *J* = 16 and 10 Hz, 1 H), 5.65 (dd, *J* = 16 and 0.5 Hz, 1 H), 5.30 (dd, *J* = 10 and 0.5 Hz, 1 H), 3.65 (m, 2 H), 2.70 (m, 2 H), 1.51 (m, 5 H) ppm. ^{13}C NMR: δ = 139.5, 136.2, 134.4, 129.3, 128.2, 126.0, 125.5, 115.1, 62.3, 32.8, 32.3, 27.0 ppm. $C_{12}H_{16}O$ (176.3): calcd. C 81.77, H 9.15; found C 81.88, H 9.25.

(2*Z*)-Octa-2,7-dien-1-ol (22): Coupling[21] of propargylic alcohol with 1-bromo-4-pentene in ammonia at −40 °C gave oct-7-en-2-yn-1-ol (**21**, 97%). Subsequent reduction with hydrogen (1 atm) in the presence of Lindlar catalyst in acetone gave the alcohol **22**[28] (90%).

(2*E*)-Octa-2,7-dien-1-ol (23): Lithium aluminum hydride reduction of the acetylenic alcohol **21** in THF gave the alcohol **23**[28] (80%).

(2*S,3*S**)-2,3-Epoxy-7-octen-1-ol (3):** Vanadyl acetylacetonate (0.013 g, 0.05 mmol) and *tert*-butyl hydroperoxide (0.320 g, 3.6 mmol) were added to a benzene solution (5 mL) of (2*Z*)-octa-2,7-dien-1-ol (**22**, 0.300 g, 2.4 mmol). After the mixture had been kept at room temp. for 6 h, the solvent was removed and the crude mixture was purified by chromatography on silica gel (diethyl ether/pentane, 50:50) to give (2*S**,3*S**)-epoxy-7-octen-1-ol (**3**) (0.243 g, 72%). The compound has been described previously.[21]

(2*S,3*R**)-2,3-Epoxy-7-octen-1-ol (4):** This compound[29] was prepared from (2*E*)-octa-2,7-dien-1-ol (**23**) by the procedure described for the preparation of compound **3** (75%).

[(2*S,3*S**)-3-(Pent-4-enyl)-2-oxiranyl]methyl Acetate (24):** Vinyl acetate (9 mL) and *Pseudomonas cepacia* lipase (0.350 g) were added to a solution of epoxide **3** (4.600 g, 0.0324 mol) in *tert*-butyl methyl ether (10 mL). After one night at room temp., the suspension was filtered and the filtrate was concentrated under vacuum. The acetate **24**[29] (5.700 g, 96%) was pure enough to be used without purification.

***cis*- and *trans*-[2,2-Dimethyl-5-(pent-4-enyl)-1,3-dioxolan-4-yl]methyl Acetates (*cis*- and *trans*-25):** Boron trifluoride−diethyl ether (0.2 mL) was added at 0 °C to [3-(pent-4-enyl)oxiranyl]methyl acetate (**24**, 2.380 g, 0.0129 mol) in acetone (40 mL). After the mixture had been kept at room temp. for 20 h, the solvent was removed under vacuum. The crude mixture (2.810 g, 90%) was used without purification for the next step. Its NMR spectra show the presence of two diastereomers. (2*S**,3*S**) diastereomer (60%): ^{1}H NMR (250 MHz): δ = 5.91−5.72 (m, 1 H), 5.08−4.95 (m, 2 H), 4.30 (dd, *J* = 2.6, 12.9 Hz, 1 H), 4.05 (dd, *J* = 6 and 8 Hz, 1 H), 3.80 (m, 2 H), 2.10 (s, 3 H), 1.70−1.20 (m and 2 s, 12 H) ppm. (2*S**,3*R**) diastereomer (40%): ^{1}H NMR (250 MHz): δ = 5.91−5.72 (m, 1 H), 5.08−4.95 (m, 2 H), 4.15 (q, *J* = 5.1 Hz, 1 H), 3.95 (m, 1 H), 3.80 (m, 2 H), 2.10 (s, 3 H), 1.70−1.00 (m and 2 s, 12 H) ppm.

[2,2-Dimethyl-(5-pent-4-enyl)-1,3-dioxolan-4-yl]methanols (5 and 6): K_2CO_3 (0.50 g) was added to the mixture of acetates **25** (2.500 g, 0.0103 mol) in methanol (50 mL) and the suspension was stirred for 1 h at room temp. After filtration, the filtrate was concentrated under vacuum and the residue was purified by chromatography (diethyl ether/pentane, 50:50). Elution gave 1.240 g (54%) of the (2*S**,3*S**) isomer and 0.820 g (36%) of the (2*S**,3*R**) isomer. (2*S**,3*S**) diastereomer **5**: ^{1}H NMR (250 MHz): δ = 5.91−5.72 (m, 1 H), 5.08−4.95 (m, 2 H), 4.07−3.93 (m, 2 H), 3.81−3.70 (m, 1 H), 3.57−3.43 (m, 1 H), 2.21−2.02 (m, 3 H), 1.78−1.22 (m and 2 s, 10 H) ppm. ^{13}C NMR: δ = 138.4, 114.7, 109.3, 79.1, 72.1, 66.1, 33.5, 33.0, 26.6, 25.3, 24.7 ppm. (2*S**,3*R**) diastereomer **6**: ^{1}H NMR (250 MHz): δ = 5.91−5.72 (m, 1 H), 5.08−4.95 (m, 2 H),

4.07−3.93 (m, 2 H), 3.80−3.69 (m, 1 H), 3.62−3.52 (m, 1 H), 2.21−2.02 (m, 3 H), 1.78−1.22 (m and 2s, 10 H) ppm.

Ethyl 2-(Pent-4-enyl)cyclopropane-1-carboxylate (26): This compound was prepared as already reported.[23] The *cis*/*trans* mixture of esters was separated by chromatography on silica gel (diethyl ether/pentane, 2:98) (60%). *trans* isomer: ^{1}H NMR (250 MHz): δ = 5.82 (m, 1 H), 4.95 (m, 2 H), 4.12 (q, *J* = 7 Hz, 2 H), 2.00 (m, 2 H), 1.50−0.98 (m, 10 H), 0.60 (m, 1 H) ppm. ^{13}C NMR: δ = 174.2, 138.3, 114.4, 60.0, 33.1, 32.2, 28.1, 22.4, 20.0, 15.2, 14.1 ppm. IR (film): $\tilde{\nu}_{max}$ = 3078, 2926, 1727, 1641, 1446, 1403, 1381, 1176, 910 cm^{-1}. *cis* isomer: ^{1}H NMR (250 MHz): δ = 5.80 (m, 1 H), 5.05 (m, 2 H), 4.15 (q, *J* = 7 Hz, 2 H), 2.06 (m, 2 H), 1.75−1.10 (m, 9 H), 1.10−0.80 (m, 2 H) ppm. ^{13}C NMR: δ = 172.8, 138.6, 114.2, 60.0, 33.3, 28.8, 26.3, 21.5, 18.0, 14.2, 13.1 ppm. IR (film): $\tilde{\nu}_{max}$ = 3078, 2980, 2928, 1726, 1641, 1447, 1409, 1176, 911 cm^{-1}.

[*cis*-2-(Pent-4-enyl)cyclopropyl]methanol (7): This alcohol was prepared by $LiAlH_4$ reduction of the *cis* ester **26** in THF by the procedure described for the preparation of alcohol **1** (96%). ^{1}H NMR (250 MHz): δ = 5.82 (m, 1 H), 5.00 (m, 2 H), 3.60 (m, 3 H), 2.10 (m, 2 H), 1.65−0.65 (m, 7 H), 0.00 (q, *J* = 5 Hz, 1 H) ppm. ^{13}C NMR: δ = 138.7, 114.2, 62.8, 33.4, 29.5, 27.8, 17.8, 15.8, 9.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3341, 3065, 2926, 1640, 1457, 1032, 909 cm^{-1}. $C_9H_{16}O$ (140.2): calcd. C 77.09, H 11.50; found C 77.35, H 11.66.

[*trans*-2-(Pent-4-enyl)cyclopropyl]methanol (8): This alcohol was prepared by the procedure used for the preparation of alcohol **7** (83%). ^{1}H NMR (250 MHz): δ = 5.80 (m, 1 H), 5.00 (m, 2 H), 3.42 (dd, *J* = 2 and 7 Hz, 2 H), 2.05 (m, 2 H), 1.60−0.50 (m, 7 H), 0.45−0.25 (m, 2 H) ppm. ^{13}C NMR 138.8, 114.2, 66.9, 33.4, 32.9, 28.7, 21.0, 16.8, 9.8 ppm. IR (film): $\tilde{\nu}_{max}$ = 3339, 3065, 2925, 1641, 1441, 1032, 909 cm^{-1}. $C_9H_{16}O$ (140.2): calcd. C 77.09, H 11.50; found C 77.71, H 11.81.

7-[(*tert*-Butyldimethylsilyl)oxy]hept-3-yn-1-ol (28): *n*BuLi (1.0 M solution in hexane, 26.30 mL, 0.042 mol) was added under argon at −78 °C to a THF solution (200 mL) of 5-[(*tert*-butyldimethylsilyl)-oxy]pent-1-yne (**27**,[30] 6.400 g, 0.0323 mol). After the mixture had been kept at −78 °C for 1.5 h, ethylene oxide (16.20 mL, 0.0323 mol) and boron trifluoride−diethyl ether (5 mL, 0.0452 mol) were added. After 3 h at −78 °C, the solution was allowed to warm to room temp. and aqueous ammonium chloride (10%, 150 mL) was added. The aqueous phase was extracted with ethyl acetate (3 × 100 mL). The organic phases were washed with brine, dried, and concentrated under vacuum. The residue was purified by chromatography on silica gel (pentane/ethyl acetate, 7:3) to give the alcohol **28** (6.360 g, 82%). ^{1}H NMR (250 MHz): δ = 3.55 (m, 4 H), 2.40 (m, 1 H), 2.23 (m, 2 H), 1.66 (m, 2 H), 1.28 (m, 2 H), 0.88 (s, 9 H), 0.02 (s, 6 H) ppm. ^{13}C NMR: δ = 81.9, 76.5, 61.6, 61.2, 31.8, 25.8, 23.0, 18.2, 15.0, −3.7 ppm. IR (film): $\tilde{\nu}_{max}$ = 3315, 2954, 2930, 2858, 1742, 1472, 1256, 1106, 836, 777 cm^{-1}.

7-[(*tert*-Butyldimethylsilyl)oxy]hept-3-yn-1-yl Acetate (29): Acetic anhydride (4.5 mL) and DMAP (0.300 g, 2.7 mmol) were added to a solution of alcohol **28** (6.000 g, 0.0248 mol) in diethyl ether (80 mL). After 16 h at room temp., the mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by chromatography on silica gel to give the acetate **29** (5.390 g, 77%). ^{1}H NMR (250 MHz): δ = 4.12 (t, *J* = 6 Hz, 2 H), 3.65 (t, *J* = 6 Hz, 2 H), 2.45 (m, 2 H), 2.22 (m, 2 H), 2.07 (s, 3 H), 1.65 (q, *J* = 6 Hz, 2 H), 0.85 (s, 9 H), 0.03 (s, 6 H) ppm. ^{13}C NMR: δ = 170.8, 81.5, 75.6, 62.8, 61.5, 31.8, 25.9, 20.8, 19.2, 18.2, 15.0, −5.4 ppm. IR (film): $\tilde{\nu}_{max}$ = 2955, 2930, 2857, 1746, 1472, 1239, 1105, 1044, 837, 777 cm^{-1}.

(3*Z*)-7-[(*tert*-Butyldimethylsilyl)oxy]hept-3-en-1-yl Acetate (30): Lindlar catalyst (48 mg) was added to a solution of acetate **29** (1.890 g, 6.65 mmol) in hexane (20 mL), and the mixture was stirred under 1 atm of hydrogen. After absorption of 1 equiv. of hydrogen (24 h), the solution was filtered and the filtrate was concentrated under vacuum (1.810 g, 95%). The olefin **30** was pure enough to be used without further purification. ^{1}H NMR (250 MHz): δ = 5.50 (m, 1 H), 5.38 (m, 1 H), 4.05 (t, *J* = 6 Hz, 2 H), 3.60 (t, *J* = 6 Hz, 2 H), 2.38 (q, *J* = 7 Hz, 2 H), 2.10 (q, *J* = 7 Hz, 2 H), 2.05 (s, 3 H), 1.57 (q, *J* = 6 Hz, 2 H), 0.9 (s, 9 H), 0.05 (s, 6 H) ppm. ^{13}C NMR: δ = 171.0, 132.2, 124.8, 63.9, 62.7, 62.4, 32.6, 25.9, 23.5, 20.9, 18.3, −5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3013, 2955, 2930, 2858, 1742, 1656, 1472, 1385, 1362, 1239, 1101, 837, 776 cm^{-1}.

2-(*cis*-2-{3-[(*tert*-Butyldimethylsilyl)oxy]propyl}cyclopropyl)ethyl Acetate (31): Diethylzinc (1 M solution in hexane, 5.73 mL, 5.73 mmol) was added under argon at 0 °C to a solution of acetate **30** (0.820 g, 2.86 mmol) in 1,2-dichloroethane (10 mL). After 15 min, chloroiodomethane (2.020 g, 11.4 mmol) was added dropwise. After warming to room temp., the mixture was stirred for 1 h. The reaction mixture was then quenched by addition of aqueous NH_4Cl (10%, 50 mL). The aqueous phase was extracted with diethyl ether (3 × 20 mL). The organic phases were dried and concentrated under vacuum, and the residue was purified by chromatography on silica gel (diethyl ether/pentane, 85:15) to give the cyclopropyl compound **31** (0.790 g, 90%). ^{1}H NMR (250 MHz): δ = 4.11 (m, 2 H), 3.65 (m, 2 H), 2.05 (s, 3 H), 1.85−1.10 (m, 7 H), 0.85 (s, 9 H), 0.85−0.55 (m, 3 H), 0.03 (s, 6 H), −0.2 (m, 1 H) ppm. ^{13}C NMR: δ = 171.2, 64.9, 62.9, 33.2, 27.7, 25.9, 24.9, 21.0, 18.3, 15.1, 12.2, 10.6, −5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3062, 2930, 2858, 1744, 1472, 1387, 1363, 1247, 1101, 837, 776 cm^{-1}.

2-[*cis*-2-(3-Hydroxypropyl)cyclopropyl]ethyl Acetate (32): Tetrabutylammonium fluoride (1 M solution in THF, 4 mL, 4 mmol) was added to a THF solution (4 mL) of silyl ether **31** (0.600 g, 1.99 mmol). After the mixture had been kept at room temp. for 12 h, the solvent was removed under vacuum and the residue was purified by chromatography on silica gel (pentane/diethyl ether, 60:40) to give the alcohol **32** (0.372 g, 100%). ^{1}H NMR (250 MHz): δ = 4.08 (t, *J* = 7 Hz, 2 H), 3.65 (t, *J* = 7 Hz, 2 H), 3.45 (m, 1 H), 2.03 (s, 3 H), 1.68 (m, 2 H), 1.48 (m, 2 H), 1.20 (m, 2 H), 0.90−0.55 (m, 3 H), −0.22 (1 H) ppm. ^{13}C NMR: δ = 171.2, 64.9, 62.6, 33.0, 27.7, 24.9, 20.9, 15.1, 12.2, 10.5 ppm. IR (film): $\tilde{\nu}_{max}$ = 3348, 3061, 2930, 2858, 1472, 1386, 1255, 1101, 1037, 836, 775 cm^{-1}.

2-[*cis*-2-(3-Oxopropyl)cyclopropyl]ethyl Acetate (33): This aldehyde was prepared by oxidation of the alcohol **32** by the procedure described for the preparation of the aldehyde **18** (70%). ^{1}H NMR (250 MHz): δ = 9.85 (br. s, 1 H), 4.13 (t, *J* = 7 Hz, 2 H), 2.55 (t, *J* = 7 Hz, 2 H), 2.05 (s, 3 H), 1.90−1.60 (m, 2 H), 1.60−1.40 (m, 2 H), 0.95−0.55 (m, 3 H), −0.22 (m, 1 H) ppm. ^{13}C NMR: δ = 202.4, 172.7, 64.7, 44.2, 27.7, 21.4, 21.0, 14.8, 12.6, 10.6 ppm. IR (film): $\tilde{\nu}_{max}$ = 3064, 2955, 1737, 1387, 1364, 1245, 1037 cm^{-1}.

2-[*cis*-2-(But-3-enyl)cyclopropyl]ethyl Acetate (34): The Wittig reaction was conducted on aldehyde **33** as reported for the preparation of the olefin **16** (53%). ^{1}H NMR (250 MHz): δ = 5.85 (m, 1 H), 5.00 (m, 2 H), 4.10 (dt, *J* = 7 and 2 Hz, 2 H), 2.13 (q, *J* = 8 Hz, 2 H), 2.03 (s, 3 H), 1.85−1.20 (m, 4 H), 0.85−0.60 (m, 3 H), −0.20 (m, 1 H) ppm. ^{13}C NMR: δ = 172.5, 138.7, 114.2, 64.8, 34.1, 28.1, 27.8, 20.9, 14.9, 12.2, 10.5 ppm. IR (film): $\tilde{\nu}_{max}$ = 3063, 2926, 2856, 1742, 1640, 1435, 1364, 1247, 1038, 911, 744, 697 cm^{-1}.

2-[*cis*-2-(But-3-enyl)cyclopropyl]ethanol (9): This alcohol was prepared by cleavage of the acetate **34** by the procedure described for the preparation of compounds **5**, **6** (70%). ^{1}H NMR (250 MHz): δ = 5.80 (m, 1 H), 5.00 (m, 2 H), 3.70 (t, *J* = 7 Hz, 2 H), 2.10 (m, 2 H), 1.90−1.10 (m, 5 H), 1.00−0.50 (m, 3 H), 0.20 (m, 1 H) ppm. ^{13}C NMR: δ = 138.8, 114.2, 63.2, 34.1, 31.6, 28.3, 14.7, 12.1, 10.5 ppm. IR (film): $\tilde{\nu}_{max}$ = 3337, 3062, 2992, 2926, 2860, 1640, 1455, 1436, 1055, 910. $C_9H_{16}O$ (140.2): calcd. C 77.09, H 11.50; found C 77.62, H 11.32 cm^{-1}.

2-(*cis*-2-{3-[(*tert*-Butyldimethylsilyl)oxy]propyl}cyclopropyl)ethanol (35): This alcohol was prepared by cleavage of the acetate **31** by the procedure used for the preparation of the alcohols **5**, **6** (95%). ^{1}H NMR (250 MHz): δ = 3.75 (q, *J* = 7 Hz, 2 H), 3.65 (t, *J* = 7 Hz, 2 H), 3.50 (d, *J* = 7 Hz, 1H (OH)], 1.70−1.20 (m, 7 H), 0.90 (s, 9 H), 0.80−0.60 (m, 2 H), 0.04 (s, 6 H), −0.20 (m, 1 H) ppm. ^{13}C NMR: δ = 63.5, 63.0, 33.2, 31.6, 25.9, 25.0, 18.3, 14.8, 12.2, 10.5, −5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3350, 3061, 2930, 2858, 1472, 1255, 1101, 836, 776 cm^{-1}.

2-(*cis*-2-{3-[(*tert*-Butyldimethylsilyl)oxy]propyl}cyclopropyl)-acetaldehyde (36): This aldehyde was prepared by oxidation of the alcohol **35** by the procedure described for the preparation of the compound **18** (83%). ^{1}H NMR (250 MHz): δ = 9.83 (t, *J* = 1 Hz, 1 H), 3.61 (t, *J* = 7 Hz, 2 H), 2.40 (dq, *J* = 14 and 6 Hz, 2 H), 1.62 (m, 2 H), 1.50−1.00 (m, 2 H), 0.88 (s, 9 H), 1.00−0.70 (m, 3 H), 0.05 (s, 6 H), 0.10 (m, 1 H) ppm. ^{13}C NMR: δ = 202.7, 62.7, 43.1, 32.9, 25.9, 25.2, 18.3, 14.7, 10.7, 9.00, −5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3062, 2929, 2712, 1729, 1689, 1472, 1387, 1255, 1100, 836, 775 cm^{-1}.

{3-[*cis*-2-(Prop-2-enyl)cyclopropyl]propoxy}(*tert*-butyl)dimethylsilane (37): The Wittig reaction was conducted on the aldehyde **36** as reported for the preparation of the olefin **16** (93%). ^{1}H NMR (250 MHz): δ = 5.95 (m, 1 H), 5.00 (m, 2 H), 3.62 (t, *J* = 6 Hz, 2 H), 2.20−1.90 (m, 2 H), 1.75−1.15 (m, 4 H), 0.90 (s, 9 H), 1.00−0.60 (m, 3 H), 0.05 (s, 6 H), 0.21 (s, 1 H) ppm. ^{13}C NMR: δ = 138.8, 114.0, 63.1, 33.3, 32.7, 25.9, 24.9, 18.3, 15.5, 14.8, 10.6, −5.2 ppm. IR (film): $\tilde{\nu}_{max}$ = 3063, 2930, 2858, 1641, 1472, 1255, 1102, 836, 775 cm^{-1}.

3-[*cis*-2-(Prop-2-enyl)cyclopropyl]propan-1-ol (11): $ClSiMe_3$ (three drops) was added at room temp. to silyl ether **37** (0.350 g, 13.7 mmol) in methanol (20 mL). After 2 h, the solvent was removed under vacuum and the residue was purified by chromatography on silica gel to give the alcohol **11** (0.164 g, 86%). ^{1}H NMR (250 MHz): δ = 5.90 (m, 1 H), 5.00 (m, 2 H), 3.65 (t, *J* = 7 Hz, 2 H), 2.05 (m, 2 H), 1.70−1.15 (m, 5 H), 0.95−0.60 (m, 3 H), 0.21 (m, 1 H) ppm. ^{13}C NMR: δ = 138.6, 114.0, 62.6, 33.0, 32.6, 24.8, 15.4, 14.7, 10.6 ppm. IR (film): $\tilde{\nu}_{max}$ = 3324, 3062, 2993, 2932, 2861, 1640, 1455, 1059, 910 cm^{-1}. $C_9H_{16}O$ (140.2): calcd. C 77.09, H 11.50; found C 77.01, H 11.87.

(4*E*)-7-[(*tert*-Butyldimethylsilyl)oxy]hept-4-enyl Acetate (39): Imidazole (2.250 g, 0.0331 mol) and (*tert*-butyl)(chloro)dimethylsilane (5.000 g, 0.034 mol) were added at room temp. to (4*E*)-7-hydroxyhept-4-enyl acetate (**38**, 4.75 g, 0.0276 mol) in DMF (250 mL). The mixture was stirred for 16 h at room temp., and water (350 mL) was added. The mixture was extracted with diethyl ether (3 × 150 mL). The organic phase was dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by chromatography on silica gel (pentane/diethyl ether, 80:20) to give the silyl ether **39** (7.400 g, 94%). ^{1}H NMR (250 MHz): δ = 5.20 (m, 2 H), 4.06 (t *J* = 7 Hz, 2 H), 3.60 (t, *J* = 7 Hz, 2 H), 2.40−1.95 (m, 4 H), 2.04 (s, 3 H), 1.67 (quint, *J* = 8 Hz, 2 H), 0.88 (s, 9 H), 0.05 (s, 6 H) ppm. ^{13}C NMR: δ = 171.2, 130.9, 127.6, 63.2, 63.9, 36.2, 28.9, 28.2, 25.9, 21.0, 18.3, −5.3 ppm.

3-(*trans*-2-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}cyclopropyl)propyl Acetate (40): The cyclopropanation was conducted on the unsaturated compound **39** as reported for the preparation of the compound **31** (93%). ^{1}H NMR (250 MHz): δ = 4.08 (t, *J* = 7 Hz, 2 H), 3.65 (t, *J* = 7 Hz, 2 H), 2.06 (s, 3 H), 1.90−1.10 (m, 6 H), 0.88 (s, 9 H), 0.90−0.00 (m, 4 H), 0.06 (s, 6 H) ppm. ^{13}C NMR: δ = 171.1, 64.3, 63.1, 37.4, 30.4, 28.5, 25.9, 20.9, 18.3, 17.8, 15.4, 11.4, −5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3062, 2929, 1743, 1472, 1364, 1254, 1100, 836, 776 cm^{-1}.

3-(*trans*-2-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}cyclopropyl)propan-1-ol (41): The cleavage of the acetate function of the compound **40** was conducted as reported for the preparation of compounds **5**, **6** (99%). ^{1}H NMR (250 MHz): δ = 3.61 (t, *J* = 7 Hz, 4 H), 1.90−1.10 (m, 6 H), 0.88 (s, 9 H), 0.55−0.10 (m, 4 H), 0.05 (s, 6 H) ppm. ^{13}C NMR: δ = 63.2, 62.7, 37.5, 32.6, 30.3, 25.9, 18;3, 18.1, 15.4, 11.4, −5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3349, 3060, 2929, 2857, 1670, 1472, 1255, 1101, 836, 775 cm^{-1}.

3-(*trans*-2-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}cyclopropyl)propionaldehyde (42): This aldehyde was prepared by oxidation of the alcohol **41** according to the procedure used for the preparation of the aldehyde **18** (73%). ^{1}H NMR (250 MHz): δ = 9.80 (t, *J* = 0.5 Hz, 1 H), 3.65 (t, *J* = 7 Hz, 2 H), 2.52 (dt, *J* = 7 and 0.5 Hz, 2 H), 1.55 (q, *J* = 7 Hz, 2 H), 1.40 (q, *J* = 7 Hz, 2 H), 0.90 (s, 9 H), 0.50 (m, 2 H), 0.25 (m, 2 H), 0.05 (s, 6 H) ppm. ^{13}C NMR: δ = 156.1, 68.2, 56.2, 52.0, 45.4, 44.9, 44.6, 39.7, 38.4, 35.9, 25.2 ppm. IR (film): $\tilde{\nu}_{max}$ = 3063, 2929, 2857, 1728, 1255, 1101, 836, 776 cm^{-1}.

{2-[*trans*-2-(But-3-enyl)cyclopropyl]ethoxy}(*tert*-butyl)dimethylsilane (43): The Wittig reaction was conducted on the aldehyde **42** as reported for the preparation of the olefin **16**. ^{1}H NMR (250 MHz): δ = 5.85 (m, 1 H), 5.00 (m, 2 H), 3.65 (t, *J* = 7 Hz, 2 H), 2.12 (m, 2 H), 1.60−1.15 (m, 4 H), 0.88 (s, 9 H), 0.60−0.10 (m, 4 H), 0.04 (s, 6 H) ppm. ^{13}C NMR: δ = 138.9, 114.2, 63.2, 37.6, 33.9, 33.7, 29.7, 25.9, 18.1, 15.4, 11.5, −5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3063, 2928, 2857, 1641, 1472, 1255, 1102, 910, 836, 775 cm^{-1}.

2-[*trans*-2-(But-3-enyl)cyclopropyl]ethanol (10): This compound was obtained by cleavage of the silyl ether **43** according to the procedure described for the preparation of the alcohol **32** (82%). ^{1}H NMR (250 MHz): δ = 5.82 (m, 1 H), 5.05 (m, 2 H), 3.65 (t, *J* = 7 Hz, 2 H), 2.12 (m, 2 H), 1.55−1.10 (m, 5 H), 0.95−0.20 (m, 4 H) ppm. ^{13}C NMR: δ = 138.8, 114.2, 62.9, 37.1, 33.8, 33.5, 17.9, 15.2, 11.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3324, 3063, 2928, 2857, 1641, 1470, 1254, 1051, 910, 836, 780 cm^{-1}. $C_9H_{16}O$ (140.2): calcd. C 77.09, H 11.50; found C 77.21, H 11.55.

(*cis*-2-{4-[(*tert*-Butyldimethylsilyl)oxy]butyl}cyclopropyl)methanol (45): Diiodomethane (3.01 mL, 0.0372 mol) and diethylzinc (1 M solution in hexane, 18.60 mL, 0.0186 mol) were added under argon at −40 °C to (2*Z*)-7-[(*tert*-butyldimethylsilyl)oxy]hept-2-en-1-ol[25] (**44**, 2.270 g, 0.0093 mol) in toluene (45 mL). After 30 min at this temperature, the mixture was allowed to warm to room temp. and quenched by addition of a 10% aqueous solution of NH_4Cl (150 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic phases were dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by chromatography on silica gel (diethyl ether/pentane, 1:9) to give the alcohol **45** (2.250 g, 92%). ^{1}H NMR (250 MHz): δ = 3.65 (m, 4 H), 1.65−1.00 (m, 7 H), 1.00−0.80 (m, 2 H), 0.90 (s, 9 H), 0.75 (m, 1 H), 0.05 (s, 6 H), −0.02 (q, *J* = 5 Hz, 1 H) ppm. ^{13}C NMR: δ = 63.1 (2C), 32.6,

28.2, 26.3, 25.9, 18.3, 18.1, 9.4, 5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3347, 2931, 2858, 1472, 1255, 1100, 836, 775 cm^{-1}.

***cis*-2-{4-[(*tert*-Butyldimethylsilyl)oxy]butyl}cyclopropane-1-carbaldehyde (46):** The oxidation of alcohol **44** was carried out as reported for the preparation of aldehyde **18** (87%). ^1H NMR (250 MHz): δ = 9.35 (d, *J* = 6 Hz, 1 H), 3.65 (t, *J* = 7 Hz, 2 H), 2.00−1.10 (m, 10 H), 0.90 (s, 9 H), 0.05 (s, 6 H) ppm. ^{13}C NMR: δ = 201.8, 63.0, 32.3, 27.9, 27.7, 26.2, 25.9, 24.7, 18.3, 14.7, −5.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 2931, 2858, 2713, 1728, 1472, 1388, 1255, 1098, 836, 776 cm^{-1}.

(*tert*-Butyl)dimethyl[4-(*cis*-2-vinylcyclopropyl)butoxy]silane (47): A Wittig reaction was conducted on the aldehyde **46** as reported for the preparation of compound **16** (87%). ^1H NMR (250 MHz): δ = 5.55 (m, 1 H), 5.05 (m, 2 H), 3.60 (t, *J* = 7 Hz, 2 H), 1.65−1.25 (m, 7 H), 1.05−0.80 (m, 2 H), 0.88 (s, 9 H), 0.25 (m, 1 H), 0.04 (s, 6 H) ppm. ^{13}C NMR: δ = 138.5, 113.7, 63.2, 32.7, 28.9, 26.0, 25.9, 19.7, 18.7, 18.3, 12.7, −5.2 ppm. IR (film): $\tilde{\nu}_{max}$ = 3078, 2930, 2857, 1641, 1472, 1255, 1103, 910, 836, 775 cm^{-1}.

4-(*cis*-2-Vinylcyclopropyl)butan-1-ol (12): This compound was obtained by cleavage of the silyl ether **47** by the procedure reported for the preparation of the alcohol **11** (93%). ^1H NMR (250 MHz): δ = 5.55 (m, 1 H), 5.00 (m, 2 H), 3.65 (t, *J* = 7 Hz, 2 H), 1.70−1.25 (m, 7 H), 1.05−0.65 (m, 3 H), 0.25 (m, 1 H) ppm. ^{13}C NMR: δ = 138.4, 113.8, 62.9, 32.5, 28.8, 25.8, 19.7, 18.6, 12.6 ppm. IR (film): $\tilde{\nu}_{max}$ = 3334, 3067, 2997, 2933, 2859, 1634, 1458, 1053, 988, 894 cm^{-1}. $C_9H_{16}O$ (140.2): calcd. C 77.09, H 11.50; found C 77.38, H 11.41.

General Procedure for the Haloetherification: A solution of unsaturated alcohol (1 mmol) in dichloromethane (5 mL) was added over 4 h at room temp. to a solution of bis(collidine)halonium(I) hexafluorophosphate (1.22 mmol) in dichloromethane (15 mL). The resulting solution was stirred for an additional 1 h, and silica gel (2 g) was added. The solvent was removed under vacuum and the resulting solid was introduced onto the top of a silica gel column. Elution with a pentane/diethyl ether mixture gave products **48**−**64**.

3-(Iodomethyl)-3,4,5,6-tetrahydro-1*H*-benzo[c]oxocine (48): Oil. ^1H NMR (250 MHz): δ = 7.33−7.12 (m, 4 H), 5.02−4.69 (2 d, AB system, *J* = 12 Hz, 2 H), 3.58−3.47 (m, 1 H), 3.31−3.13 (m, 2 H), 3.13−3.03 (m, 1 H), 2.93−2.79 (m, 1 H), 2.06−1.92 (m, 1 H), 1.86−1.48 (m, 3 H) ppm. $C_{12}H_{15}IO$ (302.2): calcd. C 47.70, H 5.00; found C 47.76, H 5.08.

3-(Bromomethyl)-3,4,5,6-tetrahydro-1*H*-benzo[c]oxocine (49): Oil. R_f = 0.66 (diethyl ether/pentane, 50:50). ^1H NMR (250 MHz): δ = 7.25−7.02 (m, 4 H), 5.02−4.69 (2 d, AB system, *J* = 15 Hz, 2 H), 3.71−3.57 (m, 1 H), 3.48−3.28 (m, 2 H), 3.18−3.00 (m, 1 H), 2.92−2.77 (m, 1 H), 2.10−1.46 (m, 4 H) ppm. ^{13}C NMR: δ = 141.2, 136.4, 130.4, 128.9, 128.3, 126.4, 77.1, 70.6, 37.0, 32.1, 31.3, 28.0 ppm. $C_{12}H_{15}BrO$ (255.2): calcd. C 56.49, H 5.93; found C 56.65, H 6.02.

2-(5-Bromo-4-fluoropentyl)benzaldehyde (50): Oil. R_f = 0.54 (diethyl ether/pentane, 50:50). ^1H NMR (250 MHz): δ = 10.28 (s, 1 H), 7.72 (dd, *J* = 7 and 1 Hz, 1 H), 7.52−7.11 (m, 3 H), 3.78−3.52 (m, 2 H), 3.45−2.95 (m, 3 H), 2.39−1.60 (m, 4 H) ppm. $C_{12}H_{14}BrFO$ (273.1): calcd. C 52.77, H 5.17; found C 52.91, H 5.50.

1-(Iodomethyl)-3,4,5,6-tetrahydro-1*H*-benzo[*c*]oxocine (51): Oil. ^1H NMR (250 MHz): δ = 7.30−7.15 (m, 4 H), 7.15−7.00 (m, 2 H), 4.65 (dd, *J* = 5 and 8 Hz, 1 H), 4.00 (q, *J* = 8 Hz, 1 H), 3.80−3.55 (m, 2 H), 3.50−3.30 (m, 2 H), 2.70−2.55 (m, 1 H), 2.05−1.85 (m, 1 H), 1.60−1.40 (m, 3 H) ppm. ^{13}C NMR: δ = 139.7 (2C), 131.6, 128.1, 127.0, 126.0, 82.4, 70.9, 32.7, 27.7, 25.9, 12.0 ppm. $C_{12}H_{15}IO$ (302.2): calcd. C 47.70, H 5.00; found C 48.15, H 5.33.

1-(Bromomethyl)-3,4,5,6-tetrahydro-1*H*-benzo[*c*]oxocine (52): Oil. ^1H NMR (250 MHz): δ = 7.30−7.15 (m, 2 H), 7.15−7.00 (m, 2 H), 4.80 (dd, *J* = 5 and 8 Hz, 1 H), 4.00 (q, *J* = 8 Hz, 1 H), 3.80−3.50 (m, 4 H), 2.65 (m, 1 H), 1.94 (m, 1 H), 1.70−1.45 (m, 3 H) ppm. ^{13}C NMR: δ = 140.2, 138.7, 131.6, 128.3, 127.1, 126.0, 82.4, 70.8, 37.6, 32.7, 27.8, 26.1 ppm. $C_{12}H_{15}BrO$ (255.2): calcd. C 56.49, H 5.93; found C 56.65, H 6.11.

4-(Iodomethyl)-3,9-dioxabicyclo[6.1.0]nonane (53): Oil (50:50 mixture of diastereomers). ^1H NMR (250 MHz): δ = 4.80 [dd, *J* = 14 and 3 Hz, 1 H, (first diastereomer)], 4.05 [dq, *J* = 13 and 3 Hz, 2 H, (second diastereomer)], 3.07−3.30 [m, 2 H, (two diastereomers)], 3.30−2.90 [m, 2 H, (two diastereomers)], 2.05−1.40 [m, 6 H, (two diastereomers)] ppm. $C_8H_{13}IO_2$ (268.1): calcd. C 35.84, H 4.89; found C 36.14, H 5.20.

4-(Bromomethyl)-3,9-dioxabicyclo[6.1.0]nonane (54): Oil (50:50 mixture of diastereomers). ^1H NMR (250 MHz): δ = 4.80 [dd, *J* = 14 and 3 Hz, 1 H, (first diastereomer)], 4.05 [dq, *J* = 13 and 3 Hz, 2 H, (second diastereomer)], 3.60−3.20 [m, 4 H, (two diastereomers)], 3.15−2.95 [m, 2 H, (two diastereomers)], 2.00−1.40 [m, 6 H, (two diastereomers)] ppm. ^{13}C NMR (first diastereomer): δ = 80.3, 67.1, 54.6, 53.2, 36.7, 31.9, 23.9, 22.6 ppm; (second diastereomer): δ = 80.1, 66.4, 55.9, 54.8, 33.3, 29.6, 27.4, 20.6 ppm. $C_8H_{13}BrO_2$ (221.1): calcd. C 43.46, H 5.93; found C 43.81, H 5.97.

(10*S,11*S**)-6-(Iodomethyl)-2,2-dimethylhexahydro-4*H*-[1,3]-dioxolo[4,5-*c*]oxocine (55):** Oil (50:50 mixture of diastereomers). ^1H NMR (250 MHz) (mixture): δ = 4.20−3.71 (m, 3 H), 3.56−3.10 (m, 4 H), 2.00−1.15 (m, 6 H), 1.45 (s, 3 H), 1.39 (s, 3 H) ppm. $C_{11}H_{19}IO_3$ (326.2): calcd. C 40.51, H 5.87; found C 40.80, H 5.89.

(10*S,11*S**)-6-(Bromomethyl)-2,2-dimethylhexahydro-4*H*-[1,3]-dioxolo[4,5-*c*]oxocine (56):** Oil (50:50 mixture of diastereomers). ^1H NMR (250 MHz) (mixture): δ = 4.23−4.04 (m, 1 H), 4.04−3.96 (m, 1 H), 3.75−3.67 (m, 1 H), 3.67−3.38 (m, 3 H), 3.38−3.30 (m, 1 H), 2.02−1.13 (m, 6 H), 1.45 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR (first isomer): δ = 109.4, 78.2, 77.7, 71.9, 65.4, 35.6, 29.5, 26.5, 26.2, 26.0, 25.5 ppm; (second diastereomer): δ = 109.5, 77.3, 76.8, 71.5, 65.6, 53.4, 32.7, 26.5, 26.1, 25.4, 17.8 ppm. $C_{11}H_{19}BrO_3$ (279.2): calcd. C 47.33, H 6.86; found C 47.64, H 6.96.

(10*S,11*R**)-6-(Iodomethyl)-2,2-dimethylhexahydro-4*H*-[1,3]-dioxolo[4,5-*c*]oxocine (57):** Oil (50:50 mixture of diastereomers). ^1H NMR (250 MHz) (mixture): δ = 4.20−4.05 (m, 1 H), 4.05−3.90 (m, 1 H), 3.90−3.75 (m, 1 H), 3.70−3.12 (m, 4 H), 2.00−1.13 (m, 6 H), 1.45 (br. s, 3 H), 1.48 (2s, 3 H) ppm. ^{13}C NMR (mixture): δ = 109.5 (A), 109.4 (B), 78.0 (A), 77.7 (B), 77.0 (A), 76.8 (B), 72.4 (A), 71.0 (B), 66.7 (A), 65.7 (B), 31.0 (A), 27.4 (B), 26.5 (A), 26.3 (A), 26.0 (A), 25.6 (B), 25.4 (B), 22.8 (A), 17.8 (B), 9.8 (A), 7.0 (B) ppm. $C_{11}H_{19}IO_3$ (326.2): calcd. C 40.51, H 5.87; found C 40.90, H 5.73.

(10*S,11*R**)-6-(Bromomethyl)-2,2-dimethylhexahydro-4*H*-[1,3]-dioxolo[4,5-*c*]oxocine (58):** Oil (50:50 mixture of diastereomers). ^1H NMR (250 MHz) (mixture): δ = 4.25−3.95 (m, 3 H), 3.85−3.40 (m, 4 H), 1.90−1.15 (m, 6 H), 1.45 (s, 3 H), 1.36 (s, 3 H) ppm. ^{13}C NMR (mixture): δ = 109.6, 109.4, 78.3, 77.8, 77.2, 76.8, 72.0, 71.6, 65.8, 65.7, 35.6, 32.7, 29.6, 26.5, 26.3, 26.1, 26.0, 25.5, 25.4, 22.6, 17.9, 15.2 ppm. $C_{11}H_{19}BrO_3$ (279.2): calcd. C 47.33, H 6.86; found C 47.66, H 6.67.

(1*S,8*S**)-4-(Iodomethyl)-4-oxabicyclo[6.1.0]nonane (59):** Oil (50:50 mixture of diastereomers). ^{1}H NMR (250 MHz) (mixture): δ = 4.40 [dd, *J* = 13 and 4 Hz, 1 H (first diastereomer)], 4.17 [dd, *J* = 11 and 2 Hz, (second diastereomer)], 3.95 [m, 1 H (second diastereomer)], 3.35−3.10 (m, 3 H), 3.00 [dd, *J* = 13 and 11 Hz, 1 H (first diastereomer)], 2.25−0.60 (m, 9 H), −0.15 (m, 1 H) ppm. ^{13}C NMR (first diastereomer): δ = 80.1, 71.1, 34.4, 26.1, 24.1, 16.1, 13.9, 13.6, 7.6 ppm; (second diastereomer): δ = 75.1, 65.2, 34.5, 29.0, 27.6, 15.8, 14.3, 13.4, 7.5 ppm. IR (film): $\tilde{\nu}_{max}$ = 3063, 2951, 1468, 1095, 1077 cm^{-1}. MS (EI): *m*/*z* (%) = 266 (0.2) [M$^+$], 255 (5), 139 (4), 97 (10), 95 (6), 93 (9), 81 (10), 79 (13), 71 (100), 69 (10), 67 (39), 55 (30), 53 (16), 43 (32), 41 (89), 39 (62). $C_9H_{15}IO$ (266.1): calcd. C 40.62, H 5.68; found C 40.86, H 5.81.

(1*S,8*S**)-5-(Iodomethyl)-4-oxabicyclo[6.1.0]nonane (60):** Oil. ^{1}H NMR (250 MHz): δ = 4.08 (dt, *J* = 13 and 2 Hz, 1 H), 3.85 (m, 1 H), 3.55 (t, *J* = 13 Hz, 1 H), 3.20 (m, 2 H), 2.15−0.50 (m, 9 H), −0.10 (m, 1 H) ppm. ^{13}C NMR: δ = 80.5, 73.4, 34.4, 32.8, 29.7, 23.9, 14.3, 12.2, 10.7 ppm. IR (film): $\tilde{\nu}_{max}$ = 3060, 2933, 2854, 1455, 1263, 1115, 1031, 613 cm^{-1}. MS (EI): *m*/*z* (%) = 266 (5) [M$^+$], 141 (3), 139 (5), 127 (6), 97 (6), 95 (11), 93 (11), 85 (17), 83 (27), 81 (18), 79 (25), 69 (11), 67 (72), 55 (100), 41 (86), 39 (70). $C_9H_{15}IO$ (266.1): calcd. C 40.62, H 5.68; found C 40.95, H 5.77.

(1*S,8*S**)-3-(Iodomethyl)-4-oxabicyclo[6.1.0]nonane (61):** Oil (50:50 mixture of diastereomers). ^{1}H NMR (250 MHz) (mixture): δ = 4.10 (m, 1 H), 3.70 (m, 1 H), 3.55−3.05 (m, 3 H), 2.30−0.60 (m, 9 H), −0.20 (m, 1 H) ppm. ^{13}C NMR (first diastereomer): δ = 82.2, 70.6, 36.6, 29.5, 23.7, 14.0, 13.7, 11.1, 10.0 ppm; (second diastereomer): δ = 78.8, 69.7, 30.8, 30.0, 28.7, 15.5, 9.7, 8.5, 8.3 ppm. IR (film) (mixture): $\tilde{\nu}_{max}$ = 3059, 2990, 2919, 2865, 1468, 1454, 1180, 1121, 1093, 1028 cm^{-1}. $C_9H_{15}IO$ (266.1): calcd. C 40.62, H 5.68; found C 41.21, H 5.50.

(1*S,8*S**)-3-(Bromomethyl)-4-oxabicyclo[6.1.0]nonane (62):** Oil (50:50 mixture of diastereomers). ^{1}H NMR (250 MHz) (mixture): δ = 4.15 (m, 1 H), 3.85−3.65 (m, 1 H), 3.65−3.47 (m, 1 H), 3.47−3.10 (m, 2 H), 2.30−0.55 (m, 9 H) ppm. ^{13}C NMR (mixture): δ = 82.0, 78.3, 70.8, 69.9, 36.7, 35.4, 34.3, 30.0 (2 diastereomers), 29.4, 28.9, 23.7, 15.5, 14.0, 13.7, 10.0, 9.8, 8.7 ppm. IR (film): $\tilde{\nu}_{max}$ = 3061, 2991, 2923, 2868, 1468, 1455, 1227, 1093, 1031, 670 cm^{-1}. $C_9H_{15}BrO$ (219.1): calcd. C 49.33, H 6.90; found C 49.61, H 7.23.

(1*S,8*S**)-2-(Iodomethyl)-3-oxabicyclo[6.1.0]nonane (63):** Oil. ^{1}H NMR (250 MHz): δ = 4.07 (dd, *J* = 13 and 7 Hz, 1 H), 3.60 (dd, *J* = 13 and 7 Hz, 1 H), 3.50−3.25 (m, 2 H), 2.95 (m, 1 H), 2.25−0.60 (m, 9 H), −0.09 (m, 1 H) ppm. ^{13}C NMR: δ = 77.5, 69.0, 29.1, 27.1, 26.9, 19.6, 14.4, 12.0, 8.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3062, 2990, 2924, 2854, 1462, 1196, 1102, 1017 cm^{-1}. MS (EI): *m*/*z* (%) = 266 (0.6) [M$^+$], 139 (0.4) [M$^+$ − I], 127 (3), 95 (4), 85 (100), 79 (12), 67 (23), 57 (15), 55 (27), 41 (45). MS (CI; NH_3): *m*/*z* (%) = 284 (42) [M$^+$ + NH_4^+], 267 (100) [M$^+$ + H$^+$], 139 (12). $C_9H_{15}IO$ (266.1): calcd. C 40.62, H 5.68; found C 41.53, H 5.74.

2-(4-Iodobut-2-enyl)tetrahydropyran (64): Oil. ^{1}H NMR (250 MHz): δ = 5.90−5.50 (m, 2 H), 4.10−3.80 (m, 3 H), 3.50−3.20 (m, 2 H), 2.25−2.05 (m, 2 H), 1.90−1.15 (m, 6 H) ppm. ^{13}C NMR: δ = 131.0, 129.7, 76.9, 68.5, 39.1, 31.4, 25.9, 23.3, 6.5 ppm. IR (film): $\tilde{\nu}_{max}$ = 3027, 2933, 2847, 1655, 1438, 1150, 1087, 1046, 964 cm^{-1}. MS (EI): *m*/*z* (%) = 266 (0.1) [M$^+$], 139 (10) [M$^+$ − I], 127 (5), 85 (100), 67 (19), 55 (24), 54 (13), 53 (8), 43 (17), 41 (40), 39 (22). MS (CI; NH_3): *m*/*z* (%) = 284 (42) [M$^+$ + NH_4^+], 267 (100) [M$^+$ + H$^+$], 139 (7). $C_9H_{15}IO$ (266.1): calcd. C 40.62, H 5.68; found C 40.31, H 5.81.

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