Synthesis of Vinylcyclopropanes by Intramolecular Epoxide Ring Opening. Application for an Enantioselective Synthesis of Dictyopterene A

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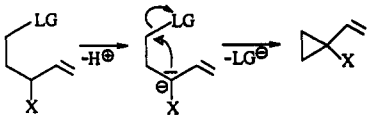
The reaction of functionalized oxiranes **1** with the sulfur- or silicon-stabilized anions **2** provides β-heteroatom-substituted γ,δ-unsaturated epoxides **5** with, for **5e,f**, a trans C=C moiety. A cis compound **9** is obtained using acetylide anion **2c** via **7** and subsequent partial hydrogenation of the C≡C bond in the intermediate oxirane **8**. Regiospecific anion generation in **5,9** is achieved by deprotonation, reductive desulfurization, and desilylation, respectively. The resulting anions **10** cyclize to 1-(hydroxyalkyl)-2-vinylcyclopropanes **11** by a stereochemically controlled S_Ni process. Starting from the optically active epoxide **1b**, the approach allows synthesis of cyclopropane **11b** with (1*S*,2*R*) configuration at the ring carbon atoms. This compound can be further elaborated to the algae sex pheromone dictyopterene A which is obtained along with the unnatural *Z* diastereomer.

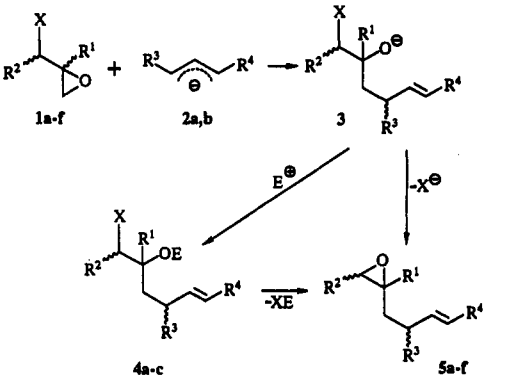
Introduction

Recently, we reported a convenient synthesis of vinylcyclopropanes nicely complementing the existing methodology.[1] The approach is based on the heteroatom-supported deprotonation of 4-alkenyl tosylates followed by S_Ni ring closure of the resulting anions (Scheme I; LG = tosylate) and could be extended to the synthesis of ethynylcyclopropanes by use of the corresponding alkynyl precursors.[2] The success of the reaction critically depends on the presence of tosylate as potential leaving group as it fails for silyl ether derivatives (homo-Peterson reaction)[1] and gives less satisfactory results for mesylates or triflates.[3] However, we now report that use of an epoxide as target of intramolecular nucleophilic attack presents an efficient and versatile modification of our approach giving 1-(2-vinylcyclopropyl)alkanols.

Scheme I



Scheme II



1a; R^1=R^2=H, X=OTHP
b; R^1=R^2=H, X=OTs
c; R^1=R^2=H, X=Cl
d; R^1=Me,R^2=H, X=OTs
(±)**e**; R^1=Me ····, R^2=Me —, X=OTs
(±)**f**; R^1=R^2=Me ····, X=OTs
2a; R^3=SPh, R^4=H
b; R^3=R^4=SiMe$_3$
4a; R^1=R^2=R^4=H, R^3=SPh, X=OTHP; E=Ts
b; R^1=R^2=R^4=E=H, R^3=SPh, X=Cl
c; R^1=R^2=E=H, R^3=R^4=SiMe$_3$, X=Cl
5a; R^1=R^2=R^4=H, R^3=SPh
b; R^1=Me, R^2=R^4=H, R^3=SPh
(±)**c**; R^1=R^2=Me ····, R^3=SPh, R^4=H
(±)**d**; R^1=Me ····, R^2=Me —, R^3=SPh, R^4=H
e; R^1=R^2=H, R^3=R^4=SiMe$_3$
f; R^1=Me, R^2=H, R^3=R^4=SiMe$_3$

Results and Discussion

Synthesis of Alkenyloxiranes 5. A practical approach to the required six-carbon units utilizes two C_3 building-blocks, i.e., the reaction of O-protected and epoxidized allyl alcohol derivatives **1** or of epichlorohydrine (**1c**) with the phenylthio- or bis(silyl)-substituted anions **2a,b** (Scheme II). In all cases, the epoxide ring of **1** is opened chemoselectively without competing substitution of X. The fate of the primary ring-opening product **3** depends on the leaving-group ability of the substituent X: tosylate in this position gives in-situ ring closure to oxiranes **5b-f** even at −78 °C, whereas use of epichlorohydrin (**1c**) allows isolation of alcohols **4b,c**. Here, subsequent treatment with base leads to epoxide ring closure, but a one-pot procedure avoiding isolation of **4** is also possible. Use of the THP-protected (hydroxymethyl)oxirane **1a** in the reaction with **2a** gives the monoprotected diol **4a** which cyclizes to **5a** via tosylation, acetal cleavage, and treatment with sodium methoxide.

The unsymmetrical anion **2a** had already shown high α selectivity in the reaction with simple oxiranes;[1,4] in the present experiments using functionalized oxiranes **1**, only trace amounts of products of γ attack (**3** with R^3 = H, R^4 = SPh), if any, were formed and could easily be removed during chromatographic workup. Moreover, transformation of the diastereomeric oxiranes **1e,f** into stereochemically pure alkenyl oxiranes **5c,d** confirms the clean trans stereochemistry of epoxide ring opening and closure. However, the configuration at the original α-carbon of the allyl anion could not be controlled.

In the reaction of **1e** with anion **2a**, product **5d** was contaminated by a small amount of the isomeric epoxide

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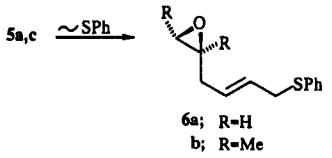
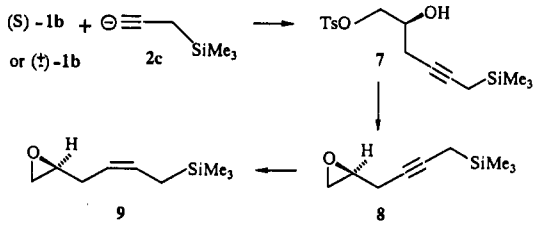
0022-3263/93/1958-0626$04.00/0

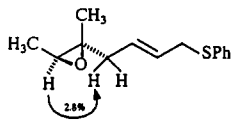
Scheme III



Scheme IV



6b with a terminal phenylthio group. Obviously, the well-documented 1,3 shift of the phenylthio group in allylic systems occurs.[5] The reaction can also be applied on a preparative scale by heating alkenyloxiranes **5a,d** with thiophenol in the presence of AIBN in refluxing carbon tetrachloride to yield isomers **6a,b** with a terminal sulfur substituent (Scheme III). This transformation does not affect the integrity or even stereochemistry of the epoxide ring as shown by an NOE experiment for **6b**:

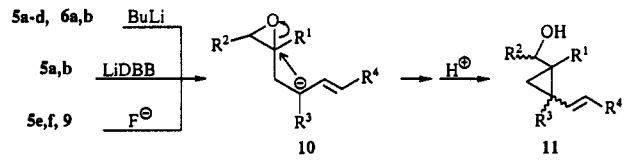


Mutatis mutandis, the NOE experiment also confirms assignment of configuration in **1e,f**.

According to the NMR spectroscopic evidence, the C=C unit has the trans configuration in the silicon derivatives **5e,f** as well as in the sulfides **6a,b**. A route to homoallyl alcohols with a cis C=C bond is demonstrated by the reaction of acetylide **2c** with oxirane **1b**.[6] The resulting tosylate **7** cyclizes by the action of base giving alkynyloxirane **8**, which eventually provides *cis*-alkenyl oxirane **9** via partial hydrogenation of the C≡C moiety (Scheme IV).

Synthesis of Vinylcyclopropanes 11. Formation of carbocycles by intramolecular nucleophilic attack on epoxides is well-documented.[7] Usually, the smaller of the possible rings is formed[8] as is also shown by the synthesis of 1-(hydroxyalkyl)-2-vinylcyclopropanes via deprotonation of γ,δ-unsaturated epoxides.[9] However, here isomerization of the oxirane ring to the corresponding allyl alcohol was a competing process. In our examples, the presence of a second-row heterosubstituent should foster anion formation and suppress the unwanted oxirane isomerization.

Scheme V



Deprotonation of epoxides **5a–d, 6a,b** proceeds smoothly by the action of *n*-butyllithium at low temperature and leads to immediate cyclization yielding invariably vinylcyclopropanes **11** (Scheme V and Table I). Thus, in accord with expectations,[8b] ring closure is regiospecific even though formation of the three-membered ring involves attack on the higher substituted oxirane ring carbon. Products of oxirane isomerization could not be detected.

Products **11a,c,f,i,j** are formed as mixtures of diastereomers with regard to the relative stereochemistry of the ring substituents. Assignment of the 1*r*,2*c* ("*Z*") configuration to the strongly predominating isomer and to the single diastereomer of **11e** is possible by NOE experiments. Thus, saturation of the ring-methyl group R^1 leads to an increase in the signal intensity of the vinylic proton by 1.5, 1.8, and 1.2% in **11c,e**, and **f**, respectively. An effect of 2.6% was observed for the main isomer of the 3,5-dinitrobenzoate of **11h**. In **11j**, additional NOE effects can be detected between exocyclic groups in the two main isomers of opposite configuration on the ring (Scheme VI). Moreover, relative to the *E* isomer, the signals of the vinylic methine proton show an upfield shift. The assignment of configurations is also supported by the ^{13}C NMR shifts of cyclopropane carbon signals.[10]

It is noteworthy that in the formation of products **11a,c,d** the stereoselectivity is much more pronounced than in the tosylate route (cf. Scheme I).[1] It appears that the conformational requirements of the epoxide ring are less flexible with the interaction between the phenylthio group and R^1 on the epoxide ring being the decisive factor. Here, route B is obviously less demanding than route A and is therefore favored (Scheme VII).

Stereochemical control in the formation of **11i,j** from **6a,b** is less efficient than from **5a–d** (Table I). Obviously, the position of the phenylthio group does not allow it to function as steering element.

Another route from alkenyl oxiranes **5** to anions **10** employs reductive desulfurization by lithium 4,4′-di-*tert*-butylbiphenylide (LiDBB)[11] giving again cyclopropane formation as exemplified by the synthesis of **11b,d** (Table I). In the products the 1*r*,2*t* ("*E*") diastereomers predominate as shown by comparison with literature data for **11b**[12] and by the ^{13}C NMR chemical shifts. This may again be understood in terms of the interactions shown in Scheme VII, if desulfurization and ring closure occur without major changes in conformation. Interestingly, LiDBB does not attack the oxirane ring though evidence

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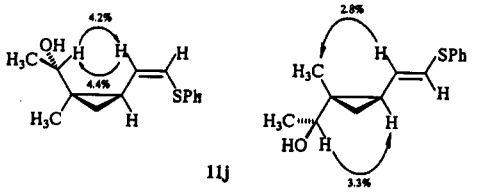
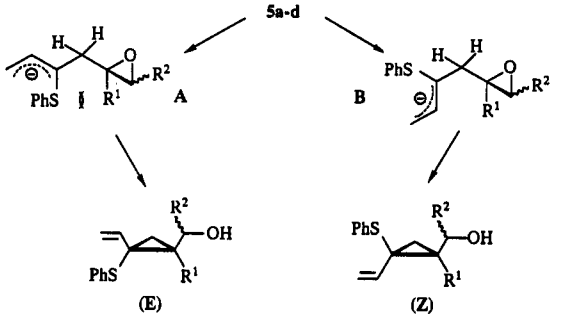
Table I. Cyclization of Epoxides 5, 6, and 9 to 1-Cyclopropylalkanols 11

precursor	reagent	product	R^1	R^2	R^3	R^4	diast ratio	yield (%)
5a	BuLi	**11a**	H	H	SPh	H	4:1	90
	LiDBB	(±)-**11b**	H	H	H	H	3:1	62
5b	BuLi	**11c**	Me	H	SPh	H	20:1	89
	LiDBB	**11d**	Me	H	H	H	6:1	64
(±)-**5c**	BuLi	**11e**	*t*-Me	Me	*r*-SPh	H	>20:1	87
(±)-**5d**	BuLi	**11f**	Me	Me	SPh	H	7:1	81
5e	Bu_4NF	**11g**	H	H	H	$SiMe_3$	4:1	80
5f	Bu_4NF	**11h**	Me	H	H	$SiMe_3$	10:1	54
6a	BuLi	**11i**	H	H	H	SPh	3:2:1.5:1	61
6b	BuLi	**11j**	Me	Me	H	SPh	5.6:4.2:1:1	59
9	Bu_4NF	(±)-**11b**	H	H	H	H	16:1	51
(*S*)-**9**	Bu_4NF	(1*S*,2*R*)-**11b**	H	H	H	H	16:1	63

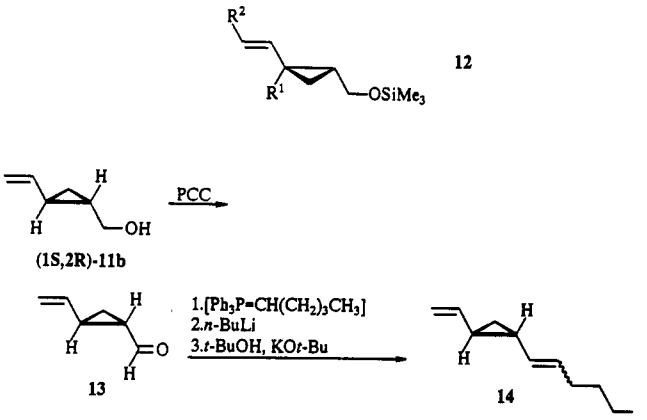
Scheme VI



Scheme VII



Scheme VIII



for this possibility is available.[13] However, reagents such as LiDBB cannot be employed in the tosylate route to vinylcyclopropanes (Scheme I)[1] as tosylate cleavage competes.[14]

Silyl substitution in an allylic position as in alkenyl oxiranes **5e,f,9** allows generation of anions **10** by fluoride-induced desilylation and provides vinylcyclopropanes **11b,g,h** (Scheme V and Table I). Here, ring closure occurs with noteworthy stereoselectivity, particularly starting from allylsilane **9** with its cis C=C unit.

Interestingly, on conventional workup of the reaction mixtures the expected cyclopropylmethanols are contaminated by their silyl ethers **12** (Scheme VIII) confirming the silylating capability of trimethylsilyl fluoride.[15] However, another desilylation step using additional tetrabutylammonium fluoride allows complete conversion into **11b,g,h**.

Synthesis of Dictyopterene A (14). Alkenyl oxiranes **5,9** are formed with control of relative configuration on the heterocyclic ring, and in vinylcyclopropane formation selectivity for trans arrangement of neighboring substituents on the carbocycle can be achieved (Table I). Therefore, it should be possible to transport the absolute configuration of an oxirane **1** into a vinylcyclopropane target. On this basis, an asymmetric synthesis of the natural product dictyopterene A[16] seems feasible. So far, this compound has been synthesized in its natural configuration by separation of enantiomeric precursors[17] or by the aid of a chiral auxiliary[18] or reagent.[19]

By analogy with the conversion of racemic **1b** into racemic vinylcyclopropane **9** (Scheme IV), (*S*)-**1b** can be transformed into the corresponding optically active oxirane (*S*)-**9**. From there, desilylation by fluoride yields cyclopropane (1*S*,2*R*)-**11b** (Table I). VPC using modified γ-cyclodextrin as a chiral stationary phase[20] confirms an enantiomeric excess of 90%. This assessment of enantiomeric purity is particularly convenient as no derivatization is required.

Optically active cyclopropane **11b** can be further elaborated by oxidation using PCC to give aldehyde **13**. For the final step of an *E*-selective olefination, we tried the dianion/reprotonation method.[21] However, in our hands the approach gave only a 1:1 ratio of the C=C diastereomers. The VPC method[20] confirmed the formation of dictyopterene A by comparison with racemic material.[22]

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The enantiomeric purity was 92% for this product and also for the unnatural *Z* isomer.

Conclusion

The present method is an extension of our vinylcyclopropane synthesis via intramolecular tosylate displacement (Scheme I).[1] If the presence of a 1-hydroxyalkyl substituent can be tolerated, intramolecular epoxide ring opening offers several advantages. Noteworthy features are the higher diastereoselectivity and the possibility of enantioselective conversion of optically active oxiranes into the corresponding vinylcyclopropanes. Here, the derivatives with a cis C=C unit appear particularly useful. For the phenylthio-substituted derivatives, the possible use of LiDBB for anion generation provides additional flexibility.

Experimental Section[23]

Starting Materials. (2*S*)-(+)-2,3-Epoxypropyl toluene-4-sulfonate (**1b**) and epichlorohydrin (**1c**) were commercially available (Merck). Epoxy tosylates **1d–f** were obtained from the corresponding epoxy alcohols using standard procedures.[24] The diastereomeric mixture of tosylates **1e,f** (1.6:1) was separated by column chromatography (petroleum ether (PE)/ethyl acetate (3.5:1)). Propargyltrimethylsilane was obtained as described.[25]

1-Chloro-4-(phenylthio)-5-hexen-2-ol (4b) was prepared according to the general procedure in ref 1 using epichlorohydrin and hydrolyzing the reaction mixture with aqueous NH_4Cl, yield 75% (two diastereomers, 1:1) along with 22% of a rearrangement product of type **6**. ^1H NMR (250 MHz; $CDCl_3$): δ 1.65–2.00 (m, 2 H, CH_2CHSPh), 2.33 (broad s, 1 H, OH), 3.48–3.70 (m, 2 H, CH_2Cl), 3.75–3.97, 4.20 (m, 2 H, CHO, CHSPh), 4.98 (m, 2 H, =CH_2), 5.60–5.90 (m, 1 H, CH=), 7.18–7.46 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 38.3, 38.5 (CH_2CHSPh)); 48.6, 48.9 (CHSPh); 50.1, 50.3 (CH_2Cl); 69.0, 69.2 (CHO); 115.5, 115.7 (=CH_2), 127.5–133.2 (CH arom), 133.7, 133.8 (quart C arom), 137.6, 138.6 (*C*=CH_2). Anal. Calcd for $C_{12}H_{15}ClOS$: C, 59.37; H, 6.23; Cl, 14.60; S, 13.21. Found: C, 59.97; H, 6.41; Cl, 13.76; S, 13.49.

4,6-Bis(trimethylsilyl)-1-chloro-5-hexen-2-ol (4c). 1,3-Bis(trimethylsilyl)propene (protonated **2b**, 4.5 g, 24 mmol)[26] was dissolved in THF (100 mL) and the solution cooled to −35 °C. Then *n*-BuLi (2.0 M, 12 mL, 24 mmol) was added dropwise followed by 3.6 mL (24 mmol) of tetramethylethylenediamine (TMEDA). The mixture was stirred at −25 °C for 15 h and cooled again to −35 °C and epichlorohydrin (2.0 mL, 25.5 mmol) added. After being stirred for 2 h at −30 °C, the cold solution was poured into a mixture of PE and aqueous NH_4Cl and the organic layer shaken with saturated brine, dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by column chromatography (PE/ethyl acetate (8:1)), yield 5.3 g (79%) of a colorless liquid which deteriorates on standing (mixture of diastereomers, 2:1*). ^1H NMR (250 MHz; $CDCl_3$): δ −0.06, 0.00* (s, 18 H), 1.5–1.95 (m, 3 H), 2.1, 2.2* (s, 1 H, OH), 3.48 (dd, *J* = 7, 10.8, 1 H, CH_2Cl), 3.52 (dd, *J* = 5.6, 10.8, 1 H, CH_2Cl), 3.62 (dd, *J* = 4, 10.8, 1 H, CH_2Cl), 3.65 (dd, *J* = 3, 10.8, 1 H, CH_2Cl), 3.80, 3.87 (m, 1 H, CHO), 5.50, 5.57 (d, *J* = 18.8, 1 H, =CHSi), 5.84 (dd, *J* = 8.8, 18.8, 1 H, SiCHC*H*=), 5.92 (dd, *J* = 9.2, 18.8, 1 H, SiCH—CH=). ^{13}C NMR ($CDCl_3$): δ −0.97, −1.02 ($Si(CH_3)_3$); 3.41, 3.48 ($Si(CH_3)_3$); 32.67, 32.72 (CH_2); 33.80, 35.38* (CHSiMe_3); 49.30*, 50.55 (CH_2Cl); 70.34, 71.52* (CHOH); 128.23*, 128.34 (*C*=C); 147.29, 147.50* (*C*=C). Anal. Calcd for $C_{12}H_{27}ClOSi_2$: C, 51.67; H, 9.75; Cl, 12.71. Found: C, 52.55; H, 10.09; Cl, 12.06.

5,6-Epoxy-1-hexen-3-yl Phenyl Sulfide (5a). (a) A few mg of 4-toluenesulfonic acid monohydrate were added to a methanolic solution of acetal **4a** (2.89 g, 6.2 mmol) as obtained from **1a** and **2a**.[1] After the solution was stirred at 20 °C for 1 h, the solvent was evaporated under reduced pressure and the residue taken up in dichloromethane and washed with $NaHCO_3$ (2×), water, and saturated brine (2×). After drying ($MgSO_4$) and concentration, the residue was treated with NaOMe in MeOH (25 mL) at 0 °C. The reaction was complete after 1 h as judged by TLC (PE/ethyl acetate (5:1)). Workup was carried out as above. Final column chromatography (PE/ethyl acetate (10:1)) gave a clear oil (58%) (two diastereomers, 1.3:1*). IR (neat): 3050, 1640, 1590, 920, 860 cm^{-1}. ^1H NMR ($CHCl_3$): δ 1.85–1.95 (m, 2 H); 2.54 (dd, *J* = 4.8, 7.6, 1 H); 2.78 (m, 1 H); 3.07*, 3.14 (m, 1 H); 3.82 (m, 1 H); 4.88–5.11 (m, 2 H); 5.63–5.90 (m, 1 H); 7.15–7.53 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 37.4 (CH_2); 47.3, 47.4* (CH_2O); 49.3*, 49.8, 50.0*, 50.3 (CHSPh, CHO); 115.8, 116.7* (=CH_2); 127.3, 127.4*, 128.7, 132.9*, 133.0 (CH arom); 133.8*, 133.9 (quart C arom); 137.5*, 138.1 (CH=). MS: *m/z* (relative intensity) 206 (37, M^+), 175 (16), 110 (100), 109 (38), 79 (53). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 69.84; H, 6.99; S, 15.49.

(b) Starting from **4b**, the same procedure without the deprotection procedure gave again **5a**, yield 70%.

General Procedure for the Synthesis of Alkenyl Sulfides 5b–d from Tosylated Epoxy Alcohols 1d–f. A THF solution of allyl anion **2a** (0.1 M) was prepared by literature methods[1] and at −78 °C added to a THF solution of 1 (0.2 M) via a cooled dropping funnel over a period of 10 min. After being stirred for 1 h at −78 °C, the mixture was hydrolyzed by addition of aqueous NH_4Cl (2 M) and diethyl ether. After separation, the organic layer was washed twice with saturated brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography.

5,6-Epoxy-5-methyl-1-hexen-3-yl Phenyl Sulfide (5b). Column chromatography (PE/ethyl acetate (12:1)) gave a clear oil (76%) (two diastereomers, 1.1:1*). IR (neat): 3077, 3057, 1634, 1584, 1068, 918 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.34, 1.37* (s, 3 H); 1.70–2.20 (m, 2 H); 2.57*, 2.60 (dd, *J* = 1.2*, 4.8*, 1.0, 4.8, 1 H); 2.66, 2.68 (d, *J* = 4.8, 1 H); 3.71 (m, 1 H); 4.80–4.98 (m, 2 H); 5.58–5.80 (m, 1 H); 7.15–7.42 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 20.9, 21.1* (CH_3); 41.4 (CH_2); 49.0, 49.4* (CHSPh), 54.0*, 54.3 (CH_2O); 55.4, 55.43* (OCCH_3); 115.6, 115.9* (=CH_2); 127.3*, 127.4, 128.6, 133.0, 133.1* (CH arom); 133.8, 134.0 (q); 138.1, 138.4* (CH=). MS: *m/z* (relative intensity) 220 (29, M^+), 189 (46), 162 (35), 123 (68), 111 (72), 110 (100), 109 (53). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32; S, 14.55. Found: C, 71.05; H, 7.31; S, 14.60.

(5*r*,6*c*)-5,6-Epoxy-5-methyl-1-hepten-3-yl Phenyl Sulfide (5c). Column chromatography (PE/ethyl acetate (10:1)) gave a clear oil (84%) (two diastereomers, 1.5:1*). IR (neat): 3076, 3058, 1634, 1584, 1025, 988, 918 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.23, 1.29* (d, *J* = 5.6, 5.4*, 3 H); 1.26, 1.32* (s, 3 H); 1.57, 1.74* (dd, *J* = 10.6, 13.6, 8.2*, 14.2*, 1 H); 2.07*, 2.21 (dd, *J* = 7.2*, 14.2*, 4.8, 13.6, 1 H); 2.83*, 2.89 (q, *J* = 5.4*, 5.6, 1 H); 3.70 (m, 1 H); 4.80–4.98 (m, 2 H); 5.59–5.80 (m, 1 H); 7.20–7.45 (m, 5 H). ^{13}C NMR ($CDCl_3$); δ 13.9, 13.92*, 16.4*, 16.7 (CH_3); 43.5*, 43.9 (CH_2); 49.3, 49.7* (CHSPh); 59.1, 59.2* (quart, OCCH_3); 59.6*, 59.7 (CHO); 115.5*, 115.9 (=CH_2); 127.4*, 127.5, 128.8, 133.0*, 133.2 (CH arom); 134.0, 134.3* (q); 138.4, 138.6* (CH=). MS: *m/z* (relative intensity) 234 (32, M^+), 190 (30), 189 (38), 162 (48), 149 (33), 137 (63), 110 (66), 109 (100), 81 (62), 79 (47). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 72.07; H, 7.78; S, 13.94.

(5*r*,6*t*)-5,6-Epoxy-5-methyl-1-hepten-3-yl Phenyl Sulfide (5d). Column chromatography (PE/ethyl acetate (10:1)) gave a clear oil (76%) (two diastereomers, 1.5:1*), contaminated with the rearranged product **6b** (8:1). IR (neat): 3077, 3059, 1635, 1584, 1069, 1026, 919 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.24, 1.32* (d, *J* = 5.6, 3 H); 1.34, 1.37* (s, 3 H); 1.75, 2.05 (dd, *J* = 10.4, 14.0, 5.2, 14.0, 2 H); 1.75 (t, *J* = 15.6, 2 H); 2.80, 2.85* (q, *J* = 5.6, 1 H); 3.75 (m, 1 H); 4.80–4.98 (m, 2 H); 5.61–5.80 (m, 1 H); 7.20–7.45 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 14.4*, 14.6, 22.5*, 22.8 (CH_3); 37.0, 37.2* (CH_2); 49.6, 50.1* (CHSPh), 59.4*, 59.5 (quart. OCCH_3); 60.2*, 60.4 (CHO); 115.6*, 116.2 (=CH_2); 127.5, 128.7*, 128.8, 133.2*, 133.3 (CH arom); 134.0, 134.3* (q); 138.1, 138.5* (CH=). MS: *m/z* (relative intensity) 234 (100, M^+), 190 (27), 189 (41),

(23) General experimental details have been described. See ref 1. *J* values are given in Hz.

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149 (29), 110 (70), 109 (87), 79 (53). HRMS: calcd for $C_{14}H_{18}OS$ 234.1078, found 234.1075.

[2,4-Bis(trimethylsilyl)-3-butenyl]oxirane (5e). (a) KOH (0.15 g, 2 mmol) was added to a solution of chlorohydrin **4c** (0.50 g, 1.8 mmol) in 50 mL of methanol and the resulting solution stirred at room temperature for 3 h. Then the mixture was transferred into a separatory funnel and diluted with PE (50 mL) and saturated aqueous NH_4Cl (50 mL). The organic layer was washed once with saturated brine, dried (Na_2SO_4), and concentrated in vacuo, yield 0.41 g (94%) (two diastereomers, 1.1:1*). IR (neat): 3042, 2954, 1600, 1249, 841 cm^{-1}. ^1H NMR (C_6D_6): δ −0.17, −0.18* ($Si(CH_3)_3$, 9 H); 0.00, −0.02* ($Si(CH_3)_3$, 9 H); 1.22–1.80 (m, 3 H); 2.00–2.09, 2.22–2.35, 2.65–2.74 (m, 1 H each), 5.41*, 5.43 (dd, J = 18.8, 18.8*, 0.9*, 1.2, 1 H); 5.83*, 5.92 (dd, J = 18.8*, 18.8, 8.6*, 8.2, 1 H). ^{13}C NMR (C_6D_6): δ −3.35, −3.39*, −0.9 ($Si(CH_3)_3$); 31.7*, 32.2 (CH_2); 35.3*, 35.6 ($CHSiMe_3$); 46.5*, 47.4 (CH_2O); 51.8*, 51.9 (CHO); 127.0*, 127.5* (=CH); 148.1*, 148.4 (CH=). Anal. Calcd for $C_{12}H_{26}OSi_2$: C, 59.43; H, 10.81. Found: C, 59.68; H, 10.58.

(b) One-pot procedure from **1c**. A solution of 1,3-bis(trimethylsilyl)propene (protonated **2b**, 3.7 g, 19.8 mmol)[26] in THF (150 mL) was cooled to −70 °C. Then a solution of *s*-BuLi (1.3 M, 16 mL, 20.8 mmol) in hexane, kept at −20 °C, was added dropwise and subsequently 3.1 mL (21 mmol) of tetramethylethylenediamine (TMEDA). The mixture was stirred at −38 °C for 4 h and cooled to −78 °C and epichlorohydrin (1.6 mL, 20.4 mmol) added. The mixture was allowed to warm to −60 °C during 2 h and stirred until TLC confirmed the disappearance of protonated **2b** (ca. 2 h). Subsequently, 10 mL of a 1 M solution of KOH (10 mmol) in methanol, kept at −20 °C, was added and the mixture allowed to warm to room temperature overnight. Then the contents of the reaction flask were poured into a mixture of PE (100 mL) and saturated aqueous NH_4Cl (100 mL). The organic layer was washed once with saturated brine, dried (Na_2SO_4), and concentrated in vacuo. The raw material was purified by column chromatography (PE/ethyl acetate (8:1)), yield 2.99 g (62%).

1-[2,4-Bis(trimethylsilyl)-3-butenyl]-1-methyloxirane (5f). A solution of *s*-BuLi (1.3 M, 10 mL, 13 mmol) in hexane was diluted with THF (100 mL). At −78 °C, a mixture of protonated **2b**[26] (2.24 g, 12 mmol) and 1.2 equiv of TMEDA was added. The mixture was stirred at −40 °C for 2 h and kept overnight at −78 °C. The resulting solution of **2b** was added dropwise to a solution of **1d** (2.91 g, 12 mmol) in 100 mL of THF at −78 °C. After being stirred at −78 °C for 15 h, the reaction mixture was poured into a mixture of PE (100 mL) and saturated aqueous NH_4Cl (100 mL). The organic layer was washed once with saturated brine and dried (Na_2SO_4), and the solvents were removed in vacuo. This resulted in separation into two phases. The lower phase was extracted with pentane and combined with the upper phase, and the solvents were removed under reduced pressure. A pure product was obtained by column chromatography (PE/ethyl acetate (8:1)) of the residue and finally distillation in a Kugelrohr apparatus (100 °C/1 Torr), yield 2.0 g (65%) (two diastereomers, 1.1:1*). ^1H NMR ($CDCl_3$); δ −0.08, −0.07*, −0.01*, 0.00 (s, 18 H, $SiCH_3$), 1.21*, 1.25 (s, 3 H, CH_3); 1.58–1.89 (m, 3 H, $CHSiMe_3$ and $SiCCH_2$); 2.44–2.57 (m, 2 H, OCH_2); 5.38*, 5.45 (d, J = 18.4, 1 H, =$CHSiMe_3$); 5.79*, 5.86 (dd, J = 18.4, 18.4*, 8.0, 7.7*, 1 H, CH=$CHSiMe_3$). ^{13}C NMR ($CDCl_3$): δ −3.51, −3.42, −1.03, −1.06 ($SiCH_3$); 20.4*, 22.0 (CCH_3); 34.3, 35.7* (CHSi); 35.2, 36.4* (CCH_2); 53.1, 55.3* (OCH_2); 57.5*, 57.7 ($MeCO$); 126.7, 127.6*; 147.8*, 148.8 (CH=CH). Anal. Calcd for $C_{13}H_{28}OSi_2$: C, 60.87; H, 11.00. Found: C, 60.96; H, 10.76.

Synthesis of the Rearranged Allyl Sulfides 6a,b. The conversion was achieved by refluxing the diastereomeric mixture of **5a,d** with a catalytic amount of azobisisobutyronitrile and 1 equiv of thiophenol in CCl_4 as reported previously.[1]

(*E*)-5,6-Epoxy-2-hexen-1-yl Phenyl Sulfide (6a). Distillation in a Kugelrohr apparatus [bp 75–80 °C (0.1 mmHg)] gave a clear oil (82%). IR (neat) 3051, 1584, 969 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.25 (m, 2 H); 2.37 (dd, J = 2.8, 5.2, 1 H); 2.66 (dd, J = 4.0, 5.2, 1 H); 3.85 (m, 1 H); 3.52 (dd, J = 0.8, 6.4, 2 H); 5.43, 5.70 (m, 2 H); 7.10–7.40 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 35.0, 36.4 (CH_2); 46.4 (CH_2O); 51.2 (CHO); 126.3, 128.0, 128.3, 128.8, 130.2 (arom, olefin CH); 135.8 (arom *C*S). MS: m/z (relative intensity) 206 (100, M^+), 110 (99), 109 (52); 79 (44), 67 (66). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 69.80; H, 6.93; S, 15.56.

(5*r*,6*c*;*E*)-5,6-Epoxy-5-methyl-2-hepten-1-yl Phenyl Sulfide (6b). Column chromatography (PE/ethyl acetate (10:1)) gave a clear oil (63%). IR (neat): 3058, 1584, 1090, 970, 861 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.10 (s, 3 H); 1.21 (d, J = 5.6, 3 H); 2.22 (m, 2 H); 2.73 (q, J = 5.6, 1 H); 3.52 (m, 2 H); 5.50 (m, 2 H); 7.25–7.40 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 14.0, 16.4 (CH_3); 36.3, 41.2 (CH_2); 58.1 (CHO); 60.1 ($OCCH_3$); 126.2, 128.5, 128.6, 128.7, 130.1 (arom, olefin CH); 135.7 (arom *C*S). MS: m/z (relative intensity) 234 (23, M^+), 189 (24), 135 (30), 125 (39), 110 (81), 109 (58), 81 (100). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.87; H, 7.81; S, 13.80.

2-Hydroxy-6-(trimethylsilyl)-4-hexynyl Tosylate (7). Propargyltrimethylsilane (1.67 g, 15 mmol) was dissolved in THF (60 mL), the solution cooled to −78 °C, and *n*-BuLi (9.3 mL, 14.9 mmol) added dropwise. After the mixture was stirred for 10 min, 1 equiv of BF_3·OEt_2 (2.13 g, 15 mmol) was added. After another 10 min, the reaction was quenched with **1b** (1.14 g, 5 mmol) in THF (10 mL) according to the general procedure given above. Column chromatography (PE/ethyl acetate (4:1)) gave 1.12 g of a clear oil (66%). IR (neat): 3524, 2222, 1599, 1363, 1250, 1190, 1178, 1098, 987, 851 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.06 (s, 9 H); 1.35 (t, J = 1.8, 2 H); 2.37 (m, 2 H); 2.42 (s, 3 H); 3.89 (m, 1 H); 4.02 (dd, J = 6.4, 10.0, 1 H); 4.13 (dd, J = 4.0, 10.0, 1 H); 7.35, 7.80 (d, J = 8.4, 4 H). ^{13}C NMR ($CDCl_3$): δ −2.1 ($Si(CH_3)_3$); 6.9 (CH_2SiMe_3); 21.6 (CH_3); 23.9 (CH_2); 68.1 (CHOH); 72.2 (CH_2OTos); 72.4, 81.5 (C≡C); 128.0, 129.9 (arom CH); 132.7, 145.0 (arom CC, CS). Anal. Calcd for $C_{16}H_{24}O_4SiS$: C, 56.44; H, 7.11; S, 9.42. Found: C, 56.32; H, 7.11; S, 9.54.

1,2-Epoxy-6-(trimethylsilyl)-4-hexyne (8). Potassium carbonate (669 mg, 4.84 mmol) was added to a solution of alcohol **7** (1.5 g, 4.4 mmol) in methanol (22 mL). After 2 h, the mixture was diluted with diethyl ether (200 mL), washed (two portions of aqueous NH_4Cl, water, and finally two portions of brine), and dried ($MgSO_4$). After careful concentration, Kugelrohr distillation [bp 100–110 °C (20 mmHg)] gave a clear liquid (89%). IR (neat): 3053, 2224, 1250, 1171, 965, 850 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.07 ($Si(CH_3)_3$); 1.41 (t, J = 2.6, 2 H); 2.50 (m, 2 H); 2.62 (dd, J = 2.4, 5.0, 1 H); 2.74 (dd, J = 3.8, 5.0, 1 H); 3.03 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −2.14 ($Si(CH_3)_3$); 6.90 (CH_2SiMe_3); 22.6 (CH_2); 46.3 (CH_2O); 50.5 (CHO); 72.6, 80.1 (C≡C). Anal. Calcd for $C_9H_{16}OSi$: C, 64.23; H, 9.58. Found: C, 63.88; H, 9.48.

(*Z*)-1,2-Epoxy-6-(trimethylsilyl)-4-hexene (9). To a solution of 589 mg (3.5 mmol) of **8** in *n*-hexane (35 mL) was added 50 mg of Lindlar catalyst. Hydrogenation was carried out at 0 °C until the calculated amount of H_2 (78 mL) was consumed. The solution was filtered, evaporated, and distilled in a Kugelrohr apparatus [bp 95 °C (20 mmHg)] to yield 474 mg (80%) of **9** as a colorless liquid. IR (neat): 3046, 3013, 1647, 1249, 1152, 971, 852 cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.03 (s, 9 H); 1.48 (dd, J = 0.6, 8.8, 2 H); 2.20, 2.35 (m, 1 H each); 2.50 (dd, J = 2.8, 5.2, 1 H); 2.73 (dd, J = 4.0, 5.2, 1 H); 2.92 (m, 1 H); 5.30 (ddd, J = 5.6, 6.8, 10.6, 1 H); 5.55 (ddd, J = 8.6, 8.8, 10.6, 1 H). ^{13}C NMR ($CDCl_3$): δ −1.8 ($(Si(CH_3)_3$); 18.7, 30.0 (CH_2); 46.7 (CH_2O); 51.7 (OCH); 120.6, 128.7 (CH=CH). MS: m/z (relative intensity) 170 (0.4, M^+), 155 (1); 116 (16), 101 (43), 75 (22), 73 (100). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.80; H, 10.80.

General Procedure for the Preparation of Vinylcyclopropanes 11 Using *n*-Butyllithium. Epoxide **5,6** was dissolved in THF (5 mL/mmol) and 1.1 equiv of *n*-BuLi (1.6 M in hexane) was added dropwise at −78 °C. The reaction was very fast and usually complete within 10 min. Consumption of the starting material was followed by TLC (PE/ethyl acetate (3:1)). The orange to red solution was then poured into a 1:3 mixture of saturated aqueous NH_4Cl and diethyl ether. The aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed twice with saturated brine, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by column chromatography or by distillation in a Kugelrohr apparatus (cf. Table I).

[2-Ethenyl-2-(phenylthio)cyclopropyl]methanol (11a). Distillation in a Kugelrohr apparatus [bp 120 °C (0.1 mmHg)] gave a clear liquid (90%) (two diastereomers, 4:1*). The spectroscopic data are consistent with those reported in ref 1.

[2-Ethenyl-1-methyl-2-(phenylthio)cyclopropyl]methanol (11c) is obtained as a mixture of diastereomers (20:1), which was separated by column chromatography (PE/ethyl acetate (4:1)), combined yield 89%. **(1*r*,2*c*)-11c** (higher R_f value). Clear oil (85%). IR (neat): 3369, 3078, 3059, 1629, 1584, 1025, 914, cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.17 (s, 2 H); 1.29 (s, 3 H); 1.70 (br, 1 H); 3.86 (s, 2 H); 5.15, 5.30 (dd, J = 1.2, 10.4, 1.2, 16.8, 2 H); 5.93 (dd, J = 10.4, 16.8, 1 H); 7.15–7.40 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 17.7 (CH_3); 25.7 (CH_2); 32.5, 37.0 (q, CCH_3, CSPh); 68.4 (CH_2O); 116.4 (=CH_2); 125.6, 127.9, 128.8 (arom CH); 136.4 (arom CS); 137.8 (CH=). MS m/z (relative intensity) 220 (19, M^+), 202 (7), 189 (63), 162 (42), 161 (41), 147 (72), 111 (98), 110 (100), 93 (50), 79 (93), 78 (78), 71 (97). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32; S, 14.55. Found: C, 70.64; H, 7.16; S, 14.65.

(1*r*,2*t*)-11c. Clear oil (4%). ^1H NMR ($CDCl_3$): δ 1.04, 1.34 (d, J = 5.6, 2 H); 1.50 (br, 1 H); 1.57 (s, 3 H); 3.55, 3.78 (d, J = 11.6, 2 H); 5.14, 5.27 (dd, J = 1.2, 10.4, 1.2, 16.8, 2 H); 6.05 (dd, J = 10.4, 16.8, 1 H); 7.15–7.40 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 18.4 (CH_3); 25.3 (CH_2); 32.5, 36.9 (q, CCH_3, CSPh); 67.5 (CH_2O); 116.7 (=CH_2); 125.3, 127.6, 128.6 (arom CH); 136.4 (arom CS); 137.2 (CH=).

(*S)-1-[(1*S**,2*S**)-2-Ethenyl-1-methyl-2-(phenylthio)cyclopropyl]ethanol (11e).** Distillation in a Kugelrohr apparatus gave a clear oil (87%) (one diastereomer). IR (neat): 3392, 3078, 3059, 1629, 1584, 1103, 1087, 1067, 923 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.16 (s, 3 H); 1.26 (s, 2 H); 1.27 (d, J = 6.4, 3 H); 1.73 (br, 1 H); 4.13 (q, J = 6.4, 1 H); 5.12, 5.22 (dd, J = 1.4, 10.2, 1.4, 16.8, 2 H); 5.86 (dd, J = 10.2, 16.8, 1 H); 7.10–7.35 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 13.3, 19.9 (CH_3); 28.1 (CH_2); 34.5, 37.4 (CCH_3, CSPh); 72.3 (CHO); 116.4 (=CH_2); 125.6, 128.5, 128.7 (arom CH); 136.2 (arom CS); 137.9 (CH=). MS: m/z (relative intensity) 234 (18, M^+), 216 (23), 201 (35), 190 (30), 189 (70), 162 (89), 161 (66), 147 (67), 129 (72), 125 (65), 110 (70), 109 (51), 81 (60), 79 (70), 71 (100). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.54; H, 7.76; S, 13.69.

(*R)-1-[(1*R**,2*R**)-2-Ethenyl-1-methyl-2-(phenylthio)cyclopropyl]ethanol (11f)** was obtained as a mixture of diastereomers (7:1), which was separated by column chromatography (PE/ethyl acetate (6:1)), combined yield 81%. **(*Z*)-11f** (higher R_f value). Clear oil (71%). IR (neat): 3436, 3078, 3058, 1629, 1584, 1099, 1049, 914 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.02, 1.18 (d, J = 5.6, 2 H); 1.20 (s, 3 H); 1.27 (d, J = 6.4, 3 H); 1.60 (br, 1 H); 4.14 (q, J = 6.4, 1 H); 5.15, 5.27 (dd, J = 1.2, 10.4, 1.2, 16.8, 2 H); 5.96 (dd, J = 10.4, 16.8, 1 H); 7.10–7.40 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 12.9, 19.6 (CH_3); 26.2 (CH_2); 35.6, 38.9 (CCH_3, CSPh); 72.0 (CHO); 116.3 (=CH_2); 125.6, 128.2, 128.7 (arom CH); 136.5 (arom CS); 138.2 (CH=). MS: m/z (relative intensity) 234 (3, M^+), 216 (6), 201 (14), 162 (33), 161 (38), 147 (51), 129 (60), 125 (26), 110 (58), 109 (56), 79 (66), 71 (10). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.83; H, 7.97; S, 13.79.

(*E*)-11f. Clear oil (10%). ^1H NMR ($CDCl_3$): δ 0.99, 1.24 (dd, J = 5.6, 2 H); 1.30 (d, J = 6.4, 3 H); 1.44 (s, 3 H); 2.30 (br, 1 H); 3.61 (q, J = 6.4, 1 H); 5.17, 5.26 (dd, J = 1.4, 10.2, 1.4, 16.8, 2 H); 6.15 (dd, J = 10.2, 16.8, 1 H); 7.10–7.35 (m, 5 H).

[2-[2-(Phenylthio)ethenyl]cyclopropyl]methanol (11i). Column chromatography (PE/ethyl acetate (3:1)) gave a clear oil (61%) (four diastereomers, 3:2:1.5*:1*, with a preponderance of the trans isomers based on the ^{13}C NMR evidence). IR (neat): 3392, 3058, 3002, 1633, 1584, 1045, 1025 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.5–2.0 (m, 4 H), 2.40 (br, 1 H); 3.40–3.85 (m, 2 H); 5.30, 5.58, 5.79 (m, 1 H); 6.05–6.34 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 11.1*, 11.8, 12.1, 12.3* (CH_2); 15.8*, 17.2, 19.0*, 20.0*, 21.2, 23.0, 23.4 (CH); 62.6*, 63.2*, 65.5, 65.6 (CH_2O); 118.3, 120.2, 121.2*, 123.6* (CH=); 125.9, 126.0, 126.2, 128.1, 128.3, 128.8, 128.83, 131.0, 135.3, 136.4, 139.5 (arom CH, =CHSPh); 136.1, 136.3 (arom CS). MS: m/z (relative intensity) 206 (100, M^+), 175 (50), 149 (21), 147 (30), 110 (88), 109 (60), 97 (36), 79 (63). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 69.89; H, 6.91; S, 15.69.

1-[2-[2-(Phenylthio)ethenyl]-1-methylcyclopropyl]ethanol (11j). Column chromatography (PE/ethyl acetate (7:1)) gave a clear oil (59%) (four diastereomers, 5.6:4.2*:1:1). Data of the two main diastereomers. IR (neat): 3392, 3060, 1584, 1105, 1072, 1025, 930, 739, 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.52*, 0.73 (dd, J = 4.8*, 5.2*, 4.7, 5.4, 1 H, CH_2); 0.91*, 0.95 (dd, J = 4.8*, 8.6*, 4.7, 8.0, 1 H, CH_2); 1.09*, 1.13 (s, 3 H, cyclopropyl); 1.21*, 1.23 (d, J = 6.3*, 6.4, 3 H, $CHCH_3$); 1.50* (ddd, J = 5.2, 8.6, 8.8, 1 H, $CHCH$=); 1.60 (broad s, 1 H, OH); 1.72 (dddd, J = 1.0, 4.7, 8.0, 9.2, 1 H, $CHCH$=); 3.15*, 3.41 (q, J = 6.3*, 6.4, 1 H, $CHCH_3$); 5.53 (t, J = 9.2, 1 H, CH=CHSPh); 5.76* (dd, J = 8.8, 14.8, 1 H, CH=CHSPh); 6.20*, 6.24 (dd, J = 0.8*, 14.8*, 1.0, 9.2, 1 H, CH=CHSPh); 7.10–7.40 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 13.0, 17.4, 19.4, 19.5 (CH_3); 20.0*, 22.6 (CH_2); 24.7*, 25.2 (CH cyclopropyl); 28.5*, 28.8 (CCH_3); 72.0, 74.9* (CHO); 120.7*, 123.6 (CH=CHSPh); 126.1–129.0 (arom CH); 131.8, 136.2* (CH=CHSPh); 136.2, 136.6 (quart arom C). MS: m/z (relative intensity) 234 (12, M^+), 216 (3), 190 (29), 189 (38), 147 (25), 129 (26), 111 (14), 110 (29), 109 (18), 107 (26), 91 (32), 85 (72), 80 (50), 79 (100), 77 (38), 65 (17). HRMS: calcd for $C_{14}H_{18}OS$ 234.1078, found 234.1077.

General Procedure for the Preparation of Vinylcyclopropanes 11 Using Lithium Di-*tert*-butylbiphenyl (LiDBB). A solution of LiDBB in THF, prepared according to ref 11a, was cooled to −78 °C. Epoxide **5a** or **b** was dissolved in THF (5 mL/mmol) and added dropwise. A 2-fold excess of LiDBB was used. The reaction was complete within seconds (TLC: PE/ethyl acetate (3:1)) and the mixture worked up as described above for vinylcyclopropanes **11a,c,e,f,j**. The solvent was carefully evaporated and the remaining solid subjected to Kugelrohr distillation. Elemental analyses were obtained after a second distillation.

(±)-[2-Ethenylcyclopropyl]methanol (11b). Kugelrohr distillation [bp 100–130 °C (20 mmHg)] gave a clear liquid (62%) (two diastereomers, 3:1). The spectroscopic data are consistent with the literature values.[12,18]

[2-Ethenyl-1-methylcyclopropyl]methanol (11d). Distillation in a Kugelrohr apparatus [bp 100–130 °C (20–40 mmHg)] gave a clear liquid (64%) (two diastereomers, 6:1*). IR (neat): 3350, 3081, 1635, 1197, 1022, 898 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.44, 0.62* (dd, J = 4.8, 5.6, 5.0*, 5.4*, 1 H); 0.75*, 0.80 (dd, J = 5.0*, 8.0*, 4.8, 8.8, 1 H); 1.15, 1.20* (s, 3 H); 1.41 (m, 1 H); 1.80 (br, 1 H); 3.39 (s, 2 H); 3.45*, 3.64 (d, J = 11.6, 2 H); 5.01 (ddd, J = 0.5, 1.9, 10.2, 1 H); 5.03* (m, 1 H); 5.13, 5.15* (ddd, J = 0.6, 1.9, 17.0, 0.6*, 1.9*, 17.0*, 1 H); 5.59, 5.65* (ddd, J = 8.4, 10.2, 17.0, 8.4*, 10.0*, 17.0*, 1 H). ^{13}C NMR ($CDCl_3$): δ 15.8, 22.1* (CH_3); 17.9, 19.0* (CH_2); 24.9, 25.5* (CCH_3); 25.6, 28.0* (CH); 67.2*, 71.4 (CH_2O); 114.7, 115.1* (=CH_2); 137.4*, 137.6 (CH=). MS: m/z (relative intensity) 112 (0.4, M^+), 97 (2), 94 (8), 81 (28), 79 (26), 58 (100). Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.43; H, 10.99.

General Procedure for the Preparation of Vinylcyclopropanes (±)- and (1*S*,2*R*)-11b,11g,h Using Tetrabutylammonium Fluoride (TBAF). This is a modification of our reported procedure.[1,6] Protodesilylation is avoided by using dried TBAF resulting in higher yields of cyclopropanes. A solution of TBAF·3H_2O in THF (3–4 mL/mmol) was cooled in an ice bath, and 3.1 equiv of freshly distilled hexamethyldisilazane was added slowly. The mixture was stirred overnight at 20 °C and then evaporated to dryness, first at 0 °C and then at room temperature. The resulting white to yellow semisolid was dissolved in THF (2–3 mL/mmol) and a THF solution of epoxides **5e,f,9** (5 mL/mmol) added dropwise at −78 °C. A 3-fold excess of TBAF was used. The reaction mixture was allowed to warm to room temperature overnight, and some TBAF·3 H_2O was added to destroy the silyl ether **12**. After TLC confirmed complete consumption of the byproduct, the red solution was poured into a mixture of diethyl ether (for **11b**) or *n*-pentane (for **11g,h**) and saturated brine. The organic phase was washed with saturated brine (5×) and dried ($MgSO_4$) and the solvent distilled. The residue was purified by column chromatography (*n*-pentane/diethyl ether (3:1) for **11b** or PE/ethyl acetate (5:1) for **11g,h**) and distilled in a Kugelrohr apparatus to afford pure products.

(±)-(2-Ethenylcyclopropyl)methanol (11b). Two diastereomers (16:1), 51% of a clear liquid with the expected spectroscopic data.[12,18]

[2-[(*E*)-2-(Trimethylsilyl)ethenyl]cyclopropyl]methanol (11g). Yield 80% (two diastereomers, 4:1), along with a trace of **11b** formed by protodesilylation. Major isomer. IR (neat): 3336, 3077, 1614, 1407, 1318, 1248, 1053, 1018, 982, 837 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.01 (s, 9 H); 0.64 (dd, J = 6.8, 6.4, 2 H); 1.09–

1.23 (m, 1 H); 1.30–1.41 (m, 1 H); 1.62 (b, 1 H); 3.45 (d, J = 6.8, 2 H); 5.50 (dd, J = 18.4, 8.0, 1 H); 5.66 (d, J = 18.4, 1 H). ^{13}C NMR ($CDCl_3$): δ -1.2 ($SiCH_3$), 12.1 (CH_2); 23.2, 23.5 (CH); 67.0 (CH_2O); 127.3, 148.7 (=CH). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.88; H, 10.92.

[1-Methyl-2-[2-(trimethylsilyl)ethenyl]cyclopropyl]-methanol (11h). Yield 54% (two diastereomers, 10:1*). Main diastereomer. IR (neat): 3339, 3063, 1612, 1446, 1248, 1211, 1027, 984, 837 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9 H); 0.49 (t, J = 5.2, 1 H); 0.78 (dd, J = 8.8, 4.8, 1 H); 1.12 (s, 3 H); 1.32–1.48 (m, 2 H); 3.32 (s, 2 H); 5.65–5.75 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ -1.1 ($SiMe_3$); 15.8 (CH_3); 18.4 (CH_2); 25.6 (CCH_3); 28.2 (CH); 71.7 (CH_2O); 130.5, 145.6 (CH=). MS: m/z (relative intensity) 184 (1.8, M^+), 169 (9). HRMS: calcd for $C_{10}H_{20}OSi$ 184.1283, found 184.1286.

Minor diastereomer. IR (neat): 3350, 1610, 1446, 1248, 1038, 982, 838 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ -1.1 ($SiMe_3$); 22.2 (CH_3); 19.7 (CH_2); 26.4 (CCH_3); 30.7 (CH); 67.4 (CH_2O); 131.2, 145.3 (CH=).

3,5-Dinitrobenzoate of the main isomer. Yield 73%. Mp 110–111 °C. ^{1}H NMR (C_6D_6): δ 0.10 (s, 9 H); 0.40 (t, J = 5.4, 1 H); 0.73 (dd, J = 8.6, 5.0, 1 H); 1.07 (s, 3 H); 1.52 (ddd, J = 8.6, 7.4, 5.4, 1 H); 3.92 (s, 2 H); 5.77 (dd, J = 17.2, 7.4, 1 H); 5.92 (d, J = 17.2, 1 H); 8.47 (s, 1 H); 8.65 (s, 2 H). ^{13}C NMR (C_6D_6): δ -1.1 ($SiMe_3$); 16.2 (CH_3); 18.8 (CH_2); 22.6 (CCH_3); 29.0 (CH); 74.7 (CH_2O); 121.9, 128.6 (arom C); 132.2 (CH=); 133.3 (arom CCOO); 144.6 (CH=); 148.3 (arom CNO_2); 162.4 (C=O).

Synthesis of (1*S*,2*R*)-(2-Ethenylcyclopropyl)methanol (11b). The synthesis of the chiral intermediates was carried out essentially as described for the corresponding racemic material.

(2*S*)-2-Hydroxy-6-(trimethylsilyl)-4-hexynyl Tosylate (7). Stirring the reaction mixture overnight instead of for 1 h improved the yield. By column chromatography, a pale yellow oil was isolated (77%). $[\alpha]_D$ +18.6 (*c* 1.7, $CHCl_3$). Anal. Calcd for $C_{16}H_{24}O_4SiS$: C, 56.44; H, 7.11; S, 9.42. Found: C, 56.45; H, 7.04; S, 9.43.

(2*S*)-1,2-Epoxy-6-(trimethylsilyl)-4-hexyne (8). Kugelrohr distillation gave a clear liquid (91%). $[\alpha]_D$ +24.5 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_9H_{16}OSi$: C, 64.23; H, 9.58. Found: C, 63.90; H, 9.39.

(*Z*)-(2*S*)-1,2-Epoxy-6-(trimethylsilyl)-4-hexene (9). Kugelrohr distillation gave a clear liquid (92%). $[\alpha]_D$ +16.9 (*c* 1.5, $CHCl_3$). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.73; H, 10.92.

(1*S*,2*R*)-11b. Column chromatography and Kugelrohr distillation gave 63% product. $[\alpha]^{22}_D$ +52.2 (*c* 1.0, EtOH abs.) (lit.[18] $[\alpha]^{27}_D$ +54 (EtOH abs.)). GC analysis on a chiral cyclodextrin phase[20a] showed an ee of 90%.

Dictyopterene (14) via (1*S*,2*R*)-2-Ethenylcyclopropane-1-carbaldehyde (13). (1*S*,2*R*)-11b (350 mg, 3.57 mmol) was dissolved in dichloromethane (2 mL) and added to a solution of PCC (2.3 g, 6.0 mmol) in dichloromethane (15 mL) at 0 °C. After being stirred overnight, the reaction mixture was filtered, the residue carefully washed with dichloromethane, and the filtrate concentrated. The residue was purified by filtration through silica gel (10 g) using a mixture of pentane/diethyl ether (5:1) as eluent to give crude 13. IR (neat): 1708 cm^{-1}.

At -78 °C, a solution of the isolated material in diethyl ether was added to a solution of the ylide as obtained from *n*-pentyltriphenylphosphonium bromide (1.86 g, 4.5 mmol) and *n*-BuLi (2.8 mL, 4.5 mmol) in diethyl ether (5 mL) and THF (10 mL). After the solution was stirred for 5 min, another equiv of *n*-BuLi was added and the mixture allowed to warm to -30 °C. After 10 min, the mixture was diluted with 2-methyl-2-propanol (371 mg, 5 mmol) and, after 20 min, KO-*t*-Bu (673 mg, 6 mmol) added. The reaction mixture was stirred overnight, diluted with pentane/diethyl ether (100 mL, 1:1), and water (15 mL) added. The organic layer was washed with water (2×) and saturated brine (2×). After drying ($MgSO_4$), the solution was carefully concentrated and filtered through silica gel (10 g). Kugelrohr distillation yielded a clear liquid (256 mg, 43%) (two diastereomers, *E*:*Z* = 1:1*). The data of the *E* isomer are consistent with the literature values.[18,27] IR (neat): 3083, 3002, 1636, 961, 895, 725 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.63* (dt, J = 5.0, 8.4, 1 H, cyclopropyl CH_2); 0.67* (t, J = 7.0, 2 H, cyclopropyl CH_2); 0.74* (dt, J = 4.9, 8.4, cyclopropyl CH_2); 0.87 (m, 3 H, CH_3); 1.28 (m, 5 H, 4 H alkyl CH_2 + 1 H cyclopropyl CH); 1.57* (m, 1 H, cyclopropyl CH); 1.92–2.05 (m, 2 H, allyl); 4.75–5.08 (m, 3 H, olefin); 5.26–5.50 (m, 2 H, olefin). ^{13}C NMR ($CDCl_3$): δ 13.93, 13.95 (CH_3); 14.7, 15.4 (cyclopropyl CH_2); 19.8*, 23.6, 24.3, 24.5* (cyclopropyl CH); 22.2, 22.3*, 27.4, 31.8, 31.9*, 32.2 (CH_2); 111.8, 111.9* (=CH_2); 129.1, 129.2*, 131.6, 131.7*, 140.6*, 140.8 (=CH).

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