Synthesis of Vinylcyclopropanes from Epoxides

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Ring-opening of epoxides **1** by heteroatom-substituted allyl anions **2** occurs with high regioselectivity. In situ tosylation of the resulting alkoxides **3** or tosylation of the corresponding alcohols **4** yields 4-pentenyl tosylates **5**. Anion generation by deprotonation or desilylation gives vinylcyclopropanes **9** by an S_{Ni} process. The approach allows annulation of vinylcyclopropanes onto existing five- and six-membered rings and synthesis of vinylcyclopropanes with functionality on the olefin.

Introduction

Vinylcyclopropanes are interesting synthetic intermediates.[1] Their most important application is the formal [1,3] sigmatropic rearrangement to cyclopentenes,[2] but their use in ring-opening,[3] ring-enlargement,[4] or cycloaddition reactions[5] is also noteworthy. Because of their synthetic potential, various routes to vinylcyclopropanes have been devised. Most frequently, vinylcyclopropanes are obtained by elaboration of the exocyclic C=C unit by elimination[6] or olefination reactions.[7] Alternatively, cyclopropane formation is the key step which occurs by a cycloelimination reaction[8] or by addition of carbenes/carbenoids to dienes.[9] In comparison, relatively few methods have been reported in which the vinylcyclopropane is generated by the addition of an activated C_3 building block in the form of a vinylcarbene or vinylcarbenoid to an alkene.[10] In the present study, we present a particularly efficient and versatile modification of this approach employing epoxides as activated alkene equivalents and second-row heteroatom-stabilized allyl anions.

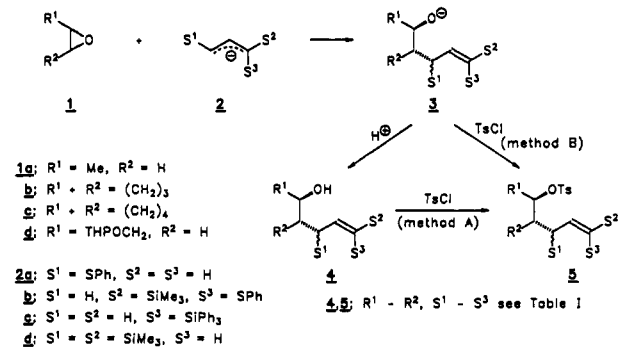
Results and Discussion

Synthesis of Tosylated Alkenols 5. Deprotonation of allyl sulfides or allyl silanes by *n*- or *sec*-butyllithium is a facile process. The resulting anions **2a–d** react readily with epoxides **1** to give ring-opened alkoxides **3** (Scheme I). In this reaction, the allylic carbanions show high regioselectivity. Thus, in line with some indications in the literature,[11] the sulfur-substituted anion **2a** reacts at the α-carbon with a preference of at least 8:1, yielding, after protonation, 3-(phenylthio)-4-alkenols **4a–d** (Table I); the minor γ-isomer can be removed by chromatography. In contrast, the silyl-substituted species **2c** opens cyclohexene oxide specifically at the γ-carbon of the allyl anion.[12] The same regioselectivity is observed for allyl derivative **2b** with mixed substitution by sulfur and silicon. It should be noted that the required precursor, protonated **2b**, can be obtained from protonated **2c** by the action of phenylsulfenyl chloride in 44% yield (cf. Experimental Section).

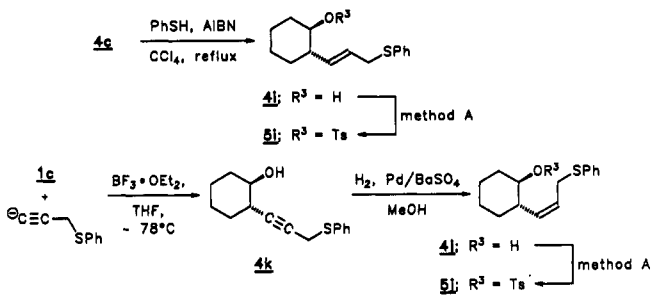
As expected, opening of epoxides **1b,c** is a clean process with trans stereochemistry. Reaction of the allyl anion at its α-carbon leads to a new stereocenter. According to the NMR spectral evidence, alcohols **4a–d,g,h** are obtained as mixtures of diastereomers. For the silyl-substituted derivative **4h**, the ratio of diastereomers is 3.5:1, although unambiguous assignment of stereochemistry or relative configuration was not possible. In **4g** overlap of NMR signals prevented determination of the ratio.

The range of available alkenols **4** can be further extended by exploiting the ready 1,3 shift of the phenylthio group in allylic systems.[13] Thus, heating of alkenol **4c** with thiophenol in the presence of AIBN in refluxing carbon tetrachloride gave a smooth conversion into isomer **4i** with a terminal sulfur substituent. From the fairly large allylic ^3J coupling of 15.1 Hz, the trans configuration of the

Scheme I



Scheme II



Scheme III

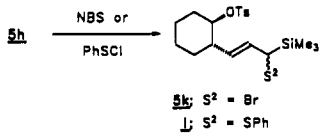


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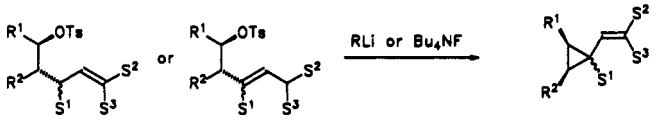
Table I. Synthesis of Tosylated Alkenols 5 (See Schemes I and II)

R^1	R^2	S^1	S^2	S^3	product	yield, %	method[a]	product	α/γ ratio	yield %
Me	H	SPh	H	H	**4a**	80	B	**5a**	8	62
$-(CH_2)_3-$		SPh	H	H	**4b**	82	A	**5b**	8	70
$-(CH_2)_4-$		SPh	H	H	**4c**	88	A (B)	**5c**	10	71 (65)
$THPOCH_2$	H	SPh	H	H	**4d**	71	B	**5d**	8	71
$-(CH_2)_4-$		H	$SiMe_3$	SPh	**4e**	–	B	**5e**	<0.1	35
$-(CH_2)_4-$		H	$SiPh_3$	H	**4f**	94	A	**5f**	<0.1	80[c]
$-(CH_2)_3-$		$SiMe_3$	$SiMe_3$	H	**4g**	59[c]	A	**5g**	–	70
$-(CH_2)_4-$		$SiMe_3$	$SiMe_3$	H	**4h**	78	A	**5h**	–	84
–		–	–	–[d]	**4i**	82	A	**5i**	–	79
–		–	–	–[d]	**4j**	83	A	**5j**	–	84

[a] Method A: alcohols 4 were isolated and subsequently tosylated. [b] Method B: tosylation of 3 was carried out in situ. [c] Crude yield given as the product tends to give protodesilylation on attempted purification. [d] See Scheme II.

Table II. Cyclization of Tosylates 5 or Epoxides 10 to Vinylcyclopropanes 9



5a - h **5i - l** **9a - l**

precursor	reagent	product	R^1	R^2	S^1	S^2	S^3	endo/exo	E/Z	yield %
5a	BuLi	**9a**	Me	H	SPh	H	H	2.3	–	70
5b	BuLi	**9b**	$-(CH_2)_3-$		SPh	H	H	2.7	–	84
5c	BuLi	**9c**	$-(CH_2)_4-$		SPh	H	H	6.3	–	68
5d	BuLi	**9d**	$HOCH_2$	H	SPh	H	H	1.1[a]	–	55[b]
5e	*sec*-BuLi	**9e**	$-(CH_2)_4-$		H	$SiMe_3$	SPh	<0.1	<0.1	54
5f	*sec*-BuLi	**9f**	$-(CH_2)_4-$		H	$SiPh_3$	H	<0.1	>10	82
5g	Bu_4NF	**9g**	$-(CH_2)_3-$		H	$SiMe_3$	H	0.3	>10	54[c]
5h	Bu_4NF	**9h**	$-(CH_2)_4-$		H	$SiMe_3$	H	<0.1	>10	61[c]
5i	BuLi	**9i**	$-(CH_2)_4-$		H	SPh	H	<0.1	1	67
5j	BuLi	**9i**	$-(CH_2)_4-$		H	SPh	H	<0.1	>8	90
5k	BuLi	**9h**	$-(CH_2)_4-$		H	$SiMe_3$	H	<0.1	>10	64
5k	Bu_4NF	**9j**	$-(CH_2)_4-$		H	Br	H	<0.1	0.3	51[c]
5l	BuLi	**9e**	$-(CH_2)_4-$		H	$SiMe_3$	SPh	<0.1	<0.1	80
5l	Bu_4NF	**9i**	$-(CH_2)_4-$		H	SPh	H	<0.1	1.2	40[c]

[a] We presume the predominant isomer to be the one with the phenylthio group in the endo (cis) position. [b] Overall yield including deprotection. [c] Protodesilylation is a side reaction.

double bond is deduced (Scheme II and Table I). The tosyl derivative of the corresponding cis compound **5j** is obtained by partial hydrogenation of alkyne **4k** (Scheme II and Table I).

Formation of carbocycles **9** from alcohols **4** requires conversion of the hydroxy function into a leaving group, and it developed that the tosyl group ideally suited our needs (vide infra). In one approach, isolated alcohols **4** were tosylated in the presence of 4-(dimethylamino)-pyridine to provide tosylates **5** (see Scheme I and Table I, method A). Alternatively, the tosyl group can be introduced in a one-pot reaction by adding tosyl chloride to alkoxides **3a–e** after they are formed as primary ring-opening products from epoxides **1** and anions **2** (Scheme I and Table I, method B). Finally, we were able to show for the example of **9b** that the overall transformation starting from **2b** can be carried out as a one-pot reaction giving a reasonable yield.

At the stage of the tosylate, the allyl silane moiety in the bis-silylated compounds offers the opportunity to replace one silyl group by another substituent. Thus, reaction of **5h** with *N*-bromosuccinimide (NBS) or phenylsulfenyl chloride converts **5h** into the multifunctional products **5k,l** (Scheme III).

Attempted Cyclization of 3h in a Homo-Peterson Reaction. Cyclization of the 3-silyl-substituted alkenol **4h** might proceed via a 1,4-C→O silyl shift at the stage of its anion **3h** giving **6** and from there annulation of a three- or five-membered ring might occur in an intramolecular displacement reaction of the siloxy group (Scheme IV). Mechanistically, this would correspond to a homo-Peterson reaction which has been verified for a single case[14] and,

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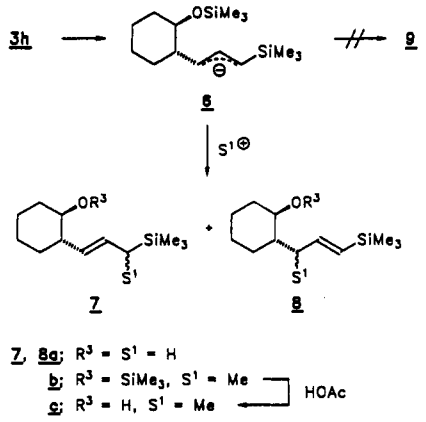
Scheme IV



very recently, shown to have a broader application.[15] However, when anion **3h** was generated from **4h** by treatment with a catalytic amount of sodium hydride and the reaction mixture hydrolyzed, the monodesilylated alcohols **7a**, **8a** were formed in a 1:8 ratio. A possible rationale is that the desired silyl shift to **6** does occur, but that the cyclization fails and **7a**, **8a** are formed via hydrolysis of the silyl ether moiety on work up.

Formation of **6** was verified in an independent experiment, in which **3h** was generated from **1c** and **2d**, and the reaction mixture was stirred at room temperature for several hours. Addition of iodomethane now led to silyl ether **7b** obviously via regiosepecific α-methylation of intermediate **6**. However, all attempts to induce a cyclization of **6** failed. Consequently, we turned our attention to derivatives with a better leaving group, i.e. tosylates **5**.

Generation of Anions from 5 and Cyclization. Deprotonation of tosylates **5a–f,i,j** proceeded smoothly by the action of *n*- or *sec*-butyllithium at low temperature. Alternatively, fluoride-induced monodesilylation of silyl derivatives **5g,h,k,l** is possible affecting only the silyl group in the allylic position of **5g,h** and leading to silyl-stabilized allyl anions. As shown by the formation of **9h** (vide infra), butyllithium induces a halogen/metal exchange in **5k**, yielding the same anion as obtained by desilylation of **5h**.

Independent of their generation, the deprotonated tosylates underwent immediate intramolecular nucleophilic attack on the tosylate moiety yielding vinylcyclopropanes **9** (Table II). In accord with expectations,[16] this ring closure is regiospecific for the formation of cyclopropanes and cyclopentenes were never observed.

It should be noted that, in the presence of a terminal trimethylsilyl group, only one configuration at the exocyclic double bond is detected probably indicating specific formation of the sterically more favored isomer (Table II).

In conclusion, we have shown that epoxides and allylic anions are very convenient building blocks for vinylcyclopropane synthesis. Vinylcyclopropanation occurs irrespective of the mode of anion generation and of the substitution pattern. Moreover, ring closure is regiospecific and occurs with considerable stereoselectivity.

Experimental Section

General Methods. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Pyridine and CH_2Cl_2 were distilled from calcium hydride. All other solvents and reagents were used without further purification. Column chromatography was carried out on Merck silica gel (70–230 mesh) unless indicated otherwise. Petroleum ether (PE) with the boiling range 60–70 °C was always used in the separations. Analytical TLC was performed on 0.2-mm silica 60 coated aluminum plates (Merck). Temperatures given for Kugelrohr distillations are oven temperatures. Melting points were determined on a Leitz hot stage and are uncorrected.

^1H and ^{13}C NMR spectra were obtained on a Bruker WP 80-FT, WH 270, WM 250, or WM 400 spectrometers; coupling constants, *J*, are given in hertz. Assignments of ^{13}C NMR signals were supported by broad band decoupled DEPT. Electron impact mass spectra were recorded at 70 eV.

Starting Materials. Epoxides 1a–c are commercially available; epoxide **1d** was prepared from the corresponding alkene using 3-chloroperoxybenzoic acid.[17] The precursors of **2a**,[18] **2c**,[19] and **2d**[20] were prepared by literature methods. Alcohol **4f** was obtained as described previously.[12]

3-(Phenylthio)-3-(trimethylsilyl)-1-propene (Protonated 2b). 1,3-Bis(trimethylsilyl)propene (**2d**, 10 mmol)[20] was dissolved in CH_2Cl_2, and a solution of PhSCl (0.8 equiv) in CCl_4 was added rapidly at −70 °C with vigorous stirring. The reaction mixture became colorless within 10 min and was then poured into a saturated $NaHCO_3$ solution which had been covered with a layer of *n*-pentane. The organic phase was washed twice with saturated brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting product was purified by column chromatography with PE/toluene (50:1). A contamination of 20% 1-(phenylthio)-3-(trimethylsilyl)-1-propene could not be removed by distillation [bp 82–87 °C (0.3 mmHg)]. The combined yield was 0.97 g (44%). The spectroscopic data are consistent with the literature values.[22]

Using the same procedure, **5h** (6.9 mmol) was converted into **2-[3-(phenylthio)-3-(trimethylsilyl)-1-propenyl]-1-cyclohexyl tosylate (5l)** as a pale yellow oil after column chromatography with PE/ethyl acetate (first 6:1, then 10:1). Yield 1.08 g (31%), only one diastereomer was isolated: IR (neat) 3050, 1595, 1575, 1360, 1180, 1170, 1240, 865, 835 cm^{-1}; ^1H NMR (C_6D_6) δ 0.21 (s, 9 H), 0.60–1.94 (m, 12 H, overlapping at 1.91 with s, 3 H), 3.15 (m, 1 H), 4.30 (m, 1 H), 5.35 (m, 2 H), 6.67–7.88 (m, 9 H); ^{13}C NMR (C_6D_6) δ −2.6 ($Si(CH_3)_3$), 21.2 (CH_3), 23.9, 24.1, 31.3, 32.0 (CH_2), 38.8 (CH), 45.6 (CHSPh), 84.7 (CHOTos), 125.8, 127.8, 128.8, 129.7, 130.2, 130.4, 131.6 (arom), 136.4, 137.8, 143.9 (q).

General Procedure for the Synthesis of Alcohols 4b,c,f–h from Epoxides 1. Protonated **2** (10 mmol) was dissolved in 50 mL of THF (for the generation of **2d**, 1 equiv of tetramethylethylenediamine (TMEDA) was added). After cooling to −78 °C, the solution was treated with 1.1 equiv of *n*-BuLi (for **2a,c**) or *sec*-BuLi (for **2d**) in hexane and stirred at this temperature (for **2a**) or at −40 °C (for **2c,d**) during 4 h. The mixture was cooled again to −78 °C, 1.1 equiv of **1** was added dropwise, and over 2 h (5 h for **4g**) the mixture was allowed to warm to −30 °C or left at −78 °C for 2–4 h (in case of **4b** and **4c**; see Formation of Tosylates **5** by in situ Tosylation). Then hydrolysis was carried out with a mixture of saturated aq NH_4Cl solution, *n*-pentane, and diethyl ether (0.5:1:1/250 mL). The organic layer was washed twice with saturated brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography.

2-[1-(Phenylthio)-2-propenyl]-1-cyclopentanol (4b) was isolated from the reaction of **2a** with cyclopenteneoxide and purified by Kugelrohr distillation ($bp_{0.01}$ 120 °C), pale yellow oil 82%, two diastereomers (2:1*) and minor impurities from the γ-adduct: IR (neat) 3350, 3060, 1630, 1580, 740, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–2.12 (m, 7 H), 2.45 (br, 1 H, OH), 3.52 (m, 1 H), 4.14 (m, 1 H), 4.80–4.95 (m, 2 H), 5.60–5.88 (m, 1 H), 7.16–7.47 (m, 5 H); ^{13}C NMR ($CDCl_3$) 22.1, 22.2, 28.6*, 28.7, 34.6*, 34.8* (CH_2), 51.2, 51.6* (CH), 56.9*, 57.1 (CHSPh), 76.3*, 77.3 (CHOH), 115.9*, 116.0 ($CH{=}CH_2$), 127.0*, 127.2, 128.6*, 128.7, 132.7*, 132.9 (arom), 134.3, 134.6* (q), 136.9, 138.1* ($CH{=}CH_2$); MS *m/z* (relative intensity) 234 (M^+, 9.3), 216 (0.9), 124 (14), 110 (100),

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55 (26). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.77; H, 7.68; S, 13.48.

2-[1-(Phenylthio)-2-propenyl]-1-cyclohexanol (4c): colorless oil after chromatography (PE/ethyl acetate, 6:1), 88%, two diastereomers, 3.2:1*: IR (neat 3350, 3050, 1630, 1580, 730, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95–1.37 (m, 9 H), 2.48 (br, 1 H), 3.35, 3.75* (m, 1 H), 4.17*, 4.26 (m, 1 H), 5.05 (m, 2 H), 5.68–6.02 (m, 1 H), 7.05–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.8*, 24.9, 25.6, 25.7*, 26.1, 26.8*, 35.8*, 36.1 (CH_2), 49.6, 50.2* (CH), 53.6, 54.4* (CHSPh), 71.2*, 71.9 (CHOH), 115.8*, 117.0 ($CH{=}CH_2$), 126.6*, 126.7, 128.6, 131.8*, 132.0 (arom), 135.6 (q), 135.8, 138.0* ($CH{=}CH_2$); MS m/z (relative intensity) 248 (M^+, 12.4), 230 (3), 150 (16), 149 (14), 135 (14), 110 (100), 109 (16), 79 (16). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12; S, 12.91. Found: C, 72.31; H, 8.19; S, 12.99.

2-[3-(Triphenylsilyl)-2-propenyl]-1-cyclohexanol (4f): pale yellow solid which after recrystallization from hexane gave colorless needles (mp 91 °C), 94%: IR (KBr) 3430, 1615, 1585, 1425, 1110, 740, 725, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91–2.22 (m, 11 H), 2.73 (m, 1 H), 3.28 (m, 1 H), 6.27 (m, 2 H), 7.36–7.69 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 24.9, 25.5, 30.5, 35.6, 40.7 (CH_2), 42.4 (CH), 74.5 (CHOH), 125.5 ($CH{=}CHSiPh_3$), 127.8, 129.4, 135.9 (arom), 134.9 (q), 151.9 ($CH{=}CHSiPh_3$). Anal. Calcd for $C_{27}H_{30}OSi$: C, 81.35; H, 7.59. Found: C, 81.37; H, 7.49.

(*E*)-2-[1,3-Bis(trimethylsilyl)-2-propenyl]-1-cyclopentanol (4g) can be separated into diastereomers by column chromatography with PE/ethyl acetate, although with substantial protodesilylation. For the subsequent tosylation, it is sufficient to distill the crude material in a Kugelrohr apparatus. Combined yield 58%. Isomer with higher R_f value: IR (neat) 3340, 1595, 1240, 860, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.02, 0.02 (2 s, 18 H), 1.11–1.97 (m, 9 H), 3.89 (m, 1 H), 5.58 (d, J = 18.0, 1 H) 6.04 (dd, J = 18.0, 9.9, 1 H); ^{13}C NMR ($CDCl_3$) δ –1.7, –1.0 (2 $Si(CH_3)_3$), 21.7, 31.1, 33.4 (CH_2), 44.6, 48.5 (CH), 80.4 (CHOH), 129.1, 148.8 ($CH{=}CH$); MS m/z (relative intensity) 270 (M^+, 0.4). Isomer with lower R_f value: IR (neat) 3320, 1595, 1240, 860–830 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.02, 0.02 (2 s, 18 H), 1.20–1.92 (m, 9 H), 3.84 (m, 1 H), 5.51 (d, J = 18.4, 1 H), 5.88 (dd, J = 18.4, 9.6, 1 H); ^{13}C NMR (C_6D_6) δ –1.9, –0.7 (2 $Si(CH_3)_3$), 22.6, 28.5, 35.0 (CH_2), 41.0, 48.6 (CH), 77.5 (CHOH), 128.7, 146.3 ($CH{=}CH$). Anal. Calcd for $C_{14}H_{30}OSi_2$: C, 62.15; H, 11.18. Found: C, 62.41; H, 11.01.

(*E*)-2-[1,3-Bis(trimethylsilyl)-2-propenyl]-1-cyclohexanol (4h) is obtained as a mixture of diastereomers (3.5:1), which can be separated and used as indicated for **4g**. Combined yield 78%. Isomer with higher R_f value (minor): oil; IR (neat) 3420, 1595, 1240, 860, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.01, 0.05 (2 s, 18 H), 1.03–1.93 (m, 10 H), 2.22 (br, 1 H), 3.41 (m, 1 H), 5.51 (d, J = 18.0, 1 H), 6.01 (dd, J = 18.0, 9.2, 1 H). Isomer with lower R_f value (major): mp 59 °C; IR (KBr) 3420, 1600, 1250, 870, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.02, 0.04 (2 s, 18 H), 1.08–1.98 (m, 10 H), 2.23 (br, 1 H), 3.26 (m, 1 H), 5.54 (d, J = 18.0, 1 H), 5.98 (dd, J = 18.4, 9.0, 1 H); ^{13}C NMR ($CDCl_3$) δ –2.1, –0.9 (2 $Si(CH_3)_3$), 25.1 26.2, 28.1, 35.1 (CH_2), 39.2, 45.8 (CH), 72.3 (CHOH), 130.3, 144.6 ($CH{=}CH$); MS m/z (relative intensity) 211 (M^+, 0.1), 194 (7), 179 (16), 120 (41), 73 (100). Anal. Calcd for $C_{15}H_{32}OSi_2$: C, 63.31; H, 11.33. Found: C, 63.67; H, 11.30.

(*E*)-2-[3-(Phenylthio)-1-propenyl]-1-cyclohexanol (4i). Refluxing the diastereomeric mixture of **4c** in CCl_4 analogous to ref 13 with 0.5 equiv of azobisisobutyronitrile (AIBN) and 1 equiv of thiophenol gave, after chromatography, 71% of **4i** as a colorless oil. No *Z* isomer could be detected in the ^1H NMR spectrum: IR (neat) 3400, 3050, 1585, 1050, 740, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92–2.08 (m, 10 H), 3.02 (dt, J = 4.0, 9.8, 1 H), 3.50 (d, J = 6.9, 2 H), 5.27 (dd, J = 8.7, 15.1, 1 H), 5.52 (ddd, J = 7.0, 7.1, 15.1, 1 H), 7.09–7.48 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.1, 31.2, 33.7, 36.7 (CH_2), 49.6 (CH), 73.0 (CHOH), 126.5 ($CH{=}CHCH_2$), 127.3, 128.7, 130.8 (arom), 135.3 (q), 135.8 ($CH{=}CHCH_2$); MS m/z (relative intensity) 248 (M^+, 4.9), 230 (1), 139 (7), 138 (12), 121 (12), 110 (100), 109 (14), 84 (30). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12; S, 12.91. Found: C, 72.33; H, 7.93; S, 13.46.

(*Z*)-2-[3-(Phenylthio)-1-propenyl]-1-cyclohexanol (4j). According to ref 23, 25 mmol of *n*-BuLi (1.6 M in hexane) was added to 25 mmol of propargyl phenyl sulfide (obtained from propargyl chloride and sodium thiophenolate[24] in 81% yield) in THF (100 mL) at –78 °C. After the mixture was stirred for 10 min, 1 equiv of $BF_3{\cdot}OEt_2$ was added, and after another 10 min, 20 mmol of cyclohexene oxide. After 30 min at –78 °C, the reaction mixture was worked up as described for **4b**. Column chromatography gave **2-[3-(phenylthio)-1-propynyl]-1-cyclohexanol (4k)** in 89% yield as a pale yellow oil: IR (neat) 3420, 3058, 2205, 1584, 1068, 741, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.15 (m, 10 H), 3.31 (dt, J = 4.2, 9.2, 1 H), 3.61 (d, J = 2.2, 2 H), 7.18, 7.56 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.1, 24.0, 24.6, 30.7, 32.9 (CH_2), 38.9 (CH), 73.3 (CHOH), 77.8, 85.1 (q), 126.9, 128.8, 130.4 (arom), 134.9 (q); MS m/z (relative intensity) 246 (M^+, 30), 123 (7), 110 (100), 109 (22), 91 (15), 81 (18). Anal. Calcd for $C_{15}H_{18}OS$: C, 73.13; H, 7.37; S, 13.02. Found: C, 73.25; H, 7.48; S, 12.99. To a solution of 3 g (12.18 mmol) of **4k** in 25 mL of methanol was added 200 mg of $Pd/BaSO_4$ (10%). Hydrogenation was carried out at room temperature over 1 week; after 3 days, another 200-mg portion of catalyst was added. The solution was filtered, and the residue was washed thoroughly with diethyl ether. The solution was washed twice with saturated brine, dried ($MgSO_4$), and concentrated in vacuo. The remaining orange oil was distilled in a Kugelrohr apparatus ($bp_{0.01}$ 125 °C) to yield 2.51 g (83%) of **4j** as a colorless oil. No trace of **4i** could be detected in the ^1H NMR spectrum: IR (neat) 3425, 3058, 3010, 1585, 1089, 1041, 739, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98–2.08 (m, 10 H), 3.18 (dt, J = 4.4, 9.8, 1 H), 3.55 (ddd, J = 1.2, 7.4, 13.0, 1 H), 3.69 (ddd, J = 1.0, 8.0, 13.0, 1 H), 5.32 (dd, J = 10.4, 10.8, 1 H), 5.70 (dt, J = 7.8, 10.8, 1 H), 7.10–7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.0, 31.3, 31.8, 33.8 (CH_2), 44.9 (CH), 73.5 (CHOH), 126.5 ($C{-}H{=}CHCH_2$), 127.3, 128.1, 130.5 (arom), 135.7 (q), 135.3 ($CH{=}CHCH_2$); MS m/z (relative intensity) 248 (M^+, 18), 230 (7), 139 (11), 138 (15), 121 (32), 110 (100), 109 (33). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12; S, 12.91. Found: C, 72.74; H, 8.17; S, 13.06.

Attempted Homo-Peterson Reaction of 4h. Formation of 7a, 8a. NaH (0.06 g, 0.25 mmol) was suspended in THF (25 mL) at –5 °C. With stirring, 15-crown-5 (4 drops) and alcohol **4h** (0.56 g, 2 mmol) were added. After 30 min, the mixture was diluted with diethyl ether (15 mL) and hydrolyzed by addition of water (10 mL). The organic layer was separated and washed with two portions of HCl (0.5 N) and then with a saturated aqueous $NaHCO_3$ solution and finally with brine. After drying over Na_2SO_4, the solvents were removed under reduced pressure and the residue was purified by column chromatography with PE/ethyl acetate (4:1). Two products could be extracted:

(*E*)-2-[3-(Trimethylsilyl)-1-propenyl]-1-cyclohexanol (7a): colorless oil; yield 0.32 g (76%); IR (neat) 3380, 1645, 1240, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.05 (s, 9 H), 1.02–1.29 (m, 4 H), 1.40 (d, J = 6.0, 2 H), 1.52–1.83 (m, 4 H), 1.89–2.13 (m, 2 H), 3.10 (m, 1 H), 5.02 (dd, J = 18.4, 6.0, 1 H), 5.49 (dt, J = 18.4, 6.0, 1 H). Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.88; H, 11.06.

(*E*)-2-[3-(Trimethylsilyl)-2-propenyl]-1-cyclohexanol (8a): colorless oil; bp 75 °C (0.5 mmHg); yield 0.04 g (9 %); IR (neat) 3350, 1615, 1240, 855, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 0.88–1.99 (m, 10 H), 2.50 (m, 1 H), 3.18 (m, 1 H), 5.63 (d, J = 18.6, 1 H), 5.99 (dt, J = 6.0, 18.6, 1 H); ^{13}C NMR ($CDCl_3$) δ –1.3 ($Si(CH_3)_3$), 24.8, 25.4, 30.3, 35.4, 40.4 (CH_2), 44.7 (CH), 74.3 (CHOH), 131.7, 145.6 ($CH{=}CH$); Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.95; H, 11.31.

Interception of 3h with Iodomethane. Formation of 7,8b and 7,8c. According to the general procedure, alkoxide **3h** was generated from **2d** and cyclohexeneoxide (20 mmol). The reaction mixture was allowed to warm to room temperature. After 8 h, iodomethane (30 mmol) was added to the solution resulting in a color change from deep red to a pale yellow. After hydrolysis with a saturated aqueous solution of $NaHCO_3$, washing of the organic phase with water, drying ($MgSO_4$), and concentration in vacuo, a residue (3.99 g) was obtained which was distilled in a Kugelrohr apparatus giving a mixture of **2-[3-(trimethylsilyl)-2-butenyl]-1-cyclohexyl trimethylsilyl ether (7b)** and **2-[1-methyl-3-(trimethylsilyl)-2-propenyl]-1-cyclohexyl**

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trimethylsilyl ether (8b): $bp_{0.04}$ 120 °C; 3.67 g (62%); IR (neat) 1240, 870, 825, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.05, 0.00 (s, 9 H), 0.08, 0.10 (s, 9 H), 0.90–2.48 (m, 14 H), 3.28 (m, 1 H), 4.75–5.50 (m, 2 H). This mixture could not be further purified, but was hydrolyzed.

The mixture of silyl ethers **7b** and **8b** (3 g, 10 mmol) was dissolved in methanol (30 mL), and acetic acid (10 mL, 2 N) was added. After 10 min, the mixture was diluted with PE/ether (30 mL, 1:1). Then, the organic layer was washed twice with a saturated aqueous $NaHCO_3$ solution and once with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue of crude **8** (2.68 g) was purified on silica gel (elution with PE/ethyl acetate, 4:1) to furnish 2.17 g (96%) of **7c** and **8c** (trace).

(*E*)-2-[3-(Trimethylsilyl)-1-butenyl]-1-cyclohexanol (7c): oil, two diastereomers (2:1*); IR (neat) 3410, 1630, 1590, 1240, 850, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.02*, −0.01 (s, 9 H), 0.98, 1.00* (s, 3 H), 1.05–2.21 (m, 11 H), 3.00–3.24 (m, 1 H), 4.93*, 5.07, 5.35, 5.55* (m, 2 H), ^{13}C NMR ($CDCl_3$) δ −3.7*, −3.5 ($Si(CH_3)_3$), 15.3*, 15.6 (CH_3), 21.6, 22.4* (CH), 24.7, 24.8*, 25.2, 25.3*, 31.1*, 32.0, 33.1*, 33.6 (CH_2), 44.7*, 44.8 (CH), 73.3*, 74.1 (CHOH), 127.8*, 129.3, 135.9, 136.6* (*C*H=*C*H); MS *m*/*z* (relative intensity) 209 (M − OH, 0.1), 136 (28), 121 (30), 75 (52), 73 (100). Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 69.92; H, 11.43.

(*E*)-2-[1-Methyl-3-(trimethylsilyl)-2-propenyl]-1-cyclohexanol (8c): oil; two diastereomers (2.5:1*); ^1H NMR ($CDCl_3$) δ 0.03*, 0.04 (s, 9 H), 0.91*, 0.93 (d, *J* = 6.0*, 7.2, 3 H), 1.07–2.09 (m, 10 H), 2.49*, 2.58 (m, 1 H), 3.26*, 3.41 (m, 1 H), 5.52*, 5.65 (d, *J* = 17.6*, 18.0, 1 H), 5.88*, 6.06 (dd, *J* = 9.40*, 17.6*, 6.0, 18.0, 1 H).

General Procedure for Formation of Tosylates 5 from Alcohols 4 (Method A). One equivalent of alcohol **4** in dry pyridine (10mL/mmol **4**) was treated with a solution of tosyl chloride (1.4 equiv) in pyridine (2 mL/mmol) at room temperature in the presence of 4-DMAP (0.1 equiv). The reactions were monitored by TLC (PE/ethyl acetate, 5:1). After complete consumption of the starting material (48–72 h), a 1:2 mixture of aqueous NH_4Cl and diethyl ether was added. The organic layer was separated, washed twice with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude product which still contained some pyridine was purified by column chromatography.

2-[1-(Phenylthio)-2-propenyl]cyclopentenyl tosylate (5b) was obtained after 72 h. Column chromatography (PE/ethyl acetate, 6:1) gave a pale yellow oil (70%); 2 diastereomers, 3:1*; IR (neat) 3075, 3060, 1634, 1599, 1584, 1361, 1190, 1177, 923, 743, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–2.00 (m, 6 H), 2.39*, 2.40 (s, 3 H), 3.39*, 3.48 (dd, *J* = 6.6*, 9.2*, 6.2, 9.6, 1 H), 4.65–4.98 (m, 3 H), 5.42–5.65 (m, 1 H), 7.15–7.40 (m, 7 H), 7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 22.9, 23.2*, 26.5, 27.5*, 32.8, 33.0* (CH_2), 49.3, 50.0* (CH), 53.8, 55.7* (CHSPh), 86.4, 86.7* (CHOTos), 116.0*, 117.9 (CH=*C*H_2), 127.3, 127.9, 128.7, 128.9, 129.7, 129.8, 132.6, 132.9, 134.9, 137.3 (CH), 134.2, 134.25 (q), 144.6*, 144.7 (CSO_3); MS *m*/*z* (relative intensity) 388 (M^+, 1.3), 216 (44), 155 (44), 149 (10), 109 (17), 107 (67), 91 (100), 79 (56). Anal. Calcd for $C_{21}H_{24}O_3S_2$: C, 65.23; H, 6.34; S, 16.66. Found: C, 64.92, H, 6.26: S, 16.51.

2-[1-(Phenylthio)-2-propenyl]cyclohexenyl tosylate (5c) was obtained after 48 h; pale yellow oil (65%) 2 diastereomers (5:1); for spectroscopic data see method B.

(*E*)-2-[3-(Triphenylsilyl)-2-propenyl]cyclohexyl tosylate (5f): 24.3 g (80%), colorless crystals; mp 114–115 °C, after recrystallization from CH_2Cl_2/pentane (1:5); IR (KBr) 3065, 3055, 3010, 1615, 1600, 1355, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96–2.08 (m, 11 H), 2.45 (s, 3 H), 2.58 (m, 1 H), 4.30 (m, 1 H), 6.03 (ddd, *J* = 5.8, 7.6, 18.8, 1 H), 6.19 (d, *J* = 18.8, 1 H), 7.27–7.83 (m, 19 H); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 24.2, 24.3, 29.9, 32.4, 39.5 (CH_2), 41.6 (CH). 85.5 (CHOTos), 126.4, 150.2 (*C*H=*C*H), 127.6, 127.8, 129.4, 129.7, 135.9 (arom), 134.8, 144.3 (q). Anal. Calcd for $C_{34}H_{36}O_3SSi$: C, 73.87; H, 6.56, S, 5.80. Found: C, 73.85; H, 6.69, S, 5.83.

(*E*)-2-[1,3-Bis(trimethylsilyl)-2-propenyl]cyclopentyl tosylate (5g) was obtained from the mixture of diastereomers of **4g** (17.8 mmol), allowing 72 h for completion of the tosylation. The sensitive product was purified by flash chromatography (eluents PE/ethyl acetate, 4:1): yield 5.3 g (70)%; oil; IR (neat) 1600, 1465, 1190, 1180, 1245, 860, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.01, 0.02 (s, 18 H), 1.02–2.33 (m, 8 H), 2.41 (s, 3 H), 4.48, 4.78 (m, 1 H), 5.05–6.04 (m, 2 H), 7.16–7.58 (m, 4 H).

(*E*)-2-[1,3-Bis(trimethylsilyl)-2-propenyl]cyclohexyl tosylate (5h) was obtained from the mixture of diastereomers of **4h** after column chromatography (toluene) as a colorless oil (84%), two diastereomers (2:1): IR (KBr) 1595, 1360, 1185, 1240, 875, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.06, −0.05*, 0.038*, 0.04 (4 s, 18 H), 1.06–2.13 (m, 10 H), 2.33, 2.44* (s, 3 H), 4.34, 4.48* (m, 1 H), 5.13, 5.42* (d, *J* = 19.8, 18.7*, 1 H), 5.67*, 5.79 (dd, *J* = 9.2*, 18.7*, 10.1, 19.8, 1 H), 7.19–7.80 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −2.3, −1.3*, −1.02*, −1.0 ($Si(CH_3)_3$), 21.6 (CH_3), 21.4*, 21.5*, 24.2, 24.9, 26.1*, 27.7*, 28.0, 32.7 (CH_2), 38.1, 38.3*, 40.2*, 42.4 (CH), 83.4*, 84.6 (CHOTos), 127.5, 127.7*, 129.5, 129.7*, (arom), 128.6*, 131.7, 142.7, 146.2* (*C*H=*C*H), 134.9*, 135.7, 143.9, 144.2* (q); MS *m*/*z* (relative intensity) 423 (0.5, $M^+ - CH_3$), 266 (6), 120 (17), 91 (16), 73 (100). Anal. Calcd for $C_{22}H_{38}O_3SSi_2$: C, 60.22; H, 8.73; S, 7.31. Found: C, 60.27; H, 8.90; S, 7.38.

(*E*)-2-[3-(Phenylthio)-1-propenyl]cyclohexyl tosylate (5i): colorless solid (79%); mp 85–86 °C; IR (KBr) 3057, 1598,, 1585, 1363, 1188, 1176, 1097 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95–1.90 (m, 7 H), 2.10 (m, 2 H), 2.43 (s, 3 H), 3.28 (d, *J* = 7.0, 2 H), 4.15 (dt, *J* = 4.4, 10.0 1 H), 5.06 (dd, *J* = 8.0, 15.2, 1 H), 5.41 (dt, *J* = 7.0, 15.2, 1 H), 7.10–7.38 (m, 7 H), 7.67 (d, *J* = 8.1, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 24.1, 24.13, 31.1, 32.5, 36.4 (CH_2), 45.6 (CH), 84.8 (CHOTos), 126.2, 134.2 (*C*H=*C*H), 126.6, 127.9, 128.8, 129.6, 129.9 (arom), 134.6, 136.0 (q), 144.3 (CSO_3); MS *m*/*z* (relative intensity) 402 (M^+, 1.3), 232 (26), 230 (13), 121 (70), 110 (31), 109 (36), 91 (57), 84 (85), 71 (52), 69 (73), 57 (100). Anal. Calcd for $C_{22}H_{26}O_3S_2$: C, 65.64; H, 6.51; S, 15.93. Found: C, 65.64; H, 6.38; S, 15.98.

(*Z*)-2-[3-(Phenylthio)-1-propenyl]cyclohexyl tosylate (5j): colorless solid (84%); mp 77–78 °C; IR (KBr) 3060, 1599, 1585, 1363, 1188, 1176, 1098 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–1.80 (m, 7 H), 2.06 (m, 1 H), 2.35 (m, 1 H), 2.42 (s, 3 H), 3.28 (ddd, *J* = 1.2, 6.4, 13.4, 1 H), 3.57 (ddd, *J* = 1.2, 9.0, 13.4, 1 H), 4.18 (dt, *J* = 4.2, 10.0, 1 H), 4.96 (dd, *J* = 10.0, 10.8, 1 H), 5.36 (dddd, *J* = 1.0, 6.4, 9.0, 10.8, 1 H), 7.10–7.40 (m, 7 H), 7.73 (d, *J* = 8.4, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 24.0, 24.1, 31.3, 31.5, 32.4 (CH_2), 41.4 (CH), 84.7 (CHOTos), 126.3, 133.3 (*C*H=*C*H), 126.8, 127.9, 128.8, 129.5, 130.1 (arom), 134.5, 136.1 (q), 144.4 (CSO_3); MS *m*/*z* (relative intensity) 402 (M^+, 2.2), 230 (43), 155 (27), 121 (85), 110 (8), 109 (23), 91 (100). Anal. Calcd for $C_{22}H_{26}O_3S_2$: C, 65.64; H, 6.51; S, 15.93. Found: C, 65.84; H, 6.43, S, 16.11.

General Procedure for Formation of Tosylates 5 by in Situ Tosylation of Alkoxides 3 (Method B). To a stirred solution of the allyl sulfide **2a** or **2b** in THF (0.1–0.5 M) was added 1.1 equiv of a 1.6 M solution of *n*-BuLi in hexane at −78 °C. The resulting orange solution was stirred at this temperature for 4 h, and then 1 equiv of epoxide **1** was added. The reaction was monitored by TLC (PE/ethyl acetate, 5:1). Monosubstituted epoxides normally needed 1–2 h, 1,2-disubstituted derivatives up to 4 h at −78 °C. The reaction mixture was then quenched with 1.1 equiv of TosCl in THF (0.5 M solution) and was slowly warmed to room temperature until TLC confirmed consumption of alkoxide **3**; 5–30 mmol of **2** were employed. The solution was poured into a two-phase system of saturated $NaHCO_3$ and *n*-pentane, stirred for 0.5 h, washed with water and brine (2×), and dried ($MgSO_4$). Concentration on the rotary evaporator resulted in a deep red oil. Filtration over a short column of approximately 50–200 g of silica gel using PE/ethyl acetate (50:1) yielded the tosylates **5** normally pure enough for conversion into **9** (^1H NMR evidence). Yields and physical data were obtained after another chromatographic purification step (PE/ethyl acetate, 6:1). α/γ ratios (see Table I) were measured independently for the alcohols **4** after quenching with a 2 M solution of NH_4Cl.

1-Methyl-3-(phenylthio)-4-pentenyl tosylate (5a): pale yellow oil (62%); two diastereomers (4:1*); IR (neat) 3050, 1610, 1590, 1570, 1350, 1180, 1170, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28, 1.30* (d, *J* = 6.1, 6.0*, 3 H), 1.70 (m, 1 H), 2.00*, 2.06 (m, 1 H), 2.39*, 2.43 (s, 3 H), 3.47*, 3.55 (m, 1 H), 4.75 (m, 1 H), 4.68–4.97 (m, 2 H), 5.51 (m, 1 H), 7.10–7.40 (m, 7 H), 7.89 (d, *J* = 8.3, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.0*, 21.2, 21.5 (CH_3), 40.9*, 41.3 (CH_2), 47.4, 48.0* (CHSPh), 77.7*, 77.9 (CHOTos), 115.7*, 117.0 (CH=*C*H_2), 127.3, 127.4, 127.6, 128.7, 128.9, 129.7, 131.4, 132.7, 133.2 (arom), 133.8, 134.6 (q), 137.1, 137.8* (*C*H=CH_2), 144.4 (CSO_3); MS *m*/*z* (relative intensity) 362 (M^+, 3.8), 190 (23), 173 (67), 155 (71), 91 (100), 81 (52). Anal. Calcd for $C_{19}H_{22}O_3S_2$: C, 62.95; H,

6.12; S, 17.67. Found: C, 62.89; H, 6.16; S, 17.64.

2-[1-(Phenylthio)-2-propenyl]cyclohexyl tosylate (5c): pale yellow oil (71%); two diastereomers (5.3:1*); IR (neat) 3040, 1630, 1600, 1580, 1350, 1190, 1180, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02–2.21 (m, 9 H), 2.32*, 2.42 (s, 3 H), 3.88*, 4.01 (dd, J = 3.2*, 8.0*, 3.3, 9.2, 1 H), 4.56 (dt, J = 4.4, 9.8, 1 H), 4.90* (m, 1 H), overlapping with a signal at 4.95 (m, 2 H), 5.63, 5.75* (m, 1 H), 7.10–7.45 (m, 7 H), 7.70*, 7.78 (d, J = 8.4*, 8.2, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 23.8*, 24.0, 24.2, 24.3*, 25.4, 32.3*, 32.4 (CH_2), 46.1, 46.7* (CH), 51.4, 51.8* (CHSPh), 82.4*, 82.9 (CHOTos), 116.4*, 118.7 (CH=CH_2), 126.3*, 126.6, 127.3, 127.7*, 128.4*, 128.6, 129.5*, 129.6, 131.2*, 131.4 (arom), 133.5, 136.7* (CH=CH_2), 134.7, 135.1 (q), 144.2*, 144.3 (CSO_3); MS m/z (relative intensity) 402 (M^+, 1.4), 230 (4), 173 (86), 155 (61), 91 (100). Anal. Calcd for $C_{22}H_{26}O_3S_2$: C, 65.64; H, 6.51; S, 15.93. Found: C, 65.82; H, 6.71; S, 15.87.

1-[[(2-Tetrahydropyranyl)oxy]methyl]-3-(phenylthio)-5-pentenyl tosylate (5d): colorless oil (71%); up to four diastereomers could be detected in the ^{13}C NMR spectrum, data are only given for the two major isomers (1.5:1*); IR (neat) 3050, 1630, 1590, 1580, 1350, 1180, 1170, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.370–1.81 (m, 6 H), 1.85–2.23 (m, 2 H), 2.40*, 2.45 (s, 3 H), 3.49–3.85 (m, 5 H), 4.45*, 4.49 (m, 1 H), 4.75–5.06 (m, 3 H), 5.46–5.78 (m, 1 H), 7.18–7.40 (m, 7 H), 7.79, 7.81* (d, J = 8.4, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.9*, 19.1, 25.3, 30.1*, 30.2 (CH_2), 21.6 (CH_3), 36.1, 36.4* (CH_2), 47.2, 47.7* (CHSPh), 61.7, 62.0*, 67.83, 67.93* (CH_2O), 79.2*, 79.3 (CHOTos), 98.5, 98.8* (OCHO), 115.9*, 117.2 (CH=CH_2), 127.3, 127.7, 127.8, 128.6, 128.7, 129.6, 129.7, 132.7, 133.4 (arom), 134.2, 134.4 (q), 136.9, 137.7 (CH=CH_2), 144.5, 144.6* (CSO_3); MS m/z (relative intensity) 462 (M^+, 1.7), 110 (11), 91 (8), 85 (100). Anal. Calcd for $C_{24}H_{30}O_5S_2$: C, 62.31; H, 6.54; S, 13.86. Found: C, 62.45; H, 6.67; S, 13.99.

2-[3-(Phenylthio)-3-(trimethylsilyl)-2-propenyl]cyclohexyl tosylate (5e): pale yellow solid (35%); mp 73–75 °C. The low yield may be due to the sluggish reaction of the anion **2b** with epoxide **1c**: IR (KBr) 3040, 1595, 1580, 1360, 1180, 1160, 1240, 860, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 1.10–1.86 (m, 8 H), 2.07 (m, 1 H), 2.15 (ddd, J = 7.6, 8.4, 14.8, 1 H), 2.39 (s, 3 H), 2.49 (ddd, J = 4.4, 6.0, 14.8, 1 H), 4.23 (dt, J = 4.0, 9.6, 1 H), 6.43 (dd, J = 6.0, 7.6, 1 H), 7.06–7.25 (m, 7 H), 7.78 (d, J = 8.3, 2 H); ^{13}C NMR ($CDCl_3$) δ 1.1 ($Si(CH_3)_3$), 21.6 (CH_3), 24.1, 24.3, 30.0, 32.4, 33.1 (CH_2), 42.0 (CH), 85.6 (CHOTos), 125.2, 127.7, 128.2, 128.6, 129.7 (arom), 134.3, 136.0, 137.5, 144.4 (q), 150.1 (CH=C); MS m/z (relative intensity) 474 (M^+, 0.4), 302 (9), 91 (13), 73 (100). Anal. Calcd for $C_{25}H_{34}O_3S_2Si$: C, 63.25; H, 7.22; S, 13.51. Found: C, 63.33; H, 7.31; S, 13.27.

Synthesis of (*E*)-2-[3-Bromo-3-(trimethylsilyl)-1-propenyl]cyclohexyl Tosylate (5k) from 5h Using *N*-Bromosuccinimide. Tosylate **5h** (10.6 mmol) in CH_2Cl_2 (50 mL) was stirred with 1.1 equiv of NBS at room temperature for 15 min. The reaction mixture was then hydrolyzed by addition of a mixture of saturated aqueous $NaHCO_3$ and CH_2Cl_2 (1:1). The organic layer was washed twice with saturated brine, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by column chromatography (eluent PE/ethyl acetate, 12:1) to give **5k** as a colorless oil, yield 3.83 g (81%), 2 diastereomers (6:1), data are only given for the major isomer: IR (neat) 1600, 1360, 1190, 1175, 1250, 850, 835, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.04–2.25 (m, 9 H), 2.45 (s, 3 H), 4.14 (dd, J = 0.8, 10.6, 1 H), 4.98 (ddd, J = 0.8, 8.2, 15.0, 1 H), 5.51 (ddd, J = 0.8, 10.6, 15.0, 1 H), 7.3–7.82 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -3.2 ($Si(CH_3)_3$), 21.5 (CH_3), 24.1, 31.6, 32.5 (CH_2, one not detected), 43.2, 45.7 (CH), 84.1 (CHOTos), 127.9, 129.6 (arom), 130.0, 132.8 (CH=CH), 134.7, 144.2 (q). Anal. Calcd for $C_{12}H_{23}BrOSi$: C, 49.48; H, 7.96; Br, 27.43. Found: C, 49.54; H, 7.85; Br, 28.66.

General Procedure for the Preparation of Vinylcyclopropanes 9 Using Butyllithium. Tosylate **5** (1 equiv) was dissolved in THF (5 mL/mmol), and at -78 °C 1.5 equiv of *n*-BuLi (1.6 M in hexane) (in the synthesis of **5e,f** *sec*-BuLi had to be used) was added dropwise. The orange solution was allowed to warm to -20 °C, and consumption of the tosylate was followed by TLC (PE/ethyl acetate, 5:1). The mixture was then poured into a 1:1:1 mixture of saturated aqueous NH_4Cl solution, *n*-pentane, and diethyl ether. The organic layer was washed twice with saturated brine, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by column chromatography.

***cis*- and *trans*-1-ethenyl-2-methyl-1-(phenylthio)cyclopropane (9a)**: eluent PE/ethyl acetate, 20:1 (70%); two diastereomers (2.3:1*); IR (neat) 3080, 3060, 3010, 1630, 1590, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83*, 0.97 (dd, J = 4.8*, 6.4*, 5.0, 6.4, 1 H), 1.20, 1.30* (d, J = 6.2, 6.0*, 3 H), 1.25*, 1.33 (dd, J = 4.8*, 8.8*, 5.0, 8.8, 1 H), 1.40*, 1.52 (m, 1 H), 4.96*, 5.15 (dd, J = 1.1*, 10.4*, 1.2, 10.2, 1 H), 5.25*, 5.33 (dd, J = 1.1*, 16.4*, 1.2, 16.8, 1 H), 5.60*, 5.79 (dd, J = 10.4*, 16.4*, 10.2, 16.8, 1 H), 7.02–7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 14.6* (CH_3), 23.8*, 24.5 (CH_2), 23.9, 24.0* (CH), 31.0, 32.2* (q), 112.8*, 116.3 (CH=CH_2), 124.5*, 124.9, 126.7*, 127.1, 128.4*, 128.5 (arom), 136.9, 142.1* (CH=CH_2), 137.4 (q); MS m/z (relative intensity) 190 (M^+, 69), 175 (13), 109 (12), 81 (100), 80 (48), 79 (73), 53 (32). Anal. Calcd for $C_{12}H_{14}S$: C, 75.74; H, 7.42; S, 16.85. Found: C, 75.89; H, 7.48; S, 17.11.

6-Ethenyl-6-(phenylthio)bicyclo[3.1.0]hexane (9b): eluent PE/ethyl acetate, 20:1 (84%); two diastereomers (2.7:1*); IR (neat) 3080, 3050, 3010, 1630, 1590, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69–2.10 (m, 8 H), 4.90, 5.20* (d, J = 10.5, 1 H), 5.22, 5.46* (d, J = 17, 1 H), 5.59, 5.82* (dd, J = 17, 10.5, 1 H), 6.98–7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.3*, 26.4, 27.1 (CH_2, one not detected), 36.6, 36.7* (CH), 34.1*, 38.8 (q), 111.8, 118.8* (CH=CH_2), 124.5, 125.3*, 126.7, 128.4*, 128.5 (arom), 133.3*, 142.5 (CH=CH_2), 137.1*, 137.5 (q); MS m/z (relative intensity) 216 (M^+, 47), 175 (19), 147 (11), 112 (10), 111 (16), 110 (8), 91 (56), 79 (100), 77 (30). Anal. Calcd for $C_{14}H_{16}S$: C, 77.73; H, 7.46; S, 14.82. Found: C, 77.76; H, 7.52; S, 14.96.

7-Ethenyl-7-(phenylthio)bicyclo[4.1.0]heptane (9c): eluent PE/ethyl acetate, 20:1 (68%); two diastereomers (6.3:1*); IR (neat) 3080, 3020, 1620, 1580, 730, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12–2.08 (m, 10 H), 4.89, 5.28* (dd, J = 1.0, 10.3, 1.8*, 10.4*, 1 H), 5.18, 5.56* (dd, J = 1.0, 16.8, 1.87*, 16.6*, 1 H), 5.58, 5.88* (dd, J = 10.3, 16.8, 10.4*, 16.6*, 1 H), 6.96–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.6*, 19.9, 21.5, 21.6* (CH_2), 24.9, 26.5* (CH), 32.7*, 35.5 (q), 111.7, 118.7* (CH=CH_2), 124.2, 124.5*, 126.2, 126.7*, 128.1, 128.3 (arom), 133.7*, 143.5 (CH=CH_2), 136.4 138.0* (q). Anal. Calcd for $C_{15}H_{18}S$: C, 78.21; H, 7.88; S, 13.92. Found: C, 78.23; H, 8.08; S, 14.11.

[2-Ethenyl-2-(phenylthio)cyclopropyl]methanol (9d): the crude product was dissolved in methanol, and 0.1 equiv of *p*-toluenesulfonic acid was added. After 1 h the mixture was diluted with diethyl ether, washed once with a solution of aqueous $NaHCO_3$ and twice with brine, dried ($MgSO_4$), and concentrated in vacuo. Column chromatography (PE/ethyl acetate, 6:1) gave a clear oil (55%), two diastereomers (1.1:1*): IR neat 3350, 3050, 3005, 1630, 1580, 1020, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05, 1.20* (dd, J = 5.2, 6.8, 5.6*, 6.2*, 1 H), 1.31. 1.37* (dd, J = 5.2, 8.8, 5.6*, 8.8*, 1 H), 1.55 (br, 1 H), 1.75, 1.84* (m, 1 H), 3.53* 3.80 (dd, J = 8.8*, 11.9*, 8.0, 12.0, 1 H), 3.83*, 3.91 (dd, J = 6.0*, 11.9*, 5.2, 12.0, 1 H), 5.05, 5.20* (dd, J = 1.0, 10.0, 1.2*, 10.4*, 1 H), 5.35, 5.36* (dd, J = 1.0, 16.8, 1.2*, 16.8*, 1 H), 5.65, 5.90* (dd, J = 10.0, 16.8, 10.4*, 16.8*, 1 H), 7.08–7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.2*, 20.7 (CH_2), 32.9, 31.5* (CH), 31.2*, 32.3 (q), 62.2*, 63.0 (CH_2OH), 113.9, 117.4*, (CH=CH_2), 125.3, 125.5*, 127.1, 127.8*, 128.6, 128.7* (arom), 136.0*, 141.2 (CH=CH_2), 136.5*, 136.6 (q); MS m/z (relative intensity) 206 (46, M^+), 188 (13, $M^+ - H_2O$), 187 (12), 176 (12), 175 (76), 155 (27), 142 (49), 110 (100), 109 (41), 97 (70), 96 (26), 79 (93). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 69.78; H, 7.04; S, 15.36.

(*Z*)-7-[2-(Phenylthio)-2-(trimethylsilyl)ethenyl]bicyclo[4.1.0]heptane (9e): eluent hexane (80% from **5l**, 54% from **5e**); pale yellow oil; IR (neat) 3070, 3010, 1585, 1240, 865, 840 cm^{-1}; ^1H NMR (C_6D_6) δ 0.11 (s, 9 H), 0.82–1.76 (m, 10 H), 2.10 (dt, J = 4.5, 9.2, 1 H), 5.97 (d, J = 9.2, 1 H), 6.84–7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ - 1.1 ($Si(CH_3)_3$), 21.5, 23.4 (CH_2), 21.3, 27.3 (CH), 124.5, 127.2, 128.5 (arom), 127.3, 138.8 (q), 157.9 (CH=C). Anal. Calcd for $C_{18}H_{26}SSi$: C, 71.46; H, 8.66; S, 10.60. Found: C, 71.25; H, 8.68; S, 10.59.

(*E*)-*exo*-7-[2-(Triphenylsilyl)-1-vinyl]bicyclo[4.1.0]heptane (9f): eluent, hexane (82%). An analytical sample was obtained by recrystallization from ethanol. Only one diastereomer was detected: mp 85–86 °C; IR (KBr) 3075, 3050, 1600, 1420, 1100, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98–1.30 (m, 6 H), 1.61–1.95 (m, 4 H), 1.33 (dt, J = 4.3, 8.6, 1 H), 5.51 (dd, J = 8.6, 18.3, 1 H), 6.08 (d, J = 18.3, 1 H), 7.26–7.58 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 20.9 (CH), 21.4, 23.2 (CH_2), 31.3 (CH), 127.7, 129.3, 135.9 (arom),

117.6, 157.2 (CH=CH), 135.9 (q). Anal. Calcd for $C_{27}H_{28}Si$: C, 85.21; H, 7.42. Found: C, 85.51; H, 7.18.

(*E*)-*exo*-7-[2-(Trimethylsilyl)-1-vinyl]bicyclo[4.1.0]heptane (9h) from 5k: eluent PE/ethyl acetate (7:1); oil (64%); IR (neat) 3010, 1610, 1245, 860, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 1.01 (m, 2 H), 1.12-1.33 (m, 5 H), 1.68-1.89 (m, 4 H), 5.53 (dd, J = 6.9, 18.2, 1 H), 5.55 (dd, J = 1.0, 18.2, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.99 ($Si(CH_3)_3$), 20.4 (CH), 21.5, 23.3 (CH_2), 30.8 (CH), 124.8, 151.0 (CH=CHSi); MS m/z (relative intensity) 194 (M^+, 9), 179 (11), 120 (31), 73 (100). Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 74.00; H, 11.24.

(*E*/*Z*)-7-[2-(Phenylthio)ethenyl]bicyclo[4.1.0]heptane (9i) from **5i** (67%, *E*/*Z** ratio 1:1*); from **5j** (90%, *E*/*Z* ratio 8:1). Column chromatography on silica using hexane provided a pure product: IR (neat) 3050, 3000, 1605, 1585, 740, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90-1.2 (m, 6 H), 1.55 (dt, J = 4.4, 9.4, 1 H (*Z*), the corresponding signal for the *E* isomer is overlapping with the cyclohexyl protons), 1.60-2.0 (m, 4 H), 5.31* (t, J = 9.4, 1 H), 5.59 (dd, J = 9.2, 14.8, 1 H), 6.02*, 6.05 (d, J = 9.4*, 14.8, 1 H), 7.10-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.3, 20.5* (CH), 21.3, 21.4*, 23.1, 23.2* (CH_2), 24.9*, 27.6 (CH), 115.4*, 117.6 (CH=CHSPh), 125.6, 125.7, 127.8, 128.2, 128.8, 128.9 (arom), 137.1*, 137.5 (q), 139.5, 143.3* (CH=CHSPh). Anal. Calcd for $C_{15}H_{18}S$: C, 78.21; H, 7.87; S, 13.92. Found: C, 78.25; H, 8.01; S, 13.79.

Vinylcyclopropane 9b from Epoxide 1b. See general procedure for in situ formation of tosylates (method B). Prior to work up of the reaction mixture after the tosylation step, another 1.5 equiv of *n*-BuLi was added, and the reaction was carried on as described above. Yield: 50%.

General Procedure for the Preparation of Vinylcyclopropanes 9 Using Tetrabutylammonium Fluoride (TBAF). At room temperature, 1 equiv of the tosylate in THF (10 mL/mmol) was treated with 1.1 equiv of TBAF in THF (5 mL/mmol). After 15 min, the reddish brown solution was poured into a 1:1 mixture of brine and hexane. The organic layer was washed twice with saturated brine, dried ($MgSO_4$), and concentrated in vacuo.

***endo*/*exo*-6-[2-(Trimethylsilyl)-1-vinyl]bicyclo[3.1.0]hexane (9g, Endo*/Exo Ratio 1*:3).** The crude product was distilled in a Kugelrohr apparatus ($bp_{0.05}$ 55 °C). The distillate was purified by column chromatography on silica gel using hexane to give a colorless oil (54%): IR (neat) 3030, 1605, 1240, 860, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04*, 0.09 (s, 9 H), 1.05-2.01 (m, 9 H), 5.51, 5.82* (dd, J = 6.7, 18.4, 6.5*, 18.6*, 1 H), 5.58, 5.89* (d, J = 18.4, 18.6*, 1 H); ^{13}C NMR (C_6D_6) δ -0.7 ($Si(CH_3)_3$), 21.3, 25.6*, 26.1*, 27.8 (CH_2), 25.9*, 26.4, 27.0*, 27.6 (CH), 125.5, 132.9*, 143.5*, 149.4 (CH=CH). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.34; H, 11.20.

9h. Distillation using a Kugelrohr apparatus provided 61%, showing identical and ^{13}C NMR spectra with the compound prepared from **5k** by action of *n*-BuLi.

(*E*/*Z*)-*exo*-7-(2-Bromo-1-vinyl)bicyclo[4.1.0]heptane (9j, *E*/*Z* Ratio 1:3.4*). Column chromatography, PE/ethyl acetate (4:1), supplied a pure product (51%): IR (neat) 3060, 2990, 1620, 680, 660 cm^{-1}; ^1H NMR (C_6D_6) δ 0.6-1.9 (m, 11 H), 5.11*, 5.5 (dd, J = 6.9*, 9.0*, 8.9, 13.4, 1 H), 5.70, 5.75* (d, J = 6.9*, 13.4, 1 H), ^{13}C NMR (C_6D_6) δ 21.6*, 23.2, 23.4* (CH_2), 19.6, 20.3*, 25.8*, 27.5 (CH), 100.4, 103.9*, 139.0*, 141.7 (CH=CH); MS m/z (relative intensity) 200 (M^+, 7), 134 (22), 132 (20), 121 (54). Anal. Calcd for $C_9H_{13}Br$: C, 53.75; H, 6.52; Br, 39.73. Found: C, 53.81; H, 6.42; Br, 39.43.

9i (from 5l, *E*/*Z* Ratio 5:4*). Column chromatography on silica gel using hexane provided a pure product (40%), identical with the compound described above.

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Stereoselective Convergent Synthesis of Hydroazulenes via an Intermolecular Cyclopropanation/Cope Rearrangement

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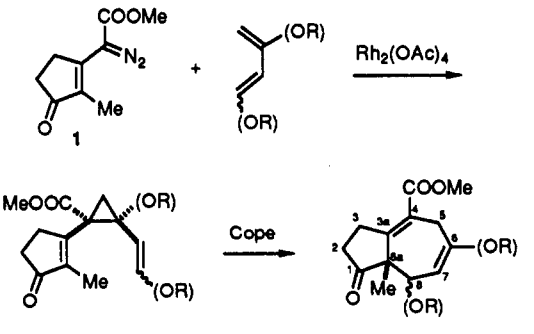
Rhodium(II) acetate catalyzed decomposition of vinyldiazomethane 1 to a vinylcarbenoid intermediate in the presence of oxygenated dienes led to the direct formation of hydroazulenes **7**, **13**, and **15-19**. The 3 + 4 annulation proceeds by a tandem cyclopropanation/Cope rearrangement sequence. The cyclopropanation is highly stereoselective, favoring the formation of *cis*-divinylcyclopropanes. Due to the boat transition state required for the Cope rearrangement of *cis*-divinylcyclopropanes, the hydroazulenes are formed with predictable stereocontrol.

The hydroazulene skeleton is an important feature of many biologically important natural products including the pseudoguaianes. Numerous synthetic strategies have been developed for the construction of this bicyclic system.[1] A particularly intriguing method, developed by Marino,[2] Wender,[3] and Piers,[4] has been the Cope rearrangement of *cis*-divinylcyclopropanes, which proceeds with predictable stereocontrol. A drawback with this approach, however, is that the isomeric *trans*-divinylcyclopropanes often undergo a competing 1,5-homodienyl rearrangement rather than equilibration to the cis isomer

Scheme I



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