Versatile Synthesis of Enantiomerically Pure 2-Alkoxy-1-ethynylcyclopropanes and Their Application in the Synthesis of Enantiomerically Pure Bicyclo-[3.3.0]oct-1-en-3-ones**

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Dedicated to Professor Manfred Regitz on the occasion of his 60th birthday

Abstract: A variety of chiral, nonracemic 2-alkoxy-1-alkynylcyclopropanes **7** were synthesized in good to very good yields from enantiomerically pure glycidol derivatives (glycidol tosylate, epichlorohydrin) by boron trifluoride promoted addition of lithium trimethylsilylacetylide followed by protection of the secondary hydroxyl group and finally a diastereoselective γ-elimination. The 2-ethoxy derivative (*S,R*)-**7b** was deprotonated with *n*-butyllithium, and the resulting 1-lithio-2-ethoxy derivative (*S,R*)-**20** functionalized by treatment with oxygen followed by tosyl chloride. Protodesilylation and catalytic hydrogenation smoothly furnished 1-ethenylcyclopropyl sulfonates, which underwent a clean Pd^0-catalyzed S_N2'-type substitution with dimethyl propargylsodiummalonate to give the (*E*)-configurated enyne (*R,E*)-**26** with a methylenecyclopropane end group. A diastereoselective Pauson–Khand reaction completed the sequence to give the enantiomerically pure spirocyclopropane-annelated bicyclo[3.3.0]octane derivative **31**.

Keywords
alkynes · asymmetric syntheses · cyclopropanes · spiro compounds

Introduction

Multifunctional cyclopropane derivatives have established their potential as useful building blocks in organic synthesis.[1] Especially functionally substituted methylenecyclopropanes,[2] ethenylcyclopropanes,[3, 4] and ethynylcyclopropanes[4, 5] can serve as so-called "composite functionalities",[5] in which the cyclopropane moiety itself takes part in the sequence of chemical transformations. In this context, we have demonstrated the utility of 1-[6b] and 2-substituted ethynylcyclopropanes,[6] and have developed an efficient, high-yielding synthesis for racemic 2-alkoxy-1-ethynylcyclopropanes.[6d] Ethynylcyclopropanes can in general be deprotonated and substituted at the 1-position—in the case of 2-alkoxy-substituted derivatives, with a high degree of diastereoselectivity—and, after partial catalytic hydrogenation to 1-substituted ethenylcyclopropanes, can be transformed to functionally substituted methylenecyclopropanes, which in turn can serve as substrates in inter-[2, 7] and intramolecular[8] cycloaddition reactions. Therefore it appeared essential to develop a simple synthesis of enantiomerically pure 2-alkoxy-1-ethynylcyclopropanes and test their applicability in sequential organic transformations. The most straightforward approach is based on our previously reported[6d] synthesis of the racemic materials, but uses enantiopure glycidol derivatives as starting materials, which are readily accessible by the Sharpless epoxidation of allyl alcohols.[9]

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Results and Discussion

Preparation of Enantiomerically Pure 2-Alkoxy-1-ethynylcyclopropanes: Racemic 4-alkoxy-5-bromo-1-pentynes as precursors to 2-alkoxy-1-ethynylcyclopropanes have been prepared by coupling bromine adducts of enol ethers with propargylmagnesium bromide.[6d] The same intermediates should also be accessible by adding lithium acetylide to epihalohydrins or analogous glycidol derivatives with subsequent protection of the secondary hydroxyl group. Such additions are known to proceed regioselectively in the presence of boron trifluoride etherate,[10] and as epichlorohydrin (**1**) and glycidyl tosylate (**2**) are readily available in enantiomerically pure form, this sequence was extended to the synthesis of enantiomerically pure 2-alkoxy-1-ethynylcyclopropanes.

In order to control the chemoselectivity, lithium trimethylsilylacetylide in the presence of 1 equiv of $BF_3 \cdot OEt_2$ was treated with (*S*)-epichlorohydrin ((*S*)-**1**) or (*S*)-glycidyl tosylate ((*S*)-**2**) at low temperature (−78 °C). Under these conditions the alcohols (*S*)-**3a** and (*S*)-**4a** were obtained in 98% and 97% yield, respectively (Scheme 1). The opening of the oxirane ring in (*S*)-**2** with 1-lithio-2-phenylethyne or 1-lithio-3,3-dimethylbutyne, respectively, gave the desired products (*S*)-**10a** or (*S*)-**11a**, re-

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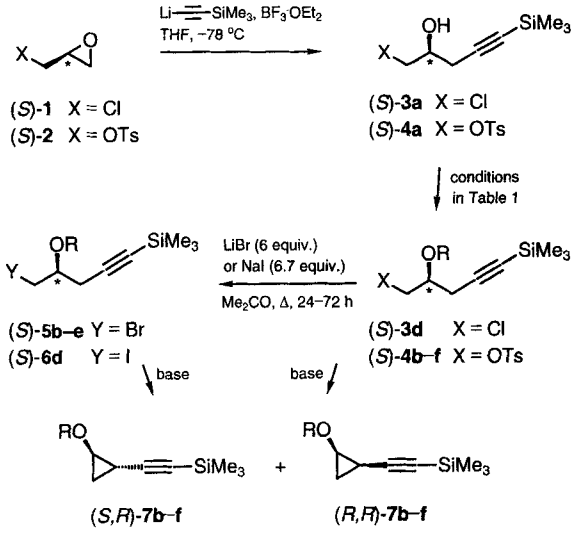
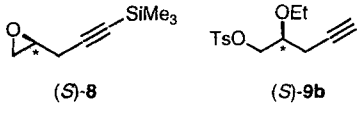
spectively, in excellent yields, too (92 and 90%, respectively). In the reaction of 1-lithio-3,3-dimethylbutyne, an unpolar by-product was isolated in 35% yield, when the reaction mixture was warmed up to room temperature. The spectroscopic data (^{11}B, ^{13}C, ^1H NMR; HRMS) and elemental analysis showed this to be tris(3,3-dimethylbut-1-ynyl)borane, which must have been formed by substitution of fluoride on boron trifluoride with lithiobutyne.

Protection of the secondary alcohols (*S*)-**3a** and (*S*)-**4a** could only be achieved under acidic or neutral conditions (Scheme 1, Table 1). Although thallium(I) ethoxide/ethyl iodide has successfully been used to protect sensitive alcohols,[11] the reaction of (*S*)-**4a** under these conditions gave only the oxirane (*S*)-**8**.



Scheme 1. For further details see Tables 1 and 2. Compounds are labeled as follows: **a**, R = H; **b**, R = Et; **c**, R = *t*Bu; **d**, R = *t*BuMe$_2$Si; **e**, R = (MeO)Me$_2$C; **f**, R = Bn.

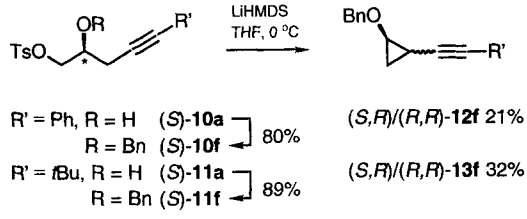
With ethyl trichloroacetimidate[12] in dichloromethane, only the desilylated product (*S*)-**9b** was observed. However, upon reaction of (*S*)-**4a** with one equivalent of triethyloxonium tetrafluoroborate, the desired product (*S*)-**4b** was formed slowly in low yield and with (*S*)-**9b** as a by-product. A large excess (5–10 equiv) of the Meerwein salt gave the product in 74% yield when the reaction was stopped at 76% conversion, in order to avoid deprotection of the alkyne terminus.



Protection of (*S*)-**3a** and (*S*)-**4a** with isobutene in the presence of a catalytic amount of sulfuric acid gave the *tert*-butyl ethers **3c** and **4c** in 88 and 76% yield, respectively. The *tert*-butyldimethylsilyl group (TBDMS) was easily attached by stirring the alcohol in DMF with TBDMSCl in the presence of imidazole (ImH) to give (*S*)-**3d** and (*S*)-**4d** in 80 and 91% yield, respectively (Scheme 1, Table 1).

The reaction of (*S*)-**4a** with 2-methoxypropene and catalytic amounts of phosphoryl chloride[13] proceeded with quantitative yield to give (*S*)-**4e**. The benzyl group was introduced by using benzyl trichloroacetimidate[12] in dichloromethane and catalytic amounts of methanesulfonic acid. The resulting benzyl ether (*S*)-**4f** was isolated in 68% yield with 75% conversion of the alcohol. The conversion could be increased by using a larger amount of acid, but polymerization of the product was then also observed.

The 1-phenyl- (**10a**) and 1-*tert*-butylpentynol (**11a**) could be converted to the corresponding benzyl ethers **10f** and **11f** in 80 and 89% yield, respectively, by using catalytic amounts of triflic acid (Scheme 2).



Scheme 2. Protection and cyclization pentynols **10a** and **11a**.

It would certainly be convenient if the addition of the acetylide to the epoxide **1** or **2** and alkylation of the resulting alkoxide could be carried out sequentially in one pot. Unfortunately, the intermediate difluoroalkoxyboranes were totally unreactive towards alkylating agents (e.g., benzyl bromide, methyl iodide, and ethyl trichloroacetimidate) and silylating agents (e.g., trimethylsilyl chloride and trimethylsilyl triflate) under the reaction conditions used. With $SnCl_4$ and Li_2CuCl_4 instead of $BF_3 \cdot OEt_2$ as catalysts in the addition of lithium (trimethylsilyl)acetylide to (*S*)-**2**, the alcohol (*S*)-**4a** was obtained after hydrolysis (39 and 29% yield), but here too the intermediate alkoxide could not be alkylated directly.

The cyclizations of the TBDMS-protected chloride (*S*)-**3d** or tosylate (*S*)-**4d** with lithium diisopropylamide (LDA) in THF according to the published procedure[6d] gave poor yields (42 and 31%, respectively; Table 2). A number of chlorides and

Table 1. Formation of protected 4-hydroxy-5-halo- (**3**, **5**, and **6**) and 4-hydroxy-5-tosyloxy-1-pentynes (**4**, **10**, and **11**) (see Schemes 1 and 2).

SM	Conditions [a]	Product	R	Yield (%)	Conditions [b] Halide	*t*/h	Product	Yield (%)
(*S*)-**4a**	$Et_3O \cdot BF_4$, $Et(iPr)_2N$, CH_2Cl_2	(*S*)-**4b**	Et	74 [c]	LiBr	24	(*S*)-**5b**	97
(*S*)-**3a**	$Me_2C{=}CH_2$, H_2SO_4, CH_2Cl_2	(*S*)-**3c**	*t*Bu	88	– [d]	–	–	–
(*S*)-**4a**	$Me_2C{=}CH_2$, H_2SO_4, CH_2Cl_2	(*S*)-**4c**	*t*Bu	76	LiBr	24	(*S*)-**5c**	96
(*S*)-**3a**	TBDMSCl, ImH, DMF	(*S*)-**3d**	*t*BuMe$_2$Si	80	–	–	–	–
(*S*)-**4a**	TBDMSCl, ImH, DMF	(*S*)-**4d**	*t*BuMe$_2$Si	91	LiBr	24	(*S*)-**5d**	92
					NaI	72	(*S*)-**6d**	98
(*S*)-**4a**	$MeC(OMe){=}CH_2$, Cl_3PO	(*S*)-**4e**	(MeO)Me$_2$C	100	LiBr	24	(*S*)-**5e**	92
(*S*)-**4a**	$Cl_3CC(NH)OBn$, $MeSO_3H$, CH_2Cl_2	(*S*)-**4f**	Bn	68 [e]	LiBr	24	(*S*)-**5f**	94
(*S*)-**10a**	$Cl_3CC(NH)OBn$, CF_3SO_3H, CH_2Cl_2	(*S*)-**10f**	Bn	80	–	–	–	–
(*S*)-**11a**	$Cl_3CC(NH)OBn$, CF_3SO_3H, CH_2Cl_2	(*S*)-**11f**	Bn	89	–	–	–	–

[a] ImH = imidazole, TBDMS = *tert*-butyldimethylsilyl. [b] All conversions were performed in refluxing acetone. [c] 76% conversion. [d] Not carried out. [e] 75% conversion.

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Table 2. Cyclization of 4-alkoxy-5-halo- and 4-alkoxy-5-tosyloxy-1-trimethylsilyl-1-pentynes to 2-alkoxy-1-ethynylcyclopropanes **7b–f**, **12f**, and **13f** (**b**, R = Et; **c**, R = *t*Bu; **d**, R = *t*BuMe$_2$Si; **e**, R = (MeO)Me$_2$C; **f**, R = Bn) (see Schemes 1 and 2).

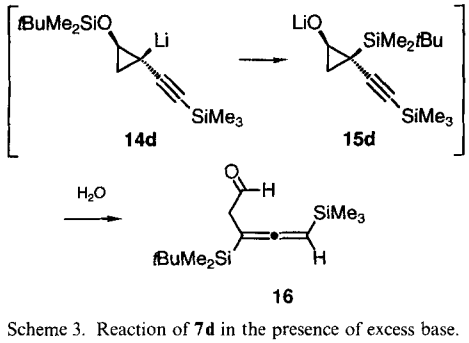
Substrate	Reagent (equiv)	Product	T/°C	Yield (%)	$(S,R)/(R,R)$ [a]	*ee* [b] (%)
(*S*)-**4b**	LiHMDS (2.5)	(*S*)-**7b**	0	89	2.0:1	95
(*S*)-**5b**	LiHMDS [c] (2.5)	(*S*)-**7b**	0	89	2.0:1	95
(*S*)-**5c**	LDA [d] (3.0)	(*S*)-**7c**	−78	92	>40:1	96
(*S*)-**3d**	LDA (1.6) [e]	(*S*)-**7d**	−78	42	20:1	98
(*S*)-**4d**	LDA (2.0) [e]	(*S*)-**7d**	−78	31	16:1	98
(*S*)-**5d**	LDA (1.16) [e]	(*S*)-**7d**	−78	75	2.6:1	98
(*S*)-**6d**	LDA (1.2) [e]	(*S*)-**7d**	−78	74	1:1	98
(*S*)-**5e**	LDA (3.0)	(*S*)-**7e**	−78	83	30:1	94
(*S*)-**4f**	LiHMDS (3.0)	(*S*)-**7f**	0	73	2.2:1	98
(*S*)-**5f**	LiHMDS (3.0)	(*S*)-**7f**	0	85	2.3:1	96
(*S*)-**10f**	LiHMDS (3.0)	(*S*)-**12f**	0	21	2.5:1	95
(*S*)-**11f**	LiHMDS (3.0)	(*S*)-**13f**	0	32	2.6:1	97

[a] Determined by GC and/or ^{1}H NMR spectroscopy. [b] Determined by GC on a chiral column [14]. [c] Lithium hexamethyldisilazide. [d] Lithium diisopropylamide. [e] Inverse addition.

tosylates were therefore converted to the corresponding bromides **5** or iodides **6** in high yields by treatment with lithium bromide or sodium iodide in refluxing acetone (Table 1).

The cyclization of the bromide (*S*)-**5b** with lithium hexamethyldisilazide (LiHMDS) in THF gave a yield of 89%, but a diastereomeric excess of only 33% ($(S,R)/(R,R) = 2.0:1$; Table 2).[6d] However, this mixture could be converted to pure (*S*,*R*)-**7b** by treatment with 4 equiv of LDA at −78 °C. The bromide (*S*)-**5c** was converted to the corresponding cyclopropane **7c** ($(S,R)/(R,R) > 40:1$) in 92% yield with 3 equiv of LDA.

The TBDMS-protected precursors [(*S*)-**3d**, (*S*)-**4d**, (*S*)-**5d**, and (*S*)-**6d**] all had to be cyclized with inverse addition of only one equivalent of LDA; a temporary or permanent excess of base led to deprotonation of the product **7d**, and the anion **14d** thus formed underwent a retro-Brook rearrangement followed by ring-opening of the cyclopropanolate to give, after aqueous workup, the pentadienal **16**, which polymerized readily (Scheme 3). With the better leaving groups bromide in (*S*)-**5d** and iodide in (*S*)-**6d** the yields were better (75 and 74%), but the diastereoselectivity was lower (Table 2).



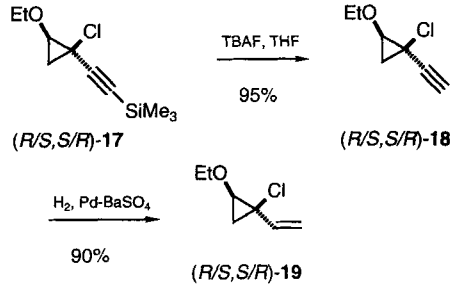
Scheme 3. Reaction of **7d** in the presence of excess base.

The acetal-protected precursor bromide (*S*)-**5e** was cyclized with 3 equiv of LDA in 83% yield and with a diastereomeric excess of more than 93% ($(S,R)/(R,R) > 30:1$). Cyclization of the stable benzyl-protected tosylate (*S*)-**4f** could be achieved in 73% yield by using LiHMDS in THF, but proceeded with poor diastereoselectivity ($(S,R)/(R,R) = 2.2:1$), like the reaction with the ethoxy analogue (*S*)-**4b**. Again, a subsequent isomerization of the product with 4 equiv of LDA produced diastereomerically pure (*S*,*R*)-**7f**. The cyclizations of the benzyl-protected derivatives (*S*)-**10f** and (*S*)-**11f** with LiHMDS gave only low yields (21 and 32%, respectively), obviously due to the lower acidity of the propargylic protons and/or polymerization.

The enantiomeric excesses of all the products were determined by gas chromatography on a chiral column[14] to be in the range between 94 and 98%. This proves that all the transformations with the epoxides (*S*)-**1** and (*S*)-**2** proceeded without any racemization.

Preparation of 1-Substituted 2-Alkoxy-1-ethynylcyclopropane Derivatives and Their Further Transformations: For one of the intended uses of the enantiomerically pure cyclopropanes (*S*)-**7**, an appropiate leaving group had to be introduced at the propargylic 1-position. As recent work has shown,[6d] 2-alkoxy-1-(trimethylsilylethynyl)cyclopropanes can readily be deprotonated at the 1-position, and substituents introduced as electrophiles. This worked particularly well with the ethoxy derivative **7b** (to give, e.g., **17**), but problems were encountered with the *tert*-butyloxy compound **7c** and the (1′-methoxyisopropyl)oxy derivative **7e**; the benzyloxy compound **7f** has not yet been tested.

In a first attempt, the previously described ethynylcyclopropane (*R*/*S*,*S*/*R*)-**17**[6d] was desilylated with tetra-*n*-butylammonium fluoride (TBAF) in THF, and (*R*/*S*,*S*/*R*)-**18** was hydrogenated over Lindlar catalyst to give the ethenylcyclopropane (*R*/*S*,*S*/*R*)-**19** (Scheme 4, 86% over two steps). Upon attempted substitution of this allylic chloride with the sodium enolate of dimethyl propargylmalonate in the presence of different palladium(0) catalysts at ambient or elevated temperatures, only ring-opening products were obtained. The bromo analogue of (*R*/*S*,*S*/*R*)-**17**[6d] did not survive the desilylation step.

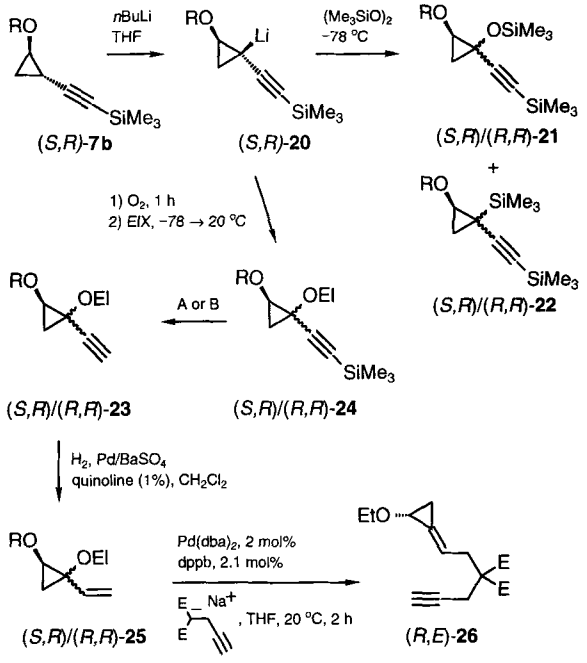


Scheme 4.

Efforts were therefore focused on the introduction of oxygen-based leaving groups into 2-alkoxy-1-ethynylcyclopropanes **7**. As **7** can cleanly be deprotonated in the 1-position with butyllithium,[6d] some of the few oxygen electrophiles known in the literature[15] were tried out on the lithium derivative (*S*,*R*)-**20**. Bis(trimethylsilyl)peroxide[16] gave only 30% of the silyloxy derivative (*S*,*R*)/(*R*,*R*)-**21** in addition to 65% of the silylated product (*S*,*R*)/(*R*,*R*)-**22** (Scheme 5). Treatment of (*S*,*R*)-**20** with bis(*p*-nitrophenylsulfonyl)peroxide led to its complete decomposition.

As oxygen has successfully been used for the preparation of cyclopropanols in reactions with organometallic cyclopropyl derivatives,[17b, c, d, e] the lithium derivative (*S*,*R*)-**20** was treated at −78 °C with dry air or oxygen, free of carbon dioxide.[18] After approximately 10 min the dark solution turned light yellow, and an electrophile (E|X) was added after 1 h at −78 °C (Scheme 5 and Table 3). The products **24** were obtained as mixtures of (*S*,*R*) and (*R*,*R*) diastereomers (ratio 2:1).

The diastereomeric excess could be increased to 50% (ratio 3:1) when the anion (*S*,*R*)-**20** was cooled to −90 °C during the



Scheme 5. For conditions see Table 3 (E = CO_2Me; R = Et; El = $SiMe_3$, Ac, Ms, Ts, Ns, or Me).

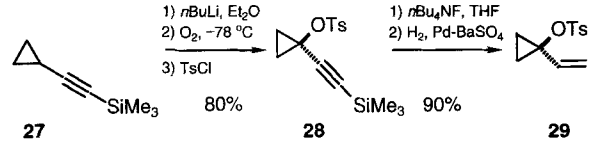
Table 3. Electrophilic substitution of (*S,R*)/(*R,R*)-**7b**, and protodesilylation and catalytic hydrogenation of (*S,R*)/(*R,R*)-**23** (see Scheme 3).

Entry	Electrophile [a]	OEl	Yield (%) **24**	Protodesilylation Yield (%), Method [b] (*S,R*)-**23**	(*R,R*)-**23**	Hydrogenation Yield (%) (*S,R*)-**25**	(*R,R*)-**25**
1	Me_3SiCl	$OSiMe_3$	93	– [c]	–	–	–
2	Ac_2O	OAc	83	95, A	90, A	–	–
3	MsCl	OMs	73	94, A	92, A	79	87
4	TsCl	OTs	78	94, B	92, B	94	94
5	NsCl	ONs	65	85, B	83, B	85	83
6	$Me_3O^+BF_4^-$	OMe	81	88, B [d]	>90, B [d]	>90 [d]	>90 [d]

[a] Ms = methanesulfonyl, Ts = *p*-toluenesulfonyl, Ns = *p*-nitrobenzenesulfonyl. [b] Method A: $Bu_4N^+F^-$/THF, 5 min; Method B: K_2CO_3/MeOH; 15 min. [c] Not carried out. [d] Mixture of (*S,R*) and (*R,R*) derivative.

treatment with oxygen, and to 60% (ratio 4:1) when precooled (−78 °C) oxygen was applied at −90 °C. The low diastereoselectivity obviously results from partial inversion of configuration during the oxygenation process; this is surprising in view of the fact that other electrophiles gave high diastereoselectivities in the reaction with (*S,R*)-**20**.[6d] Warner et al. have invoked a radical process in the oxygenation of a bicyclo[4.1.0]-heptyllithium derivative as being responsible for the formation of a mixture of *endo*- and *exo*-alcohols.[17d] A radical center in the 1-position of (*S,R*)-**7** would be stabilized by the adjacent (trimethylsilylethynyl) group, but not by chelation with the 2-alkoxy substituent, which is operative for the lithium derivative (*S,R*)-**20**. The radical might therefore relax configurationally before combining with an oxygen molecule. The primary oxygenation products, the 2-ethoxy-1-(trimethylsilylethynyl)-1-cyclopropanolates, could not only be acylated and sulfonated (Table 3, entries 2–5), but also silylated and alkylated (entries 1 and 6). This method can thus be used to prepare unsymmetrically substituted 1,2-dialkoxycyclopropane derivatives with 1-ethynyl and other substituents derived therefrom.[19]

To test whether this methodology can also be applied to other cyclopropanes without the 2-alkoxy substituent, cyclopropyltrimethylsilylethyne (**27**)[6d] was deprotonated with butyllithium, and the resulting solution treated with dry oxygen followed by tosyl chloride (Scheme 6). The resulting propargyl tosylate **28** could be protodesilylated and the terminal alkyne then converted to 1-ethenylcyclopropyl tosylate **29** by catalytic hydrogenation over Lindlar catalyst (Pd on $BaSO_4$, additionally poisoned with 1% quinoline). The overall yield in this three-step transformation was 73%.

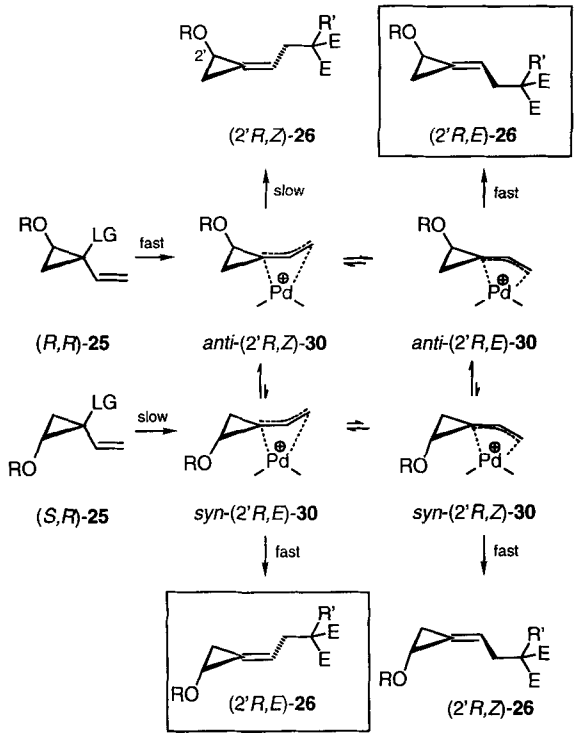


Scheme 6.

The derivatives **24** could easily be protodesilylated with tetra-*n*-butylammonium fluoride (TBAF) in THF or with potassium carbonate in methanol (Scheme 5, Table 3). The TBAF method consistently gave better results, especially with the mesylate (entry 3). Catalytic hydrogenation of the sulfonates (*S,R*)/(*R,R*)-**23** could be achieved without problems and gave the desired allylic sulfonates (*S,R*)/(*R,R*)-**25** in remarkably good to excellent yields (Table 3).

The tosylate (2*R*)-**25**-OTs reacted smoothly at room temperature with dimethyl sodiumpropargylmalonate in the presence of catalytic Pd(dppb), generated in situ from $Pd(dba)_2$ (dba = dibenzylideneacetone) and 1,4-bis(diphenylphosphano)butane (dppb). Both diastereomers gave the same single product (2*R,E*)-**26**; the *trans* isomer, however, reacted more slowly. The same product was obtained from the mesylate (*R,R*)-**25**-OMs and the nosylate (*R,R*)-**25**-ONs, but the yields were significantly lower (45% and 32%, respectively).

The (*E*) configuration of the product was assigned on the basis of NOESY spectra and by comparison with other re-



Scheme 7. Formation of a single diastereomer (2*R,E*)-**26** from both diastereomers (*S,R*)- and (*R,R*)-**25**.

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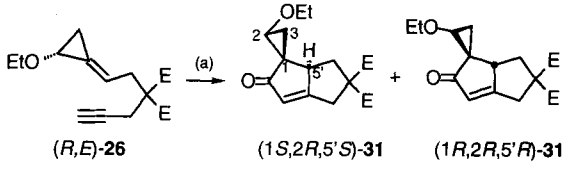
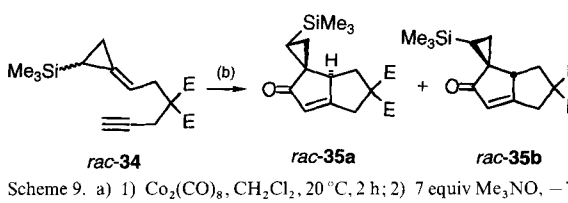
sults.[20e] The formation of a single diastereomer (2*R*,*E*)-**26** from both diastereomers (*S*,*R*)- and (*R*,*R*)-**25** can be rationalized by invoking a reasonably rapid isomerization of the four diastereomeric π-allyl complexes via the corresponding σ-allyl complexes (Scheme 7) and the rapid reaction of the two predominant (2′*R*,*E*) diastereomers with the malonate enolate.[20e] The enantiomeric excess of the product (2′*R*,*E*)-**26** was determined by gas chromatography on a chiral column to be virtually the same (94%) as that of the starting material (*S*,*R*)-**7b**.



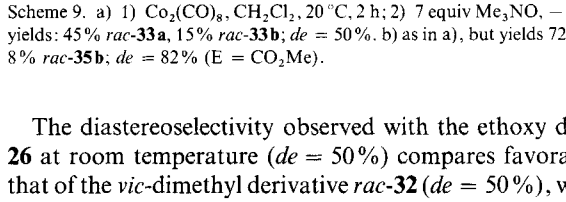
(*R*,*E*)-**26** (1*S*,2*R*,5′*S*)-**31** (1*R*,2*R*,5′*R*)-**31**

Scheme 8. a) 1) $Co_2(CO)_8$, CH_2Cl_2, 20 °C, 2 h; 2) 7 equiv Me_3NO, −78 °C or 20 °C, 50–100% *de*, 80–85% (E = CO_2Me).

Compound (*R*,*E*)-**26** was subjected to an intramolecular Pauson–Khand reaction by treatment with a stoichiometric amount of $Co_2(CO)_8$ in dichloromethane at room temperature followed by trimethylamine-*N*-oxide (TMANO)[21] at −78 °C to give a single enantiomer (^{1}H NMR, GC-MS) of the spirocyclopropanebicyclo[3.3.0]octane derivative **31** (Scheme 8). The relative configuration of the product was confirmed by NOESY spectra (NOE between the ethoxy group and the 5′-bridgehead hydrogen; no NOE between the cyclopropyl proton 2-H and the bridgehead hydrogen) and comparison with the spectra of other derivatives. When the cycloaddition was carried out by adding TMANO at room temperature, two diastereomers of **31** were obtained in a ratio of 3:1. In the NOESY spectrum of the minor isomer, no NOE was observed between the ethoxy group and the 5′-bridgehead hydrogen, but between 2-H and 5′-H.



rac-**32** *rac*-**33a** *rac*-**33b**



rac-**34** *rac*-**35a** *rac*-**35b**

Scheme 9. a) 1) $Co_2(CO)_8$, CH_2Cl_2, 20 °C, 2 h; 2) 7 equiv Me_3NO, −78 → 20 °C; yields: 45% *rac*-**33a**, 15% *rac*-**33b**; *de* = 50%. b) as in a), but yields 72% *rac*-**35a**, 8% *rac*-**35b**; *de* = 82% (E = CO_2Me).

The diastereoselectivity observed with the ethoxy derivative **26** at room temperature (*de* = 50%) compares favorably with that of the *vic*-dimethyl derivative *rac*-**32** (*de* = 50%), while that of the derivative *rac*-**34** with the yet bulkier trimethylsilyl group is even larger (*de* = 82%) (Scheme 9).

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on Bruker AW250 or WM500 instruments at 250 or 500 MHz and 62.9 MHz or 125 MHz, respectively. Chemical shifts in $CDCl_3$ or [D_6]benzene are reported in ppm relative to tetramethylsilane (TMS), chloroform or benzene as internal reference unless otherwise stated. IR spectra were registrered on a Perkin Elmer 1720 FTIR or a Bruker IFS66. Low resolution EI mass spectra were obtained on a Varian MAT CH-7 with Varian Aerograph 1740 with an ionizing voltage of 70 eV. High-resolution MS were obtained on a VG-70-250S. Optical rotations were measured with Perkin-Elmer 241 and 243 digital polarimeters. Elemental analyses were performed by the Institut für Organische Chemie der Universität Hamburg and the Mikroanalytisches Labor der Universität Göttingen, Germany. Melting points are uncorrected. Solvents for extraction and chromatography were technical grade and distilled before use. Flash chromatography was performed using Merck Kieselgel 60 (200–400 mesh). Analytical gas chromatography (GC) was performed on a Siemens Sichromat 4 with a 25 m capillary column coated with CP-Sil-55-5B (column A), 6-Me-2,3-γ-CD (chiral, column B), 6-Me-2,3-pe-β-CD (chiral, column C) [22], or heptakis(6-*O*-Me-2,3-di-*O*-pe-β-CD) (chiral, column D) [22]. Organolithium compounds were titrated by the method of Suffert [23]. All reactions were carried out under an atmosphere of dry nitrogen or argon in oven- and/or flame-dried glassware. Unless otherwise specified, solutions of NH_4Cl and $NaHCO_3$ are saturated aqueous solutions. Tetrahydrofuran and diethyl ether were distilled from potassium benzophenone ketyl, and CH_2Cl_2 was distilled from CaH_2.

Starting Materials: (2*S*)-(+)-Glycidyl tosylate [(*S*)-**2**], trimethylsilylethyne, and bis(dibenzylideneacetone)palladium [Pd(dba)$_2$] were prepared according to standard methods [9,24,25]. 1,4-Bis(diphenylphosphano)butane (dppb), 1,2-bis-(diphenylphosphano)ethane (dppe), $Co_2(CO)_8$, (*S*)-epichlorohydrin [(*S*)-**1**], and dimethyl propargylmalonate are commercially avaible (Aldrich).

(*S*)-(2-Hydroxy-5-trimethylsilyl-4-pentynyl) Tosylate [(*S*)-**4a**]: A solution of trimethylsilylethyne (4.42 g, 45 mmol) in dry THF (120 mL) was treated at −78 °C with *n*BuLi (1.50 M in hexane, 28 mL, 42 mmol). The mixture was stirred for 30 min, and $BF_3 \cdot OEt_2$ (5.6 mL, 45 mmol) then added. After another 30 min, a solution of (*S*)-**2** (6.85 g, 30 mmol) in dry THF (30 mL) was added dropwise, and the mixture stirred for 3 h at −78 °C. A solution of NH_4Cl (5 mL) was added, the cooling bath removed, and the reaction allowed to warm to RT. The reaction mixture was poured into a solution of NH_4Cl (300 mL) and extracted with diethyl ether (5 × 150 mL). The combined organic layers were washed with sat. $NaHCO_3$ and brine, dried ($MgSO_4$), concentrated under reduced pressure, and the residue purified by column chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 10/1] yielding 9.50 g (97%) of (*S*)-**4a**: M.p. 51 °C; $[\alpha]_D^{20} = +21.0$ (c = 1.75 in $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3529 (O–H), 2959 (C–H), 2178 (C≡C), 1599 (C=C), 1496, 1363 (SO_2), 1250 (Si–C), 1178 (SO_2), 1098, 989, 930, 845, 762, 734, 668 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.09 [s, 9H; $Si(CH_3)_3$], 2.28 (d, ^3J = 5.3 Hz, 1H; OH), 2.43 (s, 3H; CH_3), 2.42, 2.47 (ABX, $^3J_{AX} = {}^3J_{BX}$ = 5.9, $^2J_{AB}$ = 12.2 Hz, 2H; 3-H), 3.93–3.99 (m_c, 1H; C*H*OH), 4.01 (dd, ^3J = 6.3, ^2J = 10.0 Hz, 1H; 1-H), 4.12 (dd, ^3J = 3.9, ^2J = 10.0 Hz, 1H; 1-H), 7.34 (d, ^3J = 8.4 Hz, 2H; Ar-H), 7.79 (d, ^3J = 8.4 Hz, 2H; Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −0.15 [+, $Si(CH_3)_3$], 21.61 (+, CH_3), 24.65 (−, C-3), 67.65 (−, C-1), 72.01 (+, C-2), 88.43 (C_{quat}, C-5), 100.74 (C_{quat}, C-4), 127.98 (+, C–Ar), 129.92 (+, C–Ar), 132.55 (C_{quat}, C–Ar), 145.08 (C_{quat}, C–Ar); MS (70 eV, EI): *m*/*z* (%): 311 (3.1) [$M^+ - CH_3$], 230 (16), 229 (100) [$M^+ - C_2SiMe_3$], 215 (16), 155 (49), 149 (16), 139 (18), 109 (12), 92 (11), 91 (78) [$C_7H_7^+$], 83 (16), 75 (17), 73 (63) [$SiMe_3^+$], 65 (24), 45 (10); $C_{15}H_{22}O_4SSi$ (326.5): calcd C 55.18, H 6.79, S 9.82; found C 55.42, H 6.92, S 10.00.

(*S*)-1-Chloro-2-hydroxy-5-trimethylsilyl-4-pentyne [(*S*)-**3a**]: A solution of trimethylsilylethyne (4.42 g, 45 mmol) in dry THF (120 mL) was treated at −78 °C with *n*BuLi (1.50 M in hexane, 28 mL, 42 mmol). The mixture was stirred for 30 min, and $BF_3 \cdot OEt_2$ (5.6 mL, 45 mmol) then added. After another 30 min, a solution of (*S*)-**1** (2.68 g, 29 mmol) in dry THF (30 mL) was added dropwise, and the mixture stirred for 3 h at −78 °C. A solution of NH_4Cl (5 mL) was added, the cooling bath removed, and the reaction warmed to RT. The reaction mixture was poured into a solution of NH_4Cl (300 mL) and extracted with diethyl ether (5 × 150 mL). The combined organic layers were washed with sat. $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated under reduced pressure to afford 5.41 g (98%) of (*S*)-**3a**: $[\alpha]_D^{20} = +19.3$ (c = 1.21 in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 3401 (O–H), 2960 (C–H), 2178 (C≡C), 1430, 1251 (Si–C), 1030, 844, 761, 702, 647 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 [s, 9H; $Si(CH_3)_3$], 2.50, 2.59 (ABX, $^2J_{AB}$ = −17.0, $^3J_{AX}$ = 6.6, $^3J_{BX}$ = 5.8 Hz, 2H; 3-H), 2.66 (bs, 1H; OH), 3.60, 3.71 (ABX, $^2J_{AB}$ = −11.1, $^3J_{AX}$ = 6.0, $^3J_{BX}$ = 4.8 Hz, 2H; 1-H), 3.94 (m_c, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −0.10 [+, $Si(CH_3)_3$], 25.68 (−, C-3), 48.17 (−, C-1), 69.59 (+, C-2), 88.14 (C_{quat}, C-5), 101.24 (C_{quat}, C-4); MS (70 eV, EI): *m*/*z* (%): 192/190 (0.01/0.02) [M^+], 177/175 (0.4/0.9) [$M^+ - CH_3$], 112 (13), 100 (16), 97 (12), 95 (23), 93 (47), 91 (12), 83 (11), 81 (13), 79 (11), 75 (27), 73 (100) [$SiMe_3^+$], 65 (34), 55 (15), 53 (17), 45 (20); $C_8H_{15}ClOSi$ (190.7): calcd C 50.38, H 7.93, Cl 18.59; found C 50.41, H 7.91, Cl 18.33.

(*S*)-(2-Hydroxy-5-phenyl-4-pentynyl) Tosylate [(*S*)-**10a**]: A solution of phenylethyne (4.6 g, 45 mmol) in dry THF (120 mL) was treated at −78 °C with *n*BuLi (1.50 M in hexane, 28 mL, 42 mmol). The mixture was stirred for 30 min, and $BF_3 \cdot OEt_2$ (5.6 mL, 45 mmol) then added. After another 30 min, a solution of (*S*)-**2** (6.85 g, 30 mmol) in dry THF (30 mL) was added dropwise, and the mixture stirred for 3 h at −78 °C. A solution of NH_4Cl (5 mL) was added, the cooling bath removed, and the reaction allowed to warm to RT. The reaction mixture was poured into a solution of NH_4Cl (300 mL) and extracted with diethyl ether (5 × 150 mL). The combined organic layers were washed with sat. $NaHCO_3$ and brine, dried

($MgSO_4$), concentrated under reduced pressure, and the residue purified by column chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 10/1] yielding 9.13 g (92%) of (*S*)-**10a**: M.p. 72 °C; $[\alpha]_D^{20} = +34.8$ ($c = 1.6$ in $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3541 (O–H), 2955 (C–H), 2185 (C≡C), 1605 (C=C), 1500, 1359 (SO_2), 1182 (SO_2), 1102, 992, 762, 755, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.32 (d, ^3J = 5.2 Hz, 1H; OH), 2.44 (s, 3H; CH_3), 2.43, 2.48 (ABX, $^3J_{AX} = {}^3J_{BX}$ = 5.9, $^2J_{AB}$ = 12.3 Hz, 2H; 3-H), 3.90–4.00 (m_c, 1H; C*H*OH), 4.08 (dd, ^3J = 6.3, ^2J = 10.2 Hz, 1H; 1-H), 4.19 (dd, ^3J = 3.9, ^2J = 10.2 Hz, 1H; 1-H), 7.21–7.80 (m, 9H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.88 (+, CH_3), 24.77 (–, C-3), 67.45 (–, C-1), 75.04 (+, C-2), 89.45 (C_{quat}, C-5), 101.23 (C_{quat}, C-4), 122.45 (C_{quat}, C–Ar), 127.98 (+, C–Ar), 128.15 (+, C–Ar), 128.44 (+, C–Ar), 129.92 (+, C–Ar), 132.34 (+, C–Ar), 132.55 (C_{quat}, C–Ar), 145.08 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 315 (8) [$M^+ - CH_3$], 280 (16), 209 (55), 155 (23), 149 (16), 91 (100) [$C_7H_7^+$]; $C_{18}H_{18}O_4S$ (330.4): calcd C 65.44, H 5.49; found C 65.69, H 5.25.

(*S*)-(6,6-Dimethyl-2-hydroxy-4-heptynyl) Tosylate [(*S*)-**11a**]: A solution of 3,3-dimethylbutyne (3.7 g, 45 mmol) in dry THF (120 mL) was treated at –78 °C with *n*BuLi (1.50 M in hexane, 28 mL, 42 mmol). The mixture was stirred for 30 min, and $BF_3 \cdot OEt_2$ (5.6 mL, 45 mmol) then added. After another 30 min, a solution of (*S*)-**2** (6.85 g, 30 mmol) in dry THF (30 mL) was added dropwise, and the mixture stirred for 3 h at –78 °C. A solution of NH_4Cl (5 mL) was added, the cooling bath removed, and the reaction allowed to warm to RT. The reaction mixture was poured into a solution of NH_4Cl (300 mL) and extracted with diethyl ether (5 × 150 mL). The combined organic layers were washed with sat. $NaHCO_3$ and brine, dried ($MgSO_4$), concentrated under reduced pressure, and the residue purified by column chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 10/1] yielding 8.40 g (90%) of (*S*)-**11a**: M.p. 35 °C; $[\alpha]_D^{20} = +7.80$ ($c = 1.2$ in $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3520 (O–H), 2961 (C–H), 2169 (C≡C), 1604 (C=C), 1502, 1371 (SO_2), 1182 (SO_2), 1102, 990, 935, 845, 734, 672 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.55 [s, 9H; $C(CH_3)_3$], 2.28 (d, ^3J = 5.3 Hz, 1H; OH), 2.44 (s, 3H; CH_3), 2.40, 2.49 (ABX, $^3J_{AX} = {}^3J_{BX}$ = 5.9, $^2J_{AB}$ = 12.2 Hz, 2H; 3-H), 3.90–4.04 (m_c, 1H; C*H*OH), 4.07 (dd, ^3J = 6.3, ^2J = 10.0 Hz, 1H; 1-H), 4.18 (dd, ^3J = 3.9, ^2J = 10.0 Hz, 1H; 1-H), 7.39 (d, ^3J = 8.4 Hz, 2H; Ar–H), 7.82 (d, ^3J = 8.4 Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.95 [+, $C(CH_3)$], 20.45 [C_{quat}, $C(CH_3)_3$], 21.55 (+, CH_3), 25.03 (–, C-3), 67.88 (–, C-1), 72.09 (+, C-2), 86.78 (C_{quat}, C-5), 101.67 (C_{quat}, C-4), 128.03 (+, C–Ar), 130.56 (+, C–Ar), 132.34 (C_{quat}, C–Ar), 145.10 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 310 (3.1) [M^+], 230 (16), 155 (22), 149 (12), 139 (18), 92 (16), 91 (100) [$C_7H_7^+$], 83 (12), 75 (19), 65 (44), 45 (13); $C_{16}H_{22}O_4S$ (310.4): calcd C 61.91, H 7.14; found C 61.72, H 6.92.

(*S*)-2-Ethoxy-5-trimethylsilyl-4-pentynyl Tosylate [(*S*)-**4b**]: The alcohol (*S*)-**4a** (164 mg, 0.5 mmol) and ethyldiisopropylamine (162 mg, 1.3 mmol) were added to a solution of triethyloxonium tetrafluoroborate (190 mg, 1 mmol) in dry CH_2Cl_2 (20 mL). After 24 h of stirring at RT, the reaction mixture was poured into a solution of $NaHCO_3$ (20 mL) and extracted with diethyl ether (5 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 10/1] yielded 99 mg (56%, 74% based on conversion) of (*S*)-**4b** as a white solid: M.p. 48.5 °C; $[\alpha]_D^{20} = +24.3$ ($c = 0.98$ in $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 2959 (C–H), 2178 (C≡C), 1599 (C=C), 1496, 1363 (SO_2), 1250 (Si–C), 1178 (SO_2), 1098, 989, 930, 845, 762, 734, 668 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.11 [s, 9H; $Si(CH_3)_3$], 1.13 (t, ^3J = 7.0 Hz, 3H; CH_3CH_2O), 2.41, 2.44 (ABX, $^2J_{AB}$ = –17.0, $^3J_{AX}$ = 7.3, $^3J_{BX}$ = 6.2 Hz, 2H; 3-H), 2.44 (s, 3H; Ar–CH_3), 3.45–3.70 (m, 3H; CH_3CH_2O, 2-H), 4.03, 4.16 (ABX, $^2J_{AB}$ = –10.4, $^3J_{AX}$ = 4.0, $^3J_{BX}$ = 4.0 Hz, 2H; 1-H), 7.33 (d, ^3J = 8.0 Hz, 2H; Ar–H), 7.80 (d, ^3J = 8.0 Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –0.17 [+, $Si(CH_3)_3$], 15.20 (+, Ar–CH_3), 21.52 (+, CH_3CH_2), 22.63 (–, C-3), 65.79 (–, CH_3CH_2), 70.55 (–, C-1), 74.96 (+, C-2), 87.25 (C_{quat}, C-5), 101.73 (C_{quat}, C-4), 127.92 (+, C–Ar), 129.74 (+, C–Ar), 133.04 (C_{quat}, C–Ar), 144.50 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 243 (100) [$M^+ - C_3H_2Si(CH_3)_3$], 155 (95) [$C_7H_7SO_2^+$], 91 (74) [$C_7H_7^+$], 73 (52) [$SiMe_3^+$]; $C_{17}H_{26}O_4SSi$ (354.5): calcd C 57.59, H 7.39; found C 57.72, H 7.56.

Further elution afforded first 7 mg (5%) of (*S*)-2-ethoxy-4-pentynyl tosylate [(*S*)-**9b**] and then 40 mg (24%) (*S*)-**4b**. (*S*)-**9b**: $[\alpha]_D^{20} = +5.3$ ($c = 0.89$ in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 3280 (C≡C–H), 2959 (C–H), 2178 (C≡C), 1599 (C=C), 1496, 1363 (SO_2), 1178 (SO_2), 1098, 989, 930, 845, 762, 734, 668 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.14 (t, ^3J = 7.0 Hz, 3H; CH_3CH_2O), 1.93 (t, $^4J_{3,5}$ = 2.6 Hz, 1H; 5-H), 2.41 (dd, $^4J_{3,5}$ = 2.6, $^3J_{2,3}$ = 6.2 Hz, 2H; 3-H), 2.44 (s, 3H; Ar–CH_3), 3.52 (t, ^3J = 7.0 Hz, 2H; CH_3CH_2O), 3.50–3.65 (m_c, 1H; 2-H), 4.03, 4.16 (ABX, $^2J_{AB}$ = –11.3, $^3J_{AX}$ = 5.6, $^3J_{BX}$ = 4.5 Hz, 2H; 1-H), 7.33 (d, ^3J = 8.3 Hz, 2H; Ar–H), 7.80 (d, ^3J = 8.3 Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.19 (+, CH_3CH_2), 21.14 (–, C-3), 21.55 (+, Ar–CH_3), 65.84 (–, CH_3CH_2O), 70.03 (–, C-1), 70.64 (C_{quat}, C-4), 74.96 (+, C-2), 79.22 (+, C-5), 127.90 (+, C–Ar), 129.77 (+, C–Ar), 132.77 (C_{quat}, C–Ar), 144.82 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 243 (62) [$M^+ - C_3H_3$], 155 (82) [$C_7H_7SO_2^+$], 91 (100) [$C_7H_7^+$]; $C_{14}H_{18}O_4S$ (282.3): calcd C 59.55, H 6.43; found C 59.37, H 6.57.

(*S*)-2-*tert*-Butoxy-5-trimethylsilyl-4-pentynyl Tosylate [(*S*)-**4c**]: A solution of (*S*)-**4a** (19.0 g, 58.2 mmol) in CH_2Cl_2 (400 mL) was treated at –78 °C with a mixture of precooled (–20 °C) 2-methylpropene (500 mL, 350 g, 6.2 mol) and conc. sulfuric acid (464 mg, 4.5 mmol). The flask was stoppered, and the reaction mixture allowed to warm to RT. After 2 d it was recooled to –78 °C and then cautiously poured into a solution of $NaHCO_3$. Extraction with diethyl ether (3 × 100 mL) was followed by drying ($MgSO_4$) of the combined organic layers. Concentration under reduced pressure and purification of the crude material by flash chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 10/1], yielded 17.0 g (76%) of (*S*)-**4c**: $[\alpha]_D^{20} = +18.7$ ($c = 1.33$ in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2972 (C–H), 2177 (C≡C), 1598 (C=C), 1453, 1366 (SO_2), 1250, 1177 (SO_2), 1029, 982, 940, 843, 760, 735 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.11 [s, 9H; $Si(CH_3)_3$], 1.15 [s, 9H; $C(CH_3)_3$], 2.35, 2.38 (ABX, $^2J_{AB}$ = –17.0, $^3J_{AX}$ = 6.0, $^3J_{BX}$ = 4.7 Hz, 2H; 3-H), 2.44 (s, 3H; Ar–CH_3), 3.82 (m_c, 1H; 2-H), 3.92 (ABX, $^2J_{AB}$ = –10.0, $^3J_{AX}$ = 5.5, $^3J_{BX}$ = 5.0 Hz, 2H; 1-H), 7.35 (d, ^3J = 8.0 Hz, 2H; Ar–H), 7.80 (d, ^3J = 8.0 Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.14 [+, $Si(CH_3)_3$], 21.55 (+, Ar–CH_3), 24.93 (–, C-3), 28.14 [+, $C(CH_3)_3$], 68.08 (+, C-2), 71.57 (–, C-1), 75.56 [C_{quat}, $C(CH_3)_3$], 86.98 (C_{quat}, C-5), 102.49 (C_{quat}, C-4), 127.93 (+, C–Ar), 129.74 (+, C–Ar), 132.96 (C_{quat}, C–Ar), 144.67 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 367 (1) [$M^+ - CH_3$], 215 (100), 155 (43) [$C_7H_7SO_2^+$], 91 (27) ($C_7H_7^+$), 73 (7) ($SiMe_3^+$]; $C_{19}H_{30}O_4SSi$ (382.6): calcd C 59.65, H 7.90, S 8.38; found C 59.84, H 7.99, S 8.44.

(*S*)-2-*tert*-Butyldimethylsilyloxy-5-trimethylsilyl-4-pentynyl Tosylate [(*S*)-**4d**]: To a solution of (*S*)-**4a** (8.16 g, 25 mmol) in dry dimethylformamide (DMF) (100 mL) *tert*-butyldimethylsilylchloride (TBDMSCl) (11.25 g, 75 mmol) and imidazole (10.4 g, 153 mmol) were added, and the mixture was stirred for 16 h at RT. The solution was poured into a solution of NH_4Cl (100 mL), the aqueous layer was extracted with diethyl ether (3 × 100 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (pentane/diethyl ether = 5/1) to yield 10.03 g (91%) of (*S*)-**4d** as a white solid: M.p. 69 °C; $[\alpha]_D^{20} = +10.4$ ($c = 2.0$ in $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 2958–2855 (C–H), 2180 (C≡C), 1597 (C=C), 1471, 1349 (SO_2), 1286, 1251 (Si–C), 1191, 1173 (SO_2), 1124, 1095, 1045, 1006, 981, 927, 888, 842, 814, 780, 759, 732, 706, 681, 661, 629, 566, 554 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.05 (s, 3H; $SiCH_3$), 0.08 (s, 3H; $SiCH_3$), 0.10 [s, 9H; $Si(CH_3)_3$], 0.83 [s, 9H; $SiC(CH_3)_3$], 2.36 (m, 2H; 3-H), 2.44 (s, 3H; CH_3), 3.88–4.08 (m, 3H; 1-H, 2-H), 7.34 (d, ^3J = 8.3 Hz, 2H; Ar–H), 7.80 (d, ^3J = 8.3 Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.81 (+, $SiCH_3$), –4.77 (+, $SiCH_3$), –1.00 [+, $Si(CH_3)_3$], 17.95 [C_{quat}, $SiC(CH_3)_3$], 21.61 (+, CH_3), 25.65 (–, C-3), 25.72 [+, $SiC(CH_3)_3$], 68.96 (+, C-2), 72.34 (–, C-1), 87.27 (C_{quat}, C-5), 102.15 (C_{quat}, C-4), 127.98 (+, C–Ar), 129.83 (+, C–Ar), 133.00 (C_{quat}, C–Ar), 144.79 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 383 (9.9) [$M^+ - t$Bu], 329 (13), 231 (11), 230 (18), 229 (100) [$M^+ - C_4H_8 - C_7H_7O_2S$], 139 (14), 91 (14) [$C_7H_7^+$], 73 (28) [$SiMe_3^+$]; $C_{21}H_{36}O_4SSi_2$ (440.8): calcd C 57.23, H 8.23, S 7.27; found C 57.27, H 8.31, S 7.22.

(*S*)-2-*tert*-Butyldimethylsilyloxy-1-chloro-5-trimethylsilyl-4-pentyne [(*S*)-**3d**]: To a solution of (*S*)-**3a** (5.42 g, 28 mmol) in dry DMF (100 mL) TBDMSCl (12.7 g, 84 mmol, 3 equiv) and imidazole (10.4 g, 153 mmol) were added, and the mixture was stirred for 24 h at RT. The solution was poured into a solution of NH_4Cl (300 mL), and the aqueous layer extracted with pentane (3 × 200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel [petroleum ether (30/50)/diethyl ether = 20/1] to yield 6.90 g (80%) of (*S*)-**3d**: $R_f = 0.2$; $[\alpha]_D^{20} = +3.4$ ($c = 1.725$ in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2958–2859 (C–H), 2180 (C≡C), 1473, 1362, 1252 (Si–C), 1115, 1038, 935, 842, 778, 643 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.11 [s, 6H; $Si(CH_3)_2$], 0.16 [s, 9H; $Si(CH_3)_3$], 0.81 [s, 9H; $SiC(CH_3)_3$], 2.43, 2.55 (ABX, $^2J_{AB}$ = –16.7, $^3J_{AX}$ = 5.8, $^3J_{BX}$ = 6.1 Hz, 2H; 3-H), 3.50, 3.59 (ABX, $^2J_{AB}$ = –10.9, $^3J_{AX}$ = 5.4, $^3J_{BX}$ = 5.1 Hz, 2H; 1-H), 3.97 (m_c, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.64 [+, $Si(CH_3)_2$], –0.15 [+, $Si(CH_3)_3$], 18.06 [C_{quat}, $SiC(CH_3)_3$], 25.72 [+, $SiC(CH_3)_3$], 26.71 (–, C-3), 48.09 (–, C-1), 71.28 (+, C-2), 86.99 (C_{quat}, C-5), 102.82 (C_{quat}, C-4); MS (70 eV, EI): *m/z* (%): 289 (2.0) [$M^+ - CH_3$], 249/247 (29/69) [$M^+ - t$Bu], 195 (16), 193 (45), 169 (36), 167 (70), 147 (27), 139 (100), 115 (31), 93 (45), 83 (29), 75 (38), 73 (100) [$SiMe_3^+$], 65 (54), 59 (33); $C_{14}H_{29}ClOSi_2$ (305.0): calcd C 55.13, H 9.58, Cl 11.62; found C 55.22, H 9.69, Cl 11.45.

(*S*)-2-(2-Methoxypropyl-2-oxy)-5-trimethylsilyl-4-pentynyl Tosylate [(*S*)-**4e**]: To a solution of (*S*)-**4a** (4.897 g, 15 mmol) in dry 2-methoxypropene (10 mL) was added 1 drop of phosphorylchloride, and the mixture was stirred for 1 h at RT. Triethylamine (3 drops) was added, and the mixture concentrated under reduced pressure to yield 6.002 g (100%) of (*S*)-**4e**, which was analytically pure. $[\alpha]_D^{20} = +12.3$ ($c = 1.03$ in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2959 (C–H), 2178 (C≡C), 1599 (C=C), 1460, 1367 (SO_2), 1251 (Si–C), 1178 (SO_2), 1097, 1061, 982, 942, 843, 762, 667 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.18 [s, 9H; $Si(CH_3)_3$], 1.12 (s, 3H; CH_3), 1.15 (s, 3H; CH_3), 1.87 (s, 3H; Ar–CH_3), 2.41 (d, $^3J_{3,2}$ = 6.2 Hz, 2H; 3-H), 2.96 (s, 3H; OCH_3), 4.04 (m_c, 1H; 2-H), 4.22, 4.29 (ABX, $^2J_{AB}$ = –10.1, $^3J_{AX}$ = 4.7, $^3J_{BX}$ = 4.8 Hz, 2H; 1-H), 6.72 (d, ^3J = 8.2 Hz, 2H; Ar–H), 7.79 (d, ^3J = 8.2 Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –0.22 [+, $Si(CH_3)_3$], 20.84 (+, Ar–CH_3), 23.99 (–, C-3), 24.66 (+, CH_3), 24.77 (+, CH_3), 48.93 (+, OCH_3), 67.34 (+, C-2), 70.72 (–, C-1), 87.08 (C_{quat}, C-5), 101.17 (C_{quat}, C-2′), 102.81 (C_{quat}, C-4), 127.98 (+, C–Ar), 129.50 (+, C–Ar), 134.04 (C_{quat}, C–Ar), 143.86 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 383 (1.0) [$M^+ - CH_3$], 229 (30), 155 (15) [$C_7H_7SO_2^+$], 139 (26), 109 (17), 91 (17) [$C_7H_7^+$], 86 (12), 83 (22), 75 (14), 73 (36)

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[$SiMe_3^+$], 65 (14), 59 (21), 58 (23), 55 (10), 43 (100); $C_{19}H_{30}O_5SSi$ (398.6): calcd C 57.25, H 7.59; found C 57.01, H 7.32.

(*S*)-2-Benzyloxy-5-trimethylsilyl-4-pentynyl Tosylate [(*S*)-**4f**]: To a solution of the alcohol (*S*)-**4a** (327 mg, 1.0 mmol) and benzyloxytrichloroacetimidate (2.52 g, 10 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C was added a solution of methanesulfonic acid (11 mg, 0.1 mmol) in dry CH_2Cl_2 (2 mL). After stirring for 24 h at RT, the reaction mixture was poured into a solution of $NaHCO_3$ (20 mL) and extracted with diethyl ether (5 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 10/1] affording 212 mg (51%, 68% based on conversion) (*S*)-**4f** as a white solid: M.p. 55 °C; $[\alpha]_D^{20} = +45.2$ ($c = 1.1$ in $CHCl_3$); IR (KBr): $\tilde{\nu} = 2990-2860$ (C–H), 2182 (C≡C), 1592 (C=C), 1473, 1349 (SO_2), 1291, 1255 (Si–C), 1193, 1175 (SO_2), 1120, 1097, 1040, 1004, 986, 929, 890, 840, 818, 782, 761, 708, 689, 670, 630, 570 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.12$ [s, 9H; $Si(CH_3)_3$], 2.43 (s, 3H; CH_3), 2.48 (d, $J = 5.6$ Hz, 2H; 3-H), 3.72–3.81 (m_c, 1H; 2-H), 4.06 (dd, $J = 5.8$, $J = 10.4$, 1H; 1-H), 4.34 (dd, $J = 6.3$, $J = 10.4$, 1H; 1-H), 4.6–4.8 (m, 2H; CH_2O), 7.1–7.9 (m, 9H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -0.17$ [+, $Si(CH_3)_3$], 15.20 (+, Ar–CH_3), 22.63 (–, C-3), 65.93 (–, CH_2O), 70.55 (–, C-1), 74.96 (+, C-2), 87.25 (C_{quat}, C-5), 101.73 (C_{quat}, C-4), 127.21 (+, C–Ar), 127.92 (+, C–Ar), 128.65 (+, C–Ar), 128.78 (+, C–Ar), 129.74 (+, C–Ar), 133.04 (C_{quat}, C–Ar), 140.85 (C_{quat}, C–Ar), 144.5 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 416 (1) [M^+], 155 (43), 91 (100) [$C_7H_7^+$]; $C_{22}H_{28}O_4SSi$ (416.6): calcd C 63.43, H 6.77; found C 63.70, H 6.55.

General Procedure for the Preparation of Bromides from the Corresponding Tosylates: A solution of the tosylate (20 mmol), dry LiBr (27.3 g, 315 mmol), and ethyldiisopropylamine (1.3 mL) in dry acetone (300 mL) was heated under reflux for 24 h. After cooling to RT, the solvent was removed carefully, and the residue poured into a solution of NH_4Cl (500 mL) and extracted with pentane (3 × 200 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 6/1].

(*S*)-1-Bromo-2-ethoxy-5-trimethylsilyl-4-pentyne [(*S*)-**5b**] was obtained in 97% yield (5.11 g): $[\alpha]_D^{20} = +20.13$ ($c = 1.09$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2965$ (C–H), 2179 (C≡C), 1467, 1422, 1391, 1367, 1250 (Si–C), 1190, 1060, 843, 761, 646 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.14$ [s, 9H; $Si(CH_3)_3$], 1.22 (t, $^3J = 7.0$ Hz, 3H; CH_3), 2.55 (d, $^3J = 6.1$ Hz, 2H; 3-H), 3.44–3.65 (m, 5H; CH_2CH_3, 1-H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -0.33$ [+, $^1J_{Si,C} = 56$ Hz, $Si(CH_3)_3$], 15.30 (+, CH_3), 24.57 (–, C-3), 34.39 (–, C-1), 65.56 (–, CH_2O), 77.00 (+, C-2), 87.07 (C_{quat}, $^1J_{Si,C} = 84$ Hz, C-5), 102.35 (C_{quat}, $^2J_{Si,C} = 16$ Hz, C-4); MS (70 eV, EI): *m/z* (%): 264/262 (0.3/0.3) [M^+], 183 (17) [$M^+ - Br$], 153/151 (97/100) [$M^+ - C_3H_2Si(CH_3)_3$], 125 (45), 123 (46), 73 (65) [$Si(CH_3)_3^+$]; $C_{10}H_{19}BrOSi$ (263.3): calcd C 45.63, H 7.27; found C 45.31, H 7.01.

(*S*)-1-Bromo-2-*tert*-butoxy-5-trimethylsilyl-4-pentyne [(*S*)-**5c**] was obtained in 96% yield (5.59 g): $[\alpha]_D^{20} = +10.0$ ($c = 1.10$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2965$ (C–H), 2179 (C≡C), 1467, 1422, 1391, 1367, 1250 (Si–C), 1190, 1060, 843, 761, 646 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.12$ [s, 9H; $Si(CH_3)_3$], 1.20 [s, 9H; $C(CH_3)_3$], 2.41, 2.59 (ABX, $^2J_{AB} = -17$, $^3J_{AX} = 6.0$, $^3J_{BX} = 6.2$ Hz, 2H; 3-H), 3.39, 3.42 (ABX, $^2J_{AB} = -10$, $^3J_{AX} = 5.0$, $^3J_{BX} = 3.3$ Hz, 2H; 1-H), 3.78 (m, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.00$ [+, $Si(CH_3)_3$], 26.45 (–, C-3), 28.43 [+, $C(CH_3)_3$], 36.35 (–, C-1), 69.96 (+, C-2), 74.60 [C_{quat}, $C(CH_3)_3$], 86.63 (C_{quat}, C-5), 103.34 (C_{quat}, C-4); MS (70 eV, EI): *m/z* (%): 211 (1.2) [$M^+ - Br$], 210 (3.7) [$M^+ - HBr$], 195 (2) [$M^+ - HBr - CH_3$], 179 (6), 139 (2), 124 (3), 122 (4), 109 (11), 83 (11), 73 (100) [$Si(CH_3)_3^+$]; $C_{12}H_{23}BrOSi$ (291.3): calcd C 49.48, H 7.96; found C 49.21, H 7.77.

(*S*)-1-Bromo-2-*tert*-butyldimethylsilyloxy-5-trimethylsilyl-4-pentyne [(*S*)-**5d**] was obtained in 92% yield (6.43 g): B.p. 94 °C/4 mbar; $[\alpha]_D^{20} = +5.8$ ($c = 0.5$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2958-2858$ (C–H), 2180 (C≡C), 1473, 1421, 1362, 1251 (Si–C), 1214, 1112, 1035, 1007, 931, 841, 778, 676, 644 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.12$ [s, 9H; $Si(CH_3)_3$], 0.15 [s, 6H; $Si(CH_3)_2$], 0.92 [s, 9H; $SiC(CH_3)_3$], 2.47, 2.59 (ABX, $^2J_{AB} = -17.0$, $^3J_{AX} = 5.9$, $^3J_{BX} = 6.1$ Hz, 2H; 3-H), 3.40, 3.48 (ABX, $^2J_{AB} = -10.2$, $^3J_{AX} = 5.0$, $^3J_{BX} = 5.4$ Hz, 2H; 1-H), 3.98 (m_c, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -4.59$ [+, $Si(CH_3)_2$], 0.02 [+, $Si(CH_3)_3$], 18.07 [C_{quat}, $SiC(CH_3)_3$], 25.74 [+, $SiC(CH_3)_3$], 27.49 (–, C-3), 37.20 (–, C-1), 70.78 (+, C-2), 87.02 (C_{quat}, C-5), 102.85 (C_{quat}, C-4); MS (70 eV, EI): *m/z* (%): 293/291 (4.0/4.0) [$M^+ - t$Bu], 239/237 (13/15) [$M^+ - SiMe_3 - C_3H_2$], 169 (15), 139 (82), 137 (21), 97 (10), 96 (11), 83 (12), 75 (26), 73 (100) [$SiMe_3^+$], 65 (10), 57 (15) [$C(CH_3)_3^+$]; $C_{14}H_{29}BrOSi_2$ (349.5): calcd C 48.12, H 8.36, Br 22.86; found C 48.26, H 8.52, Br 22.97.

(*S*)-1-Bromo-2-(2-methoxypropyl-2-oxy)-5-trimethylsilyl-4-pentyne [(*S*)-**5e**] was obtained in 92% yield (5.65 g). $[\alpha]_D^{20} = +20.4$ ($c = 1.125$ in $CHCl_3$); $R_f = 0.28$; IR (neat): $\tilde{\nu} = 2992-2831$ (C–H), 2179 (C≡C), 1463, 1423, 1376, 1250 (Si–C), 1208, 1183, 1145, 1067, 1030, 955, 844, 807, 761, 699, 646 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.14$ [s, 9H; $Si(CH_3)_3$], 1.39 (s, 3H; CH_3), 1.40 (s, 3H; CH_3), 2.54, 2.63 (ABX, $^2J_{AB} = -17.0$, $^3J_{AX} = 5.6$, $^3J_{BX} = 6.8$ Hz, 2H; 3-H), 3.26 (s, 3H; OCH_3), 3.52, 3.59 (ABX, $^2J_{AB} = -10.4$, $^3J_{AX} = 3.9$, $^3J_{BX} = 5.3$ Hz, 2H; 1-H), 4.04 (m_c, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.00$ [+, $Si(CH_3)_3$], 25.09 [+, $C(CH_3)_2$], 25.59 (–, C-3), 36.15 (–, C-1), 49.51 (+, OCH_3), 68.69 (+, C-2), 87.01 (C_{quat}, C-5), 101.41 (C_{quat}, C-4*), 102.80 (C_{quat}, C-2'*); MS (70 eV, EI): *m/z* (%): 293/291 (1.2/1.2) [$M^+ - CH_3$], 277/275 (2.1/2.0) [$M^+ - OMe$], 139 (27), 137 (27), 123 (12), 75 (14), 74 (19), 73 (100) [$SiMe_3^+$], 65 (18), 43 (24); $C_{12}H_{23}BrO_2Si$ (307.3): calcd C 46.90, H 7.54, Br 26.00; found: C 47.24, H 7.57, Br 26.01.

(*S*)-2-*tert*-Butyldimethylsilyloxy-1-iodo-5-trimethylsilyl-4-pentyne [(*S*)-**6d**]: A solution of the tosylate (*S*)-**4d** (3.306 g, 7.5 mmol), NaI (7.5 g, 50 mmol, 6.7 equiv), and ethyldiisopropylamine (150 µL) in dry acetone (30 mL) was refluxed for 72 h. After cooling to RT, the solvent was removed carefully, and the residue poured into ethyl acetate (100 mL) and extracted with aqueous sodium thiosulfate (10%, 50 mL) and brine (50 mL). The combined organic layers were dried ($MgSO_4$). Concentration under reduced pressure yielded 2.914 g (98%) of iodide (*S*)-**6d**: $[\alpha]_D^{20} = +6.2$ ($c = 1.3$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2958-2858$ (C–H), 2180 (C≡C), 1472, 1412, 1362, 1251 (Si–C), 1220, 1184, 1107, 1033, 929, 888, 842, 805, 778, 761, 699, 645 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.11$ (s, 3H; $SiCH_3$), 0.12 (s, 3H; $SiCH_3$), 0.14 [s, 9H; $Si(CH_3)_3$], 0.83 [s, 9H; $SiC(CH_3)_3$], 2.45, 2.55 (ABX, $^2J_{AB} = -16.9$, $^3J_{AX} = 5.9$, $^3J_{BX} = 6.3$ Hz, 2H; 3-H), 3.32 (d, $^3J_{1,2} = 4.8$ Hz, 2H; 1-H), 3.67 (m_c, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -4.54$ [+, $Si(CH_3)_2$], 0.00 [+, $Si(CH_3)_3$], 13.07 (–, C-1), 18.04 [C_{quat}, $SiC(CH_3)_3$], 25.75 [+, $SiC(CH_3)_3$], 28.95 (–, C-3), 70.17 (+, C-2), 87.08 (C_{quat}, C-5), 102.88 (C_{quat}, C-4); MS (70 eV, EI): *m/z* (%): 381 (1.0) [$M^+ - CH_3$], 339 (68) [$M^+ - t$Bu], 169 (34), 139 (91), 73 (100) [$SiMe_3^+$]; $C_{14}H_{29}IOSi_2$ (396.5): calcd C 42.41, H 7.37, I 32.01; found C 42.45, H 7.29, I 31.81.

(*S,R*)/(*R,R*)-2-Ethoxy-1-(2-trimethylsilylethynyl)cyclopropane [(*S,R*)/(*R,R*)-**7b**] was prepared according to the literature procedure [17a] for racemic alkoxycyclopropanes to afford (*S,R*)-**7b** (59%) and (*R,R*)-**7b** (30%) as colorless liquids. (*S,R*)-**7b**: $[\alpha]_D^{20} = +76.83$ ($c = 1.54$ in $CHCl_3$). Enantiomeric purity (GC, column C): 95% *ee*; IR (neat): $\tilde{\nu} = 2973$ (C–H), 2175 (C≡C), 1449, 1375, 1257 (Si–C), 1212, 1097, 847, 764, 647 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.11$ [s, 9H; $Si(CH_3)_3$], 0.86–0.93 (m, 1H; (*Z*)-3-H), 0.90 (t, $^3J = 7.2$ Hz, 3H; CH_2CH_3), 1.06 (ddd, $^2J_{3,3} = 9.9$, $^3J_{E-3,1} = 5.6$, $^3J_{E-3,2} = 3.9$ Hz, 1H; (*E*)-3-H), 1.26–1.42 (m, 1H; 1-H), 3.39 (ddd, $^3J_{1,2} = 2.5$, $^3J_{E-3,2} = 3.9$, $^3J_{Z-3,2} = 6.4$ Hz, 1H; 2-H), 3.52, 3.54 (ABX$_3$, $^2J_{AB} = -9.4$, $^3J_{AX} = 7.2$, $^3J_{BX} = 7.2$ Hz, 2H; OCH_2CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.13$ [+, $Si(CH_3)_3$], 8.79 (+, C-1), 13.78 (+, CH_2CH_3), 16.57 (–, C-3), 60.79 (+, C-2), 70.76 (–, OCH_2CH_3), 80.76 (C_{quat}, C-2'), 107.47 (C_{quat}, C-1'); MS (70 eV, EI): *m/z* (%): 182 (5) [M^+], 73 (100) [$SiMe_3^+$]; $C_{10}H_{18}OSi$ (182.3): calcd C 65.87, H 9.95; found C 65.64, H 9.83.

(*R,R*)-**7b**: $[\alpha]_D^{20} = +153.6$ ($c = 1.26$ in $CHCl_3$). Enantiomeric purity (GC, column C): 95% *ee*; IR (neat): $\tilde{\nu} = 2972$, 2883 (C–H), 2178 (C≡C), 1447, 1357, 1256 (Si–C), 1222, 1130, 1100, 1028, 848, 763, 703, 681 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.13$ [s, 9H; $Si(CH_3)_3$], 0.89 (t, $^3J = 7.3$ Hz, 3H; CH_2CH_3), 1.53–1.65 (m, 3H; 3-H, 1-H), 3.30 (ddd, $^3J_{E-3,2} = {}^3J_{Z-3,2} = {}^3J_{1,2} = 5.4$ Hz, 1H; 2-H), 3.47, 3.56 (ABX$_3$, $^2J_{AB} = -8.9$, $^3J_{AX} = 7.3$, $^3J_{AX} = 7.3$ Hz, 2H; OCH_2CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.10$ [+, $Si(CH_3)_3$], 8.23 (+, C-1), 13.92 (+, CH_2CH_3), 15.48 (–, C-3), 57.26 (+, C-2), 70.69 (–, OCH_2CH_3), 82.50 (C_{quat}, C-2'), 105.53 (C_{quat}, C-1'); MS (70 eV, EI): *m/z* (%): 182 (5) [M^+], 73 (100) [$SiMe_3^+$]; $C_{10}H_{18}OSi$ (182.3): calcd C 65.87, H 9.95; found C 65.82, H 9.66.

(*S,R*)/(*R,R*)-2-*tert*-Butoxy-1-(2-trimethylsilylethynyl)cyclopropane [(*S,R*)/(*R,R*)-**7c**] was prepared according to the literature procedure [17a] for racemic alkoxycyclopropanes to afford (*S,R*)-**7c** (90%) and (*R,R*)-**7c** (2%) as colorless liquids. (*S,R*)-**7c**: $[\alpha]_D^{20} = -112.2$ ($c = 2.24$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 3092$, 2976 (C–H), 2158 (C≡C), 1440, 1391, 1365, 1250 (Si–C), 1196, 1163, 1088, 945, 844, 760 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.13$ [s, 9H; $Si(CH_3)_3$], 0.90 (ddd, $^2J = -5.6$, $^3J_{E-3,1} = 6.6$, $^3J_{E-3,2} = 6.6$ Hz, 1H; (*E*)-3-H), 0.99 (ddd, $^2J = -5.6$, $^3J_{Z-3,2} = 4.1$, $^3J_{Z-3,1} = 9.8$ Hz, 1H; (*Z*)-3-H), 1.28 [s, 9H; $C(CH_3)_3$], 1.32 (ddd, $^3J_{1,2} = 2.6$, $^3J_{E-3,1} = 6.6$, $^3J_{Z-3,1} = 9.8$ Hz, 1H; 1-H), 3.33 (ddd, $^3J_{1,2} = 2.6$, $^3J_{E-3,2} = 6.6$, $^3J_{Z-3,2} = 4.1$ Hz, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.19$ [+, $Si(CH_3)_3$], 10.07 (+, C-1), 15.75 (–, C-3), 28.10 [+, $C(CH_3)_3$], 54.37 (+, C-2), 75.46 [C_{quat}, $C(CH_3)_3$], 80.76 (C_{quat}, C-2'), 107.49 (C_{quat}, C-1'); MS (70 eV, EI): *m/z* (%): 154 (1.6) [$M^+ - C_4H_8$], 139 (25) [$M^+ - C_4H_8 - CH_3$], 137 (35) [$M^+ - SiMe_3$, $M^+ - OC(CH_3)_3$], 83 (17), 75 (31), 73 (43) [$SiMe_3^+$], 57 (100) [$C_4H_9^+$]; $C_{12}H_{22}OSi$ (210.4): calcd C 68.51, H 10.54; found C 68.61, H 10.64.

(*S,R*)/(*R,R*)-2-*tert*-Butyldimethylsilyloxy-1-(trimethylsilylethynyl)cyclopropane [(*S,R*)/(*R,R*)-**7d**]: To a solution of (*S*)-**5d** (301 mg, 0.86 mmol) in THF (10 mL) and HMPA (1 mL) was added a 0.5 M solution of LDA in THF (2.0 mL, 1 mmol) at −78 °C (monitored by GC, 50 min). The mixture was poured into a vigorously stirred solution of NH_4Cl (10 mL) and pentane (10 mL), and extracted with pentane (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (pentane) to yield 125 mg (54%) of (*S,R*)-**7d**: $R_f = 0.07$; B.p. 49 °C/4 mbar; $[\alpha]_D^{20} = -99.8$ ($c = 1.00$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2958-2859$ (C–H), 2162 (C≡C), 1473, 1439, 1364, 1251 (Si–C), 1209, 1165, 1086, 996, 940, 840, 779, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.12$ [s, 15H; $Si(CH_3)_3$, $Si(CH_3)_2$], 0.81–1.03 (m, 2H; 3-H), 0.89 [s, 9H; $SiC(CH_3)_3$], 1.29–1.48 (m, 1H; 1-H), 3.50–3.60 (m, 1H; 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = -4.98$ [+, $Si(CH_3)_2$], 0.15 [+, $Si(CH_3)_3$], 10.21 (+, C-1), 17.89 (–, C-3), 18.14 [C_{quat}, $SiC(CH_3)_3$], 25.73

[+, SiC(CH_3)$_3$], 55.34 (+, C-2), 80.71 (C_{quat}, C-2'), 107.61 (C_{quat}, C-1'); MS (70 eV, EI): *m/z* (%): 268 (2.0) [M^+], 211 (59) [$M^+ - t$Bu], 154 (57), 147 (12), 133 (64), 75 (20), 73 (100) [$SiMe_3^+$], 59 (17); $C_{14}H_{28}OSi_2$ (268.6): calcd C 62.62, H 10.51; found C 62.71, H 10.58.

Further elution yielded 48 mg (21%) of (*R,R*)-**7d**: $R_f = 0.05$; $[\alpha]_D^{20} = +90.7$ ($c = 0.75$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2960-2855$ (C–H), 2165 (C≡C), 1485, 1440, 1360, 1255 (Si–C), 1211, 1165, 1089, 996, 950, 840, 780, 764 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.11$ [s, 9H; Si(CH_3)$_3$], 0.15 [s, 6H; Si(CH_3)$_2$], 0.83 (ddd, $^2J_{3,3} = -5.6$, $^3J_{E-3,1} = 6.6$, $^3J_{E-3,2} = 4.1$ Hz, 1H; (*E*)-3-H), 0.90 [s, 9H; SiC(CH_3)$_3$], 0.93 (ddd, $^2J_{3,3} = -5.6$, $^3J_{Z-3,1} = 9.8$, $^3J_{Z-3,2} = 6.2$ Hz, 1H; (*Z*)-3-H), 1.32 (ddd, $^3J_{2,1} = 6.1$, $^3J_{E-3,1} = 6.6$, $^3J_{Z-3,1} = 9.8$ Hz, 1H; 1-H), 3.48 (ddd, $^3J_{1,2} = 6.1$, $^3J_{E-3,2} = 4.1$, $^3J_{Z-3,2} = 6.2$ Hz, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -5.12$ (+, $SiCH_3$), −4.57 (+, $SiCH_3$), 0.19 [+, Si(CH_3)$_3$], 8.82 (+, C-1), 16.67 (−, C-3), 18.15 [C_{quat}, SiC(CH_3)$_3$], 25.83 [+, SiC(CH_3)$_3$], 51.57 (+, C-2), 83.04 (C_{quat}, C-2'), 105.76 (C_{quat}, C-1'); MS (70 eV, EI): *m/z* (%): 268 (2.0) [M^+], 211 (50) [$M^+ - t$Bu], 154 (51), 147 (16), 133 (67), 75 (19), 73 (100) [$SiMe_3^+$], 59 (18); $C_{14}H_{28}OSi_2$ (268.6): calcd C 62.62, H 10.51; found C 62.52, H 10.43.

(*S,R*)-2-(2-Methoxypropyl-2-oxy)-1-(trimethylsilylethynyl)cyclopropane [(*S,R*)-7e]: To a solution of LDA (15 mmol) in THF (50 mL) was added at −78 °C (*S*)-**5e** (1.54 g, 5 mmol) in THF (10 mL). After stirring for 30 min, the mixture was poured into a solution of NH_4Cl (100 mL) and pentane (100 mL), and the aqueous layer was extracted with pentane (3 × 10 mL). The combined organic layers were dried ($MgSO_4$). After concentration under reduced pressure, the residue was purified by flash chromatography on silica gel (pentane/diethyl ether = 30/1) to yield 942 mg (83%) of (*S,R*)-**7e**: $R_f = 0.23$; $[\alpha]_D^{20} = -57.8$ ($c = 0.8$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2994-2831$ (C–H), 2159 (C≡C), 1440, 1372, 1251 (Si–C), 1214, 1186, 1142, 1067, 954, 907, 845, 761, 699, 642 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.05$ [s, 9H; Si(CH_3)$_3$], 0.83 (ddd, $^2J_{3,3} = -5.6$, $^3J_{Z-3,1} = 6.3$, $^3J_{Z-3,2} = 6.8$ Hz, 1H; (*Z*)-3-H), 0.95 (ddd, $^2J_{3,3} = -5.6$, $^3J_{E-3,1} = 9.8$, $^3J_{E-3,2} = 4.1$ Hz, 1H; (*E*)-3-H), 1.33 (s, 3H; CH_3), 1.37 (ddd, $^3J_{1,2} = 2.7$, $^3J_{Z-3,1} = 6.3$, $^3J_{E-3,1} = 9.8$ Hz, 1H; 1-H), 1.40 (s, 3H; CH_3), 3.21 (s, 3H; OCH_3), 3.45 (ddd, $^3J_{1,2} = 2.7$, $^3J_{E-3,2} = 4.1$, $^3J_{Z-3,2} = 6.8$ Hz, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.12$ [+, Si(CH_3)$_3$], 9.30 (+, C-1), 15.14 (−, C-3), 24.29 (+, CH_3), 25.17 (+, CH_3), 48.61 (+, OCH_3), 53.19 (+, C-2), 80.90 (C_{quat}, C-2'), 101.60 (C_{quat}, C-2'*), 107.04 (C_{quat}, C-1'*); MS (70 eV, EI): *m/z* (%): 211 (0.5) [$M^+ - CH_3$], 196 (4.3) [$M^+ - Me_2$], 195 (26), 139 (14), 137 (64), 109 (72), 97 (18), 95 (18), 83 (28), 75 (12), 74 (45), 73 (100) [$SiMe_3^+$], 59 (74), 55 (13), 45 (25), 43 (87); $C_{12}H_{22}O_2Si$ (226.4): calcd C 63.67, H 9.80; found C 63.73, H 9.91.

(*S,R*)-1-Benzyloxy-2-(trimethylsilylethynyl)cyclopropane [(*S,R*)-7f]: To a solution of LiHMDS (2.5 g, 15 mmol) in THF (100 mL) was added at 0 °C (*S*)-**4f** (2.08 g, 5.0 mmol) in THF (10 mL). After stirring for 30 min, the mixture was poured into a solution of NH_4Cl (100 mL) and pentane (100 mL), and the aqueous layer extracted with pentane (3 × 10 mL). The combined organic layers were dried ($MgSO_4$). After concentration under reduced pressure, the residue was purified by flash chromatography on silica gel (pentane/diethyl ether = 30/1), to yield 610 mg (50%) (*S,R*)-**7f**: $R_f = 0.23$; $[\alpha]_D^{20} = +34.4$ ($c = 1.0$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2994-2831$ (C–H), 2159 (C≡C), 1440, 1372, 1251 (Si–C), 1214, 1186, 1142, 1067, 954, 907, 845, 761, 699, 642 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.05$ [s, 9H; Si(CH_3)$_3$], 0.83 (ddd, $^2J_{3,3} = -5.6$, $^3J_{Z-3,1} = 6.3$, $^3J_{Z-3,2} = 6.8$ Hz, 1H; (*Z*)-3-H), 0.95 (ddd, $^2J_{3,3} = -5.6$, $^3J_{E-3,1} = 9.8$, $^3J_{E-3,2} = 4.1$ Hz, 1H; (*E*)-3-H), 1.37 (ddd, $^3J_{1,2} = 2.7$, $^3J_{Z-3,1} = 6.3$, $^3J_{E-3,1} = 9.8$ Hz, 1H; 1-H), 3.45 (ddd, $^3J_{1,2} = 2.7$, $^3J_{E-3,2} = 4.1$, $^3J_{Z-3,2} = 6.8$ Hz, 1H; 2-H), 4.2–4.6 (m, 2H; OCH_2), 7.1–7.55 (m, 5H; Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.12$ [+, Si(CH_3)$_3$], 9.30 (+, C-1), 15.14 (−, C-3), 53.19 (+, C-2), 64.23 (−, OCH_2), 80.90 (C_{quat}, C-2'), 107.04 (C_{quat}, C-1'), 127.21 (+, C–Ar), 126.89 (+, C–Ar), 128.22 (+, C–Ar), 140.79 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 244 (1) [M^+], 91 (100) [$C_7H_7^+$]; $C_{15}H_{20}OSi$ (244.4): calcd C 73.71, H 8.25; found C 74.02, H 7.99.

General Procedure for the Oxygenation of (Trimethylsilylethynyl)cyclopropanes: The ethynylcyclopropane (1.0 mmol) was dissolved in either THF or diethyl ether (10 mL) and the solution cooled to −78 °C. After addition of *n*BuLi (2.36 M in hexane, 425 μL, 1.0 mmol) and stirring for 15–60 min at −78 °C or RT dry oxygen [18] was bubbled through the mixture for 1 h at −78 °C or −90 °C, and the electrophile (1.0 mmol) was added. After 1 h the solution was allowed to warm slowly to RT and poured into a mixture of water and diethyl ether (2 × 10 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 20/1].

(*S,R*)/(*R,R*)-2-Ethoxy-1-trimethylsilyloxy-1-(2-trimethylsilylethynyl)cyclopropane [(*S,R*)/(*R,R*)-**24**-OTMS] was obtained as a mixture of diastereomers (1:2) by deprotonation of (*S,R*)-**7b** in THF at −78 °C for 15 min and treatment with oxygen and TMSCl. (*R,R*)-**24**-OTMS ($R_f = 0.12$): Clear oil (168 mg, 62%); $[\alpha]_D^{20} = -15.3$ ($c = 1.0$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2950$ (C–H), 2150 (C≡C), 1240 (Si–C), 1190, 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.13$ [s, 9H; Si(CH_3)$_3$], 0.15 [s, 9H; OSi(CH_3)$_3$], 1.05 (dd, $^3J_{Z-3,2} = 5.9$, $^2J_{3,3} = 4.8$ Hz, 1H; (*Z*)-3-H), 1.15 (dd, $^3J_{E-3,2} = 6.2$, $^2J_{3,3} = 4.8$ Hz, 1H; (*E*)-3-H), 1.20 (t, $^3J = 7.0$ Hz, 3H; CH_3), 3.20 (dd, $^3J_{Z-3,2} = 5.9$, $^3J_{E-3,2} = 6.2$ Hz, 1H; 2-H), 3.40 (dq, $^2J = -9.2$, $^3J = 7.0$ Hz, 1H; CH_2O), 3.60 (dq, $^2J = -9.2$, $^3J = 7.0$ Hz, 1H; CH_2O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -1.55$ [+, Si(CH_3)$_3$], 0.52 [+, OSi(CH_3)$_3$], 14.99 (+, CH_3), 19.28 (−, C-3), 57.30 (C_{quat}, C-1), 65.64 (+, C-2), 65.99 (−, CH_2O), 80.72 (C_{quat}, C-2'), 109.20 (C_{quat}, C-1'); MS (70 eV, EI): *m/z* (%): 270 (1) [M^+], 241 (13), 155 (14), 178 (32), 73 (100) [$SiMe_3^+$]; $C_{13}H_{26}O_2Si_2$ (270.5): calcd C 57.72, H 9.69; found C 57.41, H 10.03.

(*S,R*)-**24**-OTMS ($R_f = 0.15$): Clear oil (85 mg, 31%); $[\alpha]_D^{20} = +4.7$ ($c = 1.3$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2940$ (C–H), 2145 (C≡C), 1240 (Si–C), 1195, 840 cm^{-1}; ^1H NMR (250 MHz, C_6D_6): $\delta = 0.18$ [s, 9H; Si(CH_3)$_3$], 0.20 [s, 9H; OSi(CH_3)$_3$], 1.19 (dd, $^3J_{Z-3,2} = 5.8$, $^2J_{3,3} = 4.9$ Hz, 1H; (*Z*)-3-H), 1.22 (dd, $^3J_{E-3,2} = 6.2$, $^2J_{3,3} = 4.9$ Hz, 1H; (*E*)-3-H), 1.24 (t, $^3J = 7.0$ Hz, 3H; CH_3), 3.35 (dd, $^3J_{Z-3,2} = 5.8$, $^3J_{E-3,2} = 6.2$ Hz, 1H; 2-H), 3.37 (dq, $^2J = -9.2$, $^3J = 7.0$ Hz, 1H; CH_2O), 3.58 (dq, $^2J = -9.2$, $^3J = 7.0$ Hz, 1H; CH_2O); ^{13}C NMR (62.9 MHz, C_6D_6): $\delta = -1.88$ [+, Si(CH_3)$_3$], 0.67 [+, OSi(CH_3)$_3$], 15.23 (+, CH_3), 19.44 (−, C-3), 58.59 (C_{quat}, C-1), 66.89 (+, C-2), 67.51 (−, CH_2O), 83.62 (C_{quat}, C-2'), 105.54 (C_{quat}, C-1'); MS (70 eV, EI): *m/z* (%): 270 (1) [M^+], 241 (11), 155 (10), 178 (44), 73 (100) [$SiMe_3^+$]; $C_{13}H_{26}O_2Si_2$ (270.5): calcd C 57.72, H 9.69; found C 57.80, H 10.74.

(*S,R*)/(*R,R*)-1-Acetoxy-1-ethoxy-1-(2-trimethylsilylethynyl)cyclopropane [(*S,R*)/(*R,R*)-**24**-OAc] was obtained as a mixture of diastereomers (1:2) by deprotonation of (*R,S*)-**7b** in THF at −78 °C for 15 min and treatment with oxygen and acetic anhydride. (*R,R*)-**24**-OAc ($R_f = 0.32$): Clear oil (133 mg, 55%); $[\alpha]_D^{20} = -20.7$ ($c = 1.1$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2960$ (C–H), 2150 (C≡C), 1720 (C=O), 1330, 1200, 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.22$ [s, 9H; Si(CH_3)$_3$], 1.15 (t, $^3J = 7.2$ Hz, 3H; CH_3CH_2), 1.30 (dd, $^2J_{3,3} = 6.9$, $^3J_{E-3,2} = 4.7$ Hz, 1H; (*E*)-3-H), 1.40 (dd, $^2J_{3,3} = 6.9$, $^3J_{Z-3,2} = 6.8$ Hz, 1H; (*Z*)-3-H), 2.35 (s, 3H; CH_3CO), 3.50 (dq, $^2J = -9.2$, $^3J = 7.2$ Hz, 1H; CH_2O), 3.55 (dd, $^3J_{E-3,2} = 4.7$, $^3J_{Z-3,2} = 6.8$ Hz, 1H; 2-H), 3.92 (dq, $^2J = -9.2$, $^3J = 7.2$ Hz, 1H; CH_2O); MS (70 eV, EI): *m/z* (%): 240 (3) [M^+], 225 (4), 211 (5), 197 (10) [$M^+ - CH_3CO$], 165 (22), 125 (100) [$M^+ - C_2H_2O - SiMe_3$], 73 (72) [$SiMe_3^+$], 43 (45) [CH_3CO^+]; $C_{12}H_{20}O_3Si$ (240.4): calcd C 59.96, H 8.39; found C 59.72, H 8.05.

(*S,R*)-**24**-OAc ($R_f = 0.28$): Clear oil (67 mg, 28%); $[\alpha]_D^{20} = +7.8$ ($c = 1.0$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2960$ (C–H), 2155 (C≡C), 1720 (C=O), 1335, 1205, 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.28$ [s, 9H; Si(CH_3)$_3$], 1.15 (t, $^3J = 7.2$ Hz, 3H; CH_3CH_2), 1.27 (dd, $^2J_{3,3} = 6.9$, $^3J_{E-3,2} = 4.6$ Hz, 1H; (*E*)-3-H), 1.44 (dd, $^2J_{3,3} = 6.9$, $^3J_{Z-3,2} = 6.5$ Hz, 1H; (*Z*)-3-H), 2.27 (s, 3H; CH_3CO), 3.51 (dq, $^2J = -9.2$, $^3J = 7.2$ Hz, 1H; CH_2O), 3.58 (dd, $^3J_{E-3,2} = 4.6$, $^3J_{Z-3,2} = 6.5$ Hz, 1H; 2-H), 3.98 (dq, $^2J = -9.2$, $^3J = 7.2$ Hz, 1H; CH_2O); MS (70 eV, EI): *m/z* (%): 240 (2) [M^+], 225 (2), 211 (8), 197 (15) [$M^+ - CH_3CO$], 165 (20), 125 (100) [$M^+ - C_2H_2O - SiMe_3$], 73 (88) [$SiMe_3^+$], 43 (58) [CH_3CO^+]; $C_{12}H_{20}O_3Si$ (240.4): calcd C 59.96, H 8.39; found C 59.88, H 8.30.

(*S,R*)/(*R,R*)-2-Ethoxy-1-*p*-toluenesulfonyloxy-1-(2'-trimethylsilylethynyl)cyclopropane [(*S,R*)/(*R,R*)-**24**-OTs] was obtained as a mixture of diastereomers (1:5) by deprotonation of (*R,S*)-**7b** in THF at −78 °C for 15 min, oxygenation at −90 °C, and treatment with tosyl chloride. (*R,R*)-**24**-OTs ($R_f = 0.35$): Clear oil (230 mg, 65%); $[\alpha]_D^{20} = +98.5$ ($c = 1.05$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 2959$ (C–H), 2178 (C≡C), 1599 (C=C), 1496, 1363 (SO_2), 1250 (Si–C), 1178 (SO_2), 1098, 989, 930, 845, 762, 734, 668 cm^{-1}; ^1H NMR (250 MHz, C_6D_6): $\delta = 0.15$ [s, 9H; Si(CH_3)$_3$], 0.65 (dd, $^3J_{E-3,2} = 7.1$, $^2J_{3,3} = 7.0$ Hz, 1H; (*E*)-3-H), 1.15 (t, $^3J = 7.1$ Hz, 3H; CH_3CH_2), 1.20 (dd, $^3J_{Z-3,2} = 4.9$, $^2J_{3,3} = 7.0$ Hz, 1H; (*Z*)-3-H), 2.00 (s, 3H; Ar–CH_3), 3.25 (dd, $^3J_{Z-3,2} = 4.9$, $^3J_{E-3,2} = 7.1$ Hz, 1H; 2-H), 3.25 (dq, $^3J = 7.1$, $^2J = 9.1$ Hz, 1H; CH_2O), 3.55 (dq, $^3J = 7.1$, $^2J = 9.1$ Hz, 1H; CH_2O), 6.82 (d, $^3J = 9.3$ Hz, 2H; Ar–H), 8.00 (d, $^3J = 9.3$ Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, C_6D_6): $\delta = -0.48$ [+, Si(CH_3)$_3$], 15.05 (+, CH_3CH_2), 21.23 (+, Ar–CH_3), 22.69 (−, C-3), 55.79 (C_{quat}, C-1), 62.23 (+, C-2), 67.28 (−, CH_2O), 90.84 (C_{quat}, C-2'), 102.42 (C_{quat}, C-1'), 128.65 (+, *o*-C–Ar), 129.82 (+, *m*-C–Ar), 135.76 (C_{quat}, *p*-C–Ar), 144.43 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 352 (1) [M^+], 173 (100), 155 (77) [$C_7H_7SO_2^+$], 91 (98) [$C_7H_7^+$]; $C_{17}H_{24}O_4SSi$ (352.5): calcd C 57.92, H 6.86; found C 57.92, H 6.84.

(*S,R*)-**24**-OTs ($R_f = 0.30$): White solid (46 mg, 13%), m.p. 62.5 °C; $[\alpha]_D^{20} = +7.3$ ($c = 1.2$ in $CHCl_3$); IR (KBr): $\tilde{\nu} = 2959$ (C–H), 2178 (C≡C), 1599 (C=C), 1496, 1363 (SO_2), 1250 (Si–C), 1178 (SO_2), 1098, 989, 930, 845, 762, 734, 668 cm^{-1}; ^1H NMR (250 MHz, C_6D_6): $\delta = 0.12$ [s, 9H; Si(CH_3)$_3$], 1.00 (dd, $^3J_{Z-3,2} = 6.9$, $^2J_{3,3} = 7.0$ Hz, 1H; (*Z*)-3-H), 1.20 (t, $^3J = 7.1$ Hz, 3H; CH_3CH_2), 1.45 (dd, $^3J_{E-3,2} = 4.8$, $^2J_{3,3} = 7.0$ Hz, 1H; (*E*)-3-H), 2.05 (s, 3H; Ar–CH_3), 3.70 (dd, $^3J_{Z-3,2} = 6.9$, $^3J_{E-3,2} = 4.8$ Hz, 1H; 2-H), 3.35 (dq, $^3J = 7.1$, $^2J = -9.1$ Hz, 1H; CH_2O), 3.45 (dq, $^3J = 7.1$, $^2J = -9.1$ Hz, 1H; CH_2O), 6.84 (d, $^3J = 9$ Hz, 2H; Ar–H), 8.05 (d, $^3J = 9$ Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, C_6D_6): $\delta = -0.37$ [+, Si(CH_3)$_3$], 13.33 (+, CH_3CH_2), 21.15 (+, Ar–CH_3), 24.15 (−, C-3), 58.32 (C_{quat}, C-1), 62.83 (+, C-2), 66.38 (−, CH_2O), 93.02 (C_{quat}, C-2'), 99.65 (C_{quat}, C-1'), 128.69 (+, *o*-C–Ar), 129.92 (+, *m*-C–Ar), 135.55 (C_{quat}, *p*-C–Ar), 144.58 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 352 (1) [M^+], 173 (100), 155 (75), 91 (92); $C_{17}H_{24}O_4SSi$ (352.5): calcd C 57.92, H 6.86; found C 58.02, H 6.97.

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1-*p*-Toluenesulfonyloxy-1-(2′-trimethylsilylethynyl)cyclopropane (28) was obtained in 80% yield by deprotonation of **27** in ether at RT for 1 h and treatment with oxygen and tosyl chloride. The substance corresponds in all respects with the compound described in ref. [20c].

General Procedure for the Desilylation of (Trimethylsilyl)ethynylcyclopropanes: **Method A**, with tetrabutylammonium fluoride (TBAF): To a solution of the (trimethylsilylethynyl)cyclopropane (1.0 mmol), dissolved in moist THF (10 mL), was added TBAF (1.5 mmol). After having been stirred for 5 min at RT, the mixture was poured into a mixture of water and diethyl ether (20 mL each). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel [petroleum ether (60/80)/ diethyl ether = 20/1].

Method B, with potassium carbonate in methanol: The (trimethysilylethynyl)-cyclopropane (1.0 mmol) was dissolved in methanol (10 mL) saturated with K_2CO_3. After having been stirred for 15 min at RT, the mixture was filtered. The filtrate was poured into a mixture of water and diethyl ether (2 × 10 mL), and the aqueous layer was extracted with diethyl ether (20 mL each). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 20/1].

***(S,R)*-1-Acetoxy-2-ethoxy-1-ethynylcyclopropane** [(*S,R*)-**23**-OAc] was obtained as a clear oil from (*S,R*)-**24**-OAc by Method A (160 mg, 95%); IR (neat): $\tilde{\nu}$ = 2960 (C–H), 2150 (C≡C), 1720 (C=O), 1330, 1200, 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.10 (t, ^3J = 7.2 Hz, 3H; CH_3CH_2), 1.20 (dd, $^2J_{3,3}$ = 6.9, $^3J_{E-3,2}$ = 6.8 Hz, 1H; (*E*)-3-H), 1.75 (dd, $^2J_{3,3}$ = 6.9, $^3J_{Z-3,2}$ = 4.7 Hz, 1H; (*Z*)-3-H), 2.27 (s, 1H; 2′-H), 2.35 (s, 3H; CH_3CO), 3.15 (dd, $^3J_{E-3,2}$ = 6.8, $^3J_{Z-3,2}$ = 4.7 Hz, 1H; 2-H), 3.40 (dq, ^2J = – 9.2, ^3J = 7.2 Hz, 1H; CH_2O), 3.55 (dq, ^2J = – 9.2, ^3J = 7.2 Hz, 1H; CH_2O); MS (70 eV, EI): *m/z* (%): 139 (5) [$M^+ - C_2H_5$], 125 (10) [M^+ – MeCO], 97 (22), 43 (100) [$MeCO^+$]; $C_9H_{12}O_3$ (168.2): calcd C 64.27, H 7.19; found C 63.93, H 7.22.

***(R,R)*-2-Ethoxy-1-ethynyl-1-*p*-toluenesulfonyloxycyclopropane** [(*R,R*)-**23**-OTs] was obtained as a clear oil from (*R,R*)-**24**-OTs by Method A (258 mg, 92%): $[\alpha]_D^{20}$ = + 122.00 (*c* = 1.50 in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2970 (C–H), 2180 (C≡C), 1602 (C=C), 1500, 1379 (SO_2), 1179 (SO_2), 1102, 998, 845, 768, 734 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.1 Hz, 3H; CH_3CH_2), 1.35 (dd, $^2J_{3,3}$ = 7.9, $^3J_{Z-3,2}$ = 5.4 Hz, 1H; (*Z*)-3-H), 1.55 (dd, $^3J_{E-3,2}$ = 8.0, $^2J_{3,3}$ = 7.9 Hz, 1H; (*E*)-3-H), 1.95 (s, 3H; Ar–CH_3), 2.05 (s, 1H; 2′-H), 3.62 (dq, ^2J = – 9.4, ^3J = 7.1 Hz, 1H; CH_2O), 3.80 (dd, $^3J_{E-3,2}$ = 8.0, $^3J_{Z-3,2}$ = 5.4 Hz, 1H; 2-H), 4.00 (dq, ^2J = – 9.4, ^3J = 7.1 Hz, 1H; CH_2O), 6.75 (d, ^3J = 9.3 Hz, 2H; *m*-Ar–H), 8.00 (d, ^3J = 9.3 Hz, 2H; *o*-Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.10 (+, CH_3CH_2), 21.36 (+, Ar–CH_3), 23.63 (–, C-3), 57.64 (C_{quat}, C-1), 62.43 (+, C-2), 66.53 (–, CH_2O), 76.22 (+, C-2′), 78.22 (C_{quat}, C-1′), 127.82 (+, C–Ar), 128.10 (+, C–Ar), 135.53 (C_{quat}, C–Ar), 144.41 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 155 (100) [$C_7H_7SO_2^+$], 91 (82) [$C_7H_7^+$]; $C_{14}H_{16}O_4S$ (280.3): calcd C 59.98, H 5.75; found C 60.36, H 5.61.

***(S,R)*-2-Ethoxy-1-ethynyl-1-*p*-toluenesulfonyloxycyclopropane** [(*S,R*)-**23**-OTs] was obtained as a clear oil from (*S,R*)-**24**-OTs by Method B (263 mg, 94%): $[\alpha]_D^{20}$ = + 40.7 (*c* = 0.421 in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2970 (C–H), 2180 (C≡C), 1598 (C=C), 1502, 1371 (SO_2), 1170 (SO_2), 1101, 933, 839, 758, 735 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.10 (t, ^3J = 7.2 Hz, 3H; CH_3CH_2), 1.23 (dd, $^2J_{3,3}$ = 6.9, $^3J_{E-3,2}$ = 4.9 Hz, 1H; (*E*)-3-H), 1.85 (dd, $^2J_{3,3}$ = 6.9, $^3J_{Z-3,2}$ = 7.3 Hz, 1H; (*Z*)-3-H), 1.85 (s, 3H; Ar–CH_3), 2.05 (s, 1H; 2′-H), 3.15 (dd, $^3J_{Z-3,2}$ = 7.3, $^3J_{E-3,2}$ = 4.9 Hz, 1H; 2-H), 3.42 (dq, ^2J = – 9.2, ^3J = 7.2 Hz, 1H; CH_2O), 3.55 (dq, ^2J = – 9.2, ^3J = 7.2 Hz, 1H; CH_2O), 6.75 (d, ^3J = 9.2 Hz, 2H; *m*-Ar–H), 8.00 (d, ^3J = 9.2 Hz, 2H; *o*-Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.71 (+, CH_3CH_2), 20.91 (+, Ar–CH_3), 21.71 (–, C-3), 54.67 (C_{quat}, C-1), 61.41 (+, C-2), 66.97 (–, CH_2O), 74.09 (C_{quat}, C-1′), 80.62 (+, C-2′), 127.92 (+, C–Ar), 128.31 (+, C–Ar), 135.73 (C_{quat}, C–Ar), 144.61 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 155 (100) [$C_7H_7SO_2^+$], 91 (79) [$C_7H_7^+$]; $C_{14}H_{16}O_4S$ (280.3): calcd C 59.98, H 5.75; found C 60.21, H 5.83.

1-Chloro-1-ethynyl-2,3-dimethylcyclopropane was obtained from 1-chloro-1-trichloroethenyl-2,3-dimethylcyclopropane [26] (10.0 g, 42.7 mmol) according to the previously published procedure [20e], yield 3.65 g (67%), (*E*)/(*Z*) = 1:5.5; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.09 (d, ^3J = 6.2 Hz, 3H, 1″-H), 1.10 (d, ^3J = 6.4 Hz, 3H, 2″-H), 1.42–1.52 (m, 2H, 2-H, 3-H), 2.39 (s, 1H, 2′-H).

General Procedure for the Preparation of Ethenylcyclopropanes from Ethynylcyclopropanes by Hydrogenation: The ethynylcyclopropane (1.0 mmol) was stirred in pentane or dichloromethane (10 mL) with quinoline (2 mg) and palladium (3 mol% on $BaSO_4$, deactivated with lead, 0.005 mmol Pb) [28] under a hydrogen atmosphere (slightly pressurized by a rubber balloon). After having been stirred for 1 h to 3 d at RT, the mixture was filtered. Then the filtrate was concentrated under reduced pressure, and the residue purified by flash chromatography on silica gel [petroleum ether (60/80)/ diethyl ether = 20/1].

(1*R,2*R**)/(1*S**,2*R**)-1-Chloro-1-ethenyl-2-trimethylsilylcyclopropane** was obtained as a colorless oil from 1-chloro-1-ethynyl-2-trimethylsilylcyclopropane [28] (1.00 g, 5.79 mmol) [(*E*)/(*Z*) = 1:2.3] by hydrogenation in dichloromethane for 24 h according to the general procedure (0.74 g, 73%); IR (neat): $\tilde{\nu}$ = 3310, 2950, 1730, 1640 (C=C), 1415, 1250, 1190, 1140, 830 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.12 (s, 9H, $SiMe_3$), 0.27 (dd, ^3J = 9.5, ^3J = 11.5 Hz, 1H, 2-H), 1.23, (m, 2H, 3-H), 5.06 (dd, J_{cis} = 10.5, J_{gem} = 1.3 Hz, 1H, 2′-H), 5.34 (dd, J_{trans} = 17.0, J_{gem} = 1.3 Hz, 1H, 2′-H), 5.57 (dd, J_{trans} = 17.0, J_{cis} = 10.5 Hz, 1H, 1′-H).

(1*R,2*R**,3*S**)/(1*S**,2*R**,3*S**)-1-Chloro-2,3-dimethyl-1-ethenylcyclopropane** was obtained as a colorless oil from 1-chloro-1-ethynyl-2,3-dimethylcyclopropane (1.28 g, 10.0 mmol) [(*E*)/(*Z*) = 1:5.5] by hydrogenation in dichloromethane for 24 h according to the general procedure (1.19 g, 91%); ^1H NMR (250 MHz, $CDCl_3$): δ = 1.09–1.10 [m, 6H, 1″(2″)-H], 1.22 [m_c, 2H, 2(3)-H], 5.00 (dd, J_{gem} = 1.0, J_{cis} = 10.2 Hz, 1H, 2′-H), 5.30 (dd, J_{gem} = 1.0, J_{trans} = 16.5 Hz, 1H, 2′-H), 5.62 (dd, J_{cis} = 10.2, J_{trans} = 16.5 Hz, 1H, 1′-H).

***(R,R)*-1-Ethenyl-1-ethoxy-1-*p*-toluenesulfonyloxycyclopropane** [(*R,R*)-**25**-OTs] was obtained as a clear oil from (*R,R*)-**23**-OTs by hydrogenation for 24 h in dichloromethane (266 mg, 94%): $[\alpha]_D^{20}$ = + 243.8 (*c* = 0.390 in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2965 (C–H), 1602 (C=C), 1496, 1370 (SO_2), 1170 (SO_2), 1100, 994, 932, 843, 737, 670 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.15 (t, ^3J = 7.0 Hz, 3H; CH_3CH_2), 1.25 (dd, $^3J_{E-3,2}$ = 7.5, $^2J_{3,3}$ = 8.5 Hz, 1H; (*E*)-3-H), 1.70 (dd, $^2J_{3,3}$ = 8.5, $^3J_{Z-3,2}$ = 4.7 Hz, 1H; (*Z*)-3-H), 2.67 (s, 3H; Ar–CH_3), 3.20 (dd, $^3J_{E-3,2}$ = 7.5, $^3J_{Z-3,2}$ = 4.7 Hz, 1H; 2-H), 3.55 (dq, ^2J = 9.0, ^3J = 7.0 Hz, 1H; CH_2O), 3.65 (dq, ^2J = 9.0, ^3J = 7.0 Hz, 1H; CH_2O), 5.10 (d, $^3J_{Z-2',1'}$ = 16.9 Hz, 1H; (*Z*)-2′-H), 5.23 (d, $^3J_{E-2',1'}$ = 10.2 Hz, 1H; (*E*)-2-H), 5.87 (dd, $^3J_{Z-2',1'}$ = 16.9, $^3J_{E-2',1'}$ = 10.2 Hz, 1H; 1′-H), 7.24 (d, ^3J = 8.3 Hz, 2H; Ar-H), 7.79 (d, ^3J = 8.3 Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, C_6D_6): δ = 14.61 (+, CH_3CH_2O), 18.52 (–, C-3), 20.78 (+, Ar–CH_3), 62.18 (+, C-2), 66.03 (C_{quat}, C-1), 66.22 (–, CH_2O), 114.27 (–, C-2′), 126.15 (+, C–Ar), 129.30 (+, C–Ar), 132.65 (+, C-1′), 136.26 (C_{quat}, C–Ar), 144.03 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 155 (100) [$C_7H_7SO_2^+$], 91 (82) [$C_7H_7^+$]; $C_{14}H_{18}O_4S$ (282.4): calcd C 59.55, H 6.43; found C 59.37, H 6.21.

***(S,R)*-1-Ethenyl-2-ethoxy-1-*p*-toluenesulfonyloxycyclopropane** [(*S,R*)-**25**-OTs] was obtained as a clear oil from (*S,R*)-**23**-OTs by hydrogenation for 48 h in dichloromethane (265 mg, 94%): $[\alpha]_D^{20}$ = + 8.79 (*c* = 1.40 in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2962 (C–H), 1600 (C=C), 1496, 1369 (SO_2), 1174 (SO_2), 1092, 993, 930, 845, 762, 734, 668 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.0 Hz, 3H; CH_3CH_2), 1.35 (dd, $^3J_{Z-3,2}$ = 7.5, $^2J_{3,3}$ = 8.5 Hz, 1H; (*Z*)-3-H), 1.50 (dd, $^2J_{3,3}$ = 8.5, $^3J_{E-3,2}$ = 4.7 Hz, 1H; (*E*)-3-H), 2.67 (s, 3H; Ar–CH_3), 3.02 (dd, $^3J_{Z-3,2}$ = 7.5, $^3J_{E-3,2}$ = 4.7 Hz, 1H; 2-H), 3.45 (dq, ^2J = – 9.0, ^3J = 7.0 Hz, 1H; CH_2O), 3.65 (dq, ^2J = – 9.0, ^3J = 7.0 Hz, 1H; CH_2O), 5.05 (d, $^3J_{Z-2',1'}$ = 16.9 Hz, 1H; (*Z*)-2′-H), 5.06 (dd, $^3J_{E-2',1'}$ = 10.2 Hz, 1H; (*E*)-2′-H), 5.95 (dd, $^3J_{Z-2',1'}$ = 16.9, $^3J_{E-2',1'}$ = 10.2 Hz, 1H; 1′-H), 7.30 (d, ^3J = 8.3 Hz, 2H; Ar–H), 7.84 (d, ^3J = 8.3 Hz, 2H; Ar–H); ^{13}C NMR (62.9 MHz, C_6D_6): δ = 14.71 (+, CH_3CH_2O), 18.55 (–, C-3), 20.81 (+, Ar–CH_3), 61.85 (+, C-2), 66.03 (C_{quat}, C-1), 66.99 (–, CH_2O), 111.94 (–, C-2′), 128.25 (+, C–Ar), 129.28 (+, C–Ar), 136.06 (C_{quat}, C–Ar), 136.81 (+, C-1′), 143.74 (C_{quat}, C–Ar); MS (70 eV, EI): *m/z* (%): 155 (100) [$C_7H_7SO_2^+$], 91 (87) [$C_7H_7^+$]; $C_{14}H_{18}O_4S$ (282.4): calcd C 59.55, H 6.43; found C 59.32, H 6.14.

1-Ethenyl-1-*p*-toluenesulfonyloxycyclopropane (29) was obtained in 90% yield over two steps by protodesilylation of **28** in THF and subsequent hydrogenation for 24 h in dichloromethane. The substance corresponds in all respects with the compound described in ref. [20c].

Dimethyl (*R*)-[2-(2-Ethoxycyclopropylidene)ethyl](2-propyn-1-yl)malonate [(*R,E*)-**26**]: The tosylate (*R,R*)-**25**-OTs (150 mg, 0.53 mmol) was dissolved in dry THF (10 mL) under nitrogen and the catalyst [prepared in advance from $Pd(dba)_2$ (5.2 mg, 0.010 mmol) and dppb (4.8 mg, 0.011 mmol) in dry THF (4 mL), stirred for 5 min] was added. After the mixture had turned green (1–5 min), dimethyl 1-sodium-1-propargylmalonate (153 mg, 0.8 mmol) in THF (5 mL) was added, and the mixture stirred at RT until the tosylate disappeared (TLC, 2 h). The mixture was poured into a mixture of water and diethyl ether (10 mL each), and the aqueous layer extracted with diethyl ether (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by flash chromatography [petroleum ether (60/80)/diethyl ether = 20/1] affording (*R,E*)-**26** as a clear oil (111 mg, 75%): $[\alpha]_D^{20}$ = – 7.34 (*c* = 0.99 in $CHCl_3$); IR (neat): $\tilde{\nu}$ = 3270 (C≡C–H), 2950 (C–H), 1740 (C=O), 1430, 1190, 1040, 850 cm^{-1}; ^1H NMR (62.9 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 7.1 Hz, 3H; CH_3CH_2O), 1.20–1.30 (m, 2H; 3′-H), 1.99 (t, $^4J_{1'',3''}$ = 2.7 Hz, 1H; 3″-H), 2.78 (d, $^4J_{1'',3''}$ = 2.7 Hz, 2H; 1″-H), 2.94 (d, ^3J = 7.6 Hz, 2H; 1-H), 3.54 (q, ^3J = 7.1 Hz, 2H; CH_2O), 3.60–3.80 (m, 1H; 2′-H), 3.70 (s, 3H; CH_3O), 3.71 (s, 3H; CH_3O), 5.90 (m, 1H; 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.48 (–, C-3′), 15.03 (+, CH_3CH_2O), 22.83 (–, C-1″), 34.51 (–, C-1), 52.55 (+, CH_3O), 52.71 (+, CH_3O), 56.93 (C_{quat}, CCO_2), 62.45 (–, CH_2O), 66.10 (+, C-2′), 71.32 (C_{quat}, C-2″), 78.85 (+, C-3″), 115.33 (+, C-2), 129.37 (C_{quat}, C-1′), 170.16 (C_{quat}, CO); MS (70 eV, EI): *m/z* (%): 280 (1) [M^+], 191 (24), 161 (41), 111 (100), 83 (56), 59 (56); $C_{15}H_{20}O_5$ (280.3): calcd C 64.27, H 7.19; found C 64.22, H 7.25.

Dimethyl (2*R,3*S**)-[(2,3-Dimethyl)cyclopropylidene]ethyl](2-propyn-1-yl)malonate** (*rac*-**32**): According to the procedure for the preparation of (*R*,*E*)-**26**, the reaction of (1*R**,2*R**,3*S**)/(1*S**,2*R**,3*S**)-2,3-dimethyl-1-ethenyl-1-chlorocyclopropane (130.5 mg, 1.00 mmol) with dimethyl 1-sodio-1-propargylmalonate (298 mg, 1.50 mmol) after 2 h at 66 °C, workup, and flash chromatography on silica gel (20 g) [petroleum ether (60/80)/Et_2O 10/1] yielded 190 mg (72%) of *rac*-**32** as a colorless oil; IR (neat): $\tilde{\nu}$ = 3290, 2950, 1740 (CO), 1430, 1280, 1200, 1080, 900, 830 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.10 (d, ^3J = 6 Hz, 3H, CH_3-Cpr), 1.10 (d, ^3J = 6.1 Hz, 3H, CH_3-Cpr), 1.50–1.70 (m, 2H, Cpr-H), 2.00 (t, ^4J = 3.1 Hz, 1H, 3″-H), 2.70 (d, ^4J = 3.1 Hz, 2H, 1″-H), 2.83 (d, ^3J = 7.9 Hz, 2H, 1-H), 3.70 (s, 6H, CH_3O), 5.47 (m, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 11.13 (+, CH_3-Cpr), 11.43 (+, CH_3-Cpr), 13.00 (+, C-3′), 13.55 (+, C-2′), 22.64 (−, C-1″), 34.32 (−, C-1), 52.70 (+, CH_3O), 57.15 (C_{quat}, CCO_2), 71.12 (+, C-3″), 79.15 (C_{quat}, C-2″), 109.55 (+, C-2), 140.42 (C_{quat}, C-1′), 170.42 (C_{quat}, CO); MS (70 eV, EI): *m*/*z* (%): 264 (1) [M^+], 204 (28), 189 (29), 165 (21), 145 (100), 105 (40); $C_{15}H_{20}O_4$ (264.3): 264.1361 (HRMS correct).

Dimethyl (*E*)-[(2-Trimethylsilyl)cyclopropylidene]ethyl](2-propyn-1-yl)malonate (*rac*-**34**): According to the procedure for the preparation of (*R*,*E*)-**26**, the reaction of (1*R**,2*R**)/(1*S**,2*R**)-2-trimethylsilyl-1-ethenyl-1-chlorocyclopropane (177 mg, 1.01 mmol) with dimethyl 1-sodio-1-propargylmalonate after 4 h at 20 °C, workup, and flash chromatography on silica gel (20 g) [petroleum ether (60/80)/Et_2O 5/1] yielded 200 mg (64%) of *rac*-**34** as a colorless oil; IR (neat): $\tilde{\nu}$ = 3300, 2998, 2950, 2920, 2895, 2840, 2225, 1735, 1435, 1288, 1246, 1210, 1180, 1090, 1015, 975, 903, 837, 730, 646 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.01 [s, 9H, $Si(CH_3)_3$], 0.59 (m, 1H, Cpr-H), 0.84 (m, 1H, Cpr-H), 1.14 (m, 1H, Cpr-H), 1.99 (t, ^4J = 2.6 Hz, 1H, 3″-H), 2.78 (d, ^4J = 2.6 Hz, 2H, 1″-H), 2.94 (d, ^3J = 7.5 Hz, 1-H), 3.73 (s, 6H, OCH_3), 5.33 (m, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = −2.57 [+, $Si(CH_3)_3$], 4.63 (−, C-Cpr), 4.68 (+, C-Cpr), 22.59 (−, C-1″), 34.67 (−, C-1), 52.72 (+, OCH_3), 57.17 (C_{quat}, CCO_2), 71.11 (C_{quat}, C-3″), 79.14 (+, C-2″), 107.70 (+, C-2), 131.10 (C_{quat}, C-Cpr), 170.45 (C_{quat}, C=O).

(1*S*,2*R*,5′*S*)-7′,7′-Bis(methoxycarbonyl)-2-ethoxy-3′-oxospiro[cyclopropane-1,4′-bicyclo[3.3.0]oct-1′-ene] [(1*S*,2*R*,5′*S*)-**31**]: A solution of the enyne (*R*,*E*)-**26** (280 mg, 1.0 mmol) in dry CH_2Cl_2 (10 mL) was stirred with $Co_2(CO)_8$ (342 mg, 1.0 mmol) in the dark. After complete conversion (monitored by TLC, 2 h) the mixture was cooled to −78 °C, and trimethylamine-*N*-oxide (TMANO) (525 mg, 7.0 mmol, 7 equiv) added. The mixture was stirred under an oxygen atmosphere. The solution was warmed slowly (15 h) to RT and filtered through Celite. After removal of the solvent in vacuo the residue was purified by flash chromatography on silica gel [petroleum ether (60/80)/diethyl ether = 3:1] to yield 262 mg (85%) of bicyclooctene (1*S*,2*R*,5′*S*)-**31**: M.p. 47 °C; $[\alpha]_D^{20}$ = +19.33 (*c* = 0.90 in $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3060, 2980 (C–H), 1740 (C=O), 1700 (C=O), 1435, 1250, 1210, 840, 750 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.99 (dd, $^3J_{Z-3,2}$ = 7.3, $^2J_{3,3}$ = 9.1 Hz, 1H; (*Z*)-3-H), 1.15 (dd, $^3J_{E-3,2}$ = 5.1, $^2J_{3,3}$ = 9.1 Hz, 1H; (*E*)-3-H), 1.30 (t, ^3J = 6.9 Hz, 3H; CH_3CH_2O), 1.80 (dd, $^3J_{5',6'B}$ = 13.1, ^2J = 13.2 Hz, 1H; 6′-H_B), 2.62 (dd, ^2J = 13.2, $^3J_{5',6'A}$ = 9.3 Hz, 1H; 6′-H_A), 3.16 (dd, $^3J_{5',6'B}$ = 13.1, $^3J_{5',6'A}$ = 9.3 Hz, 1H; 5′-H), 3.35 (d, ^2J = 14.3 Hz, 1H; 8′-H), 3.50 (q, ^3J = 6.9 Hz, 2H; CH_2O), 3.57 (d, ^2J = 14.3 Hz, 1H; 8′-H), 3.70 (dd, $^3J_{2,Z-3}$ = 7.3, $^3J_{2,E-3}$ = 5.1 Hz, 1H; 2-H), 3.76 (s, 3H; CO_2CH_3), 3.80 (s, 3H; CO_2CH_3), 6.00 (s, 1H; 2′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.10 (+, CH_3CH_2), 19.85 (−, C-3), 35.76 (−, C-6′), 37.48 (−, C-8′), 39.53 (C_{quat}, C-1), 46.91 (+, C-5′), 53.14 (+, CO_2CH_3), 53.27 (+, CO_2CH_3), 61.03 (C_{quat}, C-7′), 62.11 (+, C-2), 66.77 (−, CH_2O), 125.13 (+, C-2′), 171.15 (C_{quat}, CO_2CH_3), 171.23 (C_{quat}, CO_2CH_3), 182.96 (C_{quat}, C-1′), 207.57 (C_{quat}, C-3′); MS (70 eV, EI): *m*/*z* (%): 308 (69) [M^+], 248 (35), 219 (100), 189 (99), 133 (58), 131 (97), 103 (93), 77 (83); $C_{16}H_{20}O_6$ (308.3): calcd C 62.33, H 6.54; found C 62.30, H 6.51.

(1*S,2*R**,5′*S**)-7′,7′-Bis(methoxycarbonyl)-2-trimethylsilyl-3′-oxospiro[cyclopropane-1,4′-bicyclo[3.3.0]oct-1′-ene]** (*rac*-**35a**) and **(1*R**,2*S**,5′*S*-7′,7′-Bis(methoxycarbonyl)-2-trimethylsilyl-3′-oxospiro[cyclopropane-1,4′-bicyclo[3.3.0]oct-1′-ene]** (*rac*-**35b**): According to the procedure for the preparation of (1*S*,2*R*,5′*S*)-**31**, *rac*-**34** (62 mg, 0.20 mmol) was treated and purified by flash chromatography on silica gel (10 g) [petroleum ether (60/80)/Et_2O 9/1] affording 5.4 mg (8%) of *rac*-**35b** (fraction I, R_f = 0.30) and 48 mg (72%) of *rac*-**35a** (fraction II, R_f = 0.25) as colorless solids.

rac-**35b**: IR (KBr): $\tilde{\nu}$ = 3060, 2980, 1740 (C=O), 1700 (C=O), 1435, 1250, 1210, 840, 740 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.10 (s, 9H, $Si(CH_3)_3$), 0.32 (dd, $^3J_{2-3}$ = 10.7, $^3J_{2-3}$ = 9.3 Hz, 1H, 2-H), 1.03 (dd, $^3J_{2-3}$ = 9.3, ^2J = 3.0 Hz, 1H, 3-H_Z), 1.15 (dd, $^3J_{2-3}$ = 11, ^2J = 3 Hz, 1H, 3-H_E), 1.70 (t, $^3J_{5'-6'}$ = 12.5, ^2J = 12.5 Hz, 1H, 6′-H), 2.52 (dd, ^2J = 12.5, $^3J_{5'-6'}$ = 7.5 Hz, 1H, 6′-H), 3.16 (dddd, $^3J_{5'-6'}$ = 12.5, $^3J_{5'-6'}$ = 7.5, $^4J_{2'-5'}$ = 1.1, $^4J_{5'-8'}$ = 1.0 Hz, 1H, 5′-H), 3.26 (ddd, ^2J = 18.4 Hz, ^4J = 1.1, ^4J = 1.1 Hz, 1H, 8′-H), 3.40 (ddd, $^2J_{AB}$ = 18.4, ^4J = 1.1, ^4J = 1.1 Hz, 1H, 8′-H), 3.72 (s, 3H, CO_2CH_3), 3.81 (s, 3H, CO_2CH_3), 6.00–6.02 (m, 1H, 2′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, APT): δ = −0.46 (+, $Si(CH_3)_3$), 16.68 (+, C-2), 17.89 (−, C-3), 36.57 (−, C-6′), 36.74 (−, C-8′), 38.13 (−, C-1), 52.54 (+, C-5′), 53.16 (+, CO_2CH_3), 53.29 (+, CO_2CH_3), 60.65 (−, C-7′), 126.28 (+, C-2′), 171.22 (−, CO_2CH_3), 172.01 (C_{quat}, CO_2CH_3), 182.04 (−, C-1′), 203.16 (−, C-3′); MS (70 eV, EI): *m*/*z* (%): 336 (8) [M^+], 321 (23) [M^+ − CH_3], 277 (11) [M^+ − CO_2CH_3], 261 (14), 217 (12), 115 (14), 89 (12), 73 (100) [$Si(CH_3)_3^+$]; $C_{17}H_{24}O_5Si$ (336.5): 336.1393 (HRMS correct).

rac-**35a**: IR (KBr): $\tilde{\nu}$ = 3060, 2980, 1740 (C=O), 1700 (C=O), 1435, 1250, 1210, 840, 750 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.07 (s, 9H, $Si(CH_3)_3$), 0.77 (dd, $^3J_{2-3}$ = 11.4, $^3J_{2-3}$ = 9.0 Hz, 1H, 2-H), 0.99 (dd, $^3J_{2-3}$ = 9.0, ^2J = 2.9 Hz, 1H, 3-H_Z), 1.15 (dd, $^3J_{2-3}$ = 11.4, ^2J = 2.9 Hz, 1H, 3-H_E), 1.60 (t, $^3J_{5'-6'}$ = 12.8, ^2J = 12.8 Hz, 1H, 6′-H), 2.62 (dd, ^2J = 12.8, $^3J_{5'-6'}$ = 7.2 Hz, 1H, 6′-H), 3.16 (dd, $^3J_{5'-6'}$ = 12.8, $^3J_{5'-6'}$ = 7.2 Hz, 1H, 5′-H), 3.31 (d, $^2J_{AB}$ = 18.4 Hz, 1H, 8′-H), 3.42 (d, $^2J_{AB}$ = 18.4 Hz, 1H, 8′-H), 3.72 (s, 3H, CO_2CH_3), 3.81 (s, 3H, CO_2CH_3), 6.05 (s, 1H, 2′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, APT): δ = −1.59 (+, $Si(CH_3)_3$), 14.22 (+, C-2), 18.00 (−, C-3), 35.46 (−, C-6′), 37.43 (−, C-1), 37.65 (−, C-8′), 49.82 (+, C-5′), 53.16 (+, CO_2CH_3), 53.22 (+, CO_2CH_3), 60.60 (−, C-7′), 125.47 (+, C-2′), 171.06 (−, CO_2CH_3), 171.93 (−, CO_2CH_3), 182.83 (−, C-1′), 208.93 (−, C-3′); MS (70 eV, EI): *m*/*z* (%): 336 (11) [M^+], 321 (90) [M^+ − CH_3], 277 (11) [M^+ − CO_2CH_3], 261 (14), 217 (12), 115 (14), 89 (12), 73 (100) [$Si(CH_3)_3^+$]; $C_{17}H_{24}O_5Si$ (336.5): calcd C 60.69, H 7.19; found C 60.62, H 7.25.

(1*R,5′*R**,*Z*)-7′,7′-Bis(methoxycarbonyl)-2,3-dimethyl-3′-oxospiro[cyclopropane-1,4′-bicyclo[3.3.0]oct-1′-ene]** (*rac*-**33a**) and **(1*S**,5′*R**,*Z*)-7′,7′-Bis(methoxycarbonyl)-2,3-dimethyl-3′-oxospiro[cyclopropane-1,4′-bicyclo[3.3.0]oct-1′-ene]** (*rac*-**33b**): According to the procedure for the preparation of (1*S*,2*R*,5′*S*)-**31**, *rac*-**32** (15 mg, 0.06 mmol) was treated and purified by flash chromatography on silica gel (10 g) [petroleum ether (60/80)/Et_2O 9/1] affording 7.5 mg (45%) of *rac*-**33a** (fraction I, R_f = 0.30) and 2.6 mg (15%) of *rac*-**33b** (fraction II, R_f = 0.2) as colorless oils.

rac-**33a**: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.80–0.90 (m, 1H, Cpr-H), 0.89 (d, ^3J = 6.8 Hz, 3H, CH_3-Cpr), 1.20 (d, ^3J = 6.2 Hz, 3H, CH_3-Cpr), 1.05–1.15 (m, 1H, Cpr-H), 1.68 (dd, $^3J_{5'-6'A}$ = 13, ^2J = 13 Hz, 1H, 6′-H_A), 2.47 (dd, ^2J = 13, $^3J_{5'-6'B}$ = 7.5, 1H, 6′-H_B), 3.05 (dd, $^3J'_{5'-6'B}$ = 7.5, $^3J_{5'-6'A}$ = 13 Hz, 1H, 5′-H), 3.40 (d, ^2J = 18.5 Hz, 1H, 8′-H), 3.53 (d, ^2J = 18.5 Hz, 1H, 8′-H), 3.78 (s, 3H, CH_3CO_2), 3.82 (s, 3H, CH_3CO_2), 5.91 (m, 1H, 2′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$, APT): δ = 9.52 (+, C-Cpr), 9.92 (+, C-Cpr), 24.85 (+, CH_3-Cpr), 26.94 (+, CH_3-Cpr), 34.73 (−, C-6′), 37.51 (+, C-1), 37.84 (−, C-8′), 47.66 (+, C-5′), 53.08 (+, CO_2CH_3), 53.10 (+, CO_2CH_3), 60.94 (−, C-7′), 124.67 (+, C-2′), 171.25 (−, CO_2CH_3), 172.04 (−, CO_2CH_3), 182.40 (−, C-1′), 209.3 (−, C-3′); $C_{16}H_{20}O_5$ (292.3): 292.1310 (HRMS correct).

rac-**33b**: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.80–0.90 (m, 1H, Cpr-H), 0.89 (d, ^3J = 6.8 Hz, 3H, CH_3-Cpr), 1.15 (d, ^3J = 6.2 Hz, 3H, CH_3-Cpr), 1.05–1.15 (m, 1H, Cpr-H), 1.68 (dd, $^3J_{5'-6'A}$ = 13, ^2J = 13 Hz, 1H, 6′-H_A), 2.47 (dd, ^2J = 13, $^3J_{5'-6'B}$ = 7.5, 1H, 6′-H_B), 3.05 (dd, $^3J_{5'-6'B}$ = 7.5, $^3J_{5'-6'A}$ = 13 Hz, 1H, 5′-H), 3.25 (d, $^2J_{AB}$ = 18.5 Hz, 1H, 8′-H), 3.37 (d, ^2J = 18.5 Hz, 1H, 8′-H), 3.75 (s, 3H, CH_3CO_2), 3.78 (s, 3H, CH_3CO_2), 5.91 (m, 1H, 2′-H); ^{13}C NMR (50.9 MHz, $CDCl_3$, APT): δ = 1.02 (+, C-2), 6.23 (+, C-3), 26.50 (+, CH_3-Cpr), 27.22 (+, CH_3-Cpr), 35.51 (−, C-6′), 36.01 (−, C-1), 37.28 (−, C-8′), 46.99 (+, C-5), 53.80 (+, CH_3CO_2), 53.84 (+, CH_3CO_2), 61.00 (−, C-7′), 127.66 (+, C-2′), 171.31 (−, CO_2), 171.99 (−, CO_2), 180.43 (−, C-1′), 192.92 (−, C-3′).

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[1] a) Small Ring Compounds in Organic Synthesis I–IV (Ed.: A. de Meijere), *Top. Curr. Chem.* Springer, Berlin, **1986**, *133*; **1987**, *135*; **1988**, *144*; **1990**, *155*; b) H.-U. Reißig in *The chemistry of the cyclopropyl group* (Ed. Z. Rappoport), Wiley, Chichester, **1987**, pp. 375–443; c) H. N. C. Wong, M.-Y. Hon, C.-W. Tse, Y.-C. Yip, J. Tanko, T. Hudlicky, *Chem. Rev.* **1989**, *89*, 165–198; d) J. Salaün, *ibid.* **1989**, *89*, 1247–1270; e) *Strain and its Implications in Organic Chemistry* (Eds.: A. de Meijere, S. Blechert), NATO ASI Series C, *Vol. 273*, Kluwer, Dordrecht, **1989**.

[2] a) P. Binger, U. Schuchardt, *Angew. Chem.* **1977**, *89*, 254–255; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 248–249; b) B. M. Trost, *Angew. Chem.* **1986**, *98*, 1–20; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1–19; c) P. Binger, H. M. Büch, *Top. Curr. Chem.* **1987**, *135*, 77–151; d) P. Binger, A. Brinkmann, P. Roefke, B. Schäfer, *Liebigs Ann. Chem.* **1989**, 739–750.

[3] a) R. L. Danheiser, C. Martinez-Davila, J. M. Morin, *J. Org. Chem.* **1980**, *45*, 1340–1341; b) R. L. Danheiser, C. Martinez-Davila, R. J. Auchus, J. T. Kadonaga, *J. Am. Chem. Soc.* **1981**, *103*, 2443–2446; c) T. Hudlicky, T. M. Kutchan, S. M. Naqvi, *Org. React.* **1985**, *33*, 247–335; d) R. L. Danheiser, J. J. Bronson, K. Okano, *J. Am. Chem. Soc.* **1985**, *107*, 4579–4581; e) Z. Goldschmidt, B. Crammer, *Chem. Soc. Rev.* **1988**, *17*, 229–267.

[4] a) A. de Meijere, *Bull. Soc. Chim. Belg.* **1984**, *93*, 241–260; b) A. de Meijere, *Chem. Ber.* **1987**, *23*, 865–870; c) A. de Meijere, L. Wessjohann, *Synlett* **1990**, 20–32; d) J. R. Y. Salaün, *Top. Curr. Chem.* **1990**, *144*, 1–71; e) A. de Meijere in *New Aspects of Organic Chemistry II*, (Eds.: Z.-i. Yoshida and Y. Ohshiro), Kodansha, Tokyo, **1992**, pp. 181–213.

[5] B. M. Trost in ref. [1a], **1986**, *133*, p. 3–82.

[6] a) S. Keyaniyan, M. Apel, J. P. Richmond, A. de Meijere, *Angew. Chem.* **1985**, *97*, 763–764; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 770–771; b) T. Liese, A.

de Meijere, *Chem. Ber.* **1986**, *119*, 2995–3026; c) A. de Meijere, T.-J. Schulz, R. R. Kostikov, F. Graupner, T. Murr, T. Bielfeldt, *Synthesis* **1991**, 547–560; d) H.-C. Militzer, S. Schömenauer, C. Otte, C. Puls, J. Hain, S. Bräse, A. de Meijere, *Synthesis* **1993**, 998–1012.

[7] W. A. Smit, S. L. Kireev, O. M. Nefedov, V. A. Tarasov, *Tetrahedron Lett.* **1989**, *30*, 4021–4024.

[8] a) R. T. Lewis, W. B. Motherwell, M. Shipman, *J. Chem. Soc. Chem. Commun.* **1988**, 948–950; b) S. A. Bapuji, W. B. Motherwell, M. Shipman, *Tetrahedron Lett.* **1989**, *30*, 7107–7110; c) W. B. Motherwell, M. Shipman, *ibid.* **1991**, *32*, 1103–1106; d) A. Stolle, H. Becker, J. Salaün, A. de Meijere, *ibid.* **1994**, *35*, 3517–3520, 3521–3524; e) M. Lautens, Y. Ren, P. H. M. Delanghe, *J. Am. Chem. Soc.* **1994**, *116*, 8821–8822; f) T. Heiner, S. Michalski, K. Gerke, G. Kuchta, M. Buback, A. de Meijere, *Synlett* **1995**, 355–357; g) H. Corlay, R. T. Lewis, W. B. Motherwell, M. Shipman, *Tetrahedron* **1995**, *51*, 3303–3318.

[9] a) J. M. Klunder, S. Y. Ko, K. B. Sharpless, *J. Org. Chem.* **1986**, *51*, 3710–3712; b) J. M. Klunder, T. Onami, K. B. Sharpless, *ibid.* **1989**, *54*, 1295–1304.

[10] a) M. Yamaguchi, I. Hirao, *Tetrahedron Lett.* **1983**, *24*, 391–394; b) E. Erdik, *Tetrahedron* **1984**, *40*, 641–657; c) K. Utimoto, C. Lambert, Y. Fukuda, H. Shiragami, H. Nozaki, *Tetrahedron Lett.* **1984**, *25*, 5423–5426; d) B. H. Lipshutz, R. S. Wilhelm, J. A. Kozlowski, *Tetrahedron* **1984**, *40*, 5505–5538; e) B. M. Trost, *Pure Appl. Chem.* **1991**, *64*, 315–322; f) R. Tirado, J. A. Prieto, *J. Org. Chem.* **1993**, *58*, 5666–5673.

[11] H. O. Kalinowski, D. Seebach, G. Crass, *Angew. Chem.* **1975**, *87*, 812–813; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 762–763.

[12] a) F. Cramer, K. Pawelzik, H. J. Baldauf, *Chem. Ber.* **1958**, *91*, 62–67; b) H. Stetter, M. Schwarz, A. Hirschhorn, *ibid.* **1959**, *92*, 1629–1635; c) F. Cramer, N. Hennrich; *ibid.* **1961**, *94*, 976–989; d) U. Widmer, *Synthesis* **1987**, 568–570; e) P. Barbier, F. Schneider, U. Widmer, *Helv. Chim. Acta* **1987**, *70*, 1412–1418; f) P. Eckenberg, U. Groth, T. Huhn, N. Richter, C. Schmeck, *Tetrahedron* **1993**, *49*, 1619–1624; g) U. Groth, C. Schmeck, U. Schöllkopf, *Liebigs Ann. Chem.* **1993**, 311–323.

[13] A. F. Kluge, K. G. Untel, J. H. Fried, *J. Am. Chem. Soc.* **1972**, *94*, 7827–7831.

[14] Chiral GC columns: 6-Me-2,3-γ-CD (chiral, column B), 6-Me-2,3-pe-β-CD (chiral, column C) [22], heptakis(6-*O*-Me-2,3-di-*O*-pe-β-CD) (chiral, column D) [22].

[15] d) M. S. Kharasch, O. Reinmuth, *Grignard Reactions of Non-metallic Substances*, Prentice Hall, New York, N. Y., **1954**, p. 1264; b) A. G. Davies, *Organic Peroxides*, Butterworth, London, **1961**, p. 124; c) T. G. Brilkina, V. A. Shushnov, *Reactions of Organometallic Compounds with Oxygen and Peroxides*, Iliffe, London, **1966**, p. 39; d) W. J. Wakefield, *Organolithium Methods*, Academic Press, London, **1988**, pp. 129–133; e) M. Maher-Detweiler in *Houben Weyl: Methoden der Organischen Chemie*, *Vol. E13* (Ed.: H. Kropf), p. 176.

[16] a) L. Camici, A. Ricci, M. Taddei, *Tetrahedron Lett.* **1986**, *27*, 5155–5158; b) M. Taddei, A. Ricchi, *Synthesis* **1986**, 633–635.

[17] a) C. H. DePuy, *Acc. Chem. Res.* **1968**, *1*, 33–41; b) D. T. Longone, W. D. Wright, *Tetrahedron Lett.* **1969**, 2859–2862; c) D. H. Gibson, C. H. DePuy, *Chem. Rev.* **1974**, *74*, 605–623; d) P. Warner, S.-L. Lu, *J. Org. Chem.* **1976**, *41*, 1459–1461; e) R. L. Danheiser, C. Martinez-Davila, J. M. Morin, *ibid.* **1980**, *45*, 1340–1341; f) T. Liese, A. de Meijere, *Chem. Ber.* **1986**, *119*, 2995–3026.

[18] Dry air may be used as well as dry oxygen; for larger scale operations, however, dry air is preferrable because of the moderating effect of the dilution.

[19] a) W. Kirmse, M. Zeppenfeld, *J. Chem. Soc. Chem. Commun.* **1977**, 124; b) M. Vincens, C. Dumont, M. Vidal, *Tetrahedron Lett.* **1986**, *27*, 2267–2270.

[20] a) A. Stolle, J. Salaün, A. de Meijere, *Tetrahedron Lett.* **1990**, *31*, 4593–4596; b) A. Stolle, J. Salaün, A. de Meijere, *Synlett* **1991**, 327–330; c) A. Stolle, J. Ollivier, P. P. Piras, J. Salaün, P. Aufranc, A. de Meijere, *J. Am. Chem. Soc.* **1992**, *114*, 4051–4067; d) J. Ollivier, P. P. Piras, A. Stolle, A. de Meijere, J. Salaün, *Tetrahedron Lett.* **1992**, *33*, 3307–3310; e) G. McGaffin, S. Michalski, A. Stolle, S. Bräse, J. Salaün, A. de Meijere, *Synlett* **1992**, 558–560.

[21] a) S. Shambayati, W. E. Crowe, S. L. Schreiber, *Tetrahedron Lett.* **1990**, *31*, 5289–5292; b) N. Jeong, Y. K. Chung, B. Y. Lee, S. H. Lee, S.-E. Yoo, *Synlett* **1991**, 204–206.

[22] a) We thank Prof. Dr. W. A. König, Universität Hamburg, Germany, for the determination of the enantiomeric excesses (*ee*) for the cyclopropane derivatives (*S*)-**7d** and (*S*)-**7e**. b) W. A. König, *The Practise of Enantiomer Separation by Capillary Gas Chromatography*, Hüthig, Heidelberg, **1987**. c) W. A. König, *Nachr. Chem. Tech. Lab.* **1989**, *37*, 471–476.

[23] J. Suffert, *J. Org. Chem.* **1989**, *54*, 509–510.

[24] A. B. Holmes, C. N. Sporikon, *Org. Synth.* **1987**, *65*, 61–67.

[25] M. F. Rettig, P. M. Maitlis, *Inorg. Synth.* **1977**, *17*, 135–137.

[26] W. Weber, A. de Meijere, *Chem. Ber.* **1985**, *118*, 2450–2471.

[27] T. Liese, A. de Meijere, *Chem. Ber.* **1986**, *119*, 2995–3026.

[28] The use of Lindlar catalyst without added quinoline led to partial perhydrogenation to the corresponding cyclopropylalkanes. However, ring-opening was not observed.