(−)-Sparteine-Mediated Asymmetric Cyclocarbolithiation of Alkenes Combined with a Stereospecific *retro*-[1,4]-*Brook* Rearrangement

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A novel domino-type reaction sequence consisting of an enantioselective intramolecular carbolithiation of 6-phenylhex-5-enyl carbamates and a highly stereospecific *retro*-[1,4]-*Brook* rearrangement is reported. The carbocycles are formed with high enantiomeric (er > 98:2) and diastereoisomer ratios (dr > 99:1) in good yields (47–60%). On the basis of the absolute configuration of the cyclization products, a stereoretentive mechanism is proposed for the *retro*-[1,4]-*Brook* rearrangement.

1. Introduction. – The migration of a trialkylsilyl group attached to a C-center to a nucleophilic O-atom under the cleavage of the C−Si bond and the formation of a silyl ether has been reported by *Brook* for a *C*- to *O*-[1,2]-silyl shift in the early seventies [1]. The high tendency of a Si-center with a nucleophilic O-atom in its proximity to migrate has turned out to be a common feature and has, therefore, been subject of numerous investigations. *C*- to *O*-[1,3]- [2] and -[1,4]-silyl shifts [3], generally known as [1,3]- or [1,4]-*Brook* rearrangements, have been described in recent years[3]). The reverse reaction pathway, the *O*- to *C*-silyl shift from a silyl ether to a carbanionic C-atom, is also known and has been intensively studied[4]).

We became interested in the *retro-Brook* rearrangement because of two reasons: *a*) The mechanistic studies on the *retro-Brook* rearrangement revealed these reactions to be highly stereospecific in regard to the configuration at the C-, as well as the Si-atom[5]). Since the enantiotopos-differentiating deprotonation of alkyl carbamates with *s*-BuLi/(−)-sparteine (*s*-BuLi/**1**) [12] opens an easy access to chiral non-racemic Li-carbanion pairs, we investigated whether the *retro-Brook* rearrangement can serve as a tool for intramolecularly passing in an electrophilic trialkylsilyl group [13] (*Scheme 1*). *b*) In the course of our studies towards the stereoselective intramolecular carbolithiation [14] [15][6]) of 6-phenylhex-5-enyl carbamates **2** (X = H), we could not overcome

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[1]) Taken from the dissertation of *S.H.K.*, WWU Münster.

[2]) Crystal structure analysis.

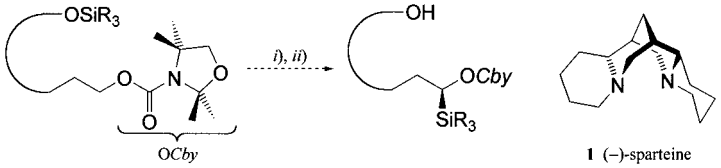
[3]) For a brief overview, see [4].

[4]) For so-called *retro*-[1,2]-, -[1,3]-, -[1,4]-, and -[1,5]-*Brook* rearrangements, see [5–7] respectively.

[5]) The stereochemical outcome of the *retro-Brook* rearrangement was elucidated for configurationally labile benzylic [8] and stable [9] γ-(silyloxy)alkyllithiums. In the former case inversion and in the latter retention of the configuration at the formerly Li-bearing C-atom was observed. The study of the *retro*-[1,2]-*Brook* rearrangement led to similar results for α-lithioalkyl- [10] and α-lithiobenzyl ethers [11].

[6]) The stereoselective intramolecular carbolithiation of alkynes [16] and conjugated systems [17] has also been reported by us quite recently.

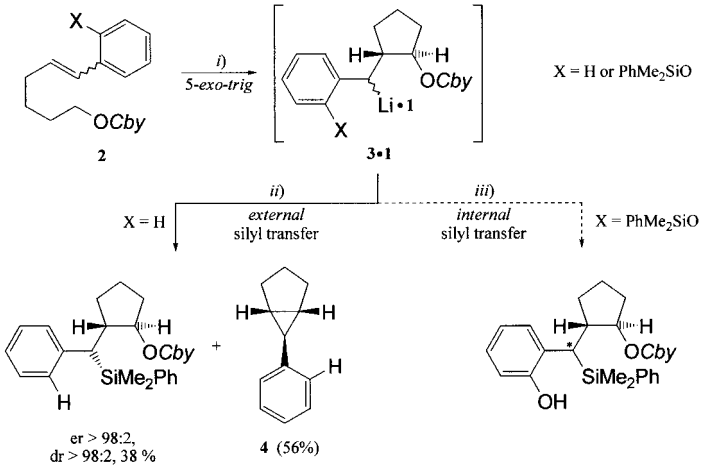
Scheme 1



i) *s*-BuLi/**1**, Et_2O, $-78°$. *ii*) MeOH, $-78°$, then r.t.; R = alkyl and/or aryl. O*Cby* = 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carbonyloxy

the problem of the 1,3-cycloelimination[7]) of the intermediate benzylic lithium carbanion pair **3**•**1** (X = H). Since the formation of the undesired bicyclic product **4** could not be completely prevented or even reduced by adding an *external* electrophile such as $PhMe_2SiCl$, we thought that an intramolecular electrophilic substitution of anionic center in **3**•**1** by an *internal* silyl group following the *retro-Brook* mechanism could be a promising domino process[8]) capable of competing with the 1,3-cycloelimination (*Scheme 2*).

Scheme 2



i) *s*-BuLi/**1**, Et_2O, $-78°$, several hours. *ii*) $PhMe_2SiCl$, $-78°$, then r.t. *iii*) MeOH, $-78°$, then r.t.

Herein, we wish to report an enantioselective domino-type reaction sequence consisting of a stereoselective cyclocarbolithiation [14] and a stereospecific *retro-Brook* rearrangement.

Results and Discussion. – The cyclization precursor **2** (X = $PhMe_2SiO$) was designed in such a fashion that a retro-[1,4]-*Brook* rearrangement – driven by the generation of the resonance-stabilized phenoxide ion – might occur after the

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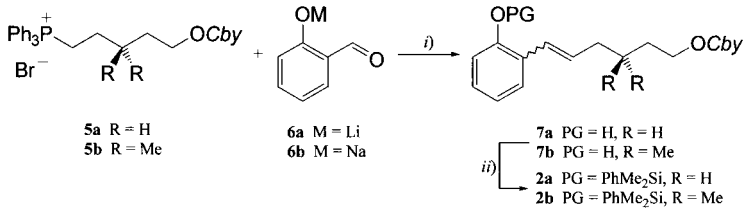
7) 1,3-Cycloeliminations with a carbamate as the leaving group have been reported by us [14] [18], and *Nakai* and co-workers [15]. Additionally, 1,3-cycloeliminations of benzyllithiums have been successfully applied in the synthesis of cyclopropanes by us [18], and *Marek*, *Normant*, and co-workers [19].

8) For the classification of domino reactions, see [20].

intramolecular carbolithiation reaction. Compounds (*E*/*Z*)-**2a** ((*E*/*Z*) 50 : 50), (*E*)-**2a** ((*E*/*Z*) 90 : 10), and (*Z*)-**2b** (*E*/*Z*) 30 : 70) were prepared from the previously described phosphonium bromides **5a** and **5b** [14], respectively, in a straightforward manner. Compounds **5a** and **5b** were reacted with the two different alkali-metal phenoxides of salicylic aldehyde **6a** or **6b** furnishing **7a** and **7b**, respectively, in moderate-to-good yield without controlling the geometry of the C=C bond[9]). The phenolic OH groups in (*E*/*Z*)-**7a**, (*E*)-**7a**, and (*Z*)-**7b** were silylated with $PhMe_2SiCl$/1*H*-imidazole in nearly quantitative yield (*Scheme 3*).

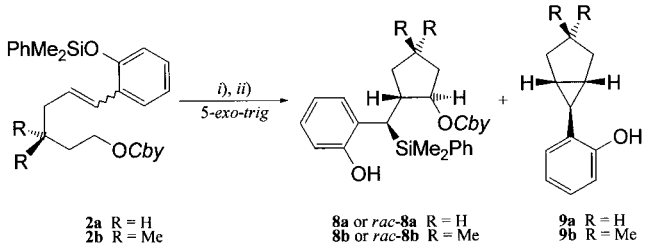
Scheme 3



i) **5a** + **6b**: NaHMDS, THF, −40°, then r.t., (*E*/*Z*)-**7a**: dr 50 : 50; 82%; **5a** + **6a**: BuLi, NaHMDS, THF, −40°, then r.t., (*E*)-**7a**: dr 90 : 10; 60%; **5b** + **6b**: NaHMDS, THF, −40°, then r.t., (*Z*)-**7b**: dr 30 : 70; 62%. *ii*) $PhMe_2SiCl$, 1*H*-imidazole, DMF, r.t., **2a**: 94%, **2b**: 93%.

The 6-{[dimethyl(phenyl)silyloxy]phenyl}hex-5-enyl carbamate (*E*/*Z*)-**2a** was treated with *s*-BuLi/**1** in Et_2O for 4 h at −78° and for further 16 h at −40°[10]), providing the cyclized and rearranged product **8a** in diastereoisomerically pure form (dr > 99 : 1) and in 58% yield (*Scheme 4* and *Table*, *Entry 1*). The bicyclic by-product **9a** resulting from the cyclocarbolithiation reaction and the subsequent 1,3-cycloelimination was isolated in only 9% yield. It is important to indicate that the undesired bicycle **4** (*Scheme 2*) is quantitatively (!) formed while warming to −40°. Consequently, the 1,3-cycloelimination is effectively restrained by the *retro*-[1,4]-*Brook* rearrangement even at higher temperatures.

Scheme 4



i) *s*-BuLi/**1** or *s*-BuLi/*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (**11**), Et_2O, −78°, then −40°, several hours. *ii*) MeOH, −78°, then r.t. See also the *Table*.

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[9]) We have already reported that the configuration of the C=C bond has no effect on the relative and absolute configuration of the cyclization products [14].

[10]) The reaction conditions have been optimized by changing the solvent (Et_2O, hexane, or cumene), the equivalents of *s*-BuLi/**1** (1.10/1.15 equiv. up to 1.40/1.45 equiv.), and the temperature program (−78°, −78°, then r.t., or −78°, then −40°) [13].

Table 1. *Domino-Type Reaction Sequence of the Hex-5-enyl Carbamates* **2**

Entry	*Alkene*	R	(*E*/*Z*)-Ratio[a])	Carbocycle	er[b])	dr[c])	Yield/%	
							2	**8**
1	(*E*/*Z*)-**2a**	H	50 : 50	**8a**	> 98 : 2	> 99 : 1	16	58[d])
2	(*E*)-**2a**	H	90 : 10	**8a**	> 98 : 2	> 99 : 1	17	60
3	(*Z*)-**2b**	Me	30 : 70	**8b**	> 98 : 2	> 99 : 1	40	47
4[e])	(*E*/*Z*)-**2a**	H	50 : 50	*rac*-**8a**	–	> 99 : 1	–	8[f])
5[e])	(*Z*)-**2b**	Me	30 : 70	*rac*-**8b**	–	> 99 : 1	–	50

[a]) Determined from the ^{1}H-NMR spectra. [b]) Determined from the ^{1}H- and ^{19}F-NMR spectra of the Mosher esters by comparison with the racemates. [c]) Determined by GC analysis and from the ^{1}H-NMR spectra. [d]) The bicyclic product **9a** was formed in 9% yield. [e]) These experiments were carried out in the presence of TMEDA (**11**) instead of (–)-sparteine (**1**). [f]) The 1,3-cycloelimination is highly favored in the presence of a 'small' diamine such as **11**.

According to the reaction conditions mentioned above, the cyclization of the precursor (*E*)-**2a** gave the carbocycle **8a** in 60% yield as a single diastereoisomer (dr > 99 : 1) in spite of the different (*E*/*Z*)-ratio of the C=C bond compared to (*E*/*Z*)-**2a** (*Scheme 2* and *Table*, *Entry 2*). This observation coincides with our previous investigations on the cyclocarbolithiation[9]).

The carbamate (*Z*)-**2b** with geminal Me groups also cyclizes smoothly upon treatment with *s*-BuLi/**1** in Et_2O at $-78° \rightarrow -40°$ to provide **8b** in diastereoisomerically pure form (dr > 99 : 1) (*Scheme 2*, *Table*, *Entry 3*) and in 47% yield. Although we expected an increase in the yield in comparison with the derivatives **2a** because of the *Thorpe-Ingold* effect [21], the cyclization of the branched precursor **2b** furnished the carbocycle **8b** in a significantly lower yield. Due to steric interactions of the bulky chiral base *s*-BuLi/**1** and the geminal Me groups, the deprotonation of the branched carbamate **2b** was not complete[11]), which was reflected by the fact that the desilylated cyclization precursor was isolated in 40% yield. Thus, any of the yield caused by the *Thorpe-Ingold*-effect is over-compensated by the restrained deprotonation[12]).

The cyclization products were also prepared in their racemic forms *rac*-**8** by performing the domino reaction in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (**11**) rather than **1** (*Table*, *Entries 4* and *5*). The carbamates **8** and *rac*-**8** were decarbamoylated according to a standard procedure [23] to furnish the diols **12** and *rac*-**12**, respectively, in high yields[13]), which were then quantitatively converted to the *Mosher* esters **13** and *rac*-**13**, respectively, in order to determine the enantiomer ratios of **8** [25] (*Scheme 5*). The diastereoisomeric ratios of **13** (dr > 98 : 2) were determined from the ^{1}H- and ^{19}F-NMR spectra of **13** and *rac*-**13**, corresponding to enantiomer ratios of > 98 : 2 for **8**.

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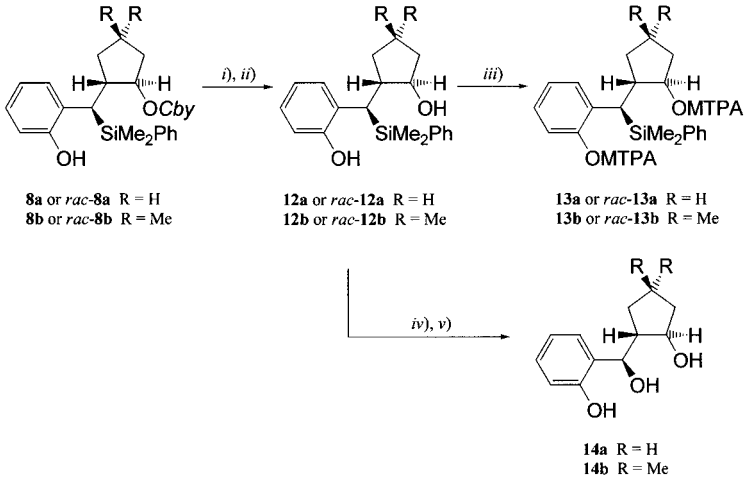
11) Experimental evidence has already been discussed for this phenomenon using a similar carbamate [14].

12) The cyclization of the branched carbamate (*Z*)-**2b** was analogously run in the presence of (1*R*,2*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine (**10**), which is assumed to be sterically less demanding than (–)-sparteine (**1**) [22]. Indeed, the carbocycle **8b** (dr > 99 : 1) was formed in 55% yield next to 24% of the starting material (*Z*)-**2b**, but the enantiomer ratio (er) dropped to 69 : 31, since **10** does not mediate the enantiotopos-differentiating deprotonation of carbamates efficiently.

13) The diols **12a** and **12b** were easily transformed into the corresponding triols **14a** and **14b**, respectively, under complete retention of the configuration in the benzylic position by applying the *Tamao* protocol [14] [24].

Scheme 5



i) $MeSO_3H$, MeOH, reflux. *ii*) $Ba(OH)_2$, MeOH, reflux, **12a**: 91%, *rac*-**12a**: 91%, **12b**: 90%, *rac*-**12b**: 90%. *iii*) (*S*)-MTPA, DCC, DMAP, CH_2Cl_2, r.t., **13a**, *rac*-**13a**, **13b**, and *rac*-**13b**: 100%. *iv*) $HBF_4 \cdot OEt_2$, CH_2Cl_2. *v*) KF, $KHCO_3$, H_2O_2, THF/MeOH, 0°, then r.t., **14a**: 58%, **14b**: 58%. MTPA = α-methoxy-α-(trifluoromethyl)phenylacetic acid; DMAP = 4-(dimethylamino)pyridine; DCC = *N*,*N*′-dicyclohexylcarbodiimide.

The relative and absolute configuration was unambigously verified on the basis of a crystal-structure analysis of the diol **12a** as (1*R*,2*R*,1′*R*) (*Fig.*). The absolute configurations at C(1) and C(2) are in accordance with those previously reported for the stereoselective cyclocarbolithiation [14] [17]. However, in contrast to the silylation of **3**·**1** by an *external* agent which results in the (1′*S*)-configuration at C(21) (*Scheme 2*), the stereospecific *retro*-[1,4]-*Brook* rearrangement provides the epimer in the benzylic position.

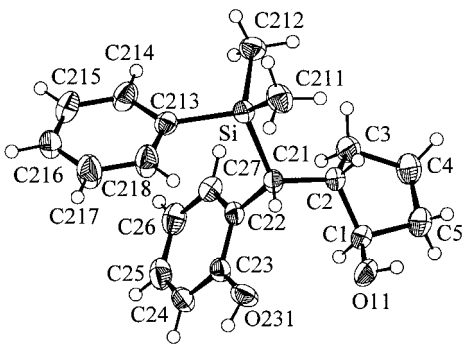


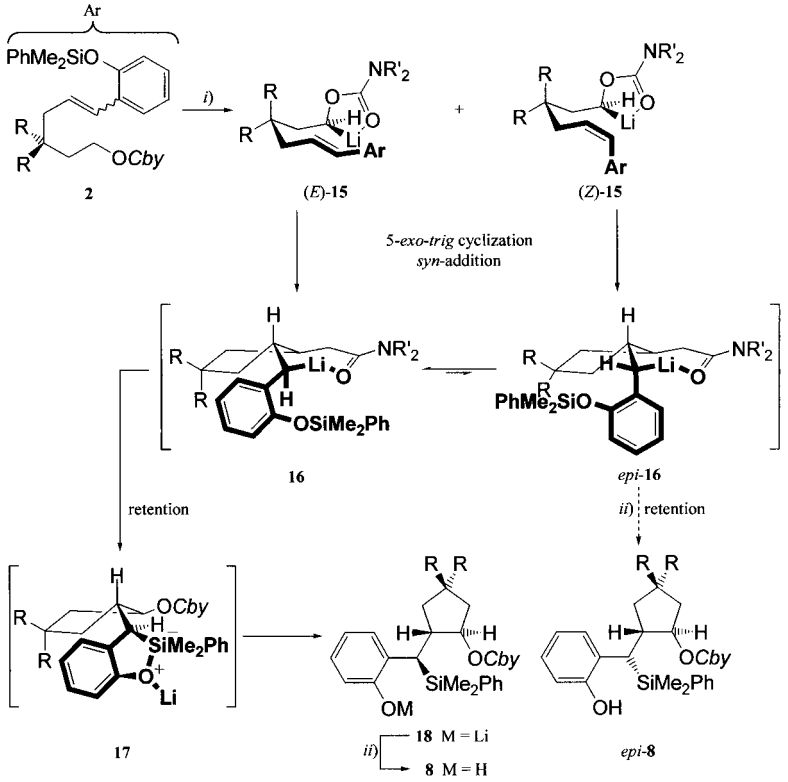
Figure. *Crystal structure of* **12a**

A mechanistic view on the domino-type cyclocarbolithiation/*retro*-[1,4]-*Brook* rearrangement reaction sequence is depicted in *Scheme 6*. The formation of the benzylic Li-carbanion pairs **16** and *epi*-**16** was discussed in detail in an earlier report [14]: the chiral base *s*-BuLi/**1** abstracts the *pro*-*S*-proton in **2** to give the lithiated carbamates (*E*)-**15** and (*Z*)-**15**, which undergo the 5-*exo*-*trig* ring closure under

retention of the configuration at the Li-bearing C-atom in a *syn*-fashion; the resulting epimeric species **16** and *epi*-**16** are presumably generated in a ratio dependent on the C=C bond geometry of **15** and epimerize, since these are configuratively labile under the reaction conditions.

Having determined the absolute configuration of **8** (*Fig.*) and *epi*-**8** [14] from X-ray crystal-structure analysis, there are two possible pathways responsible for the (1′*R*)-configuration at C(21): *a*) retention of the configuration starting from **16**, or *b*) inversion of the configuration starting from *epi*-**16**. In the latter case, the aryl substituent must move 'under' the cyclopentane backbone to allow an electrophilic attack of the silyl moiety, which is sterically disfavored. In the former case, the intermediate **16** can easily form the complex **17** with a pentacoordinated Si-center, which is reported by *Rücker* to be an intermediate of *retro*-[1,4]-*Brook* rearrangements [26][14]). The complex **17** furnishes the lithium phenoxide **18**, which is then converted to **8** by hydrolysis; **8** is isolated as a single diastereoisomer (*Scheme 6*).

Scheme 6



i) *s*-BuLi/**1**, Et_2O, $-78°$, then $-40°$, several hours. *ii*) MeOH, $-78°$, then r.t. Ligands (*e.g.*, **1**) at the Li-center are omitted for the sake of clarity.

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[14]) We assume that the stereochemically retentive mechanism is the result of the discrete steric characteristics in **16** and *epi*-**16**. Thus, the retention of the configuration in the benzylic position is only seemingly in contrast to *Kuwajima*'s observations [8].

Conclusion. – In summary, we have reported a novel modification of our stereoselective cyclocarbolithiation methodology [14][16][17] by combining this process with a highly stereospecific *retro*-[1,4]-*Brook* rearrangement. This *internal* silyl transfer proceeds with retention of the configuration at the benzylic position and provides – compared to an *external* silyl transfer [14] – a product with an epimeric stereogenic center. Additionally, the *retro*-[1,4]-*Brook* rearrangement prevents almost completely the undesired 1,3-cycloelimination. Further expansion of the stereoselective intramolecular carbolithiation of multiple bonds is currently being actively studied in our laboratories.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for generous financial support. Thanks are due to Dr. *M. Oestreich* for elaborating and writing the manuscript. *S. H. K.* would like to thank the *Fonds der Chemischen Industrie* for a fellowship, and *C. Weitkamp* for skillful technical assistance. *E. W.* would like to thank the *Academy of Finland* for financial support.

Experimental Part

General. M.p.: *Gallenkamp MFB 595* melting-point apparatus; uncorrected. Optical rotations: *Perkin-Elmer 241* polarimeter. IR and FT-IR Spectra: *Perkin-Elmer* IR spectrometer *PE 298* and a *Nicolet 5DXC* spectrometer, respectively. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM 300* or *Varian Unity Plus 600* instrument; internal reference TMS (0.00 ppm) or $CDCl_3$ (77.0 ppm). The doubling of some signals occurs as a result of the (*E*/*Z*)-isomerism of the carbamate group; these signals are given in square brackets. HR-MS: *Varian Saturn II* spectrometer. Elemental analyses were performed by the Mikroanalytische Abteilung des Organisch-chemischen Institutes der Westfälischen Wilhelms-Universität Münster on a *Perkin-Elmer CHN* analyzer *240*. All reactions were carried out in dried glassware under a static pressure of Ar; the liquids were transferred with syringes or double-ended needles. All solvents for the reactions were dried and distilled prior to use following standard procedures. The solvents for extraction and chromatography were freshly distilled before use. All products were purified by flash column chromatography (FC) on silica gel (*Merck*, 60–200 mesh). TLC: *Polygram SIL G/UV$_{254}$* foils (*Macherey, Nagel & Co.*). Starting materials and reagents were purchased from commercial sources and used without further purification unless otherwise noted. *(−)-Sparteine* (**1**) is commercially available (*Aldrich* or *Sigma*) and was dried over CaH_2, distilled, and stored under Ar; *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was distilled from CaH_2 and kept under Ar. BuLi was received as a 1.6M soln. in hexane from *Acros* and *s*-BuLi was received as a 1.4M soln. in cyclohexane/hexane 92:8 from *Fluka* and was titrated before use [27].

*(*E*)-6-(2-Hydroxyphenyl)hex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* ((*E*)-**7a**). At r.t., *5-(2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyloxy)pentyltriphenylphosphonium bromide* (**5a**) [14] (1.17 g, 2.00 mmol, 1.0 equiv.) was suspended in THF (6 ml) and treated with NaHMDS (2.00 ml, 2.00 mmol, 1.0 equiv., 1M in THF). The mixture was stirred for 15 min at this temp. and then cooled to −40°. The *lithium 2-formylphenoxide* (**6a**) was prepared separately by adding BuLi (1.25 ml, 2.00 mmol, 1.0 equiv., 1.6M) to salicylaldehyde (0.24 g, 2.00 mmol) at −40°. This soln. was then transferred to the suspension *via* syringe and stirred at −40° for 30 min. The mixture was stirred for further 4 h at ambient temp. before hydrolysis with 2N HCl (5 ml). The org. layer was separated, the aq. phase was extracted with Et_2O (3 × 5 ml), and the combined org. phases were dried ($MgSO_4$). The solvents were removed under reduced pressure, and the residue was purified by FC (Et_2O/hexanes 1:4; R_f 0.49 in Et_2O/hexanes 2:1), yielding (*E*)-**7a** (0.42 g, 60%, (*E*/*Z*)-ratio 90:10). Colorless solid. M.p. 77°. IR (neat): 3350*s* (OH); 1700*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.37 [1.43] (*s*, 6 H); 1.53 [1.56] (*s*, 6 H); 1.56 (*m*, 2 H); 1.72 (*m*, 2 H); 2.29 (*dtd*, *J* = 7.0, 7.0, 1.2, 2 H); 3.72 (*s*, 2 H); 4.13 (*t*, *J* = 6.7, 2 H); 5.32 (*s*, 1 H); 6.16 (*dt*, *J* = 16.0, 7.0, 1 H); 6.62 (*d*, *J* = 16.0, 1 H); 6.79–7.31 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.2 [25.3]; 25.3 [26.5]; 25.8; 28.3; 32.8; 59.7 [60.6]; 64.5; 76.1 [76.3]; 94.6 [95.9]; 115.9; 120.6; 124.9; 127.2; 128.0; 132.0; 135.8; 152.8. Anal. calc. for $C_{20}H_{29}NO_4$ (347.45): C 69.14, H 8.41, N 4.03; found: C 69.12, H 8.46, N 4.14.

*(*E/Z*)-6-(2-Hydroxyphenyl)hex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* ((*E*/*Z*)-**7a**). To a suspension of **5a** [14] (3.60 g, 6.16 mmol, 1.12 equiv.) in THF (10 ml) NaHMDS (8.01 ml, 8.01 mmol, 1.46 equiv., 1M in THF) was added at r.t. The mixture was stirred for 30 min at ambient temp. and was then cooled to −40° before a further charge of NaHMDS (6.16 ml, 6.16 mmol, 1.12 equiv., 1M in THF) was added. Subsequently, the

mixture was treated with salicyl aldehyde (M = Na; **6b**; 0.67 g, 5.49 mmol) in THF (1 ml) and stirred for further 60 min at $-40°$. The mixture was allowed to warm to r.t. overnight and then hydrolyzed with H_2O (8 ml) and 2N HCl (8 ml). The org. layer was separated, the aq. phase was extracted with Et_2O (3 × 20 ml), and the combined org. phases were dried ($MgSO_4$). The solvent was removed *in vacuo*, and the residue was purified by FC (Et_2O/hexanes 1:4, R_f 0.49 in Et_2O/hexanes 2:1) affording (*E*/*Z*)-**7a** (4.47 g, 82%; (*E*/*Z*)-ratio 50:50). Colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$)[15]: 1.37 [1.43] (*s*, 6 H); 1.53 [1.56] (*s*, 6 H); 1.56 (*m*, 2 H); 1.72 (*m*, 2 H); 2.29 {2.16} (*dtd*, *J* = 7.0, 7.0, 1.2 {*J* = 7.4, 7.4, 1.4}, 2 H); 3.72 (*s*, 2 H); 4.13 {4.04} (*t*, *J* = 6.7 {*J* = 6.6}, 2 H); 5.32 {5.14} (*s*, 1 H); 6.16 {5.89} (*dt*, *J* = 16.0, 7.0 {*J* = 11.3, 7.4}, 1 H); 6.62 {6.40} (*d*, *J* = 16.0 {*J* = 11.3}, 1 H); 6.79–7.31 {6.80–7.35} (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$)[15]: 24.2 [25.3]; 25.3 [26.5] {26.6}; 25.8 {26.0}, 28.3 {28.6}; 32.8; 59.7 [60.6]; 64.5 {64.3}; 76.1 [76.3]; 94.6 [95.9]; 115.9 {115.3}; 120.6 {120.2}; 124.9 {123.7}; 127.2 {128.1}; 128.0 {128.6}; 132.0 {129.6}; 135.8 {136.0}; 152.8 {152.9}.

(Z)-6-(2-Hydroxyphenyl)-3,3-dimethylhex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*Z*)-**7b**). As described for (*E*/*Z*)-**7a**, *3,3-dimethyl-5-(2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyloxy)pentyltriphenylphosphonium bromide* (**5b**) [14] (1.74 g, 2.85 mmol, 1.10 equiv.) was reacted with NaHMDS (3.70 ml, 3.70 mmol, 1.43 equiv., 1M in THF) in THF (6 ml) at r.t. After 20 min, the suspension was cooled to $-40°$ and treated again with NaHMDS (2.85 ml, 2.85 mmol, 1.10 equiv, 1M in THF). Subsequently, salicylaldehyde (M = Na; **6b**; 0.32 g, 2.59 mmol), dissolved in THF (1 ml), was added. As described above, the mixture was quenched with H_2O (5 ml) and 2N HCl (5 ml), and the aq. phase was extracted with Et_2O (3 × 10 ml). The crude product was purified by FC (hexanes/AcOEt 4:1, R_f 0.55 in Et_2O/hexanes 2:1) providing (*Z*)-**7b** (0.60 g, 62%; (*E*/*Z*)-ratio 30:70). Colorless oil. IR (neat): 3350*s* (OH); 1710*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$)[15]: 0.77 {0.84} (*s*, 6 H); 1.18 [1.27] (*s*, 6 H); 1.34 [1.41] (*s*, 6 H); 1.53 (*m*, 2 H); 2.01 {1.92} (*dd*, *J* = 7.6, 1.7 {*J* = 7.6, 1.2}, 2 H); 3.56 (*s*, 2 H); 3.86 {4.07} (*t*, *J* = 8.1 {*J* = 8.1}, 2 H); 5.82 {6.02} (*dt*, *J* = 7.6, 11.3 {*J* = 7.6, 15.7}, 1 H); 5.39 {6.18} (*s*, 1 H); 6.35 {6.54} (*d*, *J* = 11.3 {*J* = 15.7}, 1 H); 6.67–7.19 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$)[15]): 24.2 [25.3]; 25.3 [26.5]; 27.3 {27.7}; 32.7 {33.1}; 39.9 {40.4}; 45.4; 59.7 [60.6]; 61.7; 76.1 [76.4]; 94.6 [95.9]; 115.6 {116.5}; 120.1 {120.5}; 124.1; 125.5; 128.6 {128.1}; 129.8; 132.4 {132.4}; 153.0. Anal. calc. for $C_{22}H_{33}NO_4$ (375.51): C 70.37, H 8.86, N 3.73; found: C 70.36, H 9.07, N 3.81.

(E)-6-[2-(Dimethylphenylsilyloxy)phenyl]hex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*E*)-**2a**). At r.t., a soln. of (*E*)-**7a** (350 mg, 1.01 mmol) and 1*H*-imidazole (137 mg, 2.01 mmol, 2.0 equiv.) in DMF (2 ml) was treated with $PhMe_2SiCl$ (258 mg, 1.51 mmol, 1.5 equiv.). The mixture was stirred for 3 h at ambient temp. before sat. aq. NH_4Cl (3 ml) was added. The org. phase was separated, the aq. phase was extracted with Et_2O (3 × 3 ml), and the combined org. phases were neutralized with sat. aq. $NaHCO_3$ (3 ml). After drying ($MgSO_4$), the volatiles were removed under reduced pressure. The crude product was purified by FC (Et_2O/hexanes 1:4, R_f 0.69 in Et_2O/hexanes 2:1) providing (*E*)-**2a** (456 mg, 94%; (*E*/*Z*)-ratio 90:10). Colorless oil. IR (neat): 1710*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.50 (*s*, 6 H); 1.36 [1.42] (*s*, 6 H); 1.52 [1.56] (*s*, 6 H); 1.55 (*m*, 2 H); 1.69 (*m*, 2 H); 2.26 (*dtd*, *J* = *J* = *J* = 6.9, 2 H); 3.72 (*s*, 2 H); 4.11 (*t*, *J* = 6.6, 2 H); 6.15 (*dt*, *J* = 6.9, 16.0, 1 H); 6.65 (*d*, *J* = 16.0, 1 H); 6.69–7.63 (*m*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −1.0; 24.2 [25.3]; 25.3 [26.6]; 26.0; 28.5; 33.0; 59.6 [60.5]; 64.4; 76.1 [76.4]; 94.5 [95.8]; 119.8; 121.7; 125.5; 126.4; 127.6; 127.9; 129.1; 129.9; 130.5; 133.4; 137.3; 152.1. Anal. calc. for $C_{28}H_{39}NO_4Si$ (481.71): C 69.82, H 8.16, N 2.91; found: C 69.96, H 8.52, N 2.78.

(E/Z)-6-[2-(Dimethylphenylsilyloxy)phenyl]hex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*E*/*Z*)-**2a**). As described for (*E*)-**2a**, (*E*/*Z*)-**7a** was silylated providing (*E*/*Z*)-**2a** (456 mg, 94%; (*E*/*Z*)-ratio 50:50). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$)[15]): 0.50 {0.47} (*s*, 6 H); 1.36 [1.42] (*s*, 6 H); 1.52 [1.56] (*s*, 6 H); 1.55 (*m*, 2 H); 1.69 (*m*, 2 H); 2.26 (*dtd*, *J* = *J* = 6.9 {*J* = *J* = 7.1}, 2 H); 3.72 (*s*, 2 H); 4.11 {4.07} (*t*, *J* = 6.6 {*J* = 6.4}, 2 H); 6.15 {5.64} (*dt*, *J* = 16.0, *J* = 6.9 {*J* = 11.5, *J* = 7.1}, 1 H); 6.65 {6.51} (*d*, *J* = 16.0 {*J* = 11.5}, 1 H); 6.69–7.63 (*m*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$)[15]): −1.0; 24.2 [25.3]; 25.3 [26.6]; 26.0; 28.5 {28.6}; 33.0; 59.6 [60.5]; 64.5 {64.5}; 76.1 [76.4]; 94.5 [95.8]; 119.8 {119.7}; 121.7 {121.1}; 125.5 {125.6}; 126.4 {126.5}; 127.6; 127.9; 129.1 {129.5}; 129.9 {130.0}; 130.5 {132.0}; 133.4 {133.0}; 137.3; 152.1 {152.9}.

(Z)-6-[2-(Dimethylphenylsilyloxy)phenyl)-3,3-dimethylhex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*Z*)-**2b**). To a mixture of (*Z*)-**7b** (551 mg, 1.47 mmol) and 1*H*-imidazole (200 mg, 2.94 mmol, 2.0 equiv.), dissolved in DMF (3 ml), $PhMe_2SiCl$ (376 mg, 2.20 mmol, 1.5 equiv.) was added at ambient temp. The mixture was stirred for 16 h at this temp. before quenching with sat. aq. NH_4Cl (3 ml). The org. phase was separated, the aq. phase was extracted with Et_2O (3 × 3 ml), and the combined org. phases were neutralized with sat. aqueous $NaHCO_3$ (3 ml). After drying ($MgSO_4$), the solvents were removed *in vacuo*. The crude

[15]) The signals of the minor diastereoisomer are given in braces { }.

product was purified by FC (Et_2O/hexanes 1:6, R_f 0.67 in hexanes/AcOEt 4:1), giving (*Z*)-**2b** (695 mg, 93%; (*E*/*Z*)-ratio 30:70). Colorless oil. IR (neat): 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$)[15]): 0.47 {0.50} (*s*, 6 H); 0.95 {0.97} (*s*, 6 H); 1.34 [1.41] (*s*, 6 H); 1.50 [1.55] (*s*, 6 H); 1.63 (*m*, 2 H); 2.20 {2.13} (*dd*, *J* = 7.4, 1.8 {*J* = 7.4, 1.1}, 2 H); 3.71 (*s*, 2 H); 4.10 {4.18} (*t*, *J* = 7.9 {*J* = 7.9}, 2 H); 5.75 {6.20} (*dt*, *J* = 11.7, 7.4 {*J* = 16.0, 7.4}, 1 H); 6.58 {6.59} (*d*, *J* = 11.7 {*J* = 16.0}, 1 H); 6.69–7.63 (*m*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$)[15]): −1.0; 24.1 [25.3]; 25.3 [26.5]; 27.0 {27.1}; 32.7 {33.1}, 40.7 {40.1}; 46.4; 59.6 [60.5]; 61.8; 76.0 [76.3]; 94.5 [95.8]; 119.5 {119.7}; 121.0 {121.6}; 126.5; 126.9 {127.2}; 127.7 {127.8}; 128.4; 129.1; 129.8 {129.9}; 130.2; 133.4; 137.4; 152.9 {152.1}. Anal. calc. for $C_{30}H_{43}NO_4Si$ (509.76): C 70.68, H 8.50, N 2.75; found: C 70.62, H 8.84, N 3.05.

*Typical Procedure for the Cyclocarbolithiation/*retro-*[1,4]*-Brook *Rearrangement* (*TP 1*). *(−)-(1*R,2R*)-2-[(*R*)-(Dimethylphenylsilyl)(2-hydroxyphenyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**8a**). At −78°, freshly distilled (−)-sparteine (**1**) (141 mg, 0.60 mmol, 1.45 equiv.) was dissolved in Et_2O (5 ml) and treated with *s*-BuLi (0.47 ml, 0.58 mmol, 1.4 equiv., 1.25M). After 10 min, (*E*/*Z*)-**2a** (200 mg, 0.42 mmol), dissolved in Et_2O (1 ml), was added dropwise under vigorous stirring. The mixture was kept at −78° for 4 h, and at −40° for 16 h before the reaction was terminated by the addition of MeOH (1 ml) and 2N HCl (2 ml). The org. phase was separated, the aq. phase was extracted with Et_2O (3 × 3 ml), and the combined org. phases were dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the purification by FC (hexanes/AcOEt 5:1, R_f 0.62 (**8a**) and R_f 0.64 (**9a**) in Et_2O/hexanes 2:1) provided **8a** (116 mg, 58%, dr > 99:1, er > 98:2) as a colorless oil; the bicyclic product **9a** (7 mg, 9%; dr > 99:1) was isolated as a colorless solid.

Data of **9a** $[\alpha]_D^{rt} = -24.0$ (*c* = 1.00, CH_2Cl_2). IR (neat): 3350*s* (OH); 1700*s* (C=O). ^{1}H-NMR (600 MHz, $CDCl_3$, −50°): 0.09 (*s*, 3 H); 0.50 (*s*, 3 H); 1.04–1.64 (*m*, 2 H); 1.24 (*m*, 1 H); 1.41 (*m*, 1 H); 1.43 [1.49] (*s*, 6 H); 1.51 (*m*, 1 H); 1.57 [1.64] (*s*, 6 H); 1.85 (*m*, 1 H); 2.15 (*m*, 1 H); 3.14 (*d*, *J* = 16.1, 1 H); 3.73 [3.75] (*s*, 2 H); 4.69 (*m*, 1 H); 6.88–7.65 (*m*, 9 H); 8.84 (*m*, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$, −50°): −3.1; −2.8; 23.8; 23.9 [24.8]; 24.8 [26.1]; 27.9; 30.1; 31.5; 48.7; 59.6 [60.6]; 75.4 [75.5]; 80.2; 94.6 [95.6]; 117.3; 119.4; 125.7; 126.5; 127.8; 129.0; 129.6; 131.4; 133.0; 133.6; 138.1; 152.6 [153.3]; 155.5. Anal. calc. for $C_{28}H_{39}NO_4Si$ (481.71): C 69.82, H 8.16, N 2.91; found: C 69.53, H 8.15, N 2.82.

The same procedure (*TP 1*) was applied to (*E*)-**2a** (150 mg, 0.31 mmol) with **1** (106 mg, 0.45 mmol, 1.45 equiv.) and *s*-BuLi (0.35 ml, 0.44 mmol, 1.4 equiv., 1.25M), furnishing **8a** (90 mg, 60%, dr > 99:1, er > 98:2) and **9a** (5 mg, 10%, dr > 99:1).

Compound *rac*-**8a** was also prepared from (*E*/*Z*)-**2a** (150 mg, 0.31 mmol), dissolved in Et_2O (1 ml), according to *TP 1*. The reaction was performed in Et_2O (3 ml) in the presence of TMEDA (**11**; 52 mg, 0.45 mmol, 1.45 equiv.) and *s*-BuLi (0.45 ml, 0.44 mmol, 1.4 equiv., 0.97M). The purification by FC (Et_2O/hexanes 1:6) gave *rac*-**8a** (12 mg, 8%; dr > 99:1).

Data of exo-*6-(2-Hydroxyphenyl)bicyclo[3.1.0]hexane* (**9a**). M.p. 64°. IR (neat): 3350*s* (OH). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.28 (*m*, 1 H); 1.56 (*m*, 2 H); 1.59 (*m*, 1 H); 1.71 (*m*, 1 H); 1.84 (*m*, 2 H); 1.97 (*m*, 2 H); 5.29 (*m*, 1 H); 6.83–7.09 (*m*, 4 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 16.8; 21.3; 25.7; 27.6; 114.5; 120.3; 127.2; 127.3; 128.4; 154.8. HR-EI-MS calc. for $C_{12}H_{14}O$ (174.24): 174.1045; found: 174.1045.

*(−)-(1*R,2R*)-2-[(*R*)-(Dimethylphenylsilyl)(2-hydroxyphenyl)methyl]-4,4-dimethylcyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**8b**). According to *TP 1*, freshly distilled **1** (100 mg, 0.43 mmol, 1.45 equiv.) and *s*-BuLi (0.33 ml, 0.41 mmol, 1.4 equiv., 1.23M) were dissolved in Et_2O (3 ml). The chiral base was then reacted with a soln. of (*Z*)-**2b** (150 mg, 0.29 mmol) in Et_2O (1 ml). The crude product was purified by FC (hexanes/AcOEt 6:1, R_f = 0.56 (**8b**) in hexanes/AcOEt 4:1), yielding **8b** (70 mg, 47%, dr > 99:1, er > 98:2) as a colorless oil next to the desilylated cyclization precursor (44 mg, 40%). $[\alpha]_D^{rt} = -22.0$ (*c* = 1.00, CH_2Cl_2). IR (neat): 3350*s* (OH); 1710*s* (C=O). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.41 (*s*, 3 H); 0.43 (*s*, 3 H); 0.82 [0.83] (*s*, 3 H); 1.00 [1.02] (*s*, 3 H); 1.25–1.62 (*m*, 16 H); 2.54 (*m*, 1 H); 3.14 (*m*, 1 H); 3.68 [3.71] (*s*, 2 H); 4.78 (*m*, 1 H); 6.82–7.60 (*m*, 9 H); 8.32 (*m*, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): −2.9; 24.0 [24.2]; 25.0 [25.4]; 26.1 [26.6]; 28.5; 28.7; 29.5; 36.9; 43.5; 45.7; 47.6; 59.7 [60.7]; 75.9 [76.2]; 80.9; 95.1 [96.1]; 117.9; 119.5; 125.7; 126.8; 127.9; 129.0; 129.6; 132.2; 133.0; 133.8; 138.5; 156.0. Anal. calc. for $C_{30}H_{43}NO_4Si$ (509.76): C 70.68, H 8.50, N 2.75; found: C 70.71, H 8.81, N 2.94.

Compound *rac*-**8b** was prepared from (*Z*)-**2b** (150 mg, 0.29 mmol), dissolved in Et_2O (1 ml), according to *TP 1*. The reaction was performed in Et_2O (3 ml) in the presence of TMEDA (**11**; 50 mg, 0.43 mmol, 1.45 equiv.) and *s*-BuLi (0.33 ml, 0.41 mmol, 1.4 equiv., 0.23M). The crude product was purified by FC (hexanes/AcOEt 6:1, R_f 0.56 (*rac*-**8b**) in hexanes/AcOEt 4:1 and R_f 0.65 (**9b**) in Et_2O/hexanes 2:1), giving *rac*-**8b** (75 mg, 50%; dr > 99:1) as a colorless solid, m.p. 156°, and **9b** (9 mg, 15%; dr > 99:1) as colorless oil.

Data of exo-*6-(2-Hydroxyphenyl)-3,3-dimethylbicyclo[3.1.0]hexane* (**9b**). IR (neat): 3350*s* (OH). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.04 (*s*, 3 H); 1.09 (*s*, 3 H); 1.50 (*m*, 2 H); 1.58 (*m*, 1 H); 1.67 (*m*, 2 H); 1.90 (*m*, 2 H); 5.27 (*m*,

1 H); 6.83–7.09 (*m*, 4 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 28.2; 29.7; 30.7; 31.3; 31.9; 44.8; 114.6; 120.3; 127.3; 127.4; 128.1; 154.6. HR-EI-MS: calc. for $C_{14}H_{18}O$ (202.30): 202.1358; found: 202.1355.

Typical Procedure for the Decarbamoylation (*TP 2*) *[23]. (+)-(1*R,*2*R*)-2-[(*R*)-(Dimethylphenylsilyl)(2-hydroxyphenyl)methyl]cyclopentanol* (**12a**). Compound **8a** (60 mg, 0.13 mmol), dissolved in MeOH (3 ml), was reacted with MsOH (8 µl, 0.13 mmol, 1.0 equiv.) and heated at reflux for 135 min. Subsequently, $Ba(OH)_2 \cdot 8H_2O$ (118 mg, 0.37 mmol, 3.0 equiv.) was added, and the mixture was stirred at reflux for another 45 min. After cooling to r.t., the mixture was dissolved in Et_2O (3 ml) and the reaction was quenched with H_2O (1.5 ml) and 2N HCl (1.5 ml). The org. phase was separated, the aq. phase was extracted with Et_2O (3 × 3 ml), and the combined org. phases were dried ($MgSO_4$). After concentration under reduced pressure, the crude product was purified by FC (Et_2O/hexanes 1:4, R_f 0.53 in Et_2O/hexanes 2:1), providing **12a** (37 mg, 91%). Colorless solid. M.p. 119°. $[\alpha]_D^{rt} = +13.3$ ($c = 1.00$, CH_2Cl_2). IR (neat): 3650–3060*s* (OH). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.21 (*s*, 3 H); 0.43 (*s*, 3 H); 0.82–1.79 (*m*, 7 H); 2.15 (*m*, 1 H); 2.88 (*m*, 1 H); 3.48 (*m*, 1 H); 5.69 (*m*, 1 H); 6.77–7.06 (*m*, 4 H); 7.25–7.55 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −3.1; −2.0; 20.4; 27.5; 32.5; 48.7; 76.5; 116.0; 120.5; 126.3; 127.8; 129.0; 132.7; 133.0; 138.8; 154.3. Anal. calc. for $C_{20}H_{26}O_2Si$ (326.51): C 73.57, H 8.03; found: C 73.48, H 8.26.

X-Ray Crystal-Structure Analysis of **12a**. Formula $C_{20}H_{26}O_2Si$, M_r 326.50, colorless crystal, 0.30 × 0.20 × 0.10 mm, $a = 9.318(1)$, $b = 11.830(1)$, $c = 16.361(2)$ Å, $V = 1803.5(3)$ Å^3, $\varrho_{calc} = 1.202$ g cm^{-3}, $\mu = 11.96$ cm^{-1}; empirical absorption correction *via* ψ scan data ($0.716 \leq T \leq 0.890$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 2104 reflections collected ($-h$, $-k$, $-l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 2104 independent and 1941 observed reflections [$I \geq 2\,\sigma(I)$], 213 refined parameters, $R = 0.041$, $wR^2 = 0.120$, max. residual electron density 0.31 (−0.27) e Å^{-3}, *Flack* parameter 0.02(5), H-atoms calculated and riding.

Data set was collected with an *Enraf Nonius CAD4* diffractometer. Programs used: data collection EXPRESS, data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-97, graphics (with unsystematic numbering schemes) DIAMOND. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-133091. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Compound *rac*-**12a** was prepared from *rac*-**8a** (50 mg, 0.10 mmol) by decarbamoylation in the presence of MsOH (7 µl, 0.10 mmol, 1.0 equiv.) and $Ba(OH)_2 \cdot 8H_2O$ (98 mg, 0.31 mmol, 3.0 equiv.) in MeOH (3 ml) following *TP 2*; *rac*-**12a** (31 mg, 91%) was isolated as a colorless oil.

*(+)-(1*R,*2*R*)-2-[(*R*)-(Dimethylphenylsilyl)(2-hydroxyphenyl)methyl]-4,4-dimethylcyclopentanol* (**12b**). According to *TP 2*, **8b** (123 mg, 0.24 mmol) was decarbamoylated with MsOH (16 µl, 0.24 mmol, 1.0 equiv.) and $Ba(OH)_2 \cdot 8H_2O$ (228 mg, 0.72 mmol, 3.0 equiv.) in MeOH (3 ml). The purification of the crude product was accomplished by FC (Et_2O/hexanes 1:4, R_f 0.59 in Et_2O/hexanes 2:1) furnishing **12b** (77 mg, 90%). Colorless oil. $[\alpha]_D^{rt} = +17.0$ ($c = 1.00$, CH_2Cl_2). IR (neat): 3600–3150*s* (OH). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.20 (*s*, 3 H); 0.44 (*s*, 3 H); 0.81 (*s*, 3 H); 1.00 (*s*, 3 H); 1.07–1.28 (*m*, 2 H); 1.56 (*ddd*, $J = 12.7$, 7.4, 1 H); 1.66 (*ddd*, $J = 12.7$, 7.6, 1 H); 2.28 (*m*, 1 H); 2.91 (*m*, 1 H); 3.46 (*m*, 2 H); 6.79–7.53 (*m*, 10 H). ^{13}C-NMR (150 MHz, $CDCl_3$): −2.9; −2.1; 29.7; 31.5; 31.8; 34.2; 42.6; 47.3; 47.9; 75.5; 108.4; 116.0; 120.4; 126.4; 127.8; 129.1; 130.9; 133.9; 138.7; 154.4. Anal. calc. for $C_{22}H_{30}O_2Si$ (354.56): C 74.53, H 8.53; found: C 74.53, H 8.51.

Compound *rac*-**12b** was prepared from *rac*-**8b** (60 mg, 0.12 mmol) by decarbamoylation in the presence of MsOH (8 µl, 0.12 mmol, 1.0 equiv.) and $Ba(OH)_2 \cdot 8H_2O$ (111 mg, 0.35 mmol, 3.0 equiv.) in MeOH (3 ml) following *TP 2*; *rac*-**12b** (38 mg, 90%) was isolated as a colorless oil.

Typical Procedure for the Tamao *Oxidation* (*TP 3*) [24]. *(+)-(1*R,*2*R*)]-2-[(*R*)-Hydroxy(2-hydroxyphenyl)methyl]cyclopentanol* (**14a**). At 0°, to a soln. of **12a** (70 mg, 0.21 mmol) in CH_2Cl_2 (2 ml) HBF_4 (71 µl, 0.51 mmol, 2.4 equiv., 54% in Et_2O) were added. The mixture was subsequently stirred for 10 min at 0° and then stirred for further 30 min at r.t. The volatiles were removed *in vacuo*, the residue was dissolved in THF (1 ml) and MeOH (1 ml), and the resulting soln. was treated with KF (78 mg, 0.43 mmol, 2.0 equiv., 5.5 mmol · g^{-1} KF on Al_2O_3) and $KHCO_3$ (202 mg, 2.02 mmol, 10 equiv.) at 0°. The mixture was kept at this temp. for 15 min before H_2O_2 (0.28 ml, 30% in H_2O) was added. It was stirred for another 15 min at 0°, and for 4.5 h at r.t. After the addition of solid Na_2SO_3, the mixture was concentrated under reduced pressure. The residue was purified by FC (Et_2O/hexanes 2:1, R_f 0.19), giving **14a** (26 mg, 58%). Colorless oil. $[\alpha]_D^{rt} = +2.5$ ($c = 1.00$, CH_2Cl_2). IR (neat): 3600–3080*s* (OH). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.24 (*m*, 1 H); 1.39 (*m*, 1 H); 1.55–1.69 (*m*, 2 H); 2.08 (*m*, 2 H); 2.29 (*m*, 1 H); 2.68 (*m*, 1 H); 4.14 (*ddd*, $J = J = J = 8.0$, 1 H); 4.33 (*m*, 1 H); 4.72 (*d*, $J = 9.9$, 1 H); 6.80–7.17 (*m*, 4 H); 8.16 (*m*, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 20.1; 26.4; 33.9; 51.3; 79.5; 81.6; 117.2; 119.5; 126.1; 127.7; 129.1; 155.5. HR-EI-MS: calc. for $C_{12}H_{16}O_3$ (208.26): 208.1099; found: 208.1086.

*(−)-(1*R*,2*R*)-2-[(*R*)-Hydroxy(2-hydroxyphenyl)methyl]-4,4-dimethylcyclopentanol* (**14b**). According to *TP 3*, **12b** (60 mg, 0.17 mmol), dissolved in CH_2Cl_2 (2 ml), was subsequently treated with HBF_4 (56 µl, 0.41 mmol, 2.4 equiv., 54% in Et_2O), KF (62 mg, 0.34 mmol, 2.0 equiv, 5.5 mmol · g^{-1} KF on Al_2O_3), $KHCO_3$ (160 mg, 1.59 mmol, 10 equiv.), and H_2O_2 (0.22 ml, 30% in H_2O). The crude product was purified by FC (Et_2O/hexanes 2 : 1, R_f 0.31) yielding **14b** (23 mg, 58%). Colorless oil. $[\alpha]_D^{r.t.} = -14.1$ ($c = 1.00$, CH_2Cl_2). IR (neat): 3650–3100*s* (OH). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.00 (*s*, 6 H); 1.14 (*m*, 2 H); 1.50 (*dd*, *J* = 12.8, 7.7, 1 H); 1.95 (*dd*, *J* = 12.8 , 9.1, 1 H); 2.48 (*m*, 1 H); 2.70 (*m*, 1 H); 4.21 (*m*, 1 H); 4.45 (*m*, 1 H); 4.73 (*d*, *J* = 10.2, 1 H); 6.80–7.17 (*m*, 4 H); 8.23 (*m*, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 31.5; 31.7; 34.7; 41.9; 49.2; 51.1; 78.8; 81.9; 117.2; 119.5; 126.0; 127.7; 129.0; 155.5. HR-EI-MS: calc. for $C_{14}H_{20}O_3$ (236.31): 236.1413; found: 236.1408.

REFERENCES

[1] A. G. Brook, J. D. Pascoe, *J. Am. Chem. Soc.* **1971**, *93*, 6224; A. G. Brook, *Acc. Chem. Res.* **1974**, *7*, 77; A. G. Brook, A. R. Bassendale in 'Rearrangements in Ground and Excited States', Ed. P. de Mayo, Academic Press, New York, 1980, Vol. 2, pp. 149–227.

[2] P. F. Hudrlik, A. M. Hudrlik, A. K. Kulkarni, *J. Am. Chem. Soc.* **1982**, *104*, 6809; K. Yamamoto, T. Kimura, Y. Tomo, *Tetrahedron Lett.* **1985**, *26*, 4505.

[3] R. P. Woodbury, M. W. Rathke, *J. Org. Chem.* **1978**, *43*, 1947; M. Isobe, M. Kitamura, T. Goto, *Tetrahedron Lett.* **1979**, *20*, 3465.

[4] E. W. Colvin, Silicon in Organic Synthesis, Butterworths, London, 1981, pp. 30–43.

[5] R. West, H. W. Lowe, H. F. Stewart, A. Wright, *J. Am. Chem. Soc.* **1971**, *93*, 282; A. Wright, R. West, *ibid.* **1974**, *96*, 3214; *ibid.* **1974**, *96*, 3227; W. C. Still, T. L. Macdonald, *ibid.* **1974**, *96*, 5561.

[6] G. A. Gornowioz, R. West, *J. Am. Chem. Soc.* **1968**, *90*, 4478; E. J. Corey, C. Rücker, *Tetrahedron Lett.* **1984**, *25*, 4345.

[7] G. Simchen, J. Pfletschinger, *Angew. Chem.* **1976**, *88*, 444; *ibid. Int. Ed.* **1976**, *15*, 428; R. Hoffmann, R. Brückner, *Chem. Ber.* **1992**, *125*, 1471; R. W. Hoffmann, M. Bewersdorf, *Tetrahedron Lett.* **1990**, *31*, 67.

[8] D. A. Evans, J. M. Takacs, K. M. Hurst, *J. Am. Chem. Soc.* **1979**, *101*, 371; T. Cohen, B.-S. Guo, *Tetrahedron* **1980**, *42*, 2803; T. Cohen, W. M. Daniewsky, R. B. Weinsenfeld, *Tetrahedron Lett.* **1978**, *19*, 4465; S. Marumoto, I. Kuwajima, *J. Am. Chem. Soc.* **1993**, *115*, 9021.

[9] R. Hoffmann, R. Brückner, *Chem. Ber.* **1992**, *125*, 2731.

[10] R. J. Linderman, A. Ghannam, *J. Am. Chem. Soc.* **1990**, *112*, 2392.

[11] G. Boche, A. Opel, M. Marsch, K. Harms, F. Haller, J. C. W. Lohrenz, C. Thümmler, W. Koch, *Chem. Ber.* **1992**, *125*, 2265.

[12] D. Hoppe, F. Hintze, P. Tebben, *Angew. Chem.* **1990**, *102*, 1457; *ibid. Int. Ed.* **1990**, *29*, 1422; D. Hoppe, T. Hense, *Angew. Chem.* **1997**, *109*, 2376; *ibid. Int. Ed.* **1997**, *36*, 2282; P. Beak, A. Basu, D. J. Gallagher, Y. S. Park, S. Thayumanavan, *Acc. Chem. Res.* **1996**, *29*, 552; D. Hoppe, F. Hintze, P. Tebben, M. Paetow, H. Ahrens, J. Schwerdtfeger, P. Sommerfeld, J. Haller, W. Guarnieri, S. Kolczewski, T. Hense, I. Hoppe, *Pure Appl. Chem.* **1994**, *66*, 1479.

[13] S. H. Kleinfeld, Dissertation, WWU Münster, **1999**.

[14] M. J. Woltering, R. Fröhlich, D. Hoppe, *Angew. Chem.* **1997**, *109*, 1804; *ibid. Int. Ed.* **1997**, *36*, 1764; D. Hoppe, M. J. Woltering, M. Oestreich, R. Fröhlich, *Helv. Chim. Acta* **1999**, *82*, 1860.

[15] K. Tomooka, N. Komine, T. Sasaki, H. Shimizu, T. Nakai, *Tetrahedron Lett.* **1998**, *39*, 9715.

[16] M. Oestreich, R. Fröhlich, D. Hoppe, *Tetrahedron Lett.* **1998**, *39*, 1745; M. Oestreich, R. Fröhlich, D. Hoppe, *J. Org. Chem.*, accepted for publication.

[17] M. Oestreich, D. Hoppe, *Tetrahedron Lett.* **1999**, *40*, 1881.

[18] D. Hoppe, M. Paetow, F. Hintze, *Angew. Chem.* **1993**, *105*, 430; *ibid. Int. Ed.* **1993**, *32*, 394; M. Paetow, M. Kotthaus, M. Grehl, R. Fröhlich, D. Hoppe, *Synlett* **1994**, 1034.

[19] S. Norsikian, I. Marek, J.-F. Poisson, J. F. Normant, *J. Org. Chem.* **1997**, *62*, 4898; S. Norsikian, I. Marek, S. Klein, J. F. Poisson, J. F. Normant, *Chem. Eur. J.* **1999**, *5*, 2055.

[20] L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115.

[21] R. M. Beesley, C. K. Ingold, J. F. Thorpe, *J. Chem. Soc.* **1915**, *107*, 1080; N. L. Allinger, V. Zalkow, *J. Org. Chem.* **1960**, *25*, 701; A. J. Kirby, *Adv. Phys. Org. Chem.* **1980**, *17*, 183.

[22] E.-U. Würthwein, K. Behrens, D. Hoppe, *Chem. Eur. J.*, in press.

[23] F. Hintze, D. Hoppe, *Synthesis* **1992**, 1216; J. van Bebber, H. Ahrens, R. Fröhlich, D. Hoppe, *Chem. Eur. J.* **1999**, *5*, 1905.

[24] K. Tamao, N. Ishida, T. Tanaka, M. Kumada, *Organometallics* **1983**, *2*, 1694; Y. Matsumoto, T. Hayashi, Y. Ito, *Tetrahedron* **1994**, *50*, 335; I. Fleming, R. Henning, D. C. Parker, H. E. Plaut, P. E. J. Sanderson, *J. Chem. Soc., Perkin Trans. 1* **1995**, 317; I. Fleming, *Chemtracts – Org. Chem.* **1996**, *9*, 1.
[25] A. Hassner, V. Alexanian, *Tetrahedron Lett.* **1978**, *19*, 4475.
[26] C. Rücker, *Tetrahedron Lett.* **1984**, *25*, 4349.
[27] W. G. Kofron, L. M. Baclawski, *J. Org. Chem.* **1976**, *41*, 1871.

Received August 21, 1999