(−)-Sparteine-Mediated Asymmetric Intramolecular Carbolithiation of Alkenes: Synthesis of Enantiopure Cyclopentanes with Three Consecutive Stereogenic Centers

by **Dieter Hoppe***, **Michael J. Woltering**[1]), **Martin Oestreich**[1]), and **Roland Fröhlich**[2])

Organisch-chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, D-48149 Münster, Germany, Fax: (+49)251-8339772

An asymmetric intramolecular carbolithiation reaction was developed by combining the (−)-sparteine-mediated enantiotopos-differentiating deprotonation and the anionic 5-*exo-trig* cyclization. Achiral 6-phenylhex-5-enyl carbamates were efficiently cyclized furnishing regio-, diastereo- (dr > 99 : 1), and enantioselectively (er > 98 : 2) 1,2-*trans*-substituted cyclopentanes. The intermediate primary benzylic lithium-carbanion pairs were – in spite of their configurative lability – diastereoselectively substituted by versatile electrophiles creating a third consecutive stereogenic center. Additionally, some 4-functionalized 6-phenylhex-5-enyl carbamates were also cyclized in high yield to provide enantiomerically pure cyclopentanes incorporating three adjacent stereogenic centers.

Introduction. – Although the carbometalation of alkenes has been known since *Ziegler*'s pioneering work [1], this C,C bond-forming reaction still remains as one of the most lively areas in organic synthesis [2]. We became interested in the carbolithiation of alkenes when *Normant* and *Marek* reported the first enantioselective intermolecular carbolithiation mediated by (−)-sparteine (**1**) [3][4]. These studies demonstrate that complexes of the general type RLi/**1** (R = alkyl) are capable of differentiating the enantiotopic faces of C=C bonds.

We have developed an efficient method to generate highly enantiomerically enriched lithium carbanion pairs by means of asymmetric deprotonation of carbamates derived from primary alkanols with the chiral base *sec*-butyllithium/(−)-sparteine (*s*-BuLi/**1**). The intermediate lithium-carbanion species have been subsequently reacted with versatile external electrophiles under retention of the configuration at the former lithium-bearing C-atom [5]. Though, C=C bonds had not been employed as internal electrophiles so far which corresponds to an intramolecular carbolithiation [6–8]. Consequently, we thought that by fusing the concepts of the enantiotopos-differentiating deprotonation [5] and the intramolecular carbolithiation [2], the latter could be driven in an enantioselective fashion[3]) (*Scheme 1*).

In this paper, we report on our comprehensive investigations of the enantioselective intramolecular carbolithiation[4]) giving rise to enantiomerically pure cyclopentanes with three adjacent stereogenic centers [11].

---

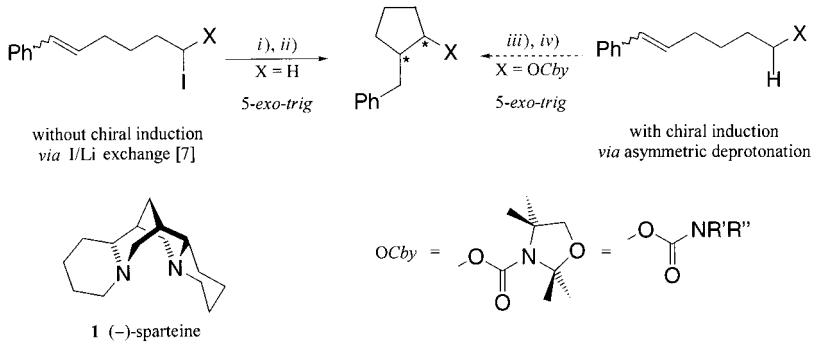
[1]) Taken in part from the Ph.D. theses of *M.J.W.* and *M.O.*

[2]) Crystal-structure analysis.

[3]) Enantiospecific intramolecular carbolithiations starting from enantiomerically enriched α-amino- [9] or α-oxystannanes [10] have also been reported.

[4]) Recently, *Nakai* and co-workers have published similar studies on a slightly modified system [12].

Scheme 1



i) *t*-BuLi, pentane/Et_2O 3 : 2, – 78° then warm. *ii*) MeOH, 95%. *iii*) *s*-BuLi/**1**, Et_2O, – 78°. *iv*) MeOH, – 78° to r.t. O*Cby* = 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyloxy.

Results and Discussion. – Our investigations began with the synthesis of the alkenes **5a** (R = H) and **5b** (R = Me). The latter, bearing the Me groups, was assumed to be the more promising cyclization precursor, since two geminal substituents are known to enhance ring closures[5]). The preparation of **5** was designed in order to provide an easy access to all C=C bond geometries. According to the straightforward three-step sequence, the 1,5-diols **2a** and **2b** [14] were converted to the phosphonium bromides **3a** and **3b**[6]), respectively, and these were subsequently reacted with PhCHO furnishing the (*Z*)-configured alkenes (*Z*)-**5** in (*E*/*Z*)-ratios of 4 : 96 for (*Z*)-**5a** and (*Z*)-**5b** [16] (*Scheme 2*). The configuration of the C=C bond in (*Z*)-**5a** was efficiently inverted by treatment with catalytic amounts of I_2 to give (*E*)-**5a** with an (*E*/*Z*)-ratio of 95 : 5 (*Scheme 2*). The alkene (*E*/*Z*)-**5b** ((*E*/*Z*)-ratio of 54 : 46) was synthesized again starting from **2b** [14] by monocarbamoylation with 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyl chloride (*Cby*Cl) [17], oxidation, and olefination with $BnPPh_3Br$ (*Scheme 2*).

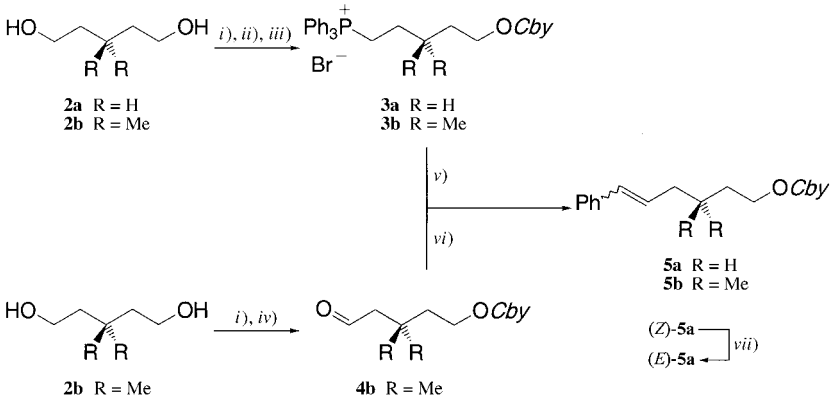
The treatment of (*Z*)-**5a** with *s*-BuLi/**1** in Et_2O at – 78° for 20 h gave 30% of **8a** in diastereomerically pure form (dr > 99 : 1) next to 32% of the cyclization precursor (*Z*)-**5a** (*Scheme 3* and *Table*, *Entry 1*). Owing to the *Thorpe-Ingold* effect [13], the alkenes (*Z*)-**5b** and (*E*/*Z*)-**5b** cyclized stereoselectively (dr > 99 : 1) to furnish **8b** independent of the configuration of the C=C bond in the somewhat higher yields of 50 and 51%, respectively (*Scheme 3* and *Table*, *Entries 9* and *10*). Furthermore, the achiral bicyclic product **9** (R = H) was isolated in small quantities in the presence of the sterically demanding diamine **1**, whereas **9** was formed in nearly quantitative yield of 93% in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) instead of **1** (*Scheme 3*). The steric bulk at the Li center and the reaction temperature were the major

---

5) This observation is often termed as the *Thorpe-Ingold* effect or gem-dialkyl effect [13].

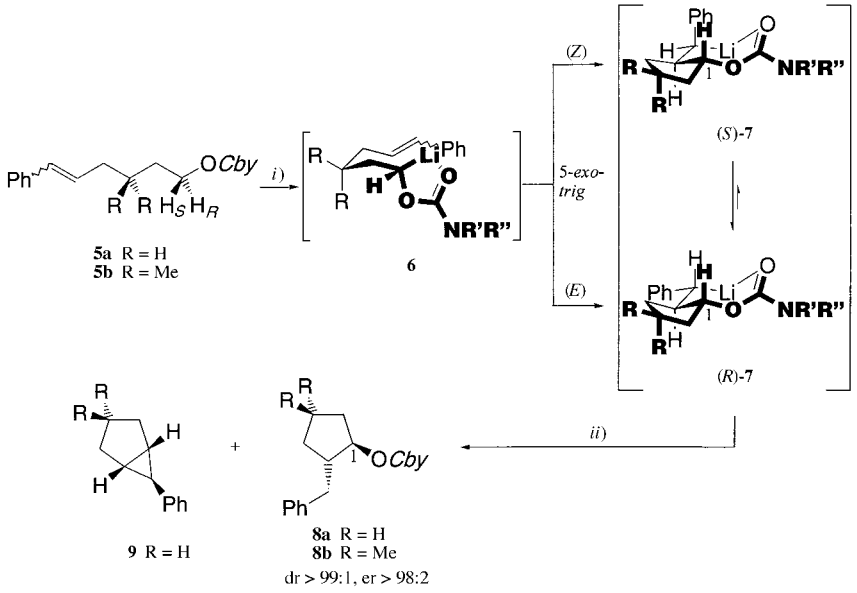
6) The synthesis of **3b** was conducted in an autoclave at 200 bar, since high pressures favor the formation of phosphonium salts [15]; the moderate yield of 41% is due to steric interactions of the geminal Me groups and the bulky phosphine.

Scheme 2



i) NaH, *Cby*Cl, THF, reflux; **32a** (R = H): 77%, **32b** (R = Me): 76%. *ii*) CBr_4, PPh_3, CH_2Cl_2, 0°; **33a** (R = H): 97%, **33b** (R = Me): 90%. *iii*) PPh_3, neat, 100°; **3a** (R = H): 95%, **3b** (R = Me): 41%. *iv*) pyridinium chlorochromate (PCC), NaOAc, CH_2Cl_2, r.t.; **4b** (R = Me): 87%. *v*) PhCHO, (*Z*)-**5a** (R = H): *t*-BuOK, Et_2O, −40°, then r.t., then reflux; 86%, (*Z*)-**5b** (R = Me): NaHMDS, THF, −50°, then r.t., 57%. *vi*) $BnPPh_3Br$, NaHMDS, THF, Et_2O, −40°, then r.t., (*E*/*Z*)-**5b** (R = Me): 81%. *vii*) I_2, hexane, r.t., (*E*)-**5a** (R = H): 78%. See also *Exper. Part.*

Scheme 3[a])



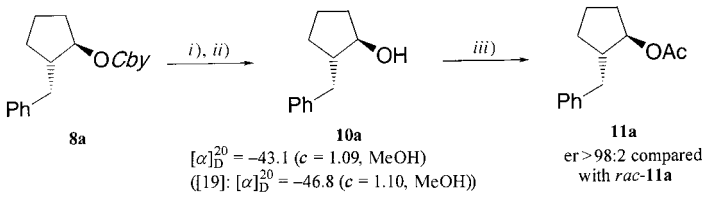
i) *s*-BuLi/**1** or *s*-BuLi/TMEDA, Et_2O, −78°. *ii*) H_2O, −78° to r.t.

[a]) Ligands (*e.g.*, **1** and TMEDA, respectively) at the Li center are omitted for the sake of clarity.

parameters affecting the intramolecular nucleophilic attack of the benzylic lithium species at the C(1), with the carbamate acting as a leaving group[7]).

The relative configuration of **8a** was assigned as *trans* by NOE measurements showing a strong NOE of the benzylic protons and the proton at C(1). The absolute configuration of **8a** was determined by chemical correlation of the decarbamoylated alcohol **10a**, which had been previously described [19]; the (1*R*,2*S*)-configuration was unambigously established by comparison of the optical rotations (*Scheme 4*).

Scheme 4



8a

10a
$[\alpha]_D^{20} = -43.1$ (c = 1.09, MeOH)
([19]: $[\alpha]_D^{20} = -46.8$ (c = 1.10, MeOH))

11a
er > 98:2 compared with *rac*-**11a**

i) $MeSO_3H$, MeOH, reflux. *ii*) K_2CO_3, MeOH, reflux, 94%. *iii*) Ac_2O, 4-(dimethylamino)pyridine (DMAP), pyridine, CH_2Cl_2, r.t.; 90%.

^{1}H-NMR Shift experiments with the acetates **11a** (*Scheme 4*) and *rac*-**11a**[8]) in the presence of 21 mol-% (+)-[Eu(hfc)$_3$] lead to a splitting of the signals of the Me groups of the antipodes; for the enantiomerically enriched sample no splitting was detected. The stereochemical outcome of the asymmetric intramolecular carbolithiation coincides with our observations that the chiral base *s*-BuLi/**1** enantioselectively abstracts the α-*pro-S*-proton in alkyl carbamates [5]. The resulting highly enantiomerically enriched, configurationally stable lithium-carbanion pair **6** inserts the C=C bond from the *Si*-face in a *syn*-fashion. The cyclization, termed 5-*exo-trig* ring closure by *Baldwin* [21], provides two epimeric, configurationally labile [22] benzylic lithium-carbanion pairs (*S*)-**7** and (*R*)-**7** in dependence on the C=C bond geometry (*Scheme 3*).

The primary benzylic lithium-carbanion pairs (*S*)-**7** and (*R*)-**7** should be initially generated by the asymmetric cyclocarbolithiation in a ratio that is directly related to the (*E*/*Z*)-ratio of the cyclization precursor. Since these species are configurationally labile [22], (*S*)-**7** and (*R*)-**7** are expected to equilibrate, and we were surprised that the reaction of **7** with versatile electrophiles provided the carbocycles **13**–**17** in excellent diastereomeric ratios of 92 : 8 up to > 98 : 2, except for the deuterolysis (*Scheme 5*, and *Table*, *Entries 2–8* and *11–17*).

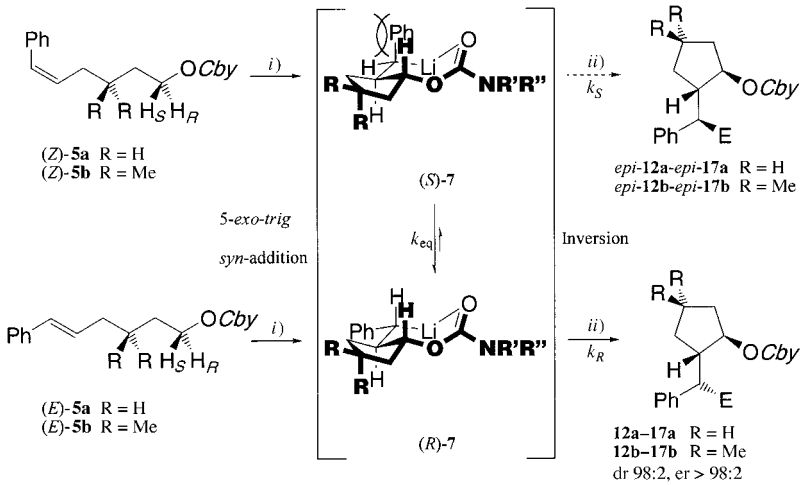
The relative configuration of compounds **12**–**17** with three consecutive stereogenic centers was exemplarily clarified by transforming the silylated carbocycle **16a** into the 1,3-diol **19a**. After the decarbamoylation of **16a**, the resulting cyclopentanol **18a** was stereospecifically oxidatively desilylated with retention of the configuration at the

---

7) Such 1,3-cycloeliminations have been observed by us [18], and later by *Normant*, *Marek* and co-workers [4], and *Nakai* and co-workers [12]; for a mechanistic view on this reaction and the assignment of the relative configuration of **9**, see [12].

8) Compound *rac*-**11a** was prepared in three steps starting from cyclopentene by epoxidation [20], addition of $PhCH_2MgBr$ [19], and subsequent acetylation.

Scheme 5



i) *s*-BuLi/**1**, Et_2O, $-78°$. *ii*) E–X, $-78°$ to r.t. For further details, see *Table 1*.

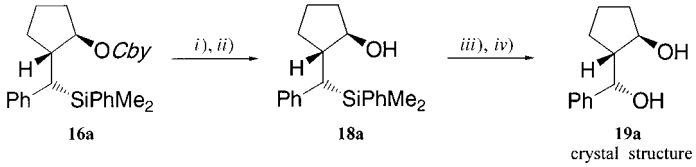
[a]) Ligands (*e.g.*, **1**) at the Li center are omitted for the sake of clarity.

Table 1. *Synthesis of Cyclopentanes with Three Consecutive Stereocenters*

Entry	Alkene	R	(*E*/*Z*)-Ratio [a])	E–X	Carbocycle	dr [b])	Yield/%
1	(*Z*)-**5a**	H	4 : 96	HO–H	**8a**	–	30
2	(*Z*)-**5a**	H	4 : 96	CH_3O–D	**12a**	33 : 67[c])	19
3	(*Z*)-**5a**	H	4 : 96	Me_3Si–Cl	**13a**	> 98 : 2	32
4	(*Z*)-**5a**	H	4 : 96	Me_3Sn–Cl	**14a**	> 98 : 2	27
5	(*Z*)-**5a**	H	4 : 96	Bu_3Sn–Cl	**15a**	> 98 : 2	14
6	(*Z*)-**5a**	H	4 : 96	$PhMe_2Si$–Cl	**16a**	> 98 : 2	38
7	(*E*)-**5a**	H	95 : 5	$PhMe_2Si$–Cl	**16a**	> 98 : 2	36
8[d])	(*Z*)-**5a**	H	4 : 96	CO_2/CH_2N_2	**17a**	97 : 3[e])[f])	32
9	(*Z*)-**5b**	Me	4 : 96	HO–H	**8b**	–	50
10	(*E*/*Z*)-**5b**	Me	54 : 46	HO–H	**8b**	–	51
11	(*E*/*Z*)-**5b**	Me	54 : 46	CH_3O–D	**12b**	43 : 57[c])	55
12	(*E*/*Z*)-**5b**	Me	54 : 46	Me_3Si–Cl	**13b**	> 98 : 2	38(28)[g])
13	(*Z*)-**5b**	Me	4 : 96	Me_3Sn–Cl	**14b**	> 98 : 2	34(25)[g])
14	(*E*/*Z*)-**5b**	Me	54 : 46	Bu_3Sn–Cl	**15b**	> 98 : 2	30
15	(*E*/*Z*)-**5b**	Me	54 : 46	$PhMe_2Si$–Cl	**16b**	> 98 : 2	48
16[d])	(*Z*)-**5b**	Me	4 : 96	CO_2/CH_2N_2	**17b**	92 : 8[e])[f])	50
17[d])	(*E*/*Z*)-**5b**	Me	54 : 46	CO_2/CH_2N_2	**17b**	92 : 8[e])[f])	43

[a]) Determined by GC analysis (R = H) or from the ^{1}H-NMR spectra by integration of the signals of the vinylic protons (R = Me). [b]) Diastereomer ratio of the epimeric benzylic substitution products determined by GC analysis and from ^{1}H-NMR spectra. [c]) Determined from the ^{1}H-NMR spectra of the mixture of the alkene and the carbocycle. [d]) CO_2 was used as the electrophile and the crude carboxylic acid was esterified with CH_2N_2. [e]) Determined by GC analysis. [f]) Some epimerization at the benzylic position might be due to enolization. [g]) Isolated yields in parentheses.

Scheme 6



16a **18a** **19a**
crystal structure

i) $MeSO_3H$, MeOH, reflux. *ii*) K_2CO_3, MeOH, reflux; 89%. *iii*) $HBF_4 \cdot OEt_2$, CH_2Cl_2. *iv*) KF, $KHCO_3$, H_2O_2, THF/MeOH, 0° then r.t.; 52%.

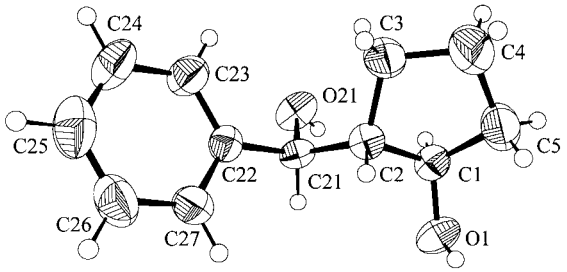


Figure. Crystal structure of **19a**[9])

benzylic stereocenter employing the *Tamao* protocol [23] (*Scheme 6*). The (1*R*,2*R*,α*S*)-configuration of **19a** was eludicated by a crystal-structure analysis[9]) (Fig.)

According to our [5][24] and other's [5][25] experience, benzylic lithium-carbanion pairs tend to react with electrophiles such as R_3SiCl, R_3SnCl (R = alkyl), and CO_2 under inversion of the configuration[10]). Consequently, it can be gathered from the (α*S*)-configuration of **13**–**17** that the predominantely reacting benzylic lithium species is (*R*)-**7**. We suggest that two – possibly co-operative – pathways might be responsible for this surprisingly high selectivity of the benzylic electrophilic substitution (*Scheme 5*): *a*) The equilibrium of (*S*)-**7** and (*R*)-**7** is strongly in favor of the latter due to 1,3-diaxial interactions in (*S*)-**7** and, therefore, the electrophile solely reacts with (*R*)-**7** to give **13**–**17**. *b*) The epimeric intermediates (*S*)-**7** and (*R*)-**7** are fastly equilibrating (k_{eq}) with the latter being preferentially substituted by the electrophile ($k_{eq} \gg k_R > k_S$) through a dynamic kinetic resolution[11]).

The moderate yields prompted us to further investigate the ring closure of either cyclization precursor **5a** or **5b** revealing three major factors: *a*) The chiral base *s*-BuLi/**1** selectively abstracts a proton from the α-position of the carbamate rather than in the allylic position. However, the kinetics for the ring closure is far from optimal, since, after electrophilic substitution, the α-functionalized carbamates (*Z*)-**20a** and (*Z*)-**21a** are isolated in considerable yields (*Scheme 7*, *Test 1* and *2*). *b*) Apart from that, the yield is also dependent on the reactivity of the electrophile, as shown for the silylation,

---

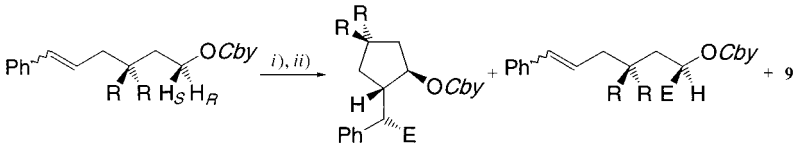
[9]) For the deposition of the crystallographic data, see [14] in [11].

[10]) In an interesting case of a domino cyclocarbolithiation/*retro*-[1,4]-*Brook*-rearrangement sequence, the benzylic electrophilic substitution is assumed to proceed under retention of the configuration [26].

[11]) For recent reviews, see [5][27]; *Beak* has also successfully applied kinetic dynamic resolutions with some (–)-sparteine (**1**) benzylic lithium complexes [25][28].

which occurs while warming from $-78°$ to ambient temperature. Therefore, not only the silylation but also the cyclocarbolithiation and the undesirable 1,3-cycloelimination is accelerated. This is reflected by the fact that, instead of the silylated open-chain product, the bicyclic compound **9** was isolated as the major product (*Scheme 7*, *Test 3*). *c*) For the branched cyclization precursor **5b**, the deprotonation is not complete because of steric interactions of the geminal Me groups and the bulky base *s*-BuLi/**1** (*Scheme 7*, *Test 4*).

Scheme 7



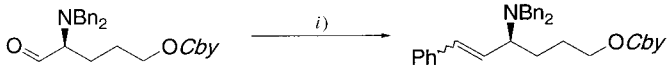
Test 1:	(*Z*)-**5a**	E-X = Bu_3SnCl	**15a**: 14%	(*Z*)-**20a**: 73%	-
Test 2:	(*Z*)-**5a**	E-X = CO_2/CH_2N_2	**17a**: 35%	(*Z*)-**21a**: 35%	-
Test 3:	(*E*)-**5a**	E-X = $PhMe_2SiCl$	**16a**: 36%	-	41%
Test 4:	(*E*/*Z*)-**5b**	E-X = CH_3OD	**12b**: 55%	(*E*/*Z*)-**5b**: 10%	-

i) *s*-Bu/Li/**1**, Et_2O, $-78°$. *ii*) E–X, $-78°$ to r.t.

When we expanded the stereoselective intramolecular carbolithiation to alkynes [29] and conjugated systems [30], a sterically demanding substituent had to be introduced in the propargylic and allylic position, respectively, in order to suppress the deprotonation in these positions. Since the ring closure of these functionalized cyclization precursors provided the cyclopentanes in high yields, we decided to study the cyclization of the (*S*)-configured 4-substituted hex-5-enyl carbamates (*E*/*Z*)-**23** and (*Z*)-**25**.

The allylic amine (*E*/*Z*)-**23** was prepared from the previously reported aldehyde **22** [29][31] in an (*E*/*Z*)-ratio of 72 : 28, without suffering racemization, employing a *Wittig* olefination [32] (*Scheme 8*). After some optimization, the *Lindlar* reduction of **24** [29] furnished the corresponding allylic alcohol (*Z*)-**25** with (*E*/*Z*)-ratio of $< 5 : 95$ (*Scheme 9*).

Scheme 8

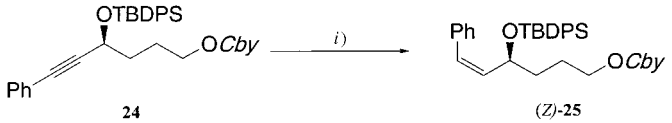


22
er > 99:1

(*E*/*Z*)-**23**
er > 99:1, (*E*)/(*Z*) 72:28

i) $BnPPh_3Br$, *t*-BuOK, Et_2O, $-18°$ to r.t.; 80%.

Scheme 9



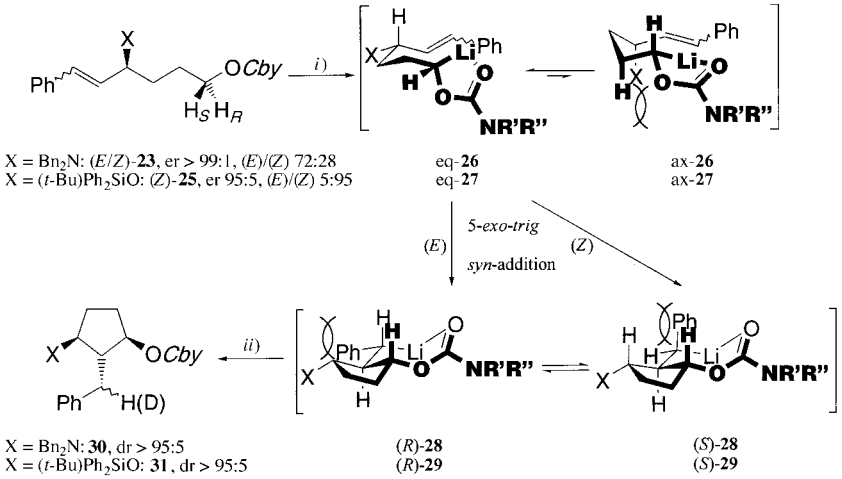
24
er 95:5

(*Z*)-**25**
er 95:5, (*E*)/(*Z*) < 5:95

i) Pd/$CaCO_3$/Pb, H_2, quinoline, toluene, r.t.; 90%. TBDPS = (*t*-Bu)Ph_2Si.

The alkenes (*E*/*Z*)-**23** and (*Z*)-**25** were transformed into the enantiomerically enriched lithium-carbanion pairs **26**/**27** upon treatment with *s*-BuLi/**1** at −78° (*Scheme 10*). Of the two feasible chair-like conformations, eq-**26**/eq-**27** should undergo the 5-*exo-trig* ring closure, whereas ring closure of ax-**26**/ax-**27** is unfavorable due to 1,3-diaxial interactions. As described above for the unsubstituted derivatives, the cyclization proceeds in a *syn*-fashion under retention of the configuration at the former lithium-bearing C-atom. Both resulting epimeric benzylic lithium species (*S*)-**28**/(*S*)-**29** and (*R*)-**28**)/(*R*)-**29**, depicted as *trans*-fused seven-membered chelates, are energetically unfavorable because of 1,3-diaxial ((*S*)-**28**/(*S*)-**29**) or 1,3-diequatorial interactions ((*R*)-**28**/(*R*)-**29**). In contrast to the intermediates (*S*)-**7** and (*R*)-**7** (*Schemes 3* and *5*), we suggest a benzylic lithium-carbanion pair not stabilized *via* a seven-membered cyclic chelate[12]) (*Scheme 10*). Methanolysis yielded the carbocycles **30** and **31**, with three adjacent stereogenic centers, in good yields of 70 and 82%, and diastereomeric ratios that directly correspond to the enantiomeric ratio of the alkenes (*E*/*Z*)-**23** and (*Z*)-**25**[13]).

Scheme 10[a])



i) *s*-BuLi/**1**, Et_2O, −78°. *ii*) MeOH, −78° to r.t., **30**: 70%, **31**: 82%.

[a]) Ligands (*e.g.*, **1**) at the Li center are omitted for the sake of clarity.

According to *Nakai* and co-workers [12], (*S*)-configured cyclization precursors such as (*E*/*Z*)-**23** and (*Z*)-**25** do not undergo the 1,3-cycloelimination for steric reasons. This and the improved kinetics for the ring closure by means of the allylic substituent might be a reasonable explanation for the increase in the yields.

12) This assumption is strongly supported by the observation that the benzylic lithium-carbanion pair could not be diastereoselectively substituted by electrophiles as demonstrated for the stannylation. *Nakai* and co-workers also discuss an 'open-chain' transition state for such intermediates [12].

13) For a more detailed discussion of the role of the existing stereogenic center in the cyclization precursor, see [29].

Conclusion. – In summary, we have presented a novel strategy for the enantioselective construction of five-membered carbocycles by fusing the asymmetric deprotonation and the intramolecular carbolithiation. The carbocycles are formed in high regio-, diastereo- (dr 92 : 8 – > 98 : 2), and enantioselectivities (er > 99 : 1). As a specific feature of these cyclizations, the intermediate, configurationally labile benzylic lithium-carbanion pair is diastereoselectively substituted by versatile electrophiles. Additionally, cyclization precursors bearing a functional group in the allylic position were also cyclized with high selectivity and good yields. This method has found further application in the synthesis of heterocycles with an indolizidine core [33].

Experimental Part

General. 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: *Merck Kieselgel 60 F_{254}* plates or *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 availabe (*Aldrich* or *Sigma*) and was stored under Ar; TMEDA was distilled from CaH_2 and kept under Ar. *s*-BuLi was received as a 1.4M soln. in cyclohexane/hexane 92 : 8 from *Fluka* and was titrated before use [34]. M.p. *Gallenkamp MFB 595* apparatus; uncorrected. Optical rotations: *Perkin-Elmer 241* polarimeter. IR and FT-IR spectra: *Perkin-Elmer* IR spectrometer *PE 298* and a *Nicolet 5DXC* spectrometer, resp. ^{1}H- and ^{13}C-NMR spectra: *Bruker AM 300* instrument; internally referenced to $CHCl_3$ (7.25 ppm) or $CDCl_3$ (77.0 ppm), resp.; the doubling of some signals occurs as a result of the (*E*)/(*Z*)-isomerism of the carbamate group; these signals are separated by slashes. MS: *Finnigan MAT 8230* instrument. Elemental analyses: performed by the Mikroanalytische Abteilung des Organisch-chemischen Institutes der Westfälischen Wilhelms-Universität Münster on a *Perkin-Elmer CHN* analyser *240*.

Typical Procedure for the Bromination of Primary Alkanols (*TP 1*). *5-Bromopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**33a**). *5-Hydroxypentyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate* (**32a**) [35] (6.000 g, 23.24 mmol) and CBr_4 (9.207 g, 27.76 mmol, 1.2 equiv.) were dissolved in CH_2Cl_2 (40 ml). At 0°, PPh_3 (7.282 g, 27.76 mmol, 1.2 equiv.) was added in portions within 20 min. After further 10 min at 0°, the mixture was allowed to warm to ambient temp. and the volatiles were removed under reduced pressure. The residue was dissolved in Et_2O (100 ml), and the white precipitate was filtered off and washed with Et_2O (4 × 50 ml). The filtrate was concentrated *in vacuo* and the resulting crude product was purified by FC (Et_2O/hexanes 1 : 3, R_f 0.29) furnishing **33a** (7.203 g, 97%). Colorless oil. IR (neat): 1680*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.37/1.42 (*s*, 6 H); 1.53/1.56 (*s*, 6 H); 1.54 (*m*, 2 H); 1.70 (*m*, 2 H); 1.91 (*tt*, *J* = 6.4, 6.9, 2 H); 3.42 (*t*, *J* = 6.7, 2 H); 3.73 (*s*, 2 H); 4.10 (*t*, *J* = 6.4, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.1/25.3/26.5; 24.8; 28.1; 32.2; 33.4; 59.6/60.5; 64.0; 76.1/76.3; 94.8/95.8; 152.1/152.8. Anal. calc. for $C_{13}H_{24}BrNO_3$ (322.24): C 48.46, H 7.51, N 4.35; found: C 48.68, H 7.60, N 4.40.

[5-(2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carbonyloxy)pentyl]triphenylphosphonium Bromide (**3a**). A vigorously stirred mixture of **33a** (8.811 g, 27.34 mmol) and Ph_3P (7.530 g, 28.71 mmol, 1.05 equiv.) was kept at 100° for 5 h without any solvent. The highly viscous mixture was cooled to r.t., and the glass-like crude product was dissolved in CH_2Cl_2 (15 ml). To this soln., Et_2O (200 ml) was added, giving rise to a white precipitate of **3a**. After decanting the solvents, this procedure was repeated twice to provide **3a** (15.154 g, 95%) as a white solid, which was dried *in vacuo*. M.p. 158°. IR (KBr): 1680*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.32/1.39 (*s*, 6 H); 1.47/1.52 (*s*, 6 H); 1.74 (*m*, 6 H); 3.70 (*s*, 2 H); 3.80 (*m*, 2 H); 4.02 (*t*, *J* = 6.2, 2 H); 7.70–7.89 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.0; 22.5 (*d*, *J* = 50); 23.9/25.1/26.3; 26.6; 28.2; 59.4/60.2; 63.5; 75.8/76.0; 94.5/95.4; 117.3; 118.5; 130.2; 130.4; 133.3; 133.4; 134.8; 151.8/152.5. Anal. calc. for $C_{31}H_{39}BrNO_3P$ (584.53): C 63.70, H 6.72, N 2.40; found: C 63.51, H 6.88, N 2.36.

3,3-Dimethyl-5-hydroxypentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (**32b**). A suspension of NaH (1.377 g, 34.44 mmol, 0.55 equiv., 60% in mineral oil) in THF (30 ml) was treated 10 min with *3,3-dimethylpentane-1,5-diol* **2b** [14] (8.277 g, 62.61 mmol). After stirring for 2 h at r.t., *2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyl chloride* (*Cby*-Cl) [17] (6.000 g, 31.31 mmol, 0.50 equiv.) was added. The mixture was

heated at reflux for 5 h and then cooled to r.t. The resulting white suspension was poured into 2N HCl (20 ml) and Et_2O (20 ml), the org. layer was separated, and the aq. phase was extracted with Et_2O (3 × 30 ml). The combined org. phases were washed with sat. aq. $NaHCO_3$ (10 ml) and brine (10 ml), dried (Na_2SO_4), and the solvents were evaporated under reduced pressure. The purification by FC (Et_2O/hexanes 4 : 1, R_f 0.39) provided **32b** (6.851 g, 76%). Colorless oil. IR (neat): 3430*s* (br., OH), 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.97 (*s*, 6 H); 1.36/1.42 (*s*, 6 H); 1.52/1.56 (*s*, 6 H); 1.57 (*t*, *J* = 7.4, 2 H); 1.64 (*m*, 3 H); 3.72 (*s*, 2 H); 3.72 (*t*, *J* = 7.4, 2 H); 4.15 (*t*, *J* = 8.0, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.1/25.3/26.5; 27.6; 31.5; 40.4; 44.5; 59.4; 59.6/60.6; 61.7; 76.1/76.3; 94.8/95.8; 153.2. Anal. calc. for $C_{15}H_{29}NO_4$ (287.40): C 62.69, H 10.17, N 4.87; found: C 62.60, H 10.32, N 5.09.

5-Bromo-3,3-dimethylpentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (**33b**). According to *TP 1*, a soln. of **32b** (7.000 g, 24.36 mmol) and CBr_4 (9.693 g, 29.23 mmol, 1.2 equiv.) were reacted with PPh_3 (7.666 g, 29.23 mmol, 1.2 equiv.) in CH_2Cl_2 (40 ml). The crude product was purified by FC (Et_2O/hexanes 1 : 5; R_f 0.49 in Et_2O/hexanes 1 : 3) to yield **33b** (7.657 g, 90%). Colorless oil. IR (neat): 1690*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.97 (*s*, 6 H); 1.36/1.42 (*s*, 6 H); 1.52/1.56 (*s*, 6 H); 1.62 (*m*, 2 H); 1.89 (*m*, 2 H); 3.39 (*m*, 2 H); 3.72 (*s*, 2 H); 4.14 (*t*, *J* = 8.0, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.1/25.3/26.6; 26.8; 28.7; 33.5; 40.1; 45.9; 59.6/60.6; 61.3; 76.1/76.4; 94.8/95.8; 152.8. Anal. calc. for $C_{15}H_{28}BrNO_3$ (350.30): C 51.43, H 8.06, N 4.00; found: C 51.44, H 8.23, N 4.34.

[3,3-Dimethyl-5-(2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyloxy)pentyl]triphenylphosphonium Bromide (**3b**). A mixture of **33b** (6.000 g, 17.13 mmol) and PPh_3 (4.717 g, 17.99 mmol, 1.05 equiv.) was heated to 100° at an Ar pressure of 200 bar in an autoclave for 21 h. After cooling to ambient temp., the crude product was dissolved in CH_2Cl_2 (10 ml), and **3b** was precipitated by the addition of Et_2O (150 ml). The solvents were decanted, and this procedure was repeated twice, affording impure **3b** as a highly viscous foam. Further purification by FC (CH_2Cl_2/MeOH 20 : 1, R_f 0.36 – 0.10) gave **3b** (4.267 g, 41%). Foaming, hygroscopic solid. M.p. 60°. IR (KBr): 1675*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*s*, 6 H); 1.33/1.39 (*s*, 6 H); 1.49/1.52 (*s*, 6 H); 1.56 – 1.70 (*m*, 4 H); 3.61 (*m*, 2 H); 3.71 (*s*, 2 H); 3.99 (*t*, *J* = 7.7, 2 H); 7.71 – 7.90 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.5 (*d*, *J* = 52); 23.9/25.1/26.2; 26.8; 33.1; 34.0; 39.3; 59.6/60.4; 60.8; 75.8/76.2; 94.6/95.5; 117.2; 118.4; 130.4; 130.5; 133.4; 133.5; 135.1; 152.2/152.9. Anal. calc. for $C_{33}H_{43}BrNO_3P$ (612.59): C 64.70, H 7.08, N 2.29; found: C 64.51, H 6.95, N 1.89.

3,3-Dimethyl-5-oxopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (**4b**). At 0°, **32b** (6.360 g, 22.13 mmol), dissolved in CH_2Cl_2 (10 ml), was slowly added to a suspension of PCC (7.155 g, 33.19 mmol, 1.5 equiv.) and AcONa (0.545 g, 6.64 mmol, 0.3 equiv.) in CH_2Cl_2 (40 ml). After 150 min at r.t., the mixture was diluted with Et_2O (40 ml) and filtered through a short silica-gel column. The silica gel was washed with Et_2O (4 × 50 ml), and the combined phases were again filtered through a silica-gel column. The volatiles were removed *in vacuo*, affording **4b** (5.517 g, 87%). Colorless oil. R_f (Et_2O/hexanes in 1 : 1) 0.32. IR (neat): 1715*s* (C=O), 1690*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*s*, 6 H); 1.36/1.42 (*s*, 6 H); 1.51/1.56 (*s*, 6 H); 1.76 (*m*, 2 H); 2.34 (*d*, *J* = 2.9, 2 H); 3.73 (*s*, 2 H); 4.17 (*t*, *J* = 7.6, 2 H); 9.86 (*t*, *J* = 2.9, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.1/25.3/26.5; 27.3; 27.5; 32.5; 40.7; 54.9; 59.6/60.6; 61.1; 76.0/76.3; 94.8/95.8; 152.7; 202.5. Anal. calc. for $C_{15}H_{27}NO_4$ (285.38): C 63.13, H 9.54, N 4.91; found: C 62.82, H 9.54, N 5.03.

(Z)-6-Phenylhex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*Z*)-**5a**). To a suspension of **3a** (7.600 g, 13.00 mmol, 1.3 equiv.) in Et_2O (45 ml), *t*-BuOK (1.347 g, 12.00 mmol, 1.2 equiv.) was added, and the resulting mixture was heated under reflux for 2 h. Subsequently, the mixture was cooled to −40°, treated with PhCHO (1.061 g, 10.00 mmol), and stirred for further 5 min at this temp. Before the reaction was quenched with H_2O (20 ml) at r.t., the mixture was stirred at ambient temp. for 30 min and heated at reflux for another 30 min. The org. layer was separated, the aq. phase was extracted with Et_2O (3 × 40 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 : 5, R_f 0.40), affording (*Z*)-**5a** (2.849 g, 86%, (*E*)/(*Z*) 4 : 96). Colorless oil. IR (neat): 1680*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.35/1.42 (*s*, 6 H); 1.51/1.56 (*s*, 6 H); 1.53 (*m*, 2 H); 1.69 (*m*, 2 H); 2.37 (*ddt*, *J* = 7.2, *J* = 1.6, 7.4, 2 H); 3.72 (*s*, 2 H); 4.08 (*t*, *J* = 6.3, 2 H); 5.65 (*dt*, *J* = 11.6, 7.2, 1 H); 6.44 (*d*, *J* = 11.6, 1 H); 7.15 – 7.37 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.1/25.3/26.6; 26.6; 28.2; 28.7; 59.6/60.5; 64.4; 76.1/76.3; 94.8/95.8; 126.5; 128.1; 128.6; 129.3; 132.2; 137.6; 152.9. Anal. calc. for $C_{20}H_{29}NO_3$ (331.46): C 72.47, H 8.82, N 4.23; found: C 72.58, H 8.97, N 4.45.

(E)-6-Phenylhex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*E*)-**5a**). A soln. of (*Z*)-**5a** (0.220 g, 0.66 mmol) and I_2 (0.003 g, 0.01 mmol) in hexane (3 ml) was stirred for 6 days at ambient temp. Then, a small amount of $Na_2S_2O_3$ was added, and the mixture was stirred for 1 h until complete bleaching of the soln. The solids were filtered off, and the volatiles were removed *in vacuo*. The crude product was purified by FC (Et_2O/hexanes 1 : 5, R_f 0.40) to give (*E*)-**5a** (0.172 g, 78%, (*E*)/(*Z*) 95 : 5). Colorless oil. IR (neat): 1686*s*

(C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.37/1.42 (*s*, 6 H); 1.53/1.56 (*s*, 6 H); 1.57 (*m*, 2 H); 1.72 (*m*, 2 H); 2.26 (*ddt*, *J* = 6.8, 1.1, 7.2, 2 H); 3.72 (*s*, 2 H); 4.12 (*t*, *J* = 6.4, 2 H); 6.20 (*dt*, *J* = 15.7, 6.8, 1 H); 6.40 (*d*, *J* = 15.7, 1 H); 7.15–7.35 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.2/25.3/26.6; 26.0; 28.5; 32.5; 59.6/60.5; 64.3; 76.2/76.4; 94.8/95.8; 125.9; 126.9; 128.5; 130.2; 130.4; 137.7; 152.7/153.6. Anal. calc. for $C_{20}H_{29}NO_3$ (331.46): C 72.47, H 8.82, N 4.23; found: C 72.37, H 8.90, N 4.46.

(Z)-3,3-Dimethyl-6-phenylhex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*Z*)-**5b**). At r.t., **3b** (3.000 g, 4.90 mmol, 1.1 equiv.), dissolved in THF (20 ml), was deprotonated with NaHMDS (4.70 ml, 4.70 mmol, 1.05 equiv., 1M in THF). After stirring for 20 min at r.t., the orange-red mixture was cooled to −50° and reacted with PhCHO (0.472 g, 4.45 mmol). The mixture was kept at −50° for further 15 min and then allowed to warm to r.t.; H_2O (10 ml) was added after 1 h at r.t. The org. layer was separated, the aq. phase extracted with Et_2O (3 × 25 ml), and the combined org. phases were dried ($MgSO_4$). The solvents were evaporated under reduced pressure, and the resulting crude product was purified by FC (Et_2O/hexanes 1:10, R_f 0.43 in Et_2O/hexanes in 1:5): (*Z*)-**5b** (0.910 g, 57%, (*E*)/(*Z*)-ratio 4:96). Colorless oil. IR (neat): 1690*s* (C=O). ^{1}H-NMR MHz, $CDCl_3$): 0.95 (*s*, 6 H); 1.34/1.41 (*s*, 6 H); 1.50/1.55 (*s*, 6 H); 1.62 (*m*, 2 H); 2.27 (*dd*, *J* = 7.4, 1.8, 2 H); 3.71 (*s*, 2 H); 4.08 (*t*, *J* = 7.9, 2 H); 5.74 (*dt*, *J* = 11.9, 7.4, 1 H); 6.54 (*d*, *J* = 11.9, 1 H); 7.16–7.37 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.2/25.3/26.6; 27.0; 27.5; 32.8; 40.0; 40.4; 59.6/60.6; 61.8; 76.1/76.4; 94.8/95.8; 126.5; 128.1; 128.7; 129.7; 130.7; 137.7; 153.0. Anal. calc. for $C_{22}H_{33}NO_3$ (359.51): C 73.50, H 9.25, N 3.90; found: C 73.26, H 9.12, N 4.15.

(E/Z)-3,3-Dimethyl-6-phenylhex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*E*/*Z*)-**5b**). To a suspension of $BnPPh_3Br$ (3.250 g, 7.50 mmol, 1.5 equiv.) in Et_2O (25 ml), NaHMDS (6.50 ml, 6.50 mmol, 1.3 equiv., 1M in THF) was added dropwise at r.t. The orange mixture was stirred for 1 h, cooled to −40°, and treated with **4b** (1.427 g, 5.00 mmol), dissolved in Et_2O (5 ml). The reaction mixture was stirred for another 60 min at this temp. and allowed to warm to r.t. overnight. The reaction was terminated by the addition of H_2O (50 ml), the org. layer was separated, the aq. phase extracted with Et_2O (3 × 50 ml), and the combined org. phases were dried ($MgSO_4$). The volatiles were evaporated under reduced pressure, and the residue was purified by FC (Et_2O/hexanes 1:10, R_f 0.43 in Et_2O/hexanes in 1:5): (*E*)-**5b**/(*Z*)-**5b** (1.460 g, 81%, (*E*)/(*Z*)-ratio 54:46). Colorless oil. IR (neat): 1690*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$)[14]): 0.99 [0.95] (*s*, 6 H); 1.35/1.43 [1.34/1.41] (*s*, 6 H); 1.51/1.57 [1.50/1.55] (*s*, 6 H); 1.62 (*m*, 2 H); 2.15 [2.27] (*dd*, *J* = 7.4, 0.7 [*J* = 7.4, 1.8], 2 H); 3.72 [3.71] (*s*, 2 H); 4.18 [4.08] (*t*, *J* = 7.9 [*J* = 7.9], 2 H); 6.24 [5.74] (*dt*, *J* = 15.8, 7.4 [*J* = 11.9, 7.4], 1 H); 6.39 [6.54] (*d*, *J* = 15.8 [*J* = 11.9], 1 H); 7.16–7.37 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$)[14]): 24.2/25.3/26.6; 27.0; 27.5; 33.1 [32.8]; 40.2 [40.0]; 45.8 [40.4]; 59.6/60.6; 61.8; 76.1/76.4; 94.8/95.8; 126.0 [126.5]; 127.0 [128.1]; 128.5 [128.7]; 128.8 [129.7]; 132.6 [130.7]; 137.7; 153.0. Anal. calc. for $C_{22}H_{33}NO_3$ (359.51): C 73.50, H 9.25, N 3.90; found: C 73.41, H 9.26, N 4.20.

*Typical Procedure for the Stereoselective Intramolecular Carbolithiation (TP 2). (−)-(1*R,2S*)-2-Benzylcyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**8a**). At −78°, a soln. of (*Z*)-**5a** (0.166 g, 0.50 mmol) in Et_2O (3 ml) was treated with *s*-BuLi (0.53 ml, 0.75 mmol, 1.5 equiv., 1.4M) in the presence of *(−)-sparteine* (**1**) (0.176 g, 0.75 mmol, 1.5 equiv.). The mixture was stirred for 20 h at this temp. before quenching with H_2O (3 ml). The org. layer was separated, the aq. phase was extracted with Et_2O (3 × 25 ml), and the combined org. phases were dried ($MgSO_4$). The evaporation of the solvents *in vacuo* gave a crude product, which was purified by FC (Et_2O/hexanes 1:10; R_f 0.43 in Et_2O/hexanes 1:3). The carbocycle **8a** (0.050 g, 30%, dr > 99:1) was isolated as a colorless oil next to (*Z*)-**5a** (0.053 g, 32%). $[\alpha]_D^{r.t.} = -20.9$ (*c* = 0.98, CH_2Cl_2). IR (neat): 1680*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.28–1.56 (*m*, 12 H); 1.64–1.87 (*m*, 5 H); 2.03 (*m*, 1 H); 2.26 (*m*, 1 H); 2.45 (*dd*, *J* = 9.7, 13.5, 1 H); 2.91 (*dd*, *J* = 5.1, 13.5, 1 H); 3.71 (*s*, 2 H); 4.90 (*ddd*, *J* = 6.7, 4.0, 5.1, 1 H); 7.14–7.30 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.2; 24.2/25.4/26.6; 29.5; 31.8; 39.4; 47.2; 59.5/60.5; 76.1/76.3; 80.9; 94.7/95.8; 125.9; 128.3; 128.8; 140.9; 152.5. Anal. calc. for $C_{20}H_{29}NO_3$ (331.46): C 72.47, H 8.82, N 4.23; found: C 72.56, H 8.86, N 4.29.

*(−)-(1*R,2S*)-2-Benzyl-4,4-dimethylcyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**8b**). According to *TP 2*, (*Z*)-**5b** (0.120 g, 0.33 mmol) was cyclized in the presence of **1** (0.117 g, 0.50 mmol, 1.5 equiv.) in Et_2O (3 ml) by treatment with *s*-BuLi (0.40 ml, 0.50 mmol, 1.5 equiv., 1.39M) for 8 h. The purification of the crude product by FC (Et_2O/hexanes 1:10; R_f 0.43 in Et_2O/hexanes 1:3) afforded a mixture of **8b** (0.060 g, 50%, dr > 99:1) and (*Z*)-**5b** (0.036 g, 30%). In analogy to *TP 2*, (*E*)-**5b**/(*Z*)-**5b** (0.180 g, 0.50 mmol) was treated with *s*-BuLi (0.56 ml, 0.75 mmol, 1.5 equiv., 1.34M) in the presence of **1** (0.176 g, 0.75 mmol, 1.5 equiv.) in Et_2O (3 ml) for 23 h. The crude product was purified by FC (Et_2O/hexanes 1:10; R_f 0.43 in Et_2O/hexanes 1:3),

[14]) The signals of the minor diastereoisomer are given in square brackets.

yielding 0.111 g of a mixture of **8b** (0.092 g, 51%, dr > 99 : 1) and (*E*/*Z*)-**5b** (0.019 g, 11%). $[\alpha]_D^{r.t.} = -29.0$ (c = 1.01, CH_2Cl_2). IR (neat): 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.03 (*s*, 3 H); 1.04 (*s*, 3 H); 1.19 (*dd*, J = 11.0, 12.9, 1 H); 1.33–1.45 (*m*, 6 H); 1.49–1.57 (*m*, 7 H); 1.62 (*dd*, J = 12.9, 7.9, 1 H); 2.02 (*dd*, J = 8.1, 13.6, 1 H); 2.42 (*m*, 1 H); 2.54 (*dd*, J = 9.1, 13.1, 1 H); 2.94 (*m*, 1 H); 3.69 (*s*, 2 H); 4.95 (*ddd*, J = 7.6, 6.2, 8.1, 1 H); 7.14–7.35 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.2/25.3/26.5; 30.3; 30.8; 36.3; 40.2; 45.2; 46.9; 47.1; 59.5/60.5; 76.1/76.3; 80.2; 94.7/95.8; 125.8; 128.3; 128.7; 141.0; 152.6. Anal. calc. for $C_{22}H_{33}NO_3$ (359.51): C 73.50, H 9.25, N 3.90; found: C 73.36, H 9.31, N 4.19.

exo-*6-Phenylbicyclo[3.1.0]hexane* (**9**). In accordance with *TP 2*, (*Z*)-**5a** (0.166 g, 0.50 mmol) was reacted with *s*-BuLi (0.54 ml, 0.75 mmol, 1.5 equiv., 1.39M) in the presence of TMEDA (0.078 g, 0.75 mmol, 1.5 equiv.) instead of **1** in Et_2O (3 ml) for 4 h. The crude product was purified by FC (Et_2O/hexanes 1 : 5, R_f 0.74) providing **9** (0.074 g, 93%, dr > 99 : 1). Colorless liquid. IR (neat): 3050*w* (C–H). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.27 (*m*, 1 H); 1.54 (*m*, 2 H); 1.59–1.69 (*m*, 2 H); 1.72–1.85 (*m*, 2 H); 1.87–1.94 (*m*, 2 H); 6.98–7.01 (*m*, 2 H); 7.06–7.11 (*m*, 1 H); 7.17–7.23 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1; 23.7; 28.0; 29.6; 124.9; 125.4; 128.1; 143.7. HR-EI-MS calc. for $C_{12}H_{14}$ (158.24): 158.10955; found: 158.10950.

*(–)-(1*R*,2*S*)-2-Benzylcyclopentanol* (**10a**). A soln. of **8a** (0.077 g, 0.23 mmol) in MeOH (3 ml) was reacted with $MeSO_3H$ (10 µl, 0.15 mmol, 0.65 equiv.) and heated at reflux for 150 min. Subsequently, K_2CO_3 (0.064 g, 0.46 mmol, 2.0 equiv.) was added, and the mixture was stirred at reflux for another 210 min. After cooling to r.t., the mixture was concentrated *in vacuo*, and the crude product was dissolved in Et_2O (10 ml). The etheral soln. was filtered to remove the solids, dried (Na_2SO_4), and again concentrated under reduced pressure. The residue was purified by FC (Et_2O/hexanes 1 : 1, R_f 0.34), providing **10a** (0.038 g, 93%). Colorless oil. The spectroscopic data were identical with those previously reported in [19]. $[\alpha]_D^{r.t.} = -43.1$ (c = 1.09, MeOH). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.20 (*m*, 1 H); 1.48–2.05 (*m*, 6 H); 1.46 (br. *s*, 1 H); 2.52 (*dd*, J = 8.3, 13.6, 1 H); 2.75 (*dd*, J = 6.9, 13.6, 1 H); 3.89 (*ddd*, J = 5.5, 5.5, 6.5, 1 H); 7.15–7.36 (*m*, 5 H).

*(–)-(1*R*,2*S*)-2-Benzylcyclopentyl Acetate* (**11a**). At r.t., **10a** (0.037 g, 0.21 mmol) was treated wtih Ac_2O (0.074 g, 0.63 mmol, 3.0 equiv.) in the presence of cat. amounts of DMAP [36] (0.004 g, 0.03 mmol) in a mixture of CH_2Cl_2 (1 ml) and pyridine (0.5 ml). The mixture was stirred for 2 h at ambient temp., the reaction was subsequently quenched with 2N HCl, and the mixture was diluted with Et_2O (4 ml). The org. layer was separated, the aq. phase extracted with Et_2O (3 × 5 ml), and the combined org. phases were dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the crude product was purified by FC (Et_2O/hexanes 1 : 5, R_f 0.45): **11a** (0.041 g, 90%, er > 98 : 2[15]). Colorless oil. The spectroscopic data were identical with those previously reported in [19]. $[\alpha]_D^{r.t.} = -6.4$ (c = 0.94, MeOH). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.27 (*m*, 1 H); 1.55–2.10 (*m*, 5 H); 1.94 (*s*, 3 H); 2.25 (*m*, 1 H); 2.50 (*dd*, J = 9.1, 13.6, 1 H); 2.81 (*dd*, J = 6.1, 13.6, 1 H); 4.85 (*ddd*, J = 4.3, 5.5, 6.9, 1 H); 7.15–7.37 (*m*, 5 H).

*(1*R*,2*S*)-2-[(*R/S*)-(Deutero)(phenyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**12a**). Following *TP 2*, (*Z*)-**5a** (0.166 g, 0.50 mmol) and **1** (0.176 g, 0.75 mmol, 1.5 equiv.), dissolved in Et_2O (3 ml) were treated with *s*-BuLi (0.57 ml, 0.75 mmol, 1.5 equiv., 1.31M) for 22 h. After deuterolysis with CH_3OD (0.2 ml), stirring for 30 min, and addition of H_2O (3 ml), the crude product was purified by FC (Et_2O/hexanes 1 : 10). The carbocycle **12a** (0.032 g, 19%, dr 67 : 33, epimers at Ph*C*D) was isolated as a colorless oil next to a mixture of the deuterated cyclization precursor (*Z*)-**5a** and **12a** (0.070 g). The spectral data were identical with those for **8a** except for the following signals: ^{1}H-NMR (300 MHz, $CDCl_3$): 2.44 (*d*, J = 9.8, 0.33 H); 2.89 (*d*, J = 4.8, 0.67 H).

*(–)-(1*R*,2*R*)-2-[(1*S*)-1-Phenyl-1-(trimethylsilyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**13a**). According to *TP 2*, (*Z*)-**5a** (0.331 g, 1.00 mmol) was cyclized in the presence of **1** (0.352 g, 1.50 mmol, 1.5 equiv.) with *s*-BuLi (1.15 ml, 1.50 mmol, 1.5 equiv., 1.30M) in Et_2O (5 ml) at –78° for 26 h. Then, Me_3SiCl (0.32 ml, 1.50 mmol, 1.5 equiv.) was added at this temp. The mixture was allowed to stir for further 5 h at –78° before warming to ambient temp. and quenching with H_2O (5 ml). The crude product was purified by FC (Et_2O/hexanes 1 : 10, R_f 0.32) yielding **13a** (0.129 g, 32%, dr > 98 : 2). Colorless needles. Compound **9** was detected by TLC. M.p. 81°. $[\alpha]_D^{r.t.} = -66.2$ (c = 1.02, CH_2Cl_2). IR (neat): 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.00 (*s*, 9 H); 1.29–1.40 (*m*, 6 H); 1.42–1.50 (*m*, 6 H); 1.52–1.85 (*m*, 5 H); 1.98 (*d*, J = 11, 1 H); 2.11 (*m*, 1 H); 2.61 (*m*, 1 H); 3.70 (*s*, 2 H); 4.89 (*ddd*, J = 3.2, 5.5, 7.8, 1 H); 7.04–7.11 (*m*, 2 H); 7.18 (*m*, 2 H); 7.36

---

15) The enantiomeric ratio was determined by NMR-shift experiments using $CDCl_3$ (0.5 ml) as a solvent: *a*) enantiomerically enriched sample: **11a** (19.0 mg) and (+)-[Eu(hfc)$_3$] (21.8 mg, 21 mol-%); ^{1}H-NMR (300 MHz): 3.92; *b*) racemic sample: *rac*-**11a** [19][20] (19.5 mg) and (+)-[Eu(hfc)$_3$] (23.5 mg, 22 mol-%); ^{1}H-NMR (300 MHz): 3.90 and 3.92.

(*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 1.2; 23.7; 24.2/25.3/25.6/26.7; 32.2; 32.3; 41.4; 47.3; 59.2/60.2; 76.1/76.3; 81.5; 94.4/95.7; 124.7; 128.3; 128.4; 143.4; 151.8. Anal. calc. for $C_{23}H_{37}NO_3Si$ (403.64): C 68.44, H 9.24, N 3.47; found: C 68.61, H 9.50, N 3.72.

*(–)-(1*R*,2*R*)-2-[(1*S*)-1-Phenyl-1-(trimethylstannyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**14a**). Following *TP 2*, (*Z*)-**5a** (0.166 g, 0.50 mmol) was treated with *s*-BuLi (0.55 ml, 0.75 mmol, 1.5 equiv., 1.36M) in the presence of **1** (0.176 g, 0.75 mmol, 1.5 equiv.) in Et_2O (3 ml) at – 78° for 23 h. Then Me_3SnCl (1.00 ml, 1.00 mmol, 2.0 equiv., 1.0M in hexane) was added at – 78°. The mixture was stirred for further 4 h at this temp., warmed to r.t., and the reaction was quenched with H_2O (2.5 ml). The crude product was purified by FC (AcOEt/hexanes 1 : 20; R_f 0.36 in Et_2O/hexanes 1 : 5), affording **14a** (0.067 g, 27%, dr > 98 : 2). Colorless solid. Compound **9** was detected by TLC. M.p. 85°. $[\alpha]_D^{r.t.} = -78.0$ ($c = 1.00$, CH_2Cl_2). IR (neat): 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): – 0.01 (*s*, 9 H); 1.25 – 1.38 (*m*, 6 H); 1.40 – 1.52 (*m*, 7 H); 1.62 – 1.80 (*m*, 3 H); 1.89 (*m*, 1 H); 2.09 (*m*, 1 H); 2.44 (*d*, *J* = 11.4, 1 H); 2.75 (*m*, 1 H); 3.66 (*s*, 2 H); 4.85 (*ddd*, *J* = 2.7, 3.5, 5.9, 1 H); 6.97 – 7.05 (*m*, 3 H); 7.10 – 7.20 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 9.2; 23.0; 24.1/25.4/26.6; 32.0; 32.7; 40.6; 48.3; 59.3; 76.1/76.3; 81.5; 95.5; 124.0; 126.9; 128.3; 145.2; 151.2/152.2. Anal. calc. for $C_{23}H_{37}NO_3Sn$ (494.26): C 55.89, H 7.55, N 2.83; found: C 56.10, H 7.54, N 2.92.

*(–)-(1*R*,2*R*)-2-[(*S*)-Phenyl(tributylstannyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**15a**) *and (+)-(1*S*,5*Z*)-6-Phenyl-1-(tributylstannyl)hex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* ((*Z*)-**20a**). In analogy to *TP 2*, (*Z*)-**5a** (0.663 g, 2.00 mmol) was reacted with *s*-BuLi (2.29 ml, 3.00 mmol, 1.5 equiv., 1.31M) in the presence of **1** (0.703 g, 3.00 mmol, 1.5 equiv.) in Et_2O (10 ml) at – 78° for 4 h. Then, Bu_3SnCl (0.89 ml, 3.30 mmol, 1.65 equiv.) was added at – 78°, and the mixture was warmed to r.t. before quenching with H_2O (8 ml). The crude product was purified by FC (Et_2O/hexanes 1 : 10; R_f 0.40 for **15a** and R_f 0.57 for (*Z*)-**20a**) affording **15a** (0.169 g, 14%, dr > 98 : 2). Colorless oil. The open-chain product (*Z*)-**20a** (0.910 g, 73%) was also isolated as a colorless oil.

Data of **15a**: $[\alpha]_D^{r.t.} = -80.7$ ($c = 1.00$, CH_2Cl_2). IR (neat): 1690*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.75 (*t*, *J* = 8.1, 6 H); 0.84 (*t*, *J* = 7.1, 9 H); 1.17 – 1.49 (*m*, 25 H); 1.64 – 1.81 (*m*, 3 H); 1.88 (*m*, 1 H); 2.09 (*m*, 1 H); 2.45 (*d*, *J* = 11.7, 1 H); 2.79 (*m*, 1 H); 3.66 (*s*, 2 H); 4.82 (*ddd*, *J* = 2.6, 3.1, 5.5, 1 H); 6.92 – 7.03 (*m*, 3 H); 7.11 – 7.18 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 10.0; 13.6; 22.9; 24.1/25.3/26.6; 27.4; 29.0; 31.8; 32.7; 40.1; 48.3; 59.2/60.3; 76.3/76.6; 81.4; 94.5/95.7; 123.8; 127.1; 128.3; 145.5; 151.3/152.1. Anal. calc. for $C_{32}H_{55}NO_3Sn$ (620.50): C 61.94, H 8.93, N 2.26; found: C 61.97, H 9.05, N 2.61.

*Data of (Z)-***20a**: $[\alpha]_D^{r.t.} = +19.2$ ($c = 2.18$, CH_2Cl_2). IR (neat): 1670*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.87 (*m*, 6 H); 0.88 (*t*, *J* = 7.1, 9 H); 1.24 – 1.54 (*m*, 26 H); 1.79 (*m*, 1 H); 1.91 (*m*, 1 H); 2.36 (*m*, 2 H); 3.71 (*s*, 2 H); 4.71 (*m*, 1 H); 5.64 (*dt*, *J* = 7.3, 11.7, 1 H); 6.42 (*d*, *J* = 11.7, 1 H); 7.17 – 7.34 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 7.8; 13.7; 24.2/25.4/26.6; 27.5; 28.3; 28.6; 29.1; 34.3; 59.4/60.5; 71.3; 76.2/76.4; 94.6/95.8; 125.9; 128.1; 128.7; 129.2; 132.5; 137.7; 152.9/153.3.

*(–)-(1*R*,2*R*)-2-[(*S*)-(Dimethylphenylsilyl)(phenyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**16a**). Following *TP 2*, (*Z*)-**5a** (0.331 g, 1.00 mmol) was cyclized with *s*-BuLi (1.14 ml, 1.50 mmol, 1.5 equiv., 1.32M) in the presence of **1** (0.352 g, 1.50 mmol, 1.5 equiv.) in Et_2O (6 ml) at – 78° for 24 h. Then, $PhMe_2SiCl$ (0.30 ml, 1.50 mmol, 1.5 equiv.) was added at – 78°, and the reaction mixture was warmed to r.t. before quenching with H_2O (5 ml). The crude product was purified by FC (Et_2O/hexanes 1 : 10; R_f 0.28 in Et_2O/hexanes 1 : 5) affording **16a** (0.177 g, 38%, dr > 98 : 2). Colorless oil. Compound **9** was detected by TLC. In a second experiment, (*E*)-**5a** (0.133 g, 0.40 mmol) was treated with *s*-BuLi (0.46 ml, 0.60 mmol, 1.5 equiv., 1.30M) in the presence of **1** (0.141 g, 0.60 mmol, 1.5 equiv.) in Et_2O (3 ml) for 20 h at – 78°. After the addition of $PhMe_2SiCl$ (0.102 g, 0.60 mmol, 1.5 equiv.), at – 78°, the mixture was warmed to ambient temp., and H_2O (3 ml) was added. Purification as described above gave **16a** (0.068 g, 36%, dr > 98 : 2), besides **9** (0.026 g, 41%). $[\alpha]_D^{r.t.} = -79.7$ ($c = 0.97$, CH_2Cl_2). IR (neat): 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.08 (*s*, 3 H); 0.32 (*s*, 3 H); 1.26/1.31 (*s*, 6 H); 1.41/1.45 (*s*, 6 H); 1.50 – 1.72 (*m*, 5 H); 1.90 (*m*, 1 H); 2.19 (*d*, *J* = 11.0, 1 H); 2.57 (*m*, 1 H); 3.64 (*s*, 2 H); 4.81 (*ddd*, *J* = 2.9 Hz, *J* = 3.1 Hz, *J* = 5.5 Hz, 1 H); 6.96 (*m*, 2 H); 7.04 (*m*, 1 H); 7.15 (*m*, 2 H); 7.26 – 7.34 (*m*, 3 H); 7.41 – 7.44 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 4.2; – 1.9; 23.6; 24.1/25.3/26.7; 32.0; 32.2; 41.1; 47.2; 59.2/60.5; 76.1/76.4; 81.5; 94.6/96.1; 124.9; 127.6; 128.1; 128.7; 128.9; 134.0; 138.7; 142.7; 152.1. Anal. calc. for $C_{28}H_{39}NO_3Si$ (465.71): C 72.21, H 8.44, N 3.01; found: C 72.29, H 8.49, N 3.26.

*(+)-(1*R*,2*S*)-2-[(*S*)-(Methoxycarbonyl)(phenyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**17a**). In analogy to *TP 2*, (*Z*)-**5a** (0.166 g, 0.50 mmol) was treated with *s*-BuLi (0.58 ml, 0.75 mmol, 1.5 equiv., 1.30M) in the presence of **1** (0.176 g, 0.75 mmol, 1.5 equiv.) in Et_2O (3 ml) at – 78° for 20 h. At this temp., a dry stream of CO_2 was bubbled through the mixture for 5 min. The mixture was kept at – 78° for further 15 min and was then allowed to warm to r.t. After the addition of 2N HCl (2 ml), the org. layer was separated, the aq. phase was extracted with Et_2O (3 × 5 ml), and the combined org. phases were dried (Na_2SO_4). The

solvents were removed *in vacuo*, and the residue was dissolved in Et_2O (83 ml). At r.t., a soln. of CH_2N_2 in Et_2O was slowly added to this soln. until the color remained yellow. The mixture was stirred for 1 h, treated with silica gel (0.050 g), and stirred for another 15 min. After filtration and concentration under reduced pressure, the crude product was purified by FC (Et_2O/hexanes 1:3, R_f 0.25). The carbocycle **17a** (0.069 g, 35%, dr 97:3) and the open-chain ester (*Z*)-**21a** (0.068 g, 35%) were isolated as a chromatographically inseparable mixture (0.137 g, 70%). To isolate pure **17a**, the mixture was dissolved in *t*-BuOH (1 ml). At 0°, this soln. was added dropwise to a suspension of *AD-mix-α* (0.225 g) in *t*-BuOH (1.0 ml) and H_2O (1.5 ml). This procedure was repeated twice in intervals of 24 h before the reaction mixture was filtered. The aq. phase was extracted wtih CH_2Cl_2 (3 × 5 ml). The combined org. phases were dried (Na_2SO_4), and the volatiles were removed *in vacuo*. The crude product was purified by FC (Et_2O/hexanes 1:3), affording pure **17a** (0.063 g, 32%, dr 97:3). Colorless, sticky oil. $[\alpha]_D^{r.t.} = +6.8$ ($c = 1.01$, CH_2Cl_2). IR (neat): 1730*s* (C=O), 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.85 (*m*, 1 H); 1.26–1.32 (*m*, 6 H); 1.38–1.45 (*m*, 6 H); 1.67–1.76 (*m*, 3 H); 1.89 (*m*, 1 H); 2.07 (*m*, 1 H); 2.73 (*m*, 1 H); 3.48 (*d*, $J = 10.7$, 1 H); 3.63 (*s*, 2 H); 3.65 (*s*, 3 H); 4.84 (*ddd*, $J = 6.2, 4.1, 2.9$, 1 H); 7.18–7.35 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.1; 24.0/25.3/25.5/26.7; 30.2; 32.9; 48.6; 51.8; 55.4; 59.3/60.4; 76.0/76.3; 78.6; 95.0/95.6; 127.4; 128.4; 128.6; 137.4; 151.0/151.7; 173.6. Anal. calc. for $C_{22}H_{31}NO_5$ (389.49): C 67.84, H 8.02, N 3.60; found: C 68.13, H 8.25, N 3.64.

*(1*R*,2*S*)-2-[(*R/S*)-(Deutero)(phenyl)methyl]-4,4-dimethylcyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**12b**). In analogy to *TP 2*, (*E*/*Z*)-**5b** (0.180 g, 0.50 mmol) and **1** (0.176 g, 0.75 mmol, 1.5 equiv.), dissolved in Et_2O (3 ml), were treated with *s*-BuLi (0.57 ml, 0.75 mmol, 1.5 equiv., 1.31M) for 26 h at −78°. The reaction was quenched with CH_3OD (0.2 ml), the mixture was stirred for further 30 min, and was hydrolyzed with H_2O (3 ml). The purification by FC (Et_2O/hexanes 1:20) gave a mixture of **12b** and (*E*/*Z*)-**5b** (0.118 g, ratio 84:16), which corresponds to a yield of 55% of **12b** (dr 43:57, epimers at Ph*C*). The spectral data were identical with those for **8b** except for the following signals: ^{1}H-NMR (300 MHz, $CDCl_3$): 2.53 (*d*, $J = 9.1$, 0.43 H), 2.92 (*m*, 0.57 H).

*(−)-(1*R*,2*R*)-4,4-Dimethyl-2-[(*S*)-(phenyl)(trimethylsilyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**13b**). Following *TP 2*, (*E*/*Z*)-**5b** (0.360 g, 1.00 mmol) was treated with *s*-BuLi (1.15 ml, 1.50 mmol, 1.5 equiv., 1.30M) in the presence of **1** (0.352 g, 1.50 mmol, 1.5 equiv.) in Et_2O (5 ml) at −78° for 26 h. Then, Me_3SiCl (0.32 ml, 1.50 mmol, 1.5 equiv.) was added at −78°. The mixture was stirred for further 5 h at this temp., warmed to r.t., and the reaction was quenched with H_2O (5 ml). The residue was purified by FC (Et_2O/hexanes 1:10; R_f 0.33 in Et_2O/hexanes 1:5) affording **13b** (0.162 g, 38%, dr > 98:2) in a mixture with (*E*/*Z*)-**5b** (0.039 g, 11%). The chromatographic purification was repeated, yielding **13b** (0.122 g, 28%, dr > 98:2). Colorless oil. $[\alpha]_D^{r.t.} = -47.5$ ($c = 1.03$, CH_2Cl_2). IR (neat): 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): −0.05 (*s*, 9 H); 1.06 (*s*, 3 H); 1.13 (*s*, 3 H); 1.19–1.43 (*m*, 14 H); 1.82 (*dd*, $J = 14.0, 8.2$, 1 H); 1.88 (*ddd*, $J = 12.4, 7.4, 2.1$, 1 H); 2.02 (*d*, $J = 10.5$, 1 H); 2.77 (*m*, 1 H); 3.61 (*s*, 2 H); 5.02 (*ddd*, $J = 3.2, 5.7, 8.2$, 1 H); 6.98–7.03 (*m*, 3 H); 7.12–7.18 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −1.1; 24.2/25.6/25.8/26.9; 28.9; 30.1; 37.9; 42.8; 47.2; 47.4; 47.8; 59.1/60.4; 76.0/76.6; 81.8; 93.9/95.8; 124.6; 128.1; 128.8; 143.6; 150.9/151.8. Anal. calc. for $C_{25}H_{41}NO_3Si$ (431.69): C 69.56, H 9.57, N 3.24; found: C 69.90, H 9.33, N 3.72.

*(−)-(1*R*,2*R*)-4,4-Dimethyl-2-[(*S*)-(phenyl)(trimethylstannyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**14b**). According to *TP 2*, (*Z*)-**5b** (0.180 g, 0.50 mmol) was treated with *s*-BuLi (0.57 ml, 0.75 mmol, 1.5 equiv., 1.31M) in the presence of **1** (0.176 g, 0.75 mmol, 1.5 equiv.) in Et_2O (3 ml) at −78° for 23 h. Then, Me_3SnCl (0.75 ml, 0.75 mmol, 1.5 equiv., 1M in hexane) was added at −78°. The mixture was stirred for further 30 min at this temp., and the reaction was quenched with H_2O (3 ml). The crude product was purified by FC (Et_2O/hexanes 1:10; $R_f = 0.43$ in AcOEt/hexanes 1:10), providing **14b** (0.088 g, 34%, dr > 98:2) in a mixture with (*Z*)-**5b** (0.023, 13%). The mixture was again subjected to FC (AcOEt/hexanes 1:10) yielding **14b** (0.064 g, 25%, dr > 98:2). Colorless oil. $[\alpha]_D^{r.t.} = -80.7$ ($c = 0.88$, CH_2Cl_2). IR (neat): 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): −0.01 (*s*, 9 H); 1.07 (*s*, 3 H); 1.13 (*s*, 3 H); 1.18–1.54 (*m*, 14 H); 1.88 (*ddd*, $J = 13.3, 7.4, 1.7$, 1 H); 1.92 (*dd*, $J = 14.1, 8.1$, 1 H); 2.54 (*d*, $J = 10.3$, 1 H); 2.92 (*m*, 1 H); 3.61 (*s*, 2 H); 4.99 (*ddd*, $J = 4.4, 6.3, 8.1$, 1 H); 6.92–7.18 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −9.0; 24.2/25.3/25.6/26.7; 29.6; 30.5; 37.1; 41.6; 47.3; 48.7; 48.8; 59.2/60.3; 76.0/76.6; 81.8; 95.0/95.8; 123.9; 127.3; 128.3; 145.5; 151.3/152.3. Anal. calc. for $C_{25}H_{41}NO_3Sn$ (522.30): C 57.49, H 7.91, N 2.68; found: C 57.83, H 7.79, N 3.02.

*(−)-(1*R*,2*R*)-4,4-Dimethyl-2-[(*S*)-(phenyl)(tributylstanyl)methyl]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**15b**). In accordance with *TP 2*, (*E*/*Z*)-**5b** (0.180 g, 0.50 mmol) was reacted with *s*-BuLi (0.77 ml, 1.00 mmol, 2.0 equiv., 1.31M) in the presence of **1** (0.176 g, 0.75 mmol, 1.5 equiv.) in Et_2O (3 ml) at −78° for 24 h. Then, Bu_3SnCl (0.30 ml, 1.12 mmol, 2.25 equiv.) was added at −78°. The mixture was stirred for another 1 h at this temp., and the reaction was quenched with H_2O (3 ml). The crude product was purified by FC (Et_2O/hexanes 1:10; R_f 0.46 in Et_2O/hexanes 1:5), giving **15b** (0.097 g, 30%, dr > 98:2), besides (*E*/*Z*)-**5b**

(0.012 g, 7%) as a colorless oil. $[\alpha]_D^{r.t.} = -79.4$ ($c = 1.01$, CH_2Cl_2). IR (neat): 1690*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.75 (*t*, *J* = 8.1, 6 H); 0.84 (*t*, *J* = 7.2, 9 H); 1.07 (*s*, 3 H); 1.13 (*s*, 3 H); 1.17–1.50 (*m*, 26 H); 1.88 (*m*, 1 H); 1.92 (*dd*, *J* = 14.0, 8.2, 1 H); 2.56 (*d*, *J* = 10.7, 1 H); 2.97 (*m*, 1 H); 3.62 (*s*, 2 H); 4.95 (*ddd*, *J* = 4.3, 5.9, 7.9, 1 H); 6.93 (*m*, 1 H); 7.00 (*m*, 2 H); 7.12 (*m*, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): 10.1; 13.6; 24.2/25.3/27.0; 27.8; 29.2; 29.6; 30.4; 37.1; 41.3; 47.4; 48.8; 48.8; 59.2/60.4; 76.0/76.4; 81.9; 95.8; 123.8; 127.5; 128.2; 145.8; 151.7/152.6. Anal. calc. for $C_{34}H_{59}NO_3Sn$ (648.56): C 62.97, H 9.17, N 2.16; found: C 63.29, H 9.38, N 2.46.

*(−)-(1*R*,2*R*)-2-[(*S*)-(Dimethylphenylsilyl)(phenyl)methyl]-4,4-dimethylcyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**16b**). According to *TP 2*, (*E*/*Z*)-**5b** (0.360 g, 1.00 mmol) was treated with *s*-BuLi (1.15 ml, 1.50 mmol, 1.5 equiv., 1.30M) in the presence of **1** (0.352 g, 1.50 mmol, 1.5 equiv.) in Et_2O (5 ml) at −78° for 24 h. Then, $PhMe_2SiCl$ (0.26 ml, 1.50 mmol, 1.5 equiv.) was added at −78°. The mixture was allowed to warm to ambient temp. overnight, and the reaction was quenched with H_2O (5 ml). The crude product was purified by FC (Et_2O/hexanes 1:20 to 1:10; R_f 0.36 in Et_2O/hexanes 1:5) providing **16b** (0.239 g, 48%, dr > 98:2). Colorless oil. $[\alpha]_D^{r.t.} = -59.4$ ($c = 0.96$, CH_2Cl_2). IR (neat): 16.85*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.12 (*s*, 3 H); 0.29 (*s*, 3 H); 0.81 (*s*, 3 H); 0.93 (*s*, 3 H); 0.98–1.30 (*m*, 14 H); 1.61 (*dd*, *J* = 13.7, 8.3, 1 H); 1.65 (*m*, 1 H); 2.17 (*d*, *J* = 10.5, 1 H); 2.62 (*m*, 1 H); 3.48 (*s*, 2 H); 4.84 (*ddd*, *J* = 3.6, 5.2, 8.3, 1 H); 6.81–7.01 (*m*, 5 H); 7.15–7.30 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −3.7; −1.9; 24.2/25.3/25.7/26.8; 28.9; 30.0; 37.8; 42.6; 47.1; 47.3; 47.7; 59.1/60.3; 76.0/76.3; 81.7; 94.0/95.6; 124.7; 127.5; 128.0; 128.8; 128.9; 134.1; 138.3; 142.9; 151.3/152.0. Anal. calc. for $C_{30}H_{43}NO_3Si$ (493.76): C 72.98, H 8.78, N 2.84; found: C 73.98, H 8.89, N 3.02.

*(+)-(1*R*,2*S*)-2-[(*S*)-(Methoxycarbonyl)(phenyl)methyl]-4,4-dimethylcyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**17b**). In analogy to *TP 2*, (*Z*)-**5b** (0.180 g, 0.50 mmol) was treated with *s*-BuLi (0.57 ml, 0.75 mmol, 1.5 equiv., 1.31M) in the presence of **1** (0.176 g, 0.75 mmol, 1.5 equiv.) in Et_2O (3 ml) at −78° for 23 h. As described for **17a**, a dry stream of CO_2 was bubbled through the mixture, the mixture was kept at −78° for further 15 min, and was allowed to warm to r.t. 2N HCl (3 ml) was added, the org. layer separated, the aq. phase was extracted with Et_2O (3 × 5 ml), and the combined org. phases were dried (Na_2SO_4). The solvents were removed *in vacuo*, and the residue was dissolved in Et_2O (3 ml). A soln. of CH_2N_2 in Et_2O was slowly added to this soln. at r.t. until the color remained yellow. The reaction mixture was stirred for 30 min, treated with silica gel (0.050 g), and stirred for another 15 min. After filtration and concentration under reduced pressure, the crude product was purified by FC (Et_2O/hexanes 1:10; R_f 0.26 in Et_2O/hexanes 1:3): **17b** (0.105 g, 50%, dr 92:8) together with (*Z*)-**5b** (0.012 g, 7%) as a colorless oil. The same experiment was conducted with (*E*/*Z*)-**5b** affording **17b** (0.090 g, 43%, dr 92:8) together with (*E*/*Z*)-**5b** (0.029 g, 16%). $[\alpha]_D^{r.t.} = +19.2$ ($c = 1.00$, CH_2Cl_2). IR (neat): 1735*s* (C=O), 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*s*, 6 H); 1.11/1.16 (*s*, 6 H); 1.24/1.30 (*s*, 6 H); 1.40–1.43 (*m*, 2 H); 1.85–1.95 (*m*, 2 H); 2.91 (*m*, 1 H); 3.54 (*d*, *J* = 10.5, 1 H); 3.58/3.59 (*s*, 2 H); 3.65 (*s*, 3 H); 5.06 (*ddd*, *J* = 8.1, 6.2, 4.1, 1 H); 7.16–7.36 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.1/25.3/26.8; 28.9; 29.9; 37.4; 45.2; 47.7; 48.5; 51.8; 56.6; 59.2/60.4; 75.9/76.3; 78.3; 95.7; 127.3; 128.4; 128.6; 137.5; 151.6; 173.7. Anal. calc. for $C_{24}H_{35}NO_5$ (417.55): C 69.04, H 8.45, N 3.35; found: C 69.27, H 8.48, N 3.49.

*(−)-(1*R*,2*R*)-2-[(*S*)-(Dimethylphenylsilyl)(phenyl)methyl]cyclopentanol* (**18a**). Compound **16a** (0.193 g, 0.41 mmol) was dissolved in MeOH (5 ml). After adding $MeSO_3H$ (0.040 g, 0.42 mmol, 1.0 equiv.), the mixture was refluxed for 4 h. Subsequently, K_2CO_3 (0.172 g, 1.25 mmol, 3.0 equiv.) was added, and the mixture was heated under reflux for another 14 h. The suspension was cooled to r.t. and filtered to remove the solids which were washed with Et_2O (25 ml). The filtrate was concentrated under reduced pressure, and the residue was purified by FC (Et_2O/hexanes 1:1, R_f 0.51), affording **18a** (0.115 g, 89%). Colorless oil. $[\alpha]_D^{r.t.} = -81.9$ ($c = 0.52$, CH_2Cl_2). IR (neat): 3380*s* (br., OH), 1685*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.00 (*s*, 3 H); 0.19 (*s*, 3 H); 0.87 (br. *s*, 1 H); 1.00 (*m*, 1 H); 1.30–1.66 (*m*, 4 H); 1.82 (*m*, 1 H); 2.02 (*d*, *J* = 11.7, 1 H); 2.19 (*m*, 1 H); 3.69 (*ddd*, *J* = 4.7, 4.7, 6.4, 1 H); 6.92–7.14 (*m*, 5 H); 7.16–7.33 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −4.1; −1.9; 22.6; 32.1; 33.7; 42.3; 49.8; 80.2; 125.2; 127.6; 128.5; 128.9; 133.0; 134.8; 138.5; 143.3. Anal. calc. for $C_{20}H_{26}OSi$ (310.51): C 77.36, H 8.44; found: C 77.21, H 8.30.

*(−)-(1*R*,2*R*)-2-[(*S*)-(Hydroxy)(phenyl)methyl]cyclopentanol* (**19a**). According to the procedure described in [23], a soln. of **18a** (0.115 g, 0.37 mmol) In CH_2Cl_2 (5 ml) was treated with HBF_4 (102 µl, 0.74 mmol, 2.0 equiv., 54% in Et_2O) at 0°. The mixture was stirred for 10 min at 0° and was then stirred for further 30 min at ambient temp. The solvents were removed under reduced pressure, the residue was dissolved in THF (2 ml) and MeOH (2 ml), and the resulting soln. was reacted with KF (0.043 g, 0.74 mmol, 2.0 equiv.) and $KHCO_3$ (0.370 g, 3.70 mmol, 10 equiv.) at 0°. The mixture was kept at this temp. for 15 min before H_2O_2 (0.45 ml, 30% in H_2O) was added. The mixture was stirred for another 15 min at 0° and for 4 h at r.t. After the addition of sat. aq. Na_2SO_3 (2 ml), the org. layer was separated, the aq. phase was extracted with Et_2O (4 × 10 ml), and the combined org. phases were dried (Na_2SO_4). The solvents were removed *in vacuo*, and the residue was purified

by FC (Et_2O; R_f 0.39), giving **19a** (= 0.037 g, 52%, dr > 98 : 2). Colorless crystals[9]). M.p. 107°. $[\alpha]_D^{r.t.} = -64.3$ ($c = 0.61$, CH_2Cl_2). IR (neat): 3380*s* (br., OH); 3280*s* (OH). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.41–1.60 (*m*, 3 H); 1.61–1.75 (*m*, 2 H); 1.76–1.93 (*m*, 2 H); 2.14 (*m*, 1 H); 2.24 (br. *s*, 1 H); 3.98 (*ddd*, *J* = 6.7, 6.9, 6.5, 1 H); 4.71 (*m*, 1 H); 7.26–7.37 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.6; 26.2; 34.3; 54.8; 74.9; 76.0; 126.4; 127.8; 128.5; 143.1. HR-EI-MS: calc. for $[C_{12}H_{16}O_2 - 2H + 2Si(CH_3)_3]$ (336.62): 336.1941; found: 336.1994.

*(−)-(4*S*,5*E/Z*)-4-(Dibenzylamino)-6-phenylhex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* ((*E*/*Z*)-**23**) [32]. A suspension of $BnPPh_3Br$ (1.55 g, 3.58 mmol, 2.0 equiv.) and *t*-BuOK (0.37 g, 3.31 mmol, 1.85 equiv.) in Et_2O (10 ml) was heated under reflux for 2 h. The resulting orange-red mixture was cooled to −18°, and the **22** [29] (0.81 g, 1.79 mmol), dissolved in Et_2O (5 ml), was injected. After stirring overnight while warming to r.t., the mixture was poured onto sat. NH_4Cl. The org. layer was separated, the aq. phase extracted with Et_2O (2 × 25 ml), and the combined org. phases were washed with H_2O (10 ml) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the crude product was purified by FC (Et_2O/hexanes 1 : 1, R_f 0.61). The mixture (*E*/*Z*)-**23** (0.75 g, 80%, (*E*)/(*Z*) 72 : 28) was isolated as a colorless oil. $[\alpha]_D^{r.t.} = -101$ (c = 1.12, $CHCl_3$). IR (neat): 1695*s* (C=O). ^{1}H-NMR[14]) (300 MHz, $CDCl_3$): 1.33/1.41/1.49/1.55 (4*s*, 12 H); 1.56–1.65 (*m*, 2 H); 1.67–1.99 (*m*, 2 H); 3.17–3.24 (*m*, 1 H); 3.44 [3.32] (*d*, *J* = 13.8 [*J* = 13.6], 2 H); 3.70 (*s*, 2 H); 3.87 [3.77] (*d*, *J* = 13.8 [*J* = 13.6], 2 H); 3.94–4.08 (*m*, 2 H); 6.22 [5.73] (*dd*, *J* = 15.8, 8.8 [*J* = 11.9, 10.6], 1 H); 6.39 [6.75] (*d*, *J* = 15.8 [*J* = 11.9], 1 H); 7.03–7.43 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.1/25.3/26.5; 25.9; 26.3; 29.3; 29.4; 53.5; 53.8; 54.1; 59.6/60.6; 60.2; 64.4; 76.1/76.3; 94.7/95.7; 126.3; 126.5; 126.7; 127.4; 127.9; 128.0; 128.2; 128.5; 128.6; 130.5; 132.3; 133.2; 137.0; 140.0; 140.2; 152.0/152.8. Anal. calc. for $C_{34}H_{42}N_2O_3$ (526.72): C 77.53, H 8.04, N 5.32; found: C 77.19, H 8.02, N 5.38.

*(−)-(4*S*,5*Z*)-4-[(*tert*-Butyl)diphenylsilyloxy]-6-phenylhex-5-enyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* ((*Z*)-**25**). At r.t., **24** [29] (0.300 g, 0.51 mmol) and quinoline (0.066 g, 0.51 mmol, 1.0 equiv.) were dissolved in toluene (15 ml). This soln. was vigorously stirred in the presence of Pd/$CaCO_3$/Pb (*Lindlar* catalyst) (0.150 g) under H_2 for 45 min at r.t. The mixture was filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by FC (Et_2O/hexanes 1 : 9; R_f = 0.67 in Et_2O/hexanes 1 : 1), affording (*Z*)-**25** (0.270 g, 90%, (*E*)/(*Z*) < 5 : 95). Colorless liquid. $[\alpha]_D^{r.t.} = -5.6$ (c = 0.52, $CHCl_3$). IR (neat): 1700*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.02/1.07 (*s*, 9 H); 1.31/1.41/1.46/1.55 (4*s*, 12 H); 1.66 (br. *s*, 4 H); 3.70 (*s*, 2 H); 3.96 (br. *s*, 2 H); 4.69–4.76 (*m*, 1 H); 5.73 (*dd*, *J* = 11.8, 9.2, 1 H); 6.29 (*d*, *J* = 11.8, 1 H); 6.78–6.82 (*m*, 2 H); 7.10–7.13 (*m*, 2 H); 7.21–7.27 (*m*, 3 H); 7.30–7.39 (*m*, 3 H); 7.51–7.57 (*m*, 4 H); 7.70–7.73 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.0/19.3; 24.6; 24.2/25.3/26.6; 27.0; 35.1; 59.6/60.5; 64.6; 69.2; 76.2/76.4; 94.8/95.8; 126.7; 127.3; 127.4; 127.7; 128.0; 128.4; 128.7; 129.4; 129.6; 134.1; 134.8; 135.3; 135.8; 135.9; 136.8; 152.0/152.8. Anal. calc. for $C_{36}H_{47}NO_4Si$ (585.86): C 73.81, H 8.09, N 2.39; found: C 73.67, H 8.08, N 2.29.

*(−)-(1*R*,2*R*,3*S*)-2-[(*R*/*S*)-(Deutero)(phenyl)methyl]-3-(dibenzylamino)cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**30**). In accordance with *TP 2*, (*E*/*Z*)-**23** (0.200 g, 0.38 mmol) was cyclized in the presence of **1** (0.133 g, 0.57 mmol, 1.5 equiv.) in Et_2O (8 ml) by treatment with *s*-BuLi (0.43 ml, 0.57 mmol, 1.5 equiv., 1.34M). The reaction was terminated by the addition of CH_3OD (1 ml) after 18 h. Purification of the crude product by FC (Et_2O/hexanes 1 : 9 to 1 : 1; R_f 0.61 in Et_2O/hexanes 1 : 1) provided **30** (0.136 g, 70%, dr > 95 : 5 and dr 50 : 50 epimers at Ph*C*) slightly contaminated with (*E*/*Z*)-**23** (less than 5%). $[\alpha]_D^{r.t.} = -12.4$ (c = 0.92, $CHCl_3$). IR (neat): 1695*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.94–1.85 (*m*, 16 H); 2.20–2.36 (*m*, 1 H); 2.46 (*d*, *J* = 8.2, 0.5 H); 2.86–2.97 (*m*, 1 H); 3.00 (*d*, *J* = 4.5, 0.5 H); 3.44 (*d*, *J* = 13.8, 2 H); 3.61 (br. *s*, 2 H); 3.88 (*d*, *J* = 13.8, 2 H); 4.79–4.86 (*m*, 1 H); 6.92–6.96 (*m*, 2 H); 7.06–7.40 (*m*, 13 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.6; 24.2/25.1/25.3/26.2; 29.5; 37.7 (*t*, *J* = 18.4); 48.7; 54.9; 59.6/60.3; 63.9; 76.1/76.3; 78.1; 94.8/95.8; 125.7; 126.6; 126.9; 127.5; 128.3; 128.8; 129.3; 140.3; 152.1/152.9. Anal. calc. for $C_{34}H_{41}DN_2O_3$ (527.73): C 77.38, H 8.02, N 5.31; found: C 77.51, H 8.06, N 5.43.

*(−)-(1*R*,2*S*,3*S*)-2-Benzyl-3-[(*tert*-butyl)diphenylsilyloxy]cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate* (**31**). Following *TP 2*, (*Z*)-**25** (0.100 g, 0.17 mmol) was treated with *s*-BuLi (0.19 ml, 0.24 mmol, 1.4 equiv., 1.23M) in the presence of **1** (0.060 g, 0.26 mmol, 1.5 equiv.) in Et_2O (3 ml) for 22 h. After quenching with MeOH (0.5 ml), the crude product was purified by FC (Et_2O/hexanes 1 : 9; R_f = 0.67 in Et_2O/hexanes 1 : 1), yielding **31** (0.082 g, 82%, dr 95 : 5), which was slightly contaminated with (*Z*)-**25** (less than 5%). $[\alpha]_D^{r.t.} = -26.6$ (c = 0.67, $CHCl_3$). IR (neat): 1694*s* (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.07/1.09 (*s*, 9 H); 1.25–1.91 (*m*, 16 H); 2.30–2.44 (*m*, 1 H); 2.46 (*dd*, *J* = 13.4, 8.6, 1 H); 2.64 (*dd*, *J* = 13.4, 5.8, 1 H); 3.66/3.67 (*s*, 2 H); 3.92 (*dd*, *J* = 10.3, 5.5, 1 H); 4.83 (*dt*, *J* = 4.9, 6.7, 1 H); 7.01–7.04 (*m*, 2 H); 7.09–7.20 (*m*, 3 H); 7.33–7.46 (*m*, 6 H); 7.63–7.75 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.1; 24.2/25.4/26.6; 27.0; 30.0; 32.7; 37.9; 55.6; 59.5/60.5; 76.2/76.4; 77.9; 78.6; 94.8/95.8; 125.9; 127.5; 128.3; 129.0; 129.6; 134.1; 134.8; 135.8; 140.0; 152.0/152.8. Anal. calc. for $C_{36}H_{47}NO_4Si$ (585.86): C 73.81, H 8.09, N 2.39; found: C 73.89, H 7.99, N 2.16.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for generous financial support. *M. J. W.* would like to thank the *Graduiertenkolleg 'Hochreaktive Mehrfachbindungssysteme'* and *M. O.* (*Kekulé* Fellow 1997–1999) the *Fonds der Chemischen Industrie* for fellowships.

REFERENCES

[1] K. Ziegler, K. Bähr, *Chem. Ber.* **1928**, *61*, 253; K. Ziegler, F. Dersch, H. Wollthan, *Liebigs Ann. Chem.* **1934**, *511*, 13; K. Ziegler, H. G. Gellert, *ibid.* **1950**, *567*, 195.

[2] I. Marek, *J. Chem. Soc., Perkin Trans. 1* **1999**, 535; I. Marek, J. F. Normant in 'Metal-Catalyzed Cross-Coupling Reaction', Eds. F. Diederich, P. J. Stang, Wiley-VCH, Weinheim, 1998, pp. 271–337; P. Knochel in 'Comprehensive Organic Synthesis', Eds. B. M. Trost, I. Fleming, Pergamon Press, New York, 1991, Vol. 4, pp. 865–911.

[3] S. Klein, I. Marek, J.-F. Poisson, J. F. Normant, *J. Am. Chem. Soc.* **1995**, *117*, 8853.

[4] C. Mück-Lichtenfeld, H. Ahlbrecht, *Tetrahedron* **1996**, *52*, 10025; S. Norsikian, I. Marek, J. F. Normant, *Tetrahedron Lett.* **1997**, *38*, 7523; 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.

[5] 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.

[6] V. N. Drozd, U. A. Ustynyuk, M. A. Tsel'eva, L. B. Dmitriev, *Zh. Obshch. Khim.* **1968**, *38*, 2114; *ibid.* **1969**, *39*, 1991.

[7] W. F. Bailey, T. T. Nurmi, J. J. Patricia, W. J. Wang, *J. Am. Chem. Soc.* **1987**, *109*, 2442; W. F. Bailey, A. D. Khanolkar, *J. Org. Chem.* **1990**, *55*, 6058; W. F. Bailey, A. D. Khanolkar, K. Gavaskar, T. V. Ovaska, K. Rossi, Y. Thiel, K. B. Wiberg, *J. Am. Chem. Soc.* **1991**, *113*, 5720; W. F. Bailey, K. V. Gavaskar, *Tetrahedron* **1994**, *50*, 5957.

[8] A. Krief, P. Barbeaux, *J. Chem. Soc., Chem. Commun.* **1987**, 1214; A. Krief, P. Barbeaux, *Synlett* **1990**, 511; A. Krief, B. Kenda, B. Remacle, *Tetrahedron Lett.* **1995**, *36*, 7917; A. Krief, J. Bousbaa, *Synlett* **1996**, 1007; A. Krief, B. Remacle, W. Dumont, *Synlett* **1999**, 1142; R. W. Hoffmann, R. Koberstein, K. Harms, *J. Chem. Soc., Perkin Trans. 2* **1999**, 183.

[9] I. Coldham, R. Hufton, D. J. Snowden, *J. Am. Chem. Soc.* **1996**, *118*, 5322; I. Coldham, J.-C. Fernàndez, D. J. Snowden, *Tetrahedron Lett.* **1999**, *40*, 1819.

[10] K. Tomooka, N. Komine, T. Nakai, *Tetrahedron Lett.* **1997**, *38*, 8939.

[11] M. J. Woltering, R. Fröhlich, D. Hoppe, *Angew. Chem.* **1997**, *109*, 1804, *ibid. Int. Ed.* **1997**, *36*, 1764.

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

[13] 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.

[14] H. E. Zimmerman, D. N. Schissel, *J. Org. Chem.* **1986**, *51*, 196; A. T. Blomquist, E. S. Wheeler, Y. Chu, *J. Am. Chem. Soc.* **1955**, *77*, 6307; J. Houk, G. M. Whitesides, *J. Am. Chem. Soc.* **1987**, *109*, 6835.

[15] W. G. Dauben, J. M. Gerdes, R. A. Bunce, *J. Org. Chem.* **1984**, *49*, 4293.

[16] M. Schlosser, *Top. Curr. Chem.* **1970**, *5*, 1; A. B. Reitz, S. O. Nortey, A. D. Jordan, Jr., M. S. Mutter, B. E. Maryanoff, *J. Org. Chem.* **1986**, *51*, 3302; M. Schlosser, B. Schaub, J. de Oliveira-Neto, S. Jeganathan, *Chimia* **1986**, *40*, 244.

[17] F. Hintze, D. Hoppe, *Synthesis* **1992**, 1216.

[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] R. Seemayer, M. P. Scheider, *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 171.

[20] L. Goodman, A. Benitez, B. R. Baker, *J. Am. Chem. Soc.* **1958**, *80*, 1680.

[21] J. E. Baldwin, *J. Chem. Soc., Chem. Commun.* **1976**, 734.

[22] R. W. Hoffmann, J. Lanz, R. Metternich, G. Tarara, D. Hoppe, *Angew. Chem.* **1987**, *99*, 1196, *ibid. Int. Ed.* **1987**, *26*, 1145.

[23] 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.

[24] D. Hoppe, A. Carstens, T. Krämer, *Angew. Chem*. **1990**, *103*, 1455; *ibid. Int. Ed*. **1990**, *29*, 1424; A. Carstens, D. Hoppe, *Tetrahedron* **1994**, *50*, 6097; C. Derwing, D. Hoppe, *Synthesis* **1996**, 149.
[25] F. Hammerschmidt, A. Hanninger, *Chem. Ber*. **1995**, *128*, 1069; M. Schlosser, D. Limat, *J. Am. Chem. Soc*. **1995**, *117*, 12342; D. J. Gallagher, H. Du, S. A. Long, P. Beak, *J. Am. Chem. Soc*. **1996**, *118*, 11391.
[26] S. H. Kleinfeld, E. Wegelius, D. Hoppe, *Helv. Chim. Acta* **1999**, *82*, in press.
[27] S. Caddick, K. Jenkins, *Chem. Soc. Rev*. **1996**, 447.
[28] S. Thayumanavan, A. Basu, P. Beak, *J. Am. Chem. Soc*. **1997**, *119*, 8209.
[29] M. Oestreich, R. Fröhlich, D. Hoppe, *Tetrahedron Lett*. **1998**, *39*, 1745; M. Oestreich, R. Fröhlich, D. Hoppe, *J. Org. Chem.*, in press.
[30] M. Oestreich, D. Hoppe, *Tetrahedron Lett*. **1999**, *40*, 1881.
[31] M. T. Reetz, *Chem. Rev*. **1999**, *99*, 1121.
[32] L. Fitjer, U. Quabeck, *Synth. Commun*. **1985**, *15*, 855.
[33] M. J. Woltering, R. Fröhlich, B. Wibbeling, D. Hoppe, *Synlett* **1998**, 797.
[34] W. G. Kofron, L. M. Baclawski, *J. Org. Chem*. **1976**, *41*, 1871.
[35] H. Ahrens, Ph. D. thesis, WWU Münster, 1994; M. Paetow, H. Ahrens, D. Hoppe, *Tetrahedron Lett*. **1992**, *33*, 5323.
[36] W. Steglich, G. Höfle, *Angew. Chem*. **1969**, *81*, 1001; *ibid. Int. Ed.* **1969**, *8*, 981.

Received August 5, 1999