(−)-Sparteine-Mediated Stereoselective Intramolecular Carbolithiation of 4-Substituted 5-Hexynyl Carbamates. Synthesis of Enantiopure 1,3-Difunctionalized Alkylidene Cyclopentanes

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The stereoselective carbolithiation of alkynes with external chiral induction has been achieved for the first time by fusing the concepts of the asymmetric deprotonation (A) with *s*-BuLi/(−)-sparteine (*s*-BuLi/**1**) and the intramolecular carbolithiation (B). Several 4-functionalized 5-hexynyl carbamates with different terminal substituents have been prepared and efficiently cyclized providing enantiopure highly substituted alkylidene cyclopentanes. The presence of a sterically demanding substituent in the propargylic position is the essential feature of these cyclizations in order to suppress the abstraction of the remaining propargylic proton. Furthermore, in dependence on the terminal substituent, the 6-phenyl-substituted precursors undergo an intramolecular carbolithiation whereas for the 6-trimethylsilyl-substituted alkynes a subsequent migration of the *O*-carbamoyl group onto the vinylic carbanionic center follows.

Introduction

The carbometalation of carbon−carbon multiple bonds ranks among the most efficient methods for the formation of new carbon−carbon bonds.[2] However, the development of asymmetric variants still remains as a major endeavor in stereoselective synthesis although some enantioselective carbometalation reactions have appeared in recent years.[3] The reports on the first asymmetric intermolecular[4] as well as intramolecular[5] carbolithiation of alkenes with external chiral induction have therefore attracted considerable interest.[6] Moreover, we were able to accomplish the first stereoselective intramolecular carbolithiation of alkynes.[7]

Our approach to stereoselective intramolecular carbolithiation reactions (C) is based on the fusion of the concepts of the enantiotopos-differentiating deprotonation (A) and the stereospecific intramolecular carbolithiation (B)[5,7] (Scheme 1).

The asymmetric deprotonation (A) of carbamic esters **2** derived from primary alkanols with the chiral base *s*-BuLi/(−)-sparteine (*s*-BuLi/**1**) and the subsequent stereospecific electrophilic substitution of the intermediate lithium−carbanion pairs with external electrophiles represent a powerful tool for the synthesis of enantioenriched secondary alkanols **3** (**2** → **3**).[8] The intramolecular carbolithiation (B) of alkenes[9] and alkynes[10,11] of type **4**, respectively, is a well-known, high-yielding process with the carbon−carbon multiple bond acting as an internal electrophile since the pioneering work of Bailey (**4** → **5**). The fusion of both methods A and B, applied to alkynes,

† Fax: (+49) 251-8339772.

(1) Crystal structure analyses.

(2) For reviews, see: (a) Marek, I.; Normant, J. F. In *Metal-catalyzed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 271−337. (b) Knochel, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 4, pp 865−911. (c) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841−871. (d) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333−2356.

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(6) For enantiospecific intramolecular carbolithiations starting from enantiomerically enriched α-amino- and α-oxy-substituted stannanes, see: (a) Coldham, I.; Hufton, R.; Snowden, D. *J. Am. Chem. Soc.* **1996**, *118*, 5322−5323. (b) Tomooka, K.; Komine, N.; Nakai, T. *Tetrahedron Lett.* **1997**, *38*, 8939−8942. For a diastereofacially controlled intramolecular carbolithiation, see: Krief, A.; Bousbaa, J. *Synlett* **1996**, 1007−1009.

(7) For a preliminary communication of our work, see: Oestreich, M.; Fröhlich, R.; Hoppe, D. *Tetrahedron Lett.* **1998**, *39*, 1745−1748.

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(11) (a) For a first report, see: Ward, H. R. *J. Am. Chem. Soc.* **1967**, *89*, 5517−5518. (b) Subsequent investigations presented convincing evidence that free radicals are involved under Ward's conditions: Ohnuki, T.; Yoshida, M.; Simamura, O. *Chem. Lett.* **1972**, 999−1004.

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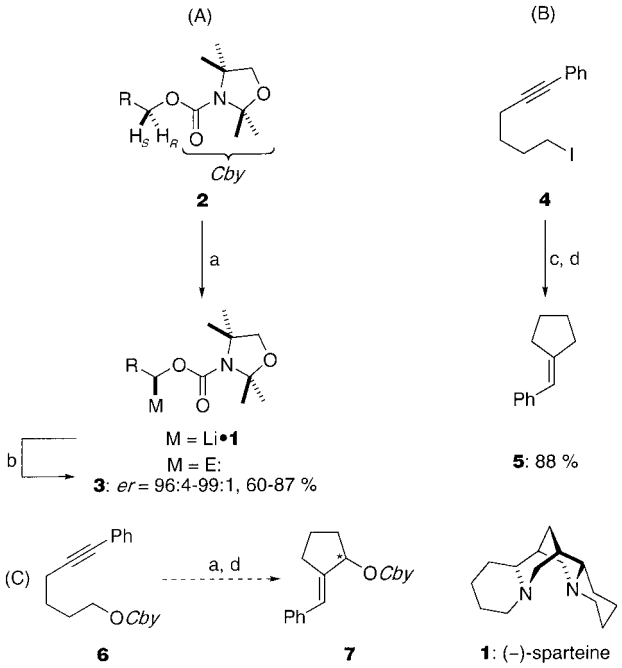
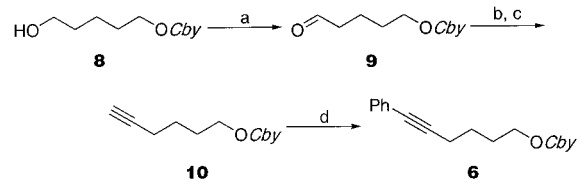
Scheme 1[a]



[a] *reagents.* a. *s*-BuLi/**1**, Et_2O, −78 °C. b. EX, −78 °C to rt. c. *t*-BuLi, Et_2O/pentane (3:2), −78 °C then warm. d. MeOH, −78 °C to rt. R = alkyl, E = electrophile. X = leaving group.

Scheme 2[a]



[a] *reagents.* a. $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C, 87%. b. CBr_4, PPh_3, CH_2Cl_2, 0 °C, 92%. c. *n*-BuLi, THF, −78 °C to rt, 90%, d. $Pd(PPh_3)_2Cl_2$, CuI, PhI, Et_3N, rt, 88%.

results in a transformation such as C (**6** → **7**) with control of the stereochemistry of the resulting double bond and stereoselectively creating a new stereocenter at the former lithium-bearing carbon atom.

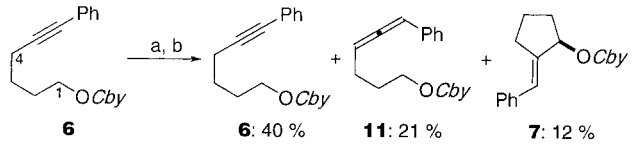
Herein, we wish to report our comprehensive studies toward the stereoselective carbolithiation (C) of several terminally substituted 5-hexynyl carbamates.[7]

Results and Discussion

Phenyl-Substituted Alkynes. The requisite 6-phenyl-5-hexynyl carbamate **6** was prepared by following the reaction sequence summarized in Scheme 2.

A Swern oxidation[12a] of the alkanol **8**[13] gave the aldehyde **9** which was then transformed into the terminal alkyne **10** by the Corey−Fuchs formyl ethynyl conversion.[14] After the cross-coupling of **10** with iodobenzene following the Sonogashira protocol[15] the cyclization precursor **6** was isolated in an overall yield of 64%.

The treatment of a solution of **6** in Et_2O with *s*-BuLi/**1** at −78 °C for 18 h (step a) produced after quenching with methanol (step b) a mixture of **6**, the allene **11**, and the desired cyclopentane **7**[16] (eq 1).



The low yield of **7** proved to be already optimal since any change of the reaction conditions (temperature, −78, −60, or −40 °C; solvent, Et_2O or toluene)[17a] lead to a decrease of the yield. These observations are due to the relatively high acidity of the propargylic protons at C-4 competing with the kinetic acidity of the activated protons at C-1 as indicated by the presence of the allene **11**. The abstraction of acidic protons, particularly terminal and propargylic, has generally been a major difficulty in the carbolithiation of alkynes.[2c] As a résumé, the formation of small amounts of **7** indicates that, in principle, the concepts A and B could be successfully fused if the deprotonation in the propargylic position is suppressed.

We became aware of a communication by Marek and Normant, who investigated in another context the deprotonation of 3-hydroxy-1,7-diynes with *s*-BuLi in THF.[18] The abstraction of a propargylic proton could be directed in dependence on the steric bulk of the hydroxy protecting group toward the less sterically hindered position with moderate regioselectivity. Consequently, a complete blocking of the deprotonation in the propargylic position could possibly be achieved by the introduction of a large substituent such as *N*,*N*-dibenzylamino, trityloxy, or silyloxy groups at C-4 in **6** *and* the use of a sterically demanding base such as *s*-BuLi/**1**.

The refinement of the 6-phenyl-5-hexynyl carbamate **6** lead to the cyclization precursors **12** and **13** which were synthesized in both enantioenriched and racemic forms. The enantiomerically pure 4-amino-6-phenyl-5-hexynyl carbamate (*S*)-**12** was prepared in six steps from the previously described alkanol (*S*)-**14** which is derived from (*S*)-glutamic acid[19] (Scheme 3).

The phenyl-substituted triple bond was again introduced by employing the four-step sequence consisting of a Swern oxidation,[12] a Corey−Fuchs conversion,[14] and a Sonogashira coupling[15] wherein the intermediate α-stereogenic aldehyde[12b] did not suffer racemization.[20] Afterward the resulting propargylic amine (*S*)-**15** was desily-

(12) (a) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480−2482. (b) For an excellent review on the synthesis and reactions of *N*,*N*-dibenzylamino aldehydes, see: Reetz, M. T. *Chem. Rev.* **1999**, *99*, 1121−1162.

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(14) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769−3772.

(15) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

(16) The (*E*)-configuration of the double bond was assigned by a nuclear Overhauser effect of the vinylic proton and the proton at the carbon bearing the carbamate group.

(17) (a) Oestreich, M. Dissertation, Universität Münster, 1999. (b) Further functionalization of the alkylidene cyclopentanes in the vinylic position was representatively demonstrated for the stannylation of the intermediate vinylic lithium species.

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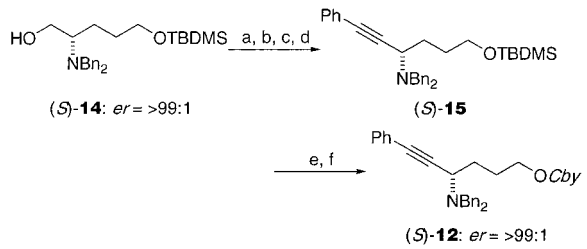
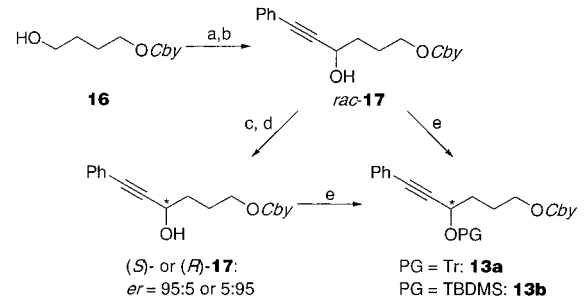
Scheme 3[a]



[a] *reagents*. a. $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C, 90%. b. CBr_4, PPh_3, CH_2Cl_2, 0 °C 69%. c. *n*-BuLi, THF, −78 °C to rt, 93%. d. $Pd(PPh_3)_2Cl_2$, CuI, PhI, Et_3N, rt, 94%. e. TBAF, Et_2O, THF, rt, 94%. f. *Cby*Cl, NaH, THF, reflux, 64%.

Scheme 4[a]



[a] *reagents*. a. $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C, 89%. b. *n*-BuLi, phenylacetylene, THF, −78 °C to −18 °C, 99%. c. PCC, sodium acetate, CH_2Cl_2, rt, 69%. d. (*S*)-Alpine borane, rt, 85% or (*R*)-Alpine borane, rt, 77%. e. PG = Tr: TrCl, Et_3N, DMAP, CH_2Cl_2, reflux, *rac*: 54%, (*S*): 45%, (*R*): 46%. PG = TBDPS: TBDPSCl, Et_3N, DMAP, CH_2Cl_2, reflux, *rac*: 100%, (*S*): 94%.

lated[21] and subsequently reacted with *Cby*Cl[22] furnishing the desired enantiopure cyclization precursor (*S*)-**12** in 33% overall yield from (*S*)-**14**.

The racemic and enantiomerically enriched 4-hydroxy-6-phenyl-5-hexynyl carbamates **13** were prepared within a straightforward synthesis as outlined in Scheme 4.

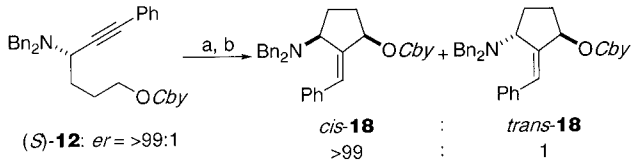
The Swern oxidation[12a] of the alkanol **16**[13] provided the corresponding aldehyde which was quantitatively alkynylated with *n*-BuLi/phenylacetylene. After the oxidation of the resulting propargylic alkanol *rac*-**17** with PCC the intermediate α,β-ynone was reduced with (*S*)- or (*R*)-Alpine-borane,[23] respectively, furnishing the alkanols (*S*)-**17** and (*R*)-**17**, respectively, in enantiomeric ratios of 95:5 and 5:95.[24] The absolute configuration of the propargylic alcohols **17** can be predicted by a model in which a six-membered transition state exhibits a boatlike conformation;[25] (*S*)-Alpine-borane provides the (*S*)-configured alkanol and vice versa in any known case if the alkynyl group is of higher priority than the alkyl group.[26] The tritylation[27] (PG = Tr) or silylation (PG = TBDMS) of the all three alkanols **17** completed the syntheses providing the cyclization precursors **13a**,**b** in overall yields of 21−48% for **13a** and 48−88% for **13b**.

Table 1. Stereoselective Cyclization of 4-Substituted 6-Phenyl-5-hexynyl Carbamates

entry	alkyne	er[a]	carbocycle[b,16]	dr[c]	yield[d]/%
1	(*S*)-**12**	>99:1	*cis*-**18**	>99:1	70
2	(*S*)-**13a**	95:5	*cis*-**19a**	95:5	88
3	(*R*)-**13a**	5:95	*trans*-**19a**	5:95	99
4	*rac*-**13a**	50:50	*cis*-/*trans*-**19a**	50:50	80[e]
5	(*S*)-**13b**	95:5	*cis*-**19b**	95:5	82
6	*rac*-**13b**	50:50	*cis*-/*trans*-**19b**	50:50	96
7[f]	(*S*)-**13b**	95:5	*cis*-/*ent*-*trans*-**19b**	50:50	89

[a] The er was determined from the ^1H NMR and ^{19}F NMR spectra of the Mosher esters (except for compound (*S*)-**12**). [b] Each diastereomer is enantiopure. [c] The dr (cis:trans ratio) was determined from the ^1H NMR spectra of the crude products. [d] Isolated yield of analytically pure product. [e] Mixture of *rac*-**13a** and *cis*-/*trans*-**19a** (20:80). [f] In this case TMEDA (**20**) was used instead of (−)-sparteine (**1**); the diastereomers *cis*-**19b** (1*R*,3*S*) and *ent*-*trans*-**19b** (1*S*,3*S*) are both formed with enantiomeric ratios of 95:5.

Using the standard conditions, to a solution of the 4-(dibenzylamino)-6-phenyl-5-hexynyl carbamate (*S*)-**12** in Et_2O, the chiral base *s*-BuLi/**1** was added at −78 °C (step a); then the reaction mixture was allowed to stir for 20 h at this temperature followed by quenching with methanol (step b). The purification, surprisingly, afforded the desired alkylidene cyclopentane *cis*-**18** in diastereomerically pure[16] form as a single product in 70% yield (eq 2, Table 1, entry 1).



This promising result prompted us to investigate the (*S*)-configured 4-alkoxy- (*S*)-**13a** and 4-siloxy-6-phenyl-5-hexynyl carbamate (*S*)-**13b** which upon treatment with *s*-BuLi/**1** in Et_2O also cyclized smoothly (Scheme 5, Table 1, entries 2 and 5).

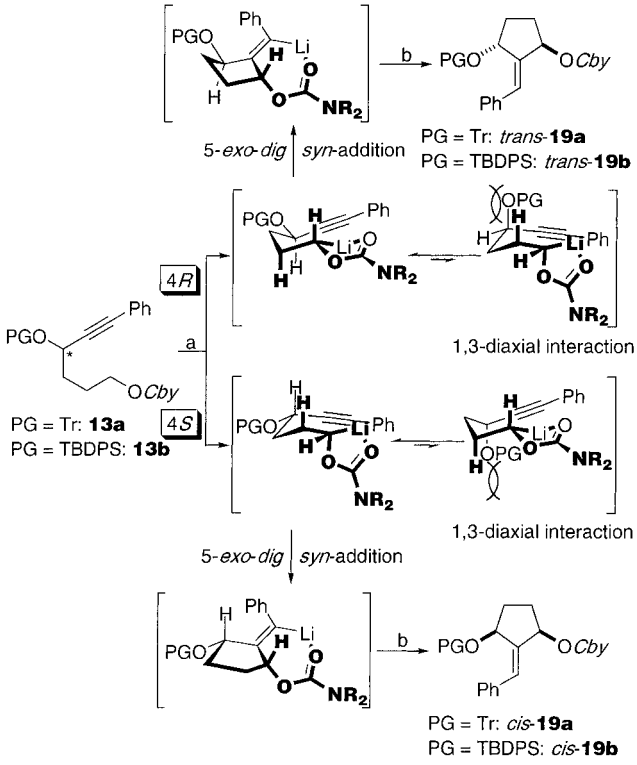
The diastereomeric ratio (cis:trans = 95:5) of the functionalized cyclopentanes *cis*-**19a** and *cis*-**19b** directly corresponded to the enantiomeric ratio (er = 95:5) of each individual cyclization precursor (*S*)-**13**. The relative configuration of the carbocycles derived from (*S*)-configured alkynes was determined on the basis of a crystal structure analysis of *cis*-**19a** (Figure 1).[28] The (1*R*)-configuration at the former lithium-bearing carbon atom coincides with our observations that carbamates of type **2** (Scheme 1) are deprotonated by chiral base *s*-BuLi/**1** with high preference for the *pro*-*S*-proton and the resulting lithium−carbanion pairs are substituted by electrophiles with retention of the configuration.[5,8a−c]

These instructive experiments (Table 1, entries 1, 2, and 5) obviously confirm that the deprotonation of

(21) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190−6191.
(22) Hintze, F.; Hoppe, D. *Synthesis* **1992**, 1216−1218.
(23) For a representative procedure, see: Brown, H. C.; Pai, G. G. *J. Org. Chem.* **1985**, *50*, 1384−1394.
(24) The enantiomeric ratios were determined by Mosher ester analysis: Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543−2549.
(25) Midland, M. M.; McLoughlin, J. I.; Gabriel, J. *J. Org. Chem.* **1984**, *49*, 1316−1317.
(26) For a review, see: Midland, M. M. *Chem. Rev.* **1989**, *89*, 1553−1561.
(27) Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, *20*, 95−98.

(28) X-ray crystal structure analysis of *cis*-**19a**: formula $C_{39}H_{41}NO_4$, M = 587.73, 0.2 × 0.1 × 0.1 mm, a = 8.837(1) Å, b = 15.141(2) Å, c = 24.831(3) Å, V = 3322.4(7) Å^3, ρ_{calc} = 1.175 g cm^{-3}, μ = 5.93 cm^{-1}, empirical absorption correction via ψ-scan data (0.950 ≤ C ≤ 0.999), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 1.541 78 Å, T = 223 K, ω/2θ scans, 3795 reflections collected (+h,−k,+l), [(sin θ)/λ] = 0.62 Å^{-1}, 3795 independent and 1737 observed reflections [$I \geq 2\sigma(I)$], 402 refined parameters, R = 0.050, wR^2 = 0.103, maximum residual electron density 0.19 (−0.18) e Å^{-3}, Flack parameter 1.0(5), hydrogens calculated and riding (structure was already published in ref 7). See also ref 35.

Scheme 5[a]



[a] *reagents*. a. *s*-BuLi/**1**, Et_2O, −78 °C. b. MeOH, −78 °C to rt. Ligands (**1** and Et_2O) at the lithium center are omitted for the sake of clearness.

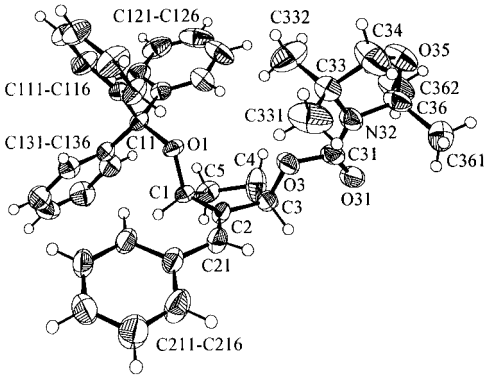
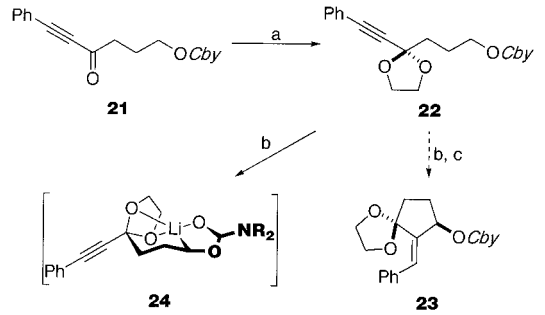


Figure 1. Crystal structure of *cis*-**19a**.

propargylic hydrogens is entirely suppressed by the introduction of a bulky substituent in this position and the use of a sterically demanding base. Nevertheless, since solely (*S*)-configured precursors were cyclized in the presence of (−)-sparteine (**1**), two questions arise concerning the influence of the existing stereocenter in the alkyne: (a) Can a racemic alkyne be kinetically resolved in the presence of **1**?[5b,c,29] (b) Can a stereoselective deprotonation be internally induced by the propargylic stereocenter using the achiral base *s*-BuLi/TMEDA (*s*-BuLi/**20**)?[19a,30]

The cyclization of the (*R*)-configured alkyne (*R*)-**13a** itself was accomplished under the standard reaction conditions furnishing the trans-substituted cyclopentane *trans*-**19a** in quantitative yield (Scheme 5, Table 1, entry 3). Thus, the chiral base *s*-BuLi/**1** selectively abstracts the *pro-S*-proton independent of the configuration of the propargylic stereocenter. The racemic precursors *rac*-**13a** and *rac*-**13b** were also treated with *s*-BuLi/**1** in Et_2O for several hours at −78 °C. The NMR analysis of the crude products exhibited a mixture of the diastereomeric carbocycles *cis*-/*trans*-**19a** or *cis*-/*trans*-**19b** in cis:trans ratios of 50:50 even when the cyclization had not been completed yet (Scheme 5, Table 1, entries 4 and 6). The fact that the er of the starting material is in full agreement with the dr of the cyclization product certifies that there is no kinetic resolution of the enantiomeric alkynes operating.

Scheme 6[a]



[a] *reagents*. a. $(TMSOCH_2)_2$, TMSOTf, CH_2Cl_2, −78 °C, 31%. b. *s*-BuLi/**1**, Et_2O, −78 °C. c. MeOH, −78 °C to rt.

The effect of the existing stereogenic center on the stereochemical course of the deprotonation step was checked in a simple experiment by replacing (−)-sparteine (**1**) by the achiral ligand TMEDA (**20**) within the cyclization of the enantioenriched carbamate (*S*)-**13b**. Since the ring closure yielded a 50:50 mixture of *cis*-/*ent-trans*-**19b**, epimers at the former lithium-bearing carbon atom, the deprotonation of (*S*)-**13b** proceeded completely unselectively indicating that the formation of the new stereocenter is not influenced by the existing one (Table 1, entry 7).[17]

Another more evident strategy to suppress propargylic deprotonation is the introduction of two substituents at C-4. The dioxolane **22** was chosen as a model system and was prepared in one step from the α,β-ynone **21** previously described in Scheme 4. Quite a number of ketalizations failed because of the lability of the aminoacetal moiety in the *Cby* group until Noyori's method[31] gave **22** in 31% yield (Scheme 6).

Upon treatment of the carbamate **22** with *s*-BuLi in the presence of **1** no ring closure was observed. Instead of isolation of the expected cyclopentane derivative **23** after methanolysis only the starting material **22** was detected in the ^1H NMR spectra of the crude reaction mixture. The intermediacy of the stable tricyclic chelate **24** appears to be very likely since such interactions had been reported by us for similar systems.[32] The intramolecular coordination of the lithium center by three oxygens delineates a thermodynamic sink preventing the precomplexation of the lithium to the triple bond (Scheme 6).

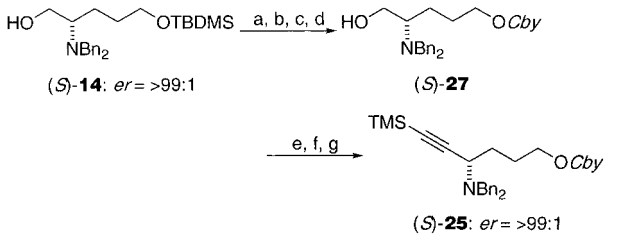
(29) For kinetic resolutions using the *s*-BuLi/**1** reagent, see also: (a) Haller, J.; Hense, T.; Hoppe, D. *Synlett* **1993**, 726−728. (b) Hense, T.; Hoppe, D. *Synthesis* **1997**, 1394−1398.

(30) See for example: Schwerdtfeger, J.; Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1505−1507.

(31) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357−1358.

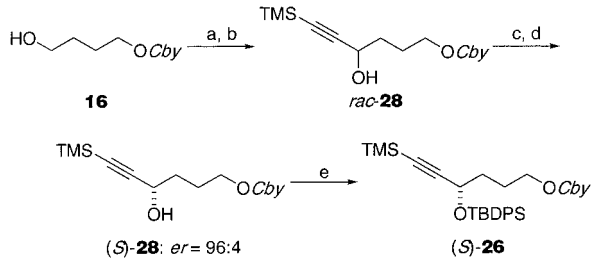
(32) An dioxolane ring acting as a chelating group during carbamate lithiation has been described before: Helmke, H.; Hoppe, D. *Synlett* **1995**, 978−980.

Scheme 7[a]



[a] *reagents.* a. TrCl, Et_3N, CH_2Cl_2, rt, 100%. b. TBAF, Et_2O, THF, rt, 100%. c. *Cby*Cl, NaH, THF, reflux, 87%. d. TFA, MeOH/CH_2Cl_2 (1:1), 0 °C to rt, 78%. e. $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C, 96%, f. CBr_4, PPh_3, CH_2Cl_2, 0 °C, 93%. g. *n*-BuLi, THF, −78 °C then TMSCl, −78 °C to rt, 83%.

Scheme 8[a]



[a] *reagents.* a. $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C, 89%. b. *n*-BuLi, trimethylsilylacetylene, THF, −78 °C to −18 °C, 96%. c. PCC, sodium acetate, CH_2Cl_2, rt, 82%. d. (*S*)-Alpine borane, rt, 96%. e. TBDPSCl, Et_3N, DMAP, CH_2Cl_2, reflux 94%.

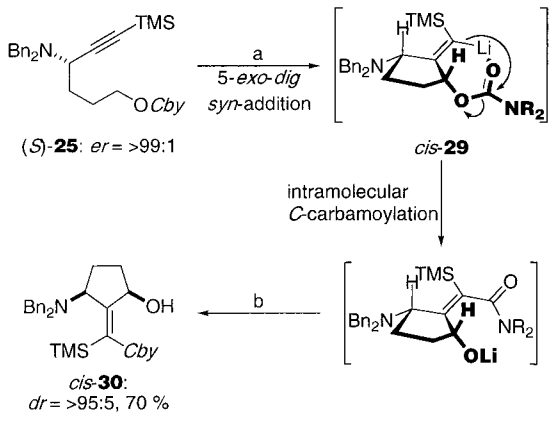
Trimethylsilyl-Substituted Alkynes. The activation of alkynes toward nucleophilic attack by terminal substituents can also be achieved by the introduction of a trimethylsilyl group[10b,d] since carbanionic centers are stabilized by α-silyl groups.[33] Therefore we synthesized the carbamates (*S*)-**25** and (*S*)-**26**—again with the essential propargylic substituent—corresponding to (*S*)-**12** and (*S*)-**13b**, respectively.

The synthesis of the 4-amino-6-(trimethylsilyl)-5-hexynyl carbamate (*S*)-**25** starting from the enantiopure alkanol (*S*)-**14**[19] is summarized in Scheme 7. After standard protecting group manipulations[19c] the alkanol (*S*)-**27** was isolated in 68% overall yield.[34] The trimethylsilyl-substituted alkyne moitey was again constructed by applying the reaction sequence of Swern oxidation[12] and a slightly modified Corey−Fuchs conversion[14] to (*S*)-**27**. The cyclization precursor (*S*)-**25** was isolated after seven steps from (*S*)-**14** in an overall yield of 52%.

The 4-hydroxy-6-(trimethylsilyl)-5-hexynyl carbamate (*S*)-**26** was prepared in analogy to the phenyl-substituted derivative (*S*)-**13b** (see Scheme 4) from **16**[13] by following the procedure depicted in Scheme 8. The (*S*)-Alpineborane[23] reduction gave the (*S*)-**28** in an enantiomeric ratio of 96:4.[24]

The cyclization experiment of (*S*)-**25** was conducted under the standard conditions (*s*-BuLi/**1**, Et_2O, −78 °C, several hours), but the analysis of the crude reaction mixture by TLC surprisingly indicated a major product of significantly higher polarity than the starting material (*S*)-**25** whereas in the case of the phenyl-substituted alkynes the cyclization precursor and product were of similar polarity and difficult to separate. The purification by flash chromatography then furnished *cis*-**30** in 70% yield along with 10% of (*S*)-**25** (Scheme 9). The constitution of *cis*-**30** was assigned on the basis of a single-crystal structure analysis (Figure 2).[35] Furthermore, the absolute configuration was determined as [2(2*R*),2(5*S*)], which is in agreement with the fact that the cyclization precursor is derived from (*S*)-glutamic acid and the observation that the (1*S*)-configured lithium−carbanion pair inserts the triple bond with retention of the configuration.

Scheme 9[a]



[a] *reagents.* a. *s*-BuLi/**1**, Et_2O, −78 °c. b. MeOH, −78 °C to rt. Ligands (**1** and Et_2O) at the lithium center are omitted for the sake of clearness.

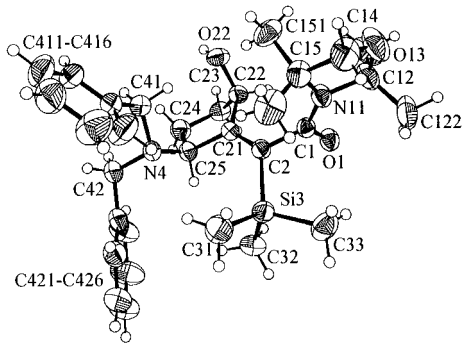


Figure 2. Crystal structure of *cis*-**30**.

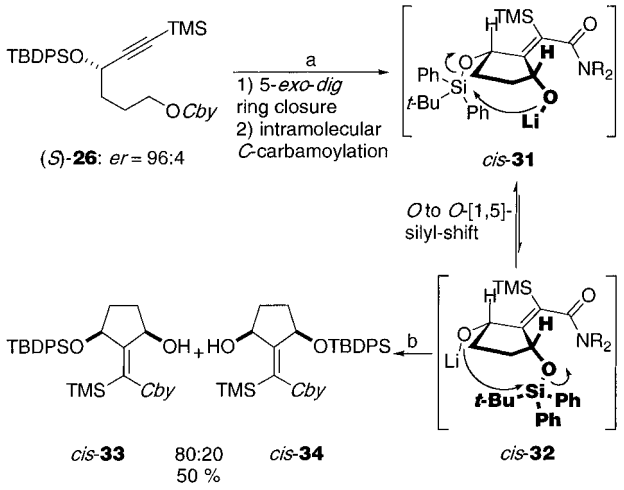
The carbocycle *cis*-**30** is the outcome of a domino-cyclization/rearrangement sequence[36] in which the intermediate vinylic lithium species *cis*-**29** is intramolecularly captured by the carbamic ester group (O*Cby*). The intramolecular carbolithiation of the trimethylsilyl-substituted triple bond proceeded highly regioselectively in a *syn*-fashion providing the vinylic lithium compound *cis*-**29**. The (1-silyl-1-alkenyl)lithium *cis*-**29** seems to be more reactive than the corresponding phenyl-substituted derivative and therefore attacks the carbonyl carbon atom in the proximity of the carbon−lithium bond giving a lithium alcoholate and, finally, the fully substituted acrylamide *cis*-**30**.

To prove whether this domino-cyclization/rearrangement sequence is a general reaction of trimethylsilyl-substituted alkynes we investigated the 4-hydroxy-6-(trimethylsilyl)-5-hexynyl carbamate (*S*)-**26**. Upon treatment with *s*-BuLi/**1** in Et_2O at −78 °C the precursor (*S*)-

(33) (a) Sakurai, H. *Organosilicon and Bioorganosilicon Chemistry: Structure, Bonding, Reactivity, and Synthetic Applications*; Halsted: New York, 1985. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

(34) Unfortunately, this lengthy sequence is required since the direct carbamoylation of (*S*)-2-(*N*,*N*-dibenzylamino)-1,5-pentanediol with *Cby*Cl[22] provided a 1:1 mixture of (*S*)-**27** and its regioisomer. After a difficult separation of the regioisomers by flash chromatography (*S*)-**27** was isolated in 29% yield.

Scheme 10[a]



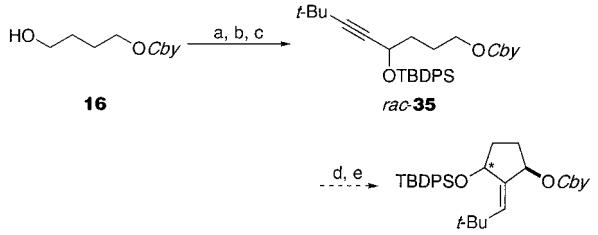
[a] *reagents*. a. *s*-BuLi/**1**, Et_2O, −78 °C. b. MeOH, −78 °C to rt. Ligands (**1** and Et_2O) at the lithium center are omitted for the sake of clearness.

26 in fact cyclizes and rearranges in the predicted manner as illustrated in Scheme 10.

But the carbocycle *cis*-**33** which is the primary product of the domino reaction was contaminated with a further cyclization product which was identified as the regioisomer *cis*-**34** from the ^{1}H NMR spectra. The formation of *cis*-**34** is due to a *O* to *O*-[1,5] silyl shift of the TBDPS ether having a lithium alcoholate in its proximity. The capability of silyl groups of type SiR_3 to undergo anionic migrations in dependence on the steric demand of the group R—the larger R, the more unlikely is the shift of SiR_3—has been extensively discussed, and examples of migrating TBDPS groups are scarce.[37] We think that the ease of this [1,5]-shift can be attributed to the steric situation in the cis-1,3-substituted carbocycles *cis*-**31** and *cis*-**32**.[38] The resulting products *cis*-**33** and *cis*-**34** were isolated in a ratio of 80:20 in 50% yield.[39]

***tert*-Butyl-Substituted Alkynes.** The above-mentioned studies are compatible with previous observations that a terminal phenyl or trimethylsilyl substituent accelerates the insertion of a carbon−carbon triple bond into a carbon−lithium bond.[10] In contrast, the activity of alkynes bearing an alkyl group in the terminal position toward nucleophilic attack is significantly lowered although Bailey has reported the cyclization of a *n*-butyl-substituted alkyne.[10a,d] The possibilty of 1,3-allylic strain[40] in the cyclization products has not been considered for the ring closures of the *tert*-butyl- as well as phenyl- and trimethylsilyl-substituted alkynes since we think that this steric effect plays a minor role in these processes.

Scheme 11[a]



[a] *reagents*. a. $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C, 89%. b. *n*-BuLi, 3,3-dimethyl-1-butyne, THF, −78 °C to −18 °C to −18 °C, 100%. c. TBDPSCl, Et_3N, DMAP, CH_2Cl_2, reflux, 88%. d. *s*-BuLi/**1**, Et_2O, −78 °C. e. MeOH, −78 °C to rt.

The racemic cyclization precursor *rac*-**35**, easily prepared from alkanol **16** by our standard reaction sequence in 78% overall yield, could not be cyclized in the presence of the chiral base *s*-BuLi/**1** in Et_2O at −78 °C (Scheme 11); *rac*-**35** was reisolated in 91% yield.

Conclusion

In summary, we have reported the first stereoselective carbolithiiation of alkynes with external chiral induction on the basis of the fusion of the concepts of the asymmetric deprotonation[8] (A) and the intramolecular carbolithiation[9,10] (B). Our studies show that the success of the cyclization is strongly dependent on two essential supplementary features in order to avoid propargylic deprotonation: a sterically demanding substituent in the propargylic position *and* the use of a large base. The 4-substituted 5-hexynyl carbamates undergo the ring closure highly regioselectively (5-*exo*-*dig* exclusively), diastereoselectively as the double bond is concerned (*syn*-addition of the lithium−carbanion pair to the triple bond), and diastereoselectively with respect to the newly formed stereocenter (retention of the configuration at the former lithium-bearing carbon atom). Terminal substituents such as a phenyl or trimethylsilyl group facilitate the insertion of the carbon−carbon triple bond into the carbon−lithium bond whereas a *tert*-butyl-substituted alkyne is too electron-rich for being nucleophilically attacked under our reaction conditions. Moreover, the intermediate (1-(trimethylsilyl)-1-alkenyl)lithium and (1-phenyl-1-alkenyl)lithium species, respectively, are of different reactivity with the further being more reactive and quantitatively intramolecularly captured by the carbamate.

This novel method allows the stereoselective synthesis of enantiopure functionalized alkylidene cyclopentanes in good to excellent yields and selectivities.

(35) X-ray crystal structure analysis of *cis*-**30**: formula $C_{31}H_{44}N_2O_3Si$, $M = 520.77$, 0.6 × 0.5 × 0.3 mm, $a = 10.259(1)$ Å, $b = 13.099(1)$ Å, $c = 23.465(2)$ Å, $V = 3153.3(5)$ Å^3, $\rho_{calc} = 1.097$ g cm^{-3}, $\mu = 8.94$ cm^{-1}, empirical absorption correction via ψ-scan data ($0.969 \le C \le 0.999$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 1.541\,78$ Å, $T = 223$ K, $\omega/2\theta$ scans, 6394 reflections collected ($-h,+k,\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 6004 independent and 5689 observed reflections [$I \ge 2\sigma(I)$], 373 refined parameters, $R = 0.038$, $wR^2 = 0.106$, max. residual electron density 0.17 (−0.17) e Å^{-3}, Flack parameter 0.01(2), disorder (51%:49%) around C15 (C14 and C151), hydrogens calculated and riding. The data set was collected with an Enraf Nonius CAD4 diffractometer. Programs used: data acquisation EXPRESS; data reduction MolEN; structure solution SHELXS-86; structure refinement SHELXL-93 and SHELXL-97; graphics DIAMOND.

(36) For domino reactions, see: Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115−136.

(37) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981.

(38) The migration of a TBDPS group in a *cis*-1,3-cyclopentanediol system has already been observed: Torisawa, Y.; Shibasaki, M.; Ikegami, S. *Chem. Pharm. Bull.* **1983**, *31*, 2607−2615. We thank one of the reviewers for drawing our attention to this reference.

(39) Another byproduct which was void of the trimethylsilyl group, compared to *cis*-**34**, was isolated in small quantities. The loss of the trimethylsilyl group may be due to the fact the lithium−oxygen bond in *cis*-**32** is in the proximity of two silyl groups. A *O* to *O*-[1, 5]-shift regenerates the primary product *cis*-**31**, and a *C* to *O*-[1, 4]-shift of the trimethylsilyl group leads to the *C*-desilylated product after aqueous workup. For an example of such a migration, see eq 2 in: Lautens, M.; Delanghe, P. H. M.; Goh, J. B.; Zhang, C. H. *J. Org. Chem.* **1992**, *57*, 3270−3272.

(40) For a comprehensive review on 1,3-allylic strain, see: Hoffmann. R. W. *Chem. Rev.* **1989**, *89*, 1841−1860.

Experimental Section

General Methods.[5c] The doubling of some signals in the NMR spectra occurs as a result of the *E*/*Z* isomerism of the carbamate group; these signals are separated by slashes. (−)-Sparteine (**1**) is commercially available (Aldrich or Sigma) and was stored under argon; TMEDA (**20**) was distilled from CaH_2 and kept under argon. *s*-BuLi was received as a 1.4 M solution in cyclohexane/*n*-hexane (92:8) from Fluka and *n*-BuLi as a 1.6 M solution in *n*-hexane from Acros; both were titrated before use.[41]

Typical Procedure for the Corey−Fuchs Formyl Ethynyl Conversion.[14] 5-Hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (10). Step A. After cooling of a solution of tetrabromomethane (5.23 g, 15.8 mmol, 2.0 equiv) and triphenylphosphine (8.28 g, 31.6 mmol, 4.0 equiv) in CH_2Cl_2 (80 mL) to 0 °C, the aldehyde **9** (2.03 g, 7.89 mmol), dissolved in CH_2Cl_2 (20 mL), was slowly added. The reaction was monitored by TLC and quenched with H_2O (10 mL) after complete conversion of **9** (1 h). The organic layer was separated, the aqueous phase extracted twice with CH_2Cl_2, and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product, dissolved in a small volume of CH_2Cl_2, purified by flash chromatography (1:1 Et_2O−hexanes; TLC, R_f = 0.53) furnishing 6,6-dibromo-5-hexenyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (**36**) (3.00 g, 92%) as a colorless liquid. IR (neat, cm^{-1}): 1695 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.37 (t, J = 7.4 Hz, 1H), 4.07 (t, J = 6.4 Hz, 2H), 3.70 (s, 2H), 2.12 (ψ-q, J = 7.4 Hz, 2H), 1.74−1.58 (m, 2H), 1.57−1.45 (2s, m, 8H), 1.39/1.34 (2s, 6H). ^{13}C NMR ($CDCl_3$, 90 MHz): δ 152.7/152.0, 138.0, 95.8/94.7, 89.3, 76.3/76.1, 63.9, 60.5/59.6, 32.5, 28.4, 24.5, 26.5/25.3/24.1. MS (EI): m/z 398 [$(M - CH_3)^+$, 100%]. Anal. Calcd for $C_{14}H_{23}NO_3Br_2$: C, 40.70; H, 5.61; N, 3.39. Found: C, 40.37; H, 5.66; N, 3.58.

Step B. At −78 °C, *n*-BuLi (3.0 mL, 4.84 mmol, 2.0 equiv, 1.6 M) was added dropwise to a solution of **36** (1.000 g, 2.42 mmol) in THF (35 mL). The solution was stirred for 1 h at −78 °C and was then allowed to warm to ambient temperature. After a further 90 min at this temperature the reaction mixture was first quenched with methanol (3 mL) and afterward hydrolyzed with H_2O (5 mL). The organic layer was separated, the aqueous phase was extracted with Et_2O, and the combined organic phases were dried with Na_2SO_4. After evaporation of the solvents in vacuo the crude product was purified by flash chromatography (1:9 Et_2O−hexanes; TLC, R_f = 0.27) yielding **10** (0.550 g, 90%) as a colorless liquid. IR (neat, cm^{-1}): 3306 (≡C−H, m), 2110 (C≡C, w), 1701 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 4.08 (t, J = 6.3 Hz, 2H), 3.69 (s, 2H), 2.21 (dt, J = 6.9 Hz, J = 2.6 Hz, 2H), 1.92 (t, J = 2.6 Hz, 1H), 1.81−1.71 (m, 2H), 1.66−1.53 (m, 2H), 1.52/1.49/1.39/1.33 (4s, 12H). ^{13}C NMR ($CDCl_3$, 90 MHz): δ 152.7/152.0, 95.7/94.7, 83.8, 76.2/76.0, 68.6, 63.9, 60.5/59.6, 28.2, 25.2, 26.5/25.3/25.1/24.1, 18.0. MS (EI): m/z 238 [$(M - CH_3)^+$, 100%]. Anal. Calcd for $C_{14}H_{23}NO_3$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.28; H, 9.24; N, 5.67.

Typical Procedure for the Sonogashira Coupling.[15] 6-Phenyl-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (6). A mixture of copper(I) iodide (1.3 mg, 6.91 μmol) and bis(triphenylphosphine)palladium(II) dichloride (9.7 mg, 13.8 μmol) was suspended in a solution of **10** (0.350 g, 1.38 mmol) and iodobenzene (0.282 g, 1.38 mmol, 1.0 equiv) in Et_3N (9 mL) at ambient temperature. The reaction mixture was stirred for 6 h at this temperature before the addition of 1 M HCl (25 mL). The organic layer was separated, and the aqueous phase was extracted with Et_2O several times. The combined organic phases were washed with H_2O and dried with Na_2SO_4. After removal of the solvents under reduced pressure the crude product was purified by flash chromatography (1:2 Et_2O−hexanes; TLC, R_f = 0.54 in 1:1 Et_2O−hexanes) furnishing the cross-coupled product **6** (0.400 g, 88%) as a colorless liquid. IR (neat, cm^{-1}): 1696 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.43−7.36 (m, 2H), 7.29−7.25 (m, 3H), 4.17 (t, J = 6.2 Hz, 2H), 3.74 (s, 2H), 2.49 (t, J = 6.8 Hz, 2H), 1.93−1.81 (m, 2H), 1.80−1.67 (m, 2H), 1.58/1.56/1.44/1.40 (4s, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.8/152.1, 131.5, 128.1, 127.5, 123.8, 95.8/94.8, 89.4, 81.0, 76.6/76.3, 64.0, 60.5/59.6, 28.2, 25.5, 26.6/25.3/24.1, 19.1. MS (EI): m/z 329 [M^+, 18%]. Anal. Calcd for $C_{20}H_{27}NO_3$: C, 72.92; H, 8.26; N, 4.25. Found: C, 72.77; H, 8.25; N, 4.51.

Typical Procedure for the Stereoselective Cyclocarbolithiation of Alkynes. (−)-[1*R*,2(1*E*)]-2-Benzylidenecyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (7). To a solution of **6** (0.300 g, 0.91 mmol) and **1** (0.320 g, 1.37 mmol, 1.5 equiv) in Et_2O (8 mL) was added *s*-BuLi (1.09 mL, 1.37 mmol, 1.5 equiv, 1.34 M) at −78 °C. This solution was stirred for 18 h at −78 °C, and after methanolysis (2.5 mL) at −78 °C the reaction mixture was brought to ambient temperature. The organic phase was washed with H_2O and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the purification of the residue by flash chromatography (1:9 Et_2O−hexanes; TLC, R_f = 0.56 in 1:1 Et_2O−hexanes) afforded **7** (0.035 g, 12%) as a white solid.[42] Mp = 87−88 °C. $[\alpha]^{20}_D$ = −21.6 (c = 0.45). IR (KBr, cm^{-1}): 1685 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.30−7.17 (m, 5H), 6.67 (s, 1H), 5.67−5.62 (m, 1H), 3.72 (s, 2H), 2.80−2.66 (m, 1H), 2.65−2.51 (m, 1H), 2.00−1.80 (m, 4H), 1.59/1.51/1.45/1.35 (4s, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.7/151.9, 143.3, 137.8, 128.3, 126.7, 126.2, 95.8/94.9, 79.1, 76.4/76.1, 60.6/59.7, 32.4, 29.6, 26.8/25.4/24.3, 23.6. MS (EI): m/z 329 [M^+, 15%]. Anal. Calcd for $C_{20}H_{27}NO_3$: C, 72.92; H, 8.26; N, 4.25. Found: C, 72.92; H, 8.27; N, 4.21.

Typical Procedure for the Swern Oxidation.[12a] (−)-(*S*)-5-(*tert*-Butyldimethylsilyloxy)-2-(*N*,*N*-dibenzylamino)-1-pentanal ((*S*)-37). A solution of oxalyl chloride (0.368 g, 2.90 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) was cooled to −78 °C and subsequently treated with a solution of DMSO (0.453 g, 5.80 mmol, 2.4 equiv) in CH_2Cl_2 (5 mL) and a solution of (*S*)-**14**[19] (1.000 g, 2.42 mmol) in CH_2Cl_2 (10 mL). The temperature of the reaction mixture was kept at −78 °C and stirred for 15 min after each addition. To this reaction mixture Et_3N (1.223 g, 12.1 mmol, 5.0 equiv) was slowly injected. The reaction mixture was stirred for further 30 min at −78 °C and after removal of the cooling bath for another 30 min at room temperature. The resulting white suspension was poured into H_2O (50 mL), and the organic layer was separated and washed with H_2O. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$). The solvents were evaporated in vacuo, and the residue was purified by flash chromatography (3:7 Et_2O−hexanes; TLC, R_f = 0.65) furnishing (*S*)-**37** (0.901 g, 90%) as a colorless liquid. $[\alpha]^{20}_D$ = −35.8 (c = 1.57). IR (neat, cm^{-1}): 1729 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 9.69 (s, 1H), 7.35−7.17 (m, 10H), 3.77 (d, J = 13.8 Hz, 2H), 3.69 (d, J = 13.8 Hz, 2H), 3.64−3.40 (m, 2H), 3.14 (ψ-t, J = 6.5 Hz, 1H), 1.82−1.65 (m, 2H), 1.58−1.49 (m, 2H), 0.87 (s, 9H), 0.01 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 203.6, 139.2, 128.8, 128.3, 127.2, 66.6, 62.5, 54.8, 30.1, 25.9, 20.5, 18.3, −5.3. MS (EI): m/z 411 [M^+, 1%]. Anal. Calcd for $C_{25}H_{37}NO_2Si$: C, 72.94; H, 9.06; N, 3.40. Found: C, 72.79; H, 8.89; N, 3.66.

(−)-(*S*)-6-(*tert*-Butyldimethylsilyloxy)-3-(*N*,*N*-dibenzylamino)-1-hexyne ((*S*)-39). Step A. According to the typical procedure for the Corey−Fuchs formyl ethynyl conversion, (*S*)-**37** (1.66 g, 4.03 mmol) was transformed into (+)-(*S*)-1,1-dibromo-6-(*tert*-butyldimethylsilyloxy)-3-(*N*,*N*-dibenzylamino)-1-hexene ((*S*)-**38**) with tetrabromomethane (2.67 g, 8.07 mmol, 2.0 equiv) and triphenylphosphine (4.23 g, 16.1 mmol, 4.0 equiv) in CH_2Cl_2 (40 mL). The crude product was purified by flash chromatography (1:1 Et_2O−hexanes; TLC, R_f = 0.76) yielding (*S*)-**38** (1.58 g, 69%) as a colorless liquid. $[\alpha]^{20}_D$ = +9.0

(41) (a) Lin, H.-S.; Paquette, L. A. *Synth. Commun.* **1994**, *24*, 2503−2506. (b) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1871−1880.

(42) The cyclization precursor **6** was reisolated in a 67:33 mixture with the allene **11**. The characteristic NMR data of **11** are as follows: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.00 (ψ-quint, J = 6.0 Hz, J = 3.1 Hz, 1H), 5.43 (ψ-quart, J = 6.8 Hz, J = 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 205.3, 95.8, 93.9.

(c = 1.09). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37−7.14 (m, 10H), 6.53 (d, J = 9.5 Hz, 1H), 3.83 (d, J = 13.8 Hz, 2H), 3.58−3.44 (m, 2H), 3.37 (d, J = 13.8 Hz, 2H), 3.41−3.36 (m, 1H), 1.80−1.61 (m, 2H), 1.58−1.40 (m, 2H), 0.86 (s, 9H), 0.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.6, 137.9, 128.7, 128.1, 126.9, 90.0, 65.8, 61.4, 54.2, 29.3, 28.3, 26.0, 18.3, −5.3. MS (EI): m/z 567 [M^+, 1%]. Anal. Calcd for $C_{26}H_{37}NOSiBr_2$: C, 55.03; H, 6.57; N, 2.47. Found: C, 55.13; H, 6.77; N, 2.75.

Step B. (*S*)-**38** (0.432 g, 0.76 mmol) was treated with *n*-BuLi (0.95 mL, 1.52 mmol, 2.0 equiv, 1.6 M) in THF (15 mL). The purification of the crude product by flash chromatography (1:4 Et_2O−hexanes; TLC, R_f = 0.71) furnished (*S*)-**39** (0.290 g, 93%) as a colorless liquid. $[\alpha]^{20}_D$ = −79.3 (c = 0.98). IR (neat, cm^{-1}): 3305 (≡C−H, m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40−7.10 (m, 10H), 3.84 (d, J = 13.8 Hz, 2H), 3.58−3.46 (m, 2H), 3.41 (d, J = 13.8 Hz, 2H), 3.44−3.39 (m, 1H), 2.32 (d, J = 2.4 Hz, 1H), 1.86−1.49 (m, 4H), 0.86 (s, 9H), 0.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.7, 128.8, 128.3, 126.9, 82.0, 72.6, 62.5, 54.8, 51.3, 30.0, 29.6, 26.0, 18.3, −5.3. MS (EI): m/z 407 [M^+, 15%]. Anal. Calcd for $C_{26}H_{37}NOSi$: C, 76.60; H, 9.15; N, 3.44. Found: C, 76.54; H, 9.40; N, 3.54.

(+)-(*S*)-6-(*tert*-Butyldimethylsilyloxy)-3-(*N*,*N*-dibenzylamino)-1-phenyl-1-hexyne ((*S*)-15). The terminal alkyne (*S*)-**39** (0.542 g, 1.33 mmol) was cross-coupled with iodobenzene (0.271 g, 1.33 mmol, 1.0 equiv) in the presence of copper(I) iodide (1.3 mg, 6.65 μmol) and bis(triphenylphosphine)palladium(II) dichloride (9.3 mg, 13.3 μmol) in Et_3N (9 mL) by following the typical procedure for the Sonogashira reaction. The crude product was purified by flash chromatography (1:9 to 1:4 Et_2O−hexanes; TLC, R_f = 0.71 in 1:4 Et_2O−hexanes) giving (*S*)-**15** (0.604 g, 94%) as a colorless liquid. $[\alpha]^{20}_D$ = +181 (c = 0.77). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51−7.20 (m, 15H), 3.89 (d, J = 13.8 Hz, 2H), 3.63−3.55 (m, 2H), 3.49 (d, J = 13.8 Hz, 2H), 3.54−3.46 (m, 1H), 1.92−1.50 (m, 4H), 0.87 (s, 9H), 0.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.8, 131.8, 128.9, 128.2, 128.0, 127.8, 126.8, 123.6, 87.9, 85.3, 62.6, 55.0, 52.1, 30.1, 29.7, 25.9, 18.3, −7.2. MS (EI): m/z 483 [M^+, 4%]. Anal. Calcd for $C_{32}H_{41}NOSi$: C, 79.45; H, 8.54; N, 2.90. Found: C, 79.39; H, 8.81; N, 3.02.

(−)-(*S*)-4-(*N*,*N*-Dibenzylamino)-6-phenyl-5-hexyn-1-ol ((*S*)-40). At room temperature, a solution of (*S*)-**15** (0.112 g, 0.23 mmol) in Et_2O (2 mL) was reacted with TBAF (0.70 mL, 0.69 mmol, 3.0 equiv, 1 M in THF) and stirred overnight. The reaction mixture was quenched with H_2O (0.5 mL), and stirring was continued for a further 2 h for complete hydrolysis. The organic layer was separated, and the aqueous phase was extracted twice with Et_2O. The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The purification of the residue by flash chromatography (1:1 Et_2O−hexanes; TLC, R_f = 0.30) afforded (*S*)-**40** (0.080 g, 94%) as a colorless oil. $[\alpha]^{20}_D$ = −299 (c = 0.29). IR (neat, cm^{-1}): 3348 (OH, m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59−7.27 (m, 15H), 3.97 (d, J = 13.6 Hz, 2H), 3.71 (dd, J = 8.1 Hz, J = 6.9 Hz, 1H), 3.59 (ψ-t, J = 6.3 Hz, 2H), 3.56 (d, J = 13.6 Hz, 2H), 2.04−1.84 (m, 3H), 1.83−1.69 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.4, 131.8, 129.0, 128.3, 128.0, 127.0, 123.4, 87.5, 85.7, 62.4, 55.1, 52.3, 30.5, 29.9. MS (EI): m/z 310 [(M − C_3H_7O)$^+$, 100%]. Anal. Calcd for $C_{26}H_{27}NO$: C, 84.51; H, 7.38; N, 3.79. Found: C, 84.24; H, 7.68; N, 3.92.

(−)-(*S*)-4-(*N*,*N*-Dibenzylamino)-6-phenyl-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*S*)-12). A solution of (*S*)-**40** (0.160 g, 0.43 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (0.012 g, 0.52 mmol, 1.2 equiv, 60% in mineral oil) in THF (1 mL). The reaction mixture was allowed to stir for 1 h at room temperature for complete deprotonation before 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyl chloride (*Cby*Cl)[22] (0.100 g, 0.48 mmol, 1.1 equiv) in THF (3 mL) was added. After being heated under reflux overnight and cooled to room temperature, the reaction mixture was poured into H_2O (1 mL) and Et_2O (10 mL). The organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were dried with $MgSO_4$, and the solvents were removed in vacuo. The crude product was purified by flash chromatography (1:9 to 1:1 Et_2O−hexanes; TLC, R_f = 0.65 in 1:1 Et_2O−hexanes) yielding (*S*)-**12** (0.145 g, 64%) as a colorless liquid. $[\alpha]^{20}_D$ = −191 (c = 0.58). IR (neat, cm^{-1}): 1701 (C═O, s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52−7.15 (m, 15H), 4.06−3.99 (m, 2H), 3.89 (d, J = 13.8 Hz, 2H), 3.70 (s, 2H), 3.51 (d, J = 13.8 Hz, 2H), 3.40 (ψ-t, J = 7.3 Hz, 1H), 1.97−1.61 (m, 4H), 1.54/1.48/1.40/1.32 (4s, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.8/152.0, 139.6, 131.8, 128.8, 128.3, 128.0, 126.9, 95.8/94.8, 87.3, 85.6, 76.3/76.1, 64.1, 60.5/59.6, 55.0, 52.1, 30.7, 26.2, 26.6/25.3/24.1. MS (EI): m/z 524 [M^+, 24%]. Anal. Calcd for $C_{34}H_{40}N_2O_3$: C, 77.83; H, 7.68; N, 5.34. Found: C, 77.65; H, 7.58; N, 5.33.

Typical Procedure for the Alkynylation of Aldehydes. *rac*-4-Hydroxy-6-phenyl-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*rac*-17). At −78 °C, to a solution of phenylacetylene (1.08 g, 10.6 mmol, 1.3 equiv) in THF (20 mL) was slowly added *n*-BuLi (6.35 mL, 10.2 mmol, 1.25 equiv, 1.6 M). The solution was allowed to warm to −18 °C and stirred for 15 min at this temperature. The cooling bath was removed, and the solution was stirred at ambient temperature for 30 min. After being cooled back to −78 °C, a solution of 4-oxobutyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (1.98 g, 8.14 mmol) in THF (20 mL) was added within 10 min. The reaction mixture was stirred for 1 h before the temperature was raised to −18 °C and kept for another 45 min at this temperature. After the hydrolysis with saturated aqueous NH_4Cl (50 mL), the organic layer was separated and the aqueous phase was extracted several times with Et_2O. Drying (Na_2SO_4), concentration in vacuo, and purification of the crude product by flash chromatography (1:1 to 3:1 Et_2O−hexanes; TLC, R_f = 0.19 in 1:1 Et_2O−hexanes) provided *rac*-**17** (2.80 g, 99%) as a colorless oil. IR (neat, cm^{-1}): 3436 (OH, s), 1707 (C═O, s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44−7.39 (m, 2H), 7.35−7.28 (m, 3H), 4.68−4.65 (m, 1H), 4.22−4.15 (m, 2H), 3.73 (s, 2H), 2.21 (bs, 1H), 1.91 (bs, 4H), 1.57/1.54/1.43/1.38 (4s, 12H). ^{13}C NMR ($CDCl_3$, 90 MHz): δ 152.8/152.1, 131.6, 128.5, 128.3, 122.5, 95.8/94.8, 89.6, 85.1, 76.3/76.1, 64.1, 62.4, 60.6/59.7, 34.5, 26.6/25.4/25.3/24.1, 24.9. MS (EI): m/z 330 [(M − CH_3)$^+$, 40%]. Anal. Calcd for $C_{20}H_{27}NO_4$: C, 69.54; H, 7.88; N, 4.05. Found: C, 69.29; H, 7.75; N, 4.25.

Typical Procedure for the PCC Oxidation. 4-Oxo-6-phenyl-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (21). At 0 °C, to a suspension of PCC (2.62 g, 12.2 mmol, 1.5 equiv) and sodium acetate (0.73 g, 8.92 mmol, 1.1 equiv) in CH_2Cl_2 (60 mL) *rac*-**17** (2.80 g, 8.11 mmol), dissolved in CH_2Cl_2 (20 mL), was added over a period of 5 min. The conversion of *rac*-**17** to **21** was monitored by TLC; after complete conversion the reaction mixture was filtrated through a short silica gel column. The volatiles were removed in vacuo, and the residue was purified by flash chromatography (1:1 Et_2O−hexanes; TLC, R_f = 0.40) yielding **21** (1.93 g, 69%) as a viscous oil which slowly solidified upon standing to give **21** as a white solid. Mp = 78−79 °C. IR (KBr, cm^{-1}): 1675 (C═O, C═O, broad, s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56−7.36 (m, 5H), 4.18 (t, J = 6.5 Hz, 2H), 3.74 (s, 2H), 2.80 (t, J = 6.9 Hz, 2H), 2.12 (ψ-quint, J = 6.9 Hz, J = 6.5 Hz, 2H), 1.57/1.55/1.43/1.39 (4s, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 186.4, 152.7/152.0, 133.0, 130.7, 128.6, 119.8, 95.8/94.8, 91.1, 87.6, 76.3/76.1, 63.4, 60.6/59.6, 42.1, 26.6/25.3/24.1, 23.5. MS (EI): m/z 328 [(M − CH_3)$^+$, 52%]. Anal. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08. Found: C, 69.97; H, 7.40; N, 4.11.

Typical Procedure for Enantioselective Reduction of α,β-Ynones with Alpine-Borane.[23] (+)-(*S*)-4-Hydroxy-6-phenyl-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*S*)-17). At 0 °C, the α,β-ynone **21** (1.20 g, 3.49 mmol) was dissolved in (*S*)-Alpine-borane (14.0 mL, 6.99 mmol, 2.0 equiv, 0.5 M in THF). The vigorously stirred reaction mixture was immediately concentrated under reduced pressure to give a sticky suspension which turned into a liquid while stirring overnight at room temperature. To destroy the excess of the reducing agent, freshly distilled acetaldehyde (1 mL) was added dropwise at 0 °C. After 15 min the cooling bath was removed and the liberated α-pinene was pumped off in vacuo at 60−70 °C (oil bath temperature) for 2 h. The reaction mixture was again cooled to 0 °C, and the residue was dissolved in Et_2O (10 mL). To this solution ethanolamine (0.47 g, 7.69 mmol, 2.2 equiv) was slowly added furnishing a white

precipitate which was then filtered off and washed with Et_2O. The etheral phase was extracted with H_2O and brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (1:1 Et_2O−hexanes) yielding (*S*)-**17** (1.03 g, 85%, er = 95:5[24]) as a colorless oil. $[\alpha]^{20}_D = +4.2$ ($c = 0.42$).

General Procedure for the Tritylation[27] of 17. *rac*-6-Phenyl-4-(triphenylmethoxy)-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*rac*-13a). At room temperature, trityl chloride (0.749 g, 2.69 mmol, 1.1 equiv) and DMAP (0.012 g, 0.10 mmol, 0.04 equiv) were dissolved in CH_2Cl_2 (15 mL). To this solution Et_3N (0.371 g, 3.66 mmol, 1.5 equiv) and *rac*-**17** (0.844 g, 2.44 mmol), dissolved in CH_2Cl_2 (5 mL), were subsequently added. After being refluxed overnight the reaction mixture was quenched with H_2O (5 mL) at room temperature. The organic layer was separated, and the aqueous phase was extracted twice with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography (1:1 Et_2O−hexanes; TLC, $R_f = 0.48$) of the residue gave *rac*-**13a** (0.387 g, 54%) as a colorless liquid. IR (neat, cm^{-1}): 1691 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.66−7.60 (m, 6H), 7.39−7.23 (m, 12H), 7.20−7.14 (m, 2H), 4.33 (t, $J = 5.5$ Hz, 1H), 4.14 (t, $J = 5.8$ Hz, 2H), 3.77 (s, 2H), 2.08−1.73 (m, 4H), 1.62/1.58/1.48/1.42 (4s, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.8/152.0, 144.4, 131.5, 129.1, 128.0, 127.9, 127.7, 127.1, 123.1, 95.8/94.8, 89.5, 87.8, 85.8, 76.4/76.1, 64.5, 60.5/59.6, 33.7, 26.6/25.4/24.2, 24.7. MS (EI): *m/z* 588 [$(M + H)^+$, 2%]. Anal. Calcd for $C_{39}H_{41}NO_4$: C, 79.70; H, 7.03; N, 2.38. Found: C, 79.54; H, 7.17; N, 2.39.

Typical Procedure for the Silylation of Alkanols. *rac*-4-(*tert*-Butyldiphenylsilyloxy)-6-phenyl-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*rac*-13b). To a solution of DMAP (0.056 g, 0.46 mmol, 0.5 equiv) in CH_2Cl_2 (10 mL) TBDPSCl (0.304 g, 1.10 mmol, 1.2 equiv), Et_3N (0.112 g, 1.10 mmol, 1.2 equiv), and *rac*-**17** (0.318 g, 0.92 mmol), dissolved in CH_2Cl_2 (5 mL), were subsequently added at room temperature. The reaction mixture was stirred under reflux overnight and hydrolyzed with H_2O (1 mL) at room temperature. The organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were dried over $MgSO_4$, and the solvents were evaporated in vacuo. The residue was purified by flash chromatography (1:9 to 1:3 Et_2O−hexanes; TLC, $R_f = 0.61$ in 1:1 Et_2O−hexanes) to give *rac*-**13b** (0.538 g, 100%) as a colorless liquid. IR (neat, cm^{-1}): 1697 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.76−7.66 (m, 4H), 7.40−7.27 (m, 6H), 7.22−7.12 (m, 5H), 4.62−4.59 (m, 1H), 4.08 (bs, 2H), 3.67 (s, 2H), 1.86 (bs, 4H), 1.52/1.47/1.38/1.31 (4s, 12H), 1.07 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.8/152.0, 136.0, 135.4, 133.6, 131.5, 129.6, 128.1, 127.6, 122.9, 95.8/94.8, 90.2, 85.2, 76.4/76.2, 64.4, 64.0, 60.5/59.6, 35.4, 27.0, 26.6/25.3/24.2, 24.6, 19.3. MS (EI): *m/z* 583 [M^+, 1%]. Anal. Calcd for $C_{36}H_{45}NO_4Si$: C, 74.06; H, 7.77; N, 2.40. Found: C, 74.37; H, 7.93; N, 2.30.

(−)-[1*R*,3*S*,2(1*E*)]-2-Benzylidene-3-(*N*,*N*-dibenzylamino)-cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*cis*-18). According to the typical procedure for the stereoselective cyclocarbolithiation of alkynes, (*S*)-**12** (0.110 g, 0.21 mmol) was cyclized with *s*-BuLi (0.25 mL, 0.31 mmol, 1.5 equiv, 1.25 M) in the presence of **1** (0.074 g, 0.31 mmol, 1.5 equiv) in Et_2O (3 mL) for 20 h at −78 °C. The crude product was purified by flash chromatography (3:7 Et_2O−hexanes; TLC, $R_f = 0.65$ in 1:1 Et_2O−hexanes) to yield *cis*-**18** (0.077 g, 70%) with traces of (*S*)-**12** as a colorless oil. $[\alpha]^{20}_D = -76.6$ ($c = 0.15$). IR (neat, cm^{-1}): 1697 (C=O, s). ^1H NMR ($CDCl_3$, 600 MHz): δ 7.40−7.16 (m, 12H), 7.04−7.02 (m, 3H), 6.92 (m, 1H), 5.56 (m, 1H), 4.20 (m, 1H), 3.85 (ψ-t, $J = 12.6$ Hz, 2H), 3.70 (2s, 2H), 3.24 (2d, $J = 12.6$ Hz, 2H), 2.28−2.18 (m, 1H), 2.04−1.96 (m, 2H), 1.85−1.78 (m, 1H), 1.60/1.56/1.49/1.45/1.42/1.39/1.33 (7s, 12H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 152.6/151.9, 141.8, 141.7, 139.2, 136.0, 135.9, 130.3, 129.3, 128.7, 128.3, 127.9, 127.6, 127.1, 126.8, 96.0/94.6, 80.3, 76.4/76.0, 60.4, 60.8/59.5, 54.9/54.8, 30.4/30.3, 22.1, 26.7/26.6/25.5/25.4/25.3/25.2/24.2/24.1. MS (EI): *m/z* 524 [M^+, 1%]. Anal. Calcd for $C_{34}H_{40}N_2O_3$: C, 77.83; H, 7.68; N, 5.34. Found: C, 77.56; H, 7.67; N, 5.41.

Stereoselective Cyclocarbolithiation of 13a. (+)-[1*R*,3*S*,2(1*E*)]-2-Benzylidene-3-(triphenylmethoxy)cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*cis*-19a). Following the typical procedure for the stereoselective cyclocarbolithiation of alkynes, (*S*)-**13a** (0.100 g, 0.17 mmol) was treated with *s*-BuLi (0.18 mL, 0.24 mmol, 1.4 equiv, 1.32 M) and **1** (0.060 g, 0.26 mmol, 1.5 equiv) in Et_2O (3 mL) for 18.5 h at −78 °C. The crude product was purified by flash chromatography (1:9 to 1:3 Et_2O−hexanes; TLC, $R_f = 0.48$ in 1:1 Et_2O−hexanes) affording *cis*-**19a** (0.088 g, 88%, dr = 95:5) as a white solid. Mp = 165−166 °C. $[\alpha]^{20}_D = +11.4$ ($c = 0.22$). ^1H NMR ($CDCl_3$, 300 MHz): 7.41−7.37 (m, 6H), 7.22−6.98 (m, 14H), 6.78 (s, 1H), 5.62 (t, $J = 6.9$ Hz, 1H), 4.32 (d, 4.7 Hz, 1H), 3.70 (s, 2H), 2.04−1.97 (m, 2H), 1.80−1.70 (m, 1H), 1.65/1.61/1.58/1.51/1.49/1.46/1.44 (7s, 12H), 1.25−1.11 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.8/152.0, 145.2, 143.6, 136.9, 132.4, 129.6, 129.3, 128.4, 127.9, 127.8, 127.5, 95.9/95.0, 86.9, 78.1, 76.6/76.2, 74.3, 60.7/59.9, 31.0, 29.5, 27.2/26.7/25.8/25.5/24.3.

(−)-[1*R*,3*R*,2(1*E*)]-2-Benzylidene-3-(triphenylmethoxy)-cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*trans*-19a). As described in the typical procedure for the stereoselective cyclocarbolithiation of alkynes, (*R*)-**13a** (0.046 g, 0.08 mmol) was cyclized with *s*-BuLi (0.10 mL, 0.11 mmol, 1.4 equiv, 1.30 M) in the presence of **1** (0.028 g, 0.12 mmol, 1.5 equiv) in Et_2O (1.5 mL) for 23 h at −78 °C. Flash chromatography (1:3 Et_2O−hexanes) of the crude product furnished *trans*-**19a** (0.046 g, 100%, dr = 5:95) as a white solid. Mp = 67−68 °C. $[\alpha]^{20}_D = -50.6$ ($c = 0.25$). ^1H NMR ($CDCl_3$, 300 MHz): 7.48−7.44 (m, 6H), 7.32−7.10 (m, 14H), 6.79 (s, 1H), 6.04−6.00 (m, 1H), 4.56 (d, $J = 4.3$ Hz, 1H), 3.72 (s, 2H), 2.41−2.33 (m, 1H), 1.74−1.23 (m, 15H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 152.6/151.9, 144.7, 143.9, 143.8, 136.5, 136.4, 129.5, 129.1, 128.9, 128.0, 127.9, 127.5, 127.3, 127.0, 95.9/94.8, 86.7, 77.5, 76.3/76.0, 74.0/73.9, 60.5/59.7, 30.5, 29.7/29.6, 28.9/26.8/26.6/25.7/25.5/25.3/24.2.

[1*R*,3*RS*,2(1*E*)]-2-Benzylidene-3-(triphenylmethoxy)-cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*cis*-/*trans*-19a). *rac*-**13a** (0.195 g, 0.33 mmol) was treated with *s*-BuLi (0.33 mL, 0.43 mmol, 1.3 equiv, 1.32 M) and **1** (0.101 g, 0.43 mmol, 1.3 equiv) in Et_2O (8 mL) for 6.5 h at −78 °C according to the typical procedure for the stereoselective cyclocarbolithiation. The purification of the crude product by flash chromatography (1:9 to 1:3 Et_2O−hexanes) gave a mixture of *cis*-/*trans*-**19a** (0.157 g, 80%, dr = 50:50) and *rac*-**13a** (0.038 g, 20%) as a white solid. IR (KBr, cm^{-1}): 1694 (C=O, s). MS (EI): *m/z* 587 [M^+, 6%]. Anal. Calcd for $C_{39}H_{41}NO_4$: C, 79.70; H, 7.03; N, 2.38. Found: C, 79.58; H, 7.12; N, 2.58.

Stereoselective Cyclocarbolithiation of 13b. (+)-[1*R*,3*S*,2(1*E*)]-2-Benzylidene-3-(*tert*-butyldiphenylsilyloxy)cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*cis*-19b). In analogy to the typical procedure for the stereoselective cyclocarbolithiation, (*S*)-**13b** (0.500 g, 0.86 mmol) was cyclized with *s*-BuLi (0.92 mL, 1.20 mmol, 1.4 equiv, 1.30 M) and **1** (0.301 g, 1.28 mmol, 1.5 equiv) in Et_2O (15 mL) for 20 h at −78 °C. The crude product was purified by flash chromatography (1:9 Et_2O−hexanes; TLC, $R_f = 0.57$ in 1:1 Et_2O−hexanes) to give *cis*-**19b** (0.410 g, 82%, dr = 95:5) as a colorless, highly viscous oil. $[\alpha]^{20}_D = +34.5$ ($c = 0.31$). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.71−7.64 (m, 4H, Ph), 7.41−7.22 (m, 8H), 7.12−7.00 (m, 3H), 6.76 (s, 1H), 5.64 (t, $J = 6.8$ Hz, 1H), 4.82 (d, $J = 4.1$ Hz, 1H), 3.72 (s, 2H), 2.24−1.90 (m, 4H), 1.60/1.59 (2bs, 6H), 1.45/1.44 (2bs, 6H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 153.0/152.2, 144.1, 136.5, 135.9, 134.8, 134.4, 133.8, 131.3, 129.6, 129.5, 128.9, 128.0, 127.5, 127.3, 95.8/95.1, 77.3, 76.6/76.1, 72.7, 60.6/59.9, 34.2, 29.3, 27.0, 26.7/25.8/25.4/24.3, 19.3.

(−)-[1*R*,3*RS*,2(1*E*)]-2-Benzylidene-3-(*tert*-butyldiphenylsilyloxy)cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*cis*-/*trans*-19b). Following the typical procedure for the stereoselective cyclocarbolithiation, *rac*-**13b** (0.100 g, 0.17 mmol) was allowed to react with *s*-BuLi (0.18 mL, 0.24 mmol, 1.4 equiv, 1.30 M) and **1** (0.060 g, 0.26 mmol, 1.5 equiv) in Et_2O (3 mL) for 23.5 h at −78 °C. Flash

chromatography (1:3 to 1:1 Et_2O−hexanes; TLC, R_f = 0.57/0.58 in 1:1 Et_2O−hexanes) afforded *cis*-/*trans*-**19b** (0.096 g, 96%, dr = 50:50) a colorless, highly viscous oil. $[\alpha]^{20}_D = -19.4$ (c = 0.48). IR (neat, cm^{-1}): 1691 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.72−7.59 (m, 4H), 7.41−7.22 (m, 8H), 7.14−7.01 (m, 3H), 6.76 (s, 0.5H, cis), 6.68 (s, 0.5H, trans), 5.88−5.86 (m, 0.5H, trans), 5.64 (t, J = 6.8 Hz, 0.5H, cis), 5.01 (m, 0.5H, trans), 4.82 (d, J = 4.1 Hz, 0.5H, cis), 3.72 (s, 1H, cis), 3.69 (bs, 1H, trans), 2.43−1.70 (m, 4H), 1.65−1.25 (m, 12H), 1.05/1.02/0.97 (3s, 9H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 153.0/152.2, 145.0, 144.1, 136.5, 135.9, 135.8, 134.8, 134.7, 133.8, 131.3, 129.6, 129.5, 128.9, 128.1, 128.0, 127.7, 127.5, 127.3, 127.2, 95.8/95.3/95.1, 77.6/77.3, 76.5/76.0, 72.8/72.7, 60.6/59.9/59.8, 34.2, 33.7, 29.7, 29.4, 27.0/26.9, 26.6/25.8/25.5/25.3/24.2, 19.3/19.0. MS (EI): m/z 583 [M^+, 1%]. Anal. Calcd for $C_{36}H_{45}NO_4Si$: C, 74.06; H, 7.77; N, 2.40. Found: C, 73.82; H, 7.79; N, 2.31.

(+)-[1*RS*,3*S*,2(1*E*)]-2-Benzylidene-3-(*tert*-butyldiphenylsilyloxy)cyclopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (*cis*-/*ent*-*trans*-19b). Analogously to the typical procedure for the stereoselective cyclocarbolithiation, (*S*)-**13b** (0.100 g, 0.17 mmol) was treated with *s*-BuLi (0.18 mL, 0.24 mmol, 1.4 equiv, 1.30 M) in the presence of TMEDA (**20**) (0.030 g, 0.26 mmol, 1.5 equiv)—instead of (−)-sparteine (**1**)—in Et_2O (3 mL) for 20 h at −78 °C. Flash chromatography of the crude product provided *cis*-/*ent*-*trans*-**19b** (0.089 g, 89%, dr = 50:50) as a colorless, highly viscous oil. $[\alpha]^{20}_D = +47.1$ (c = 0.48).

4,4-(1,2-Ethanediyldioxy)-6-phenyl-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate (22). At −78 °C, a drop of TMSOTf was dissolved in CH_2Cl_2 (1 mL). To this solution 1,2-bis(trimethylsilyloxy)ethane (0.413 g, 2.00 mmol, 1.0 equiv) and the α,β-ynone **21** (0.687 g, 2.00 mmol) in CH_2Cl_2 (3 mL) were subsequently added. The reaction was terminated with pyridine (0.2 mL) after stirring overnight at −78 °C. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (25 mL), the organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were dried (1:1 mixture of Na_2CO_3 and Na_2SO_4), and the solvents were evaporated under reduced pressure.[31] The residue was purified by flash chromatography (1:9 to 1:3 to 1:1 Et_2O−hexanes; TLC, R_f = 0.39 in 1:1 Et_2O−hexanes, silica gel passified with Et_3N) furnishing **22** (0.243 g, 31%) as colorless liquid. IR (neat, cm^{-1}): 2222 (C≡C, w), 1706 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.44−7.40 (m, 2H), 7.32−7.26 (m, 3H), 4.17 (t, J = 6.2 Hz, 2H), 4.17−4.13 (m, 2H), 4.04−3.99 (m, 2H), 3.70 (s, 2H), 2.14−2.04 (m, 2H), 2.03−1.92 (m, 2H), 1.54/1.52/1.40/1.36 (4s, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.8/152.0, 131.8, 128.7, 128.2, 121.9, 103.4, 95.8/94.8, 86.5, 84.0, 76.3/76.1, 64.8, 64.2, 60.7/59.7, 36.3, 26.6/25.3/24.1, 23.8. MS (EI): m/z 373 [M^+, 21%]. Anal. Calcd for $C_{22}H_{29}NO_5$: C, 68.20; H, 7.54; N, 3.62. Found: C, 68.07; H, 7.66; N, 3.83.

(−)-(*S*)-1-(*tert*-Butyldimethylsilyloxy)-4-(*N*,*N*-dibenzylamino)-5-(triphenylmethoxy)pentane ((*S*)-41). To a solution of trityl chloride (2.56 g, 9.17 mmol, 1.2 equiv) in CH_2Cl_2 (25 mL) a mixture of (*S*)-**14**[19] (3.16 g, 7.64 mmol) and Et_3N (1.08 g, 10.6 mmol, 1.4 equiv), dissolved in CH_2Cl_2 (25 mL), was added at room temperature. The reaction mixture was allowed to stir for 36 h before quenching with H_2O (25 mL). The organic layer was separated and the aqueous phase extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by flash chromatography (1:1 Et_2O−hexanes; TLC, R_f = 0.60) to afford (*S*)-**41** (5.00 g, 100%) as a colorless oil. $[\alpha]^{20}_D = -40.4$ (c = 1.35). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.47−7.43 (m, 5H), 7.32−7.14 (m, 20H), 3.69 (d, J = 13.8 Hz, 2H), 3.52−3.42 (m, 4H), 3.30 (dd, J = 9.3 Hz, J = 5.7 Hz, 1H), 3.13 (dd, J = 9.3 Hz, J = 5.3 Hz, 1H), 2.85 (m, 1H), 1.66−1.25 (m, 4H), 0.86 (s, 9H), 0.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.2, 140.7, 128.8, 128.0, 127.7, 126.9, 126.6, 86.9, 63.2, 63.1, 57.2, 54.1, 30.2, 26.0, 25.4, 18.3, −5.2. MS (EI): m/z 641 [$(M - CH_3)^+$, 6%]. Anal. Calcd for $C_{44}H_{53}NO_2Si$: C, 80.56; H, 8.14; N, 2.14. Found: C, 80.67; H, 8.35; N, 2.12.

(−)-(*S*)-4-(*N*,*N*-Dibenzylamino)-5-(triphenylmethoxy)-1-pentanol ((*S*)-42). At room temperature, (*S*)-**41** (8.62 g, 13.1 mmol) was desilylated with TBAF (39.4 mL, 39.4 mmol, 3.0 equiv, 1 M in THF) in Et_2O (40 mL). After being stirred overnight, the reaction mixture was treated with H_2O (15 mL) and stirred for a further 2 h at room temperature. The organic layer was separated, and the aqueous phase was extracted twice with Et_2O. The organic phases were combined, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash chromatography (1:1 Et_2O−hexanes; TLC, R_f = 0.26) to give (*S*)-**42** (7.12 g, 100%) as a colorless oil. $[\alpha]^{20}_D = -59.0$ (c = 1.24). IR (neat, cm^{-1}): 3386 (OH, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.48−7.44 (m, 5H), 7.33−7.14 (m, 20H), 3.72 (d, J = 13.7 Hz, 2H), 3.46 (d, J = 13.7 Hz, 2H), 3.50−3.43 (m, 2H), 3.34 (dd, J = 9.6 Hz, J = 5.7 Hz, 1H), 3.15 (dd, J = 9.6 Hz, J = 5.3 Hz, 1H), 2.88 (m, 1H), 2.42−2.36 (m, 1H), 1.67−1.17 (m, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.1, 140.3, 128.8, 128.1, 127.7, 126.9, 126.7, 87.0, 62.9, 62.8, 57.3, 54.1, 30.1, 25.7. MS (EI): m/z 541 [M^+, 0.4%]. HRMS Calcd for $C_{38}H_{39}NO_2$: 541.29808. Found: 541.29645.

(−)-(*S*)-4-(*N*,*N*-Dibenzylamino)-5-(triphenylmethoxy)-pentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*S*)-43). To a suspension of NaH (0.30 g, 7.50 mmol, 1.1 equiv, 60% in mineral oil) in THF (5 mL) a solution of (*S*)-**42** (3.51 g, 6.82 mmol) in THF (30 mL) was added dropwise at room temperature. The reaction mixture was stirred for 1 h at ambient temperature to achieve complete deprotonation. Then a solution of 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyl chloride (*Cby*Cl)[22] (1.44 g, 7.50 mmol, 1.1 equiv) in THF (15 mL) was injected into the reaction mixture. After being refluxed overnight and cooled to room temperature, the resulting white suspension was poured into H_2O (10 mL) and Et_2O (50 mL). The organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were dried ($MgSO_4$), and the solvents were evaporated under reduced pressure. Purification by flash chromatography (6:4 Et_2O−hexanes; TLC, R_f = 0.60) gave (*S*)-**43** (4.15 g, 87%) as a white foam. $[\alpha]^{20}_D = -34.0$ (c = 1.08). IR (neat, cm^{-1}): 1689 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.44−7.37 (m, 5H), 7.35−7.16 (m, 20H), 3.98 (m, 2H), 3.71 (d, J = 14.0 Hz, 2H), 3.70 (s, 2H), 3.46 (d, J = 14.0 Hz, 2H), 3.34 (dd, J = 9.5 Hz, J = 5.3 Hz, 1H), 3.15 (dd, J = 9.5 Hz, J = 5.3 Hz, 1H), 2.86 (ψ-dq, J = 5.3 Hz, J = 2.6 Hz, 1H), 1.86−1.81 (m, 1H), 1.71−1.32 (m, 15H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.7/152.0, 144.1, 140.4, 128.7, 128.6, 128.1, 127.7, 126.9, 126.7, 95.8/94.7, 87.0, 76.4/76.2, 64.7, 62.7, 60.5/59.6, 57.2, 54.1, 26.5, 26.2/25.3/24.1. MS (EI): m/z 696 [M^+, 0.2%]. Anal. Calcd for $C_{46}H_{52}N_2O_4$: C, 79.28; H, 7.52; N, 4.02. Found: C, 79.02; H, 7.54; N, 4.34.

(+)-(*S*)-4-(*N*,*N*-Dibenzylamino)-5-hydroxypentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*S*)-27). A solution of (*S*)-**43** (0.830 g, 1.19 mmol) in CH_2Cl_2 (15 mL) and methanol (15 mL) was cooled to 0 °C before TFA (0.679 g, 5.95 mmol, 5.0 equiv) was added dropwise. The yellowish reaction mixture was stirred for 30 min at room temperature and then carefully neutralized with saturated aqueous $NaHCO_3$ until the evolution of CO_2 had stopped. The organic layer was separated, and the aqueous phase was extracted twice with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography (1:3 to 1:1 Et_2O−hexanes; TLC, R_f = 0.55 in Et_2O) to yield (*S*)-**27** (0.420 g, 78%) as a colorless liquid. $[\alpha]^{20}_D = +62.1$ (c = 1.23). IR (neat, cm^{-1}): 3473 (OH, m), 1695 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.37−7.15 (m, 10H), 4.07 (t, J = 6.0 Hz, 2H), 3.80 (d, J = 13.5 Hz, 2H), 3.73 (s, 2H), 3.47 (m, 2H), 3.45 (d, J = 13.5 Hz, 2H), 2.99 (bs, 1H), 2.84−2.75 (m, 1H), 1.90−1.76 (m, 1H), 1.75−1.21 (m, 15H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.6/151.9, 139.1, 128.8, 128.3, 127.1, 95.7/94.6, 76.2/76.0, 64.2, 60.8, 60.5/59.5, 58.6, 53.2, 26.7, 26.5/25.3/25.2/24.0, 22.0. MS (EI): m/z 454 [M^+, 0.1%]. Anal. Calcd for $C_{27}H_{38}N_2O_4$: C, 71.34; H, 8.43; N, 6.16. Found: C, 71.12; H, 8.55; N, 6.38.

(−)-(*S*)-4-(*N*,*N*-Dibenzylamino)-5-oxopentyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*S*)-44). According to the typical procedure for the Swern oxidation, (*S*)-**27**

(0.360 g, 0.79 mmol) was oxidized with oxalyl chloride (0.121 g, 0.95 mmol, 1.2 equiv), DMSO (0.148 g, 1.90 mmol, 2.4 equiv), and Et_3N (0.401 g, 3.96 mmol, 5.0 equiv) in CH_2Cl_2 (10 mL). The purification of the crude product by flash chromatography (1:1 Et_2O−hexanes; TLC, $R_f = 0.27$) provided (*S*)-**44** (0.345 g, 96%) as a colorless liquid. $[\alpha]^{20}_D = -36.6$ ($c = 1.14$). IR (neat, cm^{-1}): 1694 (C=O, C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 9.71 (s, 1H), 7.39−7.18 (m, 10H), 4.09−4.05 (m, 2H), 3.80 (d, $J = 13.6$ Hz, 2H), 3.70 (m, 4H), 3.20−3.16 (m, 1H), 1.92−1.63 (m, 4H), 1.57/1.53/1.43/1.37 (4s, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 203.0, 152.7/151.9, 138.9, 128.7, 128.4, 127.3, 95.8/94.7, 76.3/76.1, 66.5, 64.1, 60.5/59.6, 54.8, 26.6, 26.5/25.3/24.1, 20.8. MS (EI): *m*/*z* 452 [M^+, 3%]. Anal. Calcd for $C_{27}H_{36}N_2O_4$: C, 71.65; H, 8.02; N, 6.19. Found: C, 71.65; H, 8.30; N, 5.96.

(−)-(*S*)-4-(*N*,*N*-Dibenzylamino)-6-(trimethylsilyl)-5-hexynyl 2,2,4,4-Tetramethyl-1,3-oxazolidine-3-carboxylate ((*S*)-25). Step A. Following the typical procedure for the Corey−Fuchs formyl ethynyl conversion, (*S*)-**44** (0.500 g, 1.10 mmol) was olefinated with tetrabromomethane (0.733 g, 2.21 mmol, 2.0 equiv) and triphenylphosphine (1.159 g, 4.42 mmol, 4.0 equiv) in CH_2Cl_2 (35 mL). After purification of the crude product by flash chromatography (1:9 Et_2O−hexanes; TLC, $R_f = 0.60$ in 1:1 Et_2O−hexanes), the (+)-(*S*)-6,6-dibromo-4-(*N*,*N*-dibenzylamino)-5-hexenyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate ((*S*)-**45**) (0.620 g, 93%) was isolated as a yellowish oil. $[\alpha]^{20}_D = +7.6$ ($c = 0.80$). IR (neat, cm^{-1}): 1697 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.37−7.18 (m, 10H), 6.56 (d, $J = 9.3$ Hz, 1H), 4.05−3.95 (m, 2H), 3.84 (d, $J = 13.6$ Hz, 2H), 3.71 (s, 2H), 3.44−3.40 (m, 1H), 3.39 (d, $J = 13.6$ Hz, 2H), 1.95−1.71 (m, 2H), 1.69−1.50 (m, 2H), 1.55/1.49/1.41/1.34 (4s, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.9/152.1, 139.4, 137.4, 128.7, 128.2, 127.0, 96.9/95.8, 90.5, 76.6/76.4, 64.1, 61.3, 60.6/59.6, 54.2, 28.9, 25.9, 26.6/25.5/25.3/24.2. MS (EI): *m*/*z* 608 [M^+, 0.1%]. Anal. Calcd for $C_{28}H_{36}N_2O_3Br_2$: C, 55.28; H, 5.96; N, 4.60. Found: C, 55.61; H, 6.10; N, 4.75.

Step B. In a slightly modified reaction procedure the intermediate lithium acetylide, generated from (*S*)-**45** (0.570 g, 0.94 mmol) upon treatment with *n*-BuLi (1.17 mL, 1.87 mmol, 2.0 equiv, 1.6 M) in THF (15 mL), was reacted with TMSCl (0.305 g, 2.81 mmol, 3.0 equiv). The silylated alkyne (*S*)-**25** (0.408 g, 83%) was isolated after flash chromatography (3:7 Et_2O−hexanes; TLC, $R_f = 0.65$ in 1:1 Et_2O−hexanes) of the crude product as a colorless liquid. $[\alpha]^{20}_D = -120$ ($c = 0.87$). IR (neat, cm^{-1}): 2159 (C≡C, w), 1699 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.38−7.18 (m, 10H), 4.01−3.97 (m, 2H), 3.79 (d, $J = 13.8$ Hz, 2H), 3.70 (s, 2H), 3.40 (t, $J = 7.5$ Hz, 1H), 3.38 (d, $J = 13.8$ Hz, 2H), 1.85−1.60 (m, 4H), 1.54/1.48/1.40/1.32 (4s, 12H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 152.7/151.9, 139.5, 128.7, 128.2, 126.9, 103.8, 95.7/94.4, 89.6, 76.3/76.1, 64.3, 60.8/59.8, 55.2, 52.5, 30.8, 26.4, 26.8/25.6/24.4, 0.3. MS (EI): *m*/*z* 520 [M^+, 10%]. Anal. Calcd for $C_{31}H_{44}N_2O_3Si$: C, 71.50; H, 8.52; N, 5.38. Found: C, 71.50; H, 8.70; N, 5.54.

(−)-[2(2*R*),2(5*S*),2*E*]-2-[5-(*N*,*N*-Dibenzylamino)-2-hydroxycyclopentylidene]-2-((trimethylsilyl)acetyl)-3-(2,2,4,4-tetramethyl-1,3-oxazolidinide) (*cis*-30). Following the typical procedure for the stereoselective cyclocarbolithiation, (*S*)-**25** (0.311 g, 0.60 mmol) was cyclized with *s*-BuLi (0.67 mL, 0.90 mmol, 1.5 equiv, 1.34 M) in the presence of **1** (0.210 g, 0.90 mmol, 1.5 equiv) in Et_2O (3 mL) for 20 h at −78 °C. The crude product was purified by flash chromatography (1:1 Et_2O−hexanes to Et_2O; TLC, $R_f = 0.61$ in Et_2O) affording *cis*-**30** (0.215 g, 70%, dr = >95:5) as a white solid along with (*S*)-**25** (0.030 g, 10%). Mp = 148 °C. $[\alpha]^{20}_D = -41.1$ ($c = 0.63$). IR (KBr, cm^{-1}): 3354 (OH, w), 1597 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.23−7.09 (m, 10H), 5.47 (bs, 1H), 4.35 (d, $J = 5.0$ Hz, 1H), 4.14 (d, $J = 14.1$ Hz, 2H), 3.68 (s, 2H), 3.60 (d, $J = 5.3$ Hz, 1H), 3.53 (d, $J = 14.1$ Hz, 2H), 2.39−2.27 (m, 1H), 1.92−1.70 (m, 3H), 1.74/1.68/1.60/1.58/1.57/1.54/1.49/1.35 (m, 12H), 0.12 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 168.7, 153.2, 138.0, 137.2, 129.2, 128.4, 127.3, 97.9/94.5, 76.8, 74.2, 65.9/65.8, 59.8, 55.1, 32.0, 25.8, 27.4/26.6/25.2/23.8, −0.5. MS (EI): *m*/*z* 520 [M^+, 4%]. Anal. Calcd for $C_{31}H_{44}N_2O_3Si$: C, 71.50; H, 8.52; N, 5.38. Found: C, 71.30; H, 8.59; N, 5.41.

[2(2*R*),2(5*S*),2*E*]-2-[5-(*tert*-Butyldiphenylsilyloxy)-2-hydroxycyclopentylidene]-2-((trimethylsilyl)acetyl)-3-(2,2,4,4-tetramethyl-1,3-oxazolidinide) (*cis*-33) and [2(2*S*),2(5*R*),2*Z*]-2-[5-(*tert*-Butyldiphenylsilyloxy)-2-hydroxycyclopentylidene]-2-((trimethylsilyl)acetyl)-3-(2,2,4,4-tetramethyl-1,3-oxazolidinide) (*cis*-34). As described in the typical procedure for the stereoselective cyclocarbolithiation, (*S*)-**26** (0.200 g, 0.34 mmol) was treated with *s*-BuLi (0.37 mL, 0.48 mmol, 1.4 equiv, 1.30 M) and **1** (0.121 g, 0.52 mmol, 1.5 equiv) in Et_2O (6 mL) for 20 h at −78 °C. After purification of the crude product by flash chromatography (1:1 Et_2O−hexanes; TLC, $R_f = 0.28$) a mixture of the regioisomeric cyclization products *cis*-**33** and *cis*-**34** (0.099 g, 50%, *cis*-**33**:*cis*-**34** = 80:20, dr not determined) was isolated as a white foam along with (*S*)-**26** (0.080 g, 40%). IR (neat, cm^{-1}): 3460 (OH, m), 1591 (C=O, s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.77−7.64 (m, 4H), 7.48−7.33 (m, 6H), 4.68−4.55 (m, 1H), 4.53−4.38 (m, 1H), 3.82−3.66 (m, 3H), 2.09−1.97 (m, 3H), 1.84−1.24 (m, 13H), 1.06 (s, 9H), 0.08/-0.11 (2s, 9H). MS (EI): *m*/*z* 579 [M^+, 27%]. Anal. Calcd for $C_{33}H_{49}NO_4Si_2$: C, 68.35; H, 8.52; N, 2.42. Found: C, 68.42; H, 8.41; N, 2.46.

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Supporting Information Available: Experimental procedures and characterization data for products (*S*)-**13a**, (*R*)-**13a**, (*S*)-**13b**, (*R*)-**17**, (*S*)-**26**, *rac*-**28**, (*S*)-**28**, *rac*-**35**, **46**, and *rac*-**47**, ^1H and ^{13}C NMR spectra of compounds **6**, **7**, (*S*)-**12**, **13a**, *cis*-**18**, *cis*-**19a**, *trans*-**19a**, **22**, (*S*)-**25**, and *cis*-**30**, as well as complete X-ray data for *cis*-**19a** and *cis*-**30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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