N,Se-Acetals: Preparation and Use in Diastereoselective Radical Reactions[1])

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A new facile synthesis of N,S- and N,Se-acetals starting from aldehydes and primary amines is presented (*Schemes 3–5*). These acetals are used as precursors for stereoselective radical deuteration and allylation reactions (*Schemes 6* and *7*, *Tables 1* and *2*). The stereochemical outcome of the reactions depends on the radical trap and the substituents at the N-atom. Deuterations give always *anti* products with moderate to high selectivities. The allylation reactions give either *syn* or *anti* products with low to moderate selectivities. The observed stereoselectivities can be explained with a model based on minimization of $A^{1,3}$ strain and are controlled by steric and stereoelectronic effects.

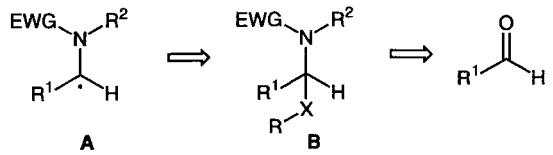
Introduction. – 1-Amidoalkyl radicals **A** are promising reactive intermediates which can be used for the synthesis of alkaloids and unusual amino acids [2]. In the precceding paper [3a] we have shown, that phthalimido-substituted radicals generated from *Barton* esters, N,Se-acetals, or seleno esters can undergo stereoselective reactions [3b]. The observed selectivities can be explained with a model based on the allylic 1,3-strain ($A^{1,3}$ strain) [4]. The attack of the radical trap is controlled by stereoelectronic and steric effects. The use of 1-amido-substituted radicals is still sparse because of the limited methods available for their generation. The homolysis of a C-halogen bond represents the most straightforward method; however, this approach is strongly limited by the instability of the precursors [5]. Sulfides and selenides are good substitutes for halides, but up to now, the preparation of N,S- and N,Se-acetals from carbonyl compounds is usually limited to highly reactive aldehydes such as formaldehyde [6] and glyoxalates [7][2]). The first part of this account describes our investigations towards the preparation of N,S- and N,Se-acetals of type **B** starting from aldehydes and their application in radical reactions (*Scheme 1*). The second part concerns the study of the factors governing 1,2-asymmetric induction in 1-amido-substituted radicals derived from chiral aldehydes. The potential for such radicals in the synthesis of enantiomerically pure compounds (EPC synthesis) is emphasized.

Preparation of N,S- and N,Se-Acetals and Radical Generation. – p-*Toluenesulfonamides*. It has been well-established that a strong electron-withdrawing group at the N-atom has a beneficial effect on the reactivity of 1-amidoalkyl radicals [1]. Therefore, in preliminary studies, we tried to generate 1-sulfonamido-substituted radicals. For this

[1]) For a preliminary communication of this work, see [1].

[2]) The preparation of N,S-acetals *via* *N*-[1-(1*H*-benzotriazol-1-yl)alkyl]amides [8] and *via* the addition of a nitrile to a β-lactam [9] was reported.

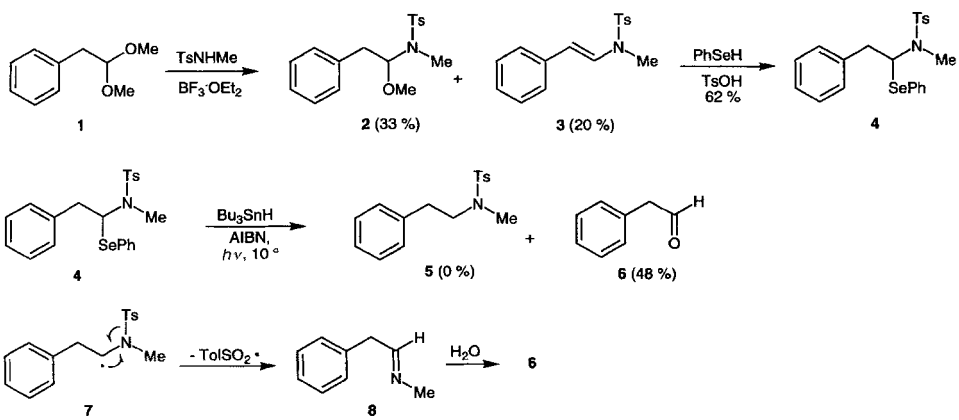
Scheme 1



EWG = electron-withdrawing group (RCO, ROCO, RSO_2, ...)
X = S, Se

purpose, N,Se-acetal **4** was prepared in two steps from commercially available phenylacetaldehyde dimethyl acetal (**1**; *Scheme 2*). Treatment of **1** with $BF_3 \cdot OEt_2$ and *N*-methyl-*p*-toluenesulfonamide (TsNHMe) at $-78°$ provided the N,O-acetal **2** (33%) contaminated with the elimination product **3** (20%). The N,O-acetal **2** was easily transformed to the N,Se-acetal **4** by treatment with selenophenol (2.5 equiv.) and a catalytic amount of *p*-toluenesulfonic acid (TsOH). Suprisingly, when **4** was irradiated with a 300-W sun lamp at 10° under standard radical-reducing conditions (Bu_3SnH, cat. 2,2′-azobis[isobutyronitrile] (AIBN)), phenylacetaldehyde (**6**), was isolated instead of the expected sulfonamide **5**. This is explained by the *β*-fragmentation of the intermediate radical **7** leading to the imine **8** which is hydrolyzed during workup to furnish **6** (*Scheme 2*)[3]).

Scheme 2

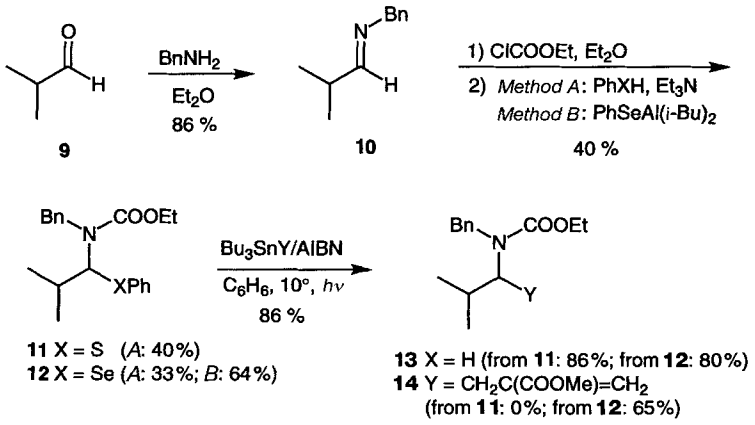


Carbamates. The first synthesis strategy investigated is based on the formation of intermediate N,O-acetals which can easily be transformed into N,S- and N,Se-acetals according to literature procedures. N,O-Acetals are obtained from aldehydes by the protocol of *Böhme* and *Hartke*, *i.e.*, the aldehyde is first converted into an imine which gives an N,O-acetal upon treatment with ethyl chloroformate (= ethyl carbonochloridate) and $MeOH/Et_3N$ [11]. Preliminary experiments with isobutyroaldehyde (**9**) showed that the formation of the intermediate N,O-acetal from **10** was not necessary; indeed, the intermediate acyliminium ion can be directly trapped with thiophenol/Et_3N to give the

[3]) For related papers on radical *β*-fragmentation of sulfonamides, see [10].

N,S-acetal **11** (*Scheme 3, Method A*). The preparation of N,Se-acetal **12** was achieved according to the same procedure (*Method A*) using selenophenol as nucleophile. Better yields (65%) were obtained when PhSeAl(i-Bu)$_2$ was used as nucleophile[4]).

Scheme 3



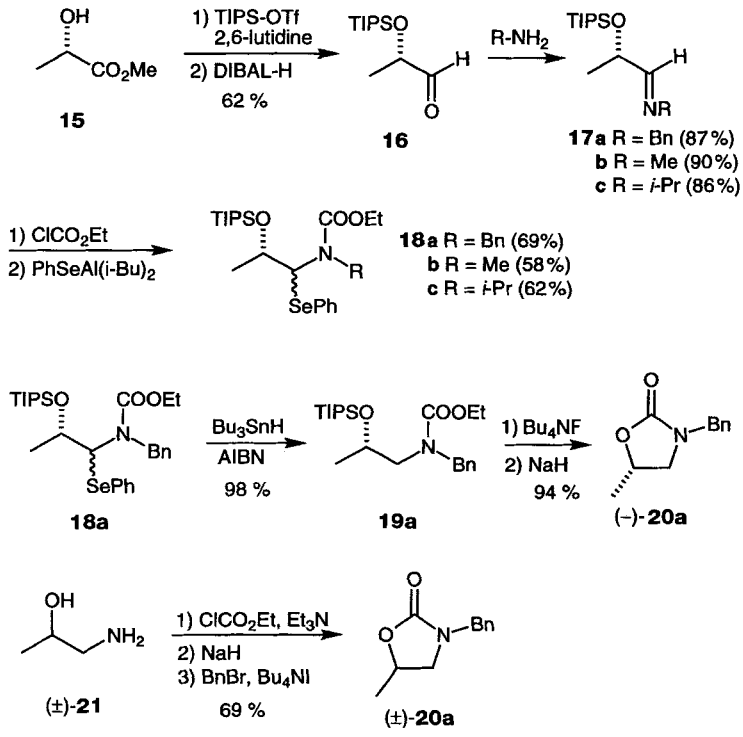
The mixed acetals **11** and **12** were then tested as precursors for radical reactions. Irradiation of **11** with a 300-W sun lamp at 10° in the presence of Bu_3SnH/AIBN gave the desulfurized product **13** in 86% yield (*Scheme 3*) proving that N,S-acetals are suitable precursors for radical generation, but the reduction was slow (12 h). The formation of C–C bonds using the *Pereyre-Keck* allylation procedure failed, and the starting material **11** was recovered unchanged after 24 h of irradiation [13]. The radical reduction of N,Se-acetal **12** in the presence of Bu_3SnH/AIBN was complete within 1 h and gave carbamate **13** in 80% yield. The allylation reaction of **12** with methyl 2-[(tributylstannyl)methyl]prop-2-enoate was also possible and provided **14** in 65% yield. Based on these results, we decided to focus exclusively on N,Se-acetals for radical reactions.

1,2-Asymmetric Induction in Radicals Generated from N,Se-Acetals. – With a good method of preparation of N,Se-acetals in hand, we next turned our attention to radical precursors derived from chiral aldehydes. The optically active aldehyde **16** was obtained in 62% yield from methyl lactate **15** by silylation of the alcohol with triisopropylsilyl trifluoromethanesulfonate ((i-Pr)$_3$SiOTf) and subsequent DIBALH reduction of the ester to the aldehyde (*Scheme 4*). Treatment of aldehyde **16** with different primary amines in Et_2O at 0° gave imines **17a–c** in good yields. Our standard procedure for the preparation of N,Se-acetals provided the radical precursors **18a–c** as mixtures of diastereoisomers in 58 to 69% yield, along with β-elimination by-products (5–20%). For synthetic applications, it was important to check that the optical purity of the starting aldehydes was preserved during the N,Se-acetal formation. For this purpose, **18** was transformed into the more volatile oxazolidinone **20a** by reduction with Bu_3SnH/AIBN (→ **19a**) followed

[4]) PhSeAl(i-Bu)$_2$ is easily prepared by treatment of diphenyl diselenide with diisobutylaluminium hydride (DIBALH) (2 equiv.) [12].

by desilylation with Bu_4NF and base-promoted cyclization. Racemic oxazolidinone (±)-**20a** was prepared in two steps starting from racemic 1-amino-propano-2-ol ((±)-**21**) according to *Scheme 4*. Gas-chromatography analysis on a chiral capillary column (30% *Diacetoxygamma* in *OV-1701*) showed that the optical purity of the final product **20a** was maintained (≥ 95% ee).

Scheme 4

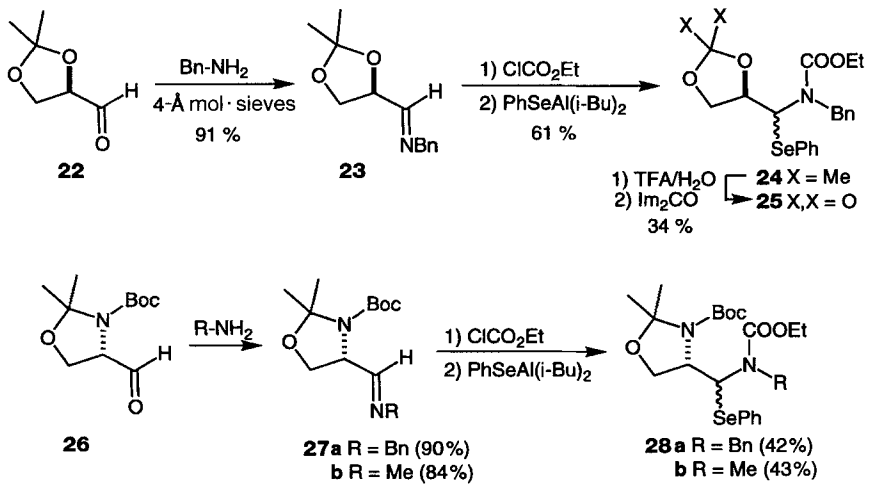


TIPS = $(i\text{-}Pr)_3Si$, Bn = $PhCH_2$

The N,Se-acetals **24** and **28a,b** were prepared according to the same procedure starting from chiral aldehydes **22** and **26** *via* **23** and **27a,b**, respectively (*Scheme 5*). To investigate possible stereoelectronic effects during the radical reactions, we transformed the acetonide **24** into the 1,3-dioxolan-2-one **25** by hydrolysis with CF_3COOH followed by treatment with 1,1′-carbonylbis[1*H*-imidazole].

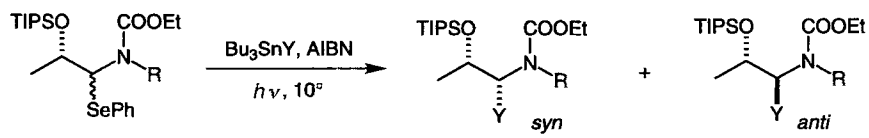
Radical Reactions. The results of the radical deuteration and allylation of the precursors **18a–c** are summarized in *Table 1* and *Scheme 6*. They show a general trend: the *anti*/*syn* ratio is always higher for the deuteration (→ **29a–c**) than for the allylation (→ **30a–c**). For instance, irradiation of N,Se-acetal **18a** with a 300-W sun lamp at 10° in benzene in the presence of Bu_3SnD and AIBN provided the deuterated product *anti*-**29a** in excellent yield and 78% ds (*Entry 1*). The selectivity was inversed for the radical allylation reaction of **18a** with methyl 2-[(tributylstannyl)methyl]prop-2-enoate which gave preferentially *syn*-**30a** (*Entry 2*). The deuteration of the methyl-substituted precursor **18b** provided again preferentially *anti*-**29b** (87% ds, *Entry 3*). A complete drop

Scheme 5



in selectivity was observed in the allylation of **18b**, the two diastereoisomers being formed in nearly equimolar amounts (*Entry 4*). Deuteration of the isopropyl-substituted precursor **18c** occurred in 80% ds (*Entry 5*), and the C–C bond forming reaction gave preferentially the *anti* isomer of **30c** with a modest selectivity of 67% (*Entry 6*).

Scheme 6



18a R = Bn
b R = Me
c R = i-Pr

29a R = Bn, Y = D
b R = Me, Y = D
c R = i-Pr, Y = D
30a R = Bn, Y = CH_2=C(COOMe)CH_2
b R = Me, Y = CH_2=C(COOMe)CH_2
c R = i-Pr, Y = CH_2=C(COOMe)CH_2

TIPS = $(i\text{-Pr})_3Si$, Bn = $PhCH_2$

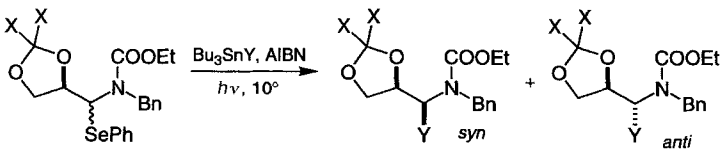
Table 1. *Radical Reactions with Precursors* **18a–c**

Entry	Precursor	R	Y	Product	Yield [%]	*syn/anti*[a])
1	**18a**	$PhCH_2$	D	**29a**	98	22:78[b])
2	**18a**	$PhCH_2$	CH_2=C(COOMe)CH_2	**30a**	65	68:32[b])
3	**18b**	Me	D	**29b**	90	13:87[c])[d])
4	**18b**	Me	CH_2=C(COOMe)CH_2	**30b**	71	55:45[b])[d])
5	**18c**	i-Pr	D	**29c**	81	20:80[c])
6	**18c**	i-Pr	CH_2=C(COOMe)CH_2	**30e**	61	33:67[b])[d])

[a]) *syn/anti* refers to the arrangement of the groups $(i\text{-Pr})_3SiO$ and Y. [b]) Selectivity determined by ^{1}H-NMR at 80° (D_6)DMSO. [c]) Selectivity determined by ^{2}H-NMR at 80° in toluene. [d]) Configuration not determined, attribution based on analogy of NMR spectra.

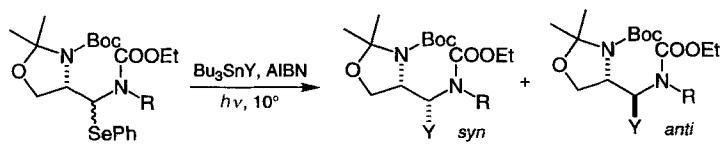
The results of the radical reactions of precursors **24**, **25**, and **28** are summarized in *Table 2* and *Scheme 7*. For the glyceraldehyde-derived precursors **24** and **25**, the reaction with Bu_3SnD gave *anti*-**31** and *anti*-**32** in 73 and 71% ds, respectively (*Entries 1* and *2*). The allylation of **24** to **33** was not diastereoselective (*Entry 3*). However, the allylation of **25** gave preferentially *anti*-**34** in 67% ds (*Entry 4*). Reaction of the oxazolidine derivatives **28a** and **28b** with Bu_3SnD yielded *anti*-**35a** and *anti*-**35b** in 76 and 86% ds (*Entries 5* and *6*), respectively, whereas the allylation of **28a** and **28b** afforded preferentially *syn*-**36a** and *syn*-**36b** in 72 and 56% ds (*Entries 7* and *8*).

Scheme 7



24 X, X = Me, Me
25 X, X = O

31 X, X = Me, Me, Y = D
32 X, X = O, Y = D
33 X, X = Me, Me, Y = CH_2=C(COOMe)CH_2
34 X, X = O, Y = CH_2=C(COOMe)CH_2



28 a R = $PhCH_2$
b R = Me

35a R = $PhCH_2$, Y = D
b R = Me, Y = D
36a R = $PhCH_2$, Y = CH_2=C(COOMe)CH_2
b R = Me, Y = CH_2=C(COOMe)CH_2

Table 2. *Radical Reactions of Precursors* **24**, **28**, *and* **28a**,**b**

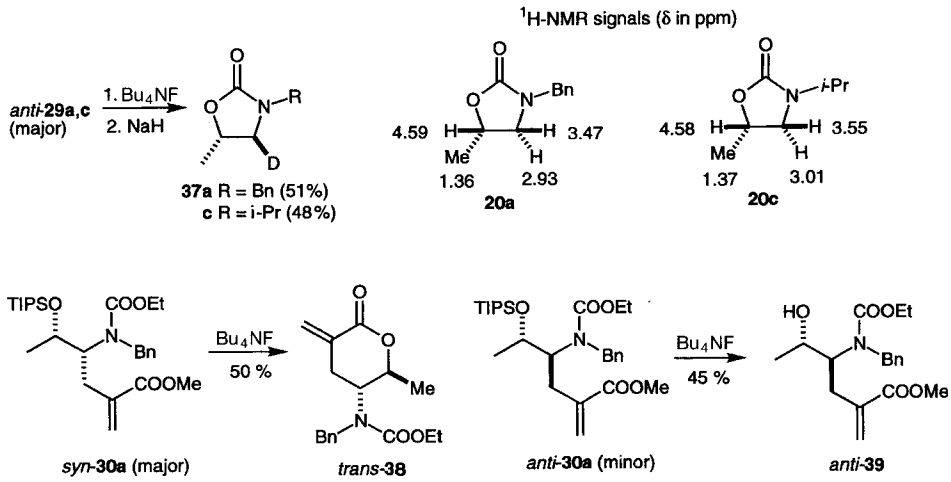
Entry	Precusor	X,X	R	Y	Product	Yield [5]	*syn*/*anti*[a])
1	**24**	Me,Me	–	D	**31**	84	27:73[b])
2	**25**	O	–	D	**32**	69	29:71[b])
3	**24**	Me,Me	–	CH_2=C(COOMe)CH_2	**33**	62	52:48[b])[c])
4	**25**	O	–	CH_2=C(COOMe)CH_2	**34**	73	33:67[b])[c])
5	**28a**	–	$PhCH_2$	D	**35a**	86	24:76[b])
6	**28b**	–	Me	D	**35b**	69	14:86[d])
7	**28a**	–	$PhCH_2$	CH_2=C(COOMe)CH_2	**36a**	58	72:28[b])[c])
8	**28b**	–	Me	CH_2=C(COOMe)CH_2	**36b**	47	56:44[b])[c])

[a]) *syn*/*anti* refers to the arrangement of the heteroatom (O or N) of the 5-ring and Y. [b]) Selectivity determined by ^{1}H-NMR at 80° in (D_6)DMSO. [c]) Configuration not determined, attribution based on analogy of NMR spectra. [d]) Selectivity determined by ^{2}H-NMR at 80° in toluene.

Determination of Relative Configuration. To establish their relative configurations, some of the products were converted into cyclic derivatives suitable for NOE measurements. The relative configuration of the other products were deduced by comparison of

the ^{1}H-NMR spectra. For instance, the major deuterated products *anti*-**29a** and *anti*-**29c** were transformed into oxazolidinones **37a** and **37c**, respectively, by treatment with Bu_4NF followed by NaH (*Scheme 8*). NOE Measurements were performed on the undeuterated analogs **20a** (*Scheme 4*) and **20c** (prepared according to the procedure for **20a** starting from **18c**). They allow to assign unambiguously the ^{1}H-NMR signals of **20a,c** (see *Scheme 8*). Based on these chemical shifts, it is possible to deduce that the *anti* isomers of **29a** and **29c** were formed preferentially during the radical deuteration. The *anti* configuration of **29b** was assigned by the strong resemblance of its ^{1}H-NMR spectrum to the one of *anti*-**29c**. The relative configuration of the allylation product **30a** was established after separation of the two diastereoisomers by prep. HPLC followed by desilylation with Bu_4NF. The major isomer cyclized directly upon deprotection to provide α-methylidene-lactone *trans*-**38**. The minor isomer gave alcohol *anti*-**39** which failed to cyclize even upon treatment with *p*-toluenesulfonic acid (*Scheme 8*). The spontaneous cyclization of the major isomer of **30a** suggested that its relative configuration was most probably *syn*; this was further confirmed by NOE measurements on **38** and from ^{1}H-NMR coupling constants. The relative configurations of **30b** and **30c** were not determined but assigned by comparison of their ^{1}H-NMR spectra with the one of **30a**.

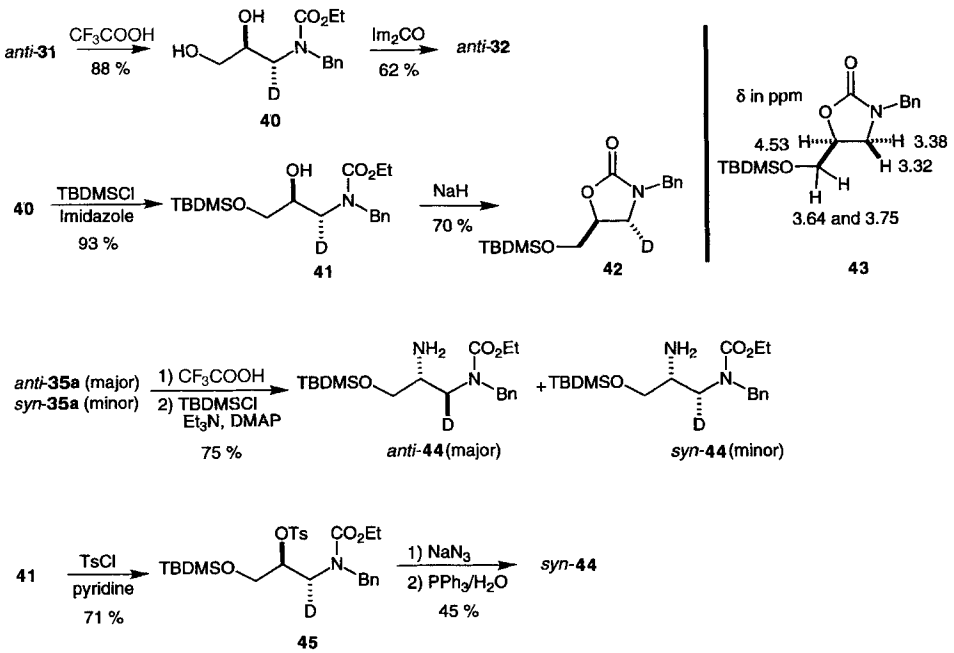
Scheme 8



Deprotection of *anti*-**31** (major isomer) with CF_3COOH provided diol **40** in 88% yield (*Scheme 9*). Monosilylation of **40** with (*tert*-butyl)chlorodimethylsilane gave **41** which afforded oxazolidinone **42** after treatment with NaH. The undeuterated analog **43** was prepared similarly using the product of Bu_3SnH-mediated radical reduction of **24**. NOE Experiments permitted to assign unambiguously the ^{1}H-NMR signals of **43** (see *Scheme 9*) and to determine the *anti* configuration of **31** (major isomer). Conversion of diol **40** into **32** by treatment with 1,1′-carbonylbis[1*H*-imidazole] allowed us to establish the relative *anti* configuration of the major isomer of **32**. The relative configuration of the allylated compounds **33** and **34** was not established but assigned based on analogies of their ^{1}H-NMR spectra with that of **30a**. The configuration of the oxazolidine deriva-

tive *anti*-**35a** (major isomer) was determined by its conversion into *anti*-**44** by hydrolysis with CF_3COOH followed by silylation with (*tert*-butyl)chlorodimethylsilane (*Scheme 9*). The relative configuration of **44** was assessed by independent synthesis from **41**. Tosylation of alcohol **41** gave **45** which was treated with NaN_3 followed by reduction with PPh_3 to give *syn*-**44** as the major isomer due to inversion of configuration during the nucleophilic substitution step. This compound was found to be identical with the minor isomer of **44** obtained from **35a**, proving that the major product of the radical deuteration had *anti* configuration. The configuration of the allylated compounds **36a** and **36b** were assessed by comparison of their ^{1}H-NMR spectra with that of **50a**.

Scheme 9



TBDMS = (*t*-Bu)Me_2Si, Bn = $PhCH_2$

Discussion. – All radical precursors demonstrate a similar trend, *i.e.*, deuteration afforded preferentially the *anti* product with higher selectivities than the corresponding allylation reactions. In some cases, a reversal of selectivity was even observed (*e.g.*, radical precursors **18a** and **28a**). A second general trend was noticed relative to the substituent at the N-atom. The $PhCH_2$ group tends to favor the production of the *syn* isomers in all investigated cases relative to the Me or i-Pr groups. To rationalize these trends, three effects have to be taken into account: *i*) the $A^{1,3}$ strain controls the conformation of 1-amidoalkyl radicals; therefore, the C–H bond at the stereogenic center prefers to be coplanar with the N–C* bond (*Fig.*, **C**); *ii*) stereoelectronic effects may favor attack *anti* to the heteroatom X (O or N) or *anti* to the group R depending on the nature of the radical trap (*Fig.*, **D** and **D′**); *iii*) the $A^{1,3}$ strain of the carbamate moiety controls the orientation of the group R′ at its N-atom, this effect is of importance only if R′ = $PhCH_2$

(*Fig.*, **E** and **E′**). The different models presented in the *Figure* have to be considered together. When the substituent at the N-atom is a Me or an i-Pr group, the radical exists in conformation **C**[5]). The stereochemistry of the reaction is governed by steric and stereoelectronic interactions. For radicals derived from **18b,c** and **28b**, steric effects favor the attack *anti* to the bulky substituted heteroatom (*anti* attack → *anti* products). The *anti* deuteration is favored by stereoelectronic effects (see **D**). Indeed, the nucleophilic character of the Bu_3SnD favors attack *anti* to the electron-withdrawing heteroatom X; therefore, with these three substrates, a good level of *anti* selectivity is observed (80–87% ds). The reaction with methyl 2-[(tributylstannyl)methyl]prop-2-enoate, an electron-poor radical trap, is favored by stereoelectronic effects in an *anti* fashion relative to the best electron-donating group, *i.e.*, the alkyl substituent R (see **D′**); this corresponds to the *syn* attack depicted in **C**. The selectivities observed in these cases are low, 55–67% ds, because of the antagonist influence of steric and stereoelectronic effects. The deuteration and allylation of **24** and **25** can be analyzed with the same model. However, steric interactions are not expected to be very important. The deuteration is mainly governed by stereoelectronic effects according to model **D**; therefore, *anti* products are formed with a moderate stereoselectivity (73 and 71% ds, resp.). The absence of selectivity for the allylation reaction of **24** is attributed to an antagonist stereoelectronic effect according to model **D′**. In the case of **25**, the electron-donating ability of the alkyl group R is lower because of the presence of the cyclic carbonate; therefore, a low selectivity for the *anti* product is still observed. The *N*-benzyl-substituted radical precursors **18a** and **28a** gave for the deuteration and for the allylation more *syn* products than the corresponding *N*-methyl (**18b** and **27b**) and *N*-isopropyl (**18c**) derivatives. This particular effect of the $PhCH_2$ group can be attributed to the second $A^{1,3}$ strain, caused by the carbamate moiety. In the most stable conformations, one of the diastereotopic benzylic H-atoms is coplanar with the C(O)–N bond, the Ph group can be either *syn* to the alkyl group R (see **E**) or *syn* to the X group (see **E′**). Because of steric hindrance (X = $(i\text{-Pr})_3SiO$ or BocN(R), the Ph group prefers to be *syn* to R (**E**) and, therefore, it shields the so-called *anti* attack leading to the *anti* isomer. For the deuteration, a moderate *anti* selectivity is still observed (76–78% ds). The stereochemical outcome of the allylation is reversed, and the *syn* products are preferentially obtained in 68 and 72% ds. This inversion is attributed to cumulative stereoelectronic effects and shielding by the Ph group at the prochiral center.

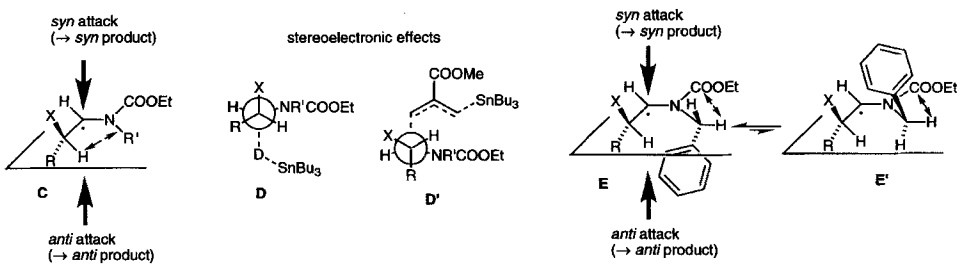


Figure. *Proposed models for the stereochemical outcome of radical reactions.* Allylic strain is indicated by a double arrow.

[5]) For convenience, all structures in the *Figure* have the same absolute configuration at the stereogenic center.

Conclusion. – We have developed an efficient transformation of aldehydes into N,Se-acetals which can be applied to substrates possessing a stereogenic center in the α-position without racemization. These N,Se-acetals are good radical precursors and can be used for stereoselective radical reactions. Interestingly, the stereochemical outcome of the reactions is not simply governed by the well established $A^{1,3}$ strain of 1-amido-substituted radicals and by steric considerations. Stereoelectronic effects also play an important role as well as the prochiral center of substituents at the N-atom because of preferential orientation due to a second $A^{1,3}$ strain. The importance of stereoelectronic effects has long been questioned in radical reactions [14]; the results presented here suggest that 1-amidoalkyl radicals are particularly sensitive to such effects. Further studies in order to separate as much as possible stereoelectronic and steric effects are underway in our laboratory.

This work was supported by the *Swiss National Science Foundation* (project No. 20-45'755.95). We thank *Ciba-Geigy*, Marly, Switzerland, for the microanalyses and *A. Saxer*, University of Bern, for GC analyses.

Experimental Part

General. See [3a]. Differing from [3a] or in addition: M.p.: not corrected; *Büchi-Tottoli* apparatus. NMR Spectra: δ(H) in ppm also rel. to (D_6)DMSO (= 2.49 ppm); no ^{13}C-NMR spectra were measured for the carbamate derivatives due to the presence of rotamers at r.t.

General Procedure 1: *'Imine' Formation.* To a 1M aldehyde soln. in dry Et_2O at 0°, an equimolar amount of the primary amine was added dropwise. The soln. was stirred at 0° for 1 h. The mixture was then washed with H_2O and brine and the org. layer dried ($MgSO_4$) and evaporated to give the crude imine which was pure enough for further use.

General Procedure 2: *Formation of N,Se-Acetals.* A 1M ethyl carbonochloridate soln. in dry Et_2O was added under N_2 to an equimolar amount of a 1M imine soln., prepared according to *GP 1*, in dry Et_2O. The mixture was stirred at r.t. for 1–5 h, cooled to 0°, and treated with a soln. of diisobutyl (phenylseleno)aluminium in toluene (1.1 equiv.; freshyl prepared by adding to 0° 0.5 equiv. of diphenyl diselenide to 1M DIBALH in toluene according to [12]). After 1 h at 0°, the mixture was treated with MeOH/H_2O 1:2.5 (1 equiv. of MeOH), the gel-like precipitate filtered through *Celite*, the filtrate washed with H_2O and sat. brine, dried ($MgSO_4$), and evaporated, and the residue purified by FC.

General Procedure 3: *Radical Reduction and Deuteration.* A soln. of the radical precursor, Bu_3SnH/Bu_3SnD (1.3 equiv.), and AIBN (0.1 equiv.) was irradiated with a 300-W sun lamp for 1.5 h at 10°. A sat. aq. KF soln. was added, and the mixture was stirred for 1 h at r.t. and poured into Et_2O. The org. phase was washed with H_2O and brine and dried ($MgSO_4$). The diastereoselectivity was determined by ^{1}H-NMR after concentration and filtration through a short column of silica gel.

General Procedure 4: *Radical Allylation.* A soln. of the radical precursor, methyl 2-[(tributylstannyl)methyl]prop-2-enoate (3.0 equiv.), and AIBN (0.1 equiv.) was irradiated with a 300-W sun lamp for several hours at 10°. Portions of AIBN (0.1 equiv.) were added every 6 h. After completion of the reaction (TLC monitoring), a sat. aq. KF soln. was added and the mixture stirred for 1 h at r.t. The aq. layer was extracted with Et_2O (3 ×) and combined org. phase washed with H_2O and brine and dried ($MgSO_4$). The diastereoselectivity was determined by ^{1}H-NMR after concentration and filtration through a short column of silica gel.

General Procedure 5: *Deprotection of the Silylated OH Groups.* The silyl ether was dissolved in 2 equiv. of 1M Bu_4NF in THF. The mixture was left overnight at r.t. The soln. was diluted with Et_2O and washed with H_2O and brine. The org. layer was dried ($MgSO_4$) and evaporated. FC of the residue gave the free alcohol.

General Procedure 6: *Preparation of Oxazolidinones.* A soln. of the alcohol in THF was cooled to 0° and treated with NaH (55% in oil; 1.3 equiv.). The mixture was stirred at 0° for 30 min and then treated with H_2O and extracted with Et_2O (3 ×). The org. phases were washed with H_2O and brine, dried ($MgSO_4$), and evaporated. FC gave the desired oxazolidinone.

N-(1-Methoxy-2-phenylethyl)-N-methyl-p-toluenesulfonamide (**2**). A soln. of **1** (831 mg, 5.00 mmol) and *N*-methyl-*p*-toluenesulfonamide (926 mg, 5.00 mmol) in dry CH_2Cl_2 (10 ml) was cooled to −78° under N_2. A soln. of $BF_3 \cdot OEt_2$ (0.70 ml, 5.50 mmol) in dry CH_2Cl_2 (5 ml) was added, and the mixture was stirred at −78°

for 2 h. A 10% Na_2CO_3 soln. was added, and the mixture was left to warm to r.t. The aq. layer was extracted with CH_2Cl_2 (2×) and the combined org. phase washed with H_2O and dried ($MgSO_4$). Evaporation and FC of the residue provided **2** (607 mg) containing 10% of N-*methyl*-N-*(2-phenylethenyl)*-p-*toluenesulfonamide* (**3**). Recrystallization in Et_2O/hexane gave pure **2** (527 mg, 33%). White solid. M.p. 87–90°. *IR* (KBr): 3061, 3026, 2944, 2834, 1933, 1819, 1595, 1452, 1325. ^{1}H-NMR (360 MHz): 7.38–7.11 (*m*, 5 arom. H); 5.26 (*dd*, *J* = 7.1, 5.7, CHN); 3.28 (*s*, MeO); 2.94 (*dd*, *J* = 14.0, 7.1, 1 H, PhCH_2); 2.71 (*s*, Me); 2.55 (*dd*, *J* = 14.0, 6.0, 1 H, PhCH_2); 2.40 (*s*, *Me*C$_6$H$_4$). ^{13}C-NMR (50.3 MHz): 143.08 (*s*); 136.69 (*s*); 136.60 (*s*); 129.51 (*d*); 129.31 (*d*); 128.51 (*d*); 127.10 (*d*); 126.62 (*d*); 89.36 (*d*); 55.74 (*q*); 39.68 (*t*); 26.67 (*q*); 21.42 (*q*). CI-MS: 289 (18), 288 (100), 228 (8). HR-FAB-MS: 320.1335 ([$C_{17}H_{21}NO_3S$ + H]$^+$; calc. 320.1320).

N-*Methyl*-N-*[2-phenyl-1-(phenylseleno)ethyl]*-p-*toluenesulfonamide* (**4**). A soln. of **2** (319 mg, 1.00 mmol), selenophenol (0.27 ml, 2.50 mmol), and TsOH · H_2O (24 mg, 0.13 mmol) in CH_2Cl_2 (1 ml) was left at r.t. for 2 h. More CH_2Cl_2 was added, the soln. washed with 10% $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated, and the residue purified by FC (AcOEt/hexane 1:5): **4** (314 mg, 69%). Colorless oil. IR (film): 3061, 3028, 2926, 1950, 1599, 1341, 1161, 941. ^{1}H-NMR (360 MHz): 7.57–7.54 (*m*, 2 arom. H); 7.34–7.23 (*m*, 8 arom. H); 7.16–7.14 (*m*, 2 arom. H); 7.09–7.07 (*m*, 2 arom. H); 6.04 (*dd*, *J* = 8.6, 6.8, CHSe); 3.12 (*dd*, *J* = 14.3, 6.8, 1 H, PhCH_2); 3.00 (*dd*, *J* = 14.3, 8.6, 1 H, PhCH_2); 2.86 (*s*, MeN); 2.37 (*s*, *Me*C$_6$H$_4$). ^{13}C-NMR (50.3 MHz): 143.03 (*s*); 137.32 (*s*); 136.04 (*d*); 136.00 (*s*); 129.38 (*d*); 129.02 (*d*); 128.58 (*d*); 128.25 (*d*); 127.89 (*s*); 127.31 (*d*); 126.91 (*d*); 63.76 (*d*); 41.37 (*t*); 29.37 (*t*); 21.41 (*q*). CI-MS: 289 (20), 288 (100, [*M* – C_6H_5Se]$^+$), 157 (9). FAB-MS: 444 (32, *M*$^+$). Anal. calc. for $C_{22}H_{23}NO_2SSe$ (444.45): C 59.45, H 5.22, N 3.15; found: C 59.59, H 5.32, N 3.13.

Phenylacetaldehyde (**6**). A soln. of **4** (327 mg, 0.72 mmol), Bu_3SnH (0.29 ml, 1.08 mmol), and AIBN (18 mg, 0.11 mmol) in benzene (7 ml) was irradiated with a 300-W sun lamp for 12 h at 10° under N_2. A sat. aq. KF soln. was added and the mixture stirred at r.t. for 1 h. The aq. layer was extracted with Et_2O (3×) and the combined org. phase washed with H_2O and brine and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:10) gave **6** (42 mg, 48%).

N-*(2-Methylpropylidene)benzenemethanamine* (**10**). According to *GP 1*, from **9** (9.13 ml, 0.10 mol) and benzenemethanamine (10.9 ml, 0.10 mol). Distillation provided **10** (13.9 g, 86%). B.p. 105°/15 mbar. ^{1}H-NMR (200 MHz): 7.65 (*dm*, *J* = 6.0, HC=N); 4.58 (*s*, PhCH_2); 2.61–2.42 (*m*, Me_2CH); 1.11 (*d*, *J* = 6.7, Me_2CH).

Ethyl Benzyl[2-methyl-1-(phenylthio)propyl]carbamate (**11**). A soln. of ethyl carbonochloridate (0.19 ml, 2.00 mmol) in Et_2O (2 ml) was added dropwise at 0° to a soln. of **10** (322 mg, 2.00 mmol) in Et_2O (2 ml). The mixture was stirred at r.t. for 3 h and then cooled to 0°. A soln. of thiophenol (0.22 ml, 2.20 mmol) and Et_3N (0.31 ml, 2.20 mmol) in Et_2O (3 ml) was added and the mixture stirred at 0° for 30 min and then filtered through *Celite*. The filtrate was washed with H_2O and brine and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:5) yielded **11** (267 mg, 39%). Colorless oil. IR (film): 3088, 2978, 2910, 1739, 1698, 1408, 1246. ^{1}H-NMR (360 MHz, (D$_6$)DMSO, 80°): 7.37–7.34 (*m*, 2 arom. H); 7.31–7.17 (*m*, 8 arom. H); 5.36 (*d*, *J* = 9.8, CHN); 4.54 (*A* of *AB*, J_{AB} = 15.9, 1 H, PhCH_2); 4.46 (*B* of *AB*, J_{AB} = 15.9, 1 H, PhCH_2); 4.00–3.90 (*m*, MeCH_2); 2.12–2.06 (*m*, MeC*H*); 1.09, 0.79 (2*d*, *J* = 6.7, Me_2CH); 1.05 (*t*, *J* = 7.0, *Me*CH$_2$). CI-MS: 344 (< 1, [*M* + 1]$^+$), 235 (16), 234 (100), 165 (9), 91 (11). Anal. calc. for $C_{20}H_{25}NO_2S$ (343.49): C 69.94, H 7.34, N 4.08; found: C 69.96, H 7.50, N 4.17.

Ethyl Benzyl[2-methyl-1-(phenylseleno)propyl]carbamate (**12**). *Method A*: With **10** (322 mg, 2.00 mmol), ethyl carbonochloridate (0.19 ml, 2.00 mmol) in Et_2O (2 ml), and selenophenol (0.27 ml, 2.50 mmol), according to the procedure for **11**. FC (AcOEt/hexane 1:5) gave **12** (293 mg, 33%).

Method B: According to *GP 2*, with **10** (322 mg, 2.00 mmol), ethyl carbonochloridate (0.19 ml). 1M DIBALH (2.2 ml), and diphenyl diselenide (344 mg, 1.10 mmol). FC (AcOEt/hexane 1:5) gave **12** (507 mg, 64%). Colorless oil. IR ($CHCl_3$): 2978, 1739, 1697. ^{1}H-NMR (360 MHz, (D$_6$)DMSO, 80°): 7.47–7.46 (*m*, 2 arom. H); 7.28–7.20 (*m*, 8 arom. H); 5.22 (*d*, *J* = 9.8, CHSe); 4.50 (*s*, PhCH_2); 4.03–3.93 (*m*, MeCH_2); 2.28 (*dsept.*, *J* = 9.9, 6.7, Me_2CH); 1.02, 0.76 (2*d*, *J* = 6.7, Me_2CH). FAB-MS: 390 (10, *M*$^+$), 235 (100), 213 (100), 160 (100), 136 (60), 119 (100). Anal. calc. for $C_{20}H_{25}NO_2Se$ (390.39): C 61.53, H 6.45; found: C 61.64, H 6.49.

Ethyl Benzyl(2-methylpropyl)carbamate (**13**). a) *Starting from* **11**: According to *GP 3*, with **11** (253 mg, 0.74 mmol), Bu_3SnH (0.29 ml, 1.11 mmol), AIBN (16 mg, 0.10 mmol), and dry benzene (5 ml); 12 h irradiation. FC (AcOEt/hexane 1:7) gave **13** (150 mg, 86%).

b) *Starting from* **12**: According to *GP 3*, with **12** (195 mg, 0.50 mmol), Bu_3SnH (0.20 ml, 0.75 mmol), AIBN (12 mg, 0.08 mmol), and dry benzene (4 ml); 2 h irradiation. FC (AcOEt/hexane 1:7) gave **13** (94 mg, 80%). Colorless oil. IR (film): 2961, 2933, 2872, 1703, 1468, 1423, 1244. ^{1}H-NMR (360 MHz, (D$_6$)DMSO, 80°): 7.34–7.22 (*m*, 5 arom. H); 4.40 (*s*, PhCH_2); 4.08 (*q*, *J* = 7.0, MeCH_2); 3.03 (*d*, *J* = 7.3, Me_2CHCH_2); 1.92 (*sept.*, *J* = 6.8, Me_2CH); 1.18 (*t*, *J* = 7.0, *Me*CH$_2$); 0.83 (*d*, *J* = 6.7, Me_2CH). CI-MS: 236 (100, [*M* + 1]$^+$), 235

(11, M^+), 192 (27), 158 (13), 91 (11). Anal. calc. for $C_{14}H_{21}NO_2$ (235.33): C 71.46, H 8.99, N 5.95; found: C 71.30, H 8.74, N 5.75.

Methyl 4-[Benzyl(ethoxycarbonyl)amino]-5-methyl-2-methylidenehexanoate (**14**). According to *GP 4*, with **12** (195 mg, 0.50 mmol), methyl 2-[(tributylstannyl)methyl]prop-2-enoate (584 mg, 1.50 mmol), AIBN (25 mg, 0.15 mmol), and dry benzene (4 ml); 20 h irradiation. FC (AcOEt/hexane 1:7, then 1:5) provided **14** (112 mg, 65%). Colorless oil. IR (film): 2963, 1721, 1693, 1439, 1220. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°): 7.29–7.19 (*m*, 5 arom. H); 5.97 (*d*, J = 1.0, 1 H, C=CH_2); 5.40 (*s*, 1 H, C=CH_2); 4.36 (*A* of *AB*, J_{AB} = 15.6, 1 H, PhCH_2); 4.24 (*B* of *AB*, J_{AB} = 15.6, PhCH_2); 4.07 (*qd*, J = 7.0, 2.1, MeCH_2); 3.71 (*td*, J = 9.5, 4.3, CHN); 3.65 (*s*, MeO); 2.65–2.52 (*m*, CH_2CHN); 1.94 (*dm*, J = 6.2, Me_2CH); 1.17 (*t*, J = 7.0, $MeCH_2$); 0.92, 0.71 (2*d*, J = 6.7, Me_2CH). CI-MS: 334 (100, $[M + 1]^+$), 288 (45), 256 (10), 234 (44), 180 (15), 155 (37), 91 (37), 41 (55). Anal. calc. for $C_{19}H_{27}NO_4$ (333.43): C 68.44, H 8.16, N 4.20; found: C 68.63, H 8.00, N 4.18.

(S)-2-[(Triisopropylsilyl)oxy]propanal (**16**) [17]. Triisopropylsilyl triflate (35.0 ml, 0.13 mol) was added at 0° under N_2 to a soln. of (–)-L-methyl lactate (**15**; 10.4 g, 0.10 mol) and freshly distilled 2,6-dimethylpyridine (29.0 ml, 0.25 mol) in dry CH_2Cl_2 (100 ml). The mixture was stirred for 30 min at 0° and then washed with 3M HCl and H_2O. The org. layer was dried ($MgSO_4$) and evaporated. The residue was distilled under vacuum to yield methyl (*S*)-2-[(triisopropylsilyl)oxy]propanoate (24.8 g, 95%). Colorless liquid. B.p. 115–118°/20 mbar. ^{1}H-NMR (200 MHz): 4.43 (*q*, J = 6.8, CHO); 3.12 (*s*, MeO); 1.42 (*d*, J = 6.7, Me); 1.06–1.02 (*m*, 21 H, (i-Pr)$_3$Si).

To a soln. of the protected ester (13.0 g, 50.0 mmol) in dry Et_2O (250 ml) at –78° under N_2, 1M DIBALH in toluene (75 ml) was added, and the mixture was stirred for 10 min, treated with MeOH (3 ml) and H_2O (7.5 ml), and allowed to warm to r.t. The gel-like precipitate was filtered through *Celite*. The filtrate was dried ($MgSO_4$) and evaporated. FC (AcOEt/hexane 1:10) gave **16** (7.48 g, 65%). Colorless liquid. ^{1}H-NMR (200 MHz): 9.62 (*d*, J = 1.7, HCO); 4.14 (*qd*, J = 6.8, 1.7, MeC*H*); 1.27 (*d*, J = 6.8, Me); 1.04–1.00 (*m*, 21 H, (i-Pr)$_3$Si).

N-{(2S)-2-[(Triisopropylsilyl)oxy]propylidene}benzenemethanamine (**17a**). According to *GP 1* with **16** (4.61 g, 20.0 mmol) and benzenemethanamine (2.18 ml, 20.0 mmol). Evaporation gave **17a** (5.59 g, 87%). Colorless liquid. IR (film): 3065, 2961, 2892, 1675, 1464, 1114, 1096. ^{1}H-NMR (360 MHz): 7.67 (*dt*, J = 5.1, 1.4, CH=N); 7.34–7.23 (*m*, 5 arom. H); 4.58 (*s*, PhCH_2); 4.46 (*quint.*, J = 6.2, CHO); 1.34 (*d*, J = 6.6, Me); 1.05–1.03 (*m*, 21 H, (i-Pr)$_3$Si). ^{13}C-NMR (50.3 MHz): 168.97 (*d*); 138.88 (*s*); 128.35 (*d*); 127.96 (*d*); 126.90 (*d*); 70.63 (*d*); 64.37 (*t*); 22.00 (*d*); 17.89 (*q*); 12.18 (*q*). CI-MS: 321 (17, $[M + 1]^+$), 320 (60, M^+), 276 (100), 277 (24), 91 (14). Unstable, not suitable for elemental analysis.

N-{(2S)-2-[(Triisopropylsilyl)oxy]propylidene}methanamine (**17b**). Prepared according to *GP 1* with **16** (6.91 g, 30.0 mmol) and $MeNH_2$ (25 ml, 563 mmol) in a sealed flask. Excess $MeNH_2$ and solvent were evaporated: **17b** (6.61 g, 90%). Yellow liquid. IR (film): 2945, 2867, 1680, 1464, 1095, 833. ^{1}H-NMR (360 MHz): 7.57–7.54 (*m*, CH=N); 4.36 (*quint.*, J = 6.1, CHO); 3.27 (*d*, J = 1.1, MeN); 1.29 (*d*, J = 6.3, Me); 1.07–1.03 (*m*, 21 H, (i-Pr)$_3$Si). ^{13}C-NMR (50.3 MHz): 169.33 (*d*); 70.55 (*d*); 47.26 (*q*); 21.82 (*d*); 17.90 (*q*); 12.17 (*q*). CI-MS: 244 (59, $[M + 1]^+$), 200 (100), 157 (14), 131 (18). Unstable, not suitable for elemental analysis.

1-Methyl-N-{(2S)-2-[(triisopropylsilyl)oxy]propylidene}ethanamine (**17c**). According to *GP 1* with **16** (2.62 g, 10.0 mmol) and (i-Pr)NH_2 (1.70 ml, 20.0 mmol). Excess (i-Pr)NH_2 and solvent were evaporated: **17c** (2.34 g, 86%). Yellow liquid. IR (film): 2986, 2944, 2867, 1670, 1096. ^{1}H-NMR (360 MHz): 7.53 (*d*, J = 5.7, CH=N); 4.36 (*qd*, J = 6.3, 5.7, CHO); 3.29 (*sept.*, J = 6.3, Me_2CH); 1.15, 1.14 (2 *d*, J = 6.3, Me_2CH); 1.28 (*d*, J = 6.3, Me); 1.07–1.03 (*m*, 21 H, (i-Pr)$_3$Si). ^{13}C-NMR (50.3 MHz): 165.24 (*d*); 70.60 (*d*); 60.63 (*d*); 23.87 (*d* or *q*); 23.62 (*d* or *q*); 22.09 (*d*); 17.87 (*q*); 12.08 (*q*). CI-MS: 272 (22, M^+), 228 (23), 173 (8), 157 (26), 131 (38), 88 (45), 61 (38). Unstable, not suitable for elemental analysis.

Ethyl Benzyl{(1R,2S)- and (1S,2S)-1-(phenylseleno)-2-[(triisopropylsilyl)oxy]propyl}carbamate (**18a**). According to *GP 2*, with **17a** (4.79 g, 15.0 mmol), ethyl carbonochloridate (1.43 ml, 15.0 mmol), 1M DIBALH (16.5 ml, 16.5 mmol), and diphenyl diselenide (2.58 g, 8.25 mmol); 3 h at r.t. FC (AcOEt/hexane 1:10) gave **18a** (4.91 g, 60%; 1:1 diastereoisomer mixture, contaminated with 20% of elimination product). Colorless oil. IR (film): 2944, 2867, 1704. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°, 1:1 mixture): 7.51–7.48 (*m*, 2 arom. H, isomer 1 or 2); 7.35–7.32 (*m*, 2 arom. H, isomer 1 or 2); 7.32–7.20 (*m*, 8 arom. H); 5.58 (*d*, J = 6.4, CHSe, isomer 1 or 2); 5.48 (*d*, J = 6.4; CHSe, isomer 1 or 2); 4.81 (*d*, J = 15.8, 1 H of PhCH_2, isomer 1 or 2); 4.56 (*s*, PhCH_2, isomer 1 or 2); 4.55 (*d*, J = 15.6, 1 H of PhCH_2, isomer 1 or 2); 4.09 (*q*, J = 7.0, MeCH_2); 3.98–3.92 (*m*, CHO); 1.30–1.01 (*m*, 27 H, $MeCH_2$, Me, (i-Pr)$_3$Si). CI-MS: 548 (0.55, M^+), 506 (4), 91 (3). Anal. calc. for $C_{28}H_{43}NO_3$SeSi (548.71) with 20% of $C_{22}H_{32}NO_3Si$ (386.58): C 62.70, H 7.99, N 2.76; found: C 62.61, H 8.29, N 2.88.

Ethyl Methyl{(1R,2S)- and (1S,2S)-1-(phenylseleno)-2-[(triisopropylsilyl)oxy]propyl}carbamate (**18b**). According to *GP 2*, with **17b** (487 mg, 2.00 mmol), ethyl carbonochloridate (0.19 ml, 2.00 mmol), 1M DIBALH (2.2 ml, 2.2 mmol), and diphenyl diselenide (344 mg, 1.10 mmol); 2 h reflux. FC (AcOEt/hexane 1:10) gave **18b** (489 mg, 52%; diastereoisomer mixture). IR (film): 2944, 2868, 1705, 1580, 1466, 1385, 1304, 1136. ^{1}H-NMR

(360 MHz, (D_6)DMSO, 80°; diastereoisomer mixture): 7.55–7.49 (*m*, 2 arom. H); 7.29–7.21 (*m*, 3 arom. H); 5.77 (*d*, $J = 5.2$, CHSe, major); 5.73 (*d*, $J = 6.7$, CHSe, minor); 4.45 (*qd*, $J = 6.1$, 5.2, CHO, major); 4.31 (*quint.*, $J = 6.1$, CHO, minor); 3.96–3.77 (*m*, $MeCH_2$); 2.97 (*s*, MeN, major); 2.85 (*s*, MeN, minor); 1.29 (*d*, $J = 6.1$, Me, minor); 1.27 (*d*, $J = 6.1$, Me, major); 1.12–1.02 (*m*, 24 H, $MeCH_2$, and $(i\text{-}Pr)_3Si$). CI-MS: 317 (21), 316 (100, $[M - C_6H_5Se]^+$), 300 (10), 157 (11), 104 (12). Anal. calc. for $C_{22}H_{39}NO_3SeSi$ (472.60): C 55.91, H 8.32, N 2.96; found: C 55.88, H 8.51, N 2.84.

Ethyl Isopropyl{(1R,2S)- and (1S,2S)-1-(phenylseleno)-2-[(triisopropylsilyl)oxy]propyl}carbamate (**18c**). According to *GP 2*, with **17c** (543 mg, 2.00 mmol), ethyl carbonochloridate (0.19 ml, 2.00 mmol), 1M DIBALH (2.2 ml, 2.2 mmol), and diphenyl diselenide (344 mg, 1.10 mmol); 12 h at r.t. FC (Et_2/hexane 1:9) gave **18c** (621 mg, 62%; 2:1 diastereoisomer mixture). Colorless oil. IR (film): 2969, 2943, 2867, 1707, 1438, 1280. ^{1}H-NMR ((D_6)DMSO, 80°; 2:1 mixture): 7.54–7.40 (*m*, 2 arom. H); 7.30–7.24 (*m*, 3 arom. H); 5.51 (br. *d*, $J = 4.0$, CHSe, major); 5.31 (br. *s*, CHSe, minor); 4.57 (*qd*, $J = 6.4$, 4.6, CHO, major); 4.49–4.41 (*m*, CHO, minor); 4.17 (*sept.*, $J = 6.7$, Me_2CH, major); 4.01 (*q*, $J = 6.9$, $MeCH_2$); 4.01–3.92 (*m*, Me_2CH, minor); 1.34, 1.32 (2 *d*, $J = 6.7$, Me_2CH); 1.24–1.06 (*m*, 27 H, Me, $(i\text{-}Pr)_3Si$, $MeCH_2$). CI-MS: 501 (< 1, M^+), 458 (7), 345 (27), 344 (100), 327 (6), 41 (19). Anal. calc. for $C_{24}H_{43}NO_3SeSi$ (500.65): C 57.58, H 8.66, N 2.80; found: C 57.63, H 8.62, N 2.69.

Ethyl Benzyl{(S)-2-[(triisopropylsilyl)oxy]propyl}carbamate (**19a**). According to *GP 3*, with **18a** (1.10 g, 2.00 mmol), Bu_3SnH (0.69 ml, 2.60 mmol), AIBN (33 mg, 0.20 mmol), and benzene (10 ml). FC (AcOEt/hexane 1:10) provided **19a** (0.77 g, 98%). Colorless oil. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 7.34–7.18 (*m*, 5 arom. H); 4.51 (*s*, $PhCH_2$); 4.19–4.13 (*m*, CHO); 4.08 (*q*, $J = 7.1$, $MeCH_2$); 3.26–3.02 (*m*, CH_2N); 1.21–0.92 (*m*, 27 H, Me, $MeCH_2$, $(i\text{-}Pr)_3Si$).

(S)-3-Benzyl-5-methyloxazolidin-2-one ((−)-**20a**). According to *GP 5*, with **19a** (348 mg, 0.88 mmol) and Bu_4NF soln. (2 ml). FC (AcOEt/hexane 1:2) provided the free alcohol (200 mg, 95%). Colorless oil. $[\alpha]_D^{20} = +3.2$ ($CHCl_3$, $c = 2.8 \cdot 10^{-3}$). IR (film): 3442, 2978, 2933, 1688, 1422, 1241, 1132. (360 MHz, (D_6)DMSO, 80°): 7.33–7.22 (*m*, 5 arom. H); 4.56 (*A* of *AB*, $J_{AB} = 15.5$, 1 H, $PhCH_2$); 4.50 (*B* of *AB*, $J_{AB} = 15.5$, 1 H, $PhCH_2$); 4.09 (*q*, $J = 7.0$, $MeCH_2$); 3.88 (*m*, CHO); 3.22–3.08 (*m*, CNH_2); 1.19 (*t*, $J = 7.0$, $MeCH_2$); 1.04 (*d*, $J = 6.4$, Me). CI-MS: 238 (100, $[M + 1]^+$), 221 (9), 220 (65), 193 (20), 192 (60), 91 (91), 41 (22). Anal. calc. for $C_{13}H_{19}NO_3$ (237.30): C 65.80, H 8.07, N 5.90; found: C 65.79, H 8.04, N 5.97.

According to *GP 6*, with the free alcohol (56 mg, 0.24 mmol), THF (1 ml), and NaH (55% in oil; 13 mg, 0.29 mmol). FC (AcOEt/hexane 1:1) gave **20a** (43 mg, 94%). Colorless liquid. $[\alpha]_D^{20} = -45.75$ ($CHCl_3$, $c = 1.33 \cdot 10^{-3}$). GC (30% *Diacetoxygamma* in *OV-1701*, 120°): t_R 182.8 ((S)) and 183.2 ((*R*)) min; ee ≥ 95%. IR (film): 2981, 2931, 1754, 1429, 1061. ^{1}H-NMR (360 MHz): 7.36–7.26 (*m*, 5 arom. H); 4.64–4.54 (*m*, $MeCHO$); 4.42 (*A* of *AB*, $J_{AB} = 14.8$, 1 H, $PhCH_2$); 4.36 (*B* of *AB*, $J_{AB} = 14.8$, 1 H, $PhCH_2$); 3.47 (*t*, $J = 8.5$, 1 H, CH_2CHO); 2.95 (*dd*, $J = 8.6$, 7.1, 1 H, CH_2CHO); 1.36 (*d*, $J = 6.3$, Me). NOE (360 MHz): 1.36 (Me) → 2.95 (1 H of CH_2N; 3.1%); 2.95 (1 H of CH_2N) → 1.36 (Me, 3.3%); 3.47 (1 H of CH_2N) → 4.64–4.54 (CHO, 7.2%); 4.64–4.54 (CHO) → 3.47 (1 H of CH_2N, 7%). ^{13}C-NMR (50.3 MHz): 158.07 (*s*); 135.87 (*s*); 128.77 (*d*); 128.07 (*d*); 127.89 (*d*); 70.2 (*d*); 50.69 (*t*); 48.23 (*t*); 20.62 (*q*). CI-MS: 192 (100, $[M + 1]^+$), 91 (19). Anal. calc. for $C_{11}H_{13}NO_2$ (191.23): C 69.09, H 6.85, N 7.32; found: C 69.00, H 6.92, N 7.37.

(±)-3-Benzyl-5-methyloxazolidin-2-one ((±)-**20a**). Ethyl carbonochloridate (5.2 ml, 55 mmol) was added dropwise within 15 min at 0° to a soln. of (±)-1-aminopropan-2-ol (**21**) (3.76 g, 50.0 mmol) and Et_3N (7.70 ml, 55.0 mmol) in CH_2Cl_2 (100 ml). The mixture was stirred for 10 min at 0° and then for 1 h at r.t. The mixture was poured into H_2O and extracted with CH_2Cl_2 (3×). The combined org. phase was dried ($MgSO_4$) and evaporated to yield crude ethyl (2-hydroxypropyl)carbamate (5.72 g, 78%) which was pure enough to be used for the next step. Yellow oil. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 6.55 (br. *s*, NH); 4.32 (*d*, $J = 4.7$, OH); 3.99 (*q*, $J = 7.1$, $MeCH_2$); 3.67–3.61 (*m*, CHO); 2.96–2.90 (*m*, CH_2NH); 1.17 (*t*, $J = 7.1$, $MeCH_2$); 1.02 (*d*, $J = 6.3$, Me).

NaH (55% in oil; 96 mg, 2.20 mmol) was added portionwise at 0° to a soln. of ethyl (2-hydroxypropyl)carbamate (146 mg, 1.00 mmol) in dry THF (3 ml). After 30 min at 0°, benzyl bromide (0.28 ml, 2.40 mmol) and Bu_4NI (37 mg, 0.10 mmol) were added. The mixture was stirred for 10 h at r.t. and then treated with H_2O, diluted with Et_2O, and washed with H_2O and brine. After drying ($MgSO_4$) and evaporation, the residue was purified by FC (AcOEt/hexane 1:1): (±)-**20a** (159 mg, 89%). Spectral data: identical with those of (−)-**27a**.

(S)-3-Isopropyl-5-methyloxazolidin-2-one (**20c**). According to *GP 3*, with **18c** (1.00 g, 2.00 mmol), Bu_3SnH (873 mg, 0.80 ml, 3.00 mmol), AIBN (49 mg, 0.30 mmol) and dry benzene (10 ml). FC (AcOEt/hexane 1:10) gave ethyl isopropyl{(*S*)-2-[(triisopropylsilyl)oxy]propyl}carbamate (588 mg, 85%). Colorless liquid. $[\alpha]_D^{20} = +17.0$ ($CHCl_3$, $c = 0.04$). IR (film): 2966, 2944, 2868, 1703, 1467, 1130, 1005, 883 (200 MHz, (D_6)DMSO, 80°): 4.26–4.14 (*m*, CHO); 4.03 (*q*, $J = 7.0$, $MeCH_2$); 4.03–3.86 (*m*, Me_2CH); 3.24–2.95 (*m*, CH_2N); 1.21–1.05

(*m*, 33 H, Me, Me_2, $(i\text{-}Pr)_3Si$, $MeCH_2$). CI-MS: 374, 346 (33, M^+), 303 (22), 302 (100), 172 (66). Anal. calc. for $C_{18}H_{39}NO_3Si$ (345.60): C 62.56, H 11.37, N 4.05; found: C 62.33, H 11.31, N 4.10.

According to *GP 5*, with ethyl isopropyl{(*S*)-2-[(triisopropylsilyl)oxy]propyl}carbamate (215 mg, 0.62 mmol) and Bu_4NF (2 ml); 36 h r.t. FC (AcOEt/hexane 1:3) provided ethyl isopropyl[(*S*)-2-hydroxypropyl]carbamate (102 mg, 87%). Colorless oil. $[\alpha]_D^{20} = -28.3$ ($CHCl_3$, $c = 0.0055$). IR (film): 3451, 2977, 2935, 1678, 1130, 774. (200 MHz, (D_6)DMSO, 80°): 4.38 (br. *s*, OH); 4.02 (*q*, $J = 7.1$, $MeCH_2$); 3.99–3.71 (*m*, CHO, Me_2CH); 3.15–2.92 (*m*, CH_2N); 1.17 (*t*, $J = 7.1$, $MeCH_2$); 1.15, 1.13 (2*d*, $J = 6.8$, Me_2CH); 1.02 (*d*, $J = 6.3$, Me). CI-MS: 191 (11, $[M + 2]^+$), 190 (100, $[M + 1]^+$), 172 (44), 144 (88), 130 (12), 102 (10). Anal. calc. for $C_9H_{19}NO_3$ (189.26): C 57.12, H 10.12, N 7.40; found: C 57.00, H 10.05, N 7.43. According to *GP 6*, with ethyl isopropyl[(*S*)-2-hydroxypropyl]carbamate (81 mg, 0.43 mmol), dry THF (1 ml), and NaH (55% in oil; 24 mg, 0.50 mmol). FC (AcOEt/hexane 1:2) yielded volatile **20c** (43 mg, 70%). Colorless liquid. $[\alpha]_D^{20} = -135$ ($CHCl_3$, $c = 0.0002$). IR (film): 2976, 1743, 1427, 1045. ^{1}H-NMR (360 MHz): 4.63–4.54 (*m*, $MeCHO$); 4.06 (*sept.*, $J = 6.7$, Me_2CH); 3.55 (*t*, $J = 8.4$, 1 H, CH_2N); 3.01 (*dd*, $J = 8.4$, 7.0, 1 H, CH_2N); 1.37 (*d*, $J = 6.3$, Me); 1.13, 1.11 (2*d*, $J = 6.7$, Me_2CH). NOE (360 MHz): 1.37 (Me) → 3.01 (1 H of CH_2N, 2.6%); 3.01 (1 H of CH_2N) → 1.37 (Me, 2.8%); 3.55 (1 H of CH_2N) → 4.63–4.54 (CHO, 12.3%). ^{13}C-NMR (50.3 MHz): 157.18 (*s*); 69.92 (*d*); 46.28 (*t*); 44.48 (*d*); 20.58 (*q*); 19.81 (*q*); 19.49 (*q*). CI-MS: 145 (20, $[M + 2]^+$), 144 (100, $[M + 1]^+$), 128 (15), 102 (13), 84 (11). HR-CI-MS: 143.0966 ($C_7H_{13}NO_2^+$; calc. 143.0966).

{[(S)-2,2-Dimethyl-1,3-dioxolan-4-yl]methylidene}benzenemethanamine (**23**). According to *GP 1*, with **22** (3.46 g, 26.6 mmol), benzenemethanamine (2.85 ml, 26.6 mmol), and 4-Å molecular sieves (800 mg). Filtration and evaporation gave **23** (5.32 g, 91%). Yellow liquid. IR (film): 2987, 2935, 2878, 1672, 1371, 1064. ^{1}H-NMR (360 MHz): 7.78–7.76 (*m*, CH=N); 7.36–7.25 (*m*, 5 arom. H); 4.66–4.63 (*m*, CHO); 4.63 (*s*, $PhCH_2$); 4.22 (*dd*, $J = 8.5$, 6.9, 1 H, CH_2O); 3.97 (*dd*, $J = 8.5$, 6.2, 1 H, CH_2O); 1.47 (*s*, Me); 1.41 (*s*, Me). ^{13}C-NMR (50.3 MHz): 163.85 (*d*); 138.23 (*d*); 128.29 (*d*); 127.71 (*d*); 126.91 (*d*); 109.91 (*s*); 76.79 (*d*); 67.12 (*d*); 64.34 (*t*); 26.31 (*q*); 25.22 (*q*). CI-MS: 220 (48, $[M + 1]^+$), 219 (7, M^+), 166 (30), 162 (32), 160 (14), 119 (11), 91 (100), 59 (30), 41 (65). Unstable, not suitable for elemental analysis.

Ethyl Benzyl{(1R)- and (1S)-[(R)-2,2-dimethyl-1,3-dioxolan-4-yl)](phenylseleno)methyl}carbamate (**24**). According to *GP 2*, with **23** (2.19 g, 10.0 mmol), ethyl carbonochloridate (0.95 ml, 10.0 mmol), 1M DIBALH (11.0 ml, 11.0 mmol), and diphenyl diselenide (1.72 g, 5.50 mmol); 3 h at r.t. FC (AcOEt/hexane 1:5) gave **24** (2.73 g, 61%; diastereoisomer mixture). Colorless oil. IR (film): 2986, 2935, 1703, 1248. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°); diastereoisomer mixture): 7.60–7.51 (*m*, 1 arom. H, minor); 7.44–7.39 (*m*, 1 arom. H, major); 7.36–7.20 (*m*, 8 arom. H); 5.70 (*d*, $J = 6.0$, CHSe, minor); 5.19 (br. *s*, CHSe, major); 4.71–4.45 (*m*, $PhCH_2$); 4.35–4.26 (*m*, CHO, major); 4.11–3.59 (*m*, 5 H, $MeCH_2$, CH_2O, CHO of minor); 1.31, 1.13 (2 *s*, 2 Me, minor); 1.26 (2 *s*, 2 Me, major); 1.09 (*t*, $J = 7.1$, $MeCH_2$, major); 1.00 (*t*, $J = 7.1$, $MeCH_2$, minor). CI-MS: 448 (< 1, M^+), 392 (10), 292 (100), 91 (18). Anal. calc. for $C_{22}H_{27}NO_4Se$ (448.43): C 58.93, H 6.07, N 3.12; found: C 59.11, H 6.12, N 3.20.

Ethyl Benzyl{(1R)- and (1S)-[(R)-2-oxo-1,3-dioxolan-4-yl](phenylseleno)carbamate (**25**). A soln. of **24** (189 mg, 0.42 mmol) and CF_3OOH (0.14 ml, 1.26 mmol) in THF/H_2O 4:1 (2 ml) was heated under reflux for 5 h. After cooling, the mixture was neutralized with NH_4OH and extracted with Et_2O (3 ×). The combined org. phase was washed with brine, dried ($MgSO_4$), and evaporated and the residue purified by FC (AcOEt/hexane 1:2, then 1:1) to provide the diol (115 mg, 67%; diastereoisomer mixture). ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 7.55–7.51 (*m*, 2 arom. H, minor); 7.43–7.39 (*m*, 2 arom. H, major); 7.37–7.18 (*m*, 8 arom. H); 5.89 (*d*, $J = 4.1$, CHSe, minor); 5.52 (br. *s*, CHSe, major); 5.02 (*d*, $J = 4.5$, $CHOH$, minor); 4.91 (*d*, $J = 5.6$, $CHOH$, major); 4.72–4.29 (*m*, $PhCH_2$, CH_2OH); 4.10–3.76 (*m*, CHOH, $MeCH_2$); 3.62–3.28 (*m*, CH_2OH); 1.04 (*t*, $J = 7.1$, $MeCH_2$, major); 0.96 (*t*, $J = 7.1$, $MeCH_2$, minor).

A soln. of the above diol (108 mg, 0.26 mmol) in dry THF (2 ml) was heated under reflux. Within 1 h, 1,1′-carbonylbis[1*H*-imidazole] (97 mg, 0.60 mmol) was added, and the mixture was heated under reflux for 2 h, then cooled to r.t., diluted with Et_2O (10 ml), washed with H_2O (3 ×) and brine, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 1:2) yielded **25** (84 mg, 74%; of diastereoisomer mixture). IR (film): 2984, 1815, 1703, 1244, 1165, 1076. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): diastereoisomer 1: 7.44–7.42 (*m*, 2 arom. H); 7.33–7.25 (*m*, 8 arom. H); 5.39–5.32 (*m*, CHO); 5.26 (*d*, $J = 8.9$, CHSe); 4.66 (*d*, $J = 15.6$, 1 H, $PhCH_2$); 4.66–4.61 (*m*, 1 H, OCH_2CHO); 4.52 (*d*, $J = 15.9$, 1 H, $PhCH_2$); 4.25–4.20 (*m*, 1 H, OCH_2CHO); 4.09 (*q*, $J = 7.0$, $MeCH_2$); 1.16 (*t*, $J = 7.0$, $MeCH_2$); diastereoisomer 2: 7.55–7.54 (*m*, 2 arom. H); 7.37–7.24 (*m*, 8 arom. H); 5.50 (*d*, $J = 4.6$, CHSe); 5.18–5.14 (*m*, CHO); 4.61 (*d*, $J = 16.2$, 1 H; $PhCH_2$); 4.50 (*d*, $J = 15.9$, 1 H, $PhCH_2$); 4.42 (*dd*, $J = 8.9$, 8.2, 1 H, OCH_2CHO); 4.16 (*dd*, $J = 8.9$, 6.4, 1 H, OCH_2CHO); 4.09–4.01 (*m*, $MeCH_2$); 1.12 (*t*, $J = 7.0$, $MeCH_2$). CI-MS: 436 (29, $[M + 2]^+$), 434 (14, M^+), 374 (23), 372 (12), 278 (100), 234 (15), 218 (32), 206 (29), 192 (12). Anal. calc. for $C_{20}H_{21}NO_5Se$ (434.35): C 55.31, H 4.87; found: C 55.38, H 4.96.

tert-*Butyl (S)-4-[(Benzylimino)methyl]-2,2-dimethyloxazolidine-3-carboxylate* (**27a**). According to *GP 1*, from **26** (1.00 g, 4.36 mmol) and benzenemethanamine (0.47 ml, 4.36 mmol) in Et_2O (5 ml). Evaporation gave **27a** (1.25 g, 90%). White solid. IR (KBr): 2990, 2820, 1694, 1397, 1371, 1173, 1096. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°): 7.75 (*d*, *J* = 4.0, N=CH); 7.32–7.20 (*m*, 5 arom. H); 4.59 (*s*, PhCH_2); 4.44–4.39 (*m*, CHN); 4.10–3.99 (*m*, CH_2O); 1.53, 1.49 (2 *s*, 2 Me). CI-MS: 319 (52, $[M + 1]^+$), 318 (3, M^+), 263 (100), 219 (24), 296 (22), 166 (20), 136 (58), 108 (21), 91 (50), 57 (24). Unstable, not suitable for elemental analysis.

tert-*Butyl (S)-2,2-Dimethyl-4-[(methylimino)methyl]oxazolidine-3-carboxylate* (**27b**). At 0°, 8M $MeNH_2$ in EtOH (3 ml) was added to **26** (1.49 g, 6.51 mmol) and 4-Å molecular sieves (600 mg) in Et_2O (7 ml). The mixture was stirred 1 h at 0°. Filtration and evaporation gave **27b** (1.33 g, 84%). Viscous oil. IR (film): 2980, 2938, 2878, 1705, 1383, 1175, 1100. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 7.26–7.55 (*m*, CH=N); 4.35–4.25 (*m*, CH_2CHN); 4.08–3.86 (*m*, CH_2O); 3.22 (*s*, MeN); 1.50, 1.45 (2 *s*, 2 Me); 1.40 (*s*, *t*-Bu). CI-MS: 243 (100, $[M + 1]^+$), 187 (70), 150 (39), 143 (17), 129 (11), 57 (18), 41 (12). Unstable, not suitable for elemental analysis.

tert-*Butyl (4S)-4-{(R)- and (S)-[Benzyl(ethoxycarbonyl)amino](phenylseleno)methyl}-2,2-dimethyloxazolidine-3-carboxylate* (**28a**). According to *GP 2*, with **26** (1.27 g, 4.00 mmol), ethyl carbonochloridate (0.38 ml, 4.00 mmol), 1M DIBALH (4.40 ml, 4.40 mmol), and diphenyl diselenide (687 mg, 2.20 mmol), 5 h at r.t. FC (AcOEt/hexane 1:7) gave **28a** (1.34 g, 61%; diastereoisomer mixture). Colorless oil. IR (film): 2981, 2935, 1710, 1700, 1377. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°, only major): 7.31–7.12 (*m*, 10 arom. H); 5.03 (*d*, *J* = 8.4, CHSe); 4.83 (*d*, *J* = 16.1, 1 H, PhCH_2); 4.59–4.42 (*m*, CH_2CHN); 4.30 (*d*, *J* = 16.1, 1 H, PhCH_2); 4.12–3.70 (*m*, MeCH_2, CH_2O); 1.48, 1.38 (2*s*, 2 Me); 1.16 (*t*, *J* = 7.1, *Me*CH_2). CI-MS: 549 (7, $[M + 1]^+$), 435 (6), 391 (29), 335 (100), 291 (62), 276 (10), 91 (16), 57 (10), 41 (32). Anal. calc. for $C_{27}H_{36}N_2O_5Se$ (547.56): C 59.23, H 6.63, N 5.12; found: C 59.34, H 6.73, N 5.06.

tert-*Butyl (4S)-4-{(R)- and (S)-[(Ethoxycarbonyl)methylamino](phenylseleno)methyl}-2,2-dimethyloxazolidine-3-carboxylate* (**28b**). According to *GP 2*, with **27b** (727 g, 3.00 mmol), ethyl carbonochloridate (0.29 ml, 3.00 mmol), 1M DIBALH (3.30 ml, 3.30 mmol), and diphenyl diselenide (515 mg, 1.65 mmol), 5 h at r.t. FC (AcOEt/hexane 1:5) gave **28b** (611 mg, 43%; diastereoisomer mixture). Colorless oil. IR (film): 2980, 2935, 2878, 1707, 1478, 1377, 1246, 1173, 1099. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°): major: 7.54–7.51 (*m*, 2 arom. H); 7.32–7.25 (*m*, 3 arom. H); 5.82 (*d*, *J* = 8.9, CHSe); 4.18–3.87 (*m*, 1 H of OCH_2CHO, MeCH_2, NCHCH_2O); 4.33 (*dd*, *J* = 8.0, 5.5, 1 H, OCH_2CHO); 2.87 (*s*, MeN); 1.55, 1.44 (2 *s*, 2 Me); 1.41 (*s*, *t*-Bu); 1.06 (*t*, *J* = 7.0, *Me*CH_2); minor: 7.52–7.50 (*m*, 2 arom. H); 7.32–7.24 (*m*, 3 arom. H); 6.02 (*d*, *J* = 7.9, CHSe); 4.28–4.22 (*m*, OCH_2CHN); 4.10–3.79 (*m*, OCH_2CHO, MeCH_2); 2.91 (*s*, Me); 1.53, 1.42 (2*s*, 2 Me); 1.48 (*s*, *t*-Bu); 1.02 (*t*, *J* = 7.1, *Me*CH_2). FAB-MS: 471 (2, M^+). Anal. calc. for $C_{21}H_{32}N_2O_5Se$ (471.46): C 53.50, H 6.84, N 5.94; found: C 53.66, H 6.93, N 5.85.

Ethyl Butyl{(1R,2S)- and (1S,2S)-2-[(triisopropylsilyl)oxy](1-$^2H_1$)propyl}carbamate (**29a**). According to *GP 3*, with **18a** (146 mg, 0.27 mmol), Bu_3SnD (110 mg, 0.38 mmol), AIBN (5 mg, 0.03 mmol), and dry benzene (2 ml). FC (AcOEt/hexane 1:10) gave **29a** (105 mg, 98%; 22:78 *syn*/*anti* mixture). Colorless oil. IR (film): 2959, 2944, 2868, 1703, 1465, 1416, 1383, 1120, 883. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°): 7.31–7.18 (*m*, 5 arom. H); 4.51 (*s*, PhCH_2); 4.19 (*quint.*, *J* = 6.1, CHO); 4.10 (*q*, *J* = 7.1, MeCH_2); 3.22 (*d*, *J* = 5.8, CHD, *anti*); 3.17 (*d*, *J* = 4.4, CHD, *syn*); 1.19 (*t*, *J* = 7.1, *Me*CH_2); 1.13 (*d*, *J* = 6.1, Me); 1.05 (*s*, (i-Pr)$_3$Si). CI-MS: 396 (5, $[M + 1]^+$), 395 (18), 392 (43), 351 (99), 221 (100), 91 (3). Anal. calc. for $C_{22}H_{38}DNO_3Si$ (394.65): C 66.96, H 10.22, N 3.55; found: C 66.86, H 10.17, N 3.59.

Ethyl Methyl{(1R,2S)- and (1S,2S)-2-[(triisopropylsilyl)oxy](1-$^2H_1$)propyl}carbamate (**29b**). According to *GP 3*, with **18b** (470 mg, 0.48 mmol), Bu_3SnD (435 mg, 0.73 mmol), AIBN (16 mg, 0.07 mmol), and benzene (6 ml). FC (AcOEt/hexane 1:10) gave **29b** (282 mg, 90%; 13:87 *syn*/*anti* mixture). Colorless oil. IR (film): 2944, 2868, 1707, 1466, 1383, 1175, 1113, 883. ^{1}H-NMR (200 MHz, (D_8)toluene, 80°): 4.15–3.98 (*m*, CHO); 3.98 (*q*, *J* = 7.1, *Me*CH_2); 3.13 (*m*, CHD, *anti*); 2.91 (br. *s*, CHD, *syn*); 2.71 (*s*, MeN); 1.20–0.90 (*m*, 27 H, Me, *Me*CH_2, (i-Pr)$_3$Si). ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 4.14 (*quint.*, *J* = 6.1, CHO); 4.00 (*q*, *J* = 7.1, MeCH_2); 3.26 (*d*, *J* = 6.2, CHD, *anti*); 3.08 (br. *s*, CHD, *syn*); 2.88 (*s*, MeN); 1.17 (*t*, *J* = 7.1, MeCH_2); 1.10 (*d*, *J* = 6.1, Me); 1.10–0.95 (*m*, 21 H, (i-Pr)$_3$Si). ^{2}H-NMR (500 MHz, toluene, 80°): 2.90 (*anti*); 3.15 (*syn*). CI-MS: 320 (18, M^+), 276 (18), 275 (100), 145 (50). Anal. calc. for $C_{16}H_{34}DNO_3Si$ (318.55): C 60.33, H 11.11, N 4.40; found: C 60.12, H 10.95, N 4.20.

Ethyl Isopropyl{(1R,2S)- and (1S,2S)-2-[(triisopropylsilyl)oxy](1-$^2H_2$)propyl}carbamate (**29c**). According to *GP 3*, with **18c** (242 mg, 0.48 mmol), Bu_3SnD (212 mg, 0.73 mmol), AIBN (11 mg, 0.07 mmol), and benzene (4 ml). FC (AcOEt/hexane 1:10) gave **29c** (135 mg, 81%; 20:80 *syn*/*anti*). Colorless oil. IR (film): 2964, 2868, 2362, 2203, 1704, 1464, 1303, 1112. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°, diastereoisomer mixture): 4.21 (*quint.*, *J* = 5.8, CHO); 4.05 (*q*, *J* = 6.9, MeCH_2); 3.92 (*sept.*, *J* = 6.7, Me_2CH); 3.21 (*d*, *J* = 5.2, CHD, *anti*); 3.03 (*d*, *J* = 7.3, CHD, *syn*); 1.21–1.07 (*m*, 33 H, Me, *Me*CH_2, *Me*$_2$CH, (i-Pr)$_3$Si). CI-MS: 347 (53, $[M + 1]^+$), 344

(30), 303 (100), 301 (16), 173 (86), 41 (19). Anal. calc. for $C_{18}H_{38}DNO_3Si$ (346.61): C 62.38, H 11.37, N 4.04; found: C 62.34, H 11.28, N 3.68.

Methyl (4R,5S)- and (4S,5S)-4-[Benzyl(ethoxycarbonyl)amino]-2-methylidene-5-[(triisopropylsilyl)oxy]-hexanoate (**30a**). According to *GP 4*, with **18a** (1.65 g, 3.00 mmol), methyl 2-[(tributylstannyl)methyl]prop-2-enoate (2.78 g, 9.00 mmol), AIBN (148 mg, 0.90 mmol), and benzene (20 ml); 24 h irradiation. FC (AcOEt/hexane 1:7) afforded **30a** (990 mg, 65%; 68:32 *syn/anti* mixture). Colorless oil. IR (film): 2945, 2868, 1722, 1701, 1464, 1232, 1140. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°; diastereoisomer mixture): 7.27–7.18 (*m*, 5 arom. H); 6.01 (*m*, 1 H of C=CH_2, *syn*); 5.97 (*m*, 1 H of C=CH_2, *anti*); 5.49 (*m*, 1 H of C=CH_2, *syn*); 5.40 (*m*, 1 H of =CH_2, *anti*); 4.53 (*A* of *AB*, J_{AB} = 16.0, 1 H of PhCH_2, *anti*); 4.47 (*B* of *AB*, J_{AB} = 15.9, 1 H of PhCH_2, *anti*); 4.37 (*A* of *AB*, J_{AB} = 15.6, 1 H of PhCH_2, *syn*); 4.34 (*B* of *AB*, J_{AB} = 15.6, 1 H of PhCH_2, *syn*); 4.22–3.86 (*m*, CHO, CHN of *anti*); 4.08 (*q*, *J* = 7.0, MeCH_2, *syn*); 4.04 (*q*, *J* = 7.0, MeCH_2, *anti*); 3.69 (*td*, *J* = 7.0, 4.0, CHN, *syn*); 1.20 (*t*, *J* = 7.0, *Me*CH$_2$, *syn*); 1.18 (*t*, *J* = 7.0, *Me*CH$_2$, *anti*); 1.09–1.05 (*m*, (i-Pr)$_3$Si, Me of *syn*); 0.99 (*d*, *J* = 6.1, Me, *anti*). CI-MS: 493 (3, $[M+1]^+$), 450 (15), 449 (42), 318 (100), 319 (21), 290 (22), 91 (6), 41 (20). Anal. calc. for $C_{27}H_{35}NO_5Si$ (491.74): C 65.95, H 9.22, N 2.85; found: C 65.86, H 9.15, N 2.89.

Methyl (4R,5S)- and (4S,5S)-4-[(Ethoxycarbonyl)methylamino]-2-methylidene-5-[(triisopropylsilyl)oxy]-hexanoate (**30b**). According to *GP 4*, with **18b** (200 mg, 0.50 mmol), methyl 2-[(tributylstannyl)methyl]prop-2-enoate (584 mg, 1.50 mmol), AIBN (25 mg, 0.15 mmol), and benzene (4 ml); 36 h irradiation. FC (AcOEt/hexane 1:7) provided **30b** (147 mg, 71%; inseparable 55:45 *syn/anti* mixture). Colorless oil. IR (film): 2945, 2868, 1724, 1703, 1456, 1443, 1315, 1140. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°, 55:45 mixture): 6.05 (*s*, 1 H of C=CH_2); 5.59 (*s*, 1 H of C=CH_2, *syn*); 5.57 (*s*, 1 H of C=CH_2, *anti*); 4.20–3.88 (*m*, CHO, MeCH_2); 3.68 (*s*, MeO, *syn*); 3.67 (*s*, MeO, *anti*); 2.76 (*s*, MeN, *syn*); 2.66 (*s*, MeN, *anti*); 1.17–1.01 (*m*, 27 H, Me, *Me*CH$_2$, (i-Pr)$_3$Si). CI-MS: 416 (14, M^+), 372 (68), 242 (100), 214 (39), 41 (9). Anal. calc. for $C_{21}H_{41}NO_5Si$ (415.65): C 60.68, H 9.94, N 3.37; found: C 60.52, H 9.94, N 3.45.

Methyl (4R,5S)- and (4S,5S)-4-[(Ethoxycarbonyl)isopropylamino]-2-methylidene-5-[(triisopropylsilyl)oxy]-hexanoate (**30c**). According to *GP 4*, with **18b** (197 mg, 0.39 mmol), methyl 2-[(tributylstannyl)methyl]prop-2-enoate (459 mg, 1.18 mmol), AIBN (20 mg, 0.12 mmol), and benzene (4 ml); 26 h irradiation. FC (AcOEt/hexane 1:10) provided **30c** (106 mg, 61%; 33:67 *syn/anti* mixture). Colorless oil. IR (film): 2946, 2868, 1723, 1698, 1442, 1288. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°; diastereoisomer mixture): 6.10 (*s*, 1 H, C=CH_2); 5.61 (*m*, 1 H of C=CH_2, *syn*); 5.58 (*s*, 1 H of C=CH_2, *anti*); 4.24–4.14 (*m*, CHO); 4.04 (*q*, *J* = 7.0, MeCH_2); 4.08–4.00 (*m*, OC*H*CHN, *syn*); 3.79 (*quint.*, *J* = 6.7, OCCHC*H*N, *anti*); 3.70 (*s*, MeO, *syn*); 3.69 (*s*, MeO, *anti*); 3.50 (*sept.*, *J* = 7.0, Me$_2$C*H*, *anti*); 3.45 (*sept.*, *J* = 7.0, Me$_2$C*H*, *syn*); 2.96–2.55 (*m*, CH$_2$C=C); 1.31–1.13 (*m*, Me, *Me*$_2$CH, *Me*CH$_2$, *anti*); 1.09 (*s*, 21 H, (i-Pr)$_3$Si); 0.89 (*t*, *J* = 7.3, *Me*CH$_2$, *syn*). CI-MS: 445 (7, $[M+1]^+$), 444 (1, M^+), 401 (13), 400 (49), 271 (16), 270 (100), 242 (47), 41 (32). Anal. calc. for $C_{23}H_{45}NO_3Si$ (443.70); C 62.26, H 10.22, N 3.16; found: C 62.22, H 10.32, N 3.12.

Ethyl Benzyl{(1R)- and (1S)-[(S)-2,2-dimethyl-1,3-dioxolan-4-yl](1-$^2H_1$)methyl}carbamate (**31**). According to *GP 3*, with **24** (160 mg, 0.36 mmol), Bu_3SnD (137 mg, 0.47 mmol), AIBN (7 mg, 0.04 mmol), and benzene (3 ml). FC (AcOEt/hexane 1:5) gave **31** (89 mg, 84%; 27:73 *syn/anti* mixture). Colorless oil. IR (film): 2983, 2936, 1701, 1454, 1424, 1248. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°): 7.35–7.22 (*m*, 5 arom. H); 4.55 (*A* of *AB*, J_{AB} = 15.6, 1 H, PhCH_2); 4.49 (*B* of *AB*, J_{AB} = 15.6, 1 H, PhCH_2); 4.21 (*q*, *J* = 6.4, OC*H*CHN); 4.10 (*q*, *J* = 7.0, MeCH_2); 3.93 (*dd*, *J* = 8.2, 6.4, 1 H, OCH_2CHO); 3.56 (*dd*, *J* = 8.2, 6.4, 1 H, OCH_2CHO); 3.37 (*d*, *J* = 4.3, CHD, *syn*); 3.26 (*d*, *J* = 6.1, CHD, *anti*); 1.33, 1.26 (2 *s*, 2 Me); 1.19 (*t*, *J* = 7.0, *Me*CH$_2$). CI-MS: 294 (1, $[M+1]^+$), 293 (2, M^+), 265 (8), 238 (15), 237 (100). Anal. calc. for $C_{16}H_{22}DNO_4$ (293.37): C 65.51, H 7.94, N 4.77; found: C 65.22, H 8.23, N 4.87.

Ethyl Benzyl{(1R)- and (1S)-[(S)-2-oxo-1,3-dioxolan-4-yl](1-$^2H_1$)methyl}carbamate (**32**). a) *From* **25**: According to *GP 3*, with **25** (113 mg, 0.26 mmol), Bu_3SnD (99 mg, 0.39 mmol), AIBN (7 mg, 0.04 mmol), and benzene (2 ml). FC (AcOEt/hexane 1:5) gave **32** (50 mg, 69%; 29:71 *syn/anti* mixture).

b) *From* **40**: A soln. of diol **40** (20 mg, 0.08 mmol; *syn/anti* 27:73) in dry THF (0.5 ml) was heated under reflux, and 1,1′-carbonylbis[1*H*-imidazole] (26 mg, 0.16 mmol) was added over 15 min. After 2 h, the mixture was cooled to r.t. Et_2O was added, the soln. washed with H_2O and brine, and the org. layer dried ($MgSO_4$) and evaporated. FC (AcOEt/hexane 1:1) provided **32** (14 mg, 62%; 27:73 *syn/anti* mixture). Colorless oil. IR (film): 3023, 1807, 1690, 1207, 1086. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 7.39–7.22 (*m*, 5 arom. H); 4.99–4.88 (*m*, OCHCH$_2$O); 4.55 (*d*, *J* = 15.6, 1 H, PhCH_2); 4.56–4.47 (*m*, 1 H, OCH_2CHO); 4.45 (*d*, *J* = 15.6, 1 H, PhCH_2); 4.22–4.14 (*m*, 1 H, OCH_2CHO); 4.10 (*q*, *J* = 7.1, MeCH_2); 3.57 (*d*, *J* = 7.3, CHD, *anti*); 3.49 (*d*, *J* = 3.9, CHD, *syn*); 1.18 (*t*, *J* = 7.0, *Me*CH$_2$). CI-MS: 281 (100, $[M+1]^+$), 193 (9), 91 (16). Anal. calc. for $C_{14}H_{16}DNO_5$ (280.30): C 59.99, H 6.15; found: C 60.04, H 6.11.

Methyl (4R)- and (4S)-4-[Benzyl(ethoxycarbonyl)amino]-4-[(S)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-methylidenebutanoate (**33**). According to *GP 4*, with **24** (242 mg, 0.54 mmol), methyl 2-[(tributylstannyl)methyl]prop-2-enoate (584 mg, 1.50 mmol), AIBN (24 mg, 0.05 mmol), and benzene (3 ml); 24 h irradiation. FC (AcOEt/hexane 1:3) gave **33** (130 mg, 62%; 52:48 *syn/anti* mixture). Colorless oil. IR (film): 2986, 2951, 1721, 1698, 1440, 1224. ^{1}H-NMR (360 MHz, (D$_6$)DMSO, 80°; 52:48 mixture): 7.32–7.19 (*m*, 5 arom. H); 6.04 (*d*, *J* = 1.5, 1 H of C=C*H*$_2$, *syn*); 6.03 (*d*, *J* = 1.2, 1 H of C=C*H*$_2$, *anti*); 5.51 (*m*, 1 H of C=C*H*$_2$, *syn*); 5.46 (*s*, 1 H of C=C*H*$_2$, *anti*); 4.42 (*A* of *AB*, J_{AB} = 15.9, 1 H of PhC*H*$_2$, *syn*); 4.40 (*A* of *AB*, J_{AB} = 15.9, 1 H of PhC*H*$_2$, *anti*); 4.39 (*B* of *AB*, J_{AB} = 15.9, 1 H of PhC*H*$_2$, *syn*); 4.36 (*B* of *AB*, J_{AB} = 15.9, 1 H of PhC*H*$_2$, *anti*); 4.28–4.22 (*m*, OCH$_2$C*H*O, *anti*); 4.13–4.03 (*m*, OCH$_2$C*H*O of *syn*, 1 H of OC*H*$_2$CHO of *anti*); 4.06 (*q*, *J* = 7.0, MeC*H*$_2$, *anti*); 4.04 (*q*, *J* = 7.0, MeC*H*$_2$, *syn*); 3.97 (*dd*, *J* = 8.2, 6.4, 1 H of OC*H*$_2$CHO, *syn*); 3.68 (*s*, MeO$_3$, *syn*); 3.65 (*s*, MeO, *anti*); 3.61 (*dd*, 1 H of OC*H*$_2$CHO, *syn*); 3.46 (*m*, 1 H of OC*H*$_2$CHO, *anti*); 2.78–2.30 (*m*, CH$_2$C=C); 1.32, 1.19 (2*s*, 2 Me, *syn*); 1.29, 1.21 (2*s*, 2 Me, *anti*). CI-MS: 392 (2, $[M + 1]^+$), 362 (11), 335 (20), 334 (100), 290 (12). Anal. calc. for $C_{21}H_{29}NO_6$ (391.47): C 64.43, H 7.47, N 3.58; found: C 64.51, H 7.40, N 3.54.

Methyl (4R)- and (4S)-4-[Benzyl(ethoxycarbonyl)amino]-2-methylidene-4-[(S)-4-oxo-1,3-dioxolan-4-yl]-butanoate (**34**). According to *GP 4*, with **25** (180 mg, 0.41 mmol), methyl 2-[(tributylstannyl)methyl]prop-2-enoate (484 mg, 1.24 mmol), AIBN (25 mg, 0.15 mmol), and benzene (4 ml); 16 h irradiation. FC (AcOEt/hexane 1:2) gave **34** (113 mg, 73%; 33:67 *syn/anti* mixture). Colorless oil. IR (film): 2984, 2955, 1809, 1701, 1443, 1235, 1171, 1082. ^{1}H-NMR (360 MHz, (D$_8$)toluene, 80°): *anti*: 7.08–6.93 (*m*, 5 arom. H); 5.88 (*d*, *J* = 1.3, 1 H C=C*H*$_2$); 5.17–5.16 (*m*, 1 H, C=C*H*$_2$); 4.41 (*q*, *J* = 7.4, OC*H*CH$_2$O); 4.25 (*s*, PhC*H*$_2$); 3.94 (*q*, *J* = 7.1, MeC*H*$_2$); 3.86–3.77 (*m*, 1 H of OC*H*$_2$CHO, CHN); 3.67–3.63 (*m*, 1 H, OC*H*$_2$CHO); 3.30 (*s*, MeO); 2.61 (*dd*, *J* = 13.9, 9.7, 1 H, CH$_2$C=C); 2.12 (*dd*, *J* = 13.9, 4.7, 1 H, CH$_2$C=C); 0.95 (*t*, *J* = 7.1, MeC*H*$_2$); *syn*: 7.51–7.06 (*m*, 5 arom. H); 5.96 (*d*, *J* = 1.6, 1 H, C=C*H*$_2$); 5.20–5.19 (*m*, 1 H, C=C*H*$_2$); 4.38 (*q*, *J* = 7.4, OC*H*CH$_2$O); 4.22 (*d*, *J* = 15.5, 1 H, PhC*H*$_2$); 4.12 (*d*, *J* = 15.5, PhC*H*$_2$); 3.91 (*q*, *J* = 7.1, MeC*H*$_2$); 3.97–3.89 (*m*, CHN); 3.56 (*dd*, *J* = 8.7, 6.7, 1 H, OC*H*$_2$CHO); 3.47 (*dd*, *J* = 8.4, 8.2, 1 H, OC*H*$_2$CHO); 3.39 (*s*, MeO); 2.63–2.59 (*m*, CH$_2$C=C); 0.95 (*t*, *J* = 7.1, *Me*CH$_2$). CI-MS: 379 (21, $[M + 2]^+$), 378 (100, $[M + 1]^+$), 290 (10), 127 (10), 99 (20), 91 (96). HR-EI-MS: 377.1490 ($C_{19}H_{23}NO_7^+$; calc. 377.1474).

tert-*Butyl (4R)-4-{(R)- and (S)-[Benzyl(ethoxycarbonyl)amino](1-$^2H_1$)methyl}-2,2-dimethyloxazolidine-3-carboxylate* (**35a**). According to *GP 3*, with **28a** (548 mg, 1.00 mmol), Bu_3SnD (380 mg, 1.30 mmol), AIBN (21 mg, 0.13 mmol), and benzene (8 ml). FC (AcOEt/hexane 1:5) gave **35a** (337 mg, 86%; 24:76 *syn/anti* mixture). Colorless oil. IR (film): 2980, 2936, 1703, 1380. ^{1}H-NMR (200 MHz, (D$_6$)DMSO, 80°; 24:76 mixture): 7.39–7.19 (*m*, 5 arom. H); 4.46 (br. *s*, PhC*H*$_2$); 4.20–4.00 (*m*, CHN); 4.09 (*q*, *J* = 7.0, MeCH$_2$); 3.89–3.78 (*m*, CH$_2$O); 3.42 (*d*, *J* = 6.9, CHD, *syn*); 3.21 (*d*, *J* = 5.2, CHD, *anti*); 1.50, 1.41 (2*s*, 2 Me); 1.40 (*s*, *t*-Bu); 1.18 (*t*, *J* = 7.0, *Me*CH$_2$). CI-MS: 394 (4, M^+), 308 (14), 294 (72), 280 (96), 100 (12), 91 (10), 57 (21), 41 (100). HR-FAB-MS: 394.2446 ($[C_{21}H_{31}DN_2O_5 + H]^+$; calc. 394.2468).

tert-*Butyl (4R)-4-{(R)- and (S)-[Ethoxycarbonyl)amino](1-$^2H_1$)methyl}-2,2-dimethyloxazolidine-3-carboxylate* (**35b**). According to *GP 3*, with **28b** (236 mg, 0.50 mmol), Bu_3SnD (190 mg, 0.65 mmol), AIBN (11 mg, 0.07 mmol), and benzene (4 ml). FC (AcOEt/hexane 1:4) gave **35b** (110 mg, 69%; 14:86 *syn/anti* mixture). Colorless oil. IR (film): 2980, 2938, 2878, 1694, 1479, 1177, 1258, 1098, 1078. ^{1}H-NMR (360 MHz, (D$_8$)toluene, 80°; 14:86 mixture): 3.97 (*qd*, *J* = 7.1, 2.4, MeC*H*$_2$); 3.86–3.84 (*m*, OCH$_2$C*H*N); 3.75 (*dd*, *J* = 9.0, 1.6, 1 H, OC*H*$_2$CHN); 3.57 (*dd*, *J* = 9.0, 5.8, 1 H, C*H*$_2$CHN); 3.41 (*d*, *J* = 7.6, CHD, *syn*); 3.15 (br. *s*, CHD, *anti*); 2.74 (*s*, MeN); 1.52, 1.38 (2 *s*, 2 Me); 1.34 (*s*, *t*-Bu); 1.01 (*td*, *J* = 7.1, 0.5, *Me*CH$_2$). ^{1}H-NMR (200 MHz, (D$_6$)DMSO, 80°): 4.03 (*q*, *J* = 7.0, MeC*H*$_2$); 3.92–3.64 (*m*, CH$_2$O, OCH$_2$C*H*N); 3.42 (*d*, *J* = 7.5, CHD, *syn*); 3.19 (*d*, *J* = 5.0, CHD, *anti*); 2.88 (*s*, MeN); 1.60–1.38 (*m*, 2 Me, *t*-Bu); 1.18 (*t*, *J* = 7.0, *Me*CH$_2$). ^{2}H-NMR (500 MHz, toluene, 80°): 3.41 (*anti*); 3.12 (*syn*). FAB-MS: 318 (55, $[M + 1]^+$). Anal. calc. for $C_{15}H_{27}DN_2O_5$ (317.41): C 56.76, H 8.93, N 8.83; found: C 56.60, H 9.15, N 8.57.

tert-*Butyl (4R)-4-{(R)- and (S)-1-[Benzyl(ethoxycarbonyl)amino]-4-methoxy-3-methylidene-4-oxobutyl}-2,2-dimethyloxazolidine-3-carboxylate* (**36a**). According to *GP 4* with **28a** (250 mg, 0.46 mmol), methyl 2-[(tributylstannyl)methyl]prop-2-enoate (584 mg, 1.50 mmol), AIBN (24 mg, 0.05 mmol), and benzene (4 ml); 27 h irradiation. FC (AcOEt/hexane 1:4) gave **36a** (130 mg, 62%; 72:28 *syn/anti* mixture). Colorless oil. IR (film): 2980, 2952, 1703, 1385, 1172. ^{1}H-NMR (200 MHz, (D$_6$)DMSO, 80°, 72:28 mixture): 7.35–7.17 (*m*, 5 arom. H); 6.04 (*s*, 1 H of C=C*H*$_2$, *syn*); 5.91 (*s*, 1 H of C=C*H*$_2$, *anti*); 5.58 (*s*, 1 H of C=C*H*$_2$, *syn*); 5.36 (*s*, 1 H of C=C*H*$_2$, *anti*); 4.55 (*d*, *J* = 16.1, 1 H, PhC*H*$_2$); 4.30–3.90 (*m*, MeC*H*$_2$, 1 H of PhC*H*$_2$, NC*H*CH$_2$O); 3.79–3.60 (*m*, NC*H*CH$_2$C=); 3.65 (*s*, MeO, *syn*); 3.06 (*s*, MeO, *anti*); 2.82–2.35 (*m*, CH$_2$C=C); 1.65 (*s*, Me); 1.45 (*s*, *t*-Bu, *anti*); 1.44 (*s*, *t*-Bu, *syn*); 1.40 (*s*, Me, *syn*); 1.38 (*s*, Me, *anti*); 1.22–1.08 (*m*, *Me*CH$_2$). CI-MS: 491 (1, M^+), 405 (11), 391 (22), 377 (100), 290 (35), 91 (19), 57 (10), 41 (53). HR-EI-MS: 490.2656 ($C_{26}H_{38}N_2O_7^+$; calc. 490.2679).

tert-*Butyl (4*R*)-4-{(*R*)- and (*S*)-1-[(Ethoxycarbonyl)methylamino]-4-methoxy-3-methylidene-4-oxobutyl}-2,2-dimethyloxazolidine-3-carboxylate* (**36b**). According to *GP 4* with **28b** (210 mg, 0.45 mmol), methyl 2-[(tributylstannyl)methyl]prop-2-enoate (584 mg, 1.50 mmol), AIBN (25 mg, 0.15 mmol), and benzene (4 ml); 12 h irradiation. FC (AcOEt/hexane 1:4) gave **36b** (116 mg, 62%; 56:44 *syn/anti* mixture). Colorless oil. IR (film): 2980, 2938, 1701, 1445, 1379, 1171. ^{1}H-NMR (360 MHz, (D$_6$)DMSO, 80°; 56:44 mixture): 6.05 (*s*, 1 H of C=CH_2, *anti*); 6.04 (*s*, 1 H of C=CH_2, *syn*); 5.58–5.55 (*m*, 1 H, C=CH_2); 4.27 (*ddd*, *J* = 10.4, 6.7, 4.3, OCH_2C*H*N, *syn*); 4.11–3.90 (*m*, OCH_2C*H*N of *anti*, MeCH_2, 1 H of OCH_2CHN of *syn*); 3.91 (*dd*, *J* = 9.8, 6.1, 1 H of OCH_2CHN, *syn*); 3.82 (*dd*, *J* = 9.2, 5.2, 1 H of OCH_2CHN, *anti*); 3.73 (br. *d*, *J* = 9.2, 1 H of OCH_2CHN, *anti*); 3.69 (*s*, MeO, *syn*); 3.68 (*s*, MeO, *anti*); 2.71 (*s*, Me); 2.66–2.51 (*m*, CH_2C=C); 1.56 (*s*, Me); 1.48 (*s*, Me, *anti*); 1.47 (*s*, *t*-Bu, *anti*); 1.44 (*s*, Me, *syn*); 1.43 (*s*, *t*-Bu, *syn*); 1.15 (*t*, *J* = 7.0, *Me*CH$_2$). CI-MS: 415 (2, M^+), 357 (7), 329 (13), 315 (38), 301 (100), 314 (8), 57 (9). HR-EI-MS 414.2354 ($C_{20}H_{34}N_2O_7^+$; calc. 414.2366).

*(4*R,*5*S*)- and (4*S,*5*S*)-3-Benzyl-5-methyl(4-$^2H_1$)oxazolidin-2-one* (**37a**). According to *GP 5*, with **29a** (163 mg, 0.41 mmol; *syn/anti* 22:78) and 1M Bu$_4$NF (1.24 ml); 7 h stirring. FC (AcOEt/hexane 1:2) provided the free alcohol (63 mg, 65%). ^{1}H-NMR (200 MHz, (D$_8$)toluene, 80°, diastereoisomer mixture): 7.18–6.96 (*m*, 5 arom. H); 4.50 (*d*, *J* = 15.0, 1 H, PhCH_2); 4.38 (*d*, *J* = 15.9, 1 H, PhCH_2); 4.05 (*q*, *J* = 7.0, MeCH_2); 3.92–3.76 (*m*, CHO); 3.13 (*d*, *J* = 9.0, CHD, *anti*); 3.08 (br. *s*, CHD, *syn*); 2.12 (br. *s*, OH); 1.01 (*t*, *J* = 7.0, *Me*CH$_2$); 0.96 (*d*, *J* = 6.5, Me$_3$).

According to *GP 6*, with the free alcohol (30 mg, 0.13 mmol) and NaH (55% in oil; 9 mg, 0.20 mmol). FC (AcOEt/hexane 1:1) gave **37a** (24 mg, 79%; 78:22 *trans/cis* mixture). ^{1}H-NMR (360 MHz): 7.36–7.26 (*m*, 5 arom. H); 4.64–4.54 (*m*, MeC*H*O); 4.42 (*A* of *AB*, J_{AB} = 14.2, 1 H, PhCH_2); 4.36 (*B* of *AB*, J_{AB} = 14.2, 1 H, PhCH_2); 3.48 (*d*, *J* = 9.9, CHD, *cis*); 2.95 (*d*, *J* = 7.2, CHD, *trans*); 1.36 (*d*, *J* = 6.3, Me).

*(4*R,*5*S*)- and (4*S,*5*S*)-3-Isopropyl-5-methyl-(4-$^2H_1$)oxazolidin-2-one* (**37c**). According to *GP 5*, with **29c** (187 mg, 0.54 mmol; *syn/anti* 20:80) and 1M Bu$_4$NF (2 ml). FC (AcOEt/hexane 1:2) gave the free alcohol (81 mg, 79%). Colorless oil. IR (film): 3450, 2977, 2935, 1678, 1428, 1111. ^{1}H-NMR (200 MHz, (D$_6$)DMSO, 80°; diastereoisomer mixture): 4.29 (*d*, *J* = 4.9, OH); 4.03 (*q*, *J* = 7.0, MeCH_2); 3.92 (*quint.*, *J* = 6.8, CHO); 3.86–3.70 (*m*, Me$_2$C*H*); 3.08 (br. *s*, CHD, *syn*); 2.98 (*d*, *J* = 6.8, CHD, *anti*); 1.18 (*t*, *J* = 7.0, *Me*CH$_2$); 1.16, 1.13 (2*d*, *J* = 2.7, *Me*$_2$CH); 1.03 (*d*, *J* = 6.3, Me). CI-MS: 192 (20, $[M + 2]^+$), 191 (100, $[M + 1]^+$), 173 (48), 145 (81), 131 (11), 103 (7). Anal. calc. for $C_9H_{18}DNO_3$ (190.26): C 56.82, H 10.12; found: C 56.77, H 10.21.

According to *GP 6*, with the free alcohol (31 mg, 0.16 mmol) and NaH (55% in oil; 9 mg, 0.20 mmol). FC (Et$_2$O/hexane 1:2) gave volatile **37c** (14 mg, 61%; 80:20 *trans/cis* mixture). Colorless oil. ^{1}H-NMR (360 MHz): 4.63–4.54 (*m*, MeC*H*O); 4.06 (*sept.*, Me$_2$C*H*); 3.55 (*d*, *J* = 9.0, CHD, *cis*); 3.02 (*d*, *J* = 7.5, CHD, *trans*); 1.37 (*d*, *J* = 6.3, Me); 1.13, 1.11 (2 *d*, *J* = 6.7, *Me*$_2$CH).

*Ethyl Benzyl{(2*S,*3*S*)-tetrahydro-2-methyl-5-methylidene-6-oxo-2*H*-pyran-3-yl}carbamate* (*trans*-**38**). According to *GP 5*, with *syn*-**30a** (major isomer; 54 mg, 0.11 mmol) and 1M Bu$_4$NF (1 ml). FC (AcOEt/hexane 1:3) gave *trans*-**38** (17 mg, 50%). Colorless oil. IR (film): 2982, 1732, 1700. ^{1}H-NMR (360 MHz, (D$_6$)DMSO, 80°): 7.36–7.18 (*m*, 5 arom. H); 6.14–6.13 (*m*, 1 H, C=CH_2); 5.55 (*s*, 1 H, C=CH_2); 4.75 (*dq*, *J* = 9.2, 6.1, CHO); 4.47 (*s*, PhCH_2); 4.13 (*q*, *J* = 7.1, MeCH_2); 3.76 (*ddd*, *J* = 11.6, 9.2, 5.5, CHN); 1.20 (*t*, *J* = 7.3, *Me*CH$_2$); 1.14 (*d*, *J* = 6.1, Me). NOE ((D$_6$)DMSO, 80°): 3.76 (CHN) → 4.47 (PhCH_2, 3.9%), 1.14 (Me, 2.8%); 4.75 (CHO) → 4.47 (PhCH_2, 1.9%). CI-MS: 304 (6, $[M + 1]^+$), 126 (4), 111 (3), 91 (5), 47 (8), 41 (100), 32 (10). HR-EI-MS: 303.1474 ($C_{17}H_{21}NO_4^+$; calc. 303.1471).

*Methyl (4*S,*5*S*)-4-[Benzyl(ethoxycarbonyl)amino]-5-hydroxy-2-methylidenehexanoate* (**39**). According to *GP 5*, with *anti*-**30a** (minor isomer; 36 mg, 0.07 mmol) and 1M Bu$_4$NF (0.5 ml). FC (AcOEt/hexane 1:3) gave **39** (11 mg, 47%). Colorless oil. IR (film): 3461, 2980, 1721, 1694, 1440, 1244. ^{1}H-NMR (200 MHz, (D$_6$)DMSO, 80°): 7.40–7.10 (*m*, 5 arom. H); 5.96 (*s*, 1 H, C=CH_2); 5.38 (*s*, 1 H, C=CH_2); 4.45 (*s*, PhCH_2); 4.01 (*q*, *J* = 7.1, MeCH_2); 4.1–3.9 (*m*, CHO); 3.85–3.80 (*m*, CHN); 3.60 (*s*, MeO); 2.60–2.35 (*m*, CH_2C=C); 1.26–1.09 (*m*, Me, *Me*CH$_2$). CI-MS: 336 (63, $[M + 1]^+$), 318 (100), 304 (48), 290 (87), 228 (16). HR-EI-MS: 335.1756 ($C_{18}H_{25}NO_5^+$; calc. 335.1733).

*Ethyl Benzyl[(1*R,*2*S*)- and (1*S,*2*S*)-2,3-dihydroxy(2-$^2H_1$)propyl]carbamate* (**40**). A soln. of **31** (305 mg, 1.03 mmol; *syn/anti* 27:73) and CH$_3$COOH (0.02 ml, 0.20 mmol) in THF/H$_2$O 4:1 (10 ml) was heated under reflux for 7 h. The mixture was cooled, diluted with Et$_2$O (50 ml), and washed with 10% aq. NaHCO$_3$ soln. H$_2$O, and brine. After drying (MgSO$_4$) and evaporation, the residue was purified by FC (AcOEt/hexane 3:1) to give **40** (230 mg, 88%; *syn/anti* 27:73). IR (film): 3425, 2982, 2934, 1680, 1425, 1242, 1128. ^{1}H-NMR (200 MHz, (D$_6$)DMSO, 80°; diastereoisomer mixture): 7.37–7.23 (*m*, 5 arom. H); 4.56 (*d*, *J* = 14.8, 1 H, PhCH_2); 4.49 (*d*, *J* = 10.9, 1 H, PhCH_2); 4.46 (*s*, OH); 4.28–4.20 (*m*, OH); 4.07 (*q*, *J* = 7.0, MeCH_2); 3.74–3.67 (*m*, CHO); 3.35–3.27 (*m*, CH$_2$O, CHD of *syn*); 3.06 (*d*, *J* = 8.0, CHD, *anti*); 1.17 (*t*, *J* = 7.0, *Me*CH$_2$). CI-MS: 256 (16,

$[M + 2]^+$), 255 (100, $[M + 1]^+$), 254 (4, M^+), 237 (29), 209 (42), 193 (24), 119 (11), 91 (76). Anal. calc. for $C_{13}H_{18}DNO_4$ (254.31): C 61.40, H 7.58, N 5.51; found: C 61.36, H 7.63, N 5.52.

*Ethyl Benzyl{(1*R,*2*S*)- and (1*S,*2*S*)-3-{[(*tert*-butyl)dimethylsilyl]oxy}-2-hydroxy(1-$^2H_1$)propyl}carbamate* (**41**). A soln. of **40** (180 mg, 0.71 mmol; *syn*/*anti* 27:73), (*t*-Bu)Me_2SiCl (128 mg, 0.85 mmol), Et_3N (0.11 ml, 0.78 mmol), and 4-(dimethylamino)pyridine (3 mg, 0.03 mmol) in dry CH_2Cl_2 (1 ml) was stirred at r.t. for 12 h and then treated with H_2O. Et_2O was added, the mixture washed with 1M HCl, H_2O, and brine, and the org. layer dried ($MgSO_4$) and evaporated. FC (AcOEt/hexane 1:2) provided **41** (318 mg, 93%; 27:73 *syn*/*anti* mixture). Colorless oil. IR (film): 3450, 2955, 2930, 2857, 2192, 1679, 1253, 1121, 838. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 7.36–7.20 (*m*, 5 arom. H); 4.56 (*A* of *AB*, J_{AB} = 15.9, 1 H, PhCH_2); 4.49 (*B* or *AB*, J_{AB} = 15.7, 1 H, PhCH_2); 4.06 (*q*, *J* = 7.1, MeCH_2); 3.80–3.68 (*m*, CHO); 3.56–3.40 (*m*, CH_2O); 3.32 (*d*, *J* = 9.1, CHD, *syn*); 3.05 (*d*, *J* = 8.8, CHD, *anti*); 1.18 (*t*, *J* = 7.1, *Me*CH_2); 0.86 (*s*, *t*-Bu); 0.02 (*s*, 2 Me). CI-MS: 370 (26, $[M + 1]^+$), 369 (100, M^+), 353 (37), 351 (20), 323 (28), 311 (68), 237 (65), 91 (24). Anal. calc. for $C_{19}H_{32}DNO_4Si$ (368.57): C 61.92, H 9.06, N 3.80; found: C 61.92, H 9.02, N 3.98.

*(4*R,*5*S*)- and (4*S,*5*S*)-3-Benzyl-5-{{[(*tert*-butyl)dimethylsilyl]oxy}methyl}(4-$^2H_1$)oxazolidin-2-one* (**42**). According to *GP 6*, with **41** (100 mg, 0.27 mmol; *syn*/*anti* 27:73), dry THF (1 ml), and NaH (55% in oil; 17 mg, 0.38 mmol). FC (AcOEt/hexane 1:2) provided **42** (61 mg, 70%; *cis*/*trans* 27:73). Colorless oil. IR (film): 2954, 2929, 2857, 2166, 1754, 1422, 838. ^{1}H-NMR (360 MHz): 7.31–7.20 (*m*, 5 arom. H); 4.46–4.42 (*m*, OC*H*CH_2O); 4.37 (*A* or *AB*, J_{AB} = 15.1, 1 H, PhCH_2); 4.34 (*B* of *AB*, J_{AB} = 15.1, 1 H, PhCH_2); 3.73–3.68 (*m*, 1 H, CH_2O); 3.63–3.59 (*m*, 1 H, CH_2O); 3.32 (*d*, *J* = 9.1, CHD, *cis*); 3.27 (*d*, *J* = 6.3, CHD, *trans*); 0.79 (*s*, *t*-Bu); 0.02 (*s*, 2 Me). ^{13}C-NMR (50.3 MHz): 157.97 (*s*); 135.81 (*s*); 128.75 (*d*); 128.06 (*d*); 127.84 (*d*); 72.88 (*d*); 63.38 (*t*); 48.24 (*t*); 45.14 (*d*); 25.75 (*q*); 18.22 (*s*); 18.22 (*s*); −5.50 (*q*). CI-MS: 324 (25, $[M + 1]^+$), 323 (100), 307 (9), 205 (20), 91 (28). Anal. calc. for $C_{17}H_{26}DNO_3Si$ (322.50): C 63.31, H 8.47, N 4.34; found: C 63.02, H 8.57, N 4.53.

*(5*S*)-3-Benzyl-5-{{[(*tert*-butyl)dimethylsilyl]oxy}methyl}oxazolidin-2-one* (**43**). According to *GP 3*, with **24** (910 mg, 2.03 mmol) Bu_3SnH (886 mg, 0.81 ml, 3.04 mmol), and AIBN (49 mg, 0.30 mmol). FC (AcOEt/hexane 1:4) gave (ethyl benzyl{[(*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]methyl}carbamate (423 mg, 71%). Colorless oil. $[\alpha]_D^{20} = -23.4$ ($CHCl_3$, $c = 0.017$). IR (film): 2985, 2936, 1703, 1420, 1242, 1068. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 7.37–7.21 (*m*, 5 arom. H); 4.57 (*d*, *J* = 15.8, 1 H, PhCH_2); 4.46 (*d*, *J* = 15.8, 1 H, PhCH_2); 4.28–4.15 (*m*, OC*H*CH_2O); 4.09 (*q*, *J* = 7.1, MeCH_2); 3.93 (*dd*, *J* = 8.4, 6.3, 1 H, CH_2O); 3.60–3.52 (*dd*, *J* = 8.4, 6.3, 1 H, CH_2O); 3.43–3.33 (*m*, 1 H, CH_2N); 3.29–3.19 (*m*, 1 H, CH_2N); 1.33, 1.25 (2 *s*, 2 Me); 1.19 (*t*, *J* = 7.1, *Me*CH_2). CI-MS: 294 (7, $[M + 1]^+$), 293 (1, M^+), 237 (14), 236 (100), 192 (8), 91 (7). Anal. calc. for $C_{16}H_{23}NO_4$ (293.37): C 65.51, H 7.0, N 4.77; found: C 65.46, H 7.79, N 4.76.

A soln. of the [(dioxolanyl)methyl]carbamate (284 mg, 0.97 mmol) and CF_3COOH (0.20 ml, 1.90 mmol) in THF/H_2O 4:1 (10 ml) was heated under reflux for 7 h. The mixture was cooled, Et_2O (50 ml), added, and the mixture washed with 10% $NaHCO_3$ soln., H_2O, and brine. After drying ($MgSO_4$) and evaporation, the residue was purified by FC (AcOEt/hexane 3:1) to give ethyl benzyl[(*S*)-2,3-dihydroxypropyl]carbamate (217 mg, 88%). $[\alpha]_D^{20} = +74.31$ ($CHCl_3$, $c = 4.3 \cdot 10^{-4}$). ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 7.37–7.19 (*m*, 5 arom. H); 4.55 (*A* of *AB*, J_{AB} = 15.9, 1 H, PhCH_2); 4.49 (*B* of *AB*, J_{AB} = 15.8, 1 H, PhCH_2); 4.41 (*s*, OH); 4.23–4.18 (*m*, OH); 4.07 (*q*, *J* = 7.0, MeCH_2); 3.78–3.60 (*m*, CHO); 3.36–3.27 (*m*, CH_2O, 1 H of CH_2N); 3.13–3.02 (*m*, 1 H, CH_2N); 1.17 (*t*, *J* = 7.0, *Me*CH_2).

A mixture of the (dihydroxypropyl)carbamate (160 mg, 0.63 mmol), (*t*-Bu)Me_2SiCl (114 mg, 0.76 mmol), Et_3N (0.10 ml, 0.70 mmol), and 4-(dimethylamino)pyridine (3 mg, 0.03 mmol) in dry CH_2Cl_2 (1 ml) was stirred at r.t. for 12 h. The mixture was treated with H_2O, diluted with Et_2O, and washed with aq. 1M HCl, H_2O, and brine. After drying ($MgSO_4$) and removal of the solvent, FC (AcOEt/hexane 1:2) provided ethyl benzyl{(*S*)-3-{[(*tert*-butyl)dimethylsilyl]oxy}-2-hydroxypropyl}carbamate (185 mg, 80%). Colorless oil. $[\alpha]_D^{20} = -8.8$ ($CHCl_3$, $c = 0.007$). IR (film): 3436, 2956, 2931, 2858, 1701, 1473, 1425, 1252. ^{1}H-NMR (200 MHz, (D_6)DMSO, 80°): 7.37–7.18 (*m*, 5 arom. H); 4.56 (*A* of *AB*, J_{AB} = 15.6, 1 H, PhCH_2); 4.50 (*d*, *J* = 4.7, OH); 4.49 (*B* of *AB*, J_{AB} = 15.6, 1 H, PhCH_2); 4.07 (*q*, *J* = 7.1, MeCH_2); 3.76–3.68 (*m*, CHO); 3.56–3.31 (*m*, CH_2O); 3.36 (*dd*, *J* = 14.0, 4.8, 1 H, CH_2N); 3.06 (*dd*, *J* = 14.0, 7.8, 1 H, CH_2N); 1.18 (*t*, *J* = 7.1, *Me*CH_2); 0.86 (*s*, *t*-Bu); 0.03 (*s*, 2 Me). CI-MS: 369 (24, $[M + 1]^+$), 368 (100, M^+), 352 (30), 310 (43), 236 (33), 91 (5). Anal. calc. for $C_{19}H_{33}NO_4Si$ (367.57): C 62.09, H 9.5, N 3.81; found: C 62.06, H 8.99, 3.89.

According to *GP 6*, with [(silyloxy)hydroxypropyl]carbamate (78 mg, 0.21 mmol) in THF (1 ml), and NaH (55% in oil; 14 mg, 0.32 mmol). FC gave **43** (54 mg, 80%). Colorless oil. $[\alpha]_D^{20} = +25$ ($CHCl_3$, $c = 0.012$). IR (film): 2954, 2929, 2857, 1754, 1442, 1256, 838. ^{1}H-NMR (360 MHz): 7.34–7.23 (*m*, 5 arom. H); 4.51–4.45 (*m*, CHO); 4.39 (*s*, PhCH_2); 3.75 (*dd*, *J* = 11.1, 4.6, 1 H, CH_2O); 3.66–3.62 (*dd*, *J* = 11.1, 3.6, 1 H, CH_2O); 3.40–3.36 (*m*, 1 H, CH_2N); 3.34–3.30 (*m*, 1 H, CH_2N); 0.83 (*s*, *t*-Bu); 0.02 (*s*, 2 Me). NOE (360 MHz): 3.75 (1 H of CH_2OSi) → 3.34–3.30 (1 H of CH_2N, 1.7%); 3.64 (1 H of CH_2OSi) → 3.34–3.30 (1 H of CH_2N, 1.6%); 4.48

(CHO) → 3.40–3.36 (1 H of CH_2N, 7.4%). ^{13}C-NMR (50.3 MHz): 157.86 (*s*); 135.73 (*s*); 128.67 (*d*); 129.97 (*d*); 127.73 (*d*); 72.88 (*d*); 63.30 (*t*); 48.16 (*t*); 45.32 (*t*); 25.67 (*q*); 18.14 (*s*); −5.59 (*q*). CI-MS: 324 (7, $[M + 2]^+$), 323 (29, $[M + 1]^+$), 322 (100, M^+), 306 (9), 264 (17), 91 (59), 41 (33). Anal. calc. for $C_{17}H_{27}NO_3Si$ (321.49): C 63.51, H 8.47, N 4.36; found: C 63.48, H 8.53, N 4.39.

*Ethyl Benzyl{(1*R,2S*)- and (1*S,2S*)-2-amino-3-{[(*tert*-butyl)dimethylsilyl]oxy}(1-$^2H_1$)-propyl}carbamate* (**44**). a) *Starting from* **45**: A mixture of **45** (750 mg, 1.43 mmol; *syn*/*anti* 27:73) and NaN_3 (650 mg, 10.0 mmol) in dry DMF (20 ml) was stirred at 60° for 24 h. Et_2O (100 ml) was added and the mixture washed with H_2O (3 × 30 ml) and brine, dried ($MgSO_4$), and evaporated. The residue was purified by FC (AcOEt/hexane 1:4) to give the azide (428 mg, 76%) as a colorless oil. Ph_3P (63 mg, 0.24 mmol) and H_2O (7 mg, 0.6 mmol) were added to a soln. of the azide (100 mg, 0.24 mmol) in THF (1 ml). After 3 h, Et_2O (10 ml) was added and the mixture washed with H_2O and brine, dried ($MgSO_4$), and evaporated. FC (CH_2Cl_2/MeOH 95:5) of the residue gave **44** (52 mg, 59%; 74:26 *syn*/*anti* mixture). ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°): 7.33–7.22 (*m*, 5 arom. H); 4.54 (*A* of *AB*, J_{AB} = 15.5, 1 H, PhCH_2); 4.46 (*B* of *AB*, J_{AB} = 15.5, 1 H, PhCH_2); 4.09 (*q*, *J* = 7.0, MeCH_2); 3.48 (*dd*, *J* = 10.0, 5.2, 1 H, CH_2O); 3.42 (*dd*, *J* = 10.0, 5.3, 1 H, CH_2O); 3.20 (*d*, *J* = 6.5, CHD, *syn*); 3.11 (*d*, *J* = 7.4, CHD, *anti*); 3.00–2.84 (C*H*NH_2); 1.28 (br. *s*, NH_2); 1.19 (*t*, *J* = 7.0, *Me*CH_2); 0.88 (*s*, *t*-Bu); 0.04 (*s*, 2 Me).

b) *Starting from* **35a**: A soln. of **35a** (424 mg, 1.21 mmol; *syn*/*anti* 24:76) and CF_3COOH (0.93 ml, 12.1 mmol) in THF/H_2O 4:1 (4 ml) was heated under reflux for 3 h. The volatiles were evaporated, and the viscous residue was dissolved in CH_2Cl_2 (1 ml). (*t*-Bu)Me_2SiCl (219 mg, 1.45 mmol), Et_3N (0.19 ml, 1.33 mmol), and 4-(dimethylamino)pyridine (7 mg, 0.06 mmol) were added, and the mixture was stirred for 1.5 h at r.t. Then H_2O was added, the mixture extracted with Et_2O (3 × 10 ml), and the combined org. phase washed with brine, dried ($MgSO_4$), and evaporated. FC (CH_2Cl_2/MeOH 95:5) gave **44** (334 mg, 75%; *syn*/*anti* 24:76 mixture). Colorless oil. IR (film): 3378, 2955, 2930, 2859, 1699, 1470, 1424, 1254, 1107. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°): 7.33–7.22 (*m*, 5 arom. H); 4.54 (*A* of *AB*, J_{AB} = 15.5, 1 H, PhCH_2); 4.46 (*B* of *AB*, J_{AB} = 15.5, 1 H, PhCH_2); 4.09 (*q*, *J* = 7.0, MeCH_2); 3.48 (*dd*, *J* = 10.0, 5.2, 1 H, CH_2O); 3.42 (*dd*, *J* = 10.0, 5.3, 1 H, CH_2O); 3.20 (*d*, *J* = 6.5, CHD, *syn*); 3.11 (*d*, *J* = 7.4, CHD, *anti*); 3.00–2.84 (C*H*NH_2); 1.28 (br. *s*, NH_2); 1.19 (*t*, *J* = 7.0, *Me*CH_2); 0.88 (*s*, *t*-Bu); 0.04 (*s*, 2 Me). CI-MS: 368 (100, M^+), 352 (12), 310 (11), 174 (9). Anal. calc. for $C_{19}H_{33}DN_2O_5Si$ (367.59): C 62.08, H 9.35, N 7.62; found: C 62.13, H 9.54, N 7.80.

*Ethyl Benzyl{(1*R,2S*)- and (1*S,2S*)-3-{[(*tert*-butyl)dimethylsilyl]oxy}-2-{[(4-methylphenyl)sulfonyl]oxy}(1-$^2H_1$)propyl}carbamate* (**45**). A soln. of **41** (904 mg, 2.45 mmol; *syn*/*anti* 27:73) and tosyl chloride (1.00 g, 5.20 mmol) in pyridine (5 ml) was stirred at 0° for 15 h. The mixture was poured into ice and extracted with Et_2O (3 × 20 ml), the combined org. phase washed with H_2O and brine, dried ($MgSO_4$), and evaporated, and the residue purified by FC (AcOEt/hexane 1.4): **45** (910 mg, 71%; *syn*/*anti* 27:73 mixture). Colorless oil. IR (film): 2955, 2932, 2859, 1703, 1664, 1366, 1252, 1179, 837. ^{1}H-NMR (360 MHz, (D_6)DMSO, 80°): 7.95 (*d*, *J* = 10.8, 2 arom. H); 7.42–7.18 (*m*, 5 arom. H); 7.10 (*d*, *J* = 10.8, 2 arom. H); 5.17–5.12 (*m*, C*H*OTs); 4.73 (*d*, *J* = 17.3, 1 H, PhCH_2); 4.58 (*d*, *J* = 17.3, 1 H, PhCH_2); 4.25 (*qd*, *J* = 7.1, 1.2, MeCH_2); 4.02 (*dd*, *J* = 13.5, 5.3, 1 H, CH_2OSi); 3.89 (*dd*, *J* = 13.7, 4.5, 1 H, CH_2Si); 3.76 (br. *s*, CHD, *syn*); 3.55 (*d*, *J* = 9.9, CHD, *anti*); 2.24 (*s*, *Me*C_6H_4); 1.30 (*t*, *J* = 7.1, *Me*CH_2); 1.08 (*s*, *t*-Bu); 0.25, 0.24 (2 *s*, 2 Me). CI-MS: 523 (10, M^+), 323 (100), 209 (50), 173 (51), 91 (75). Anal. calc. for $C_{26}H_{38}DNO_6SSi$ (522.76): C 59.74, H 7.54, N 2.68; found: C 79.76, H 7.54, N 2.70.

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Received November 13, 1997