A Useful Modification of the *Evans* Auxiliary: 4-Isopropyl-5,5-diphenyloxazolidin-2-one

by **Tobias Hintermann**[1]) and **Dieter Seebach***

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

Dedicated to Professor *Hans Bock* on the occasion of his 70th birthday

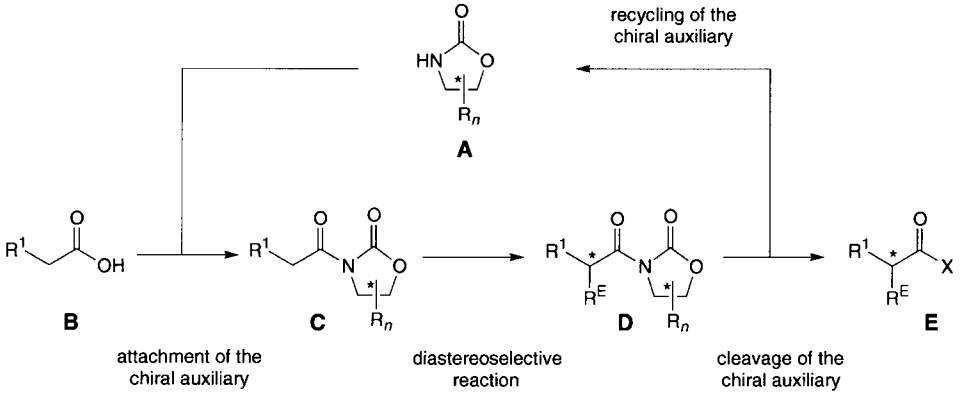
The 4-isopropyl-5,5-diphenyloxazolidinone (**1**) is readily prepared from (*R*)- or (*S*)-valine ester, PhMgBr, and ethyl chlorocarbonate. It has a melting point of *ca.* 250°, a low solubility in most organic solvents, and a C=O group which is sterically protected from nucleophilic attack. Thus, the soluble *N*-acyl-oxazolidinones (**7**–**16**) can be prepared from **1** with BuLi at temperatures around 0° instead of −78° (*Scheme 3*), their Li enolates can be generated with BuLi, rather than with LDA, and deacylation in the final step of the procedure can be achieved with NaOH at ambient temperatures (*Scheme 12*), with facile recovery of the precipitating auxiliary **1** (filtering, washing, and drying). The following reactions of *N*-acyl-oxazolidinones from **1** have been investigated: alkylations (*Scheme 4*), aminomethylations and hydroxymethylations (*Scheme 5*), aldol additions (*Schemes 6* and *7*), *Michael* additions (*Schemes 9* and *10*), and a (4+2) cycloaddition (*Scheme 11*). The well-known features of reactions following the *Evans* methodology (yield, diastereoselectivity, dependence on conditions, counter ions, additives *etc.*) prevail in these transformations. Most products, however, have higher melting points and a much more pronounced crystallization tendency than those derived from conventional oxazolidinones, and can thus be purified by recrystallization, avoiding chromatography (*Table 1*). The disadvantage of **1** having a higher molecular weight (*ca.* 150 Da) than the non-phenyl-substituted auxiliary is more than compensated by the ease of its application, especially on large scale. A number of crystal structures of oxazolidinones derived from **1** and a $TiCl_4$ complex of an oxazolidinone are described and discussed in view of the diastereoselective-reaction mechanisms.

1. Introduction. – There are only three fundamentally different methods of synthesizing enantiomerically pure compounds (EPC): resolution, enantioselective transformations, and use of starting materials from the pool of chiral building blocks [1]. Practical enantioselective transformations must be either catalytic, or the chiral auxiliary must be efficiently recycled. Of the covalently bound chiral auxiliaries (for review articles, see [2][3]), the ones which are attached to a carboxy C-atom are most useful for organic syntheses, and *the* auxiliaries in current methodology are oxazolidin-2-ones **A** (*Scheme 1*), introduced by *Evans et al.* in 1981 [4].

An ideal chiral auxiliary has to fulfil several criteria in the overall enantioselective reaction cycle (**B** → **E**; *Scheme 1*): *i*) It should be cheap, and both enantiomers should be readily available. *ii*) Attachment of the substrate to the auxiliary (**A** + **B** → **C**) should proceed in high yields by simple methods, applicable to a broad variety of substrates. *iii*) There should be many different types of reactions to be carried out with

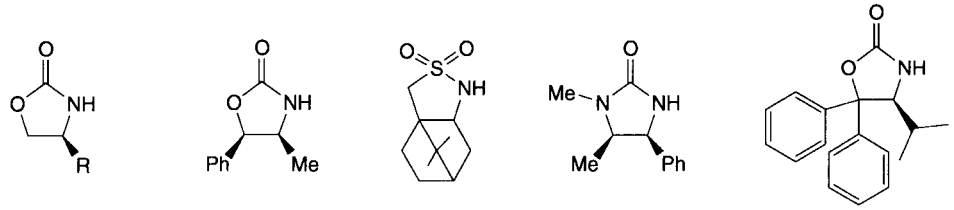
[1]) Part of the Ph. D. thesis of *T.H.*

Scheme 1



derivatives **C**. *iv*) The auxiliary must be stable under the conditions of the diastereoselective reaction (**C** → **D**). *v*) There must be a high degree of diastereoselection. *vi*) The derivatives of the chiral auxiliary (**C** and **D**) should preferably be crystalline, allowing easier purification, and removal of diastereoisomeric and other impurities (especially from **D**) by simple crystallization. *vii*) The cleavage of the auxiliary (**D** → **E** + **A**) must be possible with high yields under mild conditions, and the procedures should be generally applicable. *viii*) The auxiliary should not be destroyed under the conditions applied for cleavage, thus allowing for recycling of **A** (at least in large-scale processes). *ix*) Isolation of the enantiomerically pure product **E** and recovery of the auxiliary **A** should be possible by simple methods.

The oxazolidin-2-one auxiliaries **F**–**I** (available from valine, phenylalanine, phenylglycine, and norephedrine, resp.), all introduced by *Evans et al.* [4][5], satisfactorily fulfil most of the criteria mentioned above. Thus, they are now widely used in enantioselective syntheses. Several other oxazolidin-2-ones with partially better properties have been proposed [3][6][7], but none of them has been generally accepted by the 'synthetic community'. Other heterocyclic carboxy derivatives have also been applied with considerable succes (*e.g.*, sultams **K** [8] or ureas **L** [9]).



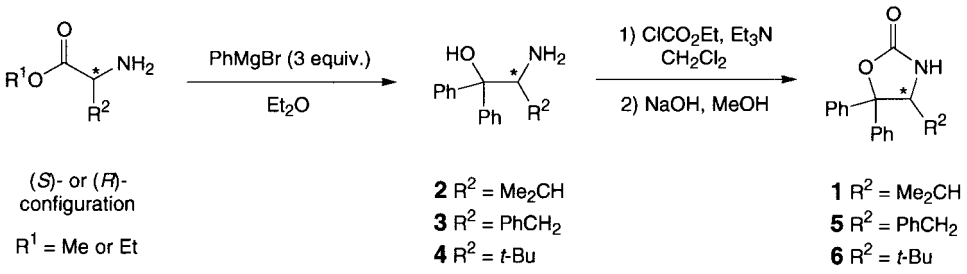
F R = Me_2CH
G R = $PhCH_2$
H R = Ph

I **K** **L** **1**

In the present paper, we report a general access to 5,5-diphenyloxazolidinones and derivatives as well as several applications of the new[2]) chiral auxiliary 4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (**1**). We will also underline the advantages of our new chiral auxiliary **1** – in every step of the reaction cycle shown in *Scheme 1* – over the well-established oxazolidinones **F**–**I** (see *Conclusions*).

2. Synthesis of the Chiral Oxazolidinone Auxiliaries 1, 5, and 6. – The 5,5-diphenyloxazolidin-2-ones **1**, **5**, and **6** were easily prepared in two steps starting from the commercially available valine methyl ester, phenylalanine ethyl ester, and leucine methyl ester (*Scheme 2*). Thus, treatment of the amino-acid esters with PhMgBr in Et_2O led to the 2-amino-1,1-diphenyl alcohols **2**–**4**. In contrast to a published procedure [12], not the hydrochloride salt of the amino esters, but the free amines, and only 3 equiv. of *Grignard* reagent (*vs.* 8 equiv.) had to be employed. Because of difficulties associated with the purification of the amino alcohols, the yields were only moderate (*ca.* 50% for **2** and **3**). For a large-scale synthesis, it would, therefore, be more reasonable to continue the process with the crude products[3]) (*ca.* 80% yield). This was done in the case of *tert*-leucine-derived amino alcohol **4**. For the cyclization to the oxazolidin-2-ones, we followed a procedure published for the preparation of *rac*-**5** [13]. The amino alcohols **2**–**4** were first ethoxycarbonylated ($ClCO_2Et$, Et_3N) and then cyclized by treatment with base (NaOH in MeOH). The yields of the cyclization were excellent (91% for (*S*)-**1**, and 86% for (*S*)-**5**), and purification was possible by simple filtration of the insoluble diphenyl-oxazolidinones from the reaction mixture and washing with H_2O, Et_2O, and pentane. The oxazolidin-2-one (*R*)-**6** was obtained in 66% overall yield (from *tert*-leucine methyl ester). The compounds **1** and **5** were shown to be >99.5% enantiomerically pure by HPLC on a chiral column (*Chiralcel OD*; see *Exper. Part* for details).

Scheme 2



---

[2]) The oxazolidinone **1** has previously been prepared by others [10][11], but, to the best of our knowledge, it has not been used as chiral auxiliary. 5,5-Disubstituted oxazolidin-2-ones with non-aryl-substituents at C(5) have also been used as chiral auxiliaries [7]. After submission of the manuscript for the present full paper, a communication, describing independent work on the use of **1**, has appeared: C. L. Gibson, K. Gillon, S. Cook, *Tetrahedron Lett.* **1998**, *39*, 6733–6736 (issue 37 of September 10). Also, in that communication, a related patent is referred to, which has escaped our notice: T. Isobe, K. Fukuda, Japanese Patent JP09143173, 1995; *Chem. Abstr.* **1997**, *127*, 50635.

[3]) The crude product contains mainly biphenyl as an impurity.

3. Acylation of the Oxazolidin-2-one Auxiliaries. – By far the most popular method of *N*-acylating an oxazolidin-2-one is the reaction of its Li salt (generated with BuLi at $-78°$) with an acyl chloride [4][14]. Generally, this procedure leads to *N*-acyl-oxazolidin-2-ones in excellent yields, but there are some limitations: *i*) acryloyl derivatives tend to polymerize under these conditions [15]; *ii*) β,γ-unsaturated carboxylic-acid derivatives isomerize to the α,β-unsaturated compounds [16]; *iii*) the method is not applicable to such carboxylic acids, which do not form stable acid halides; *iv*) due to the basicity of the lithiated oxazolidinone group, substrates with relatively acidic H-atoms or with a propensity for elimination cannot be employed; *v*) the use of RLi at $-78°$ is not desirable from an economic point of view (at least in large-scale applications). To circumvent these limitations, a number of milder methods has been proposed [15–17].

For the *N*-acylation of the 5,5-diphenyloxazolidin-2-ones **1**, **5**, and **6**, we used both, the standard *Evans* procedure [4][14] (BuLi, acyl chloride), and a method introduced by *Ho* and *Mathre* [15] (mixed anhydride, LiCl, Et_3N). Thus, lithiation of the oxazolidin-2-ones in THF with BuLi[4]) at 0° and subsequent treatment with various acyl chlorides gave the *N*-acyl-oxazolidin-2-ones **7**–**19**, mostly purified by recrystallization[5]), in good-to-excellent yields (80–98%; *Scheme 3*)[6]). *N*-Acyl-oxazolidin-2-ones containing either acidic H-atoms (**20**, **21**, and **24**), or readily eliminating substituents (**22**), or highly nucleophilic groups (**23**), were prepared by acylation with the LiCl-activated [18] pivaloyl mixed anhydride, using Et_3N as base [15] (*Scheme 3*), with somewhat lower yields of the products **20**–**24** (which had to be purified chromatographically). In summary, the *N*-acyl derivatives **7**–**24** of 5,5-diphenyloxazolidin-2-ones **1**, **5**, and **6**, containing a variety of different functional groups, are readily available in yields (of purified products!) ranging from 75 to 98%.

4. Diastereoselective Alkylations. – A typical reaction for the exploration of the potential of a chiral auxiliary is the alkylation of its propanoic-acid derivative. We, therefore, first studied the alkylation of *N*-acyl-oxazolidin-2-ones **8** (from valine), **17** (from *tert*-leucine), and **18** (from phenylalanine) (see products **25**–**30** in *Scheme 4*). Benzylation of the lithium-diisopropylamide(LDA)-generated Li-enolate from **18** turned out to be very slow, even at 0°, and the *N*-benzyl-oxazolidin-2-one[7]) was formed as the main product. With the NHMDS-generated ($-78°$) Na-enolate, the allylation product **28** was formed in good yield, however, with moderate diastereoselectivity (dr 4:1; *Entry 1* in *Scheme 4*). Better results were obtained by using the Zn-enolate, generated by transmetalation of the Li-enolate [19] (90% **28**; dr 94:6; *Entry 2*). Under the same conditions, the i-Pr-substituted derivative **8** led to the allylation product **25**

---

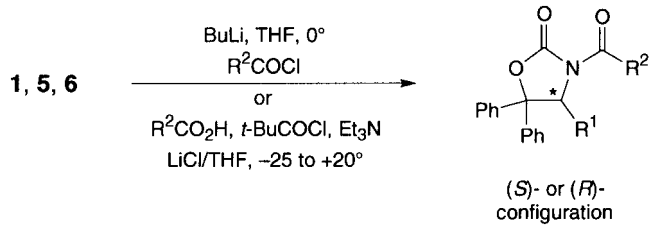
[4]) The oxazolidin-2-ones **1**, **5**, and **6** are not soluble in THF; therefore, BuLi was added to a suspension in THF, resulting in a clear solution. Although the reaction was performed at 0°, rather than at $-78°$, by-products arising from nucleophilic attack at the heterocycle were not observed.

[5]) The yields were not optimized; mother liquors from recrystallization were discarded. Purification of the *N*-acyl-oxazolidin-2-ones by flash chromatography resulted in yields of > 90%.

[6]) The acylation procedure worked equally well with **1**, **5**, and **6**, as can be seen from the yields obtained with propanoyl chloride ($\rightarrow$**8**, **17**, and **18**, 88–98%).

[7]) Probably resulting from decomposition of the enolate to the ketene and the lithiated oxazolidinone which is then benzylated.

Scheme 3



	7	**8**	**9**	**10**	**11**	**12**	**13**
R^1	Me_2CH	Me_2CH	Me_2CH	Me_2CH	$MeCH_2$	Me_2CH	Me_2CH
R^2	Me	$MeCH_2$	Me_2CHCH_2	$Me_2CH(CH_2)_2$	$Ph(CH_2)_2$	MeCH=CH(*E*)	PhCH=CH(*E*)

	14	**15**	**16**	**17**	**18**	**19**
R^1	Me_2CH	Me_2CH	Me_2CH	*t*-Bu	$PhCH_2$	$PhCH_2$
R^2	$MeOCO(CH_2)_3$	$PhthN(CH_2)_2$	$(4\text{-OBn})C_6H_4(CH_2)_2$	Me_2CH_2	Me_2CH_2	$PhthN(CH_2)_2$

	20	**21**	**22**	**23**	**24**
R^1	Me_2CH	Me_2CH	Me_2CH	Me_2CH	$PhCH_2$
R^2	$BocNH(CH_2)_2$	$CbzNH(CH_2)_2$	$MeCH(OBn)CH_2$	$[(1\text{-Cbz})\text{indol-3-yl}](CH_2)_2$	$BocNH(CH_2)_2$

Phth = phthaloyl; Boc = *t*-BuOCO; Cbz = BnOCO

with even higher diastereoselectivity (dr 96 : 4; *Entry 3*), so we tested **8** for other alkylations[8]). Indeed, reactions with BnBr and $BrCH_2CO_2(t\text{-Bu})$ afforded the corresponding products in good yields with high selectivities (*Entries 4* and *5*). Using the reactive electrophile $BrCH_2CO_2(t\text{-Bu})$, even the Li-enolates (generated with LDA, BuLi, or *t*-BuLi; *Entries 6–10*) could be alkylated at $-78°$ (→ succinic-acid derivatives **26**, **29**, and **30**). It is remarkable that the Li-enolate of **8** could be generated with BuLi, to give product **26** in essentially the same yield and selectivity as with LDA (*cf. Entries 6* and *8*)[9]). We were surprised to find that the diastereoselectivity observed with the *t*-Bu substituted auxiliary was much poorer than with the i-Pr-substituted one (3 : 1 *vs.* 19 : 1; *Entries 8* and *10*); normally, the *tert*-leucine-derived auxiliary is 'the champion'[10]). *N*-Acyl-oxazolidin-2-ones derived from other carboxylic acids can, of course, also be alkylated; see the methylation (**11** → **31**) shown on the bottom of *Scheme 4*.

The relative configuration at the newly formed stereogenic centers in compounds **29** and **30** was assigned by X-ray crystal-structure analysis (*Chapt. 9*). The configuration of the other alkylation products was assigned by analogy[11]).

---

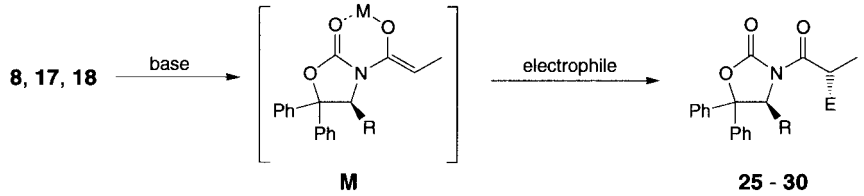
[8]) Additionally, it turned out that derivatives of **1** were generally 'more crystalline' than derivatives of **5**. It was thus possible to obtain diastereoisomerically pure products (dr > 98 : 2) by simple recrystallization.

[9]) With the isopropyl-oxazolidinone **8**, only *ca.* 5% by-products resulting from nucleophilic attack of BuLi on the propanonyl group were detected, while, with benzyl-oxazolidinone **18**, this reaction became a dominant side reaction.

[10]) *Cf.* the discussion of X-ray crystal structures in *Chapt. 9.*

[11]) As expected for such systems, the electrophile is approaching the chelated enolate **M** from the face opposite to the R group at C(4) of the heterocycle [20].

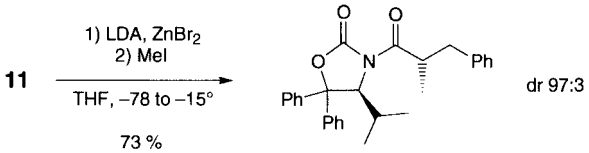
Scheme 4



	25	26	27	28	29	30
R	Me_2CH	Me_2CH	Me_2CH	$PhCH_2$	$PhCH_2$	*t*-Bu
E	$CH_2=CHCH_2$	*t*-BuOCOCH$_2$	$PhCH_2$	$CH_2=CHCH_2$	*t*-BuOCOCH$_2$	*t*-BuOCOCH$_2$

Entry	R	Base	Electrophile	Product	Temp. [°]	Yield [%][a])	dr [b])
1	$PhCH_2$	NHMDS	$CH_2=CHCH_2Br$	**28**	−78	75	4:1
2	$PhCH_2$	LDA/$ZnBr_2$	$CH_2=CHCH_2Br$	**28**	−78 to −15	90	94:6
3	Me_2CH	LDA/$ZnBr_2$	$CH_2=CHCH_2Br$	**25**	−78 to −15	72 [c])	96:4
4	Me_2CH	LDA/$ZnBr_2$	$PhCH_2Br$	**27**	−78 to −15	81 [c])	>98:2
5	Me_2CH	LDA/$ZnBr_2$	$BrCH_2CO_2$(*t*-Bu)	**26**	−78 to −15	83	92:8
6	Me_2CH	LDA	$BrCH_2CO_2$(*t*-Bu)	**26**	−78	80	95:5
7	Me_2CH	*t*-BuLi	$BrCH_2CO_2$(*t*-Bu)	**26**	−78	56	95:5
8	Me_2CH	BuLi	$BrCH_2CO_2$(*t*-Bu)	**26**	−78	82	95:5
9	$PhCH_2$ [d])	BuLi	$BrCH_2CO_2$(*t*-Bu)	**29**	−78	55	n.d. [e])
10	*t*-Bu [d])	BuLi	$BrCH_2CO_2$(*t*-Bu)	**30**	−78	49	3:1

[a]) After FC. [b]) Diastereoisomer ratio, determined by ^{1}H-NMR (300 MHz) of the crude product. [c]) After recrystallization, dr >98:2. [d]) The (*R*)-enantiomers of **17** and **18** were actually used in this experiment. [e]) n.d. = not determined (NHMDS = hexamethyldisilazane).



5. Synthesis of *β*-Amino-Acid Derivatives. – In the course of our investigation of *β*-peptides (for a review, see [21]), we needed to have a general enantioselective route to *α*-substituted *β*-amino acids (*β*^{2}-amino acids). We chose the diastereoselective aminomethylation of *N*-acyl-oxazolidin-2-one Ti-enolates, initially suggested by *Evans et al.* [22], and later also used by *Wyatt* and co-workers [23]. Initially [24], we employed *N*-(chloromethyl)benzamide as aminomethylating agent, to prepare *N*-benzoyl-protected *β*^{2}-amino acids. Since the removal of the *N*-benzoyl group requires strongly acidic conditions, under which partial racemization occurred, we switched to the *N*-(methoxymethyl) *N*-[(benzyloxy)carbonyl] (Cbz) derivative also used by *Evans* and co-workers [25][12]), which leads to *N*-Cbz-protected *β*^{2}-amino-acid derivatives, readily deprotected under neutral conditions (H_2, Pd/C).

---

[12]) *Cf.* the $TiCl_4$-mediated reactions of methoxy derivatives obtained by electrolytic oxidative decarboxylation of peptides [18][26].

We found, that best results were obtained by generating a Ti-enolate at $-20°$ ($TiCl_4$/tertiary amine), and performing the alkylation at $0°$ with the $TiCl_4$-activated electrophile[13]). Thus, *N*-acyl-oxazolidin-2-ones **8**–**11** (no functional groups in the acyl part!) led to the β^2-amino-acid derivatives **32**–**35** in good yields and with high stereoselectivities (dr 12:1–15:1; *Scheme 5*, *Entries 1–4*)[14]). The method is, however, not compatible with certain types of functional groups present in the acyl part: While an ester (in **14**) or phthalimido group (in **15**) are tolerated (→ **36**, **37**; *Entries 5* and *6*), the (benzyloxy)phenyl group in **16** prevented a satisfactory yield of **38** (*Entry 7*), and with the (*R*)-3-(benzyloxy)butanoyl and Cbz-indol-3-yl derivatives (**22** and **23**, resp.; *Entries 8* and *9*), we did not even find products[15]).

Encouraged by the successful aminoalkylation of the 3-phthalimido-propanoyl-oxazolidin-2-one **15** (→ β,β'-diamino-acid derivative **37**), we tried a hydroxymethylation of **15**, to prepare a β^2-serine: Reaction of the Ti-enolate of **15** with $ClCH_2OBn$ led to a *ca.* 1:1 mixture of starting material and product **40** (difficult to separate), but direct hydroxymethylation with trioxane [22] (→ 92% **38**) and subsequent benzylation (87%) turned out to be a superior route to this compound (*Scheme 5*).

Since the use of Boc-protected β-amino acids has proven to be the method of choice for the solution synthesis of β-peptides [21][24], a Cbz/Boc *trans*-protection by hydrogenolysis of **32**, **33**, and **35** in the presence of Boc_2O (2 h, $20°$) was performed (→ **41**–**43**, 81–87%; *Scheme 5*). Interestingly, only traces of the by-product **N** resulting from cleavage of the C(5)–O bond in the auxiliary oxazolidinone ring were detected[16]).

6. Aldol Additions. – Due to their central role in organic synthesis, stereoselective aldol additions have been the subject of intensive studies. In particular, B- [4] and Ti-enolates [17][28] of *N*-acyl-oxazolidin-2-ones are most useful reagents for the preparation of 3-hydroxy carboxylic-acid derivatives of high enantiomeric purity. Unfortunately, the simple *N*-acetyl-oxazolidin-2-ones generally undergo aldol additions with lower selectivities than their homologs [28][29]. We, therefore, chose derivative **7** as a first substrate to test the auxiliary **1** in an aldol reaction[17]).

Addition of the Li-enolate of oxazolidin-2-one **7** to PhCHO at $-78°$ afforded the aldols **44** and **45** in high yield and with good selectivity [18]) (dr 9:1; *Scheme 6*, *Entry 1*). Use of the Ti-enolate, generated by transmetalation (3 equiv. $(i\text{-PrO})_3TiCl$) from the Li-enolate [28], or of the B-enolate [14] gave poor selectivities (*Entries 2* and *3*). Direct formation of a Ti-enolate [27] (1 equiv. $TiCl_4$, $EtN(i\text{-Pr})_2$) led to a reversal of the

---

[13]) Activation of the electrophile with a second equiv. of $TiCl_4$ is required to accelerate the reaction. At lower temperatures, no alkylation was observed.

[14]) Besides the alkylation products, mainly starting material was recovered, probably resulting from proton transfer from the electrophile to the enolate. To clearly identify the minor diastereoisomer in the ^{1}H-NMR spectra, authentic samples of the epimers of **32**–**35** and **37** were prepared (acylation of (*R*)-**1** with the Cbz-protected amino acids from the reactions of (*S*)-**1** and hydrolysis).

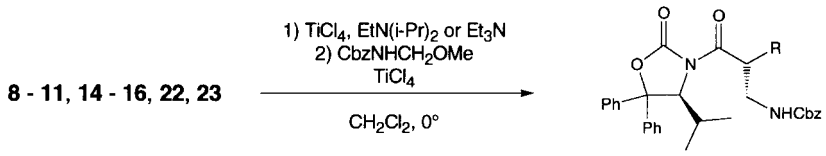
[15]) To assign the absolute configuration at the newly formed stereogenic center, **35** was transformed to the known [24] free β^2-amino acid (H_2O_2/LiOH; then H_2, Pd/C).

[16]) Hydrogenolysis for 48 h under the same conditions led exclusively to **N**.

[17]) All aldol additions were carried out under conditions as reported in the literature for the corresponding *Evans* oxazolidinones [14][27][28], in no case did we optimize for the 5,5-diphenyl derivatives.

[18]) The absolute configuration at the newly formed stereogenic center was derived by cleavage (H_2O_2/LiOH) of **45**, and comparison of the optical rotation of the free hydroxy acid [30].

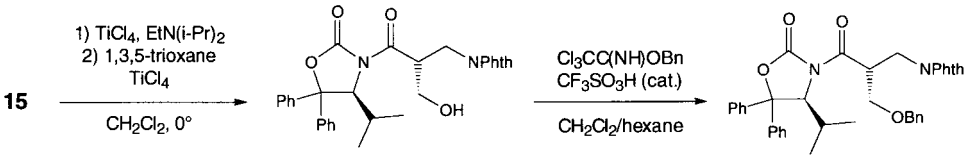
Scheme 5



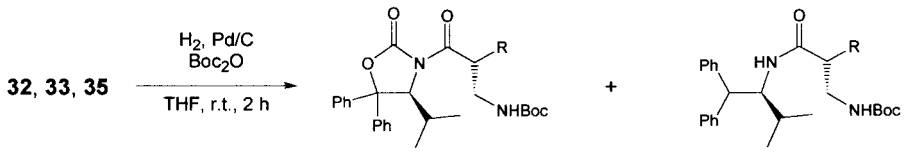
32 - 38

Entry	Substrate	R	Product	Yield [%] [a])	dr [b])
1	**8**	Me	**32**	69	93:7
2	**9**	Me_2CH	**33**	70	93:7
3	**10**	Me_2CHCH_2	**34**	64	92:8
4	**11**	$PhCH_2$	**35**	78	94:6
5	**14**	$MeOCO(CH_2)_2$	**36**	42	n.d.
6	**15**	$PhthNCH_2$	**37**	65 [c])	95:5 [c])
7	**16**	$(4\text{-OBn})C_6H_4CH_2$	**38**	30 [d])	n.d.
8	**22**	BnO(Me)CH	– [e])	–	–
9	**23**	[(1-Cbz)indol-3-yl]CH_2	– [e])	–	–

[a]) After FC. [b]) Determined by ^{1}H-NMR (300 MHz) of the crude product or after purification by FC. [c]) Determined after recrystallization. [d]) Isolated as a 3:1 mixture of **38** and **16**. [e]) No product was isolated.



39 **40**



41 R = Me
42 R = Me_2CH
43 R = $PhCH_2$

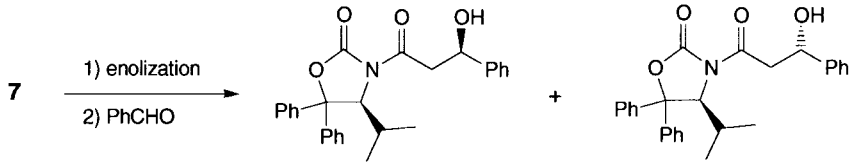
N

diastereoselectivity of the reaction (dr 1:3; *Entry 4)*, thus, aldol **45** was obtained as the major product.

In aldol additions with propanoyl-oxazolidin-2-one **8**, four diastereoisomeric products, *syn*-1, *syn*-2, *anti*-1, and *anti*-2, can be formed (**46**–**51**; see *Scheme 7*)[19]). Addition of the Li-enolate to PhCHO at −78° gave *syn*-2 aldol **48** in very good diastereoselectivity (dr 97:3; *Entry 1*). A similar result was obtained when the Li-

[19]) Assignment of the configurations of aldols **46**–**50** by cleavage ($LiOH/H_2O_2$) and comparison of ^{1}H-NMR and optical rotations of the resulting hydroxy acids with literature data [31].

Scheme 6



Entry	Base	Solvent	Temp. [°]	Yield [%] [a])	dr (**44**/**45**) [b])
1	BuLi	THF	– 78	88	90:10
2	BuLi, $(i\text{-}PrO)_3TiCl$	THF	– 78 to – 40	89	56:44
3	$EtN(i\text{-}Pr)_2$, Bu_2BOTf	CH_2Cl_2	0	74	67.33
4	$EtN(i\text{-}Pr)_2$, $TiCl_4$	CH_2Cl_2	– 78 to 0	82	25:75

[a]) Combined yield of **44** and **45** after FC. [b]) Determined by ^{1}H-NMR (300 MHz) of the crude product. Tf = CF_3SO_2.

enolate was transmetalated to the Ti-enolate (3 equiv. $(iPrO)_3TiCl$) before addition to the aldehyde (*Entry 2*). With the B-enolate, the aldol addition to PhCHO was almost nonselective (*syn*-1 **46**/*anti*-1 **50** 3:2; *Entry 3*). Surprisingly, the result was quite different when the nonaromatic isobutyraldehyde was employed: with the Li-enolate, the selectivity was significantly lower, while a dramatic improvement was observed with the B-enolate (dr 4:1 and 96:4; *Entries 4* and *5*); also lower yields were obtained.

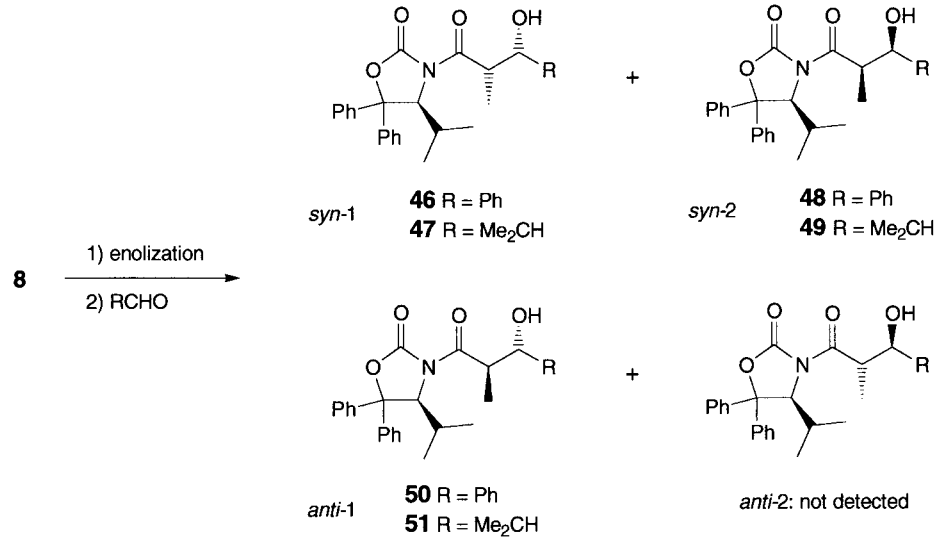
The stereochemical outcome of the aldol reactions can be discussed by using a chair-like transition-state model [32]. Thus, R_2B- and $TiCl_4$-enolate derivatives produce *syn*-1 aldols *via* intermediate **O**, and Li- or $(i\text{-}PrO)_3Ti$-enolates are thought to use an additional coordination site, to give *syn*-2 aldols *via* **P** (*Scheme 8*). Somewhat strange are the results we obtained in the B-mediated aldol addition to PhCHO: In the case of *N*-propionyl-oxazolidin-2-one **8** (*Scheme 7*, *Entry 3*), an unusually high amount of *anti*-1 aldol **50** is formed[20]). This might be explained by an attractive interaction between the Ph group of PhCHO and one of the Ph groups in the oxazolidinone ring (see **Q**)[21])[22]). In the aldol addition of *N*-acetyl-oxazolidin-2-one **7** B-enolate to PhCHO, the selectivity is also better as compared to the analogous reaction of the *Evans* oxazolidinone [4]. The stereochemical outcome of this reaction is not compatible with the model used for the propionyl derivative, since addition to the *Re* face (*cf. syn*-2 and *anti*-2) and not to the *Si* face of the aldehyde C=O group occurs. Also, the preferred formation of **44** would be in agreement with a favorable interaction between the Ph groups of the aldehyde and the auxiliary, but with a boat-like transition state (see **R**) which would only be favorable when $R^2 = H$. Further experiments would

[20]) As compared to the results with *Evans* oxazolidinones [4].

[21]) Resulting in a smaller difference of the transition-state energies between **O** and **Q**.

[22]) Since the results obtained with isobutyraldehyde are as expected, the anomalies in the case of PhCHO probably result from an interaction between the Ph rings.

Scheme 7



Entry	Base, Solvent	Aldehyde	Temp. [°]	Yield [%] [a]	dr (*s*-1/*s*-2/*a*-1) [b]
1	BuLi, THF	PhCHO	– 78	91	– [c]) : 97 : 3
2	BuLi, (i-PrO)$_3$TiCl, THF	PhCHO	– 78 to – 40	87	6 : 93 : 1
3	EtN(i-Pr)$_2$, Bu$_2$BOTf, CH_2Cl_2	PhCHO	0	77	60 : 2 : 37
4	BuLi, THF	i-PrCHO	– 78	56	6 : 80 : 14
5	EtN(i-Pr)$_2$, Bu$_2$BOTf, CH_2Cl_2	i-PrCHO	0	50	96 : – [c]) : 4

[a]) Combined yield of all isomers after FC. [b]) Determined by ^{1}H-NMR (300 MHz) of the crude product; *s* = *syn*, *a* = *anti*. [c]) A hyphen means that the corresponding isomer was not detected. Tf = CF_3SO_2.

be necessary to arrive at a more definite interpretation of the unusual selectivities in the aldol reactions of **7** and **8** with PhCHO[23]).

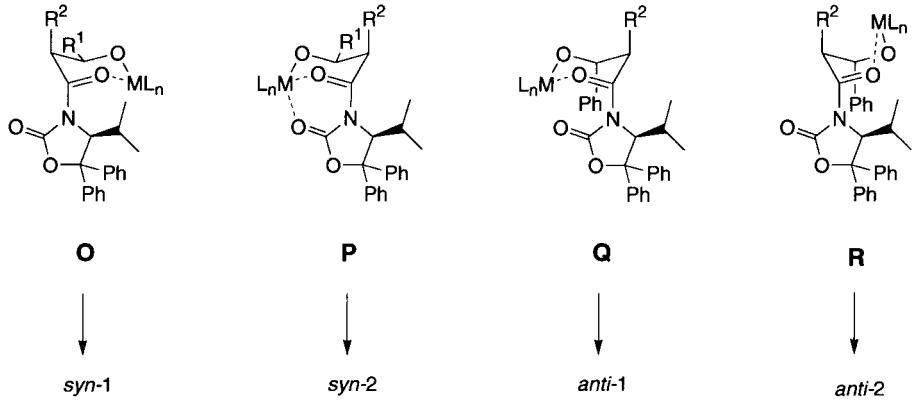
7. *Michael* and *Diels-Alder* Additions. – As a consequence of the recent discovery, that not only β-peptides [21], but also γ-peptides [33] with short chain length, form well-defined secondary structures in solution, there is now a need for efficient routes to enantiomerically pure γ-amino acids with various substitution patterns[24]).

To find out whether these would be accessible by *Michael* addition of the derivatives of oxazolidinone (*S*)-**1** to nitroolefins, we combined the Li-enolate of **8** with 1-nitro-2-phenylethene and RO-substituted nitrostyrenes (*Scheme 9*, *Entries 1–3*) and isolated the products **52**–**54** in good yields and with high selectivities (*ca.* 10 : 1); the

[23]) The aldol additions with PhCHO *via* **P** lead to significantly better selectivities than with the corresponding *Evans* auxiliaries [28].

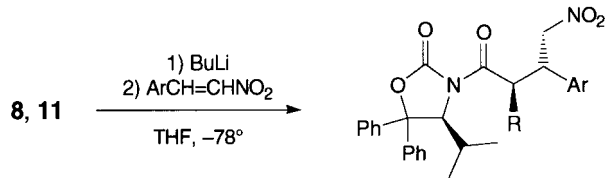
[24]) In the literature, we found only one example of a γ-amino-acid derivative, having been prepared *via* *Michael* addition of an *N*-acyl-oxazolidinone enolate to a nitroolefin and subsequent reduction of the NO_2 to the NH_2 group [34]. For our previous studies of diastereo- and enantioselective additions to nitroolefins, see [35].

Scheme 8



oxazolidinone **11** and nitrostyrene reacted with an even better selectivity (→ **55**; dr 32 : 1; *Entry 4*)[25]). These preliminary results show that the *Michael* addition of *N*-acyloxazolidin-2-one enolates to nitroolefins may well be an ideal route to γ-amino acids[26]).

Scheme 9



52 - 55

Entry	Substrate	R	Ar	Product	Yield [%] [a])	dr [b])
1	**8**	Me	Ph	**52**	78 (58)	89:11
2	**8**	Me	4-MeO – C_6H_4	**53**	80	91:9
3	**8**	Me	3,4-OCH_2O-C_6H_3	**54**	86	92:8
4	**11**	$PhCH_2$	Ph	**55**	92 (71)	97:3

[a]) After FC; numbers in brackets after recrystallization, dr > 98 : 2. [b]) Determined by ^{1}H-NMR (300 MHz) of the crude product.

In the reactions described so far, the enolate of an *N*-acyl-oxazolidin-2-one acted as a donor to combine with an acceptor reactant. With α,β-unsaturated *N*-acyl-oxazolidin-2-ones the relationship of reactants can be reversed [3]. As test reactions for the chiral auxiliary **1** in this type of transformation, we chose the *Diels-Alder* reaction and the *Michael* addition.

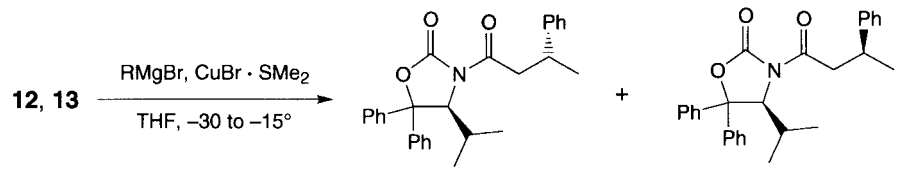
---

[25]) The relative configuration of the major diastereoisomer **55** was assigned by X-ray crystal-structure analysis, that of products **52** – **54** is assigned by analogy (the NMR spectra of the two series of epimers show characteristic resemblances). The configuration of the minor diastereoisomer is unknown.

[26]) This reaction is the subject of a separate investigation (*M. Brenner*, ETH-Zürich).

Thus, the addition of cuprates (prepared *in situ* from the corresponding *Grignard* reagents [19]) to the *Michael* acceptors **12** and **13** was studied (*Scheme 10*). Phenyl cuprate and *N*-crotonyl-oxazolidin-2-one **12** afforded a 2:1 mixture of the epimers **56** and **57** (92%), and, in turn, treatment of *N*-cinnamoyl-oxazolidin-2-one **13** with methyl cuprate led to a 1:2 mixture of these isomers, which could not be separated.

Scheme 10

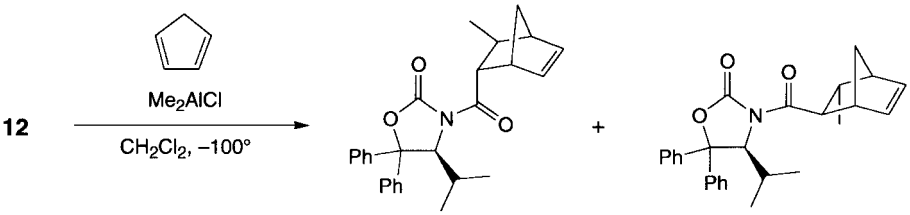


56 **57**

	Yield [%]	**56**/**57**
12 + PhMgBr	92	2:1
13 + MeMgBr	90	1:2

The *Lewis*-acid-promoted *Diels-Alder* reaction [36] of **12** with cyclopentadiene gave *endo*-product **58** with excellent yield (87%) and with almost complete selectivity (**58**(*endo*)/**59**(*exo*) 98:2, dr in **58** > 95:5; *Scheme 11*)[27]).

Scheme 11



58 (*endo*) (dr > 95:5) ratio 98:2 **59** (*exo*)

8. Cleavage of the Chiral Auxiliary. – Following a stereoselective reaction of an *N*-acyl-oxazolidin-2-one, the chiral auxiliary has to be removed, separated from the product, and preferably, recycled. There are numerous possibilities for this cleavage, which lead to different derivatives: enantiomerically pure carboxylic acids, esters, thioesters, amides, *Weinreb* amides, or alcohols are available from the same precursors [3]. As model substrate for the cleavage reactions with our modified auxiliary **1**, we chose the alkylation product **27** (see *Scheme 4*).

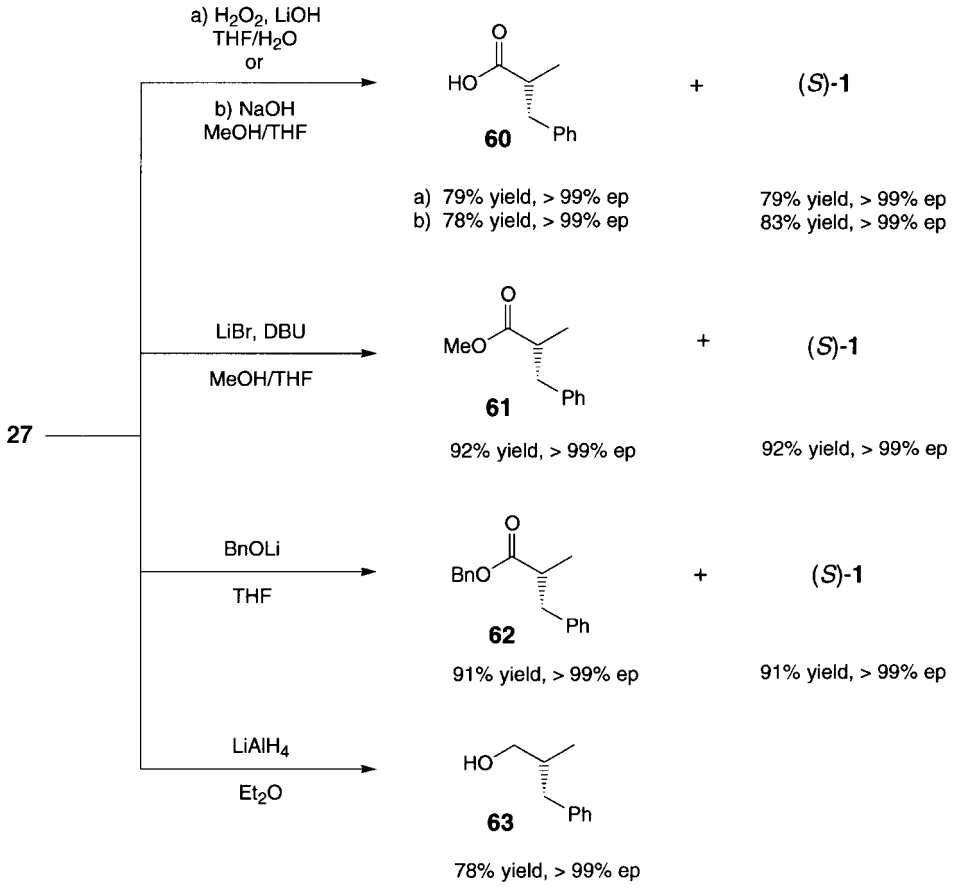
---

[27]) The relative configuration of **58** was assigned by X-ray crystal-structure analysis. The diastereoselectivity was determined by ^{1}H-NMR of the crude product, the *endo*/*exo* ratio by ^{1}H-NMR of the alcohols, obtained by reductive removal ($LiAlH_4$) of the auxiliary (*cf.* [37]).

Hydrolysis to carboxylic acids is the by far most often used method for cleavage. To prevent endocyclic cleavage (nucleophilic attack of the oxazolidinone C=O group), lithium hydroperoxide has often to be used instead of hydroxide [38]. In the case of 4-isopropyl-5,5-diphenyloxazolidin-2-ones, endocyclic cleavage is efficiently prevented by steric shielding from the Ph and i-Pr substituents. Thus, cleavage of **27** with NaOH (20°, 2.5 h) gave carboxylic acid **60** in essentially the same yield and enantiomeric purity as cleavage with $LiOH/H_2O_2$ (0°, 1.5 h; *Scheme 12*). Recycling of the auxiliary could be achieved simply by filtrating and washing with H_2O, Et_2O, and pentane, which yielded pure (*S*)-**1** after drying. Alcoholytic cleavage to methyl ester **61** (MeOH, LiBr, DBU [18][19]) or benzyl ester **62** (BnOLi [20]) proceeded with even better yields, and recovery of (*S*)-**1** was as easy as described above. Reductive cleavage ($LiAlH_4$ [20]) to the alcohol **63** was also possible, but recovery of the auxiliary turned out to be problematic in this case, because of difficulties with the separation from Al salts.

In summary, we have shown that cleavage of the chiral oxazolidin-2-one **1** is feasible under conditions commonly also used for other oxazolidinones, and recovery of the

Scheme 12



auxiliary is very simple without the need for a purification step other than filtration and washing. No partial racemization of the products **60** – **63** or of the auxiliary was detected (see enantiomeric purities, ep [%], given in *Scheme 12*)[28]).

9. X-Ray Crystal Structures. – *N*-Acyl-oxazolidin-2-ones **11**, **29**, **30**, **55**, and **58** gave crystals suitable for X-ray analysis. The asymmetric unit of the crystal of **55** contains two crystallographically independent molecules which display almost the same geometry. Thus, only one of the molecules is shown here. All other asymmetric units contain only one molecule. *Fig. 1* shows the ORTEP representations of crystal structures that were used for the determination of the relative configurations of reaction products.

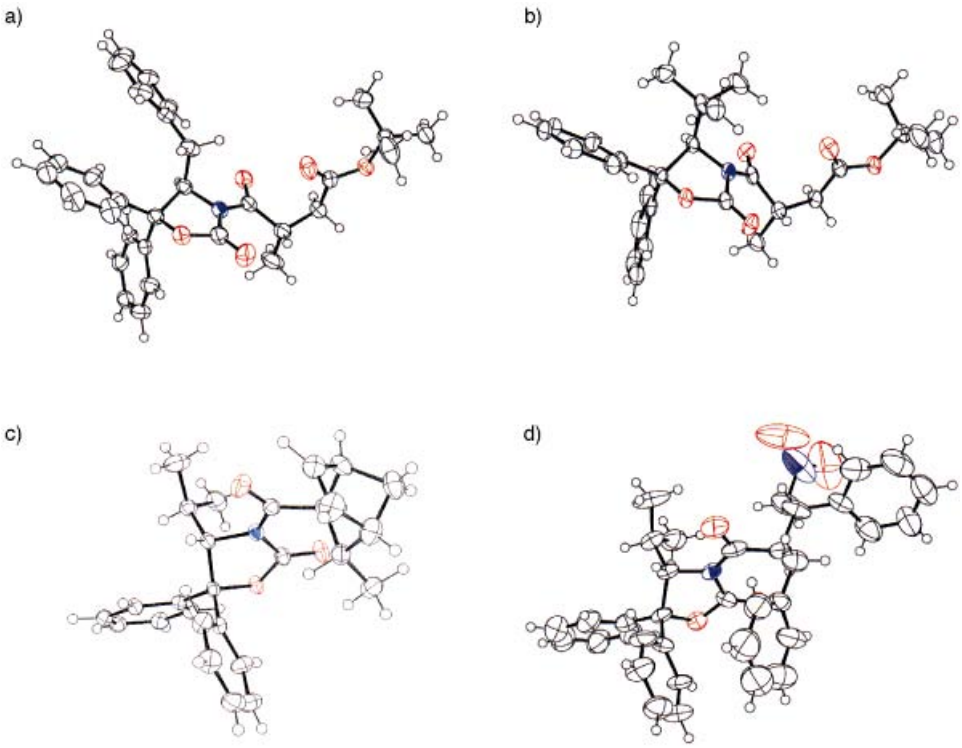


Fig. 1. *ORTEP Representations of the X-ray structures of* **29** (a), **30** (b), **58** (c), *and* **55** (d). O-Atoms in red, N-atoms in blue, C- and H-atoms in black; the thermal ellipsoids are drawn to the 50% probability level. The structures were determined by Dr. *B. Schweizer.*

The overlay of the crystal structures of oxazolidin-2-ones **29** (derived from phenylalanine), **30** (derived from *tert*-leucine), and **58** (derived from valine) shows that the oxazolidinone ring, and also the diphenylmethylene unit, have the same

[28]) The enantiomeric purity of **1** was determined by HPLC on a chiral column (*Chiralcel OD*). Acid **60** was converted to **61** (CH_2N_2). The enantiomeric purities of **61** and **63** were determined by HPLC (*Chiralcel OD*), that of **62** by optical comparison [20] (see *Exper. Part* for details).

conformation in all three compounds (*Fig. 2,a*). Small differences can be seen of the pyramidalization of the oxazolidinone N-atom and of the orientation of the substituents at C(4) of the oxazolidinone. The i-Pr group (*e.g.*, in **58**) is forced by the neighboring Ph groups to shield the face towards the acyl group in all cases (see also *Fig. 2,b*; superposition of **11**, **55**, and **58**). In contrast, the $PhCH_2$ group in the crystal structure of 4-benzyl-oxazolidin-2-one **29** is directed towards the ring Ph group (aryl/aryl interaction?); thus, the acyl group is not as efficiently shielded, which might be the cause for the slightly lower stereoselectivity obtained in the alkylation of benzyl-oxazolidinone *vs.* isopropyl-oxazolidinone (see *Scheme 4*). There is a hint for a possible interpretation of the appreciably lower selectivity obtained in this reaction with 4-(*tert*-butyl)-oxazolidin-2-one **17**, in the superposition shown in *Fig. 2,a:* the bulky *t*-Bu group induces a stronger pyramidalization of the N-atom, thus reducing the free space on the face opposite to the inducing residue. If this effect would also be present in the enolate of the corresponding *N*-acyl-oxazolidin-2-one, a lower diastereoselectivity should indeed result!

To learn more about the *N*-acyl-oxazolidin-2-ones, we also tried to crystallize their *Lewis*-acid complexes and enolates. Unfortunately, experiments with 5,5-diphenyl-

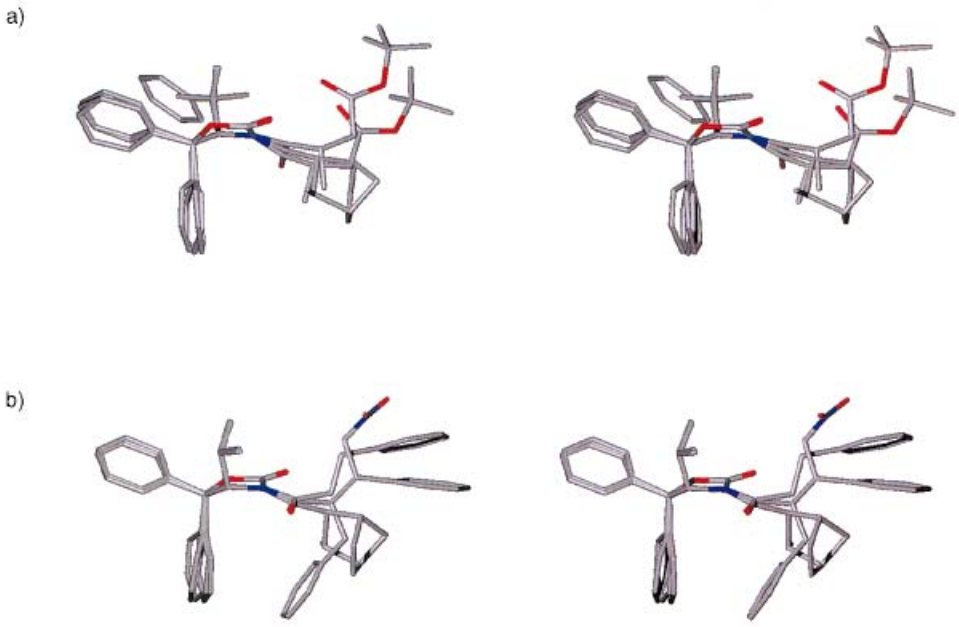


Fig. 2. *Stereo representations of overlays of the oxazolidin-2-one X-ray structures.* The structures were best fitted on the oxazolidinone ring atoms. H-Atoms have been omitted for clarity; O-atoms in red, N-atoms in blue, C-atoms in grey. The figure was generated by *K. Gademann*, using MolMol [42] and POV-Ray. *a*) Superposition of the structures of oxazolidin-2-ones **11** (auxiliary derived from L-valine; the sense of chirality of the structures of **29** and **30** was actually inverted to allow for superposition), **29** (from D-phenylalanine), and **30** (from D-*tert*-leucine). *b*) Superposition of the structures of the oxazolidin-2-ones **11**, **55**, and **58** (auxiliaries all derived from L-valine). It is remarkable that the i-Pr group has exactly the same orientation in all three structures. Obviously, the Ph substituent in *cis*-position forces the i-Pr group to present itself towards the acyl position like a *t*-Bu group!

oxazolidin-2-one derivatives were not successful. However, we were able to determine the crystal structure of the $TiCl_4$/4-benzyl-*N*-propionyloxazolidin-2-one complex (**64**; see *Fig. 3*,*a*). *Fig. 3*,*b* shows a hypothetical $TiCl_4$-enolate of 5,5-diphenyl-oxazolidin-2-one **8**, constructed from the data of the crystal structures of the $TiCl_4$-complex **64** and of the oxazolidinone **11**. It is obvious from the representation in *Fig. 3*,*b*, that one face of the enolate is efficiently shielded by the i-Pr group, but also, that the Ph group *trans* to the i-Pr group has probably no beneficial effect on the induction abilities of the auxiliary.

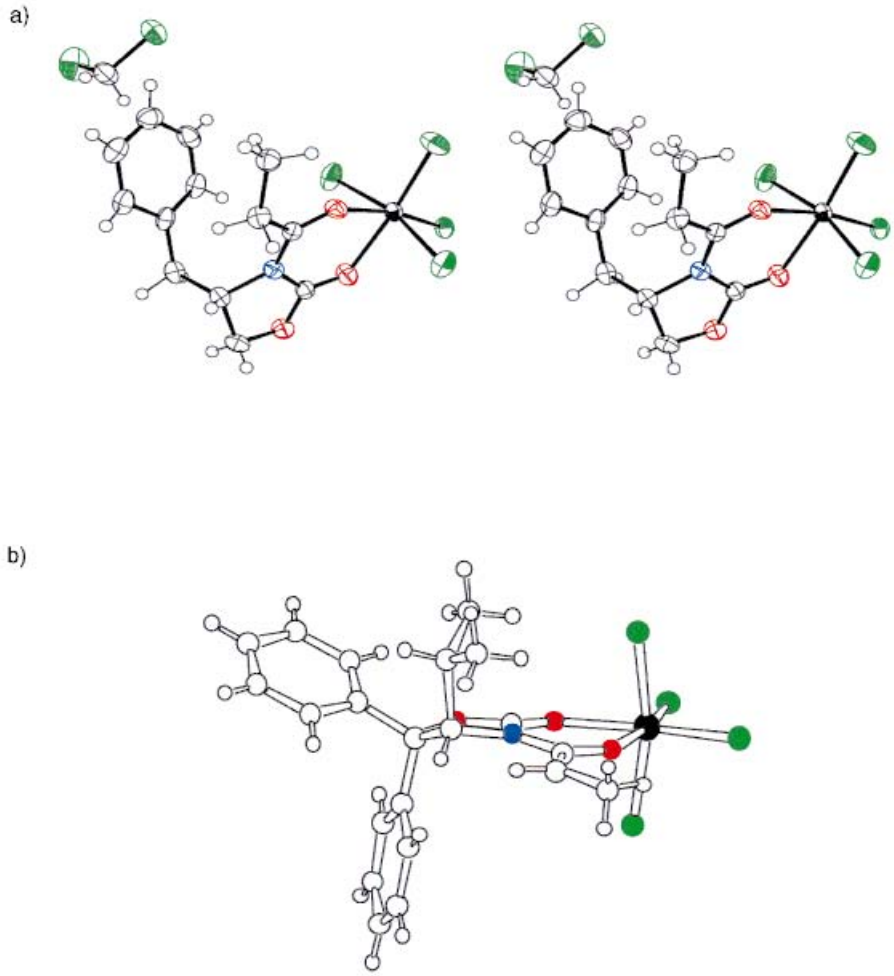


Fig. 3. a) *Stereo ORTEP representation of the X-ray crystal structure of the $TiCl_4$-complex of (*S*)-4-benzyl-3-propionyloxazolidin-2-one* (**64**). One molecule of CH_2Cl_2 is present in the unit cell. O-Atoms in red, N-atoms in blue, Cl-atoms in green, Ti-, C-, and H-atoms in black; the thermal ellipsoids are drawn to the 50% probability level. The structure was determined by Dr. *B. Schweizer*. b) *Hypothetical structure of the $TiCl_4$*-enolate of N-*propionyl-oxazolidin-2-one* **8**. The model was generated from the coordinates of **64** and of oxazolidinone **11**. O-Atoms in red, N-atom in blue, Ti-atom in black, Cl-atoms in green.

10. Conclusions and Discussion. – We have shown herein that the chiral auxiliary **1**, easily accessible from valine esters, is a useful alternative to the widely employed *Evans* oxazolidinones **F**–**I**. Thus, besides some minor drawbacks (higher molecular weight and in some cases slightly lower stereoinduction), oxazolidinone **1** has a number of advantages: *i*) *N*-Acyl-oxazolidin-2-ones of type **C** and **D** (*Scheme 1*) are generally more prone to crystallize than the corresponding derivatives of **F**–**I** (see *Table 1*). This makes purification and separation from diastereoisomeric and other impurities easier. *ii*) Because of the high insolubility of **1** in most organic solvents, recycling of the auxiliary (see **A** in *Scheme 1*) after cleavage can be achieved by simply filtering and washing (see *Chapt. 8*). *iii*) The stereoinduction of **1** in diastereoselective reactions (**C** → **D**) is generally comparable to that of *Evans* oxazolidinones [4][20][28][36]. However, in some cases there may be differences originating from aryl/aryl interactions between auxiliary and reactants (see *Chapt. 6*), which can even render **1** a superior auxiliary. *iv*) Acylation of the auxiliary **1** with BuLi may be performed at elevated temperatures[29]) (0° as compared to −78° for *Evans* oxazolidinones), which is an energetical and apparative advantage, especially in large-scale applications[30]). *v*) BuLi can be used directly for the generation of Li-enolates[29]) (see *Chapt. 4*, *6*, and *7*), while, for *Evans* oxazolidinones, the more expensive LDA is required. *vi*) The *N*-acyl-oxazolidin-2-ones can be cleaved using NaOH without detectable nucleophilic attack on the oxazolidinone ring[29]) (see *Chapt. 8*). For *Evans* oxazolidinones, the more costly system $LiOH/H_2O_2$ must generally be used.

Finally, it is worth mentioning, in view of our work on β- and γ-peptides [21][33], that we have demonstrated the usefulness of oxazolidinone **1** for the preparation of enantiomerically pure β- and γ-amino-acid derivatives (*Chapt. 5* and *7*).

Dr. *W. Pachinger* of *Novartis Pharma AG* is gratefully acknowledged for the preparation and donation of a large quantity of **1**. We thank *K. Gademann* for his help in arranging the superpositions in *Fig. 2*. *A. Häne* and *M. Frei* have carried out some of the experiments described herein, as a part of the requirements for the advanced laboratory course in organic chemistry. We thank Dr. *B. Schweizer* for the determination of the X-ray crystal structures. We thank *Novartis Pharma AG*, Basel, for continuing support.

Experimental Part

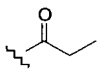
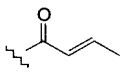
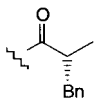
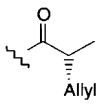
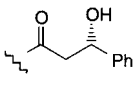
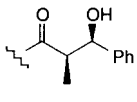
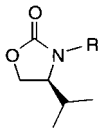
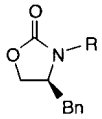
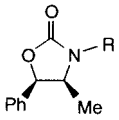
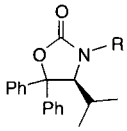
1. *General*. Abbreviations: BnOH: benzyl alcohol, Cbz: benzyloxycarbonyl, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, h.v. (high vacuum, 0.01–0.1 Torr), LDA: lithium diisopropylamide. BuLi was used as a *ca*. 1.6M soln. (hexane), $ClAlMe_2$ as 1M soln. (hexane), and Bu_2BOTf as 1M soln. (CH_2Cl_2). THF was freshly distilled over K under Ar before use. DIPA, Et_3N, BnOH, and CH_2Cl_2 (for aldol reactions) were distilled over CaH_2 and stored over 4-Å molecular sieves. Aldehydes were freshly distilled. Solvents for FC and workup procedures were distilled over *Sikkon* (anh. $CaSO_4$; *Fluka*). LiBr, LiCl, and $ZnBr_2$ were dried under h.v. at 150° overnight. BnBr, allyl bromide, MeI, and *tert*-butyl bromoacetate were filtered through basic Al_2O_3 (activity I) directly prior to use. 3-(Phthaloylamino)propanoyl chloride, (*R*)-3-(benzyloxy)butanoyl chloride, 4-methylpentanoyl chloride, and 3-[4-(benzyloxy)phenyl]propanoyl chloride were prepared from the corresponding carboxylic acids by treatment with oxalyl chloride [47]. (*R*)-3-(Benzyloxy)butanoic acid [47] and 3-[4-(benzyloxy)phenyl]propanoic acid [48] were prepared according to, 3-[(1-Cbz)indol-3-yl]propanoic acid [23] in

---

[29]) It is tempting to compare the acyl derivatives of **1** with compounds containing what we have once called sterically protected but electronically effective C=O groups [43–46]: the enolates of such compounds have been shown to be generated with BuLi [44] and their enoyl moieties to undergo *Michael* additions with RMgX and RLi reactants (without intervention of Cu^I additives) [45]; also, such compounds can be used for the reactivity *umpolung* of C-atoms in α-positions with respest to N- and O-atoms [46].

[30]) Preparation of **1** in multi-kg scale has been achieved without encountering problems.

Table 1. *Comparison of the Melting Points of Derivatives of* Evans *Oxazolidinones* **F**, **G**, **I**, *and of the Geminally Diphenyl-Substituted Auxiliary* **1**. As yet, there are no corresponding data available for 5,5-dimethyl-oxazolidin-2-ones [7]. n.k. = not known.

R	H						
	71 – 72 [4]	liquid [39]	56 – 56.5 [36]	liquid [20]	liquid [20]	65 – 66 [28]	94 [28]
	87 – 88.5 [5]	41 [40]	85 – 86 [36]	92 [40]	n.k.	n.k.	n.k.
	120 – 121 [4]	99 – 100 [41]	66 – 66.5 [36]	liquid [20]	69 – 70 [20]	n.k.	n.k.
	250 – 252	111 – 112	135 – 136	131 – 132	110 – 111	146 – 148	163 – 164

analogy to known procedures. All other reagents were used as received from *Fluka* or *Aldrich*. TLC: *Merck* silica gel *60* F_{254} plates; detection with UV or dipping into a soln. of $KMnO_4$ (1.5 g in 333 ml 1M NaOH) or a soln. of anisaldehyde (9.2 ml), AcOH (3.75 ml), conc. H_2SO_4 (12.5 ml), and EtOH (338 ml), followed by heating. FC: *Fluka* silica gel *60* (40 – 63 μm); at *ca.* 0.3 bar. Anal. HPLC: *Knauer* HPLC system (pump type *64*, *EuroChrom 2000* integration package, degaser, UV detector (variable-wavelength monitor)); *Chiralcel OD* (*Daicel Chemical Industries, Ltd.*; 4.6 × 250 mm, 10 μm). M.p.: *Büchi-510* apparatus; uncorrected. Optical rotations: *Perkin-Elmer 241* polarimeter (10 cm, 1 ml cell) at r.t. IR Spectra: *Perkin-Elmer-782* spectrophotometer. NMR Spectra: *Bruker AMX 500* (^{1}H: 500 MHz, ^{13}C: 125 MHz), *AMX 400* (^{1}H: 400 MHz, ^{13}C: 100 MHz), *Varian Gemini 300* (^{1}H: 300 MHz, ^{13}C: 75 MHz), or *Gemini 200* (^{1}H: 200 MHz, ^{13}C: 50 MHz); chemical shifts (δ) in ppm downfield from Me_4Si (= 0 ppm); *J* values in Hz. MS: *VG Tribrid* (EI) or *FG ZAB-2 SEQ* (FAB; in a 3-nitrobenzyl-alcohol matrix) spectrometer; in *m/z* (% of basis peak). Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH-Zürich.

2. *Preparation of 2-Amino-1,1-diphenyl Alcohols. General Procedure 1* (*GP 1*). The appropriate amino-acid ester salt (1 equiv.) was suspended in Et_2O (5 ml/mmol) and extracted with 1M NaOH soln. (1.5 equiv.). The aq. phase was separated and extracted with Et_2O, the org. phases were dried ($MgSO_4$) and evaporated. A soln. of the resulting amino-acid ester in Et_2O (2M) was added to a soln. of PhMgBr (3 – 4 equiv.; freshly prepared from Mg and PhBr) in Et_2O (1.2M) over a period of 30 min. After addition to the *Grignard* reagent, the mixture was refluxed for 7 – 9 h. Excess PhMgBr and Mg salts were hydrolyzed by careful addition of ice and H_2O. Individual workup yielded the amino alcohols.

3. *Preparation of 5,5-Diphenyl-oxazolidin-2-ones. General Procedure 2* (*GP 2*). To a soln. of the amino alcohol (1 equiv.) and Et_3N (1.1 equiv.) in CH_2Cl_2 (0.2M), $ClCO_2Et$ (1 equiv). was added at *ca.* −25° (dry ice/acetone bath). The mixture was allowed to warm slowly to r.t., stirred overnight, diluted with CH_2Cl_2, and washed with 1M HCl soln. The org. phase was evaporated, the residue suspended in 5 wt.-% NaOH in MeOH (0.23M), refluxed for 9 h, diluted with H_2O, and cooled to 4°. The suspension was filtered, the residue washed with H_2O, Et_2O (*ca.* 1 ml/mmol), and pentane. The resulting white powder was dried (h.v.) and used without further purification.

4. *Acylation of the Auxiliary with Acyl Chlorides. General Procedure 3* (*GP 3*). To a suspension of the auxiliary (1 equiv.) in THF (0.25M), BuLi (1.00–1.05 equiv.) was slowly added at 0° (ice bath). To the resulting clear soln., the acyl chloride (1.2 equiv.) was added in one portion. The mixture was allowed to warm slowly to r.t. overnight, treated with sat. NH_4Cl soln., and diluted with Et_2O. The org. phase was washed with 1M HCl (2×), 1M NaOH (2×) and sat. NaCl solns., dried ($MgSO_4$), and evaporated. The resulting crude product was purified by FC or recrystallization.

5. *Acylation of the Auxiliary with Mixed Anhydrides* [16]. *General Procedure 4* (*GP 4*). To a soln. of the appropriate acid (1.05 equiv.) in THF (0.2M), Et_3N (2.6 equiv.) and pivaloyl chloride (1.05 equiv.) were added at *ca.* −30°. The resulting white suspension was stirred at this temp. for 1–2 h, LiCl (1.15 equiv.) and the auxiliary (1 equiv.) were added, and the mixture was allowed to warm slowly to r.t. overnight. The mixture was treated with sat. NH_4Cl soln. and diluted with Et_2O. Workup according to *GP 4*.

6. *Alkylation of* N-*Acyl-oxazolidin-2-ones Using LDA/ZnBr*$_2$ [19]. *General Procedure 5* (*GP 5*). To a soln. of *N*-acyl-oxazolidin-2-one (1 equiv.) in THF (0.2–0.3M), a precooled soln. of LDA (1.25 equiv.) was added at −78° (LDA soln. was freshly prepared by treating a soln. of DIPA (1 equiv.) in THF (0.5M) with BuLi (1 equiv.) at *ca.* −40° for 30 min). After stirring for 30 min at −78°, a soln. of $ZnBr_2$ (1.25 equiv.) in THF (0.5M) was added. The resulting Zn-enolate was stirred for additional 30 min at −78° and then treated with the electrophile. The mixture was allowed to warm to −15°, stirred at this temp. for 24 h, treated with sat. NH_4Cl soln., and diluted with Et_2O. Workup according to *GP 4*.

7. *Alkylation of* N-*Acyl-oxazolidin-2-ones Using BuLi. General Procedure 6* (*GP 6*). To a soln. of *N*-acyl-oxazolidin-2-one (1 equiv.) in THF (0.2M), BuLi (1.1 equiv.) was added at −78°. After stirring for 30 min at −78°, the clear soln. was treated with the electrophile. The mixture was stirred at −78° for 20 h, treated with sat. NH_4Cl soln., and diluted with Et_2O. Workup according to *GP 4*.

8. *Amidoalkylation of* N-*Acyl-oxazolidin-2-ones. General Procedure 7* (*GP 7*). To a soln. of the *N*-acyl-oxazolidin-2-one (1 equiv.) in CH_2Cl_2 (0.2M), $TiCl_4$ (1.00–1.05 equiv.) was added at −20°. To the yellow soln., Et_3N or $EtN(i\text{-}Pr)_2$ (1.00–1.10 equiv.) was added and the resulting dark red soln. stirred at *ca.* −20° for 30 min before addition of a soln. of the electrophile (1.1 equiv.) in CH_2Cl_2 (0.5M) and $TiCl_4$ (1.1 equiv.). The mixture was stirred at 0° (ice-bath) for 2–3 h, treated with sat. NH_4Cl soln., and diluted with CH_2Cl_2 or Et_2O. The org. phase was washed with 1M HCl (2×), 1M NaOH, and sat. NaCl solns., dried ($MgSO_4$), and evaporated. The resulting crude product was purified by FC and, if required, recrystallization.

9. *Aldol Reaction* via *Li-Enolate* [28]. *General Procedure 8* (*GP 8*). To a soln. of the *N*-acyl-oxazolidin-2-one (1 equiv.) in THF (0.2M), BuLi (1.1 equiv.) was added at −78°. The soln. was stirred for 30 min, the aldehyde (1.1 equiv.) quickly added, and the reaction stopped after 30 s by treatment with sat NH_4Cl soln. Workup according to *GP 7*.

10. *Aldol Reaction* via *B-Enolate* [4]. *General Procedure 9* (*GP 9*). To a soln. of the *N*-acyl-oxazolidin-2-one (1 equiv.) in CH_2Cl_2 (0.4M), Bu_2BOTf (1.2 equiv.) and $EtN(i\text{-}Pr)_2$ (1.3 equiv.) was added at 0° (ice-bath). The soln. was cooled to −78° and the aldehyde (1.1 equiv.) added. The mixture was stirred at −78° for 20 min, then at 0° for 1 h, treated with phosphate buffer (pH 7, 1 ml/mmol), MeOH (3 ml/mmol), and H_2O_2/MeOH 1:2 (3 ml/mmol), and stirred at r.t. for 1 h. Et_2O was added, the org. phase washed with 0.5M HCl, sat. $NaHCO_3$, and sat. NaCl solns., dried ($MgSO_4$), and evaporated. The crude product was purified by FC.

11. *Alkylation of* N-*Acyl-oxazolidin-2-ones with ω-Nitrostyrenes. General Procedure 10* (*GP 10*). To a soln. of the *N*-acyl-oxazolidin-2-one (1 equiv.) in THF (0.2M), BuLi (1.05 equiv.) was added at −78°. The enolate was stirred for 30 min at −78°, a precooled soln. of the ω-nitrostyrene (1.1 equiv.) in THF (0.5M) added, the mixture stirred at −78° for further 2 h, then treated with sat. NH_4Cl soln., and diluted with Et_2O. The org. phase was washed with 0.5M HCl, 1M NaOH, and sat. NaCl solns., dried ($MgSO_4$), and evaporated. The crude product was purified by FC.

12. *Cbz-Deprotection/Boc-Protection of Amidoalkylation Products. General Procedure 11* (*GP 11*). To a soln. of the Cbz-protected compound (1 equiv.) and Boc_2O (1 equiv.) in THF (0.1–0.2M), Pd/C (10 wt.-%) was added. The apparatus was evacuated and flushed three times with H_2 and the mixture stirred at r.t. for 2 h under H_2 (ballon). Filtration through *Celite* and concentration under reduced pressure yielded the crude Boc-protected compound, which was purified by FC.

*(*S*)-4-(1-Methylethyl)-5,5-diphenyloxazolidin-2-one* ((*S*)-**1**). L-Valine methyl ester hydrochloride (16.8 g, 100 mmol) was treated with PhMgBr (300 mmol) according to *GP 1*. After hydrolysis, 1M HCl was added to the mixture to generate a homogenous suspension. AcOEt (500 ml) was added, and the pH adjusted to 11 with conc. aq. NH_3 soln. The org. layer was separated and the aq. phase extracted with AcOEt. The combined org. phases were dried (Na_2SO_4; *ca.* 20 ml of MeOH were added to prevent precipitation of the amino alcohol) and evaporated. Recrystallization (EtOH) gave *(S)-2-amino-3-methyl-1,1-diphenylbutanol* ((*S*)-**2**; 7.8 g). From the

mother liquor, further **2** (4.6 g) was obtained. Total yield: 12.3 g (48%). White needles. According to *GP 2*, (*S*)-**2** (10.4 g, 41 mmol), Et_3N (6.56 ml, 45 mmol), and $ClCO_2Et$ (4.10 ml, 43 mmol) were transformed to (*S*)-**1** (10.5 g, 91%). The enantiomer ratio was determined by anal. HPLC (hexane/i-PrOH 90 : 10; flow 1 ml/min, detection at 254 nm; (*S*)-**1**; t_R 8 min, (*R*)-**1**: t_R 24 min), to be > 99 : 1. White powder. M.p. 250–252°. $[\alpha]_D^{rt.} = -259.4$ ($c = 0.32$, $CHCl_3$). IR ($CHCl_3$): 3458*w*, 2967*w*, 1757*s*, 1495*w*, 1450*w*, 1003*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.69 (*d*, $J = 6.3$, Me); 0.90 (*d*, $J = 6.9$, Me); 1.80–1.95 (*m*, Me_2CH); 4.36 (*d*, $J = 3.6$, NCH); 6.44 (*s*, NH); 7.22–7.43 (*m*, 8 arom. H); 7.53–7.56 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.6, 20.8 (Me); 29.6, 65.8 (CH); 89.4 (C); 125.7, 126.3, 127.7, 128.1, 128.2, 128.5 (CH); 139.2, 143.9, 158.7 (C). EI-MS: 281 (6, M^+), 238 (4), 194 (21), 183 (100), 165 (16).

*(*S*)-4-Benzyl-5,5-diphenyloxazolidin-2-one* ((*S*)-**5**). L-Phenylalanine ethyl ester hydrochloride (23.0 g, 100 mmol) was treated with PhMgBr (300 mmol) according to *GP 1*. After hydrolysis, 1M HCl was added to the mixture to generate a homogenous suspension, and the pH adjusted to 11 with conc. aq. NH_3 soln. Et_2O (250 ml) was added, the org. layer was separated and the aq. phase extracted with Et_2O. The combined org. phases were washed with H_2O, dried (Na_2SO_4; *ca.* 20 ml of MeOH were added to prevent precipitation of the amino alcohol), and evaporated. The resulting yellow solid was triturated (toluene, 50 ml) to yield *(*S*)-2-amino-1,1,3-triphenylpropan-1-ol* ((*S*)-**3**; 11.4 g). From the residue of the mother liquor, further **3** (3.7 g) was obtained by trituration. Total yield: 15.2 g (50%). White powder. According to *GP 2*, (*S*)-**3** (12.1 g, 40 mmol), Et_3N (6.40 ml, 44 mmol), and $ClCO_2Et$ (4.00 ml, 42 mmol) were transformed to yield after trituration ($CHCl_3$, 40 ml) (*S*)-**5** (11.4 g, 86%). The enantiomer ratio was determined by anal. HPLC (hexane/i-PrOH 93 : 7; flow 1 ml/min, detection at 254 nm; (*S*)-**5**: t_R 18 min, (*R*)-**5**: t_R 37 min) to be > 99 : 1. White powder. M.p. 255–257°. $[\alpha]_D^{rt.} = -281.5$ ($c = 0.63$, $CHCl_3$). IR ($CHCl_3$): 3442*w*, 3008*w*, 1763*s*, 1495*w*, 1449*w*, 1000*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.19 (*dd*, $J = 13.7, 11.5$, 1 H, PhCH_2); 2.61 (*dd*, $J = 13.8, 3.0$, 1 H, PhCH_2); 4.68 (*dd*, $J = 11.4, 2.4$, NCH); 4.93 (*s*, NH); 7.10–7.16 (*m*, 2 arom. H); 7.20–7.48 (*m*, 11 arom. H); 7.53–7.60 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 39.9 (CH_2); 61.9 (CH); 89.1 (C); 126.4, 126.6, 127.5, 128.3, 128.6, 128.8, 128.9, 129.2, 129.4 (CH); 137.1, 139.5, 142.6, 157.5 (C). FAB-MS: 659 (49, $[2M + H]^+$), 330 (100, $[M + H]^+$).

*(*R*)-4-(*tert*-Butyl)-5,5-diphenyloxazolidin-2-one* ((*R*)-**6**). D-*tert*-Leucine methyl ester hydrochloride (1.36 g, 7.5 mmol) was treated with PhMgBr (30 mmol) according to *GP 1*. After hydrolysis, 1M HCl was added to the mixture to generate a homogenous suspension. AcOEt was added, and the pH adjusted to 11 with conc. aq. NH_3 soln. The org. layer was separated and the aq. phase extracted with AcOEt (2×). The combined org. phases were dried ($MgSO_4$) and evaporated. The resulting crude *(*R*)-2-amino-3,3-dimethyl-1,1-diphenylbutan-1-ol* ((*R*)-**4**; 2.04 g, 101%) was used without further purification. According to *GP2*, (*R*)-**4** (1.34 g, 5 mmol), Et_3N (8.80 ml, 5.5 mmol), and $ClCO_2Et$ (0.50 ml, 5 mmol) were transformed to (*R*)-**6** (974 mg, 66%). White powder. M.p. 290° (dec.). $[\alpha]_D^{rt.} = +336.5$ ($c = 0.36$, $CHCl_3$). IR ($CHCl_3$): 3467*w*, 2968*w*, 1758*s*, 1450*w*, 1002*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.80 (*s*, *t*-Bu); 4.24 (*s*, NCH); 6.27 (*s*, NH); 7.22–7.63 (*m*, arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.8 (Me); 35.5 (C); 69.1 (CH); 90.1 (C); 126.9, 127.9, 128.1, 128.3, 128.4, 128.7 (CH); 138.7, 145.1, 158.5 (C). EI-MS: 295 (3, M^+), 251 (2), 195 (98), 183 (100), 165 (37).

*(*S*)-3-Acetyl-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* ((*S*)-**7**). Compound (*S*)-**1** (8.44 g, 30 mmol) was treated with BuLi (19.8 ml, 31.5 mmol) and AcCl (2.56 ml, 36 mmol) according to *GP 3*. Recrystallization (pentane/Et_2O) yielded (*S*)-**7** (5.74 g). From the mother liquor, further **7** (3.07 g) was obtained. Total yield: 8.81 g (91%). White needles. M.p. 121–122°. $[\alpha]_D^{rt.} = -252.5$ ($c = 1.33$, $CHCl_3$). IR ($CHCl_3$): 2972*m*, 1779*s*, 1699*s*, 1494*m*, 1459*m*, 1369*m*, 1317*m*, 1177*m*, 1051*m*, 993*m*, 922*m*, 637*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.76 (*d*, $J = 6.8$, Me); 0.88 (*d*, $J = 7.0$, Me); 1.92–2.03 (*m*, CH); 2.43 (*s*, C(O)Me); 5.37 (*d*, $J = 3.4$, NCH); 7.26–7.49 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 21.7, 23.5 (Me); 29.9, 64.4 (CH); 89.4 (C); 125.6, 126.0, 128.0, 128.4, 128.6, 128.9 (CH); 138.2, 142.3, 153.2, 170.1 (C). FAB-MS: 647 (6, $[2M + H]^+$), 324 (100, $[M + H]^+$), 280 (58). Anal. calc. for $C_{20}H_{21}NO_3$ (323.39): C 74.28, H 6.54, N 4.33; found: C 74.28, H 6.77, N 4.36.

*(*S*)-4-(1-Methylethyl)-3-(1-oxopropyl)-5,5-diphenyloxazolidin-2-one* ((*S*)-**8**). Compound (*S*)-**1** (7.03 g, 25 mmol) was treated with BuLi (16.7 ml, 26 mmol) and propanoyl chloride (2.63 ml, 30 mmol) according to *GP 3*. Recrystallization (pentane/Et_2O) yielded (*S*)-**8** (6.27 g). From the mother liquor, further **8** (1.50 g) was obtained. Total yield: 7.77 g (92%). White needles. M.p. 111–112°. $[\alpha]_D^{rt.} = -239.7$ ($c = 0.74$, $CHCl_3$). IR ($CHCl_3$): 2976*w*, 1781*s*, 1706*m*, 1450*m*, 1369*m*, 1319*m*, 1177*m*, 1050*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.74 (*d*, $J = 6.8$, Me); 0.88 (*d*, $J = 7.0$, Me); 1.08 (*t*, $J = 7.4$, $MeCH_2$); 1.92–2.09 (*m*, CH); 2.68–2.78 (*m*, 1 H, CH_2); 2.88–2.98 (*m*, 1 H, CH_2); 5.38 (*d*, $J = 3.4$, NCH); 7.25–7.49 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 8.6, 16.4, 21.8 (Me); 28.9 (CH_2); 29.9, 64.4 (CH); 89.4 (C); 125.6, 125.9, 127.9, 128.4, 128.6, 128.9 (CH); 138.3, 142.4, 153.1, 174.0 (C). EI-MS: 338 (< 1, $[M + H]^+$), 294 (11), 238 (20), 220 (30), 194 (31), 183 (100). Anal. calc. for $C_{21}H_{23}NO_3$ (337.42): C 74.75, H 6.87, N 4.15; found: C 74.70, H 6.87, N 4.13.

(S)-4-(1-Methylethyl)-3-(3-methyl-1-oxobutyl)-5,5-diphenyloxazolidin-2-one ((*S*)-**9**). Compound (*S*)-**1** (8.44 g, 30 mmol) was treated with BuLi (18.9 ml, 30 mmol) and 3-methylbutanoyl chloride (4.43 ml, 36 mmol) according to *GP 3*. Recrystallization (AcOEt/hexane) yielded (*S*)-**9** (8.53 g). From the mother liquor further **9** (0.99 g) was obtained. Total yield: 9.52 g (87%). White needles. M.p. 118–119°. $[\alpha]_D^{r.t.} = -205.5$ ($c = 0.56$, $CHCl_3$). IR ($CHCl_3$): 2966*m*, 1781*s*, 1699*m*, 1450*m*, 1371*m*, 1318*m*, 1177*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.76 (*d*, *J* = 6.8, Me); 0.81 (*d*, *J* = 6.7, Me); 0.87 (*d*, *J* = 6.8, Me); 0.88 (*d*, *J* = 7.5, Me); 1.92–2.09 (*m*, 2 Me_2CH); 2.65–2.75 (*m*, CH_2); 5.37 (*d*, *J* = 3.4, NCH); 7.25–7.49 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 21.8, 22.2, 22.3 (Me); 25.4, 29.8 (CH); 43.6 (CH_2); 64.6 (CH); 89.3 (C); 125.6, 125.9, 127.9, 128.4, 128.6, 128.9 (CH); 138.2, 142.4, 153.1, 172.5 (C). FAB-MS: 731 (4, $[2M+H]^+$), 366 (100, $[M+H]^+$), 322 (31). Anal. calc. for $C_{23}H_{27}NO_3$ (365.47): C 75.59, H 7.45, N 3.83; found: C 75.58, H 7.45, N 3.92.

(S)-4-(1-Methylethyl)-3-(4-methyl-1-oxopentyl)-5,5-diphenyloxazolidin-2-one ((*S*)-**10**). Compound (*S*)-**1** (7.03 g, 25 mmol) was treated with BuLi (15.0 ml, 25 mmol) and 4-methylpentanoyl chloride (4.04 g, 30 mmol) according to *GP 3*. FC (pentane/Et_2O 9:1) yielded (*S*)-**10** (7.50 g, 79%). Colorless oil. $[\alpha]_D^{r.t.} = -202.8$ ($c = 1.60$, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2962*m*, 2873*w*, 1781*s*, 1699*s*, 1450*m*, 1366*s*, 1320*m*, 1177*s*, 1051*m*, 1001*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.76 (*d*, *J* = 6.8, Me); 0.82 (*d*, *J* = 6.3, Me); 0.84 (*d*, *J* = 6.4, Me); 0.88 (*d*, *J* = 7.0, Me); 1.35–1.50 (*m*, 3 H, Me_2CHCH_2); 1.91–2.03 (*m*, Me_2CH); 2.70–2.78 (*m*, 1 H, $C(O)CH_2$); 2.83–2.92 (*m*, 1 H, $C(O)CH_2$); 5.37 (*d*, *J* = 3.4, NCH); 7.25–7.49 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 21.8, 22.2 (Me); 27.6, 29.9 (CH); 33.3, 33.4 (CH_2); 64.5 (CH); 89.3 (C); 125.6, 125.9, 127.9, 128.4, 128.6, 128.9 (CH); 138.2, 142.4, 153.1, 173.5 (C). FAB-MS: 380 (100, $[M+H]^+$), 336 (39). Anal. calc. for $C_{24}H_{29}NO_3$ (379.50): C 75.96, H 7.70, N 3.69; found: C 75.92, H 7.73, N 3.70.

(S)-4-(1-Methylethyl)-5,5-diphenyl-3-(1-oxo-3-phenylpropyl)oxazolidin-2-one ((*S*)-**11**). Compound (*S*)-**1** (14.1 g, 50 mmol) was treated with BuLi (33 ml, 52.5 mmol) and 3-phenylpropanoyl chloride (8.93 ml, 60 mmol) according to *GP 3*. Recrystallization (pentane/Et_2O) yielded (*S*)-**11** (17.4 g, 92%). White needles. M.p. 97–98°. $[\alpha]_D^{r.t.} = -179.0$ ($c = 1.14$, $CHCl_3$). IR ($CHCl_3$): 2969*w*, 1781*s*, 1701*m*, 1496*w*, 1450*m*, 1366*m*, 1320*m*, 1176*m*, 1052*w*, 991*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.73 (*d*, *J* = 6.8, Me); 0.84 (*d*, *J* = 7.0, Me); 1.90–2.01 (*m*, Me_2CH); 2.82–2.97 (*m*, $C(O)CH_2$); 3.02–3.10 (*m*, 1 H, $PhCH_2$); 3.20–3.28 (*m*, 1 H, $PhCH_2$); 5.37 (*d*, *J* = 3.4, NCH); 7.12–7.47 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 21.7 (Me); 29.9 (CH); 30.5, 36.7 (CH_2); 64.5 (CH); 89.4 (C); 125.6, 125.9, 126.2, 128.0, 128.4, 128.4, 128.6, 128.9 (CH); 138.2, 140.3, 142.3, 153.0, 172.2 (C). FAB-MS: 827 (8, $[2M+H]^+$), 414 (100, $[M+H]^+$), 370 (34). Anal. calc. for $C_{27}H_{27}NO_3$ (413.52): C 78.42, H 6.58, N 3.39; found: C 78.56, H 6.73, N 3.38.

(S)-4-(1-Methylethyl)-3-[(E)-2-oxobut-2-enyl]-5,5-diphenyloxazolidin-2-one ((*S*)-**12**). Compound (*S*)-**1** (5.63 g, 20 mmol) was treated with BuLi (12.6 ml, 20 mmol) and (*E*)-but-2-enoylchloride (2.32 ml, 24 mmol) according to *GP 3*. Recrystallization (AcOEt/hexane) yielded (*S*)-**12** (4.32 g). From the mother liquor, further **12** (1.35 g) was obtained. Total yield: 5.67 g (81%). White solid. M.p. 135–136°. $[\alpha]_D^{r.t.} = -239.4$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 2969*m*, 1777*s*, 1685*m*, 1638*m*, 1450*m*, 1343*s*, 1177*s*, 1036*m*, 970*m*, 920*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.77 (*d*, *J* = 6.8, Me); 0.89 (*d*, *J* = 7.0, Me); 1.90 (*dd*, *J* = 6.5, 1.2, Me); 1.95–2.08 (*m*, Me_2CH); 5.46 (*d*, *J* = 3.4, NCH); 7.07–7.51 (*m*, 10 arom. H, 2 CH=). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 18.4, 21.7 (Me); 30.1, 64.3 (CH); 89.2 (C); 121.6, 125.7, 126.0, 127.9, 128.3, 128.5, 128.8 (CH); 138.3, 142.3 (C); 147.0 (CH); 153.0, 164.8 (C). FAB-MS: 699 (2, $[2M+H]^+$), 350 (100, $[M+H]^+$), 306 (31). Anal. calc. for $C_{22}H_{23}NO_3$ (349.43): C 75.62; H 6.63, N 4.01; found: C 75.33, H 6.84, N 4.03.

(S)-4-(1-Methylethyl)-3-[(E)-1-oxo-3-phenylprop-2-enyl]-5,5-diphenyloxazolidin-2-one ((*S*)-**13**). Compound (*S*)-**1** (7.03 g, 25 mmol) was treated with BuLi (16.5 ml, 26.3 mmol) and (*E*)-3-phenylprop-2-enoyl chloride (5.00 g, 30 mmol) according to *GP 3*. FC (pentane/Et_2O 6:1) yielded (*S*)-**13** (4.21 g, 41%). White solid. M.p. 160.5–161.5°. $[\alpha]_D^{r.t.} = -132.5$ ($c = 1.44$, $CHCl_3$). IR ($CHCl_3$): 3061*w*, 3032*w*, 2972*w*, 1775*s*, 1678*s*, 1617*s*, 1495*m*, 1450*m*, 1344*s*, 1177*s*, 1032*m*, 990*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.81 (*d*, *J* = 6.8, Me); 0.93 (*d*, *J* = 7.0, Me); 1.97–2.08 (*m*, Me_2CH); 5.54 (*d*, *J* = 3.4, NCH); 7.21–7.60 (*m*, arom. H); $\nu_A = 7.87$, $\nu_B = 7.80$ (*AB*, *J* = 15.7, 2 CH=). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 21.8 (Me); 30.2, 64.5 (CH); 89.4 (C); 116.8, 125.7, 126.0, 128.0, 128.4, 128.6, 128.6, 128.8, 128.9, 130.6 (CH); 134.6, 138.3, 142.3, 146.6, 153.1, 165.1 (C). FAB-MS: 412 (100, $[M+H]^+$), 368 (17). Anal. calc. for $C_{27}H_{25}NO_3$ (411.50): C 78.81, H 6.12, N 3.40; found: C 78.70, H 6.35, N 3.39.

(S)-3-[4-(Methoxycarbonyl)-1-oxobutyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one ((*S*)-**14**). Compound (*S*)-**1** (2.81 g, 10 mmol) was treated with BuLi (6.7 ml, 10.5 mmol) and monomethylglutaryl chloride (1.98 g, 12 mmol) according to *GP 3*. FC (pentane/Et_2O 3:1 → 2:1) yielded (*S*)-**14** (3.47 g, 85%). Colorless oil. $[\alpha]_D^{r.t.} = -195.9$ ($c = 0.57$, $CHCl_3$). IR ($CHCl_3$): 2966*m*, 1781*s*, 1732*m*, 1708*m*, 1450*m*, 1366*m*, 1319*m*, 1177*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.76 (*d*, *J* = 6.8, Me); 0.87 (*d*, *J* = 7.0, Me); 1.83–2.03 (*m*, 3 H, Me_2CH, CH_2); 2.29 (*t*, *J* = 7.5, $C(O)CH_2$); 2.73–2.82 (*m*, 1 H, $C(O)CH_2$); 2.90–3.00 (*m*, 1 H, $C(O)CH_2$); 3.63 (*s*, MeO); 5.37

(*d*, *J* = 3.4, NCH); 7.25–7.40 (*m*, 8 arom. H); 7.44–7.48 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4 (Me); 19.7 (CH_2); 21.8 (Me); 29.9 (CH); 32.9, 34.3 (CH_2); 51.5 (Me); 64.5 (CH); 89.5 (C); 125.6, 125.9, 128.0, 128.4, 128.6, 128.9 (CH); 138.1, 142.3, 153.0, 172.3, 173.3 (C). FAB-MS: 410 (60, $[M+H]^+$), 366 (15), 334 (17), 238 (100). Anal. calc. for $C_{24}H_{27}NO_5$ (409.48): C 70.40, H 6.65, N 3.42; found: C 70.56, H 6.67, N 3.38.

*(*S*)-4-(1-Methylethyl)-3-(1-oxo-3-phthalimidopropyl)-5,5-diphenyloxazolidin-2-one* ((*S*)-**15**). Compound (*S*)-**1** (4.22 g, 15 mmol) was treated with BuLi (9.5 ml, 15 mmol) and 3-(phthalimido)propanoyl chloride (4.27 g, 18 mmol) according to *GP 3*. Recrystallization (AcOEt) yielded (*S*)-**15** (3.76 g). From the mother liquor, further **15** (2.67 g) was obtained. Total yield: 6.43 g (89%). White solid. M.p. 181–182°. $[\alpha]_D^{rt} = -132.6$ (*c* = 0.81, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 1781*s*, 1717*s*, 1450*m*, 1381*s*, 1178*m*, 1114*w*, 1002*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.76 (*d*, *J* = 6.8, Me); 0.88 (*d*, *J* = 7.0, Me); 1.92–2.03 (*m*, Me_2CH); 3.07–3.17 (*m*, 1 H, C(O)CH_2); 3.30–3.42 (*m*, 1 H, C(O)CH_2); 3.95–4.06 (*m*, CH_2N); 5.37 (*d*, *J* = 3.2, NCH); 7.25–7.42 (*m*, 8 arom. H); 7.44–7.47 (*m*, 2 arom. H); 7.68–7.73 (*m*, 2 arom. H); 7.80–7.85 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 21.7 (Me); 30.0 (CH); 33.2, 33.9 (CH_2); 64.6 (CH); 89.7 (C); 123.3, 125.5, 125.9, 128.0, 128.4, 128.7, 129.0 (CH); 132.1 (C); 134.0 (CH); 138.1, 142.1, 152.9, 168.0, 170.2 (C). FAB-MS: 483 (70, $[M+H]^+$), 238 (69), 202 (96), 160 (100). Anal. calc. for $C_{29}H_{26}N_2O_5$ (482.54): C 72.19, H 5.43, N 5.81; found: C 72.13, H 5.33, N 5.72.

*(*S*)-3-[3-[4-(Benzyloxy)phenyl]-1-oxopropyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* ((*S*)-**16**). Compound (*S*)-**1** (7.03 g, 25 mmol) was treated with BuLi (15.7 ml, 25 mmol) and 3-[4-(benzyloxy)phenyl]-propanoyl chloride (4.43 ml, 30 mmol) according to *GP 3*. FC (pentane/Et_2O 3:1 → 1:1) yielded (*S*)-**16** (12.4 g, 96%). Colorless oil. $[\alpha]_D^{rt} = -145.0$ (*c* = 0.73, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2973*w*, 1780*s*, 1702*m*, 1511*s*, 1450*m*, 1373*m*, 1319*m*, 1180*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.72 (*d*, *J* = 6.8, Me); 0.84 (*d*, *J* = 7.0, Me); 1.90–2.01 (*m*, Me_2CH); 2.76–2.90 (*m*, $PhCH_2$); 2.99–3.07 (*m*, 1 H, C(O)CH_2); 3.16–3.24 (*m*, 1 H, C(O)CH_2); 5.02 (*s*, CH_2O); 5.36 (*d*, *J* = 3.4, NCH); 6.82–6.86 (*m*, 2 arom. H); 7.03–7.08 (*m*, 2 arom. H); 7.25–7.47 (*m*, 15 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 21.7 (Me); 29.7 (CH_2); 29.9 (CH); 37.0 (CH_2); 64.5 (CH); 70.0 (CH_2); 89.4 (C); 114.8, 125.6, 125.9, 127.4, 127.9, 128.0, 128.4, 128.5, 128.6, 128.9, 129.3 (CH); 132.7, 137.2, 138.2, 142.3, 153.0, 157.2, 172.3 (C). FAB-MS: 520 (100, $[M+H]^+$). Anal. calc. for $C_{34}H_{33}NO_4$ (519.64): C 78.59, H 6.49, N 2.70; found: C 78.63, H 6.53, N 2.76.

*(*R*)-4-(*tert*-Butyl)-3-(1-oxopropyl)-5,5-diphenyloxazolidin-2-one* ((*R*)-**17**). Compound (*R*)-**6** (886 mg, 3.0 mmol) was treated with BuLi (1.98 ml, 3.15 mmol) and propanoyl chloride (0.32 ml, 3.6 mmol) according to *GP 3*. FC (pentane/Et_2O 10:1) yielded (*R*)-**17** (923 mg, 88%). White solid. M.p. 103.5–104.5°. $[\alpha]_D^{rt} = +259.6$ (*c* = 1.19, $CHCl_3$). IR ($CHCl_3$): 2969*m*, 1782*s*, 1706*s*, 1450*m*, 1370*m*, 1339*s*, 1327*m*, 1165*m*, 1052*m*, 986*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.81 (*s*, *t*-Bu); 0.98 (*t*, *J* = 7.4, Me); 2.56–2.66 (*m*, 1 H, CH_2); 2.75–2.85 (*m*, 1 H, CH_2); 5.33 (*s*, NCH); 7.23–7.55 (*m*, 10 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 8.7, 27.7 (Me); 28.7 (CH_2); 37.0 (C); 67.0 (CH); 90.2 (C); 125.5, 127.9, 128.0, 128.4, 128.8 (CH); 137.8, 143.7, 153.6, 173.5 (C). FAB-MS: 704 (5, $[2M+H]^+$), 352 (100, $[M+H]^+$), 252 (18). Anal. calc. for $C_{22}H_{25}NO_3$ (351.44): C 75.19, H 7.17, N 3.99; found: C 75.15, H 7.18, N 4.01.

*(*S*)-3-(1-Oxopropyl)-5,5-diphenyl-4-(phenylmethyl)oxazolidin-2-one* ((*S*)-**18**). Compound (*S*)-**5** (6.59 g, 20 mmol) was treated with BuLi (12.7 ml, 20 mmol) and propanoyl chloride (2.10 ml, 24 mmol) according to *GP 3*. FC (pentane/Et_2O 6:1) yielded (*S*)-**18** (7.53 g, 98%). Colorless glass. $[\alpha]_D^{rt} = -277.4$ (*c* = 0.97, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 1782*s*, 1703*m*, 1496*w*, 1450*m*, 1372*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.03 (*t*, *J* = 7.4, Me); 2.68–2.78 (*m*, CH_2); 2.81–2.91 (*m*, CH_2); 5.62 (*dd*, *J* = 7.8, 5.0, NCH); 6.73–6.76 (*m*, 2 arom. H); 7.07–7.13 (*m*, 3 arom. H); 7.20–7.36 (*m*, 8 arom. H); 7.42–7.45 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 8.2 (Me); 29.1, 36.7 (CH_2); 61.9 (CH); 88.5 (C); 126.0, 126.5, 128.2, 128.2, 128.8, 128.9, 129.0 (CH); 136.3, 137.6, 141.5, 152.1, 173.3 (C). FAB-MS: 793 (1, $[2M+Na]^+$), 771 (2, $[2M+H]^+$), 386 (100, $[M+H]^+$), 342 (43). Anal. calc. for $C_{25}H_{23}NO_3$ (385.46): C 77.90, H 6.01, N 3.63; found: C 77.62, H 6.22, N 3.63.

*(*S*)-3-(1-Oxo-3-phthalimidopropyl)-5,5-diphenyl-4-(phenylmethyl)oxazolidin-2-one* ((*S*)-**19**). Compound (*S*)-**5** (3.29 g, 10 mmol) was treated with BuLi (6.7 ml, 10.5 mmol) and 3-phthalimidopropanoyl chloride (2.85 g, 12 mmol) according to *GP 3:* Recrystallization (AcOEt/hexane) yielded (*S*)-**19** (4.88 g, 92%). White powder. M.p. 166–167°. $[\alpha]_D^{rt} = -197.9$ (*c* = 1.01, $CHCl_3$). IR ($CHCl_3$): 3032*w*, 1782*s*, 1716*s*, 1450*w*, 1381*m*, 1114*w*, 1002*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.72 (*dd*, *J* = 14.1, 7.8, 1 H, $PhCH_2$); 2.86 (*dd*, *J* = 14.1, 5.3, 1 H, $PhCH_2$); 3.05–3.13 (*m*, 1 H, C(O)CH_2); 3.25–3.33 (*m*, 1 H, C(O)CH_2); 3.87–3.94 (*m*, CH_2N); 5.61 (*dd*, *J* = 7.8, 5.3, NCH); 6.73–6.75 (*m*, 2 arom. H); 6.99–7.03 (*m*, 1 arom. H); 7.06–7.10 (*m*, 2 arom. H); 7.19–7.28 (*m*, 5 arom. H); 7.29–7.37 (*m*, 3 arom. H); 7.41–7.44 (*m*, 2 arom. H); 7.67–7.72 (*m*, 2 arom. H); 7.79–7.84 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 33.0, 34.3, 36.6 (CH_2); 61.8 (CH); 88.8 (C); 123.3, 126.0, 126.4, 126.5, 128.2, 128.2, 128.3, 128.9, 129.0, 129.0 (CH); 132.1 (C); 134.0 (CH); 136.2, 137.5, 141.1, 152.0, 167.9, 169.6 (C). FAB-MS: 531 (100, $[M+H]^+$), 487 (44), 286 (25). Anal. calc. for $C_{33}H_{26}N_2O_5$ (530.58): C 74.70, H 4.94, N 5.28; found: C 74.64, H 4.77, N 5.25.

*(S)-3-{3-[(*tert*-Butoxycarbonyl)amino]-1-oxopropyl}-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* ((*S*)-**20**): Compound (*S*)-**1** (8.44 g, 30 mmol) was treated with pivaloyl chloride (3.90 ml, 31.5 mmol), Boc-β-alanine (5.96 g, 31.5 mmol), Et_3N (10.8 ml, 78 mmol), and LiCl (1.46 g, 34.5 mmol) according to *GP 4*. FC (pentane/Et_2O 2:1 → 1:1) yielded (*S*)-**20** (10.45 g, 77%). White solid. M.p. 113–114°. $[\alpha]_D^{r.t.} = -176.4$ ($c = 0.96$, $CHCl_3$). IR ($CHCl_3$): 3452*w*, 2980*m*, 1783*s*, 1708*s*, 1505*m*, 1450*m*, 1368*s*, 1174*s*, 1051*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.75 (*d*, $J = 6.8$, Me); 0.88 (*d*, $J = 7.0$, Me); 1.41 (*s*, *t*-Bu); 1.92–2.03 (*m*, Me_2CH); 2.84–2.92 (*m*, 1 H, C(O)CH_2); 3.11–3.19 (*m*, 1 H, C(O)CH_2); 3.38 (br. *m*, CH_2N); 4.86 (br. *s*, NH); 5.36 (*d*, $J = 3.4$, NCH); 7.26–7.48 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 21.8, 28.4 (Me); 29.9 (CH); 35.8, 36.0 (CH_2); 64.6 (CH); 79.3, 89.6 (C); 125.5, 125.9, 128.0, 128.4, 128.7, 129.0 (CH); 138.0, 142.2, 152.9, 155.7, 171.9 (C). FAB-MS: 453 (57, $[M+H]^+$), 397 (100), 353 (67), 238 (60). Anal. calc. for $C_{26}H_{32}N_2O_5$ (452.55): C 69.01, H 7.13, N 6.19; found: C 69.13, H 7.09, N 6.11.

(S)-3-{3-[(Benzyloxycarbonyl)amino]-1-oxopropyl}-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one ((*S*)-**21**). Compound (*S*)-**1** (5.63 g, 20 mmol) was treated with pivaloyl chloride (2.60 ml, 21 mmol), Cbz-β-alanine (4.69 g, 21 mmol), Et_3N (7.20 ml, 52 mmol), and LiCl (0.97 g, 23 mmol) according to *GP 4*. FC (pentane/Et_2O 1:1) yielded (*S*)-**21** (7.30 g, 75%). White solid. M.p. 131–133°. $[\alpha]_D^{r.t.} = -165.5$ ($c = 1.10$, $CHCl_3$). IR ($CHCl_3$): 3451*w*, 3011*w*, 2970*w*, 1783*s*, 1717*s*, 1511*m*, 1450*m*, 1373*m*, 1049*m*, 1002*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.74 (*d*, $J = 6.8$, Me); 0.86 (*d*, $J = 7.0$, Me); 1.91–2.02 (*m*, Me_2CH); 2.88–2.95 (*m*, 1 H, C(O)CH_2); 3.13–3.20 (*m*, 1 H, C(O)CH_2); 3.41–3.51 (*m*, CH_2N); 5.06 (*s*, CH_2O); 5.14 (br. *s*, NH); 5.35 (*d*, $J = 3.4$, NCH); 7.24–7.39 (*m*, 13 arom. H); 7.43–7.47 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 21.8 (Me); 29.9 (CH); 35.9, 36.2 (CH_2); 64.6 (CH); 66.7 (CH_2); 89.6 (C); 125.5, 125.9, 128.0, 128.1, 128.4, 128.5, 128.7, 129.0 (CH); 136.5, 138.0, 142.2, 152.9, 156.2, 171.8 (C). FAB-MS: 973 (10, $[2M+H]^+$), 487 (100, $[M+H]^+$), 443 (18). Anal. calc. for $C_{29}H_{30}N_2O_5$ (486.57): C 71.59, H 6.21, N 5.76; found: C 71.71, H 6.35, N 5.68.

(S)-3-[(R)-3-(Benzyloxy)-1-oxobutyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one ((*S*)-**22**). Compound (*S*)-**1** (4.64 g, 16.5 mmol) was treated with pivaloyl chloride (2.15 ml, 17.3 mmol), (*R*)-3-(benzyloxy)-butanoic acid (3.36 g, 17.3 mmol), Et_3N (5.94 ml, 43 mmol), and LiCl (0.80 g, 19 mmol) according to *GP 4*. FC (pentane/Et_2O 6:1 → 4:1) yielded (*S*)-**22** (5.78 g, 77%). Colorless oil. $[\alpha]_D^{r.t.} = -175.3$ ($c = 0.61$, $CHCl_3$). IR ($CHCl_3$): 2972*w*, 1781*s*, 1704*m*, 1450*m*, 1366*m*, 1320*m*, 1177*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.73 (*d*, $J = 6.8$, Me); 0.87 (*d*, $J = 7.0$, Me); 1.15 (*d*, $J = 6.2$, Me); 1.91–2.02 (*m*, Me_2CH); 2.82 (*dd*, $J = 15.8$, 5.2, 1 H, C(O)CH_2); 3.37 (*dd*, $J = 15.8$, 7.4, 1 H, C(O)CH_2); 3.96–4.04 (*m*, CHO); $\nu_A = 4.50$, $\nu_B = 4.35$ (*AB*, $J = 11.4$, CH_2O); 5.41 (*d*, $J = 3.3$, NCH); 7.22–7.51 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 19.8, 21.7 (Me); 29.9 (CH); 42.4 (CH_2); 64.5 (CH); 70.9 (CH_2); 71.9 (CH); 89.3 (C); 125.6, 125.9, 127.4, 127.6, 128.0, 128.2, 128.4, 128.6, 128.9 (CH); 138.7, 142.4, 153.0, 170.8 (C). FAB-MS: 458 (100, $[M+H]^+$), 350 (29). Anal. calc. for $C_{29}H_{31}NO_4$ (457.57): C 76.12, H 6.83, N 3.06; found: C 76.16, H 6.87, N 2.98.

(S)-3-{3-[1-(Benzyloxycarbonyl)indol-3-yl]-1-oxopropyl}-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one ((*S*)-**23**). Compound (*S*)-**1** (3.38 g, 12 mmol) was treated with pivaloyl chloride (1.57 mgl, 12.6 mmol), 3-[(1-Cbz)indol-3-yl]propanoic acid (4.07 g, 12.6 mmol), Et_3N (4.31 ml, 31.2 mmol), and LiCl (0.58 g, 13.8 mmol) according to *GP 4*. FC (pentane/Et_2O 3:1 → 1:1) yielded (*S*)-**23** (5.90 g, 84%). White foam. $[\alpha]_D^{r.t.} = -132.2$ ($c = 0.80$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2968*w*, 1781*s*, 1729*m*, 1456*m*, 1400*m*, 1356*m*, 1087*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.73 (*d*, $J = 6.8$, Me); 0.84 (*d*, $J = 7.0$, Me); 1.91–2.02 (*m*, Me_2CH); 2.88–3.04 (*m*, CH_2); 3.08–3.16 (*m*, 1 H, C(O)CH_2); 3.28–3.36 (*m*, 1 H, C(O)CH_2); 5.38 (*d*, $J = 3.4$, NCH); 5.42 (*s*, CH_2O); 7.21–7.54 (*m*, 19 arom. H); 8.14 (br. *s*, arom. NCH). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4 (Me); 19.9 (CH_2); 21.7 (Me); 29.8 (CH); 34.8 (CH_2); 64.6 (CH); 68.5 (CH_2); 89.5 (C); 115.2, 119.1 (CH); 120.3 (C); 122.3, 122.9, 124.7, 125.6, 125.9, 128.0, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9 (CH); 130.3, 135.3, 135.6, 138.1, 142.2, 150.8, 153.1, 172.2 (C). FAB-MS: 586 (100, M^+), 543 (35). Anal. calc. for $C_{37}H_{34}N_2O_5$ (586.69): C 75.75, H 5.84, N 4.77; found: C 75.78, H 5.73, N 4.79.

*(S)-3-{3-[(*tert*-Butoxycarbonyl)amino]-1-oxopropyl}-4-phenylmethyl-5,5-diphenyloxazolidin-2-one* ((*S*)-**24**). Compound (*S*)-**5** (3.29 g, 10 mmol) was treated with pivaloyl chloride (1.30 ml, 10.5 mmol), Boc-β-alanine (1.99 g, 10.5 mmol), Et_3N (3.60 ml, 26 mmol), and LiCl (0.49 g, 11.5 mmol) according to *GP 4*. FC (pentane/Et_2O 2:1 → 1:1) yielded (*S*)-**24** (3.89 g, 78%). White solid. M.p. 146–147°. $[\alpha]_D^{r.t.} = -238.7$ ($c = 1.19$, $CHCl_3$). IR ($CHCl_3$): 3454*w*, 3007*w*, 2980*w*, 1784*s*, 1707*s*, 1505*m*, 1450*m*, 1368*s*, 1168*s*, 997*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.43 (*s*, *t*-Bu); 2.67–2.87 (*m*, 3 H, PhCH_2), C(O)CH_2); 3.00–3.07 (*m*, 1 H, C(O)CH_2); 3.22–3.39 (*m*, CH_2N); 4.67 (br. *s*, NH); 5.61 (*t*, $J = 6.7$, NCH); 6.79–6.82 (*m*, 2 arom. H); 7.11–7.16 (*m*, 3 arom. H); 7.24–7.37 (*m*, 8 arom. H); 7.42–7.45 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.4 (Me); 35.3, 36.4, 37.0 (CH_2); 61.7 (CH); 79.2, 88.8 (C); 125.9, 126.3, 126.7, 128.2, 128.3, 128.4, 128.9, 129.0, 129.1 (CH); 136.2, 137.5, 141.1, 152.0, 155.6, 171.3 (C). FAB-MS: 1001 (16, $[2M+H]^+$), 501 (92, $[M+H]^+$), 445 (75), 401 (100). Anal. calc. for $C_{30}H_{32}N_2O_5$ (500.60): C 71.98, H 6.44, N 5.60; found: C 71.75, H 6.49, N 5.54.

*(*S*)-4-(1-Methylethyl)-3-[(*R*)-2-methyl-1-oxopent-4-enoyl]-5,5-diphenyloxazolidin-2-one* (**25**). The acyloxazolidinone (*S*)-**8** (814 mg, 2.4 mmol) was treated with LDA (3.1 mmol), $ZnBr_2$ (708 mg, 3.1 mmol), and allyl bromide (2.15 ml, 25 mmol) according to *GP 5*. Recrystallization (Et_2O/pentane) yielded **25** (502 mg). From the mother liquor, additional **25** (152 mg) was obtained. Total yield: 654 mg (72%). White needles. M.p. 110–111°. $[\alpha]_D^{r.t.} = -203.4$ ($c = 1.18$, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2970*w*, 1784*s*, 1706*s*, 1494*w*, 1450*m*, 1375*s*, 1321*s*, 1288*m*, 1178*m*, 1043*m*, 984*m*, 648*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.76 (*d*, $J = 6.7$, Me); 0.84 (*d*, $J = 6.8$, Me); 0.87 (*d*, $J = 7.0$, Me); 1.90–2.01 (*m*, Me_2CH); 2.12–2.19 (*m*, 1 H, CH_2); 2.50–2.58 (*m*, 1 H, CH_2); 3.74 (*sext.*, $J = 6.9$, C(O)CH); 5.01–5.11 (*m*, $CH{=}CH_2$); 5.38 (*d*, $J = 3.3$, NCH); 5.75–5.86 (*m*, $CH{=}CH_2$); 7.24–7.50 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 16.3, 21.7 (Me); 29.8, 37.0 (CH); 37.9 (CH_2); 64.6 (CH); 89.3 (C); 117.0 (CH_2); 125.7, 125.9, 127.9, 128.4, 128.6, 128.8, 135.5 (CH); 138.2, 142.4, 152.9, 176.3 (C). FAB-MS: 378 (100, $[M+H]^+$), 334 (29). Anal. calc. for $C_{24}H_{27}NO_3$ (377.48): C 76.36, H 7.21, N 3.71; found: C 76.25, H 7.23, N 3.76.

*(*S*)-3-[(*R*)-3-(*tert*-Butoxycarbonyl)-2-methyl-1-oxopropyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**26**). Compound (*S*)-**8** (844 mg, 2.5 mmol) was treated with BuLi (1.73 ml, 2.75 mmol) and *tert*-butyl bromoacetate (1.85 ml, 12.5 mmol) according to *GP 6*. FC (pentane/Et_2O 12:1) yielded **26** as a 96:4 mixture with its C(2)-epimer (924 mg, 82%), which was recrystallized (Et_2O/pentane) to yield pure **26** for anal. purposes. White solid. M.p. 111–113°. $[\alpha]_D^{r.t.} = -175.8$ ($c = 0.99$, $CHCl_3$). IR ($CHCl_3$): 2979*m*, 1782*s*, 1720*m*, 1699*m*, 1450*m*, 1393*m*, 1368*m*, 1318*m*, 1156*s*, 1052*w*, 994*w*, 845*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.73 (*d*, $J = 7.0$, Me); 0.83 (*d*, $J = 6.7$, Me); 0.88 (*d*, $J = 7.0$, Me); 1.42 (*s*, *t*-Bu); 1.91–2.02 (*m*, Me_2CH); 2.27 (*dd*, $J = 16.7$, 5.0, 1 H, CH_2); 2.76 (*dd*, $J = 16.7$, 9.9, 1 H, CH_2); 4.04–4.13 (*m*, C(O)CH); 5.33 (*d*, $J = 3.3$, NCH); 7.24–7.47 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 16.6, 21.5, 28.1 (Me); 29.9, 34.2 (CH); 38.8 (CH_2); 65.0 (CH); 80.5, 89.3 (C); 125.6, 125.9, 127.9, 128.4, 128.5, 128.8 (CH); 138.1, 142.5, 152.8, 171.0, 176.0 (C). FAB-MS: 452 (27, $[M+H]^+$), 396 (100), 334 (37), 238 (73). Anal. calc. for $C_{27}H_{33}NO_5$ (451.56): C 71.82, H 7.37, N 3.10; found: C 71.98, H 7.50, N 3.11.

*(*S*)-4-(1-Methylethyl)-3-[(*R*)-2-methyl-1-oxo-3-phenylpropyl]-5,5-diphenyloxazolidin-2-one* (**27**). Compound (*S*)-**8** (8.44 g, 25 mmol) was treated with LDA (31 mmol), $ZnBr_2$ (6.98 g, 31 mmol), and BnBr (23.8 ml, 200 mmol) according to *GP 5*. Recrystallization (Et_2O/pentane) yielded **27** (8.66 g, 81%). White solid. M.p. 131–132°. $[\alpha]_D^{r.t.} = -201.3$ ($c = 1.22$, $CHCl_3$). IR ($CHCl_3$): 2972*m*, 1778*s*, 1699*s*, 1495*m*, 1459*m*, 1370*s*, 1320*m*, 1176*s*, 1051*m*, 992*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.59 (*d*, $J = 6.8$, Me); 0.70 (*d*, $J = 7.0$, Me); 0.84 (*d*, $J = 6.8$, Me); 1.82–1.94 (*m*, Me_2CH); 2.60 (*dd*, $J = 13.4$, 7.9, 1 H, $PhCH_2$); 3.16 (*dd*, $J = 13.4$, 7.2, 1 H, $PhCH_2$); 3.99–4.08 (*m*, C(O)CH); 5.35 (*d*, $J = 3.3$, NCH); 7.14–7.49 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.1, 16.3, 21.5 (Me); 29.6, 39.2 (CH); 39.8 (CH_2); 64.5 (CH); 89.3 (C); 125.7, 125.9, 126.3, 127.9, 128.3, 128.4, 128.6, 128.8, 129.2 (CH); 138.1, 129.3, 142.3, 152.8, 176.2 (C). FAB-MS: 428 (100, $[M+H]^+$), 384 (16). Anal. calc. for $C_{28}H_{29}NO_3$ (427.54): C 78.66, H 6.84, N 3.28; found: C 78.56, H 6.83, N 3.29.

*(*S*)-4-Benzyl-3-[(*R*)-2-methyl-1-oxopent-4-enyl]-5,5-diphenyloxazolidin-2-one* (**28**). Compound (*S*)-**18** (964 mg, 2.5 mmol) was treated with LDA (3.1 mmol), $ZnBr_2$ (708 mg, 3.1 mmol), and allyl bromide (2.15 ml, 25 mmol) according to *GP 5*. FC (pentane/Et_2O 6:1) yielded **28** (959 mg, 90%). Colorless oil. $[\alpha]_D^{r.t.} = -280.2$ ($c = 0.52$, $CHCl_3$). IR ($CHCl_3$): 3037*w*, 1780*s*, 1698*m*, 1496*m*, 1450*m*, 1350*m*, 1168*m*, 993*m*, 921*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.92 (*d*, $J = 6.8$, Me); 2.03–2.11 (*m*, 1 H, CH_2); 2.38–2.46 (*m*, 1 H, CH_2); 2.74 (*dd*, $J = 14.2$, 8.1, 1 H, $PhCH_2$); 2.85 (*dd*, $J = 14.2$, 4.7, 1 H, $PhCH_2$); 3.68 (*sext.*, $J = 6.8$, C(O)CH); 4.98–5.06 (*m*, $CH_2{=}CH$); 5.61–5.75 (*m*, 2 H, NCH, $CH_2{=}CH$); 6.71–6.78 (*m*, 2 arom. H); 7.05–7.11 (*m*, 3 arom. H); 7.17–7.45 (*m*, 10 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3 (Me); 36.7 (CH_2); 37.1 (CH); 37.5 (CH_2); 62.2 (CH); 88.4 (C); 117.0 (CH_2); 126.0, 126.4, 126.5, 128.1, 128.2, 128.2, 128.8, 129.0, 135.4 (CH); 136.3, 137.4, 141.4, 151.9, 175.8 (C). FAB-MS: 426 (25, $[M+H]^+$), 382 (35), 286 (67), 268 (56), 191 (62), 167 (100). Anal. calc. for $C_{28}H_{27}NO_3$ (425.53): C 79.03, H 6.40, N 3.29; found: C 79.00, H 6.35, N 3.46.

*(*R*)-4-Benzyl-3-[(*S*)-3-(tert-butoxycarbonyl)-2-methyl-1-oxopropyl]-5,5-diphenyloxazolidin-2-one* (**29**). Compound (*R*)-**18** (771 mg, 2.0 mmol) was treated with BuLi (1.65 ml, 2.6 mmol) and *tert*-butyl bromoacetate (1.85 ml, 12.5 mmol) according to *GP 6*. FC (pentane/Et_2O 12:1 → 6:1) yielded **29** (682 mg, *ca.* 55%) as a 4:1 mixture with **18**, which was recrystallized (Et_2O/pentane) to yield pure **29** for anal. purposes. White solid. M.p. 106–107°. $[\alpha]_D^{r.t.} = +211.5$ ($c = 0.91$, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2982*w*, 1782*s*, 1722*m*, 1450*m*, 1392*m*, 1355*m*, 1156*s*, 978*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.93 (*d*, $J = 7.0$, Me); 1.40 (*s*, *t*-Bu); 2.28 (*dd*, $J = 16.7$, 5.3, 1 H, $PhCH_2$); 2.75 (*dd*, $J = 16.7$, 9.4, 1 H, $PhCH_2$); 2.83 (*dd*, $J = 14.4$, 8.9, 1 H, $C(O)CH_2$); 3.00 (*dd*, $J = 14.3$, 3.2, 1 H, $C(O)CH_2$); 4.04–4.13 (*m*, C(O)CH); 5.56 (*dd*, $J = 8.9$, 3.2, NCH); 6.64–6.69 (*m*, 2 arom. H); 7.02–7.45 (*m*, 13 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.9, 28.1 (Me); 34.4 (CH); 36.0, 38.7 (CH_2); 62.8 (CH); 80.7, 88.3 (C); 126.0, 126.2, 126.7, 128.1, 128.1, 128.1, 128.8, 128.9 (CH); 136.7, 137.3, 141.5, 151.7, 171.0, 175.8 (C).

FAB-MS: 500 (52, $[M+H]^+$), 444 (100), 400 (30), 382 (41), 286 (76), 268 (55). Anal. calc. for $C_{31}H_{33}NO_5$ (499.61): C 74.53, H 6.66, N 2.80; found: C 74.62, H 6.51, N 2.83.

*(*R*)-3-[(*S*)-3-(*tert*-Butoxycarbonyl)-2-methyl-1-oxopropyl]-4-(*tert*-butyl)-5,5-diphenyloxazolidin-2-one* (**30**). Compound (*R*)-**17** (351 mg, 1.0 mmol) was treated with BuLi (0.69 ml, 1.1 mmol) and *tert*-butyl bromoacetate (0.74 ml, 5.0 mmol) according to *GP 6*. FC (pentane/Et_2O 12:1 → 8:1) yielded **30** as a 3:1 mixture with its C(2)-epimer (230 mg, 49%), which was recrystallized (Et_2O/pentane) to yield pure **30** for anal. purposes. White needles. M.p. 141–142°. $[\alpha]_D^{r.t.} = +186.7$ ($c = 0.29$, $CHCl_3$). IR ($CHCl_3$): 2972*m*, 1784*s*, 1698*m*, 1450*m*, 1354*m*, 1155*s*, 992*m*, 840*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.43 (*d*, *J* = 7.0, Me); 0.82 (*s*, *t*-Bu); 1.40 (*s*, *t*-BuO); 2.20 (*dd*, *J* = 16.7, 5.0, 1 H, C(O)CH_2); 2.69 (*dd*, *J* = 16.7, 10.1, 1 H, C(O)CH_2); 3.94–4.02 (*m*, C(O)CH); 5.27 (*s*, NCH); 7.22–7.51 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.1, 27.7, 28.0 (Me); 33.9 (CH); 37.0 (C); 38.8 (CH_2); 67.7 (CH); 80.5, 90.2 (C); 125.4, 128.0, 128.4, 128.7 (CH); 137.6, 144.0, 153.4, 171.1, 175.4 (C). FABMS: 466 (45, $[M+H]^+$), 410 (100), 292 (42), 240 (43). Anal. calc. for $C_{28}H_{35}NO_5$ (465.59): C 72.23, H 7.58, N 3.01; found: C 72.33, H 7.73, N 2.93.

*(*S*)-4-(1-Methylethyl)-3-[(*S*)-2-methyl-1-oxo-3-phenylpropyl]5,5-diphenyloxazolidin-2-one* (**31**). Compound (*S*)-**11** (5.17 g, 12.5 mmol) was treated with LDA (15.5 mmol), $ZnBr_2$ (3.49 g, 15.5 mmol), and MeI (7.83 ml, 125 mmol) according to *GP 5*. FC (pentane/Et_2O 15:1 → 10:1) yielded **31** (3.91 g, 73%). Colorless oil. $[\alpha]_D^{r.t.} = -133.7$ ($c = 0.46$, $CHCl_3$). IR ($CHCl_3$): 2968*m*, 1778*s*, 1698*s*, 1495*m*, 1450*m*, 1372*m*, 1317*m*, 1177*s*, 991*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.77 (*d*, *J* = 6.8, Me); 0.87 (*d*, *J* = 7.0, Me); 1.23 (*d*, *J* = 6.9, Me); 1.91–2.02 (*m*, Me_2CH); 2.45 (*dd*, *J* = 13.8, 7.4, 1 H, PhCH_2); 2.81 (*dd*, *J* = 13.8, 7.1, 1 H, PhCH_2); 3.92–4.01 (*m*, C(O)CH); 5.36 (*d*, *J* = 3.4, NCH); 6.96–7.01 (*m*, 2 arom. H); 7.07–7.14 (*m*, 3 arom. H); 7.22–7.39 (*m*, 10 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 17.6, 21.8 (Me); 29.9 (CH); 38.6 (CH_2); 39.2, 64.4 (CH); 89.3 (C); 125.6, 125.9, 126.1, 127.9, 128.2, 128.4, 128.5, 128.8, 128.9 (CH); 138.2, 139.1, 142.1, 152.7, 176.2 (C). FAB-MS: 428 (100, $[M+H]^+$), 384 (25). Anal. calc. for $C_{28}H_{29}NO_3$ (427.54): C 78.66, H 6.84, N 3.28; found: C 78.51, H 6.78, N 3.29.

Benzyl N-*(Methoxymethyl)carbamate* (Cbz-NHCH_2OMe). Some modifications to the literature procedure [25] were necessary: To a suspension of *N*-benzylcarbamic acid (15.1 g, 100 mmol) in H_2O (112.5 ml), K_2CO_3 (276 mg) and HCHO (36 wt.-% soln. in H_2O, 8.5 ml, 105 mmol) were added. The mixture was stirred at 60° for 30 min, diluted with MeOH (45 ml), and cooled to 4°. The resulting white crystals were dried and purified by FC (pentane/Et_2O 1:2 → 0:1) to yield benzyl *N*-(hydroxymethyl)carbamate (8.02 g, 44%). To a soln. of benzyl *N*-(hydroxymethyl)carbamate (3.62 g, 20 mmol) in Et_2O (30 ml) and MeOH (6 ml), molecular sieves 4 Å (1.60 g) and $TsOH \cdot H_2O$ (60 mg) were added. The mixture was stirred at r.t. for 1 h, then filtered over SiO_2 (∅ = 3 cm, h = 1 cm), and the solvent removed under reduced pressure. Drying (h.v.) yielded benzyl *N*-(methoxymethyl)carbamate (3.84 g, 98%) as colorless oil that solidifies when stored at −20°. ^{1}H-NMR: in agreement with [25].

*(*S*)-3-((*R*)-2-{[(Benzyloxycarbonyl)amino]methyl}-1-oxopropyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**32**). Compound (*S*)-**8** (675 mg, 2.0 mmol) was treated with $TiCl_4$ (0.23 ml, 2.1 mmol), EtN(i-Pr)$_2$ (0.38 ml, 2.2 mmol), Cbz-NHCH_2OMe (430 mg, 2.2 mmol), and again $TiCl_4$ (0.24 ml, 2.2 mmol) according to *GP 7*. FC (pentane/Et_2O 3:1 → 1:1) yielded **32** as a 93:7 mixture with its C(2)-epimer (691 mg, 69%). For anal. purposes, a sample was recrystallized (Et_2O/pentane). White solid. M.p. 110–111°. $[\alpha]_D^{r.t.} = -161.4$ ($c = 0.83$, $CHCl_3$). IR ($CHCl_3$): 3448*w*, 2971*w*, 1782*s*, 1719*s*, 1514*m*, 1451*m*, 1365*m*, 1318*m*, 1051*m*, 1002*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.73 (*d*, *J* = 6.8, Me); 0.78 (*d*, *J* = 6.9, Me); 0.84 (*d*, *J* = 7.0, Me); 1.91–2.02 (*m*, Me_2CH); 3.34–3.46 (*m*, CH_2N); 3.81–3.89 (*m*, C(O)CH); 5.08 (*s*, CH_2O); 5.15–5.23 (br. *s*, NH); 5.31 (*d*, *J* = 3.5, NCH); 7.25–7.47 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.4, 16.5, 21.7 (Me); 29.6, 38.2 (CH); 43.6 (CH_2); 65.1 (CH); 66.7 (CH_2); 89.7 (C); 125.5, 125.9, 128.1, 128.1, 128.5, 128.5, 128.7, 128.9 (CH); 136.6, 137.8, 142.2, 152.9, 156.3, 175.5 (C). FAB-MS: 1001 (7, $[2M+H]^+$), 501 (100, $[M+H]^+$), 457 (25). Anal. calc. for $C_{30}H_{32}N_2O_5$ (500.60): C 71.98, H 6.44, N 5.60; found: C 71.75, H 6.39, N 5.37.

*(*S*)-3-((*R*)-2-{[(Benzyloxycarbonyl)amino]methyl}-3-methyl-1-oxobutyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**33**). Compound (*S*)-**9** (3.29 g, 9.0 mmol) was treated with $TiCl_4$ (1.05 ml, 9.5 mmol), EtN(i-Pr)$_2$ (1.71 ml, 9.9 mmol), Cbz-NHCH_2OMe (1.94 g, 9.9 mmol), and again $TiCl_4$ (1.08 ml, 9.9 mmol) according to *GP 7*. FC (pentane/Et_2O 2:1 → 1:1) yielded **33** as a 93:7 mixture with its C(2)-epimer (3.33 g, 70%). White foam. $[\alpha]_D^{r.t.} = -114.6$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3451*w*, 3011*w*, 2968*m*, 1780*s*, 1718*s*, 1513*s*, 1450*m*, 1363*m*, 1318*m*, 1178*m*, 1051*m*, 989*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.41 (*d*, *J* = 6.7, Me); 0.68 (*d*, *J* = 6.8, Me); 0.71 (*d*, *J* = 6.7, Me); 0.83 (*d*, *J* = 7.0, Me); 1.66–1.76 (*m*, Me_2CH); 1.94–2.02 (*m*, Me_2CH); 3.38–3.43 (*m*, CH); 3.52–3.59 (*m*, CH); 3.69–3.74 (*m*, CH); 5.06 (*s*, CH_2O); 5.14 (br. *s*, NH); 5.34 (*d*, *J* = 3.5, NCH); 7.20–7.52 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 19.0, 20.0, 21.7 (Me); 28.6, 29.6 (CH); 40.8 (CH_2); 48.7, 65.7 (CH); 66.6 (CH_2); 89.5 (C); 125.3, 125.7, 128.0, 128.1, 128.4, 128.5, 128.6, 128.9 (CH); 136.6, 137.7, 142.4, 153.3,

156.2, 174.9 (C). FAB-MS: 1058 (18, $[2M+H]^+$), 529 (60, $[M+H]^+$), 485 (100). Anal. calc. for $C_{32}H_{36}N_2O_5$ (528.65): C 72.70, H 6.86, N 5.30; found: C 72.80, H 6.79, N 5.27.

*(*S*)-3-((*R*)-2-[[(Benzyloxycarbonyl)amino]methyl]-4-methyl-1-oxopentyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**34**). Compound (*S*)-**10** (1.90 g, 5.0 mmol) was treated with $TiCl_4$ (0.58 ml, 5.25 mmol), EtN(i-Pr)$_2$ (0.95 ml, 5.5 mmol), Cbz-NHCH$_2$OMe (1.08 g, 5.5 mol), and again $TiCl_4$ (0.60 ml, 5.5 mmol) according to *GP 7*. FC (pentane/Et$_2$O 2:1 → 1:1) yielded **34** as a 92:8 mixture with its C(2)-epimer (1.73 g, 64%). For anal. purposes, a sample was recrystallized (Et$_2$O/pentane). White solid. M.p. 146–147°. $[\alpha]_D^{r.t.} = -119.4$ ($c = 0.84$, $CHCl_3$). IR ($CHCl_3$): 3444*w*, 3011*w*, 2962*m*, 1718*s*, 1515*m*, 1450*m*, 1365*m*, 1318*m*, 1051*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.39 (*d*, *J* = 6.2, Me); 0.62 (*d*, *J* = 6.1, Me); 0.71 (*d*, *J* = 6.7, Me); 0.84 (*d*, *J* = 7.0, Me); 0.88–1.01 (*m*, CH_2); 1.32–1.42 (*m*, Me$_2$C*H*); 1.93–2.01 (*m*, Me$_2$C*H*); 3.30–3.35 (*m*, 1 H, CH_2N); 3.45–3.56 (*m*, 1 H, CH_2N); 3.86–3.91 (*m*, C(O)CH); 5.06 (*s*, CH_2O); 5.26 (br. *s*, NH); 5.32 (*d*, *J* = 3.4, NCH); 7.24–7.50 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 21.7, 21.8, 22.6 (Me); 25.6, 29.6 (CH); 38.6 (CH_2); 40.7 (CH); 43.6 (CH_2); 65.7 (CH); 66.6 (CH_2); 89.8 (C); 125.3, 125.7, 128.0, 128.2, 128.4, 128.5, 128.6, 128.9 (CH); 136.6, 137.7, 142.3, 153.4, 156.2, 175.1 (C). FAB-MS: 1086 (17, $[2M+H]^+$), 543 (100, $[M+H]^+$), 499 (24). Anal. calc. for $C_{33}H_{38}N_2O_5$ (542.67): C 73.04, H 7.06, N 5.16; found: C 73.21, H 7.23, N 5.15.

*(*S*)-3-((*R*)-2-[[(Benzyloxycarbonyl)amino]methyl]-1-oxo-3-phenylpropyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**35**). Compound (*S*)-**11** (4.41 g, 10.0 mmol) was treated with $TiCl_4$ (1.16 ml, 10.5 mmol), Et_3N (1.54 ml, 11.0 mmol), Cbz-NHCH$_2$OMe (2.15 g, 11.0 mmol), and again $TiCl_4$ (1.22 ml, 11.0 mmol) according to *GP 7*. FC (pentane/Et$_2$O 2:1 → 1:1) yielded **35** (4.50 g, 78%). White solid. M.p. 126–128°. $[\alpha]_D^{r.t.} = -101.3$ ($c = 1.11$, $CHCl_3$). IR ($CHCl_3$): 3446*w*, 3008*m*, 2969*m*, 1779*s*, 1720*s*, 1514*s*, 1451*m*, 1364*m*, 1318*m*, 990*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.71 (*d*, *J* = 6.7, Me); 0.84 (*d*, *J* = 7.0, Me); 1.92–2.00 (*m*, Me$_2$C*H*); 2.51 (*dd*, *J* = 13.9, 7.2, 1 H, PhC*H*$_2$); 2.71 (*dd*, *J* = 14.0, 6.9, 1 H, PhC*H*$_2$); 3.39–3.53 (*m*, CH_2N); 4.21 (br. *m*, C(O)CH); 5.06 (*s*, CH_2O); 5.18 (br. *s*, NH); 5.33 (*d*, *J* = 3.3, NCH); 6.89–6.91 (*m*, 2 arom. H); 7.04–7.08 (*m*, 3 arom. H); 7.18–7.38 (*m*, 15 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 21.7 (Me); 29.8 (CH); 35.2, 42.4 (CH_2); 44.6, 65.1 (CH); 66.7 (CH_2); 89.6 (C); 125.3, 125.8, 126.5, 128.0, 128.1, 128.1, 128.4, 128.4, 128.5, 128.7, 128.9 (CH); 136.5, 137.6, 137.9, 142.0, 153.0, 156.1, 173.9 (C). FAB-MS: 1153 (13, $[2M+H]^+$), 577 (100, $[M+H]^+$), 533 (38), 412 (11). Anal. calc. for $C_{36}H_{36}N_2O_5$ (576.69): C 74.98, H 6.29, N 4.86; found: C 74.85, H 6.11, N 5.05.

*(*S*)-3-((*R*)-2-[[(Benzyloxycarbonyl)amino]methyl]-4-(methoxycarbonyl)-1-oxobutyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**36**). Compound (*S*)-**14** (819 mg, 2.0 mmol) was treated with $TiCl_4$ (0.22 ml, 2.0 mmol), Et_3N (0.28 ml, 2.0 mmol), Cbz-NHCH$_2$OMe (429 mg, 2.2 mmol), and again $TiCl_4$ (0.24 ml, 2.2 mmol) according to *GP 7*. FC (pentane/Et$_2$O 1:1) yielded **36** (4.82 mg, 42%). White solid. M.p. 93–95°. $[\alpha]_D^{r.t.} = -110.4$ ($c = 0.75$, $CHCl_3$). IR ($CHCl_3$): 3448*w*, 3008*m*, 2972*w*, 1779*s*, 1725*s*, 1512*m*, 1450*m*, 1364*m*, 1318*m*, 1046*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.71 (*d*, *J* = 6.7, Me); 0.83 (*d*, *J* = 7.0, Me); 1.55–1.65 (*m*, 1 H, CH_2); 1.65–1.88 (*m*, 3 H, CH_2); 1.93–2.03 (*m*, Me$_2$C*H*); 3.36–3.40 (*m*, 1 H, CH_2N); 3.49–3.56 (*m*, 1 H, CH_2N); 3.52 (*s*, MeO); 3.84–3.88 (br. *m*, 1 H, C(O)CH); 5.07 (*d*, *J* = 3.0, CH_2O); 5.23 (br. *s*, NH); 5.35 (*d*, *J* = 3.5, NCH); 7.26–7.48 (*m*, arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 16.3, 21.6 (Me); 24.5 (CH_2); 29.6 (CH); 30.7 (CH_2); 42.2 (CH); 42.9 (CH_2); 51.5 (Me); 65.3 (CH); 66.8 (CH_2); 89.8 (C); 125.4, 125.8, 128.1, 128.1, 128.2, 128.5, 128.5, 128.7, 129.0 (CH); 136.5, 137.7, 142.1, 153.1, 156.2, 172.8, 174.0 (C). FAB-MS: 1146 (28, $[2M+H]^+$), 573 (100, $[M+H]^+$), 529 (28). Anal. calc. for $C_{33}H_{36}N_2O_7$ (572.66): C 69.21, H 6.34, N 4.89; found: C 68.93, H 6.58, N 5.03.

*(*S*)-3-((*S*)-2-[[(Benzyloxycarbonyl)amino]methyl]-1-oxo-3-phthalimidopropyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**37**). Compound (*S*)-**15** (483 mg, 1.0 mmol) was treated with $TiCl_4$ (0.12 ml, 1.05 mmol), Et_3N (0.15 ml, 1.1 mmol), Cbz-NHCH$_2$OMe (215 mg, 1.1 mmol), and again $TiCl_4$ (0.12 ml, 1.1 mmol) according to *GP 7*. Recrystallization (AcOEt) yielded **37** (417 mg, 65%). White solid. M.p. 166–167°. $[\alpha]_D^{r.t.} = -116.6$ ($c = 0.88$, $CHCl_3$). IR ($CHCl_3$): 3435 (br.), 3011*w*, 2972*w*, 1777*s*, 1719*s*, 1516*m*, 1450*m*, 1365*m*, 1320*m*, 1052*w*, 990*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.72 (*d*, *J* = 6.7, Me); 0.83 (*d*, *J* = 7.0, Me); 1.90–1.98 (*m*, Me$_2$C*H*); 3.43–3.50 (*m*, 1 H, CH_2N); 3.72–3.92 (*m*, 3 H, CH_2N); 4.15–4.18 (br. *m*, C(O)CH); 5.06 (*s*, CH_2O); 5.38 (*d*, *J* = 3.0, NCH); 5.60 (br. *s*, NH); 7.09–7.13 (*m*, 1 arom. H); 7.19–7.43 (*m*, 14 arom. H); 7.68–7.77 (*m*, 4 Phth. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.9, 21.6 (Me); 30.0 (CH); 36.1, 40.7 (CH_2); 42.5, 64.9 (CH); 66.8 (CH_2); 89.7 (C); 123.5, 125.5, 125.9, 128.0, 128.0, 128.1, 128.4, 128.5, 128.5, 128.8 (CH); 131.8 (C); 134.0 (CH); 136.5, 138.1, 142.0, 152.8, 156.2, 168.0, 171.6 (C). FAB-MS: 1291 (6, $[2M+H]^+$), 646 (100, $[M+H]^+$), 602 (61), 512 (8). Anal. calc. for $C_{38}H_{35}N_3O_7$ (645.71): C 70.68, H 5.46, N 6.51; found: C 70.53, H 5.50, N 6.49.

*(*S*)-3-((*R*)-2-[[(Benzyloxycarbonyl)amino]methyl]-3-[4-(benzyloxy)phenyl]-1-oxobutyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**38**). Compound (*S*)-**16** (0.4 g, 20 mmol) was treated with $TiCl_4$ (2.32 ml, 21 mmol), EtN(i-Pr)$_2$ (3.80 ml, 22 mmol), Cbz-NHCH$_2$OMe (4.30 g, 22 mmol), and again $TiCl_4$ (2.40 ml,

22 mmol) according to *GP 7*. FC (pentane/Et_2O 2:1 → 1:1) yielded **38** (5.14 g, *ca.* 30%) as a 3:1 mixture with **16**. For anal. purposes, a sample was recrystallized (Et_2O/pentane) to yield pure **38**. white solid. M.p. 114–119°. $[\alpha]_D^{rt.} = -84.7$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3447*w*, 3008*w*, 2968*w*, 1779*s*, 1718*s*, 1610*w*, 1511*s*, 1451*m*, 1364*m*, 1318*m*, 1050*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.70 (*d*, $J = 6.7$, Me); 0.84 (*d*, $J = 7.0$, Me); 1.90–2.01 (*m*, Me_2CH); 2.45 (*dd*, $J = 14.0$, 7.1, 1 H, $PhCH_2$); 2.64 (*dd*, $J = 14.0$, 6.8, 1 H, $PhCH_2$); 3.34–3.52 (*m*, CH_2N); 4.12–4.20 (*m*, C(O)CH); 4.98 (*s*, CH_2O); 5.06 (*s*, CH_2O); 5.19 (br. *s*, NH); 5.32 (*d*, $J = 3.3$, NCH); 6.69 (*d*, $J = 8.5$, 2 arom. H); 6.80–6.82 (*m*, 2 arom. H); 7.19–7.45 (*m*, 20 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 21.7 (Me); 29.8 (CH); 34.3, 42.3 (CH_2); 44.8, 65.0 (CH); 66.7, 69.9 (CH_2); 89.5 (C); 114.7, 125.3, 125.8, 127.5, 127.9, 128.0, 128.1, 128.1, 128.4, 128.5, 128.6, 128.9, 129.7, 129.9 (CH); 136.5, 137.1, 137.9, 142.0, 153.0, 156.1, 157.3, 174.0 (C). FAB-MS: 1366 (6, $[2M + H]^+$), 683 (32, $[M + H]^+$), 639 (100), 518 (16). Anal. calc. for $C_{43}H_{42}N_2O_6$ (682.81): C 75.64, H 6.20, N 4.10; found: C 75.78, H 6.39, N 4.12.

(S)-3-[(R)-3-Hydroxy-1-oxo-2-(phthalimidomethyl)propyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (**39**). To a soln. of (*S*)-**15** (4.83 g, 10 mmol) in CH_2Cl_2 (50 ml), $TiCl_4$ (1.16 ml, 10.5 mmol) and Et_3N (1.54 ml, 11 mmol) were added at *ca.* −10°. The resulting dark red soln. was stirred at this temp. for 30 min. 1,3,5-Trioxane (0.99 g, 11 mmol) and $TiCl_4$ (1.22 ml, 11 mmol) were added, and the mixture stirred at 0° for 1 h, treated with sat. NH_4Cl soln., and diluted with Et_2O. The org. phase was washed with 1M HCl (2×), 1M NaOH, and sat. NaCl solns., dried ($MgSO_4$), and evaporated. Recrystallization (AcOEt/hexane) of the resulting crude product yielded **39** (3.66 g). FC (pentane/Et_2O 1:2) of the mother liquor yielded further **39** (1.06 g). Total yield: 4.72 g (92%). White solid. M.p. 169–172°. $[\alpha]_D^{rt.} = -108.9$ ($c = 0.90$, $CHCl_3$). IR ($CHCl_3$): 3512 (br.), 3011*w*, 1773*s*, 1714*s*, 1366*m*, 1322*m*, 1178*m*, 1098*w*, 951*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.77 (*d*, $J = 6.7$, Me); 0.94 (*d*, $J = 7.0$, Me); 1.92–2.03 (*m*, Me_2CH); 3.07 (*dd*, $J = 8.6$, 6.4, OH); 3.76–3.81 (*m*, CH); 3.88–4.00 (*m*, CH_2); 4.03–4.15 (*m*, CH_2); 5.51 (*d*, $J = 2.9$, NCH); 7.21–7.40 (*m*, 8 arom. H); 7.46–7.49 (*m*, 2 arom. H); 7.70–7.78 (*m*, 2 Phth. H); 7.79–7.84 (*m*, 2 Phth. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.9, 21.7 (Me); 30.3 (CH); 34.7 (CH_2); 45.3 (CH); 61.2 (CH_2); 64.2 (CH); 89.6 (C); 123.6, 125.6, 125.8, 127.9, 128.4, 128.7, 129.0 (CH); 131.8 (C); 134.2 (CH); 142.1, 152.8, 168.6, 171.8 (C). FAB-MS: 1025 (2, $[2M + H]^+$), 513 (100, $[M + H]^+$), 469 (13), 214 (13). Anal. calc. for $C_{30}H_{28}N_2O_6$ (512.56): C 70.30, H 5.51, N 5.47; found: C 70.26, H 5.31, N 5.40.

(S)-3-[(R)-3-(Benzyloxy)-1-oxo-2-(phthalimidomethyl)propyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (**40**). To a soln. of **39** (513 mg, 1.0 mmol) in CH_2Cl_2 (3.2 ml) and hexane (3.2 ml), benzyl trichloroacetimidate (0.22 ml, 1.1 mmol) and CF_3SO_3H (4 drops) were added at 0°. The mixture was stirred for 10 min at 0°, then at r.t. for 16 h, diluted with Et_2O, washed with 1M HCl (2×), 1M NaOH, and sat. NaCl solns., dried ($MgSO_4$), and evaporated. Purification by FC (pentane/Et_2O 1:1) yielded **40** (521 mg, 87%). For anal. purposes, a sample was recrystallized (pentane/Et_2O). White crystals. M.p. 119–121°. $[\alpha]_D^{rt.} = -114.8$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2971*w*, 1776*s*, 1718*s*, 1450*m*, 1395*m*, 1366*m*, 1322*m*, 1178*m*, 1106*m*, 1050*w*, 992*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.65 (*d*, $J = 6.7$, Me); 0.84 (*d*, $J = 7.0$, Me); 1.86–1.93 (*m*, Me_2CH); 3.76 (*dd*, $J = 9.6$, 5.5, 1 H, CH_2N); 3.82–4.04 (*m*, 3 H, CH_2N, CH_2O); 4.41–4.48 (*m*, C(O)CH); $\nu_A = 4.58$, $\nu_B = 4.45$ (*AB*, $J = 11.7$, $PhCH_2$); 5.46 (*d*, $J = 2.9$, NCH); 7.05–7.42 (*m*, 15 arom. H); 7.64–7.76 (*m*, 4 Phth. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.8, 21.6 (Me); 30.1 (CH); 36.3 (CH_2); 43.2, 64.2 (CH); 69.4, 73.3 (CH_2); 89.3 (C); 123.3, 125.6, 125.9, 127.6, 127.9, 128.0, 128.3, 128.4, 128.7 (CH); 131.9 (C); 133.8 (CH); 137.7, 138.3, 142.1, 152.5, 167.8, 171.6 (C). FAB-MS: 603 (100, $[M + H]^+$), 559 (11), 495 (17), 322 (12). Anal. calc. for $C_{37}H_{34}N_2O_6$ (602.69): C 73.74, H 5.69, N 4.65; found: C 73.57, H 5.60, N 4.53.

(S)-3-((R)-2-[[(tert-Butoxycarbonyl)amino]methyl]-1-oxopropyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (**41**). Compound **32** (250 mg, 0.50 mmol) was treated according to *GP 11* to yield, after FC (pentane/Et_2O 3:1), **41** (203 mg, 87%). White solid. M.p. 122–123°. $[\alpha]_D^{rt.} = -174.9$ ($c = 0.77$, $CHCl_3$). IR ($CHCl_3$): 3456*w*, 2972*m*, 1781*s*, 1710*s*, 1506*m*, 1450*m*, 1367*m*, 1175*s*, 1050*m*, 1000*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.77 (*d*, $J = 6.8$, Me); 0.80 (*d*, $J = 7.0$, Me); 0.87 (*d*, $J = 7.0$, Me); 1.41 (*s*, *t*-Bu); 1.94–2.02 (*m*, Me_2CH); 3.26–3.39 (*m*, CH_2N); 3.78–3.88 (*m*, C(O)CH); 4.92 (br. *s*, NH); 5.34 (*d*, $J = 3.4$, NCH); 7.26–7.47 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.3, 16.5, 21.8, 28.4 (Me); 29.7, 38.2 (CH); 43.3 (CH_2); 64.9 (CH); 79.2, 89.6 (C); 125.6, 125.9, 128.0, 128.4, 128.7, 128.9 (CH); 137.9, 142.2, 152.9, 155.8, 175.6 (C). FAB-MS: 934 (20, $[2M + H]^+$), 467 (70, $[M + H]^+$), 411 (92), 367 (89), 238 (100). Anal. calc. for $C_{27}H_{34}N_2O_5$ (466.58): C 69.51, H 7.34, N 6.00; found: C 69.39, H 7.37, N 5.95.

(S)-3-((R)-2-[[(tert-Butoxycarbonyl)amino]methyl]-3-methyl-1-oxobutyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (**42**). Compound **33** (2.22 g, 4.20 mmol) was treated according to *GP 11* to yield, after FC (pentane/Et_2O 4:1 → 2:1), **42** (1.68 g, 81%). White foam. $[\alpha]_D^{rt.} = -124.1$ ($c = 0.73$, $CHCl_3$). IR ($CHCl_3$): 3460*w*, 2970*m*, 1779*s*, 1708*s*, 1507*m*, 1450*m*, 1391*m*, 1367*m*, 1318*m*, 1175*s*, 1052*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.39 (*d*, $J = 6.6$, Me); 0.69 (*d*, $J = 6.7$, Me); 0.79 (*d*, $J = 6.7$, Me); 0.89 (*d*, $J = 7.0$, Me); 1.40 (*s*, *t*-Bu); 1.65–1.75 (*m*, Me_2CH); 1.96–2.05 (*m*, Me_2CH); 3.32–3.48 (*m*, CH_2N); 3.67–3.74 (*m*, C(O)CH); 4.88 (br. *s*, NH); 5.37

(*d*, *J* = 3.4, NCH); 7.23–7.53 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.4, 19.1, 20.0, 21.8, 28.4 (Me); 28.7, 29.7 (CH); 40.5 (CH_2); 48.7, 65.6 (CH); 79.2, 89.4 (C); 125.4, 125.7, 128.0, 128.5, 128.6, 128.9 (CH); 137.8, 142.4, 153.3, 155.6, 175.1 (C). FAB-MS: 990 (6, $[2M+H]^+$), 495 (8, $[M+H]^+$), 440 (26), 395 (100). Anal. calc. for $C_{29}H_{38}N_2O_5$ (494.63): C 70.42, H 7.74, N 5.66; found: C 70.57, H 7.82, N 5.60.

*(*S*)-3-((*R*)-2-[[(*tert*-Butoxycarbonyl)amino]methyl]-1-oxo-3-phenylpropyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**43**). Compound **35** (2.98 g, 5.20 mmol) was treated according to *GP 11* to yield, after FC (pentane/Et_2O 3:1 → 2:1), **43** (2.46 g, 87%). White solid. M.p. 141–142°. $[\alpha]_D^{r.t.} = -104.5$ (*c* = 1.26, $CHCl_3$). IR ($CHCl_3$): 3454 (br.), 3008*m*, 2978*m*, 1779*s*, 1710*s*, 1498*m*, 1450*m*, 1392*m*, 1367*s*, 1318*m*, 1175*s*, 1052*m*, 950*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.77 (*d*, *J* = 6.8, Me); 0.88 (*d*, *J* = 7.0, Me); 1.40 (*s*, *t*-Bu); 1.94–2.02 (*m*, Me_2CH); 2.52–2.56 (*m*, 1 H, $PhCH_2$); 2.71–2.76 (*m*, 1 H, $PhCH_2$); 3.30–3.48 (*m*, CH_2N); 4.21 (br. *m*, C(O)CH); 4.92 (br. *s*, NH); 5.35 (*d*, *J* = 3.3, NCH); 6.92 (br. *m*, 2 arom. H); 7.07 (br. *m*, 3 arom. H); 7.24–7.40 (*m*, 10 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 21.8, 28.4 (Me); 29.9 (CH); 35.2, 42.2 (CH_2); 44.6 (CH); 64.9 (CH_2); 79.3, 89.5 (C); 125.4, 125.8, 126.4, 128.0, 128.4, 128.4, 128.6, 128.7, 128.9 (CH); 137.8, 138.0, 142.0, 153.0, 155.6, 174.0 (C). FAB-MS: 1085 (30, $[2M+H]^+$), 543 (62, $[M+H]^+$), 487 (36), 443 (100), 412 (17), 238 (23). Anal. calc. for $C_{33}H_{38}N_2O_5$ (542.68): C 73.04, H 7.06, N 5.16; found: C 72.88, H 7.19, N 5.13.

*(*S*)-3-[(*R*)-3-Hydroxy-1-oxo-3-phenylpropyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**44**). Compound (*S*)-**7** (1.62 g, 5 mmol) was transformed with PhCHO (0.55 ml, 5.5 mmol) according to *GP 9*. Purification of the crude product by FC (pentane/Et_2O 3:1 → 1:2) gave **44** as a 89:11 mixture with its epimer **45** (1.88 g, 88%). Recrystallization (pentane/Et_2O) yielded pure **44** (0.64 g, 30%). White needles. M.p. 121–123°. $[\alpha]_D^{r.t.} = -129.7$ (*c* = 0.98, $CHCl_3$). IR ($CHCl_3$): 3544*w*, 3036*w*, 2966*w*, 1783*s*, 1692*m*, 1450*m*, 1371*s*, 1177*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.79 (*d*, *J* = 6.8, Me); 0.93 (*d*, *J* = 7.0, Me); 1.96–2.07 (*m*, Me_2CH); 3.09 (*d*, *J* = 3.1, OH); 3.15 (*dd*, *J* = 16.9, 9.3, 1 H, C(O)CH_2); 3.43 (*dd*, *J* = 16.9, 3.1, 1 H, C(O)CH_2); 5.21 (*d*, *J* = 9.3, PhC*H*); 5.43 (*d*, *J* = 3.3, NCH); 7.25–7.52 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 21.8 (Me); 29.9 (CH); 44.1 (CH_2); 64.6, 70.4 (CH); 89.7 (C); 125.5, 125.8, 125.9, 127.8, 128.0, 128.4, 128.5, 128.7, 129.0 (CH); 138.0, 142.1, 142.3, 152.9, 172.0 (C). FAB-MS: 859 (9, $[2M+H]^+$), 430 (11, $[M+H]^+$), 412 (100). Anal. calc. for $C_{27}H_{27}NO_4$ (429.51): C 75.50, H 6.34, N 3.26; found: C 75.39, H 6.46, N 3.29.

*(*S*)-3-[(*S*)-3-Hydroxy-1-oxo-3-phenylpropyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**45**). To a soln. of (*S*)-**7** (1.62 g, 5 mmol) in CH_2Cl_2 (25 ml), $TiCl_4$ (0.63 ml, 5.5 mmol) and $EtN(i\text{-}Pr)_2$ (1.03 ml, 6 mmol) were added at 0°. The resulting dark red soln. was stirred at 0° for 30 min, cooled to −78°, and PhCHO (1.01 ml, 10 mmol) was added. The mixture was allowed to warm to 0° over a period of 6 h before addition of sat. NH_4Cl soln. The mixture was diluted with CH_2Cl_2, washed with 1M HCl (2×), 1M NaOH, and sat. NaCl solns., dried ($MgSO_4$), and evaporated. Purification by FC (pentane/Et_2O 3:1 → 1:1) yielded **45** as a 87:13 mixture with its epimer **44** (1.77 g, 82%). Recrystallization (AcOEt/hexane) yielded **45** (1.22 g, 57%, dr 95:5). White crystals. M.p. 146–148°. $[\alpha]_D^{r.t.} = -189.7$ (*c* = 0.94, $CHCl_3$). IR ($CHCl_3$): 3532*w*, 3008*w*, 2970*w*, 1783*s*, 1694*m*, 1450*m*, 1372*s*, 1176. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.75 (*d*, *J* = 6.8, Me); 0.87 (*d*, *J* = 7.0, Me); 1.93–2.03 (*m*, Me_2CH); 3.10 (*dd*, *J* = 17.1, 2.9, 1 H, C(O)CH_2); 3.30 (*d*, *J* = 4.6, OH); 3.44 (*dd*, *J* = 17.1, 9.7, 1 H, C(O)CH_2); 5.06 (*ddd*, *J* = 9.6, 4.5, 2.9, PhC*H*); 5.41 (*d*, *J* = 3.4, NCH); 7.22–7.49 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 21.8 (Me); 30.0 (CH); 44.0 (CH_2); 64.7, 70.1 (CH); 89.7 (C); 125.6, 125.7, 125.9, 127.7, 128.1, 128.4, 128.5, 128.7, 129.0 (CH); 137.9, 142.2, 142.4, 153.0, 172.1 (C). FAB-MS: 430 (18, $[M+H]^+$), 412 (100), 368 (12). Anal. calc. for $C_{27}H_{27}NO_4$ (429.51): C 75.50, H 6.34, N 3.26; found: C 75.70, H 6.49, N 3.19.

*(*S*)-3-[(2*S*,3*S*)-3-Hydroxy-2-methyl-1-oxo-3-phenylpropyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**46**) *and (*S*)-3-[(2*R*,3*S*)-3-Hydroxy-2-methyl-1-oxo-3-phenylpropyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**50**). Compound (*S*)-**8** (1.69 g, 5 mmol) was treated with PhCHO (0.55 ml, 5.5 mmol) according to *GP 9*. FC (pentane/Et_2O 3:1 → 1:1) yielded **46** as a 3:2 mixture with its epimer **50** (1.71 g, 77%). For anal. purposes a sample was further purified by FC and recrystallization to yield pure **46** and **50**.

Data of **46**: White foam. $[\alpha]_D^{r.t.} = -142.5$ (*c* = 0.89, $CHCl_3$). IR ($CHCl_3$): 3600–3300 (br.), 2970*w*, 1780*s*, 1684*m*, 1450*m*, 1365*m*, 1177*m*, 990*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.77 (*d*, *J* = 6.8, Me); 0.88 (*d*, *J* = 7.0, Me); 1.21 (*d*, *J* = 7.1, Me); 1.90–2.04 (*m*, Me_2CH); 2.91 (*d*, *J* = 2.6, OH); 3.94 (*dq*, *J* = 7.1, 3.6, C(O)CH); 4.80 (*t*, *J* = 3.1, PhC*H*); 5.40 (*d*, *J* = 3.4, NCH); 7.16–7.46 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.1, 16.3, 21.8 (Me); 30.0, 44.3, 64.3, 72.9 (CH); 89.5, (C); 125.6, 125.9, 126.0, 127.4, 128.1, 128.2, 128.4, 128.7, 129.0 (CH); 138.0, 141.1, 142.1, 152.5, 176.8 (C). FAB-MS: 444 (38, $[M+H]^+$), 426 (100). Anal. calc. for $C_{28}H_{29}NO_4$ (443.54): C 75.82, H 6.59, N 3.16; found: C 75.81, H 6.72, N 3.05.

Data of **50**: Colorless oil. $[\alpha]_D^{r.t.} = -193.5$ (*c* = 0.82, $CHCl_3$). IR ($CHCl_3$): 3620*w*, 3600–3300 (br.), 3008*w*, 2973*w*, 1781*s*, 1696*m*, 1450*m*, 1370*m*, 1177*m*, 1047*m*, 1000*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.66 (*d*, *J* = 6.7, Me); 0.74 (*d*, *J* = 7.0, Me); 0.76 (*d*, *J* = 7.0, Me); 1.86–1.97 (*m*, Me_2CH); 3.24 (*d*, *J* = 7.7, OH); 4.24 (*dq*, *J* = 7.7, 7.0, C(O)CH); 4.73 (*t*, *J* = 7.7, PhC*H*); 5.34 (*d*, *J* = 3.3, NCH); 7.20–7.46 (*m*, arom. H). ^{13}C-NMR (100 MHz,

$CDCl_3$): 15.0, 16.5, 21.9 (Me); 30.1, 44.2, 65.4, 77.4 (CH); 90.0 (C); 126.0, 126.3, 126.9, 128.2, 128.4, 128.8, 128.9, 129.1, 129.3 (CH); 138.3, 142.6, 142.6, 153.7, 176.8 (C). FAB-MS: 444 (35, $[M+H]^+$), 426 (100). Anal. calc. for $C_{28}H_{29}NO_4$ (443.54): C 75.82, H 6.59, N 3.16; found: C 75.86, H 6.81, N 3.08.

*(*S*)-3-[(2*S*,3*R*)-3-Hydroxy-2,4-dimetyl-1-oxopentyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**47**). Compound (*S*)-**8** (1.69 g, 5 mmol) was transformed with isobutyraldehyde (0.46 ml, 5.5 mmol) according to *GP 9* to yield, after FC (pentane/Et_2O 3:1 → 1:1), **47** as a 96:4 mixture with its epimer **49** (1.02 g, 50%). For anal. purposes, a sample was recrystallized (pentane/Et_2O) to yield pure **47**. White solid. M.p. 104–105°. $[\alpha]_D^{r.t.} = -181.9$ ($c = 0.85$, $CHCl_3$). IR ($CHCl_3$): 3522*w*, 2969*m*, 1780*s*, 1688*m*, 1450*m*, 1364*m*, 1316*m*, 1177*m*, 990*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.71 (*d*, $J = 6.6$, Me); 0.75 (*d*, $J = 6.8$, Me); 0.78 (*d*, $J = 6.8$, Me); 0.87 (*d*, $J = 7.0$, Me); 1.26 (*d*, $J = 7.0$, Me); 1.38–1.50 (*m*, Me_2CH); 1.94–2.06 (*m*, Me_2CH); 2.36 (*d*, $J = 3.7$, OH); 3.17 (*ddd*, $J = 7.6$, 3.9, 3.7, CH(OH)); 3.78 (*dq*, $J = 7.0$, 4.0, C(O)CH); 5.37 (*d*, $J = 3.5$, NCH); 7.17–7.52 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.5, 16.4, 18.1, 19.0, 21.7 (Me); 29.8, 30.5, 39.9, 64.7, 76.6 (CH); 89.5 (C); 125.5, 125.8, 128.1, 128.5, 128.7, 128.9 (CH); 137.9, 142.4, 152.6, 177.3 (C). FAB-MS: 410 (100, $[M+H]^+$), 392 (39). Anal. calc. for $C_{25}H_{31}NO_4$ (409.52): C 73.32, H 7.63, N 3.42; found: C 73.28, H 7.90, N 3.43.

*(*S*)-3-[(2*R*,3*R*)-3-Hydroxy-2-methyl-1-oxo-3-phenylpropyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**48**) [28]. To a soln. of (*S*)-**8** (1.69 g, 5 mmol) in THF (25 ml), BuLi (3.46 ml, 5.5 mmol) was added at −78°. The clear soln. was stirred for 30 min at this temp. before addition of (i-PrO)$_3$TiCl (1.79M soln. in hexane; 8.66 ml, 15.5 mmol). The resulting yellow soln. was allowed to warm to −40° over a period of 1 h, then cooled to −78°, and PhCHO (0.56 ml, 5.5 mmol) was added. The mixture was allowed to warm to −40° over a period of 3 h, treated with sat. NH_4Cl soln. and diluted with Et_2O. The org. phase was washed with 1M HCl (2×), 1M NaOH (2×), and sat. NaCl solns., dried ($MgSO_4$), and evaporated. The resulting crude product was purified by FC (pentane/Et_2O 2:1 → 1:2) to yield **48** as a 93:7 mixture with epimers (1.92 g. 87%). Recrystallization (AcOEt/hexane) yielded pure **48** (1.46 g, 66%). M.p. 163–164°. $[\alpha]_D^{r.t.} = -158.8$ ($c = 1.34$, $CHCl_3$). IR ($CHCl_3$): 3608*w*, 3500*w*, 3008*w*, 2969*w*, 1780*s*, 1696*m*, 1450*m*, 1366*s*, 1176*s*, 1052*m*, 992*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.66 (*d*, $J = 6.7$, Me); 0.77 (*d*, $J = 7.0$, Me); 0.79 (*d*, $J = 6.9$, Me); 1.87–1.98 (*m*, Me_2CH); 2.81 (*d*, $J = 3.1$, OH); 4.04–4.11 (*m*, C(O)CH); 5.18 (*t*, $J = 3.7$, PhCH); 5.35 (*d*, $J = 3.3$, NCH); 7.22–7.46 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.5, 16.2, 21.5 (Me); 29.7, 44.0, 64.7, 74.0 (CH); 89.6 (C); 125.6, 125.9, 126.3, 127.6, 128.0, 128.3, 128.4, 128.7, 128.9 (CH); 137.9, 141.4, 142.2, 152.9, 176.1 (C). FAB-MS: 444 (31, $[M+H]^+$), 426 (100). Anal. calc. for $C_{28}H_{29}NO_4$ (443.54): C 75.82, H 6.59, N 3.16; found: C 75.76, H 6.49, N 3.12.

*(*S*)-3-[(2*R*,3*S*)-3-Hydroxy-2,4-dimethyl-1-oxopentyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**49**). Compound (*S*)-**8** (1.69 g, 5 mmol) was transformed with isobutyraldehyde (0.46 ml, 5.5 mmol) according to *GP 8* to yield, after FC (pentane/Et_2O 4:1 → 1:1), **49** as a 4:1 mixture with epimers (1.15 g, 56%). For anal. purposes, a sample was recrystallized (pentane/Et_2O) to yield pure **49**. M.p. 162–163°. $[\alpha]_D^{r.t.} = -172.0$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3526*w*, 2967*m*, 1780*s*, 1685*m*, 1450*m*, 1364*m*, 1317*m*, 1177*m*, 990*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.79 (*d*, $J = 6.8$, Me); 0.81 (*d*, $J = 7.0$, Me); 0.89 (*d*, $J = 7.0$, Me); 0.92 (*d*, $J = 6.8$, Me); 1.03 (*d*, $J = 6.6$, Me); 1.62–1.74 (*m*, Me_2CH); 1.93–2.04 (*m*, Me_2CH); 2.58 (*d*, $J = 4.0$, OH); 3.60–3.63 (*m*, CH(OH)); 3.92 (*dq*, $J = 7.0$, 3.1, C(O)CH); 5.37 (*d*, $J = 3.4$, NCH); 7.26–7.48 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 9.5, 16.4, 18.9, 19.1, 21.7 (Me); 29.8, 31.1, 39.4, 64.6, 77.0 (CH); 89.5 (C); 125.6, 125.9, 128.0, 128.4, 128.7, 128.9 (CH); 138.0, 142.2, 152.8, 177.3 (C). FAB-MS: 410 (100, $[M+H]^+$), 392 (33), 348 (19). Anal. calc. for $C_{25}H_{31}NO_4$ (409.52): C 73.32, H 7.63, N 3.42; found: C 73.49, H 7.49, N 3.35.

*(*S*)-3-[(2*R*,3*S*)-2-Methyl-4-nitro-1-oxo-3-phenylbutyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**52**). Compound (*S*)-**8** (1.69 g, 5 mmol) was treated with (*E*)-β-nitrostyrene (0.82 g, 5.5 mmol) according to *GP 10*. FC (pentane/Et_2O 10:1 → 5:1) yielded **52** as a 9:1 mixture with an epimer (1.91 g, 78%). Recrystallization (pentane/Et_2O) yielded pure **52** (1.42 g, 58%). White needles. M.p. 151–152°. $[\alpha]_D^{r.t.} = -166.8$ ($c = 0.90$, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2973*w*, 1781*s*, 1696*m*, 1557*s*, 1450*m*, 1374*m*, 1177*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.52 (*d*, $J = 6.9$, Me); 0.79 (*d*, $J = 6.8$, Me); 0.89 (*d*, $J = 7.0$, Me); 1.96–2.08 (*m*, Me_2CH); 3.74 (*dt*, $J = 10.2$, 4.2, PhCH); 4.10 (*dq*, $J = 10.3$, 6.9, C(O)CH); 4.65 (*dd*, $J = 12.3$, 4.3, 1 H, CH_2NO_2); 4.81 (*dd*, $J = 12.3$, 10.1, 1 H, CH_2NO_2); 5.33 (*d*, $J = 3.6$, NCH); 7.19–7.46 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.6, 16.7, 21.8 (Me); 29.5, 39.9, 46.6, 65.6 (CH); 78.6 (CH_2); 90.0 (C); 125.5, 125.8, 128.0, 128.2, 128.5, 128.7, 128.9, 129.0 (CH); 137.2, 142.1, 153.0, 175.1 (C). FAB-MS: 487 (100, $[M+H]^+$), 440 (15). Anal. calc. for $C_{29}H_{30}N_2O_5$ (486.57): C 71.59, H 6.21, N 5.76; found: C 71.64, H 6.08, N 5.77.

*(*S*)-3-[(2*R*,3*S*)-3-(4-Methoxyphenyl)-2-methyl-4-nitro-1-oxobutyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**53**). Compound (*S*)-**8** (1.69 g, 5 mmol) was treated with (*E*)-4-methoxy-β-nitrostyrene (0.99 g, 5.5 mmol) according to *GP 10*. FC (pentane/Et_2O 10:1 → 4:1) yielded **53** as a 92:8 mixture with an epimer (2.06 g, 80%). White foam. $[\alpha]_D^{r.t.} = -155.5$ ($c = 1.17$, $CHCl_3$). IR ($CHCl_3$): 2970*w*, 1780*s*, 1698*m*, 1556*s*, 1514*m*, 1450*m*, 1373*m*, 1035*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.52 (*d*, $J = 6.9$, Me); 0.80 (*d*, $J = 6.8$, Me); 0.90 (*d*, $J = 7.0$, Me); 1.96–2.08

(*m*, Me_2CH); 3.68 (*dt*, *J* = 10.2, 4.3, PhC*H*); 3.76 (*s*, MeO); 4.05 (*dq*, *J* = 10.3, 6.9, C(O)CH); 4.61 (*dd*, *J* = 12.1, 4.3, 1 H, CH_2NO_2); 4.75 (*dd*, *J* = 12.1, 10.2, 1 H, CH_2NO_2); 5.33 (*d*, *J* = 3.6, NCH); 6.81–6.85 (*m*, 2 arom. H); 7.10–7.14 (*m*, 2 arom. H); 7.22–7.46 (*m*, 10 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.6, 16.7, 21.8 (Me); 29.5, 40.0, 46.0 (CH); 55.2 (Me); 65.5 (CH); 78.8 (CH_2); 90.0 (C); 114.4, 125.5, 125.8, 128.2, 128.5, 128.7, 128.9, 129.0, 129.0 (CH); 137.6, 142.1, 153.1, 159.2, 175.2 (C). FAB-MS: 517 (100, $[M+H]^+$), 469 (28), 424 (17). Anal. calc. for $C_{30}H_{32}N_2O_6$ (516.59): C 69.75, H 6.24, N 5.42; found: C 69.82, H 6.24, N 5.37.

*(*S*)-4-(1-Methylethyl)-3-[(2*R*,3*S*)-3-[3,4-(methylenedioxy)phenyl]-2-methyl-4-nitro-1-oxobutyl]-5,5-diphenyloxazolidin-2-one* (**54**). Compound (*S*)-**8** (1.69 g, 5 mmol) was treated with (*E*)-3,4-(methylenedioxy)-*β*-nitrostyrene (1.06 g, 5.5 mmol) according to *GP 10*. FC (pentane/Et_2O 10:1 → 4:1) yielded **54** as a 92:8 mixture with an epimer (2.28 g, 86%). Recrystallization (pentane/Et_2O) yielded **54** (1.97 g, 74%); dr 96:4. White powder. M.p. 143–147°. $[\alpha]_D^{rt.} = -143.8$ (*c* = 1.35, $CHCl_3$). IR ($CHCl_3$): 3020*w*, 2990*w*, 1788*s*, 1705*m*, 1564*s*, 1512*m*, 1495*m*, 1457*m*, 1374*m*, 1050*m*, 945*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.53 (*d*, *J* = 6.9, Me); 0.80 (*d*, *J* = 6.8, Me); 0.90 (*d*, *J* = 7.0, Me); 1.97–2.08 (*m*, Me_2CH); 3.65 (*dt*, *J* = 10.3, 4.3, PhC*H*); 4.01 (*dq*, *J* = 10.4, 6.9, C(O)CH); 4.59 (*dd*, *J* = 12.2, 4.3, 1 H, CH_2NO_2); 4.72 (*dd*, *J* = 12.2, 10.3, 1 H, CH_2NO_2); 5.33 (*d*, *J* = 3.6, NCH); $\nu_A = 5.93$, $\nu_B = 5.92$ (*AB*, *J* = 1.5, CH_2O); 6.64–6.76 (*m*, 3 arom. H); 7.24–7.46 (*m*, 10 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.6, 16.7, 21.8 (Me); 29.5, 40.1, 46.5, 65.6 (CH); 78.7 (CH_2); 90.0 (C); 101.2 (CH_2); 108.2, 108.6, 121.8, 125.5, 125.8, 128.2, 128.5, 128.8, 128.9 (CH); 130.7, 137.6, 142.1, 147.3, 148.1, 153.1, 175.1 (C). FAB-MS: 531 (100, $[M+H]^+$), 483 (25), 438 (10). Anal. calc. for $C_{30}H_{30}N_2O_7$ (530.58): C 67.91, H 5.70, N 5.28; found: C 67.91, H 5.68, N 5.51.

*(*S*)-4-(1-Methylethyl)-3-[(2*R*,3*S*)-4-nitro-1-oxo-3-phenyl-2-(phenylmethyl)butyl]-5,5-diphenyloxazolidin-2-one* (**55**). Compound (*S*)-**11** (2.07 g, 5 mmol) was treated with (*E*)-*β*-nitrostyrene (0.82 g, 5.5 mmol) according to *GP 10*. FC (pentane/Et_2O 10:1 → 5:1) yielded **55** as a 97:3 mixture with an epimer (2.61 g, 92%). Recrystallization (AcOEt/hexane) yielded pure **55** (2.01 g, 71%). White crystals. M.p. 184–187°. $[\alpha]_D^{rt.} = -111.1$ (*c* = 0.81, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 1777*s*, 1697*m*, 1556*s*, 1495*m*, 1451*m*, 1364*m*, 1318*m*, 1178*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.67 (*d*, *J* = 6.8, Me); 0.91 (*d*, *J* = 7.1, Me); 1.97–2.04 (*m*, Me_2CH); 2.44 (*dd*, *J* = 14.2, 5.7, 1 H, PhCH_2); 2.62 (*dd*, *J* = 14.2, 7.7, 1 H, PhCH_2); 3.66–3.72 (*m*, PhC*H*); 4.64–4.74 (*m*, CH_2NO_2); 5.08 (*dd*, *J* = 12.4, 10.7, C(O)CH); 5.33 (*d*, *J* = 2.8, NCH); 6.62 (*d*, *J* = 6.8, 2 arom. H); 6.92–7.02 (*m*, 3 arom. H); 7.20–7.40 (*m*, 15 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.3, 21.8 (Me); 30.0 (CH); 35.9 (CH_2); 45.3, 46.9, 65.5 (CH); 77.9 (CH_2); 89.3 (C); 125.0, 125.7, 126.7, 128.0, 128.1, 128.1, 128.3, 128.4, 128.5, 128.7, 129.0, 129.1 (CH); 136.7, 137.3, 137.9, 142.0, 152.9, 173.4 (C). FAB-MS: 563 (100, $[M+H]^+$), 412 (39). Anal. calc. for $C_{35}H_{34}N_2O_5$ (562.66): C 74.71, H 6.09, N 4.98; found: C 74.61, H 6.15, N 4.98.

*(*S*)-4-(1-Methylethyl)-3-[(*R*)/(*S*)-1-oxo-3-phenylbutyl]-5,5-diphenyloxazolidin-2-one* (**56**/**57**) [49]. CuBr·SMe_2 (739 mg, 3.75 mmol) was suspended in THF (11 ml) and cooled to −30°. PhMgBr (7.5 mmol in 10 ml THF) was added, the mixture stirred for 5 min, and (*S*)-**12** (8.74 mg, 2.5 mmol) in THF (6 ml) was added over a period of 15 min. The mixture was allowed to warm to −15° in 1 h, treated with sat. NH_4Cl soln., and diluted with Et_2O. The org. phase was washed with 1M HCl, 1M NaOH, and sat. NaCl solns., dried ($MgSO_4$), and evaporated. The resulting crude product was purified by FC (pentane/Et_2O 12:1 → 8:1) to yield a 2:1 mixture **56**/**57** (988 mg, 92%). Reaction of (*S*)-**13** with MeMgBr under identical conditions yielded a 1:2 mixture **56**/**57** (90%). For anal. purposes, a sample was recrystallized twice to yield a 89:11 mixture of **56**/**57**. White needles. M.p. 107–109°. $[\alpha]_D^{rt.} = -182.4$ (*c* = 0.77, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2969*w*, 1778*s*, 1702*m*, 1450*m*, 1367*m*, 1318*m*, 1176*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.62 (*d*, *J* = 6.8, Me); 0.71 (*d*, *J* = 7.0, Me); 1.19 (*d*, *J* = 6.9, Me); 1.86–1.96 (*m*, Me_2CH); 2.99–3.04 (*m*, PhC*H*); 3.26–3.38 (*m*, C(O)CH_2); 5.36 (*d*, *J* = 3.3, NCH); 7.15–7.52 (*m*, arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.1, 21.5, 21.9 (Me); 29.7, 36.5 (CH); 42.7 (CH_2); 64.5 (CH); 89.2 (C); 125.6, 125.9, 126.3, 127.0, 127.9, 128.4, 128.4, 128.6, 128.9 (CH); 138.1, 142.4, 145.5, 153.0, 171.7 (C). FAB-MS: 428 (100, $[M+H]^+$), 384 (34). Anal. calc. for $C_{28}H_{29}NO_3$ (427.54): C 78.66, H 6.84, N 3.28; found: C 78.58, H 6.81, N 3.22.

*(*S*)-3-[(1*R*,2*R*,3*S*,4*S*)-3-Methylbicyclo[2.2.1]hept-5-ene-2-carbonyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**58**). To a soln. of (*S*)-**12** (874 mg, 2.5 mmol) in CH_2Cl_2 (5 ml), cyclopentadiene (5.15 ml, 62.5 mmol), and $ClAlMe_2$ (3.5 ml, 3.5 mmol) were added at −95°. The mixture stirred for 2 min at −95°, 1M HCl soln. was added, and the mixture extracted with CH_2Cl_2. The org. phase was dried ($MgSO_4$) and the solvent removed under reduced pressure. FC (pentane/Et_2O) yielded **58** (900 mg, 87%). For anal. purposes, a sample was recrystallyzed (AcOEt/hexane). White crystals. M.p. 134–135°. $[\alpha]_D^{rt.} = -69.2$ (*c* = 1.09, $CHCl_3$). IR ($CHCl_3$): 2970*m*, 2874*w*, 1777*s*, 1696*s*, 1450*m*, 1365*m*, 1325*m*, 1176*s*, 1051*m*, 912*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.78 (*d*, *J* = 6.8, Me); 0.84 (*d*, *J* = 7.0, Me); 0.93 (*d*, *J* = 7.1, Me); 1.45–1.48 (*m*, CH); 1.67 (*d*, *J* = 8.6, CH); 1.87–2.00 (*m*, Me_2CH, CH); 2.47 (*d*, *J* = 1.5, CH); 3.30 (*dd*, *J* = 4.6, 3.3, CH); 3.43 (*s*, CH); 5.36 (*d*, *J* = 3.1, NCH); 5.85 (*dd*, *J* = 5.7, 2.8, C=CH); 6.37 (*dd*, *J* = 5.7, 3.2, C=CH); 7.25–7.50 (*m*, arom. H). ^{13}C-NMR (100 MHz,

$CDCl_3$): 16.3, 20.3, 21.9 (Me); 29.9, 36.4 (CH); 47.4 (CH_2); 48.0, 49.4, 51.5, 64.4 (CH); 89.3 (C); 125.8, 126.0, 127.9, 128.3, 128.5, 128.8, 131.2 (CH); 138.4 (C); 139.7 (CH); 142.4, 153.0, 174.0 (C). FAB-MS: 416 (70, $[M+H]^+$), 350 (100), 306 (22). Anal. calc. for $C_{27}H_{29}NO_3$ (415.53): C 78.04, H 7.03, N 3.37; found: C 77.87, H 7.02, N 3.44.

*(*R*)-2-Methyl-3-phenylpropanoic Acid* (**60**). a) *Cleavage by LiOH/H_2O_2* [14]: To a soln. of **27** (1.07 g, 2.5 mmol) in THF/H_2O (10 ml/2.5 ml), H_2O_2 (30% aq. soln.; 1.03 ml, 10 mmol) and $LiOH \cdot H_2O$ (168 mg, 4.0 mmol) were added at 0°. The mixture was stirred at 0° for 1.5 h before addition of a soln. of Na_2SO_3 (1.25 g, 10 mmol) in H_2O (7.5 ml), H_2O (10 ml), and 1M NaOH soln. (10 ml). THF was removed under reduced pressure, Et_2O (20 ml) added, the suspension stirred for 15 min, and filtered. The residue was washed with 1M NaOH soln. (10 ml), H_2O, Et_2O (10 ml), and pentane (10 ml), and dried (h.v.) to yield (*S*)-**1** (552 mg, 79%) as white powder. The filtrate was diluted with Et_2O, the aq. phase separated, the pH adjusted to 1–2 with 6M HCl, and extracted with Et_2O (2×). The org. phases were washed with sat. NaCl soln., dried ($MgSO_4$), and evaporated. The crude product was purified by bulb-to-bulb distillation (0.5 Torr, 120°) to yield **60** (323 mg, 79%) as colorless liquid.

b) *Cleavage by NaOH:* To a soln. of **27** (1.07 g, 2.5 mmol) in MeOH/THF (5 ml/5 ml), 1M aq. NaOH soln. (4 ml) was added, and the mixture stirred for 2.5 h at r.t. Workup according to *a* yielded (*S*)-**1** (580 mg, 83%) as white powder and **60** (318 mg, 78%) as colorless liquid. The enantiomeric purity was determined by HPLC to be >99% after conversion to **61** with CH_2N_2 (see below). $[\alpha]_D^{rt} = -25.9$ ($c = 1.1$, $CHCl_3$) ([40]: $[\alpha]_D^{rt} = -23.1$ ($c = 1.0$, $CHCl_3$)). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.19 (*d*, $J = 6.6$, Me); 2.64–2.82 (*m*, 2 H, PhCH_2, C(O)CH); 3.08 (*dd*, $J = 13.1$, 5.9, 1 H, PhCH_2); 7.19–7.35 (*m*, arom. H).

*Methyl (*R*)-2-Methyl-3-phenylpropanoate* (**61**) [19]. To a soln. of **27** (1.07 g, 2.5 mmol) in THF (10 ml) and MeOH (25 ml), LiBr (1.09 g, 12.5 mmol) and DBU (0.75 ml, 5 mmol) were added at 0°. The mixture was stirred at r.t. for 4 h, sat. NH_4Cl soln., H_2O (50 ml), and Et_2O (20 ml) were added, and the suspension was stirred for 15 min and filtered. The residue was washed with H_2O, Et_2O (10 ml), and pentane (10 ml), and dried (h.v.) to yield (*S*)-**1** (644 mg, 92%) as white powder. The filtrate was diluted with Et_2O, the aq. phase separated, and the org. phase washed with 1M HCl and sat. NaCl solns., dried ($MsSO_4$), and evaporated. FC (pentane/Et_2O 20:1 → 15:1) of the crude product yielded **61** (408 mg, 92%) as colorless liquid. The enantiomeric purity was determined by HPLC on a *Chiralcel OD* column (hexane/i-PrOH 99.75:0.25; flow 1 ml/min, detection at 254 nm; t_R of (*R*)-**61**: 15 min, of (*S*)-**61**: 19 min) to be >99%. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*d*, $J = 6.9$, Me); 2.63–2.81 (*m*, 2 H, PhCH_2, C(O)CH); 3.03 (*dd*, $J = 12.8$, 6.2, 1 H, PhCH_2); 3.64 (*s*, MeO); 7.16–7.34 (*m*, arom. H).

*Benzyl (*R*)-2-Methyl-3-phenylpropanoate* (**62**) [20]. To a soln. of BnOH in THF (12.5 ml), BuLi (2.35 ml, 3.75 mmol) was added at 0° and the mixture stirred for 10 min before addition of **27** (1.07 g, 2.5 mmol). After 2 h at 0°, sat. NH_4Cl soln. and H_2O were added, THF was removed under reduced pressure, and Et_2O was (20 ml) added. The suspension was stirred for 15 min and filtered. The residue was washed with H_2O (50 ml), Et_2O (10 ml), and pentane (10 ml), then dried (h.v.) to yield (*S*)-**1** (642 mg, 91%) as white powder. The filtrate was diluted with Et_2O, the aq. phase separated, and the org. phase washed with 1M HCl, 1M NaOH, and sat. NaCl solns., dried ($MgSO_4$), and evaporated. FC (pentane/Et_2O 15:1) of the crude product yielded **62** (580 mg, 91%) as colorless liquid. $[\alpha]_D^{rt} = -27.8$ ($c = 6.40$, CH_2Cl_2) ([20]: $[\alpha]_D^{rt} = -26.9$ ($c = 6.12$, CH_2Cl_2)). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.19 (*d*, $J = 6.6$, Me); 2.66–2.86 (*m*, 2 H, PhCH_2, C(O)CH); 3.04 (*dd*, $J = 13.1$, 6.8, 1 H, PhCH_2); 5.08 (*s*, CH_2O); 7.14–7.38 (*m*, arom. H).

*(*R*)-2-Methyl-3-phenylpropan-1-ol* (**63**) [37]. To a soln. of **27** (428 mg, 1.0 mmol) in Et_2O (10 ml), $LiAlH_4$ (300 mg, 8 mmol) was added, and the mixture stirred at r.t. for 2 h, cooled to 0°, and 1M NaOH soln. (5 ml) and Et_2O were added. The org. layer was separated and washed with 1M HCl and sat. NaCl solns., dried ($MgSO_4$), and evaporated. FC (pentane/Et_2O 2:1 → 1:1) yielded **63** (117 mg, 78%) as colorless oil. The enantiomeric purity was determined by HPLC on a *Chiralcel OD* column (hexane/i-PrOH 97:3; flow 1 ml/min, detection at 254 nm; t_R of (*S*)-**63**: 14 min, of (*R*)-**63**: 18 min) to be >99%. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.92 (*d*, $J = 6.9$, Me); 1.34 (br. *s*, OH); 1.87–2.03 (*m*, C(O)CH); 2.43 (*dd*, $J = 13.4$, 8.0, 1 H, PhCH_2); 2.76 (*dd*, $J = 13.5$, 6.3, 1 H, PhCH_2); 3.43–3.59 (*m*, CH_2O); 7.16–7.35 (*m*, arom. H).

X-Ray Crystal-Structure Determination of **11**, **29**, **30**, **55**, **58**, *and* **64** (see *Table 2* and *Figs. 1–3*). The intensities were collected on an *Enraf-Nonius-CAD-4* four circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å, for **11**, **29**, **30**, and **64**; graphite monochromatized CuK_α radiation, $\lambda = 1.5418$ Å, for **55** and **58**). The structures were solved by direct method with SHELXS-96 (**11**, **29**, and **58**). Part of the structure was solved by direct methods, the remaining non-H-atoms were found from a difference *Fourier* map with SHELXS-96 (**30** and **55**). Part of the structure of **64** was solved by *Patterson* method, the remaining non-H-atoms were found from a difference *Fourier* map with SHELXS-96. The non-H-atoms were refined anisotropically with SHELXL-97. H-Atoms were obtained from a difference *Fourier* map and refined

isotropically (**11** and **58**). H-Atoms were calculated at idealized positions and refined isotropically (**29**). H-Atoms were calculated at idealized positions and included in the structure factor calculation with fixed isotropic displacement parameters (**30** and **55**). H-Atoms were calculated at idealized positions and refined with constrained isotropic displacement parameters (**64**).

Table 2. *Crystallographic Data for the Oxazolidin-2-ones* **11**, **29**, **30**, **55**, **58**, *and* **64**

	11	**29**	**30**	**55**	**58**	**64** · CH_2Cl_2
Crystallized from	Et_2O	Et_2O/pentane	Et_2O/pentane	AcOEt	AcOEt	CH_2Cl_2
Empirical formula	$C_{27}H_{27}NO_3$	$C_{31}H_{33}NO_5$	$C_{28}H_{35}NO_5$	$C_{35}H_{34}N_2O_5$	$C_{27}H_{29}NO_3$	$C_{14}H_{17}Cl_6NO_3Ti$
Crystal temp. [K]	180	180	220	293	170	180
Crystal dimensions [mm]	$0.3 \times 0.2 \times 0.1$	$0.3 \times 0.3 \times 0.2$	$0.4 \times 0.3 \times 0.2$	$0.1 \times 0.1 \times 0.02$	$0.4 \times 0.2 \times 0.2$	$0.4 \times 0.2 \times 0.1$
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Lattice parameters						
2θ range [°]	$3 < 2\theta < 54$	$4 < 2\theta < 50$	$3 < 2\theta < 50$	$5 < 2\theta < 121$	$8 < 2\theta < 136$	$4 < 2\theta < 56$
a [Å]	10.958(4)	10.241(6)	10.839(10)	6.436(2)	9.1028(10)	7.344(6)
b [Å]	8.554(6)	14.038(9)	9.017(10)	13.125(3)	12.618(6)	12.622(6)
c [Å]	12.761(4)	10.251(9)	13.986(8)	18.596(6)	19.248(4)	11.011(4)
α [°]	90	90	90	77.10(2)	90	90
β [°]	111.88(2)	111.60(7)	107.97(8)	83.23(3)	90	91.96(7)
γ [°]	90	90	90	89.39(3)	90	90
V [Å^3]	1110.0(9)	1370(2)	1300(2)	1520.4(8)	2210.8(12)	1020.1(10)
Space group	$P2_1$	$P2_1$	$P2_1$	P_1	$P2_12_12_1$	$P2_1$
Z	2	2	2	2	4	2
ρ_{calc} [g cm^{-3}]	1.237	1.211	1.189	1.229	1.248	1.654
μ [mm^{-1}]	0.080	0.082	0.081	0.662	0.639	1.219
Total reflections measured	2662	2518	2560	2368	2324	2750
Independent reflections	2514	2518	2437	4548	2299	2565
Reflections observed	2073	2310	1971	2368	2231	2087
Criterion	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Variables	361	434	307	756	368	276
Final R	0.0390	0.0278	0.0557	0.0672	0.0357	0.0466
wR_2	0.1078	0.0832	0.1334	0.1516	0.1065	0.1276
Goodness of fit	1.003	0.852	1.209	1.274	1.133	1.113
$\Delta\rho$ (max, min) [eÅ^{-3}]	0.25, −0.22	0.15, −0.14	0.24, −0.37	0.25, −0.38	0.32, −0.20	0.60, −0.98

REFERENCES

[1] D. Seebach, E. Hungerbühler, in 'Modern Synthetic Methods', Ed. R. Scheffold, Salle + Sauerländer, Frankfurt am Main, Aarau, 1980, p. 91 – 171; D. Seebach, R. Imwinkelried, T. Weber, in 'Modern Synthetic Methods', Ed. R. Scheffold, Springer Verlag, Berlin, 1986, p. 125 – 259; G. Helmchen, J. Mulzer, in ' Houben Weyl, Methods of Organic Chemistry', 4th edn., Eds. G. Helmchen, R. W. Hoffmann, J. Mulzer, and E. Schaumann, Thieme, Stuttgart-New York, 1995, Vol. E21a, p. 1 – 146.

[2] K. Drauz, A. Kleemann, J. Martens, *Angew. Chem.* **1982**, *94*, 590 – 613; H. Kunz, K. Rück, *ibid., Int. Ed. Engl.* **1993**, *105*, 355 – 377; W. Oppolzer, *Tetrahedron* **1987**, *43*, 1969 – 2004; J. K. Whitesell, *Chem. Rev.* **1992**, *92*, 953 – 964; A. Studer, *Synthesis* **1996**, 793 – 815.

[3] D. A. Evans, *Aldrichim. Acta* **1982**, *15*, 23; D. J. Ager, I. Prakash, D. R. Schaad, *Chem. Rev.* **1996**, *96*, 835 – 875; D. J. Ager, I. Prakash, D. R. Schaad, *Aldrichim. Acta* **1997**, *30*, 3.
[4] D. A. Evans, H. Bartroli, T. L. Shih, *J. Am. Chem. Soc.* **1981**, *103*, 2127.
[5] E. A. Evans, E. B. Sjogren, *Tetrahedron Lett.* **1985**, *26*, 3788; D. A. Evans, A. E. Weber, *J. Am. Chem. Soc.* **1986**, *108*, 6757.
[6] See *e.g.*: M. P. Bonner, E. R. Thornton, *J. Am. Chem. Soc.* **1991**, *113*, 1299; C. Palomo, F. Berrée, A. Linden, J. M. Villalgordo, *J. Chem. Soc., Chem. Commun.* **1994**, 1861; M. P. Sibi, P. K. Deshpande, A. J. La Loggia, J. W. Christensen, *Tetrahedron Lett.* **1995**, *36*, 8961.
[7] S. G. Davies, H. J. Sanganee, *Tetrahedron: Asymmetry* **1995**, *6*, 671; C. Cardillo, L. Gentilucci, C. Tomasini, L. Tomasoni, *ibid.* **1995**, *6*, 1947; G. Cardillo, E. Di Martino, L. Gentilucci, C. Tomasini, L. Tomasoni, *ibid.* **1995**, *6*, 1957.
[8] W. Oppolzer, C. Chapuis, G. Bernardinelli, *Helv. Chim. Acta* **1984**, *67*, 1397.
[9] H. Roder, G. Helmchen, E.-M. Peters, K. Peters, H.-G. von Schnering, *Angew. Chem.* **1984**, *96*, 895.
[10] P. Delair, C. Einhorn, J. Einhorn, J. L. Luche, *J. Org. Chem.* **1994**, *59*, 4680.
[11] R. E. Gawley, P. Zhang, *J. Org. Chem.* **1996**, *61*, 8103.
[12] S. Itsuno, K. Ito, A. Hirao, S. Nakahama, *J. Org. Chem.* **1984**, *49*, 555.
[13] F. Wessely, H. Pawloy, W. Rizzi, *Monatsh. Chem.* **1955**, *86*, 75 – 87.
[14] J. R. Gage, D. A. Evans, *Org. Synth.* **1990**, *68*, 83.
[15] G.-J. Ho, D. J. Mathre, *J. Org. Chem.* **1995**, *60*, 2271.
[16] A. Dobarro, D. Velasco, *Tetrahedron* **1996**, *52*, 13733.
[17] C. Thom, P. Kocienski, *Synthesis* **1996**, 582; J. Y. Lee, Y. J. Chung, B. H. Kim, *Synlett* **1994**, 197; D. J. Ager, D. R. Allen, D. E. Froen, D. R. Schaad, *Synthesis* **1996**, 1283; S. Fonquerna, A. Moyano, M. A. Pericàs, A. Riera, *Tetrahedron: Asymmetry* **1997**, *8*, 1685.
[18] D. Seebach, A. K. Beck, A. Studer, in 'Modern Synthetic Methods', Eds. B. Ernst and C. Leumann, VHCA, Basel/VCH, Weinheim, 1995, p. 1 – 178.
[19] A. Studer, T. Hintermann, D. Seebach, *Helv. Chim. Acta* **1995**, *78*, 1185 – 1206.
[20] D. A. Evans, M. D. Ennis, D. J. Mathre, *J. Am. Chem. Soc.* **1982**, *104*, 1737.
[21] D. Seebach, J. L. Matthews, *J. Chem. Soc., Chem. Commun.* **1997**, 2015.
[22] D. A. Evans, F. Urpi, T. C. Somers, J. S. Clark, M. T. Bilodeau, *J. Am. Chem. Soc.* **1990**, *112*, 8215.
[23] A. A. D'Souza, M. Motevalli, A. J. Robinson, P. B. Wyatt, *J. Chem. Soc., Perkin Trans. 1* **1995**, 1; E. Arvanitis, H. Ernst, A. A. Ludwig, A. J. Robinson, P. B. Wyatt, *ibid.* **1998**, 521.
[24] T. Hintermann, D. Seebach, *Synlett* **1997**, 437; D. Seebach, S. Abele, K. Gademann, G. Guichard, T. Hintermann, B. Jaun, J. L. Matthews, J. V. Schreiber, L. Oberer, U. Hommel, H. Widmer, *Helv. Chim. Acta* **1998**, *81*, 932 – 982.
[25] C. J. Barnett, T. M. Wilson, D. A. Evans, T. C. Somers, *Tetrahdron Lett.* **1997**, *38*, 735.
[26] D. Seebach, R. Charczuk, C. Gerber, P. Renaud, H. Berner, H. Schneider, *Helv. Chim. Acta* **1989**, *72*, 401 – 425.
[27] D. A. Evans, D. L. Rieger, M. T. Bilodeau, F. Urpi, *J. Am. Chem. Soc.* **1991**, *113*, 1047.
[28] M. Nerz-Stormes, E. R. Thornton, *J. Org. Chem.* **1991**, *56*, 2489.
[29] M. Braun, R. Devant, *Tetrahedron Lett.* **1984**, *25*, 5031.
[30] N. W. Boaz, *J. Org. Chem.* **1992**, *57*, 4289.
[31] N. A. Van Draanen, S. Arseniyadi, M. T. Crimmins, C. H. Heathcock, *J. Org. Chem.* **1991**, *56*, 2499.
[32] H. E. Zimmerman, M. D. Traxler, *J. Am. Chem. Soc.* **1957**, *79*, 1920.
[33] T. Hintermann, K. Gademann, B. Jaun, D. Seebach, *Helv. Chim. Acta* **1998**, *81*, 983; S. Hanessian, X. Luo, R. Schaum, S. Michnik, *J. Am. Chem. Soc.* **1998**, *120*, 8569.
[34] J. Mulzer, R. Zuhse, R. Schmiechen, *Angew. Chem.* **1992**, *104*, 914.
[35] G. Calderari, D. Seebach, *Helv. Chim. Acta* **1985**, *68*, 1592 – 1604; D. Seebach, A. K. Beck, J. Golinski, J. N. Hay, T. Laube, *ibid.* **1985**, *68*, 162 – 172; R. Häner, T. Laube, D. Seebach, *Chimia* **1984**, *38*, 255; D. Seebach, J. Golinski, *Helv. Chim. Acta* **1981**, *64*, 1413 – 1423; D. Seebach, H. F. Leitz, V. Ehrig, *Chem. Ber.* **1975**, *108*, 1924 – 1945; D. Seebach, H. F. Leitz, *Angew. Chem.* **1971**, *83*, 542; D. Seebach, H. F. Leitz, *ibid.* **1969**, *81*, 1047.
[36] D. A. Evans, K. T. Chapman, J. Bisaha, *J. Am. Chem. Soc.* **1988**, *110*, 1238 – 1256.
[37] D. Seebach, R. Dahinden, R. E. Marti, A. K. Beck, D. A. Plattner, F. N. M. Kühnle, *J. Org. Chem.* **1995**, *60*, 1788 – 1799.
[38] D. A. Evans, T. C. Britton, J. A. Ellman, *Tetrahedron Lett.* **1987**, *28*, 6141.
[39] D. A. Evans, R. L. Dow, T. L. Shih, J. M. Takacs, R. Zahler, *J. Am. Chem. Soc.* **1990**, *112*, 5290 – 5313.

[40] E. Tyrrell, M. W. H. Tsang, G. A. Skinner, J. Fawcett, *Tetrahedron* ***1996***, *52*, 9841.
[41] D. A. Evans, R. P. Polniaszek, K. M. DeVries, D. E. Guinn, D. S. Mathre, *J. Am. Chem. Soc.* **1991**, *113*, 7613 – 7630.
[42] R. Koradi, M. Billeter, K. Wüthrich, *J. Mol. Graphics* **1996**, *14*, 51.
[43] D. Seebach, R. Häner, T. Vettiger, *Helv. Chim. Acta* **1987**, *70*, 1507.
[44] M. Ertas, D. Seebach, *Helv. Chim. Acta* **1985**, *68*, 961; R. Häner, T. Laube, D. Seebach, *J. Am Chem. Soc*. **1985**, *107*, 5396.
[45] D. Seebach, E. Pfammatter, V. Gramlich, T. Bremi, F. N. M. Kühnle, S. Portmann, I. Tironi, *Liebigs Ann. Chem.* **1992**, 1145; D. Seebach, M. Ertas, R. Locher, W. B. Schweizer, *Helv. Chim. Acta* **1985**, *68*, 264 – 282.
[46] W. Lubosch, D. Seebach, *Helv. Chim. Acta* **1980**, *63*, 102 – 116; T. Hassel, D. Seebach, *Angew. Chem.* **1979**, *91*, 427; R. Schlecker, D. Seebach, W. Lubosch, *Helv. Chim. Acta* **1978**, *61*, 512 – 526; R. Schlecker, D. Seebach, *ibid*. **1977**, *60*, 1459 – 1471.
[47] H.-M. Müller, Diss. ETH No. 9685, ETH Zürich, 1992.
[48] D. G. Doherty, *J. Am. Chem. Soc*. **1955**, *77*, 4887.
[49] E. Nicolás, K. C. Russell, V. J. Hruby, *J. Org. Chem.* **1993**, *58*, 766.

Received September 4, 1998