Metallations and Reactions with Electrophiles of 4-Isopropyl-5,5-diphenyloxazolidin-2-one (DIOZ) with *N*-Allyl and *N*-Propargyl Substituents: Chiral Homoenolate Reagents

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N-Allyl, *N*-cinnamyl, and *N*-(3-trimethylsilyl)propargyl derivatives of 4-isopropyl-5,5-diphenyloxazolidin-2-one (DIOZ) are prepared by lithiation of the parent DIOZ (with BuLi in THF) and reaction with the corresponding bromides (*Scheme 1*). Lithiation in the same solvent, with deprotonation by BuLi on the allylic or propargylic CH_2 group at dry-ice temperature, provides colorful solutions, which are either combined with aldehydes or ketones directly or after addition (with or without warming) of $(Me_2N)_3TiCl$ or $(i\text{-}PrO)_3TiCl$. Conditions have thus been elaborated under which all three types of conjugated lithium compounds react in the γ-position with respect to the oxazolidinone N-atom: carbamoyl derivatives of enamines and allenyl amines are formed in yields ranging from 60 to 80% and with diastereoselectivities up to 98% (*Schemes 2–5*). The C=C bond of the *N*-hydroxyalkenyl groups has (*Z*)-configuration (products **5** and **8**), the allene chirality axis has (*M*)-configuration (products **9**), and the addition to aldehydes and unsymmetrical ketones has taken place preferentially from the *Si* face. A mechanistic model is proposed that is compatible with the stereochemical outcome (assuming kinetic control and disregarding the presence of Li *and* Ti species in the reaction mixture; *cf.* **L**, **M** in *Fig. 4*). Hydrolysis of the enamine derivatives leads to lactols, oxidizable to γ-lactones, with recovery of the crystalline oxazolidinone, as demonstrated in three cases (*Scheme 6*). Thus, the application of chiral oxazolidinone auxiliaries (*cf. Figs. 1* and *2*) has been extended to the overall enantioselective preparation of homoaldols.

1. Introduction. – A particularly reliable and practical method for conducting overall enantioselective transformations is the use of covalently bound recyclable chiral auxiliaries. Two of the most versatile and frequently employed auxiliaries are the oxazolidinones **A** and **B**, readily available from α-amino acids and norephedrine (*Fig. 1*)[2]). The auxiliaries **A** ($R^1 = H$) and **B** have been introduced by *Evans* [1], and, later, numerous modifications of the auxiliary **A** have been reported, but only some of them, *e.g.*, those by the groups of *Davies* ($R^1 = Me$) [2] and of *Gibson* ($R^1 = Ph$) [3], and our group ($R^1 = Ph$) [4], have led to auxiliaries with improved properties (more facile attachment, removal and recovery of the auxiliary, highly crystalline derivatives). Usually, *N*-acyl derivatives of the oxazolidinones **A** and **B** are prepared and then utilized as chiral enolates **C** or chiral *Michael* acceptors and dienophiles **D** in diastereoselective reactions (*Fig. 1*). It is surprising that there are very few reports on *N*-alkyl derivatives of **A** and **B**, and their use as chiral nucleophiles **E**.

An overview of α-metallated *N*-alkyl-oxazolidinones of type **E** is given in *Fig. 2*. The oxazolidinone organostannanes **F** [5][6] and **G** [7], and the lithiated oxazolidinone

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[1]) Part of the Ph. D. thesis of *C. G.*, ETH Zürich, Dissertation No. 14516, 2000.

[2]) For reviews on the use of oxazolidinones as chiral auxiliaries, see [1a,b] and Chapt. D in [1c].

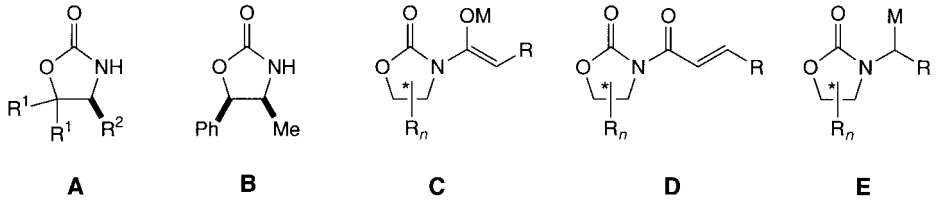

Fig. 1. *Amino acid- and norephedrine-derived oxazolidinone auxiliaries* **A** *and* **B**, *and their* N-*acyl and* N-*alkyl derivatives* **C**–**E**. For **A**, R^1 = H, Me, Ph, R^2 = i-Pr, t-Bu, Bn, Ph. For **C**–**E**, M = metal.

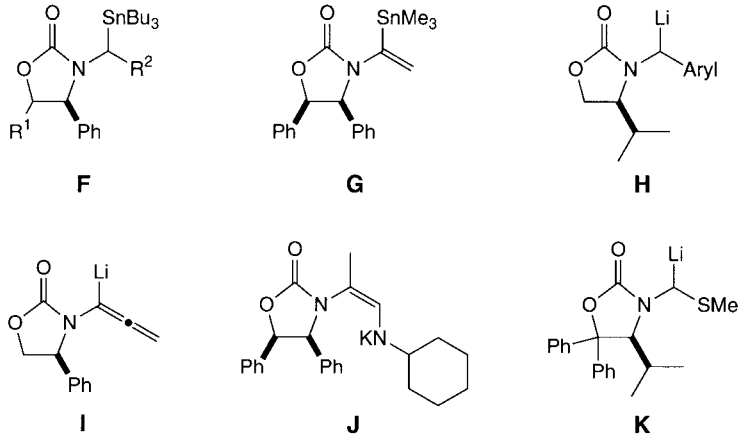

Fig. 2. N-*Alkyloxazolidinones* **F**–**K** *metallated in the α-exocyclic position*. For **F**, R^1 = H, Ph, R^2 = simple alkyl groups.

H [8] serve (in the case of **F** and **G**, after Sn/Li exchange) as 'chirally protected α-(aminoalkyl)lithium reagents' for the enantioselective preparation of α-branched amines, α-amino acids, β-amino alcohols, and γ-amino carbonyl compounds. In all cases, the oxazolidinone auxiliary is removed (and destroyed!) by hydrogenolysis or hydrolysis. The allenyl-oxazolidinone **I** is directly obtained by deprotonation with BuLi. The Li species can be alkylated and then applied to intramolecular *Pauson-Khand* reactions [9]. The oxazolidinone derivate **J** is employed for the synthesis of α,α-disubstituted amino aldehydes, with, again, destructive removal of the auxiliary [10][3])

Recently, we introduced the lithiated *N*-(methylthiomethyl)-oxazolidinone **K** as a reagent that is synthetically equivalent to a chiral formyl anion [12]. It allows for the enantioselective preparation of α-hydroxy carbonyl compounds and derivatives thereof, with recovery of the auxiliary!

We have now investigated metallated *N*-allyl and *N*-propargyl derivatives of the auxiliary **1** (*cf. Scheme 1*). Such heterosubstituted allylic and propargylic nucleophiles are especially attractive synthetic reagents when they react in the γ-position, rather than in the α-position, with respect to the heteroatom: as shown in *Fig. 3*, the resulting products are heterosubstituted enes or allenes, so that they can be hydrolyzed to

[3]) The term '*immolative* asymmetric synthesis' is suggested for a process in which the chiral auxiliary is destroyed upon removal [11].

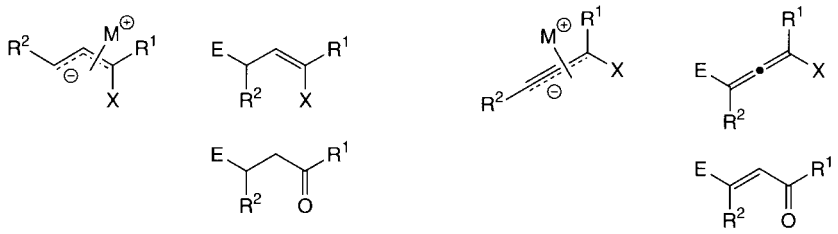

Fig. 3. *Heterosubstituted allylic and propargylic nucleophiles*; *reaction in the γ-position with respect to the heteroatom*

carbonyl or α,β-unsaturated carbonyl derivatives; the allylic reagents are thus potential d^3 reagents (sometimes referred to as 'homoenolates'). Furthermore, there is a tendency for the γ-products to be formed as (*Z*)-geometrical isomers (a stereogenic element as a gift!). Allenes from γ-attack on the propargylic system contain another stereogenic element, a chirality axis, which can lead to diastereoisomeric products (if, *e.g.*, E or X in *Fig. 3* contains a stereogenic center). The generation and reaction of 'heteroatom-stabilized allyl anions' have been the subject of an extensive review article by *Katritzky et al.* [13], and we refer the reader to publications by *Hoppe et al.* [14] for diastereoselective reactions of heterosubstituted propargylic organometallic reagents.

As we will show in the following sections, the *N*-allyl-, *N*-cinnamyl-, and *N*-propargyl-oxazolidinones[4]) **2**–**4** (*Scheme 1*) can be used for the synthesis of (*Z*)-enyl-oxazolidinones, allenyl-oxazolidinones, and enantiomerically pure homoaldol products[5]).

2. Addition of Metallated *N*-Allyl-oxazolidinones 2 to Aldehydes and Ketones. – The oxazolidinone derivatives **2**–**4** were conveniently prepared by *N*-alkylation of 5,5-diphenyl-oxazolidinone **1** with allyl, cinnamyl, and propargyl bromide, respectively (*Scheme 1*)

Deprotonation of *N*-allyl-oxazolidinone **2** in the allylic position with BuLi at −78°instantaneously gave a bright yellow solution containing the allyllithium species. Addition of isobutyraldehyde resulted in a mixture of products: compound **5a** (+ **5′a**), from reaction of isobutyraldehyde at the γ-position of the allylic system, and compound **6**, from reaction at the α-position, were obtained as a *ca.* 1:1 mixture, together with *ca.* 10% protonation product **7** (*Scheme 2*, *Entry 1*). The desired product, γ-adduct **5a**, was formed exclusively as the (*Z*)-isomer, but with low diastereoselectivity. The configuration of the newly created stereogenic center (C(4′)) and the C=C bond in **5a** were unambiguously assigned by single-crystal X-ray structure determination[6]). The results

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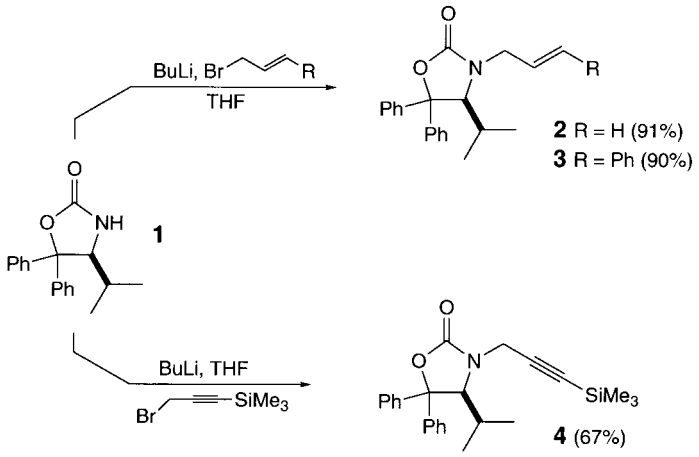
[4]) For related work, see, *e.g.*, *Helmchen*'s titanated *N*-allylimidazolidinone [15], *Hoppe*'s sparteine-mediated metallation of *O*-allyl carbamates ([16] and refs. cit. therein) and *O*-propargyl carbamates [14c], and *Beak*'s sparteine-mediated metallation of *N*-allyl carbamates [17].

[5]) For a recent review on chiral homoenolate equivalents, see [18].

[6]) The C=C bond geometry of all other γ-adducts **5** (*Scheme 3*) was assigned as (*Z*) by the magnitude of the coupling constant between the two olefinic protons ($J = 8.3–8.4$). The configuration at C(4′) of **5e** was determined by optical comparison of γ-lactone **11a** with data reported in the literature. This information, together with the X-ray crystal structure of **5a**, led to the configurational assignment of compounds **5b**–**d** by analogy.

Scheme 1. *Preparation of* N-*Allyl-*, N-*Cinnamyl- and* N-*Propargyl-oxazolidinones* **2**–**4**



of our efforts to improve the regio- and diastereoselectivity of the addition have been summarized in *Entries 2–6* of *Scheme 2*. In all cases, *N*-allyl-oxazolidinone **2** was treated successively with BuLi and an additive at $-78°$, the reaction mixture was stirred at $-25°$ for 30 min, and isobutyraldehyde was then added at the indicated temperature. Transmetallation of compound Li-**2** with $(i\text{-PrO})_4Ti$, prior to the addition of the electrophile, resulted in a change of regioselectivity in favor of the α-adduct (*Entry 2*), whereas low conversion was observed with Et_2AlCl (*Entry 3*). Better results were obtained when $(i\text{-PrO})_3TiCl$ was used as an additive[7]): γ-adduct **5a** was isolated in 54% yield as a 98:2 mixture with epimer **5′a** (*Entry 5*). We noticed that higher reaction temperatures led to increased regio- but decreased diastereoselectivities (*Entries 4* and *5*, and results that were obtained in reactions at room temperature). We also would like to point out that the separation of α- and γ-adducts by flash chromatography (as it was necessary in the experiments for *Entries 1–5*) was simple, due to their very different R_f values[8]). Finally, as can be seen from *Entry 6*, the optimal procedure involved transmetallation of Li-**2** with $(Me_2N)_3TiCl$, yielding an orange-brown solution, and addition of the aldehyde at $-25°$. γ-Adduct **5a** was obtained in 78% yield as a 94:6 mixture with epimer **5′a**.

To investigate the influence of the type of electrophile on the selectivity, and to demonstrate the general applicability of the reaction, we tested an aliphatic, an α,β-unsaturated, and an aromatic aldehyde, as well as an alkyl/aryl and a dialkyl ketone (*Scheme 3*). To our satisfaction, titanated *N*-allyl-oxazolidinone **2** added to all employed aldehydes and ketones in good yields and with excellent diastereoselectiv-

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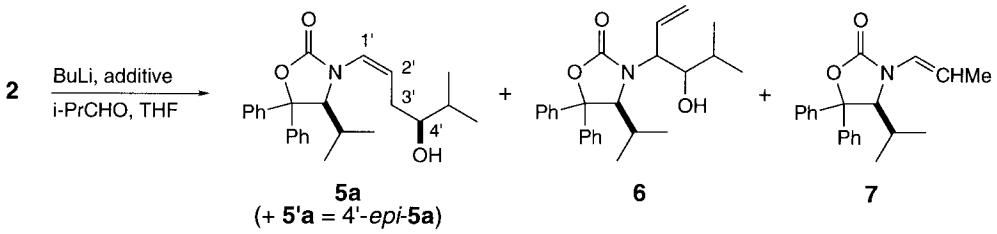
[7]) For first reports on the selectivity enhancement by Li/Ti or Mg/Ti transmetallations, see [19][20], and refs. cited therein.

[8]) A possible explanation for why the α-adducts have considerably higher R_f values ('less polar') than the corresponding γ-adducts could be as follows: the OH group of the α-adducts (*e.g.*, **6**) might form an intramolecular H-bond to the C=O O-atom of the oxazolidinone *via* a seven-membered ring, and thereby, interact with the silica gel to a lesser extent than the OH group of the γ-adducts. This type of intramolecular H-bond has previously been observed for related compounds in the solid state [12a][12b].

Scheme 2. *Addition of Metallated* N-*Allyl-oxazolidinone* **2** *to Isobutyraldehyde under Various Reaction Conditions.* The given temperature refers to the temperature of the reaction mixture during the aldehyde addition. The product ratio and the diastereoisomer ratio (dr) were determined by ^{1}H-NMR spectroscopy of the crude product. The given yield refers to a combined yield of **5a** and **5′a** after flash chromatography.



5a (+ **5'a** = 4'-*epi*-**5a**) **6** **7**

Entry	Additive	Temperature	Ratio (**5a**+**5'a**/**6**/**2**+**7**)	Yield [%]	dr (**5a**/**5'a**)
1	–	–78°	40:50:10[a])	–	44:55
2	$(i\text{-PrO})_4Ti$	–25°	5:85:10[a])	–	–
3	Et_2AlCl	–25°	38[b]):25:37	–	–
4	$(i\text{-PrO})_3TiCl$	–78°	39:56:5	–	>98:2
5	$(i\text{-PrO})_3TiCl$	–25°	65:28:7	54	98:2
6	$(Me_2N)_3TiCl$	–25°	88:<1:12	78	94:6

[a]) With traces of several unidentified products. [b]) (*E*/*Z*)-mixture.

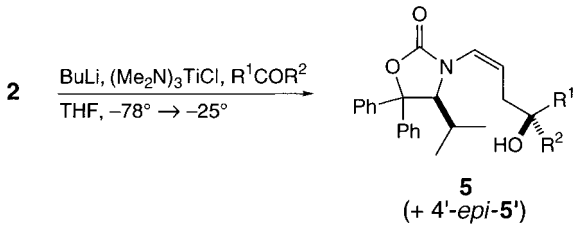
ities. In the case of PhCHO ($\rightarrow$ product **5c**), the best diastereoselectivity was obtained with $(i\text{-PrO})_3TiCl$ rather than with $(Me_2N)_3TiCl$.

3. Addition of Lithiated N-Cinnamyl-oxazolidinone 3 to Symmetrical Ketones. – Treatment of *N*-cinnamyl-oxazolidinone **3** with BuLi at $-78°$ led to the corresponding organolithium compound as a dark-red THF solution (*Scheme 4*). Reaction of Li-**3** with symmetrical ketones, such as acetone or cyclohexanone, occurred with exceptional stereoselectivities, but only moderate regioselectivities ($\gamma/\alpha \approx 70:30$)[9]). The γ-adducts **8** were obtained as single stereoisomers[10]) in 55–65 yield (*Scheme 4*). The use of titanium transmetallation reagents as additives in the reaction resulted in lower yields

[9]) The γ-adducts **8** and their corresponding α-adducts display similar NMR spectra (chemical shifts/splitting patterns). The assignment of peaks to γ- or α-adducts was achieved based on our experience from the reactions of **2** with electrophiles. Additionally, compounds **8** were unequivocally identified as γ-adducts by HMBC-NMR-spectroscopy and by the cleavage reactions shown in *Scheme 6*.

[10]) The γ-adducts **8a** and **8b** were assigned (*Z*)-configuration on the basis of the magnitude of the coupling constant between the two olefinic protons ($J = 8.4$). The configuration at C(4′) of **8a** was determined by optical comparison of γ-lactone **11b** with data reported in the literature. This information led to the configurational assignment of compound **8b** by analogy.

Scheme 3. *Addition of Titanated* N-*Allyl-oxazolidinone* **2** *to Aldehydes and Ketones.* The given yield refers to a combined yield of **5** and **5′** after flash chromatography. The diastereoisomer ratio (dr) was determined by ^{1}H-NMR spectroscopy after flash chromatography.

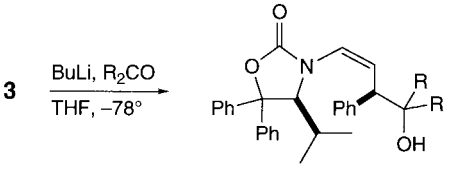


5
(+ 4′-*epi*-**5′**)

5	R^1	R^2	Yield [%]	dr (**5**/**5′**)
a	i-Pr	H	78	94:6
b		H	67	92:8
c[a])	Ph	H	62	91:9
d	Ph	Me	74	>98:2
e	i-Pr	Me	76	91:9

[a]) Reaction conditions: BuLi, $(i\text{-PrO})_3$TiCl, THF, r.t.; with $(Me_2N)_3$TiCl, the diastereoselectivity was only 66% in this case.

Scheme 4. *Addition of Lithiated* N-*Cinnamyl-oxazolidinone* **3** *to Two Symmetrical Ketones*

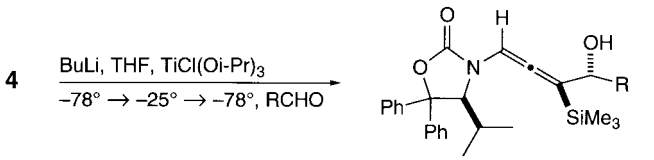


8a R = Me (65%, dr > 98:2)
8b R = –$(CH_2)_5$– (56%, dr > 98:2)

of products **8**, which were accompanied by significant amounts of decomposition products.

4. Addition of Titanated *N*-Propargyl-oxazolidinone 4 to Aldehydes. – It was also possible to lithiate *N*-propargyl-oxazolidinone **4** on the exocyclic CH_2 group (*Scheme 5*). The yellow solution of the propargyllithium species Li-**4**, when combined with PhCHO, yielded a complex mixture of products; the formation of only small amounts of propargyl and regioisomeric allenyl adducts was established by ^{1}H-NMR spectroscopy of the crude product. A drastically different reactivity was observed when Li-**4** was transmetallated[7]) with $(i\text{-PrO})_3$TiCl, prior to the addition of an aldehyde. Treatment of Li-**4** with $(i\text{-PrO})_3$TiCl for 30 min at $-25°$ to yield an orange solution, followed by addition of an aldehyde at $-78°$, gave allenyl adducts **9** with excellent

Scheme 5. *Addition of Titanated* N-*Propargyl-oxazolidinone* **4** *to Aldehydes.* The conversion of the addition reactions is 70–75%. The diastereoselectivity (ds) of the addition reaction is >95% in all four cases, as determined by ^{1}H-NMR spectroscopy of the crude product. The diastereoisomer purity (dp) of **9** was determined by ^{1}H-NMR spectroscopy after flash chromatography.



9 ((4*S*,4′*R*,*M*)-configuration)

9	R	Yield [%]	dp [%]
a	i-Pr	67	97
b	Pr	66	97
c	Methacryl	60	98
d	Ph	64	97

diastereoselectivities (ds > 95%) and complete regioselectivities (*Scheme 5*). After flash chromatography, products **9** were isolated in 60–70% yield[11]) and 97–98% diastereoisomer purity[12]). The intermediate Ti-**4** underwent addition to aldehydes with high stereoselectivities, only after the reaction mixture had been warmed to −25° for transmetallation and then cooled again to −78°[13])

5. A Model for the Stereochemical Course of the Addition Reactions. – Metallated allylic compounds can exist in three isomeric forms, which may be in equilibrium with each other, namely η^1(C(α)), η^1(C(γ)), and η^3. Similarly, substrates that were metallated in α-position to a C≡C bond can either be of propargylic nature, or rearrange ('tautomerize') to the allenylic form. It has been shown by X-ray crystal-structure [21][22] and NMR solution-structure analyses [23][24] that, in the case of metallated allylic and propargylic carbamates, the metal is held in α-position to the heteroatom (O or N) by the chelating carbamate group[14]). Therefore, it is reasonable to describe Ti-**2** and Li-**3** as η^1(C(α))-species, and Ti-**4** as a propargylic species (*Fig. 4*, left-hand side). We also suggest that the i-Pr and the allyl/cinnamyl/propargyl

[11]) The moderate yield is caused by incomplete conversion (*ca.* 70–75%).

[12]) The relative configurations of the newly formed stereogenic center (C(4′)) and axis (allene) of **9d** were elucidated by single-crystal X-ray analysis. This information led to the configurational assignment of compounds **9a–c** by analogy.

[13]) When transmetallation was carried out at −78° or the aldehyde was added at −25°, all four possible diastereoisomeric allenyl adducts were obtained with significantly reduced diastereoselectivity (ds ≈ 75%).

[14]) The Li-atom is coordinated in an η^1(C(α))-fashion in the X-ray crystal structure of *Hoppe*'s lithiated *O*-allyl carbamate [21], and it is bound in an η^3-manner in the X-ray crystal structure of *Beak*'s lithiated *N*-allyl carbamate [22]. In both cases, the C=O O-atom of the carbamate is coordinated to the Li-atom.

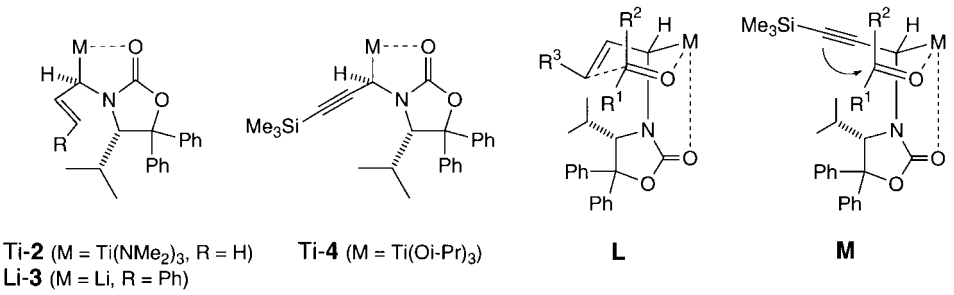


Fig. 4. *Proposed structures of Ti-***2**, *Li-***3**, *and Ti-***4**, *and models for the stereochemical course of the addition reactions to aldehydes and ketones.* For **L** and **M**, R^1 = 'large', group,R^2 = 'small' group, R^3 = H, Ph.

substituent should be on opposite sides of the bicyclic systems[15]), and that, in the case of Ti-**2** and Li-**3**, the allylic substituent should be in a *cisoid*-conformation[16]). The stereochemical outcome of the addition reactions is compatible with a six-membered chair-like transition state (*cf.* [27] and the *Zimmermann-Traxler* model of aldol reactions [28]). In this arrangement, the 'larger' substituent R^1 on the C=O C-atom adopts an equatorial position (**L** and **M**; *Fig. 4*, right-hand side); in the case of **L**, the new C,C bond is formed with relative topicity *lk*.

6. Acidic Methanolysis and Subsequent Oxidation of Some Adducts. – One useful reaction for the adducts **5** and **8** is their conversion to homoaldol products (4-hydroxy carbonyl compounds, γ-lactols) by hydrolysis of the (*Z*)-enyl-oxazolidinone moiety to the corresponding aldehyde group. Treatment of **5e**, **8a**, and **8b** with concentrated H_2SO_4 in MeOH cleanly afforded the γ-lactol ethers **10a**–**c**, with recovery of the auxiliary **1** in 80–85% yield (*Scheme 6*). It is likely that the methanolysis proceeds *via* cyclization to an N,O-acetal **N**, followed by transacetalization. It is noteworthy to mention that methanolysis of adducts **5** and **8** required rather harsh reaction conditions and long reaction times, as compared to the hydrolysis of related compounds [15][17][24][17]). γ-Lactol ethers **10** are useful synthetic intermediates. As an example, **10a**–**c** were converted almost quantitatively to γ-lactones **11a**–**c** by a procedure elaborated by *Grieco et al.* [29]. The X-ray crystal structure[18]) of spirolactone **11c** is shown in *Scheme 6*.

7. Conclusions. – An efficient method has been developed for the stereoselective transformation of *N*-allyl-, *N*-cinnamyl-, and *N*-propargyl-oxazolidinones to (*Z*)-enyl-

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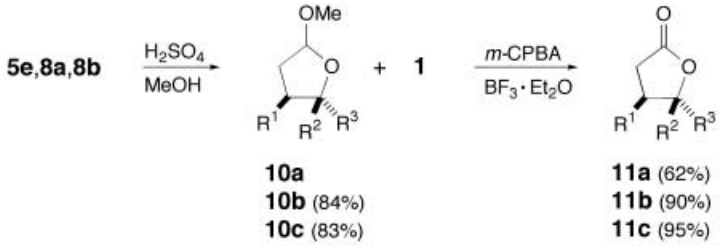
[15]) Recently, we have shown, by computational and NMR-spectroscopic methods, that the i-Pr and the MeS substituent of the lithiated oxazolidinone **K** are on opposite sides of the bicyclic system [12c].

[16]) To the best of our knowledge, all published X-ray crystal structures of N-, O-, and S-substituted metallated allylic compounds display a *cisoid*-conformation [21][22][25][26].

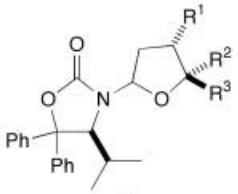
[17]) Enamides of *Helmchen* and co-workers seem to be particularly acid-sensitive: the compounds had to be purified on deactivated (Et_3N) silica gel [24].

[18]) Crystallographic data (excluding structure factors) of **11c** have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC 171704 (see also *Exper. Part*). Graphical illustrations and full crystallographic data of the X-ray crystal structures of compounds **5a**, **9d**, and of related compounds that are mentioned in [12a,b,d] will be given in an upcoming issue of this journal.

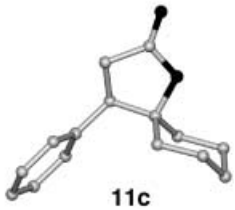
Scheme 6. *Methanolysis of Adducts* **5e**, **8a**, *and* **8b** *to γ-Lactol Ethers* **10**; *Oxidation of γ-Lactol Ethers* **10** *to γ-Lactones* **11**, *and X-Ray Crystal Structure of Spirolactone* **11c**. C-Atoms in gray, O-atoms in dark grey. The yield of γ-lactone **11a** refers to the overall yield (not optimized) from **5e**.



10,11,N:
a R^1 = H, R^2 = Me, R^3 = i-Pr
b R^1 = Ph, R^2 = R^3 = Me
c R^1 = Ph, R^2–R^3 = –$(CH_2)_5$–



N



11c

and allenyl-oxazolidinones. The products of addition are obtained in high yields and with excellent diastereo- and regioselectivities; a model for the stereochemical course of the addition reaction is proposed. We have demonstrated that (*Z*)-enyl-oxazolidinones are precursors to enantiomerically pure γ-lactol ethers and γ-lactones (homoaldol products). Further exploration of the synthetic utility of (*Z*)-enyl- and allenyl-oxazolidinones are areas of current interest. Functionalization of the electron-rich (*Z*)-C=C bond or allene moiety by epoxidation, dihydroxylation, bromination, or cycloaddition are only a few of the transformations under investigation.[19])

We are grateful to Dr. *B. Schweizer* for determination of the X-ray crystal structure of compounds **5a**, **9d**, and **11c**. We thank Prof. Dr. *G. Helmchen* for providing a copy of Dr. *H. Roder*'s dissertation. We gratefully acknowledge *Novartis Pharma AG*, Basel, for donation of 4-isopropyl-5,5-diphenyloxazolidin-2-one and for financial support.

Experimental Part

1. *General. Abbreviations: m*-CPBA: *meta*-chloroperbenzoic acid, FC: flash chromatography, dp: diastereoisomer purity, dr: diastereoisomer ratio, h.v.: high vacuum (0.01–0.1 Torr), Solvents: solvents for reactions were purchased in *puriss.* quality from *Fluka, J. T. Baker, Scharlau*, or *Merck KGaA*. THF was freshly distilled from K before use. Solvents for FC and workup procedures were purchased in technical quality and distilled from *Sikkon* (anh. $CaSO_4$; *Fluka*; pentane, hexane, CH_2Cl_2, AcOEt, MeOH) or KOH/$FeSO_4$ (Et_2O). Reagents and substrates: BuLi was used as a *ca.* 1.6M soln. (hexane). $(Me_2N)_3TiCl$ was prepared from $TiCl_4$ and $(Me_2N)_4Ti$ according to the procedure in [19c] and used undistilled as a *ca.* 0.6M soln. (hexane). $(i\text{-}PrO)_3TiCl$ was prepared from $TiCl_4$ and $Ti(i\text{-}PrO)_4$ according to the procedure in [19c] and used undistilled as a *ca.* 2M soln.

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[19]) *Hsung* and co-workers reported the base-induced isomerization of *N*-propargyl-oxazolidinones to allenyl-oxazolidinones without chirality axis (*cf. Fig. 2*). These allenes were applied to [4+2] and [4+3] cycloadditions, as well as intramolecular *Pauson-Khand* reactions [9][30].

(hexane). $Ti(i\text{-}PrO)_4$ was distilled before use, cyclopent-1-enecarbaldehyde was prepared from cyclohexene (*via trans*-cyclohexane-1,2-diol) according to the procedure in [31]. All liquid aldehydes and ketones were distilled and stored under Ar, *m*-CPBA was used in *ca.* 70% purity, and all other reagents or substrates were used as received from *Fluka* or *Aldrich*. Techniques: reactions involving air- or moisture-sensitive reagents or intermediates were performed under Ar in glassware that had been oven- or heat-gun dried under h.v. TLC: precoated silica gel *60* F_{254} glass plates (*Merck*), visualization by UV_{254} light and/or dipping into phosphomolybdic acid soln. (phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), conc. H_2SO_4 (60 ml), and H_2O (940 ml)), followed by heating with a heat gun. FC: silica gel *60* (*Fluka*, 40–63 μm), air pressure of *ca.* 0.2 bar, eluent is given in parentheses. M.p.: *Büchi 510* apparatus, determined in open capillaries, uncorrected. Optical rotation $[\alpha]_D^{r.t.}$: *Perkin-Elmer 241* polarimeter, 10 cm, 1 ml cell, concentration (*c*) in g/100 ml and solvent are given in parentheses. IR: *Perkin-Elmer 1600 FT-IR* spectrophotometer, measured as film (NaCl plates), absorption bands in cm^{-1}. NMR: *Bruker AMX-II-500* (^1H: 500 MHz, ^{13}C: 125 MHz), *AMX-400* (^1H: 400 MHz, ^{13}C: 100 MHz), *AMX-300* (^1H: 300 MHz, ^{13}C: 75 MHz), *Varian Mercury XL 300* (^1H: 300 MHz, ^{13}C: 75 MHz) spectrometer, chemical shifts (δ values) are reported in ppm with respect to Me_4Si ($\delta = 0$ ppm) as internal standard, coupling constants (*J*) are given in Hz. ^{13}C-NMR Spectra are proton broad-band-decoupled, multiplicities of the signals were determined by DEPT measurements, diastereoisomer ratios and diastereoisomer purities were determined by ^1H-NMR spectroscopy. MS: EI-MS (electron impact ionization): *VG Tribrid* spectrometer, 70 eV, FAB-MS (fast atom bombardment): *VG ZAB2-SEQ* spectrometer, 3-nitrobenzyl alcohol matrix, MALDI-FT-ICR-MS (*Fourier* transform ion-cyclotron-resonance matrix-assisted laser-desorption ionization): *IonSpec Ultima 4.7* spectrometer, 2,5-dihydroxybenzoic acid (2,5-DHB) matrix, fragment ions in *m*/*z* with relative intensities (%) in parentheses. Elemental analysis: performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH-Zürich.

2. *Reaction of Oxazolidinone* **1** *with Allyl and Propargyl Bromides. General Procedure 1* (*GP 1*). To a suspension of **1** (1 equiv.) in THF (0.4M) was added BuLi (1.1–1.2 equiv.) at 0°. After stirring for 10 min, the bromide (1.5 equiv.) was added dropwise. The mixture was warmed to r.t. and stirred for 1–2 d. Then, the mixture was treated with H_2O and diluted with Et_2O (with CH_2Cl_2 in the case of the preparation of **4**). The org. layers were separated, and the aq. layer was extracted with Et_2O or CH_2Cl_2 (3×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by trituration or recrystallization. In the case of incomplete conversion, the unreacted oxazolidinone can be separated from the product by filtration through a silica plug (CH_2Cl_2).

3. *Addition of* N-*Allyl-oxazolidinone* **2** *to Aldehydes* (non-aromatic) *and Ketones. General Procedure 2* (*GP 2*). To a soln. of **2** (1 equiv.) in THF (0.25M) was added BuLi (1.2 equiv.) at −78°. After stirring for 5 min at −78°, $(Me_2N)_3TiCl$ (1.2 equiv.) was added, and the mixture was warmed to −25°. After stirring for 30 min at −25°, the aldehyde or ketone (1.3 equiv.) was added dropwise. The mixture was kept at −25° for another 5 min, and was then treated with sat. aq. KF soln. and diluted with Et_2O. The org. layer was separated, and the aq. layer was extracted with Et_2O (3×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by FC.

4. *Addition of* N-*Cinnamyl-oxazolidinone* **3** *to Symmetrical Ketones. General Procedure 3* (*GP 3*). To a soln. of **3** (1 equiv.) in THF (0.25M) was added BuLi (1.2 equiv.) at −78°. After stirring for 5 min at −78°, the ketone (1.3 equiv.) was added dropwise. The mixture was kept at −78° for another 5 min, and was then treated with sat. aq. NH_4Cl soln. and diluted with Et_2O. The org. layer was separated, and the aq. layer was extracted with Et_2O (3×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by FC.

5. *Addition of* N-*Propargyl-oxazolidinone* **4** *to Aldehydes. General Procedure 4* (*GP 4*). To a soln. of **4** (1 equiv.) in THF (0.25M) was added BuLi (1.2 equiv.) at −78°. After stirring for 5 min at −78°, $(i\text{-}PrO)_3TiCl$ (1.2 equiv.) was added, and the mixture was warmed to −25°. After stirring for 30 min at −25°, the mixture was cooled to −78°, and the aldehyde (1.3 equiv.) was added dropwise. The mixture was kept at −78° for another 5 min, and was then treated with sat. aq. KF soln. and diluted with Et_2O. The org. layer was separated, and the aq. layer was extracted with Et_2O (3×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by FC.

6. *Acidic Hydrolysis of Adducts* **5** *and* **8** *to γ-Lactol Ethers. General Procedure 5* (*GP 5*). To a soln. of an adduct (1 equiv.) in MeOH (0.15M) was added conc. H_2SO_4 (0.125 volume equiv. to MeOH) slowly at 0°. The mixture was stirred for 5–13 d at r.t., the auxiliary **1** precipitated in the course of the reaction. After 5–13 d, the white precipitate was dissolved by adding CH_2Cl_2 to the mixture, and the clear soln. was poured into 5M NaOH (to obtain a basic pH). The org. layer was separated, and the aq. layer was extracted with CH_2Cl_2 (2×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was

triturated (Et_2O), the insoluble material was filtered off, washed with Et_2O, and dried under h.v. to recover **1**. The filtrate was concentrated under reduced pressure, and the residual oil was purified by FC to give the γ-lactol ethers.

7. Grieco *Oxidation of γ-Lactol Ethers to γ-Lactones. General Procedure 6* (*GP 6*). To a soln. of a γ-lactol ether (1 equiv.) in CH_2Cl_2 (0.2M) was added *m*-CPBA (2–3 equiv.) and $BF_3 \cdot Et_2O$ (catalytic amounts) at r.t. After stirring for 6 h, the mixture was treated with 5% aq. Na_2SO_3 soln. and diluted with CH_2Cl_2. The org. layer was separated, and the aq. layer was extracted with CH_2Cl_2 (3×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by FC.

(S)-4-(1-Methylethyl)-5,5-diphenyl-3-(prop-2-enyl)oxazolidin-2-one (**2**). Compound **1** (6.51 g, 23.1 mmol) was treated with BuLi (16.4 ml, 25.5 mmol) and allyl bromide (2.94 ml, 34.7 mmol), and the mixture was stirred for 2 d according to *GP 1*. Then, the crude product was dissolved in hexane/CH_2Cl_2 (1:1), treated with charcoal, and filtered through a *Celite* plug. The filtrate was concentrated, and the residual solid was triturated (boiling hexane, 1 × 50 ml) to yield **2** (6.76 g, 91%). White solid. M.p. 123–125°. $[\alpha]_D^{r.t.} = -303.9$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2987*w*, 1744*s*, 1493*w*, 1450*m*, 1416*m*, 1114*w*, 1040*w*, 1002*w*, 940*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.71 (*d*, $J = 6.7$, Me); 1.05 (*d*, $J = 7.4$, Me); 1.86–1.95 (*m*, Me_2CH); 3.61 (*dddd*, $J = 0.9$, 0.9, 8.1, 15.6, 1 H, CH_2); 4.37 (*d*, $J = 1.8$, NCH); 4.40 (*dddd*, $J = 1.9$, 1.9, 4.3, 15.6, 1 H, CH_2); 5.03–5.08 (*m*, 1 H, $CH{=}CH_2$); 5.11–5.15 (*m*, 1 H, $CH{=}CH_2$); 5.40–5.50 (*m*, $CH{=}CH_2$); 7.19–7.35 (*m*, 6 arom. H); 7.39–7.43 (*m*, 2 arom. H); 7.52–7.55 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.5, 22.3 (Me); 29.8 (CH); 47.2 (CH_2); 66.6 (CH); 87.9 (C); 118.8 (CH_2); 125.3, 126.0, 127.5, 128.0, 128.1, 128.5, 131.1 (CH); 139.1, 144.1, 156.9 (C). FAB-MS: 643 (35, $[2M + H]^+$), 322 (100, $[M + H]^+$), 278 (24, $[M + H - CO_2]^+$), 234 (20). Anal. calc. for $C_{21}H_{23}NO_2$ (321.41): C 78.47, H 7.21, N 4.36; found: C 78.36, H 7.30, N 4.44.

(S)-4-(1-Methylethyl)-5,5-diphenyl-3-[(E)-3-phenylprop-2-enyl]oxazolidin-2-one (**3**). Compound **1** (5.53 g, 19.7 mmol) was treated with BuLi (14.0 ml, 21.6 mmol) and cinnamyl bromide (5.81 g, 29.5 mmol), and the mixture was stirred for 1 d according to *GP 1*. Trituration of the crude product (boiling hexane, 4 × 50 ml) yielded **3** (7.03 g, 90%). White solid. M.p. 161–162°. $[\alpha]_D^{r.t.} = -226.6$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2966*w*, 1745*s*, 1494*w*, 1450*m*, 1419*m*, 1084*w*, 1040*w*, 1002*w*, 969*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.75 (*d*, $J = 6.7$, Me); 1.06 (*d*, $J = 7.3$, Me); 1.88–1.98 (*m*, Me_2CH); 3.75 (*ddd*, $J = 0.9$, 8.5, 15.6, 1 H, CH_2); 4.40 (*d*, $J = 1.9$, NCH); 4.58 (*ddd*, $J = 1.9$, 4.5, 15.6, 1 H, CH_2); 5.71 (*ddd*, $J = 4.5$, 8.5, 16.0, $PhCH{=}CH$); 6.32–6.36 (*m*, $PhCH{=}CH$); 7.15–7.32 (*m*, 11 arom. H); 7.39–7.43 (*m*, 2 arom. H); 7.52–7.55 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.6, 22.4 (Me); 30.0 (CH); 46.6 (CH_2); 66.4 (CH); 88.2 (C); 123.3, 125.4, 126.0, 126.4, 127.5, 127.9, 128.0, 128.2, 128.5, 128.6, 133.6 (CH); 136.0, 139.0, 144.2, 157.1 (C). FAB-MS: 795 (43, $[2M + H]^+$), 398 (100, $[M + H]^+$), 352 (13), 250 (26), 222 (29). Anal. calc. for $C_{27}H_{27}NO_2$ (397.52): C 81.58, H 6.85, N 3.52; found: C 81.53, H 6.86, N 3.56.

(S)-4-(1-Methylethyl)-5,5-diphenyl-3-[3-(trimethylsilyl)prop-2-ynyl]oxazolidin-2-one (**4**). Compound **1** (9.60 g, 34.1 mmol) was treated with BuLi (24.2 ml, 37.5 mmol) and 3-(trimethylsilyl)propargyl bromide (7.20 ml, 51.2 mmol), and the mixture was stirred for 2 d according to *GP 1*. Trituration of the crude product (boiling hexane, 1 × 75 ml) and subsequent recrystallization (MeOH) yielded **4** (8.90 g, 67%). White solid. M.p. 182–184°. $[\alpha]_D^{r.t.} = -268.8$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 2966*w*, 2180*w*, 1747*s*, 1494*w*, 1450*w*, 1422*w*, 1358*w*, 1252*m*, 1044*w*, 1012*w*, 846*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.21 (*s*, Me_3Si), 0.67 (*d*, $J = 6.7$, Me); 1.12 (*d*, $J = 7.4$, Me); 1.82–1.92 (*m*, Me_2CH); 3.89 (*d*, $J = 17.9$, 1 H, CH_2); 4.56 (*d*, $J = 17.9$, 1 H, CH_2); 4.68 (*d*, $J = 1.6$, NCH); 7.22–7.41 (*m*, 8 arom. H); 7.50–7.53 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): –0.2, 15.2, 22.5 (Me); 29.6 (CH); 35.9 (CH_2); 66.0 (CH); 88.1, 91.2, 98.5 (C); 126.0, 126.3, 127.6, 128.1, 128.2, 128.5 (CH); 139.2, 143.7, 156.2 (C). FAB-MS: 783 (33, $[2M + H]^+$), 392 (100, $[M + H]^+$), 348 (23, $[M + H - CO_2]^+$), 304 (15). Anal. calc. for $C_{24}H_{29}NO_2Si$ (391.58): C 73.61, H 7.46, N 3.58; found: C 73.64, H 7.35, N 3.54.

(S)-3-[(1Z,4S)-4-Hydroxy-5-methylhex-1-enyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (**5a**). Compound **2** (431 mg, 1.34 mmol) was treated with BuLi (1.04 ml, 1.61 mmol), $(Me_2N)_3TiCl$ (2.68 ml, 1.61 mmol) and isobutyraldehyde (159 µl, 1.74 mmol) according to *GP 2*. Purification of the crude product by FC (pentane/Et_2O 1:1) yielded **5a** (411 mg, 78%) as a 94:6 mixture with 4′-*epi*-**5a**. For anal. purposes a sample was recrystallized (hexane/AcOEt) to afford **5a** (dr ≥ 99:1). White solid. M.p. 140–141°. $[\alpha]_D^{r.t.} = -183.7$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3444*w*, 3008*w*, 2963*m*, 1747*s*, 1659*w*, 1493*w*, 1450*w*, 1419*w*, 1389*w*, 1002*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.72 (*d*, $J = 6.7$, Me); 0.77 (*d*, $J = 6.8$, Me); 0.85 (*d*, $J = 6.7$, Me); 1.05 (*d*, $J = 7.3$, Me); 1.51–1.62 (*m*, Me_2CH); 1.94–2.03 (*m*, 2 H, Me_2CH, CH_2); 2.10–2.17 (*m*, 1 H, CH_2); 2.34 (*d*, $J = 4.8$, OH); 3.33–3.39 (*m*, CHOH); 4.56 (*d*, $J = 1.8$, NCH); 5.35–5.41 (*m*, $CH_2CH{=}CH$); 6.06 (*ddd*, $J = 1.7$, 1.7, 8.3, $CH_2CH{=}CH$); 7.22–7.38 (*m*, 6 arom. H); 7.42–7.46 (*m*, 2 arom. H); 7.58–7.62 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.6, 17.7, 18.5, 22.1 (Me); 30.1 (CH); 31.8 (CH_2); 33.4, 70.7, 75.3 (CH); 88.0 (C); 124.5, 125.1, 125.2, 126.0, 127.7, 128.2, 128.3, 128.7 (CH); 138.7, 144.1, 155.5 (C). FAB-MS: 787 (19, $[2M + H]^+$), 394 (100, $[M + H]^+$), 332 (75,

$[M+H-CO_2-H_2O]^+$), 276 (39), 222 (47). Anal. calc. for $C_{25}H_{31}NO_3$ (393.52): C 76.30, H 7.94, N 3.56; found: C 76.25, H 7.87, N 3.65.

*(*S*)-3-[(1Z,4*S*)-4-(Cyclopent-1-enyl)-4-hydroxybut-1-enyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**5b**). Compound **2** (250 mg, 0.778 mmol) was treated with BuLi (0.60 ml, 0.933 mmol), $(Me_2N)_3TiCl$ (1.56 ml, 0.933 mmol) and cyclopent-1-enecarbaldehyde (97 µl, 1.01 mmol) according to *GP 2*. Purification of the crude product by FC (pentane/Et_2O 1:1) yielded **5b** (217 mg, 67%) as a 92:8 mixture with 4′-*epi*-**5b**. For anal. purposes, a sample was recrystallized (hexane/AcOEt) to afford **5b** (dr 98:2). White solid. M.p. 139–140°. $[\alpha]_D^{r.t.} = -209.7$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3444*w*, 3008*w*, 2966*w*, 2848*w*, 1747*s*, 1660*w*, 1493*w*, 1450*m*, 1421*m*, 1389*m*, 1326*w*, 1043*w*, 1002*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.71 (*d*, $J = 6.7$, Me); 1.04 (*d*, $J = 7.3$, Me); 1.82–1.90 (*m*, $CH_2CH_2CH_2$); 1.94–2.02 (*m*, Me_2CH); 2.11–2.22 (*m*, C=CHCH_2, 1 H of HOCHCH_2); 2.30–2.35 (*m*, CH_2C=CH); 2.36–2.44 (*m*, 1 H, HOCHCH_2); 2.56 (br. *s*, OH); 4.28–4.33 (*m*, CHOH); 4.55 (*d*, $J = 1.9$, NCH); 5.26–5.32 (*m*, CH_2CH=CH); 5.57–5.59 (*m*, C=CH); 6.01 (*ddd*, $J = 1.7$, 1.7, 8.4, CH_2CH=CH); 7.23–7.39 (*m*, 6 arom. H); 7.42–7.45 (*m*, 2 arom. H); 7.56–7.61 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.9, 22.0 (Me); 23.4 (CH_2); 30.2 (CH); 31.6, 32.2, 33.4 (CH_2); 69.6, 70.6 (CH); 88.0 (C); 122.9, 125.3, 125.4, 126.1, 127.7, 128.24, 128.28, 128.7 (CH); 138.7, 144.0, 146.1, 155.4 (C). FAB-MS: 835 (16, $[2M+H]^+$), 418 (9, $[M+H]^+$), 400 (100, $[M+H-H_2O]^+$), 356 (66, $[M+H-CO_2-H_2O]^+$), 276 (34), 222 (29). Anal. calc. for $C_{27}H_{31}NO_3$ (417.55): C 77.67, H 7.48, N 3.35; found: C 77.61, H 7.54, N 3.35.

*(*S*)-3-[(1Z,4*S*)-4-Hydroxy-4-phenylbut-1-enyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**5c**). To a soln. of **2** (384 mg, 1.19 mmol) in THF (5 ml) was added BuLi (0.94 ml, 1.43 mmol) at −78°. After stirring for 5 min at −78°, (i-PrO)$_3$TiCl (0.94 ml, 1.43 mmol) was added, and the mixture was warmed to −25°. After stirring for 30 min at −25°, the mixture was warmed to r.t., and PhCHO (156 µl, 1.55 mmol) was added dropwise. The mixture was stirred for another 5 min, and was then treated with sat. aq. KF soln. and diluted with Et_2O. The org. layer was separated, and the aq. layer was extracted with Et_2O (3×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the crude product by FC (pentane/Et_2O 2:1 → 1:1) yielded **5c** (313 mg, 62%) as a 91:9 mixture with 4′-*epi*-**5c**. For anal. purposes, a sample was recrystallized twice (hexane/CH_2Cl_2) to afford **5c** (dr 97:3). White solid. M.p. 148–150°. $[\alpha]_D^{r.t.} = -245.4$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3430*w*, 3008*w*, 2968*w*, 1745*s*, 1660*w*, 1493*w*, 1450*m*, 1421*m*, 1389*m*, 1326*w*, 1092*w*, 1046*w*, 1002*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.66 (*d*, $J = 6.7$, Me); 0.99 (*d*, $J = 7.2$, Me); 1.91–2.02 (*m*, Me_2CH); 2.30–2.37 (*m*, 1 H, CH_2); 2.57–2.64 (*m*, 1 H, CH_2); 3.29 (*d*, $J = 3.3$, OH); 4.52 (*d*, $J = 1.8$, NCH); 4.80–4.84 (*m*, CHOH); 5.21–5.27 (*m*, CH_2CH=CH); 5.95 (*ddd*, $J = 1.6$, 1.6, 8.4, CH_2CH=CH); 7.20–7.35 (*m*, 11 arom. H); 7.38–7.42 (*m*, 2 arom. H); 7.52–7.55 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.2, 22.0 (Me); 30.1 (CH); 37.1 (CH_2); 70.7, 72.3 (CH); 88.1 (C); 122.7, 125.2, 125.6, 125.8, 126.1, 127.2, 127.7, 128.23, 128.25, 128.31, 128.7 (CH); 138.6, 143.96, 144.01, 155.5 (C). FAB-MS: 855 (8, $[2M+H]^+$), 428 (14, $[M+H]^+$), 410 (84, $[M+H-H_2O]^+$), 366 (100, $[M+H-CO_2-H_2O]^+$), 276 (45), 222 (52). Anal. calc. for $C_{28}H_{29}NO_3$ (427.54): C 78.66, H 6.84, N 3.28; found: C 78.67, H 6.88, N 3.27.

*(*S*)-3-[(1Z,4*S*)-4-Hydroxy-4-phenylpent-1-enyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**5d**). Compound **2** (455 mg, 1.42 mmol) was treated with BuLi (1.10 ml, 1.70 mmol), $(Me_2N)_3TiCl$ (2.83 ml, 1.70 mmol), and acetophenone (215 µl, 1.84 mmol) according to *GP 2*. Purification of the crude product by FC (pentane/Et_2O 2:1) yielded **5d** (461 mg, 74%) as a single diastereoisomer. White solid. M.p. 153–154°. $[\alpha]_D^{r.t.} = -245.8$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3433*w*, 3008*w*, 2970*w*, 1743*s*, 1661*w*, 1493*w*, 1450*m*, 1425*m*, 1389*m*, 1093*w*, 1068*w*, 1002*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.69 (*d*, $J = 6.7$, Me); 0.97 (*d*, $J = 7.2$, Me); 1.52 (*s*, Me); 1.94–2.04 (*m*, Me_2CH); 2.46 (*ddd*, $J = 2.0$, 5.8, 14.6, 1 H, CH_2); 2.70 (*ddd*, $J = 1.1$, 9.7, 14.6, 1 H, CH_2); 3.66 (*s*, OH); 4.47 (*d*, $J = 1.9$, NCH); 5.03 (*ddd*, $J = 5.8$, 8.4, 9.7, CH_2CH=CH); 5.79 (*ddd*, $J = 1.1$, 2.0, 8.4, CH_2CH=CH); 7.18–7.39 (*m*, 11 arom. H); 7.42–7.45 (*m*, 2 arom. H); 7.55–7.60 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.5, 22.0 (Me); 30.1 (CH); 31.8 (Me); 41.9 (CH_2); 71.0 (CH); 73.1, 88.1 (C); 123.2, 124.8, 125.2, 125.5, 126.0, 126.4, 127.7, 128.0, 128.2, 128.3, 128.7 (CH); 138.5, 144.0, 147.1, 155.4 (C). FAB-MS: 883 (22, $[2M+H]^+$), 424 (92, $[M+H-H_2O]^+$), 380 (100, $[M+H-CO_2-H_2O]^+$), 276 (19), 222 (23). Anal. calc. for $C_{29}H_{31}NO_3$ (441.57): C 78.88, H 7.08, N 3.17; found: C 78.81, H 7.08, N 3.21.

*(*S*)-3-[(1Z,4*S*)-4-Hydroxy-4,5-dimethylhex-1-enyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**5e**). Compound **2** (455 mg, 1.42 mmol) was treated with BuLi (1.10 ml, 1.70 mmol), $(Me_2N)_3TiCl$ (2.83 ml, 1.70 mmol) and methyl 1-methylethyl ketone (197 µl, 1.84 mmol) according to *GP 2*. Purification of the crude product by FC (pentane/Et_2O 1:1) yielded **5e** (436 mg, 76%) as a 91:9 mixture with 4′-*epi*-**5e**. For anal. purposes a sample was recrystallized twice (hexane/CH_2Cl_2) to afford **5e** (dr 98:2). White solid. M.p. 162–164°. $[\alpha]_D^{r.t.} = -167.1$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3446*w*, 2966*m*, 2878*w*, 1748*s*, 1658*w*, 1493*w*, 1450*w*, 1407*w*, 1389*w*, 1042*w*, 1002*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.61 (*d*, $J = 6.9$, Me); 0.74 (*d*, $J = 6.7$, Me); 0.82 (*d*, $J = 6.8$, Me); 0.98 (*s*, Me); 1.05 (*d*, $J = 7.3$, Me); 1.57–1.66 (*m*, Me_2CH); 1.95–2.11 (*m*, Me_2CH, CH_2, OH); 4.57 (*d*, $J = 1.8$, NCH);

5.43–5.48 (*m*, $CH_2CH{=}CH$); 6.10 (*ddd*, *J* = 1.6, 1.6, 8.3, $CH_2CH{=}CH$); 7.23–7.38 (*m*, 6 arom. H); 7.45–7.49 (*m*, 2 arom. H); 7.62–7.66 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.6, 16.8, 17.4, 22.2, 23.0 (Me); 30.2, 36.6 (CH); 37.1 (CH_2); 71.0 (CH); 74.0, 88.0 (C); 123.6, 125.1, 125.2, 126.0, 127.7, 128.2, 128.3, 128.7 (CH); 138.6, 144.3, 155.5 (C). FAB-MS: 815 (21, $[2M+H]^+$), 408 (36, $[M+H]^+$), 390 (66, $[M+H-H_2O]^+$), 346 (100, $[M+H-CO_2-H_2O]^+$), 276 (28), 222 (40). Anal. calc. for $C_{26}H_{33}NO_3$ (407.55): C 76.62, H 8.16, N 3.44; found: C 76.66, H 8.20, N 3.45.

*(*S*)-3-[(1*Z*,4*R*)-4-Hydroxy-4-methyl-3-phenylpent-1-enyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**8a**). Compound **3** (320 mg, 0.805 mmol) was treated with BuLi (0.64 ml, 0.966 mmol) and acetone (77 µl, 1.05 mmol) according to *GP 3*. Purification of the crude product by FC (pentane/Et_2O 1:1) yielded **8a** (237 mg, 65%, including *ca.* 5% unidentified side-product) as a single diastereoisomer. For anal. purposes, the product was purified again by FC (pentane/Et_2O 1:1) to afford pure **8a**. White foam. $[\alpha]_D^{r.t.} = -281.7$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2971*w*, 1749*s*, 1660*w*, 1492*w*, 1451*w*, 1406*m*, 1326*w*, 1117*w*, 1040*w*, 1003*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.55 (*d*, *J* = 7.3, Me); 0.61 (*d*, *J* = 6.7, Me); 0.82 (*s*, Me); 0.87 (*s*, Me); 1.57 (*s*, OH); 1.81–1.92 (*m*, Me_2CH); 3.09 (*d*, *J* = 11.6, PhC*H*); 4.50 (*d*, *J* = 1.8, NCH); 5.83 (*dd*, *J* = 8.4, 11.6, CHC*H*=CH); 6.34 (*d*, *J* = 8.4, CHCH=C*H*); 7.12–7.17 (*m*, 2 arom. H); 7.21–7.39 (*m*, 7 arom. H); 7.43–7.52 (*m*, 4 arom. H); 7.72–7.77 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.8, 21.4, 27.4, 27.8 (Me); 30.4, 52.6 (CH); 72.0 (C); 72.3 (CH); 87.6 (C); 124.2, 124.9, 125.8, 126.87, 126.94, 127.7, 128.28, 128.30, 128.4, 129.1 (CH); 138.3, 139.4, 144.6, 155.9 (C). FAB-MS: 911 (12, $[2M+H]^+$), 456 (24, $[M+H]^+$), 438 (45, $[M+H-H_2O]^+$), 394 (100, $[M+H-CO_2-H_2O]^+$), 352 (41), 222 (23). Anal. calc. for $C_{30}H_{33}NO_3$ (455.60): C 79.09, H 7.30, N 3.07; found: C 78.92, H 7.38, N 3.15.

*(*S*)-3-[(1*Z*,4*R*)-3-(1-Hydroxycyclohexyl)-3-phenylprop-1-enyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**8b**). Compound **3** (470 mg, 1.18 mmol) was treated with BuLi (0.92 ml, 1.42 mmol) and cyclohexanone (159 µl, 1.53 mmol) according to *GP 3*. Purification of the crude product by FC (pentane/Et_2O 2:1) yielded **8b** (325 mg, 56%) as a single diastereoisomer. White foam. $[\alpha]_D^{r.t.} = -222.5$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3006*w*, 2934*m*, 1749*s*, 1660*w*, 1600*w*, 1492*w*, 1450*m*, 1405*m*, 1260*w*, 1102*w*, 1036*w*, 1003*w*, 909*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.46 (*d*, *J* = 7.3, Me); 0.58 (*d*, *J* = 6.7, Me); 0.78–1.45 (*m*, 11 H, cyclohexyl, OH); 1.80–1.91 (*m*, Me_2CH); 3.10 (*d*, *J* = 11.4, PhC*H*); 4.54 (*d*, *J* = 1.8, NCH); 5.86 (*dd*, *J* = 8.4, 11.4, CHC*H*=CH); 6.36 (*d*, *J* = 8.4, CHCH=C*H*); 7.18–7.38 (*m*, 9 arom. H); 7.43–7.55 (*m*, 4 arom. H); 7.76–7.81 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.7, 21.2 (Me); 21.5, 21.8, 25.3 (CH_2); 30.5 (CH); 35.1, 36.0 (CH_2); 51.1 (CH); 72.5 (C); 72.6 (CH); 87.4 (C); 124.2, 124.8, 125.8, 126.8, 126.9, 127.7, 128.2, 128.3, 128.8, 129.2 (CH); 138.3, 138.9, 144.8, 156.0 (C). FAB-MS: 992 (8, $[2M+H]^+$), 496 (10, $[M+H]^+$), 478 (83, $[M+H-H_2O]^+$), 434 (100, $[M+H-CO_2-H_2O]^+$), 396 (40), 352 (52), 222 (45). Anal. calc. for $C_{33}H_{37}NO_3$ (495.66): C 79.97, H 7.52, N 2.83; found: C 79.96, H 7.62, N 2.92.

*(*S*)-3-[(*M*,*R*)-4-Hydroxy-5-methyl-3-(trimethylsilanyl)hexa-1,2-dienyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**9a**). Compound **4** (355 mg, 0.907 mmol) was treated with BuLi (0.70 ml, 1.09 mmol), $(i\text{-}PrO)_3TiCl$ (0.54 ml, 1.09 mmol) and isobutyraldehyde (108 µl, 1.18 mmol) according to *GP 4*. Purification of the crude product by FC (pentane/Et_2O 5:1) yielded **9a** (281 mg, 67%, dp 97%). For anal. purposes, a sample was recrystallized (hexane/CH_2Cl_2) to afford **9a** (dp 98%). White solid. M.p. 160–163°. $[\alpha]_D^{r.t.} = -357.9$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2963*m*, 1749*s*, 1493*w*, 1436*s*, 1368*w*, 1016*m*, 842*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.15 (*s*, Me_3Si); 0.75 (*d*, *J* = 6.9, Me); 0.94 (*d*, *J* = 7.1, Me); 0.98 (*d*, *J* = 6.7, Me); 1.11 (*d*, *J* = 6.8, Me); 1.79 (*d*, *J* = 5.3, OH); 1.82–1.92 (*m*, Me_2CH); 1.99–2.10 (*m*, Me_2CH); 4.06–4.08 (*m*, *CH*OH); 4.41 (*d*, *J* = 3.2, NCH); 6.75 (*d*, *J* = 3.0, C=C=CH); 7.23–7.37 (*m*, 6 arom. H); 7.39–7.43 (*m*, 2 arom. H); 7.47–7.51 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): −1.0, 15.4, 17.1, 20.5, 20.9 (Me); 29.5, 33.1, 67.4, 75.3 (CH); 89.1 (C); 97.8 (CH); 118.5 (C); 125.7, 126.6, 127.8, 128.1, 128.4, 128.7 (CH); 138.5, 143.5, 154.5, 196.3 (C). MALDI-FT-ICR-MS: 486 (100, $[M+Na]^+$), 414 (76), 370 (95). Anal. calc. for $C_{28}H_{37}NO_3Si$ (463.69): C 72.53, H 8.04, N 3.02; found: C 72.67, H 8.10, N 2.94.

*(*S*)-3-[(*M*,*R*)-4-Hydroxy-3-(trimethylsilyl)hepta-1,2-dienyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**9b**). Compound **4** (370 mg, 0.945 mmol) was treated with BuLi (0.73 ml, 1.13 mmol), $(i\text{-}PrO)_3TiCl$ (0.57 ml, 1.13 mmol), and butyraldehyde (110 µl, 1.23 mmol) according to *GP 4*. Purification of the crude product by FC (pentane/Et_2O 9:2 → 4:1) yielded **9b** (288 mg, 66%, dp 97%). For anal. purposes, a sample was recrystallized (hexane/CH_2Cl_2) to afford **9b** (dp 98%). White solid. M.p. 146–148°. $[\alpha]_D^{r.t.} = -355.9$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2962*w*, 1748*s*, 1494*w*, 1435*s*, 1322*w*, 1099*w*, 1002*w*, 842*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.09 (*s*, Me_3Si); 0.69 (*d*, *J* = 6.9, Me); 0.87 (*d*, *J* = 7.1, Me); 0.92–0.96 (*m*, *Me*CH_2); 1.41–1.53 (*m*, 3 H, CH_2); 1.60–1.72 (*m*, 1 H, CH_2); 1.84 (*d*, *J* = 5.7, OH); 1.91–2.01 (*m*, Me_2CH); 4.16–4.22 (*m*, *CH*OH); 4.31 (*d*, *J* = 3.0, NCH); 6.66 (*d*, *J* = 2.7, C=C=CH); 7.18–7.30 (*m*, 6 arom. H); 7.33–7.38 (*m*, 2 arom. H); 7.41–7.45 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): −0.9, 14.0, 16.9 (Me); 18.6 (CH_2); 21.1 (Me); 29.4 (CH); 39.9

(CH_2); 67.5, 70.6 (CH); 89.1 (C); 97.7 (CH); 118.9 (C); 125.7, 126.5, 127.8, 128.1, 128.4, 128.7 (CH); 138.5, 143.5, 154.5, 196.4 (C). MALDI-FT-ICR-MS: 486 (100, $[M+Na]^+$), 446 (34, $[M+H-H_2O]^+$), 414 (34), 370 (22). Anal. calc. for $C_{28}H_{37}NO_3Si$ (463.69): C 72.53, H 8.04, N 3.02; found: C 72.36, H 8.12, N 2.97.

*(*S*)-3-[(*M,R*)-4-Hydroxy-6-methyl-3-(trimethylsilyl)hepta-1,2,6-trienyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**9c**). Compound **4** (345 mg, 0.881 mmol) was treated with BuLi (0.68 ml, 1.06 mmol), (i-PrO)$_3$TiCl (0.53 ml, 1.06 mmol), and methacrolein (94 µl, 1.15 mmol) according to *GP 4*. Purification of the crude product by FC (pentane/Et_2O 4:1) yielded **9c** (244 mg, 60%, dp 98%). For anal. purposes, a sample was recrystallized (hexane/CH_2Cl_2) to afford **9c** (dp ≥ 99%). White solid. M.p. 157–158°. $[\alpha]_D^{r.t.} = -498.6$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2966*w*, 1751*s*, 1494*w*, 1436*s*, 1370*w*, 1328*w*, 1062*w*, 911*w*, 843*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.12 (*s*, Me_3Si); 0.75 (*d*, $J = 6.9$, Me); 0.94 (*d*, $J = 7.1$, Me); 1.80–1.81 (*m*, C=CMe); 1.99–2.08 (*m*, Me_2CH); 2.35 (*d*, $J = 4.8$, OH); 4.42 (*d*, $J = 3.1$, NCH); 4.68–4.70 (*m*, *CH*OH); 4.99–5.01 (*m*, 1 H, C=CH_2); 5.09–5.10 (*m*, 1 H, C=CH_2); 6.79 (*d*, $J = 3.2$, C=C=CH); 7.24–7.38 (*m*, 6 arom. H); 7.39–7.43 (*m*, 2 arom. H); 7.47–7.52 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): –1.2, 16.9, 17.0, 20.9 (Me); 29.4, 67.5, 75.1 (CH); 89.2 (C); 98.4 (CH); 114.1 (CH_2); 117.3 (C); 125.7, 126.5, 127.9, 128.1, 128.5, 128.7 (CH); 138.4, 143.4, 145.3, 154.5, 196.3 (C). MALDI-FT-ICR-MS: 500 (8, $[M+K]^+$), 484 (58, $[M+Na]^+$), 414 (80), 370 (100). Anal. calc. for $C_{28}H_{35}NO_3Si$ (461.67): C 72.85, H 7.64, N 3.03; found: C 72.98, H 7.77, N 3.01.

*(*S*)-3-[(*M,R*)-4-Hydroxy-4-phenyl-3-(trimethylsilyl)buta-1,2-dienyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one* (**9d**). Compound **4** (280 mg, 0.715 mmol) was treated with BuLi (0.55 ml, 0.858 mmol), (i-PrO)$_3$TiCl (0.43 ml, 0.858 mmol), and PhCHO (94 µl, 0.930 mmol) according to *GP 4*. Purification of the crude product by FC (pentane/Et_2O 4:1) yielded **9d** (226 mg, 64%, dp 97%). For anal. purposes, a sample was recrystallized (hexane/CH_2Cl_2) to afford **9d** (dp ≥ 99%). White solid. M.p. 152–158°. $[\alpha]_D^{r.t.} = -451.9$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2964*w*, 1749*s*, 1493*w*, 1435*s*, 1328*w*, 1056*w*, 1002*w*, 844*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): –0.10 (*s*, Me_3Si); 0.74 (*d*, $J = 6.9$, Me); 0.95 (*d*, $J = 7.1$, Me); 1.98–2.09 (*m*, Me_2CH); 2.88 (*d*, $J = 5.3$, OH); 4.44 (*d*, $J = 3.0$, NCH); 5.24 (*dd*, $J = 3.0$, 5.3, *CH*OH); 6.71 (*d*, $J = 3.0$, C=C=CH); 7.24–7.45 (*m*, 13 arom. H); 7.48–7.52 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): –1.3, 16.8, 20.9 (Me); 29.5, 68.1, 73.5 (CH); 89.0 (C); 97.9 (CH); 118.3 (C); 125.7, 126.5, 127.4, 127.8, 128.0, 128.1, 128.4, 128.5, 128.7 (CH); 138.4, 142.4, 143.5, 154.6, 196.7 (C). FAB-MS: 995 (8, $[2M+H]^+$), 570 (10), 480 (100, $[M+H-H_2O]^+$), 346 (27), 222 (21). Anal. calc. for $C_{31}H_{35}NO_3Si$ (497.71): C 74.81, H 7.09, N 2.81; found: C 74.85, H 7.14, N 2.80.

*(*R*)-2,3,4,5-Tetrahydro-5-methoxy-2,2-dimethyl-3-phenylfuran* (**10b**). Compound **8a** (471 mg, 1.03 mmol) was treated with H_2SO_4 (0.75 ml), and the mixture was stirred for 9 d according to *GP 5*. The auxiliary **1** was recovered by filtration (241 mg, 83%). Purification of the crude product by FC (pentane/Et_2O 20:1) yielded **10b** (178 mg, 84%) as a 70:30 mixture (*C*(5)-epimers). Colorless oil. IR ($CHCl_3$): 3008*m*, 2976*m*, 2832*w*, 1602*w*, 1496*w*, 1453*w*, 1368*w*, 1136*w*, 1099*m*, 1035*s*, 976*m*, 889*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.80 (*s*, Me (major)); 1.01 (*s*, Me (minor)); 1.32 (*s*, Me (minor)); 1.47 (*s*, Me (major)); 2.19–2.25 (*m*, 1 H, CH_2 (major)); 2.36–2.68 (*m*, 1 H (major), 2 H (minor), CH_2); 3.13 (*dd*, $J = 8.6$, 11.7, PhC*H* (minor)); 3.41 (*s*, MeO (major)); 3.44 (*s*, MeO (minor)); 3.48 (*dd*, $J = 6.7$, 12.1, PhC*H* (major)); 5.08 (*dd*, $J = 5.0$, 5.0, C*H*OMe (major)); 5.12 (*dd*, $J = 4.7$, 5.9, C*H*OMe (minor)); 7.20–7.35 (*m*, 5 arom. H (major), 5 arom. H (minor)). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.0 (Me (minor)); 25.1 (Me (major)); 28.1 (Me (minor)); 30.0 (Me (major)); 37.9 (CH_2 (major)); 38.4 (CH_2 (minor)); 51.6 (CH (major)); 54.35 (Me (major)); 54.40 (CH (minor)); 55.6 (Me (minor)); 83.6 (C (minor)); 84.4 (C (major)); 103.2 (CH (major)); 104.2, 126.9 (CH (minor)); 126.8, 128.1 (CH (major)); 128.2 (CH (minor)); 128.3 (CH (major)); 128.5 (CH (minor)); 138.6 (C (minor)); 139.2 (C (major)). EI-MS: 206 (1, M^+), 174 (10, $[M-HOMe]^+$), 157 (6, $[M-OMe-H_2O]^+$), 148 (100), 116 (50).

*(*R*)-2-Methoxy-4-phenyl-1-oxaspiro[4.5]decane* (**10c**). Compound **8b** (662 mg, 1.34 mmol) was treated with H_2SO_4 (1.00 ml), and the mixture was stirred for 13 d according to *GP 5*. The auxiliary **1** was recovered by filtration (297 mg, 79%). Purification of the crude product by FC (pentane/Et_2O 20:1) yielded **10c** (273 mg, 83%) as a 70:30 mixture (*C*(2)-epimers). Colorless oil. IR ($CHCl_3$): 3007*m*, 2934*s*, 2859*m*, 1602*w*, 1497*w*, 1448*m*, 1371*w*, 1099*m*, 1037*s*, 974*m*, 866*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.56–0.68 (*m*, 1 H, CH_2 (major)); 0.68–0.79 (*m*, 1 H, CH_2 (minor)); 0.91–1.10 (*m*, 1 H (major), 1 H (minor), CH_2); 1.30–1.88 (*m*, 8 H (major), 8 H (minor), CH_2); 2.26 (*ddd*, $J = 1.1$, 7.2, 12.9, 1 H, $CH_2C(O)$ (major)); 2.35–2.50 (*m*, 1 H (major), 1 H (minor), $CH_2C(O)$); 2.62 (*ddd*, $J = 6.2$, 9.0, 13.5, 1 H, $CH_2C(O)$ (minor)); 3.03 (*dd*, $J = 9.0$, 11.2, PhC*H* (minor)); 3.35 (*dd*, $J = 7.2$, 10.9, PhC*H* (major)); 3.43 (*s*, MeO (major)); 3.50 (*s*, MeO (minor)); 5.11–5.15 (*m*, C*H*OMe (major)); 5.15–5.17 (*m*, C*H*OMe (minor)); 7.17–7.35 (*m*, 5 arom. H (major), 5 arom. H (minor)). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.2 (CH_2 (major), CH_2 (minor)); 23.3 (CH_2 (minor)); 23.5, 25.5 (CH_2 (major)); 25.7, 32.4 (CH_2 (minor)); 34.1 (CH_2 (major)); 37.2 (CH_2 (minor)); 38.2 (CH_2 (minor)); 38.3, 38.9 (CH_2 (major)); 52.4 (CH (major)); 54.4 (Me (major)); 55.2 (CH (minor)); 55.7 (Me (minor)); 84.7 (C (minor)); 85.2 (C (major)); 103.4 (CH (major)); 104.2 (CH (minor)); 126.6 (CH (major)); 126.8, 128.1 (CH (minor)); 128.2, 128.5 (CH (major));

128.9 (CH (minor)); 138.7 (C (minor)); 139.7 (C (major)). EI-MS: 246 (1, M^+), 214 (15, $[M - HOMe]^+$), 196 (2, $[M - HOMe - H_2O]^+$), 185 (10), 171 (7), 148 (100).

(S)-2,3,4,5-Tetrahydro-5-methyl-5-(2-methylethyl)furan-2-one (**11a**). Compound **5e** (228 mg, 0.559 mmol, as a 95 :5 mixture with 4′-*epi*-**5e**) was treated with H_2SO_4 (0.40 ml), and the mixture was stirred for 5 d according to *GP 5*. The auxiliary **1** was recovered by filtration (123 mg, 78%, *ca.* 95% purity). The crude product was treated without purification with *m*-CPBA (276 mg, 1.12 mmol) and $BF_3 \cdot Et_2O$ (4 drops) according to *GP 6*. Purification of the crude product by FC (pentane/Et_2O 2 :1) yielded **11a** (49 mg, 62%, *ca.* 95% purity). For anal. purposes, the product was distilled in a *Kugelrohr* apparatus (105°/0.3 Torr) to afford **11a** (33 mg, 42%). Colorless oil. $[\alpha]_D^{r.t.} = +9.8$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 2971*m*, 1758*s*, 1468*w*, 1392*w*, 1291*m*, 1087*w*, 937*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.90 (*d*, $J = 6.8$, Me); 0.97 (*d*, $J = 6.9$, Me); 1.28 (*s*, Me); 1.84 – 1.93 (*m*, 2 H, CH_2 or Me_2CH); 2.03 – 2.14 (*m*, 1 H, CH_2 or Me_2CH); 2.46 – 2.69 (*m*, $C(O)CH_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.0, 17.1, 21.8 (Me); 29.2, 31.1 (CH_2); 37.1 (CH); 89.7, 176.9 (C). The value of optical rotation is in agreement with the value reported in [15].

(R)-2,3,4,5-Tetrahydro-5,5-dimethyl-4-phenylfuran-2-one (**11b**). Compound **10b** (95 mg, 0.461 mmol) was treated with *m*-CPBA (340 mg, 1.38 mmol) and $BF_3 \cdot Et_2O$ (4 drops) according to *GP 6*. Purification of the crude product by FC (pentane/Et_2O 3 :1) yielded **11b** (79 mg, 90%). White solid. M.p. 118 – 120°. $[\alpha]_D^{r.t.} = -84.0$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 2980*w*, 1766*s*, 1499*w*, 1455*w*, 1421*w*, 1388*w*, 1376*w*, 1269*m*, 1111*m*, 959*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.05 (*s*, Me); 1.55 (*s*, Me); 2.89 (*dd*, $J = 8.5$, 17.5, 1 H, CH_2); 3.01 (*dd*, $J = 10.3$, 17.5, 1 H, CH_2); 3.53 (*dd*, $J = 8.5$, 10.3, PhC*H*); 7.20 – 7.23 (*m*, 2 arom. H); 7.29 – 7.39 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 23.2, 27.8 (Me); 34.5 (CH_2); 51.2 (CH); 87.3 (C); 127.79, 127.80, 128.7 (CH); 136.7, 175.4 (C). EI-MS: 190 (1, M^+), 175 (2), 162 (3), 131 (5), 104 (100). The physical data are in agreement with the values reported in [32][33].

(R)-4-Phenyl-1-oxaspiro[4.5]decan-2-one (**11c**). Compound **10c** (77 mg, 0.312 mmol) was treated with *m*-CPBA (231 mg, 0.938 mmol) and $BF_3 \cdot Et_2O$ (4 drops) according to *GP 6*. Purification of the crude product by FC (pentane/Et_2O 3 :1) yielded **11c** (68 mg, 95%). White solid. M.p. 102 – 103°. $[\alpha]_D^{r.t.} = -61.2$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3011*w*, 2940*m*, 2867*w*, 1764*s*, 1498*w*, 1450*w*, 1271*w*, 1133*w*, 958*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 – 0.97 (*m*, 1 H, CH_2); 1.03 – 1.15 (*m*, 1 H, CH_2); 1.42 – 1.78 (*m*, 7 H, CH_2); 1.88 – 1.95 (*m*, 1 H, CH_2); 2.88 – 3.00 (*m*, $C(O)CH_2$); 3.40 (*dd*, $J = 8.9$, 8.9, PhC*H*); 7.16 – 7.21 (*m*, 2 arom. H); 7.29 – 7.38 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.7, 22.6, 24.9, 32.3, 34.8, 36.8 (CH_2); 51.2 (CH); 88.5 (C); 127.6, 128.1, 128.6 (CH); 137.1, 175.8 (C). EI-MS: 230 (1, M^+), 202 (2), 187 (1, $[M + H - H_2O]^+$), 132 (3), 104 (100). Anal. calc. for $C_{15}H_{18}O_2$ (230.31): C 78.23, H 7.88; found: C 78.23, H 7.76. The physical data are in agreement with the values reported in [32].

X-Ray Crystal-Structure Determination of **11c**. The reflections were measured on an *Enraf-Nonius CAD-4* diffractometer with CuK_α radiation (graphite monochromator, $\lambda = 1.54184$ Å) at 293 K. The structure was solved by direct methods with SIR97 [34]. The non-H-atoms were refined anisotropically with SHELXL-97 [35]. The H-atoms were calculated at idealized positions and included in the structure factor calculation with fixed isotropic displacement parameters with SHELXL-97. Crystal size $0.30 \times 0.25 \times 0.15$ mm, monoclinic, $P2_1$, $a = 9.0270(14)$ Å, $b = 7.7820(8)$ Å, $c = 9.6730(14)$ Å, $\alpha = 90°$, $\beta = 112.488(14)°$, $\gamma = 90°$, $V = 627.84(12)$ Å^3, $D_{calc.} = 1.218$ g cm^{-3}, $Z = 2$, $\mu = 0.627$ mm^{-1}, 1219 reflections measured, 1219 independent reflections, 1118 reflections observed, 1 restraint, 154 variables, criterion $I > 2\sigma(I)$, final $R = 0.0498$, $wR_2 = 0.1494$, absolute structure parameter $= -0.2(5)$.

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