Conjugate Addition of Lithiated (*S*)-4-Isopropyl-3-[(methylthio)methyl]-5,5-diphenyloxazolidin-2-one to Cinnamoyl Derivatives: Preparation of Enantiomerically Pure 1,4-Diols

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The Li derivative of (*S*)-4-isopropyl-3-[(methylthio)methyl]-5,5-diphenyloxazolidin-2-one (Li-**2**; synthetically equivalent to a chiral formyl anion) adds to enones and enoates in a 1,4-fashion. Best results are obtained with 1,3-diarylpropenones (chalcones; *Scheme 2*), trityl enones, and 2,6-di(*tert*-butyl)-4-methoxyphenyl cinnamates (*Scheme 3*), with yields up to 80% and diastereoselectivities up to and above 99:1 of the products (**5a**–**f** and **8a**,**b**,**e**) containing three stereogenic centers! X-Ray crystal-structure analysis reveals that the C,C-bond formation occurs preferentially with relative topicity *ul* (*Re*/*Si*; *Fig. 2*). The MeS group of the 1,4-adducts can be replaced by RO groups in Hg^{2+}-assisted substitutions, with subsequent removal and facile recovery of the chiral auxiliary (*Schemes 4–6*). 4-Hydroxycarbonyl derivatives ('homoaldols') and mono-, di-, and trisubstituted 1,4-diols are, thus, accessible in enantiomerically pure forms (*cf.* **15**, **16**, and **18**–**20**).

1. Introduction. – The 4-isopropyl-5,5-diphenyloxazolidin-2-one[2]) (**1**; developed in our group[3]) and by others[4])[5]) is a useful alternative to the widely employed amino-acid- or ephedrine-derived *Evans* oxazolidinones [6][6]). *N*-Acyl derivatives of **1** were shown to be suitable substrates for diastereoselective alkylations, aldol additions, 1,4-additions, cycloadditions, and numerous other reactions [3][4][9]. Recently, we have also reported on the preparation of a new *N*-alkyl derivative of oxazolidinone **1**, the 3-[(methylthio)methyl]oxazolidin-2-one (**2**), the applicability of which as chiral reagent (synthetically equivalent to a formyl anion) was demonstrated (*Scheme 1*) [10]. The geminal Ph groups of oxazolidinone **2** protect the C=O group from nucleophilic attack, so that direct lithiation at the exocyclic CH_2 group by BuLi is possible. Addition of an aldehyde or unsymmetrical ketone to solutions of the lithium reagent Li-**2** affords adducts **3** (1,2-addition) in high yields and good-to-excellent diastereoselectivities. Hg^{2+}-Promoted hydrolysis of the *N,S*-acetal moiety of **3** yields (protected) 2-hydroxy

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[1]) Part of the Ph.D. thesis of *C. G.*, Dissertation No. 14516, ETH Zürich, 2002.

[2]) Oxazolidinone **1** and its enantiomer are commercially available as (*S*)- and (*R*)-DIOZ (5,5-*d*iphenyl-4-*i*sopropyl-1,3-*ox*a*z*olidin-2-one): *Shiratori Pharmaceutical Co., Ltd.*, Japan. DIOZ is also offered by *Onyx Scientific, Ltd.*, UK. Compound **1** has been mentioned in a patent [1]. An Organic Syntheses Procedure [2] has been submitted, a copy of which will be provided by the correspondence author upon request.

[3]) The superior properties of auxiliary **1**, as compared to the *Evans* auxiliaries, are discussed in [3].

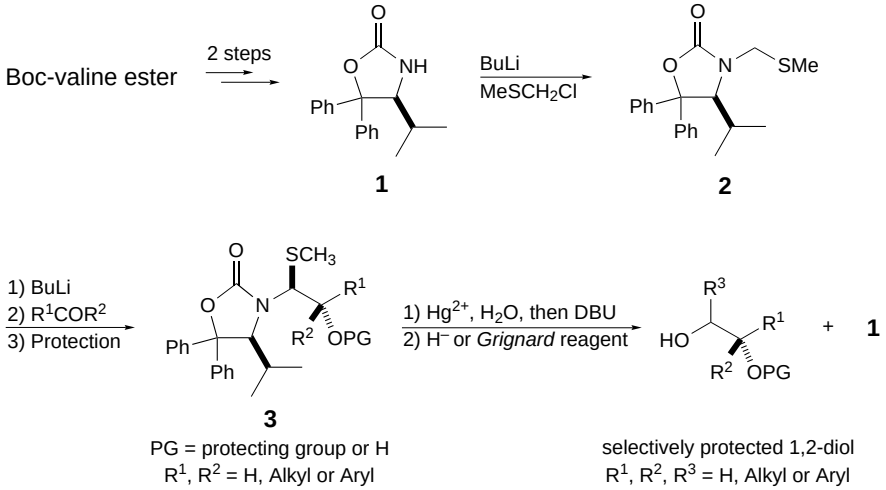
[4]) For independent work with auxiliary **1** by other groups, see [4].

[5]) Oxazolidinone **1** has also been prepared by others, but not utilized as a chiral auxiliary [5].

[6]) For earlier work with analogous thiazolidinethiones, see *Mukaiyama* [7]. For a general discussion of geminal-diarylmethanol derivatives, see Chapt. 11 in a recent review article [8a] and Scheme 17 in a book chapter [8b].

aldehydes, which can be either reduced or trapped *in situ* with carbon nucleophiles to give enantiomerically pure, selectively protected 1,2-diols, with recovery of the chiral auxiliary **1** (*Scheme 1*).

Scheme 1. *Overall Enantioselective Preparation of Specifically Protected 1,2-Diols with Formation of the Central C,C-Bond* (DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene)



We have now explored the scope and limitations of 1,4-additions of Li-**2** to conjugated enones and enoates. A survey of the literature reveals that there have been only two reagents reported for the overall enantioselective nucleophilic formylation of enones (*Fig. 1*). The synthetic use of the lithiated *S,S*-acetal *S*-oxide **A** of *Scolastico* and co-workers is rather limited [11], but formaldehyde SAMP-hydrazone **B** of *Lassaletta*, *Enders*, and their co-workers [12] undergoes conjugate addition to a wide range of α,β-unsaturated carbonyl compounds[7]), leading, after release of the masked carbonyl group, to 4-oxo aldehydes or derivatives thereof.

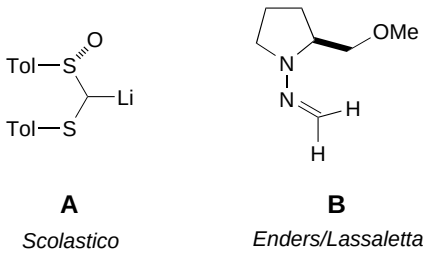


Fig. 1. *Reagents that are synthetically equivalent to a chiral formyl anion and used in 1,4-additions to α,β-unsaturated carbonyl compounds*

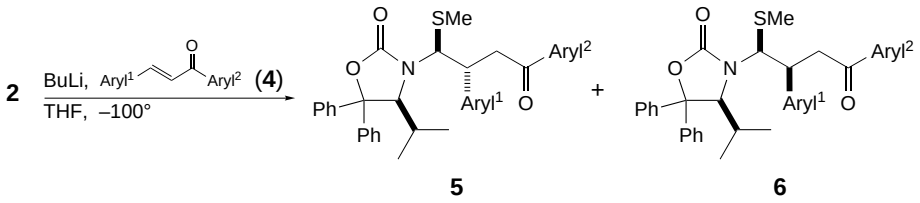
In the present paper, we describe the diastereoselective conjugate addition of [(methylthio)methyl]-oxazolidinone **2** to a series of chalcones, trityl (triphenylmethyl)-

7) For *Michael* additions of SAMP-hydrazone **B** to nitroalkenes, see [13].

enones, and a 2,6-di(*tert*-butyl)-4-methoxyphenyl (BHA) cinnamate, as well as further elaborations of the adducts to enantiomerically pure 1,4-diols, a γ-lactol ether, and a 4-hydroxytrityl ketone.

2. Addition of [(Methylthio)methyl]-oxazolidinone 2 to Chalcones, Trityl Enones, and an α,β-Unsaturated BHA Ester. – The *N*,*S*-acetal **2** was obtained from oxazolidinone **1** by *N*-alkylation with (chloromethyl) methyl sulfide (*Scheme 1*). Sequential treatment of compound **2** with BuLi at $-78°$ and a chalcone[8]) **4** at $-100°$ gave the products of conjugate addition **5** and **6** in good yields and excellent regio- and diastereoselectivities. In *Scheme 2*, we have summarized the results obtained from this addition reaction. In each case, only two of the four possibe diastereoisomers were formed. Major isomers **5** and minor isomers **6** have the same configuration at MeS–*C*(1) and are epimeric[9]) at Aryl[1]–*C*(2). After flash chromatography, 90–99% diastereoisomerically pure products **5** were obtained in 65–80% yield. The diastereoselectivity of the reaction is >90%

Scheme 2. *Addition of Lithiated [(Methylthio)methyl]-oxazolidinone Li-***2** *to Chalcones*



Entry	Products **5** and **6**[a])	Aryl[1]	Aryl[2]	Yield [%][b])	dr (**5**/**6**)[c])
1	**a**	Ph	Ph	79	98:2
2	**b**	Ph	CH=CHPh	72	>99:1
3	**c**	Ph	1-naphthyl	71	>99:1
4	**d**	Ph	5-methylfuran-2-yl	71	96:4
5	**e**	4-(MeO)C_6H_4	Ph	65	91:9
6	**f**	4-ClC_6H_4	Ph	70	96:4

[a]) Products derived from 1,2-addition can also be detected by ^{1}H-NMR of the crude product in some cases. *Entry 1*: 9%, *Entry 5*: 22%, *Entry 6*: 8%. [b]) Combined yield of both isomers **5** and **6** after FC. [c]) Determined by ^{1}H-NMR (300 MHz) after FC.

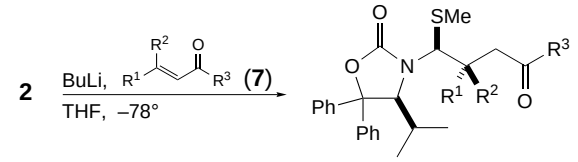
[8]) References to the preparation of compounds **4c**, **4d**, **7a**–**7c**, **7e**, and a procedure for the preparation of compound **7d** are given in the *Exper. Part*.

[9]) The relative configuration of adducts **5c**, **8b**, of *N*,*O*-acetal **10**, and of compounds **11** and **17** were unambiguously assigned by single-crystal X-ray analysis. The X-ray structures and comparison of R_f values of major and minor isomers led to configurational assignments of the other compounds by analogy (see formulae in *Schemes*). Graphical illustrations and full experimental data associated with the X-ray crystal structures of compounds **5c**, **8b**, **10**, **11**, **17**, and of related compounds that are mentioned in [10] will be published later in this journal.

in most cases, as determined by ^{1}H-NMR spectroscopy of the crude products. Formation of products derived from 1,2-addition takes place to only a small extent (< 10%, except for *Entry 5*).

We next turned our attention to the reaction of Li-**2** with trityl enones **7a**–**d** and BHA ester **7e**. The *Michael* acceptors[8]) **7a**–**e** with 'sterically protected but electronically effective carbonyl groups'[10]) are known to undergo 'sterically enforced' 1,4-additions with various carbon nucleophiles, even with the most reactive nucleophiles such as BuLi or lithiumdithiane[11]). As is evident from the data in *Scheme 3*, Li-**2** adds particularly effectively to the β-monosubstituted trityl enones **7a** (*Entry 1*) and **7b** (*Entry 2*). The adducts **8a** and **8b** were obtained as single diastereoisomers in 83% and 51% yield, respectively. The reaction of Li-**2** with β,β-disubstituted trityl enones **7c** (*Entry 3*) and **7d** (*Entry 4*), which would lead to the creation of quaternary stereogenic centers, resulted in recovery of starting material or in isolation of a complex mixture of products. We assume that proton abstraction, rather than nucleophilic addition, is the predominant reaction of Li-**2** with enone **7c**. Conjugate addition of the lithiated *N*,*S*-acetal **2** to BHA ester **7e** is possible, although the yield of the reaction is low (*Entry 5*).

Scheme 3. *Addition of Lithiated [(Methylthio)methyl]-oxazolidinone Li-***2** *to Trityl Enones and an* α,β*-Unsaturated BHA Ester* (BHA: 2,6-di(*tert*-butyl)-4-methoxyphenyl)



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Entry	Product **8**	R^1	R^2	R^3	Yield of **8** [%][a])
1	**a**	Ph	H	Ph_3C	83
2	**b**	Me	H	Ph_3C	51
3[b])	**c**	Ph	Me	Ph_3C	–[c])
4	**d**	CF_3	Ph	Ph_3C	–[d])
5	**e**	Ph	H	OBHA	30

[a]) Yield of a single diastereoisomer after FC. [b]) The C=C bond geometry of this trityl enone is unknown. [c]) No reaction. [d]) Complex mixture of products.

As reported previously [10], reactions of Li-**2** with α,β-unsaturated aldehydes (*e.g.*, methacrolein) and ketones (others than chalcones and trityl enones; *e.g.*, cyclohexenone) give exclusively 1,2-adducts. In the course of our investigations, several attempts have been undertaken to achieve conjugate addition of Li-**2** (or a derivative

[10]) For the use of this term, see, *e.g.*, [14–16].

[11]) For *Michael* additions of carbon nucleophiles to trityl enones and to BHA esters, see, *e.g.*, [15] and [16], respectively.

thereof) to 'standard' *Michael* acceptors by modifying reaction conditions and reagents. For example, hexamethylphosphoramide (HMPA) [17a] and 3,4,5,6-tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-one (DMPU) [17b,c] are frequently used as additives to cause reversal of regioselectivity (from 1,2- to 1,4-addition) in the reaction of organolithium reagents to α,β-unsaturated carbonyl compounds[12]). In our case, the presence of DMPU in the reaction of Li-**2** with cyclohexenone did not yield the desired effect; only the product of 1,2-addition could be detected by ^{1}H-NMR spectroscopy. Furthermore, it is known that lithiated *S,S*-acetals with additional anion-stabilizing groups (such as the Me_3Si group) and *S,S*-acetal *S*-oxides have an enhanced tendency toward conjugate addition as compared to simple *S,S*-acetals[13]). Therefore, we prepared the Me_3Si-substituted derivative of *N,S*-acetal **2** (**2**, BuLi, Me_3SiCl, THF)[14]) and the *S*-oxide derivative of *N,S*-acetal **2** (**2**, $NaIO_4$, H_2O, MeOH)[15]). Unfortunately, efforts to lithiate these derivatives with BuLi led to the formation of decomposition products, which were not identified. Also, transmetallation of Li-**2** to the corresponding cuprate and subsequent addition of cyclohexenone did not give the desired product of 1,4-addition but, instead, resulted in decomposition of the educt, probably caused by the high affinity of copper for sulfur in the reagent Li-**2** (α-elimination).

Based on both the data obtained by X-ray crystallography and our structural studies on Li-**2** [10c], the steric course of the *Michael* addition leading to the major isomers **5** and **8** can be deduced. The *Michael* acceptor approaches the lithiated C-atom of Li-**2** ((4*S*,1′*S*)-configuration; *Fig. 2*, left) with its *Re* face, in an orientation that allows transfer of the Li-atom from Li-**2** to the enone O-atom (*Fig. 2*, right). The reaction proceeds with relative topicity *unlike*.

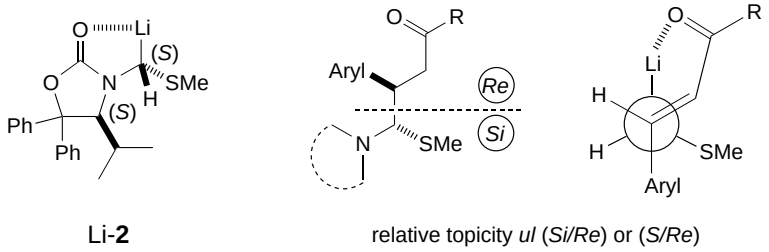

Fig. 2. *Proposed structure of Li-***2** *and a model for the stereochemical course of the conjugate addition of Li-***2** *to chalcones, trityl enones, and* α,β*-unsaturated BHA esters*

3. Conversion of the Adducts 5 and 8 to 1,4-Diols, a 'γ-Lactol Ether', and a 3-Hydroxypropyl Trityl Ketone. – The synthetic value of chalcone adducts **5** for the preparation of interesting chiral building blocks is demonstrated in *Schemes 4–6*.

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[12]) For a recent study on the effects of HMPA and DMPU on the regioselectivity of addition of organolithium reagents to enones and enals, see [17d] and references cited therein.

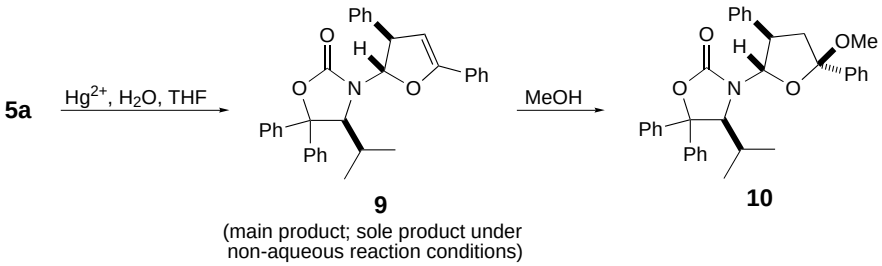
[13]) For examples of *Michael* additions of lithiated *S,S*-acetals with additional anion-stabilizing groups, lithiated *S,S*-acetal *S*-oxides, and copper *S,S*-acetals to α,β-unsaturated carbonyl compounds, see Chapt. 3.5 in a review article [18].

[14]) Obtained as a *ca.* 95:5 mixture of diastereoisomers after trituration of the crude product in hexane.

[15]) Obtained as a *ca.* 2.5:1 mixture of diastereoisomers (crude product).

Originally, we intended to hydrolyze the *N,S*-acetal moiety of **5** in order to obtain the corresponding enantiomerically pure 4-oxo aldehydes (or derivatives thereof). However, subjecting adduct **5a** to the reaction conditions that were used for the hydrolysis of 1,2-adducts **3** ($Hg(O_2CCF_3)_2$, H_2O, THF, then DBU; see *Scheme 1* and [10]) resulted in the formation of the cyclic enol ether **9** (*Scheme 4*). Obviously, compound **9** is derived from an intramolecular attack of the intermediate acyliminium ion by the carbonyl O-atom of the phenylcarbonyl moiety. Recrystallization of **9** in MeOH gave the *N,O*-acetal **10** as a single diastereoisomer. Treatment of compounds **9** or **10** with aqueous or methanolic acid did not yield the desired 4-oxo aldehydes either, but, instead, led to a complex mixture of products. Attempts to protect the phenylcarbonyl group of **5a** as an *O,O*-acetal prior to hydrolysis of the *N,S*-acetal, in order to prevent the cyclization (**5a** → **9**), were also unsuccessful.

Scheme 4. *An Unexpected Cyclization Reaction* **5a** → **9**



(main product; sole product under non-aqueous reaction conditions)

Subsequently, we decided to reduce the phenylcarbonyl moiety of **5a** and then cleave the *N,S*-acetal, with the hope to obtain '4-hydroxy aldehydes' (→'γ-lactols', 'homoaldol products') or – after an additional reduction step – 1,4-diols. Treatment of ketone **5a** with $NaBH_4$ provided the secondary alcohols **11** and **12** in excellent yield as a 1:1 mixture (*Scheme 5*). The reduction of **5a** could also be conducted diastereoselectively, *e.g.*, a 97:3 mixture **11**/**12** was obtained with i-PrOH and a chiral Ru^{II} catalyst[16]). Addition of $Hg(O_2CCF_3)_2$ to a solution of **11** in THF led to the cyclized product[17]) **13**. *N,O*-Acetal **13**, isolated in 94% yield as a single diastereoisomer, is, in contrast to the 'unsaturated' analog **9**, a stable compound, and, importantly, it can be cleaved with H_2SO_4 in MeOH to the disubstituted 'γ-lactol ether' **15** and the auxiliary **1** in very high yield.

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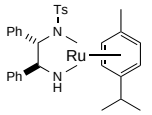
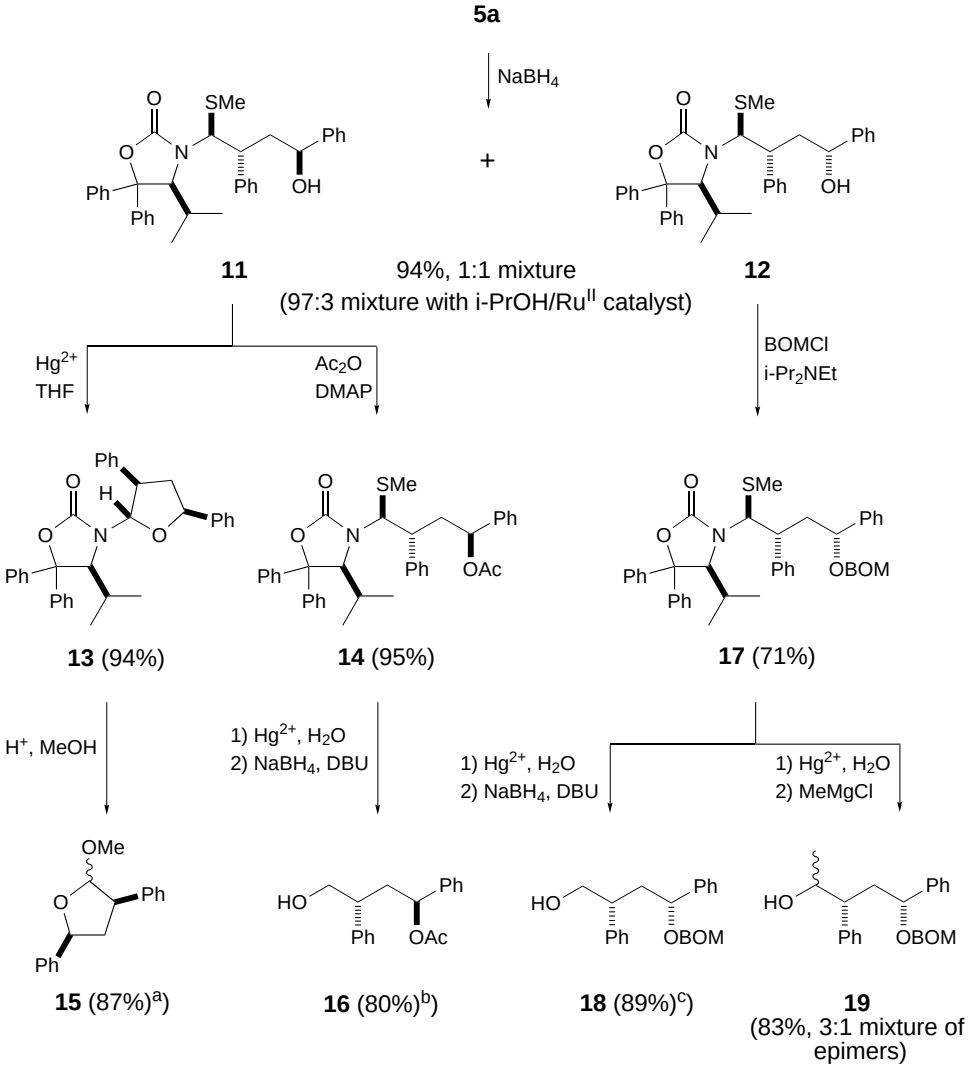
[16]) The *Noyori* catalyst (*S,S*)-**i** was used in the diastereoselective reduction of **5a** (see *Exper. Part*). For the preparation of catalyst **i**, see [19].



i

[17]) The diastereoisomeric alcohol **12** could also be cyclized to the corresponding *N,O*-acetal under the same reaction conditions.

Scheme 5. *Conversions of the Chalcone Adduct* **5a** *to a 'γ-Lactol Ether' and to Selectively Protected 1,4-Diols* (BOMCl: benzyl chloromethyl ether, DMAP: 4-(dimethylamino)pyridine)



a) Compound **15** was obtained as a 97:3 mixture with its *C*(3)-epimer. b) Compound **16** was obtained as a 97:3 mixture with its *C*(3)-epimer. c) Compound **18** was obtained as a 96:4 mixture with its *C*(2)-epimer.

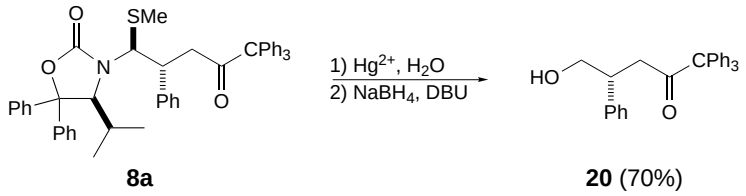
Alternatively, the OH group of alcohol **11** was protected first, *e.g.*, with Ac_2O and 4-(dimethylamino)pyridine (DMAP), to give in 95% yield the *O*-acetyl derivative **14**, which was then treated with aqueous $Hg(O_2CCF_3)_2$ to provide the corresponding *N,OH*-hemiacetal (MeS/OH displacement; OH protection prevents **14** from cyclizing). Treatment of a THF/H_2O solution of the hemiacetal with DBU generated the auxiliary

1 and the 4-OAc aldehyde, which was reduced *in situ* by $NaBH_4$ to give the selectively protected, disubstituted, enantiomerically pure 1,4-diol **16** of *unlike*-configuration (80% yield from **14** to **16**). Similarly, the diastereoisomeric alcohol **12** was BOM-protected ($\rightarrow$**17**), and treated with $Hg(O_2CCF_3)_2$ and $NaBH_4$/DBU to furnish in 89% yield the selectively protected, disubstituted, enantiomerically pure 1,4-diol **18** of *like*-configuration. It is also possible to add a *Grignard* reagent to the *N,OH*-hemiacetals to obtain trisubstituted 1,4-diols (in a C,C-bond-forming process and with generation of a third stereogenic center): thus, the diol derivative **19** was prepared from **17** in 83% yield as a 75 : 25 mixture of diastereoisomers, according to this procedure. Fortunately, no (in case of **19**) or only marginal (in case of **15**, **16**, and **18**) epimerization[18]) at *C*(3) and *C*(2), respectively, had occurred during the preparation of the 'γ-lactol ether' **15** and of the 1,4-diols **16**, **18**, and **19**, although the intermediate 2-Ph-substituted aldehyde must be highly susceptible to epimerization.

It is important to note that all processes described above involve the recycling of the chiral auxiliary **1**. Usually, oxazolidinone **1** precipitates in the course of these transformations and is isolated in 75–85% yield, ready for the next use by simple filtration, washing, and drying.

Experiments toward the elaboration of adduct **8a**, derived from conjugate addition of Li-**2** to trityl enone **7a**, were also carried out (*Scheme 6*). Hg^{2+}-Mediated hydrolysis of the *N,S*-acetal moiety of **8a**, followed by addition of $NaBH_4$ and DBU gave the 3-hydroxypropyl trityl ketone **20** in 70% yield, with recovery of the auxiliary **1**. Clearly, cyclization (*cf.* **5a** $\rightarrow$ **9**) did not occur due to the steric bulk of the trityl group. It is known that trityl ketones of type **20** can be reduced to the corresponding monosubstituted 1,4-diols with $LiBHEt_3$ (*Super-Hydride*) [15].

Scheme 6. *Conversion of the Trityl Enone Adduct* **8a** *to a 3-Hydroxypropyl Trityl Ketone*



8a **20** (70%)

4. Conclusions. – In summary, an efficient and simple method for the enantioselective preparation of selectively protected, di- and trisubstituted 1,4-diols, and disubstituted 'γ-lactol ethers' from chalcones has been developed. The procedure involves the high-yielding and diastereoselective conjugate addition of the lithiated [(methylthio)methyl]-oxazolidinone Li-**2** to chalcones (nucleophilic formylation). The reaction of Li-**2** with trityl enones also proceeds smoothly and gives access to 3-hydroxypropyl trityl ketones, which may be used for the synthesis of enantiomerically pure, monosubstituted 1,4-diols.

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[18]) To suppress epimerization, it is essential to add first $NaBH_4$, and then DBU to the solution of the *N,OH*-hemiacetal in THF/H_2O.

We are grateful to *B. Schweizer* for determination of the X-ray crystal structures of compounds **5c**, **8b**, **10**, **11**, and **17**. We thank *B. Jaun* for his help toward the elucidation of the relative configuration of compound **15** and its diastereoisomers. We gratefully acknowledge *Novartis Pharma AG*, Basel, for donation of 4-isopropyl-5,5-diphenyloxazolidin-2-one and for continuing financial support.

Experimental Part

General. Abbreviations: BOMCl: benzyl chloromethyl ether, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, DMAP: 4-(dimethylamino)pyridine, FC: flash chromatography, dp: diastereoisomer purity, dr: diastereoisomer ratio, h.v.: high vacuum (0.01–0.1 Torr). BuLi was used as a *ca.* 1.6M soln. (hexane), $AlMe_3$ as a *ca.* 1.8M soln. (heptane), and MeMgCl as a *ca.* 1.5M soln. (THF). THF was freshly distilled from K before use. Toluene was freshly distilled from Na before use. CH_2Cl_2, DBU, i-Pr_2NEt, and Et_3N were distilled from CaH_2 and stored over 4-Å molecular sieves. Solvents for FC and workup procedures were distilled from *Sikkon* (anh. $CaSO_4$, *Fluka*) or KOH/$FeSO_4$ (Et_2O). All other solvents and reagents were used as purchased from *Fluka*, *Aldrich*, *J.T. Baker*, *Scharlau*, or *Merck KGaA*. Reactions involving air- or moisture-sensitive reagents or intermediates were performed under Ar in glassware, which had been oven- or heat-gun dried under h.v. The chalcones **4c** and **4d** were prepared from the corresponding aldehydes and methyl ketones with catalytic amounts of NaOH in MeOH [20]. All other chalcones were purchased from *Fluka* or *Lancester*. The trityl enones **7a**–**7c** were prepared according to a literature procedure [15c], for the preparation of trityl enone **7d**, see *Exper. Part* below. The α,β-unsaturated BHA ester **7e** was prepared from cinnamoyl chloride and lithium 2,6-di(*tert*-butyl)-4-methoxyphenoxide in THF in 84% yield[19]). The chiral Ru^{II} catalyst **i** was prepared according to the procedure in [19]. TLC: *Merck* silica gel *60* F_{254} plates; visualization by UV_{254} light and by dipping into phosphomolybdic acid soln. (25 g of phosphomolybdic acid, 10 g of $Ce(SO_4)_2 \cdot H_2O$, 60 ml of conc. H_2SO_4, 940 ml of H_2O), followed by heating with a heat-gun. FC: *Fluka* silica gel *60* (40–63 μm, at *ca.* 0.2 bar). M.p.: *Büchi-510* apparatus, uncorrected. Optical rotations: *Perkin-Elmer 241* polarimeter (10 cm, 1-ml cell) at r.t. IR Spectra: *Perkin-Elmer 1600 FT-IR* spectrophotometer; in cm^{-1}. NMR Spectra: *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, ^{19}F: 282 MHz, ^{13}C: 75 MHz); chemical shifts (δ) in ppm downfield from internal TMS ($\delta = 0.00$ ppm); *J* values in Hz. MS: MALDI-MS (matrix-assisted laser-desorption ionization) and HR-MALDI-MS: *Ion Spec Ultima 4.7 FT Ion Cyclotron Resonance* (*ICR*) mass spectrometer, 2,5-dihydroxybenzoic acid matrix; FAB-MS (fast atom bombardment): *VG ZAB-2-SEQ* mass spectrometer, 3-nitrobenzyl alcohol matrix; fragment ions in *m*/*z* with relative intensities (%) in parentheses. Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH-Zürich. Diastereoisomer ratios were determined by ^1H-NMR spectroscopy.

1. *Addition of the* N,S-*Acetal* **2** *to Chalcones, Trityl Enones, and a BHA Ester. General Procedure 1* (*GP 1*). To a soln. of *N,S*-acetal **2** (1 equiv.) in THF (0.2M) was added BuLi (1.1–1.2 equiv.) at −78°. After stirring for 5 min, the mixture was cooled to −100° (for the addition reaction to trityl enones, and the BHA ester, the temp. was kept at −78°), and a chalcone or trityl enone (1.2–1.3 equiv.) was added as a soln. in THF (*ca.* 1M). It was allowed to warm to −78° within 10 min, and then the reaction was stopped by quenching with sat. aq. NH_4Cl soln. The mixture was diluted with Et_2O, 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 purified by FC, trituration, and/or recrystallization.

2. *Transformation of Some Adducts to 1,4-Diols and a 3-Hydroxypropyl Trityl Ketone with* $Hg(O_2CCF_3)_2$/$NaBH_4$/*DBU. General Procedure 2* (*GP 2*). To a soln. (or suspension) of adduct (1 equiv.) in THF/MeCN/H_2O (2:2:1; 0.1M) was added $Hg(O_2CCF_3)_2$ (1.1 equiv.) at r.t. After stirring for 5 min, H_2O was added, and the reaction mixture was diluted with Et_2O. The org. layer was separated, and the aq. layer was extracted with Et_2O (2×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was dissolved in THF/H_2O (4:1; 0.15M), and $NaBH_4$ (0.75 equiv.) and DBU (0.5 equiv.) were added consecutively at 0°. The auxiliary **1** precipitated in the course of the reaction. After stirring for 15 min, sat. aq. NH_4Cl soln. and Et_2O were added, and the precipitate was filtered off. The precipitate was washed with sat. aq. NH_4Cl soln., H_2O, and Et_2O, and dried under h.v. to recover **1** as a white solid. The filtrate was diluted with Et_2O,

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[19]) Compound **7e** was obtained in the manner previously described for the preparation of saturated BHA esters [21]; BHA esters are readily cleaved by CAN (cerium ammonium nitrate) [16][21].

the org. layer was separated, and the aq. layer was extracted with Et_2O (2×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by FC.

*(*S*)-4-Isopropyl-3-[(1*S*,2*R*)-1-(methylsulfanyl)-4-oxo-2,4-diphenylbutyl]-5,5-diphenyloxazolidin-2-one*[20] (**5a**). Compound **2** (350 mg, 1.02 mmol) was treated with BuLi (0.79 ml, 1.23 mmol) and chalcone **4a** (277 mg, 1.33 mmol) according to *GP 1*. Purification of the crude product by FC (CH_2Cl_2/pentane 3:1 → CH_2Cl_2 + 1% Et_2O) yielded **5a** (441 mg, 79%) as a 98:2 mixture with its *C*(2)-epimer. For anal. purposes, a sample was recrystallized (MeOH) to afford **5a** (dr ≥ 99:1). White solid. M.p. 224–226°. $[\alpha]_D^{r.t.} = -99.8$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3005*m*, 2954*w*, 1744*s*, 1682*m*, 1595*w*, 1487*m*, 1446*m*, 1405*m*, 1179*m*, 1092*w*. ^{1}H-NMR (400 MHz, CD_2Cl_2): 0.24 (*d*, *J* = 6.9, Me); 0.83 (*d*, *J* = 7.4, Me); 1.72 (*s*, MeS); 1.89–1.97 (*m*, Me_2CH); 3.25 (*dd*, *J* = 7.8, 17.1, 1 H, CH_2); 3.86 (*dd*, *J* = 4.8, 17.1, 1 H, CH_2); 4.49 (*d*, *J* = 1.7, NCH); 4.72 (*d*, *J* = 10.9, C*H*SMe); 4.80 (*ddd*, *J* = 4.8, 7.8, 10.9, PhC*H*); 7.04–7.54 (*m*, 18 arom. H); 7.82–7.85 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, CD_2Cl_2): 13.1, 15.6, 20.6 (Me); 30.0, 42.2 (CH); 45.4 (CH_2); 68.9, 69.1 (CH); 87.8 (C); 125.5, 126.9, 127.7, 127.8, 128.2, 128.3, 128.7, 128.8, 128.86, 128.90, 133.2 (CH); 137.8, 139.6, 142.1, 145.0, 157.1, 197.6 (C). MALDI-MS: 572 (100, $[M + Na]^+$), 440 (38, $[M - SMe - CO_2 - H_2O]^+$), 336 (32), 291 (50), 248 (56). Anal. calc. for $C_{35}H_{35}NO_3S$ (549.73): C 76.47, H 6.42, N 2.56, S 5.83; found: C 76.35, H 6.47, N 2.49, S 5.85.

*(*S*)-4-Isopropyl-3-[(1*S*,2*R*,E)-1-(methylsulfanyl)-4-oxo-2,6-diphenylhex-5-enyl]-5,5-diphenyloxazolidin-2-one* (**5b**). Compound **2** (350 mg, 1.02 mmol) was treated with BuLi (0.79 ml, 1.23 mmol) and **4b** (312 mg, 1.33 mmol) according to *GP 1*. Purification of the crude product by FC (CH_2Cl_2/pentane 5:1 → CH_2Cl_2 + 1% Et_2O) yielded **5b** (421 mg, 72%) as a single diastereoisomer. White solid. M.p. 196–198°. $[\alpha]_D^{r.t.} = -101.5$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): 3068*w*, 3008*m*, 1747*s*, 1610*s*, 1494*m*, 1450*m*, 1408*m*, 1324*m*, 1100*w*, 972*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.32 (*d*, *J* = 6.9, Me); 0.87 (*d*, *J* = 7.3, Me); 1.83 (*s*, MeS); 1.93–2.02 (*m*, Me_2CH); 2.94 (*dd*, *J* = 8.1, 16.5, 1 H, CH_2); 3.48 (*dd*, *J* = 4.9, 16.5, 1 H, CH_2); 4.47 (*d*, *J* = 1.6, NCH); 4.64 (*ddd*, *J* = 4.9, 8.1, 10.9, PhC*H*); 4.82 (*d*, *J* = 10.9, C*H*SMe); 6.62 (*d*, *J* = 16.1, PhCH=C*H*); 7.01–7.07 (*m*, 1 arom. H); 7.09–7.25 (*m*, 9 arom. H); 7.29–7.41 (*m*, 6 arom. H, 1 H, PhC*H*=CH); 7.43–7.47 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.1, 15.5, 20.3 (Me); 29.6, 42.1 (CH); 47.6 (CH_2); 67.9, 68.7 (CH); 87.6 (C); 125.1, 126.3, 126.6, 127.35, 127.39, 127.7, 127.8, 128.1, 128.3, 128.4, 128.5, 128.9, 130.4 (CH); 134.5, 138.9, 141.2 (C); 142.2 (CH); 144.3, 157.1, 197.3 (C). MALDI-MS: 598 (42, $[M + Na]^+$), 484 (35, $[M - SMe - CO_2]^+$), 466 (38, $[M - SMe - CO_2 - H_2O]^+$), 336 (62), 317 (43), 248 (200). Anal. calc. for $C_{37}H_{37}NO_3S$ (575.77): C 77.18, H 6.48, N 2.43, S 5.57; found: C 77.06, H 6.33, N 2.48, S 5.56.

*(*S*)-4-Isopropyl-3-[(1*S*,2*R*)-1-(methylsulfanyl)-4-(naphthalen-1-yl)-4-oxo-2-phenylbutyl]-5,5-diphenyloxazolidin-2-one* (**5c**). Compound **2** (380 mg, 1.11 mmol) was treated with BuLi (0.86 ml, 1.34 mmol) and **4c** (373 mg, 1.44 mmol) according to *GP 1*. Purification of the crude product by FC (CH_2Cl_2/pentane 3:1 → CH_2Cl_2) yielded **5c** (471 mg, 71%) as a single diastereoisomer. White solid. M.p. 188–191°. $[\alpha]_D^{r.t.} = -97.9$ (c = 1, $CHCl_3$). IR ($CHCl_3$): 3064*w*, 3008*w*, 2965*w*, 1748*s*, 1682*m*, 1494*w*, 1450*m*, 1409*m*, 1262*m*, 1101*m*, 1004*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.32 (*d*, *J* = 6.9, Me); 0.87 (*d*, *J* = 7.3, Me); 1.83 (*s*, SMe); 1.91–2.02 (*m*, Me_2CH); 3.29 (*dd*, *J* = 7.6, 16.6, 1 H, CH_2); 3.92 (*dd*, *J* = 4.7, 16.6, 1 H, CH_2); 4.48 (*d*, *J* = 1.6, NCH); 4.75–4.84 (*m*, C*H*SMe, PhC*H*); 7.03–7.27 (*m*, 9 arom. H); 7.29–7.33 (*m*, 4 arom. H); 7.39–7.48 (*m*, 5 arom. H); 7.63–7.65 (*m*, 1 arom. H); 7.79–7.82 (*m*, 1 arom. H); 7.89–7.91 (*m*, 1 arom. H); 8.10–8.12 (*m*, 1 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.2, 15.5, 20.3 (Me); 29.6, 42.4 (CH); 49.2 (CH_2); 67.9, 68.7 (CH); 87.6 (C); 124.2, 125.1, 125.7, 126.3, 126.6, 126.7, 127.40, 127.42, 127.5, 127.7, 127.8, 128.2, 128.3, 128.47, 128.49 (CH); 130.0 (C); 131.1 (CH); 133.8, 136.7, 138.9, 141.0, 144.3, 157.0, 201.9 (C). MALDI-MS: 638 (6, $[M + K]^+$), 622 (100, $[M + Na]^+$), 552 (9, $[M - SMe]^+$), 508 (63, $[M - SMe - CO_2]^+$), 490 (24, $[M - SMe - CO_2 - H_2O]^+$). Anal. calc. for $C_{39}H_{37}NO_3S$ (599.79): C 78.10, H 6.22, N 2.34; found: C 77.94, H 6.25, N 2.32.

*(*S*)-4-Isopropyl-3-[(1*S*,2*R*)-4-(5-methylfuran-2-yl)-1-(methylsulfanyl)-4-oxo-2-phenylbutyl]-5,5-diphenyloxazolidin-2-one* (**5d**). Compound **2** (355 mg, 1.04 mmol) was treated with BuLi (0.80 ml, 1.25 mmol) and **4d** (287 mg, 1.35 mmol) according to *GP 1*. Purification of the crude product by FC (CH_2Cl_2 → CH_2Cl_2/Et_2O 10:1) yielded **5d** (407 mg, 71%) as a 96:4 mixture with its *C*(2)-epimer. For anal. purposes, a sample was recrystallized (MeOH) to afford **5d** (dr ≥ 99:1). White solid. M.p. 219–222°. $[\alpha]_D^{r.t.} = -98.3$ (c = 1, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3008*w*, 1747*s*, 1665*m*, 1516*s*, 1494*w*, 1450*w*, 1409*m*, 1040*w*, 1004*w*, 926*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.33 (*d*, *J* = 7.0, Me); 0.88 (*d*, *J* = 7.3, Me); 1.86 (*s*, MeS); 1.92–2.01 (*m*, Me_2CH); 2.32–2.33 (*m*, Me); 3.06 (*dd*, *J* = 8.3, 16.3, 1 H, CH_2); 3.59 (*dd*, *J* = 4.9, 16.3, 1 H, CH_2); 4.47 (*d*, *J* = 1.6, NCH); 4.64 (*ddd*, *J* = 4.9, 8.3, 10.9, PhC*H*); 4.87 (*d*, *J* = 10.9, C*H*SMe); 6.04–6.05 (*m*, 1 H of furan); 6.95–6.96 (*m*, 1 H of furan); 6.98–7.33 (*m*, 15 arom. H); 7.43–7.45 (*m*, 2 arom.). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.2, 14.0, 15.9, 20.3 (Me); 29.6, 41.9

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[20]) The preparation and parts of the physical data of this compound have been reported before in [10b].

(CH); 44.6 (CH_2); 67.8, 68.6 (CH); 87.6 (C); 108.8, 118.7, 125.1, 126.2, 127.3, 127.4, 127.68, 127.74, 128.1, 128.37, 128.45 (CH); 139.0, 141.0, 144.3, 151.6, 157.1, 157.4, 185.9 (C). MALDI-MS: 592 (7, $[M+K]^+$), 576 (100, $[M+Na]^+$), 506 (29, $[M-SMe]^+$), 462 (58, $[M-SMe-CO_2]^+$), 444 (17, $[M-SMe-CO_2-H_2O]^+$). Anal. calc. for $C_{34}H_{35}NO_4S$ (553.72): C 73.75, H 6.37, N 2.53; found: C 73.56, H 6.20, N 2.66.

*(*S*)-4-Isopropyl-3-[(1*S*,2*R*)-2-(4-methoxyphenyl)-1-(methylsulfanyl)-4-oxo-4-phenylbutyl]-5,5-diphenyloxazolidin-2-one* (**5e**). Compound **2** (349 mg, 1.02 mmol) was treated with BuLi (0.79 ml, 1.22 mmol) and **4e** (316 mg, 1.33 mmol) according to *GP 1*. Purification of the crude product by FC (CH_2Cl_2/pentane 7:1 → CH_2Cl_2) yielded **5e** (386 mg, 65%) as a 91:9 mixture with its *C*(2)-epimer. For anal. purposes, a sample was recrystallized (MeOH) to afford **5e** (dr ≥ 99:1). White solid. M.p. 189–191°. $[\alpha]_D^{r.t.} = -106.3$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 1744*s*, 1685*m*, 1611*w*, 1513*s*, 1036*w*, 1003*w*, 834*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.46 (*d*, $J = 6.4$, Me); 0.96 (*d*, $J = 7.3$, Me); 1.97 (*s*, MeS); 2.00–2.09 (*m*, Me_2CH); 3.18 (*dd*, $J = 8.0$, 17.0, 1 H, CH_2); 3.67 (*s*, MeO); 3.84 (*dd*, $J = 4.6$, 17.0, 1 H, CH_2); 4.43 (*d*, $J = 1.6$, NCH); 4.47–4.53 (*m*, PhC*H*); 5.01 (*d*, $J = 11.3$, C*H*SMe); 6.55–6.57 (*m*, 2 arom. H); 7.13–7.21 (*m*, 8 arom. H); 7.31–7.40 (*m*, 6 arom. H); 7.45–7.52 (*m*, 1 arom. H); 7.81–7.83 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.1, 15.7, 20.3 (Me); 29.6, 41.4 (CH); 45.7 (CH_2); 54.9 (Me); 67.6, 68.3 (CH); 87.5 (C); 113.8, 124.9, 126.7, 127.36, 127.41, 127.7, 127.9, 128.3, 128.4, 128.8, 132.8 (CH); 132.9, 137.3, 139.0, 144.2, 157.2, 158.4, 197.7 (C). MALDI-MS: 602 (20, $[M+Na]^+$), 488 (31, $[M-SMe-CO_2]^+$), 470 (16, $[M-SMe-CO_2-H_2O]^+$), 366 (37), 251 (100), 248 (82). Anal. calc. for $C_{36}H_{37}NO_4S$ (579.76): C 74.58, H 6.43, N 2.42; found: C 74.64, H 6.58, N 2.44.

*(*S*)-3-[(1*S*,2*R*)-2-(4-Chlorophenyl)-1-(methylsulfanyl)-4-oxo-4-phenylbutyl]-4-isopropyl-5,5-diphenyloxazolidin-2-one* (**5f**). Compound **2** (349 mg, 1.02 mmol) was treated with BuLi (0.79 ml, 1.22 mmol) and **4f** (323 mg, 1.33 mmol) according to *GP 1*. Purification of the crude product by FC (CH_2Cl_2/pentane 3:1 → CH_2Cl_2) yielded **5f** (415 mg, 70%) as a 96:4 mixture with its *C*(2)-epimer. For anal. purposes, a sample was recrystallized (MeOH) to afford **5f** (dr ≥ 99:1). White solid. M.p. 196–198°. $[\alpha]_D^{r.t.} = -109.5$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3008*w*, 1745*s*, 1685*m*, 1598*w*, 1492*m*, 1449*m*, 1411*m*, 1093*w*, 1003*w*, 836*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.46 (*d*, $J = 7.0$, Me); 0.97 (*d*, $J = 7.3$, Me); 1.97 (*s*, MeS); 2.01–2.11 (*m*, Me_2CH); 3.18 (*dd*, $J = 8.0$, 17.2, 1 H, CH_2); 3.67 (*s*, MeO); 3.86 (*dd*, $J = 4.5$, 17.2, 1 H, CH_2); 4.41 (*d*, $J = 1.6$, NCH); 4.53–4.59 (*m*, PhC*H*); 5.00 (*d*, $J = 11.4$, C*H*SMe); 6.97–7.00 (*m*, 2 arom. H); 7.14–7.25 (*m*, 8 arom. H); 7.32–7.43 (*m*, 6 arom. H); 7.47–7.51 (*m*, 1 arom. H); 7.81–7.83 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.1, 15.7, 20.4 (Me); 29.6, 41.5 (CH); 45.4 (CH_2); 67.1, 68.8 (CH); 87.6 (C); 124.7, 126.6, 127.4, 127.6, 127.7, 127.9, 128.4, 128.5, 128.6, 129.3 (CH); 132.9 (C); 133.0 (CH); 137.0, 138.7, 139.5, 144.0, 157.1, 197.2 (C). MALDI-MS: 606 (15, $[M+Na]^+$), 492 (23, $[M-SMe-CO_2]^+$), 474 (27, $[M-SMe-CO_2-H_2O]^+$), 370 (35), 255 (47), 248 (100). Anal. calc. for $C_{35}H_{34}NO_3SCl$ (584.18): C 71.96, H 5.87, N 2.40; found: C 71.92, H 5.90, N 2.47.

*(*E*)-5,5,5-Trifluoro-1,1,1,4-tetraphenylpent-3-en-2-one* (**7d**). *1,1,1-Triphenylpropan-2-one* (3.30 g, 11.5 mmol) was dissolved in toluene (45 ml) and treated with $AlMe_3$ (8.30 ml, 14.9 mmol) at r.t. After refluxing for 4 h, the mixture was cooled to 0°, and trifluoroacetophenone (3.10 ml, 23.0 mmol) was added. The mixture was stirred for 1 h and was then poured into sat. aq. NH_4Cl soln. After stirring for another 30 min, the mixture was filtered over *Celite*. 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 to yield the crude aldol product as a yellow oil. The crude aldol product was dissolved in CH_2Cl_2 (35 ml) and Et_3N (7.00 ml, 50.0 mmol), and a soln. of $MeSO_2Cl$ (1.00 ml, 12.9 mmol) in CH_2Cl_2 (8 ml) were added dropwise at 0°. After the mesylation was complete (usually instantaneously), DBU (3.80 ml, 25.4 mmol) was added, and the mixture was stirred for 60 h at r.t. Then, H_2O was added, the org. layer was separated, and the aq. layer was extracted with Et_2O (3×). The combined org. layers were washed with 1M HCl (1×), H_2O (1×), and sat. aq. NaCl soln. (1×), dried ($MgSO_4$), and concentrated under reduced pressure. Recrystallization (hexane) of the crude product yielded **7d** (437 mg, 9%). Yellow solid. M.p. 128–131°. IR ($CHCl_3$): 3063*w*, 3009*w*, 1712*s*, 1641*w*, 1600*w*, 1494*m*, 1448*m*, 1279*s*, 1177*s*, 1136*s*, 1034*w*, 882*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.92 (*d*, $J = 1.6$, CH=C); 7.05–7.38 (*m*, 20 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 72.3 (C); 127.3, 128.1, 128.4, 129.0, 129.96, 130.03, 130.5, 131.1 (CH, C); 140.0 (*q*, J(C,F) = 30.5, CF_3); 141.2, 195.2 (C). ^{19}F-NMR (282 MHz, $CDCl_3$): −67.65 (*s*, CF_3). MALDI-MS: 465 (14, $[M+Na]^+$), 347 (18), 273 (61), 243 (100, $[Ph_3C]^+$). Anal. calc. for $C_{29}H_{21}F_3O$ (442.48): C 78.72, H 4.78; found: C 78.57, H 5.02.

*(*S*)-4-Isopropyl-3-[(1*S*,2*R*)-1-(methylsulfanyl)-4-oxo-2,5,5,5-tetraphenylpentyl]-5,5-diphenyloxazolidin-2-one* (**8a**). Compound **2** (900 mg, 2.64 mmol) was treated with BuLi (1.87 ml, 2.90 mmol) and **7a** (1.19 g, 3.17 mmol) according to *GP 1*. Purification of the crude product by FC (pentane/Et_2O 5:1) yielded **8a** (1.57 g, 83%) as a single diastereoisomer. White solid. M.p. 212–214°. $[\alpha]_D^{r.t.} = -60.2$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3062*w*, 3006*w*, 2963*w*, 1745*s*, 1712*s*, 1601*w*, 1494*m*, 1450*m*, 1409*m*, 1364*w*, 1324*w*, 1093*w*, 1035*w*, 1004*w*, 913*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.44 (*d*, $J = 7.0$, Me); 0.84 (*d*, $J = 7.3$, Me); 1.81 (*s*, MeS); 1.93–2.00 (*m*, Me_2CH); 2.84

(*dd*, *J* = 10.0, 18.3, 1 H, CH_2); 3.28 (*dd*, *J* = 2.4, 18.3, 1 H, CH_2); 4.25–4.30 (*m*, PhC*H*); 4.32 (*d*, *J* = 1.6, NCH); 4.78 (*d*, *J* = 11.3, C*H*SMe); 6.95–7.32 (*m*, 30 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.4, 16.0, 20.1 (Me); 29.6, 42.5 (CH); 48.1 (CH_2); 67.2, 68.4 (CH); 72.0, 87.4 (C); 124.8, 126.6, 126.7, 127.3, 127.38, 127.41, 127.7, 127.9, 128.41, 128.44, 130.3 (CH); 139.0, 140.4, 142.4, 144.1, 157.0, 206.2 (C). MALDI-MS: 738 (100, $[M+Na]^+$), 624 (87, $[M-SMe-CO_2]^+$), 460 (27), 457 (83), 243 (16, $[Ph_3C]^+$). Anal. calc. for $C_{48}H_{45}NO_3S$ (715.95): C 80.53, H 6.33, N 1.96, S 4.48; found: C 80.48, H 6.50, N 1.98, S 4.48.

*(*S*)-4-Isopropyl-3-[(1*S*,2*S*)-2-methyl-1-(methylsulfanyl)-4-oxo-5,5,5-triphenylpentyl]-5,5-diphenyloxazolidin-2-one* (**8b**). Compound **2** (210 mg, 0.615 mmol) was treated with BuLi (0.48 ml, 0.783 mmol) and **7b** (250 mg, 0.800 mmol) according to *GP 1*. Purification of the crude product by FC (pentane/Et_2O 5:1) and subsequent trituration (boiling hexane, 2 × 5 ml) yielded **8b** (204 mg, 51%) as a single diastereoisomer. White solid. M.p. 207–209°. $[\alpha]_D^{r.t.} = -105.0$ (*c* = 0.945, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3008*w*, 2970*w*, 1747*s*, 1709*m*, 1599*w*, 1493*m*, 1449*m*, 1410*m*, 1092*w*, 1038*w*, 1004*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.58 (*d*, *J* = 6.6, Me); 0.69 (*d*, *J* = 6.9, Me); 1.05 (*d*, *J* = 7.3, Me); 1.62 (*s*, MeS); 2.09–2.20 (*m*, Me_2CH); 2.53 (*dd*, *J* = 8.0, 18.1, 1 H, CH_2); 2.86–2.96 (*m*, MeC*H*); 3.13 (*dd*, *J* = 3.1, 18.1, 1 H, CH_2); 4.34 (*d*, *J* = 10.6, C*H*SMe); 4.51 (*d*, *J* = 1.8, NCH); 7.18–7.34 (*m*, 21 arom. H); 7.45–7.47 (*m*, 2 arom. H); 7.64–7.67 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.8, 16.2, 17.2, 20.8 (Me); 29.8, 32.0 (CH); 45.6 (CH_2); 68.5, 68.9 (CH); 73.3, 87.7 (C); 125.3, 126.5, 126.7, 127.5, 127.9, 128.0, 128.5, 130.5 (CH); 138.9, 142.5, 144.7, 156.8, 207.0 (C). MALDI-MS: 676 (14, $[M+Na]^+$), 562 (55, $[M-SMe-CO_2]^+$), 396 (56), 243 (100, $[Ph_3C]^+$). Anal. calc. for $C_{43}H_{43}NO_3S$ (653.88): C 78.99, H 6.63, N 2.14, S 4.90; found: C 78.97, H 6.74, N 2.19, S 4.95.

*2,6-Di(*tert*-butyl)-4-methoxyphenyl (1*S*,2*R*)-4-[(*S*)-4-Isopropyl-2-oxo-5,5-diphenyloxazolidin-3-yl]-4-(methylsulfanyl)-3-phenylbutanoate* (**8e**). Compound **2** (207 mg, 0.606 mmol) was treated with BuLi (0.47 ml, 0.727 mmol) and **7e** (289 mg, 0.788 mmol) according to *GP 1*. Purification of the crude product by FC (pentane/Et_2O 5:1) yielded **8e** (130 mg, 30%) as a single diastereoisomer. White solid. M.p. 228–229°. $[\alpha]_D^{r.t.} = -78.0$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2964*m*, 1751*s*, 1589*w*, 1449*w*, 1416*w*, 1366*w*, 1301*w*, 1262*w*, 1135*m*, 1105*w*, 1062*w*, 1004*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.74 (*d*, *J* = 6.9, Me); 0.90 (*s*, *t*-Bu); 1.24 (*d*, *J* = 7.5, Me); 1.38 (*s*, *t*-Bu); 1.53 (*s*, MeS); 2.25–2.34 (*m*, Me_2CH); 3.02 (*dd*, *J* = 11.5, 17.4, 1 H, CH_2); 3.55 (*dd*, *J* = 2.2, 17.4, 1 H, CH_2); 3.75 (*s*, MeO); 4.44 (*d*, *J* = 11.5, C*H*SMe); 4.69–4.73 (*m*, PhC*H*); 4.77 (*d*, *J* = 1.3, NCH); 6.72 (*d*, *J* = 3.1, 1 arom. H); 6.82 (*d*, *J* = 3.1, 1 arom. H); 7.18–7.39 (*m*, 11 arom. H); 7.42–7.44 (*m*, 2 arom. H); 7.64–7.66 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.1, 16.0, 22.4 (Me); 29.5 (CH); 30.8, 31.4 (Me); 35.0, 35.6 (C); 40.8 (CH_2); 43.2, 55.2 (Me); 67.7, 68.2 (CH); 87.8 (C); 111.56, 111.60, 125.7, 126.4, 127.2, 127.7, 128.1, 128.3, 128.4, 128.5, 128.7 (CH); 139.3, 141.3, 141.5, 143.4, 143.6, 143.7, 156.2, 157.1, 171.2 (C). MALDI-MS: 730 (94, $[M+Na]^+$), 616 (100, $[M-SMe-CO_2]^+$), 449 (39), 248 (35). Anal. calc. for $C_{44}H_{53}NO_5S$ (707.97): C 74.65, H 7.55, N 1.98, S 4.53; found: C 74.58, H 7.64, N 2.02, S 4.53.

*(*S*)-3-[(2*S*,3*R*)-2,3-Dihydro-3,5-diphenylfuran-2-yl]-4-isopropyl-5,5-diphenyloxazolidin-2-one*[20]) (**9**). To a soln. of **5a** (400 mg, 0.728 mmol) in THF (5 ml) was added $Hg(O_2CCF_3)_2$ (341 mg, 0.801 mmol) at r.t. After stirring for 20 min, H_2O was added, and the reaction mixture was diluted with Et_2O. The org. layer was separated, and the aq. layer was extracted with Et_2O (2 ×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the crude product by FC (pentane/Et_2O 4:1, 1% Et_3N) and subsequent trituration (boiling hexane, 10 ml) afforded **9** as a single diastereoisomer. Only small amounts of product could be isolated due to the instability of the compound. White solid. M.p. 211–213°. $[\alpha]_D^{r.t.} = +54.0$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3022*w*, 1754*s*, 1648*w*, 1602*w*, 1490*m*, 1445*m*, 1419*m*, 1374*m*, 1328*w*, 1252*m*, 1043*m*, 1010*m*, 1003*m*, 947*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.81 (*d*, *J* = 6.7, Me); 0.91 (*d*, *J* = 7.3, Me); 1.91–2.02 (*m*, Me_2CH); 4.32 (*dd*, *J* = 2.7, 7.3, PhC*H*); 4.68 (*d*, *J* = 1.5, NCH); 5.47 (*d*, *J* = 2.7, CCH); 5.98 (*d*, *J* = 7.3, NCHO); 6.76–6.78 (*m*, 2 arom. H); 7.10–7.16 (*m*, 2 arom. H); 7.24–7.27 (*m*, 1 arom. H); 7.30–7.40 (*m*, 10 arom. H); 7.53–7.55 (*m*, 3 arom. H); 7.67–7.69 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.6, 20.6 (Me); 29.5, 51.8, 68.6 (CH); 89.0 (C); 94.1, 98.3, 125.2, 125.3, 126.0, 127.2, 127.4, 127.7, 128.2, 128.3, 128.7, 128.86, 128.88 (CH); 129.9, 130.5, 141.3, 144.4, 155.2, 156.5 (C). MALDI-MS: 524 (100, $[M+Na]^+$), 458 (29), 248 (21). HR-MALDI-MS: 524.2196 ($C_{34}H_{31}NO_3$, $[M+Na]^+$; calc. 524.2196).

*4-Isopropyl-3-[(1*S*,2*S*,3*R*,5*R*)-5-methoxy-3,5-diphenyltetrahydrofuran-2-yl]-5,5-diphenyloxazolidin-2-one*[20]) (**10**). Compound **9** (30 mg, 0.060 mmol) was dissolved in MeOH (3 ml) at r.t. Colorless crystals were formed upon standing for 3 days. The crystals were isolated and identified as compound **10** (single diastereoisomer). White solid. M.p. 182–184°. $[\alpha]_D^{r.t.} = -28.4$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2963*w*, 1759*s*, 1602*w*, 1494*w*, 1449*w*, 1425*w*, 1381*w*, 1326*w*, 1129*w*, 1047*w*, 998*m*, 909*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.68 (*d*, *J* = 6.7, Me); 0.82 (*d*, *J* = 7.3, Me); 1.90–1.97 (*m*, Me_2CH); 2.56 (*dd*, *J* = 6.3, 13.5, 1 H, CH_2); 2.66 (*dd*, *J* = 11.4, 13.5, 1 H, CH_2); 3.11 (*s*, MeO); 4.03–4.08 (*m*, PhC*H*); 4.56 (*d*, *J* = 1.6, NCH); 5.52 (*d*, *J* = 8.3, CHO); 7.16–7.36 (*m*, 16 arom. H); 7.45–7.48 (*m*, 2 arom. H); 7.53–7.56 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$):

14.9, 20.7 (Me); 29.7, 45.0 (CH); 47.4 (CH_2); 49.4 (Me); 68.0 (CH); 88.5 (C); 92.4 (CH); 106.5 (C); 125.5, 126.0, 126.2, 126.9, 127.6, 127.9, 128.0, 128.12, 128.14, 128.4, 128.6 (CH); 138.9, 140.0, 140.2, 144.0, 156.6 (C). MALDI-MS: 556 (70, $[M+Na]^+$), 524 (47, $[M+Na-OMe]^+$), 458 (100, $[M-OMe-CO_2]^+$), 440 (44, $[M-OMe-CO_2-H_2O]^+$), 248 (67). HR-MALDI-MS: 556.2438 ($C_{35}H_{35}NO_4$, $[M+Na]^+$; calc. 556.2458).

*(*S*)-3-[(1*S*,2*R*,4*S*)-4-Hydroxy-1-(methylsulfanyl)-2,4-diphenylbutyl]-4-isopropyl-5,5-diphenyloxazolidin-2-one* (**11**) *and (*S*)-3-[(1*S*,2*R*,4*R*)-4-Hydroxy-1-(methylsulfanyl)-2,4-diphenylbutyl]-4-isopropyl-5,5-diphenyloxazolidin-2-one* (**12**). To a soln. of **5a** (1.14 g, 2.07 mmol) in THF (20 ml) and H_2O (5 ml), $NaBH_4$ (78 mg, 2.07 mmol) was added at r.t. After stirring for 4 h, sat. aq. NH_4Cl soln. was added, and the mixture was diluted with Et_2O. The org. layer was separated, and the aq. layer was extracted with Et_2O (2×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the crude product by FC (pentane/Et_2O 3:1 → 2:1) afforded **11** and **12** (1.07 g, 94%) as a 42:58 mixture. The isolated product mixture was purified again by FC (2×, pentane/Et_2O 3:1) to yield **11** (318 mg, 28%) as a single diastereoisomer and **12** (420 mg, 37%) as a 94:6 mixture with **11**.

The reduction with the chiral Ru^{II} catalyst was carried out *via* the following procedure: To a soln. of **5a** (102 mg, 0.218 mmol) in CH_2Cl_2 (3 ml), i-PrOH (1.5 ml) and catalyst **i** (13 mg, 0.022 mmol) were added at r.t. After stirring for 4 days, the mixture was concentrated and filtered through a silica plug (CH_2Cl_2) to afford **11** and **12** as a 97:3 mixture (at 40% conversion as determined by ^{1}H-NMR).

Data of **11**: White solid. M.p. 193–194°. $[\alpha]_D^{rt} = -77.5$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3612*w*, 3462*w*, 3065*w*, 3008*m*, 2966*w*, 1745*s*, 1602*w*, 1493*m*, 1450*m*, 1408*m*, 1034*m*, 1004*m*, 896*w*, 826*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.31 (*d*, *J* = 7.0, Me); 0.84 (*d*, *J* = 7.3, Me); 1.82 (*ddd*, *J* = 2.2, 12.0, 14.1, 1 H, CH_2); 1.85 (*s*, MeS); 1.90–2.05 (*m*, Me_2CH, OH); 2.65 (*ddd*, *J* = 3.1, 10.8, 14.1, 1 H, CH_2); 4.19–4.29 (*m*, CHOH, PhCH); 4.54 (*d*, *J* = 1.6, NCH); 4.60 (*d*, *J* = 9.7, CHSMe); 7.12–7.37 (*m*, 18 arom. H); 7.51–7.54 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.6, 15.7, 20.3 (Me); 29.5, 43.1 (CH); 44.6 (CH_2); 68.5, 68.6, 71.2 (CH); 87.6 (C); 125.3, 125.5, 126.6, 127.3, 127.4, 127.8, 128.36, 128.42, 128.46, 128.54 (CH); 139.0, 141.3, 144.4, 145.2, 157.1 (C). MALDI-MS: 590 (6, $[M+K]^+$), 574 (70, $[M+Na]^+$), 442 (100, $[M-SMe-CO_2-H_2O]^+$). Anal. calc. for $C_{35}H_{37}NO_3S$ (551.75): C 76.19, H 6.76, N 2.54; found: C 76.09, H 6.87, N 2.52.

Data of **12**: White solid. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.14 (*d*, *J* = 6.9, Me); 0.72 (*d*, *J* = 7.4, Me); 1.52 (*s*, MeS); 1.73 (*d*, *J* = 3.1, OH); 1.78–1.88 (*m*, Me_2CH); 2.19 (*ddd*, *J* = 5.1, 11.0, 13.3, 1 H, CH_2); 2.71 (*ddd*, *J* = 3.3, 9.1, 13.3, 1 H, CH_2); 3.73 (*ddd*, *J* = 3.3, 11.0, 11.0, PhCH); 4.29–4.35 (*m*, CHOH); 4.38 (*d*, *J* = 1.6, NCH); 4.49 (*d*, *J* = 11.0, CHSMe); 7.10–7.38 (*m*, 18 arom. H); 7.42–7.45 (*m*, 2 arom. H).

*(*S*)-3-[(2*S*,3*R*,5*S*)-2,3,4,5-Tetrahydro-3,5-diphenylfuran-2-yl]-4-isopropyl-5,5-diphenyloxazolidin-2-one* (**13**). To a soln. of **11** (885 mg, 1.60 mmol) in THF (10 ml), $Hg(O_2CCF_3)_2$ (684 mg, 1.60 mmol) was added at r.t. After stirring for 5 min, H_2O was added, and the mixture was diluted with CH_2Cl_2. 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. Purification of the crude product by trituration (boiling hexane, 10 ml) and filtration through a silica plug (CH_2Cl_2) afforded **13** (757 mg, 94%) as a single diastereoisomer. White solid. M.p. 214–216°. $[\alpha]_D^{rt} = -107.5$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3064*w*, 3008*w*, 2965*w*, 1751*s*, 1603*w*, 1603*w*, 1494*w*, 1450*m*, 1381*w*, 1326*w*, 1028*m*, 1002*m*, 945*w*, 909*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.62 (*d*, *J* = 6.7, Me); 0.87 (*d*, *J* = 7.3, Me); 1.86–1.95 (*m*, Me_2CH); 2.07 (*ddd*, *J* = 10.5, 10.5, 12.7, 1 H, CH_2); 2.82 (*ddd*, *J* = 5.7, 7.2, 12.7, 1 H, CH_2); 4.34 (*ddd*, *J* = 7.2, 7.2, 10.5, PhCH); 4.55 (*d*, *J* = 1.6, NCH); 5.16 (*dd*, *J* = 5.7, 10.5, PhCHO); 5.64 (*d*, *J* = 7.2, NCHO); 7.11–7.37 (*m*, 16 arom. H); 7.42–7.45 (*m*, 2 arom. H); 7.50–7.53 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.3, 21.1 (Me); 29.8 (CH); 43.7 (CH_2); 47.5, 68.3, 80.3 (CH); 88.4 (C); 92.7, 125.4, 125.7, 126.2, 126.9, 127.46, 127.49, 127.51, 127.9, 128.1, 128.39, 128.44, 128.7 (CH); 139.0, 140.1, 141.8, 143.9, 156.8 (C). MALDI-MS: 542 (6, $[M+K]^+$), 526 (100, $[M+Na]^+$), 442 (24). Anal. calc. for $C_{34}H_{33}NO_3$ (503.64): C 81.08, H 6.60, N 2.78; found: C 81.09, H 6.62, N 2.79.

The *C*(5)-epimer of **13** was prepared from **12** according to the same procedure. White solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.68 (*d*, *J* = 6.8, Me); 0.92 (*d*, *J* = 7.3, Me); 1.88–2.00 (*m*, Me_2CH); 2.35–2.51 (*m*, CH_2); 4.03–4.10 (*m*, PhCH); 4.56 (*d*, *J* = 1.8, NCH); 5.16–5.21 (*m*, PhCHO); 5.51 (*d*, *J* = 6.1, NCHO); 7.12–7.31 (*m*, 17 arom. H); 7.40–7.49 (*m*, 3 arom. H).

*(3*R*,5*S*)-2,3,4,5-Tetrahydro-2-methoxy-3,5-diphenylfuran* (**15**). To a soln. of **13** (544 mg, 1.08 mmol) in $CHCl_3$ (10 ml) and MeOH (10 ml), conc. H_2SO_4 (1.5 ml) was added slowly at r.t. The mixture was stirred for 14 days at r.t. Then, the white precipitate formed during the reaction was dissolved by adding CH_2Cl_2 to the mixture, and the clear soln. was poured into 5M NaOH (16 ml). 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 suspended in Et_2O (10 ml), the insoluble white solid was filtered off, washed with Et_2O, and dried under h.v. to recover **1** (254 mg, 84%). The filtrate was concentrated under reduced

pressure, and the residual oil was purified by FC (pentane/Et_2O 30:1) to afford **15** (239 mg, 87%) as a 78:22 mixture (*C*(2)-epimers), also containing 3% of its *C*(3)-epimer. For anal. purposes, a sample was purified again by FC (pentane/Et_2O 30:1) to afford (2*S*,3*R*,5*S*)-**15** (dp 95%) as major product and (2*R*,3*R*,5*S*)-**15**, (dp ≥ 98%) as minor product.

*Data of (2*S*,3*R*,5*S*)-***15***: Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.96 (*ddd*, *J* = 9.6, 10.5, 12.5, 1 H, CH_2); 2.74 (*dddd*, *J* = 0.5, 5.4, 8.2, 12.5, 1 H, CH_2); 3.42 (*s*, MeO); 3.48 (*ddd*, *J* = 3.2, 8.2, 9.6, PhC*H*); 5.13 (*d*, *J* = 3.2, C*H*OMe); 5.21 (*dd*, *J* = 5.4, 10.5, PhC*H*O); 7.19–7.38 (*m*, 8 arom. H); 7.42–7.45 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 43.2 (CH_2); 52.7 (CH); 55.5 (Me); 80.0, 111.4, 126.1, 126.6, 127.3, 127.7, 128.4, 128.6 (CH); 140.9, 141.9 (C).

*Data of (2*R*,3*R*,5*S*)-***15***: White solid. M.p. 65–68°. $[\alpha]_D^{r.t.} = -123.6$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3008*m*, 2910*w*, 2835*w*, 1604*w*, 1497*m*, 1450*w*, 1368*w*, 1326*w*, 1169*w*, 1097*w*, 1121*s*, 1048*s*, 1024*s*, 980*s*, 904*m*, 856*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.43 (*ddd*, *J* = 10.4, 11.9, 13.4, 1 H, CH_2); 2.58 (*ddd*, *J* = 6.1, 6.6, 11.9, 1 H, CH_2); 3.38 (*s*, MeO); 3.54 (*ddd*, *J* = 4.7, 6.6, 13.4, PhC*H*); 5.11 (*d*, *J* = 4.7, C*H*OMe); 5.19 (*dd*, *J* = 6.1, 10.4, PhC*H*O); 7.22–7.41 (*m*, 8 arom. H); 7.43–7.46 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 38.2 (CH_2); 50.8 (CH); 55.1 (Me); 82.0, 105.5, 126.6, 126.8, 127.5, 128.1, 128.4, 128.8 (CH); 137.3, 143.0 (C). FAB-MS: 254 (17, M^+), 223 (100, $[M - OMe]^+$), 205 (47), 194 (61, $[M - OCHOMe]^+$). Anal. calc. for $C_{17}H_{18}O_2$ (254.33): C 80.28, H 7.13; found: C 80.36, H 7.10.

*(*S*)-3-[(1*S*,2*R*,4*S*)-4-Acetyl-1-(methylsulfanyl)-2,4-diphenylbutyl]-4-isopropyl-5,5-diphenyloxazolidin-2-one* (**14**). To a soln. of **11** (339 mg, 0.614 mmol) in CH_2Cl_2 (3 ml), Ac_2O (70 µl, 0.737 mmol) and DMAP (98 mg, 0.798 mmol) were added consecutively at r.t. After stirring for 10 min, 0.1M HCl was added, and the mixture was diluted with CH_2Cl_2. The org. layer was washed with 0.1M HCl (1×) and sat. aq. $NaHCO_3$ soln. (1×), dried ($MgSO_4$), and concentrated under reduced pressure. Purification of the crude product by FC (pentane/Et_2O 5:2) afforded **14** (345 mg, 95%). White solid. M.p. 154–155°. $[\alpha]_D^{r.t.} = -60.5$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3064*w*, 3008*w*, 2962*w*, 1744*s*, 1602*w*, 1494*w*, 1450*w*, 1409*w*, 1372*w*, 1248*m*, 1097*w*, 1027*m*, 1004*m*, 820*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.08 (*d*, *J* = 6.9, Me); 0.70 (*d*, *J* = 7.4, Me); 1.67 (*s*, MeS); 1.75–1.87 (*m*, 2 H, Me_2CH, CH_2); 1.99 (*s*, Me); 2.85 (*ddd*, *J* = 3.0, 10.9, 14.1, 1 H, CH_2); 4.27–4.33 (*m*, PhC*H*); 4.40 (*d*, *J* = 11.1, C*H*SMe); 4.42 (*d*, *J* = 1.5, NCH); 5.22 (*dd*, *J* = 2.4, 10.9, C*H*OAc); 7.08–7.28 (*m*, 18 arom. H); 7.48–7.50 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.3, 15.1, 20.4, 21.0 (Me); 29.4, 41.7 (CH); 42.3 (CH); 68.4, 68.7, 73.5 (CH); 87.4 (C); 125.3, 125.9, 126.4, 127.4, 127.5, 127.6, 127.76, 127.83, 128.3, 128.4, 128.5, 128.6 (CH); 138.9, 140.6, 141.1, 144.3, 157.0, 170.0 (C). MALDI-MS: 616 (1, $[M + Na]^+$), 556 (10), 442 (74, $[M - SMe - CO_2 - HOAc]^+$), 167 (100). Anal. calc. for $C_{37}H_{39}NO_4S$ (593.79): C 74.84, H 6.62, N 2.36; found: C 74.69, H 6.84, N 2.40.

*(1*S*,3*R*)-4-Hydroxy-1,3-diphenylbutyl Acetate* (**16**). Compound **14** (301 mg, 0.506 mmol) was treated with $Hg(O_2CCF_3)_2$ (238 mg, 0.557 mmol) and $NaBH_4$ (14 mg, 0.380 mmol)/DBU (38 µl, 0.253 mmol) according to *GP 2*. The auxiliary **1** was recovered by filtration (114 mg, 80%). Purification of the crude product by FC (pentane/Et_2O 3:2) yielded **16** (115 mg, 80%) as a 97:3 mixture with its *C*(3)-epimer. For anal. purposes, a sample was purified again by FC (pentane/Et_2O 3:2) to afford **16** (dr ≥ 99:1). Colorless oil. $[\alpha]_D^{r.t.} = -34.2$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3595*w*, 3064*w*, 3008*w*, 2956*w*, 2875*w*, 1732*s*, 1603*w*, 1494*m*, 1454*m*, 1409*w*, 1373*s*, 1107*m*, 1020*s*, 946*w*, 821*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.51 (*t*, *J* = 5.9, OH); 2.02 (*s*, Me); 2.03 (*ddd*, *J* = 4.1, 10.0, 14.3, 1 H, CH_2CHOAc); 2.33 (*ddd*, *J* = 4.7, 9.5, 14.3, 1 H, CH_2CHOAc); 2.90–2.97 (*m*, PhC*H*); 3.73–3.77 (*m*, CH_2OH); 5.53 (*dd*, *J* = 4.1, 9.5, C*H*OAc); 7.15–7.18 (*m*, 2 arom. H); 7.22–7.35 (*m*, 8 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.1 (Me); 39.2 (CH_2); 45.1 (CH); 67.3 (CH_2); 74.0, 126.2, 127.1, 127.8, 128.0, 128.4, 128.9 (CH); 140.8, 141.2, 170.1 (C). MALDI-MS: 307 (100, $[M + Na]^+$), 247 (59), 207 (94). Anal. calc. for $C_{18}H_{20}O_3$ (284.35): C 76.03, H 7.09; found: C 76.15, H 7.29.

*(*S*)-3-[(1*S*,2*R*,4*R*)-4-[(Benzyloxy)methoxy]-1-(methylsulfanyl)-2,4-diphenylbutyl]-4-isopropyl-5,5-diphenyloxazolidin-2-one* (**17**). To a soln. of **12** (1.55 g, 2.80 mmol as a 90:10 mixture with its *C*(4)-epimer) in CH_2Cl_2 (8 ml), EtN(i-Pr)$_2$ (1.92 ml, 11.2 mmol) and BOMCl (1.56 ml, 11.2 mmol) were added consecutively at 0°. After stirring for 3 h at r.t., sat. aq. Na_2CO_3 soln. was added, and the mixture was stirred for 30 min to hydrolyze excess BOMCl. 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. Purification of the crude product by FC (2×; pentane/Et_2O 6:1) afforded **17** (1.33 g, 71%) as a 97:3 mixture with its *C*(4)-epimer. For anal. purposes, a sample was purified again by FC (pentane/Et_2O 6:1) to afford **17** (dr ≥ 99:1). White solid. M.p. 135–137°. $[\alpha]_D^{r.t.} = -14.5$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2961*w*, 2884*w*, 1748*s*, 1494*w*, 1451*w*, 1408*w*, 1259*w*, 1161*w*, 1096*w*, 1038*m*, 909*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.09 (*d*, *J* = 6.9, Me); 0.70 (*d*, *J* = 7.3, Me); 1.48 (*s*, MeS); 1.75–1.87 (*m*, Me_2CH); 2.21–2.28 (*m*, 1 H, CH_2); 2.79 (*ddd*, *J* = 3.2, 10.4, 13.4, 1 H, CH_2); 3.65–3.71 (*m*, PhC*H*); 4.24–4.54 (*m*, C*H*SMe, NCH, C*H*OBOM, OCH_2O, PhCH_2O); 7.08–7.38 (*m*, 23 arom. H); 7.41–7.45 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.4, 15.2, 20.3 (Me); 29.4, 41.6 (CH); 42.4 (CH_2); 68.4, 68.9

(CH); 69.3 (CH_2); 76.6 (CH); 87.4 (C); 91.9 (CH_2); 125.3, 126.4, 127.30, 127.32, 127.6, 127.75, 127.83, 128.1, 128.2, 128.3, 128.4, 128.45, 128.47, 128.6 (CH); 137.7, 138.9, 140.5, 141.2, 144.4, 156.8 (C). MALDI-MS: 694 (95, $[M+Na]^+$), 442 (100, $[M-SMe-CO_2-HOBOM]^+$), 413 (44). Anal. calc. for $C_{43}H_{45}NO_4S$ (671.90): C 76.87, H 6.75, N 2.08; found: C 76.88, H 6.87, N 2.00.

*(2*R*,4*R*)-4-[(Benzyloxy)methoxy]-2,4-diphenylbutan-1-ol* (**18**). Compound **17** (460 mg, 0.685 mmol) was treated with $Hg(O_2CCF_3)_2$ (322 mg, 0.754 mmol) and $NaBH_4$ (20 mg, 0.514 mmol)/DBU (51 µl, 0.343 mmol) according to *GP 2*. The auxiliary **1** was recovered by filtration (152 mg, 79%). Purification of the crude product by FC (pentane/Et_2O 5:2) yielded **18** (220 mg, 89%) as a 96:4 mixture with its *C*(2)-epimer. For anal. purposes, a sample was purified again by FC (pentane/Et_2O 5:2) to afford **18** (dr ≥ 99:1). Colorless oil. $[\alpha]_D^{r.t.} = +43.5$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3590*w*, 3064*w*, 3008*m*, 2946*w*, 2888*w*, 1602*w*, 1494*m*, 1454*m*, 1381*w*, 1160*w*, 1098*m*, 1037*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.54 (br. *s*, OH); 2.14 (*ddd*, $J = 5.7, 8.2, 13.7$, 1 H, CH_2); 2.26 (*ddd*, $J = 6.1, 9.2, 13.7$, 1 H, CH_2); 2.61–2.68 (*m*, PhC*H*); 3.60–3.71 (*m*, CH_2OH); 4.38 (*d*, $J = 11.5$, 1 H, OCH_2O or PhCH_2O); 4.50–4.62 (*m*, 4 H, C*H*OBOM, OCH_2O, PhCH_2O); 7.13–7.34 (*m*, 15 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 39.7 (CH_2); 44.6 (CH); 67.4, 69.6 (CH_2); 76.4 (CH); 92.2 (CH_2); 126.9, 127.3, 127.7, 127.9, 128.0, 128.1, 128.3, 128.4, 128.8 (CH); 137.7, 141.1, 141.8 (C). MALDI-MS: 385 (100, $[M+Na]^+$), 324 (2), 207 (6). Anal. calc. for $C_{24}H_{26}O_3$ (362.47): C 79.53, H 7.23; found: C 79.47, H 7.36.

*(3*R*,5*R*)-5-[(Benzyloxy)methoxy]-3,5-diphenylpentan-2-ol* (**19**). Compound **17** (506 mg, 0.754 mmol) was treated with $Hg(O_2CCF_3)_2$ (354 mg, 0.829 mmol) according to *GP 2*. The crude hemiaminal was dissolved in THF (5 ml), and MeMgCl (2.01 ml, 3.02 mmol) was added at −78°. After stirring for 10 min at −78°, the cooling bath was removed, and the mixture was stirred for another 10 min. The auxiliary **1** precipitated in the course of the reaction. Then, sat. aq. NH_4Cl soln. and Et_2O were added, and the precipitate was filtered off. The precipitate was washed with sat. aq. NH_4Cl soln., H_2O, and Et_2O, and dried under h.v. to recover **1** (163 mg, 77%) as a white solid. The filtrate was diluted with Et_2O, the org. layer was separated, and the aq. layer was extracted with Et_2O (2×). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the crude product by FC (pentane/Et_2O 5:2) afforded **19** (235 mg, 83%) as a 75:25 mixture (*C*(2)-epimers). For anal. purposes, a sample was purified again by FC (pentane/Et_2O 5:2) to afford major-**19** (dr ≥ 99:1). Colorless oil. $[\alpha]_D^{r.t.} = +72.2$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3595*w*, 3066*w*, 3008*m*, 2953*w*, 1601*w*, 1494*m*, 1454*m*, 1381*w*, 1161*w*, 1095*m*, 1038*s*, 924*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.95 (*d*, $J = 6.3$, Me); 1.61 (br. *s*, OH); 2.29–2.40 (*m*, CH_2, PhC*H*); 3.78–3.88 (*m*, C*H*OH); 4.37 (*d*, $J = 11.5$, 1 H, OCH_2O or PhCH_2O); 4.44–4.48 (*m*, C*H*OBOM); 4.49 (*d*, $J = 6.9$, 1 H, OCH_2O or PhCH_2O); 4.57 (*d*, $J = 11.5$, 1 H, OCH_2O or PhCH_2O); 4.61 (*d*, $J = 6.9$, 1 H, OCH_2O or PhCH_2O); 7.07–7.11 (*m*, 2 arom. H); 7.15–7.21 (*m*, 4 arom. H); 7.23–7.35 (*m*, 9 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.1 (Me); 38.2 (CH_2); 49.8 (CH); 69.6 (CH_2); 71.6, 76.8 (CH); 92.2 (CH_2); 126.8, 127.5, 127.7, 127.9, 128.0, 128.3, 128.4, 128.59, 128.60 (CH); 137.8, 141.0, 141.5 (C). MALDI-MS: 399 (100, $[M+Na]^+$), 221 (12). Anal. calc. for $C_{25}H_{28}O_3$ (376.49): C 79.76, H 7.50; found: C 79.52, H 7.28.

*(*R*)-5-Hydroxy-1,1,1,4-tetraphenylpentan-2-one* (**20**). Compound **8a** (821 mg, 1.15 mmol) was treated with $Hg(O_2CCF_3)_2$ (538 mg, 1.26 mmol) and $NaBH_4$ (33 mg, 0.860 mmol)/DBU (86 µl, 0.573 mmol) according to *GP 2*. The auxiliary **1** was recovered by filtration (232 mg, 72%). Purification of the crude product by FC (pentane/Et_2O 2:1) yielded **20** (325 mg, 70%). White foam. $[\alpha]_D^{r.t.} = -12.1$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3592*w*, 3434*w*, 3062*m*, 3008*m*, 2933*w*, 2878*w*, 1708*s*, 1599*m*, 1493*s*, 1448*s*, 1102*m*, 1063*m*, 1034*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.82 (br. *s*, OH); 2.78–3.02 (*m*, $CH_2C(O)$, PhC*H*); 3.54–3.60 (*m*, CH_2OH); 7.03–7.06 (*m*, 2 arom. H); 7.18–7.34 (*m*, 18 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 44.4 (CH, CH_2); 66.3 (CH_2); 73.2 (C); 126.8, 127.8, 128.0, 128.1, 128.5, 130.2, 130.3 (CH); 141.8, 142.0, 207.3 (C). MALDI-MS: 429 (100, $[M+Na]^+$), 389 (82, $[M+H-H_2O]^+$). Anal. calc. for $C_{29}H_{26}O_2$ (406.52): C 85.68, H 6.45; found: C 85.70, H 6.59.

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