

Supplementary Material for:

Lithiated 4-Isopropyl-3-methylthiomethyl-5,5-diphenyl-oxazolidin-2-one: a  
Chiral Formyl Anion Equivalent for Enantioselective Preparations of 1,2-Diols,  
2-Amino Alcohols, 2-Hydroxy Esters and 4-Hydroxy-2-alkenoates

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## 1. Abbreviations

aq.	Aqueous	<i>J</i>	Coupling constant
arom.	Aromatic	LDA	Lithium diisopropylamide
b.p.	Boiling point	M	Molecule peak (MS)
BuLi	Butyllithium	min	Minute(s)
d	Day(s)	MOMCl	Chloromethyl methyl ether
conc.	Concentrated	M.p.	Melting point
DBU	(1,8-Diazabicyclo[5.4.0]undec-7-en	MS	Mass spectrometry
DIPA	Diisopropylamine	MTMCl	Chloromethyl methyl sulfide
DME	1,2-Dimethoxyethane	M	Molar
dr	Diastereomer ratio	NMR	Nuclear Magnetic Resonance Spectroscopy
dist.	Distillation	org.	Organic
DMAP	4-(Dimethylamino)pyridine	Pd/C	Palladium on charcoal
DMF	Dimethylformamide	<i>rac</i>	Racemic
DMPU	1,3-Dimethyl-3,4,5,6-tetra-hydropyrimidin-2(1 <i>H</i> )-one	<i>R<sub>t</sub></i>	Retention time
eq.	Equivalent(s)	r.t.	Room temperature
er	Enantiomer ratio	sat.	Saturated
FC	Flash-chromatography	soln.	Solution
GC	Gas-chromatography	solv.	Solvent
GP	General Procedure	temp.	Temperature
h	Hour(s)	TFA	Trifluoroacetic acid
HPLC	High Performance Liquid Chromatography	THF	Tetrahydrofuran
h.v.	High vacuum (0.01-0.1 Torr)	TLC	Thin layer chromatography
IR	Infrared spectroscopy		

## 2 Materials and Methods

**Solvents:** THF was freshly distilled over potassium under argon before use. Et<sub>2</sub>O was freshly distilled over sodium under argon. CH<sub>2</sub>Cl<sub>2</sub> and DMSO were distilled over CaH<sub>2</sub> and stored under argon over 4 Å molecular sieves. DME was stored over KOH pellets. Solvents for chromatography and workup procedures were distilled from Sikkon (pentane, AcOEt, MeOH), P<sub>2</sub>O<sub>5</sub> (CH<sub>2</sub>Cl<sub>2</sub>) and KOH/FeSO<sub>4</sub> (Et<sub>2</sub>O).

**Reagents and methods:** (*i*Pr)<sub>2</sub>NEt, DMPU and DBU were distilled from CaH<sub>2</sub> and stored under argon over 4 Å molecular sieves. All liquid aldehydes and ketones were distilled and stored under argon. BuLi (ca. 1.6M soln. in hexane) was titrated before use according to the method of *J. Suffert* [1]. LiBr was dried in Kugelrohr apparatus (Büchi GKR-50) at 150° under h.v. for 16 h. All other reagents were used as received from *Aldrich* or *Fluka*.

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.

**Thin-layer chromatography:** *Merck* silica gel 60 F<sub>254</sub> or *Macherey-Nagel* Durasil-25 UV<sub>254</sub> plates; detection by UV and by dipping into a soln. of anisaldehyde (9.2 mL anisaldehyde, 3.75 mL HOAc, 12.5 mL conc. H<sub>2</sub>SO<sub>4</sub>, 350 mL EtOH), ninhydrine (0.6 g ninhydrine, 2 mL HOAc, 13 mL H<sub>2</sub>O, 285 mL butanol), "Mo-stain" (25 g phosphomolybdic acid, 10 g, Ce(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, 60 mL conc. H<sub>2</sub>SO<sub>4</sub> and 940 mL H<sub>2</sub>O) or KMnO<sub>4</sub> soln. (12 g NaOH, 1.5 g KMnO<sub>4</sub>, 300 mL H<sub>2</sub>O), followed by heating with a heat-gun.

**Flash chromatography:** *Fluka* silica gel 60 (40-63  $\mu\text{m}$ ) at r.t. with a pressure of *ca.* 0.2 bar.

Eluents are indicated.

**Melting points** were measured in open end glass capillary tubes on a *Büchi 510* apparatus and are uncorrected.

**IR Spectra:** Measured as film, 1%  $\text{CHCl}_3$ -soln. on a *Perkin-Elmer-782* spectrophotometer. The maxima are classified in three intensities: *s* (strong), *m* (medium) and *w* (weak) and are reported in  $\text{cm}^{-1}$ .

**NMR Spectra:**  $^1\text{H}$ -NMR spectra were recorded on a *Bruker AMX 500* (500 MHz), *AMX 400* (400 MHz), *ARX 300* (300 MHz), *Varian Gemini 300* (300 MHz), or *Varian Gemini 200* (200 MHz).  $^{13}\text{C}$ -NMR spectra were recorded on a *Bruker AMX 500* (125 MHz), *AMX 400* (100 MHz), *Varian Gemini 300* (75 MHz) or *Varian Gemini 200* (50 MHz). All  $^{13}\text{C}$ -NMR spectra are  $^1\text{H}$ -broadband decoupled.  $^{19}\text{F}$ -NMR spectra were recorded on a *Varian Gemini 300* (282 MHz).  $^{31}\text{P}$ -NMR spectra were recorded on a *Bruker AMX 400* (162 MHz). All  $^{31}\text{P}$ -NMR spectra are  $^1\text{H}$ -broadband decoupled. Chemical shifts are reported in parts per million (ppm,  $\delta$ ), downfield from internal standard tetramethylsilane (TMS) ( $\delta = 0.00$  ppm) and are referred to the solvent. Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quadruplet), *m* (multiplet or more overlapping signals), *br* (broad signal).

**Mass spectra:** *VG Tribrid* (EI), *ZAB2 SEQ* (FAB, in a 3-nitrobenzyl-alcohol matrix) or *IonSpec Ultima* (FT-ICR-MALDI, in a 2,5-Dihydroxybenzoessäure Matrix); in  $m/z$  (% of basis peak).

**Optical rotations:**  $[\alpha]_{\text{D}}^{\text{r.t.}}$  was measured on a *Perkin-Elmer 241* polarimeter (10 cm, 1 mL cell) at r.t. The solvent and the concentration (in g/100 mL) are indicated.

**Anal. HPLC:** *Knauer* HPLC system (pump type 64, *EuroChrom 2000* integration package, degaser, UV detector (variable-wavelength monitor)). The following columns were used: *Chiralcel OD* and *LiCrosorb Si-60*.

**Gas Chromatography** was performed using a *Carlo Erba Fractovap 4160* or a *CE Instruments GC 8000 Top*. Interpretation of the spectra was accomplished using the interpretation software *Chrom-Card* by *CE Instruments*. The following capillary columns were used:  $\beta$ -Dex 120 (30m x 0.25mm ID, *SUPELCO*),  $\gamma$ -Dex 120 (30m x 0.25mm ID, *SUPELCO*). Hydrogen gas was used as carrier gas. Detection was done by flame ionisation. The injection volume was 1  $\mu\text{L}$ .

**Elemental analyses** were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH-Zürich.

**Diastereoisomeric ratios** were determined by  $^1\text{H}$  NMR.

### 3. Preparations

**General Procedure 1 (GP 1) for the Methylthiomethylation of Oxazolidinones.** To a solution (or suspension) of oxazolidinone (1 eq.) in THF (1 M) was added BuLi (1.05 eq.) at 0°. After stirring for 10 min, DMSO (fivefold excess compared to the amount of THF) and MTMCl (1.2 eq.) were added consecutively to the reaction mixture. After stirring for 4 h at rt, the reaction mixture was quenched with sat. aq. NH<sub>4</sub>Cl soln. and diluted with Et<sub>2</sub>O. The org. layer was separated and the aq. layer was extracted with Et<sub>2</sub>O (2x). The combined org. layers were washed with H<sub>2</sub>O (1x), dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was purified by FC.

**General Procedure 2 (GP 2) for the Addition of *N,S*-Acetals to Aldehydes, Ketones and Imine Derivatives.** To a solution of *N,S*-acetal (1 eq.) in THF (0.2 M) or Et<sub>2</sub>O (0.2 M) was added BuLi (1.2 eq.) at –78°. After stirring for 5 min, the reaction mixture was cooled to –100° (or kept at –78°) and an aldehyde, ketone or imine derivative (1.3 eq.) was added dropwise neat or as a solution in THF (ca. 1 M) or Et<sub>2</sub>O (ca. 1 M). It was allowed to warm to –78° within 20 min and then the reaction was stopped by quenching with sat. aq. NH<sub>4</sub>Cl soln. The reaction mixture was diluted with Et<sub>2</sub>O, the org. layer was separated and the aq. layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2x). The combined org. layers were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was purified by trituration, FC or recrystallization.

**General Procedure 3 (GP 3) for the Transformation of Addition Products to 1,2-Diols Using Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>/NaBH<sub>4</sub>/DBU.** To a solution (or suspension) of addition product (1 eq.) in THF/MeCN/H<sub>2</sub>O (2:2:1; 0.1 M) was added Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (1.1 eq.) at r.t. After stirring for 5 min,

H<sub>2</sub>O was added and the reaction mixture was diluted with Et<sub>2</sub>O. The org. layer was separated and the aq. layer was extracted with Et<sub>2</sub>O (2x). The combined org. layers were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was dissolved in THF/H<sub>2</sub>O (4:1, 0.15 M), NaBH<sub>4</sub> (0.75 eq.) and DBU (0.5 eq.) were added consecutively at 0°. The auxiliary **1** precipitated in the course of the reaction. After stirring for 15 min, sat. aq. NH<sub>4</sub>Cl soln. and Et<sub>2</sub>O were added and the precipitate was filtered off. The precipitate was washed with sat. aq. NH<sub>4</sub>Cl soln., H<sub>2</sub>O and Et<sub>2</sub>O and dried under h.v. to recover **1** as a white solid. The filtrate was diluted with Et<sub>2</sub>O, the org. layer was separated and the aq. layer was extracted with Et<sub>2</sub>O (2x). The combined org. layers were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was purified by FC.

**General Procedure 4 (GP 4) for the Transformation of Addition Products to 1,2-Diols Using Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>/RLi or RMgCl.** A solution (or suspension) of addition product (1 eq.) in THF/MeCN/H<sub>2</sub>O (2:2:1; 0.1 M) was treated with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (1.1 eq.) according to GP 3. The crude product was dissolved in THF (0.25 M) and RLi (4 eq.) or RMgCl (4 eq.) was added at –78°. After stirring for 10 min at –78°, the cooling bath was removed and it was stirred for another 10 min. The auxiliary **1** precipitated in the course of the reaction. Then, sat. aq. NH<sub>4</sub>Cl soln. and Et<sub>2</sub>O were added and the precipitate was filtered off. The precipitate was washed with sat. aq. NH<sub>4</sub>Cl soln., H<sub>2</sub>O and Et<sub>2</sub>O and dried under h.v. to recover **1** as a white solid. The filtrate was diluted with Et<sub>2</sub>O, the org. layer was separated and the aq. layer was extracted with Et<sub>2</sub>O (2x). The combined org. layers were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was purified by FC.

**General Procedure 5 (GP 5) for the Transformation of Addition Products to N-Acyl-**

**oxazolidinones.** A solution (or suspension) of addition product (1 eq.) in THF/MeCN/H<sub>2</sub>O (2:2:1; 0.1 M) was treated with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (1.1 eq.) according to *GP 3*. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.15 M) and treated with PCC (2.1 eq.) and powdered 4 Å molecular sieves (1 weight eq. to PCC) at r.t. After stirring for 2.5 h, the reaction mixture was diluted with Et<sub>2</sub>O and filtered through a silica plug eluting with pentane/Et<sub>2</sub>O (1:1). The crude product was purified by FC or recrystallization.

**General Procedure 6 (GP 6) for the Methanolysis of *N*-Acyl-oxazolidinones to 2-Hydroxy Methylesters.** To a solution of *N*-acyl-oxazolidinone (1 eq.) in MeOH/THF (2:1, 0.15 M) was added DBU (2 eq.) and LiBr (5 eq.) consecutively at 0°. The auxiliary **1** precipitated in the course of the reaction. After stirring for 45 min, sat. aq. NH<sub>4</sub>Cl soln. and Et<sub>2</sub>O were added and the precipitate was filtered off. The precipitate was washed with sat. aq. NH<sub>4</sub>Cl soln., H<sub>2</sub>O and Et<sub>2</sub>O and dried under h.v. to recover **1** as a white solid. The filtrate was diluted with Et<sub>2</sub>O, the org. layer was separated and the aq. layer was extracted with Et<sub>2</sub>O (2x). The combined org. layers were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was purified by FC.

**General Procedure 7 (GP 7) for the Transformation of Addition Products to 4-Hydroxy-2-alkenoate and Butenolides.** A solution (or suspension) of addition product (1 eq.) in THF/MeCN/H<sub>2</sub>O (2:2:1; 0.1 M) was treated with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (1.1 eq.) according to *GP 3*. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.15 M), DBU (0.5 eq.) and (methoxycarbonylmethylenetriphenylphosphorane (2 eq.) were added consecutively at r.t. After stirring for 12 h at r.t, sat. aq. NH<sub>4</sub>Cl soln. was added. The org. layer was separated and the aq. layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2x). The combined org. layers were dried (MgSO<sub>4</sub>) and



concentrated under reduced pressure. The crude product was triturated in Et<sub>2</sub>O for 30 min, the insoluble material was filtered off, washed with 1 N HCl and H<sub>2</sub>O, triturated with hexane and CH<sub>2</sub>Cl<sub>2</sub> and dried under h.v. to recover **1** as a white solid. The filtrate was concentrated under reduced pressure and purified by FC.

*(S)*-4-Isopropyl-3-methoxymethyl-5,5-diphenyl-oxazolidin-2-one (**2**). To a suspension of **1** (2.00 g, 7.10 mmol) in THF (30 mL) was added BuLi (5.44 mL, 8.16 mmol) at 0°. After stirring for 10 min, MOMCl (650 µL, 8.51 mmol) was added and the reaction mixture was stirred for 5 h at r.t. Then the mixture was quenched with sat. aq. NH<sub>4</sub>Cl soln. and diluted with Et<sub>2</sub>O. The org. layer was separated and the aq. layer was extracted with Et<sub>2</sub>O (2x). The combined org. layers were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was recrystallized (AcOEt/hexane) to yield **2** (1.66 g, 72%). White solid. **M.p.** 115-117°.  $[\alpha]_D^{25} = -183.8$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3008w, 2966w, 1751s, 1600w, 1493w, 1450m, 1420m, 1387w, 1088m, 1001m. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.70 (*d*,  $J = 6.5$ , 3 H, Me); 1.05 (*d*,  $J = 7.2$ , 3 H, Me); 1.88-2.01 (*m*, 1 H, Me<sub>2</sub>CH); 2.86 (*s*, 3 H, OMe); 4.54 (*d*,  $J = 1.9$ , 1 H, NCH); 4.72 (*d*,  $J = 11.2$ , 1 H, CH<sub>2</sub>); 4.83 (*d*,  $J = 11.2$ , 1 H, CH<sub>2</sub>); 7.21-7.38 (*m*, 6 arom. H); 7.43-7.46 (*m*, 2 arom. H); 7.61-7.64 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 15.4, 21.9 (Me); 29.6 (CH); 55.8 (Me); 66.5 (CH); 76.3 (CH<sub>2</sub>); 88.4 (C); 125.3, 126.0, 127.6, 128.1, 128.6 (CH); 138.8, 144.1, 157.4 (C). **FAB-MS**: 282 (7, [*M*+H-CO<sub>2</sub>]<sup>+</sup>), 250 (100, [*M*-OMe-CO<sub>2</sub>]<sup>+</sup>). **Anal.** calc. for C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub> (325.41): C 73.82, H 7.12, N 4.30; found: C 73.54, H 7.33, N 4.39.

*(S)*-4-Isopropyl-3-methylsulfanylmethyl-5,5-diphenyl-oxazolidin-2-one (**3**) and *(S)*-4-Isopropyl-3-[[*(S)*-4-isopropyl-2-oxo-5,5-diphenyl-oxazolin-3-yl]methyl]-5,5-diphenyl-oxazolidin-2-one (**6**).

**a)** To a suspension of **1** (5.15 g, 18.3 mmol) in DME (40 mL) was added BuLi (14.4 mL, 20.1

mmol) at 0°. After stirring for 10 min, NaI (2.74 g, 18.3 mmol) and chloromethyl methyl sulfide (MTMCl) (1.89 mL, 18.3 mmol) were added consecutively to the reaction mixture. After stirring for 12 h at r.t., the reaction mixture was quenched with sat. aq. NH<sub>4</sub>Cl soln. and diluted with Et<sub>2</sub>O. The org. layer was separated and the aq. layer was extracted with Et<sub>2</sub>O (2x). The combined org. layers were washed with H<sub>2</sub>O (1x), dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. Compounds **3** and **6** were obtained as a 4:1 mixture, determined by <sup>1</sup>H-NMR of the crude product. Compounds **3** and **6** were separated by FC (pentane/AcOEt 10:1) to afford **3** (3.28 g, 53%) and **6** (yield not determined).

**b)** Compound **1** (15.7 g, 55.8 mmol) was treated with BuLi (38.8 mL, 58.6 mmol) and MTMCl (5.60 mL, 67.0 mmol) according to *GP 1*. The crude product was purified by FC (pentane/Et<sub>2</sub>O 5:1) to afford **3** (16.4 g, 86%). **3**: White solid. **M.p.** 124-125°.  $[\alpha]_D^{25} = -89.6$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 2954<sub>w</sub>, 1744<sub>s</sub>, 1451<sub>w</sub>, 1421<sub>m</sub>, 1041<sub>w</sub>, 995<sub>w</sub>. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.72 (*d*,  $J = 6.5$ , 3 H, Me); 1.04 (*d*,  $J = 7.2$ , 3 H, Me); 1.37 (*s*, 3 H, SMe); 1.88-2.03 (*m*, 1 H, Me<sub>2</sub>CH); 4.06 (*d*,  $J = 14.3$ , 1 H, CH<sub>2</sub>); 4.76 (*d*,  $J = 1.9$ , 1 H, NCH); 4.95 (*d*,  $J = 14.3$ , 1 H, CH<sub>2</sub>); 7.20-7.38 (*m*, 6 arom. H); 7.43-7.49 (*m*, 2 arom. H); 7.66-7.72 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 12.9, 15.6, 22.4 (Me); 29.7 (CH); 48.7 (CH<sub>2</sub>); 64.9 (CH); 88.3 (C); 125.3, 125.9, 127.5, 128.2, 128.6 (CH); 138.7, 144.2, 156.9 (C). **FAB-MS**: 342 (2, [M+H]<sup>+</sup>), 294 (12, [M-SMe]<sup>+</sup>), 250 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 206 (10). **Anal.** calc. for C<sub>20</sub>H<sub>23</sub>NO<sub>2</sub>S (341.47): C 70.35, H 6.79, N 4.10; found: C 70.25, H 7.08, N 4.09.

**6**: White solid. **M.p.** 190-192°.  $[\alpha]_D^{25} = -152.9$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3008<sub>w</sub>, 2966<sub>w</sub>, 1750<sub>s</sub>, 1493<sub>w</sub>, 1450<sub>w</sub>, 1392<sub>w</sub>, 1326<sub>w</sub>, 1037<sub>w</sub>, 1003<sub>w</sub>. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.59 (*d*,  $J = 6.9$ , 6 H, Me); 0.89 (*d*,  $J = 7.5$ , 6 H, Me); 1.82-1.97 (*m*, 2 H, Me<sub>2</sub>CH); 4.27 (*d*,  $J = 1.9$ , 2 H, NCH); 5.07 (*s*, 2 H, CH<sub>2</sub>); 7.10-7.30 (*m*, 16 arom. H); 7.33-7.37 (*m*, 4 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 15.6, 21.4 (Me); 29.1 (CH); 53.0 (CH<sub>2</sub>); 66.9 (CH); 88.2 (C); 125.5, 126.3,

127.6, 128.0, 128.2, 128.3 (CH); 139.0, 143.1, 157.4 (C). **FAB-MS**: 575 (23,  $[M+H]^+$ ), 530 (14,  $[M-CO_2]^+$ ), 250 (100,  $[M-CO_2-C_{18}H_{18}NO_2]^+$ ). **Anal.** calc. for  $C_{37}H_{38}N_2O_4$  (574.72): C 77.33, H 6.66, N 4.87; found: C 77.33, H 6.71, N 4.94.

*(S)*-4-Isopropyl-5,5-diphenyl-3-phenylsulfanylmethyl-oxazolidin-2-one (**4**). To a suspension of **1** (1.07 g, 3.80 mmol) in DME (8 mL) was added BuLi (2.89 mL, 4.18 mmol) at 0°. After stirring for 10 min, NaI (627 mg, 4.18 mmol) and chloromethyl phenyl sulfide (542  $\mu$ L, 4.18 mmol) were added consecutively to the reaction mixture. After stirring for 12 h at r.t., the reaction mixture was quenched with sat. aq.  $NH_4Cl$  soln. and diluted with  $Et_2O$ . The org. layer was separated and the aq. layer was extracted with  $Et_2O$  (2x). The combined org. layers were washed with  $H_2O$  (1x), dried ( $MgSO_4$ ) and concentrated under reduced pressure. The crude product was purified by FC (pentane/AcOEt 10:1) to afford **4** (807 mg, 53%). White solid. **M.p.** 137-141°.  $[\alpha]_D^{r.t.} = +9.3$  ( $c = 1$ ,  $CHCl_3$ ). **IR** ( $CHCl_3$ ): 3008w, 2966w, 1749s, 1450w, 1417m, 1040w, 1002w, 900w. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ): 0.69 (*d*,  $J = 6.8$ , 3 H, Me); 1.07 (*d*,  $J = 7.4$ , 3 H, Me); 1.88-1.98 (*m*, 1 H,  $Me_2CH$ ); 4.38 (*d*,  $J = 14.5$ , 1 H,  $CH_2$ ); 4.80 (*d*,  $J = 1.6$ , 1 H, NCH); 5.41 (*d*,  $J = 14.5$ , 1 H,  $CH_2$ ); 6.92-6.95 (*m*, 2 arom. H); 7.00-7.07 (*m*, 3 arom. H); 7.16-7.30 (*m*, 6 arom. H); 7.39-7.42 (*m*, 2 arom. H); 7.46-7.50 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz,  $CDCl_3$ ): 15.5, 22.6 (Me); 29.7 (CH); 49.3 ( $CH_2$ ); 65.6 (CH); 88.1 (C); 125.4, 126.1, 127.0, 127.6, 128.0, 128.1, 128.4, 128.9, 130.4 (CH); 132.7, 138.9, 143.8, 156.2 (C). **FAB-MS**: 294 (5,  $[M-SPh]^+$ ), 250 (100,  $[M-SPh-CO_2]^+$ ). **Anal.** calc. for  $C_{25}H_{25}NO_2S$  (403.54): C 74.41, H 6.24, N 3.47, S 7.95; found: C 74.24, H 6.36, N 3.52, S 8.04.

*(S)*-3-tert-Butylsulfanylmethyl-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**5**). To a suspension of **1** (1.05 g, 3.73 mmol) in DME (8 mL) was added BuLi (2.83 mL, 4.11 mmol) at 0°. After stirring

for 10 min, NaI (615 mg, 4.18 mmol) and chloromethyl *tert*-butyl sulfide (475  $\mu$ L, 4.11 mmol) were added consecutively to the reaction mixture. After stirring for 12 h at r.t., the reaction mixture was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  soln. and diluted with  $\text{Et}_2\text{O}$ . The org. layer was separated and the aq. layer was extracted with  $\text{Et}_2\text{O}$  (2x). The combined org. layers were washed with  $\text{H}_2\text{O}$  (1x), dried ( $\text{MgSO}_4$ ) and concentrated under reduced pressure. The crude product was purified by FC (pentane/AcOEt 9:1) to afford **5** (1.10 g, 77%). White solid. **M.p.** 174-175°.  $[\alpha]_{\text{D}}^{\text{r.t.}} = -71.6$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3007 $w$ , 2966 $m$ , 1742 $s$ , 1493 $w$ , 1450 $m$ , 1424 $m$ , 1368 $w$ , 1040 $w$ , 1002 $w$ , 880 $w$ .  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 0.69 ( $d$ ,  $J = 6.9$ , 3 H, Me); 0.97 ( $s$ , 9 H, *t*Bu); 1.07 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.83-1.98 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 4.16 ( $d$ ,  $J = 15.1$ , 1 H,  $\text{CH}_2$ ); 4.80 ( $d$ ,  $J = 1.6$ , 1 H, NCH); 5.05 ( $d$ ,  $J = 15.1$ , 1 H,  $\text{CH}_2$ ); 7.19-7.36 ( $m$ , 6 arom. H); 7.43-7.47 ( $m$ , 2 arom. H); 7.63-7.67 ( $m$ , 2 arom. H).  **$^{13}\text{C-NMR}$**  (75 MHz,  $\text{CDCl}_3$ ): 15.4, 22.7 (Me); 29.6 (CH); 30.7 (Me); 43.7 (C); 44.2 ( $\text{CH}_2$ ); 65.7 (CH); 87.9 (C); 125.6, 126.0, 127.5, 128.0, 128.1, 128.4 (CH); 139.0, 144.4, 155.8 (C). **FAB-MS**: 767 (30,  $[2M+H]^+$ ), 621 (27), 384 (7,  $[M+H]^+$ ), 294 (8,  $[M-\text{StBu}]^+$ ), 250 (100,  $[M-\text{StBu}-\text{CO}_2]^+$ ). **Anal.** calc. for  $\text{C}_{23}\text{H}_{29}\text{NO}_2\text{S}$  (383.55): C 72.02, H 7.62, N 3.65; found: C 72.13, H 7.50, N 3.66.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-1-methylsulfanyl-2-phenyl-ethyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**7b**). Compound **3** (430 mg, 1.26 mmol) was treated with BuLi (0.97 mL, 1.51 mmol) and benzaldehyde (166  $\mu$ L, 1.64 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/AcOEt 8:1) yielded **7b** (505 mg, 90%) as a 93:7 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized twice (MeOH) to afford **7b** (dr 97:3). White solid. **M.p.** 200-201°.  $[\alpha]_{\text{D}}^{\text{r.t.}} = -72.2$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3512 $w$ , 3008 $w$ , 2965 $w$ , 1729 $s$ , 1601 $w$ , 1494 $w$ , 1450 $m$ , 1422 $m$ , 1292 $w$ , 1046 $m$ .  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 0.81 ( $d$ ,  $J = 6.5$ , 3 H, Me); 1.08 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.36 ( $s$ , 3 H, SMe); 2.00-2.07 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 4.40 ( $d$ ,

$J = 9.3$ , 1 H,  $\text{CHSMe}$ ); 4.46 ( $d$ ,  $J = 5.6$ , 1 H, OH); 4.70 ( $d$ ,  $J = 2.2$ , 1 H, NCH); 5.47 ( $dd$ ,  $J = 5.6$ , 9.3, 1 H,  $\text{CH(OH)}$ ); 7.22-7.45 ( $m$ , 13 arom. H); 7.72-7.75 ( $m$ , 2 arom. H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ): 10.5, 15.5, 21.9 (Me); 29.9, 68.4, 68.7, 74.0 (CH); 89.0 (C); 125.2, 125.9, 127.0, 127.5, 128.1, 128.18, 128.21, 128.5 (CH); 138.4, 140.9, 143.8, 157.5 (C). **FAB-MS**: 446 (2,  $[M-H]^+$ ), 400 (47,  $[M-SMe]^+$ ), 356 (100,  $[M-SMe-CO_2]^+$ ), 296 (40). **Anal.** calc. for  $\text{C}_{27}\text{H}_{29}\text{NO}_3\text{S}$  (447.60): C 72.45, H 6.53, N 3.13; found: C 72.15, H 6.57, N 3.32.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-2-phenyl-1-phenylsulfanyl-ethyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**7c**). Compound **4** (403 mg, 0.999 mmol) was treated with BuLi (0.82 mL, 1.20 mmol) and benzaldehyde (131  $\mu\text{L}$ , 1.30 mmol) according to *GP* 2. Trituration of the crude product (boiling hexane, 2x 10 mL) yielded **7c** (360 mg, 71%) as a 95:5 mixture with its C(2)-OH epimer and 5 mol% of inseparable unidentified side products. White solid. **M.p.** 200-203°.  $[\alpha]_D^{+1.5} = -191.5$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3335 $w$ , 3063 $w$ , 3008 $w$ , 2962 $w$ , 1734 $s$ , 1494 $w$ , 1451 $m$ , 1423 $m$ , 1091 $w$ , 1000 $w$ .  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 0.55 ( $d$ ,  $J = 6.8$ , 3 H, Me); 0.89 ( $d$ ,  $J = 7.3$ , 3 H, Me); 1.96-2.08 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 4.37 ( $d$ ,  $J = 6.0$ , 1 H, OH); 4.51 ( $d$ ,  $J = 1.9$ , 1 H, NCH); 4.81 ( $d$ ,  $J = 8.7$ , 1 H,  $\text{CHSMe}$ ); 5.36 ( $dd$ ,  $J = 6.0$ , 8.7, 1 H,  $\text{CH(OH)}$ ); 6.78-6.81 ( $m$ , 2 arom. H); 7.06-7.42 ( $m$ , 16 arom. H); 7.53-7.59 ( $m$ , 2 arom. H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 15.2, 21.6 (Me); 29.8, 69.8, 74.0, 75.1 (CH); 88.8 (C); 125.4, 126.3, 127.65, 127.71, 127.8, 128.0, 128.2, 128.4, 128.7, 128.9, 132.8 (CH); 133.8, 138.7, 140.5, 144.0, 157.3 (C). **FAB-MS**: 492 (5,  $[M+H-H_2O]^+$ ), 448 (7), 400 (52,  $[M-SPh]^+$ ), 356 (100,  $[M-SPh-CO_2]^+$ ), 296 (11).

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-1-methylsulfanyl-2-naphthalen-2-yl-ethyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9a**). Compound **3** (357 mg, 1.05 mmol) was treated with BuLi (0.84 mL, 1.25 mmol) and a solution of 2-naphthaldehyde (212 mg, 1.36 mmol) in THF (1 mL) according to *GP*

2. Purification of the crude product by FC (pentane/AcOEt 7:1) yielded **9a** (454 mg, 87%) as a 91:9 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized twice (MeOH) to afford **9a** (dr 96:4). White solid. **M.p.** 209-211°.  $[\alpha]_D^{25} = -91.6$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3503 $w$ , 3060 $w$ , 3008 $m$ , 2967 $w$ , 1728 $s$ , 1601 $w$ , 1494 $w$ , 1450 $m$ , 1423 $m$ , 1293 $w$ , 1046 $m$ , 1002 $m$ . **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.84 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.11 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.40 ( $s$ , 3 H, SMe); 2.03-2.13 ( $m$ , 1 H, Me<sub>2</sub>CH); 4.51-4.56 ( $m$ , 2 H, CHSMe, OH); 4.74 ( $d$ ,  $J = 1.9$ , 1 H, NCH); 5.65 ( $dd$ ,  $J = 5.3, 9.3$ , 1 H, CH(OH)); 7.22-7.40 ( $m$ , 6 arom. H); 7.43-7.55 ( $m$ , 5 arom. H); 7.74-7.76 ( $m$ , 2 arom. H); 7.81-7.89 ( $m$ , 4 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 10.6, 15.7, 22.0 (Me); 30.0, 68.5, 68.6, 74.0 (CH); 89.1 (C); 124.6, 125.1, 125.3, 126.0, 126.1, 126.5, 127.6, 128.06, 128.14, 128.3, 128.6 (CH); 133.1, 133.2, 138.3, 138.5, 143.9, 157.6 (C). **FAB-MS**: 480 (8,  $[M+H-H_2O]^+$ ), 450 (46,  $[M-SMe]^+$ ), 436 (22), 406 (100,  $[M-SMe-CO_2]^+$ ), 296 (27). **Anal.** calc. for C<sub>31</sub>H<sub>31</sub>NO<sub>3</sub>S (497.66): C 74.82, H 6.28, N 2.81; found: C 74.87, H 6.48, N 2.76.

(*S*)-3-[(1*S*,2*S*)-2-Hydroxy-2-(4-methoxy-phenyl)-1-methylsulfanyl-ethyl]-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9b**). Compound **3** (357 mg, 1.05 mmol) was treated with BuLi (0.81 mL, 1.25 mmol) and *p*-anisaldehyde (165  $\mu$ L, 1.36 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/AcOEt 6:1) yielded **9b** (459 mg, 92%) as a 91:9 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized twice (MeOH) to afford **9b** (dr  $\geq$  99:1). White solid. **M.p.** 192-194°.  $[\alpha]_D^{25} = -92.2$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3500 $w$ , 3008 $m$ , 2965 $w$ , 1729 $s$ , 1612 $w$ , 1515 $m$ , 1450 $m$ , 1422 $m$ , 1304 $w$ , 1035 $m$ , 1002 $m$ , 836 $w$ . **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.83 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.10 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.36 ( $s$ , 3 H, SMe); 2.00-2.11 ( $m$ , 1 H, Me<sub>2</sub>CH); 3.97 ( $s$ , 3 H, OMe); 4.30 ( $d$ ,  $J = 5.3$ , 1 H, OH); 4.37 ( $d$ ,  $J = 9.3$ , 1 H, CHSMe); 4.70 ( $d$ ,  $J = 1.9$ , 1 H, NCH); 5.42 ( $dd$ ,  $J = 5.3, 9.3$ , 1 H, CH(OH)); 6.85-6.90 ( $m$ ,

2 arom. H); 7.22-7.39 (*m*, 8 arom. H); 7.45-7.48 (*m*, 2 arom. H); 7.72-7.75 (*m*, 2 arom. H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 10.5, 15.7, 22.0 (Me); 30.0 (CH); 55.2 (Me); 68.5, 69.0, 73.4 (CH); 89.0 (C); 113.7, 125.3, 126.0, 127.6, 128.16, 128.22, 128.6 (CH); 133.2, 138.6, 144.0, 157.5, 159.4 (C). **FAB-MS**: 460 (43, [M+H-H<sub>2</sub>O]<sup>+</sup>), 416 (63, [M+H-H<sub>2</sub>O-CO<sub>2</sub>]<sup>+</sup>), 386 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 326 (20), 296 (37). **Anal.** calc. for C<sub>28</sub>H<sub>31</sub>NO<sub>4</sub>S (477.62): C 70.41, H 6.54, N 2.93; found: C 70.25, H 6.74, N 3.09.

(S)-3-[(1S,2S)-2-[3-(*tert*-Butyl-dimethyl-silanyloxy)-phenyl]-2-hydroxy-1-methylsulfanyl-ethyl]-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9c**). Compound **3** (360 mg, 1.05 mmol) was treated with BuLi (0.84 mL, 1.27 mmol) and 3-(*tert*-butyl-dimethyl-silanyloxy)benzaldehyde (324 μL, 1.37 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/AcOEt 10:1) yielded **9c** (556 mg, 91%) as a 91:9 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized three times (MeOH) to afford **9c** (dr ≥ 99:1). White solid. **M.p.** 192-193°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -72.9 (*c* = 1, CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3493*w*, 2951*m*, 2930*m*, 2858*w*, 1728*s*, 1603*w*, 1587*w*, 1487*m*, 1450*m*, 1422*m*, 1278*m*, 1002*m*, 838*s*. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 0.19 (*s*, 6 H, Me<sub>2</sub>Si); 0.81 (*d*, *J* = 6.5, 3 H, Me); 0.98 (*s*, 9 H, *t*Bu); 1.09 (*d*, *J* = 7.5, 3 H, Me); 1.35 (*s*, 3 H, SMe); 1.97-2.11 (*m*, 1 H, Me<sub>2</sub>CH); 4.36 (*d*, *J* = 9.3, 1 H, CHSMe); 4.40 (*d*, *J* = 5.6, 1 H, OH); 4.70 (*d*, *J* = 2.2, 1 H, NCH); 5.40 (*dd*, *J* = 5.6, 9.3, 1 H, CH(OH)); 6.76-6.80 (*m*, 1 arom. H); 6.88-6.90 (*m*, 1 arom. H); 6.99-7.01 (*m*, 1 arom. H); 7.17-7.40 (*m*, 7 arom. H); 7.45-7.48 (*m*, 2 arom. H); 7.72-7.75 (*m*, 2 arom. H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): -4.5, 10.6, 15.6 (Me); 18.1 (C); 22.0, 25.6 (Me); 30.0, 68.5, 68.8, 73.9 (CH); 89.0 (C); 119.0, 119.8, 119.9, 125.3, 125.9, 127.6, 128.1, 128.2, 128.5, 129.2 (CH); 138.5, 142.5, 143.9, 155.5, 157.5 (C). **FAB-MS**: 530 (10, [M-SMe]<sup>+</sup>), 516 (13), 486 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 426 (15), 296 (5). **Anal.** calc. for C<sub>33</sub>H<sub>43</sub>NO<sub>4</sub>SiS (577.86): C 68.59, H 7.50, N 2.42; found: C 68.68, H 7.61, N 2.43.

4-[(1*S*,2*S*)-1-Hydroxy-2-((*S*)-4-isopropyl-2-oxo-5,5-diphenyl-oxazolidin-3-yl)-2-methylsulfanyl-ethyl]-benzonitrile (**9d**). Compound **3** (342 mg, 1.00 mmol) was treated with BuLi (0.80 mL, 1.20 mmol) and a solution of 4-cyanobenzaldehyde (170 mg, 1.30 mmol) in THF (1 mL) according to *GP* 2. Purification of the crude product by FC (pentane/AcOEt 5:1) yielded **9d** (362 mg, 77%) as a 85:15 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized twice (MeOH) to afford **9d** (dr  $\geq$  99:1). White solid. **M.p.** 193-194°.  $[\alpha]_{\text{D}}^{25} = -97.8$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3483<sub>w</sub>, 3067<sub>w</sub>, 3008<sub>w</sub>, 2986<sub>w</sub>, 2231<sub>m</sub>, 1728<sub>s</sub>, 1610<sub>w</sub>, 1494<sub>w</sub>, 1450<sub>m</sub>, 1422<sub>m</sub>, 1047<sub>m</sub>, 1002<sub>m</sub>, 837<sub>w</sub>. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.79 (*d*,  $J = 6.5$ , 3 H, Me); 1.05 (*d*,  $J = 7.5$ , 3 H, Me); 1.36 (*s*, 3 H, SMe); 1.98-2.12 (*m*, 1 H, Me<sub>2</sub>CH); 4.31 (*d*,  $J = 9.3$ , 1 H, CHSMe); 4.61 (*d*,  $J = 5.3$ , 1 H, OH); 4.67 (*d*,  $J = 2.2$ , 1 H, NCH); 5.51 (*dd*,  $J = 5.3, 9.3$ , 1 H, CH(OH)); 7.22-7.40 (*m*, 6 arom. H); 7.42-7.46 (*m*, 2 arom. H); 7.51-7.54 (*m*, 2 arom. H); 7.61-7.64 (*m*, 2 arom. H); 7.69-7.73 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 10.3, 15.7, 22.0 (Me); 30.0, 68.2, 68.5, 73.4 (CH); 89.3, 111.9, 118.6 (C); 125.2, 125.9, 127.7, 128.0, 128.2, 128.4, 128.6, 132.0 (CH); 138.3, 143.7, 146.2, 157.6 (C). **FAB-MS**: 945 (13, [2*M*]<sup>+</sup>), 473 (5, [M+H]<sup>+</sup>), 425 (45, [M-SMe]<sup>+</sup>), 381 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 340 (15), 296 (16). **Anal.** calc. for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>S (472.61): C 71.16, H 5.97, N 5.93; found: C 71.05, H 5.97, N 5.93.

(*S*)-3-((1*S*,2*S*)-2-Furan-2-yl-2-hydroxy-1-methylsulfanyl-ethyl)-4-isopropyl-5,5-diphenyl oxazolidin-2-one (**9e**). Compound **3** (360 mg, 1.05 mmol) was treated with BuLi (0.84 mL, 1.27 mmol) and furfural (114  $\mu$ L, 1.37 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/AcOEt 6:1) yielded **9e** (413 mg, 90%) as a 90:10 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized twice (MeOH) to afford **9e** (dr  $\geq$  99:1). White solid. **M.p.** 147-148°.  $[\alpha]_{\text{D}}^{25} = -99.6$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3518<sub>w</sub>, 3008<sub>w</sub>, 2969<sub>w</sub>, 1728<sub>s</sub>,



1599w, 1494w, 1450m, 1423m, 1150w, 1046m, 1003m, 922w. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.74 (*d*, *J* = 6.9, 3 H, Me); 1.11 (*d*, *J* = 7.2, 3 H, Me); 1.39 (*s*, 3 H, SMe); 1.97-2.11 (*m*, 1 H, Me<sub>2</sub>CH); 4.69-4.74 (*m*, 3 H, CHSMe, OH, NCH); 5.53 (*dd*, *J* = 7.2, 8.7, 1 H, CH(OH)); 6.34-6.36 (*m*, 1 arom. H); 6.38-6.40 (*m*, 1 arom. H); 7.20-7.39 (*m*, 7 arom. H); 7.45-7.47 (*m*, 2 arom. H); 7.72-7.75 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 10.4, 15.2, 21.6 (Me); 29.8, 65.3, 68.4, 68.5 (CH); 89.1 (C); 108.1, 110.4, 125.2, 125.8, 127.5, 128.1, 128.2, 128.5 (CH); 138.4, 141.8 (C); 143.8 (CH); 153.0, 157.4 (C). **FAB-MS**: 420 (9, [M+H-H<sub>2</sub>O]<sup>+</sup>), 390 (33, [M-SMe]<sup>+</sup>), 346 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 296 (32). **Anal.** calc. for C<sub>25</sub>H<sub>27</sub>NO<sub>4</sub>S (437.56): C 68.63, H 6.22, N 3.20; found: C 68.69, H 6.29, N 3.15.

(S)-3-((1S,2S)-2-Hydroxy-1-methylsulfanyl-2-thiophen-2-yl-ethyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9f**). Compound **3** (370 mg, 1.08 mmol) was treated with BuLi (0.87 mL, 1.30 mmol) and 2-thiophenecarboxaldehyde (129 μL, 1.52 mmol) according to GP 2. Purification of the crude product by FC (pentane/AcOEt 7:1) yielded **9f** (454 mg, 92%) as a 92:8 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized three times (MeOH) to afford **9f** (dr ≥ 99:1). White solid. **M.p.** 176-178°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -101.8 (*c* = 1, CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3494w, 3008w, 2968w, 1728s, 1600w, 1494w, 1450m, 1423m, 1150w, 1038m, 1002m, 844w. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.82 (*d*, *J* = 6.9, 3 H, Me); 1.10 (*d*, *J* = 7.5, 3 H, Me); 1.37 (*s*, 3 H, SMe); 1.99-2.11 (*m*, 1 H, Me<sub>2</sub>CH); 4.43 (*d*, *J* = 9.3, 1 H, CHSMe); 4.54 (*d*, *J* = 5.6, 1 H, OH); 4.71 (*d*, *J* = 1.9, 1 H, NCH); 5.57 (*dd*, *J* = 5.6, 9.3, 1 H, CH(OH)); 6.95-6.98 (*m*, 1 arom. H); 7.10-7.11 (*m*, 1 arom. H); 7.22-7.40 (*m*, 7 arom. H); 7.45-7.48 (*m*, 2 arom. H); 7.72-7.75 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 10.3, 15.6, 21.9 (Me); 30.0, 68.5, 69.0, 70.0 (CH); 89.1 (C); 124.9, 125.2, 125.7, 125.9, 126.5, 127.6, 128.1, 128.2, 128.5 (CH); 138.4, 143.8, 144.2, 157.4 (C). **FAB-MS**: 436 (24, [M+H-H<sub>2</sub>O]<sup>+</sup>), 406 (69, [M-SMe]<sup>+</sup>), 362 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>),

340 (32), 296 (45). **Anal.** calc. for  $C_{25}H_{27}NO_3S_2$  (453.63): C 66.19, H 6.00, N 3.09; found: C 66.13, H 6.10, N 3.24.

(*S*)-3-[(1*S*,2*S*)-2-Hydroxy-2-(1-methyl-1*H*-pyrrol-2-yl)-1-methylsulfanyl-ethyl]-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9g**). Compound **3** (370 mg, 1.08 mmol) was treated with BuLi (0.87 mL, 1.30 mmol) and 1-methyl-2-pyrrolicarboxaldehyde (151  $\mu$ L, 1.41 mmol) according to *GP* 2. Recrystallization (MeOH) of the crude product yielded **9g** (395 mg, 81%) as a 91:9 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized (MeOH) again to afford **9g** (dr  $\geq$  99:1). White solid. **M.p.** 222-224°.  $[\alpha]_D^{25} = -113.8$  ( $c = 1$ ,  $CHCl_3$ ). **IR** ( $CHCl_3$ ): 3490 $w$ , 3007 $w$ , 2964 $w$ , 1729 $s$ , 1600 $w$ , 1492 $w$ , 1450 $m$ , 1424 $m$ , 1305 $w$ , 1047 $w$ , 1002 $w$ , 810 $w$ . **<sup>1</sup>H-NMR** (300 MHz,  $CDCl_3$ ): 0.88 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.17 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.34 ( $s$ , 3 H, SMe); 2.02-2.14 ( $m$ , 1 H,  $Me_2CH$ ); 3.68 ( $s$ , 3 H, NMe); 3.93 ( $d$ ,  $J = 4.8$ , 1 H, OH); 4.61 ( $d$ ,  $J = 10.3$ , 1 H,  $CHSMe$ ); 4.74 ( $d$ ,  $J = 2.2$ , 1 H, NCH); 5.57 ( $dd$ ,  $J = 4.8, 10.3$ , 1 H,  $CH(OH)$ ); 6.07-6.10 ( $m$ , 2 arom. H); 6.56-6.58 ( $m$ , 1 arom. H); 7.22-7.40 ( $m$ , 6 arom. H); 7.45-7.49 ( $m$ , 2 arom. H); 7.71-7.75 ( $m$ , 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz,  $CDCl_3$ ): 10.9, 15.7, 22.2 (Me); 30.1 (CH); 34.3 (Me); 65.8, 67.7, 68.4 (CH); 89.1 (C); 106.6, 107.0, 123.0, 125.4, 126.0, 127.7, 128.2, 128.3, 128.6 (CH); 131.9, 138.6, 144.0, 157.5 (C). **FAB-MS**: 450 (6,  $[M]^+$ ), 433 (100,  $[M+H-H_2O]^+$ ), 386 (19,  $[M+H-H_2O-SMe]^+$ ), 340 (20,  $[M-H-H_2O-SMe-CO_2]^+$ ), 296 (21). **Anal.** calc. for  $C_{26}H_{30}N_2O_3S$  (450.60): C 69.30, H 6.71, N 6.22; found: C 69.22, H 6.67, N 6.23.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-1-methylsulfanyl-2-pyridin-3-yl-ethyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9h**). Compound **3** (357 mg, 1.05 mmol) was treated with BuLi (0.84 mL, 1.25 mmol) and 3-pyridinecarboxaldehyde (128  $\mu$ L, 1.36 mmol) according to *GP* 2. Recrystallization (MeOH) of the crude product yielded **9h** (339 mg, 72%) as a 96:4 mixture with its C(2)-OH

epimer. For analytical purposes a sample was recrystallized (MeOH) again to afford **9h** (dr  $\geq$  99:1). White solid. **M.p.**  $>240^{\circ}$ .  $[\alpha]_{\text{D}}^{25} = -29.6$  ( $c = 0.45$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3494 $w$ , 3007 $w$ , 2968 $w$ , 1728 $s$ , 1598 $w$ , 1494 $w$ , 1450 $m$ , 1423 $m$ , 1047 $w$ , 1002 $w$ .  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 0.82 ( $d$ ,  $J = 6.5$ , 3 H, Me); 1.06 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.33 ( $s$ , 3 H, SMe); 1.97-2.10 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 4.31 ( $d$ ,  $J = 9.3$ , 1 H,  $\text{CHSMe}$ ); 4.57 ( $d$ ,  $J = 5.6$ , 1 H, OH); 4.69 ( $d$ ,  $J = 2.2$ , 1 H, NCH); 5.53 ( $dd$ ,  $J = 5.6$ , 9.3, 1 H,  $\text{CH}(\text{OH})$ ); 7.22-7.40 ( $m$ , 7 arom. H); 7.44-7.47 ( $m$ , 2 arom. H); 7.71-7.76 ( $m$ , 3 arom. H); 8.53-8.56 ( $m$ , 1 arom. H); 8.64-8.65 ( $m$ , 1 arom. H).  **$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 10.0, 15.7, 22.2 (Me); 30.1, 68.5, 68.7, 71.8 (CH); 89.3 (C); 123.4, 125.3, 126.0, 127.8, 128.3, 128.4, 128.7, 134.6 (CH); 136.7, 138.4, 143.8 (C); 149.1, 149.5 (CH); 157.7 (C). **FAB-MS**: 449 (100,  $[\text{M}+\text{H}]^+$ ), 401 (13,  $[\text{M}-\text{SMe}]^+$ ), 357 (30,  $[\text{M}-\text{SMe}-\text{CO}_2]^+$ ). **Anal.** calc. for  $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_3\text{S}$  (448.58): C 69.62, H 6.29, N 6.24; found: C 69.59, H 6.48, N 6.41.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-1-methylsulfanyl-4-phenyl-but-3-ynyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9i**). Compound **3** (365 mg, 1.07 mmol) was treated with BuLi (0.86 mL, 1.28 mmol) and phenylpropargyl aldehyde (170  $\mu\text{L}$ , 1.39 mmol) according to GP 2. Purification of the crude product by FC (pentane/AcOEt 8:1) yielded **9i** (405 mg, 80%) as a single diastereoisomer. White solid. **M.p.** 69-78 $^{\circ}$ .  $[\alpha]_{\text{D}}^{25} = -157.9$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3354 $w$ , 3066 $w$ , 3008 $w$ , 2966 $w$ , 2226 $w$ , 1729 $s$ , 1599 $w$ , 1491 $m$ , 1450 $m$ , 1421 $m$ , 1048 $m$ , 1002 $m$ , 909 $w$ .  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 0.83 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.16 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.58 ( $s$ , 3 H, SMe); 2.04-2.16 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 4.53 ( $d$ ,  $J = 7.0$ , 1 H,  $\text{CHSMe}$ ); 4.77 ( $d$ ,  $J = 2.2$ , 1 H, NCH); 4.96 ( $d$ ,  $J = 8.7$ , 1 H, OH); 5.23 ( $dd$ ,  $J = 7.0$ , 8.7, 1 H,  $\text{CH}(\text{OH})$ ); 7.20-7.47 ( $m$ , 13 arom. H); 7.69-7.74 ( $m$ , 2 arom. H).  **$^{13}\text{C-NMR}$**  (75 MHz,  $\text{CDCl}_3$ ): 11.6, 15.6, 21.7 (Me); 30.1, 65.4, 66.8, 68.5 (CH); 86.0, 87.5, 89.4, 122.3 (C); 125.2, 126.0, 127.7, 128.2, 128.3, 128.5, 128.7, 131.7 (CH); 138.5, 143.9, 157.5 (C). **FAB-MS**: 471 (15,  $[\text{M}]^+$ ), 424 (100,  $[\text{M}-\text{SMe}]^+$ ), 380 (95,  $[\text{M}-\text{SMe}-\text{CO}_2]^+$ ), 320 (48),

296 (41). **Anal.** calc. for  $C_{29}H_{29}NO_3S$  (471.62): C 73.86, H 6.20, N 2.97; found: C 73.93, H 6.35, N 3.01.

(*S*)-3-((1*S*,2*S*)-(E)-2-Hydroxy-1-methylsulfanyl-4-phenyl-but-3-enyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9j**). Compound **3** (351 mg, 1.03 mmol) was treated with BuLi (0.82 mL, 1.23 mmol) and *trans*-cinnamaldehyde (169  $\mu$ L, 1.34 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/AcOEt 9:1) yielded **9j** (444 mg, 91%) as a 86:14 mixture with its C(2)-OH epimer. For analytical purposes a sample was purified by FC (pentane/AcOEt 9:1) to afford **9j** as a single diastereoisomer. White solid. **M.p.** 160-162°.  $[\alpha]_D^{25} = -157.3$  ( $c = 1$ ,  $CHCl_3$ ). **IR** ( $CHCl_3$ ): 3424 $w$ , 3008 $m$ , 2966 $w$ , 1728 $s$ , 1599 $w$ , 1494 $w$ , 1450 $m$ , 1422 $m$ , 1046 $w$ , 1002 $m$ , 968 $w$ . **<sup>1</sup>H-NMR** (300 MHz,  $CDCl_3$ ): 0.82 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.09 ( $d$ ,  $J = 7.2$ , 3 H, Me); 1.47 ( $s$ , 3 H, SMe); 2.01-2.14 ( $m$ , 1 H,  $Me_2CH$ ); 4.28 ( $d$ ,  $J = 8.4$ , 1 H,  $CHSMe$ ); 4.40 ( $dd$ ,  $J = 0.6, 6.2$ , 1 H, OH); 4.76 ( $d$ ,  $J = 2.2$ , 1 H, NCH); 5.01-5.09 ( $m$ , 1 H,  $CH(OH)$ ); 6.40 ( $dd$ ,  $J = 6.2, 15.9$ , 1 H,  $PhCH=CH$ ); 6.77 ( $d$ ,  $J = 15.9$ , 1 H,  $PhCH=CH$ ); 7.21-7.40 ( $m$ , 11 arom. H); 7.46-7.49 ( $m$ , 2 arom. H); 7.72-7.76 ( $m$ , 2 arom. H). **<sup>13</sup>C-NMR** (75 MHz,  $CDCl_3$ ): 10.3, 15.7, 21.8 (Me); 30.0, 67.5, 68.5, 72.2 (CH); 89.0 (C); 125.3, 125.9, 126.6, 127.6, 127.7, 128.2, 128.3, 128.4, 128.5, 128.6, 131.9 (CH); 136.5, 138.5, 143.9, 157.5 (C). **FAB-MS**: 474 (11,  $[M+H]^+$ ), 456 (100,  $[M+H-H_2O]^+$ ), 426 (98,  $[M-SMe]^+$ ), 382 (90,  $[M-SMe-CO_2]^+$ ), 340 (85), 296 (93). **Anal.** calc. for  $C_{29}H_{31}NO_3S$  (473.63): C 73.54, H 6.60, N 2.96; found: C 73.46, H 6.53, N 2.98.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-3-methyl-1-methylsulfanyl-but-3-enyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9k**). Compound **3** (355 mg, 1.04 mmol) was treated with BuLi (0.83 mL, 1.25 mmol) and methacrolein (111  $\mu$ L, 1.35 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/AcOEt 9:1) yielded **9k** (375 mg, 88%) as a 85:15 mixture with its C(2)-

OH epimer. For analytical purposes a sample was purified by FC (pentane/AcOEt 9:1) to afford **9k** (dr 98.5:1.5). White solid. **M.p.** 181-182°.  $[\alpha]_{\text{D}}^{\text{r.t.}} = -99.6$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3508 $w$ , 3007 $w$ , 2967 $w$ , 1730 $s$ , 1600 $w$ , 1493 $w$ , 1450 $m$ , 1423 $m$ , 1047 $m$ , 1003 $m$ , 911 $w$ .  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 0.85 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.10 ( $d$ ,  $J = 7.2$ , 3 H, Me); 1.38 ( $s$ , 3 H, SMe); 1.77 ( $s$ , 3 H, C=CMe); 2.00-2.14 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 3.70 ( $d$ ,  $J = 4.7$ , 1 H, OH); 4.34 ( $d$ ,  $J = 10.0$ , 1 H, CHSMe); 4.73 ( $d$ ,  $J = 2.2$ , 1 H, NCH); 4.93-4.98 ( $m$ , 2 H,  $\text{CH}(\text{OH})$ ,  $\text{C}=\text{CH}_2$ ); 5.06-5.08 ( $m$ , 1 H,  $\text{C}=\text{CH}_2$ ); 7.21-7.40 ( $m$ , 6 arom. H); 7.45-7.49 ( $m$ , 2 arom. H); 7.71-7.75 ( $m$ , 2 arom. H).  **$^{13}\text{C-NMR}$**  (125 MHz,  $\text{CDCl}_3$ ): 9.8, 15.9, 17.0, 22.0 (Me); 30.1, 65.2, 68.5, 74.2 (CH); 88.8 (C); 115.3 ( $\text{CH}_2$ ); 125.4, 126.0, 127.7, 128.2, 128.3, 128.6 (CH); 138.6, 143.5, 144.1, 157.3 (C). **FAB-MS**: 412 (7,  $[\text{M}+\text{H}]^+$ ), 364 (76,  $[\text{M}-\text{SMe}]^+$ ), 320 (100,  $[\text{M}-\text{SMe}-\text{CO}_2]^+$ ), 296 (18). **Anal.** calc. for  $\text{C}_{24}\text{H}_{29}\text{NO}_3\text{S}$  (411.56): C 70.04, H 7.10, N 3.40; found: C 70.03, H 6.97, N 3.37.

(*S*)-3-((1*S*,2*S*)-2-Cyclopent-1-enyl-2-hydroxy-1-methylsulfanyl-ethyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9l**). Compound **3** (380 mg, 1.11 mmol) was treated with BuLi (0.89 mL, 1.34 mmol) and 1-cyclopentenecarboxaldehyde (139  $\mu\text{L}$ , 1.44 mmol) according to *GP* 2. Purification of the crude product by FC pentane/AcOEt (10:1) yielded **9l** (409 mg, 84%) as a 86:14 mixture with its C(2)-OH epimer. For analytical purposes a sample was purified by FC (pentane/AcOEt 10:1) to afford **9l** (dr 98.5:1.5). White solid. **M.p.** 210-211°.  $[\alpha]_{\text{D}}^{\text{r.t.}} = -108.5$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3468 $w$ , 3006 $w$ , 2963 $m$ , 2848 $w$ , 1729 $s$ , 1600 $w$ , 1493 $w$ , 1450 $m$ , 1424 $m$ , 1046 $m$ , 1002 $m$ .  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 0.84 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.09 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.39 ( $s$ , 3 H, SMe); 1.82-1.93 ( $m$ , 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ); 2.00-2.12 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 2.21-2.50 ( $m$ , 4 H,  $\text{CCH}_2$ ,  $\text{CHCH}_2$ ); 3.81 ( $d$ ,  $J = 5.0$ , 1 H, OH); 4.35 ( $d$ ,  $J = 9.7$ , 1 H, CHSMe); 4.73 ( $d$ ,  $J = 1.9$ , 1 H, NCH); 5.12 ( $dd$ ,  $J = 5.0, 9.7$ , 1 H,  $\text{CH}(\text{OH})$ ); 5.72-5.76 ( $m$ , 1 H,  $\text{C}=\text{CH}$ ); 7.21-7.39 ( $m$ , 6 arom. H); 7.45-7.48 ( $m$ , 2 arom. H); 7.71-7.75 ( $m$ , 2 arom. H).  **$^{13}\text{C-NMR}$**  (75 MHz,  $\text{CDCl}_3$ ): 10.0, 15.8, 21.8

(Me); 23.0 (CH<sub>2</sub>); 30.0 (CH); 30.5, 32.2 (CH<sub>2</sub>); 65.7, 68.3, 69.7 (CH); 88.8 (C); 125.3, 126.0, 127.6, 128.1, 128.2, 128.5, 129.5 (CH); 138.6, 142.7, 144.0, 157.3 (C). **FAB-MS**: 420 (9, [M+H-H<sub>2</sub>O]<sup>+</sup>), 390 (29, [M-SMe]<sup>+</sup>), 376 (18, [M+H-H<sub>2</sub>O-CO<sub>2</sub>]<sup>+</sup>), 346 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 296 (25). **Anal.** calc. for C<sub>26</sub>H<sub>31</sub>NO<sub>3</sub>S (437.60): C 71.36, H 7.14, N 3.20; found: C 71.16, H 6.95, N 3.19.

(S)-3-((1S,2S)-2-Hydroxy-3-methyl-1-methylsulfanyl-butyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**9 m**) and (S)-3-((1S,2R)-2-Hydroxy-3-methyl-1-methylsulfanyl-butyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**10m**). Compound **3** (1.11 g, 3.25 mmol) was treated with BuLi (2.55 mL, 3.90 mmol) and isobutyraldehyde (384 µL, 4.23 mmol) according to *GP* 2. Trituration of the crude product (boiling hexane, 2x 6 mL) yielded **9m** (1.13 g, 84%) as a 71:29 mixture with its C(2)-OH epimer **10m**. Alternatively, purification of the crude product by FC (pentane/Et<sub>2</sub>O 10:1) yielded **9m** (61%) and **10m** (21%) as single diastereoisomers. **9m**: White solid. **M.p.** 217-218°.  $[\alpha]_D^{r.t.} = -108.3$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3520w, 2964m, 2930w, 2875w, 1730s, 1493w, 1450m, 1423m, 1049w, 1002m. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.83 (*d*,  $J = 6.9$ , 6 H, Me); 1.01 (*d*,  $J = 6.9$ , 3 H, Me); 1.07 (*d*,  $J = 7.5$ , 3 H, Me); 1.35 (*s*, 3 H, SMe); 2.00-2.21 (*m*, 2 H, Me<sub>2</sub>CH); 3.48 (*s*, 1 H, OH); 4.23-4.31 (*m*, 2 H, CHSMe, CH(OH)); 4.74 (*d*,  $J = 2.2$ , 1 H, NCH); 7.20-7.38 (*m*, 6 arom. H); 7.47-7.49 (*m*, 2 arom. H); 7.74-7.76 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 9.6, 14.1, 15.9, 20.7, 21.8 (Me); 29.1, 30.0, 65.4, 68.5, 73.2 (CH); 88.7 (C); 125.3, 126.0, 127.5, 128.1, 128.5 (CH); 138.6, 144.1, 157.4 (C). **FAB-MS**: 366 (7, [M-SMe]<sup>+</sup>), 322 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>). **Anal.** calc. for C<sub>24</sub>H<sub>31</sub>NO<sub>3</sub>S (413.58): C 69.70, H 7.55, N 3.39; found: C 69.77, H 7.57, N 3.43.

**10m**: White solid. **M.p.** 204-205°.  $[\alpha]_D^{r.t.} = -163.8$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3388w, 3007w, 2964m, 2874w, 1728s, 1466w, 1450m, 1425m, 1063w, 1002w, 908w. **<sup>1</sup>H-NMR** (300 MHz,

CDCl<sub>3</sub>): 0.76 (*d*, *J* = 6.9, 3 H, Me); 0.89 (*d*, *J* = 6.9, 3 H, Me); 1.00 (*d*, *J* = 6.5, 3 H, Me); 1.08 (*d*, *J* = 7.2, 3 H, Me); 1.58 (*s*, 3 H, SMe); 1.81-1.95 (*m*, 1 H, Me<sub>2</sub>CH); 2.05-2.18 (*m*, 1 H, Me<sub>2</sub>CH); 3.78-3.86 (*m*, 1 H, CH(OH)); 4.40 (*d*, *J* = 2.5, 1 H, CHSMe); 4.60 (*d*, *J* = 1.9, 1 H, NCH); 4.72 (*d*, *J* = 2.5, 1 H, OH); 7.22-7.39 (*m*, 6 arom. H); 7.48-7.51 (*m*, 2 arom. H); 7.69-7.72 (*m*, 2 arom. H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 13.1, 16.0, 18.4, 20.0, 21.6 (Me); 29.8, 31.3, 67.7, 71.2, 78.8 (CH); 89.0 (C); 125.1, 126.0, 127.7, 128.2, 128.3, 128.7 (CH); 138.4, 144.2, 157.6 (C). **FAB-MS**: 414 (8, [M+H]<sup>+</sup>), 366 (67, [M-SMe]<sup>+</sup>), 322 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>). **Anal.** calc. for C<sub>24</sub>H<sub>31</sub>NO<sub>3</sub>S (413.58): C 69.70, H 7.55, N 3.39; found: C 69.66, H 7.55, N 3.46.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-1-methylsulfanyl-pentyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one

**(9n)**. Compound **3** (388 mg, 1.14 mmol) was treated with BuLi (0.89 mL, 1.36 mmol) and butyraldehyde (133 μL, 1.48 mmol) according to *GP* 2. Trituration of the crude product (boiling hexane, 6 mL) yielded **9n** (391 mg, 83%) as a 70:30 mixture with its C(2)-OH epimer. For analytical purposes a sample was purified by FC (pentane/AcOEt 10:1) to afford **9n** as a single diastereoisomer. White solid. **M.p.** 171-173°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -108.3 (*c* = 1, CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3504<sub>w</sub>, 3007<sub>w</sub>, 2963<sub>m</sub>, 2873<sub>w</sub>, 1729<sub>s</sub>, 1493<sub>w</sub>, 1450<sub>m</sub>, 1423<sub>m</sub>, 1047<sub>w</sub>, 1002<sub>w</sub>, 854<sub>w</sub>. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 0.83 (*d*, *J* = 6.5, 3 H, Me); 0.91 (*t*, *J* = 7.2, 3 H, CH<sub>2</sub>Me); 1.04 (*d*, *J* = 7.5, 3 H, Me); 1.32 (*s*, 3 H, SMe); 1.36-1.47 (*m*, 2 H, CH<sub>2</sub>); 1.52-1.63 (*m*, 1 H, CH<sub>2</sub>); 1.78-1.90 (*m*, 1 H, CH<sub>2</sub>); 1.98-2.11 (*m*, 1 H, Me<sub>2</sub>CH); 3.87 (*dd*, *J* = 0.9, 5.0, 1 H, OH); 4.08 (*d*, *J* = 9.3, 1 H, CHSMe); 4.30-4.40 (*m*, 1 H, CH(OH)); 4.72 (*d*, *J* = 2.2, 1 H, NCH); 7.20-7.39 (*m*, 6 arom. H); 7.45-7.48 (*m*, 2 arom. H); 7.73-7.76 (*m*, 2 arom. H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 9.6, 14.0, 15.9, 19.0 (Me); 21.9 (CH<sub>2</sub>); 30.1 (CH); 36.8 (CH<sub>2</sub>); 67.8, 68.5, 70.3 (CH); 88.9 (C); 125.3, 126.0, 127.6, 128.2, 128.3, 128.6 (CH); 138.6, 144.1, 157.5 (C). **FAB-MS**: 366 (26, [M-SMe]<sup>+</sup>), 322 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>). **Anal.** calc. for C<sub>24</sub>H<sub>31</sub>NO<sub>3</sub>S (413.58): C 69.70, H 7.55, N 3.39; found: C

69.43, H 7.67, N 3.37.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-1-methylsulfanyl-2-phenyl-propyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11a**). Compound **3** (605 mg, 1.77 mmol) was treated with BuLi (1.45 mL, 2.13 mmol) and a solution of acetophenone (269  $\mu$ L, 2.30 mmol) in THF (1 mL) according to GP 2. The crude product was triturated (boiling hexane, 2x 7 mL) and recrystallized (MeOH) to give **11a** (456 mg, 56%) as a single diastereoisomer. White solid. **M.p.** 204-206°.  $[\alpha]_D^{25} = -118.6$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3692<sub>w</sub>, 3314<sub>w</sub>, 3008<sub>m</sub>, 2936<sub>w</sub>, 1721<sub>s</sub>, 1601<sub>w</sub>, 1494<sub>w</sub>, 1450<sub>m</sub>, 1422<sub>m</sub>, 1372<sub>w</sub>, 1036<sub>w</sub>, 1003<sub>w</sub>. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.23 (*d*,  $J = 7.1$ , 3 H, Me); 0.51 (*d*,  $J = 7.3$ , 3 H, Me); 1.67 (*s*, 3 H, SMe); 1.73 (*d*,  $J = 0.9$ , 3 H, CMe); 1.80-1.92 (*m*, 1 H, Me<sub>2</sub>CH); 4.45 (*s*, 1 H, CHSMe); 4.61 (*d*,  $J = 1.9$ , 1 H, NCH); 6.55 (*br s*, 1 H, OH); 7.13-7.34 (*m*, 11 arom. H); 7.45-7.48 (*m*, 2 arom. H); 7.58-7.61 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 13.0, 16.4, 18.3 (Me); 29.5 (CH); 31.2 (Me); 69.5, 71.6 (CH); 79.3, 89.1 (C); 125.19, 125.22, 126.6, 127.2, 127.6, 127.8, 128.1, 128.2, 128.6 (CH); 138.1, 144.1, 145.5, 158.3 (C). **FAB-MS**: 923 (5, [2*M*+H]<sup>+</sup>), 462 (14, [*M*+H]<sup>+</sup>), 444 (19, [*M*+H-H<sub>2</sub>O]<sup>+</sup>), 414 (100, [*M*-SMe]<sup>+</sup>), 370 (65, [*M*-SMe-CO<sub>2</sub>]<sup>+</sup>), 296 (28). **Anal.** calc. for C<sub>28</sub>H<sub>31</sub>NO<sub>3</sub>S (461.62): C 72.85, H 6.77, N 3.03; found: C 72.78, H 6.86, N 3.16.

(*S*)-4-Isopropyl-5,5-diphenyl-3-((1*S*,2*R*)-3,3,3-trifluoro-2-hydroxy-1-methylsulfanyl-2-phenyl-propyl)-oxazolidin-2-one (**11b**). Compound **3** (443 mg, 1.30 mmol) was treated with BuLi (1.10 mL, 1.68 mmol) and phenyl trifluoromethyl ketone (265  $\mu$ L, 1.95 mmol) according to GP 2. The crude product was recrystallized (MeOH) to give **11b** (372 mg, 55%) as a single diastereoisomer. White solid. **M.p.** >240°.  $[\alpha]_D^{25} = -99.7$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3066<sub>w</sub>, 3007<sub>m</sub>, 1746<sub>s</sub>, 1685<sub>m</sub>, 1598<sub>w</sub>, 1494<sub>m</sub>, 1449<sub>w</sub>, 1410<sub>s</sub>, 1034<sub>m</sub>, 1003<sub>m</sub>. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.77 (*d*,



$J = 7.0$ , 3 H, Me); 1.19 ( $d$ ,  $J = 7.4$ , 3 H, Me); 1.46 ( $s$ , 3 H, SMe); 2.19-2.26 ( $m$ , 1 H, Me<sub>2</sub>CH); 4.67 ( $s$ , 1 H, CHSMe); 4.81 ( $d$ ,  $J = 1.8$ , 1 H, NCH); 7.25-7.43 ( $m$ , 12 arom. H); 7.62-7.64 ( $m$ , 2 arom. H); 8.24 ( $s$ , 1 arom. H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): 14.3, 15.5, 20.7 (Me); 29.5, 68.5, 71.1 (CH); 80.8 ( $q$ ,  $J_{C,F} = 27.7$ , CF<sub>3</sub>); 90.2 (C); 125.5, 126.6, 128.0, 128.1, 128.3, 128.5, 128.62, 128.64 (CH); 137.4, 138.2, 143.7, 160.2 (C). <sup>19</sup>F-NMR (282 MHz, CDCl<sub>3</sub>): -73.82 ( $s$ , 3 F, CF<sub>3</sub>). **MALDI-MS**: 538 (100, [M+Na]<sup>+</sup>), 424 (60, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 364 (47), 249 (89), 172 (65). **Anal.** calc. for C<sub>28</sub>H<sub>28</sub>F<sub>3</sub>NO<sub>3</sub>S (515.60): C 65.23, H 5.47, N 2.72, S 6.22; found: C 65.15, H 5.54, N 2.67, S 6.21

(*S*)-3-((*1S,2S*)-2-Hydroxy-3-methyl-1-methylsulfonyl-2-phenyl-butyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11c**). Compound **3** (500 mg, 1.46 mmol) was treated with BuLi (1.15 mL, 1.76 mmol) and isobutyrophenone (287 μL, 1.93 mmol) according to *GP* 2. Trituration of the crude product (boiling MeOH, 2x 8 mL) yielded **11c** (610 mg, 85%) as a 77:23 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **11c** (dr ≥ 99:1). White solid. **M.p.** 236-240°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -110.6 ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3621 $w$ , 3323 $w$ , 2985 $m$ , 2956 $m$ , 1728 $s$ , 1595 $w$ , 1492 $w$ , 1369 $w$ , 1328 $w$ , 1246 $m$ , 1051 $m$ , 1031 $w$ , 1000 $w$ . **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.59 ( $d$ ,  $J = 6.8$ , 3 H, Me); 0.68 ( $d$ ,  $J = 7.3$ , 6 H, Me); 0.81 ( $d$ ,  $J = 6.8$ , 3 H, Me); 2.14 ( $br\ s$ , 3 H, SMe); 2.49 ( $br\ s$ , 1 H, Me<sub>2</sub>CH); 2.58-2.63 ( $m$ , 1 H, Me<sub>2</sub>CH); 4.64 ( $d$ ,  $J = 1.6$ , 1 H, NCH); 5.46 ( $s$ , 1 H, CHSMe); 6.94-7.40 ( $m$ , 15 arom. H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): 16.7, 17.2, 18.2, 18.7 (Me); 29.0, 37.6, 68.1, 68.7 (CH); 83.1, 87.7 (C); 124.5, 125.2, 126.0, 127.1, 127.38, 127.42, 127.5, 127.8, 128.5 (CH); 138.7, 144.2, 157.7 (C). **MALDI-MS**: 512 (40, [M+Na]<sup>+</sup>), 260 (100), 237 (77). **Anal.** calc. for C<sub>30</sub>H<sub>35</sub>NO<sub>3</sub>S (489.68): C 73.59, H 7.20, N 2.86; found: C 73.43, H 7.34, N 2.83.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-4-methyl-1-methylsulfanyl-2-phenyl-pentyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11d**). Compound **3** (1.00 g, 2.93 mmol) was treated with BuLi (2.20 mL, 3.51 mmol) and isovalerophenone (741 mg, 4.57 mmol) according to *GP* 2. Trituration of the crude product (hexane, 16 mL, boiling MeOH, 30 mL) yielded **11d** (1.08 g, 73%) as a single diastereoisomer. White solid. **M.p.** 221-223°.  $[\alpha]_D^{25} = -124.3$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3690w, 3322m, 3062w, 3008m, 2956s, 2869m, 1721s, 1601m, 1494m, 1450s, 1420s, 1310m, 1248m, 1133m, 1003s, 812w. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.32 (*d*,  $J = 7.2$ , 3 H, Me); 0.46 (*d*,  $J = 7.2$ , 3 H, Me); 0.58 (*d*,  $J = 6.7$ , 3 H, Me); 0.87 (*d*,  $J = 6.6$ , 3 H, Me); 1.31-1.38 (*m*, 1 H, Me<sub>2</sub>CH); 1.61-1.66 (*m*, 1 H, CH<sub>2</sub>); 1.70 (*s*, 3 H, SMe); 1.88-1.94 (*m*, 1 H, Me<sub>2</sub>CH); 2.35-2.40 (*dd*,  $J = 7.8$ , 13.9, 1 H, CH<sub>2</sub>); 4.43 (*s*, 1 H, CHSMe); 4.60 (*d*,  $J = 2.0$ , 1 H, NCH); 6.17 (*s*, 1 H, OH); 7.11-7.31 (*m*, 11 arom. H); 7.31-7.41 (*m*, 2 arom. H); 7.55-7.57 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 13.2, 17.0, 17.9, 23.8 (Me); 24.4 (CH); 24.6 (Me); 29.4 (CH); 50.7 (CH<sub>2</sub>); 69.5, 72.3 (CH); 82.2, 88.9 (C); 125.2, 126.1, 126.8, 127.0, 127.5, 127.7, 127.9, 128.1, 128.5 (CH); 138.3, 143.5, 144.2, 158.2 (C). **MALDI-MS**: 526 (70, [M+Na]<sup>+</sup>), 412 (100, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 260 (74), 237 (96). **Anal.** calc. for C<sub>31</sub>H<sub>37</sub>NO<sub>3</sub>S (503.70): C 73.92, H 7.40, N 2.78; found: C 74.03, H 7.49, N 2.73.

(*S*)-3-[(*S*)-((*S*)-1-Hydroxy-4-methoxy-indan-1-yl)-methylsulfanyl-methyl]-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11e**). Compound **3** (337 mg, 0.987 mmol) was treated with BuLi (0.76 mL, 1.18 mmol) and a solution of 4-methoxy-1-indanone (208 mg, 1.28 mmol) in THF (1 mL) according to *GP* 2. Purification of the crude product by FC (pentane/Et<sub>2</sub>O 3:1) yielded **11e** (320 mg, 64%) as a 97:3 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **11e** (dr ≥ 99:1). White solid. **M.p.** > 126° (dec.).  $[\alpha]_D^{25} = -97.8$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3346w, 3006w, 2961w, 1723s, 1591w, 1483m, 1450m, 1422m,

1268m, 1066w, 1034m, 1003w. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.01 (*d*, *J* = 6.8, 3 H, Me); 0.61 (*d*, *J* = 7.3, 3 H, Me); 1.83 (*s*, 3 H, SMe); 1.89-2.01 (*m*, 1 H, Me<sub>2</sub>CH); 2.13-2.23 (*m*, 1 H, CH<sub>2</sub>); 2.45-2.54 (*m*, 1 H, CH<sub>2</sub>); 2.63 (*br s*, 1 H, CH<sub>2</sub>); 2.87-2.94 (*m*, 1 H, CH<sub>2</sub>); 3.80 (*s*, 3 H, OMe); 4.22 (*s*, 1 H, CHSMe); 4.53 (*s*, 1 H, NCH); 6.08 (*br s*, 1 H, OH); 6.73 (*d*, *J* = 7.7, 1 arom. H); 7.17-7.38 (*m*, 10 arom. H); 7.59-7.61 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 14.8, 20.4 (Me); 25.3 (CH<sub>2</sub>); 29.3 (CH); 39.9 (CH<sub>2</sub>); 55.3 (Me); 69.4, 69.9 (CH); 87.8, 89.2 (C); 109.9, 116.8, 125.2, 126.3, 127.6, 127.9, 128.3, 128.4, 128.6 (CH); 130.3, 138.6, 144.0, 147.2, 155.8, 159.2 (C). **MALDI-MS**: 526 (85, [M+Na]<sup>+</sup>), 394 (100, [M-SMe-CO<sub>2</sub>-H<sub>2</sub>O]<sup>+</sup>), 248 (26). **Anal.** calc. for C<sub>30</sub>H<sub>33</sub>NO<sub>4</sub>S (503.66): C 71.54, H 6.60, N 2.78, S 6.37; found: C 71.48, H 6.73, N 2.67, S 6.32.

(*S*)-3-[(1*S*,2*S*)-2-Hydroxy-2-(5-methyl-furan-2-yl)-1-methylsulfanyl-propyl]-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11f**). Compound **3** (552 mg, 1.62 mmol) was treated with BuLi (1.27 mL, 1.94 mmol) and 2-acetyl-5-methylfuran (288 mg, 2.32 mmol) according to GP 2. Trituration of the crude product (boiling hexane, 2x 6 mL) yielded **11f** (542 mg, 76%) as a single diastereoisomer. White solid. **M.p.** 204-208°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -51.7 (*c* = 1, CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3313w, 3005m, 1723s, 1440m, 1415s, 1369m, 1308m, 1133m, 1093m, 1092m, 1041m. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.28 (*d*, *J* = 6.9, 3 H, Me); 0.96 (*d*, *J* = 7.4, 3 H, Me); 1.58-1.62 (*m*, 6 H, Me); 1.94-2.00 (*m*, 1 H, Me<sub>2</sub>CH); 2.19 (*d*, *J* = 0.8, 3 H, SMe); 4.44 (*s*, 1 H, CHSMe); 4.66 (*d*, *J* = 1.4, 1 H, NCH); 5.89-5.91 (*m*, 1 heteroatom. H); 6.31-6.32 (*m*, 1 heteroatom. H); 6.65 (*s*, 1 H, OH); 7.17-7.38 (*m*, 8 arom. H); 7.67-7.69 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 12.7, 13.5, 14.7, 19.8, 27.8 (Me); 29.5, 69.5, 70.5 (CH); 76.7, 89.4 (C); 106.6, 107.2, 125.3, 126.2, 127.6, 128.0, 128.3, 128.6 (CH); 138.4, 144.2, 150.3, 155.9, 158.3 (C). **MALDI-MS**: 488 (100, [M+Na]<sup>+</sup>), 356 (20, [M-SMe-CO<sub>2</sub>-H<sub>2</sub>O]<sup>+</sup>), 260 (18), 167 (23). **Anal.** calc. for C<sub>27</sub>H<sub>31</sub>NO<sub>4</sub>S (465.61): C 69.65, H 6.71, N 3.01; found: C 69.55, H 6.80, N 2.95.

(*S*)-3-((*1S,2S*)-2-Hydroxy-4-methyl-1-methylsulfanyl-2-pyridin-4-yl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11g**). Compound **3** (600 mg, 1.75 mmol) was treated with BuLi (1.40 mL, 2.11 mmol) and 4-propionylpyridine (356 mg, 2.53 mmol) according to *GP* 2. Trituration of the crude product (hexane, 10 mL, boiling MeOH, 12 mL) yielded **11g** (493 mg, 59%) as a 98:2 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **11g** as a single diastereoisomer. White solid. **M.p.** 209-211°.  $[\alpha]_{\text{D}}^{25} = -113.1$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3323<sub>w</sub>, 2974<sub>w</sub>, 1723<sub>s</sub>, 1595<sub>w</sub>, 1492<sub>w</sub>, 1446<sub>m</sub>, 1323<sub>w</sub>, 1174<sub>w</sub>, 1000<sub>m</sub>, 820<sub>m</sub>. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.40 (*d*,  $J = 7.2$ , 3 H, Me); 0.55-0.63 (*m*, 6 H, Me); 1.68-1.75 (*m*, 1 H, CH<sub>2</sub>); 1.77 (*s*, 3 H, SMe); 1.98-2.05 (*m*, 1 H, Me<sub>2</sub>CH); 2.45-2.53 (*m*, 1 H, CH<sub>2</sub>); 4.56 (*s*, 1 H, CHSMe); 4.64 (*d*,  $J = 2.1$ , 1 H, NCH); 6.05 (*br s*, 1 H, OH); 7.15-7.22 (*m*, 3 arom. H); 7.26-7.32 (*m*, 7 arom. H); 7.48-7.53 (*m*, 2 arom. H); 8.43-8.48 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 7.7, 13.6, 17.3, 18.1 (Me); 29.5 (CH); 35.3 (CH<sub>2</sub>); 69.3, 70.7 (CH); 81.3, 89.0 (C); 121.3, 125.0, 126.7, 127.7, 127.8, 128.3, 128.6 (CH); 137.9, 143.9 (C); 149.5 (CH); 152.2, 158.3 (C). **MALDI-MS**: 500 (9,  $[M+Na]^+$ ), 477 (18,  $[M]^+$ ), 340 (39), 297 (20), 296 (100). **Anal.** calc. for C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>S (476.64): C 70.56, H 6.77, N 5.88; found: C 74.50, H 6.79, N 6.00.

(*S*)-3-[(*S*)-((*S*)-2-Benzylidene-1-hydroxy-1,2,3,4-tetrahydro-naphthalen-1-yl)-methylsulfanyl-methyl]-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11h**). Compound **3** (375 mg, 1.10 mmol) was treated with BuLi (0.85 mL, 1.32 mmol) and a solution of 2-benzylidene-1-tetralone (334 mg, 1.43 mmol) in THF (1 mL) according to *GP* 2. Purification of the crude product by FC (pentane/Et<sub>2</sub>O 5:1) and subsequent trituration (boiling hexane, 5 mL) yielded **11h** (158 mg, 25%) as a single diastereoisomer. White solid. **M.p.** 236-237°.  $[\alpha]_{\text{D}}^{25} = -64.3$  ( $c = 0.965$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3278<sub>w</sub>, 3067<sub>w</sub>, 3008<sub>m</sub>, 1718<sub>s</sub>, 1599<sub>w</sub>, 1492<sub>w</sub>, 1450<sub>m</sub>, 1422<sub>m</sub>, 1286<sub>w</sub>, 1131<sub>w</sub>, 1003<sub>w</sub>.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): −0.03 (*d*, *J* = 7.0, 3 H, Me); 0.54 (*d*, *J* = 7.3, 3 H, Me); 1.73-1.82 (*m*, 1 H, Me<sub>2</sub>CH); 1.87 (*s*, 3 H, SMe); 2.40-2.49 (*m*, 1 H, CH<sub>2</sub>); 2.88-3.03 (*m*, 2 H, CH<sub>2</sub>); 3.08-3.16 (*m*, 1 H, CH<sub>2</sub>); 4.47 (*s*, 1 H, CHSMe); 4.60 (*d*, *J* = 1.7, 1 H, NCH); 6.96-6.99 (*m*, 1 H); 7.11-7.39 (*m*, 16 H); 7.57-7.62 (*m*, 2 H); 7.85-7.88 (*m*, 1 H); 7.95 (*br s*, 1 H, OH). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 14.9, 15.1, 20.0 (Me); 23.4 (CH<sub>2</sub>); 29.06 (CH); 29.09 (CH<sub>2</sub>); 70.2, 71.3 (CH); 79.6, 89.5 (C); 125.5, 126.3, 126.4, 126.6, 126.65, 126.67, 127.78, 127.83, 127.9, 128.0, 128.2, 128.4, 128.6, 129.1 (CH); 135.1, 138.4, 138.5, 141.4, 143.7, 160.2 (C). **MALDI-MS**: 598 (10, [M+Na]<sup>+</sup>), 558 (10, [M+H-H<sub>2</sub>O]<sup>+</sup>), 466 (100, [M-SMe-CO<sub>2</sub>-H<sub>2</sub>O]<sup>+</sup>), 424 (27). **Anal.** calc. for C<sub>37</sub>H<sub>37</sub>NO<sub>3</sub>S (575.77): C 77.18, H 6.48, N 2.43; found: C 77.06, H 6.63, N 2.52.

(*S*)-3-[(*S*)-1-((*S*)-1-Hydroxy-cyclohex-2-enyl)-1-methylsulfanyl-methyl]-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11i**). Compound **3** (700 mg, 2.05 mmol) was treated with BuLi (1.61 mL, 2.46 mmol) and 2-cyclohexen-1-one (257 μL, 2.67 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/Et<sub>2</sub>O 6:1) yielded **11i** (454 mg, 51%) as a 83:17 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **11i** (dr ≥ 99:1). White solid. **M.p.** 176-178°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = −113.2 (*c* = 0.5, CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3680w, 3380w, 3007m, 2934m, 1725s, 1599w, 1493w, 1450m, 1422s, 1305w, 1248m, 1153w, 1086w, 1046m, 1003m, 908m. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.74 (*d*, *J* = 6.8, 3 H, Me); 1.03 (*d*, *J* = 7.3, 3 H, Me); 1.35-1.45 (*m*, 1 H); 1.63 (*s*, 3 H, SMe); 1.76-1.83 (*m*, 2 H); 1.92-2.10 (*m*, 3 H); 2.10-2.20 (*m*, 1 H, Me<sub>2</sub>CH); 4.27 (*s*, 1 H, CHSMe); 4.73 (*d*, *J* = 2.0, 1 H, NCH); 5.29 (*s*, 1 H, OH); 5.77-5.81 (*m*, 1 H, CH<sub>2</sub>CH); 5.94 (*d*, *J* = 10.4, 1 H, CCH); 7.21-7.39 (*m*, 6 arom. H); 7.46-7.49 (*m*, 2 arom. H); 7.70-7.73 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 13.6, 15.8 (Me); 19.5 (CH<sub>2</sub>); 21.0 (Me); 25.1 (CH<sub>2</sub>); 30.2 (CH); 34.2 (CH<sub>2</sub>); 70.2, 71.4 (CH); 73.8, 89.2 (C); 125.2, 126.2, 127.6, 128.1, 128.3, 128.7, 129.9, 131.4 (CH); 138.7, 144.3, 158.5 (C). **MALDI-MS**: 460

(42,  $[M+Na]^+$ ), 444 (100,  $[M+Li]^+$ ), 328 (41,  $[M-SMe-CO_2-H_2O]^+$ ), 244 (46), 167 (36). **Anal.** calc. for  $C_{26}H_{31}NO_3S$  (437.60): C 71.36, H 7.14, N 3.20; found: C 71.15, H 6.96, N 3.22.

(*S*)-3-((1*S*,2*S*)-2-Hydroxy-2-methyl-1-methylsulfanyl-but-3-enyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11j**). Compound **3** (481 mg, 1.41 mmol) was treated with BuLi (1.13 mL, 1.69 mmol) and methyl vinyl ketone (150  $\mu$ L, 1.83 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/Et<sub>2</sub>O 2:1) and recrystallization (MeOH) afforded **11j** as a 98.5:1.5 mixture with its C(2)-OH epimer. Due to purification problems only small amounts of product could be isolated. White solid. **M.p.** 154-156°.  $[\alpha]_D^{r.t.} = -136.1$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3360w, 3008m, 1727s, 1601w, 1493m, 1450m, 1419s, 1368m, 1336m, 1248m, 1131m, 1003w, 926m. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.74 (*d*,  $J = 6.9$ , 3 H, Me); 1.06 (*d*,  $J = 7.4$ , 3 H, Me); 1.41-1.42 (*m*, 3 H, Me); 1.62 (*s*, 3 H, SMe); 2.11-2.16 (*m*, 1 H, Me<sub>2</sub>CH); 4.12 (*s*, 1 H, CHSMe); 4.72 (*d*,  $J = 1.8$ , 1 H, NCH); 5.11 (*dd*,  $J = 1.1, 10.7$ , 1 H, CH<sub>2</sub>CH); 5.46 (*dd*,  $J = 1.1, 17.1$ , 1 H, CH<sub>2</sub>CH); 5.60 (*s*, 1 H, OH); 6.04 (*dd*,  $J = 10.7, 17.1$ , 1 H, CH<sub>2</sub>CH); 7.20-7.48 (*m*, 8 arom. H); 7.68-7.70 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 13.2, 16.0, 20.9, 28.0 (Me); 30.1, 69.8, 71.2 (CH); 77.6, 89.2 (C); 113.7 (CH<sub>2</sub>); 125.3, 126.3, 127.7, 128.1, 128.3, 128.6 (CH); 138.5, 142.6, 144.2, 158.2 (C). **MALDI-MS**: 434 (100,  $[M+Na]^+$ ), 320 (31,  $[M-SMe-CO_2]^+$ ), 302 (44,  $[M-SMe-CO_2-H_2O]^+$ ), 260 (87), 237 (52). **Anal.** calc. for  $C_{24}H_{29}NO_3S$  (411.56): C 70.04, H 7.10, N 3.40; found: C 69.92, H 6.96, N 3.36.

(*S*)-3-((1*S*,2*S*)-2-Cyclopropyl-2-hydroxy-1-methylsulfanyl-propyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**11k**). Compound **3** (807 mg, 2.36 mmol) was treated with BuLi (1.85 mL, 2.83 mmol) and cyclopropyl methyl ketone (287  $\mu$ L, 3.07 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/Et<sub>2</sub>O 6:1) afforded **11k** as a single diastereoisomer. Due to

purification problems only small amounts of product could be isolated. White solid. **M.p.** 118-122°.  $[\alpha]_{\text{D}}^{25} = -135.4$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3364w, 2995m, 1723s, 1415m, 1308m, 1250m, 1133m, 1086w, 926m.  **$^1\text{H-NMR}$**  (400MHz,  $\text{CDCl}_3$ ): 0.31-0.36 (*m*, 2 H); 0.41-0.48 (*m*, 1 H); 0.71-0.75 (*m*, 1 H); 0.76 (*d*,  $J = 6.9$ , 3 H, Me); 1.03-1.19 (*m*, 1 H); 1.11 (*d*,  $J = 7.4$ , 3 H, Me); 1.20 (*d*,  $J = 0.8$ , 3 H, Me); 1.71 (*s*, 3 H, SMe); 2.18-2.27 (*m*, 1 H,  $\text{Me}_2\text{CH}$ ); 4.18 (*s*, 1 H,  $\text{CHSMe}$ ); 4.82 (*d*,  $J = 1.8$ , 1 H, NCH); 4.94 (*s*, 1 H, OH); 7.20-7.40 (*m*, 6 arom. H); 7.45-7.50 (*m*, 2 arom. H); 7.68-7.72 (*m*, 2 arom. H).  **$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 1.9, 2.4 ( $\text{CH}_2$ ); 13.8, 16.1 (Me); 20.2 (CH); 20.8, 25.3 (Me); 29.9, 70.2, 72.8 (CH); 76.2, 89.1 (C); 125.3, 126.4, 127.7, 128.1, 128.3, 128.6 (CH); 138.6, 144.3, 158.7 (C). **MALDI-MS**: 448 (41,  $[\text{M} + \text{Na}]^+$ ), 316 (42,  $[\text{M-SMe-CO}_2\text{-H}_2\text{O}]^+$ ), 274 (63), 260 (100). **Anal.** calc. for  $\text{C}_{25}\text{H}_{31}\text{NO}_3\text{S}$  (425.59): C 70.55, H 7.34, N 3.29; found: C 70.69, H 7.40, N 3.33.

(*S*)-4-Isopropyl-3-((1*S*,2*R*)-2-methyl-1-methylsulfanyl-4-oxo-2,4-diphenyl-butyl)-5,5-diphenyl-oxazolidin-2-one (**13**). Compound **3** (350 mg, 1.02 mmol) was treated with BuLi (0.79 mL, 1.23 mmol) and benzalacetophenone (277 mg, 1.33 mmol) according to GP 2. Purification of the crude product by FC ( $\text{CH}_2\text{Cl}_2$ /pentane 3:1 to  $\text{CH}_2\text{Cl}_2$  + 1%  $\text{Et}_2\text{O}$ ) yielded **13** (441 mg, 79%) as a 98:2 mixture with its C(2)-Ph epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **13** (dr  $\geq$  99:1). White solid. **M.p.** 224-226°.  $[\alpha]_{\text{D}}^{25} = -99.8$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3005m, 2954w, 1744s, 1682m, 1595w, 1487m, 1446m, 1405m, 1179m, 1092w.  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ): 0.24 (*d*,  $J = 6.9$ , 3 H, Me); 0.83 (*d*,  $J = 7.4$ , 3 H, Me); 1.72 (*s*, 3 H, SMe); 1.89-1.97 (*m*, 1 H,  $\text{Me}_2\text{CH}$ ); 3.25 (*dd*,  $J = 7.8, 17.1$ , 1 H,  $\text{CH}_2$ ); 3.86 (*dd*,  $J = 4.8, 17.1$ , 1 H,  $\text{CH}_2$ ); 4.49 (*d*,  $J = 1.7$ , 1 H, NCH); 4.72 (*d*,  $J = 10.9$ , 1 H,  $\text{CHSMe}$ ); 4.80 (*ddd*,  $J = 4.8, 7.8, 10.9$ , 1 H,  $\text{CHPh}$ ); 7.04-7.54 (*m*, 18 arom. H); 7.82-7.85 (*m*, 2 arom. H).  **$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CD}_2\text{Cl}_2$ ): 13.1, 15.6, 20.6, 30.0 (Me); 42.2 (CH); 45.4 ( $\text{CH}_2$ ); 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.

*N*-[(1*S*,2*S*)-2-((*S*)-4-Isopropyl-2-oxo-5,5-diphenyl-oxazolidin-3-yl)-2-methylsulfanyl-1-phenylethyl]-diphenylphosphinamide (**14a**). Compound **3** (257 mg, 0.753 mmol) was treated with BuLi (0.60 mL, 0.903 mmol) and a solution of *N*-diphenylphosphinoylimine (derived from benzaldehyde) [2] (299 mg, 0.978 mmol) in THF (1 mL) according to *GP* 2. Trituration of the crude product (boiling MeOH, 2x 5 mL) yielded **14a** (214 mg, 44%) as a 97:3 mixture with its C(1)-NH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **14a** (dr  $\geq$  99:1). White solid. **M.p.**  $>240^\circ$ .  $[\alpha]_D^{25} = -86.5$  ( $c = 1$ ,  $CHCl_3$ ). **IR** ( $CHCl_3$ ): 3319 $w$ , 3063 $w$ , 2986 $m$ , 1736 $s$ , 1592 $w$ , 1493 $w$ , 1451 $m$ , 1438 $m$ , 1420 $m$ , 1124 $m$ , 1003 $w$ . **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ): 0.33 ( $d$ ,  $J = 6.9$ , 3 H, Me); 0.87 ( $d$ ,  $J = 7.3$ , 3 H, Me); 1.67 ( $s$ , 3 H, SMe); 1.90-2.01 ( $m$ , 1 H,  $Me_2CH$ ); 4.61 ( $d$ ,  $J = 8.0$ , 1 H,  $CHSMe$ ); 4.79-4.87 ( $m$ , 2 H, NCH,  $CH(NH)$ ) (H,P-coupling); 5.33 ( $br s$ , 1 H, NH); 7.08-7.48 ( $m$ , 19 arom. H); 7.57-7.68 ( $m$ , 4 arom. H); 7.75-7.85 ( $m$ , 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz,  $CDCl_3$ ): 14.6, 15.4, 20.6 (Me); 29.5, 58.8, 69.2 ( $d$ ,  $J_{C,P} = 6.9$ ), 69.4 (CH); 88.7 (C); 125.4, 126.4, 127.6, 127.7, 127.89, 127.93, 128.0, 128.1, 128.25, 128.31, 128.4, 128.5, 131.18, 131.20, 131.56, 131.58, 131.8, 131.9, 132.0, 132.1 (CH) (C,P-coupling); 132.3, 133.2, 133.6, 138.8, 140.2, 143.9, 157.8 (C) (C,P-coupling). **<sup>31</sup>P-NMR** (162 MHz,  $CDCl_3$ ): 21.66. **MALDI-MS**: 669 (42,  $[M+Na]^+$ ), 599 (39,  $[M-SMe]^+$ ), 581 (12,  $[M-SMe-H_2O]^+$ ), 555 (65,  $[M-SMe-CO_2]^+$ ), 338 (100). **Anal.** calc. for  $C_{39}H_{39}N_2O_3PS$  (646.79): C 72.42, H 6.08, N 4.33, S 4.96; found: C 72.45, H 6.22, N 4.27, S 5.14.



*N*-[*(1S,2S)*-2-((*S*)-4-Isopropyl-2-oxo-5,5-diphenyl-oxazolidin-3-yl)-2-methylsulfanyl-1-phenylethyl]-4-methyl-benzenesulfonamide (**14b**). Compound **3** (326 mg, 0.955 mmol) was treated with BuLi (0.76 mL, 1.15 mmol) and a solution of *N*-tolylsulfonylimine (derived from benzaldehyde) [3] (322 mg, 1.24 mmol) in THF (1 mL) according to *GP* 2. Trituration of the crude product (boiling MeOH, 2x 6 mL) yielded **14b** (385 mg, 67%) as a 75:25 mixture with its C(1)-NH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **14b** (dr 95:5). White solid. **M.p.** >240°.  $[\alpha]_{\text{D}}^{25} = -69.0$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3278<sub>w</sub>, 3062<sub>w</sub>, 3008<sub>w</sub>, 1737<sub>s</sub>, 1599<sub>w</sub>, 1494<sub>w</sub>, 1451<sub>m</sub>, 1421<sub>m</sub>, 1331<sub>m</sub>, 1159<sub>s</sub>, 1093<sub>m</sub>, 1003<sub>w</sub>. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.21 (*d*,  $J = 6.9$ , 3 H, Me); 0.75 (*d*,  $J = 7.3$ , 3 H, Me); 1.62 (*s*, 3 H, SMe); 1.82-1.89 (*m*, 1 H, Me<sub>2</sub>CH); 2.27 (*s*, 3 H, Me); 4.51 (*d*,  $J = 7.5$ , 1 H, CHSMe); 4.67 (*d*,  $J = 1.5$ , 1 H, NCH); 5.03 (*dd*,  $J = 7.5, 9.0$ , 1 H, CH(NH)); 6.93-6.96 (*m*, 2 arom. H); 7.00-7.39 (*m*, 15 arom. H, NH); 7.64-7.67 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 14.0, 15.1, 20.5, 21.4 (Me); 29.5, 62.1, 67.2, 69.2 (CH); 89.0 (C); 125.4, 126.2, 126.9, 127.6, 127.80, 127.83, 128.0, 128.2, 128.3, 128.8, 128.9 (CH); 137.0, 138.0, 138.5, 142.5, 143.8, 157.6 (C). **MALDI-MS**: 639 (2,  $[M+K]^+$ ), 623 (100,  $[M+Na]^+$ ), 575 (5). **Anal.** calc. for C<sub>34</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (600.80): C 67.97, H 6.04, N 4.66, S 10.67; found: C 67.89, H 6.09, N 4.66, S 10.73.

*N*-[*(1S,2S)*-2-((*S*)-4-Isopropyl-2-oxo-5,5-diphenyl-oxazolidin-3-yl)-2-methylsulfanyl-1-phenylethyl]-2,4,6-trimethyl-benzenesulfonamide (**14c**). Compound **3** (341 mg, 0.999 mmol) was treated with BuLi (0.80 mL, 1.20 mmol) and a solution of *N*-mesitylsulfonylimine (derived from benzaldehyde) [3] (374 mg, 1.30 mmol) in THF (1 mL) according to *GP* 2. Trituration of the crude product (boiling MeOH, 2x 6 mL) yielded **14c** (390 mg, 62%) as a 95:5 mixture with its C(1)-NH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **14c** (dr ≥ 99:1). White solid. **M.p.** >240°.  $[\alpha]_{\text{D}}^{25} = -69.4$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3270<sub>w</sub>, 3011<sub>w</sub>,

1736s, 1604w, 1494w, 1451m, 1422m, 1328m, 1157s, 1003w. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.21 (*d*, *J* = 6.9, 3 H, Me); 0.73 (*d*, *J* = 7.3, 3 H, Me); 1.69 (*s*, 3 H, SMe); 1.80-1.89 (*m*, 1 H, Me<sub>2</sub>CH); 2.14 (*s*, 3 H, Me); 2.43 (*s*, 6 H, Me); 4.52 (*d*, *J* = 7.5, 1 H, CHSMe); 4.67 (*d*, *J* = 1.6, 1 H, NCH); 5.03 (*dd*, *J* = 7.5, 8.5, 1 H, CH(NH)); 6.62 (*d*, *J* = 0.5, 2 arom. H); 6.95-7.06 (*m*, 5 H); 7.16-7.31 (*m*, 5 H); 7.35-7.41 (*m*, 4 H); 7.65-7.68 (*m*, 2 H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 14.4, 15.0, 20.4, 22.8 (Me); 29.5, 61.8, 67.3, 69.4 (CH); 89.0 (C); 125.3, 126.2, 127.4, 127.6, 127.7, 127.9, 128.0, 128.3, 128.8, 131.4 (CH); 135.4, 136.9, 138.0, 138.5, 141.3, 143.7, 157.7 (C). **MALDI-MS**: 651 (100, [M+Na]<sup>+</sup>), 603 (3), 537 (6, [M-SMe-CO<sub>2</sub>]<sup>+</sup>), 370 (36). **Anal.** calc. for C<sub>36</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (628.86): C 68.76, H 6.41, N 4.45, S 10.20; found: C 68.83, H 6.32, N 4.48, S 10.19.

N-{(1*R*,2*S*)-2-((*S*)-4-Isopropyl-2-oxo-5,5-diphenyl-oxazolidin-3-yl)-2-methylsulfanyl-1-isopropyl-ethyl}-2,4,6-trimethyl-benzenesulfonamide (**15d**). Compound **3** (335 mg, 0.981 mmol) was treated with BuLi (0.79 mL, 1.18 mmol) and a solution of *N*-mesitylsulfonylimine (derived from isobutyraldehyde) [3] (323 mg, 1.28 mmol) in THF (1 mL) according to *GP* 2. Purification of the crude product by FC (pentane/Et<sub>2</sub>O 3:1) yielded **15d** (251 mg, 43%) as a 97:3 mixture with its C(1)-NH epimer and 5 mol% of inseparable unidentified side products. For analytical purposes a sample was recrystallized (MeOH) to afford **15d** (dr ≥ 99:1). White solid. **M.p.** 196-198°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -120.2 (*c* = 1, CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3370w, 3009m, 2976w, 1745s, 1604w, 1493w, 1450w, 1408m, 1336m, 1264m, 1158m, 1034w, 657m. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.29 (*d*, *J* = 6.9, 3 H, Me); 0.48 (*d*, *J* = 6.9, 3 H, Me); 0.78 (*d*, *J* = 7.0, 3 H, Me); 1.12-1.21 (*m*, 1 H, Me<sub>2</sub>CH); 1.19 (*d*, *J* = 7.3, 3 H, Me); 2.17 (*s*, 3 H, SMe); 2.29 (*s*, 3 H, Me); 2.29-2.36 (*m*, 1 H, Me<sub>2</sub>CH); 2.68 (*s*, 6 H, Me); 3.55-3.62 (*m*, 1 H, CH(NH)); 4.85 (*d*, *J* = 4.5, 1 H, CHSMe); 4.92 (*d*, *J* = 1.8, 1 H, NCH); 4.96 (*d*, *J* = 9.9, 1 H, NH); 6.94 (*d*, *J* = 0.5, 2 arom. H); 7.20-7.38 (*m*, 6 arom. H); 7.52-7.56 (*m*, 2 arom. H); 7.75-7.78 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 15.2, 16.9, 17.1,

17.7, 19.7, 20.9, 23.1 (Me); 29.7 30.9, 60.3, 64.3, 67.7 (CH); 89.2 (C); 125.1, 126.4, 127.6, 128.06, 128.08, 128.7, 132.0 (CH); 136.5, 137.8, 138.3, 141.9, 144.8, 157.3 (C). **MALDI-MS**: 617 (100,  $[M+Na]^+$ ), 569 (11), 503 (46,  $[M-SMe-CO_2]^+$ ), 248 (62). **Anal.** calc. for  $C_{33}H_{42}N_2O_4S_2$  (594.84): C 66.63, H 7.12, N 4.71, S 10.78; found: C 66.76, H 7.11, N 4.82, S 10.74.

*(S)*-4-Isopropyl-3-((1*S*,2*S*)-2-methoxymethoxy-1-methylsulfanyl-2-phenyl-ethyl)-5,5-diphenyl-oxazolidin-2-one (**16**). To a solution of compound **3** (500 mg, 1.46 mmol) in THF (8 mL) was added BuLi (1.20 mL, 1.76 mmol) at  $-78^\circ$ . After stirring for 15 min, the reaction mixture was cooled to  $-100^\circ$  and benzaldehyde (192  $\mu$ L, 1.90 mmol) was added dropwise. It was allowed to warm to  $-78^\circ$  within 20 min and then MOMCl (189  $\mu$ L, 2.49 mmol) was added. After stirring for 4 h at r.t., the white precipitate that developed in the course of the reaction was dissolved in  $CH_2Cl_2$  and the reaction was stopped by quenching with sat. aq.  $NH_4Cl$  soln. The org. layer was separated and the aq. layer was extracted with  $CH_2Cl_2$  (2x). The combined org. layers were dried ( $MgSO_4$ ) and concentrated under reduced pressure. The crude product was triturated (boiling hexane, 2x 5 mL) and recrystallized (MeOH/ $CH_2Cl_2$ ) to give **16** (557 mg, 77%) as a 98.5:1.5 mixture with its C(2)-OH epimer. White solid. **M.p.** 201-203 $^\circ$ .  $[\alpha]_D^{25} = -60.6$  ( $c = 1$ ,  $CHCl_3$ ). **IR** ( $CHCl_3$ ): 3008 $w$ , 1750 $s$ , 1450 $w$ , 1419 $m$ , 1101 $w$ , 1022 $m$ , 909 $w$ .  **$^1H$ -NMR** (300 MHz,  $CDCl_3$ ): 0.87 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.25 ( $d$ ,  $J = 7.2$ , 3 H, Me); 1.44 ( $s$ , 3 H, SMe); 2.13-2.23 ( $m$ , 1 H,  $Me_2CH$ ); 3.21 ( $s$ , 3 H, OMe); 4.43 ( $d$ ,  $J = 10.6$ , 1 H,  $CHSMe$ ); 4.48 ( $d$ ,  $J = 6.4$ , 1 H,  $CH_2$ ); 4.63 ( $d$ ,  $J = 1.9$ , 1 H, NCH); 4.70 ( $d$ ,  $J = 6.4$ , 1 H,  $CH_2$ ); 5.60 ( $d$ ,  $J = 10.6$ , 1 H, CHO); 7.21-7.36 ( $m$ , 11 arom. H); 7.49-7.52 ( $m$ , 2 arom. H); 7.69-7.72 ( $m$ , 2 arom. H).  **$^{13}C$ -NMR** (75 MHz,  $CDCl_3$ ): 12.9, 15.1, 21.6 (Me); 30.1 (CH); 56.1 (Me); 67.9, 69.4, 78.1 (CH); 88.0 (C); 95.6 ( $CH_2$ ); 125.4, 126.2, 127.4, 127.9, 127.96, 127.99, 128.2, 128.3, 128.4 (CH); 139.2, 139.8, 144.6, 156.4 (C). **FAB-MS**: 492 (7,  $[M+H]^+$ ), 444 (100,  $[M-SMe]^+$ ), 400 (36,  $[M-SMe-CO_2]^+$ ), 340 (16), 296 (32).

**Anal.** calc. for  $C_{29}H_{33}NO_4S$  (491.65): C 70.85, H 6.77, N 2.85; found: C 70.63, H 6.81, N 2.85.

(S)-3-((1S,2S)-2-Benzoyloxy-3-methyl-1-methylsulfanyl-but-3-enyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**17**). To a solution of compound **3** (1.58 g, 4.62 mmol) in THF (20 mL) was added BuLi (3.77 mL, 5.55 mmol) at  $-78^\circ$ . After stirring for 15 min, the reaction mixture was cooled to  $-100^\circ$  and methacrolein (493  $\mu$ L, 6.01 mmol) was added dropwise. It was allowed to warm to  $-78^\circ$  within 20 min and then BnBr (933  $\mu$ L, 7.85 mmol) and DMPU (2 mL) were added. After stirring for 5 h at r.t., the reaction was stopped by quenching with sat. aq.  $NH_4Cl$  soln. The org. layer was separated and the aq. layer was extracted with  $CH_2Cl_2$  (2x). The combined org. layers were dried ( $MgSO_4$ ) and concentrated under reduced pressure. The crude product was filtered through a silica plug (pentane/ $Et_2O$  5:1) and triturated (boiling hexane, 3x 10 mL) to give **17** (1.27 g, 55%) as a single diastereoisomer. White solid. **M.p.**  $193-195^\circ$ .  $[\alpha]_D^{25} = -104.1$  ( $c = 1$ ,  $CHCl_3$ ). **IR** ( $CHCl_3$ ): 3067 $w$ , 3005 $w$ , 1748 $s$ , 1647 $w$ , 1495 $w$ , 1450 $m$ , 1419 $m$ , 1067 $m$ , 1047 $m$ , 1003 $w$ , 912 $w$ .  **$^1H$ -NMR** (400 MHz,  $CDCl_3$ ): 0.62 ( $d$ ,  $J = 6.8$ , 3 H, Me); 1.03 ( $d$ ,  $J = 7.3$ , 3 H, Me); 1.59 ( $s$ , 3 H, SMe); 1.68 ( $d$ ,  $J = 0.5$ , 3 H,  $C=CH_2$ ); 2.01-2.13 ( $m$ , 1 H,  $Me_2CH$ ); 4.39-4.49 ( $m$ , 3 H,  $PhCH_2$ ,  $CHSMe$ ); 4.56 ( $d$ ,  $J = 1.9$ , 1 H, NCH); 5.05-5.06 ( $m$ , 1 H,  $C=CH_2$ ); 5.10 ( $d$ ,  $J = 10.0$ , 1 H, CHO); 5.13 ( $s$ , 1 H,  $C=CH_2$ ); 7.17-7.33 ( $m$ , 11 arom. H); 7.43-7.46 ( $m$ , 2 arom. H); 7.67-7.70 ( $m$ , 2 arom. H).  **$^{13}C$ -NMR** (100 MHz,  $CDCl_3$ ): 11.4, 15.2, 16.2, 21.2 (Me); 30.0, 63.4, 69.1 (CH); 71.2 ( $CH_2$ ); 81.9 (CH); 87.7 (C); 117.1 ( $CH_2$ ); 125.4, 126.3, 127.2, 127.4, 127.95, 127.98, 128.1, 128.4 (CH); 138.5, 139.1, 141.3, 144.7, 156.5 (C). **FAB-MS**: 502 (13,  $[M+H]^+$ ), 454 (100,  $[M-SMe]^+$ ), 410 (51,  $[M-SMe-CO_2]^+$ ), 350 (33). **Anal.** calc. for  $C_{31}H_{35}NO_3S$  (501.69): C 74.22, H 7.03, N 2.79; found: C 74.20, H 7.16, N 2.87.

(S)-3-[(1S,2S)-2-(tert-Butyl-dimethyl-silanyloxy)-3-methyl-1-methylsulfanyl-butyl]-4-isopropyl-

*5,5-diphenyl-oxazolidin-2-one* (**18**). To a solution of compound **9m** (503 mg, 1.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added *i*Pr<sub>2</sub>NEt (563  $\mu$ L, 3.29 mmol) and 3-(*tert*-butyl-dimethylsilanyloxy)triflate (560  $\mu$ L, 2.44 mmol) at 0°. After stirring for 10 min at 0°, the reaction mixture was quenched with MeOH (2 mL) and concentrated under reduced pressure. The crude product was purified by FC (pentane/Et<sub>2</sub>O 15:1 to 10:1) to yield **18** (560 mg, 87%). White foam.  $[\alpha]_D^{25} = -163.0$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 2964 $m$ , 2931 $m$ , 2859 $w$ , 1741 $s$ , 1492 $w$ , 1472 $w$ , 1408 $m$ , 1077 $m$ , 834 $m$ . **<sup>1</sup>H-NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>, 50°): 0.16 ( $s$ , 3 H, Me<sub>2</sub>Si); 0.40 ( $s$ , 3 H, Me<sub>2</sub>Si); 0.61 ( $d$ ,  $J = 6.5$ , 3 H, Me); 0.72 ( $d$ ,  $J = 6.5$ , 3 H, Me); 0.81 ( $d$ ,  $J = 7.5$ , 3 H, Me); 1.02-1.08 ( $m$ , 1 H, Me<sub>2</sub>CH); 1.03 ( $d$ ,  $J = 6.9$ , 3 H, Me); 1.09 ( $s$ , 9 H, *t*Bu); 2.12 ( $s$ , 3 H, SMe); 2.91-3.03 ( $m$ , 1 H, Me<sub>2</sub>CH); 3.92-3.99 ( $m$ , 1 H, CHO); 5.05 ( $d$ ,  $J = 3.7$ , 1 H, NCH); 5.20 ( $d$ ,  $J = 3.1$ , 1 H, CHSMe); 6.90-7.02 ( $m$ , 4 arom. H); 7.06-7.11 ( $m$ , 2 arom. H); 7.60-7.63 ( $m$ , 2 arom. H); 7.75-7.78 ( $m$ , 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): -4.8, -2.3, 15.8, 16.7 (Me); 18.8 (C); 19.3, 19.4, 19.8, 26.8 (Me); 29.4, 31.0, 64.3, 70.2, 83.4 (CH); 87.7 (C); 125.3, 127.48, 127.52, 127.6, 127.9, 128.2 (CH); 138.1, 145.1, 157.5 (C). **FAB-MS**: 528 (13,  $[M+H]^+$ ), 480 (100,  $[M-SMe]^+$ ), 436 (80,  $[M-SMe-CO_2]^+$ ), 352 (32). **Anal.** calc. for C<sub>30</sub>H<sub>45</sub>NO<sub>3</sub>SiS (527.84): C 68.26, H 8.59, N 2.65; found: C 68.31, H 8.50, N 2.67.

(*S*)-2-Methoxymethoxy-2-phenyl-ethanol (**21**). Compound **16** (450 mg, 0.915 mmol) was treated with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (430 mg, 1.01 mmol) and NaBH<sub>4</sub> (26 mg, 0.686 mmol)/DBU (69  $\mu$ L, 0.458 mmol) according to *GP* 3. The chiral auxiliary **1** was recovered by filtration (184 mg, 71%). Purification of the crude product by FC (pentane/AcOEt 4:1) yielded **21** (151 mg, 90%). Colorless oil. The enantiomeric purity of **21** was determined by GC on a  $\gamma$ -Dex capillary column (90°; 1°/min;  $R_t$  of (*R*)-**21**: 48.4 min, of (*S*)-**21**: 48.8 min) to be  $\geq 99:1$ .  $[\alpha]_D^{25} = +182.0$  ( $c = 2.00$ , CHCl<sub>3</sub>). **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 2.84 ( $dd$ ,  $J = 4.4, 8.7$ , 1 H, OH); 3.40 ( $s$ , 3 H, Me); 3.63-

3.79 (*m*, 2 H,  $\text{CH}_2\text{OH}$ ); 4.64 (*d*,  $J = 6.7$ , 1 H,  $\text{CH}_2\text{OMe}$ ); 4.66 (*d*,  $J = 6.7$ , 1 H,  $\text{CH}_2\text{OMe}$ ); 4.71 (*dd*,  $J = 3.9, 7.9$ , 1 H,  $\text{PhCH}$ ); 7.27-7.38 (*m*, 5 arom. H). The physical data are in agreement with the values reported in the literature [4].

(*S*)-2-Benzyloxy-3-methyl-but-3-en-1-ol (**22**). Compound **17** (616 mg, 1.23 mmol) was treated with  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  (576 mg, 1.35 mmol) and  $\text{NaBH}_4$  (35 mg, 0.921 mmol)/DBU (92  $\mu\text{L}$ , 0.614 mmol) according to *GP* 3. The chiral auxiliary **1** was recovered by filtration (287 mg, 83%). Purification of the crude product by FC (pentane/AcOEt 6:1) yielded **22** (194 mg, 82%). Colorless oil.  $[\alpha]_{\text{D}}^{\text{r.t.}} = +71.3$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3587*m*, 3076*w*, 3008*s*, 2873*m*, 1648*w*, 1496*w*, 1454*s*, 1394*m*, 1350*w*, 1260*w*, 1102*s*, 1074*s*, 1046*s*, 1011*s*, 912*s*.  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ): 1.71-1.72 (*m*, 3 H,  $\text{C}=\text{CMe}$ ); 2.31 (*br s*, 1 H, OH); 3.52-3.58 (*m*, 1 H,  $\text{CH}_2\text{OH}$ ); 3.60-3.65 (*m*, 1 H,  $\text{CH}_2\text{OH}$ ); 3.91 (*dd*,  $J = 4.2, 7.8$ , 1 H,  $\text{CHCH}_2$ ); 4.21 (*d*,  $J = 11.6$ , 1 H,  $\text{PhCH}_2$ ); 4.58 (*d*,  $J = 11.6$ , 1 H,  $\text{PhCH}_2$ ); 5.05-5.06 (*m*, 2 H,  $\text{C}=\text{CH}_2$ ); 7.23-7.36 (*m*, 5 arom. H).  **$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 18.0 (Me); 64.4, 70.5 ( $\text{CH}_2$ ); 83.7 (CH); 114.8 ( $\text{CH}_2$ ); 127.7, 127.9, 128.4 (CH); 138.1, 141.8 (C). **EI-MS**: 161 (9,  $[\text{M}-\text{CH}_2\text{OH}]^+$ ), 91 (100,  $\text{Bn}^+$ ). **Anal.** calc. for  $\text{C}_{12}\text{H}_{16}\text{O}_2$  (192.26): C 74.97, H 8.39; found: C 74.87, H 8.27.

(*S*)-2-(tert-Butyl-dimethyl-silanyloxy)-3-methyl-butan-1-ol (**23**). Compound **18** (326 mg, 0.618 mmol) was treated with  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  (290 mg, 0.680 mmol) and  $\text{NaBH}_4$  (18 mg, 0.464 mmol)/DBU (46  $\mu\text{L}$ , 0.309 mmol) according to *GP* 3. The chiral auxiliary **1** was recovered by filtration (137 mg, 79%). Purification of the crude product by FC (pentane/AcOEt 13:1) yielded **23** (112 mg, 83%). Colorless oil. The enantiomeric purity of **23** was determined by GC on a  $\gamma$ -Dex capillary column (100° isotherm;  $R_t$  of (*S*)-**23**: 17.1 min, of (*R*)-**23**: 17.6 min) to be  $\geq 99:1$ .  $[\alpha]_{\text{D}}^{\text{r.t.}} = +0.5$  ( $c = 1$ ,  $\text{CHCl}_3$ ).  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 0.05 (*s*, 6 H,  $\text{Me}_2\text{Si}$ ); 0.85-0.89

(*m*, 15 H, Me, *t*Bu); 1.74-1.87 (*m*, 2 H, Me<sub>2</sub>CH, OH); 3.42-3.52 (*m*, 2 H, CH<sub>2</sub>OH, CHCH<sub>2</sub>). The physical data are in agreement with the values reported in the literature [5].

N-((*S*)-2-Hydroxy-1-phenyl-ethyl)-2,4,6-trimethyl-benzenesulfonamide (**24**). Compound **14c** (292 mg, 0.464 mmol) was treated with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (218 mg, 0.511 mmol) and NaBH<sub>4</sub> (13 mg, 0.348 mmol)/DBU (35  $\mu$ L, 0.232 mmol) according to *GP* 3. The chiral auxiliary **1** was recovered by filtration (92 mg, 70%). Purification of the crude product by FC (CH<sub>2</sub>Cl<sub>2</sub>, 0.5% MeOH) yielded **24** (101 mg, 68%). White solid.  $[\alpha]_{\text{D}}^{\text{r.t.}} = +68.4$  (*c* = 1, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 2.04 (*t*, *J* = 6.1, 1 H, OH); 2.26 (*s*, 3 H, Me); 2.51 (*s*, 6 H, Me); 3.71-3.76 (*m*, 2 H, CH<sub>2</sub>OH); 4.31 (*dd*, *J* = 5.8, 11.5, 1 H, PhCH); 5.36 (*d*, *J* = 5.8, 1 H, NH); 6.84 (*s*, 2 arom. H); 7.03-7.09 (*m*, 2 arom. H); 7.15-7.23 (*m*, 3 arom. H). The physical data are in agreement with the values reported in the literature [6].

(*S*)-2-Phenyl-propane-1,2-diol (**25**). Compound **11a** (370 mg, 0.802 mmol) was treated with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (376 mg, 0.882 mmol) and NaBH<sub>4</sub> (23 mg, 0.601 mmol)/DBU (60  $\mu$ L, 0.401 mmol) according to *GP* 3. The chiral auxiliary **1** was recovered by filtration (192 mg, 85%). Purification of the crude product by FC (pentane/AcOEt 2:1) yielded **25** (101 mg, 82%). Colorless oil. The enantiomeric purity of **25** was determined by GC on a  $\beta$ -Dex capillary column (110°; 1°/min; *R*<sub>t</sub> of (*S*)-**25**: 31.8 min, of (*R*)-**25**: 32.3 min) to be  $\geq$  99:1.  $[\alpha]_{\text{D}}^{\text{r.t.}} = +9.8$  (*c* = 2, CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 1.52 (*s*, 3 H, Me); 2.21 (*br s*, 1 H, OH); 2.83 (*br s*, 1 H, OH); 3.60 (*d*, *J* = 11.1, 1 H, CH<sub>2</sub>OH); 3.77 (*d*, *J* = 11.1, 1 H, CH<sub>2</sub>OH), 7.24-7.46 (*m*, 5 arom. H). The physical data are in agreement with the values reported in the literature [7].

(2*S*)-4-Methyl-2-phenyl-pentane-1,2-diol (**26**). Compound **11d** (935 mg, 1.86 mmol) was treated

with  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  (871 mg, 2.04 mmol) and  $\text{NaBH}_4$  (53 mg, 1.39 mmol)/DBU (141  $\mu\text{L}$ , 0.928 mmol) according to *GP* 3. The chiral auxiliary **1** was recovered by filtration (418 mg, 80%). Purification of the crude product by FC (pentane/ $\text{Et}_2\text{O}$  6:1) yielded **26** (275 mg, 76%). White solid. **M.p.** 88-90°.  $[\alpha]_{\text{D}}^{25} = -3.6$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3573 $m$ , 3067 $w$ , 3008 $m$ , 2958 $s$ , 2870 $m$ , 1601 $w$ , 1495 $w$ , 1467 $m$ , 1446 $m$ , 1367 $m$ , 1152 $w$ , 1056 $s$ , 944 $w$ , 908 $w$ , 864 $w$ , 657 $m$ .  **$^1\text{H}$ -NMR** (400 MHz,  $\text{CDCl}_3$ ): 0.68 ( $d$ ,  $J = 6.6$ , 3 H, Me); 0.90 ( $d$ ,  $J = 6.6$ , 3 H, Me); 1.53-1.63 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 1.65-1.72 ( $m$ , 2 H); 1.72-1.80 ( $m$ , 1 H); 2.70 ( $s$ , 1 H, OH); 3.62 ( $dd$ ,  $J = 8.2$ , 11.0, 1 H,  $\text{CH}_2\text{OH}$ ); 3.76 ( $dd$ ,  $J = 4.2$ , 11.0, 1 H,  $\text{CH}_2\text{OH}$ ); 7.24-7.27 ( $m$ , 1 arom. H); 7.34-7.42 ( $m$ , 4 arom. H).  **$^{13}\text{C}$ -NMR** (100 MHz,  $\text{CDCl}_3$ ): 23.9, 24.1 (Me); 24.4 (CH); 46.8, 71.4 ( $\text{CH}_2$ ); 77.6 (C); 125.6, 126.9, 128.3 (CH); 143.8 (C). **EI-MS**: 162 (14), 147 (15), 120 (33), 105 (100). **Anal.** calc. for  $\text{C}_{12}\text{H}_{18}\text{O}_2$  (194.27): C 74.19, H 9.34; found: C 74.25, H 9.18.

(*R*)-1-Hydroxymethyl-4-methoxy-indan-1-ol (**27**). Compound **11e** (452 mg, 0.897 mmol) was treated with  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  (421 mg, 0.987 mmol) and  $\text{NaBH}_4$  (25 mg, 0.673 mmol)/DBU (67  $\mu\text{L}$ , 0.449 mmol) according to *GP* 3. The chiral auxiliary **1** was recovered by filtration (223 mg, 88%). Purification of the crude product by FC (pentane/ $\text{Et}_2\text{O}$  4:1) yielded **27** (106 mg, 61%). White solid. **M.p.** 95-96°.  $[\alpha]_{\text{D}}^{25} = +10.8$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3595 $w$ , 3465 $w$ , 3008 $m$ , 2939 $m$ , 1593 $m$ , 1482 $s$ , 1440 $w$ , 1333 $w$ , 1263 $s$ , 1076 $m$ , 1042 $m$ , 1014 $m$ , 883 $w$ .  **$^1\text{H}$ -NMR** (400 MHz,  $\text{CDCl}_3$ ): 2.00-2.08 ( $m$ , 1 H,  $\text{CH}_2$ ); 2.25 ( $br\ t$ , 1 H, OH); 2.43 ( $ddd$ ,  $J = 3.6$ , 8.3, 12.0, 1 H,  $\text{CH}_2$ ); 2.53 ( $s$ , 1 H, OH); 2.68-2.77 ( $m$ , 1 H,  $\text{CH}_2$ ); 2.98 ( $ddd$ ,  $J = 3.6$ , 9.1, 12.7, 1 H,  $\text{CH}_2$ ); 3.61 ( $dd$ ,  $J = 6.3$ , 11.1, 1 H,  $\text{CH}_2\text{OH}$ ); 3.71 ( $dd$ ,  $J = 4.3$ , 11.1, 1 H,  $\text{CH}_2\text{OH}$ ); 3.83 ( $s$ , 3 H, OMe); 6.77-6.79 ( $m$ , 1 arom. H); 6.98-7.00 ( $m$ , 1 arom. H); 7.21-7.25 ( $m$ , 1 arom. H).  **$^{13}\text{C}$ -NMR** (100 MHz,  $\text{CDCl}_3$ ): 25.9, 37.0 ( $\text{CH}_2$ ); 55.3 (Me); 68.2 ( $\text{CH}_2$ ); 84.2 (C); 110.1, 115.5, 128.5 (CH); 131.1, 146.5, 156.1 (C). **EI-MS**: 194 (1,  $[M]^+$ ), 176 (24,  $[M-\text{H}_2\text{O}]^+$ ), 163 (100,  $[M-\text{CH}_2\text{OH}]^+$ ), 147 (58). **Anal.** calc.



for  $C_{11}H_{14}O_3$  (194.23): C 68.02, H 7.26; found: C 68.03, H 7.08.

(2R,3S)-3-(tert-Butyl-dimethyl-silanyloxy)-4-methyl-pentan-2-ol (**28**). Compound **18** (615 mg, 1.17 mmol) was treated with  $Hg(O_2CCF_3)_2$  (547 mg, 1.28 mmol) and  $MeMgCl$  (4.66 mL, 4.66 mmol) according to *GP 4*. The chiral auxiliary **1** was recovered by filtration (300 mg, 91%). Purification of the crude product by FC (pentane/ $Et_2O$  15:1) yielded **28** (207 mg, 76%) as a 83:17 mixture with its C(2)-OH epimer. For analytical purposes a sample was purified by FC (pentane/ $Et_2O$  15:1) to afford **28** as a single diastereoisomer. Colorless oil. The enantiomeric purity of **28** and its C(2)-OH epimer were both determined by GC on a  $\beta$ -Dex capillary column (80°; 1°/min;  $R_t$  of (2S,3S)-**28**: 18.8 min, of (2R,3R)-**28**: 19.4 min, of (2R,3S)-**28**: 22.6 min, of (2S,3R)-**28**: 25.0 min) to be  $\geq 99:1$ .  $[\alpha]_D^{25} = -11.6$  ( $c = 1$ ,  $CHCl_3$ ). **IR** ( $CHCl_3$ ): 3599w, 2958s, 2930s, 2857m, 1472m, 1388w, 1362w, 1113m, 1049s, 1019m, 858s, 838s. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ): 0.09 (s, 3 H,  $Me_2Si$ ); 0.10 (s, 3 H,  $Me_2Si$ ); 0.89 (d,  $J = 6.9$ , 3 H, Me); 0.93 (s, 9 H, *t*Bu); 0.94 (d,  $J = 6.9$ , 3 H, Me); 1.15 (d,  $J = 6.4$ , 3 H, C(OH)Me); 1.74-1.83 (m, 1 H,  $Me_2CH$ ); 1.86 (d,  $J = 5.1$ , 1 H, OH); 3.38 (dd,  $J = 3.7, 5.0$ , 1 H, CHOSi); 3.79-3.87 (m, 1 H, CHOH). **<sup>13</sup>C-NMR** (100 MHz,  $CDCl_3$ ): -4.3, -3.9, 17.7, 18.3 (Me); 18.4 (C); 20.4, 26.1 (Me); 30.1, 69.8, 80.5 (CH). **EI-MS**: 187 (44,  $[M-MeCHOH]^+$ ), 159 (100), 115 (44). **Anal.** calc. for  $C_{12}H_{28}O_2Si$  (232.44): C 62.01, H 12.14; found: C 62.11, H 11.95.

(1R,2S)-2-(tert-Butyl-dimethyl-silanyloxy)-3-methyl-1-phenyl-butan-1-ol (**29**) and (1S,2S)-2-(tert-Butyl-dimethyl-silanyloxy)-3-methyl-1-phenyl-butan-1-ol (**29** minor). Compound **18** (555 mg, 1.05 mmol) was treated with  $Hg(O_2CCF_3)_2$  (493 mg, 1.16 mmol) and  $PhLi$  (2.63 mL, 4.20 mmol) according to *GP 4*. The chiral auxiliary **1** was recovered by filtration (258 mg, 87%). Purification of the crude product by FC (pentane/ $Et_2O$  30:1 to 25:1) yielded **29** (194 mg, 63%) and **29** minor

(50 mg, 16%) as single diastereoisomers. **29**: Colorless oil. The enantiomeric purity of **29** was determined by GC on a  $\beta$ -Dex capillary column (100°; 1°/min;  $R_t$  of (1*R*,2*S*)-**29**: 59.3 min, of (1*S*,2*R*)-**29**: 60.4 min) to be  $\geq 99:1$ .  $[\alpha]_D^{r.t.} = -21.6$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3606*w*, 2958*s*, 2930*s*, 2857*m*, 1602*w*, 1472*m*, 1388*w*, 1362*w*, 1254*m*, 1126*w*, 1043*s*, 908*s*, 836*s*. **<sup>1</sup>H-NMR** (400 MHz,  $\text{CDCl}_3$ ): -0.11 (*s*, 3 H,  $\text{Me}_2\text{Si}$ ); 0.08 (*s*, 3 H,  $\text{Me}_2\text{Si}$ ); 0.80 (*d*,  $J = 6.8$ , 3 H, Me); 0.91 (*s*, 9 H, *t*Bu); 0.94 (*d*,  $J = 6.8$ , 3 H, Me); 1.66-1.74 (*m*, 1 H,  $\text{Me}_2\text{CH}$ ); 2.43 (*br s*, 1 H, OH); 3.72 (*dd*,  $J = 3.1, 5.2$ , 1 H,  $\text{CHOSi}$ ); 4.75 (*d*,  $J = 5.2$ , 1 H,  $\text{CHOH}$ ); 7.23-7.39 (*m*, 5 arom. H). **<sup>13</sup>C-NMR** (100 MHz,  $\text{CDCl}_3$ ): -4.6, -4.4, 17.0 (Me); 18.3 (C); 21.1, 26.0 (Me); 29.3, 76.7, 80.1, 126.7, 127.4, 128.2 (CH); 141.4 (C). **EI-MS**: 277 (14,  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$ ), 237 (20), 187 (100,  $[\text{M}-\text{PhCHOH}]^+$ ). **Anal.** calc. for  $\text{C}_{17}\text{H}_{30}\text{O}_2\text{Si}$  (294.51): C 69.33, H 10.27; found: C 69.22, H 10.34.

**29** minor: Colorless oil. The enantiomeric purity of **29** minor was determined by GC on a  $\beta$ -Dex capillary column (100°; 1°/min;  $R_t$  of (1*R*,2*R*)-**29**: 57.1 min, of (1*S*,2*S*)-**29**: 57.9 min) to be  $\geq 99:1$ .  $[\alpha]_D^{r.t.} = +49.6$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ ): -0.27 (*s*, 3 H,  $\text{Me}_2\text{Si}$ ); 0.00 (*s*, 3 H,  $\text{Me}_2\text{Si}$ ); 0.90 (*s*, 9 H, *t*Bu); 0.95 (*d*,  $J = 6.9$ , 3 H, Me); 1.00 (*d*,  $J = 6.9$ , 3 H, Me); 1.74-1.83 (*m*, 1 H,  $\text{Me}_2\text{CH}$ ); 2.96 (*d*,  $J = 6.2$ , 1 H, OH); 3.63 (*t*,  $J = 4.0$ , 1 H,  $\text{CHOSi}$ ); 4.67 (*dd*,  $J = 4.0, 6.2$ , 1 H,  $\text{CHOH}$ ); 7.24-7.37 (*m*, 5 arom. H). **<sup>13</sup>C-NMR** (100 MHz,  $\text{CDCl}_3$ ): -4.9, -4.3, 17.7 (Me); 18.3 (C); 19.1, 26.0 (Me); 31.8, 73.0, 81.6, 126.2, 127.1, 128.1 (CH); 143.3 (C).

(*S*)-4-Isopropyl-3-((*S*)-methoxymethoxy-phenyl-acetyl)-5,5-diphenyl-oxazolidin-2-one (**30**). Compound **16** (557 mg, 1.13 mmol) was treated with  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  (532 mg, 1.25 mmol) and PCC (512 mg, 2.37 mmol) according to *GP* 5. Purification of the crude product by FC (pentane/AcOEt 7:1) yielded **30** (382 mg, 73%). White solid. **M.p.** 130-134°.  $[\alpha]_D^{r.t.} = -52.5$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3008*w*, 2968*w*, 1782*s*, 1710*s*, 1494*w*, 1450*w*, 1371*m*, 1177*m*, 1151*m*, 1043*m*, 1014*w*. **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ ): 0.83 (*d*,  $J = 6.9$ , 3 H, Me); 0.95 (*d*,  $J = 6.8$ ,

3 H, Me); 1.95-2.06 (*m*, 1 H, Me<sub>2</sub>CH); 3.38 (*s*, 3 H, OMe); 4.72 (*d*, *J* = 6.9, 1 H, CH<sub>2</sub>); 4.75 (*d*, *J* = 6.9, 1 H, CH<sub>2</sub>); 5.25 (*d*, *J* = 3.7, 1 H, NCH); 6.33 (*s*, 1 H, C(O)CH); 6.98-7.37 (*m*, 15 arom. H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 16.5, 21.6 (Me); 29.6 (CH); 56.0 (Me); 65.7, 76.1 (CH); 89.8 (C); 95.9 (CH<sub>2</sub>); 125.0, 125.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.6 (CH); 134.8, 137.7, 141.9, 152.6, 170.5 (C). **FAB-MS**: 460 (13, [M+H]<sup>+</sup>), 444 (37), 398 (100, [M-OCH<sub>2</sub>OCH<sub>3</sub>]<sup>+</sup>), 356 (33). **Anal.** calc. for C<sub>28</sub>H<sub>29</sub>NO<sub>5</sub> (459.54): C 73.18, H 6.36, N 3.05; found: C 73.14, H 6.36, N 3.11.

(*S*)-3-((*S*)-2-Benzoyloxy-3-methyl-but-3-enoyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**31**).

Compound **17** (512 mg, 1.02 mmol) was treated with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (479 mg, 1.12 mmol) and PCC (462 mg, 2.14 mmol) according to *GP* 5. Purification of the crude product by FC (pentane/AcOEt 13:1) yielded **31** (362 mg, 76%) with 13 mol% of a inseparable compound (later identified as compound (*S*)-3-formyl-4-isopropyl-5,5-diphenyl-oxazolidin-2-one). This mixture was used for further transformations. For analytical purposes a sample was recrystallized three times (CH<sub>2</sub>Cl<sub>2</sub>/hexane) to afford pure **31**. White solid. **M.p.** 107-108°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -83.7 (*c* = 1, CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3063<sub>w</sub>, 3008<sub>w</sub>, 2970<sub>w</sub>, 1783<sub>s</sub>, 1710<sub>s</sub>, 1495<sub>w</sub>, 1450<sub>m</sub>, 1366<sub>m</sub>, 1178<sub>m</sub>, 1094<sub>m</sub>, 989<sub>w</sub>. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.78 (*d*, *J* = 6.8, 3 H, Me); 0.91 (*d*, *J* = 7.0, 3 H, Me); 1.47 (*dd*, *J* = 0.9, 1.3, 3 H, C=CMe); 1.98-2.07 (*m*, 1 H, Me<sub>2</sub>CH); 4.45-4.46 (*m*, 1 H, C=CH<sub>2</sub>); 4.49 (*d*, *J* = 11.5, 1 H, PhCH<sub>2</sub>); 4.54-4.55 (*m*, 1 H, C=CH<sub>2</sub>); 4.56 (*d*, *J* = 11.5, 1 H, PhCH<sub>2</sub>); 5.31 (*d*, *J* = 3.6, 1 H, NCH); 5.50 (*d*, *J* = 0.4, 1 H, C(O)CH); 7.24-7.38 (*m*, 11 arom. H); 7.40-7.42 (*m*, 2 arom. H); 7.46-7.49 (*m*, 2 arom. H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): 16.5, 18.7, 21.8 (Me); 29.7, 65.9 (CH); 71.6 (CH<sub>2</sub>); 80.3 (CH); 89.8 (C); 116.3 (CH<sub>2</sub>); 125.3, 125.7, 127.8, 128.0, 128.1, 128.4, 128.46, 128.52, 128.8 (CH); 137.6, 137.8, 139.7, 142.6, 152.8, 170.1 (C). **FAB-MS**: 470 (100, [M+H]<sup>+</sup>), 426 (14, [M+H-CO<sub>2</sub>]<sup>+</sup>), 362 (52, [M-OBn]<sup>+</sup>). **Anal.** calc. for

$C_{30}H_{31}NO_4$  (469.58): C 76.73, H 6.65, N 2.98; found: C 76.67, H 6.65, N 3.01.

*(S)*-Methoxymethoxy-phenyl-acetic acid methyl ester (**32**). Compound **30** (358 mg, 0.779 mmol) was treated with DBU (233  $\mu$ L, 1.56 mmol) and LiBr (338 mg, 3.90 mmol) according to *GP* 6. The chiral auxiliary **1** was recovered by filtration (186 mg, 85%). Purification of the crude product by FC (pentane/AcOEt 7:1) yielded **32** (135 mg, 83%). Colorless oil. The enantiomeric purity of **32** was determined by HPLC on a *OD* column (hexane/*i*PrOH 500:1; flow 0.8 mL/min; detection at 220 nm;  $R_t$  of *(S)*-**32**: 25.8 min, of *(R)*-**32**: 33.8 min) to be  $\geq 99:1$ .  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 3.37 (*s*, 3 H, Me); 3.69 (*s*, 3 H, Me); 4.67 (*d*,  $J = 6.9$ , 1 H,  $\text{CH}_2$ ); 4.74 (*d*,  $J = 6.9$ , 1 H,  $\text{CH}_2$ ); 5.17 (*s*, 1 H,  $\text{C(O)CH}$ ); 7.32-7.38 (*m*, 3 arom. H); 7.42-7.46 (*m*, 2 arom. H). The physical data are in agreement with the values reported in the literature [8].

*(S)*-2-Benzylloxy-3-methyl-but-3-enoic acid methyl ester (**33**). Compound **31** (362 mg, 0.770 mmol, 13 mol% of *(S)*-3-formyl-4-isopropyl-5,5-diphenyl-oxazolidin-2-one) was treated with DBU (230  $\mu$ L, 1.54 mmol) and LiBr (334 mg, 3.85 mmol) according to *GP* 6. The chiral auxiliary **1** was recovered by filtration (203 mg, 71% overall yield from **17**). Purification of the crude product by FC (pentane/AcOEt 16:1) yielded **33** (141 mg, 63% overall yield from **17**). Colorless oil.  $[\alpha]_D^{25} = +55.0$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3008 $w$ , 2953 $w$ , 1746 $s$ , 1650 $w$ , 1496 $w$ , 1454 $m$ , 1437 $m$ , 1177 $m$ , 1096 $s$ , 1028 $m$ , 913 $m$ .  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 1.78-1.79 (*m*, 3 H,  $\text{C=CMe}$ ); 3.75 (*s*, 3 H, OMe); 4.38 (*s*, 1 H,  $\text{C(O)CH}$ ); 4.52 (*d*,  $J = 12.0$ , 1 H,  $\text{PhCH}_2$ ); 4.58 (*d*,  $J = 12.0$ , 1 H,  $\text{PhCH}_2$ ); 5.11-5.14 (*m*, 2 H,  $\text{C=CH}_2$ ); 7.26-7.37 (*m*, 5 arom. H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ): 17.9, 52.1 (Me); 70.6 ( $\text{CH}_2$ ); 81.4 (CH); 116.4 ( $\text{CH}_2$ ); 127.8, 127.9, 128.3 (CH); 137.1, 139.9, 170.8 (C). **EI-MS**: 181 (4), 161 (32,  $[M-\text{CO}_2\text{Me}]^+$ ), 114 (33,  $[M+\text{H}-\text{OBn}]^+$ ), 91 (100,  $\text{Bn}^+$ ). **Anal.** calc. for  $\text{C}_{13}\text{H}_{16}\text{O}_3$  (220.27): C 70.89, H 7.32; found: C 70.84, H 7.46.

(E)-(R)-4-Hydroxy-4-phenyl-pent-2-enoic acid methyl ester (**34**) and (R)-5-Methyl-5-phenyl-5H-furan-2-one (**35**). Compound **11a** (750 mg, 1.63 mmol) was treated with  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  (762 mg, 1.79 mmol) and DBU (122  $\mu\text{L}$ , 0.812 mmol)/Ylide (1.09 g, 3.25 mmol) according to GP 7. The chiral auxiliary **1** was recovered (365 mg, 80%). Purification of the crude product by FC ( $\text{CH}_2\text{Cl}_2$ /pentane 3:1) yielded **34** (208 mg, 62%) and **35** (75 mg, 27%) as single stereoisomers. **34**: Colorless oil.  $[\alpha]_{\text{D}}^{25} = +20.3$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3595 $w$ , 3009 $w$ , 2953 $w$ , 1718 $s$ , 1656 $w$ , 1436 $m$ , 1312 $m$ , 1281 $m$ , 1174 $m$ , 984 $w$ .  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 1.71 ( $s$ , 3 H, Me); 2.23 ( $s$ , 1 H, OH); 3.73 ( $s$ , 1 H, OMe); 6.12 ( $d$ ,  $J = 15.8$ , 1 H, C=CH); 7.17 ( $d$ ,  $J = 15.8$ , 1 H, C=CH); 7.24-7.38 ( $m$ , 3 arom. H); 7.42-7.48 ( $m$ , 2 arom. H).  **$^{13}\text{C-NMR}$**  (75 MHz,  $\text{CDCl}_3$ ): 28.9, 51.7 (Me); 74.2 (C); 118.0, 125.1, 127.6, 128.5 (CH); 144.6 (C); 153.4 (CH); 167.2 (C). **EI-MS**: 205 (1,  $[M-\text{H}]^+$ ), 188 (21,  $[M-\text{H}_2\text{O}]^+$ ), 163 (73), 131 (100). **Anal.** calc. for  $\text{C}_{12}\text{H}_{14}\text{O}_3$  (206.24): C 69.89, H 6.84; found: C 69.62, H 6.91.

**35**: Colorless oil.  $[\alpha]_{\text{D}}^{25} = +275.6$  ( $c = 1$ ,  $\text{CHCl}_3$ ).  **$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ): 1.82 ( $s$ , 3 H, Me); 6.04 ( $d$ ,  $J = 5.6$ , 1 H, C=CH); 7.28-7.40 ( $m$ , 5 arom. H); 7.64 ( $d$ ,  $J = 5.6$ , 1 H, C=CH).  **$^{13}\text{C-NMR}$**  (75 MHz,  $\text{CDCl}_3$ ): 26.2 (Me); 88.8 (C); 119.2, 124.7, 128.3, 128.8 (CH); 139.2 (C); 160.4 (CH); 172.3 (C).

(S)-3-((2S,3R)-3,5-Diphenyl-2,3-dihydro-furan-2-yl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**36**). To a solution of ketone **13** (400 mg, 0.728 mmol) in THF (5 mL) was added  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  (341 mg, 0.801 mmol) at r.t. After stirring for 20 min,  $\text{H}_2\text{O}$  was added and the reaction mixture was diluted with  $\text{Et}_2\text{O}$ . The org. layer was separated and the aq. layer was extracted with  $\text{Et}_2\text{O}$  (2x). The combined org. layers were dried ( $\text{MgSO}_4$ ) and concentrated under reduced pressure. Purification of the crude product by FC (pentane/ $\text{Et}_2\text{O}$  4:1, 1%  $\text{Et}_3\text{N}$ ) and trituration (boiling

hexane, 10 mL) afforded **36** as a single diastereoisomer. Due to purification problems only small amounts of product could be isolated. White solid. **M.p.** 211-213°.  $[\alpha]_D^{r.t.} = +54.0$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 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 $m$ .  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ): 0.81 ( $d$ ,  $J = 6.7$ , 3 H, Me); 0.91 ( $d$ ,  $J = 7.3$ , 3 H, Me); 1.91-2.02 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 4.32 ( $dd$ ,  $J = 2.7, 7.3$ , 1 H, PhCH); 4.68 ( $d$ ,  $J = 1.5$ , 1 H, NCH); 5.47 ( $d$ ,  $J = 2.7$ , 1 H, CCH); 5.98 ( $d$ ,  $J = 7.3$ , 1 H, 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).  **$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 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,  $[\text{M}+\text{Na}]^+$ ), 458 (29), 248 (21). **MALDI-HRMS**:  $m/z$  524.2196 [ $\text{C}_{34}\text{H}_{31}\text{NO}_3$  ( $\text{M}+\text{Na}$ ) $^+$  requires 524.2196]

*Isopropyl-3-((1S,2S,3R,5R)-5-methoxy-3,5-diphenyl-tetrahydro-furan-2-yl)-5,5-diphenyl-oxazolidin-2-one (37)*. Compound **36** (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 **37** (single diastereoisomer). White solid. **M.p.** 182-184°.  $[\alpha]_D^{r.t.} = -28.4$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 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 $w$ .  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ): 0.68 ( $d$ ,  $J = 6.7$ , 3 H, Me); 0.82 ( $d$ ,  $J = 7.3$ , 3 H, Me); 1.90-1.97 ( $m$ , 1 H,  $\text{Me}_2\text{CH}$ ); 2.56 ( $dd$ ,  $J = 6.3, 13.5$ , 1 H,  $\text{CH}_2$ ); 2.66 ( $dd$ ,  $J = 11.4, 13.5$ , 1 H,  $\text{CH}_2$ ); 3.11 ( $s$ , 3 H, OMe); 4.03-4.08 ( $m$ , 1 H,  $\text{CHPh}$ ); 4.56 ( $d$ ,  $J = 1.6$ , 1 H, NCH); 5.52 ( $d$ ,  $J = 8.3$ , 1 H, 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).  **$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 14.9, 20.7 (Me); 29.7, 45.0 (CH); 47.4 ( $\text{CH}_2$ ); 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). **MALDI-HRMS**:  $m/z$  556.2438 [ $C_{35}H_{35}NO_4$  ( $M+Na$ ) $^+$  requires 556.2458].

*(S)*-4-Isopropyl-3-(1-methylsulfonyl-ethyl)-5,5-diphenyl-oxazolidin-2-one (**38**). To a solution of compound **3** (210 mg, 0.615 mmol) in THF (3 mL) was added BuLi (0.48 mL) at  $-78^\circ$ . After stirring for 10 min, MeI (50  $\mu$ L, 0.800 mmol) was added dropwise. After stirring for 15 min, the reaction was stopped by quenching with sat. aq.  $NH_4Cl$  soln. The reaction mixture was diluted with  $Et_2O$ , the org. layer was separated and the aq. layer was extracted with  $CH_2Cl_2$  (2x). The combined org. layers were dried ( $MgSO_4$ ) and concentrated under reduced pressure. Trituration of the crude product (boiling hexane, 4 mL) yielded **38** (192 mg, 88%) as a 83:17 mixture with its C(1)-SMe epimer. For analytical purposes a sample was recrystallized twice ( $Et_2O$ ) to afford **38** (dr 95:5). White solid. **M.p.** 166-167 $^\circ$ .  $[\alpha]_D^{r.t.} = -138.2$  ( $c = 1$ ,  $CHCl_3$ , dr 83:17). **IR** ( $CHCl_3$ ): 3008 $w$ , 1739 $s$ , 1493 $w$ , 1450 $w$ , 1407 $w$ , 1326 $w$ , 1178 $w$ , 1025 $w$ , 1002 $w$ .  **$^1H$ -NMR** (400 MHz,  $CDCl_3$ ): 0.71 ( $d$ ,  $J = 7.0$ , 3 H, Me); 1.03 ( $d$ ,  $J = 7.3$ , 3 H, Me); 1.32 ( $s$ , 3 H, SMe); 1.52 ( $d$ ,  $J = 7.3$ , 3 H, Me); 1.97-2.08 ( $m$ , 1 H,  $Me_2CH$ ); 4.74 ( $d$ ,  $J = 1.9$ , 1 H, NCH); 4.94 ( $q$ ,  $J = 7.3$ , 1 H,  $CHSMe$ ); 7.21-7.37 ( $m$ , 6 arom. H); 7.50-7.53 ( $m$ , 2 arom. H); 7.69-7.72 ( $m$ , 2 arom. H).  **$^{13}C$ -NMR** (100 MHz,  $CDCl_3$ ): 14.0, 16.6, 19.4, 22.4 (Me); 30.0, 59.0, 67.2 (CH); 89.1 (C); 125.3, 126.5, 127.6, 128.1, 128.2, 128.6 (CH); 138.7, 144.8, 157.0 (C). **MALDI-MS**: 378 (6,  $[M+Na]^+$ ), 264 (54,  $[M-SMe-CO_2]^+$ ), 167 (100). **Anal.** calc. for  $C_{21}H_{25}NO_2S$  (355.50): C 70.95, H 7.09, N 3.94; found: C 70.99, H 7.25, N 3.95.

(*S*)-4-*tert*-Butyl-3-methylsulfanylmethyl-5,5-diphenyl-oxazolidin-2-one (**39**). (*S*)-4-*tert*-Butyl-5,5-diphenyl-oxazolidin-2-one [9] (1.52 g, 5.15 mmol) was treated with BuLi (3.65 mL, 5.66 mmol) and MTMCl (520  $\mu$ L, 6.18 mmol) according to *GP 1*. Purification of the crude product by filtering through a silica plug ( $\text{CH}_2\text{Cl}_2$ ) and subsequent trituration (boiling hexane, 10 mL) yielded **39** (1.03 g, 56%). White solid. **M.p.** 196-197°.  $[\alpha]_{\text{D}}^{\text{r.t.}} = -134.3$  ( $c = 1.03$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3007 $w$ , 2964 $w$ , 1744 $s$ , 1486 $w$ , 1450 $w$ , 1405 $m$ , 1370 $w$ , 1086 $w$ , 993 $w$ , 882 $w$ .  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ): 0.86 ( $s$ , 9 H, *t*Bu); 1.08 ( $s$ , 3 H, SMe); 4.21 ( $d$ ,  $J = 14.7$ , 1 H,  $\text{CH}_2$ ); 4.55 ( $s$ , 1 H, NCH); 4.94 ( $d$ ,  $J = 14.7$ , 1 H,  $\text{CH}_2$ ); 7.18-7.30 ( $m$ , 4 arom. H); 7.34-7.39 ( $m$ , 2 arom. H); 7.54 ( $br s$ , 2 arom. H); 7.74-7.77 ( $m$ , 2 arom. H).  **$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 13.0, 28.1 (Me); 37.3 (C); 50.9 ( $\text{CH}_2$ ); 69.1 (CH); 89.6 (C); 125.5, 127.6, 127.7, 128.2, 128.6 (CH); 138.1, 145.1, 157.7 (C). **MALDI-MS**: 378 (8,  $[M+\text{Na}]^+$ ), 264 (2,  $[M-\text{SMe}-\text{CO}_2]^+$ ), 208 (100,  $[M-\text{SMe}-\text{CO}_2-\text{isobutene}]^+$ ). **Anal.** calc. for  $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{S}$  (355.50): C 70.95, H 7.09, N 3.94, S: 9.02; found: C 70.82, H 7.15, N 3.93, S: 8.94.

(*R*)-3-Methylsulfanylmethyl-4,5,5-triphenyl-oxazolidin-2-one (**40**). (*R*)-4-Phenyl-5,5-diphenyl-oxazolidin-2-one [10] (1.81 g, 5.74 mmol) was treated with BuLi (4.07 mL, 6.31 mmol) and MTMCl (580  $\mu$ L, 6.89 mmol) according to *GP 1*. Purification of the crude product by FC (pentane/Et<sub>2</sub>O 4:1) and subsequent trituration (boiling hexane, 10 mL) yielded **40** (1.62 g, 75%). White solid. **M.p.** 129-131°.  $[\alpha]_{\text{D}}^{\text{r.t.}} = +39.8$  ( $c = 1$ ,  $\text{CHCl}_3$ ). **IR** ( $\text{CHCl}_3$ ): 3008 $w$ , 2924 $w$ , 1749 $s$ , 1494 $w$ , 1450 $w$ , 1410 $m$ , 1264 $w$ , 1080 $w$ , 1001 $w$ , 882 $w$ .  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ): 1.79 ( $s$ , 3 H, SMe); 3.60 ( $d$ ,  $J = 14.2$ , 1 H,  $\text{CH}_2$ ); 4.91 ( $d$ ,  $J = 14.2$ , 1 H,  $\text{CH}_2$ ); 5.79 ( $s$ , 1 H, NCH); 6.97-7.07 ( $m$ , 7 arom. H); 7.12-7.15 ( $m$ , 3 arom. H); 7.32-7.37 ( $m$ , 1 arom. H); 7.40-7.45 ( $m$ , 2 arom. H); 7.73-7.76 ( $m$ , 2 arom. H).  **$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 13.7 (Me); 46.7 ( $\text{CH}_2$ ); 66.6 (CH); 88.4 (C); 126.1, 126.5, 127.3, 127.6, 128.48, 128.51, 128.6, 128.7 (CH); 134.4, 138.9, 142.1, 156.8



(C). **MALDI-MS**: 398 (3,  $[M+Na]^+$ ), 284 (100,  $[M-SMe-CO_2]^+$ ), 206 (22), 167 (32). **Anal.** calc. for  $C_{23}H_{21}NO_2S$  (355.50): C 73.57, H 5.64, N 3.73, S: 8.54; found: C 73.40, H 5.76, N 3.78, S: 8.48.

(4*S*,5*R*)-4-Isopropyl-3-methylsulfanylmethyl-5-phenyl-oxazolidin-2-one (**41**). (4*S*, 5*R*)-4-Isopropyl-5-phenyl-oxazolidin-2-one [11] (798 mg, 3.89 mmol) was treated with BuLi (3.17 mL, 4.67 mmol) and MTMCl (424  $\mu$ L, 5.06 mmol) according to *GP 1*. Purification of the crude product by FC (pentane/AcOEt 8:1) yielded **41** (915 mg, 89%). White solid. **M.p.** 91-93°.  $[\alpha]_D^{r.t.} = +27.9$  ( $c = 1$ ,  $CHCl_3$ ). **IR** ( $CHCl_3$ ): 3008 $w$ , 2968 $w$ , 2924 $w$ , 1748 $s$ , 1454 $w$ , 1418 $m$ , 1267 $w$ , 1050 $w$ , 997 $w$ . **<sup>1</sup>H-NMR** (300 MHz,  $CDCl_3$ ): 0.70 ( $d$ ,  $J = 6.9$ , 3 H, Me); 0.84 ( $d$ ,  $J = 7.2$ , 3 H, Me); 1.61-1.78 ( $m$ , 1 H,  $Me_2CH$ ); 2.20 ( $s$ , 3 H, SMe); 4.10 ( $d$ ,  $J = 14.2$ , 1 H,  $CH_2$ ); 4.21 ( $dd$ ,  $J = 2.6, 8.1$ , 1 H, NCH); 5.06 ( $d$ ,  $J = 14.2$ , 1 H,  $CH_2$ ); 5.66 ( $d$ ,  $J = 8.1$ , 1 H, PhCH); 7.31-7.42 ( $m$ , 5 arom. H). **<sup>13</sup>C-NMR** (75 MHz,  $CDCl_3$ ): 14.4, 16.4, 21.0 (Me); 28.2 (CH); 48.5 ( $CH_2$ ); 61.6, 79.9, 126.1, 128.3, 128.4 (CH); 134.6, 158.2 (C). **FAB-MS**: 531 (50,  $[2M+H]^+$ ), 483 (21,  $[2M-SMe]^+$ ), 266 (13,  $[M+H]^+$ ), 218 (100,  $[M-SMe]^+$ ), 174 (84,  $[M-SMe-CO_2]^+$ ). **Anal.** calc. for  $C_{14}H_{19}NO_2S$  (265.38): C 63.36, H 7.22, N 5.28; found: C 63.41, H 7.36, N 5.25.

(*S*)-3-(2-Hydroxy-1-methyl-1-methylsulfanyl-2-phenyl-ethyl)-4-isopropyl-5,5-diphenyl-oxazolidin-2-one (**42**) and 3-[(*S*)-1-(Hydroxy-diphenyl-methyl)-2-methyl-propyl]-4-methyl-4-methylsulfanyl-5-phenyl-oxazolidin-2-one (**43**). Compound **38** (368 mg, 1.04 mmol, dr 83:17 mixture) was treated with BuLi (0.82 mL, 1.24 mmol) and benzaldehyde (136  $\mu$ L, 1.35 mmol) according to *GP 2*. Compounds **42** and **43** were obtained as a 60:40 mixture, determined by <sup>1</sup>H-NMR of the crude product. Purification of the crude product by FC (pentane/Et<sub>2</sub>O 6:1 to 3:1) yielded **42** (201 mg, 42%) as a 61:17:14:8 mixture of diastereoisomers and **43** (yield not

determined) as a 55:45 mixture of diastereoisomers. For analytical purposes a sample of **42** was recrystallized (MeOH) to afford **42** as a single diastereoisomer. **42**: White solid. **M.p.** 182-183°.  $[\alpha]_D^{25} = -83.6$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3063<sub>w</sub>, 3008<sub>w</sub>, 1721<sub>s</sub>, 1600<sub>w</sub>, 1493<sub>w</sub>, 1451<sub>m</sub>, 1387<sub>m</sub>, 1327<sub>w</sub>, 1178<sub>w</sub>, 1023<sub>m</sub>, 1002<sub>w</sub>, 909<sub>w</sub>. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): 0.71 (*d*,  $J = 7.5$ , 3 H, Me); 0.82 (*d*,  $J = 7.2$ , 3 H, Me); 1.25 (*s*, 3 H, SMe); 1.51 (*s*, 3 H, Me); 1.89-2.03 (*m*, 1 H, Me<sub>2</sub>CH); 4.63 (*d*,  $J = 2.2$ , 1 H, NCH); 4.68 (*d*,  $J = 6.5$ , 1 H, OH); 5.54 (*d*,  $J = 6.5$ , 1 H, CH(OH)); 7.18-7.39 (*m*, 9 arom. H); 7.42-7.53 (*m*, 4 arom. H); 7.71-7.76 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): 11.0, 17.5, 18.9, 22.1 (Me); 31.7, 68.1 (CH); 72.7 (C); 75.7 (CH); 88.7 (C); 125.5, 126.6, 127.4, 127.6, 127.7, 127.9, 128.2, 128.5, 128.6 (CH); 138.6, 139.2, 144.5, 157.5 (C). **MALDI-MS**: 436 (3), 370 (100,  $[M-SMe-CO_2]^+$ ), 352 (19,  $[M-H_2O-SMe-CO_2]^+$ ), 310 (54). **Anal.** calc. for C<sub>28</sub>H<sub>31</sub>NO<sub>3</sub>S (461.62): C 72.85, H 6.77, N 3.03; found: C 72.96, H 6.65, N 3.10.

**43** major: White solid. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.91 (*d*,  $J = 7.3$ , 3 H, Me); 1.07 (*d*,  $J = 7.1$ , 3 H, Me); 1.19 (*s*, 3 H, SMe); 1.54 (*s*, 3 H, Me); 2.48-2.58 (*m*, 1 H, Me<sub>2</sub>CH); 4.54 (*d*,  $J = 1.6$ , 1 H, NCH); 5.15 (*s*, 1 H, PhCH); 7.08-7.40 (*m*, 11 arom. H); 7.74-7.76 (*m*, 2 arom. H); 7.79-7.81 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 11.7, 19.7, 24.6, 24.8 (Me); 30.0, 65.9 (CH); 75.1, 82.3 (C); 85.3, 125.9, 126.3, 126.6, 126.7, 127.2, 127.6, 128.1, 128.5, 129.1 (CH); 134.1, 144.9, 146.1, 158.8 (C). **MALDI-TOF-MS**: 484 (100,  $[M+Na]^+$ ), 400 (25).

(*S*)-4-*tert*-Butyl-3-((1*S*,2*S*)-2-hydroxy-1-methylsulfonyl-2-phenyl-ethyl)-5,5-diphenyl-oxazolidin-2-one (**44**). Compound **39** (235 mg, 0.661 mmol) was treated with BuLi (0.52 mL, 0.793 mmol) and benzaldehyde (87 µL, 0.859 mmol) according to *GP* 2. Trituration of the crude product (boiling hexane, 2x 5 mL) yielded **44** (279 mg, 91%) as a 90:10 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **44** (dr 91:9). White solid. **M.p.** 239-247°.  $[\alpha]_D^{25} = -142.8$  ( $c = 1.33$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3512<sub>w</sub>, 3008<sub>m</sub>,

2964<sub>w</sub>, 1729<sub>s</sub>, 1492<sub>w</sub>, 1450<sub>m</sub>, 1416<sub>m</sub>, 1302<sub>w</sub>, 1138<sub>w</sub>, 1048<sub>m</sub>, 1002<sub>w</sub>, 857<sub>w</sub>. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.98 (*s*, 9 H, *t*Bu); 1.15 (*s*, 3 H, SMe); 4.26 (*d*, *J* = 5.0, 1 H, OH); 4.39 (*s*, 1 H, NCH); 4.46 (*d*, *J* = 9.9, 1 H, CHSMe); 5.52 (*dd*, *J* = 5.0, 9.9, 1 H, CH(OH)); 7.20-7.38 (*m*, 11 arom. H); 7.53 (*br s*, 2 arom. H); 7.75-7.78 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 9.4, 28.2 (Me); 37.6 (C); 69.6, 72.5, 73.6 (CH); 90.1 (C); 125.8, 127.3, 127.7, 127.8, 128.1, 128.26, 128.31, 128.4 (CH); 138.2, 141.1, 144.8, 158.3 (C). **MALDI-MS**: 484 (13, [*M*+Na]<sup>+</sup>), 370 (6, [*M*-SMe-CO<sub>2</sub>]<sup>+</sup>), 314 (42, [*M*-SMe-CO<sub>2</sub>-isobutene]<sup>+</sup>), 296 (100). **Anal.** calc. for C<sub>28</sub>H<sub>31</sub>NO<sub>3</sub>S (461.62): C 72.85, H 6.77, N 3.03; found: C 72.92, H 6.95, N 3.16.

(*R*)-3-((1*R*,2*R*)-2-Hydroxy-1-methylsulfanyl-2-phenyl-ethyl)-4,5,5-triphenyl-oxazolidin-2-one (**45**). Compound **40** (218 mg, 0.580 mmol) was treated with BuLi (0.45 mL, 0.697 mmol) and benzaldehyde (76 μL, 0.754 mmol) according to *GP* 2. Trituration of the crude product (boiling hexane, 2x 5 mL) yielded **45** (253 mg, 91%) as a 79:21 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **45** (dr 90:10). White solid. **M.p.** 207-213°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +12.3 (*c* = 1, CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3378<sub>w</sub>, 3064<sub>w</sub>, 3008<sub>w</sub>, 1732<sub>s</sub>, 1601<sub>w</sub>, 1495<sub>w</sub>, 1450<sub>m</sub>, 1403<sub>m</sub>, 1277<sub>w</sub>, 1033<sub>w</sub>, 1003<sub>m</sub>, 917<sub>w</sub>, 866<sub>w</sub>, 826<sub>w</sub>. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 1.83 (*s*, 3 H, SMe); 4.10 (*d*, *J* = 7.3, 1 H, OH); 4.70 (*d*, *J* = 7.0, 1 H, CHSMe); 5.25 (*dd*, *J* = 7.0, 7.3, 1 H, CH(OH)); 5.83 (*s*, 1 H, NCH); 6.87-6.93 (*m*, 2 arom. H); 6.97-7.05 (*m*, 5 arom. H); 7.12-7.27 (*m*, 7 arom. H); 7.32-7.44 (*m*, 4 arom. H); 7.65-7.68 (*m*, 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 13.7 (Me); 66.9, 69.9, 75.1 (CH); 89.0 (C); 125.9, 126.55, 126.61, 127.4, 127.5, 127.9, 128.2, 128.5, 128.69, 128.71 (CH); 133.8, 138.6, 140.5, 142.7, 157.8 (C). **MALDI-MS**: 504 (22, [*M*+Na]<sup>+</sup>), 390 (88, [*M*-SMe-CO<sub>2</sub>]<sup>+</sup>), 372 (100, [*M*-H<sub>2</sub>O-SMe-CO<sub>2</sub>]<sup>+</sup>). **Anal.** calc. for C<sub>30</sub>H<sub>27</sub>NO<sub>3</sub>S (481.61): C 74.82, H 5.65, N 2.91; found: C 74.78, H 5.53, N 3.01.

(4*S*,5*R*)-3-((1*S*,2*S*)-2-Hydroxy-1-methylsulfanyl-2-phenyl-ethyl)-4-isopropyl-5-phenyl-oxazolidin-2-one (**46**). Compound **41** (260 mg, 0.980 mmol) was treated with BuLi (0.80 mL, 1.18 mmol) and benzaldehyde (129  $\mu$ L, 1.27 mmol) according to *GP* 2. Purification of the crude product by FC (pentane/AcOEt 5:1) yielded **46** (313 mg, 86%) as a 88:12 mixture with its C(2)-OH epimer. For analytical purposes a sample was recrystallized (MeOH) to afford **46** (dr 98.5:1.5). White solid. **M.p.** 160-163°.  $[\alpha]_{\text{D}}^{\text{r.t.}} = +19.6$  ( $c = 1$ , CHCl<sub>3</sub>). **IR** (CHCl<sub>3</sub>): 3365 $w$ , 3008 $w$ , 2967 $w$ , 1735 $s$ , 1496 $w$ , 1454 $m$ , 1413 $m$ , 1041 $w$ . **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.69 ( $d$ ,  $J = 7.0$ , 3 H, Me); 0.83 ( $d$ ,  $J = 7.2$ , 3 H, Me); 1.78-1.89 ( $m$ , 1 H, Me<sub>2</sub>CH); 2.12 ( $s$ , 3 H, SMe); 4.06 ( $d$ ,  $J = 5.7$ , 1 H, OH); 4.17 ( $dd$ ,  $J = 2.7, 7.7$ , 1 H, NCH); 4.75 ( $d$ ,  $J = 8.2$ , 1 H, CHSMe); 5.35 ( $dd$ ,  $J = 5.7, 8.2$ , 1 H, CH(OH)); 5.53 ( $d$ ,  $J = 7.7$ , 1 H, PhCH); 7.29-7.41 ( $m$ , 8 arom. H); 7.48-7.50 ( $m$ , 2 arom. H). **<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): 14.6, 16.9, 19.7 (Me); 28.8, 64.8, 69.0, 74.7, 81.1 (CH); 126.2, 126.9, 128.3, 128.5, 128.6 (CH); 134.3, 140.7, 159.0 (C). **FAB-MS**: 372 (5,  $[M+H]^+$ ), 354 (15,  $[M+H-H_2O]^+$ ), 324 (100,  $[M-SMe]^+$ ), 280 (65,  $[M-SMe-CO_2]^+$ ), 264 (47). **Anal.** calc. for C<sub>21</sub>H<sub>25</sub>NO<sub>3</sub>S (371.50): C 67.90, H 6.78, N 3.77; found: C 67.96, H 6.68, N 3.85.

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