

Electro-organic Synthesis 68.¹ Diastereoselective Cathodic Reduction of Phenylglyoxylic Acid Attached to Chiral Auxiliaries

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

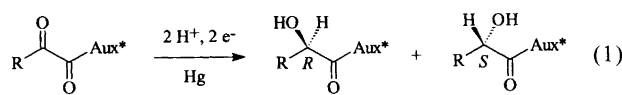
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Two chiral auxiliaries were attached to phenylglyoxylic acid as amides in 67–70% yield. Cyclic voltammetry of one amide in acetonitrile–pivalic acid (0.117 mol l^{-1}) shows that it is irreversibly reduced at -0.73 to -1.07 V (vs. Ag/AgCl) depending on the cation of the supporting electrolyte. During preparative-scale electrolysis the amides afforded the corresponding mandelic acid derivatives in 64–76% yield and 52–86% de, respectively. The diastereoselectivities depend on solvent, proton donor, supporting electrolyte, temperature and the substituent R in the 2-oxo acid amides. The results are in accordance with an ECE-reduction of the 2-oxo acid amide to an enolate anion, which subsequently undergoes a face-selective protonation to the mandelic acid amide.

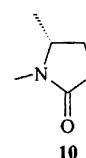
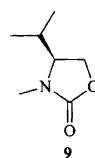
The state of art to control the diastereoselectivity in organic electro-synthesis is much less advanced than in chemical synthesis.² However, much progress has been made in recent years.³ For example in the field of cathodic reductions high diastereoselectivities have been reported for the cathodic intramolecular cyclization of keto enones⁴ and enones,⁵ for cathodic pinacolisation,⁶ for the cathodic hydrogenation of substituted cyclohexanones,⁷ and for the cyclization of pyridinium alkyl ketones.⁸ Face-selective reductions of β -amino ketones with diastereoselectivities of 92% de have been described.⁹ Auxiliary-induced diastereoselectivities with up to 95% de have been reported for the cathodic hydro-dimerization of cinnamic acid esters and amides with alcohols¹⁰ and oxazolidines¹¹ as chiral auxiliaries, respectively.

This contribution addresses the diastereoselective cathodic hydrogenation of phenylglyoxylic acid and other 2-oxo acids attached to (*S*)-4-isopropyl-1,3-oxazolidin-2-one **9** and (*R*)-5-methyl-2-oxopyrrolidine **10** [eqn. (1)]. These compounds allow the face-selectivity of the cathodic reduction of the carbonyl group to be studied.

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RCO-CO-Aux*	R	Aux*	RCH(OH)-CO-Aux*
1	C ₆ H ₅	9	11
2	C ₆ H ₅	10	12
3	CH ₃	9	13
4	CH ₃ CH ₂	9	4
5	(CH ₃) ₂ CH	9	15
6	(CH ₃) ₃ C	9	16
7	2-C ₄ H ₉ O	9	17
8	2-C ₄ H ₉ S	9	18

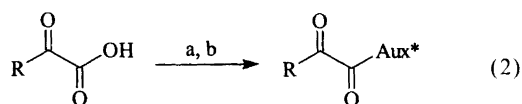


The phenylglyoxylic acid amides **1** and **2** were chosen as electrophores, because (a) both the phenyl group and the amide carbonyl group activate the keto carbonyl group towards reduction, (b) owing to the absence of acidic α -protons competing aldol condensations can be prevented, (c) a mechanistic proposal for the cathodic reduction of phenylglyoxylic acid has already been made¹² and (d) an auxiliary-induced diastereoselective

reduction of (1*R*,2*S*,5*R*)-menthyl phenylglyoxylate with 24% de has been reported.¹³ This contribution deals with the role of the solvent, the supporting electrolyte, the kind of proton donor, the temperature and the substitution of phenyl in **1** by other substituents. In another paper the influence of the auxiliary on the diastereoselectivity of the reaction will be described.

Results

Preparation of 1–8. The glyoxylamides **1**, **3–8** were prepared in two steps in 27–89% overall yield by conversion of the glyoxylic acids **19–25** into their acid chlorides and treating these with the lithium salt of the chiral auxiliary **9** [eqn. (2)]. In the case of **2** the acid **19** was activated by conversion into the mixed pivalic phenylglyoxylic acid anhydride and treated with **10** in the presence of 4-dimethylaminopyridine (DMAP).



a) (COCl)₂, DMF, CH₂Cl₂, 0 °C; b) n-BuLi, THF, **9**, –78 °C for **1**, **3–8**

a) (CH₃)₃CCOCl; Et₃N, CH₂Cl₂, 0 °C; b) **10**, CH₂Cl₂, DMAP, RT for **2**.

RCOOH	R	Aux*	RCOAAux*	Yield (%)
19	C ₆ H ₅	9	1	67
19	C ₆ H ₅	10	2	70
20	CH ₃	9	3	73
21	CH ₃ CH ₂	9	4	66
22	(CH ₃) ₂ CH	9	5	27
23	(CH ₃) ₃ C	9	6	89
24	2-C ₄ H ₃ O	9	7	74
25	2-C ₄ H ₃ S	9	8	87

The acids **19–21**, **24–25** and the sodium salt of **22** were commercially available, and **23** was obtained by permanganate oxidation of 3,3-dimethyl-2-butanone.¹⁴

Electroanalytical investigations. The reduction potential of **1** was determined by cyclic voltammetry at a hanging mercury drop electrode in acetonitrile–lithium perchlorate (0.2 mol l^{–1}) containing pivalic acid (Fig. 1). No anodic peak was detected upon scan reversal at –1.25 V, even at a scan rate of 100 V s^{–1}. The cation of the supporting electrolyte has a significant influence on the peak potential (Table 1).

As can be seen, the peak potential of **1** shifts from –1.07 V with Bu₄N⁺ to –0.74 V with Li⁺ as the supporting electrolyte cation. In acetonitrile–tetrabutylammonium perchlorate (0.2 mol l^{–1}), but without pivalic acid, partial reoxidation is observed in cyclic voltammetry at a scan rate as low as 100 mV s^{–1} (Fig. 1). Furthermore the cathodic peak current drops from –9.7 μA (with pivalic acid) to –5.0 μA (without pivalic acid).

Table 1. Influence of the supporting electrolyte cation on the reduction potential.^a

Supporting electrolyte	E _{p,c} /V ^b
Bu ₄ NClO ₄	–1.07
NaClO ₄	–0.96
LiClO ₄	–0.74
Mg(ClO ₄) ₂	–0.73

^aAcetonitrile, supporting electrolyte (0.2 mol l^{–1}), pivalic acid (0.117 mol l^{–1}), **1** (5 × 10^{–3} mol l^{–1}), scan rate 100 mV s^{–1}.

^bVs. Ag/AgCl/LiCl (sat.) in ethanol (corresponds to +0.143 V vs. NHE); ferrocene in CH₃CN–Bu₄NClO₄ (0.2 mol l^{–1}) has [E_p(Ox) + E_p(Red)]/2 = +0.51 V vs. Ag/AgCl/LiCl (sat.) in ethanol.

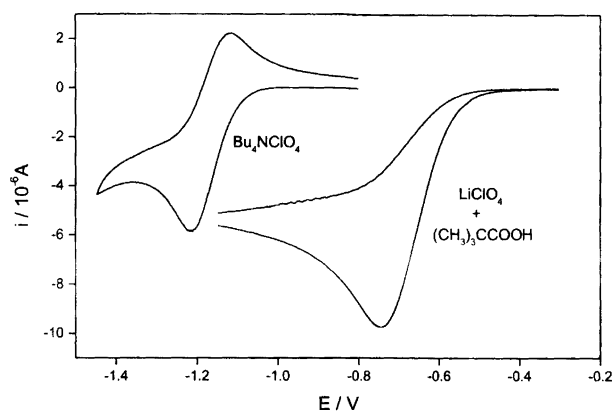


Fig. 1. Cyclic voltammograms of **1** (5 × 10^{–3} mol l^{–1}) in acetonitrile–tetrabutylammonium perchlorate (0.2 mol l^{–1}) and in acetonitrile–pivalic acid (0.117 mol l^{–1})–lithium perchlorate (0.2 mol l^{–1}) at a hanging mercury drop electrode vs. Ag/AgCl/LiCl (sat.) in ethanol; scan rate: 100 mV s^{–1}.

These results indicate a 2e-reduction of **1** with a fast follow-up reaction in the presence of acid and a 1e-reduction with a slow follow-up reduction in the absence of acid.

Preparative scale electrolysis of 1 and 2. 1.76 mmol of **1** were reduced at –1.2 V to –1.7 V vs. Ag/AgCl/LiClO₄ (0.1 mol l^{–1})/CH₃CN in a divided beaker-type cell at various temperatures. After consumption of 2.9–3.1 F this reduction afforded 59–71% of **11** with 53–86% de depending on the different reaction conditions. For identical reaction conditions the deviations are ±2% de and ±3% yield between the experiments. The structure of **11** was confirmed by the IR, ¹H and ¹³C NMR spectra, mass spectrometry and elemental analysis. The diastereomeric excess was determined by ¹H NMR analysis of the crude product or by GLC of the silylated crude product, respectively. The configuration of the new stereogenic center of the main diastereomer was assigned by methanolysis of (*R*)-**11** with sodium methoxide in methanol. The configuration of the (*R*)-methyl mandelate [(*R*)-**26**] obtained was checked by comparison with authentic (*R*)-**26** using GLC with heptakis-(2,3,6-tri-*O*-methyl)-β-cyclodextrin as the stationary phase. In meth-

analysis no racemization was observed. **11** with an *R/S* ratio of 4:1 led to **26** with the same ratio.

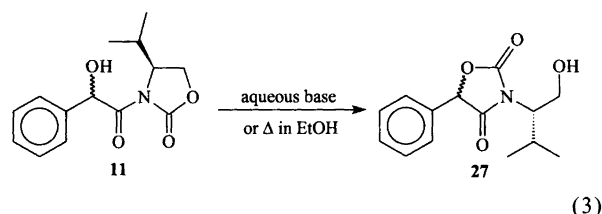
Similarly, 1.76 mmol of **2** were reduced at -1.2 V to -1.7 V vs. Ag/AgCl/LiClO₄ (0.1 mol l^{-1})/CH₃CN in a divided beaker-type cell at $+20^\circ\text{C}$ to afford, after consumption of 2.8–3.0 F, 62–76% of **12** with 37–68% de. The constitution and configuration of **12** and the diastereomeric excess were determined as described for **11**.

Influence of the solvent on the diastereoselectivity. In methanol–NaOAc (0.2 mol l^{-1}) as electrolyte only a moderate diastereoselectivity of 52% de is achieved with **2** (Table 2, entry 1). Replacement of methanol by the aprotic solvent acetonitrile increases the de to 62% (Table 2, entry 2). Exchange of acetonitrile for tetrahydrofuran, investigated with **1**, does not influence the diastereoselectivity (Table 2, entries 3 and 4).

Influence of the structure of the acid on the diastereoselectivity. The kind of acid has some influence on the diastereoselectivity. Replacement of acetic acid by pivalic acid increases the de (Table 3, entries 1, 2). Part of the increased diastereomeric excess can also be attributed to the exchange of Na⁺ for the better complexing cation Li⁺. With adamantane-1-carboxylic acid (1-AdaCOOH) and 2,2-diphenylacetic acid, which have a similar bulkiness to pivalic acid, the increase in de is smaller (Table 3, entries 3–5). Part of the increase could be due to the bulkiness of pivalic acid compared with acetic acid, but there are probably also other effects involved. In most experiments pivalic acid was used as the proton donor.

The use of 2,6-dimethylphenol (2,6-DMP) as the acid did not lead to **11** but to **27** as the main product. **27** can also be generated by either refluxing **11** in ethanol for several hours or treatment of **11** with aqueous sodium hydroxide [eqn. (3)]. **27** is the product of intramolecular

acyl transfer in **11**.¹⁵ Base-catalyzed nucleophilic attack of the α -hydroxy group at the carbonyl carbon of the 2-oxazolidinone and cleavage of the C–O bond in the lactam leads to **27**. In the presence of the weak acid 2,6-DMP **11** is probably also formed first and then rearranged to **27**.



Influence of the supporting electrolyte on the diastereoselectivity. The supporting electrolyte exerts a strong influence on the diastereoselectivity. Replacement of the tetrabutylammonium cation by a lithium or magnesium cation increases the diastereoselectivity remarkably (Table 4). The kind of supporting electrolyte anion has a small but significant influence on the diastereoselectivity (Table 5). Moreover, the diastereoselectivity depends on the concentration of the lithium cation (Table 6).

Influence of temperature on the diastereoselectivity. The diastereoselectivity of the reduction increases with decreasing temperature. With **1** at $+20^\circ\text{C}$ 72% de and at -30°C 86% de were observed (Table 7).

Influence of the substituent R in the glyoxylic acid. Compounds **3–8** were electrolyzed, as described for **1** and **2**, at a controlled potential of -1.1 to -1.8 V vs. Ag/AgCl/LiClO₄ (0.1 mol l^{-1})/CH₃CN at -20°C in acetonitrile, pivalic acid (0.117 mol l^{-1}), lithium tetra-

Table 2. Influence of the solvent on the diastereoselectivity in the cathodic reduction of **1** and **2**.

Entry	Substrate ^a	Solvent	Acid ^b	Supporting electrolyte ^c	<i>T</i> /°C	Yield (%) ^d	de (%)
1	2	CH ₃ OH	CH ₃ COOH	NaOAc	+20	76	52
2	2	CH ₃ CN	CH ₃ COOH	NaOAc	+20	68	62
3	1	CH ₃ CN	(CH ₃) ₃ CCOOH	LiClO ₄	-20	70	78
4	1	THF	(CH ₃) ₃ CCOOH	LiClO ₄	-20	66	80

^a 0.032 mol l^{-1} . ^b 0.117 mol l^{-1} . ^c 0.2 mol l^{-1} . ^dIsolated yield after separation by flash chromatography.

Table 3. Influence of the structure of the acid on the diastereoselectivity in the reduction of **1**^a in acetonitrile.

Entry	Acid ^b	Supporting electrolyte ^c	<i>T</i> /°C	Yield (%) ^d	de (%)
1	CH ₃ COOH	NaOAc	+20	65	59
2	(CH ₃) ₃ CCOOH	LiClO ₄	+20	70	72
3	(CH ₃) ₃ CCOOH	LiClO ₄	-20	70	78
4	1-AdaCOOH	LiClO ₄	-20	71	66
5	Ph ₂ CHCOOH	LiClO ₄	-20	65	72
6	2,6-DMP	LiClO ₄	-20	—	—

^a 0.032 mol l^{-1} . ^b 0.117 mol l^{-1} . ^c 0.2 mol l^{-1} . ^dIsolated yield after separation by flash chromatography.

Table 4. Influence of the supporting electrolyte cation on the diastereoselectivity of the reduction of **1^a** and **2^a** in acetonitrile–pivalic acid.^b

Entry	Substrate ^c	Supporting electrolyte ^d	T/°C	Yield (%) ^e	de (%)
1	2	Bu ₄ NBF ₄	+20	62	37
2	2	LiClO ₄	+20	64	68
3	1	Bu ₄ NBF ₄ ^f	-20	64	53
4	1	LiClO ₄	-20	70	78
5	1	LiBF ₄	-20	67	76
6	1	Mg(ClO ₄) ₂	-20	62	83

^a0.032 mol l⁻¹. ^b0.117 mol l⁻¹. ^c0.032 mol l⁻¹. ^d0.2 mol l⁻¹. ^eIsolated yield after separation by flash chromatography. ^fDepending on the work-up **27** was formed as a side product in 0–9% yield.

Table 5. Influence of the supporting electrolyte anion on the diastereoselectivity of the reduction of **1^a** in acetonitrile–pivalic acid^b at -20 °C.

Entry	Supporting electrolyte ^c	Yield (%) ^d	de (%)
1	LiOSO ₂ CF ₃	59	71
2	LiPF ₆	60	71
3	LiBF ₄	69	76
4	LiClO ₄	70	78

^a0.032 mol l⁻¹. ^b0.117 mol l⁻¹. ^c0.2 mol l⁻¹. ^dIsolated yield after separation by flash chromatography.

Table 6. Influence of lithium cation concentration on the diastereoselectivity of the reduction of **1^a** in acetonitrile–pivalic acid^b at -20 °C.

Entry	c (LiClO ₄)/mol l ⁻¹	Yield (%) ^c	de (%)
1	0.1	66	80
2	0.05	69	78
3	0.01	64	63

^a0.032 mol l⁻¹. ^b0.117 mol l⁻¹. ^cIsolated yield after separation by flash chromatography.

Table 7. Influence of the temperature on the diastereoselectivity in the reduction of **1^a** in acetonitrile–pivalic acid^b–LiClO₄.^c

Entry	T/°C	Yield (%) ^d	de (%)
1	+20	72	72
2	0	65	75
3	-20	70	78
4	-30	66	86

^a0.032 mol l⁻¹. ^b0.117 mol l⁻¹. ^c0.2 mol l⁻¹. ^dIsolated yield after separation by flash chromatography.

fluoroborate (0.2 mol l⁻¹) as electrolyte until a current consumption of 2.9–3.2 F had passed. Isolation by flash-chromatography led to the reduction products **13–18** in 47–71% yield with 50–70% de (Table 8). In general, the diastereoselectivity strongly depends on the steric and electronic properties of R. As shown in Table 8, the

change from R = phenyl (entry 5) to R = 2-furyl (entry 6) and R = 2-thienyl (entry 7) led to a significant decrease in the diastereomeric excess. Diastereomeric excesses were determined by ¹H NMR spectroscopy and isolation of the diastereomers. X-ray structures confirmed the configuration of the major diastereomers of **16–18** (Figs. 2–4) and of the minor diastereomer of **15** (Fig. 5). The chemical shift of the proton at the new stereogenic center allowed the assignment of the configuration by ¹H NMR spectroscopy in the other cases. The proton of the (*S*)-diastereomer appeared at higher field than the proton of the (*R*)-diastereomer (Table 9). For **18** the assignment is the opposite because of the CIP-rules, which assign higher priority to the 2-thienyl moiety than to the amide moiety.

Discussion

The 2-oxoacyloxazolidinones **1–8** were diastereoselectively reduced at a mercury cathode to the 2-hydroxy-acyloxazolidinones **11–18**. The chemical yields ranged from 47 to 76% and diastereoselectivities from 50 to 86% de. The yield and de depend on the structure of the 2-oxoacyloxazolidinones, the solvent, the supporting electrolyte, the acid and the temperature.

During cyclic voltammetry a chemically irreversible reduction in the presence of pivalic acid is observed, whilst in the absence of the acid the reduction becomes chemically partially reversible and the current is lowered to 50%. Taking into account the mechanistic proposal for the reduction of phenylglyoxylic acid,¹² the data can be rationalized by the reaction sequence shown in Scheme 1. At first one electron is transferred. In the presence of Li⁺ or Mg²⁺ the reduction potential is shifted to less negative values, which supports the electrophilic activation of the 2-oxo carbonyl group by the formation of **28**. Acid alone does not lead to such strong activation as found for Li⁺ or Mg²⁺. With Bu₄N⁺ as the supporting electrolyte cation the addition of pivalic acid (0.117 mol l⁻¹) shifts the reduction potential from -1.23 to -1.07 V.

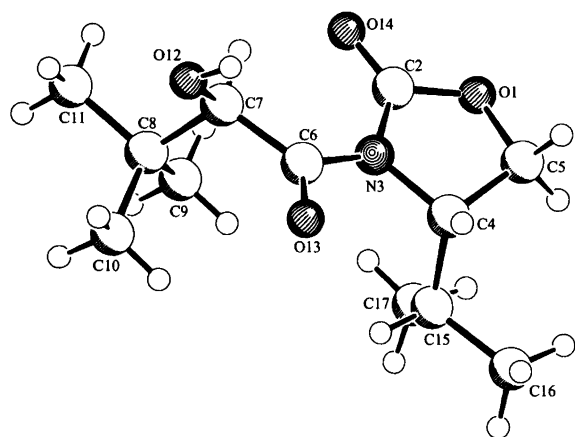
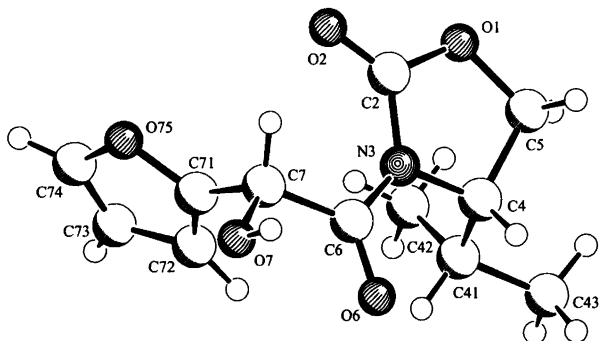
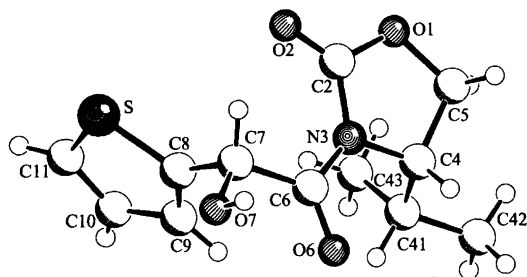
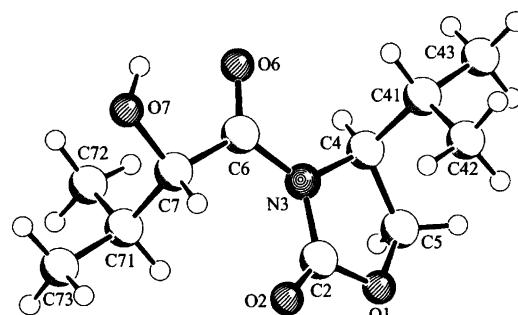
The electron transfer to **28** is the rate determining step¹² and leads to **31**. In the absence of acid and with Bu₄N⁺ as the supporting electrolyte cation a partially reversible 1e-reduction of **1** to **29** can occur. The lithium alkoxide radical **30** can be further reduced to the dilithio enediolate **32** or it can be protonated to the radical **31**. The reduction of **30** to **32** appears to be less likely, because **30** should be reduced at a more negative potential than **28**, since Li is less electronegative than H. In presence of Bu₄N⁺ the radical **31** is further reduced to the tetrabutylammonium enediolate **33** or in the presence of Li⁺ to the lithium enediolate **34**; both, as well as possibly formed **32**, are subsequently protonated to **11**.

In the presence of acid the protonation to **31** and the second electron transfer occurs rapidly. No reoxidation was detected at a scan rate of 100 V s⁻¹. In the absence of acid, when the reduction is partially chemically revers-

Table 8. Yields and diastereoselectivities in the reduction of **1**^a and **3–8**^a in acetonitrile–pivalic acid^b–LiBF₄^c at –20 °C.

Entry	Substrate	Substituent R of α -ketoacid	Potential ^d /V	Current consumption/F	Yield (%) ^e	de (%)
1	3	CH ₃	–1.24	3.2	47	50
2	4	CH ₃ CH ₂	–1.28	3.2	47	70
3	5	(CH ₃) ₂ CH	–1.24	3.0	70	62
4	6	(CH ₃) ₃ C	–1.80	3.1	70	55
5	1	C ₆ H ₅	–1.27	3.0	70	78
6	7	2-C ₄ H ₃ O	–1.15	3.0	65	64
7	8	2-C ₄ H ₃ S	–1.09	2.9	71	62

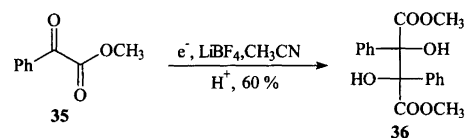
^a0.032 mol l⁻¹. ^b0.117 mol l⁻¹. ^c0.2 mol l⁻¹. ^dVs. Ag/AgCl/LiClO₄ (0.1 mol l⁻¹). ^eIsolated yield after separation by flash chromatography.

Fig. 2. X-Ray structure of (*R*)-**16**.Fig. 3. X-Ray structure of (*R*)-**17**.Fig. 4. X-Ray structure of (*S*)-**18**.Fig. 5. X-Ray structure of (*S*)-**15**.Table 9. Chemical shifts of 2-H at the new stereogenic center for the major and minor diastereomer of **11** and **13–18**.

Compound	Major diastereomer δ (ppm) ^a	Minor diastereomer δ (ppm) ^a
11	6.23 (<i>R</i>)	6.18 (<i>S</i>)
13	5.18 (<i>R</i>)	5.05 (<i>S</i>)
14	5.04 (<i>R</i>)	4.92 (<i>S</i>)
15	5.02 (<i>R</i>)	4.93 (<i>S</i>)
16	5.19 (<i>R</i>)	5.03 (<i>S</i>)
17	6.31 (<i>R</i>)	6.28 (<i>S</i>)
18	6.55 (<i>S</i>) ^b	6.49 (<i>R</i>) ^b

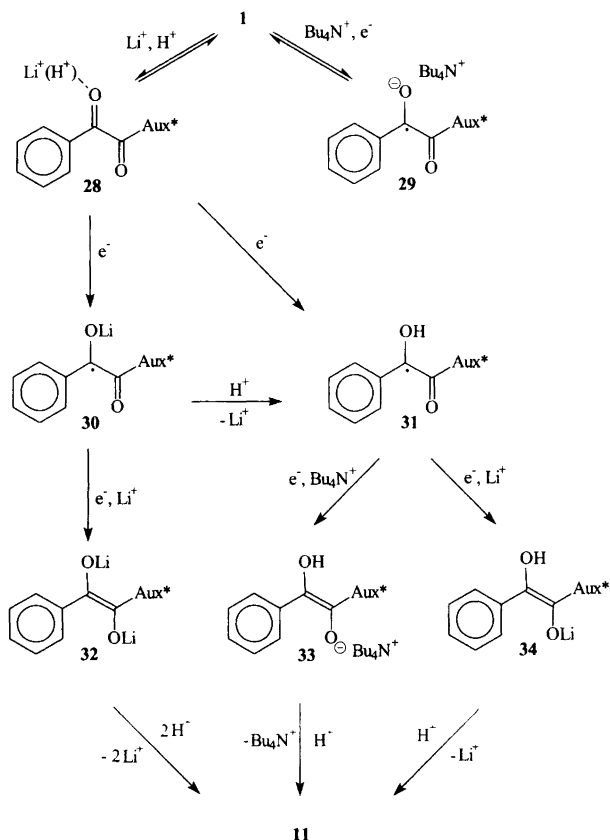
^aConfiguration at C-2. ^b(*S*)-Configuration due to priority of 2-thienyl > 2-oxazolidinone.

ible, **29** either undergoes a very slow protonation by residual water and/or undergoes dimerization. Preliminary experiments with methyl phenylglyoxalate **35** show that **35** can be hydrodimerized in aprotic medium¹⁶ [eqn. (4)].



(4)

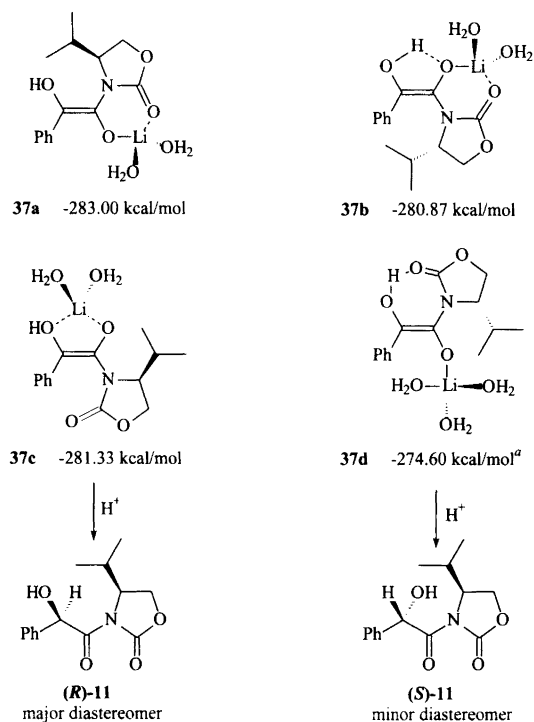
The diastereoselectivity of the reduction increases, when the polar solvent methanol is replaced by the less polar solvent acetonitrile, when the less electrophilic cation Bu₄N⁺ is replaced by the more electrophilic cation Li⁺ or Mg²⁺, when the bulkiness of the acid is increased,



Scheme 1. Proposed mechanism for the reduction of **1** to **11**.

and when the temperature is decreased. The diastereoselectivity is also remarkably influenced by the substituent R in the 2-oxoacyloxazolidinones.

The selective formation of one diastereomer occurs most probably in the final protonation of **33** or **34**. Face-selective or enantio-selective protonation of anions has been the subject of intensive research in recent years and some evidence on the features of diastereo- and enantio-selective control of this process has emerged.¹⁷ In face-selective protonation induced by an auxiliary the proton is transferred to the less shielded side of the enolate. Protonation of enolates of conjugated acids with pK_a -values >20 by acids with pK_a -values <5 is an exergonic process with an early transition state. By applying the Hammond principle, the reaction should proceed preferentially via the stereoisomer of **34**, which has the lowest ground state energy. Quantum chemical calculations (MOPAC 7.0/MOPAC 93, method: PM3, keywords: GNORM=0.1 EF PRECISE [XYZ]) have led to the structures **37a–37d** with the corresponding energies (Scheme 2). To simplify the calculations water instead of acetonitrile was used as the ligand for the lithium cation. This way the number of atoms in the calculation is reduced by 6 or 9, respectively, and the relative stabilities are not affected by this simplification. The calculations reveal that **37a** has the lowest energy and thus should predominate. As the *Re*-side of **37a** is partially shielded by the isopropyl group, it should be preferentially pro-



Scheme 2. Calculated geometries of stereoisomers **37a–d** of the intermediate enediolate **34** and their protonation. ${}^a\Delta H_f$ (H_2O) = -53.43 kcal mol $^{-1}$ and the coordination energy for the third H_2O ΔH_{coord} (3rd H_2O) = -11 ± 2 kcal mol $^{-1}$ (based on PM3 calculations) were subtracted from the calculated ground state enthalpy of **37d**.

tonated from the *Si*-side, which would lead to (*R*)-**11** as major diastereomer, as was found experimentally.

This assumption is supported by the result that Li^+ or Mg^{2+} (Table 4) leads to a much higher diastereoselectivity than Bu_4N^+ . Complex formation of the electrophilic Li^+ or Mg^{2+} with the carbonyl group of the oxazolidinone favors a preferred conformation of the oxazolidinone ring versus the enediolate (as shown in **37a–d**), which leads preferentially to (*R*)-**11**. With the less electrophilic Bu_4N^+ the stereoisomers of **33** should be less fixed, leading to decreased diastereoselectivity. The increase in the diastereoselectivity with Li^+ concentration (Table 6) could be due to a more favorable equilibrium for **37** than for species where Li is replaced by H .

The complex formation is also supported by the increase in diastereoselectivity effected by decreasing the solvent polarity (Table 2). Owing to less competition from the solvent for complexation of the cation and the lower polarity of the medium, the complex should be tighter.

The diastereoselectivity increases with the bulkiness of the proton donor (Table 3). This also supports the assumption mentioned above, because it should lead to a higher steric interaction of the proton donor with the 4-isopropyl group in the oxazolidinone and thus increase the face-selectivity. However, this effect must be analyzed

in more detail with regard to other factors, e.g. pK_a -values or dimer formation, because the interaction of adamantane-1-carboxylic acid, which also bears a quaternary α -carbon, is much less pronounced in this respect. The use of less acidic proton donors, as explored with 2,6-DMP, might possibly lead to a higher diastereoselectivity as the transition state is more advanced and thus the steric interaction of the acid and **34** is stronger. However, in this case a new product **27** was formed, whose configuration and diastereomeric excess will be established in future investigations.

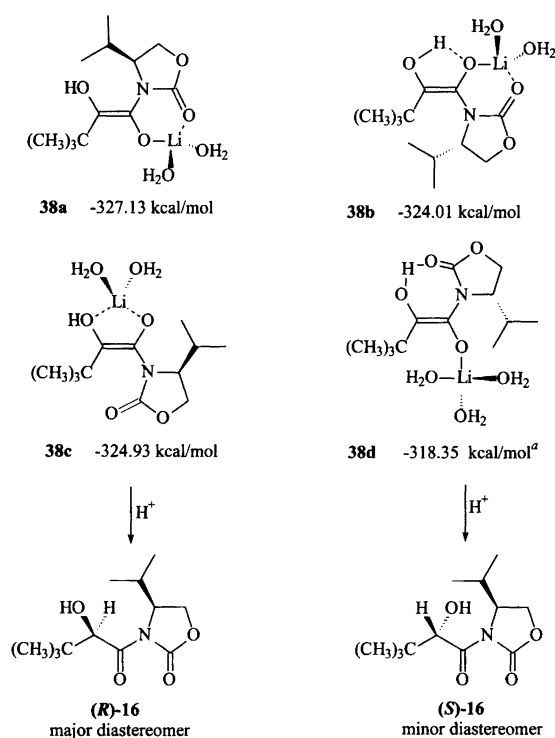
Another significant parameter influencing the diastereoselectivity is the reaction temperature. The product distribution of a kinetically controlled reaction depends on the difference in the free activation enthalpy of the transition states. Using the Arrhenius equation, k_1/k_2 for the diastereofacial protonation of **35** correlates with $\exp(1/RT)$, which means k_1/k_2 should increase with decreasing temperature.

The diastereoselectivity depends strongly on the steric and electronic properties of the substituent R in the 2-oxo acid oxazolidinone. As shown in Table 8, the change from R = phenyl (entry 5) to R = 2-furyl (entry 6) and R = 2-thienyl (entry 7) leads to a significant decrease in diastereomeric excess. 2-Furyl and 2-thienyl exhibit a +*M*-effect, which would destabilize the anion **34**. This should lead to a more exergonic protonation and thus to an earlier transition state with less interaction between the acid and the auxiliary.

No linear effects related to the successive increase of the bulkiness of alkyl substituents in the 2-oxoacyloxazolidinones have been found. The increase in the diastereomeric excess observed for substitution of R = CH₃ (50% de) against R = CH₃CH₂ (70% de) could indicate the increasing portion of the proposed *E*-enolate, e.g. **38a** (Scheme 3) relative to the *Z*-enolate, e.g. **38b**. Making the reasonable assumption that this proportion should further shift in favor of the *E*-enolate with increasing bulkiness of the substituent R, an increase of diastereoselectivity would be expected. However, the opposite is found: the change from R = CH₃CH₂ to R = (CH₃)₂CH (Table 8, entry 3) results in a decrease from 70% to 62% de. Substitution by R = (CH₃)₃C (entry 4) leads to a further decrease to 55% de. It could, however, be that the increasing bulkiness of R leads to increased shielding of both faces of the enediolate and thus decreases the face-selectivity of the isopropyl group. PM3 calculations of the ground-state energies of the enolate isomers **38a–d** with R = *tert*-butyl instead of phenyl show that **38a** is again the most stable stereoisomer. **38a** is 3 kcal mol⁻¹ more stable than **38b**.

Experimental

General. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from potassium and sodium, respectively. Dichloromethane was distilled from calcium hydride under argon. Inorganic chemicals were used without



Scheme 3. Calculated geometries of stereoisomers **38a–d** of the proposed intermediate enediolate and their protonation. ^a $\Delta H_f(\text{H}_2\text{O}) = -53.43$ kcal mol⁻¹ and the coordination energy for the third H₂O $\Delta H_{\text{coord}}(3\text{rd H}_2\text{O}) = -11 \pm 2$ kcal mol⁻¹ (based on PM3 calculations) were subtracted from the calculated ground state enthalpy of **38d**.

further purification and dried if necessary. Melting points (uncorrected): Kofler hot-stage. Optical rotation: Perkin-Elmer 241. IR: Bruker IFS 28 FT-IR-spectrometer. ¹H and ¹³C NMR: Bruker WM 300. MS: Finnigan-MAT 8230 (70 eV) in combination with Varian GLC 3400 and Varian Saturn 2 (ion trap) in combination with Varian GLC 3400; GLC-MS with capillary column HP 5 (25 m, 0.2 mm i.d., 0.33 μm film). GLC: Hewlett-Packard HP 5890 Series II; capillary columns HP 1 (25 m, 0.32 mm i.d., 0.3 μm film), HP 5 (25 m, 0.20 mm i.d., 0.52 μm film); Shimadzu GC-9A with integrator C-R3A, quartz capillary column Hydrodex β -LM (50 m, 0.25 mm i.d., 0.52 μm film). Flash chromatography: Silica gel 60 (Merck). Cyclic voltammetry: Metrohm/Eco Autolab System PG STAT 20 and Metrohm VA-Stand 663 V; hanging mercury drop cathode; glassy carbon rod cathode; reference electrode: Ag/AgCl/LiCl (sat.) in EtOH. Preparative electrolyses: Divided beaker-type glass cells, capacity 100 ml; platinum foil anode (2.8 cm²); mercury pool cathode (19.6 cm²); diaphragm: glass frit; reference electrode: Ag/AgCl/LiClO₄/CH₃CN; current source: Wenking HP 88 (Bank Electronic); Colora cryothermostat MC15.

X-Ray analyses. Crystallographic data (excluding structure factors) for the structures reported in this

paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 114110–CCDC 114113. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44 (1223) 336033, e-mail: deposit@ccdc.cam.ac.uk]. The first three data sets were collected with an Enraf-Nonius CAD4 diffractometer, the fourth data set on a Nonius KappaCCD diffractometer attached to a rotating anode. Programs used: data reduction MolEN, DENZO-SMN, and SORTAV, structure solution SHELXS-97, structure refinement SHELXL-97, graphics SCHAKAL-92.

X-Ray crystal structure analysis of (R)-16. Formula $C_{12}H_{21}NO_4$, $M=243.30$, $0.20 \times 0.15 \times 0.05$ mm, $a=6.602(2)$, $b=9.205(2)$, $c=21.832(6)$ Å, $V=1326.8(6)$ Å³, $\rho_{\text{calc}}=1.218$ g cm⁻³, $\mu=7.48$ cm⁻¹, empirical absorption correction via ψ scan data ($0.973 \leq C \leq 0.999$), $Z=4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda=1.54178$ Å, $T=223$ K, $\omega/2\theta$ scans, 1591 reflections collected ($-h, -k, +l$), $[(\sin\theta)/\lambda]=0.62$ Å⁻¹, 1591 independent and 965 observed reflections [$I \geq 2\sigma(I)$], 160 refined parameters, $R=0.053$, $wR^2=0.115$, max. residual electron density 0.21 (-0.28) e Å⁻³, Flack parameter $-0.4(6)$, hydrogens calculated and riding.

X-Ray crystal structure analysis of (R)-17. Formula $C_{12}H_{15}NO_5$, $M=253.25$, $0.20 \times 0.20 \times 0.10$ mm, $a=12.654(2)$, $c=6.786(1)$ Å, $V=941.0(3)$ Å³, $\rho_{\text{calc}}=1.341$ g cm⁻³, $\mu=8.87$ cm⁻¹, empirical absorption correction via ψ scan data ($0.949 \leq C \leq 0.999$), $Z=3$, trigonal, space group $P3_2$ (No. 145), $\lambda=1.54178$ Å, $T=223$ K, $\omega/2\theta$ scans, 1117 reflections collected ($+h, -k, -l$), $[(\sin\theta)/\lambda]=0.62$ Å⁻¹, 1117 independent and 1020 observed reflections [$I \geq 2\sigma(I)$], 166 refined parameters, $R=0.058$, $wR^2=0.179$, max. residual electron density 0.20 (-0.27) e Å⁻³, Flack parameter $0.3(6)$, hydrogens calculated and riding.

X-Ray crystal structure analysis of (S)-18. Formula $C_{12}H_{15}NO_4S$, $M=269.31$, $0.25 \times 0.20 \times 0.20$ mm, $a=12.701(3)$, $c=6.811(2)$ Å, $V=951.5(4)$ Å³, $\rho_{\text{calc}}=1.410$ g cm⁻³, $\mu=23.48$ cm⁻¹, empirical absorption correction via ψ scan data ($0.899 \leq C \leq 0.998$), $Z=3$, trigonal, space group $P3_2$ (No. 145), $\lambda=1.54178$ Å, $T=223$ K, $\omega/2\theta$ scans, 1130 reflections collected ($\pm h, -k, -l$), $[(\sin\theta)/\lambda]=0.62$ Å⁻¹, 1130 independent and 1048 observed reflections [$I \geq 2\sigma(I)$], 167 refined parameters, $R=0.030$, $wR^2=0.080$, max. residual electron density 0.17 (-0.16) e Å⁻³, Flack parameter $0.00(3)$, hydrogens calculated and riding.

X-Ray crystal structure analysis of (S)-15. Formula $C_{11}H_{19}NO_4$, $M=229.27$, $0.30 \times 0.30 \times 0.10$ mm, $a=7.269(1)$, $b=10.484(1)$, $c=8.094(1)$ Å, $\beta=99.41(1)^\circ$, $V=608.53(13)$ Å³, $\rho_{\text{calc}}=1.251$ g cm⁻³, $\mu=0.95$ cm⁻¹,

empirical absorption correction via SORTAV ($0.972 \leq T \leq 0.991$), $Z=2$, monoclinic, space group $P2_1$ (No. 4), $\lambda=0.71073$ Å, $T=198$ K, ϕ and ω scans, 3578 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda]=0.72$ Å⁻¹, 2679 independent and 2537 observed reflections [$I \geq 2\sigma(I)$], 150 refined parameters, $R=0.035$, $wR^2=0.091$, max. residual electron density 0.25 (-0.14) e Å⁻³, Flack parameter $0.1(8)$, hydrogens calculated and riding.

Auxiliaries 9, 10. The synthesis of the chiral auxiliaries (*S*)-**1** and (*R*)-**10** has already been described.¹⁸

2-Oxo carboicyclic acids. The acids **19–21** and **24–25** were commercially available. 3-Methyl-2-oxobutyric acid (**22**) was generated by acidification of the commercially available 3-methyl-2-oxo-butyric acid sodium salt with 10% sulfuric acid at 0 °C. The aqueous solution was extracted with diethyl ether (3×50 ml). The combined organic layers were dried (MgSO₄) and the ether was removed by rotary evaporation. The crude acid was used without further purification because of its instability. 3,3-Dimethyl-2-oxobutyric acid (**23**) was obtained by permanganate oxidation of 3,3-dimethyl-2-butanone in 39% yield (lit.¹⁴ 72%).

Oxazolidinones 1, 3–8: general procedure. 3.8 ml (44 mmol) of oxalyl chloride were added successively to an ice-cooled solution of 36 mmol of the α -keto acid **19–25** in 50 ml of dry CH₂Cl₂ under an argon atmosphere. After addition of 2 drops of dry dimethylformamide the reaction was stirred at 0 °C for 10 min and then slowly warmed to room temperature. After additional stirring for 12 h the solvent and the excess of oxalyl chloride were removed by rotary evaporation at room temperature. The crude product was then used without further purification. For the preparation of **3–5** light had to be excluded in the preparation of the acid chloride.

To a solution of 3.90 g (30 mmol) of (*S*)-4-isopropyl-1,3-oxazolidin-2-one (**9**) in 50 ml of dry THF at -78 °C were added dropwise 20.6 ml (33 mmol) of *n*-butyllithium in hexane (1.6 mol l⁻¹). The solution was stirred for 30 min at -78 °C after which the freshly prepared α -keto acid chloride was dissolved in 20 ml of dry THF and added in a single portion. The solution was warmed to room temperature, stirred for 1 h and then quenched by treatment with 50 ml of sat. aqueous NH₄Cl. The aqueous phase was extracted with dichloromethane (3×30 ml) and the combined organic layers were washed with aqueous sodium hydrogen carbonate solution (30 ml) and dried (MgSO₄). The solvent was evaporated off *in vacuo* to yield the crude products which were purified by crystallization or flash chromatography.

(*S*)-4-Isopropyl-2-oxo-N-(2-oxo-2-phenylethanoyl)-1,3-oxazolidine (**1**). 5.0 g (33 mmol) of **19** afforded after crystallization from the concentrated THF–CH₂Cl₂ mother liquor 5.2 g (67%) of **1** as white solid, m.p. 113 °C. $[\alpha]_D^{20} +116.3$ ($c=1.53$, ethanol). FT-IR (KBr):

$\tilde{\nu}$ (cm^{-1}) 1781 (s, C=O), 1700 (s, C=O), 1685 (s, C=O). ^1H NMR (CDCl_3): δ 0.97–1.02 [m, 6 H, $2 \times \text{CH}(\text{CH}_3)_2$], 2.57 [dsept, $^3J=3.8$ Hz, $^3J=6.9$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 4.31 [dd, $^3J=3.8$ Hz, $^3J=8.7$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 4.42 (t, $^3J=8.7$ Hz, 1 H, CH_2O), 4.48–4.54 (m, 1 H, CH_2O), 7.45–7.52 (m, 2 H, C_6H_5 , 3-H, 5-H), 7.58–7.65 (m, 1 H, C_6H_5 , 4-H), 7.82–7.88 (m, 2 H, C_6H_5 , 2-H, 6-H). ^{13}C NMR (CDCl_3): δ 14.7 [q, $\text{CH}(\text{CH}_3)_2$], 17.6 [q, $\text{CH}(\text{CH}_3)_2$], 28.3 [d, $\text{CH}(\text{CH}_3)_2$], 57.7 [d, $\text{CHCH}(\text{CH}_3)_2$], 65.2 (t, CH_2O), 128.9 (d, C_6H_5 , C-3, C-5), 129.1 (d, C_6H_5 , C-2, C-6), 132.4 (s, C_6H_5 , C-1), 134.5 (d, C_6H_5 , C-4), 153.6 (s, NCOO), 166.6 (s, $\text{C}_6\text{H}_5\text{COCO}$), 187.6 (s, $\text{C}_6\text{H}_5\text{COCO}$). MS (70 eV): m/z (%) 261 (2) [M^+], 105 (100) [$\text{C}_6\text{H}_5\text{CO}^+$], 77 (29) [C_6H_5^+]. $\text{C}_{14}\text{H}_{15}\text{NO}_4$ (261.28): calc. C 64.46, H 5.79, N 5.36; found C 64.44, H 5.83, N 5.52.

(*S*)-4-Isopropyl-2-oxo-N-(2-oxopropanoyl)-1,3-oxazolidine (**3**). 2.92 g (33 mmol) of **20** were converted following the general procedure. After flash chromatography (silica gel; cyclohexane–dichloromethane–ethyl acetate = 6:3:1), 4.4 g (73%) of **3** were obtained as a colorless oil. $[\alpha]_D^{20} + 77.0$ ($c=1.05$, CHCl_3). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) 1787 (s, C=O), 1724 (m, C=O), 1699 (s, C=O), 1214 (m, C–O). ^1H NMR (CDCl_3): δ 0.95 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.96 [d, $^3J=7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 2.43 (s, 3 H, CH_3CO), 4.41 [m, 4 H, $\text{CH}(\text{CH}_3)_2$, $\text{CHCH}(\text{CH}_3)_2$, CH_2O]. ^{13}C NMR (CDCl_3): δ 14.7 [q, $\text{CH}(\text{CH}_3)_2$], 17.6 [q, $\text{CH}(\text{CH}_3)_2$], 26.5 (q, CH_3CO), 28.0 [d, $\text{CH}(\text{CH}_3)_2$], 57.4 [d, $\text{CHCH}(\text{CH}_3)_2$], 65.5 (t, CH_2O), 154.1 (s, NCOO), 167.2 (s, CH_3COCO), 194.6 (s, CH_3CO). MS (70 eV): m/z (%) 199 (15) [M^+], 156 (9) [$M^+ - \text{CH}_3\text{CO}$], 128 (24) [$M^+ - \text{CH}_3\text{COCO}$], 86 (70) [$M^+ - \text{CH}_3\text{COCO} - \text{C}_3\text{H}_6$], 43 (100) [C_3H_7^+]. HRMS ($\text{C}_9\text{H}_{13}\text{NO}_4$): calc. 199.0845, found 199.0851. The elemental analysis led to deviating values owing to the inclusion of solvent.

(*S*)-4-Isopropyl-2-oxo-N-(2-oxobutanoyl)-1,3-oxazolidine (**4**). Transformation of 3.39 g (33 mmol) of **21** yielded, after purification by flash chromatography (silica gel; cyclohexane–dichloromethane–ethyl acetate = 6:3:1), 4.4 g (66%) of **4** as colorless oil. $[\alpha]_D^{20} + 16.8$ ($c=3.70$; methanol). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) 1789 (s, C=O), 1726 (m, C=O), 1698 (s, C=O), 1215 (s, C–O). ^1H NMR (CDCl_3): δ 0.95 [2 d, $^3J=6.7$ Hz, $^3J=6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.20 (t, $^3J=7.2$ Hz, 3 H, $\text{CH}_3\text{CH}_2\text{CO}$), 2.47 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 2.74 (q, $^3J=7.2$ Hz, 2 H, $\text{CH}_3\text{CH}_2\text{CO}$), 4.33 (dd, $^3J=3.8$ Hz, $^2J=7.4$ Hz, 1 H, CH_2O), 4.43 [m, 2 H, CH_2O , $\text{CHCH}(\text{CH}_3)_2$]. ^{13}C NMR (CDCl_3): δ 6.50 (q, CH_3CH_2), 14.7 [q, $\text{CH}(\text{CH}_3)_2$], 17.6 [q, $\text{CH}(\text{CH}_3)_2$], 28.3 [d, $\text{CH}(\text{CH}_3)_2$], 32.7 (t, CH_3CH_2), 57.5 [d, $\text{CHCH}(\text{CH}_3)_2$], 65.5 (t, CH_2O), 154.1 (s, NCOO), 167.6 (s, $\text{CH}_3\text{CH}_2\text{COCO}$), 198.0 (s, $\text{CH}_3\text{CH}_2\text{CO}$). MS (70 eV): m/z (%) 213 (6) [M^+], 158 (27), 142 (10), 86 (13) [$M^+ - \text{C}_2\text{H}_5\text{COCO} - \text{C}_3\text{H}_6$], 70 (16) [$M^+ - \text{C}_2\text{H}_5\text{COCO} - \text{CO}_2 - \text{CH}_3 + \text{H}$], 57 (100) [$\text{C}_2\text{H}_5\text{CO}^+$], 43 (22) [C_3H_7^+]. $\text{C}_{10}\text{H}_{15}\text{NO}_4$ (213.23):

calc. C 56.33, H 7.09, N 6.57; found C 56.16, H 7.14, N 6.66.

(*S*)-4-Isopropyl-2-oxo-N-(3-methyl-2-oxobutanoyl)-1,3-oxazolidine (**5**). The conversion of 3.80 g (33 mmol) of **22** led to 1.8 g (27%) of **5**, which crystallized from the concentrated solution as a white solid after purification by flash chromatography (silica gel; petroleum ether–diethyl ether = 1:1), m.p. 67 °C. $[\alpha]_D^{20} + 93.0$ ($c=1.03$; ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1784 (s, C=O), 1719 (m, C=O), 1689 (s, C=O), 1211 (s, C–O). ^1H NMR (CDCl_3): δ 0.95 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 0.97 [d, $^3J=7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 1.25 [d, $^3J=7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.27 [d, $^3J=7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 2.49 [m, 1 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 2.93 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 4.35 [m, 3 H, $\text{CHCH}(\text{CH}_3)_2$, CH_2O]. ^{13}C NMR (CDCl_3): δ 14.6 [q, $\text{CH}(\text{CH}_3)_2$, auxiliary], 16.7 [q, $\text{CH}(\text{CH}_3)_2$], 16.9 [q, $\text{CH}(\text{CH}_3)_2$], 17.4 [q, $\text{CH}(\text{CH}_3)_2$, auxiliary], 28.3 [d, $\text{CH}(\text{CH}_3)_2$, auxiliary], 37.9 [d, $\text{CH}(\text{CH}_3)_2$], 57.5 [d, $\text{CHCH}(\text{CH}_3)_2$], 65.4 (t, CH_2O), 154.0 (s, NCOO), 167.4 [s, $(\text{H}_3\text{C})_2\text{CHCOCO}$], 201.2 [s, $(\text{H}_3\text{C})_2\text{CHCO}$]. MS (70 eV): m/z (%) 227 (23) [M^+], 168 (3), 129 (17) [$M^+ - (\text{H}_3\text{C})_2\text{CHCOCO} + \text{H}$], 86 (10) [$M^+ - (\text{H}_3\text{C})_2\text{CHCOCO} - \text{C}_3\text{H}_6$], 70 (100) [$M^+ - (\text{H}_3\text{C})_2\text{CHCOCO} - \text{CO}_2 - \text{CH}_3 + \text{H}$]. $\text{C}_{11}\text{H}_{17}\text{NO}_4$ (227.26): calc. C 58.14, H 7.54, N 6.16; found C 58.41, H 7.67, N 6.26.

(*S*)-4-Isopropyl-2-oxo-N-(3,3-dimethyl-2-oxobutanoyl)-1,3-oxazolidine (**6**). Conversion of 4.31 g (33 mmol) of **23** afforded 6.4 g (89%) of **6**, which crystallized from the concentrated THF– CH_2Cl_2 mother liquor as a white solid, m.p. 94 °C. $[\alpha]_D^{20} + 81.1$ ($c=1.04$; ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1785 (s, C=O), 1714 (s, C=O), 1688 (s, C=O), 1224 (s, C–O). ^1H NMR (CDCl_3): δ 0.94 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.96 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.31 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.48 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 4.39 [m, 3 H, $\text{CHCH}(\text{CH}_3)_2$, CH_2O]. ^{13}C NMR (CDCl_3): δ 14.7 [q, $\text{CH}(\text{CH}_3)_2$], 17.6 [q, $\text{CH}(\text{CH}_3)_2$], 26.1 [q, $\text{C}(\text{CH}_3)_3$], 28.4 [d, $\text{CH}(\text{CH}_3)_2$], 42.3 [s, $\text{C}(\text{CH}_3)_3$], 57.6 [d, $\text{CHCH}(\text{CH}_3)_2$], 65.4 (t, CH_2O), 154.0 (s, NCOO), 167.4 [s, $(\text{H}_3\text{C})_3\text{CCOCO}$], 204.5 [s, $(\text{H}_3\text{C})_3\text{CCO}$]. MS (70 eV): m/z (%) 241 (6) [M^+], 158 (28), 130 (2), 86 (35) [$M^+ - (\text{H}_3\text{C})_3\text{CCOCO} - \text{C}_3\text{H}_6$], 57 (100) [C_4H_9^+]. $\text{C}_{12}\text{H}_{19}\text{NO}_4$ (241.29): calc. C 59.73, H 7.94, N 5.81; found C 59.42, H 7.92, N 5.95.

(*S*)-4-Isopropyl-2-oxo-N-[2-(2-furyl)-2-oxoethanoyl]-1,3-oxazolidine (**7**). 4.60 g (33 mmol) of **24** were converted into **7**, which crystallized from the concentrated THF– CH_2Cl_2 mother liquor. Recrystallization from ethanol afforded 5.6 g (74%) of **7** as a white solid, m.p. 118 °C. $[\alpha]_D^{20} + 102.3$ ($c=1.15$; ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1777 (s, C=O), 1692 (s, C=O), 1673 (s, C=O), 1561 (w, C=C_{arom.}), 1464 (m, C=C_{arom.}), 1216 (s, C–O). ^1H NMR (CDCl_3): δ 1.00 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.02 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 2.57 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 4.35 (dd, $^3J=2.9$ Hz, $^2J=8.6$ Hz,

1 H, CH₂O), 4.50 [m, 3 H, CH₂O, CHCH(CH₃)₂], 6.62 (dd, ³J=1.8 Hz, ³J=3.7 Hz, 1 H, C₄H₃O, 4-H), 7.34 (d, ³J=3.7 Hz, 1 H, C₄H₃O, 3-H), 7.66 (d, ³J=1.8 Hz, 1 H, C₄H₃O, 5-H). ¹³C NMR (CDCl₃): δ 14.7 (q, CH₃), 17.7 (q, CH₃), 28.3 [d, CH(CH₃)₂], 57.8 [d, CHCH(CH₃)₂], 65.3 (t, CH₂O), 113.0 (d, C₄H₃O, C-4), 120.1 (d, C₄H₃O, C-3), 148.2 (d, C₄H₃O, C-5), 149.5 (s, C₄H₃O, C-2), 153.5 (s, NCOO), 165.1 [s, (C₄H₃O)COCO], 175.3 [s, (C₄H₃O)CO]. MS (70 eV): *m/z* (%) 251 (7) [*M*⁺], 223 (4) [*M*⁺ - CO], 180 (2), 128 (2) [*M*⁺ - C₄H₃OCOCO], 95 (100) [*M*⁺ - C₄H₃OCO], 85 (2), 69 (7). C₁₂H₁₃NO₅ (251.24): calc. C 57.37, H 5.22, N 5.58; found C 57.22, H 5.29, N 5.63.

(*S*)-4-Isopropyl-2-oxo-N-[2-(2-thienyl)-2-oxoethanoyl]-1,3-oxazolidine (**8**). 5.13 g (33 mmol) of **25** were allowed to react to give **8**. 7.0 g (87%) of **8** were isolated as a white solid after crystallization from the concentrated THF-CH₂Cl₂ mother liquor and recrystallization from ethanol. M.p. 120 °C. [α]_D²⁰ +116.9 (*c*=1.10; ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) 1786 (s, C=O), 1698 (s, C=O), 1651 (s, C=O), 1511 (m), 1470 (w, C=C_{arom.}), 1207 (s, C-O). ¹H NMR (CDCl₃): δ 0.99 (d, ³J=5.9 Hz, 6 H, CH₃), 2.55 [m, 1 H, CH(CH₃)₂], 4.33 (dd, ³J=3.1 Hz, ²J=8.6 Hz, 1 H, CH₂O), 4.45 (dd, ³J=8.4 Hz, ²J=8.6 Hz, CH₂O), 4.51 [ddd, ³J=3.3 Hz, ³J=3.6 Hz, ³J=8.4 Hz, 1 H, CHCH(CH₃)₂], 6.96 (dd, ³J=3.8 Hz, ³J=5.0 Hz, 1 H, C₄H₃S, 4-H), 7.64 (d, ³J=3.8 Hz, 1 H, C₄H₃S, 3-H), 7.81 (d, ³J=5.0 Hz, 1 H, C₄H₃S, 5-H). ¹³C NMR (CDCl₃): δ 14.8 (q, CH₃), 17.7 (q, CH₃), 28.4 [d, CH(CH₃)₂], 57.9 [d, CHCH(CH₃)₂], 65.2 (t, CH₂O), 128.5 (d, C₄H₃S, C-4), 135.2 (d, C₄H₃S, C-3), 136.2 (d, C₄H₃S, C-5), 139.2 (s, C₄H₃S, C-2), 153.3 (s, NCOO), 165.4 [s, (C₄H₃S)COCO], 179.7 [s, (C₄H₃S)CO]. MS (70 eV): *m/z* (%) 267 (2) [*M*⁺], 239 (3) [*M*⁺ - CO], 154 (1), 128 (5) [*M*⁺ - C₄H₃SCOCO], 111 (100) [C₄H₃SCO⁺], 83 (6) [C₄H₃S⁺]. C₁₂H₁₃NO₄S (267.31): calc. C 53.92, H 4.90, N 5.24; found C 53.87, H 5.02, N 5.29.

(*R*)-N-(2-Oxo-2-phenylethanoyl)-5-methyl-2-oxopyrrolidine (**2**). Under an atmosphere of argon 3.9 ml (32 mmol) of pivalic acid chloride were added to a solution of 4.8 g (32 mmol) of **19** and 4.4 ml (32 mmol) of triethylamine in 30 ml of dry dichloromethane at 0 °C and the mixture was stirred for 2 h. 1.6 g (16 mmol) of **10** and 2.0 g (16 mmol) of 4-dimethylaminopyridine dissolved in 10 ml of dry dichloromethane were added to the solution and stirring was continued for 16 h. The reaction mixture was diluted with 40 ml of ether and filtered. The filtrate was successively washed with 20 ml of saturated aqueous NaHCO₃ solution and 20 ml of brine and dried over MgSO₄. After evaporation of the solvent the residue was chromatographed on silica gel (diethyl ether-petroleum ether, 1:1) to afford 2.6 g (70%) of **2** as colorless oil, that crystallized as a white solid, m.p. 62 °C. [α]_D²⁰ +62.7 (*c*=3.7; ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) 1748 (s, C=O), 1691 (s, C=O), 1678 (s, C=O).

¹H NMR (CDCl₃): δ 1.45 [d, ³J=6.4 Hz, 3 H, CH₃], 1.75–1.90 (m, 1 H, CH₂CH₂CO), 2.25–2.48 (m, 2 H, CH₂CH₂CO, CH₂CH₂CO), 2.55–2.70 (m, 1 H, CH₂CH₂CO), 4.45–4.55 [m, 1 H, NCH(CH₃)CH₂], 7.40–7.50 (m, 2 H, C₆H₅, 3-H, 5-H), 7.55–7.62 (m, 1 H, C₆H₅, 4-H), 7.78–7.84 (m, 2 H, C₆H₅, 2-H, 6-H). ¹³C NMR (CDCl₃): δ 19.3 (q, CH₃), 26.1 [t, NCH(CH₃)CH₂], 29.9 (t, CH₂CH₂CO), 51.9 [d, NCH(CH₃)CH₂], 128.8 (d, C₆H₅, C-3, C-5), 129.0 (d, C₆H₅, C-2, C-6), 132.6 (d, C₆H₅, C-4), 134.1 (s, C₆H₅, C-1), 167.1 (s, C₆H₅COCO), 175.5 (s, NCOCH₂), 188.5 (s, C₆H₅COCO). MS (70 eV): *m/z* (%) 231 (3) [*M*⁺], 203 (13) [*M*⁺ - CO], 105 (100) [C₆H₅CO⁺], 77 (29) [C₆H₅⁺]. C₁₃H₁₃NO₃ (231.25): calc. C 67.52, H 5.67, N 6.06; found C 67.72, H 5.62, N 6.13.

General procedure for the electrolyses of 1–8. 1.76 mmol of **1–8** were dissolved in 55 ml of the electrolyte. The solution was purged with argon for 10 min and electrolyzed at controlled potential (see Table 8). After consumption of 3 F the electrolysis was stopped and the mixture worked up. Depending on the supporting electrolyte different work-up procedures were used.

Work-up procedure A (electrolytes with perchlorates as supporting electrolyte). The volume of the electrolyte was reduced to 30% by removing acetonitrile under reduced pressure at 35 °C. After addition of 150 ml of ethyl acetate the solution was successively extracted with 50 ml of 10% aqueous potassium sulfate, 2 × 50 ml of 5% aqueous potassium hydrogencarbonate and 50 ml of water. The combined aqueous phases were extracted three times with 50 ml of ethyl acetate. The combined organic layers were dried (MgSO₄) and the solvent was removed under reduced pressure.

Work-up procedure B (electrolytes containing tetrafluoroborate, hexafluorophosphate and trifluoromethane sulfonate as electrolyte). The volume of the electrolyte was reduced to 25% by removing acetonitrile under reduced pressure at 35 °C. After addition of 150 ml of ethyl acetate the solution was successively extracted with 3 × 50 ml of saturated aqueous sodium hydrogencarbonate and 50 ml of water. The combined aqueous phases were extracted three times with 50 ml of ethyl acetate. The combined organic layers were dried (MgSO₄) after which the solution was passed through a short column of silica gel and the solvent was removed under reduced pressure.

Reduction of 1 to 11. 460 mg (1.76 mmol) of **1** were electrolyzed according to the general procedure and worked up following work-up procedure A. The crude product contained (*R*)-**11** as the major diastereomer with 53–86% de (¹H NMR). Purification of the crude product by flash chromatography using dichloromethane-ethyl acetate, 15:1 afforded 273–333 mg (59–72%) (*R*)- and (*S*)-**11**.

(4*S*,2'*R*)-*N*-(2-Hydroxy-2-phenylethanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*R*)-**11**: white solid, m.p.: 110 °C. $[\alpha]_D^{20} -23.4$ ($c=1.00$, ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3559 (m, OH), 1781 (s, C=O), 1699 (s, C=O). ^1H NMR (CDCl_3): δ 0.43 [d, $^3J=6.8$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.77 [d, $^3J=6.8$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 2.17 [dsept, $^3J=3.8$ Hz, $^3J=6.8$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 4.01 (d, $^3J=8.3$ Hz, 1 H, OH), 4.11 [dd, $^3J=3.8$ Hz, $^3J=9.0$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 4.28 (t, $^2J=8.7$ Hz, 1 H, CH_2O), 4.49 (dt, $^3J=3.8$ Hz, $^2J=8.7$ Hz, 1 H, CH_2O), 6.23 (d, $^3J=8.3$ Hz, 1 H, CHOH), 7.26–7.35 (m, 3 H, C_6H_5 , 2-H, 4-H, 6-H), 7.38–7.44 (m, 2 H, C_6H_5 , 3-H, 5-H). ^{13}C NMR (CDCl_3): δ 14.0 (q, CH_3), 17.5 (q, CH_3), 27.9 [d, $\text{CH}(\text{CH}_3)_2$], 58.0 [d, $\text{CHCH}(\text{CH}_3)_2$], 63.8 (t, CH_2O), 72.4 (d, CHOH), 127.3 (d, C_6H_5 , C-2, C-6), 128.5 (d, C_6H_5 , C-3, C-4, C-5), 138.3 (s, C_6H_5 , C-1), 152.9 (s, NCOO), 174.0 [s, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 408 (4) [$M+\text{Si}(\text{CH}_3)_3$] $^+$, 320 (17) [$M^+-\text{CH}_3$], 246 (59) [$M^+-\text{OSi}(\text{CH}_3)_3$], 179 (100) [$\text{C}_6\text{H}_5\text{CHOSi}(\text{CH}_3)_3$] $^+$. $\text{C}_{14}\text{H}_{17}\text{NO}_4$ (263.29): calc. C 63.85, H 6.51, N 5.32; found C 63.91, H 6.32, N 5.41.

(4*S*,2'*S*)-*N*-(2-Hydroxy-2-phenylethanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*S*)-**11**: white solid, m.p. 97 °C. $[\alpha]_D^{20} -21.8$ ($c=0.75$, ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3427 (s, OH), 1778 (s, C=O), 1703 (C=O). ^1H NMR (CDCl_3): δ 0.89–0.93 [m, 6 H, $2\times\text{CH}(\text{CH}_3)_2$], 2.50 [dsept, $^3J=3.8$ Hz, $^3J=6.9$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.80 (br s, 1 H, OH), 4.12–4.22 [m, 2 H, $\text{CHCH}(\text{CH}_3)_2$, CH_2O], 4.31–4.37 (m, 1 H, CH_2O), 6.18 (s, 1 H, CHOH), 7.28–7.41 (m, 5 H, C_6H_5). ^{13}C NMR (CDCl_3): δ 14.5 [q, $\text{CH}(\text{CH}_3)_2$], 17.9 [q, $\text{CH}(\text{CH}_3)_2$], 28.3 [d, $\text{CH}(\text{CH}_3)_2$], 59.3 [d, $\text{CHCH}(\text{CH}_3)_2$], 63.9 (t, CH_2O), 72.7 (d, CHOH), 127.5 (s, C_6H_5 , C-2, C-6), 128.6 (s, C_6H_5 , C-3, C-4, C-5), 138.1 (s, C_6H_5 , C-1), 153.2 (s, NCOO, C-2), 173.5 (s, $\text{CH}(\text{OH})\text{CO}$, C-1). MS (70 eV): m/z (%) 408 (4) [$M+\text{Si}(\text{CH}_3)_3$] $^+$, 246 (59) [$M^+-\text{OSi}(\text{CH}_3)_3$], 179 (100) [$\text{C}_6\text{H}_5\text{CHOSi}(\text{CH}_3)_3$] $^+$. $\text{C}_{14}\text{H}_{17}\text{NO}_4$ (263.29): calc. C 63.85, H 6.51, N 5.32; found C 63.88, H 6.50, N 5.42.

Reduction of 3 to 13. 350 mg (1.76 mmol) of **3** were electrolyzed according to the general procedure and worked up following work-up procedure B. The crude product contained (*R*)-**13** as the major diastereomer with 50% de (^1H NMR). Purification of the crude product by flash chromatography using dichloromethane–ethyl acetate 9:1 afforded 166 mg (47%) (*R*)- and (*S*)-**13**.

(4*S*,2'*R*)-*N*-(2-Hydroxypropanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*R*)-**13**: colorless oil. $[\alpha]_D^{20} +102.0$ ($c=1.15$, CHCl_3). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) 3482 (s, OH), 1780 (s, C=O), 1701 (s, C=O), 1250 (m, OH, def.), 1207 (s, C–O), 1126 (s, C–O). ^1H NMR (CDCl_3): δ 0.90 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.94 [d, $^3J=7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.45 [d, $^3J=6.6$ Hz, 3 H, $\text{CH}_3\text{CH}(\text{OH})$], 2.34 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.36 (s, 1 H, OH), 4.27 (dd, $^3J=3.3$ Hz, $^2J=9.1$ Hz, 1 H, CH_2O), 4.39 (dd, $^3J=8.4$ Hz, $^2J=9.1$ Hz, 1 H, CH_2O), 4.51 [ddd, $^3J=3.3$ Hz, $^3J=7.6$ Hz, $^3J=8.4$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 5.18 [q,

$^3J=6.6$ Hz, 1 H, CHOH]. ^{13}C NMR (CDCl_3): δ 14.8 [q, $\text{CH}(\text{CH}_3)_2$], 17.7 [q, $\text{CH}(\text{CH}_3)_2$], 21.3 [q, $\text{CH}_3\text{CH}(\text{OH})$], 28.4 [d, $\text{CH}(\text{CH}_3)_2$], 58.3 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.3 (t, CH_2O), 67.2 [d, CHOH], 153.4 (s, NCOO), 176.2 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 273 (1) [M^+], 258 (48) [$M^+-\text{CH}_3$], 158 (100) [$M^+-\text{H}_3\text{CCHOCO}-\text{C}_3\text{H}_7$; ($\text{H}_3\text{C})_3\text{Si}$ -shift¹⁹], 117 (96) [$\text{CH}_3\text{CHOSi}(\text{CH}_3)_3$] $^+$, 73 (88) [$\text{Si}(\text{CH}_3)_3$] $^+$. HRMS ($\text{C}_{12}\text{H}_{23}\text{NO}_4\text{Si}-\text{CH}_3$): calc. 258.1163, found 258.1159. The elemental analysis led to deviating values owing to the inclusion of solvent.

(4*S*,2'*S*)-*N*-(2-Hydroxypropanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*S*)-**13**: colorless oil. $[\alpha]_D^{20} +63.2$ ($c=0.65$, CHCl_3). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) 3500 (s, OH), 1781 (s, C=O), 1699 (s, C=O), 1251 (m, OH, def.), 1206 (m, C–O), 1124 (m, C–O). ^1H NMR (CDCl_3): δ 0.90 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.94 [d, $^3J=7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.42 [d, $^3J=6.7$ Hz, 3 H, $\text{CH}_3\text{CH}(\text{OH})$], 2.43 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.73 (s, 1 H, OH), 4.25 (dd, $^3J=3.1$ Hz, $^2J=9.0$ Hz, 1 H, CH_2O), 4.39 (dd, $^3J=7.9$ Hz, $^2J=9.0$ Hz, 1 H, CH_2O), 4.44 [ddd, $^3J=3.1$ Hz, $^3J=3.8$ Hz, $^3J=7.9$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 5.05 [q, $^3J=6.7$ Hz, 1 H, CHOH]. ^{13}C NMR (CDCl_3): δ 14.5 [q, $\text{CH}(\text{CH}_3)_2$], 17.9 [q, $\text{CH}(\text{CH}_3)_2$], 19.7 [q, $\text{CH}_3\text{CH}(\text{OH})$], 28.3 [d, $\text{CH}(\text{CH}_3)_2$], 58.9 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.3 (t, CH_2O), 67.0 [d, CHOH], 154.1 (s, NCOO), 174.9 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 273 (1) [M^+], 258 (54) [$M^+-\text{CH}_3$], 158 (100) [$M^+-\text{H}_3\text{CCHOCO}-\text{C}_3\text{H}_7$; ($\text{H}_3\text{C})_3\text{Si}$ -shift], 117 (82) [$\text{CH}_3\text{CHOSi}(\text{CH}_3)_3$] $^+$, 73 (76) [$\text{Si}(\text{CH}_3)_3$] $^+$. HRMS ($\text{C}_{12}\text{H}_{23}\text{NO}_4\text{Si}-\text{CH}_3$): calc. 258.1163, found 258.1157. The elemental analysis led to deviating values owing to the inclusion of solvent.

Reduction of 4 to 14. 375 mg (1.76 mmol) of **4** were electrolyzed according to the general procedure and worked up following procedure B. The crude product contained (*R*)-**14** as the major diastereomer with 70% de (^1H NMR). Purification of the crude product by flash chromatography using dichloromethane–ethyl acetate 9:1 afforded 178 mg (47%) (*R*)- and (*S*)-**14**.

(4*S*,2'*R*)-*N*-(2-Hydroxybutanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*R*)-**14**: colorless oil. $[\alpha]_D^{20} +87.0$ ($c=1.05$, methanol). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) 3495 (s, OH), 1783 (s, C=O), 1699 (s, C=O), 1208 (s, C–O). ^1H NMR (CDCl_3): δ 0.89 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.94 [d, $^3J=6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.04 [t, $^3J=7.4$ Hz, 3 H, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})$], 1.61 [m, 1 H, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})$], 1.95 [m, 1 H, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})$], 2.33 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.16 (s, 1 H, OH), 4.26 (dd, $^3J=3.4$ Hz, $^2J=9.1$ Hz, 1 H, CH_2O), 4.37 (dd, $^3J=8.1$ Hz, $^2J=9.1$ Hz, 1 H, CH_2O), 4.52 [ddd, $^3J=3.4$ Hz, $^3J=3.8$ Hz, $^3J=8.1$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 5.04 [dd, $^3J=3.6$ Hz, $^3J=7.4$ Hz, 1 H, CHOH]. ^{13}C NMR (CDCl_3): δ 9.2 [q, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})$], 14.7 [q, $\text{CH}(\text{CH}_3)_2$], 17.7 [q, $\text{CH}(\text{CH}_3)_2$], 28.4 [d, $\text{CH}(\text{CH}_3)_2$], 28.5 (t, CH_3CH_2), 57.2 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.2 (t, CH_2O), 71.7 [d, CHOH], 153.3 (s, NCOO), 175.7 [s, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CO}$]. MS

(70 eV): m/z (%) 287 (1) [M^+], 272 (30) [$M^+ - \text{CH}_3$], 258 (6), 229 (24) [$M^+ - \text{CH}_3\text{CH}_2\text{CHO}$; (H_3C)₃Si-shift], 201 (18) [$M^+ - \text{CH}_3\text{CH}_2\text{CHOCO}$; (H_3C)₃Si-shift], 186 (14) [$M^+ - \text{CH}_3\text{CH}_2\text{CHO} - \text{C}_3\text{H}_7$; (H_3C)₃Si-shift], 158 (88) [$M^+ - \text{CH}_3\text{CH}_2\text{CHOCO} - \text{C}_3\text{H}_7$; (H_3C)₃Si-shift], 143 (42), 131 (100) [$\text{H}_3\text{CCH}_2\text{CHSi}(\text{CH}_3)_3^+$], 101 (10), 73 (70) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{10}\text{H}_{17}\text{NO}_4$ (215.25): calc. C 55.80, H 7.96, N 6.51; found C 55.85, H 8.11, N 6.66.

(4*S*,2'*S*)-*N*-(2-Hydroxybutanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*S*)-**14**: colorless oil. $[\alpha]_D^{20} + 76.7$ ($c = 1.10$; methanol). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) 3503 (s, OH), 1782 (s, C=O), 1704 (s, C=O), 1205 (s, C-O). ^1H NMR (CDCl_3): δ 0.90 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.94 [d, $^3J = 7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.03 [t, $^3J = 7.4$ Hz, 3 H, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})$], 1.60 [m, 1 H, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})$], 1.83 [m, 1 H, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})$], 2.44 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.44 [s, 1 H, OH], 4.29 (dd, $^3J = 3.1$ Hz, $^2J = 9.1$ Hz, 1 H, CH_2O), 4.34 (dd, $^3J = 7.6$ Hz, $^2J = 9.1$ Hz, 1 H, CH_2O), 4.44 [ddd, $^3J = 3.1$ Hz, $^3J = 3.8$ Hz, $^3J = 7.6$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 4.92 [s, 1 H, CHOH]. ^{13}C NMR (CDCl_3): δ 9.5 (q, CH_3), 14.5 [q, $\text{CH}(\text{CH}_3)_2$], 17.9 [q, $\text{CH}(\text{CH}_3)_2$], 27.2 (t, CH_3CH_2), 28.2 [d, $\text{CH}(\text{CH}_3)_2$], 58.9 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.1 (t, CH_2O), 71.8 [d, CHOH], 153.9 (s, NCOO), 174.7 [s, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 287 (1) [M^+], 272 (36) [$M^+ - \text{CH}_3$], 229 (32) [$M^+ - \text{CH}_3\text{CH}_2\text{CHO}$; (H_3C)₃Si-shift], 201 (20) [$M^+ - \text{CH}_3\text{CH}_2\text{CHOCO}$; (H_3C)₃Si-shift], 186 (22) [$M^+ - \text{CH}_3\text{CH}_2\text{CHO} - \text{C}_3\text{H}_7$; (H_3C)₃Si-shift], 158 (96) [$M^+ - \text{CH}_3\text{CH}_2\text{CHOCO} - \text{C}_3\text{H}_7$; (H_3C)₃Si-shift], 143 (46), 131 (100) [$\text{H}_3\text{CCH}_2\text{CHSi}(\text{CH}_3)_3^+$], 101 (13), 73 (96) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{10}\text{H}_{17}\text{NO}_4$ (215.25): calc. C 55.80, H 7.96, N 6.51; found C 55.89, H 7.78, N 6.48.

Reduction of 5 to 15. 400 mg (1.76 mmol) of **5** were electrolyzed according to the general procedure and worked up following work-up procedure B. The crude product contained (*R*)-**15** as the major diastereomer with 62% de (^1H NMR). Purification of the crude product by flash chromatography using dichloromethane-ethyl acetate 9:1 afforded 282 mg (70%) (*R*)- and (*S*)-**15**.

(4*S*,2'*R*)-*N*-(2-Hydroxy-3-methylbutanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*R*)-**15**: colorless oil. $[\alpha]_D^{20} + 48.5$ ($c = 1.03$, methanol). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) 3492 (s, OH), 1784 (s, C=O), 1694 (s, C=O), 1209 (s, C-O). ^1H NMR (CDCl_3): δ 0.80 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.89 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 0.93 [d, $^3J = 7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 1.13 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 2.18 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 2.32 [m, 1 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 2.90 (s, 1 H, OH), 4.26 (dd, $^3J = 3.6$ Hz, $^2J = 9.2$ Hz, 1 H, CH_2O), 4.36 (dd, $^3J = 8.5$ Hz, $^2J = 9.2$ Hz, 1 H, CH_2O), 4.54 [ddd, $^3J = 3.6$ Hz, $^3J = 3.8$ Hz, $^3J = 8.5$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 5.02 [s, 1 H, CHOH]. ^{13}C NMR (CDCl_3): δ 14.5 [q, $\text{CH}(\text{CH}_3)_2$], 14.6 [q, $\text{CH}(\text{CH}_3)_2$, auxiliary], 17.9 [q, $\text{CH}(\text{CH}_3)_2$, auxiliary], 19.8 [q, $\text{CH}(\text{CH}_3)_2$], 28.5 [d, $\text{CH}(\text{CH}_3)_2$, auxiliary], 31.8 [d, $\text{CH}(\text{CH}_3)_2$], 58.2 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.0 (t, CH_2O),

74.6 [d, CHOH], 154.3 (s, NCOO), 175.5 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 301 (1) [M^+], 286 (30) [$M^+ - \text{CH}_3$], 229 (24) [$M^+ - (\text{CH}_3)_2\text{CHCHO}$; (H_3C)₃Si-shift], 201 (18) [$M^+ - (\text{CH}_3)_2\text{CHCHOCO}$; (H_3C)₃Si-shift], 186 (7), 158 (68) [$M^+ - (\text{CH}_3)_2\text{CHCHOCO} - \text{C}_3\text{H}_7$; (H_3C)₃Si-shift], 145 (100) [$(\text{H}_3\text{C})_2\text{CHCHOSi}(\text{CH}_3)_3^+$], 143 (42), 101 (8), 73 (80) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{11}\text{H}_{19}\text{NO}_4$ (229.36): calc. C 57.62, H 8.35, N 6.11; found 57.47, H 8.10, N 6.42.

(4*S*,2'*S*)-*N*-(2-Hydroxy-3-methylbutanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*S*)-**15**: colorless oil. $[\alpha]_D^{20} + 85.2$ ($c = 1.30$, methanol). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) 3504 (s, OH), 1787 (s, C=O), 1695 (s, C=O), 1208 (s, C-O). ^1H NMR (CDCl_3): δ 0.85 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.89 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 0.94 [d, $^3J = 7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 1.07 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 2.08 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 2.48 [m, 1 H, $\text{CH}(\text{CH}_3)_2$, auxiliary], 3.24 (d, $^3J = 8.3$ Hz, 1 H, OH), 4.27 (dd, $^3J = 3.1$ Hz, $^2J = 8.8$ Hz, 1 H, CH_2O), 4.33 (dd, $^3J = 7.4$ Hz, $^2J = 8.8$ Hz, 1 H, CH_2O), 4.41 [ddd, $^3J = 3.1$ Hz, $^3J = 3.3$ Hz, $^3J = 7.4$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 4.93 [dd, $^3J = 3.6$ Hz, $^3J = 8.3$ Hz, 1 H, CHOH]. ^{13}C NMR (CDCl_3): δ 14.5 [q, $\text{CH}(\text{CH}_3)_2$], 15.3 [q, $\text{CH}(\text{CH}_3)_2$, auxiliary], 18.0 [q, $\text{CH}(\text{CH}_3)_2$, auxiliary], 19.7 [q, $\text{CH}(\text{CH}_3)_2$], 28.2 [d, $\text{CH}(\text{CH}_3)_2$, auxiliary], 31.2 [d, $\text{CH}(\text{CH}_3)_2$], 59.1 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.0 (t, CH_2O), 74.8 [d, CHOH], 153.7 (s, NCOO), 174.7 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 301 (1) [M^+], 286 (30) [$M^+ - \text{CH}_3$], 229 (24) [$M^+ - (\text{CH}_3)_2\text{CHCHO}$; (H_3C)₃Si-shift], 201 (18) [$M^+ - (\text{CH}_3)_2\text{CHCHOCO}$; (H_3C)₃Si-shift], 186 (7), 158 (68) [$M^+ - (\text{CH}_3)_2\text{CHCHOCO} - \text{C}_3\text{H}_7$; (H_3C)₃Si-shift], 145 (100) [$(\text{H}_3\text{C})_2\text{CHCHOSi}(\text{CH}_3)_3^+$], 143 (42), 101 (8), 73 (80) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{11}\text{H}_{19}\text{NO}_4$ (229.36): calc. C 57.62, H 8.35, N 6.11; found C 57.78, H 8.37, N 6.17.

Reduction of 6 to 16. 424 mg (1.76 mmol) of **6** were electrolyzed according to the general procedure and worked up following work-up procedure B. The crude product contained (*R*)-**16** as the major diastereomer with 55% de (^1H NMR). Purification of the crude product by flash chromatography using dichloromethane-ethyl acetate 9:1 afforded 299 mg (70%) (*R*)- and (*S*)-**16**.

(4*S*,2'*R*)-*N*-(2-Hydroxy-3,3-dimethylbutanoyl)-4-isopropyl-2-oxo-1,3-oxazolidine (*R*)-**16**: white solid, m.p. 98 °C. $[\alpha]_D^{20} + 50.7$ ($c = 1.10$, methanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3472 (s, OH), 1754 (s, C=O), 1704 (s, C=O), 1220 (s, C-O). ^1H NMR (CDCl_3): δ 0.92 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.95 [d, $^3J = 7.2$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.04 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.29 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 2.95 [s, 1 H, OH], 4.24 (dd, $^3J = 3.6$ Hz, $^2J = 9.1$ Hz, 1 H, CH_2O), 4.32 (dd, $^3J = 8.4$ Hz, $^2J = 9.1$ Hz, 1 H, CH_2O), 4.55 [ddd, $^3J = 3.6$ Hz, $^3J = 3.6$ Hz, $^3J = 8.4$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 5.19 [s, 1 H, CHOH]. ^{13}C NMR (CDCl_3): δ 15.0 [q, $\text{CH}(\text{CH}_3)_2$], 18.1 [q, $\text{CH}(\text{CH}_3)_2$], 25.5 [q, $\text{C}(\text{CH}_3)_3$], 28.8 [d, $\text{CH}(\text{CH}_3)_2$], 36.1 [s, $\text{C}(\text{CH}_3)_3$], 58.6 [d, $\text{CHCH}(\text{CH}_3)_2$], 63.6 (t, CH_2O), 75.0 [d, CHOH], 153.6 (s, NCOO), 174.8 [s, $\text{CH}(\text{OH})\text{CO}$].

MS (70 eV): m/z (%) 315 (1) [M^+], 300 (16) [$M^+ - \text{CH}_3$], 259 (28) [$M^+ - \text{C}_4\text{H}_8$; H-shift], 229 (30) [$M^+ - (\text{CH}_3)_3\text{CCHO}$; ($\text{H}_3\text{C})_3\text{Si}$ -shift], 202 (34) [$M^+ - \text{C}_4\text{H}_8 - \text{C}_4\text{H}_6$; H-shift], 186 (17) [$M^+ - (\text{CH}_3)_3\text{CCHO} - \text{C}_3\text{H}_7$; ($\text{H}_3\text{C})_3\text{Si}$ -shift], 159 (100) [$(\text{H}_3\text{C})_3\text{CCHOSi}(\text{CH}_3)_3^+$], 101 (10), 73 (95) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{11}\text{H}_{21}\text{NO}_4$ (243.30): calc. C 59.24, H 8.70, N 5.76; found C 59.35, H 9.11, N 5.77.

(4*S*,2'*S*)-*N*-[2-Hydroxy-3,3-dimethylbutanoyl]-4-isopropyl-2-oxo-1,3-oxazolidine (*S*)-16: white solid, m.p. 114 °C. $[\alpha]_{\text{D}}^{20} + 106$ ($c = 1.04$, methanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3547 (s, OH), 1767 (s, C=O), 1697 (s, C=O), 1206 (s, C-O). ^1H NMR (CDCl_3): δ 0.91 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 0.94 [d, $^3J = 6.9$ Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 1.01 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.45 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.21 [s, 1 H, CHOH], 4.27 (m, 2 H, CH_2O), 4.41 [ddd, $^3J = 1.7$ Hz, $^3J = 4.3$ Hz, $^3J = 6.0$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 5.02 [s, 1 H, CHOH]. ^{13}C NMR (CDCl_3): δ 14.7 [q, $\text{CH}(\text{CH}_3)_2$], 18.0 [q, $\text{CH}(\text{CH}_3)_2$], 25.6 [q, $\text{C}(\text{CH}_3)_3$], 28.5 [d, $\text{CH}(\text{CH}_3)_2$], 35.7 [s, $\text{C}(\text{CH}_3)_3$], 59.2 [d, $\text{CHCH}(\text{CH}_3)_2$], 63.9 (t, CH_2O), 75.4 [d, CHOH], 154.0 (s, NCOO), 173.7 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 315 (1) [M^+], 300 (18) [$M^+ - \text{CH}_3$], 259 (28) [$M^+ - \text{C}_4\text{H}_8$; H-shift], 229 (20) [$M^+ - (\text{CH}_3)_3\text{CCHO}$; ($\text{H}_3\text{C})_3\text{Si}$ -shift], 202 (28) [$M^+ - \text{C}_4\text{H}_8 - \text{C}_4\text{H}_6$; H-shift], 186 (15) [$M^+ - (\text{CH}_3)_3\text{CCHO} - \text{C}_3\text{H}_7$; ($\text{H}_3\text{C})_3\text{Si}$ -shift], 159 (100) [$(\text{H}_3\text{C})_3\text{CCHOSi}(\text{CH}_3)_3^+$], 101 (10), 73 (50) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{11}\text{H}_{21}\text{NO}_4$ (243.30): calc. C 59.24, H 8.70, N 5.76; found C 59.21, H 8.71, N 5.85.

Reduction of 7 to 17. 442 mg (1.76 mmol) of **7** were electrolyzed according to the general procedure and worked up following work-up procedure B. The crude product contained (*R*)-**17** as the major diastereomer with 64% de (GLC). Purification of the crude product by flash chromatography using dichloromethane-ethyl acetate 9:1 afforded 289 mg (65%) (*R*)- and (*S*)-**17**.

(4*S*,2'*R*)-*N*-[2-Hydroxy-2-(2-furyl)ethanoyl]-4-isopropyl-2-oxo-1,3-oxazolidine (*R*)-**17**: white solid, m.p. 95 °C. $[\alpha]_{\text{D}}^{20} - 7.5$ ($c = 1.50$, ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3407 (s, OH), 1781 (s, C=O), 1700 (s, C=O), 1491 (m, $\text{C}=\text{C}_{\text{arom.}}$), 1212 (s, C-O). ^1H NMR (CDCl_3): δ 0.64 (d, $^3J = 6.9$ Hz, 3 H, CH_3), 0.84 (d, $^3J = 7.2$ Hz, 3 H, CH_3), 2.13 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.87 (d, $^3J = 9.0$ Hz, 1 H, OH), 4.20 (dd, $^3J = 3.6$ Hz, $^2J = 9.1$ Hz, 1 H, CH_2O), 4.35 (dd, $^3J = 8.8$ Hz, $^2J = 9.1$ Hz, 1 H, CH_2O), 4.54 [ddd, $^3J = 3.6$ Hz, $^3J = 3.6$ Hz, $^3J = 8.8$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 6.31 [d, $^3J = 9.0$ Hz, 1 H, CHOH], 6.34 (dd, $^3J = 1.9$ Hz, $^3J = 3.3$ Hz, 1 H, 4-H), 6.46 (dd, $^3J = 3.3$ Hz, 1 H, 3-H), 7.36 (d, $^3J = 1.9$ Hz, 1 H, 5-H). ^{13}C NMR (CDCl_3): δ 14.2 (q, CH_3), 17.6 (q, CH_3), 28.0 [d, $\text{CH}(\text{CH}_3)_2$], 58.3 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.1 (t, CH_2O), 66.7 [d, CHOH], 109.5 (d, $\text{C}_4\text{H}_3\text{O}$, C-4), 110.6 (d, $\text{C}_4\text{H}_3\text{O}$, C-3), 142.7 (s, $\text{C}_4\text{H}_3\text{O}$, C-5), 150.7 (d, $\text{C}_4\text{H}_3\text{O}$, C-2), 152.8 (s, NCOO), 171.6 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 310 (10) [$M^+ - \text{CH}_3$], 236 (10) [$M^+ - \text{OSi}(\text{CH}_3)_3$], 186 (15) [$M^+ - \text{C}_4\text{H}_3\text{OCHO} - \text{C}_3\text{H}_7$; ($\text{H}_3\text{C})_3\text{Si}$ -shift], 169 (100) [$\text{C}_4\text{H}_3\text{OCHOSi}(\text{CH}_3)_3^+$], 73

(54) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{12}\text{H}_{15}\text{NO}_5$ (253.25): calc. C 56.91, H 5.97, N 5.53; found C 56.69, H 6.06, N 5.59.

(4*S*,2'*S*)-*N*-[2-Hydroxy-2-(2-furyl)ethanoyl]-4-isopropyl-2-oxo-1,3-oxazolidine (*S*)-**17**: white solid, m.p. 90 °C. $[\alpha]_{\text{D}}^{20} + 165.2$ ($c = 0.90$, ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3486 (s, OH), 1766 (s, C=O), 1701 (s, C=O), 1487 (w, $\text{C}=\text{C}_{\text{arom.}}$), 1465 (w, $\text{C}=\text{C}_{\text{arom.}}$), 1206 (s, C-O). ^1H NMR (CDCl_3): δ 0.92 (d, $^3J = 6.9$ Hz, 3 H, CH_3), 0.95 (d, $^3J = 6.9$ Hz, 3 H, CH_3), 2.50 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.90 (d, $^3J = 9.3$ Hz, 1 H, OH), 4.25 (m, 2 H, CH_2O), 4.42 [ddd, $^3J = 3.8$ Hz, $^3J = 5.0$ Hz, $^3J = 5.7$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 6.28 [d, $^3J = 9.3$ Hz, 1 H, CHOH], 6.28 (dd, $^3J = 1.8$ Hz, $^3J = 3.3$ Hz, 1 H, $\text{C}_4\text{H}_3\text{O}$, 4-H), 6.41 (dd, $^3J = 3.3$ Hz, 1 H, $\text{C}_4\text{H}_3\text{O}$, 3-H), 7.37 (d, $^3J = 1.8$ Hz, 1 H, $\text{C}_4\text{H}_3\text{O}$, 5-H). ^{13}C NMR (CDCl_3): δ 14.6 (q, CH_3), 15.0 (q, CH_3), 28.4 [d, $\text{CH}(\text{CH}_3)_2$], 59.2 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.1 (t, CH_2O), 66.7 [d, CHOH], 109.3 (d, $\text{C}_4\text{H}_3\text{O}$, C-4), 110.6 (d, $\text{C}_4\text{H}_3\text{O}$, C-3), 142.9 (d, $\text{C}_4\text{H}_3\text{O}$, C-5), 150.5 (s, $\text{C}_4\text{H}_3\text{O}$, C-2), 153.1 (s, NCOO), 171.1 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 310 (12) [$M^+ - \text{CH}_3$], 236 (35) [$M^+ - \text{OSi}(\text{CH}_3)_3$], 186 (12) [$M^+ - \text{C}_4\text{H}_3\text{OCHO} - \text{C}_3\text{H}_7$; ($\text{H}_3\text{C})_3\text{Si}$ -shift], 169 (100) [$\text{C}_4\text{H}_3\text{OCHOSi}(\text{CH}_3)_3^+$], 73 (50) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{12}\text{H}_{15}\text{NO}_5$ (253.25): calc. C 56.91, H 5.97, N 5.53; found C 57.27, H 5.85, N 5.60.

Reduction of 8 to 18. 470 mg (1.76 mmol) of **8** were electrolyzed according to the general procedure and worked up following work-up procedure B. The crude product contained (*S*)-**18** as the major diastereomer with 62% de (^1H NMR). Purification of the crude product by flash chromatography using dichloromethane-ethyl acetate 9:1 afforded 336 mg (71%) (*S*)- and (*R*)-**11**.

(4*S*,2'*S*)-*N*-[2-Hydroxy-2-(2-thienyl)ethanoyl]-4-isopropyl-2-oxo-1,3-oxazolidine (*S*)-**18**: white solid, m.p. 122 °C. $[\alpha]_{\text{D}}^{20} + 32.2$ ($c = 0.98$, ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3404 (s, OH), 1777 (s, C=O), 1694 (s, C=O), 1489 (m, $\text{C}=\text{C}_{\text{arom.}}$), 1212 (s, C-O). ^1H NMR (CDCl_3): δ 0.58 (d, $^3J = 6.9$ Hz, 3 H, CH_3), 0.84 (d, $^3J = 7.2$ Hz, 3 H, CH_3), 2.25 [m, $^3J = 7.2$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.99 (d, $^3J = 8.8$ Hz, 1 H, OH), 4.21 (dd, $^3J = 3.7$ Hz, $^2J = 8.8$ Hz, 1 H, CH_2O), 4.35 (dd, $^3J = 8.6$ Hz, $^2J = 9.1$ Hz, 1 H, CH_2O), 4.53 [ddd, $^3J = 3.6$ Hz, $^3J = 3.8$ Hz, $^3J = 8.6$ Hz, 1 H, $\text{CHCH}(\text{CH}_3)_2$], 6.55 [d, $^3J = 8.8$ Hz, 1 H, CHOH], 6.96 (dd, $^3J = 3.3$ Hz, $^3J = 5.0$ Hz, 1 H, $\text{C}_4\text{H}_3\text{S}$, 4-H), 7.18 (d, $^3J = 3.3$ Hz, 1 H, $\text{C}_4\text{H}_3\text{S}$, 3-H), 7.28 (d, $^3J = 5.0$ Hz, 1 H, $\text{C}_4\text{H}_3\text{S}$, 5-H). ^{13}C NMR (CDCl_3): δ 14.3 (q, CH_3), 17.6 (q, CH_3), 28.1 [d, $\text{CH}(\text{CH}_3)_2$], 58.2 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.1 (t, CH_2O), 68.3 [d, CHOH], 126.1 (d, $\text{C}_4\text{H}_3\text{S}$, C-4), 126.6 (d, $\text{C}_4\text{H}_3\text{S}$, C-3), 126.8 (d, $\text{C}_4\text{H}_3\text{S}$, C-5), 141.5 (s, $\text{C}_4\text{H}_3\text{S}$, C-2), 153.0 (s, NCOO), 173.2 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 269 (19) [M^+], 166 (17), 140 (10) [$M^+ - \text{C}_4\text{H}_3\text{SCHOCO}$; H-shift], 130 (48), 124 (34), 113 (100) [$\text{C}_4\text{H}_3\text{SCHOH}^+$], 96 (20), 86 (44), 71 (16). $\text{C}_{12}\text{H}_{15}\text{NO}_4\text{S}$ (269.32): calc. C 53.52, H 5.61, N 5.20; found C 53.71, H 5.57, N 5.30.

(4*S*,2'*R*)-*N*-[2-Hydroxy-2-(2-thienyl)ethanoyl]-4-isopropyl-2-oxo-1,3-oxazolidine (*R*)-**18**: white solid, m.p. 92 °C. $[\alpha]_{\text{D}}^{20} + 139.8$ ($c = 1.01$, ethanol). FT-IR (KBr): $\tilde{\nu}$

(cm^{-1}) 3486 (s, OH), 1771 (s, C=O), 1698 (s, C=O), 1483 (m, C=C_{arom.}), 1205 (s, C-O). ^1H NMR (CDCl_3): δ 0.92 (d, $^3J=6.9$ Hz, 3 H, CH_3), 0.95 (d, $^3J=7.2$ Hz, 3 H, CH_3), 2.50 [m, 1 H, $\text{CH}(\text{CH}_3)_2$], 4.01 (d, $^3J=8.8$ Hz, 1 H, OH), 4.24 (m, 2 H, CH_2O), 4.38 [ddd, $^3J=3.8$ Hz, $^3J=4.1$ Hz, $^2J=6.4$ Hz, $\text{CHCH}(\text{CH}_3)_2$], 6.49 [d, $^3J=8.8$ Hz, 1 H, CHOH], 6.96 (dd, $^3J=3.6$ Hz, $^3J=5.2$ Hz, 1 H, $\text{C}_4\text{H}_3\text{S}$, 4-H), 7.10 (d, $^3J=3.6$ Hz, 1 H, $\text{C}_4\text{H}_3\text{S}$, 3-H), 7.29 (d, $^3J=5.2$ Hz, 1 H, $\text{C}_4\text{H}_3\text{S}$, 5-H). ^{13}C NMR (CDCl_3): δ 14.6 (q, CH_3), 17.9 (q, CH_3), 28.4 [d, $\text{CH}(\text{CH}_3)_2$], 59.3 [d, $\text{CHCH}(\text{CH}_3)_2$], 64.1 (t, CH_2O), 68.2 [d, CHOH], 126.3 (d, $\text{C}_4\text{H}_3\text{S}$, C-4), 126.6 (d, $\text{C}_4\text{H}_3\text{S}$, C-3), 126.8 (d, $\text{C}_4\text{H}_3\text{S}$, C-5), 141.1 (s, $\text{C}_4\text{H}_3\text{S}$, C-2), 153.2 (s, NCOO), 172.7 [s, $\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 326 (5) [$M^+ - \text{CH}_3$], 185 (100) [$\text{C}_4\text{H}_3\text{SCHOSi}(\text{CH}_3)_3^+$], 73 (50) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{12}\text{H}_{15}\text{NO}_4\text{S}$ (269.32): calc. C 53.52, H 5.61, N 5.20; found C 53.80, H 5.52, N 5.28.

Reduction of 2 to 12. 407 mg (1.76 mmol) of **2** were electrolyzed according to the general procedure. The crude product contained (*S*)-**12** as the major diastereomer with 37–76% de (GLC). Purification of the crude product by flash chromatography using dichloromethane–ethyl acetate 9:1 afforded 254–312 mg (62–76%) (*S*)- and (*R*)-**12**.

(*5R,2'S*)-*N*-(2-Hydroxy-2-phenylethanoyl)-5-methyl-2-oxopyrrolidine (*S*)-**12**: white solid, m.p. 134 °C. $[\alpha]_{\text{D}}^{20} -2.7$ ($c=1.0$, ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3555 (br, OH), 1740 (s, C=O), 1694 (s, C=O). ^1H NMR (CDCl_3): δ 1.18 (d, $^3J=6.4$ Hz, 3 H, CH_3), 1.58–1.68 (m, 1 H, $\text{CH}_2\text{CH}_2\text{CO}$), 2.14–2.28 (m, 1 H, $\text{CH}_2\text{CH}_2\text{CO}$), 2.35–2.59 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CO}$), 4.12 (d, $^3J=8.1$ Hz, 1 H, OH), 4.48–4.58 [m, 1 H, $\text{NCH}(\text{CH}_3)\text{CH}_2$], 6.10 (d, $^3J=8.1$ Hz, 1 H, CHOH), 7.25–7.38 (m, 5 H, C_6H_5). ^{13}C NMR (CDCl_3): δ 19.1 (q, CH_3), 25.3 (t, $\text{CH}_2\text{CH}_2\text{CO}$), 31.4 (t, $\text{CH}_2\text{CH}_2\text{CO}$), 53.2 [d, $\text{NCH}(\text{CH}_3)\text{CH}_2$], 73.9 (d, CHOH), 127.6 (d, C_6H_5 , C-2, C-6), 128.3 (d, C_6H_5 , C-3, C-5), 128.5 (d, C_6H_5 , C-4), 138.7 (s, C_6H_5 , C-1), 174.4 (s, NCOCH₂), 174.8 [s, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CO}$]. MS (70 eV): m/z (%) 290 (13) [$M^+ - \text{CH}_3$], 262 (2) [$M^+ - \text{CH}_3 - \text{CH}_2\text{CH}_2$], 216 (8) [$M^+ - \text{OSi}(\text{CH}_3)_3$], 179 (100) [$\text{C}_6\text{H}_5\text{CHOSi}(\text{CH}_3)_3^+$], 156 (18) [$M^+ - \text{C}_6\text{H}_5 - \text{Si}(\text{CH}_3)_3$], 90 (4) [179– $\text{OSi}(\text{CH}_3)_3$], 73 (50) [$\text{Si}(\text{CH}_3)_3^+$]. $\text{C}_{13}\text{H}_{15}\text{NO}$ (233.27): calc. C 66.94, H 6.48, N 6.00; found C 67.11, H 6.54, N 6.19.

(*5R,2'R*)-*N*-(2-Hydroxy-2-phenylethanoyl)-5-methyl-2-oxopyrrolidine (*R*)-**12**: white solid, m.p. 74 °C. $[\alpha]_{\text{D}}^{20} +51.8$ ($c=0.65$, ethanol). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3453 (s, br, OH), 1743 (s, C=O), 1679 (s, C=O). ^1H NMR (CDCl_3): δ 1.38 (d, $^3J=6.4$ Hz, 3 H, CH_3), 1.63–1.73 (m, 1 H, $\text{CH}_2\text{CH}_2\text{CO}$), 1.98–2.14 (m, 1 H, $\text{CH}_2\text{CH}_2\text{CO}$), 2.35 (dd, $^3J=1.7$ Hz, $^3J=9.3$ Hz, 1 H, $\text{CH}_2\text{CH}_2\text{CO}$), 2.58–2.74 (m, 1 H, $\text{CH}_2\text{CH}_2\text{CO}$), 4.21 (d, $^3J=8.4$ Hz, 1 H, OH), 4.36–4.47 [m, 1 H, $\text{NCH}(\text{CH}_3)\text{CH}_2$], 6.05 (d, $^3J=8.4$ Hz, 1 H, CHOH), 7.26–7.39 (m, 5 H, C_6H_5). ^{13}C NMR (CDCl_3): δ 19.1 (q, CH_3), 25.2 (t,

$\text{CH}_2\text{CH}_2\text{CO}$), 31.3 (t, $\text{CH}_2\text{CH}_2\text{CO}$), 53.9 [d, $\text{NCH}(\text{CH}_3)\text{CH}_2$], 73.8 (d, CHOH), 127.5 (d, C_6H_5 , C-2, C-6), 128.2 (d, C_6H_5 , C-3, C-5), 128.4 (d, C_6H_5 , C-4), 138.6 (s, C_6H_5 , C-1), 174.0 (s, NCOCH₂), 174.8 [s, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CO}$]. MS (70): m/z (%) 290 (25) [$M^+ - \text{CH}_3$], 216 (100) [$M^+ - \text{OSi}(\text{CH}_3)_3$], 179 (95) [$\text{C}_6\text{H}_5\text{CHOSi}(\text{CH}_3)_3^+$]. $\text{C}_{13}\text{H}_{15}\text{NO}_3$ (233.27): calc. C 66.94, H 6.48, N 6.00; found C 66.99, H 6.39, N 6.05.

Cleavage of the amides (*R*)-11 and (*S*)-12. Under an argon atmosphere 221 mg (0.84 mmol) of (*R*)-**11** were dissolved in 15 ml of methanol. At 0 °C 74 mg (1.37 mmol) of sodium methoxide were added to the solution in a single portion. After being stirred for 60 min at 0 °C the reaction was quenched with 60 ml water. The aqueous layer was extracted with ethyl acetate (3 × 20 ml) and the combined organic layers were dried (MgSO_4). Purification of the crude product by flash chromatography (petroleum ether–diethylether 2:1) afforded (*R*)-**26** in 56% yield, m.p. 54 °C. $[\alpha]_{\text{D}}^{20} +140$ ($c=1.1$, methanol). A similar result was obtained for (*S*)-**12**.

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