Applications of the Chiral Auxiliaries DIOZ and TRIOZ for Conjugate Additions and Comparison with Other Auxiliaries

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A number of *N*-acryloyl-, *N*-crotonoyl-, *N*-(3,3,3-trifluorocrotonoyl)-, *N*-cinnamoyl-, and *N*-(3nitroacryloyl)-4-isopropyl- or -4-phenyl-oxazolidin-2-ones with *geminal* diphenyl substitution, *i.e.*, **7**–**15**, have been prepared and used for conjugate additions of organocuprate reagents (Me, ⁱPr, Ph, 4-MeOPh) in the β -carbonyl (*Table 2*) and in the α -carbonyl position (NO₂-derivative **11** in *Scheme 3*). The yields and diastereoselectivities are compared with previously tested enoyl-oxazolidinones (*Table 2*). Highest diastereoselectivities (>90%) are always observed with the 4-Ph derivatives (*Hruby* effect). Nitroacryloyl-oxazolidinones and a corresponding phenylmenthol ester undergo less diastereoselective additions (*Scheme 3*). A 3-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (DIOZ)-derived Li₂-enolatenitronate was also tested for α -carbonyl alkylation (*Scheme 4*). The X-ray crystal structures of three acryloyl-oxazolidinones and of four adducts are described (*Tables 1* and 3), and they serve for configurational assignments and description of the stereochemical courses of the additions and alkylation. Possible applications of the nitro compounds for the preparation of β^2 -amino acids are discussed (*Scheme 2*).

1. Introduction. – Overall enantioselective *Michael* additions using a chiral auxiliary group (now rivaled by organocatalytic methods [1]) have been achieved by acylating chiral heterocycles with an α,β -unsaturated carboxylic acid derivative, performing a diastereoselective conjugate addition and cleaving off the auxiliary (preferably with

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recovery!) (*Scheme 1*). The most commonly used auxiliaries are the oxazolidinones popularized by *D. Evans* [2]. It turned out that, as compared to the simple value- or phenylalanine-derived oxazolidinones **1**, the geminally disubstituted derivatives **2** [3] and **3** [4]⁶) have certain general advantages (amply discussed in the literature [3-5]). In the *Michael* addition outlined in *Scheme 1*, it turned out that the phenylglycine-derived auxiliaries **1** and **2**, R = Ph, give highest diastereoselectivities (R^{Nu}MgBr/CuBr as nucleophiles) [3a][6]⁷); the 4,5,5-triphenyloxazolidin-2-one (**4**; TRIOZ) had, so far, not been used for this purpose.

Scheme 1. Principle of Enantioselective Michael Additions Using a Chiral Auxiliary Group



2. Preparation of the Starting Materials. – We have now prepared a number of oxazolidinone derivatives 5-15 and the phenylmenthol derivative 16 of α,β -unsaturated carboxylic acids, to test and compare the reactivities and diastereoselectivities in *Michael* additions to their enoylic (*i.e.*, 5, 7–10, and 12–15) or nitroolefinic (*i.e.*, 6 and 11) C=C bonds.

The substrates 5-16 for conjugate additions were prepared according to known procedures: the *classical Evans*-type acryloyl-oxazolidinone 5 [2b][7] was nitrated

⁶) Besides our group [4], the groups of *Gibson et al.* [5b], and *Davies* and wo-workers [3b] have also tested auxiliary **3**. In two papers and in a patent, the preparation of **3** has been described previously [3g][5]. The term DIOZ (=3-(1-methylethyl)-5,5-diphenyloxazolidin-2-one) for compound **3** was first used in an advertisement of the *Shiratori Pharmaceutical Company*, which offered both enantiomers for sale.

⁷⁾ A SciFinder search for N-enoyl-4-phenyloxazolidinone 1 (R=Ph) produced 200 references, 28 alone by *Hruby* and co-workers, who had first reported the superiority of this auxiliary for *Michael* additions [6].



 $(\rightarrow 6)$ by addition of NO₂Cl to the C=C bond, followed by HCl elimination with AcONa as base [8]. With a similar procedure⁸) acryloyl-DIOZ 7 gave nitro compound 11 (for crystal structure, see *Table 1*). The enoyl-oxazolidinones 7–10 and 12–15 were prepared⁹) from the corresponding parent heterocycles 3 (DIOZ) or 4 (TRIOZ), and enoyl-chlorides or anhydrides, as described in the literature [4a] and in the *Exper. Part.* The phenylmenthol-derived¹⁰) nitro-acrylate 16 was obtained according to a published procedure [9]. X-Ray crystal structures of the acryloyl-oxazolidinones 5, 11, and 12, are shown in *Table 1*. As in numerous published structures of other 3-acyl-oxazolidinones and as in the product structures, also listed in *Table 1*, the exocyclic N–CO bond has s-*trans* configuration, with OC(2)–N–C(1')=O torsion angles close to 180°.

3. Conjugate Additions to the Cinnamoyl- and Crotonoyl-Oxazolidinones 8–10, 13–15. – All reactions were carried out with excess organocuprates as nucleophiles, generated from *Grignard* reagents MeMgBr, PhMgBr, or 4-MeOPhMgBr and CuBr· SMe₂ (ratio 2:1)¹¹). In *Table 2*, the yields and diastereoselectivities are listed, together with values reported in the literature for analogous additions to enoyl-oxazolidinones (*Entries 1–7*) other than DIOZ and TRIOZ derivatives (*Entries 8–17*). With the

¹⁰) Phenylmenthol was introduced as a chiral auxiliary by *Corey* and *Ensley* [9a].

⁸⁾ We did not succeed in preparing the corresponding nitro-acryloyl-TRIOZ from acryloyl-TRIOZ 12.

⁹⁾ Compound 7 was first prepared (59% yield) by *Meinrad Brenner* (ETH-Zürich Dissertation No. 14409, 2001), using the anhydride method. Most acrylations were carried out by first treating DIOZ or TRIOZ, with BuLi or MeMgBr, and then with the corresponding acid chloride.

¹¹) The copper trick for directing *Grignard* reagents from the 1,2- to the 1,4-mode of addition to α,β unsaturated carbonyl compounds was introduced by *Kharash* and *Tawney* [10a]. For leading references to the use of CuBr · SMe₂, see [10b].







Table 1 (cont.)



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Table 2. Examples of Diastereoselective Conjugate Additions of Grignard Reagents/CuBr·SMe₂ to 3-Enoyl-4-benzyl-, -4-isopropyl-, and -4-phenyl-Substituted Oxazolidinones from the Literature (Entries 3 – 9) and from the Present Investigation (Entries 1, 2, and 10-17). Some of the data (Entries 1, 2, and 11) are taken from [11], with no experimental details given herein. In all cases, the solution of the Michael acceptor was added to the organometallic reagent at low temperatures (-30° in THF). For the X-ray crystal structure of *epi*-19, see Table 1. All diastereoisomer ratios A/*epi*-A and B/*epi*-B were determined by NMR peak integrations with the crude products. The yields are total yields of major and minor products of type A or B. In most cases, recrystallization led to diastereoisomerically pure samples of the major isomer (see Exper. Part).



Entry	Starting material	Product				
		Major	No.	Yield [%]	Ratio A/epi-A B/epi-B	Ref.
4		O O Ph O N H H H Ph		90	99:1	[6]
5		O O N H H Ph		90	74:26	[6]
6		O O Ph O N Me Me Me Ph		67	97:3	[3a]
7		O O Me O N Ph Me Ph		87	96:4	[3a]
8	(S)- 8	O O Ph O N Me Ph Ph		86 92	67:33 70:30	[4a] [11]
9	(S)- 9	O MeO N $PhPh$ Ph Ph		90	67:33	[4a]
10	(S)- 9	O $C_6H_4-4-OMe$ O N Ph Ph Ph Ph Ph Ph Ph Ph	18	88	85:15	this work
11	(S)- 10	O $PhO N C_6H_4-4-OMePh$ Ph Ph Ph Ph Ph Ph Ph	epi- 18	78	82:18	this work
12	(<i>R</i>)- 13	O O Ph O N Me Ph	19	53 71	98:2 96:4	[11] this work

Table 2 (cont.)

Table 2	(cont.)					
Entry	Starting material	Product				
		Major	No.	Yield [%]	Ratio A/epi-A B/epi-B	Ref.
13	(<i>R</i>)- 13	$\begin{array}{c c} O & O & C_{6}H_{4}-4-OMe \\ O & & Me \\ O & & Me \\ Ph & & Ph \\ Ph & Ph \end{array}$	20	74	91:9	this work
14	(<i>S</i>)-14	O O $MeCF_3Ph$ Ph Ph	21	55	61:39	this work
15	(<i>S</i>)-14	O $PhO CF_3Ph$ Ph Ph	22	60	69:31	this work
16	(<i>R</i>)-15	O O Me O N Ph Ph Ph Ph	epi- 19	71 68	93 : 7 96 : 4	[11] this work
17	(S)-15	$\begin{array}{c} O & O & C_6H_4-4-OMe \\ O & & & Ph \\ Ph & & Ph \\ Ph & Ph \\ Ph & Ph \end{array}$	23	64	97:3	this work

exception of the CF₃-substituted acceptors (*Entries 14* and *15*), the diastereoselectivities of addition to 3-enoyl-4-phenyl-oxazolidinones are above 90%; with ⁱPr groups in the 4-position, the selectivities tend to be near 2:1 (*Entries 8* and 9) or 4:1 (*Entries 10* and *11*); the yields are moderate to excellent; the configurations of the major products as shown in **A** and **B** (*Table 2*) are assigned by analogy with literature assignments, and in one case (*epi-19, Entry 16* of *Table 2*) by X-ray-structure analysis (see *Table 1*)¹²).

¹²) This is compatible with the assumption that a metal complex of the enoyl-oxazolidinone of s-*cis*configuration around the exocyclic N–CO bond [2] is approached by the nucleophile from the face of the trigonal β -carbonyl C-atom that is remote from the R group at C(4) of the heterocycle, as shown here for an (*S*)-oxazolidinone derivative (see **i**).



In view of the fact that the TRIOZ derivatives (*Entries* 12-17 of *Table* 2) do not seem to perform better than simpler 3-enoyl-4-phenyl-oxazolidinones (*Entries* 4-7), the advantage of using TRIOZ as an auxiliary for overall enantioselective conjugate additions (*Scheme* 1) remains to be the high crystallization tendency of its derivatives and the facile removal of this auxiliary group (similar to that of DIOZ [4a,e]).

4. Experiments with the NO₂ Derivatives 11, 16, and 26. – In our pursuit of new routes to β^2 -amino acids [4h], we have now employed *N*-(nitropropenyl)- and *N*-(nitropropanoyl)-oxazolidinones in two processes, which are related by *umpolung* [12] (*Scheme 2*): with respect to the C=O group, conjugate addition of a nucleophile to a 3-nitroacrylate system, where C=C-NO₂ is a much stronger *Michael* acceptor than C=C-COR, constitutes an *umpolung* (nucleophilic attack occurs in the α -carbonyl, rather than in the β -carbonyl position; see *Route a* in *Scheme 2*). On the other hand, a doubly deprotonated nitropropanoate system is attacked by *electrophiles* in β -position to the N-atom (an enolate is more reactive than a nitronate; see *Route b* in *Scheme 2*) [13].





Removal of the auxiliary from the 'common' product and hydrogenation of the NO₂ group will lead to β^2 -amino acid derivatives of the same general type, but with the R group stemming from a nucleophilic reagent (R-metal) in the first case (*Route a*) and from an electrophilic reagent (R-X) in the second case (*Route b*). Thus, the two transformations *a* and *b* are an *umpolung* of each other.

The results of addition of organomagnesium and organozinc reagents (in the presence of Cu^I salts) to nitroacryloyl derivatives **11** and **16** are shown in *Scheme 3*. The yields are generally modest, and so are the diastereoselectivities. In most cases, pure samples were prepared by flash chromatography and/or recrystallization. The configurations of two adducts, *i.e.*, **24a** and **24c**, to the nitroacryloyl-oxazolidinone **11** and of one of the adducts, **25c**, to the nitroacrylate ester **16** were determined by X-ray crystal-

Scheme 3. Conjugate Addition of Mg/Cu and Zn/Cu Reagents to N-3-(Nitroacryloyl)-DIOZ 11 and to the 3-Nitroacrylate Ester 16 of Phenylmenthol. All reactions were carried out in THF at dry-ice temperature, by adding a soln. of the nitro compound to the organometallic reagent. The yields of 24a – 24c and 25c refer to materials obtained after recrystallization. The yields of 25a and 25b are those obtained after flash chromatography. The dr values were determined by NMR spectroscopy of the crude products. For X-ray-crystal structures of 24c and 25c, see Table 1.



structure analysis (*Table 1*); the configurations of the three major products **24b**, and **25a** and **25b** are assigned by analogy¹³)¹⁴).

¹³) As in the case of 'normal' conjugate additions to 3-enoyl-oxazolidinones (*Table 2* and *Footnote 12*), the stereochemical course of reaction is compatible with the assumption that the R group of the organometallic reagent is preferentially transferred from the face opposite to the ⁱPr group at C(4) of a metal complex with s-*cis*-configuration around the exocyclic N–CO bond (see ii). The reversal observed with the Zn reagent (→ mainly *epi-24b*) may be taken as an indication that there is no metal chelation in this case, *i.e.*, the acylated oxazolidinone reacts in its preferred 'dipol-minimized' s-*trans* configuration [2] with an *anti*-arrangement of the 2 C=O groups (*cf.* the crystal structures in *Table 1* and the discussion in *Sect. 2*, above).



¹⁴) The stereochemical course of reactions of phenylmenthol derivatives is commonly explained by assuming steric hindrance of a π -face by the neighboring Ph group (' π -stacking'; see textbooks of stereochemistry, *e.g.*, [14]). This is in agreement with the assigned configuration of our major diastereoisomers **25a**-**c** (see **iii**).



Scheme 4. Methylation of the Li2-Enolate/Nitronate of N-(3-Nitropropanoyl)-DIOZ 26 with MeI



Finally, we have prepared the *N*-(nitropropanoyl)-DIOZ **26**, which was methylated through a dilithio derivative to give product **24a** (*Scheme 4*), identical with the sample obtained by methylcuprate addition to the nitroacryloyl-DIOZ **11** (*cf. Scheme 3*)¹⁵). Other, less reactive alkylating reagents, such as BnBr, gave only traces of desired product. This may not be surprising, in view of the previously observed [3b][4a] rather poor yields of Li-enolate alkylations using 5,5-diphenyl-substituted oxazolidinone derivatives¹⁶). Further experiments with other auxiliaries are in progress, in the hope that this attractive general approach to β^2 -amino acid¹⁷) precursors may eventually become general and practical.

5. Conclusions. – The triphenyl-oxazolidinone auxiliary TRIOZ has turned out to give higher diastereoselectivities in conjugate additions, and the nitroacryloyl-DIOZ may be used for diastereoselective preparations of β^2 -amino acid precursors. The yields and selectivities observed with the DIOZ and TRIOZ derivatives are not better than those reported for analogous auxiliaries, including phenylmenthol, so that the main

¹⁶) This is caused by the instability of the Li-enolates of this type with respect to Li-oxazolidinone elimination $iv \rightarrow v$ (recovery and *N*-alkylation of DIOZ!), a process, which does not occur with the corresponding Ti-enolates [4] (and which is less pronounced, with the analogous 5,5-dimethyl-substituted oxazolidinone derivatives [3b]).



¹⁷) In a preliminary experiment, reduction of **24a** with *Raney*-Ni in the presence of Boc₂O gave the DIOZ-derivative **vi** of β^2 hAla in 75% yield. The analytical data were in agreement with those reported in [4a].



¹⁵) As indicated by the drawing of the intermediate dilithio-derivative in *Scheme 4*, the configuration of the product **24a** (safely assigned by X-ray analysis; see *Table 1*) is, again (*cf. Footnotes 12–14*), compatible with a metal-chelated structure; the stereochemical course of the reaction follows the general rules for reactions of *Evans* Li-enolates with electrophiles [2].

advantage is the high crystallinity of all products, combined with the milder removal of the auxiliary groups, which has previously been demonstrated in other DIOZ applications [4]. In the preliminary experiment with a DIOZ Li₂-enolate-nitronate, another new route to β^2 -amino acid precursors has been outlined, for which, however, a better auxiliary will have to be identified. With a single exception (Zn/Cu reagent \rightarrow *epi-***24b**), the stereochemical courses of all reactions are compatible with metalchelated oxazolidinone derivatives as reactive intermediates.

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Experimental Part

1. General. All reactions were performed under Ar in dried glassware using anh. solvents except when using aq. reagents. All chemicals were of reagent grade and used as supplied, unless stated otherwise. Solvents for extractions and chromatography were of technical grade and were distilled prior to use. Sat. hydrocarbon solvents were kept over Na wire. Extracts were dried over MgSO₄. Anal. TLC: pre-coated *Merck* silica gel 60 F254 plates (0.25 mm). Flash column chromatography (FC): *Fluka* silica gel 60 (230–400 mesh). Melting points (M.p.): *Büchi 510* melting point apparatus; uncorrected. Optical rotations ($[a]_{2D}^{2D}$): *Jasco P-2000 Polarimeter*. IR Spectra: neat solid/oil on a *Perkin-Elmer precisely Universal ATR Sampling Accessory*; in cm⁻¹. ¹H-, ¹³C-, and ¹⁹F-NMR spectra: *Bruker AVANCE* (¹H: 300 MHz, ¹³C: 75 MHz), *DRX* (¹H: 400 MHz, ¹³C: 101 MHz), and *AV* (¹H: 400 MHz, ¹³C: 101 MHz) spectrometer, or *Varian Gemini-300* XL (¹H: 300 MHz, ¹⁹F: 282 MHz, ¹³C: 75 MHz) spectrometer; chemical shifts (δ) in ppm relative to Me₄Si (0.00 ppm). MS: *VG Tribrid* (EI), *IonSpecUltima 4.7-T-FT Ion Cyclotron Resonance* (ICR; HR-MALDI; in 2,5-dihydroxybenzoic acid matrix) mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratorium at the Laboratory for Organic Chemistry, ETH Zürich.

2. Preparation of the Starting Materials. (S)-3-[(E)-3-Nitroprop-2-enoyl]-4-(phenylmethyl)oxazolidin-2-one ((S)-6). Compound (S)-5 [2b] (1.15 g, 5.0 mmol) was suspended in Et₂O (25 ml) and cooled to 0°. In a separate flask, to ice-cooled 100% HNO3 (1.26 ml, 30 mmol) was added during 10 min ClSO3H (1.0 ml, 15 mmol, 3 equiv.), immediately NO₂Cl was formed, which was transferred by a slow stream of N_2 into the reaction mixture. After 1 h, additional ClSO₃H (1.0 ml, 15 mmol, 3 equiv.) was added to the HNO₃, and the NO₂Cl was transferred into the reaction mixture. The resulting yellow soln. was stirred for an additional 1 h at r.t., and then the reaction was quenched by the addition of H₂O (20 ml). The mixture was extracted with Et₂O. The org. layer was washed with H₂O and brine, dried (MgSO₄), and concentrated under reduced pressure. The crude product (1.54 g) was dissolved in Et₂O (35 ml) and treated with AcONa (410 mg, 5 mmol) and a trace hydrochinone. The mixture was heated for 5 h under reflux. After cooling to r.t., the mixture was filtered and then concentrated under reduced pressure. The residual oil was dissolved in AcOEt (5 ml) and treated with hexane (13 ml), and the precipitated (S)-6 was filtered off (130 mg). The mother liquid was concentrated under reduced pressure, and by FC (toluene) additional product was isolated to give overall (S)-6 (260 mg, 20%). Yellow crystals, M.p. 144– 150° . $[\alpha]_{20}^{20} = +77.2 (c = 0.88, CHCl_3)$. IR (CHCl_3): 3008w, 3011w, 1788s, 1692s, 1542s, 1385s, 1351s, 1113m, 1050m, 1001m, 950m. ¹H-NMR (400 MHz, CDCl₃): 2.85 (dd, J = 13.5, 9.5, 1 H, PhCH₂); 3.35 (dd, J = 13.5, 3.4, 1 H, PhCH₂); 4.26-4.35 (m, CH₂O); 4.74-4.80 (m, CHN); 7.2-7.38 (m, 10 arom. H); 7.77 (*d*, *J*=13.3, =CH); 8.47 (*d*, *J*=13.2, =CH). ¹³C-NMR (100 MHz, CDCl₃): 37.5 (CH₂); 55.4 (CH); 66.8 (CH₂); 126.9, 127.7, 129.2, 129.4 (CH); 134.4 (C); 149.1 (CH); 152.8, 161.2 (C). MS (EI): 276 (1, M⁺), 230 (13), 158 (5), 100 (9), 91 (100). Anal. calc. for C₁₃H₁₂N₂O₅ (276.25): C 56.52, H 4.38, N 10.14; found: C 56.43, H 4.53, N 9.97.

(S)-4-(1-Methylethyl)-5,5-diphenyl-3-[(E)-prop-2-enoyl]oxazolidin-2-one ((S)-7). To an ice-cold suspension of (S)-3 (2.81 g; 10.0 mmol) in THF (40 ml) was added a soln. of MeMgBr (3.5 ml, 10.5 mmol,

3M in Et₂O) during 10 min. At the end of the addition, the deprotonated DIOZ precipitated. The resulting white suspension was stirred for an additional 30 min at 0° and then cooled to -70° . Within 5 min, acroyl chloride (1 ml, 10.5 mmol) was added, and the mixture was allowed to warm to r.t. overnight. The reaction was quenched with sat. aq. NH₄Cl soln. (10 ml), and the mixture was extracted with Et₂O. The org. layer was washed with sat. aq. NH₄Cl soln., dried (MgSO₄), and concentrated under reduced pressure. The residue was triturated with hexane (30 ml) to yield (*S*)-7 (3.24 g, 90%). Colorless solid. *R*_f (hexane/AcOEt 2 : 1) 0.7. M.p. 146°. [α]₂₀²⁰ = -232 (*c* = 1.00, CH₂Cl₂). IR (CHCl₃): 3011*w*, 2969*w*, 1779*s*, 1689*m*, 1619*w*, 1494*w*, 1450*w*, 1408*m*, 1364*m*, 1322*m*, 1151*w*, 1120*w*, 1050*w*, 1002*m*, 984*w*, 958*w*. ¹H-NMR (400 MHz, CDCl₃): 0.78 (*d*, *J* = 6.8, Me); 0.90 (*d*, *J* = 7.0, Me); 1.96–2.04 (*m*, MeCH); 5.46 (*d*, *J* = 3.4, CHN); 5.85 (*dd*, *J* = 10.5, 1.8, 1 H, CH₂); 6.50 (*dd*, *J* = 17.0, 1.8, 1 H, CH₂); 7.25–7.49 (*m*, 10 arom. H). ¹³C-NMR (100 MHz, CDCl₃): 16.4, 21.8 (Me); 30.1, 65.5 (CH); 89.5 (C); 125.7, 126.0, 127.1, 128.0, 128.4, 128.6, 128.9 (CH); 131.9 (CH₂); 138.2, 142.2, 152.9, 164.8 (C). MS (EI): 335 (2, *M*⁺), 292 (13), 291 (9), 237 (11), 220 (10), 195 (36), 194 (26), 184 (12), 183 (8), 167 (19), 166 (12), 165 (26), 109 (19), 105 (22), 77 (13), 55 (100), 41 (9). Anal. calc. for C₂₁H₂₁NO₃ (335.40): C 75.20, H 6.31, N 4.18; found: C 75.28, H 6.41, N 4.20.

(S)-4-(1-Methylethyl)-3-[(E)-1-oxobut-2-enyl]-5,5-diphenyloxazolidin-2-one ((S)-8a). Starting from (S)-3, (S)-8a was prepared as described in [4a]. Yield and anal. data were in agreement with those reported in [4a].

(S)-4-(1-Methylethyl)-3-(2-methylprop-2-enoyl)-5,5-diphenyloxazolidin-2-one ((S)-8b). To an icecold suspension of (S)-3 (0.4 g, 1.42 mmol) in THF (5 ml) was added a soln. of MeMgBr (0.5 ml, 1.5 mmol, 3M in Et₂O) during 10 min. At the end of the addition, the deprotonated DIOZ precipitated. The resulting white suspension was stirred for an additional 30 min at 0° and then cooled to -70° . Within 5 min, methacroyl chloride (0.34 ml, 3.55 mmol) was added, and the reaction mixture was allowed to warm to r.t. overnight. The reaction was quenched with sat. aq. NH₄Cl soln. (10 ml), and the mixture was extracted with Et₂O. The org. layer was washed with sat. aq. NH₄Cl soln., dried (MgSO₄), and concentrated under reduced pressure. FC (pentane/Et₂O 9:1) yielded (S)-**8b** (0.42 g, 85%). Colorless solid. $R_{\rm f}$ (pentane/Et₂O 2:1) 0.8. M.p. 111–113°. $[\alpha]_{\rm D}^{20} = -181.1$ (c = 0.5, CHCl₃). IR (CHCl₃): 2968w, 1789s, 1686m, 1494w, 1450m, 1365w, 1324m, 1176m, 1001w, 918w. 1H-NMR (300 MHz, CDCl₃): 0.80 (d, J = 6.5, Me); 0.92 (d, J = 6.85, Me); 1.92 (s, Me); 2.00 – 2.04 (m, Me_2CH); 5.07 ($s, 1 H, CH_2$); 5.28 (d, J = 6.5, Me); 0.92 (d, J = 6.85, Me); 1.92 (s, Me); 2.00 – 2.04 (m, Me_2CH); 5.07 ($s, 1 H, CH_2$); 5.28 (d, J = 6.5, Me); 0.92 (d, J = 6.85, Me); 0 1.2, 1 H, CH₂); 5.38 (d, J = 3.4, CHN); 7.24 – 7.37 (m, 6 arom. H); 7.40 – 7.44 (m, 2 arom. H); 7.50 – 7.53 (m, 2 arom. H). ¹³C-NMR (75 MHz, CDCl₃): 16.4; 19.4; 21.8; 30.1; 64.9; 89.5; 119.7; 125.6; 125.8; 127.9; 128.3; 128.5; 128.8; 138.0; 139.3; 142.3; 152.1; 170.6. MS (EI): 721 ([2 M + Na]+), 388 ([M + K]+), 372 ([M + Na]⁺), 350 ([*M*+1]⁺). Anal. calc. for C₂₂H₂₃NO₃ (349.43): C 75.62, H 6.63, N 4.01; found: C 75.66, H 6.75, N 4.02.

(S)-4-(1-Methylethyl)-3-[(E)-3-phenylprop-2-enoyl]-5,5-diphenyloxazolidin-2-one ((S)-9). Starting from (S)-3, (S)-9 was prepared as described in [4a]. Yield and anal. data were in agreement with those reported in [4a].

(S)-3-[(E)-3-(3-Methoxyphenyl)prop-2-enoyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one((S)-10). To an ice-cold suspension of (S)-3 (602 mg, 2.14 mmol) in THF (10 ml) was added a soln. of BuLi (1.45 ml, 2.35 mmol, 1.6M in hexane) during 5 min. After stirring for 5 min, (E)-3-(4-methoxyphenyl)prop-2-enoyl chloride (505 mg, 2.57 mmol) in THF (2 ml) was added, and the mixture was allowed to warm to r.t. overnight. The reaction was quenched with sat. aq. NH₄Cl soln. (10 ml), and the mixture was extracted with Et₂O. The org. layer was washed with 1M HCl, 1M NaOH, and brine, dried (MgSO₄), and concentrated under reduced pressure. FC (pentane/AcOEt 15:1) yielded (S)-10 (674 mg, 71%). Colorless solid. M.p. $159-161^{\circ}$. $[\alpha]_{20}^{20} = -89.2$ (c = 1, CHCl₃). IR (CHCl₃): 3008w, 2968w, 1775s, 1676m, 1599s, 1574w, 1512s, 1450w, 1348m, 1257m, 1172s, 1030m, 987w, 829m. ¹H-NMR (300 MHz, $CDCl_3$: 0.81 (d, J = 6.9, Me); 0.93 (d, J = 6.9, Me); 1.97 – 2.09 (m, Me₂CH); 3.82 (s, MeO); 5.54 (d, J = 6.9, Me); 1.97 – 2.09 (m, Me₂CH); 3.82 (s, MeO); 1.97 – 2.09 (m, Me₂CH); 3.82 (s, MeO); 1.97 – 2.09 (m, Me₂CH); 3.82 (s, MeO); 1.97 – 2.09 (m, Me₂CH); 3.97 – 3.4, CHN); 6.86–6.92 (*m*, 2 arom. H); 7.23–7.45 (*m*, 8 arom. H); 7.50–7.56 (*m*, 4 arom. H); 7.72 (*d*, *J* = 15.7, ArylCH=CH); 7.80 (d, J=15.7, ArylCH=CH). ¹³C-NMR (75 MHz, CDCl₃): 17.0, 21.0 (Me); 28.8 (CH); 55.4 (Me); 64.4 (CH); 89.3 (C); 114.2, 114.3, 125.7, 126.0, 127.4, 127.9, 128.4, 128.9, 130.4 (CH); 138.4, 142.4 (C); 146.4 (CH); 153.1, 161.7, 165.3 (C). MS (MALDI): 480 (10, [M+K]⁺), 464 (100, [M+ $Na]^+$), 442 (6, $[M+H]^+$). Anal. calc. for $C_{28}H_{27}NO_4$ (441.53): C 76.17, H 6.16, N 3.17; found: C 76.14, H 6.23, N 3.14.

(S)-4-(1-Methylethyl)-3-[(E)-3-nitroprop-2-enoyl]-5,5-diphenyloxazolidin-2-one ((S)-11) and (S)-3-(2,3-Dichloropropanoyl)-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (17). Compound (S)-7 (5.03 g, 13.95 mmol) was suspended in Et₂O (110 ml) and cooled to 0°. In a separate flask, to ice-cooled 100% HNO₃ (3.47 ml, 83.7 mmol) was added during 10 min ClSO₃H (2.8 ml, 41.9 mmol), immediately NO₂Cl was formed, which was transferred by a slow stream of N₂ into the reaction mixture. After 1 h, additional ClSO₃H (2.8 ml, 41.9 mmol) was added to the HNO₃, and the NO₂Cl was transferred into the reaction mixture. The resulting yellow soln. was stirred for an additional 1 h at r.t., and then the reaction was quenched by the addition of H₂O (90 ml). The mixture was extracted with Et₂O. The org. layer was washed with H₂O and brine, dried (MgSO₄), and concentrated under reduced pressure. FC (pentane/ AcOEt 9:1) yielded (S)-11 (1.42 g, 22%) as yellow solid and 17 (1.31 g, 23%) as colorless solid.

Data of (S)-**11**. $R_{\rm f}$ (hexane/AcOEt 4:1) 0.53. M.p. 112°. $[a]_{10}^{20} = -185$ (c = 1.05, CH₂Cl₂). ¹H-NMR (400 MHz, CDCl₃): 0.80 (d, J = 6.8, Me); 0.92 (d, J = 7, Me); 2.02–2.09 (m, Me₂CH); 5.46 (d, J = 3.4, CHN); 7.26–7.49 (m, 10 arom. H); 7.68 (d, J = 13.2, =CH); 8.38 (d, J = 13.2, =CH). ¹³C-NMR (100 MHz, CDCl₃): 16.3; 21.8; 30.1; 65.2; 90.4; 125.4; 125.8; 126.8; 128.3; 128.6; 129.0; 129.2; 137.5; 141.6; 149.2; 152.3; 161.1. Anal. calc. for C₂₁H₂₀N₂O₅ (380.39): C 66.31, H 5.30, N 7.36; found: C 66.23, H 5.46, N 7.02.

Data of **17**. R_f (hexane/AcOEt 4 : 1) 0.63. ¹H-NMR (400 MHz, CDCl₃): 0.80 (d, J = 6.7, Me); 0.93 (d, J = 7, Me); 1.97 – 2.05 (m, Me₂CH); 3.80 (dd, J = 10.7, 4.5, 1 H, CH₂); 4.12 (dd, J = 10.7, 9.7, 1 H, CH₂); 5.41 (d, J = 3.3, CHN); 5.78 (dd, J = 9.7, 4.5, CH); 7.26 – 7.45 (m, 10 arom. H). ¹³C-NMR (100 MHz, CDCl₃): 16.2; 21.7; 29.8; 42.8; 51.3; 90.2; 125.6; 125.9; 128.2; 128.5; 128.8; 128.9; 137.6; 152.3; 166.3. Anal. calc. for C₂₁H₂₁N₁O₃Cl₂ (406.30): C 62.07, H 5.21, N 3.45, Cl 17.45; found: C 62.44, H 5.29, N 3.50, Cl 16.89.

(S)-4,5,5-*Triphenyl-3-[*(E)-*prop-2-enoyl]oxazolidin-2-one* ((S)-**12**). To an ice-cold suspension of (S)-**4** (3.15 g, 10.0 mmol) in THF (40 ml) was added a soln. of MeMgBr (3.5 ml, 10.5 mmol, 3m in Et₂O) during 10 min. At the end of the addition, the deprotonated TRIOZ precipitated. The resulting white suspension was stirred for an additional 30 min at 0° and then cooled to -70° . Within 5 min, acryloyl chloride (1.0 ml, 10.5 mmol) was added, and the mixture was allowed to warm to r.t. overnight. The reaction was quenched with sat. aq. NH₄Cl soln. (10 ml), and the mixture was extracted with Et₂O. The org. layer was washed with sat. aq. NH₄Cl soln., dried (MgSO₄), and concentrated under reduced pressure. FC (hexane/AcOEt 8:1) yielded (S)-**12** (1.58 g, 40%). Colorless solid. *R*_t (hexane/AcOEt 1:1) 0.8. M.p. 136–137°. [*a*]₂₀²⁰ = -236 (*c* = 1.00, CH₂Cl₂). ¹H-NMR (400 MHz, CDCl₃): 5.81 (*dd*, *J* = 10.3, 1.6, 1 H, =CH₂); 6.20 (*s*, CHN); 6.42 (*dd*, *J* = 17.1, 1.6, 1 H, =CH₂); 6.92–7.61 (*m*, 16 arom. H, CH=CH₂). ¹³C-NMR (100 MHz, CDCl₃): 66.1; 89.2; 126.0; 126.2; 127.2; 127.5; 127.6; 127.7; 128.2; 128.3; 128.9; 129.0; 132.3; 137.9; 141.7; 152.6; 164.0. Anal. calc. for C₂₄H₁₉NO₃ (369.41): C 78.03, H 5.18, N 3.79; found: C 77.85, H 5.37, N 3.77.

(S)- or (R)-3-[(E)-But-2-enoyl]-4,5,5-triphenyloxazolidin-2-one ((S)- or (R)-13). To an ice-cold suspension of (S)- or (R)-4 (3.70 g, 11.7 mmol) in THF (50 ml) was added BuLi (8.6 ml, 13.8 mmol, 1.6m in hexane) over a period of 25 min. During addition, the TRIOZ dissolved, and, after an additional 35 min at 0°, a clear yellow soln. was obtained. Within 15 min, crotonoyl chloride (1.73 ml, 16.2 mmol) was added, and the mixture was allowed to warm to r.t. overnight. The reaction was quenched with sat. aq. NH₄Cl soln. (25 ml), and the mixture was extracted with Et₂O. The org. layer was washed with 1M HCl, 1M NaOH, and brine, dried (MgSO₄), and concentrated under reduced pressure. FC (hexane/AcOEt 8:1) yielded (S)- or (R)-13 (ca. 3.6 g, ca. 80%). M.p. 150–152°. (S)-13: $[\alpha]_{20}^{20} = -232.3$ (c = 1, CHCl₃). (R)-13: $[\alpha]_{20}^{20} = +240.8$ (c = 1, CHCl₃). IR (CHCl₃): 3007w, 1778s, 1687m, 1638m, 1495w, 1449m, 1341s, 1179m, 1059m. ¹H-NMR (400 MHz, CDCl₃): 1.91 (d, J = 8.5, Me); 6.27 (s, CHN); 7.02–7.44 (m, 13 arom. H, CH=CH); 7.63–7.65 (m, 2 arom. H). ¹³C-NMR (100 MHz, CDCl₃): 18.5 (Me); 66.1 (CH); 89.0 (C); 121.7, 126.3, 128.9 (CH); 135.9, 138.1, 141.8 (C); 147.5 (CH); 152.8, 164.1 (C). Anal. calc. for C₂₅H₂₁NO₃ (383.44): C 78.31, H 5.52, N 3.65; found: C 78.23, H 5.48, N 3.68.

(S)-3-[(E)-4,4,4-Trifluorobut-2-enoyl]-4,5,5-triphenyloxazolidin-2-one ((S)-14). To an ice-cold suspension of (S)-4 (2.31 g, 7.3 mmol) in THF (50 ml) was added BuLi (4.85 ml, 7.8 mmol, 1.6M in hexane) over a period of 10 min. During addition, the TRIOZ dissolved, and, after an additional 35 min at 0°, a clear yellow soln. was obtained. Within 15 min, a soln. of 4,4,4-trifluorocrotonoyl chloride¹⁸) (1.28 g, 8.1 mmol) in THF (10 ml) was added, and the mixture was allowed to warm to r.t. overnight. The

¹⁸) Prepared according to a literature procedure [15].

reaction was quenched with sat. aq. NH₄Cl soln. (10 ml), and the mixture was extracted with AcOEt. The org. layer was washed with 1M HCl, 1M NaOH, and brine, dried (MgSO₄), and concentrated under reduced pressure to yield (*S*)-**14** (2.77 g, 63%). M.p. 153–154°. $[a]_D^{20} = -188.1$ (c=1, CHCl₃). IR (CHCl₃): 3032w, 1774s, 1698m, 1496w, 1450w, 1349s, 1305s, 1276m, 1150s, 1033w, 1016w, 1000w, 973w, 639w. ¹H-NMR (300 MHz, CDCl₃): 6.27 (*s*, CH); 7.78 (*dq*, *J* = 15.3, 6.3, CH=CHCF₃); 7.02–7.14 (*m*, 10 arom. H); 7.39–7.48 (*m*, 3 arom. H); 7.62–7.66 (*m*, 2 arom. H); 7.91 (*dq*, *J* = 15.3, 1.8, CH=CHCF₃). ¹³C-NMR (75 MHz, CDCl₃): 66.2 (CH); 89.7 (C); 122.0 (*q*, *J* = 269.0, CF₃); 125.8, 126.1, 127.3, 127.4, 127.6, 127.8, 128.4, 128.5, 129.1 (CH); 132.2 (*q*, *J* = 35.8, CH); 134.9, 137.5, 141.3 (C); 152.3, 161.6 (C). ¹⁹F-NMR (282 MHz, CDCl₃): - 65.20 (*dd*, *J* = 6.5, 1.7, CF₃). Anal. calc. for C₂₅H₁₈F₃NO₃ (437.42): C 68.65, H 4.15, N 3.20; found: C 68.42, H 4.41, N 3.15.

(S)- or (R)-4,5,5-Triphenyl-3-[(E)-3-phenylprop-2-enoyl]oxazolidin-2-one ((S)- or (R)-15). To an ice-cold suspension of (S)- or (R)-4 (3.60 g, 11.4 mmol) in THF (50 ml) was added BuLi (8.55 ml, 13.6 mmol, 1.6M in hexane) over a period of 10 min. During addition, the TRIOZ dissolved, and, after an additional 35 min at 0°, a clear yellow soln. was obtained. Within 15 min, a soln. of cinnamoyl chloride (2.47 g, 14.8 mmol) in THF (8 ml) was added, and the reaction mixture was allowed to warm to r.t. overnight. The reaction was quenched with sat. aq. NH₄Cl soln. (25 ml), and the mixture was extracted with AcOEt. The org. layer was washed with 1M HCl, 1M NaOH, and brine, dried (MgSO₄), and concentrated under reduced pressure. The residue was triturated twice with hot hexane (30 ml) to yield (S)- or (R)-15 (ca. 5.0 g, ca. 90%). Colorless solid. M.p. > 240°. (S)-15: $[a]_{20}^{20} = -234.6$ (c = 1, CHCl₃). (R)-15: $[a]_{20}^{20} = +242.8$ (c = 1, CHCl₃). IR (CDCl₃): 3008w, 1777s, 1681m, 1617m, 1496w, 1450m, 1344s, 1170m. ¹H-NMR (400 MHz, CDCl₃): 6.34 (s, CHN); 7.06–7.25 (m, 10 arom. H); 7.37–7.39 (m, 4 arom. H); 7.41–7.46 (m, 2 arom. H); 7.55–7.58 (m, 2 arom. H); 7.66–7.68 (m, 2 arom. H); 7.76 (d, J = 15.7, PhCH=CH); 7.92 (d, J = 15.7, PhCH=CH). ¹³C-NMR (100 MHz, CDCl₃): 66.2 (CH); 89.1 (C); 116.8, 126.9, 128.9 (CH); 134.4, 138.0, 141.8 (C); 146.9 (CH); 152.8, 164.4 (C). Anal. calc. for C₃₀H₂₈NO₃ (445.51): C 80.88, H 5.20, N 3.14; found: C 80.72, H 5.50, N 3.16.

3. Conjugate Additions to the Cinnamoyl- and Crotonoyl-oxazolidinones. General Procedure 1 (GP 1). To a Cu¹Br-DMS (1.5 equiv.) suspension in THF (2.5 ml/mmol) was added at -40° the appropriate Grignard reagent (3 equiv., as 1M soln. in THF). After 10 min, the temp. was adjusted to -40 or -70° , and the acyl-TRIOZ derivative (1 equiv.) as a soln. in THF (5 ml/mmol) was added dropwise. After stirring for 30 min at -35 or -70° , the mixture was allowed to warm to r.t. (1-2 h), and the reaction was quenched with sat. aq. NH₄Cl soln., and the mixture was extracted with AcOEt. The org. layer was washed with 1M HCl, 1M NaOH, and brine, dried (MgSO₄), and concentrated under reduced pressure to yield the crude products which were analyzed by NMR for determination of the dr. FC and crystallization yielded the 1,4-addition products.

(S)-3-[(S)- or (R)-3-(4-Methoxyphenyl)-3-phenylpropanoyl]-4-(1-methylethyl)-5,5-diphenyloxazolidin-2-one (**18** or epi-**18**). Compound (S)-**9** (113 mg, 0.275 mmol) was treated with a soln. of (4-MeOPh)MgBr (0.825 ml, 0.825 mmol, 1M in THF), or (S)-**10** (121 mg, 0.275 mmol) with a soln. of PhMgBr (0.825 ml, 0.825 mmol, 1M in THF) at -30° , according to *GP 1*. Purification of the crude product by FC (pentane/AcOEt 15:1) yielded **18** (110 mg, 88%, dr 85:15) or epi-**18** (78%, dr 82:18). Colorless solid. For anal. purposes, a sample was re-crystallized from hexane to afford diastereomerically pure **18** (dr \ge 99:1). M.p. 138–140°. [α]₂₀²⁰ = +156.9 (*c* = 1, CHCl₃). IR (CHCl₃): 3008w, 2966w, 2837w, 1779s, 1703m, 1610w, 1511s, 1450m, 1372m, 1319w, 1176s, 1034w, 831w. ¹H-NMR (400 MHz, CDCl₃): 0.61 (*d*, *J* = 6.7, Me); 0.65 (*d*, *J* = 7.0, Me); 1.82–1.92 (*m*, Me₂CH); 3.44 (*dd*, *J* = 16.5, 7.9, 1 H, CH₂); 3.74 (*s*, MeO); 3.74 (*dd*, *J* = 16.5, 7.9, 1 H, CH₂); 4.56 (*dd*, *J* = 7.9, 7.9, PhCH); 5.28 (*d*, *J* = 3.2, CHN); 6.75–6.79 (*m*, 2 arom. H); 7.08–7.20 (*m*, 7 arom. H); 7.24–7.41 (*m*, 10 arom. H). ¹³C-NMR (100 MHz, CDCl₃): 16.1, 21.4 (Me); 29.8 (CH); 40.8 (CH₂); 45.8 (CH); 55.2 (Me); 64.4 (CH); 89.4 (C); 113.9, 125.6, 125.9, 126.3, 127.5, 127.9, 128.3, 128.5, 128.9, 128.9 (CH); 135.6, 138.1, 142.2, 143.5, 153.1, 158.1, 171.1 (C). MS (MALDI): 558 (11, [*M* + K]⁺), 542 (100, [*M* + Na]⁺), 498 (32). Anal. calc. for C₃₄H₃₃NO₄ (519.64): C 78.59, H 6.40, N 2.70; found: C 78.52, H 6.46, N 2.64.

(R)-4,5,5-Triphenyl-[(S)-3-phenylbutyanoyl]oxazolidion-2-one (19). Compound (R)-13 (667 mg, 1.74 mmol) was treated at -40° with a soln. of PhMgBr (5.22 ml, 5.22 mmol, 1M in THF) according to GP 1 to yield the crude product (dr 96:4). FC (pentane/AcOEt 9:1) and crystallization from hexane/AcOEt yielded 19 (568 mg, 71%; pure diastereoisomer). Colorless solid. $R_{\rm f}$ (hexane/AcOEt 4:1) 0.48.

M.p. 112–114°. $[a]_{D}^{20} = +232.7 (c = 1, CHCl_3)$. IR (CHCl_3): 3032w, 1781s, 1705m, 1495w, 1450m, 1365m, 1333m, 1172m, 1081w, 1033w, 998w. ¹H-NMR (300 MHz, CDCl_3): 1.18 (d, J = 6.6, Me); 3.08–3.33 (m, CH₂, CH); 6.16 (s, CH); 6.91–7.22 (m, 15 arom. H); 7.43–7.46 (m, 3 arom. H); 7.63–7.67 (m, 2 arom. H). ¹³C-NMR (75 MHz, CDCl_3): 21.5 (Me); 36.1 (CH₂); 43.3 (CH); 65.9 (CH); 88.9 (C); 125.9, 126.1, 126.2, 126.8, 127.2, 127.4, 127.6, 127.9, 128.1, 128.3, 128.8, 128.9 (CH); 135.4, 137.8, 141.7, 145.2, 171.0 (C). Anal. calc. for C₃₁H₂₇NO₃ (461.55): C 80.67, H 5.90, N 3.03; found: C 80.51, H 5.98, N 3.01.

(R)-4,5,5-*Triphenyl-[*(R)-3-*phenylbutanoyl]oxazolidion-2-one* (*epi-19*). Compound (R)-15 (537 mg, 2.61 mmol) was treated at -40° with a soln. of MeMgBr (3.75 ml, 5.25 mmol, 1.4M in THF/ toluene) according to *GP1* to yield the crude product (dr 96:4). FC (hexane/AcOEt 4:1) and crystallization from hexane/AcOEt yielded *epi-19* (547 mg, 68%; pure diastereoisomer). Colorless solid. M.p. 153–155°. [a]₂₀²⁰ = +156.3 (c = 1, CHCl₃). IR (CHCl₃): 3008w, 2990w, 1780s, 1706m, 1464w, 1450m, 1367m, 1332m, 1170m, 1064w, 1034w, 999w, 629w. ¹H-NMR (300 MHz, CDCl₃): 1.20 (d, J = 6.9, Me); 3.11–3.371 (m, CH₂, CH); 6.12 (s, CH); 7.01–7.19 (m, 15 arom. H); 7.35–7.38 (m, 3 arom. H); 7.50–7.53 (m, 2 arom. H). ¹³C-NMR (75 MHz, CDCl₃): 22.2 (Me); 35.9 (CH₂); 43.2 (CH); 66.0 (CH); 125.9, 126.2, 126.7, 127.4, 127.6, 128.1, 128.2, 128.3, 128.8, 128.9 (CH); 135.7, 137.9, 141.5, 145.6, 170.9 (C). Anal. calc. for C₃₁H₂₇NO₃ (461.55): C 80.67, H 5.90, N 3.03; found: C 80.52, H 6.08, N 2.99.

(R)-3-[(S)-3-(4-Methoxyphenyl)butanoyl]-4,5,5-triphenyloxazolidin-2-one (**20**). Compound (R)-**13** (667 mg, 1.74 mmol) was treated at -40° with a soln. of 4-MeOPhMgBr (5.22 ml, 5.22 mmol, 1.4m in THF) according to *GP 1* to yield the crude product (dr 91:9). FC (pentane/AcOEt 15:1) yielded **20** (631 mg, 74%; mixture of diastereoisomers). Colorless solid. M.p. 120.5–122°. $[a]_{20}^{D}$ = +206.8 (*c* = 1, CHCl₃). IR (CHCl₃): 3032w, 2663w, 1780s, 1705m, 1611w, 1514m, 1450w, 1365m, 1332m, 1248m (br.), 1035w, 999w, 831w. ¹H-NMR (300 MHz, CDCl₃): 1.18 (*d*, *J* = 6.3, Me); 3.06–3.35 (*m*, CH, CH₂); 3.78 (*s*, MeO); 6.17 (*s*, CH); 6.75–6.79 (*m*, 2 arom. H); 6.90–7.10 (*m*, 12 arom. H); 7.41–7.50 (*m*, 3 arom. H); 7.65–7.68 (*m*, 2 arom. H). ¹³C-NMR (75 MHz, CDCl₃): 22.0 (Me); 35.7 (CH₂); 43.7 (CH); 55.3 (Me); 6.1 (CH); 88.9 (C); 113.7, 126.0, 127.2, 127.4, 127.6, 127.7, 128.0, 128.1, 128.8, 128.9 (CH); 135.5, 137.3, 137.8, 141.7, 152.6, 157.9, 171.0 (C). Anal. calc. for C₃₂H₂₉NO₄ (491.57): C 78.19, H 5.95, N 2.85; found: C 78.24, H 6.08, N 2.83.

(S)-4,5,5-*Triphenyl-3-[*(S)-4,4,4-*trifluoro-3-methylbutanoyl]oxazolidin-2-one* (**21**). Compound (S)-**14** (437 mg, 1.0 mmol) was treated at -40° with a soln. of MeMgBr (2.2 ml, 3.0 mmol, 1.4m in THF/ toluene) according to *GP 1* to yield the crude product (dr 61:39). FC (pentane/AcOEt 9:1) yielded **21** (248 mg, 55%; mixture of diastereoisomers). Colorless solid. M.p. 52–53°. [a]_D²⁰ = -184.2 (c = 1, CHCl₃). IR (CHCl₃): 3032w, 1783s, 1709m, 1496w, 1450w, 1332m, 1271m, 1174m, 1132m, 1087w, 1034w, 998w, 909w, 636w. ¹H-NMR (300 MHz, CDCl₃): 1.05 (t, J = 6.6, Me); 2.77–2.88 (m, CH); 2.93–3.35 (m, CH₂); 6.25 (s, CH, minor diastereoisomer); 6.26 (s, CH, major diastereoisomer); 7.02–7.15 (m, 10 arom. H); 7.40–7.48 (m, 3 arom. H); 7.63–7.68 (m, 2 arom. H). ¹⁹F-NMR (282 MHz; CDCl₃): -73.27 (d, J = 8.7, CF₃, major diastereoisomer); -73.28 (d, J = 8.7, CF₃, minor diastereoisomer). Anal. calc. for C₂₆H₂₂F₃NO₃ (453.45): C 68.87, H 4.89, N 3.09; found: C 66.20, H 4.85, N 2.91.

(S)-4,5,5-*Triphenyl-3-[(*R)-4,4,4-*trifluoro-3-phenylbutanoyl]oxazolidin-2-one* (**22**). Compound (S)-**14** (437 mg, 1.00 mmol) was treated at -40° with a soln. of PhMgBr (3.0 ml, 3.0 mmol, 1M in THF) according to *GP 1* to yield the crude product (dr 69:31). FC (pentane/AcOEt 9:1) yielded **22** (311 mg, 60%; mixture of diastereoisomers). Colorless solid. M.p. $103-106^{\circ}$. [α]₂₀^D = -157.3 (c = 1, CHCl₃). IR (CHCl₃): 3032w, 1782s, 1710m, 1496w, 1450w, 1390w, 1363w, 1332m, 1250m, 1166m, 1034w, 1115m, 1033w, 999w. ¹H-NMR (300 MHz, CDCl₃): 3.39-3.54 (*m*, CH); 3.75-4.03 (*m*, CH₂); 6.04 (*s*, CH, minor diastereoisomer); 6.12 (*s*, CH₂, major diastereoisomer); 6.71-7.10 (*m*, 10 arom. H); 7.23-7.62 (*m*, 10 arom. H). ¹⁹F-NMR (282 MHz, CDCl₃): -69.95 (*d*, J = 8.7, CF₃, major diastereoisomer); -69.83 (*d*, J = 8.7, CF₃, minor diastereoisomer). Anal. calc. for C₃₁H₂₄F₃NO₃ (515.52): C 72.22, H 4.69, N 2.72; found: C 72.01, H 4.97, N 2.55.

(S)-3-[(S)-3-(4-Methoxyphenyl)-3-phenylpropanoyl]-4,5,5-triphenyloxazolidin-2-one (23). Compound (S)-15 (775 mg, 1.74 mmol) was treated at -40° with a soln. of 4-MeOPhMgBr (5.22 ml, 5.22 mmol, 1.4M in THF) according to *GP 1* to yield the crude product (dr 97:3). FC (pentane/AcOEt 9:1) yielded 23 (614 mg, 64%; pure diastereoisomer). Colorless solid. M.p. 165–168°. $[a]_{2D}^{2D} = -170.6$ (c = 1, CHCl₃). IR (CHCl₃): 3008w, 1779s, 1707m, 1610w, 1512m, 1496w, 1450w, 1373m, 1332m, 1248m, 1034w, 1000w, 831w. ¹H-NMR (300 MHz, CDCl₃): 3.68, 3.72 (d, J = 7.8, CH₂); 3.75 (s, MeO); 4.50 (d,

J = 7.8, CH); 6.09 (s, CH); 6.72 - 6.75 (m, 2 arom. H); 6.87 - 7.19 (m, 17 arom. H); 7.39 - 7.41 (m, 3 arom. H); 7.52 - 7.55 (m, 2 arom. H). ¹³C-NMR (75 MHz, CDCl₃): 41.0 (CH₂); 45.7 (CH); 55.1 (CH₃); 65.8 (CH); 89.0 (C); 113.8, 126.0, 126.2, 127.2, 127.4, 127.6, 127.9, 128.1, 128.4, 128.7, 128.8, 128.9 (CH); 135.2, 135.3, 137.7, 141.5, 143.5, 152.7, 158.0, 170.5 (C). Anal. calc. for C₃₇H₃₁NO₄ (553.65): C 80.27, H 5.64, N 2.53; found: C 80.29, H 5.68, N 2.51.

(S)-4-(1-Methylethyl)-3-(2-methyl-3-nitropropanoyl)-5,5-diphenyloxazolidin-2-one (24a). a) Compound (S)-11 (380 mg, 0.83 mmol) was treated at -70° with a soln. of MeMgBr (1.0 ml, 3.0 mmol, 3M in Et₂O) according to *GP 1* to yield the crude product (dr 65:35). Crystallization from hexane yielded 24a (150 mg, 40%). The same compound was obtained by methylation of the nitropropanoyl derivative 26 as described in the following procedure.

b) A soln. of ⁱPr₂NH (0.79 ml, 4.54 mmol) in DMPU/THF (1:5; 20 ml) was cooled to -35° . To this cold soln., BuLi (2.84 ml, 4.54 mmol, 1.6M in hexane) was added, and the mixture was stirred for 10 min at $ca. -35^{\circ}$ and then for 20 min at -76° . A soln. of **26** (0.764 g, 2.0 mmol) in DMPU/THF (1:5, 5 ml) was then added at once, and stirring was continued for 60 min. To the soln. of this double deprotonated nitro-DIOZ derivative MeI (0.158 ml, 2.54 mmol) was added at -76° , and the mixture was allowed to warm to -25° over 4 h. AcOH (0.114 ml, 2.0 mmol) was added, followed after 5 min by H₂O (10 ml), and the hydrolyzed mixture was allowed to warm to r.t., H₂O and Et₂O were added, the org. layer was separated, and the aq. layer was extracted twice with Et₂O. The combined org. layers were washed successively with

and the aq. layer was extracted twice with Et₂O. The combined org. layers were washed successively with H₂O, sat. aq. NaHCO₃ soln., and brine, dried (MgSO₄), and concentrated under reduced pressure. Purification by FC (hexane/AcOEt 4:1) and crystallization from hexane/AcOEt yielded diastereomerically pure **24a** (456 mg, 58%). Colorless powder. $R_{\rm f}$ (hexane/AcOEt 4:1) 0.44. M.p. 171–173°. $[a]_{2D}^{\rm D} = -183.4$ (c = 1.0, CHCl₃). IR (CHCl₃): 2970w, 1781s, 1700m, 1555s, 1495w, 1451m, 1395s, 1378s, 1317w, 1259w, 1212m, 1178m, 1053m, 993w, 761m, 703m, 666w, 638w. ¹H-NMR (400 MHz, CDCl₃): 0.70 (d, J = 6.8, Me); 0.79 (d, J = 6.8, Me); 1.28 (d, J = 7.2, Me); 1.88–1.94 (m, Me₂CH); 4.18 (dd, J = 14.8, 4.4, 1 H, CH₂); 4.21–4.28 (m, MeCH); 4.76 (dd, J = 14.8, 10.0, 1 H, CH₂); 5.34 (d, J = 3.2, CHN); 7.21–7.35 (m, 10 arom. H). ¹³C-NMR (100 MHz, CDCl₃): 14.9, 16.3, 21.8 (Me); 29.9, 36.2, 64.3 (CH); 75.1 (CH₂); 90.1 (C); 125.8, 126.0, 128.1, 128.4, 128.9, 129.0 (CH); 138.0, 141.5, 152.5, 173.2 (C). EI-MS: 396.17 (2, M^+), 353.11, 238.08, 220.12, 195.08, 183.08, 165.07. Anal. calc. for: C₂₂H₂₄N₂O₅ (396.44): C 66.65, H 6.10, N 7.07; found: C 66.67, H 5.93, N 7.03.

(S)-4-(1-Methylethyl)-3-[(S)-2-(1-methylethyl)-3-nitropropanoyl]-5,5-diphenyloxazolidin-2-one (24b). Compound (S)-11 (380 mg, 0.83 mmol) was treated at -70° with a soln. of ⁱPrMgBr (1.5 ml, 3.0 mmol, 2M in Et₂O) according to *GP1* to yield the crude product (dr 80:20) (24b/epi-24b). Crystallization from hexane/Et₂O yielded 24b (150 mg, 40%; mixture of diastereoisomers). Colorless solid. ⁱH-NMR (300 MHz, CDCl₃; main diastereoisomer): 0.77 (d, J = 6.9, Me); 0.91 (d, J = 7.6, Me); 0.93 (d, J = 6.9, Me); 1.13 (d, J = 6.9, Me); 1.9–2.1 (m, Me₂CH); 2.25–2.4 (m, Me₂CH); 4.15–4.23 (m, CH); 4.26 (dd, J = 2.9, 14.5, 1 H, CH₂); 4.86 (dd, J = 11.2, 14.7, 1 H, CH₂); 5.45 (d, J = 3, CHN); 7.29–7.42 (m, 10 arom. H).

(S)-4-(1-Methylethyl)-3-[(R)-2-(1-methylethyl)-3-nitropropanoyl]-5,5-diphenyloxazolidin-2-one (epi-24b). A soln. of (S)-11 (380 mg (0.83 mmol) in Et₂O (10 ml) was treated at r.t. with Cu^{II}-triflate (15 mg, 0.04 mmol). The yellow soln. was cooled to -45° , and a soln. of ($^{i}Pr_{2}$)Zn (1.1 ml, 1.1 mmol, 1M in Et₂O) was added during 20 min. The resulting red soln. was stirred for an additional 40 min at -40° and then warmed to 0° during 45 min, and then the reaction was quenched with sat. aq. NH₄Cl soln., and the mixture was extracted with Et₂O. The org. layer was washed with sat. aq. NH₄Cl soln., dried (MgSO₄), and concentrated under reduced pressure to yield the crude product with a dr 75:25 (epi-24b/24b). Crystallization from hexane yielded epi-24b (150 mg, 40%; mixture of diastereoisomers). Colorless solid. ¹H-NMR (400 MHz, CDCl₃): 0.56 (d, J = 6.9, Me); 0.63 (d, J = 6.9, Me); 0.84 (d, J = 6.8, Me); 0.91 (d, J = 7, Me); 1.48 – 1.55 (m, Me₂CH); 1.97 – 2.05 (m, Me₂CH); 4.43 (dd, J = 14.8, 3.0, 1 H, CH₂); 4.51 – 4.56 (m, CH); 4.94 (dd, J = 14.8, 11.2, 1 H, CH₂); 5.39 (d, J = 3.1, CHN); 7.24 – 7.54 (m, 10 arom. H). ¹³C-NMR (100 MHz, CDCl₃): 16.0; 18.0; 19.8; 21.5; 28.7; 29.9; 45.7; 65.7; 73.2; 125.4; 125.6; 128.0; 128.5; 128.6; 128.8; 128.9; 137.6; 152.8; 172.3. MALDI-MS: 446.04 ([M + Na]⁺). Anal. calc. for C₂₄H₂₈N₂O₅ (424.49): C 67.91, H 6.65, N 6.60; found: C 67.96, H 6.71, N 6.50.

(S)-4-(1-Methylethyl)-3-[(S)-3-nitro-2-phenylpropanoyl]-5,5-diphenyloxazolidin-2-one (**24c**). Compound (S)-**11** (380 mg, 0.83 mmol) was treated at -70° with a soln. of PhMgBr (3.0 ml, 3.0 mmol, 1M in

THF) according to *GP 1* to yield the crude product (dr 95:5). Crystallization from hexane yielded diastereomerically pure **24c** (200 mg, 55%). Colorless solid. $R_{\rm f}$ (hexane/AcOEt 4:1) 0.9. M.p. 168°. $[\alpha]_{10}^{20} = -226$ (c = 1, CH₂Cl₂). ¹H-NMR (400 MHz, CDCl₃): 0.39 (d, J = 6.7, Me); 0.72 (d, J = 7, Me); 1.80 – 1.88 (m, Me₂CH); 4.46 (dd, J = 15.1, 4.16, 1 H, CH₂); 5.24 (dd, J = 15.1, 11.0, 1 H, CH₂); 5.45 (d, J = 3.1, CHN); 5.66 (dd, J = 11.0, 4.2, PhCH); 7.25 – 7.46 (m, 15 arom. H). ¹³C-NMR (100 MHz, CDCl₃): 15.6; 21.6; 30.1; 46.2; 64.3; 75.1; 89.8; 125.9; 128.0; 128.3; 128.7; 128.8; 128.9; 129.0; 129.1; 132.4; 137.9; 141.5; 152.2; 170.5. Anal. calc. for C₂₇H₂₆N₂O₅ (458.51): C 70.73, H 5.72, N 6.11; found: C 70.45, H 5.64, N 6.12.

(IR,2S,5R)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-Methyl-3-nitropropanoate (**25a**). Compound **16** (1.0 g, 3.0 mmol) was treated at -70° with a soln. of MeMgBr (3.7 ml, 10.9 mmol, 3M in THF) according to *GP 1* to yield the crude product (dr 78 :22). FC (hexane/AcOEt 10 :1) yielded **25a** (380 mg, 36%; mixture of diasterioisomers). Oily residue. IR (CHCl₃): 2955w, 2922w, 2870w, 1725s, 1601w, 1556s, 1549s, 1495w, 1473w, 1455w, 1413w, 1375m, 1345w, 1240m, 1241s, 1228m, 1199m, 1174s, 1095m, 1094m, 977m, 961m, 908w, 845w, 774w, 764m, 742m, 699s, 627m. ¹H-NMR (600 MHz, CDCl₃): 0.87, 8.8 (2d, J = 6.6, Me); 0.94, 1.05 (2d, MeCH); 0.85–0.97 (m, CH₂); 1.18, 1.19, 1.29, 1.31 (4s, MeCPh); 1.10–1.20 (m, 1 H, CH₂); 1.43–1.52 (m, MeCH); 1.66–1.71 (m, 1 H, CH₂); 2.08–2.12 (m, CH); 2.34–2.40, 2.56–2.62 (2m, MeCH); 3.91 (dd, J = 14, 6.2, 1 H, CH₂NO₂, minor diastereoisomer); 3.96 (dd, J = 14, 5.5, 1 H, CH₂NO₂, minor diastereoisomer); 4.00 (dd, J = 14, 6.2, 1 H, CH₂NO₂, major diastereoisomer); 4.21 (dd, J = 14, 7.7, 1 H, CH₂NO₂, major diastereoisomer); 4.81 (dt, J = 10.7, 4.4, CH–O, minor diastereoisomer); 7.11–7.33 (m, 5 arom. H). ¹³C-NMR (150 MHz, CDCl₃): 13.4; 14.1; 21.7; 23.3; 23.6; 26.3; 26.4; 29.1; 29.4; 31.2; 34.5; 37.3; 37.4; 39.4; 39.5; 49.2; 49.9; 50.0; 75.6; 75.65; 75.7; 76.4; 125.1; 125.2; 125.25; 125.3; 128.0; 128.1; 151.9; 151.2; 170.9; 171.5. Anal. calc. for C₂₀H₂₉NO₄ (347.45): C 69.14, H 8.41, N 4.03; found: C 69.16, H 8.41, N 4.00.

(IR,2S,5R)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 3-Methyl-2-(nitromethyl)butanoate (25b). Compound 16 (1.0 g, 3.0 mmol) was treated at -70° with a soln. of ¹PrMgBr (5.5 ml, 10.9 mmol, 2M in THF) according to *GP 1* to yield the crude product (dr 51:49). FC (hexane/AcOEt 10:1) yielded 25b (830 mg, 73%; mixture of diastereoisomers). Oily residue. IR (CHCl₃): 2956w, 2922w, 2871w, 1726s, 1601w, 1556s, 1549s, 1495w, 1473w, 1456w, 1413w, 1375m, 1346w, 1242m, 1228m, 1199m, 1175s, 1095m, 978m, 961m, 909w, 845w, 845w, 774w, 764m, 742m, 699s, 627m. ¹H-NMR (600 MHz, CDCl₃; *ca.* 1:1 mixture of epimers): 0.74, 0.82 (2d, Me); 0.86–1.00 (m, CH₂, 2 Me); 1.06–1.16 (m, CH); 1.17, 1.20, 1.30, 1.31 (4s, 2 Me); 1.43–1.52 (m, CH); 1.63–1.78, 1.83–1.88, 1.90–1.95 (3m, 2 CH₂); 2.07–2.16 (m, CH); 2.42–2.45, 2.55–2.58 (2m, CHCOO); 3.91, 4.53 (2dd, 1 H, CH₂NO₂); 4.08, 4.17 (2dd, 1 H, CH₂NO₂); 4.72, 4.85 (2dt, CH–O); 7.11–7.33 (m, 5 arom. H). ¹³C-NMR (150 MHz, CDCl₃; *ca.* 1:1 mixture of epimers): 18.8; 19.4; 19.5; 20.1; 21.7; 21.8; 23.9; 24.7; 26.5; 26.7; 27.8; 28.3; 28.5; 28.6; 31.2; 31.3; 34.5; 34.6; 39.5; 39.6; 41.3; 41.4; 48.0; 48.8; 49.6; 50.3; 72.7; 72.8; 76.0; 76.1; 125.0; 125.1; 125.3; 125.4; 127.9; 128.1; 151.7; 151.9; 170.5; 170.9. Anal. calc. for C₂₂H₃₃NO₄ (375.50): C 70.37, H 8.86, N 3.73; found: C 70.51, H 8.73, N 3.72.

(*I*R,28,5R)-5-*Methyl*-2-(1-*methyl*-1-*phenylethyl*)*cyclohexyl* 3-*Nitro*-2-*phenylpropanoate* (**25c**). Compound **16** (1.0 g, 3.0 mmol) was treated at -70° with a soln. of PhMgBr (10.9 ml, 10.9 mmol, 1m in THF) according to *GP* 1 to yield the crude product (85%, dr 80:20). Crystallization from AcOEt/ hexane yielded diastereomerically pure **25c** (520 mg, 42%). Colorless solid. M.p. 115°. [*a*]_D²⁰ = -87.9 (*c* = 0.5, CHCl₃). IR (CHCl₃): 2955*w*, 2922*w*, 2870*w*, 1725*s*, 1601*w*, 1556*s*, 1473*w*, 1455*w*, 1413*w*, 1375*m*, 1345*w*, 1240*m*, 1228*m*, 1199*m*, 1173*s*, 1094*m*, 1032*w*, 977*m*, 960*m*, 908*w*, 845*w*, 773*w*, 764*m*, 741*m*, 699*s*, 627*m*. ¹H-NMR (600 MHz, CDCl₃): 0.57 (*dd*, *J* = 23, 11, Me); 0.77 (*d*, *J* = 6.5, *Me*CH); 0.80 (*ddd*, *J* = 25.0, 13.0, 3.6, 1 H, CH₂CHMe); 1.08 (*dq*, *J* = 13.2, 3.4, 1 H, CH₂CHCPh); 1.20 (*s*, *Me*CPh): 1.34 (*s*, *Me*CPh); 1.38 – 1.44 (*m*, MeCH); 1.61 – 1.66 (*m*, 1 H each, CH₂CHMe, CH₂CHO); 1.75 – 1.80 (*m*, 1 H, CH₂CHCPh); 1.99 – 2.03 (*m*, CHCPh); 3.49 (*dd*, *J* = 8.9, 6.1, CHCOO); 4.35 (*dd*, *J* = 14.3, 6.1, 1 H, CH₂NO₂); 4.73 (*dt*, *J* = 10.7, 4.2, CH–O); 4.81 (*dd*, *J* = 14.3, 8.9, 1 H, CH₂NO₂); 6.92 – 7.37 (*m*, 10 arom. H). ¹³C-NMR (150 MHz, CDCl₃): 21.6, 23.4 (Me); 26.3 (CH₂); 29.1 (Me); 31.1 (CH); 34.5 (CH₂); 39.5 (C); 40.3 (CH₂); 48.2, 50.02 (CH); 75.5 (CH₂); 76.0 (CH); 125.2, 125.5, 127.7, 128.0, 128.2, 129.0 (CH); 133.8, 152.0, 169.73 (C). Anal. calc. for C₂₅H₃₁NO₄ (409.52): C 73.32, H 7.63, N 3.42; found: C 73.11, H 7.48, N 3.41.

(S)-4-(1-Methylethyl)-3-(3-nitropropanoyl)-5,5-diphenyloxazolidin-2-one (26). a) BuLi (33.1 ml, 52.9 mmol, 1.6M in hexane) was added slowly to a suspension of (S)-3 (14.2 g, 50.4 mmol) in THF

$\begin{array}{llllllllllllllllllllllllllllllllllll$		11	12	17	epi- 19	24a	24c	25c
Chemical $C_{13}H_{13}$ formula 231.25 M_r 231.25 Crystal size 0.5×0 [mm]		753206	753207	753208	753209	753210	753211	753212
M_r 231.25 Crystal size 0.5×0 [mm]	NO3	$\mathrm{C}_{21}\mathrm{H}_{20}\mathrm{N}_{2}\mathrm{O}_{5}$	$C_{24}H_{19}NO_3$	$C_{21}H_{21}Cl_2NO_3$	$C_{31}H_{27}NO_3$	$C_{22}H_{24}N_2O_5$	$C_{27}H_{26}N_2O_5$	$C_{25}H_{31}NO_4$
Crystal size 0.5×0.5 [mm]		380.40	369.42	406.31	461.56	396.44	458.51	409.52
	$.36 \times 0.1$	0.2 imes 0.2 imes 0.08	$0.28 \times 0.08 \times 0.06$	0.5 imes 0.14 imes 0.04	$0.4\times0.02\times0.006$	$0.21 \times 0.18 \times 0.15$	$0.28 \times 0.2 \times 0.2$	$0.42 \times 0.21 \times 0.12$
Space group $P2_1/c$,		$P2_{1}2_{1}2_{1}$,	$P2_1$,	$P2_1$,	$P2_{1}2_{1}2_{1}$,	$P2_{1}2_{1}2_{1}$,	$P2_1$,	$P2_{1}2_{1}2_{1}$,
monoc	linic	orthorhombic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
a [Å] 13.254	l (4)	8.1342(10)	6.2781(4)	11.74(9)	6.1271(4)	9.1660(2)	11.3865(4)	6.3941(10)
b [A] 5.9599	(2)	13.6164(10)	15.5661(7)	$(3)^{(3)}$	18.5938(14)	10.9238(2)	9.0646(4)	11.6222(2)
c [Å] 15.260	5 (6)	17.670(3)	20.6012(11)	9.61(2)	21.519(2)	21.3608(2)	12.3294(4)	30.7392(5)
α [°] 90.00		90.00	90.00	90.00	90.00	90.00	90.00	90.00
β [°] 105.58	35(14)	90.00	93.074(2)	91.0(4)	90.00	90.00	107.449(2)	90.00
γ [°] 90.00		90.00	90.00	90.00	90.00	90.00	90.00	90.00
V [Å ³] 1161.13	3(7)	1957.1(4)	2010.4(2)	1014.0(9)	2451.6(3)	2138.80(8)	1214.01(8)	2284.34(6)
Ζ 4		4	4	2	4	4	2	4
$ ho_{ m calc} [{ m g} \cdot { m cm}^{-3}] 1.323$		1.291	1.221	1.331	1.251	1.231	1.254	1.191
$\mu [\rm mm^{-1}] 0.095$		0.077	0.081	3.051	0.080	0.088	0.087	0.080
Temp. [K] 223		298	298	298	203	223	203	223
$\theta_{\max} \begin{bmatrix} \circ \end{bmatrix} 27.49$ $I > 2\sigma(I)$		53.87	24.93	49.90	22.47	27.48	27.52	27.46
Reflexions:								
measured 4940		1402	6148	2077	9648	4854	5097	4599
independent 2655		1387	6143	1130	3196	4838	5091	4580
observed 1882		1303	4988	820	2545	4342	4393	4185
Variables 206		333	505	219	311	358	307	271
H-Atom refined	_	refined	constr.	constr.	not refined	refined	constr.	constr.
treatment								
R(all) 0.0707		0.0595	0.1063	0.1665	0.0838	0.0588	0.0639	0.0719
R(gt) 0.0462		0.0567	0.0884	0.1226	0.0646	0.0515	0.0527	0.0648
$\Delta/\sigma_{\rm max}$ 0.004		0.002	0.041	0.040	0.000	0.006	0.024	0.000
$\Delta \rho_{\rm max}$ [e Å ³] 0.176		0.372	0.315	0.485	0.206	0.221	0.301	0.408

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(200 ml) at -40° . The mixture was allowed to warm up to -10° over 15 min. and then cooled down to -70° , followed by dropwise addition of a soln. of 3-nitropropanoyl chloride¹⁹) (6.93 g, 50.4 mmol) in THF (10 ml) so that the temp. did not exceed -50° . After addition, the mixture was stirred for 1 h at -65° , followed by slow warm-up to r.t. The reaction was then quenched with half-sat. NH₄Cl (50 ml), and the mixture was extracted with AcOEt. The org. layers were washed with sat. aq. NaHCO₃, H₂O, and brine, dried (MgSO₄), and concentrated under reduced pressure. Purification by FC (hexane/AcOEt 4:1) afforded besides **7** (product of HNO₂ elimination; 2.98 g, 17%) and (*S*)-**3** (1.87 g, 13%), **26** (4.94 g, 26%) as a colorless powder. For anal. purposes, a sample was recrystallized from hexane/AcOEt.

b) To a mixture of (*S*)-7 (1.0 g, 3 mmol) and NaNO₂ (1.5 g, 22.5 mmol) in THF (10 ml) at 50° was added AcOH (1.25 ml, 22.5 mmol) during 2 h. The reaction was quenched with sat. aq. NaHCO₃ soln., and the mixture was extracted with Et₂O. The org. layer was washed with sat. aq. NH₄Cl soln. and brine, dried (MgSO₄), and concentrated under reduced pressure. FC (pentane/Et₂O 9:1) yielded beside unreacted (*S*)-7 (0.32 g, 32%), **26** (0.43 g, 55%). Colorless solid. $R_{\rm f}$ (pentane/Et₂O 2:1) 0.5. M.p. 93–96°. [α]₁₀²⁰ = -212.2 (c = 1.0, CHCl₃). IR (CHCl₃): 2970w, 1779s, 1705m, 1556s, 1495w, 1450m, 1386s, 1372s, 1319m, 1265m, 1245w, 1211m, 1178m, 1052m, 1002m, 988m, 948w, 909w, 869w, 843w, 761m, 733m, 704m, 666w, 638w. ¹H-NMR (300 MHz, CDCl₃): 0.78 (d, J = 6.9, Me); 0.87 (d, J = 6.9, Me); 1.98 (m, CH); 3.29 (ddd, J = 19.2, 6.9, 4.2, 1 H, CH₂); 3.69 (ddd, J = 18.9, 8.1, 4.2, 1 H, CH₂); 4.58–4.75 (m, CH₂NO₂); 5.38 (d, J = 3.3, CH); 7.28–7.46 (m, 10 arom. H). ¹³C-NMR (100 MHz, CDCl₃): 16.29, 21.73 (Me); 29.9 (CH); 32.3 (CH₂); 64.8 (CH); 68.9 (CH₂); 90.1 (C); 125.6, 125.9, 128.1, 128.5, 128.8, 129.0 (CH); 137.8, 141.9, 153.0, 168.9 (C). EI-MS: 382.15 (2, M⁺), 339.09, 220.12, 195.08, 183.08, 165.07. Anal. calc. for: C₂₁H₂₂N₂O₅ (382.41): C 65.96, H 5.80, N 7.33; found: C 66.05, H 5.94, N 7.31.

4. Determination of the X-Ray Structures (Table 3). All structures were determined by the X-ray service unit of the Laboratorium für Organische Chemie, ETH-Zürich. Suitable single crystals were measured on a Bruker–Nonius Kappa CCD diffractometer with MoK_a radiation ($\lambda = 0.71073$ Å, graphite monochromator). Structures were solved by direct methods (SIR97) [17] and refined by full-matrix least-squares on F² (SHELXL97) [18]. If possible, H-atoms were located from a difference electron-density map or constrained at ideal positions and included in the refinement. The absolute configurations are derived from the known senses of chirality of the chiral auxiliaries.

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¹⁹) Prepared according to a literature procedure [16].

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