Asymmetric Reaction of Simple Nitro Compounds with Chiral 1,3-Oxazolidin-2-ones

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Dedicated to Dr. *Günther Ohloff* on the occasion of his 80th birthday

The chiral oxazolidinone **1** (=[(3a*S*,6*R*,7a*R*)-tetrahydro-8,8-dimethyl-2-oxo-4*H*-3a,6-methano-1,3-benzoxazol-3-yl](oxo)acetaldehyde) was found to react stereoselectively with simple nitro compounds in the presence of Al_2O_3 or $Bu_4NF \cdot 3\,H_2O$ (TBAF) as catalysts, affording the diastereoisomeric nitro alcohols **3**–**6** with good asymmetric induction. When Al_2O_3 was used, the (*S*)-configuration at the center bearing the OH group was generated, with the relative *syn*-configuration for the major diastereoisomers. In the case of the nitro-aldol reaction catalyzed by TBAF, an opposite asymmetric induction was found for two nitro compounds. In contrast to **1**, compound **12** (=((4*R*,5*S*)-4-methyl-2-oxo-5-phenyl-1,3-oxazolidin-3-yl)(oxo)acetaldehyde), a derivative of *Evans* auxiliary, gave rise to poor asymmetric induction in *Henry* reactions.

Introduction. – The nitro-aldol addition reaction is one of the basic methods for the construction of C–C bonds [1]. We have recently presented stereoselective reactions of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam and (1*R*)-8-phenylmenthyl glyoxylate with simple nitro compounds, reactions that proceed with high asymmetric induction and chemical yields [2][3]. This methodology has been applied in the efficient syntheses of two biologically important compounds: bestatin and the side chain of *Taxotere*® [4]. In the present paper, we would like to demonstrate extension of our investigations on the diastereoselective *Henry* reaction of nitro compounds with two new glyoximides derived from '7,7-dimethylnorbornane-(1*S*,2*R*)-oxazolidinone' [5], and (4*R*,5*S*)-4-methyl-5-phenyl-1,3-oxazolidin-2-one [6].

Results and Discussion. – The reaction of '*N*-glyoxyloyl-7,7-dimethylnorbornane-(1*S*,2*R*)-oxazolidinone'[1]) (**1**) with nitro compounds of type **2** generally afforded the nitro alcohols **3**–**6** (*Scheme 1*). In the case of the reaction of nitromethane (**2a**), carried out in the presence of neutral Al_2O_3 (*Method A1*; *Table 1*) or tetrabutylammonium fluoride trihydrate ($TBAF \cdot 3\,H_2O$; *Method B*) as catalysts, the diastereoisomeric nitro alcohols **3a** and **5a** were obtained in yields of 93 and 87%, respectively (*Table 1*, *Entries 1* and *2*). As far as the stereochemical outcome is concerned, we observed the

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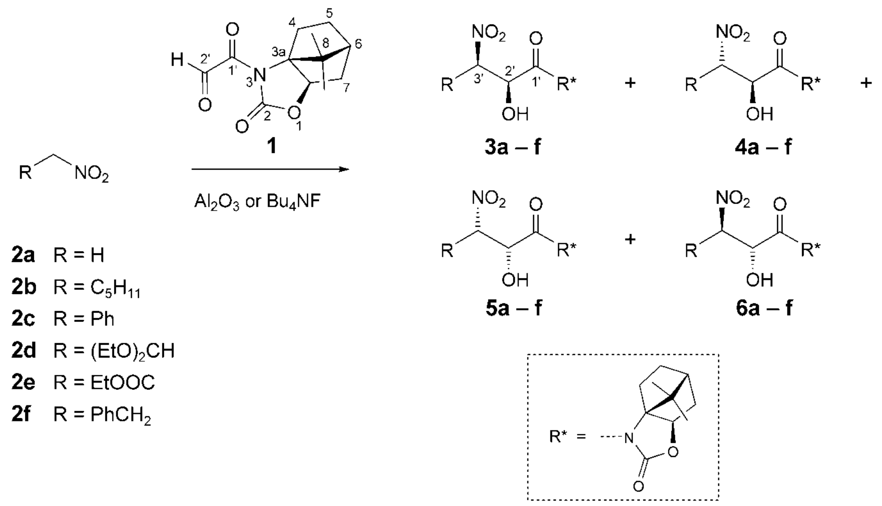
[1]) Systematic name: ((3a*S*,6*R*,7a*R*)-tetrahydro-8,8-dimethyl-2-oxo-4*H*-3a,6-methano-1,3-benzoxazol-3-yl)(oxo)acetaldehyde.

Scheme 1



formation of nitro alcohols with fair diastereoselectivities (28% and 72% de, resp.), as shown in *Table 1*. Surprisingly, in the reaction catalyzed by TBAF · 3 H_2O, we noticed inversion of asymmetric induction.

We extended our studies of the reaction between **1** and nitro compounds, and tested five more substrates: 1-nitrohexane (**2b**), (nitromethyl)benzene (**2c**), 1,1-diethoxy-2-nitroethane (**2d**), ethyl nitroacetate (**2e**), and (2-nitroethyl)benzene (**2f**). The results of these investigations are summarized in *Table 1*. Generally, all these transformations

Table 1. *Synthesis of Nitro Alcohols* **3**–**6**. For details, see the *Exper. Part*. and *Scheme 1*.

Entry	Nitro compound	Method[a])	Time [h]	Yield[b]) [%]	dr[c]) **3/4/5/6**
1	**2a**	A1	2	93	64 : 36[d])
2	**2a**	B	1	87	14 : 86[d])
3	**2b**	A1	2	88	45 : 25 : 21 : 9
4	**2b**	B	1	86	4 : 2 : 35 : 59
5	**2c**	A1	2	92	70 : 17 : 10 : 3
6	**2c**	B	1	92	55 : 19 : 11 : 15
7	**2d**	A1	2	88	67 : 17 : 11 : 5
8	**2d**	B	1	94	66 : 10 : 21 : 3
9	**2e**	A1	2	86	29 : 27 : 23 : 21
10	**2e**	B	1	91	35 : 24 : 21 : 20
11	**2f**	A1	2.5	88	34 : 28 : 21 : 17
12	**2f**	A2	1	87	42 : 31 : 15 : 12
13	**2f**	A3	36	72	41 : 39 : 10 : 10
14	**2f**	B	12	80	48 : 41 : 6 : 5

[a]) A1: Al_2O_3, r.t.; A2: activated Al_2O_3, r.t.; A3: activated Al_2O_3, $-20°$; B: TBAF · 3 H_2O, $-78°$. [b]) Isolated yield of diastereoisomeric mixtures. [c]) Diastereoisomer ratio; determined by both HPLC and ^{1}H-NMR. [d]) Compounds **3a** and **4a**, as well as **5a** and **6a**, respectively, are identical.

proceeded in high yields. Activation of Al_2O_3 by heating for 2 h at reduced pressure was not necessary, but it reduced the reaction time (*Table 1*, *Entries 11 vs. 12*). The nitro alcohols were formed with modest diastereoselectivities. In the case of processes catalyzed by TBAF·3 H_2O (*Method B*), an inversion of asymmetric induction was observed only for the reaction between **1** and **2b** (*Entry 4*).

The configurations of the diastereoisomeric nitro alcohols were assigned by means of various analytical and spectral methods, including chemical correlation, X-ray crystal-structure analysis, and NOE (nuclear *Overhauser* effect) experiments. The configuration of the major diastereoisomer **5a** (obtained from **1** and **2a** *via Method B*) was established on the basis of X-ray analysis, showing (2′*R*)-configuration at the newly formed stereogenic center (*Fig. 1*).

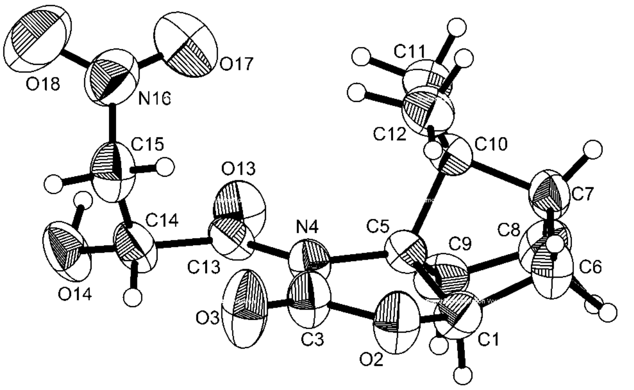
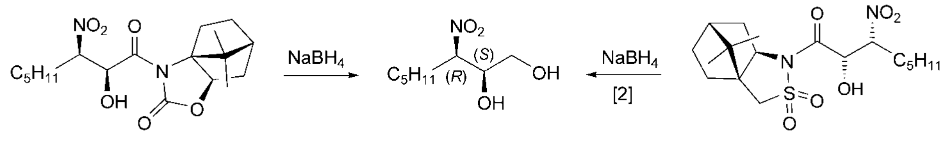


Fig. 1. *X-Ray crystal structure of* **5a**

The stereoselectivity of the reaction was much more complex to determine for the diastereoisomeric products of type **b**–**f**. The (2*S*,3*R*)- and the relative *syn*-configurations of the major product **3b** (*Method A1*; *Table 1*, *Entry 3*) were established on the basis of comparison of NMR spectra and optical rotations of the degradation product 3-nitrooctan-1,2-diol (**7**), obtained *via* two separate reductive cleavages of the chiral auxiliaries from the adduct **3b** or the sultam adduct **8**, respectively, of known configuration (*Scheme 2*) [2].

Scheme 2



3b **7** **8**

The structure and configuration of the major adduct **3c** (*Table 1*, *Entry 5*) was determined by X-ray crystal-structure analysis (*Fig. 2*). The configuration was found to be (2′*S*,3′*R*), with relative *syn*-configuration of the OH and NO_2 groups. Compound **5c**

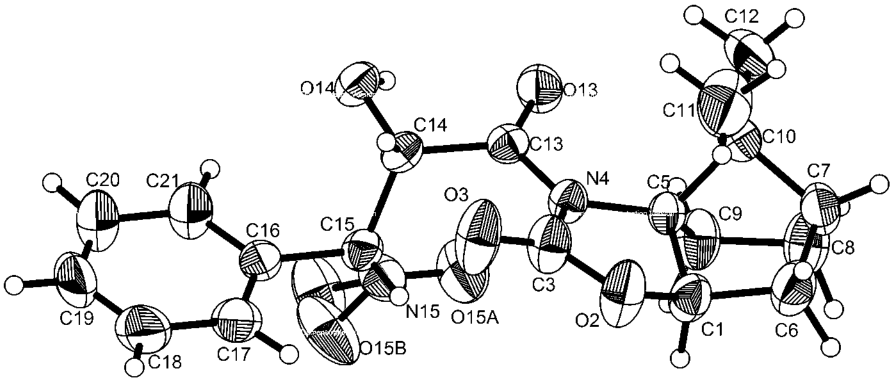


Fig. 2. *X-Ray crystal structure of* **3c**

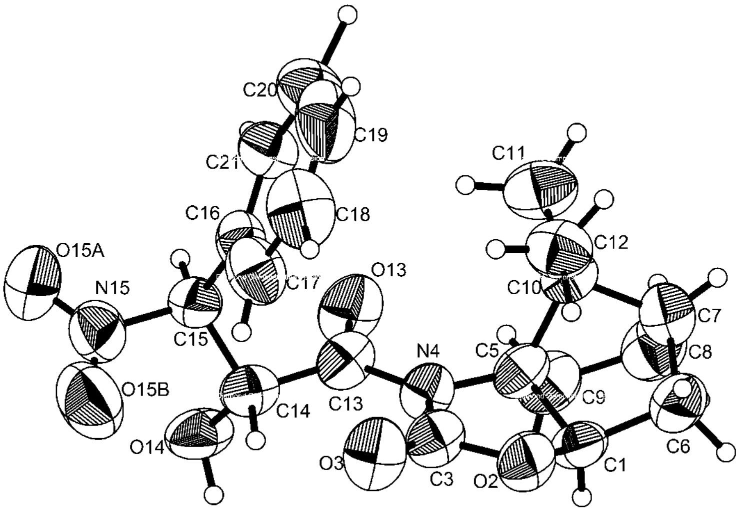


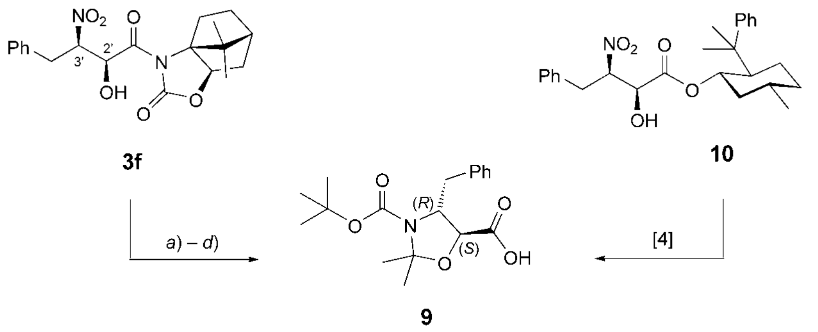
Fig. 3. *X-Ray crystal structure of* **5c**

was also identified *via* X-ray-analysis (*Fig. 3*). Here, the same *syn* relation was observed, but the opposite absolute configuration, *i.e.*, (2′*R*,3′*S*).

The absolute configuration of **3f** (*Table 1*, *Entry 12*) was confirmed by chemical correlation with the known, optically pure acid **9** [4] [7], which was obtained from **3f** in a four-step sequence in 60% overall yield (*Scheme 3*). Both the optical rotation and NMR spectra of the 'degradation' product **9** were identical with those of a sample synthesized from the menthol derivative **10**, thus corroborating the absolute configuration of **3f**.

Next, we turned our attention to *Evans* chiral auxiliary **11**, a highly efficient catalyst in various diastereoselective organic reactions [6], and converted it into '*N*-glyoxyloyl-

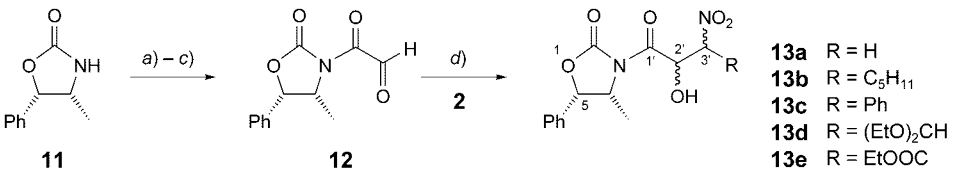
Scheme 3



a) H_2, *Raney*-Ni, MeOH. *b*) Boc_2O. *c*) DMP, *p*-TsOH. *d*) LiOH, H_2O_2.

(4*R*)-methyl-(5*S*)-phenyloxazolidinone'[2]) (**12**; *Scheme 4*). Compound **12**, which is not known in the literature, was then tested as an auxiliary in asymmetric *Henry* reactions. However, only moderate yields were obtained, even at prolonged reaction times (*Table 2*); and the same was true with compound **1**. The only exception was the reaction between **12** and **2e** (*Table 2*, *Entries 9* and *10*), which gave a mixture of nitro alcohols in more than 90% yield.

Scheme 4



a) Crotonoyl chloride, NaH. *b*) $OsO_4/NaIO_4$ or O_3. *c*) 80°, 0.2 mm Hg. *d*) Al_2O_3 or TBAF · 3 H_2O.

Table 2. *Synthesis of the Nitro Alcohols* **13a – e** (see *Scheme 4*). TBAF = $(Bu_4N^+F^-) \cdot 3\ H_2O$.

Entry	Nitro compound	Method[a])	Time [h]	Product	Yield[b]) [%]	dr[c])
1	**2a**	A	24	**13a**	62	56 : 44
2		B	24		50	65 : 35
3	**2b**	A	120	**13b**	29	50 : 25 : 20 : 5
4		B	24		57	26 : 9 : 48 : 17
5	**2c**	A	24	**13c**	63	36 : 27 : 25 : 12
6		B	24		74	12 : 11 : 57 : 20
7	**2d**	A	100	**13d**	10	35 : 34 : 29 : 2
8		B	24		16	47 : 36 : 10 : 7
9	**2e**	A	4	**13e**	95	28 : 26 : 25 : 21
10		B	1		90	26 : 32 : 20 : 22

[a]) A: Al_2O_3, r.t.; B: TBAF · 3 H_2O, – 78°. [b]) Isolated yield of diastereoisomeric mixture. [c]) Diastereoisomer ratio; determined by ^{1}H-NMR.

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[2]) Systematic name: ((4*R*,5*S*)-4-methyl-2-oxo-5-phenyl-1,3-oxazolidin-3-yl)(oxo)acetaldehyde.

Contrary to the reactions of glyoximide **1**, the diastereoselectivities of the above reactions with auxiliary **12** were unexpectedly poor. Considering this, we did not carry out the reactions in the presence of activated catalysts, because, although improving chemical yields, this lowered the degree of asymmetric induction. Moreover, the nitro alcohols were formed as inseparable mixtures of diastereoisomers, discouraging our efforts for assignment of configuration. Only for **13a** (prepared *via Method B*) we attempted to assign the configurations. Reduction of **13a** yielded 3-nitropropane-1,2-diol, whose optical rotation was compared with that of an authentic sample of known (2*S*)-configuration, with $[\alpha]_D^{20} = -6.7$ ($c = 0.99$, $CHCl_3$) [2]. The optical rotation measured for the degradation product was $[\alpha]_D^{20} = 2.2$ ($c = 1.8$, $CHCl_3$), which indicated (2*R*)-configuration of the major diastereoisomer, *i.e.*, the same as in the case of the 7,7-dimethylnorbornane-derived adduct.

Conclusions. – We have demonstrated that the chiral auxiliary **1** is an alternative to existing catalysts for the preparation of optically pure nitro alcohols, which are important starting materials for various natural products. Compounds **3**–**6** were obtained in 72–94% overall yield, with medium-to-good stereoselectivities. The new method further benefits from the fact that **1** can be recovered in 70–85% yield by means of hydrolysis or reduction.

Experimental Part

General. All reactions were carried out under Ar atmosphere in anh. solvents dried according to standard methods. Column chromatography (CC) was performed on *Kieselgel 60* (200–400 mesh; *Merck*). Thin-layer chromatography (TLC) was performed on *Kieselgel 60 F_{254}* on aluminum plates (*Merck*); visualization with a soln. of MoO_3 and $Ce_2(SO_4)_3$ in 15% aq. H_2SO_4. M.p.: *Kofler* hot-stage apparatus; uncorrected. Optical rotations: *JASCO DIP-360* polarimeter, thermally jacketed 10-cm cell. IR Spectra: *Perkin-Elmer-1640 FT-IR* apparatus; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM* and *Varian Gemini* spectrometers; chemical shifts δ (in ppm) rel. to residual $CHCl_3$ solvent signals; coupling constants *J* in Hz. Mass spectra: *AMD-604 Intectra* mass spectrometer; in *m*/*z*.

General Procedure for Al_2O_3-Catalyzed Nitro-Aldol Reactions (*Methods A1–A3*; see also *Table 1*). Compound **1** (1 mmol) and a nitro compound **2** (2 mmol) were added to a soln. of regular (*Method A1*) or activated[3] (*Methods A2* or *A3*) Al_2O_3 (2 mmol) in THF (5 ml). The mixture was stirred at r.t. or at −20° (*Method A3*), respectively, under Ar. The reaction was allowed to go to completion (TLC). The mixture was filtered and evaporated, and the products were purified by FC (hexane/AcOEt 9:1 → 6:4).

General Procedure for TBAF-Catalyzed Nitro-Aldol Reactions (*Method B*). Tetrabutylammonium fluoride trihydrate ($TBAF \cdot 3\,H_2O$; 0.5 mmol) was added to a soln. of **1** (1 mmol) in anh. THF (5 ml) at −78° under Ar atmosphere, followed by addition of a nitro compound **2** (2 mmol). The reaction was allowed to go to completion (TLC), and was then quenched by addition of brine. The mixture was extracted with AcOEt, the combined org. extracts were dried ($MgSO_4$) and evaporated, and the products were purified by FC (hexane/AcOEt 9:1 → 6:4).

(3aS,6R,7aR)-Tetrahydro-3-[(2R)-2-hydroxy-3-nitropropanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**5a**). *Method B.* Isolated yield after crystallization: 58%. M.p. 206° (MeOH). R_f (hexane/AcOEt 7:3) 0.50. $[\alpha]_D^{20} = +68.8$ ($c = 0.96$, $CHCl_3$). IR (KBr): 3482, 2970, 1784, 1710, 1550, 1379, 1322, 1176, 1077, 1055, 763. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.46 (*dd*, $J(2',3'A) = 4.6$, $J(2',3'B) = 4.8$, H−C(2′)); 4.86 (*dd*, $J = 13.8$, $J(2',3'A) = 4.6$, H_A−C(3′)); 4.90 (*dd*, $J = 13.8$, $J(2',3'B) = 4.8$, H_B−C(3′)); 4.41 (*dd*, $J(7a,7A) = 4.2$, $J(7a,7B) = 8.2$, H−C(7a)); 2.92–2.86 (*m*, H_A−C(4)); 2.35–2.25 (*m*, H_A−C(7)); 1.94–1.82 (*m*, H_A−C(5), H_B−C(7), H−C(6)); 1.40–1.30 (*m*, H_B−C(5)); 1.17, 1.05 (2*s*, 2 Me−C(8)); 1.00–0.95 (*m*, H_B−C(4)). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.0 (C(1′)); 155.3 (C(2)); 86.3 (C(7a)); 76.6 (C(3′)); 72.8 (C(3a)); 68.4 (C(2′)); 48.3

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[3] Activation was performed by heating for 2 h at 120°/0.2 Torr.

(C(8)); 42.2 (C(6)); 34.6 (C(7)); 25.7 (C(5)); 24.0 (C(4)); 21.4, 18.5 (2 *Me*−C(8)). HR-ESI-MS: 299.1228 ([*M* + H]$^+$, $C_{13}H_{19}N_6O_2^+$; calc. 299.1238). Anal. calc. for $C_{13}H_{18}N_2O_6$: C 52.34, H 6.08, N 9.39; found: C 52.14, H 6.33, N 9.20.

(3aS,6R,7aR)-Tetrahydro-3-[(2S)-2-hydroxy-3-nitropropanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**3a**). R_f (hexane/AcOEt 7:3) 0.50. ^{1}H-NMR (500 MHz, $CDCl_3$; selected signals from differential NMR): 5.47 (*dd*, *J*(2′,3′A) = 5.0, *J*(2′,3′B) = 4.5, H−C(2′)); 4.94 (*dd*, *J* = 13.3, *J*(2′,3′A) = 5.0, H_A−C(3′)); 4.90 (*dd*, *J* = 13.3, *J*(2′,3′B) = 4.5, H_B−C(3′)); 4.42 (*dd*, *J*(7a,7A) = 4.2, *J*(7a,7B) = 8.2, H−C(7a)); 1.15, 1.08 (2*s*, 2 Me−C(8)). ^{13}C-NMR (125 MHz, $CDCl_3$; selected signals): 169.8 (C(1′)); 155.0 (C(2)); 86.2 (C(7a)); 77.3 (C(3′)); 72.9 (C(3a)); 68.8 (C(2′)); 48.0 (C(8)); 43.1 (C(6)); 34.4 (C(7)); 25.8 (C(5)); 24.4 (C(4)); 20.8, 18.6 (2 *Me*−C(8)).

(3aS,6R,7aR)-Tetrahydro-3-[(2S,3R)-2-hydroxy-3-nitrooctanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**3b**). *Method B.* Isolated yield after double CC: 28%. R_f (hexane/AcOEt 7:3) 0.60. $[\alpha]_D^{20} = +27.5$ (*c* = 0.48; $CHCl_3$). IR (film): 3476, 2960, 1783, 1708, 1552, 1372, 1323, 1176, 1078, 1023, 765. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.23 (*dd*, *J*(2′,3′) = 8.8, *J*(2′,OH) = 2.4, H−C(2′)); 5.14 (*ddd*, *J*(2′,3′) = 8.8, *J*(3′,4′A) = 2.4, *J*(3′,4′B) = 5.3, H−C(3′)); 4.40 (*dd*, *J*(7a,7A) = 4.2, *J*(7a,7B) = 8.1, H−C(7a)); 3.10–2.90 (*m*, H_A−C(4)); 2.40–2.28 (*m*, H_A−C(7), CH_2(4′)); 2.13–1.80 (*m*, H_A−C(5), H_B−C(7), H−C(6)); 1.50–1.25 (*m*, H_B−C(5), CH_2(5′), CH_2(6′), CH_2(7′)); 1.20–1.05 (*m*, H_B−C(4)); 1.16, 0.92 (2*s*, 2 Me−C(8)); 0.94–0.86 (*m*, Me(8′)). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.1 (C(1′)); 154.9 (C(2)); 88.9 (C(3′)); 86.2 (C(7a)); 72.6 (C(3a)); 71.5 (C(2′)); 48.5 (C(8)); 42.3 (C(6)); 34.7 (C(7)); 31.1 (C(4′)); 29.5 (C(5′)); 26.0 (C(5)); 25.9 (C(6′)); 25.5 (C(4)); 22.1 (C(7′)); 20.4, 18.7 (2 *Me*−C(8)); 13.8 (Me(8′)). HR-LSI-MS: 369.20158 ([*M* + H]$^+$, $C_{18}H_{29}N_6O_2^+$; calc. 369.20256). Anal. calc. for $C_{18}H_{28}N_2O_6$: C 58.68, H 7.66, N 7.60; found C 58.96, H 7.43, N 7.31.

(3aS,6R,7aR)-Tetrahydro-3-[(2S,3S)-2-hydroxy-3-nitrooctanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**4b**). ^{1}H-NMR (500 MHz, $CDCl_3$; selected signals): 5.38 (*dd*, *J*(2′,3′) = 3.1, *J*(2′,OH) = 7.2, H−C(2′)); 4.86 (*ddd*, *J*(2′,3′) = 3.1, *J*(3′,4′A) = 8.6, *J*(3′,4′B) = 5.6, H−C(3′)); 4.43 (*dd*, *J*(7a,7A) = 4.2, *J*(7a,7B) = 8.2, H−C(7a)); 3.80 (*d*, *J*(2′,OH) = 7.2, OH); 1.16, 1.05 (2*s*, 2 Me−C(8)). ^{13}C-NMR (125 MHz, $CDCl_3$; selected signals): 171.8 (C(1′)); 155.0 (C(2)); 88.9 (C(3′)); 86.2 (C(7a)); 72.8 (C(3a)); 71.6 (C(2′)); 48.3 (C(8)); 42.5 (C(6)); 34.5 (C(7)); 31.1 (C(4′)); 29.4 (C(5′)); 25.7 (C(5)); 25.2 (C(6′)); 24.7 (C(4)); 24.2 (C(7′)); 21.4, 19.9 (2 *Me*−C(8)); 13.8 (Me(8′)).

(3aS,6R,7aR)-Tetrahydro-3-[(2R,3S)-2-hydroxy-3-nitrooctanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**5b**). ^{1}H-NMR (500 MHz, $CDCl_3$; selected signals): 5.22 (*dd*, *J*(2′,3′) = 8.1, *J*(2′,OH) = 6.2, H−C(2′)); 4.90 (*dt*, *J*(2′,3′) = *J*(3′,4′A) = 8.1, *J*(3′,4′B) = 3.9, H−C(3′)); 4.46 (*d*, *J*(2′,OH) = 6.2, OH); 4.39 (*dd*, *J*(7a,7A) = 4.2, *J*(7a,7B) = 8.2, H−C(7a)); 1.13, 1.04 (2*s*, 2 Me−C(8)). ^{13}C-NMR (125 MHz, $CDCl_3$; selected signals): 170.6 (C(1′)); 155.9 (C(2)); 86.3 (C(3′)); 85.9 (C(7a)); 72.6 (C(3a)); 70.4 (C(2′)); 48.4 (C(8)); 42.3 (C(6)); 34.6 (C(7)); 31.0 (C(4′)); 29.6 (C(5′)); 25.8 (C(5)); 25.1 (C(6′)); 24.7 (C(4)); 24.2 (C(7′)); 21.2, 18.9 (2 *Me*−C(8)); 13.8 (Me(8′)).

(3aS,6R,7aR)-Tetrahydro-3-[(2R,3R)-2-hydroxy-3-nitrooctanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**6b**). ^{1}H-NMR (500 MHz, $CDCl_3$; selected signals): 5.43 (*t*, *J*(2′,3′) = *J*(2′,OH) = 6.7, H−C(2′)); 3.61 (*d*, *J*(2′,OH) = 6.7, OH).

(3aS,6R,7aR)-Tetrahydro-3-[(2S,3R)-2-hydroxy-3-nitro-3-phenylpropanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**3c**). *Method A1.* Yield after crystallization: 54%. M.p. 198° (hexane/CH_2Cl_2). R_f (hexane/AcOEt 7:3) 0.5. $[\alpha]_D^{20} = +90$ (*c* = 1.05; $CHCl_3$). IR (KBr): 3470, 2966, 1795, 1684, 1553, 1387, 1175, 1073, 759. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.58–7.54 (*m*, 2 arom. H); 7.46–7.38 (*m*, 3 arom. H); 5.93 (*t*, *J*(2′,3′) = *J*(2′,OH) = 7.3, H−C(2′)); 5.81 (*d*, *J*(2′,3′) = 7.3, H−C(3′)); 4.04 (*d*, *J*(2′,OH) = 7.3, OH); 4.04 (*dd*, *J*(7a,7A) = 4.0, *J*(7a,7B) = 8.2, H−C(7a)); 2.68 (*dt*, *J*(4A,5A) = 5.2, *J*(4A,5B) = 4.0, H_A−C(4)); 2.25 (*ddt*, *J*(7a,7A) = 4.0, *J*(6,7A) = 3.6, *J*(7A,7B) = 13.9, H_A−C(7)); 2.23–1.95 (*m*, H_A−C(5)); 1.83–1.78 (*m*, H_B−C(7), H−C(6)); 1.25 (*ddd*, *J*(4,5B) = 5.2, *J*(5B,6) = 9.3, *J*(5A,5B) = 13.9, H_B−C(5)); 1.10 (2*s*, 2 Me−C(8)); 0.99–0.93 (*m*, H_B−C(4)). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.5 (C(1′)); 154.9 (C(2)); 130.7, 130.2, 128.9, 128.8 (Ph); 92.3 (C(3′)); 85.9 (C(7a)); 72.6 (C(3a)); 72.1 (C(2′)); 48.2 (C(8)); 42.4 (C(6)); 34.5 (C(7)); 25.7 (C(5)); 24.5 (C(4)); 21.3, 18.9 (2 *Me*−C(8)). HR-ESI-MS: 369.20158 ([*M* + Na]$^+$, $C_{19}H_{22}N_2NaO_6^+$; calc. 369.20256). Anal. calc. for $C_{19}H_{22}N_2O_6$: C 60.94, H 5.92, N 7.48; found: C 60.96, H 5.98, N 7.35.

(3aS,6R,7aR)-Tetrahydro-3-[(2S,3S)-2-hydroxy-3-nitro-3-phenylpropanoy])-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**4c**). *Method A1.* Yield after double CC: 10%. $[\alpha]_D^{20} = +88$ (*c* = 1.12; $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.48–7.40 (*m*, 5 arom. H); 5.90 (*d*, *J*(2′,3′) = 8.9, H−C(3′)); 5.66 (*dd*, *J*(2′,3′) = 8.9, *J*(2′,OH) = 6.2, H−C(2′)); 4.40 (*dd*, *J*(7a,7A) = 4.2, *J*(7a,7B) = 8.2, H−C(7a)); 4.25 (*d*, *J*(2′,OH) = 6.2, OH); 2.81 (*dt*, *J*(4A,5A) = 5.1, *J*(4A,5B) = *J*(4A,4B) = 12.0, H_A−C(4)); 2.25 (*ddt*, *J*(7a,7A) = *J*(6,7A) = 4.2, *J*(7A,7B) = 13.8, H_A−C(7)); 2.23–1.95 (*m*, H_A−C(5)); 1.90 (*dd*, *J*(7a,7B) = *J*(6,7B) = 8.2, *J*(7A,7B) = 13.8,

H_B–C(7)); 1.87–1.83 (*m*, H–C(6)); 1.38–1.30 (*m*, H_B–C(5)); 1.23–1.16 (*m*, H_B–C(4)); 1.13, 1.04 (2*s*, 2 Me–C(8)). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.5 (C(1')); 155.8 (C(2)); 131.5; 130.1; 129.0; 128.4 (Ph); 88.2 (C(3')); 86.4 (C(7a)); 72.7 (C(3a)); 71.0 (C(2')); 48.4 (C(8)); 42.3 (C(6)); 34.7 (C(7)); 25.8 (C(5)); 25.0 (C(4)); 21.2, 18.9 (2 *Me*–C(8)).

*(3a*S*,6*R*,7a*R*)-Tetrahydro-3-[(2*R*,3*S*)-2-hydroxy-3-nitro-3-phenylpropanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4*H*)-one* (**5c**). Yield after double CC: 6%. M.p. 158°. $[\alpha]_D^{20} = +5$ ($c = 1.65$; $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.66–7.62 (*m*, 2 arom. H); 7.45–7.38 (*m*, 3 arom. H); 6.03 (*d*, *J*(2',3') = 5.7, H–C(3')); 5.93 (*dd*, *J*(2',3') = 5.7, *J*(2',OH) = 8.3, H–C(2')); 4.33 (*dd*, *J*(7a,7A) = 4.3, *J*(7a,7B) = 8.4, H–C(7a)); 3.98 (*d*, *J*(2',OH) = 8.3, OH); 2.99–2.90 (*m*, H_A–C(4)); 2.31–2.24 (*m*, H_A–C(7)); 2.04–1.96 (*m*, H_A–C(5)); 1.86 (*dt*, *J*(7a,7B) = *J*(6,7B) = 8.4, *J*(7A,7B) = 13.7, H_B–C(7)); 1.82–1.79 (*m*, H–C(6)); 1.34–1.29 (*m*, H_B–C(5)); 1.17–1.00 (*m*, H_B–C(4)); 0.92, 0.88 (2*s*, 2 Me–C(8)). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.6 (C(1')); 155.0 (C(2)); 131.1, 130.1, 129.2, 128.8 (Ph); 91.4 (C(3')); 85.8 (C(7a)); 72.6 (C(3a)); 72.3 (C(2')); 48.4 (C(8)); 42.2 (C(6)); 34.7 (C(7)); 26.0 (C(5)); 25.8 (C(4)); 20.6, 18.7 (2 *Me*–C(8)).

*(3a*S*,6*R*,7a*R*)-Tetrahydro-3-[(2*R*,3*R*)-2-hydroxy-3-nitro-3-phenylpropanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4*H*)-one* (**6c**). ^{1}H-NMR (500 MHz, $CDCl_3$; selected signals): 5.93 (*dd*, *J*(2',3') = 8.1, *J*(2',OH) = 7.1, H–C(2')); 5.89 (*d*, *J*(2',3') = 8.1, H–C(3')); 4.38 (*dd*, *J*(7a,7B) = 8.2, *J*(7a,7A) = 4.2, H–C(7a)); 3.67 (*d*, *J*(2',OH) = 7.1, OH).

*(3a*S*,6*R*,7a*R*)-Tetrahydro-3-[(2*S*,3*S**)-4,4-diethoxy-2-hydroxy-3-nitrobutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4*H*)-one* (**3d**). Only relative configurations (*) were assigned. *Method A1*. Isolated yield after double CC: 42%. R_f (hexane/AcOEt 7:3) 0.5. $[\alpha]_D^{20} = +34$ ($c = 1.01$; $CHCl_3$). IR (film): 3474, 2977, 1783, 1703, 1555, 1372, 1328, 1176, 1117, 1076, 1025, 765. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.75 (*dd*, *J*(2',3') = 3.0, *J*(2',OH) = 8.3, H–C(2')); 5.24 (*d*, *J*(3',4') = 8.0, H–C(4')); 4.96 (*dd*, *J*(2',3') = 3.0, *J*(3',4') = 8.0, H–C(3')); 4.41 (*dd*, *J*(7a,7A) = 4.2, *J*(7a,7B) = 8.2, H–C(7a)); 3.85–3.70 (*m*, 2 MeC*H*$_2$O); 2.83–2.76 (*m*, H_A–C(4)); 2.35–2.28 (*m*, H_A–C(7)); 2.20–1.95 (*m*, H_A–C(5)); 1.94–1.84 (*m*, H_B–C(7), H–C(6)); 1.38–1.29 (*m*, H_B–C(5)); 1.23–1.18 (*m*, H_B–C(4)); 1.27, 1.17 (2*t*, *J* = 7.0 each, 2 *Me*CH$_2$O); 1.15, 1.04 (2*s*, Me–C((8)). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.6 (C(1')); 154.6 (C(2)); 99.3 (C(4')); 88.9 (C(3')); 86.1 ((C(7a)); 72.8 ((C(3a)); 69.9 ((C(2')); 64.5, 63.2 (2 MeC*H*$_2$O); 48.2 (C(8)); 42.5 (C(6)); 34.5 (C(7)); 25.7 (C(5)); 24.6 (C(4)); 21.3, 19.0 (2 *Me*–C(8)); 15.2, 14.9 (2 *Me*CH$_2$O). HR-ESI-MS: 423.1738 ($[M+H]^+$; $C_{18}H_{28}N_2NaO_8^+$; calc. 423.1738). Anal. calc. for $C_{18}H_{28}N_2O_8$: C 53.99, H 7.05, N 6.99; found: C 54.06, H 7.03, N 6.95.

*(3a*S*,6*R*,7a*R*)-Tetrahydro-3-[(2*S*,3*R**)-4,4-diethoxy-2-hydroxy-3-nitrobutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4*H*)-one* (**4d**). ^{1}H-NMR (500 MHz, $CDCl_3$; selected signals): 5.56 (*dd*, *J*(2',3') = 3.7, *J*(2',OH) = 5.6, H–C(2')); 5.15 (*d*, *J*(3',4') = 6.5, H–C(4')); 4.97 (*dd*, *J*(2',3') = 3.7, *J*(3',4') = 6.5, H–C(3')); 4.38 (*dd*, *J*(7a,7A) = 4.1, *J*(7a,7B) = 8.2, H–C(7a)). ^{13}C-NMR (125 MHz, $CDCl_3$; selected signals): 99.7 (C(4')); 87.3 (C(3')); 85.8 (C(7a)); 72.7 (C(3a)); 70.4 (C(2')); 48.3 (C(8)); 42.3 (C(6)); 34.7 (C(7)); 25.7 (C(5)); 24.9 (C(4)); 21.5, 18.5 (2 *Me*–C(8)).

*(3a*S*,6*R*,7a*R*)-Tetrahydro-3-[(2*R*,3*R**)-4,4-diethoxy-2-hydroxy-3-nitrobutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4*H*)-one* (**5d**). ^{1}H-NMR (500 MHz, $CDCl_3$; selected signals): 5.50 (*d*, *J*(3',4') = 9.9, H–C(4')); 4.33 (*dd*, *J*(7a,7A) = 4.1, *J*(7a,7B) = 8.2, H–C(7a)). ^{13}C-NMR (125 MHz, $CDCl_3$; selected signals): 88.4 (C(3')); 86.1 (C(7a)); 72.6 (C(3a)); 69.7 (C(2')); 48.5 (C(8)); 43.1 (C(6)); 34.3 (C(7)); 25.8 (C(5)); 24.0 (C(4)); 20.4, 18.4 (2 *Me*–C(8)).

*(3a*S*,6*R*,7a*R*)-Tetrahydro-3-[(2*R*,3*S**)-4,4-diethoxy-2-hydroxy-3-nitrobutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4*H*)-one* (**6d**). ^{1}H-NMR (500 MHz, $CDCl_3$; selected signals): 5.68 (*d*, *J*(3',4') = 8.4, H–C(4'); 4.24 (*dd*, *J*(7a,7A) = 4.2, *J*(7a,7B) = 8.4, H–C(7a). ^{13}C-NMR (125 MHz, $CDCl_3$; selected signals): 85.6 (C(7a)); 73.5 (C(3a)); 47.9 (C(8)); 25.6 (C(5)); 25.1 (C(4)); 21.0, 18.9 (2 *Me*–C(8)).

*(3a*S*,6*S*,7a*R*)-Tetrahydro-3-[(2*S*,3*S**)-4-ethoxy-2-hydroxy-3-nitro-4-oxobutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4*H*)-one*4) (**3e**). Inseparable mixture of nitroalcohols. Only relative configurations (*) were assigned. R_f (hexane/AcOEt 7:3) 0.5. IR (film): 3468, 2956, 1794, 1683, 1550, 1381, 1174, 1070, 758. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.68 (*d*, *J*(2',3') = 8.0, H–C(3')); 5.61 (*dd*, *J*(2',3') = 8.0, *J*(2',OH) = 6.4, H–C(2')); 4.49 (*d*, *J*(2',OH) = 6.4, OH); 4.43–4.38 (*m*, H–C(7a)); 4.35–4.28 (*m*, MeC*H*$_2$O); 2.90–2.80 (*m*, H_A–C(4)); 2.35–2.28 (*m*, H_A–C(7)); 2.12–2.01 (*m*, H_A–C(5)); 1.97–1.80 (*m*, H_B–C(7), H–C(6)); 1.40–1.26 (*m*, H_B–C(5), *Me*CH$_2$O); 1.09, 1.04 (2*s*, 2 Me–C(8)); 0.99–0.93 (*m*, H_B–C(4)). ^{13}C-NMR (125 MHz, $CDCl_3$): 169.9 (C(1')); 161.8 (C(4')); 155.5 (C(2)), 88.2 (C(3')); 86.0 (C(7a)); 72.5 (C(3a)); 70.0 (C(2')); 63.3 (MeC*H*$_2$O);

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4) Not fully systematic name. The benzoxazole nucleus was taken as the 'parent' compound (to retain atom numbering), although the COOEt group has higher priority.

48.5 (C(8)); 42.2 (C(6)); 34.6 (C(7)); 25.6 (C(5)); 24.9 (C(4)); 20.8, 18.8 (2 *Me*–C(8)); 13.7 (*Me*CH$_2$O). HR-ESI-MS: 393.1301 ([M + Na]$^+$, C$_{16}$H$_{22}$N$_2$NaO$_8^+$; calc. 393.1268).

(3aS,6S,7aR)-Tetrahydro-3-[(2S,3R*)-4-ethoxy-2-hydroxy-3-nitrobutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one*[4]) (**4e**). ^{1}H-NMR (500 MHz, CDCl$_3$; selected signals): 5.70 (*d*, J(2′,3′) = 7.2, H–C(3′)); 5.62 (*dd*, J(2′,3′) = 7.2, J(2′,OH) = 5.8, H–C(2′)); 4.51 (*d*, J(2′,OH) = 5.8, OH); 1.16, 1.07 (2*s*, 2 Me–C(8)). ^{13}C-NMR (125 MHz, CDCl$_3$; selected signals): 169.2 (C(1′)); 162.2 (C(4′)); 155.1 (C(2)); 88.0 (C(3′)); 86.3 (C(7a)); 72.6 (C(3a)); 69.8 (C(2′)); 48.3 (C(8)); 42.3 (C(6)); 34.6 (C(7)); 25.7 (C(5)); 24.9 (C(4)); 21.1, 18.8 (2 *Me*–C(8)); 13.6 (*Me*CH$_2$O).

(3aS,6R,7aR)-Tetrahydro-3-[(2R,3R*)-4-ethoxy-2-hydroxy-3-nitrobutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one*[4]) (**5e**). ^{1}H-NMR (500 MHz, CDCl$_3$; selected signals): 5.72 (*d*, J(2′,3′) = 6.6, H–C(3′)); 4.14 (*d*, J(2′,OH) = 7.9, OH); 1.13 1.11 (2*s*, 2 *Me*–C(8)). ^{13}C- NMR (125 MHz, CDCl$_3$; selected signals): 169.4 (C(1′)); 161.9 (C(4′)); 86.1 (C(7a)); 72.7 (C(3a)); 69.8 (C(2′)); 48.3 (C(8)); 42.2 (C(6)); 34.5 (C(7)); 25.3 (C(5)); 21.2, 19.0 (2*s*, 2 *Me*–C(8)); 13.7 (*Me*CH$_2$O).

(3aS,6S,7aR)-Tetrahydro-3-[(2R,3S*)-4-ethoxy-2-hydroxy-3-nitrobutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one* (**6e**). ^{1}H-NMR (500 MHz, CDCl$_3$; selected signals): 6.20 (*d*, J(2′,3′) = 6.9, H–C(3′)); 1.06, 0.97 (2*s*, 2 Me–C(8)). ^{13}C-NMR (125 MHz, CDCl$_3$; selected signals): 169.2 (C(1′)); 162.2 (C(4′)); 86.4 (C(7a)); 72.5 (C(3a)); 69.3 (C(2′)); 48.5 (C(8)); 42.3 (C(6)); 34.5 (C(7)); 25.8 (C(5)); 20.9, 19.0 (2 *Me*–C(8)); 13.8 (*Me*CH$_2$O).

(3aS,6R,7aR)-Tetrahydro-3-[(2S,3R)-2-hydroxy-3-nitro-4-phenylbutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**3f**). *Method A2*. Yield after double CC: 22%. R_f (hexane/AcOEt 7:3) 0.5. $[\alpha]_D^{20} = +29$ (c = 1.40; CHCl$_3$). IR (film): 3474, 2963, 1781, 1708, 1553, 1372, 1321, 1176, 1078, 762, 700. ^{1}H-NMR (500 MHz, CDCl$_3$): 7.33 – 7.23 (*m*, 5 arom. H); 5.45 (*ddd*, J(2′,3′) = 2.2, J(3′,4′B) = 9.0, J(3′,4′A) = 5.8, H–C(3′)); 5.16 (*dd*, J(2′,3′) = 2.2, J(2′,OH) = 8.9, H–C(2′)); 4.35 (*dd*, J(7a,7A) = 4.2, J(7a,7B) = 8.2, H–C(7a)); 4.33 (*dd*, J = 14.4, J(3′,4′A) = 5.8, H$_A$–C(4′)); 3.69 (*d*, J(2′,OH) = 8.9, OH); 3.60 (*dd*, J = 14.4, J(3′,4B) = 9.0, H$_B$–C(4′)); 3.07 – 2.98 (*m*, H$_A$–C(4)); 2.32 (*ddt*, J(7a,7A) = J(6,7A) = 3.9, J(7A,7B) = 13.7, H$_A$–C(7)); 2.21 – 2.02 (*m*, H$_A$–C(5)); 1.88 (*dd*, J(7a,7B) = J(6,7B) = 8.2, J(7A,7B) = 13.8, H$_B$–C(7)); 1.86 – 1.85 (*m*, H–C(6)); 1.37 – 1.29 (*m*, H$_B$–C(5)); 1.17 – 1.10 (*m*, H$_B$–C(4)); 1.13 (2*s*, 2 Me–C(8)). ^{13}C-NMR (125 MHz, CDCl$_3$): 172.0 (C(1′)); 154.8 (C(2)); 135.1, 129.3, 128.7, 127.3 (Ar); 89.7 (C(3′)); 86.3 (C(7a)); 72.7 (C(3a)); 71.5 (C(2′)); 48.6 (C(8)); 42.3 (C(6)); 35.6 (C(4′)); 34.8 (C(7)); 26.0 (C(5)); 25.9 (C(4)); 20.4, 18.7 (2 *Me*–C(8)). HR-ESI-MS: 389.1718 ([M + H]$^+$, C$_{20}$H$_{25}$N$_2$O$_6$; calc. 389.1707). Anal. calc. for C$_{20}$H$_{24}$N$_2$O$_6$: C 61.88, H 6.23, N 7.22; found C 61.56, H 6.06, N 6.99.

(3aS,6R,7aR)-Tetrahydro-3-[(2S,3S)-2-hydroxy-3-nitro-4-phenylbutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**4f**). ^{1}H-NMR (125 MHz, CDCl$_3$; selected signals): 5.36 (*dd*, J(2′,3′) = 2.7, J(2′,OH) = 7.1, H–C(2′)); 4.40 (*dd*, J(7a,7A) = 4.2, J(7a,7B) = 8.2, H–C(7a)); 3.86 (*d*, J(2′,OH) = 7.1, OH); 3.56 (*dd*, J = 14.4, J(3′,4′A) = 8.7, H$_A$–C(4′)); 3.32 (*dd*, J = 14.4, J(3′,4′B) = 5.8, H$_B$–C(4′)); 1.15, 1.02 (2*s*, 2 Me–C(8)). ^{13}C-NMR (125 MHz, CDCl$_3$; selected signals): 171.8 (C(1′)); 154.9 (C(2)); 135.0, 129.3, 128.7, 127.4 (Ar); 89.7 (C(3′)); 86.2 (C(7a)); 72.8 (C(3a)); 71.5 (C(2′)); 48.2 (C(8)); 42.5 (C(6)); 35.5 (C(4′)); 34.5 (C(7)); 25.8 (C(5)); 24.7 (C(4)); 21.4, 19.1 (2 *Me*–C(8)).

(3aS,6R,7aR)-Tetrahydro-3-[(2R,3S)-2-hydroxy-3-nitro-4-phenylbutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**5f**). ^{1}H-NMR (500 MHz, CDCl$_3$; selected signals): 4.29 (*dd*, J(7,7A) = 4.1, J(7,7B) = 8.2, H–C(7a)); 4.46 (*dd*, J = 14.6, J(3′,4′A) = 6.2, H$_A$–C(4′)); 1.11, 1.03 (2*s*, 2 Me–C(8)). ^{13}C-NMR (125 MHz, CDCl$_3$; selected signals): 172.3 (C(1′)); 155.5 (C(2)); 134.6, 129.1, 128.8, 127.6 (Ar); 86.4 (C(3′)); 86.3 (C(7a)); 72.7 (C(3a)); 69.5 (C(2′)); 48.4 (C(8)); 42.3 (C(6)); 35.2 (C(4′)); 34.6 (C(7)); 25.7 (C(5)); 25.0 (C(4)); 21.2, 18.9 (2 *Me*–C(8)).

(3aS,6R,7aR)-Tetrahydro-3-[(2R,3R)-2-hydroxy-3-nitro-4-phenylbutanoyl]-8,8-dimethyl-3a,6-methano-1,3-benzoxazol-2(4H)-one (**6f**). ^{1}H-NMR (500 MHz, CDCl$_3$; selected signals): 5.38 (*dd*, J(2′,3′) = 6.9, J(2′,OH) = 6.4, H–C(2′)); 5.45 (*ddd*, J(2′,3′) = 6.9, J(3′,4′B) = 8.1, J(3′,4′A) = 8.9, H–C(3′)); 4.38 (*dd*, J(7a,7A) = 4.2, J(7a,7B) = 8.2, H–C(7a)); 3.43 (*dd*, J = 14.8, J(3′,4′A) = 8.1, H$_A$–C(4′)); 3.36 (*dd*, J = 14.8, J(3′,4′B) = 3.0, H$_B$–C(4′)); 1.04, 1.01 (2*s*, 2 Me–C(8)). ^{13}C-NMR (125 MHz, CDCl$_3$; selected signals): 171.0 (C(1′)); 155.8 (C(2)); 138.4 (Ar); 72.6 (C(3a)); 70.7 (C(2′)); 48.3 (C(8)); 42.2 (C(6)); 21.2, 18.9 (2 *Me*–C(8)).

General Procedure for the Synthesis of Nitro Diols from Compounds **3** – **6**. To an ice-cold soln. of the nitro alcohol (1.0 mmol) in THF (1 ml), NaBH$_4$ (1.1 mmol) was added portionwise, and the reaction was monitored by TLC until complete. The mixture was quenched by addition of sat. aq. NaCl soln. and extracted with AcOEt. The combined org. extracts were dried (MgSO$_4$) and evaporated. All products were purified by CC (hexane/AcOEt 8:2 to 4:6).

*(2*S*,3*R*)-3-Nitrooctane-1,2-diol* ((2*S*,3*R*)-**7**). Yield: 88%. R_f (hexane/AcOEt 1 : 1) 0.2. $[\alpha]_D^{20} = 10.5$ ($c = 1.74$, MeOH). IR (film): 3371, 2958, 2931, 2863, 1554, 1464, 1377, 1099, 1039, 833. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.64 (*ddd*, *J*(2,3) = 8.3, *J*(3,4A) = 3.9, *J*(3,4B) = 10.4, H–C(3)); 4.15 (*ddd*, *J*(2,3) = 8.3, *J*(2,1A) = 3.0, *J*(2,1B) = 5.5, H–C(2)); 3.79 (*dd*, *J* = 11.9, *J*(2,1A) = 3.0, H_A–C(1)); 3.61 (*dd*, *J* = 11.9, *J*(2,1B) = 5.5, H_B–C(1)); 2.10–1.87 (*m*, H_A–C(4)); 1.83–1.63 (*m*, H_B–C(4)); 1.50–1.10 (*m*, CH_2(5), CH_2(6), CH_2(7)); 0.88–0.82 (*m*, Me(8)). ^{13}C-NMR (50 MHz, $CDCl_3$): 90.3 (C(3)); 72.5 (C(2)); 62.9 (C(1)); 30.9 (C(4)); 29.9 (C(5)); 25.2 (C(6)); 22.2 (C(7)); 13.8 (Me(8)). HR-ESI-MS: 214.1054 ($[M + Na]^+$, $C_8H_{17}NNaO_4^+$; calc. 214.1050). Anal. calc. for $C_8H_{17}NO_4$: C 50.25, H 8.96, N 7.32; found: C 50.03, H 8.83, N 7.20.

*(2*S*,3*S*)-3-Nitrooctane-1,2-diol* ((2*S*,3*S*)-**7**). Yield: 85%. R_f (hexane/AcOEt 1 : 1) 0.2. $[\alpha]_D^{20} = -21.0$ ($c = 1.70$, MeOH). ^{1}H-NMR (200 MHz, $CDCl_3$): 4.63 (*ddd*, *J*(2,3) = 5.8, *J*(3,4A) = 3.5, *J*(3,4B) = 10.3, H–C(3)); 4.09 (*dd*, *J*(2,3) = *J*(2,1A) = 5.8, *J*(2,1B) = 3.8, H–C(2)); 3.76 (*dd*, *J* = 11.7, *J*(2,1B) = 3.8, H_B–C(1)); 3.66 (*dd*, *J* = 11.7, *J*(2,1A) = 5.8, H_A–C(1)); 2.30–1.80 (*m*, CH_2(4)); 1.60–1.30 (*m*, CH_2(5), CH_2(6), CH_2(7)); 0.99–082 (*m*, Me(8)). ^{13}C-NMR (50 MHz, $CDCl_3$): 89.4 (C(3)); 72.2 (C(2)); 62.7 (C(1)); 31.0 (C(4)); 29.0 (C(5)); 25.4 (C(6)); 22.2 (C(7)); 13.8 (Me(8)).

*(4*R*,5*S*)-4-Benzyl-3-[(*tert*-butoxy)carbonyl]-2,2-dimethyl-1,3-oxazolidine-5-carboxylic acid* (**9**). H_2 was bubbled through a soln. of **3f** (0.39 mmol) in MeOH (5 ml) in the presence of a cat. amount of *Raney*-Ni. When the reaction was finished (TLC), the catalyst was filtered off and the solvent was evaporated. The residue was dissolved in AcOEt/sat. $NaHCO_3$ soln. 1 : 1 (10 ml), and $(Boc)_2O$ (0.43 mmol) was added. After 2 h of stirring, the layers were separated, and the aq. phase was extracted with CH_2Cl_2. The org. phase was dried ($MgSO_4$), and the solvents were removed under reduced pressure. The residue was dissolved in toluene (2 ml). Then, dimethoxypropane (0.21 mmol) and a cat. amount of 4-methylbenzenesulfonic acid (TsOH) were added. The mixture was heated at 50° (TLC control). After 5 h, the mixture was cooled, the solvents were evaporated, and the residue was dissolved in THF/H_2O 3 : 1 (4 ml). This mixture was cooled to 0°, and LiOH (3 equiv.) in aq. 28% H_2O_2 (6 equiv.) was added. After 2 h at r.t., peroxides were decomposed by addition of an excess of aq. Na_2SO_3 soln. The mixture was extracted with CH_2Cl_2 (3 ×), the combined extracts were dried ($MgSO_4$), evaporated *in vacuo*, and purified by CC (SiO_2; hexane/AcOEt 8 : 2 → 6 : 4) to give the recovered prosthetic group in 50% overall yield. The aq. phase was acidified with 3N aq. HCl and extracted with CH_2Cl_2 (3 ×). The combined org. layers were dried ($MgSO_4$), evaporated, and the residue was subjected to CC (SiO_2; CH_2Cl_2/MeOH 95 : 5 → 9 : 1) to afford **9** in 60% overall yield. $[\alpha]_D^{20} = 17.5$ ($c = 1.56$, $CHCl_3$); lit. $[\alpha]_D^{20} = 16.6$ ($c = 0.81$, $CHCl_3$) [4b].

*(4*R*,5*S*)-4-Methyl-2-oxo-5-phenyl-1,3-oxazolidin-3-yl](oxo)acetaldehyde* (**12**). *Method 1.* To a soln. of (4*R*,5*S*)-*N*-crotonoyl-4-methyl-5-phenyloxazolidinone [10] (4.66 g, 19 mmol) in dioxane/H_2O 3 : 1 (80 ml), OsO_4 (5.7 ml of a 0.05M soln. in *t*-BuOH; 0.285 mmol) was added. After 15 min, $NaIO_4$ (10.16 g, 47 mmol) was added. The reaction was monitored by TLC. After 12 h, the two phases were separated, and the aq. layer was extracted with AcOEt (3 ×). The combined extracts were dried ($MgSO_4$), evaporated, and the residue was purified by CC (hexane/AcOEt 8 : 2 → 1 : 1) to give a mixture of the corresponding glyoximide and its hydrate. This mixture was heated at 80° under reduced pressure (0.2 mm Hg) for 2 h to give **12** in 88% yield. For characterization, see below.

Method 2. A soln. of (4*R*,5*S*)-*N*-crotonoyl-4-methyl-5-phenyloxazolidinone (4.19 g, 17.1 mmol) [10] in MeOH/CH_2Cl_2 2 : 5 (280 ml) was cooled to −78°. O_3 was bubbled through this mixture until the blue color persisted. The excess of O_3 was purged with O_2, followed by addition of Me_2S. After stirring for 16 h, the solvents were evaporated and the residue was purified by CC (hexane/AcOEt 8 : 2 → 1 : 1) to give a mixture of the glyoximide and its hydrate. This mixture was heated at 80° under reduced pressure (0.2 mm Hg) for 2 h to give compound **12** in 80% yield. R_f (hexane/AcOEt 1 : 1) 0.2. $[\alpha]_D^{20} = 73.5$ ($c = 0.67$; $CHCl_3$). IR (film): 3455, 2983, 1787, 1711, 1354, 1200, 1149, 1122, 1032, 957, 765, 701. ^{1}H-NMR (200 MHz, $CDCl_3$): 9.91 (*s*, CHO); 7.51–7.25 (*m*, Ph); 5.91 (*d*, *J*(4,5) = 7.5, H–C(5)); 4.78 (*dq*, *J*(4,5) = 7.5, *J*(Me,4) = 6.7, H–C(4)); 1.00 (*d*, *J* = 6.7, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 184.8 (CHO); 162.8 (N–C=O); 153.5 (C(2) = O); 132.3, 129.1, 128.8, 125.6 (Ph); 81.5 (C(5)); 54.0 (C(4)); 14.3 (Me). HR-ESI-MS[5]): 302.0991 ($[M + H]^+$, $C_{14}H_{17}NO_5^+$; calc. 302.0999). Anal. calc. for $C_{12}H_{11}NO_4$: C 61.80, H 4.75, N 6.00; found C 61.77, H 4.99, N 5.81.

*(4*R*,5*S*)-3-[(2*R*)-2-Hydroxy-3-nitropropanoyl]-4-methyl-5-phenyl-1,3-oxazolidin-2-one* ((2′*R*)-**13a**). R_f (hexane/AcOEt 6 : 4) 0.5. IR (film): 3416, 2981, 1784, 1750, 1713, 1557, 1455, 1353, 1201, 1150, 1122, 1067, 957, 766, 701. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.46–7.37 (*m*, 4 arom. H); 7.33–7.28 (*m*, 1 arom. H); 5.84 (*d*, *J*(4,5) = 7.2, H–C(5)); 5.52–5.47 (*m*, H–C(2′)); 4.91 (*dd*, *J* = 13.9, *J*(2′,3′A) = 4.7, H_A–C(3′)); 4.84 (*dd*, *J* = 13.9, *J*(2′,3′B) =

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[5]) Data refer to the corresponding methyl acetal.

5.5, H$_B$–C(3′)); 4.89–4.78 (*m*, H–C(4)); 0.97 (*d*, *J* = 6.6, Me). ^{13}C-NMR (125 MHz, CDCl$_3$): 169.6 (C(1′)); 153.4 (C(2)); 132.2, 128.7, 125.6 (Ph); 80.5 (C(3′)); 76.2 (C(5)); 68.1 (C(2′)); 55.6 (C(4)); 14.2 (Me). HR-ESI-MS: 317.0758 ([*M* + Na]$^+$, $C_{13}H_{14}N_2NaO_6^+$; calc. 317.0744). Anal. calc. for $C_{13}H_{14}N_2O_6$: C 53.06, H 4.80, N 9.52; found: C 52.84, H 5.17, N 8.98.

*(4*R*,5*S*)-3-[(2*S*)-2-Hydroxy-3-nitropropanoyl]-4-methyl-5-phenyl-1,3-oxazolidin-2-one* ((2′*S*)-**13a**). ^{1}H-NMR (500 MHz, CDCl$_3$; selected signals): 4.97 (*dd*, *J* = 13.6, *J*(2′,3′A) = 5.0, H$_A$–C(3′)); 4.91 (*dd*, *J* = 13.6, *J*(2′,3′B) = 4.2, H$_B$–C(3′)); 0.97 (*d*, *J* = 6.7, Me–C(4)). ^{13}C-NMR (125 MHz, CDCl$_3$; selected signals): 170.0 (C(1′)); 153.0 (C(2)); 132.5, 129.1, 125.6 (Ph); 80.4 (C(3′)); 77.2 (C(5)); 68.4 (C(2′)); 55.1 (C(4)); 14.3 (*Me*–C(4)).

*(4*R*,5*S*)-3-(2-Hydroxy-3-nitrooctanoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one* (**13b**). Four diastereoisomers; configurations not determined. *R*$_f$ (hexane/AcOEt 6 :4) 0.6. IR (film): 3382, 2958, 2932, 2872, 1784, 1738, 1699, 1557, 1537, 1455, 1372, 1353, 1201, 1151, 1124, 766, 702. ^{1}H- and ^{13}C-NMR: see below. HR-ESI-MS: 387.1564 ([*M* + Na]$^+$, $C_{18}H_{24}N_2NaO_6^+$; calc. 387.1527). Anal. calc. for $C_{18}H_{24}N_2O_6$: C 59.33, H 6.64, N 7.69; found C 60.00, H 7.00, N 7.39.

Selected NMR Data for Diastereoisomer 1 of **13b**. ^{1}H-NMR (200 MHz, CDCl$_3$): 7.50–7.20 (*m*, 5 arom. H); 5.84 (*d*, *J*(4,5) = 7.2, H–C(5)); 5.34 (*dd*, *J*(2′,3′) = 3.5, *J*(2′,OH) = 7.8, H–C(2′)); 4.97 (*ddd*, *J*(2′,3′) = 5.3, *J*(3′,4′B) = 13.9, *J*(3′,4′A) = 8.8, H–C(3′)); 4.98–4.65 (*m*, H–C(4)); 3.79 (*d*, *J*(2,OH) = 7.8, OH); 4.36–2.15 (*m*, H$_A$–C(4′)); 2.14–1.89 (*m*, H$_B$–C(4′)); 1.58–1.10 (*m*, CH$_2$(5′), CH$_2$(6′), CH$_2$(7′)); 0.94–0.84 (*m*, Me(8′)). ^{13}C-NMR (50 MHz, CDCl$_3$): 170.5 (C(1′)); 153.0 (C(2)); 132.2, 129.1, 128.9, 125.5 (Ph); 88.7 (C(3′)); 80.5 (C(5)); 71.2 (C(2′)); 55.9 (C(4)); 31.1 (C(4′)); 29.4 (C(5′)); 25.2 (C(6′)); 22.2 (C(7′));14.2 (Me(4)); 13.8 (Me(7′)).

Selected NMR Data for Diastereoisomer 2 of **13b**. ^{1}H-NMR (200 MHz, CDCl$_3$): 5.81 (*d*, *J*(4,5) = 7.8, H–C(5)); 5.32 (*dd*, *J*(2′,3′) = 2.7, *J*(2′,OH) = 8.5, H–C(2′)); 5.11 (*ddd*, *J*(2′,3′) = 2.7, *J*(3′,4′B) = 5.5, *J*(3′,4′A) = 8.8, H–C(3′)); 3.64 (*d*, *J*(2′,OH) = 8.5, OH); 0.97 (*d*, *J* = 6.7, Me–C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 170.7 (C(1′)); 152.8 (C(2)); 132.5, 128.8, 125.7 (Ph); 88.8 (C(3′)); 80.3 (C(5)); 71.2 (C(2′)); 55.0 (C(4)); 31.1 (C(4′)); 29.3 (C(5′)); 25.2 (C(6′)); 22.2 (C(7′)); 14.3 (*Me*–C(4)); 13.8 (Me(8′)).

Selected NMR Data for Diastereoisomer 3 of **13b**. ^{1}H-NMR (200 MHz, CDCl$_3$): 5.80 (*d*, *J*(4,5) = 7.2, H–C(5)); 5.47 (*dd*, *J*(2′,3′) = 7.2, *J*(2′,OH) = 7.3, H–C(2′)); 4.93 (*ddd*, *J*(2′,3′) = 7.2, *J*(3′,4′B) = 2.2, *J*(3′,4′A) = 4.1, H–C(3′)); 4.04 (*d*, *J*(2′,OH) = 7.3, OH); 0.91 (*d*, *J* = 6.6, Me–C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 169.8 (C(1′)); 153.4 (C(2)); 132.5, 129.1, 125.6 (Ph); 86.2 (C(3′)); 80.3 (C(5)); 70.7 (C(2′)); 55.0 (C(4)); 31.1 (CH$_2$(4′)); 28.9 (CH$_2$(5′)); 24.9 (CH$_2$(6′)); 22.2 (CH$_2$(7′)); 14.3 (*Me*–C(4)); 13.8 (Me(8′)).

Selected NMR Data for Diastereoisomer 4 of **13b**. ^{1}H-NMR (200 MHz, CDCl$_3$): 5.79 (*d*, *J*(4,5) = 7.3, H–C(5)); 5.23 (*dd*, *J*(2′,3′) = 6.3, *J*(2′,OH) = 8.5, H–C(2′)). ^{13}C-NMR (50 MHz, CDCl$_3$): 169.1 (C(1′)); 154.0 (C(2)); 140.4, 129.8, 125.9 (Ar); 85.6 (C(3′)); 80.6 (C(5)); 69.9 (C(2′)); 55.4 (C(4)); 31.0 (CH$_2$(4′)); 29.8 (CH$_2$(5′)); 24.7 (CH$_2$(6′)); 22.2 (CH$_2$(7′)); 14.1 (*Me*–C(4)); 12.6 (Me(8′)).

*(4*R*,5*S*)-3-(2-Hydroxy-3-nitro-3-phenylpropanoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one* (**13c**). Yield after repeated CC: 12%. Four diastereoisomers; configurations not determined.

Data for Diastereoisomer 1 of **13c**. *R*$_f$ (hexane/AcOEt 6 :4) 0.5. $[\alpha]_D^{20}$ = 10.6 (*c* = 0.98; CHCl$_3$). IR (film): 3419, 2984, 1782, 1706, 1557, 1456, 1455, 1353, 1200, 1150, 1123, 1067, 765, 700. ^{1}H-NMR (200 MHz, CDCl$_3$): 7.67–7.59 (*m*, 2 arom. H); 7.48–7.36 (*m*, 6 arom. H); 7.29–7.21 (*m*, 2 arom. H); 6.03 (*d*, *J*(2′,3′) = 5.8, H–C(3′)); 5.91 (*dd*, *J*(2′,3′) = 5.8, *J*(2′,OH) = 7.8, H–C(2′)); 5.76 (*d*, *J*(4,5) = 7.7, H–C(5)); 4.81 (*dq*, *J*(4,5) = 7.7, *J*(4,Me) = 6.6, H–C(4)); 4.06 (*d*, *J*(2′,OH) = 7.8, OH); 0.74 (*d*, *J* = 6.6, Me–C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 169.5 (C(1′)); 152.9 (C(2)); 132.5, 130.7, 129.2, 129.1, 128.8, 125.6 (Ph); 91.5 (C(3′)); 80.0 (C(5)); 71.7 (C(2′)); 54.7 (C(4)); 14.2 (*Me*–C(4)). HR-LSI-MS: 371.12121 ([*M* + H]$^+$, $C_{19}H_{19}N_2O_6^+$; calc. 371.12431). Anal. calc. for $C_{19}H_{18}N_2O_6$: C 61.62, H 4.90, N 7.56; found: C 62.03, H 5.26, N 7.62.

Selected NMR Data for Diastereoisomer 2 of **13c**. ^{1}H-NMR (200 MHz, CDCl$_3$): 5.84 (*d*, *J*(2′,3′) = 7.3, H–C(3′)); 5.44 (*d*, *J*(4,5) = 7.1, H–C(5)); 4.56 (*dq*, *J*(4,5) = 7.1, *J*(4,Me) = 6.6, H–C(4)); 0.88 (*d*, *J* = 6.6, Me–C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 168.6 (C(1′)); 153.0 (C(2)); 132.1, 130.7, 130.2, 128.9, 128.7, 125.4 (Ph); 91.6 (C(3′)); 80.0 (C(5)); 71.4 (C(2′)); 55.4 (C(4)); 14.0 (Me(4)).

Selected NMR Data for Diastereoisomer 3 of **13c**. ^{1}H-NMR (200 MHz, CDCl$_3$): 5.81 (*d*, *J*(2′,3′) = 7.6, H–C(3′)); 0.80 (*d*, *J* = 6.5, Me–C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 169.5 (C(1′)); 153.2 (C(2)); 132.5, 130.9, 130.2, 129.1, 128.9, 128.7 (Ph); 88.3 (C(3′)); 80.2 (C(5)); 70.9 (C(2′)); 54.9 (C(4)); 14.3 (*Me*–C(4)).

Selected NMR Data for Diastereoisomer 4 of **13c**. ^{1}H-NMR (200 MHz, CDCl$_3$): 4.79 (*dq*, *J*(4,5) = 6,7, *J*(4,Me) = 6.6, H–C(4)); 0.95 (*d*, *J* = 6.6, Me–C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 169.1 (C(1′)); 153.7 (C(2)); 132.3, 131.5, 130.0, 129.9, 128.3, 125.5 (Ph); 88.1 (C(3′)); 80.4 (C(5)); 70.2 (C(2′)); 55.2 (C(4)); 13.8 (*Me*–C(4)).

*(4*R*,5*S*)-3-(4,4-Diethoxy-2-hydroxy-3-nitrobutanoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one* (**13d**). Four diastereoisomers; configurations not determined. R_f (hexane/AcOEt 6:4) 0.5. IR (film): 3464, 2981, 2935, 1786, 1738, 1708, 1555, 1353, 1221, 1200, 1149, 1121, 1067, 1033, 979, 765, 701. ^{1}H- and ^{13}C-NMR: see below. HR-ESI-MS: 419.1427 ([*M* + Na]$^+$, $C_{18}H_{24}N_2NaO_8^+$; calc. 419.1425). Anal. calc. for $C_{18}H_{24}N_2O_8$: C 54.54, H 6.10, N 7.07; found: C 54.41, H 6.30, N 6.78.

NMR Data for Diastereoisomer 1 of **13d**. ^{1}H-NMR (200 MHz, CDCl$_3$): 7.46 – 7.38 (*m*, 4 arom. H); 7.33 – 7.28 (*m*, 1 arom. H); 5.82 (*d*, *J*(4,5) = 7.0, H−C(5)); 5.72 (*dd*, *J*(2′,3′) = 3.4, *J*(2′,OH) = 8.8, H−C(2′)); 5.27 (*d*, *J*(3′,4′) = 7.9, H−C(4′)); 5.09 (*dd*, *J*(2′,3′) = 3.4, *J*(3′,4′) = 7.9, H−C(3′)); 4.74 (*dq*, *J*(4,5) = 7.0, *J*(4,Me) = 6.6, H−C(4)); 3.86 – 3.71 (*m*, 2 MeC*H*$_2$O); 1.28 (*t*, *J* = 7.0, *Me*CH$_2$O); 1.18 (*t*, *J* = 7.0, *Me*CH$_2$O); 0.96 (*d*, *J* = 6.6, Me−C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 170.4 (C(1′)); 152.6 (C(2)); 132.3, 129.1, 128.8, 125.6 (Ph); 99.2 (C(4′)); 88.6 (C(3′)); 80.3 (C(5)); 69.8 (C(2′)); 64.6 (Me*C*H$_2$O)); 63.2 (Me*C*H$_2$O); 55.8 (C(4)); 15.2 (*Me*−C(4)); 14.9 (*Me*CH$_2$O); 14.2 (*Me*CH$_2$O).

Selected NMR Data for Diastereoisomer 2 of **13d**. ^{1}H-NMR (200 MHz, CDCl$_3$): 5.63 (*d*, *J*(3′,4′) = 3.0, H−C(4′)); 5.29 (*dd*, *J*(2′,3′) = 8.0, H−C(2′)); 5.25 (*dd*, *J*(2′,3′) = 8.0, *J*(3′,4′) = 3.0, H−C(3′)); 4.82 (*dq*, *J*(4,5) = 6.8, *J*(4,Me) = 6.7, H−C(4)); 0.95 (*d*, *J* = 6.6, Me−C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 169.3 (C(1′)); 152.5 (C(2)); 132.6, 128.8, 125.6 (Ph); 99.8 (C(4′)); 88.5 (C(3′)); 80.3 (C(5)); 70.0 (C(2′)); 65.9 (Me*C*H$_2$O); 65.1 (Me*C*H$_2$O); 55.0 (C(4)); 15.1 (*Me*−C(4)); 14.1 (*Me*CH$_2$O); 14.0 (*Me*CH$_2$O).

Selected NMR Data for Diastereoisomer 3 of **13d**. ^{1}H-NMR (200 MHz, CDCl$_3$): 5.66 (*d*, *J*(4,5) = 7.8, H−C(5)); 5.16 (*d*, *J*(3′,4′) = 6.0, H−C(4′)); 5.10 (*dd*, *J*(2′,3′) = 4.6, *J*(3′,4′) = 6.0, H−C(3′)); 4.46 (*dq*, *J*(4,5) = 7.8, *J*(4,Me) = 6.6, H−C(4)); 0.96 (*d*, *J* = 6.6, Me−C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 168.0 (C(1′)); 152.6 (C(2)); 132.3, 129.1, 128.8 (Ph); 80.3 (C(5)); 55.9 (C(4)).

Selected NMR Data for Diastereoisomer 4 of **13d**. ^{1}H-NMR (200 MHz, CDCl$_3$): 4.68 (*dq*, *J*(4,5) = 6.8, *J*(4,Me) = 6.7, H−C(4)); 0.93 (*d*, *J* = 6.7, Me−C(4)). ^{13}C-NMR (50 MHz, CDCl$_3$): 169.3 (C(1′)); 152.7 (C(2)); 132.1, 129.0 (Ph); 80.3 (C(5)), 53.3 (C(4)).

*(4*R*,5*S*)-3-(4-Ethoxy-2-hydroxy-3-nitro-4-oxobutanoyl)-4-methyl-5-phenyl-1,3-oxazolidin-2-one*[4]) (**13e**). R_f (hexane/AcOEt 6:4) 0.5. IR (film): 3475, 2987, 2935, 1780, 1706, 1568, 1372, 1202, 1153, 1124, 1031, 767, 701. ^{1}H- and ^{13}C-NMR: see below. HR-LSI-MS: 367.11317 ([*M* + H]$^+$, $C_{16}H_{19}N_2O_8^+$; calc. 367.11414). Anal. calc. for $C_{16}H_{18}N_2O_8$: C 52.46, H 4.95, N 7.65; found: C 52.56, H 5.04, N 7.55.

NMR Data for Diastereoisomer 1 of **13e**. ^{1}H-NMR (500 MHz, C$_6$D$_6$): 7.05 – 6.96 (*m*, 5 arom. H); 6.20 (*d*, *J*(2′,3′) = 7.2, H−C(3′)); 5.99 (*d*, *J*(2′,3′) = 7.2, H−C(2′)); 4.70 (*d*, *J*(4,5) = 7.6, H−C(5)); 4.23 – 4.01 (*m*, H−C(4)); 4.01 – 3.77 (*m*, MeC*H*$_2$O); 0.80 (*t*, *J* = 7.1, *Me*CH$_2$O); 0.62 (*d*, *J* = 6.6, Me−C(4)). ^{13}C-NMR (125 MHz, C$_6$D$_6$): 169.0 (C(1′)); 162.3 (C(4′)); 153.1 (C(2)); 133.1, 128.8, 128.1, 125.8 (Ph); 89.2 (C(3′)); 79.8 (C(5)); 70.0 (C(2′)); 63.3 (Me*C*H$_2$O); 54.8 (C(4)); 13.7 (*Me*−C(4)); 13.6 (*Me*CH$_2$O).

Selected NMR Data for Diastereoisomer 2 of **13e**. ^{1}H-NMR (500 MHz, C$_6$D$_6$): 6.13 (*d*, *J*(2′,3′) = 5.6, H−C(3′)); 5.88 (*d*, *J*(2′,3′) = 5.6, H−C(2′)); 4.62 (*d*, *J*(4,5) = 7.4, H−C(5)); 0.82 (*t*, *J* = 7.1, *Me*CH$_2$O); 0.56 (*d*, *J* = 6.6, Me−C(4)). ^{13}C-NMR (125 MHz, C$_6$D$_6$): 168.6 (C(1′)); 162.7 (C(4′)); 153.5 (C(2)); 132.9, 128.8, 128.0, 125.7 (Ph); 87.4 (C(3′)); 79.9 (C(5)); 69.9 (C(2′)); 63.3 (Me*C*H$_2$O); 55.1 (C(4)); 13.7 (*Me*−C(4)); 13.6 (*Me*CH$_2$O).

Selected NMR Data for Diastereoisomer 3 of **13e**. ^{1}H-NMR (500 MHz, C$_6$D$_6$): 6.10 (*d*, *J*(2′,3′ = 8.7, H−C(3′)); 5.97 (*d*, *J*(2′,3′) = 8.7, H−C(2′)); 4.72 (*d*, *J*(4,5) = 7.7, H−C(5)); 0.86 (*t*, *J*(5,6) = 7.1, *Me*CH$_2$O); 0.51 (*d*, *J* = 6.6, Me−C(4)). ^{13}C-NMR (125 MHz, C$_6$D$_6$): 169.0 (C(1′)); 162.9 (C(4′)); 153.2 (C(2)); 133.1, 128.9, 128.2, 125.8 (Ph); 88.8 (C(3′)); 79.9 (C(5)); 70.0 (C(2′)); 63.2 (Me*C*H$_2$O); 54.8 (C(4)); 13.8 (*Me*−C(4)); 13.4 (*Me*CH$_2$O).

Selected NMR Data for Diastereoisomer 4 of **13e**. ^{1}H-NMR (500 MHz, C$_6$D$_6$): 6.04 (*d*, *J*(2′,3′) = 7.8, H−C(3′)); 5.94 (*d*, *J*(2′,3′) = 7.8, H−C(2′)); 4.63 (*d*, *J*(4,5) = 7.3, H−C(5)); 0.89 (*t*, *J*(5,6) = 6.7, *Me*CH$_2$O); 0.52 (*d*, *J* = 6.6, Me−C(4)). ^{13}C-NMR (125 MHz, C$_6$D$_6$): 168.6 (C(1′)); 162.7 (C(4′)); 153.8 (C(2)); 132.9, 128.8, 128.1, 125.7 (Ph); 86.8 (C(3′)); 79.0 (C(5)); 69.6 (C(2′)); 64.1 (Me*C*H$_2$O); 55.2 (C(4)); 13.9 (*Me*−C(4)); 13.4 (*Me*CH$_2$O).

X-Ray Crystal-Structure Analyses. Measurements were made on a *Kuma KM4CCD* diffractometer, using the Express software, and without absorption corrections. The structures were solved by direct methods [8] and refined with the SHELXL97 program [9]. The known configuration of the asymmetric centers has been confirmed by *Flack*-parameter refinement. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Center* as supplementary publication numbers CCDC-230269 (**5a**), CCDC-230270 (**3c**), and CCDC-230271 (**5c**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk), or *via* internet (www.ccdc.cam.ac.uk/retrieving.html).

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