REVISED !

SUPPORTING INFORMATION (15 pages)

**Chiral-Auxiliary-Controlled Diastereoselectivity in the Epoxidation
of Enecarbamates with DMD and *m*CPBA**

Waldemar Adam, Sara G. Bosio*, Barbara T. Wolff

*Institut für Organische Chemie, Universität Würzburg, Am Hubland,
D-97074 Würzburg, GERMANY*

E-mail: adam@chemie.uni-wuerzburg.de

General Remarks

The ^1H - and ^{13}C -NMR spectra were recorded on a Bruker AC 200 (^1H : 200 MHz, ^{13}C : 50 MHz) or on a Bruker Avance 400 (^1H : 400 MHz, ^{13}C : 101 MHz) spectrometer, the IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrophotometer. The HPLC analyses were carried out on chiral columns (Daicel CHIRALCEL OD-H) by means of a Kontron instrument, furnished with a spectrophotometer UVIKON 720 and a CHIRALYSER 1.6, the latter from IBZ Masstechnik (Hannover, Germany). Silicia gel (20 - 63 mm, Woelm) was used for flash chromatography. Solvents and commercially available chemicals were purified by standard procedures. The enantiomerically pure 4-(*R*)-isopropylloxazolidinone, 4-(*S*)-*tert*-butylloxazolidinone, 4-(*S*)-phenylloxazolidinone were generous gifts from Degussa AG, Hanau, Germany. The enecarbamates **1a-d** were prepared according to the literature procedure.⁸

General Procedure for the Epoxidation of the Enecarbamates **1** with Dimethyldioxirane (GP1)

The enecarbamate **1** (1.0 equiv.) was dissolved in acetone (30 mL) and 0.50 g of molecular sieves (5 Å) was added under an argon-gas atmosphere. The solution was cooled to 0 °C and after 10 min magnetic stirring, 1.0 equiv. of dimethyldioxirane (0.09 M in acetone) was added. The reaction mixture was allowed to warm up to ca. 20 °C while stirring, and the reaction progress was monitored for the presence of DMD by iodometry (KI/HOAc). After complete DMD consumption (the reaction times are given for the individual cases), the reaction mixture was centrifuged to remove the molecular sieves, the sieves were washed with acetone (2x15 mL) and centrifuged again. From the combined centrifugates, the acetone was removed (20 °C, 30 mbar) and the epoxide **2** was obtained as only product.

The epoxides **2** were too labile for purification by silica-gel chromatography, and were characterized by their ^1H - and ^{13}C - NMR spectra and exact mass determination on the diastereomeric mixture [except epoxide 2a, which decomposed completely already at room temperature (ca. 20 °C) in a couple of hours].

The diastereomeric ratio was determined by ^1H -NMR analysis directly on the crude reaction mixture, through integration of the areas under the characteristic NMR signals. In the case of nearly 1:1 mixtures of the diastereomers, COSY, HMBC and HMQC experiments were carried out for rigorous assignment. For the configurational assignment of the individual diastereomers, see General Procedure GP3.

The epoxides **2b-d** persist as neat solids for several months at -20 °C, but they readily decompose in solution in the presence of acid traces at room temperature (ca. 20 °C). For

this reason, after formation, the labile epoxides must be immediately worked up to remove the solvent and the molecular sieves to minimize decomposition.

Epoxidation of the Enecarbamate **Z-1a** by DMD

According to the general procedure GP1, 397.5 mg (1.96 mmol) of enecarbamate **Z-1a** were epoxidized with DMD during 1 h. After work-up, the racemic epoxide (**1S*,2S*-2a**) was obtained as colorless oil in 94% yield (403.8 mg). The material decomposed at ca. 20 °C within a couple of hours, such that an exact-mass determination was not possible. Characterisation rests only on the NMR-spectral data.

(1S*,2S*)-3-(3-Methyl-3-phenyloxyranyl)oxazolidin-2-one [(1S*,2S*)-2a].

¹H-NMR (400 MHz, CDCl₃) δ 1.64 (s, 3 H), 2.27-2.39 (m, 1 H), 3.05-3.16 (m, 1 H), 3.89-4.00 (m, 1 H), 4.04-4.14 (m, 1 H), 4.97 (s, 1 H), 7.18-7.56 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃) δ 24.4 (q), 41.6 (d), 62.6 (t), 63.4 (s), 69.6 (d), 126.4 (d), 128.1 (d), 128.5 (d), 137.8 (s), 158.4 (s).

Epoxidation of the Enecarbamate **Z-1b** by DMD

According to the general procedure GP1, 433.1 mg (1.77 mmol) of the enecarbamate **Z-1b** were dissolved in 50 mL acetone and epoxidized with DMD for 2 h. After work-up, a diastereomeric mixture (60:40) of the epoxides (**1S,2S-2b** and (**1R,2R-2b**) was obtained as a colorless powder in ca. 100% yield (462.1 mg).

IR (KBr) 2966, 1757, 1445, 1393, 1315, 1234 ; exact mass for C₁₅H₁₉NO₃ Calcd. 261.1364; Found 261.1359.

(1S,2S)-4-Isopropyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1S,2S)-2b].

¹H NMR (400 MHz, CDCl₃) δ 0.54 (d, *J* = 7.0 Hz, 3 H), 0.65 (d, *J* = 6.8 Hz, 3 H), 1.60-1.70 (m, 1 H), 1.67 (s, 3 H), 2.62-2.71 (m, 1 H), 3.49-3.57 (m, 1 H), 3.75-3.88 (m, 1 H), 4.45 (s, 1 H), 7.12-7.53 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃) δ 14.8 (q), 17.5 (q), 22.8 (q), 29.7 (d), 59.0 (d), 63.8 (t), 62.0 (s), 68.5 (d), 126.8 (d), 128.1 (d), 128.2 (d), 137.2 (s), 158.7 (s).

(1R,2R)-4-Isopropyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1R,2R)-2b].

¹H-NMR (400 MHz, CDCl₃) δ 0.71 (d, *J* = 7.1 Hz, 3 H), 0.83 (d, *J* = 6.9 Hz, 3 H), 1.60 (s, 3 H), 1.93-2.06 (m, 1 H), 3.02-3.10 (m, 1 H), 3.57-3.83 (m, 1 H), 3.75-3.88 (m, 1 H), 4.58 (s, 1 H), 7.12-7.53 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃) δ 15.4 (q), 17.5 (q), 22.5 (q), 29.6 (d), 59.3 (d), 64.2 (t), 64.7 (s), 68.0 (d), 126.2 (d), 128.1 (d), 128.2 (d), 137.2 (s), 158.9 (s).

Epoxidation of the Enecarbamate **Z-1b** by DMD at -25 °C

According to the general procedure GP1 (except at -25 °C instead of 20 °C), a solution of 253.5 mg (1.03 mmol) of the enecarbamate **Z-1b** in 30 mL of acetone was epoxidized with DMD for 18 h. After work-up, a diastereomeric mixture (63:37) of the epoxides (1*S*,2*S*)-**2b** and (1*R*,2*R*)-**2b** was obtained as a colorless powder in 83% yield (209.0 mg).

Epoxidation of the Enecarbamate **Z-1c** by DMD

According to the general procedure GP1, 619.8 mg (2.22 mmol) of the enecarbamate **Z-1c** were epoxidized with DMD for 4 h. After work-up, a diastereomeric mixture (92:8) of the epoxides (1*R*,2*R*)-**2c** and (1*S*,2*S*)-**2c** was obtained as colorless oil in ca. 100% yield (655.1 mg).

IR (neat) 2974, 1763, 1456, 1396, 1320, 1224; exact mass for C₁₈H₁₇NO₃ Calcd. 295.1208; Found 295.1205.

(1*R*,2*R*)-4-Phenyl-3-(3-methyl-3-phenyloxiranyl)oxazolidin-2-one [(1*R*,2*R*)-**2c**].

¹H-NMR (400 MHz, CDCl₃) δ 1.46 (s, 3 H), 3.78-3.85 (m, 1 H), 3.87-3.95 (m, 1 H), 4.19-4.27 (m, 1 H), 4.52 (s, 1 H), 6.76-6.82 (m, 2 H), 7.11-7.25 (m, 8 H); ¹³C-NMR (151 MHz, CDCl₃) δ 22.9 (q), 58.4 (d), 62.2 (s), 69.1 (t), 70.7 (d), 125.9 (d), 126.8 (d), 127.9 (d), 128.0 (d), 128.6 (d), 128.9 (d), 136.7 (s), 138.4 (s), 158.6 (s).

(1*S*,2*S*)-4-Phenyl-3-(3-methyl-3-phenyloxiranyl)oxazolidin-2-one [(1*S*,2*S*)-**2c**].

¹H-NMR (400 MHz, CDCl₃) δ 1.52 (s, 3 H), 3.77-4.16 (m, 3 H, overlap with the signals of the major isomer), 4.45 (s, 1 H), 6.76-6.82 (m, 5 H), 7.11-7.25 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃): δ = 22.5 (q), 59.1 (d), 65.1 (s), 68.1 (t), 70.6 (d), 126.1 (d), 126.5 (d), 127.9 (d), 128.2 (d), 128.5 (d), 129.1 (d), 136.8 (s), 139.0 (s), 159.1 (s).

Epoxidation of the Enecarbamate **Z-1d** by DMD

According with the general procedure GP1, 556.8 mg (2.15 mmol) of the enecarbamate **Z-1d** were epoxidized with DMD for 4 h. After work-up, a diastereomeric mixture (93:7) of the epoxides (1*R*,2*R*)-**2d** and (1*S*,2*S*)-**2d** was obtained as a colorless powder in 95% yield (561.7 mg).

IR (KBr) 2965, 1774, 1446, 1418, 1368, 1238; exact mass for C₁₆H₂₁NO₃ Calcd. 275.1521; Found 275.1521.

(1*R*,2*R*)-4-*tert*-Butyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*R*,2*R*)-2*d*].

¹H-NMR (400 MHz, CDCl₃) δ 0.73 (s, 9 H), 1.68 (s, 3 H), 2.14-2.23 (m, 1 H), 3.51-3.59 (m, 1 H), 3.78-3.84 (m, 1 H), 4.50 (s, 1 H), 7.10-7.49 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃) δ 20.7 (q), 25.1 (q), 34.4 (d), 61.6 (s), 63.3 (d), 64.9 (t), 68.2 (d), 126.4 (d), 127.9 (d), 128.1 (d), 136.8 (s), 158.0 (s).

(1*S*,2*S*)-4-*tert*-Butyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*S*,2*S*)-2*d*].

¹H-NMR (400 MHz, CDCl₃) δ 0.68 (s, 9 H), 1.61 (s, 3 H), 2.14-2.23 (m, 1 H), 3.51-3.59 (m, 1 H), 4.02-4.06 (m, 1 H), 4.49 (s, 1 H), 7.10-7.49 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃) δ 21.8 (q), 25.6 (q), 34.4 (d), 61.6 (s), 63.3 (d), 64.9 (t), 69.4 (d), 126.4 (d), 127.9 (d), 128.5 (d), 140.0 (s), 158.0 (s).

Epoxidation of the Enecarbamate *E*-1*a* by DMD

According to the general procedure GP1, the enecarbamate *E*-1*a* (111.2 mg, 0.55 mmol) was epoxidized with DMD for 1 h. After work-up, the racemic epoxide (1*S**,2*R**)-2*a* was obtained as colorless oil in 94% yield (403.8 mg). The material decomposed at ca. 20 °C within a couple of hours, such that an exact-mass determination was not possible. Characterisation rests only on the NMR-spectral data.

(1*S,2*R**)-3-(3-Methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*S**,2*R**)-2*a*].**

¹H-NMR (400 MHz, CDCl₃) δ 1.70 (s, 3 H), 3.61-3.70 (m, 2 H), 4.19 (s, 1 H), 4.27-4.40 (m, 2 H), 7.10-7.40 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃) δ 18.0 (q), 43.6 (t), 63.0 (t), 63.1 (s), 70.0 (d), 125.3 (d), 127.9 (d), 128.4 (d), 139.5 (s), 157.4 (s).

Epoxidation of the Enecarbamate *E*-1*b* by DMD

According to the general procedure GP1, 752.7 mg (3.07 mmol) of the enecarbamate *E*-1*b* in 50 mL acetone were epoxidized with DMD for 1 h. After work-up, a diastereomeric mixture (53:47) of the epoxides (1*S*,2*R*)-2*b* and (1*R*,2*S*)-2*b* was obtained as a colorless powder in 97% yield (779.0 mg).

IR (KBr) 3454, 1729, 1707, 1431, 1241, 1051; exact mass for C₁₅H₁₉NO₃ Calcd. 261.1364; Found 261.1364.

(1*R*,2*S*)-4-Isopropyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*R*,2*S*)-2*b*].

¹H-NMR (400 MHz, CDCl₃) δ 0.84 (d, *J* = 7.9 Hz, 3 H), 0.88 (d, *J* = 6.8 Hz, 3 H), 1.72 (s, 3 H), 2.11-2.24 (m, 1 H), 3.74-3.80 (m, 1 H), 3.83 (s, 1 H), 3.92-4.00 (m, 1 H), 4.13-4.18 (m, 1 H), 7.14-7.34 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃) δ 15.1 (q), 17.5 (q), 19.0 (q), 28.3 (d), 62.0 (t), 62.1 (t), 64.0 (s), 70.0 (d), 125.2 (d), 127.7 (d), 128.2 (d), 139.8 (s), 157.4 (s).

(1*S*,2*R*)-4-Isopropyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*S*,2*R*)-2*b*].

¹H-NMR (400 MHz, CDCl₃) δ 0.82 (d, *J* = 7.2 Hz, 3 H), 0.86 (d, *J* = 7.0 Hz, 3 H), 1.60 (s, 3 H), 2.06-2.17 (m, 1 H), 3.80-3.86 (m, 1 H), 4.05-4.10 (m, 1 H), 4.08 (d, *J* = 7.2 Hz, 1 H), 4.17-4.23 (m, 1 H), 7.14-7.53 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃): δ 15.0 (q), 17.3 (q), 17.7 (q), 28.8 (d), 59.2 (t), 63.5 (t), 64.2 (s), 67.5 (d), 125.2 (d), 127.6 (d), 128.1 (d), 139.1 (s), 156.3 (s).

Epoxidation of the Enecarbamate *E*-1*c* by DMD

According to the general procedure GP1, 649.0 mg (2.32 mmol) of the enecarbamate *E*-1*c* in 40 mL acetone were epoxidized with DMD for 2 h. After work-up, a diastereomeric mixture (60:40) of the epoxides (1*R*,2*S*)-2*c* and (1*S*,2*R*)-2*c* was obtained as a colorless powder in ca. 100% yield (685.0 mg)

IR (KBr) 1779, 1458, 1397, 1250, 1060, 1035; exact mass for C₁₈H₁₇NO₃ Calcd. 295.1208; Found 295.1210.

(1*R*,2*S*)-4-Phenyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*R*,2*S*)-2*c*].

¹H-NMR (400 MHz, CDCl₃) δ 1.75 (d, *J* = 0.2 Hz, 3 H), 4.07 (d, *J* = 0.3 Hz, 1 H), 4.12-4.21 (m, 1 H), 4.62-4.69 (m, 1 H), 4.95-5.02 (m, 1 H), 7.20-7.45 (m, 10 H); ¹³C-NMR (151 MHz, CDCl₃) δ 19.2 (q), 61.3 (d), 61.9 (s), 70.3 (d), 70.8 (t), 125.3 (d), 127.0 (d), 127.7 (d), 128.2 (d), 129.0 (d), 129.4 (d), 137.4 (s), 139.8 (s), 157.7 (s).

(1*S*,2*R*)-4-Phenyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*S*,2*R*)-2*c*].

¹H-NMR (400 MHz, CDCl₃) δ 1.78 (d, *J* = 0.4 Hz, 3 H), 3.91 (d, *J* = 0.2 Hz, 1 H), 4.30-4.35 (m, 1 H), 4.69-4.75 (m, 1 H), 4.90-4.95 (m, 1 H), 7.20-7.45 (m, 10 H); ¹³C-NMR (151 MHz, CDCl₃) δ 18.4 (q), 58.9 (d), 61.9 (s), 67.4 (d), 70.6 (t), 125.4 (d), 126.6 (d), 127.8 (d), 128.2 (d), 129.0 (d), 129.1 (d), 137.7 (s), 139.2 (s), 156.1 (s).

Epoxidation of the Enecarbamate *E*-1*d* by DMD

According to the general procedure GP1, 574.1 mg (2.21 mmol) of the enecarbamate *E*-1*d* in 40 mL acetone were epoxidized with DMD for 4 h. After work-up, a diastereomeric mixture (75:25) of the epoxides (1*R*,2*S*)-2*d* and (1*S*,2*R*)-2*d* was isolated as a colorless powder in 88% yield (534.3 mg).

IR (KBr) 2964, 1758, 1487, 1418, 1371, 1235; exact mass for C₁₆H₂₁NO₃ Calcd. 275.1521; Found 275.1520.

(1*R*,2*S*)-4-*tert*-Butyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*R*,2*S*)-2*d*].

¹H-NMR (400 MHz, CDCl₃) δ 0.97 (s, 9 H), 1.75 (s, 3 H), 3.56-3.61 (m, 1 H), 3.98-4.05 (m, 1 H), 4.15-4.24 (m, 1 H), 3.83 (s, 1 H), 7.10-7.43 (m, 5 H); ¹³C-NMR (151 MHz,

CDCl_3) δ 19.3 (q), 25.9 (q), 34.4 (d), 64.2 (s), 65.1 (t), 67.3 (d), 70.8 (d), 125.4 (d), 127.8 (d), 128.3 (d), 140.1 (s), 158.4 (s).

(1*S*,2*R*)-4-*tert*-Butyl-3-(3-methyl-3-phenyloxyranyl)oxazolidin-2-one [(1*S*,2*R*)-2d].

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.95 (s, 9 H), 1.59 (s, 3 H), 3.60-3.63 (m, 1 H), 4.04-4.09 (m, 1 H), 4.23 (s, 1 H), 4.25-4.30 (m, 1 H), 7.10-7.43 (m, 5 H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 18.0 (q), 25.6 (q), 34.4 (d), 63.0 (s), 64.4 (t), 66.5 (d), 68.9 (d), 125.5 (d), 127.5 (d), 128.3 (d), 140.4 (s), 157.2(s).

General Procedure for the Epoxidation of the Enecarbamates 1 by *meta*-Chloroperbenzoic Acid (GP2)

The enecarbamate **1** (1.0 equiv.) was dissolved in 10 mL of CHCl_3 and 1.1 equiv. of *m*CPBA was added. The solution was stirred magnetically at 20 °C and the reaction progress was monitored by TLC until negative peroxide test (KI/HOAc). After complete consumption of the enecarbamate **1** (the reaction times are specified for the individual cases), 1.00 g of K_2CO_3 was added and the solution was stirred another 30 min. The suspension was removed by filtration, the filtrate washed with saturated, aqu. NaHCO_3 (3 x 5 mL) and water (2 x 5 mL), the organic phase dried over MgSO_4 , and after evaporation of the solvent (20 °C, 10 mbar), the ester **3** was obtained as a mixture of diastereomers (except **3a**, which was obtained as a mixture of enantiomers). The esters **3** were characterized by their ^1H - and ^{13}C -NMR spectra and after recrystallization of the diastereomeric mixture from ethyl ether, an elemental analysis was carried out.

The diastereomeric ratio was determined by ^1H -NMR analysis directly on the crude reaction mixture, through integration of the areas under the characteristic NMR signals.

Epoxidation of the Enecarbamate Z-1a by *m*CPBA

According to the general procedure GP2, 1.32 g (6.52 mmol) of the enecarbamate Z-1a and the *m*CPBA (1.24 g, 7.17 mmol) in 65 mL of chloroform were allowed to react for 8 h. After work-up, the racemic ester (1*R**,2*S**)-3a was obtained as colorless powder, mp 139-140°C, in 93% yield (1.35 g).

(1*R,2*S**)-2-Hydroxy-1-(2-oxo-oxazolidin-3-yl)-2-phenylpropyl 3-Chlorobenzoate**

[(1*R**,2*S**)-3a]. IR (KBr): 3431, 1732, 1482, 1427, 1235, 1082; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.57 (s, 3 H), 3.31-3.49 (m, 1 H), 3.67-3.78 (m, 1 H), 3.92-4.10 (m, 2 H), 6.59 (s, 1 H), 7.12- 7.56 (m, 7 H), 7.93- 8.07 (m, 2 H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 27.7 (q), 42.3 (t), 61.9 (t), 77.5 (s), 81.7 (d), 123.6 (d), 124.6 (d), 127.2 (d), 127.5 (d), 128.0 (d), 129.0 (d),

130.0 (s), 132.8 (d), 133.8 (s), 141.6 (s), 156.8 (s), 163.0 (s); Anal. Calc. for $C_{19}H_{18}ClNO_5$ (375.8): C, 60.72; H, 4.83; N, 3.73. Found: C, 60.83; H, 5.02; N, 3.51;

Epoxidation of the Enecarbamate **Z-1b** by *m*CPBA

According to the general procedure GP2, 1.60 g (6.52 mmol) of the enecarbamate **Z-1b** and *m*CPBA (1.24 g, 7.17 mmol) in 65 mL of chloroform were allowed to react for 8 h. After work-up, a diastereomeric mixture (70:30) of the esters (1*R*,2*S*)-**3b** and (1*S*,2*R*)-**3b** was obtained as a colorless powder in 93% yield (1.58 g).

IR (KBr) 3419, 1736, 1429, 1261, 1233, 1084; Anal. Calc. for $C_{22}H_{24}ClNO_5$ (417.9): C, 63.23; H, 5.79; N, 3.35. Found: C, 63.32; H, 5.99; N, 3.05.

(1*R*,2*S*)-2-Hydroxy-1-(4-isopropyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl

3-Chlorobenzoate [(1*R*,2*S*)-**3b**]. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.61 (d, $J = 7.0$ Hz, 3 H), 0.74 (d, $J = 7.0$ Hz, 3 H), 1.56 (s, 3 H), 2.04-2.16 (m, 1 H), 3.04-3.12 (m, 1 H), 3.62-3.70 (m, 1 H), 3.87-3.93 (m, 1 H), 6.24 (s, OH), 6.30 (s, 1 H), 7.21- 7.63 (m, 7 H), 8.02- 8.20 (m, 2 H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 13.1 (q), 18.2 (q), 28.9 (q), 29.0 (d), 59.8 (d), 63.3 (t), 76.8 (s), 83.0 (d), 124.7 (d), 127.5 (d), 128.2 (d), 128.4 (d), 129.9 (d), 130.0 (d), 130.6 (d), 130.7 (s), 134.7 (d), 143.0 (s), 158.5 (s), 164.4 (s).

(1*S*,2*R*)-2-Hydroxy-1-(4-isopropyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl

3-Chlorobenzoate [(1*S*,2*R*)-**3b**]. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.37 (d, $J = 6.8$ Hz, 3 H), 0.80 (d, $J = 7.1$ Hz, 3 H), 1.61 (s, 3 H), 2.05-2.24 (m, 1 H), 3.73-3.83 (m, 1 H), 3.88-3.97 (m, 1 H), 4.04-4.12 (m, 1 H), 5.03 (br. s, OH), 6.72 (s, 1 H), 7.16- 7.64 (m, 7 H), 8.02- 8.20 (m, 2 H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 13.8 (q), 18.7 (q), 29.4 (q), 29.4 (d), 60.3 (d), 63.8 (t), 77.5 (s), 83.5 (d), 125.2 (d), 127.9 (d), 128.9 (d), 128.9 (d), 130.4 (d), 130.4 (d), 131.1 (s), 134.2 (d), 135.2 (s), 143.5 (s), 159.0 (s), 164.9 (s).

Epoxidation of the Enecarbamate **Z-1c** by *m*CPBA

According to the general procedure GP2, 1.42 g (5.10 mmol) of the enecarbamate **Z-1c** and 1.26 mg (5.61 mmol) of *m*CPBA in 50 mL of chloroform were allowed to react for 24 h. After work-up, a diastereomeric mixture (92:8) of the esters (1*S*,2*R*)-**3c** and (1*R*,2*S*)-**3c** was obtained as a colorless powder in 67% yield (1.54 g).

IR (KBr): $\nu = 3381$, 1713, 1432, 1258, 1231, 1109; Anal. Calc. for $C_{25}H_{22}ClNO_5$ (451.9): C, 66.45; H, 4.91; N, 3.10. Found: C, 66.08; H, 5.19; N, 2.88.

(1*S*,2*R*)-2-Hydroxy-1-(4-phenyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl 3-Chlorobenzoate

[(1*S*,2*R*)-**3c**]. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.35 (s, 3 H), 3.91-3.98 (m, 1 H), 4.11-4.18 (m, 2 H), 5.93 (br. s, OH), 6.05 (s, 1 H), 7.00- 7.50 (m, 12 H), 7.77- 7.88 (m, 2 H);

^{13}C -NMR (151 MHz, CDCl_3) δ 27.3 (q), 62.8 (t), 71.4 (t), 77.5 (s), 82.5 (d), 124.6 (d), 127.2 (d), 127.4 (d), 128.1 (d), 128.5 (d), 129.1 (d), 129.3 (d), 129.7 (d), 129.8 (d), 130.4 (s), 133.5 (d), 134.4 (s), 136.5 (s), 144.2 (s), 158.7 (s), 163.0 (s).

(1*R*,2*S*)-2-Hydroxy-1-(4-phenyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl 3-Chlorobenzoate [(1*R*,2*S*)-3*c*]: ^1H -NMR (400 MHz, CDCl_3) δ 1.41 (s, 3 H), 3.83-4.18 (m, 3 H, overlap with the signals of the major isomer), 6.55 (s, 1 H), 7.00- 7.50 (m, 12 H), 7.77- 7.88 (m, 2 H); ^{13}C -NMR (151 MHz, CDCl_3) δ 28.5 (q), 62.8 (t), 70.7 (t), 76.9 (s), 82.0 (d), 124.7 (d), 127.2 (d), 127.4 (d), 128.1 (d), 128.4 (d), 129.2 (d), 129.5 (d), 129.7 (d), 130.2 (d), 130.4 (s), 133.5 (d), 134.2 (s), 136.5 (s), 142.4 (s), 157.6 (s), 163.8 (s).

Epoxidation of the Enecarbamate **Z-1d** by *m*CPBA

According to the general procedure GP2, the enecarbamate **Z-1d** (644.4 mg, 2.49 mmol) and *m*CPBA (614 mg, 2.74 mmol) in 30 mL of chloroform were allowed to react for 24 h. After work-up, a diastereomeric mixture (93:7) of the esters (1*S*,2*R*)-**3d** and (1*R*,2*S*)-**3d** was obtained as a colorless powder in 95% yield (1.02 g).

IR (KBr) 3423, 1723, 1433, 1412, 1261, 1234; Anal. Calc. for $\text{C}_{23}\text{H}_{26}\text{ClNO}_5$ (431.9): C, 63.96; H, 6.07; N, 3.24. Found: C, 63.72; H, 6.04; N, 2.96.

(1*S*,2*R*)-2-Hydroxy-1-(4-*tert*-butyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl

3-Chlorobenzoate [(1*S*,2*R*)-3*d*]. ^1H -NMR (400 MHz, CDCl_3) δ 0.80 (s, 9 H), 1.57 (s, 3 H), 2.63-2.98 (m, 1 H), 3.12-3.20 (m, 1 H), 4.01 -4.06 (m, 1 H), 5.80 (br. s, OH), 6.29 (s, 1 H), 7.20- 7.60 (m, 9 H); ^{13}C -NMR (151 MHz, CDCl_3): δ = 25.3 (q), 27.9 (q), 34.5 (s), 66.3 (t), 68.8 (d), 79.7 (s), 86.8 (d), 124.8 (d), 127.7 (d), 128.5 (d), 128.7 (d), 130.0 (d), 130.3 (d), 130.7 (s), 133.9 (d), 134.9 (s), 144.3 (s), 160.6 (s), 164.2 (s).

(1*R*,2*S*)-2-Hydroxy-1-(4-*tert*-butyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl

3-Chlorobenzoate [(1*R*,2*S*)-3*d*]. ^1H -NMR (400 MHz, CDCl_3): δ = 0.83 (s, 9 H), 1.58 (s, 3 H), 2.60-4.06 (m, 3 H, overlap with the signals of the main isomer), 6.30 (s, 1 H), 7.20- 7.60 (m, 9 H); ^{13}C -NMR (151 MHz, CDCl_3) δ 25.4 (q), 27.7 (q), 35.3 (s), 64.8 (t), 68.0 (d), 79.3 (s), 85.6 (d), 124.2 (d), 127.8 (d), 128.6 (d), 128.8 (d), 130.0 (d), 130.2 (d), 130.7 (s), 133.9 (d), 134.9 (s), 142.1 (s), 160.6 (s), 164.6 (s).

Epoxidation of the Enecarbamate **E-1a** by *m*CPBA

According to the general procedure GP2, 1.53 g (7.59 mmol) of the enecarbamate **E-1a** and 1.87 g (8.32 mmol) of *m*CPBA in 65 mL of chloroform were allowed to react for 8 h. After work-up, the ester (1*R**,2*R**)-**3a** was isolated as a colorless powder, mp 143-144°C, in 76% yield (2.17 g).

(1*R,2*R**)-2-Hydroxy-1-(2-oxo-oxazolidin-3-yl)-2-phenylpropyl 3-Chlorobenzoate**

[(1*R**,2*R**)-3a]. IR (KBr) 3397, 1736, 1428, 1248, 1089, 1071; ¹H-NMR (400 MHz, CDCl₃) δ 1.60 (s, 3 H), 3.46-3.55 (m, 1 H), 3.77-3.86 (m, 1 H), 4.18-4.33 (m, 2 H), 6.60 (s, 1 H), 7.12- 7.56 (m, 7 H), 7.71- 7.76 (m, 2 H); ¹³C-NMR (151 MHz, CDCl₃): δ = 26.5 (q), 42.2 (t), 62.9 (t), 83.7 (d), 86.7 (s), 125.6 (d), 127.5 (d), 128.0 (d), 128.4 (d), 129.1 (d), 129.5 (d), 130.3 (s), 133.5 (d), 134.8 (s), 143.4 (s), 158.2 (s), 163.1 (s); Anal. Calc. for C₁₉H₁₈ClNO₅ (375.8): C, 60.72; H, 4.83; N, 3.73. Found: C, 61.17; H, 5.12; N, 3.53.

Epoxidation of the Enecarbamate *E*-1b by *m*CPBA

According to the general procedure GP2, the enecarbamate *E*-1b (1.44 g, 6.34 mmol) and *m*CPBA (1.57 g, 6.98 mmol) in 65 mL of chloroform were allowed to react for 8 h. After work-up, a diastereomeric mixture (50:50) of the esters (1*S*,2*S*)-3b and (1*R*,2*R*)-3b was obtained as a colorless powder in 73% yield (2.17 g).

IR (KBr) 3440, 1742, 1719, 1393, 1282, 1229; Anal. Calc. for C₂₂H₂₄ClNO₅ (417.9): C, 63.23; H, 5.79; N, 3.35. Found: C, 63.63; H, 5.97; N, 3.22.

(1*S*,2*S*)-2-Hydroxy-1-(4-isopropyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl

3-Chlorobenzoate [(1*S*,2*S*)-3b]. ¹H-NMR (400 MHz, CDCl₃) δ 0.77 (d, *J* = 6.9 Hz, 3 H), 0.81 (d, *J* = 6.9 Hz, 3 H), 1.68 (s, 3 H), 2.12-2.30 (m, 1 H), 3.66-3.73 (m, 1 H), 4.07-4.30 (m, 2 H), 5.22 (br. s, OH), 6.11 (s, 1 H), 7.04- 7.53 (m, 7 H), 7.68- 7.90 (m, 2 H); ¹³C-NMR (151 MHz, CDCl₃) δ 13.5 (q), 17.9 (q), 26.2 (q), 28.2 (d), 60.1 (d), 63.9 (t), 76.5 (s), 83.7 (d), 125.5 (d), 127.4 (d), 128.0 (d), 128.1 (d), 129.7 (d), 129.8 (d), 130.3 (s), 133.5 (d), 134.5 (s), 143.6 (s), 159.3 (s), 162.8 (s).

(1*R*,2*R*)-2-Hydroxy-1-(4-isopropyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl

3-Chlorobenzoate [(1*R*,2*R*)-3b]. ¹H-NMR (400 MHz, CDCl₃) δ 0.67 (d, *J* = 6.8 Hz, 3 H), 0.79 (d, *J* = 6.8 Hz, 3 H), 1.62 (s, 3 H), 2.12-2.30 (m, 1 H), 4.07-4.30 (m, 3 H), 4.71 (br. s, OH), 6.47 (s, 1 H), 7.04- 7.53 (m, 7 H), 7.68- 7.90 (m, 2 H); ¹³C-NMR (151 MHz, CDCl₃) δ 13.9 (q), 18.2 (q), 27.0 (q), 28.9 (d), 62.3 (d), 63.6 (t), 76.2 (s), 83.1 (d), 125.0 (d), 127.4 (d), 127.8 (d), 128.2 (d), 129.7 (d), 129.8 (d), 130.4 (s), 133.4 (d), 134.5 (s), 143.8 (s), 158.8 (s), 163.7 (s).

Epoxidation of the Enecarbamate *E*-1c by *m*CPBA

According to the general procedure GP2, the enecarbamate *E*-1c (1.72 g, 6.68 mmol) and *m*CPBA (1.65 mg, 7.34 mmol) in 65 mL of chloroform were allowed to react for 8 h. After work-up, the NMR spectrum of the crude product showed a (2:48:50) mixture of the esters (1*R*,2*R*)-3c and (1*S*,2*S*)-3c and the epoxide (1*S*,2*R*)-2c. After purification by silica-gel flash

chromatography (petroleum ether/ ethyl acetate 4:1), the diastereomeric esters (1*S*,2*S*)-**3c** and (1*R*,2*R*)-**3c** were isolated in 46% yield (1.39 g) as a colorless oil.

(1*S*,2*S*)-2-Hydroxy-1-(4-phenyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl 3-Chlorobenzoate [(1*S*,2*S*)-**3c**]. IR (KBr) 3469, 1751, 1720, 1261, 1235, 1084 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 1.57 (s, 3 H), 4.16-4.22 (m, 1 H), 4.54-4.61 (m, 1 H), 4.66-4.72 (m, 1 H), 6.20 (s, 1 H), 7.00-7.60 (m, 14 H); ¹³C-NMR (151 MHz, CDCl₃): δ = 26.4 (q), 60.3 (d), 71.6 (d), 76.1 (s), 84.5 (d), 125.1 (d), 127.1 (d), 127.2 (d), 127.8 (d), 128.0 (d), 129.2 (d), 129.2 (d), 129.4 (d), 129.6 (d), 130.4 (s), 133.2 (d), 134.4 (s), 138.7 (s), 143.2 (s), 159.1 (s), 162.5 (s); Anal. Calc. for C₂₅H₂₂ClNO₅ (451.9): C, 66.45; H, 4.91; N, 3.10. Found: C, 66.27; H, 5.03; N, 2.80.

Epoxidation of the Enecarbamate *E*-**1d** by *m*CPBA

According to the general procedure GP2, 1.72 g (6.68 mmol) of the enecarbamate *E*-**1d** and 1.65 mg (7.34 mmol) of *m*CPBA in 65 mL of chloroform were allowed to react for 24 h. After work-up, a diastereomeric mixture (79:21) of the esters (1*S*,2*S*)-**3d** and (1*R*,2*R*)-**3d** was obtained as a colorless powder in 93% yield (2.68 g).

IR (KBr): ν = 3404, 1737, 1428, 1258, 1226, 1118; Anal. Calc. for C₂₃H₂₆ClNO₅ (431.9): C, 63.96; H, 6.07; N, 3.24. Found: C, 63.93; H, 6.05; N, 2.99.

(1*S*,2*S*)-2-Hydroxy-1-(4-*tert*-butyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl

3-Chlorobenzoate [(1*S*,2*S*)-**3d**]. ¹H-NMR (400 MHz, CDCl₃) δ 1.06 (s, 9 H), 1.77 (s, 3 H), 3.76-3.82 (m, 1 H), 4.19-4.25 (m, 2 H), 6.23 (s, 1 H), 7.01- 7.48 (m, 5 H), 7.74- 7.83 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃) δ 25.3 (q), 28.0 (q), 35.0 (s), 65.3 (d), 66.6 (t), 75.1 (s), 86.0 (d), 125.0 (d), 125.6 (d), 127.1 (d), 128.2 (d), 129.7 (d), 129.9 (d), 130.5 (s), 133.5 (d), 134.4 (s), 144.1 (s), 160.6 (s), 164.6 (s).

(1*R*,2*R*)-2-Hydroxy-1-(4-*tert*-butyl-2-oxo-oxazolidin-3-yl)-2-phenylpropyl

3-Chlorobenzoate [(1*R*,2*R*)-**3d**]. ¹H-NMR (400 MHz, CDCl₃) δ 0.83 (s, 9 H), 1.73 (s, 3 H), 3.16-3.21 (m, 1 H), 3.99-4.15 (m, 2 H), 6.12 (s, 1 H), 7.01- 7.48 (m, 5 H), 7.74- 7.83 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃): δ = 25.5 (q), 25.6 (q), 34.7 (s), 65.7 (t), 67.8 (d), 78.3 (s), 86.6 (d), 125.9 (d), 127.4 (d), 127.5 (d), 128.2 (d), 129.7 (d), 129.9 (d), 130.8 (s), 133.5 (d), 134.5 (s), 143.5 (s), 158.9 (s), 163.1 (s).

Epoxidation of the Enecarbamate *E*-**1a** by *m*CPBA under Buffered Conditions

A sample of 231.4 mg (1.14 mmol) of the enecarbamate *E*-**1a** was dissolved in 11.4 mL of methylene chloride and 3.4 mL of a 0.5 M aqueous NaHCO₃ solution were added. To this buffered two-phase mixture were added in small portions 255.7 mg (1.14 mmol) of *m*CPBA

and stirred magnetically at ca. 20 °C for 2 d. The phases were separated and the organic layer was washed with 3 mL of 1 M NaOH solution and 3 mL water. The organic phase was dried over MgSO₄ and the solvent was evaporated (20 °C, 10 mbar), to afford the ester (1*R**,2*R**)-**3a** as colorless powder, mp 143-144 °C, in 82% yield (309.2 mg).

General Procedure for the Assignment of the Absolute Configuration of the Epoxide **2** (GP3)

The epoxide **2** (1.0 equiv.) was dissolved in a ca. 3:1 acetone/water mixture (15 mL) and 0.2 equiv. of *p*-toluenesulfonic acid (*p*TsOH) were added. After 30 min at 20 °C, 15 mL of ethyl acetate were added and most of the acetone was evaporated (20 °C, 50 mbar). The organic phase was separated, washed with saturated aqu. NaCl solution (10 mL) and with water (10 mL), dried over MgSO₄, and the solvent was evaporated (20 °C, 10 mbar). The crude product was dissolved in a 4:1 THF/water mixture (10 mL), cooled to 0 °C, and 28.5 mg (0.75 equiv.) of NaBH₄ and 1.1 mL of a 0.468 M solution in a 4:1 THF/water mixture of DBU (0.50 equiv.) were added. After 15 min of magnetic stirring, 10 mL of a saturated, aqu. NH₄Cl solution were added, the THF was evaporated (20 °C, 10 mbar), the aqueous layer was extracted with ethyl acetate (2x10 mL), the combined organic layers dried over MgSO₄, and the solvent evaporated (20 °C, 10 mbar). The enantiomeric ratio of the diol **5** was determined by chiral HPLC analysis directly on the crude product mixture. All attempts failed to separate the mixture of diol **5** and the oxazolidinone by chromatography.

The crude mixture of the diol **5** and the chiral oxazolidinone was repeatedly recrystallized from ethyl ether to remove the oxazolidinone. In the first recrystallisation, most of the oxazolidinone was obtained as pure substance (this is specified as the yield of recovered oxazolidinone). Subsequent recrystallizations gave mixtures of the oxazolidinone and the diol **5**, and the recrystallization was repeated until no more oxazolidinone could be detected (according to ¹H-NMR) in the ethyl ether solution. The diol **5** was isolated after evaporation (20 °C, 10 mbar) of the ethyl ether; the low yield is the consequence of fractional recrystallization.

1,2-Dihydroxy-2-phenylpropane (diol 5): ¹H-NMR (400 MHz, CDCl₃): δ = 1.50 (s, 3 H), 3.57 (d, *J* = 11.2 Hz, 1 H), 3.73 (d, *J* = 11.2 Hz, 1 H), 7.23-7.46 (m, 5 H); ¹³C-NMR (151 MHz, CDCl₃): δ = 26.0 (q), 70.4 (d), 74.3 (s), 125.1 (d), 127.1 (d), 128.4 (d), 144.9 (s).

Transformation of the Epoxide **2b** Derived from Enecarbamate **Z-1b** to the 1,2-Diol **5**

According to the general procedure GP3, 392 mg (1.50 mmol) of the diastereomeric epoxide mixture (1*S*,2*S*)-**2b** : (1*R*,2*R*)-**2b** (60:40) were treated with *p*TsOH (57.1 mg, 0.30 mmol),

followed by NaBH₄ (33.7 mg, 0.89 mmol) and DBU (1.26 ml, 0.59 mmol), and the mixture magnetically stirred at 0 °C for 15 min. After work-up, the crude product mixture was submitted to chiral HPLC and the *S*:*R* ratio of the diol **5** was determined to be 57:43. On repetitive fractional recrystallisation for the removal of the oxazolidinone (54%), the diol **5** was isolated as colorless oil in 42% yield (95.0 mg).

Transformation of the Epoxide **2c Derived from Enecarbamate **Z-1c** to the 1,2-Diol **5****

According to the general procedure GP3, 505.7 mg (1.71 mmol) of the diastereomeric epoxide mixture of (1*R*,2*R*)-**2c** and (1*S*,2*S*)-**2c** (92:8) was converted to the diol **5**. HPLC analysis of the crude product mixture showed a *S*:*R* ratio of 10:90 for the diol **5**, which was isolated as colorless oil in 53% yield (96.0 mg), by removal of the oxazolidinone (66%) on repetitive recrystallisation from ethyl ether.

Transformation of the Epoxide **2d Derived from Enecarbamate **Z-1d** to the 1,2-Diol **5****

According to the general procedure GP3, 562.8 mg (2.04 mmol) of the diastereomeric epoxide mixture of (1*R*,2*R*)-**2d** and (1*S*,2*S*)-**2d** (93:7) was converted to the diol **5**. The crude product mixture was submitted to chiral HPLC analysis and the *S*:*R* ratio of diol **5** was determined to be 6:94. The diol **5** was isolated as colorless oil in 53% (164 mg) yield by removal of the oxazolidinone (67%) on repetitive fractional recrystallization from ethyl ether.

Transformation of the Epoxide **2b Derived from Enecarbamate **E-1b** to the 1,2-Diol **5****

According to the general procedure GP3 700.4 mg (2.68 mmol) of the diastereomeric epoxide mixture of (1*S*,2*R*)-**2b** and (1*R*,2*S*)-**2b** (53:47) was converted to the diol **5**. Chiral HPLC analysis of the crude product mixture gave a *S*:*R* ratio of 47:53 for the diol **5**. The diol **5** was isolated as colorless oil in 51% yield (207 mg) by removal of the oxazolidinone (55%) on repetitive fractional recrystallisation from ethyl ether.

Transformation of the Epoxide **2c Derived from Enecarbamate **E-1c** to the 1,2-Diol **5****

According to the general procedure GP3, 554.2 mg (1.88 mmol) of the diastereomeric epoxide mixture of (1*R*,2*S*)-**2c** and (1*S*,2*R*)-**2c** (60:40) was converted to the diol **5**. The crude product mixture was submitted to chiral HPLC analysis and the *S*:*R* ratio of the diol **5** was determined to be 58:42. The purification of the diol **5** by removal of the oxazolidinone (37%) through repetitive fractional recrystallization (four times) from ethyl ether was in this

case particularly difficult and accompanied with a great loss of the diol **5** [29% yield (83.0 mg)].

Transformation of the Epoxide **2d Derived from Enecarbamate **E-1d** to the 1,2-Diol **5****

According to the general procedure GP3, 440.9 mg (1.60 mmol) of the diastereomeric epoxide mixture of (1*R*,2*S*)-**2d** and (1*S*,2*R*)-**2d** (75:25) was converted to the diol **5**. The crude product mixture was analyzed with chiral HPLC and the *S*:*R* ratio for diol **5** determined to be 75:25. After removal of the oxazolidinone (38% yield) by repetitive fractional recrystallization (four times) from ethyl ether, the diol **5** was obtained as a colorless oil in 26% yield (71.0 mg). The low yield is due to the large losses in the repetitive fractional recrystallization.

Transformation of the Ester **3c Derived from the Enecarbamate **Z-1c** to the 1,2-Diol **5****

A sample of 517.3 mg (1.18 mmol) of the diastereomeric ester mixture (1*S*,2*R*)-**3c** and (1*R*,2*S*)-**3c** (92:8), obtained in the oxidation of the enecarbamate **Z-1c** by mCPBA, was dissolved in 20 mL ethanol and treated with 22.3 mg (0.59 mmol) NaBH₄. After magnetic stirring for 24 h at ca. 20 °C, 20 mL of a saturated, aqu. NH₄Cl solution was added to the reaction mixture, extracted with ethyl acetate (4 x 40 mL), the phases were separated, the organic layer was dried over MgSO₄, and the solvent was evaporated (20 °C, 10 mbar). The crude product mixture was submitted to chiral HPLC analysis and the *R*:*S* ratio of the diol **5** was determined to be 90:10. After removal of the oxazolidinone (71% yield) by repetitive recrystallisation from ethyl ether, the diol **5** was obtained as colorless oil in 78% yield (138 mg).

Determination of the Absolute Configuration of the Diol **5 Obtained from the Epoxides **2** and Esters **3****

The configuration of the diol **5** was determined by comparison of the HPLC retention times on a chiral AS column with an authentic sample of 2*R*-(-)-1,2-dihydroxy-2-phenylpropane (93% ee), prepared according to the literature procedure.¹² Clean separation of the enantiomers was achieved by elution with a 90:10 isopropanol/hexane mixture at a flow rate of 1 mL/min; the retention times were 10.4 min for the *S*(+) and 12.9 min for the *R*(-) enantiomer.

DFT Calculations for the Determination of the Preferred Conformations for the Diastereomeric Pair of *tert*-Butyl Enecarbamates **E-1d** and **Z-1d**

PM3^{S1} calculations were carried out to determine the energy profile for the rotation about the CN bond in the enecarbamates **E-1d** and **Z-1d** (structures are shown below). The absolute

energy minima were refined at B3LYP/3-21G* level.^{S1}

^{S1} Semiempirical and density functional calculations were carried out by using the Gaussian 98 package: Gaussian 98, Revision A.7, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.