Supporting Information (Experimental Section: 15 pages)

Opposite π-Face Selectivity for the DMD and *m*-CPBA Epoxidations of Chiral 2,2-Dimethyloxazolidine Derivatives of Tiglic Amides: Control by Steric Interactions *versus* Hydrogen Bonding

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We report herein the synthetic details and characteristic spectral data of the α,β-unsaturated amides (*S*)-**1a-c**, the optically active epoxides *ul*-**2a-c** and *lk*-**2a-c**, the *N,N*-diethyl tiglic amide **3** and the *N,N*-diethyl dimethyloxiranecarboxamide **4**.

General Aspects

^{1}H- and ^{13}C-NMR spectra were measured on a Bruker AC 200 (^{1}H: 200 MHz, ^{13}C: 50 MHz), Bruker AC 250 (^{1}H: 250 MHz, ^{13}C: 63 MHz) or Bruker DMX 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz), with $CHCl_3$ (δ 7.26), acetonitrile (δ 1.93) and MeOH (δ 3.39) for the ^{1}H and $CDCl_3$ (δ 77.0 ppm)

for the ^{13}C resonances as internal standard. IR spectra were recorded on a FT-IR Perkin-Elmer 1600 Infrared Ratio-Recording spectrophotometer. Melting points were taken on a Büchi B-545 apparatus and are not corrected. Optical rotations were measured on a Perkin-Elmer Polarimeter 241 MC.

TLC analysis was conducted on precoated silicia-gel aluminum sheets 60 F_{254} (40×80 mm) from Merck (Darmstadt, Germany). Spots were visualized by irradiation under an UV lamp or with the phosphomolybdic acid test spray. Silica gel (32-63 μm, Woelm) was used for flash chromatography.

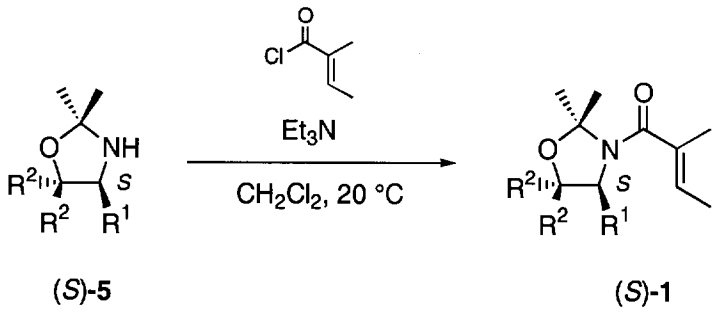
Materials

The DMD solution in acetone was prepared by the standard procedure[21] and 3-chloroperoxy benzoic acid (*m*-CPBA) was commercially available from Acros (70-75% of purity). All the optically active amino alcohols were gift samples from Degussa AG, Hanau, for which we are thankful. Tiglic acid chloride, prepared from tiglic acid according to the literature procedure,[22] was freshly distilled before use.

Synthesis of 2,2-Dimethyl-3-tigloyloxazolidines *(S)*-1a-c

The optically active 2,2-dimethyl-3-tigloyloxazolidines (*S*)-**1** were synthesized by acylation of the 2,2-dimethyloxazolidines (*S*)-**5** (prepared from the corresponding *S*-configured amino alcohols by the literature method[15a]) with tiglic acid chloride and triethylamine as base (Scheme 3).

Scheme 3



General Procedure for 2,2-Dimethyl-3-tigloyloxazolidines (*S*)**-1a-c.** The appropriate 2,2-dimethyloxazolidine (*S*)**-5** (25.0 mmol) and Et_3N (2.53 g, 25.0 mmol) were dissolved in CH_2Cl_2 (50 mL) under an argon-gas atmosphere. After slow (ca. 30 min) addition of the tiglic acid chloride (2.96 g, 25.0 mmol) at 0 °C, the mixture was stirred at this temperature for 0.5 h, warmed to 20 °C, and stirred for 16 h more. The reaction mixture was treated with saturated, aqueous $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (4×20 mL). The combined extracts were dried ($MgSO_4$), the solvent evaporated (20 °C/ 7.5 torr), and the residue was purified by silica-gel chromatography or Kugelrohr distillation.

[*S*-(*E*)]-2,2-Dimethyl-3-(2-methyl-1-oxo-2-butenyl)-4-phenylmethyloxazolidine [(S)-1a]: Colorless oil (silica-gel chromatography, eluted first with 1:1.2 and subsequently with 1:1 Et_2O/petroleum ether; R_f = 0.16, 1:2 Et_2O/petroleum ether), 71% yield. An analytical sample was obtained by Kugelrohr distillation (oven temperature 190 °C/ 0.015 torr); $[\alpha]^{25}_D$ = -58.5 ° (c = 1.00, $CHCl_3$); IR (neat) 1630 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.55 (s, 3 H), 1.71 (s, 3 H), 1.77 (d, *J* = 7.0 Hz, 3 H), 1.87 (s, 3 H), 2.76 (dd, *J* = 13.1 Hz, *J* = 8.4 Hz, 1 H), 2.93 (dd, *J* = 13.1 Hz, *J* = 3.4 Hz, 1 H), 3.75-3.88 (m, 2 H), 4.10-4.25 (m, 1 H), 5.73 (qq, *J* = 7.0 Hz, *J* = 1.2 Hz, 1 H), 7.05-7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.2 (q), 14.0 (q), 23.8 (q), 27.0 (q), 40.6 (t), 60.2 (d), 66.3 (t), 95.2 (s), 125.3 (d), 126.8 (d), 128.8 (2×d), 129.1 (2×d), 134.1

(s), 137.8 (s), 170.5 (s); Anal. Found: C, 74.39; H, 8.18; N, 5.19%. Calcd for $C_{17}H_{23}NO_2$ (273.4): C, 74.69; H, 8.48; N, 5.12%.

[*S*-(*E*)]-2,2,5,5-Tetramethyl-3-(2-methyl-1-oxo-2-butenyl)-4-phenylmethyloxazolidine [(S)-1b]: Colorless prisms (silica-gel chromatography, eluted first with 1:1.2 and subsequently with 1:1 Et_2O/petroleum ether; R_f = 0.50, 1:2 Et_2O/petroleum ether), 81% yield. An analytical sample was obtained by recrystallization from 1:8 Et_2O/petroleum ether at -20 °C, mp 73.8-74.8 °C; $[\alpha]^{25}_D$ = -110.6 °(c = 1.08, $CHCl_3$); IR (KBr) 1620 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.21 (s, 3 H), 1.36 (s, 3 H), 1.44-1.48 (m, 3 H), 1.62 (dq, *J* = 6.9 Hz, *J* = 1.1 Hz, 3 H), 1.68 (s, 3 H), 1.73 (s, 3 H), 2.77 (dd, *J* = 14.0 Hz, *J* = 6.7 Hz, 1 H), 2.95 (dd, *J* = 14.0 Hz, *J* = 7.6 Hz, 1 H), 4.27 (dd, *J* = 7.6 Hz, *J* = 6.7 Hz, 1 H), 5.58 (qq, *J* = 6.8 Hz, *J* = 1.4 Hz, 1 H), 7.30-7.08 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.2 (q), 13.4 (q), 24.1 (q), 27.7 (q), 29.1 (q), 29.2 (q), 39.0 (t), 67.1 (d), 80.3 (s), 93.9 (s), 126.2 (d), 126.4 (d), 128.6 (2×d), 129.3 (2×d), 134.2 (s), 138.0 (s), 171.0 (s); Anal. Found: C, 75.72; H, 8.80; N, 4.59%. Calcd for $C_{19}H_{27}NO_2$ (301.4): C, 75.70; H, 9.03; N, 4.65%.

[*S*-(*E*)]-2,2-Dimethyl-3-(2-methyl-1-oxo-2-butenyl)-4-phenyloxazolidine [(S)-1c]: Colorless prisms (silica-gel chromatography, eluted first with 1:1.2 and subsequently with 1:1 Et_2O/petroleum ether; R_f = 0.25 in 1:2 Et_2O/petroleum ether), 67% yield. An analytical sample was obtained by recrystallization from 1:4 Et_2O/petroleum ether at -20 °C, mp 82.7-83.7 °C; $[\alpha]^{25}_D$ = +126.3 ° (c = 1.00, $CHCl_3$); IR (KBr) 1619 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.20 (s, 3 H), 1.45 (dq, *J* = 6.9 Hz, *J* = 1.1 Hz, 3 H), 1.68 (s, 3 H), 1.85 (s, 3 H), 3.83 (dd, *J* = 9.2 Hz, *J* = 6.4 Hz, 1 H), 4.30 (dd, *J* = 9.2 Hz, *J* = 6.6 Hz, 1 H), 4.94 (dd, *J* = 6.6 Hz, *J* = 6.4 Hz, 1 H), 5.47 (qq, *J* = 6.8 Hz, *J* = 1.4 Hz, 1 H), 7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 12.7 (q), 12.9 (q), 24.6 (q), 24.8 (q), 63.3 (d), 71.5 (t), 95.7 (s), 125.1 (d), 126.9

(2×d), 127.6 (d), 128.6 (2×d), 134.5 (s), 140.8 (s), 171.3 (s); Anal. Found: C, 73.75; H, 8.19; N, 5.21%. Calcd for $C_{16}H_{21}NO_2$ (259.4): C, 74.10; H, 8.16; N, 5.40%.

General Procedure for the DMD Epoxidation of Amides (*S*)-1

The tiglic acid amide (*S*)-**1** (1.00 mmol) was dissolved in 0.08 *M* solution of DMD in acetone (19 mL; 1.50 mmol). After stirring at 20 °C for 8 h, 19 mL (1.50 mmol) of a fresh DMD solution were added and the reaction mixture was allowed to react for 16 h. The solvent was removed (20 °C/ 30 torr) to give the diastereomeric mixture of the corresponding epoxides **2** with *ul-2* as the major diastereomer.

DMD Epoxidation of (*S*)-1a: After application of the general procedure, the diastereomeric mixture of epoxides (d.r. 91:09) was purified by silica-gel chromatography, eluted with 1:2 Et_2O/petroleum ether (R_f = 0.29), 87% yield. The major diastereomer ***ul-2a*** was obtained in pure form (d.r. > 95:5) after recrystallization from *n*-pentane at -20 °C.

[*S-(R*, 2S*, 3R*)*]-2,2-Dimethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenylmethyl oxazolidine (*ul-2a*): Colorless prisms (from *n*-pentane at –20 °C), mp 52.0-53.0 °C; $[\alpha]^{25}_D$ = -134.2 ° (c = 1.01, $CHCl_3$); IR (KBr) 1638 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.40 (d, *J* = 5.5 Hz, 3 H), 1.54 (s, 3 H), 1.57 (s, 3 H), 1.68 (s, 3 H), 2.71 (t, *J* = 11.9 Hz, 1 H), 3.13 (dm, *J* = 12.5 Hz, 1 H), 3.24 (q, *J* = 5.4 Hz, 1 H), 3.71 (ddd, *J* = 9.1 Hz, *J* = 4.5 Hz, *J* = 1.8 Hz, 1 H), 3.83 (d, *J* = 8.8 Hz, 1 H), 4.25 (ddd, *J* = 11.3 Hz, *J* = 4.3 Hz, *J* = 3.1 Hz, 1 H), 7.10-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.5 (q), 15.6 (q), 22.7 (q), 26.8 (q), 40.6 (t), 57.0 (d), 59.6 (d), 62.0 (s), 66.2 (t), 95.4 (s), 126.5 (d), 128.6 (2×d), 129.5 (2×d), 138.4 (s), 167.7

(s); Anal. Found: C, 70.63; H, 7.81; N, 4.85%. Calcd for $C_{17}H_{23}NO_3$ (289.4): C, 70.56; H, 8.01; N, 4.84%.

[*S*-(*R, 2*R**, 3*S**)]-2,2-Dimethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenylmethyl oxazolidine (*lk*-2a):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.41 (d, *J* = 5.2 Hz, 3 H), 1.48 (s, 3 H), 1.58 (s, 3 H), 1.75 (s, 3 H), 2.78 (dd, *J* = 12.8 Hz, *J* = 11.0 Hz, 1 H), 3.02-3.09 (m, 1 H), 3.14 (q, *J* = 5.5 Hz, 1 H), 3.70 (m, 1 H), 3.79 (dd, *J* = 9.2 Hz, *J* = 1.5 Hz, 1 H), 4.85 (m, 1 H), 7.20-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.5 (q), 15.7 (q), 23.1 (q), 26.6 (q), 41.4 (t), 57.4 (d), 58.1 (d), 61.2 (s), 66.5 (t), 96.1 (s), 126.8 (d), 128.6 (2×d), 129.4 (2×d), 137.6 (s), 168.1 (s).

DMD Epoxidation of (*S*)-1b: After application of the general procedure, the diastereomeric mixture of epoxides (d.r. 90:10) was purified by silica-gel chromatography, eluted with 1:2 Et_2O/petroleum ether (R_f = 0.41), 95% yield. The major diastereomer *ul*-**2b** was obtained in pure form (d.r > 95:5) after recrystallization from *n*-pentane at -20 °C.

[*S*-(*R, 2*S**, 3*R**)]-2,2,5,5-Tetramethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenylmethyl oxazolidine (*ul*-2b):** Colorless prisms (from *n*-pentane at –20 °C), mp 81.0-82.0 °C; $[\alpha]^{25}_D$ = -151.7 ° (c = 1.00, $CHCl_3$); IR (KBr) 1646 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.03 (s, 3 H), 1.33 (s, 3 H), 1.35 (d, *J* = 5.5 Hz, 3 H), 1.61 (s, 3 H), 1.62 (s, 3 H), 1.73 (s, 3 H), 2.99 (d, *J* = 8.8 Hz, 1 H), 3.00 (d, *J* = 4.6 Hz, 1 H), 3.14 (q, *J* = 5.4 Hz, 1 H), 4.40 (dd, *J* = 8.8 Hz, *J* = 4.9 Hz, 1 H), 7.18 (m, 1 H), 7.29 (m, 2 H), 7.41 (dm, *J* = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.5 (q), 15.8 (q), 24.6 (q), 27.5 (q), 28.5 (q), 29.1 (q), 39.8 (t), 57.0 (d), 62.2 (s), 65.6 (d), 81.4 (s), 94.1 (s), 126.1 (d), 128.4 (2×d), 128.9 (2×d), 138.8 (s), 167.5 (s); Anal. Found: C, 71.84; H, 8.42; N, 4.40%. Calcd for $C_{19}H_{27}NO_3$ (317.4): C, 71.89; H, 8.57; N, 4.41%.

[*S*-(*R, 2*R**, 3*S**)]-2,2,5,5-Tetramethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenylmethyl oxazolidine (*lk*-2b):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.90 (s, 3 H), 1.21 (s, 3 H), 1.26 (s, 3 H), 1.27 (d, *J* = 5.5 Hz, 3 H), 1.60 (s, 3 H), 1.77 (s, 3 H), 2.82 (dd, *J* = 14.2 Hz, *J* = 7.8 Hz, 1 H), 2.92-2.98 (m, 2 H), 5.04 (t, *J* = 7.5 Hz, 1 H), 7.12-7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.5 (q), 14.0 (q), 24.0 (q), 27.4 (q), 28.8 (q), 29.0 (q), 39.2 (t), 58.4 (d), 61.2 (s), 63.9 (d), 80.8 (s), 94.7 (s), 126.5 (d), 128.6 (2×d), 129.8 (2×d), 137.8 (s), 169.7 (s).

DMD Epoxidation of (*S*)-1c: After application of the general procedure, the diastereomeric mixture of epoxides (d.r. 83:17) was purified by silica-gel chromatography, eluted first with a 3:1 Et_2O/petroleum ether mixture and subsequently with Et_2O; both diastereomers were obtained in pure form.

[*S*-(*R, 2*S**, 3*R**)]-2,2-Dimethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenyloxazolidine (*ul*-2c):** Colorless prisms (from 1:5 CH_2Cl_2/petroleum ether at –20 °C), 74% yield, mp 153.0-154.0 °C; R_f = 0.36, 3:1 Et_2O/petroleum ether; $[\alpha]^{25}_D$ = -104.2 ° (c = 1.01, $CHCl_3$); IR (KBr) 1643 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.18 (d, *J* = 5.8 Hz, 3 H), 1.19 (s, 3 H), 1.66 (s, 3 H), 1.89 (s, 3 H), 2.91 (q, *J* = 5.4 Hz, 1 H), 3.91 (dd, *J* = 9.0 Hz, *J* = 1.4 Hz, 1 H), 4.32 (dd, *J* = 8.9 Hz, *J* = 6.1 Hz, 1 H), 5.17 (d, *J* = 5.5 Hz, 1 H), 7.22-7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.2 (q), 15.0 (q), 22.9 (q), 25.3 (q), 56.7 (d), 60.9 (d and s), 71.6 (t), 96.6 (s), 125.5 (2×d), 127.3 (d), 128.4 (2×d), 142.7 (s), 169.0 (s); Anal. Found: C, 69.63; H, 7.44; N, 5.01%. Calcd for $C_{16}H_{21}NO_3$ (275.4): C, 69.79; H, 7.69; N, 5.09%.

[*S*-(*R, 2*R**, 3*S**)]-2,2-Dimethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenyloxazolidine (*lk*-2c):** 17% yield; R_f = 0.54, 3:1 Et_2O/petroleum ether; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.83 (s, 3 H), 1.14 (d, *J* = 5.5 Hz, 3 H), 1.58 (s, 3 H), 1.87 (s, 3 H), 2.98 (q, *J* = 5.4 Hz, 1 H), 3.83 (dd,

J = 9.0 Hz, *J* = 4.7 Hz, 1 H), 4.29 (dd, *J* = 9.0 Hz, *J* = 6.9 Hz, 1 H), 5.44 (dd, *J* = 6.9 Hz, *J* = 4.7 Hz, 1 H), 7.25-7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.3 (q), 13.6 (q), 23.9 (q), 24.8 (q), 58.6 (d), 60.1 (d), 61.4 (s), 71.9 (t), 96.6 (s), 126.9 (2×d), 127.9 (d), 128.7 (2×d), 141.4 (s), 169.3 (s).

General Procedure for the *m*-CPBA Epoxidation of Amides (*S*)-1

A solution of the tiglic acid amide (3.5 mmol) and *m*-CPBA (1.73 g, 7.0 mmol) in CH_2Cl_2 (20 mL) was stirred at 20 °C for 24 h. After washing with $NaHCO_3$ (3×20 mL), the organic layer was dried over $MgSO_4$. The solvent was removed (20 °C/ 30 torr) to give the diastereomeric mixture of the corresponding epoxides with ***lk-2*** as the major diastereomer.

m*-CPBA Epoxidation of *(S)* -1a:** After application of the general procedure, the diastereomeric mixture of epoxides (d.r. 85:15) was purified by silica-gel chromatography, eluted first with a 1:3 and subsequently with a 1:1 Et_2O/petroleum ether mixture (R_f = 0.34, 1:1 Et_2O/petroleum ether), 78% yield. The major diastereomer ***lk-2a was obtained in pure form (d.r. > 95:5) after recrystallization from 1:4 Et_2O/ petroleum ether at -20 °C.

[*S*-(*R, 2*R**, 3*S**)]-2,2-Dimethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenylmethyl oxazolidine (*lk-2a*):** Colorless prisms (from 1:4 Et_2O/ petroleum ether at -20 °C), mp 116.1-116.6 °C; $[\alpha]^{25}_D$ = -87.1 ° (c = 1.00, $CHCl_3$); IR (KBr) 1633 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.39 (d, *J* = 5.5 Hz, 3 H), 1.47 (s, 3 H), 1.57 (s, 3 H), 1.74 (s, 3 H), 2.76 (dd, *J* = 12.8 Hz, *J* = 11.0 Hz, 1 H), 3.05 (dd, *J* = 13.0 Hz, *J* = 3.8 Hz, 1 H), 3.14 (q, *J* = 5.4 Hz, 1 H), 3.68 (ddd, *J* = 9.2 Hz, *J* = 5.3 Hz, *J* = 1.1 Hz, 1 H), 3.77 (dd, *J* = 9.2 Hz, *J* = 1.2 Hz, 1 H), 4.75-4.83 (m, 1 H), 7.19-7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.5 (q), 15.7 (q), 23.1 (q), 26.5

(q), 41.4 (t), 57.3 (d), 58.0 (d), 61.2 (s), 66.5 (t), 96.1 (s), 126.7 (d), 128.6 (2×d), 129.4 (2×d), 137.6 (s), 168.1 (s); Anal. Found: C, 70.37; H, 8.26; N, 5.05%. Calcd for $C_{17}H_{23}NO_3$ (289.4): C, 70.56; H, 8.01; N, 4.84%.

[*S*-(*R, 2*S**, 3*R**)]-2,2-Dimethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenylmethyl oxazolidine (*ul*-2a):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.40 (d, *J* = 5.2 Hz, 3 H), 1.55 (s, 3 H), 1.58 (s, 3 H), 1.69 (s, 3 H), 2.72 (t, *J* = 12.2 Hz, 1 H), 3.13 (m, 1 H), 3.25 (q, *J* = 5.5 Hz, 1 H), 3.66-3.85 (m, 2 H), 4.26 (ddd, *J* = 10.7 Hz, *J* = 4.6 Hz, *J* = 2.5 Hz, 1 H), 7.20-7.54 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.5 (q), 15.6 (q), 22.7 (q), 26.8 (q), 40.6 (t), 57.0 (d), 59.7 (d), 62.0 (s), 66.3 (t), 95.5 (s), 126.6 (d), 128.6 (2×d), 129.5 (2×d), 138.4 (s), 167.8 (s).

***m*-CPBA Epoxidation of (*S*)-1b:** After application of the general procedure, the diastereomeric mixture of epoxides (d.r. 93:07) was purified by silica-gel chromatography, eluted first with a 1:3 and subsequently with a 1:1 Et_2O/petroleum ether mixture (R_f = 0.58, 1:1 Et_2O/petroleum ether), 88% yield. An analytical sample was obtained by Kugelrohr distillation (150 °C/ 0.1 torr) as a colorless oil.

For both diastereomers: $[\alpha]^{25}_D$ = -149.2 ° (c = 1.01, $CHCl_3$); IR (KBr) 1634 (C=O) cm^{-1}; Anal. Found: C, 71.74; H, 8.65; N, 4.38%. Calcd for $C_{19}H_{27}NO_3$ (317.4): C, 71.89; H, 8.57; N, 4.41%.

[*S*-(*R, 2*R**, 3*S**)]-2,2,5,5-Tetramethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenylmethyl oxazolidine (*lk*-2b):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.92 (s, 3 H), 1.22 (s, 3 H), 1.26 (s, 3 H), 1.27 (d, *J* = 6.1 Hz, 3 H), 1.61 (s, 3 H), 1.78 (s, 3 H), 2.83 (dd, *J* = 14.0 Hz, *J* = 7.6 Hz, 1 H), 2.93-3.01 (m, 2 H), 5.04 (t, *J* = 7.4 Hz, 1 H), 7.19-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz):

δ 13.5 (q), 14.1 (q), 24.0 (q), 27.4 (q), 28.8 (q), 29.1 (q), 39.3 (t), 58.5 (d), 61.2 (s), 63.9 (d), 80.9 (s), 94.7 (s), 126.6 (d), 128.7 (2×d), 129.9 (2×d), 137.9 (s), 169.8 (s).

[*S*-(*R, 2*S**, 3*R**)]-2,2,5,5-Tetramethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenylmethyl oxazolidine (*ul*-2b):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.03 (s, 3 H), 1.33 (s, 3 H), 1.36 (d, J = 5.5 Hz, 3 H), 1.61 (s, 3 H), 1.62 (s, 3 H), 1.73 (s, 3 H), 2.96-3.02 (m, 2 H), 3.15 (q, J = 5.5 Hz, 1 H), 4.41 (dd, J = 8.3 Hz, J = 4.9 Hz, 1 H), 7.19-7.57 (m, 5 H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 13.4 (q), 15.8 (q), 24.5 (q), 27.5 (q), 28.5 (q), 29.0 (q), 39.8 (t), 57.1 (d), 62.1 (s), 65.8 (d), 81.5 (s), 94.3 (s), 126.2 (d), 128.4 (2×d), 128.9 (2×d), 138.7 (s), 167.9 (s).

***m*-CPBA Epoxidation of (*S*)-1c:** After application of the general procedure, the diastereomeric mixture of epoxides (d.r. 85.15) was purified by silica-gel chromatography, eluted first with a 1:3 and subsequently with a 2:1 Et_2O/petroleum ether mixture to give both diastereomers in pure form.

[*S*-(*R, 2*R**, 3*S**)]-2,2-Dimethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenyloxazolidine (*lk*-2c):** Colorless prisms (from 1:1 Et_2O /petroleum ether at–20 °C), 57% yield, mp 86.1-86.8 °C; R_f = 0.54, 3:1 Et_2O/petroleum ether; $[\alpha]^{25}_D$ = +85.5 ° (c = 1.00, $CHCl_3$); IR (KBr) 1639 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.83 (s, 3 H), 1.14 (d, J = 5.5 Hz, 3 H), 1.57 (s, 3 H), 1.86 (s, 3 H), 2.97 (q, J = 5.4 Hz, 1 H), 3.83 (dd, J = 9.0 Hz, J = 4.7 Hz, 1 H), 4.29 (dd, J = 9.2 Hz, J = 7.0 Hz, 1 H), 5.44 (dd, J = 6.9 Hz, J = 4.7 Hz, 1 H), 7.27-7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.3 (q), 13.6 (q), 23.9 (q), 24.8 (q), 58.5 (d), 60.1 (d), 61.4 (s), 71.9 (t), 96.5 (s), 126.9 (2×d), 127.9 (d), 128.7 (2×d), 141.4 (s), 169.2 (s); Anal. Found: C, 69.49; H, 7.41; N, 5.05%. Calcd for $C_{16}H_{21}NO_3$ (275.4): C, 69.79; H, 7.69; N, 5.09%.

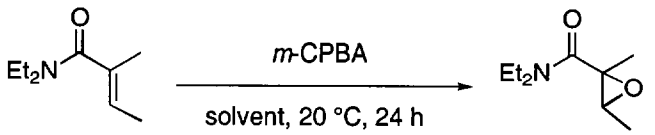
[*S*-(*R, 2*S**, 3*R**)]-2,2-Dimethyl-3-[(2,3-dimethyloxiranyl)carbonyl]-4-phenyloxazolidine (*ul*-2c):** 15% yield, R_f = 0.36, 3:1 Et_2O/petroleum ether; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.18 (d, *J* = 5.5 Hz, 3 H), 1.20 (s, 3 H), 1.65 (s, 3 H), 1.89 (s, 3 H), 2.88 (q, *J* = 5.8 Hz, 1 H), 3.92 (dd, *J* = 8.9 Hz, *J* = 1.5 Hz, 1 H), 4.31 (dd, *J* = 8.9 Hz, *J* = 6.1 Hz, 1 H), 5.16 (d, *J* = 5.5 Hz, 1 H), 7.21-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 13.2 (q), 15.0 (q), 22.9 (q), 25.3 (q), 56.9 (d), 61.1 (d and s), 71.7 (t), 96.7 (s), 125.6 (2×d), 127.4 (d), 128.4 (2×d), 142.5 (s), 169.4 (s).

***(E)*-*N,N*-Diethyl-2-methyl-2-butenamide[23] (3):** Tiglic acid chloride (3.00 g, 25.3 mmol) was slowly (ca. 30 min) added to a solution of diethylamine (3.70 g, 50.6 mmol) in CH_2Cl_2 (50 mL) at 0 °C. After stirring at 20 °C for 2 h, the reaction mixture was poured into saturated aqueous $NaHCO_3$ (50 mL) and the aqueous phase was extracted with CH_2Cl_2 (5×15 mL). The combined extracts were dried over $MgSO_4$ and evaporated (20 °C/ 200 torr) to dryness. The crude product was purified by Kugelrohr distillation (150 °C/ 14 torr) to give the amide in 90% yield. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.10 (t, *J* = 7.2 Hz, 6 H), 1.65 (dq, *J* = 6.9 Hz, *J* = 1.1 Hz, 3 H), 1.80 (m, 3 H), 3.33 (q, *J* = 7.1 Hz, 4 H), 5.54 (qq, *J* = 6.8 Hz, *J* = 1.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 12.6 (q), 13.1 (2×q), 13.7 (q), 38.5 (t), 42.4 (t), 124.1 (d), 133.2 (s), 174.1 (s).

(*R, *S**)-*N,N*-Diethyl-2,3-Dimethyloxirane carboxamide (4):** A solution of the tiglic amide **3** (3.00 g, 19.3 mmol) and *m*-CPBA (9.53 g, 38.7 mmol) in CH_2Cl_2 (100 mL) was stirred at 20 °C for 24 h. The reaction mixture was washed with saturated aqueous Na_2SO_3 (4×50 mL) and dried over $MgSO_4$. After removal of the solvent (20 °C/ 20 torr), the crude product was purified by Kugelrohr distillation (140 °C/ 15 torr) to give **4** in 87% yield. IR (KBr) 1636 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.04 (t, *J* = 7.2 Hz, 3 H), 1.13 (t, *J* = 7.0 Hz, 3 H), 1.28 (d, *J* = 5.5 Hz, 3 H), 1.42 (s, 3 H), 3.08 (q, *J* =5.5 Hz, 1 H), 3.13-3.54 (m, 4 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 12.4 (q), 13.3 (q), 14.0 (q), 15.2 (q), 39.1 (t), 41.1 (t), 57.6 (d), 60.8 (s), 170.0 (s); EM (70 eV) m/z = 171

(M^+, 4), 100 (44), 72 (100), 58 (45). Exacts mass for $C_9H_{17}NO_2$, calcd: 171.1259; found: 171.1260.

Table 2: Epoxidation of *N,N*-diethyl tiglic amide (3) by *m*-CPBA



3 4

entry	solvent	mass balance (%)[a]	convn (%)[b]
1	CH_2Cl_2	87	>95
2	CH_3CN	85	>95
3	MeOH	81	30

[a] Determined gravimetrically; [b] determined by ^{1}H-NMR analysis of characteristic signals directly on the crude product (error ± 5 of the stated value)

Configurational Assignment of *ul*-2a-c and *lk*-2a-c Amides

The configuration of the major diastereomer obtained in the *m*-CPBA epoxidation of the tiglic amide (*S*)-**1c** was determined to be *lk*-**2c** by X-ray analysis[24] (Figure 1).

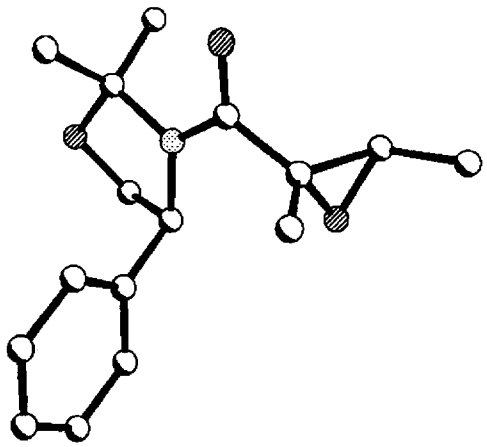


Figure 1: Crystal structure of the epoxide *lk*-**2c**; oxygen atoms are hatched, the nitrogen atom is dotted

By analogy, the configurations of the major diastereomers obtained in the *m*-CPBA epoxidation of the amides (*S*)-**1a** and (*S*)-**1b** were assigned to be *lk*-**2a** and *lk*-**2b**; consequently, the minor diastereomers are *ul*-**2a-c**.

Ab Initio and Semiempirical Calculations to Determine the Preferred Conformation of the Amides (*S*)-1a-c

The AM1 calculations,[25] with the energy minima corrected at the 6-31G* level,[26] were performed on the tiglic acid amide (*S*)-**1d** as a model compound. The energy profile for the rotation (α angle) about the sp^2-sp^2 single bond of the *N*-tigloyl moiety is depicted in Figure 2 and displays two energy minima at α = 56 ° and α = 249 °.

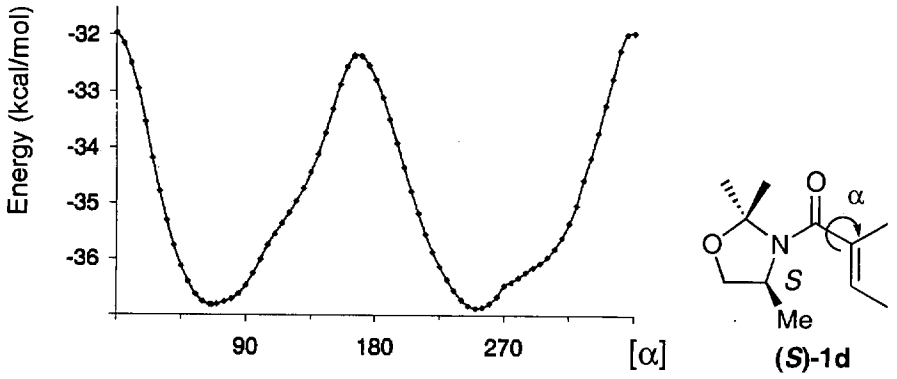
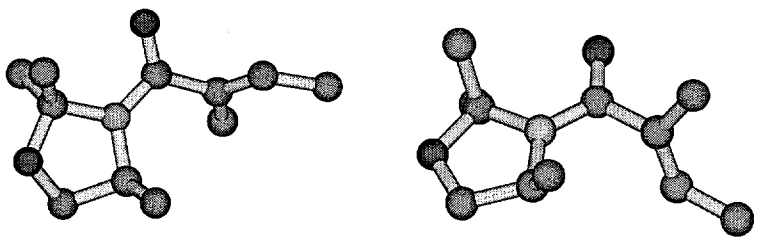


Figure 2: Energy profile for the rotation about the C-C bond of the tiglic amide (*S*)-**1d**

The lowest-energy conformers are represented by the structures **A** (α = 56 °) and **B** (α = 249 °), the energy difference amounts to 1.37 kcal/mol in favor of conformer **B**.



A (α = 56 °) **B** (α = 249 °)

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