Supplementary Information

General Procedures:

General procedure 1. Cycloaddition of nitrone (–)-**1** and allyl glycosides **2**:

Allyl glycosides **2** (1 mmol) and nitrone **1** (1.2 mmol) are dissolved in 5 ml toluene and refluxed for appr. 3 days. After completeness (checked by TLC) of the reaction the solvent is reduced under reduced pressure and the remaining product is purified by column chromatography (silica gel, petrol ether/ ethyl acetate = 1:1) and can be isolated as a colourless oil.

General procedure 2. Sm^{II}-mediated cleavage of isoxazolidines **3**:

Preparation of a fresh solution of SmI_2: To Sm powder (150 mg, 1 mmol) in 2 ml THF under argon atmosphere $C_2H_4I_2$ (160 mg,) is added and stirred at room temperature, until all Sm has been oxidized. The solutions becomes dark blue. (We always used freshly prepared SmI_2 solutions)

To this solution isoxazolidine **3** (0.2 mmol, dissolved in 3 ml THF and 0.5 ml abs. methanol) is added and stirred at room temperature until the colour of the solution has turned from blue to yellow. Subsequently, NH_4Cl (sat.) is added and the reaction mixture extracted with ethyl acetate. The combined organic phases are dried over $MgSO_4$, the solvent is evaporated and the remaining oily residue is purified by chromatography (silica gel, petrol ether/ ethyl acetate = 1:1). The product can be isolated as a colourless oil.

General procedure 3. Cleavage of the chiral auxiliary and of the amide in **4**:

N,N-acetal **4** (0.12 mmol) is dissolved in 2N HCl (12 ml) and acetic acid (10 ml) and the reaction mixture is heated up to 80 °C for 2 h. After cleavage of the chiral auxiliary, the reaction mixture is evaporated to dryness. The remaining residue is dissolved in THF (4 ml) and H_2O (4 ml) and treted with LiOH (80 mg, 3.3 mmol). After appr. 2 h (TLC-control) the cleavage of the amide bond is completed and the residue is again evaporated to dryness. After CH_2Cl_2 (10 ml) has been added and neutralization (H_2O, 2x5ml), the amont of solvent is diminished by evaporation. Subsequently, by addition of petrol ether the product **5** can be isolated as a colourless solid in quantitative yield.

α-**3b**: R_f = 0.56 (silica, petrol ether/EtOAc = 1/1); $[\alpha]_D^{20}$= +58.9° (c = 0.87, CH_2Cl_2); IR: $\tilde{\nu}_{max}$ = 3022, 2956, 2919, 2862, 1698, 1450, 1382, 1093; ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C): δ =

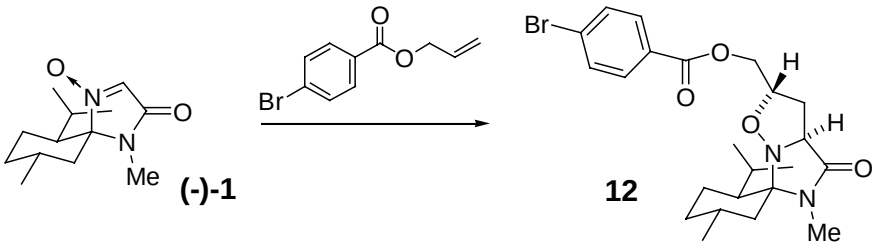
7.46 – 7.11 (m, 20H, CH-Benzyl), 4.99 – 4.49 (m, 8H, CH_2-Benzyl), 4.40 –4.29 (m, 1H, CH), 3.99 –4.03 (m, 2H, 2xCH), 3.62 – 3.80 (m, 6H, 4xCH, CH_2), 2.63 (s, 4H, NCH_3, *H*CH), 2,29 – 1.19 (m, 12H, 3xCH, 5xCH_2), 1.02 (d, ^3J = 4.9 Hz, 3H, CH_3), 0.91 (d, ^3J = 6.5 Hz, 6H, 2xCH_3); ^{13}C-NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 173.40 (C=O), 139.14 (q), 138.66 (q), 138.52 (q), 138.47 (q), 128.02 – 128.81 (CH-Benzyl), 89.95 (q), 82.60 (CH), 79.78 (CH), 78.39 (CH), 75.83 (CH_2-Benzyl), 75.41 (CH_2-Benzyl), 73.96 (CH_2-Benzyl), 73.44 (CH_2), 73.06 (CH-Benzyl), 72.07 (CH_2), 71.64 (CH), 69.45 (CH_2), 66.51 (CH), 48.60 (CH), 40.85 (CH_2), 39.20 (CH_2), 35.18 (CH_2), 30.31 (CH), 28.41 (CH_2), 26.36 (NCH_3), 24.82 (CH), 24.62 (CH_3), 22.94 (CH_2), 22.85 (CH_3), 18.92 (CH_3); elemental analysis: cal. $C_{50}H_{62}N_2O_7$: C 74.48, H 7.78, N 3.49; found: C 74.70, H 7.76, N 3.80.

α-**4b**: R_f = 0.23 (silica, petrol ether/EtOAc = 1/1); $[\alpha]_D^{20}$= +43.4° (c = 0.94, CH_2Cl_2); IR: $\tilde{\nu}_{max}$ = 3337, 3027, 2955, 2867, 1698,1455, 1093; ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.45 – 7.15 (m, 20H, CH-Benzyl), 5.03 – 4.48 (m, 8H, CH_2-Benzyl), 4.11 – 4.00 (m, 1H, CH), 3.85 –3.67 (m, 8H, 6xCH, CH_2), 2.77 (s, 3H, NCH_3), 1.98 – 1.25 (m, 13H, 5xCH_2, 3xCH), 1.07 – 0.87 (m, 9H, 3xCH_3); ^{13}C-NMR (50 MHz, $CDCl_3$, 25 °C): δ = 175.01 (C=O), 139.14 (q), 138.63 (q), 138.53 (q), 138.43 (q), 128.81 – 128.03 (CH-Benzyl), 82.61 (CH), 81.61 (q), 79.98 (CH), 78.47 (CH), 75.77 (CH_2-Benzyl), 75.37 (CH_2-Benzyl), 73.88 (CH_2-Benzyl), 73.20 (CH_2-Benzyl), 72.05 (CH), 71.07 (CH), 69.49 (CH_2, C-6), 66.69 (CH_2), 58.69 (CH), 48.44 (CH_2), 47.15 (CH), 41.09 (CH_2), 34.95 (CH_2), 33,19 (CH_2), 29.30 (CH), 25.79 (NCH_3), 25.06 (CH), 24.38 (CH_3), 22.68 (CH_3), 22.60 (CH_2), 18.89 (CH_3); elemental analysis: cal. $C_{50}H_{64}N_2O_7$: C 74.60, H 8.01, N 3.48; found: C 74.20, H 7.67, N 3.41.

α-**5b**: R_f = 0.16 (silica, CH_2Cl_2/MeOH = 98/2); $[\alpha]_D^{20}$= +17.2° (c = 1.16, CH_2Cl_2); IR: $\tilde{\nu}_{max}$ = 3379, 3011, 2929, 2846, 1734, 1650, 1100, 1036; ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.49 – 7.34 (m, 20H, CH-Benzyl), 4.65 – 4.46 (CH_2-Benzyl), 3.94 – 3.58 (m, 9H, 7XCH, CH_2), 2.13 – 2.01 (m, 2H, CH_2), 1.89 – 1.60 (m, 2H, CH_2); ^{13}C-NMR (50 MHz, $CDCl_3$, 25 °C): δ = 178.76 (C=O), 141.32 (q), 140.90 (q), 14.82 (q), 140.48 (q), 131.27 – 130.81 (CH-Benzyl), 84.54 (CH), 82.09 (CH), 80.69 (CH), 78.13 (CH_2-Benzyl), 77.77 (CH_2-Benzyl), 76.37 (CH_2-Benzyl), 75.65 (CH_2-Benzyl), 74.46 (CH), 73.15 (CH), 71.91 (CH_2), 67.03 (CH), 54.45 (CH), 38.00 (CH_2), 36.27 (CH_2); elemental analysis: cal. $C_{39}H_{45}NO_8$: C 71.43, H 6.92, N 2.14; found: C 71.17, H 6.95, N 2.72.

X-ray structure of **12**:

prepared by general procedure 1



$C_{23}H_{31}BrN_2O_4$, M_r = 479.4, orthorhombic, space group P 2_12_12 (No 18), T = 203(2) K, a = 13.052(3), b = 18.329(5), c = 9.700(9) Å, V = 2321(3) Å³, Z = 4, D_c = 1.372 g/cm³, μ(MoKα) = 1.802 mm^{-1}, F(000) = 1000, crystal size 0.60 x 0.50 x 0.10 mm³; Bruker AXS P4 diffractometer, MoKα radiation, graphite monochromator, ω-scan, 2.6 < Θ < 25°, h: 0/-14, k: 0/-20, l: 1/-11, 1938 reflections collected, absorption correction via psi-scans, min/max transmission 0.357/0.773. Structure solved by Direct and conventional Fourier methods, full-matrix least-squares refinement based on F^2 and 272 parameters, all but H-atoms refined anisotropically, H-atoms ‚riding' at idealized positions, refinement converged at R1(I > 2σ(I)) = 0.079, wR2(all data) = 0.175, S = 1.055, absolute structure parameter refined to 0.00(3), min/max height in final ΔF map –0.30/0.46 e/Å³. Programs used: SHELXTL NT V5.10.

Figure 2. Molecular structure of **12.** Displacement ellopsoids shown at the 50% level, H-atoms omitted for clarity.