Supplementary Material

Synthesis of modified miuraenamides – the Ugi approach

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General procedures

GP 1: Ugi reactions

To a solution of aldehyde (1.0 eq) and amine (1.0 eq) in the corresponding solvent (1.0 mL/mmol) Boc-L-alanine (1.2 eq) was added after 15 min. Methyl isocyanoacetate (1.0 eq) was added at 0 °C. After stirring at room temperature or heating in a microwave the reaction mixture was hydrolyzed with saturated $NaHCO_3$ solution. The organic layer was washed with 1 M $KHSO_4$ and 0.5 M HCl solution and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate).

GP 2: Saponification of esters with LiOH solutions

To a solution of the ester (1.0 eq) in THF/MeOH (3:1; 5–8 mL/mmol) a solution of LiOH (1.05 eq) in dest. H_2O (2 mL/mmol ester) was added at 0 °C. After complete conversion (TLC-control), the solvent was evaporated *in vacuo* and the residue was acidified with 1 M HCl solution to pH 2. The aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over Na_2SO_4 and the solvent was evaporated *in vacuo*.

GP 3a: Steglich Esterifications with EDC·HCl/DMAP

To a solution of the tripeptide acid (1.0 eq) in dry CH_2Cl_2 (8 mL/mmol) alcohol **(*S*)-6** (1.1 eq), 4-(dimethylamino)pyridine (DMAP) (0.1 eq) and *N*-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC·HCl) (1.2 eq) in dry CH_2Cl_2 (2 mL/mmol) were added. After stirring the mixture overnight at room temperature, the solvent was evaporated *in vacuo* and the residue was dissolved in Et_2O. The organic layer was washed with 1 M $KHSO_4$ and sat. $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate).

GP 3b: Steglich Esterifications with DCC/DMAP[1]

To a solution of the tripeptide acid (1.0 eq) in dry CH_2Cl_2 (8 mL/mmol) alcohol **3** (1.0-1.2eq), 4-(dimethylamino)pyridine (DMAP) (0.1 eq) and N,N'-dicyclohexyl-carbodiimide (DCC) (1.2 eq) in dry CH_2Cl_2 (3 mL/mmol) were added. After stirring the mixture overnight at room temperature, the solvent was evaporated *in vacuo* and the residue was dissolved in Et_2O. The precipitated urea derivative was filtered off, the solvent was evaporated and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate).

GP 4: Palladium-catalyzed allyl-cleavages

To a solution of allylester (1.0 eq) in dry THF (20 mL/mmol) $Pd(PPh_3)_4$ (10 mol%) and morpholin (2.0 eq) was added. The solution was stirred overnight at room temperature, before it was diluted with ethyl acetate. The solution was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of the solvent *in vacuo*, the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate).

GP 5: Macrolactamizations via the pentafluorophenyl ester method[2]

To a solution of the cyclization precursor (1.0 eq) and pentafluorophenol (1.1 eq) in dry CH_2Cl_2 (10 mL/mmol) *N*-(3-dimethylaminopropyl-N'-ethylcarbodiimide hydrochloride (EDC·HCl) (1.0 eq) was added at 0 °C. After stirring overnight at room temperature, the mixture was diluted with ethyl acetate. The organic layer was washed with sat. $NaHCO_3$ solution, dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. The activated

[1] B. Neises, W. Steglich, *Angew. Chem.* **1978**, *90*, 556-557; *Angew. Chem. Int. Ed. Engl*. **1978**, *17*, 522-523.

[2] a) U. Schmidt, M. Kroner, H. Griesser, *Synthesis* **1991**, 294-300; b) U. Schmidt, V. Leitenberger, H. Griesser, J. Schmidt, R. Meyer, *Synthesis* **1992**, 1248-1254.

ester was then diluted in DCM/TFA (4:1, 10 mL/mmol). After complete Boc-deprotection (2-3 h, tlc-control), the reaction mixture was diluted with dry CH_2Cl_2 (10-20 mL/mmol) and slowly added unter vigorously stirring to a two-phase-mixture of $CHCl_3$/sat. $NaHCO_3$ (7:1, 400 mL/mmol) at 40 °C. After complete addition, the mixture was heated to 60 °C and stirred overnight. The reaction mixture was diluted with H_2O and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. Column chromatography (silica gel, petroleum ether/ ethyl acetate) gave rise to the desired macrocycle.

GP 6: TBS-Deprotections with TBAF

To a solution of a silyl-protected depsipeptide (1.0 eq) in dry THF (3 mL/mmol) a solution of TBAF·3 H2O (1.1 eq) in dry THF (2.2 mL/mmol) was added. After complete deprotection (TLC-control), the reaction mixture was diluted with ethyl acetate, washed with 1 M HCl- and saturated NaCl solution and was dried over Na2SO4. After evaporation of the solvent and purification by column chromatography, the desired alcohol was obtained.

GP 7: Jones Oxidations

Jones solution (3 M): 1.0 g CrO_3, 2.91 mL H_2O, 0.84 mL H_2SO_4

To a solution of alcohol (1.0 eq) in acetone (7 mL/mmol) a 3 M Jones solution (3.0 eq) was added. After complete oxidation (TLC-control, 10–20 min), the reaction was hydrolyzed with isopropanol and the solvent was evaporated *in vacuo*. The residue was diluted with dest. H_2O and extracted with ethyl acetate. The combined organic layers were washed with saturated NaCl solution and dried over Na_2SO_4. After evaporation of the solvent *in vacuo*, the residue was purified by column chromatography.

Ugi Reactions

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-(*N*-methyl-phenylglycyl)-glycine methyl ester (7b)

According to **GP 1** 250 µL (2.50 mmol) benzaldehyde in 0.5 mL EtOH was reacted with 310 µL (2.50 mmol) methylamine (33 % in EtOH), 680 mg (3.00 mmol) Boc-L-alanine and 225 µL (2.50 mmol) methyl isocyanoacetate in the microwave (80 °C, 150 W, 30 min). Column chromatography (silica gel, petroleum ether/ethyl acetate 1:1) gave rise to the desired tripeptide **7b** (330 mg, 800 µmol, 32 % diastereomer 1; 320 mg, 780 µmol, 31 % diastereomer 2) as yellow foam. Diastereomer 1: R_f = 0.21 (petroleum ether/ethyl acetate 1:1). Mp: 42–46 °C. $[\alpha]_D^{20}$= –59.6° (c = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.32 (d, *J* = 6.8 Hz, 3 H), 1.44 (s, 9 H), 2.95 (s, 3 H), 3.77 (s, 3 H), 4.01 (dd, *J* = 17.8, 5.2 Hz, 1 H), 4.16 (dd, *J* = 17.8, 5.5 Hz, 1 H), 4.63 (qd, *J* = 7.0, 7.0 Hz, 1 H), 5.44 (d, *J* = 6.8 Hz, 1 H), 6.34 (s, 1 H), 6.78 (bs, 1 H), 7.34–7.40 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.1 (q), 28.3 (q), 32.3 (q), 41.2 (t), 46.8 (d), 52.3 (q), 61.1 (d), 79.8 (s), 128.4 (d), 128.8 (d), 129.5 (d), 163.1 (s), 165.0 (s), 169.2 (s) ppm. The ^{13}C signal of the tertiary carbon of the phenyl group is not visible in the background noise of the spectrum. Diastereomer 2: R_f = 0.17 (petroleum ether/ethyl acetate 1:1). Mp: 42–46 °C. $[\alpha]_D^{20}$= +63.1° (c = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.38 (d, *J* = 7.0 Hz, 3 H), 1.44 (s, 9 H), 2.91 (s, 3 H), 4.00 (dd, *J* = 18.3, 5.3 Hz, 1 H), 4.16 (dd, *J* = 18.3, 5.5 Hz, 1 H), 4.65 (qd, *J* = 7.5, 7.5 Hz, 1 H), 5.49 (d, *J* = 8.0 Hz, 1 H), 6.37 (s, 1 H), 6.27 (bs, 1 H), 7.36–7.42 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 18.7 (q), 28.3 (q), 32.2 (q), 41.2 (t), 46.8 (d), 52.4 (q), 60.7 (d), 79.5 (s), 128.7 (d), 128.9 (d), 129.5 (d), 167.5 (s), 169.4 (s), 169.9 (s) ppm. The ^{13}C signal of the tertiary carbon of the phenyl group is not visible in the background noise of the spectrum. HRMS (CI) calcd for: $C_{20}H_{30}N_3O_6^+$ $[M+H]^+$: 408.2129, found: 408.2133.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-[*N*-methyl-(4-allyloxy-3-bromo)-phenylglycyl]-glycine methyl ester (7c)

According to **GP 1** 241 mg (1.00 mmol) 3-bromo-4-allyloxybenzaldehyde in 1.0 mL trifluoroethanol was reacted with 124 µL (1.00 mmol) methylamine (33 % in EtOH), 227 mg (1.20 mmol) Boc-L-alanine and 90 µL (1.00 mmol) methyl isocyanoacetate in 0.2 mL trifluoroethanol in the microwave (100 °C, 150 W, 75 min). Column chromatography (silica gel, petroleum ether/ethyl acetate 1:1) gave rise to the desired tripeptide **7c** (129 mg, 240 µmol, 24 % diastereomer 1; 150 mg, 280 µmol, 28 % diastereomer 2) as brown oil. Diastereomer 1: R_f = 0.25 (petroleum ether/ethyl acetate 1:1) $[\alpha]_D^{20}$= –-55.4° (c = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.32 (d, *J* = 6.8 Hz, 3 H), 1.44 (s, 9 H), 2.95 (s, 3 H), 3.77 (s, 3 H), 3.97 (dd, *J* = 18.2, 5.7 Hz, 1 H), 4.17 (m, 1 H), 4.58–4.65 (m, 3 H), 5.33 (dd, *J* = 10.5, 0.8 Hz, 1 H), 5.36 (bs, 1 H), 5.49 (dd, *J* = 17.3, 1.3 Hz, 1 H), 6.06 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1 H), 6.28 (s, 1 H), 6.85 (m, 1 H), 6.89 (d, *J* = 8.5, 1 H), 7.30 (dd, *J* = 8.8, 1.2 Hz, 1 H), 7.57 (d, *J* = 1.5 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 17.9 (q), 28.3 (q), 32.1 (q), 41.3 (t), 46.8 (d), 52.4 (q), 59.6 (d), 69.7 (t), 80.0 (s), 113.3 (d), 118.0 (t), 123.4 (s), 128.9 (d), 131.3 (d), 132.3 (s), 134.5 (d), 154.3 (s), 165.6 (s), 169.1 (s), 169.3 (s), 169.9 (s) ppm. Diastereomer 2: R_f = 0.20 (petroleum ether/ethyl acetate 1:1) $[\alpha]_D^{20}$= +73.4° (c = 1.0, $CHCl_3$).^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.39 (d, *J* = 6.8 Hz, 3 H), 1.45 (s, 9 H), 2.92 (s, 3 H), 3.78 (s, 3 H), 4.01 (dd, *J* = 18.1, 5.2 Hz, 1 H), 4.14 (dd, *J* = 18.3, 5.8 Hz, 1 H), 4.61–4.66 (m, 3 H), 5.34 (dd, *J* = 10.6, 1.3 Hz, 1 H), 5.43 (d, *J* = 8.0 Hz, 1 H), 5.50 (dd, *J* = 17.1, 1.5 Hz, 1 H), 6.07 (ddt, *J* = 17.3, 10.5, 5.0 Hz, 1 H), 6.20 (bs, 1 H), 6.28 (s, 1 H), 6.90 (d, *J* = 8.6 Hz, 1 H), 7.30 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.60 (d, *J* = 2.2 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.6 (q), 28.4 (q), 32.5 (q), 41.3 (t), 46.8 (d), 52.5 (q), 59.6 (d), 69.7 (t), 80.2 (s), 113.4 (d), 118.0 (t), 123.4 (s), 128.9 (d), 131.3 (d), 132.2 (s), 134.4 (d), 154.3 (s), 165.6 (s), 169.1 (s), 169.3 (s), 169.9 (s) ppm. HRMS (CI) calcd for: $C_{23}H_{32}BrN_3O_7^+$ $[M+H]^+$: 543.1398, found: 543.1422.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-(*N*-methyl-(4-allyloxy-3-chlor)-phenylglycyl)-glycine methyl ester (7d)

According to **GP 1** 298 mg (1.52 mmol) 3-chloro-4-allyloxybenzaldehyde in 1.5 mL trifluoroethanol was reacted with 226 µL (1.82 mmol) methylamine (33 % in EtOH), 345 mg (1.82 mmol) Boc-L-alanine and 137 µL (1.52 mmol) methyl isocyanoacetate in 0.2 mL trifluoroethanol in the microwave (100 °C, 150 W, 60 min). Column chromatography (silica gel, petroleum ether/ethyl acetate 1:1) gave rise to the desired tripeptide 7d (213 mg, 430 µmol, 28 %, *dr* = 1:1) as brown foam. Diastereomer 1: R_f = 0.12 (petroleum ether/ethyl acetate 1:1). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.33 (d, *J* = 6.8 Hz, 3 H), 1.44 (s, 9 H), 2.95 (s, 3 H), 3.77 (s, 3 H), 3.97 (dd, *J* = 18.0, 5.2 Hz, 1 H), 4.17 (dd, *J* = 17.8, 5.8 Hz, 1 H), 4.61–4.65 (m, 3 H), 5.33 (dd, *J* = 10.6, 1.3 Hz, 1 H), 5.37 (m, 1 H), 5.47 (dd, *J* = 17.3, 1.5 Hz, 1 H), 6.07 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1 H), 6.28 (s, 1 H), 6.87 (t, *J* = 6.3 Hz, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 7.25 (dd, *J* = 8.5, 2.2 Hz, 1 H), 7.40 (d, *J* = 2.2 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 17.9 (q), 28.3 (q), 32.1 (q), 41.3 (t), 46.8 (d), 52.4 (q), 60.0 (d), 69.7 (t), 113.6 (d), 118.1 (t), 123.2 (s), 129.0 (d), 131.9 (d), 132.3 (d), 168.9 (s), 168.9 (s), 170.0 (s) ppm. The tertiary carbons of the phenyl and silyl groups and the carboxy atom of the silyl group are in the background noise of the ^{13}C-NMR spectrum. Diastereomer 2: R_f = 0.08 (petroleum ether/ethyl acetate 1:1) ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.38 (d, *J* = 6.8 Hz, 3 H), 1.45 (s, 9 H), 2.92 (s, 3 H), 3.77 (s, 3 H), 3.99 (dd, *J* = 18.3, 5.3 Hz, 1 H), 4.15 (dd, *J* = 18.0, 5.5 Hz, 1 H), 4.62–4.65 (m, 3 H), 5.33 (dd, *J* = 10.5, 1.2 Hz, 1 H), 5.44 (m, 1 H), 5.48 (dd, *J* = 17.1, 1.3 Hz, 1 H), 6.06 (ddt, *J* = 17.0, 10.5, 5.0 Hz, 1 H), 6.29 (s, 1 H), 6.32 (bs, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 7.24 (d, *J* = 8.8 Hz, 1 H), 7.43 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.6 (q), 28.3 (q), 32.0 (q), 41.3 (t), 46.8 (d), 52.5 (q), 59.6 (d), 69.7 (t), 113.6 (d), 118.1 (t), 123.4 (s), 128.9 (d), 131.4 (d), 132.3 (d), 154.3 (s), 165.6 (s), 169.1 (s), 169.9 (s) ppm. A tertiary carbon of the phenyl group, a tertiary carbon of the silyl group and the carboxy atom of the silyl group are in the background noise of the ^{13}C-NMR spectrum. HRMS (CI) calcd for $C_{18}H_{24}ClN_3O_5$ $[M\text{-}C_5H_9O_2]^+$: 397.1399, found: 397.1405.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-(*N*-methyl-phenylalanyl)-glycine methyl ester (7f)

According to **GP 1** 300 mg (2.50 mmol) 2-phenylacetaldehyde in 2.5 mL dichloroethan was reacted with 310 µL (2.50 mmol) methylamine (33 % in EtOH), 681 mg (3.00 mmol) Boc-L-alanine and 225 µL (2.50 mmol) methyl isocyanoacetate in the microwave (100 °C, 150 W, 120 min). Column chromatography (silica gel, petroleum ether/ethyl acetate 1:1) gave rise to the desired tripeptide **7f** (351 mg, 830 µmol, 33 %, *dr* =1:1) as yellowish oil. R_f = 0.14 (petroleum ether/ethyl acetate 1:1). Diastereomer 1: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.44 (m, 3 H), 1.46 (s, 9 H), 2.96 (s, 3 H), 3.00 (m, 1 H), 3.44 (dd, *J* = 15.0, 5.5 Hz, 1 H), 3.76 (s, 3 H), 3.86 (dd, *J* = 17.8, 5.3 Hz, 1 H), 4.16 (m, 1 H), 4.40 (qd, *J* = 7.0, 7.0 Hz, 1 H), 5.23 (m, 1 H), 5.65 (m, 1 H), 6.90 (m, 1 H), 7.13–7.31 (m, 5 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 16.4 (q), 28.3 (q), 33.3 (q), 34.0 (t), 41.1 (t), 52.4 (d), 52.9 (q), 79.1 (s), 128.4 (d), 128.7 (d), 129.0 (d), 129.4 (s), 159.1 (s), 169.8 (s), 169.9 (s), 170.0 (s) ppm. Diastereomer 2 (selected signals): ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 7.0 Hz, 3 H), 1.40 (s, 9 H), 2.97 (s, 3 H), 3.05 (m, 1 H), 3.37 (dd, *J* = 14.6, 3.2 Hz, 1 H), 3.74 (s, 3 H), 3.95 (m, 1 H), 4.10 (m, 1 H), 4.24 (m, 1 H), 5.01 (m, 1 H), 5.23 (dd, *J* = 7.3, 7.3 Hz, 1 H), 7.13–7.31 (m, 5 H), 8.32 (dd, *J* = 5.3, 5.3 Hz, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 17.3 (q), 28.3 (q), 33.4 (t), 34.0 (q), 41.1 (t), 52.3 (d), 53.0 (q), 79.1 (s), 128.4 (d), 128.7 (d), 129.0 (d), 129.4 (s), 159.1 (s), 169.8 (s), 169.9 (s), 170.0 (s) ppm. HRMS (CI) calcd for: $C_{21}H_{32}N_3O_6^+$ $[M+H]^+$: 422.2286, found: 422.2301.

Saponification of Ugi Products

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-(*N*-methyl-phenylglycyl)-glycine (8b)

According to **GP 2** 269 mg (660 µmol) tripeptide **7b** in 3.3 mL THF/MeOH (3:1) was reacted with 16.6 mg (693 µmol) LiOH·H_2O in 1.3 mL H_2O. After aqueous workup acid **8b** (218 mg, 550 µmol, 84 %, *dr* = 52:48) could be obtained as white foam. R_f = 0.06 (petroleum ether/ethyl acetate 1:1). Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.30 (d, *J* = 7.0 Hz, 3 H), 1.44 (s, 9 H), 2.90 (s, 3 H), 4.09 (m, 2 H), 4.66 (qd, *J* = 6.8, 6.8 Hz, 1 H), 5.51 (d, *J* = 7.3 Hz, 1 H), 6.32 (s, 1 H), 6.99 (s, 1 H), 7.30–7.37 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.0 (q), 28.3 (q), 32.5 (q), 41.2 (t), 46.9 (d), 61.2 (d), 80.1 (s), 128.5 (d), 128.8 (d), 129.3 (d), 134.3 (s), 155.6 (s), 169.5 (s), 172.1 (s), 174.5 (s) ppm. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.34 (d, *J* = 6.8 Hz, 3 H), 1.43 (s, 9 H), 2.93 (s, 3 H), 4.09 (m, 2 H), 4.66 (qd, *J* = 6.8, 6.8 Hz, 1 H), 5.55 (d, *J* = 6.8 Hz, 1 H), 6.39 (s, 1 H), 6.79 (s, 1 H), 7.30–7.37 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.2 (q), 28.3 (q), 32.4 (q), 41.2 (t), 46.8 (d), 60.9 (d), 79.8 (s), 128.6 (d), 128.8 (d), 129.3 (d), 134.3 (s), 155.3 (s), 169.6 (s), 171.9 (s), 174.5 (s) ppm. HRMS (CI) calcd for: $C_{19}H_{28}N_3O_6^+$ $[M+H]^+$: 394.1973, found: 394.1960.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-[*N*-methyl-(4-allyloxy-3-brom)-phenylglycyl]-glycine (8c)

According to **GP 2** 176 mg (320 µmol) tripeptide **7c** in 1.6 mL THF/MeOH (3:1) was reacted with 7.8 mg (340 µmol) LiOH·H_2O in 0.7 mL H_2O. After aqueous workup acid **8c** (159 mg, 300 µmol, 93 %, *dr* = 1:1) could be obtained as orange foam. R_f = 0.09 (petroleum ether/ethyl acetate 1:1). Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.32 (d, *J* = 7.0 Hz, 3 H), 1.44 (s, 9 H), 2.97 (s, 3 H), 3.98 (dd, *J* = 18.6, 5.3 Hz, 1 H), 4.23 (dd, *J* = 18.3, 6.0 Hz, 1 H), 4.62 (d, *J* = 5.0 Hz, 2 H), 4.65 (m, 1 H), 5.33 (dd, *J* = 10.6, 0.8 Hz, 1 H), 5.40 (m, 1 H), 5.49 (dd, *J* = 17.3, 1.5 Hz, 1 H), 6.06 (ddt, *J* = 17.3, 10.8, 5.0 Hz, 1 H), 6.27 (s, 1 H), 6.88 (d, *J* = 8.6 Hz, 1 H), 7.00 (m, 1 H), 7.25 (m, 1 H), 7.54 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.0 (q), 28.4 (q), 32.5 (q), 41.3 (t), 46.9 (d), 60.4 (d), 69.7 (t), 113.4 (d), 118.0 (t), 123.4 (s), 127.4 (d), 129.7 (d), 132.2 (s), 155.9 (s), 156.8 (s), 169.2 (s), 169.8 (s), 174.5 (s) ppm. The ^{13}C signal of the tertiary carbon of the carbamate is not visible in the background noise of the spectrum. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.36 (d, *J* = 7.0 Hz, 3 H), 1.45 (s, 9 H), 2.93 (s, 3 H), 4.07–4.17 (m, 2 H), 4.62 (d, *J* = 5.0 Hz, 2 H), 4.65 (m, 1 H), 5.33 (dd, *J* = 10.6, 0.8 Hz, 1 H), 5.43 (m, 1 H), 5.49 (dd, *J* = 17.3, 1.5 Hz, 1 H), 6.06 (ddt, *J* = 17.3, 10.8, 5.0 Hz, 1 H), 6.32 (s, 1 H), 6.64 (m, 1 H), 6.88 (d, *J* = 8.6 Hz, 1 H), 7.25 (m, 1 H), 7.57 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.3 (q), 28.4 (q), 32.5 (q), 41.4 (t), 46.9 (d), 60.4 (d), 69.7 (t), 113.4 (d), 118.0 (t), 123.4 (s), 127.4 (d), 129.7 (d), 132.2 (s), 132.2 (d), 155.9 (s), 156.8 (s), 169.2 (s), 169.8 (s), 174.6 (s) ppm. The ^{13}C signal of the tertiary carbon of the carbamate is not visible in the background noise of the spectrum. HRMS (CI) calcd for: $C_{17}H_{22}BrN_3O_5^+$ $[M+H]^+$: 427.0737, found: 427.0759.

Preparation of the tripeptide esters

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-(*N*-methyl-phenylglycyl)-glycine-(2*S*,6*E*)-10-(allyloxy-carbonyl)-7-methyl-dec-6-en-2-yl ester (9b)

According to **GP 3a** 190 mg (480 µmol) acid **8b** in 3.8 mL dry CH_2Cl_2 was reacted with 127 mg (530 µmol) **(*S*)-6**, 6.10 mg (50.0 µmol) DMAP and 111 mg (580 µmol) EDC·HCl in 1.4 mL dry CH_2Cl_2. Purification by column chromatography (silicagel, petroleum ether/ethyl acetate 6:4) gave rise to **9b** (197 mg, 320 µmol, 67 %, *dr* = 1:1)

as yellow resin. R_f = 0.25 (petroleum ether/ethyl acetate 6:4). Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.23 (d, *J* = 6.5 Hz, 3 H), 1.32 (d, *J* = 6.8 Hz, 3 H), 1.26–1.38 (m, 4 H), 1.44 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.31 (t, *J* = 8.0 Hz, 2 H), 2.44 (t, *J* = 7.5 Hz, 2 H), 2.92 (s, 3 H), 3.99 (m, 1 H), 4.10 (m, 1 H), 4.57 (dt, *J* = 5.8, 1.24 Hz, 2 H), 4.65 (qd, *J* = 7.3, 7.3 Hz, 1 H), 4.96 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.12 (m, 1 H), 5.23 (dd,*J* = 10.5, 1.2 Hz, 1 H), 5.31 (dd, *J* = 17.3, 1.5 Hz, 1 H), 5.45 (d, *J* = 8.3 Hz, 1 H), 5.91 (ddt, *J* = 17.0, 10.5, 5.8 Hz, 1 H), 6.20 (dd, *J* = 5.3, 5.3 Hz, 1 H), 6.31 (s, 1 H), 7.34–7.43 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 15.9 (q), 18.8 (q), 19.9 (q), 25.4 (t), 27.5 (t), 28.4 (q), 32.3 (q), 33.1 (t), 34.6 (t), 35.4 (t), 41.6 (t), 46.8 (d), 60.8 (d), 64.9 (t), 72.7 (d), 118.1 (t), 124.8 (d), 128.7 (d), 128.9 (q), 129.6 (q), 132.3 (s), 133.8 (s), 133.8 (d), 156.5 (s), 169.0 (s), 169.1 (s), 169.2 (s), 169.3 (s) ppm. The ^{13}C signal of the tertiary carbon of the carbamate is not visible in the background noise of the spectrum. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.24 (d, *J* = 6.3 Hz, 3 H), 1.40 (d, *J* = 6.8 Hz, 3 H), 1.26–1.38 (m, 4 H), 1.44 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.31 (t, *J* = 8.0 Hz, 2 H), 2.44 (t, *J* = 8.5 Hz, 2 H), 2.95 (s, 3 H), 3.95 (m, 1 H), 4.15 (m, 1 H), 4.57 (dt, *J* = 5.8, 1.24 Hz, 2 H), 4.65 (qd, *J* = 7.3, 7.3 Hz, 1 H), 4.96 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.12 (m, 1 H), 5.23 (dd, *J* = 10.5, 1.2 Hz, 1 H), 5.31 (dd, *J* = 17.3, 1.5 Hz, 1 H), 5.47 (d, *J* = 9.0 Hz, 1 H), 5.91 (ddt, *J* = 17.0, 10.5, 5.8 Hz, 1 H), 6.67 (m, 1 H), 6.36 (s, 1 H), 7.34–7.43 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 15.9 (q), 18.6 (q), 19.9 (q), 25.3 (t), 27.5 (t), 28.4 (q), 32.3 (q), 32.2 (t), 34.6 (t), 35.3 (t), 41.6 (t), 46.7 (d), 60.8 (d), 64.9 (t), 72.6 (d), 118.1 (t), 124.8 (d), 128.7 (d), 128.8 (d), 129.5 (q), 132.3 (s), 133.8 (s), 133.8 (d), 156.5 (s), 169.0 (s), 169.1 (s), 169.2 (s), 169.3 (s) ppm. The ^{13}C signal of the tertiary carbon of the carbamate is not visible in the background noise of the spectrum. HRMS (CI) calcd for: $C_{33}H_{50}N_3O_8^+$ $[M+H]^+$: 616.3592, found: 616.3595.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-[*N*-methyl-(3-brom-4-allyloxy)-phenylglycyl]-glycine-(2*S*,6*E*)-10-(allyloxy-carbonyl)-7-methyl-dec-6-en-2-yl ester (9c)

According to **GP 3a** 319 mg (600 µmol) acid **8c** in 4.8 mL dry CH_2Cl_2 was reacted with 160 mg (660 µmol) **(*S*)-6**, 7.3 mg (60.0 µmol) DMAP and 139 mg (720 µmol) EDC·HCl in 1.8 mL dry CH_2Cl_2. Purification by column chromatography (silicagel, petroleum ether/ethyl acetate 6:4) gave rise to **9c** (270 mg, 360 µmol, 60 %, *dr* = 1:1) as yellow resin. R_f = 0.25 (petroleum ether/ethyl acetate 6:4). Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.23 (d, *J* = 6.2 Hz, 3 H), 1.28–1.40 (m, 4 H), 1.32 (d, *J* = 6.8 Hz, 3 H), 1.43 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.30 (t, *J* = 7.3 Hz, 2 H), 2.44 (t, *J* = 7.0 Hz, 2 H), 2.92 (s, 3 H), 4.02 (m, 1 H), 4.56 (d, *J* = 5.5 Hz, 2 H), 4.60–4.65 (m, 3 H), 4.96 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.13 (m, 1 H), 5.23 (dd, *J* = 10.3, 1.0 Hz, 1 H), 5.27–5.35 (m, 2 H), 5.40 (d, *J* = 6.5 Hz, 1 H), 5.49 (d, *J* = 17.3 Hz, 1 H), 5.91 (ddt, *J* = 16.8, 10.8, 5.5 Hz, 1 H), 6.05 (ddt, *J* = 17.1, 10.6, 5.0 Hz, 1 H), 6.26 (s, 1 H), 6.81 (m, 1 H), 6.88 (d, *J* = 8.5 Hz, 1 H), 7.29 (d, *J* = 8.6 Hz, 1 H), 7.56 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 15.9 (q), 18.0 (q), 19.9 (q), 25.4 (t), 27.5 (t), 28.3 (q), 32.1 (q), 33.1 (t), 34.6 (t), 35.3 (t), 41.6 (t), 46.8 (d), 60.4 (d), 65.0 (t), 69.7 (t), 72.7 (d), 79.9 (s), 110.0 (s), 113.4 (d), 118.1 (t), 118.1 (t), 124.8 (s), 128.1 (d), 129.8 (d), 132.3 (s), 133.8 (s), 134.4 (d), 155.2 (s), 158.9 (s), 168.7 (s), 168.9 (s). 169.0 (s), 173.0 (s) ppm. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.23 (d, *J* = 6.5 Hz, 3 H), 1.28–1.40 (m, 4 H), 1.38 (d, *J* = 6.8 Hz, 3 H), 1.43 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.30 (t, *J* = 7.3 Hz, 2 H), 2.44 (t, *J* = 7.0 Hz, 2 H), 2.95 (s, 3 H), 4.02 (m, 1 H), 4.56 (d, *J* = 5.5 Hz, 2 H), 4.60–4.65 (m, 3 H), 4.96 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.13 (m, 1 H), 5.23 (dd, *J* = 10.3, 1.0 Hz, 1 H), 5.27–5.35 (m, 2 H), 5.40 (d, *J* = 6.5 Hz, 1 H), 5.49 (d, *J* = 17.3 Hz, 1 H), 5.91 (ddt, *J* = 16.8, 10.8, 5.5 Hz, 1 H), 6.05 (ddt, *J* = 17.1, 10.6, 5.0 Hz, 1 H), 6.29 (s, 1 H), 6.81 (m, 1 H), 6.88 (d, *J* = 8.5 Hz, 1 H), 7.29 (d, *J* = 8.6 Hz, 1 H), 7.58 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 15.9 (q), 18.0 (q), 19.9 (q), 25.3 (t), 27.5 (t), 28.3 (q), 32.0 (q), 33.1 (t), 34.6 (t), 35.3 (t), 41.5 (t), 46.8 (d), 60.4 (d), 65.0 (t),

69.7 (t), 72.5 (d), 79.9 (s), 110.0 (s), 113.3 (d), 118.1 (t), 118.1 (t), 124.8 (s), 128.1 (d), 129.7 (d), 132.3 (s), 133.8 (s), 134.4 (d), 134.4 (d), 155.2 (s), 158.9 (s), 168.7 (s), 168.9 (s), 169.0 (s), 173.0 (s) ppm.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-[*N*-methyl-(3-chlor-4-allyloxy)-phenylglycyl]-glycine-(2*S*,6*E*)-10-(allyloxy-carbonyl)-7-methyl-dec-6-en-2-yl ester (9d)

According to **GP 2** 294 mg (590 µmol) tripeptide **7d** in 3.0 mL THF/MeOH (3:1) was reacted with 26.5 mg (620 µmol) LiOH·H_2O in 0.6 mL H_2O to the free acid **8d** (277 mg, 570 µmol, 96%). According to **GP 3a** the crude acid (246 mg, 510 µmol) in 4.1 mL dry CH_2Cl_2 was reacted with 135 mg (560 µmol) **(*S*)-6**, 6.20 mg (50.0 µmol) DMAP and 117 mg (610 µmol) EDC·HCl in 1.5 mL dry CH_2Cl_2. Purification by column chromatography (silicagel, petroleum ether/ethyl acetate 6:4) gave rise to **9d** (217 mg, 310 µmol, 60 %, *dr* = 1:1) as brown resin. R_f = 0.26 (petroleum ether/ethyl acetate 6:4). Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.23 (d, *J* = 6.2 Hz, 3 H), 1.25–1.56 (m, 4 H), 1.32 (d, *J* = 6.8 Hz, 3 H), 1.44 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.31 (t, *J* = 7.3 Hz, 2 H), 2.44 (t, *J* = 7.3 Hz, 2 H), 2.92 (s, 3 H), 3.97 (dd, *J* = 18.0, 5.0 Hz, 1 H), 4.09 (m, 1 H), 4.57 (d, *J* = 5.8 Hz, 2 H), 4.59–4.67 (m, 3 H), 4.96 (qt, *J* = 6.5, 6.5 Hz, 1 H), 5.13 (m, 1 H), 5.23 (dd, *J* = 10.3, 1.2 Hz, 1 H), 5.28–5.36 (m, 2 H), 5.40 (d, *J* = 6.0 Hz, 1 H), 5.47 (d, *J* = 17.3 Hz, 1 H), 5.91 (ddt, *J* = 16.6, 10.8, 5.8 Hz, 1 H), 6.06 (ddt, *J* = 17.3, 10.8, 5.0 Hz, 1 H), 6.26 (s, 1 H), 6.80 (m, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 7.24 (dd, *J* = 8.6, 2.2 Hz, 1 H), 7.40 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 15.9 (q), 18.0 (q), 19.9 (q), 25.4 (t), 27.5 (t), 28.3 (q), 32.2 (q), 33.1 (t), 34.6 (t), 35.3 (t), 41.5 (t), 46.8 (d), 60.3 (d), 65.0 (t), 69.7 (t), 72.7 (d), 79.9 (s), 113.6 (d), 118.1 (t), 118.1 (t), 123.4 (s), 124.8 (d), 131.4 (d), 132.3 (s), 132.3 (d), 133.8 (s), 133.8 (d), 155.1 (s), 158.9 (s), 168.7 (s), 168.9 (s), 169.0 (s), 173.0 (s) ppm. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.24 (d, *J* = 6.3 Hz, 3 H), 1.25–1.56 (m, 4 H), 1.38 (d, *J* = 6.8 Hz, 3 H), 1.43 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.31 (t, *J* = 7.3 Hz, 2 H), 2.44 (t, *J* = 7.3 Hz, 2 H), 2.95 (s, 3 H), 3.92 (dd, *J* = 16.6, 5.0 Hz, 1 H), 4.13 (m, 1 H), 4.57 (d, *J* = 5.8 Hz, 2 H), 4.59–4.67 (m, 3 H), 4.96 (qt, *J* = 6.5, 6.5 Hz, 1 H), 5.13 (m, 1 H), 5.23 (dd, *J* = 10.3, 1.2 Hz, 1 H), 5.28–5.36 (m, 2 H), 5.40 (d, *J* = 6.0 Hz, 1 H), 5.47 (d, *J* = 17.3 Hz, 1 H), 5.91 (ddt, *J* = 16.6, 10.8, 5.8 Hz, 1 H), 6.06 (ddt, *J* = 17.3, 10.8, 5.0 Hz, 1 H), 6.29 (s, 1 H), 6.80 (m, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 7.24 (dd, *J* = 8.6, 2.2 Hz, 1 H), 7.42 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 15.9 (q), 18.0 (q), 19.9 (q), 25.4 (t), 27.5 (t), 28.3 (q), 32.2 (q), 33.1 (t), 34.6 (t), 35.4 (t), 41.6 (t), 46.8 (d), 60.1 (d), 65.0 (t), 69.7 (t), 72.7 (d), 79.9 (s), 113.6 (d), 118.1 (t), 123.4 (s), 124.8 (d), 131.4 (d), 132.3 (s), 132.3 (d), 133.8 (s), 133.8 (d), 155.1 (s), 158.9 (s), 168.7 (s), 168.9 (s), 169.0 (s), 173.0 (s) ppm. HRMS (CI) calcd for: $C_{31}H_{44}ClN_3O_7^+$ $[M+H]^+$: 605.2861, found: 605.2860.

(*S*)-*N*-*tert*-Butoxcarbonyl-alanyl-(*N*-methyl-2-naphthylglycyl)-glycine-(2*S*,6*E*)-10-(allyloxycarbonyl)-7-methyl-dec-6-en-2-yl ester (9e)

According to **GP 2** methyl ester **7e** (251 mg, 570 mol) in THF/MeOH (3:1, 2.8 mL) was saponified with a solution of LiOH (25.7 mg, 600 mol) in H_2O (1.9 mL). The crude acid **8e** (250 mg, 570 mol, quant., dr 1:1) was directly used without further purification. For that, the acid (222 mg, 500 mol) in 4.0 mL dry CH_2Cl_2 was converted according to **GP 3a** with 132 mg (550 µmol) **(*S*)-6**, 6.1 mg (50.0 µmol) DMAP and 115 mg (600 µmol) EDC·HCl in 1.5 mL dry CH_2Cl_2. Purification by column chromatography (silicagel, petroleum ether/ethyl acetate 6:4) gave rise to **9e** (198 mg, 296 µmol, 59 %, *dr* = 54:46) as colorless oil. Diastereomer 1: R_f = 0.20 (petroleum ether/ethyl acetate 6:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, *J* = 6.3 Hz, 3 H), 1.27-1.56 (m, 4 H), 1.33 (d, *J* = 6.5 Hz, 3 H), 1.44 (s, 9 H), 1.60 (s, 3 H), 1.97 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.30 (m, 2 H), 2.42 (m, 2 H), 2.94 (s, 3 H), 4.02 (dd, *J* = 17.6 Hz, 5.0 Hz, 1 H), 4.17 (m, 1 H), 4.55 (m, 2 H), 4.67 (dq, *J* = 7.0, 7.0 Hz, 1 H), 4.97 (m, 1 H), 5.12 (t, *J* = 6.8 Hz, 1 H), 5.22 (d, *J* = 10.3 Hz, 1 H), 5.30 (d, *J* = 17.0 Hz, 1 H), 5.50 (m, 1 H), 5.90 (m, 1 H), 6.39 (bs, 1 H), 6.50 (s, 1 H),

7.40 (m, 1 H), 7.47-7.55 (m, 2 H), 7.80-7.90 (m, 3 H), 7.94 (s, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 15.9 (q), 18.2 (q), 19.9 (q), 25.3 (t), 27.5 (t), 28.3 (q), 32.4 (q), 33.1 (t), 34.6 (t), 35.4 (t), 41.6 (t), 46.8 (d), 60.3 (d), 64.9 (t), 72.6 (d), 79.5 (s), 118.0 (t), 124.8 (d), 126.4, 126.5, 126.6 (3 d), 127.6 (s),128.2 (s),128.7 (s),129.0 (d), 131.9 (s), 132.2 (d), 133.0 (s),133.1 (s),133.8 (s),155.5 (s), 169.0 (s), 169.2 (s), 169.3 (s), 173.0 (s) ppm. Diastereomer 2: R_f = 0.16 (petroleum ether/ethyl acetate 6:4). (selected signals): ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 6.8 Hz, 3 H), 1.59 (s, 9 H), 2.30 (m, 2 H), 2.42 (m, 2 H), 2.97 (s, 3 H), 3.98 (dd, *J* = 17.8 Hz, 4.6 Hz, 1 H), 4.55 (m, 2 H), 5.11 (t, *J* = 6.2 Hz, 1 H), 5.50 (m, 1 H), 6.54 (s, 1 H), 6.82 (bs, 1 H), 7.37 (d, *J* = 9.6 Hz, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 18.7 (q), 25.3 (t), 27.5 (t), 32.2 (q), 35.3 (t), 41.6 (t), 72.5 (d), 79.8 (s), 124.8 (d), 126.6 (d), 126.7 (d), 126.7 (d), 129.0 (d), 131.5 (s), 133.0 (s), 133.1 (s), 133.8 (s), 155.1 (s) ppm. HRMS (CI) calcd for: $C_{37}H_{52}N_3O_8^+$ $[M+H]^+$: 666.3749, found: 666.3750.

(*S*)-*N*-*tert*-Butoxcarbonyl-alanyl-(*N*-methyl-phenylalanyl)-glycine-(2*S*,6*E*)-10-(allyloxycarbonyl)-7-methyl-dec-6-en-2-yl ester (9f)

According to **GP 2** 307 mg (728 µmol) Tripeptide **7f** in 3.6 mL THF/MeOH (3:1) was reacted with 18.3 mg (764 µmol) LiOH·H_2O in 1.5 mL H_2O. After aqueous workup, 181 mg (440 µmol, 60%) crude acid **8f** in 3.5 mL dry CH_2Cl_2 was converted directly according to **GP 3a** with 115 mg (480 µmol) **(*S*)-6**, 5.40 mg (44.0 µmol) DMAP and 102 mg (530 µmol) EDC·HCl in 3.5 mL dry CH_2Cl_2. Purification by column chromatography (silicagel, petroleum ether/ethyl acetate 6:4) gave rise to **9f** (166 mg, 263 µmol, 60 %, *dr* = 63:37) as colorless oil. R_f = 0.21 (petroleum ether/ethyl acetate 6:4). Diastereomer 1: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.8 Hz, 3 H), 1.27 (d, *J* = 7.3 Hz, 3 H), 1.30-1.58 (m, 4 H), 1.40 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 7.3, 7.3 Hz, 2 H), 2.31 (t, *J* = 7.3 Hz, 2 H), 2.44 (t, *J* = 7.6 Hz, 2 H), 2.96 (s, 3 H), 3.05 (m, 1 H), 3.43 (dd, *J* = 15.0, 5.3 Hz, 1 H), 3.85 (m, 1 H), 4.08 (m, 1 H), 4.49 (m, 1 H), 4.57 (d, *J* = 5.8 Hz, 2 H), 4.93 (m, 1 H), 5.13 (t, *J* = 6.8 Hz, 1 H), 5.23 (d, *J* = 10.5 Hz, 1 H), 5.24 (bs, 1 H), 5.31 (dd, *J* = 17.3, 1.3 Hz, 1 H), 5.64 (m, 1 H), 5.91 (ddt, *J* = 16.8, 10.6, 5.8 Hz, 1 H), 6.84 (m, 1 H), 7.12-7.31 (m, 5 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 15.9 (q), 17.3 (q), 19.9 (q), 25.3 (t), 27.5 (t), 28.3 (3 q), 30.8 (q), 33.1 (t), 33.4 (t), 34.6 (t), 35.4 (t), 41.3 (t), 46.5 (d), 56.8 (d), 65.0 (t), 72.4 (d), 79.8 (s), 118.1 (t), 124.8 (d), 128.4 (d), 128.4 (d), 128.7 (d), 132.2 (d), 133.7 (s), 137.7 (s), 155.6 (s), 169.1 (s), 169.5 (s), 170.1 (s), 173.0 (s) ppm. Diastereomer 2 (selected signals): ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.16-1.34 (m, 6 H), 1.37 (s, 9 H), 2.97 (s, 3 H), 3.05 (m, 1 H), 3.22 (m, 1 H), 3.85 (m, 1 H), 4.08 (m, 1 H), 4.94 (m, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 28.2 (q), 72.1 (d), 80.6 (s), 129.4 (d), 129.4 (d) ppm. Rotamer (selected signals): ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.16-1.34 (m, 6 H), 1.36 (s, 9 H), 3.05 (m, 1 H), 3.22 (m, 1 H), 3.85 (m, 1 H), 4.08 (m, 1 H) ppm. HRMS (CI) calcd for: $C_{34}H_{52}N_3O_8^+$ $[M+H]^+$: 630.3749, found: 630.3755.

(*S*)-(*N*-*tert*-Butoxycarbonyl-alanyl)-(*R*)-(*O*-allyl-3-bromo-*N*-methyl-tyrosyl)-glycine-(2*S*,6*E*)-10-(allyloxycarbonyl)-7-methyl-dec-6-en-2-yl ester (9g)

According to **GP 3a** 180 mg (380 µmol) crude acid **8g**[3] in 3.0 mL dry CH_2Cl_2 was reacted with 101 mg (420 µmol) **(*S*)-6**, 4.6 mg (38.0 µmol) DMAP and 88.2 mg (460 µmol) EDC·HCl in 1.1 mL dry CH_2Cl_2. Purification by column chromatography (silicagel, petroleum ether/ethyl acetate 1:1) gave rise to **9g** (142 mg, 186 µmol, 49 %) as colorless oil. R_f = 0.33 (petroleum ether/ethyl acetate 1:1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 7.0 Hz, 3 H), 1.21 (d, *J* = 6.2 Hz, 3 H), 1.40 (s, 9 H), 1.25-1.37 (m, 4 H), 1.60 (s, 3 H), 1.97 (td, *J* = 7.3, 7.3 Hz, 2 H), 2.30 (t, *J* = 8.0 Hz, 2 H), 2.43 (t, *J* = 8.3 Hz, 2 H), 2.91 (m, 1 H), 2.96 (s, 3 H), 3.35 (dd, *J* = 15.3, 5.5 Hz, 1 H), 3.78 (dd, *J* =

[3] a) L. Karmann, K. Schulz, J. Herrmann, R. Müller, U. Kazmaier, *Angew. Chem.* **2015**, 127, 4585–4590; *Angew. Chem. Int. Ed.* **2015**, *54*, 4502–4507.b) S. Kappler, L. Karmann, C. Prudel, J. Herrmann, G. Caddeu, R. Müller, A. M. Vollmar, S. Zahler, U. Kazmaier, *Eur. J. Org. Chem.* **2018**, 6952–6965.

17.8, 4.8 Hz, 1 H), 4.12 (m, 1 H), 4.43 (qd, *J* = 6.8, 6.8 Hz, 1 H), 4.54-4.58 (m, 4 H), 4.93 (qt, *J* = 6.2, 6.2 Hz, 1 H), 5.12 (t, *J* = 7.0 Hz, 1 H), 5.19-5.34 (m, 4 H), 5.44 (dd, *J* = 17.8, 1.5 Hz, 1 H), 5.55 (dd, *J* = 10.8, 5.8 Hz, 1 H), 5.90 (ddt, *J* = 17.1, 11.3, 5.8 Hz, 1 H), 6.02 (ddt, *J* = 17.3, 10.5, 5.0 Hz, 1 H), 6.78 (d, *J* = 8.3 Hz, 1 H), 6.88 (bs, 1 H), 7.07 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.34 (d, *J* = 1.8 Hz, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 15.9 (q), 17.4 (q), 19.9 (q), 25.3 (t), 27.5 (t), 28.3 (q), 30.8 (q), 32.2 (t), 33.1 (t), 34.6 (t), 35.3 (t), 41.3 (t), 46.5 (d), 56.6 (d), 64.9 (t), 69.9 (t), 72.3 (d), 79.9 (s), 112.0 (s), 113.6 (d), 117.7 (t), 118.0 (t), 124.8 (d), 128.6 (d), 130.8 (s), 132.2 (d), 132.5 (d), 133.4 (d), 133.7 (s), 153.6 (s), 155.7 (s), 169.1 (s), 169.9 (s), 173.0 (s), 174.9 (s) ppm. HRMS (CI) calcd for: $C_{37}H_{47}BrN_3O_7^+$ $[M+H]^+$: 664.2592, found: 664.2587.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-(*N*-methyl-phenylglycyl)-glycine-(2*S*,6*E*)-10-carboxy-7-methyl-dec-6-en-2-yl ester (10b)

According to **GP 4** 164 mg (270 µmol) allylester **9b** in 5.4 mL dry THF was reacted with 31.2 mg (30.0 µmol) $Pd(PPh_3)_4$ and 46.7 µL (640 µmol) morpholin. After column chromatography (silica gel, petroleum ether/ethyl acetate 1:1) acid **10b** (80.7 mg, 140 µmol, 52 % d. Th., *dr* = 2:1) could be isolated as yellow resin. Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.22 (d, *J* = 6.3 Hz, 3 H), 1.31 (d, *J* = 6.8 Hz, 3 H), 1.24–1.40 (m, 4 H), 1.43 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 6.8, 6.8 Hz, 2 H), 2.30 (t, *J* = 7.0 Hz, 2 H), 2.43 (t, *J* = 7.0 Hz, 2 H), 2.94 (s, 3 H), 3.96 (dd, *J* = 18.0, 5.2 Hz, 1 H), 4.13 (dd, *J* = 18.1, 6.0 Hz, 1 H), 4.67 (qd, *J* = 7.0, 7.0 Hz, 1 H), 4.98 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.14 (t, *J* = 6.5 Hz, 1 H), 5.64 (d, *J* = 7.3 Hz, 1 H), 6.33 (s, 1 H), 6.98 (dd, *J* = 5.3, 5.3 Hz, 1 H), 7.32–7.41 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 15.9 (q), 19.7 (q), 20.8 (q), 25.0 (t), 27.3 (t), 28.3 (q), 32.4 (q), 32.9 (t), 34.6 (t), 34.9 (t), 41.6 (t), 46.8 (d), 61.2 (d), 72.4 (d), 79.6 (s), 124.8 (d), 128.4 (d), 128.5 (d), 128.8 (d), 132.0 (s), 132.1 (s), 155.6 (s), 169.2 (s), 175.9 (s) ppm. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.19 (m, 3 H), 1.37 (d, *J* = 6.8 Hz, 3 H), 1.24–1.40 (m, 4 H), 1.44 (s, 9 H), 1.60 (s, 3 H), 1.98 (td, *J* = 6.8 Hz, 2 H), 2.30 (t, *J* = 7.0 Hz, 2 H), 2.43 (t, *J* = 7.0 Hz, 2 H), 2.92 (s, 3 H), 4.03 (d, *J* = 5.5 Hz, 2 H), 4.67 (qd, *J* = 7.0, 7.0 Hz, 1 H), 4.98 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.14 (t, *J* = 6.5 Hz, 1 H), 5.59 (d, *J* = 8.3 Hz, 1 H), 6.36 (s, 1 H), 6.59 (dd, *J* = 5.3, 5.3 Hz, 1 H), 7.32–7.41 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 15.9 (q), 19.8 (q), 20.8 (q), 25.02(t), 27.2 (t), 28.3 (3 q), 32.3 (q), 32.8 (t), 34.5 (t), 35.0 (t), 41.6 (t), 46.8 (d), 61.2 (d), 72.6 (d), 79.8 (s), 124.8 (d), 128.4 (d), 128.5 (q), 128.9 (d), 131.8 (s), 131.9 (s), 155.6 (s), 169.2 (s), 175.9 (s) ppm. HRMS (CI) calcd for: $C_{30}H_{46}N_3O_8$ $[M+H]^+$: 576.3279, found: 576.3286.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-[*N*-methyl-(3-brom-4-hydroxy)-phenylglycyl]-glycine-(2*S*,6*E*)-10-carboxy-7-methyl-dec-6-en-2-yl ester (10c)

According to **GP 4** 242 mg (320 µmol) allylester **9c** in 6.4 mL dry THF was reacted with 37.2 mg (30.0 µmol) $Pd(PPh_3)_4$ and 33.5 µL (390 µmol) morpholin. After aqueous workup and evaporation of the solvent acid **10c** (179 mg, 270 µmol, 83 % d. Th., *dr* = 1:1) could be isolated as yellow resin. R_f = 0.11 (petroleum ether/ethyl acetate 1:1). Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.24 (m, 3 H), 1.28–1.41 (m, 4 H), 1.32 (d, *J* = 7.0 Hz, 3 H), 1.45 (s, 9 H), 1.61 (s, 3 H), 1.99 (m, 2 H), 2.31 (m, 2 H), 2.45 (t, *J* = 6.8 Hz, 2 H), 2.95 (s, 3 H), 4.04 (m, 2 H), 4.66 (qd, *J* = 6.8 Hz, 1 H), 4.99 (qt, *J* = 6.0 Hz, 1 H), 5.14 (t, *J* = 7.3 Hz, 1 H), 5.56 (d, *J* = 8.3 Hz, 1 H), 6.27 (s, 1 H), 6.71 (dd, *J* = 5.5, 5.5 Hz, 1 H), 6.99 (d, *J* = 8.3 Hz, 1 H), 7.21 (d, *J* = 8.3 Hz, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 15.9 (q), 17.9 (q), 19.8 (q), 25.2 (t), 27.1 (t), 28.3 (3 q), 32.3 (q), 32.5 (t), 34.4 (t), 34.9 (t), 41.7 (t), 46.9 (d), 60.4 (d), 72.7 (d), 79.9 (s), 110.5 (s), 116.4 (d), 125.1 (d), 128.5 (d), 130.2 (s), 132.1 (d), 133.2 (s), 152.9 (s), 155.3 (s), 169.1 (s), 169.3 (s), 174.4 (s), 176.2 (s) ppm. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.25 (m, 3 H), 1.28–1.41 (4 H, 17-H), 1.37 (d, *J* = 6.8 Hz, 3 H), 1.44 (s, 9 H), 1.61 (s, 3 H), 1.99 (m, 2 H), 2.31 (m, 2 H), 2.45 (t, *J* = 6.8 Hz, 2 H), 2.95 (s, 3 H), 4.04 (m, 2 H), 4.66 (qd, *J* = 6.8, 6.8 Hz, 1 H), 4.99 (qt, *J* = 6.0,

6.0 Hz, 1 H), 5.14 (t, *J* = 7.3 Hz, 1 H), 5.65 (d, *J* = 7.3 Hz, 1 H), 6.28 (s, 1 H), 6.71 (dd, *J* = 5.5, 5.5 Hz, 1 H), 6.99 (d, *J* = 8.6 Hz, 1 H), 7.21 (d, *J* = 8.5 Hz, 1 H), 7.50 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 15.9 (q), 17.9 (q), 19.8 (q), 25.2 (t), 27.2 (t), 28.3 (3 q), 32.3 (q), 32.5 (t), 34.8 (t), 34.9 (t), 41.7 (t), 46.9 (d), 60.4 (d), 72.5 (d), 79.9 (s), 110.5 (s), 116.3 (d), 125.1 (d), 128.6 (d), 130.4 (s), 132.2 (d), 133.3 (s), 152.7 (s), 155.3 (s), 169.1 (s), 169.3 (s), 174.4 (s), 176.2 (s) ppm.

(*S*)-*N*-*tert*-Butoxycarbonyl-alanyl-[*N*-methyl-(3-chlor-4-hydroxy)-phenylglycyl]-glycine-(2*S*,6*E*)-10-carboxy-7-methyl-dec-6-en-2-yl ester (10d)

According to **GP 4** 199 mg (280 µmol) allylester **9d** in 5.6 mL dry THF was reacted with 32.4 mg (30.0 µmol) $Pd(PPh_3)_4$ and 29.2 µL (340 µmol) morpholin. After aqueous workup and evaporation of the solvent acid **10d** (173 mg, 280 µmol, 98 % d. Th., *dr* = 1:1) could be isolated as brown resin. R_f = 0.11 (petroleum ether/ethyl acetate 1:1). Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.25 (d, *J* = 7.3 Hz, 3 H), 1.28–1.40 (m, 4 H), 1.31 (d, *J* = 7.0 Hz, 3 H), 1.44 (s, 9 H), 1.60 (s, 3 H), 1.98 (m, 2 H), 2.30 (t, *J* = 6.5 Hz, 2 H), 2.44 (m, 2 H), 2.93 (s, 3 H), 3.94 (m, 2 H), 4.64 (qd, *J* = 7.0, 7.0 Hz, 1 H), 4.98 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.14 (t, *J* = 7.0 Hz, 1 H), 5.57 (d, *J* = 8.0 Hz, 1 H), 6.25 (s, 1 H), 6.71 (dd, *J* = 5.2, 5.2 Hz, 1 H), 6.95 (d, *J* = 6.8 Hz, 1 H), 7.14 (d, *J* = 8.3 Hz, 1 H), 7.35 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 15.9 (q), 17.9 (q), 19.8 (q), 25.2 (t), 27.2 (t), 28.3 (q), 32.3 (q), 32.6 (t), 34.4 (t), 34.9 (t), 41.7 (t), 46.9 (d), 60.3 (d), 72.6 (d), 79.9 (s), 116.7 (d), 120.4 (s), 125.0 (d), 128.5 (d), 130.3 (s), 132.0 (d), 133.6 (s), 152.0 (s), 155.4 (s), 169.2 (s), 171.2 (s), 174.5 (s), 176.5 (s) ppm. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.27 (d, *J* = 7.0 Hz, 3 H), 1.28–1.40 (m, 4 H), 1.36 (d, *J* = 7.0 Hz, 3 H), 1.43 (s, 9 H), 1.60 (s, 3 H), 1.98 (m, 2 H), 2.30 (t, *J* = 6.5 Hz, 2 H), 2.43 (m, 2 H), 2.95 (s, 3 H), 3.94 (m, 2 H), 4.64 (qd, *J* = 7.0 Hz, 1 H), 4.98 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.14 (t, *J* = 7.0 Hz, 1 H), 5.63 (d, *J* = 7.3 Hz, 1 H), 6.27 (s, 1 H), 6.71 (dd, *J* = 5.2, 5.2 Hz, 1 H), 6.97 (d, *J* = 7.3 Hz, 1 H), 7.14 (d, *J* = 8.3 Hz, 1 H), 7.35 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 15.8 (q), 18.3 (q), 19.6 (q), 24.9 (t), 27.2 (t), 28.3 (3 q), 32.2 (q), 32.7 (t), 34.5 (t), 34.9 (t), 41.7 (t), 46.9 (d), 60.3 (d), 72.5 (d), 80.1 (s), 116.6 (d), 120.3 (s), 125.1 (d), 128.6 (d), 130.4 (s), 132.1 (d), 133.6 (s), 151.8 (s), 155.8 (s), 169.3 (s), 171.2 (s), 174.4 (s), 176.4 (s) ppm. HRMS (CI) calcd for: $C_{25}H_{35}ClN_3O_7^+$ [(M-Boc)+H]$^+$: 524.2158, found: 524.2139.

(*S*)-*N*-*tert*-Butoxcarbonyl-alanyl-(*N*-methyl-(4-allyloxy-3-chlor)-phenylglycyl)-glycine-(2*S*,5*E*)-10-(*tert*-butyldimethylsiloxy)-5-methyl-dec-5-en-2-yl ester (12d)

According to **GP 2** 294 mg (590 µmol) tripeptide **7d** in 3.0 mL THF/MeOH (3:1) was reacted with 26.5 mg (620 µmol) $LiOH·H_2O$ in 0.6 mL H_2O. After aqueous workup, 277 mg (570 µmol, 96%) crude acid **8d** in 4.6 mL dry CH_2Cl_2 was converted according to **GP 3b** with 189 mg (630 µmol) **(*S*)-2**, 83.1 mg (680 µmol) DMAP and 140 mg (680 µmol) DCC in 1.7 mL dry CH_2Cl_2. Purification by column chromatography (silicagel, petroleum ether/ethyl acetate 6:4) gave rise to **12d** (206 mg, 266 µmol, 47 %, *dr* = 1:1) as colorless oil. Additionally alcohol **(*S*)-2** (95.4 mg, 317 µmol, 50 %) could be reisolated. R_f = 0.25 (petroleum ether/ethyl acetate 6:4). Diastereomer 1: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 6 H), 0.89 (s, 9 H), 1.25 (d, *J* = 6.1 Hz, 3 H), 1.35 (m, 2 H), 1.38 (d, *J* = 7.0 Hz, 3 H), 1.43 (s, 9 H), 1.50 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.58 (s, 3 H), 1.74 (m, 2 H), 1.93-2.03 (m, 4 H), 2.92 (s, 3 H), 3.60 (t, *J* = 6.5 Hz, 2 H), 3.96 (dd, *J* = 18.2, 5.2 Hz, 1 H), 4.10 (dd, *J* = 19.1, 5.4 Hz, 1 H), 4.59-4.67 (m, 3 H), 4.94 (m, 1 H), 5.12 (m, 1 H), 5.23 (d, *J* = 10.5 Hz, 1 H), 5.40 (d, *J* = 6.6 Hz, 1 H), 5.47 (d, *J* = 17.4 Hz, 1 H), 6.06 (ddt, *J* = 17.1, 10.8, 5.3 Hz, 1 H), 6.29 (s, 1 H), 6.83 (m, 1 H), 6.91 (dd, *J* = 8.4, 2.3 Hz, 1 H), 7.24 (d, *J* = 8.4 Hz, 1 H), 7.39 (d, *J* = 1.8 Hz, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = –5.3 (q), 15.9 (q), 18.3 (q), 19.8 (q), 26.0 (t, q, C-23), 27.6 (t), 28.3 (q), 32.1 (t), 32.5 (q), 34.2 (t), 35.3 (t), 41.6 (t), 46.8 (d), 60.0 (d), 63.1 (t), 69.7 (t), 72.6 (d), 79.9 (s), 113.6 (d), 118.0 (t), 123.4 (s), 125.1 (d), 127.7 (s), 128.9 (d), 131.3 (d), 132.3 (d), 133.8 (s), 154.3 (s), 155.6 (s), 168.7 (s), 169.0 (s),

174.1 (s) ppm. Diastereomer 2 (selected signals): ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, *J* = 6.2 Hz, 3 H), 1.32 (d, *J* = 7.0 Hz, 3 H), 1.44 (s, 9 H), 2.95 (s, 3 H), 7.42 (d, *J* = 1.8 Hz, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 15.9 (q), 32.0 (t), 34.1 (t), 41.5 (t), 59.6 (d), 72.5 (d), 79.6 (s), 113.6 (d), 118.1 (t), 125.1 (d), 129.0 (d), 131.4 (d), 132.3 (d), 133.9 (s), 154.1 (s), 168.9 (s), 169.1 (s), 174.0 (s) ppm.

(9*S*,5*E*)-9-((*S*)-(*N*-*tert*-Butoxycarbonyl-alanyl)-(*N*-methyl-(4-allyloxy-3-chlor)-phenylglycyl)-glycinyl-oxy)-6-methyldec-5-enoic acid (13d)

According to **GP 6** 203 mg (265 µmol) silylester **12d** in 0.8 mL THF was reacted with 92.0 mg (292 µmol) TBAF·3 H_2O in 0.6 mL H_2O. After complete deprotection and aqueous workup, the corresponding alcohol (159 mg, 238 µmol, 90%) was directly subjected to Jones oxidation. According to **GP 7** 88.3 mg (135 µmol) alcohol in 1.0 mL acetone was reacted with 135 µL (405 µmol) Jones reagent at 0 °C. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 1:1 + 1 % AcOH) gave rise to acid **13d** (41.7 mg, 63.0 µmol, 51 %, *dr* = 58:42) as colorless oil. R_f = 0.26 (petroleum ether/ethyl acetate 1:1 + 1 % AcOH). Diastereomer 1: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, *J* = 6.3 Hz, 3 H), 1.33 (d, *J* = 7.0 Hz, 3 H), 1.43 (s, 9 H), 1.57 (s, 3 H), 1.60-1.79 (m, 4 H), 1.96-2.08 (m, 4 H), 2.24 (m, 2 H), 2.92 (s, 3 H), 3.94 (dd, *J* = 18.3, 5.0 Hz, 1 H), 4.08 (dd, *J* = 18.3, 5.3 Hz, 1 H), 4.61 (m, 2 H), 4.66 (m, 1 H), 4.90 (qt, *J* = 6.0, 6.0 Hz, 1 H), 5.07 (t, *J* = 6.5 Hz, 1 H), 5.31 (d, *J* = 11.3 Hz, 1 H), 5.46 (d, *J* = 17.3 Hz, 1 H), 5.65 (d, *J* = 7.6 Hz, 1 H), 6.05 (ddt, *J* = 16.3, 10.8, 5.3 Hz, 1 H), 6.30 (s, 1 H), 6.90 (d, *J* = 8.6 Hz, 1 H), 7.16 (m, 1 H), 7.22 (d, *J* = 8.5 Hz, 1 H), 7.37 (d, *J* = 1.5 Hz, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 15.7 (q), 18.4 (q), 20.0 (q), 24.6 (t), 27.0 (t), 28.3 (q), 32.1 (q), 33.3 (t), 33.6 (t), 35.5 (t), 41.4 (t), 46.8 (d), 60.1 (d), 69.6 (t), 72.0 (d), 79.7 (s), 113.5 (d), 118.0 (t), 123.3 (s), 124.1 (d), 127.1 (s), 128.8 (d), 131.2 (d), 132.3 (d), 134.8 (s), 154.2 (s), 155.2 (s), 169.0 (s), 169.3 (s), 174.3 (s), 177.7 (s) ppm. Diastereomer 2 (selected signals): ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, *J* = 6.3 Hz, 3 H), 1.36 (d, *J* = 6.5 Hz, 3 H), 1.45 (s, 9 H), 2.93 (s, 3 H), 3.81 (m, 1 H), 4.22 (dd, *J* = 17.8, 5.0 Hz, 1 H), 5.56 (d, *J* = 7.5 Hz, 1 H), 6.91 (d, *J* = 8.8 Hz, 1 H), 7.39 (d, *J* = 1.5 Hz, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 15.6 (q), 18.1 (q), 20.2 (q), 24.7 (t), 27.1 (t), 33.6 (t), 33.6 (t), 41.5 (t), 72.3 (d), 80.2 (s), 113.6 (d), 118.0 (t), 123.2 (s), 124.2 (d), 129.0 (d), 131.4 (d), 132.3 (d), 154.0 (s), 155.8 (s) ppm.

Cyclization towards miuraenamide derivatives

(9*S*,19*S*,14*E*)-6-Phenyl-7,9,14,19-tetramethyl-1-oxa-4,7,10-triazacylono-nadec-14-en-2,5,8,11-tetraon (11b)

According to **GP 5** 41.8 mg (71.6 µmol) acid **10b**, 14.7 mg (79.9 µmol) pentafluorophenol and 15.3 mg (79.9 µmol) EDC·HCl were reacted in 0.8 mL dry CH_2Cl_2. The corresponding active ester was dissolved in 0.8 mL dry CH_2Cl_2/TFA (4:1). After Boc deprotection the reaction mixture was diluted with 1.0 mL dry CH_2Cl_2 and added dropwise to 29 mL $CHCl_3$/sat. $NaHCO_3$ (7:1). Column chromatography (silica gel, petroleum ether/ethyl acetate 3:7) gave rise to macrocycle **11b** (16.2 mg, 35.4 µmol, 44 %, *dr* = 9:1) as colorless resin. R_f = 0.12 (petroleum ether/ethyl acetate 3:7) ppm. Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.25 (d, *J* = 6.3 Hz, 3 H), 1.34 (d, *J* = 6.8 Hz, 3 H), 1.37–1.61 (m, 4 H), 1.64 (s, 3 H), 2.01 (td, *J* = 7.3, 7.3 Hz, 2 H), 2.18–2.49 (m, 4 H), 2.88 (s, 3 H), 3.76 (dd, *J* = 17.6, 4.5 Hz, 1 H), 4.33 (dd, *J* = 17.6, 7.3 Hz, 1 H), 4.93 (qd, *J* = 6.8 Hz, 1 H), 5.01 (m, 1 H), 5.22 (t, *J* = 6.0 Hz, 1 H), 6.32 (s, 1 H), 6.41 (m, 1 H), 6.79 (d, *J* = 6.5 Hz, 1 H), 7.32–7.41 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 16.3 (q), 18.4 (q), 20.0 (q), 24.8 (t), 27.8 (t), 32.1 (q), 33.9 (t), 34.0 (t), 35.7 (t), 42.0 (t), 45.9 (d), 60.5 (d), 72.3 (d), 126.1 (d), 128.6 (d), 128.9 (d), 129.4 (d), 133.3 (s), 134.0 (s), 168.5 (s), 169.2 (s), 172.0 (s), 173.8 (s) ppm. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.25 (d, *J* = 6.3 Hz, 3 H), 1.34 (d, *J* = 6.8 Hz, 3 H), 1.37–1.61 (m, 4 H), 1.64 (s, 3 H), 2.01 (td, *J* = 7.3, 7.3 Hz, 2 H), 2.18–2.49 (m, 4 H), 2.86 (s, 3 H), 3.76 (dd, *J* = 17.6, 4.5 Hz, 1

H), 4.33 (dd, *J* = 17.6, 7.3 Hz, 1 H), 4.93 (qd, *J* = 6.8, 6.8 Hz, 1 H), 5.01 (m, 1 H), 5.22 (t, *J* = 6.0 Hz, 1 H), 6.32 (s, 1 H), 6.48 (m, 1 H), 6.79 (d, *J* = 6.5 Hz, 1 H), 7.32–7.41 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 16.3 (q), 18.4 (q), 20.0 (q), 24.8 (t), 27.8 (t), 32.1 (q), 33.9 (t), 34.0 (t), 35.7 (t), 42.0 (t), 45.9 (d), 60.5 (d), 72.3 (d), 126.1 (d), 128.6 (d), 128.9 (d), 129.4 (d), 133.3 (s), 134.0 (s), 168.5 (s), 169.2 (s), 172.0 (s), 173.8 (s). HRMS (CI) cald for: $C_{25}H_{36}N_3O_5^+$ $[M+H]^+$: 458.2649, found: 458.2654.

(9*S*,19*S*,14*E*)-6-(3-chlor-4-hydroxy)-phenyl-7,9,14,19-tetramethyl-1-oxa-4,7,10-triazacylononadec-14-en-2,5,8,11-tetraon (11d)

According to **GP 5** 176 mg (280 µmol) acid **10d**, 55.9 mg (310 µmol) pentafluorophenol and 59.2 mg (310 µmol) EDC·HCl were reacted in 2.8 mL dry CH_2Cl_2. The corresponding active ester was disolved in 2.8 mL dry CH_2Cl_2/TFA (4:1). After Boc deprotection the reaction mixture was diluted with 4.2 mL dry CH_2Cl_2 and added dropwise to 112 mL $CHCl_3$/sat. $NaHCO_3$ (7:1). Column chromatography (silica gel, petroleum ether/ethyl acetate 3:7) gave rise to macrocycle **11d** (54.2 mg, 110 µmol, 38 %, *dr* = 7:3) as yellow resin. R_f = 0.13 (petroleum ether/ethyl acetate 3:7). Diastereomer 1: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.24 (m, 3 H), 1.30–1.57 (m, 4 H), 1.34 (m, 3 H), 1.62 (s, 3 H), 1.99 (td, *J* = 5.8 Hz, 2 H), 2.29–2.56 (m, 4 H), 2.88 (s, 3 H), 3.80 (dd, *J* = 14.1, 3.8 Hz, 2 H), 4.37 (m, 1 H), 4.90 (qd, *J* = 5.0, 5.0 Hz, 1 H), 5.01 (m, 1 H), 5.19 (t, *J* = 5.3 Hz, 1 H), 6.23 (s, 1 H), 6.61 (m, 1 H), 6.79 (m, 1 H), 6.99 (d, *J* = 6.8 Hz, 1 H), 7.15 (m, 1 H), 7.36 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 14.6 (q), 18.2 (q), 19.9 (q), 24.8 (t), 27.7 (t), 31.9 (q), 32.6 (t), 34.0 (t), 35.6 (t), 42.0 (t), 46.0 (d), 59.6 (d), 72.4 (d), 116.7 (d), 120.4 (s), 126.0 (d), 128.0 (d), 129.4 (s), 130.4 (d), 133.2 (s), 152.0 (s), 168.5 (s), 169.0 (s), 172.3 (s), 173.7 (s) ppm. Diastereomer 2: ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 1.24 (m, 3 H), 1.30–1.57 (m, 4 H), 1.34 (m, 3 H), 1.60 (s, 3 H), 1.95 (td, *J* = 6.3 Hz, 2 H), 2.29–2.56 (m, 4 H), 2.85 (s, 3 H), 3.73 (m, 2 H), 4.25 (m, 1 H), 4.86 (qd, *J* = 6.0, 6.0 Hz, 1 H), 5.01 (m, 1 H), 5.53 (t, *J* = 5.6 Hz, 1 H), 5.81 (s, 1 H), 6.99 (d, *J* = 6.8 Hz, 1 H), 7.15 (m, 1 H), 7.27 (m, 1 H), 7.41 (m, 1 H), 7.89 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* = 15.0 (q), 18.2 (q), 19.9 (q), 24.8 (t), 28.4 (t), 31.9 (q), 32.9 (t), 34.0 (t), 35.6 (t), 42.1 (t), 46.4 (d), 61.3 (d), 72.8 (d), 116.7 (d), 120.5 (s), 126.0 (d), 128.0 (d), 129.6 (s), 130.4 (d), 133.5 (s), 152.3 (s), 168.7 (s), 169.2 (s), 172.3 (s), 173.7 (s) ppm. HRMS (CI) calcd for: $C_{25}H_{34}ClN_3O_6^+$ $[M+H]^+$: 509.2101, found: 509.2138.

(9*S*,19*S*,14*E*)-7,9,14,19-tetramethyl-6-(2-naphthyl)-1-oxa-4,7,10-triazacylononadec-14-en-2,5,8,11-tetraon (11e)

According to **GP 4** 197 mg (296 µmol) allylester **9e** in 5.9 mL dry THF was reacted with 34.2 mg (29.6 µmol) $Pd(PPh_3)_4$ and 51.2 µL (592 µmol) morpholin. According to **GP 5** 197 mg (296 µmol) of the crude acid **10e**, 60.0 mg (326 µmol) pentafluorophenol and 62.5 mg (326 µmol) EDC·HCl were reacted in 3.0 mL dry CH_2Cl_2. The corresponding active ester was dissolved in 3.0 mL dry CH_2Cl_2/TFA (4:1). After Boc deprotection the reaction mixture was diluted with 4.4 mL dry CH_2Cl_2 and added dropwise to 118 mL $CHCl_3$/sat. $NaHCO_3$ (7:1). Column chromatography (silica gel, petroleum ether/ethyl acetate 3:7) gave rise to macrocycle **11e** (20.1 mg, 39.6 µmol, 13 %, *dr* = 1:1) as yellow oil. R_f = 0.18 (petroleum ether/ethyl acetate 3:7). Diastereomeric mixture: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.21-1.29 (m, 3 H), 1.29-1.59 (m, 7 H), 1.60, 1.68 (s, 3 H), 2.01 (m, 2 H), 2.14-2.60 (m, 4 H), 2.96 (s, 3 H), 2.99 (s, 3 H), 3.72 (m, 1 H), 4.54 (m, 1 H), 4.73-5.27 (m, 3 H), 6.39 (m, 1 H), 6.54 (s, 1 H), 6.58 (s, 1 H), 7.32-7.42 (m, 2 H), 7.47-7.55 (m, 2 H), 7.81-7.90 (m, 3 H), 7.98, 7.00 (s, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 15.6 (q), 17.3, 17.5 (q), 20.5, 20.8 (q), 23.8, 24.2 (t), 26.8, 27.3 (t), 32.2 (q), 33.5 (t), 35.0 (t), 36.4 (t), 41.6 (t), 45.9, 46.2 (d), 61.3 (d), 71.3, 71.7 (d), 117.0, 117.1 (d), 126.0 (d), 126.4 (d), 126.6 (d), 127.1 (d), 127.2 (d), 127.5

(d), 127.6 (d), 128.2, 128.4 (d), 131.7 (s), 132.9 (s), 133.2 (s), 133.6 (s), 168.5 (s), 168.6 (s), 168.7 (s), 169.2 (s), 173.5 (s) ppm. HRMS (CI) calcd for: $C_{29}H_{38}N_3O_5^+$ $[M+H]^+$: 508.2806, found: 508.2824.

(9*S*,19*S*,14*E*)-6-benzyl-7,9,14,19-tetramethyl-1-oxa-4,7,10-triazacylononadec-14-en-2,5,8,11-tetraon (11f)

According to **GP 4** 165 mg (260 µmol) allylester **9f** in 5.2 mL dry THF was reacted with 30.0 mg (26.0 µmol) $Pd(PPh_3)_4$ and 27.0 µL (310 µmol) morpholin. According to **GP 5** the crude acid **10f** (150 mg, 258 µmol) was reacted with 53.4 mg (290 µmol) pentafluorophenol and 55.6 mg (290 µmol) EDC·HCl in 2.6 mL dry CH_2Cl_2. The corresponding active ester was converted in 2.6 mL dry CH_2Cl_2/TFA (4:1). After Boc deprotection the reaction mixture was diluted with 3.9 mL dry CH_2Cl_2 and added dropwise to 104 mL $CHCl_3$/sat. $NaHCO_3$ (7:1). Column chromatography (silica gel, petroleum ether/ethyl acetate 3:7) gave rise to two fractions of macrocycle **11f** as colorless oils. Diastereomer 1: 33.4 mg (70.8 µmol, 27 %). R_f = 0.27 (petroleum ether/ethyl acetate 3:7). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.41 (d, *J* = 6.8 Hz, 3 H), 1.22 (d, *J* = 6.3 Hz, 3 H), 1.37-1.54 (m, 4 H), 1.56 (s, 3 H), 1.90 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.25-2.58 (m, 4 H), 2.95 (s, 3 H), 3.07 (m, 1 H), 3.29 (m, 1 H), 3.83 (dd, *J* = 17.1 Hz, 5.0 Hz, 1 H), 4.23-4.44 (m, 2 H), 4.80-5.11 (m, 3 H), 5.94 (bs, 1 H), 7.12-7.32 (m, 5 H), 8.33 (t, *J* = 6.0 Hz, 1 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 16.2 (q), 16.4 (q), 19.6 (q), 24.2 (t), 25.8 (t), 29.1 (q), 33.5 (t), 34.0 (t), 34.1 (t), 34.2 (t), 41.8 (t), 44.4 (d), 62.5 (d), 71.1 (d), 125.5 (d), 128.6 (d), 128.9 (d), 129.3 (d), 132.3 (s), 137.8 (s), 169.2 (s), 169.4 (s), 173.0 (s), 73.2 (s) ppm. Diastereomer 2: 32.2 mg (68.2 µmol, 26 %). R_f = 0.17 (petroleum ether/ethyl acetate 3:7). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.8 Hz, 3 H), 1.24 (d, *J* = 6.3 Hz, 3 H), 1.26-1.54 (m, 4 H), 1.59 (s, 3 H), 1.96 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.25-2.47 (m, 4 H), 2.93 (s, 3 H), 3.04 (dd, *J* = 15.3, 10.5 Hz, 1 H), 3.34 (dd, *J* = 15.1, 6.3 Hz, 1 H), 3.82 (dd, *J* = 17.6, 4.5 Hz, 1 H), 4.18 (dd, *J* = 17.8, 7.0 Hz, 1 H), 4.74 (m, 1 H), 4.98 (m, 1 H), 5.09 (t, *J* = 6.8 Hz, 1 H), 5.50 (dd, *J* = 10.5, 6.2 Hz, 1 H), 6.57 (d, *J* = 6.5 Hz, 1 H), 6.67 (bs, 1 H), 7.16-7.30 (m, 5 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 16.6 (q), 17.9 (q), 20.0 (q), 25.2 (t), 27.4 (t), 30.6 (q), 33.0 (t), 33.5 (t), 34.0 (t), 35.5 (t), 41.7 (t), 45.8 (d), 56.7 (d), 72.2 (d), 124.8 (d), 126.7 (d), 128.5 (d), 128.7 (d), 132.0 (s), 136.6 (s), 168.4 (s), 170.1 (s), 171.7 (s), 174.6 (s) ppm. HRMS (CI) calcd for: $C_{26}H_{37}N_3O_5^+$ $[M+H]^+$: 472.2806, found: 472.2832.

(6*R*,9*S*,19*S*,14*E*)-6-(4-allyloxy-3-bromobenzyl)-7,9,14,19-tetramethyl-1-oxa-4,7,10-triazacylononadec-14-en-2,5,8,11-tetraon (11g)

According to **GP 4** 143 mg (160 µmol) allylester **9g** in 3.8 mL dry THF was reacted with 22.0 mg (19.0 µmol) $Pd(PPh_3)_4$ and 32.4 µL (374 µmol) morpholin. According to **GP 5** 130 mg (160 µmol) of the crude acid **10g**, 32.4 mg (176 µmol) pentafluorophenol and 33.7 mg (176 µmol) EDC·HCl were reacted in 1.6 mL dry CH_2Cl_2. The corresponding active ester was converted in 1.6 mL dry CH_2Cl_2/TFA (4:1). After Boc deprotection the reaction mixture was diluted with 2.4 mL dry CH_2Cl_2 and added dropwise to 64 mL $CHCl_3$/sat. $NaHCO_3$ (7:1). Column chromatography (silica gel, petroleum ether/ethyl acetate 3:7) gave rise to macrocycle **11g** (6.6 mg, 12.0 µmol, 9 %) as yellow oil. R_f = 0.30 (petroleum ether/ethyl acetate 3:7). $[\alpha]_D^{20}$= –21.3 (c=1.0, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.0 Hz, 3 H), 1.24-1.46 (m, 4 H), 1.27 (d, *J* = 7.0 Hz, 3 H), 1.57 (s, 3 H), 1.91 (td, *J* = 7.0, 7.0 Hz, 2 H), 2.26-2.46 (m, 4 H), 2.94 (s, 3 H), 2.98 (m, 1 H), 3.22 (dd, *J* = 14.8, 3.5 Hz, 1 H), 3.84 (dd, *J* = 17.3, 5.4 Hz, 1 H), 4.38 (dd, *J* = 17.4, 7.6 Hz, 1 H), 4.43 (qd, *J* = 6.6, 6.6 Hz, 1 H), 4.74 (m, 1 H), 4.81 (qt, *J* = 7.0, 7.0 Hz, 1 H), 5.02 (t, *J* = 6.7 Hz, 1 H), 6.15 (d, *J* = 5.1 Hz, 1 H), 6.92 (m, 1 H), 7.02 (dd, *J* = 8.2, 2.2 Hz, 1 H), 7.30 (d, *J* = 2.2 Hz, 1 H), 6.88 (m, 1 H) ppm.^{13}C-NMR (125 MHz, $CDCl_3$): δ = 16.1 (q), 18.3 (q), 19.7 (q), 24.2 (t), 25.9 (t), 29.2 (q), 32.8 (t), 33.6 (t), 34.2 (t), 35.4 (t), 41.8 (t), 44.5 (d), 62.4 (d), 71.1 (d), 72.9 (s), 110.4 (s), 125.5 (d), 129.5 (d), 129.7 (t), 130.5 (s), 132.8 (d), 133.8 (s), 152.2 (s), 169.1 (s), 169.2 (s), 173.3 (s), 173.4 (s). HRMS (CI) calcd for: $C_{26}H_{37}BrN_3O_6^+$ $[M+H]^+$: 566.1860, found: 566.1859.

(9*S*,19*S*,5*E*)-6-(4-allyloxy-3-chlorophenyl)-7,9,16,19-tetramethyl-1-oxa-4,7,10-triazacyclononadec-15-en-2,5,8,11-tetraon (14d)

According to **GP 5** 41.0 mg (63.0 µmol) acid **13d** was reacted with 12.8 mg (69.3 µmol) pentafluorophenol and 13.3 mg (69.3 µmol) EDC·HCl in 0.6 mL dry CH_2Cl_2. The corresponding active ester was dissolved in 630 µL dry CH_2Cl_2/TFA (4:1). After Boc deprotection the reaction mixture was diluted with 950 µL dry CH_2Cl_2 and added dropwise to 25.2 mL $CHCl_3$/sat. $NaHCO_3$ (7:1). Column chromatography (silica gel, petroleum ether/ethyl acetate 1:1, 4:6, 3:7) gave rise to macrocycle **14d** (24.6 mg, 44.9 µmol, 71 %, *dr* = 66:34) as colorless foam. Diastereomer 1: R_f = 0.23 (petroleum ether/ethyl acetate 3:7). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.27 (m, 3 H), 1.41 (d, *J* = 6.6 Hz, 3 H), 1.60 (s, 3 H), 1.60-1.88 (m, 4 H), 1.95-2.28 (m, 6 H), 2.82 (s, 3 H), 4.07 (m, 1 H), 4.63 (m, 2 H), 4.93 (td, *J* = 7.0, 7.0 Hz, 1 H), 4.97 (qt, *J* = 6.6, 6.6 Hz, 1 H), 5.10 (t, *J* = 6.3 Hz, 1 H), 5.33 (d, *J* = 10.75 Hz, 1 H), 5.47 (d, *J* = 17.4 Hz, 1 H), 5.65 (d, *J* = 7.6 Hz, 1 H), 6.06 (m, 1 H), 6.30 (s, 1 H), 6.89 (m, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 7.37 (d, *J* = 8.5 Hz, 1 H), 7.54 (m, 1 H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 16.1 (q), 17.6 (q), 19.6 (q), 25.6 (t), 26.2 (t), 31.2 (q), 32.9 (t), 34.6 (t), 35.2 (t), 41.1 (t), 46.0 (d), 58.1 (d), 69.7 (t), 71.4 (d), 113.4 (d), 118.1 (t), 123.2 (s), 125.4 (d), 126.4 (s), 128.8 (d), 131.3 (d), 132.4 (d), 134.4 (s), 154.0 (s), 168.9 (s), 170.0 (s), 173.1 (s), 173.4 (s) ppm. Diastereomer 2: R_f = 0.17 (petroleum ether/ethyl acetate 3:7) (selected signals): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 5.6 Hz, 3 H), 1.58 (s, 3 H), 6.91 (d, *J* = 8.2 Hz, 1 H), 7.36 (d, *J* = 8.5 Hz, 1 H), 7.53 (m, 1 H) ppm. HRMS (CI) calcd for: $C_{28}H_{39}ClN_3O_6^+$ $[M+H]^+$: 548.2522, found: 548.2550.

