

Synthesis and Characterization of Peptides

Melting points were determined with a Janako MP-J3 (Kyoto, Japan) apparatus and are uncorrected. Silica-gel column chromatography was carried out with Merck (Darmstadt, Germany) silica-gel 60 (70-230 mesh). Analytical ^1H NMR spectra were recorded on a Jeol JNM-EX 270 (Tokyo, Japan) or a Bruker model AM 400 (Karlsruhe, Germany) spectrometer. Peptide mass-number were determined by fast-atom bombardment mass spectrometry (FAB-MS) using a Jeol JMS-HX 100 spectrometer. Specific optical rotations were measured with a Horiba SEPA-200 polarimeter (Kyoto, Japan).

HCl·H-A₂pr(Z)-OMe (A₂pr, α,β -diaminopropionic acid; Z, benzyloxycarbonyl). To a solution of Boc-A₂pr(Z)-OH·DCHA (Boc, *tert*-butyloxycarbonyl; DCHA, dicyclohexyl ammonium salt) (25.0 g, 48.1 mmol) in ethyl acetate (AcOEt) (150 mL) an excess of citric acid was added. The organic layer was quickly washed with 10% aqueous citric acid (30 mL x 3), and water (30 mL x 3), dried over MgSO₄, and concentrated *in vacuo* to give an oily residue. To a solution of this residue in a methanol (MeOH) / N,N-dimethylformamide (DMF) (1:1) mixture (200 mL) CH₃I (89.8 mL, 1.44 mol) and KHCO₃ (72.1 g, 0.721 mol) were added at room temperature. After stirring for 2 h at room temperature, the insoluble KHCO₃ was filtered off, and the filtrate was concentrated *in vacuo*. The residue was dissolved in AcOEt (30 mL) and the solution was washed with 10% aqueous citric acid (75 mL x 5), saturated aqueous NaHCO₃ (75 mL x 3), and brine (75 mL x 5). The organic layer was dried over anhydrous MgSO₄ and then concentrated *in vacuo*. To a solution of the oily residue in AcOEt (10 mL) a 4 M HCl/AcOEt solution (10 mL) was added at room temperature. After stirring for 1 h the reaction mixture was concentrated *in vacuo*. The residue was triturated with diethyl ether. The ester hydrochloride was used for the subsequent reaction without further purification. Yield 12.7 g (91 %).

pBrBz-A₂pr(Z)-OMe (pBrBz, *para*-bromobenzoyl). To a solution of HCl·H-A₂pr(Z)-OMe (1.20 g, 4.15 mmol) in DMF (5 mL) pBrBz-Cl (0.913 g, 4.15 mmol) and triethylamine (TEA) (1.27 mL, 9.13 mmol) were added in ten equal and alternate portions over 100 min at 0 °C. The mixture was stirred for 2 h at 0 °C, and then overnight at room temperature. The precipitated TEA·HCl was filtered off and the filtrate was concentrated *in vacuo*. The residue was triturated with water and the

resulting crystalline product was collected by filtration, followed by recrystallization from AcOEt-diethyl ether-*n*-hexane. Yield 1.66 g (92 %); mp 113-116 °C; $[\alpha]_D^{24} +13.9^\circ$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃), δ 3.69-3.76 (2H, m, β -CH₂/A₂pr), 3.78 (3H, s, CH₃/OMe), 4.74-4.82 (1H, m, α -CH/A₂pr), 5.05-5.16 (1H, m, α -NH/A₂pr), 5.11 (2H, s, CH₂/Z), 5.19-5.27 (1H, m, β -NH/A₂pr), 7.32 (5H, m, Ph/Z), 7.54-7.71 (4H, m, Ph/BrBz); FAB-MS: m/z 435 (M + H)⁺ (calcd. for C₁₉H₁₉N₂O₅Br + H = 435.1), 437 (M + 2 + H)⁺ as an isotope peak.

***p*BrBz- Δ Ala-OMe.** To a solution of *p*BrBz-A₂pr(Z)-OMe (0.750 g, 1.72 mmol) in acetic acid (AcOH) (2 mL) 25% HBr/AcOH (5 mL) was added at room temperature. After stirring for 2 h the reaction mixture was concentrated *in vacuo*. The residue was crystallized by trituration with diethyl ether and the *p*BrBz-A₂pr-OMe was used for the subsequent reaction without further purification. To a solution of the above mentioned hydrobromide (0.640 g, 1.67 mmol) in a MeOH/DMF (1:3) mixture (64 mL) CH₃I (4 mL, 64.2 mmol) and KHCO₃ (3.21 g, 32.1 mmol) were added. After stirring for 6 h at room temperature, AcOEt (200 mL) was added to the reaction mixture. The precipitated insoluble material was filtered off and the filtrate was concentrated *in vacuo*. AcOEt (100 mL) and water (20 mL) were added to the residue. The AcOEt layer was washed with water (20 mL x 3), 10% aqueous citric acid (20 mL x 3), saturated aqueous NaHCO₃ (20 mL x 3), and brine (20 mL x 3). The organic layer was dried over anhydrous MgSO₄ and concentrated *in vacuo* below 25 °C. The residue was crystallized by trituration with *n*-hexane. The crystalline product was collected by filtration and recrystallized from AcOEt/*n*-hexane. Yield 0.352 g (82 %); mp 94-96 °C. ¹H NMR (CDCl₃), δ 3.91 (3H, s, CH₃/OMe), 6.03 (1H, d, β -CH₂/ Δ Ala), 6.77 (1H, s, β -CH₂/ Δ Ala); 7.59-7.77 (4H, m, Ph/BrBz); 8.45 (1H, br.s, NH/ Δ Ala); FAB-MS: m/z 284 (M + H)⁺ (calcd. for C₁₁H₁₀NO₃Br + H = 284.2), 286 (M + 2 + H)⁺ as an isotope peak.

Boc-[A₂pr(Z)]₂-OMe. To a stirred solution of Boc-A₂pr(Z)-OSu (OSu, N-hydroxysuccinimido)¹⁴ (1.50 g, 3.44 mmol) and HCl·H-A₂pr(Z)-OMe (0.994 g, 3.27 mmol) in DMF (15 mL) TEA (30.3 mL, 2.19 mmol) was added at 0 °C. After stirring for 1 h at 0 °C and overnight at room temperature, the precipitated TEA·HCl was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in CHCl₃ (10 mL) and washed with 10% aqueous citric acid (5 mL x 3), brine (5 mL x 3), saturated aqueous NaHCO₃ (5 mL x 3), and brine (5 mL x 3). The organic layer was dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The residue was crystallized by trituration with *n*-hexane. The crystalline product was collected by filtration and recrystallized from AcOEt-*n*-hexane. Yield 1.55 g (79 %); mp 119-122 °C; $[\alpha]_D^{25} -0.6^\circ$ (c 1.0, CHCl₃). ¹H NMR

[DMSO (dimethylsulfoxide)-d₆], δ 1.43 (9H, s, CH₃/Boc), 3.46-3.66 (4H, m, β -CH₂ A₂pr x 2), 3.74 (3H, s, CH₃/OMe), 4.19-4.58 (2H, 2m, α -CH A₂pr x 2), 4.91-5.16 (4H, m, CH₂/Z x 2), 5.29-5.36 (2H, br.m, β -NH/A₂pr x 2), 5.66-5.77 (2H, br.m, α -NH/A₂pr x 2), 7.23-7.35 (10H, m, Ph/Z x 2). FAB-MS: m/z 573 (M + H)⁺ (calcd. for C₂₈H₃₆N₄O₉ + H = 573.3).

HCl·H-[A₂pr(Z)]₂-OMe. To a solution of Boc-[A₂pr(Z)]₂-OMe (1.53 g, 2.67 mmol) in AcOEt (25 mL) 4 M HCl/AcOEt (20 mL) was added at room temperature. After stirring for 1 h the mixture was concentrated *in vacuo* and the residue was crystallized by trituration with diethyl ether. The resulting ester hydrochloride was used for the subsequent reaction without further purification. Yield 1.32 g (97 %).

Boc-[A₂pr(Z)]₃-OMe. To a solution of Boc-A₂pr(Z)-OSu (8.28 g, 19.0 mmol) and HCl·H-[A₂pr(Z)]₂-OMe (9.71 g, 19.0 mmol) in DMF (100 mL) TEA (30.3 mL, 2.19 mmol) was added at 0 °C. After stirring for 1 h at 0 °C and overnight at room temperature, the precipitated TEA·HCl was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in CHCl₃ (200 mL) and worked up as described above for Boc-[A₂pr(Z)]₂-OMe. The crude product was recrystallized from CHCl₃-*n*-hexane. Yield 12.7 g (84 %); mp 153-155 °C; $[\alpha]_D^{25}$ -18.0° (c 1.0, CHCl₃). ¹H NMR (CDCl₃), δ 1.45 (9H, s, CH₃/Boc), 3.38-3.66 (6H, m, β -CH₂ A₂pr x 3), 3.71 (3H, s, CH₃/OMe), 4.13, 4.46, 4.55 (3H, 3m, α -CH A₂pr x 3), 4.90-5.14 (6H, m, CH₂/Z x 3), 5.64-5.76 (3H, br.m, β -NH/A₂pr x 3), 5.96 (3H, br.m, α -NH/A₂pr x 3), 7.22-7.34 (15H, m, Ph/Z x 3). FAB-MS: m/z 793 (M + H)⁺ (calcd. for C₃₉H₄₈N₆O₁₂ + H = 793.3).

HCl·H-[A₂pr(Z)]₃-OMe. To a solution of Boc-[A₂pr(Z)]₃-OMe (12.4 g, 15.6 mmol) in AcOEt (50 mL) 4 M HCl/AcOEt (30 mL) was added at room temperature. The mixture was worked up as described above for HCl·H-[A₂pr(Z)]₂-OMe and the ester hydrochloride was used for the subsequent reaction without further purification. Yield 10.9 g (96 %).

Boc-[A₂pr(Z)]₄-OMe. To a solution of HCl·H-[A₂pr(Z)]₃-OMe (10.5 g, 14.4 mmol) and Boc-A₂pr(Z)-OSu (6.27 g, 14.4 mmol) in DMF (80 mL) TEA (2.00 mL, 14.4 mmol) was added under stirring at 0 °C. After stirring for 1 h at 0 °C and overnight at room temperature the precipitated TEA·HCl was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in CHCl₃ (200 mL) and worked up as described above for Boc-[A₂pr(Z)]₂-OMe. The crude product was recrystallized from CHCl₃-*n*-hexane. Yield 12.6 g (86 %); mp 193-196 °C; $[\alpha]_D^{23}$ -23.1° (c 1.0,

DMF). ^1H NMR (DMSO- d_6), δ 1.36 (9H, s, CH_3/Boc), 3.20-3.53 (8H, m, $\beta\text{-CH}_2$ $\text{A}_2\text{pr} \times 4$), 3.56 (3H, s, CH_3/OMe), 4.04-4.44 (4H, m, $\alpha\text{-CH}$ $\text{A}_2\text{pr} \times 4$), 4.95-5.07 (8H, m, $\text{CH}_2/\text{Z} \times 4$), 6.58-7.12 (4H, br.m, $\beta\text{-NH}/\text{A}_2\text{pr} \times 4$), 7.22-7.37 (4H, br.m, $\alpha\text{-NH}/\text{A}_2\text{pr} \times 4$), 7.87-8.10 (20H, m, $\text{Ph}/\text{Z} \times 4$). FAB-MS: m/z 1013 ($\text{M} + \text{H}$) $^+$ (calcd. for $\text{C}_{50}\text{H}_{60}\text{N}_8\text{O}_{15} + \text{H} = 1013.4$).

HCl·H-[A₂pr(Z)]₄-OMe. To a solution of Boc-[A₂pr(Z)]₄-OMe (12.3 g, 12.2 mmol) in AcOEt (50 mL) 4 M HCl/AcOEt (30 mL) was added at room temperature. The mixture was worked up as described above for HCl·H-[A₂pr(Z)]₂-OMe and the ester hydrochloride was used for the subsequent reaction without further purification. Yield 11.2 g (97 %).

Boc-[A₂pr(Z)]₅-OMe. To a solution of HCl·H-[A₂pr(Z)]₄-OMe (7.38 g, 7.77 mmol) and Boc-A₂pr(Z)-OSu (4.06 g, 9.32 mmol) in DMF (60 mL) TEA (2.00 mL, 14.4 mmol) was added under stirring at 0 °C. After stirring for 2 h at 0 °C and overnight at room temperature the precipitated TEA·HCl was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in CHCl_3 (200 mL) and worked up as described above for Boc-[A₂pr(Z)]₂-OMe. The crystalline residue was recrystallized from DMF-water. Yield 9.44 g (99 %); mp 218-220 °C (decomp.); $[\alpha]_{\text{D}}^{23}$ -25.8° (c 1.0, DMF). ^1H NMR (DMSO- d_6), δ 1.35 (9H, s, CH_3/Boc), 3.18-3.52 (10H, m, $\beta\text{-CH}_2$ $\text{A}_2\text{pr} \times 5$), 3.55 (3H, s, CH_3/OMe), 3.96-4.14 (5H, m, $\alpha\text{-CH}$ $\text{A}_2\text{pr} \times 5$), 4.31-4.45 (10H, m, $\text{CH}_2/\text{Z} \times 5$), 6.56-7.12 (5H, br.m, $\beta\text{-NH}/\text{A}_2\text{pr} \times 5$), 7.22-7.34 (5H, br.m, $\alpha\text{-NH}/\text{A}_2\text{pr} \times 5$), 7.87-8.11 (25H, m, $\text{Ph}/\text{Z} \times 5$). FAB-MS: m/z 1234 ($\text{M} + \text{H}$) $^+$ (calcd. for $\text{C}_{61}\text{H}_{72}\text{N}_{10}\text{O}_{18} + \text{H} = 1233.5$).

HCl·H-[A₂pr(Z)]₅-OMe. To a solution of Boc-[A₂pr(Z)]₅-OMe (9.05 g, 7.34 mmol) in AcOEt (10 mL) 4 M HCl/AcOEt (20 mL) was added at room temperature. The mixture was worked up as described above for HCl·H-[A₂pr(Z)]₂-OMe and the ester hydrochloride was used for the subsequent reaction without further purification. Yield 8.30 g (97 %).

Boc-[A₂pr(Z)]₆-OMe. To a solution of HCl·H-[A₂pr(Z)]₅-OMe (10.5 g, 14.4 mmol) and Boc-A₂pr(Z)-OSu (4.02 g, 3.44 mmol) in DMF (40 mL) TEA (2.00 mL, 14.4 mmol) was added under stirring at 0 °C. After stirring for 1 h at 0 °C and overnight at room temperature the precipitated TEA·HCl was filtered off and the filtrate was concentrated *in vacuo*. The residue was recrystallized with water to give Boc-[A₂pr(Z)]₆-OMe and then washed with diethyl ether. The crystalline residue was recrystallized from DMF-water. Yield 4.93 g (99 %); mp 119-122 °C; $[\alpha]_{\text{D}}^{25}$ -0.6° (c 1.0, DMF). ^1H NMR (DMSO- d_6), δ 1.35 (9H, s, CH_3/Boc), 3.18-3.51 (12H, m, $\beta\text{-CH}_2$ $\text{A}_2\text{pr} \times 6$), 3.55

(3H, s, CH₃/OMe), 3.99-4.44 (6H, m, α -CH A₂pr x 6), 4.94-5.06 (12H, m, CH₂/Z x 6), 6.54-7.14 (6H, br.m, β -NH/A₂pr x 6), 7.21-7.37 (6H, br.m, α -NH/A₂pr x 6), 7.23-7.35 (30H, m, Ph/Z x 6). FAB-MS: m/z 1454 (M + H)⁺ (calcd. for C₇₂H₈₄N₁₂O₂₁ + H = 1453.6).

HCl·H-[A₂pr(Z)]₆-OMe. To a solution of Boc-[A₂pr(Z)]₅-OMe (4.60 g, 3.16 mmol) in AcOEt (5 mL) 4 M HCl/AcOEt (20 mL) was added at room temperature. The mixture was worked up as described above for HCl·H-[A₂pr(Z)]₂-OMe and the ester hydrochloride was used for the subsequent reaction without further purification. Yield 4.08 g (93 %).

pBrBz-[A₂pr(Z)]₂-OMe. HCl·H-[A₂pr(Z)]₂-OMe (1.31 g, 2.57 mmol) dissolved in DMF (7 mL) was reacted with pBrBz-Cl (0.565 g, 2.57 mmol) in the presence of TEA (0.784 mL, 5.65 mmol) and worked up as described above for pBrBz-A₂pr(Z)-OMe. The crude product was recrystallized from DMF-water. Yield 1.37 g (81 %); mp 212-214 °C; [α]_D²⁵ -24.3° (c 1.0, DMF). ¹H NMR (DMSO-d₆), δ 3.27-3.56 (4H, m, β -CH₂/A₂pr x 2), 3.59 (3H, s, CH₃/OMe), 4.36-4.66 (2H, m, α -CH/A₂pr x 2), 4.97 and 5.01 (4H, 2s, CH₂/Z x 2), 7.11 (2H, br.m, β -NH/A₂pr x 2), 7.25-7.35 (10H, m, Ph/Z x 2), 7.61-7.83 (4H, m, Ph/BrBz), 8.19 and 8.34 (2H, 2d, α -NH/A₂pr x 2). FAB-MS: m/z 655 (M + H)⁺ (calcd. for C₃₀H₃₁N₄O₈Br + H = 655.1), 657 (M + 2 + H)⁺ as an isotope peak.

pBrBz-[A₂pr(Z)]₃-OMe. A suspension of HCl·H-[A₂pr(Z)]₃-OMe (0.250 g, 0.342 mmol) in DMF (40 mL) was reacted with pBrBz-Cl (75.2 mg, 0.342 mmol) and TEA (0.104 mL, 0.752 mmol). The reaction mixture was worked up as described above for pBrBz-A₂pr(Z)-OMe. The crude product was recrystallized from DMF-water. Yield 0.280 g (93 %); mp 212-214 °C; [α]_D²⁵ -24.3° (c 1.0, DMF). ¹H NMR (DMSO-d₆), δ 3.25-3.54 (6H, m, β -CH₂/A₂pr x 3), 3.57 (3H, s, CH₃/OMe), 4.36-4.56 (3H, m, α -CH/A₂pr x 3), 4.97-5.02 (6H, m, CH₂/Z x 3), 6.87, 7.09 and 7.18 (3H, 3 br.m, β -NH/A₂pr x 3), 7.27-7.38 (15H, m, Ph/Z x 3), 7.60-7.82 (4H, m, Ph/BrBz), 8.42 (3H, m, α -NH/A₂pr x 3). FAB-MS: m/z 875 (M + H)⁺ (calcd. for C₄₁H₄₃N₆O₁₁Br + H = 875.1), 877 (M + 2 + H)⁺ as an isotope peak.

pBrBz-[A₂pr(Z)]₄-OMe. A suspension of HCl·H-[A₂pr(Z)]₄-OMe (3.50 g, 3.68 mmol) in DMF (40 mL) was reacted with pBrBz-Cl (0.892 g, 4.05 mmol) and TEA (1.12 mL, 8.11 mmol). The reaction mixture was worked up as described above for pBrBz-A₂pr(Z)-OMe. The crude product was recrystallized from DMF-water. Yield 3.62 g (88 %); mp 234-242 °C (decomp.); [α]_D²³ -38.2° (c 1.0, DMF). ¹H NMR (DMSO-d₆), δ 3.18-3.53 (8H, m, β -CH₂/A₂pr x 4), 3.57 (3H, s, CH₃/OMe), 4.28-4.60 (4H, m, α -CH/A₂pr x 4), 4.93-5.14 (8H, m, CH₂/Z x 4), 6.70-7.24 (4H, br.m, β -NH/A₂pr

x 4), 7.25-7.35 (20H, m, Ph/Z x 4), 7.60-7.82 (4H, m, Ph/BrBz), 7.92-8.44 (4H, 4d, α -NH/A₂pr x 4). FAB-MS: m/z 1095 (M + H)⁺ (calcd. for C₅₂H₅₅N₈O₁₄Br + H = 1095.2), 1097 (M + 2 + H)⁺ as an isotope peak.

***p*BrBz-[A₂pr(Z)]₅-OMe.** A suspension of HCl·H-[A₂pr(Z)]₅-OMe (3.50 g, 2.99 mmol) in DMF (40 mL) was reacted with *p*BrBz-Cl (0.724 g, 3.29 mmol) and TEA (0.913 mL, 6.58 mmol). The reaction mixture was worked up as described above for *p*BrBz-A₂pr(Z)-OMe. The crude product was recrystallized from DMF-water. Yield 3.83 g (97 %); mp 250-259 °C (decomp.); $[\alpha]_D^{21}$ -38.1° (c 1.0, DMF). ¹H NMR (DMSO-d₆), δ 3.24-3.53 (10H, m, β -CH₂/A₂pr x 5), 3.56 (3H, s, CH₃/OMe), 4.30-4.59 (5H, m, α -CH/A₂pr x 5), 4.93-5.00 (10H, m, CH₂/Z x 5), 6.77-7.20 (5H, br.m, β -NH/A₂pr x 5), 7.23-7.35 (25H, m, Ph/Z x 5), 7.57-7.81 (4H, m, Ph/BrBz), 7.92-8.43 (5H, 5d, α -NH/A₂pr x 5). FAB-MS: m/z 1315 (M + H)⁺ (calcd. for C₆₃H₆₇N₁₀O₁₇Br + H = 1315.3), 1317 (M + 2 + H)⁺ as an isotope peak.

***p*BrBz-[A₂pr(Z)]₆-OMe.** A suspension of HCl·H-[A₂pr(Z)]₆-OMe (3.80 g, 2.63 mmol) in DMF (40 mL) was reacted with *p*BrBz-Cl (0.662 g, 3.01 mmol) and TEA (0.834 mL, 6.01 mmol). The reaction mixture was worked up as described above for *p*BrBz-A₂pr(Z)-OMe. The crude product was recrystallized from DMF-water. Yield 3.79 g (90 %); mp 212-214 °C (decomp.); $[\alpha]_D^{25}$ -24.3° (c 1.0, DMF). ¹H NMR (DMSO-d₆), δ 3.25-3.53 (12H, m, β -CH₂/A₂pr x 6), 3.55 (3H, s, CH₃/OMe), 4.30-4.60 (6H, m, α -CH/A₂pr x 6), 4.91-5.03 (12H, m, CH₂/Z x 6), 6.73-7.19 (6H, br.m, β -NH/A₂pr x 6), 7.21-7.37 (30H, m, Ph/Z x 6), 7.57-7.81 (4H, m, Ph/BrBz), 7.94-8.43 (6H, 6d, α -NH/A₂pr x 6). FAB-MS: m/z 1535 (M + H)⁺ (calcd. for C₇₄H₇₉N₁₂O₂₀Br + H = 1535.4), 1537 (M + 2 + H)⁺ as an isotope peak.

***p*BrBz-(Δ Ala)₂-OMe.** To a solution of *p*BrBz-[A₂pr(Z)]₂-OMe (1.26 g, 1.92 mmol) in AcOH (5 mL) 25% HBr/AcOH (10 mL) was added at room temperature and the mixture was worked up as described above for *p*BrBz- Δ Ala-OMe to give the ester dihydrobromide which was used for the subsequent reaction without further purification. Yield 1.04 g (90 %). A part of the ester dihydrobromide (1.07 g, 1.95 mmol) was dissolved in a MeOH/DMF (1 : 3) mixture (20 mL) and then CH₃I (3.63 mL, 58.4 mmol) and KHCO₃ (2.92 g, 29.2 mmol) were added to the solution. The reaction mixture was stirred for 15 h at room temperature and then worked up as described above for *p*BrBz- Δ Ala-OMe. Yield 0.416 g (61 %); mp 119-122 °C. ¹H NMR (CDCl₃), δ 3.91 (3H, s, CH₃/OMe), 5.51 and 6.79 (2H, dd and d, β -CH₂/ Δ Ala¹), 6.03 and 6.65 (2H, m and s, β -CH₂/ Δ Ala²),

7.59-7.77 (4H, m, Ph/BrBz), 8.59 (1H, br.s, NH/ Δ Ala²), 8.86 (1H, br.s, NH/ Δ Ala¹). FAB-MS: m/z 353 ($M + H$)⁺ (calcd. for C₁₄H₁₃N₂O₄Br + H = 353.2), 355 ($M + 2 + H$)⁺ as an isotope peak.

***p*BrBz-(Δ Ala)₃-OMe.** To a solution of *p*BrBz-[A₂pr(Z)]₃-OMe (1.04 g, 1.19 mmol) in AcOH (3 mL) 25% HBr/AcOH (5 mL) was added at room temperature and the mixture was worked up as described above for *p*BrBz- Δ Ala-OMe to give the ester trihydrobromide. Yield 0.820 g (96 %). To a solution of the ester trihydrobromide in a MeOH/DMF (1 : 3) mixture (80 mL) CH₃I (4.26 mL, 68.6 mmol) and KHCO₃ (3.44 g, 34.4 mmol) were added. The reaction mixture was stirred for 57 h at room temperature and then worked up as described above for *p*BrBz- Δ Ala-OMe. Recrystallization of the crude product was carried out from CHCl₃-*n*-hexane. Yield 310 mg (59 %); mp >270 °C (decomp.). ¹H NMR (CDCl₃), δ 3.91 (3H, s, CH₃/OMe), 5.51 and 6.65 (2H, dd and d, β -CH₂/ Δ Ala²), 5.55 and 6.80 (2H, dd and d, β -CH₂/ Δ Ala¹), 6.04 and 6.65 (2H, m and s, β -CH₂/ Δ Ala³), 7.61-7.76 (4H, m, Ph/BrBz), 8.56 (1H, br.s, NH/ Δ Ala³), 8.86 (1H, br.s, NH/ Δ Ala¹), 8.96 (1H, br.s, NH/ Δ Ala²). FAB-MS: m/z 422 ($M + H$)⁺ (calcd. for C₁₇H₁₆N₃O₅Br + H = 422.2), 424 ($M + 2 + H$)⁺ as an isotope peak.

***p*BrBz-(Δ Ala)₄-OMe.** To a solution of *p*BrBz-[A₂pr(Z)]₄-OMe (3.30 g, 3.01 mmol) in AcOH (3 mL) 25% HBr/AcOH (18 mL) was added at room temperature and the mixture was worked up as described above for *p*BrBz- Δ Ala-OMe to give the ester tetrahydrobromide. Yield 2.46 g (93 %). To a solution of a part of the ester tetrahydrobromide (0.900 g, 1.02 mmol) in a MeOH/DMF (1 : 3) mixture (90 mL) CH₃I (3.80 mL, 61.1 mmol) and KHCO₃ (3.05 g, 30.5 mmol) were added. The reaction mixture was stirred for 39 h at room temperature and then worked up as described above for *p*BrBz- Δ Ala-OMe. Recrystallization of the crude product was carried out from CHCl₃-*n*-hexane. Yield 290 mg (58 %); mp >210 °C (decomp.). ¹H NMR (CDCl₃), δ 3.91 (3H, s, CH₃/OMe), 5.52, 5.56, 5.64 and 6.04 (4H, 4m, β -CH₂/ Δ Ala), 6.66 (3H, m, β -CH₂/ Δ Ala), 6.80 (1H, m, β -CH₂/ Δ Ala), 7.61-7.75 (4H, m, Ph/BrBz), 8.56, 8.86, 8.95 and 8.97 (4H, 4 br.s, NH/ Δ Ala). FAB-MS: m/z 491 ($M + H$)⁺ (calcd. for C₂₀H₁₉N₄O₆Br + H = 491.1), 493 ($M + 2 + H$)⁺ as an isotope peak.

***p*BrBz-(Δ Ala)₅-OMe.** To a solution of *p*BrBz-[A₂pr(Z)]₅-OMe (3.33 g, 2.53 mmol) in AcOH (3 mL) 25% HBr/AcOH (15 mL) was added at room temperature and the mixture was worked up as described above for *p*BrBz- Δ Ala-OMe to give the ester pentahydrobromide. Yield 2.39 g (90 %). To a solution of a part of the ester pentahydrobromide (1.20 g, 1.14 mmol) in a MeOH/DMF (1 : 3) mixture (120 mL) CH₃I (8.53 mL, 137 mmol) and KHCO₃ (6.85 g, 68.5 mmol) were added. The reaction mixture was stirred for 11 h at room temperature and then worked up as described above

for *p*BrBz- Δ Ala-OMe. Recrystallization of the crude product was carried out from CHCl₃-*n*-hexane. Yield 190 mg (30 %); mp >210 °C (decomp.). ¹H NMR (CDCl₃), δ 3.91 (3H, s, CH₃/OMe), 5.52-5.57 (4H, m, β -CH₂/ Δ Ala), 6.04 (1H, m, β -CH₂/ Δ Ala), 6.66 (4H, m, β -CH₂/ Δ Ala), 6.80 (1H, m, β -CH₂/ Δ Ala), 7.59-7.77 (4H, m, Ph/BrBz), 8.56, 8.86, 8.95, 8.95 and 8.97 (5H, 4 br.s, NH/ Δ Ala). FAB-MS: *m/z* 560 (M + H)⁺ (calcd. for C₂₃H₂₂N₅O₇Br + H = 560.1), 562 (M + 2 + H)⁺ as an isotope peak.

*p*BrBz-(Δ Ala)₆-OMe. To a solution of *p*BrBz-[A₂pr(Z)]₆-OMe (3.79 g, 2.47 mmol) in AcOH (3 mL) 25% HBr/AcOH (10 mL) was added at room temperature and the mixture was worked up as described above for *p*BrBz- Δ Ala-OMe to give the ester hexahydrobromide. Yield 2.87 g (95 %). To a solution of a part of the ester hexahydrobromide (1.20 g, 0.984 mmol) in a MeOH/DMF (1 : 3) mixture (120 mL) CH₃I (7.35 mL, 118 mmol) and KHCO₃ (8.86 g, 88.6 mmol) were added. The reaction mixture was stirred for 6 h at room temperature and then worked up as described above for *p*BrBz- Δ Ala-OMe. Recrystallization of the crude product was carried out from DMF-water. Yield 134 mg (22 %); mp >210 °C (decomp.). ¹H NMR (CDCl₃), δ 3.90 (3H, s, CH₃/OMe), 5.53-5.57 (5H, m, β -CH₂/ Δ Ala), 6.04 (1H, m, β -CH₂/ Δ Ala), 6.66 (5H, m, β -CH₂/ Δ Ala), 6.80 (1H, m, β -CH₂/ Δ Ala), 7.60-7.77 (4H, m, Ph/BrBz), 8.56 and 8.86 (2H, 2 br.s, NH/ Δ Ala), 8.96 (4H, m, NH/ Δ Ala). FAB-MS: *m/z* 629 (M + H)⁺ (calcd. for C₂₆H₂₅N₆O₈Br + H = 629.1), 631 (M + 2 + H)⁺ as an isotope peak.

Table 1. Crystal data and structure refinement for 1.

Identification code	mor97	
Empirical formula	C11 H10 Br N O3	
Formula weight	284.11	
Temperature	293(2) K	
Wavelength	0.71070 Å	
Crystal system	Triclinic	
Space group	P1-	
Unit cell dimensions	a = 8.899(1) Å	alpha = 96.2(1) deg.
	b = 13.709(2) Å	beta = 89.9(1) deg
	c = 4.895(1) Å	gamma = 107.2(1) deg
Volume	566.8(2) Å ³	
Z	2	
Density (calculated)	1.665 Mg/m ³	
Absorption coefficient	3.616 mm ⁻¹	
F(000)	284	
Crystal size	0.2 x 0.2 x 0.1 mm	
Theta range for data collection	2.40 to 28.01 deg.	
Index ranges	-11<=h<=11, -18<=k<=17, 0<=l<=6	
Reflections collected	2752	
Independent reflections	2749 [R(int) = 0.0164]	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2749 / 0 / 133	
Goodness-of-fit on F ²	0.940	
Final R indices [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.1383	
R indices (all data)	R1 = 0.1596, wR2 = 0.1838	
Largest diff. peak and hole	0.478 and -0.760 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br1	934(1)	6363(1)	393(2)	84(1)
C01	1608(4)	7754(2)	-120(8)	54(1)
C02	1004(4)	8448(2)	1458(7)	61(2)
C03	1528(4)	9486(2)	1112(7)	52(1)
C04	2656(4)	9831(2)	-812(7)	48(1)
C05	3261(4)	9138(3)	-2391(7)	60(2)
C06	2737(4)	8100(2)	-2045(7)	62(2)
C07	3264(7)	10935(4)	-1330(11)	51(1)
O0	3788(6)	11167(3)	-3555(8)	71(1)
N1	3191(5)	11630(3)	755(9)	52(1)
C1A	3636(6)	12693(4)	754(11)	48(1)
C1B	4649(7)	13235(5)	-908(12)	64(2)
C1	2800(7)	13185(4)	2906(12)	56(1)
O1	1763(5)	12707(3)	4209(9)	65(1)
OT	3337(5)	14215(3)	3148(8)	65(1)
CT	2595(8)	14748(5)	5206(15)	78(2)

Table 3. Bond lengths [Å] and angles [deg] for 1.

Br1-C01	1.867(3)
C01-C02	1.39
C01-C06	1.39
C02-C03	1.39
C03-C04	1.39
C04-C05	1.39
C04-C07	1.498(6)
C05-C06	1.39
C07-O0	1.220(6)
C07-N1	1.334(7)
N1-C1A	1.393(6)
C1A-C1B	1.326(8)
C1A-C1	1.503(8)
C1-O1	1.191(7)
C1-OT	1.342(6)
OT-CT	1.452(7)
C02-C01-C06	120.0
C02-C01-Br1	120.0(2)
C06-C01-Br1	120.0(2)
C03-C02-C01	120.0
C02-C03-C04	120.0
C05-C04-C03	120.0
C05-C04-C07	116.9(3)
C03-C04-C07	123.1(3)
C06-C05-C04	120.0
C05-C06-C01	120.0
O0-C07-N1	123.0(5)
O0-C07-C04	120.7(5)
N1-C07-C04	116.3(4)
C07-N1-C1A	127.0(4)
C1B-C1A-N1	126.2(5)
C1B-C1A-C1	122.3(5)
N1-C1A-C1	111.5(4)
O1-C1-OT	124.4(6)
O1-C1-C1A	123.2(5)
OT-C1-C1A	112.4(5)
C1-OT-CT	115.7(5)

Table 4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 1.
 The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Br1	84(1)	50(1)	114(1)	20(1)	7(1)	10(1)
C01	55(3)	50(3)	59(4)	6(3)	-2(3)	18(3)
C02	54(3)	63(4)	60(4)	12(3)	5(3)	7(3)
C03	47(3)	46(3)	63(4)	9(3)	9(3)	12(2)
C04	54(3)	42(3)	43(3)	2(2)	-9(2)	8(2)
C05	70(4)	57(3)	54(3)	3(3)	6(3)	23(3)
C06	67(4)	60(3)	64(4)	7(3)	9(3)	27(3)
C07	64(4)	54(3)	37(3)	12(3)	0(3)	20(3)
O0	114(4)	54(2)	45(2)	14(2)	13(2)	24(2)
N1	71(3)	45(2)	40(2)	9(2)	11(2)	12(2)
C1A	52(3)	45(3)	47(3)	8(2)	-3(2)	13(2)
C1B	78(4)	53(3)	66(4)	19(3)	12(3)	21(3)
C1	57(3)	48(3)	60(4)	15(3)	-5(3)	8(3)
O1	66(3)	52(2)	78(3)	10(2)	23(2)	18(2)
OT	68(3)	51(2)	72(3)	-1(2)	13(2)	15(2)
CT	79(5)	59(4)	95(5)	-4(4)	8(4)	24(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.

	x	y	z	U(eq)
H02	248(5)	8217(3)	2745(9)	73
H03	1123(6)	9950(3)	2168(10)	63
H05	4016(5)	9369(3)	-3678(9)	72
H06	3142(6)	7636(3)	-3101(10)	75
H1	2831(5)	11396(3)	2262(9)	63
H1B1	5136(7)	12904(5)	-2230(12)	77
H1B2	4872(7)	13946(5)	-752(12)	77
HT1	3063(8)	15476(5)	5236(15)	116
HT2	2741(8)	14545(5)	6980(15)	116
HT3	1490(8)	14574(5)	4764(15)	116

Table 6. Selected torsion angles [deg] for 1.

C06-C01-C02-C03	0.0
Br1-C01-C02-C03	178.8(3)
C01-C02-C03-C04	0.0
C02-C03-C04-C05	0.0
C02-C03-C04-C07	179.2(4)
C03-C04-C05-C06	0.0
C07-C04-C05-C06	-179.2(4)
C04-C05-C06-C01	0.0
C02-C01-C06-C05	0.0
Br1-C01-C06-C05	-178.8(3)
C05-C04-C07-O0	25.3(6)
C03-C04-C07-O0	-153.8(4)
C05-C04-C07-N1	-154.8(4)
C03-C04-C07-N1	26.0(6)
O0-C07-N1-C1A	1.9(9)
C04-C07-N1-C1A	-178.0(5)
C07-N1-C1A-C1B	-23.2(9)
C07-N1-C1A-C1	156.2(5)
C1B-C1A-C1-O1	171.4(6)
N1-C1A-C1-O1	-8.0(7)
C1B-C1A-C1-OT	-7.5(7)
N1-C1A-C1-OT	173.1(4)
O1-C1-OT-CT	1.6(8)
C1A-C1-OT-CT	-179.5(5)

Table 1. Crystal data and structure refinement for 1.

Identification code	mor96
Empirical formula	C14 H13 Br N2 O4
Formula weight	353.17
Temperature	293(2) K
Wavelength	0.71074 Å
Crystal system	Triclinic
Space group	P1-
Unit cell dimensions	a = 9.937(2) Å alpha = 102.3(1) deg b = 11.187(2) Å beta = 94.2(1) deg c = 6.743(1) Å gamma = 93.7(1) deg.
Volume	727.9(2) Å ³
Z	2
Density (calculated)	1.611 Mg/m ³
Absorption coefficient	2.840 mm ⁻¹
F(000)	356
Crystal size	0.4 x 0.4 x 0.2 mm
Theta range for data collection	2.06 to 28.01 deg.
Index ranges	-13<=h<=13, -14<=k<=14, -1<=l<=8
Reflections collected	3525
Independent reflections	3513 [R(int) = 0.0188]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3510 / 0 / 179
Goodness-of-fit on F ²	0.854
Final R indices [I>2sigma(I)]	R1 = 0.0668, wR2 = 0.1620
R indices (all data)	R1 = 0.2254, wR2 = 0.2386
Extinction coefficient	0.002(3)
Largest diff. peak and hole	0.673 and -0.698 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br1	4078(1)	5581(1)	3101(1)	84(1)
C01	2602(4)	5870(5)	1421(7)	61(2)
C02	1561(5)	6506(4)	2297(5)	63(2)
C03	499(4)	6790(4)	1065(6)	53(2)
C04	478(4)	6437(4)	-1043(6)	47(2)
C05	1519(5)	5801(4)	-1919(5)	60(2)
C06	2581(4)	5517(4)	-687(7)	67(2)
C07	-570(8)	6786(7)	-2453(13)	63(2)
O0	-409(6)	6755(6)	-4216(8)	81(2)
N1	-1726(6)	7169(5)	-1624(9)	58(2)
C1A	-2854(7)	7627(7)	-2547(11)	55(2)
C1B	-2946(8)	7804(8)	-4432(12)	73(2)
C1	-3884(7)	7918(7)	-1047(11)	54(2)
O1	-3578(5)	7937(5)	757(8)	73(2)
N2	-5079(6)	8192(5)	-1776(9)	58(2)
C2A	-6155(7)	8669(6)	-719(11)	52(2)
C2B	-6251(8)	8819(7)	1255(12)	64(2)
C2	-7192(8)	9028(7)	-2126(12)	59(2)
O2	-7054(6)	8917(6)	-3917(9)	85(2)
OT	-8244(5)	9455(5)	-1253(8)	68(2)
CT	-9257(8)	9855(9)	-2607(14)	83(3)

Table 3. Bond lengths [Å] and angles [deg] for 1.

Br1-C01	1.874(4)
C01-C02	1.39
C01-C06	1.39
C02-C03	1.39
C03-C04	1.39
C04-C05	1.39
C04-C07	1.485(9)
C05-C06	1.39
C07-O0	1.205(8)
C07-N1	1.367(9)
N1-C1A	1.419(9)
C1A-C1B	1.325(10)
C1A-C1	1.493(10)
C1-O1	1.227(8)
C1-N2	1.331(8)
N2-C2A	1.400(9)
C2A-C2B	1.317(10)
C2A-C2	1.481(10)
C2-O2	1.206(9)
C2-OT	1.305(9)
OT-CT	1.464(9)
C02-C01-C06	120.0
C02-C01-Br1	119.3(3)
C06-C01-Br1	120.6(3)
C01-C02-C03	120.0
C02-C03-C04	120.0
C05-C04-C03	120.0
C05-C04-C07	116.9(4)
C03-C04-C07	122.9(4)
C04-C05-C06	120.0
C05-C06-C01	120.0
O0-C07-N1	121.6(8)
O0-C07-C04	122.3(7)
N1-C07-C04	116.1(6)
C07-N1-C1A	128.9(6)
C1B-C1A-N1	124.6(7)
C1B-C1A-C1	125.7(7)
N1-C1A-C1	109.6(6)
O1-C1-N2	124.1(7)
O1-C1-C1A	119.4(6)
N2-C1-C1A	116.4(6)
C1-N2-C2A	129.3(6)
C2B-C2A-N2	126.1(7)
C2B-C2A-C2	123.3(7)
N2-C2A-C2	110.6(6)
O2-C2-OT	124.2(7)
O2-C2-C2A	121.7(7)
OT-C2-C2A	114.0(7)
C2-OT-CT	114.8(6)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.
 The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Br1	68(1)	105(1)	83(1)	30(1)	-2(1)	29(1)
C01	57(5)	62(5)	69(5)	16(4)	20(4)	22(4)
C02	63(5)	74(5)	57(5)	22(4)	16(4)	15(4)
C03	50(4)	63(5)	50(4)	11(4)	9(3)	28(4)
C04	51(4)	49(4)	40(4)	9(3)	10(3)	10(3)
C05	64(5)	79(5)	32(4)	-5(4)	5(3)	19(4)
C06	60(5)	82(6)	63(5)	16(4)	16(4)	28(4)
C07	68(5)	72(5)	54(5)	18(4)	16(4)	19(4)
O0	92(4)	114(5)	45(3)	23(3)	14(3)	35(4)
N1	54(4)	76(4)	52(4)	30(3)	1(3)	12(3)
C1A	57(4)	64(5)	47(4)	17(4)	0(3)	6(4)
C1B	67(5)	110(7)	56(5)	42(5)	7(4)	32(5)
C1	50(4)	66(5)	53(5)	25(4)	5(3)	22(4)
O1	71(4)	100(4)	56(3)	31(3)	2(3)	28(3)
N2	57(4)	79(4)	41(3)	16(3)	-1(3)	23(3)
C2A	55(4)	49(4)	50(4)	8(3)	4(3)	5(3)
C2B	64(5)	76(6)	57(5)	21(4)	8(4)	15(4)
C2	61(5)	69(5)	52(5)	24(4)	3(4)	4(4)
O2	82(4)	119(5)	55(4)	15(3)	0(3)	41(4)
OT	55(3)	82(4)	74(4)	27(3)	10(3)	26(3)
CT	64(5)	99(7)	99(7)	47(6)	2(5)	35(5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.

	x	y	z	U(eq)
H02	1575(7)	6742(7)	3707(5)	75
H03	-198(5)	7216(6)	1651(8)	64
H05	1505(7)	5565(6)	-3329(5)	72
H06	3278(5)	5091(6)	-1273(9)	80
H1	-1775(6)	7127(5)	-373(9)	70
H1B1	-2239(8)	7624(8)	-5248(12)	87
H1B2	-3717(8)	8107(8)	-4938(12)	87
H2	-5208(6)	8056(5)	-3082(9)	70
H2B1	-5561(8)	8600(7)	2080(12)	76
H2B2	-7008(8)	9145(7)	1823(12)	76
HT1	-9993(8)	10155(9)	-1850(14)	124
HT2	-9592(8)	9175(9)	-3694(14)	124
HT3	-8851(8)	10498(9)	-3165(14)	124

Table 6. Selected torsion angles [deg] for 1.

C06-C01-C02-C03	0.0
Br1-C01-C02-C03	176.3(4)
C01-C02-C03-C04	0.0
C02-C03-C04-C05	0.0
C02-C03-C04-C07	-175.5(6)
C03-C04-C05-C06	0.0
C07-C04-C05-C06	175.8(5)
C04-C05-C06-C01	0.0
C02-C01-C06-C05	0.0
Br1-C01-C06-C05	-176.2(4)
C05-C04-C07-O0	-14.8(10)
C03-C04-C07-O0	160.8(6)
C05-C04-C07-N1	166.5(5)
C03-C04-C07-N1	-17.9(9)
O0-C07-N1-C1A	-3.0(13)
C04-C07-N1-C1A	175.7(6)
C07-N1-C1A-C1B	-2.6(13)
C07-N1-C1A-C1	179.5(7)
C1B-C1A-C1-O1	-166.1(8)
N1-C1A-C1-O1	11.8(10)
C1B-C1A-C1-N2	11.4(12)
N1-C1A-C1-N2	-170.8(6)
O1-C1-N2-C2A	7.6(13)
C1A-C1-N2-C2A	-169.7(7)
C1-N2-C2A-C2B	-8.2(13)
C1-N2-C2A-C2	170.3(7)
C2B-C2A-C2-O2	177.4(8)
N2-C2A-C2-O2	-1.1(11)
C2B-C2A-C2-OT	-3.0(11)
N2-C2A-C2-OT	178.5(6)
O2-C2-OT-CT	-2.5(12)
C2A-C2-OT-CT	177.9(6)

Table 7 Intramolecular H-bond parameters for 1.

Donor	Acceptor	Distance	Distance	Angle
D-H	A	D...A	H...A	D-H...A
		()	()	($\frac{1}{2}$)
N1-H	O1	2.599(8)	2.174(8)	110.2(2)
N2-H	O2	2.624(8)	2.218(8)	108.8(2)

p-Br₂(ΔA₆)-OMe₃

Table 1. Crystal data and structure refinement for 1.

Identification code	mor98
Empirical formula	C17 H16 Br N3 O5
Formula weight	422.24
Temperature	293(2) K
Wavelength	0.71070 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 9.885(1) Å alpha = 90.0 deg. b = 6.779(1) Å beta = 98.3(1) deg. c = 26.339(2) Å gamma = 90.0 deg.
Volume	1746.5(3) Å ³
Z	4
Density (calculated)	1.606 Mg/m ³
Absorption coefficient	2.388 mm ⁻¹
F(000)	856
Crystal size	0.4 x 0.2 x 0.1 mm
Theta range for data collection	2.08 to 28.02 deg.
Index ranges	-13 ≤ h ≤ 12, 0 ≤ k ≤ 8, 0 ≤ l ≤ 34
Reflections collected	4316
Independent reflections	4207 [R(int) = 0.0291]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4207 / 0 / 223
Goodness-of-fit on F ²	0.869
Final R indices [I > 2σ(I)]	R1 = 0.0432, wR2 = 0.1069
R indices (all data)	R1 = 0.1214, wR2 = 0.1390
Largest diff. peak and hole	0.530 and -0.416 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Br1	4442(1)	7049(1)	4561(1)	70(1)
C01	4279(2)	8741(3)	3993(1)	54(1)
C02	3731(2)	8014(3)	3514(1)	52(1)
C03	3559(2)	9260(3)	3091(1)	50(1)
C04	3935(2)	11233(3)	3146(1)	47(1)
C05	4483(2)	11960(3)	3626(1)	55(1)
C06	4655(2)	10714(3)	4049(1)	59(1)
C07	3685(4)	12705(6)	2714(1)	51(1)
O0	3756(4)	14458(4)	2791(1)	88(1)
N1	3325(3)	11961(4)	2239(1)	56(1)
C1A	2857(3)	12939(5)	1784(1)	46(1)
C1B	2650(4)	14863(6)	1735(1)	56(1)
C1	2546(3)	11474(6)	1357(1)	50(1)
O1	2610(3)	9708(4)	1449(1)	66(1)
N2	2238(3)	12223(4)	879(1)	54(1)
C2A	1912(3)	11220(6)	417(1)	49(1)
C2B	1798(4)	9281(6)	363(1)	60(1)
C2	1684(4)	12700(6)	-17(1)	51(1)
O2	1738(3)	14453(4)	78(1)	71(1)
N3	1426(3)	11941(5)	-491(1)	58(1)
C3A	1034(3)	12955(6)	-957(1)	50(1)
C3B	891(4)	14882(6)	-1015(1)	62(1)
C3	758(4)	11516(6)	-1382(1)	52(1)
O3	865(3)	9766(5)	-1319(1)	74(1)
OT	382(3)	12347(4)	-1839(1)	64(1)
CT	76(5)	11007(7)	-2261(1)	79(1)

Table 3. Bond lengths [Å] and angles [deg] for 1.

Br1-C01	1.872(2)
C01-C02	1.39
C01-C06	1.39
C02-C03	1.39
C03-C04	1.39
C04-C05	1.39
C04-C07	1.508(4)
C05-C06	1.39
C07-O0	1.205(4)
C07-N1	1.349(4)
N1-C1A	1.388(4)
C1A-C1B	1.323(5)
C1A-C1	1.498(5)
C1-O1	1.221(4)
C1-N2	1.352(4)
N2-C2A	1.390(4)
C2A-C2B	1.325(5)
C2A-C2	1.512(5)
C2-O2	1.214(4)
C2-N3	1.341(4)
N3-C3A	1.412(4)
C3A-C3B	1.320(5)
C3A-C3	1.478(5)
C3-O3	1.201(4)
C3-OT	1.333(4)
OT-CT	1.433(5)

C02-C01-C06	120.0
C02-C01-Br1	119.01(12)
C06-C01-Br1	120.96(13)
C01-C02-C03	120.0
C04-C03-C02	120.0
C03-C04-C05	120.0
C03-C04-C07	123.0(2)
C05-C04-C07	116.8(2)
C06-C05-C04	120.0
C05-C06-C01	120.0
O0-C07-N1	121.8(3)
O0-C07-C04	121.7(3)
N1-C07-C04	116.5(3)
C07-N1-C1A	129.2(3)
C1B-C1A-N1	125.6(3)
C1B-C1A-C1	124.6(3)
N1-C1A-C1	109.7(3)
O1-C1-N2	123.4(3)
O1-C1-C1A	120.2(3)
N2-C1-C1A	116.4(3)
C1-N2-C2A	128.6(3)
C2B-C2A-N2	125.7(3)
C2B-C2A-C2	125.2(3)
N2-C2A-C2	109.1(3)
O2-C2-N3	124.4(3)
O2-C2-C2A	119.7(3)
N3-C2-C2A	115.9(3)
C2-N3-C3A	127.9(4)
C3B-C3A-N3	126.4(4)
C3B-C3A-C3	124.1(3)
N3-C3A-C3	109.5(3)

O3-C3-C3A	123.0(3)
OT-C3-C3A	113.7(3)
C3-OT-CT	115.7(3)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Br1	84(1)	76(1)	47(1)	12(1)	4(1)	3(1)
C01	51(2)	65(2)	45(2)	-2(2)	7(2)	5(2)
C02	62(2)	49(2)	45(2)	-1(2)	3(2)	-5(2)
C03	57(2)	47(2)	43(2)	-9(2)	-3(2)	-1(2)
C04	50(2)	48(2)	42(2)	-6(2)	3(1)	2(2)
C05	64(2)	53(2)	45(2)	-7(2)	3(2)	-5(2)
C06	65(2)	65(3)	43(2)	-9(2)	-3(2)	-3(2)
C07	58(2)	52(2)	41(2)	-3(2)	2(2)	-4(2)
O0	155(3)	46(2)	55(2)	-5(1)	-13(2)	-11(2)
N1	79(2)	43(2)	44(2)	3(1)	2(1)	7(2)
C1A	52(2)	44(2)	41(2)	-2(2)	6(1)	1(2)
C1B	69(2)	51(2)	48(2)	1(2)	5(2)	4(2)
C1	50(2)	51(2)	47(2)	2(2)	4(2)	5(2)
O1	100(2)	44(2)	50(1)	1(1)	-3(1)	7(2)
N2	78(2)	44(2)	39(1)	0(1)	2(1)	-2(2)
C2A	51(2)	49(2)	45(2)	1(2)	1(2)	-1(2)
C2B	75(3)	58(3)	46(2)	0(2)	2(2)	-3(2)
C2	55(2)	52(3)	46(2)	2(2)	3(2)	-4(2)
O2	113(2)	46(2)	50(2)	0(1)	-1(1)	-5(2)
N3	79(2)	49(2)	43(2)	1(1)	-1(1)	1(2)
C3A	50(2)	53(2)	45(2)	5(2)	3(1)	0(2)
C3B	76(3)	57(3)	51(2)	6(2)	0(2)	-4(2)
C3	58(2)	49(2)	48(2)	1(2)	5(2)	-2(2)
O3	101(2)	55(2)	61(2)	0(1)	-3(1)	5(2)
OT	84(2)	63(2)	43(1)	2(1)	1(1)	-5(1)
CT	106(3)	82(3)	45(2)	-10(2)	-4(2)	-12(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.

	x	y	z	U(eq)
H02	3479(4)	6695(3)	3477(1)	63
H03	3192(3)	8774(4)	2770(1)	60
H05	4734(4)	13280(3)	3663(1)	66
H06	5022(3)	11200(4)	4370(1)	70
H1	3395(3)	10701(4)	2214(1)	67
H1B1	2821(4)	15678(6)	2021(1)	68
H1B2	2334(4)	15399(6)	1415(1)	68
H2	2244(3)	13489(4)	857(1)	65
H2B1	1941(4)	8469(6)	651(1)	72
H2B2	1576(4)	8731(6)	39(1)	72
H3	1509(3)	10682(5)	-514(1)	69
H3B1	1054(4)	15708(6)	-731(1)	75
H3B2	627(4)	15413(6)	-1340(1)	75
HT1	-242(5)	11735(7)	-2567(1)	119
HT2	-620(5)	10101(7)	-2191(1)	119
HT3	886(5)	10288(7)	-2307(1)	119

Table 6. Selected torsion angles [deg] for 1.

C06-C01-C02-C03	0.0
Br1-C01-C02-C03	177.9(2)
C01-C02-C03-C04	0.0
C02-C03-C04-C05	0.0
C02-C03-C04-C07	-175.4(2)
C03-C04-C05-C06	0.0
C07-C04-C05-C06	175.7(2)
C04-C05-C06-C01	0.0
C02-C01-C06-C05	0.0
Br1-C01-C06-C05	-177.9(2)
C03-C04-C07-O0	164.5(3)
C05-C04-C07-O0	-11.0(5)
C03-C04-C07-N1	-12.9(4)
C05-C04-C07-N1	171.6(2)
O0-C07-N1-C1A	-7.1(6)
C04-C07-N1-C1A	170.3(3)
C07-N1-C1A-C1B	-1.3(6)
C07-N1-C1A-C1	-178.2(3)
C1B-C1A-C1-O1	-171.0(4)
N1-C1A-C1-O1	6.0(5)
C1B-C1A-C1-N2	10.8(5)
N1-C1A-C1-N2	-172.3(3)
O1-C1-N2-C2A	1.8(6)
C1A-C1-N2-C2A	179.9(3)
C1-N2-C2A-C2B	2.4(6)
C1-N2-C2A-C2	-178.5(3)
C2B-C2A-C2-O2	175.8(4)
N2-C2A-C2-O2	-3.4(5)
C2B-C2A-C2-N3	-4.1(5)
N2-C2A-C2-N3	176.8(3)
O2-C2-N3-C3A	-7.2(6)
C2A-C2-N3-C3A	172.6(3)
C2-N3-C3A-C3B	2.5(6)
C2-N3-C3A-C3	-175.8(3)
C3B-C3A-C3-O3	-178.3(4)
N3-C3A-C3-O3	0.0(5)
C3B-C3A-C3-OT	1.9(5)
N3-C3A-C3-OT	-179.9(3)
O3-C3-OT-CT	1.4(6)
C3A-C3-OT-CT	-178.8(3)
