

**General:** NMR experiments were conducted on a Bruker WM-300 (300 MHz for  $^1\text{H}$  and 75,4 MHz para  $^{13}\text{C}$ ), a Bruker DPX-250 (250 MHz for  $^1\text{H}$  and 62,8 MHz para  $^{13}\text{C}$ ) or a Bruker WM-500 (500 MHz for  $^1\text{H}$ ) spectrometer, in  $\text{CDCl}_3$  solutions unless otherwise stated. The following abbreviations are used: s (singlet), t (triplet), q (quartet) an m (multiplet). Infrared spectra were recorded on a MIDAC Prospect-IR spectrometer. Mass spectra were recorded using direc insertion probe on a Hewlett Packard 5988A in EI mode. High resolution mass spectra were recorded on a Kratos MS-50 spectrometer. Melting points were recorded on a Köfler-Thermogerate apparatus and are uncorrected.. Chemicals were purchased from Aldrich or Avocado. Dry solvents were distilled according to standard procedures prior to use. Column chromatography was performed on 60 Merck 230-400 mesh sílica (flash, 0,04-0,063).

**6-Nitro-3,5-di-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene- $\alpha$ -D-glucofuranose (1):** A solution of triphenylphosphine (0.31 g, 1.19 mmol) in dry dichloromethane (1 ml) was added to a solution of 6-azido-3,5-di-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene- $\alpha$ -D-glucofuranose (0.46 g, 1.08 mmol) in dry dichloromethane (1 ml) and the resulting mixture was stirred at room temperature for 16 h. The reaction was then diluted with dry dichloromethane (10 ml), added to a solution of dry dichloromethane saturated with ozone (90 ml) at  $-78^\circ\text{C}$  and stirred at this temperature for 10 min. Argon was then bubbled through the mixture until a colourless solution was obtained. The mixture was allowed to warm up to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography (ethyl acetate/hexane 2:11) to give 6-nitro-3,5-di-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene- $\alpha$ -D-glucofuranose (**1**) (0.22 g, 48% yield) as a yellow oil.  $[\alpha]_{\text{D}}^{20} -33^\circ$  (c, 6.0 in chloroform).  $^1\text{H}$ -NMR (250 MHz,  $\text{CDCl}_3$ ): 1.31, 1.47 (2 x s, 6 H, 2 x  $-\text{CH}_3$ ); 4.06 (d, 1 H,  $J = 3.1$  Hz); 4.21-4.25 (m, 1 H); 3.41-4.82 (m, 6 H); 5.89 (d, 1 H,  $J_{1,2} = 3.7$  Hz, H-1); 7.15-7.38 (m, 10 H, 10 x Ar-H).  $^{13}\text{C}$ -NMR (62.8 MHz,  $\text{CDCl}_3$ ): 26.71, 27.21, 72.22, 73.85, 74.19, 77.91, 79.87, 81.74, 81.89, 105.36, 112.58, 128.02, 128.17, 128.25, 128.41, 128.66, 128.87, 137.26, 137.69. IR (NaCl):  $\nu$  1554, 1376  $\text{cm}^{-1}$ . MS ( $m/z$ , %): 428  $[(\text{M} - \text{H})^+]$ , 0.6; 338; 180 (17); 105 (3); 91 (100). Anal calcd for  $\text{C}_{23}\text{H}_{27}\text{NO}_7$ : C, 64.32; H, 6.34; N, 3.26. Found C, 64.20; H, 6.33; N, 3.44.

**3,5-Di-*O*-benzyl-6-deoxy-6-nitro-D-glucofuranose (2):** 6-Nitro-3,5-di-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene- $\alpha$ -D-glucofuranose (**1**) (0.23 g, 0.54 mmol) was dissolved in a mixture of trifluoroacetic acid/water (1:1, 10 ml) and the reaction mixture was stirred at room temperature until the starting material had been consumed (tlc, ethyl acetate/hexane 1:5) (17 h). The solvent was evaporated *in vacuo* and the residue was coevaporated with toluene (3 x 5 ml) to give 3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucofuranose (**2**) as a clear gum, which was used in the next step without further purification.

**3,5-Di-*O*-benzyl-6-deoxy-6-nitro-D-glucono-1,4-lactone (3):** 3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucofuranose (**2**) (0.20 g, 0.51 mmol) was dissolved in dioxane/water (2:1, 9 ml). Barium carbonate (0.11 g, 0.56 mmol) and then bromine (0.07 ml, 1.18 mmol) were added and the reaction mixture was stirred for 4 h at room temperature with the exclusion of light. The reaction was quenched with saturated aqueous sodium thiosulphate solution (until the mixture was colourless) and the mixture was then extracted with ethyl acetate (3 x 25 ml). The combined ethyl acetate extracts were dried over anhydrous sodium sulphate and evaporated to dryness. The crude residue was purified by flash column chromatography (ethyl acetate/hexane 2:5) to give 3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucono-1,4-lactone (**3**) (0.12 g, 58% over the last two steps) as a clear, unstable gum. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 4.10-4.17 (m, 1 H); 4.38-4.87 (m, 10 H); 7.08-7.36 (m, 10 H, 10 x Ar-H). MS (*m/z*, %): 386 [(M - H)<sup>+</sup>, 2]; 296 (15); 180 (20); 165 (8); 107 (16); 91 (100); 65 (10). IR (NaCl): ν 3443, 1792, 1555, 1380 cm<sup>-1</sup>.

**2-*O*-Trifluoromethanesulphonyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucono-1,4-lactone (4):** 3,5-Di-*O*-benzyl-6-deoxy-6-nitro-D-glucono-1,4-lactone (**3**) (1.66 g, 4.29 mmol) was dissolved in dry dichloromethane (29 ml) and the solution was cooled to -30 °C under nitrogen. Pyridine (1.04 ml, 12.87 mmol) and trifluoromethanesulphonic anhydride (1.10 ml, 6.43 mmol) were added and the mixture was stirred for 1.5 h at -30 °C. The reaction was diluted with dichloromethane (250 ml), washed with dilute hydrochloric acid (125 ml) and brine (125 ml). The organic layer was dried (anhydrous sodium sulphate) and concentrated to dryness to give 2-*O*-trifluoromethanesulphonyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucono-1,4-lactone (**4**) as a clear gum, which was used in the next step without further purification.

**(5*S*,6*R*,7*R*)-6,7-Bis-benzyloxy-5-nitro-2-oxa-bicyclo[2.2.1]heptan-3-one (5):** A 1M solution of tetrabutylammonium fluoride in THF (4.4 ml) was added to a solution of the 2-*O*-trifluoromethanesulphonyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucono-1,4-lactone (**4**) previously obtained in THF (42 ml) and the resulting mixture was stirred under argon for 4 h. The solvent was evaporated and the residue dissolved in dichloromethane (250 ml). The solution was washed with water (3 x 125 ml) and the solvent was evaporated *in vacuo*. The resulting gum was purified by flash column chromatography (ethyl acetate/hexane 1:5) to give (5*S*,6*R*,7*R*)-6,7-bis-benzyloxy-5-nitro-2-oxa-bicyclo[2.2.1]heptan-3-one (**5**) (0.65 g, 41% yield over the last two steps) as a yellow oil. [ $\alpha$ ]<sub>D</sub><sup>21</sup> -35° (c, 0.85 in chloroform). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 4.03 (s, 1 H, H-1); 4.28-4.30, 4.51-4.54 (2 x m, 4 H, -OCH<sub>2</sub>Ph, H-6, H-7); 4.67 (dd, 1 H, *J*<sub>4,5</sub> = 2.3 Hz, *J*<sub>5,6</sub> = 4.0 Hz, H-5); 4.79 (d, 1 H, *J* = 11.9 Hz, -OCH<sub>2</sub>Ph); 4.81 (d, 1 H, *J* = 11.9 Hz, -OCH<sub>2</sub>Ph); 5.05 (d, 1 H, *J*<sub>4,5</sub> = 2.3 Hz, H-4); 7.17-7.40 (m, 10 H, 10 x Ar-H). <sup>13</sup>C-NMR (75.4 MHz, CDCl<sub>3</sub>): 50.29, 72.57, 72.66, 80.22, 81.42, 82.19, 84.78, 127.97, 128.21, 128.31, 128.63, 128.71, 128.79, 135.39, 136.60, 169.33. MS (*m/z*, %): 352 (M<sup>+</sup> - 17, 0.02); 314 (1); 187 (1); 181 (1); 91 (100); 65 (6). IR (NaCl): ν 1804, 1554, 1361 cm<sup>-1</sup>. HRMS: calcd for C<sub>20</sub>H<sub>18</sub>NO<sub>5</sub> (M<sup>+</sup> - 17), 352.1180; found 352.1184.

**(5*S*,6*R*,7*R*)-5-Amino-6,7-bis-benzyloxy-2-oxa-bicyclo[2.2.1]heptan-3-one (6):** (5*S*,6*R*,7*R*)-6,7-Bis-benzyloxy-5-nitro-2-oxa-bicyclo[2.2.1]heptan-3-one (**5**): (0.34 g, 0.91 mmol) was dissolved in methanol (30 ml) and the solution was deoxygenated by bubbling argon through. Raney-nickel (10% in water) (3.4 ml) was added and the suspension was stirred at room temperature under an atmosphere of hydrogen for 20 h. The reaction mixture was then filtered through Celite, eluted with methanol and the filtrate evaporated *in vacuo* to give (5*S*,6*R*,7*R*)-5-amino-6,7-bis-benzyloxy-2-oxa-bicyclo[2.2.1]heptan-3-one (**6**) as a clear gum, which was used in the next step without further purification.

**(5*S*,6*R*,7*R*)-(6,7-Bis-benzyloxy-3-oxo-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (7):** Ethyl chloroformate (0.87 ml, 0.91 mmol) was added to a cooled (-15 °C), stirred solution of Z-glycine (0.19 g, 0.91 mmol) and triethylamine (0.13 ml, 0.91 mmol) in a mixture of THF (7 ml) and CH<sub>3</sub>CN (7 ml) and the reaction mixture was stirred until a precipitate appeared. A solution of (5*S*,6*R*,7*R*)-5-amino-6,7-Bis-benzyloxy-2-oxa-bicyclo[2.2.1]heptan-3-one (**6**) and pyridine (0.13 ml) in DMF (7 ml) was slowly added and the mixture was stirred at -10 °C for 1 h, and then at room temperature for 4 h. The liquids were evaporated and the residue preabsorbed onto silica and purified by flash column chromatography (ethyl acetate/hexane 10:9→3:2) to give (5*S*,6*R*,7*R*)-(6,7-bis-benzyloxy-3-oxo-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (**7**) (0.25 g, 53% yield over the last two steps) as clear gum.  $[\alpha]_D^{23}$  -15° (c, 0.4 in chloroform). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 2.84 (bs, 1 H, H-7); 3.75-3.76 (m, 2 H, H-8, H-8'); 4.05 (bs, 1 H, H-1); 4.22 (bs, 1 H, H-6); 4.44-4.55 (m, 5 H, 3 x -OCH<sub>2</sub>Ph, H-4, H-5); 4.68 (d, 1 H, *J* = 12.0 Hz, -OCH<sub>2</sub>Ph); 5.09 (s, 2 H, -OCOCH<sub>2</sub>Ph); 5.36 (bs, 1 H, -NH); 6.63 (d, 1 H, *J*<sub>5,NH</sub> = 9.5 Hz); 7.21-7.36 (m, 15 H, 15 x Ar-H). <sup>13</sup>C-NMR (75.4 MHz, CDCl<sub>3</sub>): 44.73, 51.69, 52.59, 67.25, 71.87, 73.07, 80.28, 82.87, 84.93, 128.01, 128.18, 128.36, 128.60, 129.08, 135.79, 136.02, 136.96, 156.53, 167.51, 170.72. MS (*m/z*, %): 530 (M<sup>+</sup>, 0.12); 331 (4); 272 (6); 91 (100). IR (NaCl): ν 3406, 3326, 1679, 1723, 1799 cm<sup>-1</sup>.

**(1*S*,2*R*,3*S*,4*R*,5*S*)-(2,4-Bis-benzyloxy-5-hydrazinocarbonyl-3-hydroxy-cyclopentyl)-carbamic acid benzyl ester (8):** Hydrazine hydrate (0.23 ml, excess) was added to a solution of (5*S*,6*R*,7*R*)-(6,7-bis-benzyloxy-3-oxo-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (**7**) (0.1 g, 0.18 mmol) in methanol (5 ml) and the reaction mixture was stirred at room temperature for 24 h. The solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography (chloroform/methanol 12:1) to give (1*S*,2*R*,3*S*,4*R*,5*S*)-(2,4-bis-benzyloxy-5-hydrazinocarbonyl-3-hydroxy-cyclopentyl)-carbamic acid benzyl ester (**8**) as a white, unstable solid.

**(1*S*,2*R*,3*S*,4*R*,5*S*)-[(2,4-Bis-benzyloxy-5-benzyloxycarbonylamino-3-hydroxy-cyclopentanecarbonyl)-amino]-acetic acid methyl ester (10):** A solution of the (1*S*,2*R*,3*S*,4*R*,5*S*)-(2,4-bis-benzyloxy-5-hydrazinocarbonyl-3-hydroxy-cyclopentyl)-carbamic acid benzyl ester (**8**) previously obtained in dry DMF (3 ml) was cooled to -20 °C and 3.35 N solution of hydrochloric acid in dioxane (0.13 ml, 0.45 mmol) was added. The temperature of the reaction was increased to -15 °C and *tert*-butylnitrite (0.023 ml, 0.2 mmol) was added. The mixture was left at -10 °C for 10 min and a solution of glycine methyl ester hydrochloride (19 mg, 0.16 mmol) in dry DMF (12 ml) was added dropwise at -15 °C. Triethylamine (0.055 g, 0.55 mmol) was added and the reaction mixture was stirred at 0 °C for 24 h; during the first 6 h triethylamine (0.003 ml) was added every hour. The reaction mixture was poured into a mixture of ice and 1% aqueous acetic acid (18 ml). The resulting solution was evaporated *in vacuo* and the residue was dissolved in ethyl acetate (18 ml) and filtered through Celite. The solvent was evaporated and the resulting residue purified by flash column chromatography (ethyl acetate/hexane 3:1) to give (1*S*,2*R*,3*S*,4*R*,5*S*)-[(2,4-bis-benzyloxy-5-benzyloxycarbonylamino-3-hydroxy-cyclopentanecarbonyl)-amino]-acetic acid methyl ester (**10**) (72 mg, 65% yield over the last three steps) as an amorphous white solid.  $[\alpha]_D^{23}$  -3.2° (c, 1.05 in methanol). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 2.86 (m, 1 H, H-1); 3.64 (s, 3 H, -OCH<sub>3</sub>); 3.75 (ABq, 2 H,  $J_{8,8'} = 3.8$  Hz, H-8, H-8'); 3.91 (ABq, 2 H,  $J_{7,7'} = 5.2$  Hz, H-7, H-7'); 3.98 (s, 1 H, H-3); 4.13, 4.14 (2 x s, 2 H, H-2, H-4); 4.34 (d, 1 H,  $J_{2,9} = 6.6$  Hz, H-5); 4.55-4.70 (m, 4 H, 2 x -OCH<sub>2</sub>Ph); 5.05 (s, 2 H, -OCOCH<sub>2</sub>Ph); 5.72 (bs, 1 H, -NH); 7.03 (d, 1 H,  $J = 6.7$  Hz, -NH, H-9); 7.23-7.30 (m, 15 H, 15 x Ar-H); 7.41 (bs, 1 H, -NH). <sup>13</sup>C-NMR (75.4 MHz, CDCl<sub>3</sub>): 41.35, 44.49, 52.07, 52.28, 55.45, 67.13, 72.29, 74.14, 81.35, 84.18, 127.84, 128.06, 128.26, 128.40, 128.55, 136.12, 137.51, 137.80, 156.69, 169.95, 170.44, 172.22. MS (*m/z*, %): 620 [(M + H)<sup>+</sup>, 0.2]; 619 (M<sup>+</sup>, 0.1); 312 (8); 296 (30); 108 (43); 91 (100). IR (NaCl): ν 3295, 1732, 1691, 1654, 1551 cm<sup>-1</sup>. Anal calcd for C<sub>33</sub>H<sub>37</sub>N<sub>3</sub>O<sub>9</sub>: C, 63.96; H, 6.02; N, 6.78. Found C, 63.64; H, 5.98; N, 6.56.

**Methyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucofuranoside (11):** Acetyl chloride (0.65 ml, 0.72 mmol) was added to a cooled (0 °C) solution of 3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucofuranose (**2**) (0.66 g, 1.53 mmol) in dry methanol (10 ml) and the resulting mixture was stirred at 0 °C for 14 h and at room temperature for a further 9 h. The reaction was basified with sodium carbonate, water (20 ml) was added and mixture was extracted with dichloromethane (4 x 20 ml). The combined organic extracts were washed with brine (5 ml), dried over anhydrous sodium sulphate and concentrated to dryness. The residue was purified by flash column chromatography (ethyl acetate/hexane 2:3) to give methyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucofuranoside (**11**) (0.56 g, 90%) as a 1:1 mixture of epimers.

Small quantities of each epimer were isolated and the spectroscopic data are as follows:

Spectroscopic data for **11α**:  $[\alpha]_D^{22}$  -6.0° (c, 1.0 in chloroform). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 2.84 (d, 1 H,  $J_{2,OH} = 5.9$  Hz, -OH); 3.50 (s, 3 H, -OCH<sub>3</sub>); 4.04-4.06 (m, 1 H); 4.24-4.34 (m, 2 H); 4.51-4.82 (m, 7 H, 2 x -OCH<sub>2</sub>Ph, H-6, H-6'); 5.03 (d, 1 H, H-1,  $J_{1,2} = 4.2$  Hz); 7.21-7.36 (m, 10 H, 10 x Ar-H). <sup>13</sup>C-NMR (75.4 MHz, CDCl<sub>3</sub>): 56.05, 71.66, 73.17, 74.54, 76.30, 77.19, 77.78, 83.34, 102.10, 127.81, 127.84, 127.98, 128.06, 128.46, 128.61,

137.30, 137.45. MS ( $m/z$ , %): 403 ( $M^+$ , 5); 402 [( $M - H$ ) $^+$ , 11]; 370 (29); 181 (90); 179 (66); 91 (100). IR (NaCl):  $\nu$  3448, 1551, 1379  $\text{cm}^{-1}$ . Anal calcd for  $\text{C}_{21}\text{H}_{25}\text{NO}_7$ : C, 62.52; H, 6.25; N, 3.47. Found C, 62.51; H, 6.24; N, 3.50.

Spectroscopic data for **11 $\beta$** : Mp 91-93°C.  $[\alpha]_D^{22} -77^\circ$  (c, 1.0 in chloroform).  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ): 1.71 (d, 1 H,  $J_{2,\text{OH}} = 4.4$  Hz, -OH); 3.41 (s, 3 H, - $\text{OCH}_3$ ); 3.96 (d, 1 H,  $J_{3,4} = 4.6$  Hz, H-3); 4.26 (d, 1 H, H-2); 4.41-4.43 (m, 1 H, H-4); 4.50 (m, 1 H,  $J = 11.8$  Hz, - $\text{OCHPh}$ ); 4.55-4.56 (m, 2 H, - $\text{OCH}_2\text{Ph}$ ); 4.58-4.69 (m, 3 H, - $\text{OCHPh}$ , H-5, H-6'); 4.82 (s, 1 H, H-1); 4.89 (dd, 1 H,  $J_{5,6} = 2.8$  Hz,  $J_{6,6'} = 13.2$  Hz, H-6); 7.20-7.38 (m, 10 H, 10 x Ar-H).  $^{13}\text{C-NMR}$  (75.4 MHz,  $\text{CDCl}_3$ ): 56.20, 72.11, 72.96, 75.22, 77.55, 77.79, 80.74, 82.53, 110.13, 127.91, 127.96, 128.11, 128.45, 128.60, 137.20, 137.30. MS ( $m/z$ , %): 403 ( $M^+$ , 5); 402 [( $M - H$ ) $^+$ , 11]; 370 (29); 181 (90); 179 (66); 91 (100). IR (NaCl):  $\nu$  3448, 1551, 1379  $\text{cm}^{-1}$ . Anal calcd for  $\text{C}_{21}\text{H}_{25}\text{NO}_7$ : C, 62.52; H, 6.25; N, 3.47. Found C, 62.55; H, 6.30; N, 3.40.

**Methyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-2-*O*-trifluoromethanesulphonyl-D-glucufuranoside (12)**: Methyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-D-glucufuranoside (**11**) (1.32 g, 3.28 mmol) was dissolved in dry dichloromethane (24 ml) and the solution cooled to -30 °C under nitrogen. Pyridine (0.8 ml, 9.85 mmol) and trifluoromethanesulphonic anhydride (0.72 ml, 4.27 mmol) were added and the mixture was stirred for 1.5 h at -30 °C. The reaction was diluted with dichloromethane (190 ml), washed with dilute hydrochloric acid (95 ml) and brine (125 ml). The organic layer was dried (anhydrous sodium sulphate) and concentrated to dryness, to give methyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-2-*O*-trifluoromethanesulphonyl-D-glucufuranoside (**12**) as a clear gum, which was used in the next step without further purification.

**(3*R*,5*S*,6*R*,7*R*)-6,7-Bis-benzyloxy-3-methoxy-5-nitro-2-oxa-bicyclo[2.2.1]heptane (13)**: A 1M solution of tetrabutylammonium fluoride in THF (7.5 ml) was added to a solution of methyl-3,5-di-*O*-benzyl-6-deoxy-6-nitro-2-*O*-trifluoromethanesulphonyl- $\alpha,\beta$ -D-glucufuranoside (**12**) in THF (33 ml) and the resulting mixture was stirred under argon for 14 h. The solvent was removed and the residue dissolved in dichloromethane (190 ml). The organic phase was washed with water (3 x 125 ml) and the solvent evaporated *in vacuo*. The resulting gum was purified by flash column chromatography (ethyl acetate/hexane 1:4) to give (3*R*,5*S*,6*R*,7*R*)-6,7-bis-benzyloxy-3-methoxy-5-nitro-2-oxa-bicyclo[2.2.1]heptane (**13**) (0.59 g, 46% yield over two steps) as a yellow solid. m.p. 99-101°C.  $[\alpha]_D^{19} -47.2^\circ$  (c, 1.0 in chloroform).  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ): 3.49 (s, 3 H, - $\text{OCH}_3$ ); 3.67 (s, 1 H, H-4); 4.12 (s, 1 H, H-7); 4.24-4.28 (m, 2 H, - $\text{OCHPh}$ , H-1); 4.48 (d, 1 H,  $J = 11.5$  Hz, - $\text{OCHPh}$ ); 4.77 (d, 1 H,  $J = 12.2$  Hz, H-6); 4.82-4.84 (m, 2 H, - $\text{OCH}_2\text{Ph}$ ); 4.99 (s, 1 H, H-5); 5.16 (d, 1 H,  $J = 2.7$  Hz, H-3); 7.27-7.47 (m, 10 H, 10 x Ar-H).  $^{13}\text{C-NMR}$  (75.4 MHz,  $\text{CDCl}_3$ ): 47.97, 56.18, 72.02, 72.16, 79.10, 81.45, 83.19, 83.57, 101.93, 127.81, 127.85, 127.89, 128.18, 128.39, 136.44, 137.83. MS ( $m/z$ , %): 386 [( $M + H$ ) $^+$ , 2.4]; 385 ( $M^+$ , 0.6); 384 [( $M - H$ ) $^+$ , 2.5]; 181(57); 91 (100). IR (NaCl):  $\nu$  1552, 1371  $\text{cm}^{-1}$ . Anal calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}_6$ : C, 65.44; H, 6.02; N, 3.63. Found C, 64.99; H, 6.05; N, 3.67.

**(3*R*,5*S*,6*R*,7*R*)-(6,7-Bis-benzyloxy-3-methoxy-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (15):** (3*R*,5*S*,6*R*,7*R*)-6,7-bis-benzyloxy-3-methoxy-5-nitro-2-oxa-bicyclo[2.2.1]heptane (**13**) (0.59 g, 1.52 mmol) was dissolved in methanol (60 ml) and the solution was deoxygenated by bubbling argon through. Raney-nickel (10% in water) (1.2 ml) was added and the suspension was stirred at room temperature under an atmosphere of hydrogen for 19 h. The reaction mixture was filtered through Celite, eluted with methanol and the filtrate evaporated *in vacuo* to give amine **14** as a clear gum. The amine was dissolved in ethyl acetate (12 ml) and saturated aqueous sodium bicarbonate (8 ml) and benzyl chloroformate (0.32 ml) were added. The resulting mixture was stirred at room temperature for 3 h. and then decanted and the aqueous portion extracted with ethyl acetate (3 x 17 ml). The combined organic layers were dried over anhydrous sodium sulphate, filtered and the solvent evaporated. The residue was purified by flash column chromatography (ethyl acetate/hexane 4:9) to give (3*R*,5*S*,6*R*,7*R*)-(6,7-bis-benzyloxy-3-methoxy-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (**15**) (0.52 g, 70% yield over the last two steps) as a gum.  $[\alpha]_D^{21} -32^\circ$  (c, 1.2 in chloroform).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 3.48 (s, 3 H,  $-\text{OCH}_3$ ); 3.86 (s, 1 H); 4.10-4.15 (m, 3 H); 4.47-4.82 (m, 5 H); 5.04-5.19 (m, 3 H); 5.48 (d, 1 H,  $J_{3,\text{NH}} = 10.5 \text{ Hz}$ ,  $J = 1.3 \text{ Hz}$ ); 7.20-7.39 (m, 15 H, 15 x Ar-H).  $^{13}\text{C-NMR}$  (75.4 MHz,  $\text{CDCl}_3$ ): 49.60, 50.60, 56.04, 66.63, 71.39, 72.57, 78.76, 82.92, 86.66, 102.52, 127.51, 127.66, 127.71, 127.85, 127.92, 128.06, 128.15, 128.27, 128.40, 128.52, 128.73, 136.67, 137.75, 138.11, 155.14. MS ( $m/z$ , %): 354 ( $\text{M}^+ - \text{OCOBn}$ , 0.5); 290 (1); 230 (4); 181(2); 91 (100). IR  $\nu$ : 3433, 1722  $\text{cm}^{-1}$ .

**(5*S*,6*R*,7*R*)-(6,7-Bis-benzyloxy-3-hydroxy-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (16):** (3*R*,5*S*,6*R*,7*R*)-(6,7-bis-benzyloxy-3-methoxy-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (**15**) (0.51 g, 1.03 mmol) was dissolved in a mixture of trifluoroacetic acid/water (1:1, 10 ml) and the reaction mixture was stirred at room temperature until the starting material had been consumed (tlc, ethyl acetate/hexane 1:1) (4 h). The solvent was evaporated *in vacuo* and the residue was coevaporated with toluene (3 x 8 ml) to give (5*S*,6*R*,7*R*)-(6,7-bis-benzyloxy-3-hydroxy-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (**16**) as an unstable mixture of isomers.

**(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-Trihydroxy-5-hydroxymethyl-cyclopentyl-ammonium chloride (17):** A solution of sodium borohydride (13 mg, 0.34 mmol) in a mixture of ethanol/water 1:1 (2 ml) was added to a solution of the (5*S*,6*R*,7*R*)-(6,7-bis-benzyloxy-3-hydroxy-2-oxa-bicyclo[2.2.1]hept-5-yl)-carbamic acid benzyl ester (**16**) in ethanol (6 ml). The reaction mixture was stirred at room temperature for 1 h. Ammonium chloride (19 mg, 0.36 mmol) was added and the reaction mixture was evaporated to dryness. The residue was partitioned between water (10 ml) and dichloromethane (20 ml) and the aqueous layer was extracted with dichloromethane (4 x 20 ml). The combined organic layers were dried over anhydrous sodium sulphate and the solvent evaporated to give a gum. The gum was dissolved in acetic acid (4 ml) and the resulting solution was deoxygenated. 10% Palladium/carbon (83 mg) was added and the suspension was stirred at room temperature under an atmosphere

of hydrogen for 3 d. The reaction mixture was filtered through Celite, eluted with methanol and the filtrate evaporated to dryness. The residue was purified using an ion-interchange column (DOWEX 50x8-200) to give a white solid, which was solved in water. 20% Hydrochloric acid was then added to adjust the pH of this solution to 4 and the resulting precipitate was filtered off to give the hydrochloride salt of (1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-trihydroxy-5-hydroxymethyl-cyclopentyl-ammonium chloride (**17**) (104 mg, 50% from **15**).  $[\alpha]_D^{22}$  -13.0° (c, 0.65 in methanol). <sup>1</sup>H-NMR (300 MHz, D<sub>2</sub>O): 2.02-2.15 (m, 1 H, H-5); 3.47-3.94 (m, 6 H). <sup>13</sup>C-NMR (75.4 MHz, D<sub>2</sub>O): 42.00, 60.77, 66.54, 72.90, 78.24, 78.48. MS (*m/z*, %, FAB): 164 [(M + H)<sup>+</sup>, 1]; 150 (10); 133 (13).