SUPPORTING INFORMATION

Photoinduced Formation of β-oxy-α,α-Disubstituted-α-Amino Acid Derivatives from Ketoximes

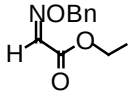
Susana Torrente and Ricardo Alonso

Departamento de Química Orgánica y Unidad Asociada al CSIC, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain

General. NMR spectra were determined on Bruker DPX-250 and AMX-300 instruments. Low resolution mass data were recorded on a Hewlett-Packard 5988A spectrometer.

Ethyl 2-(*O*-benzyloxyimine)-ethanoate (3).

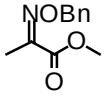
A solution of ethyl glyoxalate (200 mg, 1.96 mmol), *O*-benzylhydroxylamine hydrochloride (343 mg, 2.15 mmol) and piridine (210 μL, 2.15 mmol) in toluene was refluxed for 4 h. The solvent was evaporated and the residue purified by flash chromatography (Ø=2 cm, L=12 cm, ethyl acetate/hexane 30/70) to afford **3** (245 mg, 60%).



^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.55 (s, 1H), 7.37-7.32 (m, 5H, ArH), 5.29 (s, 2H, CH_2Ar), 4.30 (q, J=7.1, 2H, O-CH_2), 1.33 (t, J=7.1, 3H, CH_3). **^{13}C-NMR** (62.90 MHz, $CDCl_3$)δ: 161.7 (C=O), 141.1 (C=N), 135.8 (C_{ipso}), 128.4, 128.3 (ArH), 77.8 (CH_2Ar), 61.4 (-O-CH_2), 14.0 (CH_3). **MS** (FAB^+): 208 (94.4, M^++1), 154 (100).

Methyl 2-(*O*-benzyloxyimine)-propanoate (5a).

A solution of methyl pyruvate (1g, 9.8 mmol), *O*-benzylhydroxylamine hydrochloride (1.87 g, 11.75 mmol) and triethylamine (1.6 mL, 11.75 mmol) in benzene was refluxed for 4 h with azeotropic removal of water using a Dean-Stark condenser. The solvent was evaporated and the residue purified by flash chromatography (Ø=3 cm, L=12 cm, ethyl acetate/hexane 20/80) to afford **5a** as a E/Z mixture (1.91 g, 94%, E/Z=6/1).

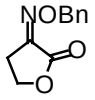


E-isomer. **^{1}H-NMR** (250 MHz, $CDCl_3$)δ : 7.39-7.32 (m, 5H, ArH), 5.31 (s, 2H, CH_2), 3.84 (s, 3H, -OCH_3), 2.1 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 164.0 (C=O), 149.1 (C=N), 136.4 (Ar_{ipso}), 128.3, 128.1, 128.0 (ArH), 77.4 (CH_2), 52.3 (-OCH_3), 11.4

(CH_3). **Z-isomer.** **^{1}H-NMR** (250 MHz, $CDCl_3$)δ : 7.39-7.32 (m, 5H, ArH), 5.13 (s, 2H, CH_2), 3.81 (s, 3H, -OCH_3), 2.03 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 164.0 (C=O), 149.1 (C=N), 136.4 (Ar_{ipso}), 128.3, 128.1, 128.0 (ArH), 76.0 (CH_2), 51.9 (-OCH_3), 16.8 (CH_3). **MS** (CI): 210 (3.4, M+3), 209 (21.9, M+2), 208 (M+1), 91 (67.3, C_7H_7).

α-Benzyloxyimine-γ-butyrolactone (5b).

A mixture of α-hydroxy-γ-butyrolactone (1g, 9.79 mmol), periodinane (4.5g, 10.77 mmol) and *tert*-butanol (1 mL, 11.26 mmol) in acetonitrile (0.2M, 45 mL) was stirred at room temperature for 19 hours, then *O*-benzylhydroxylamine hydrochloride (1.5g, 9.79 mmol) and triethylamine (1.3 mL, 9.79 mmol) were added. After 5 hours, the reaction mixture was diluted with ether and treated with a mixture of sodium thiosulfate and sodium hydrogen carbonate (1:1). The organic phase was extracted, washed with a saturated aqueous solution of NaCl and dried over anhydrous sodium sulfate. Purification of the residue by column chromatography (Ø=3 cm, L=12 cm, ethyl acetate/hexane 30/70), afforded **5b** (153 mg, 7.6%) as a colorless oil.



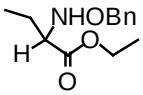
^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.39-7.35 (m, 5H, ArH), 5.34 (s, 2H, CH_2), 4.46 (t, J=7.2, 2H, CH_2), 3.02 (t, J=7.2, 2H, CH_2). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 165.3 (C=O), 145.8 (C=N), 136.0 (Ar_{ipso}), 128.6, 128.5 (ArH), 78.5 (CH_2Ar), 64.9 (CH_2-O), 24.6 (CH_2). MS (EI): 205 (0.7, M^+), 91 (100, C_7H_7), 77 (10.6, C_5H_5).

General procedure for photochemistry reaction.

A solution of the oxime ether in the appropriate solvent (0.02M) is degassed in a Pyrex flask with a stream of argon for 10 minutes. Benzophenone (1 eq.) is added and then the mixture is irradiated using a 450w medium pressure Hanovia mercury lamp. The solvent is evaporated and the residue purified by column chromatography.

Ethyl 2-(*O*-benzylhydroxylamin)-butanoate (4).

A solution of ethyl 2-(*O*-benzyloxyimine)-ethanoate (50 mg, 0.24 mmol) and triethyl borane (1.2 mL, 1.20 mmol) in toluene was refluxed for 20 min. The solvent was evaporated and the residue purified by column chromatography (Ø=0.8 cm, L=12 cm, ethyl acetate/hexane 15/85) to afford **4** (52 mg, 91%).

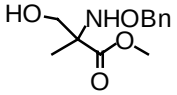


^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.35-7.27 (m, 5H, ArH), 5.95 (s broad, 1H, NH), 4.70 (s, 2H, CH_2Ar), 4.22 (q, J=7.1, 2H, -O-CH_2), 3.52 (m, 1H), 1.28 (t, J=7.1, 3H, CH_3), 0.92 (t,

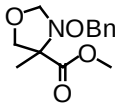
J=7.4, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 174.1 (C=O), 137.8 (C_{ipso}), 128.4, 128.2, 127.7 (ArH), 76.0 (CH_2Ar), 65.1 (CH), 60.8 (-O-CH_2), 22.9 (CH_2), 14.2 (CH_3), 10.5 (CH_3). **MS** (EI): 237 (0.78, M^++1), 236 (5.4, M^+), 164 (39), 91 (100, C_7H_7).

Methyl 2-(*O*-benzylhydroxylamine)-3-hydroxy-2-methyl propanoate (6) and methyl 3-(benzyloxy)-4-methyl-1,3-oxazolane-4-carboxylate (7).

A solution of methyl 2-(benzyloxyimine)propanoate (50 mg, 0.24 mmol) in methanol was irradiated for 2 hours 20 minutes following the general procedure. Purification by flash chromatography (Ø=2 cm, L=12 cm, ethyl acetate/hexane 10/90), afforded **6** and **7** (10 mg, 17%, and 19 mg, 31%, respectively), and 6% of starting material recovered.



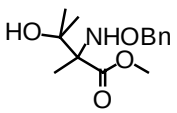
6: ^{1}H-NMR (300 MHz, $CDCl_3$)δ : 7.39-7.31 (m, 5H, ArH), 4.70 (s, 2H, CH_2Ar), 3.76 (s, 3H, CH_3), 3.74 (s, 2H, CH_2), 1.25 (s, 3H, CH_3). **^{13}C-NMR** (75.47 MHz, $CDCl_3$)δ : 174.3 (C=O), 137.2 (Ar_{ipso}), 128.5, 128.4, 128.1 (ArH), 77.0 (CH_2Ar), 66.0 (C), 64.3 (CH_2), 52.3 (-OCH_3), 18.0 (CH_3). **MS** (EI): 239 (0.27, M^+), 208 (22.4, M^+-OCH_3), 91 (100, C_7H_7), 77 (8.8, C_5H_5). **MS** (FAB$^+$): 241 (14.2, M^++2), 240 (100, M^++1), 208 (10.1, M^+-OCH_3). **HR-MS** (FAB$^+$): Calcd for $C_{12}H_{18}NO_4$: 240.1236. Found: 240.1236.



7: ^{1}H-NMR (250 MHz, C_6D_6, 343 k)δ : 7.27-7.10 (m, 5H, ArH), 4.85 (d, J=11.2, 1H, CH_2), 4.74 (d, J=11.2, 1H, CH_2), 4.70 (d, J=8.2, 1H, CH_2), 4.58 (d, J=8.2, 1H, CH_2), 4.45 (d, J=7.6, 1H, CH_2), 3.63 (d, J=7.6, 1H, CH_2), 3.40 (s, 3H, CH_3), 1.29 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, C_6D_6, 343 k)δ : 171.7 (C=O), 138.5 (Ar_{ipso}), 90.1 (CH_2), 77.5 (CH_2Ar), 75.5 (C), 71.9 (CH_2), 52.2 (-OCH_3), 21.4 (CH_3). **MS** (FAB$^+$): 254 (2.0, M^++3), 253 (13.6, M^++2), 252 (90, M^++1), 154 (100). **HR-MS** (FAB$^+$): Calcd for $C_{13}H_{18}NO_4$: 252.1235. Found: 252.1236.

Methyl 2-(*O*-benzylhydroxylamine)-3-hydroxy-2,3-dimethyl butanoate (8).

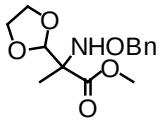
A solution of methyl 2-(benzyloxyimine)propanoate (47 mg, 0.2 mmol) in 2-propanol was irradiated for 2 hours following the general procedure. Purification by flash chromatography (Ø=1 cm, L=12 cm, ethyl acetate/hexane 20/80) afforded **8** (35 mg, 58%) and 4% of starting material recovered.



^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.33-7.27 (m, 5H, ArH), 4.69 (ABq, J=11.7, CH_2Ar), 3.76 (s, 3H, CH_3), 2.97 (s ancho, 1H, OH), 1.38 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.14 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 175.8 (C=O), 137.5 (Ar_{ipso}), 128.5, 128.2, 127.7 (ArH), 77.2 (CH_2Ar), 73.6 (C), 71.3 (C), 52.2 (-OCH_3), 26.3 (CH_3), 24.1 (CH_3), 16.2 (CH_3). **MS** (IE): 268 (0.7, M^++1), 252 (2.6, M^+-CH_3), 208 (29), 176 (9.3, M^+-C_7H_7), 102 (43), 91 (100, C_7H_7). **MS** (FAB^+): 269 (17.2, M^++2), 268 (100, M^++1). **HR-MS** (FAB^+): Calcd for $C_{14}H_{22}NO_4$: 268.1548. Found: 268.1556. **Anal**.: Calcd for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.92; N, 5.24%. Found: C, 63.13; H, 8.11; N, 5.06%.

Methyl 2-(*O*-benzylhydroxylamine)-2-(1,3-dioxolan-2-yl) propanoate (9).

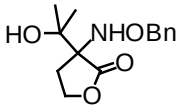
A solution of methyl 2-(benzyloxyimine)propanoate (52 mg, 0.25 mmol) in 1,3-dioxolane was irradiated for 2 hours following the general procedure. Purification by flash chromatography (Ø=1 cm, L=12 cm, ethyl acetate/hexane 20/80) afforded **9** (52 mg, 74%) and 5% of starting material recovered.



^{1}H-NMR (300 MHz, $CDCl_3$)δ : 7.36-7.27 (m, 5H, ArH), 6.29 (s, 1H, NH), 5.07 (s, 1H), 4.72 (ABq, J=11.6, CH_2Ar), 3.98-3.85 (m, 4H, CH_2, CH_2O-), 3.76 (s, 3H, -OCH_3), 1.40 (s, 3H, CH_3). **^{13}C-NMR** (75.47 MHz, $CDCl_3$)δ : 172.3 (C=O), 137.2 (Ar_{ipso}), 128.3, 128.3, 127.8 (ArH), 104 (CH), 68.5 (C), 65.6 (CH_2, CH_2), 52.4 (-OCH_3), 15.2 (CH_3). **MS** (IE): 281 (14.5, M^+), 149 (100, $CH_3CNHOC_7H_7$). **Anal**.: Calcd for $C_{14}H_{19}NO_5$: C, 59.78; H, 6.81; N, 4.98%. Found: C, 59.52; H, 7.03; N, 4.97%.

3-(*O*-Benzylhydroxylamine)-3-(1-hydroxy-1-methylethyl)tetrahydro-2-furanone (10).

A solution of α-benzyloxyimine-γ-butyrolactone (19 mg, 0.09 mmol) in 2- propanol was irradiated for 20 minutes following the general procedure. Purification by flash chromatography (Ø=0.8 cm, L=12 cm, ethyl acetate/hexane 30/70) afforded **10** (18 mg, 73%) as a colorless oil.

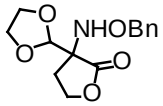


^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.33 (m, 5H, ArH), 6.59 (s, 1H, NH), 4.71 (ABq, 2H, CH_2), 4.31-4.20 (m, 2H, CH_2), 3.21 (s, 1H, OH), 2.26 (m, 2H, CH_2), 1.26 (s, 3H, CH_3), 1.25 (s, 3H, CH_3). **^{13}C-NMR** (75.47 MHz, $CDCl_3$)δ : 179.7 (C=O), 136.9 (Ar_{ipso}), 128.7, 128.4, 128.1 (ArH), 77.2 (CH_2Ar), 73.4 (C), 70.8 (C), 66.2 (CH_2-O), 28.6 (CH_2), 26.1 (CH_3), 23.5 (CH_3). **MS** (IE): 207 (2.1, M^+-C_3H_7O), 116 (8.5, M^+-(C_3H_7O)-(C_7H_7)), 91 (100, C_7H_7), 77 (8.5, C_5H_5), 59 (9.9, C_3H_7O). **MS** (FAB^+): 268 (3.4, M^++3), 267 (16.3, M^++2), 266 (M^++1),

154 (54). **HR-MS** (FAB$^+$): Calcd for $C_{14}H_{20}NO_4$: 266.1392. Found: 266.1401. **Anal**.: Calcd for $C_{14}H_{19}NO_4$: C, 63.39; H, 7.22; N, 5.28%. Found: C, 63.63; H, 7.51; N, 5.31%.

3-(*O*-Benzylhydroxylamine)-3-(1,3-dioxolan-2-yl)tetrahydro-2-furanone (11).

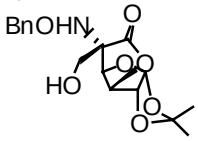
A solution of α-benzyloxyimine-γ-butyrolactone (33 mg, 0.16 mmol) in 1,3-dioxolane was irradiated for 20 minutes following the general procedure. Purification by flash chromatography (Ø=1 cm, L=12 cm, ethyl acetate/hexane 30/70) afforded **11** (33 mg, 73%).



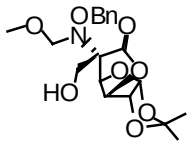
^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.33-7.29 (m, 5H, ArH), 6.18 (s, 1H, NH), 5.04 (s, 1H), 4.73 (ABq, J=11.7, 2H, CH_2), 4.32-4.26 (m, 2H, CH_2O-), 4.05-3.93 (m, 2H, CH_2O-), 3.91-3.85 (m, 2H, CH_2O-), 2.53-2.29 (m, 2H, CH_2). **^{13}C-NMR** (75.47 MHz, $CDCl_3$)δ : 174.8 (C=O), 137.0 (ArH_{ipso}), 128.5, 128.4, 128.0 (ArH), 103.4 (CH), 77.3 (CH_2Ar), 68.5 (C), 65.8 (CH_2, CH_2,CH_2), 27.0 (CH_2). **MS** (FAB$^+$): 280 (100, M$^+$+1). **HR-MS** (FAB$^+$): Calcd for $C_{14}H_{18}NO_5$: 280.1185. Found: 280.1197. **Anal**.: Calcd for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.13; N, 5.01%. Found: C, 59.94; H, 6.41; N, 4.82%.

5-C-(*O*-benzylhydroxylamine)-5-deoxy-5-C-(hydroxymethyl)-1,2-*O*-isopropilidene-β-L-idofuranose-3,6-lactone (12a).

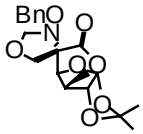
A solution of **5c** (1g, 3.13 mmol) in methanol (150 mL, 0.02M) was irradiated for 20 minutes following the general procedure. Purification by flash chromatography (Ø=3 cm, L=12 cm, ethyl acetate/hexane 15/85, 30/70, 40/60) afforded **12a** (42%), **12b** (0.6%) and **12c** (3%).



12a: ^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.39-7.33 (m, 5H, ArH), 6.3 (s, 1H, NH), 5.96 (d, J=3.7, 1H, H_1), 4.90 (s, 2H, C$\underline{H}_2$-OH), 4.79 (d, J=3.7, 1H, H_2), 4.76 (s, 2H, C$\underline{H}_2$-ArH), 3.87 (m, 2H, H_3, H_4), 2.12 (m, 1H, -OH), 1.52 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 172.5 (C_6), 136.6 (Ar_{ipso}), 128.9, 128.5, 128.3 (ArH), 113.2 ($\underline{C}(OCH_3)_2$), 106.2 (C_1), 83.0, 82.7, 80.4 (C_4, C_3, C_2), 77.3 ($\underline{C}H_2Ar$), 70.9 (C_5), 62.5 ($\underline{C}H_2$-OH), 27.0, 26.5 (CH_3, CH_3). **MS** (EI): 351 (0.02, M$^+$), 336 (0.3, M$^+$-CH_3), 91 (100, C_7H_7), 77 (4.4, C_6H_5). **MS** (CI$^+$): 354 (9.0, M$^+$+3), 353 (32.4, M$^+$+2), 352 (100, M$^+$+1). **HR-MS** (CI$^+$): Calcd for $C_{17}H_{22}NO_7$: 352.1396. Found: 352.1402.

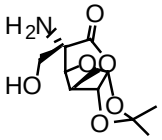


12b: **^{1}H-NMR** (250 MHz, $CDCl_3$, in a mixture with the alcohol N)δ : 7.43-7.28 (m, 5H, ArH), 5.97 (H_1), 4.98-4.72 (m, 7H, -CH_2, H_2, -CH_2, -CH_2), 3.98-3.86 (m, 2H, H_3, H_4), 3.51 (s, 3H, -OCH_3), 1.51 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 171.4 (C_6), 136.2 (Ar_{ipso}), 128 (ArH), 113.1 ($\underline{C}(OCH_3)_2$), 106.1 (C_1), 86.0 ($\underline{C}H_2$-OCH_3), 82.5, 82.4, 81.5 (C_4, C_3, C_2), 77.0 ($\underline{C}H_2Ar$), 74.4 (C_5), 62.7 ($\underline{C}H_2$-O), 57.3 (O$\underline{C}H_3$), 27.0, 26.5 (CH_3, CH_3).



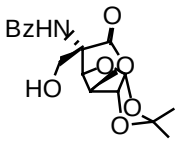
12c: **^{1}H-NMR** (250 MHz, $CDCl_3$)δ : 7.44-7.3 (m, 5H, ArH), 6.13 (d, J=3.7, 1H, H_1), 5.06 (d, J=9.8, 1H, CH_2), 4.96 (d, J=2.5, 1H, H_3^*), 4.87 (d, J=3.7, 1H, H_2), 4.82 (d, J=9.8, 1H, CH_2-ArH), 4.72 (d, J=2.5, 1H, H_4^*), 3.94 (d, J=8.0, 1H, CH_2), 3.83 (d, J=8.0, 1H, CH_2), 1.55 (s, 3H, CH_3), 1.39 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 171.4 (C=O), 136.3 (Ar_{ipso}), 129.5, 128.3, 128.3 (ArH), 113.3 ($\underline{C}(OCH_3)_2$), 106.5 (C_1), 91.1 (N-CH_2-O), 82.3, 82.0, 81.5 (C_4, C_3, C_2), 77.9 (C), 76.9 (CH_2Ar), 68.0 (CH_2-O), 26.9, 26.5 (CH_3, CH_3). **MS** (EI): 348 (0.6, M^+-CH_3), 91 (100, C_7H_7). **Anal**.: Calcd for $C_{18}H_{21}NO_7$: C, 59.49; H, 5.82; N, 3.85%. Found: C, 59.69; H, 6.13; N, 3.83%.

5-Amino-5-deoxy-5-C-(hydroxymethyl)-1,2-*O*-isopropilidene-β-L-idofuranose-3,6-lactone. A mixture of **12a** (192 mg, 0.54 mmol) and Pearlmann's catalyst $Pd(OH)_2$ (38 mg, 0.27mmol) in methanol (20 mL) under hydrogen (40 psi) was stirred for 13 h. Additional catalyst (80 mg, 0.54 mmol) was added and the mixture was stirred for 10 hours. Filtration over celite and evaporation of solvent afforded the pure aminoalcohol (116 mg, 86%).



^{1}H-NMR (300 MHz, $CDCl_3$)δ : 5.95 (d, J=3.4, 1H, H_1), 4.91-4.82 (m, 3H, H_4, H_3, H_2), 3.61 (s, 2H, CH_2), 2.54 (s ancho, 3H, -OH, -NH_2), 1.51 (s, 3H, CH_3), 1.35 (s, 3H, CH_3). **^{13}C-NMR** (75.47 MHz, $CDCl_3$)δ : 177.9 (C_6), 113.3 ($\underline{C}(OCH_3)_2$), 106.1 (C_1), 82.9, 82.4, 81.6 (C_4, C_3, C_2), 77.2 (C_5), 64.2 (CH_2Ar), 27.0, 26.6 (CH_3, CH_3). **MS** (EI): 245 (18, M^+), 230 (100, M^+-CH_3), 215 (63.8, M^+-(CH_3)-(NH_3)), 214 (51.8, M^+-(CH_3)-(NH_2)), 202 (49.9, M^+-(CH_3)-(CH_2OH)). **HR-MS** (EI): Calcd for $C_{10}H_{15}NO_6$: 245.0899. Found: 245.0891. Cristalized from methanol: mp=110-112ºC.

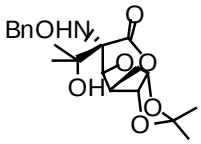
5-Benzamido-5-deoxy-5-C-(hydroxymethyl)-1,2-*O*-isopropilidene-β-L-idofuranose-3,6-lactone (13). A solution of the aminoalcohol (50 mg, 0.2 mmol) and benzoyc anhydride (135 mg, 0.6 mmol) in methanol (3 mL) was stirred for 36 h at room temperature. Removal of solvent and chromatography (Ø=1 cm, L=12 cm, ethyl acetate/hexane 30/70; ethyl acetate/hexane 50/50) afforded **13** (36 mg, 50%) as a colorless oil.



^{1}H-NMR (300 MHz, $CDCl_3$)δ : 7.80 (m, 2H, ArH_o), 7.57-7.43 (m, 3H, ArH), 6.74 (s, 1H, NH), 5.94 (d, J=3.7, 1H, H_1), 5.32 (d, J=3.4, 1H, H_3*), 5.08 (d, J=3.4, 1H, H_4*), 4.88 (d, J=3.7, 1H, H_2), 4.19 (d, J=11.9, 1H, CH_2), 3.94 (d, J=11.9, 1H, CH_2), 1.52 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). **^{13}C-NMR** (75.47 MHz, $CDCl_3$)δ : 173.3 (C=O), 168.8 (C=O), 113.5 ($\underline{C}(OCH_3)_2$), 106.4 (C_1), 83.6, 82.9, 80.0 (C_4, C_3, C_2), 66.7 (C_5), 64.3 (CH_2), 27.0, 26.6 (CH_3, CH_3). **MS** (EI): 349 (15.1, M^+), 334 (100, M^+-CH_3). **HR-MS** (EI): Calcd for $C_{17}H_{19}NO_7$: 349.1161. Found: 349.1153. **Anal**.: Calcd for $C_{17}H_{18}NO_7$: 348.1083. Found 348.1079. $[\alpha]_D$= +30.8 (c=1.0, $CHCl_3$) (Reported: $[\alpha]_D$= +33 (c=1.0, $CHCl_3$)).

5-C-(*O*-Benzylhydroxylamine)-5-deoxy-5-C-(1-hydroxy-1-methylethyl)-1,2-*O*-isopropilidene-β-L-idofuranose-3,6-lactone (12d).

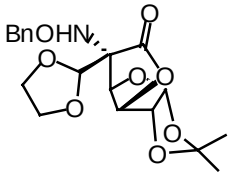
A solution of **5c** (103 mg, 0.32 mmol) in 2-propanol (12 mL, 0.03M) was irradiated for 30 minutes following the general procedure. Purification by flash chromatography (Ø=1 cm, L=12 cm, ethyl acetate/hexane 30/70) afforded **12d** (86 mg, 70%).



^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.32 (m, 5H, ArH), 6.3 (s, 1H, NH), 5.98 (d, J=3.4, 1H, H_1), 5.20 (d, J=5.4, 1H, H_4*), 4.91 (d, J=5.4, 1H, H_3*), 4.76 (ABq, 2H, CH_2Ar), 4.70 (d, J=3.4, 1H, H_2), 2.94 (s ancho, 1H, -OH), 1.54 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.33 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 172.8 (C_6), 136.5 (Ar_{ipso}), 128.5, 128.4, 128.0 (ArH), 113.5 ($\underline{C}(CH_3)_2$), 106.6 (C_1), 84.0, 83.3, 79.9 (C_4, C_3, C_2), 76.6 ($\underline{C}H_2Ar$), 74.5, 73.2 (C_5, C), 27.4, 26.8, 26.0, 24.9 (CH_3, CH_3, CH_3, CH_3). **MS** (FAB^+): 380 (M^++1). **HR-MS** (FAB^+): Calcd for $C_{19}H_{26}NO_7$: 380.1709. Found: 380.1706.

5-C-(*O*-benzylhydroxylamine)-5-C-(1,3-dioxolan-2-yl)-5-deoxy-1,2-*O*-isopropilidene-β-L-idofuranose-3,6-lactone (12e).

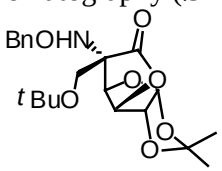
A solution of **5c** (98 mg, 0.3 mmol) in 1,3-dioxolane (12 mL, 0.03M) was irradiated for 30 minutes following the general procedure. Purification by flash chromatography (Ø=1 cm, L=12 cm, ethyl acetate/hexane 30/70) afforded **12e** (89 mg, 74%).



^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.37-7.28 (m, 5H, ArH), 6.38 (s, 1H, NH), 6.0 (d, J=3.6, 1H, H_1), 5.32 (s, 1H), 4.97 (s, 2H, CH_2Ar), 4.83-4.75 (m, 3H, H_2, H_3, H_4), 4.05-3.89 (m, 4H, CH_2, CH_2), 1.53 (s, 3H, CH_3), 1.36 (s, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 170.7 (C_6), 136.9 (Ar_{ipso}), 128.6, 128.3, 128.1 (ArH), 113.2 ($\underline{C}(OCH_3)_2$), 106.5 (C_1), 102.3 (CH), 83.7, 83.1, 79.6 (C_4, C_3, C_2), 77.2 ($\underline{C}H_2Ar$), 71.7 (C), 66.0, 65.4 (CH_2, CH_2), 27.2, 26.7 (CH_3, CH_3). **MS** (FAB^+): 396 (3.9, M^++3), 395 (20.5, M^++2), 394 (100, M^++1), 154 (18.8). **HR-MS** (FAB^+): Calcd for $C_{19}H_{24}NO_8$: 394.1502. Found: 394.1502.

5-C-(*O*-Benzylhydroxylamine)-5-C-(*tert*-butoxymethyl)-5-deoxy-1,2-*O*-isopropilidene-β-L-idofuranose-3,6-lactone (12f).

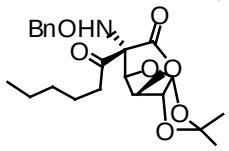
A solution of **5c** (50 mg, 0.15 mmol) in *tert*-butyl methyl ether (8 mL, 0.02 M) was irradiated for 1 h 10 minutes following the general procedure. Purification by flash chromatography (Ø=1 cm, L=12 cm, ethyl acetate/hexane 17/83) afforded **12f** (30 mg, 47%).



^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.37-7.32 (m, 5H, ArH), 6.27 (s, 1H, NH), 5.94 (d, J=3.7, 1H, H_1), 4.87 (s, 2H, CH_2Ar), 4.75 (m, 3H, H_2, H_3, H_4), 3.63 (ABq, 2H, CH_2), 1.54 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.1 (s, 9H, $-C(CH_3)_3$). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 173.7 (C_6), 137.1 (Ar_{ipso}), 129.0, 128.3, 128.0 (ArH), 113.0 ($\underline{C}(CH_3)_2$), 106.0 (C_1), 83.8, 82.8, 82.1 (C_4, C_3, C_2), 77.3 ($\underline{C}H_2Ar$), 74.1, 70.3 (C5, $\underline{C}(CH_3)_3$), 27.1, 26.6 (CH_3, $C(\underline{C}H_3)_3$). **MS** (EI): 407 (0.1, M^+), 392 (0.6, M^+-CH_3), 91 (100, C_7H_7).

5-C-(*O*-Benzylhydroxylamine)-5-deoxy-5-C-(1-hexanoyl)-1,2-*O*-isopropilidene-β-L-idofuranose-3,6-lactone (12g).

A solution of **5c** (120 mg, 0.37 mmol) and capronaldehyde (460 μL, 3.75 mmol) in acetonitrile (12 mL, 0.03M) was irradiated for 15 minutes from 0ºC to 32ºC following the general procedure. Purification by flash chromatography (Ø=3 cm, L=12 cm, ethyl acetate/hexane 10/90) afforded **12h** (88 mg, 57%).



^{1}H-NMR (250 MHz, $CDCl_3$)δ : 7.39-7.30 (m, 5H, ArH), 6.38 (s, 1H, NH), 5.93 (d, J=3.7, 1H, H_1), 5.24 (d, J=3.1, 1H, H_3*), 5.0 (d, J=3.1, 1H, H_4*), 4.86-4.74 (m, 3H, H_2, CH_2Ar), 2.94-2.74 (m, 2H, CH_2), 1.57-1.49 (m, 4H, CH_2, CH_2), 1.55 (s, 3H, CH_3), 1.35 (s, 3H, CH_3),

0.88 (t, J=7.0, 3H, CH_3). **^{13}C-NMR** (62.83 MHz, $CDCl_3$)δ : 203.5 (C=O), 167.4 (C_6), 136.2 (Ar_{ipso}), 128.4, 128.3, 128.2 (ArH), 113.4 ($\underline{C}(OCH_3)_2$), 106.0 (C_1), 84.4, 82.8, 79.8 (C_4, C_3, C_2), 79.4 (C), 76.4 ($\underline{C}H_2Ar$), 37.4, 31.0, 22.6, 22.4 (4 CH_2), 27.0, 26.6 (CH_3, CH_3). **MS** (IE): 419 (11.6, M^+), 404 (100, M^+-CH_3). **Anal**.: Calcd for $C_{22}H_{29}NO_7$: C, 62.98; H, 6.96; N, 3.33%. Found: C, 62.90; H, 7.16; N, 3.21%.