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Two new examples of the rare C→O migration of ethoxycarbonyl groups

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Abstract—Two new examples of a carbon→oxygen ethoxycarbonyl group shift are described. Treatment of 3-ethoxycarbonylnitromethyl-1,2-*O*-isopropylidene-6-*O*-*p*-toluenesulfonyl-α-D-allofuranose (**4**) with Bu_4NF leads to a rearrangement to 5-*O*-ethoxycarbonyl-1,2-*O*-isopropylidene-3-nitromethyl-6-*O*-*p*-toluenesulfonyl-α-D-allofuranose (**8**). Similar treatment of ethyl-3-*O*-benzyl-6-deoxy-6-nitro-D,L-glycero-D-glucoheptofuronate (**12**) gives 3-*O*-benzyl-4-*O*-ethoxycarbonyl-6-deoxy-6-nitro-D-glucopyranose (**16**).

A wide range of C→C migrations involving alkoxycarbonyl groups have been reported[1] but, in contrast, C→N and C→O alkoxycarbonyl shifts[2] are much less common. The first C→O alkoxycarbonyl migration, reported in 1972, involved the migration of an ethoxycarbonyl group in a compound resulting from the reaction between ethyl nitroacetate and a 1,5-dialdehyde.[3] To the best of our knowledge, only one other example[4] has been described and this occurred in the context of an unusual decarboxylation of β-ethoxycarbonyl-ketones. We report here two new, closely related C→O ethoxycarbonyl migrations that were observed during the course of a project aimed at the synthesis of cyclic α-nitro acids from sugars by intramolecular Henry reactions between appropriate sugar derivatives and ethyl nitroacetate. More specifically, compounds **4** and **12**, upon treatment with Bu_4NF, rearranged to give compounds **8** and **16**, respectively.

When diacetone-D-glucose derivative **1**[5] was reacted with ethyl nitroacetate and ammonium acetate in DMF, compound **2** was formed in 26% yield as a 15:1 mixture of epimers (Scheme 1). As expected,[6] the resulting *R* configuration at C-3 was controlled by the starting material, which facilitates attack by the ethyl nitroacetate anion on the less hindered face of the carbonyl group in ketone **1**. However, the relatively long distance between the methylene group in ethyl nitroacetate and the stereogenic centers in compound **1** did not allow full stereocontrol at the carbon bearing the ethoxycarbonyl and nitro groups.

Subsequent treatment of nitroester **2** with a mixture of methanol, acetic acid and water allowed selective hydrolysis of the exocyclic acetonide protecting group. The resulting unstable mixture of compounds **3** was directly treated with one equivalent of tosyl chloride at low temperature to yield the expected tosyl compound **4** (64% yield for the last two steps), which results from the selective tosylation of the less hindered hydroxy group at C-6. Finally, compound **4** was reacted with Bu_4NF in order to promote the intramolecular cyclization leading to bicycle **5**. However, compound **8** was obtained as the only isolable component of a complex reaction mixture {59% yield, $[\alpha]_D^{21}=+9.60°$ (*c*, 1.6 in $CHCl_3$)}.

The isomeric nature of compounds **4** and **8** was easily established from their HRMS data, which indicated the same molecular formula ($C_{20}H_{28}NO_{12}S$) from the corresponding (M^++H) peak.

The structure of **8** was established from its spectroscopic data. The IR spectrum contains at 1559 and 1357 cm^{-1} two bands due to the nitro group, and a band at 1746 cm^{-1}, corresponding to the carbonyl group. The ^1H NMR spectrum contains the expected signals for aromatic protons of the OTs group: a doublet (2H) at 7.31 ppm and a doublet (2H) at 7.75 ppm. Additional information about the structure of compound **8** was obtained from its ^{13}C NMR spectrum, particularly the signals at 65.01, 68.00 and 75.78 ppm due to the three methylene groups. These signals clearly indicate the internal displacement of the ethoxycarbonyl group.

Transformation of compound **4** into **8** might occur in the following way: the hydroxy group at C-5 in compound **4** takes part in an intramolecular attack on the ethoxycarbonyl group to give a cyclic intermediate **6**. This compound

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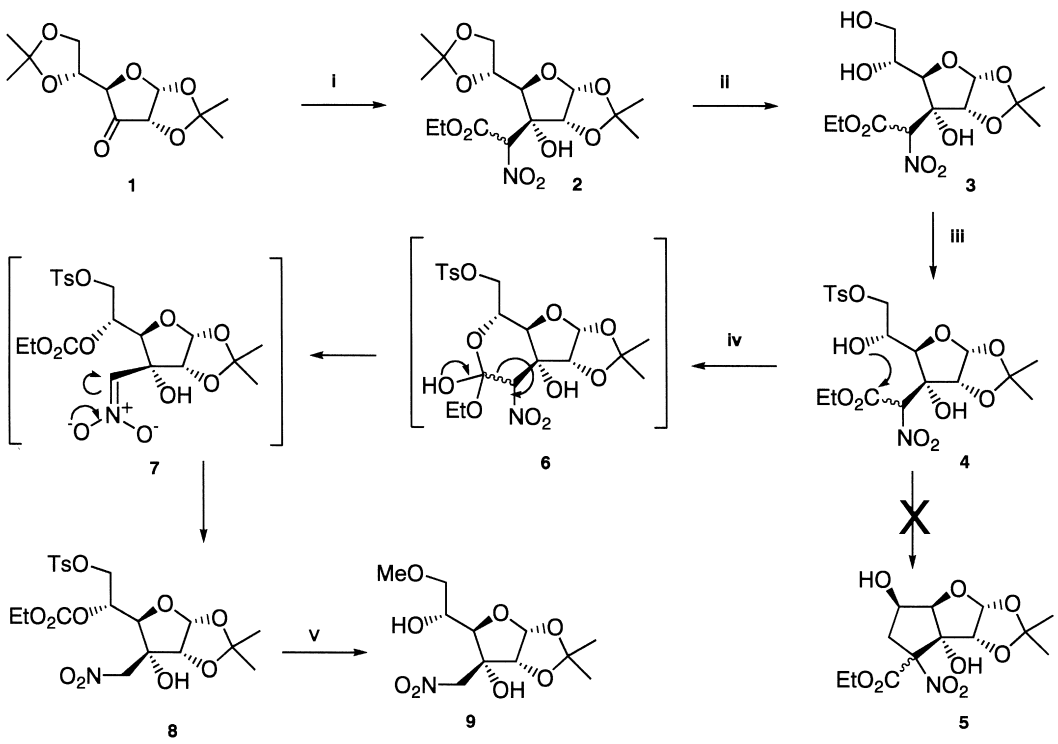


Scheme 1. *Conditions*: (i) Ethyl nitroacetate, $AcONH_4$, DMF (26% yield); (ii) $CH_3OH/CH_3CO_2H/H_2O$, 1:1:1; (iii) *p*-toluenesulfonyl chloride, dry pyridine (64% yield over the two last steps); (iv) Bu_4NF (1 M solution in THF), dry THF (59% yield); (v) K_2CO_3 1% methanolic solution (43% yield).

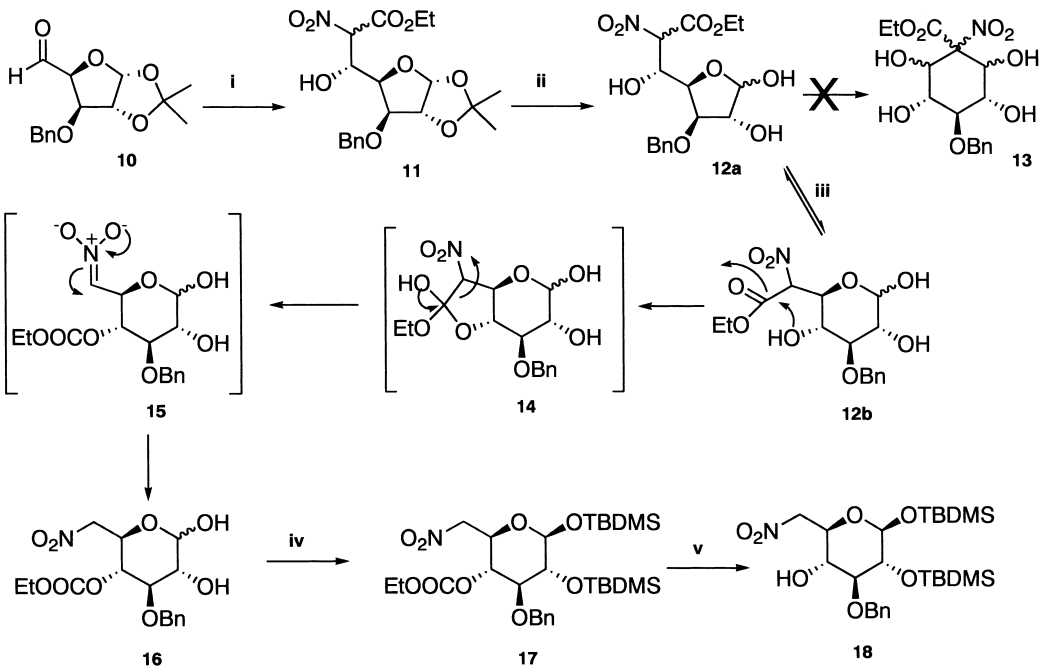
readily rearranges to the more stable anionic intermediate **7**, which is finally protonated in the reaction medium.

In an attempt to further confirm the aforementioned displacement of the ethoxycarbonyl group in compound **4**, compound **8** was treated with 1% methanolic potassium carbonate solution. Under these conditions compound **9** was formed in 43% yield as an oil {$[\alpha]_D^{20}=+32.20°$ (*c*, 0.9 in $CHCl_3$)} as a result of the removal of the ethoxycarbonyl group at C_5 and the displacement of the tosyl group by methanol. The mass spectrum confirmed the molecular weight expected for this compound and the IR and ^1H NMR spectra do not show any evidence for the presence of an ethoxycarbonyl group. Moreover, this compound shows a NOE between the nitromethylene chain and the hydrogen at position C_2. Therefore, this confirm that the *R* configuration at C_3 is maintained along the reactions sequence starting from compound **2**.

The second rearrangement described here involved nitroacetate derivative **11** (Scheme 2), which was obtained in 40% yield as a 59:41 epimeric mixture when diacetoneglucose derivative **10**[7] was allowed to react with ethyl nitroacetate under basic conditions.[8] Hydrolysis of compound **11** with a 1:1 mixture of trifluoroacetic acid/water gave the unstable hemiacetal derivative **12a**, which was directly reacted with Bu_4NF in order to promote its intramolecular Henry reaction to compound **13**. However, in this case the only isolable component from the resulting complex reaction mixture was compound **16**, which was obtained in 26% yield (for the two last steps) as an oil and was identified from its analytical and spectroscopic data. The HRMS (CI) shows the molecular formula $C_{16}H_{22}NO_9$ from the (M^++H) peak. The IR spectrum shows at 1560 and 1373 cm^{-1} two bands due the nitro group and a band at 1748 cm^{-1} corresponding to the carbonyl of the ethoxycarbonyl group. The presence of this group was confirmed from the ^1H NMR spectrum, which showed a triplet at 1.29 ppm (J=7.23 Hz) due to the methyl of the ethoxy substituent. In addition, the ^{13}C NMR spectrum clearly shows two signals at 65.07 and 75.35 ppm, the last one corresponding to the highly deshielded methylene contiguous to the nitro group.

A mechanism similar, but slightly more complex, to that discussed above for the transformation of compound **4** into compound **8** can be proposed for the rearrangement of compound **12** to **16**: furanose **12a** can easily isomerize to pyranose **12b**, which experiences intramolecular attack by the C-4 hydroxy group on the ethoxycarbonyl group. This step results in the bicyclic intermediate **14**, which irreversibly opens to the more stable anionic intermediate **15**. Protonation of this compound in the reaction medium yields the unstable rearranged compound **16**, which was finally converted into its stable derivative **17** by protecting the free hydroxy groups as TBDMS derivatives. The stereochemistry at the anomeric position of this compound was easily established from its ^1H NMR spectrum, which includes a doublet at 4.83 ppm due to the proton at C_1. The coupling constant for this doublet ($J_{1,2}$=11.24 Hz) allowed us to establish the diaxial disposition of the protons at C_1 and at C_2.

Migration of the ethoxycarbonyl group in **12** was corroborated by chemical means in a similar way as for compound **8**: treatment of compound **17** with a methanolic K_2CO_3 solution resulted in the formation of compound **18** in 61% yield as a solid {mp: 101–103°C (hexane), $[\alpha]_D^{20}=-1.33°$



Scheme 2. *Conditions*: (i) ethyl nitroacetate, Bu_4NF, Et_3N, *t*-$BuMe_2SiCl$ (40% yield); (ii) CF_3CO_2H/H_2O, 1:1; (iii) Bu_4NF (1 M solution in THF), dry THF (26% yield over the two last steps); (iv) *t*-$BuMe_2SiCl$, imidazole, DMF (67% yield); (v) K_2CO_3 1% aqueous solution, CH_3OH (61% yield).

(*c*, 1 in $CHCl_3$)} due to removal of the ethoxycarbonyl group at C-4. The structure of compound **18** was confirmed from its analytical and spectroscopic data. The IR spectrum does not show evidence of a carbonyl group and has a band at 3505 cm^{-1} due to the hydroxy group.

In summary, we report two new examples of rare carbon→oxygen rearrangements. The chemistry described here also represents an interesting contribution to the knowledge of the Henry reaction. The application of this reaction to the synthesis of sugar amino acids is currently under investigation in our laboratory.[9]

1. Experimental

1.1. General

Melting points were determined using a Kofler Thermogerate apparatus and are uncorrected. Specific rotations were recorded on a JASCO DIP-370 optical polarimeter. Infrared spectra were recorded on a MIDAC FTIR spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Bruker WM-300 or a Bruker AMX-500 apparatus, using deuterochloroform solutions containing tetramethylsilane as internal standard. NMR assignments were made by a combination of 1D, COSY, NOESY and DEPT-135 experiments. Mass spectra were obtained on a Kratos MS 50 TC mass spectrometer by electronic impact unless otherwise specified. Elemental analyses were obtained from the Elemental Analysis Service at the University of Santiago de Compostela. Thin layer chromatography (TLC) was performed using Merck GF-254 type 60 silica gel and ethyl acetate/hexane mixtures as eluants; the TLC spots were visualized with Hannesian mixture. Column chromatography was carried out using Merck type 9385 silica gel. Solvents were purified as per Ref. [10]. Solutions of extracts in organic solvents were dried with anhydrous sodium sulfate.

1.1.1. 3-Ethoxycarbonylnitromethyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (2). Ethyl nitroacetate (1.83 ml, 16.5 mmol) and ammonium acetate (1.65 g, 21.45 mmol) were added to a solution of compound **1** (3.87 g, 15 mmol) in DMF (80 ml) and the resulting mixture was stirred at room temperature for 40 h. The solvent was evaporated in vacuo, the residue dissolved in dichloromethane (150 ml) and the solution washed with water (3×100 ml). The organic layers were dried, filtered and the solvent evaporated. The residue was submitted to flash column chromatography (ethyl acetate/hexane, 1:3) to give the title compounds (1.5 g, 26% yield) as a gum-like mixture of isomers in a 15:1 ratio. $[\alpha]_D^{20}=+40.20°$ (*c*, 1.3 in MeOH). Spectroscopic data for the main epimer: ν_{max} (NaCl): 3440 (–OH), 1747 (C=O), 1570 ($-NO_2$), 1376 ($-NO_2$). δ_H (300 MHz, $CDCl_3$): 1.25–1.44 (m, 9H, $-O-CH_2-CH_3$ and 2×$-CH_3$), 1.52 (s, 6H, 2×$-CH_3$), 3.61 (bs, 1H, –OH), 4.03–4.39 (m, 5H), 4.58 (d, 1H, *J*=6.4 Hz), 4.82 (d, 1H, *J*=3.6 Hz), 5.84 (s, 1H, H_2), 5.93 (d, 1H, $J_{1,2}$=4.0 Hz, H_1). δ_C (75.3 MHz, $CDCl_3$): 13.72 (q, $-CH_3$), 24.86 (q, $-CH_3$), 25.60 (q, $-CH_3$), 26.45 (q, $-CH_3$), 26.53 (q, $-CH_3$), 63.16 (t, $-CH_2-$), 67.23 (t, $-CH_2-$), 73.00 (d, –CH–), 80.26 (d, –CH–), 81.23 (s, –C–), 85.78 (d, –CH–), 89.20 (d, –CH–), 104.43 (d, –CH–), 110.09 (s, –C–), 113.16 (s, –C–), 162.46 (s, C=O). *m/z* (%): 490 [(M^+-15), 8], 318 (6), 212 (14), 259 (3), 143 (8), 101 (100), 59 (70). HRMS: $C_{15}H_{22}NO_{10}$ (M^+-15), calcd 376.1244; found 376.1251.

1.1.2. 3-Ethoxycarbonylnitromethyl-1,2-*O*-isopropylidene-6-*O*-*p*-toluenesulfonyl-α-D-allofuranose (4). Compound **2** (1.2 g, 3.07 mmol) was dissolved in a 1:1:1 mixture of methanol/water/acetic acid (18 ml) and the solution stirred at room temperature for 22 h. The solvent was evaporated in vacuo, the traces of acetic acid were

co-evaporated with toluene (3×1 ml) and the resulting unstable compound **3** was immediately dissolved in dry pyridine (10 ml). Tosyl chloride (0.62 g, 3.37 mmol) was then added slowly to this cooled (−20°C) solution and the resulting mixture was stirred at −20°C for 10 h. The solvent was evaporated in vacuo and the residue submitted to flash column chromatography (ethyl acetate/hexane, 2:3) to give a mixture of compounds **4** (0.407 g, 64% over the two last steps) as a clear gum. $[\alpha]_D^{22}$=+29.0° (*c*, 0.6 in $CHCl_3$). Spectroscopic data for the main epimer: ν_{max} (NaCl): 3432 (–OH), 1750 (C═O), 1564 (–NO_2), 1379 (–NO_2). δ_H (500 MHz, $CDCl_3$): 1.31–1.33 (m, 6H, –CH_3 and –O–CH_2–CH_3), 1.63 (s, 3H, –CH_3), 2.45 (s, 3H, –CH_3), 4.11–4.15 (m, 2H, H_5 and H_6), 4.26–4.34 (m, 3H, $H_{6'}$ and –O–CH_2–CH_3), 4.55 (d, 1H, $J_{4,5}$=7.4 Hz, H_4), 4.81 (d, 1H, $J_{1,2}$=3.7 Hz, H_2), 5.85 (d, 1H, $J_{1,2}$=3.7 Hz, H_1), 5.91 (s, 1H, H_7), 7.35 (d, 2H, *J*=8.2 Hz, 2×Ar-H), 7.80 (d, 2H, *J*=8.2 Hz, 2×Ar-H). δ_C (75.3 MHz, $CDCl_3$): 13.72 (q, –CH_3), 21.69 (q, –CH_3), 26.42 (q, –CH_3), 26.55 (q, –CH_3), 63.34 (t, –CH_2–), 67.89 (d, –CH–), 72.24 (t, –CH_2–), 78.55 (d, –CH–), 81.28 (s, –C–), 85.49 (d, –CH–), 89.27 (d, –CH–), 104.25 (d, –CH–), 113.32 (s, –C–), 128.06 (d, –CH–), 130.00 (d, –CH–), 132.35 (s, –C–), 145.25 (s, –C–), 162.66 (s, C═O). *m/z* (%): 496 [(M^+−15), 0.5], 290 (2), 155 (60), 91 (100). HRMS (FAB): $C_{20}H_{28}NO_{12}S$ (M^++H), calcd 506.1332; found 506.1330.

1.1.3. 5-*O*-Ethoxycarbonyl-1,2-*O*-isopropylidene-3-nitromethyl-6-*O*-*p*-toluenesulfonyl-α-D-allofuranose (8). Tetrabutylammonium fluoride (0.32 ml, 1 M in THF) was added to a solution of compound **4** (0.16 g, 0.32 mmol) in dry THF (5 ml) and the mixture was stirred at room temperature for 7 h. The reaction mixture was evaporated in vacuo and the residue submitted to flash column chromatography (ethyl acetate/hexane, 1:2) to give the title compound (94 mg, 59%) as a clear gum. $[\alpha]_D^{21}$=+9.6° (*c*, 1.6 in $CHCl_3$). ν_{max} (NaCl): 3446 (–OH), 1746 (C═O), 1559 (–NO_2), 1357 (–NO_2). δ_H (500 MHz, $CDCl_3$): 1.27–1.29 (m, 6H, –O–CH_2–CH_3 and –CH_3), 1.46 (s, 3H, –CH_3), 2.42 (s, 3H, –CH_3), 4.02 (d, 1H, $J_{4,5}$=6.7 Hz, H_4), 4.14–4.18 (m, 3H, –O–CH_2–CH_3 and H_6), 4.47 (d, 1H, $J_{6,6'}$=11.5 Hz, $H_{6'}$), 4.56–4.58 (m, 2H, H_2 and H_7), 4.76 (d, 1H, *J*=14.6 Hz, $H_{7'}$), 4.95–4.97 (m, 1H, H_5), 5.86 (d, 1H, $J_{1,2}$=2.8 Hz, H_1), 7.31 (d, 2H, *J*=7.5 Hz, 2×Ar-H), 7.75 (d, 2H, *J*=7.5 Hz, 2×Ar-H). δ_C (75.3 MHz, $CDCl_3$): 14.11 (q, –CH_3), 21.67 (q, –CH_3), 26.41 (q, –CH_3), 26.99 (q, –CH_3), 65.01 (t, –CH_2–), 68.00 (t, –CH_2–), 71.66 (d, –CH–), 75.78 (t, –CH_2–), 77.70 (d, –CH–), 79.53 (s, –C–), 85.19 (d, –CH–), 104.65 (d, –CH–), 113.42 (s, –C–), 128.07 (d, –CH–), 129.86 (d, –CH–), 132.57 (s, –C–), 144.95 (s, –C–), 153.81 (s, C═O). *m/z* (%, FAB): 490 [(M^++H), 25], 334 (12), 185 (100). HRMS (FAB): $C_{20}H_{28}NO_{12}S$ calcd 506.1332; found 506.1336.

1.1.4. 1,2-*O*-Isopropylidene-6-*O*-methyl-3-nitromethyl-α-D-allofuranose (9). A solution of compound **8** (0.037 g, 0.07 mmol) and potassium carbonate (0.03 g) in methanol (3 ml) was stirred at room temperature for 16 h. The reaction mixture was neutralized with DOWEX 50W acidic resin, filtered and the solvents removed. The residue was submitted to flash column chromatography (ethyl acetate/hexane, 1:7) to give the title compound (0.009 g, 43% yield) as an oil. {$[\alpha]_D^{20}$=+32.20° (*c*, 0.9 in $CHCl_3$)}. ν_{max} (NaCl): 3410 (–OH); 1585 (–NO_2), 1376 (–NO_2). δ_H (500 MHz, $CDCl_3$): 1.32 (s, 3H, –CH_3), 1.51 (s, 3H, CH_3), 2.58 (bs, 1H, –OH), 3.41 (s, 3H, –CH_3), 3.48–3.51 (m, 1H, H_6), 3.61–3.64 (m, 1H, $H_{6'}$), 3.79 (d, 1H, $J_{4,5}$=8.6 Hz, H_4), 4.10–4.12 (m, 1H, H_5), 4.58 (d, 1H, $J_{1,2}$=3.5 Hz, H_2), 4.78 (d, 1H, $J_{7,7'}$=14.5 Hz, H_7), 5.01 (d, 1H, $J_{7,7'}$=14.5 Hz, $H_{7'}$), 5.92 (d, 1H, $J_{1,2}$=3.5 Hz, H_1). *m/z* (%, CI): 294 [(M^++H), 16], 278 (M^+−15, 12); 236 (100). HRMS (CI): $C_{11}H_{20}NO_8$ (M^++H), calcd 294.1188; found 294.1179.

1.1.5. 3-*O*-Benzyl-4-*O*-ethoxycarbonyl-6-deoxy-6-nitro-D-glucopyranose (16). Compound **11** (0.23 g, 0.57 mmol) was dissolved in a 1:1 mixture of trifluoroacetic acid/water (4 ml) and the solution was stirred at room temperature for 9 h. The solvent was evaporated in vacuo, the traces of acetic acid were co-evaporated with toluene (3×1 ml) and the resulting unstable compound **12** was immediately dissolved in dry THF (10 ml). Tetrabutylammonium fluoride (0.48 ml, 1 M in THF) was added to this solution and the resulting mixture was stirred at room temperature for 16 h. The solvent was evaporated in vacuo and the residue was submitted to flash column chromatography (ethyl acetate/hexane, 2:3) to give the title compounds (0.08 g, 26% yield over the two last steps) as a yellow oil. $[\alpha]_D^{20}$=−11.8° (*c*, 1.0 in $CHCl_3$). ν_{max} (NaCl): 3437 (–OH), 1748 (C═O), 1560 (–NO_2), 1373 (–NO_2). δ_H (300 MHz, $CDCl_3$): 1.29 (t, 3H, *J*=7.23 Hz, –O–CH_2–CH_3), 3.68–3.90 (m, 2H), 4.14–4.22 (m, 3H), 4.44–4.86 (m, 5H), 5.18 (d, 1H, *J*=3.6 Hz, H_1), 7.32 (s, 5H, 5×Ar-H). δ_C (75.3 MHz, $CDCl_3$): 14.15 (q, –CH_3), 65.07 (t, –CH_2–), 66.61 (d, –CH–), 72.26 (d, –CH–), 74.76 (d, –CH–), 75.35 (t, –CH_2–), 75.93 (t, –CH_2–), 79.40 (d, –CH–), 92.13 (d, –CH–), 127.86 (d, –CH–), 127.94 (d, 2×–CH–), 128.42 (d, 2×–CH–), 137.88 (s, –C–), 154.51 (C═O). *m/z* (%, CI): 372 [(M^++H), 10], 217 (24), 91 (100). HRMS (CI): $C_{16}H_{22}NO_9$ (M^++H), calcd 372.1295; found 372.1291.

1.1.6. 3-*O*-Benzyl-1,2-di-*O*-*tert*-butyldimethylsilyl-4-*O*-ethoxycarbonyl-6-deoxy-6-nitro-β-D-glucopyranose (17). A solution of compound **16** (0.07 g, 0.19 mmol) in dry DMF (1.5 ml) was added to a mixture of *tert*-butyldimethylsilyl chloride (0.28 g, 1.89 mmol) and imidazole (0.22 g, 3.02 mmol) in dry DMF (3 ml). The reaction mixture was stirred at room temperature for 18 h. The DMF was evaporated in vacuo and the residue was dissolved in chloroform (20 ml) and washed with water (3×10 ml). The organic layer was dried, filtered and evaporated. The residue was submitted to flash column chromatography (ethyl acetate/hexane, 1:12) to give the title compound (0.08 g, 67%) as an oil. {$[\alpha]_D^{22}$=−9.0° (*c*, 0.6 in $CHCl_3$)}. ν_{max} (NaCl): 1751 (C═O), 1563 (–NO_2), 1373 (–NO_2). δ_H (500 MHz, $CDCl_3$): 0.04 (s, 3H, –$SiCH_3$), 0.06 (s, 3H, –$SiCH_3$), 0.08 (s, 3H, –$SiCH_3$), 0.10 (s, 3H, –$SiCH_3$), 0.87 [s, 9H, –$SiC(CH_3)_3$], 0.90 [s, 9H, –$SiC(CH_3)_3$], 1.19 (t, 3H, *J*=7.0 Hz, –O–CH_2–CH_3), 3.49–3.54 (m, 2H, H_3 and H_4), 4.04–4.10 (m, 2H, –O–CH_2–CH_3), 4.21–4.25 (m, 1H, H_5), 4.40–4.43 (d, 1H, $J_{6,6'}$=13.3 Hz, H_6). 4.49–4.61 (m, 1H, $H_{6'}$), 4.60–4.68 (m, 3H, H_2 and –O–CH_2–Ph), 4.83 (d, 1H, $J_{1,2}$=11.24 Hz, H_1), 7.25–7.32 (m, 5H, 5×Ar-H). δ_C (75.3 MHz, $CDCl_3$): −5.11 (q, –$SiCH_3$), −4.25 (q, –$SiCH_3$), −4.12 (q, –$SiCH_3$), −3.78 (q, –$SiCH_3$), 14.01 (q, –O–CH_2–CH_3), 17.96 [s, –Si$C(CH_3)_3$], 18.05 [s, –Si$C(CH_3)_3$], 25.85 [q, –$SiC(CH_3)_3$], 25.95 [q,

$SiC(CH_3)_3$], 64.91 (t, $-CH_2-$), 70.74 (d, –CH–), 75.23 (d, –CH–), 75.78 (t, $-CH_2-$), 75.99 (d, –CH–), 76.03 (t, $-CH_2-$), 82.94 (d, –CH–), 98.28 (d, –CH–), 127.47 (d, –CH–), 127.48 (d, 2×–CH–), 128.19 (d, 2×–CH–), 138.06 (s, –C–), 154.44 (s, C=O). *m/z* (%): 542 [(M^+-57), 0.1], 434 (1), 360 (1), 259 (3), 147 (7), 91 (100), 73 (20). Anal: $C_{28}H_{49}NO_9Si_2$ requires: C, 56.06; H, 8.23; N, 2.33; found: C, 56.42; H, 8.32; N, 2.32.

1.1.7. 3-*O*-Benzyl-1,2-di-*O*-*tert*-butyldimethylsilyl-6-deoxy-6-nitro-β-D-glucopyranose (18). A solution of compound **17** (0.08 g, 0.13 mmol) and potassium carbonate (0.04 g) in methanol (9 ml) was stirred at room temperature for 16 h. The reaction mixture was neutralized with DOWEX 50W acidic resin, filtered and the solvents removed. The residue was submitted to flash column chromatography (ethyl acetate/hexane, 1:7) to give the title compound (0.042 g, 61% yield) as a solid. Mp: 101–103°C (hexane). $\{[\alpha]_D^{20}=-1.33°$ (*c*, 1.0 in $CHCl_3)\}$. ν_{max} (NaCl): 3505 (–OH), 1560 ($-NO_2$), 1362 ($-NO_2$). δ_H (500 MHz, $CDCl_3$): 0.05 (s, 3H, $-SiCH_3$), 0.07 (s, 3H, $-SiCH_3$), 0.14 (s, 3H, $-SiCH_3$), 0.15 (s, 3H, $-SiCH_3$), 0.87 [s, 9H, $-SiC(CH_3)_3$], 0.95 [s, 9H, $-SiC(CH_3)_3$], 3.26–3.32 (m, 2H, H_4 and H_5), 3.42 (dd, 1H, $J_{3,4}=J_{3,2}=7.30$ Hz, H_3), 3.99–4.02 (m, 1H, H_6), 4.40 (dd, 1H, $J_{6,6'}=13.0$ Hz, $J_{6',5}=9.8$ Hz, $H_{6'}$), 4.55–4.58 (m, 2H, H_2 and –O–CH_2–Ph), 4.66 (d, 1H, $J=11.5$ Hz, –O–CH_2–Ph), 4.99 (d, 1H, $J_{1,2}=12.2$ Hz, H_1), 7.34–7.40 (m, 5H, 5×Ar-H). δ_C (75.3 MHz, $CDCl_3$): −5.04 (q, $-SiCH_3$), −4.21 (q, $-SiCH_3$), −4.05 (q, $-SiCH_3$), −3.61 (q, $-SiCH_3$), 17.99 [s, $-SiC(CH_3)_3$], 18.10 [s, $-SiC(CH_3)_3$], 25.91 [q, $-SiC(CH_3)_3$], 26.03 [q, $-SiC(CH_3)_3$], 70.46 (d, –CH–), 72.24 (d, –CH), 75.82 (t, $-CH_2-$), 76.09 (d, –CH–), 76.46 (t, $-CH_2-$), 85.35 (d, –CH–), 98.27 (d, –CH–), 127.97 (d, 2×–CH–), 128.37 (d, –CH–), 129.02 (d, 2×–CH–), 138.45 (s, –C–). *m/z* (%): 542 [(M^+-57), 0.1], 378 (0.3), 187 (3), 91 (100), 73 (23). Anal: $C_{25}H_{45}NO_7Si_2$ requires: C, 56.89; H, 8.59; N, 2.65; found: C, 56.62; H, 8.70; N, 2.69.

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