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A NOVEL CLASS OF GLYCOSYL DONORS: ANOMERIC *S*-XANTHATES OF 2-AZIDO-2-DEOXY-D-GALACTOPYRANOSYL DERIVATIVES[1]

Alberto Marra, Françoise Gauffeny and Pierre Sinaÿ*
Ecole Normale Supérieure, Laboratoire de Chimie, UA 1110,
24 Rue Lhomond, 75231 Paris Cedex 05, France

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Abstract – Variously substituted *O*-ethyl *S*-(2-azido-2-deoxy-D-galactopyranosyl) dithiocarbonates have been easily prepared *via* a two-step azidoxanthation reaction of the corresponding galactals (1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitols). They are efficient glycosyl donors for the stereoselective synthesis of protected precursors of biologically important galactosamine-containing oligosaccharides.

INTRODUCTION

Aryl and alkyl *S*-glycosides are stable under major classical chemical carbohydrate transformations and have been converted, over the last few years, into efficient glycosyl donors by various electrophilic reagents[2], heavy metal salts[3], oxidations[4], and very recently, heterogeneous[5] or homogeneous[6] one-electron transfer from sulfur. Consequently, *S*-glycosides are currently at the front scene in this field[7].

We have demonstrated[8] that a *S*-glycosyl xanthate of *N*-acetylneuraminic acid is a stereoselective glycosylating agent. This was a novel application of a class of *S*-glycosides (*O*-alkyl *S*-glycosyl dithiocarbonates) which have attracted attention mainly for the preparation of 1-thio sugars[9] and thioglycosides[10].

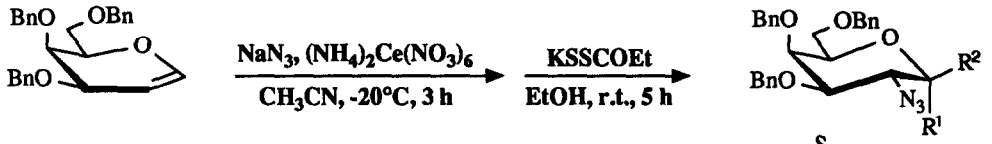
The azidonitration[11] of galactals, despite its rather moderate efficiency, still constitute a welcome entry to anomeric nitrates of 2-azido-2-deoxy-D-galactopyranose derivatives. A problem is therefore the one-step high-yield conversion of these nitrates into potentially efficient *S*-glycosyl donors for the stereoselective synthesis of protected precursors of biologically important galactosamine-containing oligosaccharides. We demonstrate in this work that anomeric *S*-xanthates provide a solution to this problem.

RESULTS

Azidonitration of tri-*O*-benzyl-D-galactal (**1**) gave a crude mixture[12,13] which was directly treated with commercially available *O*-ethyl *S*-potassium dithiocarbonate in ethanol at room temperature to give *O*-ethyl *S*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl) dithiocarbonate (**3**) (37% yield, based on **1**) together with 6% of the crystalline α-anomer **2** isolated by chromatography on silica gel (Scheme 1). Other minor products were not investigated.

Acetylation of known[14] 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-*lyxo*-hex-1-enitol (**4**) gave the acetate **5** which was next submitted to azidonitration, following established procedures. After column chromatography of the crude mixture, the α-D-*galacto* azidonitrate **7** was obtained in crystalline form in 44% yield. A small amount (~4%) of α-D-*talo* azidonitrate **8** was also isolated, probably contaminated by β-D-*galacto* isomer. A comparison of these results with those originally obtained by Lemieux and Ratcliffe[11] on tri-*O*-acetyl-D-galactal shows that

the presence of the 4,6-*O*-benzylidene fused ring, introducing rigidity onto the galactal ring, increased the selectivity of the addition of the azido group at C-2.



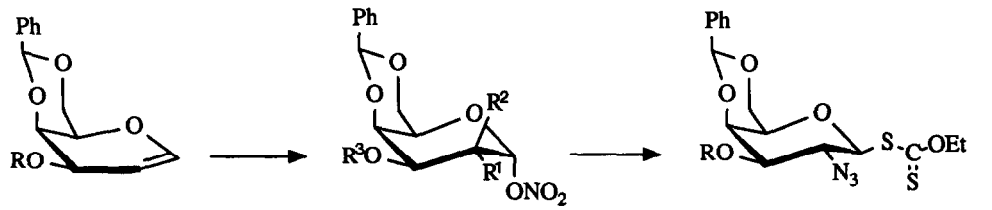
1

2 R^1 = S-C(=S)-OEt, R^2 = H

3 R^1 = H, R^2 = S-C(=S)-OEt

Scheme 1

Similarly, azidonitration of 3-*O*-benzyl-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*lyxo*-hex-1-enitol[14] (**6**) gave, after column chromatography, the α-D-*galacto* azidonitrate **9** in crystalline form in 40% yield. No trace of β-D-*galacto* or D-*talo* azidonitrates was found. Displacement of α-nitrates **7** and **9** with *O*-ethyl *S*-potassium dithiocarbonate in acetonitrile for 5 h at room temperature gave the β-*S*-xanthates **10** and **11** in 97 and 90% yield, respectively (Scheme 2).



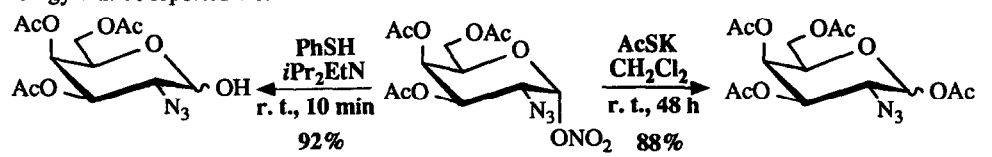
4 R = H
5 R = Ac
6 R = Bn

7 R^1 = N_3, R^2 = H, R^3 = Ac
8 R^1 = H, R^2 = N_3, R^3 = Ac
9 R^1 = N_3, R^2 = H, R^3 = Bn

10 R = Ac
11 R = Bn

Scheme 2

When the direct anomeric S_N2 displacement of the α-D-nitrates with alkyl and aryl thiolates was attempted, almost quantitative denitration was observed. This reaction, which is in sharp contrast with the successful anomeric S_N2 displacement of nitrates with sodium alkoxides[15,16], was in retrospect not unexpected since the mechanism of denitration of nitrate esters by sulfide or polysulfide ions was previously studied and discussed[17]. Anomeric denitration is usually achieved[12] with sodium nitrite in aqueous dioxane at 80°C for about 6 h. We found that 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl nitrate[11] (**12**) is conveniently denitrated using the conditions shown in Scheme 3 to give known[18] **13**. The generalization of this useful methodology will be reported elsewhere.

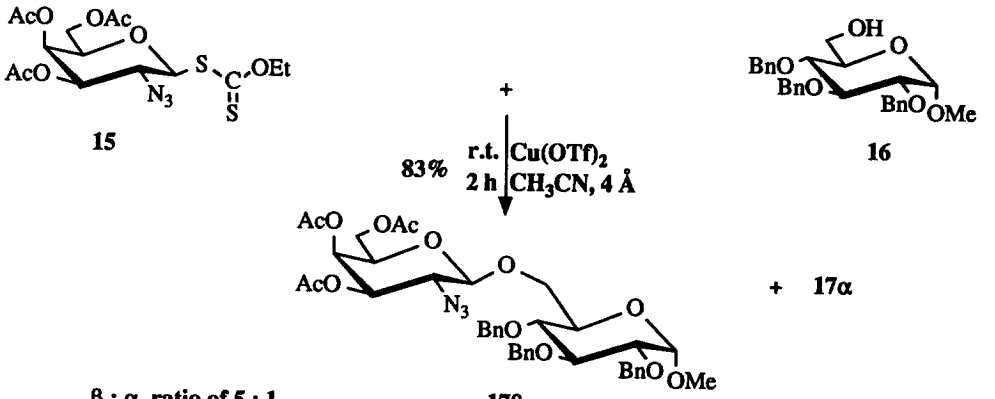


13 **12** **14**

Scheme 3

We observed a similar reluctance for anomeric displacement of nitrates with potassium thioacetate in dichloromethane at room temperature when high yields of 1-*O*-acetyl derivatives[19] were obtained (Scheme 3).

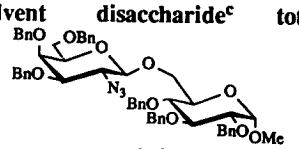
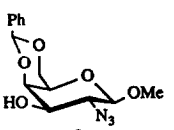
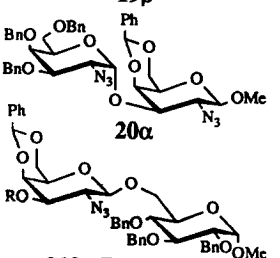
With various anomeric *S*-xanthates on hand, their glycosylating properties were then evaluated. As an introduction to the field, the xanthate[20] **15** was reacted at room temperature with methyl 2,3,4-tri-*O*-benzyl-α-D--glucopyranoside[21] (**16**) in acetonitrile in the presence of copper(II) triflate and 4 Å molecular sieves to give selectively the crystalline β-disaccharide **17β** (Scheme 4).The formation of the corresponding α-disaccharide **17α** was also observed (β:α ratio of 5:1). The β-selectivity obtained in acetonitrile is due to the stereoselective kinetic formation[22] of a reactive α-nitrilium intermediate acting as the glycosylating species[23]. We assumed that the formation of the nitrilium was the rate-determining step.



Scheme 4

We then demonstrated (Table I) the excellent capacity of xanthate **3**, **10** and **11** to act as selective α or β glycosyl donors.

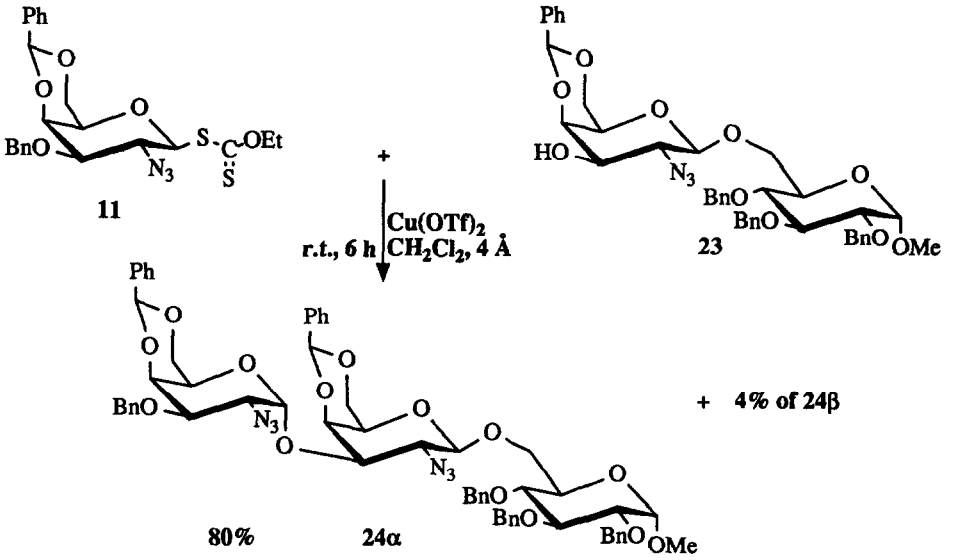
Table I. Glycosylation *via* *S*-Glycosyl Xanthates[a]

entry	xanthate	alcohol	promoter[b]/solvent	disaccharide[c]	total yield (%)	α:β ratio
1	3	16	B/CH_3CN	 **19β**	92	1:6
2	3	 **18**[24]	B/CH_2Cl_2	 **20α**	90	16:1
3	10	16	A/CH_3CN	**21β** R = Ac	86	1:6
4	11	16	B/CH_3CN	**22β** R = Bn	85	1:5.5

[a] Donor/acceptor ratio of 1.5:1. [b] Promoter A: DMTST; B: $Cu(OTf)_2$. [c] Only the major anomer was shown.

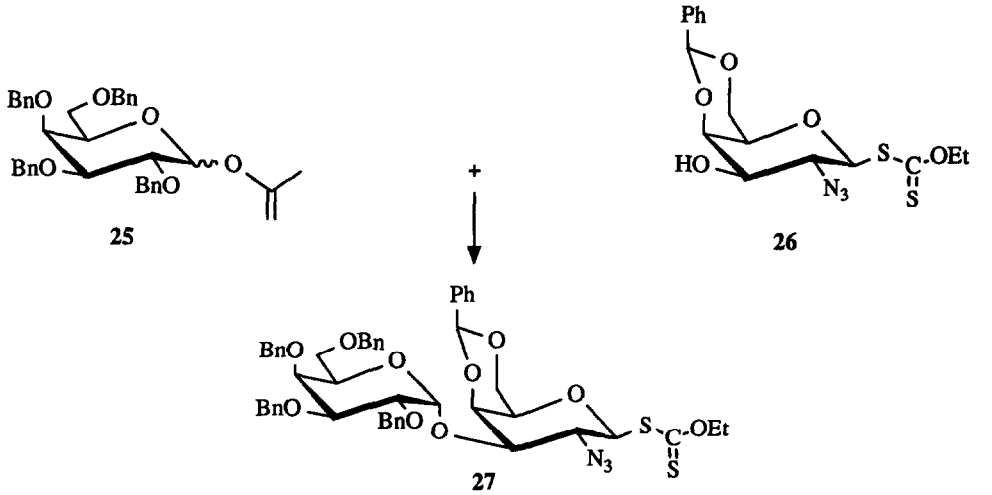
According to specific cases, dimethyl(methylthio)sulfonium triflate[25] (DMTST), promoter A, or copper(II) triflate, promoter B, were found to be the best promoters. The reaction time was 1-5 h, except in the case of the CH_2Cl_2/promoter B combination where the completion of the reaction takes about 18 h (entry 2), resulting in an excellent stereoselectively (β:α ratio of 16:1). Also isolated in these reactions were small amounts of the corresponding disaccharides **19α**, **20β**, **21α**, and **22α**.

Higher saccharides have also been selectively synthesized. Deacetylation of the disaccharide **21β** gave the alcohol **23** which was very selectively (α:β ratio of 20:1) glycosylated with xanthate **11** (Scheme 5).



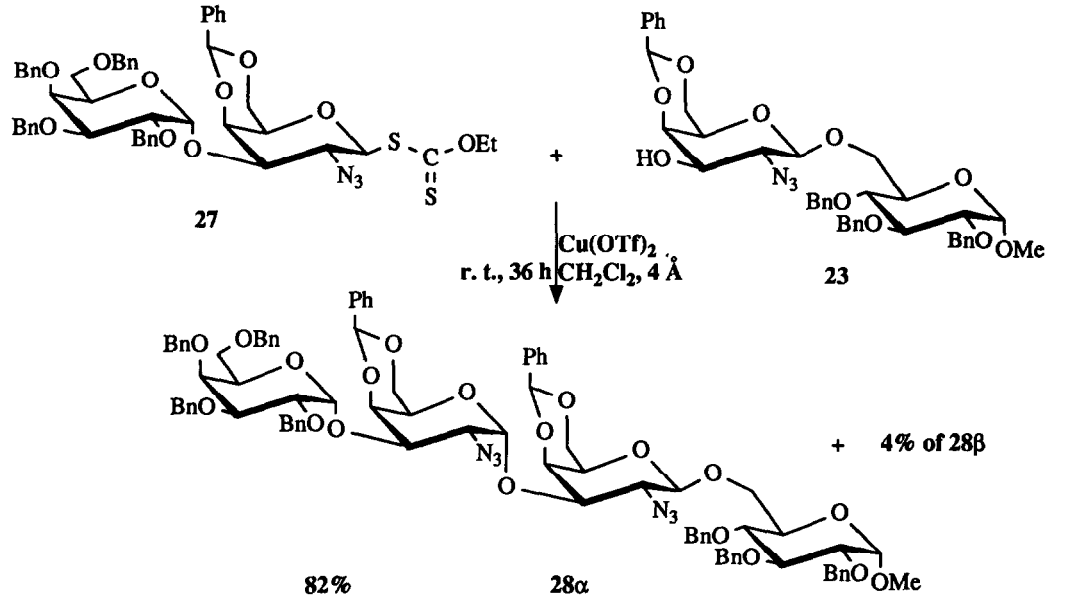
Scheme 5

Finally, the xanthate **27** was first prepared according to a novel glycosylation procedure[26] (Scheme 6).



Scheme 6

Condensation of this xanthate with the acceptor **23** in dichloromethane and in the presence of $Cu(OTf)_2$ very selectively (α:β ratio of 20:1) gave the protected tetrasaccharide **28α** (Scheme 7). The corresponding β-tetrasaccharide **28β** was also isolated and characterized.



Scheme 7

We very recently discovered[6] that xanthate **2** can also be activated in acetonitrile by a novel kind of promoter, commercially available tris(4-bromophenyl)ammoniumyl hexachloroantimonate.

In conclusion, anomeric *S*-xanthates were conveniently prepared by a two-step azidoxanthation sequence from a series of galactals which were in turn easily derived from thiophenyl galactosides by a well-established reductive lithiation-elimination sequence[14]. They constitute a novel class of glycosyl donors for the stereoselective preparation of either α- or β-protected precursors of biologically important galactosamine--containing oligosaccharides. Further developments of this strategy are now being achieved in our group.

EXPERIMENTAL

General methods. – Melting points were determined with a Büchi Model 510 capillary apparatus and are uncorrected. Optical rotations were measured at 20 ± 2° with a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed at the Service Central d'Analyse (C.N.R.S., Vernaison). ^{1}H-N.m.r. spectra were recorded with Bruker AC-250 and AM-400 spectrometers for solutions in $CDCl_3$ (internal Me_4Si). ^{13}C-N.m.r. spectra (62.90 MHz) were recorded for solutions in $CDCl_3$, adopting δ 77.0 for the central line of $CDCl_3$. Reactions were monitored by t.l.c. on Silica Gel 60 F_{254} (Merck) with detection by charring with sulfuric acid. Flash column chromatography was performed on Silica Gel 60 (230-400 mesh, Merck). Commercial *O*-ethyl *S*-potassium dithiocarbonate (potassium xanthogenate) was crystallized from acetone-ether, then dried under *vacuum*.

O-Ethyl S-(2-azido-3,4,6-tri-O-benzyl-2-deoxy-α- and -β-D-galactopyranosyl) dithiocarbonate (**2** *and* **3**).

– To a vigorously stirred, cooled (-20°) mixture of **1** (5.00 g, 12 mmol), sodium azide (1.17 g, 18 mmol), and anhydrous acetonitrile (70 mL) was added cerium(IV) ammonium nitrate (19.70 g, 36 mmol). Stirring was continued for 3 h, then the suspension was diluted with ice-cold dichloromethane (300 mL), washed with cold water (50 mL), neutralized with cold, saturated aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and concentrated. The residue was treated with *O*-ethyl *S*-potassium dithiocarbonate (3.80 g, 24 mmol) and ethanol (50 mL) for 5 h at room temperature. The solution was diluted with dichloromethane (200 mL), washed with water (40 mL), dried ($MgSO_4$), and concentrated. The residue was eluted from a column of silica gel with carbon tetrachloride-diisopropylic ether (from 20:1 to 10:1) to give, first, **2** (0.42 g, 6%), m.p. 62-63° (from ether-hexane), $[\alpha]_D$ +111° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data (250 MHz): δ 7.40-7.24 (m, 15 H, 3 Ph), 6.33 (d, 1 H, $J_{1,2}$ 5.6 Hz, H-1), 4.88 and 4.53 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.73 and 4.67 (2 d, 2 H, *J* 11.4 Hz, PhCH_2), 4.64 (q, 2 H, *J* 7.1 Hz, CH_2CH$_3$), 4.49 (dd, 1 H, $J_{2,3}$ 10.6 Hz, H-2), 4.46 and 4.39 (2 d, 2 H, *J* 11.6 Hz, PhCH_2), 4.04-3.99 (m, 2 H, H-4,5), 3.63 (dd, 1 H, $J_{5,6a}$ 8.0, $J_{6a,6b}$ 9.0 Hz, H-6a), 3.52 (dd, 1 H, $J_{5,6b}$ 5.6 Hz, H-6b), 3.51 (dd, 1 H, $J_{3,4}$ 2.3 Hz, H-3), 1.40 (t, 3 H, CH$_2$CH_3).

Anal. Calc. for $C_{30}H_{33}N_3O_5S_2$: C, 62.15; H, 5.74; N, 7.25. Found: C, 61.84; H, 5.75; N, 7.20.

Eluted second was **3** (2.57 g, 37%), $[\alpha]_D$ +40° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data (250 MHz): δ 7.40-7.26 (m, 15 H, 3 Ph), 5.16 (d, 1 H, $J_{1,2}$ 10.8 Hz, H-1), 4.87 and 4.56 (2 d, 2 H, *J* 11.4 Hz, PhCH_2), 4.75 and 4.68 (2 d, 2 H, *J* 11.6 Hz, PhCH_2), 4.63 (q, 2 H, *J* 7.0 Hz, CH_2CH$_3$), 4.48 and 4.39 (2 d, 2 H, *J* 11.6 Hz, PhCH_2), 4.03-3.95 (m, 2 H), 3.68-3.52 (m, 4 H), 1.39 (t, 3 H, CH$_2$CH_3).

Anal. Found: C, 61.88; H, 5.70; N, 7.21.

*3-O-Acetyl-1,5-anhydro-4,6-O-benzylidene-2-deoxy-*D*-lyxo-hex-1-enitol* (**5**). – A solution of **4** (1.97 g, 8.4 mmol), pyridine (25 mL), acetic anhydride (25 mL), and 4-dimethylaminopyridine (~10 mg) was kept for 15 min at room temperature, then concentrated. The residue was eluted from a column of silica gel with 2:1 hexane-ethyl acetate to give **5** (2.20 g, 95%), m.p. 95-96° (from ethyl acetate-hexane), $[\alpha]_D$ +159° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data (250 MHz): δ, amongst others, 6.55 (dd, 1 H, $J_{1,2}$ 6.5, $J_{1,3}$ 2.2 Hz, H-1), 5.63 (s, 1 H, PhC*H*), 5.50 (m, 1 H, H-3), 2.12 (s, 3 H, Ac).

Anal. Calc. for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.03; H, 6.01.

*3-O-Acetyl-2-azido-4,6-O-benzylidene-2-deoxy-*α*-*D*-galactopyranosyl nitrate* (**7**). – A solution of **5** (1.93 g, 7 mmol) in anhydrous acetonitrile (60 mL) was added dropwise to a stirred, cooled (-20°) mixture of sodium azide (680 mg, 10.5 mmol) and cerium(IV) ammonium nitrate (11.34 g, 21 mmol). The suspension was stirred vigorously for 4 h at -20°, then diluted with ice-cold dichloromethane (200 mL), washed with cold water (50 mL), neutralized with cold, saturated aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and concentrated. Column chromatography of the residue (from 4:1 to 3:1 hexane-ethyl acetate, containing 0.3% of triethylamine) gave, first, **7** (1.17 g, 44%), m.p. 117-118° (from ethyl acetate-hexane), $[\alpha]_D$ +189° (*c* 0.4, $CHCl_3$). ^{1}H-N.m.r. data (250 MHz): δ 7.52-7.38 (m, 5 H, Ph), 6.43 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.55 (s, 1 H, PhC*H*), 5.20 (dd, 1 H, $J_{2,3}$ 11.3, $J_{3,4}$ 3.3 Hz, H-3), 4.54 (dd, 1 H, $J_{4,5}$ ~0.5 Hz, H-4), 4.39 (dd, 1 H, H-2), 4.30 (dd, 1 H, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 12.8 Hz, H-6a), 4.06 (dd, 1 H, $J_{5,6b}$ 1.6 Hz, H-6b), 3.97 (ddd, 1 H, H-5), 2.17 (s, 3 H, Ac).

Anal. Calc. for $C_{15}H_{16}N_4O_8$: C, 47.37; H, 4.24. Found: C, 47.50; H, 4.25.

Eluted second was 3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-talopyranosyl nitrate (**8**; 106 mg, 4%) contaminated by an unknown product. ^{1}H-N.m.r. data (250 MHz): δ 7.59-7.36 (m, 5 H, Ph), 6.34 (d, 1 H, $J_{1,2}$ ~1.0 Hz, H-1), 5.52 (s, 1 H, PhC*H*), 5.24 (dd, 1 H, $J_{2,3} = J_{3,4}$ 4.0 Hz, H-3), 4.46 (ddd, 1 H, $J_{4,5} = J_{2,4}$ ~0.5 Hz, H-4), 4.34 (dd, 1 H, $J_{5,6a}$ 1.4, $J_{6a,6b}$ 12.9 Hz, H-6a), 4.10 (dd, 1 H, $J_{5,6b}$ 1.8 Hz, H-6b), 4.03 (ddd, 1 H, H-2), 3.93 (ddd, 1 H, H-5), 2.18 (s, 3 H, Ac).

2-Azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl nitrate (**9**). – Treatment of **6** (1.36 g, 4 mmol) as for the preparation of **7** gave, after column chromatography (3:1 hexane-ethyl acetate, containing 0.3% of triethylamine), **9** (685 mg, 40%), m.p. 131-132° (from ethyl acetate-hexane), $[a]_D$ +161° (*c* 1.5, $CHCl_3$). ^{1}H-N.m.r. data (250 MHz): δ 7.56-7.32 (m, 10 H, 2 Ph), 6.38 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.47 (s, 1 H, PhC*H*), 4.80 and 4.74 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.32 (dd, 1 H, $J_{2,3}$ 10.8, $J_{3,4}$ 4.0 Hz, H-3), 4.26 (dd, 1 H, $J_{5,6a}$ 1.7, $J_{6a,6b}$ 12.7 Hz, H-6a), 4.23 (dd, 1 H, $J_{4,5}$ ~0.5 Hz, H-4), 4.00 (dd, 1 H, $J_{5,6b}$ 1.6 Hz, H-6b), 3.90 (dd, 1 H, H-2), 3.80 (ddd, 1 H, H-5).

Anal. Calc. for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.71. Found: C, 56.27; H, 4.59.

O-Ethyl S-(3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-β-D-galactopyranosyl) dithiocarbonate (**10**). – A solution of **7** (0.95 g, 2.5 mmol) and *O*-ethyl *S*-potassium dithiocarbonate (0.80 g, 5 mmol) in acetonitrile (20 mL) was kept for 5 h at room temperature, then diluted with dichloromethane (200 mL), washed with water (30 mL), dried ($MgSO_4$), and concentrated. The residue was eluted from a column of silica gel with 4:1 hexane-ethyl acetate (containing 0.3% of triethylamine) to give **10** (1.06 g, 97%), $[\alpha]_D$ +75° (*c* 0.5, $CHCl_3$). ^{1}H-N.m.r. data (250 MHz): δ 7.52-7.32 (m, 5 H, Ph), 5.52 (s, 1 H, PhC*H*), 5.35 (d, 1 H, $J_{1,2}$ 10.6 Hz, H-1), 4.95 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 3.4 Hz, H-3), 4.68 (q, 2 H, *J* 7.1 Hz, CH_2CH$_3$), 4.44 (dd, 1 H, $J_{4,5}$ ~1.0 Hz, H-4), 4.32 (dd, 1 H, $J_{5,6a}$ 1.6, $J_{6a,6b}$ 12.6 Hz, H-6a), 4.12 (dd, 1 H, H-2), 4.02 (dd, 1 H, $J_{5,6b}$ 1.8 Hz, H-6b), 3.63 (ddd, 1 H, H-5), 2.18 (s, 3 H, Ac), 1.42 (t, 3 H, CH$_2$CH_3)

Anal. Calc. for $C_{18}H_{21}N_3O_6S_2$: C, 49.19; H, 4.82. Found: C, 49.20; H, 4.88.

O-Ethyl S-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-galactopyranosyl) dithiocarbonate (**11**). – Treatment of **9** (0.86 g, 2 mmol) as for the preparation of **10** (reaction time: 2 h) gave **11** (0.88 g, 90%), m.p. 126-127° (from ethyl acetate-hexane), $[\alpha]_D$ + 55° (*c* 0.9, $CHCl_3$). ^{1}H-N.m.r. data (250 MHz): δ 7.54-7.33 (m, 10 H, 2 Ph), 5.48 (s, 1 H, PhC*H*), 5.22 (d, 1 H, $J_{1,2}$ 10.7 Hz, H-1), 4.78 (s, 2 H, PhCH_2), 4.66 (q, 2 H, *J* 7.1 Hz, CH_2CH$_3$), 4.30 (dd, 1 H, $J_{5,6a}$ 1.4, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.18 (dd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ ~0.5 Hz, H-4), 4.05 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 3.98 (dd, 1 H, $J_{5,6b}$ 1.6 Hz, H-6b), 3.61 (dd, 1 H, H-3), 3.47 (ddd, 1 H, H-5), 1.41 (t, 3 H, CH$_2$CH_3).

Anal. Calc. for $C_{23}H_{25}N_3O_5S_2$: C, 56.65; H, 5.17. Found: C, 56.57; H, 5.13.

Denitration of 3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl nitrate. – A solution of **12** (113 mg, 0.3 mmol) in thiophenol (1.5 mL) was treated at room temperature with *N,N*-diisopropylethylamine (28 μL, 0.3 mmol). After 10 min the mixture was concentrated and eluted from a column of silica gel with 1:1 ethyl acetate-hexane to give known **13**[18] (91 mg, 92%). ^{1}H-N.m.r. spectrum (250 MHz) was consistent with the assigned structure.

Treatment of azidonitrate **12** *with potassium thioacetate.* – A mixture of **12** (113 mg, 0.3 mmol), anhydrous potassium thioacetate (0.10 g, 0.9 mmol), and anhydrous dichloromethane (4 mL) was stirred for 48 h at room temperature , then filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 2:1 hexane-ethyl acetate to give, first, **14** (98 mg, 88%) as an ~3:1 mixture of β and α[19] anomers. ^{1}H-N.m.r. data (250 MHz): δ, amongst others, 6.33 (d, $J_{1,2}$ 3.6 Hz, H-1α), 5.56 (d, $J_{1,2}$ 8.4 Hz, H-1β), 5.48 (dd, $J_{3,4}$ 3.1, $J_{4,5}$ 1.2 Hz, H-4α), 5.38 (dd, $J_{3,4}$ 3.4, $J_{4,5}$ 1.0 Hz, H-4β), 5.31 (dd, $J_{2,3}$ 11.0 Hz, H-3α), 4.90 (dd, $J_{2,3}$ 10.9 Hz, H-3β), 3.95 (dd, H-2α), 3.84 (dd, H-2β), 2.21, 2.17, 2.07, and 2.04 (4 s, 4 Acβ), 2.18, 2.17, 2.08, and 2.04 (4 s, 4 Acα). C.i. (ammonia) mass spectrum: *m/z* 391 $(M + 18)^+$.

Further elution gave **13** (7 mg, 7%).

Methyl 6-O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α- and -β-D-galactopyranosyl)-2,3,4-tri-O-benzyl-α-D--glucopyranoside (**17**α *and* **17**β). – A mixture of **16** (93 mg, 0.2 mmol), **15** (130 mg, 0.3 mmol), activated 4 Å

powdered molecular sieves (0.20 g), and anhydrous acetonitrile (2 mL) was stirred for 15 min at room temperature. Copper(II) triflate (0.43 g, 1.2 mmol) was added and stirring was continued for 2 h at room temperature. The suspension was treated with an excess of diisopropylamine, then concentrated, diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 6:1 toluene-ethyl acetate to give a mixture (130 mg, 83%) of **17β** and **17α** in a 5:1 ratio (^{1}H-n.m.r. analysis). Crystallization from ethyl acetate-hexane gave pure **17β**, m.p. 144-146°, $[\alpha]_D$ -8° (*c* 0.8, $CHCl_3$). ^{1}H-N.m.r. data (400 MHz): δ 7.37-7.26 (m, 15 H, 3 Ph), 5.30 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 0.8 Hz, H-4'), 4.99 and 4.82 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.94 and 4.63 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.80 and 4.65 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.76 (dd, 1 H, $J_{2',3'}$ 10.8 Hz, H-3'), 4.62 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.20 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1'), 4.14-4.07 (m, 3 H, H-6a,6'a,6'b), 4.01 (dd, 1 H, $J_{2,3}$ 9.7, $J_{3,4}$ 9.0 Hz, H-3), 3.82 (ddd, 1 H, $J_{4,5}$ 10.2, $J_{5,6a}$ 1.8, $J_{5,6b}$ 4.7 Hz, H-5), 3.77 (ddd, 1 H, $J_{5',6'a} = J_{5',6'b}$ 6.8 Hz, H-5'), 3.72 (dd, 1 H, H-2'), 3.70 (dd, 1 H, $J_{6a,6b}$ 10.8 Hz, H-6b), 3.55 (dd, 1 H, H-2), 3.54 (dd, 1 H, H-4), 3.39 (s, 3 H, MeO), 2.11, 2.05, and 2.02 (3 s, 9 H, 3 Ac).

Anal. Calc. for $C_{40}H_{47}N_3O_{13}$: C, 61.77; H, 6.09; N, 5.40. Found: C, 61.89; H, 5.95; N, 5.30.

^{1}H-N.m.r. data (250 MHz) of **17α**: δ, amongst others, 7.36-7.26 (m, 15 H, 3 Ph), 5.39 (dd, 1 H, $J_{3',4'}$ 3.3, $J_{4',5'}$ ~0.6 Hz, H-4'), 5.27 (dd, 1 H, $J_{2',3'}$ 11.2 Hz, H-3'), 5.06 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), 4.58 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 3.38 (s, 3 H, MeO), 2.17, 2.05, and 1.98 (3 s, 9 H, 3 Ac).

When the reaction was carried out in the presence of DMTST instead of $Cu(OTf)_2$, poor yields of disaccharide derivatives were obtained.

Methyl 6-O-(2-azido-tri-O-benzyl-2-deoxy-α- and -β-D-galactopyranosyl)-2,3,4-tri-O-benzyl-α-D-gluco-pyranoside (**19α** *and* **19β**). – A mixture of **16** (93 mg, 0.2 mmol), **3** (174 mg, 0.3 mmol), activated 4 Å powdered molecular sieves (0.20 g), and anhydrous acetonitrile (2 mL) was stirred for 15 min at room temperature, then cooled to 0°. Copper(II) triflate (0.43 g, 1.2 mmol) was added and stirring continued for 5 h at 0°. The suspension was treated with an excess of diisopropylamine, then concentrated, diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 3:1 carbon tetrachloride-diisopropyl ether to give, first, **19α** (26 mg, 14%), $[\alpha]_D$ +81° (*c* 1, $CHCl_3$). N.m.r. data: ^{1}H (400 MHz), δ, amongst others, 7.40-7.22 (m, 30 H, 6 Ph), 4.98 and 4.80 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.98 (d, 1 H, $J_{1',2'}$ 3.3 Hz, H-1'), 4.87 and 4.52 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.87 and 4.55 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.78 and 4.65 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.72 and 4.64 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.57 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.44 and 4.37 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 3.33 (s, 3 H, Meo); ^{13}C, δ, amongst others, 98.52 (C-1'), 97.85 (C-1).

Anal. Calc. for $C_{55}H_{59}N_3O_{10}$: C, 71.64; H, 6.45; N, 4.56. Found: C, 71.85; H, 6.42; N, 4.54.

Eluted second was **19β** (144 mg, 78%), m.p. 92-93° (from ethyl acetate-hexane), $[\alpha]_D$ +3° (*c* 1.6, $CHCl_3$). N.m.r. data: ^{1}H (400 MHz), δ 7.40-7.23 (m, 30 H, 6 Ph), 4.97 and 4.80 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.90 and 4.64 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.86 and 4.52 (2 d, 2 H, *J* 11.4 Hz, PhCH_2), 4.78 and 4.64 (2 d, 2 H, *J* 11.6 Hz, PhCH_2), 4.70 and 4.65 (2 d, 2 H, *J* 11.8 Hz, PhCH_2), 4.59 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.43 and 4.39 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.09 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.08 (dd, 1 H, $J_{5,6a}$ 1.8, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.98 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3), 3.87 (dd, 1 H, $J_{3',4'}$ 2.8, $J_{4',5'}$ ~0.5 Hz, H-4'), 3.85 (dd, 1 H, $J_{2',3'}$ 10.3 Hz, H-2'), 3.79 (ddd, 1 H, $J_{4,5}$ 10.2, $J_{5,6b}$ 4.6 Hz, H-5), 3.63 (dd, 1 H, $J_{6a,6b}$ 10.8 Hz, H-6b), 3.60 (dd, 1 H, $J_{5',6'a}$ 7.6, $J_{6'a,6'b}$ 9.0 Hz, H-6'a), 3.56-3.51 (m, 3 H, H-2,4,6'b), 3.44 (ddd, 1 H, $J_{5',6'b}$ 5.6 Hz, H-5'), 3.35 (s, 3 H, MeO), 3.29 (dd, 1 H, H-3'); ^{13}C, δ, amongst others, 102.47 (C-1'), 98.06 (C-1).

Anal. Found: C, 71.34; H, 6.40; N, 4.48.

Use of **2** as glycosyl donor gave similar results.

When the reaction was carried out in the presence of DMTST (0°, 1.5 h) instead of $Cu(OTf)_2$, 70% of a 5:1 mixture of **19β** and **19α** was isolated together with ~20% of unreacted **16**.

Methyl 2-azido-3-O-(2-azido-3,4,6-tri-O-benzyl-2-deoxy-α- and -β-D-galactopyranosyl)-4,6-O-benzylidene-2-deoxy-β-D-galactopyranoside (**20α** *and* **20β**). – A mixture of **18**[24] (61 mg, 0.2 mmol), **3** (174 mg, 0.3 mmol), activated 4 Å powdered molecular sieves (0.20 g), and anhydrous dichloromethane (2 mL) was stirred for 15 min at room temperature. Copper(II) triflate (0.43 g, 1.2 mmol) was added and stirring was continued for 18 h at room temperature. The suspension was treated with an excess of diisopropylamine, diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 4:1 toluene-ethyl acetate (containing 0.3% of triethylamine) to give a mixture (138 mg, 90%) of **20α** and **20β** in a 16:1 ratio (^{1}H-n.m.r. analysis). Pure samples were obtained by elution of the mixture from a column of silica gel with cyclohexane-ethyl acetate (from 3:1 to 1.5:1). Eluted first was **20α**, m.p. 126-127° (from ethyl acetate-hexane), $[\alpha]_D$ +109° (*c* 1.1, $CHCl_3$). ^{1}H-N.m.r. data (400 MHz): δ 7.57-7.55 and 7.41-7.26 (2 m, 20 H, 4 Ph), 5.58 (s, 1 H, PhC*H*), 5.17 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1'), 4.89 and 4.54 (2 d, 2 H, *J* 11.3 Hz, PhCH_2), 4.73 and 4.70 (2 d, 2 H, *J* 10.8 Hz, PhCH_2), 4.52 and 4.48 (2 d, 2 H, *J* 11.8 Hz, PhCH_2), 4.36 (dd, 1 H, $J_{5,6a}$ 1.4, $J_{6a,6b}$ 12.6 Hz, H-6a), 4.27 (dd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ ~0.6 Hz, H-4), 4.21 (ddd, $J_{4',5'}$ ~0.5, $J_{5',6'a}$ 6.5, $J_{5',6'b}$ 6.3 Hz, H-5'), 4.12 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.11 (dd, 1 H, $J_{2',3'}$ 10.7, $J_{3',4'}$ 2.8 Hz, H-3'), 4.06 (dd, 1 H, $J_{5,6b}$ 1.8 Hz, H-6b), 4.05 (dd, 1 H, H-4'), 3.89 (dd, 1 H, H-2'), 3.88 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2), 3.66 (dd, 1 H, H-3), 3.61 (dd, 1 H, $J_{6'a,6'b}$ 9.8 Hz, H-6'a), 3.57 (s, 3 H, MeO), 3.55 (dd, 1 H, H-6'b), 3.31 (ddd, 1 H, H-5).

Anal. Calc. for $C_{41}H_{44}N_6O_9$: C, 64.39; H, 5.80; N, 10.99. Found: C, 64.23; H, 5.74; N, 10.68.

Eluted second was **20β** $[\alpha]_D$ +25° (*c* 1.3, $CHCl_3$). ^{1}H-N.m.r. data (400 MHz): δ 7.52-7.49 and 7.41-7.24 (2 m, 20 H, 4 Ph), 5.49 (s, 1 H, PhC*H*), 4.90 and 4.56 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.73 and 4.69 (2 d, 2 H, *J* 11.8 Hz, PhCH_2), 4.52 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.43 and 4.40 (2 d, 2 H, *J* 11.8 Hz, PhCH_2), 4.27 (dd, 1 H, $J_{5,6a}$ 1.3, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.20 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ ~0.5 Hz, H-4), 4.17 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.93 (dd, 1 H, $J_{5,6b}$ 1.6 Hz, H-6b), 3.88 (dd, 1 H, $J_{2,3}$ 10.6 Hz, H-2), 3.88 (dd, 1 H, $J_{2',3'}$ 10.4 Hz, H-2'), 3.82 (dd, 1 H, $J_{3',4'}$ 2.8, $J_{4',5'}$ ~0.5 Hz, H-4'), 3.61-3.49 (m, 3 H, H-5',6'a,6'b), 3.57 (s, 3 H, MeO), 3.49 (dd, 1 H, H-3), 3.33 (dd, 1 H, H-3'), 3.29 (ddd, 1 H, H-5).

Anal. Found: C, 64.53; H, 5.72.

Use of **2** as glycosyl donor gave similar results.

The same glycosylation reaction had also been performed using other promoters: DMTST (1 h; 90% yield; α:β ratio of 4:1), AgOTf (2 h; 80% yield; α:β ratio of 9:1), MeOTf (18 h; 60% yield; α:β ratio of 7:1).

Methyl 6-O-(3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-α- and -β-D-galactopyranosyl)-2,3,4-tri-O--benzyl-α-D-glucopyranoside (**21α** *and* **21β**). – A mixture of **16** (372 mg, 0.8 mmol), **10** (527 mg, 1.2 mmol), activated 4 Å powdered molecular sieves (0.60 g), and anhydrous acetonitrile (10 mL) was stirred for 15 min at room temperature. Dimethyl(methylthio)sulfonium triflate (1.24 g, 2.4 mmol, of a 1:1 mixture of DMTST and activated 3 Å powdered molecular sieves) was added and stirring was continued for 1 h at room temperature. The suspension was treated with an excess of diisopropylamine, diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with toluene-ethyl acetate (from 10:1 to 5:1), to give, first, **21α** (81 mg, 13%), $[\alpha]_D$ +76° (*c* 0.9, $CHCl_3$). ^{1}H-N.m.r. data (400 MHz): δ 7.48-7.16 (m, 20 H, 4 Ph), 5.47 (s, 1 H, PhC*H*), 5.22 (dd, 1 H, $J_{2',3'}$ 11.2, $J_{3',4'}$ 3.5 Hz, H-3'), 5.11 (d, 1 H, $J_{1',2'}$ 3.4 Hz, H-1'), 4.99 and 4.80 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.96 and 4.60 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.79 and 4.65 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.57 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.37 (dd, 1 H, $J_{4',5'}$ ~0.8 Hz, H-4'), 4.13 (dd, 1

H, $J_{5',6'a}$ 1.0, $J_{6'a,6'b}$ 12.4 Hz, H-6'a), 4.00 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 9.1 Hz, H-3), 3.90 (dd, 1 H, H-2'), 3.88 (dd, 1 H, $J_{5',6'b}$ 1.3 Hz, H-6'b), 3.81-3.67 (m, 3 H, H-5,6a,6b), 3.56 (ddd, 1 H, H-5'), 3.53 (dd, 1 H, H-2), 3.53 (dd, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 3.38 (s, 3 H, MeO), 2.15 (s, 3 H, Ac).

Anal. Calc. for $C_{43}H_{47}N_3O_{11}\cdot 0.5\ H_2O$: C, 65.30; H, 6.12. Found: C, 65.47; H, 6.19.

Eluted second was **21β** (456 mg, 73%), $[\alpha]_D$ +30° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data (400 MHz): δ 7.52-7.31 (m, 20 H, 4 Ph), 5.52 (s, 1 H, PhC*H*), 5.02 and 4.85 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.97 and 4.67 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.82 and 4.69 (2 d, 2 H, *J* 12.4 Hz, PhCH_2), 4.72 (dd, 1 H, $J_{2',3'}$ 10.8, $J_{3',4'}$ 3.5 Hz, H-3'), 4.65 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.33 (dd, 1 H, $J_{4',5'}$ ~0.5 Hz, H-4'), 4.31 (dd, 1 H, $J_{5',6'a}$ 1.0, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 4.26 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.20 (dd, 1 H, $J_{5,6a}$ 1.8, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.05 (dd, 1 H, $J_{5',6'b}$ 1.5 Hz, H-6'b), 4.03 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.6 Hz, H-3), 3.99 (dd, 1 H, H-2'), 3.88 (ddd, 1 H, $J_{4,5}$ 10.0, $J_{5,6b}$ 5.0 Hz H-5), 3.74 (dd, 1 H, H-6b), 3.59 (dd, 1 H, H-2), 3.57 (dd, 1 H, H-4), 3.42 (s, 3 H, MeO), 3.41 (ddd, 1 H, H-5'), 2.18 (s, 3 H, Ac).

Anal. Calc. for $C_{43}H_{47}N_3O_{11}\cdot H_2O$: C, 64.57; H, 6.17. Found: C, 64.66; H, 6.11.

*Methyl 6-O-(2-azido-4,6-O-benzylidene-2-deoxy-*β*-*D*-galactopyranosyl)-2,3,4-tri-O-benzyl-*α*-*D*-glucopyranoside* (**23**). – Deacetylation of **21β** with sodium methoxide in methanol, quantitatively gave **23**, m.p. 148-149° (from ethyl acetate-hexane), $[\alpha]_D$ +6° (*c* 0.8, $CHCl_3$). N.m.r. data: ^{1}H (400 MHz), δ, amongst others, 5.54 (s, 1 H, PhC*H*), 4.62 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.14 (d, 1 H, 8.0 Hz, H-1'), 3.52 (ddd, 1 H, $J_{2',3'} = J_{3',OH}$ 10.0, $J_{3',4'}$ 3.5 Hz, H-3'), 2.54 (d, 1 H, OH-3); ^{13}C, δ, amongst others, 102.36 (C-1'), 101.34 (PhCH), 98.10 (C-1).

Anal. Calc. for $C_{41}H_{45}N_3O_{10}\cdot H_2O$: C, 64.98; H, 6.25. Found: C, 64.92; H, 6.23.

*Methyl 6-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-*α*- and -*β*-*D*-galactopyranosyl)-2,3,4-tri-O-benzyl-*α*-*D*-glucopyranoside* (**22α** *and* **22β**). – Glycosylation of **16** (93 mg, 0.2 mmol) with **11** (146 mg, 0.3 mmol) as for the preparation of **17β** (reaction time: 1 h) gave, after column chromatography (5:1 toluene-ethyl acetate, containing 0.3% of triethylamine), first, **22α** (21 mg, 13%), m.p. 124-125° (from ethyl acetate-hexane), $[\alpha]_D$ +34° (*c* 0.6, $CHCl_3$). ^{1}H-N.m.r. data (400 MHz): δ, amongst others, 5.43 (s, 1 H, PhC*H*), 5.05 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1'), 4.57 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 3.33 (s, 3 H, MeO).

Anal. Calc. for $C_{48}H_{51}N_3O_{10}\cdot H_2O$: C, 67.99; H, 6.30. Found: C, 67.53; H, 5.83.

Eluted second was **22β** (120 mg, 72%), m.p. 166-167° (from ethyl acetate-hexane), $[\alpha]_D$ +23° (*c* 0.4, $CHCl_3$). ^{1}H-N.m.r. data (400 MHz): δ 7.51-7.24 (m, 25 H, 5 Ph), 5.45 (s, 1 H, PhC*H*), 4.98 and 4.81 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.93 and 4.66 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.78 and 4.65 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.72 (s, 2 H, PhCH_2), 4.62 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.26 (dd, 1 H, $J_{5',6'a}$ 1.2, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 4.14 (dd, 1 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.11 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.04 (dd, 1 H, $J_{3',4'}$ 3.5, $J_{4',5'}$ ~0.6 Hz, H-4'), 4.00 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 9.0 Hz, H-3), 3.97 (dd, 1 H, $J_{5',6'b}$ 1.6 Hz, H-6'b), 3.91 (dd, 1 H, $J_{2',3'}$ 10.4 Hz, H-2'), 3.82 (ddd, 1 H, $J_{4,5}$ 10.2, $J_{5,6b}$ 4.6 Hz, H-5), 3.69 (dd, 1 H, H-6b), 3.57 (dd, 1 H, H-4), 3.56 (dd, 1 H, H-2), 3.39 (s, 3 H, MeO), 3.33 (dd, 1 H, H-3'), 3.20 (ddd, 1 H, H-5').

Anal. Calc. for $C_{48}H_{51}N_3O_{10}$: C, 69.46; H, 6.19. Found: C, 69.21; H, 6.10.

When the reaction was carried out in the presence of DMTST (r.t., 1 h) instead of $Cu(OTf)_2$, 75% of a 2:1 mixture of **22β** and **22α** was isolated.

*Methyl O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-*α*- and -*β*-*D*-galactopyranosyl)-(1 → 3)-O-(2-azido-4,6-O-benzylidene-2-deoxy-*β*-*D*-galactopyranosyl)-(1 → 6)-2,3,4-tri-O-benzyl-*α*-*D*-glucopyranoside* (**24α** *and* **24β**). – Glycosylation of **23** (74 mg, 0.1 mmol) with **11** (73 mg, 0.15 mmol) as for the preparation of **20α** (reaction time: 6 h) gave, after column chromatography (2:1 toluene-ethyl acetate, containing 0.3% of triethylamine), first, **24α** (88 mg, 80%), m.p. 184-185° (from ethyl acetate-hexane), $[\alpha]_D$ +118° (*c* 0.4, $CHCl_3$).

^{1}H-N.m.r. data (400 MHz): δ 7.55-7.26 (m, 30 H, 6 Ph), 5.56 and 5.47 (2 s, 2 H, 2 PhC*H*), 5.25 (d, 1 H, $J_{1'',2''}$ 3.5 Hz, H-1''), 4.98 and 4.80 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.93 and 4.64 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.78 and 4.65 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.76 and 4.70 (2 d, 2 H, *J*, 12.0 Hz, PhCH_2), 4.62 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.31 (dd, 1 H, $J_{5',6'a}$ 1.0, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 4.27 (dd, 1 H, $J_{3',4'}$ 3.5, $J_{4',5'}$ ~0.6 Hz, H-4'), 4.25 (dd, 1 H, $J_{5'',6''a}$ 1.2, $J_{6'',6''b}$ 12.6 Hz, H-6''a), 4.25 (dd, 1 H, $J_{3'',4''}$ 3.2, $J_{4'',5''}$ ~0.6 Hz, H-4''), 4.17 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.16 (dd, 1 H, $J_{5,6a}$ 1.6, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.13 (dd, 1 H, $J_{2'',3''}$ 10.7 Hz, H-3''), 4.05 (m, 2 H, H-6'b,6''b), 4.00 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.0 Hz, H-3), 3.93 (dd, 1 H, $J_{2',3'}$ 10.4 Hz, H-2'), 3.88 (dd, 1 H, H-2''), 3.84 (ddd, 1 H, H-5''), 3.83 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6b}$ 4.8 Hz, H-5), 3.69 (dd, 1 H, H-6b), 3.61 (dd, 1 H, H-3'), 3.55 (dd, 1 H, H-2), 3.55 (dd, 1 H, H-4), 3.38 (s, 3 H, MeO), 3.30 (ddd, 1 H, H-5').

Anal. Calc. for $C_{61}H_{64}N_6O_{14}$: C, 66.29; H, 5.84. Found: C, 66.07; H, 5.54.

Eluted second was unreacted **23** (6 mg, 8%).

Eluted third was **24β** (4.5 mg, 4%) contaminated by **23**. ^{1}H-N.m.r. data (400 MHz): δ, amongst others, 5.57 and 5.47 (2 s, 2 H, 2 PhC*H*), 4.63 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1''), 4.61 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.23 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.38 (s, 3 H, MeO).

Use of DMTST instead of $Cu(OTf)_2$ as promoter led to lower α:β ratio of trisaccharide derivatives.

O-Ethyl S-[2-azido-4,6-O-benzylidene-2-deoxy-3-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-β-D--galactopyranosyl] dithiocarbonate (**27**). – Compound **27** had been prepared from donor **25** and xanthate **26** according to a novel glycosylation procedure already reported by us[26] and had $[\alpha]_D$ +75° (*c* 1.1, $CHCl_3$). N.m.r. data: ^{1}H (400 MHz), δ 7.56-7.09 (m, 25 H, 5 Ph), 5.52 (s, 1 H, PhC*H*), 5.35 (d, 1 H, $J_{1',2'}$ 3.3 Hz, H-1'), 5.26 (d, 1 H, $J_{1,2}$ 10.8 Hz, H-1), 5.00 and 4.63 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.88 and 4.74 (2 d, 2 H, *J* 11.8 Hz, PhCH_2), 4.71 (q, 2 H, *J* 7.0 Hz, CH_2CH$_3$), 4.62 and 4.59 (2 d, 2 H, *J* 11.8 Hz, PhCH_2), 4.54 and 4.52 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.42 (ddd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ ~0.6 Hz, H-4), 4.32 (dd, 1 H, $J_{5,6a}$ 1.2, $J_{6a,6b}$ 12.6 Hz, H-6a), 4.20 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 4.17-4.11 (m, 3 H, H-2',3',5'), 4.01 (m, 1 H, H-4'), 4.00 (dd, 1 H, $J_{5,6b}$ 1.5 Hz, H-6b), 3.89 (dd, 1 H, H-3), 3.66 (dd, 1 H, $J_{5',6'a}$ 6.7, $J_{6'a,6'b}$ 9.8 Hz, H-6'a), 3.55 (dd, 1 H, $J_{5',6'b}$ 5.8 Hz, H-6'b), 3.38 (ddd, 1 H, H-5), 1.46 (t, 3 H, CH$_2$CH_3); ^{13}C, δ, amongst others, 101.20 (Ph*C*H), 92.92 (C-1'), 86.90 (C-1).

Anal. Calc. for $C_{50}H_{53}N_3O_{10}S_2$: C, 65.27; H, 5.81. Found: C, 65.11; H, 5.85.

Methyl O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-(1 → 3)-O-(2-azido-4,6-O-benzylidene-2--deoxy-α- and -β-D-galactopyranosyl)-(1 → 3)-O-(2-azido-4,6-O-benzylidene-2-deoxy-β-D-galactopyranosyl)-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**28α** *and* **28β**). – Glycosylation of **23** (74 mg, 0.1 mmol) with **27** (138 mg, 0.15 mmol) as for the preparation of **20α** (reaction time: 36 h) gave, after column chromatography (from 4:1 to 2:1 toluene-ethyl acetate, containing 0.3% of triethylamine), first, **28α** (126 mg, 82%), $[\alpha]_D$ +93° (*c* 1.1, $CHCl_3$). N.m.r. data: ^{1}H (400 MHz), δ, amongst others, 7.57-7.05 (m, 45 H, 9 Ph), 5.58 and 5.44 (2 s, 2 H, 2 PhC*H*), 5.31 (d, 1 H, $J_{1'',2''}$ 3.5 Hz, H-1''), 5.25 (d, 1 H, $J_{1''',2'''}$ 3.2 Hz, H-1'''), 4.61 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.17 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.37 (s, 3 H, MeO); ^{13}C, δ, amongst others, 102.04 (C-1'), 100.94 and 100.60 (2 Ph*C*H), 98.05 (C-1), 94.42 (C-1''), 93.95 (C-1''').

Anal. Calc. for $C_{88}H_{92}N_6O_{19}$: C, 68.73; H, 6.03. Found: C, 68.46; H, 6.09.

Eluted second was **28β** (6 mg, 4%), $[\alpha]_D$ +51° (*c* 0.9, $CHCl_3$). N.m.r. data: ^{1}H (400 MHz), δ, amongst others, 7.57-7.07 (m, 45 H, 9 Ph), 5.61 and 5.54 (2 s, 2 H, 2 PhC*H*), 5.24 (m, 1 H, H-1'''), 4.66 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.63 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1''), 4.30 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.42 (s, 3 H, MeO); ^{13}C, δ, amongst others, 103.00 (C-1''), 102.75 (C-1'), 101.08 and 100.53 (2 Ph*C*H), 98.03 (C-1), 92.86 (C-1''').

Anal. Found: C, 69.03; H, 6.25.

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