Synthesis of α-*C*-Glycopyranosides of D-Galactosamine and D-Glucosamine *via* Iodocyclization of Corresponding Glycals and Silver Tetrafluoroboranuide-Promoted Alkynylation at the Anomeric Centre

Christine Leteux and Alain Veyrières*
Université d'Orléans, UFR-Faculté des Sciences, Laboratoire de Biochimie Structurale, URA 499, BP 6759, 45067 Orléans, France

Iodocyclization of O-stannylated D-galactal **1**, followed by azide ion displacement, gave 1,6-anhydro-2-azido-2-deoxy-β-D-galactopyranose **9** in an expeditious way. Transformation into bromide **12** allowed coupling of various alkynyltributylstannanes in the presence of silver tetrafluoroboranuide (silver tetrafluoroborate), thus affording the corresponding α,β-*C*-(D-galacto-pyranosyl)alkynes **13–17**. Application of this methodology to the D-*gluco* isomeric bromide **24** gave a *C*-(D-glucopyranosyl)octyne **25** with total α-stereoselectivity. Conventional deprotection and saturation of the acetylenic linkage led to *C*-octyl-α-glycopyranosides of D-galactosamine **20** and D-glucosamine **28**.

Carbon-linked glycosyl compounds have become important materials in biochemistry as stable analogues of naturally occurring sugars used in enzymic and metabolic studies.[1] They have also a potential interest as a source of chiral intermediates possessing more carbon functionality than do *O*-glycosides.[2] From a biological point of view, amino sugars such as D-glucosamine and D-galactosamine are among the most important carbohydrates, being integral components of glycoproteins, a class of natural products playing a crucial role in molecular recognition phenomena.[3] Thus *N*-acetylgalactosamine with an α-linkage to the hydroxy group of serine or threonine is found in mucin-type *O*-glycans, a family of glycoproteins synthesized by the respiratory mucosa and involved in antimicrobial defence and several intercellular recognition processes.[4]

C-Glycosides of amino sugars have scarcely been reported in the literature.[5] The Lewis acid-catalysed addition of *C*-nucleophiles to activated carbohydrate derivatives has been reported[6] to be incompatible with the presence of amino or amido substituents at C-2, and previous methods for the synthesis of amino sugar *C*-glycosides mostly relied upon a Wittig-type reaction at the anomeric centre followed by electrophilic recyclization.[7] Whereas the use of 2-azido sugars as substrates for direct Lewis acid-promoted nucleophilic additions of alcohols has met with great success in the synthesis of *O*-glycosides,[8] only anomeric cyanides[9] and *C*-glycosylpropene and -allene[10] have been obtained with trimethylsilyl cyanide, and allyl- and propargyl-trimethylsilane respectively; the two latter, unsaturated *C*-glycosides are valuable compounds, but being unstable they have to be converted rapidly into the corresponding aldehydes by ozonolysis.

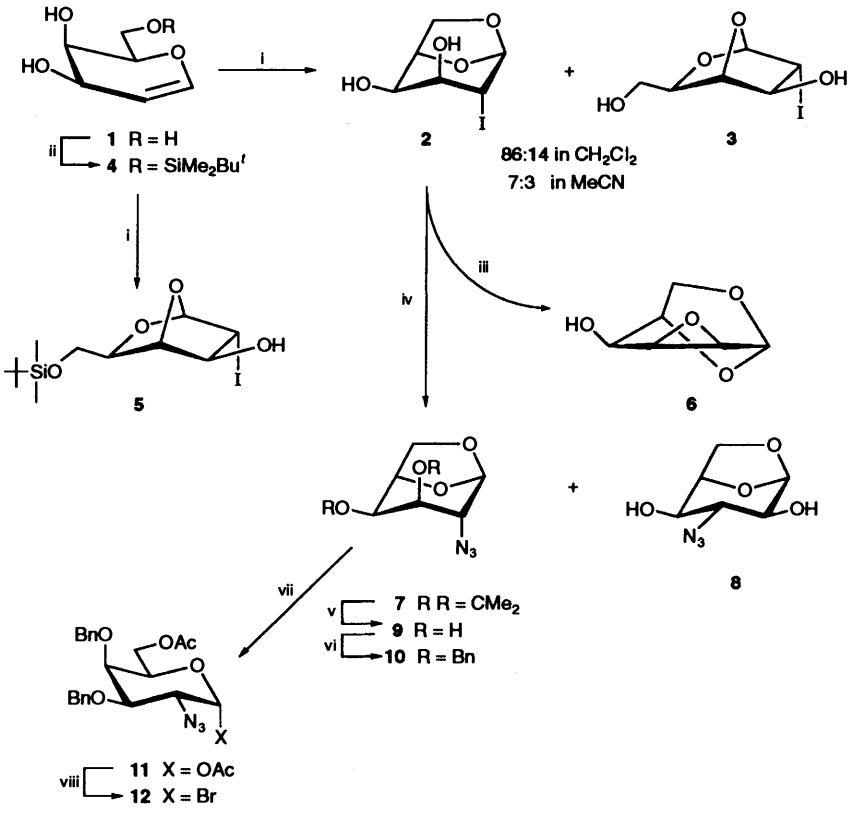
Radical-promoted additions to the anomeric centre of a suitably activated 2-azido sugar derivative could be an alternative solution to this problem, especially after the two recent reports[11] on the direct synthesis of phenyl 2-azido-2-deoxy-1-selenoglycosides from glycals. However, attempted reactions of the known[12] compound, 6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl bromide **24**, with allyltributylstannane or tributylstannane itself in the presence of azoisobutyronitrile (AIBN) as a thermal initiator led only to glucal derivatives.[13] Cathodic reduction of vicinal iodo azides has been reported[14] to give a quantitative elimination, reminiscent of the behaviour of 1,2-dihalides[15] or β-chloro phenyl sulfides[16] in radical reactions.

We describe herein a new procedure for the coupling of alkynylstannanes with 2-azido sugar bromides leading to stable *C*-glycosylacetylenes which can be conveniently converted into amino sugar *C*-glycosides. A new access to 2-azido-2-deoxy-D-galactopyranose derivatives from D-galactal is also reported.

Results and Discussion

Iodocyclization of D-*Galactal*.—We recently reported[17] that oxidative 1,6-iodocyclization of D-glucal can be easily performed after activation of hydroxy groups by O-tributylstannylation. The crystalline 1,6-anhydro-2-deoxy-2-iodo-β-D-glucopyranose is obtained in high yield and has been used in radical reactions.[18] Tailler *et al.*[19] have shown that it can be converted into 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose in a fully stereoselective reaction occurring with retention of configuration; a transient 2,3-*manno*-epoxide is opened in a *trans*-diaxial fashion by azide ions. This methodology is now applied to D-galactal **1** where the presence of an axial hydroxy group at C-4 of the preferred $^4H_5$ half-chair conformation is expected to give different results.

It is known[20] that treatment of a polyol with bis(tributyltin) oxide affords an equilibrium mixture among various O-stannylated species and the starting material; dibutylstannanediyl acetals themselves are susceptible to migrations particularly when treated with bulky electrophilic reagents.[21] Addition of various Lewis bases such as alkylammonium halides, *N*-methylimidazole, and polar solvents [dimethylformamide (DMF), MeCN] alters the composition of the equilibrium probably by preferential coordination of some O-stannylated molecules. When D-galactal **1** was treated with 0.8 molar equiv. of bis(tributylstannyl) oxide in refluxing acetonitrile, then with 1.2 mol equiv. of iodine at 0 °C, a mixture of iodocyclized products **2** and **3** was obtained in the ratio 7:3 (Scheme 1). Careful removal of acetonitrile after O-stannylation, then replacement by dry dichloromethane in the iodocyclization step, modified this ratio to 86:14. Since there was no evidence that the cyclization process was reversible, it is tempting to speculate that acetonitrile favours to some extent a stannylation reaction at O-4 with a tin atom coordinated to the adjacent pseudo-equatorial hydroxy group at C-3. 1,4-Iodocyclization will then occur easily without the need for a deep conformational change in the intermediate iodonium species. Attempts to reduce the amount of 1,4-cyclized product by running the O-stannylation step in less polar solvents (refluxing chloroform or 1,2-dichloroethane) were indeed successful, but led to recovery of large amounts of unchanged D-galactal which is sparingly soluble under such conditions. 1,6-Iodocyclization



Scheme 1 *Reagents and conditions:* i, $(Bu_3Sn)_2O$ (0.8 mol equiv.), MS 3 Å, MeCN, reflux, 3 h; then I_2 (1.2 mol equiv.), 0 °C, 30 min; ii, Bu_2SnO (2 mol equiv.), MS 3 Å, MeCN, reflux, 150 min; then TBDMSCl (1.2 mol equiv.), room temp., 1 h; iii, NaOMe, CH_2Cl_2–MeOH (3:2), room temp., 3 h; iv, LiN_3 (3 mol equiv.), DMF, 100 °C, 12 h; then $Me_2C(OMe)_2$ (5 mol equiv.), CSA, MeCN, room temp., 5 h; v, 60% AcOH, 100 °C, 1 h; vi, $PhCH_2Br$, NaH, DMF, room temp., 1 h; vii, Ac_2O–TFA (9:1), room temp., 12 h; viii, $TiBr_4$ (1.5 mol equiv.), CH_2Cl_2–AcOEt (10:1), room temp., 12 h

still remains the main pathway whatever the solvent and must occur in a similar fashion to that of D-glucal with a change of conformation towards the $^5H_4$ half-chair conformer.[17]

The ^{1}H NMR spectrum of the 1,6-anhydro compound **2** revealed low values for $J_{1,2}$ and $J_{2,3}$ (< 1 Hz), indicating a $^1C_4$ chair conformation.[22] The structure of the 1,4-anhydro isomer **3** was established as follows: the anomeric bridgehead proton appeared as a narrow doublet at δ 5.55 ($J_{1,2}$ 2.5 Hz), thus confirming the presence of an *exo*-proton at C-2, coupling of an *endo*-proton being normally zero. Signal at δ 3.48 ($J_{4,5}$ ~ 0 Hz) could be attributed to 5-H in agreement with a dihedral angle of ~ 90°. A long-range coupling ($J_{2,4}$ 1.5 Hz) was also in accord with the strained bicyclic structure.[23]

D-Galactal **1** was also treated with dibutyltin oxide in refluxing acetonitrile, then with *tert*-butyldimethylsilyl chloride (TBDMSCl) at room temperature. A high yield of the 6-O-silylated product **4** was thus obtained with no trace of other silylated compound, a result which confirms the preferential reactivity of a 4,6-*O*-stannanediyl acetal.[21] It is noteworthy that usual conditions for regioselective silylation of a primary hydroxy group (2.25 mol equiv. of imidazole and 1.1 mol equiv. of TBDMSCl in DMF at 0 °C) gave the 3,6-di-O-silylated D-galactal as a side-product in 11% yield.[24] Treatment of compound **4** with bis(tributyltin) oxide in refluxing acetonitrile, then with iodine at 0 °C, gave the 1,4-anhydro derivative **5** in 79% yield (Scheme 1); ^{1}H NMR spectrum of compound **5** showed the same characteristics as did the spectrum of compound **3**.

The rigid structure of 1,4-anhydro-β-D-galactopyranoses **3** and **5** prevents the formation of an *exo*-2,3-*talo*-epoxide under alkaline conditions [sodium methoxide in methanol or sodium hydride in tetrahydrofuran (THF)] as well as any S_N2 displacement of the iodine atom by a nucleophile (no reaction occurred with sodium azide in aqueous DMF at 120 °C), but should be highly favourable for radical-mediated formation of carbon–carbon bonds at C-2, then at C-3.

As expected, 1,6-anhydro-2-deoxy-2-iodo-β-D-galactopyranose **2** gave high yields of the known[25] 2,3-*talo*-epoxide **6** by treatment with sodium methoxide in methanol at room temperature. An expeditious synthesis of this valuable material from D-galactal is therefore now available.

Syntheses of 2-Azido-2-deoxy-D-galactopyranose Derivatives.—Treatment of 1,6-anhydro-2-deoxy-2-iodo-β-D-galactopyranose **2** with sodium azide in aqueous DMF at 120 °C gave a mixture (72%) of 1,6-anhydro-3-azido-3-deoxy-β-D-idopyranose **8**, 1,6-anhydro-2-azido-2-deoxy-β-D-galactopyranose **9** and 2,3-*talo*-epoxide **6** in the proportions 15:3:2 as judged by ^{1}H NMR spectroscopy in deuteriated dimethyl sulfoxide (DMSO) [δ 5.14, 5.37 and 5.65 for 1-H in **8**, **9** and **6** respectively]. Therefore a preferential abnormal ring opening of the intermediate 2,3-epoxide is now observed under conditions where the isomeric *manno*-epoxide behaves normally.[19] A possible explanation[26] may come from unfavourable polar repulsions between the adjacent nearly eclipsed 4-OH and a developing negatively charged oxygen at C-3 in a 'normal' ^5H_O half-chair transition state. A change to a $B_{3,O}$ boat conformation in the transition state where the negatively charged oxygen at C-2, the incoming nucleophile at C-3, and 4-OH are all in axial positions will lead to the major D-*ido*-compound **8** (Fig. 1). It is worth noting that opening of the *manno*-epoxide leading only to 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose[19] involves a 'normal' ^5H_O half-chair transition state with substituents at C-2, -3 and -4 *all axial* as well. Drastic conditions (high temperature, prolonged reaction times) are necessary to obtain conversion of iodide **2** into azides **8** and **9** under non-

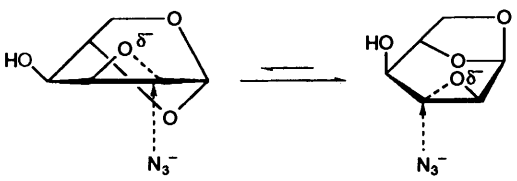


Fig. 1 Half-chair ^5H_O–boat $B_{3,O}$ equilibrium of 1,6:2,3-dianhydro-β-D-talopyranose **6** in ring-opening reaction with azide ions

acidic conditions and it is therefore not surprising that tetrabutylammonium azide[27] in refluxing acetonitrile afforded only the epoxide **6**. Paulsen *et al.*[28] reported a 73% yield of azide **9** by treatment of epoxide **6** with 7 mol equiv. of sodium azide and 8.6 mol equiv. of ammonium chloride in refluxing 85% aq. ethanol for 48 h; in our hands these conditions led to uncomplete transformation, although the 'normal' product **9** now became predominant. Variable amounts of D-*ido*-compounds have been reported[29] in similar ring-opening reactions of 1,6:2,3-dianhydro-β-D-talopyranose with a substituent at O-4. It is known[30] that some metal salts such as lithium or magnesium perchlorate catalyse the ring opening of epoxides in non-protic solvents, the Lewis acid metal ion being able to coordinate the epoxide oxygen. When compound **2** was heated in dry DMF at 100 °C in the presence of 3 mol equiv. of *lithium azide* a complete conversion into a mixture of azides **8** and **9** in the ratio 1:3 was obtained after 12 h. This reversal of regioselectivity can be explained by chelation of a lithium cation between O-3 and O-4 in the ^5H_O half-chair transition state relieving their polar repulsions. Similar chelation effects have been put forward[31] in regioselective ring opening of 2,3-epoxy alcohols by trimethylsilyl azide-catalysed by titanium or aluminium alkoxides.

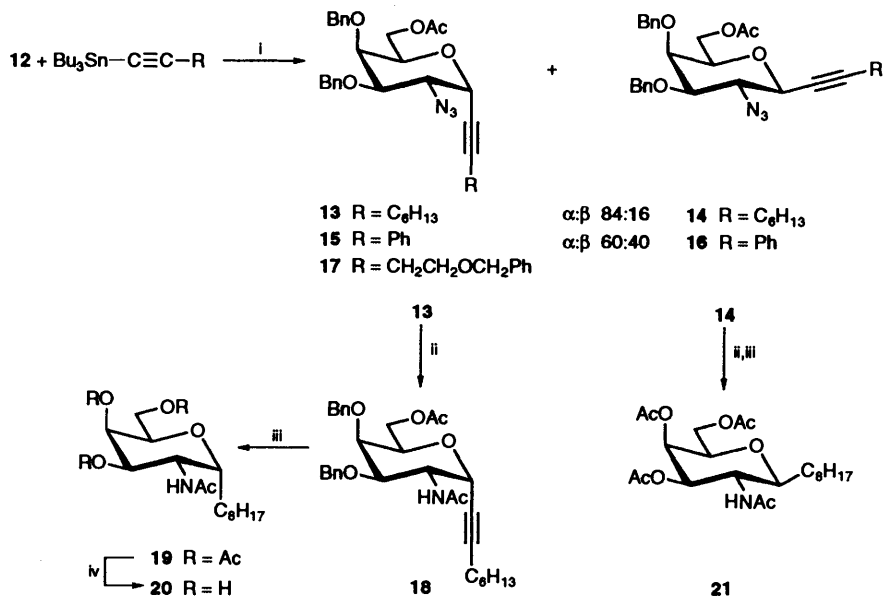
The mixture of azides **8** and **9** was easily separated by selective conversion of 2-azide **9** into its 3,4-*O*-isopropylidene derivative **7** with 2,2-dimethoxypropane in acetonitrile under acid catalysis. Known[28] azido compound **7** is thus obtained in 43% overall yield from D-galactal with only three steps (Scheme 1). The structure of the D-*ido* compound **8** which has an equatorial azido group at C-3 was confirmed by ^{1}H NMR spectroscopy in deuteriated DMSO: a large coupling constant ($J_{3,4}$ 9 Hz) was noticed in the signal of 4-H at δ 3.49, whereas the D-*galacto* isomer **9** has its 4-H signal at δ 3.67 ($J_{3,4}$ 5 Hz).

Acid hydrolysis, followed by conventional O-benzylation, converted isopropylidene compound **7** into the known[28] 3,4-di-*O*-benzyl derivative **10**. Acetolysis of the 1,6-anhydro bridge by acetic anhydride and trifluoroacetic acid (TFA) gave a mixture of α,β-1,6-diacetates **11** in the approximate ratio 1:1. Finally bromination of diacetates **11** with titanium tetrabromide according to the described[28] procedure gave the syrupy α-bromide **12** in 69% overall yield from compound **7** (Scheme 1).

Syntheses of C-*Glycosides of* N-*Acetylgalactosamine.*—Alkyne transfer to the anomeric centre of 2-azido-2-deoxy sugars was selected as a means of preparing *C*-glycosides of amino sugars. Sinaÿ[32] has reported a fully stereospecific synthesis of (β-D-glucopyranosyl)-1-alkynes by addition of lithium acetylides to glucopyranolactones followed by reduction with triethylsilane in the presence of a Lewis acid. To our knowledge this methodology has not been extended to 2-azido-2-deoxypyranolactones, perhaps because of easy epimerization at C-2 of these compounds[33] (sodium acetate or sodium azide in DMF at room temperature). Acetylated D-glucal and 2-acetoxy-D-glucal have been treated with silylacetylenes under Lewis acid catalysis to give stereospecifically α-*C*-alkynyl unsaturated glucopyranosides in high yields;[34] it is interesting that the alkynyl group could be epimerized through cobalt complexes leading to mixtures of α-and β-*C*-alkynyl glycosides in the ratio 1:6. Williams[35] has reported the alkynylation of sugar bromides by alkynylstannanes in boiling tetrachloromethane; zinc chloride was the promoter, average yields of 50% being obtained from tetrabenzylglucopyranosyl bromide with a significant α-selectivity. The alkyne π-system adds preferentially to the α-face of the oxonium species generated from the bromide, giving rise to a vinyl cation stabilized by the β-tin atom. The kinetic anomeric effect of the pyranose ring oxygen is generally put forward[36] as an explanation for α-stereoselectivity.

Titanium tetrachloride-promoted coupling of alkynylsilanes with acetals at low temperature has been reported[37] to give high yields of propargylic ethers. We therefore investigated first the addition of trimethyl(octynyl)silane or tributyl(octynyl)-stannane with various 1,6-anhydro-β-D-hexopyranose derivatives in the hope of getting high α-selectivity by Lewis acid-catalysed opening of the 1,6-anhydro bridge. Unfortunately no clean reaction could be obtained whatever the promoter (titanium tetrachloride, boron trifluoride–diethyl ether, trimethylsilyl triflate, zinc bromide, *etc.*). Complexation of protecting *O*-benzyl groups by the Lewis acid[38] occurred to a large extent and led to decomposition under forcing conditions. However, successful couplings of allylic silanes with 1,6-anhydro sugars in the presence of boron trifluoride–diethyl ether have been reported,[39] but the lower nucleophilicity of metallated alkynes required more electrophilic sugar derivatives. Chlorides and bromides prepared by acetolysis of the 1,6-anhydro bridge reacted with tributyl(octynyl)stannane under Williams' conditions, but in modest yields and low reproducibility.[40] In search of a more efficient promoter we found that silver tetrafluoroboranuide (2 mol equiv.) was able to initiate a smooth and clean coupling reaction at 0 °C in 1,2-dichloroethane, 5 mol equiv. of stannane being, however, necessary in order to reach a complete transformation. Silver tetrafluoroboranuide has already been used for allylation of β-bromo ethers by allylsilanes[41] and more relevantly for alkynylation of thiol esters by alkynylsilanes.[42] Acetylenic silanes and stannanes are apparently not cleaved by silver ions in aprotic solvents of low polarity, although complexation of the triple bond can be expected. On the other hand, glycosyl fluorides have been obtained by reaction of the corresponding chlorides with silver tetrafluoroboranuide,[43] the oxonium species being trapped in that case by fluoride ions with concomitant release of boron trifluoride. We observed the formation of a 2-azido-2-deoxy-α-D-glycopyranosyl fluoride when the reaction was quenched with sodium hydrogen carbonate before completion. 2-*O*-Benzyl-α-D-glycopyranosyl chlorides in the absence of an external nucleophile gave rise to a very efficient intramolecular Friedel–Crafts reaction instead,[44] which demonstrated the highly electrophilic character of the oxonium intermediate generated under such conditions. Boron trifluoride–diethyl ether is known to promote additions of alcohols[45] and reactive *C*-nucleophiles[5] as well to glycosyl fluorides and, in the absence of complexing diethyl ether, boron trifluoride is a much stronger Lewis acid, quite comparable to aluminium trichloride.[46]

Following this new methodology, bromide **12** was coupled with octynyl-, phenylethynyl- and 4-benzyloxybut-1-ynyl-tributylstannanes to give the 1-(α,β-D-galactopyranosyl)oct-1-yne **13** and **14** in 62% yield (ratio 5:1), the 1-(α,β-D-galactopyranosyl)-2-phenylacetylene **15** and **16** in 65% yield (ratio 3:2) and the 4-benzyloxy-1-(α-D-galactopyranosyl)but-1-yne **17** in 46% yield respectively (Scheme 2). The poorer α-selectivity encountered with the metallated phenylacetylene comes from its greater nucleophilicity, an observation which has often been made in O-glycosylation of reactive alcohols. ^{1}H NMR spectra of α-*C*-glycosides **13**, **15** and **17** in deuteriated chloroform showed signals for 1-H at δ 4.81, 5.06 and 4.81 respectively with



Scheme 2 *Reagents and conditions:* i, $AgBF_4$ (2 mol equiv.), MS 3 Å, $ClCH_2CH_2Cl$, −30 to 0 °C; ii, PPh_3 (1.5 mol equiv.), THF, room temp., 3 h; then water, 40 °C, 12 h; then Ac_2O–Py (1 : 1), room temp., 12 h; iii, 10% Pd–C, H_2, AcOEt–MeOH–water (15 : 4 : 1), 1 atm, 18 h; then Ac_2O–Py (1 : 1), room temp., 12 h; iv, MeOH–water–NEt_3 (10 : 10 : 1), room temp., 18 h

$J_{1,2}$ 5.5 Hz; a propargylic coupling constant $J(CH_2)$ 2 Hz was observed in compounds **13** and **17**. Other coupling constants are characteristic of a D-galactopyranose ring in a $^4C_1$ chair conformation. The 1-H proton of isomeric β-*C*-glycosides **14** and **16** appears at δ 3.84 [$J_{1,2}$ 10, $J(CH_2)$ 2 Hz] and 4.08 ($J_{1,2}$ 10 Hz) evaluated in deuteriated benzene, since in deuteriated chloroform the 1-H signal shows virtual coupling to 3-H and cannot be analysed at first order). A $^4C_1$ chair conformation can also be deduced from the other coupling constants. The phenylethynyl α-*C*-glycoside **15** crystallized from ethanol (m.p. 88–89 °C) and its structure was confirmed by an X-ray diffraction analysis which will be reported elsewhere. The torsion angles about the skeletal bonds of the pyranose ring are given in Table 1. Comparison with the torsion angles of α-D-galactopyranose in a $^4C_1$ chair geometry shows very little distortion.

Eliel[47] has reported that, in non-polar solvents, axial isomers of 2-ethynyl- and 2-phenylethynyl-*cis*-4,6-dimethyl-1,3-dioxanes predominate at equilibrium over their equatorial epimers. This axial stability (ΔG^0 +0.315 kcal mol^{-1}* for the 2-phenylethynyl compound) was attributed to a generalized anomeric effect involving a partial ionic character of the sp–sp^3 bond. This anomeric effect is most probably operative in α-*C*-alkynyl D-hexopyranosides, but being much smaller than in *O*-glycosides[36] (ΔG^0 ~ +1.4 kcal mol^{-1}) could not be detected by appreciable changes in bond lengths. Besides, Isobe[34] has recently shown that an α-*C*-trimethylsilylethynyl 2,3-unsaturated glycoside adopts a conformation where the alkynyl group is axially disposed, but flips to a conformation where a bulky dicobalt hexacarbonyl complex of the triple bond will be equatorial. Steric effects become predominant in such complexes, but are negligible in the free alkyne.

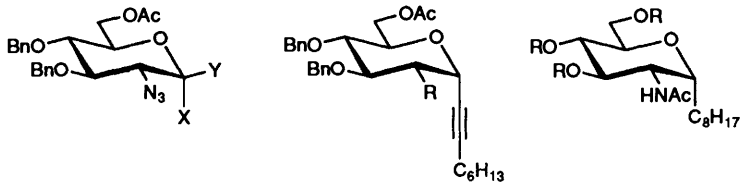
Attempted hydrogenation of alkyne **13** in the presence of palladium on charcoal gave a complex mixture of products, perhaps because of the vicinity of azide and acetylenic functions. Therefore the azido group was first reduced by treatment with triphenylphosphine in THF, followed by hydrolysis of the intermediate iminophosphorane.[48] N-Acetylation, then hydrogenation and O-acetylation, afforded compound **19** in high yield. Finally, hydrolysis of *O*-acetyl groups gave 1-(2-acetamido-2-deoxy-α-D-galactopyranosyl)octane **20** as an amorphous material sparingly soluble in water and quite soluble in methanol (Scheme 2). Its ^{1}H NMR spectrum in deuteriated methanol shows a multiplet signal at δ 4.06 and a doublet of doublets at δ 4.23 ($J_{1,2}$ 5, $J_{2,3}$ 10 Hz) attributed to 1-H and 2-H respectively; coupling constants $J_{3,4}$ 3 Hz and $J_{4,5}$ 2.5 Hz seem to indicate a slight distortion of the usual $^4C_1$ chair conformation in the neighbourhood of the axial 4-OH group; that distortion is also present in the tri-*O*-acetyl derivative **19**. 1-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)octane **21** was obtained from compound **14** in a similar sequence of reactions; its ^{1}H NMR spectrum in deuteriated chloroform indicates a $^4C_1$ chair conformation. A more refined analysis of ^{1}H NMR spectra for the α- and β-*C*-octyl glycosides of *N*-acetylgalactosamine will be reported elsewhere.

Table 1 Ring torsion angles for (i) 1-(6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-2-phenylacetylene **15** and (ii) α-D-galactose

	(i)	(ii)
O(5)–C(1)–C(2)–C(3)	60.0	58.7
C(1)–C(2)–C(3)–C(4)	−59.3	−58.1
C(2)–C(3)–C(4)–C(5)	59.5	55.0
C(3)–C(4)–C(5)–O(5)	−61.0	−55.2
C(4)–C(5)–O(5)–C(1)	62.1	59.6
C(5)–O(5)–C(1)–C(2)	−61.0	−60.6
Mean absolute value	60.5	57.9

Synthesis of α-C-*Octyl Glycoside of* N-*Acetylglucosamine.*— The above methodology was applied to 6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl bromide **24**, a known[12] crystalline compound easily prepared by sequential iodocyclization of D-glucal,[17,18] stereoselective introduction of azide functionality,[19] O-benzylation, acetolysis and titanium tetrabromide-mediated bromination. When the reaction of compound **24** with tributyl(octynyl)stannane and silver tetrafluoroboranuide was stopped after 1 h at 0 °C, work-up of the reaction mixture delivered some of the addition product **25** and large amounts of the α-fluoride **23**. A sample of anomeric mixture of fluorides was independently prepared as follows: the

* 1 cal = 4.184 J.



22 X,Y = H, OH
23 X,Y = H, F
24 X = Br, Y = H

25 R = N_3
26 R = NHAc

27 R = Ac
28 R = H

intermediate acetolysis product in the preparation of bromide **24** was regioselectively deacetylated at the anomeric position by benzylamine in diethyl ether[49] to give a mixture of α,β-hemiacetals **22**. This mixture was then treated with (diethylamino)sulfur trifluoride (DAST) in THF[50] to give, quantitatively, α- and β-D-glucopyranosyl fluorides **23** in an approximate 1:3 ratio. The characteristic ^{1}H NMR signal at δ 5.63 ($J_{1,2}$ 2.8, $J_{1,F}$ 53 Hz) attributed to 1-H of the α-isomer in the above mixture allowed identification of the transient fluoride in coupling reaction. This fluoride was absent after a reaction time of 12 h at 0 °C. After work-up the α-*C*-glycoside **25** was isolated in 74% yield without evidence for the presence of the β-isomer. The ^{1}H NMR spectrum of compound **25** in deuteriated chloroform indicated an usual $^4C_1$ chair conformation with signals at δ 4.77 [$J_{1,2}$ 5.5, J(CH$_2$) 2 Hz] and 3.55 ($J_{2,3}$ 10 Hz) attributed to 1-H and 2-H, respectively.

The total α-selectivity in the coupling reaction of the *gluco*-bromide **24** with an alkynylstannane may reflect a better match between the electrophilic and nucleophilic partners; the more reactive *galacto*-bromide **12** shows less stereoselectivity as it often does in O-glycosylation of alcohols.

1-(2-Acetamido-2-deoxy-α-D-glucopyranosyl)octane **28** was obtained from azide **25** by the same sequence of reactions as in the *galacto*-series. Its ^{1}H NMR spectrum in deuteriated DMSO showed signals at δ 3.78 ($J_{1,2}$ 5.2 Hz and two couplings with the diastereotopic protons of the first methylene unit in the carbon chain, J 5 and 11 Hz) and 3.68 ($J_{2,3}$ 10, $J_{2,NH}$ 8 Hz) attributed to 1-H and 2-H, respectively.

Experimental

General Methods.—M.p.s were recorded with a Büchi apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. [α]$_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded on a Philips Pye-Unicam SP3-100 spectrometer. ^{1}H NMR spectra were recorded with a Bruker AM-300 WB (300.013 MHz) spectrometer. Chemical shifts are reported in δ values relative to tetramethylsilane, and J-values are given in Hz. Mass spectra were recorded with a Ribermag R-10-10 instrument in the desorption, chemical-ionization mode. TLC was conducted on precoated silica gel 60 F 254 (Art. 5554; Merck) with detection by UV fluorescence and charring with H_2SO_4–EtOH (1:10). Flash chromatography was performed using silica gel 60 (Merck, 3–63 μm). Ether refers to diethyl ether. All solvents were dried and distilled using standard methods.[51] Elemental analyses were performed by the Service Central de Micro-Analyse du Centre National de la Recherche Scientifique.

1,6-*Anhydro*-2-*deoxy*-2-*iodo*-β-D-*galactopyranose* **2** *and* 1,4-*Anhydro*-2-*deoxy*-2-*iodo*-β-D-*galactopyranose* **3**.—A mixture of D-galactal[24,52] **1** (1.46 g, 10 mmol), bis(tributyltin) oxide (4.77 g, 8 mmol), 3 Å molecular sieves (3 g) and dry acetonitrile (60 cm^3) was heated at reflux for 3 h. The solvent was evaporated off under reduced pressure and the residue was dried *in vacuo* (0.1 mmHg). Dichloromethane (60 cm^3) was added and the mixture was cooled in an ice–water-bath under argon. Iodine (3.05 g, 12 mmol) was then added and the resulting mixture was stirred at 0 °C under argon for 10 min. TLC (toluene–acetone, 1:1) showed the complete conversion of D-galactal (R_f 0.14) into title products **2** (R_f 0.38) and **3** (R_f 0.27). The dark brown solution was filtered through Celite and concentrated. Saturated aq. sodium thiosulfate (50 cm^3) and hexane (50 cm^3) were added and the biphasic mixture was vigorously stirred for 3 h. The aqueous phase was then extracted continuously with ethyl acetate for 8 h. The extract was concentrated and the residue was purified by flash chromatography with hexane–acetone (3:2) as eluent.

The 1,6-anhydro derivative **2** was eluted first and was crystallized from ethanol (1.55 g, 57%), m.p. 87–88 °C; [α]$_D$ + 68 (*c* 1, MeOH); δ_H[(CD$_3$)$_2$SO] 3.50 (1 H, dd, $J_{5,6a}$ 4.7, $J_{6a,6b}$ 7, 6-H^a), 4.04 (1 H, m, 4-H), 4.10 (1 H, m, 2-H), 4.13 (1 H, m, $J_{2,3}$ 0.5, $J_{3,4}$ 5, 3-H), 4.27 (1 H, m, $J_{4,5}$ 4.7, 5-H), 4.38 (1 H, d, 6-H^b), 5.02 (1 H, d, *J* 7, exch. with D$_2$O, 4-OH), 5.36 (1 H, d, *J* 3.5, exch. with D$_2$O, 3-OH) and 5.48 (1 H, s, 1-H) (Found: C, 26.8; H, 3.3. $C_6H_9IO_4$ requires C, 26.49; H, 3.33%).

The 1,4-anhydro derivative **3** was eluted next and was crystallized from ethanol (245 mg, 9%), m.p. 83–84 °C; [α]$_D$ +118 (*c* 1, MeOH); δ_H[(CD$_3$)$_2$SO] 3.13 (1 H, dd, $J_{5,6a}$ 8, $J_{6a,6b}$ 11, 6-H^a), 3.22 (1 H, dd, $J_{5,6b}$ 6, 6-H^b), 3.48 (1 H, dd, 5-H), 3.58 (1 H, m, 2-H), 4.00 (1 H, dd, $J_{2,3}$ 2.5, 3-H), 4.37 (1 H, d, $J_{2,4}$ 1.5, 4-H), 4.82 (1 H, t, *J* 6, exch. with D$_2$O, 6-OH), 5.55 (1 H, d, $J_{1,2}$ 2.5, 1-H) and 5.75 (1 H, d, *J* 5, exch. with D$_2$O, 3-OH) (Found: C, 26.6; H, 3.55%).

1,4-*Anhydro*-6-O-(tert-*butyldimethylsilyl*)-2-*deoxy*-2-*iodo*-β-D-*galactopyranose* **5**.—A mixture of D-galactal **1** (585 mg, 4 mmol), dibutyltin oxide (1.99 g, 8 mmol), 3 Å molecular sieves (1 g) and dry acetonitrile (25 cm^3) was heated at reflux for 150 min, then was cooled under argon to room temperature. TBDMSCl (724 mg, 4.8 mmol) was added and the mixture was stirred for 1 h at room temperature, then was filtered over Celite. TLC (hexane–ethyl acetate, 3:2) showed complete conversion of D-galactal (R_f 0.01) into a new compound (R_f 0.38). The filtrate was concentrated and the residue was purified by flash chromatography (hexane–ethyl acetate, 7:3) to give 1,5-anhydro-6-O-(*tert*-butyldimethylsilyl)-2-deoxy-D-*lyxo*-hex-1-enitol **4** (884 mg, 85%), δ_H(CDCl$_3$) 0.11 (6 H, s, 2 × Me), 0.92 (9 H, s, Bu^t), 2.72 (1 H, d, *J* 10, OH), 3.17 (1 H, d, *J* 5, OH), 3.85–4.01 (3 H, m, 5-H and 6-H$_2$), 4.10 (1 H, m, 4-H), 4.32 (1 H, m, 3-H), 4.72 (1 H, ddd, $J_{2,3}$ ~ $J_{2,4}$ ~ 2, 2-H) and 6.38 (1 H, dd, $J_{1,2}$ 6.2, $J_{1,3}$ 2, 1-H).

A mixture of glycal **4** (884 mg, 3.4 mmol), bis(tributyltin) oxide (1.22 g, 2 mmol), 3 Å molecular sieves (1 g) and dry acetonitrile (25 cm^3) was heated at reflux for 2 h, then was cooled under argon to 0 °C. Iodine (1.03 g, 4.1 mmol) was added and the mixture was stirred at 0 °C for 30 min. TLC (hexane–ethyl acetate, 3:2) showed complete conversion of glycal **4** (R_f 0.34) into the title compound (R_f 0.66). The mixture was filtered over Celite, then was concentrated. The residue was taken up in dichloromethane and the solution was washed with saturated aq. sodium thiosulfate, dried, and concentrated. Flash

chromatography (hexane–ethyl acetate, 4:1) gave iodide **5** (1.03 g, 79%), $[\alpha]_D$ +67 (*c* 2.1, $CHCl_3$); $\delta_H(CDCl_3)$ 0.05 (6 H, s, 2 × Me), 0.90 (9 H, s, Bu^t), 2.28 (1 H, d, $J_{3,OH}$ 8, 3-OH), 3.35 (1 H, dd, $J_{5,6a} \sim J_{6a,6b} \sim 10$, 6-H^a), 3.55 (1 H, dd, $J_{5,6b}$ 4.5, 6-H^b), 3.66 (2 H, m, 2- and 5-H), 4.19 (1 H, dd, $J_{2,3}$ 2, $J_{3,OH}$ 8, 3-H), 4.51 (1 H, d, $J_{2,4}$ 1.5, 4-H) and 5.47 (1 H, d, $J_{1,2}$ 2.5, 1-H) (Found: C, 37.1; H, 6.1. $C_{12}H_{23}IO_4Si$ requires C, 37.31; H, 6.00%).

1,6:2,3-*Dianhydro*-β-D-*talopyranose* **6**.—To a solution of iodide **2** (1.088 g, 4 mmol) in dry dichloromethane (40 cm^3) cooled in an ice–water-bath was added 0.78 mol dm^{-3} sodium methoxide in methanol (26 cm^3, 20 mmol). The mixture was allowed to warm to room temperature, then was stirred for 3 h. TLC (hexane–acetone, 3:2) showed complete conversion of compound **2** (R_f 0.56) into the title compound (R_f 0.44). Water (60 cm^3) was added and the solution was extracted with ethyl acetate. The extract was dried and concentrated to give title compound **6** (461 mg, 80%), m.p. 127–128 °C (lit.,[25] 134–135 °C), $[\alpha]_D$ −90 (*c* 1.08, water) {lit.,[25] $[\alpha]_D$ −88 (*c* 0.7, water)}; $\delta_H[(CD_3)_2SO]$ 3.17 (1 H, ddd, $J_{2,3}$ 4, $J_{3,4}$ 3, $J_{3,5}$ 1, 3-H), 3.38 (1 H, dd, $J_{5,6a}$ 6, $J_{6a,6b}$ 7, 6-H^a), 3.52 (1 H, dd, $J_{1,2}$ 3, 2-H), 3.87 (1 H, dd, $J_{5,6b}$ 2, 6-H^b), 4.02 (1 H, ddd, $J_{4,5} \sim J_{4,OH} \sim 6$, 4-H), 4.25 (1 H, m, 5-H), 5.50 (1 H, d, OH) and 5.65 (1 H, d, 1-H).

1,6-*Anhydro*-2-*azido*-2-*deoxy*-3,4-O-*isopropylidene*-β-D-*galactopyranose* **7** *and* 1,6-*Anhydro*-3-*azido*-3-*deoxy*-β-D-*idopyranose* **8**.—A solution of compound **2** (2.72 g, 10 mmol) and lithium azide[53] (1.47 g, 30 mmol) in dry DMF (30 cm^3) was heated at 100 °C for 12 h. TLC (Et_2O) showed the complete conversion of compound **2** (R_f 0.77) into a mixture of azides (R_f 0.46). The solution was concentrated and the residue was dissolved in water. Continuous extraction with ethyl acetate for 15 h, followed by evaporation of the extract, gave a mixture of isomers **8** and **9** (1.9 g) in the ratio 1:3 as judged by ^{1}H NMR spectroscopy.

To a solution of azides **8** and **9** (1.9 g) in dry acetonitrile (10 cm^3) were added 2,2-dimethoxypropane (5.2 g, 50 mmol) and (±)-camphor-10-sulfonic acid (CSA) (25 mg). The mixture was stirred at room temperature for 5 h, then was neutralized with triethylamine. TLC (hexane–ethyl acetate, 7:3) showed the formation of the isopropylidene derivative **7** (R_f 0.45) and unchanged diol **8** (R_f 0.04). After concentration the residue was purified by flash chromatography (hexane–ethyl acetate, 4:1) to give compound **7** (1.73 g, 75%); $[\alpha]_D$ −23 (*c* 1, $CHCl_3$) {lit.,[28] $[\alpha]_D$ −27.9 (*c* 1, $CHCl_3$)}; $\delta_H(CDCl_3)$ 1.37 and 1.53 (6 H, 2 s, 2 × Me), 3.54 (1 H, br s, 2-H), 3.61 (1 H, dd, $J_{6a,6b}$ 7.5, 6-H^a), 4.14 (1 H, dd, 6-H^b), 4.25 (1 H, dd, $J_{2,3} < 1$, 3-H), 4.41 (1 H, dd, $J_{3,4}$ 7, 4-H), 4.53 (1 H, ddd, $J_{4,5}$ 6, $J_{5,6a}$ 5.5, $J_{5,6b}$ 0.5, 5-H) and 5.45 (1 H, br s, 1-H).

Elution with acetone gave compound **8** (287 mg, 15%); $[\alpha]_D$ −98 (*c* 1.01, MeOH); ν_{max}(film)/cm^{-1} 2110 (N_3); $\delta_H[(CD_3)_2SO]$ 3.26 (2 H, m, 2- and 3-H), 3.49 (1 H, m, $J_{3,4}$ 9, 4-H), 3.58 (1 H, dd, 6-H^a), 3.97 (1 H, dd, $J_{6a,6b}$ 7.5, 6-H^b), 4.32 (1 H, ddd, $J_{4,5}$ 4.5, $J_{5,6a}$ 5, $J_{5,6b} < 1$, 5-H), 5.14 (1 H, br s, 1-H) 5.55 (1 H, d, *J* 6, OH) and 5.71 (1 H, d, *J* 5.5, OH); *m/z* 205 ($M^+ + 18$) and 160 ($M^+ + 1 - N_2$).

6-O-*Acetyl*-2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-α-D-*galactopyranosyl Bromide* **12**.—A solution of compound **7** (2.27 g, 10 mmol) in 60% aq. acetic acid (35 cm^3) was heated at 100 °C for 1 h. TLC (Et_2O) showed complete conversion of substrate **7** (R_f 0.74) into the diol **9** (R_f 0.30). The cold solution was concentrated and the residue was dried by several co-evaporations with toluene. Sodium hydride (60% dispersion in oil; 1.6 g, 40 mmol) was added portionwise to a stirred solution of crude diol **9** (1.81 g) in dry DMF (40 cm^3) containing benzyl bromide (2.85 cm^3, 24 mmol) at 0 °C. The solution was stirred at room temperature for 1 h, then was cooled to 0 °C. Methanol (13 cm^3) was added to decompose the excess of sodium hydride. The solution was diluted with dichloromethane (300 cm^3), washed with brine, dried, and concentrated. The residue was chromatographed with hexane–ethyl acetate (4:1) as eluent to give compound **10** (3.32 g, 90%) as a syrup; $[\alpha]_D$ +30 (*c* 1.09, $CHCl_3$) {lit.,[28] $[\alpha]_D$ +32.8 (*c* 1, $CHCl_3$)}; $\delta_H(CDCl_3)$ 3.56 (1 H, dd, $J_{2,3}$ 1.5, 2-H), 3.68 (1 H, m, $J_{5,6a}$ 5, 6-H^a) 3.83 (1 H, m, 4-H), 3.87 (1 H, m, $J_{3,4}$ 5.5, 3-H), 4.49 (1 H, m, 5-H), 4.59 (1 H, dd, $J_{5,6b} < 1$, $J_{6a,6b}$ 7, 6-H^b), 4.53 and 4.62 (2 H, 2 d, *J* 11.5, PhCH_2), 4.68 (2 H, m, PhCH_2), 5.43 (1 H, dd, $J_{1,2} \sim J_{1,3} \sim 1.5$, 1-H) and 7.35 (10 H, m, 2 × Ph).

A solution of compound **10** (3.32 g) in acetic anhydride (40 cm^3)–TFA (4 cm^3) was stirred at room temperature for 12 h. TLC (hexane–ethyl acetate, 4:1) showed the complete conversion of compound **10** (R_f 0.47) into diacetate **11** (R_f 0.21). The solution was concentrated and the residue was dried by several co-evaporations with toluene; $\delta_H(CDCl_3)$ 1.97, 2.00, 2.12 and 2.16 (6 H, 4 s, OAc), 5.41 (0.5 H, d, $J_{1,2}$ 8.5, β-acetate 1-H) and 6.26 (0.5 H, d, $J_{1,2}$ 3.5, α-acetate 1-H).

Crude anomeric mixture of acetates **11** (4.24 g) was treated with titanium tetrabromide as described[28] to give, after flash chromatography (hexane–ethyl acetate, 4:1), syrupy bromide **12** (3.36 g, 69% overall yield from compound **7**); $[\alpha]_D$ +174 (*c* 1.28, MeCN) {lit.,[28] $[\alpha]_D$ +141 (*c* 1, MeCN)}; $\delta_H(CDCl_3)$ 2.02 (3 H, s, OAc), 3.95 (1 H, dd, $J_{3,4}$ 2.5, $J_{4,5} < 1$, 4-H), 3.99 (1 H, dd, $J_{2,3}$ 10, 3-H), 4.12 (1 H, dd, $J_{1,2}$ 3.5, 2-H), 4.17 (3 H, m, 5-H and 6-H$_2$), 4.56 and 4.93 (2 H, 2 d, *J* 11.5, PhCH_2), 4.79 (2 H, m, PhCH_2), 6.48 (1 H, d, 1-H) and 7.35 (10 H, m, 2 × Ph).

Tributyl(*oct*-1-*ynyl*)*stannane*.—Butyllithium (75 cm^3 of a 1.6 mol dm^{-3} solution in hexane; 120 mmol) was added to a solution of oct-1-yne (14.7 cm^3, 100 mmol) in dry THF (175 cm^3) under argon at −78 °C. The mixture was stirred for 2 h at −78 °C; tributyltin chloride (32.4 cm^3, 120 mmol) was added and the solution was allowed to reach room temperature, then was heated for a few min at 90 °C until precipitation of lithium chloride occurred. After cooling, the mixture was poured into saturated aq. ammonium chloride (300 cm^3). The organic layer was extracted with dichloromethane (3 × 100 cm^3). The combined extracts were washed with brine, dried, and concentrated. The residue was distilled, b.p. 120 °C at 2 mmHg (32 g, 80%), $\delta_H(CDCl_3)$ 0.88–0.98 (12 H, m, Me), 1.25–1.70 (26 H, m, CH_2) and 2.22 (2 H, t, *J* 7, $CH_2C{\equiv}C$).

1-(6-O-*Acetyl*-2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-α,β-D-*galactopyranosyl*)*oct*-1-*yne* **13** *and* **14**.—A mixture of bromide **12** (1.96 g, 4 mmol), tributyl(oct-1-ynyl)stannane (7.98 g, 20 mmol) and 3 Å molecular sieves (1 g) in dry 1,2-dichloroethane (12 cm^3) was stirred at room temperature under argon for 30 min, then was cooled to −30 °C. Dry silver tetrafluoroboranuide (1.56 g, 8 mmol) was rapidly added and the temperature was allowed to rise slowly 0 °C. The mixture was stirred under argon overnight at 0 °C, then was diluted with dichloromethane (120 cm^3) and filtered over Celite. The filtrate was washed successively with saturated aq. sodium hydrogen carbonate and water, dried, and concentrated. Flash chromatography (hexane–ethyl acetate, 7:3) gave pure α-*C*-glycoside **13** (1.08 g, 52%) as a syrup; $[\alpha]_D$ +74 (*c* 1.05, $CHCl_3$); ν_{max}(film)/cm^{-1} 2215 (C≡C), 2090 (N_3) and 1730 (C=O); $\delta_H(CDCl_3)$ 0.90 (3 H, t, *J* 7, Me), 1.25–1.55 (8 H, m, CH_2), 2.00 (3 H, s, OAc), 2.24 [2 H, dt, *J* 7, *J*(1, CH_2) 2, $CH_2C{\equiv}C$], 3.86 (1 H, dd, $J_{2,3}$ 10, $J_{3,4}$ 2.8, 3-H), 3.89 (1 H, dd, $J_{4,5}$ 1, 4-H), 4.04 (1 H, dd, $J_{1,2}$ 5.5, 2-H), 4.04–4.13 (3 H, m, 5-H and 6-H$_2$), 4.55 and 4.90 (2 H, 2 d, *J* 11.5, PhCH_2), 4.77 (2 H, m, PhCH_2), 4.81 (1 H, dt, 1-H) and 7.35 (10 H, m, 2 × Ph) (Found: C, 69.1; H, 7.3; N, 7.8. $C_{30}H_{37}N_3O_5$ requires C, 69.34; H, 7.18; N, 8.08%).

β-*C*-Glycoside **14** was eluted next (218 mg, 10%) as a syrup;

$[\alpha]_D$ +26 (*c* 1.02, $CHCl_3$); ν_{max}(film)/cm^{-1} 2230 (C≡C), 2090 (N_3) and 1730 (C=O); δ_H($CDCl_3$) 0.88 (3 H, t, *J* 7, Me), 1.20–1.60 (8 H, m, CH_2), 1.98 (3 H, s, OAc), 2.24 [2 H, dt, *J* 7, *J*(1, CH_2) 2, $CH_2C{\equiv}C$], 3.30 (1 H, dd, $J_{2,3}$ 9.5, $J_{3,4}$ 2.5, 3-H), 3.48 (1 H, ddd, $J_{4,5}$ 1, $J_{5,6a}$ 5.5, $J_{5,6b}$ 6.5, 5-H), 3.78 (1 H, dd, 4-H), 3.84 (1 H, dt, $J_{1,2}$ 10, 1-H), 3.92 (1 H, dd, 2-H), 4.06 (1 H, dd, $J_{6a,6b}$ 11.5, 6-H[a]), 4.17 (1 H, dd, 6-H[b]), 4.60 and 4.93 (2 H, 2 d, *J* 11.5, PhCH_2), 4.76 (2 H, m, PhCH_2) and 7.35 (10 H, m, 2 × Ph) (Found: C, 69.45; H, 7.2; N, 8.0%).

1-(6-O-*Acetyl*-2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-α,β-D-*galactopyranosyl*)-2-*phenylacetylene* **15** *and* **16**.—Bromide **12** (980 mg, 2 mmol) was treated with tributyl(phenylethynyl)stannane (Aldrich, 3.91 g, 10 mmol) and silver tetrafluoroboranuide (779 mg, 4 mmol) as described for the preparation of compounds **13** and **14**, except that a complete reaction occurred after the temperature was raised from −40 to 0 °C within 4 h. Flash chomatography (hexane–ethyl acetate, 3:1) gave compound **15** (394 mg, 39%), m.p. 88–89 °C (from EtOH); $[\alpha]_D$ +89 (*c* 1.03, $CHCl_3$); δ_H($CDCl_3$) 2.02 (3 H, s, OAc), 3.97 (2 H, m, 3- and 4-H), 4.17 (4 H, m, 2- and 5-H and 6-H_2), 4.59 and 4.94 (2 H, 2 d, *J* 11.5, PhCH_2), 4.77 and 4.83 (2 H, 2 d, *J* 11, PhCH_2), 5.06 (1 H, d, $J_{1,2}$ 5.5, 1-H) and 7.25–7.45 (15 H, m, 3 × Ph); δ_H(C_6D_6) 1.70 (3 H, s, OAc), 3.72 (1 H, dd, $J_{3,4}$ 2.5, $J_{4,5}$ 1, 4-H), 3.89 (1 H, dd, $J_{2,3}$ 10.5, 3-H), 4.05 (1 H, dd, $J_{1,2}$ 5.5, 2-H), 4.32–4.47 (6 H, m, 5-H, 6-H_2, PhCH_2, PhCH^xH^y), 4.82 (1 H, d, *J* 11, PhCH$^xH^y$), 4.86 (1 H, d, 1-H) and 7.00–7.50 (15 H, m, 3 × Ph); *m*/*z* 529 (M^+ + 18) and 484 (M^+ + 1 − N_2) (Found: C, 70.2; H, 5.8; N, 8.1. $C_{30}H_{29}N_3O_5$ requires C, 70.43; H, 5.71; N, 8.21%).

β-*C*-Glycoside **16** was eluted next as a syrup (262 mg, 26%), $[\alpha]_D$ +34 (*c* 1.56, $CHCl_3$), δ_H($CDCl_3$) 2.00 (3 H, s, OAc), 3.37 (2 H, m, 2- and 3-H), 3.56 (1 H, ddd, $J_{4,5}$ < 1, $J_{5,6a}$ 5.5, $J_{5,6b}$ 6.8, 5-H), 3.81 (1 H, dd, $J_{3,4}$ 2.5, 4-H), 4.08 (1 H, m, 1-H), 4.10 (1 H, dd, $J_{6a,6b}$ 11.5, 6-H[a]), 4.20 (1 H, dd, 6-H[b]), 4.63 and 4.95 (2 H, 2 d, *J* 11.5, PhCH_2), 4.78 (2 H, m, PhCH_2) and 7.25–7.50 (15 H, m, 3 × Ph); δ_H(C_6D_6) 1.63 (3 H, s, OAc), 2.98 (1 H, dd, $J_{2,3}$ 10, $J_{3,4}$ 3, 3-H), 3.26 (1 H, ddd, $J_{4,5}$ 1, $J_{5,6a}$ 5, $J_{5,6b}$ 7, 5-H), 3.50 (1 H, dd, 4-H), 3.96 (1 H, d, $J_{1,2}$ 10, 1-H), 4.21 (1 H, dd, $J_{6a,6b}$ 11.5, 6-H[a]), 4.24 (1 H, dd, 2-H), 4.37 (1 H, dd, 6-H[b]), 4.44 and 4.85 (2 H, 2 d, *J* 11.5, PhCH_2), 4.40 and 4.48 (2 H, 2 d, *J* 11.5, PhCH_2) and 6.85–7.40 (15 H, m, 3 × Ph); *m*/*z* 529 (M^+ + 18) and 484 (M^+ + 1 − N_2) (Found: C, 70.4; H, 5.8; N, 7.8%).

(4-*Benzyloxybut*-1-*ynyl*)*tributylstannane*.—Butyllithium (40 cm^3 of a 2.5 mol dm^{-3} solution in hexane; 100 mmol) was added to a solution of 4-benzyloxybut-1-yne[54] (16 g, 100 mmol) in dry THF (175 cm^3) under argon at −30 °C. The mixture was stirred for 15 min at −30 °C; tributyltin chloride (27.1 cm^3, 100 mmol) was then added and the solution was stirred for 1 h at −30 °C, then for 12 h at room temperature. Dry hexane (120 cm^3) was added; the mixture was filtered, and the filtrate was washed with water (2 × 200 cm^3), dried, and concentrated (44 g, 98%), δ_H($CDCl_3$) 0.90 (9 H, m, Me), 1.30–1.60 (18 H, m, CH_2), 2.57 (2 H, t, *J* 7, $CH_2C{\equiv}C$), 3.60 (2 H, t, *J* 7, CH_2OCH_2Ph), 4.55 (2 H, s, PhCH_2) and 7.35 (5 H, m, Ph).

1-(6-O-*Acetyl*-2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-α-D-*galactopyranosyl*)-4-*benzyloxybut*-1-*yne* **17**.—Bromide **12** (980 mg, 2 mmol) was treated with (4-benzyloxybut-1-ynyl)tributylstannane (6.29 g, 14 mmol) and silver tetrafluoroboranuide (779 mg, 4 mmol) as described for the preparation of compound **13** and **14**. Flash chromatography (hexane–ethyl acetate, 4:1) gave compound **17** (527 mg, 46%) as a syrup, $[\alpha]_D$ +64 (*c* 0.75, $CHCl_3$); δ_H($CDCl_3$) 1.98 (3 H, s, OAc), 2.57 [2 H, dt, *J* 7, *J*(1, CH_2) 2, $CH_2C{\equiv}C$], 3.61 (2 H, t, *J* 7, CH_2OCH_2Ph), 3.84 (2 H, m, 3- and 4-H), 4.07 (4 H, m, 2- and 5-H and 6-H_2), 4.54 (2 H, s, PhCH_2), 4.54 and 4.89 (2 H, 2 d, *J* 11.5, PhCH_2), 4.67 (2 H, m, PhCH_2), 4.81 (1 H, dt, $J_{1,2}$ 5.5, 1-H) and 7.35 (15 H, m, 3 × Ph); δ_H(C_6D_6) 1.64 (3 H, s, OAc), 2.28 [2 H, dt, *J* 6.5, *J*(1, CH_2) 2, $CH_2C{\equiv}C$], 3.32 (2 H, m, CH_2OCH_2Ph), 3.70 (1 H, d, $J_{3,4}$ 2.5, 4-H), 3.90 (1 H, dd, $J_{2,3}$ 10.5, 3-H), 4.00 (1 H, dd, $J_{1,2}$ 5.5, 2-H), 4.28 (2 H, s, PhCH_2), 4.29–4.42 (6 H, m, 5-H, 6-H_2, PhCH_2 and PhCH^xH^y), 4.68 (1 H, dt, 1-H), 4.81 (1 H, d, *J* 11, PhCH$^xH^y$) and 7.00–7.40 (15 H, m, 3 × Ph); *m*/*z* 587 (M^+ + 18) and 542 (M^+ + 1 − N_2) (Found: C, 68.6; H, 6.2; N, 7.5. $C_{33}H_{35}N_3O_6{\cdot}0.5H_2O$ requires C, 68.50; H, 6.10; N, 7.26%).

1-(2-*Acetamido*-2-*deoxy*-α-D-*galactopyranosyl*)*octane* **20**.—Triphenylphosphine (393 mg, 1.5 mmol) was added to a solution of azide **13** (520 mg, 1 mmol) in dry THF (5 cm^3). The solution was stirred at room temperature for 3 h. Water (1.3 cm^3) was added and the mixture was stirred at 40 °C for 12 h. The solution was concentrated and the residue was dried by several co-evaporations with toluene, then was treated with pyridine–acetic anhydride (1:1; 13 cm^3) at room temperature for 12 h. Methanol was added and the solution was concentrated. The residue was taken up in toluene and the solution was washed with water, dried, and concentrated. Flash chromatography of the residue (hexane–ethyl acetate, 3:2) gave compound **18** (441 mg, 82% overall yield from **13**).

A solution of compound **18** (441 mg) in ethyl acetate–methanol–water (15:4:1; 25 cm^3) was stirred for 18 h under hydrogen at normal pressure and room temperature in the presence of 10% palladium on charcoal (100 mg). The catalyst was filtered off over a layer of silica gel, then was washed with ethyl acetate. The combined filtrate and washings were concentrated, and the dried residue was treated with pyridine–acetic anhydride (1:1; 50 cm^3) at room temperature for 12 h. Work-up gave chromatographically pure triacetate **19** (330 mg, 90%); δ_H($CDCl_3$) 0.88 (3 H, t, *J* 7, Me), 1.25–1.70 (14 H, m, CH_2), 1.98, 2.05, 2.07 and 2.12 (12 H, 4 s, 4 × Ac), 4.00 (1 H, m, 5-H), 4.11 (2 H, m, 6-H_2), 4.23 (1 H, m, 1-H), 4.47 (1 H, ddd, $J_{1,2}$ 4.8, $J_{2,3}$ 9.8, $J_{2,NH}$ 8.5, 2-H), 5.14 (1 H, dd, $J_{3,4}$ 3.2, 3-H), 5.31 (1 H, dd, $J_{4,5}$ 3, 4-H) and 5.58 (1 H, d, NH).

A solution of compound **19** (330 mg) in methanol–water–triethylamine (10:10:1; 63 cm^3) was stirred overnight at room temperature, then was concentrated. The residue was dried by several co-evaporations with ethanol, then under good reduced pressure to give triol **20** (215 mg, 91%), $[\alpha]_D$ +96 (*c* 1, MeOH); δ_H(CD_3OD) 0.89 (3 H, t, *J* 7, Me), 1.25–1.75 (14 H, m, CH_2), 1.97 (3 H, s, NAc), 3.66 (1 H, ddd, $J_{4,5}$ 2.5, 5-H), 3.67–3.82 (2 H, m, 6-H_2), 3.71 (1 H, dd, $J_{2,3}$ 10, $J_{3,4}$ 3, 3-H), 3.89 (1 H, dd, 4-H), 4.06 (1 H, m, 1-H) and 4.23 (1 H, dd, $J_{1,2}$ 5, 2-H) (Found: C, 60.3; H, 9.9; N, 4.7. $C_{16}H_{31}NO_5$ requires C, 60.53; H, 9.84; N, 4.41%).

1-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*galactopyranosyl*)*octane* **21**.—The β-*C*-glycoside **14** (104 mg, 0.2 mmol) was converted into triacetate **21** as described above (53 mg, 60% overall yield); δ_H($CDCl_3$) 0.88 (3 H, t, *J* 7, Me), 1.25–1.70 (14 H, m, CH_2), 1.97, 2.01, 2.05 and 2.17 (12 H, 4 s, 4 × Ac), 3.22 (1 H, m, 1-H), 3.79 (1 H, ddd, $J_{4,5}$ 1.2, $J_{5,6a}$ ~ $J_{5,6b}$ ~ 6.8, 5-H), 4.06 (1 H, dd, $J_{6a,6b}$ 11, 6-H[a]), 4.14 (1 H, dd, 6-H[b]), 4.20 (1 H, dd, $J_{1,2}$ 10, $J_{2,3}$ 11, 2-H), 4.96 (1 H, dd, $J_{3,4}$ 3.2, 3-H), 5.25 (1 H, d, $J_{2,NH}$ 9.8, NH) and 5.35 (1 H, dd, 4-H).

6-O-*Acetyl*-2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-α,β-D-*glucopyranosyl Fluoride* **23**.—A mixture of 1,6-di-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranose[12] (2.35 g, 5 mmol) and benzylamine (2.73 cm^3, 25 mmol) in ether (20 cm^3) was stirred at room temperature for 12 h. TLC (hexane–ethyl acetate, 7:3) showed complete conversion of starting material (R_f 0.47) into a major compound (R_f 0.30). The solution was concentrated and the residue was taken up in dichloromethane; the extract was washed successively with aq. hydrochloric acid (1 mol dm^{-3}), brine and water, then was dried and concentrated. Flash

chromatography (hexane–ethyl acetate, 7:3) gave the hemiacetal **22** (1.46 g, 68%), $\delta_H(CDCl_3$; major isomer) 2.06 (3 H, s, OAc), 3.01 (1 H, br d, OH), 3.42 (1 H, dd, $J_{1,2}$ 3.2, $J_{2,3}$ 10, 2-H), 3.54 (1 H, dd, $J_{3,4}$ 9, $J_{4,5}$ 10, 4-H), 4.03 (1 H, dd, 3-H), 4.10 (1 H, ddd, 5-H), 4.20 (1 H, dd, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 12, 6-H^a), 4.33 (1 H, dd, $J_{5,6b}$ 2, 6-H^b), 5.29 (1 H, dd, $J_{1,2}$ ~ $J_{1,OH}$ ~ 3.2, 1-H) and 7.35 (10 H, m, 2 × Ph).

DAST (660 mg, 4.1 mmol) was added to a solution of compound **22** (1.46 g, 3.42 mmol) in dry THF (10 cm^3) at −30 °C. The mixture was allowed to reach room temperature and was stirred at this temperature for 20 min. TLC (hexane–ethyl acetate, 7:3) showed complete conversion of substrate **22** (R_f 0.23) into the title compound (R_f 0.45). The solution was cooled to −30 °C and methanol (3 cm^3) was added to decompose the excess of DAST. Solvents were evaporated off and the residue was taken up in dichloromethane. The extract was washed successively with saturated aq. sodium hydrogen carbonate, brine and water, dried, and concentrated to give fluoride **23** (1.39 g, 95%), $\delta_H(CDCl_3)$ 2.04 (0.75 H, s, α-fluoride OAc), 2.05 (2.25 H, s, β-fluoride OAc), 3.46 (0.25 H, ddd, $J_{1,2}$ 2.8, $J_{2,3}$ 10, $J_{2,F}$ 26, α-fluoride 2-H), 3.98 (0.25 H, dd, $J_{3,4}$ 9, α-fluoride 3-H), 4.04 (0.25 H, ddd, $J_{5,6a}$ 4.5, $J_{5,6b}$ 2.5, α-fluoride 5-H), 4.19 (0.75 H, dd, $J_{5,6a}$ 4, $J_{6a,6b}$ 12, β-fluoride 6-H^a), 4.23 (0.25 H, dd, $J_{5,6a}$ 4, $J_{6a,6b}$ 12, α-fluoride 6-H^a), 4.35 (0.25 H, dd, α-fluoride 6-H^b), 4.37 (0.75 H, dd, $J_{5,6b}$ 1, β-fluoride 6-H^b), 5.06 (0.75 H, dd, $J_{1,2}$ 7, $J_{1,F}$ 52, β-fluoride 1-H), 5.63 (0.25 H, dd, $J_{1,2}$ 2.8, $J_{1,F}$ 53, α-fluoride 1-H) and 7.35 (10 H, m, 2 × Ph).

1-(6-O-*Acetyl*-2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-α-D-*glucopyranosyl*)*oct*-1-*yne* **25**.—6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl bromide[12] **24** (980 mg, 2 mmol) was treated with tributyl(oct-1-ynyl)stannane (3.99 g, 10 mmol) and silver tetrafluoroboranuide (779 mg, 4 mmol) as described for the preparation of compounds **13** and **14**. After 1 h at 0 °C TLC (hexane–ethyl acetate, 4:1) was performed upon a sample of the reaction mixture quenched with dry ether; it showed the formation of the title compound (R_f 0.50) and the fluoride **23** (R_f 0.42). Following work-up of the sample, ^{1}H NMR analysis demonstrated the α-configuration of the fluoride. After 12 h at 0 °C, TLC analysis of the reaction mixture showed the absence of fluoride. Flash chromatography (hexane–ethyl acetate, 17:3) gave title compound **25** (723 mg, 74%), $[\alpha]_D$ +57.5 (*c* 1.06, $CHCl_3$); $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 7, Me), 1.25–1.60 (8 H, m, CH_2), 2.04 (3 H, s, OAc), 2.27 [2 H, dt, *J* 7, *J*(1, CH_2) 2, $CH_2C{\equiv}C$], 3.51 (1 H, dd, $J_{3,4}$ 8.5, $J_{4,5}$ 10, 4-H), 3.55 (1 H, dd, $J_{1,2}$ 5.5, $J_{2,3}$ 10, 2-H), 3.92 (1 H, dd, 3-H), 4.06 (1 H, ddd, $J_{5,6a}$ 4, $J_{5,6b}$ 2.5, 5-H), 4.26 (1 H, dd, $J_{6a,6b}$ 12, 6-H^a), 4.32 (1 H, dd, 6-H^b), 4.57 and 4.85 (2 H, 2 d, *J* 11, PhCH_2), 4.77 (1 H, dt, 1-H), 4.88 and 4.93 (2 H, 2 d, *J* 11, PhCH_2) and 7.35 (10 H, m, 2 × Ph) (Found: C, 69.3; H, 7.3; N, 8.0. $C_{30}H_{37}N_3O_5$ requires C, 69.34; H, 7.18; N, 8.08%).

1-(2-*Acetamido*-2-*deoxy*-α-D-*glucopyranosyl*)*octane* **28**.—Compound **25** (520 mg, 1 mmol) was treated with triphenylphosphine (393 mg, 1.5 mmol), then water (1.3 cm^3) as described above. N-Acetylation gave the acetamide **26** (421 mg, 78%) after flash chromatography (hexane–ethyl acetate, 3:2); $\delta_H(CDCl_3)$ 0.90 (3 H, t, *J* 7, Me), 1.25–1.55 (8 H, m, CH_2), 1.80 (3 H, s, NAc), 2.07 (3 H, s, OAc), 2.22 [2 H, dt, *J*(1, CH_2) 2, $CH_2C{\equiv}C$), 3.58 (1 H, dd, $J_{3,4}$ 8.5, $J_{4,5}$ 9.5, 4-H), 3.72 (1 H, dd, $J_{2,3}$ 10.5, 3-H), 4.00 (1 H, ddd, $J_{5,6a}$ 4.5, $J_{5,6b}$ 2.5, 5-H), 4.18 (1 H, ddd, $J_{1,2}$ 5.5, $J_{2,NH}$ 9, 2-H), 4.27 (1 H, dd, $J_{6a,6b}$ 12, 6-H^a), 4.36 (1 H, dd, 6 H^b), 4.61, 4.68, 4.87 and 4.89 (4 H, 4 d, *J* 11, 2 × PhCH_2), 4.96 (1 H, d, NH) and 7.35 (10 H, m, 2 × Ph).

Compound **26** (421 mg) was hydrogenated, then acetylated as described above to give triacetate **27** (314 mg, 90%), $\delta_H(CDCl_3)$ 0.88 (3 H, t, *J* 7, Me), 1.25–1.70 (14 H, m, CH_2), 1.97, 2.06, 2.08 and 2.09 (12 H, 4 s, 4 × Ac), 3.83 (1 H, ddd, $J_{4,5}$ 7, $J_{5,6a}$ 3.5, $J_{5,6b}$ 6.5, 5-H), 4.12 (2 H, m, 1-H and 6-H^a), 4.26 (1 H, ddd, $J_{1,2}$ 4.5, $J_{2,3}$ 9, $J_{2,NH}$ 8.5, 2-H), 4.31 (1 H, dd, $J_{6a,6b}$ 12, 6-H^b), 4.96 (1 H, dd, $J_{3,4}$ 7, 4-H), 5.04 (1 H, dd, 3-H) and 5.80 (1 H, d, NH); $\delta_H(C_6D_6)$ 4.16 (1 H, dd, 6-H^a) and 4.18 (1 H, m, 1-H).

De-O-acetylation of triacetate **27** (314 mg) gave triol **28** (202 mg, 90%), $[\alpha]_D$ +79 (*c* 0.53, MeOH); $\delta_H[(CD_3)_2SO]$ 0.85 (1 H, t, *J* 7, Me), 1.10–1.65 (14 H, m, CH_2), 1.80 (3 H, s, NAc), 3.10 (1 H, m, 4-H), 3.20 (1 H, m, 5-H), 3.42 (2 H, m, 3-H and 6-H^a), 3.60 (1 H, m, 6-H^b), 3.68 (1 H, ddd, $J_{2,3}$ 10, 2-H), 3.78 [1 H, ddd, $J_{1,2}$ 5.2, *J*(1, C*H*^{x}H^y) 11, *J*(1, CH^x*H*^{y}) 5, 1-H], 4.41 (1 H, t, *J* 3.5, 6-OH), 4.69 (1 H, d, *J* 4, 3-OH), 4.88 (1 H, d, *J* 4, 4-OH) and 7.68 (1 H, d, $J_{2,NH}$ 8, NH) (Found: C, 59.25; H, 9.8; N, 4.6. $C_{16}H_{31}NO_5{\cdot}0.33H_2O$ requires C, 59.43; H, 9.87; N, 4.33%).

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