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Ethereal Glycoconjugated Azodyes (GADs): A New Group of Water-Soluble, Naturalised Dyes

Roberto Bianchini,*[a] Giorgio Catelani,*[b] Riccardo Cecconi,[c] Felicia D'Andrea,[b] Lorenzo Guazzelli,[b] Jalal Isaad,[a] and Massimo Rolla[a]

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This report deals with azodyes naturalised through glycoconjugation with a very common saccharide – lactose – and with its galactose and glucose components. The conjugation takes place through a bifunctional linker, here a terminal dibromoalkane, so the final products are very stable diether derivatives of the starting dyes. These transformations produce naturalised dyes – indeed, water-soluble and multipurpose – that are able to dye different materials without addition of chemical additives such as surface agents.

Introduction

The topic of naturalised dyes can be regarded as a huge field of investigation into ways to prepare classes of dyes essentially based upon two main properties: considerable hydrosolubility and universality of application. This is poorly compatible with the starting disperse azodyes, which are almost but not completely insoluble in water. These disperse azodyes experienced fast growth in the last decades of the past century, especially since they were the most suitable for dyeing of polyester fibres,[1] their absorption on all hydrophobic polymers being the consequence of the combined action of weak dispersion forces together with strong hydrogen bonds.[2] Here, however, what we call "naturalised dyes",[3] exhibit the advantages of the potential both to carry out dyeing processes in water and also to avoid the use of surfactant agents and other additives that cause not only increased cost, but also further environmental problems in the attempted depuration of such materials. In addition, the reduction of the number of these dyes needed in textile activity, due to the ability of these new dyes to colour different textile materials, whether natural, synthetic, or artificial, should also offer the potential for effective depuration, beside further reductions in costs associated with general technological improvements in this area.

As we have recently highlighted,[3] "naturalised" is a term referring to the bonding of chromophores, primarily azo moieties, to a natural saccharide – lactose – and to its derivatives glucose and galactose, through a bivalent linker capable of chemically bonding both the dye and the sugar, a process we have called "glycation". "Naturalisation" also refers to natural dyes, which often feature sugar moieties as well as the chromophore in order to provide acceptable solubilities in biological liquids[4] such as lymph.

The initially proposed linker was succinic acid, providing diester derivatives. The succinyl bridge worked very well from the synthetic point of view, even though its ester bonds would not appear to be the most stable. This kind of derivatization raised a concern in a referee involving the stabilities of this first series of naturalised dyes in the dyeing, a chemical procedure involving conditions far from ambient, with pHs sometime far from neutrality, and also in the presence of many aggressive chemicals. Although our dyes changed the procedures of dyeing, since they are able to dye without any addition of surfactants of other chemicals, at neutral pH, we nevertheless took this comment into serious consideration, and here we report on a different kind of bonding, based not on a diester but on a much more stable and resistant diether model. Glycoazodyes (GADs) based on diether links between the spacer and the dye at one end and with the saccharide at the other were synthesised and proved to be at least as effective as the diester derivatives in dyeing.

Results

Three azodyes (**1**–**3**, Figure 1), either commercially available or easily synthesised,[5] were derivatised by the procedure of putting a linker between the dye and the glycidic moieties. As far as the saccharide is concerned, this time we also first took into consideration the two monosaccharides,

[a] Dipartimento di Chimica Organica "Ugo Schiff", Università di Firenze,
Via della Lastruccia 13, 50019 Sesto Fiorentino (FI), Italy
E-mail: roberto.bianchini@unifi.it
[b] Dipartimento di Chimica Bioorganica e Biofarmacia, Università di Pisa,
Via Bonanno 33, Pisa 56126, Italy
E-mail: giocate@farm.unipi.it
[c] Lanartex snc laboratory,
Via 1 Maggio, Montemurlo (PO) 59013, Italy

galactose and glucose, that are the constituents of the lactose disaccharide that was also used to glycoconjugate the dyes.

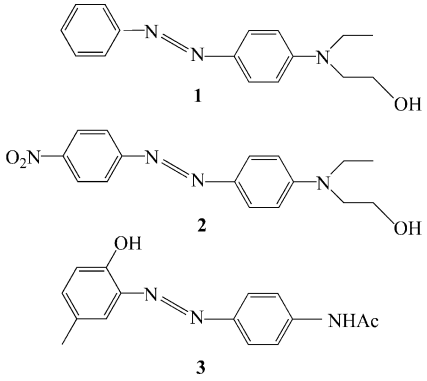


Figure 1. Starting azodyes.

We therefore used three different glycides, but in the case of lactose we selected two differently protected derivatives in order to examine possible tinctorial effects depending on the position of lactose at which the derivatization had been carried out. Isopropylidene protection was chosen in all cases, since it is easy to accomplish and its removal under mild conditions is also possible. We used the commercially available 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (**4**) and 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (**5**) (Figure 2).

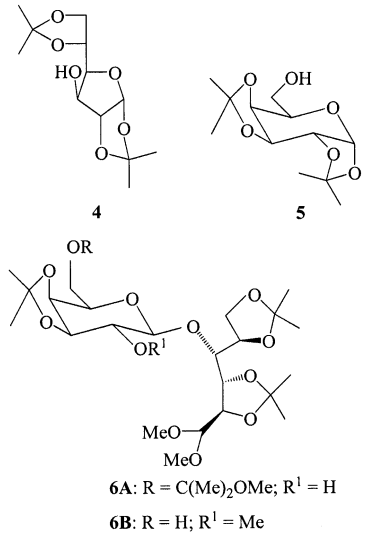
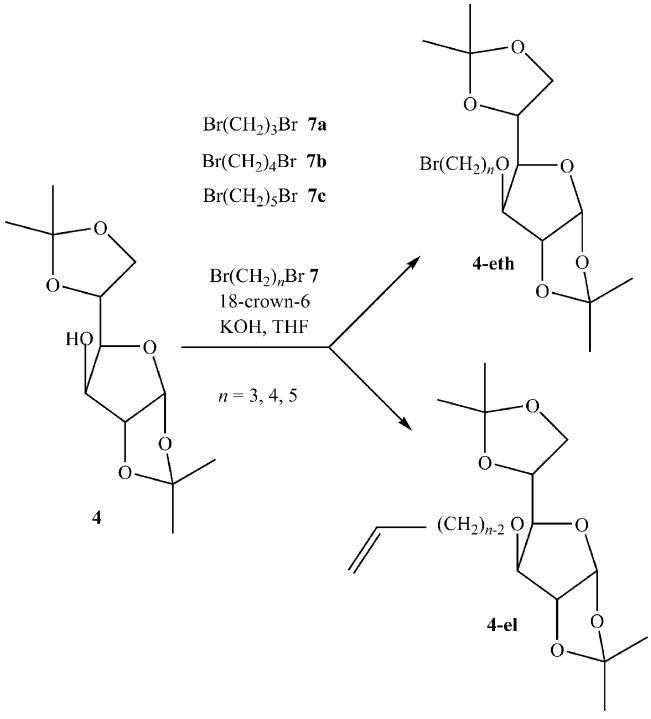


Figure 2. Protected saccharides.

With lactose, we resorted both to derivative **6A**, prepared by a known procedure,[6] and to protected lactose **6B**, bearing a methoxy substituent in the 2′ position, easily obtained in high yields from **6A** through *O*-methylation followed by selective deprotection of O-6′ under mild acid conditions (Figure 2).

As far as the third component of the glycoconjugation is concerned, we set out to use linkers capable of forming ethereal bonds between the linker and the dye on one side and with the glycide on the other, and we therefore resorted to terminal dibromoalkanes to bind the OH groups of the selected dye and a free OH of a protected saccharide, as they had given satisfactory results in similar reactions aimed towards linking two saccharidic moieties with each other.[7] The reaction is a classic nucleophilic substitution of the oxygen atom in the protected sugar at the carbon atom linked to the bromine atom and was carried out with KOH as strong inorganic base and 18-crown-6 as phase-transfer agent.[8] We used non-anhydrous THF, because it helps KOH to dissolve and does not affect the yield by competing with the crown ether. Reagents with smaller numbers of carbon atoms showed the formation of larger quantities of by-products, mainly originating from the competing hydrogen bromide elimination reaction (Scheme 1, Table 1).



Scheme 1. Products obtained on treatment of **4** with α,ω-dibromoalkanes **7**.

Table 1. Yields of reactions shown in Scheme 1.

Reactant	Product	Yield	$(CH_2)_n$	By-product	Yield
7a	**2f**	12%	$n = 3$	**7f**	35%
7b	**2g**	70%	$n = 4$	**7g**	12%
7c	**2h**	83%	$n = 5$	**7h**	10%

In light of the results obtained we decided to use 1,5-dibromopentane and 1,4-dibromobutane as linkers in our reactions for the synthesis of the second generation of GADs. We finally treated **7b** or **7c** with protected glycides **4**, **5**, **6A** and **6B**, the substrate producing the best yield being **5**, but we may note that all saccharides gave very good yields with comparable reaction times, only glucose derivative **4** suffering from detectable elimination, as reported in

Table 1. In conclusion, as reported in Figure 3, we obtained four monoethers from **4** and **5** – the bromobutoxy ether **4-eth4** and the bromopentoxy ether **4-eth5** from **4**, and the bromobutoxy ether **5-eth4** and the bromopentoxy ether **5-eth5** from **5** – together with the two monoethers **6A-eth5** and **6B-eth4** originating from the differently protected lactoses. As well as the monoether derivatives, traces of elimination products occurred, but their yields were so low that they are not reported in Figure 3.

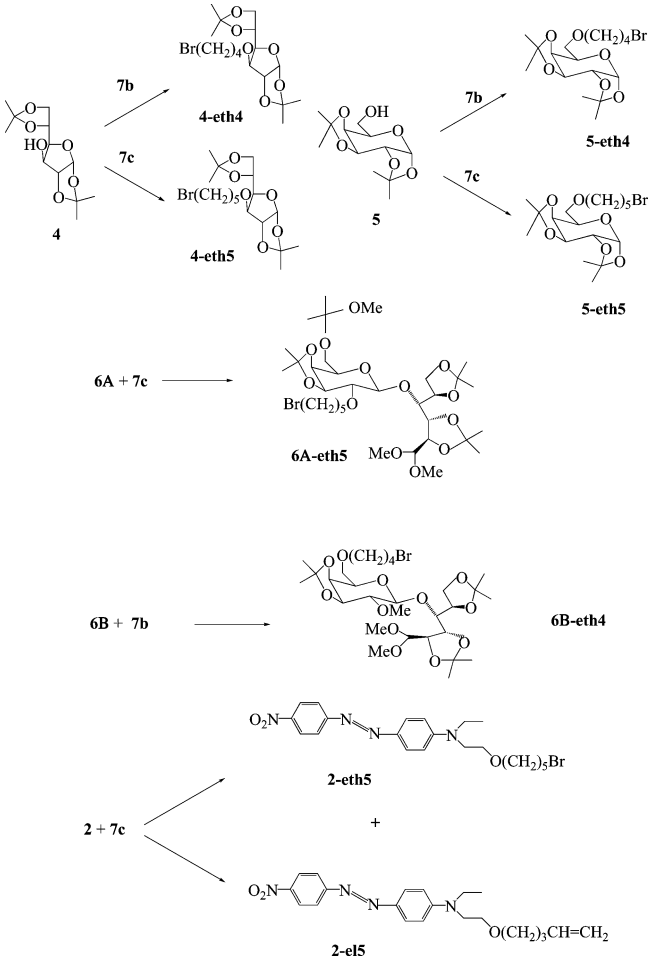


Figure 3. Monoethers (**eth**) and elimination products (**el**) prepared from dibromoalkanes **7** and glycides or dye **2**.

We also investigated the preparation of final GADs starting from the monoether of the dye. A single case is reported here for reasons of brevity: dye **2** was treated in the presence of **7c**, with the results illustrated in Figure 3, in particular the azobenzene derivative **2-eth5**.

The further step, to obtain the target products – that is, diethereal GADs – consisted of the replication of a substitution reaction in which the obtained bromo ethers were intended to react with the appropriate nucleophile, the dye or the glycide, in an identical procedure. The production of elimination products, indicated in Figure 4, was variable but detectable. This aspect appears to be different from the reactions leading to monoethers, in which the elimination products, generally speaking, did not influence the yield.

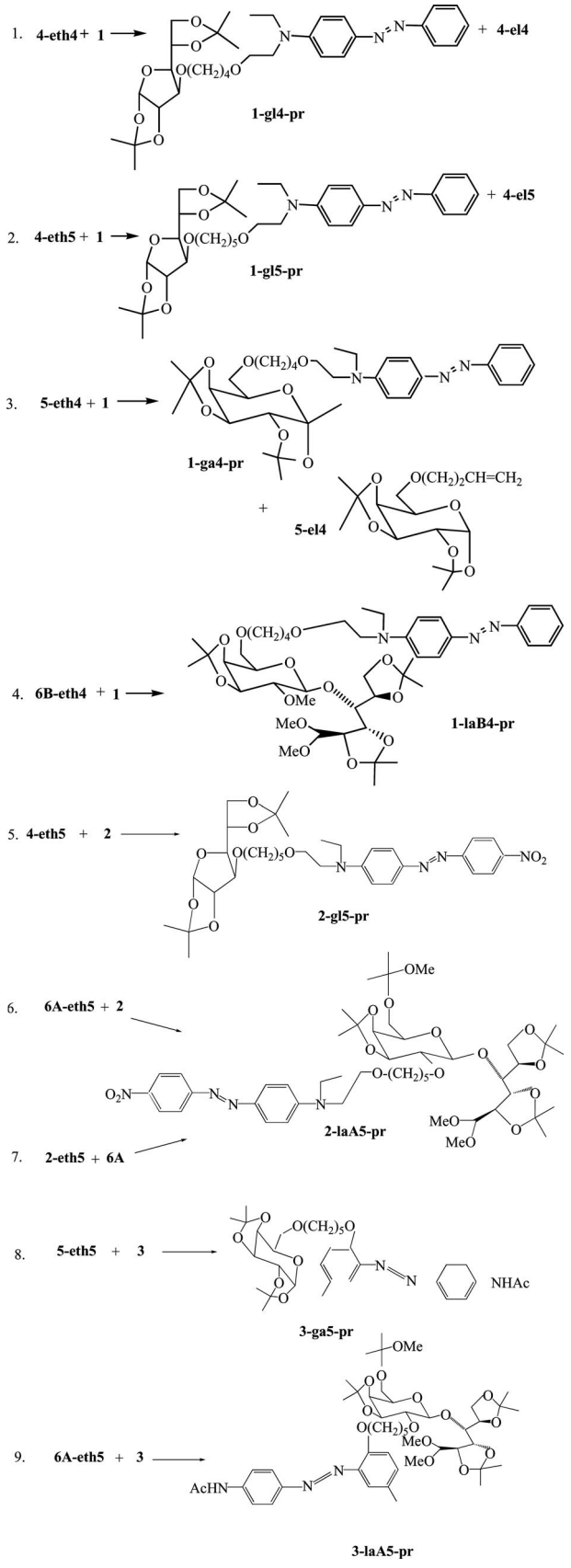


Figure 4. Preparation of protected diethers [GADs; **eth** stands for ether, **gl** for glucose, **gal** for galactose, **la** for lactose (A and B), the number indicates the carbons in the linker, and **pr** means protected].

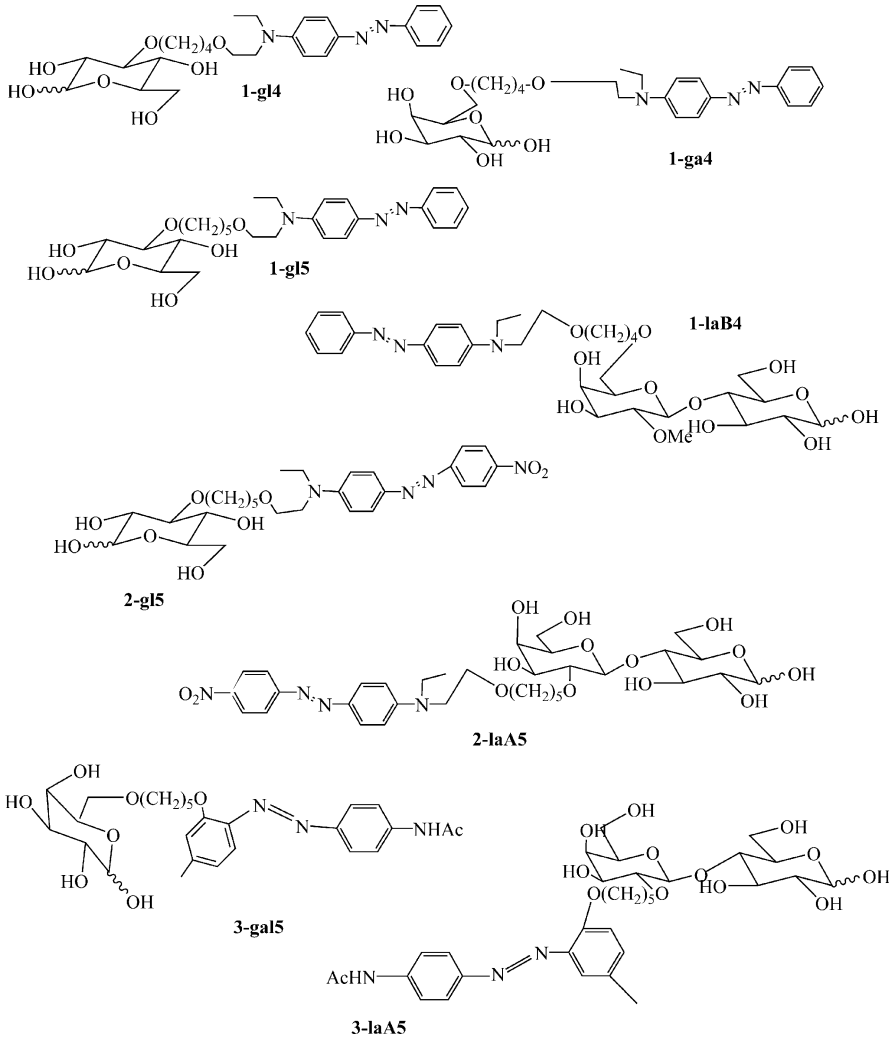


Figure 5. Final deprotected GADs as diethers.

Here, however, the reacting species each bear a single heteroatom, not two as in the case of species **7b** and **7c**, and moreover in this case we used 1 equiv. of the bromoethers, while in the formation of monoethers the dibromides were added as 5 equiv. Finally, the nucleophiles in the paths under comparison are different, and in particular the species on which the substitutions occur – dibromides and bromoethers – are different, and all these considerations might explain the greater importance of the competing elimination in the preparation of the final protected products.

It is worth stressing that in a single case we obtained the same product – **2-laA5-pr** – by two different strategies, the first (reaction 6) consisting of the early preparation of a glycidyl ether bromide, followed by treatment with the dye, and the second (reaction 5) first involving preparation of the dye bonded to a bromide ether, followed by treatment of this product with the protected glycide. As a matter of fact, the products can be prepared by either pathway without appreciable differences (Figure 4).

The next step, to arrive at the final products, consists of the deprotection of the various diethers illustrated in Figure 4 by trifluoroacetic cleavage. Finally the products reported below (Figure 5) were obtained. It also deserves mention that products **1**, **1-ga4**, **1-gl4**, **1-gl5** and **1-laB4** – that is, dye **1** and its ethereal glyconjugated derivatives – all exhibit the same λ_{max}, as expected, at around 412 nm.

Tinctorial Tests

The materials described above, the final products of the approach in the title, exist as powders, as is also the case with diesters.[3] Moreover, their solubilities are comparable to those of the previously described succinate GADs. The dyeing procedure, furthermore, is as attractive as its diesteric GAD counterpart, since these diethers dye the same kind of materials – polyacetates, nylon, wool, acrylic, polyester and cotton – uniformly and efficaciously (Figure 6). Dyeing was carried out with a 1% solution of the dye, 1% of added acetic acid, at 50:1 ratio (bath/fabric), over a 15–30 min period and at average temperature of 80–98 °C, polyester included. In conclusion, diethers derivatives of textile glycoconjugated dyes behave as well as expected, besides being more stable, and they represent an augmentation in the efficiency of GADs that we are studying.

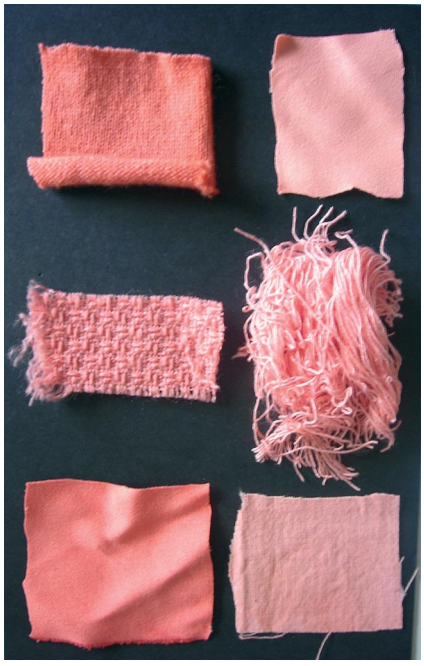


Figure 6. Tinctorial test on **2-laA5** carried out on (from the line up, right-hand side): 1) cotton, 2) nylon, 3) polyacrylic, 4) wool, 5) polyacetate, 6) polyester.

Some typical luminosity values: polyester, dyed with **1-laB4**: 71 920, with chromaticity 32 502 and tone 29 776. The same dye on wool: 53 936, 39 920, 32 778, respectively. For acetate the values were 43 921, 65 709, and 41 513.

Experimental Section

General: Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at 20±2 °C. ^{1}H NMR spectra were recorded in appropriate solvents (internal standard Me_4Si) with a Bruker AC 200 instrument at 200 MHz, with a Varian Gemini instruments at 200 MHz and with a Bruker Avance II operating at 250 MHz. ^{13}C NMR spectra were recorded with the spectrometers operating at 50 and 62.9 MHz. Assignments were made with the aid of DEPT, HETCOR and COSY experiments and by comparison with values for known compounds and application of the known additivity rules.[9] In the case of anomeric mixtures, the assignments were made by referring to the differences in the peak intensities. All reactions were followed by TLC on Kieselgel 60 F_{254} with detection under UV light and/or with ethanolic 10% phosphomolybdic or sulfuric acid, and heating. Kieselgel 60 (E. Merck, 70–230 and 230–400 mesh, respectively) was used for column and flash chromatography. Solvents were dried by distillation according to standard procedures,[10] followed by storage over 4-Å molecular sieves activated at 250 °C for at least 24 h. Red azodyes **2** (Disperse Red 1) and **3** (Disperse yellow 3) are commercially available (Sigma–Aldrich); yellow dye **1** was prepared according to the literature.[5] 1,2:5,6-Di-*O*-isopropylidene-D-glucofuranose (**4**) and 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (**5**) are commercially available (Fluka). Literature methods were used to prepare 4-*O*-[6-*O*-(1-methoxy-1-methylethyl)-3,4-*O*-isopropylidene-β-D-galactopyranosyl]-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (**6A**).[6] UV/Vis spectra were recorded in methanol on a Varian Cary 4000 instrument, under the conditions reported in the Results section.

2,3:5,6-Di-*O*-isopropylidene-4-*O*-[3,4-*O*-isopropylidene-2-*O*-methyl-β-D-galactopyranosyl]-*aldehydo*-D-glucose Dimethyl Acetal (6B): A solution of **6A** (1.03 g, 1.77 mmol) in dry DMF (20 mL) was cooled to 0 °C and treated slowly with NaH in mineral oil (60%, 0.278 g, 7.00 mmol), and the suspension was stirred at room temperature for 20 min. The mixture was cooled to 0 °C, treated with CH_3I (0.22 mL, 3.49 mmol) and further stirred for 15 min at 0 °C and 2 h at room temperature. TLC analysis (hexane/EtOAc, 1:1) revealed the complete disappearance of the starting material (R_f = 0.29) and the formation of a major faster-moving product (R_f = 0.49). The reaction was quenched by the addition of MeOH (3.0 mL), and the solvent was evaporated under reduce pressure. The residue was taken up in EtOAc, (50 mL) and the solution was treated with aqueous HCl (20%) until TLC analysis (hexane/EtOAc, 1:1) revealed the complete disappearance of the product with R_f = 0.49 and the formation of a minor faster-moving product (R_f = 0.26). The aqueous phase was further extracted with EtOAc, (3 × 20 mL), and the organic extracts were dried with $MgSO_4$, filtered and concentrated under diminished pressure. The crude residue (1.25 g) was subjected to flash chromatographic purification (hexane/EtOAc, 3:2) to yield **6B** as a syrup (0.864 g, 94%). R_f = 0.26 (hexane/EtOAc, 1:1). $[\alpha]_D$ = +19.2 (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, CD_3CN): δ = 4.66 (dd, $J_{1,2}$ = 7.0, $J_{2,3}$ = 7.8 Hz, 1 H, 2-H), 4.49 (d, $J_{1',2'}$ = 8.1 Hz, 1 H, 1′-H), 4.38 (d, 1 H, 1-H), 4.29 (dt, $J_{5,6a}$ = $J_{5,6b}$ = 6.4 Hz, 1 H, 5-H), 4.03 (m, 2 H, 3′-H, 4′-H), 4.00 (m, 2 H, 6a-H, 6b-H), 3.96 (dd, $J_{3,4}$ = 7.8, $J_{4,5}$ = 1.2 Hz, 1 H, 4-H), 3.92 (m, 1 H, 3-H), 3.80–3.70 (m, 3 H, 5′-H, 6′a-H, 6′b-H), 3.09 (dd, $J_{2',3'}$ = 6.7 Hz, 2′-H), 3.57 (s, 3 H, 2-OCH_3), 3.49 (s, 6 H, 2 × 1-OCH_3), 1.51, 1.45, 1.41, 1.40, 1.36, 1.34 [6 × s, each 3 H, 3 × C(CH_3)$_2$] ppm. ^{13}C NMR (62.9 MHz, CD_3CN) see Table 5 and: δ = 110.1, 109.8, 108.4 [3 × C(CH_3)$_2$], 60.4 (2-OCH_3), 57.6, 53.8 (2 × 1-OCH_3), 28.0, 27.2, 26.3, 26.1, 26.0, 25.4 [3 × C-(CH_3)$_2$] ppm. $C_{24}H_{42}O_{12}$ (522.60): calcd. C 55.10, H 8.10; found C 55.43, H 8.39.

Alternatively, pure **6B** was prepared by methylation of the crude mixture (1.00 g) obtained by double isopropylidenation of lactose (0.555 g, 0.423 mmol) with DMP and TsOH, according to the procedure described in the literature,[6] followed by selective de-*O*-methoxyisopropylation as reported above. Flash chromatography (hexane/EtOAc, 2:3) of the crude product gave pure **6B** (0.176 g) in 70% yield calculated from lactose.

General Procedure for Etherification of 4, 5, 6A and 6B: A mixture of the appropriate sugar (1.0 mmol), KOH (4.0 equiv.) and 18-crown-6 (0.01 equiv.) in THF/H_2O (99.5:0.5, 10 mL) was stirred at room temperature for 1 h, the dibromide (5 equiv.) was then added, and the mixture was stirred under the same conditions for several hours. The reaction mixture was neutralised with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was dried with Na_2SO_4, filtered and concentrated under diminished pressure, and the resulting residue was purified by flash chromatography.

3-*O*-(3-Bromopropyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4-eth3) and 3-*O*-Allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4-el3): Flash chromatography (hexane/EtOAc, 4:1) of the crude product obtained by etherification of **4** (2.00 g, 7.68 mmol) afforded **4-eth3** (0.409 g, 12% yield) and **4-el3** (0.809 g, 35% yield).

Data for 4-eth3: Syrup. R_f = 0.33 (hexane/EtOAc, 4:1). $[\alpha]_D$ = –27.1 (c = 1.0, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 3.70 (m, 2 H, CH_2O), 3.52 (t, J = 6.1 Hz, 2 H, CH_2Br), 2.07 (m, 2 H, CH_2), 1.50, 1.43, 1.35, 1.32 [4 × s, each 3 H, 2 × C-

(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 111.3, 109.0 [2 × C(CH$_3$)$_2$], 67.7 (CH_2O), 32.6 (CH_2Br), 30.3 (CH_2), 26.8, 26.7, 26.2, 25.3 [4 × C(CH_3)$_2$] ppm. $C_{15}H_{25}BrO_6$ (381.27): calcd. C 47.25, H 6.61; found C 47.52, H 6.78.

Data for 4-el3: Syrup. R_f = 0.36 (hexane/EtOAc, 4:1). [a]$_D$ = –23.5 (c = 1.0, $CHCl_3$); ref.[11] [a]$_D$ = –24.0 (c = 1.0, $CHCl_3$). NMR spectroscopic data were in good agreement with those reported.[12]

3-*O*-(4-Bromobutyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4-eth4) and 3-*O*-Butenyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4-el4): Flash chromatography (hexane/EtOAc, 4:1) of the crude product obtained by etherification of **4** (1.00 g, 3.84 mmol) afforded **4-eth4** (1.06 g, 70% yield) and **4-el4** (0.144 g, 12% yield).

Data for 4-eth4: Syrup. R_f = 0.39 (hexane/EtOAc, 4:1). [a]$_D$ =–24.8 (c = 1.0, $CHCl_3$), ref.[7] [a]$_D$ = –24.6 (c = 1.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 3.67 (dt, J = 5.9, J = 9.5 Hz, 1 H, CH_2O), 3.55 (dt, J = 6.1, J = 9.5 Hz, 1 H, CH_2O), 3.44 (t, J = 6.6 Hz, 2 H, CH_2Br), 1.96, 1.71 [2 × m, each 2 H, (CH_2)$_2$], 1.50, 1.42, 1.35, 1.32 [4 × s, each 3 H, 2 × C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 111.7, 108.9 [2 × C(CH$_3$)$_2$], 69.4 (CH_2O), 33.4 (CH_2Br), 29.4, 28.2 [(CH_2)$_2$], 26.8, 26.7, 26.2, 25.4 [2 × C(CH_3)$_2$] ppm. NMR spectroscopic data were in good agreement with the reported ones.[7]

Data for 4-el4: Syrup. R_f = 0.44 (hexane/EtOAc, 4:1). [a]$_D$ = –30.5 (c = 1.0, $CHCl_3$), ref.[13] [a]$_D$ = –31.0 (c = 0.76, $CHCl_3$). NMR spectroscopic data were in good agreement with those reported.[13]

3-*O*-(5-Bromopentyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4-eth5) and 1,2:5,6-Di-*O*-isopropylidene-3-*O*-pentenyl-α-D-glucofuranose (4-el5): Flash chromatography (hexane/EtOAc, 4:1) of the crude product obtained by etherification of **4** (1.00 g, 3.84 mmol) afforded **4-eth5** (1.30 g, 83% yield) and **4-el5** (0.126 g, 10% yield).

Data for 4-eth5: Syrup, R_f = 0.63 (hexane/EtOAc, 1:1). [a]$_D$ = –26.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 3.53 (dt, J = 6.1, J = 9.3 Hz, 1 H, CH_2O), 3.41 (t, J = 6.7 Hz, 2 H, CH_2Br), 1.85 (m, 2 H, CH_2CH$_2$Br), 1.60 [m, 4 H, (CH_2)$_2$], 1.50, 1.43, 1.35, 1.32 [4 × s, each 3 H, 2 × C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 111.6, 108.8 [2 × C(CH$_3$)$_2$], 70.1 (CH_2O), 33.5 (CH_2Br), 32.3, 28.7, 24.6 [(CH_2)$_3$], 26.7, 26.6, 26.1, 25.3 [2 × C(CH_3)$_2$] ppm. $C_{17}H_{29}BrO_6$ (409.32): calcd. C 49.88, H 7.14; found C 49.82, H 7.11.

Data for 4-el5: Syrup. R_f = 0.57 (hexane/EtOAc, 1:1). [a]$_D$ = –30.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): see Table 2 and δ = 5.81 (m, 1 H, CH=), 4.95 (m, 2 H, CH_2=), 3.57 (m, 2 H, CH_2O), 2.17 (m, 2 H, CH_2CH$_2$=), 1.71 (m, 2 H, CH_2CH$_2$O), 1.49, 1.42, 1.35, 1.31 [4 × s, each 3 H, 2 × C(CH_3)$_2$] ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): see Table 3 and δ = 138.0 (CH=), 114.9 (CH_2=), 111.7; 108.8 [2 × C(CH$_3$)$_2$], 69.6 (CH_2O), 30.1, 28.8 (CH_2CH_2), 26.8, 26.7, 26.2, 25.3 [4 × C(CH_3)$_2$] ppm. $C_{17}H_{28}O_6$ (328.41): calcd. C 62.18, H 8.59; found C 62.11, H 8.55.

6-*O*-(4-Bromobutyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5-eth4): The etherification of **5** (1.80 g, 6.92 mmol) afforded **5-eth4** (2.46 g, 90% yield) as a clear syrup after flash chromatographic purification (hexane/EtOAc, 4:1). R_f = 0.23 (hexane/EtOAc, 4:1). [a]$_D$ = –24.1 (c = 1.0, $CHCl_3$), ref.[7] [a]$_D$ = –24.6 (c = 1.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 3.51 (t, J = 6.0 Hz, 2 H, CH_2O), 3.45 (t, J = 6.7 Hz, 2 H, CH_2Br), 1.93, 1.71 [2 × m, each 2 H, (CH_2)$_2$], 1.54, 1.45, 1.34, 1.33 [4 × s, each 3 H, 2 × C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3

Table 2. ^{1}H NMR spectroscopic data (δ, ppm; J, Hz) for the glycide portions for protected 3-*O*-D-glucoyl and 6-*O*-D-galactoyl derivatives (n.d. = not determined).

Compound	Solvent	1-H	2-H	3-H	4-H	5-H	6a-H	6b-H	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
4-eth3	$CDCl_3$	5.88	4.56	3.90	4.11	4.28	3.97	4.07	3.7	0	3.0	n.d.	5.9	n.d.	8.5
4-eth4	$CDCl_3$	5.87	4.50	3.86	4.10	4.28	3.96	4.09	3.7	0	3.0	7.5	5.8	5.9	8.6
4-eth5	$CDCl_3$	5.87	4.53	3.85	4.11	3.29	3.99	4.08	3.7	0	3.1	7.5	5.7	5.9	8.5
4-el5	$CDCl_3$	5.87	4.53	3.85	4.12	4.31	3.97	4.09	3.7	0	3.1	7.5	5.9	6.0	8.5
1-gl4-pr	$CDCl_3$	5.87	4.52	3.85	4.30	4.08	3.98	4.08	3.7	0	3.1	7.6	5.9	6.1	8.5
1-gl5-pr	$CDCl_3$	5.56	4.51	3.84	4.31	4.03	4.03	4.03	3.7	0	3.0	n.d.	n.d.	n.d.	n.d.
2-gl5-pr	$CDCl_3$	5.88	4.52	3.85	4.12	4.24	3.95	3.95	3.8	0	2.8	7.4	6.0	6.2	8.4
5-eth4	$CDCl_3$	5.53	4.31	4.60	4.25	3.96	3.56	3.63	5.0	2.4	7.9	1.9	6.8	5.7	10.2
5-eth5	$CDCl_3$	5.40	4.18	4.47	4.13	3.82	3.38	3.46	5.0	2.4	8.0	2.0	n.d.	n.d.	n.d.
1-ga5-pr	$CDCl_3$	5.54	4.32	4.59	4.24	3.95	3.60	3.60	5.0	2.6	7.9	1.8	n.d.	n.d.	n.d.
3-ga5-pr	$CDCl_3$	5.53	4.33	4.62	4.23	4.03	3.60	3.62	5.0	2.5	7.9	1.9	n.d.	n.d.	n.d.

Table 3. ^{13}C NMR spectroscopic data (δ, ppm) for the glycide portions for protected 3-*O*-D-glucoyl and 6-*O*-D-galactoyl derivatives.

Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6
4-eth3	$CDCl_3$	105.3	82.4	81.2	82.2	72.4	67.4
4-eth4	$CDCl_3$	105.2	82.4	81.2	82.4	72.3	67.4
4-eth5	$CDCl_3$	105.2	82.4	82.1	81.1	72.4	67.2
4-el5	$CDCl_3$	105.2	82.4	82.0	81.1	72.4	67.3
1-gl4-pr	$CDCl_3$	105.2	82.4	81.2	82.1	72.5	67.2
1-gl5-pr	$CDCl_3$	105.2	82.4	81.1	82.0	72.4	67.1
2-gl5-pr	$CDCl_3$	105.2	82.5	81.2	82.1	72.5	67.3
5-eth4	$CDCl_3$	95.9	70.8[a]	70.3[a]	70.2[a]	66.4	69.1
5-eth5	$CDCl_3$	96.0	70.9	70.7	70.3	66.4	69.0
1-ga4-pr	$CDCl_3$	96.0	70.9[a]	70.2[a]	70.1[a]	66.4	69.0
3-ga5-pr	$CDCl_3$	96.2	71.1	70.6	70.6	66.8	69.4

[a] Assignments may have to be interchanged.

and δ = 108.7, 108.1 [2 × $C(CH_3)_2$], 69.8 (CH_2O), 33.4 (CH_2Br), 29.3, 27.8 [$(CH_2)_2$], 25.7, 25.6, 24.6, 24.1 [2 × $C(CH_3)_2$] ppm. NMR spectroscopic data were in good agreement with the reported ones.[7]

6-*O*-(5-Bromopentyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5-eth5): The etherification of **5** (1.00 g, 3.84 mmol) afforded **5-eth5** (1.47 g, 93% yield) as a clear syrup after flash chromatographic purification (hexane/EtOAc, 9:1). R_f = 0.41 (hexane/EtOAc, 9:1). $[\alpha]_D$ = –25.7 (c = 1.0, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 3.54 (m, 2 H, CH_2O), 3.25 (m, 2 H, CH_2Br), 1.76 (m, 2 H, CH_2CH_2Br), 1.52 [m, 4 H, $(CH_2)_2$], 1.41, 1.32, 1.22, 1.21 [4 × s, each 3 H, 2 × $C(CH_3)_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 111.4, 108.1 [2 × $C(CH_3)_2$], 70.2 (CH_2O), 33.4 (CH_2Br), 32.2, 28.4, 24.5 [$(CH_2)_3$], 25.8, 25.7, 24.7, 24.2 [2 × $C(CH_3)_2$] ppm. $C_{17}H_{29}BrO_6$ (409.32): calcd. C 49.88, H 7.14; found C 49.52, H 6.98.

4-*O*-[2-*O*-(5-Bromopentyl)-3,4-*O*-isopropylidene-6-*O*-(1-methoxy-1-methylethyl)-β-D-galactopyranosyl]-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (6A-eth5): The etherification of **6A** (1.40 g, 2.41 mmol) afforded **6A-eth5** (1.60 g, 91% yield) as a clear syrup after flash chromatographic purification (hexane/EtOAc, 7:3). R_f = 0.65 (hexane/EtOAc, 7:3). $[\alpha]_D$ = –6.4 (c = 1.0, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.6 (d, $J_{1',2'}$ = 7.80 Hz, 1 H, 1′-H), 4.52 (dd, $J_{1,2}$ = 6.1 Hz, $J_{2,3}$ = 7.4 Hz, 1 H, 2-H), 4.39 (d, 1 H, 1-H), 4.26 (m, 1 H, 5-H), 4.18–4.00 (m, 6 H, 3-H, 4-H, 6a-H, 6b-H, 3′-H, 4′-H), 3.77–3.51 (m, 6 H, 5′-H, 6′a-H, 6′b-H, 2′-H, 1 × CH_2O), 3.46 (m, 2 H, CH_2Br), 3.42, 3.41(2 × s, each 3 H, 2 × OCH_3), 3.20 [s, 3 H, $C(CH_3)_2OCH_3$],1.81 (m, 2 H, CH_2CH_2O), 1.70 (m, 4 H, CH_2CH_2), 1.50, 1.44, 1.39, 1.38, 1.33, 1.32 [6 × s, each 3 H, 3 × $C(CH_3)_2$], 1.31, 1.30 [2 × s, each 3 H, $C(CH_3)_2OCH_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 5 and δ = 111.8, 111.1, 110.1 [3 × $C(CH_3)_2$], 100.8 [$C(CH_3)_2OCH_3$], 70.8 (CH_2O), 56.1, 54.3 (2 × OCH_3), 50.4 [$C(CH_3)_2OCH_3$], 35.2 (CH_2Br), 30.5, 28.8, 24.9 [$(CH_2)_3$], 28.4, 27.7, 27.1, 26.8, 26.5, 25.6, 25.4, 25.3 [3 × $C(CH_3)_2$, $C(CH_3)_2OCH_3$] ppm. $C_{32}H_{57}BrO_{13}$ (729.71): calcd. C 52.67, H 7.87; found C 52.43, H 7.77.

4-*O*-[6-*O*-(5-Bromobutyl)-3,4-*O*-isopropylidene-2-*O*-methyl-β-D-galactopyranosyl]-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (6B-eth4): The etherification of **6B** (1.00 g, 1.91 mmol) afforded **6B-eth4** (1.11 g, 88% yield) as a clear syrup after flash chromatographic purification (hexane/EtOAc, 7:3). R_f = 0.19 (hexane/EtOAc, 7:3). $[\alpha]_D$ = –5.00 (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, CD_3CN): δ = 4.53 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 4.36 (dd, $J_{1,2}$ = 6.0 Hz, $J_{2,3}$ = 7.9 Hz, 1 H, 2-H), 4.35 (d, 1 H, 1-H), 4.19 (dt, $J_{5,6a}$ = $J_{5,6b}$ = 6.1 Hz, 1 H, 5-H), 4.11 (dd, $J_{3',4'}$ = 5.6 Hz, $J_{4',5'}$ = 2.0 Hz, 1 H, 4′-H), 4.08–3.95 (m, 4 H, 3′-H, 3-H, 6a-H, 6b-H), 3.82 (m, 2 H, 4-H, 5′-H), 3.50 (m, 2 H, 6′a-H, 6′b-H), 3.00 (dd, $J_{2',3'}$ = 7.0 Hz, 2′-H), 3.56 (t, J = 6.6 Hz, 2 H, CH_2O), 3.48 (m, 2 H, CH_2Br), 3.47 (s, 3 H, 2-OCH_3), 3.38, 3.37 (2 × s, each 3 H, 2 × 1-OCH_3), 1.90 (m, 2 H, CH_2CH_2O), 1.71 (m, 2 H, CH_2CH_2Br), 1.46, 1.36, 1.34, 1.32, 1.29, 1.28 [6 × s, each 3 H, 3 × $C(CH_3)_2$] ppm. ^{13}C NMR (62.9 MHz, CD_3CN): see Table 5 and δ = 110.7, 110.1, 109.1 [3 × $C(CH_3)_2$], 70.1 (CH_2O), 60.5 (2-OCH_3), 56.1, 54.3 (2 × 1-OCH_3), 35.2 (CH_2Br), 30.5 (CH_2CH_2O), 28.8 (CH_2CH_2Br), 28.4, 27.7, 27.1, 26.8, 26.5, 25.6 [3 × $C(CH_3)_2$] ppm. $C_{28}H_{49}BrO_{12}$ (657.60): calcd. C 51.14, H 7.51; found C 51.09, H 7.49.

***N*-[2-(5-Bromopentyloxy)ethyl]-*N*-ethyl-4-(4-nitrophenylazo)aniline (2-eth5) and *N*-Ethyl-4-(4-nitrophenylazo)-*N*-[2-(pent-4-enyloxy)-ethyl]aniline (2-el5):** A mixture of **2** (1.00 g, 3.18 mmol), KOH, (0.715 g, 12.7 mmol) and 18-crown-6 (0.01 equiv.) in THF/H_2O (99.5:0.5, 10 mL) was stirred at room temperature for 1 h, the dibromide **7c** (1.30 mL, 9.54 mmol) was then added, and the mixture was stirred under the same conditions until TLC analysis (hexane/EtOAc, 5:1) revealed the complete disappearance of the starting material (R_f = 0.11) and the formation of a major faster-moving product (R_f = 0.79). The mixture reaction was neutralised with saturated aqueous NH_4Cl (15 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was dried with Na_2SO_4, filtered and concentrated under diminished pressure, and the resulting residue was purified by flash chromatography (hexane/EtOAc, 5:1) to yield **2-eth5** (1.15 g, 78%) and **2-el5** (0.061 g, 5%).

Data for 2-eth5: Syrup. R_f = 0.79 (hexane/EtOAc, 5:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.33, 7.93 (AA′XX′ system, 4 H, 2′-H, 2′-H, 5′-H, 6′-H), 7.87, 6.77 (AA′XX′ system, 4 H, 8′-H, 9′-H, 11′-H, 12′-H), 3.63–3.36 (m, 10 H, 2 × CH_2O, CH_2CH_2N, CH_3CH_2N, CH_2Br), 1.85 (m, 2 H, CH_2CH_2O), 1.51 [m, 4 H, $(CH_2)_2$], 1.25 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 156.5 (C-1′), 151.5 (C-10′), 147.2 (C-4′), 143.4 (C-7′), 126.3, 124.6, 122.4, 111.5 (Ar-CH), 71.3, 68.5 [2 × CH_2O], 50.5, 46.2 (2 × CH_2N), 33.8 (CH_2Br), 32.6, 29.0, 25.0 [$(CH_2)_3$], 12.5 (CH_3) ppm. $C_{21}H_{27}BrN_4O_3$ (463.38): calcd. C 54.43, H 5.87; found C 54.33, H 5.76.

Data for 2-el5: Syrup. R_f = 0.69 (hexane/EtOAc, 5:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.34, 7.91 (AA′XX′ system, 4 H, 2′-H, 2′-H, 5′-H, 6′-H), 7.88, 6.77 (AA′XX′ system, 4 H, 8′-H, 9′-H, 11′-H, 12′-H), 5.74 (m, 1 H, =CH), 5.04, 4.96 (m, 2 H, =CH_2), 3.61–3.37 (m, 8 H, 2 × CH_2O, CH_2CH_2N, CH_3CH_2N), 1.95 (m, 2 H, CH_2), 1.51 [m, 2 H, (CH_2)], 1.15 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 157.5 (C-1′), 152.2 (C-10′), 147.5 (C-4′), 143.4 (C-7′), 126.3, 124.6, 122.4, 111.5 (Ar-CH), 135.1 (=CH), 115.7 (=CH_2), 71.3, 68.5 [2 × CH_2O], 50.5, 46.2 (2 × CH_2N), 32.6, 29.0 [$(CH_2)_2$], 12.5 (CH_3) ppm. $C_{21}H_{26}N_4O_3$ (382.47): calcd. C 65.95, H 6.85; found C 65.87, H 6.81.

General Procedure for the Preparation of Protected GADs: A mixture of the dye (1.0 mmol), KOH (5.0 equiv.) and 18-crown-6 (0.01 equiv.) in THF/H_2O (99.5:0.5, 10 mL) was stirred at room temperature for 1 h, the appropriate etherified bromo sugar (1.0 equiv.) was then added, and the mixture was left stirring under the same conditions for several hours. The reaction mixture was neutralised with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was dried with $MgSO_4$, filtered and concentrated at reduced pressure, and the resulting residue was purified by flash chromatography.

GAD 1-gl4-pr: Flash chromatography (hexane/EtOAc, 2:3) of the crude product obtained by condensation of **4-eth4** (1.76 g, 4.46 mmol) and **1** (1.17 g, 4.46 mmol) afforded **1-gl4-pr** (1.58 g, 60% yield) and **4-el4** (0.44 g, 32% yield).

Data for 1-gl4-pr: Syrup. R_f = 0.52 (hexane/EtOAc, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 7.83 (m, 4 H, 2′-H, 6′-H, 8′-H, 12-H), 7.42 (m, 3 H, 3′-H, 4′-H, 5′-H), 6.75 (m, 2 H, 9′-H, 11′-H), 3.65–3.43 (m, 10 H, 2 × CH_2N, 3 × CH_2O), 1.64 [m, 4 H, $(CH_2)_2$], 1.50, 1.42, 1.34, 1.31 [4 × s, each 3 H, 2 × $C(CH_3)_2$], 1.22 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 152.2 (C-1′), 150.2 (C-10′), 143.4 (C-7′), 129.2, 128.9, 125.1, 122.1, 111.1 (Ar-CH), 111.1, 108.8 [2 × $C(CH_3)_2$], 71.1, 70.2, 68.3 (3 × CH_2O), 50.2 (CH_3CH_2N), 45.8 (CH_2CH_2N), 26.4 [$(CH_2)_2$], 26.8, 26.3, 26.2, 25.4 [2 × $C(CH_3)_2$], 12.2 (CH_3) ppm. $C_{32}H_{45}N_3O_7$ (583.73): calcd. C 65.84, H 7.77, N 7.20; found C 65.80, H 7.74, N 7.17.

GAD 1-gl5-pr: Flash chromatography (hexane/EtOAc, 35:65) of the crude product obtained by condensation of **4-eth5** (1.10 g, 2.69 mmol) and **1** (0.72 g, 2.69 mmol) afforded **1-gl5-pr** (0.90 g, 56% yield) and **4-el5** (0.24 g, 37% yield).

Data for 1-gl5-pr: Syrup. R_f = 0.58 (hexane/EtOAc, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 7.84 (m, 4 H, 2′-H, 6′-H,

8′-H, 12′-H), 7.41 (m, 3 H, 3′-H, 4′-H, 5′-H), 6.73 (m, 2 H, 9′-H, 11′-H), 3.56–3.40 (m, 10 H, 2×CH_2N, 3×CH_2O), 1.58 [m, 6 H, $(CH_2)_3$], 1.49, 1.42, 1.34, 1.30 [4×s, each 3 H, 2×C(CH_3)$_2$], 1.20 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 153.1 (C-1′), 150.2 (C-10′), 143.3 (C-7′), 129.1, 128.8, 125.1, 122.0, 111.1 (Ar-CH), 111.6, 108.7 [2×C(CH_3)$_2$], 71.2, 70.3, 68.2 (3×CH_2O), 50.2 (CH_3CH_2N), 45.7 (CH_2CH_2N), 29.3, 29.2, 22.6 [(CH_2)$_3$], 26.8, 26.7, 26.2, 25.3 [2×C(CH_3)$_2$], 12.2 (CH_3) ppm. $C_{33}H_{47}N_3O_7$ (597.76): calcd. C 66.31, H 7.93, N 7.03; found C 66.28, H 7.90, N 7.00.

GAD 1-ga4-pr: Flash chromatography (hexane/EtOAc, 7:3) of the crude product obtained by condensation of **5-eth4** (1.00 g, 2.53 mmol) and **1** (0.68 g, 2.53 mmol) afforded **1-ga4-pr** (1.08 g, 73% yield) and **5-el4** (0.20 g, 25% yield).

Data for 1-ga4-pr: Syrup. R_f = 0.21 (hexane/EtOAc, 3:2). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 7.85 (m, 4 H, 2′-H, 6′-H, 8′-H, 12′-H), 7.46 (m, 3 H, 3′-H, 4′-H, 5′-H), 6.74 (m, 2 H, 9′-H, 11′-H), 3.70–3.40 (m, 10 H, 2×CH_2N, 3×CH_2O), 1.64 [m, 4 H, $(CH_2)_2$], 1.53, 1.51, 1.44, 1.33 [4×s, each 3 H, 2×C(CH_3)$_2$], 1.21 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 152.8 (C-1′), 149.9 (C-10′), 142.9 (C-7′), 128.8, 128.5, 124.9, 121.8, 110.7 (Ar-CH), 108.7, 108.0 [2×C(CH_3)$_2$], 70.8, 70.7, 67.9 (3×CH_2O), 49.9 (CH_3CH_2N), 45.3 (CH_2CH_2N), 26.0, 25.9 [(CH_2)$_2$], 25.7, 25.6, 24.6, 24.1 [2×C(CH_3)$_2$], 11.8 (CH_3) ppm. $C_{32}H_{45}N_3O_7$ (583.73): calcd. C 65.84, H 7.77, N 7.20; found C 65.78, H 7.74, N 7.18.

Data for 5-el4: Syrup. R_f = 0.52 (hexane/EtOAc, 3:2). $[\alpha]_D$ = –60.3 (c = 1.0, $CHCl_3$), ref.[13] $[\alpha]_D$ = –61.0 (c = 1.13, $CHCl_3$). NMR spectroscopic data were in good agreement with the reported ones.[13]

GAD 1-laB4-pr: The condensation of **6B-eth4** (1.18 g, 1.79 mmol) and **1** (0.48 g, 1.79 mmol) afforded **1-laB4-pr** (1.05 g, 69% yield) as a yellow syrup after flash chromatographic purification (hexane/EtOAc, 65:35). R_f = 0.45 (hexane/EtOAc, 2:3). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.84 (m, 4 H, 2′-H, 6′-H, 8′-H, 12′-H), 7.42 (m, 3 H, 3′-H, 4′-H, 5′-H), 6.75 (m, 2 H, 9′-H, 11′-H), 4.60 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.51 (dd, $J_{1,2}$ = 6.3 Hz, $J_{2,3}$ = 7.1 Hz, 1 H, 2-H), 4.35 (d, 1 H, 1-H), 4.25 (m, 1 H, 5-H), 4.16–3.95 (m, 7 H, 4′-H, 3′-H, 3-H, 4-H, 6a-H, 6b-H), 3.80 (m, 1 H, 5′-H), 3.70–3.41 (m, 12 H, 6′a-H, 6′b-H, 2×CH_2N, 3×CH_2O), 3.55 (s, 3 H, 2-OCH$_3$), 3.42, 3.40 (2×s, each 3 H, 2×1-OCH$_3$), 3.09 (dd, $J_{2',3'}$ = 6.9 Hz, 2′-H), 1.64 [m, 4 H, $(CH_2)_2$], 1.51, 1.43, 1.40, 1.39, 1.35 1.32 [6×s, each 3 H, 3×C(CH_3)$_2$], 1.22 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (62.9 MHz, CD_3CN): see Table 5 and δ = 153.2 (C-1′), 150.2 (C-10′), 143.3 (C-7′), 129.2, 128.9, 125.1, 122.1, 111.1 (Ar-CH), 110.2, 109.6, 108.4 [3×C(CH_3)$_2$], 71.1, 69.3, 68.3 (3×CH_2O), 60.2 (2-OCH$_3$), 55.4, 53.2 (2×1-OCH$_3$), 50.2 (CH_3CH_2N), 45.8 (CH_2CH_2N), 28.0, 27.5, 26.5, 26.4, 26.2, 25.5 [3×C(CH_3)$_2$], 26.3 [(CH_2)$_2$], 12.2 (CH_3) ppm. $C_{44}H_{67}N_3O_{13}$ (846.04): calcd. C 62.47, H 7.98, N 4.97; found C 62.44, H 7.79, N 4.94.

GAD 2-gl5-pr: The condensation of **4-eth5** (0.87 g, 2.13 mmol) and **2** (0.67 g, 2.13 mmol) afforded **2-gl5-pr** (1.16 g, 85% yield) as a red syrup after flash chromatographic purification (hexane/EtOAc, 3:7). R_f = 0.29 (hexane/EtOAc, 3:7). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 8.33, 7.93 (AA′XX′ system, 4 H, 2′-H, 3′-H, 5′-H, 6′-H), 7.91, 6.78 (AA′XX′ system, 4 H, 8′-H, 9′-H, 11′-H, 12′-H), 3.63–3.42 [m, 10 H, CH_2CH_2N, CH_3CH_2N, 3×CH_2O], 1.85 [m, 6 H, $(CH_2)_3$], 1.50, 1.43, 1.35, 1.32 [4×s, each 3 H, 2×C(CH_3)$_2$], 1.26 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 157.6 (C-1′), 152.6 (C-10′), 148.2 (C-4′), 144.2 (C-7′), 127.0, 125.7, 123.3, 122.5, 112.5 (Ar-CH), 111.8, 109.3 [2×C(CH_3)$_2$], 71.5, 70.5, 68.4 (3×CH_2O), 50.4, 46.0 (2×CH_2N), 29.5, 29.4, 22.7 [(CH_2)$_3$], 26.9, 26.8, 26.3, 25.5 [2×C(CH_3)$_2$], 12.2 (CH_3) ppm. $C_{33}H_{46}N_4O_9$ (642.74): calcd. C 61.67, H 6.76, N 8.72; found C 61.81, H 6.92, N 8.89.

GAD 2-laA5-pr. Method A: The condensation of **6A-eth5** (1.59 g, 2.18 mmol) and **2** (0.70 g, 2.18 mmol), by the General Procedure, afforded **2-laA5-pr** (1.12 g, 54% yield) as a red syrup after flash chromatographic purification (hexane/EtOAc, 7:3). R_f = 0.27 (hexane/EtOAc, 7:3). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.32, 7.93 (AA′XX′ system, 4 H, 2′-H, 2′-H, 5′-H, 6′-H), 7.88, 6.76 (AA′XX′ system, 4 H, 8′-H, 9′-H, 11′-H, 12′-H), 4.59 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 4.52 (dd, $J_{1,2}$ = 6.4 Hz, $J_{2,3}$ = 7.4 Hz, 1 H, 2-H), 4.37 (d, 1 H, 1-H), 4.26 (m, 1 H, 5-H), 4.18–3.98 (m, 6 H, 3-H, 4-H, 6a-H, 6b-H, 3′-H, 4′-H), 3.77–3.35 (m, 14 H, 5′-H, 6′a-H, 6′b-H, 2′-H, 3×CH_2O, CH_2CH_2N, CH_3CH_2N), 3.42, 3.41(2×s, each 3 H, 2×1-OCH_3), 3.20 [s, 3 H, C(CH_3)$_2$OCH_3], 1.60 [m, 6 H, (CH_2)$_3$], 1.50, 1.44, 1.39, 1.38, 1.33, 1.32 [6×s, each 3 H, 3×C(CH_3)$_2$], 1.31, 1.30 [2×s, each 3 H, C(CH_3)$_2$OCH$_3$], 1.25 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 5 and δ = 156.6 (C-1′), 152.3 (C-10′), 147.2 (C-4′), 143.5 (C-7′), 126.2, 124.6, 122.5, 111.3 (Ar-CH), 110.1, 109.4, 108.4 [3×C(CH_3)$_2$], 100.0 [C(CH_3)$_2$-OCH$_3$], 72.1 71.9, 68.2 [3×CH_2O], 55.5, 53.1 (2×1-OCH_3), 48.5 [C(CH_3)$_2$OCH_3], 50.4, 46.0 (2×CH_2N), 29.8, 29.6, 22.6 [(CH_2)$_3$], 28.1, 27.5, 26.6, 26.5, 26.3, 25.7 [3×C(CH_3)$_2$], 24.4, 24.3 [C(CH_3)$_2$-OCH$_3$], 12.4 (CH_3) ppm. $C_{48}H_{74}N_4O_{16}$ (963.12): calcd. C 59.86, H 7.74, N 5.82; found C 59.50, H 7.69, N 5.71.

Method B: A mixture of **6A** (1.00 g, 1.37 mmol), KOH (0.39 g, 6.85 mmol) and 18-crown-6 (0.01 equiv.) in THF/H_2O (99.5:0.5, 10 mL) was stirred at room temperature for 1 h, **2-eth5** (0.64 g, 1.38 mmol) was then added, and the mixture was stirred under the same conditions for several hours. TLC analysis (hexane/EtOAc, 5:1) revealed the complete disappearance of the starting material (R_f = 0.79) and the formation of a minor faster-moving product (R_f = 0.29). The mixture reaction was neutralised with saturated aqueous NH_4Cl (20 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic phase was dried with Na_2SO_4, filtered and concentrated under diminished pressure, and the resulting residue was purified by flash chromatography (hexane/EtOAc, 5:1) to yield **2-laA5-pr** (0.77 g, 57%), with NMR parameters identical to those of the sample prepared above.

GAD 3-ga5-pr: The condensation of **5-eth5** (0.85 g, 2.08 mmol) and **3** (0.31 g, 2.08 mmol) afforded **3-ga5-pr** (0.70 g, 56% yield) as a red syrup after flash chromatographic purification (hexane/EtOAc, 1:1). R_f = 0.34 (hexane/EtOAc, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 2 and δ = 7.90, 7.71 (AA′XX′ system, 4 H, 2′-H, 3′-H, 6′-H, 5′-H), 7.47 (d, J = 2.0 Hz, 1 H, 12′-H), 7.19 (dd, J = 8.6 Hz, 1 H, 10′-H), 6.97 (d, 1 H, 9′-H), 4.14 (t, J = 7.0 Hz, 2 H, CH_2OPh), 3.50 (m, 2 H, CH_2O), 2.32 (s, 3 H, CH_3Ph), 2.03 (s, 3 H, CH_3CO), 1.90 (m, 2 H, CH_2); 1.70 (m, 4 H, CH_2CH_2), 1.51, 1.41, 1.32, 1.31 [4×s, each 3 H, 2×C(CH_3)$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 168.9 (C=O), 154.6, 149.4, 142.3, 140.3 (C-1′, C-4′, C-7′, C-8′), 130.5 (C-11′), 132.7, 123.9, 123.8, 119.6, 116.9, 115.0, (Ar-CH), 109.2, 108.6 [2×C(CH_3)$_2$], 71.5, 70.1 (2×CH_2O), 29.3, 29.1, 22.7 [(CH_2)$_3$], 26.0, 25.9, 24.9, 24.4 [2×C(CH_3)$_2$], 24.6 (CH_3Ph), 21.5 (CH_3CO) ppm. $C_{32}H_{43}N_3O_7$ (597.71): calcd. C 64.30, H 7.25, N 7.03; found C 64.50, H 7.31, N 6.87.

GAD 3-laA5-pr: The condensation of **6A-eth5** (2.00 g, 2.74 mmol) and **3** (0.74 g, 2.74 mmol) afforded **3-laA5-pr** (1.18 g, 47% yield) as a red syrup after flash chromatographic purification (hexane/EtOAc, 1:2). R_f = 0.37 (hexane/EtOAc, 1:2). ^{1}H NMR (200 MHz, $CDCl_3$): see Table 3 and δ = 7.91, 7.73 (AA′XX′ system, 4 H, 2′-H, 3′-H, 6′-H, 5′-H), 7.46 (d, J = 2.0 Hz, 1 H, 12′-H), 7.19 (dd, J

= 8.2 Hz, 1 H, 10′-H), 6.97 (d, 1 H, 9′-H), 4.59 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 4.52 (dd, $J_{1,2}$ = 6.4 Hz, $J_{2,3}$ = 7.4 Hz, 1 H, 2-H), 4.37 (d, 1 H, 1-H), 4.26 (m, 1 H, 5-H), 4.18–3.98 (m, 6 H, 3-H, 4-H, 6a-H, 6b-H, 3′-H, 4′-H), 3.81 (t, J = 6.8 Hz, 2 H, CH_2OPh), 3.77–3.51 (m, 6 H, 5′-H, 6′a-H, 6′b-H, 2′-H, 2 × CH_2O), 3.42, 3.41 (2 × s, each 3 H, 2 × 1-OCH_3), 3.20 [s, 3 H, C(CH_3)$_2$OCH_3], 2.33 (s, 3 H, CH_3Ph), 2.02 (s, 3 H, CH_3CO), 1.81 (m, 2 H, CH_2), 1.70 (m, 4 H, CH_2CH_2), 1.50, 1.44, 1.39, 1.38, 1.33, 1.32 [6 × s, each 3 H, 3 × C(CH_3)$_2$], 1.31, 1.30 [2 × s, each 3 H, C(CH_3)$_2$OCH$_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3 and δ = 168.9 (C=O), 154.6, 149.4, 142.3, 140.3 (C-1′, C-4′, C-7′, C-8′), 132.7 (C-10′), 131.5 (C-11′), 126.0, 123.9, 123.8, 121.6, 121.5, 116.2 (C-12′, C-2′, C-6′, C-3′, C-5′,C-9′), 111.8, 111.1, 110.1 [3 × C(CH$_3$)$_2$], 100.8 [C(CH$_3$)$_2$OCH$_3$], 71.5, 70.1 (2 × CH$_2$O), 56.1, 54.3 (2 × OCH_3), 50.4 [C(CH$_3$)$_2$OCH_3], 30.5, 29.7, 28.8 [(CH_2)$_3$], 28.4, 27.7, 27.1, 26.8, 26.5, 25.6, 25.4, 25.3 [3 × C(CH$_3$)$_2$, C(CH$_3$)$_2$OCH$_3$], 24.9, 24.3 (CH_3Ar, CH$_3$CO) ppm. $C_{47}H_{71}N_3O_{15}$ (918.10): calcd. C 61.49, H 7.79, N 4.58; found C 61.54, H 7.71, N 4.47.

Deprotected GAD 1-ga4: A solution of **1-ga4-pr** (0.59 g, 1.00 mmol) in aqueous CF_3COOH (90%, 10 mL) was stirred at room temperature until the starting material had been completely consumed [TLC (EtOAc/MeOH 9:1), 30 min]. The violet solution was repeatedly co-evaporated with toluene (5 × 10 mL) at reduced pressure, and the resulting residue was diluted with CH_2Cl_2 (15 mL), neutralised with saturated aqueous $NaHCO_3$ until the disappearance of the violet colour and the return of the yellow-orange colouration. The aqueous phase was further extracted with CH_2Cl_2 (3 × 10 mL) up to the decolouration of the aqueous solution and the organic extract were dried with Na_2SO_4, filtered and concentrated at reduce pressure. Purification of the crude residue (0.495 g) by flash column chromatography (EtOAc/MeOH 9:1) afforded **1-ga4** (0.44 g, 87% yield) as an orange amorphous solid. R_f = 0.19 (EtOAc/MeOH 9:1) as a mixture of α-pyranose, β-pyranosic and β-furanosic anomers in the ratio of 29:53:18, calculated on the basis of the relative C-1 signal intensities (see Table 4). Selected ^{1}H NMR (200 MHz, Me_2SO): δ = 7.76 (m, 4 H, 2′-H, 6′-H, 8′-H, 12′-H, all anomers), 7.46 (m, 3 H, 3′-H, 4′-H, 5′-H, all anomers), 6.79 (m, 2 H, 9′-H, 11′-H, all anomers), 1.50 [m, 4 H, (CH_2)$_2$, all anomers], 1.11 (m, 3 H, CH$_3$, all anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 4 for the glycide portion and, for the ethereal and dye portions, δ = 152.5 (C-1′), 150.4 (C-10′), 142.3 (C-7′), 129.5, 129.2, 125.0. 121.8, 111.2 (ArCH), 70.3, 70.2, 67.9 (3 × CH_2O), 49.6 (CH$_3$$CH_2$N), 45.1 (CH$_2$$CH_2$N), 26.6 [($CH_2$)$_2$], 12.0 (CH$_3$) ppm. $C_{26}H_{37}N_3O_7$ (503.60): calcd. C 62.01, H 7.41, N 8.34; found C 62.06, H 7.51, N 8.33.

Table 4. ^{13}C NMR spectroscopic data (δ, ppm) for the glycide portions for deprotected 3-*O*-D-glucoyl (**1-gl4**, **1-gl5** and **2-gl5**) and 6-*O*-D-galactoyl (**1-ga4** and **3-ga4**) derivatives.

Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6
1-gl4-α*p*	Me_2SO	92.4	72.1	81.9	72.1	70.0	61.2
1-gl5-α*p*	Me_2SO	92.4	72.1	82.0	72.1	70.0	61.2
2-gl5-α*p*	Me_2SO	92.1	72.1	81.9	72.1	70.1	61.1
1-ga4-α*p*	Me_2SO	92.7	69.3	69.5	69.5	68.5	70.3
3-ga5-α*p*	Me_2SO	92.3	69.4	69.6	69.6	68.4	70.2
1-gl4-β*p*	Me_2SO	96.9	76.7	85.2	74.6	69.8	61.2
1-gl5-β*p*	Me_2SO	97.0	76.7	85.2	74.7	69.8	61.2
2-gl5-β*p*	Me_2SO	97.4	77.2	85.6	75.1	70.3	61.6
1-ga4-β*p*	Me_2SO	97.4	73.4	72.0	68.9	73.4	70.3
3-ga5-β*p*	Me_2SO	97.4	73.3	72.1	68.8	73.3	70.3
1-ga4-β*f*	Me_2SO	101.8	81.5	75.9	82.5	68.5	70.3
3-ga5-β*f*	Me_2SO	101.7	81.5	75.9	82.3	68.4	70.3

Deprotected GAD 1-gl4: Hydrolysis of pure **1-gl4-pr** (0.60 g, 1.03 mmol) with aqueous CF_3COOH (90%, 10 mL) by the same procedure as described above for the preparation of **1-ga4** afforded **1-gl4** (0.42 g, 82% yield) as an orange solid after flash chromatography (CH_2Cl_2/*i*PrOH, 8:2). R_f = 0.32 (CH_2Cl_2/*i*PrOH 8:2) as a mixture of α- and β-pyranosic anomers in the ratio of 40:60, calculated on the basis of the relative C-1 signal intensities (see Table 4). Selected ^{1}H NMR (200 MHz, Me_2SO): δ = 7.76 (m, 4 H, 2′-H, 6′-H, 8′-H, 12-H, both anomers), 7.46 (m, 3 H, 3′-H, 4′-H, 5′-H, both anomers), 6.80 (m, 2 H, 9′-H, 11′-H, both anomers), 1.53 [m, 4 H, (CH_2)$_2$, both anomers], 1.11 (t, J = 6.7 Hz, 3 H, CH$_3$, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 4 for the glycide portion and, for the ethereal and dye portions, δ = 152.5 (C-1′), 150.5 (C-10′), 142.9 (C-7′), 129.5, 129.2, 125.1, 121.8, 111.3 (ArCH), 71.6, 70.5, 67.9 (3 × CH_2O), 49.6 (CH$_3$$CH_2$N), 45.1 (CH$_2$$CH_2$N), 26.7, 26.0 [($CH_2$)$_2$], 12.1 (CH$_3$) ppm. $C_{26}H_{37}N_3O_7$ (503.60): calcd. C 62.01, H 7.41, N 8.34; found C 61.98, H 7.39, N 8.36.

Deprotected GAD 1-gl5: Hydrolysis of **1-gl5-pr** (0.80 g 1.34 mmoli) with aqueous CF_3COOH (90%, 13 mL) by the same procedure as described above for the preparation of **1-ga4** afforded **1-gl5** (0.55 g, 78% yield) as an orange solid after flash chromatography (CH_2Cl_2/*i*PrOH 8:2). R_f = 0.11 (EtOAc) as a mixture of α- and β-pyranosic anomers in the ratio of 45:55, calculated on the basis of the relative C-1 signal intensities (see Table 4). Selected ^{1}H NMR data (200 MHz, Me_2SO): δ = 7.76 (m, 4 H, 2′-H, 6′-H, 8′-H, 12-H, both anomers), 7.46 (m, 3 H, 3′-H, 4′-H, 5′-H, both anomers), 6.78 (m, 2 H, 9′-H, 11′-H, both anomers), 1.56–1.30 [m, 6 H, (CH_2)$_3$, both anomers], 1.11 (t, J = 6.7 Hz, 3 H, CH$_3$, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 4 for the glycide portion and, for the ethereal and dye portions, δ = 152.5 (C-1′), 150.5 (C-10′), 142.4 (C-7′), 129.5, 129.2, 125.0, 121.8, 111.3 (ArCH), 71.8, 70.6, 67.9 (3 × CH_2O), 49.6 (CH$_3$$CH_2$N), 45.1 (CH$_2$$CH_2$N), 29.7, 29.2, 22.2 [($CH_2$)$_2$], 12.0 (CH$_3$) ppm. $C_{27}H_{39}N_3O_7$ (517.63): calcd. C 62.65, H 7.59, N 8.12; found C 62.70, H 7.54, N 8.09.

The treatment of crude **1-gl5-pr** (8.42 g), obtained by condensation of **4-eth4** (4.80 g, 11.7 mmol) and **1** (3.20 g, 11.8 mmol), by an identical procedure led to pure **1-gl5**, after flash chromatography (3.63 g), in 60% yield calculated from **4-eth4**.

Deprotected GAD 1-laB4: Hydrolysis of **1-laB4-pr** (0.21 g 0.25 mmol) with aqueous CF_3COOH (90%, 3 mL) by the same procedure as described above for the preparation of **1-ga4** afforded **1-laB4** (0.16 g, 94% yield) as an orange solid after flash chromatography (CH_2Cl_2/*i*PrOH 8:2). R_f = 0.11 (EtOAc) as a mixture of α- and β-pyranosic anomers in the ratio of 50:50, calculated on the basis of the relative C-1 signal intensities (see Table 5). Selected ^{1}H NMR data (250 MHz, Me_2SO): δ = 7.74 (m, 4 H, 2′-H, 6′-H, 8′-H, 12′-H, both anomers), 7.44 (m, 3 H, 3′-H, 4′-H, 5′-H, both anomers), 6.81 (m, 2 H, 9′-H, 11′-H, both anomers), 1.54 [m, 4 H, (CH_2)$_2$, both anomers], 1.08 (t broad, 3 H, CH$_3$, both anomers) ppm. ^{13}C NMR (62.9 MHz, Me_2SO): see Table 5 for the glycide portion and, for the ethereal and dye portions, δ = 152.4 (C-1′), 150.5 (C-10′), 142.4 (C-7′), 129.5, 129.3, 125.2, 121.8, 111.5 (Ar-CH), 70.3, 70.2, 69.6 (3 × CH_2O), 60.2 (2-OCH$_3$), 49.7 (CH$_3$$CH_2$N), 45.3 (CH$_2$$CH_2$N), 25.9 [($CH_2$)$_2$], 12.0 (CH$_3$) ppm. $C_{32}H_{47}N_3O_{12}$ (665.74): calcd. C 57.73, H 7.12, N 6.31; found C 57.65, H 7.19, N 6.14.

Deprotected GAD 2-gl5: Hydrolysis of **2-gl5-pr** (1.00 g, 1.55 mmol) with aqueous CF_3COOH (90%, 10 mL) by the same procedure as described above for the preparation of **1-ga4** afforded **2-gl5** (0.78 g, 87% yield) as a red solid as a mixture of α- and β-pyranosic anomers in the ratio of 50:50, calculated on the basis of the relative C-

Table 5. ^{13}C NMR spectroscopic data (δ, ppm) for the glycide portions for protected and deprotected lactose derivatives.

Compound	Solvent	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-1	C-2	C-3	C-4	C-5	C-6
6B	CD_3CN	103.1	83.0	79.2	73.7	74.2	62.3	107.2	74.8	78.0	74.3	77.5	65.3
6B-eth4	CD_3CN	103.3	83.9	79.7	74.7	72.5	71.0	106.3	76.4	78.5	76.6	77.7	66.4
6A-eth5	$CDCl_3$	102.5	81.3	79.3	73.6	72.0	60.0	105.2	75.0	78.0	74.3	77.7	65.6
1-laB4-pr	$CDCl_3$	102.6	82.8	78.8	74.5	71.6	71.2	105.1	75.0	77.9	73.6	77.6	65.5
2-laA5-pr	$CDCl_3$	102.5	81.1	79.3	74.3	71.5	59.6	105.1	74.9	77.9	73.5	77.6	65.6
3-laA5-pr	$CDCl_3$	102.4	82.5	79.1	73.7	72.4	60.2	105.6	75.1	78.6	73.9	77.9	65.2
β-lactose[a]	D_2O	103.7	72.0	73.5	69.5	76.2	62.0	96.6	74.8	75.3	79.2	75.6	61.1
1-laB4-β	Me_2SO	103.1	72.5	73.6	68.7	75.0	67.5	96.6	74.6	75.1	80.6	75.2	60.2
2-laA5-β	Me_2SO	103.2	72.6	73.2	68.8	74.9	67.4	96.6	74.5	75.3	80.5	75.5	60.4
3-laA5-β	Me_2SO	102.9	72.7	73.4	68.6	75.2	67.5	96.5	74.4	75.4	80.0	75.1	60.4
α-lactose[a]	D_2O	103.6	72.0	73.5	69.5	76.2	62.0	92.7	72.2	72.4	79.3	71.0	61.0
1-laB4-α	Me_2SO	103.1	72.5	73.6	68.7	75.0	67.8	92.1	72.6	72.2	81.0	71.3	60.2
2-laA5-α	Me_2SO	103.0	72.4	73.5	68.5	74.9	66.9	92.6	72.4	72.4	81.3	71.1	60.0
3-laA5-α	Me_2SO	103.1	72.5	73.6	68.4	74.9	67.4	92.4	72.6	72.1	81.5	71.4	59.8

[a] Taken from ref.[9].

1 signal intensities (see Table 4). Selected ^1H NMR data (200 MHz, CD_3OD): δ = 8.38, 7.96 (AA′XX′ system, 4 H, 2′-H, 3′-H, 5′-H, 6′-H, α- and β-pyranose), 7.89, 6.90 (AA′XX′ system, 4 H, 8′-H, 9′-H, 11′-H, 12′-H, α- and β-pyranose), 5.11 (d, $J_{1,2}$ = 3.8 Hz, 1-H, α-pyranose), 4.51 (d, $J_{1,2}$ = 7.7 Hz, 1-H, β-pyranose), 3.85–3.15 (m, 16 H, 2-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, CH_2CH_2N, CH_3CH_2N, $3\times CH_2O$, α- and β-pyranose), 1.80–1.40 [m, 6 H, $(CH_2)_3$, α- and β-pyranose], 1.27 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 5 for the glycide portion and, for the ethereal and dye portions, δ = 156.6 (C-1′), 152.1 (C-10′), 147.1 (C-4′), 143.0 (C-7′), 126.5, 125.3, 122.8, 120.6, 112.0 (Ar-CH), 72.3, 71.0, 68.4 ($3\times CH_2O$), 50.3, 45.9 ($2\times CH_2N$), 30.3, 29.7, 22.8 [$(CH_2)_3$], 12.6 (CH_3) ppm. $C_{27}H_{38}N_4O_9$ (562.26): calcd. C 57.64, H 6.81, N 9.96; found C 57.45, H 6.69, N 9.88.

Deprotected GAD 3-ga5: Hydrolysis of **3-ga5-pr** (1.00 g, 1.67 mmol) with aqueous CF_3COOH (90%, 10 mL) by the same procedure as described above for the preparation of **1-ga4** afforded **3-ga5** (0.78 g, 90% yield) as an orange solid as a mixture of α- and β-pyranosic anomers in the ratio of 45:55, calculated on the basis of the relative C-1 signal intensities (see Table 4). Selected ^1H NMR (200 MHz, Me_2SO): δ = 7.80, 7.61 (4 H, 2′-H, 3′-H, 6′-H, 5′-H, both anomers), 7.47 (d, J = 2.0 Hz, 1 H, 12′-H), 6.98 (dd, J = 8.6 Hz, 1 H, 10′-H, both anomers), 6.77 (d, 1 H, 9′-H, both anomers), 4.14 (t, J = 7.0 Hz, 2 H, CH_2OPh, both anomers), 3.50 (m, 2 H, CH_2O, both anomers), 2.32 (s, 3 H, CH_3Ph), 2.03 (s, 3 H, CH_3CO, both anomers), 1.90 (m, 2 H, CH_2, both anomers); 1.70 (m, 4 H, CH_2CH_2, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 4 for the glycide portion and, for the ethereal and dye portions, δ = 168.9 (C=O), 155.6, 148.8, 142.3, 140.1 (C-1′, C-4′, C-7′, C-8′), 131.7 (C-10′), 130.5 (C-11′), 126.0, 123.9, 123.5, 121.6, 121.5, 116.2 (C-12′, C-2′, C-6′, C-3′, C-5′, C-9′), 71.5, 70.1 ($2\times CH_2O$), 30.5, 29.7, 28.8 [$(CH_2)_3$],24.9, 24.3 (CH_3Ar, CH_3CO) ppm. $C_{26}H_{35}N_3O_8$ (517.58): calcd. C 60.34, H 6.82, N 8.12; found C 60.24, H 6.64, N 8.09.

Deprotected GAD 2-laA5: Hydrolysis of **2-laA5-pr** (1.00 g, 1.03 mmol) with aqueous CF_3COOH (90%, 3 mL) by the same procedure as described above for the preparation of **1-ga4** afforded **2-laA5** (0.70 g, 96% yield) as a red solid as a mixture of α- and β-pyranosic anomers in the ratio of 50:50, calculated on the basis of the relative C-1 signal intensities (see Table 5). Selected ^1H NMR data (200 MHz, Me_2SO): δ = 8.38, 7.96 (AA′XX′ system, 4 H, 2′-H, 3′-H, 5′-H, 6′-H, α- and β-pyranose), 7.89, 6.90 (AA′XX′ system, 4 H, 8′-H, 9′-H, 11′-H, 12′-H, α- and β-pyranose), 5.11 (d, $J_{1,2}$ = 3.8 Hz, 1-H, α-pyranose), 4.51 (d, $J_{1,2}$ = 7.7 Hz, 1-H, β-pyranose), 3.85–3.15 (m, 16 H, 2-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, CH_2CH_2N, CH_3CH_2N, $3\times CH_2O$, α- and β-pyranose), 1.80–1.40 [m, 6 H, $(CH_2)_3$, α- and β-pyranose], 1.27 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 5 for the glycide portion and, for the ethereal and dye portions, δ = 156.6 (C-1′), 152.1 (C-10′), 147.1 (C-4′), 143.0 (C-7′), 126.5, 125.3, 122.8, 120.6, 112.0 (Ar-CH), 72.3, 71.0, 68.4 ($3\times CH_2O$), 50.3, 45.9 ($2\times CH_2N$), 30.3, 29.7, 22.8 [$(CH_2)_3$], 12.6 (CH_3) ppm. $C_{32}H_{46}N_4O_{14}$ (710.74): calcd. C 54.08, H 6.52, N 7.88; found C 54.21, H 6.64, N 7.74.

Deprotected GAD 3-laA5: Hydrolysis of **3-laA5-pr** (1.00 g, 1.18 mmol) with aqueous CF_3COOH (90%, 10 mL) by the same procedure as described above for the preparation of **1-ga4** afforded **3-laA5** (0.76 g, 95% yield) as a yellow solid as a mixture of α- and β-pyranosic anomers in the ratio of 50:50, calculated on the basis of the relative C-1 signal intensities (see Table 5). Selected ^1H NMR data (200 MHz, Me_2SO): δ = 7.80, 7.61 (4 H, 2′-H, 3′-H, 6′-H, 5′-H, both anomers), 7.47 (d, J = 2.0 Hz, 1 H, 12′-H), 6.98 (dd, J = 8.6 Hz, 1 H, 10′-H, both anomers), 6.77 (d, 1 H, 9′-H, both anomers), 4.14 (t, J = 7.0 Hz, 2 H, CH_2OPh, both anomers), 3.50 (m, 2 H, CH_2O, both anomers), 2.32 (s, 3 H, CH_3Ph), 2.03 (s, 3 H, CH_3CO, both anomers), 1.90 (m, 2 H, CH_2, both anomers); 1.70 (m, 4 H, CH_2CH_2, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 5 for the glycide portion and, for the ethereal and dye portions, δ = 168.9 (C=O), 155.6, 148.8, 142.3, 140.1 (C-1′, C-4′, C-7′, C-8′), 131.7 (C-10′),130.5 (C-11′), 126.0, 123.9, 123.5, 121.6, 121.5, 116.2 (C-12′, C-2′, C-6′, C-3′, C-5′, C-9′), 71.5, 70.1 ($2\times CH_2O$), 30.5, 29.7, 28.8 [$(CH_2)_3$], 24.9, 24.3 (CH_3Ar, CH_3CO) ppm. $C_{32}H_{45}N_3O_{13}$ (679.73): calcd. C 56.55, H 6.67, N 6.18; found C 54.51, H 6.61, N 6.08.

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