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Synthesis and Photochromic Properties of Configurationally Varied Azobenzene Glycosides

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Spatial orientation of carbohydrates is a meaningful parameter in carbohydrate recognition processes. To vary orientation of sugars with temporal and spatial resolution, photosensitive glycoconjugates with favorable photochromic properties appear to be opportune. Here, a series of azobenzene glycosides were synthesized, employing glycoside synthesis and Mills reaction, to allow "switching" of carbohydrate orientation by reversible E/Z isomerization of the azobenzene N=N double bond. Their photochromic properties were tested and effects of azobenzene substitution as well as the effect of anomeric configuration and the orientation of the sugar's 2-hydroxy group were evaluated.

Introduction

Photoswitchable glycoconjugates have recently received increasing attention for their potential of spatial and temporal control of carbohydrate recognition.[1] This is because photoisomerization of such "sweet switches" allows for a reversible shifting between two structurally different states in which carbohydrate orientation is significantly altered. Thus, photoswitchable glycoconjugates might be utilized on surfaces to control cell adhesion or to influence other processes of cell biology.[2] Moreover, they may eventually lead to the development of designer surfaces for further applications.[3]

We have shown earlier that, among photosensitive glycoconjugates, the azobenzene glycosides are suitable tools in the context of molecular switching.[4] In azobenzene glycosides, the well-known azobenzene substructure serves as a reliable photoresponsive unit that is glycosidically attached to a specific carbohydrate glycone moiety. Irradiation of the planar and more stable E-form of an azobenzene glycoside with UV light ($\lambda \approx 365$ nm) effects transition to the bent Z isomer.[5] By exposure to visible light ($\lambda > 440$ nm) or by thermal equilibration, the azobenzene Z isomer relaxes back to the E-form with a half-life $\tau_{1/2}$ which is an individual parameter of a specific azobenzene derivative.[6] Hence, E/Z isomerization of the N=N double bond in azobenzene glycosides can be employed to effect a considerable change in the spatial orientation of the conjugated sugar moiety (Figure 1).

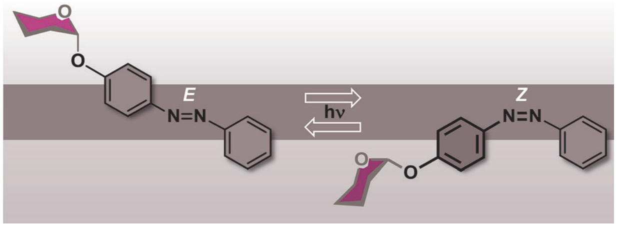

Figure 1. Irradiation of azobenzene glycosides effects E/Z isomerization accompanied by a significant change in orientation of the ligated carbohydrate moiety.

For the application of photosensitive azobenzene glycosides, the kinetics of photoswitching are critical. The photoinduced $E \rightarrow Z$ isomerization of azobenzene derivatives is known to be fast and can be performed in a few femtoseconds using an appropriate light source.[6] The rate of the $Z \rightarrow E$ relaxation process, on the other hand, greatly depends on the structure of the molecule. Here, both slow and fast $Z \rightarrow E$ back isomerization can be desired depending on the planned application. Slow $Z \rightarrow E$ isomerization, for example, is required to investigate the two photoisomeric states of an azobenzene glycoside in a biological assay independently of each other. Fast relaxation in turn is crucial for the application of azobenzene derivatives in real-time information-transmitting systems.

For $Z \rightarrow E$ back isomerization of azobenzene glycosides, it is especially interesting to test the influence of configurational characteristics; in particular, the relevance of the configuration at the 2-position of the sugar ring, adjacent to the anomeric center, which often influences the properties of glycosides specifically. Secondly, the impact of the anomeric configuration on $Z \rightarrow E$ relaxation has to be tested. Consequently, we have commenced a corresponding study on the photochromic proper-

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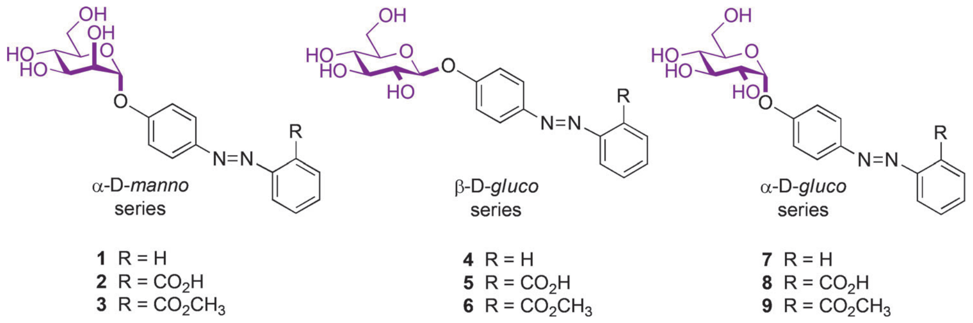


Figure 2. Target azobenzene glycosides: Configurational characteristics were systematically varied to study their effect on the photochromic properties of the respective molecule.

ties of azobenzene glycosides, mainly employing a series of nine representatives, the α-D-mannosides **1**–**3**, the β-D-glucosides **4**–**6**, and the α-D-glucosides **7**–**9** (Figure 2). Substituents at the azobenzene moiety were expected to alter the photochromic properties of the respective glycosides but also were installed to influence solubility as well as to provide a functional handle for later conjugation.

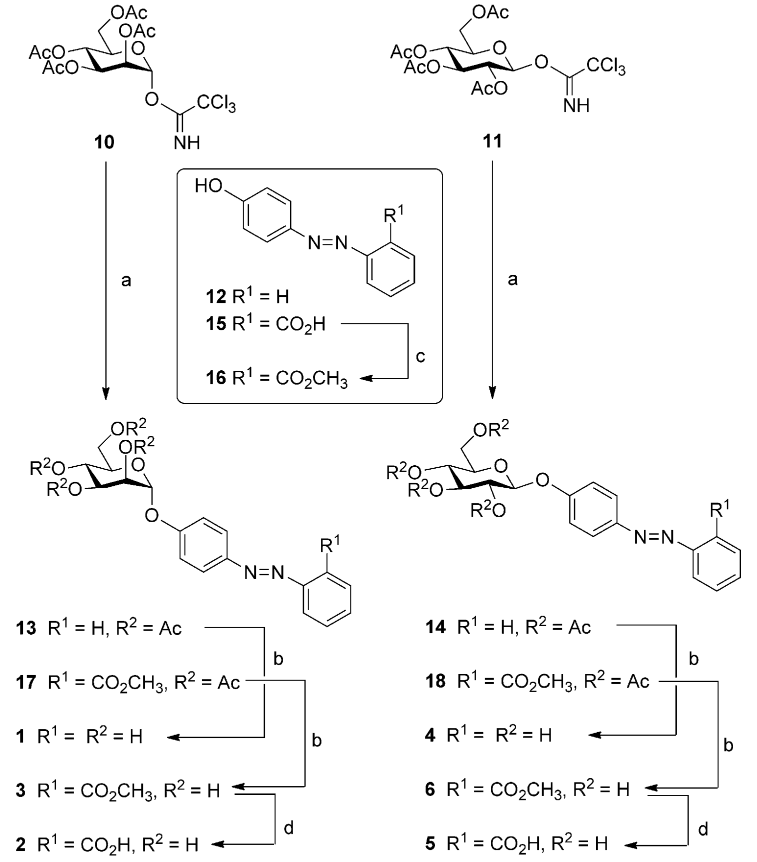
Results and Discussion

Synthesis of azobenzene glycosides

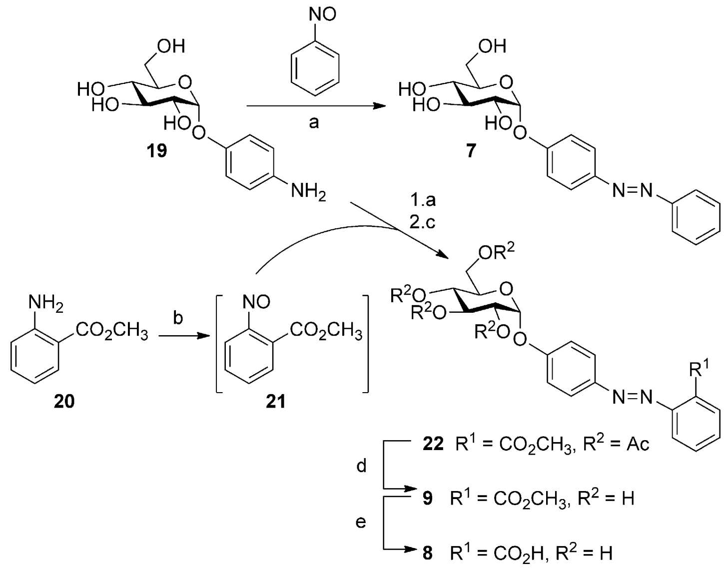
Synthesis of the desired azobenzene glycosides (Figure 2) started with the preparation of the 1,2-*trans*-configured α-D-mannosides **1**–**3** and the 1,2-*trans*-configured β-D-glucosides **4**–**6**. Azobenzene glycosides of the 1,2-*trans*-type can be obtained in a stereospecific glycosylation reaction, employing an O-acylated glycosyl donor and the appropriate azobenzene alcohol. The neighbouring group participation of the 2-*O*-acyl group of the sugar ring ensures the stereospecific course of the glycosylation reaction.[7] Thus, the O-acetylated glycosyl trichloroacetimidates **10**[8] and **11**,[9] respectively, were employed for glycosylation of commercially available 4-hydroxyazobenzene (**12**) according to Schmidt's procedure[10] in a Lewis acid-catalyzed reaction. We have described this approach for the synthesis of the α-configured mannoside **13** earlier,[4] and here it was extended to the synthesis of **14**. Deprotection under Zemplén conditions[11] led to the known α-mannoside **1**[4] and to its analogue, the β-glucoside **4**, the first two target glycosides of this study (Scheme 1).

Next we aimed at introducing a carboxyl group at the azobenzene aglycone moiety in order to improve water solubility of the azobenzene glycosides. The required carboxyl-substituted azobenzene derivative **15**, *o*-(*p*-hydroxyphenylazo)benzoic acid (HABA), is commercially available. For glycosylation, it was converted into its methyl ester **16**, and then again Lewis acid-promoted reaction with glycosyl donors **10** and **11**, respectively, led to the methoxycarbonyl-substituted azobenzene glycosides **17** and **18**. Zemplén deacetylation[11] gave the next two target glycosides **3** and **6**, and treatment with LiOH in a subsequent step delivered the unprotected *o*′-carboxyl-substituted azobenzene glycosides **2** and **5**. Notably, the water solubility of the methyl esters **3** and **6** was better than that of the carboxylic acids **2** and **5**. Overall, the synthesis of the first two sets of azobenzene glycosides, **1**–**3** and **4**–**6** required only a handful of high-yielding steps, furnishing the final products as colored crystalline compounds.

The series of synthetic azobenzene glycosides was complemented by α-D-glucosides **7**–**9**. These glucosides are representatives of the 1,2-*cis*-glycoside type, and therefore more difficult to synthesize stereoselectively. A number of methods providing a stereospecific access to α-glucosides have been introduced,[12] often requiring a higher number of synthetic steps. We therefore refrained from a glycosylation approach for the synthesis of **7**–**9**. Instead Mills reaction[13] was utilized comprising acid-promoted condensation of amino-substituted aryl de-



Scheme 1. Synthesis of azobenzene glycosides **1**–**6**. a) BF$_3$·Et$_2$O, CH$_2$Cl$_2$, 0 °C→RT, **13** (with **12**: 81 %), **14** (with **12**: 73 %), **17** (with **16**: 84 %), **18** (with **16**: 79 %); b) NaOMe, MeOH, RT, **1** (92 %), **3** (89 %), **4** (90 %), **6** (83 %); c) MeOH/HCl, reflux, 5 h, 85 %; d) LiOH, THF/H$_2$O (2:1), RT, **2** (93 %), **5** (91 %).



Scheme 2. Synthesis of azobenzene glycosides **7**, **8**, and **9**. a) Acetic acid, RT, **7** (96 %); b) oxone, CH_2Cl_2/H_2O (16:20), RT; c) pyridine, acetic anhydride, RT, **22** (89 % over two steps); d) NaOMe, MeOH, RT, overnight, 96 %; e) LiOH, THF/H_2O (2:1), RT, 18 h, 95 %.

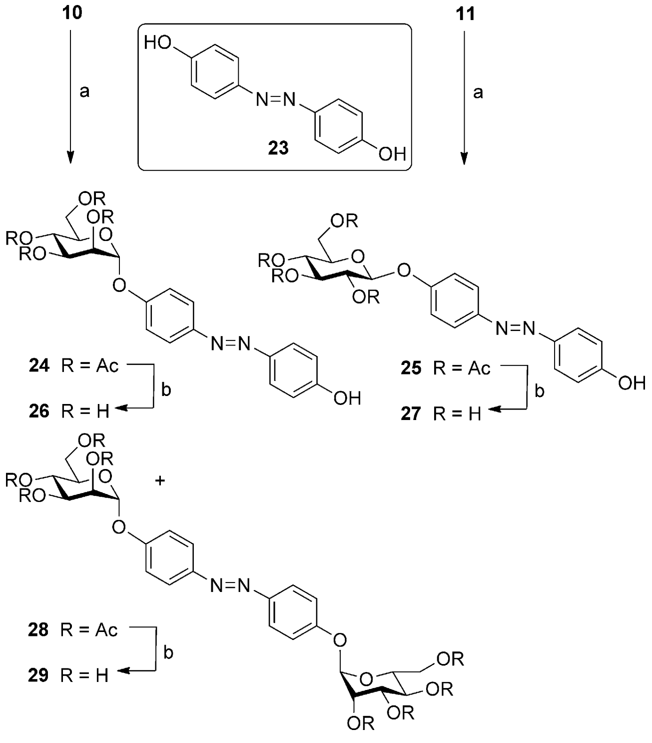
rivatives and nitrosoarenes. Thus, synthesis of the target α-azobenzene glucosides started with *p*-aminophenyl α-D-glucoside **19**, which can be obtained by catalytic reduction of commercially available *p*-nitrophenyl α-D-glucoside in a quantitative reaction (Scheme 2).[14] Acid-catalyzed condensation of **19** with nitrosobenzene delivered the unprotected target glucoside **7** in high yield. Likewise, target glucoside **8** was derived from condensation of **19** with the nitrosobenzene derivative **21**, which was obtained from its carboxylic acid ester **20**[15] and employed in situ. In order to facilitate purification of the condensation product, it was submitted to O-acetylation, using acetic anhydride in pyridine to yield the fully protected glucoside **22**, which could be easily purified. Then, de-O-acetylation furnished the methoxycarbonyl-substituted glucoside **9** in pure form, and subsequent saponification of **9** with LiOH gave the carboxylic acid derivative **8**.

In addition to the nine target azobenzene glycosides **1**–**9**, we were interested in the properties of *p*′-hydroxy-substituted azobenzene glycosides, which were derived from the azobenzene acceptor diol **23** by monoglycosylation. Diol **23** was prepared according to the literature (Scheme 3).[16] Thus, O-acetylated glycosides **24** and **25** were received employing **10** and **11**, respectively, as the glycosyl donors. Yields were limited in this case, due to only partial glycosylation of diol **23**. Usual deprotection of **24** and **25** gave the OH-free azobenzene glycosides **26** and **27**, respectively. We also aimed at the divalent azobenzene mannnoside **29**, as it is a promising antagonists of the mannose-specific bacterial lectin FimH.[17] When an appropriate amount of mannosyl donor **10** was employed in the glycosylation reaction with **23**, a mixture of the mono- and bis-α-mannosylated azobenzene derivatives **24** and **28** was obtained in 37 % and 31 % respective yields after separation by column chromatography. Subsequent de-O-acetylation proceeded in high yields. The bis-glycosylated glycoside **29** is a symmetric molecule, which displays one signal set for both mannosyl moieties in its NMR spectra.

Photochromic properties

With this collection of new azobenzene glycosides in hand, $E \rightarrow Z$ photoisomerization was studied. Photostationary states (PSS) were reached after irradiation at 365 nm for approx. 30 min. Resulting *E*/*Z* ratios were determined in ^{1}H NMR spectra, as *E* and *Z* isomers display well-separated and easily distinguishable resonances for the aromatic and the anomeric protons (Table 1). Thus, *E*/*Z* ratios of the isomeric mixtures in the ground state (GS) as well as in the PSS were quantified by integration of the respective NMR peaks. It is noteworthy that the solutions used for NMR spectroscopy had millimolar concentrations (≈40 mmol). On the other hand, rate constants κ and half-lives $\tau_{1/2}$ of thermal $Z \rightarrow E$ back isomerization were determined by UV/Vis spectroscopy employing 50 μM solutions in DMSO (cf. Supporting Information). The photochromic data obtained for the synthetic azobenzene glycosides are collected in Table 2.

As expected, all azobenzene glycosides are completely *E*-configured in their GS within the experimental error (Table 2). Their UV/Vis spectra display very similar absorption maxima. The carbohydrate moiety does not alter these electronic properties owing to lack of conjugation. The different *o*′-substituents influence the maxima somewhat, their effect on the thermal $Z \rightarrow E$ back isomerization rate, however, is much more pro-



Scheme 3. Synthesis of azobenzene glycosides **26**, **27**, and **29**. a) $BF_3{\cdot}Et_2O$, CH_2Cl_2, 0 °C→RT, **24** (37 %), **25** (31 %), **28** (31 %); b) NaOMe, MeOH, RT, **26** (88 %), **27** (89 %), **29** (93 %).

Table 1. Chemical shifts δ [ppm] of anomeric protons (H-1) of *E*- and *Z*-configured azobenzene glycosides.[a]

H-1	**1**	**1**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**29**
E isomer	5.54	5.53	5.53	5.04	4.99	5.00	5.55	5.57	5.57	5.51
Z isomer	5.34	5.30	5.31	4.80	4.78	4.80	5.35	5.34	5.35	5.34

[a] ^{1}H NMR ([D$_6$]DMSO, 500 MHz).

Table 2. Comparison of photochromic properties of synthesized azobenzene glycosides with different types of azobenzene substitutions, in particular carboxyl (CO_2H) and methoxycarbonyl (CO_2Me).

Compd	Substituent	GS *E/Z* ratios by NMR[a] (ε)[b]	$\lambda_{max}(E)$, $\lambda_{max}(Z)$ [nm][c]	$\tau_{1/2}$ [h][d]	PSS *E/Z* ratios by NMR[a] (ε)[b]	PSS *E/Z* ratios by UV/Vis[c]
1 (α-man)	H	99:1 (25907)	347, 440	89	3:97 (2635)	5:95
4 (β-glc)	H	98:2 (23274)	347, 439	94	4:96 (1704)	5:95
7 (α-glc)	H	99:1 (15804)	356, 439	36	2:98 (1712)	5:95
2 (α-man)	*ortho*′-CO_2H	99:1 (29362)	341, 423	2	85:15 (3106)	25:75
5 (β-glc)	*ortho*′-CO_2H	99:1 (28335)	337, 425	4	41:59 (2521)	25:75
8 (α-glc)	*ortho*′-CO_2H	98:2 (13715)	341, 424	2.5	76:24 (1407)	30:70
3 (α-man)	*ortho*′-CO_2Me	98:2 (21694)	345, 426	5	10:90 (3452)	20:80
6 (β-glc)	*ortho*′-CO_2Me	98:2 (18722)	346, 425	5	39:61 (2071)	20:80
9 (α-glc)	*ortho*′-CO_2Me	99:1 (16943)	345, 426	2	45:55 (1734)	20:80
26 (α-man)	*para*′-OH	98:2 (19804)	363, 480	–	–	–
29	*para*′-α-man	98:2 (18810)	358, 446	24	5:95 (1395)	5:95

[a] *E/Z* ratios are based on the integrals of the respective anomeric protons H-1 in the ^{1}H NMR spectrum (at millimolar concentration, namely 10 mg sample in 600 µL [D$_6$]DMSO, 500 MHz). [b] ε: Extinction coefficient [L mol^{-1} cm^{-1}]. [c] UV/Vis absorption maxima $\lambda_{max}(E)$ and $\lambda_{max}(Z)$ [nm]. [d] Half-life $\tau_{1/2}$ as determined by UV/Vis spectroscopy (50 µM samples in DMSO). PSS = Photostationary states. [e] Rounded values based on estimated accuracy of ±5% (cf. Supporting Information).

nounced. Inclusion of a carboxyl- or methoxycarbonyl group shortens the half-life $\tau_{1/2}$ from ~90 h to ~2 h and 5 h, respectively. These shorter life times of a less-stable *Z* isomer suggest that the barrier for thermal relaxation is lowered. This can be clearly seen in case of the *p*′-OH-substituted azobenzene mannoside **26**. Here, thermal *Z*→*E* back isomerization was too fast to allow monitoring by NMR spectroscopy. This finding is in line with reports from the literature, showing that *p*-hydroxy-substituted azobenzene derivatives are characterized by fast kinetics of thermal relaxation of the *Z* isomer, leading to relaxation times in the millisecond range.[6,18] This feature is also emphasized by our observation that the *p*′-OH-substituted azobenzene glucoside **27** behaves exactly the same as the analogous mannoside **26** (Scheme 3).

Most strikingly, significant substituent effects are observed in the PSS *E/Z* ratios determined by NMR spectroscopy. These further deviate significantly from the PSS ratio estimated from the UV data. An *o*′-substitution reduces conversion to the *Z* isomer from near completeness to about 80% under UV conditions. Under NMR conditions, in particular conversion of the *o*′-carboxyl-substituted compounds is moderately to severely hindered (15% Z isomer for **2**, 24% for **8**, and 59% for **5**) depending on the sugar moiety.

The source of these surprising results lies in differing solution properties of the azobenzene glycosides as highlighted by the exemplary ^{1}H NMR spectra of the α-D-glucoside **8** (Figure 3). At low concentration (UV conditions), unassociated monomeric glycosides are present, giving rise to sharp NMR resonances (Figure 3 a). Partial and dynamic association is apparent for **8** at intermediate concentrations where strong exchange-broadened resonances in particular for the *o*′-substituted phenyl ring protons can be observed. At high concentrations, all resonances are again observed with reasonable line widths owing to the presence of a stable aggregate (Figure 3 c). Most strongly, this aggregation behavior is observed in the NMR-determined PSS ratios of the *o*′-carboxylates **2**, **5**, and **8**. The differences in these show a further dependency on the anomeric configuration and the configuration at C-2 of the sugar ring, presumably reflecting close steric contact of the carbohydrate moieties in the associated form of the respective azobenzene glycosides.

A detailed characterization of this unexpected observation and delineation of the type of aggregates is beyond the scope of this synthetic paper and is the focus of ongoing research. Nevertheless, similar effects of *o*-substitution have been reported in the literature.[18] Here, the formation of inter- as well as intramolecular hydrogen bonds between azobenzene substituents (e.g., hydroxy or carboxyl) and the azobenzene N_2 moiety similarly affect the thermal *Z*→*E* isomer-

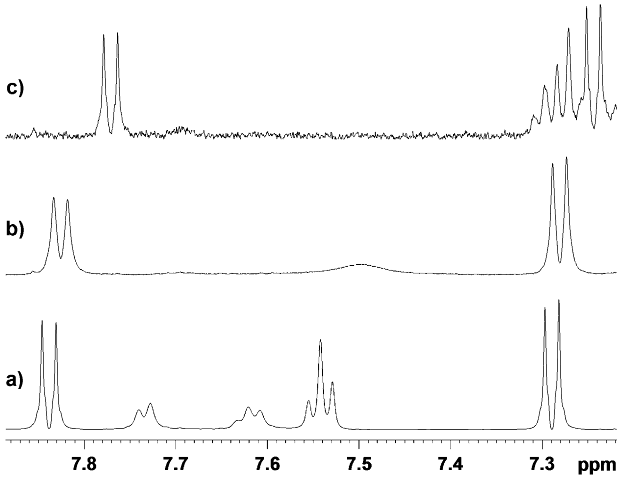


Figure 3. Aromatic region of ^{1}H NMR spectra of **8** in [D$_6$]DMSO at concentrations of a) 5 mM, b) 500 µM and c) 50 µM. Spectra were acquired with a Bruker Avance II 600 MHz spectrometer, using a standard 1D experiment with excitation sculpting for solvent line suppression acquiring 64 scans. In c) and a) sharp resonances are obtained for the monomeric and aggregated compound, respectively. At intermediate concentration (b), broadening is observed most pronouncedly for the *o*-carboxyl-substituted phenyl ring of the azobenzene moiety, owing to the presence of intermediate timescale exchange between monomeric and aggregated species.

ization. The energy barrier of $Z \rightarrow E$ relaxation can be significantly lowered when azobenzene substituents favor a hydrazone-type distribution of electron density and thus promote a tautomeric form of the molecule by which thermal $Z \rightarrow E$ recovery is facilitated. It was also suggested that substituents at the azobenzene substructure can alter the isomerization mechanism (rotation versus inversion mechanism).[6,19,20] Moreover, azobenzene substitution can influence pH sensitivity of photoisomerization and solvent dependency of isomerization.[21] Our results strongly suggest, that substitution may also dramatically affect the tendency of the compounds to interact via π–π stacking or hydrogen-bond mechanisms, and thus may lead to strongly varying photochromic properties.

Conclusions

While substitution effects in azobenzene glycosides are difficult to predict, it can be concluded that indeed the anomeric linkage of a glycoside (cf. **5** versus **8**) as well as the configuration of the 2-OH group (cf. **3** versus **6**) can be crucial for the photoisomerization behavior, possibly via steric differences in associated glycosides. These two important characteristics of a glycoside thus provide additional parameters to regulate the photochromic properties of this class of "sweet switches", which can be employed to facilitate future applications in the field of carbohydrate recognition.

Experimental Section

General methods: *p*-Hydroxyazobenzene and *o*-(*p*-hydroxyphenylazo)benzoic acid were purchased from Sigma–Aldrich and used without further purification. Air/moisture-sensitive reactions were carried out under nitrogen in dry glassware. Thin-layer chromatography was performed on silica gel plates (GF 254, Merck), using UV detection and subsequent charring with 10% sulfuric acid in EtOH followed by heat treatment at ~180 °C. Flash chromatography was performed on silica gel 60 (Merck, 230–400 mesh, particle size 0.040–0.063 mm) using distilled solvents. Melting points (mp) were determined on a Büchi 510 apparatus (Flawil, Switzerland). Optical rotations were measured with a PerkinElmer 241 polarimeter (sodium D-line: 589 nm, length of cell: 1 dm) in the solvents indicated. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-500 and AV-600 spectrometers at 300 K. Chemical shifts δ are reported relative to internal tetramethylsilane ($\delta = 0.00$ ppm) or D_2O ($\delta = 4.76$ ppm) in ppm. Full assignment of the peaks was achieved with the aid of 2D NMR techniques (^{1}H–^{1}H COSY and ^{1}H–^{13}C HSQC). For photostationary state (PSS) determination, all ^{1}H NMR spectra were recorded in [D$_6$]DMSO (cf. Table 2). NMR assignments are in accordance with the compound numbering indicated in Figure 4. The glycoside glycone moiety is numbered from 1–6, aglycone numbering is ascending from 7, starting with the atom adjacent to the glycosidic bond. UV/Vis absorption spectra were performed on Perkin-Elmer Lambda-14 and Varian Cary-5000 at 18 ± 1 °C. Irradiation ($E \rightarrow Z$ isomerization) was carried out with a high-pressure mercury lamp UV-P 250C from Panacol-Elosol (Steinbach, Germany). The band-pass filters were obtained from laser components. IR spectra were measured with a PerkinElmer FT-IR Paragon 1000 (ATR) spectrometer. ESI mass spectra were recorded on a Mariner instrument 5280. MALDI-TOF mass spectra were recorded on a Bruker Biflex III instrument with 19 kV acceleration voltage, and 2,5-dihydroxybenzoic acid (DHB) was used as a matrix. High-resolution mass spectra (HRMS) were measured using a Thermo Scientific LTQ Velos Orbitrap mass spectrometer equipped with nano-electrospray source in positive ion mode. Elemental analyses were performed using a Euro Vector CHNS-O-element analyzer (Euro EA 3000) at the Institute of Inorganic Chemistry, Christiana Albertina University of Kiel.

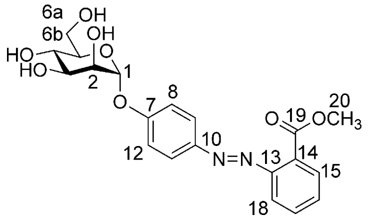


Figure 4. Numbering of hydrogen and carbon atoms for assignment of NMR data exemplified for mannoside **3**.

Irradiation of *E*-configured azobenzene glycosides: The respective *E*-configured azobenzene glycoside (≈10 mg) was dissolved in [D$_6$]DMSO (600 μL) in a NMR tube and irradiated for 30 min at 365 nm. Photostationary states (PSS) were reached after approx. 30 min. Then, the sample was kept in the dark, and ^{1}H NMR spectroscopy was performed immediately afterwards. NMR data of *Z* isomers are given in the Supporting Information. In analogy, for UV/Vis spectroscopy, the *E*-configured azobenzene glycoside was dissolved in DMSO in a UV cuvette, irradiated for 30 min at 365 nm, and UV/Vis spectra were recorded immediately afterwards. Extinction coefficients ε were deduced from UV/Vis spectra measured at five different concentrations (10 μM, 20 μM, 30 μM, 40 μM and 50 μM; for details see the Supporting Information).

Half-life determination: Half-life $\tau_{1/2}$ determination of thermal $Z \rightarrow E$ back isomerization was determined using UV/Vis spectroscopy (for details see the Supporting Information).

***E*-*p*-(Phenylazo)phenyl α-D-mannopyranoside (1)**: NaOMe (15 mg) was added under N_2 atmosphere to a solution of the protected glycoside **13** (600 mg, 1.14 mmol) in dry MeOH (6 mL), and the reaction mixture was stirred at RT overnight. The reaction mixture was neutralized with Amberlite IR 120 ion exchange resin and was filtered. The filtrate was evaporated under reduced pressure, and the crude product purified by flash column chromatography (10% MeOH in CH_2Cl_2) to yield deprotected **1**. Recrystallization from MeOH gave a pale yellow solid (376 mg, 1.04 mmol, 92%): mp: 183–185 °C; $R_f = 0.33$ (CH_2Cl_2/MeOH, 4:1); $[\alpha]_D^{20} = +1.40$ ($c = 1.0$, DMSO); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.86$ (d, $J = 8.7$ Hz, 2H, H-9, H-11), 7.82 (d, $J = 7.7$ Hz, 2H, H-14, H-18), 7.56 (t, $J = 7.6$ Hz, 2H, H-15, H-17), 7.52 (d, $J = 7.3$ Hz, 1H, H-16), 7.26 (d, $J = 8.7$ Hz, 2H, H-8, H-12), 5.53 (bs, 1H, H-1), 3.89 (dd~bs, 1H, H-2), 3.73 (dd, $J_{3,4} =$

9.2 Hz, $J_{3,2}=3.0$ Hz, 1H, H-3), 3.58–3.47 (m, 3H, H-6a, H-4, H-6b), 3.38 (m_c, 1H, H-5); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta=158.9$ (C-7), 155.5 (C-13), 151.9 (C-10), 130.9 (C-16), 129.4 (C-15, C-17), 124.3 (C-9, C-11), 122.3 (C-14, C-18), 117.1 (C-8, C-12), 98.7 (C-1), 75.2 (C-5), 70.6 (C-3), 69.9 (C-2), 66.6 (C-4), 60.9 (C-6); IR (ATR): $\tilde{\nu}=3337$, 2920, 1599, 1584, 1496, 1227 cm^{-1}; $\varepsilon=25907\pm529$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): m/z $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_6$: 361.36, found: 361.21; HRMS: m/z $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_6$: 361.1394, found: 361.1388; Anal. calcd for $C_{18}H_{20}N_2O_6 \times 0.1\,H_2O$ (360.13): C 59.99, H 5.59, N 7.77, found: C 59.69, H 5.62, N 7.74.

***E-p-*(*o*-Carboxyphenylazo)phenyl α-D-mannopyranoside (2)**: LiOH (14.8 mg, 0.622 mmol) was added to a solution of methyl ester **3** (200 mg, 0.478 mmol) in THF/H_2O (2:1, 3 mL), and the reaction mixture was stirred overnight at RT. It was neutralized with Amberlite IR 120 ion exchange resin, diluted with MeOH (25 mL), and filtered. The filtrate was evaporated under reduced pressure to get pure glycoside **2** as a pale yellow solid (180 mg, 0.45 mmol, 93 %): mp: 116–117 °C; $R_f=0.21$ (EtOAc/MeOH, 8:2); $[\alpha]_D^{20}=+1.21$ ($c=0.9$, DMSO); ^{1}H NMR (500 MHz, CD_3OD): $\delta=7.94$ (d, $J=9.0$ Hz, 2H, H-9, H-11), 7.92 (dd, $J=7.7$, 1.3 Hz, 1H, H-15), 7.73 (dd, $J=8.1$, 1.1 Hz, H-18), 7.68 (dt, $J=7.7$, 1.5, 7.3 Hz, 1H, H-17), 7.59 (dt, $J=7.5$, 7.4, 1.3 Hz, 1H, H-16), 7.34 (d, $J=9.0$ Hz, 2H, H-8, H-12), 5.65 (d, $J=1.8$ Hz, 1H, H-1), 4.08 (dd, $J_{2,3}=3.4$, $J_{2,1}=1.9$ Hz, 1H, H-2), 3.96 (dd, $J_{3,4}=9.5$, $J_{3,2}=3.4$ Hz, 1H, H-3), 3.83–3.74 (m, 3H, H-4, H-6a, H-6b), 3.61 (ddd, $J_{5,4}=9.8$, $J_{5,6a}=5.4$ Hz, $J_{5,6b}=2.5$, 1H, H-5); ^{13}C NMR (125 MHz, CD_3OD): $\delta=170.9$ (C-19), 161.0 (C-7), 152.5 (C-13), 149.1 (C-10), 133.1 (C-17), 131.2 (C-16), 130.9 (C-15), 126.8 (C-14), 126.2 (C-9, C-11), 118.6 (C-18), 118.1 (C-8, C-12), 100.1 (C-1), 75.8 (C-5), 72.4 (C-3), 71.8 (C-2), 68.3 (C-4), 62.7 (C-6); IR (ATR): $\tilde{\nu}=3394$, 2936, 1719, 1595, 1498, 1243 cm^{-1}; $\varepsilon=29362\pm1037$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): m/z $[M+Na]^+$ calcd for $C_{19}H_{20}N_2O_8$: 427.37, found: 427.10; HRMS: m/z $[M+H]^+$ calcd for $C_{19}H_{20}N_2O_8$: 405.1292, found: 405.1282.

***E-p-*(*o*-Methoxycarbonylphenylazo)phenyl α-D-mannopyranoside (3)**: A catalytic amount of NaOMe was added under N_2 atmosphere to a solution of the acetylated mannoside **17** (2.00 g, 3.41 mmol) in dry MeOH (20 mL). The reaction mixture was stirred at RT overnight, neutralized with Amberlite IR 120 ion exchange resin and filtered. The filtrate was concentrated under reduced pressure. Purification by flash column chromatography (EtOAc/MeOH, 9:1) gave **3** as an orange solid (1.20 g, 2.87 mmol, 89 %): mp: 108–110 °C; $R_f=0.29$ (EtOAc/MeOH, 9:1); $[\alpha]_D^{20}=+1.34$ ($c=1.0$, MeOH); ^{1}H NMR (500 MHz, D_2O): $\delta=7.85$ (d, $J=8.4$ Hz, H-15), 7.84(d, J=9.0 Hz, 2H, H-9, H-11), 7.65 (t, $J=7.6$ Hz, 1H, H-17), 7.53 (t, $J=7.9$ Hz, H-16), 7.47 (d, $J=7.7$ Hz, 1H, H-18), 7.24 (d, $J=8.8$ Hz, 2H, H-8, H-12), 5.67 (d, 1H, $J_{1,2}=1.2$ Hz H-1), 4.14 (dd, $J_{1,2}=1.6$, $J_{1,3}=3.2$ Hz,1H, H-2), 4.02 (dd, $J_{3,4}=9.6$, $J_{2,3}=3.3$ Hz, 1H, H-3), 3.83 (s, 3H, CO_2CH_3), 3.75–3.66 (m, 3H, H-4, H-6$_a$,H-6$_b$), 3.64–3.30 (m, 1H, H-5); ^{13}C NMR (125 MHz, D_2O): $\delta=170.1$ (C-19), 169.8 (C-7), 158.7 (C-13), 147.2 (C-10), 133.1 (C-17), 130.1 (C-15), 129.9 (C-16), 126.0 (C-14), 124.8 (C-9/C-11), 119.8 (C-18), 117.3 (C-8/C-12), 97.8 (C-1), 73.5 (C-5), 70.3 (C-3), 69.7 (C-2), 66.5 (C-4), 60.6 (C-6), 53.0 (C-20); IR (ATR): $\tilde{\nu}=3344$, 2930, 1715, 1596, 1497, 1231 cm^{-1}; $\varepsilon=21694\pm696$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): m/z $[M+Na]^+$ calcd for $C_{20}H_{22}N_2O_8$: 441.14, found: 441.08; HRMS: m/z $[M+H]^+$ calcd for $C_{20}H_{22}N_2O_8$: 419.1376, found: 419.1372; Anal. calcd for $C_{20}H_{22}N_2O_8$ (418.13): C 57.41, H 5.30, N 6.70, found: C 57.27, H 5.48, N 6.68.

***E-p-*(Phenylazo)phenyl β-D-glucopyranoside (4)**: The protected glycoside **14** (300 mg, 0.568 mmol) was dissolved in dry MeOH (3 mL) and treated with NaOMe (6 mg), under N_2 atmosphere. The reaction mixture was stirred at RT overnight, then it was neutralized with Amberlite IR 120 ion exchange resin, filtered and the filtrate evaporated under reduced pressure. The crude product was purified by flash column chromatography (10 % MeOH in CH_2Cl_2) to yield unprotected glycoside **4** as yellow solid (185 mg, 0.514 mmol, 90 %): mp: 180–181 °C; $R_f=0.29$ (cyclohexane/MeOH, 4:1); $[\alpha]_D^{20}=-0.37$ ($c=0.85$, DMSO); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta=7.90$ (d, $J=8.8$ Hz, 2H, H-9, H-11), 7.87 (d, $J=7.4$ Hz, 2H, H-14, H-18), 7.61–7.58 (m, 2H, H-15, H-17), 7.54 (m_c, 1H, H-16), 7.23 (d, $J=8.9$ Hz, 2H, H-8, H-12), 5.04 (d, $J=7.3$ Hz, 1H, H-1), 3.73 (dd, $J_{6a,6b}=11.6$, $J_{5,6a}=5.2$ Hz, 1H, H-6a), 3.51 (dd~t, $J_{5,6a}=5.9$ Hz, $J_{6a,6b}=11.8$, 1H, H-6b), 3.42 (ddd, $J_{5,6a}=5.7$, $J_{5,6b}=2.8$ Hz, $J_{4,5}=9.2$ Hz 1H, H-5), 3.32–3.28 (m, 2H, H-3, H-2), 3.23–3.19 (m, 1H, H-4); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta=159.9$ (C-7), 151.9 (C-13), 146.9 (C-10), 130.9 (C-16), 129.4 (C-15, C-17), 124.3 (C-9, C-11), 122.3 (C-14, 18), 116.7 (C-8, C-12), 100.0 (C-1), 77.1 (C-5), 76.5 (C-3), 73.2 (C-2), 69.6 (C-4), 60.6 (C-6); IR (ATR): $\tilde{\nu}=3242$, 1600, 1589, 1495, 1232 cm$^{-1;}$ $\varepsilon=23274\pm1121$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): m/z $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_6$: 361.36, found: 361.17; HRMS: m/z $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_6$: 361.1394, found: 361.1385; Anal. calcd for $C_{18}H_{20}N_2O_6$ (360.13): C 59.99, H 5.59, N 7.77, found: C 59.55, H 5.59, N 7.13.

***E*-4-(2′-Carboxyphenylazo)phenyl β-D-glucopyranoside (5)**: Methyl ester **6** (100 mg, 0.24 mmol) was dissolved in THF/H_2O (2:1, 3 mL), LiOH (7.5 mg, 0.31 mmol) was added, and the reaction mixture stirred at RT overnight. The reaction mixture was neutralized with Amberlite IR 120 ion exchange resin, diluted with MeOH (20 mL) and filtered. The filtrate was evaporated under reduced pressure to yield glycoside **5** as a pale yellow solid (88 mg, 0.22 mmol, 91 %): mp: 194–195 °C; $R_f=0.22$ (EtOAc/MeOH, 8:2); $[\alpha]_D^{20}=-0.39$ ($c=0.78$, DMSO); ^{1}H NMR (500 MHz, CD_3OD): $\delta=7.94$ (d, $J=9.0$ Hz, 2H, H-9, H-11), 7.82 (dd, $J=7.6$, 1.3 Hz, 1H, H-15), 7.71 (dd, $J=7.8$ H, 0.9 Hz, 1H, H-18), 7.60 (dt, $J=8.0$, 7.7, 1.5 Hz, 1H, H-17), 7.54 (dt, $J=7.4$, 7.4, 1.3, 1H, H-16), 7.28 (d, $J=9.0$ Hz, 2H, H-8, H-12), 5.07 (d, $J=7.6$ Hz, 1H, H-1), 3.95 (dd, $J_{6a,6b}=12.1$, $J_{5,6a}=2.2$ Hz, 1H, H-6a), 3.75 (dd, $J_{6a,6b}=12.1$, $J_{5,6b}=5.7$ Hz, 1H, H-6b), 3.56–3.52 (m, 3H, H-2, H-3, H-5), 3.45 (m_c, 1H, H-4); ^{13}C NMR (125 MHz, CD_3OD, 125 MHz): $\delta=173.3$ (C-19), 161.9 (C-7), 151.8 (C-13), 149.3 (C-10), 134.2 (C-14), 132.0 (C-17), 131.2 (C-16), 130.2 (C-15), 126.0 (C-9, C-11), 118.4 (C-18), 117.9 (C-8, C-12), 101.9 (C-1), 78.3 (C-5), 77.9 (C-3), 74.7 (C-2), 71.3 (C-4), 62.5 (C-6); IR (ATR): $\tilde{\nu}=3329$, 2498, 1699, 1592, 1499, 1246 cm^{-1}; $\varepsilon=28335\pm345$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): m/z $[M+Na]^+$ calcd for $C_{19}H_{20}N_2O_8$: 427.37, found: 427.14; HRMS: m/z $[M+H]^+$ calcd for $C_{19}H_{20}N_2O_8$: 405.1292, found: 405.1283.

***E*-*p*-(*o*-Methoxycarbonylphenylazo)phenyl β-D-glucopyranoside (6)**: Protected glucoside **18** (152 mg, 0.259 mmol) was dissolved in dry MeOH (2 mL), and a catalytic amount of NaOMe was added under N_2 atmosphere. The reaction mixture was stirred at RT overnight, neutralized with Amberlite IR 120 ion exchange resin and filtered. The filtrate was evaporated under reduced pressure, and the crude product was purified by flash chromatography (EtOAc/MeOH, 9:1) to yield **6** as a pale yellow solid (90 mg, 215 mmol, 83 %): mp: 142–143 °C; $R_f = 0.29$ (EtOAc/MeOH, 4:1); $[\alpha]_D^{20} = -0.66$ ($c = 1.0$, MeOH); ^{1}H NMR (500 MHz, CD_3OD): $\delta = 7.88$ (d, $J = 9.0$ Hz, 2H, H-9, H-11), 7.76 (d, $J = 7.4$ Hz, 1H, H-15), 7.67-7.64 (m, 2H, H-17, H-18), 7.53 (m_c, 1H, H-16), 7.26 (d, $J = 9.0$ Hz, 2H, H-8, H-12), 5.05 (d, $J = 7.6$ Hz, 1H, H-1), 3.93 (dd, $J_{6a,6b} = 12.1$, $J_{5,6a} = 2.3$ Hz, 1H, H-6a), 3.87 (s, 3H, CO_2CH_3), 3.72 (dd, $J_{6a,6b} = 12.1$, $J_{5,6b} = 5.7$ Hz, 1H, H-6b), 3.54–3.48 (m, 3H, H-2, H-3, H-5), 3.42 (m_c, 1H, H-4); ^{13}C NMR (125 MHz, CD_3OD): $\delta = 169.9$ (C-19), 161.9 (C-7), 152.9 (C-13), 149.2 (C-10), 133.0 (C-17), 130.8 (C-16), 130.5 (C-15), 130.0 (C-14), 125.9 (C-9, C-11), 120.3 (C-18), 118.0 (C-8, C-12), 101.9 (C-1), 78.3 (C-5), 77.9 (C-3), 74.8 (C-2), 71.3 (C-4), 62.5 (C-6), 52.9 (C-20); IR (ATR): $\tilde{\nu} = 3323$, 2942, 1723, 1598, 1498, 1235 cm^{-1}; $\varepsilon = 18\,722 \pm 400$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): m/z $[M+Na]^+$ calcd for $C_{20}H_{22}N_2O_8$: 441.14, found: 441.12; HRMS: m/z $[M+H]^+$ calcd for $C_{20}H_{22}N_2O_8$: 419.1376, found: 419.1362; Anal. calcd for $C_{20}H_{22}N_2O_8 \times 1.4\ H_2O$ (418.14): C 55.96, H 5.45, N 6.53, found: C 56.06, H 5.52, N 6.34.

***E*-*p*-(Phenylazo)phenyl α-D-glucopyranoside (7)**: Glucoside **19** (238 mg, 0.89 mmol) and nitrosobenzene (103 mg, 0.97 mmol, 1.1 equiv) were dissolved in glacial acid (20 mL), and the reaction mixture was stirred at RT for 18 h. After it was concentrated under reduced pressure, the residual was purified by flash column chromatography (EtOAc/MeOH, 9:1→MeOH) to obtain glucoside **7** as an orange solid (305 mg, 0.85 mmol, 96 %): mp: 206–207 °C; $R_f = 0.62$ (EtOAc/MeOH, 1:1); $[\alpha]_D^{20} = +2.21$ ($c = 0.2$, DMSO); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.88$ (d, $J = 8.9$ Hz, 2H, H-9, H-11), 7.84 (d, $J = 7.2$ Hz, 2H, H-14, H-18), 7.58 (t, $J = 7.4$ Hz, 2H, H-15, H-17), 7.52 (d, $J = 7.2$ Hz, 1H, H-16), 7.28 (d, $J = 8.9$ Hz, 2H, H-8, H-12), 5.55 (d, $J_{1,2} = 3.6$ Hz, 1H, H-1), 3.66 (dd~t, $J = 9.2$ Hz, 1H, H-3), 3.56 (m_c, 1H, H-6a), 3.47 (m_c, 1H, H-6b), 3.44 (m_c, 1H, H-5), 3.42 (dd, $J_{2,3} = 9.7$, $J_{2,1} = 3.6$ Hz, 1H, H-2), 3.21 (dd~t, $J = 9.1$ Hz, 1H, H-4); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 158.9$ (C-7), 155.5 (C-13), 151.9 (C-10), 130.9 (C-16), 129.4 (C-15, C-17), 124.3 (C-9, C-11), 122.3 (C-14, C-18), 117.2 (C-8, C-12), 97.6 (C-1), 73.9 (C-5), 72.8 (C-3), 71.3 (C-2), 69.6 (C-4), 60.5 (C-6); IR (ATR): $\tilde{\nu} = 3382$, 3288, 2918, 1597, 1496, 1234; cm^{-1}; $\varepsilon = 15\,804 \pm 256$ L mol^{-1} cm^{-1}; MS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{20}N_2O_6$: 383.121, found: 383.138; HRMS: m/z $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_6$: 361.1394, found: 361.1379.

***E*-*p*-(*o*-Carboxyphenylazo)phenyl α-D-glucopyranoside (8)**: Methyl ester **9** (430 mg, 1.03 mmol) was dissolved in THF/H_2O (1:1, 10 mL), LiOH (49 mg, 2.06 mmol, 2 equiv) was added, and the reaction mixture was stirred overnight at RT. After neutralization with Amberlite IR 120 ion exchange resin, the reaction mixture was filtered, and the filtrate concentrated under reduced pressure to obtain pure glycoside **8** as a yellow solid (395 mg, 0.78 mmol, 95 %): mp: 173–174 °C; $R_f = 0.36$ (EtOAc/MeOH, 1:1); $[\alpha]_D^{20} = +1.93$ ($c = 0.18$, DMSO); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.84$ (d, $J = 9.0$ Hz, 2H, H-9, H-11), 7.77 (m_c, 1H, H-15), 7.66 (m_c, 1H, H-17), 7.56 (m_c, 2H, H-16, H-18), 7.29 (d, $J = 9.0$ Hz, 2H, H-8, H-12), 5.57 (d, $J_{1,2} = 3.6$ Hz, 1H, H-1), 3.66 (dd~t, $J_{3,4} = 9.2$ Hz, 1H, H-3), 3.57 (m_c, 1H, H-6a), 3.48 (m_c, 1H, H-6b), 3.45 (m_c, 1H, H-5), 3.43 (dd, $J_{2,3} = 9.7$, $J_{1,2} = 3.6$ Hz, 1H, H-2), 3.21 (dd~t, $J_{4,3} = 9.2$ Hz, 1H, H-4); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 168.3$ (C-19), 159.9 (C-7), 150.7 (C-13), 146.9 (C-10), 131.6 (C-17), 130.0 (C-14), 129.9 (C-16), 129.1 (C-15), 124.6 (C-9, C-11), 118.1 (C-18), 117.2 (C-8, C-12), 97.6 (C-1), 74.0 (C-5), 72.8 (C-3), 71.3 (C-2), 69.7 (C-4), 60.6 (C-6); IR (ATR): $\tilde{\nu} = 3366$, 2921, 1728, 1597, 1479, 1240 cm^{-1}; $\varepsilon = 13\,715 \pm 2132$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): m/z $[M+Na]^+$ calcd for $C_{19}H_{20}N_2O_8$: 427.11, found: 427.10; HRMS: m/z $[M+H]^+$ calcd for $C_{19}H_{20}N_2O_8$: 405.1292, found: 405.1276.

***E*-*p*-(*o*-Methoxycarbonylphenylazo)phenyl α-D-glucopyranoside (9)**: NaOMe (18 mg) was added under N_2 atmosphere to a solution of glycoside **22** (630 mg, 1.07 mmol) in dry MeOH (12 mL), and the reaction mixture was stirred at RT for 18 h. It was neutralized with Amberlite IR 120 ion exchange resin and filtered, and the filtrate concentrated under reduced pressure. The residual was purified by GPC on Sephadex LH-20 (MeOH) to yield **9** as an orange solid (431 mg, 1.03 mmol, 96 %): mp: 144–145 °C; $R_f = 0.72$ (EtOAc/MeOH, 1:1); $[\alpha]_D^{20} = +1.81$ ($c = 0.2$, DMSO); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.84$ (d, $J = 8.9$ Hz, 2H, H-9, H-11), 7.76 (dd, $J = 7.6$, 1.4 Hz, 1H, H-15), 7.70 (m_c, 1H, H-17), 7.63 (dd, $J = 8.0$, 1.2 Hz, 1H, H-18), 7.58 (dt, $J = 7.4$, 1.3 Hz, 1H, H-16) 7.29 (d, $J = 9.0$ Hz, 2H, H-8, H-12), 5.55 (d, $J_{1,2} = 3.6$ Hz, 1H, H-1), 3.81 (s, 3H, CO_2CH_3), 3.66 (dd~t, $J_{3,4} = 9.2$ Hz, 1H, H-3), 3.57 (dd, $J_{5,6a} = 11.4$, $J_{6a,6b} = 1.6$ Hz, 1H, H-6a), 3.48 (m_c, 1H, H-6b), 3.46 (m_c, 1H, H-5), 3.43 (dd, $J_{2,3} = 9.7$, $J_{2,1} = 3.5$ Hz, 1H, H-2), 3.21 (dd~t, $J_{4,3} = 9.2$ Hz, 1H, H-4); ^{13}C NMR (150 MHz, [D$_6$]DMSO): $\delta = 167.6$ (C-19), 160.22 (C-7), 150.8 (C-13), 146.9 (C-10), 132.2 (C-17), 130.1 (C-16), 129.3 (C-15), 128.4 (C-14), 124.7 (C-9, C-11), 119.5 (C-18), 117.4 (C-8, C-12), 97.7 (C-1), 74.1 (C-5), 72.9 (C-3), 71.4 (C-2), 69.8 (C-4), 60.6 (C-6), 52.4 (C-20); IR (ATR): $\tilde{\nu} = 3327$, 2921, 2853, 1715, 1596, 1497, 1230 cm^{-1}; $\varepsilon = 16\,943 \pm 383$ L mol^{-1} cm^{-1}; MS (ESI): m/z $[M+K]^+$ calcd for $C_{20}H_{22}N_2O_8$: 457.14, found: 457.11; HRMS: m/z $[M+H]^+$ calcd for $C_{20}H_{22}N_2O_8$: 419.1449, found: 419.1439.

***E*-*p*-(Phenylazo)phenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (13)**: $BF_3 \cdot Et_2O$ (347 µL, 2.74 mmol, 1.2 equiv) was added at 0 °C under N_2 atmosphere to a solution of mannosyl donor **10** (900 mg, 1.83 mmol) and *p*-hydroxyazobenzene (**12**, 398 mg, 2.01 mmol) in dry CH_2Cl_2 (18 mL). The reaction mixture was stirred at RT overnight, and quenched by addition of saturated aq $NaHCO_3$ (18 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3×30 mL). The combined organic phases were washed with H_2O (2×20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (cyclohexane/EtOAc, 3:7) gave glycoside **13** as an orange crystalline solid (780 mg, 1.47 mmol, 81 %): mp: 53–55 °C; $R_f = 0.25$ (cyclohexane/EtOAc, 7:3); $[\alpha]_D^{20} = +0.86$ ($c = 0.9$, DMSO); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.92$ (d, $J = 9.1$ Hz, 2H, H-9, H-11), 7.90–7.87 (m, 2H, H-14, H-18), 7.52–7.49 (m, 2H, H-15, H-17), 7.46 (dt, $J = 4.9$, 1.9 Hz, 1 H, H-16), 7.23 (d, $J = 9.1$ Hz, 2 H, H-8, H-12), 5.62 (d, $J_{1,2} = 1.8$ Hz, 1 H, H-1), 5.39 (dd, $J_{3,4} = 10.0$, $J_{2,3} = 3.6$ Hz, 1 H, H-3), 5.49 (dd, $J_{2,3} = 3.5$ Hz, $J_{1,2} = 1.8$ Hz, 1 H, H-2), 5.39 (dd ~ t, $J_{4,3} = J_{4,5} = 10.1$ Hz, 1 H, H-4), 4.28 (m_c, 1 H, H-6a), 4.12–4.07 (m, 2 H, H-5, H-6b), 2.21, 2.06, 2.05, 2.03 (each s, each 3 H, 4 OAc); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.5$, 169.9, 169.9, 169.7 (4 C=O), 157.6 (C-7), 152.6 (C-13), 148.4 (C-10), 130.8 (C-16), 128.9 (C-15, C-17), 124.6 (C-9, C-11), 123.1 (C-14, 18), 116.8 (C-8, C-12), 95.7 (C-1), 69.4 (C-5), 69.3 (C-2), 68.8 (C-3), 65.9 (C-4), 62.1 (C-6), 20.9, 20.7, 20.7, 20.6 (4 CO_2CH_3); IR (ATR): $\tilde{\nu} = 2929$, 1743, 1598, 1496, 1366, 1209, 1029 cm^{-1}; MS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{28}N_2O_{10}$: 551.57, found: 551.17.

***E-p*-(Phenylazo)phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (14)**: Glucosyl donor **11** (500 mg, 1.02 mmol) and *p*-hydroxyazobenzene (**12**, 221 mg, 1.12 mmol) were dissolved in dry CH_2Cl_2 (10 mL), and $BF_3{\cdot}Et_2O$ (128 μL, 1.02 mmol) was added at 0 °C. The reaction mixture was stirred at RT overnight, and the reaction was quenched by addition of saturated aq $NaHCO_3$ (1 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (25 mL). The combined organic phases were washed with H_2O (2×10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residual was purified by flash chromatography (cyclohexane/EtOAc, 3:7) to yield glucoside **14** as an orange solid (390 mg, 0.74 mmol, 73 %): mp: 166–167 °C; $R_f = 0.27$ (cyclohexane/EtOAc, 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 9.0$ Hz, 2 H, H-9, H-11), 7.89 (d, $J = 7.2$ Hz, 2 H, H-14, H-18), 7.53–7.49 (m, 2 H, H-15, H-17), 7.46 (m_c, 1 H, H-16), 7.11 (d, $J = 8.9$ Hz, 2 H, H-8, H-12), 5.33–5.31 (m, 2 H, H-2, H-3), 5.21–5.27 (m, 2 H, H-1, H-4), 4.31 (dd, $J_{6a,6b} = 12.3$, $J_{5,6a} = 5.5$ Hz, 1 H, H-6a), 4.20 (dd, $J_{6a,6b} = 12.3$, $J_{5,6b} = 2.4$ Hz, 1 H, H-6a), 3.92 (ddd, $J_{5,6a} = 5.5$, $J_{5,6b} = 2.4$ Hz, $J_{4,5} = 9.9$ Hz 1 H, H-5), 2.09, 2.08, 2.06, 2.05 (each s, each 3 H, 4 OAc); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.6$, 170.2, 169.4, 169.3 (4 C=O), 158.8 (C-7), 152.6 (C-13), 148.6 (C-10), 130.8 (C-16), 129.1 (C-15, C-17), 124.5 (C-9, C-11), 122.7 (C-14, C-18), 117.1 (C-8, C-12), 98.7 (C-1), 72.6 (C-5), 72.3 (C-2), 71.2 (C-3), 68.3 (C-4), 61.9 (C-6), 20.7, 20.7, 20.6, 20.6 (4 CO_2CH_3); IR (ATR): $\tilde{\nu} = 1740$, 1598, 1497, 1366, 1220 cm^{-1}; MS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{28}N_2O_{10}$: 551.51, found: 551.17.

***E-p*-(*o*-Methoxycarbonylphenylazo)phenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (17)**: $BF_3{\cdot}Et_2O$ (927 μL, 7.32 mmol, 1.2 equiv) was added at 0 °C under N_2 atmosphere to a solution of mannosyl donor **10** (3.00 g, 6.09 mmol) and *p*-(*o*-methoxycarbonylphenylazo)phenol (**16**, 1.72 g, 6.72 mmol) in dry CH_2Cl_2 (45 mL). The reaction mixture was stirred at RT overnight, and the reaction was quenched by addition of saturated aq $NaHCO_3$ (30 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with H_2O (2×50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residual by flash column chromatography (cyclohexane/EtOAc, 1:4) gave glycoside **17** as a yellow crystalline solid (3.00 g, 5.12 mmol, 84 %): mp: 120–121 °C; $R_f = 0.21$ (cyclohexane/EtOAc, 1:4), $[\alpha]_D^{20} = +0.806$ ($c = 1.0$, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 8.9$ Hz, 2 H, H-9, H-11), 7.82 (d, $J = 7.5$ Hz, 1 H, H-15), 7.61-7.56 (m, 2 H, H-17, H-18), 7.49–7.46 (m, 1 H, H-16), 7.23 (d, $J = 8.9$ Hz, 2 H, H-8, H-12), 5.63 (d, $J_{1,2} = 1.7$ Hz, 1 H, H-1), 5.58 (dd, $J_{3,4} = 10.0$, $J_{3,2} = 3.5$ Hz, 1 H, H-3), 5.48 (dd, $J_{2,3} = 3.5$ Hz, $J_{1,2} = 1.8$ Hz, 1 H, H-2), 5.39 (t, $J_{4,3} = J_{4,5} = 9.9$ Hz, 1 H, H-4), 4.30 (dd, $J_{6a,6b} = 12.7$, $J_{5,6a} = 5.9$ Hz, 1 H, H-6a), 4.08–4.11 (m, 2 H, H-5, H-6b), 3.91 (s, 3 H, CO_2CH_3), 2.22, 2.06, 2.05, 2.03 (each s, each 3 H, 4 OAc); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.4$, 169.9, 169.9, 169.7 (4 C=O), 167.9 (C-19), 157.9 (C-7), 151.9 (C-13), 148.4 (C-10), 131.9 (C-17), 129.7 (C-15), 129.6 (C-16), 128.5 (C-14), 125.0 (C-9, C-11), 118.8 (C-18), 116.8 (C-8, C-12), 95.6 (C-1), 69.5 (C-5), 69.2 (C-3), 68.7 (C-2), 65.8 (C-4), 62.0 (C-6), 52.3 (C-20), 20.9, 20.7, 20.7, 20.6 (4 CO_2CH_3); IR (ATR): $\tilde{\nu} = 2954$, 1744, 1715, 1597, 1498, 1366, 1210 cm^{-1}; MS (ESI): m/z $[M+Na]^+$ calcd for $C_{28}H_{30}N_2O_{12}$: 609.58, found: 609.16.

***E-p*-(*o*-Methoxycarbonylphenylazo)phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (18)**: Glucosyl donor **11** (170 mg, 0.345 mmol) and *o*-(*p*-hydroxyphenylazo)methyl benzoate (**16**, 97.3 mg, 0.38 mmol) were dissolved in dry CH_2Cl_2 (5 mL), and $BF_3{\cdot}Et_2O$ (53 μL, 0.42 mmol, 1.2 equiv) was added at 0 °C. The reaction mixture was stirred at RT overnight, and the reaction was quenched with saturated aq $NaHCO_3$ (10 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (20 mL). The combined organic phases were washed with H_2O (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residual by column chromatography (cyclohexane/EtOAc, 7:3) gave glucoside **18** as an orange solid (160 mg, 0.273 mmol, 79 %): mp: 118–119 °C; $R_f = 0.24$ (cyclohexane/EtOAc, 7:3); $[\alpha]_D^{20} = -0.20$ ($c = 1.0$, MeOH); ^{1}H NMR (500 MHz, CD_3OD): $\delta = 7.89$ (d, $J = 9.0$ Hz, 2 H, H-9, H-11), 7.77 (td, $J = 7.6$, 1.0 Hz, 1 H, H-15), 7.65–7.64 (m, 2 H, H-17, H-18), 7.54 (m_c, 1 H, H-16), 7.19 (d, $J = 9.1$ Hz, 2 H, H-8, H-12), 5.49 (d, $J_{1,2} = 7.9$ Hz, 1 H, H-1), 5.42 (dd ~ t, $J_{3,4} = J_{2,3} = 9.5$ Hz, 1 H, H-3), 5.22 (dd, $J_{2,3} = 9.6$ Hz, $J_{1,2} = 7.9$ Hz, 1 H, H-2), 5.14 (dd ~ t, $J_{4,3} = J_{4,5} = 9.7$ Hz, 1 H, H-4), 4.33 (dd, $J_{6a,6b} = 12.3$, $J_{5,6a} = 5.1$ Hz, 1 H, H-6a), 4.19 (dd, $J_{6a,6b} = 12.3$ Hz, $J_{5,6b5} = 2.4$ Hz, 1 H, H-6b), 3.87 (s, 3 H, CO_2CH_3), 2.06, 2.06, 2.04, 2.01 (each s, each 3 H, 4 OAc); ^{13}C NMR (125 MHz, CD_3OD): $\delta = 172.2$, 171.5, 171.2, 171.1 (4 C=O), 169.8 (C-19), 160.8 (C-7), 152.9 (C-13), 149.7 (C-10), 133.1 (C-17), 130.9 (C-16), 130.5 (C-15), 130.1 (C-14), 125.9 (C-9, C-11), 120.2 (C-18), 118.1 (C-9, C-12), 99.1 (C-1), 74.3 (C-3), 73.2 (C-5), 72.6 (C-2), 69.7 (C-4), 63.1 (C-6), 52.9 (C-20), 20.6, 20.5, 20.5, 20.5 (4 CO_2CH_3); IR (ATR): $\tilde{\nu} = 1739$, 1598, 1501, 1367, 1211 cm^{-1}; MS (ESI): m/z $[M+Na]^+$ calcd for $C_{28}H_{30}N_2O_{12}$: 609.58, found: 609.17.

***E-p*-(*o*-Methoxycarbonylphenylazo)phenyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (22)**: Aniline **20** (966 mg, 6.39 mmol) and CH_2Cl_2 (20 mL) were added to a solution of oxone (7.86 g, 12.8 mmol) in H_2O (20 mL), and the reaction mixture was stirred at RT for 20 h under N_2 atmosphere. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (50 mL). The combined organic phases were successively washed with aq HCl (1 M, 50 mL), saturated aq $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$, filtered and concentrated to yield the crude nitroso intermediate **21** (1.05 g, 6.36 mmol), which was processed without further purification. It was added to the amino-functionalized mannoside

19[14] (648 mg, 2.39 mmol), dissolved in glacial acid (20 mL) and stirred for 18 h at RT. The solution was concentrated, and the crude product dissolved in pyridine (5 mL) and treated with Ac_2O (1.13 mL, 11.9 mmol, 5 equiv) at RT for 52 h under N_2 atmosphere. The solution was concentrated and co-evaporated with toluene. The residual was purified by flash column chromatography (EtOAc/cyclohexane, pure EtOAc→1:1) to yield protected glycoside **22** as an orange solid (1.25 g, 2.13 mmol, 89%): mp: 55 °C; $R_f = 0.5$ (MeOH/EtOAc, 1:2); $[\alpha]_D^{20} = +1.83$ ($c = 0.26$, DMSO););; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 8.9$ Hz, 2H, H-9, H-11), 7.81 (m_c, 1H, H-15), 7.58 (m_c, 2H, H-17, H-18), 7.47 (ddd, $J = 7.7$, 6.4, 2.2 Hz, 1H, H-16), 7.22 (d, $J = 8.9$ Hz, 2H, H-8, H-12), 5.83 (d, $J_{1,2} = 3.6$ Hz, 1H, H-1), 5.72 (dd, $J_{2,3} = 10.0$, $J_{3,4} = 9.6$ Hz, 1H, H-3), 5.18 (dd, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 10.1$ Hz, 1H, H-4), 5.08 (dd, $J_{1,2} = 3.6$ Hz, $J_{2,3} = 10.2$ 1H, H-2), 4.26 (dd, $J_{5,6a} = 12.3$, $J_{6a,6b} = 4.52$ Hz, 1H, H-6a), 4.11 (m_c, 1H, H-5), 4.07 (dd, $J_{5,6b} = 12.2$, $J_{6a,6b} = 2.3$ Hz, 1H, H-6b), 3.91 (s, 3H, CO_2CH_3), 2.08, 2.06, 2.05, 2.04 (each s, each 3H, 4OAc); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.5$, 170.2, 169.5, 167.9 (4 C=O), 158.9 (C-7), 151.9 (C-13), 148.5 (C-10), 131.9 (C-17), 129.7 (C-15). 129.6 (C-16), 125.1 (C-9, C-11), 118.8 (C-18), 116.8 (C-8, C-12), 94.7 (C-1), 70.3 (C-2), 69.9 (C-3), 68.3 (C-5), 68.2 (C-4), 61.5 (C-6), 52.3 (C-20), 20.7, 20.66, 20.63, 20.59 (4CO_2CH_3); IR (ATR): $\tilde{\nu} = 1741$, 1596, 1498, 1367, 1214 cm^{-1}; MS (ESI): m/z $[M+Na]^+$ calcd for $C_{28}H_{30}N_2O_{12}$: 609.169, found: 609.167.

***E*-*p*-(*o*-Hydroxyphenylazo)phenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (24) and *E*-*p*-[*p*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxy)]phenylazophenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (28):** $BF_3 \cdot Et_2O$ (260 μL, 2.01 mmol) was added at 0 °C under N_2 atmosphere to a solution of mannosyl donor **10** (1.00 g, 2.03 mmol) and *p,p'*-dihydroxyazobenzene[16] (23, 200 mg, 0.93 mmol) in dry CH_3CN (15 mL). The reaction mixture was stirred at RT overnight, and saturated aq $NaHCO_3$ (5 mL) was added to quench the reaction. After dilution with EtOAc (100 mL), the phases were separated. The organic phase was washed with H_2O (2×15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (cyclohexane/EtOAc, 6:4) gave the monoglycosylated product **24** (190 mg, 0.349 mmol, 37%) as the first fraction, followed by the divalent glycoside **28** (268 mg, 0.307 mmol, 31%) as pale yellow solids.

24: mp: 109–110 °C; $R_f = 0.26$ (cyclohexane/EtOAc, 1:1); $[\alpha]_D^{20} = +0.75$ ($c = 1.0$, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.85$ (d, $J = 9.0$ Hz, 2H, H-14, H-18), 7.83 (d, $J = 8.9$ Hz, 2H, H-9, H-11), 7.19 (d, $J = 9.0$ Hz, 2H, H-15, H-17), 6.94 (d, $J = 8.8$ Hz, 2H, H-8, H-12), 5.61 (d, $J_{1,2} = 1.6$ Hz, 1H, H-1), 5.59 (dd, $J_{3,4} = 10.0$, $J_{3,2} = 3.4$ Hz, 1H, H-3), 5.48 (dd, $J_{2,3} = 3.5$ Hz, $J_{1,2} = 1.8$ Hz, 1H, H-2), 5.39 (dd~t, $J_{3,4} = J_{4,5} = 10.1$ Hz, 1H, H-4), 4.30 (dd, $J_{5,6a} = 12.1$, $J_{6a,6b} = 5.3$ Hz, 1H, H-6a), 4.12–4.08 (m, 2H, H-5, H-6b), 2.22, 2.07, 2.06, 2.04 (each s, each 3H, 4OAc); ^{13}C NMR (150 MHz, CD_3OD): $\delta = 170.7$, 170.3, 170.1, 169.8 (4C=O), 158.3 (C-7), 157.2 (C-16), 148.5 (C-13), 147.1 (C-10), 124.8 (C-14, C-18), 124.3 (C-9, C-11), 116.8 (C-15, C-17), 115.8 (C-8, C-12), 95.7 (C-1), 69.4 (C-5), 69.3 (C-2), 68.9 (C-3), 65.9 (C-4), 62.1 (C-6), 20.9, 20.7, 20.7, 20.7 (CO_2CH_3); IR (ATR): $\tilde{\nu} = 3407$, 1744, 1587, 1498, 1368; 1211 cm^{-1}; MS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{28}N_2O_{11}$: 567.51, found: 567.16.

28: mp: 167–169 °C; $R_f = 0.15$ (cyclohexane/EtOAc, 1:1); $[\alpha]_D^{20} = +0.89$ ($c = 1.0$, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.89$ (dd, $J = 9.0$ Hz, 4H, H-9, H-11, H-14, H-18), 7.22 (d, $J = 9.0$ Hz, 4H, H-8, H-12, H-15, H-17), 5.61 (d, $J_{1,2} = 1.7$ Hz, 2H, 2 H-1), 5.58 (dd, $J_{3,4} = 10.0$, $J_{2,3} = 3.5$ Hz, 2H, 2 H-3), 5.48 (dd, $J_{2,3} = 3.5$ Hz, $J_{1,2} = 1.8$ Hz, 2H, 2 H-2), 5.38 (dd~t, $J_{3,4} = J_{4,5} = 10.1$ Hz, 2H, 2 H-4), 4.31–4.26 (m, 2H, 2 H-6a), 4.11-4.07 (m, 4H, 2 H-5, 2 H-6b), 2.21, 2.06, 2.05, 2.03 (each s, each 6H, 8OAc); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.5$, 169.9, 169.9, 169.7 (8 C=O), 157.5 (C-7, C-16), 148.4 (C-13, C-10), 124.5 (C-9, C-11, C-14, C-18), 116.8 (C-8, C-12, C-15, C-17), 95.7 (C-1), 69.5 (C-5), 69.3 (C-2), 68.8 (C-3), 65.9 (C-4), 62.1 (C-6), 20.9, 20.7, 20.7, 20.7 (8CO_2CH_3C); IR (ATR): $\tilde{\nu} = 2992$, 1748, 1599, 1582, 1496, 1368, 1213 cm^{-1}; MS (ESI): m/z $[M+Na]^+$ calcd for $C_{40}H_{46}N_2O_{20}$: 897.26, found: 897.23.

***E*-*p*-(p-Hydroxyphenylazo)phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (25):** $BF_3 \cdot Et_2O$ (280 μL, 2.16 mmol) was added at 0 °C under N_2 atmosphere to a solution of the glucosyl donor **11** (907 mg, 1.84 mmol) and *p,p'*-dihydroxyazobenzene[16] (**23**, 304 mg, 1.42 mmol) in dry THF (5 mL). The reaction mixture was stirred at RT overnight, and saturated aq $NaHCO_3$ (5 mL) was added to quench the reaction. The solution was extracted with CH_2Cl_2 (3×5 mL). The combined organic phases were washed with H_2O (2×5 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (cyclohexane/EtOAc, 1:1) gave the monoglycosylated product **25** as a yellow solid (239 mg, 0.440 mmol, 31%): mp: 89–91 °C; $R_f = 0.46$ (cyclohexane/EtOAc, 1:3) $[\alpha]_D^{20} = -1.27$ ($c = 0.92$, MeOH); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.77$ (d, $J = 9.0$ Hz, 2H, H-9, H-11), 7.75 (d, $J = 8.9$ Hz, 2H, H-14, H-18), 7.00 (d, $J = 9.0$ Hz, 2H, H-8, H-12), 6.86 (d, $J = 8.9$ Hz, 2H, H-15, H-17), 6.19 (s, br, 1H, OH), 5.25 (m_z, 2H, H-2, H-3), 5.12 (t, $J = 9.8$ Hz, 1H, H-4), 5.09 (d, $J_{1,2} = 7.2$ Hz, 1H, H-1), 4.30 (dd, $J = 12.3$, 5.3 Hz, 1H, 1H-6a), 4.13 (dd, $J = 2.5$, 12.3, 1H, H-6b), 3.84 (ddd, $J = 10$, 5.4, 2.5 Hz, 1H, H-5), 2.02 (s, 3H, OAc-6), 2.01, (s, 3H, OAc-2), 1.99, (s, 3H, OAc-4), 1.98 (s, 3H, OAc-3); ^{13}C NMR (150 MHz, CDCl3): $\delta = 170.8$ (CO_2CH_3-6) 170.4 (CO_2CH_3-4), 169.5 (CO_2CH_3-2), 169.5 (CO_2CH_3-4), 158.6 (C-16), 158.3 (C-7), 148.7 (C-10), 146.9 (C-13), 124.8 (C-14, C-18), 124.2 (C-9, C-11), 117.1 (C-8, C-12), 115.8 (C-15, C-17), 98.8 (C-1), 72.7 (C-2), 72.2 (C-5), 71.2 (C-3), 68.3 (C-4), 62.0 (C-6), 20.7, 20.6, 20.6, 20.5 (4CO_2CH_3); IR (ATR): $\tilde{\nu} = 3367$, 2940, 2874, 1743, 1586, 1366, 1211 cm^{-1}; MS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{28}N_2O_{11}$: 545.2, found: 545.3.

***E*-*p*-(*p*-Hydroxyphenylazo)phenyl α-D-mannopyranoside (26):** Protected mannoside **24** (100 mg, 0.184 mmol) was dissolved in dry MeOH (2 mL), and a catalytic amount of NaOMe was added. The reaction mixture stirred at RT overnight and then neutralized with Amberlite IR 120 ion exchange resin. After filtration, the filtrate evaporated under reduced pressure to yield pure **26** as a light orange solid (61 mg, 0.162 mmol, 88%): mp: 206–207 °C; $R_f = 0.18$ (CH_2Cl_2/MeOH, 9:1); $[\alpha]_D^{20} = +1.02$ ($c = 1.0$, MeOH); ^1H NMR (500 MHz, CD_3OD): $\delta = 7.82$ (d, $J = 9.0$ Hz, 2H, H-9, H-11), 7.78 (d, $J=8.9$ Hz, 2H, H-14, H-18), 7.25 (d, $J=9.0$ Hz, 2H, H-8, H-12), 6.90 (d, $J=8.9$ Hz, 2H, H-15, H-17), 5.58 (d, $J_{1,2}=1.8$ Hz, 1H, H-1), 4.04 (dd, $J_{2,3}=3.4$ Hz, $J_{1,2}=1.9$ Hz, 1H, H-2), 3.92 (dd, $J_{2,3}=3.4$ Hz, $J_{3,4}=9.5$, 1H, H-3), 3.79–3.71 (m, 3H, H-4, H-6a, H-6b), 3.60 (ddd, $J_{4,5}=9.8$ Hz, $J_{5,6a}=5.3$ Hz, $J_{5,6b}=2.5$ Hz, 1H, H-5); ^{13}C NMR (125 MHz, CD_3OD): $\delta=161.7$ (C-16), 159.7 (C-7), 149.4 (C-10), 147.5 (C-13), 125.6 (C-15, C-17), 124.9 (C-8, C-12), 117.9 (C-9, C-11), 116.7 (C-14, C-18), 100.2 (C-1), 75.6 (C-5), 72.4 (C-3), 71.9 (C-2), 68.3 (C-4), 62.7 (C-6); IR (ATR): $\tilde{\nu}=3210$, 1586, 1493, 1225 cm^{-1}; $\varepsilon=19804\pm750$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_7$: 377.36, found: 377.17; HRMS: *m/z* $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_7$: 377.1343, found: 377.1339.

***E-p*-[*p*-(α-D-Mannopyranosyloxy)]phenylazophenyl α-D-mannopyranoside (29)**: Protected bis-glycoside **28** (100 mg, 0.114 mmol) was dissolved in dry MeOH (2 mL), and a catalytic amount of NaOMe was added. The reaction mixture was stirred at RT overnight, then neutralized with Amberlite IR 120 ion exchange resin and filtered. The filtrate was evaporated under reduced pressure to yield bivalent glycoside **29** as a yellow solid (57 mg, 0.105 mmol, 93%): mp: 204–206 °C; $R_f=0.21$ (CH_2Cl_2/MeOH, 6:4); $[\alpha]_D^{20}=+1.92$ ($c=0.9$, DMSO); ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta=7.84$ (d, $J=8.9$ Hz, 4H, H-9, H-11, H-14, H-18), 7.26 (d, $J=8.9$ Hz, 4H, H-8, H-12, H-15, H-17), 5.51 (bs, 2H, 2 H-1), 5.09 (d, $J=4.3$ Hz, 2H, 2 OH), 4.86 (d, $J=5.8$ Hz, 2H, 2 OH), 4.79 (d, $J=5.9$ Hz, 2H, 2OH), 4.47 (t, $J=5.9$ Hz, 2H, 2 OH), 3.87 (bs, 2H, 2 H-2), 3.70 (m$_c$, 2H, 2 H-3), 3.60 (dd, $J_{5,6a}=10.1$, $J_{6a,6b}=5.8$ Hz, 2 H-6a), 3.54–3.46 (m, 4H, 2 H-4, 2 H-6b), 3.40–3.36 (m, 2H, 2 H-5); ^{13}C NMR (150 MHz, [D$_6$]DMSO): $\delta=158.6$ (C-7, C-16), 146.9 (C-13, C-10), 124.51 (C-9, C-11, C-14, C-18), 117.1 (C-8, C-12, C-15, C-17), 98.7 (2 C-1), 75.2 (2 C-5), 70.7 (2 C-3), 69.9 (2 C-2), 66.7 (2 C-4), 61.0 (2 C-6); IR (ATR): $\tilde{\nu}=3301$, 2914, 1599, 1583, 1498, 1227 cm^{-1}; $\varepsilon=18810\pm252$ L mol^{-1} cm^{-1}; MS (MALDI-TOF): *m/z* $[M+Na]^+$ calcd for $C_{24}H_{30}N_2O_{12}$: 561.50, found: 561.26; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{30}N_2O_{12}$: 539.1871, found: 539.1860.

***E-p*-(p-Hydroxyphenylazo)phenyl β-D-glucopyranoside (27)**: Protected glycoside **25** (87 mg, 0.16 mmol) was dissolved in dry MeOH (2 mL) and a catalytic amount of NaOMe was added. The reaction mixture was stirred at RT overnight, then neutralized with Amberlite IR 120 ion exchange resin and filtered. The filtrate was evaporated under reduced pressure to yield glycoside **27** as a yellow solid (53 mg, 0.14 mmol, 89%): mp: 186–188 °C; $R_f=0.75$ (EtOAc/MeOH 3:2), $[\alpha]_D^{20}=-3.42$ ($c=0.92$, DMSO); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta=7.79$ (d, $J=8.8$ Hz, 2H, H-9, H-11), 7.75 (d, $J=8.8$ Hz, 2H, H-15, H-17), 7.18 (d, $J=8.9$ Hz, 2H, H-8, H-12), 6.93 (d, $J=8.8$ Hz, 2H, H-14, H-18), 4.99 (d, $J=7.3$ Hz, 1H, H-1), 3.70 (dd, $J=12.1$, 1.9 Hz, 1H, H-6a), 3.48 (dd. $J=5.83$, 12.1 Hz, 1H, H-6b), 3.39 (dt, $J=2.0$, 5.76 Hz, 1H, H-5), 3.30 (t, $J=9.0$ Hz, 1H H-3), 3.27 (t, $J=8.3$ Hz, 1H, H-2), 3.18 (d, $J=7.9$ Hz, 1H, H-4); ^{13}C NMR (150 MHz, [D$_6$]DMSO): $\delta=160.7$ (C-15, C-17), 159.5 (C-7), 147.4 (C-10), 145.7 (C-13), 124.7 (C-15, C-17), 124.0 (C-9, C-11) 117.1 (C-8, C-12), 116.2 (C-14, C-18), 100.4 (C-1), 77.5 (C-5). 76.7 (C-3), 73.5 (C-2), 69.9 (C-4), 61.0 (C-6); IR (ATR): $\tilde{\nu}=3276$, 2882, 1587, 1495, 1231; $\varepsilon=17871\pm788$ L mol^{-1} cm^{-1}; MS (EI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_7$: 377.1, found: 377.1.

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