Synthesis of Triazole-Linked Fluorescent Saccharides and Glycosyl Amino Esters

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Abstract: Synthesis of fluorescent carbohydrates and glycopeptides has been emerging as an attractive research field because of various biological roles of carbohydrates and glycoproteins. Fluorescent glycosides and C-glycosides were synthesized by copper(I)-catalyzed Huisgen reaction between 6-*O*-(2-azidoacetyl) glycopyranosides and alkyne-functionalized fluorophores. For the fluorescent disaccharides as well as glycosyl amino acids derivatives, glycosylation of azido-functionalized thioglycosides, followed by click reaction with corresponding fluorophores is preferred than the inversed procedure (click reaction before the glycosylation). Fluorophores like dansyl, NBD, or rhodamine have been successfully introduced on the sugar ring. All the newly synthesized fluorescent glycosides and glycoconjugates showed similar photophysical properties to the native fluorophores, with a higher quantum yield for the dansyl derivatives.

Key words: fluorescence, saccharides, glycosyl amino acids, copper(I), Huisgen cycloaddition reaction, glycosylation

Oligosaccharides and glycoconjugates play key roles in various biological events, including signal transduction, cell–cell communication, cancer metastasis, as well as bacterial and viral infection.[1] Development of chemical tools is indispensable in order to understand and control the biological functions of carbohydrates. Fluorescent labeling of biomolecules has been proven to be a powerful method to investigate various biological phenomena at molecular level because of the high sensitivity and efficiency of fluorescence spectroscopy.[2] Different aspects of fluorescence output like steady-state intensity, Stokes shift, life-time, steady-state and time-resolved anisotropies, and resonance energy transfer could be used for studying biological structures, dynamics, and functions, and for visualizing intracellular processes or molecular interactions.[3] Consequently, synthesis of fluorescent carbohydrates and glycoconjugates has attracted increasing attention since the last decade. Fluorescent sugar derivatives have been utilized as protein ligands,[4] enzyme substrates or inhibitors,[5] molecular probes for the investigation of cell membrane,[6] glucose uptake,[7] protein glycosylation[8] or for the direct observation of target cells.[9] Fluorophores have been introduced into the sugar moiety through amide/ester formation,[4–7,9,10] reductive amination,[11] Sonogashira coupling,[12] aldol reaction,[13] oxime-based synthesis,[14] as well as the recently developed copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC, also qualified as click reaction).[4,8,15] Although the CuAAC reaction has been used to synthesize the fluorescent sugars, the reactivity of triazole-linked fluorescent glycosyl donors have never been investigated. As a continuing program on the synthesis of carbohydrate conjugates and amino acid derivatives with click chemistry,[16] we were interested in the synthesis of fluorescent sugars and glycopeptides from azido-functionalized sugars as the common starting materiel.

In order to functionalize the sugar ring with a fluorophore and also realize the glycosylation reaction so as to obtain fluorescent oligosaccharides as well as glycosyl amino acids, phenyl thioglycoside has been chosen as the glycosyl donor due to its compatibility with click reaction conditions. Since the 6-hydroxy-free thioglycosides are readily accessible, we decided to introduce the azido function through an ester linkage. From azido-functionalized thioglycosides, the target molecules are accessible either through click reaction with fluorophores followed by glycosylation with different glycosyl acceptors or through glycosylation before introduction of different fluorophores (Scheme 1). As fluorophores, dansyl, rhodamine, and NBD (7-nitrobenz-2-oxa-1,3-diazole) chromophores have been chosen because of their excellent photophysical properties and fluorescence in the visible. Herein we report the investigation of these two synthetic approaches and photophysical properties of synthesized fluorescent sugar derivatives.

Azido group was first introduced into the 6-position of thioglycosides through esterification of phenyl β-D-gluco- and galactopyranosides **1** and **2** with chloroacetyl chloride followed by treatment with sodium azide. The desired azido derivatives **3** and **4** were obtained in excellent yields (Scheme 2). Click reaction of **3** or **4** with NBD alkyne **5**[16h] in the presence of $CuSO_4$/Na ascorbate afforded the NBD-functionalized thioglycosides **6** and **7**, with a better yield for the *gluco* derivative. Similarly, click reaction with dansyl alkyne **8**[16h] furnished the corresponding dansyl sugars **9** and **10**. We have also prepared the rhodamine alkyne **11**[17] by DCC-catalyzed coupling of rhodamine B with propargylamine in 62% yield. Cycloaddition between **3** or **4** with rhodamine alkyne **11** led to **12** and **13**. With the fluorescent thioglycosides in hand, we have then tried to realize the glycosylation reaction so as to investigate the possibility of synthesis of fluorescent glycoconjugates. Glycosylation of **7** with diacetone α-D-galactose using NIS in the presence of TfOH in MeCN[18] led, how-

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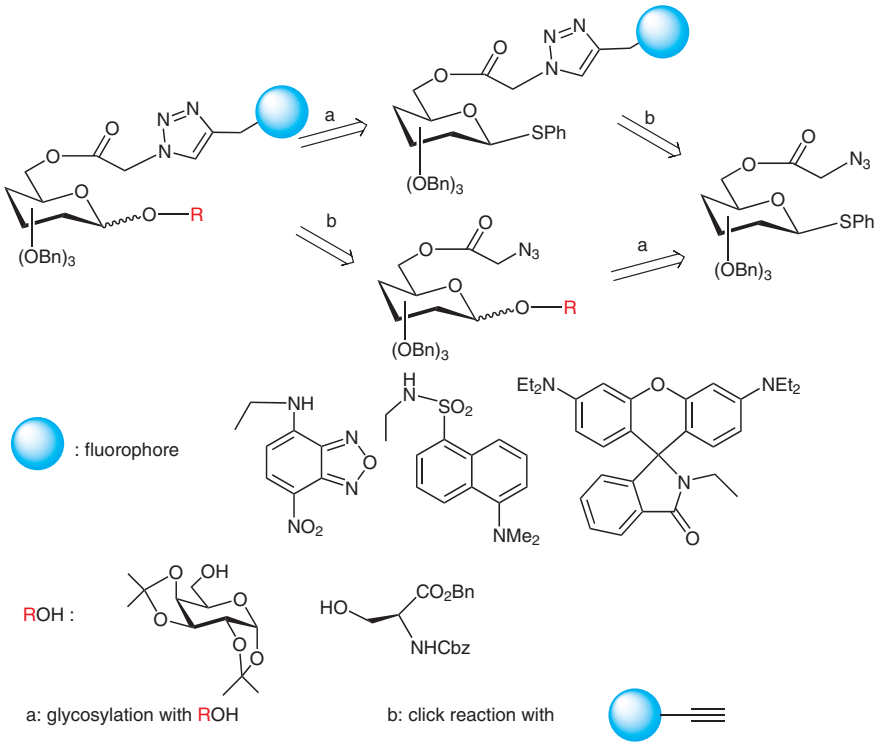


Scheme 1 Retrosynthesis of fluorescent saccharides and glycosyl amino acids derivatives

ever, to a mixture of products, whatever the reaction conditions (quantity of catalyst, temperature, concentration, etc.). Elimination of the NBD fluorophore from the sugar unit has also been observed.

To circumvent the difficulty, it was decided to realize first the glycosylation reaction before introduction of the fluorophore (Scheme 3). Glycosylation of **3** or **4** with diacetone α-D-galactose using NIS in the presence of TfOH in MeCN at –40 °C afforded stereoselectively the corresponding β-disaccharides **14** (α/β = 1:10) and **15** (only β) in excellent yields. Click reaction of **14** or **15** with NBD alkyne **5**, dansyl alkyne **8**, and rhodamine alkyne **11** took place smoothly to afford the corresponding fluorescent disaccharides **16** to **21** in good yields.

We have also tried to prepare fluorescent glycosyl amino acid derivatives (Scheme 4). Glycosylation of thioglucoside **3** with CbzSerOBn by employing NIS/TfOH in MeCN at –40 °C led, however, to compound **22** as a mixture of anomers (α/β = 1:3). A better selectivity was obtained with the *galacto* derivative **23** (α/β = 1:9). Cycloaddition reaction of **22** or **23** with alkynes **8** and **11** afforded the corresponding fluorescent glycosyl amino esters **24** to **27** in good yields.

C-Allyl glycosides have proven to be a very useful synthetic intermediates.[19] Synthesis of fluorescent *C*-allyl glycosides may contribute to the development of various enzymatically stable glycomimetics. The azido-functionalized α-*C*-allyl glucoside **29** was prepared either from the α-*C*-allyl glucoside **28**[19a] (chloroacetylation followed by azidation) or from methyl α-D-glucoside **30** (chloroacety-

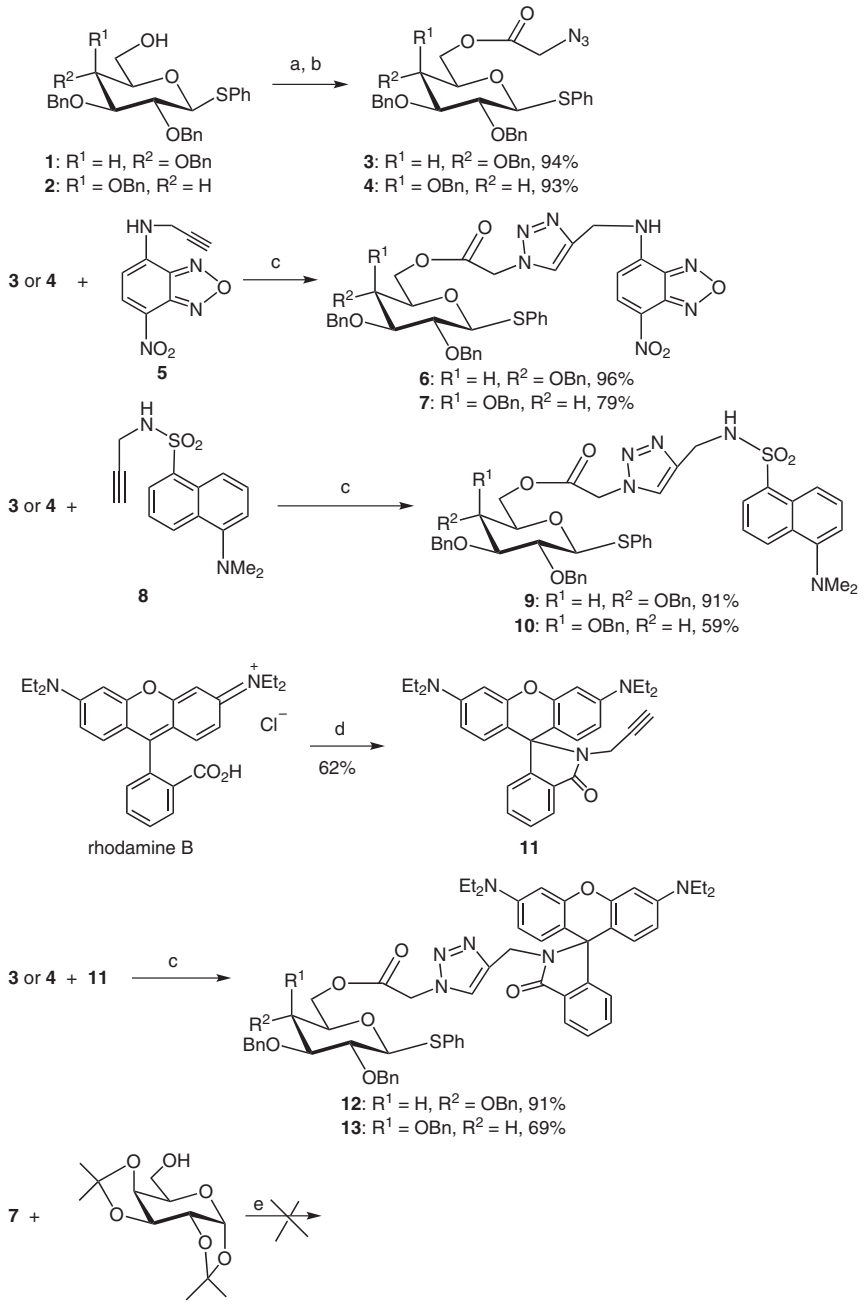
Table 1 Photophysical Properties of Fluorescent Saccharides

	Solvent	λ^{abs} (nm)	λ^{em} (nm)[a]	Δν (cm^{-1})	Φ_F
8	DMSO–H_2O	328	569	12913	0.20[b]
	EtOH	330	532	1506	0.84[b]
9	DMSO–H_2O	341	496	9164	0.30[b]
	EtOH	340	527	10436	0.95[b]
24	DMSO–H_2O	341	495	9124	0.38[b]
	EtOH	338	527	10611	0.98[b]
18	DMSO–H_2O	342	498	9159	0.60[b]
	EtOH	338	529	10682	0.96[b]
5	DMSO–H_2O	466	551	3310	0.01[c]
	EtOH	451	528	3234	0.23[c]
7	DMSO–H_2O	460	566	4071	0.04[c]
	EtOH	454	531	3194	0.16[c]
11	CH_2Cl_2	314	466	10387	0.09[b]
13	CH_2Cl_2	314	427	8428	0.07[b]
21	CH_2Cl_2	315	472	10560	0.06[b]
27	CH_2Cl_2	315	469	10424	0.07[b]

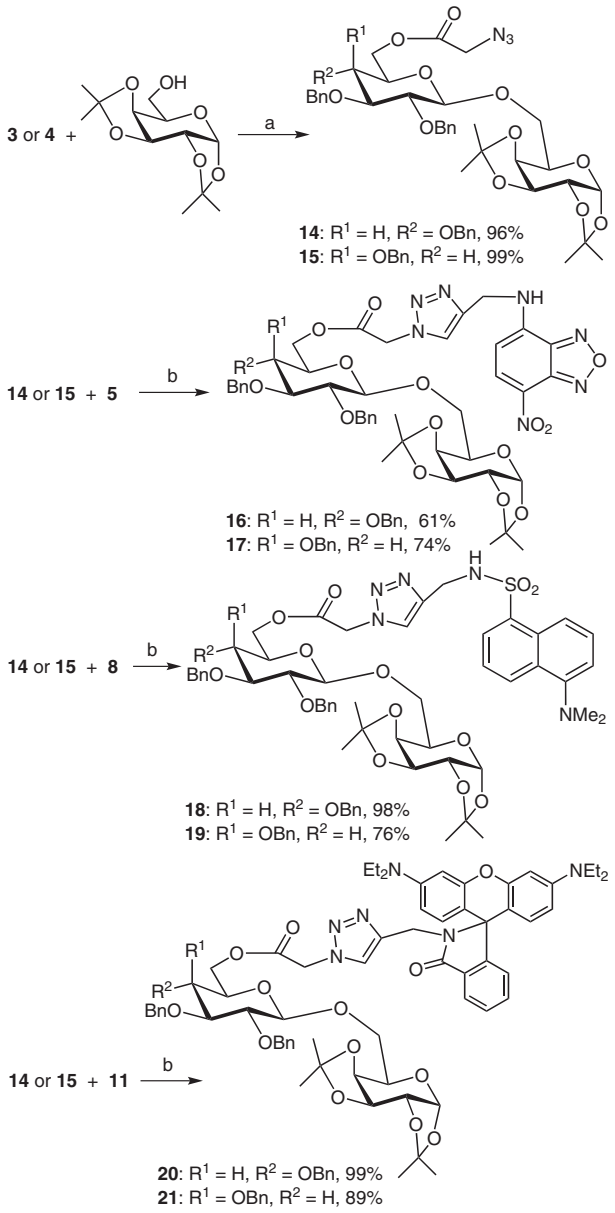
[a] Excitation was set equal to λ^{abs}.
[b] Quantum yields (Φ_F) were determined using as reference a solution of quinine sulfate.
[c] Quantum yields (Φ_F) were determined using as reference a solution of coumarin 153.

lation, azidation then α-C-allylation with TMSAllyl–TMSOTf) (Scheme 5). Subsequent click reaction with **8** or **11** afforded the corresponding glucosides **31** and **32**.

The photophysical properties of synthetic compounds were then investigated in DMSO–water (2:8), ethanol, or CH_2Cl_2. The fluorescence quantum yields were determined by using quinine sulfate for dansyl and rhodamine derivatives, and coumarin 153 for NBD derivatives. As shown in Table 1, spectroscopic properties of the newly synthesized NBD **7** and dansyl **9**, **18**, and **24** glycoconjugates were similar to the native fluorophores **5** and **8**: they exhibited large Stokes shifts and higher quantum yields in ethanol. Their fluorescent emissions were also affected by solvent polarity, with a blue shift for the dansyl alkyne **8** and NBD derivatives **5**, **7**, and a red shift for compounds **9**, **18**, and **24** in ethanol. All three tested dansyl glycoconjugates, which had quantitatively similar absorption and emission spectra, displayed a red shift of about 10 nm in absorption and a higher quantum yield as compared to the native molecule **8**. Only slight difference could be observed in the absorption and emission spectra between NBD derivatives **5** and **7**. Due to the spirolactam structure, the rhodamine derivatives **11**, **13**, **21**, and **27** scarcely showed absorption or emission bands in the visible region. Further photophysical study of these rhodamine derivatives is ongoing in our laboratory.



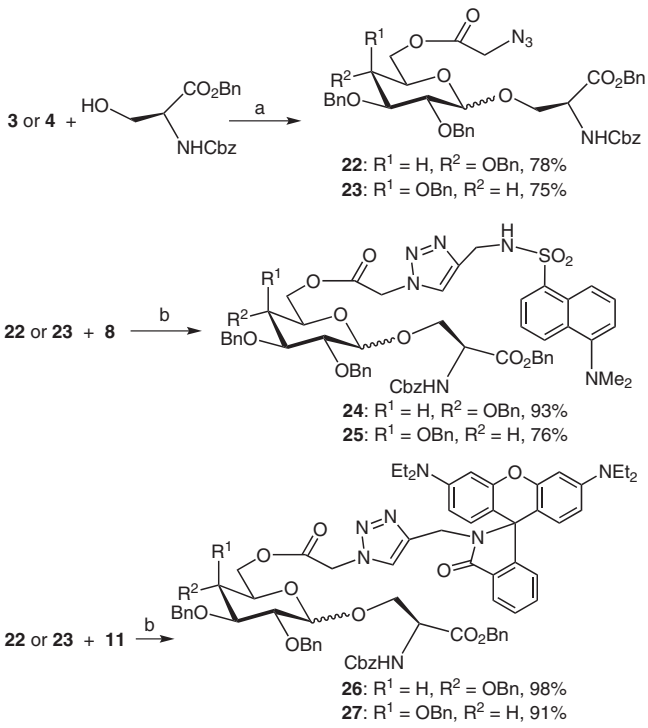
Scheme 2 *Reagents and conditions*: (a) chloroacetyl chloride, Et_3N, CH_2Cl_2; (b) NaN_3, NaI, acetone; (c) Na ascorbate, $CuSO_4$, CH_2Cl_2, H_2O; (d) propargylamine, Et_3N, DCC, HOBt, CH_2Cl_2; (e) NIS, TfOH, 4 Å MS, MeCN.



Scheme 3 *Reagents and conditions*: (a) NIS, TfOH, 4 Å MS, MeCN, –40 °C; (b) Na ascorbate, $CuSO_4$, CH_2Cl_2, H_2O.

In summary, the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition has been successfully used for the synthesis of fluorescent glycosides and C-glycosides by reaction of 6-*O*-(2-azidoacetyl) glycopyranosides with dansyl, NBD, or rhodamine alkynes. For the synthesis of fluorescent disaccharides as well as glycosyl amino esters, it is preferred to realize the glycosylation of 6-*O*-(2-azidoacetyl) thioglycosides first before the introduction of fluorophore with click reaction. All the newly synthesized fluorescent glycosides and glycoconjugates showed similar photophysical properties to the native fluorophores, with a higher quantum yield for dansyl derivatives.

Melting points (Mp) were obtained without correction using a Kofler melting point apparatus. Column chromatography was performed on silica gel 40–63 μm. Analytical TLC was performed on



Scheme 4 *Reagents and conditions*: (a) NIS, TfOH, 4 Å MS, MeCN, –40 °C; (b) Na ascorbate, $CuSO_4$, CH_2Cl_2, H_2O.

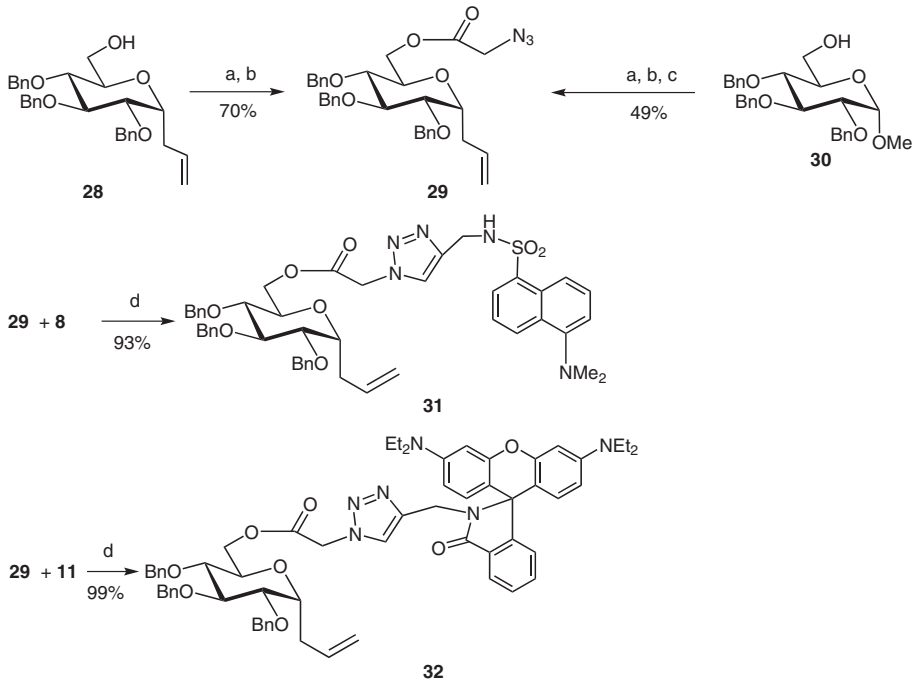
aluminum percolated plates of Silica Gel 60F-254 with detection by UV and by spraying with 10% H_2SO_4 in EtOH solution and heating for about 20 sec at 400 °C. Petroleum ether (PE) used refers to the fraction boiling in the 40–65 °C range. ^1H and ^{13}C NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer. The spectra were taken with TMS as a proton standard reference (0 ppm). For ^{13}C spectra, central peak of the residual solvent multiplets were used as a chemical shift reference ($CDCl_3$: 77.00 ppm). ESI-HRMS mass spectra were recorded on a Bruker micrOTOF-Q II spectrometer. UV/vis absorption spectra were recorded on a Uvikon-940 KONTRON spectrophotometer. The fluorescence quantum yields (Φ_F) were determined by the standard method using a solution of 1.0×10^{-5} M quinine sulfate in 0.5 N H_2SO_4 or coumarin 153 in EtOH as reference. Only diluted and degassed solutions with an absorbance below 0.1 at the excitation wavelength λ_{ex} were used.

6-*O*-Azidoacetyl Glycopyranosides; General Procedure 1 (GP 1)

To a solution of partially protected glycopyranoside (0.3 mmol) and Et_3N (0.63 mmol) in CH_2Cl_2 (10 mL) at 0 °C, was added chloroacetyl chloride (0.6 mmol). The mixture was stirred for 2 h at 0 °C and then the temperature was gradually raised to r.t. and stirred for 12 h. After evaporation, the residue was dissolved in EtOAc (20 mL), and the EtOAc layer was washed with sat. aq $NaHCO_3$ (3 × 10 mL) and brine (3 × 10 mL). The organic layer was dried ($MgSO_4$) and concentrated under vacuum to give a crude product, which was used without purification in the next step. To a solution of crude 6-*O*-chloroacetyl glycopyranoside in acetone (10 mL), was added NaN_3 (1.5 mmol) and KI (10 mg). After stirring for 24 h at r.t., the mixture was evaporated. The residue was dissolved in EtOAc (20 mL), and the EtOAc layer was washed with sat. aq $NaHCO_3$ (3 × 10 mL) and brine (3 × 10 mL). The organic layer was dried ($MgSO_4$) and concentrated under vacuum to give a crude product, which was purified by column chromatography.

Glycosylation; General Procedure 2 (GP 2)

A mixture of thioglycoside (0.5 mmol), glycosyl acceptor (0.55 mmol), NIS (0.6 mmol), and powdered 4 Å molecular sieves (1 g)



Scheme 5 *Reagents and conditions*: (a) chloroacetyl chloride, Et_3N, CH_2Cl_2; (b) NaN_3, NaI, acetone; (c) TMSallyl, TMSOTf, MeCN; (d) Na ascorbate, $CuSO_4$, CH_2Cl_2, H_2O.

in MeCN (10 mL) was stirred for 30 min at –40 °C before the addition of TfOH (0.015 mmol). The mixture was stirred at –40 °C for 2 h and the temperature was then gradually raised to r.t. After the completion of the reaction, Na_2SO_3 (1 g), $NaHCO_3$ (1 g), and a few drops of H_2O were added to the reaction mixture. The mixture was stirred for 5 min, then diluted with CH_2Cl_2 (25 mL), filtered through Celite, and the CH_2Cl_2 layer was washed with sat. aq $NaHCO_3$ (3 × 10 mL) and brine (3 × 10 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuum to give a crude product, which was purified by chromatography.

Click Reaction; General Procedure 3 (GP 3)

To a solution of alkyne (0.05 mmol) and azide (0.05 mmol) in CH_2Cl_2 (5 mL) and H_2O (5 mL), were added $CuSO_4 \cdot 5H_2O$ (0.01 mmol) and Na ascorbate (0.01 mmol) successively. The reaction mixture was vigorously stirred at r.t. for 12 to 20 h. CH_2Cl_2 (10 mL) was then added. After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (2 × 20 mL), dried ($MgSO_4$), evaporated, and the residue purified by column chromatography.

Phenyl 6-*O*-(2-Azido)acetyl-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (3)

Phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**1**; 1.112 g, 2.049 mmol) was treated successively with $ClCH_2COCl$ and NaN_3 according to GP 1. Purification by column chromatography (EtOAc–PE, 1:9) gave 1.210 g (94%) of compound **3** as a white solid; mp 65 °C; $[\alpha]_D^{20}$ +26.8 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.47–3.57 (m, 3 H, H-2,4,5), 3.72 (t, *J* = 8.2 Hz, 1 H, H-3), 3.73 (d, *J* = 17.0 Hz, 1 H), 3.79 (d, *J* = 17.0 Hz, 1 H), 4.27 (dd, *J* = 5.3, 11.9 Hz, 1 H, H-6), 4.43 (dd, *J* = 1.8, 11.9 Hz, 1 H, H-6′), 4.59 (d, *J* = 11.4 Hz, 1 H), 4.65 (d, *J* = 9.6 Hz, 1 H, H-1), 4.74 (d, *J* = 10.1 Hz, 1 H), 4.85 (d, *J* = 11.0 Hz, 1 H), 4.86 (d, *J* = 11.0 Hz, 1 H), 4.91 (d, *J* = 10.1 Hz, 1 H), 4.94 (d, *J* = 11.0 Hz, 1 H), 7.25–7.39 (m, 18 H), 7.51–7.53 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.2, 64.4, 75.1, 75.6, 76.0, 76.6, 77.1, 86.8, 87.6, 127.8, 127.9, 128.3, 128.6, 128.7, 129.0, 132.3, 137.6, 137.9, 138.2, 168.0.

HRMS (ESI): *m*/*z* calcd for $C_{35}H_{35}N_3O_6S$ + Na [M + Na^+]: 648.2144; found: 648.2127.

Phenyl 6-*O*-(2-Azido)acetyl-2,3,4-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (4)

Phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-galactopyranoside (**2**; 1.012 g, 1.867 mmol) was treated successively with $ClCH_2COCl$ and NaN_3 according to GP 1. Purification by column chromatography (EtOAc–PE, 1:9) gave 1.060 g (93%) of compound **4** as a white solid; mp 84 °C; $[\alpha]_D^{20}$ –21.3 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58–3.62 (m, 2 H, H-3,5), 3.66 (d, *J* = 17.0 Hz, 1 H), 3.74 (d, *J* = 17.0 Hz, 1 H), 3.83 (d, *J* = 1.8 Hz, 1 H, H-4), 3.95 (t, *J* = 9.6 Hz, 1 H, H-2), 4.13 (dd, *J* = 5.5, 11.4 Hz, 1 H, H-6), 4.36 (dd, *J* = 6.9, 11.0 Hz, 1 H, H-6′), 4.62 (d, *J* = 9.6 Hz, 1 H, H-1), 4.76 (d, *J* = 11.9 Hz, 1 H), 4.74–4.84 (m, 4 H), 4.99 (d, *J* = 11.9 Hz, 1 H), 7.23–7.40 (m, 18 H), 7.53–7.59 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.2, 64.8, 73.0, 73.4, 74.3, 75.8, 75.9, 77.3, 84.2, 88.0, 127.8, 128.0, 128.4, 128.5, 128.6, 128.7, 128.9, 132.0, 133.9, 138.1, 138.2, 168.0.

HRMS (ESI): *m*/*z* calcd for $C_{35}H_{35}N_3O_6S$ + Na [M + Na^+]: 648.2144; found: 648.2126.

Phenyl 2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(7-nitrobenzo[1,2,5]oxadiazol-4-ylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-1-thio-β-D-glucopyranoside (6)

From 7-nitro-*N*-(prop-2-ynyl)benzo[*c*][1,2,5]oxadiazol-4-amine (**5**; 30 mg, 0.13 mmol) and azidoacetyl thioglucoside **3** (34 mg, 0.054 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 2:8) led to **6** as an orange solid (44 mg, 96%); mp 85 °C; $[\alpha]_D^{20}$ +16.5 (c 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (t, *J* = 10.1 Hz, 1 H, H-2), 3.46 (t, *J* = 9.6 Hz, 1 H, H-4), 3.50–3.53 (m, 1 H, H-5), 3.72 (t, *J* = 8.7 Hz, 1 H, H-3), 4.23 (dd, *J* = 5.5, 11.4 Hz, 1 H, H-6), 4.45 (dd, *J* = 1.8, 11.5 Hz, 1 H, H-6′), 4.53 (d, *J* = 11.0 Hz, 1 H, H-1), 4.65 (d, *J* = 9.6 Hz, 1 H), 4.73–4.95 (m, 7 H), 5.03 (d, *J* = 17.4 Hz, 1 H), 5.12 (d, *J* = 17.4 Hz, 1 H), 6.30 (d, *J* = 8.2 Hz, 1 H, ArH), 6.75 (t, *J* = 5.5 Hz, 1 H, NH), 7.23–7.48 (m, 20 H), 7.64 (s, 1 H), 8.44 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.5, 50.9, 64.9, 75.1, 75.6, 75.9, 76.9, 80.9, 86.7, 87.6, 99.7, 125.5, 127.9, 128.3, 128.3, 128.6, 128.7, 129.0, 132.1, 133.3, 136.1, 138.0, 142.7, 144.4, 165.7.

HRMS (ESI): *m*/*z* calcd for $C_{44}H_{41}N_7O_9S$ + Na [M + Na^+]: 866.2584; found: 866.2562.

Phenyl 2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(7-nitrobenzo[1,2,5]oxadiazol-4-ylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-1-thio-β-D-galactopyranoside (7)

From **5** (36 mg, 0.165 mmol) and azidoacetyl thiogalactoside **4** (102 mg, 0.163 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 5:5 to 7:3) led to **7** as orange pellets (110 mg, 79%); mp 100 °C (dec.); $[\alpha]_D^{20}$ –5.5 (*c* 0.33, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.61–3.65 (m, 2 H, H-3,5), 3.82 (d, *J* = 1.8 Hz, 1 H, H-4), 3.95 (t, *J* = 9.6 Hz, 1 H, H-2), 4.09 (dd, *J* = 4.6, 11.4 Hz, 1 H, H-6), 4.66 (dd, *J* = 7.8, 11.4 Hz, 1 H, H-6′), 4.59 (d, *J* = 11.9 Hz, 1 H), 4.63 (d, *J* = 9.6 Hz, 1 H, H-1), 4.73–4.81 (m, 6 H), 5.00 (d, *J* = 11.4 Hz, 1 H), 5.03 (d, *J* = 17.4 Hz, 1 H), 5.09 (d, *J* = 17.4 Hz, 1 H), 6.30 (d, *J* = 8.7 Hz, 1 H, ArH), 7.03 (m, 1 H, NH), 7.20–7.40 (m, 18 H), 7.51–7.53 (m, 2 H), 7.72 (s, 1 H), 8.41 (d, *J* = 9.7 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.4, 50.8, 60.5, 65.5, 73.3, 73.4, 74.3, 75.7, 75.8, 77.4, 84.1, 87.7, 99.8, 123.9, 124.8, 127.5, 127.8, 128.0, 128.3, 128.4, 128.5, 128.7, 129.0, 133.9, 136.3, 138.0, 138.2, 142.8, 143.3, 143.9, 144.4, 165.9, 171.3.

HRMS (ESI): *m*/*z* calcd for $C_{44}H_{41}N_7O_9S$ + Na [M + Na^+]: 866.2584; found: 866.2581.

Phenyl 2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(5-dimethylaminonaphthalene-1-sulfonylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-1-thio-β-D-glucopyranoside (9)

From 5-(dimethylamino)-*N*-(prop-2-ynyl)naphthalene-1-sulfonamide (**8**; 28 mg, 0.097 mmol) and azidoacetyl thioglucoside **3** (38 mg, 0.06 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 7:3) led to **9** as a red/brown solid (51 mg, 91%); mp 64 °C; $[\alpha]_D^{20}$ +34.4 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 6 H, 2 × CH_3), 3.39 (t, *J* = 8.9 Hz, 1 H, H-4), 3.48–3.53 (m, 2 H, H-2,5), 3.72 (t, *J* = 8.9 Hz, 1 H, H-3), 4.17–4.21 (m, 3 H, H-6, NCH_2), 4.43 (dd, *J* = 2.3, 11.9 Hz, 1 H, H-6′), 4.47 (d, *J* = 11.0 Hz, 1 H), 4.65 (d, *J* = 10.1 Hz, 1 H, H-1), 4.76–4.99 (m, 7 H), 5.38 (t, *J* = 6.0 Hz, 1 H, NH), 7.25–7.51 (m, 24 H), 8.20 (dd, *J* = 0.9, 7.4 Hz, 1 H), 8.25 (d, *J* = 8.7 Hz, 1 H), 8.52 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.9, 45.5, 50.6, 64.8, 75.0, 75.6, 75.9, 76.4, 77.0, 80.9, 86.7, 87.5, 115.4, 118.7, 123.2, 123.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.6, 128.7, 129.1, 129.7, 129.9, 130.7, 132.3, 133.2, 134.5, 137.5, 137.9, 138.1, 144.6, 152.1, 165.7.

HRMS (ESI): *m*/*z* calcd for $C_{50}H_{51}N_5O_8S_2$ + Na [M + Na^+]: 936.3077; found: 936.3075.

Phenyl 2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(5-dimethylaminonaphthalene-1-sulfonylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-1-thio-β-D-galactopyranoside (10)

From **8** (32 mg, 0.111 mmol) and azidoacetyl thiogalactoside **4** (22 mg, 0.054 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 5:5) led to **10** (29 mg, 59%) as a brown solid; mp 72–74 °C (dec.); $[\alpha]_D^{20}$ –12.5 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 6 H, 2 × CH_3), 3.57–3.61 (m, 2 H, H-3,5), 3.80 (d, *J* = 1.8 Hz, 1 H, H-4), 3.93 (t, *J* = 9.6 Hz, 1 H, H-2), 4.08 (dd, *J* = 5.5, 11.5 Hz, 1 H, H-6), 4.16 (d, *J* = 6.4 Hz, 2 H, NCH_2), 4.38 (dd, *J* = 7.4, 11.0 Hz, 1 H, H-6′), 4.58 (d, *J* = 11.4 Hz, 1 H), 4.62 (d, *J* = 9.6 Hz, 1 H, H-1), 4.73–4.81 (m, 4 H), 4.89 (s, 2 H, CH_2), 4.98 (d, *J* = 11.9 Hz, 1 H), 5.68 (t, *J* = 6.0 Hz, 1 H, NH), 7.12–7.56 (m, 24 H), 8.21–8.25 (m, 2 H), 8.51–8.53 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.8, 45.5, 50.6, 60.5, 64.1, 73.1, 73.3, 74.3, 75.6, 75.8, 77.3, 84.0, 87.7, 115.4, 118.8, 123.3, 124.0, 127.5, 127.7, 127.9, 128.3, 128.4, 128.5, 128.6, 128.7, 129.0, 129.7, 131.8, 133.9, 138.1, 138.3, 144.6, 152.1, 165.9.

HRMS (ESI): *m*/*z* calcd for $C_{50}H_{51}N_5O_8S_2$ + Na [M + Na^+]: 936.3077; found: 936.3054.

3′,6′-Bis(diethylamino)-2-(prop-2-ynyl)spiro[isoindoline-1,9′-xanthen]-3-one (11)

To a solution of rhodamine B (196 mg, 0.4 mmol) in CH_2Cl_2 (25 mL) at 0 °C were added Et_3N (0.2 mL, 1.4 mmol), propargylamine (102 μL, 0.402 mmol), DCC (160 mg, 0.8 mmol), and HOBt (80 mg, 0.6 mmol). After stirring 18 h at r.t., the reaction mixture was filtered and the filtrate evaporated. The residue was dissolved in EtOAc (20 mL) and the solution was washed successively with H_2O (10 mL) and brine (10 mL), dried ($MgSO_4$), evaporated, and purified by column chromatography (EtOAc–PE, 1:9 to 1:4) to give 120 mg of **11** (62%) as a pink solid; mp 163 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (t, *J* = 6.9 Hz, 12 H, 4 × CH_3), 1.75 (t, *J* = 2.8 Hz, 1 H, CH≡), 3.24 (q, *J* = 6.9 Hz, 8 H, 4 × CH_2), 3.93 (d, *J* = 2.4 Hz, 2 H, CH_2), 6.26 (dd, *J* = 2.7, 9.2 Hz, 2 H, ArH), 6.37 (d, *J* = 2.3 Hz, 2 H, ArH), 6.45 (d, *J* = 8.7 Hz, 2 H, ArH), 7.07–7.11 (m, 1 H, ArH), 7.40–7.44 (m, 2 H, ArH), 7.89–7.93 (m, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 28.7, 44.5, 64.9, 70.1, 77.5, 97.9, 105.2, 108.1, 123.2, 123.9, 128.1, 129.3, 130.6, 132.8, 149.1, 153.6, 153.9, 167.5.

HRMS (ESI): *m*/*z* calcd for $C_{31}H_{34}N_3O_2$ [M + H^+]: 480.2651; found: 480.2633.

Phenyl 2,3,4-Tri-*O*-benzyl-6-*O*-[2-(4-{[3′,6′-bis(diethylamino)-3-oxospiro(isoindoline-1,9′-xanthene)-2-yl]methyl}-1*H*-1,2,3-triazol-1-yl)]acetyl-1-thio-β-D-glucopyranoside (12)

From **11** (12 mg, 0.025 mmol) and azidoacetyl thioglucoside **3** (13 mg, 0.021 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:9 to 1:4) led to **12** as a pink solid (21 mg, 91%); mp 102–104 °C; $[\alpha]_D^{20}$ +24.5 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, *J* = 6.8 Hz, 12 H, 4 × CH_3), 3.28 (q, *J* = 6.8 Hz, 8 H, 4 × CH_2), 3.55 (t, *J* = 9.2 Hz, 1 H), 3.46–3.51 (m, 2 H), 3.71 (t, *J* = 8.7 Hz, 1 H), 4.17 (dd, *J* = 6.0, 11.9 Hz, 1 H, H-6), 4.39 (dd, *J* = 2.3, 11.9 Hz, 1 H, H-6′), 4.49 (s, 2 H, NCH_2), 4.51 (d, *J* = 11.0 Hz, 1 H, C*H*Ph), 4.65 (d, *J* = 9.6 Hz, 1 H, H-1), 4.73–4.85 (m, 5 H), 4.91–4.94 (m, 2 H, CH_2), 6.13 (dd, *J* = 2.7, 8.7 Hz, 2 H), 6.29 (d, *J* = 8.7 Hz, 2 H, ArH), 6.34 (d, *J* = 2.8 Hz, 2 H, ArH), 7.09–7.51 (m, 24 H, ArH), 7.91–7.93 (m, 1 H, CH=).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 35.3, 44.4, 50.2, 64.7, 65.1, 75.0, 75.6, 75.9, 76.5, 77.3, 80.9, 86.7, 87.6, 97.9, 105.3, 108.0, 123.0, 123.9, 124.0, 127.9, 128.2, 128.3, 128.5, 128.6, 128.7, 128.9, 129.1, 131.0, 132.2, 132.6, 133.4, 137.5, 137.9, 138.2, 145.0, 148.8, 153.5, 153.7, 165.9, 168.0.

HRMS (ESI): *m*/*z* calcd for $C_{66}H_{68}N_6O_8S$ + Na [M + Na^+]: 1127.4717; found: 1127.4649.

Phenyl 2,3,4-Tri-*O*-benzyl-6-*O*-[2-(4-{[3′,6′-bis(diethylamino)-3-oxospiro(isoindoline-1,9′-xanthene)-2-yl]methyl}-1*H*-1,2,3-triazol-1-yl)]acetyl-1-thio-β-D-galactopyranoside (13)

From **11** (20 mg, 0.042 mmol) and azidoacetyl thiogalactoside **4** (31 mg, 0.050 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:9 to 1:4) led to **13** as a pink solid (32 mg, 69%); mp 103 °C (dec.); $[\alpha]_D^{20}$ +3.0 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 6.9 Hz, 12 H, 4 × CH_3), 3.29 (q, *J* = 6.9 Hz, 8 H, 4 × CH_2), 3.55 (t, *J* = 6.0 Hz, 1 H, H-5), 3.60 (dd, *J* = 2.7, 9.2 Hz, 1 H, H-3), 3.77 (m, 1 H, H-4), 3.93 (t, *J* = 9.6 Hz, 1 H, H-2), 4.06 (dd, *J* = 5.5, 11.4 Hz, 1 H, H-6), 4.34 (dd, *J* = 6.7, 11.0 Hz, 1 H, H-6′), 4.46 (s, 2 H, NCH_2), 4.57 (d, *J* = 11.9

Hz, 1 H, C*H*Ph), 4.62 (d, *J* = 9.6 Hz, 1 H, H-1), 4.71– 4.82 (m, 6 H, NCH_2, 2 × OCH_2), 4.98 (d, *J* = 11.4 Hz, 1 H, C*H*Ph), 6.13–6.16 (m, 2 H, ArH), 6.28–6.34 (m, 4 H, ArH), 7.07–7.54 (m, 24 H, ArH), 7.91–7.94 (m, 1 H, CH=).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 35.4, 44.5, 50.2, 64.9, 65.2, 73.1, 73.3, 74.3, 75.6, 75.8, 77.3, 84.1, 87.7, 97.9, 105.2, 108.1, 123.0, 123.9, 124.0, 127.8, 127.9, 128.2, 128.4, 128.5, 128.6, 128.9, 130.9, 131.8, 132.7, 133.8, 138.0, 138.2, 145.0, 148.8, 153.5, 153.6, 165.8, 168.0.

HRMS (ESI): *m*/*z* calcd for $C_{66}H_{68}N_6O_8S$ + Na [M + Na^+]: 1127.4717; found: 1127.4714.

6-*O*-(2-Azido)acetyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (14)

Compound **3** (375 mg, 0.6 mmol) was treated with diacetone α-D-galactose (178 mg, 0.68 mmol) according to GP 2. Purification by chromatography (EtOAc–PE, 1:4) gave 446 mg (96%) of **14** (β/α = 10:1) as a colorless oil; $[\alpha]_D^{20}$ –10.5 (*c* 1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31, 1.32, 1.45, 1.49 (4 s, 12 H, 4 × CH_3), 3.48 (t, *J* = 8.5 Hz, 1 H, H-2′), 3.49–3.50 (m, 2 H), 3.65–3.75 (m, 2 H), 3.73 (d, *J* = 17.4 Hz, 1 H), 3.83 (d, *J* = 17.4 Hz, 1 H), 4.07–4.12 (m, 2 H), 4.22 (dd, *J* = 1.4, 8.2 Hz, 1 H), 4.30 (dd, *J* = 4.6, 8.7 Hz, 1 H), 4.32 (dd, *J* = 2.3, 5.0 Hz, 1 H), 4.41–4.44 (m, 1 H), 4.48 (d, *J* = 8.0 Hz, 1 H, H-1′), 4.56 (d, *J* = 11.4 Hz, 1 H), 4.60 (dd, *J* = 2.2, 7.8 Hz, 1 H), 4.72 (d, *J* = 11.4 Hz, 1 H), 4.79 (d, *J* = 10.5 Hz, 1 H), 4.86 (d, *J* = 11.0 Hz, 1 H), 5.00 (d, *J* = 11.0 Hz, 1 H), 5.06 (d, *J* = 11.4 Hz, 1 H), 5.57 (d, *J* = 5.0 Hz, 1 H, H-1), 7.24–7.44 (m, 15 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 25.1, 26.1, 50.1, 64.3, 67.4, 70.1, 70.5, 70.9, 71.5, 72.6, 74.5, 74.9, 75.8, 76.8, 81.5, 84.6, 96.5, 104.5, 108.7, 109.5, 127.7, 127.8, 128.0, 128.2, 128.4, 128.5, 128.6, 128.7, 137.8, 138.5, 138.6, 168.6.

HRMS (ESI): *m*/*z* calcd for $C_{41}H_{49}N_3O_{12}$ + Na [M + Na^+]: 798.3214; found: 798.3203.

6-*O*-(2-Azido)acetyl-2,3,4-tri-*O*-benzyl-β-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (15)

Compound **4** (400 mg, 0.639 mmol) was treated with diacetone α-D-galactose (189 mg, 0.726 mmol) according to GP 2. Purification by chromatography (EtOAc–PE, 1:9–1:4) gave 490 mg (99%) of **15** as a white solid; mp 80 °C; $[\alpha]_D^{20}$ –58.4 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30, 1.31, 1.44, 1.48 (4 s, 12 H, 4 × CH_3), 3.51–3.53 (m, 2 H, H-3, 3′), 3.62–3.74 (m, 4 H), 3.85 (dd, *J* = 7.8, 9.6 Hz, 1 H, H-2′), 4.06–4.13 (m, 3 H), 4.21 (dd, *J* = 1.8, 7.8 Hz, 1 H), 4.26 (dd, *J* = 6.4, 11.0 Hz, 1 H), 4.30 (dd, *J* = 2.3, 5.0 Hz, 1 H, H-2), 4.41 (d, *J* = 7.4 Hz, 1 H, H-1′), 4.58 (dd, *J* = 2.3, 7.8 Hz, 1 H), 4.65 (d, *J* = 11.9 Hz, 1 H), 4.73 (d, *J* = 11.0 Hz, 1 H), 4.74 (d, *J* = 11.9 Hz, 1 H), 4.85 (d, *J* = 11.9 Hz, 1 H), 4.94 (d, *J* = 11.9 Hz, 1 H), 5.05 (d, *J* = 11.9 Hz, 1 H), 5.55 (d, *J* = 5.0 Hz, 1 H, H-1), 7.25–7.46 (m, 15 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 25.1, 26.1, 50.1, 64.2, 67.5, 69.8, 70.6, 70.9, 71.5, 71.8, 72.6, 73.7, 74.2, 74.9, 79.0, 81.9, 96.5, 104.7, 108.7, 109.4, 127.5, 127.6, 127.7, 127.9, 128.2, 128.4, 128.5, 128.7, 128.9, 138.2, 138.5, 139.0, 167.9.

HRMS (ESI): *m*/*z* calcd for $C_{41}H_{49}N_3O_{12}$ + Na [M + Na^+]: 798.3214; found: 798.3200.

2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(7-nitrobenzo[1,2,5]oxadiazol-4-yl-amino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (16)

From NBD alkyne **5** (29 mg, 0.132 mmol) and azidoacetyl disaccharide **14** (107 mg, 0.138 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 3:7) led to **16** as an orange powder (80 mg, 61%); mp 98 °C; $[\alpha]_D^{20}$ –39.1 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 6 H, CH_3), 1.43 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 3.36–3.42 (m, 2 H), 3.46–3.52 (m, 1 H), 3.66 (t, *J* = 9.0 Hz, 1 H), 3.71 (dd, *J* = 8.5, 10.1 Hz, 1 H), 4.05–4.09 (m, 2 H), 4.20–4.24 (m, 2 H), 4.32 (dd, *J* = 2.3, 7.4 Hz, 1 H, H-2), 4.43–4.50 (m, 3 H), 4.58 (dd, *J* = 2.3, 7.8 Hz, 1 H, CH), 4.71 (d, *J* = 11.4 Hz, 1 H), 4.76 (d, *J* = 11.0 Hz, 1 H), 4.78–4.79 (m, 2 H), 4.81 (d, *J* = 11.4 Hz, 1 H), 4.97 (d, *J* = 11.0 Hz, 1 H), 5.03 (d, *J* = 11.0 Hz, 1 H), 5.08 (d, *J* = 17.4 Hz, 2 H, 2 × CH), 5.16 (d, *J* = 17.4 Hz, 2 H, 2 × CH), 5.56 (d, *J* = 5.0 Hz, 1 H, H-1), 6.31 (d, *J* = 8.7 Hz, 1 H), 7.18–7.41 (m, 15 H), 7.76 (s, 1 H), 8.39 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 25.0, 26.08, 26.13, 39.4, 50.9, 64.9, 67.2, 69.8, 70.5, 70.8, 71.4, 72.4, 74.4, 74.8, 75.8, 76.7, 77.4, 81.4, 84.5, 96.4, 99.8, 104.3, 108.7, 109.5, 123.9, 124.6, 127.6, 127.6, 127.8, 128.0, 128.3, 128.5, 128.6, 128.8, 136.4, 137.7, 138.4, 138.5, 142.9, 143.4, 143.9, 144.3, 166.0.

HRMS (ESI): *m*/*z* calcd for $C_{50}H_{56}N_7O_{15}$ [M + H^+]: 994.3834; found: 994.3822.

2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(7-nitrobenzo[1,2,5]oxadiazol-4-yl-amino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-β-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (17)

From NBD alkyne **5** (27 mg, 0.126 mmol) and azidoacetyl disaccharide **15** (97 mg, 0.126 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 3:7) led to **17** as an orange powder (92 mg, 74%); mp 66 °C (dec.); $[\alpha]_D^{20}$ +6.7 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 3.50–3.53 (m, 2 H, H-3′, H-4), 3.67 (dd, *J* = 6.9, 10.1 Hz, 1 H, H-6′), 3.72 (m, 1 H, H-5), 3.83 (dd, *J* = 7.8, 9.6 Hz, 1 H, H-2′), 4.03–4.12 (m, 3 H, H-3, H-5′, H-6), 4.21 (dd, *J* = 1.6, 8.0 Hz, 1 H, CH), 4.31 (m, 2 H, H-2, H-4′), 4.40 (d, *J* = 7.8 Hz, 1 H, H-1′), 4.57 (dd, *J* = 2.3, 7.8 Hz, 1 H, CH), 4.60 (d, *J* = 12.7 Hz, 1 H, CH), 4.72 (d, *J* = 11.0 Hz, 1 H, CH), 4.74 (d, *J* = 11.9 Hz, 1 H, CH), 4.80 (d, *J* = 5.5 Hz, 2 H, CH_2NH), 4.85 (d, *J* = 11.7 Hz, 1 H, CH), 4.94 (d, *J* = 11.9 Hz, 1 H, CH), 5.00–5.11 (m, 3 H), 5.55 (d, *J* = 5.0 Hz, 1 H, H-1), 6.31 (d, *J* = 8.7 Hz, 1 H), 7.13 (t, *J* = 5.5 Hz, 1 H, NH), 7.24–7.43 (m, 15 H), 7.76 (s, 1 H), 8.40 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 25.1, 26.1, 39.4, 50.8, 65.2, 67.3, 69.5, 70.6, 70.8, 71.4, 71.8, 72.8, 73.7, 74.2, 74.9, 77.3, 78.9, 81.8, 96.4, 99.8, 104.5, 108.8, 109.5, 123.9, 124.7, 127.6, 127.7, 127.8, 128.0, 128.3, 128.5, 128.58, 128.55, 128.8, 136.4, 138.1, 138.4, 138.8, 142.8, 143.3, 143.9, 144.3, 165.9.

HRMS (ESI): *m*/*z* calcd for $C_{50}H_{56}N_7O_{15}$ [M + H^+]: 994.3834; found: 994.3816.

2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(5-dimethylaminonaphthalene-1-sulfonylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (18)

From dansyl alkyne **8** (19 mg, 0.066 mmol) and azidoacetyl disaccharide **14** (52 mg, 0.067 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 5:5) led to **18** as a beige powder (69 mg, 98%); mp 94 °C (dec.); $[\alpha]_D^{20}$ –3.97 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30, 1.31, 1.44, 1.48 (4 s, 12 H, 4 × CH_3), 2.87 (s, 6 H, 2 × NCH_3), 3.37–3.48 (m, 3 H), 3.63–3.73 (m, 2 H), 4.06–4.19 (m, 5 H), 4.24 (dd, *J* = 1.4, 7.8 Hz, 1 H), 4.31 (dd, *J* = 2.3, 5.0 Hz, 1 H), 4.40–4.45 (m, 2 H), 4.46 (d, *J* = 7.8 Hz, 1 H, H-1′), 4.59 (dd, *J* = 2.3, 7.8 Hz, 1 H), 4.72 (d, *J* = 11.0 Hz, 1 H), 4.76 (d, *J* = 11.0 Hz, 1 H), 4.79 (d, *J* = 10.5 Hz, 1 H), 4.88 (d, *J* = 17.4 Hz, 1 H), 4.97–5.07 (m, 3 H), 5.52 (t, *J* = 6.0 Hz, 1 H, NH), 5.56 (d, *J* = 5.0 Hz, 1 H, H-1), 7.12–7.55 (m, 19 H), 8.21 (dd, *J* = 1.4, 7.4 Hz, 1 H), 8.25 (d, *J* = 8.7 Hz, 1 H), 8.52 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 25.1, 26.1, 38.9, 45.5, 50.6, 64.7, 67.3, 69.9, 70.5, 70.8, 71.4, 72.4, 74.4, 74.8, 75.8, 76.8, 81.5, 84.5, 96.4, 104.4, 108.7, 109.5, 115.4, 118.8, 123.3, 123.8, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.5, 128.6, 128.7, 129.7, 130.0, 130.7, 134.6, 137.7, 138.4, 138.6, 144.6, 152.1, 165.8.

HRMS (ESI): *m*/*z* calcd for $C_{56}H_{65}N_5O_{14}S$ + Na [M + Na^+]: 1086.4146; found: 1086.4157.

2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(5-dimethylaminonaphthalene-1-sulfonylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-β-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (19)

From dansyl alkyne **8** (26 mg, 0.090 mmol) and azidoacetyl disaccharide **15** (62 mg, 0.080 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 5:5) led to **19** (65 mg, 76%) as a yellow/brown solid; mp 90 °C; $[\alpha]_D^{20}$ –98.2 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30, 1.43, 1.48 (3 s, 12 H, 4 × CH_3), 2.87 (s, 6 H, 2 × NCH_3), 3.48–3.52 (m, 2 H, H-3,3′), 3.67 (dd, *J* = 6.9, 9.6 Hz, 1 H), 3.70 (d, *J* = 2.3 Hz, 1 H), 3.83 (dd, *J* = 7.4, 9.6 Hz, 1 H, H-2′), 4.05–4.13 (m, 3 H), 4.18 (d, *J* = 6.4 Hz, 2 H), 4.21 (dd, *J* = 1.4, 7.8 Hz, 1 H), 4.27 (dd, *J* = 6.9, 11.0 Hz, 1 H), 4.30 (dd, *J* = 2.3, 4.6 Hz, 1 H), 4.40 (d, *J* = 7.8 Hz, 1 H, H-1′), 4.57–4.58 (m, 1 H), 4.60 (d, *J* = 11.9 Hz, 1 H), 4.72 (d, *J* = 11.0 Hz, 1 H), 4.73 (d, *J* = 11.9 Hz, 1 H), 4.83 (d, *J* = 11.9 Hz, 1 H), 4.87 (d, *J* = 6.9 Hz, 2 H, CH_2), 4.93 (d, *J* = 11.9 Hz, 1 H), 5.05 (d, *J* = 11.0 Hz, 1 H), 5.55 (d, *J* = 4.6 Hz, 1 H, H-1), 5.56–5.63 (m, 1 H, NH), 7.16 (d, *J* = 7.3 Hz, 1 H), 7.25–7.53 (m, 18 H), 8.23–8.26 (m, 2 H), 8.52 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 25.1, 26.1, 38.8, 45.5, 50.5, 64.8, 67.4, 69.7, 70.6, 70.8, 71.5, 71.7, 72.7, 73.7, 74.2, 74.9, 79.0, 81.8, 96.5, 104.6, 108.7, 109.5, 115.4, 118.8, 123.3, 123.9, 127.5, 127.6, 127.7, 128.0, 128.2, 128.4, 128.5, 128.6, 128.7, 128.8, 129.6, 129.7, 130.0, 130.7, 134.6, 138.2, 138.5, 139.0, 144.6, 152.1, 165.8.

HRMS (ESI): *m*/*z* calcd for $C_{56}H_{65}N_5O_{14}S$ + Na [M + Na^+]: 1086.4146; found: 1086.4135.

2,3,4-Tri-*O*-benzyl-6-*O*-[2-(4-{[3′,6′-bis(diethylamino)-3-oxospiro(isoindoline-1,9′-xanthene)-2-yl]methyl}-1*H*-1,2,3-triazol-1-yl)]acetyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (20)

From rhodamine alkyne **11** (53 mg, 0.110 mmol) and azidoacetyl disaccharide **14** (85 mg, 0.110 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 5:5) led to **20** (137 mg, 99%) as a red solid; mp 88 °C; $[\alpha]_D^{20}$ –7.5 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 6.9 Hz, 12 H, 4 × CH_3), 1.30, 1.31, 1.43, 1.48 (4 s, 12 H, 4 × CH_3), 3.28 (q, *J* = 6.9 Hz, 8 H, 4 × CH_2), 3.38–3.42 (m, 3 H), 3.64 (t, *J* = 9.2 Hz, 1 H, H-3′), 3.68–3.73 (m, 1 H), 4.05–4.13 (m, 2 H), 4.16 (dd, *J* = 5.0, 11.9 Hz, 1 H), 4.23 (dd, *J* = 1.4, 7.8 Hz, 1 H), 4.31 (dd, *J* = 2.8, 5.0 Hz, 1 H, H-2), 4.37 (dd, *J* = 1.8, 11.4 Hz, 1 H), 4.44 (d, *J* = 7.8 Hz, 1 H, H-1′), 4.47–4.49 (m, 3 H), 4.59 (dd, *J* = 2.3, 7.8 Hz, 1 H), 4.70 (d, *J* = 11.0 Hz, 1 H), 4.75 (d, *J* = 11.0 Hz, 1 H), 4.80–4.87 (m, 3 H), 4.97 (d, *J* = 10.6 Hz, 1 H), 5.04 (d, *J* = 11.0 Hz, 1 H), 5.55 (d, *J* = 4.4 Hz, 1 H, H-1), 6.14–6.15 (m, 2 H), 6.27–6.33 (m, 4 H), 7.08–7.43 (m, 19 H), 7.90–7.91 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 24.5, 25.1, 26.1, 31.0, 35.3, 44.4, 50.1, 64.6, 65.1, 67.4, 70.5, 70.8, 71.5, 72.5, 74.4, 74.9, 75.7, 81.4, 84.5, 96.4, 97.9, 104.4, 105.3, 108.0, 108.6, 109.5, 122.9, 123.9, 124.1, 127.6, 127.7, 128.0, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 132.6, 137.7, 138.5, 138.6, 144.9, 148.8, 153.4, 166.0, 168.0.

HRMS (ESI): *m*/*z* calcd for $C_{72}H_{82}N_6O_{14}S$ + Na [M + Na^+]: 1277.5787; found: 1277.5562.

2,3,4-Tri-*O*-benzyl-6-*O*-[2-(4-{[(3′,6′-bis(diethylamino)-3-oxospiro(isoindoline-1,9′-xanthene)-2-yl)methyl]-1*H*-1,2,3-triazol-1-yl)]acetyl-β-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (21)

From rhodamine alkyne **11** (28 mg, 0.058 mmol) and azidoacetyl disaccharide **15** (42 mg, 0.054 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 5:5) led to **21** as a pink solid (60 mg, 89%); mp 113 °C (dec.); $[\alpha]_D^{20}$ –5.68 (*c* 0.62, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (t, *J* = 6.9 Hz, 12 H, 4 × CH_3), 1.30, 1.41, 1.43, 1.48 (4 s, 12 H, 4 × CH_3), 3.29 (q, *J* = 6.9 Hz, 8 H, 4 × CH_2), 3.37 (t, *J* = 6.4 Hz, 1 H), 3.50 (dd, *J* = 2.8, 9.6 Hz, 1 H, H-3′), 3.64–3.68 (m, 2 H), 3.83 (dd, *J* = 7.8, 9.6 Hz, 1 H, H-2′), 4.02–4.13 (m, 3 H), 4.20–4.24 (m, 2 H), 4.30 (dd, *J* = 2.3, 4.6 Hz, 1 H, H-2), 4.40 (d, *J* = 7.8 Hz, 1 H, H-1′), 4.47 (s, 2 H, OCH_2), 4.58 (dd, *J* = 2.3, 5.5 Hz, 1 H), 4.59 (d, *J* = 11.9 Hz, 1 H, C*H*Ph), 4.71–4.76 (m, 4 H), 4.85 (d, *J* = 11.9 Hz, 1 H, C*H*Ph), 4.92 (d, *J* = 11.9 Hz, 1 H, C*H*Ph), 5.06 (d, *J* = 11.0 Hz, 1 H, C*H*Ph), 5.55 (d, *J* = 5.0 Hz, 1 H, H-1), 6.13–6.15 (m, 2 H), 6.29 (dd, *J* = 3.2, 8.7 Hz, 2 H, ArH), 6.33–6.35 (m, 2 H), 7.07–7.09 (m, 1 H, ArH), 7.25–7.44 (m, 18 H, ArH), 7.90–7.93 (m, 1 H, CH=).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 24.5, 25.1, 26.1, 27.0, 35.4, 44.4, 50.2, 64.5, 65.1, 67.5, 70.9, 71.5, 73.7, 74.2, 74.9, 78.9, 81.8, 87.5, 96.5, 97.9, 104.7, 105.1, 108.0, 108.7, 109.4, 123.0, 123.9, 124.0, 128.1, 128.2, 128.5, 128.7, 128.8, 130.9, 132.7, 138.0, 138.6, 139.0, 145.0, 148.8, 153.4, 153.8, 165.6.

HRMS (ESI): *m*/*z* calcd for $C_{72}H_{82}N_6O_{14}S$ + Na [M + Na^+]: 1277.5787; found: 1277.5680.

O-[2,3,4-Tri-*O*-benzyl-6-*O*-(2-azido)acetyl-D-glucopyranosyl]-*N*-benzyloxycarbonyl-L-serine Benzyl Ester (22)

Compound **3** (314 mg, 0.502 mmol) was treated with *N*-Z-L-Ser-OBn (176 mg, 0.534 mmol) according to GP 2. Purification by chromatography (EtOAc–PE, 1:9 to 3:7) gave 330 mg (78%) of **22** as a mixture of β/α (3:1) anomers; white solid.

β-Anomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30–3.46 (m, 4 H), 3.60–3.88 (m, 4 H), 4.18–4.40 (m, 3 H), 4.34 (d, *J* = 7.8 Hz, 1 H, H-1), 4.53–4.97 (m, 6 H), 5.08–5.20 (m, 4 H), 5.66–5.68 (d, *J* = 8.2 Hz, 1 H, NH), 7.20–7.33 (m, 25 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.0, 54.5, 64.1, 67.1, 67.4, 67.7, 72.6, 74.9, 75.0, 75.7, 76.7, 76.8, 81.8, 84.5, 103.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 135.3, 136.2, 137.6, 138.0, 138.3, 156.0, 168.1, 169.8.

HRMS (ESI): *m*/*z* calcd for $C_{47}H_{48}N_4O_{11}$ + Na [M + Na^+]: 867.3217; found: 867.3206.

O-[2,3,4-Tri-*O*-benzyl-6-*O*-(2-azido)acetyl-D-galactopyranosyl]-*N*-benzyloxycarbonyl-L-serine Benzyl Ester (23)

Compound **4** (202 mg, 0.323 mmol) was treated with *N*-Z-L-Ser-OBn (112 mg, 0.340 mmol) according to GP 2. Purification by chromatography (EtOAc–PE, 1:9 to 1:3) gave 204 mg (75%) of **23** (β/α = 9:1) as a beige solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48–3.53 (m, 2 H), 3.70 (s, 2 H, CH_2), 3.77–3.82 (m, 2 H), 3.83 (dd, *J* = 2.3, 10.6 Hz, 1 H), 4.13 (dd, *J* = 6.0, 11.0 Hz, 1 H), 4.24–4.29 (m, 1 H), 4.30 (d, *J* = 7.8 Hz, 1 H), 4.38 (dd, *J* = 2.3, 10.1 Hz, 1 H), 4.57–4.59 (m, 1 H), 4.65 (d, *J* = 11.5 Hz, 1 H), 4.70 (d, *J* = 11.0 Hz, 1 H), 4.76 (d, *J* = 11.4 Hz, 2 H), 4.82 (d, *J* = 11.9 Hz, 1 H), 4.99 (d, *J* = 11.5 Hz, 1 H), 5.06 (d, *J* = 12.3 Hz, 1 H), 5.10 (d, *J* = 12.3 Hz, 1 H), 5.19 (d, *J* = 12.4 Hz, 1 H), 5.23 (d, *J* = 12.4 Hz, 1 H), 5.77 (d, *J* = 7.8 Hz, 1 H, NH), 7.18–7.40 (m, 25 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.1, 54.6, 64.3, 67.1, 67.5, 70.0, 72.1, 72.9, 73.6, 74.5, 75.5, 75.9, 79.0, 82.0, 104.3, 127.7, 127.9, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 135.4, 136.4, 138.1, 138.2, 138.3, 156.1, 168.0, 169.8.

HRMS (ESI): *m*/*z* calcd for $C_{47}H_{48}N_4O_{11}$ + Na [M + Na^+]: 867.3217; found: 867.3211.

***O*-{2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(5-dimethylaminonaphthalene-1-sulfonylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-D-glucopyranosyl}-*N*-benzyloxycarbonyl-L-serine Benzyl Ester (24)**

From dansyl alkyne **8** (15 mg, 0.052 mmol) and azidoacetyl glucosyl amino ester **22** (44 mg, 0.052 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 5:5) led to **24** (β/α = 3:1) as a beige solid (55 mg, 93%).

β-Anomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (s, 6 H, 2 × CH_3), 3.30–3.36 (m, 3 H), 3.59 (t, *J* = 9.2 Hz, 1 H), 3.88 (dd, *J* = 3.6, 10.5 Hz, 1 H), 4.08–4.18 (m, 4 H), 4.31 (d, *J* = 7.8 Hz, 1 H, H-1), 4.35–4.38 (m, 1 H), 4.45–4.48 (m, 1 H), 4.56–4.67 (m, 2 H), 4.75–4.94 (m, 6 H), 5.07–5.18 (m, 4 H), 5.67–5.69 (m, 1 H, NH), 5.79 (d, *J* = 7.8 Hz, 1 H, NH), 7.15–7.55 (m, 29 H), 8.21 (dd, *J* = 0.9, 7.3 Hz, 1 H), 8.27 (d, *J* = 8.3 Hz, 1 H), 8.52 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.9, 45.5, 50.6, 54.7, 60.5, 64.6, 67.2, 67.6, 69.6, 72.5, 74.9, 75.0, 75.8, 77.3, 81.8, 84.4, 103.6, 115.4, 118.9, 123.3, 123.9, 127.8, 127.9, 128.0, 128.1, 128.2, 128.5, 128.6, 128.7, 129.7, 130.7, 134.6, 135.3, 136.2, 137.6, 138.1, 138.2, 144.7, 152.0, 156.1, 165.8, 170.0.

HRMS (ESI): *m*/*z* calcd for $C_{62}H_{64}N_6O_{13}S$ + Na [M + Na$^+$]: 1155.4150; found: 1155.4149.

***O*-{2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(5-dimethylaminonaphthalene-1-sulfonylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-D-galactopyranosyl}-*N*-benzyloxycarbonyl-L-serine Benzyl Ester (25)**

From dansyl alkyne **8** (14 mg, 0.048 mmol) and azidoacetyl glucosyl amino ester **23** (43 mg, 0.051 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 5:5) led to **25** (44 mg, 76%) (β/α = 9:1) as a beige solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (s, 6 H, 2 × CH_3), 3.42–3.50 (m, 2 H), 3.67 (s, 2 H, CH_2), 3.72–3.78 (m, 2 H), 3.84 (dd, *J* = 3.7, 10.5 Hz, 1 H), 3.99 (dd, *J* = 4.6, 11.0 Hz, 1 H), 4.15–4.29 (m, 4 H), 4.57 (d, *J* = 11.9 Hz, 2 H), 4.65–5.20 (m, 10 H), 5.57 (t, *J* = 6.0 Hz, 1 H, NH), 5.82 (d, *J* = 7.8 Hz, 1 H, NH), 7.12–7.52 (m, 29 H), 8.21–8.26 (m, 2 H), 8.52 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.9, 45.6, 50.7, 54.7, 65.1, 67.2, 67.6, 69.9, 72.0, 73.1, 73.6, 74.5, 75.4, 79.0, 81.9, 104.2, 115.5, 118.8, 123.3, 124.0, 127.8, 127.9, 128.2, 128.5, 128.6, 128.7, 129.8, 130.0, 130.7, 134.6, 135.3, 136.3, 138.1, 138.3, 138.4, 144.8, 152.1, 156.2, 165.8, 170.0.

HRMS (ESI): *m*/*z* calcd for $C_{62}H_{64}N_6O_{13}S$ + Na [M + Na$^+$]: 1155.4150; found: 1155.4142.

***O*-{2,3,4-Tri-*O*-benzyl-6-*O*-[2-(4-{[3′,6′-bis(diethylamino)-3-oxospiro(isoindoline-1,9′-xanthene)-2-yl]methyl}-1*H*-1,2,3-triazol-1-yl)]acetyl-D-glucopyranosyl}-*N*-benzyloxycarbonyl-L-serine Benzyl Ester (26)**

From rhodamine alkyne **11** (33 mg, 0.069 mmol) and azidoacetyl glucosyl amino ester **22** (58 mg, 0.069 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:4 to 5:5) led to **26** (89 mg, 98%) (β/α = 3:1) as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10–1.14 (m, 12 H, 4 × CH_3), 3.24–3.34 (m, 11 H), 3.59 (t, *J* = 8.7 Hz, 0.75 H, H-3$_\beta$), 3.70 (t, *J* = 6.9 Hz, 0.25 H, H-3$_\alpha$), 3.81–3.83 (m, 0.25 H), 3.88 (dd, *J* = 3.7, 10.6 Hz, 0.75 H), 3.88–4.20 (m, 1 H), 4.33 (d, *J* = 7.8 Hz, 0.75 H, H-1$_\beta$), 4.29–4.37 (m, 1.25 H), 4.46–4.54 (m, 3 H), 4.57–4.62 (m, 3 H), 4.73–4.93 (m, 6 H), 5.02–5.19 (m, 4 H), 5.85 (d, *J* = 7.8 Hz, 1 H, NH), 6.11–6.13 (m, 2 H, ArH), 6.27–6.34 (m, 4 H, ArH), 7.07 (d, *J* = 6.4 Hz, 1 H, ArH), 7.19–7.52 (m, 28 H, ArH), 7.91 (d, *J* = 6.4 Hz, 1 H, CH=).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 35.4, 44.4, 50.2, 54.7, 60.5, 64.5, 65.1, 67.1, 67.4, 69.7, 72.6, 74.9, 75.0, 75.7, 77.3, 81.2, 84.5, 98.0, 103.6, 105.3, 108.0, 123.0, 123.9, 124.2, 127.9, 128.0, 128.2, 128.5, 128.6, 128.7, 128.8, 130.9, 132.6, 135.4, 136.3, 137.5, 138.1, 138.3, 144.9, 148.8, 153.5, 156.1, 166.0, 168.0, 169.9.

HRMS (ESI): *m*/*z* calcd for $C_{78}H_{81}N_7O_{13}$ + Na [M + Na$^+$]: 1346.5790; found: 1346.5746.

***O*-{2,3,4-Tri-*O*-benzyl-6-*O*-[2-(4-{[(3′,6′-bis(diethylamino)-3-oxospiro(isoindoline-1,9′-xanthene)-2-yl]methyl}-1*H*-1,2,3-triazol-1-yl)]acetyl-D-galactopyranosyl}-*N*-benzyloxycarbonyl-L-serine Benzyl Ester (27)**

From rhodamine alkyne **11** (21 mg, 0.044 mmol) and azidoacetyl glucosyl amino ester **23** (37 mg, 0.044 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 5:5) led to **27** as a pink solid (53 mg, 91%) (β/α = 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (t, *J* = 6.9 Hz, 12 H, 4 × CH_3), 3.29 (q, *J* = 6.9 Hz, 8 H, 4 × CH_2), 3.41 (t, *J* = 6.0 Hz, 1 H, H-5), 3.46 (dd, *J* = 2.3, 9.6 Hz, 1 H, H-3), 3.66 (m, 1 H, H-4), 3.74 (dd, *J* = 7.8, 9.6 Hz, 1 H, H-2), 3.82 (dd, *J* = 3.2, 10.6 Hz, 1 H, OCH_{Ser}), 4.02 (dd, *J* = 5.5, 11.0 Hz, 1 H, H-6), 4.20 (dd, *J* = 6.4, 11.0 Hz, 1 H, H-6′), 4.27 (d, *J* = 7.8 Hz, 1 H, H-1), 4.35 (dd, *J* = 2.8, 10.1 Hz, 1 H, OCH_{Ser}), 4.45 (s, 2 H, OCH_2), 4.55 (d, *J* = 11.9 Hz, 1 H, C*H*Ph), 4.56–4.57 (m, 1 H, NCH), 4.67 (d, *J* = 11.0 Hz, 1 H, C*H*Ph), 4.72–4.79 (m, 4 H), 4.94 (d, *J* = 11.9 Hz, 1 H, C*H*Ph), 4.92 (d, *J* = 11.9 Hz, 1 H, C*H*Ph), 5.02–5.10 (m, 2 H), 5.14–5.22 (m, 2 H), 5.80 (d, *J* = 8.2 Hz, 1 H, NH), 6.12–6.14 (m, 2 H, ArH), 6.28–6.34 (m, 4 H, ArH), 7.07–7.09 (m, 1 H, ArH), 7.25–7.31 (m, 28 H, ArH), 7.89–7.91 (m, 1 H, CH=).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 29.8, 35.4, 44.4, 50.2, 54.6, 64.5, 65.2, 67.1, 67.5, 70.0, 71.9, 72.8, 73.5, 74.5, 79.0, 82.0, 98.0, 104.2, 105.2, 108.0, 123.0, 123.9, 124.2, 128.6, 128.7, 132.7, 135.3, 138.1, 138.2, 145.0, 148.8, 153.5, 153.7, 156.1, 165.8, 168.0, 169.9.

HRMS (ESI): *m*/*z* calcd for $C_{78}H_{81}N_7O_{13}$ + Na [M + Na$^+$]: 1346.5790; found: 1346.5567.

3-[6-*O*-(2-Azido)acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl]prop-1-ene (29)

α-*C*-Allyl glucopyranoside **28** (259 mg, 0.546 mmol) was treated successively with $ClCH_2COCl$ and NaN_3 according to GP 1. Purification by column chromatography (EtOAc–PE, 1:9) gave 213 mg (70%) of compound **29** as a white solid; mp 72 °C; $[\alpha]_D^{20}$ +54.9 (*c*, 0.5 $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (t, *J* = 6.9 Hz, 2 H, CH_2), 3.41 (dd, *J* = 8.7, 10.1 Hz, 1 H, H-4), 3.67–3.69 (m, 1 H, H-5), 3.71 (dd, *J* = 5.5, 9.2 Hz, 1 H, H-2), 3.73 (d, *J* = 17.4 Hz, 1 H), 3.79 (d, *J* = 17.4 Hz, 1 H), 3.82 (t, *J* = 9.2 Hz, 1 H, H-3), 4.02–4.08 (m, 1 H, H-1), 4.24 (dd, *J* = 5.0, 11.4 Hz, 1 H, H-6), 4.31 (dd, *J* = 2.3, 11.4 Hz, 1 H, H-6′), 4.56 (d, *J* = 11.0 Hz, 1 H), 4.61 (d, *J* = 11.4 Hz, 1 H), 4.68 (d, *J* = 11.9 Hz, 1 H), 4.79 (d, *J* = 11.0 Hz, 1 H), 4.86 (d, *J* = 11.0 Hz, 1 H), 4.94 (d, *J* = 10.5 Hz, 1 H), 5.05–5.11 (m, 2 H, CH_2=), 5.69–5.75 (m, 1 H, CH=), 7.25–7.35 (m, 15 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.0, 50.2, 64.8, 69.5, 73.3, 73.7, 75.1, 75.6, 77.4, 80.1, 82.3, 117.3, 128.0, 128.1, 128.2, 128.3, 128.6, 128.7, 134.5, 137.8, 138.1, 138.6, 168.2.

HRMS (ESI): *m*/*z* calcd for $C_{32}H_{35}N_3O_6$ + Na [M + Na$^+$]: 580.2424; found: 580.2435.

3-{2,3,4-Tri-*O*-benzyl-6-*O*-{4-[(5-dimethylaminonaphthalene-1-sulfonylamino)methyl]-1*H*-1,2,3-triazol-1-yl}acetyl-α-D-glucopyranosyl}prop-1-ene (31)

From dansyl alkyne **8** (15 mg, 0.052 mmol) and azidoacetyl *C*-glucoside **29** (29 mg, 0.052 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 1:9 to 1:4) led to **31** (41 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43–2.47 (m, 2 H, CH_2), 2.87 (s, 6 H, 2 × CH_3), 3.30 (dd, *J* = 8.2, 9.6 Hz, 1 H, H-4), 3.65 (ddd, *J* = 2.2, 4.6, 10.1 Hz, 1 H, H-5), 3.72 (dd, *J* = 5.5, 9.2 Hz, 1 H, H-2), 3.81 (t, *J* = 9.2 Hz, 1 H, H-3), 4.04–4.09 (m, 1 H, H-1), 4.15–4.19 (m, 3 H, H-6, NCH_2), 4.33 (dd, *J* = 2.3, 11.9 Hz, 1 H, H-6′), 4.45 (d, *J* = 11.4 Hz, 1 H), 4.62 (d, *J* = 11.4 Hz, 1 H), 4.71 (d, *J* = 10.2 Hz, 1 H), 4.78 (d, *J* = 11.0 Hz, 1 H), 4.80 (d, *J* = 11.0 Hz, 1 H), 4.87–4.99 (m, 5 H), 5.06–5.10 (m, 2 H, CH_2=), 5.43 (t, *J* = 6.4 Hz, 1 H,

NH), 5.70–5.78 (m, 1 H, CH=), 7.23–7.54 (m, 18 H), 8.20 (dd, *J* = 1.4, 7.6 Hz, 2 H), 8.23 (d, *J* = 8.3 Hz, 1 H), 8.52 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.0, 39.0, 50.7, 65.2, 69.4, 73.2, 73.6, 75.0, 75.6, 77.4, 79.9, 82.2, 115.5, 117.3, 118.8, 123.3, 123.9, 127.9, 128.0, 128.1, 128.2, 128.3, 128.6, 128.7, 128.8, 129.7, 130.1, 130.8, 134.5, 134.6, 137.8, 138.1, 138.4, 144.6, 152.1, 167.8.

HRMS (ESI): *m*/*z* calcd for $C_{47}H_{51}N_5O_8S$ + Na [M + Na$^+$]: 868.3356; found: 868.3390.

3-{2,3,4-Tri-*O*-benzyl-6-*O*-[2-(4-{[(3′,6′-bis(diethylamino)-3-oxospiro(isoindoline-1,9′-xanthene)-2-yl]methyl}-1*H*-1,2,3-triazol-1-yl)]acetyl-α-D-glucopyranosyl}prop-1-ene (32)

From rhodamine alkyne **11** (19 mg, 0.040 mmol) and azidoacetyl C-glucoside **29** (30 mg, 0.054 mmol), click reaction according to GP 3 and purification by column chromatography (EtOAc–PE, 2:8 to 5:5) led to **32** as a red solid (55 mg, 99%); mp 81 °C; $[\alpha]_D^{20}$ +57.8 (*c*, 0.5 $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (m, 12 H, 4 × CH_3), 2.43–2.46 (m, 2 H, CH_2), 3.25–3.35 (m, 9 H, 4 × CH_2, H-4), 3.65 (ddd, *J* = 2.2, 4.6, 10.1 Hz, 1 H, H-5), 3.69 (dd, *J* = 5.5, 9.6 Hz, 1 H, H-2), 3.79 (t, *J* = 8.7 Hz, 1 H, H-3), 4.01–4.08 (m, 1 H, H-1), 4.14 (dd, *J* = 5.5, 11.4 Hz, 1 H, H-6), 4.29 (dd, *J* = 2.3, 11.9 Hz, 1 H, H-6′), 4.48–4.51 (m, 3 H), 4.62 (d, *J* = 11.4 Hz, 1 H), 4.68 (d, *J* = 11.4 Hz, 1 H), 4.76–4.84 (m, 4 H), 4.93 (d, *J* = 11.0 Hz, 1 H), 5.05–5.10 (m, 2 H, CH_2=), 5.65–5.73 (m, 1 H, CH=), 6.12–6.15 (m, 2 H), 6.27–6.33 (m, 4 H), 7.06–7.45 (m, 19 H), 7.90–7.93 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 30.0, 35.3, 44.4, 50.2, 65.0, 69.4, 73.2, 73.5, 74.9, 75.4, 77.4, 79.9, 82.1, 97.9, 105.3, 108.0, 117.2, 123.0, 123.9, 124.1, 127.8, 127.9, 128.0, 128.2, 128.3, 128.6, 128.7, 128.9, 130.9, 132.6, 134.4, 137.7, 138.1, 138.5, 144.8, 148.8, 153.4, 153.7, 166.0, 168.0.

HRMS (ESI): *m*/*z* calcd for $C_{63}H_{68}N_6O_8S$ + Na [M + Na$^+$]: 1059.4996; found: 1127.4833.

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