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Fluorous-Assisted One-Pot Oligosaccharide Synthesis

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A new method for oligosaccharide assembly that combines the advantages of one-pot synthesis and fluorous separation is described. After one-pot glycosylations are completed, a fluorous tag is introduced into the reaction mixture to selectively "catch" the desired oligosaccharide, which is rapidly separated from non-fluorous impurities by fluorous solid-phase extraction (F-SPE). Subsequent "release" of the fluorous tag and F-SPE achieved the purification of the desired oligosaccharide without the use of time- and solvent-consuming silica gel chromatography. Linear and branched oligosaccharides have been synthesized with this approach in just a few hours (for the overall oligosaccharide assembly and purification process).

Introduction

Carbohydrates are widely present in nature with important roles in numerous biological processes.[1,2] In order to illustrate the functions of carbohydrates, carbohydrate synthesis has been extensively studied over the past three decades. Traditional oligosaccharide assembly is a time-consuming process because of the need for multiple protective group adjustments and aglycon manipulations on oligosaccharide intermediates. Many novel methods to expedite oligosaccharide assembly have been introduced,[3–8] which include orthogonal glycosylation,[9,10] active-latent activation,[11–13] reactivity-based armed-disarmed glycosylation,[14–16] reactivity-independent chemoselective glycosylation,[17–20] and automated solid-phase synthesis.[21] Several of these strategies have been adopted into one-pot protocols, by which multiple glycosylation reactions can be carried out in a single flask without the need to purify the intermediates, thus greatly enhancing the efficiencies for oligosaccharide assembly.[22,23] Many large complex oligosaccharides have been assembled through one-pot methods, such as the phytoalexin elicitor heptasaccharide,[24] dimeric LewisX antigens,[25,26] Globo-H hexasaccharide,[27,28] the Lewis Y carbohydrate hapten,[29] and the core-fucosylated bi-antennary N-glycan dodecasaccharide.[30] Common to all one-pot methodologies, upon completion of the synthesis, silica gel chromatography is required to purify the desired product from side products such as disulfide and decomposed donors generated in the reaction, which can be time- and solvent-consuming. It would be desirable if purification of the final product from one-pot reactions could also be expedited to improve the overall efficiencies.

Recently, fluorous chemistry has become popular to facilitate organic synthesis and catalysis.[31–34] Highly fluorinated (fluorous) compounds have strong affinities with fluorinated silica gel. This property is utilized in F-SPE, which is an attractive technique to expedite purification.[32,35] F-SPE separates compounds containing fluorous tags from non-fluorous counterparts regardless of polarities through solid-phase extraction. As it does not require large amounts of solvents to elute the samples, F-SPE is faster than traditional silica gel chromatography and uses less organic solvents.[32,35] In order to take advantage of this unique property in carbohydrate synthesis, a fluorous tag can be introduced into a building block, typically a glycosyl acceptor, prior to glycosylation.[35–42] The fluorous acceptor is then coupled to a glycosyl donor to yield a fluorous disaccharide, which can be purified by F-SPE. This process can be repeated, which leads to fluorous oligosaccharides. As an alternative to tagging glycosyl acceptors, fluorous tags can also be introduced into glycosyl donors as protective groups[43–45] or the aglycon leaving group.[46] Recently, another method has been developed where a fluorinated silyl protective group has been used to selectively tag the desired product after oligosaccharide assembly on the solid phase.[47] This facilitated purification of a model trisaccharide product from the deletion sequences in an automated solid-phase synthesis.

One of the goals of our research program is to develop new methodologies expediting oligosaccharide assembly. Our initial foray into fluorous chemistry involved the development of a fluorous thiol as the aglycon leaving group for thioglycoside building blocks.[46] In this paper, we report our results on the use of fluorous reagents to aid one-pot oligosaccharide assembly.

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Results and Discussion

Our journey started by attaching a fluorous group to the glycosyl acceptor prior to glycosylation. Serious difficulties were encountered with this approach,[48] as the fluorous disaccharide acceptor **2a** reacted poorly with trisaccharide donor **1** (Figure 1a); main side products resulted from donor decomposition or hydrolysis. In contrast, under identical reaction conditions, the reaction of the corresponding non-fluorous lactoside **2b** with **1** produced pentasaccharide **3b** in 70% yield (Figure 1b). The exact reason for the poor reactivity of **2a** is not clear as other fluorous acceptors have successfully been glycosylated.[35–39] Addition of a fluorous solvent 1-(ethoxy)nonafluorobutane to the reaction to enhance solubility or elevation of the reaction temperature did not improve the outcome.[48] Another potential complication of the introduction strategy of this pre-glycosylation fluorous tag is that, in the synthesis of large oligosaccharides, the original fluorous chain installed may not be sufficient to retain the growing oligosaccharides during F-SPE with the increasing size of the organic components. These considerations led us to explore an alternative strategy for fluorous-assisted carbohydrate synthesis.

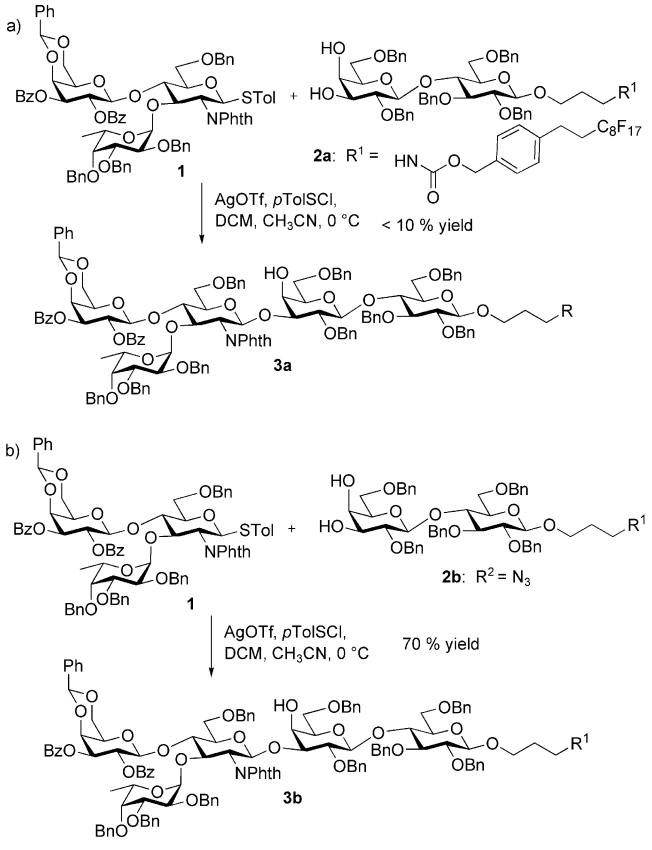


Figure 1. While glycosylation of trisaccharide donor **1** failed with (a) the fluorous acceptor **2a**, its glycosylation with (b) acceptor **2b** was successfully performed under identical reaction conditions.

As outlined in Figure 2, this new approach combines a fluorous "catch and release" protocol[46–54] with a preactivation-based one-pot synthesis, which begins by activation of a thioglycosyl donor by the promoter *p*TolSCl/AgOTf, thereby generating a reactive intermediate[55] in the absence of an acceptor.[20] Upon addition of a thioglycosyl acceptor to the preactivated donor, a disaccharide will be formed, which can be activated for the next round of glycosylation. This process can be repeated in the same flask until the desired oligosaccharide length is achieved. The last acceptor at the reducing end of the oligosaccharide will bear a functionalized linker, which can react with a fluorous tag. After one-pot glycosylation reactions are completed, the fluorous tag is added into the reaction mixture to selectively "catch" the desired oligosaccharide, which is easily separated from non-fluorous impurities by F-SPE. Subsequent release of the tag and F-SPE will lead to the pure desired oligosaccharide product without the need for any silica gel column purification.

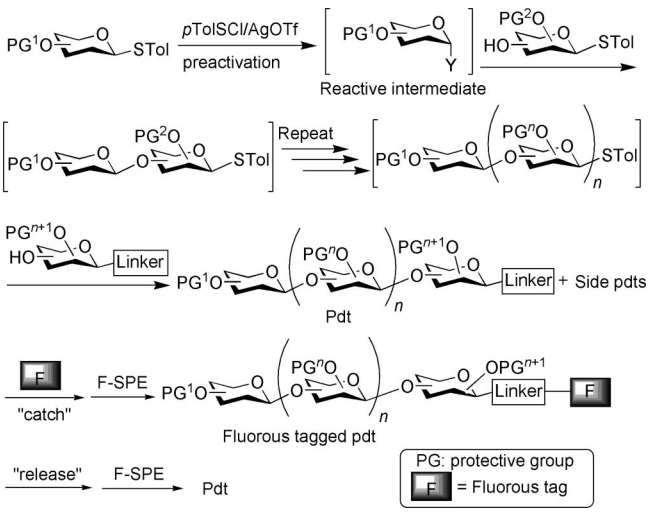
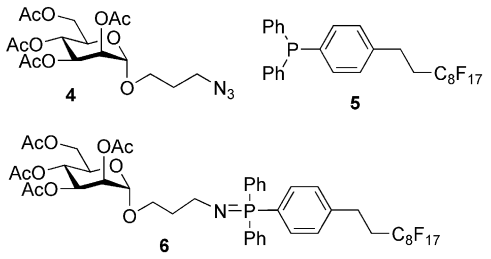


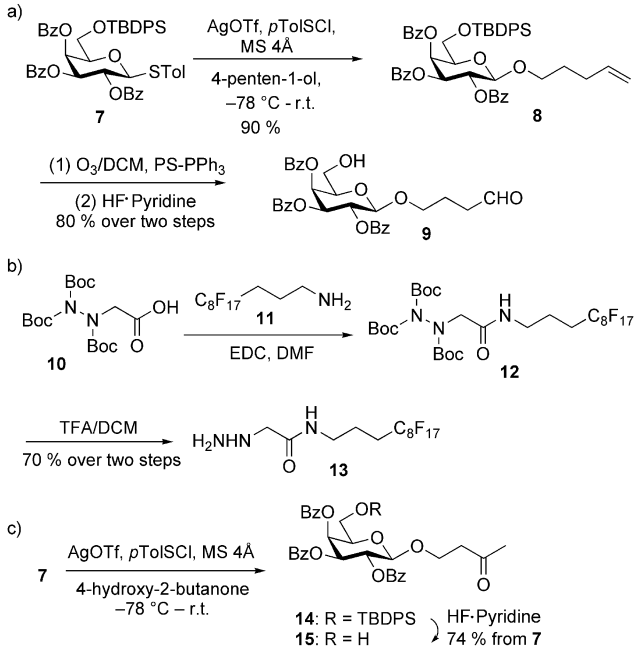
Figure 2. Fluorous-assisted one-pot oligosaccharide synthesis.

We envisioned that this fluorous "catch and release" protocol could potentially address the aforementioned limitations of the introduction of the pre-glycosylation tag. As no fluorous groups are present during glycosylation, typical glycosylation conditions can directly be adopted without extensive optimization of the reaction conditions. Furthermore, the post-glycosylation introduction of the fluorous tag allows the flexibility of choosing the appropriate fluorous groups to "catch" the oligosaccharides. In order for the fluorous "catch and release" protocol to be successful, the functionalized linker should be inert under glycosylation conditions and must not interfere with the glycosylation. Furthermore, the "catch" and "release" reactions must be highly chemoselective in the presence of the heavily functionalized oligosaccharides, and the reactions should be rapid, ideally completed within minutes.

The first reaction we examined is the Staudinger reaction between mannosyl azide **4**[56] and the commercially available fluorous phosphane **5**. However, the resulting aza-ylide **6** was hydrolyzed during F-SPE after the "catch" reaction.

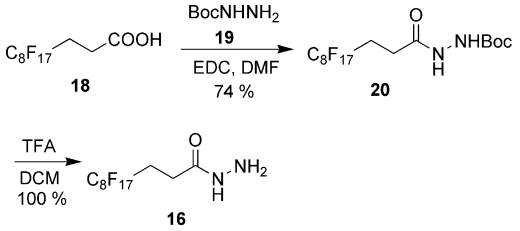


Hydrazone formation was explored next with aldehyde **9** and fluorous hydrazine **13**. Aldehyde **9** was synthesized from compound **7**,[14] which was first glycosylated with 4-penten-1-ol to give compound **8** followed by ozonolysis to introduce the aldehyde moiety (Scheme 1a). Triphenylphosphane was used initially to reduce the trioxolane intermediate from ozonolysis. Although the reaction was successful, it turned out to be difficult to separate cleanly the desired product from triphenylphosphane oxide generated in the reaction. This problem was solved by employing the solid-phase-supported triphenylphosphane (PS-PPh_3), which was easily removed after the reaction by simple filtration. Removal of the TBDPS group in **8** by HF in pyridine led to aldehyde **9**. Hydrazine **13** was obtained by 1-ethyl-3-(3-dimethyl-aminopropyl)carbodiimide hydrochloride (EDC) mediated coupling of compound **10**[63] and compound **11** and subsequent deprotection with trifluoroacetic acid (TFA) (Scheme 1b). The "catch and release" reactions between **9** and **13** were then performed. Unfortunately, aldehyde **9** was found to be unstable as it oxidized in air. To overcome this obstacle, ketone **15** was prepared. Glycosylation of compound **7** with 4-hydroxy-2-butanone gave compound **14**, which was treated with HF in pyridine to yield ketone **15** (Scheme 1c). However, with increased steric hindrance around the carbonyl group in ketone **15**, its "catch" reaction with fluorous hydrazine **13** turned out to be very slow and required more than 24 h to complete, which rendered it unattractive.

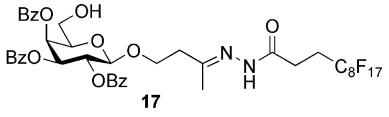


Scheme 1. Synthesis of aldehyde **9**, fluorous hydrazine **13**, and ketone **15**.

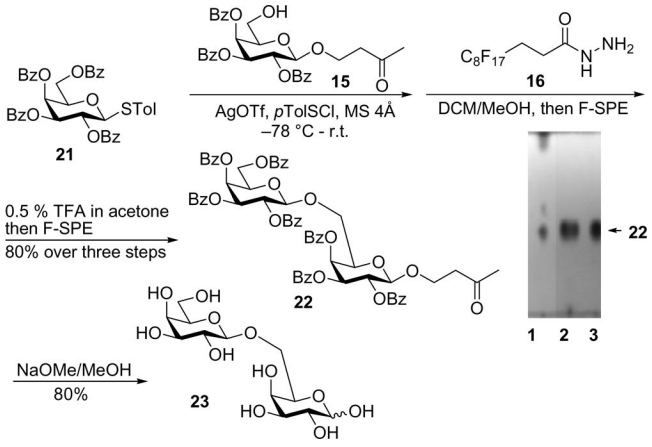
The slow reaction rate of **15** with hydrazine **13** prompted the design of fluorous hydrazide **16**. The preparation of hydrazide **16** started from fluorous carboxylic acid **18**, which was first coupled to *tert*-butyl carbazate **19** to provide compound **20** in 74% yield. Removal of the Boc group from **20** by TFA gave fluorous tag **16** in 100% yield (Scheme 2). Hydrazide **16** was much more reactive, reacting with ketone **15** in 5 min to lead to **17**. Compound **17** was stable under neutral conditions; the hydrazone bond can be cleaved with 0.5% TFA in acetone to release ketone **15** within 10 min in quantitative yield.



Scheme 2. Synthesis of fluorous hydrazide **16**.



With compound **16** in hand, its utility in oligosaccharide synthesis was examined first in a single-step glycosylation reaction. Glycosylation of acceptor **15** by donor **21**[14] promoted by *p*TolSCl/AgOTf led to disaccharide **22**. Upon completion of the reaction, the reaction mixture (Scheme 3, TLC Lane 1, and Figure 3a) was redispersed in DCM and methanol (1:1), followed by addition of fluorous hydrazide **16**. The "catch" reaction was completed in 5 min, followed by F-SPE, which removed all non-fluorous compounds. The fluorous fraction was then dissolved in acetone with 0.5% TFA to cleave the hydrazone bond in 10 min (Lane 2). After subsequent F-SPE, pure disaccharide **22** was obtained in 80% yield after the overall purification process (Lane 3, and Figure 3b). The purity and structure of the product were confirmed by NMR spectroscopy, MS, and HPLC analysis. The success of this reaction proved that the ketone moiety is stable and it does not interfere with the glycosylation reaction. The whole "catch and release" purification process took less than 1 h to complete with less than 30 mL organic solvent. In contrast, a typical silica gel chromatography separation requires a few hours and consumes several hundred milliliters of solvent. The speed in obtaining **22** highlights the advantage of our approach. The linker in **22** was removed through a reverse Michael reaction under basic conditions, together with the benzoyl protective groups, to produce **23** in 80% yield.



Scheme 3. Synthesis of disaccharide **23**. TLC: Lane 1, reaction mixture after glycosylation; Lane 2, reaction mixture after "catch", first F-SPE, and "release"; Lane 3, organic fraction after the second F-SPE.

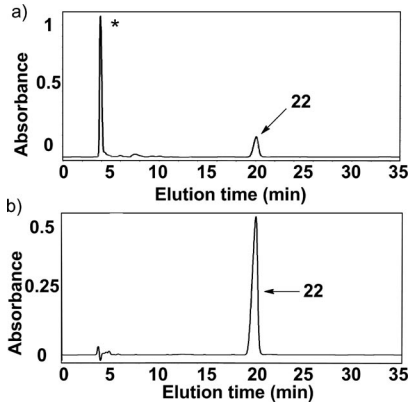
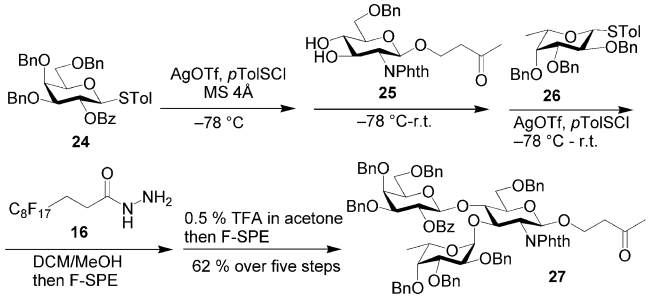


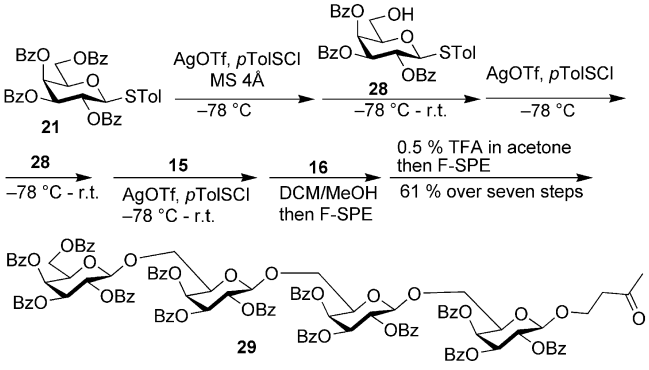
Figure 3. (a) HPLC chromatogram of the crude reaction mixture of compound **22** after the glycosylation reaction. The peak marked with an * was ditolyl disulfide, which was a side product from donor activation and has a strong UV absorbance band. This chromatogram corresponds to lane 1 of the TLC shown in Scheme 3; (b) HPLC chromatogram of the organic fraction after the second F-SPE, which corresponds to lane 3 of the TLC shown in Scheme 3. (HPLC mobile phase: hexanes/ethyl acetate = 2:1, flow rate 1 mL/min, UV monitoring at 256 nm, HPLC column: SupelCOSIL LC-Si, 25 cm × 4.6 mm, 5-μm particle size).

On the basis of the success of disaccharide synthesis, we moved on to test the feasibility of the fluorous-assisted assembly of a branched oligosaccharide, LewisX trisaccharide. LewisX is biologically important[57,58] and has been shown to be a good testing candidate for new synthetic methodologies.[25,26,59,60] For our synthesis, donor **24**[27] was first preactivated by *p*TolSCl/AgOTf, which regiospecifically glycosylated glucosamine diol **25** at its 4-hydroxy group. Upon complete consumption of the acceptor **25**, the resulting disaccharide was immediately subject to fucosylation by fucosyl donor **26**[14] in the same reaction flask, which led to the formation of LewisX trisaccharide **27** in 3 h (Scheme 4). One potential obstacle of the fluorous-assisted one-pot synthesis was the incomplete consumption of acceptors that leads to multiple products bearing the functionalized linker. To solve this problem, we found that by raising the reaction temperature to room temperature after each glycosylation, the acceptor was completely consumed and no deletion sequences were observed. The fluorous hydrazide **16** then successfully caught and released pure trisaccharide **27** from the reaction mixture. The overall process of acquiring trisaccharide **27** through a one-pot synthesis and "catch and release" purification took 4 h with an overall yield of 62% starting from donor **24**.



Scheme 4. Synthesis of LewisX trisaccharide **27**.

To further examine the scope of our method, a linear tetrasaccharide was synthesized through a four–component, one-pot synthesis. Sequential preactivation-based one-pot glycosylations of **21**,[14] **28**,[61] **28**, and **15** gave tetrasaccharide **29** (Scheme 5). The temperature-cycling protocol was adopted to minimize deletion sequences. F-SPE purification with hydrazide **16** generated pure tetrasaccharide **29** in 61% yield from galactoside donor **21** within just a few hours.



Scheme 5. Synthesis of tetrasaccharide **29**.

A potential concern with the acidic conditions employed for detagging is acid-mediated glycosidic linkage cleavage. Although, in general, glycosidic linkages can be sensitive to acids, the cleavage rate is dependent on the amount of acid used. The LewisX trisaccharide **27** with the acid-labile fucosyl linkage was stable under the mild acidic conditions employed for tag removal (0.5% TFA in acetone, 10 min). Control experiments have shown that **27** was un-affected in 5% TFA over 30 min. Thus, the fluorous catch-and-release protocol can be of general utility.

During our work, Seeberger and co-workers have reported a fluorinated silyl triflate to cap the non-fluorous oligosaccharide bearing a free hydroxy group assembled on a solid phase,[47] which was the first time a fluorous-capping

protocol on a desired product was adopted for carbohydrate synthesis. Our fluorous hydrazide offers an alternative to the silyl triflate chemistry, as it does not require a free hydroxy group in the oligosaccharide product with very fast rates of tagging and release.

Conclusions

We have developed a new fluorous "catch and release" protocol, which facilitates the purification of the desired oligosaccharide after a one-pot synthesis without the need for any silica gel chromatography. Among several reactions examined, the easily accessible hydrazide **16** was found to be the most suitable; it rapidly reacted with ketone-functionalized oligosaccharides. Both linear and branched oligosaccharides can be constructed with this strategy as exemplified by the one-pot assemblies of LewisX trisaccharide **27** and the galactose containing tetrasaccharide **29**. Because of the rapid reaction rates and substantially reduced volume of organic solvents employed for purification, this post-glycosylation tagging strategy provides an attractive alternative to the current practice of pre-glycosylation introduction of fluorous tags.

Experimental Section

General Experimental Procedures: All reactions were carried out under nitrogen with anhydrous solvents in flame-dried glassware, unless otherwise noted. Glycosylation reactions were performed in the presence of molecular sieves, which were flame-dried right before the reaction under high vacuum. Glycosylation solvents were dried by using a solvent purification system and used directly without further drying. HPLC grade hexanes and ethyl acetate were used as the HPLC solvents. The HPLC column used was SupelCOSIL LC-Si, with the dimensions of 25 cm × 4.6 mm and a 5-μm particle size. The chemicals used were of reagent grade as supplied, except where noted. Compound **5** and the fluorous silica gel were purchased from Fluorous Technologies Incorporated. Analytical thin-layer chromatography was performed by using silica gel 60 F254 glass plates. The compounds were visualized by a UV light (254 nm) and by staining with a yellow solution containing $Ce(NH_4)_2(NO_3)_6$ (0.5 g) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (24.0 g) in 6% H_2SO_4 (500 mL). Flash column chromatography was performed on silica gel 60 (230–400 Mesh). Fluorous column chromatography was performed on a 40-μm fluorous silica gel purchased from Fluorous Technologies. NMR spectra were referenced by using residual $CHCl_3$ (δ = ^{1}H NMR 7.26 ppm, ^{13}C NMR 77.0 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, ^{1}H-^{1}H gCOSY and/or ^{1}H-^{13}C gHMQC and ^{1}H-^{13}C gHMBC experiments. All optical rotations were measured at 25 °C by using the sodium D line.

Characterization of Anomeric Stereochemistry: The stereochemistries of the newly formed glycosidic linkages in disaccharide **22**, LewisX trisaccharide **27**, and tetrasaccharide **29** were determined by $^3J_{H1,H1}$ through ^{1}H NMR and/or $^1J_{C1,H1}$ through gHMQC 2-D NMR (without ^{1}H decoupling) spectroscopy. Smaller coupling constants of $^3J_{H1,H2}$ (about 3 Hz) indicate α linkages and larger coupling constants of $^3J_{H1,H1}$ (7.2 Hz or larger) indicate β linkages. $^1J_{C1,H1}$ of about 170 Hz suggests α linkages and 160 Hz suggests β linkages.[62]

4-Oxobutyl 2,3,4-Tri-*O*-benzoyl-β-D-galactopyranoside (9): *p*-Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyl-diphenylsilyl-1-thio-β-D-galactopyranoside **7**[14] (540 mg, 0.65 mmol) was dissolved in DCM (5 mL) and stirred at –78 °C with freshly activated molecular sieves (MS 4 Å, 1 g) for 30 min. Silver triflate (498 mg, 1.94 mmol) dissolved in acetonitrile (0.3 mL) was added to the reaction mixture. Five minutes later, orange *p*TolSCl (102 μL, 0.65 mmol) was added directly into the reaction mixture. This addition needs to be performed quickly in order to prevent *p*TolSCl from freezing inside the syringe tip or on the flask wall. The yellow color of the solution quickly dissipated within a few seconds, which indicates the complete consumption of *p*TolSCl. 4-Penten-1-ol (80 μL, 0.7746 mmol, dried by dissolving in DCM and by stirring with MS 4 Å molecular sieves overnight before use) was then added slowly along the wall of the flask. The reaction mixture was warmed to room temperature whilst stirring for 2 h. The reaction mixture was then diluted with DCM and filtered through Celite. The Celite was washed with DCM until no organic compounds were present in the filtrate. The filtrate was extracted with a saturated solution of $NaHCO_3$. The organic layer was then dried with Na_2SO_4 and concentrated to dryness. The residue was purified by silica gel column chromatography (hexanes/EtOAc, 4:1) to give compound 4-oxobutyl 2,3,4-tri-*O*-benzoyl-6-*tert*-butyl-diphenylsilyl-β-D-galactopyranoside **8** (464 mg, 90%). $[\alpha]_D^{20}$ = +83, (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02–7.08 (m, 25 H, CO*Ph*, *Ph*), 6.01 (dd, $J_{3,4}$ = 3.5, $J_{4,5}$ = 1 Hz, 1 H, 4-H), 5.68 (dd, $J_{1,2}$ = 7.5, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 5.64–5.60 (m, 1 H, $OCH_2CH_2CH_2CHCH_2$), 5.59 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 4.81–4.76 (m, 2 H, $OCH_2CH_2CH_2CHCHH$), 4.71 (d, $J_{1,2}$ = 7.5 Hz, 1 H, 1-H), 4.03 (dt, $J_{4,5}$ = 1, $J_{5,6}$ = 7 Hz, 1 H, 5-H), 3.91–3.87 (m, 1 H, $OCHHCH_2CH_2CHCH_2$), 3.81 (d, $J_{5,6}$ = 7 Hz, 2 H, 6-H), 3.52–3.47 (m, 1 H, $OCHHCH_2CH_2CHCH_2$), 1.97–1.91 (m, 2 H, $OCH_2CH_2CHHCHCH_2$), 1.65–1.55 (m, 2 H, $OCH_2CHHCHCHCH_2$), 0.98 [s, 9 H, $C(CH_2)_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6, 165.4, 165.2 (3 C, *C*OPh), 137.7, 136.4, 135.5, 135.4, 133.2, 133.0, 132.9, 132.6, 130.1, 129.9, 129.8, 129.7, 129.6, 129.6, 129.5, 129.5, 129.3, 129.0, 128.4, 128.3, 128.2, 127.7, 127.6, 127.5, 114.7, 101.5, 73.8, 71.9, 70.1, 69.3, 67.9, 61.4, 29.7, 28.5, 26.6 [$C(CH_3)_3$], 18.9 [$C(CH_3)_3$] ppm. HRMS: calcd. for $C_{48}H_{50}O_9SiNa$ [M + Na]$^+$ 821.3122; found 821.3162. This compound was dissolved in pyridine (4 mL) in a plastic flask, followed by addition of 65–70% an HF·pyridine solution (4 mL) at 0 °C. The solution was stirred overnight until complete disappearance of the starting material as judged from TLC analysis. The reaction mixture was diluted with EtOAc and washed with 10% aqueous $CuSO_4$ solution. The aqueous phase was extracted with EtOAc twice, and the combined organic layers were washed with saturated aqueous $NaHCO_3$ solution. After drying over Na_2SO_4 and after concentration, the residue was purified by silica gel column chromatography (hexanes/EtOAc, 5:2 then 2:1). The product was dissolved in DCM (3 mL) in a three-neck flask and stirred at –78 °C, and O_3 was bubbled into the solution. The solution turned blue after a few seconds, and polymer-supported triphenylphosphane (3.0 mmol/g, 600 mg) was added into the flask. The reaction mixture was further stirred overnight at room temperature. The polymer was removed by filtration, and the solution was concentrated and purified by silica gel chromatography (hexanes/EtOAc, 1:1) to give compound **9** (228 mg, 80%). However, this compound was not very stable and was partially oxidized to carboxylic acid over time, as evidenced by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.53 (t, *J* = 1 Hz, 1 H, C*HO*, this peak became smaller over time), 8.11–7.22 (m, 15 H, CO*Ph*), 5.83–5.79 (m, 2 H, 2-H, 4-H), 5.58 (dd, $J_{2,3}$ = 10, $J_{3,4}$ = 3 Hz, 1 H, 3-H), 4.77 (dd, $J_{1,2}$ = 8 Hz, 1 H, 1-H), 4.01–

3.95 (m, 2 H, 5-H, OC*H*HCH$_2$CH$_2$CHO), 3.83–3.80 (m, 1 H, 6-H), 3.66–3.59 (m, 2 H, 6′-H, OC*H*HCH$_2$CH$_2$CHO), 2.47–2.35 (m, 2 H, OCH$_2$CH$_2$C*H*HCHO), 1.89–1.80 (m, 2 H, OCH$_2$C*H*HCH$_2$CHO) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.5 (*C*HO), 173.9 (*C*OOH, formed from oxidation of aldehyde), 165.0, 164.9, 164.6 (3 C, *C*OPh), 133.7, 133.6, 133.6, 129.1, 129.1, 129.0, 128.9, 128.8, 128.8, 128.8, 128.7, 128.6, 99.7, 72.9, 71.9, 70.1, 68.3, 68.2, 68.1, 58.9, 29.7, 24.5, 21.7 ppm.

Fluorous Alkyl Hydrazine (13): Tri-Boc-protected α-hydrazinoacetic acid **10**[63] (378 mg, 0.97 mmol) and 3-(perfluorooctyl)propylamine **11** (463 mg, 0.97 mmol) were dissolved in DMF (6 mL), and EDC (278 mg, 1.46 mmol) and 4-dimethylaminopyridine (177 mg, 1.46 mmol) were added to the solution. The reaction mixture was stirred at room temperature overnight. DMF was removed, and the residue was purified by silica gel column chromatography (hexanes/EtOAc, 3:1) to yield tri-Boc-protected ester, which was dissolved in DCM (3 mL), followed by treatment with trifluoroacetic acid (3 mL) overnight at room temperature. The solvent was removed and dried under high vacuum to provide compound **13** (450 mg, 70% over two steps) in the form of a salt. ^{1}H NMR (500 MHz, CD_3OD): δ = 3.64, 3.51 (s, 2 H, NH$_2$NHC*H*HCO), 3.33 (t, 2 H, C*H*HC$_8$F$_{17}$), 2.27–2.16 (m, 2 H, CONHC*H*H), 1.99–1.85 (m, 2 H, NHCH$_2$C*H*HCH$_2$C$_8$F$_{17}$) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 170.5 (*C*O of TFA), 169.3 (*C*ONH), 50.5, 38.1, 28.2, 20.3 ppm. ^{19}F NMR (282 MHz, CD_3OD): δ = –77.18 (s, 3 F), –82.43 (t, 3 F), –115.31 (m, 2 F), –122.91 (m, 6 F), –123.76 (m, 2 F), –124.40 (m, 2 F), –127.31 (m, 2 F) ppm. HRMS : calcd. for $C_{13}H_{13}F_{17}N_3O$ [M + H]$^+$ 550.0800; found 550.0787.

3-Oxobutyl 2,3,4-Tri-*O*-benzoyl-β-D-galactopyranoside (15): *p*-Tolyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyl-diphenylsilyl-1-thio-β-D-galactopyranoside **7**[64] (299 mg, 0.36 mmol) and 4-hydroxy-2-butanone (37 μL, 0.43 mmol, dried by dissolving in DCM and by stirring with MS 4 Å molecular sieves overnight before use) were dissolved in DCM (5 mL) and stirred at –78 °C with freshly activated molecular sieves (MS 4 Å, 600 mg) for 30 min. Silver triflate (276 mg, 1.07 mmol) dissolved in acetonitrile (0.3 mL) was added to the reaction mixture. Five minutes later, orange *p*TolSCl (56.6 μL, 0.36 mmol) was added directly into the reaction mixture. This addition needs to be performed quickly in order to prevent *p*TolSCl from freezing inside the syringe tip or on the flask wall. The yellow color of the solution quickly dissipated within one minute, which indicates the complete consumption of *p*TolSCl. The reaction mixture was warmed to room temperature whilst stirring for 2 h. The reaction mixture was then diluted with DCM and filtered through Celite. The Celite was washed with DCM until no organic compounds were present in the filtrate. The filtrate was extracted with a saturated solution of $NaHCO_3$. The organic layer was then dried with Na_2SO_4 and concentrated to dryness. The residue was purified by silica gel column chromatography (hexanes/EtOAc, 4:1). The product was dissolved in pyridine (4 mL) in a plastic flask followed by addition of a 65–70% HF·pyridine solution (2.5 mL) at 0 °C. The solution was stirred overnight until complete disappearance of the starting material as judged from TLC analysis. The reaction mixture was diluted with EtOAc and washed with 10% aqueous $CuSO_4$ solution. The aqueous phase was extracted with EtOAc twice, and the combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution. After drying over Na_2SO_4 and after concentration, the residue was purified by silica gel column chromatography (hexanes/EtOAc, 1:1 then 1:2) to give compound **15** (148 mg, 74% over two steps). $[a]_D^{20}$ = +162 (c = 0.2, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07–7.18 (m, 15 H, CO*Ph*), 5.83–5.81 (m, 1 H, 4-H), 5.75 (dd, $J_{1,2}$ = 7.5, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 5.59 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 3 Hz, 1 H, 3-H), 4.86 (d, $J_{1,2}$ = 7.5 Hz, 1 H, 1-H), 4.18–4.15 (m, 1 H, OC*H*HCH$_2$CO), 4.05 (dt, $J_{4,5}$ = 1, $J_{5,6}$ = 9 Hz, 1 H, 5-H), 3.97–3.92 (m, 1 H, OC*H*HCH$_2$CO), 3.84–3.82 (m, 1 H, 6-H), 3.69–3.65 (m, 1 H, 6-H), 2.82 (m, 1 H, O*H*), 2.76–2.69 (m, 1 H, OCH$_2$C*H*HCO), 2.66–2.61 (m,1 H, OCH$_2$C*H*HCO), 1.99 (s, 1 H, COC*H*$_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.6 (*C*OCH$_3$), 166.5, 165.4, 165.3 (3 C, *C*OPh), 133.6, 133.2, 133.1, 129.9, 129.6, 129.2, 128.7, 128.7, 128.5, 128.2, 128.2, 101.8, 74.0, 71.7, 69.8, 68.8, 65.3, 60.5, 43.3, 30.3, 20.9, 14.0 ppm. HRMS : calcd. for $C_{13}H_{13}F_{17}N_3O$ [M + H]$^+$ 585.1737; found 585.1726.

Fluorous Acyl Hydrazide (16): 2H,2H,3H,3H-Perfluoroundecanoic acid **18** (241 mg, 0.49 mmol) and *tert*-butyl carbazate **19** (77.6 mg, 0.59 mmol) were dissolved in DMF (5 mL), followed by the addition of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (141 mg, 0.74 mmol). The resulting solution was stirred overnight at room temperature. DMF was removed, and the residue was purified by silica gel column chromatography (hexanes/EtOAc, 3:1) to give Boc-protected **20**, which was further treated with trifluoroacetic acid (3 mL) in DCM (3 mL). After stirring the mixture at room temperature overnight, the solvent was removed, and the residue was dried under high vacuum to give compound **16** (225 mg, 74% over two steps) in the form of salt. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.61 (m, 4 H) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 171.4 (*C*O of TFA), 162.6 (*C*ONHNH$_2$), 27.1, 25.3 ppm. ^{19}F NMR (282 MHz, CD_3OD): δ = –77.01 (m, 2 F), –82.59 (t, 3 F), –115.84 (m, 1 F), –123.01 (m, 3 F), –123.87 (m, 1 F), –124.64 (m, 1 F), –127.44 (m, 1 F) ppm. HRMS : calcd. for $C_{11}H_8F_{17}N_2O$ [M + H]$^+$ 507.0365; found 507.0369.

General Procedure for "Catch" and "Release": The reaction mixture was dispersed in DCM/MeOH (1:1, 2 mL). Fluorous hydrazide (2 equiv., by assuming that the glycosylation yield was quantitative) was added to the solution. After stirring at room temperature for 5 min, the solution was neutralized by $NaHCO_3$ to pH 6–7. Following the removal of the solvent, the residue was loaded into a short fluorous silica gel column (5 g fluorous silica) with MeOH (0.3 mL). The column was first flushed with MeOH/H_2O (4:1, 5 mL), and all the non-fluorous compounds came out immediately. This was followed by flushing with MeOH (5 mL) to elute the fluorous compounds. The fluorous fraction was collected and concentrated to dryness. The residue was then dissolved in a solution of 0.5% TFA in acetone (2 mL). After stirring the solution at room temperature for 10 min, the solvent was removed, and the residue was loaded onto a fluorous column. After flushing with MeOH/H_2O (4:1, 5 mL), the desired product came out immediately, which was concentrated and dried under high vacuum to provide the pure product.

3-Oxobutyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (22): *p*-Tolyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside[14] (29 mg, 0.041 mmol) and compound **15** (19 mg, 0.034 mmol) were dissolved in DCM (3 mL) and stirred at –78 °C with freshly activated molecular sieves (MS 4 Å, 150 mg) for 30 min. Silver triflate (32 mg, 0.12 mmol) dissolved in acetonitrile (30 μL) was added to the reaction mixture. Five minutes later, orange *p*TolSCl (6.53 μL, 0.041 mmol) was added directly into the reaction mixture. This addition needs to be performed quickly in order to prevent *p*TolSCl from freezing inside the syringe tip or on the flask wall. The yellow color of the solution quickly dissipated within a few seconds, which indicates the complete consumption of *p*TolSCl. The reaction mixture was warmed to room temperature whilst stirring for 2 h. The reaction mixture was then concentrated to dryness and redispersed in DCM/MeOH (1:1). Compound **16** (51 mg, 0.082 mmol) was

added to the solution. Following the general procedure for "catch and release", compound **22** (31 mg, 80%) was obtained. $[\alpha]_D^{20}$ = +100 (c = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09–7.19 (m, 35 H, CO*Ph*), 5.96–5.91 (m, 1 H, 4′-H), 5.87–5.81 (m, 1 H, 4-H), 5.76 (dd, $J_{1',2'}$ = 8, $J_{2',3'}$ = 10.5 Hz, 1 H, 2′-H), 5.65–5.57 (m, 2 H, 2-H, 3′-H), 5.47 (dd, $J_{2,3}$ = 10, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 4.93 (d, $J_{1',2'}$ = 8 Hz, 1 H, 1′-H), 4.68 (d, $J_{1,2}$ = 8 Hz, 1 H, 1-H), 4.44 (m, 1 H, 6′-H), 4.29–4.24 (m, 2 H, 5′-H, 6′-H), 4.16–4.12 (m, 2 H, 5-H, 6-H), 3.88–3.78 (m, 2 H, 6-H, OC*H*HCH$_2$CO), 3.66–3.61 (m, 1 H, OC*H*HCH$_2$CO), 2.55–2.50 (m, 1 H, OCH$_2$C*H*HCO), 2.31–2.27 (m, 1 H, OCH$_2$C*H*HCO), 1.87 (s, 3 H, COC*H*H$_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.6 (*C*OCH$_3$), 165.9, 165.5, 165.5, 165.3, 165.3, 165.2, 165.0 (7 C, *C*OPh), 133.5, 133.4, 133.2, 133.2, 133.1, 133.1, 130.0, 129.9, 129.7, 129.7, 129.7, 129.3, 129.3, 129.3, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 101.6 ($J_{C1,H1}$ = 160.9 Hz, 1 C), 101.1 ($J_{C1',H1'}$ = 161.5 Hz, 1 C), 73.2, 71.5, 71.5, 71.2, 69.8, 69.7, 68.6, 68.0, 67.9, 64.9, 61.7, 43.0, 30.4, 29.6 ppm. HRMS : calcd. for $C_{65}H_{56}O_{19}Na$ [M + Na]$^+$ 1163.3314; found 1163.3339.

6-*O*-β-D-Galactopyranosyl-D-galactose (23): To compound **22** (38 mg, 0.033 mmol) dissolved in MeOH (4 mL) was added dropwise 0.1 M NaOMe/MeOH, until the pH was 11. The reaction mixture was stirred at room temperature for 4 h. After the reaction was complete, the solution was neutralized by acidic resin. After filtration and size-exclusion chromatography by using Sephadex G-15, compound **23** was isolated in 80% yield. The identity of compound **23** was confirmed by comparison with literature NMR spectroscopic data and MS analysis.[64]

3-Oxobutyl 6-*O*-Benzyl-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (25): *p*-Tolyl 6-*O*-benzyl-2-deoxy-2-*N*-phthalimido-1-thio-β-D-glucopyranoside[65] (292 mg, 0.58 mmol) and 4-hydroxy-2-butanone (498 μL, 5.78 mmol, dried by dissolving in DCM and by stirring with MS 4 Å molecular sieves overnight before use) were dissolved in DCM (5 mL) and stirred at –78 °C with freshly activated molecular sieves (MS 4 Å, 800 mg) for 30 min. Silver triflate (445 mg, 1.73 mmol) dissolved in acetonitrile (0.3 mL) was added to the reaction mixture. Five minutes later, orange *p*TolSCl (91.3 μL, 0.58 mmol) was added directly into the reaction mixture. This addition needs to be performed quickly in order to prevent *p*TolSCl from freezing inside the syringe tip or on the flask wall. The yellow color of the solution quickly dissipated within a few seconds, which indicates the complete consumption of *p*TolSCl. The reaction mixture was warmed to room temperature whilst stirring for 2 h. The reaction mixture was then diluted with DCM and filtered through Celite. The Celite was washed with DCM until no organic compounds were present in the filtrate. The filtrate was extracted with a saturated solution of $NaHCO_3$. The organic layer was then dried with Na_2SO_4 and concentrated to dryness. The residue was purified by silica gel column chromatography (hexanes/EtOAc, 1:2) to give compound **25** (243 mg, 90%). $[\alpha]_D^{20}$ = –45 (c = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.24 (m, 9 H, CH$_2$*Ph*, *H* of NPhth), 5.16 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H), 4.54–4.63 (m, 2 H, C*H*$_2$Ph), 4.33–4.29 (m, 1 H, 3-H), 4.06 (d, $J_{1,2}$ = 8.5, $J_{2,3}$ = 11 Hz, 1 H, 2-H), 3.99–3.94 (m, 1 H, OC*H*HCH$_2$CO), 3.80–3.68 (m, 3 H, 5-H, 6-H, OC*H*HCH$_2$CO), 3.62–3.55 (m, 2 H, 4-H, 6-H), 3.24 (d, $J_{H\text{-}4,OH\text{-}4}$ = 2.5 Hz, 1 H, OH-4), 2.82 (d, $J_{H\text{-}3,OH\text{-}3}$ = 4.5 Hz, 1 H, OH-3), 2.60–2.54 (m, 1 H, OCH$_2$C*H*HCO), 2.48–2.43 (m, 1 H, OCH$_2$C*H*HCO), 1.87 (s, 3 H, COC*H*H$_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.5 (*C*OCH$_3$), 168.3 (1 C, *C*OPh), 137.6, 134.0, 131.7, 128.5, 127.9, 127.7, 123.3, 98.5, 73.8, 71.5, 70.3, 64.8, 56.1, 43.1, 30.2 ppm. HRMS : calcd. for $C_{25}H_{27}NO_8Na$ [M + Na]$^+$ 492.1634; found 492.1612.

3-Oxobutyl 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (27): *p*-Tolyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside **24**[27] (40.3 mg, 0.061 mmol) was dissolved in DCM (5 mL) and stirred at –78 °C with freshly activated molecular sieves (MS 4 Å, 300 mg) for 30 min. Silver triflate (47 mg, 0.19 mmol) dissolved in acetonitrile (50 μL) was added to the reaction mixture. Five minutes later, orange *p*TolSCl (9.65 μL, 0.061 mmol) was added directly into the reaction mixture. This addition needs to be performed quickly in order to prevent *p*TolSCl from freezing inside the syringe tip or on the flask wall. The yellow color of the solution quickly dissipated within a few seconds, which indicates the complete consumption of *p*TolSCl. Glucosamine acceptor **25** (23 mg, 0.049 mmol) dissolved in DCM (0.2 mL) was then added dropwise to the reaction mixture. The mixture was stirred for a further 1 h, at which point the temperature reached room temperature and glucosamine acceptor **25** was completely consumed. The fucose donor **26** (53.5 mg, 0.099 mmol) dissolved in DCM (1 mL) was added to the mixture. The solution was cooled back to –78 °C, and silver triflate (50.3 mg, 0.196 mmol) dissolved in acetonitrile (50 μL) was added. Five minutes later, orange *p*TolSCl (15.6 μL, 0.099 mmol) was added directly into the reaction mixture. The reaction mixture was warmed to room temperature whilst stirring for 1 h. The reaction mixture was then concentrated to dryness and redispersed in DCM/MeOH (1:1). Compound **16** (61 mg, 0.098 mmol) was added to the solution. Following the general procedure for fluorous "catch and release", pure **27** (44 mg, 62%) was obtained. $[\alpha]_D^{20}$ = –49 (c = 0.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93–6.87 (m, 44 H, CH$_2$*Ph*, CO*Ph*, *H* of NPhth), 5.11 (dd, $J_{1',2'}$ = 10, $J_{2',3'}$ = 8 Hz, 1 H, 2′-H), 4.90–4.80 (m, 3 H, 1-H), 4.67–4.26 (m, 15 H, 1′-H, 1′′-H), 4.17–4.04 (m, 3 H), 3.86–3.72 (m, 6 H, OC*H*HCH$_2$CO), 3.64–3.17 (m, 7 H, OC*H*HCH$_2$CO), 2.51–2.45 (m, 1 H, OCH$_2$C*H*HCO), 1.78 (s, 3 H, COC*H*H$_2$), 1.21 (d, J = 6.5 Hz, 3 H, C*H*$_3$ of fucose) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.3 (*C*OCH$_3$), 164.6 (1 C, *C*OPh), 139.3, 139.1, 138.6, 138.2, 138.1, 137.8, 137.7, 133.9, 133.0, 129.8, 129.7, 128.7, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.4, 127.1, 127.0, 126.9, 126.9, 123.4, 99.8 ($J_{C1',H1'}$ = 162.2 Hz, 1 C), 98.5 ($J_{C1,H1}$ = 163.8 Hz, 1 C), 96.9 ($J_{C1'',H1''}$ = 170.2 Hz, 1 C), 80.2, 79.4, 78.5, 75.4, 74.9, 74.8, 74.2, 73.8, 73.5, 73.4, 72.9, 72.7, 72.4, 72.0, 71.9, 71.6, 71.1, 67.7, 66.5, 64.6, 56.3, 43.0, 30.2, 29.6, 16.3 ppm. HRMS : calcd. for $C_{86}H_{87}NO_{18}Na$ [M + Na]$^+$ 1444.5821; found 1444.5787.

3-Oxobutyl (2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-[(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)]-[(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)]-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (29): *p*-Tolyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside **21**[14] (50 mg, 0.071 mmol) was dissolved in DCM (5 mL) and stirred at –78 °C with freshly activated molecular sieves (MS 4 Å, 400 mg) for 30 min. Silver triflate (55 mg, 0.21 mmol) dissolved in acetonitrile (50 μL) was added to the reaction mixture. Five minutes later, orange *p*TolSCl (11.25 μL, 0.071 mmol) was added directly into the reaction mixture. This addition needs to be performed quickly in order to prevent *p*TolSCl from freezing inside the syringe tip or on the flask wall. The yellow color of the solution quickly dissipated within a few seconds, which indicates the complete consumption of *p*TolSCl. Acceptor **28** (34 mg, 0.057 mmol) dissolved in DCM (1 mL) was then added dropwise to the reaction mixture. This mixture was warmed up to room temperature whilst stirring for 1 h. The reaction mixture was kept at room temperature for 0.5 h to completely decompose the excess activated donor. The solution was then cooled back to –78 °C. Silver triflate (29 mg, 0.11 mmol) dissolved in acetonitrile

(50 μL) was added to the reaction mixture. Five minutes later, orange *p*TolSCl (9 μL, 0.057 mmol) was added directly into the reaction mixture. After 5 min, acceptor **28** (26.8 mg, 0.045 mmol) dissolved in DCM (1 mL) was added dropwise to the reaction mixture. The reaction mixture was warmed up to room temperature whilst stirring for 1 h and kept at room temperature for 0.5 h to completely decompose the excess activated donor. Acceptor **15** (14.7 mg, 0.026 mmol) dissolved in DCM (1 mL) was then added to the reaction mixture. The solution was cooled back to –78 °C. Silver triflate (23 mg, 0.090 mmol) dissolved in acetonitrile (50 μL) was added to the reaction mixture. Five minutes later, *p*TolSCl (7 μL, 0.045 mmol) was added directly into the reaction mixture. This was warmed up to room temperature whilst stirring for 1 h. The reaction mixture was then concentrated to dryness and redispersed in DCM/MeOH (1:1). Compound **16** (34 mg, 0.052 mmol) was added to the solution. Following the general procedure for fluorous "catch and release", pure **29** (34 mg, 61%) was obtained. $[\alpha]_D^{20}$ = +68 (*c* = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06–7.17 (m, 65 H, CO*Ph*), 5.89–5.79 (m, 4 H, 4-H, 4′-H, 4′′-H, 4′′′-H), 5.66–5.38 (m, 8 H, 2-H, 2′-H, 2′′-H, 2′′′-H, 3-H, 3′-H, 3′′-H, 3′′′-H), 4.79 (d, *J* = 8 Hz, 1 H, 1′′′-H), 4.66 (d, *J* = 8 Hz, 1 H, 1-H), 4.53–4.49 (m, 2 H, H′, H′′), 4.22-. 3.72 (m, 11 H, 5-H, 5′-H, 5′′-H, 5′′′-H, 6-H, 6′-H, 6′′-H, 6′′-H, 6′′′-H, 6′′′-H, OC*H*HCH$_2$CO), 3.65–3.60 (m, 1 H, OC*H*HCH$_2$CO), 3.56–3.52 (m, 1 H, 6′-H), 3.34–3.31 (m, 1 H, 6-H), 2.52–2.47 (m, 1 H, OCH$_2$C*H*HCO), 2.30–2.25 (m, 1 H, OCH$_2$C*H*HCO), 1.84 (s, 3 H, COCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.3 (*C*OCH$_3$), 165.7, 165.5, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0, 164.9 (13 C, *C*OPh), 133.4, 133.2, 133.1, 133.1, 133.0, 133.0, 132.9, 130.1, 130.0, 130.0, 129.9, 129.8, 129.7, 129.7, 129.7, 129.7, 129.6, 129.4, 129.4, 129.3, 129.3, 129.2, 129.0, 128.9, 128.9, 128.7, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 101.6 ($J_{C1''',H1'''}$ = 162.5 Hz, 1 C), 101.0 ($J_{C1,H1}$ = 162.5 Hz, 1 C), 100.8, 100.7 ($J_{C1',H1'}$ = 160.1, $J_{C1'',H1''}$ = 160.1 Hz, 2 C), 72.9, 72.5, 72.2, 71.6, 71.5, 71.1, 69.9, 69.8, 69.8, 69.7, 68.5, 67.8, 67.8, 67.7, 67.5, 66.3, 66.2, 64.9, 61.3, 43.0, 36.6, 30.3, 29.6, 24.6 ppm. HRMS : calcd. for $C_{119}H_{100}O_{35}Na$ $[M + Na]^+$ 2111.5943; found 2111.5969.

Supporting Information (see footnote on the first page of this article): TLC for "catch and release" of compounds **27** and **29**, HPLC chromatogram for reaction mixtures and pure compounds **27** and **29** after "catch and release", and NMR spectroscopic data of all new compounds.

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