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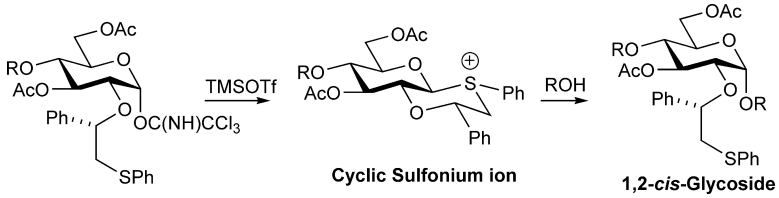

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A General Strategy for Stereoselective Glycosylations

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Abstract: The principal challenge that the synthesis of oligosaccharides of biological importance presents is the development of a general approach for the stereoselective introduction of a glycosidic linkage. It is shown here that a (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety at C-2 of a glycosyl donor can perform neighboring group participation to give a quasi-stable anomeric sulfonium ion. Due to steric and electronic factors, the sulfonium ion is formed as a *trans*-decalin ring system. Displacement of the sulfonium ion by a hydroxyl leads to the stereoselective formation of α-glycosides. NMR experiments were employed to show convincingly the presence of the β-linked sulfonium ion intermediate. The (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety could be introduced by reaction of a sugar alcohol with acetic acid (1*S*)-phenyl-2-(phenylsulfanyl)ethyl ester in the presence of BF_3-OEt_2. Furthermore, it could be removed by conversion into acetate by treatment with BF_3-OEt_2 in acetic anhydride. The introduction as well as the cleavage reaction proceeds through the formation of an intermediate episulfonium ion. The use of the new methodology in combination with traditional neighboring group participation by esters to introduce β-glycosides makes it possible, for the first time, to synthesize a wide variety of oligosaccharides by routine procedures. The latter was demonstrated by the synthesis of the Galili trisaccharide, which has been identified as an epitope that can trigger acute rejections in xeno-transplantations, by the one-pot two-step glycosylation sequence.

Introduction

Glycoconjugates are the most functionally and structurally diverse molecules in nature, and it is now well established that protein- and lipid-bound saccharides play essential roles in many molecular processes impacting eukaryotic biology and disease.[1−3] Examples of such processes include fertilization, embryogenesis, neuronal development, hormone activities, the proliferation of cells, and their organization into specific tissues. Remarkable changes in the cell-surface carbohydrates occur with tumor progression, which appears to be intimately associated with the dreaded state of metastasis. Furthermore, carbohydrates are capable of inducing a protective antibody response, which is a major contributor to the survival of the organism during infection.

The development of routine procedures for the chemical synthesis of oligonucleotide fragments (DNA and RNA) and peptides has altered the face of modern biology. Although significant improvements have been made,[4−6] there is still no general method for the preparation of complex carbohydrates of biological importance. In general, the chemical synthesis of a target compound is a research project that may require many months and perhaps years to be completed. These problems are compounded by the fact that, in biological samples, complex carbohydrates are often found in low concentrations and in microheterogeneous forms, which greatly complicates their isolation and characterization.

The chemical synthesis of complex carbohydrates involves the coupling of a fully protected glycosyl donor bearing a leaving group at its anomeric center, with a suitably protected glycosyl acceptor that contains often only one free hydroxyl group.[7] In many cases, these reactions lead to a mixture of two stereoisomers that differ in the configuration of the anomeric center. The most reliable method for stereoselective glycosylations is based on the neighboring group participation by a 2-*O*-acyl functionality (Scheme 1a).[4] In these reactions, a promoter activates an anomeric leaving group resulting in its departure and the formation of an oxocarbenium ion. Subsequent, neighboring group participation of the 2-*O*-acyl protecting group will give a more stable acetoxonium ion. An alcohol can attack the anomeric center of the acetoxonium ion from only one face providing a 1,2-*trans*-glycoside. Thus, in the case of glucosyl-type donors, β-linked products will be formed while mannosides will give α-glycosides. The introduction of 1,2-*cis*-glycosidic linkages, such as α-glucosides and α-galactosides, requires glycosyl donors with a nonassisting functionality at C-2. Invariably, the use of these glycosyl donors leads to the formation of mixtures of anomers.[5] Separation of these anomers requires time-consuming purification protocols resulting in loss of material. It also limits the use of one-pot multistep glyco-

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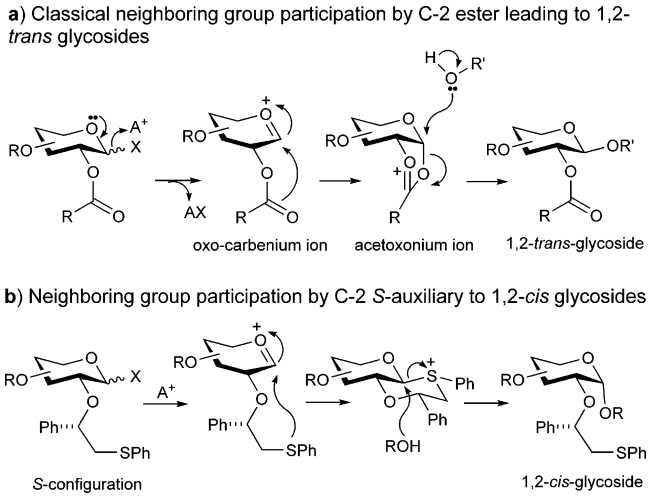
Scheme 1. Conventional and New Approaches for Stereoselective Glycosylation



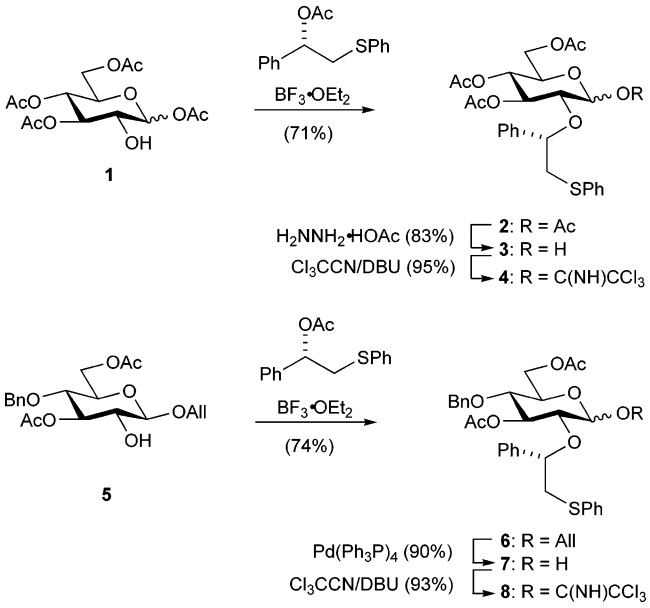
sylations[6,8] and automated polymer-supported synthesis[9−11] to oligosaccharides that only contain 1,2-*trans*-glycosides. Thus, the stereoselective formation of 1,2-*cis*-glycosides is the principal challenge of complex oligosaccharide synthesis.

We describe here a novel strategy for the stereoselective introduction of 1,2-*cis*-glycosides, which in combination with conventional methods using neighboring group participation by C-2 esters[5] will allow the routine preparation of a wide variety of complex oligosaccharides. The new glycosylation approach is based on neighboring group participation of a (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety at C-2 of a glycosyl donor (Scheme 1b). Upon formation of an oxocarbenium ion, the nucleophilic phenylsulfanyl moiety of the C-2 functionality will participate, leading to the formation of an intermediate sulfonium ion as either *trans*- or *cis*-decalin. The formation of the *trans*-decalin is expected due to the absence of unfavorable gauche interactions. In addition, the *cis*-decalin system will place the phenyl substituent in an axial position inducing further unfavorable steric interactions.[12] Displacement of the equatorial anomeric sulfonium ion by a sugar alcohol will then lead to the formation of a 1,2-*cis*-glycoside.

Results and Discussion

The (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety could easily be installed by reaction with a sugar alcohol, such as **1**[13] and **5**,[14] with acetic acid (1*S*)-phenyl-2-(phenylsulfanyl)ethyl ester in the presence of BF_3-OEt_2.[15] This reaction proceeds by a BF_3-OEt_2-promoted departure of the acetate with concomitant formation of an episulfonium ion. Subsequently, nucleophilic attack at the benzylic position of the episulfonium ion by a sugar hydroxyl leads to the required substituted benzyl ether with overall retention of configuration. Detailed NMR analysis of products **2** and **6** revealed that no other regio- or stereoisomers had been formed. Compounds **2** and **6** could be converted into glycosyl donors **4** and **8** by either removal of the anomeric acetyl ester or allyl ether followed by conversion of the hemiacetals into anomeric trichloroacetimidate using standard reaction conditions (Scheme 2).[16]

Scheme 2. Preparation of Glycosyl Donors **4** and **8**



With glycosyl donors **4** and **8** at hand, attention was focused on the glycosylation of a range of different glycosyl acceptors (Scheme 3). Thus, coupling of **4** or **8** with glycosyl acceptor **9** using a catalytic amount of TMSOTf in dichloromethane at −78 °C followed by gradual warming to 10 °C gave, after a reaction time of 3 h, disaccharides **10** and **11** as only the α-glycosides in good yields (protocol A). To demonstrate the generality of the approach, glycosyl acceptors **12**, **15**, and **18** were also coupled with **4** and **8** and as can be seen in Scheme 3; in each case, only the expected α-anomer was isolated.

TLC analysis of the reaction mixture indicated that the glycosyl donor had been consumed within 10 min after adding TMSOTf. The glycoside products were, however, formed over a period of 3 h indicating the presence of a quasi-stable intermediate anomeric sulfonium ion. Furthermore, it was observed that some degradation had occurred probably due to the acidic nature of the reaction conditions. To address the latter problem, the glycosylations were performed by an alternative protocol (Scheme 3, protocol B) whereby the glycosyl donor was first activated with TMSOTf followed by the addition of the acceptor in the presence of the base 2,6-di-*tert*-butyl-4-methylpyridine. As expected, under these conditions no degradation was observed and, in each case, the disaccharides were isolated in improved and near quantitative yield.

The fact that the glycosylations lead to the formation of exclusively α-anomers provides strong support that the reactions proceed through an equatorially substituted anomeric sulfonium ion. To confirm the presence of this intermediate, glycosyl donor **8** in CD_2Cl_2 at −50 °C was treated with 1 equiv of TMSOTf, and after the temperature was raised to −20 °C, ^{1}H, ^{1}H-TOCSY, HSQC, and HMBC NMR spectra were recorded. The collected

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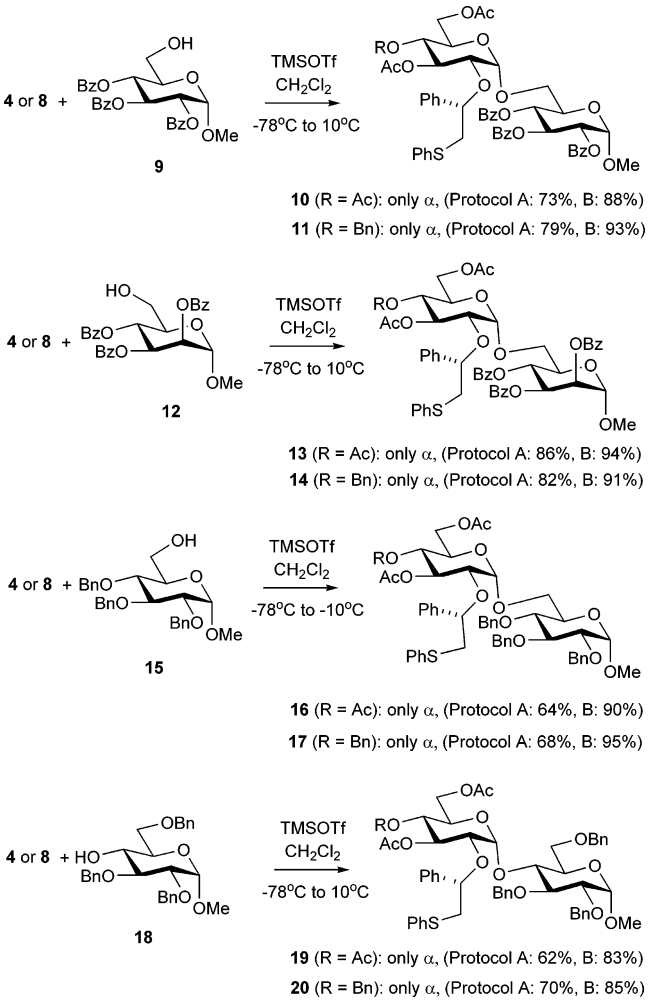
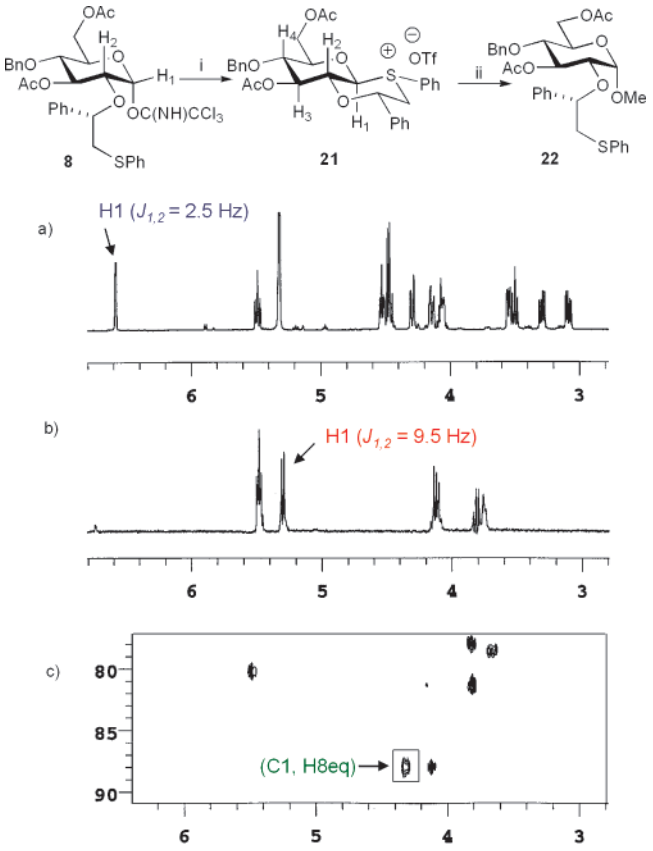
Scheme 3. Stereoselective Glycosylations with Glycosyl Donors **4** and **8**



data showed the formation of a single new compound, which was unambiguously identified as the sulfonium ion **21** (Scheme 4). Upon activation, the anomeric proton of **8** (δ 6.58, d, $J_{1,2}$ = 2.5 Hz) shifted upfield (δ 5.30, d, $J_{1,2}$ = 9.5 Hz) and its large vicinal coupling constant established an equatorial orientation of the anomeric substituent. The coupling constants of the other saccharide protons showed that no conformational distortion of the saccharide ring had occurred. The HMBC spectrum, which allows the determination of three-bond proton−carbon couplings, showed a correlation between C-1 and H8eq, proving that the *trans*-decalin system of **21** had been formed. Treatment of **21** with methanol resulted in the clean formation of the α-methyl glycoside **22**, demonstrating that the glycosylation proceeds by inversion of configuration of the anomeric center.

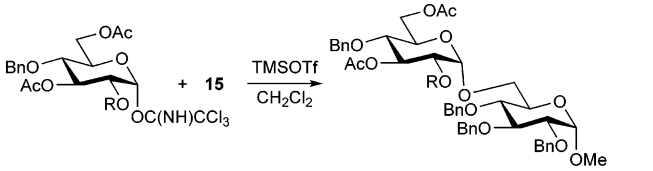
Next, a number of experiments were performed to establish which features of the (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety are important for controlling the α-anomeric selectivity. In this respect, a reaction of an intermediate oxocarbenium ion with an externally delivered sulfide may also lead to the formation of an equatorially substituted sulfonium ion, which may be displaced by a sugar alcohol to give an α-glycoside. Furthermore, the chiral center of the (1*S*)-phenyl-2-(phenylsulfanyl)-ethyl moiety may not be essential for achieving absolute α-anomeric selectivity. It may well be possible that *trans*- vs *cis*-decalin formation in combination with stereoelectronic effects is sufficient to induce the formation of a β-substituted

Scheme 4 [a]



[a] Key: (i) TMSOTf, CD_2Cl_2, −50 to 0 °C; (ii) MeOH, −20 to 0 °C. (a) ^{1}H NMR spectrum of glycosyl donor **8**. (b) ^{1}H TOCSY 1D spectrum on irradiation of H4 of sulfonium ion **21**. (c) HMBC spectrum of sulfonium ion **21**.

Scheme 5. Glycosylations with Glycosyl Donors **23**, **25**, **27**, and **8**



23: R = Bn

24: R = Bn
a. TMSOTf, CH_2Cl_2, α/β = 3/1 **(94%)**
b. TMSOTf, CH_2Cl_2, PhSEt, α/β = 6/1 **(92%)**

25: R = $(CH_2)_2$SPh

26: R = $(CH_2)_2$SPh, α/β = 8/1 **(86%)**

27: R = (*R*)-CH(Ph)CH_2SPh

28: R = (*R*)-CH(Ph)CH_2SPh, α/β = 1/1 **(88%)**

8: R = (*S*)-CH(Ph)CH_2SPh

17: R = (*S*)-CH(Ph)CH_2SPh, α **only (95%)**

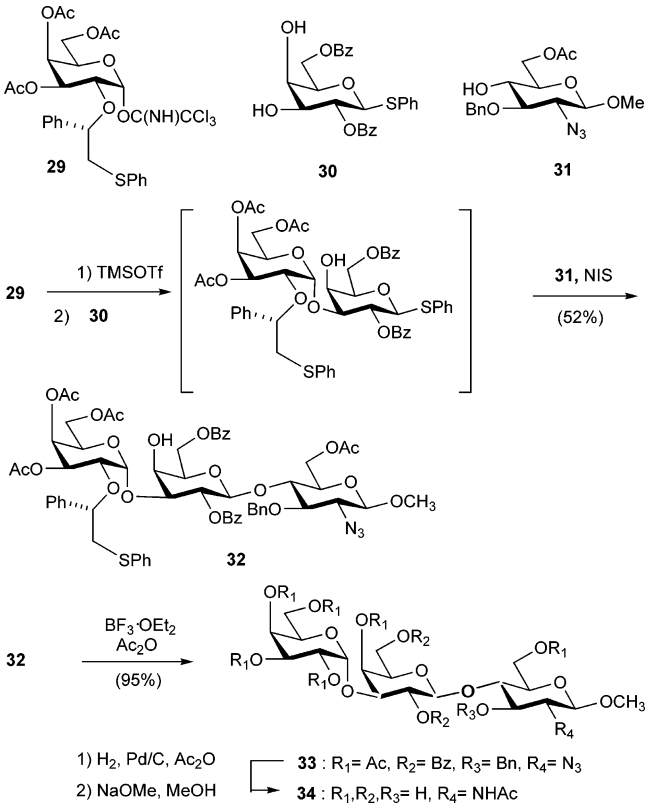
sulfonium ion reacting to an α-glycoside. To investigate these issues, trichloroacetimidates **23**, **25**, and **27** were coupled with **15** using TMSOTf as a promoter and the results were compared with a similar coupling with glycosyl donor **8** (Scheme 5). A standard glycosylation of trichloroacetimidate **23**, which has a C-2 benzyl ether, gave the disaccharide **24** as a 3/1 mixture of α/β anomers. When the glycosylation was performed in the presence of ethyl phenyl sulfide (5 equiv), only a marginal increase in α-anomeric selectivity (α/β = 6/1) was observed. With the establishment that intramolecular delivery of the phenylsulfanyl moiety is important for obtaining absolute α-anomeric selectivity, glycosylations were performed with glycosyl donors **25** and **27**, which have modified C-2 functionalities. In the case of **25**, the C-2 functionality lacks the (1*S*)-

phenyl moiety whereas, in the glycosyl donor **27**, it has an opposite (1*R*)-stereochemistry. In the latter case, the formation of a β-substituted sulfonium ion will place the (1*R*)-phenyl substituent in an axial orientation inducing unfavorable steric interactions. In the alternative α-substituted sulfonium ion (*cis*-decalin), the (1*R*)-phenyl group will adopt an equatorial orientation; however, this intermediate will experience unfavorable gauche interactions. Displacement of the α-sulfonium ion would lead to the formation of β-glycoside. Thus, a standard glycosylation with glycosyl donor **25** gave the disaccharide **26** as a 8/1 mixture of α/β anomers. A similar glycosylation with **27** resulted in the formation of **28** as an anomeric mixture (α/β = 1/1). These results indicate that a combination of an equatorially oriented (1*S*)-phenyl substituent and *trans*-decalin formation are important features for controlling the α-anomeric selectivity.

The new glycosylation protocol described here in combination with traditional neighboring group participation by esters should allow the installment of α- as well as β-glycosides. To demonstrate the combined use of these methodologies trisaccharide **34**,[17−24] which has been identified as an epitope that can trigger acute rejections in xeno-transplantations,[25,26] was prepared. It was anticipated that this compound could be assembled from the monomeric building blocks **29**, **30**, and **31** using a one-pot two-step glycosylation sequence. Galactosyl donor **29**, which possesses a (1*S*)-phenyl-2-(phenylsulfanyl)-ethyl functionality at C-2, will direct the formation of an α-galactoside, whereas the C-2 benzoyl of **30** will induce the formation of a β-galactoside. The novel galactosyl donor **29** could be prepared in a good overall yield starting from 1,3,4,6-tetra-*O*-acetyl-α-D-galactose[27] using a sequence of reactions similar to that used for the synthesis of compound **4** (Scheme 6). Glycosyl donor **29** was treated with TMSOTf to form an intermediate anomeric sulfonium ion, which was reacted with glycosyl acceptor **30** for 4 h at 0 °C. Next, methyl glycoside **31** and NIS were added to the reaction mixture, and within 2 h, trisaccharide **32** was formed. This compound was isolated in a yield of 52% as a single anomer with expected anomeric configuration. Interestingly, the NIS/TMSOTf promoter system does not affect the (1*S*)-phenyl-2-(phenylsulfanyl)ethyl group. Furthermore, preactivation of **29** was required to achieve a high yield.

Finally, we explored reaction conditions for the removal of the (1*S*)-phenyl-2-(phenylsulfanyl)ethyl group. It was anticipated that this functionality could be converted into an acetyl ester by treatment with BF_3-OEt_2 in acetic anhydride. In this reaction, an acetoxonium ion, generated from a reaction of BF_3-OEt_2 with acetic anhydride, will react with oxygen of the (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety. An intramolecular nucleophilic substitution of sulfur of the resulting intermediate should lead to the formation of an episulfonium ion and acetyl ester. Nucleophilic attack of acetic acid at the benzylic position of the episulfonium ion should regenerate acetic acid (1*S*)-phenyl-2-(phenylsulfanyl)ethyl ester. Indeed, treatment of **32** with BF_3-OEt_2 in acetic anhydride gave, after a reaction time of 30 min, a quantitative yield of C-2″ acetate **33** and full recovery of acetic acid (1*S*)-phenyl-2-(phenylsulfanyl)ethyl ester. The latter compound could be reused for the installment of an (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety. Compound **33** could be further deprotected under standard conditions to give the target compound **34**.

Scheme 6. Preparation of Glycosyl Donor **29**, One-Pot Two-Step Synthesis of Trisaccharide **32**, and Deprotection



Conclusion

It has been shown that a (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety at C-2 of a glycosyl donor can direct the formation of α-gluco and α-galactosides. These glycosyl donors react through a new reaction mechanism whereby the phenylsulfanyl moiety of the C-2 functionality performs neighboring group participation to give a quasi-stable anomeric sulfonium ion. Due to steric and electronic effects, the sulfonium ion is only formed as a *trans*-decalin. Displacement of the sulfonium ion by a sugar hydroxyl leads exclusively to the formation of an α-glycoside. The formation of an intermediate cyclic β-linked sulfonium ion was convincingly demonstrated by NMR experiments. This (1*S*)-phenyl-2-(phenylsulfanyl)ethyl moiety can be introduced and removed under mild reaction conditions by exploiting the high reactivity of an episulfonium ion. It is to be expected that the new methodology can be expanded to include the synthesis of 1,2-*cis*-amino sugars. A combined use of a new approach to introduce α-glycosides and traditional neighboring group par-

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ticipation by C-2 esters to give β-glycosides provides a general strategy for the synthesis of a wide variety of oligosaccharides.

Experimental Section

Acetyl 3,4,6-Tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)-ethyl}-α-D-glucopyranose (2). Boron trifluoride diethyl etherate (381 μL, 3.0 mmol) was added to a solution of acetyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranose (**1**) (697 mg, 2.0 mmol), acetic acid (1*S*)-phenyl-2-(phenylsulfanyl)ethyl ester (**39**) (817 mg, 3.0 mmol), and activated molecular sieves (4Å) in dichloromethane (10 mL) at 0 °C. After 30 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic phase was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (25% ethyl acetate in hexane) to afford **2** (796 mg, 71%): colorless syrup; R_f = 0.37 (ethyl acetate/hexane, 1/2); $[\alpha]^{20}_D = +124.6°$ (c = 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.17 (m, 10H, aromatic), 6.46 (d, 1H, J = 3.6 Hz, H-1), 5.39 (t, 1H, J = 9.6 Hz, H-3), 4.46 (t, 1H, J = 9.6 Hz, H-4), 4.46 (dd, 1H, J = 4.8, 8.1 Hz, H-7), 4.27−4.23 (m, 1H, H-6a), 4.08−3.98 (m, 2H, H-6b, H-5), 3.58 (dd, 1H, J = 3.6, 9.6 Hz, H-2), 3.22 (dd, 1H, J = 8.1, 13.8 Hz, H-8a), 3.04 (dd, 1H, J = 4.8, 13.8 Hz, H-8b), 2.18 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.82 (s, 3H, $COCH_3$); HR MALDI-TOF MS (*m*/*z*) calcd for $C_{28}H_{32}O_{10}S$ $[M + Na]^+$ 583.1614, found 583.1622.

3,4,6-Tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-α-D-glucopyranosyl Trichloroacetimidate (4). Hydrazinium acetate (144 mg, 1.56 mmol) was added to a solution of **2** (796 mg, 1.42 mmol) in DMF (10 mL) at room temperature. The reaction mixture was stirred overnight and then quenched with saturated aqueous $NaHCO_3$ (20 mL). The reaction mixture was extracted with ethyl acetate (20 mL × 2). The combined organic phase was washed with saturated aqueous NH_4-Cl (20 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (25% ethyl acetate in hexane) to afford 3,4,6-tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-D-glucopyranose (**3**) (612 mg, 83%). Trichloroacetonitrile (1.18 mL, 11.8 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (71 μL, 0.47 mmol) were added to a solution of **3** (612 mg, 1.18 mmol, 1 equiv) in dichloromethane (5 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 1 h and then concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **4** (743 mg, 95%): R_f = 0.29 (ethyl acetate/hexane, 1/3); $[\alpha]^{20}_D = +50.0°$ (c = 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H, N*H*), 7.36−7.16 (m,10H, aromatic), 6.66 (d, 1H, J = 3.6 Hz, H-1), 5.44 (t, 1H, J = 9.6 Hz, H-3), 4.93 (t, 1H, J = 9.6 Hz, H-4), 4.53 (t, 1H, J = 6.3 Hz, H-7), 4.26−4.16 (m, 2H, H-5, H-6a), 4.06−4.03 (m, 1H, H-6b), 3.67 (dd, 1H, J = 3.6, 9.6 Hz, H-2), 3.21 (dd, 1H, J = 7.5, 13.8 Hz, H-8a), 3.06 (dd, 1H, J = 6.3, 13.8 Hz, H-8b), 2.02 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.76 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.53, 169.90, 169.68, 160.86, 139.68, 136.17, 129.34, 129.02, 128.56, 126.99, 126.19, 93.02, 81.34, 75.31, 71.22, 69.77, 67.99, 61.51, 41.50, 20.65, 20.59 (2); HR MALDI-TOF MS (*m*/*z*) calcd for $C_{28}H_{30}Cl_3NO_9S$ $[M + Na]^+$ 684.0604, found 684.0602.

Allyl 3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-β-D-glucopyranoside (6). Boron trifluoride diethyl etherate (572 μL, 4.5 mmol) was added to a solution of allyl 3,6-di-*O*-acetyl-4-*O*-benzyl-β-D-glucopyranoside (**5**) (1.18 g, 3.0 mmol), acetic acid (1*S*)-phenyl-2-(phenylsulfanyl)ethyl ester (**39**) (1.23 g, 4.5 mmol), and activated molecular sieves (4 Å) in dichloromethane (10 mL) at 0 °C. After 10 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic phase was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (25% ethyl acetate in hexane) to afford **6** (1.35 g, 74%): colorless syrup; R_f = 0.30 (ethyl acetate/hexane, 1/3); $[\alpha]^{20}_D = +8.8°$ (c = 1.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.10 (m,15H, aromatic), 5.96−5.83 (m, 1H, OCH_2CHCH_2), 5.30−5.13 (m, 3H, H-3, OCH_2CHCH_2), 4.96 (t, 1H, J = 6.9 Hz, H-7), 4.43 (d, 1H, J = 8.4 Hz, H-1), 4.49−4.26 (m, 3H, H-6a, $OCHHCHCH_2$, $CHHPh$), 4.17−4.10 (m, 2H, H-6b, $OCHHCHCH_2$), 3.53−3.35 (m, 3H, H-4, H-5, H-8a), 3.23 (dd, 1H, J = 8.4, 9.6 Hz, H-2), 3.08 (dd, 1H, J = 6.9, 13.5 Hz, H-8b), 2.01 (s, 3H, $COCH_3$), 1.76 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.58, 169.75, 140.32, 137.26, 136.89, 133.71, 128.78, 128.49, 128.347, 128.29, 128.01, 127.89, 127.69, 125.69, 118.15, 102.66, 81.41, 77.19, 76.24, 75.09, 74.42, 72.49, 70.73, 62.80, 40.38, 21.09, 20.81; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{34}H_{38}O_8S$ $[M + Na]^+$ 629.2185, found 629.2203.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)-ethyl}-α-D-glucopyranosyl Trichloroacetimidate (8). Tetrakis(triphenylphosphine)palladium (2.56 g, 2.22 mmol) was added to a solution of **6** (1.35 g, 2.22 mmol) in acetic acid (15 mL) at room temperature. The reaction mixture was stirred overnight and then diluted with dichloromethane (20 mL) and quenched with saturated aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (25% ethyl acetate in hexane) to afford 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-D-glucopyranose (**7**) (1.13 g, 90%): R_f = 0.19 (ethyl acetate/hexane, 1/2). Trichloroacetonitrile (1.99 mL, 19.9 mmol) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) (119 μL, 0.8 mmol) were added to a solution of **7** (1.13 g, 1.99 mmol) in dichloromethane (10 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 1 h and then concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **8** (1.32 g, 93%): R_f = 0.45 (dichloromethane/acetone, 100/1); $[\alpha]^{20}_D = -0.03°$ (c = 6.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H, N*H*), 7.37−7.16 (m, 15H, aromatic), 6.62 (d, 1H, J = 3.6 Hz, H-1), 5.57 (t, 1H, J = 9.6 Hz, H-3), 4.52−4.42 (m, 1H, H-7), 4.50 (d, 1H, J = 10.5 Hz, C*H*HPh), 4.44 (d, 1H, J = 10.5 Hz, C*H*HPh), 4.29−4.17 (m, 2H, H-6a, H-6b), 4.13−4.08 (m, 1H, H-5), 3.55 (dd, 1H, J = 3.6, 9.6 Hz, H-2), 3.49 (t, 1H, J = 9.6 Hz, H-4), 3.25 (dd, 1H, J = 6.9, 13.5 Hz, H-8a), 3.05 (dd, 1H, J = 6.6, 13.5 Hz, H-8b), 2.00 (s, 3H, $COCH_3$), 1.81 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.44, 169.49, 161.08, 139.80, 137.07, 136,21, 129.35, 128.97, 128.54, 128.53, 128.13, 127.22, 126.11, 93.07, 80.86, 75.51, 75.47, 74.54, 72.70, 70.96, 62.33, 41.27, 20.95, 20.77; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.44, 169.49, 161.08, 139.80, 137.07, 136,21, 129.35, 128.97, 128.54, 128.53, 128.13, 127.22, 126.11, 93.07, 80.86, 75.51, 75.47, 74.54, 72.70, 70.96, 62.33, 41.27, 20.95, 20.77; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{33}H_{34}Cl_3NO_8S$ $[M + Na]^+$ 732.0968, found 732.0957.

General Procedure for the Glycosylation Reaction Employing Glycosyl Donors 4 and 8. Protocol A. A mixture of donor **4** or 8 (0.04 mmol), glycosyl acceptor (0.06 mmol), and activated molecular sieves (4 Å) in DCM (5 mL) was stirred for 10 min under an atmosphere of argon at room temperature. After the mixture was cooled to −78 °C, trimethylsilyl trifluoromethanesulfonate (2.2 μL, 0.012 mmol) was added. The reaction mixture was allowed to warm slowly to 10 °C. After the donor was consumed, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ (5 mL) and separated. The organic phase was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane)

Protocol B. A mixture of donor **4** or 8 (0.04 mmol) and activated molecular sieves (4 Å) in DCM (5 mL) was stirred for 10 min under an atmosphere of argon at room temperature. After the mixture was cooled to −78 °C, trimethylsilyl trifluoromethanesulfonate (7.2 μL, 0.04 mmol) was added, and the reaction mixture was allowed to warm to 0 °C over a period of 40 min. After cooling of the reaction mixture to −78 °C, glycosyl acceptor (0.06 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (16 mg, 0.08 mmol) were added. The reaction mixture was allowed to warm slowly to room temperature and kept overnight at room temperature. After quenching with aqueous saturated $NaHCO_3$ (5 mL), the organic phase was dried ($MgSO_4$) and filtered, and the

filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane)

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)-ethyl}-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (10): $[\alpha]^{20}_D = +56.8°$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99−7.86 (m, 6H, aromatic), 7.53−7.08 (m, 19H, aromatic), 6.19 (t, 1H, $J = 9.5$ Hz, H-3), 5.45 (t, 1H, $J = 10.0$ Hz, H-3′), 5.41 (t, 1H, $J = 10.0$ Hz, H-4), 5.26 (dd, 1H, $J = 4.0$, 9.5 Hz, H-2), 5.23 (d, 1H, $J = 4.0$ Hz, H-1), 5.07 (d, 1H, $J = 3.0$ Hz, H-1′), 4.82 (t, 1H, $J = 9.5$ Hz, H-4′), 4.43−4.37 (m, 2H, H-5, H-7′), 4.24−4.16 (m, 2H, H-5′, H-6a′), 4.04−4.02 (m, 1H, H-6a), 3.93−3.89 (m, 1H, H-6b′), 3.79−3.77 (m, 1H, H-6b), 3.54 (s, 3H, OCH_3), 3.48 (dd, 1H, $J = 3.0$, 10.0 Hz, H-2′), 3.24 (dd, 1H, $J = 9.0$, 14.0 Hz, H-8a′), 3.06 (dd, 1H, $J = 3.5$, 14.0 Hz, H-8b′), 2.06(s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$), 1.64 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.69, 170.02, 169.82, 165.87, 165.77, 165.56, 140.57, 136.40, 133.54, 133.366, 133.16, 133.09, 130.01, 129.96, 129.92, 129.67, 129.25, 129.09, 128.89, 128.80, 128.63, 128.58, 128.50, 128.43, 128.28, 126.54, 125.94, 96.68, 96.30, 82.20, 77.19, 72.26, 71.29, 70.47, 70.11, 68.71(2), 67.35, 67.10, 62.01, 55.61, 41.67, 20.76, 20.63, 20.56; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{54}H_{54}O_{17}S$ $[M + Na]^+$ 1029.2979, found 1029.2910.

Methyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (11): $[\alpha]^{20}_D = -14.6°$ ($c = 0.3$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99−7.85 (m, 6H, aromatic), 7.52−7.09 (m, 24H, aromatic), 6.17 (t, 1H, $J = 10.0$ Hz, H-3), 5.54 (t, 1H, $J = 9.0$ Hz, H-3′), 5.42 (t, 1H, $J = 10.0$ Hz, H-4), 5.26(dd, 1H, $J = 4.0$, 10.0 Hz, H-2), 5.19 (d, 1H, $J = 4.0$ Hz, H-1), 5.01 (d, 1H, $J = 3.0$ Hz, H-1′), 4.48 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.43 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.38−4.36 (m, 2H, H-5, H-7′), 4.27−4.10 (m, 3H, H-5′, H-6a′,H-6b′), 3.89 (t, 1H, $J = 10.0$ Hz, H-6a), 3.75 (d, 1H, $J = 10.0$ Hz, H-6b), 3.51 (s, 3H, OCH_3), 3.38−3.34 (m, 2H, H-2′, H-4′), 3.26 (dd, 1H, $J = 8.5$, 14.0 Hz, H-8a′), 3.03 (dd, 1H, $J = 5.0$, 14.0 Hz, H-8b′), 2.04 (s, 3H, $COCH_3$), 1.70 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.66, 169.71, 165.81, 165.76, 165.57, 140.69, 137.53, 136.46, 133.46, 133.29, 133.04, 129.96, 129.93, 129.67, 129.28, 129.22, 129.14, 128.82, 128.59, 128.54, 128.46, 128.43, 128.39, 128.25, 128.08, 127.85, 127.06, 126.74, 125.85, 96.62, 96.19, 81.74, 77.22, 76.14, 73.81, 72.74, 72.23, 70.53, 69.93, 68.67, 68.34, 67.12, 62.87, 55.69, 41.43, 21.98, 20.88; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{59}H_{58}O_{16}S$ $[M + Na]^+$ 1077.3342, found 1077.3396.

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)-ethyl}-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-manopyranoside (13): $[\alpha]^{20}_D = -11.0$ ° ($c = 0.4$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13−7.81 (m, 6H, aromatic), 7.64−7.08 (m, 19H, aromatic), 5.91 (dd, 1H, $J = 3.5$, 10.0 Hz, H-3), 5.81 (t, 1H, $J = 10.0$ Hz, H-4), 5.69 (m, 1H, H-2), 5.45 (t, 1H, $J = 9.5$ Hz, H-3′), 5.06 (d, 1H, $J = 3.50$ Hz, H-1′), 4.93 (s, 1H, H-1), 4.82 (t, 1H, $J = 9.5$ Hz, H-4′), 4.41−4.37 (m, 2H, H-5, H-7′), 4.22−4.19 (m, 1H, H-5′), 4.13−4.10 (m, 1H, H-6a′), 4.01−3.98 (m, 21H, H-6a, H-6b′), 3.81−3.79 (m, 1H, H-6b), 3.57 (s, 3H, OCH_3), 3.47 (dd, 1H, $J = 3.0$, 10.0 Hz, H-2′), 3.23 (dd, 1H, $J = 8.5$, 14.0 Hz, H-8a′), 2.94 (dd, 1H, $J = 4.5$, 14.0 Hz, H-8b′), 1.96 (s, 3H, $COCH_3$), 1.92 (s, 3H, $COCH_3$), 1.69 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.61, 169.94, 169.81, 165.78, 165.55, 165.40, 129.97, 129.83, 129.72, 129.37, 129.13, 128.96, 128.91, 128.70, 128.61, 128.51, 128.36, 98.51, 96.37, 81.83, 77.22, 71.32, 70.68, 70.01, 69.76, 68.66, 67.58, 67.43, 67.23, 61.98, 55.52, 41.34, 20.64 (3); HR MALDI-TOF MS (*m*/*z*) calcd for $C_{54}H_{54}O_{17}S$ $[M + Na]^+$ 1029.2979, found 1029.2934.

Methyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-manopyranoside (14): $[\alpha]^{20}_D = -181.4°$ ($c = 1.5$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12−7.81 (m, 6H, aromatic), 7.63−7.08 (m, 24H, aromatic), 5.90 (dd, 1H, $J = 3.0$, 10.0 Hz, H-3), 5.80 (t, 1H, $J = 10.0$ Hz, H-4), 5.67 (s, 1H, H-1), 5.57 (t, 1H, $J = 10.0$ Hz, H-3′), 5.04 (d, 1H, $J = 3$ Hz, H-1′), 4.90 (s, 1H, H-2), 4.96 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.43 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.39−4.32 (m, 2H, H-5, H-7′), 4.23−4.21 (m, 1H, H-6a′), 4.14−4.09 (m, 2H, H-5′, H-6b′), 3.99−3.95 (m, 1H, H-6a), 3.78−3.76 (m, 1H, H-6b), 3.54 (s, 3H, OCH_3), 3.39−3.34 (m, 2H, H-2′, H-4′), 3.25 (dd, 1H, 2.06, $J = 8.0$, 14.0 Hz, H-8a′), 2.92 (dd, 1H, $J = 5.0$, 14.0 Hz, H-8b′), 1.92 (s, 3H, $COCH_3$), 1.74 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.59, 169.65, 165.76, 165.56, 165.41, 140.59, 137.59, 136.44, 133.48, 133.45, 133.08, 129.99, 129.87, 129.73, 129.40, 129.18, 128.93, 128.69, 128.58, 128.51, 128.47, 128.43, 128.32, 128.26, 127.88, 127.84, 126.81, 125.85, 98.47, 96.22, 81.40, 77.23, 76.06, 73.78, 72.82, 70.67, 70.07, 69.72, 68.32, 67.47, 62.87, 55.59, 41.14, 21.04, 20.74; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{59}H_{58}O_{16}S$ $[M+Na]^+$ 1077.3342, found 1077.3392.

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)-ethyl}-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (16): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33−7.05 (m, 25H, aromatic), 5.36 (t, 1H, $J = 9.5$ Hz, H-3′), 5.19 (d, 1H, $J = 3.5$ Hz, H-1′), 4.97−4.90 (m, 2H, C*H*HPh), 4.84−4.79 (m, 2H, C*H*HPh, H-4′), 4.73−4.69 (m, 2H, C*H*HPh), 4.61−4.56 (m, 2H, C*H*HPh, H-1), 4.49 (dd, 1H, $J = 5.0$, 8.0 Hz, H-7′), 4.18−4.12 (m, 2H, H-4, H-6a′), 4.06 (d, 1H, $J = 11.0$ Hz, H-6b′), 4.01−3.95 (m, 3H, H-3, H-6a, H-6b), 3.60 (dd, 1H, $J = 3.5$, 9.5 Hz, H-2), 3.54−3.51 (m, 2H, H-5′, H-5), 3.51 (dd, 1H, $J = 3.5$, 9.5 Hz, H-2′), 3.42 (s, 3H, OCH_3), 3.25 (dd, 1H, $J = 8.0$, 14.0 Hz, H-8a′), 3.07 (dd, 1H, $J = 5.0$, 14.0 Hz, H-8b′), 1.99 (s, 3H, $COCH_3$), 1.94 (s, 3H, $COCH_3$), 1.65 (s, 3H, $COCH_3$); HR MALDI-TOF MS (*m*/*z*) calcd for $C_{54}H_{60}O_{14}S$ $[M + Na]^+$ 987.3601, found 987.3659.

Methyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (17): $[\alpha]^{20}_D = -221.7°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34−7.07 (m, 30H, aromatic), 5.51 (t, 1H, $J = 9.5$ Hz, H-3′), 5.14 (d, 1H, $J = 3.0$ Hz, H-1′), 4.96 (d, 1H, $J = 12.0$ Hz, C*H*HPh), 4.94 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.82 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.69 (d, 1H, $J = 12.0$ Hz, C*H*HPh), 4.67 (d, 1H, $J = 12.0$ Hz, C*H*HPh), 4.59 (d, 1H, $J = 3.0$ Hz, H-1), 4.58 (d, 1H, $J = 12.0$ Hz, C*H*HPh), 4.47 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.48−4.41 (m, 1H, H-7′), 4.40 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.20 (dd, 1H, $J = 2.0$, 12.0 Hz, H-6a′), 4.13 (dd, 1H, $J = 4.0$, 12.0 Hz, H-6b′), 3,99 (t, 1H, $J = 9.5$ Hz, H-3), 3.92−3.91 (m, 1H, H-5′), 3.85−3.83 (m, 1H, H-5), 3.80 (m, 2H, H-6a, H-6b), 3.64 (t, 1H, $J = 9.5$ Hz, H-4), 3.58 (dd, 1H, $J = 3.0$, 9.5 Hz, H-2), 3.40 (s, 3H, OCH_3), 3.38−3.34(m, 2H, H-2′, H-4′), 3.31(dd, 1H, $J = 7.0$, 13.5 Hz, H-8a′), 3.05(dd, 1H, $J = 5.0$, 13.5 Hz, H-8b′), 1.99 (s, 3H, $COCH_3$), 1.72 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.61, 169.66, 140.41, 138.88, 138.40, 138.22, 137.50, 136.53, 128.94, 128.75, 128.49, 128.45, 128.40, 128.34, 128.27, 128.06, 127.92, 127.76, 127.62, 127.49, 126.87, 125.85, 97.88, 96.60, 82.27, 80.93, 80.24, 78.02, 77.23, 76.12, 75.69, 75.03, 74.03, 73.27, 73.05, 70.18, 68.32, 66.37, 62.80, 55.26, 41.49, 20.91, 20.84; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{59}H_{64}O_{13}S$ $[M + Na]^+$ 1035.3965, found 1035.3988.

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)-ethyl}-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (19): $[\alpha]^{20}_D = +66.5°$ ($c = 0.4$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−6.97 (m, 25H, aromatic), 5.71 (d, 1H, $J = 3.5$ Hz, H-1′), 5.35 (t, 1H, $J = 10.0$ Hz, H-3′), 5.07 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.96 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.78 (t, 1H, $J = 10.0$ Hz, H-4′), 4.71 (d, 1H, $J = 9.5$ Hz, C*H*HPh), 4.63−4.54 (m, 3H, H-1, C*H*HPh), 4.35 (t, 1H, $J = 7.0$ Hz, H-7′), 4.17 (t, 1H, $J = 9.5$ Hz, H-3), 4.10−3.93 (m, 4H, H-4, H-5, H-6a, H-5′), 3.85−3.82 (m, 1H, H-6b), 3.76−3.74 (m, 1H, H-6b′), 3.67−3.65 (m, 1H, H-6′), 3.60 (dd, 1H, $J = 3.5$, 9.5 Hz, H-2), 3.38 (s, 3H, OCH_3), 3.34 (dd, 1H, $J = 3.5$, 10.0 Hz, H-2′), 3.25 (dd, 1H, $J = 7.0$, 13.0 Hz, H-8a′), 2.89 (dd, 1H, $J = 7.0$, 13.0 Hz, H-8b′), 1.97 (s, 3H, $COCH_3$), 1.94 (s, 3H, $COCH_3$), 1.73 (s, 3H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.55, 170.04, 169.64, 140.08 139.31, 138.06, 137.97, 136.60, 128.87, 128.53, 128.54, 128.36, 128.28, 128.15, 127.92, 127.61, 127.36, 127.09, 126.87, 126.83, 125.68, 97.91, 94.97, 81.35, 81.28, 80.13, 77.22, 76.13, 74.23, 73.42,

73.29, 71.21, 69.66, 68.83, 68.69, 67.50, 61.92, 55.36, 40.83, 20.73, 20.65, 20.20; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{54}H_{60}O_{14}S$ [M + Na]$^+$ 987.3601, found 987.3666.

Methyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (20): $[\alpha]^{20}_D = -103.65°$ (c = 2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−6.98 (m, 30H, aromatic), 5.63 (d, 1H, J = 3.0 Hz, H-1′), 5.45 (t, 1H, J = 10.0 Hz, H-3′), 5.06 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.97 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.72 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.61 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.61(d, 1H, J = 3.0 Hz, H-1), 4.53 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.50 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.47 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.38 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.33 (t, 1H, J = 6.0 Hz, H-7′), 4.14 (t, 1H, J = 9.0 Hz, H-3), 4.08−3.89 (m, 5H, H-6a′, H-6b′, H-5′, H-5, H-6b), 3.71−3.69 (m, 1H, H-6a), 3.63−3.61 (m, 1H, H-4), 3.58 (dd, 1H, J = 3.0, 9.0 Hz, H-2), 3.37 (s, 3H, OCH_3), 3.34−3.29 (m, 2H, H-4′, H-8b′), 3.22 (dd, 1H, J = 3.0, 10.0 Hz, H-2′), 2.87 (dd, 1H, J = 6.0, 14.0 Hz, H-8a′), 1.96 (s, 3H, $COCH_3$), 1.81 (s, 3H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.51, 169.67, 140.08 139.45, 138.12, 138.02, 137.60, 136.70, 128.81, 128.47, 128.43, 128.33, 128.25, 128.21, 128.16, 127.92, 127.41, 127.141, 127.06, 126.95, 125.56, 97.91, 94.95, 81.55, 80.90, 80.01, 77.22, 76.80, 76.11 (2), 74.36, 74.23, 73.27 (2), 72.87, 69.66, 68.74, 62.82, 55.28, 40.53, 21.04, 20.86; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{59}H_{64}O_{13}S$ [M + Na]$^+$ 1035.3965, found 1035.3979.

Procedure for Low-Temperature NMR Experiments. The ^{1}H NMR spectrum of **8** (14 mg, 0.02 mmol) in CD_2Cl_2 (0.5 mL) was recorded: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.67 (s, 1H, N*H*), 7.39−7.18 (m, 15H, aromatic), 6.58 (d, 1H, J = 3.0 Hz, H-1)**,** 5.48 (t, 1H, J = 10.0 Hz, H-3), 4.53 (t, 1H, J = 6.5 Hz, H-7), 4.49 (d, 1H, J = 10.5 Hz, C*H*HPh), 4.46 (d, 1H, J = 10.5 Hz, C*H*HPh), 4.30−4.08 (m, 1H, H-6a), 4.16−4.12 (m, 1H, H-6b), 4.09−4.05 (m, 1H, H-5), 3.55 (dd, 1H, J = 3.0, 10.0 Hz, H-2), 3.51 (t, 1H, J = 10.0 Hz, H-4), 3.29 (dd, 1H, J = 7.0, 14.0 Hz, H-8a), 3.08 (dd, 1H, J = 7.0, 14.0 Hz, H-8b), 1.98 (s, 3H, $COCH_3$), 1.85 (s, 3H, $COCH_3$).

Trimethylsilyl trifluoromethanesulfonate (3.6 μL, 0.02 mmol) was added to the above solution at −50 °C. The reaction mixture was allowed to warm slowly to 0 °C. The NMR spectra of **21** (^{1}H, ^{1}H TOCSY 1D, HSQC, and HMBC) were recorded at −20 °C. **21**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.89−7.87 (m, 2H, aromatic), 7.76−7.74 (m, 1H, aromatic), 7.65−7.62 (m, 2H, aromatic), 7.41−7.16 (m, 10H, aromatic), 5.48 (t, 1H, J = 9.5 Hz, H-3), 5.35 (d, 1H, J = 11.0 Hz, H-7), 5.30 (d, 1H, J = 9.5 Hz, H-1)**,** 4.56 (d, 1H, J = 11.5 Hz, C*H*HPh), 4.50 (d, 1H, J = 11.5 Hz, C*H*HPh), 4.32 (d, 1H, J = 11.0 Hz, H-8eq), 4.16−4.08 (m, 3H, H-2, H-6a, H-6b), 3.81 (t, 1H, J = 9.5 Hz, H-4), 3.77 (m, 1H, H-5), 3.66 (t, 1H, J = 11.0 Hz, H-8ax), 1.96 (s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$).

Methanol was added to the reaction mixture at the same temperature, and the ^{1}H NMR spectrum of **22** was recorded at 0 °C. **22**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.39−7.18 (m, 15H, aromatic), 5.47 (t, 1H, J = 9.0 Hz, H-3), 4.84 (d, 1H, J = 3.5 Hz, H-1), 4.44 (d, 1H, J = 11.5 Hz, C*H*HPh), 4.39 (d, 1H, J = 11.5 Hz, C*H*HPh), 4.39 (t, 1H, J = 5.5 Hz, H-7), 4.27−4.11 (m, 2H, H-6a, H-6b), 3.81−3.77 (m, 1H, H-5), 3.40 (s, 3H, OCH_3), 3.36−3.26 (m, 3H, H-2, H-4, H-8a), 3.10 (dd, 1H, J = 5.5, 14.0 Hz, H-8b), 1.96 (s, 3H, $COCH_3$), 1.72 (s, 3H, $COCH_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.18 (m, 15H, aromatic), 5.49 (t, 1H, J = 9.6 Hz, H-3), 4.94 (d, 1H, J = 3.6 Hz, H-1), 4.49 (d, 1H, J = 11.1 Hz, C*H*HPh), 4.42 (d, 1H, J = 11.1 Hz, C*H*HPh), 4.40 (t, 1H, J = 6.3 Hz, H-7), 4.25−4.22 (m, 2H, H-6a, H-6b), 3.92−3.86 (m, 1H, H-5), 3.44 (s, 3H, OCH_3), 3.41−3.30 (m, 3H, H-2, H-4, H-8a), 3.10 (dd, 1H, J = 4.8, 13.8 Hz, H-8b), 2.03 (s, 3H, $COCH_3$), 1.66 (s, 3H, $COCH_3$).

The ^{1}H NMR spectrum of **21** showed that the anomeric proton (H1) signal (δ 6.58, d, $J_{1,2}$ = 2.5 Hz, α-configuration) was shifted to upfield (δ 5.30, d, $J_{1,2}$ = 9.5 Hz, β-configuration). The change of anomeric configuration indicate that the α-imidate donor **8** was completely transformed to a new intermediate **21** after activation. H1, H7, H8eq, and H8ax signals of **21** were assigned from ^{1}H TOCSY 1D data irradiated on H4 and H7. The anomeric carbon signal (C1, δ 88.0) of **21** was assigned from HSQC data. The HMBC spectrum of **21** showed the three-bond coupling between C1 (δ 88.0) and H8eq (δ 4.32), which confirmed the presence of the C1−H8eq bond. So, the *trans*-decalin structure of the sulfonium ion **21** was proved directly from the low-temperature NMR experiments.

3,6-Di-*O*-acetyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (23): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H, NH), 7.35−7.24 (m, 10H, aromatic), 6.47 (d, 1H, J = 3.5 Hz, H-1), 5.62 (t, 1H, J = 9.5 Hz, H-3), 4.68 (d, 1H, J = 12.0 Hz, CHHPh), 4.59 (d, 1H, J = 11.0 Hz, CHHPh), 4.55 (d, 1H, J = 12.0 Hz, CHHPh), 4.53 (d, 1H, J = 11.0 Hz, CHHPh), 4.31 (dd, 1H, J = 2.5, 12.5 Hz, H-6a), 4.24 (dd, 1H, J = 4.5, 12.5 Hz, H-6b), 4.14−4.09 (m, 1H, H-5), 3.66 (dd, 1H, J = 3.5, 9.5 Hz, H-2), 3.62 (t, 1H, J = 9.5 Hz, H-4), 2.03 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$).

Methyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (24) (mixture as α/β = 3/1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (t, 1H, J = 9.5 Hz, H-3′-α), 5.22 (t, 1H, J = 9.0 Hz, H-3′-β), 4.96 (d, 1H, J = 3.0 Hz, H-1′-α), 4.38 (d, 1H, J = 8.5 Hz, H-1′-β), 3.36 (s, 3H, OCH_3-α), 3.34 (s, 3H, OCH_3-β), 2.01 (s, 3H, $COCH_3$-β), 2.00 (s, 3H, $COCH_3$-α), 1.97 (s, 3H, $COCH_3$-α), 1.86 (s, 3H, $COCH_3$-β).

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(2-(phenylsulfanyl)ethyl)-α-D-glucopyranosyl trichloroacetimidate (25): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (s, 1H, =N*H*), 7.38−7.17 (m,10H, aromatic), 6.51 (d, 1H, J = 3.6 Hz, H-1), 5.56 (t, 1H, J = 9.6 Hz, H-3), 4.60 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.54 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.34−4.21 (m, 2H, H-6a, H-6b), 4.14−4.09 (m, 1H, H-5), 3.86−3.49 (m, 4H, H-7a, H-7b, H-4, H-2), 3.08−2.99 (m, 2H, H-8a, H-8b), 2.04 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.49, 169.71, 161.24, 137.09, 135.76, 129.64, 129.46, 129.02, 128.60, 128.26, 128.22, 128.18, 128.07, 126.40, 126.32, 93.45, 77.84, 75.25, 74.55, 72.93, 71.19, 69.82, 62.38, 33.39, 21.11, 20.78.

Methyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-(2-(phenylsulfanyl)ethyl)-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (26) (mixture as α/β = 8/1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (t, 1H, J = 10.0 Hz, H-3′-α), 5.17 (t, 1H, J = 9.5 Hz, H-3′-β), 5.02 (d, 1H, J = 3.5 Hz, H-1′-α), 4.31 (d, 1H, J = 7.5 Hz, H-1′-β), 3.35 (s, 3H, OCH_3-α), 3.33 (s, 3H, OCH_3-β), 2.017 (s, 3H, $COCH_3$-α), 2.006 (s, 3H, $COCH_3$-β), 2.001 (s, 3H, $COCH_3$-β), 1.99 (s, 3H, $COCH_3$-α).

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*R*)-phenyl-2-(phenylsulfanyl)-ethyl}-α-D-glucopyranosyl Trichloroacetimidate (27). Compound **27** was synthesized according to the procedure described for the synthesis of compound **8**: colorless syrup; R_f = 0.43 (dichloromethane/acetone = 100/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H, NH), 7.26−7.36 (m, 15H, aromatic), 5.79 (d, 1H, J = 4.0 Hz, H-1), 5.68 (t, 1H, J = 10.0 Hz, H-3), 4.60 (d, 1H, J = 11.0 Hz, CHHPh), 4.53 (d, 1H, J = 11.0 Hz, CHHPh), 4.50 (dd, 1H, J = 5.0, 8.0 Hz, H-7), 4.23−4.16 (m, 2H, H-6a, H-6b), 4.03−4.00 (m, 1H, H-5), 3.65 (dd, 1H, J = 4.0, 10.0 Hz, H-2), 3.60 (t, 1H, J = 10.0 Hz, H-4), 3.25 (dd, 1H, J = 8.0, 13.5 Hz, H-8a), 3.05 (dd, 1H, J = 5.0, 13.5 Hz, H-8b), 2.08 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$).

Methyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-{(1*R*)-phenyl-2-(phenylsulfanyl)ethyl}-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (28) (mixture as α/β = 1/1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.59 (t, 1H, J = 10.0 Hz, H-3′-α), 5.28 (t, 1H, J = 9.0 Hz, H-3′-β), 4.24 (d, 1H, J = 6.5 Hz, H-1′-β), 4.23 (d, 1H, J = 3.5 Hz, H-1′-α), 2.04 (s, 3H, $COCH_3$-α), 2.00 (s, 3H, $COCH_3$-β), 1.98 (s, 3H, $COCH_3$-β), 1.95 (s, 3H, $COCH_3$-α).

Acetyl 3,4,6-Tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)-ethyl}-α-D-galactopyranose (51). Boron trifluoride diethyl etherate (190 μL, 1.5 mmol) was added to a solution of acetyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranose (348 mg, 1.0 mmol), acetic acid (1*S*)-phenyl-2-(phenylsulfanyl)ethyl ester (408 mg, 1.5 mmol), and activated molecular sieves (4 Å) in dichloromethane (5 mL) at 0 °C. After 20 min, the

reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic phase was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (25% ethyl acetate in hexane) to afford **51** (504 mg, 90%): colorless syrup; $R_f = 0.37$ (ethyl acetate/hexane, 1/2); $[\alpha]^{20}_D = -9.0°$ ($c = 4.0$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.14 (m,10H, aromatic), 6.49 (d, 1H, $J = 3.6$ Hz, H-1), 5.37−5.36 (m, 1H, H-4), 5.24 (dd, 1H, $J = 3.3$, 10.2 Hz, H-3), 4.51 (dd, 1H, $J = 4.8$, 9.6 Hz, H-7), 4.27−4.23 (m, 1H, H-5), 4.03−3.96 (m, 2H, H-6b, H-6a), 3.83 (dd, 1H, $J = 3.6$, 10.2 Hz, H-2), 3.20 (dd, 1H, $J = 9.6$, 13.8 Hz, H-8a), 3.07 (dd, 1H, $J = 4.8$, 13.8 Hz, H-8b), 2.18 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 1.92 (s, 3H, $COCH_3$), 1.76 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.38, 169.98, 169.97, 169.42, 140.06, 136.39, 129.28, 128.99, 128.95, 128.92, 128.88, 128.68, 128.38, 126.85, 126.75, 126.16, 89.61, 81.24, 71.55, 68.84, 68.33, 67.67, 61.26, 41.77, 21.171, 20.65, 20.48, 20.43; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{28}H_{32}O_{10}S$ $[M + Na]^+$ 583.1614, found 583.1611.

3,4,6-Tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-α-D-galatopyranosyl Trichloroacetimidate (29). Hydrazinium acetate (91 mg, 0.99 mmol) was added to a solution of **51** (504 mg, 0.9 mmol) in DMF (5 mL) at room temperature. The reaction mixture was stirred overnight and then quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (20 mL). The combined organic phases were washed with saturated aqueous NH_4Cl (20 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (25% ethyl acetate in hexane) to afford 3,4,6-tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-D-galactopyranose (**52**) (434 mg, 93%). Trichloroacetonitrile (0.84 mL, 8.4 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (50 μL, 0.33 mmol) were added to a solution of **52** (434 mg, 0.84 mmol) in dichloromethane (10 mL) at 0 °C. The reaction mixture was stirred at this temperature for 1 h and then concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **29** (505 mg, 91%): $R_f = 0.32$ (ethyl acetate/hexane, 1/3); $[\alpha]^{20}_D = -56.37°$ ($c = 3.0$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H, N*H*), 7.34−7.18 (m, 10H, aromatic), 6.70 (d, 1H, $J = 3.3$ Hz, H-1), 5.43−5.42 (m, 1H, H-4), 5.28 (dd, 1H, $J = 3.3$, 10.5 Hz, H-3), 4.57 (dd, 1H, $J = 5.7$, 7.8 Hz, H-7), 441−4.37 (m, 1H, H-5), 4.11−3.99 (m, 2H, H-6a, H-6b), 3.94 (dd, 1H, $J = 3.3$, 10.5 Hz, H-2), 3.21 (dd, 1H, $J = 7.8$, 13.8 Hz, H-8a), 3.11 (dd, 1H, $J = 5.7$, 13.8 Hz, H-8b), 1.99 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$), 1.69 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.33, 169.92, 169.84, 160.99, 140.26, 129.27, 129.02, 128.37, 128.25, 126.67, 126.14, 94.00, 81.41, 72.48, 69.10, 68.84, 67.71, 61.36, 41.86, 20.64, 20.45, 20.36; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{28}H_{30}Cl_3NO_9S$ $[M+Na]^+$ 684.0604, found 684.0612.

Methyl 3,4,6-Tri-*O*-acetyl-2-*O*-{(1*S*)-phenyl-2-(phenylsulfanyl)ethyl}-α-D-galatopyranosyl-(1→3)-2,6-di-*O*-benzoyl-β-D-galatopyranosyl-(1→4)-6-*O*-acetyl-3-*O*-benzyl-2-deoxy-2-azido-β-D-glucopyranoside (32). Trimethylsilyl trifluoromethanesulfonate (9.0 μL, 0.05 mmol) was added to a solution of **29** (66 mg, 0.1 mmol) and activated molecular sieves (4 Å) in DCM (10 mL) at 0 °C. After 5 min, phenyl 2,6-di-*O*-benzoyl-1-thio-β-D-galatopyranoside (30) (48 mg, 0.1 mmol) was added to the reaction mixture at the same temperature. After the temperature was raised gradually to room temperature over a period of 4 h, methyl 6-*O*-acetyl-3-*O*-benzyl-2-deoxy-2-azido-β-D-glucopyranoside (**31**) (70.3 mg, 0.2 mmol) and *N*-iodosuccinimide (45.0 mg, 0.2 mmol) were added at −78 °C. The reaction mixture was allowed to warm gradually to room temperature over a period of 2 h and then quenched with aqueous saturated $NaHCO_3$ (10 mL). The organic phase was washed with aqueous solution of sodium thiosulfate (1 M, 10 mL) and then dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (25% ethyl acetate in hexane) to afford the trisaccharide **32** (63 mg, 52%) as a colorless syrup: $R_f = 0.32$ (ethyl acetate/ hexane, 1/1); $[\alpha]^{20}_D = +19.5°$ ($c = 0.2$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13−7.97 (m, 4H, aromatic), 7.57−7.19 (m, 21H, aromatic), 5.61 (t, 1H, $J = 9.0$ Hz, H-2′), 5.49 (d, 1H, $J = 4.0$ Hz, H-1″), 5.11 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 5.08−5.06 (m, 1H, H-4″), 5.05 (dd, 1H, $J = 3.0$, 10.0 Hz, H-3″), 4.77 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.64 (d, 1H, $J = 8.5$ Hz, H-1′), 4.54 (dd, 1H, $J = 3.0$, 10.0 Hz, H-7″), 4.54−4.52 (m, 1H), 4.45 (dd, 1H, $J = 7.0$, 10.0 Hz), 4.33 (m, 1H, H-4′), 4.21−4.18 (m, 1H), 4.04 (d, 1H, $J = 7.5$ Hz, H-1), 4.03−4.02 (m, 1H, H-3′), 3.89−3.78 (m, 4H, H-2″, H-4), 3.72−3.68 (m, 2H), 3.46 (s, 3H, OCH_3), 3.48−3.43 (m, 1H, H-3), 3.34−3.31 (m, 2H), 3.25 (t, 1H, $J = 9.0$ Hz, H-2), 3.20 (dd, 1H, $J = 3.0$, 10.0 Hz, H-8a″), 3.01 (dd, 1H, $J = 10.0$, 14.0 Hz, H-8b″), 1.93 (s, 3H, $COCH_3$), 1.92 (s, 3H, $COCH_3$), 1.77 (s, 3H, $COCH_3$), 1.19 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.60, 169.95, 169.75, 169.45, 166.24, 164.79, 141.20, 138.12, 135.43, 133.51, 133.08, 129.83, 129.78, 129.54, 129.34, 129.09, 128.73, 128.63, 128.42, 128.32, 128.19, 127.98, 127.65, 126.71, 125.32, 102.60, 100.93, 96.22, 84.42, 80.75, 78.94, 77.22, 77.02, 77.01, 75.46, 72.78, 72.18, 71.17, 69.73, 67.61, 66.77, 65.83, 65.57, 62.89, 62.19, 60.48, 57.18, 43.54, 20.69, 20.49, 19.65; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{62}H_{67}N_3O_{21}S$ $[M + Na]^+$ 1244.3884, found 1244.3809.

Methyl 2,3,4,6-Tetra-*O*-acetyl-α-D-galatopyranosyl-(1→3)-4-*O*-acetyl-2,6-di-*O*-benzoyl-β-D-galatopyranosyl-(1→4)-6-*O*-acetyl-3-*O*-benzyl-2-deoxy-2-azido-β-D-glucopyranoside (33). To a solution of the trisaccharide **32** (63 mg, 0.051 mmol) in acetic anhydride (3 mL) was added boron trifluoride diethyl etherate (9.7 μL, 0.077 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 40 min and then quenched with aqueous saturated $NaHCO_3$ (10 mL). After dilution with DCM (10 mL), the reaction mixture was separated. The organic phase was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (25% ethyl acetate in hexane) to afford trisaccharide **33** (53 mg, 95%) as colorless syrup: $R_f = 0.24$ (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D = +41.8$ ° ($c = 0.6$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12−7.97 (m, 4H, aromatic), 7.63−7.28 (m, 11H, aromatic), 5.57 (dd, 1H, $J = 7.5$, 9.0 Hz, H-2′), 5.46 (d, 1H, $J = 3.0$ Hz, H-1″), 5.21−5.19 (m, 2H, H-2″, H-4″), 5.05 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.99 (dd, 1H, $J = 3.0$, 10.0 Hz, H-3″), 4.83 (d, 1H, $J = 11.0$ Hz, C*H*HPh), 4.83−4.81 (m, 1H, H-4′), 4.70 (d, 1H, $J = 9.0$ Hz, H-1′), 4.28−4.11 (m, 4H), 4.06 (d, 1H, $J = 7.5$ Hz, H-1), 4.03 (dd, 1H, $J = 3.5$, 10.0 Hz, H-3′), 3.98 (t, 1H, $J = 7.0$ Hz), 3.86 (t, 1H, $J = 7.0$ Hz), 3.83−3.73 (m, 3H), 3.47 (s, 3H, OCH_3), 3.43 (t, 1H, $J = 9.0$ Hz), 3.40−3.27 (m, 2H), 2.16 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.93 (s, 3H, $COCH_3$), 1.87 (s, 3H, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.44, 170.13(2), 169.95, 169.63, 169.40, 165.87, 164.69, 138.23, 133.88, 133.46, 129.89, 129.77, 129.29, 128.83, 128.65, 128.54, 128.24, 127.29, 127.60, 102.65, 100.92, 93.74, 80.81, 77.22, 76.77, 75.14, 73.67, 72.68, 70.94, 67.63, 66.88, 66.66, 66.47, 65.72, 64.78, 61.69, 61.30, 61.15, 57.22, 20.77, 20.73, 20.66, 20.62, 20.52, 20.49; HR MALDI-TOF MS (*m*/*z*) calcd for $C_{52}H_{59}N_3O_{23}$ $[M + Na]^+$ 1116.3436, found 1116.3418.

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Supporting Information Available: General procedures, experimental method for the preparation of compound **25** and acetic acid (1*S*)-phenyl-2-phenylsulfanyl-ethyl ester, alternative preparation of compound **8**, ^{1}H NMR spectra of all compounds, and ^{1}H, ^{1}H-TOCSY, HSQC, and HMBC NMR spectra of episulfonium ion **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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