Coupling of Glycal Derived Thioethyl Glycosyl Donors with Glycal Acceptors. An Advance in the Scope of the Glycal Assembly

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Abstract: Glycals were converted into thioethyl glycosyl donors through 1,2-anhydrosugar intermediates. Various participating groups in the C-2 position were examined for formation of β-glucosyl, β-galactosyl, and α-mannosyl linkages. A number of disaccharides was prepared employing a novel coupling protocol involving thioethyl 2-pivaloyl glycosyl donors and glycal acceptors. Using this methodology, a linear tetrasaccharide containing exclusively β-glucosyl-(1→4) linkages was prepared in high yields. Ready application to α-mannosylation and C2 branching are other hallmarks of the method.

Introduction and Purpose of the Investigation

Complex biomolecules carry detailed structural information which serves to mediate a range of biological events including inflammation, immunological response, and metastasis.[1] Not surprisingly, there has been a continuing quest to develop a broader range of glycosyl donors to service increasingly sophisticated oligosaccharide construction problems.[2] Trichloroacetimidates,[3] *N*-pentenylglycosides,[4] anomeric fluorides,[5] anomeric aryl sulfoxides,[6] and anomeric thioglycosyl donors have been successfully applied to this problem.[7]

Our laboratory has explored the use of glycals for the synthesis of oligosaccharides and glycoconjugates.[8] Glycals may be converted into a number of glycosyl donors.[9] For instance, epoxidation of glycals provides access to 1,2-anhydrosugars, which, in the presence of Lewis acid catalysts, proved to be excellent glycosyl donors in a range of glycosylation reactions. The heart of our method involves the use of glycal derived donors with suitably differentiated glycal acceptors, thereby providing the feature of smooth reiterability. Indeed, the adaptability of the logic of glycal assembly to solid phase synthesis has been demonstrated.[8]

Glycal derived epoxy donors (such as cyclic carbonate **A**) are particularly effective in enabling *β-galactosylation*. They function well even when the acceptor hydroxyl site is secondary and surrounded by protecting groups as is typical in oligosaccharide synthesis (see **A** → **B**). By contrast, the analogous glucal derived epoxides (*cf.* **C**), lacking a comparable interlocking pattern between C3 and C4, are considerably more labile with respect to typical Lewis acid promoters (*cf.* anhydrous zinc chloride). This heightened reactivity brings with it significant limitations to the scope of their effectiveness as β-glycosyl donors. When the acceptor sites have been primary alcohols or relatively unhindered secondary alcohol centers, β-glucosidations are achieved in decent overall yields of 50−75%. However, when the hydroxyl site is hindered, donor decomposition and oligomerization can undermine the projected reaction (**C** → **D**). After extensive study, β-glucosidation via direct use of 1,2-α epoxides was realized to be problematic when the acceptor reactivity of the hydroxyl group in ROH is diminished. Two particularly vulnerable cases involve glucosidations of donor type **C** with acceptor types **E** and **F**. The former case (**C** + **E**) would be required to build 1,4-β glucoside linkages, while the second instance (**C** + **F**) would be of strategic importance for the synthesis of certain branched glycosides.

For these reasons, it was necessary to upgrade the 1,2-α-glucal epoxide method. The thought was to use epoxide type **C** to produce a new donor generalized as **G**. The nature of the C2 substituent would be such as to favor β-glucoside in the glycosylation event. A key condition to be met by the method is that it be applicable to hindered glycal acceptors such as **E**. In this way, product **H** would be generated. The presence of the glycal linkage in **H** would invite reiteration of the scheme.

Another purpose of this investigation was to deal with the question of mannosylation. In particular we sought to generate an α-mannosyl donor (**I**) from a glucal epoxide (*cf.* **C**). Once again the condition for success that we set was that donor **I** might react with glycal acceptor (*cf.* **J**) to furnish a product of the type **K**. The possibility of translating such a paradigm to the solid phase did not escape our notice.

Thioalkyl or -aryl glycosyl donors have previously been shown in impressive studies of the Garegg school to provide access to β-glucosyl-(1→4) linkages in good yield. Donor activation is accomplished by either heavy metal salts[7] or

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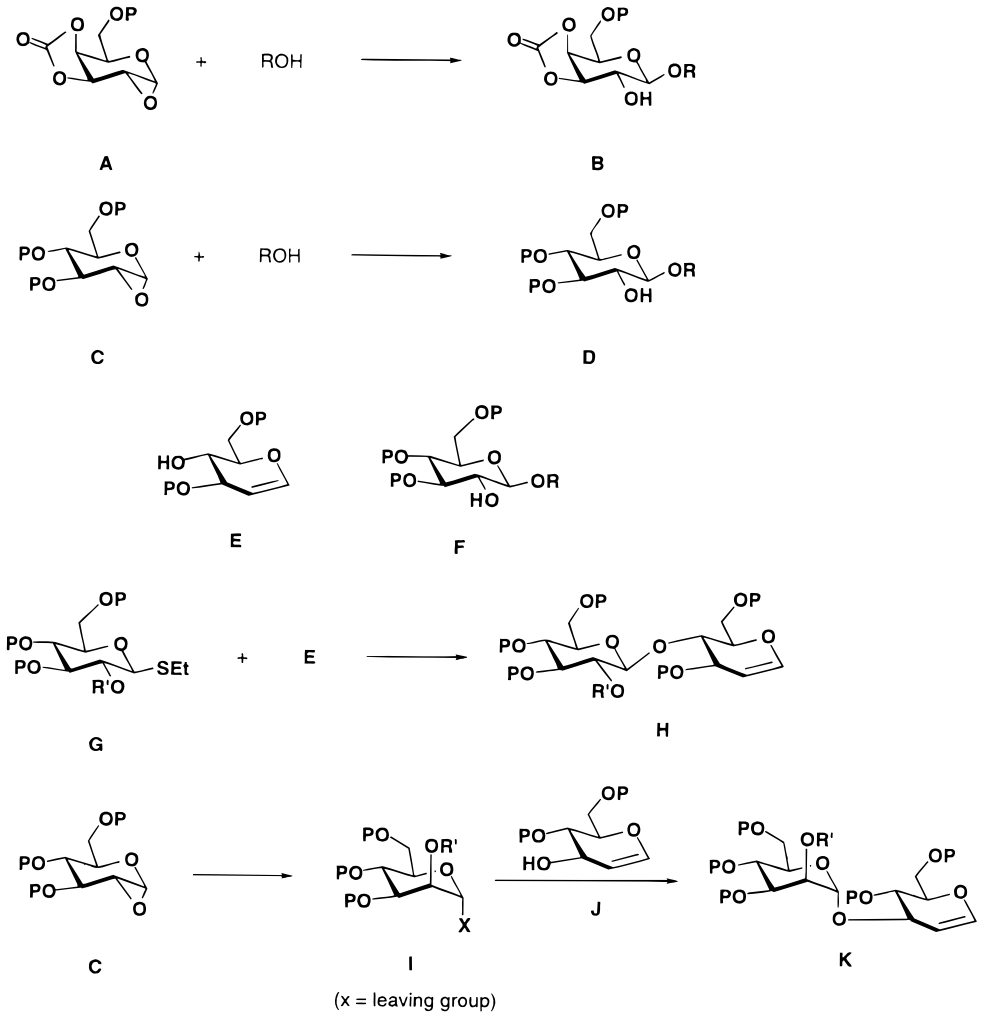
Scheme 1. Glycosylation Using Glycal Derived Donors



directly and more efficiently by thiophilic reagents.[10,11] The stereoselectivity of the glycosylation reaction is greatly influenced by the nature of the protecting group on the C2-hydroxyl. Neighboring group participation of the C2 blocking group can be used to ensure a very high degree of stereoselectivity for the glycosylation reaction.

We first addressed the conversion of glycals into thioalkyl glycosyl donors and coupling of these glycosyl donors with glycal acceptors. Such a scheme takes advantage of the relative ease of exposing specific acceptor sites on glycals.[8] Moreover, it was critical to develop conditions which would allow for the coupling of such donors with glycal acceptors with maintenance of the sensitive 1,2-double bond in the acceptor. This reasoning has been reduced to practice as demonstrated by the synthesis of a β-(1→4) linked tetrasaccharide, branched trisaccharides, and α-mannosides.

Results and Discussion

Protected glycal derivatives **1**−**3** are either commercially available or can be easily derived from unprotected glycals. We had previously described the conversion of **1** to thioethyl glycoside **4** by epoxidation with dimethyldioxirane to produce the 1,2 anhydrosugar. Opening of the epoxide with ethanethiolate in the presence of zinc chloride was achieved, but the reaction proceeded in only modest yield (35%).[9,12] Sharp improvement of this procedure was accomplished by opening the 1,2-anhydrosugar intermediate in a mixture of ethanethiol and dichloromethane (1:1) in the presence of a trace of trifluoroacetic acid. The thioethyl glucosides **4** and **5** and galactoside **6** were obtained in significantly higher yields (71−78%).

The thioethyl glycosides **4** and **5** could be converted into the mannosides (**7** and **8**). This overall inversion of configuration started with oxidation (DMSO/acetic anhydride)[13] of the glucosides to produce the C2 ketones. This step was followed by reduction of the ketone with sodium borohydride to provide the mannose derivative exclusively. Protection of the C2-hydroxyl could now be accomplished by acylation. The reagents we used for acylation were either acetic anhydride, benzoyl chloride, 4-methoxybenzoylchloride, or pivaloylchloride in the presence of DMAP. These reaction sequences furnished the protected thioethyl glycosides **9**−**21** in very good yields (Figure 1). With thioethyl glycosyl donors **9**−**21** in hand, glycosylation conditions using glycals as acceptors were studied. The goal was to achieve reliable, stereoselective formation of glycosidic bonds.

Initially, glycosylations using donors carrying C2-acetyl protecting groups (**9**−**11**, **17**, **18**) were explored. While it was possible to activate the thioglycosides by using methyltriflate as a thiophile, partial degradation of the glycal double bond,

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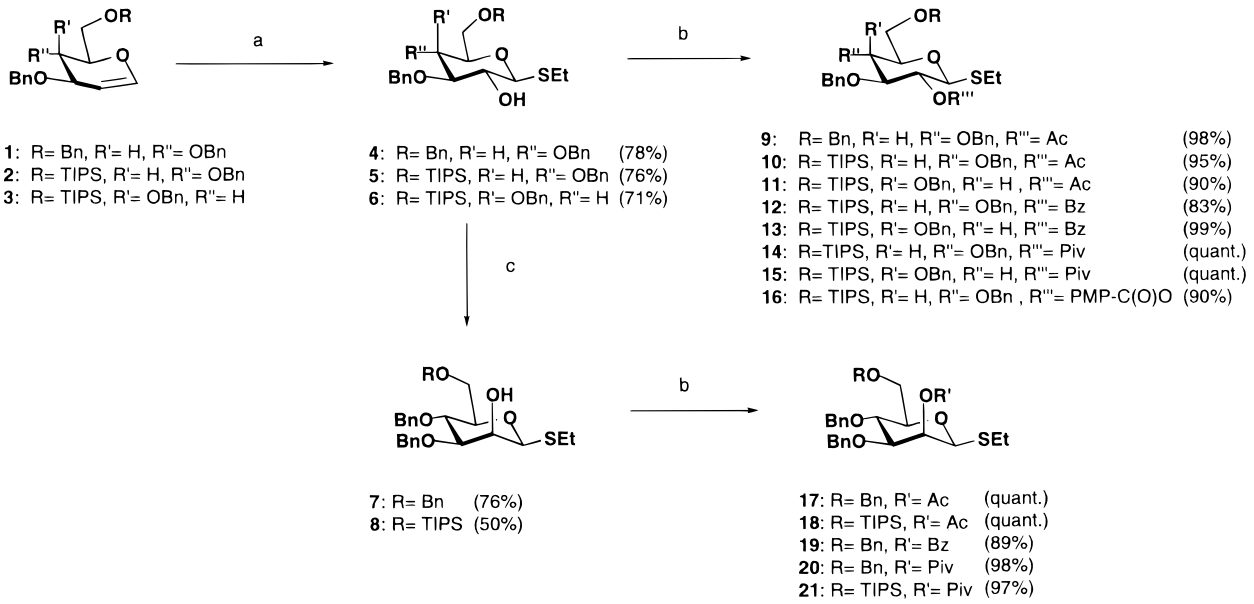


Figure 1. Synthesis of glycosyl thioethyl donors from glycal precursors: (a) 1. DMDO, acetone, CH_2Cl_2, 2. EtSH, CH_2Cl_2, cat. TFAA; (b) Ac_2O, pyridine, CH_2Cl_2, DMAP; or PivCl, DMAP; or BzCl, DMAP; or PMB-Cl, DMAP; (c) 1. Ac_2O, DMSO, pyridine, 2. $NaBH_4$, MeOH, CH_2Cl_2.

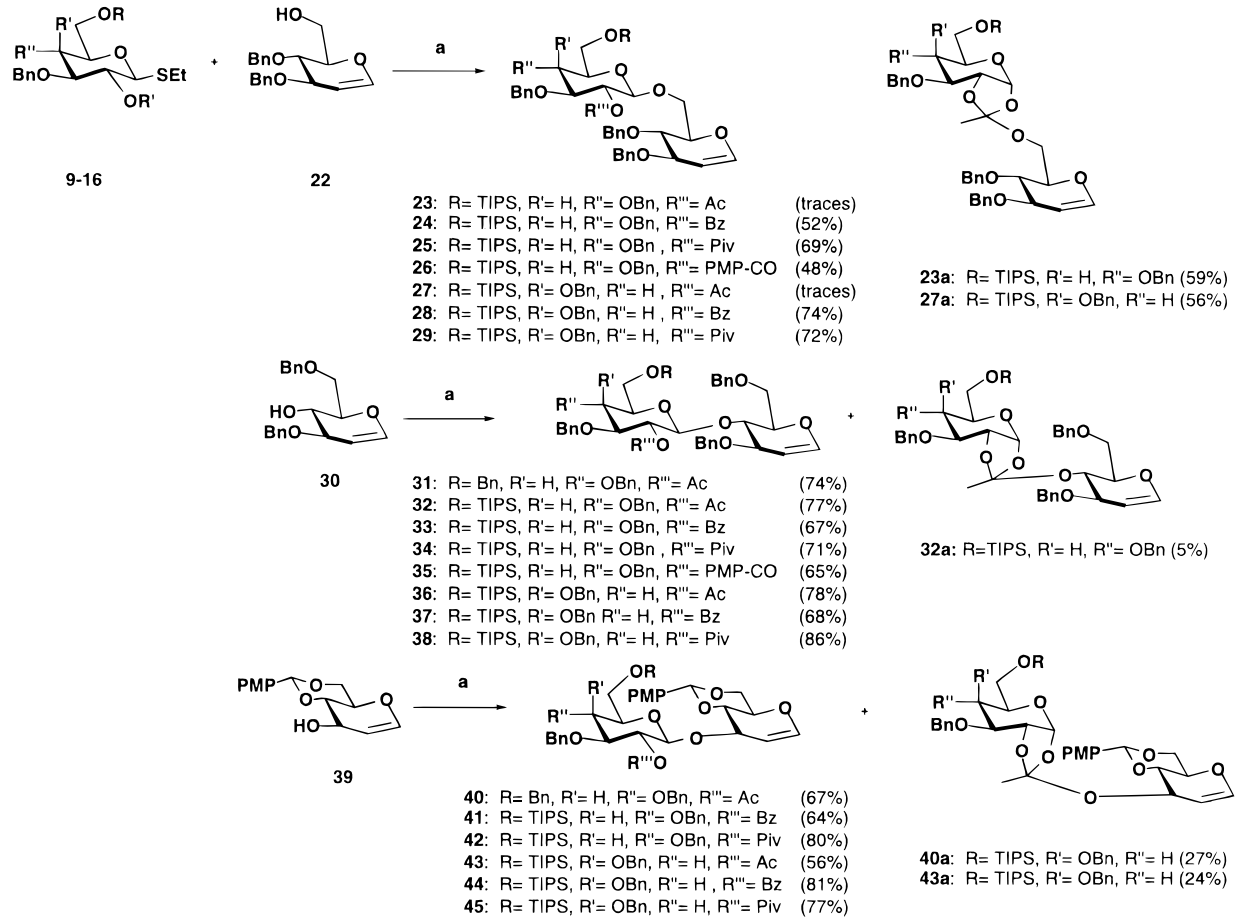


Figure 2. Synthesis of glucosyl and galactosyl disaccharides using thioethyl glycosyl donors; (a) MeOTf, DTBP, 4 Å MS, CH_2Cl_2, 0 °C.

presumably by the liberated triflic acid, was observed when longer reaction times were required. However, addition of 1 equiv of the non-nucleophilic base di-*tert*-butylpyridine (DTBP) sufficed to provide for stability of the glycal linkage during the coupling experiments.

It soon became clear that using these mild conditions, reactions involving C2-acetyl protected thioglycosides became unpredictable. While in some cases (**9** + **39** → **40**) the desired disaccharide was the major product, other attempted glycosylations (**10** + **22** → **23**) yielded exclusively the undesired orthoester product **23a**. Orthoester formation was found to be much suppressed with sterically hindered acceptors (e.g., **39**). Similar unpredictable results were obtained for the thioethyl mannosyl donors (**17** and **18**). Often these experiments resulted in significant amounts of orthoester products (see **18** + **22** → **46** + **46a**, **18** + **39** → **52** + **52a**).

These findings were certainly not unexpected. Thus the formation of orthoesters had previously been reported with a

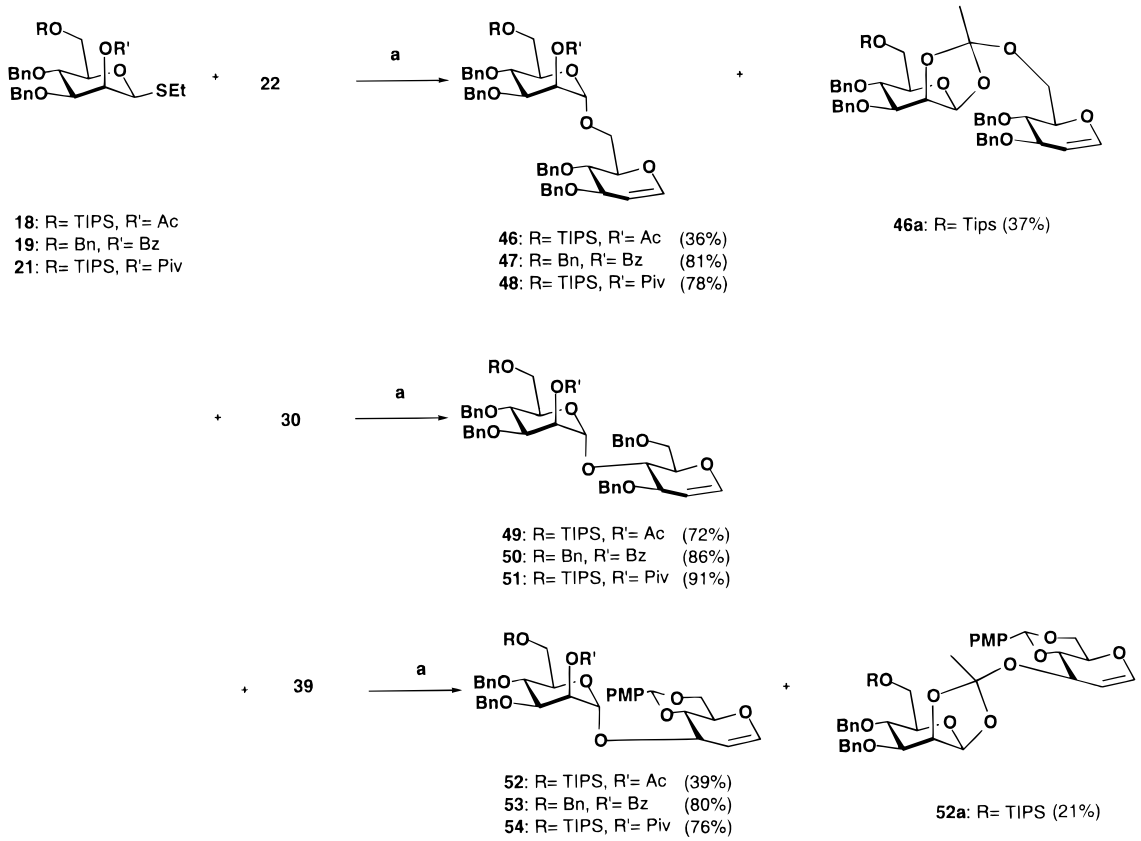
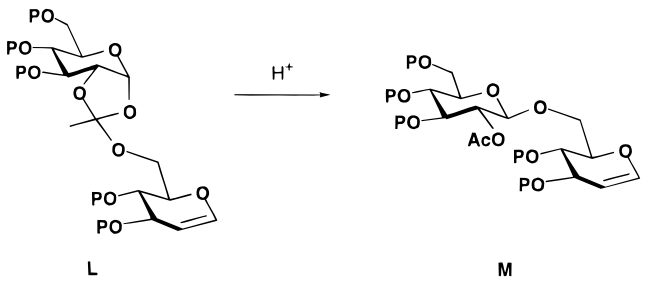


Figure 3. Synthesis of mannosyl disaccharides using thioethyl glycosyl donors: (a) MeOTf, DTBP, 4 Å MS, CH_2Cl_2, 0 °C.

Scheme 2. Rearrangement of Orthoesters to Glycosides



number of different glycosyl donors which react through an oxonium ion intermediate and contain a C2-acetyl group.[14] Reaction conditions involving more acidic conditions may also favor orthoester formation at the kinetic level. The latter can suffer rearrangement to the thermodynamically more stable and desired glycosidic product.[15]

The use of C2-benzoyl protected glycosyl donors **12**, **13**, and **19** resulted in improved glycosylation reactions. Formation of the desired product dominated in all cases over orthoester formation. The benzoyl protected mannosyl donor **19** resulted in very good coupling yields (80−86%), while only trace amounts of side products were obtained. The use of benzoyl protected glucosyl donor **13** and galactosyl donor **14** resulted in improved selectivity in the coupling. In reactions involving the secondary hydroxyl acceptors **30** and **39**, only small amounts of side products, presumably orthoesters, were observed (<6%). Coupling with the primary C6-hydroxyl of acceptor **22** furnished not only the desired disaccharides **24** and **28** in moderate yields (52% and 74%) but also mixtures of side products. Purification of the disaccharide products did not prove feasible in all cases. Application of the 4-methoxybenzoyl protected glucosyl donor **16** resulted in some improvement. The desired disaccharides **26** and **35** were obtained. However, this participating group did not provide full relief in all cases. Difficultly removable side products were occasionally encountered with this C2 directing function.

Thioethyl glycosyl donors **14**, **15**, **20**, and **21** carrying a C2-pivaloyl protecting group performed in a superior fashion in all coupling reactions. The only case where a side product was noted arose in the preparation of the β-glucosyl (1→6) linked disaccharide **25**. In all other couplings, the desired product was formed either exclusively or with massive preponderance. These glycosylation reactions on donors bearing a C2 pivaloyl resident group were free of contaminating side products. The synthetically challenging C1→C2 linkage between thioethyl galactosyl donor **15** and disaccharide glycal **55** as acceptor was established in 68% yield (Figure 4). The versatility of the method is seen from the fact that acceptor **55** had itself been fashioned in one step from coupling of tribenzylglucal a-epoxide with 3,4-dibenzyl glucal.[8] Thus, for unhindered C_6 alcohol acceptors, direct coupling with epoxy donor is preferred on the grounds of conciseness. However, with seriously hindered acceptor sites, thioethyl donors bearing C_2-pivaloyloxy directing groups are vastly superior.

Mannosyl donor **20** was used in a dimannosylation reaction of acceptor glycal **57** to provide the 3,6-branched trisaccharide **59** in 63% yield (Figure 5). This result constitutes dramatic progress over a dimannosylation reaction involving acetyl

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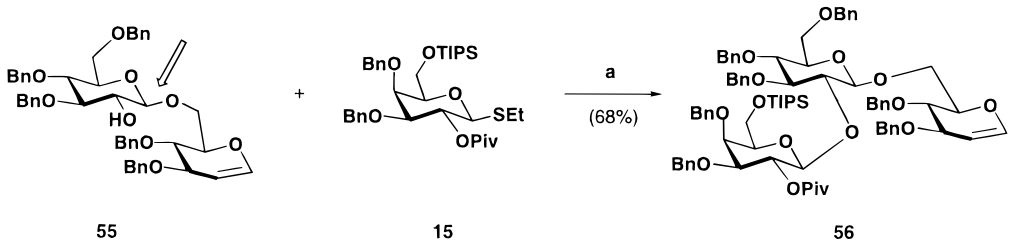

Figure 4. Galactosylation of a C2 hydroxyl group: (a) MeOTf, DTBP, 4 Å MS, CH_2Cl_2, 0 °C.

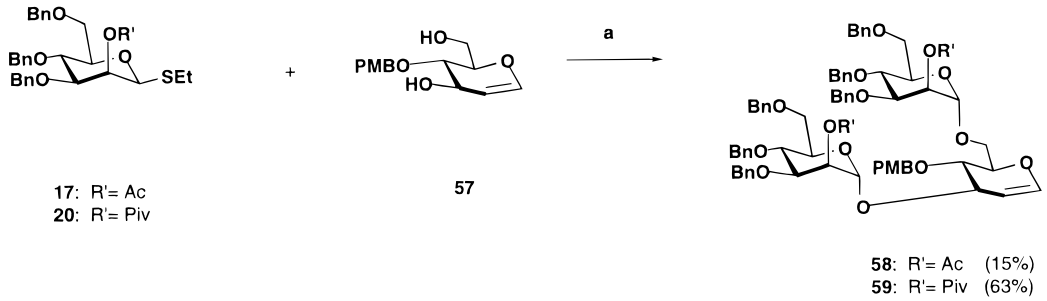

Figure 5. Synthesis of a trisaccharide by dimannosylation: (a) MeOTf, DTBP, 4 Å MS, CH_2Cl_2, 0 °C.

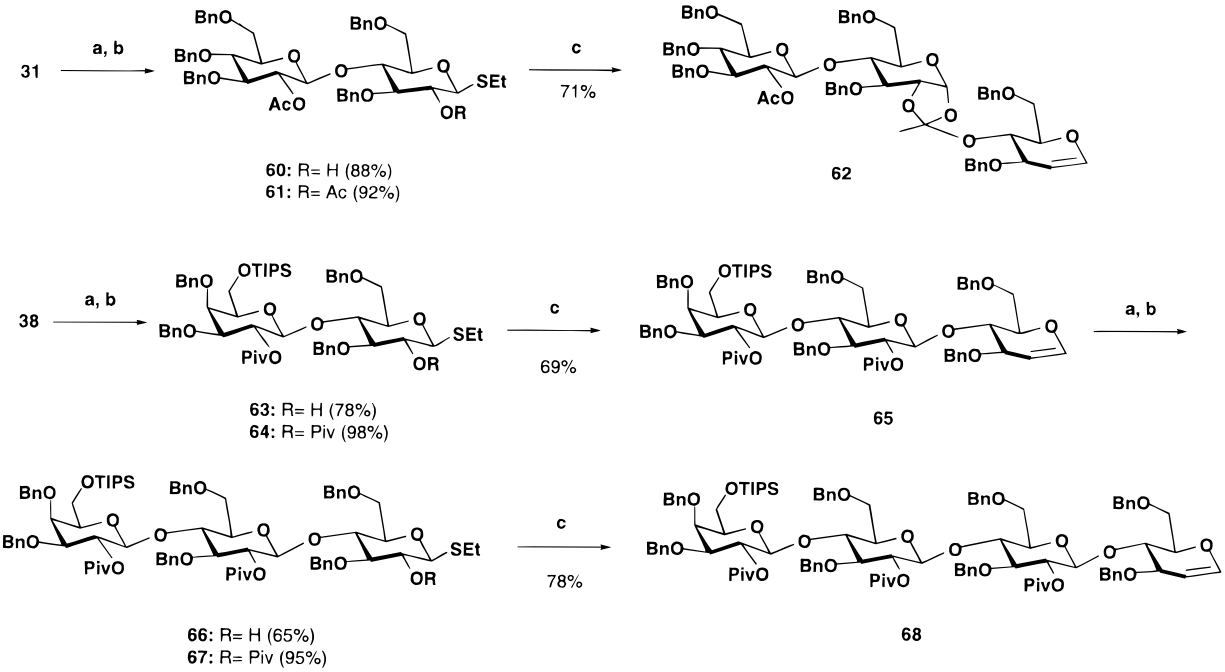

Figure 6. Synthesis of a β-(1→4) linked tetrasaccharide: (a) 1. DMDO, acetone, CH_2Cl_2, 2. EtSH, CH_2Cl_2, cat. TFAA; (b) PivCl, DMAP; (c) **30**, MeOTf, DTBP, 4 Å MS.

protected mannosyl donor **17**, which gave only 15% of the desired trisaccharide **58** in addition to a variety of orthoester containing side products.

After establishing a protocol for the efficient coupling of thioethyl glycosyl donors with glycal acceptors, we set out to apply this methodology to the synthesis of oligosaccharides. The preparation of a β-glucosyl (1→4) linked trisaccharide had not been possible using acetyl protecting groups since the coupling to the trisaccharide yielded almost exclusively orthoester **62**. Use of a C2-pivaloyl group allowed for the synthesis of tetrasaccharide **68** in good yield (Figure 6). A similar result was obtained for the synthesis of a β-glucosyl (1→3) linked trisaccharide (Figure 7). While disaccharide **40** could be obtained using acetylated glucosyl donor **9**, coupling of disaccharide donor **70** to glycal acceptor **39** afforded 81% of trisaccharide orthoester **73a**. Only 3% of the desired trisaccharide **73** was obtained. Benzoyl donor **71** provided trisaccharide **74** only in 45% yield, whereas pivaloyl donor **72** furnished **75** in 74% yield.

Finally, we return to the question of the need of buffering of the methyltriflate solutions in the application of glycals to the coupling with thioethyl donors. Interestingly, the synthesis of a β-(1→6) linked trisaccharide could be accomplished with a protocol not employing DTBP. Short reaction times allowed for the minimization of glycal degradation due to exposure to acid. For instance, the disaccharide **23** could be obtained in 89% yield. Moreover, glycosidation involving the more complex donor **77** furnished the trisaccharide **78** in 78% yield. More complex acceptors, requiring longer reaction times, were completely degraded under these more acidic conditions. With the more hindered and less reactive acceptors the reactivity ratio of glycosidation to destruction tilts in favor of the latter process thereby requiring the buffering procedure for success of the experiment.

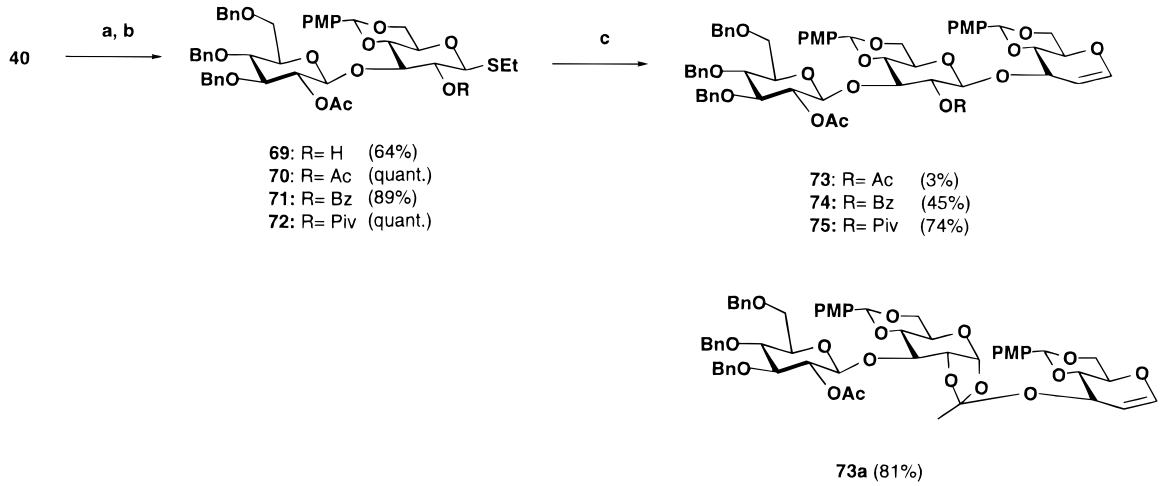

Figure 7. Synthesis of a β-(1→3) linked trisaccharide: (a) 1. DMDO, acetone, CH_2Cl_2, 2. EtSH, CH_2Cl_2, cat. TFAA; (b) PivCl, DMAP; or BzCl DMAP; or Ac_2O, DMAP, pyridine; (c) **39**, MeOTf, DTBP, 4 Å MS.

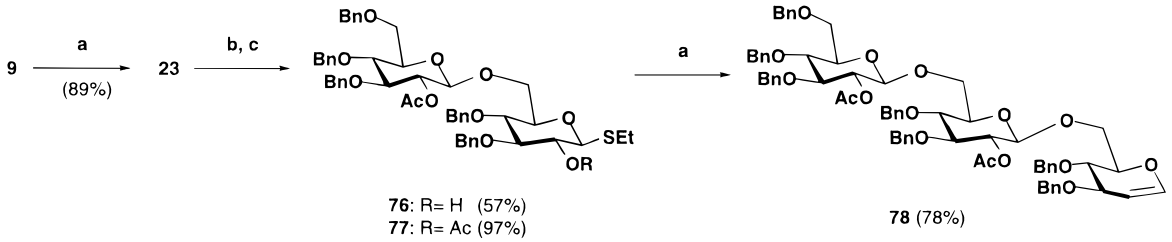

Figure 8. Synthesis of a β-(1→6) linked trisaccharide: (a) **22**, MeOTf, 4 Å MS, CH_2Cl_2, 0 °C; (b) 1. DMDO, acetone, CH_2Cl_2, 2. EtSH, CH_2Cl_2, cat. TFAA; (c) Ac_2O, DMAP.

Conclusions

A novel protocol for the preparation of differentially protected thioethyl glycosyl donors from glycal precursors has been developed. We were able to establish a coupling procedure by which C2-pivaloyl glucosyl, galactosyl, and mannosyl donors bearing β-thioethyl functions at their anomeric carbons can be coupled to various glycal acceptors in high yield. This new protocol was successfully extended to the synthesis of a β-(1→4) linked tetrasaccharide, a β-(1→3) linked trisaccharide, and two branched trisaccharides.

We certainly lay no claim to the uniqueness of glycal assembly[8] for reaching the targets described above. However, the methodological advance reported here substantially expands the range of glycosidic linkages which may be fashioned using glycal acceptors. Most importantly, it is now possible to prepare oligosaccharides containing glucosyl β-(1→4) and α-mannosyl linkages. These were previously not reliably accessible by glycal methodology. We emphasize that contrary to many other protocols, our solution phase constructions are being conducted with near stoichiometric equivalences of donors and acceptors. Moreover, as will be disclosed, the method described here has been extended to the solid phase synthesis of complex oligosaccharides.[16]

Experimental Section

Synthesis of Thioethyl β-D-Glycopyranosides 4−6. General Procedure A. Protected glycal (2.4 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and cooled to 0 °C. Dimethyldioxirane (36.0 mL in acetone, 2.9 mmol) was added, and the solution was stirred for 20 min. The solvent was removed in a stream of N_2. After drying for 30 min under vacuum, the epoxide was dissolved in CH_2Cl_2 (5 mL), and EtSH (5 mL) was added. The mixture was cooled to −78 °C, and trifluoroacetic acid anhydride (30 μL) was added dropwise. The reaction mixture was stirred at −78 °C for 20 min and then warmed up to room temperature. The solvents were removed in a stream of N_2, and the residue was purified by silica gel chromatography.

Thioethyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside 4: (78%) $[\alpha]^{24}_D$: −12.8° (*c* 2.05, CH_2Cl_2); IR (thin film) 3458, 1496, 1453, 1359, 1054 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.31−7.16 (m, 13H), 7.11−7.08 (m, 2H), 4.86 (d, J = 11.3 Hz, 1H), 4.77 (d, J = 11.3 Hz, 1H), 4.76 (d, J = 12.1 Hz, 1H), 4.22 (d, J = 9.1 Hz, 1H), 3.67 (dd, J = 1.8, 10.9 Hz, 1H), 3.61 (dd, J = 4.5, 10.9 Hz, 1H), 3.56−3.39 (m, 4H), 2.70−2.60 (m, 2H), 1.24 (d, J = 4.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ 138.6, 138.2, 138.0, 128.4, 128.3, 127.9, 127.9, 127.7, 127.7, 127.5, 86.1, 86.0, 79.4, 75.2, 75.0, 73.4, 73.2, 69.0, 24.2, 15.4; HRMS (FAB) calcd for $C_{29}H_{34}O_5S$: 494.2127, found: 494.2136.

Thioethyl 3,4-di-*O*-benzyl-6-*O*-triisopropylsilyl-β-D-glucopyranoside 5: (76%) $[\alpha]^{24}_D$: −12.3° (*c* 1.5, CH_2Cl_2); IR (thin film) 3030, 2942, 2864, 1454, 1151, 1087 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.41−7.22 (m, 10H); 4.94 (d, J = 5.6 Hz, 1H), 4.86 (d, J = 5.1 Hz, 2H), 4.70 (d, J = 5.4 Hz, 1H), 4.27 (d, J = 4.8 Hz, 1H), 3.91 (m, 2H), 3.68 (t, J = 6.1 Hz, 2H); 3.58 (t, J = 4.6 Hz, 1H), 3.51 (t, J = 4.1 Hz, 1H), 3.30 (d, J = 1.0 Hz, 1H), 2.66 (m, 2H), 2.58 (s, 1H), 1.24 (t, J = 3.7 Hz, 3H), 1.04 (m, 21 H); ^{13}C-NMR ($CDCl_3$) δ 138.8, 138.5, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 86.3, 85.6, 80.6, 77.1, 75.5, 75.2, 73.2, 62.7, 23.6, 18.2, 15.5, 12.7; MS (ES+): 583.2 ($M^+ + Na^+$); (ES−): 595.1 ($M^- + Cl^-$).

Thioethyl 3,4-di-*O*-benzyl-6-*O*-triisopropylsilyl-β-D-galactopyranoside 6: (71%) $[\alpha]^{24}_D$: −3.8° (*c* 1.48, CH_2Cl_2); IR (thin film) 3440, 3029, 2941, 1454, 1104, 882 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.35−714 (m, 10H); 4.88 (d, J = 11.5 Hz, 1H); 4.70 (s, 1H), 4.63 (d, J = 11.5 Hz, 1H), 4.26 (d, J = 9.6 Hz, 1H), 3.97 (m, 2H), 3.73 (d, J = 7.0 Hz, 2H), 3.40 (m, 2H), 2.65 (m, 2H), 2.41 (s, br, 1H), 1.21 (t, J = 7.5 Hz, 3H), 0.98 (m, 21H); ^{13}C-NMR ($CDCl_3$) δ 138.8, 138.0, 128.4, 128.0, 127.7, 127.6, 127.2, 86.0, 83.1, 79.2, 74.4, 73.0, 72.3, 69.6, 61.5, 23.7, 17.9, 15.0, 11.7; MS (ES+): 583.2 ($M^+ + Na^+$); (ES−): 595.1 ($M^- + Cl^-$).

Synthesis of Thioethyl 3,4-Di-*O*-benzyl-6-*O*-triisopropylsilyl-β-D-mannopyranoside 8. Thioethyl β-D-glucoside **5** (18.7 mmol) was treated with DMSO/Ac_2O (100 mL/50 mL) for 72 h at room temperature. It was then diluted with ether (100 mL) and washed with H_2O (5 × 200 mL), saturated aqueous Na_2CO_3 (3 × 200 mL), and saturated aqueous NaCl. The crude ketone was dried with $MgSO_4$ and

concentrated to dryness. It was dissolved in CH_2Cl_2/MeOH (60 mL/60 mL) and cooled to 0 °C. $NaBH_4$ (2.13 g, 37.8 mmol) was added in several portions. The reaction mixture was allowed to warm up to room temperature and stirred for another 20 min. The reaction was quenched with H_2O (20 mL), and the aqueous phase was extracted with ether (3 × 300 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ (200 mL) and saturated aqueous NaCl (300 mL) and dried ($MgSO_4$). The crude material was purified by flash column chromatography (15% EtOAc−hexanes): (50%) $[\alpha]^{24}_D$: −30.1° (*c* 1.25, CH_2Cl_2); IR (thin film) 3482, 3063, 3030, 2941, 2865, 1454, 1128, 882, 745 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.49−7.35 (m, 10H); 5.01 (d, J = 14.3 Hz, 1H), 4.84 (d, J = 11.7 Hz, 1H), 4.72 (d, J = 11.0 Hz, 2H), 4.68 (s, 1H), 4.27 (s, 1H), 4.04 (d, J = 11.0 Hz, 1H), 4.01−3.87 (m, 2H), 3.56 (m, 1H), 3.40 (m, 1H), 2.79 (m, 2H), 2.55 (d, J = 3.1 Hz, 1H), 1.39 (t, J = 7.3 Hz, 3H), 1.14 (m, 21H); ^{13}C-NMR ($CDCl_3$) δ 137.1, 136.5, 127.4, 127.2, 127.0, 126.8, 126.6, 126.4, 125.9, 82.3, 79.9, 73.9, 72.7, 68.3, 61.6, 23.7, 16.6, 13.8, 10.7; MS (ES+): 583.2 ($M^+ + Na^+$); (ES−): 595.1($M^- + Cl^-$).

Synthesis of Thioethyl 2-*O*-Pivaloyl-D-glycopyranosides 14, 15, 20, and 21. General Procedure C. Thioethyl glycoside (1.0 mmol) was dissolved in 5 mL of CH_2Cl_2 and DMAP (0.24 g, 2.0 mmol), and benzoyl chloride, pivaloyl chloride, or 4-methoxybenzoyl chloride (1.5 mmol) were added. The reaction mixture was stirred at room temperature for 30 min. The reaction was diluted with EtOAc (100 mL), washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. Purification by silica column chromatography afforded the C2-protected thioethyl glycopyranosides.

Thioethyl 3,4-di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-glucopyranoside 14: (quant.) $[\alpha]^{24}_D$: −22.9° (*c* 1.8, CH_2Cl_2); IR (thin film) 2910, 2885, 1738, 1454, 1137, 1087 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.38−7.18 (m, 10H); 5.03 (t, J = 9.0 Hz, 1H), 4.78 (d, J = 5.8 Hz, 1H), 4.73 (d, J = 6.0 Hz, 1H), 4.63 (m, 2H), 4.30 (d, J = 9.9 Hz, 1H), 3.98−3.85 (m, 2H), 3.73−3.62 (m, 2H), 3.29 (m, 2H), 2.60 (m, 2H), 1.26 (m, 12H), 1.02−0.98 (m, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.7, 138.1, 128.3, 128.2, 127.8, 127.6, 127.5, 127.3, 84.6, 82.7, 80.4, 75.1, 74.8, 71.4, 62.3, 27.0, 22.7, 14.6, 11.8; MS (ES+): 667.7 ($M^+ + Na^+$); (ES−): 679.4 ($M^- + Cl^-$).

Thioethyl 3,4-di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-galactopyranoside 15: (quant.) $[\alpha]^{24}_D$: −4.3° (*c* 1.16, CH_2Cl_2); IR (thin film) 2958, 2941, 2865, 1736, 1455, 1365, 1276, 1157, 1108, 1067, 882, 732, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.38−7.19 (m, 10H), 5.48 (t, J = 9.7 Hz, 1H), 4.97 (d, J = 11.4 Hz, 1H), 4.62 (d, J = 12.5 Hz, 1H), 4.38 (d, J = 9.8 Hz, 1H), 4.01 (s, 1H), 3.81 (d, J = 6.7 Hz, 2H), 3.62 (dd, J = 9.5, 2.2 Hz, 1H), 3.47 (t, J = 6.6 Hz, 1H), 2.79−2.60 (m, 2H), 1.28−1.14 (m, 12H), 1.04 and 1.03 (2 s, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.9, 138.8, 137.9, 128.0, 127.7, 127.7, 127.4, 127.2, 83.5, 81.8, 79.2, 74.4, 73.0, 72.3, 69.3, 61.5, 38.7, 27.2, 23.1, 18.0, 14.7, 11.8; MS (ES+): 667.4 ($M^+ + Na^+$); (ES−): 679.4 ($M^- + Cl^-$).

Thioethyl 3,4,6-tri-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-mannopyranoside 20: (98%) $[\alpha]^{24}_D$: −0.3° (*c* 1.04, CH_2Cl_2); IR (thin film) 2968, 2868, 1732, 1454, 1363, 1281, 1154, 1109 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.41−7.25 (m, 13H), 7.22−7.18 (m, 2H); 5.66 (d, J = 3.1 Hz, 1H), 4.87 (d, J = 10.8 Hz, 1H), 4.79 (d, J = 11.81 Hz, 1H),4.70 (s, 1H), 4.69 (d, J = 11.2 Hz, 1H), 4.61, (d, J = 12.1 Hz, 1H), 4.57 (d, J = 10.8 Hz, 1H), 4.51 (d, J = 11.1 Hz, 1H), 3.85−3.67 (m, 4H), 3.54 (m, 1H), 2.77 (q, J = 7.4 Hz, 1H), 1.33 (t, J = 7.4 Hz, 3H), 1.30 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 177.6, 138.5, 138.1, 137.8, 128.3, 128.2, 128.2, 128.1, 127.7, 127.6, 127.4, 82.3, 81.6, 79.7, 75.2, 74.0, 73.2, 71.4, 69.3, 39.1, 27.2, 25.7, 15.0; MS (ES+): 601.2 ($M^+ + Na^+$); (ES−): 613.3 ($M^- + Cl^-$).

Thioethyl 3,4-di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-mannopyranoside 21: (97%) $[\alpha]^{24}_D$: −47.7° (*c* 1.04, CH_2Cl_2); IR (thin film) 3030, 2940, 2865, 1454, 1281, 1111 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.38−7.18 (m, 10H); 5.57 (d, J = 3.0 Hz, 1H), 4.81 (d, J = 10.7 Hz, 1H), 4.70 (d, J = 11.0 Hz, 1H), 4.61 (m, 2H), 4.40 (d, J = 11.0 Hz, 1H), 3.92 (m, 2H), 3.82 (t, J = 9.5 Hz, 1H), 3.28 (m, 1H), 2.61 (m, 2H), 1.23 (m, 12H), 1.03 (m, 21H); ^{13}C-NMR ($CDCl_3$) δ 177.5, 138.4, 137.9, 128.2, 128.1, 128.0, 127.9, 127.5, 127.4, 82.0, 81.5, 80.5, 75.2, 73.6, 71.3, 69.2, 62.5, 38.9, 25.2, 17.9, 14.9, 11.8; MS (ES+): 667.5 ($M^+ + Na^+$); (ES−): 679.4 ($M^- + Cl^-$).

Synthesis of Disaccharides. General Procedure D. A mixture of thioethyl glycosyl donor (1 equiv) and glycosyl acceptor (1.2 equiv) was azeotroped with benzene (3 × 50 mL) and dried under vacuum for 1 h. Freshly dried 4 Å molecular sieves (30 mg) were added. Into the mixture was added CH_2Cl_2 (3 mL) and di-*tert*-butylpyridine (4 equiv). The suspension was stirred at room temperature for 30 min and cooled to 0 °C. Methyl triflate (4 equiv) was added dropwise. After stirring at 0 °C for 15 h, the reaction mixture was slowly warmed to room temperature, and triethylamine (0.2 mL) was added, followed by EtOAc (50 mL). Extraction with saturated aqueous $NaHCO_3$ (100 mL) and saturated aqueous NaCl (100 mL) was followed by drying over Na_2SO_4. The crude product was purified by silica gel chromatography.

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-glucopyranoside-(1→6)-3,4-di-*O*-benzyl-D-glucal 25: (58%) $[\alpha]^{24}_D$: −10.3° (*c* 2.02, CH_2Cl_2); IR (thin film) 2939, 2866, 1740, 1650, 1457, 1135, 1095, 1065, 738 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.36−7.21 (m, 20H), 6.35 (dd, J = 6.2, 0.6 Hz, 1H), 5.03 (m, 1H), 4.87 (m, 1H), 4.82−4.45 (m, 9H), 4.16 (m, 1H), 4.09−3.95 (m, 4H), 3.83−3.67 (m, 3H), 3.62 (m, 1H), 3.36−3.27 (m, 1H), 1.19 (s, 9H), 1.05 and 1.04 (2 s, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.9, 144.3, 138.3, 138.3, 138.0, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 101.4, 99.5, 83.2, 76.4, 76.2, 75.0, 74.9, 74.2, 73.8, 73.1, 72.9, 71.9, 67.8, 62.2, 38.8, 27.1, 18.0, 18.0, 12.0; MS (ES+): 931.6 ($M^+ + Na^+$), (ES−): 943.4 ($M^- + Cl^-$).

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-galactopyranoside-(1→6)-3,4-di-*O*-benzyl-D-glucal 29: (72%) $[\alpha]^{24}_D$: −3.4° (*c* 2.05, CH_2Cl_2); IR (thin film) 2941, 2865, 1739, 1648, 1454, 1103, 1067, 734 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.36−7.17 (m, 20H), 6.35 (d, J = 6.2 Hz, 1H), 5.45 (dd, J = 10.0, 8.1 Hz, 1H), 4.96 (d, J = 11.4 Hz, 1H), 4.86 (dd, J = 6.1, 3.3 Hz, 1H), 4.72 (d, J = 11.7 Hz, 1H), 4.67−4.45 (m, 7H), 4.17 (m, 1H), 4.05−3.93 (m, 3H), 3.87−3.73 (m, 3H), 3.65 (m, 1H), 3.57 (m, 1H), 3.40 (m, 1H), 1.21 (s, 9H), 1.03 and 1.02 (2 s, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.9, 144.3, 138.7, 138.2, 137.9, 128.3, 128.0, 128.0, 127.8, 127.7, 127.6, 127.6, 127.4, 127.3, 101.7, 99.3, 80.6, 76.2, 75.3, 74.5, 73.7, 73.4, 72.7, 72.6, 72.3, 71.0, 70.2, 67.3, 61.5, 18.8, 27.1, 18.0, 18.0, 11.8, 11.5; MS (ES+): 931.6 ($M^+ + Na^+$), (ES−): 943.6 ($M^- + Cl^-$).

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-glucopyranoside-(1→4)-3,6-di-*O*-benzyl-D-glucal 34: (71%) $[\alpha]^{24}_D$: −20.3° (*c* 2.97, CH_2Cl_2); IR (thin film) 3063, 3029, 2940, 2864, 1741, 1648, 1454, 1132 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.32−7.17 (m, 20H), 6.33 (d, J = 6.3 Hz, 1H), 4.96 (t, J = 9.2 Hz, 1H), 4.81 (m, 1H), 4.72 (m, 2H), 4.68 (m, 2H), 4.56−4.43 (m, 6H), 4.26 (m, 1H), 4.03 (m, 1H), 3.92−3.86 (m, 3H), 3.78−3.69 (m, 2H), 3.58 (m, 2H), 3.23 (m, 1H), 1.13 (s, 9H), 0.98 (br s, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.2, 143.8, 138.0, 137.8, 137.7, 137.6, 128.0, 127.92, 127.9, 127.8, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 98.5, 98.1, 82.8, 75.9, 74.5, 74.0, 73.0, 72.6, 71.5, 70.0, 69.5, 67.8, 61.9, 38.3, 26.7, 17.8, 11.5; MS (ES+): 931.5 ($M^+ + Na^+$), (ES−): 943.5 ($M^- + Cl^-$).

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-galactopyranoside-β-(1→4)-3,6-di-*O*-benzyl-D-glucal 38: (86%) $[\alpha]^{24}_D$: −6.1° (*c* 2.24, CH_2Cl_2); IR (thin film) 2941, 2865, 1741, 1650, 1454, 1366, 1278, 1131, 1100, 1075, 734, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.36−7.17 (m, 20H), 6.35 (d, J = 6.2 Hz, 1H), 5.39 (dd, J = 10.1, 8.0 Hz, 1H), 4.95 (d, J = 9.3 Hz, 1H), 4.82 (m, 1H), 4.65−4.48 (m, 8H), 4.17−4.09 (m, 2H), 4.05 (m, 1H), 3.95 (d, J = 2.3 Hz, 1H), 3.84−3.13 (m, 4H), 3.47 (dd, J = 10.2, 2.7 Hz, 1H), 3.36 (m, 1H), 1.17 (s, 9H), 1.01 and 1.00 (2 s, 21H); ^{13}C-NMR ($CDCl_3$) δ 177.1, 144.5, 139.0, 138.3, 138.1, 128.7, 128.5, 128.4, 128.2, 128.2, 128.0, 128.0, 127.8, 127.7, 127.6, 127.6, 100.1, 99.7, 81.2, 75.6, 74.8, 73.8, 72.8, 72.6, 72.5, 71.6, 71.0, 67.6, 61.8, 39.1, 27.6, 18.3, 18.3, 12.1; MS (ES+): 931.6 ($M^+ + Na^+$), (ES−): 943.5 ($M^- + Cl^-$).

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-glucopyranoside-(1→3)-4,6-*O*-(4-methoxy)benzylidene-D-glucal 42: (80%) $[\alpha]^{24}_D$: −41.5° (*c* 2.92, CH_2Cl_2); IR (thin film) 3064, 3030, 2939, 2864, 1741, 1518, 1251, 1095, 883 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.37 (d, J = 9.0 Hz, 2H), 7.28−7.17 (m, 11H), 6.83 (d, J = 8.3 Hz, 2H), 6.31 (d, J = 6.3 Hz, 1H), 5.48 (s, 1H), 4.97 (t, J = 8.6 Hz, 1H), 4.71−4.58 (m, 5H), 4.52 (d, J = 8.0 Hz, 1H), 4.39 (d, J = 6.4 Hz, 1H), 4.27 (d, J = 5.8 Hz, 1H), 3.91 (t, J = 7.1 Hz, 1H), 3.80−3.66 (m, 8H), 3.59 (t, J = 7.7 Hz, 1H), 3.08 (d, J = 9.3 Hz, 1H), 1.18 (s, 9H), 1.01 (m, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.5, 160.0, 144.8, 138.1, 138.0, 129.5, 128.5, 128.3, 128.2, 127.8, 127.6, 127.4, 127.3, 127.2, 113.5, 101.3, 101.0,

100.2, 83.1, 78.8, 75.8, 74.8, 74.1, 73.5, 68.5, 68.3, 61.9, 55.1, 38.7, 27.0, 17.9, 14.0, 11.8; MS (ES+): 869.6 ($M^+ + Na^+$), (ES−): 881.6 ($M^- + Cl^-$).

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-*β*-D-galactopyranoside-*β*-(1→3)-4,6-*O*-(4-methoxy)benzylidene-D-glucal 45: (77%) $[\alpha]^{24}_D$: −34.9° (*c* 2.75, CH_2Cl_2); IR (thin film) 2941, 2865, 1740, 1645, 1615, 1518, 1463, 1366, 1278, 1251, 1235, 1172, 1128, 1097, 1071, 1029, 1009, 883, 825, 734, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.41 (d, *J* = 8.7 Hz, 2H), 7.35−7.16 (m, 10H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.31 (dd, *J* = 6.1, 1.2 Hz, 1H), 5.55 (s, 1H), 5.41 (dd, *J* = 10.1, 8.0 Hz, 1H), 4.97 (d, *J* = 11.2 Hz, 1H), 4.70 (dd, *J* = 6.2, 2.0 Hz, 1H), 4.66−4.54 (m, 4H), 4.43 (m, 1H), 4.30 (m, 1H), 3.99 (m, 2H), 3.86 (t, *J* = 10.0 Hz, 1H), 3.83−3.75 (m, 5H), 3.64 (m, 1H), 3.57 (dd, *J* = 10.2, 2.7 Hz, 1H), 3.39 (m, 1H), 1.20 (s, 9H), 0.98 and 0.97 (2 s, 21H); ^{13}C-NMR ($CDCl_3$) *δ* 176.8, 159.9, 144.7, 138.8, 137.9, 129.8, 128.3, 128.0, 127.8, 127.6, 127.4, 127.2, 113.5, 101.6, 100.8, 100.7, 80.7, 78.7, 75.1, 74.4, 74.1, 72.6, 72.1, 71.8, 68.7, 68.1, 61.3, 55.2, 38.8, 27.2, 18.0, 11.8; MS (ES+): 869.5 ($M^+ + Na^+$), (ES−): 881.5 ($M^- + Cl^-$).

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-α-D-mannopyranoside-(1→6)-3,4-di-*O*-benzyl-D-glucal 48: (78%) $[\alpha]^{24}_D$: +22.4° (*c* 2.01, CH_2Cl_2); IR (thin film) 3030, 2940, 2865, 1733, 1648, 1454, 1102, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.34−7.11 (m, 20H), 6.31 (d, *J* = 6.0 Hz, 1H), 5.43 (br s, 1H), 4.83−4.78 (m, 3H), 4.71 (s, 1H), 4.62−4.41 (m, 6H), 4.17 (m, 1H), 3.96−3.65 (m, 8H), 3.55 (m, 1H), 1.15 (s, 9H), 0.98 (m, 21H); ^{13}C-NMR ($CDCl_3$) *δ* 177.5, 144.5, 138.6, 138.0, 128.3, 128.2, 128.0, 127.8, 127.6, 127.5, 127.3, 127.2, 99.6, 98.0, 78.2, 75.9, 75.7, 75.0, 74.0, 73.8, 73.4, 72.5, 71.2, 70.3, 67.9, 65.6, 62.4, 38.7, 27.0, 17.9, 11.8; MS (ES+): 931.6 ($M^+ + Na^+$), (ES−): 943.6 ($M^- + Cl^-$).

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-α-D-mannopyranoside-(1→4)-3,6-di-*O*-benzyl-D-glucal 51: (91%) $[\alpha]^{24}_D$: +16.1° (*c* 2.71, CH_2Cl_2); IR (thin film) 3064, 3030, 2940, 2865, 1732, 1648, 1140, 1073, 883 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.31−7.15 (m, 20H), 6.38 (d, *J* = 6.1 Hz, 1H), 5.32 (m, 1H), 5.20 (d, *J* = 7.3 Hz, 1H), 4.80 (m, 2H), 4.65−4.39 (m, 7H), 4.08 (s, 3H), 3.90−3.79 (m, 3H), 3.71−3.54 (m, 4H), 1.11 (s, 9H), 0.99 (m, 21H); ^{13}C-NMR ($CDCl_3$) *δ* 177.4, 144.8, 138.6, 138.3, 137.8, 128.2, 128.1, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 99.2, 97.2, 78.3, 75.0, 74.0, 73.6, 73.1, 73.0, 71.3, 69.8, 69.2, 68.3, 62.1, 38.7, 26.9, 17.8, 11.7; MS (ES+): 931.6 ($M^+ + Na^+$), (ES−): 839.4 ($M^- + Cl^-$).

3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-α-D-mannopyranoside-(1→3)-4,6-*O*-(4-methoxy)benzylidene-D-glucal 54: (76%) $[\alpha]^{24}_D$: −30.1° (*c* 3.05, CH_2Cl_2); IR (thin film), 3030, 2940, 2865, 1732, 1641, 1517, 1021 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.38 (d, *J* = 12.0 Hz, 2H), 7.27−7.18 (m, 11H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.53 (s, 1H), 5.39 (m, 1H), 5.15 (s, 1H), 4.81 (d, *J* = 10.6 Hz, 1H), 4.69 (m, 1H), 4.62 (d, *J* = 11.0 Hz, 1H), 4.53 (d, *J* = 10.7 Hz, 1H), 4.45 (d, *J* = 11.1 Hz, 1H), 4.29 (m, 1H), 3.96−3.78 (m, 8H), 3.74 (s, 3H), 1.12 (s, 9H), 1.03 (m, 21H); ^{13}C-NMR ($CDCl_3$) *δ* 177.5, 159.8, 144.7, 138.4, 138.2, 129.4, 128.2, 128.0, 127.6, 127.5, 127.2, 127.1, 113.3, 102.2, 100.8, 97.7, 79.3, 78.3, 75.1, 74.0, 72.8, 71.2, 71.1, 68.5, 68.1, 62.7, 55.1, 38.7, 26.9, 17.9, 11.8; MS (ES+): 869.6 ($M^+ + Na^+$), (ES−): 881.5 ($M^- + Cl^-$).

Synthesis of 3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-*β*-D-galactopyranoside-(1→2)-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside-(1→6)-3,4-di-*O*-benzyl-glucal 56: (68%) $[\alpha]^{24}_D$: −1.1° (*c* 1.19, CH_2Cl_2); IR (thin film) 2939, 2865, 1740, 1648, 1454, 1363, 1100, 1069 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.38−7.13 (m, 32H), 7.08 (m, 2H), 6.36 (d, *J* = 5.9 Hz, 1H), 5.49 (dd, *J* = 9.9, 8.2 Hz, 1H), 5.03−4.83 (m, 5H), 4.76−4.65 (m, 3H), 4.62−4.44 (m, 9H), 4.21−4.12 (m, 3H), 4.03−3.93 (m, 2H), 3.87−3.71 (m, 4H), 3.68−3.55 (m, 4H), 3.49−3.35 (m, 3H), 1.12 (s, 9H), 1.04 (br. s, 21H); ^{13}C-NMR ($CDCl_3$) *δ* 176.5, 144.3, 139.0, 138.8, 138.5, 138.4, 138.2, 138.1, 137.9, 128.3, 128.3, 128.1, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.2, 127.1, 102.6, 100.0, 84.9, 81.5, 80.2, 77.5, 76.8, 75.4, 74.9, 74.8, 74.7, 74.6, 74.3, 73.4, 72.2, 72.0, 70.3, 69.0, 68.9, 61.2, 38.7, 27.2, 18.1, 18.0, 14.2, 11.9; MS (ES+): 1363.9 ($M^+ + Na^+$), (ES−): 1375.8 ($M^- + Cl^-$).

Synthesis of 3,4,6-Tri-*O*-benzyl-2-*O*-pivaloyl-α-D-mannopyranoside-(1→6)[3,4,6-tri-*O*-benzyl-2-*O*-pivaloyl-α-D-mannopyranoside-(1→3)]-4-*O*-(4-methoxy)benzyl-D-glucal 59. A mixture of donor **20** (310 mg, 0.536 mmol) and acceptor **57** (46 mg, 0.172 mmol) was azeotroped with benzene (3 × 50 mL) and dried under vacuum for 1 h. Freshly dried 4 Å molecular sieves (300 mg) were added. Into the mixture was added CH_2Cl_2 and di-*tert*-butylpyridine (0.48 mL, 12.4 mmol). The mixture was stirred at room temperature for 30 min and cooled to 0 °C, and MeOTf (0.24 mL, 12.4 mmol) was added slowly. After being stirred at 0 °C for 24 h, the reaction mixture was diluted with EtOAc (500 mL) and washed with saturated aqueous $NaHCO_3$ (100 mL) and saturated aqueous NaCl (100 mL), dried ($MgSO_4$), and purified by flash column chromatography.

59: (63%) $[\alpha]^{24}_D$: +0.3° (*c* 2.72, $CHCl_3$); IR (film) 3030, 2970, 2870, 1732, 1649, 1514, 1454, 1279, 835 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.38−7.12 (m, 32 H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.21 (d, *J* = 6.1 Hz, 1H), 5.45 (m, 1H), 5.36 (m, 1H), 5.10 (s, 1H), 4.92−4.82 (m, 4H), 4.84 (d, *J* = 10.8 Hz, 2H), 4.79 (d, *J* = 2.0 Hz, 1H), 4.78 (d, *J* = 11.7 Hz, 1H), 4.76−4.62 (m, 5H), 4.57−4.46 (m, 7H), 4.49−4.34 (m, 1H), 4.05−3.66 (m, 18H), 1.22 and 1.21 (2 s, 17H); ^{13}C-NMR ($CDCl_3$) *δ* 177.5, 159.3, 144.5, 138.4, 138.3, 138.1, 129.8, 129.7, 129.5, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.6, 127.5, 127.4, 127.3, 127.3, 127.2, 114.0, 101.5, 99.1, 98.3, 78.2, 79.9, 79.1, 75.0, 75.0, 74.8, 74.6, 74.0, 73.1, 73.0, 72.6, 72.3, 72.1, 68.5, 67.9, 65.8, 55.2, 38.9, 27.1, 25.4; MS (ES+): 1321.8 ($M^+ + Na^+$), (ES−): 1333.6 ($M^- + Cl^-$).

Synthesis of Thioethyl 3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-*β*-D-galactopyranoside-(1→4)-3,6-di-*O*-benzyl-*β*-D-glucopyranoside 63. Disaccharide **38** was converted into **63** using general procedure A: (78%) $[\alpha]^{24}_D$: −9.4° (*c* 1.05, CH_2Cl_2); IR (thin film) 3470, 2940, 2865, 1741, 1454, 1276, 1087, 1028, 801 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.36−7.18 (m, 20H), 5.40 (dd, *J* = 9.0, 8.0 Hz, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 4.98 (d, *J* = 11.1 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.56 (d, *J* = 6.4 Hz, 1H), 4.53 (d, *J* = 5.6 Hz, 1H), 4.45 (d, *J* = 2.5 Hz, 1H), 4.43 (s, 1H), 4.32 (d, *J* = 9.1 Hz, 1H), 4.14−4.08 (m, 2H), 3.83−3.71 (m, 3H), 3.71 (m, 1H), 3.46 (m, 2H), 3.40−3.32 (m, 2H), 3.27 (m, 1H), 2.71 (m, 2H), 2.49 (s, 1H), 1.30 (t, *J* = 7.4 Hz, 3H), 1.17 (s, 9H), 1.02 (m, 21H); ^{13}C-NMR ($CDCl_3$) *δ* 176.8, 138.9, 138.6, 138.1, 137.8, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.7, 127.6, 127.5, 127.3, 127.2, 127.1, 99.8, 85.4, 84.0, 80.8, 79.4, 75.2, 74.8, 74.5, 74.4, 73.6, 72.5, 72.0, 71.8, 68.2, 38.8, 27.3, 24.0, 18.0, 18.0, 15.2, 11.8; MS (ES+): 1009.5 ($M^+ + Na^+$), (ES−): 1021.6 ($M^- + Cl^-$).

Synthesis of Thioethyl 3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-*β*-D-galactopyranoside-(1→4)-3,6-di-*O*-benzyl-2-O-pivaloyl-*β*-D-glucopyranoside 64. Thioethyl disaccharide **63** was protected using general procedure C to afford **64** (98%): $[\alpha]^{24}_D$: −8.8° (*c* 2.73, CH_2Cl_2); IR (thin film) 3030, 2940, 2865, 1739, 1454, 1277, 1143 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.32−7.10 (m, 15H), 7.08−6.94 (m, 5H), 5.33 (t, *J* = 8.0 Hz, 1H), 4.92 (m, 2H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.68 (d, *J* = 9.2 Hz, 1H), 4.42 (t, *J* = 11.5 Hz, 1H), 4.39 (m, 1H), 4.30 (m, 4H), 4.00 (t, *J* = 10.8 Hz, 1H), 3.90 (m 1H), 3.78−3.61 (m, 3H), 3.50 (m, 2H), 3.38 (m, 2H), 3.29 (m, 2H), 3.19 (m, 1H), 2.60 (m, 2H), 1.20 (t, *J* = 7.5 Hz, 3H), 1.12 (m, 18H), 0.90 (m, 21H); ^{13}C-NMR ($CDCl_3$) *δ* 176.7, 176.6, 138.8, 138.6, 138.4, 138.0, 128.3, 128.1, 128.0, 127.9, 127.6, 127.5, 127.3, 127.1, 127.0, 126.6, 99.7, 83.4, 81.9, 80.6, 79.4, 74.6, 73.4, 72.3, 72.1, 71.8, 70.5, 67.9, 60.5, 38.7, 38.5, 27.2, 26.9, 23.3, 17.9, 14.8, 11.6; MS (ES+): 1093.7 ($M^+ + Na^+$), (ES−): 1105.6 ($M^- + Cl^-$).

Synthesis of 3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-*β*-D-galactopyranoside-(1→4)-3,6-di-*O*-benzyl-2-O-pivaloyl-*β*-D-glucopyranoside-(1→4)-3,6-di-O-benzyl-D-glucal 65. Coupling of donor **64** and acceptor **30** was accomplished using general procedure D to yield 69% of **65**: $[\alpha]^{24}_D$: −14.4° (*c* 2.4, CH_2Cl_2); IR (thin film) 3029, 2949, 2865, 1740, 1454, 1096 cm^{-1}; ^{1}H-NMR ($CDCl_3$) *δ* 7.38−7.10 (m, 25H), 7.07−6.92 (m, 5H), 6.32 (d, *J* = 6.2 Hz, 1H), 5.34 (t, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 11.2 Hz, 1H), 4.89−4.85 (m, 2H), 4.76 (m, 1H), 4.65−4.38 (m, 10H), 4.32−4.26 (m, 3H), 4.11−3.96 (m, 4H), 3.86 (m, 1H), 3.78−3.59 (m, 4H), 3.48−3.29 (m, 3H), 3.25 (m, 1H), 3.18−3.12 (m, 2H), 1.11 (s, 9H), 1.09 (s, 9H), 0.91 (m, 21H); ^{13}C-NMR ($CDCl_3$) *δ* 176.6, 176.3, 144.2, 138.8, 138.7, 137.9, 137.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.3, 127.1, 127.0, 126.6, 100.0, 99.7, 99.4, 80.6, 75.7, 75.0, 74.8, 74.4, 74.3, 73.4, 72.7, 72.3, 71.8, 71.7, 70.5, 67.8, 60.4, 38.6, 27.2, 27.0, 17.9, 17.8, 11.6; MS (ES+): 1358.9 ($M^+ + Na^+$), (ES−): 1370.8 ($M^- + Cl^-$).

Synthesis of Thioethyl 3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triiso-

propylsilyl-β-D-galactopyranoside-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-D-glucopyranoside-(1→4)-3,6-di-*O*-benzyl-β-D-glucopyranoise 66. Trisaccharide glycal **65** was converted into **66** (65%) using general procedure A: $[\alpha]^{24}_D$: −19.9° (*c* 2.23, CH_2Cl_2); IR (thin film) 3566, 2960, 2940, 2565, 1740, 1454, 1276, 1142, 1066, 1028 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.40−7.17 (m, 26H), 7.09−6.97 (m, 4H), 5.40 (dd, *J* = 9.8, 8.2 Hz, 1H), 5.11−5.03 (m, 2H), 4.98−4.90 (m, 2H), 4.78−4.25 (m, 12H), 4.09−3.98 (m, 2H), 3.94 (br. s, 1H), 3.80−3.64 (m, 4H), 3.50−3.15 (m, 9H), 2.70 (m, 2H), 2.48 (br. s, 1H), 1.29 (t, *J* = 7.4 Hz, 3H), 1.27 (s, 9H), 1.11 (s, 9H), 0.97 and 0.95 (2 s, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.8, 176.5, 139.0, 138.8, 138.2, 137.9, 137.6, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.4, 127.2, 127.2, 127.0, 126.6, 99.8, 99.6, 85.4, 83.8, 80.8, 80.7, 79.2, 75.2, 74.8, 74.6, 74.6, 74.5, 73.7, 73.4, 72.7, 72.4, 72.0, 71.9, 71.8, 67.8, 60.4, 38.8, 38.7, 27.4, 27.2, 24.0, 18.0, 18.0, 15.2, 11.8; MS (ES+): 1435.9 ($M^+ + Na^+$), (ES−): 1447.7 ($M^- + Cl^-$).

Synthesis of Thioethyl 3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-galactopyranoside-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-D-glucopyranoside-(1→4)-3,6-di-*O*-pivaloyl-β-D-glucopyranoside 67. Thioethyl trisaccharide **66** was protected using general procedure C to afford **67** in 95% yield: $[\alpha]^{24}_D$: −29.2° (*c* 1.76, CH_2Cl_2); IR (thin film) 2964, 2866, 1740, 1479, 1277, 1143, 1061 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.37−6.98 (m, 30H), 5.37 (dd, *J* = 9.6, 8.1 Hz, 1H), 5.12 (d, *J* = 11.8 Hz, 1H), 5.09−5.01 (m, 2H), 4.96−4.90 (m, 2H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.54−4.25 (m, 9H), 4.11−4.03 (m, 2H), 3.99 (t, *J* = 9.2 Hz, 1H), 3.92 (m, 1H), 3.78 (dd, *J* = 10.9, 2.8 Hz, 1H), 3.69 (d, *J* = 10.3 Hz, 1H), 3.62−3.53 (m, 3H), 3.48−3.12 (m, 7H), 2.68 (m, 2H), 1.23 (t, *J* = 7.3 Hz, 3H), 1.14 (s, 9H), 1.11 (s, 9H), 1.09 (s, 9H), 0.96 and 0.94 (2 s, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.9, 176.8, 176.6, 139.2, 139.0, 138.8, 138.3, 137.9, 137.6, 128.7, 128.3, 128.3, 128.2, 128.0, 127.9, 127.9, 127.7, 127.6, 127.4, 127.2, 127.2, 127.1, 126.9, 126.7, 99.8, 99.6, 83.5, 82.6, 80.8, 80.7, 79.3, 75.3, 75.2, 75.0, 74.7, 74.5, 73.7, 73.3, 72.7, 72.5, 72.0, 71.8, 70.5, 67.7, 60.5, 38.8, 38.7, 38.6, 27.3, 27.2, 27.0, 23.4, 18.0, 18.0, 14.9, 11.8; MS (ES+): 1521.0 ($M^+ + Na^+$), (ES−): 1532.9 ($M^- + Cl^-$).

Synthesis of Thioethyl 3,4-Di-*O*-benzyl-2-*O*-pivaloyl-6-*O*-triisopropylsilyl-β-D-galactopyranoside-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-D-glucopyranoside-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-D-glucopyranoside-(1→4)-3,6-di-*O*-benzyl-glucal 68. Coupling of donor **67** and acceptor **30** was accomplished using general procedure D to yield 71% of **65**: $[\alpha]^{24}_D$: −29.5° (*c* 3.0, CH_2Cl_2); IR (thin film) 2963, 2940, 2866, 1740, 1650, 1479, 1276, 1140, 1058 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.38−6.99 (m, 40H), 6.37 (d, *J* = 6.1 Hz, 1H), 5.37 (dd, *J* = 9.7, 8.3 Hz, 1H), 5.08−4.91 (m, 4H), 4.80 (dd, *J* = 5.0, 3.2 Hz, 1H), 4.70−4.42 (m, 10H), 4.33−4.21 (m, 5H), 4.15−3.92 (m, 7H), 3.86−3.52 (m, 6H), 3.48−3.36 (m, 3H), 3.31−3.10 (m, 5H), 1.15 (s, 9H), 1.11 (s, 9H), 1.05 (s, 9H), 0.97 and 0.95 (2 s, 21H); ^{13}C-NMR ($CDCl_3$) δ 176.9, 144.4, 139.2, 139.0, 138.8, 138.3, 137.9, 137.8, 137.5, 128.7, 128.5, 128.3, 128.3, 128.3, 128.2, 128.0, 127.9, 127.9, 127.7, 127.6, 127.4, 127.3, 127.2, 127.2, 127.0, 126.9, 126.7, 126.6, 100.1, 99.8, 99.5, 81.2, 80.7, 80.7, 75.7, 75.3, 75.2, 75.1, 74.9, 74.6, 74.5, 74.5, 74.4, 73.7, 73.6, 73.3, 72.8, 72.7, 72.5, 72.3, 71.9, 71.8, 70.6, 68.0, 67.7, 67.5, 60.4, 38.8, 38.7, 38.6, 27.3, 27.2, 27.1, 18.0, 18.0, 11.8; MS (ES+): 1785.1 ($M^+ + Na^+$), (ES−): 1797.0 ($M^- + Cl^-$).

Synthesis of Thioethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside-(1→3)-4,6-*O*-(4-methoxy)benzylidene-β-D-glucopyranoside 69. Disaccharide glucal **40** (86 mg, 0.116 mmol) was treated according to general procedure A giving **69** (61 mg (64%)) as a white foam: $[\alpha]^{23}_D$: −28.5° (*c* 2.70, $CHCl_3$); IR (thin film): 3440, 3010, 2830, 1730, 1605, 1505, 1480, 1360, 1165 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.42−7.25 (m, 15H), 7.20−7.12 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.41 (s, 1H), 5.03 (t, *J* = 8.6 Hz, 1H), 4.84−4.63 (m, 4H), 4.59−4.43 (m, 4H), 4.31 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.88−3.42 (m, 9H), 3.77 (s, 3H), 3.28 (br d, *J* = 9.5 Hz, 1H), 3.03 (d, *J* = 2.2 Hz, 1H), 2.83−2.72 (m, 2H), 1.92 (s, 3H), 1.34 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ 170.8, 160.5, 138.6, 138.5, 138.2, 130.1, 128.8, 128.8, 128.5, 128.3, 128.2, 128.1, 127.9, 1140.0, 102.0, 101.2, 86.3, 83.1, 82.8, 80.0, 78.1, 77.9, 77.5, 77.1, 75.5, 75.3, 74.2, 73.8, 72.7, 71.2, 69.0, 68.5, 55.6, 24.8, 21.4, 15.5; HRMS (FAB) calcd for $C_{45}H_{52}O_{12}SNa$: 839.3077, found *m*/*z* 839.3099 (M + Na).

Synthesis of Thioethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside-(1→3)-4,6-*O*-(4-methoxy)benzylidene-2-*O*-pivaloyl-β-D-glucopyranoside 72. Disaccharide **70** (21 mg, 0.026 mmol) was reacted according to general procedure C to give **72** (24 mg (quant.)) as a white foam: $[\alpha]^{23}_D$: −38.8° (*c* 7.20, $CHCl_3$); IR (thin film): 3050, 2950, 2855, 1730, 1605, 1505, 1445, 1360, 1295, 1220 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.38−7.17 (m, 15H), 6.73 (d, *J* = 8.8 Hz, 1H), 5.48 (s, 1H), 5.07 (t *J* = 9.4 Hz, 1H), 5.01 (t, *J* = 8.7 Hz, 1H), 4.81−4.72 (m, 2H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.58−4.51 (m, 2H), 4.45−4.30 (m, 4H), 4.02 (t, *J* = 9.1 Hz, 1H), 3.83−3.62 (m, 5H), 3.66 (s, 3H), 3.55 (t, *J* = 9.2 Hz, 1H), 3.49−3.39 (m, 2H), 2.75−2.62 (m, 2H), 1.97 (s, 3H), 1.24 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 170.3, 160.2, 138.9, 138.4, 138.1, 130.2, 128.9, 128.7, 128.7, 128.4, 128.4, 128.1, 128.1, 127.9, 127.9, 113.7, 101.8, 101.0, 84.5, 83.0, 78.9, 78.7, 78.4, 77.7, 76.1, 75.5, 75.1, 74.2, 72.9, 72.3, 71.7, 69.8, 68.9, 55.5, 39.0, 27.8, 24.1, 21.3, 15.1; HRMS (FAB) calcd for $C_{50}H_{60}O_{13}SNa$ = 923.3652, found *m*/*z* 923.3652 (M + Na).

Synthesis of 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside-(1→3)-2-*O*-pivaloyl-4,6-*O*-(4-methoxy)benzylidene-β-D-glucopyranoside(1→3)-4,6-*O*-(4-methoxy)benzylidene-D-glucal 75. Thioethyl donor **72** (13.9 mg, 0.015 mmol) and glucal acceptor **40** (5.0 mg, 0.019 mmol) were reacted according to general procedure D giving **75** (12.6 mg (74%)) as a white foam: $[\alpha]^{23}_D$: −24.64° (*c* 6.30, $CHCl_3$); IR (thin film) 3050, 2860, 1735, 1630, 1510, 1445, 1365, 1280, 1225 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.36−7.19 (m, 17H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.37 (dd, *J* = 6.2, 1.2 Hz, 1H), 5.58 (s, 1H), 5.28 (s, 1H), 5.03−4.98 (m, 2H), 4.77 (t, *J* = 11.0 Hz, 2H), 4.69−4.63 (m, 3H), 4.58−4.53 (m, 2H), 4.50−4.44 (m, 2H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.35 (dd, *J* = 9.7, 4.2 Hz, 1H), 4.12 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.99−3.65 (m, 9H), 3.77 (s, 3H), 3.67 (s, 3H), 3.58 (t, *J* = 9.2 Hz, 1H), 3.46−3.42 (m, 1H), 3.37−3.31 (m, 1H), 1.98 (s, 3H), 1.24 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 176.5, 160.8, 145.5, 138.9, 138.5, 138.1, 130.2, 128.9, 128.8, 128.7, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 114.1, 113.8, 102.0, 101.6, 101.2, 100.4, 99.9, 83.1, 78.9, 78.7, 78.6, 77.5, 76.1, 75.4, 75.2, 74.4, 74.2, 73.6, 73.0, 69.5, 69.2, 69.1, 68.6, 66.9, 55.6, 55.5, 39.2, 27.8, 21.4; HRMS (FAB) calcd for $C_{62}H_{70}O_{18}Na$: 1125.4460, found *m*/*z* 1125.4456 (M + Na).

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Supporting Information Available: Experimental procedures for **9**−**11**, **17**, and **18**, general procedure B for **12**, **13**, **16**, **19**, **23**, **23a**, **24**, **26**, **27a**, **28**, **31**, **32**, **32a**, **33**, **35**−**37**, **40**, **40a**, **41**, **43**, **44**, **46**, **46a**, **47**, **49**, **50**, **52**, **52a**, **53**, **58**, **60**, **61**, **62**, **70**, **71**, and **73a**, general procedure E for **76**−**78** and ^{1}H and ^{13}C NMR spectra for **25**, **29**, **34**, **38**, **42**, **45**, **48**, **51**, **54**, **56**, **59**, **68**, **75**, and **78** (43 pages). See any current masthead page for ordering and Internet access instructions.

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