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Applications of 5-*exo*-trig Thiyl Radical Cyclizations for the Synthesis of Thiosugars

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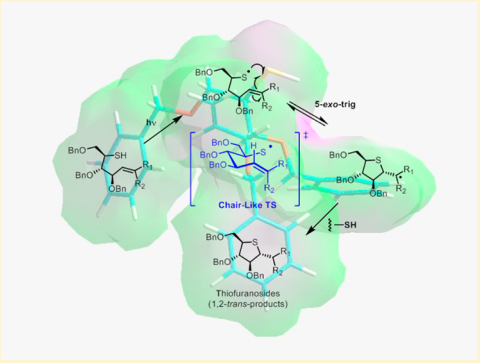
Supporting Information

ABSTRACT: The application of thiyl-radical-mediated 5-*exo*-trig cyclization reactions for the preparation of a series of C-linked 4-thiofuranoside sugars has been investigated. The cyclization reactions were found to proceed in high yield with complete regioselectivity and moderate to excellent diastereoselectivity for a number of benzyl-protected precursors. The diastereoselectivity of the radical cyclization was determined by a number of factors, primarily the stereochemistry at the C-2 position and the nature of the substituents attached to the olefin. The cyclization reactions proceed via transition-state intermediates that favor formation of the 1,2-*trans* products. For D-sugars, a chairlike transition state is proposed. For L-sugars, both chair- and boatlike transition states could be considered. Inversion of the stereochemistry at C-4 also induced a significant effect on the diastereoselectivity of the radical process. The synthetic route is general for both D- and L-sugars and offers a highly novel and efficient strategy for accessing C-linked 4-thiofuranosides. A fluorescently labeled thiosugar was prepared as a putative glycosidase inhibitor.



INTRODUCTION

Thiosugars are carbohydrate analogues in which one or more oxygen atoms are substituted with sulfur in both furanoside and pyranoside structures.[1,2] Because of the unique conformational and electronic properties conferred by the presence of the sulfur atom, these compounds offer fascinating prospects for medicinal chemistry[3] and have been shown to demonstrate potent biological activity as antiviral,[4,5] antidiabetic,[6] and anticancer compounds.[7,8] The potent, naturally occurring α-glucosidase inhibitor salacinol (**1**) (Figure 1) contains a 1-deoxy-4-thioarabinofuranosyl sulfonium cation, which is essential for the biological activity of the molecule.[9,10] The related family of sulfonium salts isolated from the *Salacia* species all contain an identical thioarabinofuranosyl core structure.[11] The replacement of the furanose-ring oxygen with sulfur also confers potent biological activity on naturally occurring nucleosides.[12,13] Examples such as 4-thiothymidine (**2**)[14,15] and 2-deoxy-4-thiocytidine (**3**)[14] (Figure 1), in which a heterocyclic group is attached directly to C-1 of the thiofuranose ring, have been demonstrated to possess extremely potent antiviral and anticancer activity.[16] The structurally related 4-thio analogues of C-nucleosides are also of considerable interest as potential glycosidase inhibitors, but currently there are a limited number of synthetic strategies available to access these compounds.[17,18] Recently, Haraguchi and co-workers developed a method for the synthesis of the β-anomer of 4-thio-C-ribonucleosides starting from a 3,5-*O*-(di-*tert*-butylsilylene)-4-thiofuranoid glycal.[19] Because of the potential applications of thiosugars as bioactive compounds, the development of new methodologies for accessing new classes of thiosugars remains highly relevant. In particular, synthetic routes to 4-thio analogues of C-nucleosides and related C-linked thiofuranosides are of considerable interest. Several efficient and elegant methodologies have been developed for the preparation of thiosugars[20−26] and their C-analogues,[19] but the application of thiyl-radical-mediated intramolecular cyclizations remains unexplored. The free-radical approach offers several advantages over current strategies for thiofuranose synthesis due to the high regio- and diastereoselectivity available from these reactions, the mild conditions required for initiation, and the tolerance of a wide range of protecting groups.[27] The radical cyclization also allows for formation of the C-linked thiofuranosides in one step as part of the cyclization reaction. Examples of intramolecular thiyl radical cyclizations onto alkenes for the preparation of sulfur-containing heterocycles are rare,[28−34] but the analogous

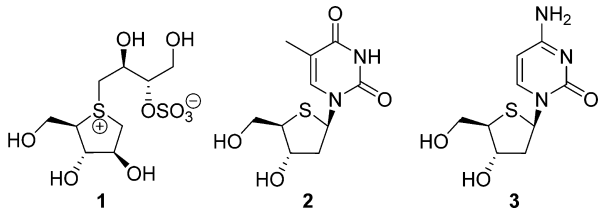


Figure 1. Salacinol (**1**), 4-thiothymidine (**2**), and 2-deoxy-4-thiocytidine (**3**).

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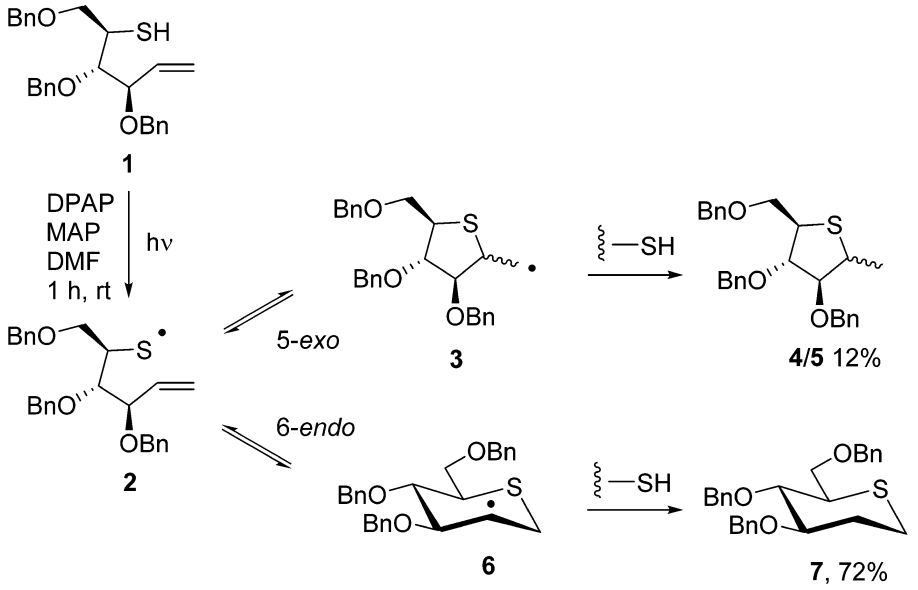
Scheme 1. Product Distribution Obtained from Intramolecular Thiyl-Radical-Mediated Cyclization onto a Terminal Alkene



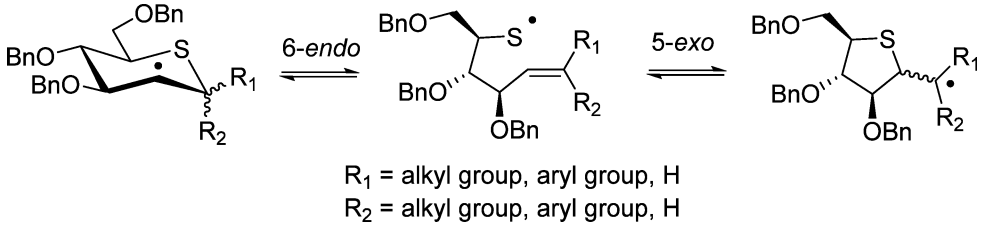
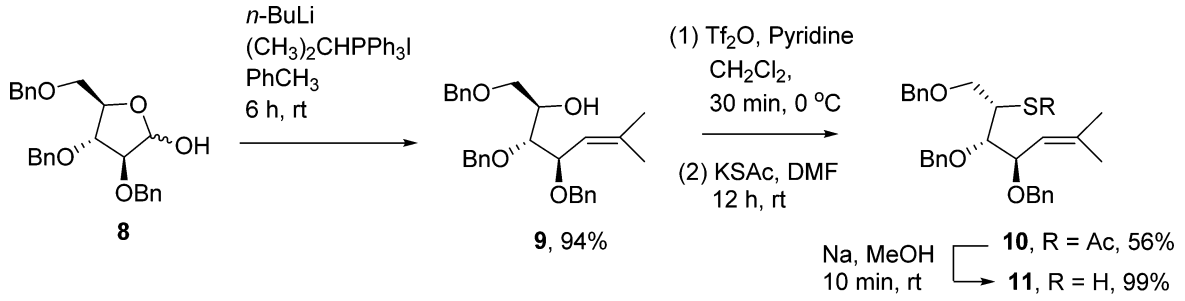


Figure 2. Radical species formed upon thiyl radical cyclization onto substituted alkenes.

Scheme 2. Preparation of Thiyl Radical Precursor 11



intermolecular thiol−ene click (TEC) reaction is becoming widely used in carbohydrate and peptide chemistry for the synthesis of glycopeptides and glycoproteins.[27,35−37] Taking advantage of the reversible nature of the radical cyclization[32] and promoting the 5-*exo* radical cyclization process makes possible the preparation of 4-thiofuranosides in high yield with high diastereoselectivity. Herein we report the results of our investigation into the use of 5-*exo*-trig thiyl radical cyclizations for the synthesis of C-linked thiofuranosides as putative glycosidase inhibitors.

RESULTS AND DISCUSSION

In our recent study of the applications of intramolecular thiyl-radical-mediated cyclization reactions for the preparation of pyranosyl thiosugars, we observed that the 5-*exo*-trig cyclization products **4** and **5** were not the dominant products emerging from cyclization onto a terminal alkene. Rather, the 6-*endo* process dominated, resulting in almost exclusive formation of the thiopyranose ring **7**.[38] Conditions for this photochemically initiated reaction were optimized using 2,2-dimethoxy-2-phenylacetophenone (DPAP) as an initiator and 4-methoxyacetophenone (MAP) as a photosensitizer (Scheme 1).

We rationalized that this product distribution was due to the relative stability of the secondary alkyl radical intermediate **6** formed during the 6-*endo* cyclization process over the less stable radical **3** derived from the 5-*exo* cyclization pathway. As outlined in the Introduction, C-linked thiofuranosides are extremely interesting sugars with a range of biological applications. We therefore set out to develop a method where we could promote the formation of the 5-*exo*-trig products under radical cyclization conditions to furnish the C-linked thiofuranoside products exclusively. It was anticipated that this could be achieved by using substituted alkenes for which the stability of the radical formed upon 5-*exo* cyclization

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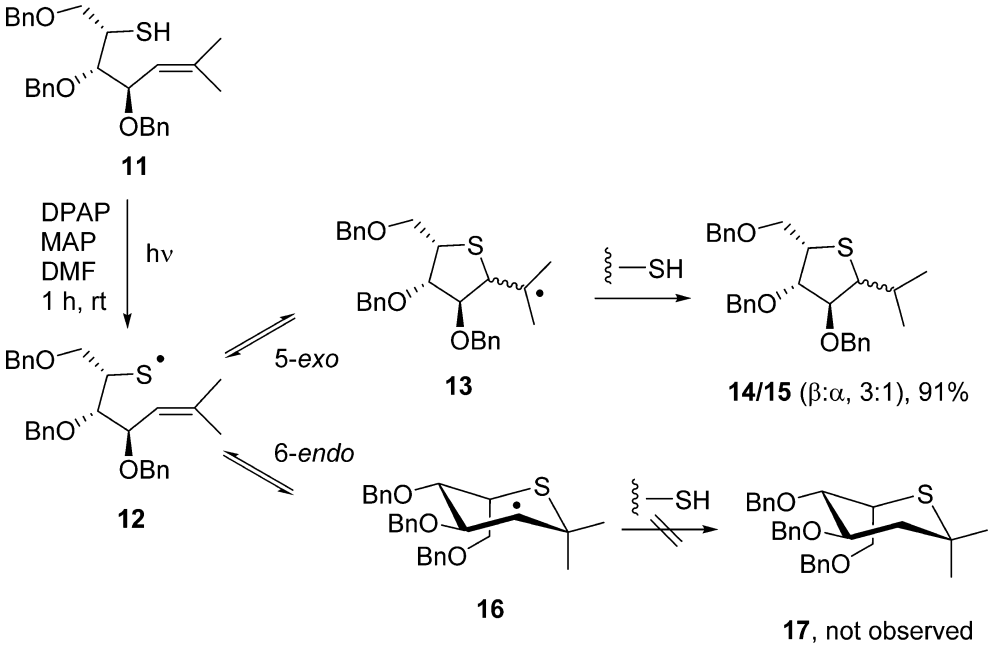
Scheme 3. Thiyl Radical Cyclization Reaction from Precursor 11



would be greater than that of the competing 6-*endo* product (Figure 2). The 5-*exo* radical cyclization process would also result in the formation of a new stereocenter at C-1, and we were interested in studying the diastereoselectivity of the radical cyclization reaction process.

In order to investigate the effect of using a substituted olefin in the radical cyclization reaction, we prepared thiyl radical precursor **11** containing a terminal isopropylidene olefin using the procedure shown in Scheme 2. Treatment of commercially available benzyl-protected D-arabinose hemiacetal **8** with the appropriate isopropyl Wittig reagent furnished the desired isopropylidene olefin **9**. Olefin **9** was reacted with triflic anhydride, and an S_N2 substitution reaction with KSAc was used to introduce the protected thiol group with inversion of configuration at C-4. Treatment of the thioester with catalytic sodium methoxide in methanol released the free thiol, furnishing the desired thiyl radical precursor **11**.

Once precursor **11** was available, we set out to investigate the intramolecular radical cyclization reaction. Conditions for the photochemically initiated intramolecular thiol−ene reaction had previously been optimized for 6-*endo* cyclization onto a terminal alkene,[38] and these optimized conditions were applied to precursor **11**. Gratifyingly, the expected 5-*exo* products **14** and **15** were the only products observed in this reaction and were isolated in an excellent yield of 91% as an inseparable mixture of diastereoisomers [**14**:**15** (β:α) = 3:1] (Scheme 3). The diastereomeric ratio was determined by ^{1}H NMR analysis (see the Supporting Information for details). The competing 6-*endo* product **17** was not observed under these conditions. The free-radical cyclization reaction proceeded in high yield with complete regioselectivity and good diastereoselectivity in favor of the 1,2-*trans* product. This result clearly demonstrated that 5-*exo*-trig radical cyclizations of a thiyl radical onto a substituted alkene can be used to prepare C-linked thiofuranosides in high yield. We have previously demonstrated that benzyl-protected thiosugars can be readily deprotected in good yield by employing Birch conditions.[38] The presence of the sulfur atom does not appear to hinder the removal of the benzyl protecting group under these conditions.

Both the product distribution and the diastereomeric ratio of 5-*exo*-trig products observed for this reaction require some rationalization. The distribution of products formed from the intramolecular thiyl radical cyclization depends on a number of factors, including the relative stability of the alkyl radicals formed upon cyclization and the rate of the radical chain transfer step. For the diastereomeric ratio of the 5-*exo* products, steric factors relating to the stereochemistry of the benzyl-protected hydroxyl groups and the conformation of the transition state should be considered. The kinetics of the intermolecular thiol−ene polymerization reaction have been investigated by a number of groups.[39,40] The major factor governing the overall kinetics of the thiol−ene polymerization reaction is the ratio of the propagation rate to the chain transfer rate. For the intramolecular process, we can assume that the chain transfer step is rate-limiting and that the overall process is first order with respect to thiol concentration. We anticipated that the 5-*exo*-trig products would dominate because of the relative stability of the tertiary alkyl radical **13** formed upon 5-*exo* cyclization. In terms of the diastereoselectivity of the radical reaction, four possible transition-state structures can be adopted (**A**−**D** in Figure 3). Beckwith,[41] Houk,[42] and others have reported that hex-5-enyl radical cyclizations normally proceed through either a "chairlike" or "boatlike" transition state, with the chairlike state usually being favored. Beckwith proposed that the major product would arise from a conformation where the substituents could occupy quasi-equatorial orientations. RajanBabu has carried out detailed studies on the cyclization of hex-5-enyl radicals derived from carbohydrates.[43−45] His studies have concluded that in systems with a C_4 substituent present, the local allylic conformation dictates the choice between the "chairlike" and "boatlike" transition states, with the conformation that results in the least allylic strain being dominant.[45] In the case of thiyl radical **12**, formation of the chairlike transition structure **A** is favored since it minimizes steric interactions between the isopropyl group at C-1 and the benzyl protecting

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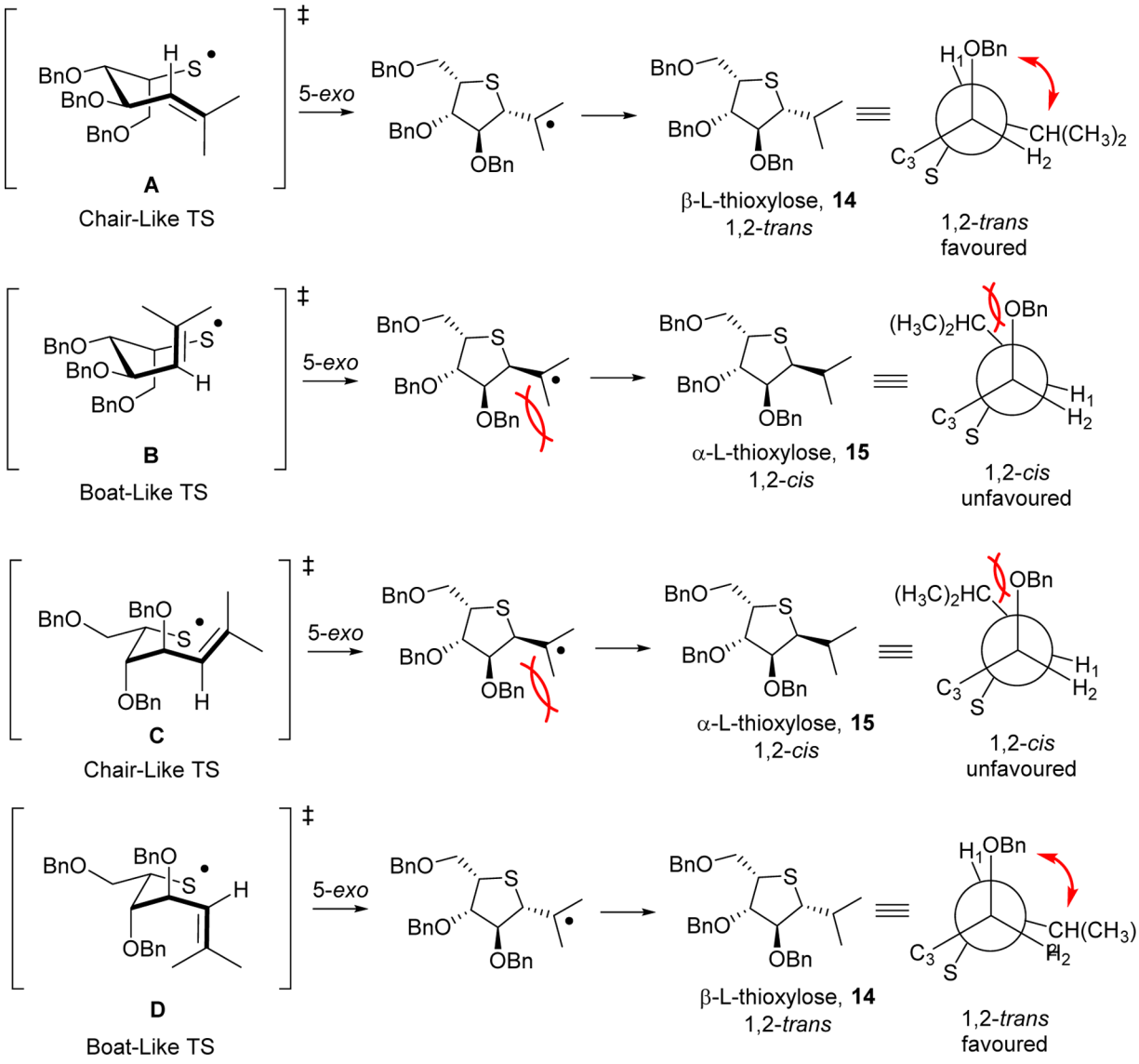

Figure 3. Transition-state structures for thiyl radical **11**.

group at C-2 which results in the formation of 1,2-*trans* product **14** as the major diastereoisomer (Figure 3). The 1,2-*cis* product **15** is the minor product. The formation of the new C-1−H bond in both **14** and **15** was confirmed by the presence of the strong correlation between H-1 and H-2 in the COSY experiment. The structures of diastereoisomers **14** and **15** were confirmed by detailed NMR analysis techniques, including rotating-frame nuclear Overhauser effect spectroscopy (ROESY) (see the Supporting Information for details). An alternative pair of transition-state structures (**C** and **D**) can also be proposed for the formation of **14** and **15** whereby the benzyloxymethyl group occupies an equatorial orientation and the two benzyloxy protecting groups are both axial. This alternative TS places the majority of the substituents in a quasi-axial orientation. The alternative TS is worth considering since it is known that in L-hexose sugars the bulky hydroxymethyl group can lock the structure into a conformation in which this group is equatorial even if this means that other substituents have to adopt an axial orientation. In this case it would be the boatlike TS **D** that would result in the formation of the observed 1,2-*trans* product. It is difficult to predict whether **A** or **D** is more favorable for this cyclization without recourse to detailed computational studies.

After demonstrating that 5-*exo* radical cyclizations can be employed for the preparation of the novel C-thiofuranosides **14** and **15** possessing the unusual L-xylose configuration, we set out to investigate other substituted olefin groups that would promote the 5-*exo* cyclization process. Aromatic rings are well-known to promote radical cyclization reactions by facilitating stabilization of the cyclized radical intermediates through delocalization onto the aromatic ring.[46] We carried out the olefination reaction on D-arabinose hemiacetal **8** using a modified version of the procedure described by Motoshima and co-workers,[47] wherein potassium carbonate was used as the base and 18-crown-6 was added as a phase transfer catalyst. Using 3 equiv of the phosphonium salt and base gave the desired olefin **18** in 72% yield as a 50:50 mixture of *E* and *Z* isomers (Scheme 4). The resulting olefin was treated with triflic anhydride and KSAc in a manner analogous to that for the preparation of thioester **10**, again with inversion of stereochemistry at C-4. Treatment with sodium methoxide in methanol released the free thiol **20** in good yield. In order to investigate the scope of this methodology and to apply it to a

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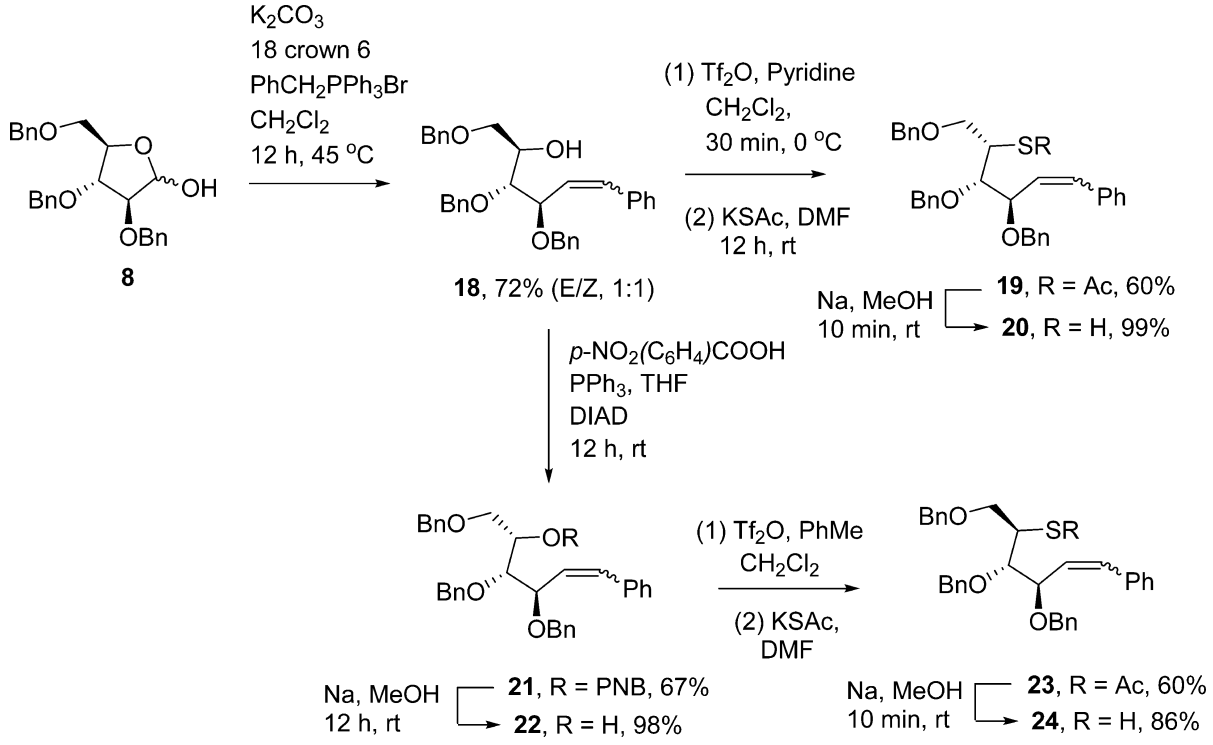
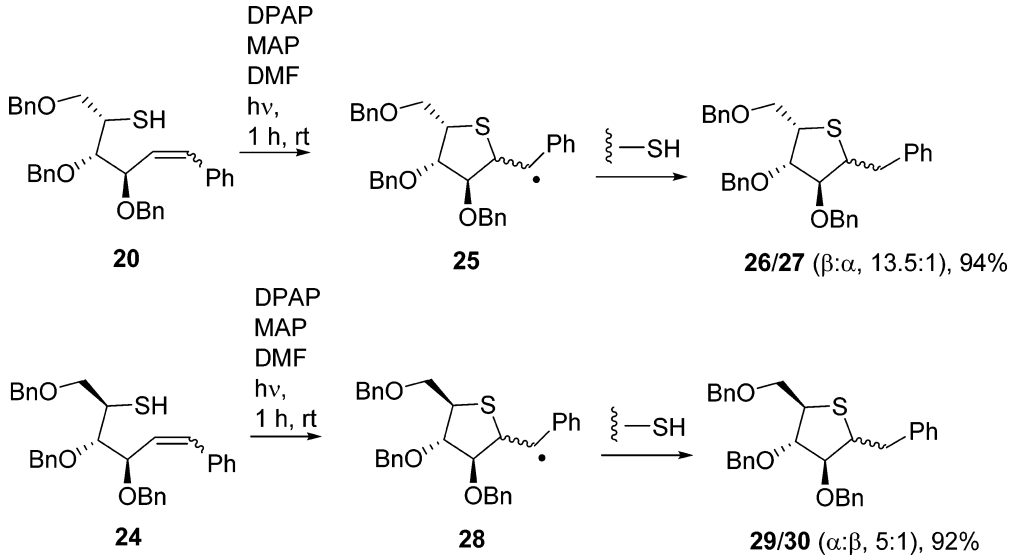
Scheme 4. Synthesis of Phenyl-Containing Derivatives 18 and 22



Scheme 5. Results of Radical Cyclization Reactions from Radical Precursors 18 and 20



broad range of furanosides, we also prepared the D-arabinose analogue **24**, wherein the stereochemistry at C-4 was maintained using a double inversion strategy.[48] We were also interested in investigating how this variation in stereochemistry would affect the overall diastereoselectivity of the 5-*exo* cyclization reaction.

With both thiols **20** and **24** in hand, we investigated their intramolecular radical cyclization reactions. The results of these radical reactions are outlined in Scheme 5. In both cases, the radical reactions gave excellent yields of the desired 5-*exo* cyclization products. The diastereoselectivity of the radical cyclization was maintained in favor of the 1,2-*trans* products, but the cyclization starting from L-sugar **20** exhibited a significantly enhanced diastereoselectivity relative to the corresponding D-sugar, suggesting that the formation of the chairlike transition-state structure **E** (Figure 4) is highly favored. Once again, it is possible that the benzyloxymethyl group occupies an equatorial orientation and that the major product **26** may be formed via a boat-type TS as outlined in TS-**D** above. Since the amounts of allylic strain in these two systems should be identical, we rationalized that an additional stabilizing interaction must be participating in the stabilization of transition state **E**. This may be a π-stacking interaction between the olefin phenyl group and the C-6 OBn protecting group, which occupy the same face in the L-sugar. This type of π-stacking-promoted diastereoselectivity in intramolecular reactions has been described previously by a number of groups.[49,50] In the case of the D-sugar there would be no

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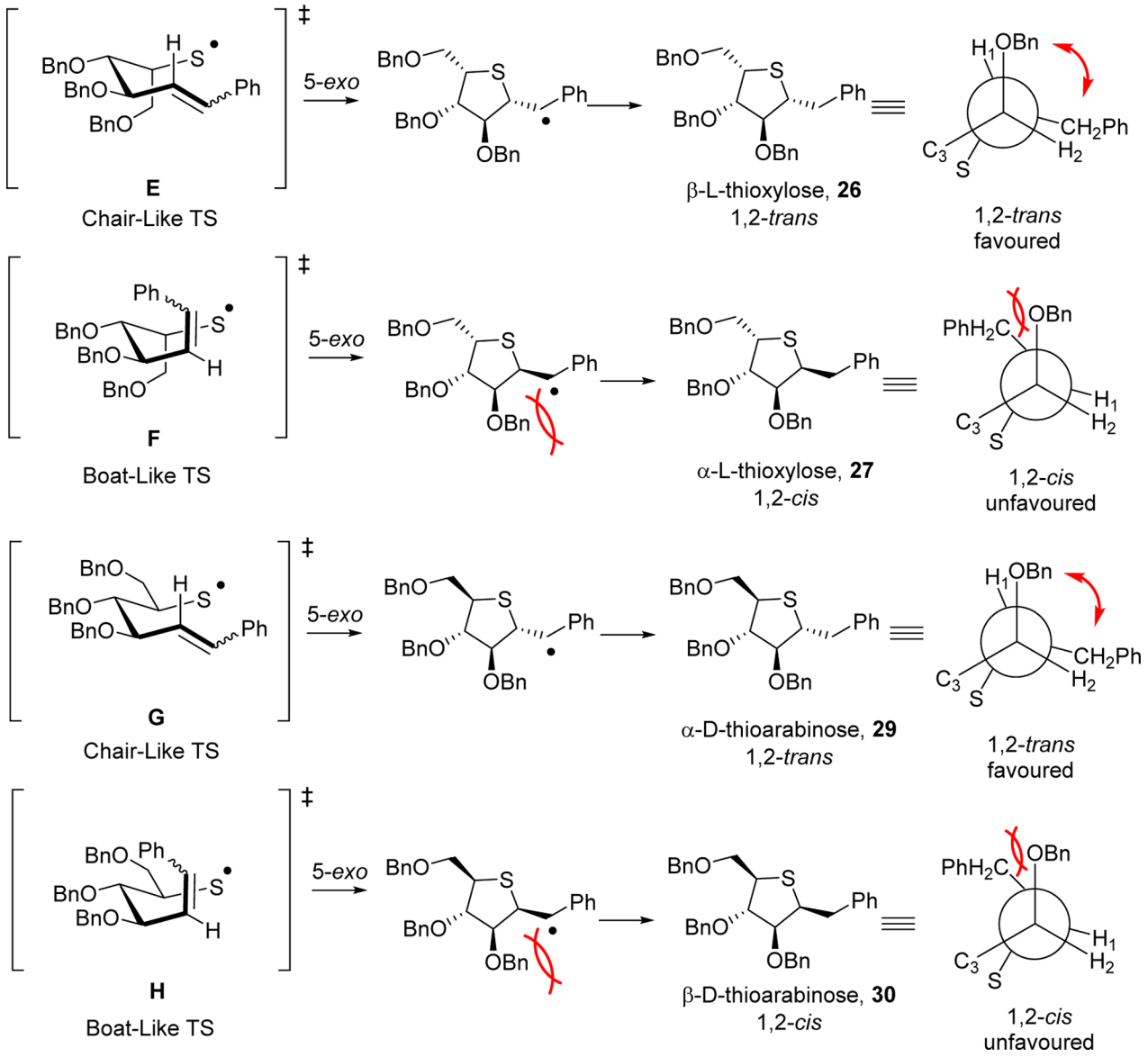

Figure 4. Transition-state structures for the thiyl radical cyclizations of **18** and **20**.

possibility of such a π-stacking interaction, and although D-sugar **24** furnished the 1,2-*trans* compound **29** as the major product, the diastereoselectivity was more comparable to that of the isopropylidene example. This variation in the diastereoselectivity suggests that the stereochemistries at both C-2 and C-4 are important in determining the stereochemical outcome of the intramolecular radical cyclization. This observation is consistent with observations reported by Beckwith and others for related systems.[41,42,45] It is also noteworthy that using a mixture of *E* and *Z* isomers in the olefin starting material did not appear to affect the product distribution, as both isomers furnished the 1,2-*trans* product **26** or **29** as the major product.

In order to further investigate the scope and limitations of this methodology, in particular the excellent diastereoselectivity observed when using benzyl-protected L-sugar **20** for the radical-mediated cyclization onto an olefin substituted with an aromatic group, we set out to investigate the radical cyclization onto an olefin substituted with a methylbenzoate group. The presence of the methylbenzoate group would allow us to investigate the effect of carrying out the radical cyclization onto a more electron-deficient alkene.[51] In addition, we envisaged that the methyl ester group could be readily hydrolyzed to the corresponding acid following cyclization and used as a "synthetic handle" for introducing a fluorescent label onto the thiosugar. Fluorescently labeled sugars[52,53] and thiosugars[54] have a wide range of biological applications, and we were interested in accessing fluorescently labeled versions of our C-linked thiosugars as putative glycosidase inhibitors. The synthesis of the methylbenzoate-containing thiol **33** was carried out in a manner similar to that described for the phenyl-containing systems **20** and **24**, and the desired olefin was prepared as a mixture of *E* and *Z* isomers in 63% isolated yield (Scheme 6). The olefin was then converted into the desired thiol using the conditions described previously. In this case, thioester **32** had to be deprotected at low temperature in order to prevent spontaneous ring closure of the thiolate onto the electron-deficient alkene. The free-radical cyclization reaction was carried out under the standard conditions and furnished the 5-*exo*-trig products in 89% yield, but the high diaster-

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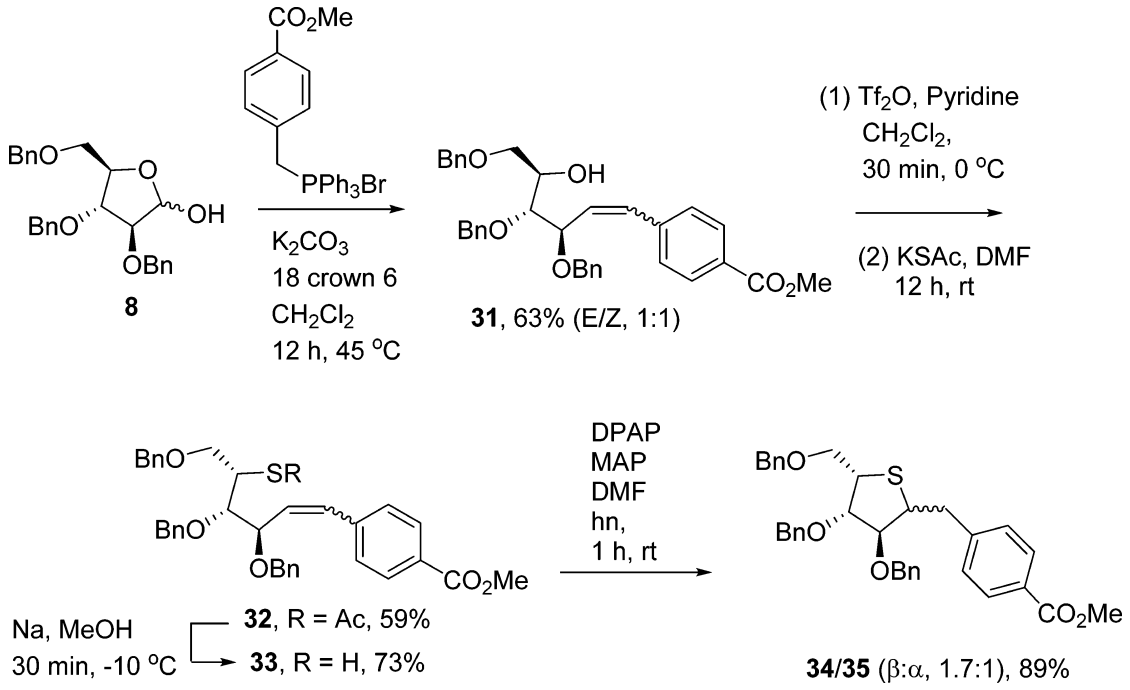
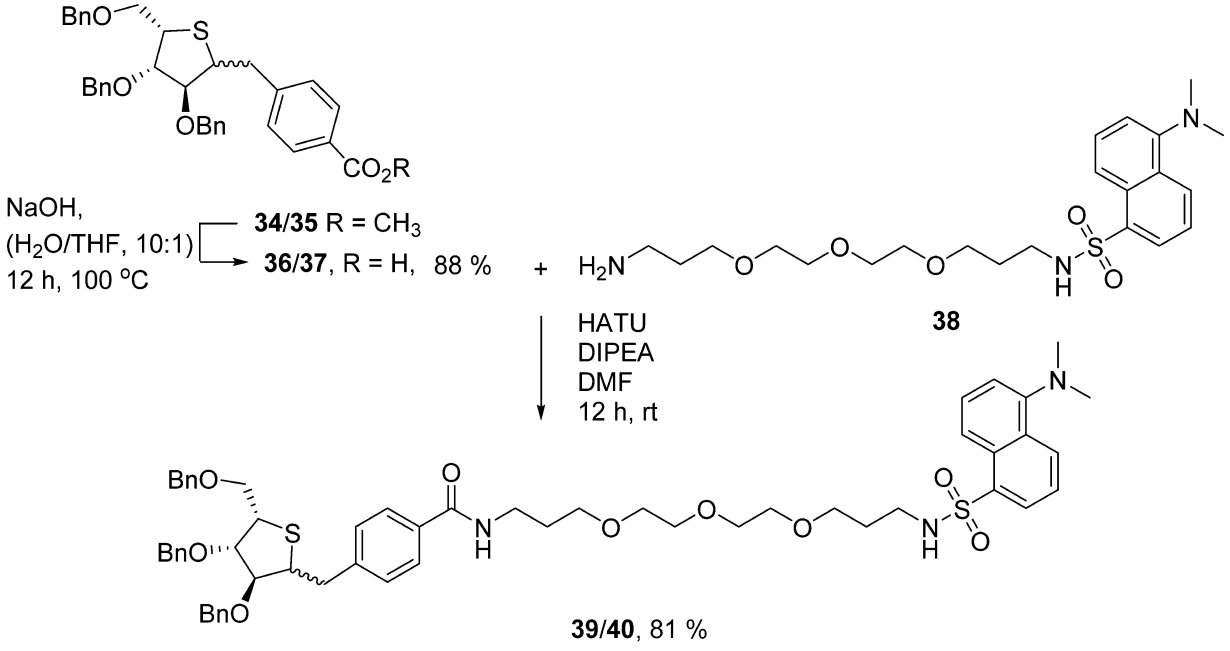
Scheme 6. Synthesis of Methylbenzoate-Containing Derivatives 32 and 33



Scheme 7. Preparation of Fluorescently Labeled Thiosugars 37 and 38



eoselectivity observed in the phenyl system was not observed in this case. The 1,2-*trans* isomer **34** was still the major product, but significant quantities of the *cis* isomer **35** were also observed. The diastereomeric ratio of 1.7:1 was the lowest observed for any of the intramolecular free-radical cyclizations. This result suggests that the presence of the electron-deficient alkene may have a significant effect on the diastereoselectivity of the cyclization reaction. This may be attributed to the increased rate of cyclization onto the activated alkene.

Following the successful preparation of thiosugars **34** and **35**, we proceeded to couple these compounds with a 5-(dimethylamino)naphthalene-1-sulfonyl (Dansyl) fluorophore in order to furnish fluorescently labeled thiosugars **39** and **40**. Since diastereoisomers **34** and **35** were inseparable by chromatography, we carried the mixture forward to the fluorescently labeled products. The synthetic approach is outlined in Scheme 7. Following hydrolysis of the methyl ester mixture **34**/**35** to furnish the free-acid mixture **36**/**37**, an *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate (HATU)-promoted amide coupling reaction was used to introduce the poly(ethylene glycol)-linked dansyl fluorophore **38** to give the fluorescently labeled thiosugars **39** and **40** in good yield. This approach clearly demonstrates that further modification of the thiosugar can be carried out

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following the free-radical-mediated cyclization reaction and further highlights the synthetic potential of this methodology.

CONCLUSIONS

We have demonstrated for the first time that 5-*exo*-trig thiyl radical cyclizations can be employed for the efficient synthesis of C-linked thiofuranose products. The synthetic utility of the methodology was demonstrated through the preparation of a number of novel C-linked thiofuranosides. The methodology is robust and diastereoselective, allowing rapid access to thiofuranose derivatives in high yields under carefully controlled conditions. The level of diastereocontrol observed is remarkable given that the systems contain multiple stereogenic centers and that all of the reactions were carried out at room temperature. Investigations into the use of this methodology for the preparation of other sulfur-containing heterocycles are ongoing in our laboratory, and the results will be reported in due course.

EXPERIMENTAL SECTION

General Experimental Methods. For NMR spectra, a 400 MHz spectrometer was employed for ^{1}H (400.13 MHz) and ^{13}C (100.61 MHz) spectra and a 600 MHz spectrometer for ^{1}H (600.13 MHz) and ^{13}C (150.90 MHz) spectra. Resonances (δ) are reported in parts per million downfield from an internal reference in $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.0 ppm) or MeOH (δ_H = 3.31 ppm, δ_C = 49.0 ppm). Mass spectrometry analysis was performed with a MALDI quadrupole time-of-flight (Q-Tof) mass spectrometer equipped with Z-spray electrospray ionization (ESI). Silica gel (200 mesh) was used for column chromatography. Analytical thin-layer chromatography was performed using silica gel (precoated sheets, 0.2 mm thick, 20 cm × 20 cm) and visualized by UV irradiation or molybdenum staining. All UV reactions were carried out in a Luzchem photoreactor (LZC-EDU, 110 V/60 Hz) containing 10 UVA lamps (8 W) centered at 350 nm (unfiltered). DCM, MeOH, THF, and toluene were dried over flame-dried 3 Å or 4 Å sieves. Dimethylformamide (DMF), triethylamine (Et_3N), and trifluoroacetic acid (TFA) were used dry from Sure/Seal bottles. Other reagents were purchased from an industrial supplier.

General Procedure for the Synthesis of Thioesters. Sugar−OH (1 equiv) in dry CH_2Cl_2 (0.5 mmol/mL) was added to an oven-dried round-bottom flask (RBF) equipped with a Teflon stirring bar. The reaction mixture was cooled to 0 °C, and pyridine (2.5 equiv) was added, followed by the dropwise addition of triflic anhydride (1.2 equiv). The solution was stirred at 0 °C for 30 min. The reaction mixture was diluted in CH_2Cl_2 and washed with cold $NaHCO_3$, water, and brine. The organic layer was dried over magnesium sulfate and concentrated in vacuo. The crude triflate was dried under high vacuum and resuspended in dry DMF. KSAc (5 equiv) was added in one portion, and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted in ether and washed with brine, and the ethereal layer was dried over magnesium sulfate and concentrated in vacuo. The reaction mixture was purified by column chromatography.

General Procedure for Thioacetate Hydrolysis. To a degassed solution of sugar−thioacetate (1 equiv) in MeOH was added freshly prepared NaOMe (0.1 M soln). After the mixture was stirred for 10 min, the reaction was quenched by the addition of Dowex H^+ ion-exchange resin until the mixture was pH-neutral. The resin was removed by filtration and washed with MeOH, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

General Procedure for Radical Cyclization. Sugar−thiol (1 equiv) was dissolved in dry DMF (0.03 mmol/mL), and the solution was degassed under argon. 2,2-Dimethoxy-2-phenylacetophenone (DPAP) (0.1 equiv) and 4-methoxyacetophenone (MAP) (0.1 equiv) were added in one portion, and the resultant solution was UV-irradiated for 1 h without agitation. DMF was removed in vacuo, and the crude reaction mixture was purified by column chromatography.

Compound 9. To a suspension of isopropyltriphenylphosponium iodide (3.08 g, 7.15 mmol) in dry toluene (30 mL) was added dropwise a 1.6 M solution of *n*-butyllithium in hexane (4.31 mL, 6.90 mmol) at 0 °C under N_2, and the reaction mixture was stirred for 30 min at room temperature. A suspension of 2,3,4-tri-*O*-benzyl-α-D-arabinofuranose (**8**) (1.00 g, 2.38 mmol) in dry toluene (10 mL) was added, and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched with acetone (5 mL), and the mixture was diluted with ether and extracted with water (50 mL). The aqueous phase was extracted with ether (50 mL), and the organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography (10:1 hexane/ethyl acetate) to afford **9** (990 mg, 2.22 mmol, 94%) as a colorless oil. $[\alpha]_D^{20}$ +17.1° (c = 0.1, $CHCl_3$); ν_{max} (thin film) 1180 (C−O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42−7.28 (15H, m, Ar−H), 5.34 (1H, bd, $J_{2,1}$ = 9.1 Hz, H-2), 4.68 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.62 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.60 (1H, d, J = 11.1 Hz, Bn-CH_2), 4.53 (2H, app s, Bn-CH_2), 4.35 (1H, dd, $J_{3,2}$ = 9.1 Hz, $J_{3,4}$ = 4.5 Hz, H-3), 4.34 (1H, d, J = 11.1 Hz, Bn-CH_2), 4.04 (1H, m, H-5), 3.60 (3H, m, H-4, H-6, and H-6′), 2.96 (1H, bs, OH), 1.80 (3H, s, CH_3), 1.57 (3H, s, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 138.1, 138.1 (q-Ar), 137.9 (C-1), 128.2, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 127.5, 127.4 (Ar-C), 121.9 (C-2), 80.9 (C-4), 75.1 (C-3), 74.1 (Bn-CH_2), 73.3 (Bn-CH_2), 71.0 (C-6), 70.5 (C-5), 69.8 (Bn-CH_2), 26.1, 18.5 (CH_3); HRMS (ES$^+$) m/z calcd for $C_{29}H_{34}O_4$ [M + Na]$^+$ 469.2355, found 469.2370.

Compound 10. The general procedure for the synthesis of thioesters was carried out to prepare **10**, which was purified by column chromatography (10:1 hexane/EtOAc, R_f = 0.42) to yield a colorless oil (426 mg, 0.85 mmol, 56%). $[\alpha]_D^{20}$ −45.8° (c = 0.1, $CHCl_3$); ν_{max} (thin film) 1785 (C═O), 1150 (C−O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.26 (15H, m, Ar−H), 5.06 (1H, dt, J_{2,CH_3} = 1.1 Hz, $J_{2,3}$ = 10.0 Hz, H-2), 5.03 (1H, d, J = 11.5 Hz, Bn-CH_2), 4.62 (1H, d, J = 11.5 Hz, Bn-CH_2), 4.57 (1H, d, J = 11.3 Hz, Bn-CH_2), 4.50 (1H, d, J = 11.3 Hz, Bn-CH_2), 4.40 (1H, dd, $J_{3,2}$ = 10.0 Hz, $J_{3,4}$ = 8.5 Hz, H-3), 4.39 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.38 (1H, d, J = 11.3 Hz, Bn-CH_2), 4.08 (1H, dd, $J_{4,3}$ = 8.5 Hz, $J_{4,5}$ = 1.5 Hz, H-4), 3.93 (1H, ddd, $J_{5,4}$ = 1.5 Hz, $J_{5,6}$ = 5.3 Hz, $J_{5,6'}$ = 10.2 Hz, H-5), 3.64 (1H, app t, $J_{6',5}$ = $J_{6',6}$ = 10.2 Hz, H-6′), 3.38 (1H, dd, $J_{6,5}$ = 5.3 Hz, $J_{6,6'}$ = 10.2 Hz, H-6), 2.29 (3H, s, SCH_3), 1.80 (3H, d, $J_{CH_3,2}$ = 1.1 Hz, CH_3), 1.61 (3H, d, $J_{CH_3,2}$ = 1.1 Hz, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.8 (C═O), 139.2 (C-1), 139.1, 138.9, 138.1 (q-Ar), 128.3, 128.2, 128.2, 127.7, 127.7, 127.6, 127.6, 127.3, 127.3 (Ar-C), 121.7 (C-2), 79.9 (C-4), 79.6 (C-3), 75.6, 72.3, 70.1 (Bn-CH_2), 70.1 (C-6), 45.6 (C-5), 30.6 (SCH_3), 26.2, 18.5 (CH_3); HRMS (ES$^+$) m/z calcd for $C_{31}H_{36}O_4S$ [M + Na]$^+$ 527.2232, found 527.2220.

Compound 11. The general procedure for the hydrolysis of thioesters was carried out to prepare **11**, which was purified by column chromatography (15:1 hexane/EtOAc, R_f = 0.20) to yield a colorless oil (388 mg, 0.84 mmol, 99%). $[\alpha]_D^{20}$ −36.8° (c = 0.1, $CHCl_3$); ν_{max} (thin film) 1022 (C−O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40−7.25 (15H, m, Ar−H), 5.08 (2H, m, H-2 and Bn-CH_2), 4.60 (3H, m, H-3 and Bn-CH_2 × 2), 4.41 (3H, m, Bn-CH_2 × 3), 3.96 (1H, dd, $J_{4,3}$ = 8.6 Hz, $J_{4,3}$ = 2.2 Hz, H-4), 3.54 (2H, m, H-6 and H-6′), 3.02 (1H, dddd, $J_{5,4}$ = 2.2 Hz, $J_{5,SH}$ = 10.8 Hz, $J_{5,6}$ = 6.0 Hz, $J_{5,6'}$ = 8.1 Hz, H-5), 1.83 (1H, d, $J_{CH_3,2}$ = 1.4 Hz, CH_3), 1.80 (1H, d, $J_{CH_3,2}$ = 1.4 Hz, CH_3), 1.72 (1H, d, $J_{SH,5}$ = 10.8 Hz, SH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.2, 139.1, 139.1 (q-Ar), 138.0 (C-1), 128.4, 128.2, 128.2, 127.8, 127.7, 127.7, 127.3, 127.4 (Ar-C), 122.1 (C-2), 79.7 (C-4), 79.5 (C-3), 75.4 (Bn-CH_2), 73.3 (C-6), 72.9 (Bn-CH_2), 70.4 (Bn-CH_2), 41.5 (C-5), 26.3, 19.1 (CH_3); HRMS (ES$^+$) m/z calcd for $C_{29}H_{34}O_3S$ [M + Na]$^+$ 485.2126, found 485.2138.

Compounds 14 and 15. The general procedure for radical cyclization was carried out to prepare **14** and **15** as a mixture of diastereoisomers (3:1, β:α). Purification by column chromatography (15:1 hexane/EtOAc, R_f = 0.22) furnished the mixture of isomers as a colorless oil (351 mg, 0.76 mmol, 91%).

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Data for β-Anomer **14** *(Major Product).* ν_{max} (thin film) 1130 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.38−7.27 (15H, m, Ar−H), 4.73 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.62 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.57 (4H, m, 4 × Bn-CH_2), 4.57 (1H, app t, $J_{3,4} = J_{3,2}$ = 5.4 Hz, H-3), 3.95 (1H, app t, $J_{2,1} = J_{2,3}$ = 5.4 Hz, H-2), 3.86 (1H, dd, $J_{5,4}$ = 6.7 Hz, $J_{5,5'}$ = 9.6 Hz, H-5), 3.68 (1H, m, H-4), 33.57 (1H, dd, $J_{5',4}$ = 6.9 Hz, $J_{5',5}$ = 9.6 Hz, H-5′), 3.11 (1H, dd, $J_{1,CH(CH_3)_2}$ = 7.5 Hz, $J_{1,2}$ = 5.4 Hz, H-1), 1.94 (1H, m, $CH(CH_3)_2$), 0.94 (3H, d, $J_{CH_3,CH(CH_3)_2}$ = 7.1 Hz, CH_3), 0.93 (3H, d, $J_{CH_3,CH(CH_3)_2}$ = 6.7 Hz, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.3, 137.9 (q-Ar), 128.4, 128.4, 128.4, 128.3, 128.3, 127.9, 127.8, 127.8, 127.7 (Ar-C), 85.2 (C-3), 84.8 (C-2), 73.3, 72.6, 72.2 (Bn-CH_2), 70.4 (C-5), 55.6 (C-1), 45.1 (C-4), 31.9 ($CH(CH_3)_2$), 21.6, 20.0 (CH_3); HRMS (ES^+) m/z calcd for $C_{29}H_{34}O_3S$ $[M + Na]^+$ 485.2126, found 485.2140.

Data for α-Anomer **15** *(Minor Product).* ν_{max} (thin film) 1130 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37−7.25 (15H, m, Ar−H), 4.63 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.56 (4H, m, 4 × Bn-CH_2), 4.34 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.21 (1H, dd, $J_{3,2}$ = 3.8 Hz, $J_{3,4}$ = 2.0 Hz, H-3), 3.97 (1H, m, H-4), 3.86 (2H, m, H-2 and H-5), 3.63 (1H, app dd, $J_{5,4}$ = 5.8 Hz, $J_{5,5'}$ = 9.2 Hz, H-5), 3.39 (1H, dd, $J_{1,CH(CH_3)_2}$ = 10.9 Hz, $J_{1,2}$ = 3.1 Hz, H-1), 2.09 (1H, m, $CH(CH_3)_2$), 0.99 (3H, d, $J_{CH_3,CH(CH_3)_2}$ = 6.7 Hz, CH_3), 0.81 (3H, d, $J_{CH_3,CH(CH_3)_2}$ = 6.5 Hz, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 138.2, 137.9 (q-Ar), 128.4, 128.3, 128.3, 127.9, 127.9, 127.7, 127.6, 127.6, 127.6 (Ar-C), 83.2 (C-2), 81.9 (C-3), 73.3, 72.9, 71.8 (Bn-CH_2), 69.0 (C-5), 58.6 (C-1), 48.5 (C-4), 29.2 ($CH(CH_3)_2$), 23.2 (CH_3), 21.1 (CH_3); HRMS (ES^+) m/z calcd for $C_{29}H_{34}O_3S$ $[M + Na]^+$ 485.2126, found 485.2140.

Compound 18. 2,3,4-Tri-*O*-benzyl-α-D-arabinofuranose (**8**) (1.00 g, 2.38 mmol), benzyltriphenylphosphonium bromide (2.77 g, 7.14 mmol), potassium carbonate (1.08 g, 7.85 mmol), and 18-crown-6 (377 mg, 1.43 mmol) were added to an oven-dried RBF. The reaction mixture was solubilized in dry CH_2Cl_2 (50 mL) under argon and refluxed at 45 °C overnight. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with water (50 mL × 2) and brine (50 mL). The organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. Purification by column chromatography (10:1 hexane/EtOAc) afforded **18** as a mixture of isomers (1:1, *E*:*Z*) as a colorless oil (847 mg, 1.71 mmol, 72%).

Data for the E Isomer. ν_{max} (thin film) 1180 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.41−7.08 (20H, m, Ar−H), 6.62 (1H, d, $J_{1,2}$ = 16.5 Hz, H-1), 6.33 (1H, dd, $J_{2,1}$ = 16.5 Hz, $J_{2,3}$ = 7.8 Hz, H-2), 4.68−4.42 (6H, m, Bn-CH_2), 4.29 (1H, dd, $J_{3,2}$ = 7.8 Hz, $J_{3,4}$ = 3.7 Hz, H-3), 4.10 (1H, m, H-5), 3.71 (1H, dd, $J_{4,5}$ = 3.7 Hz, $J_{4,5}$ = 6.7 Hz, H-4), 3.66 (2H, m, H-6 and H-6′), 2.85 (1H, d, $J_{OH,5}$ = 5.5 Hz, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.1, 138.1, 137.9 (q-Ar), 136.5 (q-Ph), 133.6 (C-1), 128.7, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.7, 127.7, 127.7 (Ar-C), 127.6 (C-2), 126.6 (C-1), 81.1 (C-4), 79.8 (C-3), 74.3, 73.4 (Bn-CH_2), 71.0 (C-6), 70.7 (Bn-CH_2), 70.4 (C-5); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_4$ $[M + Na]^+$ 517.2355, found 517.2347.

Data for the Z Isomer. ν_{max} (thin film) 1180 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.41−7.08 (20H, m, Ar−H), 6.84 (1H, d, $J_{1,2}$ = 12.1 Hz, H-1), 5.95 (1H, dd, $J_{2,1}$ = 12.1 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 4.72 (1H, dd, $J_{3,2}$ = 9.5 Hz, $J_{3,4}$ = 3.1 Hz, H-3), 4.68−4.42 (6H, m, Bn-CH_2), 4.12 (1H, m, H-5), 3.75 (1H, dd, $J_{4,3}$ = 3.1 Hz, $J_{4,5}$ = 6.7 Hz, H-4), 3.58 (1H, dd, $J_{6,5}$ = 5.4 Hz, $J_{6,6'}$ = 9.7 Hz, H-6), 3.49 (1H, dd, $J_{6',5}$ = 4.1 Hz, $J_{6',6}$ = 9.7 Hz, H-6′), 2.90 (1H, d, $J_{OH,5}$ = 5.8 Hz, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.1, 138.0 137.6 (q-Ar), 136.4 (q-Ph), 133.9 (C-1), 129.5 (C-2), 128.6, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 127.9, 127.7, 127.7, 127.3, 126.6 (Ar-C), 80.8 (C-4), 74.0 (Bn-CH_2), 73.4, (C-3 and CH_2), 71.2 (C-6), 70.5 (C-5), 70.2 (Bn-CH_2); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_4$ $[M + Na]^+$ 517.2355, found 517.2347.

Compound 19. The general procedure for the synthesis of thioesters was carried out to prepare **19** as a mixture of isomers (1:1, *E*:*Z*). Purification by column chromatography (12:1 hexane/EtOAc) furnished **19** as a colorless oil (566 mg, 1.03 mmol, 60%).

Data for the E Isomer. ν_{max} (thin film) 1782 (C═O), 1110 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.45−7.23 (20H, m, Ar−H), 6.65 (1H, d, $J_{1,2}$ = 16.2 Hz, H-1), 6.14 (1H, dd, $J_{2,1}$ = 16.2 Hz, $J_{2,3}$ = 7.7 Hz, H-2), 5.01 (1H, d, J = 11.3 Hz, Bn-CH_2), 4.69 (3H, m, Bn-CH_2), 4.53 (2H, m, Bn-CH_2), 4.31 (1H, app t, $J_{3,2} = J_{3,4}$ = 7.7 Hz, H-3), 4.17 (1H, m, H-4), 4.08 (1H, ddd, $J_{5,4}$ = 2.3 Hz, $J_{5,6}$ = 5.1 Hz, $J_{5,6'}$ = 9.7 Hz, H-5), 3.69 (1H, app t, $J_{6,5} = J_{6,6'}$ = 9.7 Hz, H-6), 3.46 (1H, dd, $J_{6',5}$ = 5.1 Hz, $J_{6'6}$ = 9.7 Hz, H-6′), 2.32 (3H, s, $SOCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.7 (C═O), 138.7, 138.4, 138.1 (q-Ar), 136.6 (q-Ph), 134.3 (C-1), 128.5, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.4, 127.4, 127.2 (Ar-C), 125.9 (C-2), 83.3 (C-3), 80.1 (C-4), 75.1, 72.7, 70.9 (Bn-CH_2), 69.9 (C-6), 45.6 (C-5), 30.9 ($SCOCH_3$); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_4S$ $[M + Na]^+$ 575.2232, found 575.2261.

Data for the Z Isomer. ν_{max} (thin film) 1782 (C═O), 1110 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.45−7.23 (20H, m, Ar−H), 6.80 (1H, d, $J_{1,2}$ = 12.1 Hz, H-1), 5.63 (1H, dd, $J_{2,1}$ = 12.1 Hz, $J_{2,3}$ = 10.8 Hz, H-2), 4.91 (1H, d, J = 11.4 Hz, Bn-CH_2), 4.69 (2H, m, Bn-CH_2), 4.51 (1H, d, J = 12.4 Hz, Bn-CH_2), 4.43 (2H, m, Bn-CH_2), 4.85 (1H, dd, $J_{3,2}$ = 10.8 Hz, $J_{3,4}$ = 7.1 Hz, H-3), 4.17 (1H, dd, $J_{4,3}$ = 7.1 Hz, $J_{4,5}$ = 2.3 Hz, H-4), 4.05 (1H, ddd, $J_{5,4}$ = 2.3 Hz, $J_{5,6}$ = 4.9 Hz, $J_{5,6'}$ = 9.4 Hz, H-5), 3.63 (1H, app t, $J_{6',5} = J_{6',6}$ = 9.4 Hz, H-6′), 3.39 (1H, dd, $J_{6,5}$ = 4.9 Hz, $J_{6,6'}$ = 9.4 Hz, H-6), 2.08 (3H, s, $SCOCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.4 (C═O), 138.6, 138.3, 138.0 (q-Ar), 136.4 (q-Ph), 134.1 (C-1), 128.7 (C-2), 128.6, 128.3, 128.2, 128.2, 127.9, 127.7, 127.7, 127.6, 127.4, 127.4, 127.2, 126.7 (Ar-C), 79.6 (C-4), 77.2 (C-3), 75.2, 72.7, 70.5 (Bn-CH_2), 69.8 (C-6), 45.3 (C-5), 30.4 ($SCOCH_3$); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_4S$ $[M + Na]^+$ 575.2232, found 575.2261.

Compound 20. The general procedure for the hydrolysis of thioesters was carried out to prepare **20** as a mixture of isomers (1:1, *E*:*Z*). Purification by column chromatography (15:1 hexane/EtOAc) furnished **20** as a colorless oil (520 mg, 1.02 mmol, 99%).

Data for the E Isomer. ν_{max} (thin film) 1154 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.50−7.13 (20H, m, Ar−H), 6.78 (1H, d, $J_{1,2}$ = 16.0 Hz, H-1), 6.15 (1H, dd, $J_{2,1}$ = 16.0 Hz, $J_{2,3}$ = 8.5 Hz, H-2), 5.07 (1H, d, J = 11.2 Hz, Bn-CH_2), 4.97 (1H, d, J = 11.2 Hz, Bn-CH_2), 4.68 (3H, d, J = 11.5 Hz, Bn-CH_2), 4.51 (1H, d, J = 11.5 Hz, Bn-CH_2), 4.50 (1H, app t, $J_{3,2} = J_{3,4}$ = 8.5 Hz, H-3), 4.06 (1H, dd, $J_{4,3}$ = 8.5 Hz, $J_{4,5}$ = 2.3 Hz, H-4), 3.59 (1H, app t, $J_{6,5} = J_{6,6'}$ = 9.3 Hz, H-6), 3.53 (1H, dd, $J_{6',5}$ = 5.0 Hz, $J_{6',6}$ = 9.3 Hz, H-6′), 3.09 (1H, dddd, $J_{5,4}$ = 2.3 Hz, $J_{5,6}$ = 5.0 Hz, $J_{5,6'}$ = 9.3 Hz, $J_{5,SH}$ = 10.5 Hz, H-5), 1.76 (1H, d, $J_{SH,5}$ = 10.5 Hz, SH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.9, 138.6, 137.9 (q-Ar), 136.5 (q-Ph), 134.6 (C-1), 128.9, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5 (Ar-C), 126.1 (C-2), 84.1 (C-3), 79.5 (C-4), 75.6, 75.3 (Bn-CH_2), 72.9 (C-6), 70.9 (Bn-CH_2), 41.3 (C-5); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_3S$ $[M + Na]^+$ 533.2126, found 533.2120.

Data for the Z Isomer. ν_{max} (thin film) 1154 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.50−7.13 (20H, m, Ar−H), 6.68 (1H, d, $J_{1,2}$ = 11.9 Hz, H-1), 5.68 (1H, dd, $J_{2,1}$ = 11.9 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 4.86 (1H, dd, $J_{3,2}$ = 10.1 Hz, $J_{3,4}$ = 6.9 Hz, H-3), 4.57 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.45 (2H, d, J = 12.1 Hz, Bn-CH_2), 4.43 (1H, d, J = 10.9 Hz, Bn-CH_2), 4.37 (1H, d, J = 10.9 Hz, Bn-CH_2), 4.27 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.01 (1H, dd, $J_{4,3}$ = 6.9 Hz, $J_{4,5}$ = 3.3 Hz, H-4), 3.50 (1H, app t, $J_{6,5} = J_{6,6'}$ = 9.1 Hz, H-6), 3.44 (1H, dd, $J_{6',5}$ = 4.9 Hz, $J_{6',6}$ = 9.1 Hz, H-6′), 3.21 (1H, dddd, $J_{5,4}$ = 3.3 Hz, $J_{5,6}$ = 9.1 Hz, $J_{5,6'}$ = 4.9 Hz, $J_{5,SH}$ = 10.0 Hz, H-5), 1.78 (1H, d, $J_{SH,5}$ = 10.0 Hz, SH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.8, 138.3, 137.9 (q-Ar), 136.3 (q-Ph), 134.7 (C-1), 129.0 (C-2), 128.9, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.9, 127.8, 127.8, 127.4 (Ar-C), 80.7 (C-4), 76.3 (C-3), 72.9 (Bn-CH_2), 72.8 (C-6), 72.7, 70.3 (Bn-CH_2), 41.3 (C-5); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_3S$ $[M + Na]^+$ 533.2126, found 533.2120.

Compound 21. To a stirred solution of **18** (608 mg, 1.2 mmol) in dry THF (10 mL) were added 4-nitrobenzoic acid (801 mg, 4.8 mmol) and PPh_3 (968 mg, 3.7 mmol). The reaction mixture was cooled to 0 °C, and DIAD (0.94 mL, 4.8 mmol) was added dropwise under N_2. The reaction mixture was stirred for 12 h at room temperature and then concentrated in vacuo, and the residue was purified by column chromatography (15:1 hexane/ethyl acetate) to

afford **21** (517 mg, 0.80 mmol, 67%) as a mixture of isomers (1:1, *E*:*Z*) and as a colorless oil.

Data for the E Isomer. ν_{max} (thin film) 1725, 1643 (C═O), 1067 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.17 (2H, d, J = 9.0 Hz, Ar−H), 8.08 (2H, d, J = 9.0 Hz, Ar−H), 7.38−7.21 (15H, m, Ar−H), 7.10 (5H, m, Ar−H), 6.54 (1H, d, $J_{1,2}$ = 16.2 Hz, H-1), 6.24 (1H, dd, $J_{2,1}$ = 16.2 Hz, $J_{2,3}$ = 7.5 Hz, H-2), 5.62 (1H, app dd, $J_{5,6}$ = 4.9 Hz, $J_{5,6'}$ = 10.3 Hz, H-5), 4.86 (1H, d, J = 11.4 Hz, Bn-CH_2), 4.68 (1H, d, J = 11.4 Hz, Bn-CH_2), 4.69 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.51 (1H, d, J = 12.1 Hz, Bn-CH_2), 4.42 (1H, d, J = 12.1 Hz, Bn-CH_2), 4.40 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.21 (1H, dd, $J_{3,2}$ = 7.5 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 4.01 (1H, app t, $J_{4,3}$ = $J_{4,5}$ = 5.1 Hz, H-4), 3.76 (1H, dd, $J_{6,5}$ = 4.9 Hz, $J_{6,6'}$ = 10.3 Hz, H-6), 3.68 (1H, dd, $J_{6',5}$ = 5.8 Hz, $J_{6',6}$ = 10.3 Hz, H-6′); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (C═O), 150.4 (OCOCCH), 138.1, 137.9, 137.8 (q-Ar), 136.2 (q-Ph), 135.5 (CNO_2), 133.5 (C-1), 130.8, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7 (Ar-C), 126.1 (C-2), 123.4 (Ar-C), 79.9 (C-4), 79.8 (C-3), 75.1 (Bn-CH_2), 73.7 (C-5), 73.2, 70.7 (Bn-CH_2), 68.0 (C-6); HRMS (ES^+) m/z calcd for $C_{40}H_{37}NO_7$ $[M + Na]^+$ 666.2468, found 666.2458.

Data for the Z Isomer. ν_{max} (thin film) 1725, 1643 (C═O), 1067 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.32 (2H, d, J = 8.7 Hz, Ar−H), 8.25 (2H, d, J = 8.7 Hz, Ar−H), 7.36−7.21 (15H, m, Ar−H), 7.10 (5H, m, Ar−H), 6.83 (1H, d, J = 12.3 Hz, H-1), 5.85 (1H, dd, $J_{2,1}$ = 12.3 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 5.57 (1H, m, H-5), 4.87 (1H, d, J = 11.5 Hz, Bn-CH_2), 4.69 (1H, d, J = 11.5 Hz, Bn-CH_2), 4.68 (1H, dd, $J_{3,2}$ = 9.9 Hz, $J_{3,4}$ = 3.9 Hz, H-3), 4.67 (1H, d, J = 12.2 Hz, Bn-CH_2), 4.42 (1H, d, J = 12.2 Hz, Bn-CH_2), 4.34 (1H, d, J = 11.7 Hz, Bn-CH_2), 4.26 (1H, d, J = 11.7 Hz, Bn-CH_2), 4.11 (1H, dd, $J_{4,3}$ = 3.9 Hz, $J_{4,5}$ = 6.0 Hz, H-4), 3.68 (1H, dd, $J_{6,5}$ = 4.1 Hz, $J_{6,6'}$ = 11.0 Hz, H-6), 3.46 (1H, dd, $J_{6',5}$ = 4.9 Hz, $J_{6',6}$ = 11.0 Hz, H-6′); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.3 (C═O), 150.6 (OCOCCH), 138.0, 137.8, 137.5 (q-Ar), 136.2 (q-Ph), 135.5 (CNO_2), 134.3 (C-1), 130.7 (Ar-C), 129.1 (C-2), 129.2, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.2, 123.4 (Ar-C), 80.5 (C-4), 75.5 (Bn-CH_2), 74.8 (C-5), 73.1 (Bn-CH_2), 72.9 (C-3), 69.9 (Bn-CH_2), 67.9 (C-6); HRMS (ES^+) m/z calcd for $C_{40}H_{37}NO_7$ $[M + Na]^+$ 666.2468, found 666.2458.

Compound 22. To a stirred solution of glycosyl *p*-nitrobenzoate **21** (500 mg, 0.78 mmol) in MeOH (10 mL) was added NaOMe (4 mg, 0.08 mmol). The solution was stirred at room temperature for 12 h and neutralized with Dowex H^+ ion-exchange resin. The resin was removed by filtration and washed with MeOH, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (10:1 hexane/ethyl acetate) to give **22** (378 mg, 0.76 mmol, 98%) as a mixture of isomers (1:1, *E*:*Z*) and as a colorless oil.

Data for the E Isomer. ν_{max} (thin film) 2968 (OH), 1021 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (2H, m, Ar−H), 7.40−7.30 (18H, m, Ar−H), 6.71 (1H, d, $J_{1,2}$ = 16.3 Hz, H-1), 6.23 (1H, dd, $J_{2,1}$ = 16.3 Hz, $J_{2,3}$ = 8.2 Hz, H-2), 4.96 (1H, d, J = 11.3 Hz, Bn-CH_2), 4.74 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.67 (1H, d, J = 11.3 Hz, Bn-CH_2), 4.51 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.49 (1H, d, J = 11.7 Hz, Bn-CH_2), 4.48 (1H, d, J = 11.7 Hz, Bn-CH_2), 4.34 (1H, app t, $J_{3,2}$ = $J_{3,4}$ = 8.2 Hz, H-3), 4.02 (1H, m, H-5), 3.75 (1H, dd, $J_{4,3}$ = 8.2 Hz, $J_{4,5}$ = 2.6 Hz, H-4), 3.52 (1H, dd, $J_{6,5}$ = 6.2 Hz, $J_{6,6'}$ = 9.3 Hz, H-6), 3.49 (1H, dd, $J_{6',5}$ = 6.1 Hz, $J_{6',6}$ = 9.3 Hz, H-6′), 2.56 (1H, d, $J_{OH,5}$ = 6.9 Hz, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.3, 137.9, 136.3 (q-Ar), 134.1 (C-1), 128.6, 128.3, 128.3, 128.3, 128.3, 127.9, 127.9, 127.9, 127.7, 127.7, 127.5 (Ar-C), 126.5 (C-2), 126.5 (Ar-C), 81.9 (C-3), 80.7 (C-4), 75.2, 73.3 (Bn-CH_2), 71.3 (C-6), 70.8 (Bn-CH_2), 70.2 (C-5); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_4$ $[M + Na]^+$ 517.2355, found 517.2350.

Data for the Z Isomer. ν_{max} (thin film) 2968 (OH), 1021 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.39−7.28 (15H, m, Ar−H), 7.23 (3H, m, Ar−H), 7.09 (2H, m, Ar−H), 6.88 (1H, d, $J_{1,2}$ = 11.7 Hz, H-1), 5.75 (1H, dd, $J_{2,1}$ = 11.7 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 4.92 (1H, d, J = 11.4 Hz, Bn-CH_2), 4.71 (1H, dd, $J_{3,2}$ = 10.2 Hz, $J_{3,4}$ = 6.3 Hz, H-3), 4.62 (1H, d, J = 11.4 Hz, Bn-CH_2), 4.55 (1H, d, J = 11.7 Hz, Bn-CH_2), 4.51 (1H, d, J = 12.1 Hz, Bn-CH_2), 4.43 (1H, d, J = 12.1 Hz, Bn-CH_2), 4.16 (1H, d, J = 11.7 Hz, Bn-CH_2), 4.05 (1H, m, H-5), 3.79 (1H, dd, $J_{4,3}$ = 6.3 Hz, $J_{4,5}$ = 3.0 Hz, H-4), 3.45 (1H, dd, $J_{6,5}$ = 5.9 Hz, $J_{6,6'}$ = 9.6 Hz, H-6), 3.42 (1H, dd, $J_{6',5}$ = 5.8 Hz, $J_{6,6'}$ = 9.6 Hz, H-6′), 2.58 (1H, d, $J_{OH,5}$ = 6.9 Hz, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.0, 138.0, 136.4 (q-Ar), 134.6 (C-1), 128.9 (C-2), 128.9, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.4, 128.3 (Ar-C), 80.7 (C-4), 75.4 (C-3), 75.4 (Bn-CH_2), 73.3 (Bn-CH_2), 71.1 (C-6), 70.2 (Bn-CH_2), 70.1 (C-5); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_4$ $[M + Na]^+$ 517.2355, found 517.2350.

Compound 23. The general procedure for the synthesis of thioesters was carried out to prepare **23** as a mixture of isomers (1:1, *E*:*Z*). Purification by column chromatography (12:1 hexane/EtOAc) furnished **23** as a colorless oil (252 mg, 0.46 mmol, 60%).

Data for the E Isomer. ν_{max} (thin film) 1680 (C═O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.41−7.15 (20H, m, Ar−H), 6.56 (1H, d, $J_{1,2}$ = 16.0 Hz, H-1), 6.29 (1H, dd, $J_{2,1}$ = 16.0 Hz, $J_{2,3}$ = 8.3 Hz, H-2), 4.78 (1H, d, J = 11.1 Hz, Bn-CH_2), 4.73 (1H, d, J = 11.1 Hz, Bn-CH_2), 4.66 (1H, d, J = 12.1 Hz, Bn-CH_2), 4.48 (1H, d, J = 12.1 Hz, Bn-CH_2), 4.43 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.38 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.23 (1H, dd, $J_{3,2}$ = 8.3 Hz, $J_{3,4}$ = 5.4 Hz, H-3), 3.90 (1H, app t, $J_{4,3}$ = $J_{4,5}$ = 5.4 Hz, H-4), 3.69 (3H, m, H-5, H-6, and H-6′) 2.31 (3H, s, SCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.2 (C═O), 138.2, 138.0, 137.9, 136.3 (q-Ar), 134.0 (C-1), 128.6, 128.5, 128.2, 128.1, 128.1 128.0, 127.9, 127.8, 127.4, 127.4, 127.3, 127.3 (Ar-C), 126.7 (C-2), 81.7 (C-4), 81.4 (C-3), 74.7, 72.8, 70.4 (Bn-CH_2), 68.8 (C-6), 44.7 (C-5), 30.4 (SCH_3); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_4S$ $[M + Na]^+$ 575.2232, found 575.2230.

Data for the Z Isomer. ν_{max} (thin film) 1680 (C═O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.41−7.17 (18H, m, Ar−H), 7.09 (2H, m, Ar−H), 6.82 (1H, d, $J_{1,2}$ = 11.9 Hz, H-1), 5.92 (1H, dd, $J_{2,1}$ = 11.9 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.70 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.65 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.59 (1H, dd, $J_{3,2}$ = 9.6 Hz, $J_{3,4}$ = 3.7 Hz, H-3), 4.59 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.35 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.32 (1H, m, H-5), 4.27 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.18 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.02 (1H, dd, $J_{4,3}$ = 3.7 Hz, $J_{4,5}$ = 5.9 Hz, H-4), 3.57 (1H, dd, $J_{6,5}$ = 6.1 Hz, $J_{6,6'}$ = 10.2 Hz, H-6), 3.28 (1H, dd, $J_{6',5}$ = 6.8 Hz, $J_{6',6}$ = 10.2 Hz, H-6′), 2.31 (3H, s, SCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.7 (C═O), 137.8, 137.5, 137.5, 136.4 (q-Ar), 133.5 (C-1), 129.9 (C-2), 128.7, 128.6, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.5, 127.3, 127.3, 126.5 (Ar-C), 80.1 (C-4), 74.1 (Bn-CH_2), 73.0 (C-3), 72.9, 70.0 (Bn-CH_2), 69.0 (C-6), 44.2 (C-5), 30.4 (SCH_3); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_4S$ $[M + Na]^+$ 575.2232, found 575.2230.

Compound 24. The general procedure for the hydrolysis of thioesters was carried out to prepare **24** as a mixture of isomers (1:1, *E*:*Z*). Purification by column chromatography (15:1 hexane/EtOAc) furnished **24** as a colorless oil (201 mg, 0.39 mmol, 86%).

Data for the E Isomer. ν_{max} (thin film) 1174 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.42−7.23 (20H, m, Ar−H), 6.64 (1H, d, $J_{1,2}$ = 16.3 Hz, H-1), 6.28 (1H, dd, $J_{2,1}$ = 16.3 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 4.73 (2H, d, J = 11.4 Hz, Bn-CH_2), 4.69 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.64 (2H, d, J = 11.4 Hz, Bn-CH_2), 4.51 (1H, dd, $J_{3,2}$ = 8.1 Hz, $J_{3,4}$ = 3.9 Hz, H-3), 4.40 (1H, d, J = 11.6 Hz, Bn-CH_2), 3.90 (1H, dd, $J_{4,3}$ = 3.9 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 3.72 (2H, m, H-6 and H-6′), 3.36 (1H, m, H-5), 1.88 (1H, d, $J_{SH,5}$ = 9.3 Hz, SH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.0, 137.9, 136.9 (q-Ar), 133.4 (C-1), 128.9, 128.7, 128.6, 128.4, 128.3, 128.3, 128.3, 127.9, 127.8, 127.7, 127.6, 127.3 (Ar-C), 126.6 (C-2), 84.1 (C-4), 80.1 (C-3), 75.6, 75.5 (Bn-CH_2), 71.5 (C-6), 70.6 (Bn-CH_2), 40.7 (C-5); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_3S$ $[M + Na]^+$ 533.2126, found 533.2119.

Data for the Z Isomer. ν_{max} (thin film) 1074 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35−7.19 (17H, m, Ar−H), 7.15 (3H, m, Ar−H), 6.98 (2H, d, J = 7.6 Hz, Ar−H), 6.73 (1H, d, $J_{1,2}$ = 12.0 Hz, H-1), 5.83 (1H, dd, $J_{2,1}$ = 12.0 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 4.92 (1H, dd, $J_{3,2}$ = 9.8 Hz, $J_{3,4}$ = 2.4 Hz, H-3), 4.59 (1H, d, J = 12.2 Hz, Bn-CH_2), 4.50 (4H, m, Bn-CH_2 × 4), 4.15 (1H, d, J = 12.2 Hz, Bn-CH_2), 3.94 (1H, dd, $J_{6,5}$ = 4.3 Hz, $J_{6,6'}$ = 9.4 Hz, H-6), 3.74 (1H, dd, $J_{4,3}$ = 2.4 Hz, $J_{4,5}$ = 9.0 Hz, H-4), 3.59 (1H, dd, $J_{6',5}$ = 3.3 Hz, $J_{6,6'}$ = 9.4 Hz, H-6′), 3.35 (1H, dddd, $J_{5,SH}$ = 9.2 Hz, $J_{5,4}$ = 9.0 Hz, $J_{5,6}$ = 4.3 Hz, $J_{5,6'}$ = 3.3 Hz, H-5), 1.65 (1H, d, $J_{SH,5}$ = 9.2 Hz, SH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.2, 138.0, 136.5 (q-Ar), 133.6 (C-1), 130.5 (C-2), 128.9, 128.6, 128.44, 128.4, 128.3, 128.3, 128.3, 127.8, 127.7, 127.7, 127.6, 127.5 (Ar-C), 84.8 (C-4), 73.1, 73.0 (Bn-CH_2), 72.5 (C-3), 71.2 (C-

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6), 70.1 (Bn-CH_2), 40.6 (C-5); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_3S$ $[M + Na]^+$ 533.2126, found 533.2119.

Compounds 26 and 27. The general procedure for radical cyclization was carried out to prepare **26** and **27** as a mixture of isomers (13.5:1, β:α). Purification by column chromatography (15:1 hexane/EtOAc, R_f = 0.22) furnished **26**/**27** as a colorless oil (351 mg, 0.96 mmol, 94%).

*Data for β-Anomer **26** (Major Product).* ν_{max} (thin film) 1185 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.41−7.12 (20H, m, Ar−H), 4.59 (2H, s, Bn-CH_2), 4.56 (2H, d, J = 8.9 Hz, Bn-CH_2), 4.46 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.42 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.16 (1H, app t, $J_{3,2} = J_{3,4}$ = 5.1 Hz, H-3), 3.94 (1H, app t, $J_{2,1} = J_{2,3}$ = 5.1 Hz, H-2), 3.87 (1H, dd, $J_{5,4}$ = 6.6 Hz, $J_{5,5'}$ = 9.3 Hz, H-5), 3.78 (1H, m, H-4), 3.61 (1H, dd, $J_{5',4}$ = 6.1 Hz, $J_{5',5}$ = 9.3 Hz, H-5′), 3.57 (1H, ddd, J_{1,CH_2Ph} = 8.3 Hz, $J_{1,CH_2Ph'}$ = 7.1 Hz, $J_{1,2}$ = 5.1 Hz, H-1), 3.10 (1H, dd, $J_{CH_2Ph,CH_2Ph'}$ = 13.4 Hz, $J_{CH_2Ph,1}$ = 8.3 Hz, CH_2Ph), 2.88 (1H, dd, J_{CH_2Ph',CH_2Ph} = 13.4 Hz, $J_{CH_2Ph',1}$ = 7.1 Hz, CH_2Ph'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5, 138.1, 137.9 (q-Ar), 137.9 (q-Ph), 128.9, 128.3, 128.3, 128.2, 128.2, 127.7, 127.6, 127.6, 127.5, 127.4, 126.8, 126.2 (Ar-C), 85.5 (C-2), 84.8 (C-3), 73.4, 72.5, 71.8 (Bn-CH_2), 69.7 (C-5), 50.2 (C-1), 46.8 (C-4), 42.0 (CH_2Ph); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_3S$ $[M + Na]^+$ 533.2126, found 533.2130.

*Data for α-Anomer **27** (Minor Product).* This compound was formed in such small quantities that full characterization could not be carried out.

Compounds 29 and 30. The general procedure for radical cyclization was carried out to prepare **29** and **30** as a mixture of isomers (5:1, α/β). Purification by column chromatography (15:1 hexane/EtOAc) furnished **29**/**30** as a colorless oil (182 mg, 0.36 mmol, 92%).

*Data for α-Anomer **29** (Major Product).* ν_{max} (thin film) 1100, 1093 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37−7.16 (20H, m, Ar−H), 4.65 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.61 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.54 (2H, d, J = 12.1 Hz, Bn-CH_2), 4.51 (2H, d, J = 12.4 Hz, Bn-CH_2), 4.13 (1H, app t, $J_{3,2} = J_{3,4}$ = 4.7 Hz, H-3), 3.96 (1H, app t, $J_{2,1} = J_{2,3}$ = 4.7 Hz, H-2), 3.67 (1H, dd, $J_{5,4}$ = 8.1 Hz, $J_{5,5'}$ = 9.3 Hz, H-5), 3.60 (2H, m, H-1 and H-4), 3.51 (1H, dd, $J_{5',4}$ = 6.4 Hz, $J_{5',5}$ = 9.3 Hz, H-5′), 3.21 (1H, dd, $J_{CH_2Ph,CH_2Ph'}$ = 13.7 Hz, $J_{CH_2Ph,1}$ = 6.3 Hz, CH_2Ph), 2.81 (1H, dd, J_{CH_2Ph',CH_2Ph} = 13.7 Hz, $J_{CH_2Ph',1}$ = 8.6 Hz, CH_2Ph'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.4 (q-Ph), 138.1, 138.1, 137.9 (q-Ar), 128.9, 128.9, 128.4, 128.4, 128.4, 128.3, 128.3, 127.8, 127.8, 127.7, 127.7, 127.7 (Ar-C), 88.9 (C-2), 86.9 (C-3), 73.0 (Bn-CH_2), 72.4 (C-5), 72.3, 72.2 (Bn-CH_2), 50.4 (C-1), 48.3 (C-4), 41.3 (CH_2Ph); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_3S$ $[M + Na]^+$ 533.2126, found 533.2132.

*Data for β-Anomer **30** (Minor Product).* ν_{max} (thin film) 1100, 1093 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.39−7.17 (20H, m, Ar−H), 4.67−4.44 (5H, m, Bn-CH_2), 4.36 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.23 (1H, app t, $J_{3,2} = J_{3,4}$ = 2.8 Hz, H-3), 3.93 (1H, app t, $J_{2,1} = J_{2,3}$ = 2.8 Hz, H-2), 3.88 (1H, m, H-1), 3.69 (1H, m, H-5), 3.61 (1H, m, H-4), 3.53 (1H, m, H-5′), 3.15 (1H, dd, $J_{CH_2Ph,CH_2Ph'}$ = 13.8 Hz, $J_{CH_2Ph,1}$ = 6.5 Hz, CH_2Ph), 2.91 (1H, dd, J_{CH_2Ph',CH_2Ph} = 13.8 Hz, $J_{CH_2Ph',1}$ = 8.7 Hz, CH_2Ph'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.0 (q-Ph), 138.2, 138.0, 137.8 (q-Ar), 128.9, 128.4, 128.4, 127.9, 127.8, 127.6, 127.6, 127.6, 127.6, 126.4, 126.4, 126.4, 126.4 (Ar-C), 85.3 (C-2), 83.4 (C-3), 73.0 (Bn-CH_2), 72.5 (C-5), 71.7, 71.6 (Bn-CH_2), 51.2 (C-1), 49.7 (C-4), 36.1 (CH_2Ph); HRMS (ES^+) m/z calcd for $C_{33}H_{34}O_3S$ $[M + Na]^+$ 533.2126, found 533.2132.

Compound 31. 2,3,4-Tri-*O*-benzyl-α-D-arabinofuranose (**8**) (1.00 g, 2.38 mmol), 4-(methoxycarbonyl)benzyltriphenylphosphonium bromide (3.18 g, 7.14 mmol), potassium carbonate (1.08 g, 7.85 mmol), and 18-crown-6 (377 mg, 1.43 mmol) were added to an oven-dried RBF. The reaction mixture was solubilized in dry CH_2Cl_2 (50 mL) under argon and refluxed at 45 °C overnight. The reaction mixture was diluted in CH_2Cl_2 (50 mL) and washed with water (50 mL × 2) and brine (50 mL). The organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. Purification by column chromatography (10:1 hexane/EtOAc) afforded **31** as a mixture of isomers (1:1, *E*:*Z*) as a colorless oil (828 mg, 1.49 mmol, 63%).

Data for the E Isomer. ν_{max} (thin film) 3453 (OH), 1733 (C═O) 1021 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (2H, d, J = 8.5 Hz, Ar−H), 7.42−7.19 (17H, m, Ar−H), 6.64 (1H, d, $J_{1,2}$ = 16.2 Hz, H-1), 6.41 (1H, dd, $J_{2,1}$ = 16.2 Hz, $J_{2,3}$ = 7.3 Hz, H-2), 4.72−4.40 (6H, m, Bn-CH_2), 4.31 (1H, dd, $J_{3,2}$ = 7.7 Hz, $J_{3,4}$ = 3.9 Hz, H-3), 4.08 (1H, m, H-5), 3.90 (3H, s, CO_2CH_3) 3.70 (1H, dd, $J_{4,3}$ = 3.9 Hz, $J_{4,5}$ = 6.8 Hz, H-4), 3.66 (2H, m, H-6 and H-6′) 2.78 (1H, bd, J = 5.2 Hz, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.8 (q-CO_2Me), 137.9, 137.7, 137.6, 137.3 (q-Ar), 132.2 (C-1), 131.5 (C-2), 129.8, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 127.8, 127.7, 127.6 (Ar-C), 80.8 (C-4), 79.4 (C-3), 74.2, 73.4, 71.1 (Bn-CH_2), 70.8 (C-6), 70.4 (C-5), 52.0 (CO_2Me); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_6$ $[M + Na]^+$ 575.2410, found 575.2413.

Data for the Z Isomer. ν_{max} (thin film) 3453 (OH), 1733 (C═O) 1021 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.88 (2H, d, J = 8.3 Hz, Ar−H), 7.34−7.14 (15H, m, Ar−H), 6.76 (1H, d, $J_{1,2}$ = 12.1 Hz, H-1), 5.98 (1H, dd, $J_{2,1}$ = 12.1 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 4.63 (1H, dd, $J_{3,2}$ = 9.9 Hz, $J_{3,4}$ = 3.0 Hz, H-3), 4.55 (3H, d, J = 11.2 Hz, Bn-CH_2), 4.46 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.41 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.17 (1H, d, J = 11.2 Hz, Bn-CH_2), 4.07 (1H, m, H-5), 3.90 (3H, s, CO_2CH_3), 3.68 (1H, dd, $J_{4,3}$ = 3.0 Hz, $J_{4,5}$ = 7.0 Hz, H-4), 3.55 (1H, dd, $J_{6,5}$ = 5.5 Hz, $J_{6,6'}$ = 9.9 Hz, H-6), 3.47 (1H, dd, $J_{6',5}$ = 4.2 Hz, $J_{6',6}$ = 9.9 Hz, H-6′), 2.83 (1H, d, $J_{OH,5}$ = 5.7 Hz, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.8 (q-CO_2Me), 137.9, 137.7, 137.6, 137.3 (q-Ar), 132.7 (C-1), 129.6 (C-2), 129.5, 129.1, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.6 (Ar-C), 80.5 (C-4), 78.3 (Bn-CH_2), 73.4 (C-3), 73.4 (Bn-CH_2), 71.03 (C-6), 70.5 (Bn-CH_2), 70.3 (C-5), 52.0 (CO_2Me); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_6$ $[M + Na]^+$ 575.2410, found 575.2413.

Compound 32. The general procedure for the synthesis of thioesters was carried out to prepare **32** as a mixture of isomers (1:1, *E*:*Z*). Purification by column chromatography (12:1 hexane/EtOAc) furnished **32** as a colorless oil (539 mg, 0.88 mmol, 59%).

Data for the E Isomer. ν_{max} (thin film) 1740, 1680 (C═O), 1027 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (2H, d, J = 8.1 Hz, Ar−H), 7.44 (2H, d, J = 8.1 Hz, Ar−H), 7.37−7.24 (15H, m, Ar−H), 6.64 (1H, d, $J_{1,2}$ = 16.1 Hz, H-1), 6.23 (1H, dd, $J_{2,1}$ = 16.1 Hz, $J_{2,3}$ = 4.5 Hz, H-2), 4.94 (1H, d, J = 10.9 Hz, Bn-CH_2), 4.93 (1H, d, J = 11.3 Hz, Bn-CH_2), 4.65 (1H, d, J = 11.3 Hz, Bn-CH_2), 4.63 (1H, d, J = 10.9 Hz, Bn-CH_2), 4.49 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.40 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.29 (1H, app t, $J_{3,2} = J_{3,4}$ = 7.4 Hz, H-3), 4.13 (1H, dd, $J_{4,3}$ = 7.4 Hz, $J_{4,5}$ = 2.1 Hz, H-4), 4.03 (1H, m, H-5), 3.94 (3H, s, CO_2Me), 3.64 (1H, app t, $J_{6,5} = J_{6,6'}$ = 9.7 Hz, H-6), 3.41 (1H, dd, $J_{6',5}$ = 5.6 Hz, $J_{6',6}$ = 9.7 Hz, H-6′), 2.29 (3H, s, SCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.7 (C═O), 140.9 (q-CO_2Me), 138.6, 138.6, 138.3, 137.9 (q-Ar), 132.7 (C-1), 129.9 (Ar-C), 128.9 (C-2), 128.7, 128.4, 128.3, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 126.5 (Ar-C), 82.7 (C-3), 79.9 (C-4), 75.4, 75.1, 70.7 (Bn-CH_2), 69.9 (C-6), 52.1 (CO_2Me), 45.1 (C-5), 30.6 (SCH_3); HRMS (ES^+) m/z calcd for $C_{37}H_{38}O_6S$ $[M + Na]^+$ 633.2287, found 633.2298.

Data for the Z Isomer. ν_{max} (thin film) 1740, 1680 (C═O), 1027 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.90 (2H, d, J = 8.2 Hz, Ar−H), 7.36−7.25 (14H, m, Ar−H), 7.22 (1H, m, Ar−H), 6.76 (1H, d, $J_{1,2}$ = 12.3 Hz, H-1), 5.69 (1H, app t, $J_{2,1} = J_{2,3}$ = 12.3 Hz, H-2), 4.75 (1H, m, H-3), 4.64 (2H, m, Bn-CH_2), 4.47 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.46 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.39 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.38 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.14 (1H, dd, $J_{4,3}$ = 4.9 Hz, $J_{4,5}$ = 2.4 Hz, H-4), 3.94 (3H, s, CO_2Me), 3.98 (1H, m, H-5), 3.59 (1H, app t, $J_{6,5} = J_{6,6'}$ = 9.7 Hz, H-6), 3.36 (1H, dd, $J_{6',5}$ = 5.1 Hz, $J_{6',6}$ = 9.7 Hz, H-6′), 2.06 (3H, s, SCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.4 (C═O), 140.9 (q-CO_2Me), 138.6, 138.6, 138.3, 137.9 (q-Ar), 133.5 (C-1), 130.5 (C-2), 129.5, 128.7, 128.4, 128.4, 128.4, 128.3, 128.3, 127.8, 127.7, 127.6, 127.5 (Ar-C), 79.4 (C-4), 76.9 (C-3), 72.8, 72.7, 71.3 (Bn-CH_2), 69.9 (C-6), 52.1 (CO_2Me), 45.4 (C-5), 30.4 (SCH_3); HRMS (ES^+) m/z calcd for $C_{37}H_{38}O_6S$ $[M + Na]^+$ 633.2287, found 633.2298.

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Compound 33. To a degassed solution of **32** in MeOH was added freshly prepared NaOMe (0.01 M soln) at −10 °C. After the reaction mixture was stirred for 30 min, the reaction was quenched by the addition of Dowex H^+ ion-exchange resin until the mixture was pH-neutral. The resin was removed by filtration and washed with MeOH, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography to afford **33** as a colorless oil (366 mg, 0.64 mmol, 73%).

Data for the E Isomer. ν_{max} (thin film) 1039 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (2H, d, J = 8.3 Hz, Ar−H), 7.47 (2H, t, J = 7.2 Hz, Ar−H), 7.40−7.15 (15H, m, Ar−H), 6.78 (1H, d, $J_{1,2}$ = 16.1 Hz, H-1), 6.26 (1H, dd, $J_{2,1}$ = 16.1 Hz, $J_{2,3}$ = 8.2 Hz, H-2), 4.67−4.63 (4H, m, Bn-CH_2), 4.49 (1H, app t, $J_{3,2}$ = $J_{3,4}$ = 8.2 Hz, H-3), 4.36 (1H, d, J = 12.2 Hz, Bn-CH_2), 4.27 (1H, d, J = 12.2 Hz, Bn-CH_2), 4.05 (1H, dd, $J_{4,3}$ = 8.2 Hz, $J_{4,5}$ = 2.3 Hz, H-4), 3.56 (2H, m, H-6 and H-6′), 3.06 (1H, m, H-5), 3.94 (3H, s, CO_2Me), 1.75 (1H, d, $J_{5,SH}$ = 10.6 Hz, SH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.5 (C═O), 139.0 (q-CO_2Me), 138.7, 138.3, 138.0, 136.3 (q-Ar), 133.4 (C-1), 130.1, 129.6 (Ar-C), 129.4 (C-2), 128.4, 128.4, 128.3, 128.3, 128.2, 127.8, 127.7, 127.6, 127.6 (Ar-C), 83.7 (C-3), 79.5 (C-4), 75.3, 75.1 (Bn-CH_2), 72.8 (C-6), 72.5 (Bn-CH_2), 52.4 (CO_2Me), 41.1 (C-5); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_5S$ $[M + Na]^+$ 591.2181, found 591.2192.

Data for the Z Isomer. ν_{max} (thin film) 1039 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.96 (2H, d, J = 8.1 Hz, Ar−H), 7.40−7.15 (17H, m, Ar−H), 6.83 (1H, d, $J_{1,2}$ = 12.4 Hz, H-1), 5.75 (1H, app t, $J_{2,1}$ = $J_{2,3}$ = 12.4 Hz, H-2), 5.03 (1H, d, J = 12.2 Hz, Bn-CH_2), 4.95 (1H, d, J = 12.2 Hz, Bn-CH_2), 4.83 (1H, dd, $J_{3,2}$ = 12.4 Hz, $J_{3,4}$ = 6.9 Hz, H-3), 4.67−4.63 (4H, m, Bn-CH_2), 4.01 (1H, dd, $J_{4,3}$ = 6.9 Hz, $J_{4,5}$ = 3.1 Hz, H-4), 3.46 (2H, m, H-6 and H-6′), 3.15 (1H, m, H-5), 3.94 (3H, s, CO_2Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3 (C═O), 140.9 (q-CO_2Me), 138.3, 137.9, 134.9, 134.3 (q-Ar), 133.4 (C-1), 130.6 (C-2), 129.8, 129.7, 129.4, 128.7, 128.4, 128.3, 128.1, 128.1, 127.8, 127.5, 126.8 (Ar-C), 80.3 (C-4), 76.3 (C-3), 73.2, 72.8 (Bn-CH_2), 72.8 (C-6), 72.6 (Bn-CH_2), 51.9 (CO_2Me), 41.1 (C-5); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_5S$ $[M + Na]^+$ 591.2181, found 591.2192.

Compounds 34 and 35. The general procedure for radical cyclization was carried out to prepare **34** and **35** as a mixture of isomers (1.5:1, β:α). Purification by column chromatography (15:1 hexane/EtOAc) furnished **34**/**35** as a colorless oil (81 mg, 0.14 mmol, 89%).

*Data for β-Anomer **34** (Major Product).* ν_{max} (thin film) 1762 (C═O), 1050 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37−7.23 (17H, m, Ar−H), 7.17 (1H, d, J = 8.3 Hz, Ar−H), 7.13 (1H, m, Ar−H), 4.58 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.57 (2H, d, J = 12.2 Hz, Bn-CH_2), 4.53 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.52 (2H, d, J = 11.5 Hz, Bn-CH_2), 4.18 (1H, app t, $J_{3,2}$ = $J_{3,4}$ = 4.8 Hz, H-3), 3.91 (1H, app t, $J_{2,1}$ = $J_{2,3}$ = 4.8 Hz, H-2), 3.86 (1H, dd, $J_{5,4}$ = 6.9 Hz, $J_{5,5'}$ = 9.4 Hz, H-5), 3.79 (1H, m, H-4), 3.62 (1H, dd, $J_{5',4}$ = 5.6 Hz, $J_{5',5}$ = 9.4 Hz, H-5′), 3.61 (3H, s, CO_2Me), 3.54 (1H, m, H-1), 3.15 (1H, dd, $J_{CH_2Ar,1}$ = 6.7 Hz, $J_{CH_2Ar,CH_2Ar'}$ = 13.5 Hz, CH_2Ar), 2.91 (1H, dd, $J_{CH_2Ar',1}$ = 8.2 Hz, J_{CH_2Ar',CH_2Ar} = 13.5 Hz, CH_2Ar'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6 (C═O), 145.1, 137.8, 137.7, 137.6, 137.5 (q-Ar), 130.3, 128.9, 128.9, 128.7, 127.9, 127.6, 127.4, 127.4, 127.3, 127.3, 126.9 (Ar-C), 85.1 (C-2), 84.7 (C-3), 73.4, 72.2, 71.6 (Bn-CH_2), 68.9 (C-5), 52.1 (CO_2Me), 49.7 (C-1), 48.5 (C-4), 41.7 (CH_2Ar); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_5S$ $[M + Na]^+$ 591.2181, found 591.2194.

*Data for α-Anomer **35** (Minor Product).* ν_{max} (thin film) 1762 (C═O), 1050 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (4H, m, C_2H_4), 7.39−7.22 (15H, m, Ar−H), 4.62 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.59 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.52 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.51 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.42 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.34 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.18 (1H, app t, $J_{3,2}$ = $J_{3,4}$ = 3.5 Hz, H-3), 3.94 (2H, m, H-2 and H-4), 3.92 (3H, s, CO_2Me), 3.84 (1H, app t, $J_{5,4}$ = $J_{5,5'}$ = 8.6 Hz, H-5), 3.78 (1H, m, H-1), 3.56 (1H, dd, $J_{5',5}$ = 8.6 Hz, $J_{5',4}$ = 6.8 Hz, H-5′), 3.09 (1H, dd, $J_{CH_2Ar,CH_2Ar'}$ = 13.3 Hz, $J_{CH_2Ar,1}$ = 7.2 Hz, CH_2Ar), 3.01 (1H, dd, J_{CH_2Ar',CH_2Ar} = 13.3 Hz, $J_{CH_2Ar',1}$ = 8.8 Hz, CH_2Ar'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0 (C═O), 145.0, 137.9, 137.8, 137.8, 137.5 (q-Ar), 130.3, 128.9, 128.9, 128.8, 128.5, 128.4, 127.7, 127.3, 127.1, 126.9, 126.8, (Ar-C), 83.6 (C-2), 81.7 (C-3), 72.8, 72.6, 71.9 (Bn-CH_2), 69.8 (C-5), 52.2 (CO_2Me), 50.2 (C-1), 46.8 (C-4), 36.3 (CH_2Ar); HRMS (ES^+) m/z calcd for $C_{35}H_{36}O_5S$ $[M + Na]^+$ 591.2181, found 591.2194.

Compounds 26 and 37. **34**/**35** (80 mg, 0.14 mmol) was dissolved in THF (1 mL), and water (10 mL) was added. To this mixture was added dropwise with stirring and aqueous solution of NaOH (2.5 M, 3.5 mmol). The reaction mixture was heated to 100 °C overnight and then acidified with 1 M HCl at 0 °C until pH-neutral, saturated with NaCl (50 mL), and extracted with ethyl acetate (25 mL × 4). The crude reaction mixture was dried over magnesium sulfate, concentrated in vacuo, and used directly in the following step (69 mg, 0.12 mmol, 88%).

*Data for β-Anomer **36**.* ν_{max} (thin film) 1710 (CO_2H), 1041 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.41−7.22 (17H, m, Ar−H), 7.21 (1H, d, J = 8.2 Hz, Ar−H), 7.16 (1H, m, Ar−H), 4.81 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.60 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.59 (1H, d, J = 11.5 Hz, Bn-CH_2), 4.52 (1H, d, J = 11.5 Hz, Bn-CH_2), 4.44 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.36 (1H, d, J = 11.8 Hz, Bn-CH_2), 4.20 (1H, app t, $J_{3,2}$ = $J_{3,4}$ = 4.8 Hz, H-3), 3.94 (1H, app t, $J_{2,1}$ = $J_{2,3}$ = 4.8 Hz, H-2), 3.89 (1H, dd, $J_{5,4}$ = 6.7 Hz, $J_{5,5'}$ = 9.3 Hz, H-5), 3.82 (1H, m, H-4), 3.65 (1H, dd, $J_{5',4}$ = 6.1 Hz, $J_{5',5}$ = 9.3 Hz, H-5′), 3.58 (1H, m, H-1), 3.18 (1H, dd, $J_{CH_2Ar,1}$ = 7.8 Hz, $J_{CH_2Ar,CH_2Ar'}$ = 13.8 Hz, CH_2Ar), 2.94 (1H, dd, $J_{CH_2Ar',1}$ = 8.4 Hz, J_{CH_2Ar',CH_2Ar} = 13.8 Hz, CH_2Ar'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5 (C═O), 145.9 (CCO_2H), 137.9, 137.7, 137.7, 137.6 (q-Ar), 129.0, 128.8, 128.4, 128.4, 128.3, 128.3, 127.7, 127.7, 127.7, 127.7, 127.5, 127.7 (Ar-C), 85.4 (C-2), 84.6 (C-3), 73.2, 72.6, 71.9 (Bn-CH_2), 69.6 (C-5), 49.7 (C-1), 46.9 (C-4), 41.6 (CH_2Ar); HRMS (ES^+) m/z calcd for $C_{34}H_{34}O_5S$ $[M + Na]^+$ 577.2025, found 577.2038.

*Data for α-Anomer **37**.* ν_{max} (thin film) 1710 (CO_2H), 1041 (C−O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (2H, m, C_2H_4), 7.41−7.22 (17H, m, Ar−H), 4.61 (2H, m, Bn-CH_2), 4.54 (4H, m, Bn-CH_2), 4.21 (1H, m, H-3), 3.92 (2H, m, H-1 and H-4), 3.88 (1H, app t, $J_{5,4}$ = $J_{5,5'}$ = 8.6 Hz, H-5), 3.82 (1H, m, H-2), 3.61 (1H, dd, $J_{5',4}$ = 6.3 Hz, $J_{5',5}$ = 8.6 Hz, H-5′), 3.12 (1H, dd, $J_{CH_2Ar,CH_2Ar'}$ = 13.5 Hz, $J_{CH_2Ar,1}$ = 6.9 Hz, CH_2Ar), 3.04 (1H, dd, J_{CH_2Ar',CH_2Ar} = 13.5 Hz, $J_{CH_2Ar',1}$ = 8.6 Hz, CH_2Ar'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.6 (C═O), 146.4 (CCO_2H), 137.9, 137.8, 137.7, 137.6 (q-Ar), 130.2, 128.8, 128.4, 128.3, 127.8, 127.8, 127.7, 127.7, 127.5, 127.5, 127.4 (Ar-C), 83.5 (C-2), 81.7 (C-3), 73.2, 72.8, 71.9 (Bn-CH_2), 67.8 (C-5), 50.3 (C-1), 48.5 (C-4), 36.3 (CH_2Ar); HRMS (ES^+) m/z calcd for $C_{34}H_{34}O_5S$ $[M + Na]^+$ 577.2025, found 577.2038.

Compounds 39 and 40. To a solution of **36** (66 mg, 0.12 mmol) in CH_2Cl_2 (0.5 mL) was added TFA (1 mL), and the reaction mixture was allowed to stir for 10 min at room temperature. The solvent was removed in vacuo and coevaporated with DIPEA (0.02 mL, 1.2 mmol). The resultant residue was dissolved in dry DMF (1 mL) under argon, and **36**/**37** (55 mg, 0.1 mmol) was added. To the reaction mixture were added *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate (HATU) (57 mg, 0.15 mmol) and DIPEA (35 μL, 0.2 mmol), and the reaction mixture was left to stir overnight at room temperature under argon. The solvent was removed in vacuo, and the residue was purified by column chromatography (4:1 EtOAc/hexane) to yield **37**/**38** as a yellow oil (80 mg, 0.08 mmol, 81%).

*Data for β-Anomer **39**.* ν_{max} (thin film) 3059, 1692, 1045 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.52 (1H, d, $J_{3,4}$ = 8.6 Hz, H-3), 8.35 (1H, d, $J_{8,9}$ = 8.6 Hz, H-8), 8.24 (1H, d, $J_{5,4}$ = 8.6 Hz, H-5), 7.68 (2H, t, $J_{23,24}$ = 6.8 Hz, H-23), 7.55 (1H, app t, $J_{9,8}$ = $J_{9,10}$ = 8.6 Hz, H-9), 7.52 (1H, app t, $J_{4,3}$ = $J_{4,5}$ = 8.6 Hz, H-4), 7.40−7.22 (14H, m, Ar−H), 7.21 (1H, d, J = 8.6 Hz, H-10), 7.16 (1H, d, J = 7.9 Hz, Bn-Ar−H), 7.12 (2H, d, $J_{24,23}$ = 6.8 Hz, H-24), 7.03 (1H, t, J = 5.3 Hz, CONH), 5.81 (1H, t, J = 5.7 Hz, $NHSO_2$), 4.61 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.58 (1H, d, J = 11.9 Hz, Bn-CH_2), 4.56 (1H, d, J = 11.6 Hz, Bn-CH_2), 4.54−4.48 (3H, m, Bn-CH_2), 4.17 (1H, app t, $J_{29,28}$ = $J_{29,30}$ = 5.1 Hz, H-29), 3.93 (1H, app t, $J_{28,27}$ = $J_{28,29}$ = 5.1 Hz, H-28), 3.87 (1H, dd, $J_{31,30}$ = 6.8 Hz, $J_{31,31'}$ = 9.3 Hz, H-31), 3.78 (1H, m, H-30), 3.62−3.60 (11H, m, H-31′, H-14 × 2, H-15 × 2, H-16 × 2, H-18 × 2, H-20 × 2), 3.52 (1H, m, H-

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27), 3.43 (2H, m, H-17), 3.39 (2H, t, J = 5.9 Hz, H-13), 3.13 (1H, dd, $J_{26,27}$ = 6.7 Hz, $J_{26,26'}$ = 13.7 Hz, H-26), 3.02 (2H, q, J = 5.9 Hz, H-11), 2.92 (6H, s, NMe_2), 2.86 (1H, dd, $J_{26',27}$ = 8.6 Hz, $J_{26',26}$ = 13.7 Hz, H-26′), 1.89 (2H, m, H-19 × 2), 1.62 (2H, quintet, J = 5.8 Hz, H-12 × 2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4 (C-21), 151.3 (C-1), 143.1 (C-25), 138.2, 137.9, 137.9 (q-Bn-Ar), 135.1 (C-6), 132.8 (C-22), 129.9 (C-3), 129.7 (C-2), 129.5 (C-5), 129.0 (C-24) 128.5, 128.4, 128.4 (Ar-C), 128.2 (C-9), 127.8, 127.8, 127.8 (Ar-C), 127.1 (C-23), 119.5 (C-7), 119.5 (C-8), 115.3 (C-10), 113.5 (C-4), 85.8 (C-28), 84.7 (C-29), 73.3, 72.7, 72.1 (Bn-CH_2), 70.5 (C-15), 70.4 (C-16), 70.2 (C-18), 70.1 (C-14), 69.9 (C-13), 69.8 (C-17), 69.7 (C-31), 50.0 (C-27), 46.9 (C-30), 45.5 (NMe_2), 42.1 (C-11), 41.6 (C-26), 38.4 (C-20), 29.0 (C-19), 28.6 (C-12); HRMS (ES$^+$) m/z calcd for $C_{56}H_{67}N_3O_9S_2$ $[M + Na]^+$ 1012.4217, found 1012.4225.

Data for α-Anomer ***40****.* ν_{max} (thin film) 3059, 1692, 1045 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (1H, d, $J_{3,4}$ = 8.6 Hz, H-3), 8.35 (1H, d, $J_{8,9}$ = 8.6 Hz, H-8), 8.24 (1H, d, $J_{5,4}$ = 8.6 Hz, H-5), 7.67 (2H, t, $J_{23,24}$ = 6.8 Hz, H-23), 7.55 (1H, app t, $J_{9,8}$ = $J_{9,10}$ = 8.6 Hz, H-9), 7.52 (1H, app t, $J_{4,3}$ = $J_{4,5}$ = 8.6 Hz, H-4), 7.40−7.22 (15H, m, Ar−H), 7.21 (1H, d, $J_{10,9}$ = 8.6 Hz, H-10), 7.18 (2H, d, $J_{24,23}$ = 6.8 Hz, H-24), 7.03 (1H, t, $J_{NH,20}$ = 5.3 Hz, CONH), 5.81 (1H, t, $J_{NH,11}$ = 5.7 Hz, $NHSO_2$), 4.54−4.48 (4H, m, Bn-CH_2), 4.41 (1H, d, J = 12.6 Hz, Bn-CH_2), 4.39 (1H, d, J = 12.6 Hz, Bn-CH_2), 4.16 (1H, app t, $J_{29,28}$ = $J_{29,30}$ = 4.3 Hz, H-29), 3.98 (1H, m, H-30), 3.92 (1H, app t, $J_{28,27}$ = $J_{28,29}$ = 4.3 Hz, H-28), 3.86 (1H, m, H-27), 3.82 (1H, dd, $J_{31,30}$ = 5.9 Hz, $J_{31,31'}$ = 10.1 Hz, H-31), 3.68 (1H, dd, $J_{31',30}$ = 5.2 Hz, $J_{31',31}$ = 10.1 Hz, H-31′), 3.66 (10H, m, H-14 × 2, H-15 × 2), H-16 × 2, H-18 × 2, H-20 × 2), 3.43 (2H, m, H-17 × 2), 3.39 (2H, t, J = 5.9 Hz, H-13), 3.07 (1H, dd, $J_{26,27}$ = 6.7 Hz, $J_{26,26'}$ = 13.8 Hz, H-26), 3.02 (2H, q, J = 5.9 Hz, H-11), 2.96 (1H, d, $J_{26',27}$ = 8.1 Hz, $J_{26',26}$ = 13.8 Hz, H-26′), 2.92 (6H, s, NMe_2), 1.89 (2H, m, H-19 × 2), 1.62 (2H, quintet, J = 5.8 Hz, H-12 × 2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4 (C-21), 151.3 (C-1), 143.6 (C-25), 138.2, 137.9, 137.9 (q-Bn-Ar), 135.1 (C-6), 132.7 (C-22), 129.9 (C-3), 129.7 (C-2), 129.5 (C-5), 128.6, 128.5, 128.4 (Ar-C), 128.3 (C-24), 128.2 (C-9), 127.9, 127.8, 127.8 (Ar-C), 127.1 (C-23), 119.5 (C-7), 119.5 (C-8), 115.3 (C-10), 113.5 (C-4), 83.7 (C-28), 81.8 (C-29), 73.3, 72.8, 72.0 (Bn-CH_2), 70.5 (C-15), 70.4 (C-16), 70.2 (C-18), 70.1 (C-14), 69.9 (C-13), 69.8 (C-17), 69.1 (C-31), 50.6 (C-27), 48.6 (C-30), 45.5 (NMe_2), 42.1 (C-11), 36.1 (C-26), 38.4 (C-20), 29.0 (C-19), 28.6 (C-12); HRMS (ES$^+$) m/z calcd for $C_{56}H_{67}N_3O_9S_2$ $[M + Na]^+$ 1012.4217, found 1012.4225.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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