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Reactivity switching and selective activation of *C*-1 or *C*-3 in 2,3-unsaturated thioglycosides

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Dedicated to Professor Dr. András Lipták on the occasion of his 75th birthday

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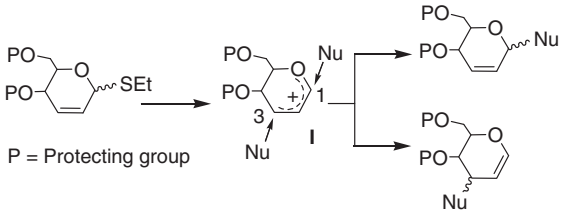
ABSTRACT

Reactivity switching and selective activation of *C*-1 or *C*-3 in 2,3-unsaturated thioglycosides, namely, 2,3-dideoxy-1-thio-D-hex-2-enopyranosides are reported. The reactivity switching allowed activation of either *C*-1 or *C*-3, with the use of either *N*-iodosuccinimide (NIS)/triflic acid (TfOH) or TfOH alone. *C*-1 glycosylation with alcohol acceptors occurred in the presence of NIS/TfOH, without the acceptors reacting at *C*-3. On the other hand, reaction of 2,3-unsaturated thioglycosides with alcohols mediated by triflic acid led to transposition of *C*-1 ethylthio-moiety to *C*-3 intramolecularly, to form 3-ethylthio-glycals. Resulting glycals underwent glycosylation with alcohols to afford 3-ethylthio-2-deoxy glycosides. However, when thiol was used as an acceptor, only a stereoselective addition at *C*-3 resulted, so as to form *C*-1, *C*-3 dithio-substituted 2-deoxypyranosides.

1. Introduction

Thioglycosides are common activated glycosyl donors, on account of their ease of preparation, stabilities, orthogonal reactivities in the presence of other functionalities, and facile activation methods.[1] On the other hand, 2,3-dideoxy-hex-2-enopyranosides, referred to as Ferrier products, serve as excellent intermediates in derivatizations of monosaccharides with varied functionalities.[2] Such products are formed, in turn, from 1,2-unsaturated sugars, namely, glycals, having a 3-*O*-acyl/alkyl group, through acid catalysis. In our efforts to utilize glycals, the method of treating glycals with ethanethiol, in the presence of cerium(IV) salt, was identified, in order to prepare activated 2-deoxy glycosyl donors.[3] In addition to the formation of 2-deoxy-1-thioglycosides, the method also led to the formation of the Ferrier product, namely, 2,3-dideoxy-1-thio-D-hex-2-enopyranosides. Glycosylations involving activated 2-deoxy-1-thioglycosides afforded a variety of 2-deoxy sugars, linear, and cyclic-oligosaccharides.[4] Continuing to explore the synthetic potential of thioglycosides formed from glycals, glycosylations of 2,3-unsaturated thioglycosides, namely, 2,3-dideoxy-1-thio-D-hex-2-enopyranosides, appeared attractive. Oxocarbenium ion[5] is the reactive intermediate during activation of a glycosyl donor, and in the case of a 2,3-unsaturated thioglycoside, the oxocarbenium ion may stabilize further by the presence of a *C*-2–*C*-3 unsaturation, as shown in Scheme 1. Reaction of a nucleophile with dihydropyrylium ion **I** may lead to two regio-isomers. Studies of the reaction of 1,5-anhydro-2-deoxy-hex-1-enitol, namely, glycals and 2,3-dideoxy-2-enopyranosides with thiols were studied previously by Zamojski[6] and Fraser-Reid[7] groups, respectively. 2,3-Unsaturated thioglycosides undergo equilibration to afford 3-*S*-alkyl-3-thio glycals[6] in an acid-catalyzed condition (HCl or $SnCl_4$). On the other hand, glycals react with thiols, in the presence of $BF_3{\cdot}Et_2O$, to afford 2,3-unsaturated 1-thioglycosides, along with allylic rearrangement isomer 3-*S*-aryl-3-thio glycals and aryl 1,3-dithio-2-deoxy glycosides.[8–11] Further, Blattner and Ferrier showed that glycals reacted with thiophenol, in the presence of $BF_3{\cdot}Et_2O$ along with catalytic amount of water, to afford *S*-phenyl 2-deoxy-3-phenylthio-1-thioglycosides.[12] With the knowledge that thioglycosides are activated by *N*-iodosuccinimide (NIS)/triflic acid (TfOH), a commonly used promoter system of thioglycosides, we undertook to study the glycosylation of 2,3-unsaturated thioglyco-



Scheme 1.

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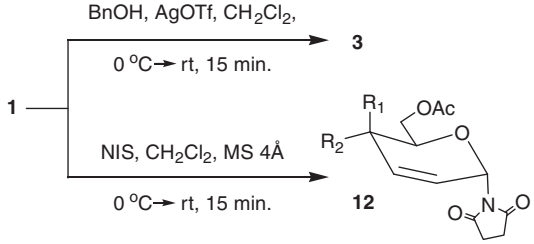
sides. The studies showed that it was possible to activate either *C*-1 or *C*-3 selectively, depending on the choice of the activation agent. Details of this reactivity switching potential of 2,3-unsaturated thioglycosides are presented herein.

2. Results and discussion

Precursors of 2,3-unsaturated thioglycoside, namely, ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-1-thio-D-*erythro*-hex-2-enopyranoside (**1**), and the *threo*-analog (**2**), were obtained by reaction of 3,4,6-tri-*O*-acetyl glucal with EtSH, in the presence of $(NH_4)_2Ce(NO_3)_6$.[3] Glycosylation of thioglycoside **1** was undertaken with few aglycosyl and glycosyl acceptors, in the presence of NIS/TfOH (cat.), in CH_2Cl_2 (Scheme 2). Product formed in the reaction was found to be *O*-glycosides **3**–**11**, with both aglycosyl and glycosyl acceptors. *O*-Glycosides with α-anomeric configuration were predominant in the above reactions. The observation that only *O*-glycosides **3**–**11** formed in the reaction illustrated that *C*-1 was the preferred reactive center under NIS/TfOH reaction condition. It was also observed that O-glycosylation at *C*-1 occurred in the presence of NIS, without TfOH. Thus, products **4** and **6** were obtained without TfOH in Scheme 2. Illustrative studies on glycosylations involving allyl phenylthio-glycosides were demonstrated previously by Fraser-Reid and co-workers, under iodonium-ion promoted condition, in the absence of a Lewis acid.[7] Our results are in agreement with this report. Further, reaction of 2,3-unsaturated thioglycosides with benzyl alcohol in the presence of AgOTf, without TfOH, also afforded *O*-glycoside product **3**, as an α-anomer (Scheme 3). In the absence of an acceptor, succinimide, generated during the reaction with NIS, reacted at *C*-1, and glycosyl derivative **12** was isolated (Scheme 3).

Constitutions of 2,3-unsaturated *O*-glycosides **3**–**13** were confirmed by NMR spectroscopies and mass spectrometry. Unsaturations at C*H*-2–C*H*-3 were confirmed by the presence of resonances at ~6 and 5.8 ppm in ^{1}H NMR spectra. Anomeric carbon in **3**–**11** showed resonance at ~96–102 and ~92–94 ppm for β- and α-anomeric configurations, respectively, in ^{13}C NMR spectra. Thioglycoside **1** showed resonance at ~78–80 ppm, for α- and β-configurations of *C*-1.

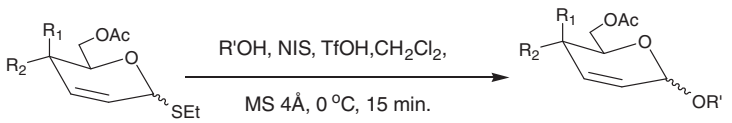
With the inability to identify a product with alcohol reacting at *C*-3 in intermolecular reactions, an intramolecular reaction of **I** with an acceptor was undertaken. For this purpose, *C*-4-*O*-*tert*-butyloxycarbonyl (*O*-Boc)-protected thioglycoside derivative **13**



Scheme 3.

was prepared (Scheme 4) and subjected to NIS/TfOH promoted glycosylation, as in Scheme 2. Analysis of the product showed that glycosyl carbonate at *C*-4, formed under the reaction condition, reacted at *C*-3 to afford 6-*O*-benzoyl-3,4-di-*O*-carbonyl glucal **14**. We presume that an altered reactivity profile of carbonate may have caused nucleophile entry at *C*-3 of dihydropyrylium ion **I**. Zamojski and co-workers put-forth the possibility of hard–soft acid–base principle[13] to account for the reactivity preferences at *C*-1 and *C*-3 of allyl thioglycosides under acidic conditions.[6] It is likely that both carbonate and succinimide nucleophiles exhibit borderline hard–soft nucleophilicities, leading to entry at *C*-1 or *C*-3 which is somewhat unpredictable. Alternatively, it might be that the proximity effect led to reaction at *C*-3, than at *C*-1 in **13** in the above reaction.

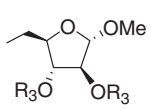
Reactivities of 2,3-unsaturated thioglycosides were assessed further with TfOH, in the absence of NIS, with the anticipation that the double bond might be activated selectively. Thus, reactions were performed with **1**, in the presence of TfOH (0.7 molar equiv) and an alcohol acceptor (Scheme 5). Analysis of the product showed that 2-deoxy glycosides **16**–**18** formed, with transposition of *C*-1 ethylthio-moiety to *C*-3. The transformation appeared to occur through (i) shift of *C*-1 ethylthio-moiety to *C*-3 to afford 3-*S*-alkyl-3-thioglycal **II** and (ii) subsequent glycosylation of **II** under the reaction conditions, leading to 2-deoxy glycoside **16**–**18**. The reaction did not occur when catalytic amount of TfOH was used. Further, this transformation also occurred when TMSOTf was used in place of TfOH. Important observations of the reaction were (i) *C*-1 ethylthio-moiety transposition led to an equatorial configuration at *C*-3, even when anomeric mixture of **1** was used and (ii) product with α-anomeric configuration formed predominantly. When the reaction was conducted in the absence of a glycosyl acceptor,



1: R_1 = H, R_2 = OAc
2: R_1 = OAc, R_2 = H

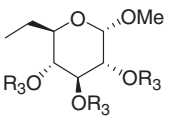
3: R' = Bn: R_1 = H, R_2 = OAc; α/β = 2.2:1
4: R' = Bn: R_1 = OAc, R_2 = H; only α
5: R' = cyclohexyl: R_1 = H, R_2 = OAc; only α
6: R' = cyclohexyl: R_1 = OAc, R_2 = H; α/β = 4.7:1

R' =



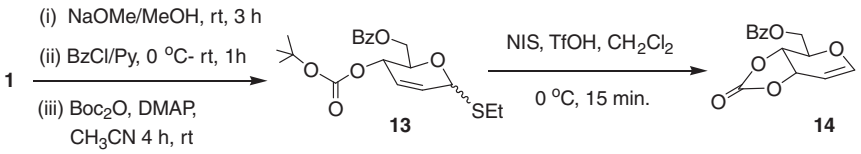
7: R_1 = H, R_2 = OAc, R_3 = Bz; only α
8: R_1 = OAc, R_2 = H, R_3 = Bz; α/β = 1.75:1
9: R_1 = H, R_2 = OAc, R_3 = Bn; only α

R' =

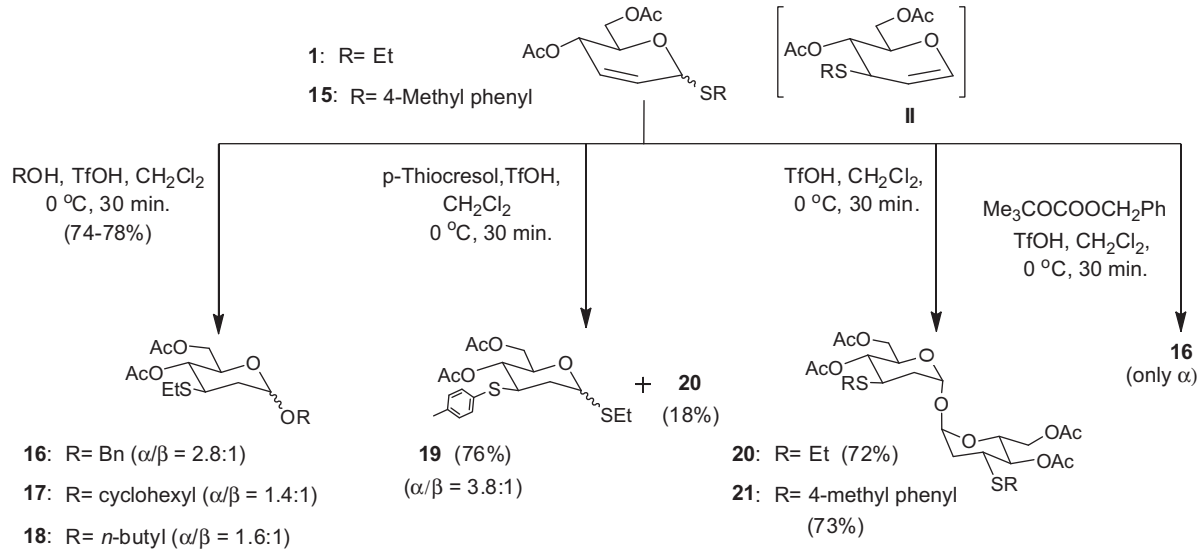


10: R_1 = H, R_2 = OAc, R_3 = Bz; only α
11: R_1 = H, R_2 = OAc, R_3 = Bn; α/β = 3.6:1

Scheme 2.



Scheme 4.



Scheme 5.

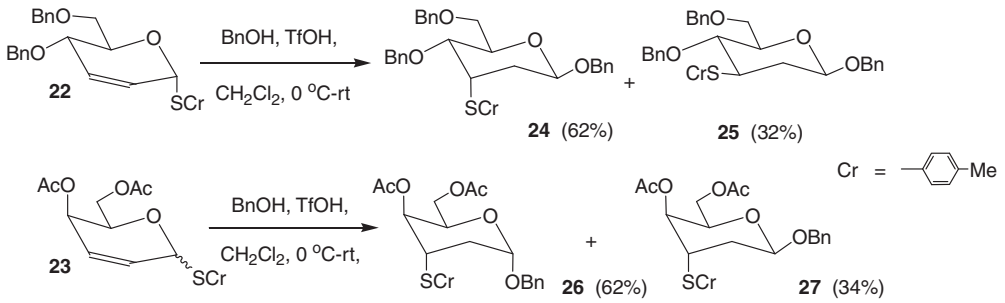
2,2′-dideoxy trehalose derivative (**20**) formed, with *C*-1 ethylthio-moiety transposed to *C*-3, which might have occurred as a result of hydrolysis and subsequent glycosylation involving lactol. Reaction of 2,3-unsaturated *p*-cresylthioglycoside **15** led similarly to trehalose derivative **20**, with transposed 4-methylphenylthio-moiety.

When *p*-thiocresol was used as an acceptor, in the reaction with **1**, addition across *C*-2–*C*-3 double bond occurred and the major product was ethyl 3-(4-methylphenyl)thio-2-deoxy-1-thioglycoside **19** (76%). The transposition and subsequent glycosylation at *C*-1 led to **20** (18%) as a minor product. As observed previously, **20** would result by the formation of lactol and subsequent glycosylation. Reaction of benzyl *tert*-butylcarbonate with ethyl thioglycoside **1** in the presence of TfOH provided **16**, with transposed ethylthio-moiety at *C*-3 and benzyl group at *C*-1. An anchimeric assistance arising from *C*-4 acetoxy group is likely,[2a,14] which, in turn would permit facial selectivity of ethylthio-moiety at *C*-3. In order to verify this possibility, 2,3-unsaturated thioglycosides **22** and **23**[15] were treated with BnOH in the presence of TfOH (Scheme 6).

Whereas **22** afforded *O*-glycosides **24** and **25** as an epimeric mixture, galactosyl derivative **23** led to the formation of 3-(4-methylphenylthio)-*O*-glycosides **26** and **27**, as an anomeric mixture, with axial orientation of the substituent at *C*-3. These reactions reiterate the role of the *C*-4 substituent on carbocation at *C*-3, through the presence or absence of anchimeric assistance.

In the absence of an ability of TfOH or TMSOTf alone to activate thioglycoside moiety, preferred activation would occur at the double bond. Upon activation, a facile 1→3 shift would lead to transposition of *C*-1 ethylthio-moiety to *C*-3, with concomitant glycal **II** (Scheme 5) formation. A glycosylation, under acidic condition, led to the formation of 2-deoxy glycoside. Glycals providing 2-deoxy glycosides under acidic conditions are known previously.[16–21]

Such a type of 1→3 shift in allyl thioglycosides is known so far in the presence of $BF_3{\cdot}Et_2O$[7–12] and $SnCl_4$.[6] A sigmatropic shift occurring with 3-azido glycals to 2,3-dideoxy-hex-2-enopyranosyl azides under catalysis by $BF_3{\cdot}Et_2O$,[22] as also shifts in 3,4,6-tri-*O*-benzyl-D-glycals to 2,3-unsaturated α/β-benzyl glycosides by $BF_3{\cdot}Et_2O$[23] and $InCl_3$[24] are known. The observed transposition in



Scheme 6.

this study thus appeared general, although hard–soft nature of carbon centers and those of acceptors seemed to be important. This view is supported when comparing the reactions of **1** with alcohols and thiocresol, in the presence of TfOH. Whereas 2-deoxy glycosides **16**–**18** formed with alcohols, derivative **19** formed as the major product, when thiocresol was used (Scheme 5). TfOH-mediated activation of the double bond is probably prone to attack by a soft nucleophile, arising either intra- or intermolecularly, thereby leading to either *C*-1→*C*-3 transposition or incorporation of externally added of thio-functionality, respectively. This observation also confirms that addition across *C*-2–*C*-3 double bond predominates in the presence of TfOH or TMSOTf, without affecting *C*-1 thioethyl-moiety. Hard–soft acid–base principle, put-forth by Zamojski and co-workers for reactivities arising from glycals,[6] appears to be reasonable in order to rationalize the observed addition pattern upon allylic bond activation.

Structures of **16**–**21** were confirmed by NMR spectroscopies and mass spectrometry. In addition, heteronuclear multiple quantum coherence, correlated spectroscopy, and proton decoupling NMR techniques were utilized to identify the resonances of individual nuclei and configurations in few cases. Absence of olefinic protons in ^{1}H NMR spectra and appearance of resonance at ~91–98 ppm in ^{13}C NMR spectra confirmed 2-deoxy glycoside formation in **16**–**18**, **20,** and **21**. *trans*-diequatorial configuration of substituents at C-3–C-4 was confirmed through proton decoupling experiments, through which a *J* value of ~10.5 Hz was observed. Presence of resonances at ~1.9 and ~2.1 ppm corresponded to *C*-2 methylene protons in ^{1}H NMR spectra, as also a resonance at ~36 ppm, in the ^{13}C NMR spectra. In the case of *C*-3 with ethylthio-moiety, signal at ~39–41 ppm appeared, whereas, that with (4-methylphenyl)thio-moiety, *C*-3 appeared at ~45–47 ppm. In the case of **24** and **25**, the epimeric nature was identified through *C*-3 resonances that appeared at 45.5 and 46.9 ppm, respectively. The anomers **26** and **27** were adjudged through ^{13}C NMR values of *C*-1, appearing at 95.1 and 97.2 ppm, for α- and β-anomers, respectively. β-Anomers showed generally resonances in the range of 96–98 ppm, whereas, those in α-anomers were observed in the range of 92–95 ppm.

3. Conclusion

From the series of studies, the possibility of selective activation of either thioglycoside moiety or allylic bond in 2,3-unsaturated thioglycoside is established. A reactivity switching between these two functionalities was possible by a choice of activation reagent. Thus, whereas NIS or AgOTf activated thioglycoside moiety, double bond activation occurred in the presence of TfOH or TMSOTf. This activation led to the formation of a glycal with *C*-1 thioglycoside moiety transposed to *C*-3. The newly formed glycal underwent a glycosylation at *C*-1 with available acceptor under the reaction conditions. Soft thiol nucleophile afforded allylic bond addition as the major product, with stereoselective substitution at *C*-3, thereby leading to the formation of *C*-1, *C*-3 dithio-substituted 2-deoxy pyranosides.

4. Experimental

4.1. General procedure for the synthesis of 2,3-unsaturated-*O*-glycosides

Alcohol (1.2 mmol), NIS (1.2 mmol), and molecular sieves (MS) 4 Å were added to a stirred solution of **1** (1 mmol) in CH_2Cl_2. A solution of TfOH (10 mol % in CH_2Cl_2) was added subsequently, the reaction mixture stirred for ~15 min at 0 °C, diluted with CH_2Cl_2, washed with aq $Na_2S_2O_3$ (5%) solution, brine, concentrated in vacuo, and purified by column chromatography (SiO_2) to afford the desired 2,3-unsaturated *O*-glycosides.

4.2. Benzyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3)

Yield: 62%. R_f = 0.3 (12% EtOAc/pet. ether). $[\alpha]_D$ +0.75 (*c* 0.44, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.36–7.26 (m, 5H), 5.97–5.86 (m, 2H), 5.33 (app. d, *J* = 12 Hz, 1H), 5.23 (app. s, 1H), 4.80 (d, *J* = 12 Hz, 1H), 4.59 (d, *J* = 12 Hz, 1H), 4.31–4.20 (m, 2H), 4.17–4.06 (m, 1H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.2, 137.5, 130.4, 128.0, 127.9, 125.9, 93.6, 72.7, 70.2, 67.0, 65.2 62.8, 20.9, 20.7. HR-MS: *m/z* calcd for $C_{17}H_{20}O_6$: 343.1158 $[M+Na]^+$. Found: 343.1108.

Alternatively, benzyl alcohol (0.1 mL, 1.2 mmol) and AgOTf (0.25 g, 0.98 mmol) were added to a solution of **1** (0.3 g, 1.09 mmol) in CH_2Cl_2 at 0 °C and stirred at room temperature for ~15 min. The reaction mixture was then concentrated in vacuo and purified by column chromatography (SiO_2) to afford **3**. Yield: 0.32 g (91%).

4.3. Benzyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (4)

Yield: 91%. R_f = 0.2 (12% EtOAc/pet. ether). $[\alpha]_D$ −0.83 (*c* 0.27, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.44–7.26 (m, 5H), 6.12 (dd, *J* = 5.2, 10 Hz, 1H), 6.04 (dd, *J* = 2.6, 10 Hz, 1H), 5.17 (d, *J* = 2.6 Hz, 1H), 5.04 (dd, *J* = 5.2, 2.6 Hz, 1H), 4.79 (d, *J* = 8 Hz, 1H), 4.53 (d, *J* = 8 Hz, 1H), 4.44–4.41 (m, 1H), 4.31–4.11 (m, 2H), 2.09 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.3, 137.3, 130.5, 128.5, 128.1, 127.9, 125.3, 92.8, 69.8, 66.9, 62.8, 20.8, 20.7. HR-MS: *m/z* calcd for $C_{17}H_{20}O_6$: 343.1158 $[M+Na]^+$. Found: 343.1154.

4.4. Cyclohexyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5)

Yield: 87%. R_f = 0.35 (12% EtOAc/pet. ether). $[\alpha]_D$ +86 (*c* 0.67, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.85–5.82 (m, 2H), 5.29 (app. d, *J* = 9.2 Hz, 1H), 5.17 (app. s, 1H), 4.25–4.15 (m, 2H), 3.67–3.62 (m, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.93–1.89 (m, 1H), 1.74 (d, *J* = 5.2 Hz, 2H), 1.67 (s, 1H), 1.56–1.53 (m, 1H), 1.41–1.17 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.3, 128.7, 128.5, 92.8, 72.6, 66.7, 63.5, 33.7, 32.1, 25.5, 24.3, 20.9, 20.7. HR-MS: *m/z* calcd for $C_{16}H_{24}O_6$: 335.1471 $[M+Na]^+$. Found: 335.1473.

4.5. Cyclohexyl 4,6-di-*O*-acetyl-2,3-dideoxy α-D-*threo*-hex-2-enopyranoside (6)

Yield: 89%. R_f = 0.3 (12% EtOAc/pet. ether). $[\alpha]_D$ −0.79 (*c* 0.38, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 6.09 (dd, *J* = 5.2, 10.0 Hz, 1H), 6.02 (dd, *J* = 2.8, 10.0 Hz, 1H), 5.28 (d, *J* = 2.8 Hz, 1H), 5.02 (dd, *J* = 2.3, 5.2 Hz, 1H), 4.50- 4.31 (m, 1H), 4.28–4.19 (m, 1H), 3.68–3.65 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.00–1.95 (m, 2H), 1.78–1.65 (m, 2H), 1.56–1.54 (band, 1H), 1.46–1.17 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.3, 131.2, 124.2, 92.3, 70.9, 66.5, 62.9, 33.7, 32.0, 25.5, 24.4, 20.8, 20.7. HR-MS: *m/z* calcd for $C_{16}H_{24}O_6$: 335.1471 $[M+Na]^+$. Found: 335.1479.

4.6. Methyl-5-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (7)

Yield: 78%. R_f = 0.3 (30% EtOAc/pet. ether). $[\alpha]_D$ −19.2 (*c* 0.67, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.08–8.03 (m, 5H), 7.61–7.54 (m, 1H), 7.46–7.37 (m, 4H), 5.98–5.82 (m, 2H), 5.55 (d, *J* = 4.8 Hz, 1H), 5.47 (d, *J* = 2.5 Hz, 1H), 5.45–5.42 (m, 1H), 5.34–5.31 (m, 1H), 5.18–5.15 (m, 1H), 4.41–4.38 (m, 1H), 4.32–4.16 (m, 2H), 4.07–

4.03 (m, 1H), 3.94 (d, J = 2.2 Hz, 1H), 3.95–3.89 (m, 1H), 3.47 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.2, 165.7, 165.4 133.4, 129.9, 129.7, 128.4, 127.5, 106.8, 94.6, 82.1, 70.2, 67.1, 65.0, 62.7, 55.4, 54.9, 20.9,20.7. HR-MS: m/z calcd for $C_{30}H_{32}O_{12}$: 607.1791 $[M+Na]^+$. Found: 607.1782.

4.7. Methyl-5-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α/β-D-*threo*-hex-2-enopyranosyl)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (8)

Yield: 67%. αβ = 1.75:1. R_f = 0.5 (30% EtOAc/pet. ether). ^{1}H NMR ($CDCl_3$): δ 8.05 (t, J = 8.4 Hz, 12.3H), 7.62–7.51 (m, 4.17H), 7.42 (q, J = 7.2, 10.5 Hz, 16.3H), 7.39–7.37 (m, 3.52H), 6.09–6.03 (m, 4.50H), 5.52 (d, J = 4.6 Hz, 2.63H), 5.48 (br s, 1.75H), 5.19 (s, 1.50H), 5.13 (s, 1.57H), 4.92 (d, J = 1.2 Hz, 1.27H), 4.41–4.32 (m, 3.62H), 4.03 (d, J = 6.8 Hz, 6.02H), 3.96 (d, J = 2.8 Hz, 1H), 3.93 (d, J = 4.6 Hz, 1.75H), 3.48 (s, 4.11H), 3.43 (s, 1.05H) 2.13–2.04 (m, 12.7H), 1.98 (s, 8.78H); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.3, 167.0, 165.7, 165.3, 133.5, 133.3, 130.3, 129.9, 129.5, 128.5, 125.2, 125.1, 106.8, 101.3, 94.1, 82.1, 79.3, 69.9, 67.0 62.7, 55.5, 54.9, 52.0, 20.8, 20.6. HR-MS: m/z calcd for $C_{30}H_{32}O_{12}$: 607.1791 $[M+Na]^+$. Found: 607.1747.

4.8. Methyl-5-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (9)

Yield: 75%. R_f = 0.4 (30% EtOAc/pet. ether). $[\alpha]_D$ +0.82 (c 0.45, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.29–7.18 (band, 10H), 5.74 (app. q, J = 7.4, 10.0 Hz, 2H), 5.23 (app. d, J = 10.0 Hz, 1H), 5.02 (app. s, 1H), 4.85 (s, 1H) 4.53–4.38 (m, 6H), 4.16–4.03 (m, 2H), 3.92–3.79 (m, 2H), 3.66 (dd, J = 3.8, 11.2 Hz, 2H), 3.30 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.2, 137.7, 137.3, 129.0, 128.4, 127.9, 127.6, 107.3, 94.6, 87.6, 83.4, 82.5, 80.6, 72.3, 72.1, 67.7, 66.8, 65.1, 62.7, 62.2, 54.9, 54.8, 20.9, 20.4. HR-MS: m/z calcd for $C_{30}H_{36}O_{10}$: 579.2206. Found: 579.2206.

4.9. Methyl-6-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-*erythro*-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzoyl-α-D- glucopyranoside (10)

Yield: 62%. R_f = 0.2 (30% EtOAc/pet. ether). $[\alpha]_D$ +23 (c 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.94 (m, 4H), 7.81 (d, J = 7.2 Hz, 2H), 7.51 (m, 2H), 7.44–7.36 (m, 4H), 7.29–7.25 (m, 3H), 5.94 (app. d, J = 5.2 Hz, 2H), 5.76 (m, 1H), 5.63 (app. t, J = 9.6 Hz, 1H), 5.53–5.45 (m, 2H), 5.28 (d, J = 8.4 Hz, 1H), 5.05 (br s, 1H), 4.73 (d, J = 7.9 Hz, 1H), 4.12–4.05 (m, 1H), 4.02–3.86 (m, 3H), 3.81–3.76 (m, 1H), 3.55 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.2, 165.8, 165.1, 133.4, 133.2, 129.9, 129.2, 128.9, 128.5, 128.2, 127.2, 102.0, 94.5, 76.6, 74.5, 73.1, 71.7, 69.5, 65.0, 62.6, 57.2, 20.9, 20.6. HR-MS: m/z calcd for $C_{38}H_{38}O_{14}$: 741.2159 $[M+Na]^+$. Found: 741.2151.

4.10. Methyl-6-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α/β-D-*erythro*-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (11)

Yield: 68%. R_f = 0.3 (30% EtOAc/pet. ether). αβ = 3.6:1. ^{1}H NMR ($CDCl_3$): δ 7.25–7.26 (band, 68.8H), 5.85 (br s, 3.58H), 5.29 (d, J = 5.2 Hz, 6.89H), 5.10 (br s, 2.98H), 4.97 (d, J = 10.6 Hz, 9.32H), 4.78 (dd, J = 2.8, 11.6 Hz, 10.76H), 4.64 (m, J = 11.6 Hz, 10.79H), 4.62–4.60 (m, 3.65H), 4.58–4.56 (m, 1H), 4.40 (m, 3.08H), 4.16 (dd, J = 4.4, 11.6 Hz, 10.3H), 4.04–3.97 (m, 9.5H), 3.77–3.60 (m, 9.56H), 3.57 (s, 15.92H), 3.37 (s, 13.9H), 2.07 (s, 13.9H), 2.01 (s, 8.76H); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.2, 138.6, 138.3, 128.9, 128.4, 128.1, 127.9, 127.7, 98.0, 94.7, 82.1, 79.9, 75.7, 74.8, 73.3, 69.9, 67.0, 66.9, 65.1, 62.7, 55.1, 50.8, 20.9, 20.6. HR-MS: m/z calcd for $C_{38}H_{44}O_{11}$: 699.2781, $[M+Na]^+$. Found: 699.2772.

4.11. 4,6-Di-*O*-acetyl-2,3-dideoxy-1-succinimido-α-D-*erythro*-hex-2-enopyranoside (12)

N-Iodosuccinamide (1.2 mmol) and molecular sieves 4 Å were added to a stirred solution of **1** (1 mmol) in CH_2Cl_2, stirred for 25 min at 0 °C, diluted with CH_2Cl_2, washed with aq $Na_2S_2O_3$ (5%) solution, brine, concentrated in vacuo and purified by column chromatography (SiO_2).

Yield: 84%. R_f = 0.5 (35% EtOAc/pet. ether). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.11 (d, J = 10.2 Hz, 1H), 5.78 (d, J = 10.2 Hz, 1H), 5.73 (m, 1H), 5.46 (s, 1H) 4.33 (m, 1H), 4.25–4.15 (m, 2H), 2.15 (s, 3H), 2.08 (s, 3H), 2.77–2.73 (band, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.9, 175.4, 170.2, 129.3, 128.8, 126.7, 125.9, 89.8, 74.7, 70.8, 62.5, 29.5, 28.0, 20.9, 20.8. HR-MS: m/z calcd for $C_{14}H_{17}O_7N$ 334.0903 $[M+Na]^+$. Found: 334.0911.

4.12. Ethyl 6-*O*-benzoyl-4-*tert*-butyl-*O*-carbonate-2,3-dideoxy-1-thio-α-D-*erythro*-hex-2-enopyranoside (13)

Di-*tert*-butyl dicarbonate (1.2 mmol) and *N*,*N*-dimethylaminopyridine (cat.) were added to a solution of ethyl 6-*O*-benzoyl 2,3-dideoxy-1-thio-α-D-erythro-hex-2-enopyranoside (1 mmol) in CH_3CN (5 mL). After stirring at rt for 4 h, the reaction mixture was evaporated in vacuo, and purified by column chromatography (SiO_2).

Yield: 74%. R_f = 0.2 (40% EtOAc/pet. ether). ^{1}H NMR ($CDCl_3$): δ 8.07–8.05 (m, 2H), 7.58–7.54 (m, 1H), 7.45–7.42 (m, 2H), 5.96 (app. d, J = 10.2 Hz, 1H), 5.88 (app. d, J = 10.2 Hz, 1H), 5.57 (app. s, 1H), 5.25 (app. d, J = 7.1 Hz, 1H), 4.54–4.48 (band, 3H), 2.66 (dt, J = 7.2, 14.4 Hz, 2H), 1.47 (s, 9H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 166.3, 152.7, 133.0, 129.8, 129.6, 129.2, 128.3, 126.6, 83.0, 79.9, 68.0, 66.8, 63.7, 27.6, 25.9, 15.1. HR-MS: m/z calcd for $C_{20}H_{26}O_6S$: 417.1348 $[M+Na]^+$. Found: 417.1345.

4.13. 1, 5 Anhydro-6-*O*-benzoyl-3,4-*O*-carbonate-2-deoxy-D-arabino-hex-1-enitol (14)

Yield: 71%. R_f = 0.2 (40% EtOAc/pet. ether). ^{1}H NMR ($CDCl_3$): δ8.10–8.04 (m, 2H), 7.61–7.58 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.78 (d, J = 6 Hz, 1H), 5.21 (dd, J = 4.8, 6 Hz, 1H), 5.10–5.07 (m, 1H), 4.86–4.82 (m, 1H), 4.74 (dd, J = 2.8, 12.4 Hz, 1H), 4.60 (dd, J = 4.8, 12.4 Hz, 1H), 4.08–4.04 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 165.9, 153.5, 150.0, 133.4, 129.7, 128.5, 127.6, 96.9, 72.0, 71.2, 69.0, 64.0, 62.0. HR-MS: m/z calcd for $C_{14}H_{12}O_6$: 299.0532 $[M+Na]^+$. Found: 299.0531.

4.14. 4-Methylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-1-thio-α-D-*erythro*-hex-2-enopyrano-side (15)

A mixture of *tri*-*O*-acetyl glycal (1 mmol), $(NH_4)_6Ce(NO_3)_4$ (10 mol %) in MeCN was stirred at 0 °C for 15 min. A solution of *p*-cresol (5 mmol) in MeCN was added drop-wise to the reaction mixture and stirring was continued for 15 h at room temperature, the reaction mixture extracted with Et_2O, dried, concentrated in vacuo, and purified by column chromatography to afford **15**.

Yield: 76%. R_f = 0.5 (15% EtOAc/pet. ether). $[\alpha]_D$ +0.128 (c 0.67, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.45–7.34 (m, 2H), 7.13–7.01 (m, 2H), 6.05 (d, J = 10.2 Hz, 1H), 5.84 (d, J = 10.2 Hz, 1H), 5.68 (s, 1H), 5.37 (d, J = 9.6 Hz, 1H), 4.51–4.46 (m, 1H), 4.29–4.20 (m, 2H), 2.34 (s, 3H), 2.11–2.01 (band, 6H); ^{13}C NMR ($CDCl_3$) δ 170.7, 170.3, 138.2, 133.3, 132.4, 130.9, 129.9, 128.6, 127.4, 84.0, 74.7, 67.1, 65.1, 63.2, 20.9, 20.8. HR-MS: m/z calcd for $C_{17}H_{20}O_5S$: 359.0929 $[M+Na]^+$. Found 359.0933.

4.15. General procedure for the synthesis of 2,3-dideoxy-3-thioethyl-*O*-glycosides

TfOH/TMSOTf (70 mol % in CH_2Cl_2) was added to a stirred solution of 2,3-dideoxy-1-thioglycoside (1 mmol), alcohol/thiol

(1.2 mmol), CH_2Cl_2 (6 mL), and stirred at 0 °C for ~30 min. The reaction mixture was concentrated in vacuo and purified by column chromatography (SiO_2).

4.16. Benzyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-ethylthio-α-D-*arabino*-hexopyranoside (16)

Yield: 78%. R_f = 0.2 (15% EtOAc/pet. ether). $[\alpha]_D$ −0.76 (*c* 0.27, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.39–7.30 (m, 5H), 4.97 (app. d, *J* = 2.4 Hz, 1H), 4.90 (app. t, *J* = 10.2 Hz, 1H), 4.68 (d, *J* = 12 Hz, 1H), 4.55 (d, *J* = 12 Hz, 1H), 4.25 (dd, *J* = 4.8, 12 Hz, 1H), 3.98–3.93 (m, 2H), 3.18–3.11 (m, 1H), 2.58–2.52 (m, 2H), 2.24 (dd, *J* = 4.4, 13.4 Hz, 1H), 2.09 (s, 6H), 1.94 (ddd, *J* = 3.2, 13.4, 13.6 Hz, 1H), 1.25–1.19 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 170.8, 169.7, 137.2, 128.4, 127.9, 127.7, 95.8, 69.6, 69.4, 69.0, 62.9, 41.4, 37.0, 23.9, 20.9, 14.7. HR-MS: *m/z* calcd for $C_{19}H_{26}O_6S$: 405.1348 $[M+Na]^+$. Found: 405.1351.

4.17. Cyclohexyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-ethylthio-α/β-D-*arabino*-hexopyranoside (17)

Yield: 75%. R_f = 0.3 (15% EtOAc/pet. ether). αβ = 1.4:1. ^{1}H NMR ($CDCl_3$): δ 5.03–4.94 (m, 1.85H), 4.89 (app. t, *J* = 10.4 Hz, 1.43H), 4.40–4.18 (m, 3.10H), 4.15–4.11 (m, 0.59H), 4.07–3.97 (m, 3.10H), 3.65–3.50 (m, 3.16H), 3.31–3.29 (m, 0.75H), 3.16–3.09 (m, 1H), 2.72–2.60 (m, 1.53H), 2.59–2.52 (m, 5.16H), 2.25–2.16 (m, 1H), 2.14 (dd, *J* = 3.6, 13.4 Hz, 1.4H), 2.09–2.04 (m, 20.3H), 1.94 (dd, *J* = 3.6, 13.4 Hz, 1H), 1.91–1.88 (m, 4.83H), 1.86–1.67 (m, 3.58H), 1.53 (d, *J* = 8.4 Hz, 2.45H), 1.39–1.18 (m, 16.9H); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.1, 169.8, 97.6, 95.7, 75.6, 71.4, 70.6, 66.2, 41.4, 40.8, 36.6, 33.3, 31.5, 26.4, 24.2, 23.9, 20.9, 14.7. HR-MS: *m/z* calcd for $C_{18}H_{30}O_6S$: 397.1661 $[M+Na]^+$. Found: 397.1666.

4.18. Butyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-ethylthio-α/β-D-*arabino*-hexopyranoside (18)

Yield: 74%. R_f = 0.4 (20% EtOAc/pet. ether). αβ = 1.6:1. ^{1}H NMR ($CDCl_3$): δ 5.02–4.95 (m, 1.18H), 4.90–4.80 (m, 2.1H), 4.79 (dd, *J* = 2.6, 6.8 Hz, 0.91H), 4.30–4.22 (m, 3.46H), 4.16–4.07 (m, 1.28H), 4.06–4.01 (m, 1.96H), 3.93–3.87 (m, 1.06H), 3.84–3.80 (m, 1.40H), 3.66–3.59 (m, 1.28H), 3.55–3.49 (m, 1.12H), 3.479–3.38 (m, 2.48H), 3.14–3.06 (m, 1.05), 2.85–2.49 (band, 5.25H), 2.35–2.24 (band, 0.46H), 2.22–2.15 (dd, *J* = 3.8, 18 Hz, 1.02H), 2.12–2.05 (m, 16.6H), 2.01–1.96 (m, 1H), 1.95–1.90 (m, 1.6H), 1.62–1.52 (m, 5.04H), 1.55 −1.35 (m, 5.25H), 1.33–1.18 (m, 9.7H), 0.97–0.87 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.0, 169.8, 98.1, 96.4, 71.7, 69.7, 69.1, 68.9, 67.2, 63.0, 41.4, 40.1, 37.1, 35.2, 31.6 26.2, 23.8, 20.7, 19.4, 19.1, 14.7, 13.8. HR-MS: *m/z* calcd for $C_{16}H_{28}O_6S$: 371.1504 $[M+Na]^+$. Found: 371.1503.

4.19. Ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-(4-methylphenylthio)-1-thio-α/β-D-*arabino*-hexopyranoside (19)

Yield: 76%. R_f = 0.5 (15% EtOAc/pet. ether). αβ = 3.8:1. ^{1}H NMR ($CDCl_3$): δ 7.42–7.26 (m, 13.4H), 7.14–7.02 (m, 13.4H), 5.50 (d, *J* = 5.6 Hz, 1.86H), 5.03 (app. t, *J* = 8 Hz, 1H) 4.94–4.86 (m, 3.82H), 4.33–4.23 (m, 6.16H), 4.21–3.99 (m, 4.4H), 3.18–3.14 (m, 1.99H), 2.77–2.70 (m, 3.30H), 2.60–2.52 (m, 7.23H), 2.33–2.30 (band, 17.9H), 2.10 (dd, *J* = 3.8, 6 Hz, 5.03H), 2.08–2.06 (band, 17.9H), 2.01 (dd, *J* = 3.8, 6 Hz, 4.89H), 2.03 (s, 5.15H), 1.38–1.30 (m, 0.48H), 1.29–1.18 (m, 17.6H); ^{13}C NMR ($CDCl_3$): δ 170.7, 169.9, 138.0, 137.7, 133.8, 132.5, 130.2, 129.7, 80.5, 78.2, 72.9, 70.3, 69.5, 62.7, 47.7, 45.4, 36.8, 36.3, 25.0, 24.6, 21.0, 20.4, 15.0, 14.8. HR-MS: *m/z* calcd for $C_{19}H_{26}O_5S_2$: 421.1119 $[M+Na]^+$. Found: 421.1115.

4.20. General procedure for the synthesis of 2,3-dideoxy-(1→1)-disaccharide

TfOH/TMSOTf (70 mol % in CH_2Cl_2) was added to a stirred solution of 2,3-dideoxy-1-thioglycoside (1 mmol) in CH_2Cl_2 (6 mL), stirred at 0 °C for 30 min, the reaction mixture concentrated in vacuo, and purified by column chromatography to afford the disaccharide.

4.21. 4,6-Di-*O*-acetyl-2,3-dideoxy-3-ethylthio-α-D-*arabino*-pyranosyl-(1→1)-4,6-di-*O*-acetyl-2,3-dideoxy-3-ethylthio-α-D-*arabino*-pyranose (20)

Yield: 72%. R_f = 0.4 (40% EtOAc/pet. ether). $[\alpha]_D$ 61.73 (*c* 0.18, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.18 (d, *J* = 2.6 Hz, 2H), 4.90 (d, *J* = 10.2 Hz, 2H), 4.23 (dd, *J* = 5.2, 12.4 Hz, 2H), 4.01 (dd, *J* = 2.6, 12.4 Hz, 2H), 3.88–3.84 (m, 2H), 3.12–3.05 (m, 2H), 2.62–2.58 (m, 4H), 2.16 (dd, *J* = 4.4, 13.6 Hz, 2H), 2.12 (s, 6H), 2.08 (s, 6H), 1.98 (dd, *J* = 3.6, 13.6 Hz, 2H), 1.23 (t, *J* = 7.2, Hz 6H); ^{13}C NMR ($CDCl_3$): δ 170.7, 169.6, 91.7, 69.8, 69.4, 62.9, 41.0, 36.4, 23.6, 20.8, 20.7, 14.6. HR-MS: *m/z* calcd for $C_{24}H_{38}O_{11}S_2$ 589.1753 $[M+Na]^+$. Found: 589.1755.

4.22. 4,6-Di-*O*-acetyl-2,3-dideoxy-3-(4-methylphenylthio)-α-D-*arabino*-pyranosyl-(1→1)-4,6-di-*O*-acetyl-2,3-dideoxy-3-(4-methylphenylthio)-α-D-*arabino*-pyranose (21)

Yield: 73%. R_f = 0.5 (35% EtOAc/pet. ether). $[\alpha]_D$ −39.8 (*c* 0.44, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.41–7.26 (m, 4H), 7.15–7.04 (m, 4H), 5.15 (d, *J* = 2.4 Hz, 2H), 4.97 (app. t, *J* = 9.6 Hz, 2H), 4.92 (dd, *J* = 4.0, 9.6 Hz, 2H), 4.31–4.23 (m, 2H), 4.22–4.08 (m, 2H), 4.05–3.76 (m, 2H), 2.33 (s, 6H), 2.12 (dd, *J* = 3.4, 16.4 Hz, 2H), 2.07–2.04 (band, 12H), 1.96 (dd, *J* = 3.4, 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 170.7, 169.9, 137.6, 134.8, 131.7, 129.8, 129.6, 92.5, 75.2, 69.3, 65.4, 62.7, 45.0, 36.6, 20.9, 20.6. HR-MS: *m/z* calcd for $C_{34}H_{42}O_{11}S_2$: 713.2066 $[M+Na]^+$. Found: 713.2064.

4.23. Benzyl 4,6-di-*O*-benzyl-2,3-dideoxy-3-(4-methylphenylthio)-β-D-*ribo*-hexopyrano side (24)

Yield: 62%. R_f = 0.5 (15% EtOAc/pet. ether). $[\alpha]_D$ −63.45 (*c* 0.57, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.36–7.21 (m, 17H), 7.07–7.02 (m, 2H), 5.03 (app. d, *J* = 5.6 Hz, 1H), 4.86 (d, *J* = 12 Hz, 1H), 4.64 (d, *J* = 12 Hz, 1H), 4.58–4.50 (m, 3H), 4.45 (d, *J* = 12 Hz, 1H), 4.13–4.09 (m, 1H), 3.89–3.70 (m, 4H), 2.31 (s, 3H), 2.16–2.11 (m, 1H), 1.90–1.84 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 138.2, 137.7, 137.3, 132.8, 130.7, 129.8, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 97.0, 74.2, 73.6, 73.3, 71.0, 70.1, 69.8, 45.5, 34.2, 21.0. HR-MS: *m/z* calcd for $C_{34}H_{36}O_4S$: 563.2232 $[M+Na]^+$. Found: 563.2231.

4.24. Benzyl 4,6-di-*O*-benzyl-2,3-dideoxy-3-(4-methylphenylthio)-α-D-*arabino*-hexopyrano side (25)

Yield: 32%. R_f = 0.55 (15% EtOAc/pet. ether). $[\alpha]_D$ −82.27 (*c* 0.38, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.45–7.21 (m, 17H), 7.02–7.00 (m, 2H), 4.94 (br s, 1H), 4.81 (d, *J* = 12 Hz, 1H), 4.68–4.42 (m, 4H), 4.31–4.21 (m, 2H), 3.90–3.87 (m, 1H), 3.83–3.72 (m, 2H), 3.67–3.59 (m, 1H), 2.34 (s, 3H), 2.23–2.18 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 138.0, 137.8, 133.0, 129.4, 128.3, 128.2, 128.0, 127.8, 127.5, 127.4, 127.2, 96.1, 74.9, 73.4, 71.6, 69.2, 68.9, 68.5, 46.9, 34.4, 21.0. HR-MS: *m/z* calcd for $C_{34}H_{36}O_4S$: 563.2232 $[M+Na]^+$. Found: 563.2240.

4.25. Benzyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-(4-methylphenyl thio)-α-D-*xylo*-hexopyrano side (26)

Yield: 62%. R_f = 0.57 (15% EtOAc/pet. ether). $[\alpha]_D$ −61.87 (*c* 0.46, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.45–7.43 (m, 1H), 7.40–7.25 (m, 7H),

7.14–7.08 (m, 1H), 5.00 (app. d, J = 2.8 Hz, 1H), 4.90 (app. d, J = 2 Hz, 1H), 4.83 (d, J = 12 Hz, 1H), 4.71 (app. t, J = 6.2 Hz, 1H), 4.62–4.58 (m, 1H), 4.53 (d, J = 12 Hz, 1H), 4.13–4.10 (m, 1H), 3.45–3.42 (m, 1H), 2.44 (ddd, J = 4.2, 12, 15.4 Hz, 1H), 2.32 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.00–1.98 (m, 1H), ^{13}C NMR ($CDCl_3$) δ 170.6, 170.2, 137.5, 137.2, 131.9, 131.3, 129.8, 128.4, 127.9, 127.7, 127.6, 127.5, 95.1, 69.3, 68.9, 66.0, 63.5, 62.7, 42.8, 30.2, 21.0, 20.9, 20.7. HR-MS: m/z calcd for $C_{24}H_{28}O_6S$: 467.1504 $[M+Na]^+$. Found: 467.1504.

4.26. Benzyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-(4-methyl phenylthio)-β-D-*xylo*-hexopyrano side (27)

Yield: 34%. R_f = 0.55 (15% EtOAc/pet. ether). $[\alpha]_D$ −78.31 (c 0.39, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.37–7.32 (m, 7H), 7.14–7.12 (m, 2H), 4.95 (dd, J = 2.8 Hz, 1H), 4.94 (d, J = 12 Hz, 1H), 4.77 (dd, J = 1.2, 2.4 Hz, 1H), 4.62 (d, J = 12 Hz, 1H), 4.43–4.40 (m, 1H), 4.26–4.21 (m, 1H), 4.17–4.13 (m, 1H), 3.65–3.62 (m, 1H), 2.32 (s, 3H), 2.19–2.14 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 1.98–1.92 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.2, 138.0, 137.2, 130.0, 129.3, 128.1, 127.9, 127.6, 97.2, 70.4, 69.9, 67.9, 62.9, 44.9, 31.8, 21.1, 20.9, 20.7. HR-MS: m/z calcd for $C_{24}H_{28}O_6S$: 467.1504 $[M+Na]^+$. Found: 467.1504.

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