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Stereoselective Construction of 2,8-Dioxabicyclo[3.3.1]nonane/nonene Systems from 3-*C*-Branched Glycals

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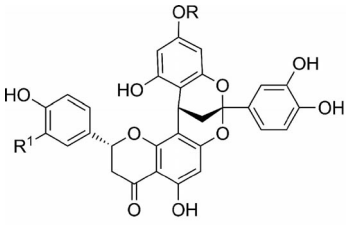
Dedicated to Professor M. Periasamy on the occasion of his 60th birthday

Keywords: Carbohydrates / Chiral pool / Acetals / Fused-ring systems / Diastereoselectivity / Rearrangement

A stereoselective approach for the formation of 2,8-dioxabicyclo[3.3.1]nonane/nonene frameworks through the formation of 3-*C*-branched glycals encompassing the Claisen rearrangement of the carbohydrate-derived allyl-vinyl ethers and TMSOTf-catalyzed acetalization reactions as key steps is revealed. A novel acetalization of 3-*C*-branched glycals with a tentative mechanism is proposed. The expedient protocol is evaluated by synthesizing a number of 2,8-dioxabicyclo[3.3.1]nonane/nonene architectures.

Introduction

Bicyclic acetals/ketals possessing the [3.3.1] skeleton exist ubiquitously in nature as a rigid conformation in a number of bioactive natural products.[1] As part of this group of bicycles, the 2,8-dioxabicyclo[3.3.1]nonane architecture is one of most important skeletons, and is present in biologically active compounds such as diinsininol (**1**), diinsinin (**2**), and procyanidin A1 (**3**) and A2 (**4**).[2] Natural products **1** and **2** have been shown to be potent inhibitors of prostaglandin synthesis as well as platelet activating-factor (PAF) induced exocytosis. Bridged bicyclic ketal **3** has been found to suppress human peripheral blood mononuclear cell (PBMC) proliferation activated with phytohemagglutinin (PHA), possibly by blocking interleukin-2 (IL-2) and interferon-γ (IFN-γ) production.[3] The diastereomer of **3**, compound **4**, has been discovered to be highly active in vitro as an antiviral agent, relative to the ribavirin, against the canine distemper virus (CDV).[4] Interestingly, in all the above compounds the [3.3.1]-bicyclic system is linearly fused with diaromatic rings (Figure 1).



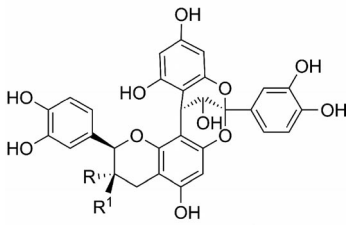


Figure 1. Some bioactive natural products containing a 2,8-dioxabicyclo[3.3.1]nonane framework fused with aromatic rings.

On the other hand, semburin (**5**), isosemburin (**6**), and neosemburin (**7**), possessing the 2,8-dioxabicyclo[3.3.1]-nonane framework, are volatile monoterpenoids that are isolated from the herb *Swertia Japonica* (Gentianaceae; Japanese name, semburi).[5] The extract of this herb is commonly used in Japan as a folk medicine for stomach disorders. (+)-Lineatin (**8**), a pheromone used for mass trapping of *Trypodendron lineatum* Olivier, which is a deleterious pest responsible for the infestation of coniferous forests in Europe and North America,[6] also possesses the 2,8-dioxabicyclo[3.3.1]nonane framework. Monoterpenoids **5**–**8** are fully aliphatic bridged bicyclic/tricyclic acetals possessing intriguing biological properties (Figure 2).

Despite their wide occurrence, synthetic methods for the straightforward construction of the 2,8-dioxabicyclo[3.3.1]-nonane/nonene motifs are scarce.[7] Recently, synthesis of aryl-ring-fused 2,8-dioxabicyclo[3.3.1]nonane systems has been reported by using the Pd^{II}-catalyzed cascade reaction

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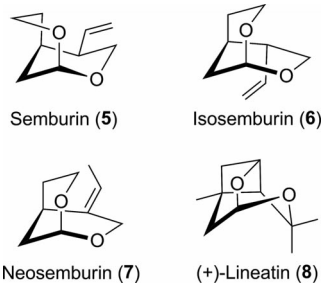


Figure 2. Some aliphatic bioactive natural products possessing a 2,8-dioxabicyclo[3.3.1]nonane framework.

through (2-hydroxyphenyl)boronic acid[8] or AgOTf-catalyzed domino reaction of phenols/naphthols,[9] with a series of 2-hydroxychalcone derivatives. A catalyst-free[10] or iodine-catalyzed[11] Michael condensation of 2-hydroxychalcones with the activated methylene groups followed by bicyclization reaction to provide 2,8-dioxabicyclo[3.3.1]nonane derivatives has also recently been reported. However, all the above methods have been directed to the synthesis of mono- or bi-aryl fused 2,8-dioxabicyclo[3.3.1]nonane systems involving 2-hydroxy chalcone derivatives as one of the common precursors. Very recently, Franzén et al. reported an organocatalytic approach towards the synthesis of N,O- and O,O-acetals in an asymmetric fashion by condensing 5-amino/5-hydroxy α,β-unsaturated aldehydes, replacing the 2-hydroxy chalcone, and 1,3-diketones.[12] Except for this report, to the best of our knowledge, there has been no straightforward methodology for the construction of fully aliphatic 2,8-dioxabicyclo[3.3.1]nonane/nonene skeleton.

Carbohydrates have long been the source of unique chiral raw materials for the synthesis of biologically relevant small molecular libraries.[13] In a continuation of our efforts to develop the use of carbohydrate building blocks for the construction of chiral architectures relevant to bioactive natural products, we previously reported the synthesis of *cis*-fused perhydrofuro[2,3-*b*]furans and perhydro-5-oxofuro-[2,3-*b*]furans from 3-*C*-branched sugar derivatives.[14] In our further investigations in this direction, herein, we report an efficient methodology for the stereoselective formation of the completely aliphatic 2,8-dioxabicyclo[3.3.1]nonane/nonene systems from the 3-*C*-branched glycal derivatives (Figure 3).

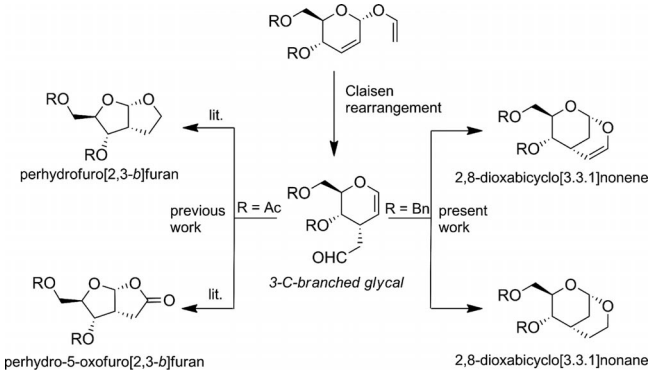
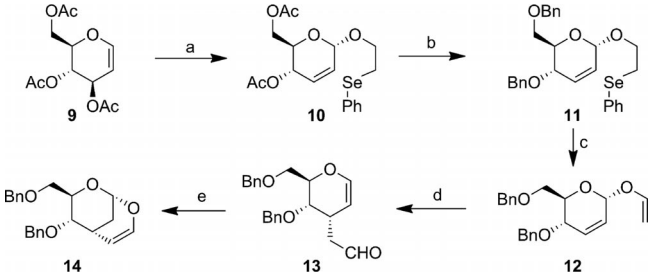


Figure 3. Stereoselective synthesis of bicyclic acetals from 3-*C*-branched glycal derivatives.

Results and Discussion

We planned to synthesize the precursor 3-*C*-branched glycals by the Claisen rearrangement[15] of the sugar derived allyl-vinyl ethers of type **12**, which could be obtained from glycals by following the procedure reported previously from our laboratory.[14a] Thus, hydrolysis of glycoside **10**,[14a] obtained by the Ferrier rearrangement[16] of 3,4,6-tri-*O*-acetyl-D-glucal **9**, followed by benzylation, provided glycoside **11**. Oxidation of **11** with $NaIO_4$ followed by treatment with *N*,*N*-diisopropylamine gave allyl-vinyl ether **12**. The Claisen rearrangement of **12**, upon heating in nitrobenzene and *N*,*N*-dimethylaniline at 160 °C, provided the 3-*C*-branched aldehyde derivative **13** in 80% yield. Serendipitously, exposure of aldehyde **13** to TMSOTf in CH_2Cl_2 at –40 °C provided a single diastereomer in 83% yield. A careful spectroscopic analysis revealed that the product was a 2,8-dioxabicyclo[3.3.1]non-6-ene derivative **14** (Scheme 1). To the best of our knowledge, this is the first observation of the formation of an acetal by the reaction between aldehyde and vinyl ether.

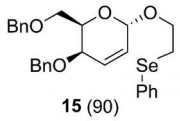
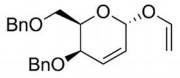
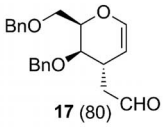
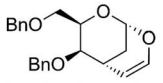
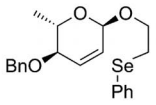
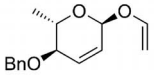
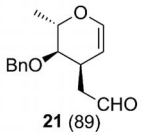
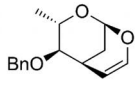
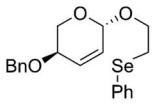
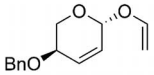
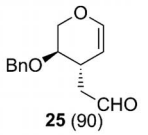
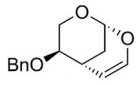
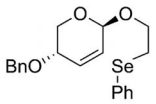
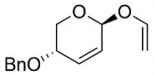
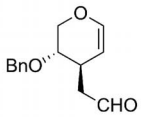
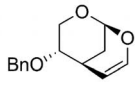
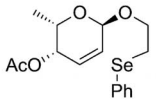
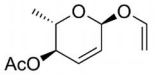
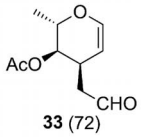
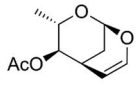
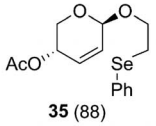
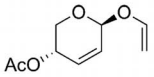
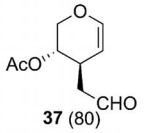
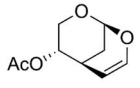


Scheme 1. Synthesis of D-allose-based 2,8-dioxabicyclo[3.3.1]non-6-ene derivative **14**. *Reagents and conditions*: (a) $PhSeCH_2CH_2OH$, $BF_3{\cdot}OEt_2$, benzene, 0–25 °C, 5 min, 88%; (b) i. K_2CO_3, MeOH; ii. NaH, BnBr, THF, 95% (two steps); (c) i. $NaIO_4$, $NaHCO_3$, $MeOH/H_2O$ (6:1), 1 h; ii. DIPA, benzene, reflux, 30 min, 75% (two steps); (d) *N*,*N*-dimethylaniline, nitrobenzene, 160 °C, 3 h, 80%; (e) TMSOTf (15 mol-%), CH_2Cl_2, 4 Å MS, –40 °C, 83%. DIPA = *N*,*N*-diisopropylamine. TMSOTf = trimethylsilyl trifluoromethanesulfonate.

Encouraged with the above results, a series of 2-phenylselenenylethyl glycosides, **15**, **19**, **23**, **27**, **31**, and **35**, were prepared[17] from the corresponding protected glycals and subjected to oxidative elimination to give sugar-derived allyl vinyl ethers **16**, **20**, **24**, **28**, **32** and **36**, respectively, in good yield. Claisen rearrangement of these vinyl glycosides by heating in nitrobenzene and *N*,*N*-dimethylaniline at 160 °C resulted the formation of 3-*C*-branched glycal derivatives **17**, **21**, **25**, **29**, **33**,[14a] and **37**.[14a] Subjecting these 3-*C*-branched glycals to TMSOTf-mediated cyclization reaction provided 2,8-dioxabicyclo[3.3.1]non-6-ene frameworks **18**, **22**, **26**, **30**, **34** and **38**. In all the above cases, the reactions proceeded efficiently and provided the products as single diastereomers (Table 1).

A plausible mechanism for TMSOTf-catalyzed formation of bridged bicyclic acetal **14** from 3-*C*-branched glycal **13** is proposed, based on the observed products. As shown in Scheme 2, activation of aldehyde by TMSOTf would give the silyl-vinyl ether **39** and triflic acid. Addition of triflic

Table 1. Stereoselective synthesis of carbohydrate-derived 2,8-dioxabicyclo[3.3.1]non-6-ene systems.

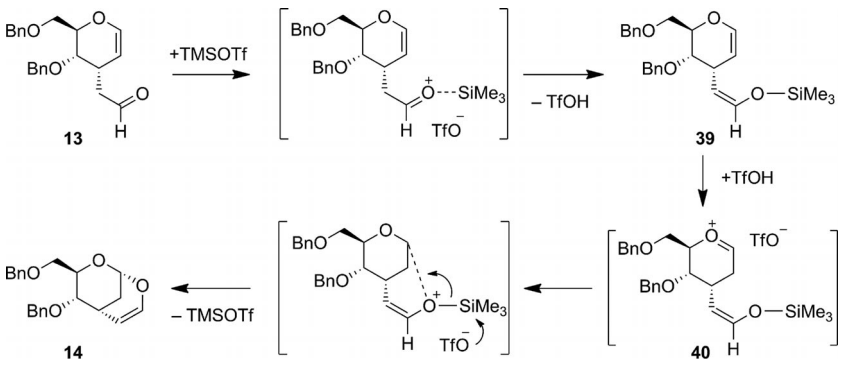
Entry	2-Phenyl selenoethyl glycoside	Vinyl ether (%)[a]	3-*C*-Branched glycal (%)[a]	Dioxabicyclo[3.3.1] non-6-ene (%)[a]
1	 **15** (90)	 **16** (78)	 **17** (80)	 **18** (85)
2	 **19** (94)	 **20** (84)	 **21** (89)	 **22** (83)
3	 **23** (90)	 **24** (79)	 **25** (90)	 **26** (81)
4	 **27** (95)	 **28** (80)	 **29** (88)	 **30** (80)
5	 **31** (87)	 **32** (74)	 **33** (72)	 **34** (72)
6	 **35** (88)	 **36** (73)	 **37** (80)	 **38** (84)

[a] Isolated yield after column chromatography.

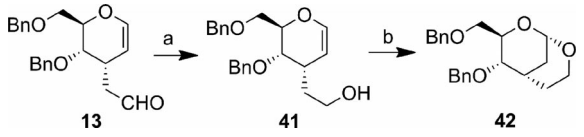
acid on glucal would lead to the formation of intermediate oxonium ion **40**. Trapping of this intermediate in an intramolecular fashion by the silyl-vinyl ether would result the formation of 2,8-dioxabicyclo[3.3.1]non-6-ene derivative **14** along with the regeneration of catalyst, TMSOTf (Scheme 2).

After successful evaluation of the generality of the methodology, we envisaged that an intramolecular hydroetherification reaction would be enable access to the 2,8-dioxabicyclo[3.3.1]nonane framework. Thus, aldehyde **13** was reduced to alcohol **41** and subjected to catalytic TMSOTf-mediated acetalization reaction. As expected, the reaction proceeded very smoothly and provided the fully saturated 2,8-dioxabicyclo[3.3.1]nonane derivative **42** as a single diastereomer in excellent yield (Scheme 3).

The generality of this reaction was also investigated by applying it to a series of 3-*C* branched alcohols **43**, **45**, **47** and **50**,[14a] which were obtained by reduction of aldehydes



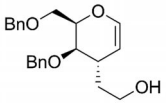
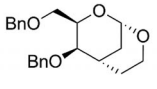
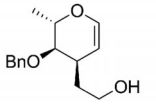
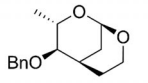
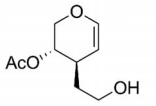
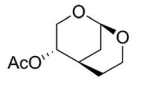
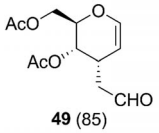
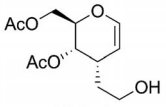
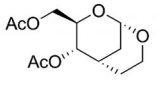
Scheme 2. Proposed mechanism for formation of 2,8-dioxabicyclo[3.3.1]non-6-ene derivative **14**.



Scheme 3. Synthesis of D-allose-based 2,8-dioxabicyclo[3.3.1]-nonane derivative **42**. *Reagents and conditions:* (a) $NaBH_4$, EtOH, 0 °C, 30 min, 96%; (b) TMSOTf (15 mol-%), CH_2Cl_2, 4 Å MS, 0 °C, 92%.

17, **33**, **37** and **49**, respectively. Reaction of these alcohols with catalytic TMSOTf in CH_2Cl_2 provided bridged bicyclic acetals **44**, **46**, **48** and **51** in good yield (Table 2).

Table 2. Stereoselective synthesis of carbohydrate derived 2,8-dioxabicyclo[3.3.1]nonane systems.

Entry	3-*C*-Branched aldehyde	3-*C*-Branched alcohol (%)[a]	Dioxabicyclo[3.3.1] nonane (%)[a]
1	**17**	 **43** (98)	 **44** (85)
2	**33**	 **45** (95)	 **46** (88)
3	**37**	 **47** (92)	 **48** (78)
4	 **49** (85)	 **50** (95)	 **51** (90)

[a] Isolated yield after column chromatography.

Conclusions

A stereoselective methodology for the formation of the 2,8-dioxabicyclo[3.3.1]nonane/nonene architecture starting from 3-*C*-branched carbohydrates has been revealed. The developed methodology has been successfully applied for the synthesis of a number of bicyclic systems possessing the above skeleton. The methodology was shown to be effective with benzyl and acetyl protective groups, which are the two most important protecting groups in carbohydrate chemistry. Application of the developed methodology for the stereoselective synthesis of bioactive natural products possessing this skeleton is in progress.

Experimental Section

General Methods: All the chemicals were purchased from Carbosynth, Spectrochem, Merck and Sigma–Aldrich Chemical Companies and were of the highest purity. The reactions were carried out under an inert atmosphere and monitored by thin-layer chromatography (TLC) using silica gel GF_{254} plates with detection by charring with 5% (v/v) H_2SO_4 in methanol or by phosphomolybdic acid (PMA) stain or by ultra violet (UV) detection unless otherwise mentioned. Benzene, *N*,*N*-diisopropylamine, CH_2Cl_2, THF, methanol and TMSOTf used in the reactions were distilled from dehydrating agents prior to use. Silica gel (100–200 mesh) was used for column chromatography. ^1H, ^{13}C, DEPT, COSY, NOESY spectra were recorded with Bruker 400 MHz or 500 MHz spectrometers in $CDCl_3$. ^1H NMR chemical shifts are reported in ppm (δ) with TMS as internal standard (δ = 0.00 ppm); ^{13}C NMR data are reported in chemical shifts with solvent reference ($CDCl_3$, δ = 77.00 ppm). IR spectra were recorded with a JASCO FT/IR-5300 spectrometer. High-resolution mass spectra were recorded with a Bruker maXis ESI-TOF spectrometer.

2-Phenylselenenylethyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10):[14a] To a solution of 3,4,6-tri-*O*-acetyl-D-glucal (0.75 g, 2.76 mmol) in anhydrous benzene (10 mL) was added 2-(phenylselenenyl)ethanol (0.55 g, 2.76 mol) and the mixture was cooled to 0–5 °C. $BF_3{\cdot}Et_2O$ (0.1 mL, 0.8 mmol) was added dropwise and the solution was stirred until complete disappearance of the starting material (30 min). Et_3N (0.4 mL) was added at 0–5 °C to quench the reaction. The solvent was completely evaporated under reduced pressure to obtain the crude compound **10**. Purification by column chromatography over silica gel (hexanes/ethyl acetate) provided **10** (1.05 g, 88%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.23 (m, 5 H), 5.88–5.77 (m, 2 H), 5.30 (dd, *J* = 1.6, 8.0 Hz, 1 H), 5.03 (br. s, 1 H), 4.24 (dd, *J* = 5.6, 12.0 Hz, 1 H), 4.15–4.09 (m, 2 H), 4.01–3.05 (m, 4 H), 2.07 (s, 3 H), 2.04 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 170.2, 132.4, 129.5, 129.1, 129.0, 127.4, 126.9, 94.5, 68.3, 66.9, 65.0, 62.8, 26.7, 20.9, 20.7 ppm.

2-Phenylselenenylethyl 4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (11): To a solution of **10** (2.50 g, 6.02 mmol) in methanol (20 mL) under an inert atmosphere was added K_2CO_3 (8.3 mg, 0.06 mmol) and the solution was stirred until completion of reaction (ca. 3 h). Methanol was completely evaporated under reduced pressure to obtain the crude deacetylated derivative. The crude material thus obtained was dissolved in anhydrous THF under an inert atmosphere and the mixture was cooled to 0 °C. NaH (60%, 0.26 g, 18.06 mmol) was added portionwise with stirring over a period of 20 min. After continuous stirring for a further 1 h at 0 °C, benzyl bromide (3.08 g, 18.06 mmol) and TBAI (cat) were added and the mixture was stirred overnight at 25 °C. The reaction was quenched with slow addition of cold water and extracted with CH_2Cl_2. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain crude benzylated derivative. Purification of the crude product by column chromatography over silica gel (hexanes/ethyl acetate) provided pure **11** (2.91 g, 95%). R_f = 0.65 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3663, 3024, 2865, 1742, 1572, 1457 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 2 H), 7.35–7.24 (m, 13 H), 6.10 (d, *J* = 10.4 Hz, 1 H), 5.77 (td, *J* = 2.4, 10.4 Hz, 1 H), 5.05 (d, *J* = 0.8 Hz, 1 H), 4.66–4.60 (m, 2 H), 4.52 (dd, *J* = 12.4, 18.0 Hz, 2 H), 4.20 (dd, *J* = 1.2, 9.2 Hz, 1 H), 4.03–3.97 (m, 2 H), 3.83–3.66 (m, 3 H), 3.15–3.11 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 138.0, 132.5, 130.8, 129.8, 129.0, 128.3, 128.3, 127.7, 127.6, 126.9, 126.2, 94.8, 73.4, 71.0, 70.2, 69.3, 68.8, 68.0, 27.0 ppm. HRMS (ESI): calcd. for $C_{28}H_{30}O_4SeNa$ $[M + Na]^+$ 533.1207; found 533.1211.

Vinyl 4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (12): To a solution of **11** (10.55 g, 20.70 mmol) in methanol/water

(6:1, 280 mL), sodium periodate (6.64 g, 31.05 mmol) and sodium hydrogen carbonate (1.91 g, 22.77 mmol) were added sequentially, and the mixture was stirred at 25 °C. After complete disappearance of the starting material (1 h), the suspension was filtered through a Celite 545 plug and concentrated under reduced pressure. The crude material thus obtained was taken into ethyl acetate and washed with water and the organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The obtained crude selenoxide was dissolved in anhydrous benzene (100 mL), *N*,*N*-diisopropylamine (14.76 mL, 96.95 mmol) was added and the mixture was heated to reflux for 30 min. After completion of the reaction, the solvent was evaporated and purified over silica gel (hexanes/ethyl acetate) to obtain pure **12** (5.47 g, 75% after two steps). R_f = 0.65 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3035, 2915, 2860, 1638, 1452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 10 H), 6.55 (dd, *J* = 6.4, 14.0 Hz, 1 H), 6.19 (d, *J* = 10.4 Hz, 1 H), 5.84 (td, *J* = 2.0, 10.6 Hz, 1 H), 5.36 (br. s, 1 H), 4.69–4.47 (m, 5 H), 4.28 (dd, *J* = 1.2, 9.2 Hz, 1 H), 4.21 (dd, *J* = 1.2, 6.4 Hz, 1 H), 3.80–3.69 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 138.1, 137.9, 131.9, 128.4, 128.3, 127.9, 127.8, 127.8, 127.6, 125.1, 93.9, 91.7, 73.3, 71.2, 69.8, 68.4 ppm. HRMS (ESI): calcd. for $C_{22}H_{24}O_4Na$ $[M + Na]^+$ 375.1573; found 375.1567.

2-[(2*R*,3*S*,4*S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2*H*-pyran-4-yl]acetaldehyde (13): To vinyl glycoside **12** (5.0 g, 14.18 mmol) in nitrobenzene (40 mL) was added *N*,*N*-dimethylaniline (0.4 mL) and the mixture was heated at 150–170 °C until the disappearance of the starting material was observed (5–6 h). After cooling the reaction mixture to 25 °C, the mixture was directly loaded onto a silica-gel column and the product was purified by column chromatography over silica gel (hexanes/ethyl acetate) to obtain 3-*C*-branched glucal derivative **13** (4.0 g, 80%). R_f = 0.45 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3063, 2865, 1715, 1643, 1651, 1457 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.74 (t, *J* = 1.2 Hz, 1 H), 7.35–7.22 (m, 10 H), 6.35 (dd, *J* = 1.2, 6.0 Hz, 1 H), 4.69 (dd, *J* = 4.8, 6.0 Hz, 1 H), 4.60 (d, *J* = 4.4 Hz, 2 H), 4.51 (d, *J* = 10.8 Hz, 2 H), 3.99–3.95 (m, 1 H), 3.88–3.85 (m, 1 H), 3.75–3.74 (m, 2 H), 3.11–3.08 (m, 1 H), 2.79 (ddd, *J* = 1.6, 7.2, 17.6 Hz, 1 H), 2.40 (ddd, *J* = 1.2, 6.8, 17.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2, 143.1, 137.9, 137.5, 128.4, 128.4, 128.1, 127.8, 101.39, 73.67, 73.01, 72.5, 72.1, 69.0, 45.8, 28.9 ppm. HRMS (ESI): calcd. for $C_{22}H_{24}O_4Na$ $[M + Na]^+$ 375.1573; found 375.1574.

(1*S*,3*R*,4*S*,5*R*)-4-(Benzyloxy)-3-(benzyloxymethyl)-2,8-dioxabicyclo[3.3.1]non-6-ene (14): To a solution of 3-*C*-branched glycal **13** (0.10 g, 0.28 mmol) in anhydrous CH_2Cl_2 (10 mL) under an inert atmosphere was added powdered 4 Å molecular sieves and the mixture was cooled to –40 °C. Freshly distilled TMSOTf (15 mol-%) was added and the mixture was stirred until completion of the reaction (1 h). Upon complete disappearance of the starting material, the reaction was quenched with Et_3N at –40 °C and brought to 25 °C, filtered, and concentrated under reduced pressure. The crude material thus obtained was purified by column chromatography over silica gel (hexanes/ethyl acetate) to obtain compound **14** (83 mg, 83%). R_f = 0.55 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3063, 2926, 2854, 1649, 1463 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.25 (m, 10 H), 6.66 (d, *J* = 6.0 Hz, 1 H), 5.39 (d, *J* = 1.6 Hz, 1 H), 4.99 (dt, *J* = 1.2, 7.6 Hz, 1 H), 4.67 (d, *J* = 12.4 Hz, 1 H), 4.62 (d, *J* = 11.6 Hz, 1 H), 4.54 (d, *J* = 12.4 Hz, 1 H), 4.44 (d, *J* = 11.6 Hz, 1 H), 3.91 (td, *J* = 2.8, 9.6 Hz, 1 H), 3.74–3.70 (m, 3 H), 2.76–2.74 (m, 1 H), 1.96 (ddd, *J* = 2.0, 4.0. 12.8 Hz, 1 H), 1.89 (ddd, *J* = 2.0, 4.0, 12.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 138.2, 138.1, 128.4, 128.3, 127.8, 127.7, 127.5, 101.1, 91.9, 75.4, 73.4, 72.4, 70.9, 69.0, 28.2, 25.8 ppm. HRMS (ESI): calcd. for $C_{22}H_{24}O_4Na$ $[M + Na]^+$ 375.1573; found 375.1571.

2-Phenylselenenylethyl 4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (15): Synthesized from 2-phenylselenenylethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside[14a] by following the procedure described for **11**, yield 90%. IR (neat): $\tilde{\nu}_{max}$ = 3063, 2915, 2865, 1572, 1479, 1457 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 2 H), 7.35–7.23 (m, 13 H), 6.15 (dd, *J* = 5.2, 10.0 Hz, 1 H), 5.98 (dd, *J* = 3.2, 10.0 Hz, 1 H), 5.10 (d, *J* = 2.8 Hz, 1 H), 4.65 (dd, *J* = 8.0, 12.0 Hz, 2 H), 4.57 (dd, *J* = 1.6, 11.6 Hz, 2 H), 4.31 (dt, *J* = 2.8, 6.4 Hz, 1 H), 4.05–3.99 (m, 1 H), 3.83–3.78 (m, 2 H), 3.76–3.71 (m, 2 H), 3.19–3.09 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 138.2, 132.5, 129.8, 129.3, 129.1, 128.4, 128.3, 127.8, 127.7, 127.6, 127.2, 126.9, 94.0, 73.4, 71.1, 69.6, 69.4, 67.8, 67.2, 27.0 ppm. HRMS (ESI): calcd. for $C_{28}H_{30}O_4SeNa$ $[M + Na]^+$ 533.1207; found 533.1209.

Vinyl 4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (16): Synthesized from **15** by following the procedure described for **12**, yield 78%. R_f = 0.40 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3029, 2914, 2859, 1643, 1456 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.28 (m, 10 H), 6.56 (dd, *J* = 6.8, 14.0 Hz, 1 H), 6.23 (dd, *J* = 5.2, 10.0 Hz, 1 H), 6.04 (dd, *J* = 2.8, 10.0 Hz, 1 H), 5.40 (d, *J* = 2.4 Hz, 1 H), 4.66–4.55 (m, 5 H), 4.31 (dt, *J* = 2.4, 6.4 Hz, 1 H), 4.22 (dd, *J* = 1.2, 6.4 Hz, 1 H), 3.88 (dd, *J* = 6.8, 10.0 Hz, 1 H), 3.79–3.74 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 138.2, 138.1, 128.3, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 93.3, 91.7, 73.3, 71.3, 69.9, 68.9, 66.8 ppm. HRMS (ESI): calcd. for $C_{22}H_{28}NO_4$ $[M + NH_4]^+$ 370.2018; found 370.2027.

2-[(2*R*,3*R*,4*S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2*H*-pyran-4-yl]acetaldehyde (17): Synthesized from **16** by following the procedure described for **13**, yield 80%. R_f = 0.50 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3441, 3063, 2915, 2865, 1715, 1643, 1452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.71 (t, *J* = 1.6 Hz, 1 H), 7.37–7.28 (m, 10 H), 6.42 (dd, *J* = 1.6, 6.0 Hz, 1 H), 4.69–4.61 (m, 2 H), 4.57 (dd, *J* = 9.2, 12.0 Hz, 2 H), 4.45 (d, *J* = 12.0 Hz, 1 H), 4.06–4.02 (m, 1 H), 3.75 (dd, *J* = 7.2, 10.0 Hz, 1 H), 3.56 (dd, *J* = 4.4, 10.0 Hz, 1 H), 3.46–3.44 (m, 1 H), 2.83–2.78 (m, 1 H), 2.47 (dt, *J* = 0.8, 6.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5, 143.1, 137.8, 137.7, 128.4, 128.3, 127.9, 127.7, 101.4, 74.0, 73.5, 72.8, 71.3, 68.5, 48.8, 28.8 ppm. HRMS (ESI): calcd. for $C_{22}H_{28}NO_4$ $[M + NH_4]^+$ 370.2018; found 370.2039.

(1*S*,3*R*,4*R*,5*R*)-4-(Benzyloxy)-3-(benzyloxymethyl)-2,8-dioxabicyclo[3.3.1]non-6-ene (18): Synthesized from **17** by following the procedure described for **14**, yield 85%. R_f = 0.80 (EtOAc/hexanes, 30%). IR (neat): $\tilde{\nu}_{max}$ = 3040, 2920, 2849, 1632, 1452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.29 (m, 10 H), 6.68 (d, *J* = 6.0 Hz, 1 H), 5.45 (s, 1 H), 4.96–4.92 (m, 1 H), 4.67 (d, *J* = 12.0 Hz, 1 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 4.51 (t, *J* = 11.6 Hz, 2 H), 4.25 (dt, *J* = 2.0, 6.0 Hz, 1 H), 3.64 (d, *J* = 6.4 Hz, 2 H), 3.42 (br. s, 1 H), 2.67–2.66 (m, 1 H), 2.44 (dd, *J* = 2.0, 12.8 Hz, 1 H), 1.54 (d, *J* = 12.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 138.1, 138.0, 128.2, 127.7, 127.5, 101.9, 93.1, 74.1, 73.4, 71.4, 70.2, 70.0, 25.4, 23.6 ppm. HRMS (ESI): calcd. for $C_{22}H_{28}NO_4$ $[M + NH_4]^+$ 370.2018; found 370.2037.

2-Phenylselenenylethyl 4-*O*-Benzyl-2,3-dideoxy-β-L-*rhamno*-2-enopyranoside (19): Synthesized from 2-phenylselenenylethyl 4-*O*-acetyl-2,3-dideoxy-β-L-rhamno-2-enopyranoside[14a] by following the procedure described for **11**, yield 94%. R_f = 0.50 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3068, 2975, 2926, 2871, 1578, 1484, 1457 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.33 (m, 2 H), 7.32–7.24 (m, 8 H), 6.09 (d, *J* = 10.4 Hz, 1 H), 5.76 (td, *J* = 2.4, 10.4 Hz, 1 H), 4.95 (br. s, 1 H), 4.68 (d, *J* = 11.6 Hz, 1 H), 4.55 (d, *J* = 11.6 Hz, 1 H), 4.00–3.90 (m, 2 H), 3.79–3.71 (m, 2 H), 3.12 (t,

J = 7.2 Hz, 2 H), 1.28 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 132.5, 130.8, 129.7, 129.0, 128.3, 127.7, 126.9, 126.4, 94.5, 76.2, 70.7, 67.7, 65.7, 26.9, 18.1 ppm.

Vinyl 4-*O*-Benzyl-2,3-dideoxy-β-L-*rhamno*-2-enopyranoside (20): Synthesized from **19** by following the procedure described for **12**, yield 84%. R_f = 0.60 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3033, 2975, 2898, 2860, 1638, 1457 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.30 (m, 5 H), 6.51 (dd, J = 6.4, 14.0 Hz, 1 H), 6.16 (d, J = 10.4 Hz, 1 H), 5.82–5.79 (m, 1 H), 5.24 (s, 1 H), 4.70–4.52 (m, 3 H), 4.18 (dd, J = 1.2, 6.4 Hz, 1 H), 3.96–3.89 (m, 1 H), 3.74 (dd, J = 1.6, 9.2 Hz, 1 H), 1.31 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 137.9, 131.8, 128.4, 127.8, 125.3, 93.7, 91.5, 75.9, 70.9, 66.4, 18.1 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}O_3Na$ [M + Na]$^+$ 269.1154; found 269.1155.

2-[(2*S*,3*R*,4*R*)-3-(Benzyloxy)-2-methyl-3,4-dihydro-2*H*-pyran-4-yl]-acetaldehyde (21): Synthesized from **20** by following the procedure described for **13**, yield 89%. R_f = 0.40 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3413, 2975, 2871, 1720, 1457 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, J = 1.2 Hz, 1 H), 7.37–7.30 (m, 5 H), 6.29 (dd, J = 1.2, 6.0 Hz, 1 H), 4.66 (dd, J = 4.4, 5.6 Hz, 1 H), 4.56 (q, J = 11.6, 20.0 Hz, 2 H), 3.99–3.92 (m, 1 H), 3.49 (dd, J = 5.6, 8.0 Hz, 1 H), 3.13–3.06 (m, 1 H), 2.80 (ddd, J = 1.2, 6.8, 17.2 Hz, 1 H), 2.41 (ddd, J = 1.2, 6.8, 17.6 Hz, 1 H), 1.32 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 143.0, 137.6, 128.4, 128.1, 127.9, 101.3, 72.0, 69.8, 45.7, 28.6, 17.6 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}O_3Na$ [M + Na]$^+$ 269.1154; found 269.1157.

(1*R*,3*S*,4*R*,5*S*)-4-(Benzyloxy)-3-methyl-2,8-dioxabicyclo[3.3.1]non-6-ene (22): Synthesized from **21** by following the procedure described for **14**, yield 83%. R_f = 0.50 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3073, 2964, 2931, 2859, 1643, 1462 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 5 H), 6.64 (d, J = 6.0 Hz, 1 H), 5.29 (d, J = 1.6 Hz, 1 H), 4.98 (t, J = 6.4 Hz, 1 H), 4.69 (d, J = 11.6 Hz, 1 H), 4.53 (d, J = 11.6 Hz, 1 H), 3.89–3.82 (m, 1 H), 3.24 (dd, J = 3.6, 9.2 Hz, 1 H), 2.73–2.71 (m, 1 H), 1.87 (t, J = 0.8 Hz, 2 H), 1.28 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 138.1, 128.4, 127.7, 101.2, 91.8, 81.6, 70.8, 68.6, 28.6, 25.8, 18.2 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}O_3Na$ [M + Na]$^+$ 269.1154; found 269.1154.

2-Phenylselenenylethyl 4-*O*-Benzyl-2,3-dideoxy-α-L-*arabino*-2-enopyranoside (23): Synthesized from 2-phenylselenenylethyl 4-*O*-acetyl-2,3-dideoxy-α-L-arabino-2-enopyranoside[14a] by following the procedure described for **11**, yield 90%. R_f = 0.45 (EtOAc/hexanes, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.24 (m, 10 H), 6.13 (dd, J = 4.8, 10.0 Hz, 1 H), 5.97–5.93 (m, 1 H), 5.03 (t, J = 2.8 Hz, 1 H), 4.65 (dd, J = 4.0, 12.0 Hz, 1 H), 4.60 (dd, J = 4.0, 11.6 Hz, 1 H), 4.09–4.05 (m, 1 H), 4.03–3.92 (m, 2 H), 3.81–3.74 (m, 1 H), 3.77–3.69 (m, 1 H), 3.13–3.08 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 132.6, 129.3, 129.1, 128.4, 127.7, 127.1, 127.0, 93.5, 70.4, 67.4, 67.2, 61.5, 27.1 ppm.

Vinyl 4-*O*-Benzyl-2,3-dideoxy-α-L-*arabino*-2-enopyranoside (24): Synthesized from **23** by following the procedure described for **12**, yield 79%. R_f = 0.55 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3030, 2915, 1860, 1693, 1457 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.34 (m, 5 H), 6.52 (dd, J = 6.4, 14.0 Hz, 1 H), 6.21–6.16 (m, 1 H), 6.03 (ddd, J = 0.8, 3.2, 10.0 Hz, 1 H), 5.34 (dd, J = 0.4, 2.8 Hz, 1 H), 4.63 (s, 1 H), 4.60 (s, 1 H), 4.58 (dd, J = 1.6, 14.0 Hz, 1 H), 4.21 (dd, J = 0.4, 6.4 Hz, 1 H), 4.03 (d, J = 2.8 Hz, 1 H), 4.02 (t, J = 1.6 Hz, 1 H), 3.73–3.71 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 138.0, 128.5, 128.1, 127.8, 92.6, 91.6, 70.5, 66.9, 61.9 ppm. HRMS (ESI): calcd. for $C_{14}H_{16}O_3Na$ [M + Na]$^+$ 255.0997; found 255.1473.

2-[(3*R*,4*S*)-3-(Benzyloxy)-3,4-dihydro-2*H*-pyran-4-yl]acetaldehyde (25): Synthesized from **24** by following the procedure described for **13**, yield 90%. R_f = 0.50 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3435, 2926, 2876, 1720, 1649, 1452 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (t, J = 1.6 Hz, 1 H), 7.36–7.31 (m, 5 H), 6.36 (dd, J = 2.0 Hz, 1 H), 4.65–4.53 (m, 3 H), 4.10 (dd, J = 3.2 Hz, 1 H), 3.75 (dd, J = 8.4, 10.8 Hz, 1 H), 3.44–3.40 (m, 1 H), 2.87–2.80 (m, 1 H), 2.55 (ddd, J = 2.8, 7.2, 16.4 Hz, 1 H), 2.43 (ddd, J = 1.6, 6.8, 16.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 143.8, 137.6, 128.4, 127.9, 101.4, 74.5, 71.6, 65.5, 47.9, 32.6 ppm. HRMS (ESI): calcd. for $C_{14}H_{16}O_3Na$ [M + Na]$^+$ 255.0997; found 255.1497.

(1*R*,4*R*,5*R*)-4-(Benzyloxy)-2,8-dioxabicyclo[3.3.1]non-6-ene (26): Synthesized from **25** by following the procedure described for **14**, yield 81%. R_f = 0.60 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3068, 2964, 2931, 2876, 1643, 1452 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.27 (m, 5 H), 6.67 (d, J = 6.0 Hz, 1 H), 5.40 (s, 1 H), 4.98 (dt, J = 1.6, 6.8 Hz, 1 H), 4.65 (dd, J = 12.4, 16.4 Hz, 2 H), 3.95 (dd, J = 2.0, 12.4 Hz, 1 H), 3.86 (d, J = 12.8 Hz, 1 H), 3.34 (d, J = 0.8 Hz, 1 H), 2.63–2.62 (m, 1 H), 2.51–2.46 (m, 1 H), 1.54–1.50 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.8, 138.3, 128.4, 127.6, 127.5, 102.4, 93.0, 74.1, 70.7, 62.1, 26.1, 24.0 ppm. HRMS (ESI): calcd. for $C_{14}H_{16}O_3Na$ [M + Na]$^+$ 255.0997; found 255.0999.

2-Phenylselenenylethyl 4-*O*-Benzyl-2,3-dideoxy-α-D-*arabino*-2-enopyranoside (27): Synthesized from 2-phenylselenenylethyl 4-*O*-acetyl-2,3-dideoxy-α-D-*arabino*-2-enopyranoside[14a] by following the procedure described for **11**, yield 95%. R_f = 0.40 (EtOAc/hexanes, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.24 (m, 10 H), 6.13 (dd, J = 4.8, 10.0 Hz, 1 H), 5.97–5.93 (m, 1 H), 5.03 (t, J = 2.8 Hz, 1 H), 4.65 (dd, J = 4.0, 12.0 Hz, 1 H), 4.60 (dd, J = 4.0, 11.6 Hz, 1 H), 4.09–4.05 (m, 1 H), 4.03–3.92 (m, 2 H), 3.81–3.74 (m, 1 H), 3.77–3.69 (m, 1 H), 3.13–3.08 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 132.6, 129.3, 129.1, 128.4, 127.7, 127.1, 127.0, 93.5, 70.4, 67.4, 67.2, 61.5, 27.1 ppm.

Vinyl 4-*O*-Benzyl-2,3-dideoxy-α-D-*arabino*-2-enopyranoside (28): Synthesized from **27** by following the procedure described for **12**, yield 80%. R_f = 0.55 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 3030, 2915, 1860, 1693, 1457 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.34 (m, 5 H), 6.52 (dd, J = 6.4, 14.0 Hz, 1 H), 6.21–6.16 (m, 1 H), 6.03 (ddd, J = 0.8, 3.2, 10.0 Hz, 1 H), 5.34 (dd, J = 0.4, 2.8 Hz, 1 H), 4.63 (s, 1 H), 4.60 (s, 1 H), 4.58 (dd, J = 1.6, 14.0 Hz, 1 H), 4.21 (dd, J = 0.4, 6.4 Hz, 1 H), 4.03 (d, J = 2.8 Hz, 1 H), 4.02 (t, J = 1.6 Hz, 1 H), 3.73–3.71 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 138.0, 128.5, 128.1, 127.8, 92.6, 91.6, 70.5, 66.9, 61.9 ppm. HRMS (ESI): calcd. for $C_{14}H_{16}O_3Na$ [M + Na]$^+$ 255.0997; found 255.1473.

2-[(3*S*,4*R*)-3-(Benzyloxy)-3,4-dihydro-2*H*-pyran-4-yl]acetaldehyde (29): Synthesized from **28** by following the procedure described for **13**, yield 88%. R_f = 0.50 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3435, 2926, 2876, 1720, 1649, 1452 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (t, J = 1.6 Hz, 1 H), 7.36–7.31 (m, 5 H), 6.36 (dd, J = 2.0 Hz, 1 H), 4.65–4.53 (m, 3 H), 4.10 (dd, J = 3.2 Hz, 1 H), 3.75 (dd, J = 8.4, 10.8 Hz, 1 H), 3.44–3.40 (m, 1 H), 2.87–2.80 (m, 1 H), 2.55 (ddd, J = 2.8, 7.2, 16.4 Hz, 1 H), 2.43 (ddd, J = 1.6, 6.8, 16.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 143.8, 137.6, 128.4, 127.9, 101.4, 74.5, 71.6, 65.5, 47.9, 32.6 ppm. HRMS (ESI): calcd. for $C_{14}H_{16}O_3Li$ [M + Li]$^+$ 239.1259; found 239.1541.

(1*S*,4*S*,5*S*)-4-(Benzyloxy)-2,8-dioxabicyclo[3.3.1]non-6-ene (30): Synthesized from **29** by following the procedure described for **14**, yield 80%. R_f = 0.60 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3068, 2964, 2931, 2876, 1643, 1452 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.27 (m, 5 H), 6.67 (d, J = 6.0 Hz, 1 H), 5.40 (s,

1 H), 4.98 (dt, J = 1.6, 6.8 Hz, 1 H), 4.65 (dd, J = 12.4, 16.4 Hz, 2 H), 3.95 (dd, J = 2.0, 12.4 Hz, 1 H), 3.86 (d, J = 12.8 Hz, 1 H), 3.34 (d, J = 0.8 Hz, 1 H), 2.63–2.62 (m, 1 H), 2.51–2.46 (m, 1 H), 1.54–1.50 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.8, 138.3, 128.4, 127.6, 127.5, 102.4, 93.0, 74.1, 70.7, 62.1, 26.1, 24.0 ppm. HRMS (ESI): calcd. for $C_{14}H_{16}O_3Na$ $[M + Na]^+$ 255.0997; found 255.0999.

2-Phenylselenenylethyl 4-*O*-Acetyl-2,3-dideoxy-α-L-*rhamno*-2-enopyranoside (31):[14a] To a solution of 3,4-di-*O*-acetyl-L-rhamnal (2.0 g, 9.33 mmol) in anhydrous benzene (50 mL) was added 2-(phenylselenenyl)ethanol (1.87 g, 9.33 mmol) and the mixture was cooled to 0–5 °C. $BF_3{\cdot}Et_2O$ (0.23 mL, 1.86 mmol) was added dropwise and the solution was stirred until complete disappearance of the starting material was observed (30 min). Et_3N (1 mL) was added at 0–5 °C to quench the reaction. The solvent was completely evaporated under reduced pressure and purification of the obtained crude product by column chromatography over silica gel (hexanes/ethyl acetate) provided pure **31** (2.90 g, 87%). R_f = 0.70 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3466, 2978, 2934, 1743, 1579, 1477 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.51–7.49 (m, 2 H), 7.24–7.23 (m, 3 H), 5.84 (d, J = 10.4 Hz, 1 H), 5.76 (dd, J = 0.8, 10.4 Hz, 1 H), 5.04 (d, J = 9.2 Hz, 1 H), 4.95 (s, 1 H), 4.00–3.93 (m, 2 H), 3.79–3.73 (m, 1 H), 3.10 (t, J = 6.8 Hz, 2 H), 2.06 (s, 3 H), 1.19 (d, J = 6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 132.5, 129.6, 128.9, 127.4, 126.8, 94.3, 70.6, 67.8, 64.8, 26.9, 20.9, 17.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{20}O_4SeNa$ $[M + Na]^+$ 379.0425; found 379.0425.

Vinyl 4-*O*-Acetyl-2,3-dideoxy-α-L-*rhamno*-2-enopyranoside (32):[14a] Synthesized from **31** by following the procedure described for **12**, yield 74%. R_f = 0.30 (EtOAc/hexanes, 10%). IR (neat): $\tilde{\nu}_{max}$ = 2982, 2934, 1743, 1641 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.47 (dd, J = 6.4, 14.0 Hz, 1 H), 5.92 (d, J = 10.0 Hz, 1 H), 5.83 (td, J = 2.4, 10.4 Hz, 1 H), 5.24 (s, 1 H), 5.06 (dd, J = 1.6, 9.2 Hz, 1 H), 4.54 (dd, J = 1.6, 14.0 Hz, 1 H), 4.17 (dd, J = 1.2, 6.4 Hz, 1 H), 3.97–3.90 (m, 1 H), 2.06 (s, 3 H), 1.20 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 149.1, 130.6, 126.3, 93.4, 91.6, 70.4, 65.4, 20.9, 17.7 ppm. HRMS (ESI): calcd. for $C_{10}H_{14}O_4Na$ $[M + Na]^+$ 221.0790; found 221.0790.

(2*S*,3*R*,4*R*)-2-Methyl-4-(2-oxoethyl)-3,4-dihydro-2*H*-pyran-3-yl Acetate (33):[14a] Synthesized from **32** by following the procedure described for **13**, yield 72%. R_f = 0.40 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3468, 2982, 2939, 1732, 1649 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (t, J = 1.2 Hz, 1 H), 6.29 (dd, J = 2.0, 6.4 Hz, 1 H), 4.93 (t, J = 5.6 Hz, 1 H), 4.57 (dd, J = 3.6, 6.4 Hz, 1 H), 4.06 (t, J = 6.4 Hz, 1 H), 3.10–3.04 (m, 1 H), 2.62 (ddd, J = 1.6, 7.2, 17.6 Hz, 1 H), 2.44 (ddd, J = 1.6, 6.4, 17.6 Hz, 1 H), 2.03 (s, 3 H), 1.25 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 169.9, 142.5, 100.1, 70.9, 69.8, 45.2, 26.9, 20.7, 16.8 ppm. HRMS (ESI): calcd. for $C_{10}H_{14}O_4Na$ $[M + Na]^+$ 221.0790; found 221.0790.

(1*R*,3*S*,4*R*,5*S*)-3-Methyl-2,8-dioxabicyclo[3.3.1]non-6-en-4-yl Acetate (34): Synthesized from **33** by following the procedure described for **14**, yield 72%. R_f = 0.65 (EtOAc/hexanes, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.63 (d, J = 6.0 Hz, 1 H), 5.28 (d, J = 1.2 Hz, 1 H), 4.88 (dt, J = 1.6, 6.4 Hz, 1 H), 4.62 (dd, J = 4.0, 9.6 Hz, 1 H), 3.92–3.85 (m, 1 H), 2.67–2.64 (m, 1 H), 2.04 (s, 3 H), 2.00 (dd, J = 2.0, 12.8 Hz, 1 H), 1.84 (ddd, J = 2.0, 4.4, 12.8 Hz, 1 H), 1.16 (d, J = 6.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 145.6, 100.5, 91.7, 76.0, 67.2, 28.6, 26.6, 21.0, 17.7 ppm. HRMS (ESI): calcd. for $C_{10}H_{14}O_4Na$ $[M + Na]^+$ 221.0790; found 221.0790.

2-Phenylselenenylethyl 4-*O*-Acetyl-2,3-dideoxy-β-D-*arabino*-2-enopyranoside (35):[14a] To a solution of 3,4-di-*O*-acetyl-D-arabinal (2.0 g, 9.99 mmol) in anhydrous benzene (50 mL) was added 2-(phenylselenenyl)ethanol (2.0 g, 9.99 mmol) and the mixture was cooled to 0–5 °C. $BF_3{\cdot}Et_2O$ (0.246 mL, 1.99 mmol) was added dropwise and the solution was stirred until complete disappearance of the starting material was observed (30 min). Et_3N (1 mL) was added to quench the reaction at 0–5 °C. The solvent was completely evaporated under reduced pressure to obtain crude product, which was purified by column chromatography over silica gel (hexanes/ethyl acetate) to give pure **35** (3.0 g, 88%). R_f = 0.50 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3059, 2932, 1732, 1371 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.51–7.49 (m, 2 H), 7.24–7.23 (m, 3 H), 6.07 (dd, J = 5.2, 10 Hz, 1 H), 5.99 (dd, J = 2.8, 10 Hz, 1 H), 5.00 (d, J = 2.4 Hz, 1 H), 4.93 (d, J = 2.8 Hz, 1 H), 4.17 (dd, J = 2.8, 13.2 Hz, 1 H), 4.00–3.94 (m, 1 H), 3.82 (d, J = 12.8 Hz, 1 H), 3.77–3.74 (m, 1 H), 3.10 (t, J = 6.8 Hz, 2 H), 2.06 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 132.5, 130.4, 129.5, 128.9, 126.8, 124.9, 92.9, 67.7, 63.0, 61.1, 26.8, 20.9 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}O_4SeNa$ $[M + Na]^+$ 365.0268; found 365.0268.

Vinyl 4-*O*-Acetyl-2,3-dideoxy-α-D-*arabino*-2-enopyranoside (36):[14a] Synthesized from **35** by following the procedure described for **12**, yield 73%. R_f = 0.70 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3445, 2920, 1726, 1364 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.47 (dd, J = 6.4, 14.0 Hz, 1 H), 6.15 (dd, J = 5.2, 10.0 Hz, 1 H), 6.06 (dd, J = 3.2, 10.4 Hz, 1 H), 5.30 (d, J = 3.2 Hz, 1 H), 4.96 (dd, J = 2.8, 5.2 Hz, 1 H), 4.55 (dd, J = 1.6, 14.0 Hz, 1 H), 4.19 (dd, J = 2.6, 6.8 Hz, 1 H), 4.13 (dd, J = 2.8, 13.2 Hz, 1 H), 3.87 (dd, J = 1.2, 13.2 Hz, 1 H), 2.06 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 149.0, 129.3, 125.7, 92.0, 91.7, 62.7, 61.6, 20.9 ppm. HRMS (ESI): calcd. for $C_9H_{12}O_4Na$ $[M + Na]^+$ 207.0364; found 207.0364.

(3*S*,4*R*)-4-(2-Oxoethyl)-3,4-dihydro-2*H*-pyran-3-yl Acetate (37):[14a] Synthesized from **36** by following the procedure described for **13**, yield 80%. R_f = 0.50 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3430, 2876, 2728, 1736, 1643, 1364, 1250, 1090, 1046, 964, 926 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (s, 1 H), 6.39 (dd, J = 1.6, 6.0 Hz, 1 H), 4.80 (dd, J = 5.6, 8.0 Hz, 1 H), 4.65 (dd, J = 3.6, 6.0 Hz, 1 H), 3.96 (dd, J = 2.8, 11.2 Hz, 1 H), 3.88 (dd, J = 6.64, 11.2 Hz, 1 H), 2.80 (d, J = 2.8 Hz, 1 H), 2.60 (dd, J = 1.2, 6.0 Hz, 1 H), 2.56 (dd, J = 1.2, 6.0 Hz, 1 H), 2.07 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.9, 170.1, 143.7, 100.8, 69.2, 64.0, 48.2, 30.4, 20.8 ppm. HRMS (ESI): calcd. for $C_9H_{12}O_4Na$ $[M + Na]^+$ 207.0634; found 207.0634.

(1*S*,4*S*,5*S*)-2,8-Dioxabicyclo[3.3.1]non-6-en-4-yl Acetate (38): Synthesized from **37** by following the procedure described for **14**, yield 84%. R_f = 0.60 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 2980, 2942, 1731, 1643, 1369 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.65 (d, J = 6.0 Hz, 1 H), 5.37 (br. s, 1 H), 5.00–4.97 (m, 1 H), 4.63 (br. s, 1 H), 4.02 (dd, J = 2.4, 13.2 Hz, 1 H), 3.71 (d, J = 13.2 Hz, 1 H), 2.52 (br. s, 1 H), 2.32 (dd, J = 2.0, 13.2 Hz, 1 H), 2.09 (s, 3 H), 1.54 (d, J = 12.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 147.1, 101.5, 92.5, 69.4, 62.2, 25.8, 24.0, 21.1 ppm. HRMS (ESI): HRMS (ESI): calcd. for $C_9H_{12}O_4Na$ $[M + Na]^+$ 207.0634; found 207.0634.

2-[(2*R*,3*S*,4*S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2*H*-pyran-4-yl]ethanol (41): To a solution of aldehyde **13** (0.93 g, 2.63 mmol) in absolute ethanol (10 mL) at 0–5 °C was added $NaBH_4$ (0.129 g, 3.4 mmol) and the mixture was stirred for 15 min at the same temperature. After complete disappearance of the starting material, the reaction was quenched by slow addition of aq. NH_4Cl solution (2 mL) and filtered through Celite 545. The filtrate

obtained was concentrated under reduced pressure and purified by column chromatography over silica gel (hexanes/ethyl acetate) to obtain alcohol **41** (0.89 g, 96%). R_f = 0.35 (EtOAc/hexanes, 40%). IR (neat): $\tilde{\nu}_{max}$ = 3424, 3024, 2871, 1649, 1501, 1452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.26 (m, 10 H), 6.35 (d, J = 6.0 Hz, 1 H), 4.71–4.55 (m, 5 H), 4.12–4.08 (m, 1 H), 3.87 (dd, J = 5.6, 13.6 Hz, 1 H), 3.77 (d, J = 4.0 Hz, 2 H), 3.73–3.62 (m, 2 H), 2.59–2.53 (m, 1 H), 2.03 (br. s, 1 H), 1.99–1.90 (m, 1 H), 1.57–1.48 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2, 137.9, 137.7, 128.3, 128.2, 127.8, 127.6, 127.5, 101.6, 73.4, 73.0, 72.8, 71.3, 69.2, 60.4, 34.6, 30.1 ppm. HRMS (ESI): calcd. for $C_{22}H_{26}O_4Na$ $[M + Na]^+$ 377.1729; found 377.1733.

(1*S*,3*R*,4*S*,5*S*)-4-(Benzyloxy)-3-(benzyloxymethyl)-2,8-dioxabicyclo[3.3.1]nonane (42): To a solution of 3-*C*-branched alcohol **41** (0.66 g, 1.86 mmol) in anhydrous CH_2Cl_2 (60 mL) under an inert atmosphere, was added powdered 4 Å molecular sieves and the mixture was cooled to 0 °C. Freshly distilled TMSOTf (15 mol-%) was added and the mixture was stirred until completion of the reaction (1 h). After complete disappearance of starting material, the reaction was quenched with slow addition of Et_3N at 0 °C and brought to 25 °C. The reaction mixture was filtered and concentrated under reduced pressure, and the crude material thus obtained was purified over silica gel (hexanes/ethyl acetate) to obtain **42** (0.60 g, 92%). R_f = 0.60 (EtOAc/hexanes, 30%). IR (neat): $\tilde{\nu}_{max}$ = 2926, 2860, 1501, 1457, 1367 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.24 (m, 10 H), 5.28 (s, 1 H), 4.70–4.36 (m, 4 H), 4.19–4.16 (m, 1 H), 4.01–3.96 (m, 1 H), 3.80–3.68 (m, 4 H), 2.55 (br. s, 1 H), 2.25–2.19 (m, 1 H), 2.16 (qd, J = 2.0, 13.5 Hz, 1 H), 1.82–1.70 (m, 1 H), 1.70 (d, J = 13.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 138.1, 128.3, 128.2, 127.7, 127.5, 127.4, 92.3, 74.9, 73.3, 71.2, 70.3, 69.8, 60.4, 28.2, 23.9, 22.2 ppm. HRMS (ESI): calcd. for $C_{22}H_{30}NO_4$ $[M + NH_4]^+$ 372.2175; found 372.2185.

2-[(2*R*,3*R*,4*S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2*H*-pyran-4-yl]ethanol (43): Synthesized from **17** by following the procedure described for **41**, yield 98%. R_f = 0.25 (EtOAc/hexanes, 30%). IR (neat): $\tilde{\nu}_{max}$ = 3441, 3063, 3024, 2931, 2871, 1643, 1452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 10 H), 6.41 (d, J = 6.4 Hz, 1 H), 4.69 (t, J = 4.8 Hz, 1 H), 4.63–4.62 (m, 5 H), 4.10–4.07 (m, 1 H), 3.77 (dd, J = 7.8, 10.0 Hz, 1 H), 3.67 (dt, J = 2.0, 6.0 Hz, 2 H), 3.61 (dd, J = 4.4, 10.0 Hz, 1 H), 3.52 (br. s, 1 H), 2.34–2.33 (m, 1 H), 1.59–1.49 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.3, 137.9, 137.8, 128.5, 128.4, 128.3, 127.9, 127.9, 127.7, 102.6, 74.6, 73.5, 72.8, 71.4, 68.7, 60.1, 38.1, 31.0 ppm. HRMS (ESI): calcd. for $C_{22}H_{30}NO_4$ $[M + NH_4]^+$ 372.2175; found 372.2181.

(1*S*,3*R*,4*R*,5*S*)-4-(Benzyloxy)-3-(benzyloxymethyl)-2,8-dioxabicyclo[3.3.1]nonane (44): Synthesized from **43** by following the procedure described for **42**, yield 85%. R_f = 0.60 (EtOAc/hexanes, 30%). IR (neat): $\tilde{\nu}_{max}$ = 3030, 2926, 2871, 1720, 1463 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.27 (m, 10 H), 5.33 (s, 1 H), 4.66 (d, J = 11.6 Hz, 1 H), 4.62 (d, J = 12.0 Hz, 1 H), 4.52–4.44 (m, 3 H), 3.96–3.90 (m, 1 H), 3.81–3.71 (m, 2 H), 3.67 (dd, J = 6.0, 9.2 Hz, 1 H), 3.33 (br. s, 1 H), 2.45 (br. d, J = 10.0 Hz, 1 H), 2.18 (d, J = 13.6 Hz, 1 H), 2.02–1.94 (m, 1 H), 1.83 (d, J = 13.6 Hz, 1 H), 1.74–1.66 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 138.1, 128.2, 127.7, 127.5, 127.4, 93.5, 73.3, 71.3, 69.8, 66.9, 59.5, 25.4, 23.3, 22.5 ppm. HRMS (ESI): calcd. for $C_{22}H_{30}NO_4$ $[M + NH_4]^+$ 372.2175; found 372.2180.

2-[(2*S*,3*R*,4*R*)-3-(Benzyloxy)-2-methyl-3,4-dihydro-2*H*-pyran-4-yl]-ethanol (45): Synthesized from **33** by following the procedure described for **41**, yield 95%. R_f = 0.20 (EtOAc/hexanes, 20%). IR (neat): $\tilde{\nu}_{max}$ = 3397, 3063, 3030, 2926, 2871, 1649, 1501, 1452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.30 (m, 5 H), 6.28 (dd, J = 1.6, 6.0 Hz, 1 H), 4.67 (dd, J = 4.8, 6.0 Hz, 1 H), 4.64 (dd, J = 11.6, 26.0 Hz, 2 H), 4.08–4.02 (m, 1 H), 3.76–3.70 (m, 1 H), 3.69–3.63 (m, 1 H), 3.47 (dd, J = 5.6, 7.6 Hz, 1 H), 2.61–2.55 (m, 1 H), 2.30 (s, 1 H), 1.97–1.88 (m, 1 H), 1.57–1.49 (m, 1 H), 1.32 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 137.7, 128.3, 127.8, 127.7, 101.5, 77.6, 71.3, 69.6, 60.5, 34.0, 29.8, 17.7 ppm. HRMS (ESI): calcd. for $C_{15}H_{21}O_3$ $[M + H]^+$ 249.1491; found 249.1492.

(1*R*,3*S*,4*R*,5*R*)-4-(Benzyloxy)-3-methyl-2,8-dioxabicyclo[3.3.1]-nonane (46): Synthesized from **45** by following the procedure described for **42**, yield 88%. R_f = 0.60 (EtOAc/hexanes, 30%). IR (neat): $\tilde{\nu}_{max}$ = 3030, 2926, 2865, 1457 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 5 H), 5.17 (br. s, 1 H), 4.63 (d, J = 11.6 Hz, 1 H), 4.46 (d, J = 11.6 Hz, 1 H), 4.17–4.10 (m, 1 H), 3.99–3.93 (m, 1 H), 3.79–3.72 (m, 1 H), 3.24 (dd, J = 4.0, 9.2 Hz, 1 H), 2.51 (br. d, J = 4.0 Hz, 1 H), 2.24 (dd, J = 8.4, 15.6 Hz, 1 H), 2.17–2.12 (m, 1 H), 1.79–1.71 (m, 1 H), 1.63 (d, J = 13.6 Hz, 1 H), 1.30 (d, J = 6.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 128.3, 127.6, 127.5, 92.1, 81.5, 70.26, 67.01, 60.49, 28.4, 23.8, 22.1, 19.3 ppm. HRMS (ESI): calcd. for $C_{15}H_{20}O_3Na$ $[M + Na]^+$ 271.1310; found 271.1311.

(3*S*,4*R*)-4-(2-Hydroxyethyl)-3,4-dihydro-2*H*-pyran-3-yl Acetate (47):[14a] Synthesized from **37** by following the procedure described for **41**, yield 92%. R_f = 0.5 (EtOAc/hexanes, 40%). IR (neat): $\tilde{\nu}_{max}$ = 3398, 2924, 1736, 1649 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.34 (d, J = 6.4 Hz, 1 H), 4.79 (s, 1 H), 4.65 (t, J = 4.8 Hz, 1 H), 3.90 (dd, J = 4.0, 11.6 Hz, 1 H), 3.84 (d, J = 11.2 Hz, 1 H), 3.73–3.61 (m, 2 H), 2.76 (s, 1 H), 2.23 (s, 1 H), 2.02 (s, 3 H), 1.61–1.46 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 142.9, 102.0, 69.9, 63.5, 59.3, 37.5, 32.0, 20.9 ppm. HRMS (ESI): calcd. for $C_9H_{14}O_4Na$ $[M + Na]^+$ 209.0790; found 209.0790.

(1*R*,4*S*,5*R*)-2,8-Dioxabicyclo[3.3.1]nonan-4-yl Acetate (48): Synthesized from **47** by following the procedure described for **42**, yield 78%. R_f = 0.60 (EtOAc/hexanes, 50%). IR (neat): $\tilde{\nu}_{max}$ = 2931, 1736, 1441, 1364, 1249 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.79 (d, J = 2.0 Hz, 1 H), 4.10–4.04 (m, 2 H), 3.99 (dd, J = 5.5, 10.5 Hz, 1 H), 3.58 (t, J = 10.5 Hz, 1 H), 3.24–3.19 (m, 1 H), 2.0 (s, 3 H), 2.01–1.99 (m, 1 H), 1.96 (dd, J = 7.0, 13.0 Hz, 1 H), 1.90 (dd, J = 3.5, 13.0 Hz, 1 H), 1.41–1.35 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 98.2, 79.8, 62.5, 62.2, 35.2, 32.3, 31.9, 21.0 ppm. HRMS (ESI): calcd. for $C_{09}H_{14}O_4Na$ $[M + Na]^+$ 209.0790; found 209.0790.

[(2*R*,3*S*,4*S*)-3-Acetoxy-4-(2-oxoethyl)-3,4-dihydro-2*H*-pyran-2-yl]-methyl Acetate (49):[14a] To a solution of **10** (3.1 g, 7.5 mmol) in MeOH/H_2O (6:1, 28 mL) was added $NaIO_4$ (2.40 g, 11.25 mmol) and $NaHCO_3$ (0.693 g, 8.25 mol) and the mixture was stirred until the disappearance of starting material was observed (1 h). The reaction mass was filtered through a Celite 545 plug and the filtrate was concentrated under reduced pressure. The crude product obtained was dissolved in ethyl acetate (100 mL) and washed with water. The aqueous layer was extracted with ethyl acetate (2 × 25 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain the crude selenoxide derivative. To a solution of crude selenoxide derivative in anhydrous benzene (25 mL) was added *N*,*N*-diisopropylamine (5.14 mL, 36.1 mmol) and the mixture was heated to reflux until the disappearance of starting material was observed (20 min). The solvent was evaporated under reduced pressure to obtain the crude vinyl glycoside. Purification of the crude product by column chromatography over silica gel (hexanes/ethyl acetate) provided

pure vinyl glycoside, yield 55% (two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.43 (dd, J = 2.0, 14.0 Hz, 1 H), 5.92–5.81 (m, 2 H), 5.27 (s, 2 H), 4.53 (dd, J = 1.2, 14.0 Hz, 1 H), 4.23–4.05 (m, 4 H), 2.03 (s, 3 H), 2.02 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.0, 148.8, 130.0, 126.3, 93.2, 92.1, 67.3, 64.6, 62.3, 20.7, 20.6 ppm.

Compound **49** was synthesized form the above vinyl glycoside by following the procedure described for **13**, yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (t, J = 1.2 Hz, 1 H), 6.35 (dd, J = 2.0, 6.4 Hz, 1 H), 5.19 (dd, J = 5.6, 7.6 Hz, 1 H), 4.69 (d, J = 4.4, 6.0 Hz, 1 H), 4.33 (dd, J = 6.0, 12.0 Hz, 1 H), 4.21 (dd, J = 3.2, 12.0 Hz, 1 H), 4.12–4.09 (m, 1 H), 3.15–3.10 (m, 1 H), 2.66 (dd, J = 1.2, 7.2 Hz, 1 H), 2.47 (dd, J = 1.2, 6.4 Hz, 1 H), 2.03 (s, 3 H), 2.02 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.8, 170.5, 169.5, 142.6, 101.0, 71.1, 66.7, 62.0, 45.3, 27.5, 20.6 ppm.

[(2*R*,3*S*,4*S*)-3-Acetoxy-4-(2-hydroxyethyl)-3,4-dihydro-2*H*-pyran-2-yl]methyl Acetate (50):[14a] Synthesized from **49** by following the procedure described for **41**, yield 95%. R_f = 0.25 (EtOAc/hexanes, 40%). IR (neat): $\tilde{\nu}_{max}$ = 3449, 2947, 1743, 1649, 1437 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.28 (dd, J = 2.0, 6.0 Hz, 1 H), 5.07 (t, J = 6.0 Hz, 1 H), 4.66 (dd, J = 4.0, 6.0 Hz, 1 H), 4.26–4.22 (m, 1 H), 4.17–4.11 (m, 2 H), 3.69–3.62 (m, 2 H), 2.61–2.58 (m, 1 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 1.75–1.66 (m, 1 H), 1.51–1.42 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 170.1, 141.5, 101.5, 71.7, 67.5, 62.4, 59.8, 33.3, 28.8, 20.7, 20.6 ppm. HRMS (ESI): calcd. for $C_{12}H_{18}O_6Na$ [M + Na]$^+$ 281.1001; found 281.1001.

[(1*S*,3*R*,4*S*,5*S*)-4-Acetoxy-2,8-dioxabicyclo[3.3.1]nonan-3-yl]methyl Acetate (51): Synthesized from **50** by following the procedure described for **42**, yield 90%. R_f = 0.40 (EtOAc/hexanes, 50%). IR (neat): $\tilde{\nu}_{max}$ = 2953, 2926, 1742, 1369 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (s, 1 H), 4.85 (dd, J = 4.4, 10.4 Hz, 1 H), 4.31–4.27 (m, 1 H), 4.21 (dd, J = 4.8, 12.0 Hz, 1 H), 4.14 (dd, J = 2.0, 12.0 Hz, 1 H), 3.96–3.90 (m, 1 H), 3.75–3.68 (m, 1 H), 2.54 (br. d, J = 3.6 Hz, 1 H), 2.14–2.09 (m, 2 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 1.82–1.72 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 169.9, 92.5, 69.9, 67.6, 63.7, 60.0, 27.8, 24.9, 22.3, 21.0, 20.9 ppm. HRMS (ESI): calcd. for $C_{12}H_{18}O_6Na$ [M + Na]$^+$ 281.1001; found 281.1002.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H, ^{13}C, DEPT NMR and HRMS spectra of all new compounds and 2D spectra of ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY of bridged bicycles **14** and **42**.

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[17] The major diastereomer obtained after Ferrier rearrangement was used further to obtain the allyl vinyl ether.

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