ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 329 (2000) 731–744

CARBOHYDRATE RESEARCH

Preparation of various C-2 branched carbohydrates using intramolecular radical reactions

Sung Won Tina Choe [a,*], Michael E. Jung [b]

[a] *Department of Chemistry and Biochemistry, Loyola Marymount University, 7900 Loyola Boulevard, Los Angeles, CA 90045-8225, USA*

[b] *Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90024, USA*

Received 6 July 2000; accepted 10 August 2000

Abstract

A new and efficient method for the facile synthesis of C-2 branched carbohydrates has been developed using an intramolecular radical cyclization–fragmentation reaction. The desired C-2 branched glucopyranosides were isolated in 40–84% yield. Additionally, an unexpected furanoside was obtained from a tributyltin iodide-promoted rearrangement of the radical intermediate. The C-2 formyl glycal was also isolated in good yield using tris(trimethylsilyl)silane (TTMSS) as the reducing agent. This method was extended to synthesize a β C-2 branched glucopyranoside, a C-2 branched galactoside and a C-2 cyano glucopyranoside.

Keywords: C-2 Branched carbohydrates; Intramolecular radical cyclization–fragmentation reaction; Formyl glycal

1. Introduction

While investigating the synthesis of the potential antiviral agents cyclophellitol **1**β and **1**α, an efficient method was required to construct α C-2 formyl glucopyranoside **4**α [1]. The sequence of reactions used in the synthesis of cyclophellitol was lengthy and repetitive, although the overall yield was acceptable [2]. The sequence required a Swern oxidation of the mannopyranoside **2**, followed by a Wittig olefination to produce **3** in 70% yield (two steps). Hydroboration of the olefin **3** afforded a mixture of hydroxymethylglucopyranosides that was oxidized to give C-2 formyl adducts **4**αβ. The aldehydes were treated under mild basic conditions overnight to furnish the desired C-2 formyl glucopyranoside **4**α (Scheme 1).

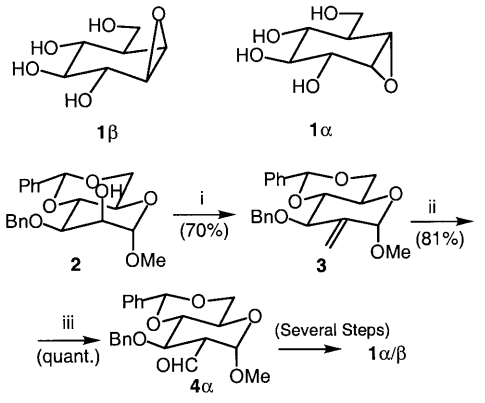
Various methods have been reported for the preparation of C-2 branched sugars [3]. Balasubramanian and co-workers published a short route to C-2 formyl glycals using the Vilsmeier–Haack reaction [4]. The reported reaction conditions, however, were too harsh for acid-labile protective groups. The most direct approach was accomplished by Kahne and co-workers using an intermolecular radical trapping of carbon monoxide (CO). However, the reported low yields (5–37%) and the required reaction conditions (1200–1400 psi CO) made it less attractive as a general method for the preparation of C-2 branched sugars [5].

This paper describes a new method to synthesize α C-2 formyl carbohydrates using commercially available glucals by employing an intramolecular cyclization–fragmentation rad-

* Corresponding author. Tel.: +1-310-3387405; fax: +1-310-3382905.

E-mail address: tchoe@lmumail.lmu.edu (S.W.T. Choe).

0008-6215/00/$ - see front matter
PII: S0008-6215(00)00246-9



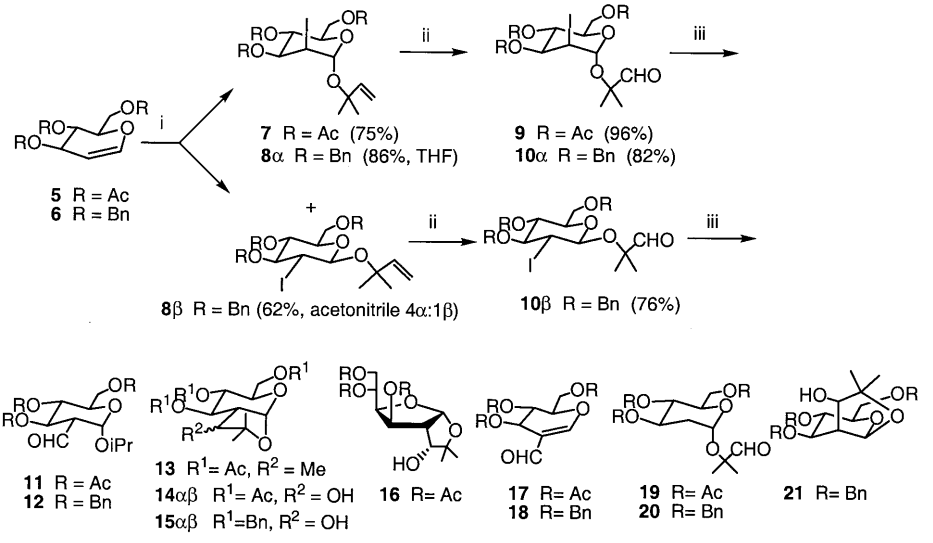
Scheme 1. Synthesis of 2-*C*-formyl glucoside **3**α. Reagents: (i) (a) DMSO, TFAA, TEA, (b) Wittig; (ii) (a) BH_3·DMS, THF, (b) DMSO, TFAA, TEA; (iii) TEA.

ical reaction (Scheme 2) [6]. The functionalizable formyl moiety is ideal to further branch the sugar if needed. The mechanism for the formation of the desired C-2 formyl sugar requires the generation of a secondary alkyl radical from iodoaldehydes **9** and **10**. The resulting radical adds intramolecularly to the aldehyde group at the C-1 center of the sugar to give the highly reactive bicyclic alkoxy radical. The radical intermediate undergoes β-scission to produce an α-isopropoxy radical, which upon reduction affords the formyl-transfer products **11** and **12**. A conceptually similar process was reported by Fraser-Reid and co-workers [7]. They reported a number of examples that transposes an aldehyde group upon β-scission onto the side chains of carbohydrates.

2. Results and discussion

2-Iodo glucopyranoside **7** was prepared in 75% yield from commercially available tri-*O*-acetyl-D-glucal (**5**) by addition of *N*-iodosuccinimide and commercially available dimethylvinyl carbinol (Scheme 2) [8]. Ozonolysis and reduction with methyl sulfide furnished the desired iodoaldehyde **9** in 96% yield. To test the feasibility of the radical cyclization, **7** was subjected to tributyltin hydride-promoted radical cyclization, which successfully furnished the cyclized product **13** in 68% yield as a 1:1 mixture of diastereomers.

The free-radical promoted cyclization of the aldehyde **9** produced a mixture of products in varying yields depending on the reaction conditions. The products from the radical reactions were separated using flash column chromatography. The desired formyl-transfer product **11** was isolated in 40% yield under optimal conditions (Table 1, Method A). In addition to the C-2 formyl glucopyranoside **11**, the bicyclic alcohols **14**αβ as a 1:1 mixture of diastereomers, the C-2 formyl glycal **17**, and the directly reduced sugar **19** were isolated from the reaction. An unexpected furanoside **16** was isolated, and the structure was determined by careful spectroscopic analysis.

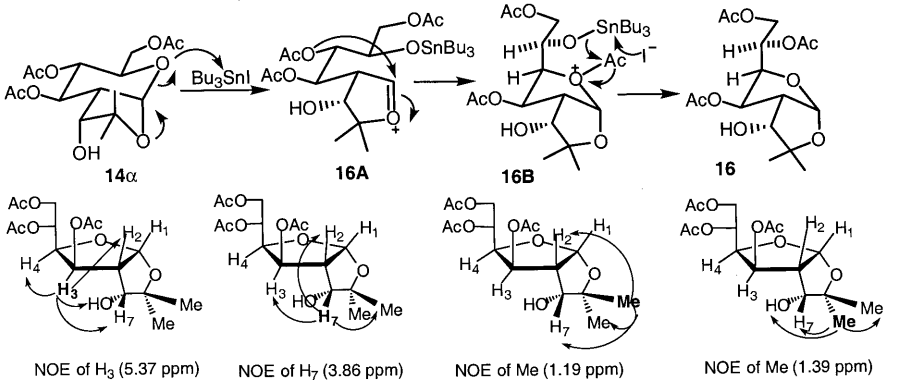


Scheme 2. Synthesis of the radical substrates and the products from the radical reactions. Reagents: (i) NIS, dimethylvinyl carbinol, acetonitrile; (ii) O_3, DMS; (iii) Bu_3SnH, AIBN, PhH.

Table 1
Representative reaction conditions and product distribution for the radical reaction [a,b]

Method	[9][c]	Time (h) [d]	[11]	[14]	[16]	[17]	[19]
A	0.004	0.5			60		
A	0.005	2	40		27		23
A	0.01	0.5	16		42		
A	0.02	6	21	20	38	10	
A	0.03	5			42		9
B	0.006	5		17		65	
B	0.01	1.5	20	20		17	
B	0.021	3	30	13		32	
B	0.024	1.5	41	33		11	
B	0.024	3	17	13		31	

[a] Method A: typical reaction was conducted in benzene with 1.0–1.5 equiv of Bu_3SnH and 0.01–0.5 equiv of AIBN under reflux.
[b] Method B: typical reaction was conducted in toluene with 1.0–1.5 equiv of TTMSS and 0.01–0.5 equiv of AIBN under reflux.
[c] Initial concentrations (mol/L) of the deoxyiodoglucoside **9**.
[d] Time required to deliver the reducing agent using a syringe pump.



Scheme 3. Proposed mechanism for the formation of the furanoside and NOE data.

NMR analysis of **16** indicated the absence of large trans-diaxial coupling constants and axial–equatorial coupling constants typical for glucopyranosides. Instead, coupling constants expected from a furanoside ring system were observed. We propose that the furanoside **16** is formed from a tributyltin iodide-catalyzed rearrangement of the radical intermediate **14**α (Scheme 3). The mechanism involves the complexation of the pyran oxygen with the iodostannane, followed by a pyranoside ring opening to give **16A**. The resulting oxonium ion **16A** would then be attacked by the C-4 acetate group to afford **16B**, followed by an internal (or intermolecular) acetate transfer to give the furanoside **16**. The stereochemistry of the alcohol was determined using NOE difference spectra (Scheme 3). The NOE difference spectra of H-3 (5.37 ppm) showed a strong enhancement of the signal for H-4 (4.74 ppm) and a weak enhancement of the signal for H-7 (3.86 ppm), H-2 (2.45 ppm) and OH (2.46 ppm). Irradiation of H-7 (3.86 ppm) showed weak enhancement of H-3 (5.37 ppm) but a strong enhancement of the signal for H-2 (2.45 ppm) and one of the methyl singlets (1.19 ppm). Irradiation of the methyl singlet at 1.19 ppm showed a strong NOE to both H-2 and H-7, which added further evidence that this methyl group is cis to both H-2 and H-7. Lastly, irradiation of the methyl singlet at 1.39 ppm showed a strong enhancement of OH (2.46 ppm) but a weak enhancement of H-7 and no NOE enhancement of H-2. The methyl singlet at 1.39 ppm was therefore assigned cis to OH and trans to both H-2 and H-7.

Chatgilialoglu and co-workers reported that tris(trimethylsilyl)silane (TTMSS) rivaled tri-

butyltin hydride in efficiency as a reducing agent with several advantages [9]. They found that the silane was less reactive as a hydrogen donor than the stannanes since the Si–H bond is 5 kcal mol^{-1} stronger than the Sn–H bond. In addition, removal of the byproducts from the radical reaction using TTMSS was reported to be much easier than with the tin reagent. To diminish the formation of **14** and **19**, the radical precursor **9** was subjected to TTMSS radical conditions. Furthermore, the sterically bulky nature of the intermediate tris(trimethylsilyl)silyl iodide was expected to function as a poor catalyst for the rearrangement needed to give the furanoside **16**. As anticipated, the radical reactions using TTMSS (Table 1, Method B) did not form any of the furanoside **16**. However, a 65% yield of the C-2 formyl glycal **17** was isolated. This route to C-2 formyl glycals is more general by allowing for acid-sensitive protecting groups than the known method via the Vilsmeier–Haack reaction. Along with the glycal, the bicyclic alcohols **14**αβ were isolated in varying yields depending on the reaction conditions. The desired formyl-transfer product **11** was isolated in 41% yield under optimal conditions. Efforts towards increasing the yield of **11** using in situ generation of the reducing agent and attempts using hexabutyldistannane under photolytic conditions were unsuccessful.

Table 2
Product distribution for the radical reaction

[**10**]	Time (h)	[**12**]	[**15**]	[**18**]	[**21**]
0.009 [a]	3.4	14	30	17	
0.009 [a]	6.5	20	20	21	
0.01 [a]	3	20	58		
0.02 [a]	6.5	11	60		
0.02 [a]	3	17	53		
0.004 [b]	0.5				67
0.005 [b]	3				82
0.03 [b]	3				67
0.009[c]	3.5		45		

[a] Typical reaction was conducted in benzene with **10a**, 1.0–1.5 equiv of Bu_3SnH and 0.01–0.5 equiv of AIBN under reflux.

[b] Typical reaction was conducted in benzene with **10b**, 1.0–1.5 equiv of Bu_3SnH and 0.01–0.5 equiv of AIBN under reflux.

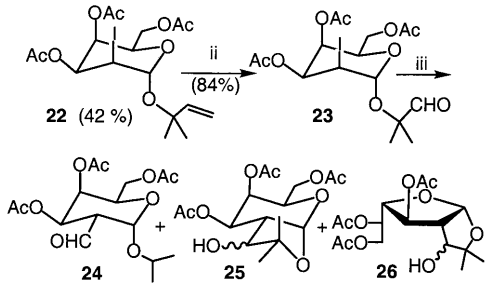
[c] Radical reaction with **10a** using TTMSS as the reducing agent.

Conversion of the commercially available tri-*O*-benzyl-D-glucal (**6**) [8] by the same two-step procedure furnished the desired radical precursor **10** (Scheme 2). A solvent effect was observed on the iodoetherification of **6**. Namely, a reaction using tetrahydrofuran as the solvent afforded the diaxial α glucoside **8**α exclusively in 86% yield. However, using acetonitrile as the solvent, the diaxial glucoside **8**α and the diequatorial glucoside **8**β were isolated as a 4:1 mixture in 62% yield. The two diastereomers were separated and ozonized to give an 82% yield of the diaxial iodoaldehyde **10**α and a 76% yield of the diequatorial iodoaldehyde **10**β. Easy access to the two isomers allowed us to investigate not only the α-formyl transfer reactions but also the feasibility of extending this process to generate the β-branched sugars.

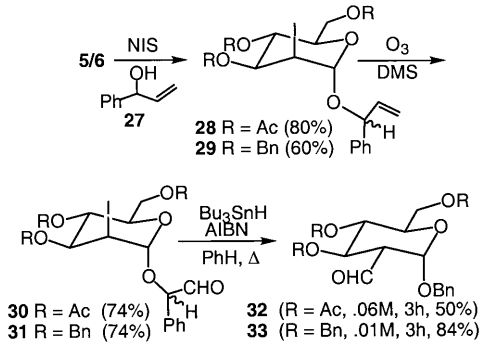
The formyl-transfer reaction of **10**α using tributyltin hydride gave **12** in 20% yield under optimal conditions (Table 2). Under most experimental conditions, the alcohols **15**αβ were isolated as the major product. Formyl glycal **18** was isolated in 21% yield. No furanosides and only traces of the directly reduced product **20** were detected in the radical reactions of **10**αβ. Using TTMSS on the radical substrate **10**α yielded the bicyclic alcohol **15** with only traces of other byproducts.

Extending the formyl-transfer reaction to β branched sugars, the iodoaldehyde **10**β was subjected to radical reaction conditions (Table 2). The reaction yielded the alcohol **21** as the major product with yields as high as 82% with no traces of the β C-2 formyl product.

The radical reactions for the tri-*O*-acetyl and the tri-*O*-benzyl glucal substrates furnished substantial amounts of the bicyclic alcohols **14**, **15**, and **21**. Therefore, in order to increase the yields of **11** and **12**, these intermediates were subjected to reaction conditions that regenerate the alkoxy radical, thus allowing the β-fission to complete the rearrangement process [10]. However, attempts at converting the alcohols to the desired formyl-transfer products were unsuccessful. In several cases the 1:1 mixture of the alcohols **14**αβ epimerized to give mostly one isomer upon reaction with mercuric oxide and iodine under photolysis. This result indicated the formation of the hypoiodite and the generation of the aldehyde but that the bicyclic alcohol had reformed to give the thermody-



Scheme 4. Synthesis of C-2 branched galactoside. Reagents used were the same as Scheme 2.



Scheme 5. Synthesis of 2-*C*-formyl glucosides. Reaction conditions were the same as Scheme 2.

namically stable bicyclic alcohol. The NMR of the photolyzed product showed H-2 as an apparent doublet of triplets with $J = 5.7$, 11.5 Hz. Thus H-2 should be nearly trans-diaxial to both H-3 and H-7, indicating **14**β as the epimerized product. Similar photochemically induced inversions of configuration of alcohols were reported by Binkley and co-workers [11].

The application of this formyl-transfer method to commercially available tri-*O*-acetyl-D-galactal was explored. The same two-step sequence of reactions (Scheme 2) was repeated to synthesize the radical precursor **23** (Scheme 4). Iodoetherification of the galactal gave only the diaxial galactoside **22** in 42% yield. Ozonolysis of **22** furnished the radical precursor **23** in 84% yield. Radical reaction of the galactoside **23** using tributyltin hydride conditions successfully produced the desired formyl-transfer product **24** in 50% yield (0.05 M, 2 h) along with an inseparable mixture of what appeared to be the bicyclic alcohol **25** and the rearranged furanoside **26**. The structures of these byproducts were not confirmed since the two compounds were inseparable.

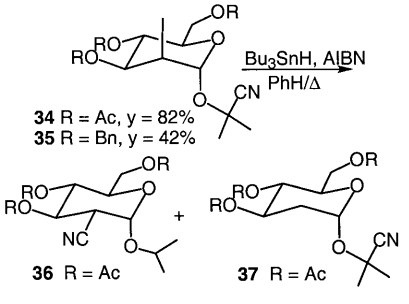
The collective results of the radical reactions indicated that the initial radical cyclization to the aldehyde occurred but the subsequent fragmentation of the alkoxyl radical to form the α-isopropoxy radical was problematic. Therefore, the intermediate α-isopropoxy radical was not stable enough to drive the reaction to completion. With this in mind, a modified radical substrate was synthesized to favor the fragmentation process by increasing the stability of the resulting radical. Initially, we tried changing the substrate such that the resulting radical from the fragmentation would be an α,α-diphenyl radical. In order to synthesize the radical substrate it was necessary to add α,α-diphenyl allyl alcohol (easily prepared from benzophenone and vinylmagnesium bromide) to **5** and **6**. However, many attempts at the iodoetherification reaction were unsuccessful presumably due to the low reactivity of the diphenyl allyl alcohol towards electrophilic reactions and also its propensity to rearrange to β-phenylcinnamyl alcohol with traces of acid. Next, α-phenyl allyl alcohol **27** was added to **5** and **6** since these substrates would produce a stable benzyl radical upon fragmentation (Scheme 5). The radical substrates **30** and **31** were prepared by reacting the glucals with α-phenyl allyl alcohol and *N*-iodosuccinimide in acetonitrile. The iodoetherification reaction furnished only the diaxial products as a 1:1 diastereomeric mixture at the allylic centers of the glucosides. Although the mixture of diastereomers were inseparable, the newly generated chiral center was not important since the radical reaction would produce a benzyl group. The mixture of diastereomers was ozonized to afford the key aldehydes **30** and **31** in 74% yields.

The modified radical precursor **30** yielded the formyl-transfer adduct **32** in 50% yield under optimal conditions. Radical reaction of the tri-*O*-benzyl iodoglucoside **31** produced the desired glucoside **33** in 84% yield with only traces of the glycal **18**. Therefore, the driving force of producing a benzyl radical caused the fragmentation to occur more efficiently, leading to higher yields of the desired C-2 formyl glucopyranosides. Thus, this simple three-step procedure of iodoetherification, ozonolysis, and radical cyclization–fragmentation efficiently converts glucals into α C-2 formyl pyranosides.

To further explore this radical fragmentation process, this reaction was extended to nitrile-transfer reactions. Curran and co-workers reported several examples of intramolecular nitrile-transfer reactions on non-carbohydrate systems [12]. The radical substrates were prepared from **5** and **6** using acetone cyanohydrin and *N*-iodosuccinimide. This reaction successfully furnished **34** in 82% yield and **35** in 42% yield (Scheme 6). The iodoetherification reaction using mandelonitrile as the nucleophile gave unsatisfactory yields of the radical substrates, presumably due to the same reasons given for α,α-diphenyl allyl alcohol.

The iodoglucoside **34** successfully produced the nitrile-transfer product **36**, albeit in 30% yield along with the directly reduced glucoside **37**. The cyano-transfer reactions with the tri-*O*-benzyl glucoside **35** led to decomposition of the starting material.

A new method for the construction of C-2 branched sugars was developed using an intramolecular formyl- and cyano-transfer reactions via a radical cyclization–fragmentation process. The desired formyl-transfer product **11** was isolated in 41% yield along with the furanoside **16**. Tris(trimethylsilyl)silane gave good yields of the formyl glycal **17**, a compound otherwise difficult to synthesize directly. In addition, this study showed that the formyl-transfer method is a viable means to afford not only the α C-2 branched sugars but also the β C-2 branched sugar **21**. The yields of the formyl-transfer reactions were improved by changing the radical substrates to give a benzyl radical upon fragmentation. This method was also used to synthesize α C-2 branched galactopyranoside and α C-2 cyano glucoside **36**.



Scheme 6. Synthesis of 2-*C*-cyanoglucoside.

3. Experimental

General methods.—^{1}H NMR spectra were recorded on a Bruker AF 200 spectrometer, operating at 200.132 MHz, a Bruker AM 360 spectrometer, operating at 360.134 MHz, and the Bruker ARX 400 spectrometer, operating at 400.130 MHz, and are so indicated. ^{13}C NMR spectra were recorded on the AF 200, operating at 50.323 MHz, the AM 360, operating at 90.556 MHz, the ARX 400, operating at 100.625 MHz, and the ARX 500 spectrometer, operating at 125.767 MHz, and are also specified. IR spectra were recorded on a Nicolet 510 FTIR as a liquid film (neat) on sodium chloride plates, and the spectra were referenced to a polystyrene standard. High-resolution mass spectra were obtained from the Mass Spectrometry Facilities at the University of California, Riverside and at the University of California, Los Angeles using ZAB 7070 HP spectrometers. The chemical-impact high-resolution mass spectra (CIHRMS) were obtained using ammonia as the reagent gas. All optical rotations were obtained from a Perkin–Elmer 243 polarimeter at ambient temperature and referenced to the sodium D line (589 nm). Thin-layer chromatography (TLC) was performed using E. Merck Silica Gel 60 F_{254} 0.2 mm aluminum-backed plates. Visualization was accomplished using ultraviolet light or by using an anisaldehyde stain [*p*-anisaldehyde (2 mL) in EtOH (85 mL), glacial AcOH (10 mL), and concd H_2SO_4 (2 mL)]. Silica gel column chromatography was conducted on E. Merck Silica Gel 60 (70–230 mesh). Concentration in vacuo refers to the removal of solvent using a Büchi rotary evaporator.

1,1-Dimethyl-2-propenyl 3,4,6-tri-O-*acetyl-2-deoxy-2-iodo-α*-D-*mannopyranoside* (**7**). A solution of commercially available tri-*O*-acetyl-D-glucal (3 g, 11.0 mmol) in dry MeCN (30 mL) was stirred for 30 min with *N*-iodosuccinimide (2.5 g, 11.0 mmol) in the dark. To the reaction mixture was added dropwise 2-methyl-3-buten-2-ol (5.7 mL, 55.0 mmol), and the mixture was stirred at rt for an additional 16 h. The reaction mixture was diluted with EtOAc, then washed several times with aq sodium thiosulfate until the organic layer

turned clear. The organic layer was combined, dried over $MgSO_4$ and concentrated in vacuo. The resulting yellow oil was purified by flash column chromatography (1:5 EtOAc–hexane) to give 3 g (84% based on recovered starting material) of the desired iodo sugar **7** as a clear liquid along with 1 g of recovered tri-*O*-acetyl-D-glucal: $[\alpha]_D$ +18.3° (*c* 12.2, CH_2Cl_2); R_f 0.73 (1:1 EtOAc–hexane); IR (neat): 2982, 2940, 1752, 1433, 1416, 1368, 1231, 1113, 1030, 938, 920 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 5.81 (dd, 1 H, $J_{8,9}$ 10.7, $J_{8,9'}$ 17.5 Hz, H-8), 5.35 (t, 1 H, $J_{3,5}$ 9.6 Hz, H-4), 5.28 (bs, 1 H, H-1), 5.19 (m, 2 H, H-9, H-9′), 4.68 (dd, 1 H, $J_{2,3}$ 4.1, $J_{3,4}$ 9.5 Hz, H-3), 4.40 (dd, 1 H, $J_{1,2}$ 1.3, $J_{2,3}$ 4.1 Hz, H-2), 4.23 (m, 3 H, H-5, H-6, H-6′), 2.09, 2.07, 2.05 (each s, 9 H, OAc), 1.35, 1.32 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.4, 169.6, 169.3, 142.0, 115.1, 96.4, 78.3, 68.9, 68.7, 67.6, 62.2, 31.4, 27.6, 24.9, 20.8, 20.6, 20.5; CIHRMS (*m*/*z*): 485.0672 (M^+). Calcd for $C_{17}H_{25}IO_8$ 485.0641 (M^+).

1,1-Dimethyl-2-propenyl 3,4,6-tri-O-*benzyl-2-deoxy-2-iodo-α-*D-*mannopyranoside* (**8**α). Prepared from **6** (1 g, 2.4 mmol) using dry THF in the manner as described for **7** to yield 460 mg (86% based on recovered starting material): $[\alpha]_D$ +12.2° (*c* 0.9, CH_2Cl_2); R_f 0.61 (1:2 EtOAc–hexane); IR (neat): 3031, 2979, 2926, 2861, 1497, 1455, 1364, 1144, 1113, 1053, 1028, 1000 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 7.30 (m, 15 H, Ph), 5.82 (dd, 1 H, $J_{8,9}$ 10.7, $J_{8,9'}$ 17.5 Hz, H-8), 5.36 (d, 1 H, $J_{1,2}$ 0.7 Hz, H-1), 5.16 (d, 1 H, H-9), 5.14 (d, 1 H, H-9′), 4.87 4.75, 4.72, 4.56, 5.11, 4.99 (each d, 6 H, *J* 10.5 Hz, benzyl), 4.37 (dd, 1 H, $J_{1,2}$ 1.4, $J_{2,3}$ 4.0 Hz, H-2), 4.07 (m, 1 H, H-5), 3.97 (dd, 1 H, $J_{3,4}$ 8.8, $J_{4,5}$ 9.7 Hz, H-4), 3.83 (dd, 1 H, $J_{5,6}$ 4.2, $J_{6,6'}$ 10.7 Hz, H-6), 3.69 (dd, 1 H, H-6′), 3.40 (dd, 1 H, $J_{2,3}$ 4.0, $J_{3,4}$ 8.7 Hz, H-3), 1.34, 1.28 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 142.7, 138.4, 138.2, 137.8, 128.3 (2C), 128.2, 128.1, 128.0, 127.7, 127.6 (2C), 127.3, 114.6, 96.7, 77.8, 76.9, 76.1, 75.2, 73.2, 71.9, 70.9, 68.8, 35.7, 27.8, 25.1; HRMS FAB (*m*/*z*): 627.1608 ($M^+ - H$). Calcd for $C_{32}H_{36}IO_5$ 627.1581 ($M^+ - H$).

1,1-Dimethyl-2-propenyl 3,4,6-tri-O-*benzyl-2-deoxy-2-iodo-β-*D-*glucopyranoside* (**8**β). Prepared from **6** (517 mg, 24 mmol) using MeCN in the manner described for **7** to yield 201 mg (62% based on recovered starting material): R_f 0.61 (1:2 EtOAc–hexane); ^1H NMR (360 MHz, $CDCl_3$): δ 7.29 (m, 15 H, Ph), 6.13 (dd, 1 H, $J_{8,9}$ 10.8, $J_{8,9'}$ 17.6 Hz, H-8), 5.22 (d, 1 H, H-9), 5.13 (d, 1 H, H-9′), 4.97 (d, 1 H, $J_{8,9}$ 10.1 Hz, benzyl), 4.85–4.78 (m, 2 H), 4.64–4.50 (m, 3 H), 4.59 (d, 1 H, $J_{1,2}$ 9.2 Hz, H-1), 3.92 (t, 1 H, $J_{1,3}$ 9.0 Hz, H-2), 3.74–3.58 (m, 3 H), 3.55 (t, 1 H, $J_{2,4}$ 9.7 Hz, H-3), 3.45 (m, 1 H), 1.41, 1.38 (each s, 6 H, Me).

1,1-Dimethyl-2-oxoethyl 3,4,6-tri-O-*acetyl-2-deoxy-2-iodo-α-*D-*mannopyranoside* (**9**). To a solution **7** (1.2 g, 2.6 mmol) in dry CH_2Cl_2 (120 mL) at −78 °C was added a steady stream of ozone until the clear solution turned dark blue (15 min). The excess ozone was purged with nitrogen (10 min) methyl sulfide (0.94 mL, 12.8 mmol) was added and the mixture was allowed to stir at −78 °C for an additional hour before warming to rt. The solvent was removed in vacuo and the resulting yellow residue was purified by flash column chromatography (3:7 EtOAc–hexane) to give 1.2 g (96%) of the desired aldehyde **9** as a clear oil: $[\alpha]_D$ +22.2° (*c* 3.7, CH_2Cl_2); R_f 0.64 (1:1 EtOAc–hexane); IR (neat): 2986, 2940, 1748, 1435, 1370, 1231, 1161, 1115, 1040, 1013, 968, 949, 920 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 9.44 (s, 1 H, CHO), 5.28 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.25 (t, 1 H, $J_{3,5}$ 9.2 Hz, H-4), 4.60 (dd, 1 H, H-3), 4.47 (dd, 1 H, H-2), 4.14 (m, 2 H), 3.98 (m, 1 H), 2.07, 2.06, 2.03 (each s, 9 H, OAc), 1.34, 1.33 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 200.8, 170.5, 169.7, 169.3, 97.1, 82.1, 69.4, 68.7, 67.6, 62.2, 29.7, 21.5, 21.1, 20.8, 20.6, 20.5; CIHRMS (*m*/*z*): 504.0731 ($M + NH_4^+$). Calcd for $C_{16}H_{27}INO_9$ 504.0751 ($M + NH_4^+$).

1,1-Dimethyl-2-oxoethyl 3,4,6-tri-O-*benzyl-2-deoxy-2-iodo-α-*D-*mannopyranoside* (**10**α). Prepared from **8**α (690 mg, 1.09 mmol) using the same procedure described for **9** to yield 0.60 g (86%): $[\alpha]_D$ +13.0° (*c* 1.5, CH_2Cl_2); R_f 0.69 (1:2 EtOAc–hexane); IR (neat): 2923, 2865, 1736, 1455, 1374, 1267, 1246, 1115, 1046, 911 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 9.54 (s, 1 H, CHO), 7.36 (m, 15 H, Ph), 5.46 (d, 1 H, $J_{1,2}$ 1.58 Hz, H-1), 4.87, 4.75, 4.72 (each d, 3 H, *J* 10.1 Hz, benzyl), 4.56 (m, 4 H), 4.09 (m, 1 H), 3.97 (dd, 1 H, $J_{3,4}$ 8.4, $J_{4,5}$

8.6 Hz, H-4), 3.80 (dd, 1 H, $J_{5,6}$ 4.6, $J_{6,6'}$ 10.7 Hz, H-6), 3.69 (dd, 1 H, H-6′), 3.41 (dd, 1 H, $J_{2,3}$ 4.0, $J_{3,4}$ 8.4 Hz, H-3), 1.34, 1.33 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 201.6, 138.2, 137.9, 137.5, 128.3 (2C), 128.2, 128.0 (2C), 127.8, 127.7, 127.5, 127.4, 97.3, 81.6, 76.7, 75.8, 75.1, 73.3, 72.5, 71.0, 68.7, 33.8, 21.6, 21.1; CIHRMS (m/z): 629.1415 ($M^+ - H$). Calcd for $C_{31}H_{34}IO_6$ 629.1400 ($M^+ - H$).

1,1-Dimethyl-2-oxoethyl 3,4,6-tri-O-*benzyl-2-deoxy-2-iodo-β*-D-*glucopyranoside* (**10**β). Prepared from **8**β (52 mg, 0.083 mmol) using the same procedure described for **9** to yield 39.4 mg (76%): $[\alpha]_D$ +28.2° (*c* 0.4, CH_2Cl_2); IR (neat): 3031, 2926, 2855, 1732, 1497, 1455, 1360, 1310, 1273, 1213, 1111, 1074, 1045, 1028, 911 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$): δ 9.66 (s, 1 H, CHO), 7.32 (m, 15 H, Ph), 4.97, 4.86, 4.79, 4.60, 4.58, 4.49 (each d, 6 H, *J* 10.1 Hz, benzyl), 4.68 (d, 1 H, $J_{1,2}$ 8.9 Hz, H-1), 3.95 (dd, 1 H, $J_{1,2}$ 8.9, $J_{2,3}$ 9.1 Hz, H-2), 3.70 (m, 4 H), 3.42 (m, 1 H), 1.39, 1.34 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 202.5, 137.9, 137.7, 137.6, 128.5, 128.4 (2C), 128.1 (2C), 127.9, 127.8 (2C), 127.7, 98.3, 87.1, 82.5, 79.2, 75.3, 75.2 (2C), 73.5, 68.7, 32.6, 22.6, 19.2; CIHRMS (m/z): 648.1820 ($M + NH_4^+$). Calcd for $C_{31}H_{34}INO_6$ 648.1822 ($M + NH_4^+$).

Typical radical reaction using tributyltin hydride. To a refluxing solution of **9** (99.6 mg, 0.205 mmol) in degassed benzene (31 mL) was added a solution of tributyltin hydride (0.055 mL, 0.205 mmol) and AIBN (0.01 g, 0.061 mmol) over 2 h using a syringe pump. The reaction was allowed to heat to reflux for an additional 3 h then cooled to rt. The solvent was removed in vacuo, and the yellow residue was diluted with MeCN and washed with pentane several times to remove all the tin byproducts. The MeCN layers were combined and concentrated in vacuo to give a pale yellow oil. The products of the radical reaction were purified by flash column chromatography (3:7 EtOAc–hexane). Depending on the reaction conditions, i.e., the concentrations and the rate of addition of the tin hydride, we observed different products (see Tables 1 and 2).

Typical radical reaction using tris-(trimethylsilyl)silane (TTMSS). To a refluxing solution of **9** (236 mg, 0.484 mmol) in degassed toluene (15 mL) was added a solution of tris(trimethylsilyl)silane (0.15 mL, 0.484 mmol), and AIBN (0.04 g, 0.242 mmol) in toluene (5 mL) via syringe pump over a 1.5 h period. The reaction was allowed to heat at reflux for an additional 4 h before cooling to rt. The reaction mixture was concentrated in vacuo, then the products were purified by flash column chromatography (3:7 EtOAc–hexane). Depending on the reaction conditions, i.e., the concentrations and the rate of addition of the tin hydride, we observed different products (see Tables 1 and 2).

Isopropyl 3,4,6-tri-O-*acetyl-2-deoxy-2*-C-*formyl-α*-D-*glucopyranoside* (**11**): IR (neat): 2967, 1750, 1373, 1229, 1119, 1051 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (d, 1 H, $J_{2,CHO}$ 2.5 Hz, CHO), 5.81 (t, 1 H, $J_{3,5}$ 9.3 Hz, H-4), 5.25 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.03 (t, 1 H, $J_{2,4}$ 9.7 Hz, H-3), 4.30 (dd, 1 H, $J_{5,6}$ 4.5, $J_{6,6'}$ 12.1 Hz, H-6), 4.15 (m, 1 H, H-5), 4.08 (dd, 1 H, H-6′), 3.88 (septet, 1 H, H-7), 2.78 (ddd, 1 H, H-2), 2.09, 2.05, 2.01 (each s, 9 H, OAc), 1.22, 1.11 (each d, 6 H, $J_{7,Me}$ 6.2 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 170.6, 170.2, 169.8, 95.2, 77.1, 71.0, 68.9, 68.2, 68.1, 67.7, 61.9, 56.6, 23.0, 20.6 (2C); CIHRMS (m/z): 378.1761 ($M + NH_4^+$). Calcd for $C_{16}H_{28}NO_9$ 378.1764 ($M + NH_4^+$).

Isopropyl 3,4,6-tri-O-*benzyl-2-deoxy-2*-C-*formyl-α*-D-*glucopyranoside* (**12**): R_f 0.73 (1:2 EtOAc–hexane); ^{1}H NMR (360 MHz, $CDCl_3$): δ 9.47 (d, 1 H, $J_{2,CHO}$ 2.6 Hz, CHO), 7.30 (m, 15 H, Ph), 5.19 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.90, 4.82, 4.77, 4.66, 4.56, 4.52 (each d, 6 H, *J* 11.0 Hz, benzyl), 4.36 (dd, 1 H, $J_{3,4}$ 8.9, $J_{4,5}$ 11.0 Hz, H-4), 3.94–3.65 (m, 5 H), 2.71 (ddd, 1 H, H-2), 1.16, 1.05 (each d, 6 H, $J_{7,Me}$ 6.2 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 138.0, 137.8, 137.7, 128.4, 128.3, 128.2, 128.0, 127.8 (2C), 127.7, 127.6, 127.5, 95.4, 79.1, 74.9, 74.7, 73.5, 70.9, 69.8, 68.3, 58.5, 23.1, 21.2. (one aliphatic carbon not resolved); CIHRMS (m/z): 522.2832 ($M + NH_4^+$). Calcd for $C_{31}H_{40}NO_6$ 522.2856 ($M + NH_4^+$).

*[4*R - *(3αβ,3aβ,4β,5α,6β,7aβ)] - 6 - [(Acetyloxy)methyl]hexahydro - 2,2,3 - trimethyl - 4*H-*furo[2,3-*b*]pyran-4,5-diol, diacetate* (**13**). Prepared from **7** (373 mg, 0.77 mmol) using typical radical reaction conditions described above to yield 113 mg (68% based on recovered starting material): R_f 0.44 (1:1 EtOAc–hexane); IR (neat): 2973, 1744, 1456, 1437, 1372, 1231, 1165, 1130, 1032, 963, 916 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.49–5.39 (m, 2 H), 5.30–5.29 (m, 1 H), 5.00–4.92 (m, 1 H), 4.92–5.00 (m, 1 H), 4.48–4.10 (m, 7 H), 3.15–3.21 (m, 1 H, H-2), 2.52 (m, 1 H), 2.32 (m, 2 H), 2.10, 2.09, 2.07, 2.04, 2.03, 2.02 (each s, 18 H, OAc), 1.58, 1.52, 1.32, 1.30 (each s, 12 H, Me), 1.26, 0.94 (each d, 6 H, $J_{7,Me}$ 6.8 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 169.6 (2C), 97.3, 83.1, 70.9, 68.8, 67.3, 63.2, 48.0, 43.0, 27.5, 22.3, 20.9, 20.8, 20.7, 13.3; CIHRMS (*m/z*): 376.1976 ($M + NH_4^+$). Calcd for $C_{17}H_{30}NO_8$ 376.1971 ($M + NH_4^+$).

*[3*R-*(3α,3aβ,4β,5α,6β,7aβ)]-6-[(Acetyloxy)-methyl]hexahydro-2,2-dimethyl-4*H-*furo[2,3-*b*] pyran-3,4,5-triol, 4,5-diacetate* (**14**). Data for **14**α: ^1H NMR (360 MHz, $CDCl_3$): δ 5.45 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 5.39 (dd, 1 H, $J_{3,4}$ 8.7, $J_{4,5}$ 8.8 Hz, H-4), 5.15 (t, 1 H, $J_{2,4}$ 8.9 Hz, H-3), 4.32–4.12 (m, 3 H), 2.34 (ddd, 1 H, H-2), 2.06, 2.05, 2.04 (each s, 9 H, OAc), 1.41, 1.21 (each s, 6 H, Me). Data for **14**β: ^1H NMR (360 MHz, $CDCl_3$): δ 5.51 (d, 1 H, $J_{1,2}$ 5.5 Hz, H-1), 5.14 (t, 1 H, $J_{3,5}$ 6.4 Hz, H-4), 5.02 (dd, 1 H, $J_{2,3}$ 6.5, $J_{3,4}$ 9.2 Hz, H-3), 4.29 (dd, 1 H, $J_{5,6}$ 5.1, $J_{6,6'}$ 12.2 Hz, H-6), 4.13–3.99 (m, 3 H, H-5, H-6′, H-7), 2.34 (ddd, 1 H, $J_{1,2}$ 5.7, $J_{2,7}$ 5.7, $J_{2,3}$ 11.5 Hz, H-2), 2.08, 2.07, 2.06 (each s, 9 H, OAc), 1.44, 1.21 (each s, 6 H, Me). Data for the mixture of isomers **14**αβ: IR (neat): 3480, 2977, 2938, 1748, 1435, 1370, 1237, 1161, 1113, 1036, 916 cm^{-1}; ^{13}C NMR (90 MHz, $CDCl_3$): δ 171.1, 170.8, 169.8, 169.5, 97.5, 97.4, 83.3, 82.1, 78.5, 76.6, 71.3, 69.8, 69.3, 68.5, 68.3, 68.2, 62.6, 62.4, 50.5, 48.2, 27.8, 27.7, 23.0, 22.1, 20.9, 20.7 (2C); CIHRMS (*m/z*): 378.1773 ($M + NH_4^+$). Calcd for $C_{16}H_{28}NO_9$ 378.1764 ($M + NH_4^+$).

*4*R-*(3αβ,3aβ,4β,5α,6β,7aβ) Hexahydro-2,2-dimethyl - 4,5 - bis(phenylmethoxy) - 6 - [(phenylmethoxy)methyl] - 4*H - *furo[2,3 -* b*]pyran - 3 - ol* (**15**αβ). Data for **15**α: R_f 0.50 (1:2 EtOAc–hexane); ^1H NMR (360 MHz, $CDCl_3$); δ 7.34 (m, 15 H, Ph), 5.19 (d, 1 H, $J_{1,2}$ 4.3 Hz, H-1), 4.63–4.32 (m, 7 H, benzyl, H-7), 4.04 (bs, 1 H, OH), 3.94 (dt, 1 H, $J_{2,3}$ 1.4, $J_{3,4}$ 7.4 Hz, H-3), 3.80 (t, 1 H, J 7.2 Hz), 3.60 (m, 3 H), 2.64 (ddd, 1 H, $J_{1,2}$ 4.3, $J_{2,7}$ 4.3, $J_{2,3}$ 7.1 Hz, H-2), 1.36, 1.20 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 137.6, 136.5, 128.5 (2C), 128.4, 128.3, 128.1, 128.0, 127.8 (2C), 127.7, 127.6, 100.9, 87.9, 79.0, 76.5, 73.4, 72.3, 71.9, 71.1, 71.0, 68.3, 47.9, 28.9, 23.9. Data for **15**β: R_f 0.35 (1:2 EtOAc–hexane); IR (neat): 3445, 3031, 2930, 2867, 1497, 1455, 1366, 1275, 1207, 1111, 1067, 1028 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 7.31 (m, 15 H, Ph), 5.50 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 4.80, 4.78, 4.68, 4.56, 4.55, 4.43 (each d, 6 H, J 11.6 Hz, benzyl), 4.19 (dd, 1 H, $J_{3,4}$ 7.7, $J_{4,5}$ 7.7 Hz, H-4), 3.94 (dd, 1 H, $J_{2,3}$ 8.2, $J_{3,4}$ 8.2 Hz, H-3), 3.86 (m, 2 H), 3.68 (m, 2 H), 2.61 (ddd, 1 H, $J_{1,2}$ 5.7, $J_{2,7}$ 5.7, $J_{2,3}$ 10.9 Hz, H-2), 2.60 (bs, 1 H, OH), 1.37, 1.19 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 138.2, 137.7, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8 (2C), 127.7, 127.6, 98.4, 84.9, 77.2, 76.8, 75.6, 73.9, 73.4, 73.0, 69.4, 49.7, 27.8, 23.4, 1. (one aromatic and one aliphatic carbon not resolved); CIHRMS (*m/z*): 522.2856 ($M + NH_4^+$). Calcd for $C_{31}H_{40}NO_6$ 522.2867 ($M + NH_4^+$).

*[3*R - *(3α,3aβ,4β,5β(*R**),6aβ)] - 5 - [1,2 - Bis-(acetyloxy)ethyl]hexahydro - 2,2 - dimethyl - furo - [2,3-*b*]furan - 3,4 - diol, 4 - acetate* (**16**). $[\alpha]_D$ −18.8° (*c* 0.8, CH_2Cl_2); R_f 0.36 (2:3 EtOAc–hexane); IR (neat): 3567, 2975, 2938, 1744, 1435, 1372, 1233, 1154, 1125, 1098, 1049, 984, 953 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 5.37 (bd, 1 H, H-3), 5.19 (d, 1 H, $J_{1,2}$ 4.1 Hz, H-1), 4.74 (dd, 1 H, $J_{3,4}$ 1.9, $J_{4,5}$ 2.1 Hz, H-4), 4.08 (m, 2 H, H-6, H-6′), 4.05 (m, 1 H, H-5), 3.86 (dd, 1 H, $J_{2,7}$ 6.1, $J_{7,OH}$ 12.0 Hz, H-7), 2.46 (d, 1 H, OH), 2.45 (m, 1 H, H-2), 2.11, 2.10, 2.05 (each s, 9 H, OAc), 1.39, 1.19 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.6, 169.3, 169.1, 101.1, 87.7, 76.5, 70.2, 68.3, 66.5, 62.1, 47.2, 28.3, 23.5, 20.9, 20.8, 20.7; CIHRMS (*m/z*): 361.1488 ($M + H^+$). Calcd for $C_{16}H_{25}O_9$ 361.1498 ($M + H^+$).

*1,5-Anhydro-3,4,6-tri-*O*-acetyl-2-deoxy-2-*C*-formyl-α-*D*-arabino-hex-1-enitol* (**17**). $[\alpha]_D$ 34.7° (*c* 0.5, CH_2Cl_2); R_f 0.30 (1:1 EtOAc–hexane); IR (neat): 2963, 2924, 2853, 1748,

1682, 1634, 1424, 1372, 1032, 1229, 1194, 1125, 1032 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 9.36 (bs, 1 H, CHO), 7.46 (s, 1 H, H-1), 5.68 (bd, 1 H, H-3), 5.18 (t, 1 H, $J_{3,5}$ 3.5 Hz, H-4), 4.62 (m, 1 H, H-5), 4.47 (dd, 1 H, $J_{5,6}$ 7.7, $J_{6,6'}$ 12.2 Hz, H-6), 4.17 (dd, 1 H, H-6′), 2.09, 2.06, 2.04 (each s, 9 H, OAc); ^{13}C NMR (90 MHz, $CDCl_3$): δ 188.1, 170.3, 169.4, 169.2, 163.6, 115.7, 76.3, 65.6, 60.8, 60.6, 20.6; CIHRMS (*m*/*z*): 301.0931 (MH^+). Calcd for $C_{13}H_{17}O_8$ 301.0923 (MH^+).

1,5-Anhydro-3,4,6-tri-O-*benzyl-2-deoxy-2*-C-*formyl-α*-D-*arabino-hex-1-enitol* (**18**) *[4a].* R_f 0.12 (1:2 EtOAc–hexane); ^1H NMR (360 MHz, $CDCl_3$): δ 9.41 (s, 1 H, CHO), 7.29 (m, 15 H, Ph), 4.75–4.41 (m, 9 H), 3.84–3.77 (m, 2 H), 3.62 (dd, 1 H, $J_{5,6}$ 4.6, $J_{6,6'}$ 10.8 Hz, H-6); CIHRMS (*m*/*z*): 445.2006 (MH^+). Calcd for $C_{28}H_{29}O_5$ 445.2015 (MH^+).

1,1-Dimethyl-2-oxoethyl 3,4,6-tri-O-*acetyl-2-deoxy-α*-D-*mannopyranoside* (**19**). IR (neat): 2978, 1746, 1437, 1370, 1231, 1152, 1123, 1090, 1047, 1005, 924 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 9.53 (s, 1 H, CHO), 5.37 (m, 1 H, H-3), 5.19 (bd, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.96 (t, 1 H, $J_{3,5}$ 9.7 Hz, H-4), 4.27 (dd, 1 H, $J_{5,6}$ 5.4, $J_{6,6'}$ 12.0 Hz, H-6), 4.16 (m, 1 H, H-5), 3.98 (dd, 1 H, H-6′), 2.22 (dd, 1 H, $J_{1,2'}$ 5.3, $J_{2,2'}$ 12.8 Hz, H-2′), 2.08, 2.04, 2.01 (each s, 9 H, OAc), 1.87 (td, 1 H, $J_{1,2}$ 3.8, $J_{2,2'}$ 12.8 Hz, H-2), 1.33 (s, 6 H, 2Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 201.8, 170.7, 170.3, 169.9, 92.6, 81.2, 69.5, 68.7, 68.2, 62.4, 35.6, 21.8, 20.9, 20.8, 20.7 (2C); CIHRMS (*m*/*z*): 378.1768 ($M + NH_4^+$). Calcd for $C_{16}H_{28}NO_9$ 378.1764 ($M + NH_4^+$).

*4*R-*(3αβ,3aα,4β,5α,6β,7aβ) Hexahydro-2,2-dimethyl-4,5-bis(phenylmethoxy)-6-[(phenylmethoxy)methyl]-4*H-*furo[2,3-*b*]pyran-3-ol* (**21**). Data for one diastereomer: R_f 0.52 (1:2 EtOAc–hexane); IR (neat): 3463, 3032, 2924, 1497, 1455, 1366, 1321, 1076, 1028 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 7.30 (m, 15 H, Ph), 4.99 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.84, 4.78, 4.73, 4.69, 4.67, 4.54 (each d, 6 H, benzyl), 4.40 (d, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 3.98 (m, 2 H), 3.81 (dd, 1 H, $J_{5,6}$ 3.6, $J_{6,6'}$ 11.0 Hz), 3.71 (dd, 1 H, H-6), 3.28 (m, 1 H), 2.71 (m, 1 H), 2.62 (bs, 1 H), 1.49, 1.19 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 138.4, 138.2, 137.7, 128.7, 128.5, 128.3, 128.1, 127.9, 127.8 (2C), 127.6, 127.5, 99.4, 80.7, 77.2, 76.1, 74.9, 74.1, 73.5 (2C), 68.8, 50.0, 29.5, 23.2. (one aliphatic carbon not resolved); CIHRMS (*m*/*z*): 522.2850 ($M + NH_4^+$). Calcd for $C_{31}H_{40}NO_6$ 522.2856 ($M + NH_4^+$).

1,1-Dimethyl-2-propenyl 3,4,6-tri-O-*acetyl-2-deoxy-2-iodo-α*-D-*galactopyranoside* (**22**). Prepared from commercially available tri-*O*-acetyl-D-galactal (1 mL, 4.52 mmol) in the same manner described for **7** to give 488 mg (42% based on recovered starting material): $[\alpha]_D$ +46.1° (*c* 1.7, CH_2Cl_2); R_f 0.82 (2:3 EtOAc–hexane); IR (neat): 2978, 2928, 1750, 1497, 1455, 1370, 1231, 1105, 1028, 988, 930 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 5.81 (dd, 1 H, $J_{7,8}$ 10.7, $J_{7,8'}$ 17.5 Hz, H-7), 5.41 (bs, 1 H, H-1), 5.35 (m, 1 H), 5.20 (d, 1 H, H-8), 5.18 (d, 1 H, H-8′), 4.93 (dd, 1 H, $J_{2,3}$ 3.6, $J_{3,4}$ 4.2 Hz, H-3), 4.47 (ddd, 1 H, *J* 1.8, 6.5, 13.2 Hz), 4.12 (m, 3 H), 2.16, 2.05, 2.02 (each s, 9 H, OAc); ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.4, 170.1, 169.6, 142.3, 115.1, 98.1, 78.4, 66.4, 65.5, 65.3, 62.1, 27.8, 25.1, 23.4, 21.0, 20.9, 20.6; CIHRMS (*m*/*z*): 502.0938 ($M + NH_4^+$). Calcd for $C_{17}H_{29}INO_8$ 502.0957 ($M + NH_4^+$).

1,1-Dimethyl-2-oxoethyl 3,4,6-tri-O-*acetyl-2-deoxy-2-iodo-α*-D-*galactopyranoside* (**23**). Prepared from **22** (218 mg, 0.45 mmol) using the same procedure described for **9** to give 184 mg (84%): $[\alpha]_D$ +61.3° (*c* 1.5, CH_2Cl_2); R_f 0.60 (2:3 EtOAc–hexane); IR (neat): 2982, 1752, 1464, 1435, 1373, 1231, 1169, 1109, 1040, 992, 955, 914 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 9.44 (s, 1 H, CHO), 5.38 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1), 5.30 (dd, 1 H, $J_{2,3}$ 2.8, $J_{3,4}$ 3.0 Hz, H-3), 4.92 (t, 1 H, $J_{3,5}$ 4.0 Hz, H-4), 4.39 (m, 1 H), 4.22 (m, 1 H), 4.11 (dd, 1 H, $J_{5,6}$ 7.7, $J_{6,6'}$ 11.6 Hz, H-6), 4.01 (dd, 1 H, H-6′), 2.07, 1.99, 1.96 (each s, 9 H, OAc), 1.26, 1.25 (each s, 6 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.1, 170.5, 170.0, 169.6, 98.2, 82.0, 67.5, 65.5, 61.9, 22.2, 21.8, 21.0, 20.9, 20.7. (Two aliphatic carbons not resolved); CIHRMS (*m*/*z*): 504.0731 ($M + NH_4^+$). Calcd for $C_{16}H_{27}INO_9$ 504.0749 ($M + NH_4^+$).

Isopropyl 3,4,6-tri-O-*acetyl-2-deoxy-2*-C-*formyl-α*-D-*galactopyranoside* (**24**). Prepared from **23** (59 mg, 0.12 mmol) using Bu_3SnH

radical reaction conditions (0.01 M, 3 h) to give 18.5 mg (43%) of **24** and 14 mg (32%) of a mixture of **25** and **26**: $[\alpha]_D$ +154.5° (*c* 0.62, CH_2Cl_2); IR (neat): 2977, 2930, 1750, 1437, 1372, 1233, 1163, 1125, 1071, 1017, 950, 928 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.48 (d, 1 H, $J_{2,CHO}$ 2.7 Hz, CHO), 5.70 (dd, 1 H, $J_{3,4}$ 3.1, $J_{2,3}$ 11.8 Hz, H-3), 5.43 (bd, 1 H, H-4), 5.29 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.31 (t, 1 H, *J* 6.9 Hz), 4.09 (m, 2 H), 3.87 (septet, 1 H, H-7), 2.95 (ddd, 1 H, H-2), 2.13, 2.04, 1.98 (each s, 9 H, OAc), 1.20, 0.92 (each d, 6 H, $J_{7,Me}$ 6.1 Hz, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 198.9, 170.4, 170.2, 170.0, 95.8, 71.1, 66.9, 66.2, 66.0, 62.1, 51.4, 23.0, 21.4, 22.7, 20.6 (2C); CIHRMS (*m*/*z*): 378.1758 ($M+NH_4^+$). Calcd for $C_{16}H_{28}NO_9$ 378.1764 ($M+NH_4^+$).

*4*R - *(3αβ,3aβ,4β,5α,6β)] - 6 - [(Acetyloxy)-methyl]hexahydro-2,2-dimethyl-4*H-*furo[2,3-*b*]pyran-3,4,5-triol*, *4,5-diacetate* (**25**), *4*R-*(3αβ,3aβ,4β,5α(*R**),6aβ)] - 5 - [1,2 - bis(acetyloxy)-ethyl]-hexahydro-2,2-dimethylfuro[2,3-*b*]furan-3,4-diol*, *4-acetate* (**26**). Data for the mixture of **25** and **26**: IR (neat): 3470, 2926, 1748, 1462, 1433, 1372, 1231, 1047 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 5.66 (t, 1 H, *J* 3.7 Hz), 5.56 (d, 1 H, *J* 4.3 Hz), 5.35–3.31 (m, 3 H), 5.05 (dd, 1 H, *J* 3.0, 9.8 Hz), 4.65–3.92 (m), 2.74 (m, 1 H), 2.58 (m, 1 H), 2.11, 2.08, 2.07, 2.05, 2.04, 2.03 (each s, 18 H, OAc), 1.42, 1.27, 1.25, 1.23 (s, 12 H, Me); CIHRMS (*m*/*z*): 378.1766 ($M+NH_4^+$). Calcd for $C_{16}H_{28}NO_9$ 378.1764 ($M+NH_4^+$).

1-Phenyl-2-propen-1-ol (**27**). To a stirred solution of benzaldehyde (1 g, 9.42 mmol) in dry tetrahydrofuran (50 mL) was added dropwise vinylmagnesium bromide (1.0 M in THF, 1.9 ml, 14.3 mmol) at 0 °C. The reaction mixture was allowed to warm to rt and stirred for an additional hour before quenching with aq NH_4Cl. The reaction mixture was concentrated, diluted with ether and washed with brine several times. The organic layer was combined, dried over $MgSO_4$ and concentrated in vacuo. Flash column chromatography (1:9 EtOAc–hexane) of the resulting oil gave 0.82 g (65%) of the desired alcohol **90** as a clear oil: R_f 0.52 (1:2 EtOAc–hexane); ^1H NMR (360 MHz, $CDCl_3$): δ 7.27 (m, 5 H, Ph), 5.99 (ddd, 1 H, $J_{1,2}$ 6.0, $J_{2,3}$ 10.3, $J_{2,3'}$ 16.8 Hz, H-2), 5.27 (d, 1 H, H-3), 5.13 (d, 1 H, H-31), 5.12 (bd, 1 H, H-1), 2.23 (bs, 1 H, OH).

*1-Phenyl-2-propenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-*D*-mannopyranoside* (**28**). Prepared from **5** (28.8 g, 10.2 mmol) and **27** (1.5 g, 11.2 mmol) in the manner described for **7** to give 2.92 g (80% based on recovered starting material). Data for the mixture of diastereomers: R_f 0.36 (2:3 EtOAc–hexane); IR (neat): 3031, 2986, 2940, 1748, 1493, 1456, 1431, 1370, 1296, 1231, 1175, 1119, 1038, 945, 916 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 7.30 (m, 10 H, Ph), 5.97 (m, 1 H), 5.94 (m, 1 H), 5.42–5.16 (m, 11 H), 4.71 (dd, 1 H, $J_{2,3}$ 4.2, $J_{3,4}$ 9.4 Hz, H-3), 4.61 (m, 1 H), 4.47 (dd, 1 H, $J_{1,2}$ 1.1, $J_{2,3}$ 4.4 Hz, H-2), 4.25–4.05 (m, 4 H), 3.89 (m, 12 H), 3.82 (m, 1 H), 2.12, 2.08, 2.06, 2.05, 2.02, 1.99 (each s, 18 H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.5 (2C), 169.7, 169.4, 169.3, 139.6, 138.5, 137.7, 136.3, 128.7, 128.5, 128.4, 127.9, 127.2, 126.5, 118.6, 115.9, 99.0, 98.4, 80.3, 79.5, 69.3 (2C), 69.1, 69.0, 67.4, 67.2, 62.1, 61.8, 29.7, 29.6, 20.9, 20.8, 20.7, 20.6 (2C), 20.5; CIHRMS (*m*/*z*): 550.0920 ($M+NH_4^+$). Calcd for $C_{21}H_{29}INO_8$ 550.0938 ($M+NH_4^+$).

*1-Phenyl-2-propenyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-iodo-α-*D*-mannopyranoside* (**29**). Prepared from **6** (2.1 g, 4.9 mmol) and **27** (0.73 g, 5.42 mmol) in the manner described for **7** to yield 2 g (60%). Data for the mixture of diastereomers: R_f 0.68 (1:6 EtOAc–hexane); IR (neat): 3088, 3063, 3031, 2865, 1605, 1497, 1455, 1362, 1308, 1291, 1265, 1208, 1113, 1028, 932, 912 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 7.36 (m, 40 H, Ph), 5.98 (dd, 1 H, *J* 6.1, 10.4 Hz), 5.95 (dd, 1 H, *J* 6.2, 10.3 Hz), 5.84 (dd, 1 H, *J* 7.7, 10.1 Hz), 5.79 (dd, 1 H, *J* 7.7, 9.9 Hz), 5.48–4.47 (m, 19 H), 3.98 (m, 4 H), 3.87–3.58 (m, 5 H), 3.46 (dd, 1 H, *J* 4.1, 8.2 Hz), 3.36 (dd, 1 H, *J* 4.1, 8.7 Hz); ^{13}C NMR (90 MHz, $CDCl_3$): δ 140.2, 139.3, 138.5, 138.3, 138.2, 137.9, 137.8, 136.7, 128.5 (2C), 128.4 (2C), 128.3 (2C), 128.2 (2C), 127.9 (2C), 127.8, 127.7, 127.6, 127.5, 126.8, 126.7, 118.8, 115.8, 99.3, 99.0, 98.8, 85.9, 80.4, 79.5, 78.9, 77.6, 77.2, 76.2, 75.5 (2C), 75.4, 75.3, 74.9, 73.5, 73.4 (2C), 72.6 (2C), 71.1 (2C), 68.9, 68.8, 68.6, 60.4, 34.0, 33.9, 21.1, 14.3. (Several carbons not resolved); CIHRMS (*m*/*z*): 675.1627 (M − H). Calcd for $C_{36}H_{36}IO_5$ 675.1608 (M − H).

1-Phenyl-2-oxoethyl 3,4,6-tri-O-*acetyl-2-deoxy-2-iodo-α*-D-*mannopyranoside* (**30**). Prepared from **28** (0.10 g, 0.19 mmol) using the same procedure described for **9** to yield 76 mg (74%): IR of mixture (neat): 2937, 1746, 1494, 1455, 1370, 1232, 1124, 1061, 913 cm^{-1}; Data for one of the diastereomers: ^1H NMR (360 MHz, $CDCl_3$): δ 9.61 (bs, 1 H, CHO), 7.42 (m, 5 H, Ph), 5.46 (bs, 1 H, H-1), 5.38 (t, 1 H, $J_{3,5}$ 9.8 Hz, H-4), 5.11 (bs, 1 H, H-7), 4.81 (dd, 1 H, $J_{1,2}$ 1.2, $J_{2,3}$ 4.4 Hz, H-2), 4.65 (dd, 1 H, $J_{2,3}$ 4.4, $J_{3,4}$ 9.6 Hz, H-3), 4.06 (dd, 1 H, H-6), 3.89 (dd, 1 H, H-6′), 3.77 (ddd, 1 H, H-5), 2.09, 2.07, 2.00 (each s, 9 H, OAc); ^{13}C NMR (90 MHz, $CDCl_3$): δ 196.3, 170.5, 169.8, 169.4, 132.7, 129.4, 129.3, 127.7, 101.3, 83.6, 70.0, 68.7, 67.3, 61.8, 28.5, 20.9, 20.7, 20.6. Data for one of the diastereomers: ^1H NMR (360 MHz, $CDCl_3$): δ 9.64 (d, 1 H, J 1.7 Hz, CHO), 7.42 (m, 5 H, Ph), 5.40 (t, 1 H, $J_{3,5}$ 9.4 Hz, H-4), 5.20 (d, 1 H, J 1.4 Hz, H-1 or H-7), 4.99 (d, 1 H, J 1.4 Hz, H-1 or H-7), 4.77 (dd, 1 H, $J_{2,3}$ 4.4, $J_{3,4}$ 9.3 Hz, H-3), 4.62 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 4.3 Hz, H-2), 4.21 (m, 3 H, H-5, H-6, H-6′), 2.13, 2.10, 2.09 (each s, 9 H, OAc); ^{13}C NMR (90 MHz, $CDCl_3$): δ 195.8, 170.6, 169.8, 169.5, 132.3, 129.6, 129.4, 127.7, 99.6, 83.8, 70.0, 69.0, 67.3, 62.1, 28.4, 20.9, 20.7, 20.6; CIHRMS (m/z): 552.0720 ($M + NH_4^+$). Calcd for $C_{20}H_{27}INO_9$ 552.0731 ($M + NH_4^+$).

1-Phenyl-2-oxoethyl 3,4,6-tri-O-*benzyl-2-deoxy-2-iodo-α*-D-*mannopyranoside* (**31**). Prepared from **29** (570 mg, 0.84 mmol) using the same procedure described for **9** to yield 425 mg (74%). Data for one of the diastereomers: ^1H NMR (360 MHz, $CDCl_3$): δ 9.60 (s, 1 H, CHO), 7.36 (m, 20 H, Ph), 5.54 (bs, 1 H), 5.21 (s, 1 H), 4.85, 4.78, 4.68, 4.58, 4.50, 4.49 (each d, 6 H, J 10.6 Hz, benzyl), 4.82 (dd, 1 H, J 1.2, 4.2 Hz), 3.95 (t, 1 H, J 9.4 Hz), 3.73 (m, 2 H), 3.58 (m, 1 H), 3.37 (dd, 1 H, J 4.1, 8.7 Hz). Data for one of the diastereomers: ^1H NMR (360 MHz, $CDCl_3$): δ 9.60 (d, 1 H, J 1.4 Hz, CHO), 7.36 (m, 20 H, Ph), 5.26 (d, 1 H, J 1.1 Hz), 5.04 (d, 1 H, J 1.5 Hz), 4.89, 4.76, 4.74, 4.61, 4.56, 4.52 (each d, 6 H, J 10.7 Hz, benzyl), 4.58 (d, 1 H, J 1.6 Hz), 4.02 (m, 2 H), 3.82 (dd, 1 H, $J_{5,6}$ 4.5, $J_{6,6'}$ 10.9 Hz, H-6), 3.75 (dd, 1 H, J 1.5, 10.9 Hz), 3.51 (dd, 1 H, J 4.1, 8.2 Hz). Data of the mixture of diastereomers: IR (neat): 3031, 2924, 1734, 1497, 1455, 1362, 1267, 1101, 1028 cm^{-1}; ^{13}C NMR (90 MHz, $CDCl_3$): δ 197.0, 196.4, 138.2, 138.0, 137.9, 137.5, 132.6, 129.3, 129.2, 129.1 (2C), 128.4 (3C), 128.3(2C), 128.2, 128.1 (2C), 128.0, 127.8 (2C), 127.6 (2C), 127.5 (2C), 101.1, 99.6, 83.2, 82.7, 76.8, 76.5, 75.8, 75.7, 75.4, 75.3, 73.4, 73.3, 73.0, 72.8, 71.2, 71.0, 68.6, 68.5, 32.5, 29.7. (Several carbons not resolved); CIHRMS (m/z): 696.1805 ($M + NH_4^+$). Calcd for $C_{35}H_{39}INO_6$ 696.1822 ($M + NH_4^+$).

Benzyl 3,4,6-tri-O-*acetyl-2-deoxy-2*-C-*formyl-α*-D-*glucopyranoside* (**32**). Prepared from **30** (75 mg, 0.14 mmol) using Bu_3SnH (0.046 mL, 0.17 mmol) radical reaction conditions (0.60 M, 3 h) to yield 28.5 mg (50%): $[\alpha]_D$ + 141.9° (c 0.0016, CH_2Cl_2); IR (neat): 3034, 2957, 1748, 1455, 1433, 1370, 1229, 1125, 1024, 922 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.51 (d, 1 H, $J_{2,CHO}$ 2.4 Hz, CHO), 7.33 (m, 5 H, Ph), 5.81 (t, 1 H, $J_{3,5}$ 9.7 Hz, H-4), 5.23 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 5.05 (t, 1 H, $J_{2,4}$ 9.7 Hz, H-3), 4.68, 4.52 (each d, 2 H, J 11.9 Hz, benzyl), 4.30 (dd, 1 H, $J_{5,6}$ 4.2, $J_{6,6'}$ 12.1 Hz, H-6), 4.06 (m, 2 H, H-5, H-6′), 2.84 (ddd, 1 H, $J_{2,CHO}$ 2.7, $J_{1,2}$ 3.6, $J_{2,3}$ 8.4 Hz, H-2), 2.11, 2.04, 2.00 (each s, 9 H, OAc); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.8, 170.5, 170.1, 169.7, 135.9, 128.5, 128.2, 128.0, 95.7, 69.8, 68.7, 67.9, 61.8, 56.6, 30.8, 20.6 (2C), 20.5; CIHRMS (m/z): 426.1752 ($M + NH_4^+$). Calcd for $C_{20}H_{28}NO_9$ 426.1764 ($M + NH_4^+$).

Benzyl 3,4,6-tri-O-*benzyl-2-deoxy-2*-C-*formyl-α*-D-*glucopyranoside* (**33**). Prepared from **31** (76.5 mg, 0.112 mmol) using Bu_3SnH (0.03 mL, 0.112 mmol) radical reaction conditions (0.01 M, 3 h) to yield 26 mg (84% based on recovered starting material): $[\alpha]_D$ + 96.6° (c 0.4, CH_2Cl_2); R_f 0.52 (1:2 EtOAc–hexane); IR (neat): 3032, 2924, 2853, 1727, 1497, 1455, 1360, 1273, 1125, 1059, 1026 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 9.51 (d, 1 H, $J_{2,CHO}$ 2.6 Hz, CHO), 7.35–7.17 (m, 20 H, Ph), 5.20 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.90–4.45 (m, 8 H, benzyl), 4.39 (dd, 1 H, $J_{3,4}$ 8.8, $J_{4,5}$ 8.9 Hz, H-4), 3.90–3.87 (m, 1 H), 3.78 (m, 2 H), 3.66 (dd, 1 H, J 1.9, 10.6 Hz), 2.78 (ddd, 1 H, $J_{2,CHO}$ 2.6, $J_{1,2}$ 3.8, $J_{2,3}$ 6.5 Hz, H-2); ^{13}C NMR (90 MHz, $CDCl_3$): δ 199.4, 138.2, 138.0, 137.8, 136.9, 128.5 (2C), 128.4 (2C), 127.9, 127.8 (3C), 96.5, 79.1, 76.5, 75.0, 74.9, 73.6, 71.2, 69.3, 68.3, 58.6. (Several aromatic car-

bons not resolved); CIHRMS (m/z): 551.2448 ($M^+ - H$). Calcd for $C_{35}H_{35}O_6$ 551.2434 ($M^+ - H$).

1-Cyano-1-methylethyl 3,4,6-tri-O-*acetyl-2-deoxy-2-iodo-α*-D-*mannopyranoside* (**34**). Prepared from **5** (2 g, 7.35 mmol) and acetone cyanohydrin (2.68 mL, 29.4 mmol) in the manner described for **7** to yield 1.4 g (82% based on recovered starting material): $[\alpha]_D$ +4.26° (*c* 10.8, CH_2Cl_2); R_f 0.48 (1:1 EtOAc–hexane); IR (neat): 2994, 2963, 2942, 2200, 1748, 1435, 1372, 1221, 1167, 1119, 1084, 1032, 1007, 916 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 5.55 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 5.37 (t, 1 H, $J_{3,5}$ 9.6 Hz, H-4), 4.56 (dd, 1 H, $J_{2,3}$ 4.3, $J_{3,4}$ 9.3 Hz, H-3), 4.46 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 4.3 Hz, H-2), 4.23–4.10 (m, 3 H, H-5, H-6, H-6′), 2.07, 2.06, 2.03 (each s, 9 H, OAc), 1.64, 1.63 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.5, 169.8, 169.3, 120.0, 98.5, 70.5, 70.1, 68.6, 67.2, 61.8, 28.8, 27.9, 26.6, 20.9, 20.6 (2C); CIHRMS (m/z): 501.0716 ($M + NH_4^+$). Calcd for $C_{16}H_{26}IN_2O_8$ 501.0734 ($M + NH_4^+$).

1-Cyano-1-methylethyl 3,4,6-tri-O-*benzyl-2-deoxy-2-iodo-α*-D-*mannopyranoside* (**35**). Prepared from **6** (1.22 g, 2.93 mmol) and acetone cyanohydrin (1.5 mL, 14.7 mmol) in the manner described for **7** to yield 0.78 g (42%): $[\alpha]_D$ +20.0° (*c* 1.0, CH_2Cl_2); R_f 0.43 (1:2 EtOAc–hexane); IR (neat): 3088, 3063, 3031, 2992, 2919, 2867, 1497, 1455, 1364, 1293, 1267, 1208, 1171, 1113, 1028, 999 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 7.43–7.15 (m, 15 H, Ph), 5.65 (bs, 1 H, H-1), 4.85 (d, 1 H, *J* 10.5 Hz, benzyl), 4.76–4.70 (m, 2 H), 4.55–4.44 (m, 4 H), 4.04–3.95 (m, 1 H), 3.82 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.8 Hz, H-3), 3.73 (dd, 1 H, *J* 1.5, 11.0 Hz), 3.28 (dd, 1 H, *J* 4.1, 7.6 Hz), 1.63, 1.60 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 138.2, 138.0, 137.5, 128.4 (2C), 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 120.4, 98.9, 76.5, 75.6, 75.3, 73.4, 73.2, 71.0, 70.4, 68.3, 32.8, 27.7, 27.2; CIHRMS (m/z): 645.1841 ($M + NH_4^+$). Calcd for $C_{31}H_{38}IN_2O_5$ 645.1826 ($M + NH_4^+$).

1-Methylethyl 3,4,6-tri-O-*acetyl*-C-*cyano-2-deoxy-2-α*-D-*glucopyranoside* (**36**). Prepared from **34** (122 mg, 0.25 mmol) using Bu_3SnH (0.08 mL, 0.28 mmol) radical reaction conditions (0.13 M, 2 h) to yield 26 mg (30%) of **36** and 26 mg (30%) of **37**: $[\alpha]_D$ +187.5° (*c* 0.08, CH_2Cl_2); IR (neat): 2977, 2932, 2255, 1752, 1456, 1372, 1227, 1119, 1047, 959, 924 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.58 (t, 1 H, $J_{2,4}$ 9.3 Hz, H-3), 5.20 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.93 (t, 1 H, $J_{3,5}$ 9.8 Hz, H-4), 4.27 (dd, 1 H, $J_{5,6}$ 4.5, $J_{6,6'}$ 12.3 Hz, H-6), 4.13 (ddd, 1 H, *J* 2.2, 4.4, 10.2 Hz), 4.06 (m, 1 H), 3.98 (septet, 1 H, H-7), 3.07 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 11.3 Hz, H-2), 2.04, 2.03, 2.01 (each s, 9 H, OAc), 1.27, 1.25 (each d, 6 H, $J_{7,Me}$ 6.1 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 169.6, 169.4, 115.1, 94.0, 77.1, 72.3, 68.3 (2C), 67.8, 61.6, 38.8, 30.8, 22.9, 21.3, 20.5; CIHRMS (m/z): 375.1763 ($M + NH_4^+$). Calcd for $C_{16}H_{27}N_2O_8$ 375.1767 ($M + NH_4^+$).

1-Cyano-1-methylethyl 3,4,6-tri-O-*acetyl-2-deoxy-α*-D-*glucopyranoside* (**37**). IR (neat): 2994, 2963, 1746, 1441, 1370, 1304, 1233, 1173, 1154, 1123, 1088, 1049, 1017, 1003 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): δ 5.42 (bd, 1 H, $J_{1,2}$ 2.2 Hz, H-1), 5.30 (m, 1 H, H-3), 5.02 (t, 1 H, $J_{3,5}$ 9.8 Hz, H-4), 4.34 (dd, 1 H, $J_{5,6}$ 4.2, $J_{6,6'}$ 12.2 Hz, H-6), 4.13–4.04 (m, 2 H, H-5, H-6′), 2.19 (m, 1 H, H-2), 2.07, 2.04, 2.01 (each s, 9 H, OAc), 1.91 (m, 1 H, H-2′), 1.65, 1.64 (each s, 6 H, Me); ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.6, 170.2, 169.8, 120.5, 94.2, 70.0, 69.0, 68.9, 68.5, 61.9, 35.4, 28.1, 26.7, 20.9, 20.7 (2C); CIHRMS (m/z): 375.1758 ($M + NH_4^+$). Calcd for $C_{16}H_{27}N_2O_8$ 375.1767 ($M + NH_4^+$).

Acknowledgements

This work was supported in part by the Camille and Henry Dreyfus Faculty Start-up Grant for Undergraduate Institutions. S.W.T.C. would like to thank B.S. Safina and J.N. Bashara for their contributions to the work with mandelonitrile.

References

[1] (a) D.H.R. Barton, P. Dalko, S.D. Gero, *Tetrahedron Lett.*, 32 (1991) 2471–2474. (b) K. Tatsuta, Y. Niwata, K. Umezawa, K. Toshima, M. Nakata, *Tetrahedron Lett.*, 31 (1990) 1171–1172. (c) S. Atsumi, H. Iinuma, C. Nosaka, K. Umezawa, *J. Antibiot.*, (1990) 1579–1585.

[2] M.E. Jung, S.W.T. Choe, *J. Org. Chem.*, 60 (1995) 3280–3281.

[3] (a) B. Giese, *Angew. Chem., Int. Ed. Engl.*, 22 (1983) 753–764. (b) B. Giese, *Pure Appl. Chem.*, 60 (1988) 1655–1658. (c) D.P. Curran, J. Tamine, *J. Org. Chem.*, 56 (1991) 2746–2750.
[4] (a) N.G. Ramesh, K.K. Balasubramanian, *Tetrahedron Lett.*, 32 (1991) 3875–3878. (b) J.C. Lopez, E. Lameignere, G. Lukacs, *J. Chem. Soc., Chem. Commun.*, (1988) 514–515.
[5] V. Gupta, D. Kahne, *Tetrahedron Lett.*, 34 (1993) 591–593.
[6] M.E. Jung, S.W.T. Choe, *Tetrahedron Lett.*, 34 (1993) 6247–6250.
[7] (a) R. Tsang, J.K. Dickson, H. Pak, R. Walton, B. Fraser-Reid, *J. Am. Chem. Soc.*, 109 (1987) 3484–3486. (b) R. Tsang, B. Fraser-Reid, *J. Am. Chem. Soc.*, 108 (1986) 2116–2117. (c) B. Fraser-Reid, G.D. Vite, B.W.A. Yeung, R. Tsang, *Tetrahedron Lett.*, 29 (1988) 1645–1648.
[8] (a) S.H. Chen, R.F. Horvath, J. Joglar, M.J. Fisher, S.J. Danishefsky, *J. Org. Chem.*, 56 (1991) 5834–5845. (b) J. Thiem, H. Karl, J. Schwentner, *Synthesis*, (1978) 696–698.
[9] (a) C. Chatgilialoglu, M. Ballestri, K.B. Clark, D. Griller, B. Giese, B. Kopping, *J. Org. Chem.*, 56 (1991) 678–683. (b) C. Chatgilialoglu, D. Griller, M. Lesage, *J. Org. Chem.*, 54 (1989) 2492–2494. (c) B. Giese, B. Kopping, *Tetrahedron Lett.*, 30 (1989) 681–684.
[10] H. Suginome, S. Yamada, *Tetrahedron*, 43 (1987) 3371–3386.
[11] R.W. Binkley, D.J. Kolohic, *J. Org. Chem.*, 44 (1979) 2047–2048.
[12] D.P. Curran, C.M. Seong, *Tetrahedron*, 48 (1992) 2175–2190.