The Cobalt-Catalyzed Oxygenative Radical Route from Hexopyranosides to Carbapentofuranoses

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Cobalt-catalyzed radical cyclization/oxygenation of various 6-iodohex-1-enitols gave in one step the carbocyclic analogs of pentofuranoses. The reaction was run under very mild conditions and gave moderate to good yields of carbapentofuranoses within a few hours. All the possible 6-iodohex-1-enitol stereoisomers were prepared, and the influence of relative configurations and protecting groups was studied.

Introduction

Carbocyclic analogs of pentofuranoses[1−5] and nucleosides[1,6] are biologically important products, exhibiting enzyme inhibitor activities[7,8] or antiviral and antibiotic properties.[1,9] Synthetic studies geared towards the elaboration of these polyoxygenated cyclopentanes have been described, starting from sugar precursors,[10−17] or from non-carbohydrate materials.[8,18−23] For the approach to carbasugars from non-carbohydrate starting materials, diastereo- and enantioselective methods for the sequential introduction of the oxygenated substituents are required. On the other hand, carbohydrates already have the polyoxygenated substitution pattern and are available in enantiomerically pure form, but manipulation of protective groups and formation of the carbocycle can be lengthy. The first synthesis of all stereoisomeric carbafuranoses, some of them in enantiopure form, from a single precursor − norborn-5-en-2-one − has been reported.[24] Other methodologies relevant to the synthesis of polyoxygenated cyclopentanes from carbohydrates, using samarium diiodide, have also been described.[25−29]

Our strategy for the synthesis of carbafuranosides from carbohydrates relies on the reductive ring-opening of *O*-protected 6-deoxy-6-iodohexopyranosides with zinc, as reported by Vasella[30,31] (Figure 1), and further elaboration of the aldehyde function of the open-chain sugar to a radical precursor group. Cobalt-catalyzed radical cyclization with molecular oxygen[32,33] of the 6-iodohex-1-enitol would then give the required hydroxymethyl-substituted cyclopentane core of the carbafuranoses in one step.[34]

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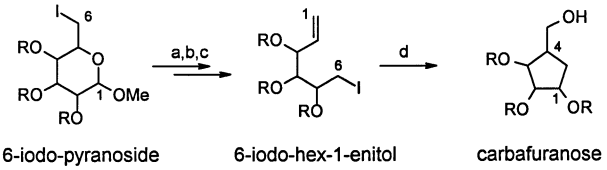

Figure 1. From hexopyranosides to carbafuranoses: a: zinc-catalyzed opening reaction; b: $NaBH_4$ reduction; c: iodation; d: cobalt-catalyzed oxygenative radical cyclization

All the possible relative configurational isomers of 1,2-dideoxyhex-1-enitols were studied; they could be conveniently prepared from readily available D-hexopyranosides. Thus, reductive ring-opening of 6-deoxy-6-iodo-α-D-*gluco*-hexopyranoside **1** (Figure 2) followed by reduction of the aldehyde group gave 1,2-dideoxyhex-1-enitol **16** (Figure 3) with the L-*xylo* configuration. In an analogous manner, 1,2-dideoxyhex-1-enitols in the L-*lyxo*, D-*arabino*, and L-*ribo* series are available from D-*galacto*-, D-*manno*-, and D-*allo*-hexopyranosides, respectively. Furthermore, in order to improve some cyclization yields, and to look at the influence of the protecting groups on the stereochemical outcome of the radical cyclization reaction, conformational restrictions were introduced on some substrates. Hence, methylethylidene-protected 6-iodohex-1-enitols **29**, **30**, and **32** were synthesized and cyclized. The acetamido-hexenitol **34** was prepared from D-glucosamine; cyclization of compounds of this class would give a new entry into the synthesis of carbanucleosides.[13]

Preparation of 1,2,6-Trideoxy-6-iodohex-1-enitols

Preparation of 6-Deoxy-6-iodohexopyranosides

Iodination of methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexopyranoside[35] with iodine and triphenylphosphane[36] proceeded in 80% yield and gave iodide **1**.

Selective monotritylation[37] (trityl chloride, DMAP, pyridine, 77%) of methyl β-D-*allo*-pyranoside[38] **2** followed by perbenzylation and trityl ether hydrolysis (formic acid, diethyl ether) gave methyl 2,3,4-tri-*O*-benzyl-β-D-*allo*-pyrano-

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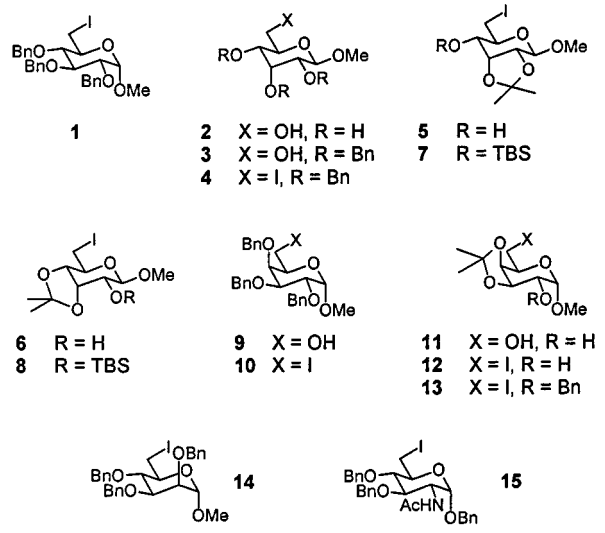


Figure 2. Hexopyranosides **1**−**15**

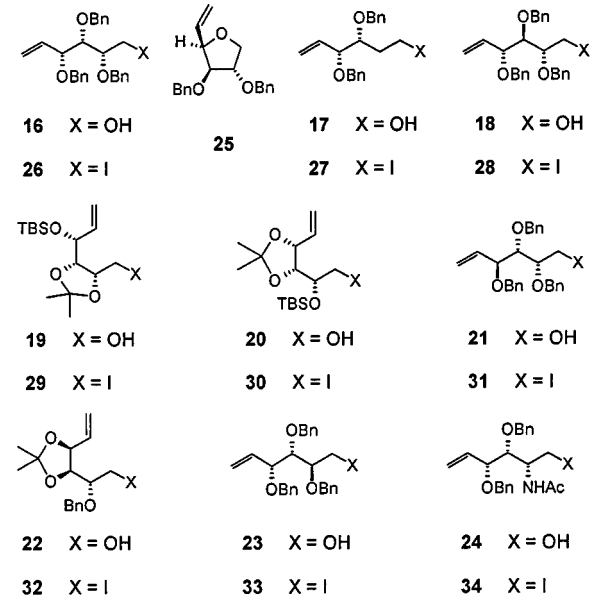


Figure 3. Hex-1-enitols **16**−**34**

side **3** (55%, 2 steps), which was iodinated as above to give methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-β-D-*allo*-pyranoside **4** in high yield (87%).

For the synthesis of 1,2,6-trideoxy-6-iodo-L-*ribo*-hex-1-enitols **29** and **30**, compound **2** was treated with 2,2-dimethoxypropane and camphorsulfonic acid in DMF, and the mixture of 2,3- and 3,4-*O*-methylethylidene-protected β-D-*allo*-pyranosides was directly iodinated. Thus, we isolated 30% of 6-deoxy-6-iodo-2,3-*O*-methylethylidene-β-D-*allo*-pyranoside **5**, and 20% of the 3,4-regioisomer **6** after chromatography. The 4-hydroxy group of **5** was then protected as the *tert*-butyldimethylsilyl ether and gave compound **7** in 90% yield. In a similar manner, **8** was obtained in 89% yield from the silylation of **6**.

Starting from methyl α-D-*galacto*-pyranoside, the 2,3,4-tri-*O*-benzyl-protected compound **9** was obtained in four steps and 68% overall yield according to literature procedures.[39,40] Iodination as above gave methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-α-D-*galacto*-pyranoside **10** in 71% yield.

For the synthesis of the conformationally rigid methylethylidene-hexenitol **22**, methyl 3,4-*O*-methylethylidene-α-D-*galacto*-pyranoside **11**[41] was selectively iodinated at the 6-position (58%) and the 2-hydroxy group of iodide **12** was then benzylated (NaH, BnBr) to give **13** in 96% yield.

The last configurational isomer **14** was prepared in 76% yield by iodination of methyl 2,3,4-tri-*O*-benzyl-α-D-*manno*-pyranoside.[35]

Finally, benzyl 2-acetamido-3,4-*O*-dibenzyl-2,6-dideoxy-6-iodo-α-D-*gluco*-pyranoside **15** was obtained from benzyl 2-acetamido-2-deoxy-α-D-*gluco*-pyranoside[42] by the four-step sequence described above for the preparation of **4**: tritylation at the 6-position (86%), benzylation of the secondary hydroxy groups (80%), detritylation (71%), and iodination at the 6-position (84%).

Preparation of 1,2,6-Trideoxy-6-iodohex-1-enitols

The ring-opening of 6-deoxy-6-iodo sugars was carried out using activated zinc in refluxing aqueous ethanol according to the procedure of Vasella.[30,31] The crude extract from this reaction was immediately reduced with $NaBH_4$ in ethanol, and the hexenitols were isolated by chromatography. In the cases of compounds **7**, **8**, and **13** (see Figure 2), good yields of hexenitols could only be achieved when 10 equivalents of pyridine were added to the zinc reaction. Results are summarized in Table 1. For unclear reasons, the opening of the mannose derivative **14** proved to be sluggish despite being mentioned in the literature.[28] The glucosamine derivative **15** gave a moderate yield of the expected hexenitol **24**, and considerable degradation of the reaction products was observed. As already mentioned by Vasella, small amounts of hexenitols lacking the 5-benzyloxy group were observed in some reactions; up to 25% of the deoxygenated product **17** was isolated from the zinc-promoted opening of **1**. This compound was also used in the radical cyclization.

The hex-1-enitols were then converted into substrates for radical cyclization, by transformation of their primary hydroxy groups into iodides. Direct substitution of the hydroxy group of **16** with triphenylphosphane/iodine[36] (procedure A) was plagued by competitive intramolecular attack by the oxygen atom of the C-3 benzyloxy group,[43] resulting in the formation of the tetrahydrofuran **25** (30%, Figure 3), together with 35% of the expected product **26**. A two-step sequence was investigated (procedure B); alcohol **16** was tosylated (tosyl chloride, pyridine, 80%) and the tosylate was then displaced with a large excess of sodium iodide in HMPA at 60 °C to give the required 3,4,5-tri-*O*-benzyl-1,2,6-trideoxy-1-iodo-L-*xylo*-hex-1-enitol **26** in an acceptable yield of 50%. Although the improvement with this substrate was only marginal (40% overall instead of 35% with procedure A), this two-step procedure proved to give much higher yields for other compounds and was used for all benzyl-protected hexenitols as well as for compound **19**. 3,4-Ketal-protected compounds **20** and **22** were directly

Table 1. Synthesis of 6-deoxy-6-iodohex-1-enitols

6-Iodohexopyranoside	Reflux time [h][a]	Hexenitol (yield in %)[b][c]	Iodination procedure[d]	Iodohexenitol (yield in %)[b]
1	1.5	**16** (70)	B	**26** (40)
		17 (25)	B	**27** (46)
4	2.5	**18** (65)	B	**28** (77)
7	0.5	**19** (87)	B	**29** (59)
8	0.5	**20** (78)	A	**30** (98)
10	2	**21** (73)	B	**31** (61)
13	1.5	**22** (60)	A	**32** (92)
14	2	**23** (48)	B	**33** (63)
15	2.5	**24** (38)	A	**34** (70)

[a] Reflux time for the ring-opening reaction with zinc. – [b] Isolated yields of homogeneous products, see experimental Section. – [c] Yields for the two-steps sequence: ring-opening and $NaBH_4$ reduction. – [d] A and B refer to procedures A and B respectively, see text.

iodinated in high yield, as the presence of the methylethylidene group precluded any competitive attack by the C-3 oxygen atom (see Table 1). Surprisingly, and in sharp contrast with the results obtained with **16**, nucleophilic displacement by sodium iodide of the tosylate derived from **24** could not be achieved even under forcing conditions (HMPA, 120 °C). Iodohexenitol **34** was eventually obtained by direct iodination[36] of **24**, the yield was 70% and no tetrahydrofuran product was isolated.

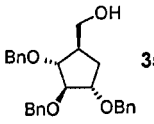
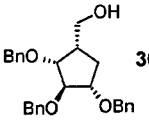
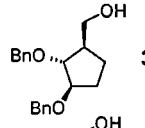
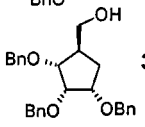
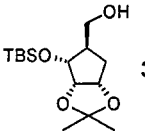
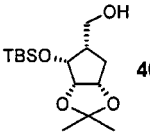
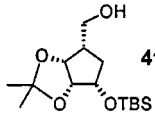
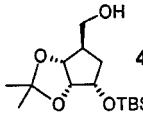
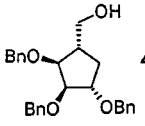
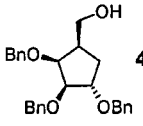
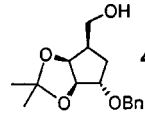
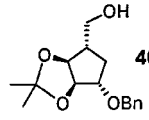
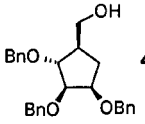
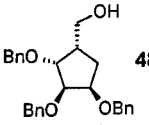
Synthesis of Carbafuranoses

Radical Cyclization/Oxygenation of 6-Iodohex-1-enitols

6-Iodohex-1-enitols were treated at 40 °C in ethanol with a catalytic amount of cobalt(salen) complex[44] (3–5%) under air.[32,33] Radical cyclization followed by oxygenation of the cyclized radical took place and a mixture of carbafuranosides were obtained in moderate to good yield (see Table 2). Only products of 5-*exo* cyclization[45] were observed and the main by-product was the hexenitol resulting from oxygenation of the uncyclized radical; some starting material and very small amounts of reduced compounds were also observed in some reactions.

Assignment of the stereochemistry of the products was performed by ^1H NMR spectroscopy and comparison, when possible, with known compounds. When benzyl protecting groups were the only ones present, the major cyclized product had the 3- and 4-substituents (see Figure 1 for numbering) in a *trans* relationship in every case, in full agreement with the rules proposed by Babu,[46] which favor a pseudo-chair transition state for the radical closure. Cyclisation of the hexenitols **26** and **27**, in which all benzyloxy groups were able to occupy pseudo-equatorial positions in the transition state, gave higher selectivities than that of hexenitols **31** and **33**, in which one benzyloxy group is forced into a pseudo-axial position. The case of 6-iodo-hexenitols with the L-*ribo* configuration is worth commenting upon. The tri-*O*-benzyl-protected compound **28** gave only 35% of carbafuranose **38**, but as a single isomer, together with 25% of hexenitol **18**. In this case, the cyclization rate of the intermediate radical is not high enough, and competitive radical oxygenation occurs prior to cyclization. When positions 4 and 5 of the L-*ribo*-hexenitol were constrained with a methylethylidene group, as in **29**, a better cyclization yield (50%) was obtained, once again with high selectivity, for the 3,4-*trans* compound **39**. Further improve-

Table 2. Cyclization/oxygenation of 6-iodo-6-deoxyhex-1-enitols

s.m.	time	products/yield			
26	20 h	 **35**	 **36**	69%	12/1
27	6 h	 **37**	**17**	57%	4/1
28	20 h	 **38**	35% **18**	25%	
29	16 h	 **39**	 **40**	50%	10/1
30	2.5 h	 **41**	 **42**	74%	1/1
31	5 h	 **43**	 **44**	50%	4/1
32	4 h	 **45**	 **46**	80%	1.2/1
33	6 h	 **47**	 **48**	33%	4/1
34	48 h	no reaction			

ment of the yield of carbafuranoses (75%) was observed in the cyclization of the 3,4-restricted L-*ribo*-hexenitol **30**, but at the expense of the selectivity, which was completely lost (1:1).

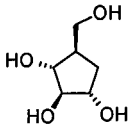
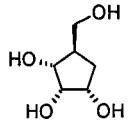
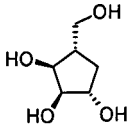
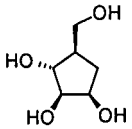
The very same effect was observed with hexenitols in the L-*lyxo* series **31** and **32**. A much higher yield of carbafuranoses was obtained from the cyclization of compound **32**, constrained at positions 3 and 4 (80% instead of 50% with **31**), but with concomitant loss of stereoselectivity. Compound **32** is the only case in which the major product of the cyclization was the 3,4-*cis* product, although the excess was modest (1.2:1). These results could also be rationalized by examination of examples found in the literature on radical cyclization of products of this type.[47,48] Low selectivities were obtained and no preference for a chair versus a boat transition state was observed for 1,2-disubstituted double bonds of (*Z*) configuration.

Iodohexenitol **34** could not be cyclized under any conditions we tried, and the starting material was recovered at the end of the reaction. This compound was also completely unreactive towards the tributyltin hydride/air system;[33,49] once again, **34** was recovered and formation of the radical from the primary iodide could not be achieved.

Preparation of Carbafuranoses

Carbapentofuranoses were obtained in high yield from compounds **35**, **39**, **43**, and **47** after deprotection (see Table 3). Benzyl groups were hydrogenolyzed in the presence of 10% palladium on charcoal in methanol, while *tert*-butyldimethylsilyl and acetal groups were removed in one step using dilute methanolic HCl. All carbafuranoses are known products and gave spectral data in full agreement with the literature (see Experimental Section).

Table 3. Synthesis of carbafuranoses

s.m.	carbafuranose	yield	$[\alpha]_D^{20}$
35	 **49**	85%	+45 (*c* 1.08, MeOH)
39	 **50**	91%	$[\alpha]_D^{20}$ +30 (c 0.80, MeOH)
43	 **51**	99%	$[\alpha]_D^{20}$ -4 (c 1.70, MeOH)
47	 **52**	98%	$[\alpha]_D^{20}$ +4 (c 1.00, MeOH)

Conclusion

The cobalt-catalyzed radical cyclization/oxygenation sequence[32,33] was successfully applied to the efficient preparation of the carbocyclic analogs of pentofuranoses from 6-iodohex-1-enitols, easily available from common hexopyranosides. Further work is in progress towards the extension of this methodology to the synthesis of carbanucleosides.

Experimental Section

General: All reactions were performed under standard anhydrous conditions under argon, reagents were used as received, and solvents were distilled under argon just before use. Chromatographic separations were performed on 35−70 μm silica. − NMR spectra were recorded with Bruker AM 250 and Avance DPX 250 spectrometers, working at 250 MHz for ^{1}H and 62.89 MHz for ^{13}C; chemical shifts (δ) are expressed in ppm from internal tetramethylsilane. − Optical rotations were measured with a Perkin−Elmer 41 polarimeter. − Mass spectra were recorded with a Ribermag R10−10 spectrometer (chemical ionization with ammonia CI/NH_3) at the University of Orleans (France). Analytical data were obtained from the Service Central de Microanalyse du CNRS at Vernaison (France) and from the Laboratoire de Chimie de Coordination at Toulouse (France).

Methyl 2,3,4-Tri-*O*-benzyl-β-D-*allo*-pyranoside (3): A solution of methyl β-D-*allo*-pyranoside (750 mg, 3.86 mmol) in CH_2Cl_2/pyridine (2:1, v/v, 12 mL) was treated with trityl chloride (1.60 g, 5.79 mmol) and 4-dimethylaminopyridine (25 mg, 0.19 mmol) for 14 h at room temperature. The solvents were evaporated, the residue was coevaporated once with toluene and taken up in CH_2Cl_2. The organic phase was washed with water and dried. Filtration on silica (petroleum ether/ethyl acetate, 1:6) and concentration gave a white foam (1.37 g) which was dissolved in DMF (4 mL) and treated at 0 °C with benzyl bromide (1.40 mL, 11.77 mmol) and NaH (420 mg of a 60% dispersion in mineral oil, 10.50 mmol). After warming to room temperature, the mixture was left overnight, neutralized with methanol, and concentrated. The crude product from CH_2Cl_2/water extraction was dissolved in formic acid/diethyl ether (1:1, v/v, 12 mL) and left at room temperature for 10 h before dilution with ether. The organic phase was washed with saturated $NaHCO_3$ and dried. Chromatography (petroleum ether/ethyl acetate, 2:1) gave **3** as a colorless oil (780 mg, 43%). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (m, 1 H, 6-OH), 3.20 (dd, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 2.5 Hz, 1 H, 2-H), 3.44 (dd, $J_{4,5}$ = 9.5 Hz, $J_{4,3}$ = 2.5 Hz, 1 H, 4-H), 3.57 (m, 1 H, 6-H), 3.91 (m, 1 H, 6′-H), 4.00 (ddd, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 4.0 Hz, $J_{5,6'}$ = 3.0 Hz, 1 H, 5-H), 4.14 (m, $J_{3,4} \approx J_{3,2} \approx$ 2.5 Hz, 1 H, 3-H), 4.41−4.95 (6d, 6 × 1 H, 3 × OC*H*$_2$Ph), 4.87 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 7.20−7.42 (m, 15 H, arom). − $C_{28}H_{32}O_6$ (464.6): calcd. C 72.39, H 6.94; found C 72.58, H 6.72.

General Procedure for Iodination of Hexopyranosides:[36] The hexopyranoside in toluene (0.15 M) was refluxed with PPh_3 (1.2 equiv.) for 10 min. After cooling to 80 °C, imidazole (3.0 equiv.) and iodine

(1.3 equiv.) were added and the mixture was refluxed for 20 min before concentration. The residue was taken up in ethyl acetate and the organic phase was washed with saturated $Na_2S_2O_3$ solution and water, and dried. Concentration and chromatography gave the 6-deoxy-6-iodohexopyranoside.

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-β-D-*allo*-pyranoside (4): From **3** (700 mg, 1.51 mmol), chromatography with heptane/ethyl acetate (4:1), yield 760 mg, 87%. − $[\alpha]_D^{20}$ = +15 (*c* = 1.03, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.20 (dd, $J_{4,5}$ = 9.2 Hz, $J_{4,3}$ = 2.5 Hz, 1 H, 4-H), 3.23 (dd, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 2.5 Hz, 1 H, 2-H), 3.27 (dd, $J_{6,6'}$ = 10.2 Hz, $J_{6,5}$ = 7.0 Hz, 1 H, 6-H), 3.55 (dd, $J_{6',6}$ = 10.2 Hz, $J_{6',5}$ = 2.5 Hz, 1 H, 6′-H), 3.58 (s, 3 H, OCH_3), 3.73 (ddd, $J_{5,4}$ = 9.2 Hz, $J_{5,6}$ = 7.0 Hz, $J_{5,6'}$ = 2.5 Hz, 1 H, 5-H), 4.09 (t, $J_{3,2} \approx J_{3,4} \approx$ 2.5 Hz, 1 H, 3-H), 4.35−4.92 (6d, 6×1 H, 3×OCH_2Ph), 4.85 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 56.9, 71.1, 71.5, 73.0, 74.2, 74.5, 79.1, 79.4, 101.9, 127.5, 127.5, 127.6, 127.96, 128.00, 128.2, 128.3, 128.5, 137.4, 138.7. − $C_{28}H_{31}IO_5$ (574.5): calcd. C 58.54, H 5.44; found C 58.56, H 5.38.

Methyl 6-Deoxy-6-iodo-2,3-*O*,*O*-methylethylidene-β-D-*allo*-pyranoside (5) and Methyl 6-Deoxy-6-iodo-3,4-*O*,*O*-methylethylidene-β-D-*allo*-pyranoside (6): Methyl β-D-*allo*-pyranoside (2.20 g, 11.33 mmol), 2,2-dimethoxypropane (1.39 mL, 11.33 mmol), and camphorsulfonic acid (260 mg, 1.13 mmol) were stirred at 70 °C in anhydrous DMF (10 mL) for 90 min. The reaction was quenched with a few drops of NEt_3 and concentrated. Chromatography (CH_2Cl_2/methanol, 9:1) gave a mixture of 2,3- and 3,4-methylethylidene-β-D-*allo*-pyranosides. This mixture was then iodinated. Chromatography (petroleum ether/ethyl acetate, 3:2) gave **5** (1.18 g, 30%) and **6** (0.76 g, 20%).

Compound 5: $[\alpha]_D^{20}$ = −1.5 (*c* = 1.43, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 and 1.54 (2s, 2×3 H, CH_3-methylethylidene), 2.58 (d, $J_{OH,4}$ = 10.0 Hz, 1 H, 4-OH), 3.32 (dd, $J_{6,6'}$ = 10.5 Hz, $J_{6,5}$ = 7.0 Hz, 1 H, 6-H), 3.51 (m, 1 H, 5-H), 3.54 (s, 3 H, OCH_3), 3.60 (dd, $J_{6',6}$ = 10.5 Hz, $J_{6',5}$ =2.5 Hz, 1 H, 6′-H), 3.81 (ddd, $J_{4,OH}$ = 10.0, $J_{4,5}$ = 9.5 Hz, $J_{4,3}$ = 4.0 Hz, 1 H, 4-H), 4.13 (dd, $J_{2,3}$ = 6.2 Hz, $J_{2,1}$ = 4.5 Hz, 1 H, 2-H), 4.51 (dd, $J_{3,2}$ = 6.2 Hz, $J_{3,4}$ = 4.0 Hz, 1 H, 3-H), 4.53 (d, $J_{1,2}$ = 4.5 Hz, 1 H, 1-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 25.2, 27.0 56.7, 60.3, 68.9, 72.3, 73.9, 76.1, 100.9, 110.3. − $C_{10}H_{17}IO_5$ (344.1): calcd. C 34.90, H 4.98; found C 34.74, H 4.49.

6: $[\alpha]_D^{20}$ = +3.2 (*c* = 1.38, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 and 1.53 (2s, 2×3 H, CH_3-methylethylidene), 3.20 (dd, $J_{6,6'}$ = 10.5 Hz, $J_{6,5}$ = 7.5 Hz, 1 H, 6-H), 3.41 (m, 1 H, 5-H), 3.51 (dd, $J_{6',6}$ = 10.5 Hz, $J_{6',5}$ = 2.5 Hz, 1 H, 6′-H), 3.60 (s, 3 H, OCH_3), 3.77 (dd, $J_{2,1}$ = 7.0 Hz, $J_{2,3}$ = 4.7 Hz, 1 H, 2-H), 3.91 (dd, $J_{4,5}$ = 8.5 Hz, $J_{4,3}$ = 4.7 Hz, 1 H, 4-H), 4.53 (dd, $J_{3,4} \approx J_{3,2} \approx$ 4.7 Hz, 1 H, 3-H), 4.60 (d, $J_{1,2}$ = 7.0 Hz, 1 H, 1-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 25.7, 27.9, 56.8, 60.2, 68.7, 74.7, 75.0, 101.5, 110.6. − $C_{10}H_{17}IO_5$ (344.1): calcd. C 34.90, H 4.98; found C 34.49, H 4.71.

Methyl 4-*O*-*tert*-Butyldimethylsilyl-6-deoxy-6-iodo-2,3-*O*,*O*-methylethylidene-β-D-*allo*-pyranoside (7): Compound **5** (1.10 g, 3.19 mmol) was dissolved in CH_2Cl_2 (55 mL) containing pyridine (2.50 mL, 31.9 mmol) at 0 °C, and *tert*-butyldimethylsilyl triflate (2.20 mL, 9.59 mmol) was added. The reaction mixture was kept 1 h at 0 °C before workup and chromatography (petroleum ether/ethyl acetate, 12:1), to give 1.32 g of **7** (90%). − $[\alpha]_D^{20}$ = +8 (*c* = 1.07, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 and 0.13 (2s, 2×3 H, $SiCH_3$), 0.90 (s, 9 H, *t*Bu), 1.32 and 1.53 (2s, 2×3 H, CH_3-methylethylidene), 3.24 (dd, $J_{6,6'}$ = 10.5 Hz, $J_{6,5}$ = 7.0 Hz, 1 H, 6-H), 3.48−3.58 (m, 2 H, 5-H, 6′-H), 3.53 (s, 3 H, OCH_3), 3.79 (dd, $J_{4,5}$ = 9.0, $J_{4,3}$ = 4.0 Hz, 1 H, 4-H), 3.94 (dd, $J_{2,3} \approx J_{2,1} \approx$ 5.7 Hz, 1 H, 2-H), 4.34 (dd, $J_{3,2}$ = 5.7 Hz, $J_{3,4}$ = 4.0 Hz, 1 H, 3-H), 4.43 (d, $J_{1,2}$ = 5.7 Hz, 1 H, 1-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = −4.4, −4.3, 7.9, 18.1, 25.4, 25.7, 27.8, 57.1, 70.6, 72.0, 75.4, 76.8, 102.6, 110.2. − $C_{16}H_{31}IO_5Si$ (458.4): calcd. C 41.92, H 6.82; found C 42.18, H 6.46.

Methyl 2-*O*-*tert*-Butyldimethylsilyl-6-deoxy-6-iodo-3,4-*O*,*O*-methylethylidene-β-D-*allo*-pyranoside (8): The same procedure as described above for the preparation of **7** was used for the silylation of **6** (680 mg, 1.97 mmol), giving **8** (800 mg, 89%). − $[\alpha]_D^{20}$ = −12 (*c* = 0.80, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 and 0.12 (2s, 2×3 H, $SiCH_3$), 0.90 (s, 9 H, *t*Bu), 1.34 and 1.50 (2s, 2 × 3 H, CH_3-methylethylidene), 3.19 (dd, $J_{6,6'}$ = 10.0 Hz, $J_{6,5}$ = 7.0 Hz, 1 H, 6-H), 3.44 (m, 1 H, 5-H), 3.49 (dd, $J_{6',6}$ = 10.0 Hz, $J_{6',5}$ = 2.5 Hz, 1 H, 6′-H), 3.55 (s, 3 H, OCH_3), 3.76 (dd, $J_{2,1}$ = 7.0 Hz, $J_{2,3}$ = 4.7 Hz, 1 H, 2-H), 3.85 (dd, $J_{4,5}$ = 8.5 Hz, $J_{4,3}$ = 4.7 Hz, 1 H, 4-H), 4.36 (dd, $J_{3,2} \approx J_{3,4} \approx$ 4.7 Hz, 1 H, 3-H), 4.56 (d, $J_{1,2}$ = 7.0 Hz, 1 H, 1-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = −5.1, −3.0, 18.3, 25.6, 25.7, 25.8, 28.1, 57.0, 70.1, 74.5, 76.2, 76.3, 102.2, 110.2. − $C_{16}H_{31}IO_5Si$ (458.4): calcd. C 41.92, H 6.82; found C 42.18, H 7.06.

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-α-D-*galacto*-pyranoside (10): From **9** (6.80 g, 14.64 mmol), chromatography with heptane/ethyl acetate (4:1), yield 6.07 g, 71%. − $[\alpha]_D^{20}$ = +23 (*c* = 1.10, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.08 (dd, $J_{6,6'}$ =10.0 Hz, $J_{6,5}$ = 6.5 Hz, 1 H, 6-H), 3.22 (dd, $J_{6',6}$ = 10.0 Hz, $J_{6',5}$ = 8.0 Hz, 1 H, 6′-H), 3.41 (s, 3 H, OCH_3), 3.84 (m, 1 H, 5-H), 3.92 (dd, $J_{3,2}$ = 10.0 Hz, $J_{3,4}$ = 2.8 Hz, 1 H, 3-H), 4.02 (m, 2 H, 2-H, 4-H), 4.60−5.06 (6d, 6 × 1 H, 3 × OCH_2Ph), 4.64 (d, $J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.7, 71.2, 73.5, 74.9, 75.7, 75.9, 79.0, 98.8, 127.5, 127.6, 127.7, 127.8, 128.1, 128.3, 128.8, 138.2, 138.3, 138.6. − $C_{28}H_{31}IO_5$ (574.5): calcd. C 58.54, H 5.44; found C 58.78, H 5.16.

Methyl 6-Deoxy-6-iodo-3,4-*O*,*O*-methylethylidene-α-D-*galacto*-pyranoside (12): From **11**[41] (7.35 g, 31.38 mmol), chromatography with heptane/ethyl acetate (2:1), yield 6.30 g, 58%. − $[\alpha]_D^{20}$ = +111 (*c* = 1.22, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37 and 1.50 (2s, 2×3 H, CH_3-methylethylidene), 2.41 (d, $J_{OH,2}$ = 5.0 Hz, 1 H, OH), 3.31 (dd, $J_{6,6'}$ = 10.2, $J_{6,5}$ = 8.0 Hz, 1 H, 6-H), 3.37 (dd, $J_{6',6}$ = 10.2, $J_{6',5}$ = 6.0 Hz, 1 H, 6′-H), 3.53 (s, 3 H, OCH_3), 3.88 (m, 1 H, 2-H), 4.14 (ddd, $J_{5,6}$ = 8.0, $J_{5,6'}$ = 6.0, $J_{5,4}$ = 2.0 Hz, 1 H, 5-H), 4.29 (dd, $J_{3,4} \approx J_{3,2} \approx$ 6.0 Hz, 1 H, 3-H), 4.32 (dd, $J_{4,3}$ = 6.0, $J_{4,5}$ = 2.0 Hz, 1 H, 4-H), 4.78 (d, $J_{1,2}$ = 4.0 Hz, 1 H, 1-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 25.7, 27.3, 55.6, 68.6, 69.3, 73.5, 75.7, 98.2, 109.7. − $C_{10}H_{17}IO_5$ (344.1): calcd. C 34.90, H 4.98; found C 34.93, H 4.66.

Methyl 2-*O*-Benzyl-6-deoxy-6-iodo-3,4-*O*,*O*-methylethylidene-α-D-*galacto*-pyranoside (13): Compound **12** (2.0 g, 5.81 mmol) was dissolved in DMF (5 mL) and treated at 0 °C with benzyl bromide (0.90 mL, 7.57 mmol) and NaH (280 mg, 11.67 mmol) for 6 h before neutralization with methanol and concentration. Dichloromethane/water extraction and chromatography (petroleum ether/ethyl acetate, 3:1) gave **13** as a slightly yellow oil (2.45 g, 96%). − $[\alpha]_D^{20}$ = +93 (*c* = 3.10, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37 and 1.40 (2 s, 2 × 3 H, CH_3-methylethylidene), 3.37 (m, 2 H, 6-H, 6′-H), 3.45 (s, 3 H, OCH_3), 3.53 (dd, $J_{2,3}$ = 7.5, $J_{2,1}$ = 3.5 Hz, 1 H, 2-H), 4.11 (m, 1 H, 5-H), 4.32 (dd, $J_{4,3}$ = 5.5, $J_{4\cdot5}$ = 2.5 Hz, 1 H, 4-H), 4.38 (dd, $J_{3,2}$ = 7.5, $J_{3,4}$ = 5.5 Hz, 1 H, 3-H), 4.68 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.79 (2d, 2 ×1 H, OCH_2Ph), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 26.3, 28.0,

55.7, 68.0, 72.4, 73.9, 75.8, 76.0, 98.5, 101.2, 127.8, 128.0, 128.3, 138.0. − $C_{17}H_{23}IO_5$ (434.3): calcd. C 47.02, H 5.34; found C 47.46, H 5.38.

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-α-D-*manno*-pyranoside (14): From methyl 2,3,4-tri-*O*-benzyl-α-D-*manno*-pyranoside[35] (2.60 g, 5.60 mmol), chromatography with heptane/ethyl acetate (3:1), yield 2.60 g, 76%. − $[\alpha]_D^{20}$ = +26 (*c* = 1.39, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.34 (m, 1 H, 6-H), 3.37 (s, 3 H, OCH_3), 3.50 (dd, $J_{6',6}$ = 9.0, $J_{6',5}$ = 2.0, Hz, 1 H, 6′-H), 3.57 (m, 1 H, 5-H), 3.79 (m, 2 H, 2-H, 4-H), 3.89 (dd, $J_{3,4}$ = 9.5, $J_{3,2}$ = 3.0 Hz, 1 H, 3-H), 4.60 (s, 2 H, OCH_2Ph), 4.64−5.01 (4d, 4 × 1 H, 2 × OCH_2Ph), 4.75 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.0, 71.3, 72.0, 72.6, 74.5, 75.4, 78.5, 79.9, 99.0, 127.6, 127.6, 127.8, 128.0, 128.3, 128.4, 128.4, 138.1, 138.2. − $C_{28}H_{31}IO_5$ (574.5): calcd. C 58.54, H 5.44; found C 58.41, H 5.26.

Benzyl 2-Acetamido-3,4-di-*O*-benzyl-2,6-dideoxy-6-iodo-α-D-*gluco*-pyranoside (15): Benzyl 2-acetamido-2-deoxy-α-D-*gluco*-pyranoside[42] (2.0 g, 6.72 mmol) was dissolved in pyridine (16 mL) and treated with trityl chloride (2.25 g, 8.07 mmol) for 5 h at 100 °C. The solvent was evaporated and the residue extracted with dichloromethane/water. Chromatography (dichloromethane/methanol, 4:1) gave 3.20 g (86%) of benzyl 2-acetamido-2-deoxy-6-*O*-trityl-α-D-*gluco*-pyranoside. This compound (2.88 g, 5.38 mmol) was dissolved in THF (30 mL) and treated with benzyl bromide (2.0 mL, 16.81 mmol) and NaH (1.00 g of a 60% suspension in mineral oil, 25.00 mmol). The mixture was then refluxed for 40 min before neutralization and extraction with dichloromethane. Chromatography (heptane/ethyl acetate, 2:1 then 1:1) gave 3.15 g (80%) of a pale yellow solid. This solid was taken up in dichloromethane/methanol (3:7, 65 mL), and aqueous HCl (3 N solution, 14 mL) was added. The mixture was left overnight at room temperature, the solvents were evaporated, and the residue was extracted with dichloromethane/10% $NaHCO_3$. Recrystallization of the residue from ethanol gave benzyl 2-acetamido-3,4-di-*O*-benzyl-2-deoxy-α-D-*gluco*-pyranoside (1.50 g, 71%). A portion of this solid (1.3 g, 2.64 mmol) was iodinated to give **15** (1.33 g, 84%) after chromatography with heptane/ethyl acetate (1:1). − $[\alpha]_D^{20}$ = +61 (*c* = 1.32, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.80 (s, 3 H, NH*Ac*), 3.32 (dd, $J_{6,6'}$ = 10.5, $J_{6,5}$ = 6.0 Hz, 1 H, 6-H), 3.53 (m, 3 H, 4-H, 5-H, 6′-H), 3.77 (dd, $J_{3,2}$ = 10.5, $J_{3,4}$ = 8.0 Hz, 1 H, 3-H), 4.32 (ddd, $J_{2,3}$ = 10.5, $J_{2,NH}$ = 9.5, $J_{2,1}$ = 4.0 Hz, 1 H, 2-H), 4.55−4.97 (6d, 6 × 1 H, 3 × OCH_2Ph), 4.88 (d, $J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 5.33 (d, $J_{NH,2}$ = 9.5 Hz, 1 H, N*H*), 7.15−7.45 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 23.4, 52.5, 69.7, 70.5, 75.1, 75.5, 80.1, 82.0, 96.9, 127.2, 127.9, 128.12, 128.18, 128.51, 128.58, 128.6, 136.9, 137.7, 138.1, 169.7. − $C_{29}H_{32}INO_5$ (601.5): calcd. C 57.91, H 5.36; found C 57.62, H 5.48.

General Procedure for the Preparation of Hex-1-enitols from 6-Deoxy-6-iodohexopyranosides: The 6-deoxy-6-iodohexopyranoside was dissolved in 94% aqueous ethanol (0.75 M) and treated with activated zinc powder (10 equiv.) at reflux for 0.5−2 h (for methylethylidene-protected compounds, 10 equiv. of pyridine were added before refluxing with Zn). After cooling to room temperature, the reaction mixture was filtered through Celite, diluted with water, and extracted with diethyl ether. The solvent was evaporated and the residue was coevaporated once with absolute ethanol. The crude enal was taken up in absolute ethanol and treated with an excess of sodium tetrahydroborate for 15 min at room temperature, before addition of a few drops of 2 N HCl and extraction with ethyl acetate. The organic phase was washed with 10% NH_4Cl solution, dried with $MgSO_4$ and the solvent was evaporated. Chromatography with petroleum ether/ethyl acetate (3:1) gave the hex-1-enitol.

3,4,5-Tri-*O*-benzyl-1,2-dideoxy-L-*xylo*-hex-1-enitol (16): From **1** (2.60 g, 4.53 mmol), chromatography with heptane/ethyl acetate (4:1), yield 1.30 g, 70%. − $[\alpha]_D^{20}$ = −2.4 (*c* = 1.17, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.20 (t, 1 H, OH), 3.55 (m, 4 H, 4-H, 5-H, 6-H, 6′-H), 4.11 (m, 1 H, 3-H), 4.38 and 4.64 (2 d, 2 × 1 H, OCH_2Ph), 4.61 (s, 2 H, OCH_2Ph), 4.74 (s, 2 H, OCH_2Ph), 5.27−5.36 (m, 2 H, 1-H, 1′-H), 5.89 (ddd, $J_{2,1}$ = 17.5, $J_{2,1'}$ = 10.0, $J_{2,3}$ = 7.5 Hz, 1 H, 2-H), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 61.4, 65.3, 70.7, 72.8, 74.8, 79.5, 80.4, 81.7, 118.9, 126.9, 127.61, 127.66, 127.7, 127.9, 128.0, 128.32, 128.36, 128.4, 128.5, 135.1, 137.9, 138.2, 138.4. − $C_{27}H_{30}O_4$ (418.5): calcd. C 77.48, H 7.22; found C 77.26, H 7.43.

3,4-Di-*O*-benzyl-1,2,5-trideoxy-D-*threo*-hex-1-enitol (17): From **1** (5.80 g, 10.10 mmol), chromatography with heptane/ethyl acetate (3:1), yield 800 mg, 25% together with **16** (2.00 g, 48%). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.77 (m, 2 H, 5-H, 5′-H), 2.20 (s, 1 H, OH), 3.72 (m, 3 H, 4-H, 6-H, 6′-H), 3.99 (m, 1 H, 3-H), 4.42−4.79 (4 d, 4 × 1 H, OCH_2Ph), 5.32 (m, 1 H, 1-H), 5.37 (m, 1 H, 1′-H), 5.83 (ddd, *J* 17.5, 10.5, 7.5 Hz, 1 H, 2-H), 7.20−7.40 (m, 10 H, arom). − $C_{20}H_{24}O_3$ (312.4): calcd. C 76.89, H 7.74; found C 77.01, H 7.53.

3,4,5-Tri-*O*-benzyl-1,2-dideoxy-L-*ribo*-hex-1-enitol (18): From **4** (700 mg, 1.22 mmol), chromatography with heptane/ethyl acetate (4:1), yield 320 mg, 65%. − $[\alpha]_D^{20}$ = −36 (*c* = 1.66, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.28 (t, 1 H, OH), 3.57 (ddd, $J_{5,6'}$ = 8.5, $J_{5,4}$ = 6.5, $J_{5,6}$ = 4.0 Hz, 1 H, 5-H), 3.79 (m, 2 H, 6-H, 6′-H), 3.88 (dd, $J_{4,5}$ = 6.5, $J_{4,3}$ = 3.7 Hz, 1 H, 4-H), 4.08 (dd, $J_{3,2}$ = 8.0, $J_{3,4}$ = 3.7 Hz, 1 H, 3-H), 4.36−4.86 (6 d, 6 × 1 H, 3 × OCH_2Ph), 5.18 (ddd, $J_{1,2}$ = 17.5, $J_{1,1'}$ = 2.0, $J_{1,3}$ = 1.0 Hz, 1 H, 1-H), 5.34 (ddd, $J_{1',2}$ = 10.5, $J_{1',1}$ = 2.0, $J_{1',3}$ = 0.5 Hz, 1 H, 1′-H), 5.91 (ddd, $J_{2,1}$ = 17.5, $J_{2,1'}$ = 10.5, $J_{2,3}$ = 8.0 Hz, 1 H, 2-H), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 61.0, 70.4, 71.7, 74.2, 78.4, 81.1, 81.2, 119.7, 127.5, 127.6, 127.71, 127.77, 127.9, 128.1, 128.3, 128.4, 135.0, 137.9, 138.2, 138.3. − $C_{27}H_{30}O_4$ (418.5): calcd. C 77.48, H 7.22; found C 76.99, H 7.27.

3-*O*-*tert*-Butyldimethylsilyl-1,2-dideoxy-4,5-*O*,*O*-methylethylylidene-L-*ribo*-hex-1-enitol (19): From **7** (1.20 g, 2.62 mmol), chromatography with heptane/ethyl acetate (10:1), yield 695 mg, 87%. − $[\alpha]_D^{20}$ = −14 (*c* = 1.01, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.09 and 0.13 (2 s, 2 × 3 H, $SiCH_3$), 0.91 (s, 9 H, *t*Bu), 1.36 and 1.47 (2 s, 2 × 3 H, CH_3-methylethylidene), 2.84 (dd, $J_{OH,6}$ = 7.5, $J_{OH,6'}$ = 6.0 Hz, 1 H, OH), 3.72 (m, 2 H, 6-H, 6′-H), 4.07 (t, $J_{4,3} \approx J_{4,5}$ 5.5 Hz, 1 H, 4-H), 4.20 (m, 1 H, 5-H), 4.49 (ddd, $J_{3,2}$ = 6.5, $J_{3,4}$ = 5.5, $J_{3,1}$ = 1.0 Hz, 1 H, 3-H), 5.30 (m, 2 H, 1-H, 1′-H), 5.86 (ddd, $J_{2,1'}$ = 17.0, $J_{2,1}$ = 10.0, $J_{2,3}$ = 6.5 Hz, 1 H, 2-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = −4.7, −4.1, 18.1, 25.5, 25.8, 27.8, 61.5, 72.7, 76.5, 77.6, 79.2, 108.0, 117.6, 137.3. − $C_{15}H_{30}O_4Si$ (302.5): calcd. C 59.56, H 10.00; found C 59.53, H 10.30.

5-*O*-*tert*-Butyldimethylsilyl-1,2-dideoxy-3,4-*O*,*O*-methylethylylidene-L-*ribo*-hex-1-enitol (20): From **8** (670 mg, 1.46 mmol), chromatography with heptane/ethyl acetate (10:1), yield 342 mg, 78%. − $[\alpha]_D^{20}$ = +32 (*c* = 1.46, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 and 0.11 (2 s, 2 × 3 H, $SiCH_3$), 0.89 (s, 9 H, *t*Bu), 1.38 and 1.48 (2 s, 2 × 3 H, CH_3-methylethylidene), 3.72 (m, 2 H, 6-H, 6′-H), 3.82 (ddd, $J_{5,4}$ = 7.5, $J_{5,6'}$ = 5.0, $J_{5,6}$ = 3.0 Hz, 1 H, 5-H), 4.20 (dd, $J_{4,5}$ = 7.5, $J_{4,3}$ = 6.0 Hz, 1 H, 4-H), 4.63 (dd, $J_{3,2}$ = 7.0, $J_{3,4}$ = 6.0 Hz, 1 H, 3-H), 5.27 (ddd, $J_{1,2}$ = 10.0, $J_{1,1'}$ = 2.8, $J_{1,3}$ = 1.0 Hz, 1 H, 1-H), 5.38 (ddd, $J_{1',2}$ = 17.0, $J_{1',1}$ = 2.8,

$J_{1',3}$ = 1.0 Hz, 1 H, 1′-H), 5.94 (ddd, $J_{2,1'}$ = 17.0, $J_{2,1}$ = 10.0, $J_{2,3}$ = 7.0 Hz, 1 H, 2-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = −4.4, −3.7, 18.0, 25.4, 25.8, 27.8, 29.7, 65.0, 70.7, 78.8, 79.5, 108.5, 118.4, 134.0. − $C_{15}H_{30}O_4Si$ (302.5): calcd. C 59.56, H 10.00; found C 59.67, H 10.42.

3,4,5-Tri-*O*-benzyl-1,2-dideoxy-L-*lyxo*-hex-1-enitol (21): From **10** (1.00 g, 1.74 mmol), chromatography with heptane/ethyl acetate 3:1, yield 530 mg, 73%. − $[\alpha]_D^{20}$ = +13.2 (*c* = 1.17, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.00 (m, 1 H, OH), 3.69 (m, 4 H, 4-H, 5-H, 6-H, 6′-H), 4.06 (dd, *J* = 5.0, 8.0 Hz, 1 H, 3-H), 4.28−4.79 (6d, 6 × 1 H, 3 × OCH_2Ph), 5.37 (m, 2 H, 1-H, 1′-H), 5.99 (m, 1 H, 2-H), 7.25−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 61.7, 64.9, 70.1, 73.1, 74.3, 79.4, 80.3, 81.3, 119.7, 126.8, 127.4, 127.5, 127.6, 127.9, 128.2, 128.3, 128.33, 128.8, 129.5, 130.0, 133.3, 135.5, 138.0, 138.2. − $C_{27}H_{30}O_4$ (418.5): calcd. C 77.48, H 7.22; found C 77.31, H 7.01.

5-*O*-Benzyl-1,2-dideoxy-3,4-*O*,*O*-methylethylylidene-L-*lyxo*-hex-1-enitol (22): From **13** (2.40 g, 5.53 mmol), chromatography with heptane/ethyl acetate (3:1), yield 920 mg, 60%. − $[\alpha]_D^{20}$ = −9.7 (*c* = 1.71, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37 and 1.52 (2 s, 2 × 3 H, CH_3-methylethylidene), 2.81 (t, $J_{1,OH}$ = 6.0 Hz, 1 H, OH), 3.42−3.62 (m, 2 H, 6′-H, 2-H), 3.71 (m, 1 H, 6-H), 4.33 (dd, $J_{4,3} \approx J_{4,5}$ 6.5 Hz, 1 H, 4-H), 4.51 (dd, $J_{3,2}$ = 8.5, $J_{3,4}$ = 6.5 Hz, 1 H, 3-H), 4.72 (2d, 2×1 H, OCH_2Ph), 5.24 (dd, $J_{1',2}$ = 10.5, $J_{1',1}$ = 1.5 Hz, 1 H, 1′-H), 5.31 (dd, $J_{1,2}$ = 17.5, $J_{1,1'}$ = 1.5 Hz, 1 H, 1-H), 5.91 (ddd, $J_{2,1}$ = 17.5, $J_{2,1'}$ = 10.5, $J_{2,3}$ = 8.5 Hz, 1 H, 2-H), 7.20−7.40 (m, 5 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 25.6, 27.8, 61.7, 72.6, 77.8, 79.1, 79.2, 109.1, 119.5, 127.7, 128.4, 134.2, 138.4. − $C_{16}H_{22}O_4$ (278.3): calcd. C 69.04, H 7.97; found C 68.68, H 7.60.

3,4,5-Tri-*O*-benzyl-1,2-dideoxy-D-*arabino*-hex-1-enitol (23): From **14** (1.0 g, 1.74 mmol), chromatography with heptane/ethyl acetate (4:1), yield 355 mg, 48%. − $[\alpha]_D^{20}$ = −6.5 (*c* = 1.39, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.66−3.82 (m, 4 H, 4-H, 5-H, 6-H, 6′-H), 4.04 (dd, $J_{3,2}$ = 8.0, $J_{3,4}$ = 4.0 Hz, 1 H, 3-H), 4.31−4.69 (4 d, 4 × 1 H, 2 × OCH_2Ph), 4.73 (s, 2 H, OCH_2Ph), 5.34 (m, 2 H, 1-H, 1′-H), 5.94 (ddd, $J_{2,1'}$ = 17.5, $J_{2,1}$ = 10.2, $J_{2,3}$ = 8.0 Hz, 1 H, 2-H), 7.17−7.42 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 60.7, 70.4, 71.6, 75.1, 78.8, 80.5, 81.4, 118.8, 127.6, 127.7, 128.1, 128.2, 128.3, 128.4, 135.8, 138.0, 138.1, 138.2. − $C_{27}H_{30}O_4$ (418.5): calcd. C 77.48, H 7.22; found C 77.68, H 7.12.

5-Acetamido-3,4-di-*O*-benzyl-1,2,5-trideoxy-L-*xylo*-hex-1-enitol (24): From **15** (600 mg, 0.99 mmol), chromatography with ethyl acetate/heptane (3:1), yield 135 mg, 38%. − $[\alpha]_D^{20}$ = −45 (*c* = 0.66, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.92 (s, 3 H, NHA*c*), 3.50 (dd, *J* = 11.0, 6.5 Hz, 1 H, 6′-H), 3.64 (dd, *J* = 11.0, 5.5 Hz, 1 H, 6-H), 3.74 (dd, *J* = 6.5, 2.0 Hz, 1 H, 4-H), 3.97 (dd, *J* = 8.0, 6.5 Hz, 1 H, 3-H), 4.15 (m, 1 H, 5-H), 4.91−4.36 (4 d, 4 × 1 H, 2 × OCH_2Ph), 5.38 (m, 1 H, 1-H), 5.33 (m, 1 H, 1′-H), 5.81 (ddd, *J* = 18.0, 11.0, 8.0 Hz, 1 H, 2-H), 5.99 (d, *J* = 8.0 Hz, 1 H, N*H*), 7.38−7.27 (m, 10 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 23.2 (Ac), 51.6 (C-5), 63.4 (C-6), 70.6, 74.8 (O*C*H_2Ph), 79.2 (C-4), 81.8 (C-3), 119.8 (C-1), 127.5, 127.6, 127.7, 127.8, 128.0, 128.3, 128.4 (arom), 134.2 (C-2). − No satisfactory analytical data could be obtained for this compound.

General Procedures for the Preparation of 6-Iodohex-1-enitols. − Procedure A: A solution of hexenitol in anhydrous toluene (0.1 M) was treated at reflux with PPh_3 (1.2 equiv.), imidazole (3.0 equiv.), and iodine (1.3 equiv.). The mixture was heated at reflux for 15 min before cooling and concentration. The residue was taken up in ethyl acetate and the organic phase washed with saturated $Na_2S_2O_3$ and water. Chromatography (petroleum ether/ethyl acetate) gave the product (see Table 1 for yields). − **Procedure B:** To a solution of the hexenitol (0.3 M) in anhydrous pyridine was added tosyl chloride (2.0 equiv.) and the mixture was left overnight at room temperature. Aqueous HCl (1 M) was added before extraction with CH_2Cl_2. Chromatography (petroleum ether/ethyl acetate) gave the pure tosylate. The tosylate (0.5 M solution) in HMPA was treated with sodium iodide (10 equiv.) at 60 °C in the dark for 1−1.5 h. The reaction mixture was diluted with ether and washed with 10% sodium thiosulfate. Chromatography gave the iodo hexenitol.

3,4,5-Tri-*O*-benzyl-1,2,6-trideoxy-6-iodo-L-*xylo*-hex-1-enitol (26): − Procedure B. − $[\alpha]_D^{20}$ = −15 (*c* = 1.26, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.13 (dd, $J_{6,6'}$ = 10.2, $J_{6,5}$ = 5.0 Hz, 1 H, 6-H), 3.33 (dd, $J_{6',6}$ = 10.2, $J_{6',5}$ = 6.5 Hz, 1 H, 6′-H), 3.67 (ddd, $J_{5,6'}$ = 6.5, $J_{5,6}$ = 5.0, $J_{5,4}$ = 4.5 Hz, 1 H, 5-H), 3.76 (dd, $J_{4,3}$ = 5.5, $J_{4,5}$ = 4.5 Hz, 1 H, 4-H), 4.07 (m, 1 H, 3-H), 4.35−4.88 (6 d, 6 × 1 H, 3 × OCH_2Ph), 5.28 (m, 2 H, 1-H, 1′-H), 5.81 (ddd, $J_{2,1}$ = 18.0, $J_{2,1'}$ = 10.0, $J_{2,3}$ = 7.5 Hz, 1 H, 2-H), 7.20−7.35 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 5.4, 70.5, 72.9, 75.5, 79.5, 81.1, 82.0, 119.1, 127.6, 127.8, 128.0, 128.3, 128.4, 135.0, 138.0, 138.1, 138.4. − MS (CI/NH_3): *m*/*z* = 546 [M + 18]. − $C_{27}H_{29}IO_3$ (528.4): calcd. C 61.37, H 5.53; found C 61.74, H 5.58.

3,4-Di-*O*-benzyl-1,2,5,6-tetradeoxy-6-iodo-D-*threo*-hex-1-enitol (27): − Procedure B. − $[\alpha]_D^{20}$ = +39 (*c* = 1.39, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.00 (m, 2 H, 5-H, 5′-H), 3.22 (m, 2 H, 6-H, 6′-H), 3.64 (ddd, $J_{4,5}$ = 9.0, $J_{4,3}$ = 5.5, $J_{4,5'}$ = 3.5 Hz, 1 H, 4-H), 3.93 (dd, $J_{3,2}$ = 7.5, $J_{3,4}$ = 5.5 Hz, 1 H, 3-H), 4.40, 4.59, 4.63, 4.80 (4 d, 4 ×1 H, 2 × OCH_2Ph), 5.31 (m, 2 H, 1-H, 1′-H), 5.81 (ddd, $J_{2,1}$ = 17.5, $J_{2,1'}$ = 10.5, $J_{2,3}$ = 7.5 Hz, 1 H, 2-H), 7.20−7.40 (m, 10 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 3.4, 35.0, 70.6, 73.8, 77.2, 80.6, 81.8, 119.2, 127.6, 127.7, 128.1, 128.4, 128.4, 134.8, 138.3, 138.4. − MS (CI/NH_3): *m*/*z* = 440 [M + 18]. − $C_{20}H_{23}IO_2$ (422.3): calcd. C 56.88, H 5.49; found C 57.07, H 5.24.

3,4,5-Tri-*O*-benzyl-1,2,6-trideoxy-6-iodo-L-*ribo*-hex-1-enitol (28): − Procedure B. − $[\alpha]_D^{20}$ = −15 (*c* = 1.01, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.22 (m, 1 H, 5-H), 3.46 (dd, $J_{6,6'}$ = 11.0, $J_{6,5}$ = 3.2 Hz, 1 H, 6-H), 3.59 (dd, $J_{6',6}$ = 11.0, $J_{6',5}$ = 4.2 Hz, 1 H, 6′-H), 3.81 (dd, $J_{4,5}$ = 7.0, $J_{4,3}$ = 3.5 Hz, 1 H, 4-H), 4.12 (dd, $J_{3,2}$ = 8.0, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 4.30−5.00 (6 d, 6 × 1 H, 3 × OCH_2Ph), 5.16 (dd, $J_{1,2}$ = 17.5, $J_{1,1'}$ = 1.5 Hz, 1 H, 1-H), 5.31 (dd, $J_{1',2}$ = 10.5, $J_{1',1}$ = 1.5 Hz, 1 H, 1′-H), 5.90 (ddd, $J_{2,1}$ = 17.5, $J_{2,1'}$ = 10.5, $J_{2,3}$ = 8.0 Hz, 1 H, 2-H), 7.20−7.50 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 8.8, 70.3, 71.5, 74.6, 76.7, 81.2, 82.1, 119.8, 127.4, 127.6, 127.6, 127.8, 128.17, 128.20, 128.30, 128.32, 128.39, 135.1, 137.5, 138.4. − MS (CI/NH_3): *m*/*z* = 546 [M + 18]. − $C_{27}H_{29}IO_3$ (528.4): calcd. C 61.37, H 5.53; found C 61.23, H 5.52.

3-*O*-*tert*-Butyldimethylsilyl-1,2,6-trideoxy-6-iodo-4,5-*O*,*O*-methylethylidene-L-*ribo*-hex-1-enitol (29): Procedure B. − $[\alpha]_D^{20}$ = −48 (*c* = 1.22, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.07 and 0.09 (2 s, 2 × 3 H, SiCH_3), 0.89 (s, 9 H, *t*Bu), 1.37 and 1.49 (2 s, 2 × 3 H, CH_3-methylethylidene), 3.27 (dd, $J_{6,5} \approx J_{6,6'} \approx$ 10.5 Hz, 1 H, 6-H), 3.50 (dd, $J_{6',6}$ = 10.5, $J_{6',5}$ = 2.5 Hz, 1 H, 6′-H), 3.98 (t, $J_{4,3} \approx J_{4,5} \approx$ 6.0 Hz, 1 H, 4-H), 4.36 (m, 2 H, 3-H, 5-H), 5.31 (m, 2 H, 1-H, 1′-H), 5.83 (ddd, $J_{2,1'}$ = 17.0, $J_{2,1}$ = 10.0, $J_{2,3}$ = 6.5 Hz, 1 H, 2-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = −4.7, −3.8, 7.7, 18.1, 25.6, 25.8, 28.1, 29.7, 63.2, 72.4, 78.6, 79.8, 108.6, 117.7, 137.7. − $C_{15}H_{29}IO_3Si$ (412.4): calcd. C 43.69, H 7.09; found C 43.71, H 7.08.

5-*O*-*tert*-Butyldimethylsilyl-1,2,6-trideoxy-6-iodo-3,4-*O*,*O*-methylethylidene-L-*ribo*-hex-1-enitol (30): From **20** (300 mg, 0.99 mmol), procedure A, chromatography with heptane/ethyl acetate (12:1),

yield 402 mg, 98%. − $[\alpha]_D^{20}$ = +55 (*c* = 1.03, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.07 and 0.16 (2 s, 2 × 3 H, $SiCH_3$), 0.91 (s, 9 H, *t*Bu), 1.39 and 1.47 (2 s, 2 × 3 H, CH_3-methylethylidene), 3.23 (m, 1 H, 5-H), 3.29 (dd, $J_{6,6'}$ = 10.5, $J_{6,5}$ = 3.5 Hz, 1 H, 6-H), 3.59 (dd, $J_{6',6}$ = 10.5, $J_{6',5}$ = 2.0 Hz, 1 H, 6′-H), 4.13 (dd, $J_{4,5}$ = 7.0, $J_{4,3}$ = 6.0 Hz, 1 H, 4-H), 4.60 (ddd, $J_{3,2}$ = 7.0, $J_{3,4}$ = 6.0, $J_{3,1}$ = 1.0 Hz, 1 H, 3-H), 5.24 (ddd, $J_{1,2}$ = 10.0, $J_{1,1'}$ = 2.8, $J_{1,3}$ = 1.0 Hz, 1 H, 1-H), 5.37 (ddd, $J_{1',2}$ = 17.0, $J_{1',1}$ = 2.8, $J_{1',3}$ = 1.0 Hz, 1 H, 1′-H), 5.91 (ddd, $J_{2,1'}$ = 17.0, $J_{2,1}$ = 10.0, $J_{2,3}$ = 7.0 Hz, 1 H, 2-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = −4.5, −3.5, 14.6, 18.0, 25.2, 25.8, 27.8, 68.0, 78.1, 80.2, 108.3, 118.2, 134.3. − $C_{15}H_{29}IO_3Si$ (412.4): calcd. C 43.69, H 7.09; found C 43.79, H 7.13.

3,4,5-Tri-*O*-benzyl-1,2,6-trideoxy-6-iodo-L-*lyxo*-hex-1-enitol (31): − Procedure B. − $[\alpha]_D^{20}$ = +3 (*c* = 1.62, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.23 (dd, $J_{6,6'}$ = 10.0, $J_{6,5}$ = 5.5 Hz, 1 H, 6-H), 3.34 (dd, $J_{6',6}$ = 10.0, $J_{6,5}$ = 6.5 Hz, 1 H, 6′-H), 3.64 (m, 2 H, 4-H, 5-H), 4.05 (dd, $J_{3,2}$ = 8.0, $J_{3,4}$ = 6.0 Hz, 1 H, 3-H), 4.22−4.80 (6 d, 6 × 1 H, 3 × OCH_2Ph), 5.41 (m, 2 H, 1-H, 1′-H), 5.97 (ddd, $J_{2,1}$ = 18.0, $J_{2,1'}$ = 10.0, $J_{2,3}$ = 8.0 Hz, 1 H, 2-H), 7.20−7.35 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 5.2, 70.0, 73.3, 74.8, 79.7, 80.2, 81.4, 119.9, 127.5, 127.7, 127.7, 127.8, 127.9, 128.1, 128.2, 128.28, 128.33, 128.4, 136.0, 138.0, 138.2, 138.3. − $C_{27}H_{29}IO_3$ (528.4): calcd. C 61.37, H 5.53; found C 61.72, H 5.60.

5-*O*-Benzyl-1,2,6-trideoxy-6-iodo-3,4-*O*,*O*-methylethylidene-L-*lyxo*-hex-1-enitol (32): − Procedure B. − $[\alpha]_D^{20}$ = −7 (*c* = 1.40, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 3.28 (m, 2 H, 6-H, 6′-H), 3.46 (dd, $J_{5,6}$ = 11.0, $J_{5,4}$ = 4.5 Hz, 1 H, 5-H), 4.42 (dd, $J_{4,3}$ = 6.5, $J_{4,5}$ = 5.5 Hz, 1 H, 4-H), 4.59 (dd, $J_{3,2}$ = 8.5, $J_{3,4}$ = 6.5 Hz, 1 H, 3-H), 4.70 (s, 2 H, OCH_2Ph), 5.28 (m, 1 H, 1′-H), 5.36 (m, 1 H, 1-H), 5.91 (ddd, $J_{2,1}$ = 18.0, $J_{2,1'}$ = 10.2, $J_{2,3}$ = 8.2 Hz, 1 H, 2-H), 7.25−7.45 (m, 5 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 4.3, 25.6, 27.5, 72.5, 77.6, 78.9, 79.9, 109.3, 119.6, 127.6, 128.3, 134.0, 138.0. − $C_{16}H_{21}IO_3$ (388.2): calcd. C 49.50, H 5.45; found C 49.75, H 5.53.

3,4,5-Tri-*O*-benzyl-1,2,6-trideoxy-6-iodo-D-*arabino*-hex-1-enitol (33): − Procedure B. − $[\alpha]_D^{20}$ = −17 (*c* = 1.80, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.44−3.66 (m, 4 H, 4-H, 5-H, 6-H, 6′-H), 4.10 (dd, $J_{3,2}$ = 7.5, $J_{3,4}$ = 3.2, Hz, 1 H, 3-H), 4.27−4.68 (4 d, 4 × 1 H, 2 × OCH_2Ph), 4.77 (s, 2 H, OCH_2Ph), 5.35 (m, 2 H, 1-H, 1′-H), 5.94 (ddd, $J_{2,1'}$ = 17.5, $J_{2,1}$ = 10.2, $J_{2,3}$ = 7.7 Hz, 1 H, 2-H), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 70.3, 71.7, 75.2, 79.8, 118.5, 128.1, 128.2. MS (CI/NH_3): *m*/*z* = 546 [M + 18]. − $C_{27}H_{29}IO_3$ (528.4): calcd. C 61.37, H 5.53; found C 61.02, H 5.86.

5-Acetamido-3,4-di-*O*-benzyl-1,2,5,6-tetradeoxy-6-iodo-L-*xylo*-hex-1-enitol (34): From **24** (55 mg, 0.15 mmol), procedure A, chromatography with heptane/ethyl acetate (1:1), yield 50 mg, 70%. − $[\alpha]_D^{20}$ = −45 (*c* = 0.66, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.92 (s, 3 H, NH*Ac*), 3.50 (dd, $J_{6,6'}$ = 11.0, $J_{6,5}$ = 6.5 Hz, 1 H, 6-H), 3.64 (dd, $J_{6',6}$ = 11.0, $J_{6',5}$ = 5.5 Hz, 1 H, 6′-H), 3.74 (dd, $J_{4,3}$ = 6.5, $J_{4,5}$ = 2.0 Hz, 1 H, 4-H), 3.97 (dd, $J_{3,2}$ = 8.0, $J_{3,4}$ = 6.5 Hz, 1 H, 3-H), 4.15 (m, 1 H, 5-H), 4.36−4.91 (4 d, 4 × 1 H, 2 × OCH_2Ph), 5.33 (m, 1 H, 1′-H), 5.38 (m, 1 H, 1-H), 5.81 (ddd, $J_{2,1}$ = 18.0, $J_{2,1'}$ = 11.0, $J_{2,3}$ = 8.0 Hz, 1 H, 2-H), 5.99 (d, $J_{NH,5}$ = 8.0 Hz, 1 H, NH), 7.27−7.38 (m, 10 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 23.2, 51.6, 63.4, 70.6, 74.8, 79.2, 81.8, 119.8, 127.5, 127.6, 127.7, 127.8, 128.0, 128.3, 128.4, 134.3.

General Procedure for the Cobalt-Catalyzed Radical Cyclization Under Oxygen:[33] The iodo-hexenitol was dissolved in absolute ethanol (0.06 M) at 40 °C. Sodium hydroxide (10 N aqueous solution, 1.7 equiv.) and solid sodium tetrahydroborate (2 equiv.) were added and a stream of ethanol-saturated air was passed through the solution before addition of the cobalt(salen) catalyst (0.03−0.05 equiv.). The reaction mixture was left at 40 °C under air for 4−20 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and the organic phase washed with water. Chromatography gave the carbafuranosides. − The diastereoisomeric ratio was determined by ^{1}H NMR spectroscopy of the purified mixture of carbafuranosides before any attempted separation. Assignment of the stereochemistry of purified isomers was performed using NOESY and, when possible, comparison with known compounds. Some minor isomers were not fully characterized.

(1*S*,2*R*,3*R*,4*R*)-1,2,3-Tribenzyloxy-4-hydroxymethylcyclopentane (35): From **26** (50 mg, 0.09 mmol); chromatography with petroleum ether/ethyl acetate (2:1), yield 27 mg, 69%, diastereoisomeric ratio 12:1. − $[\alpha]_D^{20}$ = +38 (*c* = 0.85, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.72 (ddd, $J_{5,5'}$ = 13.5, $J_{5,4}$ = 9.8, $J_{5,1}$ = 6.8 Hz, 1 H, 5-H) 1.93 (m, $J_{5,5'}$ = 13.5, *J* = 8.0, *J* = 3.6, $J_{5,2}$ = 1.0 Hz, 1 H, 5-H), 2.39 (m, 1 H, 4-H), 3.62 (d, $J_{6,4}$ = 6.0 Hz, 2 H, 6-H), 3.73 (dd, $J_{3,4}$ = 8.2, $J_{3,2}$ = 5.5 Hz, 1 H, 3-H), 3.90 (m, $J_{1,5}$ = 6.8, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.03 (m, $J_{2,3}$ = 5.5, $J_{2,1}$ = 3.6, $J_{2,5}$ = 1.0 Hz, 1 H, 2-H), 4.45−4.76 (6 d, 6 × 1 H, 3 × OCH_2Ph), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 30.1, 43.0, 64.9, 70.9, 72.00, 72.02, 81.3, 85.8, 90.0, 127.6, 127.7, 127.8, 128.4, 138.1, 138.2, 138.3. MS (CI/NH_3): *m*/*z* = 366 [M + 1]. − $C_{27}H_{30}O_4$ (418.5): calcd. C 77.48, H 7.22; found C 77.67, H 7.02.

(1*R*,2*R*,3*R*)-1,2-Dibenzyloxy-3-hydroxymethylcyclopentane (37): From **27** (83 mg, 0.19 mmol); chromatography with petroleum ether/ethyl acetate (3:1), yield 35 mg, 57%, 4:1 mixture with **18**. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.45−1.63 (m, 1 H, 4-H), 1.71−2.02 (m, 3 H, 4-H, 5-H, 5′-H), 2.19 (m, 1 H, 3-H), 3.62 (dd, $J_{6,6'}$ = 10.7, $J_{6,4}$ = 6.5 Hz, 1 H, 6-H), 3.68 (dd, $J_{6',6}$ = 10.7, $J_{6',4}$ = 5.5 Hz, 1 H, 6′-H), 3.78 (dd, *J* = 5.5, 3.5 Hz, 1 H, 2-H), 4.00 (m, 1 H, 1-H), 4.44−4.78 (4 d, 4 × 1 H, 2 × OCH_2Ph), 7.20−7.40 (m, 10 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 24.0, 29.0, 46.1, 65.4, 71.1, 71.7, 84.4, 87.6, 125.8, 127.6, 127.66, 127.70, 127.74, 128.1, 128.4, 128.5, 138.2, 138.4. − MS (CI/NH_3): *m*/*z* = 313 [M + 1]. − $C_{20}H_{24}O_3$ (312.4): calcd. C 76.89, H 7.74; found C 77.14, H 7.40.

(1*S*,2*S*,3*R*,4*R*)-1,2,3-Tribenzyloxy-4-hydroxymethylcyclopentane (38): From **28** (40 mg, 0.075 mmol); chromatography with petroleum ether/ethyl acetate (7:3), yield 11 mg, 35%. − $[\alpha]_D^{20}$ = +53.7 (*c* = 0.41, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.69 (ddd, $J_{5,5'}$ = 14.0, $J_{5,1}$ = 8.0, $J_{5,4}$ = 6.5 Hz, 1 H, 5-H), 2.12 (ddd, $J_{5',5}$ = 14.0, $J_{5',1}$ = 8.0, $J_{5',4}$ = 6.5 Hz, 1 H, 5′-H), 2.57−2.69 (m, 1 H, 4-H), 3.53−3.68 (m, 3 H, 3-H, 6-H, 6′-H), 3.83 (ddd, $J_{1,5'}$ = 8.0, $J_{1,5}$ = 8.0, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.04 (dd, $J_{2,3}$ = 3.5, $J_{2,1}$ = 3.5 Hz, 1 H, 2-H), 4.38, 4.61, 4.80, 4.90 (4 d, 4 × 1 H, 2 × OCH_2Ph), 4.53 (s, 2 H, OCH_2Ph), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 29.5, 42.5, 64.9, 71.3, 71.9, 72.8, 78.2, 80.6, 81.1, 127.4, 127.5, 127.7, 127.9, 128.2, 128.3, 128.4, 138.1, 139.0. − MS (CI/NH_3): *m*/*z* = 436 [M + 18]. − $C_{27}H_{30}O_4$ (418.5): calcd. C 77.48, H 7.22; found C 77.57, H 7.20.

(1*S*,2*S*,3*R*,4*R*)-3-*tert*-Butyldimethylsilyloxy-4-hydroxymethyl-1,2-*O*,*O*-(methylethylidenedioxy)cyclopentane (39): From **29** (50 mg, 0.12 mmol); chromatography with petroleum ether/ethyl acetate (3:1), yield 18 mg, 50%, 10:1 diastereoisomeric ratio and 10 mg **19**. − $[\alpha]_D^{20}$ = +8 (*c* = 1.80, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 and 0.13 (2 s, 2 × 3 H, $SiCH_3$), 0.92 (s, 9 H, *t*Bu), 1.27 (m, 1 H, 5-H), 1.29 and 1.48 (2 s, 2 × 3 H, CH_3-methylethylidene),

1.73 (m, 1 H, 5′-H), 2.04 (s, 1 H, OH), 2.33 (dddd, J = 18.0, J = 15.5, J = 11.0, $J_{4,3}$ = 5.5 Hz, 1 H, 4-H), 3.59−3.77 (m, 3 H, 1-H, 6-H, 6′-H), 4.36 (m, $J_{2,1}$ = 5.0, $J_{2,3}$ = 5.0 Hz, 1 H, 2-H), 4.52 (m, $J_{3,4}$ = 5.5, $J_{3,2}$ = 5.0 Hz, 1 H, 3-H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = −4.8, −4.3, 18.2, 24.2, 25.8, 26.0, 30.3, 42.5, 64.2, 77.6, 77.7, 79.3, 109.9.

(1*S*,2*R*,3*S*,4*S*)-1,2,3-Tribenzyloxy-4-hydroxymethylcyclopentane (43): From **31** (45 mg, 0.085 mmol); chromatography with heptane/ethyl acetate (4:1), yield 10 mg, 50%, diastereoisomeric ratio 4:1. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30 (ddd, $J_{5,5'}$ = 14.5, $J_{5,1}$ = 7.5, $J_{5,4}$ = 4.5 Hz, 1 H, 5-H), 1.93 (br s, 1 H, OH), 2.30 (ddd, $J_{5',5}$ = 14.5, $J_{5',4}$ = 8.5, $J_{5',1}$ = 2.5 Hz, 1 H, 5′-H), 2.41 (m, 1 H, 4-H), 3.56−3.74 (m, 2 H, 6-H, 6′-H), 3.82 (dd, $J_{3,4}$ = 7.5, $J_{3,2}$ = 4.8 Hz, 1 H, 3-H), 3.88 (dd, $J_{2,3}$ = 4.8, $J_{2,1}$ = 2.5 Hz, 1 H, 2-H), 4.00 (ddd, $J_{1,5}$ = 7.5, $J_{1,5'}$ = 4.5, $J_{1,2}$ = 2.5 Hz, 1 H, 1-H), 4.42−4.65 (6 d, 6 × 1 H, 3 × OCH_2Ph), 7.20−7.45 (m,15 H, arom). − MS (CI/NH_3): m/z = 519 [M + 1]. − $C_{27}H_{30}O_4$ (418.5): calcd. C 77.48, H 7.22; found C 76.92, H 7.29.

(1*S*,2*R*,3*S*,4*R*)-1-Benzyloxy-4-hydroxymethyl-2,3-*O*,*O*-(methylethylidenedioxy)cyclopentane (45) and (1*S*, 2*R*, 3*S*, 4*S*)-1-Benzyloxy-4-hydroxymethyl-2,3-*O*,*O*-(methylethylidenedioxy)cyclopentane (46): From **32** (200 mg, 0.51 mmol); chromatography with heptane/ethyl acetate (4:1), yield 115 mg, 80%, 1.2:1 mixture of **45**/**46**.

Compound 45: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32 and 1.44 (2 s, 2 × 3 H, CH_3-methylethylidene), 1.76−1.86 (m, $J_{5,5'}$ = 13.5, J = 6.8, J = 1.0 Hz, 1 H, 5-H), 1.84−1.97 (m, $J_{5,5'}$ = 13.5, $J_{5',4}$ = 4.3 Hz, 1 H, 5′-H), 2.29−2.46 (m, 1 H, 4-H), 3.76 (dd, $J_{6,6'}$ = 11.2, $J_{6,4}$ = 6.5 Hz, 1 H, 6-H), 3.90 (d, J = 4.5 Hz, 1 H, 1-H), 3.94 (dd, $J_{6',6}$ = 11.2, $J_{6',4}$ = 4.0, Hz, 1 H, 6′-H), 4.53 (s, 2 H, OCH_2Ph), 4.57 (dd, $J_{2,3}$ = 5.5, $J_{2,1}$ = 1.5 Hz, 1 H, 2-H), 4.79 (t, $J_{3,4} \approx J_{3,2}$ 5.5 Hz, 1 H, 3-H), 7.20−7.40 (m, 5 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 23.7, 25.9, 29.9, 42.7, 61.9, 70.7, 81.6, 82.4, 84.4, 110.4, 127.5, 127.6, 128.4, 128.4, 128.5, 138.1. − MS (CI/NH_3): m/z = 279 [M + 1]. − $C_{16}H_{22}O_4$ (278.3): calcd. C 69.04, H 7.97; found C 69.03, H 7.83.

Compound 46: $[\alpha]_D^{20}$ = +6 (c = 0.60, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30 and 1.44 (2 s, 2 × 3 H, CH_3-methylethylidene), 1.60−1.70 (m,1 H, 5-H), 2.26−2.42 (m, 2 H, 4-H, 5′-H), 2.95 (m, 1 H, OH), 3.59−3.71 (m, 2 H, 6-H, 6′-H), 3.92 (m, 1 H, 1-H), 4.53, 4.64 (2d, 2×1 H, OCH_2Ph), 4.58 (m, 1 H, 4-H), 4.72 (dd, $J_{2,3}$ = 6.0, $J_{2,1}$ = 1.5 Hz, 1 H, 2-H), 7.20−7.35 (m, 5 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 23.9, 26.5, 33.4, 47.1, 64.7, 71.3, 71.4, 83.4, 84.6, 85.1, 110.0, 127.5, 127.7, 127.9, 128.5, 137.2. − MS (CI/NH_3): m/z = 279 [M + 1].

(1*R*,2*R*,3*R*,4*R*)-1,2,3-Tribenzyloxy-4-hydroxymethylcyclopentane (47): From **33** (75 mg, 0.14 mmol); chromatography with heptane/ethyl acetate (3:1), yield 19 mg, 33%, diastereoisomeric ratio 4:1. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.71 (m, $J_{5,5'}$ = 13.5 Hz, 1 H, 5-H), 2.01−2.23 (m, 2 H, 4-H, 5-H), 3.60−3.73 (m, 2 H, 6-H), 3.87 (dd, J = 5.5, 4.0 Hz, 1 H, 2-H), 3.94−4.04 (m, 2 H, 1-H, 3-H), 4.51−4.71 (6 d, 6 × 1 H, 3 × OCH_2Ph), 7.20−7.40 (m, 15 H, arom). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 29.5, 43.1, 65.6, 71.4, 71.9, 72.2, 77.2, 84.4, 84.6, 127.6, 127.67, 127.70, 127.76, 127.8, 128.4, 128.4, 128.4, 128.6, 138.1, 138.2, 138.5. MS (CI/NH_3): m/z = 419 [M + 1]. − $C_{27}H_{30}O_4$ (418.5): calcd. C 77.48, H 7.22; found C 77.25, H 7.30.

(1*S*,2*R*,3*R*,4*R*)-1,2,3-Trihydroxy-4-hydroxymethylcyclopentane (49): Hydrogenolysis of **35** (40 mg, 0.096 mmol) with H_2 and 10% Pd/C in ethanol (2 mL) gave **49**[50] (12 mg, 85%). − $[\alpha]_D^{20}$ = +45 (c = 1.08, methanol). − Ref.[50] $[\alpha]_D^{20}$ = +40 (methanol). − Ref.[51] $[\alpha]_D^{16}$ = −40.5 (c = 0.84, methanol) for the enantiomer. − ^{1}H NMR (250 MHz, CD_3OD): δ = 1.65−1.91 (m, 2 H, 5-H, 5′-H), 2.03 (m, 1 H, 4-H), 3.44−3.59 (m, 4 H, 3-H, 9-H, 6′-H), 3.80 (ddd, J = 5.0, 3.7, 3.0 Hz, 1 H, 1-H). − ^{13}C NMR (62.89 MHz, CD_3OD): δ = 33.1, 44.9, 64.5, 75.5, 78.5, 85.6. − MS (CI/NH_3): m/z = 166 [M + 18].

(1*S*,2*S*,3*R*,4*R*)-1,2,3-Trihydroxy-4-hydroxymethylcyclopentane (50): Compound **39** (18 mg, 0.059 mmol) in methanol (0.5 mL) was treated at room temperature with HCl (50 μL of a 6 N aqueous solution) for 2 h. Neutralization with a basic resin and chromatography (CH_2Cl_2/methanol, 3:1) gave **50** (8 mg, 91%). − $[\alpha]_D^{20}$ = +30 (c = 0.80, methanol). − Ref.[52] $[\alpha]_D^{24}$ = +33 (c = 0.80, methanol). − Ref.[53] $[\alpha]_D^{25}$ = +33.3 (c = 0.40, methanol). − Ref.[18] $[\alpha]_D^{25}$ = +47.1 (c = 0.85, methanol). − ^{1}H NMR (250 MHz, CD_3OD): δ = 1.59 (ddd, J = 13.5, 7.5, 5.5 Hz, 1 H, 5-H), 1.93 (ddd, J = 13.5, 10.5, 3.5 Hz, 1 H, 5′-H), 2.30 (m, 1 H, 4-H), 3.53 (d, J = 5.5 Hz, 2 H, 6-H, 6′-H), 3.89 (m, 2 H, 2-H, 3-H), 4.11 (m, 1 H, 1-H). − ^{13}C NMR (62.89 MHz, CD_3OD): δ = 34.0, 48.0, 64.9, 74.1, 75.4, 75.7.

(1*S*,2*R*,3*S*,4*S*)-1,2,3-Trihydroxy-4-hydroxymethylcyclopentane (51): Compound **43** (40 mg, 0.096 mmol) was hydrogenolyzed (H_2, 10% Pd/C) in ethanol (2 mL) and gave **51** (14 mg, 99%). − $[\alpha]_D^{20}$ = −4 (c = 1.70, methanol). − Ref.[53] $[\alpha]_D^{20}$ = +8 (c = 2.9, methanol) for the enantiomer. − Ref.[51] $[\alpha]_D^{20}$ = +6.6 (c = 1.00, methanol) for the enantiomer. − ^{1}H NMR (250 MHz, CD_3OD): δ = 1.25 (ddd, J = 13.5, 8.0, and 6.0 Hz, 1 H, 5-H), 2.05 (m, 1 H, 4-H), 2.22 (ddd, J = 13.5, 9.3 and 7.0 Hz, 1 H, 5-H), 3.54 (dd, J = 10.5 and 6.5 Hz, 1 H, 6-H), 3.63 (dd, J = 10.5 and 5.5 Hz, 1 H, 6-H), 3.70 (m, J = 4.5 Hz, 1 H, 2-H), 3.87 (m, J = 5 Hz, 1 H, 3-H), 4.00 (m, J = 6.5 and 4.5 Hz, 1 H, 1-H). − ^{13}C NMR (62.89 MHz, CD_3OD): δ = 33.7, 46.0, 65.3, 74.6, 76.7, 79.7. − MS (CI/NH_3): m/z = 149 [M + 1].

(1*R*,2*R*,3*R*,4*R*)-1,2,3-Trihydroxy-4-hydroxymethylcyclopentane (52):[50] Hydrogenolysis of **47** (28 mg, 0.067 mmol) with H_2 and 10% Pd/C in ethanol gave **52** (10 mg, 98%). − $[\alpha]_D^{20}$ = +4 (c = 1.00, methanol). − Ref.[50] $[\alpha]_D^{20}$ = +6 (methanol). − Ref.[54] $[\alpha]_D^{14}$ = −19.2 (c = 1.00, methanol) for the enantiomer. − Ref.[55] $[\alpha]_D^{23}$ = −8.8 (c = 0.56, methanol) for the enantiomer. − ^{1}H NMR (250 MHz, CD_3OD): δ = 1.42 (ddd, $J_{5,5'}$ = 13.5, $J_{5,4}$ = 7.5, $J_{5,1}$ = 4.0 Hz, 1 H, 5-H), 1.86−2.01 (m, 1 H, 4-H), 2.28 (ddd, $J_{5',5}$ = 13.5, $J_{5',4}$ = 9.5, $J_{5',1}$ = 6.5 Hz, 1 H, 5′-H), 3.58 (dd, $J_{6,6'}$ = 11.0, $J_{6,5}$ = 7.5 Hz, 1 H, 6-H), 3.73 (dd, $J_{6',6}$ = 11.0, $J_{6',5}$ = 5.5 Hz, 1 H, 6′-H), 3.81 (m, 2 H, 2-H, 3-H), 4.11 (ddd, $J_{1,5'}$ = 6.5, $J_{1,5} \approx J_{1,2}$ 4.0 Hz, 1 H, 1-H).). − ^{13}C NMR (62.89 MHz, CD_3OD): δ = 33.9, 46.2, 65.2, 71.6, 79.2, 80.7.

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