Fragmentation of Carbohydrate Anomeric Alkoxy Radicals: A New Synthesis of Chiral 1-Halo-1-iodo Alditols

Concepción C. González,[a] Alan R. Kennedy,[b] Elisa I. León,[a] Concepción Riesco-Fagundo,[a] and Ernesto Suárez*[a]

Abstract: Treatment of 1,2-fluorohydrins, 1,2-chlorohydrins, 1,2-bromohydrins, and 1,2-iodohydrins of the D-*gluco*, D-*galacto*, D-*lacto*, L-*rhamno*, D-*allo*, L-*arabino*, 3-deoxy-D-*gluco*, and 3,4-dideoxy-D-*gluco* families of carbohydrates with the (diacetoxyiodo)benzene/iodine system afforded 1-fluoro-1-iodo, 1-chloro-1-iodo, 1-bromo-1-iodo, and 1,1-diiodo alditols, respectively, in excellent yields. The reaction was achieved by radical fragmentation of the C1–C2 bond, triggered by the initially formed anomeric alkoxy radical, and subsequent trapping of the C2-radical by iodine atoms. This methodology is compatible with the stability of the protective groups most frequently used in carbohydrate chemistry. The potential utility of these 1-halo-1-iodo alditols as chiral synthons was evaluated by their transformation into alk-1-enyl iodides and in the Takai *E*-olefination reaction.

Keywords: Halogen compounds · alditols · carbohydrates · iodine · radical reactions

Introduction

1,1-Dihaloalkanes, and in particular the highly reactive 1,1-diiodoalkanes, are an important class of organic compounds extensively used in organic synthesis.[1] Several methods for the preparation of these compounds have been developed,[2] among them the iodolysis of 1,1-bis(diisobutylalumino)alkanes,[2a] the alkylation of diiodomethyllithium or diiodomethylsodium with reactive electrophiles,[2b] treatment of 1,1-bistrifluoromethylsulfonyloxy-alkanes with magnesium iodide,[2c–e] and the oxidation of aldehyde hydrazones with iodine.[2f,g] None of these is mild enough to be used with highly functionalized or sensitive molecules. In consequence, in the great majority of cases the 1,1-diiodoalkanes obtained are derivatives of relatively simple hydrocarbons.[3]

This situation is similar to that found for the synthesis of the mixed halo-iodo species, 1-fluoro-1-iodo,[4] 1-chloro-1-iodo,[5] and 1-bromo-1-iodo[6] compounds. Halogen exchange by means of a Finkelstein reaction can be used to prepare specific compounds.[7] Thus, the synthesis of 1-fluoro-1-iodo compounds is generally accomplished from the more easily available 1-fluoro-1-chloro or 1-fluoro-1-bromo derivatives.[4] The oxidative decarboxylations of α-bromo- and α-chlorobutyric acid with lead tetraacetate and iodine (modified Hunsdiecker reaction) to give 1-bromo-1-iodopropane and 1-chloro-1-iodopropane, respectively, albeit in low yield, have also been described.[8]

Methodology for the asymmetric synthesis of mixed geminal haloiodides has scarcely been described in the literature, although the resolution of racemic chloro-iodo-acetic acid through recrystallization of diastereomeric brucine salts was described as early as 1927.[9] To the best of our knowledge, the only previous syntheses of optically pure 1-fluoro-1-iodide compounds by resolution of racemic mixtures was reported by Bailey et al. and Myers et al.[10] The trapping of highly enantiomerically enriched α-halo-2-phenylethylmagnesium chloride with trifluoroiodoethane afforded (*S*)-1-chloro-1-iodo-2-phenylethane, with retention of configuration.[11]

Since the synthetic utility of these compounds owes a great deal to the ease and mildness with which they are prepared, the need for a more general and practical synthesis proved justified. Moreover, several products possessing this 1,1-halo-iodo grouping have been isolated from marine natural sources.[12]

[a] Prof. E. Suárez, Dr. C. C. González, Dr. E. I. León, C. Riesco-Fagundo
Instituto de Productos Naturales y Agrobiología del C.S.I.C.
Carretera de La Esperanza 3
38206 La Laguna, Tenerife (Spain)
Fax: (+34) 922-260-135
E-mail: esuarez@ipna.csic.es

[b] Dr. A. R. Kennedy
Department of Pure and Applied Chemistry
University of Strathclyde
295 Cathedral Street, Glasgow G1 1XL, Scotland (UK)
E-mail: a.r.kennedy@strath.ac.uk

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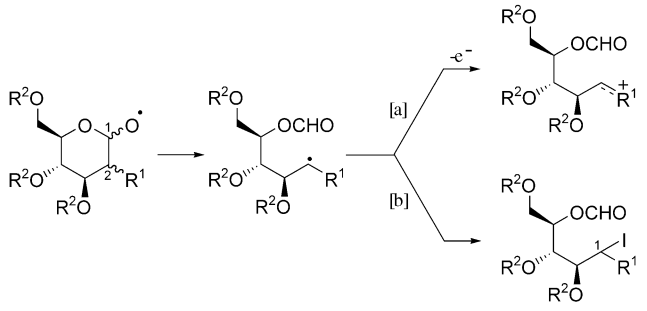
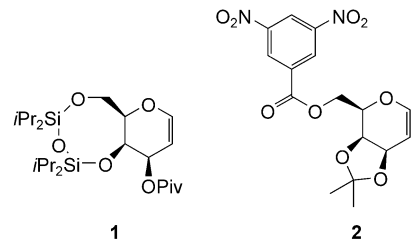
Recently, the facile formation of glycopyran-1-*O*-yl and glycofuran-1-*O*-yl radicals was achieved in our laboratories by treatment of carbohydrate anomeric alcohols with hypervalent iodine reagents in the presence of iodine.[13] The reaction presumably proceeds by homolytic fragmentation of an



Scheme 1. Mechanism of alkoxy radical fragmentation (ARF): a) R^1 = O-alkyl; R^2 = protective group. b) R^1 = OC(O)-alkyl, halogen; R^2 = protective group.

alkyl hypoiodite intermediate.[14] The newly formed alkoxy radical subsequently undergoes β-fragmentation of the C1–C2 bond and gives rise to a C2 radical (Scheme 1). The nature of the substituent at the 2-position may have a strong influence on the ultimate fate of the radical. Indeed, when the substituent is an ether group the radical is rapidly oxidized by an excess of the hypervalent iodine reagent to give an oxycarbenium ion (path a). This ion can be trapped inter- or intramolecularly by nucleophiles, leading to a variety of modified carbohydrate derivatives with one carbon fewer.[13] The presence at C2 of a substituent with a more strongly electron-withdrawing ability (e.g., an ester group, path b) should decrease the electron density at this position and the oxidation of the radical should be more difficult. This offers the possibility of competitive trapping of the intermediate C2 radical by atoms of iodine from the reaction medium. The α-iodoalkyl esters thus formed are difficult to synthesize by other methods and may be interesting chiral synthons.[13f]

Based on the above results, we decided to carry out the alkoxy radical fragmentation (ARF) reaction with 2-deoxy-2-halo carbohydrates in order to develop an advantageous methodology for the preparation of 1-halo-1-iodo-alditol derivatives. We have described the obtained preliminary results in a previous communication,[15]



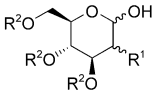
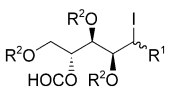
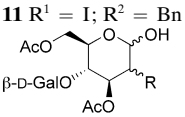
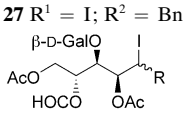
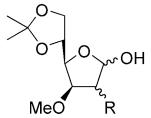
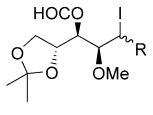
1 **2**

and we now report full details of these experiments and their extension to a number of new models.

Results and Discussion

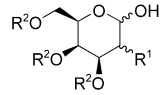
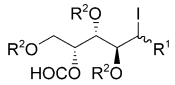
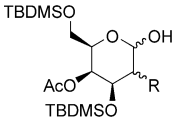
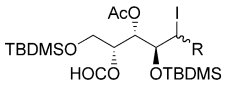
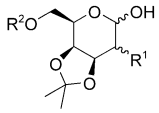
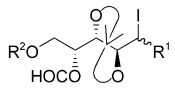
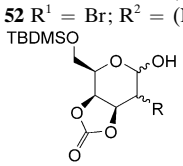
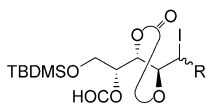
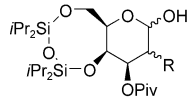
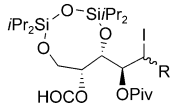
We have synthesized 1,2-halohydrins of carbohydrates in pyranose and furanose form as outlined in Table 1, Table 2, and Table 3. 1,2-Fluorohydrins, 1,2-chlorohydrins, 1,2-bromohydrins, and 1,2-iodohydrins were prepared from the corresponding 2-deoxy-hex-1-enitol by treatment with Selectfluor,[16] *N*-chlorosuccinimide[17] or chloramine-T,[18] *N*-bromoacetamide,[19] and *N*-iodosuccinimide,[20] respectively. The required 2-deoxy-hex-1-enitols were known compounds, except for 2,6-anhydro-5-deoxy-4-*O*-pivaloyl-1,3-*O*-(tetraisopropyldisiloxane-1,3-diyl)-D-*arabino*-hex-5-enitol (**1**) and 2,6-anhydro-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-3,4-*O*-isopropylidene-D-*arabino*-hex-5-enitol (**2**), which were prepared from 2,6-anhydro-5-deoxy-D-*arabino*-hex-5-enitol by well established procedures as described in the Supporting Information. The fluorohydrin **3** was synthesized by treatment of

Table 1. Synthesis of 1-halo-1-iodo-D-arabinitol derivatives.[a]

Entry	Substrate	*t* [h]	Product	Yield [%](*dr*)
				
1	**3** R^1 = F; R^2 = Ac	1	**19** R^1 = F; R^2 = Ac	96 (1:1)
2	**4** R^1 = Cl; R^2 = Ac	3	**20** R^1 = Cl; R^2 = Ac	95 (1:1)
3	**5** R^1 = Br; R^2 = Ac	1.5	**21** R^1 = Br; R^2 = Ac	99 (1:1)
4	**6** R^1 = I; R^2 = Ac	0.75	**22** R^1 = I; R^2 = Ac	92
5	**7** R^1 = F; R^2 = TBDMS	1	**23** R^1 = F; R^2 = TBDMS	94 (3:2)
6	**8** R^1 = Cl; R^2 = TBDMS	0.5	**24** R^1 = Cl; R^2 = TBDMS	84 (2:1)
7	**9** R^1 = Br; R^2 = TBDMS	1	**25** R^1 = Br; R^2 = TBDMS	91 (2:1)
8	**10** R^1 = I; R^2 = TBDMS	1	**26** R^1 = I; R^2 = TBDMS	91
9	**11** R^1 = I; R^2 = Bn	2.5	**27** R^1 = I; R^2 = Bn	86
				
10	**12** R = F	1	**28** R = F	84 (4:3)
11	**13** R = Cl	2.5	**29** R = Cl	85 (1:1)
12	**14** R = Br	3	**30** R = Br	82 (1:1)
13	**15** R = I	4	**31** R = I	80
				
14	**16** R = Cl	0.5	**32** R = Cl	83 (3:2)
15	**17** R = Br	0.5	**33** R = Br	92 (3:2)
16	**18** R = I	0.5	34 R = I	69

[a] Halohydrin (1 mmol) in CH_2Cl_2 (50 mL) containing (diacetoxyiodo)benzene (1.5 mmol) and iodine (1.5 mmol) was irradiated with two 80 W tungsten-filament lamps at reflux temperature.

Table 2. Synthesis of 5-halo-5-iodo-D-arabinitol derivatives.[a]

Entry	Substrate	t [h]	Product	Yield [%](*dr*)
				
1	**35** R^1 = F; R^2 = Ac	1	**61** R^1 = F; R^2 = Ac	94 (1:1)
2	**36** R^1 = Cl; R^2 = Ac	1.5	**62** R^1 = Cl; R^2 = Ac	96 (3:2)
3	**37** R^1 = Br; R^2 = Ac	2	**63** R^1 = Br; R^2 = Ac	98 (3:2)
4	**38** R^1 = I; R^2 = Ac	0.5	**64** R^1 = I; R^2 = Ac	84
5	**39** R^1 = F; R^2 = TBDMS	1	**65** R^1 = F; R^2 = TBDMS	95 (1:1)
6	**40** R^1 = Cl; R^2 = TBDMS	1	**66** R^1 = Cl; R^2 = TBDMS	92 (1:1)
7	**41** R^1 = Br; R^2 = TBDMS	1	**67** R^1 = Br; R^2 = TBDMS	95 (1:1)
8	**42** R^1 = I; R^2 = TBDMS	1.5	**68** R^1 = I; R^2 = TBDMS	87
				
9	**43** R = F	0.5	(*R*,*S*)-**69** R = F	83 (1:1)[b]
10	**44** R = Cl	1	**70** R = Cl	91 (3:2)
11	**45** R = Br	0.5	**71** R = Br	95 (5:4)
				
12	**46** R^1 = F; R^2 = Bn	1	(*R*,*S*)-**72** R^1 = F; R^2 = Bn	79 (3:2)[b]
13	**47** R^1 = Cl; R^2 = Bn	1	(*R*,*S*)-**73** R^1 = Cl; R^2 = Bn	92 (3:2)[b]
14	**48** R^1 = Br; R^2 = Bn	1.5	(*R*,*S*)-**74** R^1 = Br; R^2 = Bn	93 (3:2)[b]
15	**49** R^1 = I; R^2 = Bn	1	**75** R^1 = I; R^2 = Bn	90
16	**50** R^1 = F; R^2 = $(NO_2)_2$Bz[c]	1	(*R*,*S*)-**76** R^1 = F; R^2 = $(NO_2)_2$Bz	92 (5:4)[b]
17	**51** R^1 = Cl; R^2 = $(NO_2)_2$Bz	1.5	(*R*,*S*)-**77** R^1 = Cl; R^2 = $(NO_2)_2$Bz	92 (2:1)[b]
18	**52** R^1 = Br; R^2 = $(NO_2)_2$Bz	1	(*R*,*S*)-**78** R^1 = Br; R^2 = $(NO_2)_2$Bz	93 (2:1)[b]
				
19	**53** R = F	1	**79** R = F	70 (3:2)
20	**54** R = Cl	3	(*R*,*S*)-**80** R = Cl	65 (4:3)[b]
21	**55** R = Br	3	**81** R = Br	60 (1:1)
22	**56** R = I	0.5	**82** R = I	75
				
23	**57** R = F	1	**83** R = F	96 (3:2)
24	**58** R = Cl	0.5	**84** R = Cl	92 (1:1)
25	**59** R = Br	1	**85** R = Br	92 (4:3)
26	**60** R = I	0.5	**86** R = I	84

[a] Halohydrin (1 mmol) in CH_2Cl_2 (50 mL) containing (diacetoxyiodo)benzene (1.5 mmol) and iodine (1.5 mmol) was irradiated with two 80 W tungsten-filament lamps at reflux temperature. [b] *R* and *S* isomers were separated by chromatography. [c] $(NO_2)_2$Bz = 3,5-dinitrobenzoyl.

3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol with xenon difluoride,[21] followed by acid hydrolysis of the anomeric fluoride, peracetylation, and subsequent selective anomeric *O*-deacetylation with hydrazine acetate.[22] As detected spectroscopically, the halohydrins were diastereoisomeric mixtures in most cases.[23]

The ARF reactions were performed under the conditions stated in the tables, with (diacetoxyiodo)benzene (DIB) and iodine in CH_2Cl_2 at reflux temperature and irradiation with two 80 W tungsten-filament lamps. The reaction yields were determined on chromatographically homogeneous halohydrin mixtures giving correct elemental analyses, and in all cases complete consumption of the starting material was observed. In Table 1 we compare the reactions of several halohydrins **3–15** of the 2-deoxy-2-halo-glucopyranose type. The reaction proceeded smoothly to afford 1-halo-1-iodo-D-arabinitol derivatives **19–31** in excellent yield. During each reaction the integrity of the adjacent stereogenic center was preserved and no generation of diastereoisomers at this carbon atom were detected. As may be expected, the level of diastereoselection achieved was very low for the mixed halogen compounds, which in the great majority of cases were obtained as chromatographically inseparable equimolar mixtures of isomers. The mild reaction conditions were fully compatible with the acetate and TBDMS protective groups (Table 1, entries 1–8) and also with the β-(1→4)-glycosidic linkage present in the disaccharide derivatives **12–15** (Table 1, entries 10–13). The results with iodohydrin **11** (Table 1, entry 9) indicate that benzyl ethers also survive the conversion well, in spite of the recent use of the DIB/I_2 system for the deprotection of carbohydrate benzyl ethers.[24]

To extend the scope of the described method further, we investigated the feasibility of applying this methodology to the five-membered glucofuranose halohydrins **16–18**. In these three cases the reaction proceeded analogously to give a new set of halo-iodo-D-*arabino* derivatives **32–34** with a very different protection pattern (Table 1, entries 14–16).

A number of differently protected D-galactopyranose halohydrins **35–60** (Table 2) were prepared in order to study the influence of the intramolecular environments on the selectivity of the fragmentation reaction. These compounds provided a new series of 5-halo-5-iodo-D-arabinitol (1-halo-1-iodo-D-lyxitol)[25] derivatives **61–86**. In the examples shown in the first 11 entries of Table 2 little if any diastereoselectivity was observed. Nevertheless, a modest increment in the diastereoselectivity is observed as the steric demand of the starting halohydrin increases (compare entries 1 or 6,7 versus 12 or 17,18 in Table 2). The mixed fluoro-iodo

(**72**), chloro-iodo (**73**), and bromo-iodo (**74**) derivatives could now be separated by careful Chromatotron chromatography. Unfortunately, none of these diastereoisomers could be crystallized, and so we prepared the 3,5-dinitrobenzoates **76–78** in order to establish the absolute configurations at C1[25] by X-ray crystallographic analysis. Crystallization of the major isomers (*R*)-**76**, (*R*)-**77**, and (*R*)-**78** from *n*-hexane/EtOAc yielded colorless crystals suitable for X-ray studies, which permitted the determination of the stereochemistry as stated.[26]

The X-ray crystal structure of (*R*)-**76** shows that the fluorine atom exhibits a nearly antiperiplanar disposition with the oxygen at C2 (F-C1-C2-O torsion angle of 172.3°). The observed deshielding of the C1 signal in the ^{13}C NMR spectrum of the *R* isomer ($\delta_R-\delta_S$ = 3.4 ppm) and principally the differences between the ^2J(F,C) in both isomers (28.4 Hz for the *R* and 18.0 Hz for the *S*), from the X-ray crystallographic data, permit the assignment of the C1 stereochemistry in the closely related iodo-fluoro compound **72** [$\delta_R-\delta_S$ = 2 ppm, ^2J(F,C) (*R*) = 29.8 Hz, ^2J(F,C) (*S*) = 17.2 Hz]. Although the differences are smaller in the case of the fluoro-iodo compound **69** we tentatively assigned the *R* stereochemistry to the isomer with the higher ^2J(C,F) value.

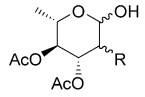
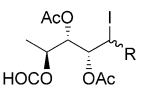
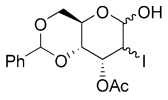
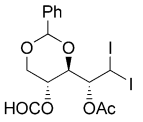
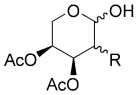
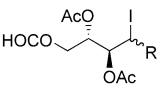
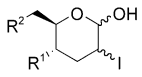
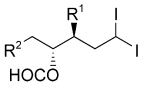
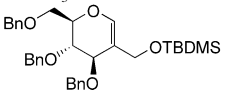
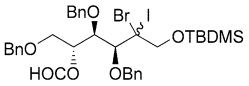
The configurations at C1 of the chloro-iodo and bromo-iodo series can now be assigned on the basis of the significant deshielding of the C3 signal in the ^{13}C NMR spectra of the *S* isomers. The observed deshielding ($\delta_S-\delta_R$ = 1.6–2.5 ppm for the mixed chloro-iodo and $\delta_S-\delta_R$ = 1.3–1.8 ppm for the bromo-iodo compound) is possibly due to restricted rotation around the C1–C2 bond. The use of the sensitive cyclic carbonate as the protective group (Table 2, entries 19–22) resulted in a significant reduction in the yield of the fragmentation reaction. On the other hand, treatment of 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl (TIPDS) group derivatives (Table 2, entries 23–26) proceeded efficiently with high yield.

Next, the reaction was examined with other types of carbohydrates or modified carbohydrates as substrates in order to test the generality and applicability of this methodology further. The results summarized in Table 3 showed that halohydrins derived from hexenitols such as 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-*arabino*-hex-1-enitol (Table 3, entries 1–4) and 3-*O*-acetyl-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enitol (Table 3, entry 5) and pentenitols such as 3-di-*O*-acetyl-1,5-anhydro-4-deoxy-D-*erythro*-pent-4-enitol (Table 3, entries 6–9) gave the corresponding 1-halo-1-iodo compounds **99–107** in similar yields.

This process could also be applied successfully to 3-deoxy and 3,4-dideoxy iodohydrins **96** and **97** (Table 3, entries 10 and 11), which were synthesized from 4,6-di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-D-*erythro*-hex-1-enitol[27] and 1,5-anhydro-1,2,3,4-tetradeoxy-6-*O*-(triisopropylsilyl)-D-*glycero*-hex-1-enitol,[28] respectively. The obtained *gem*-diiodo alditols **109** and **108** may be interesting chiral synthons when the introduction of one or two stereogenic centers, respectively, is required.

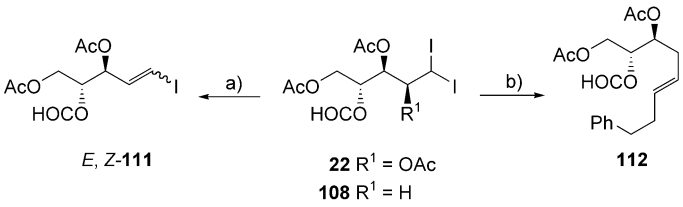
The reaction of the 2-*C*-hydroxymethyl branched carbohydrate **98**[29] (Table 3, entry 12) also proceeded effectively, providing the 2-bromo-2-iodo-D-*arabino*-hexitol derivative **110**. In this case the inherent instability of the tertiary halide intermediate precluded isolation and so it was used without purification in the fragmentation reaction.

Table 3. Synthesis of 1-halo-1-iodo compounds.[a]

Entry	Substrate	*t* [h]	Product	Yield [%](dr)
				
1	**87** R = F	0.5	**99** R = F	90 (1:1)
2	**88** R = Cl	4	**100** R = Cl	89 (1:1)
3	**89** R = Br	2	**101** R = Br	84 (1:1)
4	**90** R = I	0.5	**102** R = I	90
				
5	**91**	1	**103**	76
				
6	**92** R = F	0.5	**104** R = F	96 (3:2)
7	**93** R = Cl	1	**105** R = Cl	73 (3:2)
8	**94** R = Br	1	**106** R = Br	87 (4:3)
9	**95** R = I	0.5	**107** R = I	82
				
10	**96** R^1 = OAc; R^2 = OAc	0.5	**108** R^1 = OAc; R^2 = OAc	94
11	**97** R^1 = H; R^2 = OSi*i*Pr$_3$	2	**109** R^1 = H; R^2 = OSi*i*Pr$_3$	90
				
12[b]	**98**	2.5	**110**	69 (1:1)

[a] Halohydrin (1 mmol) in CH_2Cl_2 (50 mL) containing (diacetoxyiodo)benzene (1.5 mmol) and iodine (1.5 mmol) was irradiated with two 80 W tungsten-filament lamps at reflux temperature. [b] Crude bromohydrin was used, two-step yield.

The synthetic usefulness of these compounds as chiral synthons has been assessed in the *E*-olefination of aldehydes with chromium(II) chloride. Our initial attempts to use these 1,1-diiodo compounds in a Takai[30] reaction were unsuccessful, and only β-elimination products were isolated. These results, however, provide the possibility to obtain chiral vinyl iodides from 1,1-diiodo compounds oxygenated at the α-position. For example, treatment of 1,1-diiodo **22** with the chromium(II) chloride/DMF complex afforded a mixture of the corresponding (1*Z*)- and (1*E*)-1-iodo-D-*erythro*-pent-1-enitol derivatives **111** in excellent yield and moderate diastereoselectivity (*Z*/*E* 3:2) (Scheme 2). An iodo-chromium carbenoid may be involved in this reaction, followed by chromium-induced β-elimination of the oxygenated function at C2. As far as we know, no examples of chromium-mediated β-elimination of 2-*O*-acetyl-1,1-diiodo compounds have been reported until now.[31] Alk-1-enyl iodides are probably the most widely used organic electrophiles in the Stille and Suzuki coupling reactions.[32]



E, Z-**111** **22** R^1 = OAc **108** R^1 = H **112**

Scheme 2. Reactions of 1,1-diiodo compounds. a) $CrCl_2$ (4 equiv), DMF (4 equiv), THF, RT, 30 min, 89%, (*Z*/*E* 3:2); b) $CrCl_2$ (3 equiv), hydrocinnamaldehyde ($Ph(CH_2)_2CHO$; 1 equiv), DMF (3 equiv), THF, RT, 2.5 h, 70%.

On the other hand, the 2-deoxy-pentitol **108**, when subjected to the normal Takai reaction conditions in the presence of hydrocinnamaldehyde, gave the expected *E* olefin **112** in good yield (Scheme 2). It is worth noting the stability of the highly sensitive formyl ester under the reaction conditions.

The synthetic utility of the Takai reaction owes a great deal to the ease with which the 1,1-diiodo compounds can be synthesized. As a consequence of the difficulty in the preparation of the 1,1-diiodo compounds of highly functionalized substrates, this reaction, in the majority of cases, has been used simply as an *E*-ethylenation of aldehydes with diiodoethane.[33]

Conclusions

This new ARF reaction offers special advantages for the synthesis of these *gem*-dihalocompounds, including the ready accessibility of the starting materials, experimental simplicity, high yields, and mild conditions compatible with the stability of the protective groups most commonly used in carbohydrate chemistry. It is hoped that these 1-halo-1-iodo compounds will be powerful building blocks for organic synthesis by virtue of the fact that the carbohydrate would potentially be amenable to prior manipulation to provide more specific or complex synthons.

Experimental Section

General methods: Melting points were determined with a hot-stage apparatus. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded in $CHCl_3$ solutions unless otherwise stated. NMR spectra were determined at 500 MHz for ^1H and 125.7 MHz for ^{13}C in $CDCl_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in H_2SO_4/EtOH (4:1) and further heating until development of color.

General procedure for the synthesis of fluorohydrins: H_2O (1.5 mL) and F-TEDA-BF_4 (Selectfluor, 1.5 mmol) were added to a solution of the corresponding 2-deoxy-hex-1-enitol (1 mmol) in nitromethane (8.5 mL), and the mixture was stirred at room temperature (1–5 h) until the disappearance of the starting material was observed by TLC. The reaction mixture was then heated to reflux for 0.5 h, poured into brine, and extracted with EtOAc. The organic layer was dried and concentrated in vacuo. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the required fluorohydrin compounds. The fluorohydrin corresponding to 3,4,6-tri-*O*-acetyl-D-glucal **3** was prepared by the procedure described in the Supporting Information.

General procedure for the synthesis of chlorohydrins: A solution of the corresponding 2-deoxy-hex-1-enitol (1 mmol) in THF (45 mL) and H_2O (5 mL), containing *N*-chlorosuccinimide (2 mmol), was heated at reflux for 8 h. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the required chlorohydrin compounds. Alternatively, a solution of the 2-deoxy-hex-1-enitol (1 mmol) in acetone (10 mL) and H_2O (10 mL) was cooled to 0°C and chloramine-T trihydrate (1.5 mmol) and pyridinium *p*-toluenesulfonate (1.5 mmol) were added. The reaction mixture was kept at this temperature for 5 min and was then stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with EtOAc. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the required iodohydrin compounds.

General procedure for the synthesis of bromohydrins: A solution of the corresponding 2-deoxy-hex-1-enitol (1 mmol) in THF (35 mL) and H_2O (4 mL), containing recently crystallized *N*-bromoacetamide (1.5 mmol), was stirred at room temperature for 4 h. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo. Column chromatography of the residue (hexanes/EtOAc mixtures) afforded the required bromohydrin compounds.

General procedure for the synthesis of iodohydrins: A solution of the corresponding 2-deoxy-hex-1-enitol (1 mmol) in THF (10 mL) and H_2O (10 mL), containing *N*-iodosuccinimide (1.2 mmol), was stirred at room temperature for 20 min. The reaction mixture was diluted with EtOAc, poured into water, and extracted with EtOAc. The organic layer was washed with 10% aqueous sodium thiosulfate, dried, and concentrated in vacuo. Chromatotron chromatography of the residue (hexanes/EtOAc mixtures) afforded the required iodohydrin compounds.

General procedure for the synthesis of 1-halo-1-iodo compounds: A solution of the halohydrin (1 mmol) in CH_2Cl_2 (50 mL) containing (diacetoxyiodo)benzene (1.5 mmol) and iodine (1.5 mmol) was irradiated with two 80 W tungsten-filament lamps at reflux temperature. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was washed with 10% aqueous sodium thiosulfate, dried, and concentrated in vacuo. Chromatotron chromatography of the residue (hexanes/EtOAc mixtures) afforded the required halo-iodine compounds.

2,3,5-Tri-*O*-acetyl-1-deoxy-4-*O*-formyl-1,1-diiodo-D-arabinitol (22): Crystalline solid (92%): m.p. 109–110°C (from *n*-hexane/EtOAc); $[\alpha]_D = +45$ ($c = 1.42$); ^1H NMR: $\delta = 2.04$ (s, 3H), 2.12 (s, 3H), 2.14 (s, 3H), 4.08 (dd, $J = 5.9$, 12.4 Hz, 1H), 4.27 (dd, $J = 3.3$, 12.4 Hz, 1H), 5.06 (d, $J = 7.5$ Hz, 1H), 5.18 (m, 1H), 5.25 (dd, $J = 3.0$, 7.5 Hz, 1H), 5.76 (dd, $J = 3.0$, 7.3 Hz, 1H), 7.98 (s, 1H) ppm; ^{13}C NMR: $\delta = -33.9$ (CH), 20.6 ($3\times CH_3$), 61.5 (CH_2), 68.6 (CH), 68.9 (CH), 73.4 (CH), 159.4 (CH), 169.3 ($2\times C$), 170.4 (C) ppm; IR: $\tilde{\nu} = 3013$, 1754 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 542 (<1) $[M]^+$, 482 (3), 207 (100); HRMS (EI): found 541.8989; $C_{12}H_{16}I_2O_8$ calcd 541.8935; elemental analysis calcd (%) for $C_{12}H_{16}I_2O_8$ (542.1): C 26.59, H 2.98; found: C 26.72, H 2.82.

2,3,5-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-1-deoxy-4-*O*-formyl-1,1-diiodo-D-arabinitol (26): Oil (91%): $[\alpha]_D = +5.0$ ($c = 2.38$); ^1H NMR: $\delta = 0.03$ (s, 3H), 0.04 (s, 3H), 0.13 (s, 3H), 0.13 (s, 3H), 0.15 (s, 3H), 0.30 (s, 3H), 0.87 (s, 9H), 0.92 (s, 9H), 1.01 (s, 9H), 3.76 (dd, $J = 4.8$, 5.0 Hz, 1H), 3.76 (dd, $J = 6.7$, 11.6 Hz, 1H), 3.90 (dd, $J = 2.8$, 11.6 Hz, 1H), 4.07 (dd, $J = 1.9$, 5.0 Hz, 1H), 5.22 (ddd, $J = 2.8$, 4.8, 6.7 Hz, 1H), 5.62 (d, $J = 1.9$ Hz, 1H), 8.09 (s, 1H) ppm; ^{13}C NMR: $\delta = -24.1$ (CH), -5.3 (CH_3), -5.0 (CH_3), -4.6 (CH_3), -4.6 (CH_3), -4.0 (CH_3), -3.7 (CH_3), 18.0 (C), 18.0 (C), 18.3 (C), 26.0 ($9\times CH_3$), 62.3 (CH_2), 74.0 (CH), 74.4 (CH), 81.2 (CH), 160.7 (CH) ppm; IR: $\tilde{\nu} = 2930$, 1726, 1110 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 713 (15) $[M-C_3H_9]^+$, 655 (9), 581 (100), 555 (84), 453 (44); HRMS (EI): found: 713.0515; $C_{21}H_{43}I_2O_5Si_3$ calcd 713.0508; elemental analysis calcd (%) for $C_{24}H_{52}I_2O_5Si_3$ (758.7): C 37.99, H 6.91; found: C 37.80, H 7.26.

2,3,5-Tri-*O*-benzyl-1-deoxy-4-*O*-formyl-1,1-diiodo-D-arabinitol (27): Oil (86%): $[\alpha]_D = +22.7$ ($c = 1.046$); ^{1}H NMR: $\delta = 3.68$ (dd, $J = 4.4$, 5.6 Hz, 1H), 3.67 (dd, $J = 5.4$, 5.4 Hz, 1H), 3.89 (dd, $J = 5.2$, 10.3 Hz, 1H), 4.11 (dd, $J = 4.5$, 5.6 Hz, 1H), 4.51 (d, $J = 11.9$ Hz, 1H), 4.55 (d, $J = 11.9$ Hz, 1H), 4.71 (d, $J = 11.1$ Hz, 1H), 4.79 (d, $J = 11.1$ Hz, 1H), 4.83 (d, $J = 10.7$ Hz, 1H), 5.03 (d, $J = 10.7$ Hz, 1H), 5.19 (ddd, $J = 4.8$, 4.8, 4.8 Hz, 1H), 5.39 (d, $J = 4.4$ Hz, 1H), 7.26–7.46 (m, 15H), 8.03 (s, 1H) ppm; ^{13}C NMR: $\delta = -25.1$ (CH), 67.2 (CH_2), 72.6 (CH), 73.5 (CH_2), 75.1 (CH_2), 75.4 (CH_2), 80.4 (CH), 83.9 (CH), 127.8 (5×CH), 128.3 (5×CH), 128.5 (5×CH), 137.3 (C), 137.5 (C), 137.7 (C), 159.9 (CH) ppm; IR: $\tilde{\nu} = 3016$, 1726, 1174 cm^{-1}; MS (70 eV, EI): m/z (%): 595 (1) $[M-PhCH_2]^+$, 503 (0.5), 427 (0.5), 91 (100); HRMS (EI): found: 594.9494; $C_{20}H_{21}I_2O_5$ calcd 594.9479; elemental analysis calcd (%) for $C_{27}H_{28}I_2O_5$ (686.3): C 47.25, H 4.11; found: C 47.29, H 4.02.

2,5-Di-*O*-acetyl-1-deoxy-4-*O*-formyl-1,1-diiodo-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-D-arabinitol (31): Oil (80%): $[\alpha]_D = +28.4$ ($c = 1.02$); ^{1}H NMR: $\delta = 1.95$ (s, 3H), 2.05 (s, 3H), 2.06 (s, 6H), 2.14 (s, 3H), 2.16 (s, 3H), 3.96 (dd, $J = 6.6$, 7.0 Hz, 1H), 4.02 (dd, $J = 5.6$, 12.4 Hz, 1H), 4.19 (dd, $J = 7.0$, 11.3 Hz, 1H), 4.30 (dd, $J = 6.3$, 11.3 Hz, 1H), 4.51 (dd, $J = 2.7$, 12.4 Hz, 1H), 4.56 (d, $J = 8.0$ Hz, 1H), 4.57 (dd, $J = 1.8$, 4.7 Hz, 1H), 4.97 (dd, $J = 3.5$, 10.4 Hz, 1H), 5.04 (m, 1H), 5.17 (dd, $J = 8.0$, 10.4 Hz, 1H), 5.33 (dd, $J = 1.8$, 9.6 Hz, 1H), 5.36 (m, 1H), 5.37 (d, $J = 9.7$ Hz, 1H), 7.98 (s, 1H) ppm; ^{13}C NMR: $\delta = -27.6$ (CH), 20.5 (CH_3), 20.6 (CH_3), 20.7 (2×CH_3), 20.8 (CH_3), 20.9 (CH_3), 61.1 (CH_2), 61.3 (CH_2), 66.7 (CH), 68.8 (CH), 69.9 (CH), 70.9 (CH), 71.2 (CH), 73.9 (CH), 75.4 (CH), 101.6 (CH), 159.4 (CH), 169.1 (C), 169.8 (C), 170.0 (C), 170.1 (C), 170.2 (C), 170.4 (C) ppm; IR: $\tilde{\nu} = 3026$, 1751, 1232, 1076 cm^{-1}; MS (FAB) m/z (%): 853 (100) $[M+Na]^+$, 831 (42), 703 (49); HRMS (EI): found: 770.9581; $C_{22}H_{29}I_2O_{14}$ calcd 770.9647; elemental analysis calcd (%) for $C_{24}H_{32}I_2O_{16}$ (830.3): C 34.72, H 3.88; found: C 34.75, H 3.91.

1-Deoxy-3-*O*-formyl-1,1-diiodo-2-*O*-methyl-4,5-*O*-isopropylidene-D-arabinitol (34): Oil (69%): $[\alpha]_D = +12$ ($c = 1.04$); ^{1}H NMR: $\delta = 1.35$ (s, 3H), 1.46 (s, 3H), 3.60 (dd, $J = 3.0$, 7.0 Hz, 1H), 3.72 (s, 3H), 3.85 (dd, $J = 5.3$, 8.9 Hz, 1H), 4.02 (dd, $J = 6.1$, 8.9 Hz, 1H), 4.18 (ddd, $J = 5.3$, 6.1, 8.1 Hz, 1H), 5.14 (d, $J = 7.0$ Hz, 1H), 5.49 (dd, $J = 3.0$, 8.1 Hz, 1H), 8.09 (s, 1H) ppm; ^{13}C NMR: $\delta = -27.8$ (CH), 25.4 (CH_3), 26.7 (CH_3), 62.0 (CH_3), 66.8 (CH_2), 72.6 (CH), 74.4 (CH), 84.3 (CH), 110.1 (C), 160.0 (CH) ppm; IR: $\tilde{\nu} = 2992$, 2938, 1732 cm^{-1}; MS (70 eV, EI): m/z (%): 470 (1) $[M]^+$, 455 (22), 438 (6), 343 (8), 101 (100); HRMS (EI): found: 469.9064; $C_{10}H_{16}I_2O_5$ calcd 469.9087; elemental analysis calcd (%) for $C_{10}H_{16}I_2O_5$ (470.0): C 25.54, H 3.43; found: C 25.66, H 3.26.

1,3,4-Tri-*O*-acetyl-5-deoxy-2-*O*-formyl-5,5-diiodo-D-arabinitol (64): Crystalline solid (84%): m.p. 122–123°C (from *n*-hexane/EtOAc); $[\alpha]_D = +11$ ($c = 0.32$); ^{1}H NMR: $\delta = 1.99$ (s, 3H), 2.14 (s, 3H), 2.15 (s, 3H), 3.85 (dd, $J = 7.6$, 11.8 Hz, 1H), 4.29 (dd, $J = 4.7$, 11.8 Hz, 1H), 5.02 (dd, $J = 2.7$, 8.4 Hz, 1H), 5.21 (dd, $J = 1.2$, 8.4 Hz, 1H), 5.24 (d, $J = 2.7$ Hz, 1H), 5.38 (ddd, $J = 1.2$, 4.7, 7.6 Hz, 1H), 7.97 (s, 1H) ppm; ^{13}C NMR: $\delta = -32.3$ (CH), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 62.0 (CH_2), 67.2 (CH), 72.1 (CH), 73.4 (CH), 159.7 (CH), 169.1 (2×C), 170.3 (C) ppm; IR: $\tilde{\nu} = 3027$, 2953, 1753 cm^{-1}; MS (70 eV, EI): m/z (%): 482 (19) $[M-AcOH]^+$, 415 (10), 327 (59), 313 (100); HRMS (EI): found: 481.8750; $C_{10}H_{12}I_2O_6$ calcd 481.8723; elemental analysis calcd (%) for $C_{12}H_{16}I_2O_8$ (542.1): C 26.59, H 2.98; found: C 26.82, H 2.64.

1,3,4-Tris-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-5,5-diiodo-2-*O*-formyl-D-arabinitol (68): Oil (87%): $[\alpha]_D = -6.4$ ($c = 1.43$); ^{1}H NMR: $\delta = 0.07$ (s, 3H), 0.08 (s, 3H), 0.15 (s, 3H), 0.22 (s, 3H), 0.24 (s, 3H), 0.35 (s, 3H), 0.91 (s, 18H), 0.98 (s, 9H), 3.74 (dd, $J = 4.5$, 11.5 Hz, 1H), 3.80 (dd, $J = 4.3$, 11.5 Hz, 1H), 3.90 (dd, $J = 4.3$, 6.4 Hz, 1H), 4.22 (dd, $J = 3.4$, 5.4 Hz, 1H), 5.08 (ddd, $J = 4.3$, 4.5, 5.4 Hz, 1H), 5.55 (d, $J = 6.4$ Hz, 1H), 8.08 (s, 1H) ppm; ^{13}C NMR (100.6 MHz): $\delta = -17.8$ (CH), −5.4 (CH_3), −5.2 (CH_3), −4.3 (CH_3), −3.5 (CH_3), −3.4 (CH_3), −3.2 (CH_3), 18.2 (C), 18.3 (C), 18.7 (C), 25.9 (3×CH_3), 26.1 (3×CH_3), 26.5 (3×CH_3), 61.2 (CH_2), 70.4 (CH), 74.8 (CH), 81.7 (CH), 160.5 (CH) ppm; IR: $\tilde{\nu} = 3017$, 1722, 1472, 1257, 1187 cm^{-1}; MS (70 eV, EI): m/z (%): 701 (1) $[M-C(CH_3)_3]^+$, 673 (1), 655 (1), 569 (3), 527 (2), 73 (100); HRMS (EI): found: 701.0542; $C_{20}H_{43}I_2O_2Si_3$ calcd 701.0508; elemental analysis calcd (%) for $C_{24}H_{52}I_2O_5Si_3$ (758.7): C 37.99, H 6.91; found: C 38.07, H 6.79.

(5*RS*)-3-*O*-Acetyl-1,4-bis-*O*-[*tert*-butyl(dimethyl)silyl]-5-deoxy-5-fluoro-2-*O*-formyl-5-iodo-D-arabinitol (69): Diastereoisomeric mixture (1:1), separated by careful column chromatography (hexanes/EtOAc 98:2). Compound (*S*)-**69**: crystalline solid (40.8%): m.p. 40–41.5°C (from *n*-hexane/EtOAc); $[\alpha]_D = +8.4$ ($c = 0.25$); ^{1}H NMR (C_6D_6): $\delta = 0.01$ (s, 3H), 0.02 (s, 3H), 0.06 (s, 6H), 0.94 (s, 9H), 0.95 (s, 9H), 1.71 (s, 3H), 3.74 (dd, $J = 5.0$, 11.1 Hz, 1H), 3.81 (dd, $J = 5.7$, 11.1 Hz, 1H), 4.24 (ddd, $J = 4.0$, 6.5 Hz, ^3J(F,H) = 10.1 Hz, 1H), 5.46 (ddd, $J = 5.0$, 5.0, 5.0 Hz, 1H), 5.80 (dd, $J = 4.0$, 4.0 Hz, 1H), 6.82 (dd, $J = 6.5$ Hz, ^2J(F,H) = 11.1 Hz, 1H), 7.65 (s, 1H) ppm; ^{13}C NMR (C_6D_6): $\delta = -5.4$ (CH_3), −5.3 (CH_3), −4.7 (CH_3), −4.6 (CH_3), 18.4 (2×C), 20.3 (CH_3), 25.9 (3×CH_3), 26.0 (3×CH_3), 62.0 (CH_2), 71.3 (CH), 72.0 (CH), 74.9 (^1J(F,C) = 256.8 Hz, CH), 77.0 (^2J(F,C) = 19.5 Hz, CH), 159.8 (CH), 168.7 (C); IR (CCl_4): $\tilde{\nu} = 1754$, 1732, 1257, 1175 cm^{-1}; MS (70 eV, EI): m/z (%): 521 (16) $[M-C_4H_9]^+$, 441 (8), 333 (10), 301 (14), 207 (13), 174 (16), 117 (81), 73 (100); HRMS (EI): found: 521.0691; $C_{16}H_{31}FIO_6Si_2$ calcd 521.0688; elemental analysis calcd (%) for $C_{20}H_{40}FIO_6Si_2$ (578.6): C 41.51, H 6.97; found: C 41.57, H 6.79.

Compound (*R*)-**69**: amorphous solid (41.5%): $[\alpha]_D = +4.5$ ($c = 0.22$); ^{1}H NMR: $\delta = 0.05$ (s, 3H), 0.06 (s, 3H), 0.13 (s, 3H), 0.14 (s, 3H), 0.89 (s, 9H), 0.93 (s, 9H), 2.09 (s, 3H), 3.69 (dd, $J = 5.5$, 11.3 Hz, 1H), 3.72 (dd, $J = 5.5$, 11.3 Hz, 1H), 3.80 (ddd, $J = 3.1$, 6.6 Hz, ^3J(F,H) = 10.2 Hz, 1H), 5.11 (dd, $J = 3.5$, 6.6 Hz, 1H), 5.21 (ddd, $J = 3.5$, 5.5, 5.5 Hz, 1H), 6.85 (dd, $J = 3.1$ Hz, ^2J(F,H) = 48.1 Hz, 1H), 8.11 (s, 1H) ppm; ^{13}C NMR: $\delta = -5.55$ (CH_3), −5.48 (CH_3), −4.6 (CH_3), −3.9 (CH_3), 18.2 (2×C), 20.7 (CH_3), 25.7 (3×CH_3), 25.9 (3×CH_3), 61.7 (CH_2), 72.0 (2×CH), 73.6 (^2J(F,C) = 21.1 Hz, CH), 78.0 (^1J(F,C) = 256.0 Hz, CH), 160.1 (CH), 169.1 (C) ppm; IR (CCl_4): $\tilde{\nu} = 1760$, 1734, 1222, 1173 cm^{-1}; MS (70 eV, EI): m/z (%): 521 (30) $[M-C_4H_9]^+$, 441 (12), 415 (11), 333 (15), 301 (20), 174 (16), 117 (72), 73 (100); HRMS (EI): found: 521.0675; $C_{16}H_{31}FIO_6Si_2$ calcd 521.0688; elemental analysis calcd (%) for $C_{20}H_{40}FIO_6Si_2$ (578.6): C 41.51, H 6.97; found: C 41.60, H 6.61.

(5*RS*)-1-*O*-Benzyl-5-deoxy-5-fluoro-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (72): Diastereoisomeric mixture (3:2), separated by careful Chromatotron chromatography (hexanes/EtOAc 98:2). Compound (*R*)-**72**: Oil (42%); $[\alpha]_D = +54$ ($c = 0.2$); ^{1}H NMR: $\delta = 1.39$ (s, 3H), 1.47 (s, 3H), 3.67 (ddd, $J = 5.2$, 5.2, 13.1 Hz, 2H), 4.41 (ddd, $J = 4.9$, 9.2 Hz, ^3J(F,H) = 4.5 Hz, 1H), 4.52 (dd, $J = 4.9$, 5.2 Hz, 1H), 4.53 (d, $J = 11.8$ Hz, 1H), 4.56 (d, $J = 11.8$ Hz, 1H), 5.39 (ddd, $J = 5.2$, 5.2, 5.2 Hz, 1H), 6.84 (dd, $J = 9.2$ Hz, ^2J(F,H) = 48.5 Hz, 1H), 7.29–7.37 (m, 5H), 8.09 (s, 1H) ppm; ^{13}C NMR: $\delta = 25.1$ (CH_3), 27.4 (CH_3), 68.2 (CH_2), 68.5 (CH), 73.4 (CH_2), 73.6 (^1J(F,C) = 268.4 Hz, CH), 74.5 (CH), 79.7 (^2J(F,C) = 29.8 Hz, CH), 109.4 (C), 127.7 (2×CH), 127.9 (CH), 128.5 (2×CH), 137.4 (C), 159.9 (CH) ppm; IR: $\tilde{\nu} = 3032$, 1735, 1375, 1223, 1166 cm^{-1}; MS (70 eV, EI): m/z (%): 438 (1) $[M]^+$, 423 (2), 380 (2), 185 (10), 147 (40), 91 (100); HRMS (EI): found: 438.0313; $C_{16}H_{20}FIO_5$ calcd 438.0340; elemental analysis calcd (%) for $C_{16}H_{20}FIO_5$ (438.2): C 43.83, H 4.60; found: C 43.78, H 4.67.

Compound (*S*)-**72**: Oil (37%); $[\alpha]_D = +13.1$ ($c = 0.13$); ^{1}H NMR: $\delta = 1.42$ (s, 3H), 1.54 (s, 3H), 3.58 (dd, $J = 7.0$, 9.8 Hz, 1H), 3.70 (dd, $J = 5.3$, 9.8 Hz, 1H), 4.39 (t, $J = 6.3$ Hz, 1H), 4.47 (ddd, $J = 3.3$, 6.3 Hz, ^3J(F,H) = 24.3 Hz, 1H), 4.53 (s, 2H), 5.39 (ddd, $J = 6.3$, 6.3, 6.0 Hz, 1H), 6.92 (dd, $J = 3.3$ Hz, ^2J(F,H) = 49.8 Hz, 1H), 7.28–7.39 (m, 5H), 8.09 (s, 1H) ppm; ^{13}C NMR: $\delta = 25.6$ (CH_3), 26.3 (CH_3), 68.5 (CH_2), 69.1 (CH), 71.6 (^1J(F,C) = 261.1 Hz, CH), 73.7 (CH_2), 76.3 (CH), 81.3 (^2J(F,C) = 17.2 Hz, CH), 110.3 (C), 127.9 (2×CH), 128.2 (CH), 128.6 (2×CH), 136.9 (C), 159.9 (CH) ppm; IR: $\tilde{\nu} = 3032$, 1733, 1372, 1220, 1169, 1134 cm^{-1}; MS (70 eV, EI): m/z (%): 438 (1) $[M]^+$, 423 (3), 380 (1), 185 (7), 147 (19), 91 (100); HRMS (EI): found: 438.0349; $C_{16}H_{20}FIO_5$ calcd 438.0340; elemental analysis calcd (%) for $C_{16}H_{20}FIO_5$ (438.2): C 43.85, H 4.60; found: C 43.62, H 5.04.

(5*RS*)-1-*O*-Benzyl-5-chloro-5-deoxy-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (73): Diastereoisomeric mixture (3:2), separated by careful Chromatotron chromatography (hexanes/EtOAc 98:2). Compound (*R*)-**73**: Oil (52%); $[\alpha]_D = +43$ ($c = 1.33$); ^{1}H NMR: $\delta = 1.40$ (s, 3H), 1.52 (s, 3H), 3.63 (dd, $J = 6.9$, 9.6 Hz, 1H), 3.67 (dd, $J = 6.1$, 9.7 Hz, 1H), 4.45 (dd, $J = 5.9$, 9.7 Hz, 1H), 4.50 (dd, $J = 2.2$, 5.8 Hz, 1H), 4.54 (s, 2H), 5.45 (m, 1H), 5.69 (d, $J = 9.3$ Hz, 1H), 7.29–7.36 (m, 5H), 8.10 (s, 1H) ppm; ^{13}C NMR (50.3 MHz): $\delta = 25.3$ (CH_3), 25.8 (CH), 26.8 (CH_3), 68.2 (CH_2), 68.5 (CH), 73.3 (CH_2), 74.2 (CH), 82.2 (CH), 109.3 (C), 127.7 (2×CH), 127.9 (CH), 128.4 (2×CH), 137.4 (C), 160.2 (CH) ppm; IR: $\tilde{\nu} = 1728$ cm^{-1}; MS (70 eV, EI): m/z (%): 441/439 (2/5) $[M-Me]^+$, 398/396 (0.3/1), 277/275 (2/6), 185 (12); HRMS (EI):

found: 440.9737; $C_{15}H_{17}{}^{37}ClIO_5$ calcd 440.9780; elemental analysis calcd (%) for $C_{16}H_{20}ClIO_5$ (454.7): C 42.27, H 4.43; found: C 42.47, H 4.17.

Compound (*S*)-**73**: Oil (40%); $[\alpha]_D = -25$ ($c = 0.5$); ^{1}H NMR: δ = 1.42 (s, 3H), 1.58 (s, 3H), 3.59 (dd, J = 6.8, 9.8 Hz, 1H), 3.68 (dd, J = 5.9, 9.9 Hz, 1H), 4.42 (dd, J = 4.7, 5.9 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.55 (d, J = 11.8 Hz, 1H), 4.71 (dd, J = 6.5, 6.5 Hz, 1H), 5.53 (ddd, J = 6.1, 6.1, 6.1 Hz, 1H), 5.75 (d, J = 6.8 Hz, 1H), 7.30–7.38 (m, 5H), 8.10 (s, 1H) ppm; ^{13}C NMR (50.3 MHz): δ = 25.4 (CH), 25.6 (CH_3), 26.3 (CH_3), 68.6 (CH_2), 68.6 (CH), 73.6 (CH_2), 76.7 (CH), 82.9 (CH), 110.4 (C), 127.8 (2×CH), 128.0 (CH), 128.6 (2×CH), 137.1 (C), 160.1 (CH) ppm; IR: $\tilde{\nu}$ = 1725 cm^{-1}; MS (70 eV, EI): m/z (%): 456/454 (0.2/0.6) $[M]^+$, 441/439 (1/3), 277/275 (1/3), 185 (9); HRMS (EI): found: 454.0011; $C_{16}H_{20}{}^{35}ClIO_5$ calcd 454.0044; elemental analysis calcd (%) for $C_{16}H_{20}ClIO_5$ (454.7): C 42.27, H 4.43; found: C 42.35, H 4.27.

(5*RS*)-1-*O*-Benzyl-5-bromo-5-deoxy-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (74): Diastereoisomeric mixture (3:2) separated by careful Chromatotron chromatography. Compound (*R*)-**74**: Oil (56%); $[\alpha]_D = +38$ ($c = 0.64$); ^{1}H NMR: δ = 1.41 (s, 3H), 1.54 (s, 3H), 3.62 (dd, J = 6.8, 9.8 Hz, 1H), 3.66 (dd, J = 6.3, 9.8 Hz, 1H), 4.50 (dd, J = 1.5, 5.9 Hz, 1H), 4.54 (s, 2H), 4.58 (dd, J = 6.0, 10.0 Hz, 1H), 5.41 (d, J = 10.0 Hz, 1H), 5.50 (ddd, J = 1.3, 6.6, 6.6 Hz, 1H), 7.28–7.34 (m, 5H), 8.11 (s, 1H) ppm; ^{13}C NMR: δ = 6.3 (CH), 25.4 (CH_3), 26.7 (CH_3), 68.3 (CH_2), 68.5 (CH), 73.4 (CH_2), 74.6 (CH), 82.1 (CH), 109.4 (C), 127.8 (2×CH), 127.9 (CH), 128.4 (2×CH), 137.5 (C), 160.2 (CH) ppm; IR: $\tilde{\nu}$ = 1725 cm^{-1}; MS (70 eV, EI): m/z (%): 500/498 (<1) $[M]^+$, 485/483 (3), 321/319 (3), 209/207 (15); HRMS (EI): found: 499.9565; $C_{16}H_{20}{}^{81}BrIO_5$ calcd 499.9518; elemental analysis calcd (%) for $C_{16}H_{20}BrIO_5$ (499.1): C 38.50, H 4.04; found: C 38.72, H 3.98.

Compound (*S*)-**74**: Oil (37%): $[\alpha]_D = -12$ ($c = 0.73$); ^{1}H NMR: δ = 1.42 (s, 3H), 1.58 (s, 3H), 3.61 (dd, J = 6.8, 9.9 Hz, 1H), 3.66 (dd, J = 6.2, 9.9 Hz, 1H), 4.46 (dd, J = 3.3, 6.1 Hz, 1H), 4.54 (d, J = 11.9 Hz, 1H), 4.55 (d, J = 11.9 Hz, 1H), 4.74 (dd, J = 6.1, 8.4 Hz, 1H), 5.44 (d, J = 8.4 Hz, 1H), 5.54 (ddd, J = 3.5, 6.8, 6.8 Hz, 1H), 7.30–7.37 (m, 5H), 8.11 (s, 1H) ppm; ^{13}C NMR: δ = 6.1 (CH), 25.5 (CH_3), 26.5 (CH_3), 68.4 (CH_2), 68.5 (CH), 73.5 (CH_2), 76.4 (CH), 82.7 (CH), 110.2 (C), 127.8 (2×CH), 128.0 (CH), 128.6 (2×CH), 137.3 (C), 160.2 (CH) ppm; IR: $\tilde{\nu}$ = 1725 cm^{-1}; MS (70 eV, EI): m/z (%): 500/498 (<1) $[M]^+$, 485/483 (1), 321/319 (2), 209/207 (9); HRMS (EI): found: 499.9483; $C_{16}H_{20}{}^{81}BrIO_5$ calcd 499.9518; elemental analysis calcd (%) for $C_{16}H_{20}BrIO_5$ (499.1): C 38.50, H 4.04; found: C 38.67, H 3.93.

1-*O*-Benzyl-5-deoxy-2-*O*-formyl-5,5-diiodo-3,4-*O*-isopropylidene-D-arabinitol (75): Oil (90%): $[\alpha]_D = +29$ ($c = 1.88$); ^{1}H NMR: δ = 1.40 (s, 3H), 1.54 (s, 3H), 3.60 (dd, J = 6.6, 9.9 Hz, 1H), 3.63 (dd, J = 6.4, 9.9 Hz, 1H), 4.50 (dd, J = 1.8, 5.9 Hz, 1H), 4.53 (s, 1H), 4.54 (s, 1H), 4.62 (dd, J = 5.9, 10.1 Hz, 1H), 4.91 (d, J = 10.1 Hz, 1H), 5.50 (ddd, J = 1.8, 6.4, 6.6 Hz, 1H), 7.97–7.27 (m, 5H), 8.10 (s, 1H) ppm; ^{13}C NMR: δ = −34.2 (CH), 25.5 (CH_3), 26.7 (CH_3), 68.2 (CH), 68.5 (CH_2), 73.3 (CH_2), 75.0 (CH), 82.6 (CH), 109.6 (C), 127.8 (2×CH), 127.8 (CH), 128.5 (2×CH), 137.4 (C), 160.3 (CH) ppm; IR: $\tilde{\nu}$ = 3010, 2938, 1724 cm^{-1}; MS (70 eV, EI): m/z (%): 546 (<1) $[M]^+$, 531 (2), 91 (100); HRMS (EI): found: 545.9393; $C_{16}H_{20}I_2O_5$ calcd 545.9400; elemental analysis calcd (%) for $C_{16}H_{20}I_2O_5$ (546.1): C 35.17, H 3.69; found: C 35.41, H 3.60.

(5*RS*)-5-Deoxy-1-*O*-(3,5-dinitrobenzoyl)-5-fluoro-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (76): Diastereoisomeric mixture (92%, 5:4), partially separated by careful Chromatotron chromatography (hexanes/EtOAc 85:15). Compound (*R*)-**76**: crystalline solid (51.3%): m.p. 122–124°C (from *n*-hexane/EtOAc); $[\alpha]_D = +43.2$ ($c = 0.8$); ^{1}H NMR: δ = 1.43 (s, 3H), 1.52 (s, 3H), 4.48 (dd, J = 3.4, 5.7 Hz, 1H), 4.59–4.63 (m, 1H), 4.78 (dd, J = 3.4, 12.0 Hz, 1H), 5.70–5.71 (m, 2H), 6.87 (dd, J = 8.8 Hz, ^2J(F,H) = 48.7 Hz, 1H), 8.14 (s, 1H), 9.14 (d, J = 2.1 Hz, 2H), 9.25 (dd, J = 2.1, 2.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz): δ = 25.2 (CH_3), 27.2 (CH_3), 65.7 (CH_2), 67.2 (^3J(F,C) = 3.2 Hz, CH), 71.6 (^1J(F,C) = 248.6 Hz, CH), 75.1 (CH), 80.3 (^2J(F,C) = 28.4 Hz, CH), 110.2 (C), 122.7 (CH), 129.6 (2×CH), 133.2 (C), 148.7 (2×C), 159.7 (CH), 162.2 (C); IR $\tilde{\nu}$ = 3094, 2984, 1742, 1372, 1240, 1170 cm^{-1}; MS (70 eV, EI): m/z (%): 527 (40) $[M-Me]^+$, 415 (21), 195 (100), 149 (32); HRMS (EI): found: 526.9603; $C_{15}H_{13}FIN_2O_{10}$ calcd 526.9599; elemental analysis calcd (%) for $C_{16}H_{16}FIN_2O_{10}$ (542.2): C 35.44, H 2.97, N 5.17; found: C 35.71, H 2.74, N 5.13.

Crystal data and structure refinement for (*R*)-**76**: $C_{16}H_{16}FIN_2O_{10}$, M_τ = 542.21, monoclinic, space group $P2_1$, a = 7.9686 (1), b = 7.5629 (1), c = 17.7602 (3) Å, β = 102.262 (1), V = 1045.91 (3) Å^3, Z = 2, ρ_{calcd} = 1.722 Mg m^{-3}, $\mu(Mo_{K\alpha})$ = 0.71073 Å, $F(000)$ = 536, T = 150(2) K; colorless crystal, 0.20×0.16×0.08 mm, collected reflections 27779. The structure was solved by direct methods, all hydrogen atoms were refined anisotropically by use of full-matrix, least-squared based F^2 to give R_1 = 0.0356, wR_2 = 0.0726 for 6094 independently observed reflections ($|F_o| > 2\sigma(|F_o|)$) and 274 parameters.

Compound (*S*)-**76**: Oil (40.3%): $[\alpha]_D = -17.9$ ($c = 0.47$); ^{1}H NMR: δ = 1.46 (s, 3H), 1.60 (s, 3H), 4.46 (dd, J = 2.6, 6.5 Hz, 1H), 4.54 (dd, J = 7.5, 11.9 Hz, 1H), 4.73 (dd, J = 3.6, 11.9 Hz, 1H), 4.81 (ddd, J = 6.5, 6.5 Hz, ^3J(F,H) = 15.8 Hz, 1H), 5.70 (ddd, J = 0.8, 3.6, 7.5 Hz, 1H), 6.76 (dd, J = 6.5 Hz, ^2J(F,H) = 50.2 Hz, 1H), 8.17 (s, 1H), 9.13 (d, J = 2.1 Hz, 2H), 9.25 (dd, J = 2.1, 2.1 Hz, 1H) ppm; ^{13}C NMR: δ = 25.5 (CH_3), 26.4 (CH_3), 65.6 (CH_2), 67.7 (CH), 68.2 (^1J(F,C) = 257.7 Hz, CH), 75.2 (^3J(F,C) = 3.2 Hz, CH), 81.3 (^2J(F,C) = 18.0 Hz, CH), 111.7 (C), 122.7 (CH), 129.5 (2×CH), 133.0 (C), 148.7 (2×C), 159.9 (CH), 162.2 (C); IR $\tilde{\nu}$ = 3102, 2939, 1735, 1551, 1343, 1276, 1171 cm^{-1}; MS (70 eV, EI): m/z (%): 527 (51) $[M-CH_3]^+$, 371 (16), 254 (12), 195 (100), 149 (31); HRMS (EI): found 526.9588; $C_{15}H_{13}FIN_2O_{10}$ calcd 526.9599; elemental analysis calcd (%) for $C_{16}H_{16}FIN_2O_{10}$ (542.2): C 35.44, H 2.97, N 5.17; found: C 35.61, H 3.04, N 4.95.

(5*RS*)-5-Chloro-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (77): Diastereoisomeric mixture (92%, 2:1), partially separated by careful Chromatotron chromatography (hexanes/EtOAc 85:15). Compound (*R*)-**77**: crystalline solid (67%): m.p. 102.5–104°C (from *n*-pentane/EtOAc); $[\alpha]_D = +28.6$ ($c = 0.22$); ^{1}H NMR (400 MHz): δ = 1.45 (s, 3H), 1.57 (s, 3H), 4.50 (ddd, J = 1.3, 1.3, 6.0 Hz, 1H), 4.60 (dd, J = 7.3, 12.1 Hz, 1H), 4.63 (dd, J = 5.8, 10.6 Hz, 1H), 4.75 (dd, J = 3.7, 11.9 Hz, 1H), 5.64 (d, J = 10.3 Hz, 1H), 5.76 (dddd, J = 1.3, 1.3, 3.7, 7.2 Hz, 1H), 8.19 (s, 1H), 9.14 (d, J = 2.1 Hz, 2H), 9.24 (dd, J = 2.3, 2.3 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz): δ = 23.4 (CH), 25.3 (CH_3), 26.5 (CH_3), 65.9 (CH_2), 67.6 (CH), 74.6 (CH), 82.6 (CH), 110.1 (C), 122.7 (CH), 129.5 (2×CH), 133.2 (C), 148.7 (2×C), 160.0 (CH), 162.2 (C) ppm; IR: $\tilde{\nu}$ = 3102, 1736, 1549 cm^{-1}; MS (70 eV, EI): m/z (%): 545/543 (19/59) $[M-Me]^+$, 433/431 (6/20), 405/403 (2/7), 347/345 (2/8), 277/275 (7/24), 195 (100); HRMS (EI): found: 544.9273; $C_{15}H_{13}{}^{37}ClIN_2O_{10}$ calcd 544.9274; elemental analysis calcd (%) for $C_{16}H_{16}ClIN_2O_{10}$ (558.7): C 34.40, H 2.89, N 5.01; found: C 34.75, H 2.83, N 4.74.

Crystal data and structure refinement for (*R*)-**77**: $C_{16}H_{16}ClIN_2O_{10}$, M_τ = 558.66, monoclinic, space group $P2_1$, a = 8.0771 (1), b = 7.5186 (1), c = 17.4913 (2) Å, β = 101.362 (1), V = 1041.40 (2) Å^3, Z = 2, ρ_{calcd} = 1.782 Mg m^{-3}, $\mu(Mo_{K\alpha})$ = 0.71073 Å, $F(000)$ = 552, T = 150(2) K; colorless crystal, 0.45×0.42×0.32 mm, collected reflections 22552. The structure was solved by direct methods, all hydrogen atoms were refined anisotropically by use of full-matrix, least-squared based F^2 to give R_1 = 0.0162, wR_2 = 0.0355 for 4757 independently observed reflections ($|F_o| > 2\alpha(|F_o|)$) and 273 parameters.

Compound (*S*)-**77**: oil (33%): $[\alpha]_D = +24.6$ ($c = 0.24$); ^{1}H NMR (400 MHz): δ = 1.47 (s, 3H), 1.60 (s, 3H), 4.51 (ddd, J = 1.3, 1.3, 6.0 Hz, 1H), 4.55 (dd, J = 7.4, 11.7 Hz, 1H), 4.72 (dd, J = 4.0, 11.4 Hz, 1H), 4.82 (dd, J = 6.1, 9.8 Hz, 1H), 5.53 (d, J = 10.1 Hz, 1H), 5.77 (dddd, J = 1.3, 1.3, 4.0, 7.7 Hz, 1H), 8.20 (s, 1H), 9.14 (d, J = 2.1 Hz, 2H), 9.24 (dd, J = 2.1, 2.1 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz): δ = 23.0 (CH), 25.6 (CH_3), 26.6 (CH_3), 65.7 (CH_2), 67.6 (CH), 76.2 (CH), 82.9 (CH), 111.5 (C), 122.7 (CH), 129.6 (2×CH), 133.1 (C), 148.8 (2×C), 160.1 (CH), 162.2 (C) ppm; IR: $\tilde{\nu}$ = 3102, 1737, 1549 cm^{-1}; MS (70 eV, EI): m/z (%): 545/543 (19/53) $[M-Me]^+$, 433/431 (1/3), 277/275 (7/23), 195 (100); HRMS (EI): found: 544.9225; $C_{15}H_{13}{}^{37}ClIN_2O_{10}$ calcd 544.9274; elemental analysis calcd (%) for $C_{16}H_{16}ClIN_2O_{10}$ (558.7): C 34.40, H 2.89, N 5.01; found: C 34.73, H 3.00, N 4.82.

(5*RS*)-5-Bromo-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (78): Diastereoisomeric mixture (93%, 2:1), partially separated by careful Chromatotron chromatography (hexanes/EtOAc 98:2→90:10). Compound (*R*)-**78**: crystalline solid (66%); m.p. 99–100°C (from *n*-hexane/EtOAc); $[\alpha]_D = +23$ ($c = 0.45$); ^{1}H NMR: δ = 1.46 (s, 3H), 1.58 (s, 3H), 4.52 (d, J = 5.8 Hz, 1H), 4.58 (dd, J = 7.6, 11.7 Hz, 1H), 4.72 (dd, J = 6.1, 10.5 Hz, 1H), 4.73 (dd, J = 4.7,

11.0 Hz, 1H), 5.32 (d, J = 10.8 Hz, 1H), 5.78 (dd, J = 3.6, 7.2 Hz, 1H), 8.20 (s, 1H), 9.13 (d, J = 1.8 Hz, 2H), 9.24 (dd, J = 2.0, 2.0 Hz, 1H) ppm; ^{13}C NMR: δ = 3.6 (CH), 25.4 (CH_3), 26.6 (CH_3), 65.9 (CH_2), 67.6 (CH), 74.8 (CH), 82.4 (CH), 110.2 (C), 122.6 (CH), 129.5 (2×CH), 133.2 (C), 148.7 (2×C), 160.1 (CH), 162.2 (C) ppm; IR: $\tilde{\nu}$ = 3100, 1731, 1549 cm^{-1}; MS (70 eV, EI): m/z (%): 589/587 (90) $[M-Me]^+$, 477/475 (9), 321/319 (28), 195 (100); HRMS (EI): found: 588.8742; $C_{15}H_{13}{}^{81}BrIN_2O_{10}$ calcd 588.8778; elemental analysis calcd (%) for $C_{16}H_{16}BrIN_2O_{10}$ (603.1): C 31.86, H 2.67, N 4.64; found: C 31.95, H 2.51, N 4.51.

Crystal data and structure refinement for (*R*)-**78**: $C_{16}H_{16}BrIN_2O_{10}$, M_r = 603.12, monoclinic, space group $P2_1$, a = 8.0662 (2), b = 9.0388 (3), c = 14.8243 (6) Å, β = 105.710 (2)°, V = 1040.45 (6) Å^3, Z = 2, ρ_{calcd} = 1.925 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 0.71073 Å, $F(000)$ = 588, T = 150 (2) K; colorless crystal, 0.55×0.40×0.25 mm, Rigaku AFC7-S diffractometer, collected reflections 6834. The structure was solved by direct methods, all nonhydrogen atoms were refined anisotropically by use of full-matrix, least-squared based on F^2 to give R_1 = 0.0247, wR_2 = 0.0631 for 3585 independently observed reflections ($|F_o| > 2\alpha(|F_o|)$) and 274 parameters.

Compound (*S*)-**78**: Crystalline solid (34%): m.p. 129–129.5°C (from *n*-hexane/EtOAc); $[\alpha]_D$ = −10 (c = 0.88); ^{1}H NMR: δ = 1.47 (s, 3H), 1.60 (s, 3H), 4.53 (d, J = 5.8 Hz, 1H), 4.55 (dd, J = 7.2, 11.7 Hz, 1H), 4.71 (dd, J = 4.0, 11.7 Hz, 1H), 4.83 (dd, J = 6.1, 10.5 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H), 5.76 (dd, J = 4.0, 7.6 Hz, 1H), 8.20 (s, 1H), 9.13 (d, J = 1.8 Hz, 2H), 9.24 (dd, J = 2.0, 2.0 Hz, 1H) ppm; ^{13}C NMR: δ = 3.3 (CH), 25.6 (CH_3), 26.6 (CH_3), 65.7 (CH_2), 67.5 (CH), 76.1 (CH), 82.7 (CH), 111.2 (C), 122.7 (CH), 129.5 (2×CH), 133.2 (C), 148.7 (2×C), 160.1 (CH), 162.1 (C) ppm; IR: $\tilde{\nu}$ = 3101, 1728, 1549 cm^{-1}; MS (70 eV, EI): m/z (%): 589/587 (20) $[M-Me]^+$, 393/395 (14), 321/319 (35), 195 (57); HRMS (EI): found: 588.8747; $C_{15}H_{13}{}^{81}BrIN_2O_{10}$ calcd 588.8778; elemental analysis calcd (%) for $C_{16}H_{16}BrIN_2O_{10}$ (603.1): C 31.86, H 2.67, N, 4.64; found: C 31.97, H 2.64, N, 4.39.

(5*RS*)-1-*O*-[*tert*-Butyl(dimethyl)silyl]-5-chloro-5-deoxy-2-*O*-formyl-5-iodo-3,4-*O*-(oxomethylene)-D-arabinitol (80): Diastereoisomeric mixture (65%, 4:3) separated by careful column chromatography (hexanes/EtOAc 98:2); Compound (*R*)-**80**: crystalline solid; m.p. 130–132°C (from *n*-hexane/EtOAc); $[\alpha]_D$ = −4.8 (c = 0.44); ^{1}H NMR: δ = 0.1 (s, 6H), 0.89 (s, 9H), 3.69 (dd, J = 9.0, 9.5 Hz, 1H), 3.79 (dd, J = 5.7, 9.5 Hz, 1H), 5.09 (dd, J = 7.3, 10.0 Hz, 1H), 5.16 (d, J = 7.3 Hz, 1H), 5.38 (dd, J = 5.7, 9.0 Hz, 1H), 5.64 (d, J = 10.0 Hz, 1H), 8.08 (s, 1H) ppm; ^{13}C NMR: δ = −5.7 (CH_3), −5.6 (CH_3), 16.9 (CH), 18.2 (C), 25.6 (3×CH_3), 59.4 (CH_2), 68.8 (CH), 74.7 (CH), 81.8 (CH), 151.1 (C), 159.2 (CH); IR (CCl_4): $\tilde{\nu}$ = 1844, 1736, 1163, 1086 cm^{-1}; MS (79 eV, EI): m/z (%): 409/407 (2/5) $[M-C_4H_9]^+$, 319/317 (4/11), 245/243 (6/18), 190 (12), 117 (32), 103 (100); HRMS (EI): found: 406.9234; $C_9H_{13}{}^{35}ClIO_6Si$ calcd 406.9215; elemental analysis calcd (%) $C_{13}H_{22}ClIO_6Si$ (464.7): C 33.60, H 4.77; found: C 33.66, H 4.63.

Compound (*S*)-**80**: crystalline solid; m.p. 73–75°C (from *n*-hexane/EtOAc); $[\alpha]_D$ = −26.8 (c = 0.40); ^{1}H NMR: δ = 0.09 (s, 6H), 0.87 (s, 9H), 3.70 (dd, J = 9.0. 9.7 Hz, 1H), 3.79 (dd, J = 5.7, 9.7 Hz, 1H), 5.05 (dd, J = 2.9, 7.1 Hz, 1H), 5.20 (dd, J = 7.1, 8.5 Hz, 1H), 5.50 (ddd, J = 2.9, 5.7, 9.0 Hz, 1H), 5.71 (d, J = 8.5 Hz, 1H), 8.07 (s, 1H) ppm; ^{13}C NMR: δ = −5.5 (CH_3), −5.4 (CH_3), 18.1 (C), 20.0 (CH), 25.7 (3×CH_3), 60.1 (CH_2), 68.3 (CH), 76.5 (CH), 82.4 (CH), 152.1 (C), 159.2 (CH); IR (CCl_4): $\tilde{\nu}$ = 1842, 1736, 1161, 1085 cm^{-1}; MS (70 eV, EI): m/z (%): 409/407 (1/3) $[M-C_4H_9]^+$, 319/317 (3/7), 245/243 (5/15), 190 (10), 117 (30), 103 (100); HRMS (EI): found: 316.9261; $C_7H_{11}{}^{35}ClIO_2Si$ calcd 316.9264; elemental analysis calcd (%) for $C_{13}H_{22}ClIO_6Si$ (464.7): C 33.60, H 4.77; found: C 33.85, H 4.75.

1-*O*-[*tert*-Butyl(dimethyl)silyl]-5-deoxy-2-*O*-formyl-5,5-diiodo-3,4-*O*-(oxomethylene)-D-arabinitol (82): Crystalline solid (75%): m.p. 138.4–140.3°C (from *n*-hexane/EtOAc); $[\alpha]_D$ = −14 (c = 0.53); ^{1}H NMR: δ = 0.09 (s, 6H), 0.88 (s, 9H), 3.69 (dd, J = 9.0, 9.6 Hz, 1H), 3.75 (dd, J = 5.8, 9.7 Hz, 1H), 4.84 (d, J = 10.4 Hz, 1H), 5.15 (d, J = 6.9 Hz, 1H), 5.18 (dd, J = 6.9, 10.4 Hz, 1H), 5.44 (dd, J = 5.8, 8.8 Hz, 1H), 8.07 (s, 1H) ppm; ^{13}C NMR: δ = −42.8 (CH), −5.5 (CH_3), −5.4 (CH_3), 18.1 (C), 25.7 (3×CH_3), 59.5 (CH_2), 68.1 (CH), 75.4 (CH), 80.2 (CH), 151.3 (C), 159.3 (CH) ppm; IR: $\tilde{\nu}$ = 2955, 2931, 1833, 1814, 1731 cm^{-1}; MS (70 eV, EI): m/z (%): 499 (4) $[M-C_4H_9]^+$, 103 (100); HRMS (EI): found: 498.8576; $C_9H_{13}I_2O_6Si$ calcd 498.8571; elemental analysis calcd (%) for $C_{13}H_{22}I_2O_6Si$ (556.2): C 28.06, H 3.99; found: C 28.14, H 3.75.

5-Deoxy-4-*O*-(2,2-dimethylpropanoyl)-2-*O*-formyl-5-diiodo-1,3-*O*-(tetraisopropyldisiloxane-1,3-diyl)-D-arabinitol (86): Crystalline solid (84%): m.p. 76.9–78.2°C (from *n*-hexane/EtOAc); $[\alpha]_D$ = −19 (c = 0.84); ^{1}H NMR: δ = 1.01–1.30 (m, 28H), 1.31 (s, 9H), 3.76 (dd, J = 10.4, 10.4 Hz, 1H), 3.82 (dd, J = 5.9, 10.4 Hz, 1H), 4.17 (d, J = 8.5 Hz, 1H), 4.96 (dd, J = 5.8, 10.3 Hz, 1H), 5.07 (dd, J = 1.8, 8.5 Hz, 1H), 5.56 (d, J = 1.9 Hz, 1H), 7.92 (s, 1H) ppm; ^{13}C NMR: δ = −27.9 (CH), 12.3 (CH), 13.2 (2×CH), 15.2 (CH), 17.0 (CH_3), 17.1 (2×CH_3), 17.3 (CH_3), 17.4 (2×CH_3), 17.6 (CH_3), 17.9 (CH_3), 27.1 (3×CH_3), 39.2 (C), 57.6 (CH_2), 69.7 (CH), 71.1 (CH), 75.4 (CH), 160.2 (CH), 176.5 (C) ppm; IR: $\tilde{\nu}$ = 2948, 2869, 1727, 1725 cm^{-1}; MS (70 eV, EI): m/z (%): 699 (16) $[M-C_3H_7]^+$, 57 (100); HRMS (EI): found: 699.0163; $C_{20}H_{37}I_2O_7Si_2$ calcd 699.0167; elemental analysis calcd (%) for $C_{23}H_{44}I_2O_7Si_2$ (742.6): C 37.20, H 5.97; found: C 37.29, H 5.69

2,3-Di-*O*-acetyl-1,5-dideoxy-4-*O*-formyl-1,1-diiodo-L-arabinitol (102): Oil (90%): $[\alpha]_D$ = −65 (c = 0.48); ^{1}H NMR: δ = 1.27 (d, J = 6.5 Hz, 3H), 2.14 (s, 3H), 2.16 (s, 3H), 5.02 (d, J = 7.8 Hz, 1H), 5.04 (dddd, J = 6.5, 6.5, 6.5, 6.7 Hz, 1H), 5.31 (dd, J = 2.8, 7.9 Hz, 1H), 5.64 (dd, J = 2.8, 6.7 Hz, 1H), 7.97 (s, 1H) ppm; ^{13}C NMR: δ = −32.9 (CH), 16.1 (CH_3), 20.77 (CH_3), 20.83 (CH_3), 68.0 (CH), 71.8 (CH), 73.4 (CH), 159.7 (CH), 169.3 (C), 169.6 (C) ppm; IR: $\tilde{\nu}$ = 3018, 2940, 1754, 1728 cm^{-1}; MS (70 eV, EI): m/z (%): 485 (<1) $[M+H]^+$, 439 (76), 269 (100); HRMS (EI): found: 484.8932; $C_{10}H_{15}I_2O_6$ calcd 484.8958; elemental analysis calcd (%) for $C_{10}H_{14}I_2O_6$ (484.0): C 24.81, H 2.92; found: C 24.92, H 2.96.

2-*O*-Acetyl-3,5-*O*-benzylidene-1-deoxy-4-*O*-formyl-1,1-diiodo-D-ribitol (103): Oil (76%): $[\alpha]_D$ = +2.4 (c = 0.74); ^{1}H NMR: δ = 2.21 (s, 3H), 3.62 (dd, J = 9.5, 10.9 Hz, 1H), 4.01 (dd, J = 7.6, 9.3 Hz, 1H), 4.47 (dd, J = 5.3, 10.9 Hz, 1H), 4.96 (dd, J = 2.6, 7.6 Hz, 1H), 5.12 (ddd, J = 5.3, 9.3, 9.5 Hz, 1H), 5.53 (s, 1H), 5.55 (d, J = 2.6 Hz, 1H), 7.40–7.42 (m, 3H), 7.46–7.48 (m, 2H), 7.95 (s, 1H) ppm; ^{13}C NMR: δ = −28.0 (CH), 20.9 (CH_3), 65.3 (CH), 67.1 (CH_2), 76.6 (CH), 78.9 (CH), 101.2 (CH), 126.9 (2×CH), 128.3 (2×CH), 129.3 (CH), 136.2 (C), 158.6 (CH), 159.5 (C) ppm; IR: $\tilde{\nu}$ = 3024, 1752, 1373, 1144, 1004 cm^{-1}; MS (70 eV, EI): m/z (%): 546 (3) $[M]^+$, 486 (2), 419 (9), 101 (100); HRMS (EI): found: 545.9064; $C_{15}H_{16}I_2O_6$ calcd 545.9036; elemental analysis calcd (%) for $C_{15}H_{16}I_2O_6$ (546.1): C 32.99, H 2.95; found: C 32.88, H 2.67.

2,3-Di-*O*-acetyl-4-deoxy-1-*O*-formyl-4,4-diiodo-L-erythritol (107): Crystalline solid (82%): m.p. 60.9–61.1°C (from *n*-hexane/EtOAc); $[\alpha]_D$ = −52 (c = 1.31); ^{1}H NMR: δ = 2.11 (s, 3H), 2.22 (s, 3H), 4.15 (dd, J = 3.5, 12.5 Hz, 1H), 4.49 (dd, J = 2.4, 12.5 Hz, 1H), 5.10 (m, 1H), 5.10 (m, 1H), 5.34 (d, J = 2.9 Hz, 1H), 8.03 (s, 1H) ppm; ^{13}C NMR: δ = −31.5 (CH), 20.8 (2×CH_3), 60.0 (CH_2), 72.4 (CH), 73.8 (CH), 160.2 (CH), 169.1 (C), 169.2 (C) ppm; IR: $\tilde{\nu}$ = 3029, 2959, 1753 cm^{-1}; MS (70 eV, EI): m/z (%): 470 (1) $[M]^+$, 410 (47), 343 (29), 241 (100); HRMS (EI): found: 469.8680; $C_9H_{12}I_2O_6$ calcd 469.8723; elemental analysis calcd (%) for $C_9H_{12}I_2O_6$ (470.0): C 23.00, H 2.57; found: C 23.15, H 2.42.

3,5-Di-*O*-acetyl-1,2-dideoxy-4-*O*-formyl-1,1-diiodo-D-*erythro*-pentitol (108): Oil (94%): $[\alpha]_D$ = +5 (c = 0.44); ^{1}H NMR: δ = 2.05 (s, 3H), 2.06 (s, 3H), 2.65 (ddd, J = 9.9, 10.7, 15.2 Hz, 1H), 2.86 (ddd, J = 2.6, 3.6, 15.2 Hz, 1H), 4.14 (dd, J = 7.0, 12.1 Hz, 1H), 4.23 (dd, J = 4.0, 12.1 Hz, 1H), 4.93 (dd, J = 3.6, 10.7 Hz, 1H), 5.03 (ddd, J = 2.6, 3.5, 9.9 Hz, 1H), 5.39 (ddd, J = 3.5, 4.0, 7.0 Hz, 1H), 8.06 (s, 1H) ppm; ^{13}C NMR: δ = −36.7 (CH), 20.6 (CH_3), 20.7 (CH_3), 47.7 (CH_2), 61.6 (CH_2), 70.0 (CH), 73.0 (CH), 159.6 (CH), 169.8 (C), 170.3 (C) ppm; IR: $\tilde{\nu}$ = 3025, 2945, 1738 cm^{-1}; MS (70 eV, EI): m/z (%): 484 (<1) $[M]^+$, 357 (23), 209 (100); HRMS (EI): found: 483.8832; $C_{10}H_{14}I_2O_6$ calcd 483.8880; elemental analysis calcd (%) for $C_{10}H_{14}I_2O_6$ (484.0): C 24.81, H 2.92; found: C 25.05, H 2.90.

1,1-Diiodo-4-*O*-formyl-1,2,3-trideoxy-6-*O*-(triisopropylsilyl)-D-*glycero*-pentitol (109): Oil (90%): $[\alpha]_D$ = +0.6 (c = 1.08); ^{1}H NMR: δ = 1.05 (m, 21H), 1.80 (m, 1H), 1.89 (m, 1H), 2.38 (m, 2H), 3.75 (dd, J = 5.0, 10.6 Hz, 1H), 3.79 (dd, J = 5.6, 10.6 Hz, 1H), 5.05 (dddd, J = 4.9, 4.9, 4.9, 9.4 Hz, 1H), 5.15 (dd, J = 6.2, 6.2 Hz, 1H), 8.10 (s, 1H) ppm; ^{13}C NMR: δ = −27.7 (CH), 11.9 (3×CH), 17.9 (6×CH_3), 32.7 (CH_2), 43.6 (CH_2), 64.3 (CH_2), 72.6 (CH), 160.7 (CH) ppm; IR: $\tilde{\nu}$ = 1721, 1185 cm^{-1}; MS (70 eV, EI): m/z (%): 541 (2) $[M+H]^+$, 495 (35), 367 (4), 159 (100); HRMS (EI): found: 541.0208; $C_{15}H_{31}I_2O_3Si$ calcd 541.0132; elemental analysis calcd (%) for $C_{15}H_{30}I_2O_3Si$ (540.3): C 33.35, H 5.60; found: C 33.33, H 5.93.

(1*E*)-3,5-Di-*O*-acetyl-1,2-dideoxy-4-*O*-formyl-1-iodo-D-*erythro*-pent-1-enitol ((*E*)-111) and (1*Z*)-3,5-di-*O*-acetyl-1,2-dideoxy-4-*O*-formyl-1-iodo-D-*erythro*-pent-1-enitol ((*Z*)-111): Dry, deoxygenated DMF (48 μL, 0.62 mmol) was added to a suspension of $CrCl_2$ (76 mg, 0.62 mmol) in dry, deoxygenated THF (2 mL), and the mixture was stirred at room temperature under nitrogen for 30 min. A solution of compound **22** (82.4 mg, 0.15 mmol) in dry THF (1.5 mL) was then added, and stirring was continued at this temperature for 30 min. The reaction mixture was poured into ice/water and extracted with EtOAc. The organic extracts were washed with brine, dried, and evaporated. The residue was purified by column chromatography (*n*-hexane/EtOAc, 90:10→80:20) to provide vinyl iodides (*E*)-**111** (18.2 mg, 0.051 mmol, 34%) and (*Z*)-**111** (29.8 mg, 0.084 mmol, 55%). Compound (*E*)-**111**: Oil, $[\alpha]_D$ +52.5 (c = 1.14); ^{1}H NMR: δ = 2.07 (s, 3H), 2.09 (s, 3H), 4.19 (dd, J = 12.4, 6.6 Hz, 1H), 4.26 (dd, J = 3.8, 12.4 Hz, 1H), 5.34 (ddd, J = 3.8, 4.6, 6.6 Hz, 1H), 5.42 (dd, J = 4.6, 7.4 Hz, 1H), 6.53 (dd, J = 7.4, 14.6 Hz, 1H), 6.65 (d, J = 14.6 Hz, 1H), 8.08 (s, 1H) ppm; ^{13}C NMR (50.3 MHz): δ = 20.7 (CH_3), 20.8 (CH_3), 61.4 (CH_2), 70.2 (CH), 73.3 (CH), 83.8 (CH), 138.4 (CH), 159.7 (CH), 169.3 (C), 170.4 (C) ppm; IR: $\tilde{\nu}$ = 3024, 2943, 1734 cm^{-1}; MS (70 eV, EI): m/z (%): 356 (<1) $[M]^+$, 313 (<1), 311 (<1), 229 (<1), 183 (100); HRMS (EI): found 355.9768; $C_{10}H_{13}IO_6$ calcd 355.9757; elemental analysis calcd (%) for $C_{10}H_{13}IO_6$ (356.1): C 33.73, H 3.68; found: C 33.61, H 3.92.

Compound (*Z*)-111: Oil, $[\alpha]_D$ −2.8 (c = 1.35); ^{1}H NMR δ = 2.07 (s, 6H), 4.18 (dd, J = 7.3, 12.1 Hz, 1H), 4.26 (dd, J = 4.0, 12.1 Hz, 1H), 5.49 (ddd, J = 4.0, 4.2, 7.3 Hz, 1H), 5.72 (dd, J = 4.2, 8.5 Hz, 1H), 6.32 (dd, J = 8.0, 8.5 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 8.10 (s, 1H) ppm; ^{13}C NMR δ = 20.69 (CH_3), 20.74 (CH_3), 61.6 (CH_2), 70.4 (CH), 74.3 (CH), 88.5 (CH), 134.4 (CH), 159.7 (CH), 169.3 (C), 170.4 (C) ppm; IR: $\tilde{\nu}$ = 3025, 2939, 1736 cm^{-1}; MS (70 eV, EI): m/z (%): 356 (1) $[M]^+$, 229 (<1), 183 (100); HRMS (EI): found 355.9695; $C_{10}H_{13}IO_6$ calcd 355.9698; elemental analysis calcd (%) for $C_{10}H_{13}IO_6$ (356.1): C 33.73, H 3.68; found: C 33.58, H 4.07.

(1*S*,3*E*)-1-[(1*R*)-2-Acetyloxy-1-(formyloxy)ethyl]-6-phenyl-3-hexenyl acetate (112): Dry, deoxygenated DMF (38 μL, 0.49 mmol) was added to a suspension of $CrCl_2$ (60 mg, 0.49 mmol) in dry, deoxygenated THF (1 mL), and the mixture was stirred at room temperature under nitrogen for 30 min. A solution of compound **108** (82 mg, 0.17 mmol) and hydrocinnamaldehyde (23 mg, 0.17 mmol) in dry THF (1 mL) was then added, and stirring was continued at this temperature for 2.5 h. The reaction mixture was poured into ice/water and extracted with EtOAc. The organic extracts were washed with brine, dried, and evaporated. The residue was purified by column chromatography (*n*-hexane/EtOAc, 90:10) to give compound **112** (41 mg, 0.12 mmol, 70%): Oil, $[\alpha]_D$ +25.5 (c = 1.71); ^{1}H NMR δ = 2.04 (s, 3H), 2.06 (s, 3H), 2.34 (m, 4H), 2.66 (dd, J = 7.9, 7.9 Hz, 2H), 4.18 (dd, J = 7.2, 12.4 Hz, 1H), 4.32 (dd, J = 3.1, 12.4 Hz, 1H), 5.11 (ddd, J = 5.1, 5.1, 7.5 Hz, 1H), 5.29 (ddd, J = 3.7, 3.7, 7.2 Hz, 1H), 5.36 (ddd, J = 7.3, 7.3, 14.8 Hz, 1H), 5.56 (ddd, J = 7.2, 7.2, 14.7 Hz, 1H), 7.18 (m, 3H), 7.28 (m, 2H), 8.06 (s) ppm; ^{13}C NMR δ = 20.7 (CH_3), 20.8 (CH_3), 33.5 (CH_2), 34.2 (CH_2), 35.6 (CH), 61.7 (CH), 71.0 (2×CH), 124.0 (CH), 125.8 (CH), 128.3 (2×CH), 128.5 (2×CH), 134.2 (CH), 141.6 (C), 159.9 (C), 170.0 (C), 170.6 (C) ppm; IR: $\tilde{\nu}$ = 3027, 2938, 1732 cm^{-1}; MS (70 eV, EI): m/z (%): 348 (<1) $[M]^+$, 289 (<1), 288 (<1), 243 (<1), 242 (<1), 228 (18), 182 (16), 109 (35), 91 (100); HRMS (EI): found 348.1499; $C_{19}H_{24}O_6$ calcd 348.1573; elemental analysis calcd (%) for $C_{19}H_{24}O_6$ (348.4): C 65.50, H 6.94; found: C 65.83, H 6.57.

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[26] CCDC-212682 [(*R*)-**76**], CCDC-212683 [(*R*)-**77**], and CCDC-155002 [(*R*)-**78**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

[27] The 3-deoxy-D-glucal precursor of **96** was prepared in two steps by BF_3-catalyzed rearrangement of commercially available tri-*O*-acetyl-D-glucal, and $LiAlH_4$ reduction of the hex-2-enopyranoside formed, 84% overall yield (R. J. Ferrier, *Methods Carbohydr. Chem.* **1972**, *6*, 307–311; B. Fraser-Reid, S. Y-K. Tam, B. Radatus, *Can. J. Chem.* **1975**, *53*, 2005–2016). A one-step method is available as well, also starting from tri-*O*-acetyl-D-glucal, although with a lower yield of 58% (N. Greenspoon, E. Keinan, *J. Org. Chem.* **1988**, *53*, 3723–3731).

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