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Chromium(II) chloride-promoted reductive β-elimination of 1,1-dihalo alditols. Synthesis of highly functionalized alk-1-enyl halides

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ABSTRACT

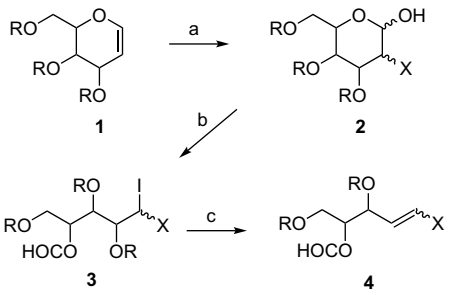
A new general synthetic route to obtain highly functionalized (*Z*)- and (*E*)-alk-1-enyl halides is described, where the halogen can be indistinctly F, Cl, Br, and I. The procedure involves $CrCl_2$-promoted reductive elimination of β-*O*-substituted *gem*-dihalo alditols easily accessible from carbohydrates. The simplicity and mildness of the reaction conditions and their compatibility with different functional groups increase the synthetic potential of this methodology.

1. Introduction

Alk-1-enyl halides are useful synthetic intermediates[1] and probably the most widely used organic electrophiles in the Stille, Suzuki, Nozaki–Hiyama–Kishi, and Heck cross-coupling reactions.[2] Moreover, new strategic reactions are emerging for C–N and C–O bond formation that employ this type of compounds as starting materials and their importance as valuable synthons is increasing accordingly.[3] The synthetic utility of these reactions owes a great deal to the ease with which the coupling partners can be synthesized.

There are many methods for obtaining alk-1-enyl halides, but very few of them are mild enough to be used with highly functionalized or sensitive substrates.[4] An overview reveals few general procedures and these usually have to be optimized for each class of vinyl halides. Elimination reactions are well known among the earliest routes toward vinyl halides, especially base-promoted dehydrohalogenation of vicinal or geminal dihalo compounds.[5] Zinc-promoted reductive elimination of β-heterosubstituted polyhalogenated compounds have also been used but to a lesser extent.[6] Some years ago the preparation of vinyl halides by a stereoselective reductive β-elimination of non-fluorinated *O*-acetylated *gem*-dihaloalkanols with samarium(II) iodide was reported.[7] Recent advances, for instance, involve the use of transition-metal reagents in the reductive dehalogenation of *gem*-trihalo compounds promoted by $CrCl_2$ or CuCl/2,2′-bipyridine.[8]

Herein we describe a facile and general synthetic route to chiral polyhydroxylated alk-1-enyl halides **4** by chromium(II)-mediated reductive β-elimination reaction of 1,1-dihalo alditols **3** (Scheme 1). These *gem*-dihalo derivatives are easily available from glycals **1** by an advantageous two-step methodology previously developed in our laboratory,[9] with the alkoxyl radical β-fragmentation (ARF) reaction of 2-deoxy-2-halo pyranoses **2** as the key step.



Scheme 1. General scheme for the synthesis of 1-halo-1-iodo-alditols. Reagents and conditions: (a) Fluorohydrins: Selectfluor™, CH_3NO_2/H_2O (4:1), rt, 14 h and then refluxed 30 min. Chlorohydrins: *N*-chlorosuccinimide, THF/H_2O, reflux, 8 h. Bromohydrins: *N*-bromoacetamide, THF/H_2O, rt, 4 h. Iodohydrins: *N*-iodosuccinimide, THF/H_2O, rt, 20 min; (b) $PhI(OAc)_2$, I_2, CH_2Cl_2, *hν*; (c) $CrCl_2$, THF/DMF, rt; R=protective group; X=F, Cl, Br, I.

2. Results and discussion

Treatment of β-*O*-acetyl or β-*O*-benzyl-1,1-haloiodo alditols with an excess of chromium(II) chloride as reducing agent has allowed the formation of highly functionalized vinyl iodides, vinyl bromides, vinyl chlorides, and vinyl fluorides as summarized in Table 1. As far as we know, no examples of chromium-mediated β-elimination of dihalo compounds have been previously reported.

The reaction proceeds at room temperature in THF with an excess of a preformed complex of $CrCl_2$ and DMF, since this donor ligand enhances the reductive power of chromium(II),[11a] to give

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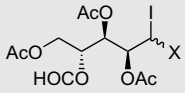
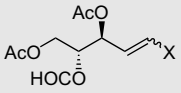
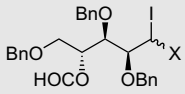
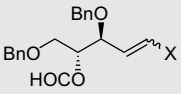
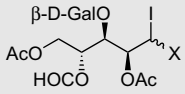
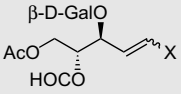
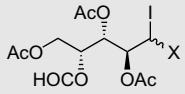
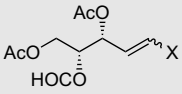
Table 1
Reductive β-elimination of 1-halo-1-iodo alditols[a]

Entry	Substrate	Time (h)	Product	Yield (%, *Z*/*E*)
				
1	**5** X=F	24	**9** X=F	85, 1:1
2	**5** X=F	0.5	**9** X=F	52, 3:1[b]
3	**6** X=Cl	1	**10** X=Cl	92, 3:1
4	**6** X=Cl	0.3	**10** X=Cl	85, 5:1[b]
5	**7** X=Br	3	**11** X=Br	96, 3:2[c]
6	**7** X=Br	0.5	**11** X=Br	72, 5:1[b]
7	**8** X=I	0.5	**12** X=I	90, 3:2
8	**8** X=I	0.5	**12** X=I	77, 5:1[b]
				
9	**13** X=F	24	**17** X=F	99, 1:1
10	**14** X=Cl	24	**18** X=Cl	80, 2:1
11	**15** X=Br	5	**19** X=Br	81, 7:3[c]
12	**16** X=I	1.5	**20** X=I	81, 3:1[d]
				
13[e]	**21** X=F	24	**25** X=F	79, 3:1
14[e]	**22** X=Cl	2.5	**26** X=Cl	81, 2:1[f]
15[e]	**23** X=Br	6	**27** X=Br	92, 4:1[c]
16[e]	**24** X=I	0.5	**28** X=I	93, 3:2
				
17	**29** X=F	24	**33** X=F	84, 1:1
18	**30** X=Cl	1	**34** X=Cl	96, 1:1
19	**31** X=Br	3	**35** X=Br	84, 3:2[c]
20	**32** X=I	1	**36** X=I	90, 1:1

[a] Reactions were performed with $CrCl_2$–DMF in dry THF.
[b] Reactions were performed with SmI_2 in dry THF.
[c] Vinyl iodide (3–11%) was also obtained.
[d] **20*E*** contaminated with 20% of **20*Z***.
[e] Gal in this case refers to the peracetylated moiety of galactose.
[f] **26*E*** contaminated with 15% of starting material **22**.

(*Z*)- and (*E*)-vinyl halides in good to excellent yields but with moderate diastereoselectivity (Table 1).

For the preparation of vinyl fluorides a higher excess of $CrCl_2$–DMF complex and in general longer reaction time (24 h) were necessary (entries 1, 9, 13, and 17, Table 1). In preliminary experiments we studied different temperature conditions and no effect was observed in the diastereoisomeric ratio. However, yields became lower as the temperature increased.

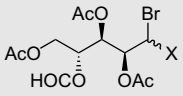
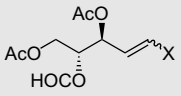
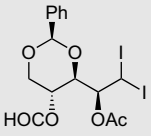
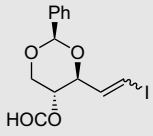
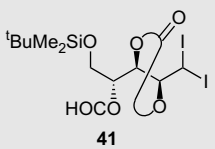
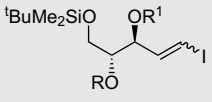
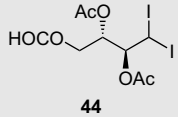
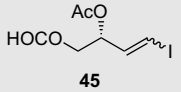
The reaction is compatible with *O*-acetyl or *O*-benzyl protecting groups present in the structure of all *gem*-haloiodo alditols studied, especially with the sensitive *O*-formyl protecting group. The glycosidic linkage of *O*-acetylated derivatives **25**–**28** also remains unaffected too. Iodides are considerably more reactive than fluorides and chlorides in the reductive elimination reaction. Consequently, vinyl fluorides (entries 1, 9, 13, and 17) and vinyl chlorides (entries 3, 10, 14, and 18) were exclusively obtained. However, this does not appear to be the case for 1-bromo-1-iodo alditols (**7**, **15**, **23**, and **31**), since bromine was eliminated competitively and the vinyl bromides (entries 5, 11, 15, and 19) were contaminated by small amounts of the corresponding vinyl iodides. In contrast with the fact that vinyl fluorides were obtained with lower yields than the other vinyl halides from each series of *O*-acetyl-1,1-haloiodo alditols, vinyl fluoride **17** was obtained almost quantitatively from β-*O*-benzyl-1-fluoro-1-iodo alditol **13** (entry 9). This could suggest that the reductive elimination of a β-*O*-benzyl group is the best option when a fluorine atom is present.

In comparison, preformed[10] SmI_2 was used at room temperature as an alternative reducing agent for the elimination of the β-*O*-acetyl-1,1-haloiodo alditols **6**–**8** to obtain vinyl halides **10**–**12** (entries 4, 6, and 8, Table 1), with higher diastereoselectivity but in somewhat lower yields. Although vinyl fluoride **9** (entry 2) could also be obtained from 1,1-fluoroiodo-alditol **5**, heating to 50 °C was necessary and a notable decrease in yield was observed (entry 2, Table 1). SmI_2 failed to lead to the reductive elimination of β-*O*-benzylated-1,1-diiodo alditol **16**, which afforded complex mixtures of compounds, even when temperature and amounts of reagent were reduced.

In order to test the scope and generality of our methodology the reaction was examined with other types of *gem*-dihalo alditols as substrates such as *O*-acetyl 1,1-dibromo- and 1,1-bromochloro alditols **37** and **38** (Table 2).[9b] These were also suitable for the cromium(II)-promoted β-elimination and vinyl bromide **10** and vinyl chloride **11** were formed under the usual conditions with good yields (entries 1 and 2, Table 2).

Similar results were obtained when experiments using *gem*-diiodo alditols **39**, **41**, and **44** were carried out. The reaction showed tolerance to other *O*-protecting groups such as benzylidene acetal of **39** and *tert*-butyldimethysilyl of **41** (entries 3 and 4, Table 2). Elimination of this last alditol afforded mixtures of the expected vinyl iodides **42** and their corresponding transesterification products **43**. As can be observed in this case the presence of a cyclic carbonate at the β-position had a decisive influence on the steric course of the elimination, probably due to the conformational restriction introduced, and the diastereoselectivity improved

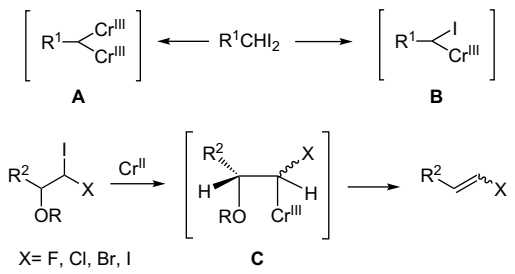
Table 2
Reductive β-elimination of 1,1-dihalo alditols[a]

Entry	Substrate	Time (h)	Product	Yield (%, *Z*/*E*)
				
1	**37** X=Br	1.5	**11** X=Br	82, 1:1
2	**38** X=Cl	1.5	**10** X=Cl	83, 3:2
3	 **39**	1	 **40**	91, 3:2
4	 **41**	0.5	 **42** R=OCOH; R^1=H **43** R=H; R^1=OCOH	85, 3:7[b]
5	 **44**	0.5	 **45**	86, 3:2[c]

[a] All reactions were performed with $CrCl_2$–DMF in dry THF.
[b] Inseparable mixtures of **42*E*** with **43*E*** and **42*Z*** with **43*Z***.
[c] Inseparable mixture of isomers.

significantly toward the (*E*)-isomer (*Z*/*E*, 3:7). Reductive elimination of a less substituted *gem*-dihalo alditol **44** afforded vinyl iodide **45**, which may be an alternative chiral synthon when the introduction of only one stereogenic center is required.

Mechanistically, details of the formation of vinyl halides from β-*O*-substituted *gem*-dihalo alditols have yet to be elucidated. The most important chromium-mediated reaction of *gem*-dihaloalkanes, the *E*-olefination of carbonyl compounds developed by Takai,[11] is believed to proceed via a *gem*-dichromium carbenoid (**A**), which nucleophilically attacks the carbonyl compounds, although a *gem*-halo-chromium intermediate (**B**) may be involved (Scheme 2). When we attempted the olefination of hydrocinnamaldehyde using different β-substituted *gem*-diiodo alditols β-elimination products were exclusively obtained.[9a] It is probable that initially an oxidative addition of chromium into the C–X bond (I≥Br≫Cl>F) takes place to generate the *gem*-halo-chromium intermediate (**C**), followed by chromium-induced β-elimination of the oxygenated function at C-2, which must be faster than the possible second reduction toward a geminal dichromium species (Scheme 2).



Scheme 2. Tentative mechanism for $CrCl_2$-promoted β-elimination of *gem*-dihalo alditols.

In general, reductive elimination of 1:1 diastereoisomeric mixtures of *gem*-haloiodo alditols (3:2 for **30** and **31**) afforded (*Z*)- and (*E*)-vinyl halides with ratios different from those of the starting material. β-Elimination of the different *gem*-diiodo alditols studied took place with variable diastereoselectivity. The observed stereochemical course can be explained by a low degree of control in the transition state. It is known that stereoselective reactions of *gem*-trihalogenated compounds promoted by $CrCl_2$ involve a *gem*-dihalogenated monochromium intermediate whose conformation is fixed by intramolecular coordination of chromium(III) with an oxygen atom of a β-group.[12] Since *gem*-dihalo alditols show a high number of oxygenated functions several chromium(III)–oxygen coordinations are feasible and different conformations of the *gem*-halo-chromium intermediate (**C**) are possible with the subsequent loss of stereocontrol during the elimination.

3. Conclusion

In summary we have described an efficient and general new methodology to obtain highly functionalized (*Z*)- and (*E*)-vinyl halides by reductive elimination of β-*O*-acetyl- and β-*O*-benzyl-1,1-dihalo alditols. The easy accessibility of these starting products from carbohydrates combined with the simplicity and mildness of the elimination conditions and the exceptional tolerance of the $CrCl_2$ reagent toward different functional groups increase the potential of this method to obtain those valuable synthons. The synthesis of libraries of both (*Z*)- and (*E*)-vinyl halides is of interest for comparative studies in biochemistry as well as in physical organic chemistry, especially for vinyl fluorides since the presence of a fluorine atom modifies their biological activity by altering their physicochemical properties.[13]

4. Experimental section

4.1. General

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, 100.6 MHz for ^{13}C, and 376.4 MHz for ^{19}F in $CDCl_3$ unless otherwise stated. TMS was used as internal standard for ^1H and ^{13}C nuclei, while CCl_3F was used as internal standard for ^{19}F nucleus. 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. Anhydrous $CrCl_2$ was purchased from Aldrich. Samarium powder was purchased from Strem. 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, and the glassware was oven-dried. 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.

4.2. General procedure for the synthesis of vinyl halides with $CrCl_2$

To a suspension of $CrCl_2$ (4 mmol) in dry THF (8 mL) was added, under nitrogen, dry DMF (4 mmol) and the mixture stirred for 30 min. A solution of the 1,1-dihalo alditol (1 mmol) in THF (10 mL) was then added and the stirring continued at room temperature, for the time specified in the tables. The reaction mixture was poured into water and extracted with EtOAc, the organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography (hexanes–EtOAc mixtures). For vinyl fluorides **9**, **17**, **25**, and **33**, $CrCl_2$ (6 mmol) in dry THF (18 mL) and dry DMF (6 mmol) were used.

4.3. General procedure for the synthesis of vinyl halides with SmI_2

A solution of freshly prepared SmI_2 (3 mmol) in dry THF (30 mL) was added dropwise over 30 min, under nitrogen, to a solution of the 1,1-dihalo alditol (1 mmol) in THF (10 mL) at room temperature, with the exception of the fluoride derivative, which was heated to 50 °C. Stirring was continued for the time specified in Table 1, the reaction mixture was treated with 10% aqueous HCl, and after usual work up the residue was purified by chromatography (hexanes–EtOAc mixtures).

4.4. Spectral and analytical data of alk-1-enyl halides

*4.4.1. (Z)-3,5-Di-O-acetyl-1,2-dideoxy-1-fluoro-4-O-formyl-D-erythro-pent-1-enitol (**9Z**) and (E)-3,5-di-O-acetyl-1,2-dideoxy-1-fluoro-4-O-formyl-D-erythro-pent-1-enitol (**9E**)*

Yield with $CrCl_2$ 85%, *Z*/*E* dr: 1:1. Yield with SmI_2 52%, *Z*/*E* dr: 3:1. Compound **9*Z***: oil, $[\alpha]_D$ +15.5 (*c* 0.67); IR 1734 cm^{-1}; ^1H NMR δ_H 2.06 (3H, s), 2.07 (3H, s), 4.16 (1H, dd, *J*=12.1, 7.2 Hz), 4.24 (1H, dd, *J*=12.1, 4.1 Hz), 4.93 (1H, ddd, $^3J_{FH}$=39.4 Hz, *J*=9.2, 4.9 Hz), 5.46 (1H, ddd, *J*=7.2, 4.3, 4.1 Hz), 5.93 (1H, dd, *J*=9.2, 4.3 Hz), 6.61 (1H, dd, $^2J_{FH}$=82.1 Hz, *J*=4.9 Hz), 8.10 (1H, s); ^{13}C NMR δ_C 20.6 (CH_3), 20.8 (CH_3), 61.6 (CH_2), 64.9 (CH, $^3J_{FC}$=6.5 Hz), 70.7 (CH, $^4J_{FC}$=2.2 Hz), 105.3 (CH, $^2J_{FC}$=2.2 Hz), 151.2 (CH, $^1J_{FC}$=268.6 Hz), 159.8 (CH), 169.4 (C), 170.4 (C); ^{19}F NMR δ_F −119.8 (dd, $^2J_{FH}$=82.6 Hz, $^3J_{FH}$=41.3 Hz); MS *m*/*z* (rel intensity) 203 (M^+−HOCO, 10), 189 (8), 160 (30), 131 (50), 117 (100); HRMS

m/*z* calcd for $C_9H_{12}FO_4$ 203.0720, found 203.0728. Anal. Calcd for $C_{10}H_{13}FO_6$: C, 48.39; H, 5.28. Found: C, 48.37; H, 5.10. Compound **9*E***: oil, $[\alpha]_D$ +21.7 (*c* 0.72); IR 1734 cm^{-1}; ^1H NMR δ_H 2.06 (3H, s), 2.07 (3H, s), 4.18 (1H, dd, *J*=12.1, 6.5 Hz), 4.23 (1H, dd, *J*=12.1, 3.9 Hz), 5.36 (3H, m), 6.82 (1H, dd, $^2J_{FH}$=81.3 Hz, *J*=10.3 Hz), 8.09 (1H, s); ^1H NMR (C_6D_6) δ_H 1.54 (3H, s), 1.61 (3H, s), 3.94 (1H, dd, *J*=11.9, 6.2 Hz), 3.98 (1H, dd, *J*=11.9, 3.3 Hz), 5.21 (1H, ddd, $^3J_{FH}$=16.2 Hz, *J*=11.0, 9.1 Hz), 5.31 (2H, m), 6.31 (1H, dd, $^2J_{FH}$=81.5 Hz, *J*=11.0 Hz), 7.42 (1H, s); ^{13}C NMR δ_C 20.6 (CH_3), 20.9 (CH_3), 61.5 (CH_2), 67.6 (CH, $^3J_{FC}$=11.4 Hz), 70.7 (CH, $^4J_{FC}$=3.2 Hz), 106.3 (CH, $^2J_{FC}$=11.2 Hz), 154.6 (CH, $^1J_{FC}$=266.6 Hz), 159.7 (CH), 169.5 (C), 170.4 (C); ^{19}F NMR δ_F −119.5 (dd, $^2J_{FH}$=82.6 Hz, $^3J_{FH}$=13.8 Hz); MS *m*/*z* (rel intensity) 203 (M^+−HOCO, 18), 189 (7), 160 (32), 130 (40), 117 (100); HRMS *m*/*z* calcd for $C_9H_{12}FO_4$ 203.0720, found 203.0705. Anal. Calcd for $C_{10}H_{13}FO_6$: C, 48.39; H, 5.28. Found: C, 48.24; H, 4.98.

*4.4.2. (Z)-3,5-Di-O-acetyl-1-chloro-1,2-dideoxy-4-O-formyl-D-erythro-pent-1-enitol (**10Z**) and (E)-3,5-di-O-acetyl-1-chloro-1,2-dideoxy-4-O-formyl-D-erythro-pent-1-enitol (**10E**)*

Yield with $CrCl_2$ 92%, *Z*/*E* dr: 3:1. Yield with SmI_2 85%, *Z*/*E* dr: 5:1. Compound **10*Z***: oil, $[\alpha]_D$ +4.0 (*c* 0.38); IR 1738 cm^{-1}; ^1H NMR δ_H 2.06 (3H, s), 2.08 (3H, s), 4.15 (1H, dd, *J*=12.2, 7.3 Hz), 4.24 (1H, dd, *J*=12.1, 4.0 Hz), 5.48 (1H, ddd, *J*=8.0, 3.9, 3.9 Hz), 5.82 (1H, dd, *J*=8.7, 7.4 Hz), 5.98 (1H, dd, *J*=8.9, 4.1 Hz), 6.35 (1H, dd, *J*=7.4, 0.8 Hz), 8.09 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.6 (CH_3), 20.7 (CH_3), 61.6 (CH_2), 67.8 (CH), 70.6 (CH), 124.4 (CH), 125.1 (CH), 159.7 (CH), 169.3 (C), 170.4 (C); MS *m*/*z* (rel intensity) 229 (M^+−Cl, 8), 133 (100); HRMS *m*/*z* calcd for $C_{10}H_{13}O_6$ 229.0712, found 229.0721. Anal. Calcd for $C_{10}H_{13}ClO_6$: C, 45.38; H, 4.95. Found: C, 45.25; H, 5.02. Compound **10*E***: oil, $[\alpha]_D$ +44.1 (*c* 0.15); IR 1738 cm^{-1}; ^1H NMR δ_H 2.07 (3H, s), 2.08 (3H, s), 4.18 (1H, dd, *J*=12.2, 6.5 Hz), 4.25 (1H, dd, *J*=12.1, 3.9 Hz), 5.36 (1H, ddd, *J*=5.2, 5.2, 4.7 Hz), 5.48 (1H, dd, *J*=8.3, 4.7 Hz), 5.93 (1H, dd, *J*=13.4, 8.3 Hz), 6.42 (1H, dd, *J*=13.5, 0.8 Hz), 8.09 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.6 (CH_3), 20.8 (CH_3), 61.4 (CH_2), 70.3 (CH), 70.6 (CH), 125.8 (CH), 126.5 (CH), 159.6 (CH), 169.4 (C), 170.4 (C); MS *m*/*z* (rel intensity) 229 (M^+−Cl, 15), 81 (100); HRMS *m*/*z* calcd for $C_{10}H_{13}O_6$ 229.0712, found 229.0713. Anal. Calcd for $C_{10}H_{13}ClO_6$: C, 45.38; H, 4.95. Found: C, 45.52; H, 5.02.

*4.4.3. (Z)-3,5-Di-O-acetyl-1-bromo-1,2-dideoxy-4-O-formyl-D-erythro-pent-1-enitol (**11Z**) and (E)-3,5-di-O-acetyl-1-bromo-1,2-dideoxy-4-O-formyl-D-erythro-pent-1-enitol (**11E**)*

Yield with $CrCl_2$ 96%, *Z*/*E* dr: 3:2. Yield with SmI_2 72%, *Z*/*E* dr: 5:1. Compound **11*Z***: oil, $[\alpha]_D$ −1.7 (*c* 0.24); IR 1735 cm^{-1}; ^1H NMR δ_H 2.06 (3H, s), 2.07 (3H, s), 4.17 (1H, dd, *J*=12.2, 7.4 Hz), 4.26 (1H, dd, *J*=12.2, 4.0 Hz), 5.50 (1H, ddd, *J*=7.6, 4.0, 4.0 Hz), 5.91 (1H, dd, *J*=8.6, 4.0 Hz), 6.18 (1H, dd, *J*=8.6, 7.7 Hz), 6.54 (1H, d, *J*=7.7 Hz), 8.10 (1H, s); ^{13}C NMR δ_C 20.6 (CH_3), 20.7 (CH_3), 61.6 (CH_2), 70.2 (CH), 70.5 (CH), 114.0 (CH), 128.3 (CH), 159.7 (CH), 169.3 (C), 170.4 (C); MS *m*/*z* (rel intensity) 251/249 (M^+−CH_3CO_2, 29/25), 222/220 (15/16), 183 (29), 179/177 (39/39), 162/160 (11/13), 141 (46), 81 (100); HRMS *m*/*z* calcd for $C_8H_{10}^{81}BrO_4$ 250.9742, found 250.9760. Anal. Calcd for $C_{10}H_{13}BrO_6$: C, 38.86; H, 4.24. Found: C, 38.90; H, 4.11. Compound **11*E***: oil, $[\alpha]_D$ +59.2 (*c* 1.14); IR 1734 cm^{-1}; ^1H NMR δ_H 2.07 (3H, s), 2.08 (3H, s), 4.19 (1H, dd, *J*=12.2, 6.6 Hz), 4.25 (1H, dd, *J*=12.2, 3.9 Hz), 5.36 (1H, ddd, *J*=5.2, 5.2, 4.7 Hz), 5.45 (1H, dd, *J*=8.0, 4.7 Hz), 6.21 (1H, dd, *J*=13.8, 8.0 Hz), 6.56 (1H, d, *J*=13.8 Hz), 8.08 (1H, s); ^{13}C NMR δ_C 20.6 (CH_3), 20.8 (CH_3), 61.4 (CH_2), 70.4 (CH), 71.5 (CH), 113.3 (CH), 130.5 (CH), 159.6 (CH), 169.3 (C), 170.4 (C); MS *m*/*z* (rel intensity) 251/249 (M^+−CH_3CO_2, 5/5), 222 (15), 183 (26), 179/177 (30/32), 163/161 (13/13), 141 (43), 81 (100), HRMS *m*/*z* calcd for $C_8H_{10}^{81}BrO_4$ 250.9742, found 250.9780. Anal. Calcd for $C_{10}H_{13}BrO_6$: C, 38.86; H, 4.24. Found: C, 38.89; H, 4.13.

*4.4.4. (Z)-3,5-Di-O-acetyl-1,2-dideoxy-4-O-formyl-1-iodo-D-erythro-pent-1-enitol (**12Z**) and (E)-3,5-di-O-acetyl-1,2-dideoxy-4-O-formyl-1-iodo-D-erythro-pent-1-enitol (**12E**)*

Yield with $CrCl_2$ 90%, *Z*/*E* dr: 3:2. Yield with SmI_2 77%, *Z*/*E* dr: 5:1. Compound **12*Z***: oil, $[\alpha]_D$ −2.8 (*c* 1.35); IR 1736 cm^{-1}; ^1H NMR δ_H 2.07 (6H, s), 4.18 (1H, dd, *J*=12.1, 7.3 Hz), 4.26 (1H, dd, *J*=12.1, 4.0 Hz), 5.49 (1H, ddd, *J*=7.3, 4.2, 4.0 Hz), 5.72 (1H, dd, *J*=8.5, 4.2 Hz), 6.32 (1H, dd, *J*=8.5, 8.0 Hz), 6.74 (1H, d, *J*=8.0 Hz), 8.10 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 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); MS *m*/*z* (rel intensity) 356 (M^+, 1), 229 (<1), 183 (100); HRMS *m*/*z* calcd for $C_{10}H_{13}IO_6$ 355.9698, found 355.9695. Anal. Calcd for $C_{10}H_{13}IO_6$: C, 33.73; H, 3.68. Found: C, 33.58; H, 4.07. Compound **12*E***: oil, $[\alpha]_D$ +52.5 (*c* 1.14); IR 1734 cm^{-1}; ^1H NMR δ_H 2.07 (3H, s), 2.09 (3H, s), 4.19 (1H, dd, *J*=12.4, 6.6 Hz), 4.26 (1H, dd, *J*=12.4, 3.8 Hz), 5.34 (1H, ddd, *J*=6.6, 4.6, 3.8 Hz), 5.42 (1H, dd, *J*=7.4, 4.6 Hz), 6.53 (1H, dd, *J*=14.6, 7.4 Hz), 6.65 (1H, d, *J*=14.6 Hz), 8.08 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.6 (CH_3), 20.8 (CH_3), 61.3 (CH_2), 70.2 (CH), 73.3 (CH), 83.8 (CH), 138.3 (CH), 159.6 (CH), 169.3 (C), 170.4 (C); MS *m*/*z* (rel intensity) 356 (M^+, <1), 313 (<1), 311 (<1), 229 (<1), 183 (100); HRMS *m*/*z* calcd for $C_{10}H_{13}IO_6$ 355.9757, found 355.9768. Anal. Calcd for $C_{10}H_{13}IO_6$: C, 33.73; H, 3.68. Found: C, 33.61; H, 3.92.

*4.4.5. (Z)-3,5-Di-O-benzyl-1,2-dideoxy-1-fluoro-4-O-formyl-D-erythro-pent-1-enitol (**17Z**) and (E)-3,5-di-O-benzyl-1,2-dideoxy-1-fluoro-4-O-formyl-D-erythro-pent-1-enitol (**17E**)*

Yield 99%, *Z*/*E* dr: 1:1. Compound **17*Z***: oil, $[\alpha]_D$ +24.5 (*c* 0.31); IR 1727 cm^{-1}; ^1H NMR δ_H 3.64 (1H, dd, *J*=10.7, 4.3 Hz), 3.68 (1H, dd, *J*=10.7, 6.0 Hz), 4.41 (1H, d, *J*=11.7 Hz), 4.49 (1H, d, *J*=12.0 Hz), 4.55 (1H, d, *J*=12.0 Hz), 4.59 (1H, d, *J*=11.7 Hz), 4.65 (1H, dd, *J*=9.7, 5.7 Hz), 4.90 (1H, ddd, $^3J_{FH}$=41.2 Hz, *J*=9.7, 4.8 Hz), 5.30 (1H, ddd, *J*=5.7, 5.7, 5.7 Hz), 6.70 (1H, dd, $^1J_{FH}$=84.0 Hz, *J*=4.8 Hz), 7.26–7.35 (10H, m), 8.11 (1H, s); ^{13}C NMR δ_C 68.2 (CH_2), 69.5 (CH, $^3J_{FC}$=5.4 Hz), 70.8 (CH_2), 73.1 (CH), 73.3 (CH_2), 108.0 (CH, $^2J_{FC}$=3.2 Hz), 127.67 (2×CH), 127.74 (2×CH), 127.8 (2×CH), 128.36 (2×CH), 128.39 (2×CH), 137.68 (C), 137.74 (C), 151.3 (CH, $^1J_{FC}$=264.4 Hz), 160.4 (CH); ^{19}F NMR δ_F −123.9 (dd, $^2J_{FH}$=82.6 Hz, $^3J_{FH}$=41.3 Hz); MS *m*/*z* (rel intensity) 344 (M^+, <1), 253 (<1), 165 (3), 91 (100); HRMS *m*/*z* calcd for $C_{20}H_{21}FO_4$ 344.1424, found 344.1413. Anal. Calcd for $C_{20}H_{21}FO_4$: C, 69.75; H, 6.15. Found: C, 69.82; H, 6.31. Compound **17*E***: oil, $[\alpha]_D$ +18.4 (*c* 0.51); IR 1727 cm^{-1}; ^1H NMR δ_H 3.63 (1H, dd, *J*=10.6, 4.3 Hz), 3.70 (1H, dd, *J*=10.6, 5.5 Hz), 4.02 (1H, dd, *J*=9.5, 5.8 Hz), 4.37 (1H, d, *J*=11.8 Hz), 4.50 (1H, d, *J*=12.1 Hz), 4.52 (1H, d, *J*=12.0 Hz), 4.60 (1H, d, *J*=11.8 Hz), 5.24 (1H, ddd, *J*=5.8, 5.8, 5.8 Hz), 5.35 (1H, ddd, $^3J_{FH}$=17.1 Hz, *J*=11.3, 9.5 Hz), 6.63 (1H, dd, $^1J_{FH}$=82.8 Hz, *J*=11.3 Hz), 7.26–7.35 (10H, m), 8.09 (1H, s); ^{13}C NMR δ_C 67.8 (CH_2), 70.3 (CH_2), 72.8 (CH, $^3J_{FC}$=12.9 Hz), 73.1 (CH, $^4J_{FC}$=3.2 Hz), 73.4 (CH_2), 108.5 (CH, $^2J_{FC}$=8.6 Hz), 127.7 (4×CH), 127.8 (2×CH), 128.5 (4×CH), 137.5 (C), 137.6 (C), 152.8 (CH, $^1J_{FC}$=264.4 Hz), 160.2 (CH); ^{19}F NMR δ_F −121.8 (dd, $^2J_{FH}$=82.6 Hz, $^3J_{FH}$=18.4 Hz); MS *m*/*z* (rel intensity) 344 (M^+, <1), 253 (<1), 165 (3), 91 (100); HRMS *m*/*z* calcd for $C_{20}H_{21}FO_4$ 344.1424, found 344.1427. Anal. Calcd for $C_{20}H_{21}FO_4$: C, 69.75; H, 6.15. Found: C, 70.04; H, 5.76.

*4.4.6. (Z)-3,5-Di-O-benzyl-1-choro-1,2-dideoxy-4-O-formyl-D-erythro-pent-1-enitol (**18Z**) and (E)-3,5-di-O-benzyl-1-choro-1,2-dideoxy-4-O-formyl-D-erythro-pent-1-enitol (**18E**)*

Yield 80%, *Z*/*E* dr: 2:1. Compound **18*Z***: oil, $[\alpha]_D$ +0.9 (*c* 0.22); IR 1728 cm^{-1}; ^1H NMR δ_H 3.65 (1H, dd, *J*=10.8, 4.1 Hz), 3.68 (1H, dd, *J*=10.8, 6.3 Hz), 4.44 (1H, d, *J*=12.1 Hz), 4.49 (1H, d, *J*=12.1 Hz), 4.56 (1H, d, *J*=11.7 Hz), 4.58 (1H, d, *J*=11.7 Hz), 4.72 (1H, dd, *J*=9.0, 5.4 Hz), 5.34 (1H, ddd, *J*=5.4, 5.4, 5.4 Hz), 5.83 (1H, dd, *J*=9.0, 7.2 Hz), 6.38 (1H, d, *J*=7.2 Hz), 7.27–7.35 (10H, m), 8.10 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 68.2 (CH_2), 71.0 (CH_2), 72.6 (CH), 73.0 (CH), 73.3 (CH_2), 123.8 (CH), 127.6–128.4 (10×CH), 128.4 (CH), 137.66 (C),

137.73 (C), 160.3 (CH); MS *m/z* (rel intensity) 271/269 (M^+−Bn, <1/<1), 183/181 (1/2), 91 (100); HRMS *m/z* calcd for $C_{13}H_{14}^{37}ClO_4$ 271.0551, found 271.0557. Anal. Calcd for $C_{20}H_{21}ClO_4$: C, 66.65; H, 5.88. Found: C, 66.55; H, 6.04. Compound **18*E***: oil, $[\alpha]_D$ +29.8 (*c* 0.28); IR 1727 cm^{-1}; ^1H NMR δ_H 3.63 (1H, dd, *J*=10.6, 4.3 Hz), 3.70 (1H, dd, *J*=10.8, 5.8 Hz), 4.11 (1H, dd, *J*=8.7, 5.9 Hz), 4.22 (1H, d, *J*=11.7 Hz), 4.50 (1H, d, *J*=12.1 Hz), 4.53 (1H, d, *J*=12.1 Hz), 4.60 (1H, d, *J*=11.7 Hz), 5.22 (1H, ddd, *J*=5.4, 5.4, 5.4 Hz), 5.90 (1H, dd, *J*=13.5, 8.6 Hz), 6.24 (1H, d, *J*=13.5 Hz), 7.27–7.35 (10H, m), 8.08 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 67.7 (CH_2), 70.9 (CH_2), 72.9 (CH), 73.3 (CH_2), 76.1 (CH), 123.4 (CH), 127.7–128.4 (10×CH), 129.8 (CH), 137.4 (C), 137.6 (C), 160.2 (CH); MS *m/z* (rel intensity) 271/269 ($M^+-C_7H_7$,<1/<1), 183/181 (1/2), 91 (100); HRMS *m/z* calcd for $C_{13}H_{14}^{37}ClO_4$ 271.0551, found 271.0548. Anal. Calcd for $C_{20}H_{21}ClO_4$: C, 66.65; H, 5.88. Found: C, 66.72; H, 5.97.

*4.4.7. (Z)-3,5-Di-O-benzyl-1-bromo-1,2-dideoxy-4-O-formyl-D-erythro-pent-1-enitol (**19Z**) and (E)-3,5-di-O-benzyl-1-bromo-1,2-dideoxy-4-O-formyl-D-erythro-pent-1-enitol (**19E**)*

Yield 81%, *Z*/*E* dr: 7:3. Compound **19*Z***. The isolated vinyl bromide was contaminated with ca. 8% of vinyl iodide **20*Z*** that could not be completely removed by chromatography, nevertheless a small analytical sample was obtained. Oil, IR 1727 cm^{-1}; ^1H NMR δ_H 3.66 (1H, dd, *J*=10.6, 4.4 Hz), 3.69 (1H, dd, *J*=10.5, 5.9 Hz), 4.51 (1H, d, *J*=11.6 Hz), 4.56 (1H, d, *J*=11.8 Hz), 4.63 (1H, d, *J*=11.8 Hz), 4.66 (1H, d, *J*=11.6 Hz), 4.72 (1H, dd, *J*=8.9, 5.5 Hz), 5.41 (1H, ddd, *J*=5.5, 5.0, 4.4 Hz), 6.24 (1H, dd, *J*=8.8, 7.4 Hz), 6.61 (1H, d, *J*=7.3 Hz), 7.32–7.41 (10H, m), 8.17 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 68.1 (CH_2), 71.0 (CH_2), 72.9 (CH), 73.3 (CH_2), 75.0 (CH), 113.4 (CH), 127.6–128.4 (10×CH), 131.5 (CH), 137.6 (C), 137.7 (C), 160.3 (CH); MS *m/z* (rel intensity) 325 (M^+−Br, <1), 315/313 (<1/<1), 227/225 (1/1), 91 (100); HRMS *m/z* calcd for $C_{20}H_{21}O_4$ 325.1440, found 325.1431. Anal. Calcd for $C_{20}H_{21}BrO_4$: C, 59.27; H, 5.22. Found: C, 59.25; H, 5.57. Compound **19*E***. The isolated vinyl bromide was contaminated with ca. 3% of vinyl iodide **20*E*** that could not be completely removed by chromatography, nevertheless a small analytical sample was obtained. Oil, IR 1727 cm^{-1}; ^1H NMR δ_H 3.63 (1H, dd, *J*=10.6, 4.3 Hz), 3.70 (1H, dd, *J*=10.6, 5.5 Hz), 4.09 (1H, dd, *J*=8.3, 5.7 Hz), 4.39 (1H, d, *J*=11.8 Hz), 4.49 (1H, d, *J*=12.1 Hz), 4.52 (1H, d, *J*=12.1 Hz), 4.60 (1H, d, *J*=11.7 Hz), 5.22 (1H, ddd, *J*=5.2, 5.2, 5.2 Hz), 6.33 (1H, dd, *J*=13.7, 8.3 Hz), 6.36 (1H, d, *J*=13.7 Hz), 7.26–7.35 (10H, m), 8.08 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 67.7 (CH_2), 71.0 (CH_2), 72.6 (CH), 73.3 (CH_2), 77.4 (CH), 110.9 (CH), 127.7–128.4 (10×CH), 133.9 (CH), 137.3 (C), 137.6 (C), 160.2 (CH); MS *m/z* (rel intensity) 325 (M^+−Br, <1), 315/313 (<1/<1), 227/225 (2/2), 91 (100); HRMS *m/z* calcd for $C_{20}H_{21}O_4$ 325.1440, found 325.1451. Anal. Calcd for $C_{20}H_{21}BrO_4$: C, 59.27; H, 5.22. Found: C, 59.21; H, 5.55.

*4.4.8. (Z)-3,5-Di-O-benzyl-1,2-dideoxy-4-O-formyl-1-iodo-D-erythro-pent-1-enitol (**20Z**) and (E)-3,5-di-O-benzyl-1,2-dideoxy-4-O-formyl-1-iodo-D-erythro-pent-1-enitol (**20E**)*

Yield 81%, *Z*/*E* dr: 3:1. Compound **20*Z***: oil, $[\alpha]_D$ −15.8 (*c* 2.12); IR 1727 cm^{-1}; ^1H NMR δ_H 3.66 (1H, dd, *J*=10.4, 6.4 Hz), 3.70 (1H, dd, *J*=10.6, 5.8 Hz), 4.45 (1H, d, *J*=11.8 Hz), 4.47 (1H, dd, *J*=8.6, 5.9 Hz), 4.50 (1H, d, *J*=12.1 Hz), 4.58 (1H, d, *J*=12.1 Hz), 4.59 (1H, d, *J*=11.8 Hz), 5.35 (1H, ddd, *J*=5.3, 5.3, 5.3 Hz), 6.28 (1H, dd, *J*=8.0, 8.0 Hz), 6.69 (1H, d, *J*=8.0 Hz), 7.28–7.35 (10H, m), 8.10 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 68.1 (CH_2), 71.0 (CH_2), 72.8 (CH), 73.3 (CH_2), 79.2 (CH), 87.8 (CH), 127.6–128.4 (10×CH), 137.5 (CH), 137.6 (C), 137.7 (C), 160.3 (CH); MS *m/z* (rel intensity) 361 (M^+−Bn, <1), 325 (<1), 273 (5), 91 (100); HRMS *m/z* calcd for $C_{13}H_{14}IO_4$ 360.9937, found 360.9946. Anal. Calcd for $C_{20}H_{21}IO_4$: C, 53.11; H, 4.68. Found: C, 53.42; H, 4.87. Compound **20*E***. The material isolated was contaminated with ca. 20% of the isomer **20*Z*** that could not be removed chromatographically. Oil, IR 1728 cm^{-1}; ^1H NMR δ_H 3.62 (1H, dd, *J*=10.6, 4.2 Hz), 3.69 (1H, dd, *J*=10.6, 5.6 Hz), 4.06 (1H, dd, *J*=7.8, 5.7 Hz), 4.40 (1H, d, *J*=11.8 Hz), 4.50 (2H, s), 4.60 (1H, d, *J*=11.7 Hz), 5.21 (1H, ddd, *J*=5.7, 5.6, 4.2 Hz), 6.43 (1H, d, *J*=14.6 Hz), 6.52 (1H, dd, *J*=14.6, 7.8 Hz), 7.27–7.35 (10H, m), 8.07 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 67.6 (CH_2), 71.0 (CH_2), 72.5 (CH), 73.3 (CH_2), 72.4 (CH), 81.5 (CH), 127.5–128.4 (10×CH), 137.7 (2×C), 142.1 (CH), 160.2 (CH); MS *m/z* (rel intensity) 361 (M^+−Bn, <1), 325 (<1), 273 (18), 91 (100). HRMS *m/z* calcd for $C_{13}H_{14}IO_4$ 360.9937, found 360.9953. Anal. Calcd for $C_{20}H_{21}IO_4$: C, 53.11; H, 4.68. Found: C, 53.28; H, 4.88.

*4.4.9. (Z)-5-O-Acetyl-1,2-dideoxy-1-fluoro-4-O-formyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-erythro-pent-1-enitol (**25Z**) and (E)-5-O-acetyl-1,2-dideoxy-1-fluoro-4-O-formyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-erythro-pent-1-enitol (**25E**)*

Yield 79%, *Z*/*E* dr: 3:1. Compound **25*Z***: crystalline solid, mp 121.5–122.2 °C (from *n*-hexane–EtOAc); $[\alpha]_D$ +9.2 (*c* 0.62); IR 1749 cm^{-1}; ^1H NMR δ_H 1.97 (3H, s), 2.03 (3H, s), 2.06 (3H, s), 2.07 (3H, s), 2.14 (3H, s), 3.89 (1H, ddd, *J*=6.7, 6.7, 0.6 Hz), 4.06 (1H, dd, *J*=12.1, 7.1 Hz), 4.08 (1H, dd, *J*=11.6, 4.1 Hz), 4.13 (1H, dd, *J*=11.3, 6.9 Hz), 4.35 (1H, dd, *J*=12.1, 3.3 Hz), 4.58 (1H, d, *J*=8.0 Hz), 4.78 (1H, dd, *J*=9.2, 5.3 Hz), 5.00 (1H, dd, *J*=10.5, 3.4 Hz), 5.04 (1H, ddd, $^3J_{FH}$=39.9 Hz, *J*=9.2, 4.3 Hz), 5.18 (1H, dd, *J*=10.5, 8.0 Hz), 5.29 (1H, m), 5.37 (1H, dd, *J*=3.4, 0.6 Hz), 6.55 (1H, dd, $^2J_{FH}$=83.1 Hz, *J*=4.8 Hz), 8.05 (1H, s); ^{13}C NMR δ_C 20.5 (CH_3), 20.55 (CH_3), 20.62 (CH_3), 20.64 (CH_3), 20.7 (CH_3), 61.3 (CH_2), 61.8 (CH_2), 67.0 (CH), 68.7 (CH), 70.8 (CH), 71.0 (CH), 71.4 (CH, $^4J_{FC}$=2.2 Hz), 72.1 (CH, $^3J_{FC}$=6.4 Hz), 102.0 (CH), 108.3 (CH, $^2J_{FC}$=2.1 Hz), 150.2 (CH, $^1J_{FC}$=264.4 Hz), 159.7 (CH), 169.4 (C), 170.1 (C), 170.2 (C), 170.37 (C), 170.42 (C); ^{19}F NMR δ_F −123.7 (dd, $^2J_{FH}$=82.6 Hz, $^3J_{FH}$=36.7 Hz); MS *m/z* (rel intensity) 491 (M^+−OCHO, <1), 476 (<1), 348 (<1), 331 (19), 189 (100); HRMS *m/z* calcd for $C_{21}H_{28}FO_{12}$ 491.1565, found 491.1560. Anal. Calcd for $C_{22}H_{29}FO_{14}$: C, 49.26; H, 5.45. Found: C, 49.40; H, 5.32. Compound **25*E***: oil, $[\alpha]_D$ +5.7 (*c* 0.14); IR 1736 cm^{-1}; ^1H NMR δ_H 1.98 (3H, s), 2.05 (3H, s), 2.06 (3H, s), 2.07 (3H, s), 2.16 (3H, s), 3.88 (1H, ddd, *J*=6.8, 6.8, 0.5 Hz), 4.09 (1H, dd, *J*=11.7, 6.0 Hz), 4.09 (1H, dd, *J*=11.7, 6.0 Hz), 4.14 (1H, dd, *J*=11.4, 7.2 Hz), 4.24 (1H, dd, *J*=8.3, 5.2 Hz), 4.38 (1H, dd, *J*=12.2, 3.1 Hz), 4.55 (1H, d, *J*=7.7 Hz), 5.01 (1H, dd, *J*=10.5, 3.5 Hz), 5.20 (1H, dd, *J*=10.5, 7.9 Hz), 5.22 (1H, m), 5.37 (1H, dd, *J*=3.5, 0.5 Hz), 5.48 (1H, ddd, $^3J_{FH}$=16.8 Hz, *J*=11.2, 8.3 Hz), 6.75 (1H, dd, $^1J_{FH}$=82.0 Hz, *J*=11.2 Hz), 8.06 (1H, s); ^{13}C NMR δ_C 20.5 (2×CH_3), 20.6 (2×CH_3), 20.7 (CH_3), 61.5 (CH_2), 61.6 (CH_2), 67.0 (CH), 68.7 (CH), 70.7 (CH), 71.0 (CH), 71.8 (CH, $^4J_{FC}$=3.2 Hz), 75.6 (CH, $^3J_{FC}$=12.9 Hz), 101.3 (CH), 108.9 (CH, $^2J_{FC}$=12.9 Hz), 152.7 (CH, $^1J_{FC}$=264.4 Hz), 159.6 (CH), 169.4 (C), 170.1 (C), 170.2 (C), 170.4 (C), 170.5 (C); ^{19}F NMR δ_F −122.4 (dd, $^2J_{FH}$=82.6 Hz, $^3J_{FH}$=13.8 Hz); MS *m/z* (rel intensity) 491 (M^+−OCHO, <1), 476 (<1), 431 (<1), 331 (31), 189 (100); HRMS *m/z* calcd for $C_{21}H_{28}FO_{12}$ 491.1565, found 491.1559. Anal. Calcd for $C_{22}H_{29}FO_{14}$: C, 49.26; H, 5.45. Found: C, 49.32; H, 5.54.

*4.4.10. (Z)-5-O-Acetyl-1-chloro-1,2-dideoxy-4-O-formyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-erythro-pent-1-enitol (**26Z**) and (E)-5-O-acetyl-1-chloro-1,2-dideoxy-1-fluoro-4-O-formyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-erythro-pent-1-enitol (**26E**)*

Yield 81%, *Z*/*E* dr: 2:1. Compound **26*Z***: oil, $[\alpha]_D$ −11.7 (*c* 1.03); IR 1747 cm^{-1}; ^1H NMR δ_H 1.97 (3H, s), 2.03 (3H, s), 2.06 (3H, s), 2.07 (3H, s), 2.13 (3H, s), 3.89 (1H, dd, *J*=6.7, 6.3 Hz), 4.06 (1H, dd, *J*=12.2, 7.2 Hz), 4.07 (1H, dd, *J*=6.5 Hz, not observed), 4.10 (1H, dd, *J*=11.1, 6.9 Hz), 4.34 (1H, dd, *J*=12.1, 3.1 Hz), 4.58 (1H, d, *J*=8.1 Hz), 4.83 (1H, dd, *J*=8.5, 4.9 Hz), 5.00 (1H, dd, *J*=10.8, 3.6 Hz), 5.18 (1H, dd, *J*=10.8, 8.1 Hz), 5.33 (1H, m), 5.37 (1H, d, *J*=3.1 Hz), 5.96 (1H, dd, *J*=8.5, 7.2 Hz), 6.26 (1H, d, *J*=7.2 Hz), 8.05 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.5 (CH_3), 20.6 (2×CH_3), 20.7 (2×CH_3), 61.3 (CH_2), 61.8 (CH_2), 66.9 (CH), 68.7 (CH), 70.7 (CH),

71.1 (CH), 71.2 (CH), 75.3 (CH), 102.1 (CH), 122.3 (CH), 128.0 (CH), 159.6 (CH), 169.4 (C), 170.0 (C), 170.2 (C), 170.35 (C), 170.39 (C); MS (FAB) *m/z* (rel intensity) 577/575 (M^++Na, 4/10), 331 (65), 207/205 (7/20); HRMS *m/z* calcd for $C_{22}H_{29}^{37}ClNaO_{14}$ 577.1114, found 577.1093. Anal. Calcd for $C_{22}H_{29}ClO_{14}$: C, 47.79; H, 5.29. Found: C, 47.52; H, 5.66. Compound **26*E***. The material isolated was contaminated with ca. 15% starting material **22** that could not be completely removed by chromatography, nevertheless a small analytical sample was obtained. Oil, IR ($CHCl_3$) 1751 cm^{-1}; ^1H NMR δ_H 1.98 (3H, s), 2.050 (3H, s), 2.055 (3H, s), 2.07 (3H, s), 2.16 (3H, s), 3.87 (1H, dd, *J*=6.5, 6.4 Hz), 4.03 (1H, m), 4.106 (1H, d, *J*=6.4 Hz), 4.109 (1H, d, *J*=6.7 Hz), 4.31 (1H, dd, *J*=6.0, 6.0 Hz), 4.35 (1H, dd, *J*=12.3, 3.2 Hz), 4.55 (1H, d, *J*=8.1 Hz), 5.00 (1H, dd, *J*=10.6, 3.5 Hz), 5.19 (1H, dd, *J*=10.7, 7.9 Hz), 5.22 (1H, m), 5.37 (1H, d, *J*=3.2 Hz), 5.97 (1H, dd, *J*=13.3, 7.4 Hz), 6.36 (1H, dd, *J*=13.3, 1.1 Hz), 8.06 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.5 (CH_3), 20.6 (4×CH_3), 61.4 (2×CH_2), 67.0 (CH), 68.7 (CH), 70.7 (CH), 71.0 (CH), 71.7 (CH), 78.3 (CH), 101.5 (CH), 123.6 (CH), 128.9 (CH), 159.6 (CH), 169.3 (C), 170.0 (C), 170.2 (C), 170.4 (2×C); MS (FAB) *m/z* (rel intensity) 555/553 (M^++H, 1/2), 331 (2), 207/205 (16/6); HRMS *m/z* calcd for $C_{22}H_{30}^{37}ClO_{14}$ 555.1295, found 555.1292. Anal. Calcd for $C_{22}H_{29}ClO_{14}$: C, 47.79; H, 5.29. Found: C, 47.67; H, 5.60.

*4.4.11. (Z)-5-O-Acetyl-1-bromo-1,2-dideoxy-4-O-formyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-erythro-pent-1-enitol (**27Z**) and (E)-5-O-acetyl-1-bromo-1,2-dideoxy-4-O-formyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-erythro-pent-1-enitol (**27E**)*

Yield 92%, *Z*/*E* dr: 4:1. Compound **27*Z***. The isolated vinyl bromide was contaminated with ca. 11% of vinyl iodide **28*Z*** that could not be completely removed by chromatography, nevertheless a small analytical sample was obtained. Oil, IR 1747 cm^{-1}; ^1H NMR δ_H 1.97 (3H, s), 2.03 (3H, s), 2.05 (3H, s), 2.07 (3H, s), 2.13 (3H, s), 3.89 (1H, dd, *J*=6.5, 6.5 Hz), 4.07 (1H, dd, *J*=11.9, 7.3 Hz), 4.10 (1H, d, *J*=7.2 Hz), 4.11 (1H, d, *J*=7.3 Hz), 3.84 (1H, dd, *J*=12.1, 3.3 Hz), 4.59 (1H, d, *J*=8.0 Hz), 4.56 (1H, dd, *J*=8.4, 5.0 Hz), 5.0 (1H, dd, *J*=10.5, 3.3 Hz), 5.18 (1H, dd, *J*=10.3, 8.0 Hz), 5.34 (1H, ddd, *J*=7.6, 4.2, 4.2 Hz), 5.36 (1H, d, *J*=3.5 Hz), 6.26 (1H, dd, *J*=8.6, 7.4 Hz), 6.42 (1H, d, *J*=7.3 Hz), 8.05 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.5 (CH_3), 20.6 (4×CH_3), 61.2 (CH_2), 61.7 (CH_2), 66.9 (CH), 68.7 (CH), 70.7 (CH), 71.08 (2×CH), 77.7 (CH), 102.1 (CH), 111.8 (CH), 131.1 (CH), 159.6 (CH), 169.4 (C), 170.0 (C), 170.1 (C), 170.3 (C), 170.4 (C); MS (FAB) *m/z* (rel intensity) 620/618 (M^++Na−H, 5/5), 539/537 (1/1), 331 (100), 251/249 (26/26); HRMS *m/z* calcd for $C_{22}H_{28}^{81}BrNaO_{14}$ 620.0540, found 620.0547. Anal. Calcd for $C_{22}H_{29}BrO_{14}$: C, 44.23; H, 4.89. Found: C, 44.13; H, 5.07. Compound **27*E***. The isolated vinyl bromide was contaminated with ca. 8% of vinyl iodide **28*E*** that could not be completely removed by chromatography, nevertheless a small analytical sample was obtained. Oil, IR 1749 cm^{-1}; ^1H NMR δ_H 1.98 (3H, s), 2.06 (6H, s), 2.07 (3H, s), 2.16 (3H, s), 3.87 (1H, dd, *J*=6.7, 6.7 Hz), 4.10 (1H, m), 4.110 (1H, d, *J*=6.7 Hz), 4.113 (1H, d, *J*=6.7 Hz), 4.28 (1H, dd, *J*=6.1, 5.7 Hz), 4.34 (1H, dd, *J*=12.6, 3.1 Hz), 4.56 (1H, d, *J*=8.0 Hz), 5.01 (1H, dd, *J*=10.3, 3.4 Hz), 5.20 (1H, dd, *J*=10.5, 7.8 Hz), 5.23 (1H, m), 5.37 (1H, d, *J*=3.5 Hz), 6.25 (1H, dd, *J*=13.4, 6.9 Hz), 6.50 (1H, s), 8.06 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.5 (CH_3), 20.7 (4×CH_3), 61.3 (CH_2), 61.4 (CH_2), 66.9 (CH), 68.7 (CH), 70.6 (CH), 71.0 (CH), 71.4 (CH), 79.6 (CH), 101.5 (CH), 111.1 (CH), 132.9 (CH), 159.6 (CH), 169.4 (C), 170.0 (C), 170.2 (C), 170.4 (2×C); 620/618 (M^++Na−H, 4/4), 539/537 (1/1), 331 (100), 251/249 (17/17); HRMS *m/z* calcd for $C_{22}H_{28}^{81}BrNaO_{14}$ 620.0540, found 620.0547. Anal. Calcd for $C_{22}H_{29}BrO_{14}$: C, 44.29; H, 4.90. Found: C, 44.03; H, 5.23.

*4.4.12. (Z)-5-O-Acetyl-1,2-dideoxy-4-O-formyl-1-iodo-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-erythro-pent-1-enitol (**28Z**) and (E)-5-O-acetyl-1,2-dideoxy-4-O-formyl-1-iodo-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-erythro-pent-1-enitol (**28E**)*

Yield 93%, *Z*/*E* dr: 3:2. Compound **28*Z***: crystalline solid, mp 99.6–101.6 °C (from *n*-hexane–EtOAc); $[\alpha]_D$ −20.9 (*c* 1.85); IR (neat) 1747 cm^{-1}; ^1H NMR δ_H 1.97 (3H, s), 2.04 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 2.14 (3H, s), 3.90 (1H, dd, *J*=6.9, 6.5 Hz), 4.07 (1H, dd, *J*=12.1, 7.2 Hz), 4.106 (1H, d, *J*=6.9 Hz), 4.11 (1H, d, *J*=6.9 Hz), 4.34 (1H, dd, *J*=12.1, 3.3 Hz), 4.58 (1H, dd, *J*=8.5, 5.2 Hz), 4.61 (1H, d, *J*=8.0 Hz), 5.01 (1H, dd, *J*=10.5, 3.4 Hz), 5.18 (1H, dd, *J*=10.5, 7.9 Hz), 5.34 (1H, ddd, *J*=7.2, 5.2, 3.3 Hz), 5.37 (1H, d, *J*=3.4 Hz), 6.36 (1H, dd, *J*=8.2, 8.1 Hz), 6.57 (1H, d, *J*=7.9 Hz), 8.05 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.5 (CH_3), 20.7 (4×CH_3), 61.2 (CH_2), 61.7 (CH_2), 66.9 (CH), 68.7 (CH), 70.7 (CH), 71.1 (2×CH), 82.1 (CH), 86.4 (CH), 102.1 (CH), 137.0 (CH), 159.5 (CH), 169.4 (C), 170.1 (C), 170.2 (C), 170.3 (C), 170.4 (C); MS (FAB) *m/z* (rel intensity) 667 (M^++Na, 2), 331 (23), 297 (18); HRMS *m/z* calcd for $C_{22}H_{29}INaO_{14}$ 667.0500, found 677.0494. Anal. Calcd for $C_{22}H_{29}IO_{14}$: C, 41.01; H, 4.54. Found: C, 41.15; H, 4.47. Compound **28*E***: oil, $[\alpha]_D$ +20 (*c* 0.09); IR 1749 cm^{-1}; ^1H NMR δ_H 1.98 (3H, s), 2.06 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 2.17 (3H, s), 3.72 (1H, dd, *J*=6.7, 6.0 Hz), 4.09 (1H, dd, *J*=12.1, 7.1 Hz), 4.11 (2H, d, *J*=6.6 Hz), 4.26 (1H, dd, *J*=4.7, 4.7 Hz), 4.33 (1H, dd, *J*=12.3, 3.1 Hz), 4.56 (1H, d, *J*=7.8 Hz), 5.00 (1H, dd, *J*=10.5, 3.4 Hz), 5.20 (1H, dd, *J*=10.3, 7.9 Hz), 5.22 (1H, ddd, *J*=7.9, 4.7, 3.1 Hz), 5.37 (1H, d, *J*=3.3 Hz), 6.58 (1H, d, *J*=4.6 Hz), 6.59 (1H, s), 8.06 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.5 (CH_3), 20.7 (3×CH_3), 20.8 (CH_3), 61.3 (CH_2), 61.4 (CH_2), 66.9 (CH), 68.7 (CH), 70.7 (CH), 70.9 (CH), 71.3 (CH), 81.5 (CH), 81.6 (CH), 101.6 (CH), 140.8 (CH), 159.6 (CH), 169.4 (C), 170.1 (C), 170.2 (C), 170.4 (2×C); MS *m/z* (rel intensity) 644 (M^+, <1), 584 (<1), 297 (100); HRMS *m/z* calcd for $C_{22}H_{29}IO_{14}$ 644.0602, found 644.0577. Anal. Calcd for $C_{22}H_{29}IO_{14}$: C, 41.01; H, 4.54. Found: C, 41.36; H, 4.33.

*4.4.13. (Z)-3,5-Di-O-acetyl-1,2-dideoxy-1-fluoro-4-O-formyl-D-threo-pent-1-enitol (**33Z**) and (E)-3,5-di-O-acetyl-1,2-dideoxy-1-fluoro-4-O-formyl-D-threo-pent-1-enitol (**33E**)*

Yield 84%, *Z*/*E* dr: 1:1. Compound **33*Z***: oil, $[\alpha]_D$ +140.7 (*c* 0.17); IR 1744 cm^{-1}; ^1H NMR δ_H 2.06 (6H, s), 4.12 (1H, dd, *J*=12.2, 6.4 Hz), 4.33 (1H, dd, *J*=12.2, 3.6 Hz), 4.85 (1H, ddd, $^3J_{FH}$=39.3 Hz, *J*=9.0, 4.9 Hz), 5.37 (1H, ddd, *J*=6.4, 6.4, 3.6 Hz), 5.95 (1H, dd, *J*=9.0, 6.4 Hz), 6.57 (1H, dd, $^2J_{FH}$=81.8 Hz, *J*=4.9 Hz), 8.11 (1H, s); ^{13}C NMR δ_C 20.6 (CH_3), 20.8 (CH_3), 61.9 (CH_2), 64.8 (CH, $^3J_{FC}$=4.6 Hz), 70.9 (CH, $^4J_{FC}$=1.8 Hz), 105.8 (CH, $^2J_{FC}$=2.0 Hz), 151.1 (CH, $^1J_{FC}$=268.8 Hz), 159.8 (CH), 169.4 (C), 170.4 (C); ^{19}F NMR δ_F −119.1 (dd, $^2J_{FH}$=82.8 Hz, $^3J_{FH}$=41.1 Hz); MS *m/z* (rel intensity) 247 (M^+−H, <1), 203 (13), 189 (7), 160 (30), 130 (34), 117 (100); HRMS *m/z* calcd for $C_{10}H_{12}FO_6$ 247.0618, found 247.0625. Anal. Calcd for $C_{10}H_{13}FO_6$: C, 48.39; H, 5.28. Found: C, 48.10; H, 5.59. Compound **33*E***: oil, $[\alpha]_D$ +17.3 (*c* 1.8); IR 1736 cm^{-1}; ^1H NMR δ_H 2.05 (3H, s), 2.06 (3H, s), 4.05 (1H, dd, *J*=12.1, 6.3 Hz), 4.37 (1H, dd, *J*=12.1, 3.9 Hz), 5.35 (2H, m), 5.47 (1H, dd, *J*=9.3, 6.1 Hz), 6.84 (1H, dd, $^2J_{FH}$=81.4 Hz, *J*=11.1 Hz), 8.10 (1H, s); ^{13}C NMR δ_C 20.6 (CH_3), 20.9 (CH_3), 61.7 (CH_2), 67.4 (CH, $^3J_{FC}$=14.6 Hz), 70.8 (CH, $^4J_{FC}$=3.1 Hz), 106.4 (CH, $^2J_{FC}$=13.2 Hz), 154.6 (CH, $^1J_{FC}$=266.7 Hz), 159.7 (CH), 169.6 (C), 170.3 (C); ^{19}F NMR δ_F −119.6 (dd, $^2J_{FH}$=82.8 Hz, $^3J_{FH}$=15.1 Hz); MS *m/z* (rel intensity) 203 (M^+−HCO_2, 18), 189 (8), 160 (35), 130 (50), 117 (100); HRMS *m/z* calcd for $C_9H_{12}FO_4$ 203.0720, found 203.0672. Anal. Calcd for $C_{10}H_{13}FO_6$: C, 48.39; H, 5.28. Found: C, 48.30; H, 5.56.

*4.4.14. (Z)-3,5-Di-O-acetyl-1-chloro-1,2-dideoxy-4-O-formyl-D-threo-pent-1-enitol (**34Z**) and (E)-3,5-di-O-acetyl-1-chloro-1,2-dideoxy-4-O-formyl-D-threo-pent-1-enitol (**34E**)*

Yield 96%, *Z*/*E* dr: 1:1. Compound **34*Z***: oil, $[\alpha]_D$ +36.4 (*c* 0.40); IR 1737 cm^{-1}; ^1H NMR δ_H 2.07 (3H, s), 2.08 (3H, s), 4.10 (1H, dd, *J*=12.1, 6.7 Hz), 4.34 (1H, dd, *J*=12.1, 4.1 Hz), 5.42 (1H, ddd, *J*=5.8, 5.8, 3.6 Hz), 5.74 (1H, dd, *J*=8.5, 7.6 Hz), 6.00 (1H, dd, *J*=8.6, 5.9 Hz), 6.32 (1H, dd, *J*=7.2, 0.9 Hz), 8.10 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.65

(CH_3), 20.7 (CH_3), 61.8 (CH_2), 67.7 (CH), 70.5 (CH), 124.3 (CH), 125.5 (CH), 159.7 (CH), 169.3 (C), 170.4 (C); MS *m/z* (rel intensity) 229 (M^+−Cl, 5), 103 (100), HRMS *m/z* calcd for $C_{10}H_{13}O_6$ 229.0746, found 229.0740. Anal. Calcd for $C_{10}H_{13}ClO_6$: C, 45.38; H, 4.95. Found: C, 45.41; H, 5.11. Compound **34*E***: oil, $[\alpha]_D$ +2.2 (*c* 0.27); IR 1740 cm^{-1}; ^1H NMR δ_H 2.07 (3H, s), 2.09 (3H, s), 4.05 (1H, dd, *J*=12.1, 6.7 Hz), 4.36 (1H, dd, *J*=12.2, 3.6 Hz), 5.33 (1H, ddd, *J*=6.3, 5.9, 3.5 Hz), 5.52 (1H, dd, *J*=7.7, 5.9 Hz), 5.87 (1H, dd, *J*=13.5, 7.7 Hz), 6.42 (1H, d, *J*=13.5 Hz), 8.10 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.6 (CH_3), 20.8 (CH_3), 61.7 (CH_2), 70.0 (CH), 70.4 (CH), 125.7 (CH), 126.6 (CH), 159.6 (CH), 169.4 (C), 170.3 (C); MS *m/z* (rel intensity) 266/264 (M^+, <1/<1), 229 (8), 103 (100); HRMS *m/z* calcd for $C_{10}H_{13}^{37}ClO_6$ 266.0371, found 266.0341. Anal. Calcd for $C_{10}H_{13}ClO_6$: C, 45.38; H, 4.95. Found: C, 45.31; H, 5.11.

4.4.15. *(Z)-3,5-Di-O-acetyl-1-bromo-1,2-dideoxy-4-O-formyl-D-threo-pent-1-enitol (**35Z**) and (E)-3,5-di-O-acetyl-1-bromo-1,2-dideoxy-4-O-formyl-D-threo-pent-1-enitol (**35E**)*

Yield 84%, *Z*/*E* dr: 3:2. Compound **35*Z***. The isolated vinyl bromide was contaminated with ca. 4% of vinyl iodide **36*Z*** that could not be completely removed by chromatography, nevertheless a small analytical sample was obtained. Oil, IR 1740 cm^{-1}; ^1H NMR δ_H 2.07 (3H, s), 2.08 (3H, s), 4.10 (1H, dd, *J*=12.1, 6.7 Hz), 4.34 (1H, dd, *J*=12.1, 3.9 Hz), 5.44 (1H, m), 5.92 (1H, dd, *J*=8.4, 5.7 Hz), 6.10 (1H, dd, *J*=8.3, 7.6 Hz), 6.54 (1H, dd, *J*=7.5, 0.8 Hz), 8.10 (1H, s); ^{13}C NMR δ_C 20.7 (CH_3), 20.8 (CH_3), 61.8 (CH_2), 69.9 (CH), 70.4 (CH), 113.7 (CH), 128.7 (CH), 159.7 (CH), 169.3 (C), 170.4 (C); MS *m/z* (rel intensity) 229 (M^+−Br, 1), 81 (100); HRMS *m/z* calcd for $C_{10}H_{13}O_6$ 229.0712, found 229.0691. Anal. Calcd for $C_{10}H_{13}BrO_6$: C, 38.86; H, 4.24. Found: C, 38.81; H, 4.33. Compound **35*E***. The isolated vinyl bromide was contaminated with ca. 3% of vinyl iodide **36*Z*** that could not be completely removed by chromatography, nevertheless a small analytical sample was obtained. Oil, IR 1736 cm^{-1}; ^1H NMR δ_H 2.07 (3H, s), 2.10 (3H, s), 4.06 (1H, dd, *J*=12.1, 6.4 Hz), 4.36 (1H, dd, *J*=12.1, 4.0 Hz), 5.33 (1H, ddd, *J*=6.1, 6.1, 6.1 Hz), 5.49 (1H, dd, *J*=7.2, 6.1 Hz), 6.15 (1H, dd, *J*=13.7, 7.6 Hz), 6.56 (1H, d, *J*=13.7 Hz), 8.10 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.6 (CH_3), 20.8 (CH_3), 61.6 (CH_2), 70.1 (CH), 71.3 (CH), 113.2 (CH), 130.6 (CH), 159.5 (CH), 169.4 (C), 170.3 (C); MS *m/z* (rel intensity) 229 (M^+−Br, 2), 81 (100); HRMS *m/z* calcd for $C_{10}H_{13}O_6$ 229.0712, found 229.0681. Anal. Calcd for $C_{10}H_{13}BrO_6$: C, 38.86; H, 4.24. Found: C, 39.03; H, 4.35.

4.4.16. *(Z)-3,5-Di-O-acetyl-1,2-dideoxy-4-O-formyl-1-iodo-D-threo-pent-1-enitol (**36Z**) and (E)-3,5-di-O-acetyl-1,2-dideoxy-4-O-formyl-1-iodo-D-threo-pent-1-enitol (**36E**)*

Yield 90%, *Z*/*E* dr: 1:1. Compound **36*Z***: crystalline solid, mp 45.9–47.5 °C (from *n*-hexane–EtOAc); $[\alpha]_D$ +51.6 (*c* 1.12); IR 1740 cm^{-1}; ^1H NMR δ_H 2.069 (3H, s), 2.072 (3H, s), 4.09 (1H, dd, *J*=12.0, 6.7 Hz), 4.34 (1H, dd, *J*=12.0, 3.9 Hz), 5.44 (1H, ddd, *J*=6.7, 5.8, 3.9 Hz), 5.72 (1H, dd, *J*=8.3, 5.8 Hz), 6.24 (1H, dd, *J*=8.2, 8.2 Hz), 6.70 (1H, d, *J*=8.0 Hz), 8.09 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 20.67 (CH_3), 20.74 (CH_3), 61.7 (CH_2), 70.2 (CH), 74.1 (CH), 88.1 (CH), 134.7 (CH), 159.7 (C), 169.3 (C), 170.4 (C); MS *m/z* (rel intensity) 357 (M^++H, 3), 356 (M^+, 1), 311 (15), 297 (80), 183 (100); HRMS *m/z* calcd for $C_{10}H_{13}IO_6$ 355.9757, found 355.9794. Anal. Calcd for $C_{10}H_{13}IO_6$: C, 33.73; H, 3.68. Found: C, 33.86; H, 3.66. Compound **36*E***: oil, $[\alpha]_D$ −14.2 (*c* 0.94); IR 1739 cm^{-1}; ^1H NMR δ_H 2.07 (3H, s), 2.10 (3H, s), 4.05 (1H, dd, *J*=12.1, 6.3 Hz), 4.35 (1H, dd, *J*=12.1, 4.0 Hz), 5.33 (1H, ddd, *J*=6.3, 6.2, 4.0 Hz), 5.45 (1H, dd, *J*=6.4, 6.2 Hz), 6.48 (1H, dd, *J*=14.6, 7.0 Hz), 6.64 (1H, d, *J*=14.6 Hz), 8.09 (1H, s). ^{13}C NMR (125.7 MHz) δ_C 20.6 (CH_3), 20.7 (CH_3), 61.6 (CH_2), 69.9 (CH), 73.0 (CH), 83.4 (CH), 138.4 (CH), 159.6 (CH), 169.3 (C), 170.3 (C); MS *m/z* (rel intensity) 356 (M^+, 1), 310 (3), 297 (3), 229 (<1), 183 (100); HRMS *m/z* calcd for $C_{10}H_{13}IO_6$ 355.9757, found 355.9770. Anal. Calcd for $C_{10}H_{13}IO_6$: C, 33.73; H, 3.68. Found: C, 33.62; H, 3.67.

4.4.17. *(Z)-3,5-O-Benzylidene-1,2-dideoxy-4-O-formyl-1-iodo-D-erythro-pent-1-enitol (**40Z**) and (E)-3,5-O-benzylidene-1,2-dideoxy-4-O-formyl-1-iodo-D-erythro-pent-1-enitol (**40E**)*

Yield 91%, *Z*/*E* dr: 3:2. Compound **40*Z***: crystalline solid, mp 73.9–74.6 °C (from *n*-hexane–AcOEt); $[\alpha]_D$ −60.5 (*c* 0.81); IR 1733 cm^{-1}; ^1H NMR δ_H 3.84 (1H, dd, *J*=10.5, 10.5 Hz), 4.41 (1H, dd, *J*=10.8, 5.3 Hz), 4.65 (1H, dd, *J*=8.9, 8.8 Hz), 5.14 (1H, ddd, *J*=9.9, 9.8, 5.6 Hz), 5.64 (1H, s), 6.36 (1H, dd, *J*=8.0, 8.0 Hz), 6.66 (1H, d, *J*=8.0 Hz), 7.38 (3H, m), 7.51 (2H, m), 8.04 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 64.8 (CH), 67.7 (CH_2), 81.1 (CH), 87.8 (CH), 101.2 (CH), 126.1 (2×CH), 128.3 (2×CH), 129.3 (CH), 136.8 (C), 140.5 (CH), 159.4 (CH); MS *m/z* (rel intensity) 360 (M^+, <1), 314 (4), 233 (<1), 208 (7), 107 (100); HRMS *m/z* calcd for $C_{13}H_{13}IO_4$ 359.9859, found 359.9840. Anal. Calcd for $C_{13}H_{13}IO_4$: C, 43.36; H, 3.64. Found: C, 43.55; H, 3.48. Compound **40*E***: crystalline solid, mp 100.2–100.6 °C (from *n*-hexane–AcOEt); $[\alpha]_D$ +11.6 (*c* 0.51); IR 1735 cm^{-1}; ^1H NMR δ_H 3.70 (1H, dd, *J*=10.5, 10.5 Hz), 4.28 (1H, dd, *J*=9.6, 2.4 Hz), 4.44 (1H, dd, *J*=10.8, 5.3 Hz), 4.93 (1H, ddd, *J*=10.0, 9.6, 5.4 Hz), 5.56 (1H, s), 6.63 (1H, d, *J*=2.2 Hz), 6.64 (1H, s), 7.39 (3H, m), 7.49 (2H, m), 8.05 (1H, s); ^{13}C NMR (125.7 MHz) δ_C 65.7 (CH), 67.7 (CH_2), 80.7 (CH), 81.8 (CH), 101.3 (CH), 126.2 (2×CH), 128.3 (2×CH), 129.4 (CH), 136.8 (C), 140.5 (CH), 159.3 (CH); MS *m/z* (rel intensity) 360 (M^+, <1), 314 (4), 233 (<1), 208 (2), 107 (100); HRMS *m/z* calcd for $C_{13}H_{13}IO_4$ 359.9859, found 359.9845. Anal. Calcd for $C_{13}H_{13}IO_4$: C, 43.36; H, 3.64. Found: C, 43.42; H, 3.53.

4.4.18. *5-O-[tert-Butyl(dimethyl)silyl]-1,2-dideoxy-4-O-formyl-1-iodo-D-threo-pent-1-enitol (**42EZ**) and 5-O-[tert-butyl(dimethyl)silyl]-1,2-dideoxy-3-O-formyl-1-iodo-D-threo-pent-1-enitol (**43EZ**)*

Yield 85%, *Z*/*E* dr: 3:7, the four products were isolated as two mixtures (**42*E***, **43*E*** and **42*Z***, **43*Z***) that could not be separated. Inseparable mixture of compounds **42*E*** and **43*E*** (71%, 68:32): IR 3611, 3468, 1727 cm^{-1}; MS *m/z* (rel intensity) 387 (M^++H, 5), 341 (3), 73 (100); HRMS *m/z* calcd for $C_{12}H_{23}IO_4Si$ 387.0489, found 387.0466. Anal. Calcd for $C_{12}H_{23}IO_4Si$: C, 37.31; H, 6.00. Found: C, 37.34; H, 6.04. Compound **42*E***: ^1H NMR δ_H −0.07 (3H, s), −0.06 (3H, s), 0.86 (9H, s), 2.06 (1H, br s), 3.47 (1H, dd, *J*=11.0, 4.9 Hz), 3.57 (1H, dd, *J*=11.0, 4.8 Hz), 3.99 (1H, dd, *J*=4.6, 4.6 Hz), 4.76 (1H, ddd, *J*=4.8, 4.8, 4.8 Hz), 6.24 (1H, d, *J*=14.5 Hz), 6.36 (1H, dd, *J*=14.4, 5.2 Hz), 7.50 (1H, s); ^{13}C NMR (125.7 MHz) δ_C −5.5 (2×CH_3), 18.3 (C), 25.9 (3×CH_3), 62.0 (CH_2), 73.3 (CH), 74.6 (CH), 79.1 (CH), 144.3 (CH), 159.9 (CH). Compound **43*E***: ^1H NMR δ_H −0.07 (3H, s), −0.06 (3H, s), 0.86 (9H, s), 2.06 (1H, br s), 3.33 (2H, d, *J*=4.2 Hz), 3.37 (1H, ddd, *J*=6.3, 4.2, 4.2 Hz), 5.34 (1H, dd, *J*=7.0, 6.3 Hz), 6.29 (1H, d, *J*=14.6 Hz), 6.42 (1H, dd, *J*=14.6, 7.4 Hz), 7.46 (1H, s); ^{13}C NMR (125.7 MHz) δ_C −5.5 (2×CH_3), 18.3 (C), 25.9 (3×CH_3), 63.2 (CH_2), 72.1 (CH), 75.3 (CH), 82.5 (CH), 140.5 (CH), 159.4 (C). Inseparable mixture of compounds **42*Z*** and **43*Z*** (14%, 57:43): IR 3592, 3468, 1727 cm^{-1}; MS (FAB) *m/z* (rel intensity) 409 (M^++Na, 1), 391 (4). Anal. Calcd for $C_{12}H_{23}IO_4Si$: C, 37.31; H, 6.00. Found: C, 37.63; H, 5.71. Compound **42*Z***: ^1H NMR δ_H −0.05 to 0.10 (6H, s), 0.91 (9H, s), 2.86 (1H, d, *J*=4.6 Hz), 3.89 (1H, dd, *J*=11.0, 3.7 Hz), 3.93 (1H, dd, *J*=11.0, 5.0 Hz), 4.74 (1H, ddd, *J*=7.8, 4.6, 3.4 Hz), 5.04 (1H, ddd, *J*=4.9, 3.7, 3.4 Hz), 6.35 (1H, dd, *J*=7.8, 7.8 Hz), 6.51 (1H, d, *J*=7.8 Hz), 8.14 (1H, s); ^{13}C NMR (125.7 MHz) δ_C −5.5 to −5.4 (2×CH_3), 18.2 (C), 25.8 (3×CH_3), 62.4 (CH_2), 74.0 (CH), 74.4 (CH), 84.7 (CH), 139.1 (CH), 160.4 (CH). Compound **43*Z***: ^1H NMR δ_H −0.05 to 0.10 (6H, s), 0.91 (9H, s), 2.50 (1H, d, *J*=6.5 Hz), 3.67 (1H, dd, *J*=10.2, 5.9 Hz), 3.69 (1H, dd, *J*=10.2, 4.8 Hz), 3.86 (1H, dddd, *J*=6.5, 5.9, 4.8, 4.8 Hz), 5.68 (1H, dd, *J*=8.3, 4.8 Hz), 6.42 (1H, dd, *J*=8.2, 8.1 Hz), 6.65 (1H, d, *J*=8.0 Hz), 8.12 (1H, s); ^{13}C NMR (125.7 MHz) δ_C −5.5 to −5.4 (2×CH_3), 18.2 (C), 25.8 (3×CH_3), 63.0 (CH_2), 72.2 (CH), 76.2 (CH), 86.6 (CH), 136.2 (CH), 159.9 (C).

*4.4.19. (Z,E)-3-O-Acetyl-1,2-dideoxy-4-O-formyl-1-iodo-D-glycero-tetra-1-enitol (**45ZE**)*

Yield 86%, *Z*/*E* dr: 3:2. Inseparable mixture of compounds **45*Z*** and **45*E***: Oil, IR 1732 cm^{-1}; MS *m*/*z* (rel intensity) 284 (M^+, 7), 238 (1), 225 (41), 196 (58), 111 (100); HRMS *m*/*z* calcd for $C_7H_9IO_4$ 283.9546, found 283.9565. Anal. Calcd for $C_7H_9IO_4$: C, 29.60; H, 3.19. Found: C, 29.77; H, 3.16. Compound **45*Z***: ^1H NMR δ_H 2.10 (3H, s), 4.28 (1H, dd, *J*=11.9, 6.2 Hz), 4.38 (1H, dd, *J*=11.9, 3.6 Hz), 5.71 (1H, ddd, *J*=7.9, 6.2, 3.6 Hz), 6.33 (1H, dd, *J*=7.9, 7.9 Hz), 6.64 (1H, d, *J*=8.0 Hz), 8.08 (1H, s); ^{13}C NMR (50.3 MHz) δ_C 20.8 (CH_3), 62.9 (CH_2), 74.0 (CH), 86.5 (CH), 135.5 (CH), 160.3 (CH), 169.7 (C). Compound **45*E***: ^1H NMR δ_H 2.10 (3H, s), 4.18 (1H, dd, *J*=11.8, 6.5 Hz), 4.32 (1H, dd, *J*=11.9, 4.0 Hz), 5.40 (1H, ddd, *J*=6.6, 6.6, 3.9 Hz), 6.52 (1H, dd, *J*=14.6, 6.7 Hz), 6.62 (1H, d, *J*=14.6 Hz), 8.04 (1H, s); ^{13}C NMR (50.3 MHz) δ_C 20.8 (CH_3), 63.1 (CH_2), 72.6 (CH), 82.6 (CH), 139.2 (CH), 160.3 (CH), 169.7 (C).

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References and notes

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