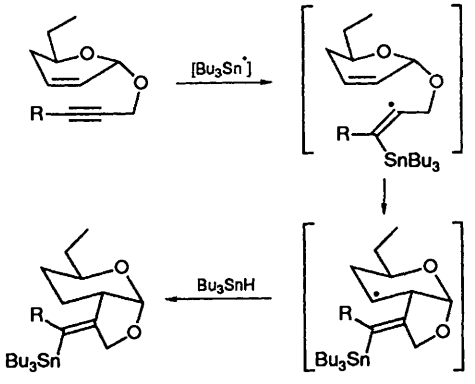
Radical Cyclization of Some Unsaturated Carbohydrate-derived Propargyl Ethers and Acetals†

Nadira Moufid, Yves Chapleur* and Patrick Mayon
Laboratoire de Chimie Organique 3, Unité Associée au CNRS 486, Université de Nancy I, BP 239, F-54506 Vandoeuvre les Nancy, France

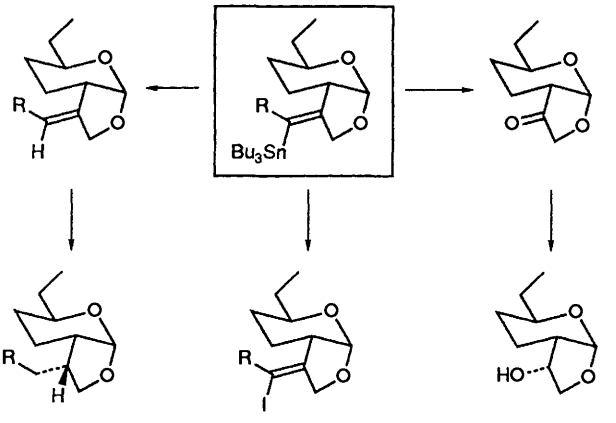
Treatment of propargyl ethers and acetals derived from deoxy-D-hexenopyranosides of *erythro* and *threo* configuration with tributyltin hydride with a radical initiator gave fused pyranofuranosides. This vinylic radical cyclization allowed the completely stereo- and regio-specific introduction, at the C-2 or C-3 position, of a functionalized carbon chain which can be further manipulated to create new chiral centres.

The continuing exploration of free-radical reactions in organic synthesis has led to a number of new methodologies of formation of carbon–carbon bonds.[2] A great deal of success has been obtained in this area because radical reactions are well suited for the synthesis of complex molecules containing a number of functional groups and/or protecting groups. Carbohydrates were often used to demonstrate examples of new radical reactions.[3] We,[4] and others,[5,6] have demonstrated the validity of radical cyclizations for the stereo- and regio-specific introduction of a functional chain on a sugar template by using a primary detachable radical and an unsaturated carbohydrate as the radical acceptor. However, the primary nature of the involved radicals precluded the introduction of highly functionalized carbon chains. In this regard, the cyclization of vinyl radicals may afford a good alternative. This reaction could provide us with new synthetic intermediates bearing an olefinic appendage which could be further elaborated by oxidative cleavage and/or new carbon–carbon bond-forming reactions. We have pursued our investigations on the cyclization of vinyl radicals readily formed from the addition of tributyltin hydride to alkynes according to Scheme 1, and we report here in full our results along these lines.



Scheme 1

We first investigated the cyclization of the unsaturated glycoside **1** readily available from tri-*O*-acetyl-D-glucal.[7] The slow addition of tributyltin hydride to the glycoside **1** in refluxing, degassed benzene gave a mixture of two compounds, which were identified as the expected cyclization product **6** and the uncyclized one **25**. In the case of the uncyclized compound **25** the *Z*/*E* ratio was also determined by ^{1}H NMR spectroscopy and in this case it was possible to attribute the *Z* and *E* stereochemistry on the basis of the coupling constants $^3J_{H,Sn}$ (50 Hz) for the *E*-isomer and 110 Hz for the *Z*-one.[8] The ^{1}H NMR spectrum of the *Z*/*E* mixture of the vinylstannane **6** was in agreement with the expected *cis* cyclization; however, if the *Z*/*E* ratio was estimated on the integration of the vinylic protons, the *Z*/*E* stereochemistry could not be firmly established. It is assumed that the major isomer was of *Z* configuration because of large steric interaction between the tributyltin moiety and the pyranose ring in the *E* isomer as seen from molecular models. Several representative examples were examined including propargyl glycosides and ethers. These compounds were prepared by Ferrier glycosidation or standard alkylation of the corresponding allylic alcohols and were submitted to the cyclization reaction. The results are summarized in Table 1.

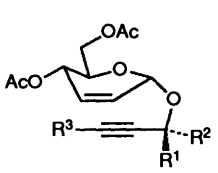


Scheme 2

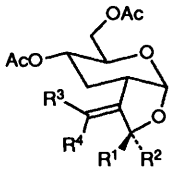
As seen from Table 1, the expected cyclized vinylstannanes were isolated in good yields even in the case of the disubstituted functionalized alkyne **3** (entry 3). The cyclization of vinyl radicals with a chiral centre derived from the diastereomerically pure propargyl derivatives **4** and **5** gave excellent results with both stereoisomers without alteration of the stereochemistry α to the radical (entries 5 and 6). The cyclization of vinyl radicals proceeded well on the substituted olefin **29** (entry 11). In contrast to the primary radicals, the 6-*exo* cyclization of vinylic radicals gave cyclized products **33** albeit in low yield (entry 7). Finally it is interesting to note that hydrostannylation, resulting from the reaction of the intermediate vinylic radicals with tributyltin hydride, occurred only with propargyl glycosides **1**, **3**, **4**, **5** and **14**. This was in full agreement with the observed reduction of the corresponding primary radicals,[4c] and could be explained by a slower cyclization rate.

The synthetic usefulness of the vinylstannanes is well known.[9]

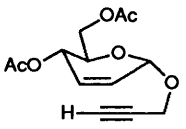
† Contribution from the Laboratoire de Procédés Moléculaires, Université de Nancy I, Institut National Polytechnique de Lorraine.



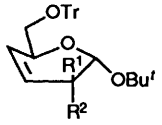
1 $R^1 = R^2 = R^3 = H$
2 $R^1 = R^2 = H$, $R^3 = CH_2OH$
3 $R^1 = R^2 = H$, $R^3 = CH_2OAc$
4 $R^1 = Me$, $R^2 = R^3 = H$
5 $R^2 = Me$, $R^1 = R^3 = H$



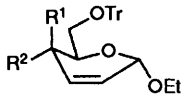
6 $R^1 = R^2 = R^3 = H$, $R^4 = SnBu_3$
7 $R^1 = R^2 = H$, R^3, $R^4 = CH_2OAc$, $SnBu_3$
8 $R^1 = Me$, $R^2 = H$, R^3, $R^4 = SnBu_3$
9 $R^1 = H$, $R^2 = Me$, R^3, $R^4 = H$, $SnBu_3$
10 $R^1 = R^2 = R^3 = R^4 = H$
11 $R^1 = R^2 = H$, R^3, $R^4 = H$,I
12 $R^1 = R^2 = H$, R^3, $R^4 = H$, CH_2OAc
13 $R^1 = R^2 = H$, R^3, $R^4 = I$, CH_2OAc



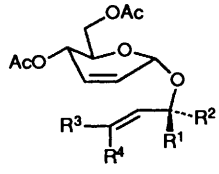
14



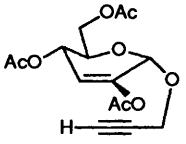
15 $R^1 = H$, $R^2 = OH$
16 $R^1 = H$, $R^2 = OCH_2C{\equiv}CH$
17 $R^1 = OBz$, $R^2 = H$
18 $R^1 = OH$, $R^2 = H$
19 $R^1 = OCH_2C{\equiv}CH$, $R^2 = H$



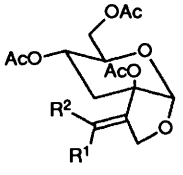
20 $R^1 = H$, $R^2 = OH$
21 $R^1 = H$, $R^2 = OCH_2C{\equiv}CH$
22 $R^1 = OBz$, $R^2 = H$
23 $R^1 = OH$, $R^2 = H$
24 $R^1 = OCH_2C{\equiv}CH$, $R^2 = H$



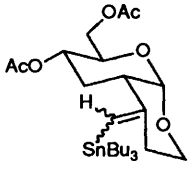
25 $R^1 = R^2 = R^3 = H$, $R^4 = SnBu_3$
26 $R^1 = R^2 = H$, R^3, $R^4 = CH_2OAc$, $SnBu_3$
27 $R^1 = Me$, $R^2 = H$, R^3, $R^4 = H$, $SnBu_3$
28 $R^1 = H$, $R^2 = Me$, R^3, $R^4 = H$, $SnBu_3$



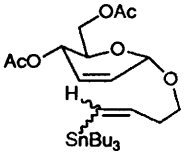
29



30 R^1, $R^2 = H$, $SnBu_3$
31 $R^1 = R^2 = H$
32 R^1, $R^2 = H$, I



33



34

Table 1 Radical cyclization of propargyl acetals and ethers

Entry	Starting compound	Method	Time (h)	Cyclized product (yield %)	$Z:E$ ratio[a]	Hydrostannylated product yield (%)	$Z:E$ ratio[b]
1	**1**	C	0.5	**6**(66)	Z	**25**(12)	1:3
2	**1**	D	4	**6**(75)	Z	**25**(11)	1:3
3	**3**	C	0.5	**7**(54)	5:1	**26**(42)	4.5:1
4	**3**	D	4	**7**(77)	5:1	**26**(16)	4.5:1
5	**4**	C	2	**8**(65)	5:1	**27**(16)	1:33
6	**5**	C	2	**9**(63)	4:1	**28**(18)	1:35
7	**14**	C	0.5	**33**(21)	3.5:1	**34**(59)	1:4.5
8	**16**	C	0.75	**36**(61)	16:1		
9	**19**	D	3	**37a**(36) **37**(34)			
10	**24**	D	2.5	**39**(44) **40**(39)			
11	**29**	D	7	**30a**(50) **30b**(34)			

[a] Mixtures of Z,E isomers (stereochemistry not determined) estimated by integration of the vinylic proton in NMR spectrum. [b] $E:Z$ Ratio estimated by integration of the vinylic protons in NMR spectrum, the stereochemistry being determined on the basis of the $^3J_{H,Sn}$ (see text).

Table 2 Protiodestannylation of vinylstannanes

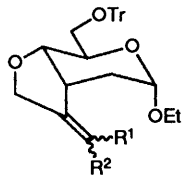
Entry	Starting compound	Method	Time (h)	Product (yield %)
1	**6**	E	48	**10**(82)
2	**6**	F	1.5	**10**(90)
3	**7**	E	48	**12**(0)
4	**7**	F	7	**12**(90)
5	**30a**	F	2	**31**(98)
6	**37**	F	48	**38**(89)
7	**39**	F	36	**40**(99)

Table 3 Iodination of vinylstannanes

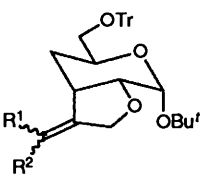
Entry	Starting compound	Time (min)	Product
1	**6**	5	**11**(92)
2	**7**	5	**13**(80)
3	**30b**	5	**32**(69)

They can be used as precursors of vinyl halides,[10] vinylcarbanions,[11] of olefins *via* protiodestannylation[12] or coupling,[13] and of carbonyl compounds *via* epoxidation.[14] Having easy access to sugar-derived vinylstannanes, we have explored some of their potentialities, which are summarized in Scheme 2. The model compound **6** was found to undergo protiodestannylation on silica gel or in slightly acidic medium to give the expected olefin **10**. Catalytic reduction of the double bond of compound **10** gave the expected furanopyranoside **46** as a single isomer. The configuration at C-4′ was established on the basis of ^1H NMR and Nuclear Overhauser Effect (NOE) difference spectroscopic results. Clearly, the reduction occurred from the less hindered *exo* face of the bicyclic system. On treatment with iodine, the vinylstannane **6** gave the expected vinyl iodide **11** in excellent yield. These reactions were extended to other vinylstannanes and proceeded well as can be seen from the results summarized in Tables 2 and 3.

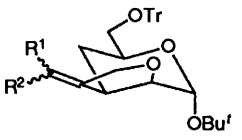
Finally, we focused our attention on the oxidative cleavage of the olefinic bond of vinylstannanes, which would open the way to more functionalized furans. Although ozonolysis of the vinylstannane **6** gave the ketone **45** in an acceptable yield (60%), the osmium tetraoxide–sodium periodate system (0.1/5 mol equiv.) in a diethyl ether–water mixture (1:1) was found to be more efficient. This method has been applied to the olefins **6**, **35**, **36**, **37** and **39**. The results are summarized in Table 4. These ketones are potentially useful intermediates for the synthesis of multichiral arrays, because it would be possible to take



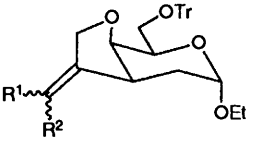
35 R^1, R^2 = H, $SnBu_3$



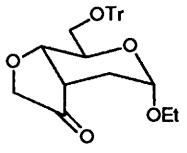
36 R^1, R^2 = H, $SnBu_3$



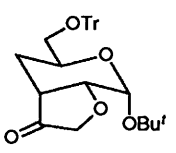
37 R^1, R^2 = H, $SnBu_3$
38 R^1 = R^2 = H



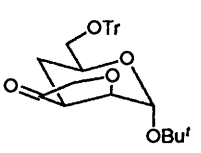
39 R^1, R^2 = H, $SnBu_3$
40 R^1 = R^2 = H



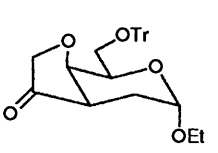
41



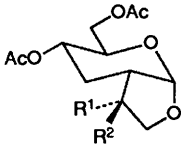
42



43



44



45 R^1, R^2 = O
46 R^1 = Me, R^2 = H
47 R^1 = OH, R^2 = H

Table 4 Oxidative cleavage of vinylstannanes

Entry	Starting compound	Method	Time (h)	Product (yield %)
1	**6**	I	2	**45**(90)
2	**30**	I	48	(0)
3	**35**	H	1	**41**(60)
4	**35**	I	2.5	**41**(99)
5	**36**	I	2	**42**(95)
6	**37**	I	24	**43**(86)
7	**39**	I	5	**44**(88)

advantage of such biased systems to introduce new chiral centres on the furan ring. This was exemplified by the stereospecific reduction ($NaBH_4$, EtOH, 90%) of the ketone **45** to the single alcohol **47**. The stereochemistry of this centre was found to be *R* by proton NMR spectroscopy, resulting from the reduction from the *exo* face as in the case of the catalytic reduction of olefin **10**. This whole transformation could be viewed as a fully stereocontrolled aldol reaction.[15]

The radical cyclization of β-stannyl vinyl radicals derived from carbohydrates proceeded well, whatever the configuration of the starting allylic alcohol, to give *Z,E* mixtures of vinylstannanes, without epimerization of a chiral centre α to the intermediate radical. As in the case of primary radicals, reaction of a vinyl radical anchored at the anomeric centre with tributyltin hydride was found to compete with the cyclization reaction. This could be explained, in either case, in terms of the *exo*-anomeric effect. This effect tends to orientate the O–C bond of the aglycone antiperiplanar to the C-1–C-2 bond of the sugar for stereoelectronic reasons.[16] This stabilization has to be overcome to reach the correct geometry of the cyclization transition state, thus lowering the cyclization rate.

The vinylstannanes can be transformed into a number of synthetic intermediates, such as ketones, *via* oxidative cleavage of the double bond. This new sequence allows the stereocontrolled acylation of carbohydrates at C-2 or C-3 to occur.[17] It is worthy of note that this radical cyclization allowed the highly stereocontrolled introduction of new chiral centres out of the sugar templates and is a good alternative to other approaches.[18] The coupling of the intermediate vinylstannanes, for example, with vinyl iodides could be a method of choice for the synthesis of C–C (pseudo) disaccharides.[19] This point is currently under study in our laboratories.

Experimental

General conditions and the preparation of compounds **15**, **17**, **18**, **20**, **22** and **23** are described in the preceding paper.

General Procedure A: Glycosylation.—To a stirred solution of the D-glucal (1 mmol) in methylene dichloride (5 cm^3) at room temperature were added successively the alcohol (1.1 mmol) and boron trifluoride–diethyl ether (0.03 cm^3, 0.1 mmol). The mixture was stirred until TLC control indicated complete reaction. Pyridine (0.1 cm^3) was added and the reaction mixture was extracted with methylene dichloride and the combined extracts were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Purification by chromatography on silica gel afforded the unsaturated glycoside.

General Procedure B: Etherification.—To a suspension of NaH (53 mg, 1.1 mmol) in dry tetrahydrofuran (THF) (1.5 cm^3) at 0 °C was added slowly under nitrogen a solution of the alcohol (1 mmol) in dry THF (3.5 cm^3). After the mixture had been stirred for 30 min, propargyl bromide (0.32 cm^3, 2.2 mmol) was added and the mixture was stirred at 0 °C for 30 min, then at room temperature until TLC control (SiO_2) indicated complete reaction. After addition of methanol, the solvent was removed under reduced pressure and the residue was extracted with methylene dichloride; the combined extracts were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography on silica gel gave the products.

General Procedure C: Cyclization by Slow Addition.—To a solution of iodo or bromo compound (1 mmol) with azoisobutyronitrile (AIBN) (16 mg, 0.1 mmol) in refluxing, degassed benzene (50 cm^3) under nitrogen was added tributyltin hydride (0.3 cm^3) and the mixture was stirred until TLC indicated complete reaction. The solvent was removed, and the products were separated by column chromatography on silica gel.

General Procedure D: Cyclization.—The acetylenic compound (1 mmol) was dissolved in degassed benzene (50 cm^3) containing AIBN (16 mg, 0.1 mmol) and the solution was refluxed under argon. A solution of tributyltin hydride (0.3 cm^3, 1.1 mmol) in benzene (5 cm^3) was slowly added with a motor-driven syringe over a period of 4 h. The mixture was stirred under these conditions until TLC indicated complete reaction. After removal of the solvent, the products were separated by chromatography on silica gel.

General Procedure E: Protiodestannylation on Silica Gel.—The vinyltributylstannane (1 mmol) was stirred in methylene dichloride (10 cm^3) with silica gel (1 g) at room temperature until completion was indicated by TLC. The reaction mixture was filtered, and the filtrate was filtered through a pad of Celite

which was then washed with ethyl acetate. After concentration of the combined filtrate and washings under reduced pressure, column chromatography gave the olefin.

General Procedure F: Protiodestannylation in Acidic Medium.—To a solution of the vinyltributylstannane (1 mmol) in methanol (10 cm^3) was added 0.1 mol dm^{-3} HCl (1 cm^3, 0.1 mmol). The reaction mixture was stirred at room temperature until TLC (SiO_2) indicated completion. 3 mol dm^{-3} Sodium hydroxide was then added (to neutrality) and the reaction mixture was concentrated and coevaporated with ethanol. Without further purification the residue was taken up in a mixture of pyridine (5 cm^3) and acetic anhydride (1 cm^3) for acetylation. After conventional work-up, column chromatography on silica gel gave the olefin.

General Procedure G: Iodination.—To a solution of the vinyltributylstannane (1 mmol) in methylene dichloride (10 cm^3) was added iodine (1.05 mmol). The reaction mixture was stirred at room temperature until TLC indicated completion (SiO_2; 5 min). The reaction mixture was diluted with methylene dichloride, washed successively with aq. saturated sodium thiosulfate and water, dried ($MgSO_4$), and concentrated under reduced pressure. The vinyl iodide was purified on silica gel column chromatography.

General Procedure H for Olefin Cleavage: Ozonolysis.—Ozonized oxygen was passed through a solution of the olefin (1 mmol) in anhydrous methylene dichloride (15 cm^3) at −40 °C until no starting material remained on TLC. The reaction mixture was warmed to 0 °C, dimethyl sulfide was added and the mixture was stirred overnight. The residue obtained on evaporation was extracted with methylene dichloride (3 × 50 cm^3), and the organic phase was washed with water until neutral, dried ($MgSO_4$), and evaporated to dryness. Column chromatography of the residue gave the pure ketone.

General procedure I for Olefin Cleavage: Sodium Periodate–Osmium Tetroxide.—To a solution of the olefin in a diethyl ether–water mixture (1:1; 10 cm^3 $mmol^{-1}$) was added a solution of osmium tetraoxide in *tert*-butyl alcohol (2 cm^3 $mmol^{-1}$; 1% w/v) and sodium periodate (5 mol equiv.). The mixture was stirred until no starting material remained on TLC. The product was extracted with diethyl ether and the extract washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Column chromatography of the residue gave the pure ketone.

Prop-2′-ynyl 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α,β-D-erythro-*hex*-2-*enopyranoside* **1**.—Obtained quantitatively according to general procedure A as a *crystalline solid* (α:β 12:1; 1 mmol, 269 mg), m.p. 61 °C (from hexane–ethyl acetate); R_f 0.4 (H:E 1:3); $[\alpha]_D^{20}$ +145 (*c* 1, $CHCl_3$) (Found: C, 58.3; H, 6.1. $C_{13}H_{16}O_6$ requires C, 58.20; H, 6.01%); ν_{max}/cm^{-1} 3300 (H–C≡), 2120 (C≡C), 1745 (C=O) and 1605 (C=C); δ_H 2.08 (3 H, s, OAc), 2.14 (3 H, s, OAc), 2.49 (1 H, s, 3′-H), 4.10 (1 H, ddd, $J_{4,5}$ 9.5 $J_{5,6}$ 2.5 $J_{5,6'}$ 5, 5-H), 4.19 (1 H, dd, J_{gem} 11, 6-H), 4.26 (1 H, dd, 6-H′), 4.34 (1 H, d, J_{gem} 16, 1′-H), 4.35 (1 H, d, 1-H′), 5.17 (0.08 H, dd, $J_{1,2}$ 3.5, 1-H$^\beta$), 5.25 (0.92 H, d, $J_{1,2}$ 3.5, 1-H$^\alpha$), 5.35 (1 H, dd, $J_{2,4}$ 2, 4-H), 5.85 (0.92 H, dd, $J_{2,3}$ 10, 2-H$^\alpha$), 5.93 (0.92 H, d, 3-H$^\alpha$), 5.99 (0.08 H, d, $J_{2,3}$ 10, 3-H$^\beta$) and 6.04 (0.08 H, dd, 2-H$^\beta$).

4′-Acetoxybut-2′-ynyl 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α,β-D-*hex*-2-*enopyranoside* **3**.—General procedure A gave the alcohol **2** accompanied by the dimer; the crude products were acetylated and separated to give pure acetate **3** (α:β 10:1; 146 mg, 43%), R_f 0.30 (H:A 2:1); $[\alpha]_D^{20}$ +112.9 (*c* 0.95, $CHCl_3$) (Found: C, 56.6; H, 5.8. $C_{16}H_{20}O_8$ requires C, 56.47; H, 5.92%); ν_{max}/cm^{-1} 2200 (C≡C), 1750 (C=O) and 1605 (C=C); δ_H 2.04 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.11 (3 H, s, OAc), 4.08 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 2.5, $J_{5,6'}$ 5, 5-H), 4.19 (1 H, dd, J_{gem} 11.5, 6-H), 4.26 (1 H, dd, 6-H′), 4.34–4.37 (1.8 H, m, 1′-H$^\alpha_2$), 4.39–4.41 (0.2 H, m, 1′-H$^\beta_2$), 4.70–4.73 (2 H, m, 4′-H$_2$), 5.19 (0.1 H, t, $J_{1,2}$ = $J_{1,3}$ = 4, 1-H$^\beta$), 5.22 (0.9 H, dd, $J_{1,2}$ 3, $J_{1,3}$ 1, 1-H$^\alpha$), 5.31 (0.1 H, dd, 4-H$^\beta$), 5.35 (0.9 H, ddd, $J_{2,4}$ 1.5, $J_{3,4}$ 1, 4-H$^\alpha$), 5.84 (0.9 H, ddd, $J_{2,3}$ 10, 2-H$^\alpha$), 5.93 (0.9 H, ddd, 3-H$^\alpha$), 5.98 (0.1 H, ddd, $J_{2,3}$ 10, 3-H$^\beta$) and 6.02 (0.1 H, ddd, 2-H$^\beta$).

The dimer was a crystalline solid, m.p. 106 °C (from hexane–ethylacetate) (α:β 10:1; 140 mg, 27%), R_f 0.17 (H:A 2:1); $[\alpha]_D^{20}$ 136.4 (*c* 1, $CHCl_3$); ν_{max}/cm^{-1} 2210 (C≡C), 1750 (C=O) and 1605 (C=C); δ_H 2.08 (6 H, s, 2 × OAc), 2.11 (6 H, s, 2 × OAc), 4.31–4.42 (4 H, m, 2 × 1′-H$_2$), 5.16 (0.2 H, t, $J_{1,2}$ = $J_{1,3}$ 4, 2 × 1-H$^\beta$), 5.22 (1.8 H, dd, $J_{1,2}$ 3, $J_{1,3}$ 1, 2 × 1-H$^\alpha$), 5.32 (0.2 H, dd, 2 × 4-H$^\beta$), 5.34 (1.8 H, dd, $J_{2,4}$ 1.5, 2 × 4-H$^\alpha$), 5.84 (1.8 H, ddd, $J_{2,3}$ 10, 2 × 2-H$^\alpha$), 5.93 (1.8 H, dd, 2 × 3-H$^\alpha$), 5.98 (0.2 H, dd, 2 × 3-H$^\beta$) and 6.04 (0.2 H, ddd, 2 × 2-H$^\beta$).

3,4,6-Tri-*O*-acetyl-D-glucal (5 mmol) was treated with the racemic alcohol but-1-yn-3-ol according to general procedure A to give compounds **4** and **5**.

(S)-1′-*Methylprop*-2′-*ynyl* 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α,β-D-erythro-*hex*-2-*enopyranoside* **4**.—Obtained as a *crystalline solid* (α:β 25:1; 684 mg, 49%), m.p. 62 °C (from hexane–ethyl acetate); R_f 0.35 (H:A 4:1); $[\alpha]_D^{20}$ +185.2 (*c* 1, $CHCl_3$) (Found: C, 59.4; H, 6.3. $C_{14}H_{18}O_6$ requires C, 59.57; H, 6.43%); ν_{max}/cm^{-1} 3300 (H–C≡), 2120 (C≡C), 1745 (C=O) and 1605 (C=C); δ_H 1.49 (3 H, d, $J_{1',Me}$ 7, 1′-Me), 2.08 (3 H, s, OAc), 2.10 (3 H, s, OAc), 2.45 (1 H, d, $J_{1',3'}$ 2, 3′-H), 4.07 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 2.5, $J_{5,6'}$ 5, 5-H), 4.18 (1 H, dd, J_{gem} 11, 6-H), 4.23 (1 H, dd, 6-H′), 4.57 (0.96 H, dq, 1′-H$^\alpha$), 4.70 (0.04 H, ddd, 1′-H$^\beta$), 5.33 (1 H, ddd, $J_{2,4}$ 1.5, $J_{3,4}$ 1, 4-H), 5.39 (0.96 H, dd, $J_{1,2}$ 2.5, $J_{1,3}$ 1, 1-H$^\alpha$), 5.48 (0.04 H, dd, 1-H$^\beta$), 5.85 (0.96 H, ddd, $J_{2,3}$ 10, 2-H$^\alpha$), 5.92 (0.96 H, ddd, 3-H$^\alpha$), 5.97 (0.04 H, ddd, 2-H$^\beta$) and 6.02 (0.04 H, ddd, 3-H$^\beta$).

(R)-1′-*Methylprop*-2′-*ynyl* 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α,β-D-erythro-*hex*-2-*enopyranoside* **5**.—Obtained as a *syrup* (α:β 25:1; 714 mg, 51%); R_f 0.29 (H:A 4:1); $[\alpha]_D^{20}$ +76.1 (*c* 1, $CHCl_3$) (Found: C, 59.25; H, 6.4%); ν_{max}/cm^{-1} 3300 (H–C≡), 2120 (C≡C), 1740 (C=O) and 1605 (C=C); δ_H 1.48 (3 H, d, $J_{1',Me}$ 7, 1′-Me), 2.09 (3 H, s, OAc), 2.11 (3 H, s, OAc), 2.46 (1 H, d, $J_{1'',3'}$ 2, 3′-H), 4.19–4.25 (2 H, m, 5- and 6-H), 4.31 (1 H, dd, $J_{5,6'}$ 5, J_{gem} 12, 6-H′), 4.47 (1 H, qd, $J_{1',Me}$ 7, 1′-H), 5.21 (1 H, dd, $J_{1,2}$ 2.5, $J_{1,3}$ 1, 1-H), 5.40 (1 H, dd, $J_{2,4}$ 1, $J_{4,5}$ 9.5, 4-H), 5.81 (1 H, ddd, $J_{2,3}$ 10, 2-H) and 5.92 (1 H, ddd, 3-H).

Compound **1**, treated according to general procedure C (0.25 mmol), gave compounds **6** (*Z*, 92 mg, 66%) and **25** (*Z*:*E* 1:3; 17 mg, 12%); general procedure D (4.29 mmol) gave compounds **6** (*Z*, 1.79 g, 75%) and **25** (*Z*:*E* 1:3; 253 mg, 11%).

4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*tributylstannylmethylene*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **6**.—R_f 0.38 (H:A 8:1); $[\alpha]_D^{20}$ +78.4 (*c* 0.4, $CHCl_3$); ν_{max}/cm^{-1} 1760 (C=O) and 1650 (C=C); δ_H 0.90–0.97 (9 H, m, 3 × Me), 1.24–1.60 (18 H, m, 9 × CH_2), 1.69 (1 H, dt, $J_{2,3a}$ = $J_{3a,4}$ = 9, J_{gem} 13, 3-H^a), 2.03 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.23 (1 H, ddd, $J_{2,3e}$ 7.5, $J_{3e,4}$ 5, 3-H^e), 2.77 (1 H, m, $J_{1,2}$ 4.5, $J_{2,3''}$ 2, 2-H), 4.03 (1 H, ddd, $J_{4,5}$ 9, $J_{5,6}$ 2.5, $J_{5,6'}$ 5.5, 5-H), 4.15 (1 H, dd, J_{gem} 12, 6-H), 4.24 (1 H, dd, $J_{CH=,5'}$ 2, J_{gem} 13, 5′-H), 4.29 (1 H, dd, 6-H′), 4.57 (1 H, ddd, $J_{CH=,5'}$ 2, 5′-H), 4.78 (1 H, ddd, 4-H), 5.38 (1 H, d, 1-H) and 5.88 (1 H, ddd, $J_{CH=,Sn}$ 50, CH=).

(E)-3′-(*Tributylstannyl*)*prop*-2′-*enyl* 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α-D-erythro-*hex*-2-*enopyranoside* **25**.—R_f 0.3 (H:A 8:1); ν_{max}/cm^{-1} 1750 (C=O), 1640 (C=C) and 1605 (C=C); δ_H 0.86–0.97 (9 H, m, 3 × Me), 1.24–1.56 (18 H, m, 9 × CH_2), 2.08

(3 H, s, OAc), 2.11 (3 H, s, OAc), 4.15–4.20 (3 H, m, $J_{5,6}$ 2, $J_{5,6'}$ 5.5, J_{gem} 11, 5-H and 6-H_2), 4.24–4.34 (2 H, m, J_{gem} 12, 1'-H_2), 5.08 (1 H, d, $J_{1,2}$ 2, 1-H), 5.33 (1 H, dd, $J_{3,4}$ 2, $J_{4,5}$ 10, 4-H), 5.85 (1 H, dd, $J_{2,3}$ 10, 3-H), 5.90 (1 H, dd, 2-H), 6.05 (1 H, m, $J_{1',2'}$ = $J_{1',2'}$ 5, $J_{2',3'}$ 20, $J_{2',Sn}$ 50, 2'-H) and 6.25 (1 H, dd, $J_{3',Sn}$ 53, 3'-H).

Compound **3**, treated according to general procedure C (0.3 mmol), gave compounds **7** (*Z*:*E* 5:1; 102 mg, 54%) and **26** (*Z*:*E* 4.5:1; 80 mg, 42%); general procedure D (2.35 mmol) gave compounds **7** (*Z*:*E* 5:1; 1.0 g, 77%) and **26** (*Z*:*E* 4.5:1; 232 mg, 16%).

4'-[2-*Acetoxy*-1-(*tributylstannyl*)*ethylidene*-4,6-*di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5'-*tetrahydro*-α-D-ribo*hexopyranoso*[1,2-b]*furan* **7**.—R_f 0.65 (H:A 2:1) ν_{max}/cm^{-1} 1750 (C=O) and 1640 (C=C); δ_H major isomer 0.82–1.04 (9 H, m, 3 × Me), 1.23–1.59 (19 H, m, 9 × CH_2, 3-H^a), 2.02–2.06 (9 H, m, 3 × OAc), 2.20 (1 H, ddd, $J_{2,3e}$ 4.5, J_{gem} 12, $J_{3e,4}$ 6.5, 3-H^e), 3.12 (1 H, ddd, $J_{1,2}$ 4, $J_{2,3a}$ 9.5, 2-H), 4.08 (1 H, ddd, $J_{4,5}$ 9.5 $J_{5,6}$ 2, $J_{5,6'}$ 4.5, 5-H), 4.16 (1 H, dd, J_{gem} 11.5, 6-H), 4.20 (1 H, d, J_{gem} 13, 5'-H), 4.31 (1 H, dd, 6-H'), 4.57 (1 H, d, J_{gem} 12.5, AcOC*H*H), 4.58 (1 H, d, 5'-H), 4.79 (1 H, dt, $J_{3a,4}$ 9.5, 4-H), 4.83 (1 H, d, AcOCH*H*) and 5.38 (1 H, d, 1-H).

(Z)-4'-*Acetoxy*-3'-*tributylstannyl*)*but*-2'-*enyl* 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α-D-erythro-*hex*-2-*enopyranoside* **26**.—R_f 0.7 (H:A 2:1); ν_{max}/cm^{-1} 1750 (C=O), 1650 (C=C) and 1605 (C=C); δ_H 0.82–1.04 (9 H, m, 3 × Me), 1.23–1.58 (18 H, m, 9 × CH_2), 2.02–2.15 (9 H, m, 3 × OAc), 4.09 (1 H, ddd, $J_{4,5}$ 9, $J_{5,6}$ 2.5, $J_{5,6'}$ 5, 5-H), 4.16 (1 H, dd, J_{gem} 12, 6-H), 4.22–4.33 (2 H, m, 4'-H and 6-H'), 4.40 (1 H, dd, J_{gem} 13, $J_{4'',Sn}$ 43, 4'-H), 4.48–4.55 (2 H, m, 1'-H_2), 5.05 (1 H, d, $J_{1,2}$ 3, 1-H), 5.32 (1 H, dd, $J_{2,4}$ 1.5, 4-H), 5.81 (1 H, ddd, $J_{2,3}$ 10, 2-H), 5.88 (1 H, d, 3-H) and 6.40 (1 H, m, $J_{1',2'}$ = $J_{1'',2'}$ = 7, $J_{2',Sn}$ 114, 2'-H).

Compound **4** (0.5 mmol), treated according to general procedure C gave compounds **8** (*Z*:*E* 5:1; 185 mg, 65%) and **27** (*Z*:*E* 1:33; 45 mg, 16%).

(5'S)-4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5'-*tetrahydro*-5'-*methyl*-4'-*tributylstannylmethylene*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **8**.—R_f 0.26 (H:A 9:1); ν_{max}/cm^{-1} 1750 (C=O) and 1650 (C=C); δ_H major isomer 0.80–1.00 (15 H, m, 3 × CH_2Me), 1.20–1.60 (15 H, m, 3 × CH_2CH_2Sn, 5'-Me), 1.99–2.09 (7 H, m, 2 × OAc, 3-H^a), 2.11 (1 H, ddd, $J_{2,3e}$ 6.5, J_{gem} 13, $J_{3e,4}$ 4.5, 3-H^e), 2.53 (1 H, ddd, $J_{1,2}$ 3.5, $J_{2,3a}$ 9, 2-H), 4.05 (1 H, ddd, $J_{4,5}$ 9, $J_{5,6}$ 2.5, $J_{5,6'}$ 5, 5-H), 4.12 (1 H, dd, J_{gem} 11.5, 6-H), 4.31 (1 H, dd, 6-H'), 4.75 (1 H, ddd, $J_{3a,4}$ 9.5, 4-H), 4.82 (1 H, dq, $J_{5',CH=}$ 1.5, $J_{5',Me}$ = $J_{5',Me}$ = 6.5, 5'-H), 5.35 (1 H, d, 1-H) and 5.61 (1 H, dd, $J_{CH=,Sn}$ 54, CH=).

(S)-1'-*Methyl*-3'-(*tributylstannyl*)*prop*-2'-*enyl* 4,6-*Di*-O-*acetyl*-α-D-erythro-*hex*-2-*enopyranoside* **27**.—R_f 0.33 (H:A 9:1); ν_{max}/cm^{-1} 1750 (C=O) and 1640 (C=C); δ_H 0.80–1.00 (15 H, m, 3 × CH_2Me), 12.0–1.60 (15 H, m, 3 × CH_2CH_2Sn, 1'-Me), 2.08 (3 H, s, OAc), 2.10 (3 H, s, OAc), 4.17 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 2, $J_{5,6'}$ 5, 5-H), 4.19–4.24 (2 H, m, 1'- and 6-H), 4.26 (1 H, dd, J_{gem} 10, 6-H'), 5.09 (1 H, dd, $J_{1,2}$ 3, $J_{1,4}$ 1, 1-H), 5.31 (1 H, m, $J_{2,4}$ 1.5, $J_{3,4}$ 1, 4-H), 5.80 (1 H, ddd, $J_{2,3}$ 10, 2-H), 5.82 (1 H, ddd, $J_{1',2'}$ 6.5, $J_{2',3'}$ 19, $J_{2',Sn}$ 56, 2'-H), 5.88 (1 H, dd, 3-H) and 6.14 (1 H, dd, $J_{3',Sn}$ 58, 3'-H).

Compound **5** (0.5 mmol), treated according to general procedure C, gave compounds **9** (*Z*:*E* 4:1; 181 mg, 63%) and **28** (*Z*:*E* 1:35; 52 mg, 18%).

(5'R)-4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2'3',4',5'-*tetrahydro*-5'-*methyl*-4'-(*tributylstannylmethylene*)-α-D-ribo-*hexopyranoso*-[1,2-b]*furan* **9**.—R_f 0.19 (H:A 9:1); ν_{max}/cm^{-1} 1750 (C=O) and 1650 (C=C); δ_H major isomer 0.84–0.98 (15 H, m, 3 × CH_2Me), 1.24–1.54 (15 H, m, 3 × CH_2CH_2Sn, 5'-Me), 1.88 (1 H, dt, $J_{2,3}$ = $J_{3,4}$ = 6, J_{gem} 13, 3-H), 2.01 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.24 (1 H, dt, $J_{2,3}$ = $J_{3,4}$ = 6, 3-H), 2.94 (1 H, m, $J_{1,2}$ 5.5, $J_{CH=,2}$ 1.5, $J_{2,5'}$ 2, 2-H), 3.91 (1 H, ddd, $J_{4,5}$ 9, $J_{5,6}$ 2, $_{5,6'}$ 5, 5-H), 4.12 (1 H, dd, J_{gem} 11.5, 6-H), 4.21 (1 H, dd, 6-H'), 4.78 (1 H, ddd, $J_{CH=,5'}$ 1.5, $J_{5',Me}$ 7, 5'-H), 4.82 (1 H, dt, 4-H), 5.52 (1 H, d, 1-H) and 5.80 (1 H, ddd, $J_{CH=,Sn}$ 49, CH=).

(R)-1'-*Methyl*-3'-(*tributylstannyl*)*prop*-2'-*enyl* 4,6-*Di*-O-*acetyl*-α-D-erythro-*hex*-2-*enopyranoside* **28**.—R_f 0.30 (H:A 9:1); ν_{max}/cm^{-1} 1750 (C=O), 1640 (C=C) and 1605 (C=C); δ 0.80–1.00 (15 H, m, 3 × CH_2Me), 1.20–1.65 (15 H, m, 3 × CH_2CH_2Sn, 1'-Me), 2.09 (3 H, s, OAc), 2.11 (3 H, s, OAc), 4.13 (1 H, ddd, $J_{4,5}$ 9, $J_{5,6}$ 2, $J_{5,6'}$ 5, 5-H), 4.15 (1 H, dd, J_{gem} 12, 6-H), 4.34 (1 H, dd, 6-H'), 5.16 (1 H, ddd, $J_{2,4}$ 1, $J_{3,4}$ 1.5 4-H), 5.25 (1 H, d, $J_{1,2}$ 4.5, 1-H), 5.73 (1 H, ddd, $J_{1',2'}$ 7, $J_{2',3'}$ 19, $J_{2',Sn}$ 50, 2'-H), 5.92 (1 H, dd, $J_{2,3}$ 10.5, 3-H), 5.98 (1 H, ddd, 2-H) and 6.15 (1 H, ddd, $J_{1',3'}$ 5, $J_{3',Sn}$ 53, 3'-H).

4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5-*tetrahydro*-4'-*methylene*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **10**.—Obtained from compound **6** according to the general procedure E (0.38 mmol; 85 mg, 82%) or general procedure F (2.3 mmol; 557 mg, 90%) as a crystalline solid, m.p. 49–50 °C (from hexane–ethyl acetate); R_f 0.33 (H:A 2:1); $[\alpha]_D^{20}$ +46.2 (*c* 1.2, $CHCl_3$) (Found: C, 57.75; H, 6.6. $C_{13}H_{18}O_6$ requires C, 57.83; H, 6.77%); ν_{max}/cm^{-1} 1750 (C=O) and 1655 (C=C); δ_H 1.69 (1 H, dt, $J_{2,3a}$ = $J_{3a,4}$ = 9, J_{gem} 13, 3-H^a), 2.03 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.21 (1 H, ddd, $J_{2,3e}$ 5, $J_{3e,4}$ 6.5, 3-H^e), 2.80 (1 H, m, $J_{1,2}$ 4.5, $J_{2,5'}$ 2, 2-H), 4.03 (1 H, ddd, $J_{4,5}$ 9, $J_{5,6}$ 2.5, $J_{5,6'}$ 5.5, 5-H), 4.15 (1 H, dd, J_{gem} 12, 6-H), 4.29 (1 H, dd, 6-H'), 4.34 (1 H, dt, $J_{CH=,5'}$ = $J_{CH=,5'}$ = 1.5, J_{gem} 13, 5'-H), 4.65 (1 H, m, $J_{CH=,5'}$ = $J_{CH=,5'}$ = 1.5, 5'-H), 4.79 (1 H, dt, 4-H), 4.95 (1 H, dt, J_{gem} 2, C*H*H=), 5.02 (1 H, dt, CH*H*=) and 5.37 (1 H, d, 1-H).

4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5'-*tetrahydro*-4'-*iodomethylene*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **11**.—Obtained from compound **6** (0.32 mmol) according to general procedure G (116 mg, 92%); R_f 0.36 (H:A 3:1); $[\alpha]_D^{20}$ +109.4 (*c* 1.2, $CHCl_3$) (Found: C, 39.5; H, 4.3; I, 32.2. $C_{13}H_{17}IO_6$ requires C, 39.41; H, 4.32; I, 32.03%); ν_{max}/cm^{-1} 1745 (C=O) and 1650 (C=C); δ_H 1.74 (1 H, dt, $J_{2,3a}$ = $J_{3a,4}$ = 9, J_{gem} 13, 3-H^a), 2.04 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.21 (1 H, ddd, $J_{2,3e}$ 7, J_{3e4} 5, 3-H^e), 2.91 (1 H, m, $J_{1,2}$ 4.5, $J_{2,5'}$ 2, 2-H), 4.06 (1 H, ddd, $J_{4,5}$ 8.5, $J_{5,6}$ 2.5, $J_{5,6'}$ 5.5, 5-H), 4.17 (1 H, dd, J_{gem} 12, 6-H), 4.22 (1 H, dd, $J_{CH=,5'}$ 2.5, J_{gem} 14, 5'-H), 4.29 (1 H, dd, 6-H'), 4.52 (1 H, ddd, $J_{CH=,5'}$ 2, 5'-H), 4.78 (1 H, ddd, 4-H), 5.45 (1 H, d, 1-H, d, 1-H) and 6.08 (1 H, dd, CHI).

4'-(2-*Acetoxyethylidene*)-4,6-*di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5'-*tetrahydro*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **12**.—Obtained from compound **7** (0.49 mmol) according to general procedure F (*Z*:*E* 2.3:1; 160 mg, 90%); R_f 0.5 (H:A 2:1) (Found: C, 56.25; H, 6.3. $C_{16}H_{22}O_8$ requires C, 56.14; H, 6.48%); ν_{max}/cm^{-1} 1750 (C=O) and 1650 (C=C); δ_H 1.99–2.14 (10 H, m, 3 × OAc, 3-H^a), 2.22 (1 H, ddd, $J_{2,3e}$ 7, J_{gem} 13, $J_{3e,4}$ 4.5, 3-H^e), 3.04 (1 H, ddd, $J_{1,2}$ 5, $J_{2,3a}$ 10, 2-H), 4.09 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 2.5, $J_{5,6'}$ 6.5, 5-H), 4.16 (1 H, dd, J_{gem} 10, 6-H), 4.19–4.88 (5 H, m, AcOCH_2CH=, 5'-H_2, and 6-H'), 5.07 (1 H, dt, $J_{3a,4}$ 9.5, 4-H), 5.30 (1 H, d, 1-H) and 5.44 (1 H, dd, $J_{CH=,CHOAc}$ 2.5, $J_{CH=,CHOAc}$ 5.5, CH=).

4'-(2-*Acetoxy*-1-*iocloethylidene*)-4,6-*di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5'-*tetrahydro*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **13**.—Obtained from compound **7** (0.53 mmol) according to general procedure G (*Z*:*E* 2.2:1; 200 mg, 80%), R_f 0.29 (H:A 2:1); $[\alpha]_D^{20}$ +48.4 (*c* 1.2, $CHCl_3$) (Found: C, 41.3; H, 4.5; I, 26.95. $C_{16}H_{21}IO_8$ requires C, 41.04; H, 4.52; I, 27.10%); ν_{max}/cm^{-1} 1745 (C=O) and 1670 (C=C); δ_H major isomer 1.39 (1 H, dt, $J_{2,3a}$ =

$J_{3a,4}$ = 10, J_{gem} 12, 3-H^a), 2.03 (3 H, s, OAc), 2.05 (3 H, s, OAc), 2.07 (3 H, s, OAc), 2.23 (1 H, ddd, $J_{2,3e}$ 6.5, $J_{3e,4}$ 4.5, 3-H^e), 3.22 (1 H, ddd, $J_{1,2}$ 4.5, 2-H), 4.11 (1 H, ddd, $J_{4,5}$ 10, $J_{5,6}$ 2.5, $J_{5,6'}$ 5, 5-H), 4.14 (1 H, d, J_{gem} 13.5, 5'-H), 4.17 (1 H, dd, J_{gem} 12, 6-H), 4.30 (1 H, dd, 6-H'), 4.47 (1 H, d, J_{gem} 15, C*H*HOAc), 4.64 (1 H, d, CH*H*OAc), 4.80 (1 H, dt, 4-H), 4.90 (1 H, d, 5'-H) and 5.37 (1 H, d, 1-H).

But-3'-ynyl 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α,β-D-erythro-*hex*-2-*enopyranoside* **14**.—Obtained according to general procedure A (α:β 10:1; 282 mg, 100%), R_f 0.4 (H:E 1:3); $[\alpha]_D^{20}$ +131 (*c* 1.2, $CHCl_3$) (Found: C, 59.8; H, 6.3. $C_{14}H_{18}O_6$ requires C, 59.57; H, 6.43%); ν_{max}/cm^{-1} 3300 (H–C≡), 2120 (C≡C), 1750 (C=O) and 1605 (C=C); δ_H 2.08 (3 H, s, OAc), 2.12 (3 H, s, OAc), 2.50 (1.80 H, ddd, J_{gem} 9.5, 2 × 2'-H$^\alpha$), 2.54 (0.20 H, ddd, J_{gem} 9.5 2 × 2'-H$^\beta$), 3.66 (0.10 H, dt, J_{gem} 9.5, $J_{1',2'} = J_{1',2''}$ = 7, 1'-H$^\beta$), 3.70 (0.90 H, dt, $J_{1',2'} = J_{1',2''}$ = 7, J_{gem} 9.5 1'-H$^\alpha$), 3.87 (0.90 H, dt, $J_{1'',2'} = J_{1'',2''}$ = 7, 1'-H$^\alpha$), 3.95 (0.10 H, dt, $J_{1'',2'} = J_{1'',2''}$ = 7, 1'-H$^\beta$), 4.15 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 2.5, $J_{5,6'}$ 5, 5-H), 4.20 (1 H, dd, J_{gem} 11, 6-H), 4.24 (1 H, dd, 6-H'), 5.08 (0.90 H, dd, $J_{1,2}$ 3, $J_{1,3}$ 1, 1-H$^\alpha$), 5.17–5.20 (0.20 H, m, 1- and 4-H$^\beta$), 5.31 (0.90 H, ddd, $J_{2,4}$ 1.5, $J_{3,4}$ 1,4-H$^\alpha$), 5.84 (0.90 H, ddd, $J_{2,3}$ 10, 2-H$^\alpha$), 5.90 (0.90 H, dd, 3-H$^\alpha$), 5.96 (0.10 H, dd, $J_{2,3}$ 10, 3-H$^\beta$) and 6.00 (0.10 H, ddd, $J_{1,2}$ 3.5, 2-H$^\beta$).

tert-*Butyl* 3,4-*Dideoxy*-2-O-(*prop*-2'-*ynyl*)-6-O-*trityl*-α-D-erythro-*hex*-3-*enopyranoside* **16**.—Obtained from compound **15** (2 mmol), according to general procedure B, as a *crystalline solid* (814 mg, 85%), m.p. 60 °C (from hexane–ethyl acetate); R_f 0.44 (H:A 4:1); $[\alpha]_D^{20}$ −10.6 (*c* 1.1, $CHCl_3$) (Found: C, 79.45; H, 7.2. $C_{32}H_{34}O_4$ requires C, 79.64; H, 7.10%); ν_{max}/cm^{-1} 3300 (H–C=), 2150 (C≡C) and 1605 (C=C); δ_H 1.31 (9 H, s, Bu^t), 2.38 (1 H, t, $J_{1',3'} = J_{1'',3'}$ = 2.5, 3'-H), 3.11 (1 H, dd, $J_{5,6}$ 5.5, J_{gem} 10, 6-H), 3.23 (1 H, dd, $J_{5,6'}$ 6.5, 6-H'), 4.22–4.28 (2 H, m, 1'-H_2), 4.29 (1 H, ddd, $J_{1,2}$ 5, $J_{2,3}$ 3.5, $J_{2,4}$ 1.5, 2-H), 4.41 (1 H, m, $J_{3,5}$ 1, $J_{4,5}$ 2.5, 5-H), 5.33 (1 H, d, 1-H), 5.75 (1 H, ddd, $J_{3,4}$ 10, 3-H), 5.82 (1 H, ddd, 4-H) and 7.12–7.50 (15 H, m, Ph).

tert-*Butyl* 3,4-*Dideoxy*-2-O-(*prop*-2'-*ynyl*)-6-O-*trityl*-α-D-threo-*hex*-3-*enopyranoside* **19**.—Obtained from compound **18** (1.5 mmol), according to general procedure B, as a *crystalline solid* (600 mg, 83%), m.p. 98–99 °C (from hexane–ethyl acetate); R_f 0.66 (H:A 4:1); $[\alpha]_D^{20}$ +28.3 (*c* 1, $CHCl_3$) (Found: 79.5; H, 7.2%); ν_{max}/cm^{-1} 3300 (H–C≡), 2165 (C≡C) and 1605 (C=C); δ_H 1.60 (9 H, s, Bu^t), 2.70 (1 H, t, $J_{1',3'} = J_{1'',3'}$ = 2.5, 3'-H), 3.48 (1 H, dd, $J_{5,6}$ 6, J_{gem} 9, 6-H), 3.65 (1 H, dd, $J_{5,6'}$ 6, 6-H'), 4.08 (1 H, ddd, $J_{1,2}$ 2, $J_{2,3}$ 4, $J_{2,4}$ 1, 2-H), 4.55 (1 H, dd, J_{gem} 16, 1'-H), 4.60 (1 H, dd, 1'-H), 4.75 (1 H, m, $J_{3,5}$ 2, $J_{4,5}$ 2, 5-H), 5.5 (1 H, d, 1-H), 6.18 (1 H, ddd, $J_{3,4}$ 10, 3-H), 6.36 (1 H, ddd, 4-H) and 7.46–7.86 (15 H, m, Ph).

Ethyl 2,3-*Dideoxy*-4-O-(*prop*-2'-*ynyl*)-6-O-*trityl*-α-D-erythro-*hex*-2-*enopyranoside* **21**.—Obtained from compound **20** (2 mmol), according to general procedure B, as a *crystalline solid* (782 mg, 86%), m.p. 98 °C (from hexane–ethyl acetate); R_f 0.39 (H:A 4:1); $[\alpha]_D^{20}$ +42.2 (*c* 1, $CHCl_3$) (Found: C, 79.2; H, 6.6. $C_{30}H_{30}O_4$ requires C, 79.27; H, 6.65%); ν_{max}/cm^{-1} 3300 (H–C≡), 2120 (C≡C) and 1600 (C=C); δ_H 1.25 (3 H, t, OCH_2Me), 2.24 (1 H, t, $J_{1',3'} = J_{1'',3'}$ = 2, 3'-H), 3.21 (1 H, dd, $J_{5,6}$ 5.5, J_{gem} 10, 6-H), 3.44 (1 H, dd, $J_{5,6'}$ 2, 6-H'), 3.60 (1 H, m, OC*H*HMe), 3.90–3.99 (2 H, m, 5-H and OCH*H*Me), 4.00 (2 H, t, 1'-H_2), 4.19 (1 H, ddd, $J_{2,4}$ 1.5, $J_{3,4}$ 1, $J_{4,5}$ 9.5, 4-H), 5.06 (1 H, d, $J_{1,2}$ 3, 1-H), 5.78 (1 H, ddd, $J_{2,3}$ 10.5, 2-H), 6.05 (1 H, dd, 3-H) and 7.19–6.60 (15 H, m, Ph).

Ethyl 2,3-*Dideoxy*-4-O-(*prop*-2'-*ynyl*)-6-O-*trityl*-α-D-threo-*hex*-2-*enopyranoside* **24**.—Obtained from compound **23** (3 mmol), according to general procedure B (1.28 g, 95%), R_f 0.76 (H:A 3:2); $[\alpha]_D^{20}$ −73.1 (*c* 1, $CHCl_3$) (Found: C, 79.4; H, 6.75%); ν_{max}/cm^{-1} 3300 (H–C≡), 2110 (C≡C) and 1605 (C=C); δ_H 1.32 (3 H, t, OCH_2Me), 2.33 (1 H, t, $J_{1',3'} = J_{1'',3'}$ = 2, 3'-H), 3.32 (1 H, dd, $J_{5,6}$ 6, J_{gem} 10, 6-H), 3.55 (1 H, dd, $J_{5,6}$ 6, 6-H'), 3.62 (1 H, m, OC*H*HMe), 3.86 (1 H, dd, $J_{3,4}$ 5.5, $J_{4,5}$ 2.5, 4-H), 4.0 (1 H, m, OCH*H*Me), 4.11 (1 H, dd, J_{gem} 16, 1'-H), 4.18 (1 H, dd, 1'-H), 4.31 (1 H, dt, 5-H), 5.10 (1 H, dd, $J_{1,2}$ 3, $J_{1,3}$ 1, 1-H), 6.04 (1 H, dd, $J_{2,3}$ 10, 2-H), 6.24 (1 H, ddd, 3-H) and 7.15–7.60 (15 H, m, Ph).

Prop-2'-ynyl 2,4,6-*Tri*-O-*acetyl*-3-*deoxy*-α,β-D-erythro-*hex*-2-*enopyranoside* **29**.—Obtained according to general procedure A (α:β 16:1; 458 mg, 94%); R_f 0.68 (H:A 3:2); $[\alpha]_D^{20}$ +100.2 (*c* 1.2, $CHCl_3$) (Found: C, 55.5; H, 5.4. $C_{15}H_{18}O_8$ requires C, 55.21; H, 5.56%); ν_{max}/cm^{-1} 3290 (H–C≡), 2120 (C≡C), 1750 (C=O) and 1705 (C=C); δ_H 2.10 (6 H, s, 2 × OAc), 2.20 (3 H, s, OAc), 2.53 (1 H, t, $J_{1',3'} = J_{1'',3'}$ = 2, 3'-H), 4.14 (1 H, dt, $J_{4,5}$ 9.5, $J_{5,6}$ = $J_{5,6}$ = 9.5, 5-H), 4.23 (2 H, d, 6-H_2), 4.32 (2 H, d, 1'-H_2), 5.28 (0.94 H, s, 1-H$^\alpha$), 5.33 (0.06 H, s, 1H$^\beta$), 5.44 (0.06 H, dd, 4-H$^\beta$), 5.49 (0.94 H, dd, $J_{3,4}$ 2, 4-H$^\alpha$), 5.73 (0.06 H, d, 3-H$^\beta$) and 5.76 (0.94 H, d, 3-H$^\alpha$).

Compound **29** (0.47 mmol), treated according to general procedure D, gave compounds **30a** (143 mg, 50%) and **30b** (97 mg, 34%).

2,4,6-*Tri*-O-*acetyl*-1,3-*dideoxy*-2',3',4',5'-*tetrahydro*-4'-*tributylstannylmethylene*-α-D-arabino-*hexopyranoso*[1,2-b]*furan* **30a** *and* **30b**.—Isomer **30a** R_f 0.74 (H:A 3:2); $[\alpha]_D^{20}$ +41.9 (*c* 1.1, $CHCl_3$); ν_{max}/cm^{-1} 1750 (C=O) and 1640 (C=C); δ_H 0.85–1.0 (9 H, m, 3 × Me), 1.25–1.50 (18 H, m, 9 × CH_2), 2.02–2.13 (10 H, m, 3 × OAc, 3-H^a), 2.34 (1 H, dd, J_{gem} 14, $J_{3e,4}$ 4.5, 3-H^e), 4.03 (1 H, ddd, $J_{4,5}$ 8, $J_{5,6}$ 2.5, $J_{5,6'}$ 5.5, 5-H), 4.20 (1 H, dd, J_{gem} 12, 6-H), 4.28 (1 H, dd, 6-H'), 4.53 (1 H, dd, $J_{CH=,5'}$ 2.5, J_{gem} 13, 5'-H), 4.63 (1 H, dd, $J_{CH=,5'}$ 2.5, 5'-H), 4.96 (1 H, m, $J_{3a,4}$ 7.5, 4-H), 5.79 (1 H, s, 1-H) and 5.91 (1 H, ddd, $J_{CH=,Sn}$ 48, CH=).

Isomer **30b**. R_f 0.66 (H:A 3:2); $[\alpha]_D^{20}$ +10.8 (*c* 1, $CHCl_3$); ν_{max}/cm^{-1} 1750 (C=O) and 1640 (C=C); δ_H 0.85–1.0 (9 H, m, 3 × Me), 1.20–1.60 (18 H, m, 9 × CH_2), 1.99 (3 H, s, OAc), 2.05 (6 H, s, 2 × OAc), 2.30 (1 H, dd, J_{gem} 13, $J_{3a,4}$ 10.5, 3-H^a), 3.17 (1 H, dd, $J_{3e,4}$ 5, 3-H^e), 3.82 (1 H, ddd, $J_{4,5}$ 10, $J_{5,6}$ 6, $J_{5,6'}$ 2, 5-H), 4.03 (1 H, dd, J_{gem} 12.5, 6-H), 4.17 (1 H, dd, 6-H'), 4.49 (1 H, dd, $J_{CH=,5'}$ 2, J_{gem} 13, 5'-H), 4.57 (1 H, ddd, 4-H), 5.51 (1 H, s, 1-H) and 6.65 (1 H, ddd, $J_{CH=,Sn}$ 48, CH=).

2,4,6-*Tri*-O-*acetyl*-1,3-*dideoxy*-2',3',4',5'-*Tetrahydro*-4'-*methylene*-α-D-arabino-*hexopyranoside* **31**.—Obtained from isomer **30a** (0.2 mmol) according to general procedure F (64 mg, 98%); R_f 0.48 (H:A 3:2); $[\alpha]_D^{20}$ +23.7 (*c* 1.1, $CHCl_3$) (Found: C, 54.7; H, 6.3. $C_{15}H_{20}O_8$ requires C, 54.88; H, 6.14%); ν_{max}/cm^{-1} 1750 (C=O) and 1650 (C=C); δ_H 2.01 (3 H, s, OAc), 2.06 (3 H, s, OAc), 2.10 (3 H, s, OAc), 2.20 (1 H, dd, J_{gem} 14, $J_{3a,4}$ 7.5, 3-H^a), 2.38 (1 H, dd, $J_{3e,4}$ 4.5, 3-H^e), 4.04 (1 H, ddd, $J_{4,5}$ 8, $J_{5,6}$ 3 $J_{5,6'}$ 5.5, 5-H), 4.21 (1 H, dd, J_{gem} 12, 6-H), 4.28 (1 H, dd, 6-H'), 4.62 (1 H, dt, $J_{CH=,5'} = J_{CH=,5'}$ = 2, J_{gem} 13, 5'-H), 4.72 (1 H, dt, $J_{CH=,5'} = J_{CH=,5'}$ = 2.5, 5'-H), 4.97 (1 H, ddd, 4-H), 5.03 (1 H, dt, J_{gem} 2, CH=), 5.08 (1 H, dt, CH=) and 5.76 (1 H, s, 1-H).

2,4,6-*Tri*-O-*acetyl* 1,3-*dideoxy*-2',3',4',5'-*tetrahydro*-4'-*iodomethylene*-α-D-arabino-*hexopyranoso*[1,2-b]*furan* **32**.—Obtained from compound **30** (0.07 mmol) according to general procedure G (22 mg, 69%); R_f 0.12 (H:A 4:1); $[\alpha]_D^{20}$ +9.31 (*c* 0.9, $CHCl_3$) (Found: C, 39.45; H, 4.2; I, 28.1. $C_{15}H_{19}IO_8$ requires C, 39.67; H, 4.22; I, 27.93%); ν_{max}/cm^{-1} 1750 (C=O) and 1650 (C=C); δ_H 2.01 (3 H, s, OAc), 2.05 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.16 (1 H, dd, J_{gem} 13, $J_{3a,4}$ 10.5, 3-H^a), 3.31 (1 H, dd, $J_{3e,4}$ 5, 3-H^e), 3.80 (1 H, ddd, $J_{4,5}$ 10, $J_{5,6}$ 6, $J_{5,6'}$ 2.5, 5-H), 4.10 (1 H, dd, J_{gem} 12, 6-H), 4.21 (1 H, dd, 6-H'), 4.50 (1 H, dd, $J_{CH=,5'}$ 2.5, J_{gem} 13, 5'-H), 4.55 (1 H, dd, $J_{CH=,5'}$ 2.5, 5'-H), 4.61 (1 H, ddd, 4-H), 5.52 (1 H, s, 1-H) and 6.98 (1 H, t, CH=).

Compound **14** (0.97 mmol) was treated according to general procedure C to give compounds **33** (*Z*:*E* 3.5:1; 114 mg, 21%) and **34** (*Z*:*E* 1:4.5; 318 mg, 59%).

4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*tributylstannylmethylene*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **33**.—R_f 0.34 (H:A 4:1); ν_{max}/cm^{-1} 1750 (C=O) and 1640 (C=C); δ_H major isomer 0.79–1.01 (15 H, m, 3 × CH_2Me), 1.20–1.39 (6 H, m, 3 × CH_2), 1.40–1.58 (6 H, m, 3 × CH_2Sn), 1.60 (1 H, ddd, $J_{2.3a}$ 5, J_{gem} 13, $J_{3a,4}$ 9, 3-H^a), 2.05 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.20 (1 H, dt, $J_{5',6'} = J_{5',6'} = 4$, J_{gem} 14, 5′-H), 2.33 (1 H, ddd, $J_{5',6'}$ 5, $J_{5',6'}$ 9, 5′-H), 2.59 (1 H, dt, $J_{2.3e} = J_{3e,4} = 5$, 3-H^e), 2.75 (1 H, m, $J_{1,2}$ 3, $J_{CH=,2}$ 1.5, 2-H), 3.71 (1 H, ddd, J_{gem} 10, 6′-H), 3.79 (1 H, ddd, $J_{4,5}$ 8, $J_{5,6}$ 5, $J_{5,6'}$ 2, 5-H), 3.99 (1 H, ddd, 6′-H), 4.13 (1 H, dd, J_{gem} 12, 6-H), 4.25 (1 H, dd, 6-H′), 4.88 (1 H, ddd, 4-H), 4.96 (1 H, d, 1-H) and 5.91 (1 H, dd, $J_{CH=,Sn}$ 60, CH=).

(E)-4′-(*Tributylstannyl*)*but*-3′-*enyl* 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α-D-erythro-*hex*-2-*enopyranoside* **34**.—R_f 0.38 (H:A 4:1); ν_{max}/cm^{-1} 1750 (C=O), 1650 (C=C) and 1605 (C=C); δ_H major isomer 0.80–1.00 (15 H, m, 3 × CH_2Me), 1.21–1.39 (6 H, m, 3 × CH_2), 1.40–1.60 (6 H, m, 3 × CH_2Sn), 2.08 (3 H, s, OAc), 2.11 (3 H, s, OAc), 2.46 (1 H, t, $J_{1'',2''} = J_{1'',2'} = 6$, 2′-H), 2.48 (1 H, t, $J_{1',2''} = J_{1'',2''} = 7$, 2′-H), 3.58 (1 H, ddd, J_{gem} 10, 1′-H), 3.84 (1 H, ddd, 1′-H), 4.11 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 2, $J_{5,6'}$ 5, 5-H), 4.17 (1 H, dd, J_{gem} 12, 6-H), 4.27 (1 H, dd, 6-H′), 5.05 (1 H, ddd, $J_{1,2}$ 2.5, $J_{1,4}$ 1, 1-H), 5.35 (1 H, m, $J_{2,4}$ 1.5 $J_{3,4}$ 1, 4-H), 5.83 (1 H, ddd, $J_{2,3}$ 10, 2-H), 5.88 (1 H, dd, 3-H), 5.94 (1 H, dd, $J_{3',4'}$ 19, $J_{3',Sn}$ 56, 3′-H) and 6.02 (1 H, dd, $J_{4',Sn}$ 58, 4′-H).

2,3,4-*Trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*tributylstannylmethylene*-6-O-*trityl*-(*ethyl* α-D-ribo-*hexopyranosido*)[4,3-b]*furan* **35**.—Obtained from compound **20** (1 mmol) according to general procedure C (658 mg, 90%); R_f 0.56 (H:A 6:1); ν_{max}/cm^{-1} 1640 (C=C); δ_H major isomer 0.80–1.00 (15 H, m, 3 × CH_2Me), 1.20–1.40 (15 H, m, 3 × CH_2CH_2Sn, OCH_2Me), 1.76 (1 H, ddd, $J_{1,2a}$ 6.5, J_{gem} 14, $J_{2a,3}$ 11, 2-H^a), 2.06 (1 H, dt, $J_{1,2e} = J_{2e,3}$ 6, 2-H^e), 2.70 (1 H, ddd, $J_{3,4}$ 7, 3-H), 3.23 (1 H, dd, $J_{5,6}$ 2.5, J_{gem} 10, 6-H), 3.30 (1 H, dd, $J_{5,6'}$ 6.5, 6-H′), 3.56 (1 H, m, OC*H*HMe), 3.89 (1 H, dd, $J_{4,5}$ 9, 4-H), 3.94 (1 H, ddd, 5-H), 4.03 (1 H, m, OCH*H*Me), 4.17 (1 H, dd, $J_{CH=,5'}$ 2, J_{gem} 13, 5′-H), 4.30 (1 H, ddd, $J_{CH=,5'}$ 2, $J_{3,5'}$ 1.5, 5′-H), 4.93 (1 H, dd, 1-H), 5.84 (1 H, dt, $J_{CH=,Sn}$ 57, CH=) and 7.20–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*tributylstannylmethylene*-6-O-*trityl*-(tert-*butyl* α-D-ribo-*hexopyranosido*)[2,3-b]*furan* **36**.—Obtained from compound **15** (1.4 mmol) according to general procedure C (660 mg, 61%); R_f 0.48 (H:A 6:1); ν_{max}/cm^{-1} 1635 (C=C); δ_H major isomer 0.80–1.00 (15 H, m, 3 × CH_2Me), 1.20–1.40 (12 H, m, 3 × CH_2CH_2Sn), 1.73 (1 H, dt, $J_{3,4a}$ 6.5, $J_{4a,5} = J_{gem} = 13$, 4-H^a), 1.94 (1 H, ddd, $J_{3,4e}$ 1.5, $J_{4e,5}$ 2, 4-H^e), 2.83 (1 H, m, $J_{CH=,3}$ 2, $J_{2,3}$ 8.5, $J_{3,5'} = J_{3,5'} = 1.5$, 3-H), 2.97 (1 H, dd, $J_{5,6}$ 4.5, J_{gem} 9.5, 6-H), 3.15 (1 H, dd, $J_{5,6'}$ 5.5, 6-H′), 4.13 (1 H, m, 5-H), 4.18 (1 H, dd, $J_{1,2}$ 5, 2-H), 4.35 (1 H, ddd, $J_{CH=,5'}$ 2, J_{gem} 12, 5′-H), 4.53 (1 H, dd, 5′-H), 5.11 (1 H, d, 1-H), 5.65 (1 H, ddd, $J_{CH=,Sn}$ 57, CH=) and 7.19–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*tributylstannylmethylene*-6-O-*trityl*-(tert-*butyl* α-D-lyxo-*hexopyranosido*)[2,3-b]*furan* **37a** *and* **37b**.—Obtained from compound **18** (1 mmol) according to general procedure D.

Isomer **37a**: (278 mg, 36%), R_f 0.88 (H:A 4:1); $[\alpha]_D^{20}$ +3.8 (*c* 1, $CHCl_3$); ν_{max}/cm^{-1} 1630 (C=C); δ_H 0.80–1.0 (15 H, m, 3 × CH_2Me), 1.25–1.36 (16 H, m, 4-H^a, Bu^t, 3 × CH_2), 1.41–1.51 (6 H, m, 3 × CH_2Sn), 1.64 (1 H, ddd, $J_{3,4e}$ 7, J_{gem} 14, $J_{4e,5}$ 2,4-H^e), 2.79 (1 H, ddd, $J_{2,3}$ 4, $J_{3,4a}$ 10, 3-H), 2.88 (1 H, dd, J_{gem} 9, $J_{5,6}$ 5.5, 6-H), 3.24 (1 H, dd, $J_{5,6'}$ 6, 6-H′), 3.59 (1 H, d, 2-H), 4.12 (1 H, dd, $J_{CH=,5'}$ 2, J_{gem} 13, 5′-H), 4.15 (1 H, m, $J_{4a,5}$ 11, 5-H), 4.42 (1 H, dd, $J_{CH=,5'}$ 2, 5′-H), 5.22 (1 H, s, 1-H), 5.79 (1 H, dt, $J_{CH=,Sn}$ 60, CH=) and 7.20–7.50 (15 H, m, Ph).

Isomer **37b**: (263 mg, 34%); R_f 0.80 (H:A 4:1); $[\alpha]_D^{20}$ +60.5 (*c* 1, $CHCl_3$); ν_{max}/cm^{-1} 1630 (C=C); δ_H 0.80–1.0 (15 H, m, 3 × CH_2Me), 1.20–1.40 (15 H, m, 3 × CH_2, Bu^t), 1.43–1.53 (6 H, m, 3 × CH_2Sn), 1.50 (1 H, ddd, $J_{3,4a}$ 10, J_{gem} 13, $J_{4a,5}$ 12, 4-H^a), 1.60 (1 H, ddd, $J_{3,4e}$ 6.5, $J_{4e,5}$ 12, 4-H^e), 2.58 (1 H, ddd, $J_{2,3}$ 3.5, 3-H), 2.88 (1 H, $J_{5,6}$ 5, J_{gem} 10, 6-H), 3.26 (1 H, dd, $J_{5,6'}$ 6, 6-H′), 3.58 (1 H, d, 2-H), 4.11 (1 H, m, 5-H), 4.20 (1 H, dd, $J_{CH=,5'}$ 2, J_{gem} 13, 5′-H), 4.50 (1 H, dd, $J_{CH=,5'}$ 2, 5′-H), 5.20 (1 H, s, 1-H), 5.55 (1 H, dt, $J_{CH=,Sn}$ 57, CH=), and 7.10–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*methylene*-6-O-*trityl*-(tert-*butyl* α-D-lyxo-*hexopyranosido*)[2,3-b]*furan* **38**.—Obtained from compound **37** (0.12 mmol) according to general procedure E (50 mg, 89%); R_f 0.36 (H:A 9:1); $[\alpha]_D^{20}$ +49.8 (*c* 1.1, $CHCl_3$) (Found: C, 79.1; H, 7.3. $C_{32}H_{36}O_4$ requires C, 79.31; H, 7.49%); ν_{max}/cm^{-1} 1675 (C=C); δ_H 1.27 (1 H, ddd, $J_{3,4a}$ 11, J_{gem} 14, $J_{4a,5}$ 8, 4-H^a), 1.30 (9 H, s, Bu^t), 1.61 (1 H, ddd, $J_{3,4e}$ 7, $J_{4e,5}$ 2, 4-H^e), 2.83 (1 H, ddd, $J_{2,3}$ 4, 3-H), 2.89 (1 H, dd, $J_{5,6}$ 5, J_{gem} 9.5, 6-H), 3.23 (1 H, dd, $J_{5,6'}$ 6, 6-H′), 3.55 (1 H, d, 2-H), 4.15 (1 H, m, 5-H), 4.21 (1 H, ddd, $J_{CH=,5'}$ 1.5, $J_{CH=,5'}$ 2.5, J_{gem} 13.5, 5′-H), 4.49 (1 H, ddd, $J_{CH=,5'}$ 2, $J_{CH=,5'}$ 2.5, 5′-H), 4.80 (1 H, dd, CH=), 4.97 (1 H, dd, CH=), 5.23 (1 H, s, 1-H) and 7.18–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*tributylstannylmethylene*-6-O-*trityl*-(*ethyl* α-D-lyxo-*hexopyranosido*)[4,3-b]*furan* **39**.—Obtained from compound **24** (0.86 mmol) according to general procedure D (280 mg, 44%), accompanied by compound **40** (153 mg, 39%); R_f 0.83 (H:A 3:1); ν_{max}/cm^{-1} 1635 (C=C); δ_H major isomer 0.80–1.00 (15 H, m, 3 × CH_2Me), 1.20–1.36 (9 H, m, OCH_2*Me*, 3 × CH_2CH_2Sn), 1.40–1.55 (6 H, m, $SnCH_2$), 1.70 (1 H, ddd, $J_{1,2e}$ 3, J_{gem} 12, $J_{2e,3}$ 6, 2-H^e), 1.73 (1 H, ddd, $J_{1,2a}$ 4, $J_{2a,3}$ 9, 2-H^a), 2.88 (1 H, ddd, $J_{3,4}$ 6, 3-H), 3.30 (1 H, dd, $J_{5,6}$ 5, J_{gem} 10, 6-H), 3.45 (1 H, dd, $J_{5,6'}$ 6, 6-H′), 3.50 (1 H, m, OC*H*HMe), 3.84 (1 H, dd, $J_{4,5}$ 2, 4-H), 3.88 (1 H, m, OCH*H*Me), 4.00 (1 H, ddd, 5-H), 4.12 (1 H, dd, $J_{CH=,5'}$ 2.5, J_{gem} 13, 5′-H), 4.38 (1 H, dd, $J_{CH=,5'}$ 2, 5′-H), 4.88 (1 H, dd, 1-H), 5.79 (1 H, ddd, $J_{CH=,Sn}$ 60, CH=) and 7.20–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*methylene*-6-O-*trityl*-(*ethyl* α-D-lyxo-*hexopyranosido*)[4,3-b]*furan* **40**.—Obtained quantitatively from compound **39** (0.1 mmol), according to general procedure E (47 mg), as a *syrup*; R_f 0.74 (H:A 3:1); $[\alpha]_D^{20}$ +11.3 (*c* 0.8, $CHCl_3$) (Found: C, 78.6; H, 7.1. $C_{30}H_{32}O_4$ requires C, 78.92; H, 7.06%); ν_{max}/cm^{-1} 1650 (C=C); δ_H 1.28 (3 H, t, OCH_2*Me*), 1.70 (1 H, m, $J_{1,2e}$ 3, J_{gem} 14, $J_{2e,3}$ 8, 2-H^e), 1.76 (1 H, ddd, $J_{1,2a}$ 4, $J_{2a,3}$ 9, 2-H^a), 2.90 (1 H, ddd, $J_{3,4}$ 5, 3-H), 3.31 (1 H, dd, $J_{5,6}$ 5, J_{gem} 10, 6-H), 3.44 (1 H, dd, $J_{5,6'}$ 7, 6-H′), 3.51 (1 H, m, OC*H*HMe), 3.81 (1 H, dd, $J_{4,5}$ 2, 4-H), 3.88 (1 H, m, OCH*H*Me), 4.20 (1 H, dt, $J_{CH=,5'} = J_{CH=,5'} = 2$, J_{gem} 13.5, 5′-H), 4.46 (1 H, dt, $J_{CH=,5'} = J_{CH=,5'}$ 2, 5′-H), 4.81 (1 H, ddd, 5-H), 4.83 (1 H, dd, CH=), 4.88 (1 H, dd, 1-H), 4.95 (1 H, dd, CH=), 7.26–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2′,3′,4′,5′-*tetrahydro*-4′-*oxo*-6-O-*trityl*-(*ethyl* α-D-ribo-*hexapyranosido*)[4,3-b]*furan* **41**.—Obtained from compound **35** according to general procedure H (61 mg, 60%) or general procedure I (48 mg, 99%); R_f 0.38 (H:A 4:1); $[\alpha]_D^{20}$ +74 (*c* 0.7, $CHCl_3$) (Found: C 75.65; H, 6.6. $C_{29}H_{30}O_5$ requires C, 75.96; H, 6.59%); ν_{max}/cm^{-1} 1770 (C=O); δ_H 1.20 (3 H, t, OCH_2*Me*), 2.05 (1 H, ddd, $J_{1,2a}$ 4.5, J_{gem} 14, $J_{2a,3e}$ 7.5, 2-H^a), 2.19 (1 H, ddd, $J_{1,2e}$ 2.5, $J_{2e,3}$ 4, 2-H^e), 2.58 (1 H, m, $J_{3,5'}$ 1, $J_{3,4}$ 9, 3-H), 3.34 (1 H, dd, $J_{5,6}$ 6.5, J_{gem} 10, 6-H), 3.39 (1 H, dd, $J_{5,6'}$ 2.5, 6-H′), 3.49 (1 H, m, OC*H*HMe), 3.74–3.85 (2 H, m, 5-H,

OCH*H*Me), 3.89 (1 H, d, J_{gem} 16.5, 5'-H), 3.97 (1 H, dd, 5'-H), 4.31 (1 H, t, $J_{4,5}$ 9, 4-H), 4.88 (1 H, dd, 1-H) and 7.20–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2',3',4',5'-*tetrahydro*-4'-*oxo*-6-O-*trityl*-(tert-*butyl* α-D-ribo-*hexopyranosido*)[2,3-b]*furan* **42**.—Obtained from compound **36** (0.18 mmol) according to general procedure I (87 mg, 95%) as a *crystalline solid*, m.p. 156 °C (from hexane–ethyl acetate); R_f 0.43 (H:A 4:1); $[\alpha]_D^{20}$ −2.4 (*c* 1, $CHCl_3$) (Found: C, 76.25; H, 7.0. $C_{31}H_{34}O_5$ requires C, 76.52; H, 7.04%); ν_{max}/cm^{-1} 1770 (C=O); δ_H 1.20–1.30 (9 H, s, Bu^t), 1.63 (1 H, dt, $J_{3,4a}$ 7.5, $J_{gem} = J_{4a,5}$ = 13, 4-H^a), 2.13 (1 H, ddd, $J_{3,4e}$ 1.5, $J_{4e,5}$ 3, 4-H^e), 2.63 (1 H, m, $J_{2,3}$ 9, $J_{3,5'}$ 1.5, 3-H), 2.97 (1 H, dd, $J_{5,6}$ 4, J_{gem} 9.5, 6-H), 3.12 (1 H, dd, $J_{5,6'}$ 5.5, 6-H'), 3.99 (1 H, dd, J_{gem} 15, 5'-H), 4.1 (1 H, m, 5-H), 4.22 (1 H, d, 5'-H), 4.48 (1 H, dd, $J_{1,2}$ 4.5, 2-H), 5.11 (1 H, d, 1-H) and 7.20–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2',3',4',5'-*tetrahydro*-4'-*oxo*-6-O-*trityl*-(tert-*butyl* α-D-lyxo-*hexopyranosido*)[2,3-b]*furan* **43**.—Obtained from compound **37** (0.17 mmol), according to general procedure I (70 mg, 86%), as a *crystalline solid*, m.p. 131 °C (from hexane–ethyl acetate); R_f 0.68 (H:A 3:1); $[\alpha]_D^{20}$ +56.2 (*c* 1, $CHCl_3$) (Found: C, 76.2; H, 7.1. $C_{31}H_{34}O_5$ requires C, 76.52; H, 7.04%); ν_{max}/cm^{-1} 1770 (C=O); δ_H 1.25 (9 H, s, Bu^t), 1.32 (1 H, dt, J_{gem} 13, $J_{3,4a} = J_{4a,5}$ = 11, 4-H^a), 1.80 (1 H, ddd, $J_{3,4e}$ 7, $J_{4e,5}$ 2, 4-H^e), 2.67 (1 H, ddd, $J_{2,3}$ 4.5, 3-H), 2.95 (1 H, dd, $J_{5,6}$ 5.5, J_{gem} 9, 6-H), 3.25 (1 H, dd, $J_{5,6}$ 5.5, 6-H'), 3.84 (1 H, d, J_{gem} 17, 5'-H), 3.88 (1 H, d, 2-H), 4.16 (1 H, ddt, 5-H), 4.20 (1 H, d, 5'-H), 5.25 (1 H, s, 1-H) and 7.30–7.50 (15 H, m, Ph).

2,3,4-*Trideoxy*-2',3',4',5'-*tetrahydro*-4'-*oxo*-6-O-*trityl*-(*ethyl* α-D-lyxo-*hexopyranosido*)[4,3-b]*furan* **44**.—Obtained from compound **39** (0.1 mmol) according to general procedure I (45 mg, 88%); R_f 0.50 (H:A 3:1); $[\alpha]_D^{20}$ −32.8 (*c* 0.5 $CHCl_3$) (Found: C, 75.6; H, 6.6. $C_{29}H_{30}O_5$ requires C, 75.96; H, 6.59%); ν_{max}/cm^{-1} 1770 (C=O); δ_H 1.23 (3 H, t, OCH_2Me), 1.66 (1 H, dt, $J_{1,2a}$ 6, J_{gem} 14, $J_{2a,3}$ 6, 2-H^a), 2.26 (1 H, dt, $J_{1,2e} = J_{2e,3}$ = 5,2-H^e), 2.67 (1 H, dt, $J_{3,4}$ 7.5, 3-H), 3.32 (1 H, dd, J_{gem} 10, $J_{5,6}$ 4,6-H), 3.43–3.53 (2 H, m, OC*H*HMe, 6-H'), 3.89 (1 H, d, J_{gem} 16.5, 5'-H), 3.91 (1 H, m, OCH*H*Me), 3.98–4.02 (2 H, m, 5- and 5'-H), 4.38 (1 H, dd, $J_{4,5}$ 2.5, 4-H), 4.87 (1 H, dd, 1-H) and 7.20–7.50 (15 H, m, Ph).

4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5'-*tetrahydro*-4'-*oxo*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **45**.—Obtained from compound **6** (1.1 mmol), according to general procedure I (280 mg, 90%), as a *crystalline compound* m.p. 74 °C (from hexane–ethyl acetate); R_f 0.36 (H:A 1:1); $[\alpha]_D^{20}$ +3.5 (*c* 1.1, $CHCl_3$) (Found: C, 52.6; H, 5.8. $C_{12}H_{16}O_7$ requires C, 52.94; H, 5.92%); ν_{max}/cm^{-1} 1765 C=O, ketone) and 1745 (C=O, ester); δ_H 2.0 (3 H, s, OAc), 2.11 (3 H, s, OAc), 2.12 (1 H, ddd, $J_{2,3a}$ 7.5, J_{gem} 15, $J_{3a,4}$ 4.5, 3-H^a), 2.27 (1 H, dt, $J_{2,3e} = J_{3e,4}$ = 4.5, 3-H^e), 2.58 (1 H, ddd, $J_{1,2}$ 5.5, 2-H), 4.09 (1 H, ddd, $J_{4,5}$ 4.5, $J_{5,6}$ 4, $J_{5,6'}$ 6, 5-H), 4.11 (1 H, d, J_{gem} 17, 5'-H), 4.19 (1 H, dd, J_{gem} 12, 6-H), 4.32 (1 H, dd, 6-H'), 4.33 (1 H, d, 5'-H), 4.9 (1 H, q, 4-H) and 5.81 (1 H, d, 1-H).

(4'R)-4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5'-*tetrahydro*-4'-*methyl*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **46**.—The olefin **10** (270 mg, 1 mmol) was dissolved in ethyl acetate (10 cm^3) the solution was stirred with 10% palladium on charcoal (80 mg) under hydrogen for 1 h (TLC, H:A 2:1). The reaction mixture was filtered through a cake of Celite and concentrated under reduced pressure. Column chromatography on silica gel gave crystalline *compound* **46** (214 mg, 79%), m.p. 79–80 °C (from hexane–ethyl acetate); R_f 0.3 (H:A 2:1); $[\alpha]_D^{20}$ +107.5 (*c* 1, $CHCl_3$) (Found: C, 57.6; H, 7.3. $C_{13}H_{20}O_6$ requires C, 57.34; H, 7.29%); ν_{max}/cm^{-1} 1750 (C=O); δ_H 0.95 (3 H, d, $J_{4',Me}$ 7.5, 4'-Me), 1.38 (1 H, dt, $J_{2,3a} = J_{3a,4}$ = 11.5, J_{gem} 12.5, 3-H^a), 2.03 (1 H, ddd, $J_{2,3e}$ 6.5, $J_{3e,4}$ 4.5, 3-H^e), 2.05–2.14 (6 H, m, 2 × OAc), 2.21 (1 H, m, $J_{1,2}$ 4, $J_{2,4'}$ 4.5, 2-H), 2.57 (1 H, m, $J_{4',5'}$ 10.5, $J_{4',5'}$ 8,4'-H), 3.65 (1 H, dd, J_{gem} 8, 5'-H), 3.97 (1 H, ddd, $J_{4,5}$ 10, $J_{5,6}$ 2, $J_{5,6'}$ 5, 5-H), 3.98 (1 H, t, 5'-H), 4.13 (1 H, dd, J_{gem} 12, 6-H), 4.33 (1 H, dd, 6-H'), 4.79 (1 H, ddd, 4-H) and 5.37 (1 H, d, 1-H).

(4'R)-4,6-*Di*-O-*acetyl*-1,2,3-*trideoxy*-2',3',4',5'-*tetrahydro*-4'-*hydroxy*-α-D-ribo-*hexopyranoso*[1,2-b]*furan* **47**.—To a solution of compound **6** (139 mg, 0.49 mmol) stirred at room temperature in dry ethanol (2.5 cm^3) was added sodium borohydride (20 mg, 0.53 mmol). Completion was indicated by TLC (H:A 1:3) after 5 min. 3 mol dm^{-3} HCl was added to neutrality and the solvent was removed. The product was extracted with methylene dichloride and the organic layers were washed with water, dried ($MgSO_4$) and concentrated to dryness. Column chromatography on silica gel (H:A 1:3) gave *title compound* **47** quantitatively (135 mg), R_f 0.36 (H:A 1:3); $[\alpha]_D^{20}$ +61.8 (*c* 0.5, $CHCl_3$) (Found: C, 52.8; H, 6.5. $C_{12}H_{18}O_7$ requires C, 52.55; H, 6.61%); ν_{max}/cm^{-1} 3470 (OH) and 1745 (C=O); δ_H 1.71 (1 H, dt, $J_{2,3a} = J_{3a,4}$ = 10, J_{gem} 12.5, 3-H^a), 2.04–2.11 (7 H, m, 2 × OAc, OH), 2.17 (1 H, ddd, $J_{2,3e}$ 7, $J_{3e,4}$ 4.5, 3-H^e) 2.43 (1 H, m, $J_{1,2}$ 4, $J_{4,2}$ 7, 2-H), 3.86 (1 H, dd, $J_{4',5'}$ 7, J_{gem} 9, 5'-H), 4.04 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 3.5, $J_{5,6'}$ 6, 5-H), 4.07 (1 H, dd, $J_{4',5'}$ 7, 5'-H), 4.15 (1 H, dd, J_{gem} 12, 6-H), 4.31 (1 H, dd, 6-H'), 4.61 (1 H, q, 4'-H), 4.84 (1 H, ddd, 4-H) and 5.35 (1 H, d, 1-H).

References

1 Free Radicals in Carbohydrate Chemistry. Part 4: for Part 3, see the preceding paper.

2 B. Giese, *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon Press, New York, 1986; M. Ramaiah, *Tetrahedron*, 1987, **43**, 3541; D. P. Curan, *Synthesis*, 1988, 417, 489.

3 W. Hartwig, *Tetrahedron*, 1983, **39**, 2609 and references cited therein; B. Giese and K. Gröninger, *Tetrahedron Lett.*, 1984, **25**, 2743; for a review on radical anomeric chemistry see: G. Descotes, *J. Carbohydr. Chem.*, 1988, **7**, 1.

4 (*a*) Y. Chapleur and N. Moufid, *J. Chem. Soc., Chem. Commun.*, 1989, 39; (*b*) N. Moufid and Y. Chapleur, *Tetrahedron Lett.*, 1991, **32**, 1799; (*c*) N. Moufid, Y. Chapleur and P. Mayon, preceding paper.

5 (*a*) C. E. McDonald and R. W. Dugger, *Tetrahedron Lett.*, 1988, **29**, 2413; (*b*) A. De Mesmaeker, P. Hoffmann and B. Ernst, *Tetrahedron Lett.*, 1988, **29**, 6585; (*c*) R. J. Ferrier, P. M. Petersen and M. A. Taylor, *J. Chem. Soc., Chem. Commun.*, 1989, 1247; (*d*) J. C. Lopez and B. Fraser-Reid, *J. Am. Chem. Soc.*, 1989, **111**, 3450; (*e*) R. J. Ferrier and P. M. Petersen, *Tetrahedron*, 1990, **46**, 1; (*f*) R. Nouguier, C. Lesueur, E. De Riggi, M. P. Bertrand and A. Virgili, *Tetrahedron Lett.*, 1990, **31**, 3541; (*g*) A. V. Rama Rao, J. S. Yadav, C. Srinivas Rao and S. Chandrasekhar, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1211.

6 For carbohydrates as radical donors see: C. Audin, J. M. Lancelin and J. M. Beau, *Tetrahedron Lett.*, 1988, **29**, 3691; A. De Mesmaeker, P. Hoffmann and B. Ernst, *Tetrahedron Lett.*, 1989, **30**, 57. For anomeric radicals see: A. De Mesmaeker, P. Hoffmann, B. Ernst, P. Hug and T. Winkler, *Tetrahedron Lett.*, 1989, **30**, 6307, 6310; A. De Mesmaeker, A. Waldner, P. Hoffmann, T. Mindt, P. Hug and T. Winkler, *Synth. Lett.*, 1990, 687; G. V. M. Sharma and S. R. Vepachedu, *Tetrahedron*, 1991, **47**, 519; J. C. Wu, Z. Xi, C. Gioeli and J. Chattopadhyaya, *Tetrahedron*, 1991, **47**, 2237; S. Velazquez, S. Huss and M.-J. Camarasa, *J. Chem. Soc., Chem. Commun.*, 1991, 1263. See also Y. Araki, T. Endo, Y. Arai and M. Tanji, *Tetrahedron Lett.*, **30**, 2829.

7 R. J. Ferrier and N. Prasad, *J. Chem. Soc. C*, 1969, 570.

8 D. W. Moore and J. A. Happe, *J. Phys. Chem.*, 1961, **65**, 224.

9 M. Peyrere, J. P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworth, London, 1987.

10 J. L. Musachio and J. R. Lever, *Tetrahedron Lett.*, 1989, **30**, 3613.

11 E. Negishi, *Organometallics in Organic Synthesis*, Wiley Interscience, New York, 1980, vol. 1, pp. 394–454; S. L. Schreiber and J. A. Porco, Jr., *J. Org. Chem.*, 1989, **54**, 4721; S. Hanessian, M. Martin and R. C. Desai, *J. Chem. Soc., Chem. Commun.*, 1986, 926; P. Lesimple, J. M. Beau, G. Jaurand and P. Sinaÿ, *Tetrahedron Lett.*, 1986, **27**, 6201.

12 J. Ardisson, J. P. Férézou, M. Julia and A. Pancrazi, *Tetrahedron Lett.*, 1987, **28**, 2001.

13 For leading references see: coupling with vinyl iodides: A. S. Rende and R. J. De Vita, *Tetrahedron Lett.*, 1990, **31**, 307; Coupling with triflates: N. Tamayo, A. M. Echavarren, M. C. Paredes, F. Farina and P. Noheda, *Tetrahedron Lett.*, 1990, **31**, 5189. Coupling with acyl halides: M. T. Reetz and P. Hois, *J. Chem. Soc., Chem. Commun.*, 1989, 1081; Palladium catalysis: L. Del Valle, J. K. Stille and L. S. Hegedus, *J. Org. Chem.*, 1990, **55**, 3019; J. P. Férézou, M. Julia, Y. Li, L. W. Liu and A. Pancrazi, *Synth. Lett.*, 1991, 53 and references cited therein. Application to carbohydrates: R. W. Friesen and C. F. Sturino, *J. Org. Chem.*, 1990, **55**, 2572; E. Dubois and J. M. Beau, *J. Chem. Soc., Chem. Commun.*, 1990, 1191.

14 A. Nishida, M. Shibasaki and S. Ikegami, *Tetrahedron Lett.*, 1981, **22**, 4819.

15 For aldolisation of sugar enolates see: Y. Chapleur, F. Longchambon and H. Gillier, *J. Chem. Soc., Chem. Commun.*, 1988, 564; S. Handa, R. Tsang, A. T. McPhail and B. Fraser-Reid, *J. Org. Chem.*, 1987, **52**, 3489.

16 R. U. Lemieux, S. Koto and D. Voisin, A.C.S. Symposium Series, ed. W. A. Szarek and D. Horton, 1979, vol. 87, p. 17; I. Tvaroska and T. Bleha, *Adv. Carbohydr. Chem. Biochem.*, 1989, **47**, 45.

17 For the use of acyl radicals see: D. Crich and S. M. Fortt, *Tetrahedron Lett.*, 1987, **28**, 2895; D. L. Boger and R. J. Mathvink, *J. Am. Chem. Soc.*, 1990, **112**, 4003 and references cited.

18 For studies on the 'off-template' problem see: B. F. Molino, L. Magdzinski and B. Fraser-Reid, *Tetrahedron Lett.*, 1983, **24**, 5819; B. Fraser-Reid, B. F. Molino, L. Magdzinski and D. R. Mootoo, *J. Org. Chem.*, 1987, **52**, 4505; Y. Chapleur and M.-N. Euvrard, *J. Chem. Soc., Chem. Commun.*, 1987, 884; A. A. Ghini, C. Burnouf, J. C. Lopez, A. Olesker and G. Lukacs, *Tetrahedron Lett.*, 1990, **30**, 2301; C. Burnouf, J. C. Lopez, F. Garcia Calvo-flores, M. de los Angeles Laborde, A. Olesker and G. Lukacs, *J. Chem. Soc., Chem. Commun.*, 1990, 823; A. Rashid, G. M. Taylor, W. W. Wood and D. Alker, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1289. See also ref. 5.

19 R. R. Schmidt and R. Preuss, *Tetrahedron Lett.*, 1989, **30**, 3409; A. Boschetti, F. Nicotra, L. Panza, G. Russo and L. Zucchelli, *J. Chem. Soc., Chem. Commun.*, 1989, 1085; S. A. Babirad, Y. Wang and Y. Kishi, *J. Org. Chem.*, 1987, **52**, 1370; M. A. Tius, J. Gomez-Galeno, X. Gu and J. H. Zaidi, *J. Am. Chem. Soc.*, 1991, **113**, 5775; R. Friesen and R. W. Loo, *J. Org. Chem.*, 1991, **56**, 4821.

Paper 2/00061J
Received 6*th January* 1992
Accepted 21*st January* 1992