Some Studies on Proximal Addition–Elimination Procedures in Intermolecular Carbon–Carbon Bond-forming Free Radical Reactions. Convenient Synthesis of Ethyl (*E*)-(Ethyl 2,3,6,7,8-Pentadeoxy-α-D-*erythro*-nona-2,7-dienopyranosid)uronate

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Et_3B-Induced hydrostannation of ethyl propiolate with tributyltin hydride afforded a mixture of ethyl (*Z*)- and (*E*)-3-(tributylstannyl)propenoate which, after purification, could be used as such in radical carbon–carbon bond-forming reactions with iodides as the sources of the carbon radicals. The radical-coupling reactions took place without significant loss of yield or stereoselectivity when compared with the same reactions carried out with the pure (*Z*)-stannylacrylate. Use of ethyl (*Z*)-3-(phenylsulfanyl)propenoate in the presence of carbon-centred radicals, generated with Bu_3SnH from alkyl iodides, resulted in the formation of reduced and coupled products where the intermediate β-phenylsulfanyl radicals had experienced hydrogen transfer from Bu_3SnH rather than 1,2-elimination of phenylsulfanyl radicals.

Two areas of interest in our research group for several years have been: (i) the use of 2,3-unsaturated sugars,[1] of which ethyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, **1a**, is one of the most readily available,[2] and (ii) the synthesis of carbocycles from carbohydrates.[3] As part of some synthetic studies underway in our laboratory on radical processes for the latter objective, we had need of the *E* and *Z* isomers of the ethyl octa-2,6-dienopyranosiduronate, **3**, and of the ethyl (*E*)-nona-2,7-dienopyranosiduronate **4a**. We have recently reported on stereocontrolled access to the *E* and *Z* isomers of compound **3** from compound **1a**,[4] and here we disclose our efforts aimed at the transformation **1** ⟶ **4**.

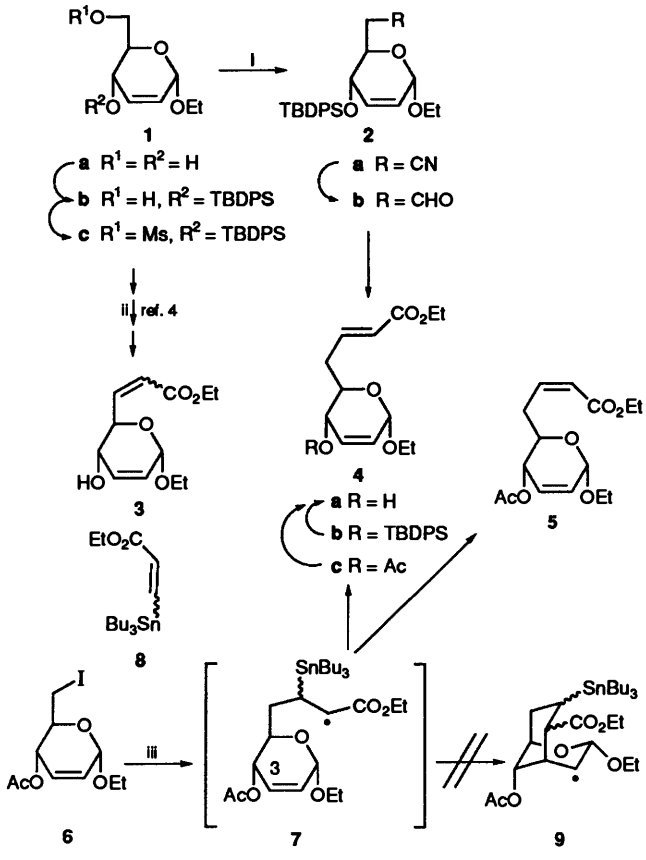
Results and Discussion

Our initial route to ester **4a** (Scheme 1) involved a one-carbon homologation effected by cyanide-induced displacement of an intermediate mesyl ester **1c**, to obtain the nitrile **2a**, followed by a Wittig reaction on the derived aldehyde **2b**, and desilylation of the resulting material, compound **4b**, Although this route provided gram amounts of compound **4a** we considered it to be lengthy, and furthermore some of the steps were not high yielding (see Experimental section).

In considering better alternatives for the preparation of our title compound **4a**, we then turned our attention to the radical addition–elimination reactions of tributylstannylpropenoates, **8**, initially studied by Russell's group[5] and subsequently developed as a synthetically useful method by Baldwin *et al.*[6] (Scheme 2a). Application of Baldwin's reaction conditions [azoisobutyronitrile (AIBN), (*Z*)-**8**, toluene, 85 °C, 2 days][6] to iodide **6**[7] gave the desired compound **4c** along with some *Z* isomer **5** (88% yield; 3:1 ratio) as the only reaction products. Chemoselective deacetylation of compound **4c** (MeOH, NEt_3, water; 8:2:1) cleanly afforded target compound **4a**.

The cyclized product was not observed, thereby showing that intermediate **7** underwent a 'proximal' radical-elimination process[6] faster than the potential intramolecular 6-*exo*-*trig* ring closure leading to the bicyclic radical **9**. Therefore Baldwin's addition–elimination-type radical carbon–carbon bond-forming reaction appeared to be the method of choice for the preparation of compound **4a**.

However, the procedure was compromised by problems having to do with the preparation of the required (*Z*)-(tributylstannyl)propenoate (*Z*)-**8**. Examination of the literature indicated three approaches (Scheme 2b–d): (i) hydrostannation of ethyl propiolate,[8–10] (ii) conjugate addition of a tributylstannylcuprate to ethyl propiolate,†[11] and (iii) addition



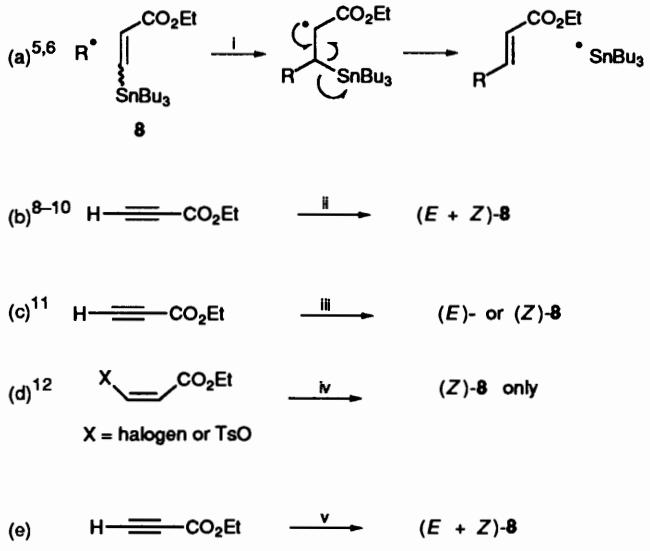
Scheme 1 TBDPS = *tert*-butyldiphenylsilyl; Ms = methylsulfonyl. *Reagents:* i, **1c**, NaCN: ii, **1a**; iii, **8**.

† Piers *et al.*[11] have studied the addition of the corresponding trimetyltin reagent to α,β-acetylenic esters, and have developed procedures for obtaining the *E* and *Z* derivatives with complete stereoselectivity.

Table 1 Reaction of ethyl propiolate with Bu_3SnH and Et_3B in toluene

Entry	Temperature (T/°C)	(Z + E)-**8** Observed ratio[a]	Yield (%)
1	20	1.25:1	76
2	0	2.7:1	78
3	−35	2.8:1	75
4	−78	5.5:1	70

[a] Based on ^1H NMR (300 MHz) of the crude reaction mixture.



Scheme 2 *Reagents:* i, **8**; ii, Bu_3SnH; iii, ($Bu_3SnCuSPh$) Li; iv, Bu_3SnLi, CuI; v, Bu_3SnH, Et_3B

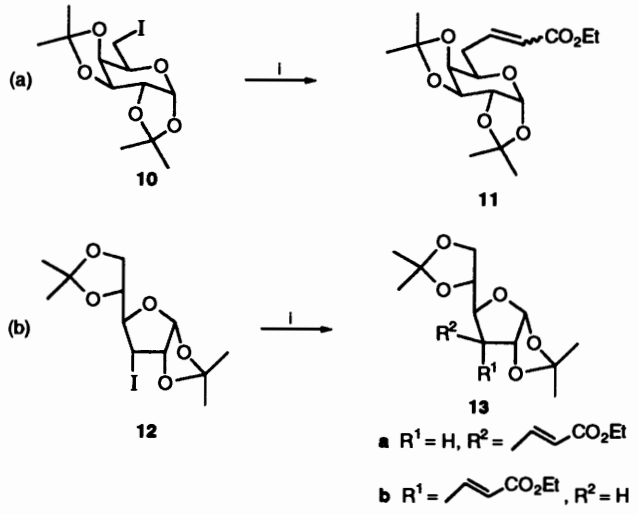
of tributylstannylcopper[12] to β-substituted acrylates. Method (i) is non-stereospecific and yielded E/Z mixtures of the stannylacrylates.[8–10] On the other hand, although the addition of tributylstannyllithium in the presence of copper(I) iodide to β-substituted acrylates[12] is highly stereospecific, the preparation of the required (Z)-halogeno[13] or (Z)-tosyloxy[14] acrylates involves multistep procedures.

We now report (Scheme 2e) that the stannylacrylates (E)-**8** and (Z)-**8**, can be easily obtained by column chromatography of the material prepared by Et_3B-induced hydrostannation, as described by Oshima and co-workers,[15] of ethyl propiolate with Bu_3SnH in toluene. In addition, we report that the geometric mixture of acrylates can be used directly in the radical-coupling reaction without significant loss of yield or stereoselectivity as compared with the reaction using pure acrylate (Z)-**8**.[6]

Radical addition of Bu_3SnH to ethyl propiolate in the presence of Et_3B as initiator[15] gave good yields of β-stannylacrylates, **8**, as a mixture of E/Z isomers that could be cleanly separated by column chromatography.*,[16] In contrast with previous reports by Oshima's group on the addition of Ph_3SnH to unactivated terminal acetylenic compounds,[15] we have observed that the E/Z ratios of compound **8** were affected by the reaction temperature †,[17] (Table 1).

In searching for an experimental simplification of Baldwin's procedure,[6] we first treated iodide **6** with compound (E)-**8**, under the above mentioned conditions. Compound **4c** was now obtained as the only isomer, although a longer time was required for the reaction to go to completion (Table 2, entry ii). We next treated iodide **6** with an E/Z mixture of stannylacrylates (Table 2, entry iii) and were able to obtain good yields of the coupled products **4c** and **5** (3:1 ratio).

Analogously, primary iodide **10**, and secondary allofuranosyl iodide **12**, were treated with the mixture of stannylacrylates to afford coupled products (E + Z)-**11** and **13**(**a** + **b**) respectively (Scheme 3 and Table 2, entries vi–xi).



Scheme 3 *Reagents:* i, (Z)- and/or (E)-**8**, AIBN

It is clear from Table 2 that, in the case of acrylate **8**, use of the pure Z isomer does not cause spectacular improvements in yield or stereoselectivity as compared with the E/Z mixture (*e.g.*, entries i *vs* v; vi *vs* viii; and ix *vs* xi). On the other hand compound (Z)-**8** reacted faster than did isomer (E)-**8** (compare entries i and ii; vi and vii; ix and x, but the latter displayed a higher stereoselectivity in the formation of E olefins[5] (entries ii, vii) (see also below).

In the study reported in Scheme 3b, the origin of the facial selectivity displayed by compound **8** (E and Z) in reacting with the biased substrate **12** (entries ix–xi) is unclear at this time.

A detailed study on the stereochemical aspects of this process has been carried out by the Russell group,[5a] who have shown that the relative rates of 1,2-radical elimination and bond rotation are prime factors in influencing the stereochemical composition of the product. Hence their results were dependent, among other things on the nature of the leaving group (LVG) (Scheme 4a). However when $Bu_3Sn^{\bullet}$ is the leaving group, there are several examples which show that use of E-alkenes leads largely to retention of configuration whereas with Z-alkenes low stereospecificities are observed.[18]

In our case, two factors could be added to relative lifetime of the intermediate radical in order to account for the stereochemical mixtures shown in Table 2. They are: isomerizations of (a) the initially used stannylacrylates and/or (b) the initially formed enoate.

That the latter indeed was a contributihg factor was demonstrated by a control experiment (Scheme 4b) in which compound (Z)-**3** was treated with acrylate (Z)-**8** in the presence of AIBN under standard conditions. After 16 h of reaction, partial isomerization had occurred to give a 1.2:1 mixture of compounds (Z)- and (E)-**3**.

For the isomerization of the stannylacrylates, the addition–elimination pathway suggested in Scheme 4c could be discounted because the conjugate addition to give radical **14** would be much slower than transfer of an iodine atom from the substrate. We addressed this issue by the series of experiments

* Purification of these products by vacuum distillation resulted in partial isomerization. See ref. 16.

† In the case of uncatalysed hydrostannation, the E/Z ratios depend on the reaction temperature as described in ref. 17.

Table 2 Reaction of alkyl iodides with stannyl- and phenylsulfanyl-propenoates

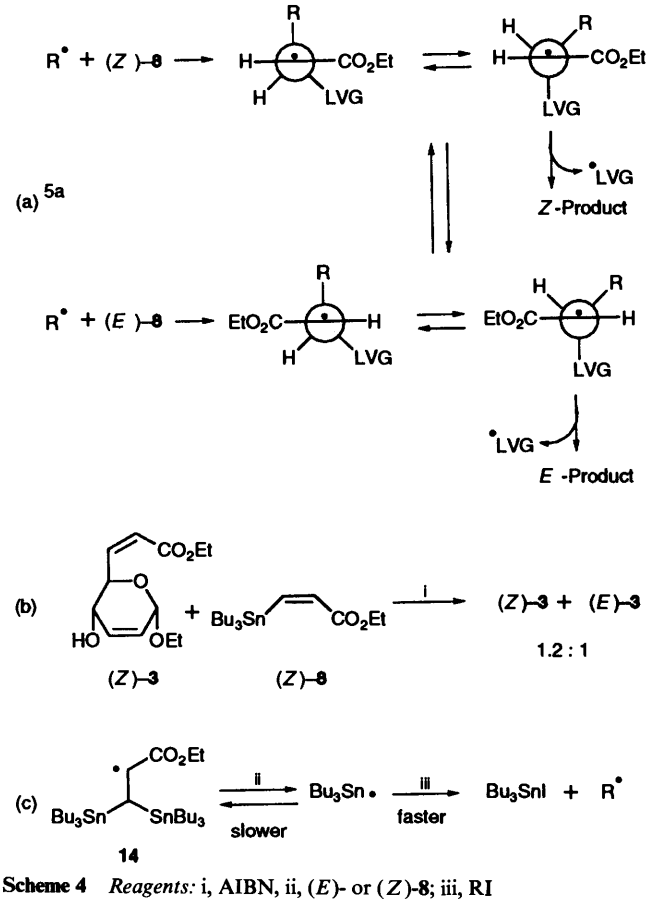
Entry	Substrate	Propenoates (ratio)	Time (days)	Products (% Yield)
i	**6**	(*Z*)-**8**	2	**4c** (66) + **5** (22)
ii	**6**	(*E*)-**8**	7	**4c** (72)[a]
iii	**6**	(*Z* + *E*)-**8** (1.4:1)	3	**4c** (51) + **5** (17)
iv	**6**	(*Z* + *E*)-**8** (1.1:1)	4	**4c** (59) + **5** (20)
v	**6**	(*Z* + *E*)-**8** (6:1)	3	**4c** (60) + **5** (26)
vi	**10**	(*Z*)-**8**	1.5	(*E*)-**11** (76) + (*Z*)-**11** (18)
vii	**10**	(*E*)-**8**	3	(*E*)-**11** (79)[a]
viii	**10**	(*Z* + *E*)-**8** (1.3:1)	2	(*E*)-**11** (63) + (*Z*)-**11** (7)
ix	**12**	(*Z*)-**8**	1.7	**13a** (72) + **13b** (11)
x	**12**	(*E*)-**8**	4	**13a** (19) + **13b** (10)[b]
xi	**12**	(*Z* + *E*)-**8** (1.3:1)	3	**13a** (49) + **13b** (14)
xii	**6**	**15**		**16** (35)
xiii	**10**	**15**		**17** (37) + **18** (51)

[a] No *Z*-isomer was detected by ^{1}H NMR (300 MHz) spectroscopy. [b] Only 50% conversion.

Table 3 Reaction of iodide **10** with (*Z*)- and (*E*)-stannylpropenoates **8**

Entry	Stannane reagent	Reaction time (*t*/h)	Conversion[a] (%)	Products[b] (*Z* + *E*)-**11** (ratio)	Unchanged stannane[b]
i	(*Z*)-**8**	16	70	(2.2:1)	(*Z*)-**8**
ii	(*Z*)-**8**	24	80	(2.7:1)	(*Z*)-**8**
iii	(*Z*)-**8**	30	90	(3:1)	(*Z*)-**8**
iv	(*Z*)-**8**	40	100	(3.5:1)	(*Z* + *E*)-**8**
v	(*E*)-**8**	16	20	1:0	(*E*)-**8**
vi	(*E*)-**8**	24	35	1:0	(*E*)-**8**
vii	(*E*)-**8**	40	50	1:0	(*E*)-**8**
viii	(*E*)-**8**	72	100	1:0	(*Z* + *E*)-**8**

[a] Based on unchanged starting material **10**. [b] Based on ^{1}H NMR (300 MHz) analysis of an aliquot taken from the reaction mixture.

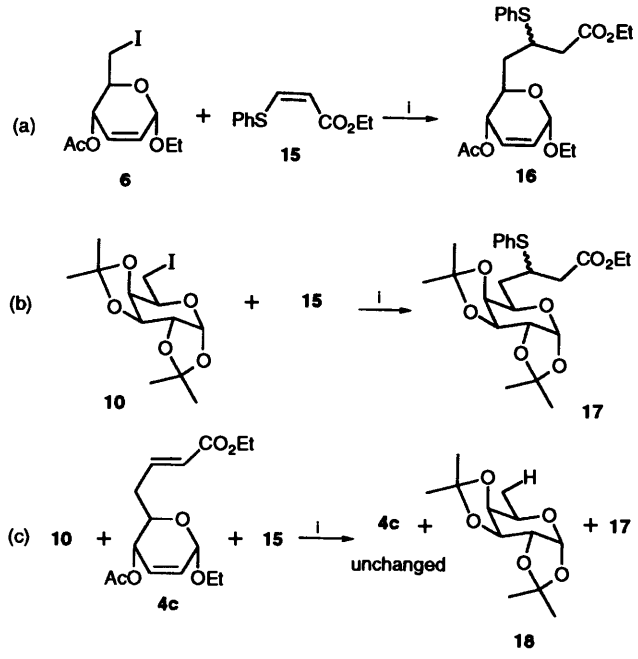


Scheme 4 *Reagents:* i, AIBN, ii, (*E*)- or (*Z*)-**8**; iii, RI

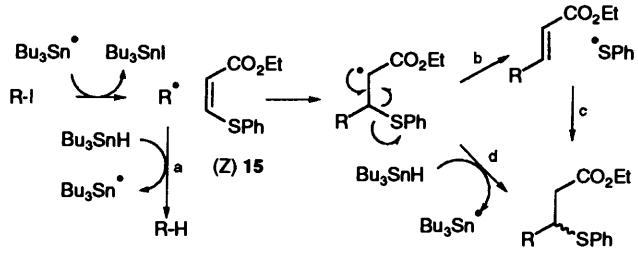
reported in Table 3. Thus it is seen that isomerization of the starting stannylacrylates did not occur as long as some alkyl iodide was present (entries i–iii, v–vii). However, once the alkyl iodide was consumed, then isomerization of the acrylates took place (entries iv and viii). These observations are in contrast with the results of Russell and Ngoviwatchai[5b] on vinylic free radical substitution where the carbon-centred radicals were generated by photolysis of alkylmercury(II) chlorides. These authors concluded that the starting stannylacrylates, as well as the initially formed products, underwent isomerizations under their reaction conditions.

Finally, since it is known that β-elimination of a phenylsulfanyl radical is a very rapid process,[19,20] we attempted an addition–elimination-type radical carbon–carbon bond-forming reaction by using ethyl (*Z*)-(phenylsulfanyl)propenoate **15**,[21] (Scheme 5a, b). Thus we treated iodides **6** and **10** with Bu_3SnH (generated from catalytic Bu_3SnCl and sodium cyanoboranuide[22]) and AIBN in the presence of an excess of acylate **15** (10 mol equiv.). We were able to isolate coupled phenyl sulfides **16** and **17** in 35 and 37% yield, respectively, along with the reduced products (Table 2, entries xii, xiii).

Reduction of R• by Bu_3SnH was therefore the major pathway (a, Scheme 6). Sulfides **16** and **17** were formed by addition of the carbon-centred radicals, R•, to propenoate **15**, followed by hydrogen transfer from Bu_3SnH to the β-phenylsulfanyl radical (d, Scheme 6). The alternative route, involving a 1,2-radical-elimination process followed by addition of the phenylsulfanyl radical to an intermediate propenoate (b and c in Scheme 6), was ruled out when, in a cross-experiment (Scheme 5c), compounds **10** and **4c** were treated with Bu_3SnH and AIBN in the presence of propenoate **15** (10 mol equiv.). Olefin **4c** was recovered unchanged together with the reduction product **18**[23] and coupled product **17**.



Scheme 5 *Reagents:* i, Bu_3SnCl, $NaCNBH_3$, AIBN



Scheme 6

The reduction of the intermediate β-phenylsulfanyl radical contrasts with the previous results by Ueno *et al.*,[20] and must be associated with a stabilizing effect of the ethoxycarbonyl group adjacent to the radical.

Experimental

^1H NMR spectra were recorded in deuteriochloroform at 300 MHz with a Varian XL-300 spectrometer. Chemical shifts are reported in δ-values relative to tetramethylsilane, and *J*-values are given in Hz. ^{13}C NMR spectra were recorded in deuteriochloroform at 75 MHz with a GE QE-300 spectrometer. Chemical shifts are reported in δ-values relative to internal solvent standard (δ_C 77.0). Mass spectra were recorded on a Hewlett-Packard 59-88A GCMS by chemical ionization (with $CH_4 + NH_3$ as the reagent gas). Optical rotations were measured in chloroform solutions using a Perkin-Elmer 241 instrument. $[\alpha]_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}. TLC was conducted on precoated Kieselgel 60 F254 (Art. 5554; Merck). Detection was first by UV (254 nm), then by charring with a solution of ammonium molybdate(VI) tetrahydrate (12.5 g), and cerium(IV) sulfate tetrahydrate (5.0 g) in 10% aq. sulfuric acid (500 cm^3). Stannylpropenates **8** were visualized with a solution resulting from mixing of 1% aq. potassium permanganate (100 cm^3) with an equal volume of 5% aq. sodium carbonate. Column chromatography was carried out on Kieselgel (230–400 mesh) with the eluent specified. All reactions were conducted under argon. Organic extracts were dried over $MgSO_4$ and evaporated at aspirator pressure using a rotary evaporator, unless otherwise stated. Solvents were dried and purified using standard methods.[24] Alkyl iodides **10** and **12** were prepared according to the procedure of Garegg and Samuelsson.[25] Petroleum spirit refers to the fraction boiling in the range 35–60 °C.

Ethyl 4-O-(tert-*Butyldiphenylsilyl*)-2,3-*dideoxy*-α-D-erythro-*hex*-2-*enopyranoside* **1b**.—Prepared from compound **1a**[2] according to ref. 4; $[\alpha]_D^{21}$ +93.5 (*c* 1.0) (Found: C, 70.1; H, 7.9. $C_{24}H_{32}O_4Si$ requires C, 69.9; H, 7.8%); δ_H(300 MHz) 1.06 (9 H, s, Bu^t), 1.25 (3 H, t, *J* 7.1, Me), 1.66 (1 H, d, *J* 6.8, OH), 3.52 (1 H, m, OCH_2Me), 3.65 (1 H, m, 6-H), 3.83 (2 H, m, 6-H′ and OCH_2Me), 3.92 (1 H, m, 5-H), 4.27 (1 H, dd, $J_{4,5}$ 9.0, $J_{3,4}$ 2.6, 4-H), 4.90 (1 H, s, 1-H), 5.58 (1 H, dt, $J_{2,3}$ 10.3, *J* 2.6, 3-H), 5.78 (1 H, d, $J_{2,3}$ 10.3, 2-H), 7.42 (6 H, m, ArH) and 7.69 (4 H, m, ArH); δ_C(75 MHz) 15.4 (Me), 19.4 (CSi), 26.9 (CMe_3), 62.3 (C-6), 64.1 (OCH_2), 65.3 (C-4), 71.6 (C-5), 94.2 (C-1), 125.5 (C-3), 127.7, 127.8, 129.8, 130.0, 132.9 and 133.7 (C-arom), 133.8 (C-2) and 135.9 and 136.0 (C-arom) [Found $(M - 1)^+$, 411.1975. $C_{24}H_{32}O_4Si$ requires (M − 1), 411.2070].

Ethyl 4-O-(tert-*Butyldiphenylsilyl*)-2,3,6-*trideoxy*-α-D-erythro-*hept*-2-*enopyranurononitrile* **2**.—Ethyl 4-*O*-(*tert*-butyldiphenylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside **1b**[4] (16.0 g, 38.8 mmol) was dissolved in dry methylene dichloride (400 cm^3) at 0 °C and treated with triethylamine (32.71 cm^3, 232.8 mmol, 6 mol equiv.) and mesyl chloride (6.0 cm^3, 77.6 mmol, 2 mol equiv.) for 1 h, after which time the reaction was complete by TLC. The reaction mixture was poured onto saturated aqueous sodium hydrogen carbonate (400 cm^3) and the organic layer was separated. Two further extractions with CH_2Cl_2, washing with water (400 cm^3), drying and removal of the solvents by azeotroping with toluene afforded crude mesyl ester **1c**, which was used without further purification in the next step. The sulfonate was dissolved in anhydrous dimethyl sulfoxide (125 cm^3). Sodium cyanide (7.6 g, 155.2 mmol, 4 mol equiv.) was added to the solution and the mixture was stirred at 50 °C overnight. The reaction mixture was poured into water containing ammonium chloride (250 cm^3) and extracted with CH_2Cl_2 (3 × 250 cm^3). The organic extracts were washed well with water, dried, and evaporated to afford a residue, which was purified by flash chromatography [petroleum spirit–ethyl acetate (9 : 1)], to afford pure nitrile **2a** (12.2 g, 74.6% two steps), $[\alpha]_D^{21}$ +71.9 (*c* 0.54) (Found: C, 71.3; H, 7.3; N, 3.2. $C_{25}H_{31}NO_3Si$ requires C, 71.2; H, 7.4; N, 3.3%); δ_H(300 MHz) 1.07 (9 H, s, Bu^t), 1.27 (3 H, t, *J* 7.1, Me), 2.36 (1 H, dt, $J_{6,6'}$ 16.8, *J* 4.1, 6-H), 2.74 (1 H, dd, $J_{6,6'}$ 16.8, $J_{5,6'}$ 1.9, 6-H′), 3.55 (1 H, m, OCH_2Me), 3.92 (1 H, m, OCH_2Me), 4.08 (2 H, m, 4- and 5-H), 4.91 (1 H, d, *J* 2.1, 1-H), 5.61 (1 H, d, $J_{2,3}$ 10.3, 3-H), 5.79 (1 H, d, $J_{2,3}$ 10.3, 2-H), 7.42 (6 H, m, ArH) and 7.69 (4 H, m, ArH); δ_C(75 MHz) 15.3 (Me), 19.3 (CSi), 21.2 (C-6), 26.9 (CMe_3), 64.3 (OCH_2), 67.8 and 68.6 (C-4 and -5), 94.3 (C-1), 117.3 (CN) and 127.9, 128.1, 128.2, 130.1, 130.3, 132.4, 132.7 and 133.2 (C-arom, -2 and -3); *m/z* 450 $(M + NH_4)^+$.

Ethyl(E)-[*Ethyl*4-O-(tert-*Butyldiphenylsilyl*)-2,3,6,7,8-*pentadeoxy*-α-D-erythro-*nona*-2,7-*dienopyranosid*]*uronate* **4b**.—To a cooled (−40 °C) solution of nitrile **2a** (12.2 g, 28.95 mmol) in CH_2Cl_2 (350 cm^3) was slowly added diisobutylaluminium hydride (DIBAL) (1 mol dm^{-3} in hexane; 86.85 cm^3, 86.85 mmol, 3 mol equiv.). The reaction mixture was allowed to warm to −20 °C and was stirred for 6 h. Recooling of the solution to −40 °C was followed by slow addition of a 1 : 1 solution of acetic acid–water (15 cm^3). The reaction mixture was stirred at this temperature for 30 min and was then poured into an Erlenmeyer flask containing conc. aq. $NaHCO_3$ (1 dm^3) and CH_2Cl_2 (1 dm^3). The layers were separated and the aqueous fraction was further extracted with CH_2Cl_2 (800 cm^3). The

combined organic extracts were washed successively with conc. aq. $NaHCO_3$ (800 cm^3), water (2 × 800 cm^3) and brine (800 cm^3) and dried. Evaporation of the solvents furnished crude aldehyde **2b** that, without further purification, was subjected to the Wittig reaction.

To a cooled (0 °C) solution of aldehyde **2b** in CH_2Cl_2 (250 cm^3) was added (ethoxycarbonylmethylene)triphenylphosphorane (50.4 g, 144.75 mmol, 5 mol equiv.). After being stirred at room temperature for 36 h the mixture was evaporated and the residue was purified by flash chromatography with petroleum spirit–EtOAc (95:5) to afford compound **4b** (9.75 g, 69.8%), $[\alpha]_D^{21}$ +35.4 (*c* 0.72) (Found: C, 70.7; H, 7.6. $C_{29}H_{38}O_5Si$ requires C, 70.4; H, 7.75%); δ_H(300 MHz) 1.05 (9 H, s, Bu^t), 1.23 (3 H, t, *J* 7.1, Me), 1.28 (3 H, t, *J* 7.1, Me), 2.13 (1 H, dt, $J_{6,6'}$ 15.0, *J* 6.8, 6-H), 2.70 (1 H, dd, $J_{6,6'}$ 15.0, *J* 6.8, 6-H'), 3.49 (1 H, m, OCH_2Me), 3.77 (1 H, m, OCH_2Me), 3.97 (2 H, m, 4- and 5-H), 4.18 (2 H, q, *J* 7.1, OCH_2Me), 4.83 (1 H, d, *J* 1.3, 1-H), 5.61 (1 H, d, $J_{2,3}$ 9.8, 3-H), 5.78 (2 H, m, 2- and 8-H), 6.94 (1 H, dt, $J_{7,8}$ 15.1, *J* 6.8, 7-H), 7.42 (6 H, m, ArH) and 7.69 (4 H, m, ArH); δ_C(75 MHz) 14.3 and 15.3 (2 × Me), 19.4 (CSi), 26.9 (CMe_3), 34.3 (C-6), 60.1 and 64.3 (2 × OCH_2), 69.0 and 70.4 (C-4 and -5), 94.2 (C-1), 123.3 (C-8), 125.7, 127.7, 127.8, 127.9, 129.8, 130.0, 133.7 and 135.9 (C-arom, -2 and -3), 145.4 (C-7) and 166.3 (CO); *m/z* 450 $(M + NH_4)^+$.

Ethyl (E)-(*Ethyl* 2,3,6,7,8-*Pentadeoxy*-α-D-erythro-*nona*-2,7-*dienopyranosid*)*uronate* **4a**.—To a cooled (0 °C) solution of silyl derivative **4b** (1.03 g, 2.13 mmol) in dry tetrahydrofuran (49 cm^3) was added pyridine (14 cm^3) followed by hydrogen fluoride–pyridine complex (7 cm^3). The solution was allowed to warm to room temperature and was stirred for 24 h. After being cooled to 0 °C the mixture was treated with saturated aq. $NaHCO_3$ added dropwise and the reaction mixture was extracted with CH_2Cl_2 (3 × 200 cm^3). The combined organic extracts were washed successively with conc. $NaHCO_3$ and water and dried. Evaporation of the solvents gave a residue, which was purified by flash chromatography with petroleum spirit–EtOAc (7:3) to afford compound **4a** (304 mg, 52.3%), $[\alpha]_D^{21}$ +30.1 (*c* 1.1) (Found: C, 65.1; H, 8.4. $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.4%); δ_H(300 MHz) 1.20 (3 H, t, *J* 7.1, Me), 1.26 (3 H, t, *J* 7.1, Me), 2.39 (1 H, m, 6-H), 2.74 (1 H, m, 6-H'), 3.51 (1 H, m, OCH_2Me), 3.74 (2 H, m, OCH_2Me and 5-H), 3.91 (1 H, m, 4-H), 4.16 (2 H, q, *J* 7.1, OCH_2Me), 4.92 (1 H, s, 1-H), 5.72 (1 H, dt, *J* 7.1, OCH_2Me), 4.92 (1 H, s, 1-H), 5.72 (1 H, dt, $J_{2,3}$ 10.1, *J* 2.3, 3-H), 5.90 (1 H, d, $J_{2,3}$ 10.1, 2-H), 5.93 (1 H, dt, $J_{7,8}$ 15.7, $J_{6,8}$ 1.4, 8-H) and 7.01 (1 H, dt, $J_{7,8}$ 15.7, $J_{6,7}$ 6.8, 7-H); δ_C(75 MHz) 14.2 and 15.2 (2 × Me), 34.4 (C-6), 60.3 and 64.1 (2 × OCH_2), 67.3 and 70.6 (C-4 and -5), 94.0 (C-1), 123.5, 126.7 and 133.4 (C-2, -3 and -8), 145.2 (C-7) and 166.5 (CO); *m/z* 450 $(M + NH_4)^+$.

Ethyl (Z)- *and* (E)-*3*-(*Tributylstannyl*)*propenoates* **8**.—To a stirred solution of ethyl propiolate (1.0 mol equiv.) and tributyltin hydride (1.1 mol equiv.) in toluene (10 cm^3 $mmol^{-1}$) was added triethylborane (0.1 mol equiv. of a 1 mol dm^{-3} solution in hexane) under argon at the desired temperature. The reaction mixture was stirred for 24 h and was then concentrated under reduced pressure. The residue was purified by flash chromatography. Elution was carried out initially with petroleum spirit to remove tributylethyltin and then with petroleum spirit–EtOAc (98:2) to isolate compound (*Z*)-**8** as a clear liquid, δ_H(300 MHz) 0.86 (9 H, t, *J* 7.1, 3 × Me), 0.94 (6 H, m, 3 × CH_2), 1.28 (3 H, t, *J* 7.1, Me), 1.29 (6 H, m, 3 × CH_2), 1.47 (6 H, m, 3 × CH_2), 4.20 (2 H, q, *J* 7.1, OCH_2Me), 6.72 (1 H, d, $J_{2,3}$ 12.9, 2-H) and 7.15 (1 H, d, $J_{2,3}$ 12.9, 3-H); δ_C(75 MHz) 11.0 (CH_2), 13.7 and 14.3 (2 × Me), 27.4 and 29.2 (2 × CH_2), 60.4 (OCH_2), 135.3 (C-2), 157.0 (C-3) and 167.7 (CO); followed by petroleum spirit–EtOAc (95:5) to elute the isomer (*E*)-**8** as a clear liquid; δ_H(300 MHz) 0.86 (9 H, t, *J* 7.1, 3 × Me), 0.94 (6 H, m, 3 × CH_2), 1.28 (3 H, t, *J* 7.1, Me), 1.29 (6 H, m, 3 × CH_2), 1.47 (6 H, m, 3 × CH_2), 4.11 (2 H, q, *J* 7.3, OCH_2Me), 6.22 (1 H, d, *J* 19.7, 2-H) and 7.65 (1 H, d, *J* 19.7, 3-H); δ_C(75 MHz) 9.6 (CH_2), 13.6 and 14.3 (2 × Me), 27.3 and 28.9 (2 × CH_2), 60.3 (OCH_2), 136.4 (C-2), 152.4 (C-3) and 164.9 (CO).

General Procedure for Baldwin's Reaction.—Typically, a thoroughly degassed (argon) solution of alkyl iodide (1 mol equiv.), ethyl 3-(tributylstannyl)propenoate **8** (2 mol equiv.) and AIBN (16 mol% every 12 h) in toluene (1 cm^3 $mmol^{-1}$ of iodide) was heated at 85 °C until TLC showed complete consumption of the starting material. The solvent was removed under reduced pressure and the resulting material was chromatographed over silica gel.

Ethyl (E)-(6,7,8-*Trideoxy*-1,2:3,4-*di*-O-*isopropylidene*-α-D-galacto-*non*-7-*enopyranosid*)*uronate* (E)-**11**. This compound was prepared from iodide **10** (424 mg, 1.14 mmol) and acrylate (*E*)-**8** (887 mg, 2.28 mmol) according to the general method. Chromatography with petroleum spirit–EtOAc (95:5) as eluent gave compound (*E*)-**11** as an oil (309 mg, 79%); $[\alpha]_D^{21}$ −50.9 (*c* 1.10) (Found: C, 59.5; H, 7.8. $C_{17}H_{26}O_7$ requires C, 59.6; H, 7.7%); δ_H(300 MHz) 1.27 (3 H, t, *J* 7.1, Me), 1.32 (3 H, s, Me), 1.33 (3 H, s, Me), 1.45 (3 H, s, Me), 1.51 (3 H, s, Me), 2.50 (2 H, m, 6-H_2), 3.86 (1 H, m, 5-H), 4.12 (1 H, dd, $J_{3,4}$ 7.7, $J_{4,5}$ 1.7, 4-H), 4.17 (2 H, q, *J* 7.1, OCH_2), 4.30 (1 H, dd, $J_{1,2}$ 5.0, $J_{2,3}$ 2.4, 2-H), 4.59 (1 H, dd, $J_{3,4}$ 7.7, $J_{2,3}$ 2.4, 3-H), 5.52 (1 H, d, $J_{1,2}$ 5.0, 1-H), 5.96 (1 H, d, $J_{7,8}$ 15.7, 8-H) and 6.95 (1 H, dt, $J_{7,8}$ 15.7, $J_{6,7}$ 7.0, 7-H); δ_C(75 MHz) 24.5, 24.9, 26.0, 26.6 and 29.1 (5 × Me), 32.9 (C-6), 60.2 (OCH_2), 66.4, 70.3, 70.8 and 72.2 (C-2, -3, -4, -5), 96.5 (C-1), 108.5 and 109.3 (2 × OCO), 123.6 (C-8), 149.4 (C-7) and 166.5 (CO); *m/z* 360 $(M + NH_4)^+$ and 343 $(MH)^+$.

Ethyl (Z)-(6,7,8-*Trideoxy*-1,2:3,4-*di*-O-*isopropylidene*-α-D-galacto-*non*-7-*enopyranosid*)*uronate* (Z)-**11**. According to the general method, iodide **10** (264 mg, 0.71 mmol) was treated with ethyl (*Z*)-3-(tributylstannyl)propenoate **8** (552 mg, 1.42 mmol) to give a 4:1 mixture of (*E*)- and (*Z*)-**11** (^{1}H NMR). Flash chromatography with petroleum spirit–EtOAc (95:5) as eluent gave compound (*Z*)-**11** (42 mg, 18%); $[\alpha]_D^{21}$ −79.5 (*c* 0.60) (Found: C, 59.95; H, 7.5%); δ_H(300 MHz) 1.32 (3 H, t, *J* 7.1, Me), 1.38 (3 H, s, Me), 1.41 (3 H, s, Me), 1.45 (3 H, s, Me), 1.49 (3 H, s, Me), 2.85 (1 H, m, 6-H), 3.02 (1 H, m, 6-H), 3.85 (1 H, dd, $J_{5,6}$ 9.0, $J_{4,5}$ 2.3, 5-H), 4.15 (2 H, q, *J* 7.1, CH_2Me), 4.16 (1 H, m, 4-H), 4.29 (1 H, dd, $J_{1,2}$ 4.9, $J_{2,3}$ 1.9, 2-H), 4.58 (1 H, dd, $J_{3,4}$ 7.8, $J_{2,3}$ 1.9, 3-H), 5.52 (1 H, d, $J_{1,2}$ 4.9, 1-H), 5.85 (1 H, d, $J_{7,8}$ 11.6, 8-H) and 6.39 (1 H, dt, $J_{7,8}$ 11.6, $J_{6,7}$ 7.0, 7-H); δ_C(75 MHz) 24.5, 24.9, 26.0, 26.7 and 29.1 (5 × Me), 32.9 (C-6), 60.2 (OCH_2), 66.4, 70.3, 70.8 and 72.2 (C-2, -3, -4, -5), 96.5 (C-1), 108.5 and 109.2 (2 × OCO), 123.6 (C-8), 144.4 (C-7) and 166.4 (CO); *m/z* 360 $(M + NH_4)^+$ and 343 $(MH)^+$; followed by the *E*-isomer (186 mg, 76%).

Ethyl (E)-(*ethyl* 4-O-*acetyl*-2,3,6,7,8-*pentadeoxy*-α-D-erythro-*nona*-2,7-*dienopyranosid*)*uronate* **4c**. Prepared from iodide **6** (400 mg, 1.22 mmol) and (*E*)-stannylacrylate **8** (949 mg, 2.44 mmol) according to the general method. Chromatography with petroleum spirit–EtOAc (8:2) as eluent gave compound **4c** as an oil (262 mg, 72%), $[\alpha]_D^{21}$ +47.0 (*c* 1.45) (Found: C, 60.5; H, 7.3. $C_{15}H_{22}O_6$ requires C, 60.4; H, 7.4%); δ_H(300 MHz) 1.21 (3 H, t, *J* 7.1, Me), 1.26 (3 H, t, *J* 7.1, Me), 2.33 (3 H, s, Me), 2.39 (1 H, m, 6-H), 2.49 (1 H, m, 6-H'), 3.52 (1 H, m, OCH_2Me), 3.78 (1 H, m, 6-H), 4.00 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 8.6, $J_{5,6'}$ 3.7, 5-H), 4.16 (2 H, q, *J* 7.1, OCH_2Me), 4.96 (1 H, s, 1-H), 5.12 (1 H, d, $J_{4,5}$ 9.5, 4-H), 5.81 (2 H, s, 2- and 3-H), 5.90 (1 H, d, $J_{7,8}$ 15.7, 8-H) and 6.96 (1 H, dt, $J_{7,8}$ 15.7, $J_{6,7}$ 7.1, 7-H); δ_C(75 MHz) 14.2, 15.2 and 21.0 (3 × Me), 34.7 (C-6), 60.2 and 64.3 (2 × OCH_2Me), 67.3 and 68.9 (C-4 and -5), 94.1 (C-1), 123.7 (C-8) 128.0 and 129.3 (C-2 and -3), 144.1 (C-7) and 166.2 and 170.4 (2 × CO);

m/z 316 $(M + NH_4)^+$, 299 $(MH)^+$, 253 $(MH - EtOH)^+$ and 239 $(MH - AcOH)^+$.

Ethyl (E)-*nona*-2,7-*dienopyranosiduronate* **4a** *from the acetate* **4c**. Acetyl derivative **4c** (15.6 g, 52.3 mmol) was dissolved in a mixture of methanol–triethylamine–water (8:2:1) (750 cm^3). After 24 h the solvents were evaporated off and the residue was azeotroped with chloroform (2 ×) and toluene (3 ×) to afford compound **4a** (13.8 g, 99%).

Ethyl (Z)-(*ethyl* 4-O-*acetyl*-2,3,6,7,8-*pentadeoxy*-α-D-erythro-*nona*-2,7-*dienopyranosid*)*uronate* **5**. By the general method, iodide **6** (2.4 g, 7.3 mmol) and (*Z*)-stannylacrylate **8** (5.7 g, 14.7 mmol) gave a 3:1 mixture (^1H NMR) of stereoisomers **4c** and **5**. Flash chromatography with petroleum spirit–EtOAc (95:5) as eluent gave *Z*-isomer **5** (480 mg, 22%), $[\alpha]_D^{21}$ +83.7 (*c* 1.1) (Found: C, 60.5; H, 7.2%); δ_H(300 MHz) 1.15 (3 H, t, *J* 7.1, Me), 1.19 (3 H, t, *J* 7.1, Me), 1.99 (3 H, s, Me), 2.89 (2 H, m, 6-H_2), 3.45 (1 H, m, OCH_2Me), 3.73 (1 H, m, OCH_2Me), 3.93 (1 H, m, 5-H), 4.07 (2 H, q, *J* 7.1, OCH_2Me), 4.90 (1 H, s, 1-H), 5.05 (1 H, dd, *J* 9.3 and 1.3, 4-H), 5.76 (3 H, m, 2-, 3- and 8-H) and 6.26 (1 H, dt, $J_{7,8}$ 11.5, $J_{6,7}$ 7.1 7-H); δ_C(75 MHz) 14.2, 15.2 and 21.0 (3 × Me), 31.0 (C-6), 59.8 and 64.0 (2 × OCH_2Me), 67.9 (C-5), 68.6, (C-4), 94.0 (C-1), 121.6, 127.8 and 129.4 (C-2, -3 and -8), 144.9 (C-7), 166.0 and 170.3 (2 × CO); *m/z* 316 $(M + NH_4)^+$, 299 $(MH)^+$ and 253 $(MH - EtOH)^+$; followed by the *E*-isomer **5** (1.45 g, 66%).

3-*Deoxy*-3-[2-(*ethoxycarbonyl*)*vinyl*]-1,2:5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* **13a** *and* 3-*deoxy*-3-[2-(*ethoxycarbonyl*)*vinyl*]-1,2:5,6-*di*-O-*isopropylidene*-α-D-*allofuranose* **13b**. By the general method, iodide **12** (500 mg, 1.35 mmol) and ethyl (*Z*)-3-(tributylstannyl) propenoate **8** (997 mg, 2.70 mmol) gave a 7:1 mixture (^1H NMR) of stereoisomers **13a** and **13b**. Flash chromatography with petroleum spirit–EtOAc (9:1) as eluent afforded compound **13a** as an oil (333 mg, 72%), $[\alpha]_D^{21}$ +102.7 (*c* 1.1) (Found: C, 59.5; H, 7.5. $C_{17}H_{26}O_7$ requires C, 59.6; H, 7.7%); δ_H(300 MHz) 1.27 (3 H, t, *J* 7.1, Me), 1.29 (3 H, s, Me), 1.31 (3 H, s, Me), 1.40 (3 H, s, Me), 1.53 (3 H, s, Me), 3.13 (1 H, dd, *J* 9.9 and 4.3, 3-H), 3.90–4.24 (6 H, m, 4- and 5-H, 6-H_2, OCH_2), 4.55 (1 H, d, $J_{1,2}$ 3.6, 2-H), 5.88 (1 H, d, $J_{1,2}$ 3.6, 1-H), 5.95 (1 H, d, *J* 16.0, =C*H*CO_2Et) and 6.77 (1 H, dd, *J* 16.0, $J_{3,H}$ 9.9, *H*C=CHCO_2Et); δ_C(75 MHz) 14.2, 25.1, 26.0, 26.5 and 26.8 (5 × Me), 49.4 (C-3), 60.4 and 67.8 (OCH_2 and C-6), 73.5, 80.6 and 84.1 (C-2, -4 and -5), 104.9 (C-1), 109.3 and 111.6 (2 × OCO), 124.9 (C=*C*HCO_2Et), 141.8 (*C*=CHCO_2Et) and 165.6 (CO); *m/z* 360 $(M + NH_4)^+$ and 343 $(MH)^+$, followed by the allo-isomer **13b** as a syrup (53 mg, 11%); $[\alpha]_D^{21}$ −5.1 (*c* 1.0) (Found: C, 59.8; H, 7.5%); δ_H(300 MHz) 1.29 (3 H, t, *J* 7.1, Me), 1.31 (3 H, s, Me), 1.32 (3 H, s, Me), 1.40 (3 H, s, Me), 1.54 (3 H, s, Me), 2.76 (1 H, dt, *J* 9.3 and 4.6, 3-H), 3.82 (1 H, dd, $J_{6,6'}$ 8.5, $J_{5,6}$ 5.6, 6-H), 4.00 (1 H, dd, $J_{6,6'}$ 8.5, $J_{5,6'}$ 6.6, 6-H'), 4.11 (1 H, t, *J* 4.6, 4-H), 4.17 (3 H, m, OCH_2 and 5-H), 4.65 (1 H, dd, $J_{2,3}$ 4.6, $J_{1,2}$ 3.6, 2-H), 5.84 (1 H, d, $J_{1,2}$ 3.6, 1-H), 6.02 (1 H, d, *J* 15.9, =C*H*CO_2Et) and 6.95 (1 H, dd, *J* 15.9, $J_{3,H}$ 9.3, *H*C=CHCO_2Et); δ_C(75 MHz) 14.3, 25.1, 26.2, 26.5 and 26.8 (5 × Me), 49.4 (C-3), 60.5 and 66.2 (OCH_2 and C-6), 76.3, 80.3 and 83.5 (C-2, -4 and -5), 105.0 (C-1), 109.7 and 112.4 (2 × OCO), 124.7 (C=*C*HCO_2Et), 142.2 (*C*=CHCO_2Et) and 165.9 (CO); *m/z* 360 $(M + NH_4)^+$ and 343 $(MH)^+$.

General Procedure for Coupling Reactions of Iodides with Ethyl (Z)-3-(*Phenylsulfanyl*)*propenoate*.—Typically, to a thoroughly degassed (argon) solution of alkyl iodide (1 mol equiv.), ethyl (*Z*)-3-(phenylsulfanyl)propenoate **15** (10 mol equiv.), $ClSnBu_3$ (0.10 mmol) and AIBN (0.10 mmol) in *tert*-butyl alcohol, (0.02 mol dm^{-3}) was added $NaCNBH_3$ (2.0 mol equiv.) and the reaction mixture was immediately refluxed in a preheated bath for 4 h. The reaction mixture was diluted with CH_2Cl_2 and shaken with 3% ammonium hydroxide, followed by brine and separation of the organic phase. The aqueous layer was extracted twice with CH_2Cl_2 and dried. CH_2Cl_2 and *tert*-butyl alcohol were removed by azeotroping with toluene and the residue was subjected to flash chromatography.

Phenyl sulfides **16**. Prepared from iodide **6** (506 mg, 1.55 mmol) according to the general method. Flash chromatography with petroleum spirit–EtOAc (95:5) as eluent gave the corresponding reduced product ethyl 2,3,6-trideoxy-4-*O*-acetyl-α-D-*erythro*-hex-2-enopyranoside[7] (125 mg, 56%); further elution with petroleum spirit–EtOAc (9:1) afforded phenyl sulfides **16** as a 1:1 mixture of diastereoisomers (173 mg, 35%), δ_H(300 MHz) (selected data) 1.15 (3 H, t, *J* 7.1, Me one isomer), 1.17 (3 H, t, *J* 7.1, Me other isomer), 1.24 (6 H, t, *J* 7.0, CH_2Me), 2.04 (3 H, s, Me one isomer), 2.07 (3 H, s, Me other isomer), 4.90 (2 H, s, 2 × 1-H), 5.04 (2 H, d, $J_{4,5}$ 9.2, 2 × 4-H), 5.79 (4 H, m, 2 × 2- and 2 × 3-H) and 7.30 (10 H, m, 2 × SPh); δ_C(75 MHz) 14.1, 14.2, 15.1 and 15.2 (2 × Me), 21.0 (Me), 33.5, 34.0, 36.1 and 36.8 (2 × C-6 and 2 × -8), 41.6 and 42.1 (2 × C-7), 60.7 (2 × OCH_2), 66.4, 66.5, 69.2 and 69.5 (2 × C-4 and 2 × -5), 93.8 and 93.9 (2 × C-1), 126.6, 126.7, 127.9, 128.0, 128.9, 129.1, 129.3, 130.3, 130.4, 130.6, 130.7, 135.4 and 135.5 (C-arom, -2 and -3) and 170.3, 170.5, 173.8 and 174.0 (C=O); *m/z* 336 $(M + NH_4)^+$ and 318 $(MH)^+$.

Phenyl sulfides **17** *and reduced product* **18**. Prepared from iodide **10** (503 mg, 1.36 mmol) according to the general method. Flash chromatography with petroleum spirit–EtOAc (9:1) as eluent gave the reduced product **18**[23] (170 mg, 51%); further elution with petroleum spirit–EtOAc (1:1) afforded phenyl sulfides **17** as a 1:1 mixture of diastereoisomers (230 mg, 37%); δ_H(300 MHz) (selected data) 1.20 (6 H, t, *J* 7.1, 2 × Me), 1.28 (6 H, s, 2 × Me), 1.31 (6 H, s, 2 × Me), 1.42 (12 H, s, 4 × Me), 1.87 (2 H, m, 6-H_2 one isomer), 1.95 (1 H, m, 6-H other isomer), 2.11 (1 H, m, 6-H' other isomer), 2.87 (2 H, m, 2 × 7-H), 3.16 (4 H, m, 2 × 8-H_2), 3.76 (2 H, m, 2 × 5-H), 4.08 (6 H, m, 2 × 4-H and 2 × OCH_2), 4.24 (1 H, dd, $J_{2,3}$ 5.3, $J_{1,2}$ 4.6, 2-H one isomer), 4.25 (1 H, dd, $J_{2,3}$ 5.3, $J_{1,2}$ 4.6, 2-H other isomer), 4.53 (1 H, dd, $J_{2,3}$ 5.3, $J_{3,4}$ 3.2, 3-H one isomer), 4.54 (1 H, dd, $J_{2,3}$ 5.3, $J_{3,4}$ 3.2, 3-H other isomer), 5.45 (1 H, d, $J_{1,2}$ 4.6, 1-H one isomer), 5.47 (1 H, d, $J_{1,2}$ 4.6, 1-H other isomer) and 7.26 (10 H, m 2 × SPh); δ_C(75 MHz) 14.2 (Me), 24.4, 24.5, 24.9 and 25.8 (4 × Me), 25.9 and 26.0 (2 × Me), 31.3, 32.0, 34.8 and 36.6 (C-6 and -8 both isomers), 60.6 and 60.7 (OCH_2), 64.8, 65.4, 70.3, 70.9, 71.0, 72.5 and 73.1 (C-2, -3, -4 and -5 both isomers), 96.4 and 96.5 (C-1 both isomers), 108.3, 109.1 and 109.2 (OCO), 126.1, 126.1, 126.2, 126.3, 128.8, 128.9, 129.6, 129.7, 129.9, 130.0 and 135.9 (C-arom) and 174.0 and 174.1 (C=O); *m/z* 476 $(M + NH_4)^+$ and 453 $(MH)^+$.

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