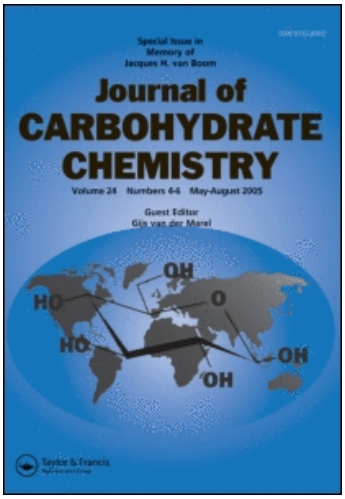

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From Sugar Allyltin Derivatives to Chiral Dienoaldehydes and Trienoates[1]

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FROM SUGAR ALLYLTIN DERIVATIVES TO CHIRAL DIENOALDEHYDES AND TRIENOATES[1]

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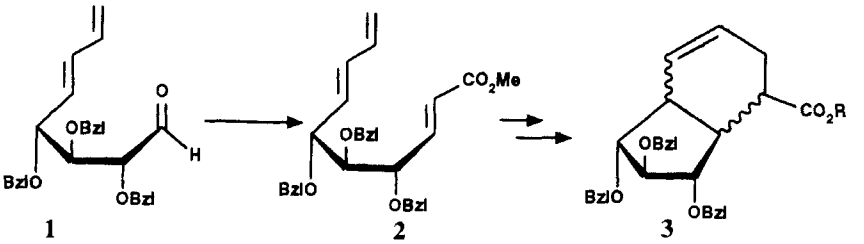
ABSTRACT

Sugar dialdoses **5**, **9**, **15**, and **16** were converted into allyltin derivatives **4**, **12**, **13**, and **14**, in yields of 35 - 47% respectively. Treatment of **4**, **12**, and **13** with a mild Lewis acid ($ZnCl_2$) in methylene chloride caused rearrangement to appropriate dienoaldehydes **1**, **19**, and **20** which were converted into trienes **2**, **21**, and **22**, respectively, by reaction with $Ph_3P{=}CHCO_2Me$.

INTRODUCTION

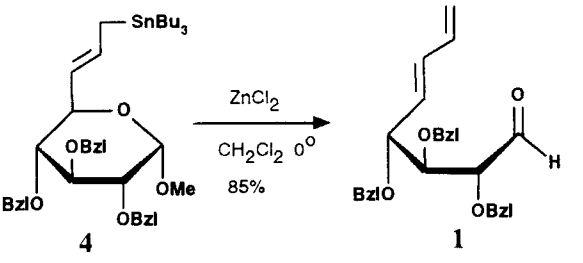
Intramolecular Diels-Alder reactions allow the preparation of bi(and poly)-cyclic systems, that are present in many natural compounds. Highly oxygenated dienoaldehydes such as **1** may be used as starting materials in the preparation of



SCHEME 1

bicyclic systems[2] (*e.g.*, **3**) from which chiral cyclopentanones or cyclohexanones may easily be obtained. The Diels-Alder reaction in systems such as **2** creates three new chiral centers and the stereochemistry of the products depend on the configurations of the starting materials.

Recently we observed that the Lewis acid catalyzed reaction of the allyltin derivative **4** led to aldehyde **1**[3] in high (*ca.* 85%) yield. This result prompted us to perform more detailed studies on the preparation of chiral dienoaldehydes from different allyltin derivatives. The latter should be readily available from simple monosaccharides of different configurations. In this paper the preparation of several sugar allyltin derivatives as well as their transformation to appropriate dienoaldehydes is presented. Preparation of these compounds will be exemplified by the synthesis of methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-(tri-*n*-butyl)stannyl-α-D-*gluco*-oct-6(*E*)-enopyranoside (**4**) and its conversion to dienoaldehyde **1**.

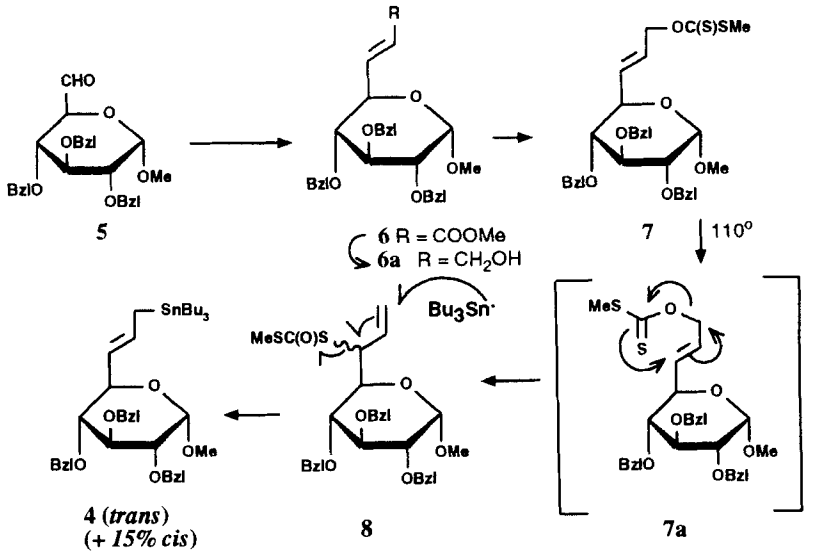


4 **1**

RESULTS AND DISCUSSION

Allyltin derivatives are available by many methods: *a)* reaction of carbanions with tributyltin oxide[4a] or tributyltin chloride,[4b] *b)* reaction of allylic acetates with diethylaluminum tributyltin,[4c] *c)* reactions of tin anions (R_3Sn^-) with allylic halides,[4d] *d)* reaction of allyltin Wittig-type reagents ($Bu_3SnCH_2CH{=}PPh_3$) with aldehydes,[4e] or *e)* by S_R2 reaction of trialkyltin radicals with allylic sulphones[4f] or thiocarbonates.[5]

We have found that the last of these methods[5] is most suitable for the preparation of sugar allyltin derivatives (see Scheme 2). Methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranose[6] (**5**) was treated with $Ph_3P{=}CHCOOMe$ and the crude product **6**, after reduction of the ester function with DIBAL-H to an alcohol **6a**, was converted into xanthate **7** under standard conditions. Thermal rearrangement of **7** in boiling toluene afforded (as indicated in **7a**) allylic thiocarbonate **8** as a mixture (*ca.*

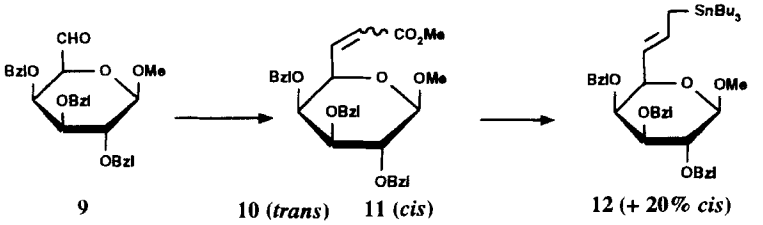


SCHEME 2

1:1) of diastereoisomers. Reaction of **8** with tri-*n*-butyltin hydride afforded *trans* allyltin derivative **4** (together with *ca.* 15% of the *cis* isomer) in 47% overall yield (from **5**).

The 3,3-rearrangement of **7** was completely non-stereoselective; from a single **7**-*trans* isomer a 1:1 mixture of thiocarbonates **8** was formed. However, this mixture when treated with tributyltin radical at 110 °C, afforded mainly the *trans* isomer **4**. It is clear that this reaction is under thermodynamic control and we obtained the more thermodynamically stable[7] isomer. In other words, the configuration of **8** has no influence on the geometry of **4**; hence, the configuration of xanthate **7** is also not important.

To prove this hypothesis we performed the same sequence of reactions (*i.* reduction with DIBAL-H, *ii.* formation of a xanthate, *iii.* thermal rearrangement, *iv.* reaction with Bu_3SnH) on the *cis* ester **11** and the *trans/cis* mixture (**10/11**). In both reactions the *trans* isomer **12** was obtained as the main product and the proportion of **12** *trans* : **12** *cis* isomers was estimated in both cases at 4:1 (see Scheme 3).



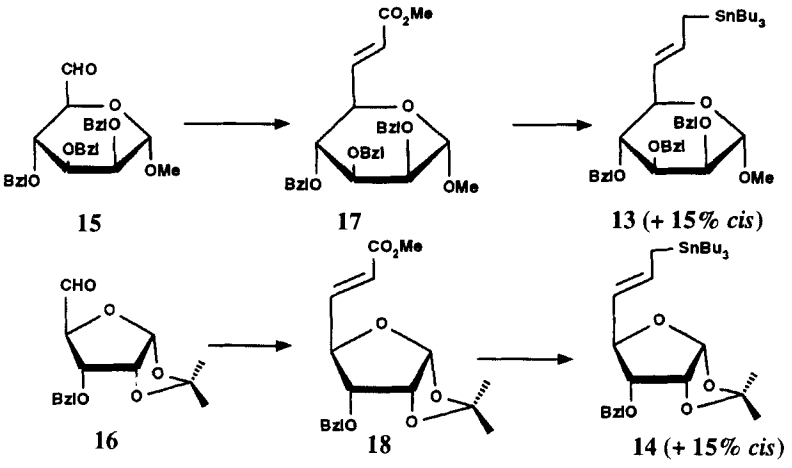
SCHEME 3

Treatment of allyltin derivative **4** with ethereal zinc chloride in methylene chloride at room temperature afforded dienoaldehyde **1** in high (85%) yield. The high resolution ^{1}H NMR spectrum of the isolated product revealed the presence of mainly one isomer of **1** which was contaminated with tri-*n*-butyltin species. Careful examination of the vinylic region allowed the assignment of the *trans* (J = 15.3 Hz) configuration to the newly created (*C5-C6*) double bond. To free aldehyde **1** from tri-*n*-butyltin species, it was treated with $Ph_3P{=}CHCO_2Me$ to afford chromatographically pure methyl 4(*S*),5(*S*),6(*R*)-tri-*O*-benzyl-dec-2(*E*),7(*E*)-9-trienoate (**2**).

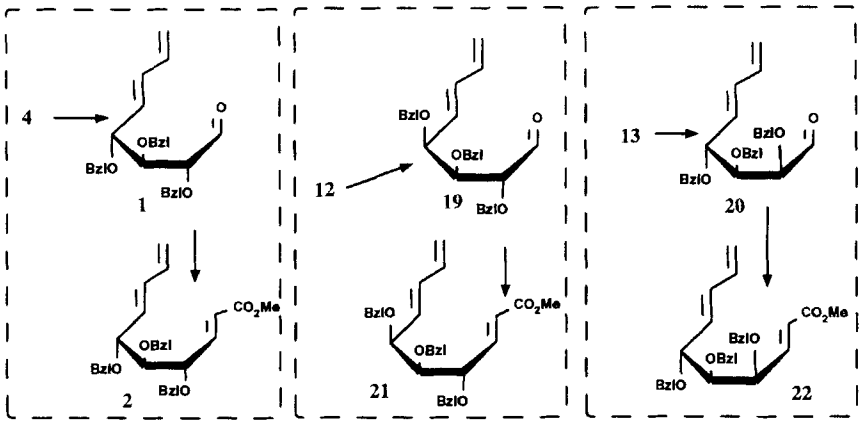
The same methodology was applied for the preparation of methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-(tri-*n*-butyl)stannyl-α-D-*manno*-oct-6(*E*)-eno-1,5-pyranoside (**13**) and 3-*O*-benzyl-1,2-*O*-isopropylidene-5,6,7-trideoxy-7-(tri-*n*-butyl)stannyl-α-D-*ribo*-hept-5(*E*)-eno-1,4-furanose (**14**) from aldehydes **15**[10] and **16**,[11] respectively.

Isomerisation of allyltins: **12** (β-D-*galacto* configuration) and **13** (α-D-*manno*) in the presence of zinc chloride afforded dienoaldehydes **19** and **20** which were treated with $Ph_3P{=}CHCO_2Me$ to afford methyl 4(*S*),5(*S*),6(*S*)- and 4(*R*),5(*S*),6(*R*)-tri-*O*-benzyl-dec-2(*E*),7(*E*),9-trienoates, **21** and **22**, respectively (Scheme 5).

The method presented here allows the simple preparation of sugar allyltin derivatives in 35 - 47% overall yield from appropriate dialdoses. These compounds are suitable starting materials for the preparation of chiral dienoaldehydes (by rearrangement in the presence of mild Lewis acid) which react with $Ph_3P{=}CHCO_2Me$ to afford trienoates **2**, **21** and **22** (having the D-*xylo*, L-*arabino* and D-*lyxo* configurations respectively). These trienoates will be used for studies on asymmetric Diels-Alder reaction leading to bicyclic systems such as **3**.



SCHEME 4



SCHEME 5

EXPERIMENTAL

General. ^1H NMR spectra were recorded with Bruker AM 500 or Varian 200 Gemini spectrometers for $CDCl_3$ solutions (internal Me_4Si). Column chromatography was performed on silica gel (Merck 230-400 mesh). Mass spectra were recorded on ADM 604 Intectrta GmbH. Aldehydes **5**, **9**, and **15** were prepared by the Swern oxidation[11] of appropriate alcohols and were used without purification.

Methyl 2,3,4-Tri-*O*-benzyl-6,7,8-trideoxy-8-(tri-*n*-butyl)stannyl-α-D-*gluco*-oct-6(*E*)-enopyranoside (4). To a solution of aldehyde **5** (6.93 g, 15 mmol) in benzene (100 mL) $Ph_3P{=}CHCO_2Me$ (6.5 g, 19.5 mmol, 1.3 equiv) was added and the mixture was stirred for 3 h at room temperature. The product - *trans* ester **6** [^{1}H NMR data: 7.03 (dd, 1H, $J_{6,7}$ = 15.7, $J_{5,6}$ = 4.6 Hz, **H-6**), 6.11 (dd, 1H, $J_{5,7}$ = 1.7 Hz, **H-7**), 4.26 (ddd, 1H, $J_{4,5}$ = 9.8 Hz, **H-5**), 4.02 (dd, 1H, $J_{3,4}$ = 9.0 Hz, **H-3**), 3.80 (s, 3H, **OMe** - ester), 3.52 (dd, 1H, $J_{2,3}$ = 9.7 Hz, **H-2**), 3.23 (dd, 1H, **H-4**), 3.35 (s, 3H, **OMe**)] was isolated by column chromatography (hexane - ethyl acetate 4:1) and reduced with DIBAL-H (45 mmol) in CH_2Cl_2 solution at 0 °C for 30 min. Excess of DIBAL-H was decomposed with water, the organic phase was washed with 5% HCl and water, dried and concentrated. Crude product was dissolved in THF (100 mL), sodium hydride (60% in oil, 2 g) was added followed by CS_2 (3 mL). After the mixture was stirred for 20 min at room temperature, methyl iodide (3 mL) was added and the stirring was continued at room temp for another 2 h. Water (50 mL) was carefully added, and the product was extracted with ether. The organic phase was washed with water, dried and concentrated. The residue was dissolved in toluene (100 mL) and refluxed under an argon atmosphere for 2 h. After this time, TLC (hexane - ethyl acetate, 3:1) showed the formation of slightly less polar products (D/L isomers in *ca.* 1:1 ratio) and disappearance of the starting material. Tri-*n*-butyltin hydride (5.4 mL, 20 mmoles) was added dropwise to the refluxing mixture followed by AIBN (*ca* 50 mg) and the mixture was refluxed for another 3 h. After the mixture was cooled to room temperature toluene was evaporated *in vacuo* and the residue was purified by column chromatography (first with hexane to remove excess of Bu_3SnH, then with hexane - ethyl acetate, 95:5) to afford **4** as an oil (5.38 g, 7.05 mmol, 47% overall) as a 6:1 mixture of *trans/cis* isomers. ^{1}H NMR data, *trans* isomer: 5.95 (dd, 1 H, **H-7**), 5.23 (dd, 1 H, $J_{6,7}$ = 15.0, $J_{5,6}$ = 7.7 Hz, **H-6**), 4.56 (d, 1 H, $J_{1,2}$ = 3.6 Hz, **H-1**), 3.98 (dd, 1 H, $J_{4,5}$ = 9.4 Hz, **H-5**), 3.95 (t, 1 H, $J_{3,4}$ = 9.3 Hz, **H-4**), 3.51 (dd, 1 H, $J_{2,3}$ = 9.7 Hz, **H-2**), 3.35 (s, 3 H, **OMe**), 3.21 (dd, 1 H, **H-3**), 1.75 (m, 2 H, **H-8,8'**); for *cis* isomer: 5.86 (m, 1H, **H-7**), 5.07 (dd, 1H, $J_{5,6}$ = 8.7, $J_{6,7}$ = 10.6 Hz, **H-6**), 3.43 (s, 3H, **OMe**); MS(EI) m/z: 764 (0.6), 707.27617 (M^+-Bu [$C_{38}H_{51}O_5Sn$] = 707.27584), 707 (13.3), 383 (7.9), 291 (27.0), 265 (26.0), 235 (32.0), 179 (31.0).

Methyl 2,3,4-Tri-*O*-benzyl-6,7,8-trideoxy-8-(tri-*n*-butyl)stannyl-β-D-*galacto*-oct-6(*E*)-enopyranoside (12). Methyl 2,3,4-tri-*O*-benzyl-β-D-*galacto*-hexodialdo-1,5-pyranoside[8] (**9**) was treated with $Ph_3P{=}CHCO_2Me$ as described above to give a 3:2 *cis/trans* mixture of **11/10** [^{1}H NMR data for *cis* **11** *inter alia*: 6.36 (dd, 1 H, $J_{6,7}$ = 11.7, $J_{5,6}$ = 6.8 Hz, **H-6**), 5.69 (dd, $J_{5,7}$ = 1.5 Hz, **H-7**), 4.31 (d, 1 H, $J_{1,2}$ = 7.5 Hz, **H-1**), 4.08 (m, 1 H, **H-5**), 3.66 and 3.54 (2s, 6 H, 2 x **OMe**); for *trans* isomer **10**: 6.74 (dd, 1 H, $J_{6,7}$ = 15.7, $J_{5,6}$ = 4.0 Hz, **H-6**), 6.14 (dd, $J_{5,7}$ = 1.9 Hz, **H-7**), 4.32 (d, 1 H, $J_{1,2}$ = 7.6 Hz, **H-1**), 3.97 (m, 1 H, **H-5**), 3.85 (dd, 1 H, $J_{2,3}$ = 9.7 Hz, **H-2**), 3.76 and 3.58 (2s, 6 H, 2 x **OMe**), 3.55 (dd, 1 H, $J_{3,4}$ = 3.1 Hz, **H-3**)]. Pure *cis* isomer (isolated by column chromatography) and, separately, a *trans/cis* mixture were treated under the conditions described above to give the title compound **12** in 37% overall yield. In both cases the proportion of *trans/cis* isomers of **12** was estimated (from ^{1}H NMR spectrum) at 4:1. ^{1}H NMR data, *trans* isomer: 5.85 (dd, 1 H, **H-7**), 5.42 (dd, 1 H, $J_{6,7}$ = 15.2, $J_{5,6}$ = 7.3 Hz, **H-6**), 4.26 (d, 1 H, $J_{1,2}$ = 7.7 Hz, **H-1**), 3.80 (dd, 1 H, $J_{2,3}$ = 9.7 Hz, **H-2**), 3.71 (d, 1 H, $J_{4,5}$ = 0 Hz, **H-5**), 3.63 (d, 1 H, $J_{3,4}$ = 2.9 Hz, **H-4**), 3.51 (dd, 1 H, **H-3**), 3.53 (s, 3 H, **OMe**), 1.62 (m, 2 H, **H-8,8'**); for *cis* isomer: 4.29 (s, 1H, $J_{1,2}$ = 7.7 Hz, **H-1**), 3.68 (d, 1H, $J_{3,4}$ = 2.1 Hz, **H-4**), 3.55 (s, 3H, **OMe**); MS(EI) m/z: 707.27478 (M^+-Bu [$C_{38}H_{51}O_5Sn$] = 707.27584), 707 (3.0), 383 (2.5), 341 (7.4), 291 (10.0), 265 (9.4), 235 (19.6), 179 (15.3), 91(100).

Methyl 2,3,4-Tri-*O*-benzyl-6,7,8-trideoxy-8-(tri-*n*-butyl)stannyl-α-D-*manno*-oct-6(*E*)-enopyranoside (13). From aldehyde **15**[9] [*via trans* ester **17**; ^{1}H NMR data *inter alia*: 7.13 (dd, 1H, $J_{6,7}$ = 15.8, $J_{5,6}$ = 4.7 Hz, **H-6**), 6.22 (dd, 1H, $J_{5,7}$ = 1.7 Hz, **H-7**), 4.19 (ddd, 1H, $J_{4,5}$ = 9.7 Hz, **H-5**), 3.90 (dd, 1H, $J_{2,3}$ = 3.0, $J_{3,4}$ = 9.3, **H-3**), 3.75 and 3.28 (2s, 6H, 2 x **OMe**)] the title compound (**13**) was prepared in 33% overall yield as a 6:1 mixture of *trans:cis* isomers. ^{1}H NMR data, *trans* isomer: 5.97 (dd, 1 H, **H-7**), 5.39 (dd, 1 H, $J_{6,7}$ = 15.0, $J_{5,6}$ = 7.7 Hz, **H-6**), 4.66 (d, 1 H, $J_{1,2}$ = 1.7 Hz, **H-1**), 3.92 (dd, 1 H, $J_{4,5}$ = 9.0 Hz, **H-5**), 3.83 (dd, 1 H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.3 Hz, **H-3**), 3.76 (dd, 1 H, **H-2**), 3.70 (d, 1 H, **H-4**), 3.28 (s, 3 H, **OMe**), 1.75 (m, 2 H, **H-8,8'**) ; for *cis* isomer: 5.86 (m, 1H, **H-7**), 5.25 (m, 1H, **H-6**), 3.35 (s, 3H, **OMe**); MS(EI) m/z: 707.27548 (M^+-Bu (4.3) [$C_{38}H_{51}O_5Sn$] = 707.27584), 383, (4.4), 341 (12.0), 291 (15.0), 265 (5.9), 235 (10.0), 173 (17.6), 91 (100).

3-*O*-Benzyl-1,2-*O*-isopropylidene-5,6,7-trideoxy-7-(tri-*n*-butyl)stannyl-α-D-*ribo*-hept-5(*E*)-eno-1,4-furanose (14) From aldehyde **16**[10] [*via trans* ester **18**; ^{1}H NMR data: 6.93 (dd, 1H, $J_{5,6}$ = 15.8, $J_{4,5}$ = 5.1 Hz, **H-5**), 6.13 (dd, $J_{4,6}$ = 1.6 Hz, **H-6**), 5.71 (d, 1H, $J_{1,2}$ = 3.6 Hz, **H-1**), 4.61 (m, 1H, **H-4**), 4.58 (dd, 1H, $J_{2,3}$ = 9.2 Hz, **H-2**), 3.53 (dd, 1H, $J_{3,4}$ = 4.2 Hz, **H-3**), 1.61 and 1.36 (CMe_2)] the title compound (**14**) was prepared in 38% yield as a 6:1 mixture of *trans:cis* isomers. ^{1}H NMR data, *trans* isomer: 6.01 (m, 1H, **H-6**), 5.68 (d, 1H, $J_{1,2}$ = 3.8 Hz, **H-1**), 5.16 (dd, 1H, $J_{5,6}$ = 15.0, $J_{4,5}$ = 8.4 Hz, **H-5**), 4.50 (dd, 1H, $J_{2,3}$ = 4.4 Hz, **H-2**), 4.40 (dd, 1H, $J_{3,4}$ = 8.9 Hz, **H-4**), 3.44 (dd, 1H, **H-3**); for *cis* isomer: 5.91 (1H, **H-6**), 5.70 (d, 1H, $J_{1,2}$ = 3.8, **H-1**), 3.49, (dd, 1H, $J_{2,3}$ = 4.3, $J_{3,4}$ = 8.9 Hz, **H-3**). MS (EI) m/z: 565 (M-15, 0.2), 539 (1.2), 523 (0.6), 465 (5.9), 329 (4.7), 291 (2.7), 235 (26.0), 173 (47.0), 91 (100).

Conversion of 4 to Dienoaldehyde 1. To a solution of allyltin derivative **4** (380 mg, 0.5 mmol) in methylene chloride (5 mL) at 0 °C an ethereal zinc chloride (0.55 mL of 1.0 M solution) was added and the mixture was stirred for 1 h at room temperature. After this time TLC (hexane - ethyl acetate, 2:1) showed disappearance of the starting material and formation of a new, more polar product. Water was added followed by ether, the product was separated, washed with water, dried and concentrated, and the residue was purified by chromatography (hexane - ethyl acetate, 3:1) to afford dienoaldehyde **1**. ^{1}H NMR data: 9.64 (s, 1 H, **CHO**), 6.29 (m, 1 H, **H-7**), 6.20 (dd, 1 H, $J_{6,7}$ = 10.0, $J_{5,6}$ = 15.3 Hz, **H-6**), 5.61 (dd, 1 H, $J_{4,5}$ = 7.3 Hz, **H-5**), 5.21 (dd, 1 H, $J_{8,8'}$ = 1.6 $J_{7,8}$ = 16.5 Hz, **H-8**), 5.13 (dd, 1 H, $J_{7,8'}$ = 10.0 Hz, **H-8'**). Aldehyde **1** contaminated with tri-*n*-butyltin species, was dissolved in benzene (20 mL) and Ph_3P=$CHCO_2Me$ was added. The mixture was stirred overnight at room temperature, the solvent was removed *in vacuo* and the product was isolated by chromatography to give **methyl 4(*S*),5(*S*),6(*R*)-tri-*O*-benzyl-dec-2(*E*),7(*E*),9-trienoate 2**. ^{1}H NMR data: 6.86 (dd, 1H, $J_{2,3}$ = 15.9, $J_{3,4}$ = 6.2 Hz, **H-3**), 6.01 (dd, 1H, $J_{2,4}$=1.3, **H-2**), 5.19 (dd, 1H, $J_{10,10'}$ = 1.9, $J_{9,10}$ = 17.4 Hz, **H-10**), 5.12 (dd, 1H, $J_{9,10'}$ = 9.3 Hz, **H-10'**), 3.50 (s, 3H, **OMe**). Signals **H-7**, **H-8** and **H-9** formed a complicated multiplet from which $J_{7,8}$ value could not be established, but, because the main isomer of **1** had the *trans* configuration of this double bond (J = 15.3) we assumed the same *trans* configuration of this double bond in **2**. MS(LS) m/z: 521.23085 ($M+Na^+$ [$C_{32}H_{34}O_5$] = 521.23039), 498 (1.8), 467 (2.5), 407 (18.8), 299 (70.5), 191 (59.0), 91 (100).

Using this procedure trienoates **21** and **22** were also prepared (from allyltins **12** and **13**).

Methyl 4(*S*),5(*S*),6(*S*)-Tri-*O*-benzyl-dec-2(*E*),7(*E*),9-trienoate (21). ^{1}H NMR data: 6.93 (dd, 1H, $J_{2,3}$ = 15.8, $J_{3,4}$ = 6.1 Hz, **H-3**), 6.44 - 6.24 (m, 2H, **H-8** and **H-9**), 6.07 (dd, 1H, $J_{2,4}$ = 1.4 Hz, **H-2**), 5.64 (dd, 1H, $J_{7,8}$ = 14.4, $J_{6,7}$ = 8.3 Hz, **H-7**), 5.24 (dd, 1H, $J_{10,10'}$ = 2.0, $J_{9,10}$ = 16.8 Hz, **H-10**), 5.14 (dd, 1H, $J_{9,10'}$ = 9.2 Hz, **H-10'**), 3.74 (s, 3H, **OMe**). MS(LS) m/z: 521.23110 (M+Na$^+$ [$C_{32}H_{34}O_5$] = 521.23039).

Methyl 4(*R*),5(*S*),6(*R*)-Tri-*O*-benzyl-dec-2(*E*),7(*E*),9-trienoate (22). ^{1}H NMR data: 6.95 (dd, 1H, $J_{2,3}$ = 15.8, $J_{3,4}$ = 6.3 Hz, **H-3**), 6.32 - 6.14 (m, 2H, **H-8** and **H-9**), 6.02 (dd, $J_{2,4}$ = 1.2 Hz, **H-2**), 5.58 (dd, $J_{7,8}$ = 14.4, $J_{6,7}$ = 8.1 Hz, **H-7**), 5.18 (dd, 1H, $J_{10,10'}$ = 1.2, $J_{9,10}$ = 15.9 Hz, **H-10**), 5.08 (dd, 1H, $J_{9,10'}$ = 9.6 Hz, **H-10'**) 3.68 (s, 3H, **OMe**). MS(LS) m/z: 521.23083 (M+Na$^+$ [$C_{32}H_{34}O_5$] = 521.23039).

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