STEREOSELECTIVE PREPARATION OF PRECURSORS OF α-*C*-(1→3)-DISACCHARIDES

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The stereoselectivity of cycloaddition of sugar-containing substituted 1-(thiazol-2-yl)but-2-en-1-ones **1** and vinyl ethers was studied using the achiral vinyl ether/chiral catalyst as well as the chiral vinyl ether/achiral catalyst combinations. It has been shown that Eu(fod)$_3$-catalyzed cycloaddition of oxadienes **1a**–**1e** with the chiral vinyl ethers **9** and **10** affords stereoselectively almost pure cycloadducts **11a**–**11e** and **12a**–**12e**, respectively. The obtained cycloadducts are suitable precursors for the synthesis of α-*C*-(1→3)-disaccharides, containing 2-deoxy-*arabino*-hexopyranose moiety of D- or L-configuration.

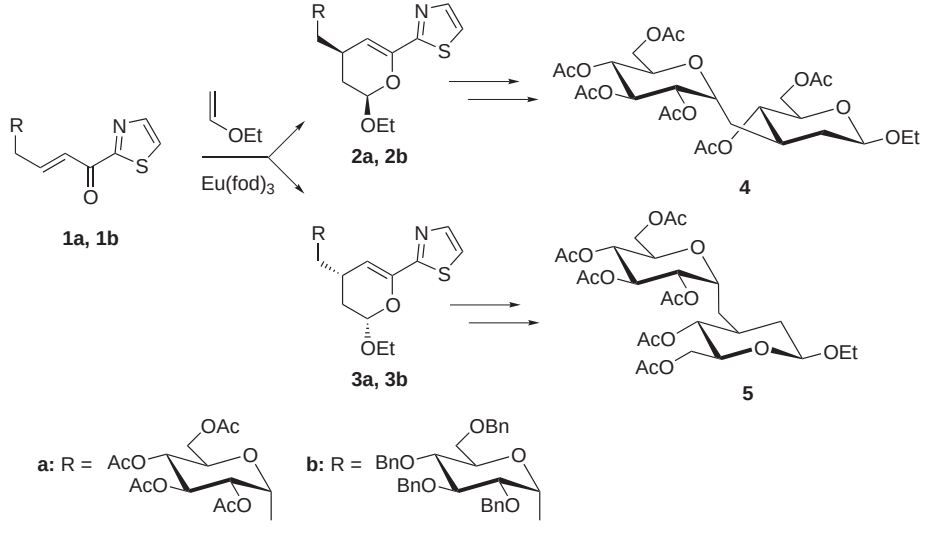
Keywords: Hetero-Diels–Alder reactions; Cycloadditions; Saccharides; Carbohydrates; Disaccharides; Carba-analogues; Stereoselective synthesis; X-ray diffraction; Thiazoles; Dihydropyrans; *C*-glycosides.

The cell-surface carbohydrates play essential role in cell communication system and can significantly influence many vital processes. It is assumed that *C*-disaccharides, which are analogues of natural disaccharides but in which the glycosidic oxygen atom has been substituted with a methylene group mimic well the disaccharide structure but they resist acidic as well as enzyme hydrolysis. The *C*-disaccharides as disaccharide mimetics could form nonhydrolyzable epitopes of cell surface glycoconjugates, thus disturbing their interactions with proteins, or they could inhibit the enzymes involved in the biosynthesis of glycoconjugates. For these reasons, there is

an increased interest in the search for new synthetic pathways leading to *C*-disaccharides and in the study of their properties[1].

Recently we described a short and efficient synthesis of α-*C*-(1→3)-disaccharides, containing 2-deoxy-*arabino*-hexopyranose moiety[2], in which the key step was the hetero-Diels–Alder reaction of ethyl vinyl ether with chiral 1-oxa-1,3-butadienes **1a** or **1b** (see Scheme 1). Under catalysis with $Eu(fod)_3$ (Europium(III) tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) this cycloaddition was highly *endo*- selective and afforded a mixture of only two diastereoisomeric cycloadducts **2** and **3** in the ca 1:1 ratio. With acetyl protecting groups, the obtained diastereoisomers **2a** and **3a** were not separable by preparative chromatography on silica gel; however, in the case of benzyl protecting groups the cycloadducts **2b** and **3b** were separated without any problems and each of them was converted into the final α-*C*-(1→3)-disaccharide with D- (compound **4**) or L- (compound **5**) configuration of the new deoxyhexopyranose.

The necessary separation of the obtained mixture of diastereoisomers **2** and **3** is a weak point of the mentioned synthesis significantly limiting a more general utilization of this pathway because it cannot be predicted whether other oxadienes **1**, containing monosaccharides of other configuration or with other protecting groups, will afford chromatographically well



SCHEME 1
Synthetic route to α-*C*-(1→3)-disaccharides

separable cycloadducts. To avoid problems associated with the separation of the cycloadducts, we tried to study whether the cycloaddition could be performed with even higher stereoselectivity, leading to only one of the two *endo*-cycloadducts, either to compound **2** or **3**.

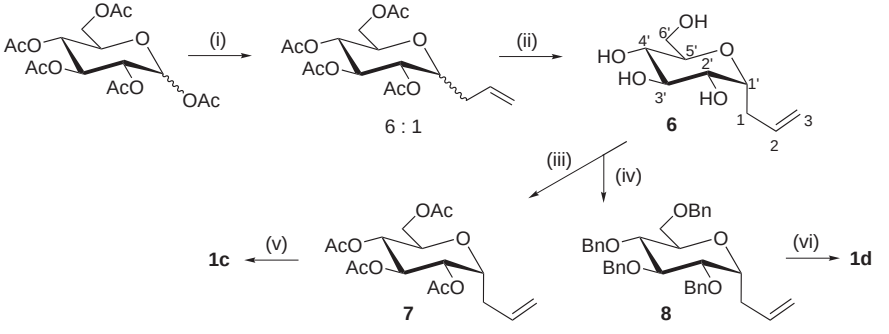
The formation of the two cycloadducts **2** and **3** in the 1:1 ratio indicates that in the studied cycloaddition the monosaccharide moiety present in the starting oxadiene **1a** or **1b** has practically no chiral influence. We can therefore assume that for the facial stereoselectivity control of the cycloaddition one could use procedures of classical enantioselective synthesis, irrespective of whether the present additional chiral element will form a matched or mismatched pair with the starting chiral oxadiene **1**.

The enantioselectivity of hetero-Diels–Alder reaction of structurally very similar oxadienes, i.e. β,γ-unsaturated α-keto esters, has already been studied. In the reactions of these oxadienes, high enantioselectivity was achieved by replacement of the ester group by a chiral auxiliary group[3], using chiral catalysis[4,5] or chiral enol ethers[6]. We decided to study whether also in the case of oxadienes **1**, containing a thiazole ring, the facial stereoselectivity of the cycloaddition can be controlled by the chiral catalysis or by the use of chiral enol ethers.

Stereoselectivity of the cycloaddition was studied with oxadienes **1a**–**1e** (see Scheme 3) containing monosaccharide moieties of various configurations with various protecting groups. The starting oxadienes **1a**–**1e** can be easily obtained from the corresponding α-pyranosylpropenes; however, the situation is complicated by the fact that chromatographic separation of α-pyranosylpropenes from the minor β-epimers is usually difficult. Purification of α-pyranosylpropenes, required for the synthesis of oxadienes **1a** and **1b**, is described in our previous paper[2]. Isopropylidene-protected α-mannopyranosylpropene, precursor of oxadiene **1e**, is crystalline and can be separated from the minor β-epimer by crystallization[7]. On the other hand, isolation of pure galactopyranosylpropenes, precursors of oxadienes **1c** and **1d**, was not trivial. 1-(Tetra-*O*-acetyl-α-D-galactopyranosyl)prop-2-ene[8] has already been synthesized from the corresponding pyranosyl bromide and allylic sulfide in the presence of hexabutyldistannane under photolytic conditions, however, the description in the experimental part of the cited paper[8] does not mention possible contamination with β-epimer. An even much simpler synthesis of this propene by reaction of penta-*O*-acetyl-D-galactose with commercial allyltrimethylsilane under catalysis with $BF_3 \cdot Et_2O$ is described[9]. The authors state that after 48 h in acetonitrile at 4 °C the desired α-epimer is obtained in 80% yield, the stereoselectivity being 95:5. In our hands, the reaction under these conditions gave neither

the stated yield nor the selectivity. Finally we found that the entirely pure α-epimer can be easily obtained by the following efficient procedure. Heating at reflux a solution of penta-*O*-acetyl-D-galactose, allyltrimethylsilane and $BF_3 \cdot Et_2O$ in acetonitrile for 4 h gave a 6:1 mixture of α- and β-epimers of 1-(tetra-*O*-acetyl-D-galactopyranosyl)prop-2-ene in 98% yield (Scheme 2). Zemplén deacetylation afforded quantitatively the same mixture of epimeric 1-(D-galactopyranosyl)prop-2-enes, which was dissolved in ethanol and treated with ether to turbidity, affording in 60% yield crystalline, completely pure α-epimer **6**, melting at 134–135 °C, which, to our knowledge, has not been so far described. Its acetylation and benzylation afforded in high yield and purity the respective compounds **7** and **8**, precursors for the synthesis of oxadienes **1c** and **1d**.

To obtain the oxadienes **1c**–**1e**, the prepared α-galactopyranosylpropenes **7** and **8** as well as the isopropylidene-protected α-mannopyranosylpropene[7], were subjected to ozonolysis. We found that ozonides, formed from α-galactopyranosylpropenes with acetyl or isopropylidene protecting groups, can be decomposed[10] with stabilized 2-phosphoranylidene-1-(thiazol-2-yl)ethan-1-one[11] with direct formation of oxadienes **1c** or **1e**. With the benzyl protecting groups, this procedure gave only a mixture of products and it was necessary to decompose the arising ozonide with dimethyl sulfide to give the aldehyde that subsequently, in a Wittig reaction with the above mentioned ylide, gave oxadiene **1d**.



(i) allyltrimethylsilane, $BF_3 \cdot Et_2O$, MeCN, reflux, 4 h
(ii) 1. MeONa/MeOH, 2. crystalization from EtOH/Et_2O; (iii) Ac_2O, pyridine; (iv) NaH, BnBr, DMF
(v) 1. O_3, CH_2Cl_2, 2. 2-phosphoranylidene-1-(thiazol-2-yl)ethan-1-one
(vi) 1. O_3, CH_2Cl_2, 2. Me_2S, 3. 2-phosphoranylidene-1-(thiazol-2-yl)ethan-1-one

SCHEME 2
Synthesis of 1-(α-D-galactopyranosyl)prop-2-enes

The *trans*-configuration at the C=C bond in oxadienes **1c** and **1e** was unequivocally confirmed on the basis of vicinal interaction of olefinic protons in the ^{1}H NMR spectrum. On the other hand, it was not possible to confirm the *trans*-configuration in **1d** directly from the coupling constants because the pertinent signals were overlapped by signals of aromatic protons. The *trans*-configuration of this compound was assigned in an indirect way, on the basis of the fact that the cycloaddition with ethyl vinyl ether afforded only two perbenzylated cycloadducts **2** and **3** of the same configuration as the peracetylated cycloadducts arising from oxadiene **1c** in which the *trans*-configuration had already been confirmed.

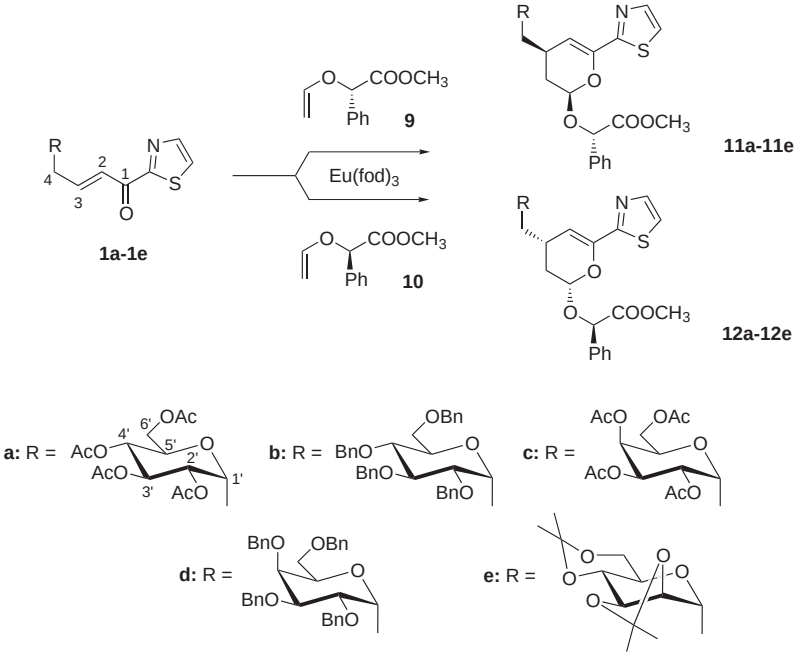
First, we tried to affect the cycloaddition stereoselectivity by the use of chiral catalysts. To be able to compare the effectivity and stereoselectivity of various catalysts, we performed several reactions of oxadiene **1b** under identical conditions, i.e. with 10 mole % of catalyst, in dichloromethane solution and at room temperature. Firstly, we used both enantiomers of Eu(hfc)$_3$ (Europium(III) tris[3-(heptafluoropropylhydroxymethylene)-camphorate]) instead of the achiral Eu(fod)$_3$. Unfortunately, this did not lead to any marked increase in reaction stereoselectivity: the ratio of the two cycloadducts changed only insignificantly. Moreover, in both cases we observed a significant prolongation of the reaction time (from 7 to about 16 h) and the ^{1}H NMR spectrum of the reaction mixture exhibited also new signals probably corresponding to the *trans*-isomers (ca 15%).

As further catalysts we tried the derivatives of another lanthanide, ytterbium. The reaction of oxadienes **1** in the presence of achiral Yb(OTf)$_3$ was slower than with Eu(fod)$_3$ (it was complete only after 4 days) and the ^{1}H NMR spectrum again contained also signals corresponding to supposed *trans*-cycloadducts. In spite of this we tried to influence the facial stereoselectivity by the use of chiral catalysts that had been successfully employed in cycloadditions by Kobayashi[12] and Nakagawa[13] and which are formed in situ from Yb(OTf)$_3$, a tertiary amine and biaryl chiral ligands. As chiral ligands we used both enantiomers of 1,1′-binaphthalene-2,2′-diol, (*S*)-2′-benzamido-1,1′-binaphthalen-2-ol and (*S*)-*N*,*N*′-dibenzoyl-1,1′-binaphthalene-2,2′-diamine and the selected tertiary amine was diisopropylethylamine. Unfortunately, even the use of these catalysts did not lead to significant changes in stereoselectivity, the cycloaddition being even slower than that with Yb(OTf)$_3$.

As found in the literature, cycloadditions of the structurally similar β,γ-unsaturated α-keto esters led to outstanding enantioselectivity with catalysts based on the chiral bisoxazoline copper(II) complexes, particularly with *tert*-butyl-substituted bisoxazoline copper(II) triflate[4,5] or indane-

derived bisoxazoline copper(II) triflate[14]. Using $Cu(OTf)_2$ we observed about the same activity as $Yb(OTf)_3$ (under the same conditions, the reaction was completed after about 6 days and the reaction mixture again contained also supposed *trans*-cycloadducts). With chiral *tert*-butyl-substituted bisoxazoline copper(II) triflate[4,5] the reaction mixture after 9 days still contained 60% of the starting oxadiene **1b**, moreover, the arising product again showed no significant change in the facial stereoselectivity.

As the mentioned chiral catalysts have not afforded the desired stereoselectivity enhancement, we turned our attention to the use of chiral enol ethers. The literature data show that in cycloadditions of β,γ-unsaturated α-keto esters, the best results were obtained by Dujardin[6] et al. with chiral vinyl ethers **9** and **10** (Scheme 3) which can be easily obtained from cheap and commercially accessible enantiomers of mandelic acid. Therefore, we synthesized these chiral vinyl ethers and to our delight we found that their cycloaddition with thiazole-substituted oxadienes **1b** is highly stereoselective, affording only one diastereoisomer in almost pure form.



SCHEME 3
Cycloaddition of substituted oxadienes with chiral vinyl ethers

The similar stereoselectivity showed reactions with all other starting oxadienes **1a**–**1e**. Their cycloadditions with the chiral vinyl ether **9** under catalysis with $Eu(fod)_3$ afforded diastereoisomers **11a**–**11e** as principal products and diastereoisomers **12a**–**12e** as minor products. On the other hand the cycloaddition with the vinyl ether **10** gave, with practically the same selectivity, diastereoisomers **12a**–**12e** as the main products (see Table I). The obtained results confirm that the monosaccharide moieties in the starting oxadienes **1a**–**1e** indeed have no chiral influence in this cycloaddition and the chiral vinyl ethers **9** and **10** do not form matched and mismatched pairs with the starting oxadienes.

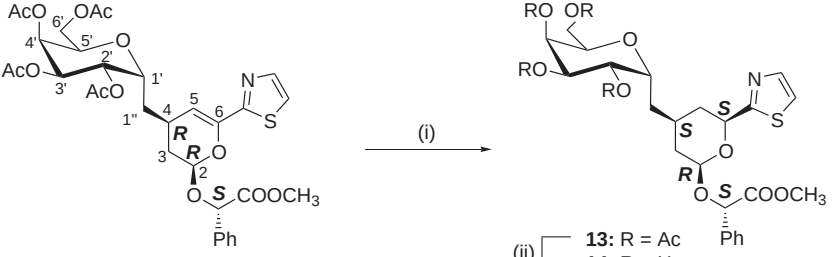
All the isolated cycloadducts **11a**–**11e** and **12a**–**12e** exhibited a strong NOEs between protons H-2 and H-4 on the 3,4-dihydro-2*H*-pyran ring that confirm their relative *cis*-configuration. Thus, cycloadducts **11a**–**11e** and **12a**–**12e**, similarly to cycloadducts **2** and **3** [2], must differ in the absolute configuration at the chiral atoms C-2 and C-4 of the 3,4-dihydro-2*H*-pyran ring.

To assign unequivocally the absolute configuration in cycloadducts **11** and **12**, we tried to obtain a crystalline derivative suitable for X-ray diffraction analysis. Hydrogenation of compound **11c** and subsequent deacetylation of **13** afforded crystalline tetrahydropyran derivative **14** (Scheme 4) the X-ray analysis of which (Fig. 1) confirmed the 2*R*,4*S*,6*S*-configuration at the chiral carbon atoms of the tetrahydropyran ring. From this it follows

TABLE I
Selectivity of cycloadditions with chiral vinyl ethers

Starting oxadiene	Chiral vinyl ether	Reaction time, days	Ratio of cycloadducts **11**:**12**
1a	**9**	9	98:2
1b	**9**	4	95:5
1c	**9**	6	95:5
1d	**9**	5	94:6
1e	**9**	2	95:5
1a	**10**	9	5:95
1b	**10**	4	6:94
1c	**10**	6	2:98
1d	**10**	5	4:96
1e	**10**	2	5:95

that cycloadduct **11c** must have the 2*R*,4*R*-configuration at the chiral carbon atoms of the 3,4-dihydro-2*H*-pyran ring. This result confirms that cycloaddition reaction of oxadienes **1a**–**1e** with the vinyl ether **9** of *S*-configuration leads to the cycloadducts **11a**–**11e** with 2*R*,4*R*-configuration of the 3,4-dihydro-2*H*-pyran ring, whereas the reaction with the vinyl ether **10** of *R*-configuration affords the cycloadducts **12a**–**12e** of the opposite configuration, i.e. 2*S*,4*S*.



(i) H_2, 10% Pd(C), methanol; (ii) KCN/methanol

SCHEME 4

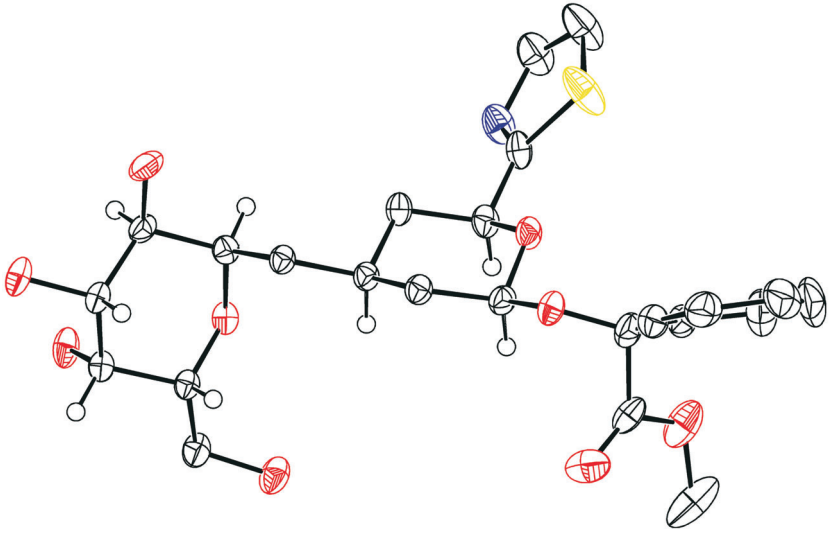


FIG. 1

ORTEP drawing of **14** (30% probability ellipsoids). The hydrogen atoms (except ring hydrogens) and molecule of methanol are omitted for clarity

In conclusion, the chiral vinyl ethers **9** and **10**, prepared from both enantiomers of mandelic acid, enable a highly diastereoselective preparation of cycloadducts **11** or **12**, which are direct precursors of α-*C*-(1→3)-disaccharides. The configuration of the monosaccharide moiety and the protecting groups in the starting oxadiene **1** has no effect on the stereoselectivity of the reaction. X-ray analysis of compound **14** confirmed that the reaction of the chiral vinyl ether **9** of *S*-configuration leads to precursors **11a**–**11e**, convertible into α-*C*-(1→3)-disaccharides in which the 2-deoxy-*arabino*-hexopyranose moiety has D-configuration (as in compound **4**). On the other hand, the use of chiral vinyl ether **10** of *R*-configuration leads to precursors **12a**–**12e** that on further transformation can afford α-*C*-(1→3)-disaccharides with L-configuration of the 2-deoxy-*arabino*-hexopyranose moiety (like in compound **5**).

EXPERIMENTAL

The synthesis of oxadienes **1a** and **1b** was described in our previous paper[2]. Chiral enol ethers **10** and **11** were synthesized according to the procedure described in ref.[6]

The melting points are not corrected. TLC was performed on HF_{254} plates (Merck), detection with UV light or by spraying with a solution of 5 g of $Ce(SO_4)_2 \cdot 4H_2O$ in 500 ml 10% H_2SO_4 and subsequent heating. Flash column chromatography was performed on silica gel (Merck, 100–160 μm) in solvents distilled prior to use. Specific optical rotations were measured at 25 °C on a Jasco DIP-370 spectropolarimeter and are given in 10^{-1} deg cm^2 g^{-1}. ^{1}H and ^{13}C NMR spectra were taken on a Bruker DRX 500 Avance spectrometer at 500.132 MHz (^{1}H NMR) and at 125.767 MHz (^{13}C NMR) using tetramethylsilane as internal standard. Chemical shifts in ^{1}H and ^{13}C NMR spectra are given in ppm (δ), coupling constants *J* in Hz. ^{1}H and ^{13}C NMR signal assignments were confirmed by 2D COSY and HMQC when necessary. NOE connectivities were obtained using 1D ^{1}H DPFGSE-NOE experiment. Mass spectra were taken on a Q TOF micromass spectrometer with direct inlet (ESI) or on a ZAB-EQ (VG Analytical) instrument (FAB) with Xe ionization, accelerating voltage 8 kV. HPLC was performed using an Agilent 1100 instrument equipped with gradient pump, column thermostat and UV detector, on a 250 × 4.6 mm column packed with 5 μm Supelco BDS Hypersil C-18, mobile phase methanol–water.

1-(α-D-Galactopyranosyl)prop-2-ene (**6**)

Allyltrimethylsilane (16.3 ml, 11.67 g, 102 mmol) and $BF_3 \cdot Et_2O$ (13.2 ml, 14.78 g, 104 mmol) were added to a solution of penta-*O*-acetyl-D-galactose (10 g, 25.64 mmol) in dry acetonitrile (160 ml). The reaction mixture was refluxed under argon for 4 h, cooled, poured into saturated solution of $NaHCO_3$ (400 ml) and extracted with dichloromethane (3 × 100 ml). The organic phase was washed with water (3×), dried, the solvent was evaporated and the residue subjected to chromatography on silica gel (petroleum ether–ethyl acetate 4:1). Yield 9.1 g (97%) of 1-(tetra-*O*-acetyl-D-galactopyranosyl)prop-2-ene as 6:1 mixture of α- and β-epimers (according to ^{1}H NMR). This mixture was dissolved in 200 ml of 0.1 M MeONa in MeOH and after stirring for 2 h it was neutralized by addition of Dowex, suspended in methanol. The

ion exchanger was removed by filtration and the solvent was evaporated. The residue (4.97 g) was dissolved in ethanol (10 ml), and ether was slowly added to persistent turbidity. After 12 h the solution deposited 3.1 g of the title compound, m.p. 134–135 °C. $[\alpha]_D$ +113.1 (*c* 1.0, H_2O). ^{1}H NMR (D_2O) (for numbering of atoms see Scheme 2): 2.31 ddd, 1 H, *J*(1a,1b) = 14.9, *J*(1a,2) = 6.1, *J*(1a,1′) = 4.5 (H-1a); 2.44 ddd, 1 H, *J*(1a,1b) = 14.9, *J*(1b,2) = 7.9, *J*(1b,1′) = 11.8 (H-1b); 3.63 d, 2 H, *J*(6′ab,5′) = 6.1 (H-6′a, H-6′b); 3.73–3.77 m, 2 H (H-3′,H-5′); 3.91 dd, 1 H, *J*(3′,4′) = 3.9, *J*(4′,5′) = 3.9 (H-4′); 3.93 dd, 1 H, *J*(2′,3′) =10.1, *J*(1′,2′) = 6.1 (H-2′); 4.04 ddd, 1 H, *J*(1a,1′) = 4.5, *J*(1b,1′) = 11.8, *J*(1′,2′) = 6.1 (H-1′); 5.07 d, 1 H, *J*(2,3*cis*) = 10.2 (H-3*cis*); 5.13 d, 1 H, *J*(2,3*trans*) = 17.1 (H-3*trans*); 5.79 dddd, 1 H, *J*(1a,2) = 6.1, *J*(1b,2) = 7.9, *J*(2,3*cis*) = 10.2, *J*(2,3*trans*) = 17.1 (H-2). ^{13}C NMR (D_2O): 29.91 (C-1); 62.03 (C-6′); 69.37 (C-2′); 70.12 (C-4′); 70.81 (C-3′); 72.80 (C-5′); 76.04 (C-1′); 118.45 (C-3); 136.11 (C-2). For **6** ($C_9H_{16}O_5$) calculated: relative molecular mass 204.22, monoisotopic mass 204.09. MS (FAB), *m/z*: 205.1 $[M + H]^+$. For $C_9H_{16}O_5$ (204.2) calculated: 52.93% C, 7.90% H; found: 52.95% C, 7.98% H.

1-(Tetra-*O*-acetyl-α-D-galactopyranosyl)prop-2-ene (**7**)

Compound **6** (5.8 g, 28.4 mmol) was added to a mixture of pyridine (40 ml) and Ac_2O (20 ml) and the formed suspension was stirred at room temperature to dissolution (18 h). The reaction mixture was then poured onto ice (200 g) and extracted with dichloromethane (3 × 100 ml). The organic phase was washed with satureted solution of Na_2CO_3, water, and dried. Evaporation of the solvent afforded 10.1 g (95%) of product **7**, identical with the known compound[8].

1-(Tetra-*O*-benzyl-α-D-galactopyranosyl)prop-2-ene (**8**)

A suspension of NaH in mineral oil (60%; 6.8 g, 170 mmol) was added to a solution of compound **6** (5.8 g, 28.4 mmol) and tetrabutylammonium iodide (0.6 g) in DMF (80 ml) and THF (400 ml). After stirring at room temperature for 2 h, benzyl bromide (4 × 5 ml) was added dropwise to the reaction mixture in 45 min intervals, and after stirring at room temperature for another 3 h the reaction was quenched by addition of methanol (50 ml). The solvents were evaporated in vacuo and the residue was partitioned between a saturated solution of $NaHCO_3$ and dichloromethane. The organic phase was washed with water, dried and taken down. Subsequent chromatography of the residue on silica gel afforded 15.2 g (95%) of product **8**, R_F 0.43 (petroleum ether–ethyl acetate 10:1), identical with the known compound[15].

(*E*)-4-(Tetra-*O*-acetyl-α-D-galactopyranosyl)-1-(thiazol-2-yl)but-2-en-1-one (**1c**)

A solution of 1-(tetra-*O*-acetyl-α-D-galactopyranosyl)prop-2-ene (**7**) (2.3 g, 6.18 mmol) in dichloromethane (40 ml) was cooled to –75 °C and subjected to ozonolysis till the blue coloration persisted. The solution was then decolorized by introduction of oxygen, and 2-phosphoranylidene-1-(thiazol-2-yl)ethan-1-one[11] (4.1 g, 10.5 mmol) was immediately added. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Evaporation of the solvent in vacuo and chromatography afforded 2.18 g (73%) of oily **1c**. R_F 0.4 (petroleum ether–ethyl acetate 2:1). $[\alpha]_D$ +73.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) (for numbering of atoms see Scheme 3): 1.99 s, 3 H (C**H**$_3$CO); 2.05 s, 3 H (C**H**$_3$CO); 2.11 s, 3 H (C**H**$_3$CO); 2.13 s, 3 H (C**H**$_3$CO); 2.51–2.61 m, 1 H (H-4a); 2.69–2.81 m, 1 H (H-4b); 4.06 dd, 1 H, *J*(6′a,6′b) = 11.4, *J*(6′a,5′) = 4.5 (H-6′a); 4.08–4.13 m, 1 H (H-5′); 4.29 dd, 1 H, *J*(6′a,6′b) =

11.4, *J*(5′,6′b) = 7.9 (H-6′b); 4,47 ddd, 1 H, *J*(4a,1′) = 9.5, *J*(4b,1′) = 5.2, *J*(1′,2′) = 4.8 (H-1′); 5.26 dd, 1 H, *J*(2′,3′) = 9.0, *J*(3′,4′) = 2.9 (H-3′); 5.32 dd, 1 H, *J*(2′,3′) = 9.0, *J*(1′,2′) = 4.8 (H-2′); 5.54 dd, 1 H, *J*(3′,4′) = 2.9, *J*(4′,5′) = 2.7 (H-4′); 7.25 ddd, 1 H, *J*(2,3) = 15.6, *J*(3,4a) = 7.0, *J*(3,4b) = 3.4 (H-3); 7.41 d, 1 H, *J*(2,3) = 15.6 (H-2); 7.71 d, 1 H, *J* = 2.9 (**H**-thiazole); 8.03 d, 1 H, *J* = 2.9 (**H**-thiazole). ^{13}C NMR ($CDCl_3$): 20.43, 20.51, 20.57, 20.61 (CH_3CO); 30.21 (C-4); 61.19 (C-6′); 68.05 (C-3′); 68.27 (C-4′); 69.15 (C-5′); 69.75 (C-2′); 70.88 (C-1′); 126.61 (CH-thiazole); 126.79 (C-2); 144.65 (C-3); 144.95 (CH-thiazole); 167.78 (thiazole C-2); 170.57, 169.92, 169.75, 169.42 (CH_3CO). For **1c** ($C_{21}H_{25}NO_{10}S$) calculated: relative molecular mass 483.49, monoisotopic mass 483.12. MS (ESI), *m/z*: 484.2 $[M + H]^+$. For $C_{21}H_{25}NO_{10}S$ (483.5) calculated: 52.17% C, 5.21% H, 2.90% N; found: 51.97% C, 5.32% H, 2.81% N.

(*E*)-4-(2,3:4,6-Di-*O*-isopropylidene-α-D-mannopyranosyl)-1-(thiazol-2-yl)but-2-en-1-one (**1e**)

The title compound was prepared in the same manner as described in the preceding experiment. Reaction of 1-(2,3;4,6-di-*O*-isopropylidene-α-D-mannopyranosyl)prop-2-ene[7] (0.2 g, 0.7 mmol), dichloromethane (5 ml) and 2-phosphoranylidene-1-(thiazol-2-yl)ethan-1-one[11] (0.46 g, 1.19 mmol) afforded 0.2 g (72%) of oily **1e**. R_F 0.72 (petroleum ether–ethyl acetate 2:1). $[\alpha]_D$ + 12.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (C_6D_6–CD_3OD 9:1): 1.16 s, 3 H ($(CH_3)_2C$); 1.23 s, 3 H ($(CH_3)_2C$); 1.41 s, 3 H ($(CH_3)_2C$); 1.42 s, 3 H ($(CH_3)_2C$); 2.25–2.18 m, 2 H (H-4a, H-4b); 3.26 ddd, 1 H, *J*(4′,5′) = 10.5, *J*(5′,6′a) = 10.3, *J*(5′,6′b) = 5.5 (H-5′); 3.55 dd, 1 H, *J*(6′a,6′b) = 10.8, *J*(5′,6′a) = 10.3 (H-6′a); 3.71–3.67 m, 1 H (H-2′); 3.78 dd, 1 H, *J*(6′a,6′b) = 10.8, *J*(5′,6′b) = 5.5 (H-6′b); 3.88 ddd, 1 H, *J*(4a,1′) = 12.9, *J*(4b,1′) = 6.8, *J*(1′,2′) = 6.0 (H-1′); 3.98 dd, 1 H, *J*(3′,4′) = 7.3, *J*(4′,5′) = 10.5 (H-4′); 4.06 dd, 1 H, *J*(3′,4′) = 7.3, *J*(3′,2′) = 7.0 (H-3′); 6.76 d, 1 H, *J* = 2.7 (**H**-thiazole); 7.38 ddd, 1 H, *J*(2,3) = 15.6, *J*(3,4a) = 7.5, *J*(3,4b) = 7.5 (H-3); 7.50 d, 1 H, *J*(2,3) = 15.6 (H-2); 7.56 d, 1 H, *J* = 2.7 (**H**-thiazole). ^{13}C NMR (C_6D_6–CD_3OD 9:1): 18.72, 25.31, 27.67, 29.19 (4 × $(CH_3)_2C$); 35.48 (C-4); 62.17 (C-6′); 64.59 (C-5′); 72.77 (C-4′); 72.87 (C-1′); 75.56 (C-3′); 75.96 (C-2′); 99.51 ($(CH_3)_2C$); 109.65 ($(CH_3)_2C$); 127.09 (CH-thiazole); 127.52 (C-3); 144.76 (CH-thiazole); 146.39 (C-2); 168.53 (thiazole C-2); 181.48 (C-1). For **1e** ($C_{19}H_{25}NO_6S$) calculated: relative molecular mass 395.47, monoisotopic mass 395.14. MS (FAB), *m/z*: 396.1 $[M + H]^+$. For $C_{19}H_{25}NO_6S$ (395.5), calculated: 57.70% C, 6.37% H, 3.54% N; found: 57.52% C, 6.48% H, 3.44% N.

(*E*)-4-(Tetra-*O*-benzyl-α-D-galactopyranosyl)-1-(thiazol-2-yl)but-2-en-1-one (**1d**)

A solution of propene **8** (10 g, 17.7 mmol) in dichloromethane (85 ml) and methanol (15 ml) was cooled to –75 °C and ozonized to persistent blue coloration. Then, at the same temperature, the solution was decolorized by introducing oxygen. Dimethyl sulfide (12.9 ml, 10.9 g, 176 mmol) and solid $NaHCO_3$ (2.5 g, 29.7 mmol) were added and the reaction mixture was stirred at room temperature for 24 h and then filtered. The solvents were evaporated in vacuo and chromatography of the residue on silica gel afforded 2-(tetra-*O*-benzyl-α-D-galactopyranosyl)ethanal (9.7 g, 89%). R_F 0.35 (petroleum ether–ethyl acetate 5:1), identical with the authentic compound[16]. To a solution of the aldehyde (5 g, 8.82 mmol) in chloroform (25 ml) was added 2-phosphoranylidene-1-(thiazol-2-yl)ethan-1-one[11] (6.85 g, 17.64 mmol) and the reaction mixture was stirred at 60 °C for 96 h. Evaporation of the solvent in vacuo and chromatography on silica gel gave 4.8 g (81%) of oily oxadiene **1d**. R_F 0.8 (petroleum ether–ethyl acetate 5:1). $[\alpha]_D$ +48.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CHCl_3$): 2.59–2.80 m, 2 H (H-4a, H-4b); 3.70 dd, 1 H, *J*(6′a,6′b) = 10.6, *J*(5′,6′a) = 4.7 (H-6′a); 3.87 dd, 1 H, *J*(6′a,6′b) = 10.6, *J*(5′,6′b) = 7.3 (H-6′b); 3.74–4.13 m, 4 H (H-2′, H-3′, H-4′, H-5′); 4.15–4.24 m, 1 H (H-1′);

4.44–4.80 m, 8 H (4 × C_6H_5-C**H**$_2$); 7.21–7.41 m, 22 H (4 × C_6**H**$_5$, H-2, H-3); 7.65 d, 1 H, *J* = 2.9 (**H**-thiazole); 7.99 d, 1 H, *J* = 2.9 (**H**-thiazole). ^{13}C NMR ($CHCl_3$): 31.95 (C-4); 67.39 (C-6′); 70.61 (C-1′); 73.05, 74.32, 76.58 (C-2′, C-3′, C-4′, C-5′, one of them overlapped by C_6H_5-CH_2); 73.47, 76.92, 77.35, 77.76 (4 × C_6H_5-CH_2); 126.55 (CH-thiazole); 127.68–128.70 (20 × C_6H_5, C-3); 138.23, 138.58, 138.66, 138.67 (4 × *ipso* C_6H_5); 144.93 (CH-thiazole); 148.02 (C-2); 168.51 (thiazole C-2); 181.57 (C-1). For **1d** ($C_{41}H_{41}NO_6S$) calculated: relative molecular mass 675.84, monoisotopic mass 675.27. MS (ESI), *m/z*: 676.4 $[M + H]^+$. For $C_{41}H_{41}NO_6S$ (675.8) calculated: 72.86% C, 6.11% H, 2.07% N; found: 72.96% C, 6.31% H, 1.95% N.

Cycloaddition of Oxadienes **1a**–**1e** with Chiral Enol Ether **9** or **10**. General Procedure

Eu(fod)$_3$ was added to a solution of the corresponding oxadiene **1** and vinyl ether **9** or **10** in dry dichloromethane and the reaction mixture was stirred at room temperature under argon. The reaction was monitored by TLC and after disappearance of the starting oxadiene it was analyzed by HPLC. The reaction times and cycloadduct ratios for the products are given in Table I. After evaporation of the solvent in vacuo, the product was isolated by chromatography on silica gel. In this manner, the following compounds **11** and **12** were prepared.

Methyl (S)-2-phenyl-2-({(2R,4R)-4-[(tetra-O-acetyl-α-D-glucopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**11a**). Reaction of oxadiene **1a** (128 mg, 0.27 mmol), vinyl ether **9** (89 mg, 0.46 mmol) and Eu(fod)$_3$ (25 mg, 0.026 mmol) afforded 140 mg (78%) of compound **11a**. R_F 0.59 (petroleum ether–diethyl ether–dichloromethane 1:1:4). $[\alpha]_D$ +63.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) (for numbering of atoms see Scheme 4): 1.77–1.84 m, 1 H (H-1″a); 1.88 s, 3 H (C**H**$_3$CO); 1.97–2.12 m, 19 H (3 × C**H**$_3$CO); 2.12–2.19 m, 1 H (H-1″b); 2.22–2.32 m, 2 H (H-3eq, H-3ax); 2.53–2.58 m, 1 H (H-4); 3.74 s, 3 H (CH-COOC**H**$_3$); 4.04–4.09 m, 1 H (H-5′); 4.15 dd, 1 H, *J*(5′,6′a) = 2.0, *J*(6′a,6′b) = 12.3 (H-6′a); 4.28 dd, 1 H, *J*(5′,6′a) = 4.9, *J*(6′a,6′b) = 12.3 (H-6′b); 4.31–4.39 m, 1 H (H-1′); 5.03 dd, 1 H, *J*(3′,4′) = 9.1, *J*(4′,5′) = 9.3 (H-4′); 5.07 dd, 1 H, *J*(1′,2′) = 5.8, *J*(2′,3′) = 9.6 (H-2′); 5.25 dd, 1 H, *J*(2′,3′) = 9.2, *J*(3′,4′) = 9.3 (H-3′); 5.44 s, 1 H (C**H**-COOCH$_3$); 5.51 dd, 1 H, *J*(2,3ax) = 5.9, *J*(2,3eq) = 3.1 (H-2); 6.04 d, 1 H, *J*(4, 5) = 4.3 (H-5); 7.24–7.39 m, 6 H (C_6**H**$_5$, **H**-thiazole); 7.76 d, 1 H, *J* = 3.1 (**H**-thiazole). ^{13}C NMR ($CDCl_3$): 20.52 (CH$_3$CO); 26.63 (C-4); 30.09 (C-1″); 31.33 (C-3); 52.24 (CH-COOCH$_3$); 61.18 (C-6′); 68.54 (C-5′); 68.67 (C-4′); 69.91 (C-2′); 70.33 (C-3′); 71.98 (C-1′); 77.67 (CH-COOCH$_3$); 97.18 (C-2); 103.92 (C-5); 118.59 (CH-thiazole); 127.03–128.53 (5 × C_6H_5); 135.99 (*ipso* C_6H_5); 142.97 (C-6); 143.18 (CH-thiazole); 163.67 (thiazole C-2); 2 × 169.37, 169.89, 170.58, 170.68 (4 × CH_3CO, CH-COOCH$_3$). For **11a** ($C_{32}H_{37}NO_{13}S$) calculated: relative molecular mass 675.71, monoisotopic mass 675.19. MS (FAB), *m/z*: 676.2 $[M + H]^+$, 698.3 $[M + Na]^+$. For $C_{32}H_{37}NO_{13}S$ (675.7) calculated: 56.88% C, 5.52% H, 2.07% N; found: 56.74% C, 5.63% H, 1.95% N.

Methyl (S)-2-phenyl-2-({(2R,4R)-4-[(tetra-O-benzyl-α-D-glucopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**11b**). Reaction of oxadiene **1b** (1.45 g, 2.14 mmol), vinyl ether **9** (700 mg, 3.64 mmol) and Eu(fod)$_3$ (230 mg, 0.22 mmol) afforded 1.48 g (80%) of compound **11b**. R_F 0.18 (petroleum ether–ethyl acetate 6:1). $[\alpha]_D$ +61.3 (*c* 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.93–1.99 m, 1 H (H-1″a); 2.05–2.14 m, 1 H (H-1″b); 2.16–2.23 m, 1 H (H-3ax); 2.26–2.32 m, 1 H (H-3eq); 2.56–2.65 m, 1 H (H-4); 3.63–3.82 m, 9 H (H-2′, H-3′, H-4′, H-5′, H-6′a, H-6′b, CH-COOC**H**$_3$); 4.16–4.23 m, 1 H (H-1′); 4.51–4. 96 m, 8 H (4 × C_6H_5-C**H**$_2$); 5.49 dd, 1 H, *J*(2,3eq) = 2.5, *J*(2,3ax) = 4.5 (H-2); 5.51 s, 1 H (C**H**-COOCH$_3$); 6.09 d, 1 H, *J*(4,5) = 3.9 (H-5); 7.19–7.46 m, 26 H (5 × C_6**H**$_5$, **H**-thiazole); 7.82 d, 1 H, *J* = 3.2

(**H**-thiazole). ^{13}C NMR ($CDCl_3$): 27.21 (C-4); 30.82 (C-1″); 32.22 (C-3); 52.29 (CH-COO**C**H$_3$); 68.99 (C-6′); 72.98 (C-1′); 73.02, 73.48, 74.88, 75.39 (4 × C_6H_5-**C**H$_2$); 71.31, 77.25, 77.99, 79.98, 82.33 (C-2′, C-3′, C-4′, C-5′, **C**H-COOCH$_3$); 97.81 (C-2); 105.02 (C-5); 118.56 (**C**H-thiazole); 128.50–127.27 (25 × **C**$_6$H$_5$); 136.06–138.72 (5 × *ipso* **C**$_6$H$_5$); 142.95 (C-6); 143.22 (**C**H-thiazole); 164.14 (thiazole C-2); 170.98 (CH-**C**OOCH$_3$). For **11b** ($C_{52}H_{53}NO_9S$) calculated: relative molecular mass 868.06, monoisotopic mass 867.34. MS (FAB), *m/z*: 868.3 $[M + H]^+$. For $C_{52}H_{53}NO_9S$ (868.1) calculated: 71.95% C, 6.15% H, 1.61% N; found: 72.36% C, 6.11% H, 1.67% N.

Methyl (S)-2-phenyl-2-({(2R,4R)-4-[(tetra-O-acetyl-α-D-galactopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**11c**). Reaction of oxadiene **1c** (500 mg, 1.03 mmol), vinyl ether **9** (332 mg, 1.75 mmol) and Eu(fod)$_3$ (107 mg, 0.1 mmol) afforded 546 mg (78%) of compound **11c**. R_F 0.59 (petroleum ether–diethyl ether–dichloromethane 1:1:4). $[\alpha]_D$ +71.2 (*c* 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.63–1.76 m, 2 H (H-1″a, H-1″b); 1.96–2.15 m, 13 H, (4 × C**H**$_3$CO, H-3ax); 2.29 ddd, 1 H, *J*(3eq,3ax) = 13.5, *J*(3eq,4) = 7.1, *J*(2,3eq) = 1.9 (H-3eq); 2.62 m, 1 H (H-4); 3.76 s, 3 H (CH-COOC**H**$_3$); 3.90–3.95 m, 1 H (H-5′); 4.08 dd, 1 H, *J*(6′a,6′b) = 11.5, *J*(5′,6′a) = 5,5 (H-6′a); 4.22 dd, 1 H, *J*(6′a,6′b) = 11.5, *J*(5′,6′b) = 7.7 (H-6′b); 4.37–4.43 m, 1 H (H-1′); 5.14 dd, 1 H, *J*(2′,3′) = 9.2, *J*(3′,4′) = 3.2 (H-3′); 5.27 dd, 1 H, *J*(2′,3′) = 9.2, *J*(1′,2′) = 5.1 (H-2′); 5.32–5.36 m, 1 H (H-4′); 5.47 s, 1 H (C**H**-COOCH$_3$); 5.49–5.52 m, 1 H (H-2); 6.05 d, 1 H, *J*(4,5) = 3.8 (H-5); 7.27–7. 44 m, 6 H (C_6**H**$_5$, **H**-thiazole); 7.77 d, 1 H, *J* = 2.9 (**H**-thiazole). ^{13}C NMR ($CDCl_3$): 20.69 (**C**H$_3$CO); 26.81 (C-4); 31.19 (C-1″); 31.33 (C-3); 52.38 (CH-COO**C**H$_3$); 61.18 (C-6′); 67.47 (C-4′); 67.87 (C-3′); 68.22 (C-5′); 68.31 (C-2′); 70.29 (C-1′); 77.57 (**C**H-COOCH$_3$); 97.68 (C-2); 105.39 (C-5); 118.59 (**C**H-thiazole); 128.64–127.14 (5 × **C**$_6$H$_5$); 136.09 (*ipso* **C**$_6$H$_5$); 143.09 (C-6); 143.34 (**C**H-thiazole); 163.77 (thiazole C-2); 2 × 169.77, 170.05, 170.47, 170.84 (4 × CH$_3$**C**O, CH-**C**OOCH$_3$). For **11c** ($C_{32}H_{37}NO_{13}S$) calculated: relative molecular mass 675.71, monoisotopic mass 675.19. MS (FAB), *m/z*: 676.2 $[M + H]^+$, 698.3 $[M + Na]^+$. For $C_{32}H_{37}NO_{13}S$ (675.7) calculated: 56.88% C, 5.52% H, 2.07% N; found: 56.93% C, 5.81% H, 1.83% N.

Methyl (S)-2-phenyl-2-({(2R,4R)-4-[(tetra-O-benzyl-α-D-galactopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**11d**). Reaction of oxadiene **1d** (2.12 g, 3.14 mmol), vinyl ether **9** (1 g, 5.34 mmol) and Eu(fod)$_3$ (0.33 g, 0.31 mmol) afforded 2.25 g (83%) of compound **11d**. R_F 0.30 (petroleum ether–ethyl acetate 3:1). $[\alpha]_D$ +53.7 (*c* 0.14, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.64–1.78 m, 1 H (H-1″a); 1.90–2.06 m, 2 H (H-1″b, H-3ax); 2.30 ddd, 1 H, *J*(3eq,3ax) = 13.8, *J*(3eq,4) = 6.7, *J*(2,3eq) = 2.4 (H-3eq); 2.48–2. 65 m, 1 H (H-4); 3.63–3.82 m, 9 H (H-2′, H-3′, H-4′, H-5′, H-6′a, H-6′b, CH-COOC**H**$_3$); 4.02–4. 21 m, 1 H (H-1′); 4.45–4.79 m, 8 H (4 × C_6H_5-C**H**$_2$); 5.41 dd, 1 H, *J*(2,3ax) = 5.6, *J*(2,3eq) = 2.4 (H-2); 5.49 s, 1 H (C**H**-COOCH$_3$); 6.04 d, 1 H, *J*(4,5) = 3.5 (H-5); 7.18–7. 51 m, 26 H (5 × C_6**H**$_5$, C**H**-thiazole); 7.78 d, 1 H, *J* = 3.2 (**H**-thiazole). ^{13}C NMR ($CDCl_3$): 27.58 (C-4); 33.48 (C-1″); 33.54 (C-3); 52.63 (CH-COO**C**H$_3$); 67.86 (C-6′); 72.53 (C-1′); 73.24, 73.44, 73.59, 73.63 (4 × C_6H_5-**C**H$_2$); 74.62, 77.25, 77.32, 77.42, 77.75 (C-2′, C-3′, C-4′, C-5′, **C**H-COOCH$_3$); 97.56 (C-2); 105.19 (C-5); 118.82 (**C**H-thiazole); 127.98–128.85 (25 × **C**$_6$H$_5$); 136.45, 138.51, 138.71, 138.79, 138.84 (5 × *ipso* **C**$_6$H$_5$); 143.41 (C-6); 143.49 (**C**H-thiazole); 164.44 (C-2 thiazole); 171.24 (CH-**C**OOCH$_3$). For **11d** ($C_{52}H_{53}NO_9S$) calculated: relative molecular mass 868.06, monoisotopic mass 867.34. MS (FAB), *m/z*: 868.3 $[M + H]^+$. For $C_{52}H_{53}NO_9S$ (868.1) calculated: 71.95% C, 6.15% H, 1.61% N; found: 72.23% C, 6.11% H, 1.48% N.

Methyl (S)-2-phenyl-2-({(2R,4R)-4-[(2,3:4,6-di-O-isopropylidene-α-D-mannopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**11e**). Reaction of oxadiene **1e** (490 mg, 1.24 mmol), vinyl ether **9** (405 mg, 2.11 mmol) and Eu(fod)$_3$ (130 mg, 0.124 mmol) af-

forded 590 mg (83%) of compound **11e**. R_F 0.4 (petroleum ether–ethyl acetate 2:1). $[\alpha]_D$ +59.6 (*c* 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.32 s, 3 H (($CH_3)_2$C); 1.44 s, 3 H (($CH_3)_2$C); 1.49 s, 3 H (($CH_3)_2$C); 1.55 s, 3 H (($CH_3)_2$C); 1.82–1.95 m, 2 H (H-1″a, H-1″b); 2.01–2.09 m 1 H (H-3ax); 2.25–2.32 m, 1 H (H-3eq); 2.65–2.74 m, 1 H (H-4); 3.37–3.44 m, 1 H (H-6′a); 3.72–3.79 m, 4 H (H-5′, CH-COOCH_3); 3.89–3.98 m, 3 H (H-6′b, H-3′, H-2′); 4.10 dd, 1 H, *J* = 7.6, *J* = 7.2 (H-4′); 4.16–4.22 m, 1 H (H-1′); 5.48–5.51 m, 2 H (H-2, C**H**-COOCH_3); 6.07 d, 1 H, *J*(4,5) = 3.1 (H-5); 7.27–7.51 m, 6 H (5 × C_6H_5, **H**-thiazole); 7.77 d, 1 H (**H**-thiazole). ^{13}C NMR ($CDCl_3$): 18.92 (C-4); 25.49, 26.47, 27.79, 29.06 (4 × ($CH_3)_2$C); 32.65 (C-1′); 37.19 (C-3); 52.39 (CH-COOCH_3); 62.73 (C-6′); 62.58 (C-3′); 71.87 (C-2′); 72.62 (C-4′); 75.18 (C-5′); 75.26 (C-1′); 77.62 (CH-COOCH_3); 97.79 (C-2); 99.56 ($(CH_3)_2$C); 103.86 (C-5); 109.34 ($(CH_3)_2$C); 118.63 (CH-thiazole); 127.25, 128.48, 128.64, 128.76, 128.96 (5 × C_6H_5); 136.06 (*ipso* C_6H_5); 143.25 (CH-thiazole); 143.35 (C-6); 169.95 (C-2 thiazole); 170.94 (CH-COOCH_3). For **11e** ($C_{30}H_{37}NO_9S$) calculated: relative molecular mass 587.69, monoisotopic mass 587.22. MS (ESI), *m/z*: 610.4 $[M + Na]^+$. For $C_{30}H_{37}NO_9S$ (587.7) calculated: 61.31% C, 6.35% H, 2.38% N; found: 61.58% C, 6.11% H, 2.07% N.

Methyl (R)-2-phenyl-2-({(2S,4S)-4-[(tetra-O-acetyl-α-D-glucopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**12a**). Reaction of oxadiene **1a** (130 mg, 0.27 mmol), vinyl ether **10** (89 mg, 0.46 mmol) and Eu(fod)$_3$ (25 mg, 0.026 mmol) afforded 137 mg (75%) of compound **12a**. R_F 0.59 (petroleum ether–diethyl ether–dichloromethane 1:1:4). $[\alpha]_D$ +15.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.71–1.79 m, 1 H (H-1″a); 1.93–2.09 m, 13 H (4 × CH_3CO, H-3ax); 2.12–2.22 m, 1 H (H-1″b); 2.24–2.32 m, 1 H (H-3eq); 2.54–2.63 m, 1 H (H-4); 3.67–3.78 m, 4 H (CH-COOCH_3, H-5′); 3.93–3.07 m, 1 H (H-6′a); 4.20 dd, 1 H, *J*(6a′,6b′) = 12.3, *J*(5′,6′b) = 4.7 (H-6′b); 4.31–4.39 m, 1 H (H-1′); 4.98 dd, 1 H, *J*(3′,4′) = 9.0, *J*(4′,5′) = 8.9 (H-4′); 5.06 dd, 1 H, *J*(1′,2′) = 5.7, *J*(2′,3′) = 9.2 (H-2′); 5.22 dd, 1 H, *J*(2′,3′) = 9.0, *J*(3′,4′) = 9.0 (H-3′); 5.44 s, 1 H (C**H**-COOCH_3); 5.46–5.52 m, 1 H (H-2); 6.07 d, 1 H, *J*(4,5) = 3.8 (H-5); 7.23–7.41 m, 6 H (C_6H_5, **H**-thiazole); 7.74 d, 1 H, *J* = 2.9 (**H**-thiazole). ^{13}C NMR ($CDCl_3$): 20.51 (CH_3CO); 26.50 (C-4); 30.62 (C-1″); 31.14 (C-3); 52.26 (CH-COOCH_3); 61.82 (C-6′); 68.36 (C-4′); 68.83 (C-5′); 69.97 (C-2′); 70.18 (C-3′); 71.09 (C-1′); 77.58 (CH-COOCH_3); 97.45 (C-2); 105.06 (C-5); 118.52 (CH-thiazole); 126.92–128.51 (5 × C_6H_5); 135.99 (*ipso* C_6H_5); 142.99 (C-6); 143.24 (CH-thiazole); 163.55 (thiazole C-2); 169.32, 169.48, 169.81, 170.52, 170.69 (4 × CH_3CO, CH-COOCH_3). For **12a** ($C_{32}H_{37}NO_{13}S$) calculated: relative molecular mass 675.71, monoisotopic mass 675.19. MS (FAB), *m/z*: 676.2 $[M + H]^+$, 698.3 $[M + Na]^+$. For $C_{32}H_{37}NO_{13}S$ (675.7) calculated: 56.88% C, 5.52% H, 2.07% N; found: 56.93% C, 5.43% H, 1.96% N.

Methyl (R)-2-phenyl-2-({(2S,4S)-4-[(tetra-O-benzyl-α-D-glucopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**12b**). Reaction of oxadiene **1b** (150 mg, 0.22 mmol), vinyl ether **10** (73 mg, 0.38 mmol) and Eu(fod)$_3$ (24 mg, 0.023 mmol) afforded 150 mg (78%) of compound **12b**. R_F 0.19 (petroleum ether–ethyl acetate 6:1). $[\alpha]_D$ +19.0 (*c* 0.079, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.83–1.97 m, 2 H (H-1″a, H-3ax); 2.02–2.13 m, 1 H (H-1″b); 2.28–2.36 m, 1 H (H-3eq); 2.56–2.66 m, 1 H (H-4); 3.47–3.80 m, 9 H (H-2′, H-3′, H-4′, H-5′, H-6′a, H-6′b, CH-COOCH_3); 4.15–4.23 m, 1 H (H-1′); 4.42–4. 93 m, 8 H (4 × C_6H_5-CH_2); 5.41–5.47 m, 1 H (H-2); 5.50 s, 1 H (C**H**-COOCH_3); 6.01 d, 1 H, *J*(4,5) = 3.5 (H-5); 7.09–7.46 m, 26 H (5 × C_6H_5, **H**-thiazol); 7.74 d, 1 H, *J* = 3.1 (**H**-thiazol). ^{13}C NMR ($CDCl_3$): 27.05 (C-4); 30.17 (C-1″); 31.82 (C-3); 52.37 (CH-COOCH_3); 68.79 (C-6′); 71.35 (C-3′); 72.11 (C-1′); 72.93, 73.47, 74.91, 75.42 (4 × C_6H_5-CH_2); 77.79, 77.95, 77.99, 79.68, 82.31 (C-2′, C-4′, C-5′, CH-COOCH_3); 98.34 (C-2); 106.92 (C-5); 118.50 (CH-thiazol); 128.58–128.56 (25 × C_6H_5); 136.06–138.72 (5 × *ipso* C_6H_5); 142.86 (CH-thiazol); 142.88 (C-6); 164.02 (thiazol C-2);

170.95 (CH-COOCH$_3$). For **12b** ($C_{52}H_{53}NO_9S$) calculated: relative molecular mass 868.06, monoisotopic mass 867.34. MS (FAB), *m/z*: 868.3 $[M + H]^+$. For $C_{52}H_{53}NO_9S$ (868.1) calculated: 71.95% C, 6.15% H, 1.61% N; found: 72.13% C, 6.04% H, 1.43% N.

Methyl (R)-2-phenyl-2-({(2S,4S)-4-[(tetra-O-acetyl-α-D-galactopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**12c**). Reaction of oxadiene **1c** (500 mg, 1.03 mmol), vinyl ether **10** (337 mg, 1.75 mmol) and Eu(fod)$_3$ (107 mg, 0.103 mmol) afforded 470 mg (71%) of compound **12c**. R_F 0.51 (petroleum ether–diethyl ether–dichloromethane 1:1:4). $[\alpha]_D$ +22.2 (*c* 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.73–1.86 m, 2 H (H-1″a, H-1″b); 1.90–2.20 m, 13 H (4 × C**H**$_3$CO, H-3ax); 2.27–2.35 m, 1 H (H-3eq); 2.56–2.63 m, 1 H (H-4); 3.75 s, 3 H (CH-COOC**H**$_3$); 4.09–4.29 m, 3 H (H-5′, H-6′a, H-6′b); 4.36–4.44 m, 1 H (H-1′); 5.14 dd, 1 H, *J*(2′,3′) = 9.4, *J*(3′,4′) = 2.9 (H-3′); 5.27 dd, 1 H, *J*(2′,3′) = 9.4, *J*(1′,2′) = 5.3 (H-2′); 5.40–5.45 m, 2 H (C**H**-COOCH$_3$, H-5′); 5.50–5.56 m, 1 H (H-2); 6.05 d, 1 H, *J*(4,5) = 3.7 (H-5); 7.26–7.39 m, 6 H (C_6**H**$_5$, **H**-thiazole); 7.77 d, 1 H, *J* = 2.5 (**H**-thiazole). ^{13}C NMR ($CDCl_3$): 20.71 (4 × C**H**$_3$CO); 26.86 (C-4); 30.88 (C-1″); 31.93 (C-3); 52.35 (CH-COOC**H**$_3$); 62.71 (C-6′); 67.94–68.01 (C-2′, C-3′, C-4′, C-5′); 71.34 (C-1′); 77.89 (C**H**-COOCH$_3$); 97.57 (C-2); 104.01 (C-5); 118.68 (C**H**-thiazole); 127.15, 127.23, 128.60, 128.66, 128.85 (5 × C_6H_5); 136.07 (*ipso* C_6H_5); 143.25 (C**H**-thiazole); 143.14 (C-6); 163.85 (C-2 thiazole); 169.72, 170.12, 170.57, 170.86 (4 × CH_3CO, CH-C**O**OCH$_3$). For **12c** ($C_{32}H_{37}NO_{13}S$) calculated: relative molecular mass 675.71, monoisotopic mass 675.19. MS (FAB), *m/z*: 676.2 $[M + H]^+$, 698.3 $[M + Na]^+$. For $C_{32}H_{37}NO_{13}S$ (675.7) calculated: 56.88% C, 5.52% H, 2.07% N; found: 56.64% C, 5.59% H, 1.84% N.

Methyl (R)-2-phenyl-2-({(2S,4S)-4-[(tetra-O-benzyl-α-D-galactopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**12d**). Reaction of oxadiene **1d** (110 mg, 0.16 mmol), vinyl ether **10** (52 mg, 0.27 mmol) and Eu(fod)$_3$ (9 mg, 0.016 mmol) afforded 113 mg (83%) of compound **12d**. R_F 0.28 (petroleum ether–ethyl acetate 3:1). $[\alpha]_D$ +13.8 (*c* 0.26, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.58–1.72 m, 1 H (H-1″a); 1.85 ddd, 1 H, *J*(3ax,4) = 13.5, *J*(3ax,3eq) = 13.2, *J*(2,3ax) = 6.5 (H-3ax); 2.00–2.12 m, 1 H (H-1″b); 2.30 ddd, 1 H, *J*(3ax,3eq) = 13.2, *J*(3eq,4) = 6.7, *J*(2,3eq) = 2.1 (H-3eq); 2.60–2.74 m, 1 H (H-4); 3.59–4.00 m, 9 H (H-2′, H-3′, H-4′, H-5′, H-6′a, H-6′b, CH-COOC**H**$_3$); 4.06–4.21 m, 1 H (H-1′); 4.45–4.79 m, 8 H (4 × C_6H_5-C**H**$_2$); 5.42 dd, 1 H, *J*(2,3ax) = 6.2, *J*(2,3eq) = 2.1 (H-2); 5.48 s, 1 H (C**H**-COOCH$_3$); 6.02 d, 1 H, *J*(4,5) = 3.5 (H-5); 7.18–7.44 m, 26 H (5 × C_6**H**$_5$, **H**-thiazole); 7.76 d, 1 H, *J* = 3.2 (**H**-thiazole). ^{13}C NMR ($CDCl_3$): 27.43 (C-4); 32.09 (C-1″); 32.95 (C-3); 52.60 (CH-COOC**H**$_3$); 67.74 (C-6′); 72.30 (C-1′); 73.24, 73.41, 73.51, 73.59 (4 × C_6H_5-C**H**$_2$); 74.55, 77.14, 77.31, 77.73, 77.99 (C-2′, C-3′, C-4′, C-5′, C**H**-COOCH$_3$); 98.76 (C-2); 106.80 (C-5); 118.75 (C**H**-thiazole); 127.56–128.79 (25 × C_6H_5); 136.53, 138.46, 138.63, 138.77, 138.86 (5 × *ipso* C_6H_5); 143.32 (C-6); 143.50 (C**H**-thiazole); 164.41 (C-2 thiazole); 171.14 (CH-C**O**OCH$_3$). For **12d** ($C_{52}H_{53}NO_9S$) calculated: relative molecular mass 868.06, monoisotopic mass 867.34. MS (FAB), *m/z*: 868.3 $[M + H]^+$. For $C_{52}H_{53}NO_9S$ (868.1) calculated: 71.95% C, 6.15% H, 1.61% N; found: 72.14% C, 6.26% H, 1.50% N.

Methyl (R)-2-phenyl-2-({(2S,4S)-4-[(2,3:4,6-di-O-isopropylidene-α-D-mannopyranosyl)methyl]-6-(thiazol-2-yl)-3,4-dihydro-2H-pyran-2-yl}oxy)acetate (**12e**). Reaction of oxadiene **1e** (490 mg, 1.24 mmol), vinyl ether **10** (405 mg, 2.11 mmol) and Eu(fod)$_3$ (130 mg, 0.124 mmol) afforded 600 mg (85%) of compound **12e**. R_F 0.4 (petroleum ether–ethyl acetate 2:1). $[\alpha]_D$ +17.6 (*c* 0.24, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.34 s, 3 H ((C**H**$_3$)$_2$C); 1.46 s, 3 H ((C**H**$_3$)$_2$C); 1.54 s, 3 H ((C**H**$_3$)$_2$C); 1.58 s, 3 H ((C**H**$_3$)$_2$C); 1.82–1.95 m, 2 H (H-1″a, H-1″b); 2.02–2.08 m, 2 H (H-3ax); 2.25–2.32 m, 1 H (H-3eq); 2.66–2.73 m, 1 H (H-4); 3.37–3.45 m, 1 H (H-6′a); 3.71–3.79 m, 4 H (H-5′, CH-COOC**H**$_3$); 3.88–3.99 m, 3 H (H-6′b, H-3′, H-2′); 4.11 dd, 1 H,

J(3′,4′) = 7.6, *J*(4′,5′) = 7.6 (H-4′); 4.16–4.22 m, 1 H (H-1′); 5.45–5.52 m, 2 H (H-2, C**H**-COOCH$_3$); 6.07 d, 1 H, *J*(4,5) = 3.9 (H-5); 7.25–7.52 m, 6 H (C$_6$**H**$_5$, **H**-thiazole); 7.78 d, 1 H (**H**-thiazole). ^{13}C NMR (CDCl$_3$): 18.86 (C-4); 25.52, 26.22, 28.44, 29.09 (4 × (**C**H$_3$)$_2$C); 32.72 (C-1″); 37.30 (C-3); 52.37 (CH-COO**C**H$_3$); 62.79 (C-6′); 63.66 (C-3′); 71.93 (C-2′); 72.77 (C-4′); 74.01 (C-5′); 75.01 (C-1′); 77.38 (**C**H-COOCH$_3$); 97.85 (C-2); 99.57 ((CH$_3$)$_2$**C**); 103.95 (C-5); 109.36 ((CH$_3$)$_2$**C**); 118.63 (**C**H-thiazole); 127.50, 128.47, 128.81, 129.02, 128.74 (**C**$_6$H$_5$); 136.14 (*ipso* **C**$_6$H$_5$); 143.28 (**C**H-thiazole); 143.35 (C-6′); 169.84 (C-2 thiazole); 170.94 (CH-**C**OOCH$_3$). For **12e** (C$_{30}$H$_{37}$NO$_9$S) calculated: relative molecular mass 587.69, monoisotopic mass 587.22. MS (ESI), *m/z*: 610.4 [M + Na]$^+$. For C$_{30}$H$_{37}$NO$_9$S (587.7) calculated: 61.31% C, 6.35% H, 2.38% N; found: 61.43% C, 6.16% H, 2.07% N.

Methyl (*S*)-2-Phenyl-2-({(2*R*,4*S*,6*S*)-4-[(tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-6-(thiazol-2-yl)tetrahydropyran-2-yl}oxy)acetate (**13**)

Compound **11c** (100 mg, 0.15 mmol) in methanol (4 ml) was hydrogenated over Pd/C (10%; 60 mg) under atmospheric pressure for 12 h. The catalyst was removed by filtration, the solvent evaporated in vacuo and the residue chromatographed on silica gel. Yield 80 mg (80%) of compound **13**. R_F 0.63 (petroleum ether–ethyl acetate 1:4). [α]$_D$ +200 (*c* 0.013, CHCl$_3$). ^{1}H NMR (CDCl$_3$): 1.25–1.55 m, 3 H (H-1″a, H-3ax, H-5ax); 1.74–1.83 m, 1 H (H-1″b); 1.95–2.15 m, 13 H (H-4, 4 × C**H**$_3$CO); 2.18–2.22 m, 1 H (H-3eq); 2.30–2.36 m, 1 H (H-5eq); 3.73 s, 1 H (CH-COOC**H**$_3$); 4.05–4.14 m, 2 H (H-5′, H-6′a); 4.23–4.30 m, 1 H (H-6′b); 4.32–4.39 m, 1 H (H-1′); 4.81 dd, 1 H, *J*(5ax,6) = 11.0, *J*(5eq,6) = 1.9 (H-6); 4.87 dd, 1 H, *J*(2,3ax) = 9.0, *J*(2,3eq) = 1.2 (H-2); 5.15–5.19 m, 1 H (H-3′); 5.20–5.24 m, 1 H (H-2′); 5.32–5.43 m, 1 H (H-4′); 5.53 s, 1 H (C**H**-COOCH$_3$); 7.30 d, 1 H, *J* = 3.2 (**H**-thiazole); 7.32–7.46 m, 5 H (C$_6$**H**$_5$); 7.73 d, 1 H, *J* = 3.2 (**H**-thiazole). ^{13}C NMR (CDCl$_3$): 20.63–20.74 (4 × **C**H$_3$CO); 30.69 (C-4); 32.05 (C-1″); 36.25 (C-5); 37.61 (C-3); 52.26 (CH-COO**C**H$_3$); 61.28 (C-6′); 67.36 (C-2′); 67.74 (C-3′); 68.29 (C-4′); 68.59 (C-5′); 69.23 (C-1′); 75.33 (C-6); 76.75 (**C**H-COOCH$_3$); 100.46 (C-2); 118.95 (**C**H-thiazole); 127.41, 128.54, 128.62 (**C**$_6$H$_5$); 136.13 (*ipso* **C**$_6$H$_5$); 142.16 (**C**H-thiazole); 169.67, 169.83, 169.99, 170.64, 171.14, 171.23 (4 × CH$_3$**C**O, CH-**C**OOCH$_3$, C-2 thiazole). For **13** (C$_{32}$H$_{39}$NO$_{13}$S) calculated: relative molecular mass 677.73, monoisotopic mass 677.21. MS (FAB), *m/z*: 610.4 [M + Na]$^+$. For C$_{32}$H$_{39}$NO$_{13}$S (677.7) calculated: 56.71% C, 5.80% H, 2.07% N; found: 56.86% C, 5.69% H, 1.93% N.

Methyl (*S*)-2-Phenyl-2-({(2*R*,4*S*,6*S*)-4-[(α-D-galactopyranosyl)methyl]-6-(thiazol-2-yl)tetrahydropyran-2-yl}oxy)acetate (**14**)

Potassium cyanide (53 mg, 0.81 mmol) was added to a solution of compound **13** (850 mg, 1.26 mmol) in methanol (15 ml) and the reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel, affording 590 mg (93%) of compound **14** which crystallized from methanol with one molecule of solvent, m.p. 206–208°C (methanol). R_F 0.45 (chloroform–MeOH 20:1). [α]$_D$ +18.1 (*c* 1.18, MeOH). ^{1}H NMR (CD$_3$OD$_3$): 1.13–1.40 m, 3 H (H-3ax, H-4, H-5ax); 1.48–1.55 m, 1 H (H-1″a); 1.81–1.89 m, 1 H (H-1″b); 2.11–2.20 m, 1 H (H-3eq); 2.33–2.40 m, 1 H (H-5eq); 3.72 s, 3 H (CH-COOC**H**$_3$); 3.28–3.89 m, 6 H (H-2′, H-3′, H-4′, H-5′, H-6′a, H-6′b); 4.11–4.20 m, 1 H (H-1′); 4.85–4.89 m, 1 H (H-6); 4.93–4.96 m, 1 H (H-2); 5.54 s, 1 H (C**H**-COOCH$_3$); 7.34–7.46 m, 5 H (C$_6$**H**$_5$); 7.53 d, 1 H, *J* = 3.0 (**H**-thiazole); 7.75 d, 1 H, *J* = 2.9 (**H**-thiazole). ^{13}C NMR (CDCl$_3$): 31.60 (C-4); 32.29 (C-1″); 39.13 (C-5); 52.75

(CH-COOCH$_3$); 62.42 (C-6′); 70.19, 71.85, 72.97, 74.15, 76.36, 78.83 (C-6, CH-COOCH$_3$, C-5′, C-4′, C-3′, C-2′, C-1′); 102.30 (C-2); 120.58 (CH-thiazole); 128.39, 128.47, 129.49, 129.58, 129.72 (C_6H_5); 137.99 (*ipso* C_6H_5); 142.78 (CH-thiazole); 173.08 (thiazole C-2); 173.84 (CH-COOCH$_3$). For **14** ($C_{24}H_{31}NO_9S$) calculated: relative molecular mass 509.58, monoisotopic mass 509.17. MS (FAB), *m/z*: 510.2 $[M + H]^+$. For $C_{24}H_{31}NO_9S$ (509.6) calculated: 56.57% C, 6.13% H, 2.57% N; found: 56.42% C, 6.22% H, 2.46% N.

X-ray Structure Analysis of Compound **14**

The diffraction-quality crystals of compound **18** were grown from methanol at room temperature. Selected colourless crystal was mounted on glass fibres in random orientation using silicone fat. Diffraction data were collected using Nonius Kappa CCD diffractometer (Enraf–Nonius) at 150(1) K (Cryostream Cooler Oxford Cryosytem) and analyzed using the HKL program package[17]. The structures were solved by the direct, and refined by full-matrix least-squares techniques (SIR92 [18], SHELXL97 [19]). Scattering factors for the neutral atoms used were included in the program SHELXL97. The hydrogen atoms on non-C atoms were found on diference Fourier map and refined isotropically; the hydrogen ones on C-atoms were kept in theoretical positions (SHELXL97). Final geometric calculations were carried out with SHELXL97 and recent version of the PLATON program[20].

Pertinent crystallographic data for compound **14**: $C_{25}H_{34}NO_{10}S$, M_W = 540.59, monoclinic, space group $P2_1$ (No. 4), Z = 2, unit cell parameters a = 12.5130(3) Å, b = 8.1850(2) Å, c = 13.6220(3) Å, α = γ = 90°, β = 103.808(1)°, V = 1354.83(6) Å^{-3}, D_{calc} = 1.325 g cm^{-3}, F(000) = 574, λ (MoKα) = 0.71073 Å, μ = 0.175 mm^{-1}, θ in range from 3.08 to 27.47° (6173 measured reflections, 6171 unique data), R_1 = 0.0460, wR_2 = 0.1268 for 5857 observed reflections ($\geq 4\sigma(F_o)$), goodness-of-fit S = 1.058. The residual electron density was found between –0.606 and 0.717 e Å^{-3}. In the crystal, only weak hydrogen bonds (2.71–3.08 Å) were observed. The MeOH molecule is connected with the atom O3A (O···O distance is 2.71 Å).

CCDC 268332 (structure **14**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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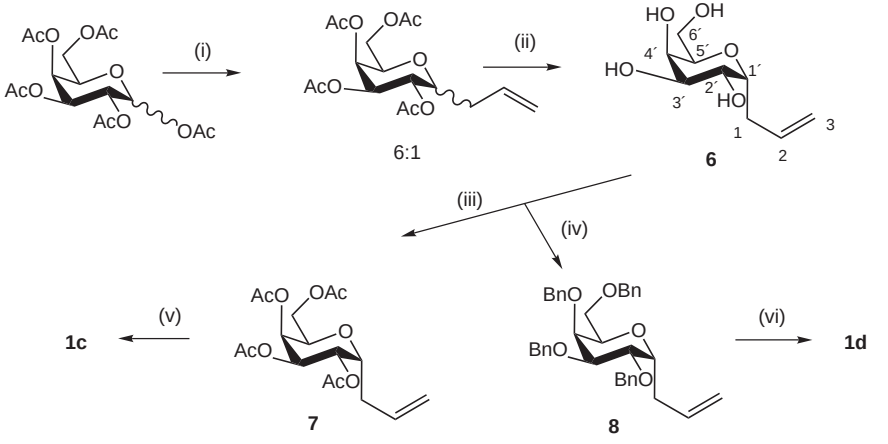
Erratum

Paper published in 2005, Vol. 70, No. 9, pp. 1411–1428:

Please replace the wrong Scheme 2 on page 1414 with the following:



(i) allyltrimethylsilane, $BF_3.Et_2O$, MeCN, reflux 4 h;

(ii) 1. MeONa/MeOH, 2. crystallization from EtOH/Et_2O; (iii) Ac_2O, pyridine; (iv) NaH, BnBr, DMF

(v) 1. O_3, CH_2Cl_2, 2. 2 phosphoranylidene-1-(thiazol-2-yl)-ethan-1-one

(vi) 1. O_3, CH_2Cl_2, 2. Me_2S, 3. 2 phosphoranylidene-1-(thiazol-2-yl)-ethan-1-one.

SCHEME 2