Use of the Cationic Iridium Complex 1,5-Cyclooctadiene-bis[methyldiphenylphosphine]-iridium Hexafluorophosphate in Carbohydrate Chemistry: Smooth Isomerization of Allyl Ethers to 1-Propenyl Ethers

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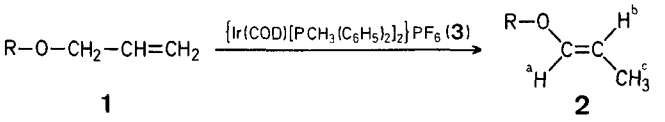
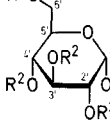
Protection of hydroxy functions of sugar derivatives by the allyl group has been shown to be a useful step[1] in the synthesis of oligosaccharides. Removal of the *O*-allyl group is achieved by a two-step process: isomerization of the allyl ether to the 1-propenyl ether (e.g., **1**→**2**), and conversion of the propenyl ether into the free alcoholic group using acid[2] or the $HgCl_2/HgO$ reagent[3].

Up to now, the method of choice to effect this isomerization consisted of treating the allyl ether (e.g. **1**) with tris[triphenylphosphine]-rhodium chloride at elevated temperature[4]. However, one of the drawbacks of the rhodium catalyst is that part of the allyl ether is reduced to the propyl ether. The occurrence of this side reaction has been reported earlier[5,6] and it has recently[7] also been observed in the isomerization of **1a** to **2a** (e.g., 10% of the reduced derivative was observed). This undesired reduction renders the rhodium catalyst less attractive and unreliable in the synthesis of complex glucophospholipids and oligosaccharides.

It has been reported[8] that allyl ethers (**1**, R = alkyl, aryl) can be isomerized stereoselectively to give the corresponding *trans*-1-propenyl ethers (**2**) in high yield using the hydrogen-activated cationic iridium complex **3**. We describe here the use of complex **3**, 1,5-cyclooctadiene-bis[methyldiphenylphosphine]-iridium hexafluorophosphate, for the isomerization of allyl ethers (**1**) of glycerol or glucose having various protective groups to the corresponding 1-propenyl ethers (**2**).



1 2

1,2	R
a	$R^1 = H$, $R^2 = -CH_2-C_6H_5$
b	$R^1 = Ac$, $R^2 = -CH_2-C_6H_5$
c	
d	$R^1 = H$, $R^2 = -CH_2-C_6H_5$
e	$R^1 = -\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (levulinyl), $R^2 = -CH_2-C_6H_5$

1,2	R
f	$R^1 = H$
g	$R^1 = Ac$
h	$R^1 = R^2 = H$
i	$R^1 = R^2 = Ac$
j	$R^1 = -P(O)(Cl)-O-CH_2-CCl_3$, $R^2 = H$

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Treatment of 1-*O*-allyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-*sn*-glycerol[7] in peroxide-free tetrahydrofuran with a catalytic amount of the hydrogen-activated iridium complex **3** for 2 hours at room temperature gave, after work-up, the 1-propenyl ether derivative **2a** as an oil. The absence of a propyl group was established unambiguously by ^{1}H- and ^{13}C-N.M.R. spectroscopy as well as by chemical means. The reaction of product **2a** with the $HgCl_2$/HgO reagent[3], as monitored by T.L.C., led to complete conversion of **2a** into a product with a lower R_f value. It should be noted that the purified product **2a** prepared by the present method can be crystallized from ether/petroleum ether to give isomerically pure *trans*-**2a**. Compounds **2b–e** are also obtained in the *trans* form.

It was found that the present method is also applicable to glucose derivatives such as **1f**[10] and **1h**[10] containing the sensitive tetraisopropyldisiloxane-1,3-diyl group[9] and to glucose derivatives of the type **1j** containing the tetraisopropyldisiloxane-1,3-diyl and the *O*-(2-chlorophenyl)-*O*-(2,2,2-trichloroethyl)-phosphoryl group; in these cases, the silyl and phosphoryl groups are not cleaved under the reaction conditions. The structures of products **2f, h, j** were confirmed by C,H analyses, ^{1}H-, ^{13}C-, and (for **2j**) ^{31}P-N.M.R. spectrometry, and by chemical means such as *O*-acetylation (**2f→2g, 2h→2i**) and complete cleavage (as monitored by T.L.C.) of the *O*-propenyl group using the $HgCl_2$/HgO reagent. It is worth mentioning that the attempted isomerization of the *O*-allyl group in compound **1j** using tris[triphenylphosphine]-rhodium chloride was unsuccessful; under the conditions employed, not only reduction of the allyl group occurred but also degradation of the phosphotriester function into a phosphodiester function.

The data reported here show that the isomerization of allyl ethers using complex **3** represents a preparatively useful method which is performed under neutral and mild conditions and which can be applied to substrates containing sensitive groups. The propenyl ethers thus obtained may be converted into the free hydroxy compounds by treatment with the $HgCl_2$/HgO reagent. In contrast, the method using palladium on charcoal in the presence of a strong acid at elevated temperatures for removal of the *O*-allyl group[16] which involves allyl-propenyl isomerization and *in situ* cleavage of the intermediate 1-propenyl group can only be applied to substrates not containing acid-labile protective groups. A further advantage of the iridium catalyst procedure is the potential use of the product propenyl ethers **2** in the synthesis of valuable sugar derivatives. Thus, for example, 2-deoxy-2-aminosugar derivatives having a propenyloxy group on the anomeric center can be easily converted[17] into intermediates which can be used for the formation of interglycosidic linkages[18].

T.L.C. analysis was carried out on silica gel (TLC-Ready Plastic Sheets LS 254 Silica Gel, Schleicher & Schüll) in solvent A: ether/petroleum ether (b.p. 40–60 °C), 5:2, v/v; B: ether/petroleum ether (b.p. 40–60 °C), 7:2 v/v; C: ether/petroleum ether (b.p. 40–60 °C), 1:1, v/v. Visualization of compounds **1a–j** and **2a–j** was obtained either by U.V. spectroscopy (254 nm) or by spraying with a solution of potassium permanganate (1%, w/v) in aqueous sodium carbonate (2%, w/v) or with sulfuric acid (20%, v/v) in methanol. Short-column chromatography was carried out on silica gel (Merck, Kieselgel 60). The ^{1}H-N.M.R. spectra were recorded on a Jeol JNM PS 100 spectrometer at 100 MHz. The ^{13}C(^{1}H)-N.M.R. spectra and the ^{31}P-N.M.R. spectra were recorded on a Jeol JNM PS 100 at 25.15 MHz on line with a EC-100 computer for Fourier transformation. Optical rotations were measured at 25 °C with a Perkin-Elmer 141 Polarimeter.

Complex **3**, *1,5-cyclooctadiene-bis[methyldiphenylphosphine]-iridium hexafluorophosphate*, was prepared following the procedure of Ref.[11].

3-*O*-*trans*-1-Propenyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-*sn*-glycerol (2a); Typical Isomerization Procedure:

To a solution of 3-*O*-allyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-*sn*-glycerol[7] [homogeneous syrup, R_f (solvent A): 0.35; **1a**; 0.49 g, 0.75 mmol] in peroxide-free tetrahydrofuran (freshly distilled from lithium aluminium hydride) is added the iridium catalyst (**3**; 0.75 mg, 0.9 mmol). The stirred solution is degassed, placed under dry and oxygen-free nitrogen, and degassed once more. The catalyst is activated by hydrogen during which operation the slightly red suspension becomes colourless. To effect isomerization, the solution is degassed once more after 5 min and left at room temperature for 2 h under an atmosphere of dry and oxygen-free nitrogen. T.L.C. analysis (solvent A) shows complete conversion of the allyl ether (**1a**; R_f 0.35) into the propenyl ether **2a** (R_f 0.37). The solvent is evaporated and the residual oil is dissolved in chloroform (50 ml). The solution is washed with aqueous 10% sodium hydrogen carbonate (10 ml) and water (10 ml). The organic layer is dried with magnesium sulfate, and concentrated to an oil. The oily product is purified by short-column chromatography (8 g) using ether/petroleum ether (2:1, v/v). Elution of the column with the same solvent mixture and concentration of the appropriate fractions affords **2a** as a glass; yield: 444 mg (91%). The product is crystallized from ether/petroleum ether; m.p. 87–87.3 °C; R_f (solvent A): 0.37; $[\alpha]_D^{25}$: +48.3 (*c* 0.27, chloroform).

$C_{40}H_{46}O_8$	calc.	C 73.37	H 7.08	O 19.55
(654.8)	found	72.67	7.46	19.82

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 1.5–1.6 (dd, 3H, —CH=CH—CH$_3$, $J_{c,b}$ = 6 Hz, $J_{c,a}$ = 2 Hz); 2.: (broad, 1H, —OH); 4.7–5.1 (m, 1H, CH=CH—CH$_3$); 5.1 (d, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 6.1–6.3 (dd, 1H, —CH=CH—CH$_3$, $J_{a,b}$ = 13 Hz, $J_{a,c}$ = 2 Hz); 7.1–7.3 ppm (broad, 20 H_{arom}).

^{13}C{^{1}H}-N.M.R. ($CDCl_3$/TMS_{int}): δ = 12.5 (s, —CH=CH—CH$_3$); 97.1 (s, C-1′); 98.9 (s, —CH=CH—CH$_3$); 137.6, 137.9, 138.0, 138.6 (s, 4 C-1_{arom}); 146.2 ppm (s, —CH=CH—CH$_3$).

1-*O*-Acetyl-3-*O*-allyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-*sn*-glycerol (1b):

3-*O*-Allyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-*sn*-glycerol[7] (**1a**; 0.28 g, 0.43 mmol) is stirred with acetic anhydride (1 ml) and dry pyridine (2 ml). After 2 h, T.L.C. analysis (solvent A) shows the reaction to be complete. After concentration under reduced pressure the resulting oil is twice co-evaporated with toluene (10 ml) and alcohol (10 ml) to give **1b** as a homogeneous glass: yield: 0.31 g (100%); R_f (solvent A): 0.55.

$C_{42}H_{48}O_9$	calc.	C 72.40	H 6.94
(696.8)	found	72.16	7.15

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 2.0 (s, 3H, —CO—CH$_3$); 5.15 (s, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 5.0–5.4 (m, 2H, —CH$_2$—CH=CH$_2$); 5.6–6.1 (m, 1H, —CH$_2$—CH=CH$_2$); 7.1–7.5 ppm (broad, 20 H_{arom}).

1-*O*-Acetyl-3-*O*-*trans*-1-propenyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-*sn*-glycerol (2b):

Compound **2b** is obtained by treating **1b** (0.14 g, 0.2 mmol) in the same manner as described for the isomerization of **1a**; yield of homogeneous glassy **2b**: 0.13 g (95%); R_f (solvent A): 0.6.

$C_{42}H_{48}O_9$	calc.	C 72.40	H 6.94
(696.8)	found	72.20	7.13

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 1.5–1.6 (dd, 3H, —CH=CH—CH$_3$, $J_{c,a}$ = 2 Hz, $J_{c,b}$ = 6 Hz); 2.0 (s, 3H, —CO—CH$_3$); 4.8–5.2 (m, 1H, CH=CH—CH$_3$); 5.1 (s, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 6.2–6.35 (dd, 1H, —CH=CH—CH$_3$, $J_{a,b}$ = 13 Hz, $J_{a,c}$ = 2 Hz); 7.1–7.5 ppm (broad, 20 H_{arom}).

1,2-*O*-Isopropylidene-3-*O*-*trans*-1-propenyl-*sn*-glycerol (2c):

Compound **2c** is obtained by treating 3-*O*-allyl-1,2-*O*-isopropylidene-*sn*-glycerol[12] (**1c**; b.p. 97 °C/35 torr; 0.17 g, 1 mmol) in the same manner as described for the isomerization of **1a**; yield of **2c** as an oil: 0.16 g (95%); b.p. 22 °C/0.1 torr (Ref.[12], b.p. 44 °C/0.8 torr): R_f (ether/petroleum ether 1/4): 0.60.

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 1.5–1.6 (dd, 3H, —CH=CH—CH$_3$, $J_{c,b}$ = 6 Hz, $J_{c,a}$ = 2 Hz); 3.6–4.4 (m, 5H, glycerol protons); 4.5–5.0 (sext, 1H, —CH=CH—CH$_3$, $J_{b,a}$ = 13 Hz, $J_{b,c}$ = 6 Hz); 6.2–6.5 ppm (dd, 1H, CH=CH—CH$_3$, $J_{a,b}$ = 13 Hz, $J_{a,c}$ = 2 Hz).

***trans*-1-Propenyl 2,3,4-Tri-*O*-benzyl-α-D-glucopyranoside (2d):**
Compound **2d** is obtained by treating allyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[13] [**1d**; colorless oil; R_f (solvent C): 0.35; 0.11 g, 0.2 mmol] in the same manner as described for the isomerization of **1a**; yield of homogeneous **2d** as an oil: 0.09 g (90%); R_f (solvent C): 0.35.

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 1.4–1.8 (dd, 3H, —CH CH—CH$_3$, $J_{c,b}$ = 6 Hz, $J_{c,a}$ = 2 Hz); 4.0–5.3 (m, 1H, —CH CH—CH$_3$); 5.0 (d, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 5.9–6.2 (dd, 1H, —CH=CH—CH$_3$, $J_{a,b}$ = 13 Hz, $J_{a,c}$ = 2 Hz); 7.1–7.4 ppm (broad, 15 H_{arom}).

Allyl 2,3,4-Tri-*O*-benzyl-6-*O*-levulinyl-α-D-glucopyranoside (1e):
Allyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[13] (**1d**; 0.07 g, 0.15 mmol) is *O*-acylated with levulinic anhydride[14] (0.04 g, 0.2 mmol) in pyridine (3 ml) in the presence of a catalytic amount of 4-dimethylaminopyridine. When, after 2 h, T.L.C. analysis (solvent C) shows the reaction to be complete, water (1 ml) is added. The pyridine is removed by evaporation under reduced pressure and the residue is partitioned between chloroform (50 ml) and 10% aqueous sodium hydrogen carbonate (20 ml). The organic layer is washed with water (20 ml), dried with magnesium sulfate, and concentrated to an oil, which is purified by short-column chromatography on silica gel (3 g) in solvent C. Elution of the column with the same solvent mixture and concentration of the appropriate fractions affords **1e** as an oil; yield: 0.08 g (87%); R_f (solvent C): 0.50.

$C_{35}H_{40}O_8$	calc.	C 71.41	H 6.85
(588.7)	found	70.99	7.07

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 2.1 (s, CH_{3lev}); 2.4–2.8 (m, 4H, —CH_2—CH_2—$_{lev}$); 5.0 (1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 5.0–5.4 (m, 2H, —CH_2—CH=CH_2); 5.7–6.1 (m, 1H, —CH_2—CH=CH_2); 7.2–7.5 ppm (broad, 15 H_{arom}).

***trans*-1-Propenyl 2,3,4-Tri-*O*-benzyl-6-*O*-levulinyl-α-D-glucopyranoside (2e):**
Compound **2e** is obtained by treating **1e** (0.08 g, 0.14 mmol) in the same manner as described for the isomerization of **1a**; yield of **2e** as a homogeneous oil: 0.065 g (85%); R_f (solvent C): 0.55.

$C_{35}H_{40}O_8$	calc.	C 71.41	H 6.85
(588.7)	found	70.97	7.19

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 1.5–1.6 (dd, 3H, —CH CH—CH$_3$, $J_{c,a}$ = 2 Hz, $J_{c,b}$ = 6 Hz); 2.1 (s, 3H, CH_{3lev}); 2.5–2.8 (m, 4H, —CH_2—CH_2—$_{lev}$); 5.1 (d, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 5.0–5.3 (m, 1H, —CH CH—CH$_3$); 6.1–6.2 (dd, 1H, —CH=CH—CH$_3$, $J_{a,b}$ = 13 Hz, $J_{a,c}$ = 2 Hz); 7.3–7.4 ppm (broad, 15 H_{arom}).

Allyl 4,6-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (1f):
Allyl α-D-glucopyranoside[19] (4.4 g, 20 mmol) is stirred with 1,3-dichlorotetraisopropyldisiloxane[10] (6 g, 20 mmol) in pyridine (40 ml) for 1 h at 0 °C. The reaction is stopped by the addition of methanol (0.5 ml) and the mixture concentrated under reduced pressure. The resultant oil is dissolved in chloroform (200 ml), the solution washed with 10% aqueous sodium hydrogen carbonate (50 ml) and water (50 ml), dried with magnesium sulfate, and concentrated to an oil, which is purified by short-column chromatography on silica gel (150 g) in chloroform/aceton (100–96: 0–4, v/v). Elution of the column with the same solvent mixture and concentration of the appropriate fractions gives **1f** (5 g, 54%) as an oil, which is crystallized from aqueous acetonitrile; yield: 3.28 g (36%); m.p. 95–96°; R_f (solvent B): 0.30; $[\alpha]_D^{25}$: +54.91 (*c* 7.3, chloroform).

$C_{21}H_{42}O_7Si_2$	calc.	C 54.51	H 9.15
(462.7)	found	54.45	9.20

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 1.0–1.2 [broad, 28H, 4 CH(CH_3)$_2$]; 4.95 (d, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 5.1–5.4 (m, 2H, —CH_2—CH=CH_2); 5.7–6.1 ppm (m, 1H, —CH_2—CH=CH_2).

$^{13}C\{^1H\}$-N.M.R. ($CDCl_3$/TMS_{int}): δ = 12.5, 13.3, 13.6 [s, CH(CH$_3$)$_2$]; 17.3 [s, CH(CH$_3$)$_2$]; 68.5 (s, —CH_2—CH=CH_2); 97.6 (s, C-1′); 117.8 (s, —CH_2—CH=CH_2); 133.6 ppm (s, —CH_2—CH=CH_2).

***trans*-1-Propenyl 4,6-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (2f):**
Compound **2f** is obtained by treating **1f** (0.105 g, 0.23 mmol) in the same manner as described for the isomerization of **1a**; yield of **2f** as a homogeneous glassy product: 0.10 g (96%); R_f (solvent B): 0.33.

$C_{21}H_{42}O_7Si_2$	calc.	C 54.51	H 9.15
(462.7)	found	54.46	9.10

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 1.0–1.2 [broad, 28H, 4 CH(CH_3)$_2$]; 1.4–1.6 (dd, 3H, —CH CH—CH$_3$); 5.1 (d, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 4.9–5.2 (m, 1H, —CH CH—CH$_3$); 6.0–6.2 ppm (dd, 1H, —CH=CH—CH$_3$, $J_{a,b}$ = 13 Hz, $J_{a,c}$ = 2 Hz).

Allyl 2,3-Di-*O*-acetyl-4,6-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (1g):
Compound **1f** (1.05 g, 2.3 mmol) is acetylated with acetic anhydride (5 ml) in pyridine (10 ml). After 24 h, T.L.C. analysis (solvent B) shows the reaction to be complete. Workup as described for **1b** affords compound **1g** as a homogeneous oil; yield: 1.26 g (100%); R_f (solvent B): 0.62; $[\alpha]_D^{25}$: +52.2 (*c* 1.53, chloroform).

$C_{25}H_{46}O_9Si_2$	calc.	C 54.91	H 8.48
(546.8)	found	54.73	8.63

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 0.9–1.2 [broad, 28H, 4 CH(CH_3)$_2$]; 2.0 (s, 6H, 2 —CO—CH$_3$); 4.6–4.8 (dd, 1H, 2′-H, $J_{2',1'}$ = 3.5 Hz, $J_{2',3'}$ = 10.5 Hz); 5.0 (d, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 5.0–5.5 (m, 2H, —CH_2—CH=CH_2); 5.3–5.5 (t, 1H, 3′-H, $J_{2,3'}$ = 10.5 Hz); 5.7–6.1 ppm (m, 1H, —CH_2—CH=CH_2).

$^{13}C\{^1H\}$-N.M.R. ($CDCl_3$/TMS_{int}): δ = 12.6, 13.3, 13.6 [s, CH(CH_3)$_2$]; 17.1, 17.2 [CH(CH_3)$_2$]; 20.6, 21.0 (s, —CO—CH_3); 68.4 (s, CH_2—CH=CH_2); 95.0 (s, 1′-C); 117.6 (s, —CH_2—CH=CH_2); 133.4 (s, —CH_2—CH=CH_2); 169.6, 170.1 ppm (s, —CO—CH$_3$).

***trans*-1-Propenyl 2,3-Di-*O*-acetyl-4,6-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (2 g):**
Compound **2f** (0.11 g, 0.24 mmol) is acetylated as described for the synthesis of **1b** to give **2g** as a homogeneous oil; yield: 0.13 g (100%); R_f (solvent B): 0.64.

$C_{25}H_{46}O_9Si_2$	calc.	C 54.91	H 8.48
(546.8)	found	54.37	8.69

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 0.9–1.1 [broad, 28H, 4 CH(CH_3)$_2$]; 1.5–1.6 (dd, 3H, CH=CH—CH$_3$, $J_{c,a}$ = 2 Hz, $J_{c,b}$ = 6 Hz); 2.0 (s, 6H, 2 —CO—CH$_3$); 4.7–4.9 (dd, 1H, 2′-H, $J_{2',1'}$ = 3.5 Hz, $J_{2',3'}$ = 10.5 Hz); 5.1 (s, 1H, 1′-H, $J_{1',2'}$ = 3.5 Hz); 5.0–5.3 (m, 1H, —CH CH—CH$_3$); 5.5 (t, 1H, 3′-H, $J_{2,3'}$ = 10.5 Hz); 6.1–6.2 ppm (dd, 1H, —CH=CH—CH$_3$, $J_{a,b}$ = 13 Hz, $J_{a,c}$ = 2 Hz).

$^{13}C\{^1H\}$-N.M.R. ($CDCl_3$/TMS_{int}): δ = 12.4, 12.6, 13.2, 13.6 [s, CH(CH_3)$_2$, —CH CH—CH_3]; 20.7, 21.1 (s, —CO—CH_3); 95.1 (s, C-1′); 104.8 (s, —CH=CH—CH$_3$); 142.4 (s, —CH=CH—CH$_3$); 169.8, 170.2 ppm (s, —CO—CH$_3$).

Allyl 3,4-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (1h):
Compound **1f** (102 mg, 2.2 mmol) is rearranged[10] by stirring with mesitylenesulfonic acid (40 mg, 0.2 mmol) in dry dimethylformamide for 12 h. The mixture is then neutralized with methanolic ammonia (half saturated at 0 °C) and concentrated under reduced pressure. The resultant oil is dissolved in chloroform (100 ml), washed with aqueous sodium hydrogen carbonate (10%, w/v, 20 ml) and water (20 ml), dried with magnesium sulfate, and concentrated to an oil, which is purified by short-column chromatography on silica gel (20 g) in chloroform/aceton (99 : 1, v/v). Elution of the column with the same solvent mixture and concentration of the appropriate fractions affords **1h** as a homogeneous glass; yield: 0.72 g (80%); R_f (solvent B): 0.42; $[\alpha]_D^{25}$: +72.3 (*c* 1.4, chloroform).

$C_{21}H_{42}O_7Si_2$	calc.	C 54.51	H 9.15
(462.7)	found	54.42	9.22

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 0.9–1.1 [broad, 28H, 4 CH(CH_3)$_2$]; 4.9 (d, 1H, 1′-H, $J_{1',2}$ = 3.5 Hz); 5.2–5.4 (m, 2H, —CH_2—CH=CH_2); 5.8–6.2 ppm (m, 1H, —CH_2—CH=CH_2).

$^{13}C\{^1H\}$-N.M.R. ($CDCl_3$/TMS_{int}): δ = 12.1, 12.2, 12.8, 12.9 [s, CH(CH_3)$_2$]; 17.3 [s, CH(CH_3)$_2$]; 68.6 (s, —CH_2—CH=CH_2); 97.1 (*C*-1′); 117.7 (s, —CH_2—CH=CH_2); 133.7 ppm (s, —CH_2—CH=CH_2).

Allyl 2,6-Di-*O*-acetyl-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (1i):
Compound **1h** (0.11 g, 0.24 mmol) is acetylated as described for the synthesis of **1b** to give **1i** as a homogeneous oil; yield: 0.13 g (100%); R_f (solvent B): 0.64; $[\alpha]_D^{25}$: +66.1 (*c* 7.15, chloroform).

$C_{25}H_{46}O_9Si_2$	calc.	C 54.91	H 8.48
(546.8)	found	54.41	8.75

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 0.9$–1.1 [broad, 28H, 4 CH(CH$_3$)$_2$]; 2.1 (s, 6H, 2 —CO—CH$_3$); 4.7–4.9 (dd, 1H, 2′-H, $J_{2',3'} = 9$ Hz, $J_{2',1'} = 3.5$ Hz); 5.0 (d, 1H, 1′-H, $J_{1',2'} = 3.5$ Hz); 5.1–5.4 (m, 2H, —CH$_2$—CH=CH$_2$); 5.7–6.1 ppm (m, 1H, —CH$_2$—CH=CH$_2$).

^{13}C{^{1}H}-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 12.2$, 12.8, 12.9, 13.7 [s, CH(CH$_3$)]; 17.2 [s, CH(CH$_3$)$_2$]; 20.7, 20.8 (s, —CO—CH$_3$); 68.3 (s, —CH$_2$—CH=CH$_2$); 92.2 (s, C-1′); 117.4 (s, —CH$_2$—CH=CH$_2$); 133.5 (s, —CH$_2$—CH=CH$_2$); 170.1, 170.6 ppm (s, —CO—CH$_3$).

***trans*-1-Propenyl 3,4-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (2h):**

Compound **2h** is obtained by treating **1h** (80 mg, 0.18 mmol) in the same manner as described for the isomerization of **1a**; yield of **2h** as a homogeneous glass: 75 mg (90%); R_f (solvent B): 0.44; $[\alpha]_D^{25}$: +64.8 (*c* 3, chloroform).

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 1.0$–1.2 [broad, 28H, 4 CH(CH$_3$)$_2$]; 1.5–1.6 (dd, 3H, —CH=CH—CH$_3$, $J_{c,a} = 2$ Hz, $J_{c,b} = 6.8$ Hz); 5.1 (s, 1H, 1′-H, $J_{1',2'} = 3.5$ Hz); 5.1–5.5 (m, 1H, —CH=CH—CH$_3$, $J_{b,c} = 6.8$, $J_{b,a} = 13$ Hz); 6.1–6.3 ppm (dd, 1H, —CH=CH—CH$_3$, $J_{a,b} = 13$ Hz, $J_{a,c} = 2$ Hz).

^{13}C{^{1}H}-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 12.1$, 12.2, 12.8, 12.9 [s, CH(CH$_3$)$_2$ and —CH=CH—CH$_3$]; 17.2 (s, CH(CH$_3$)$_2$]; 97.3 (s, C-1′); 105.4 (s, —CH=CH—CH$_3$); 142.6 ppm (s, —CH=CH—CH$_3$).

***trans*-1-Propenyl 2,6-Di-*O*-acetyl-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (3i):**

Compound **2h** (0.06 g, 0.13 mmol) is acetylated as described for the synthesis of **1b** to afford **2i** as an oil; yield: 0.07 g (100%); R_f (solvent B): 0.68; $[\alpha]_D^{25}$: +65.1 (*c* 2.5, chloroform).

$C_{25}H_{46}O_9Si_2$	calc.	C 54.91	H 8.48
(546.8)	found	54.53	8.96

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $d = 0.9$–1.1 [broad, 28H, CH(CH$_3$)$_2$]; 1.5–1.6 (dd, 3H, —CH=CH—CH$_3$, $J_{c,a} = 2$ Hz, $J_{c,b} = 6$ Hz); 2.1 (s, 6H, 2 —CO—CH$_3$); 4.8–4.9 (dd, 1H, 2′-H, $J_{2',1'} = 3.5$ Hz, $J_{2',3'} = 9$ Hz); 5.1 (d, 1H, 1′-H, $J_{1',2'} = 3.5$ Hz); 5.1–5.3 (m, 1H, —CH=CH—CH$_3$); 6.1–6.3 ppm (dd, 1H, —CH=CH—CH$_3$, $J_{a,b} = 16$ Hz, $J_{a,c} = 2$ Hz).

^{13}C{^{1}H}-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 12.1$, 12.4, 12.7, 12.8 [s, CH(CH$_3$)$_2$, —CH=CH—CH$_3$]; 17.2 [s, CH(CH$_3$)$_2$]; 20.7 (s, —CO—CH$_3$); 95.4 (s, C-1′); 105.3 (s, —CH=CH—CH$_3$); 142.5 (s, —CH=CH—CH$_3$); 170.2, 170.6 ppm (s, —CO—CH$_3$).

Allyl-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranosyl 6-*O*-[2,2,2-Trichloroethyl 2-Chlorophenyl Phosphate] (1j):

2,2,2-Trichloroethyl 2-chlorophenyl phosphochloridate[15] (0.41 g, 1.13 mmol) is added to a stirred solution of **1h** (0.52 g, 1.13 mmol) in dry pyridine (5 ml). After 1 h, T.L.C. analysis (solvent B) indicates the reaction to be complete. The mixture is concentrated to an oil and the residue dissolved in chloroform (50 ml). The solution is washed with 5% aqueous sodium hydrogen carbonate (20 ml) and water (20 ml). The organic layer is dried with magnesium sulfate and concentrated to an oil, which is purified by short-column chromatography on silica gel (10 g) in chloroform/acetone (99:1, v/v). Elution of the column with the same solvent system and concentration of the appropriate fractions gives **1j** as an oil; yield: 0.56 g (63%); R_f (solvent B): 0.37; $[\alpha]_D^{25}$: +52.3 (*c* 1.30, chloroform).

$C_{29}H_{47}Cl_4O_{10}PSi_2$	calc.	C 44.39	H 6.04
(784.6)	found	44.02	6.39

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$) of a mixture of diastereoisomers of **1j**: $\delta = 0.9$–1.1 [broad, 28H, 4 CH(CH$_3$)$_2$]; 2.1 (broad, 1H, 2′-OH); 4.7 (2H, —CH$_2$—CCl$_3$, $^3J_{P,H} = 6$ Hz); 4.8–4.9 (dd, 1H, 1′-H, $J_{1',2'} = 3.5$ Hz); 5.1–5.4 (m, 2H, —CH$_2$—CH=CH$_2$); 5.7–6.1 (m, 1H, —CH$_2$—CH=CH$_2$); 7.0–7.6 ppm (m, 4H$_{arom}$).

^{13}C{^{1}H}-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 12.1$, 12.2, 12.7, 12.8 [s, CH(CH$_3$)$_2$]; 17.3 [s, CH(CH$_3$)$_2$]; 68.5 (s, —CH$_2$—CH=CH$_2$); 77.1, 77.3 (d, —CH$_2$—CCl$_3$, $^2J_{C,P} = 4.6$ Hz); 94.4, 93.7 (d, —CH$_2$—CCl$_3$, $^3J_{C,P} = 11.8$ Hz); 96.8 (s, C-1′); 117.9 (s, —CH$_2$—CH=CH$_2$); 133.4 (s, —CH$_2$—CH=CH$_2$); 146.1, 146.4 ppm (d, C—Cl$_{arom}$, $^3J_{C,P} = 6.5$ Hz).

^{31}P-N.M.R. ($CDCl_3/H_3PO_{4ext}$): $\delta = -8.60$, -8.64 ppm (s).

***trans*-1-Propenyl-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranosyl 6-*O*-[2,2,2-Trichloroethyl 2-Chlorophenyl Phosphate] (2j):**

Compound **2j** is obtained by treating **1j** (0.56 g, 0.71 mmol) in the same manner as described for the isomerization of **1a**; yield of homogeneous **2j** as an oil: 0.52 g (95%); R_f (solvent B): 0.45.

$C_{29}H_{47}Cl_4O_{10}PSi_2$	calc.	C 44.39	H 6.04
(784.6)	found	44.12	6.28

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$) of a mixture of diastereoisomers of **2j**: $\delta = 0.9$–1.1 [broad, 28H, 4 CH(CH$_3$)$_2$]; 1.4–1.6 (dd, 3H, —CH=CH—CH$_3$, $J_{c,b} = 6.8$ Hz, $J_{c,a} = 2$ Hz); 2.2 (broad, 1H, 2′-OH); 4.6–4.8 (d, 2H, —CH$_2$—CCl$_3$, $^3J_{H,P} = 6$ Hz); 4.9–5.3 (m, 1H, —CH=CH—CH$_3$, $J_{b,c} = 6.8$ Hz, $J_{b,a} = 13$ Hz); 4.9–5.1 (dd, 1H, 1′-H, $J_{1',2'} = 3.5$ Hz); 7.0–7.6 ppm (m, 4H$_{arom}$).

^{13}C{^{1}H}-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 12.1$, 12.3, 12.7, 12.9 [s, CH(CH$_3$)$_2$ and —CH=CH—CH$_3$]; [s, CH(CH$_3$)$_2$]; 77.1, 77.3 (d, —CH$_2$—CCl$_3$, $^2J_{C,P} = 4.5$ Hz); 94.3, 94.8 (d, —CH$_2$—CCl$_3$, $^3J_{C,P} = 12.1$ Hz); 97.3 (s, C-1′); 105.3 (s, —CH=CH—CH$_3$); 142.7 (s, —CH=CH—CH$_3$); 146.2, 146.4 ppm (d, C—Cl$_{arom}$, $^3J_{C,P} = 5.4$ Hz).

^{31}P-N.M.R. ($CDCl_3/H_3PO_{4ext}$): $\delta = -8.68$, -8.70 ppm (s).

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