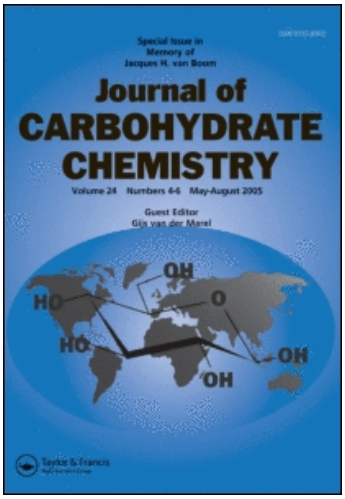

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Ramza, Jan , Descotes, Gerard , Basset, Jean-Marie and Mutch, Andy(1996) 'Metathesis Of Ω-Unsaturated Glycosides with Chloro-Aryloxide Complexes of Tungsten, as a New Synthetic Route Leading to Unsaturated Neutral Bolaforms', Journal of Carbohydrate Chemistry, 15: 2, 125 — 136
To link to this Article: DOI: 10.1080/07328309608005433
URL: http://dx.doi.org/10.1080/07328309608005433

J. CARBOHYDRATE CHEMISTRY, 15(2), 125-136 (1996)

Metathesis of Ω-Unsaturated Glycosides with Chloro-Aryloxide Complexes of Tungsten, as a New Synthetic Route Leading to Unsaturated Neutral Bolaforms

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Received December 15, 1994 - Final Form November 9, 1995

ABSTRACT

Glucosides of unsaturated alcohols, bearing different functional groups on the carbohydrate units, underwent catalytic metathesis reaction affording neutral bolaforms in good yields. Tungsten aryloxo-complexes (**1** and **2**), due to large steric hindrance, were found to be superior catalysts for this process.

INTRODUCTION

Bolaforms represent a group of compounds which consist of two hydrophilic heads joined together by a long hydrophobic spacer (aliphatic chain). During recent years interest in this group of compounds has grown, because of their unusual properties as surfactants[1,2] (they are able to form micelles and vesicles), and their ability to form very thin monolayer lipid membranes.[3] Bolaforms have also been used for studying mechanisms of membrane processes,[2] as well as some enzymatic reactions,[4,5] and have

been investigated as liquid crystals.[6] Consequently, the practical use of these compounds is expected to grow in the near future. Among one of the most interesting classes of bolaforms is the neutral form containing carbohydrate units at both ends of the long aliphatic chain.

As previously reported,[7] one of the most simple and effective synthetic routes leading to carbohydrate-based bolaforms is the olefin metathesis - a well known catalytic reaction intensively studied for thirty years, because of numerous practical applications.[8,9,10] This reaction was mainly applied to acyclic and cyclic olefins, and in a few cases to olefins bearing single functional groups[11,12] (e.g., esters, ethers, thioethers, quaternary ammonium salts, nitriles). Application of this catalytic reaction for polyfunctional, polyoxygenated substrates, as carbohydrates has extended the scope of synthetic utility of this method. Here we present full experimental details for our preliminary results in this area, and an extension of the investigation employing glucoside substrates bearing more than one olefinic function.

RESULTS AND DISCUSSION

Recently developed by us, a new generation of chloro-aryloxide complexes of tungsten, (**1** and **2**, Figure 1) are among the most active catalysts in metathesis of olefins bearing functional groups (e.g., esters, thioethers, phosphoranes).[13,14] Catalyst **1** is a bicomponent system, associating an air stable chloro-aryloxide tungsten (VI) complex with an alkylating agent such as SnR_4 and preferably PbR_4 (R = Et, Bu). It is considered, that the alkylating agent is necessary to carry out a double alkylation of the tungsten, followed by α-hydrogen transfer to generate *in situ* the metallocarbene. The most active and stereoselective catalyst **2** is derived from **1**, a cyclo metallated aryloxo (chloro) neopentylidene tungsten (VI) complex.[12,15]

Since the ligand environment around the tungsten atom is an extremely bulky (*O*, *O'*- diphenylphenoxy) group, and since bulky groups have difficulty coordinating to the metallocarbene, these catalysts are expected to tolerate a wide range of functional groups, especially esters and ethers. So it was logical to test these complexes with unsaturated *O*-protected carbohydrates, namely ω-unsaturated *O*-protected glucosides. The use of protecting groups on the sugar residue would seem to be necessary to prevent deactivation of the oxophilic and moisture sensitive catalysts with a d^o configuration. Some of the most commonly used *O*-protecting groups, namely acetyl, *t*-butyldimethylsilyl and benzyl were selected for preliminary experiments. Classical glycosylation[16] of 10-undecen-1-ol by 2,3,4,6-tetra-*O*-acetylglucopyranosyl bromide in the presence of the silver triflate, following deprotection and reprotection procedures[17,18] afforded the desired ω-unsaturated substrates **3,4,5**.

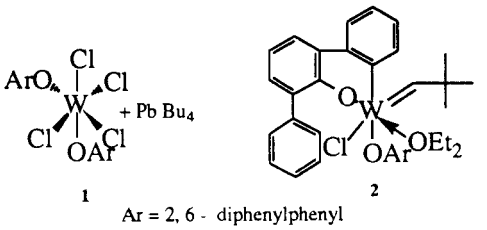


Figure 1

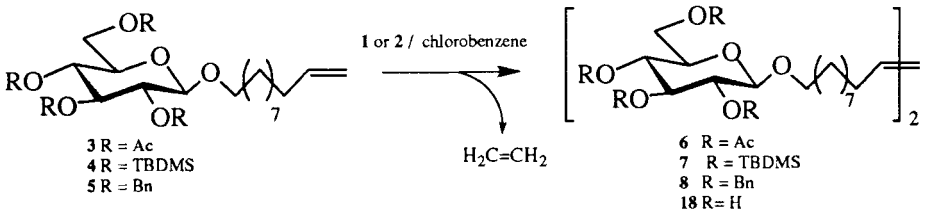


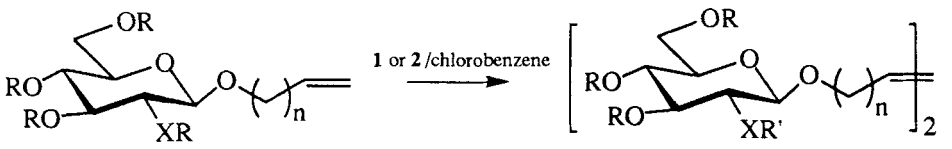
Figure 2

These substrates in the presence of catalysts **1** or **2** in chlorobenzene at 80 °C under argon gave expected metathesis products as shown in Figure 2.

Glucosides protected as acetyl esters or silyl ethers were found to be superior substrates in the metathesis reaction to the benzyl ether protected carbohydrate, the latter deactivating the catalyst and resulting in lower yield, even when a higher catalyst / substrate ratio was employed. (see Table 1).

The scope of this reaction was extended to *N*-acetyl aminosugars by successful application of glucosamine derivative **9** as another metathesis substrate (Figure 3).

4-Pentenyl and allyl glucosides **10** and **11**, prepared by the same glycosylation procedure as above, using 4-penten-1-ol and allyl alcohol, respectively, were also tested. Catalysts **1** and **2** were also active for the pentenyl glucoside **10** and results were as good as for the undecenyl substrate, whereas allyl glucoside **11** did not give any metathesis product. As we expected, in the case of allyl glucoside **11** as well as the benzyl protected substrate **5**, catalysts were deactivated by competitive coordination of the ether oxygen atoms to the metallocarbene. For silylated substrate **4**, the steric hindrance from the TBDMS group was large enough to inhibit this kind of complexation with the also sterically hindered tungsten. Similar steric effects were found to occur in metathesis of thioethers.[19]



9 R = Ac, X = NH, n = 9
10 R = Ac, X = O, n = 3
11 R = Ac, X = O, n = 1

12 R = R' = Ac, X = NH, n = 9
13 R = R' = Ac, X = O, n = 3

Figure 3

For the substrate **4** the catalyst developed by Mol[11] (Re_2O_7 / Al_2O_3 - SiO_2 /Pb Bu_4), gave no metathesis product. This result supports our hypothesis that steric hindrance effects play a key role in the metathesis reaction of polyfunctional compounds as the protection factor against catalyst deactivation.

Finally, we applied compounds **14** and **15** bearing two different olefinic groups as metathesis substrates. These substrates were prepared according to the method of Ferrier and Prasad[20] from 3,4,6-tri-*O*-acetyl-D-glucal with apropriate ω-unsaturated alcohols in the presence of BF_3 etherate. In both cases only the terminal isolated double bond was involved in the catalytic process (Figure 4). No sign of reaction involving the olefin part of the sugar ring was observed. We also did not observe any detectable increase in the deactivation rate of the catalyst by the ring olefin bearing three oxygen atoms at allylic positions.

Separations of products by column chromatography afforded for all metathesis reactions inseparable *E*/*Z* mixtures, but with predominance of one isomer. All reaction products were analysed by ^1H and ^{13}C NMR spectroscopy: proton and carbon atom signals of terminal double bond for substrates were replaced in products spectra by signals of symmetrically substituted olefins (results are summarized in Tables 1 and 2). However, it was not possible even after ^1H and ^{13}C NMR analysis to prove which isomer was the major reaction product.

Finally compound **6** was deprotected, by treatment with sodium methoxide in methanol, affording neutral bolaform **18**.

In conclusion, catalysts **1** and **2** appeared to be very efficient even in the presence of numerous functional groups. The steric hindrance from crowded aromatic substituents probably prohibits deactivation of the active metallocarbene by oxygen, and nitrogen atoms from functional groups of substrates. As result, metathesis was shown to be very effective for carbohydrate substrates, and an efficient method leading to unsaturated neutral bolaforms was developed.

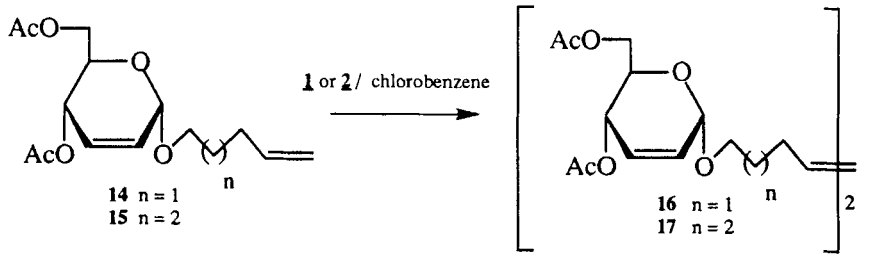


Figure 4

Table 1. Results obtained for catalytic metathesis reactions.

Substrate	Catalyst	Catalyst/substrate ratio	Reaction time hrs	Reaction temp. °C	Product	Yield %
3	**2**	1 : 10	12	80	**6**	64
3	**1**	1 : 5	12	80	**6**	52
4	**1**	1 : 12	12	65	**7**	51
4	**2**	1 : 12	12	65	**7**	92
5	**1**	1 : 5	12	80	**8**	37
5	**2**	1 : 15	12	80	no reaction	0
9	**1**	1 : 10	12	80	**12**	62
10	**1**	1 : 20	6	80	**13**	65
11	**2**	1 : 10	12	80	no reaction	0
11	**1**	1 : 8	12	80	no reaction	0
14	**1**	1 : 15	6	80	**16**	53
15	**1**	1 : 20	12	80	**17**	55

Table 2. Characteristic NMR data for olefinic protons and carbon atoms.

Substrates						Products		
N°	Hα	Hα'	Hβ	Cα	Cβ	N°	Hα=Hβ	Cα=Cβ
3	5.08	4.87	5.82	114.4	139.3	**6**	5.38	130.5
4	5.06	4.92	5.81	113.8	139.5	**7**	5.37	130.4
5	4.99	4.91	5.82	114.2	139.4	**8**	5.39	130.3
9	5.07	4.90	5.81	114.7	139.6	**12**	5.36	130.3
10	5.02	4.85	5.71	115.0	137;7	**13**	5.38	129.0
14	5.10	4.85	5.10	115.0	138.1	**16**	5.41	129.0
15	5.10	4.90	5.85	114.4	140.6	**17**	5.39	129.5

EXPERIMENTAL

General methods. All reactions were performed under argon atmosphere in flame dried reactions flasks. All solvents were distilled prior to use. Chlorobenzene and methylene chloride were dried according to standard procedures.[21] For column chromatography silica gel 60, 400-230 mesh (E. Merck) was employed. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker AM-200 spectrometer with TMS and $CDCl_3$ as internal standards respectively, with $CDCl_3$, as a solvent. For some cases decoupling experiments were done to ensure proton assignments. IR spectra were obtained using a Perkin Elmer 681 Infrared Spectrometer. Optical rotations were measured using a Perkin Elmer 241 Polarimeter.

10-Undecenyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside 3. To a solution of 2,3,4,6-tetra-*O*-acetyl-glucopyranosyl bromide (5 g, 12.2 mM) and 10-undecen-1-ol (3.71 g, 12.8 mM) in CH_2Cl_2 (25 mL) dried molecular sieves were added and after the mixture was stirred for 45 min at rt AgOTf (3.28 g, 12.8 mM) was added at 0 °C in one portion. The mixture was stirred overnight at rt. Triethylamine (2.04 mL, 14.6 mM) was added and the mixture was filtered (celite). Chromatography of the oily residue after solvent evaporation (hexane/ethyl acetate 7:1) gave compound **3** (4.09 g, 67%) as an oil: $[\alpha]_D$ -17.4 (*c* 0.7 , chloroform); IR ν_{max} 2920, 1750, 1640, 1225, 1040 cm^{-1}; ^1H NMR δ 5.80 (dddd, $J_{10'11'cis}$ 10.2, $J_{10'11'trans}$ 17.0, 2x $J_{9',10'}$ 6.6, 1H, H-10'), 5.21 (dd, $J_{3,4}$ 9.5, 1H,H-3), 5.12 (dd, $J_{4,5}$ 9.6, 1H, H-4), 5.03 (dd, $J_{2,3}$ 9.1, 1H, H-2), 4.97 (m, 2H, H-11'), 4.50 (d, $J_{1,2}$ 7.9, 1H, H-1), 4.28 (dd, $J_{5,6}$ 4.6, 1H, H-6), 4.14 (dd, $J_{6,6'}$ 12.3, 1H, H-6'), 3.88 (ddd, $J_{1',1''}$ 9.6, 2x$J_{1',2'}$ 6.2, 1H, H-1'), 3.70 (ddd, $J_{5,6'}$ 2.4, 1H, H-5), 3.47 (ddd, 2x$J_{1'',2'}$ 6.5, 1H, H-1''), 2.09, 2.04, 2.03, 2.01 (4xs, 12H, 4xCH_3CO), 2.0 (m, 2H H-9'), 1.56 (m, 2H, H-2'), 1.27 (m, 12H, $CH_{2\ alkyl}$); ^{13}C NMR 170.8, 170.4, 169.6, 169.4 (4 x CO), 139.3 (C-10'), 114.7 (C-11'), 101.0 (C-1), 73.0 (C-3), 71.9 (C-5), 71.5 (C-2), 70.4 (C-1'), 68.7 (C-4), 62.2 (C-6), 34.0-26.0 (8xC_{alkyl}), 20.9-20.8 (4 x CH_3 CO).

Anal. Calcd for $C_{25}H_{40}O_{10}$: C, 59.98; H, 8.05. Found: C, 59.98; H, 8.25.

10-Undecenyl 2,3,4,6-Tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside 4. To the solution of compound **3** (1.0 g, 2.0 mM) in methanol (15 mL) K_2CO_3 (0.2 g) was added and the mixture was stirred 4 h at rt. Chromatography through a short column of silica gel (CH_2Cl_2/MeOH 4:1) of the oily residue after solvent evaporation gave deprotected compound (0.63 g, 95%); IR ν_{max} 3600, 2920, 1640, 1225, 1040 cm^{-1}, which was silylated by a standard procedure[17] using imidazole (10 equiv) and *tert*-butyldimethylsilyl chloride (10 equiv). After purification compound **4** was obtained as colourless oil (76 %): $[\alpha]_D$ -16.1 (*c* 2.1 , chloroform); IR ν_{max} 2930, 1640, 1220, 1030

cm^{-1}; ^1H NMR δ 5.82 (dddd, $J_{10'11'cis}$ 10.2, $J_{10'11'trans}$ 17.0, 2x $J_{9',10'}$ 6.6, 1H, H-10'), 4.97 (m, 2H, H-11'), 4.67 (d, $J_{1,2}$ 6.7, 1H, H-1), 3.95-3.65 (m, 6H, H-3, 4, 5, 6, 6', 1'), 3.57 (dd, $J_{2,3}$ <1.0, 1H, H-2), 3.38 (ddd, $2xJ_{1',2'}$ 6.5, $J_{1',1''}$ 8.9, 1H, H-1''), 2.0 (m, 2H H-9'), 1.62 (m, 2H, H-2'), 1.28 (m, 12H, $CH_{2\ alkyl}$), 0.89-0.87 (4xs, 36H, $4x(CH_3)_3CSi$), 0.09-0.05 (8xs, 24H, $8XCH_3Si$); ^{13}C NMR: 139.3 (C10'), 114.2 (C-11'), 101.8 (C-1), 82.4 (C-3), 79.3 (C-2), 77.9 (C-4), 70.2 (C-5), 69.6 (C-1'), 64.3 (C-6), 34.0-26.3 ($8xC_{alkyl}$), 26.2-25.9 ($12xCH_{3\ t\text{-}butyl}$), 18.4-18.0 ($4xSiCMe_3$), -4.0-5.1.($8xSiCH_3$).

Anal. Calcd for $C_{41}H_{88}O_6Si_4$: C, 62.38; H, 11.24. Found: C, 62.66; H, 11.30.

10-Undecenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside 5. Deacetylation of **3** was performed as above, and deprotected compound was benzylated by a standard procedure[18] with NaH (6 equiv) and benzyl bromide (6 equiv). After purification, compound **5** was obtained as a colourless oil (63 %): $[\alpha]_D$ -6.7 (*c* 0.08 , chloroform); IR ν_{max} 3005, 2920, 1640, 1550, 1225, 1040 cm^{-1}; ^1H NMR δ 7.5-7.2 (m, 20H, arom), 5.88 (dddd, $J_{10'11'cis}$ 10.2, $J_{10'11'trans}$ 17.0, 2x $J_{9',10'}$ 6.6, 1H, H-10'), 4.99 (m, 2H, H-11'), 4.85, 4.83, 4.68, 5.59 (4 x ABq, J_{AB} 11.4, 11.3, 10.8, 12.4, 8H, CH_2Ph), 4.40 (d, $J_{1,2}$ 7.7, 1H, H-1), 3.97 (ddd, $2xJ_{1',2'}$ 6.3, $J_{1',1''}$ 9.3, 1H, H-α), 3.74 (dd, $J_{5,6}$ 2.0, $J_{6,6'}$ 10.5, 1H, H-6), 3.72-3.38 (m, 6H, H-2, 3, 4, 5, 6', 1''), 2.03 (m, 2H, H-9'), 1.62 (m, 2H, H-2'), 1.29 (m, 12H, $CH_{2\ alkyl}$); ^{13}C NMR: 139.4 (C-10'), 138.7-138;2 ($4xC_{arom}$), 128.4-127.6 (C_{arom}), 114.2 (C-11'), 103.7 (C-1), 84.7 (C-3), 82.3 (C-2), 78.0 (C-4), 75.7, 75.0, 74.7, 73.5 ($4xCH_{2\ benzyl}$), 74.8 (C-5), 70.2 (C-1'), 69.0 (C-6), 32.6-26.2 (C_{alkyl}).

Anal. Calcd for $C_{45}H_{56}O_6$: C, 78.00; H, 8.15. Found: C, 77.64; H, 7.91.

4-Pentenyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside 10. This compound was prepared by the same procedure as **3** using 2,3,4,6-tetra-*O*-acetyl-glucopyranosyl bromide (5 g, 12.2 mM), 4-penten-1-ol (1.10 g, 12.8 mM) and AgOTf (3.28 g, 12.8 mM). Chromatography of the oily residue after solvent evaporation (hexane/ethyl acetate 7:1) gave compound **10** (3.21 g, 63%) as an oil $[\alpha]_D$ -13.2 (*c* 1.4 , chloroform); IR ν_{max} 2930, 1740, 1640, 1225, 1040 cm^{-1}; ^1H NMR δ 5.72 (dddd, $J_{4',5'cis}$ 10.3, $J_{4'5'trans}$ 17.0, 2x $J_{3',4'}$ 6.7, 1H, H-4'), 5.15 (dd, $J_{3,4}$ 9.5, 1H,H-3), 5.04 (dd, $J_{4,5}$ 9.3, 1H, H-4), 4.93 (dd, $J_{2,3}$ 9.0, 1H, H-2), 4.90 (m, 2H, H-5'), 4.46 (d, $J_{1,2}$ 7.9, 1H, H-1), 4.22 (dd, $J_{5,6}$ 4.8, 1H, H-6), 4.08 (dd, $J_{6,6'}$ 12.3, 1H, H-6'), 3.82 (ddd, $J_{1',1''}$ 9.7, $2xJ_{1',2'}$ 6.2, 1H, H-1'), 3.65 (ddd, $J_{5,6'}$ 2.4, 1H, H-5), 3.46 (ddd, $2xJ_{1'',2'}$ 6.5, 1H, H-1''), 2.03, 1.99, 1.97, 1.95 (4xs, 12H, $4xCH_3CO$), 2.0 (m, 2H H-3'), 1.62 (m, 2H, H-2'); ^{13}C NMR: 170.5, 170.2, 169.3, 169.2 (4 x CO), 137.7 (C-4'), 115.0 (C-5'), 100.7 (C-1), 72.8 (C-3), 71.7 (C-5), 71.3 (C-2), 69.2 (C-1'), 68.4 (C-4), 61.9 (C-6), 29.8, 28.5 ($2xCH_{2\ alkyl}$), 20.6-20.5 (4 x CH_3 CO).

Anal. Calcd for $C_{19}H_{28}O_{10}$: C, 54.80; H, 6.78. Found: C, 54.35; H, 6.91.

4-Pentenyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-eno-pyranoside 14. To the solution of 3,4,6-tri-*O*-acetyl-D-glucal (1.08 g, 3.96 mM) in dry toluene (10 mL) 4-penten-1-ol (0.818 mL, 7.90 mM) was added, followed by boron trifluoride etherate (0.268 mL, 2.05 mM). The resulting mixture was stirred at rt for 3 h. An excess of aqueous $NaHCO_3$ was added, and after extraction, drying and solvent evaporation the product was purified by column chromatography (hexane/ethyl acetate 4:1) affording **14** (1.02 g, 82%) as a colourless oil: $[\alpha]_D$ +94.4 (*c* 5.0 , chloroform); IR ν_{max} 2900, 1750, 1640, 1225, 1030 cm^{-1}; ^1H NMR δ 5.83 (m, 2H, H-2, H-3), 5.82 (dddd, $J_{4'5'cis}$ 10.2, $J_{4'5'trans}$ 16,9, 2x $J_{3',4'}$ 6.7, 1H, H-4'), 5.30 (dd, $J_{5,4}$ 9.4, $J_{3,4}$ 0.8, 1H, H-4), 5.02 (m, 2H, H-5'), 4.99 (bs, $J_{1,2}=J_{1,3}$ 1.6, 1H, H-1), 4.20 (m, 2H, H-6, H-6'), 4.09 (ddd, $J_{5,6}$ 2.4, $J_{5,6'}$ 5.1, 1H, H-5), 3.79 (ddd, $J_{1',1''}$ 9.6, $2xJ_{1',2'}$ 6.7, 1H, H-1'), 3.51 (ddd, $2xJ_{1'',2'}$ 6.5, 1H, H-1''), 2.15 (m, 2H H-3'), 2.09, 2.08 (2xs, 6H, $2xCH_3CO$), 1.71 (m, 2H, H-2'); ^{13}C NMR: 170.8, 170.3 (2x CO), 138.1 (C-4'), 130.6 (C-3), 126.2 (C-2), 114.9 (C-5'), 95.3 (C-1), 72.8 (C-5), 67.8 (C-1'), 64.5 (C-4), 63.5 (C-6), 30.3, 28.9 ($2xCH_2$ alkyl), 21.0, 20.9 (2 x CH_3 CO).

Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43. Found: C, 60.48; H, 7.38.

5-Hexenyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-eno-pyranoside 15. This compound was prepared by the same procedure as for **14.** Purified product **15** was obtained in 60% yield as a colourless oil: $[\alpha]_D$ +61.2 (*c* 2.5, chloroform); IR ν_{max} 2910, 1750, 1640, 1220, 1040 cm^{-1}; ^1H NMR δ 5.86 (m, 2H, H-2, H-3), 5.80 (dddd, $J_{6'5'cis}$ 10.2, $J_{6'5'trans}$ 16,9, 2x $J_{4',5'}$ 6.7, 1H, H-5'), 5.31 (dd, $J_{5,4}$ 9.5, $J_{3,4}$ 0.8, 1H, H-4), 5.03 (bs, $J_{1,2}=J_{1,3}$ 1.6 1H, H-1), 4.96 (m, 2H, H-6'), 4.24 (dd, $J_{5,6}$ 4.9, 1H, H-6), 4.17 (dd, $J_{6,6'}$ 12.3, $J_{5,6'}$ 2.4, 1H, H-6'), 4.09 (ddd, 1H, H-5), 3.78 (ddd, $J_{1',1''}$ 9.7, $2xJ_{1',2'}$ 6.7, 1H, H-1'), 3.52 (ddd, 1H, H-1''), 2.10, 2.08 (2xs, 6H, $2xCH_3CO$), 2.07 (m, 2H H-4'), 1.63 (m, 2H, H-2'), 1.48 (m, 2H, H-3'); ^{13}C NMR: 170.0, 170.0 (2x CO), 140.6 (C-5'), 129.2 (C-3), 126.8 (C-2), 114.4 (C-6'), 102.0 (C-1), 77.8 (C-5), 73.0 (C-4), 65.9 (C-6), 64.5 (C-1'), 33.5, 31.5, 26.3 ($3xCH_2$ alkyl), 17.7, 17.3 (2 x CH_3 CO).

General procedures for the metathesis reaction:

a. with the bicomponent catalyst **1**; to a solution of tetrachloro-bis-(2,6-diphenylphenoxy)tungsten **1** (8.2 mg, 0.01 mM) in dry chlorobenzene (2 mL) 2 equiv of $PbBu_4$ (6.9 μL) were added by syringe and the solution was stirred 15 min at 80 °C. The unsaturated substrate (5-20 equiv) was added at the same temperature, and stirring was continued overnight. Products were separated by column chromatography after evaporation of solvent under reduced pressure.

b. with the monocomponent catalyst **2**; to a solution of complex **2** (8.5 mg, 0.01 mM) in dry chlorobenzene (2 mL) the unsaturated substrate (5-20 equiv) was added at 80 °C, and the mixture was stirred overnight. Products were separated by column chromatography after evaporation of solvent under reduced pressure.

(*E*,*Z*)-Di-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-1,20-eicos-10-ene 6. Product obtained from substrate **3** by procedure **a**, (catalyst / substrate ratio - 1:5), yield: 52%, as an oil: $[\alpha]_D$ -1.78 (*c* 0.23 , chloroform); IR ν_{max} 2920, 1750, 1640, 1225, 1040 cm^{-1}; ^1H NMR δ 5.38 (m, 1H, H-10'), 5.19 (dd, $J_{3,4}$ 9.3, 1H,H-3), 5.10 (dd, $J_{4,5}$ 9.5, 1H, H-4), 4.99 (dd, $J_{2,3}$ 9.3, 1H, H-2), 4.49 (d, $J_{1,2}$ 7.9, 1H, H-1), 4.27 (dd, $J_{5,6}$ 4.6, 1H, H-6), 4.15 (dd, $J_{6,6'}$ 12.2, 1H, H-6'), 3.86 (ddd, $J_{1',1''}$ 9.6, $2xJ_{1',2'}$ 6.4, 1H, H-1'), 3.69 (ddd, $J_{5,6'}$ 2.4, 1H, H-5), 3.46 (ddd, $2xJ_{1'',2'}$ 6.4, 1H, H-1''), 2.09, 2.04, 2.03, 2.01 (4xs, 12H, $4xCH_3CO$), 1.97 (m, 2H H-9'), 1.57 (m, 2H, H-2'), 1.26 (m, 12H, $CH_{2\ alkyl}$); ^{13}C NMR: 170.9, 170.6, 169.8, 169.5 (4 x CO), 130.6, 130.1 (*cis* and *trans* C-10'), 101.0 (C-1), 73.1 (C-3), 71.9 (C-5), 71.5 (C-2), 70.5 (C-1'), 68.7 (C-4), 62.2 (C-6), 32.8-26.0 ($8xC_{alkyl}$), 21.0-20.9 (4 x CH_3 CO). FABMS: 996.0 $(M+Na)^+$, 990.9 $(M+NH_4)^+$, 523.5, 331.4.

Anal. Calcd for $C_{48}H_{76}O_{20}$: C, 59.25; H, 7.87. Found: C, 58.98; H, 7.85.

The same product **6** was obtained by procedure **b**, (catalyst / substrate ratio - 1:10), yield: 64%.

(*E*,*Z*) Di-*O*-(2,3,4,6-tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyloxy)-1,20-eicos-10-ene 7. The product was obtained from substrate **4** by procedure **a**, (catalyst / substrate ratio - 1:12), yield: 51%, as an oil: $[\alpha]_D$ -15.9 (*c* 3.8 , chloroform); IR ν_{max} 2960, 1640, 1225, 1105, 1040 cm^{-1}; ^1H NMR δ 5.39 (m, 1H, H-10'), 4.68 (d, $J_{1,2}$ 6.7, 1H, H-1), 3.95-3.65 (m, 6H, H-3, 4, 5, 6, 6', 1'), 3.58 (dd, $J_{2,3}$ <1.0, 1H, H-2), 3.37 (ddd, $2xJ_{1'',2'}$ 6.5, $J_{1',1''}$ 9.0, 1H, H-1''), 1.97 (m, 2H, H-9'), 1.61 (m, 2H, H-2'), 1.29 (m, 12H, $CH_{2\ alkyl}$), 0.89-0.87 (4xs, 36H, $4x(CH_3)_3CSi$), 0.09-0.05 (8xs, 24H, $8XCH_3Si$); ^{13}C NMR δ: 130.3, 129.9 (*cis* and *trans* C-10'), 101.7 (C-1), 82.3 (C-3), 79.2 (C-2), 77.8 (C-4), 70.1 (C-5), 69.5 (C-1'), 64.1 (C-6), 32.6-26.3 ($8xC_{alkyl}$), 26.1-25.8 ($12xCH_{3\ t\text{-butyl}}$), 18.3-17.9 ($4xSiCMe_3$), -4.1--5.3.($8xSiCH_3$); FABMS: 797.9 $(M+2Na)^{++}$, 863.6, 848.6, 834.8, 811.7.

Anal. Calcd for $C_{80}H_{172}O_{12}Si_8$: C, 61.96; H, 11.18. Found: C, 62.67; H, 10.75.

The same product **7** was obtained by procedure **b** (catalyst / substrate ratio - 1:12), yield: 92%.

(*E*,*Z*) Di-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyloxy)1,20-eicos-10-ene 8. The product was obtained from substrate **5** by procedure **a**, (catalyst / substrate ratio - 1:5), yield: 37%, as an oil, $[\alpha]_D$ -15.9 (*c* 0.85 , chloroform); IR ν_{max}

2920, 1640, 1630, 1585, 1225, 1040 cm^{-1}; ^1H NMR δ 7.4-7.2 (m, 20H, arom), 5.37 (bt, 1H, H-10'), 4.84, 4.82, 4.67, 5.58 (4 x ABq, J_{AB} 11.0, 11.0, 10.8, 12.3, 8H,$CH_{2benzyl}$), 4.38 (d, $J_{1,2}$ 7.7, 1H, H-1), 3.95 (ddd, $2xJ_{1',2'}$ 6.3, $J_{1',1''}$ 9.3, 1H, H-1'), 3.74 (dd, $J_{5,6}$ 2.0, $J_{6,6'}$ 10.9, 1H, H-6), 3.72-3.39 (m, 6H, H-2, 3, 4, 5, 6', 1''), 2.10 (m, 2H , H-9'), 1.65 (m, 2H, H-2'), 1.29 (m, 12H, $CH_{2\ alkyl}$); ^{13}C NMR: 138.7-138;2 (4xC_{arom}), 130.4 (C-10'), 128.4-127.6 (C_{arom}), 103.7 (C-1), 84.8 (C-3), 82.3 (C-2), 78.0 (C-4), 75.7, 75.0, 74.7, 73.5 (4x$CH_{2\ benzyl}$), 74.8 (C-5), 70.2 (C-1'), 69.0 (C-6), 32.6-26.2 (C_{alkyl}).

Anal. Calcd for $C_{88}H_{108}O_{12}Si_8$: C, 77.84; H, 8.02. Found: C, 78.02; H, 7.78.

The same product **8** was not obtained by procedure **b**, (catalyst / substrate ratio - 1:15),

(*E*,*Z*) Di-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyloxy)-1,20-eicos-10-ene 12. The product was obtained from substrate **9** by procedure **a**, (catalyst / substrate ratio - 1:10), yield: 62%, as an oil: $[\alpha]_D$ -13.5 (*c* 1.3, chloroform); IR ν_{max} 2920, 1760, 1640, 1240, 1050 cm^{-1}; ^1H NMR δ 5.63 (bd, $J_{1,NH}$ 8.6, 1H, NH), 5.37 (bt, 1H, H-10'), 5.29 (dd, $J_{3,4}$ 9.0, 1H,H-3), 5.07 (dd, $J_{4,5}$ 9.5, 1H, H-4), 4.69 (d, $J_{1,2}$ 8.3, 1H, H-1), 4.28 (dd, $J_{5,6}$ 4.6, 1H, H-6), 4.13 (dd, $J_{6,6'}$ 12.3, 1H, H-6'), 3.86 (ddd, $J_{2,3}$ 9.5, 1H, H-2), 3.84 (ddd, $J_{1',1''}$ 9.6, $2xJ_{1',2'}$ 6.4, 1H, H-1'), 3.71 (ddd, $J_{5,6'}$ 2.1, 1H, H-5), 3.48 (ddd, $2xJ_{1'',2'}$ 6.4, 1H, H-1''), 2.08, 2.03, 2.02, 1.94 (4xs, 12H, 4xCH_3CO), 1.97 (m, 2H, H-9'), 1.56 (m, 2H, H-2'), 1.26 (m, 12H, $CH_{2\ alkyl}$); ^{13}C NMR 170.8, 170.7, 170.1, 169.4 (4 x CO), 130., 129.8 (*cis* and *trans* C-10'), 100.6 (C-1), 72.3 (C-3), 71.7 (C-5), 69.9 (C-1'), 68.7 (C-4), 62.2 (C-6), 54.8 (C-2), 32.5-25.8 (8xC_{alkyl}), 23.3 (CH_{3amide}), 20.7-20.6 (3 x CH_3 CO). FABMS: 994.8 $(M+Na)^+$, 972.4 $(M+H)^+$, 951.1, 330.3.

Anal. Calcd for $C_{48}H_{78}O_{18}N_2$: C, 59.37; H, 8.10; N, 2.88. Found: C, 59.29; H, 8.14; N, 2.74.

(*E*,*Z*) Di-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-1,8-oct-4-ene 13. The product obtained from substrate **10** by procedure **a**, (catalyst / substrate ratio - 1:20), yield: 65%, as an oil, $[\alpha]_D$ -17.5 (*c* 1.0 , chloroform); IR ν_{max} 2950, 1745, 1620, 1220, 1040 cm^{-1}; ^1H NMR δ 5.38 (m, 1H, H-4'), 5.18 (dd, $J_{3,4}$ 9.5, 1H,H-3), 5.10 (dd, $J_{4,5}$ 9.3, 1H, H-4), 4.98 (dd, $J_{2,3}$ 9.2, 1H, H-2), 4.49 (d, $J_{1,2}$ 7.9, 1H, H-1), 4.27 (dd, $J_{5,6}$ 4.6, 1H, H-6), 4.13 (dd, $J_{6,6'}$ 12.3, 1H, H-6'), 3.86 (ddd, $J_{1',1''}$ 9.6, $2xJ_{1',2'}$ 6.2, 1H, H-1'), 3.69 (ddd, $J_{5,6'}$ 2.4, 1H, H-5), 3.48 (ddd, $2xJ_{1'',2'}$ 6.5, 1H, H-1''), 2.08, 20.4, 20.2, 20.1 (4xs, 12H, 4xCH_3CO), 2.05 (m, 2H , H-3'), 1.62 (m, 2H, H-2'); ^{13}C NMR 170.6, 170.2, 169.4, 169.2 (4 x CO), 129.9, 129.4 (*cis* and *trans* C-4'), 100.7 (C-1), 72.8 (C-3), 71.7 (C-5), 71.3 (C-2), 69.4 (C-1'), 68.4 (C-4), 61.9 (C-

6), 29.1, 28.5 (2xCH_2 alkyl), 20.7-20.6 (4 x CH_3 CO). FABMS: 827.3 $(M+Na)^+$, 805.4 $(M+H)^+$, 518.3, 331.6.

Anal. Calcd for $C_{36}H_{52}O_{20}$: C, 53.73; H, 6.51. Found: C, 53.51; H, 6.52.

No metathesis product was obtained from allyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside **11** either by the procedure **a** or the procedure **b**.

(*E*,*Z*)-Di-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythrohex-2-eno-pyranosyloxy)-1,8-oct-4-ene 16. The product was obtained from substrate **14** by procedure **a**, (catalyst / substrate ratio - 1:20), yield: 52%, as an oil, $[\alpha]_D$ +100.0 (*c* 0.2 , chloroform); IR ν_{max} 2920, 1750, 1640, 1225, 1040 cm^{-1}; ^1H NMR δ 5.87 (m, 2H, H-2, H-3), 5.42 (bt, 1H, H-4'), 5.32 (dd, $J_{5,4}$ 9.4, $J_{3,4}$ 0.8, 1H, H-4), 5.02 (bs, $J_{1,2}=J_{1,3}$ 1.6, 1H, H-1), 4.23 (dd, $J_{5,6}$ 5.2, 1H, H-6), 4.18 (dd, $J_{6,6'}$ 12.1, $J_{5,6'}$ 2.3, 1H, H-6'), 4.09 (ddd, 1H, H-5), 3.79 (ddd, $J_{1',1''}$ 9.6, 2x$J_{1',2'}$ 6.5, 1H, H-1'), 3.50 (ddd, 2x$J_{1'',2'}$ 6.5, 1H, H-1''), 2.15 (m, 2H , H-3'), 2.10, 2.08 (2xs, 6H, 2xCH_3CO), 1.66 (m, 2H, H-2'); ^{13}C NMR: 170.8, 170.3 (2x CO), 129.5, 129.0 (*cis* and *trans* C-4'), 130.0 (C-3), 127.9 (C-2), 94.5 (C-1), 68.3 (C-1'), 66.8 (C-5), 65.2 (C-4), 63.0 (C-6), 29.6, 29.2 (2xCH_2 alkyl), 21.0, 20.8 (2 x CH_3 CO).

Anal. Calcd for $C_{28}H_{40}O_{12}$: C, 59.14; H, 7.09. Found: C, 58.92; H, 7.16.

(*E*,*Z*) Di-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-2-eno-pyranosyloxy)-1,10-dec-5-ene 17. The product was obtained from substrate **15** by procedure **a**, (catalyst / substrate ratio - 1:27), yield: 55%, as an oil, $[\alpha]_D$ +88.3 (*c* 1.8, chloroform); IR ν_{max} 2920, 1750, 1640, 1225, 1040 cm^{-1}; ^1H NMR δ 5.83 (m, 2H, H-2, H-3), 5.39 (bt, 1H, H-5'), 5.30 (dd, $J_{5,4}$ 9.4, $J_{3,4}$ 0.8, 1H, H-4), 5.01 (bs, $J_{1,2}=J_{1,3}$ 1.6, 1H, H-1), 4.25 (dd, $J_{5,6}$ 5.2, 1H, H-6), 4.18 (dd, $J_{6,6'}$ 12.1, $J_{5,6'}$ 2.3, 1H, H-6'), 4.10 (ddd, 1H, H-5), 3.79 (ddd, $J_{1',1''}$ 9.6, 2x$J_{1',2'}$ 6.5, 1H, H-1'), 3.50 (ddd, 2x$J_{1'',2'}$ 6.5, 1H, H-1''), 2.10, 2.08 (2xs, 6H, 2xCH_3CO), 2.02 (m, 2H H-4'), 1.60 (m, 2H, H-2'), 1.40 (m, 2H, H-3'); ^{13}C NMR: 169.7, 169.2 (2x CO), 129.5 (C-3), 129.2, 129.0 (*cis* and *trans* C-5'), 126.8 (C-2), 93.3 (C-1), 67.7 (C-5), 65.8 (C-1'), 64.2 (C-4), 61.9 (C-6), 31.2, 28.2 (2xCH_2 alkyl), 19.9, 19.7 (2 x CH_3 CO).

Anal. Calcd for $C_{30}H_{44}O_{12}$: C, 60.39; H, 7.43. Found: C, 60.46; H, 7.53.

(*E*,*Z*) Di-*O*-(β-D-glucopyranosyloxy)-1,20-eicos-10-ene 18. To a solution of compound **6** (100 mg, 0.10 mM) in methanol (5 mL) a catalytic amount of MeONa was added and the resulting mixture was stirred overnight. After neutralisation (acetic acid) and solvent evaporation, the residue was filtered through a short column (CH_2Cl_2/MeOH 2:1) affording **18** as an oil (52%), $[\alpha]_D$ +26.7 (*c* 0.06, methanol); IR ν_{max} 3500, 2920, 1225, 1040 cm^{-1}; ^1H NMR (CD_3OD) δ 5.37 (m, 1H, H-10'), 4.24 (d, $J_{1,2}$ 7.7, 1H, H-1), 3.97-3.12 (m, 8H, H-2,3, 4, 5, 6, 6', 1', 1''), 2.02 (m, 2H , H-9'), 1.65 (m, 2H, H-2'), 1.31 (m, 12H, CH_2 alkyl); ^{13}C NMR (CD_3OD) δ: 131.5, 129.9 (*cis*

and *trans* C-10'), 104.4 (C-1), 78.1 (C-3), 77.9 (C-5), 75.1 (C-2), 71.7 (C-4), 70.9 (C-1'), 62.8 (C-6), 33.6-27.1 (8xC $_{alkyl}$); FABMS: 659.4 $(M+Na)^+$, 429.3, 413.4, 409.4, 393.4, 351.4, 317.3.

ACKNOWLEDGMENT

We thank Dr. Lafont (Lyon) and Dr. E. Yaacoub (Braunschweig) for gifts of two substrates (**9** and **15**), and Dr. J. Banoub (Canada) for obtaining FAB mass spectra. One of co-authors (J.R.) thanks CNRS for granting of a postdoctorate position.

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