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Stereoselective Formation of Tetrahydrofurans during Allyltrimethylsilane Additions to L-Xylose Derivatives

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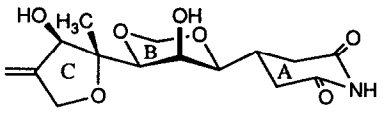
Key Words: Stereoselectivity; α-Alkoxy Aldehydes; L-Xylose; Acetals; Chelation.

Abstract: *Stereoselective addition reactions to the aldehyde function of some L-xylose derivatives, under the influence of Lewis acid catalysts, lead to the formation of tetrahydrofuran derivatives at low temperatures, depending on the acetal protecting groups used. Via separate reactions it was shown, that these tetrahydrofurans seemed to be intermediates in the formation of homoallyl alcohols.*

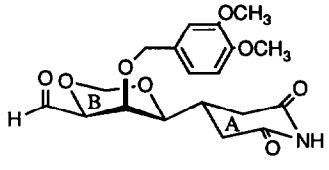
Introduction

The use of carbohydrates as chiral synthons has received a great deal of attention in recent years[1]. In addition to the fact, that carbohydrates provide stereochemically defined carbon frameworks, which can be incorporated into new chiral structures, molecules of (protected) saccharides can also serve as templates for communicating chirality to new chiral centres being generated in an adjacent emerging chain[2], followed by a sacrificial destruction of one or more original chiral centres (sacrificial asymmetric synthesis).

Both the aforementioned principles have been applied in our laboratory for a variety of synthetic objectives. Thus, the synthesis of both enantiomers of the anti tumour alkaloid Sesbanimide A, **1** (Fig. 1) has utilized protected (L- and D -) xylose as an integral moiety of the target molecule[3a,b].



1 Sesbanimide A



2

Figure 1.

Furthermore, the synthetic strategy employed the communication of chirality of the carbohydrate in the construction of ring C of the alkaloid. This was realized by a reaction of aldehyde **2** with a suitably substituted allylsilane using a Lewis acid catalyst[4]. To study these reactions, model experiments were carried out with carbohydrate derivatives and allylsilanes under catalytic influence of different Lewis acids. Recent publications by *Hideyuki Sugimura et.al.*[5a-d] prompt us to present our results obtained in these studies.

Results and Discussion

In connection with the synthesis of Sesbanimide A and some analogues, the first model experiments were performed with the protected L-xylose derivative **3** (Fig. 2) as a chiral template. The choice of the methylene acetal as protecting group was obvious since the 1,5-acetal could be incorporated into the target molecule. L-Xylose derivative **3** was obtained from L-sorbitol in three simple steps as described by *Ness et.al.*[6] and *Bourne et.al.*[7].

Figure 2.

From earlier experiments by *Cram et.al.*[8] and *Reetz et.al.*[9] it is known, that reactions of nucleophiles with chiral α-alkoxy aldehydes under influence of Lewis acids exhibit diastereofacial selectivity which is dependent on the nature of the electrophile. With Lewis acids, capable of forming chelates with both the carbonyl oxygen as well as with the α-alkoxy oxygen atoms (titanium and tin derivatives) (projection **A**, Fig. 3) the approach of the nucleophile will be from the opposite direction than by application of boron electrophiles (projection **B**), where the two complexing oxygen atoms might prefer the opposite orientation, due to electrostatic repulsion[8]. Thus, it should be possible to direct the stereochemistry of the new formed chiral centre in both directions, by simple variation of the Lewis acid,. On basis of molecular orbital considerations the nucleophilic attack should be non-perpendicular as postulated by *Anh et.al.*[10].

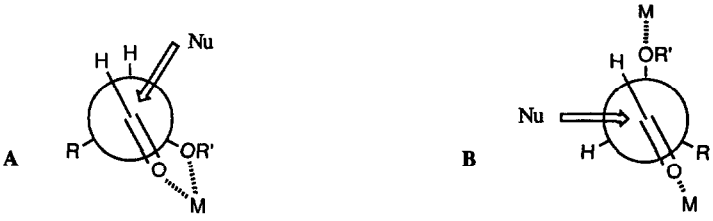
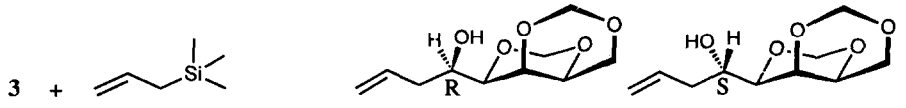


Figure 3.

Complete stereospecificity was found in reactions of aldehyde **3** with allyltrimethylsilane, **4** (Fig. 4) in dichloromethane. Using titanium tetrachloride, capable of forming a six-coordinate octahedral complex[11], homoallyl alcohol **6** was obtained with very high selectivity, which was in keeping with the cyclic Cram model[8]. On the contrary, use of boron trifluoride etherate as Lewis acid gave predominately alcohol **5**.

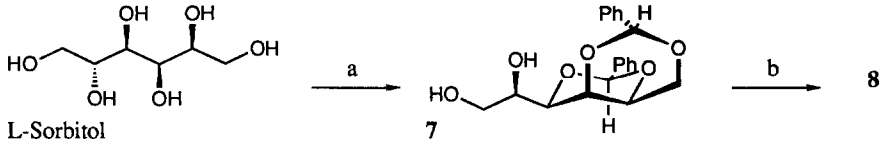


4	Lewis acid (mol. eq.)	5	+	6
	$BF_3.OEt_2$ (3.3), 0° C	60 %		9 %
	$TiCl_4$ (1.1), -10° C	4 %		68 %

Figure 4.

In the synthesis of Sesbanimide A and its analogues the 2,4-methylene acetal of L-xylose served not only as a protecting group, but was also incorporated in the target molecule. However, if one wants the carbohydrate to serve only as a temporary chiral auxiliary, the use of acetal protecting groups which can be removed under milder conditions is more desirable.

In this context L-xylose derivative **8** (Fig. 2) was synthesized from L-sorbitol, using benzylidene acetals to protect the hydroxy functionalities (Scheme 1). Treating L-sorbitol with benzaldehyde and sulphuric acid, under azeotropic removal of water, yielded diol **7**. The distribution of the acetals can be explained by consideration of both free energy calculations[12] as well as normal conformational principles. Both the phenyl groups occupy the equatorial position[13]. Oxidation of diol **7** with sodium metaperiodate gave aldehyde **8** partially as its hydrate. The free aldehyde **8** was obtained after azeotropic distillation with toluene followed by crystallization.

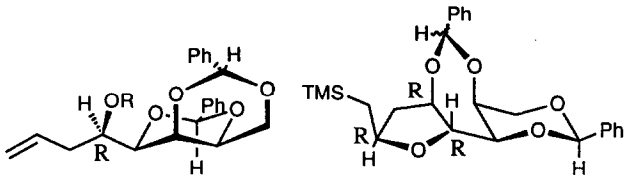


(a) PhCHO, H_2SO_4, cyclohexane, Δ, 4 hr, 58%; (b) $NaIO_4$, H_2O, dioxane, RT, 17 hr, 76%.

Scheme 1.

Performing addition reactions of allylsilane **4** with aldehyde **8** in dichloromethane at low temperature to our surprise yielded only one diastereomer of homoallyl alcohol **9a**, using both chelating Lewis acids as well as non-chelating ones (Fig. 4). Probably, steric hindrance upon the formation of a chelate by the phenyl group of the benzylidene acetal adjacent to the carbonyl function, plays a crucial role in the stereochemical outcome of the reaction.

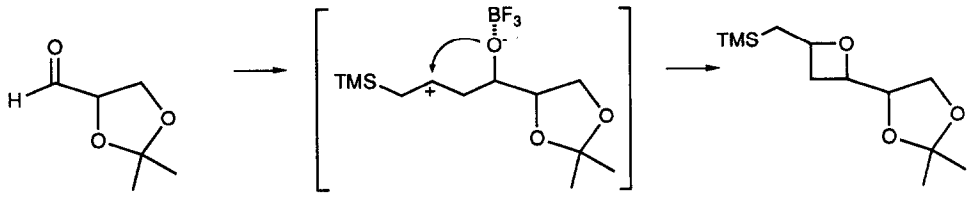
At low temperature the trimethylsilyl ether **9b** seemed to be stable and was isolated in some cases (Fig. 5). Removal of the TMS group of **9b** gave homoallyl alcohol **9a**.



8 + **4**	Lewis acid (mol.eq.)	**9a**: R = H	+ **9b**: R = TMS	+ **10**
	$BF_3.OEt_2$ (3.3), -78° C	40 %	12 %	21 %
	$TiCl_4$ (1.1), -78° C	18 %	-	-
	$SnCl_4$ (1.1), -78° C	9 %	5 %	10 %
	$ZnCl_2$ (5.0), 20° C	34 %	19 %	-

Figure 5.

In first instance the structure of the third, apolar product **10** could not be elucidated. However, *Sugimura et.al.*[5a,b] claimed to have isolated oxetanes under the same reaction conditions, using comparable carbohydrate derivatives protected with the isopropylidene group. The mechanism of the formation of oxetanes they proposed, a direct attack of the negatively charged oxygen atom on the carbenium ion, stabilized by the silyl group in the β position, was quite acceptable (Scheme 2).

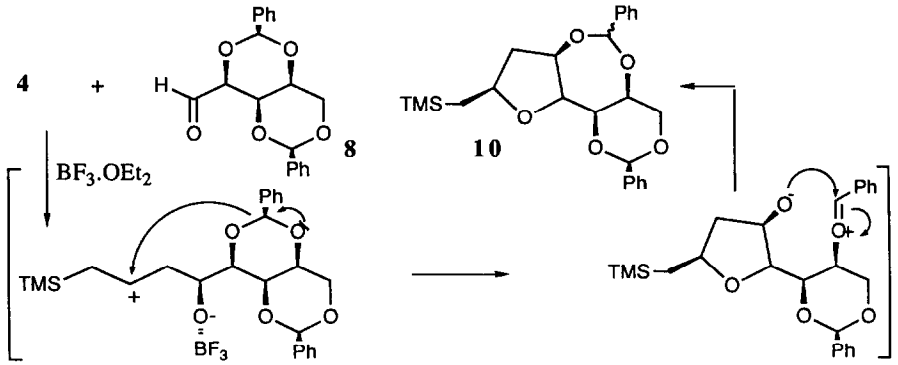


Scheme 2.

Structure elucidation of the products was carried out by the authors via proton NMR. In our point of view complete stereochemical structure elucidation is not possible in this way. Our attempts to obtain crystals of **10** suitable to be used for X-ray analysis failed repeatedly. This kept us from publishing our results at that time.

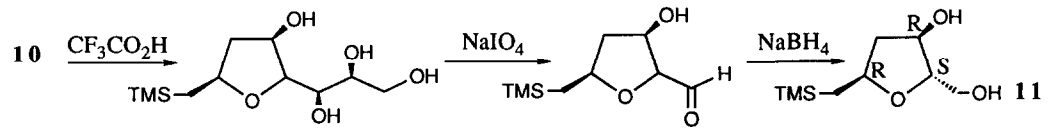
However, later *Sugimura et.al.* published a rectification of their earlier results[5c]. X-ray analysis of one of the former 'oxetanes' showed that tetrahydrofuran derivatives had been formed instead. The brief mechanism they proposed was not very clear[5c].

The formation of these tetrahydrofuran derivatives can be explained more readily via an attack of one of the acetal oxygen atoms on the carbenium ion, stabilized by the silyl group in the β position, followed by neutralization of the resulting intermediate oxonium ion by the negatively charged oxygen atom. This is shown in Scheme 3 with **8** as the starting material. The tricyclic product **10** was isolated as a single diastereomer.



Scheme 3.

Because attempts to obtain crystals suitable for X-ray analysis failed, the structural and stereochemical elucidation of tetrahydrofuran derivative **10** was performed by means of chemical transformations (Scheme 4). In a one-pot-procedure **10** could be converted into derivative **11**. First the benzylidene acetals of **10** were removed by acid hydrolysis. After neutralization with sodium hydrogen carbonate, the resulting tetraol was cleaved by oxidation with sodium metaperiodate. A subsequent reduction with sodium borohydride provided tetrahydrofuran derivative **11**. Elucidation of the configurations of the two new formed stereogenic centres was performed by means of nOe experiments.

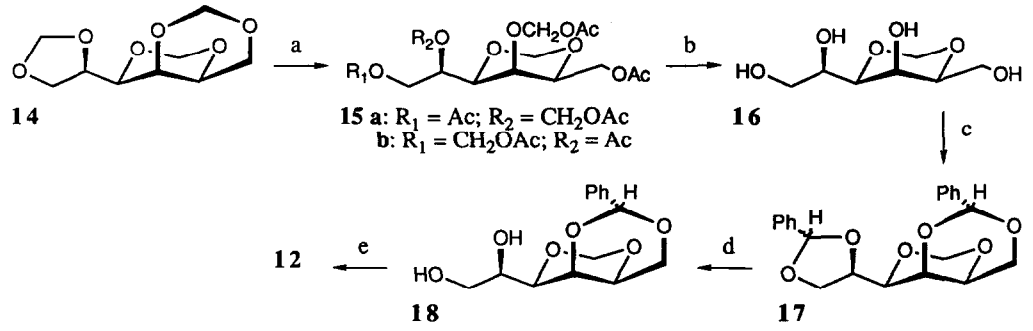


Scheme 4.

To study the steric influence of the acetal protection on the stereoselectivity of the reactions, and on the formation of tetrahydrofuran derivatives like compound **10**, allylsilane additions were also performed with aldehydes **12** and **13** (Fig. 6).

Figure 6.

The synthesis of aldehyde **12** was performed starting from L-sorbitol. Trimethylene sorbitol, **14** was obtained via the method described by *Ness et.al.*[6]. Acetolysis of **14** with acetic anhydride, acetic acid and sulphuric acid[6] afforded 62 % of a 3 / 1 mixture of derivatives **15a** and **15b** respectively (Scheme 5). Treatment of this mixture with sodium methanolate gave **16**. Acetal formation of **16** with benzaldehyde, under azeotropic removal of water, yielded 88 % of an isomeric mixture of derivative **17**. The two isomers formed are most likely to be epimers at the carbon of the dioxolane ring system. Selective hydrolysis of the five membered ring acetal[14] of the isomeric mixture of **17** with formic acid afforded one diastereomer of diol **18**. The presence of two epimers at the dioxolane acetal carbon was also established at this point. Oxidation of diol **18** with sodium metaperiodate gave aldehyde **12**, partially as its hydrate. Water was removed via azeotropic distillation with toluene followed by crystallization.



(a) OAc_2, HOAc, H_2SO_4, 0° C, 10 min, 62%; (b) $NaOCH_3$, CH_3OH, $CHCl_3$, 5° C, 3 d, 91%; (c) PhCHO, H_2SO_4, cyclohexane, Δ, 4 hr, 88%; (d) HCO_2H, CH_3CH_2OH, Δ, 3 hr, 71%; (e) $NaIO_4$, H_2O, dioxane, RT, 17 hr, 67%.

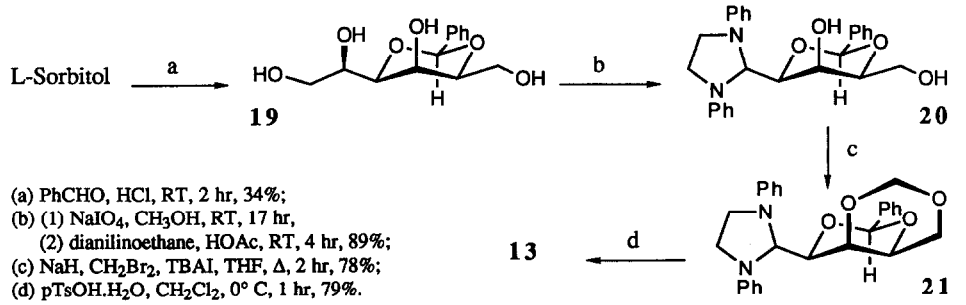
Scheme 5.

Aldehyde **13** was synthesized starting from L-sorbitol (Scheme 6). Treatment of L-sorbitol with benzaldehyde and concentrated hydrochloric acid afforded the mono benzylidene derivative **19**[14,15]. In the oxidation of the geminal diol system in **19** with sodium metaperiodate the product could be monitored via TLC analysis, but attempts to isolate the resulting aldehyde failed, due to its low stability. However, when the oxidation was performed in methanol until the conversion was completed, followed by addition of dianilinoethane and a catalytic amount of acetic acid, aminal **20** was obtained in high yield. This aldehyde protecting group[16] is well known to stimulate crystallization, leading to pure **20** on a large scale.

Introduction of the methylene acetal at the remaining two hydroxy functions was performed under basic conditions using sodium hydride and dibromomethane as reagents and tetrabutylammonium iodide as phase transfer catalyst. This procedure provided derivative **21** in reasonable yield. The presence of the acid sensitive

aminal and benzylidene acetal in **20** did not allow acid conditions to be used for the introduction of this methylene acetal.

Deprotection of the aldehyde was performed under very mild conditions. Treatment of derivative **21** with *p*-toluenesulphonic acid monohydrate at 0°C in dry dichloromethane afforded the free aldehyde **13**.



Scheme 6.

Additions of allylsilane **4** to aldehyde **12** (Fig. 7) were performed under the same conditions as described for aldehydes **3** and **8**.

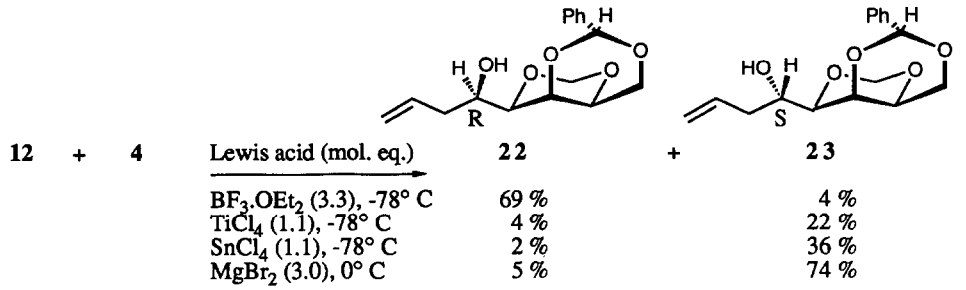
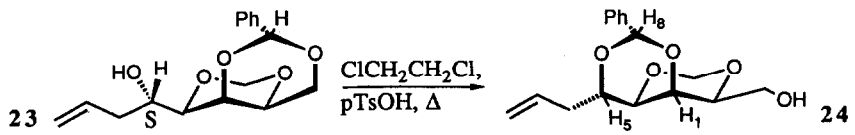


Figure 7.

With boron trifluoride etherate as the catalyst only the 'Cram' product **22**, was obtained. However, when chelation-promoting Lewis acids like titanium tetrachloride, tin tetrachloride or magnesium bromide etherate were used, the other possible diastereomeric homoallyl alcohol **23** predominated in the product mixture.

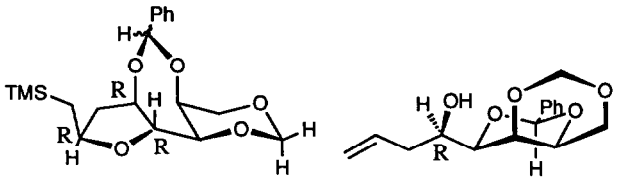
The elucidation of the configuration of the newly formed asymmetric centre in the latter compound was realized as follows: the benzylidene acetal in **23** could be rearranged to the secondary hydroxy function under acid conditions, affording compound **24** (Scheme. 7). NOe experiments with this compound showed the proximity of H1 and H8 to the proton at the new chiral carbon atom, H5. Model studies showed that the proximity of those three protons could only be possible if C5 of derivative **24** has the S-configuration. Consequently, homoallyl alcohol **23** also has the S-configuration at C5.



Scheme 7.

The use of boron trifluoride etherate as Lewis acid in the addition reaction of allylsilane **4** to aldehyde **13** leads also to the formation of a tetrahydrofuran derivative, compound **25** (Fig. 8), which is structurally related to derivative **10**. However, the homoallyl alcohol **26** was still the major product. Chemical degradation of **25**, analogous to the procedure described for **13** (Scheme 4) afforded the same tetrahydrofuran derivative **11**.

Similar to the reactions of **4** with aldehyde **8**, both chelating as well as non-chelating Lewis acids gave the same diastereomer of homoallyl alcohol, the 'Cram' product **26**.



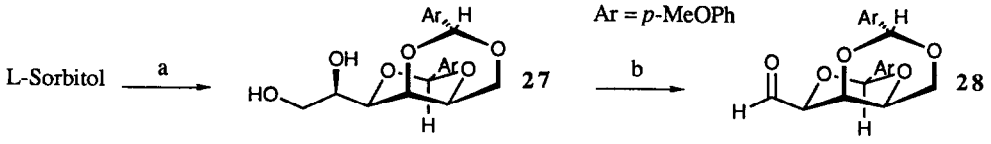
13 + **4**	Lewis acid (mol.eq.)	**25**	+	**26**
	$BF_3.OEt_2$ (3.3), -78° C	23 %		57 %
	$TiCl_4$ (1.1), -78° C	-		34 %
	$SnCl_4$ (1.1), -78° C	-		52 %

Figure 8.

Comparing our results with those obtained by *Sugimura et.al.*[5c,d], who used the isopropylidene protection, the electron donating nature of the acetal group, adjacent to the carbonyl function seems to be important for the formation of the tetrahydrofuran derivatives. A strong electron donating group will stabilize the intermediate oxonium ion (Scheme 3) and, therefore, stimulating the formation of the tetrahydrofuran derivatives.

To prove this statement we performed addition reactions with aldehyde **28** (Scheme 8), with *p*-methoxybenzaldehyde as the protecting group. Because of the stronger electron donating nature of this group compared to the benzylidene acetal we expected the formation of tetrahydrofuran derivative **29** (Fig. 9) to be more favoured

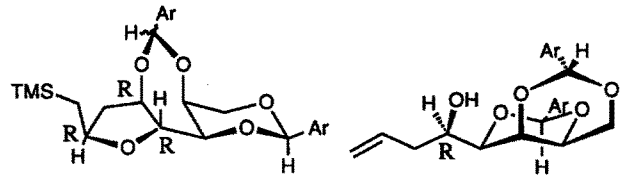
The synthesis of aldehyde **28** (Scheme 8) was performed in a straightforward way. Treating L-sorbitol with *p*-methoxybenzaldehyde and concentrated hydrochloric acid afforded diol **27**. Oxidation of this diol with sodium metaperiodate gave aldehyde **28**.



(a) *p*-MeOPhCHO, HCl, RT, 17 hr, 95%; (b) $NaIO_4$, H_2O, dioxane, RT, 17 hr, 79%.

Scheme 8.

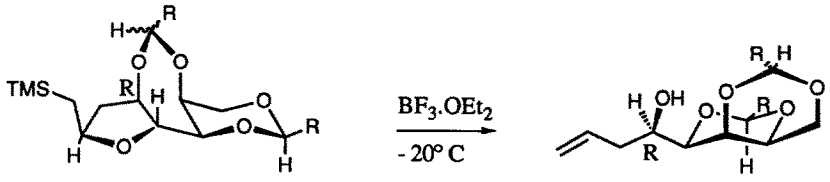
Performing the addition reaction of allylsilane **4** with aldehyde **28** in dichloromethane with boron trifluoride etherate as the Lewis acid afforded tetrahydrofuran derivative **29** (Fig. 9) as the sole product in high yield, according to our expectations. Chemical degradation of this compound similar to the procedure as described for compounds **10** and **25** gave also the same tetrahydrofuran derivative **11** in high overall yield. Titanium tetrachloride and tin tetrachloride gave homoallyl alcohol **30** as the sole product, be it in very low yield.



28 + 4	Lewis acid (mol.eq.)	29	+	30
	$BF_3.OEt_2$ (3.3), -78° C	83 %		-
	$TiCl_4$ (1.1), -78° C	-		13 %
	$SnCl_4$ (1.1), -78° C	-		17 %

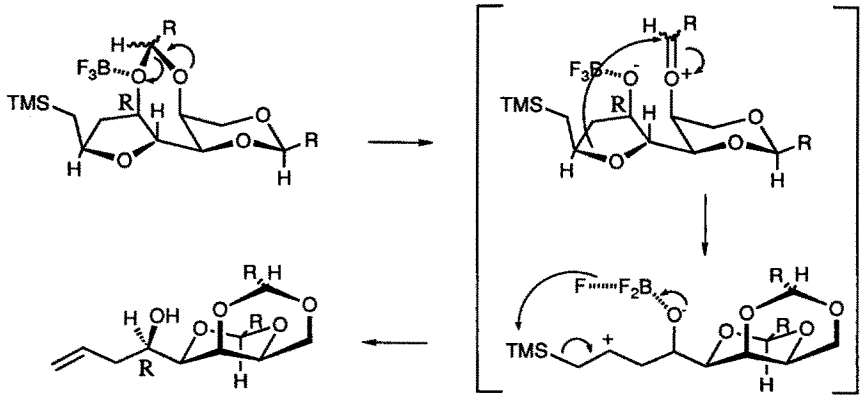
Figure 9.

To our surprise tetrahydrofuran derivatives **10**, **25** and **29** could be converted to homoallyl alcohols **9a**, **26**, and **30** respectively, when treated with boron trifluoride etherate at -20° C (Scheme 9).



Scheme 9.

A proposed mechanism for this reaction is shown in Scheme 10. First complexation of boron trifluoride with one of the acetal oxygen atoms takes place, followed by opening of the acetal ring to an oxonium ion intermediate. Subsequent opening of the furan ring to the carbon atom of the oxonium ion leads to a carbenium ion, stabilized by the silyl group. Intra- or intermolecular nucleophilic attack of a fluoride ion upon the silyl group gives after hydrolysis the homoallyl alcohol.



Scheme 10.

Since at -78° C both the tetrahydrofuran derivative as well as the homoallyl alcohol were formed (except for the reactions with aldehyde **28** in which the tetrahydrofuran derivative **29** was the only product formed) it seems reasonable to assume that these tetrahydrofuran derivatives are intermediates in the formation of the homoallyl alcohols in these cases. Further studies concerning the mechanism of the reactions are necessary. In this context the variations in the product ratios at different reaction temperatures are worth studying.

Conclusions

In the reactions described, stereoselectivity in additions of allyltrimethylsilane to acetal protected L-xylose aldehydes in presence of a Lewis acid is dependent on the acetal group adjacent to the carbonyl function.

With a methylene acetal at this position, the reactions were highly stereoselective and the configuration at the new formed chiral centre could be directed by the choice of chelating or non-chelating Lewis acids. However, when more bulky protecting acetal groups were used at this position, like benzylidene and *p*-methoxybenzylidene acetal, the influence of the catalyst on the stereoselectivity was completely lost, most likely due to the steric hindrance of these groups upon the formation of chelates.

Remarkable was the formation of tetrahydrofuran derivatives with boron trifluoride etherate as Lewis acid at low reaction temperature, which was also dependent on the nature of the neighbouring acetal group. Stronger electron donating properties of the acetal at this position favoured the formation of these compounds. These results were in keeping with the proposed mechanism.

At higher temperatures however, these tetrahydrofuran derivatives could be converted to homoallyl alcohols in the presence of boron trifluoride etherate. Further studies are necessary to prove if these tetrahydrofuran derivatives are also intermediates in the formation of the homoallyl alcohols under the reaction conditions applied.

Acknowledgement

We gratefully acknowledge the financial support by the Ministry of Economic Affairs of The Netherlands.

Experimental

General methods and materials

IUPAC nomenclature[17] is used. Infrared (IR) spectra were recorded on a Perkin Elmer 298 spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) were recorded on Bruker AC-200, Bruker WM-250 or Bruker WM-300 instruments. Carbon nuclear magnetic resonance (^{13}C-NMR) were recorded on the Bruker AC-200 and Bruker WM-250 instruments at 50 and 62.9 MHz, respectively. Chemical shifts are given in ppm downfield of tetramethylsilane (TMS). As is indicated ^{1}H-NMR shift correlation spectroscopy (COSY)[18], attached proton test (APT)[19] and double resonance experiments were occasionally used for signal assignments. Accurate mass measurements were performed on a Varian MAT 711 instrument. Thin layer chromatography (TLC) was performed on silicagel coated plastic sheets (Merck silicagel 60 F_{254}). Flash chromatography was performed on silicagel 60 (230-400 mesh)[20]. Optical rotations were measured on a Perkin Elmer 241 polarimeter. Melting points (m.p.) were determined on a Leitz melting point microscope and are uncorrected.

(1S,5S,6R)-2,4,7,9-tetraoxabicyclo[4.4.0]decane-5-carboxaldehyde 3

Aldehyde **3** was prepared from L-sorbitol in two steps, as described by *Ness et.al.*[6] and *Bourne et.al.*[7] with 51% overall yield. Before use the free aldehyde **3** was obtained by sublimation *in vacuo* at 130-140° C of the initially formed hydrate. Aldehyde **3** was obtained as small white needles; M.p.: 176-181° C (lit.[6]: 186-189° C).

(1S,3S,5R,6R,8R)-5-[(1R)-1,2-dihydroxyethyl]-3,8-diphenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane 7

To a suspension of 54.6 g L-sorbitol (0.300 mol) in cyclohexane/DMF (300/15 ml) was added freshly distilled benzaldehyde (61.0 ml, 0.60 mol) and 50% aq. sulphuric acid (0.6 ml). The reaction mixture was stirred vigo-

rously and heated to reflux while water was removed by azeotropic distillation with a Dean-Stark apparatus. Within thirty minutes the product started to deposit. After four hours no more water was formed and the reaction mixture was cooled to room temperature. The acid was neutralized by addition of a saturated aqueous $NaHCO_3$ solution (100 ml) under vigorous stirring during one hour. The product was filtered off, washed with hot water (200 ml) and, after cooling, diethyl ether. The product was dried *in vacuo*. The yield of diol **7** was 62.3 g (0.174 mol, 58 %); M.p.: 206-208° C; IR (KBr) 3300, 2860, 1590, 1550, 733 and 693 cm^{-1}; ^{1}H-NMR (D_6-DMSO, 200 MHz) δ = 3.4-4.3 (m, 8H, H1, H1', H2'a, H2'b, H5, H6, H10'a and H10b'), 4.46 (t, J = 4.2 Hz, 1H, OH2'), 4.89 (d, J = 5.4 Hz, 1H, OH1'), 5.69 (s, 2H, H3 and H8), 7.38-7.51 (m, 10H, HAr).

(1S,3S,5S,6R,8R)-3,8-diphenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane-5-carboxaldehyde ***8***
To an ice cooled suspension of powdered diol **7** (21.48 g, 60.0 mmol) in dioxane/water (96/24 ml) a solution of 12.84 g sodium metaperiodate (60.0 mmol) was added. After stirring for one hour the reaction mixture was allowed to warm to room temperature and stirred for seventeen hours. The milky suspension was poured into 300 ml of a ice/water mixture whereupon the product started to deposit. After stirring vigorously for one hour, the product was filtered off, washed twice with cold water (100 ml) and dried repeatedly on phosphorous pentoxide *in vacuo*. IR spectroscopy showed that aldehyde **8** was still partial in its hydrate form. The product was suspended in toluene (300 ml) and the remaining water was removed by azeotropic distillation with a Dean--Stark apparatus. The suspension became clear after one hour. Upon cooling to room temperature white 'soft' needles deposited which were filtered off and washed with petroleum ether 40-60 (50 ml). Addition of petroleum ether 40-60 (150 ml) to the mother liquor afforded an additional deposit of crystalline product. The combined crops were dried *in vacuo*, yielding 14.87 g of the free aldehyde **8** (45.6 mmol, 76 %) as white crystals. M.p.: 169-171° C; IR (KBr) 2870, 2860, 1740, 1495, 1450, 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 3.87 (bs, 1H, H1'), 4.16 (dd, J10'a-10'b = 12.7, J1'-10'a = 1.9 Hz, 1H, H10'a), 4.35 (d, J5'-6' = 2.0 Hz, 1H, H6'), 4.38 (d, J5'-6' = 2.0 Hz, 1H, H5'), 4.41 (dd, J10'a-10'b = 12.7, J1'-10'b = 1.3 Hz, 1H, H10'b), 5.57 (s, 1H, -OCPhHO-), 5.71 (s, 1H, -OCPhHO-), 7.34-7.67 (m, 10H, HAr), 9.73 (s, 1H, H1).

(1S,5R,6R)-5-[(4R)-1,3-dioxalan-4-yl]-2,4,7,9-tetraoxabicyclo[4.4.0]decane ***14***
Compound **14** was prepared from L-sorbitol and benzaldehyde, as described by *Ness et.al.*[6]

(4R,5R,6S)-4-[1(R)-1-acetyloxymethoxy-2-acetyloxyethyl]-5-acetyloxymethoxy-6-acetyloxymethyl-1,3-dioxane ***15a*** *and (4S,5R,6S)-4-[1(R)-1-acetyloxy-2-acetyloxy-methoxyethyl]-5-acetyloxymethoxy-6-acetyloxymethyl-1,3-dioxane* ***15b***.
Derivative **14** (100.04 g, 460 mmol) was added to a ice-cooled acetic anhydride/acetic acid/sulphuric acid mixture (220/95/3 ml). The suspension was stirred vigorously for ten minutes and the resulting clear reaction mixture was poured out into 2,5 l ice water. After stirring vigorously for one hour the product started to deposit. The mixture was extracted three with dichloromethane (200 ml). The combined organic layers were washed twice with water (200 ml) and a saturated aqueous $NaHCO_3$ solution (200 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Yield: 121.32 g (287 mmol, 62 %) as a light yellow oil. TLC analysis (eluent: ethyl acetate/petroleum ether 60-80, 30/70, v/v) showed two products (R_f = 0.29 and R_f = 0.32). Part of the product (168 mg) was purified by flash column chromatography (eluent: ethyl acetate/ petroleum ether 60-80, 25/75, v/v).
Concentrating *in vacuo* the fractions containing the product with the Rf value of 0.32 yielded 112 mg of derivative **15a** as a colourless oil IR ($CHCl_3$) 3020, 3010, 2960, 2865, 2770, 1745 and 1430 cm^{-1}; ^{1}H-NMR (D_6-benzene, 250 MHz) δ = 3.39 (ddd, J1"a-6 = 4.7, J1"b-6 = 7.6, J5-6 = 1.4 Hz, 1H, H6), 3.43 (m, 1H, H4), 3.59 (m, 1H, H5), 3.89 (ddd, J1'-2'a = 3.7, J1'-2'b = 2.3, J1'-4 = 8.9 Hz, 1H, H1'), 4.10 (dd, J2'a-2'b = 12.6, J1'-2'a = 3.7, Hz, 1H, H2'a), 4.28 (dd, J1"a-1"b = 11.5, J1"a-6 = 4.7 Hz, 1H, H1"a), 4.31 (m, 1H, H2a), 4.42 (dd, J1"a-1"b = 11.5, J1"b-6 = 7.6 Hz, 1H, H1"b), 4.69 (dd, J2'a-2'b = 12.6, J1'-2'b = 2.3 Hz, 1H, H2'b), 4.88 (d, J2a-2b = 6.1 Hz, 1H, H2b), 5.01 (d, J = 6.4 Hz, 1H, -OCH$_2$OAc), 5.15 (d, J = 6.1 Hz, 1H, -OCH$_2$OAc), 5.44 (d, J = 6.4 Hz, 1H, -OCH$_2$OAc), 5.49 (d, J = 6.1 Hz, -OCH$_2$OAc).
Concentrating the fractions containing the product with R_f value 0.29 gave 36 mg of a colourless oil, most likely being *(4S,5R,6S)-4-[1(R)-1-acetyloxy-2-acetyloxy-methoxyethyl]-5-acetyloxymethoxy-6-acetyloxymethyl-1,3-dioxane* ***15b***. IR ($CHCl_3$) 3020, 3000, 2950, 2865, 2770, 2760 and 1745 cm^{-1}; ^{1}H-NMR (D_6-benzene, 250 MHz) δ = 3.41 (dd, J1"a-6 = 5.3, J5-6 = 1.6 Hz, 1H, H6), 3.59 (bs, 1H, H5), 3.73 (dd, J4-5 = 1.4, J1'-4 = 7.8 Hz, 1H, H4), 3.89 (dd, J1'-2'a = 4.3, J2'a-2'b = 11.2 Hz, 1H, H2'a), 4.08 (dd, J1"a-6 = 5.3, J1"a-1"b = 11.4 Hz, 1H, H1"a), 4.11 (dd, J2'a-2'b = 11.2 Hz, J1'-2'b = 2.1 Hz, 1H, H2'b), 4.28 (d, J1"a-1"b = 11.4 Hz, 1H, H1"b), 4.31 (d, J2a-2b= 6.1 Hz, 1H, H2a), 4.93 (d, J2a-2b = 6.1 Hz, 1H, H2b), 5.02 (d, J = 6.4 Hz, 1H, -OCH$_2$OAc), 5.05 (d, J = 6.1 Hz, 1H, -OCH$_2$OAc), 5.06 (d, J = 6.1 Hz, 1H, -OCH$_2$OAc), 5.18 (ddd, J1'-2'a = 4.3, J1'-2'b = 2.1, J1'-4 = 7.8 Hz, 1H, H1'), 5.25 (d, J = 6.4 Hz, 1H, -OCH$_2$OAc).

(2S,4R,5R,6S)-4-[(1R)-1,2-dihydroxyethyl]-5-hydroxy-6-hydroxymethyl-1,3-dioxane **16**
A solution of 42.0 g of the isomeric tetra acetate mixture (**15a** and **15b**) (100 mmol) in chloroform (250 ml) was cooled in an ice bath under a dry nitrogen atmosphere. A sodium methanolate solution (200 mg sodium in 25 ml methanol) was added dropwise to the acetate solution. Soon the product started to deposit. After keeping in the refrigerator (5° C) during three days the product was filtered off and washed three times with diethyl ether (30 ml) and dried. Recrystallization from ethanol (200 ml). Yield 17.56 g (91 mmol, 91 %) of white needles; M.p.: 157-161° C (lit.[6] : 163-164° C); IR (KBr) 3260, 3000, 2960, 2930, 2860, 2780 cm^{-1}; ^{1}H-NMR (D_6-DMSO, 250 MHz) δ = 3.35 (m, 2H, H4 and H6), 3.56 (m, 6H, H1"a, H1"b, H5, H1', H2'a and H2'b), 4.39 (m, 2H, -OH), 4.58 (m, 2H, -OH), 4.63 (d, J2a-2b = 6.3 Hz, 1H, H2a), 4.93 (d, J2a-2b = 6.3 Hz, 1H, H2b).

(1S,5R,6R,8R)-5-[(4R)-2-phenyl-1,3-dioxalan-4-yl]-8-phenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane **17**
To a suspension of 7.77 g of powdered **16** (40.0 mmol) in cyclohexane/DMF (150/10 ml) was added freshly distilled benzaldehyde (8.49 g, 80.0 mmol, 8.13 ml) and 50% sulphuric acid (1 ml). Under vigorous stirring the reaction mixture was heated to reflux while water was removed by azeotropic distillation. After three hours product started to deposit. After four hours the reaction mixture was cooled to room temperature and the acid was neutralized by adding a saturated aqueous $NaHCO_3$ solution (100 ml). The product was filtered off, washed twice with water (25 ml), three times with diethyl ether (25 ml) and dried *in vacuo*, yielding 10.82 g of one diastereomer of the desired product (29.2 mmol, 73 %); M.p.: 174-175° C; IR ($CHCl_3$) 3090, 3070, 3030, 3000, 2870, 2770, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 3.65 (s, 1H, H1), 3.93 (dd, J4'-5 = 5.8, J5-6 = 1.6 Hz, 1H, H5), 4.05 (s, 1H, H6), 4.10 (dd, J1-10a = 1.5, J10a-10b = 12.7 Hz, 1H, H10a), 4.1-4.3 (m, 2H, H5'a, H5'b), 4.34 (dd, J1-10b = 1.2, J10a-10b = 12.7 Hz, 1H, H10b), 4.85 (d, J3a-3b = 6.3 Hz, 1H, H3a), 5.27 (d, J3a-3b = 6.3 Hz, 1H, H3b), 5.59 (s, 1H, -OCPhHO-), 5.93 (s, 1H, -OCPhHO-), 7.31-7.52 (m, 10H, HAr). Micro analysis: Calculated: C, 68.11; H, 5.95. Found: C, 67.89; H, 6.06 (1.5 % H_2O).
From the filtrate the organic layer was separated, washed once with water (100 ml), dried ($MgSO_4$) and concentrated *in vacuo*. TLC analyses (eluent: ethyl acetate/petroleum ether 60-80, 40/60, v/v) of the resulting syrup showed two main products which were separated by flash column chromatography using the same eluent. This afforded another 593 mg of the product which was isolated as described above (1.60 mmol, 4 %) (R_f = 0.31). The yield of the other diastereomer of **17** was 1.63 g (4.40 mmol, 11 %) (R_f = 0.34).This product was crystallized from ethyl acetate and petroleum ether 60-80. M.p.: 187-188.5° C; IR ($CHCl_3$) 3090, 3070, 3000, 2870, 2770, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 3.60 (bs, 1H, H1), 3.70 (dd, J4'-5 = 7.8, J5-6 = 1.4 Hz, 1H, H5), 4.04 (bs, 1H, H6), 4.01-4.12 (m, 2H, H10a and H5'a), 4.29-4.38 (m, 2H, H10b and H5'b), 4.49 (m, 1H, H4'), 4.83 (d, J3a-3b = 6.3 Hz, 1H, H3a), 5.24 (d, J3a-3b = 6.3 Hz, 1H, H3b), 5.60 (s, 1H, -OCPhHO-), 5.78 (s, 1H, -OCPhHO-), 7.3-7.4 (m, 6H, HAr), 7.4-7.5 (m, 4H, HAr).

(1S,5R,6R,8R)-5-[(1R)-1,2-dihydroxyethyl]-8-phenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane **18**
Derivative **17** (5.70 g, 15.4 mmol) was dissolved in a hot mixture of ethanol/1,2-dichloroethane (30/90 ml) After all the starting material had dissolved, 90% ethanol (400 ml) was added together with formic acid (60 ml). The reaction mixture was heated to reflux, stirred for three hours, cooled to room temperature and concentrated *in vacuo*. The residue was coevaporated with toluene (75 ml). Crystallization from ethanol (80 ml) yielded 3.07 g of diol **18** (10.9 mmol, 71 %) as white crystals; M.p.: 188-189° C; IR (KBr) 3500, 3480, 3010, 2985, 2940 and 2885 cm^{-1}; ^{1}H-NMR (D_6-DMSO, 200 MHz) δ = 3.3-4.1 (m, 8H, H1, H1', H2'a, H2'b, H5, H6, H10a and H10b), 4.42 (t, J = 5.8 Hz, 1H, OH2'), 4.72 (d, J3a-3b = 6.1 Hz, 1H, H3a), 4.81 (d, J = 4.9 Hz, 1H, -OH1'), 5.03 (d, J3a-3b = 6.1 Hz, 1H, H3b), 5.63 (s, 1H, H8), 7.37-7.46 (m, 5H, HAr); ^{13}C-NMR (D_6-DMSO, 50 MHz) (Assignments with APT) δ = 62.51 (s, C2'), 67.51, 69.14, 69.46 and 77.20 (s, C1, C1', C5 and C6), 69.28 (s, C10), 91.91 (s, C3), 99.22 (s, C8), 126.03, 127.81, 128.43 and 138.64 (s, CAr). Micro analysis: Calculated: C, 59.57; H, 6.38. Found: C, 59.61; H, 6.53.

(1S,5S,6R,8R)-8-phenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane-5-carboxaldehyde **12**
Diol **18** (1.00 g, 3.54 mmol) was dissolved in peroxide free dioxane (35 ml) and a solution of 850 mg of sodium metaperiodate (3.92 mmol) in water (35 ml) together with $NaHCO_3$ (1 g) was added. After stirring for two hours at room temperature the reaction mixture was poured out into water (150 ml). Sodium chloride (~12 g) was added and the mixture was extracted three times with dichloromethane (50 ml). The dichloromethane solution was dried ($MgSO_4$) and concentrated *in vacuo*. To the residue toluene (60 ml) was added and water was removed by azeotropic distillation. After concentration to half its original volume the solution was cooled slowly to 5° C after which aldehyde **12** started to deposit as small white needles. The product was filtered off and dried *in vacuo* to constant weight, yielding 595 mg (2.37 mmol, 67 %) of aldehyde **12**. M.p.: 165-166° C; IR ($CHCl_3$) 3060, 3030, 2990, 2970, 2920, 2850, 2770 and 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 3.65 (d, J1'-10'b = 1.4 Hz, 1H, H1'), 4.10 (m, 2H, H10'a and H6'), 4.31 (s, 1H, H5'), 4.35 (dd, J1'-10'b =

1.4, J10'a-10'b = 12.8 Hz, 1H, H10'b), 4.87 (d, J3'a-3'b = 6.4 Hz, 1H, H3'a), 5.36 (d, J3'a-3'b = 6.4 Hz, 1H, H3'b), 5.55 (s, 1H, H8'), 7.31-7.52 (m, 5H, HAr), 9.68 (s, 1H, H1). ^{13}C-NMR ($CDCl_3$, 50 MHz) (Assignments with APT) δ = 69.79 (s, C10'), 69.25 and 71.38 (s, C1' and C6'), 81.51 (s, C5'), 92.44 (s, C3'), 100.58 (s, C8'), 126.07, 128.09 and 128.97 (s, CAr), 137.13 (s, CAr quart.), 199.75 (s, C1). MS: (EI) accurate mass: observed 250.0819; calculated for $C_{13}H_{14}O_5$: 250.0841

(2S,4R,5R,6S)-4-[(1R)-1,2-dihydroxyethyl]-5-hydroxy-6-hydroxymethyl-2-phenyl-1,3-dioxane ***19***
The synthesis of the benzylidene derivative **19** was performed as described by *Vargha et.al.*[15]. The overall yield was 36 %. M.p.: 175-176.5°C (lit.[14] 176-177°C).

2-[(2S,4S,5R,6S)-5-hydroxy-6-hydroxymethyl-2-phenyl-1,3-dioxan-4-yl]-1,3-diphenylimidazolidine ***20***
To a solution of 540 mg of **19** (2.0 mmol) in methanol (15 ml) 470 mg sodium metaperiodate (2.2 mmol) was added and the reaction mixture was stirred for seventeen hours at room temperature. 848 mg dianilinoethane (4.0 mmol) was added together with a catalytic amount of acetic acid (0.5 ml). The reaction mixture was stirred for four hours at room temperature, *in vacuo*. The residue was dissolved in dichloromethane (25 ml) and washed with a saturated aqueous $NaHCO_3$ solution (25 ml) and twice with water (25 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Crystallization from ethyl acetate and petroleum ether 60 - 80 afforded aminal **20** as white crystals. Yield: 748 mg (1.78 mmol, 89 %) (R_f = 0.42 (eluent: methanol/ dichloromethane, 5/95, v/v)). M.p.: 167-168°C; IR ($CHCl_3$) 3420, 3080, 3060, 3000, 2940, 2870, 1590, 1495, 1470, 1445, 1360, 1280, 1140, 1020, 1010, 990, 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 3.56-3.94 (m, 7H), 4.04-4.08 (m, 2H), 5.61 (s, 1H, H2'), 5.69 (d, J2-4' = 5.3 Hz, 1H, H2), 6.85 (d, J = 8.0 Hz, 4H, HAr), 6.98 (d, J = 8.0 Hz, 2H, HAr), 7.21-7.36 (m, 9H, HAr); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) (Assignments with APT) δ = 47.31, 47.65 (s, C4, C5), 62.69 (s, -$\underline{C}H_2OH$), 64.77, 76.03, 79.83, 80.48 (s, C2, C4', C5', C6'), 101.49 (s, C2), 114.60, 114.78, 118.93, 119.06, 126.11, 128.09, 128.88, 129.24, 129.28, 137.45, 147.32, 147.52 (s, CAr).

2-[(1S,3S,5S,6R)-3-phenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decan-5-yl]-1,3-diphenylimidazolidine ***21***
Diol **20** (420 mg, 1.0 mmol) was dissolved in dry THF (20 ml). The solution was cooled in ice under a dry nitrogen atmosphere. Of a 55-60% dispersion of sodium hydride in mineral oil, 131 mg (~ 3 mmol) was washed twice with a small amount of dry pentane (2 ml), partially dried under a dry nitrogen flow, and added in one portion to the stirred solution of **20**. The temperature was allowed to rise to room temperature. After stirring for one hour, dibromomethane (209 ml, 3.0 mmol) and tetrabutyl ammoniumchloride (37 mg, 0.1 mmol) was added and the reaction mixture was refluxed for two hours after which it was cooled again on an ice bath. The excess of sodium hydride was destroyed by adding some methanol (3 ml) and the reaction mixture was concentrated *in vacuo*. To the residue, dichloromethane (20 ml) and water (10 ml) was added. The organic layer was washed twice with water (10 ml), dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica, eluent: ethyl acetate/petroleum ether 60-80, 40/60, v/v). Crystallization from ethyl acetate/petroleum ether 60-80 yielded 336 mg (0.78 mmol, 78 %) of aminal **21** as white crystals (*Rf* = 0.40 (eluent: ethyl acetate/petroleum ether 60-80, 50/50, v/v)); M.p.: 149.5-151°C; IR ($CHCl_3$) 3000, 2850, 1590, 1495, 1470, 1445, 1335, 1280, 1175, 1090, 1045, 1030, 990, 920 and 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 3.48-3.64 (m, 2H), 3.47 (bs, 3H), 3.80 (dd, J1'-10'a = 1.6, J10'a-10'b = 12.5 Hz, 1H, H10'a), 3.86 (bs, 1H), 3.91 (bs, 1H), 4.24 (d, J10'a-10'b = 12.5 Hz, 1H, H10'b), 4.65 (d, J8'a-8'b = 6.3 Hz, 1H, H8'a), 5.24 (d, J8'a-8'b = 6.3 Hz, 1H, H8'b), 5.59 (s, 1H, H3'), 5.95 (d, J2-5' = 8.5 Hz, 1H, H2), 6.73-6.84 (m, 2H, HAr), 6.95 (d, J = 8.2 Hz, 4H, HAr), 7.17-7.42 (m, 9H, HAr); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) (Assignments with APT) δ = 45.97 and 47.68 (s, C4 and C5), 69.42 (s, C10), 69.48, 71.36, 73.06 and 80.58 (s, C1', C2, C5' and C6'), 92.93 (s, C8'), 100.71 (s, C3'), 113.79, 114.74, 117.49, 119.02, 126.21, 127.80, 128.41, 128.72, 129.13, 137.43 and 147.50 (s, CAr).

(1S,3S,5S,6R)-3-phenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane-5-carboxaldehyde ***13***
Aminal **21** (216 mg, 0.50 mmol) was dissolved in dry dichloromethane (10 ml). The solution was cooled in ice under a dry nitrogen atmosphere. A solution of 190 mg *p*-toluenesulphonic acid monohydrate (1.00 mmol) in dichloromethane/methanol (4/1 ml) was added dropwise to the stirred solution of the aminal. After five minutes, a white precipitate, the di-*p*-toluenesulphonate salt of dianilinoethane, was formed. After stirring at 0°C for one hour the reaction mixture was filtered through Hyflow. The residue was washed twice carefully with dichloromethane (5 ml). The dichloromethane solution was washed three times with a saturated aqueous $NaHCO_3$ solution (10 ml) and once with water (10 ml), dried ($MgSO_4$) and concentrated in *vacuo*. To the residue toluene (10 ml) was added and water was removed by azeotropic distillation. After concentration to half its original volume the solution was cooled slowly to 5°C after which aldehyde **13** started to crystallize as small white needles. The product was filtered off and dried *in vacuo*, yielding 99 mg (0.395 mmol, 79 %) of the

desired aldehyde **13**. M.p.: 170-172° C; IR ($CHCl_3$) 3000, 2940, 2880, 1735, 1450, 1400, 1180, 1090, 1025, 920 and 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 3.84 (m, 1H, H1'), 3.92 (dd, J1'-10'a = 1.9, J10'a-10'b = 12.7 Hz, 1H, H10'a), 4.11 (m, 1H, H6'), 4.27 (d, J10'a-10'b = 12.7 Hz, 1H, H10'b), 4.32 (d, J5'-6' = 2.2 Hz, 1H, H5'), 4.74 (d, J8'a-8'b = 6.4 Hz, 1H, H8'a), 5.11 (d, J8'a-8'b = 6.4 Hz, 1H, H8'b), 5.70 (s, 1H, H3'), 7.39-7.42 (m, 3H, HAr), 7.61-7.66 (m, 2H, HAr), 9.74 (s, 1H, H1); ^{13}C-NMR ($CDCl_3$, 50 MHz) (Assignments with APT) δ = 69.77 (s, C10'), 69.19 and 71.44 (s, C1' and C6'), 80.97 (s, C5'), 92.36 (s, C8'), 101.38 (s, C3'), 126.69, 127.91, 128.38 (s, CAr), 136.69 (s, CAr quart.), 199.67 (s, C1).

(1S,3S,5R,6R,8R)-5-[(1R)-1,2-dihydroxyethyl]-3,8-di[4-methoxyphenyl]-2,4,7,9-tetraoxabicyclo[4.4.0]-decane **27**

To a solution of 100.10 g of L-sorbitol (0.55 mol) in water/DMF (150/50 ml) 25 ml of freshly distilled *p*-methoxybenzaldehyde (0.20 mol) was added, followed by 25 ml concentrated aqu.HCl. The solution was stirred vigorously. After three hours the product started to deposit. After stirring overnight the resulting suspension was cooled on an ice bath and the product was filtered off and washed twice with a saturated aqueous $NaHCO_3$ (200 ml) and twice with water (200 ml). The product was dried *in vacuo*, yielding 39.80 g of diol **27** (95 mmol, 17 % (95 % based on the amount of *p*-methoxybenzaldehyde used)) as a white powder. M.p.: 185-187° C; IR (KBr) 3300, 2960, 2840, 1585, 1550, 1105, 735 and 695 cm^{-1}; ^{1}H-NMR (D_6-DMSO, 200 MHz) δ = 3.4 - 4.2 (m, 8H, H1, H1', H2'a, H2'b, H5, H6, H10a and H10b), 3.76 (s, 6H, -O<u>C</u>H$_3$ (2x)), 4.47 and 4.85 (bs, 1H, -O<u>H</u>), 5.61 (s, 2H, H3 and H8), 6.94 (m, 4H, HAr), 7.39 (m, 4H, HAr).

(1S,3S,5S,6R,8R)-3,8-di[4-methoxyphenyl]-2,4,7,9-tetraoxabicyclo[4.4.0]decane-5-carboxaldehyde **28**

Powdered diol **27** (20.9 g, 50.0 mmol) was suspended in dioxane/water (100/25 ml). To the cooled suspension was added a solution of 12.84 g sodium metaperiodate (60.0 mmol). After stirring for one hour the reaction mixture was allowed to warm to room temperature and stirred overnight. The milky suspension was poured into 300 ml of a mixture of ice and water and stirred vigorously for one hour. The product was filtered off, washed twice with cold water (100 ml), partially dried on the air during one night, suspended in toluene (300 ml) and the remaining water was removed by azeotropic distillation with a Dean-Stark apparatus. The suspension became almost clear after one hour. The hot solution was filtered and cooled to room temperature. The product (white needles) was filtered off and washed with petroleum ether 40-60 (50 ml). Addition of petroleum ether 40-60 (150 ml) to the mother liquor afforded an additional deposit of product. The combined crops were dried *in vacuo*, yielding 15.25 g of aldehyde **28** (39.5 mmol, 79 %) as white crystals. M.p.: 167-168° C; IR ($CHCl_3$) 2960, 2860, 2830, 1735, 1610, 1510, 1390, 1250, 1170, 1100, 1035, 995, 830 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 3.80-3.82 (m, 7H, -OC<u>H</u>$_3$ (2x) and H1'), 4.12 (dd, J1'-10'a = 1.8, J10'a-10'b = 12.7 Hz, 1H, H10'a), 4.30 (bs, 1H, H6'), 4.34 (s, 1H, H5'), 4.36 (dd, J1'-10'b = 1.1, J10'a-10'b = 12.7, H10'b), 5.51 (s, 1H, -OCPh<u>H</u>O-), 5.66 (s, 1H, -OCPh<u>H</u>O-), 6.87 (d, J = 8.8 Hz, 2H, HAr), 6.93 (d, J = 8.8 Hz, 2H, HAr), 7.41 (d, J = 8.8 Hz, 2H, HAr), 7.56 (d, J = 8.8 Hz, 2H, HAr), 9.70 (s, 1H, H1).

The general procedure for the additions of allyltrimethylsilane **4** *to L-xylose derivatives* **3**, **8**, **12**, **13** *and* **28**:

The aldehyde (1.00 mmol) was dissolved in dry dichloromethane (25 ml). The solution was cooled to the desired reaction temperature under a dry nitrogen atmosphere. The Lewis acid was added dropwise using a syringe. An exception was made for magnesium bromide etherate and zink dichloride which were added as their pure solid forms. After stirring for fifteen minutes. 198 µl allyltrimethylsilane (1.25 mmol) was added dropwise. The reactions were monitored by TLC-analysis. After complete conversion of all the starting material the reaction was quenched by adding dropwise 1.5 mol. equivalents (with respect to the amount of Lewis acid used) of triethyl amine. The reaction mixture was allowed to warm to room temperature. Successively a saturated aqueous $NaHCO_3$ solution (20 ml) was added and the mixture was stirred for one hour. The dichloromethane layer was separated and washed twice with water (20 ml). The solution was dried ($MgSO_4$) and concentrated *in vacuo*. The products were separated with flash column chromatography

Results for aldehyde **3**: TLC analysis (eluent: ethyl acetate/dichloromethane, 10/90, v/v). Flash column chromatography was performed using silica (eluent: acetone/dichloromethane, 3/97, v/v).

The product with R_f value 0.27 was *(1S,5R,6R)-5-[(1R)-1-hydroxy-3-butenyl]-2,4,7,9-tetraoxabicyclo-[4.4.0]decane* **5**; M.p.(ethyl acetate): 189-192° C; IR (KBr) 3610, 3580, 2870, 1640, 1460, 1405, 1340, 1180, 1100, 1025, 830, 690 cm^{-1}; ^{1}H-NMR (D_6-DMSO, 200 MHz) δ = 2.07 (m, 1H, H2'a), 2.58 (m, 1H, H2'b), 3.47 (m, 2H, H1 and H5), 3.57 (m, 1H, H10a, H10b and H6), 4.13 (m, 1H, H1'), 4.63 (d, J = 6.4 Hz, 1H, -OC<u>H</u>$_2$O-), 4.67 (d, J = 6.4 Hz, 1H, -OC<u>H</u>$_2$O-), 4.94 (d, J = 6.4 Hz, 1H, -OC<u>H</u>$_2$O-), 4.96 (d, J = 6.4 Hz, 1H, -OC<u>H</u>$_2$O-), 5.04 (s, 1H, H4'a), 5.21 (d, J3'-4'b = 7.1 Hz, 1H, H4'b), 5.94 (m, 1H, H3').

The product with R_f value 0.19 was *(1S,5R,6R)-5-[(1S)-1-hydroxy-3-butenyl]-2,4,7,9-tetraoxabicyclo-*

[4.4.0]decane ***6***; M.p.(methanol): 195-196.5° C; IR (KBr) 3600, 2870, 1640, 1455, 1405, 1345, 1180, 1100, 1030, 830 and 690 cm^{-1}; ^{1}H-NMR (D_6-DMSO, 200 MHz) δ = 2.19 (m, 1H, H2'a), 2.49 (m, 1H, H2'b), 3.4-3.5 (m, 2H, H1 and H5), 3.55-3.65 (m, 3H, H10a, H10b and H6), 4.31 (m, 1H, H1'), 4.68 (d, J = 6.3 Hz, 1H, -OC$\underline{H}_2$O-), 4.71 (d, J = 6.3 Hz, 1H, -OC$\underline{H}_2$O-), 4.95 (d, J = 6.3 Hz, 1H, -OC$\underline{H}_2$O-), 4.99 (d, J = 6.3 Hz, 1H, -OC$\underline{H}_2$O-), 5.19 (s, 1H, H4'a), 5.23 (d, J3'-4'b = 7.0 Hz, 1H, H4'b), 6.02 (m, 1H, H3').

Results for aldehyde **8**: TLC analysis (eluent: ethyl acetate/petroleum ether 60-80, 50/50, v/v) Flash column chromatography was performed using silica (eluent: ethyl acetate/petroleum ether 60-80, 40/60, v/v).
The product with R_f value 0.61 was *(1S,3S,5R,6R,8R)-3,8-diphenyl-5-[(1R)-1-trimethylsilyloxy-3-butenyl]-2,4,7,9-tetraoxabicyclo[4.4.0]decane* ***9b***; M.p.(petroleum ether 60-80): 158-159° C; IR ($CHCl_3$) 2875, 1640, 1455, 1405, 1100, 830, 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 0.02 (s, 9H, -OSi(C$\underline{H}_3$)$_3$), 2.25-2.37 (m, 1H, H2'a), 2.40-2.48 (m, 1H, H2'b), 3.70 (dd, J1'-5 = 9.2, J5-6 = 1.5 Hz, 1H, H5), 3.78 (d, J1-10a = 1.2 Hz, 1H, H1), 4.02 (s, 1H, H), 4.12-4.21 (m, 2H, H1' and H10a), 4.39 (dd, J1-10b = 1.0, J10a-10b = 12.5 Hz, 1H, H10b), 5.07 (d, J3'-4'a = 4.0 Hz, 1H, H4'a), 5.13 (s, 1H, H4'b), 5.56 and 5.58 (s, 1H, H3/H8), 5.78-5.95 (m, 1H, H3'), 7.32-7.38 (m, 6H, HAr), 7.52-7.59 (m, 4H, HAr).
The product with R_f value 0.51 was *(1R,3R,5R,7R,9S,12R,14R)-7,12-diphenyl-3-trimethyl-silylmethyl-2,6,8,11,13-pentaoxatricyclo[9.3.0.0^{9,14}]tetradecane* ***10***;. M.p.(petroleum ether 60-80): 176-178° C; IR ($CHCl_3$) 3000, 2955, 2900, 1450, 1248, 1120, 1100, 1045, 855, 840, 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 0.00 (s, 9H, -Si(C$\underline{H}_3$)$_3$), 1.00 (dd, J1'a-1'b = 13.9, J1'a-3 = 10.0 Hz, 1H, H1'a), 1.24 (dd, J1'a-1'b = 13.9, J1'a-3 = 5.1 Hz, 1H, H1'b), 1.74-1.86 (m, 1H, H4a), 2.45-2.56 (m, 1H, H4b), 3.99 (d, J1-14 = 5.3 Hz, 1H, H1), 4.18-4.37 (m, 6H, H3, H5, H9, H10a, H10b and H14), 5.57 (s, 1H, -OCPhHO-), 5.59 (s, 1H, -OCPhHO-), 7.31-7.37 (m, 6H, HAr), 7.50-7.56 (m, 4H, HAr); MS: (EI) accurate mass: observed 440.6089; calculated for $C_{25}H_{32}O_5Si$: 440.6116.
The product with R_f value 0.25 was *(1S,3S,5R,6R,8R)-3,8-diphenyl-5-[(1R)-1-hydroxy-3-butenyl]-2,4,7,9-tetraoxabicyclo-[4.4.0]decane* ***9a***; M.p.(ethyl acetate/petroleum ether 60-80): 167-168° C; IR ($CHCl_3$) 3610, 3580, 2870, 1642, 1460, 1405, 1345, 1175, 1100, 1030, 828 and 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 2.12-2.32 (m, 1H, H2'a), 2.58-2.67 (m, 1H, H2'b), 3.74 (dd, J1'-5 = 8.4, J5-6 = 1.9 Hz, 1H, H5), 3.82 (d, J1-10a = 1.4 Hz, 1H, H1), 3.86-4.22 (m, 3H, H1', H6 and H10a), 4.40 (dd, J1-10b = 1.2, J10a-10b = 12.6 Hz, 1H, H10b), 5.13 (s, 1H, H4'a), 5.18 (d, J3'-4'b = 6.7 Hz, 1H, H4'b), 5.62 (s, 1H, -OCPhHO-), 5.63 (s, 1H, -OCPhHO-), 5.81-5.95 (m, 1H, H3'), 7.33-7.39 (m, 6H, HAr), 7.45-7.59 (m, 4H, HAr).

Results for aldehyde **12**: TLC analysis (eluent: methanol/dichloromethane, 10/90, v/v). Flash column chromatography was performed using silica (eluent: methanol/dichloromethane, 3/97, v/v).
The product with R_f value 0.39 was *(1S,5R,6R,8R)-5-[(1R)-1-hydroxy-3-butenyl]-8-phenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane* ***22***; M.p.(ethyl acetate): 186-188° C; IR ($CHCl_3$) 3550, 3065, 3000, 2850, 2765, 1635, 1450, 1395, 1360, 1335, 1190, 1120, 1085, 995, 915, 830, 805 and 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 2.19-3.30 (m, 1H, H2'a), 2.53-2.58 (m, 1H, H2'b), 3.49 (dd, J1'-5 = 8.2, J5-6 = 1.7 Hz, 1H, H5), 3.59 (d, J1-10b = 1.2 Hz, 1H, H1), 4.11 (dd, J1-10a = 1.9, J10a-10b = 12.8 Hz, 1H, H10a), 4.10 (m, 1H, H1'), 4.14 (s, 1H, H6), 4.35 (dd, J1-10b = 1.2, J10a-10b = 12.8 Hz, 1H, H10b), 4.80 (d, J3a-3b = 6.3 Hz, 1H, H3a), 5.14 (s, 1H, H4'a), 5.21 (d, J3'-4'b = 7.3 Hz, 1H, H4'b), 5.25 (d, J3a-3b = 6.3 Hz, 1H, H3b), 5.62 (s, 1H, H8), 5.77-5.95 (m, 1H, H3'), 7.34-7.39 (m, 3H, HAr), 7.51-7.56 (m, 2H, HAr).
The product with R_f value 0.30 was *(1S,5R,6R,8R)-5-[(1S)-1-hydroxy-3-butenyl]-8-phenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane* ***23***; M.p.(ethyl acetate): 193-194° C; IR ($CHCl_3$) 3550, 3060, 3000, 2850, 1635, 1450, 1395, 1365, 1335, 1180, 1120, 1090, 995, 830, 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 2.25-3.51 (m, 2H, H2'a, H2'b), 3.57 (bs, 2H, H1, H5), 3.97 (s, 1H, H6), 4.10 (dd, J1-10a = 2.0, J10a-10b = 12.8 Hz, 1H, H10a), 4.12 (m, 1H, H1'), 4.36 (dd, J1-10b = 1.0, J10a-10b = 12.8 Hz, 1H, H10b), 4.82 (d, J3a-3b = 6.3 Hz, 1H, H3a), 5.11 (s, 1H, H4'a), 5.18 (d, J3'-4'b = 8.7 Hz, 1H, H4'b), 5.31 (d, J3a-3b = 6.3 Hz, 1H, H3b), 5.57 (s, 1H, H8), 5.83-6.03 (m, 1H, H3'), 7.33-7.36 (m, 3H, HAr), 7.48-7.51 (m, 2H, HAr).

Results for aldehyde **13**: TLC analysis (eluent: methanol/dichloromethane, 10/90, v/v). Flash column chromatography was performed using silica (eluent: methanol/dichloromethane, 3/97, v/v).
The product with R_f value 0.86 was *(1R,3R,5R,7R,9S,14R)-7-phenyl-3-trimethylsilylmethyl-2,6,8,11,13-pentaoxatricyclo[9.3.0.0^{9,14}]tetradecane* ***25***; M.p.(petroleum ether 60-80): 176-178.5° C; IR ($CHCl_3$) 3010, 2950, 2900, 1450, 1248, 1120, 1100, 1045, 855, 840, 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 0.00 (s, 9H, -Si(C$\underline{H}_3$)$_3$), 1.04 (dd, J1'a-1'b = 13.9, J1'a-3 = 10.4 Hz, 1H, H1'a), 1.25 (dd, J1'a-1'b = 13.9, J1'a-3 = 5.1 Hz, 1H, H1'b), 1.81 (ddd, J = 9.0, J = 9.2, J4a-4b = 12.2 Hz, 1H, H4a), 2.50 (ddd, J3-4b ≈ J4b-5 = 6.1, J4a-4b = 12.2 Hz, 1H, H4b), 3.96-4.34 (m, 7H, H1, H3, H5, H9, H10a, H10b and H14), 4.76 (d, J12a-12b = 6.1 Hz, 1H, H12a), 5.14 (d, J12a-12b = 6.1 Hz, 1H, H12b), 5.55 (s, 1H, H7), 7.30-7.40 (m,

3H, HAr), 7.49-7.54 (m, 2H, HAr); MS(EI): accurate mass: obs. 364.5112; calc. for $C_{19}H_{32}O_5Si$: 364.5138.
The product with R_f value 0.36 was *(1S,3S,5R,6R)-5-[(1R)-1-hydroxy-3-butenyl]-3-phenyl-2,4,7,9-tetraoxabicyclo[4.4.0]decane* **26**; M.p.(ethyl acetate and petroleum ether 60-80): 186-187.5° C; IR ($CHCl_3$) 3550, 3065, 3000, 2850, 2765, 1635, 1450, 1395, 1360, 1335, 1190, 1120, 1085, 995, 915, 830, 805 and 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 2.28 (m, 1H, H2'a), 2.65 (m, 1H, H2'b), 3.68 (dd, J1'-5 = 8.5, J5-6 = 1.8 Hz, 1H, H5), 3.80 (bs, 1H, H1), 3.93 (dd, J1-10a = 1.9, J10a-10b = 12.7 Hz, 1H, H10a), 3.95 (s, 1H, H6), 4.09 (m, 1H, H1'), 4.28 (d, J10a-10b = 12.7 Hz, 1H, H10b), 4.83 (d, J8a-8b = 6.3 Hz, 1H, H8a), 5.16 (s, 1H, H4'a), 5.20 (d, J8a-8b = 6.3 Hz, 1H, H8b), 5.23 (d, J3'-4'b = 5.1 Hz, 1H, H4'b), 5.61 (s, 1H, H3), 5.79-5.99 (m, 1H, H3'), 7.34-7.42 (m, 3H, HAr), 7.54 - 7.59 (m, 2H, HAr).

Results for aldehyde **28**: TLC analysis (eluent: methanol/dichloromethane, 10/90, v/v). Flash column chromatography was performed using silica (eluent: methanol/dichloromethane, 5/95, v/v).
The product with R_f value 0.69 was *(1R,3R,5R,7R,9S,12R,14R)-7,12-di[4-methoxyphenyl]-3-trimethylsilylmethyl-2,6,8,11,13-pentaoxatricyclo[9.3.0.0^{9,14}]tetradecane* **29**; M.p.(petroleum ether 60-80): 184-185.5° C; IR ($CHCl_3$) 3000, 2940, 2900, 1450, 1255, 1120, 1100, 1045, 855, 840, 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 0.02 (s, 9H, -Si($C\underline{H}_3$)$_3$), 1.00 (dd, J1'a-1'b = 13.9, J1'a-3 = 11.9 Hz, 1H, H1'a), 1.24 (dd, J1'a-1'b = 13.9, J1'a-3 = 5.0 Hz, 1H, H1'b), 1.75 (m, 1H, H4a), 2.50 (m, 1H, H4b), 3.79 (s, 6H, -O$C\underline{H}_3$), 3.97 (bs, 1H, H9), 4.21-4.36 (m, 6H, H1, H3, H5, H10a, H10b, H14), 5.55 (s, 2H, H7 and H12), 6.87 (m, 4H, HAr), 7.45 (m, 4H, HAr); MS(EI): accurate mass: obs. 500.6117; calc. for $C_{27}H_{36}O_7Si$: 500.6642.
The product with R_f value 0.36 was *(1S,3S,5R,6R)-5-[(1R)-1-hydroxy-3-butenyl]-3,8-di[4-methoxyphenyl]-2,4,7,9-tetraoxabicyclo[4.4.0]decane* **30**; M.p.(ethyl acetate/petroleum ether 60-80): 182 - 183.5° C; IR ($CHCl_3$) 3550, 3065, 3000, 2850, 2765, 1635, 1450, 1395, 1360, 1335, 1190, 1120, 1085, 995, 915, 830, 805 and 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 2.26 (m, 1H, H2'a), 2.64 (m, 1H, H2'b), 3.72 (dd, J1'-5 = 8.2, J5-6 = 1.7 Hz, 1H, H5), 3.81 (bs, 1H, H1), 3.93 (dd, J1-10a = 1.8, J10a-10b = 12.7 Hz, 1H, H10a), 3.95 (s, 1H, H6), 4.09 (m, 1H, H1'), 4.28 (d, J10a-10b = 12.7 Hz, 1H, H10b), 4.85 (d, J8a-8b = 6.3 Hz, 1H, H8a), 5.14 (s, 1H, H4'a), 5.20 (d, J8a-8b = 6.3 Hz, 1H, H8b), 5.23 (d, J3'-4'b = 5.1 Hz, 1H, H4'b), 5.61 (s, 1H, H3), 5.79-6.01 (m, 1H, H3'), 7.31-7.40 (m, 3H, HAr), 7.53- 7.62 (m, 2H, HAr).

(1R,3S,5S,6R,10S)-10-hydroxymethyl-3-phenyl-5-[2-propenyl]-2,4,7,9-tetraoxabicyclo[4.4.0]decane **24**.
Homoallyl alcohol **23** (292 mg, 1.00 mmol) was dissolved in dry 1,2-dichloroethane (10 ml) and brought under a dry nitrogen atmosphere. *p*-Toluenesulphonic acid monohydrate, 38 mg (0.2 mmol), was added and the solution was heated to reflux for two hours. After cooling to room temperature a saturated aqueous $NaHCO_3$ solution (10 ml) was added and the mixture was stirred vigorously for fifteen minutes. The mixture was diluted with dichloromethane (15 ml) and was washed twice with water (20 ml), dried ($MgSO_4$) and concentrated *in vacuo*. The product was purified with flash column chromatography (silica, eluent: ethyl acetate/petroleum ether 60-80, 80/20, v/v) and crystallized from ethyl acetate; M.p.: 191-194°C; IR ($CHCl_3$) 3400, 3060, 3000, 2850, 1635, 1450, 1395, 1365, 1335, 1180, 1120, 1090, 995, 915, 830, 805 and 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 2.54 (t, J1'a-2' = 1.4,J1'a-1'b≈J1'a-5 = 7.0 Hz, 1H, H1'a), 2.55 (t, J1'b-2' = 1.4,J1'a-1'b≈J1'b-5 = 7.0 Hz, 1H, H1'b), 3.53 (bs, 1H, H10), 3.91 (dt, J1'a-5≈J1'b-5 = 7.0, J5-6 = 1.6 Hz, 1H, H5), 3.83-4.14 (m, 4H, -$C\underline{H}_2$OH, H1 and H6), 4.80 (d, J8a-8b = 6.2 Hz, 1H, H8a), 5.13 (dd, J3'a-3'b = 0.9, J2'-3'a = 10.0 Hz, 1H, H3'a), 5.20 (dd, J3'a-3'b = 1.8, J2'-3'b = 18.0 Hz, 1H, H3'b), 5.27 (d, J8a-8b = 6.2 Hz, H8b), 5.59 (s, 1H, H3), 5.84 (dddd, J1'a-2' = 1.4, J1'b-2' = 1.4, J2'-3'a = 10.0, J2'-3'b = 18.0 Hz, 1H, H2'), 7.33-7.40 (m, 3H, HAr), 7.49-7.54 (m, 2H, HAr); NOE : Irradiation at the signal of H3 (s, 5.59 ppm) showed a strong nOe effect on both H10 (bs, 3.53 ppm) and H5 (dt, 3.91 ppm).

(2S,3R,5R)-3-hydroxy-2-hydroxymethyl-5-trimethylsilylmethyl-tetrahydrofuran **11**
Of tricyclic products **10**, **25** and **29** 0.25 mmol was dissolved in a dioxane/water mixture (3/2 ml). Trifluoroacetic acid (77 µl, 1.00 mmol) was added and the reaction mixture was heated to reflux. Reaction times for the different starting materials were thirty minutes, two hours and fifteen minutes respectively. After compete conversion of the starting material the reaction mixture was cooled to room temperature and the acid was neutralized by carefully adding 126 mg sodium hydrogen carbonate (1.50 mmol) and stirring for fifteen minutes. A solution of 214 mg sodium metaperiodate (1.00 mmol) in water (3 ml) was added dropwise to the reaction mixture. After stirring for fifteen minutes 76 mg sodium borohydride (2.00 mmol) was added. After stirring for one hour the reaction mixture was diluted with dichloromethane (10 ml). The resulting mixture was stirred vigorously for thirty minutes and the layers were separated. This procedure was repeated and the combined organic extracts were washed with water (20 ml), dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified with flash column chromatography (silica, eluent: ethyl acetate/dichloromethane, 5/95, v/v). The main product **11** had a R_f value of 0.27 and could be recrystallized from methanol. The yields

were 78, 34 and 81% respectively. M.p.: 123-127°C; IR ($CHCl_3$) 3420, 3050, 2930, 1450, 1400, 1390, 1370, 1070 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) (Assignments with COSY) δ = 0.03 (s, 9H, -Si(CH_3)$_3$), 0.96 (dd, J1"a-1"b = 13.9, J1"a-5 = 9.5 Hz, 1H, H1"a), 1.17 (dd, J1"a-1"b = 13.9, J1"b-5 = 5.6 Hz, 1H, H1"b), 1.60 (ddd, J4a-5 = 8.7, J4a-4b = 12.3, J3-4a = 7.6 Hz, 1H, H4a), 2.37 (ddd, J4b-5 = 7.0, J4a-4b = 12.3, J3-4b = 6.0 Hz, 1H, H4b), 3.62 (dd, J1'a-2 = 5.2, J1'a-1'b = 11.6 Hz, 1H, H1'a), 3.69 (dd, J1'b-2 = 4.2, J1'a-1'b = 11.6 Hz, 1H, H1'b), 3.82 (ddd, J2-3 = 5.7, J1'a-2 = 5.2, J1'b-2 = 4.2 Hz, 1H, H2), 4.16 (dddd, J1"a-5 = 9.5, J1"b-5 = 5.6, J4a-5 = 8.7, J4b-5 = 7.0 Hz, 1H, H5), 4.28 (ddd, J3-4a = 7.6, J3-4b = 6.0, J2-3 = 5.7 Hz, 1H, H3); NOE : Irradiation at the H2-signal (ddd, 3.82 ppm) resulted in a strong NOE effect on the H4a-signal (ddd, 1.60 ppm) and weak NOE effects on the signals of H1"a (dd, 0.96 ppm) and H1"b (dd, 1.17 ppm). Irradiation at the H3-signal (ddd, 4.28 ppm) resulted in a NOE effect on the H4b-signal (ddd, 2.37 ppm). Irradiation at the H5-signal (dddd, 4.16 ppm) resulted in a strong NOE effect on the H4b-signal (ddd, 2.37 ppm) and weak effects on the signals of H1"a (dd, 0.96 ppm) and H1"b (dd, 1.17 ppm).

(1S,3S,5R,6R,8R)-3,8-diphenyl-5-[(1R)-1-hydroxy-3-butenyl]-2,4,7,9-tetraoxabicyclo[4.4.0]decane ***12a*** *from derivative* ***10***

Tricyclic derivative **10** (110 mg, 0.25 mmol) was dissolved in dry dichloromethane (5 ml). The solution was cooled to -78° C under a dry nitrogen atmosphere. Boron trifluoride etherate (62 µl, 0.50 mmol) was added dropwise using a syringe. The reaction mixture was allowed to warm to -20°C. The reaction mixture was stirred at this temperature for one hour. After complete conversion of all the starting material the reaction was quenched by adding dropwise 139 µl of triethyl amine (1.00 mmol). The reaction mixture was allowed to warm to room temperature. Successively a saturated aqueous $NaHCO_3$ solution (10 ml) was added and the mixture was stirred vigorously for one hour. The dichloromethane layer was separated and washed twice with water (10 ml). The solution was dried ($MgSO_4$) and concentrated *in vacuo*. The product was purified with flash column chromatography (silica, eluent: ethyl acetate/petroleum ether 60-80, 40/60, v/v). Crystallization was performed from ethyl acetate and petroleum ether 60-80 yielding 78 mg of homoallyl alcohol **9a** (0.21 mmol, 85 %) as white needles. M.p.: 165-167.5° C. Analytical data was similar to those written above. Following the same procedure starting with 91 mg of derivative **25** (0.25 mmol) yielded 59 mg of homoallyl alcohol **26** (0.20 mmol, 81 %). Starting with 125 mg of derivative **29** (0.25 mmol) yielded 101 mg of homoallyl alcohol **30** (0.24 mmol, 94 %).

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