Stereoselectivity of the hydrogenation of galactofuranosyl *exo*glycals

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Dedicated to Professor Alain Krief

Abstract
This work describes a study of the α/β-diastereoselectivity of the hydrogenation of phosphonylated exoglycals in the galactofuranose series. Nine exoglycals displaying sterically hindering groups on the α or the β face have been synthesized and hydrogenated using Pearlman's catalyst. These reactions gave the expected *C*-glycoside with good to excellent α -selectivities.

Keywords: Exoglycal, C-glycoside, hydrogenation, phosphonate

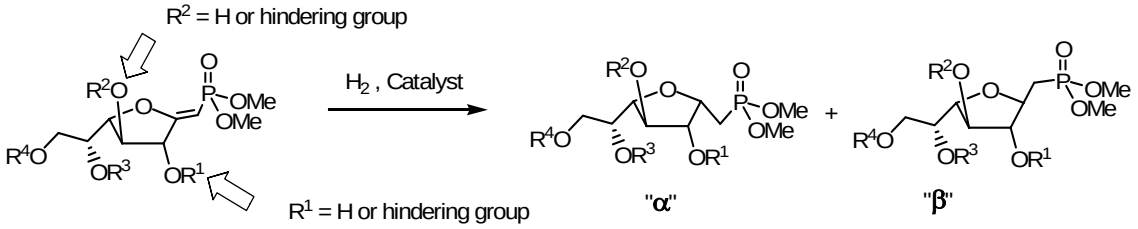
Introduction

In the course of our study involving the exploration of the mechanism of glycosyl processing enzymes, we have developed an approach to generate *C*-glycosidic phosphonates in the galactofuranose series (Gal*f*). First we developed conformational probes mimicking UDP-Gal*f* the substrate of key enzymes implied in the biosynthesis of the mycobacterial cell wall: UDP-galactose mutase (UGM) and Galacto*furanosyl* transferases.[1,2] We then prepared nucleotide-exoglycals, fluorinated[3] or not,[4] that displayed interesting time-dependent inactivation properties against UDP-galactose mutase.

In our studies, exoglycals became key intermediates: for instance we found that once protected with four TBDMS groups, the enol ether could be hydrogenated selectively to give a α-phosphonate (Scheme 1) thus yielding a *C*-glycosidic analog of the natural Gal*f*-1- α-phosphate.[4] In some cases, glycoconjugates whose anomeric configuration is inverted compared to the natural substrate displayed interesting inhibition properties.[5] A survey of the literature in the Gal*f* series showed that there is no published method to synthesize the corresponding Gal*f*-1- β-

phosphonate. Therefore, we addressed the question of the obtention of β-phosphonates from phosphonylated exoglycals.

The purpose of this study is to define the α/β stereoselectivity of the hydrogenation as a function of the protective group pattern of the phosphonylated exoglycal. Since both α and β diastereomers can be transformed into biologically relevant molecules, we found it interesting to assess the scope of these hydrogenations as a function of i) the selective steric hindrance of one of the two faces of the exoglycal ii) the directing effect of a OH group at the 2- or the 3- or the 5-position of the galactofuranosyl moiety (scheme 1). In the early eighties, it had already been acknowledged that hydroxyl-directed hydrogenations are of considerable generality.[6,7] The addition of hydrogen usually occurs from the same face of a cyclic system than the directing group.[8,9] Thus, we developed the chemistry to differentiate the 2- and the 3-positions of the starting exoglycal and selectively install a hindering group, or a OH group, on either face of the carbohydrate (Scheme 1).



Scheme 1

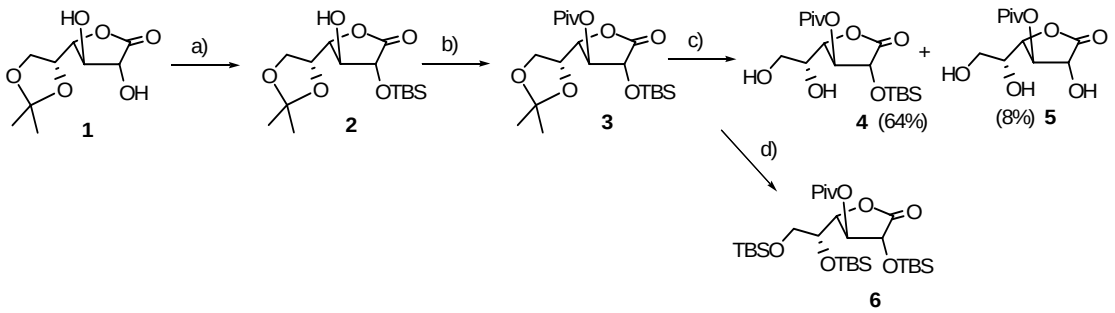
Results and Discussion

Selective protections of the intermediate lactones

First, we developed a synthetic pathway for selectively protecting the 3-position of the starting d-1,4-galactonolactone.

The synthesis starts from known 5,6-*O*-(dimethyl-methylidene)-d-galactono-1,4-lactone **1** (Scheme 2).[10] Despite the steric hindrance of the 5 and 6 positions, alcohol **1** was selectively silylated in presence of a slight excess of TBDMSCl giving **2** in 85% yield. This regioselectivity may be explained by the fact that the carbonyl group of the lactone decreases the p*K*a of the adjacent secondary alcohol, thus increasing its reactivity towards electrophiles. Intermediate alcohol **2** was transformed into lactone **3** (in 93% yield) by addition of pivaloyl chloride. This key intermediate is of particular interest since all the secondary alcohols in lactone **3** are differentiated. Under published conditions ($AcOH/H_2O$, 60°C),[10] the acetonide could be hydrolyzed to afford an intermediate 5,6-diol **4** in an expected 60% yield. This moderate yield can be explained by the concomitant deprotection of the TBDMS group at the 2-position (the resulting triol **5** was isolated in 8%). However, we had planned to install two TBDMS groups at

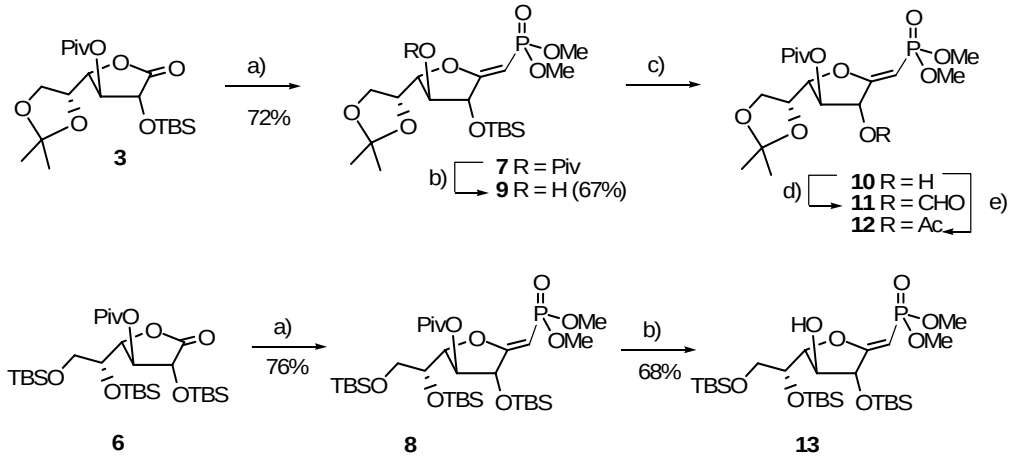
positions 5 and 6: therefore, instead of isolating intermediate diol **4**, we performed the persilylation on the crude hydrolysis mixture yielding **6** in 74% yield for two steps.



Scheme 2. a) TBDMSCl, Im, DMF (85%) b) PivCl, Py, CH_3CN, 80°C (93%) c) AcOH, H_2O, 60°C. d) conditions c then TBDMSCl, Im, DMF, 60°C (74%).

Synthesis of the phosphonylated exoglycals

From lactones **3** and **6** we could synthesize two exoglycals **7** and **8** according to the one-pot procedure developed by Lin *et al*. in 72 and 76% yield, respectively (Scheme 3).[11,12]



Scheme 3. a) $LiCH_2PO(OMe)_2$ then $(CF_3CO)_2O$, Py. b) MeOH, NaH, RT. c) TBAF, THF (73%). d) DCC, HCO_2H, RT (79%). e) Ac_2O, Py, RT (96%).

Since their protective groups patterns were orthogonal, the two key molecules **7** and **8** could easily be transformed into a broad range of exoglycals presenting different functional groups on all the four available alcohols of the galactofuranose moiety. The pivaloates could be chemoselectively hydrolyzed without deprotection of the TBDMS, the acetonide or the phosphonate methyl esters, to give alcohol **9** and **13** in 67 and 68% yield, respectively. A TBAF deprotection could in turn lead to alcohol **10** that was further acylated into formate **11** and acetate **12**. At this stage we had in hand seven exoglycals (molecules **7** to **13**) that could be used in

hydrogenation assays. This series of molecules can be divided into two families: the first one displays a sterically hindering TBDMS group at the 2-position (α face of the exoglycal) and the second one presents a pivaloate at the 3-position hindering the β-face. Moreover, we also tested exoglycals **14** and **15** (Figure 1) whose synthesis had been previously described.[1,4]

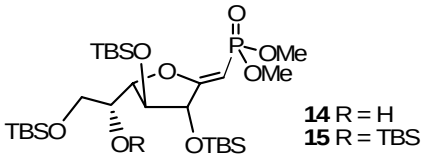


Figure 1

Hydrogenations of the exoglycals

The results of the hydrogenation experiments from exoglycals **7** to **15** are summarized in Table 1. The structures of the major products and some side-products are represented in Figure 2.

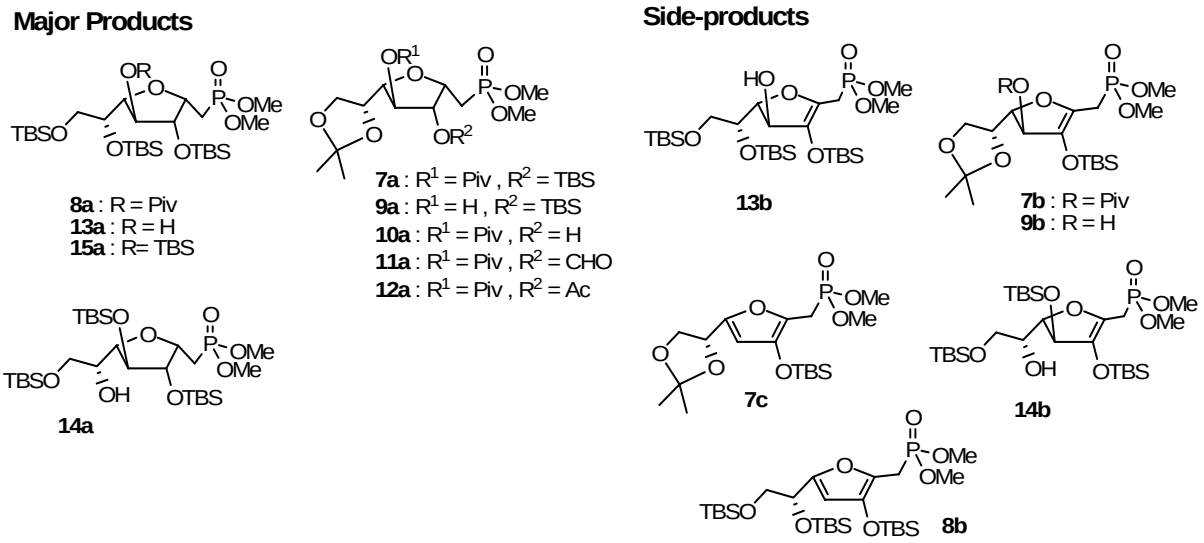


Figure 2

We first had to find the most efficient catalyst for this reaction (Table 1, entries 1 to 4). Exoglycal **13**, presenting a totally hindered **α** face and no bulky group on the **β** face was selected for this series. Interestingly, under high hydrogen pressure (100 bars) and vigorous stirring, the saturation of the enol ether was only observed with Pearlman's catalyst (entry 4), yielding ether **13a** in 89% yield. A single diastereomer was observed by ^{1}H and ^{31}P-NMR of the crude final reaction mixture. The expected α configuration was unambiguously determined by the H1-H2 coupling constant ($J_{1\text{-}2}$ = 4.8 Hz), indicating a *cis* relationship between these two protons. For β-configured galactofuranosides, the $J_{1\text{-}2}$ value would have been lower than 1.0 Hz.[13,14] Moreover,

a NOESY experiment clearly showed a correlation between protons H-1 and H-4 of **13a**, thus confirming the α-configuration. Other standard homogeneous or heterogeneous catalysts (entries 1-3) either did not produce any product or yielded 10% of unidentified side-products. We then systematically performed this reaction with $Pd(OH)_2$ (0.4 equivalent/w) in AcOEt at room temperature under H_2 atmosphere (1.5 bar). Good to excellent yields (72 to 95%) have been obtained for the 9 starting exoglycals (entries 5 to 13). It should be noted that some side-products could be formed (Table 1, entries 5, 7, 8 and 11). We could isolate and characterize some of them (structures depicted in Figure 2). Interestingly, these molecules resulted from a migration of the double bond to give 2-alkoxy-*endo*glycals. In one case, we could even isolate a furan **7c**, likely resulting from an elimination of dihydrofuran **7b**. These side-reactions are quite unusual and consequently the yields were not quantitative. Nevertheless, replacing AcOEt by MeOH as the solvent improved the yield and decreased the amount of side-products (entry 6).

Table 1. Hydrogenations of exoglycals **8-15**

Entry	Substrate	Catalyst	Solvent	H_2 (bar)	Yield[a]	α / β [b]	Product	J_{1-2} (Hz)[c]	Side products
1	**13**	Pd/C	AcOEt	100	0	-	-[d]	-	-[d]
2	**13**	PtO_2	AcOEt	100	0	-	-	-	-[e]
3	**13**	$(Ph_3P)_3RhCl$	CH_2Cl_2	100	0	-	-	-	-[e]
4	**13**	$Pd(OH)_2$	AcOEt	100	89	100/0	**13a**	4.8	-
5	**15**	$Pd(OH)_2$	AcOEt	1.5	82	100/0	**15a**	2.8	**15b** (8%)
6	**15**	$Pd(OH)_2$	MeOH	1.5	95	100/0	**15a**	2.8	-
7	**8**	$Pd(OH)_2$	AcOEt	1.5	72	100/0	**8a**	3.2	**8b** (8%)
8	**14**	$Pd(OH)_2$	AcOEt	1.5	76	100/0	**14a**	3.7	**14b** (10%)
9	**7**	$Pd(OH)_2$	AcOEt	1.5	95	100/0	**7a**	2.9	-
10	**9**	Pd(OH)2	AcOEt	1.5	89	100/0	**9a**	3.4	-
11	**10**	Pd(OH)2	AcOEt	1.5	55	80/20	**10a**	-	(25%) [f]
12	**11**	Pd(OH)2	AcOEt	1.5	82	82/18	**11a**	-	-
13	**12**	Pd(OH)2	AcOEt	1.5	70	84/16	**12a**	-	-
14	**10**	$(Ph_3P)_3RhCl$	CH_2Cl_2	1.5	0	-	-	-	-

(a) isolated yield. (b) determined by ^1H- and ^{31}P-NMR. (c) coupling constant of the α isomer. (d) no reaction. (e) 10% conversion of the starting *exo*-glycal into two unidentified side-products. (f) unidentified side-products.

Diastereoselectivity of the hydrogenations

The exoglycals bearing a bulky protective group at the 2-position (Piv or TBDMS, molecules **7**, **8**, **13**, **14** and **15**) gave exclusively the " α " *C*-galactosides. For each final ether, we performed NOESY experiments to confirm the "anomeric" configuration. In each case, a NOE effect

between protons H-1 and H-4 was observed which corroborated with the configuration assigned from $J_{1\text{-}2}$ coupling constants. Whatever the steric hindrance of the group at the 3-position (H, Piv or TBDMS), the addition occurred always from the β face specifically. For all these molecules, the "β"-ether has never been observed. From this set of data, the steric hindrance at position 2 seems to be the only parameter governing the α-specificity.

Then, we performed hydrogenations with a bulky pivaloate group at the 3-position and a less hindering functionality at the 2-position (OH, OCHO, OAc, entries 11, 12 and 13). Surprisingly, α-diastereoselectivities were observed in the three cases, the β-phosphonate being formed, at best, in 20% yield. Exoglycal **10** gave a greater amount of side-products thus resulting in a poorer yield (entry 11). A better β-selectivity was expected with substrate **10** for two reasons: i) the steric hindrance of the OH group is rather small ii) OH groups have been shown to direct hydrogenations such a way that the H_2 addition occurs from the same face of a cyclic system. Clearly, this directing effect does not apply with Pearlman catalyst. The directing effect of hydroxyl groups for the hydrogenation reaction has been often observed with rhodium and iridium catalysts.[6] We thus used Crabtree's[6] and Wilkinson's catalysts, under basic or non-basic conditions, using alcohols **10**, **13** and **14** as substrates. Unfortunately, the expected phosphonates were never formed under these conditions (data not shown).

In conclusion, this study showed that the hydrogenation of exoglycals in the galactofuranose series, even unprotected at the 2-position, give a good to excellent α-selectivity. Other parameters than the relative steric hindrance of the two faces of the glycal may be invoked to explain this result: owing to the abundant literature related to the stereoselectivity of reactions taking place at the anomeric center, it is quite reasonable to suggest that stereoelectronic or conformational effects may strongly contribute to the systematic α-selectivity we observed. Conformationally, furanoses are usually less resticted than pyranoses. However, the presence of a trigonal sp^2 hybrized anomeric carbon atom may favour a conformation placing the functional group in a position preventing the H_2 addition from the α-face. Moreover, the mechanism of the hydrogenation under heterogeneous catalysis being still poorly understood, we cannot rule out a directing effect of the two free doublets of the endocyclic oxygen, in other words, a stereoelectronic effect favoring the addition from the β-face of these *exo*glycals.

Experimental Section

General Procedures. All chemicals were purchased from Sigma, Aldrich or Fluka and were used without further purification. Tetrahydrofuran and toluene were freshly distilled over sodium benzophenone, dichloromethane over P_2O_5 and nitromethane over CaH_2. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded with Bruker AC-250 and AMX-400 spectrometers. All new compounds were characterized by ^{1}H, ^{13}C, ^{31}P-NMR as well as by ^{1}H-^{1}H and ^{1}H-^{13}C correlation experiments. Specific optical rotations were measured on a Perkin Elmer 241 Polarimeter in a 1 dm cell. Melting points were determined with a Büchi 535 apparatus. Purification by chromatography

was performed on silica gel Kieselgel Si 60 (40-63 μm) using cyclohexane (Cy) and AcOEt as eluent. Molecule **1** was prepared following literature data.[10] Compounds **14, 15** and **15a** were previously described.[1,4]

Atom and position numberings. We systematically numbered the phosphonate methylene group 1' and adopted the usual numbering for carbohydrates from 1 to 6 with 1 for the anomeric position.

General procedure for exoglycal formation from lactones

To a cooled (-70°C) solution of dimethyl methylphosphonate (1 eq.) in anhydrous THF (18 mL) under Ar was added first butyl lithium (1 eq., 2.5 M solution in hexane) and after 20 min, a solution of lactone (0.4 eq.) in anhydrous THF. The temperature was maintained at –70°C during 10 min, the reaction mixture was then allowed to reach –40°C over a 1 h period. The solution was then diluted with phosphate buffer (1 M, pH = 7) and extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered and concentrated. The residue was dissolved in anhydrous CH_2Cl_2. At 0°C were added pyridine (10 eq.) and trifluoroacetic anhydride (5 eq.). After 3 h at 0°C, the reaction was stopped by addition of saturated aqueous $NaHCO_3$ followed by extraction with AcOEt. The organic phase was dried over $MgSO_4$, filtered and concentrated at reduced pressure. The exoglycal was purified by chromatography on silica gel with cyclohexane/AcOEt (2:1).[1,4]

General procedure for exoglycals hydrogenation

To a solution of exoglycal in AcOEt (final concentration 0.15 M), was added wet $Pd(OH)_2$ (0.4 equiv./w) and the resulting suspension was degassed three times (the solution was left a few seconds under vacuum then under H_2 atmosphere). The suspension was vigorously stirred under H_2 (1.5 bar) for 24 hours, filtrated over celite and concentrated under vacuum.

2-*O*-*tert*-Butyldimethylsilyl-5,6-*O*-(dimethyl-methylidene)-D-galactono-1,4-lactone (2). A suspension of lactone **1**[10] (890 mg, 4.08 mmol), TBDMSCl (1.65 g, 4.28 mmol, 1.05 eq.) and imidazole (415 mg, 6.11 mmol, 1.5 eq.) in anhydrous DMF (12 mL) was stirred, under argon, one hour at 0°C, then overnight at room temperature. The solvent was removed and the resulting mixture was suspended in ether (15 mL) and washed twice with water (10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The resulting crude reaction mixture was submitted to purification by chromatography on silica gel (Cy/AcOEt : 3/1) to give **2** (880 mg, 85 %) as a white solid. $[\alpha]_D^{23}$ -7.1 (c 1.0, $CHCl_3$); m.p. 118°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.42 (d, $J_{2\text{-}3}$ = 8.5 Hz, 1H, H-2), 4.39 (td, $J_{4\text{-}5}$ = 3.9 Hz, $J_{5\text{-}6a,b}$ = 6.8 Hz, 1H, H-5), 4.32 (dd, $J_{2\text{-}3}$ = 8.5 Hz, $J_{3\text{-}4}$ = 8.1 Hz, 1H, H-3), 4.13 (ABX, $J_{5\text{-}6a}$ = 6.8 Hz, $J_{6a\text{-}6b}$ = 8.7 Hz, 1H, H-6a), 4.10 (dd, $J_{3\text{-}4}$ = 8.1 Hz, $J_{4\text{-}5}$ = 3.9 Hz, 1H, H-4), 4.00 (ABX, $J_{5\text{-}6b}$ = 6.8 Hz, $J_{6a\text{-}6b}$ = 8.7 Hz, 1H, H-6b), 1.44, 1.40 (2s, 6H, $C(CH_3)_2$, acetonide), 0.96 (s, 9H, Si-*t*Bu), 0.16 (s, 3H, Si-Me), 0.13 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.57 (C-1), 110.16 ($C(CH_3)_2$, acetonide), 78.35 (C-4), 75.56

(C-2), 74.90 (C-3), 73.73 (C-5), 64.84 (C-6), 26.06 (C(CH_3)$_2$, acetonide), 25.58 (Si-C(CH_3)$_3$), 25.36 (C(CH_3)$_2$, acetonide), 18.19 (Si-*C*(CH_3)$_3$), -4.67 (Si-Me), -5.12 (Si-Me); **MS** (CI-NH_3) *m/z* 350 $[M + NH_4]^+$; **El. Anal.** for $C_{15}H_{28}O_6Si$: calc. (%) C 54.19 H 8.19. mes. C 54.04 H 8.67.

2-*O*-*tert*-Butyldimethylsilyl-5,6-*O*-(dimethyl-methylidene)-3-*O*-pivaloyl-D-galactono-1,4-lactone (3). To a suspension of lactone **2** (1.0 g, 3.0 mmol) in anhydrous acetonitrile (20 mL) were added pyridine (5 mL) and pivaloyl chloride (0.74 mL, 6 mmol, 2 eq.). The mixture was then stirred overnight at 80°C, concentrated and dried under vacuum. The resulting crude mixture was chromatographed on silica gel (Cy/AcOEt : 4/1) to give 3 (2.79g, 93 %) as a white solid. $[\alpha]_D^{23}$ +12.1 (c 1.0, $CHCl_3$); m.p. 69-70°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.34 (t $J_{2\text{-}3} = J_{3\text{-}4}$ = 5.7 Hz, 1H, H-3), 4.52 (d, $J_{2\text{-}3}$ = 5.7 Hz, 1H, H-2), 4.43 (td, $J_{4\text{-}5}$ = 3.9 Hz, $J_{5\text{-}6a,b}$ = 6.6 Hz, 1H, H-5), 4.20 (dd, $J_{3\text{-}4}$ = 5.7 Hz, $J_{4\text{-}5}$ = 3.9 Hz, 1H, H-4), 4.11 (ABX, $J_{5\text{-}6a}$ = 6.6 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 1H, H-6a), 3.94 (ABX, $J_{5\text{-}6b}$ = 6.6 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 1H, H-6b), 1.45, 1.37 (2s, 6H, C(CH_3)$_2$, acetonide), 1.26 (s, 9H, Piv), 0.92 (s, 9H, Si-*t*Bu), 0.16 (s, 3H, Si-Me), 0.13 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.46 (C-1), 172.00 (C=O, Piv), 110.41 (*C*(CH_3)$_2$, acetonide), 79.73 (C-4), 76.17 (C-3), 74.77 (C-5), 73.17 (C-2), 65.04 (C-6), 38.67 (CO-*C*(CH_3)$_3$, Piv), 27.03 (CO-C(*C*H_3)$_3$, Piv), 26.88 (C(*C*H_3)$_2$, acetonide), 25.99 (Si-C(*C*H_3)$_3$), 25.48 (C(*C*H_3)$_2$, acetonide), 17.79 (Si-*C*(CH_3)$_3$), -4.66 (Si-Me), -5.39 (Si-Me); MS (CI-NH_3) *m/z* 434 $[M + NH_4]^+$; El. Anal. for $C_{20}H_{36}O_7Si$: calc. (%) C 57.66 H 8.71. mes. C 57.57 H 8.85.

2,5,6-Tri-*O*-*tert*-butyldimethylsilyl-3-*O*-pivaloyl-D-galactono-1,4-lactone (6). A solution of lactone **3** (500 mg, 1.2 mmol) in AcOH/H_2O 4/1 (9.0 mL) was stirred at 80°C for 3 hours. After concentration under *vacuum*, the resulting oil was submitted three times to azeotropic distillation with toluene and dried overnight under vacuum before being dissolved in anhydrous DMF (7 mL). To this solution were added TBDMSCl (1.2 g, 8 mmol, 6.7 eq.) and imidazole (0.81g, 11.9 mmol, 10 eq.). This mixture was then heated 5 hours at 60°C. The solvent was removed under reduced pressure and the resulting mixture was suspended in ether (15 mL) and washed twice with water (10 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. The crude reaction mixture was purified by chromatography on silica gel (Cy/AcOEt : 35/1) to give **6** (536 mg, 74 %) as a colourless oil. $[\alpha]_D^{23}$ -10.4 (c 0.9, $CHCl_3$); m.p. 52-53°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.41 (t, $J_{2\text{-}3} = J_{3\text{-}4}$ = 5.6 Hz, 1H, H-3), 4.57 (d, $J_{2\text{-}3}$ = 5.6 Hz, 1H, H-2), 4.41 (dd, $J_{3\text{-}4}$ = 5.6 Hz $J_{4\text{-}5}$ = 1.6 Hz, 1H, H-4), 3.97 (ddd, $J_{4\text{-}5}$ = 1.6 Hz, $J_{5\text{-}6a}$ = 8.9 Hz, $J_{5\text{-}6b}$ = 5.4 Hz, 1H, H-5), 3.66 (ABX, $J_{5\text{-}6a}$ = 8.9 Hz, $J_{6a\text{-}6b}$ = 9.8 Hz,1H, H-6a), 3.59 (ABX, $J_{5\text{-}6b}$ = 5.4 Hz, $J_{6a\text{-}6b}$ = 9.8 Hz, 1H, H-6b), 1.25 (s, 9H, Piv), 0.93 (s, 9H, Si-*t*Bu), 0.90 (s, 9H, Si-*t*Bu), 0.89 (s, 9H, Si-*t*Bu), 0.20 (s, 3H, Si-Me), 0.19 (s, 3H, Si-Me), 0.16 (s, 3H, Si-Me), 0.12 (s, 3H, Si-Me), 0.08 (s, 3H, Si-Me), 0.07 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.52 (C=O, Piv), 172.58 (C-1), 79.90 (C-4), 76.47 (C-3), 73.56 (C-2), 71.99 (C-5), 62.51 (C-6), 38.58 (CO-*C*(CH_3)$_3$, Piv), 27.02 (CO-C(*C*H_3)$_3$, Piv), 25.76 (Si-C(*C*H_3)$_3$), 25.72 (Si-C(*C*H_3)$_3$), 25.51 (Si-C(*C*H_3)$_3$), 18.11 (Si-*C*(CH_3)$_3$), 18.08 (Si-*C*(CH_3)$_3$), 17.92 (Si-*C*(CH_3)$_3$), -4.11 (Si-Me), -4.71 (Si-Me), -4.90 (Si-Me), -5.39 (Si-Me), -5.48 (Si-Me), -5.51 (Si-Me); MS (CI-NH_3) *m/z* 622 $[M + NH_4]^+$; El. Anal. for $C_{29}H_{60}O_7Si_3$: calc. (%) C 57.57 H 9.99. mes. C 57.50 H 10.02.

(1(1')*Z*)-2-*O*-*tert*-Butyldimethylsilyl-1-(dimethoxyphosphoryl) methylidene-5,6-*O*-(dimethyl-ethylidene)-3-*O*-pivaloyl-D-galactofuranose (7). The product **6** was prepared according to the general procedure for exoglycal formation from lactones. After chromatography on silica gel (Cy/AcOEt : 1/2), compound **7** (72 %) was isolated as a white solid. $[\alpha]_D^{21}$ +28.6 (c 0.9, $CHCl_3$); m.p. 49-50°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.13 (t, $J_{2\text{-}3} = J_{3\text{-}4} = 4.5$ Hz, 1H, H-3), 4.70 (td, $J_{1'\text{-}2} = 1.3$ Hz, $J_{2\text{-}P} = J_{2\text{-}3} = 4.5$ Hz, 1H, H-2), 4.62 (dd, $J_{1'\text{-}2} = 1.3$ Hz, $J_{1'\text{-}P} = 9.4$ Hz, 1H, H-1'), 4.41 (td, $J_{4\text{-}5} = 4.5$ Hz, $J_{5\text{-}6} = 6.8$ Hz, 1H, H-5), 4.30 (t, $J_{3\text{-}4} = J_{4\text{-}5} = 4.5$ Hz, 1H, H-4), 4.06 (ABX, $J_{5\text{-}6a} = 6.8$ Hz, $J_{6a\text{-}6b} = 8.3$ Hz, 1H, H-6a), 3.98 (ABX, $J_{5\text{-}6b} = 6.8$ Hz, $J_{6a\text{-}6b} = 8.3$ Hz, 1H, H-6b), 3.77 (d, $J_{H\text{-}P} = 11.3$ Hz, 3H, OMe), 3.75 (d, $J_{H\text{-}P} = 11.4$ Hz, 3H, OMe), 1.45, 1.37 (2s, 6H, $C(CH_3)_2$, acetonide), 1.23 (s, 9H, Piv), 0.92 (s, 9H, Si-*t*Bu), 0.16 (s, 3H, Si-Me), 0.13 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.53 (C=O, Piv), 171.30 (d, $J_{1\text{-}P} = 2.3$ Hz, C-1), 109.99 ($C(CH_3)_2$, acetonide), 85.64 (C-4), 82.84 (d, $J_{1'\text{-}P} = 196.1$ Hz, C-1'), 77.43 (C-3), 77.10 (d, $J_{2\text{-}P} = 14.0$ Hz, C-2), 74.77 (C-5), 64.96 (C-6), 52.40 (d, $J_{C\text{-}P} = 5.7$ Hz, OMe), 52.10 (d, $J_{C\text{-}P} = 5.6$ Hz, OMe), 38.67 (CO-$C(CH_3)_3$, Piv), 27.02 (CO-C(CH_3)$_3$, Piv), 26.02 (C(CH_3)$_2$, acetonide), 25.49 (Si-C(CH_3)$_3$), 25.24 (C(CH_3)$_2$, acetonide), 17.79 (Si-$C(CH_3)_3$), -4.74 (Si-Me), -4.78 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 20.49; MS (CI-NH_3) *m/z* 523 $[M + H]^+$; El. Anal. for $C_{23}H_{43}O_9PSi$: calc. (%) C 52.86 H 8.29. mes. C 52.53 H 8.56.

Dimethyl (2-*O*-*tert*-butyldimethylsilyl-5,6-*O*-(dimethyl-methylidene)-3-*O*-pivaloyl-α-D-galactofuranosyl) methanephosphonate (7a). The "general procedure for exoglycals hydrogenation" was applied. After chromatography on silica gel (AcOEt), compound **7a** (95%) was isolated as a colourless oil. $[\alpha]_D^{19}$ -9.5 (c 0.77, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.79 (d, $J_{3\text{-}4} = 2.2$ Hz, 1H, H-3), 4.31 (q, $J_{4\text{-}5} = 6.8$ Hz, 1H, H-5), 4.22 (tdd, $J_{1\text{-}2} = 2.9$ Hz, $J_{1'a,b\text{-}1} = 6.4$ Hz, $J_{1\text{-}P} = 11.4$ Hz, 1H, H-1), 4.00 (ABX, $J_{5\text{-}6a} = 6.8$ Hz, $J_{6a\text{-}6b} = 8.6$ Hz, 1H, H-6a), 3.96 (d, $J_{1\text{-}2} = 2.9$ Hz, 1H, H-2), 3.88 (ABX, $J_{5\text{-}6b} = 6.1$ Hz, $J_{6a\text{-}6b} = 8.6$ Hz, 1H, H-6b), 3.83 (dd, $J_{3\text{-}4} = 2.2$ Hz, $J_{4\text{-}5} = 6.8$ Hz, 1H, H-4), 3.76 (d, $J_{H\text{-}P} = 11.3$ Hz, 3H, OMe), 3.73 (d, $J_{H\text{-}P} = 11.3$ Hz, 3H, OMe), 2.23 (ABXX', $J_{1'a\text{-}1'b} = 15.3$ Hz, $J_{1'a\text{-}1} = 6.4$ Hz, $J_{1'a\text{-}P} = 18.2$ Hz, 1H, H-1'a), 2.15 (ABXX', $J_{1'a\text{-}1'b} = 15.3$ Hz, $J_{1'b\text{-}1} = 6.4$ Hz, $J_{1'b\text{-}P} = 18.3$ Hz, 1H, H-1'b), 1.40, 1.33 (2s, 6H, $C(CH_3)_2$, acetonide), 1.19 (s, 9H, Piv), 0.91 (s, 9H, Si-*t*Bu), 0.17 (s, 3H, Si-Me), 0.11 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.30 (C=O, Piv), 109.64 ($C(CH_3)_2$, acetonide), 84.50 (C-4), 79.82 (C-3), 76.92 (C-1), 76.90 (d, $J_{2\text{-}P} = 8.4$ Hz, C-2), 75.60 (C-5), 65.40 (C-6), 52.57 (d, $J_{C\text{-}P} = 6.5$ Hz, OMe), 52.00 (d, $J_{C\text{-}P} = 6.5$ Hz, OMe), 38.48 (CO-$C(CH_3)_3$, Piv), 26.88 (CO-C(CH_3)$_3$, Piv), 26.38 (C(CH_3)$_2$, acetonide), 25.66 (Si-C(CH_3)$_3$), 24.88 (C(CH_3)$_2$, acetonide), 24.71 (d, $J_{1'\text{-}P} = 141.6$ Hz, C-1'), 17.95 (Si-$C(CH_3)_3$), -4.64 (Si-Me), -5.61 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 31.33; MS (CI-NH_3) *m/z* 525 (25 %) $[M + H]^+$, 542 (100 %) $[M + NH_4]^+$; El. Anal. for $C_{23}H_{45}O_9PSi$: calc. (%) C 52.65 H 8.65. mes. C 52.51 H 8.82.

(1(1')*Z*)-2,5,6-Tri-*O*-*tert*-butyldimethylsilyl-1-(dimethoxyphosphoryl)methylidene-3-*O*-pivaloyl-D-galactofuranose (8). Product **8** was prepared according to the general procedure for exoglycal formation from lactones. After chromatography on silica gel (Cy/AcOEt : 3/1), compound **8** (76 %) was isolated as a white solid. $[\alpha]_D^{22}$ +8.15 (c 1.2, $CHCl_3$); m.p. 61°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.25 (t, $J_{2\text{-}3} = J_{3\text{-}4} = 5.0$ Hz, 1H, H-3), 4.85 (ddd, $J_{1'\text{-}2} = 1.6$ Hz, $J_{2\text{-}3} =$

5.0 Hz, $J_{2\text{-}P}$ = 4.1 Hz, 1H, H-2), 4.53 (dd, $J_{1'\text{-}2}$ = 1.6 Hz, $J_{1'\text{-}P}$ = 10.1 Hz, 1H, H-1'), 4.41 (dd, $J_{3\text{-}4}$ = 5.0 Hz, $J_{4\text{-}5}$ = 1.8 Hz, 1H, H-4), 4.01 (ddd, $J_{4\text{-}5}$ = 1.8 Hz, $J_{5\text{-}6a}$ = 8.8 Hz, $J_{5\text{-}6b}$ = 5.3 Hz, 1H, H-5), 3.72 (ABX, $J_{5\text{-}6a}$ = 8.8 Hz, $J_{6a\text{-}6b}$ = 9.6 Hz, 1H, H-6a), 3.72 (d, $J_{H\text{-}P}$ = 11.3 Hz, 3H, OMe), 3.70 (d, $J_{H\text{-}P}$ = 11.5 Hz, 3H, OMe), 3.58 (ABX, $J_{5\text{-}6b}$ = 5.3 Hz, $J_{6a\text{-}6b}$ = 9.6 Hz, 1H, H-6b), 1.21 (s, 9H, Piv), 0.90 (s, 9H, Si-*t*Bu), 0.87 (s, 9H, Si-*t*Bu), 0.86 (s, 9H, Si-*t*Bu), 0.17 (s, 3H, Si-Me), 0.13 (s, 3H, Si-Me), 0.08 (s, 6H, Si-Me), 0.06 (s, 3H, Si-Me), 0.05 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.71 (C=O, Piv), 172.10 (d, $J_{1\text{-}P}$ = 2.1 Hz, C-1), 85.77 (C-4), 80.34 (d, $J_{1'\text{-}P}$ = 195.8 Hz, C-1'), 77.77 (C-3), 77.34 (d, $J_{2\text{-}P}$ = 13.9 Hz, C-2), 72.78 (C-5), 62.65 (C-6), 52.16 (d, $J_{C\text{-}P}$ = 5.6 Hz, OMe), 52.00 (d, $J_{C\text{-}P}$ = 5.2 Hz, OMe), 38.52 (CO-*C*$(CH_3)_3$, Piv), 27.02 (CO-C(*C*$H_3)_3$, Piv), 25.72 (2Si-C(*C*$H_3)_3$), 25.53 (Si-C(*C*$H_3)_3$), 18.02 (Si-*C*$(CH_3)_3$), 17.91 (Si-*C*$(CH_3)_3$), 17.78 (Si-*C*$(CH_3)_3$), -4.16 (Si-Me), -4.70 (Si-Me), -4.99 (Si-Me), -5.08 (Si-Me), -5.54 (Si-Me), -5.62 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 21.85; MS (CI-NH_3) m/z 711 (100 %) $[M + H]^+$, 728 (80 %) $[M + NH_4]^+$; El. Anal. for $C_{32}H_{67}O_9PSi_3$: calc. (%) C 54.05 H 9.50. mes. C 53.93 H 9.63.

Dimethyl (2,5,6-tri-*O*-*tert*-butyldimethylsilyl-3-*O*-pivaloyl-α-D-galactofuranosyl) methanephosphonate (8). The "general procedure for exoglycals hydrogenation" was applied. After chromatography on silica gel (Cy/AcOEt : 2/1), compound **8a** (72%) and **8b** (8%) were isolated. $[\alpha]_D^{21}$ -7.1 (c 0.6, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.08 (dd, $J_{2\text{-}3}$ = 1.3 Hz, $J_{3\text{-}4}$ = 2.4 Hz, 1H, H-3), 4.32 (tdd, $J_{1\text{-}2}$ = 3.2 Hz, $J_{1'a\text{-}1}$ = 6.9 Hz, $J_{1'b\text{-}1}$ = 5.6 Hz, $J_{1\text{-}P}$ = 9.8 Hz, 1H, H-1), 3.93 (dd, $J_{3\text{-}4}$ = 2.4 Hz, $J_{4\text{-}5}$ = 7.1 Hz, 1H, H-4), 3.91 (d, $J_{2\text{-}P}$ = 9.8 Hz, 1H, H-2), 3.87 (ddd, $J_{4\text{-}5}$ = 7.1 Hz, $J_{5\text{-}6a}$ = 4.1 Hz, $J_{5\text{-}6b}$ = 5.4 Hz,1H, H-5), 3.79 (d, $J_{H\text{-}P}$ = 11.0 Hz, 3H, OMe), 3.77 (d, $J_{H\text{-}P}$ = 11.0 Hz, 3H, OMe), 3.72 (ABX, $J_{5\text{-}6a}$ = 4.1 Hz, $J_{6a\text{-}6b}$ = 10.6 Hz, 1H, H-6a), 3.59 (ABX, $J_{5\text{-}6b}$ = 5.4 Hz, $J_{6a\text{-}6b}$ = 10.6 Hz, 1H, H-6b), 2.21 (ABXX', $J_{1'a\text{-}1'b}$ = 15.5 Hz, $J_{1'a\text{-}1}$ = 6.9 Hz, $J_{1'a\text{-}P}$ = 17.8 Hz, 1H, H-1'a), 2.14 (ABXX', $J_{1'a\text{-}1'b}$ = 15.5 Hz, $J_{1'b\text{-}1}$ = 5.6 Hz, $J_{1'b\text{-}P}$ = 18.4 Hz, 1H, H-1'b), 1.21 (s, 9H, Piv), 0.95 (s, 9H, Si-*t*Bu), 0.91 (s, 9H, Si-*t*Bu), 0.90 (s, 9H, Si-*t*Bu), 0.23 (s, 3H, Si-Me), 0.13 (s, 3H, Si-Me), 0.11 (s, 3H, Si-Me), 0.10 (s, 3H, Si-Me), 0.06 (s, 3H, Si-Me), 0.05 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.20 (C=O, Piv), 84.38 (C-4), 79.21 (C-3), 77.29 (d, $J_{2\text{-}P}$ = 9.8 Hz, C-2), 75.26 (d, $J_{1\text{-}P}$ = 0.9 Hz, C-1), 73.66 (C-5), 65.64 (C-6), 52.54 (d, $J_{C\text{-}P}$ = 6.4 Hz, OMe), 52.15 (d, $J_{C\text{-}P}$ = 6.5 Hz, OMe), 38.4 (CO-*C*$(CH_3)_3$, Piv), 27.05 (CO-C(*C*$H_3)_3$, Piv), 25.98 (Si-C(*C*$H_3)_3$), 25.87 (2Si-C(*C*$H_3)_3$), 25.12 (d, $J_{1'\text{-}P}$ = 141.8 Hz, C-1'), 18.35 (Si-*C*$(CH_3)_3$), 18.17 (Si-*C*$(CH_3)_3$), 18.07 (Si-*C*$(CH_3)_3$), -4.41 (Si-Me), -4.59 (2Si-Me), -5.39 (2Si-Me), -5.50 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 32.05; MS (CI-NH_3) *m/z* 713 (100 %) $[M + H]^+$, 730 (45 %) $[M + NH_4]^+$; El. Anal. for $C_{32}H_{69}O_9PSi_3$: calc. (%) C 53.90 H 9.75. mes. C 53.73 H 9.94.

Dimethyl (2,5,6-tri-*O*-*tert*-butyldimethylsilyl-1,3-dienyl-D-galactofuranosyl)methane phosphonate (8). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.99 (s, 1H, H-3), 4.60 (dd, $J_{5\text{-}6a}$ = 5.6 Hz, $J_{5\text{-}6b}$ = 6.7 Hz, 1H, H-5), 3.82 (ABX, $J_{5\text{-}6a}$ = 5.6 Hz, $J_{6a\text{-}6b}$ = 10.0 Hz, 1H, H-6a), 3.74 (2d, $J_{H\text{-}P}$ = 11.0 et 10.8 Hz, 6H, OMe), 3.71 (ABX, $J_{5\text{-}6b}$ = 6.7 Hz, $J_{6a\text{-}6b}$ = 10.0 Hz, 1H, H-6b), 3.18 (AX, $J_{1'\text{-}P}$ = 19.9 Hz, 2H, H-1'a, H-1'b), 0.99 (s, 9H, Si-*t*Bu), 0.89 (s, 9H, Si-*t*Bu), 0.88 (s, 9H, Si-*t*Bu), 0.19 (s, 3H, Si-Me), 0.18 (s, 3H, Si-Me), 0.09 (s, 3H, Si-Me), 0.05 (s, 3H, Si-Me), 0.04 (s, 3H, Si-Me), 0.02 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.50 (d, $J_{4\text{-}P}$ = 4.3 Hz, C-4), 140.06 (d, $J_{1,2\text{-}P}$ = 10.1 Hz, C-1 and C-2), 129.46 (d, $J_{1,2\text{-}P}$ = 14.2 Hz, C-1 and C-2), 75.62 (d, $J_{3\text{-}P}$ = 3.8 Hz,

C-3), 70.30 (d, $J_{5\text{-}P}$ = 1.3 Hz, C-5), 66.79 (d, $J_{6\text{-}P}$ = 1.4 Hz, C-6), 52.65 (d, $J_{C\text{-}P}$ = 6.5 Hz, OMe), 52.62 (d, $J_{C\text{-}P}$ = 6.5 Hz, OMe), 25.85 (Si-C(CH$_3$)$_3$), 25.71 (Si-C(CH$_3$)$_3$), 25.56 (Si-C(CH$_3$)$_3$), 22.60 (d, $J_{1'\text{-}P}$ = 143.8 Hz, C-1'), 18.27 (Si-C(CH$_3$)$_3$), 18.20 (Si-C(CH$_3$)$_3$), 17.97 (Si-C(CH$_3$)$_3$), -4.67 (Si-Me), -4.69 (Si-Me), -4.93 (Si-Me), -5.05 (Si-Me), -5.43 (Si-Me), -5.51 (Si-Me); ^{31}P-NMR (101 MHz, CDCl3) δ 25.84; MS (CI-NH$_3$) *m/z* 609 (10 %) [M + H]$^+$, 626 (90 %) [M + NH$_4$]$^+$; HRMS for $C_{27}H_{61}O_7NPSi_3$: calc. 626.3494 mes. 626.3492.

(1(1')*Z*)- 2-*O*-*tert*-butyldimethylsilyl-1- (dimethoxyphosphoryl)methylidene-5,6-*O*-(dimethyl-methylidene)- D-galactofuranose (9). To a solution of exoglycal **7** (269 mg, 0.52 mmol) in anhydrous MeOH (10 mL) was added at 0°C NaH (62 mg, 60% in mineral oil). The solution was stirred 12 hours at room temperature followed by addition of silica gel (3 g). The solution was filtered, concentrated and purified by chromatography on silica gel (AcOEt) to yield **9** (151 mg, 67%) as a white solid. $[\alpha]_D^{20}$ -2.9 (c 1.3, $CHCl_3$); m.p. 128-129°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.78 (d, $J_{3\text{-}OH}$ = 9.3 Hz, 1H, OH-3), 4.69 (ddd, $J_{1'\text{-}2}$ = 1.6 Hz, $J_{2\text{-}3}$ = 8.3 Hz, $J_{2\text{-}P}$ = 4.4 Hz, 1H, H-2), 4.59 (dd, $J_{1'\text{-}2}$ = 1.6 Hz, $J_{1'\text{-}P}$ = 11.3 Hz, 1H, H-1'), 4.37-4.30 (m, 2H, H-4, H-5), 4.10 (ABX, $J_{5\text{-}6a}$ = 6.4 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 1H, H-6a), 4.00 (dd, $J_{2\text{-}3}$ = 8.3 Hz, 1H, H-3), 3.99 (ABX, $J_{5\text{-}6b}$ = 7.8 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 1H, H-6b), 3.74 (d, $J_{H\text{-}P}$ = 11.4 Hz, 3H, OMe), 3.71 (d, $J_{H\text{-}P}$ = 11.2 Hz, 3H, OMe), 1.46, 1.38 (2s, 6H, C(CH$_3$)$_2$, acetonide), 0.96 (s, 9H, Si-*t*Bu), 0.23 (s, 3H, Si-Me), 0.17 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.51 (d, $J_{1\text{-}P}$ = 1.2 Hz, C-1), 109.60 (C(CH$_3$)$_2$, acetonide), 85.55 (C-4), 80.15 (d, $J_{1'\text{-}P}$ = 197.9 Hz, C-1'), 77.94 (d, $J_{2\text{-}P}$ = 12.5 Hz, C-2), 75.98 (C-3), 74.62 (C-5), 65.00 (C-6), 53.03 (d, $J_{C\text{-}P}$ = 5.8 Hz, OMe), 51.60 (d, $J_{C\text{-}P}$ = 6.0 Hz, OMe), 26.14 (C(CH$_3$)$_2$, acetonide), 25.71 (Si-C(CH$_3$)$_3$), 25.43 (C(CH$_3$)$_2$, acetonide), 17.93 (Si-C(CH$_3$)$_3$), -4.23 (Si-Me), -5.06 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 21.02; MS (CI-NH$_3$) *m/z* 438 (100 %) [M + H]$^+$, 456 (10 %) [M + NH$_4$]$^+$; El. Anal. for $C_{18}H_{35}O_8PSi$: calc. (%) C 49.30 H 8.04. mes. C 49.29 H 8.08.

Dimethyl(2-*O*-*tert*-butyldimethylsilyl-5,6-*O*-(dimethyl-methylidene)-α-D-galactofuran -osyl) methanephosphonate (9a). The "general procedure for exoglycals hydrogenation" was applied. After chromatography on silica gel (Cy/AcOEt : 2/1), compound **9a** (89%) was isolated as a colourless oil. $[\alpha]_D^{21}$ -6.1 (c 0.76, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.37 (tdd, $J_{1\text{-}2}$ = 3.4 Hz, $J_{1'a,b\text{-}1}$ = 6.5 Hz, $J_{1\text{-}P}$ =9.3 Hz, 1H, H-1), 4.30 (q, $J_{4\text{-}5}$ = $J_{5\text{-}6a}$ = $J_{5\text{-}6b}$ = 6.7 Hz, 1H, H-5), 4.06 (d, $J_{1\text{-}2}$ = 3.4 Hz, 1H, H-2), 4.03 (ABX, $J_{5\text{-}6a}$ = 6.9 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 1H, H-6a), 3.92 (ABX, $J_{5\text{-}6b}$ = 6.4 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 1H, H-6b), 3.88 (d, $J_{3\text{-}4}$ = 3.3 Hz, 1H, H-3), 3.81 (dd, $J_{3\text{-}4}$ = 3.3 Hz, $J_{4\text{-}5}$ = 6.9 Hz, 1H, H-4), 3.78 (d, $J_{H\text{-}P}$ = 10.9 Hz, 3H, OMe), 3.75 (d, $J_{H\text{-}P}$ = 10.9 Hz, 3H, OMe), 2.21 (ABXX', $J_{1'a\text{-}1'b}$ = 15.4 Hz, $J_{1'a\text{-}1}$ = 6.5 Hz, $J_{1'a\text{-}P}$ = 18.1 Hz, 1H, H-1'a), 2.17 (ABXX', $J_{1'a\text{-}1'b}$ = 15.4 Hz, $J_{1'b\text{-}1}$ = 6.5 Hz, $J_{1'\text{-}P}$ = 20.9 Hz, 1H, H-1'b), 1.46, 1.37 (2s, 6H, C(CH$_3$)$_2$, acetonide), 0.93 (s, 9H, Si-*t*Bu), 0.16 (s, 3H, Si-Me), 0.14 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 109.63 (C(CH$_3$)$_2$, acetonide), 86.62 (C-4), 79.61 (C-3), 79.19 (d, $J_{2\text{-}P}$ = 8.5 Hz, C-2), 76.11 (C-1), 75.90 (C-5), 65.44 (C-6), 52.78 (d, $J_{C\text{-}P}$ = 6.4 Hz, OMe), 52.03 (d, $J_{C\text{-}P}$ = 6.4 Hz, OMe), 26.57 (C(CH$_3$)$_2$, acetonide), 25.73 (Si-C(CH$_3$)$_3$), 24.85 (d, $J_{1'\text{-}P}$ = 141.4 Hz, C-1'), 24.14 (C(CH$_3$)$_2$, acetonide), 18.00 (Si-C(CH$_3$)$_3$), -4.50 (Si-Me), -5.19 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ

32.27; MS (CI-NH_3) *m/z* 441 (100 %) $[M + H]^+$, 458 (75 %) $[M + NH_4]^+$; HRMS for $C_{18}H_{38}O_8PSi$: calc. 441.2074 mes. 441.2065.

(10) (1(1')*Z*)-1-(dimethoxyphosphoryl)methylidene-5,6-*O*-(dimethyl-methylidene)-3-*O*-pivaloyl-D-galactofuranose. To a solution of **7** (1.28 g, 2.45 mmol) in distilled THF (10 mL) was added tetrabutyl ammonium trihydrate (850 mg, 2.69 mmol) at 0°C. The solution was stirred 30 minutes at 0°C and concentrated. Compound **10** (727 mg, 73 %) was obtained as a white solid after chromatography on silica gel (AcOEt). $[\alpha]_D^{19}$ +78.8 (c 0.9, $CHCl_3$); m.p. 77-78°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.01 (d, 1H, H-3), 4.76 (d, $J_{1'\text{-P}}$ = 9.9 Hz, 1H, H-1'), 4.71 (s_l, 1H, OH-2), 4.49 (m, 1H, H-2), 4.41-4.37 (m, 2H, H-4, H-5), 4.08 (ABX, $J_{5\text{-}6a}$ = 6.5 Hz, $J_{6a\text{-}6b}$ = 8.3 Hz, 1H, H-6a), 4.01 (ABX, $J_{5\text{-}6b}$ = 7.7 Hz, $J_{6a\text{-}6b}$ = 8.3 Hz, 1H, H-6b), 3.68 (2d, $J_{H\text{-P}}$ = 11.3 Hz, 6H, OMe), 1.39, 1.34 (2s, 6H, $C(CH_3)_2$, acetonide), 1.15 (s, 9H, Piv); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.88 (C=O, Piv), 172.33 (d, $J_{1\text{-P}}$ = 3.1 Hz, C-1), 110.48 ($C(CH_3)_2$, acetonide), 85.40 (C-4), 82.04 (d, $J_{1'\text{-P}}$ = 195.5 Hz, C-1'), 78.55 (d, $J_{3\text{-P}}$ = 1.3 Hz, C-3), 76.19 (d, $J_{2\text{-P}}$ = 14.3 Hz, C-2), 74.96 (C-5), 65.05 (C-6), 52.17 (d, $J_{C\text{-P}}$ = 5.5 Hz, OMe), 52.02 (d, $J_{C\text{-P}}$ = 5.8 Hz, OMe), 38.47 (CO-$C(CH_3)_3$, Piv), 26.75 (CO-C(CH_3)$_3$, Piv), 25.40, 25.29 (C(CH_3)$_2$, acetonide); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 20.36; MS (CI-NH_3) *m/z* 409 (100 %) $[M + H]^+$, 426 (30 %) $[M+ NH_4]^+$; El. Anal. for $C_{17}H_{29}O_9P$: calc. (%) C 50.00 H 7.16. mes. C 49.87 H 7.22.

Dimethyl (5,6-*O*-(dimethyl-methylidene)-3-*O*-pivaloyl-α-D-galactofuranosyl)methane phosphonate (10a). The "general procedure for exoglycals hydrogenation" was applied. After chromatography on silica gel (Cy/AcOEt : 2/1), compound **10a** (56%) was isolated as a colourless oil (α/β:80/20).^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.08 (t, $J_{2\text{-}3}$ = $J_{3\text{-}4}$ = 3.0 Hz, 0.25H, H-3_β), 5.00 (s, 1H, H-3_α), 4.46 (td, $J_{4\text{-}5}$ = 2.0 Hz, $J_{5\text{-}6a,b}$ = 8.2 Hz, 1H, H-5_α), 4.42 (dd, $J_{5\text{-}6a}$ = 3.1 Hz, $J_{5\text{-}6a}$ = 7.1 Hz, 0.25H, H-5_β), 4.36 (tdd, $J_{1\text{-}2}$ = 1.9 Hz, $J_{1'a,b\text{-}1}$ = 6.3 Hz, $J_{1\text{-P}}$ =10.6 Hz, 0.25H, H-1_β), 4.30 (tdd, $J_{1'b\text{-}1}$ = 2.6 Hz, $J_{1\text{-}2}$ = $J_{1'a\text{-}1}$ = 6.8 Hz, $J_{1\text{-P}}$ =13.9 Hz, 1H, H-1_α), 4.15 (d, $J_{2\text{-}3}$ = 3.0 Hz, 0.25H, H-2_β), 4.00 (m, 1.25, H-$6a_\alpha$-$6a_\beta$), 3.98 (d, $J_{1\text{-}2}$ = 6.8 Hz, 1H, H-2_α), 3.99 (m, 1.5H, H-$6b_\alpha$H-$6b_\beta$H-4_β), 3.82 (d, $J_{4\text{-}5}$ = 2.0 Hz, 1H, H-4_α), 3.80, 3.78 (2d, $J_{H\text{-P}}$ = 11.1, 11.0 Hz, 6H, OMe_α), 3.78, 3.74 (2d, $J_{H\text{-P}}$ = 11.0, 10.9 Hz, 0.75H, OMe_β), 2.26 (ABXX', $J_{1'a\text{-}1}$ = 6.8 Hz, $J_{1'a\text{-P}}$ = 18.4 Hz, 2.75H, H-$1'a_{\alpha\beta}$ H-$1'b_{\alpha\beta}$, 1.45, 1.41 (2s, 6H, $C(CH_3)_2$, $acetonide_\alpha$), 1.46, 1.40 (2s, 1.5H, $C(CH_3)_2$, $acetonide_\alpha$), 1.23 (s, 2.25H, Piv_β), 1.21 (s, 9H, Piv_α); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.13 (C=O, Piv_β), 177.80 (C=O, Piv_α), 110.04 ($C(CH_3)_2$, acetonide), 110.00 ($C(CH_3)_2$, acetonide), 82.23 (C-4_α), 81.97 (C-4_β), 81.79 (C-3_β), 80.94 (C-3_α), 80.71 (C-1_β), 79.45 (d, $J_{2\text{-P}}$ = 6.6 Hz, C-2_β), 77.37 (C-1_α), 76.08 (C-5_β), 75.68 (C-5_α), 74.83 (d, $J_{2\text{-P}}$ = 8.5 Hz, C-2_α), 65.56 (C-6_β), 65.51 (C-6_α), 52.63 (d, $J_{C\text{-P}}$ = 6.1 Hz, OMe_α), 52.61 (d, $J_{C\text{-P}}$ = 6.6 Hz, OMe_β), 52.51 (d, $J_{C\text{-P}}$ = 6.3 Hz, OMe_β), 52.24 (d, $J_{C\text{-P}}$ = 6.4 Hz, OMe_α), 38.48 (CO-$C(CH_3)_3$, $Piv_{\alpha\beta}$, 29.63 (d, $J_{1'\text{-P}}$ = 137.9 Hz, C-$1'_\beta$), 26.96 (CO-C(CH_3)$_3$, Piv_β), 26.92 (CO-C(CH_3)$_3$, Piv_α), 25.85, 25.18 (C(CH_3)$_2$, $acetonide_\beta$), 25.70, 25.60 (C(CH_3)$_2$, $acetonide_\alpha$), 24.48 (d, $J_{1'\text{-P}}$ = 141.0 Hz, C-$1'_\alpha$); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 31.27 (α), 30.20 (β); MS (CI-NH_3) *m/z* 379 (100 %) $[M - 32 + H]^+$, 411 (27 %) $[M + H]^+$; HRMS for $C_{16}H_{28}O_8P$: calc. 379.1522 mes. 379.1517.

(1(1')*Z*)-2-*O*-formyl-1-(dimethoxyphosphoryl)methylidene-5,6-*O*-(dimethyl-methyl -idene)-3-*O*-pivaloyl-D-galactofuranose (11). To a solution of DCC (378 mg, 1.83 mmol) in anhydrous

CH_2Cl_2 (15 mL) was added, at 0°C under argon, formic acid (65 µL, 1.73 mmol). After 10 minutes at 0°C, a solution of **10** in anhydrous CH_2Cl_2 (3 mL) was added. The resulting mixture was stirred overnight at room temperature, concentrated, dried 1 hour under vacuum, dissolved in Et_2O and filtered on filter paper. The filtrate was concentrated under rotary evaporation and the resulting crude residue was purified by chromatography on silica gel with AcOEt as eluent, to yield **11** (118 mg, 79%) as a colourless oil. $[\alpha]_D^{21}$ +67.9 (c 1.2, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.14 (s_l, 1H, CHO), 5.94 (tdd, $J_{1'\text{-}2}$ = 1.4 Hz, $J_{2\text{-}3}$ = $J_{2\text{-}P}$ = 4.1 Hz, $J_{2\text{-}H(OCHO)}$ = 1.2 Hz, 1H, H-2), 5.35 (t, $J_{2\text{-}3}$ = $J_{3\text{-}4}$ = 4.1 Hz, 1H, H-3), 4.72 (dd, $J_{1'\text{-}2}$ = 1.4 Hz, $J_{1'\text{-}P}$ = 8.2 Hz, 1H, H-1'), 4.47-4.39 (m, 2H, H-4, H-5), 4.11 (ABX, $J_{5\text{-}6a}$ = 6.6 Hz, $J_{6a\text{-}6b}$ = 8.5 Hz, 1H, H-6a), 4.03 (ABX, $J_{5\text{-}6b}$ = 6.4 Hz, $J_{6a\text{-}6b}$ = 8.5 Hz, 1H, H-6b), 3.78 (d, $J_{H\text{-}P}$ = 11.4 Hz, 3H, OMe), 3.76 (d, $J_{H\text{-}P}$ = 11.3 Hz, 3H, OMe), 1.44, 1.38 (2s, 6H, $C(CH_3)_2$, acetonide), 1.23 (s, 9H, Piv); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.59 (C=O, Piv), 166.35 (d, $J_{1\text{-}P}$ = 1.4 Hz, C-1), 159.25 (C=O, CHO), 110.24 ($C(CH_3)_2$, acetonide), 85.53 (C-4), 85.39 (d, $J_{1'\text{-}P}$ = 196.1 Hz, C-1'), 75.76 (d, $J_{2\text{-}P}$ = 14.4 Hz, C-2), 75.57 (d, $J_{3\text{-}P}$ = 1.0 Hz, C-3), 74.40 (C-5), 64.87 (C-6), 52.52 (d, $J_{C\text{-}P}$ = 5.8 Hz, OMe), 52.21 (d, $J_{C\text{-}P}$ = 5.7 Hz, OMe), 38.63 (CO-$C(CH_3)_3$, Piv), 26.84 (CO-C(CH_3)$_3$, Piv), 25.78 (C(CH_3)$_2$, acetonide), 25.17 (C(CH_3)$_2$, acetonide); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 18.78; MS (CI-NH_3) *m/z* 437 (100 %) $[M + H]^+$, 454 (20 %) $[M + NH_4]^+$; HRMS for $C_{18}H_{30}O_{10}P$ calc. 437.1577 mes. 437.1570.

Dimethyl (2-*O*-formyl-5,6-*O*-(dimethyl-methylidene)-3-*O*-pivaloyl-α-D-galactofuranosyl) methanephosphonate (11a). The "general procedure for exoglycals hydrogenation" was applied. After chromatography on silica gel (AcOEt), compound **11a** (70%) was isolated as a colourless oil (α̃/β:82/18). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H, CHO_α), 8.07 (s, 0.18H, CHO_β), 5.30 (m, 0.18H, H-2_β), 5.28 (d, $J_{1\text{-}2}$ = 3.4 Hz, $J_{2\text{-}3}$ = 0.7 Hz, 1H, H-2_α), 5.20 (t, $J_{2\text{-}3}$ = $J_{3\text{-}4}$ = 3.4 Hz, 0.18H, H-3_β), 4.98 (d, $J_{3\text{-}4}$ = 4.0 Hz, 1H, H-3_α), 4.53 (m, 0.18H, H-1_β), 4.41 (ddd, $J_{1\text{-}2}$ = 3.4 Hz, $J_{1'a\text{-}1}$ = 6.9 Hz, $J_{1'b\text{-}1}$ = $J_{1\text{-}P}$ = 10.8 Hz, 1H, H-1_α), 4.33 (q, $J_{4\text{-}5}$ = $J_{5\text{-}6a,b}$ = 6.3 Hz, 1H, H-5_α), 4.29 (m, 0.18H, H-5_β), 4.05 (ABX, $J_{5\text{-}6a}$ = 6.3 Hz, $J_{6a\text{-}6b}$ = 8.6 Hz, 1H, H-$6a_\alpha$), 4.04 (m, 0.18H, H-$6a_\beta$), 3.97 (m, 0.18H, H-4_β), 3.87 (m, 0.18H, H-$6b_\beta$), 3.86 (ABX, $J_{5\text{-}6b}$ = 6.2 Hz, $J_{6a\text{-}6b}$ = 8.6 Hz, 1H, H-$6b_\alpha$), 3.80 (dd, $J_{3\text{-}4}$ = 4.0 Hz, $J_{4\text{-}5}$ = 6.2 Hz, 1H, H-4_α), 3.77, 3.75 (2d, $J_{H\text{-}P}$ = 11.1, 10.9 Hz, 7.1H, $OMe_{\alpha\beta}$), 2.26-2.17 (m, 0.36H, H-1'a_β, H-1'b_β), 2.26 (ABXX', $J_{1'a\text{-}1'b}$ = 15.3 Hz, $J_{1'a\text{-}1}$ = 6.9 Hz, $J_{1'a\text{-}P}$ = 18.9 Hz, 1H, H-1'a_α), 2.17 (ABXX', $J_{1'b\text{-}1}$ = 10.8 Hz, $J_{1'b\text{-}P}$ = 17.5 Hz, 1H, H-1'b_α), 1.47, 1.38 (2s, 6H, $C(CH_3)_2$, $acetonide_\beta$), 1.43, 1.37 (2s, 1.08H, $C(CH_3)_2$, $acetonide_\alpha$), 1.23 (s, 9H, Piv_α), 1.21 (s, 1.62H, Piv_β); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.10 (C=O, $Piv_{\alpha\beta}$), 159.53 (CHO_β), 159.33 (CHO_α), 109.85 ($C(CH_3)_2$, $acetonide_{\alpha\beta}$), 84.11 (C-4_α), 82.77 (C-4_β), 80.17 (C-2_β), 78.56 (C-3_β), 78.33 (C-3_α), 77.70 (d, $J_{1\text{-}P}$ = 2.9 Hz, C-1_β), 77.16 (d, $J_{2\text{-}P}$ = 7.7 Hz, C-2_α), 75.69 (C-5_β), 75.20 (C-5_α), 75.13 (C-1_α), 65.50 (C-6_α), 65.41 (C-6_β), 52.82 (d, $J_{C\text{-}P}$ = 6.5 Hz, $OMe_{\alpha\beta}$), 52.24 (d, $J_{C\text{-}P}$ = 6.5 Hz, $OMe_{\alpha\beta}$), 38.56 (CO-$C(CH_3)_3$, $Piv_{\alpha\beta}$), 28.67 (d, $J_{1'\text{-}P}$ = 140.7 Hz, C-1'$_\beta$), 26.89 (CO-C(CH_3)$_3$, Piv_α), 26.86 (CO-C(CH_3)$_3$, Piv_β), 26.21, 25.48 (C(CH_3)$_2$, $acetonide_\alpha$), 26.12, 25.13 (C(CH_3)$_2$, $acetonide_\beta$), 24.77 (d, $J_{1'\text{-}P}$ = 141.9 Hz, C-1'$_\alpha$); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 29.37 (α) , 28.65 (β); MS (CI-NH_3) *m/z* 439 $[M + H]^+$; HRMS for $C_{18}H_{32}O_{10}P$ calc. 439.1733 mes. 439.1729.

(1(1')*Z*)-2-*O*-Acetyl-1-(dimethoxyphosphoryl)methylidene-5,6-*O*-(dimethyl-methylidene)-3-*O*-pivaloyl-D-galactofuranose (12). To a solution of **10** (209 mg, 0.51 mmol) in anhydrous pyridine (10 mL) was slowly added, at 0°C under argon, acetic anhydride (145 µL, 1.54 mmol). The resulting solution was stirred 12 hours at room temperature and the solvent was removed under vacuum. The residue was dissolved in AcOEt and washed with sat. $NaHCO_3$ and water. The organic phases were dried over $MgSO_4$, filtered and concentrated. Acetate **12** (221 mg, 96 %) was obtained as a white solid after silica gel chromatography (AcOEt).$[\alpha]_D^{20}$ +31.7 (c 0.8, $CHCl_3$); m.p. 81-82°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.83 (td, $J_{1'\text{-}2}$ = 1.4 Hz, $J_{2\text{-}P}$ = $J_{2\text{-}3}$ = 4.0 Hz, 1H, H-2), 5.30 (t, $J_{2\text{-}3}$ = $J_{3\text{-}4}$ = 4.0 Hz, 1H, H-3), 4.69 (dd, $J_{1'\text{-}2}$ = 1.4 Hz, $J_{1'\text{-}P}$ = 8.4 Hz, 1H, H-1'), 4.43-4.37 (m, 2H, H-4, H-5), 4.10 (ABX, $J_{5\text{-}6a}$ = 6.5 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 1H, H-6a), 4.02 (ABX, $J_{5\text{-}6b}$ = 6.5 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 1H, H-6b), 3.77 (d, $J_{H\text{-}P}$ = 11.3 Hz, 3H, OMe), 3.76 (d, $J_{H\text{-}P}$ = 11.3 Hz, 3H, OMe), 2.15 (s, 3H, Ac), 1.44, 1.37 (2s, 6H, $C(CH_3)_2$, acetonide), 1.22 (s, 9H, Piv); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.58 (C=O, Piv), 169.61 (C=O, Ac), 166.97 (d, $J_{1\text{-}P}$ = 2.1 Hz, C-1), 110.14 ($C(CH_3)_2$, acetonide), 85.19 (C-4), 84.71 (d, $J_{1'\text{-}P}$ = 196.3 Hz, C-1'), 76.23 (d, $J_{2\text{-}P}$ = 14.0 Hz, C-2), 75.51 (d, $J_{3\text{-}P}$ = 1.3 Hz, C-3), 74.35 (C-5), 64.85 (C-6), 52.45 (d, $J_{C\text{-}P}$ = 5.4 Hz, OMe), 52.20 (d, $J_{C\text{-}P}$ = 5.4 Hz, OMe), 38.60 (CO-$C(CH_3)_3$, Piv), 26.84 (CO-C(CH_3)$_3$, Piv), 25.82 (C(CH_3)$_2$, acetonide), 25.17 (C(CH_3)$_2$, acetonide), 21.22 (CO-CH_3, Ac); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 19.14; MS (CI-NH_3) *m/z* 451 (100 %) $[M + H]^+$, 468 (35 %) $[M + NH_4]^+$; El. Anal. for $C_{19}H_{31}O_{10}P$: calc. (%) C 50.66 H 6.94. mes. C 50.46 H 7.13.

Dimethyl (2-*O*-acetyl-5,6-*O*-(dimethyl-methylidene)-3-*O*-pivaloyl-α-D-galactofuranosyl) methanephosphonate (12a). The "general procedure for exoglycals hydrogenation" was applied. After chromatography on silica gel (AcOEt), compound **12a** (82%) was isolated as a colourless oil (α̃β 84/16). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.14 (d, $J_{1\text{-}2}$ = 3.4 Hz, 1H, H-2$_\alpha$), 5.15-5.12 (m, 0.46H, H-2$_\beta$, H-3$_\beta$), 4.94 (d, $J_{3\text{-}4}$ = 3.8 Hz, 1H, H-3$_\alpha$), 4.48 (tdd, $J_{1\text{-}2}$ = 4.1 Hz, $J_{1'a,b\text{-}1}$ = 7.1 Hz, $J_{1\text{-}P}$ =11.1 Hz, 0.23H, H-1$_\beta$), 4.36 (tdd, $J_{1\text{-}2}$ = 3.4 Hz, $J_{1'a,b\text{-}1}$ = 7.1 Hz, $J_{1\text{-}P}$ =10.7 Hz, 1H, H-1$_\alpha$), 4.31 (q, $J_{4\text{-}5}$ = $J_{5\text{-}6a,b}$ = 6.7 Hz, 1H, H-5$_\alpha$), 4.04 (ABX, $J_{5\text{-}6a}$ = 6.7 Hz, $J_{6a\text{-}6b}$ = 8.4 Hz, 0.23H, H-6a$_\beta$), 4.03 (ABX, $J_{5\text{-}6a}$ = 6.8 Hz, $J_{6a\text{-}6b}$ = 8.6 Hz, 1H, H-6a$_\alpha$), 3.93 (m, 0.23H, H-4$_\beta$), 3.84 (ABX, $J_{5\text{-}6b}$ = 6.2 Hz, $J_{6a\text{-}6b}$ = 8.6 Hz, 1.23H, H-6b$_\alpha$, H-6$_\beta$), 3.75, 3.73 (2d, $J_{H\text{-}P}$ = 11.1, 11.0 Hz, 6H, OMe$_\alpha$), 3.76, 3.74 (2d, $J_{H\text{-}P}$ = 11.0, 10.9 Hz, 1.38H, OMe$_\beta$), 3.75 (m, 1H, H-5$_\beta$), 2.26-2.12 (ABXX', $J_{1'a\text{-}1'b}$ = 15.1 Hz, $J_{1'a\text{-}1}$ = 7.1 Hz, $J_{1'a\text{-}P}$ = 18.4 Hz, 2.46H, H-1'a$_{\alpha\beta}$, H-1'b$_{\alpha\beta}$, 2.10 (s, 3H, Ac$_\alpha$), 2.08 (s, 0.69H, Ac$_\beta$), 1.44, 1.36 (2s, 6H, $C(CH_3)_2$, acetonide$_\beta$), 1.40, 1.34 (2s, 1.38H, $C(CH_3)_2$, acetonide$_\alpha$), 1.20 (s, 11H, Piv$_{\alpha\beta}$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.03 (C=O, Piv$_{\alpha\beta}$), 169.74 (C=O, Ac$_\beta$), 169.35 (C=O, Ac$_\alpha$), 109.68 ($C(CH_3)_2$, acetonide$_{\alpha\beta}$), 84.19 (C-4$_\alpha$), 82.74 (C-4$_\beta$), 80.69 (d, $J_{2\text{-}P}$ = 12.0 Hz, C-2$_\beta$), 78.45 (C-3$_\beta$), 78.37 (C-3$_\alpha$), 77.70 (d, $J_{1\text{-}P}$ = 2.9 Hz, C-1$_\beta$), 77.41 (d, $J_{2\text{-}P}$ = 8.1 Hz, C-2$_\alpha$), 75.65 (C-5$_\beta$), 75.29 (C-5$_\alpha$), 75.16 (C-1$_\alpha$), 65.40 (C-6$_\alpha$), 65.37 (C-6$_\beta$), 52.73 (d, $J_{C\text{-}P}$ = 6.2 Hz, OMe$_\alpha$), 52.55 (d, $J_{C\text{-}P}$ = 6.5 Hz, OMe$_\beta$), 52.23 (d, $J_{C\text{-}P}$ = 6.7 Hz, OMe$_\beta$), 52.14 (d, $J_{C\text{-}P}$ = 6.3 Hz, OMe$_\alpha$), 38.48 (CO-$C(CH_3)_3$, Piv$_{\alpha\beta}$), 28.67 (d, $J_{1'\text{-}P}$ = 140.7 Hz, C-1'$_\beta$), 26.84 (CO-C(CH_3)$_3$, Piv$_\beta$), 26.82 (CO-C(CH_3)$_3$, Piv$_\alpha$), 26.19, 25.21 (C(CH_3)$_2$, acetonide$_\alpha$), 26.09, 25.11 (C(CH_3)$_2$, acetonide$_\beta$), 24.78 (d, $J_{1'\text{-}P}$ = 141.8 Hz, C-1'$_\alpha$), 20.70 (CO-CH_3, Ac$_\beta$), 20.59 (CO-CH_3, Ac$_\alpha$); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 29.69 (α), 28.89 (β); MS (CI-NH_3) *m/z* 453 [M +

H]$^+$; HRMS for $C_{19}H_{34}O_{10}P$ calc. 453.18.90 mes. 453.1894.

(1(1')*Z*)-2,5,6-Tri-*O*-*tert*-butyldimethylsilyl-1-(dimethoxyphosphoryl)methylidene-D-galactofuranose. To a solution of exoglycal **8** (940 mg, 1.32 mmol) in anhydrous MeOH (30 mL) was added at 0°C NaH (160 mg, 60% in mineral oil). The solution was stirred 12 hours at room temperature and quenched by adding silica gel (3 g). The suspension was filtrated, concentrated and chromatographed on silica gel (Cy/AcOEt 3/1) to yield **13** (530 mg, 68 %) as viscous solid. $[\alpha]_D^{22}$ -7.3 (c 0.46, $CHCl_3$); m.p. 91-92°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.65 (ddd, $J_{1'\text{-}2}$ = 1.7 Hz, $J_{2\text{-}3}$ = 5.9 Hz, $J_{2\text{-}P}$ = 4.3 Hz, 1H, H-2), 4.60 (dd, $J_{1'\text{-}2}$ = 1.7 Hz, $J_{1'\text{-}P}$ = 10.4 Hz, 1H, H-1'), 4.04 (m, 2H, H-3, H-5), 3.83 (d, *J* = 2.1 Hz, 1H, H-4), 3.79-3.76 (m, 3H, 1H, H-6a, H-6b, OH-2), 3.72 (2d, $J_{H\text{-}P}$ = 11.1 Hz, 6H, OMe), 0.96 (s, 9H, Si-*t*Bu), 0.94 (s, 9H, Si-*t*Bu), 0.92 (s, 9H, Si-*t*Bu), 0.21 (s, 3H, Si-Me), 0.19 (s, 6H, Si-Me), 0.16 (s, 3H, Si-Me), 0.15 (s, 3H, Si-Me), 0.14 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.19 (d, $J_{1\text{-}P}$ = 2.1 Hz, C-1), 86.47 (C-4), 79.59 (d, $J_{1'\text{-}P}$ = 197.1 Hz, C-1'), 77.46 (d, $J_{2\text{-}P}$ = 13.1 Hz, C-2), 75.11 (C-3), 73.06 (C-5), 64.59 (C-6), 51.80 (d, $J_{C\text{-}P}$ = 5.5 Hz, OMe), 51.78 (d, $J_{C\text{-}P}$ = 5.3 Hz, OMe), 25.54 (Si-C(CH$_3$)$_3$), 25.52 (Si-C(CH$_3$)$_3$), 25.51 (Si-C(CH$_3$)$_3$), 17.89 (Si-C(CH$_3$)$_3$), 17.80 (Si-C(CH$_3$)$_3$), 17.78 (Si-C(CH$_3$)$_3$), -4.54 (Si-Me), -5.13 (Si-Me), -5.20 (Si-Me), -5.24 (Si-Me), -5.61 (Si-Me), -5.77 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 21.88; MS (CI-NH_3) : m/z 627 (100 %) [M+H]$^+$, 644 (25 %) [M+NH_4]$^+$; El. Anal. for $C_{27}H_{59}O_8PSi_3$ calc. (%) C 51.72 H 9.48. mes. C 51.70 H 9.47.

Dimethyl (2,5,6-tri-*O*-*tert*-butyldimethylsilyl-α-D-galactofuranosyl) methanephosphonate (13a). The "general procedure for exoglycals hydrogenation" was applied. After chromatography on silica gel (Cy/AcOEt 2/1), compound **13a** (89%) was isolated as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.26 (tdd, $J_{1\text{-}2}$ = 4.8 Hz, $J_{1'a\text{-}1}$ = 4.8 Hz, $J_{1'b\text{-}1}$ = 7.8 Hz, $J_{1\text{-}P}$ = 10.7 Hz, 1H, H-1), 4.14 (dd, $J_{1\text{-}2}$ = 4.8 Hz, $J_{2\text{-}3}$ = 3.0 Hz, 1H, H-2), 3.94 (dd, $J_{2\text{-}3}$ = 3.0 Hz, $J_{3\text{-}4}$ = 6.6 Hz, 1H, H-3), 3.78 (d, $J_{H\text{-}P}$ = 11.0 Hz, 3H, OMe), 3.77 (d, $J_{H\text{-}P}$ = 10.8 Hz, 3H, OMe), 3.76 (m, 1H, H-5), 3.71 (m, 2H, H-6a, H-6b), 3.56 (t, $J_{3\text{-}4}$ = $J_{4\text{-}5}$ = 6.6 Hz, 1H, H-4), 2.81 (d, $J_{OH\text{-}3}$ = 1.9 Hz, 1H, OH-3), 2.21 (ABXX', $J_{1'a\text{-}1'b}$ = 15.8 Hz, $J_{1'a\text{-}1}$ = 4.8 Hz, $J_{1'a\text{-}P}$ = 18.7 Hz, 1H, H-1'a), 2.08 (ABXX', $J_{1'a\text{-}1'b}$ = 15.8 Hz, $J_{1'b\text{-}1}$ = 7.8 Hz, $J_{1'b\text{-}P}$ = 16.9 Hz, 1H, H-1'b), 0.94 (s, 9H, Si-*t*Bu), 0.93 (s, 9H, Si-*t*Bu), 0.92 (s, 9H, Si-*t*Bu), 0.15 (s, 3H, Si-Me), 0.13 (s, 3H, Si-Me), 0.12 (s, 3H, Si-Me), 0.12 (s, 6H, Si-Me), 0.11 (s, 3H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 86.37 (C-4), 79.93 (C-3), 79.42 (d, $J_{2\text{-}P}$ = 10.1 Hz, C-2), 75.47 (d, $J_{1\text{-}P}$ = 2.7 Hz, C-1), 73.78 (C-5), 65.93 (C-6), 52.37 (d, $J_{C\text{-}P}$ = 6.4 Hz, OMe), 52.26 (d, $J_{C\text{-}P}$ = 6.5 Hz, OMe), 25.94 (2Si-C(CH$_3$)$_3$), 25.86 (Si-C(CH$_3$)$_3$), 25.72 (d, $J_{1'\text{-}P}$ = 143.4 Hz, C-1'), 18.32 (Si-C(CH$_3$)$_3$), 18.26 (Si-C(CH$_3$)$_3$), 18.10 (Si-C(CH$_3$)$_3$), -4.44 (2Si-Me), -4.57 (2Si-Me), -4.73 (2Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 32.61; MS (CI-NH_3) *m/z* 629 (85 %) [M + H]$^+$, 646 (100 %) [M+NH_4]$^+$; El. Anal. for $C_{27}H_{61}O_8PSi_4$ calc. (%) C 51.56 H 9.77. mes. C 51.76 H 9.56.

(1(1')*Z*)-2,3,6-Tri-*O*-*tert*-butyldimethylsilyl-1-(dimethoxyphosphoryl)methylidene-D-galactofuranose (14). The general procedure for preparing *exo*glycals was followed starting from known lactone.[10] A white solid was obtained (63%). $[\alpha]_D^{24}$ +50.3 (c 1.0, $CHCl_3$); m.p. 95-96°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.68 (dd, $J_{1'\text{-}2}$ = 1.5 Hz, $J_{1'\text{-}P}$ = 12.0 Hz, 1H, H-1'), 4.55 (ddd, $J_{1'\text{-}2}$ = 1.5 Hz, $J_{2\text{-}P}$ = 4.0 Hz, $J_{2\text{-}3}$ = 6.3 Hz, 1H, H-2), 4.45 (d, $J_{3\text{-}4}$ = 5.9 Hz, 1H, H-4), 4.35

(t, $J_{2\text{-}3} = J_{3\text{-}4}$ = 6.3 Hz, 1H, H-3), 3.76 (d, $J_{H\text{-}P}$ = 11.6 Hz, 3H, OCH_3), 3.74 (d, $J_{H\text{-}P}$ = 11.3 Hz, 3H, OCH_3), 3.81-3.69 (m, 3H, H-5, H-6a, H-6b), 0.98 (s, 9H, Si-*t*Bu), 0.93 (s, 9H, Si-*t*Bu), 0.92 (s, 9H, Si-*t*Bu), 0.18 (s, 3H, Si-Me), 0.17 (s, 3H, Si-Me), 0.14 (s, 3H, Si-Me), 0.09 (s, 9H, 3Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.31 (d, $J_{1\text{-}P}$ = 2.0 Hz, C-1), 84.71 (C-4), 82.82 (d, $J_{1'\text{-}P}$ = 193.3 Hz, C-1'), 78.46 (d, $J_{2\text{-}P}$ = 12.5 Hz, C-2), 75.80 (C-3), 70.43 (C-5), 62.91 (C-6), 52.44 (d, $J_{C\text{-}P}$ = 5.6 Hz, OCH_3), 51.99 (d, $J_{C\text{-}P}$ = 5.5 Hz, OCH_3), 25.82 (Si-C(CH_3)$_3$), 25.77 (Si-C(CH_3)$_3$), 25.69 (Si-C(CH_3)$_3$), 18.16 (Si-*C*(CH_3)$_3$), 17.86 (Si-*C*(CH_3)$_3$), 17.82 (Si-*C*(CH_3)$_3$), -4.05 (Si-Me), -4.19 (Si-Me), -4.29 (Si-Me), -4.58 (Si-Me), -5.44 (Si-Me), -5.57 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 22.60; MS (IC-NH_3) *m/z* 627 (100 %) $[M+H]^+$, 644 (70 %) $[M+NH_4]^+$; El. Anal. for $C_{27}H_{59}O_8PSi_3$ calc. (%) C 51.72 H 9.48. mes. C 51.57 H 9.64.

Dimethyl (2,3,6-tri-*O*-*tert*-butyldimethylsilyl-α-D-galactofuranosyl) methanephosphonate (14a). The "general procedure for exoglycals hydrogenation" was applied. After chromatography on silica gel (Cy/AcOEt 3/1), compounds **14a** (76%) and **14b** (10 %) were isolated as colourless oils. $[\alpha]_D^{19}$ -2.5 (c 0.4, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.38 (tdd, $J_{1\text{-}2}$ = 3.7 Hz, $J_{1'a\text{-}1}$ = 8.0 Hz, $J_{1'b\text{-}1}$ = 4.4 Hz, $J_{1\text{-}P}$ = 12.3 Hz, 1H, H-1), 4.16 (dd, $J_{2\text{-}3}$ = 3.2 Hz, $J_{3\text{-}4}$ = 2.5 Hz, 1H, H-3), 4.03 (dd, $J_{3\text{-}4}$ = 2.5 Hz, $J_{4\text{-}5}$ = 1.8 Hz, 1H, H-4), 3.96 (dd, $J_{2\text{-}3}$ = 3.2 Hz, 1H, H-2), 3.79 (2d, $J_{H\text{-}P}$ = 10.9 Hz, 6H, OMe), 3.70-3.59 (m, 3H, H-5, H-6a, H-6b), 2.19 (ABXX', $J_{1'a\text{-}1'b}$ = 15.4 Hz, $J_{1'a\text{-}1}$ = 8.0 Hz, $J_{1'a\text{-}P}$ = 16.9 Hz, 1H, H-1'a), 2.00 (ABXX', $J_{1'a\text{-}1'b}$ = 15.4 Hz, $J_{1'b\text{-}1}$ = 4.4 Hz, $J_{1'b\text{-}P}$ = 19.7 Hz, 1H, H-1'b), 0.94 (s, 9H, Si-*t*Bu), 0.91 (s, 9H, Si-*t*Bu), 0.9 (s, 9H, Si-*t*Bu), 0.17 (s, 3H, Si-Me), 0.14 (s, 3H, Si-Me), 0.12 (s, 3H, Si-Me), 0.11 (s, 3H, Si-Me), 0.07 (s, 6H, Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 84.99 (C-4), 79.50 (C-3), 79.47 (d, $J_{2\text{-}P}$ = 10.9 Hz, C-2), 75.33 (d, $J_{1\text{-}P}$ = 3.5 Hz, C-1), 71.08 (C-5), 63.64 (C-6), 52.53 (d, $J_{C\text{-}P}$ = 6.3 Hz, OMe), 52.35 (d, $J_{C\text{-}P}$ = 6.2 Hz, OMe), 25.87 (Si-C(CH_3)$_3$), 25.80 (d, $J_{1'\text{-}P}$ = 142.4 Hz, C-1'), 25.78 (Si-C(CH_3)$_3$), 25.69 (Si-C(*C*H_3)$_3$), 18.23 (Si-*C*(CH_3)$_3$), 18.01 (Si-*C*(CH_3)$_3$), 17.81 (Si-*C*(CH_3)$_3$), -4.41 (Si-Me), -4.46 (Si-Me), -4.55 (Si-Me), -4.91 (Si-Me), -5.39 (Si-Me), -5.48 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 32.50; MS (DIC-NH_3) *m/z* 629 (100 %) $[M+H]^+$, 646 (60 %) $[M+NH_4]^+$; El. Anal. for $C_{27}H_{61}O_8PSi_3$ calc. (%) C 51.56 H 9.77. mes. C 51.59 H 9.70.

Dimethyl (2,3,6-tri-*O*-*tert*-butyldimethylsilyl-1-enyl-D-galactofuranosyl)methanephosphonate (14b). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.83 (dd, $J_{3\text{-}4}$ = 2.0 Hz, $J_{4\text{-}5}$ = 6.5 Hz, 1H, H-4), 4.42 (d, $J_{3\text{-}4}$ = 2.0 Hz, 1H, H-3), 3.82 (d, $J_{H\text{-}P}$ = 11.2 Hz, 3H, OMe), 3.78 (d, $J_{H\text{-}P}$ = 11.0 Hz, 3H, OMe), 3.78-3.67 (m, 3H, H-5, H-6a, H-6b), 3.01 (ABX, $J_{1'a\text{-}1'b}$ = 15.7 Hz, $J_{1'a\text{-}P}$ = 19.0 Hz, 1H, H-1'a), 2.67 (ABX, $J_{1'a\text{-}1'b}$ = 15.7 Hz, $J_{1'b\text{-}P}$ = 21.2 Hz, 1H, H-1'b), 0.98 (s, 9H, Si-*t*Bu), 0.93 (s, 9H, Si-*t*Bu), 0.92 (s, 9H, Si-*t*Bu), 0.22 (s, 3H, Si-Me), 0.20 (s, 3H, Si-Me), 0.13 (2s, 6H, 2Si-Me), 0.08 (s, 6H, 2Si-Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 134.61 (d, $J_{1,2\text{-}P}$ = 14.6 Hz, C-1 and C-2), 134.38 (d, $J_{1,2\text{-}P}$ = 12.4 Hz, C-1 and C-2), 84.56 (C-4), 77.80 (d, $J_{3\text{-}P}$ = 2.8 Hz, C-3), 74.09 (C-5), 63.09 (C-6), 52.73 (d, $J_{C\text{-}P}$ = 6.6 Hz, OMe), 52.71 (d, $J_{C\text{-}P}$ = 6.8 Hz, OMe), 25.92 (Si-C(*C*H_3)$_3$), 25.87 (Si-C(*C*H_3)$_3$), 25.63 (Si-C(*C*H_3)$_3$), 23.31 (d, $J_{1'\text{-}P}$ = 139.8 Hz, C-1'), 18.23 (Si-*C*(CH_3)$_3$), 17.99 (Si-*C*(CH_3)$_3$), 17.88 (Si-*C*(CH_3)$_3$), -3.66 (Si-Me), -4.08 (Si-Me), -4.18 (Si-Me), -4.26 (Si-Me), -5.42 (Si-Me), -5.54 (Si-Me); ^{31}P-NMR (101 MHz, $CDCl_3$) δ 29.44; MS (FAB+) *m/z* 626

(100 %) [M], 649 (90 %) $[M+Na]^+$; HRMS for $C_{27}H_{59}O_8PSi_3$ calc. 626.3255 mes. 626.3239; HRMS for $C_{27}H_{59}O_8PSi_3Na$ calc. 649.3153 mes. 649.3151.

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