Synthesis, regioselective hydrogenolysis, partial hydrogenation and conformational study of dioxane and dioxolane type (9'-anthracenyl)methylene acetals of sugars

Zsolt Jakab, Attila Mándi, Anikó Borbás, Attila Bényei, István Komáromi, László Lázár, Sándor Antus, András Lipták

PII: S0008-6215(09)00444-3
DOI: 10.1016/j.carres.2009.09.007
Reference: CAR 5156

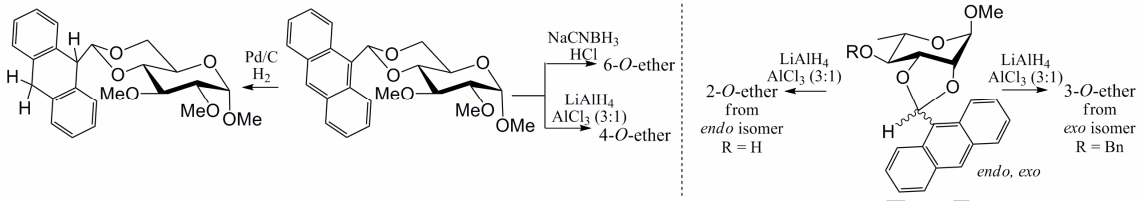
To appear in: *Carbohydrate Research*

Received Date: 15 July 2009
Revised Date: 26 August 2009
Accepted Date: 9 September 2009

Please cite this article as: Jakab, Z., Mándi, A., Borbás, A., Bényei, A., Komáromi, I., Lázár, L., Antus, S., Lipták, A., Synthesis, regioselective hydrogenolysis, partial hydrogenation and conformational study of dioxane and dioxolane type (9'-anthracenyl)methylene acetals of sugars, *Carbohydrate Research* (2009), doi: 10.1016/j.carres.2009.09.007

Synthesis, regioselective hydrogenolysis, partial hydrogenation and conformational study of dioxane and dioxolane type (9'-anthracenyl)methylene acetals of sugars

Zsolt Jakab, Attila Mándi, Anikó Borbás*, Attila Bényei, István Komáromi, László Lázár, Sándor Antus and András Lipták



Synthesis, regioselective hydrogenolysis, partial hydrogenation and conformational study of dioxane and dioxolane type (9'-anthracenyl)methylene acetals of sugars

Zsolt Jakab[a], Attila Mándi[a], Anikó Borbás[a,*], Attila Bényei[b], István Komáromi[c], László Lázár[a], Sándor Antus[a,d], András Lipták[a]

[a]*Research Group for Carbohydrates of the Hungarian Academy of Sciences, University of Debrecen, H-4010, Debrecen, PO Box 94, Hungary*

[b]*Institute of Physical Chemistry, Faculty of Science, University of Debrecen, Debrecen, PO Box 7, H-4010 Hungary*

[c]*Haemostasis, Thrombosis and Vascular Biology Research Group of the Hungarian Academy of Sciences, University of Debrecen, H-4032 Debrecen, Hungary*

[d]*Department of Organic Chemistry, University of Debrecen, H-4010, Debrecen, PO Box 20*

Dedicated to Professor Károly Lempert on the occasion of his 85th birthday

Abstract

Dioxane-type (9'-anthracenyl)methylene acetal of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside was cleaved with $LiAlH_4$-$AlCl_3$ (3:1) or with $Na(CN)BH_3$-HCl regioselectively to provide the 4- or 6-*O*-(9'-anthracenyl)methyl ether, respectively. Hydrogenolytic reaction of the *exo* and *endo* isomers of dioxolane-type acetals proved to be directed by the configuration of the acetalic carbon as well as the intramolecular participation of the adjacent free hydroxyl; ring opening reaction of the *endo* isomer of the methyl 2,3-*O*-(9'-anthracenyl)methylene-α-L-rhamnopyranoside took place with complete selectivity

resulting in the axial (9'-anthracenyl)methyl ether, whereas a 1:1 mixture of the axial and equatorial ethers was formed upon same reaction of the *exo* isomer. Catalytic hydrogenation of the sugar acetals resulted in (9',10'-dihydro-9'-anthracenyl)methylene derivatives without affecting the acetalic center. High-temperature molecular dynamics simulations and DFT (Density Functional Theory) geometry optimizations were carried out to study the conformation of the dioxane-type (9',10'-dihydro-9'-anthracenyl)methylene acetal.

Keywords 9-Anthracenylmethylene acetal, Regioselective, Hydrogenolysis, High-temperature MD, DFT

Corresponding author. Tel.: +36 52512900/22462; fax: +36 52512900/22342.
E-mail address: *borbasa@puma.unideb.hu (A. Borbás).*

1. Introduction

Regioselective transformation of polyhydroxy compounds, such as carbohydrates, necessitates the application of protective groups which can be attached or cleaved in a selective manner to obtain partially substituted molecules. Modification of simple sugars and synthesis of higher oligosaccharides can not be carried out without the use of these methodologies.[1]

The acetal-type protecting groups possess significant advantages such as simultaneous protection of two hydroxyls, the easy removal and the possibility of a partial deprotection. By the adequate selection of the hydride donor and various protic or Lewis acid reagents as well as solvents, any of the two protected hydroxyls can be liberated regioselectively.[2]

Most recently the 9-anthraldehyde acetal as a new protecting group was proposed by Ellervik[3] reporting the synthesis of (9'-anthracenyl)methylene acetals of the 2-(trimethylsilyl)ethyl β-D-glucopyranoside and the phenyl 1-thio-β-D-galactopyranoside in an acetal exchange reaction. The anthraldehyde acetals can be cleaved under reductive conditions with $Na(CN)BH_3$ and HCl/Et_2O in THF to give 6-*O*-(9'-anthracenyl)methyl ethers, and can be selectively removed in the presence of benzylidene acetals. Due to the good crystalline properties and strong absorbance and fluorescence the (9'-anthracenyl)methylene acetal and (9'-anthracenyl)methyl ether may become useful as new protecting groups.

These results prompted us to investigate the regioselective ring opening reaction and deprotection procedures of dioxane- and dioxolane-type (9'-anthracenyl)methylene-acetals of sugars.

2. Results and discussion

2.1. Synthesis and reactivity of dioxane-type (9'-anthracenyl)methylene acetals

To prepare the dioxane-type acetal **2**, methyl α-D-glucopyranoside **1** was treated with anthraldehyde dimethyl acetal in the presence of (±)10-camphorsulfonic acid (CSA). The OH groups of position 2 and **3** were methylated to obtain the fully protected methyl 4,6-*O*-(9'-anthracenyl)methylene-2,3-di-*O*-methyl-α-D-glucopyranoside **3** (Scheme 1).

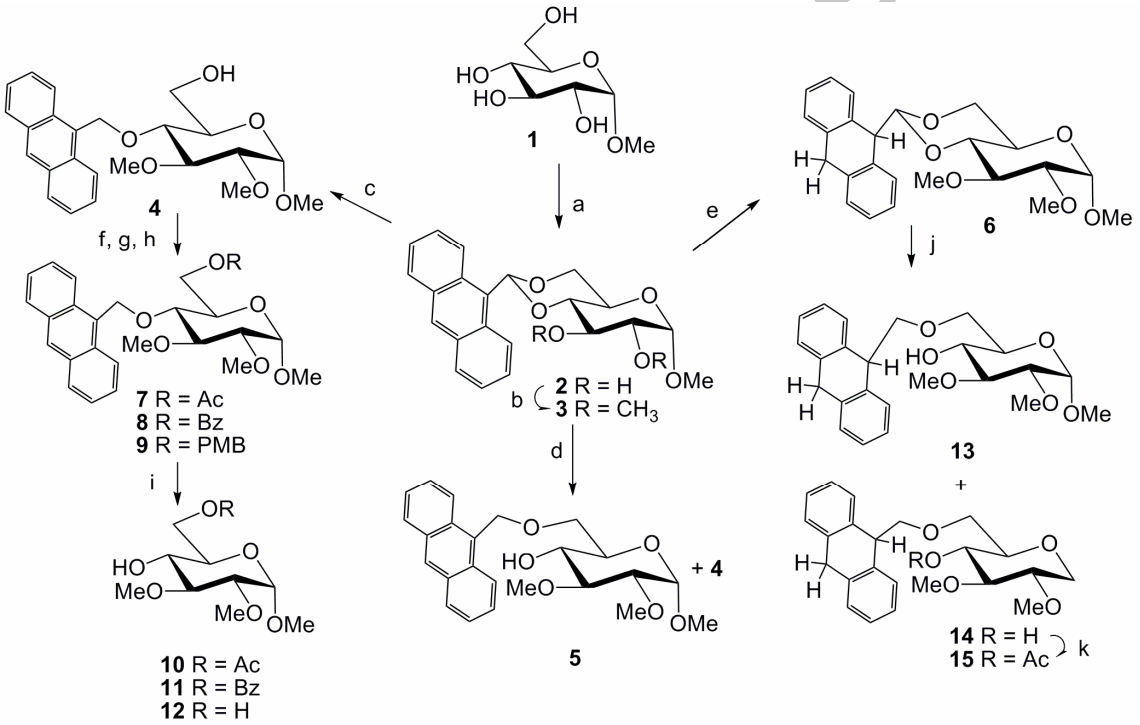
Upon treatment of compound **3** with $LiAlH_4$-$AlCl_3$[4] (3:1) the methyl 4-*O*-(9'-anthracenyl)methyl-2,3-di-*O*-methyl-α-D-glucopyranoside **4** could be isolated in crystalline form in a yield of 70%. Transformation of **3** with $Na(CN)BH_3$ and HCl/Et_2O in dry THF[5] mainly resulted in methyl 6-*O*-(9'-anthracenyl)methyl-2,3-di-*O*-methyl-α-D-glucopyranoside **5,** and its regioisomer **4** was also formed as a minor product.

It has been known since 1936 that 4,6-*O*-benzylidene acetals of glucose can be catalytically reduced into the corresponding 4,6-diols.[6] However, catalytic hydrogenation of **3** surprisingly did not affect the acetalic center, but affected the antracenyl ring resulting in methyl 4,6-*O*-(9',10'-dihydro-9'-anthracenyl)methylene-2,3-di-*O*-methyl-α-D-glucopyranoside **6** which was stable under hydrogen atmosphere in the presence of Pd catalyst for as long as 5 days. The structure of compound **6** was determined on the basis of ^{1}H- and ^{13}C-NMR spectroscopy and X-ray crystallography as well. Molecular modeling was also applied to investigate the conformation of the (9',10'-dihydro-9'-anthracenyl)methylene moiety.

In order to study the selective removal of the (9'-anthracenyl)methyl ether moiety in the presence of acetyl, benzoyl or *p*-methoxybenzyl (PMB) groups the free hydroxyl of compound **4** was substituted by a simple acetylation, benzoylation and *p*-methoxybenzylation to furnish compounds **7**-**9**, respectively. All three fully protected derivatives **7**-**9** were treated with $BF_3{\cdot}OEt_2$ in dry CH_2Cl_2 at 0 °C. Selective cleavage of the (9'-anthracenyl)methyl group of **7** and **8** liberating the OH-4 took place in 20 minutes to afford compounds **10**[7] and **11**,[8,9] respectively. In the case of compound **9** not only the (9'-anthracenyl)methyl group but also the PMB group was cleaved under these conditions to give the diol **12**.[10]

Reductive ring opening reaction of the partially hydrogenated acetal derivative **6** was also studied. We assumed that the acetalic center of 4,6-*O*-acetal ring anchored to the aliphatic 9'-carbon is less reactive under hydrogenolytic conditions than that of compound **3** anchored to an aromatic carbon. Compound **6** was treated with $LiAlH_4$-$AlCl_3$ (3:1) under the conditions applied for the conversion of **3** into **4**, however no reaction could be observed. Interestingly, the reaction of **6** with Et_3SiH in the presence of $BF_3{\cdot}OEt_2$[11] in dry CH_2Cl_2 resulted in two products, **13** and **14**. Unreacted starting material **6** also remained after 24 h. Compound **13** proved to be methyl 6-*O*-(9',10'-dihydro-9'-anthracenyl)methyl-2,3-di-*O*-

methyl-α-D-glucopyranoside. The byproduct **14** could be purified after acetylation (**14**→**15**) and was identified as 1,5-anhydro-4-*O*-acetyl-6-*O*-(9',10'-dihydro-9'-anthracenyl)methyl-2,3-di-*O*-methyl-D-glucitol on the basis of NMR. This result has experimentally proved the high stability of this type of acetal **6** and the formation of **14** is assumed to take place *via* compound **13**. Hydrogenolysis of the glycosidic acetal resulting in a glucitol derivative is extremely rare upon reductive cleavage of benzylidene type acetals,[12] since glycosides are more stable than the aromatic acetals.

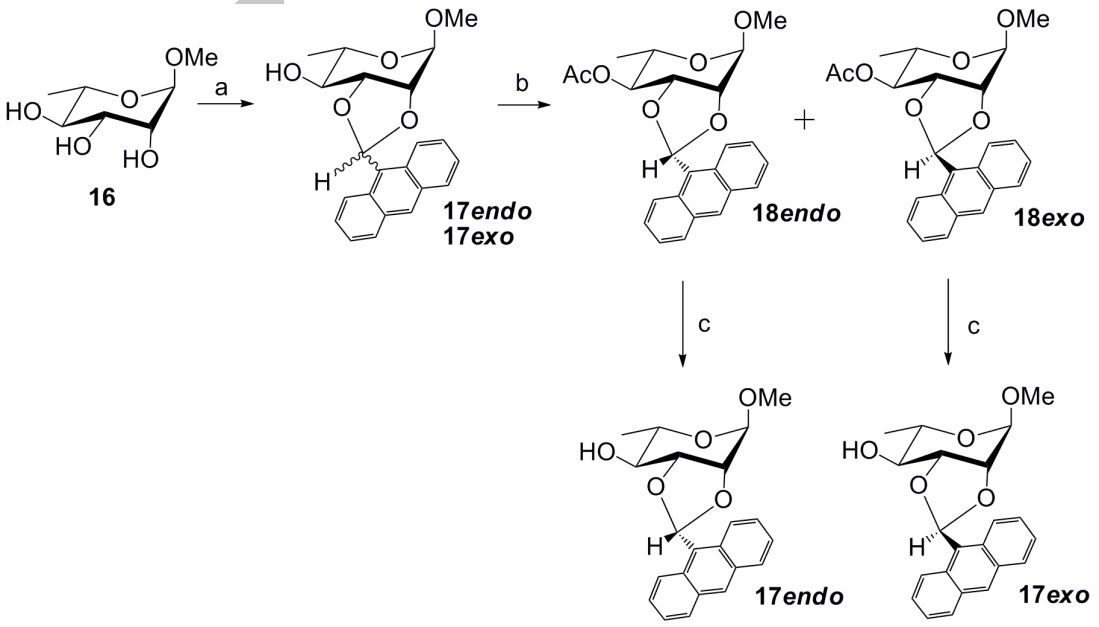


Scheme 1. Reagents and conditions: (a) anthraldehyde dimethylacetal, cat. CSA, dry MeCN, rt, 3 h, 79%; (b) MeI, NaH, DMF, 0 °C, 3 h, 90%; (c) from **3**: $LiAlH_4$, $AlCl_3$ (3:1), Et_2O, CH_2Cl_2, rt, 4 h, 70%; (d) from **3**: $Na(CN)BH_3$ in THF, HCl/Et_2O, rt, 5 min, 48% for **5**, 12% for **4**; (e) Pd(C), H_2, EtOH, rt, 6 h, 90%; (f) Ac_2O, pyridine, rt, 2 h, 80% for **7**; (g) BzCl, pyridine, CH_2Cl_2, 0 °C, 2 h, 89% for **8**; (h) PMBCl, NaH, DMF, 0 °C, 2 h, 82% for **9**; (i)

$BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 20 min, 75% for **10**, 76% for **11**, 79% for **12;** (j) $BF_3{\cdot}OEt_2$, Et_3SiH, CH_2Cl_2, 0 °C, overnight, 20% for **13**; (k) Ac_2O, pyridine, rt, 2 h, 14% for two steps.

2.2. Synthesis and reactivity of dioxolane-type (9'-anthracenyl)methylene acetals

The vicinal *cis*-axial/equatorial hydroxyl groups of pyranosides react with acetalating reagents to form dioxolane-type acetal derivatives. The corresponding anthraldehyde dimethylacetal have not been used as protecting group for vicinal diols so far. Methyl α-L-rhamnopyranoside was considered to be an excellent model compound to study the synthesis and hydrogenolysis of dioxolane-type (9'-anthracenyl)methylene acetals. Treatment of methyl α-L-rhamnopyranoside **16** with anthraldehyde dimethylacetal resulted in a 1:4.5 mixture of the **17*endo*** and **17*exo*** isomers, in a moderate yield (55%). Since these isomers could not be completely separated by column chromatography, the mixture was acetylated, and the separation of the obtained mixture of **18*endo*** and **18*exo*** was successful. After deacetylation of **18*endo*** and **18*exo***, respectively, the **17*endo***- and ***exo*-**acetals could be obtained in crystalline form (Scheme 2).



Scheme 2. Reagents and conditions: (a) anthraldehyde dimethylacetal, cat. CSA, dry MeCN, rt, 1 d, 46% for **17*exo***, 9% for **17*endo***. (b) Ac_2O, pyridine, rt, 1 h; (c) NaOMe, MeOH, rt, 1 h.

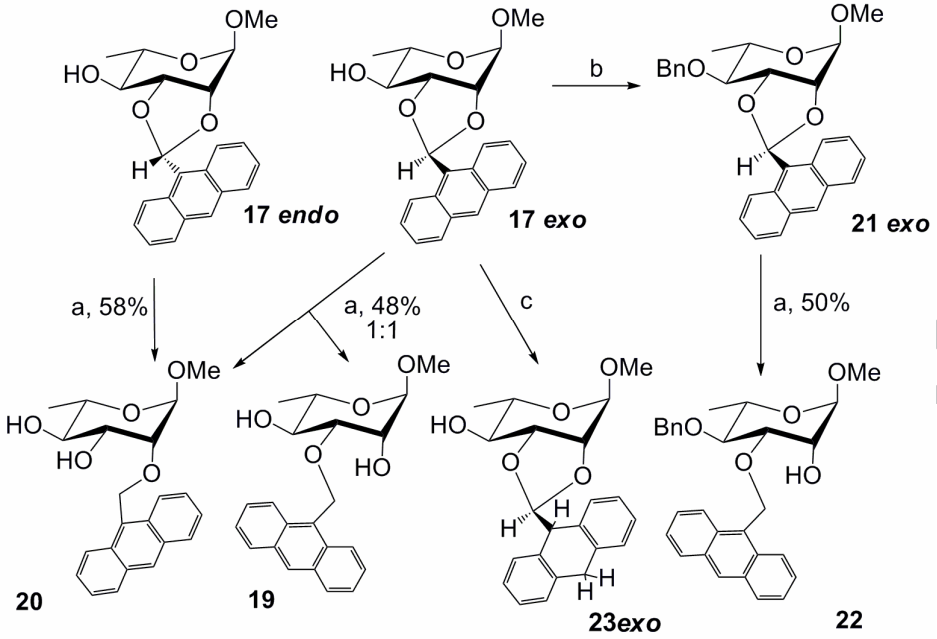
The determination of the absolute configuration of the dioxolane-type acetals is a rather complex task although the ^{1}H-NMR spectra can help if both isomers are available. Since the late seventies the chemical shift values of acetalic protons and carbons have been applied for the structure elucidation of the dioxolane-type structures.[13] The acetalic configuration of compounds **17** and **18** were proven by ^{1}H-NMR spectroscopy; H-acetalic of **17**- and **18*endo*** isomers resonate at higher field (δ 7.08 and 7.12 ppm) while H-acetalic signals of **17**- and **18*exo*** isomers are at lower field (δ 7.47 and 7.58 ppm). Resonance values of the acetalic carbons are the followings: **17*endo***: 102.2 ppm, **18*endo***: 101.8 ppm and **17*exo***:100.3 ppm, **18*exo***:100.8 ppm.

We studied ring-opening reaction of the dioxolane-type acetals **17*endo*** and **17*exo*** possessing an extremely bulky anthracenyl substituent at the acetalic center. It was earlier shown that the cleavage of the five-membered benzylidene-type acetal rings is directed by the stereochemistry of the acetalic center. Namely, upon exo arrangement of the bulky substituent, the reagent attacks the axial oxygen atom forming the axial hydroxyl and equatorial benzyl-ether derivatives, selectively. On the contrary, in the case of *endo* arrangement of the bulky group, the equatorial oxygen atom is attacked leading to the formation of the equatorial hydroxyl and axial ether type products, also with full selectivity. Recently a rule of thumb (x, x, x) was formulated for the ring opening reactions of the dioxolane acetals by the following way: exo isomer gives axial hydroxyl.[14] In good agreement with our expectations the cleavage of **17*endo*** with $LiAlH_4$-$AlCl_3$ (3:1) gave methyl 2-*O*-(9'-anthracenyl)methyl-α-L-rhamnopyranoside **20**, exclusively. Surprisingly, treatment of **17*exo*** with $LiAlH_4$-$AlCl_3$ (3:1) resulted in a 1:1 mixture of the equatorial (9'-anthracenyl)methyl-

ether derivative **19** and the axial (9'-anthracenyl)methyl-ether derivative **20**. The loss of selectivity in the ring opening reaction of the **17*exo*** acetal is seemed to disagree with the rule of thumb. In fact, we supposed, that the rule is valid, and the formation of the axial hydroxyl derivative **19** is due to the directing effect of the bulky *exo*-substituent of the acetalic carbon. However, an opposite directing effect of the free OH-4 next to the acetal ring also appears and gives rise to the formation of the axial ether **20**. We demonstrated earlier[15,16] in the course of symmetrical acetals of sugars that an adjacent free hydroxyl could participate in the opening reaction of the acetal ring. Being a free hydroxyl present at the acetal derivative first the reagents reacted with the OH free forming an aluminate derivative, then the cleavage of the acetal occurred through an intramolecular complexation of the adjacent oxygen of the acetal ring. The formation of the axial ether derivative **20** upon hydrogenolysis of **17*exo*** was assumed *via* this mechanism.

In order to prove our assumption compound **17*exo*** was benzylated, and the fully protected **21*exo*** was subjected to reductive ring opening reaction using $LiAlH_4$ and $AlCl_3$ (3:1) as the reagents. The reaction gave exclusively the equatorial (9'-anthracenyl)methyl-ether derivative **22** as expected. In the course of hydrogenolytic cleavage, hydrolysis of the dioxolane acetals also occured decreasing the yields of compounds **19**, **20** and **22**.

Catalytic hydrogenation of compound **17*exo*** took place in a similar manner as observed in the case of compound **3**; the acetalic center stayed intact and the 9',10'-positions of the anthracenyl ring were saturated to afford compound **23*exo*** (Scheme 3).



Scheme 3. Reagents and conditions: (a) $LiAlH_4$, $AlCl_3$ (3:1), Et_2O, CH_2Cl_2, 0 °C, 2 h; (b) BnBr, NaH, dry DMF, 0 °C, 1 h, 92%; (c) Pd(C), H_2, EtOH, rt, 8 h, 95%.

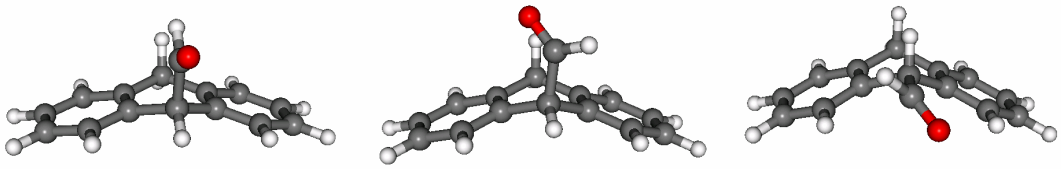
The (9',10'-dihydro-9'-anthracenyl)methylene acetals of sugars have not been known in the literature and this kind of structure could be interesting in a sterical point of view. Therefore, conformational studies of the presumed roof-like structure of the (9',10'-dihydro-9'-anthracenyl)methylene acetal ring of **6** was performed by means of computational and X-ray crystallographic methods.

2.3. Computational study of the 9,10-dihydro-9-anthraldehyde (24) and the (9',10'-dihydro-9'-anthracenyl)methylene acetal of glucopyranoside (6) and comparison to the X-ray experiment

First, a simple aldehyde was chosen as a model compound for the computational studies. 100ns constant temperature molecular dynamics simulation has been carried out at 1200K on the partially hydrogenated 9,10-dihydro-9-anthraldehyde **24** in order to explore the

low energy regions of the conformational energy (hyper) surface. 100 thousands geometries (snapshots) have been saved and each of them was minimized applying the GAFF empirical force field. Due to the relatively high temperature molecular dynamics simulations it can be plausibly assumed, that the low energy region of the conformational energy surface is sufficiently sampled, i.e. geometry optimization from the saved trajectory snapshots will find all the conformers corresponding to local energy minima which are non-negligibly populated. The geometries obtained this way constituted three distinct clusters of conformers. The geometry of a representative member of each cluster (with the lowest energy) was further optimized at the B3LYP/6-31G(d) level of theory. The computed energies and populations of the stable conformers of compound **24** are given in Table 1. As it is immediately apparent, the axial position of the aldehyde group is substantially more preferable than the equatorial one. In addition, while the axial position of the aldehyde group can exist in two (three, if the mirrored conformers are counted independently) stable conformations differing only in the relative orientation of the carbonyl oxygen, only one (two mirror related) conformer found with equatorial aldehyde group. It is especially interesting, that interchanging the aldehyde O and H atoms at the conformer **24c** causes a conformational (equatorial→axial) transition to the most stable conformer **24a**.

Table 1. Computed empirical force field (GAFF) and zero point vibrational energy corrected density functional (B3LYP/6-31G(d)) energies and relative energies as well as the estimated percentage populations (based on the corrected density functional energies and the Boltzmann energy distribution) of conformers for compound **24.**

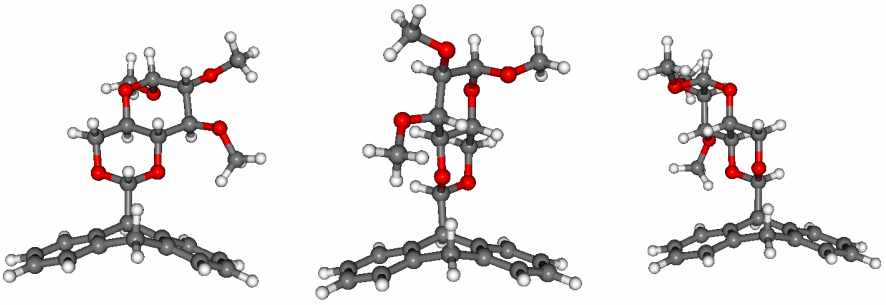


24a 24b 24c

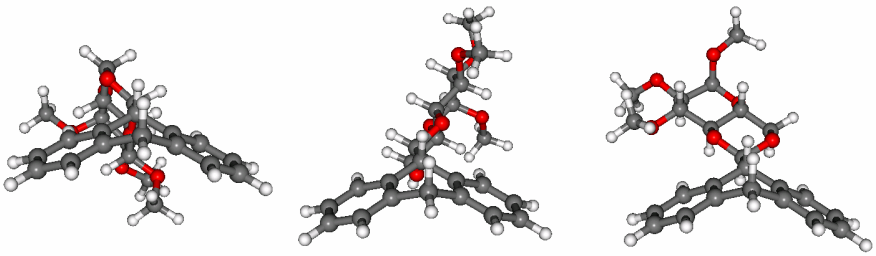
Geometry	GAFF		B3LYP/6-31G(d)		Percentage population (at 300K)(%)
	E (kJ/mol)	ΔE (kJ/mol)	E+ZPVE (a.u.)	ΔE (kJ/mol)	
24a	44.354	0	-653.822281	0	70.98
24b	56.223	11.869	-653.821431	2.232	29.01
24c	69.973	25.619	-653.813038	24.267	0.01

The computational protocol detailed above was applied for the methyl 4,6-*O*-(9',10'-dihydro-9'-anthracenyl)methylene-2,3-di-*O*-methyl-α-D-glucopyranoside **6**. It resulted in six structures which are schematically depicted and the corresponding numerical results are summarized in Table 2. Not surprisingly, the partially hydrogenated anthracenylmethylene group favors the equatorial position to the sugar ring. On the other hand, acetalic C became axial to C-9' as it was expected, based on the conformational analysis of the model compound **24**.

Table 2. Computed empirical force field (GAFF) and zero point vibrational energy corrected density functional (B3LYP/6-31G(d)) energies and relative energies as well as the estimated percentage populations (based on the corrected density functional energies and the Boltzmann energy distribution) of conformers for compound **6.**



6a 6b 6c



6d 6e 6f

Geometry	GAFF		B3LYP/6-31G(d)		Percentage population (at 300K)(%)
	E (kJ/mol)	ΔE (kJ/mol)	E+ZPVE (a.u.)	ΔE (kJ/mol)	
6a	245.396	0	-1382.220653	1.366	28.75
6b	246.792	1.396	-1382.220375	2.095	21.46
6c	252.835	7.439	-1382.221173	0	49.71
6d	269.563	24.167	-1382.214537	17.423	0.05
6e	274.761	29.365	-1382.214000	18.823	0.03
6f	281.164	35.768	-1382.213114	21.159	0.01

The structure of methyl 4,6-*O*-(9',10'-dihydro-9'-(*R*)-anthracenyl)methylene-α-D-glucopyranoside determined by X-ray measurements (shown in Figure 1), corresponds perfectly to **6a**, which is predicted as the most stable structure by GAFF empirical force field and showed one of the considerably populated one suggested by B3LYP/6-31G(d) method (Table 2). Figure 2 shows the correlation between X-ray geometry of **6** and DFT optimized geometry of **6a**.

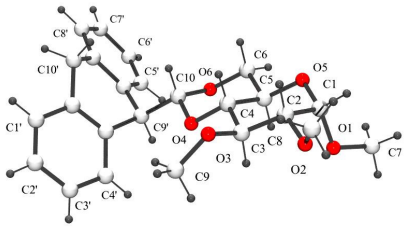


Figure 1. Structure of compound **6** determined by single crystal X-ray diffraction together with partial numbering scheme.

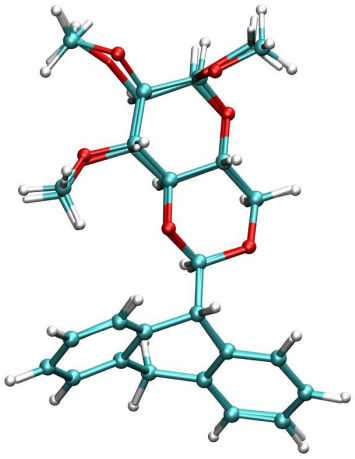


Figure 2. Correlation of X-ray structure of **6** and DFT optimized **6a** structure.

3. Conclusion

Dioxane- and dioxolane-type (9'-anthracenyl)methylene acetal of sugars could be readily prepared by means of acetal exchange reaction. Reductive hydrogenolysis of the (9'-anthracenyl)methylene acetal ring showed the similar pattern of regioselectivity as observed in the case of benzylidene acetals. Reaction of methyl 4,6-*O*-(9'-anthracenyl)methylene-2,3-di-*O*-methyl-α-D-glucopyranoside with $LiAlH_4$-$AlCl_3$ (3:1) or with $Na(CN)BH_3$-HCl provided regioselectively the 4- or 6-*O*-(9'-anthracenyl)methyl ether, respectively. Hydrogenolytic reaction of the *exo* and *endo* isomers of dioxolane-type acetals with AlH_3 was directed by the configuration of the acetalic carbon as well as the intramolecular participation of the adjacent free hydroxyl. Due to the joint effects the *endo* isomer of the methyl 2,3-*O*-(9'-anthracenyl)methylene-α-L-rhamnopyranoside afforded the axial (9'-anthracenyl)methyl ether exclusively, whereas the *exo* isomer resulted in a 1:1 mixture of the axial and equatorial ethers upon ring opening reaction. The ring cleavage of the fully protected *exo* isomer (**21exo**) afforded the expected equatorial (9'-anthracenyl)methyl ether exclusively, in the lack of directing effect of an adjacent free hydroxyl. The (9'-anthracenyl)methyl group could be removed selectively with $BF_3{\cdot}OEt_2$ in the presence of acetyl or benzoyl groups. To remove the (9'-anthracenyl)methylene acetal catalytic hydrogenation proved to be inefficient, and resulted in the stable (9',10'-dihydro-9'-anthracenyl)methylene derivatives without affecting the acetalic center. Catalytic hydrogenation of 9-anthraldehyde into 9-methyl-1,2,3,4,5,6,7,8-octahydro-anthracene is known from the literature,[17] the unexpected stability of the 9',10'-dihydro-9'-anthracenyl)methylene derivatives of sugars was explained by computational methods.

The computational studies outlined above show that more than one local energy minimum with non-negligible population are exist which correspond to axial acetalic orientations and they are substantially more stable than the equatorial ones. It means that although the X-ray experiment shows the global minimum in solid phase, in solution the

existence of other axial conformation also might have contribution to the observed properties. Another consequence of the axial acetal conformation and the roof-type shape of the hydrogenated anthracenyl group is the loss of tight fit to the surface of catalysator and this way the loss of full hydrogenation.

4. Experimental

4.1. General Methods

Optical rotations were measured at room temperature with a Perkin-Elmer 241 automatic polarimeter. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. TLC was performed on Kieselgel 60 F254 (Merck) with detection by 5% sulfuric acid in ethanol. Column chromatography was performed on Silica Gel 60 (E. Merck 0.062–0.200 nm). The organic solutions were dried over $MgSO_4$ and concentrated in vacuum. The ^1H (200.13, 360.13 and 500.13 MHz) and ^{13}C NMR (50.3, 90.54, 125.76 MHz) spectra were recorded with Bruker WP-200SY, Bruker AM-360 and Bruker DRX-500 spectrometers for solutions in $CDCl_3$. Internal references: TMS (0.00 ppm for ^1H), $CDCl_3$ (77.00 ppm for ^{13}C). MALDI-TOF MS spectra were recorded on a Bruker Biflex III spectrometer in positive, linear mode using saturated 2,4,6-trihydroxy-acetofenon in water as matrix. X-ray diffraction data was collected at 293 K, Enraf Nonius MACH3 diffractometer, Mo Kα radiation λ= 0.71073 Å. The structure was solved by SIR-92 program[18] and refined by full-matrix least-squares method on F^2, with all non-hydrogen atoms refined with anisotropic thermal parameters using the SHELXL-97 package[19], publication material was prepared with the WINGX- suite.[20] All hydrogen atoms were located geometrically and refined in the rigid mode. The molecular dynamics simulations and the preliminary geometry optimizations using the suitably developed GAFF empirical force field on the trajectory snapshot geometries were

carried out by means of the Amber molecular dynamics simulation package.[21] B3LYP/6-31G(d) density functional calculations were carried out using the Gaussian 03 package.[22] At the B3LYP/6-31G(d) minima the zero point vibrational energy correction at the same level of theory also were computed. Ball-and-stick representations of the conformers were generated by the Molekel[23] and VMD[24] softwares.

4.1.1. Methyl 4,6-*O*-(9'-anthracenyl)methylene-α-D-glucopyranoside (2)

To a mixture of methyl α-D-glucopyranoside **1** (3.0 g 15.4 mmol) and anthraldehyde dimethylacetal[3] (4.56 g 18.1 mmol) in MeCN (20 mL) was added catalytic amount of (±)10-camphorsulfonic acid (CSA) and was stirred at room temperature for 3 h. The mixture was neutralized by addition of Et_3N and concentrated, then co-evaporated with toluene three times. The residue was crystallized from Et_2O-hexane to give **2** (4.64 g, 79%) as white needles: mp 192-194 °C; $[\alpha]_D$ +106 (c 0.14, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.59 (d, 2H, *J* 8.5 Hz), 8.46 (s, 1H), 7.97 (d, 2H, *J* 8.0 Hz), 7.58-7.37 (m, 4H), 6.80 (s, 1H, acetalic), 4.50 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.33 (dd, 1H, *J* 10.4 Hz, *J* 4.7 Hz), 4.0 (dt, 1H, *J* 9.9 Hz, *J* 4.7 Hz), 3.87 (dd, 1H, *J* 9.3 Hz, *J* 2.4 Hz), 3.82 (d, 1H, *J* 11.6 Hz), 3.7 (d, 1H, *J* 10.3 Hz), 3.50-3.35 (m, 2H), 3.31 (s, 3H, OCH_3), 2.73 (d, 1H, *J* 8.7 Hz, OH); ^{13}C NMR: (50 MHz, $CDCl_3$): δ (ppm) 131.5, 129.9, 129.6, 129.0, 126.6, 126.2, 124.8 (aromatic), 100.5 (C acetalic), 99.9 (C-1), 82.1 (C-4), 72.5, 71.3 (C-2, C-3), 69.9 (C-6), 62.3 (C-5), 55.6 (OCH_3); Anal. Calcd. for $C_{22}H_{22}O_6$ (382.41): C 69.10, H 5.80. Found: C 69.43, H 5.71.

4.1.2. Methyl 4,6-*O*-(9'-anthracenyl)methylene-2,3-di-*O*-methyl-α-D-glucopyranoside (3)

Compound **2** (1.58 g, 4.36 mmol) was stirred in dry DMF (10 mL), treated with NaH (0.40 g, 60%, 3 equiv) at 0 °C. Methyl iodide (0.70 mL, 11.2 mmol, 2.71 equiv) was added dropwise and the reaction temperature was kept at 0 °C for 1 h. Then it was allowed to warm up to rt, and no starting material was indicated by TLC after 2 h. To the mixture MeOH was added to decompose the unreacted NaH and then it was concentrated, diluted with CH_2Cl_2, washed twice with water, dried ($MgSO_4$) and concentrated. After column chromatography (6:4 hexane-EtOAc) compound **3** (1.52 g, 90%) was isolated as a syrup: $[\alpha]_D$ +85 (c 0.16, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.66 (d, 2H, *J* 8.7 Hz), 8.42 (s, 1H), 7.93 (dd, 2H, *J* 8.4 Hz, *J* 0.8 Hz), 7.55-7.36 (m, 4H), 6.89 (s, 1H, acetalic), 4.89 (d, 1H, *J* 3.8 Hz, H-1), 4.43 (dd, 1H, *J* 10.1 Hz, *J* 4.7 Hz), 4.26-4.11 (m, 1H), 4.09 (dd, 1H, *J* 14.3 Hz, *J* 7.2 Hz), 3.90 (t, 1H, *J* 10.2 Hz), 3.80-3.72 (m, 1H), 3.52 (2s, 6H, 2 x OCH_3), 3.41 (s, 3H, OCH_3), 3.34 (dd, 1H, $J_{2,3}$ 8.9 Hz, H-2); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 131.4, 129.6, 129.6, 128.8, 126.9, 125.9, 124.9, 124.7 (aromatic), 100.6 (C acetalic), 98.5 (C-1), 83.1, 81.4, 79.8 (C-2, C-3, C-4), 69.9 (C-6), 62.3 (C-5), 60.8, 59.2 (2 x OCH_3), 55.5 (anomeric OCH_3). MALDI-TOF MS *m/z* calcd. for $C_{24}H_{26}O_6$: 410.17. Found: 410.42 $[M]^+$ and 433.38 $[M+Na]^+$. Anal. Calcd. for $C_{24}H_{26}O_6$: C 70.23, H 6.38. Found: C 70.33, H 6.32.

4.1.3. Methyl 4-*O*-(9'-anthracenyl)methyl-2,3-di-*O*-methyl-α-D-glucopyranoside (4)

To a stirred suspension of the starting acetal **3** (2.1 g, 5.1 mmol) in dry CH_2Cl_2 and Et_2O (30 mL, 2:1) $LiAlH_4$ (0.86 g, 4.5 equiv) and solution of $AlCl_3$ (1.0 g, 1.5 equiv) in Et_2O (10 mL) were added carefully under argon at 0 °C, then stirred for 4 h at rt. After complete conversion 2-3 mL of EtOAc and 1-5 drops of water were added, the mixture was diluted with EtOAc, washed 3 times with water, dried and concentrated. The crude syrup was crystallized from EtOH to give pale yellow crystalline product and mother liquor was purified by column

chromatography (7:3 hexane-acetone) to give **4** with 70% overall yield (1.46 g): mp 145-146 °C; $[\alpha]_D$ +112 (c 0.10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.47 (d, 2H, *J* 9.0 Hz, H-1', H-8'), 8.44 (s, 1H, H-10'), 7.98 (d, 2H, *J* 8.5 Hz, H-4', H-5'), 7.55-7.40 (m, 4H, H-2', H-3', H-6', H-7'), 5.81 (d, 1H, *J* 11.0 Hz, ArCH_2), 5.71 (d, 1H, *J* 11.0 Hz, ArCH_2), 4.80 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 3.80 (s, 3H, OCH_3), 3.75-3.60 (m, 4H), 3.55-3.50 (m, 1H), 3.53 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.29 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-2), 1.80 (bs, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 131.4, 130.9, 129.0, 128.7, 128.5, 126.3, 124.9, 124.3 (aromatic), 97.2 (C-1), 83.5, 82.8, 76.6 (C-2, C-3, C-4), 70.6 (C-5), 66.6 (Ar*C*H_2-), 61.7 (C-6), 61.3, 58.6 (2 x OCH_3), 55.0 (OCH_3 anomeric); Anal. Calcd. for $C_{24}H_{28}O_6$ (412.48): C 69.88, H 6.84. Found: C 69.96, H 6.75.

4.1.4. Methyl 6-*O*-(9'-anthracenyl)methyl-2,3-di-*O*-methyl-α-D-glucopyranoside (5) and compound (4)

To a stirred suspension of the starting acetal **3** (0.39 g, 0.96 mmol) and $Na(CN)BH_3$ (0.54 g, 9 equiv) in dry THF (5 mL) containing 3 Å MS was added HCl in Et_2O dropwise until the evolution of gas ceased. After 5 min TLC showed complete conversion of the starting material. The mixture was diluted with CH_2Cl_2 (100 mL), washed with satd $NaHCO_3$ and water, then dried ($MgSO_4$) and concentrated. After column chromatography (1:1 hexane-EtOAc) compound **5** (227 mg, 48%) was isolated as a syrup: $[\alpha]_D$ +63 (c 0.17, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 8.39 (d, 3H), 7.95 (d, 2H, *J* 8.4 Hz), 7.47 (dt, 4H), 5.55 (d, 1H, *J* 11.5 Hz, ArCH_2), 5.47 (d, 1H, *J* 11.6 Hz, ArCH_2), 4.84 (s, 1H, $J_{1,2}$ 3.4 Hz, H-1), 3.90-3.75 (m, 2H), 3.68 (m, 1H, H-5), 3.60-3.33 (m, 12H, incl. 3x OCH_3), 3.17 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-2); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 130.9, 130.5, 128.5, 128.3, 127.9, 125.7, 124.5, 124.0 (aromatic), 97.0 (C-1, $J_{C1,H1}$ 170 Hz), 82.5, 81.2, 70.2, 70.0 (C-2, C-3, C-4, C-5),

69.2 (Ar*C*H_2-), 65.3 (C-6), 60.5, 58.1 (2 x OCH_3), 54.7 (OCH_3 anomeric); Anal. Calcd. for $C_{24}H_{28}O_6$ (412.48): C 69.88, H 6.84. Found: C 70.06, H 6.63.

Compound **4** was also formed (56 mg, 12%).

4.1.5. Methyl 4,6-*O*-(9',10'-dihydro-9'-anthracenyl)methylene-2,3-di-*O*-methyl-α-D-glucopyranoside (6)

Compound **3** (0.45 g, 1.1 mmol) was dissolved in 96% EtOH (25 mL) and stirred under H_2 atmosphere in the presence of 10% Pd/C (75 mg) for 6 h. The catalyst was removed by filtration through a layer of Celite, washed with EtOH, and the solvent was evaporated. The residue was crystallized from MeOH to give **6** (360 mg, 79%) as white needles: mp 172-174 °C; $[\alpha]_D$ +51 (c 0.19, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 7.40-7.10 (m, 8H, aromatic), 4.72 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.63 (d, 1H, *J* 5.2 Hz, H-acetalic), 4.22 (d, 1H, *J* 4.4 Hz, H-9'), 4.17 (d, 1H, *J* 16.9 Hz, H-10'a), 3.99 (dd, 1H, *J* 10 Hz, *J* 4.6 Hz), 3.78 (d, 1H, *J* 18.1 Hz, H-10'b), 3.60-3.40 (m, 8H, incl. 2 x OCH_3), 3.33 (s, 3H, anomeric OCH_3), 3.30 (t, 1H, *J* 10.1 Hz), 3.14 (t, 1H, *J* 9.4 Hz), 3.12 (dd, 1H, $J_{2,3}$ 9.3 Hz, H-2); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 137.3, 137.2, 135.1, 134.9, 130.0, 129.8, 127.4, 127.3, 126.7, 125.6 (aromatic), 103.5 (C-acetalic), 98.3 (C-1), 81.8, 80.9, 79.8 (C-2, C-3, C-4), 68.6 (C-6), 61.9 (C-5), 60.6, 59.3 (2 x OCH_3), 55.0 (anomeric OCH_3), 51.0 (C-9'), 35.8 (C-10'). MALDI-TOF MS *m/z* calcd. for $C_{24}H_{28}O_6$: 412.19. Found: 435.40 $[M+Na]^+$. Anal. Calcd. for $C_{24}H_{28}O_6$: C 69.88, H 6.84. Found: C 70.03, H 6.69.

4.1.6. Methyl 6-*O*-acetyl-4-*O*-(9'-anthracenyl)methyl-2,3-di-*O*-methyl-α-D-glucopyranoside (7)

To a solution of **4** (250 mg, 0.61 mmol) in pyridine (2 mL) was added Ac_2O (1 mL), and stirred for 2 hours. Then the reaction mixture was concentrated and co-evaporated twice with toluene. After column chromatography (7:3 hexane-EtOAc) compound **7** was isolated (220 mg, 80%) as a syrup: $[\alpha]_D$ +144 (c 0.11, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.42 (d, 2H, *J* 9.0 Hz, H-1', H-8'), 8.40 (s, 1H, H-10'), 7.96 (d, 2H, *J* 8.5 Hz, H-4', H-5'), 7.60-7.40 (m, 4H, H-2', H-3', H-6', H-7'), 5.75 (d, 1H, *J* 11.5 Hz, ArCH_2), 5.70 (d, 1H, *J* 11.5 Hz, ArCH_2), 4.80 (s, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.12-4.08 (m, 1H), 3.95 (dd, 1H, *J* 12.0 Hz, *J* 3.5 Hz), 3.81 (s, 3H, OCH_3), 3.75-3.60 (m, 3H), 3.59 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.40-3.30 (dd, 1H, *J* 4.0 Hz), 1.77 (s, 3H, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 170.3 (*C*O) 131.5, 131.0, 129.0, 128.6, 126.4, 125.0, 124.3 (aromatic), 97.2 (C-1), 83.9, 82.5, 76.0, 68.4 (C-2, C-3, C-4, C-5), 66.3 (Ar*C*H_2), 62.9 (C-6) 61.5, 58.7 (2 x OCH_3), 55.1 (anomeric OCH_3) 20.2 (OCO*C*H_3); Anal. Calcd. for $C_{26}H_{30}O_7$ (454.51): C 68.71, H 6.65. Found: C 68.52, H 6.77.

4.1.7. Methyl 4-*O*-(9'-anthracenyl)methyl-6-*O*-benzoyl-2,3-di-*O*-methyl-α-D-glucopyranoside (8)

To a solution of **4** (123 mg, 0.30 mmol) in dry CH_2Cl_2 (2 mL) and dry pyridine (2 mL) was added BzCl (42 µL, 1.2 equiv) at 0 °C and the mixture was stirred for 2 h. Then the reaction mixture was diluted with CH_2Cl_2, washed twice with water, dried ($MgSO_4$) and concentrated. After column chromatography (7:3 hexane-EtOAc) compound **8** (138 mg, 89%) was isolated as a syrup: $[\alpha]_D$ +102 (c 0.12, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.43 (d, 2H, *J* 9.0 Hz, H-1', H-8'), 8.26 (s, 1H, H-10'), 7.88 (d, 2H, *J* 8.5 Hz, H-4', H-5'), 7.82 (d, 2H, *J* 9.0 Hz,) 7.55-7.45 (m, 3H) 7.40-7.30 (m, 4H, H-2', H-3', H-6', H-7'), 5.83 (d, 1H, *J* 11.5 Hz, ArCH_2), 5.76 (d, 1H, *J* 11.5 Hz, ArCH_2), 4.82 (s, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.42

(dd, 1H, *J* 11.8 Hz, *J* 2.0 Hz), 4.23 (dd, 1H, *J* 12.0 Hz, *J* 3.5 Hz), 3.85 (s, 3H, OCH_3), 3.85-3.76 (m, 4H), 3.55 (s, 3H, OCH_3), 3.36 (s, 4H, incl. OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 165.8 (*C*OPh) 132.9, 131.4, 131.0, 129.8, 129.5, 129.1, 128.7, 128.4, 126.4, 125.0, 124.2 (aromatic), 97.2 (C-1), 84.0, 82.7, 76.3, 68.6 (C-2, C-3, C-4, C-5), 66.5 (Ar*C*H_2), 63.2 (C-6) 61.5, 58.7 (2 x OCH_3), 55.2 (anomeric OCH_3); Anal. Calcd. for $C_{31}H_{32}O_7$ (516.58): C 72.08, H 6.24. Found: C 72.66, H 6.01.

4.1.8. Methyl 4-*O*-(9'-anthracenyl)methyl-6-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-α-D-glucopyranoside (9)

To a solution of **4** (127 mg, 0.31 mmol) in dry DMF (3 mL) was added NaH (20 mg, 80%, 1.5 equiv) at 0 °C and the mixture was stirred for 20 min, then PMBCl (50 μL, 1.2 equiv) was added and stirred for 4 h. Then the reaction mixture was diluted carefully with MeOH and concentrated. The residue was dissolved in CH_2Cl_2, washed twice with water, dried ($MgSO_4$) and concentrated. After column chromatography (7:3 hexane-EtOAc) compound **9** (135 mg, 82%) was isolated as a syrup: $[\alpha]_D$ +118 (c 0.09, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.41 (s, 1H, H-10'), 8.41 (d, 2H, *J* 8.5 Hz, H-1', H-8'), 7.97 (d, 2H, *J* 8.0 Hz, H-4', H-5'), 7.50-7.40 (m, 4H, H-2', H-3', H-6', H-7'), 7.18 (d, 2H, *J* 8.5 Hz), 6.81 (d, 2H, *J* 8.5 Hz), 5.77 (d, 1H, *J* 11.0 Hz, ArCH_2), 5.66 (d, 1H, *J* 11.0 Hz, H- ArCH_2), 4.86 (s, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.30 (s, 2H, *p*CH_3OPhCH_2), 3.82 (t, 1H, *J* 8.0 Hz), 3.76-3.65 (m, 9H, incl. 2 x OCH_3) 3.65-3.60 (m, 4H, incl. OCH_3), 3.39-3.35 (m, 4H, incl. OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.2, 131.6, 131.0, 130.2, 129.2, 128.0, 126.2, 124.9, 124.6, 113.8 (aromatic), 97.3 (C-1), 83.8, 82.7, 76.7, 70.1 (C-2, C-3, C-4, C-5), 73.0 (*p*CH_3OPh*C*H_2), 66.5 (anthr-*C*H_2), 66.6 (C-6), 61.5, 58.7 (2 x OCH_3), 55.2, 55.1

(*p*CH_3OPhCH_2, anomeric OCH_3); Anal. Calcd. for $C_{32}H_{36}O_7$ (532.62): C 72.16, H 6.81. Found: C 72.32, H 6.71.

4.1.9. Methyl 6-*O*-acetyl-2,3-di-*O*-methyl-α-D-glucopyranoside (10)

To a solution of **7** (42 mg, 0.09 mmol) in dry CH_2Cl_2 (1 mL) at 0 °C was added $BF_3{\cdot}OEt_2$ (2 μL) and the mixture was stirred for 20 min. When TLC (4:6 hexane-EtOAc) showed complete conversion of the starting material (R_f 0.65) into the title compound (R_f 0.22) 1 drop of Et_3N was added and the solvent was evaporated. After column chromatography (3:7 hexane-EtOAc, R_f 0.27) compound **10**[7] (18 mg, 75%) was isolated as a syrup: $[\alpha]_D$ = +85 (c 1.28, $CHCl_3$), lit.[7] +85 (CH_2Cl_2); ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 4.86 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.45 (d, 1H, $J_{6a,6b}$ 12.1 Hz, $J_{6a,5}$ 4.8 Hz, H-6a), 4.27 (d, 1H, $J_{6b,5}$ 2.1 Hz, H-6b), 3.80-3.70 (m, 1H, H-5), 3.65 (s, 3H, OCH_3), 3.55-3.35 (m, 8H, 2 x OCH_3, H-3, H-4), 3.25 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-2), 2.77 (bs, 1H, 4-OH), 2.12 (s, 3H, OCOC*H*$_3$); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 97.5 (C-1), 82.5, 81.7 (C-2, C-3), 69.9, 69.3 (C-4, C-5), 63.2 (C-6), 61.3, 58.6 (2 x OCH_3), 55.3 (anomeric OCH_3), 20.8 (OCO*C*H_3); Anal. Calcd. for $C_{11}H_{20}O_7$ (264.27): C 49.99, H 7.63. Found: C 50.38, H 7.42.

4.1.10. Methyl 6-*O*-benzoyl-2,3-di-O-methyl-α-D-glucopyranoside (11)

To a solution of **8** (47 mg, 0.09 mmol) in dry CH_2Cl_2 (1 mL) at 0 °C was added $BF_3{\cdot}OEt_2$ (2 μL) and the mixture was stirred for 20 min. TLC (4:6 hexane-EtOAc) showed complete conversion of the starting material (R_f 0.72) into the title compound (R_f 0.32). Then 1 drop of TEA was added and the solution was evaporated. After column chromatography (3:7 hexane-EtOAc, R_f 0.52) compound **11**[8,9] (22 mg, 76%) was isolated as a syrup: $[\alpha]_D$ +81

(c 0.11, $CHCl_3$), lit.[9] +75 (CH_2Cl_2); ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 8.06 (d, 2H, *J* 7.4 Hz, *o*-H aromatic), 7.57 (t, 1H, *J* 7.4 Hz, *p*-H aromatic), 7.44 (t, 2H, *J* 7.7 Hz, *m*-H aromatic), 4.87 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.67 (d, 1H, $J_{6a,6b}$ 12.1 Hz, $J_{6a,5}$ 4.9 Hz, H-6a), 4.55 (d, 1H, $J_{6b,5}$ 2.1 Hz, H-6b), 3.9-3.8 (m, 1H, H-5), 3.66 (s, 3H, OCH_3), 3.55-3.4 (m, 8H, 2 x OCH_3, H-3, H-4), 3.25 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-2), 2.96 (bs, 1H, 4-OH); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 166.8 (O*C*OPh), 133.2 (*m* aromatic), 129.7, 128.4 (*o* and *p* aromatic), 97.4 (C-1), 82.6, 81.7 (C-2, C-3), 70.1, 69.5 (C-4, C-5), 63.7 (C-6), 61.3, 58.6 (2 x OCH_3), 55.2 (anomeric OCH_3); Anal. Calcd. for $C_{16}H_{22}O_7$ (326.34): C 58.89, H 6.79. Found: C 58.63, H 6.89.

4.1.11. Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (12)

To a solution of **9** (67 mg, 0.13 mmol) in dry CH_2Cl_2 (1 mL) at 0 °C was added $BF_3{\cdot}OEt_2$ (2 μL) and the mixture was stirred for 20 min. TLC (1:1 hexane-EtOAc) showed complete conversion of the starting material (R_f 0.82) into the title compound (R_f 0.22). Then 1 drop of TEA was added and the solution was evaporated. After column chromatography (1:1 hexane-EtOAc) compound **12**[10] (24 mg, 86%) was isolated as a syrup: $[\alpha]_D$ +170 (c 0.98, $CHCl_3$), lit.[10b] +174; ^{1}H- and ^{13}C-NMR datas were in very good agreement with those reported in the literature.[10b]

4.1.12. Methyl 6-*O*-(9',10'-dihydro-9'-anthracenyl)methyl-2,3-di-*O*-methyl-α-D-glucopyranoside (13) and 1,5-anhydro-6-*O*-(9',10'-dihydro-9'-anthracenyl)methyl-2,3-di-*O*-methyl-D-glucitol (14)

To a solution of **6** (250 mg, 0.60 mmol) in dry CH_2Cl_2 (2 mL) was added Et_3SiH (484 μL, 5 equiv) at 0 °C, then $BF_3{\cdot}OEt_2$ (154 μL, 2 equiv) was also added and the mixture was

stirred overnight at rt. After TLC (7:3 hexane-acetone) indicated the formation of two products, the reaction mixture was diluted with CH_2Cl_2, washed with water, satd $NaHCO_3$, then again with water, dried ($MgSO_4$) and concentrated. After column chromatography (8:2→7:3 hexane-acetone) compound **13** (R_f 0.42, 49 mg, 20%), compound **14** (R_f 0.46, 52 mg) and unreacted **6** (34 mg, 14%) were isolated as syrups. Compound **13**: $[\alpha]_D$ +62 (c 0.14, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.36-7.19 (m, 8H, aromatic), 4.78 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.22 (t, 1H, *J* 7.3 Hz, H-9'), 4.13 (d, 1H, *J* 18.5 Hz, H-10'a), 3.88 (d, 1H, *J* 18.5 Hz, H-10'b), 3.65-3.56 (m, 6H), 3.61 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.47-3.36 (m, 2H), 3.35 (s, 3H, OCH_3), 3.15 (dd, 1H, *J* 9.1 Hz, H-1); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 137.1, 137.0, 136.1, 128.8, 128.7, 127.7, 127.7, 126.5, 126.1, 126.0 (aromatic), 97.3 (C-1), 82.6, 81.6 (C-2, C-3) 75.6 (C-11'), 71.0, 69.8 (C-4, C-5), 70.9 (C-6), 61.0, 58.5 (2 x OCH_3), 55.0 (OCH_3 anomeric), 47.5 (C-9'), 35.1 (C-10'). MALDI-TOF MS *m/z* calcd. for $C_{24}H_{30}O_6$: 414.20. Found: 437.42 $[M+Na]^+$. Anal. Calcd. for $C_{24}H_{30}O_6$ (414.49): C 69.54, H 7.30. Found: C 69.43, H 7.38.

Compound **14** containing impurities was purified and characterized after acetylation.

4.1.13. 4-*O*-acetyl-1,5-anhydro-6-*O*-(9',10'-dihydro-9'-anthracenyl)methyl-2,3-di-*O*-methyl-D-glucitol (15)

The isolated **14** (52 mg) containing impurities was acetylated with Ac_2O (0.5 mL) in pyridine (1 mL). The mixture was diluted with CH_2Cl_2, washed twice with water, dried and concentrated. After column cromatography (7:3 hexane-acetone) compound **15** (37 mg, 14% for two steps) was isolated as a syrup: $[\alpha]_D$ +16 (c 0.14, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.31-7.19 (m, 8H, aromatic), 4.66 (t, 1H, *J* 9.3 Hz), 4.18 (t, 1H, *J* 7.1 Hz, H-9'), 4.12 (d, 1H, *J* 18.0 Hz, H-10'a), 4.02 (dd, 1H, *J* 11.3 Hz, *J* 5.3 Hz), 3.87 (d, 1H, *J* 18.5

Hz, H-10'b), 3.63 (dd, 1H, *J* 8.2 Hz, *J* 6.6 Hz), 3.56-3.45 (m, 7H, incl. 2 x OCH_3), 3.40-3.20 (m, 4H), 3.17 (t, 1H, *J* 9.0 Hz), 3.04 (t, 1H, *J* 11.0 Hz), 2.0 (s, 3H, OCOCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 169.8 (*C*O), 137.2, 137.0, 136.3, 136.2, 129.0, 128.8, 128.7, 127.6, 127.6, 126.5, 126.4, 126.2, 126.1 (aromatic), 84.9, 79.3, 78.0 (C-2, C-3, C-4), 75.8 (C-11'), 71.0 (C-6), 70.7 (C-5), 67.5 (C-1), 60.52 (OCH_3), 58.8 (OCH_3), 47.6 (C-9'), 35.2 (C-10'), 20.9 (OCO*C*H_3). MALDI-TOF MS *m/z* calcd. for $C_{25}H_{30}O_6$: 426.20. Found: 449.39 $[M+Na]^+$. Anal. Calcd. for $C_{25}H_{30}O_6$: C 70.40, H 7.09. Found: C 70.29, H 7.17.

4.1.14. Methyl 2,3-*O*-(9'-anthracenyl)methylene-α-L-rhamnopyranoside (17*exo*, 17*endo*) and methyl-4-*O*-acetyl-2,3-*O*-(9'-anthracenyl)methylene-α-L-rhamnopyranoside (18*exo*, 18*endo*)

Crystalline methyl α-L-rhamnopyranoside **16**[25] (5.35 g, 30.2 mmol) was converted into the title compound according to the method described for **2**. The crude product was crystallized from EtOAc-hexane to give the **17*exo*** isomer (4.80 g, 43%). The mother liquor containing the *exo* and *endo* isomers could not be separated by crystallization therefore it was acetylated with Ac_2O (2 mL) in pyridine (3 mL). TLC (8:4 hexane-EtOAc) showed two new spots (R_f 0.41 acetylated *endo* and R_f 0.49 acetylated *exo* isomers). The mixture was diluted with CH_2Cl_2, washed twice with water, dried and concentrated. The isomers were separated with column chromatography on silica gel (8:2 hexane-EtOAc) to yield 1.276 g of **18*endo*** and 410 mg of **18*exo*** isomers. Deacetylation of compound **18*endo*** and **18*exo*** with cat. amount of NaOMe in MeOH (3 mL) followed by neutralization with Amberlite IR-120 H^+ resin, evaporated and **17*endo*** (1.03 g, 90%) and **17*exo*** (324 mg, 88%) were yielded, respectively. In summary 5.124 g **17*exo*** (46%) and 1.03 g **17*endo*** (9%) were isolated.

Compound **17*exo***: mp 201-202 °C; $[\alpha]_D$ +26 (c 0.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.50 (d, 2H, *J* 9.0 Hz, H-1', H-8'), 8.46 (s, 1H, H-10'), 7.97 (d, 2H, *J* 8.4 Hz, H-4', H-5'), 7.50-7.40 (m, 5H, H-2', H-3', H-6', H-7', H acetalic), 4.99 (s, 1H, H-1), 4.76 (t, 1H, *J* 6.5 Hz, H-3), 4.56 (d, 1H, $J_{2,3}$ 6.2 Hz, H-2), 3.85-3.75 (m, 2H, H-4, H-5), 3.44 (s, 1H, OH), 3.39 (s, 3H, OCH_3), 1.43 (d, 3H, $J_{6,5}$ 6 Hz, CH_3-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 131.2, 130.5, 130.3, 129.0, 126.2, 124.8, 124.6, 123.7 (aromatic), 100.3 (C acetalic), 98.8 (C-1), 80.3 (C-3), 76.0 (C-2), 70.4 (C-4), 65.1 (C-5), 54.7 (OCH_3), 17.4 (C-6). MALDI-TOF MS *m/z* calcd. for $C_{22}H_{22}O_5$: 366.15. Found: 367.37 $[M+H]^+$ and 389.34 $[M+Na]^+$ and 397.24 $[M+K]^+$. Anal. Calcd. for $C_{22}H_{22}O_5$: C 72.12, H 6.05. Found: C 72.01, H 6.15.

Compound **17*endo***: mp 182-184 °C; $[\alpha]_D$ -32 (c 0.13; $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.70 (d, 2H, *J* 9.5 Hz, H-1', H-8'), 8.45 (s, 1H, H-10'), 7.94 (d, 2H, *J* 8.5 Hz, H-4', H-5'), 7.50-7.40 (m, 4H, H-2', H-3', H-6', H-7'), 7.08 (s, 1H, acetalic), 5.08 (s, 1H, H-1), 4.36 (bt, 1H, *J* 6.5 Hz, *J* 7.0 Hz, H-3), 4.30 (d, 1H, $J_{2,3}$ 7.5 Hz, H-2), 3.78-3.74 (m, 1H, H-5), 3.62 (dd, 1H, $J_{4,5}$ 8.5 Hz, $J_{4,3}$ 6.0 Hz, H-4), 3.41 (s, 3H, OCH_3), 3.01 (bs, 1H, OH), 1.22 (d, 3H, $J_{6,5}$ 6.5 Hz, CH_3-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 131.4, 130.5, 129.1, 126.4, 124.8, 124.6, 124.0 (aromatic), 102.2 (C acetalic), 98.4 (C-1), 78.0, 77.4 (C-2, C-3), 73.5 (C-4), 66.3 (C-5), 55.0 (OCH_3), 18.0 (C-6). Anal. Calcd. for $C_{22}H_{22}O_5$ (366.41): C 72.12, H 6.05. Found: C 72.26, H 5.90.

Compound **18*exo*** (4-*O*-acetyl): mp 213-214 °C; $[\alpha]_D$ +90 (c 0.14; $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 8.54 (d, 2H, *J* 9.0 Hz, H-1', H-8'), 8.48 (s, 1H, H-10'), 7.98 (d, 2H, *J* 8.0 Hz, H-4', H-5'), 7.58 (s, 1H, H acetalic), 7.55-7.40 (m, 4H, H-2', H-3', H-6', H-7'), 5.35 (dd, 1H, $J_{4,5}$ 9.2 Hz, H-4), 5.06 (s, 1H, H-1), 4.84 (dd, 1H, $J_{3,4}$ 7.7 Hz, H-3), 4.62 (d, 1H, $J_{2,3}$ 5.8 Hz, H-2), 3.95-3.88 (m, 1H, H-5), 3.43 (s, 3H, OCH_3), 2.11 (s, 3H, OCOCH_3), 1.34 (d, 3H, $J_{6,5}$ 6.3 Hz, CH_3-6); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 170.2 (***C***O), 131.4, 130.7, 130.6, 129.1, 126.5, 124.8, 123.9 (aromatic), 100.8 (C acetalic), 98.8 (C-1), 77.9, 76.3, 70.2

(C-2, C-3, C-4), 63.2 (C-5), 55.1 (OCH_3), 20.9 ($CO\mathit{C}H_3$), 17.2 (C-6); Anal. Calcd. for $C_{24}H_{24}O_6$ (408.44): C 70.57, H 5.92. Found: C 70.60, H 5.99.

Compound **18*endo*** (4-*O*-acetyl): mp 194-196 °C; $[\alpha]_D$ +43 (c 0.16; $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.69 (d, 2H, *J* 9 Hz, H-1', H-8'), 8.49 (s, 1H, H-10'), 7.98 (d, 2H, *J* 8.3 Hz, H-4', H-5'), 7.55-7.40 (m, 4H, H-2', H-3', H-6', H-7'), 7.12 (s, 1H, H acetalic), 5.20 (dd, 1H, $J_{4,5}$ 9.5 Hz, H-4), 5.14 (s, 1H, H-1), 4.57 (dd, 1H, $J_{3,4}$ 5.7 Hz, H-3), 4.43 (d, 1H, $J_{2,3}$ 7.6 Hz, H-2), 3.95-3.88 (m, 1H, H-5), 3.45 (s, 3H, OCH_3), 2.02 (s, 3H, $OCOC\mathit{H}_3$), 1.34 (d, 3H, $J_{6,5}$ 6.4 Hz, $C\mathit{H}_3$-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 169.6 (*C*O), 131.4, 130.8, 130.7, 129.1, 126.4, 124.8, 124.4, 123.4 (aromatic), 101.8 (C acetalic), 98.8 (C-1), 77.4, 75.8, 74.5 (C-2, C-3, C-4), 63.9 (C-5), 55.1 (OCH_3), 20.9 ($CO\mathit{C}H_3$), 18.1 (C-6), Anal. Calcd. for $C_{24}H_{24}O_6$ (408.44): C 70.57, H 5.92. Found: C 70.46, H 6.06.

4.1.15. Methyl 3-*O*-(9'-anthracenyl)methyl-α-L-rhamnopyranoside (19) and methyl 2-*O*-(9'-anthracenyl)methyl-α-L-rhamnopyranoside (20)

Prepared from **17*exo*** (100 mg, 0.27 mmol) according to the same procedure as described for **4.** After column chromatography (7:3 hexane-acetone) compound **19** (20 mg, 20%) and compound **20** (36 mg, 32%) were isolated as syrups.

Compound **19**: $[\alpha]_D$ +22 (c 0.06, $CHCl_3$); ^{1}H NMR (500 MHz, OCH_3): δ (ppm) 8.50 (s, 1H, H-10'), 8.36 (d, 2H, *J* 8.9 Hz, H-1', H-8'), 8.03 (d, 2H, *J* 8.5 Hz, H-4', H-5'), 7.60-7.40 (m, 4H, H-2', H-3', H-6', H-7'), 5.73 (d, 1H, *J* 11.3 Hz, Ar-CH_2), 5.53 (d, 1H, *J* 11.2 Hz, Ar-CH_2), 4.76 (s, 1H, H-1), 4.29 (d, 1H, $J_{2,1}$ 1.5 Hz, H-2), 3.86 (dd, 1H, $J_{3,4}$ 9.2 Hz, *J* 3.25 Hz, H-3), 3.69-3.64 (m, 1H, H-5), 3.51 (t, 1H, $J_{4,5}$ 9.3 Hz, H-4), 3.38 (s, 3H, OCH_3), 1.29 (d, 3H, $J_{6,5}$ 6.25 Hz, $C\mathit{H}_3$-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 131.4, 130.9, 129.3, 128.9, 127.8, 126.8, 125.1, 123.6 (aromatic), 100.5 (C-1), 80.0, 71.6, 68.0, 67.5 (C-2, C-3, C-4, C-5), 63.6

(Ar*C*H_2), 54.9 (OCH_3), 17.6 (C-6); Anal. Calcd. for $C_{22}H_{24}O_5$ (368.42): C 71.72, H 6.57. Found: C 71.40, H 6.88.

Compound **20**: $[\alpha]_D$ +34 (c 0.12, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.32 (s, 1H, H-10'), 8.29 (d, 2H, *J* 9.0 Hz, H-1', H-8'), 7.88 (d, 2H, *J* 8.4 Hz, H-4', H-5'), 7.55-7.37 (m, 4H, H-2', H-3', H-6', H-7'), 5.60 (d, 1H, *J* 11.3 Hz, Ar-CH_2), 5.37 (d, 1H, *J* 11.2 Hz, Ar-CH_2), 5.00 (s, 1H, H-1), 3.81 (dd, 1H, $J_{2,3}$ 3.7 Hz, $J_{2,1}$ 1.1 Hz, H-2), 3.62 (dd, 1H, $J_{3,4}$ 9.4 Hz, H-3), 3.58-3.50 (m, 1H, H-5), 3.36 (s, 3H, OCH_3), 3.19 (t, 1H, $J_{4,5}$ 9.4 Hz, H-4), 1.24 (d, 3H, $J_{6,5}$ 6.2 Hz, CH_3-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 131.3, 130.8, 129.0, 128.7, 127.8, 126.5, 125.0, 123.9 (aromatic), 97.8 (C-1), 78.0, 73.6, 71.4, 67.7 (C-2, C-3, C-4, C-5), 64.4 (Ar*C*H_2), 54.8 (OCH_3), 17.5 (C-6); Anal. Calcd. for $C_{22}H_{24}O_5$ (368.42): C 71.72, H 6.57. Found: C 71.56, H 6.65.

Starting from **17*endo*** (150 mg, 0.41 mmol) the previous ring-opening method gave only **20** (88 mg, 58%).

4.1.16. Methyl 2,3-*O*-(9'-anthracenyl)methylene-4-*O*-benzyl-α-L-rhamnopyranoside (21exo)

To a solution of **17*exo*** (220 mg, 0.6 mmol) in dry DMF (3 mL) was added NaH (35 mg, 2 equiv.) at 0 °C and stirred for 30 min. Benzyl bromide (79 µL, 1.2 equiv.) was added to the mixture and stirred for another 30 min. After complete conversion 2-3 mL of EtOAc and 1-5 drops of water were added, the mixture was diluted with EtOAc, washed 3 times with water, dried and concentrated. After column chromatography (8:2 hexane-EtOAc, R_f 0.48) compound **21*exo*** (253 mg, 92%) was isolated as an amorf material. Crystallization of **22*exo*** from hexane-EtOAc afforded pale yellow crystals: mp 142 °C; $[\alpha]_D$ +47.2 (c 0.04, $CHCl_3$);^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 8.50 (s, 1H, aromatic), 8.46 (d, 2H, *J* 8.9 Hz, aromatic),

8.00 (d, 2H, *J* 8.2 Hz, aromatic), 7.56-7.41 (m, 4H, aromatic), 7.37 (s, 1H, H-acetalic), 7.35-7.25 (m, 5H), 5.03-4.97 (m, 2H), 4.95 (d, 1H, *J* 11.9 Hz, PhC*H*H), 4.77 (d, 1H, *J* 11.8 Hz, PhCH*H*), 4.62 (d, 1H, *J* 6.3 Hz), 3.94-3.84 (m, 1H, H-5), 3.58 (dd, 1H, *J* 9.6 Hz, *J* 6.9 Hz), 3.39 (s, 3H, OCH_3), 1.43 (d, 3H, *J* 6.2 Hz, C*H*$_3$-6); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 137.8, 131.5, 130.7, 130.6, 129.2, 128.4, 128.3, 127.7, 126.4, 125.0, 124.8, 123.9 (aromatic), 100.3 (C acetalic), 99.0 (C-1), 80.5, 76.4, 76.2, 63.6 (C-2, C-3, C-4, C-5), 72.3 (Ph*C*H$_2$), 18.1 (C-6). MALDI-TOF MS *m/z* calcd. for $C_{29}H_{28}O_5$: 456.53. Found: 456.51 $[M]^+$ 479.50 $[M+Na]^+$. Anal. Calcd. for $C_{29}H_{28}O_5$: C 76.30, H 6.18. Found: C 76.46, H 6.09.

4.1.17. Methyl 3-*O*-(9'-anthracenyl)methyl-4-*O*-benzyl-α-L-rhamnopyranoside (22)

Prepared from **21*exo*** (133 mg, 0.3 mmol) according to the same method as described for the synthesis of **4**. Column chromatography (75:25 hexane-EtOAc, R_f 0.21) of the mixture gave compound **22** (86 mg, 65%) as a syrup: $[\alpha]_D$ -32.8 (c 0.12, $CHCl_3$);^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 8.47 (s, 1H, aromatic), 8.33 (d, 2H, *J* 8.5 Hz, aromatic), 8.00 (d, 2H, *J* 8.0 Hz, aromatic), 7.50-7.10 (m, 9H, aromatic), 5.71 (d, 1H, *J* 10.8 Hz, anthr-C*H*H), 5.52 (d, 1H, *J* 10.8 Hz, anthr-CH*H*), 4.77 (d, 1H, *J* 11.2 Hz, PhC*H*H), 4.76 (s, 1H, H-1), 4.48 (d, 1H, *J* 11.2 Hz, PhCH*H*), 4.32 (s, 1H), 4.12 (dd, 1H, *J* 9.1 Hz *J* 3.2 Hz), 3.83-3.74 (m, 1H, C-5), 3.43-3.35 (m, 5H, OCH_3), 1.31 (d, 3H, *J* 6.2 Hz, C*H*$_3$-6); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 138.5, 131.4, 130.8, 129.1, 128.7, 128.2, 127.5, 126.6, 125.0, 123.8 (aromatic), 100.1 (C-1), 80.59, 79.60 (C-3, C-4), 75.2 (Ph*C*H$_2$), 68.5, 67.3 (C-2, C-5), 63.9 (anthr-*C*H$_2$), 54.81 (OCH_3), 17.9 (C-6). MALDI-TOF MS *m/z* calcd. for $C_{29}H_{30}O_5$: 458.55. Found: 481.52 $[M+Na]^+$. Anal. Calcd. for $C_{29}H_{30}O_5$: C 75.96, H 6.59. Found: C 76.05, H 6.51.

4.1.18. Methyl 2,3-*O*-(9',10'-dihydro-9'-anthracenyl)methylene-α-L-rhamnopyranoside (23)

Prepared from **17*exo*** (2.14 g, 5.84 mmol) according to the same method as described for the synthesis of **6**. After 8 h the reaction was completed according to TLC (6:4 hexane-aceton, R_f 0.55). After column chromatography compound **23*exo*** (2.06 g, 95%) was isolated as a syrup: $[\alpha]_D$ -22 (c 0.17, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.35-7.10 (m, 8H, aromatic), 5.44 (d, 1H, *J* 2.8 Hz, H-acetalic), 4.67 (s, 1H, H-1), 4.24 (d, 1H, *J* 18.3 Hz, Ar-C*H*$_2$), 4.16 (s, 1H), 3.89 (dd, 1H, *J* 7.4 Hz, *J* 5.2 Hz), 3.81 (d, 1H, *J* 18.4 Hz, Ar-C*H*$_2$), 3.50-3.40 (m, 1H, H-5), 3.25 (s, 3H, OCH_3), 3.20-3.10 (m, 2H), 2.15 (bs, 1H, OH), 1.19 (d, 3H, $J_{6,5}$ 6.2 Hz, C*H*$_3$-6); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 137.6, 137.6, 134.1, 134.0, 129.6, 129.2, 127.7, 127.6, 126.9, 126.0, 125.8 (aromatic), 107.4 (C-acetalic), 97.7 (C-1), 79.0, 75.5, 71.4, (C-2, C-3, C-4), 64.8 (C-5), 54.7 (OCH_3), 51.7 (C-9'), 35.9 (C-10'), 17.2 (C-6). MALDI-TOF MS *m/z* calcd. for $C_{22}H_{24}O_5$: 368.16. Found: 391.41 $[M+Na]^+$. Anal. Calcd. for $C_{22}H_{24}O_5$: C 71.72, H 6.57. Found: C 71.62, H 6.67.

Supplementary data

Complete crystallographic data for the structural analysis of 4,6-*O*-(9',10'-dihydro-9'-anthracenyl)methylene-2,3-di-*O*-methyl-α-D-glucopyranoside (**6**) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 736551. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).

Acknowledge

This work was supported by the Hungarian National Fund (NK48798 to A.L. and K62802 to A.B.).

References

1. Kocienski, P. J. *Protecting Groups*; Thieme: New York, **1994**.
2. Lipták, A.; Borbás, A.; Bajza, I. Protecting Group Manipulations in Carbohydrate Synthesis. In *Comprehensive Glycoscience*; Kamerling, J. P., Boons, G.-J., Lee, Y. C., Suzuki, A., Taniguchi, N., Voragen, A. G. J., Eds; Elsevier, 2007, 1; pp 203-259.
3. Ellervik U. *Tetrahedron Lett.* **2003**, *44*, 2279-2281.
4. Lipták, A.; Jodál, I.; Nánási, P. *Carbohydr. Res.* **1975**, *44*, 1-11.
5. Garegg, P. J.; Hultberg, H. *Carbohydr. Res.* **1975**, *93*, C10-C11.
6. Zervas, L. *Ber*. **1939**, *64*, 2289-2296.
7. Petitou, M.; Imberty, A.; Duchaussoy, P.; Driguez, P.-A.; Ceccato, M.-L.; Gourvenec, F.; Sizun, P.; Hérault, J.-P.; Pérez, S.; Herbert, J.-M. *Chem. Eur. J.* **2001**, *7*, 858-873.
8. Sato, K; Igarashi, T.; Yanagisawa, Y.; Kawauchi, N.; Hashimoto, H.; Yoshimura, J. *Chem. Lett.* **1988**, 1699-1702.
9. Luzzio, F. A.; Bobb, R. A. *Tetrahedron Lett.* **1997**, *38*, 1733-1736.
10. (a) Irvine, J. C.; Scott, J. P. *J. Chem. Soc*. **1913**, *109*, 575-586. (b) Robertson, G. J., Lamb, R. A. *J. Chem. Soc*. **1934**, 1321.
11. Debenham, S. D.; Toone, E. J. *Tetrahedron: Asymmetry* **2000**, *11*, 385-387.
12. (a) Lipták, A.; Neszmélyi, A.; Kováč, P; Hirsch, J. *Tetrahedron* **1981**, *37*, 2379-2382; (b) Gigg, R.; Conant, R. *J. Carb. Chem.* **1982-83**, *1*, 331-336; (c) Gigg, R.; Conant, R. *Carbohydr. Res*. **1982**, *104*, C14-C17.
13. (a) Bagett, N.; Buck, K. W.; Foster, A. B.; Webber, J. M. *J. Chem. Soc*. **1965**, 3401-3407; (b) Neszmélyi, A.; Lipták, A.; Nánási, P. *Carbohydr. Res*. **1977**, *58*, C7-C9.

14. Oscarson, S. Protective Group Strategies. In *The Organic Chemistry of Sugars*; Fügedi, P., Levy, D. E., Eds.; Taylor & Francis, 2006; pp 53-87.

15. Borbás, A.; Hajkó, J.; Kajtár-Peredy, M.; Lipták, A. *J. Carbohydr. Chem.* **1993**, *12*, 191-200.

16. Hajkó, J.; Borbás, A.; Szabovik, G.; Kajtár-Peredy, M.; Lipták, A. *J. Carbohydr. Chem*. **1997**, *16*, 1123-1144.

17. Rigaudy J, Tardieu P. *Compt. rend.* **1956**, *242*, 2730-2733.

18. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst.* **1993,** *26*, 343-350.

19. Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

20. Farrugia, L. J. *J. Appl. Cryst.* **1999,** *32*, 837-838.

21. Case, D. A.; Darden, T. A.; Cheatham III, T. E.; Simmerling, C. L.; Wang, J.; Duke, R. E.; Luo, R.; Crowley, M.; Walker, R. C.; Zhang, W.; Merz, K. M.; Wang, B.; Hayik, S.; Roitberg, A.; Seabra, G.; Kolossváry, I.; Wong, K. F.; Paesani, F.; Vanicek, J.; Wu, X.; Brozell, S. R.; Steinbrecher, T.; Gohlke, H.; Yang, L.; Tan, C.; Mongan, J.; Hornak, V.; Cui, G.; Mathews, D. H.; Seetin, M. G.; Sagui, C.; Babin, V.; Kollman, P.A. AMBER 10, University of California, San Francisco, 2008.

22. Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G.

A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.

23. (a) Flükiger P.; Lüthi H. P.; Portmann S.; Webere J. MOLEKEL 5.2 Swiss Center for Scientific Computing, Manno (Switzerland) 2000-2002; (b) Portmann S.; Lüthi H. P. *Chimia* **2000**, *54*, 766-770.
24. Humphrey, W.; Dalke, A.; Schulten, K. *J. Molec. Graphics* **1996**, *14*, 33-38.
25. Clode, D. M.; Horton, D.; Weckerle, W. *Carbohydr. Res.* **1976**, *49*, 305-314.