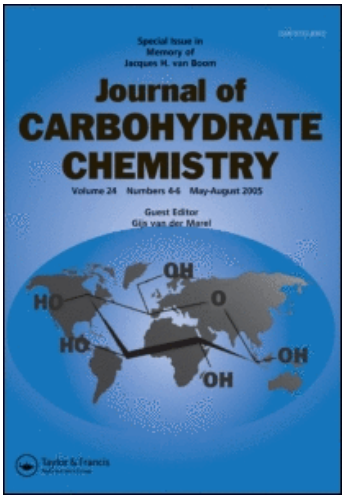

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MONO-GLYCOSYLATED 3-*N*-ALKYLCATECHOLS: DIRECT SYNTHESIS FROM GLYCOSYLACETATES, ^{1}H NMR ANALYSIS AND CONFORMATIONAL STUDIES

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ABSTRACT

The direct coupling of 3-*n*-alkyl catechols to the acetate or trichloroacetimidate derivatives of β-D- or α-D-glycosides (glucose, galactose, xylose, mannose and maltose) catalyzed by $BF_3{\cdot}OEt_2$ has been studied. β-Glycosides with an equatorial acetate group at position 2 formed exclusively β adducts with yields of 60-80%. α-Glycosides with an equatorial acetate group at position 2 formed β adducts, while β-glycosides with an axial acetate group formed α adducts when activated as trichloroacetimidates, with yields of 70-85%. This was applied to the coupling of 3-*n*-alkylcatechols of increasing chain length (up to C15) to sugar derivatives. The coupling position of glycosides on the catechol was determined either by differential NOE experiments and by the regioselective synthesis of 1-(*O*-β-D-glucopyranosyl)-3-pentadecylcatechol, a water soluble analogue of the poison ivy skin allergen. ^{1}H NMR of acetylated and deprotected compounds were investigated and the conformational preferences of the C_6 side chain determined using molecular modeling.

INTRODUCTION

One of the foremost goals in the area of toxicological testing over the next few years will be development of *in vitro* "alternative" tests to detect the pharmacological and toxic properties of xenobiotic molecules.[1] Although such tests have been developed in certain areas, an *in vitro* test for detecting the allergenic properties of molecules has yet to be

established. One obstacle to its development is that many allergens are hydrophobic and thus not soluble in cell culture media. During our studies on the mechanism of contact allergy, we have been confronted, for example, with the problem of dissolving several highly hydrophobic molecules, such as the alkylcatechols, the principal allergens[2] of poison ivy and poison oak, in water.

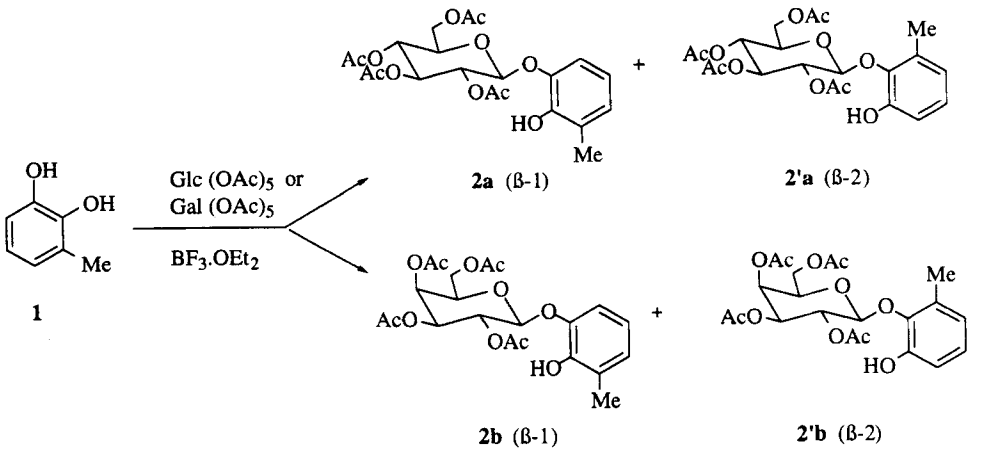
Among the different methods envisaged for increasing the water-solubility of alkylcatechols, one which seems particularly attractive is the introduction of a glycoside on the aromatic nucleus, by means of an *O*-glycosidic linkage. In addition to improved solubility, glycosides are not intrinsically cytotoxic, an important consideration for their subsequent *in vitro* use, and the relative lability of the glycosidic linkage should release the unmodified allergen on contact with cells.

In the plant kingdom, many hydrophobic substances are found in solution in the form of glycosides,[3] e.g. the tuliposides A and B, which are hydrolyzed to the tulipalines A and B, the principal allergens of the tulip bulb.[4] To our surprise, despite the existence of natural substances containing *O*-ß-D-glycosylated catechols,[5] we were unable to find any literature method for the direct glycosylation of catechols. This might be explained by the extreme lability of these molecules which are highly sensitive to oxidation and especially unstable in basic media. We had little success in applying methods generally used for phenols[6] to catechols. We therefore developed a direct coupling method[7] of ß-D-glycosyl pentaacetates to 3-alkylcatechols, using acid catalysis ($BF_3{\cdot}OEt_2$).

RESULTS AND DISCUSSION

Direct Synthesis of β-*O*-Glycosylated Alkylcatechols. The use of $BF_3{\cdot}OEt_2$ with penta-*O*-acetyl-ß-D-glycopyranosides is a simple and rapid method for the preparation of glycosylated derivatives of catechols. Our method is relatively easy and can be performed on a large scale, starting from precursors either commercially available or prepared by simple acetylation of the corresponding glycosides. In order to optimize the coupling reaction, we have studied the effects of solvent, temperature, and time of reaction on the yield of the reaction product and on the ratio of 1-*O*- and 2-*O*-(acetyl-ß-D-glycopyranosyl)-3-alkylcatechol. It should be noted that, in all cases, the two isomers are separable by column chromatography over SiO_2. This study was performed using two glycosides, penta-*O*-acetyl-ß-D-glucopyranoside and penta-*O*-acetyl-ß-D-galactopyranoside, and 3-methylcatechol **1** as a model.

The coupling reaction of the model substrate 3-methylcatechol **1** to ß-Glc$(OAc)_5$ and ß-Gal$(OAc)_5$ in the presence of $BF_3{\cdot}OEt_2$ was carried out in various solvents at 25 °C. In



Scheme 1

complexing solvents, such as ethyl ether or THF, no coupling occurred; this was also the case using DMF or acetonitrile. Optimal yields (about 70%) were obtained in methylene chloride, chloroform or toluene. Although the results in toluene were slightly better, methylene chloride seemed to us to be more convenient to use. In all cases, the yields observed and the rate of coupling in the 1-*O*-ß- position (ß-1) were higher with galactose.

We then investigated the effect of temperature on the coupling reaction in methylene chloride, in the presence of $BF_3{\cdot}OEt_2$, between the model substrate 3-methylcatechol **1** and ß-Glc$(OAc)_5$ or ß-Gal$(OAc)_5$. Despite substantially longer reaction times, useful yields were only obtained at, or above, 25 °C. It should be noted that increasing the temperature, while giving higher yields (76% yield for ß-Glc$(OAc)_5$), also resulted in a lower 1-*O*-ß-/2-*O*-ß- ratio, which, for glucose, was essentially constant (80/20) up to 25 °C but fell to only 60/40 on refluxing. For both ß-Glc$(OAc)_5$ and ß-Gal$(OAc)_5$, the optimal reaction time was 60 min, after which time the yield started to slowly decrease.

Optimal conditions have thus been established as 0.8 equiv of $BF_3{\cdot}OEt_2$ and a reaction time of 1 hour in methylene chloride at 25 °C, these were then applied to the coupling of different sugar derivatives to the model 3-methylcatechol **1**. The yields and 1-*O*-ß-/2-*O*-ß- ratio are shown in Table 1.

In all cases, ß adducts were formed, except in the case of mannose, when only the α adduct was obtained in low yield (12%). Experiments using penta-*O*-acetyl-α-D-glycoside yielded ß adducts, but again only in very low yield (5-10%). It is known that equatorial acetate groups at position 2 of glycosides can have a very important assisting role during

Table 1: Coupling reaction of compound **1** with various peracetylated sugars.

Substrate	Yield %
ß-Glc(OAc)$_5$	68 (82/18)[a]
ß-Gal(OAc)$_5$	76 (86/14)
ß-Xyl(OAc)$_4$	64 (80/20)
ß-Man(OAc)$_5$	12 (100/0)[b]
ß-Malt(OAc)$_8$	61 (82/18)

a. 1-*O*-ß- / 2-*O*-ß- ratio. b. Only the 1-*O*-α- adduct was observed.

anomeric reactions.[8] In the case of the ß derivatives of glucose, galactose, xylose and maltose, it is possible that the acetate group at position 2 supports the cleavage of the anomeric acetate to form an intermediate, which can only form a ß adduct when attacked by one of the oxygens of the catechol. This mechanism is no longer possible if the acetate at position 2 is axial (mannose), or if the sugar has an α configuration, thus explaining the low yields obtained.

The replacement of acetate groups in the anomeric position with better leaving groups, such as trichloroacetimidates, could possibly compensate for the lack of assistance of acetate at position 2. Indeed, trichloroacetimidates have been described in the coupling of benzylated sugars.[9] We therefore tried to couple catechols to trichloroacetimidate derivative of glycosides, which can be easily prepared in two steps from the pentaacetate derivatives. Under similar reaction conditions to those used for the acetates, the trichloroacetimidate derivative of α-D-glucose gave the ß conjugate with a yield of 95% and the trichloroacetimidate derivative of ß-D-mannose gave the α conjugate with a yield of 85%.

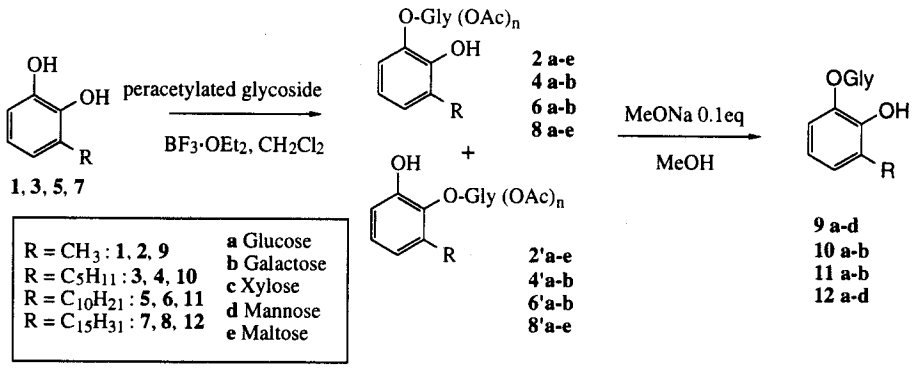
We assume, in this case, that the reaction proceeds via an oxycarbenium intermediate. In the presence of an equatorial acetate group at position 2, this oxycarbenium would form the same intermediate as described above and lead to the ß adduct, whereas with an axial non-participating acetate group, only the α adduct would be formed. With $BF_3{\cdot}OEt_2$ catalysis we succeeded in efficiently coupling a large number of acetylated or imidate derivatized sugars to catechols.

We then used the optimal conditions described above for the coupling of different 3-*n*-alkylcatechols of increasing chain length to glycoside derivatives. The yields and the 1-*O*-ß- /2-*O*-ß- ratios are shown in Table 2.

Table 2: Coupling reaction of 3-*n*-alkylcatechols **3**, **5**, **7** and peracetylated or trichloroacetimidate glycosyl derivatives using $BF_3{\cdot}OEt_2$.

Substrate	R = C_5H_{11} %	R = $C_{10}H_{21}$ %	R = $C_{15}H_{31}$ %
ß-Glc(OAc)$_5$	67 (88/12)[a]	63 (92/8)	62 (96/4)
ß-Gal(OAc)$_5$	72 (89/11)	68 (95/5)	69 (97/3)
ß-Xyl(OAc)$_4$	-	-	79 (96/4)
ß-Man(OAc)$_4$-Imidate[b]	-	-	85 (100/0)[c]
ß-Malt(OAc)$_8$	-	-	65 (99/1)

a. 1-*O*-ß- /2-*O*-ß- ratio. b. Trichloroacetimidate derivative. c. Only the 1-*O*-α adduct was observed.

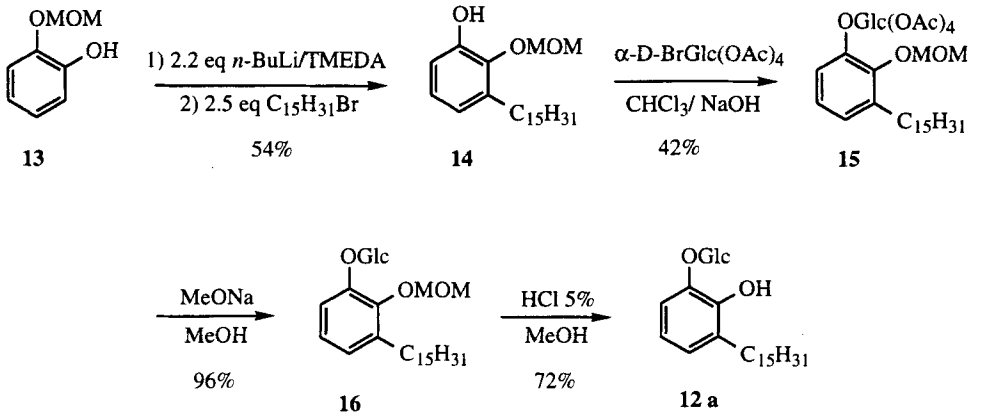


Scheme 2

Yields were not influenced by chain length, while the 1-*O*-ß- /2-*O*-ß- ratio increased with the number of carbons and bulkiness. Coupling a disaccharide such as maltose was also easy, giving a yield of 65%.

The glycosides were then quantitatively deprotected using sodium methanolate in methanol.[10] Other methods, such as NH_3 in methanol or K_2CO_3/MeOH, were also tried but without the least success. The glycosylated derivatives were finally crystallized from cold ethanol.

Regiospecific Synthesis of 1-(*O*-ß-D-Glucopyranoside)-3-pentadecyl catechol. To unambiguously confirm the linkage of the sugar at position 1-*O*-ß- and



Scheme 3

produce a reference compound, we performed a regiospecific synthesis of 1-(*O*-ß-D-glucopyranosyl)-3-pentadecylcatechol **12a** (Scheme 3), the glycosylated analogue of the major allergen of poison ivy and poison oak. The monomethoxymethyl derivative of pyrocatechol[11] **13** was treated with 2.2 equiv of *n*-BuLi in the presence of TMEDA, forming the dianion, which was then treated with 2.5 equiv of bromopentadecane to give the ortho-alkylation product **14** with a yield of 54%. A phase transfer reaction, known to lead to ß-glycosylation,[6b] made it possible to couple the acetylated bromoglucose to the phenol **14**. After deprotection of the acetate groups by sodium methanolate in methanol to give **16**, the methoxymethyl group was selectively removed without affecting the glycosidic bond by treatment with a 5% solution of HCl in methanol to give **12a**.
The spectra of this compound were identical to those of the product obtained by direct glycosylation of 3-*n*-pentadecylcatechol in the presence of $BF_3{\cdot}OEt_2$.

^{1}H NMR Analysis of Glycosyl Derivatives. As the NMR of unprotected glycosylated derivatives is often highly complex, we determined the configuration (α/ß) and the linkage position on *O*-(2',3',4',6'-tetra-*O*-acetyl-ß-D-glucopyranosyl)-3-methylcatechol **2a**. The ^{1}H NMR signals of the H-1', H-2', H-3' and H-4' protons of the 3-methylcatechol glycosides in $CDCl_3$ showed a highly complex spectrum at 200 MHz. This complexity presents a problem in analyzing the spectra, especially in observing the anomeric proton. The signal of the anomeric proton, expected to be a doublet, whose coupling constant makes it possible to determine if the configuration is α or ß,[12] showed a complex form due to the higher order spin system. This splitting pattern could be

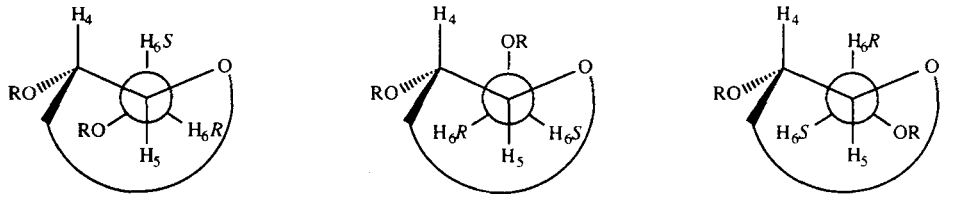
simplified either by increasing the field (400 MHz) or by changing the solvent: in CD_2Cl_2 or $C_2D_2Cl_4$, a doublet was obtained with a coupling constant of 8.0 Hz, characteristic for a ß linkage. This was confirmed using the programme geNMR FPU, version 3.4M (1992) to simulate the 200 MHz spectrum, using the coupling constants (field independent) determined from the 400 MHz spectrum. The simulated and experimental spectra were entirely superimposable, confirming the assignments of the coupling constants and the chemical shifts.

Confirmation of the linkage position: No reference to the chemical shifts of such compounds exists in the literature. The complete assignment of the proton and carbon signals of the molecule, determined mainly by ^1H-^{13}C and inversed long range ^1H-^{13}C correlations, did not allow a correlation to be made between the coupling constants or the chemical shift and the position of the glycoside on the catechol. However, a differential NOE experiment showed a NOE of 8% between the proton on the free phenol and the methyl group at position 3 of the catechol, confirming the linkage of the sugar at position 1. This was also confirmed by the regiospecific synthesis of 1-(*O*-ß-D-glucopyranosyl)-3-pentadecylcatechol.

NMR of the deprotected derivatives: Although NMR analysis of the acetylated molecules was easily solved with the glycosylated catechols, this was not the case for the deprotected molecules. We encountered problems relating to the solubility of certain amphiphilic glycosylated catechols, namely **11a-b** and **12a-d**, which have a long carbon chain and an hydrophilic region. To record the spectra it was therefore necessary to use mixtures of polar (CD_3OD) and non-polar ($CDCl_3$ or C_6D_6) solvents.

Conformational Analysis. The two protons at position 6 of the glycoside are magnetically and chemically non-equivalent and thus appear as an AB system split by the H-5 proton of the ring. When the molecule is acetylated, the signal with the large $J_{5,6}$ value is at higher chemical shift than that with the small $J_{5,6}$ value whereas the reverse is true with the deacetylated molecule. These constants reflect the relative disposition of the electron spins and thus the dihedral angle linking these two coupled protons. A clear difference would be seen between the behavior of the acetylated and deprotected derivatives. Such variations have already been reported in the literature and attributed to inversions of conformer populations.[13] We have therefore calculated the energy values for each of the three staggered positions of the H-6*S*, H-6*R* and H-5 protons for the glycosylated derivatives of 3-methylcatechol, both acetylated and free, using a molecular mechanics MM2(91) force-field programme (MacMimic 2.0).

1-O-(2',3',4,'6'-Tetra-O-acetyl-ß-D-glucopyranosyl)-3-methylcatechol **2a***:* Three staggered conformations can be envisaged (Fig 1). The **A** *tg* conformation, with strong



	A *tg*	B *gg*	C *gt*
2 a; R = Ac	0/0	68/66	32/34
9 a; R = H	25.5/26	73.5/74	1/0

Figure 1: Calculated vs experimental distribution (%) of the three staggered conformations of compounds **2a** and **9a** at 25 °C.

repulsive interactions between the acetyl groups, is clearly not favored and represents a local minimum of high energy which will develop towards the **B** *gg* conformer. This high energy barrier, estimated from the temperature of coalescence (see below), explains the lack of free rotation of the 5-6 bond. The difference of energy between the **B** *gg* conformer with an H-5,H-6*S* dihedral angle of -61.3° and the **C** *gt* conformer with an H-5,H-6*S* angle of +68.1° is estimated to 0.5 kcal (the higher energy of **C** accounts for the unfavorable gauche interaction of the acetate at position 6 with H-5). This difference of energy gives a Boltzmann distribution of 68% conformer **B** *gg* and 32% conformer **C** *gt* for the C_5-C_6 bond at 25 °C. This distribution is confirmed by the analysis of the H-5, H-6*S* and H-5, H-6*R* coupling constants. According to the Karplus equation, the large coupling constant with H-5 (5.7 Hz) corresponding to the H-6*R* proton (low-field) reflects a dihedral angle of 180 ±60° (conformer **C**) while the small constant (2.5 Hz) corresponding to the H-6*S* proton (high-field) reflects a dihedral angle of 60 ±60° (conformer **B**). The additivity of coupling constants balanced by the molar fraction of each rotamer gives an experimental distribution of 66% conformers **B** *gg* and 34% conformer **C** *gt*. This fully supports the calculated values.

1-O-ß-D-Glucopyranosyl-3-methylcatechol **9a**: The difference of energy calculated for the three conformers indicates a most stable **B** *gg* followed by the **A** *tg* conformation. The **C** *gt* conformation has a much higher energy due to gauche interactions between the hydroxyl at position 6 and the H-5 proton. The difference of energy between the **B** *gg* and the **A** *tg* conformers, calculated for H_5-H_{6S} angles of -60.9° and 180°, respectively, is estimated to 0.65 kcal. The **C** *gt* conformation, with a difference of energy of +2.58 kcal for an angle of +63.17°, compared to the **B** *gg* conformation, is the less populated. These

calculated values give a Boltzman distribution of 25.5% conformer **A** *tg*, 73.5% conformer **B** *gg* and 1% conformer **C** *gt* for the C_5-C_6 bond at 25 °C. As previously, the large coupling constant (4.8 Hz) with H-5 corresponding to the H-6*S* proton (high-field) reflects a diedral angle of 180 ± 60° (conformer **A**) and the small constant (2.0 Hz) corresponding to the H-6*R* proton (low-field) reflects a dihedral angle of 60 ±60° (conformer **B**). The additivity principle of coupling constants balanced by the molar fraction of each rotamer gives an experimental distribution of 76% conformers **B** *gg* and 26% conformer **A** *tg* . Again this fully supports the calculated values.

These energy calculations indicate that for **2a** and **9a** the predominant conformation places the acetate or the hydroxyl group *anti* to H-5 (*gg* conformation) in equilibrium with the *gt* conformation for **2a** and the *tg* conformation for **9a**. The similarity of the chemical shifts and coupling constants seen with pentyl, decyl and pentadecyl derivatives, whether acetylated or protected, demonstrates that the lengh of the alkyl chain has no effect on the percentage of rotamers calculated on the 3-methyl derivatives. This inversion of conformer populations might explain the clear spectral differences between the acetylated and deprotected derivatives.

Measurement of the temperature of coalescence of 1-O-(2',3,'4,'6'-tetra-O-acetyl-ß-D-glucopyranosyl)-3-methylcatechol **2a***:* Energy calculations indicate the presence of a rotation barrier about the C_5-C_6 bond. The temperature of coalescence gives access to the energy which must be provided to the system to transform the AB system into an X_2 system. From the temperature of coalescence, it is possible to calculate the rate constant and thus the activation energy.[14] The main difficulty is the choice of solvent, which must give good solubility and also be capable of being heated to high temperatures. To avoid using very high temperatures, experiments were performed at 200 MHz. The temperature of coalescence depends on the field in the apparatus, and increases with increased field.[14] To make the AB system more amenable to study, the H-5 proton was selectively decoupled. 1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-glucopyranosyl)-3-methylcatechol **2a** was dissolved in $C_2D_2Cl_4$, with no noticeable effect on the chemical shift or coupling constants, then gradually heated to the coalescence point (Fig 2) at 450 ± 5 K. The rate constant was then calculated by:

$$k_c = 2.22 \sqrt{\Delta\nu^2 + 6\, J_{AB}{}^2} \quad \text{thus } k_c = 83 s^{-1} \qquad (1)$$

the activation energy was then calculated using the equation (2).

$$\Delta G^{\ddagger} = 4.58\ T_c\ (10.32 + \log T_c/k_c) \text{ thus } \Delta G^{\ddagger} = 23 \text{ kcal mol}^{-1} \qquad (2)$$

This high value confirms the magnitude of the rotation barrier predicted by modeling and the equilibrium between two conformations of the compound **2a**.

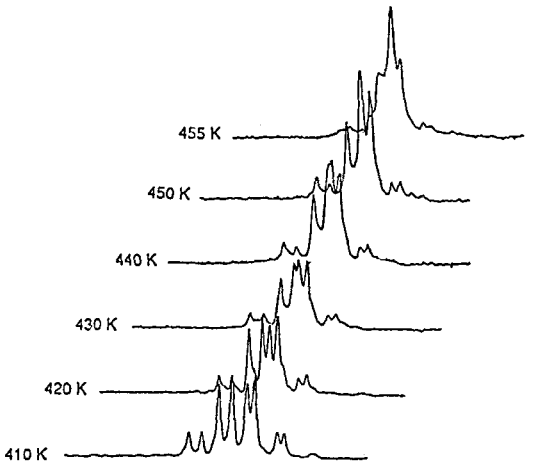


Figure 2: Measurement of the temperature of coalescence of the H-6*S*, H-6*R* of compound **2a.**

CONCLUSION

$BF_3{\cdot}OEt_2$ catalysis makes it possible to efficiently couple a large number of acetylated or imidated derivatized glycosides to 3-*n*-alkylcatechols. Yields are not influenced by chain length while the 1-*O*-ß- / 2-*O*-ß- ratio increases with the number of carbons. Conformational preferences of glucose derivatives may be determined through a combination of NMR data and molecular modeling, and explain changes observed in the ^1H NMR spectra of acetylated versus non acetylated adducts. The biological activity of these compounds and their use in *in vitro* tests[15] is under investigation.

EXPERIMENTAL

General methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400MHz spectrometer in $CDCl_3$ unless otherwise specified. Chemical shifts are reported in ppm (δ) with respect to TMS, and $CHCl_3$ was used as internal standard (δ = 7.27 ppm). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), m (multiplet). Infrared spectra were obtained on a FTIR Perkin-Elmer spectrometer; peaks are reported in reciprocal centimeters. Melting points were determined on a Buchi Tottoli 510 apparatus and are uncorrected. Dried solvents were freshly distilled before use. Tetrahydrofuran and ethyl ether were distilled from sodium benzophenone. Methylene chloride was dried over

P_2O_5 before distillation. All air- or moisture-sensitive reactions were conducted in flame-dried glassware under an atmosphere of dry argon. Chromatographic purifications were conducted on silica gel columns according to the flash chromatography technique.

Molecular Modeling. Conformational searches were performed using MacMimic 2.0 using the MM2(91) force field. Bonds between C_5 and C_6 were rotated using a 120° resolution. Structures were then energy minimized until there was a change of less than 0.001 cal between minimization cycles.

General procedure for the glycosylation of 3-*n*-alkylcatechols. 1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-glucopyranosyl)-3-methylcatechol (2a) and 2-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-glucopyranosyl)-3-methylcatechol (2'a). To 3-methylcatechol **1** (2.48 g; 20 mmol) in CH_2Cl_2 (40 mL) and 4 Å molecular sieves was added penta-*O*-acetyl-ß-D-glucopyranose (8 g, 20 mmol, 1 equiv) and $BF_3{\cdot}OEt_2$ (2.1 mL, 16 mmol, 0.8 equiv). The reaction mixture was stirred at room temperature for 1 h and hydrolysed with water (2 mL). The organic solution was washed with water, brine and dried over $MgSO_4$. Organic solvents were removed under vacuum and the crude adduct purified by column chromatography over SiO_2 (35% AcOEt, hexane) to give 5.3 g (11.3 mmol) of the catechol adduct **2a** and 1.2 g (2.7 mmol) of the catechol adduct **2'a**.

(2a). white solid, mp 128-128.5 °C. ^1H NMR ($CDCl_3$, 200 MHz) δ 6.89 (d, 1H, $J_{4,5}$ = 7.2 Hz, H-4), 6.80 (d, 1H, $J_{5,6}$ = 8.0 Hz, H-6), 6.71 (dd, t like, 1H, H-5), 6.03 (s, 1H, OH), 5.29 (m, 2H, H-2', H-3'), 5.20 (m, 1H, H-4'), 4.93 (d, 1H, $J_{1'-2'}$ = 8.0 Hz, H-1'), 4.31 (dd, 1H, $J_{6'a,6'b}$ = 12.4 Hz, $J_{6'a,5'}$= 5.4 Hz, H-6'a), 4.17 (dd, 1H, $J_{6'b,5'}$ = 2.4 Hz, H-6'b), 3.83 (ddd, 1H, $J_{5',4'}$=9.4Hz, H-5'), 2.24 (s, 3H, Ar-CH_3), 2.11, 2.10, 2.04, 2.03 (4s, 12H, OAc). ^1H NMR (CD_2Cl_2) δ 6.84 (d, 1H, $J_{4,5}$ = 7.5 Hz, H-4), 6.79 (d, 1H, $J_{5,6}$ = 8.1 Hz, H-6), 6.69 (dd, t like, 1H, H-5), 6.04 (s, 1H, OH), 5.32 (dd, 1H, H-3'), 5.23 (dd, 1H, $J_{2',3'}$ = 9.9 Hz, $J_{2',1'}$=7.8 Hz, H-2'), 5.13 (dd, 1H, $J_{3',4'}$ = 9.3Hz, $J_{5',4'}$ = 10.0 Hz, H-4'), 4.98 (d, 1H, H-1'), 4.26 (dd, 1H, $J_{6'a,5'}$= 5.7 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6'a), 4.17 (dd, 1H, $J_{6',5'}$ = 2.4 Hz, H-6'b), 3.88 (ddd, 1H, H-5'), 2.22 (s, 3H, CH_3-Ar), 2.09, 2.07, 2.03 (3s, 12H, OAc). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.1, 169.7, 169.6, 169.1, 145.1, 143.7, 126.1, 125.3, 118.9, 114.6, 101.0, 72.1, 71.8, 71.1, 68.0, 61.6, 20.3, 20.2, 20.1, 15.3. IR ($CHCl_3$) cm^{-1} 3522 (O-H), 1752 (C=O).

Anal. Calcd for $C_{21}H_{26}O_{11}$: C, 55.54; H, 5.77. Found: C, 55.58; H, 5.73.

(2'a). White solid, mp 112-113 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.92 (dd, t like, 1H, H-5), 6.79 (dd, 1H, $J_{5,6}$ = 7.6 Hz, $J_{4,6}$ = 1.0 Hz, H-6), 6.65 (dd, 1H, $J_{4,5}$ =7.4 Hz, H-4), 6.09 (s, 1H, OH), 5,29 (dd, 1H, $J_{3',4'}$ = 9.4 Hz, H-3'), 5.23 (dd, 1H, $J_{2',3'}$ = 9.8 Hz, $J_{2',1'}$ = 7.9 Hz, H-2'), 5.13 (dd, t like, 1H, H-4'), 4.78 (d, 1H, H-1'),

4.24 (dd, 1H, $J_{6'a,5'}$= 5.6 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6'a), 4.09 (dd, 1H, $J_{6'b,5'}$= 2.4 Hz, H-6'b), 3.74 (ddd, 1H, $J_{4',5'}$ = 9.9 Hz, H-5'), 2.18 (s, 3H, CH_3-Ar), 2.08, 2.06, 2.03, 2.00 (4s, 12H, OAc). ^{13}C NMR ($CDCl_3$) δ 170.4, 170.4, 169.2, 169.0, 149.5, 142.4, 131.3, 126.2, 122.1, 114.9, 102.6, 72.5, 72.1, 71.1, 68.0, 61.3, 20.5, 20.5, 20.4, 15.9. IR ($CHCl_3$) cm^{-1} 3518 (O-H), 1752 (C=O).

Anal. Calcd for $C_{21}H_{26}O_{11}$: C, 55.54; H, 5.77. Found: C, 55.41; H, 5.79

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-galactopyranosyl)-3-methylcatechol (2b). White crystals, mp 96.5-98 °C. ^1H NMR ($CDCl_3$, 200 MHz) δ 6.86 (m, 1H, H-4), 6.78 (dd, 1H, $J_{5,6}$ = 8.2 Hz, H-6), 6.71 (dd, t like, 1H, $J_{4,5}$ = 7.2 Hz, H-5), 6.04 (s, 1H, Ar-OH), 5.51-5.42 (m, 2H, H-2', H-4'), 5.11 (dd, 1H, $J_{2',3'}$ = 10.4 Hz, $J_{3',4'}$ = 3.4 Hz, H-3'), 4.90 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.24 (dd, 1H, $J_{6'a,5'}$ = 5.6 Hz, $J_{6'a,6'b}$ = 11.2 Hz, H-6'a), 4.24 (dd, 1H, $J_{6'b,5'}$= 5.6 Hz, H-6'b), 4,03 (ddd, 1H, $J_{4',5'}$ = 1.2 Hz, H-5'), 2.24 (s, 3H, Me-Ar), 2.20, 2.13, 2.07, 2.02 (4s, 12H, OAc). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 170.2, 170.1, 170.0, 145.4, 144.0, 126.4, 125.6, 119.2, 114.5 101.9, 71.2, 70.4, 69.0, 66.7, 61.2, 20.8, 20.5, 20.5, 15.6. IR ($CHCl_3$) cm^{-1} 3522 (O-H), 1748 (C=O).

Anal. Calcd for $C_{21}H_{26}O_{11}$: C, 55.54; H, 5.77. Found: C, 55.55; H, 5.77.

2-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-galactopyranosyl)-3-methylcatechol (2'b). White crystals, mp 91-92 °C. ^1H NMR ($CDCl_3$, 200 MHz) δ 6.96 (dd, t like, 1H, H-5), 6.78 (dd, 1H, $J_{5,6}$ = 8.0 Hz, H-6), 6.67 (dd, 1H, $J_{4,5}$ = 7.4 Hz, $J_{4,6}$ =1.2 Hz, H-4), 6.03 (s, 1H, Ar-OH), 5.58 (dd, 1H, $J_{2',3'}$ = 10.2 Hz, H-2'), 5.40 (dd, 1H, H-4'); 5,08 (dd, 1H, $J_{3',4'}$ = 3,4 Hz, H-3'), 4.76 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.20 (dd, 1H, $J_{6'a,5'}$ = 5.5 Hz, $J_{6'a,6'b}$ =11.5 Hz, H-6'a), 4.17 (dd, 1H, $J_{6'b,5'}$ = 5.7 Hz, H-6'b), 4.01 (ddd, 1H, $J_{4',5'}$ = 1.2 Hz, H-5'), 2.22 (s, 3H, Me-Ar), 2.20, 2.14, 2.07, 2.04 (4s, 12H, OAc). ^{13}C ($CDCl_3$, 100 MHz) δ 170.3, 170.2, 170.1, 169.9, 144.4, 142.5, 126.3, 122.0, 114.8, 103.3, 7.5, 70.6, 69.0, 66.7, 61.0, 20.8, 20.5 (2C), 15.6. IR ($CHCl_3$) cm^{-1} 3536 (O-H), 1752 (C=O).

Anal. Calcd for $C_{21}H_{26}O_{11}$: C, 55.54; H, 5.77. Found: C, 55.42; H, 5.86.

1-*O*-(2',3',4'-Tri-*O*-acetyl-ß-D-xylopyranosyl)-3-methylcatechol (2c). White crystals, mp 106 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.76 (dd, t like, 2H, H-6, H-4), 6.60 (dd, t like, 1H, $J_{5,6}$ = $J_{4,5}$ = 7.8 Hz, H-5), 6.36 (s, 1H, OH), 5.24 (dd, 1H, $J_{3',4'}$ = 8.4 Hz, H-3'), 5.19 (dd, 1H, $J_{2',3'}$ = 8.6 Hz, $J_{2',1'}$ = 6.6 Hz, H-2'), 5.00 (m, 2H, H-1', H-4'), 4.11 (dd, 1H, $J_{5'a,4'}$ = 5.0 Hz, $J_{5'a,5'b}$ = 12.0 Hz, H-5'a), 3.40 (dd, 1H, $J_{5'b,4'}$ = 9.0 Hz, H-5'b), 2.14 (s, 3H, Ar-CH_3), 2.00, 1.98, 1.96 (3s, 9H, OAc). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.6, 169.5, 169.1, 145.1, 143.3, 125.6, 125.0, 118.8, 113.9, 100.4, 70.7, 70.6, 68.2, 61.9, 20.1, 20.1, 20.1, 15.1. IR ($CHCl_3$) cm^{-1} 3534 (O-H), 1751 (C=O).

Anal. Calcd for $C_{18}H_{22}O_9$: C, 56.54; H, 5.80. Found: C, 56.47; H, 5.96.

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-α-D-mannopyranosyl)-3-methylcatechol (2d). White crystals mp 96.5-98 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.01 (dd, 1H, $J_{4,5}$ = 8.0 Hz, $J_{4,6}$ = 1.6 Hz, H-4), 6.85 (dd, 1H, $J_{5,6}$ = 7.6 Hz, H-6), 6.70 (dd, t like, 1H, H-5), 5.80 (s, 1H, Ar-OH), 5.50 (m, 3H, H-1', H-2', H-3'), 5.35 (ddd, 1H, $J_{4',3'}$ = 11.0 Hz, $J_{5',4'}$ = 9.4 Hz, $J_{4',6'a}$ = 1.2 Hz, H-4'), 4.90 (d, 1H, $J_{1',2'}$ = 7,9 Hz, H-1'), 4.30 (ddd, 1H, $J_{6'a,5'}$ = 5.0 Hz, $J_{6'a,6'b}$ = 11.3 Hz, H-6'a), 4.14 (ddd, 1H, H-5'), 4.12 (dd, 1H, $J_{6'b,5'}$ = 2.3 Hz, H-6'b), 2.25 (s, 3H, Me-Ar), 2.19, 2.07, 2.06, 2.04 (4s, 12H, OAc). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.4, 170.1, 169.9, 169.7, 144.2, 143.1, 125.5 (2C), 119.3, 113.2, 97.2, 69.4, 69.3, 68.9, 66.0, 62.1, 20.7, 20.5 (3C), 15.5. IR ($CHCl_3$) cm^{-1} 3524 (O-H), 1745 (C=O).

Anal. Calcd for $C_{21}H_{26}O_{11}$: C, 55.54; H, 5.77. Found: C, 55.71; H, 5.84.

1-*O*-[4-*O*-(2",3",4",6"-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2',3',6'-tri-*O*-acetyl-ß-D-glucopyranosyl]-3-methylcatechol (2e). White crystals mp 67-69 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.88 (dd, 1H, $J_{4,6}$ = 1.2 Hz, $J_{4,5}$ = 7.2 Hz, H-4), 6.76 (m, 2H, H-6, H-5), 5,99 (s, 1H, OH), 5.50 (d, 1H, $J_{1",2"}$ = 4 .0 Hz, H-1"), 5.36 (m, 2H, H-3', H-3"), 5.10 (dd, 1H, $J_{2',3'}$ = 9.6Hz, $J_{2',1'}$ = 7.8 Hz, H-2'), 5.04 (dd, t like, 1H, $J_{3',4'}$ = 10.0 Hz, H-4'), 4.96 (d, 1H, H-1'), 4.83 (dd, 1H, $J_{2",3"}$ = 10.6 Hz, H-2"), 4.48 (dd, 1H, $J_{6'a,5'}$ = 2.6 Hz, $J_{6'a,6'b}$ = 12.0 Hz, H-6'a), 4.28 (m, 2H, H-6'b, H-6"a), 4.07 (m, 2H, H-4', H-6"b), 3.96 (ddd, 1H, $J_{5",4"}$ = 10.0 Hz, H-5"), 3.83 (ddd, 1H, $J_{5',4'}$ = 9.9Hz, H-5'), 2.24 (s, 3H, CH_3-Ar), 2.13, 2.10, 2.09, 2.04, 2.02, 2.00 (6s, 21H, 0Ac). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.3, 119.2, 170.2, 169.9, 169.9, 169.7, 169.2, 145.5, 143.7, 126.3, 125.7, 115.2, 100.9, 95.6, 74.8, 72.7, 72.5, 72.0, 70.0, 69.2, 68.6, 67.9, 62.5, 61.5, 20.7 (2 C), 20.5 (3 C), 20.4 (2 C), 16.1. IR ($CHCl_3$) cm^{-1} 3530 (O-H), 1752 (C=O).

Anal. Calcd for $C_{33}H_{42}O_{19}$: C, 53.51; H, 5.70. Found: C, 53.41; H, 5.76.

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-glucopyranosyl)-3-*n*-pentylcatechol (4a). White crystals, mp 79.5-80 °C. ^{1}H NMR (CD_2Cl_2) δ 6.86 (m, 2H, $J_{4,6}$ = 1.6 Hz, $J_{4,5}$ = 7.7 Hz, H-6, H-4), 6.64 (dd, t like, 1H, $J_{5,6}$ = 8.0 Hz, H-5), 6.16 (s, 1H, OH), 5.36 (dd, t like, 1H, H-3'), 5.26 (dd, 1H, $J_{2',3'}$ = 9.7 Hz, $J_{2',1'}$ = 7.9 Hz, H-2'), 5.16 (dd, t like, 1H, $J_{3',4'}$ = 9.5 Hz, H-4'), 4.98 (d, 1H, H-1'), 4.31 (dd, 1H, $J_{6'a,5'}$ = 5.8 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6'a), 4.18 (dd, 1H, $J_{6'b,5'}$ = 2.4 Hz, H-6'b), 3.93 (ddd, 1H, $J_{5',4'}$ = 10.0 Hz, H-5'), 2.61 (m, 2H, CH_2-Ar), 2.09, 2.07, 2.04, 2.02 (4s, 12H, OAc), 1.60 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.33 (m, 4H, -CH_2-), 0.91 (t, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 170.7, 170.3, 170.3 169.7, 145.6, 144.5, 130.8, 125.8, 119.6, 115.0, 101.6, 72.6, 72.6, 71.9, 68.7, 62.2, 32.1, 30.1, 29.8, 22.9, 20.9, 20.7, 20.7 (2C), 14.2. IR ($CHCl_3$) cm^{-1} 3508 (O-H), 1760 (C=O).

Anal. Calcd for $C_{25}H_{34}O_{11}$: C, 58.82; H, 6.71. Found: C, 58.64; H, 6.71.

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-galactopyranosyl)-3-*n*-pentylcatechol (4b). White crystals, mp 66-68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.88 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{4,5}$ = 8.1 Hz, H-4), 6.81 (dd, 1H, $J_{5,6}$ = 7.2 Hz, H-6), 6.71 (dd, 1H, H-5), 5.97 (s, 1H, OH), 5.46 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.44 (dd, 1H, $J_{4',3'}$ = 3.4 Hz, $J_{5',4'}$ = 1.0 Hz, H-4'), 5,10 (dd, 1H, H-3'), 4.91 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.23 (dd, 1H, $J_{6'a,5'}$ = 7.4 Hz, $J_{6'a,6'b}$ = 11.4 Hz, H-6'a), 4.16 (dd, 1H, $J_{6'b,5'}$ = 5.9 Hz, H-6'b), 4.04 (ddd, 1H, H-5'), 2.60 (m, 2H, CH_2-Ar), 2.18, 2.11, 2.06, 2.01 (4s, 12H, OAc), 1.60 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.32 (m, 4H, -CH_2-), 0.87 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7 (2C), 169.6, 169.3, 144.5, 143.7, 129.7, 124.8, 118.7, 113.8, 101.0, 70.7, 70.0, 68.7, 66.5, 60.9, 31.1, 29.2, 28.8, 22.0, 20.1, 19.8, 19.8 (2C), 13.5. IR ($CHCl_3$) cm^{-1} 3520 (O-H), 1750 (C=O).

Anal. Calcd for $C_{25}H_{34}O_{11}$: C, 58.82; H, 6.71. Found C, 58.86; H, 6.77.

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-glucopyranosyl)-3-*n*-decylcatechol (6a). White crystals, mp 58.5-59.5 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 6.89 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{4,5}$ = 7.5 Hz, H-4), 6.85 (dd, 1H, $J_{5,6}$ = 8.2 Hz, H-6), 6.75 (dd, 1H, H-5), 6.11 (s, 1H, OH), 5.35 (dd, t like, 1H, H-3'), 5.26 (dd, 1H, $J_{2',3'}$ = 9.7 Hz, $J_{1',2'}$ = 7.8 Hz, H-2'), 5.16 (dd, 1H, $J_{3',4'}$ = 9.3 Hz, $J_{5',4'}$ = 10.0 Hz, H-4'), 5.03 (d, 1H, H-1'), 4.30 (dd, 1H, $J_{6'a,5'}$ = 5.7 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6'a), 4.18 (dd, 1H, $J_{6'b,5'}$ = 2.4 Hz, H-6'b), 3.91 (ddd, 1H, H-5'), 2.62 (m, 2H, CH_2-Ar), 2.10, 2.08, 2.05, 2.03 (4s, 12H, OAc), 1.58 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.30 (m, 14H, -CH_2-), 0.89 (t, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 170.7, 170.4, 170.2, 169.7, 145.6, 144.4, 130.9, 125.9, 119.7, 115.0, 101.7, 72.7, 72.6, 71.9, 62.2, 68.7, 32.3, 30.2, 30.2, 30.1 (3C), 30.0, 29.7, 23.1, 21.0, 20.8, 20.8 (2C), 14.3. IR ($CHCl_3$) cm^{-1} 3524 (O-H), 1756 (C=O).

Anal. Calcd for $C_{30}H_{44}O_{11}$: C, 62.05; H, 7.64. Found: C, 61.83; H, 7.61.

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-galactopyranosyl)-3-*n*-decylcatechol (6b). White crystals, mp 64-65 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86 (dd, 1H, $J_{4,6}$ = 1.9 Hz, $J_{4,5}$ = 8.1 Hz, H-4), 6.76 (dd, 1H, $J_{5,6}$ = 7.1 Hz, H-6), 6.71 (dd, 1H, H-5), 5.98 (s, 1H, OH), 5.45 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.43 (dd, 1H, $J_{4',3'}$ = 3.4 Hz, $J_{5',4'}$ = 1.0 Hz, H-4'), 5,09 (dd, 1H, H-3'), 4.90 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.22 (dd, 1H, $J_{6'a,5'}$ = 7.6 Hz, $J_{6'a,6'b}$ = 11.1 Hz, H-6'a), 4.15 (dd, 1H, $J_{6'b,5'}$ = 5.6 Hz, H-6'b), 4.03 (ddd, 1H, H-5'), 2.61 (m, 2H, CH_2-Ar), 2.19, 2.12, 2.06, 2.02 (4s, 12H, OAc), 1.58 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.28 (m, 14H, -CH_2-), 0.87 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 169.9, 169.9, 169.0, 144.8, 143.9, 130.1, 125.1, 118.9, 114.1, 101.4, 71.0, 70.2, 68.9, 66.7, 61.1, 31.1, 29.6, 29.4, 29.4 (3C), 29.3, 29.1, 22.4, 20.5, 20.2 (2C), 20.2, 14.3. IR ($CHCl_3$) cm^{-1} 3530 (O-H), 1752 (C=O).

Anal. Calcd for $C_{30}H_{44}O_{11}$: C, 62.05; H, 7.64. Found: C, 61.93; H, 7.79

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-glucopyranosyl)-3-*n*-pentadecylcatechol (8a). White crystals, mp 76.5-77.5 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 6.88 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{4,5}$ = 8.2 Hz, H-4), 6.80 (dd, 1H, $J_{5,6}$ = 7.6 Hz, H-6), 6.73 (dd, 1H, H-5), 5.94 (s, 1H, OH), 5.30 (dd, t like, 1H, H-3'), 5.27 (dd, 1H, $J_{2',3'}$ = 9.7 Hz, $J_{1',2'}$ = 7.6 Hz, H-2'), 5.15 (dd, 1H, $J_{3',4'}$ = 9.3 Hz, $J_{5',4'}$ = 9.9 Hz, H-4'), 4.94 (d, 1H, H-1'), 4.30 (dd, 1H, $J_{6'a,5'}$ = 5.5 Hz, $J_{6'a,6'b}$ = 12.2 Hz, H-6'a), 4.17 (dd, 1H, $J_{6'b,5'}$ = 2.3 Hz, H-6'b), 3.83 (ddd, 1H, $J_{5',4'}$ = 9.9 Hz, H-5'), 2.61 (t, 2H, CH_2-Ar), 2.11, 2.10, 2.04, 2.04 (4s, 12H, OAc), 1.58 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.25 (m, 14H, -CH_2-), 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.4, 170.0, 169.9, 169.3, 145.1, 143.1, 130.5, 125.6, 119.3, 114.6, 101.0, 72.3, 72.2, 71.4, 68.2, 61.8, 31.9, 29.8, 29.6, 29.5 (4C), 29.3, 29.1, 22.6 (2C), 20.5 (2C), 14.1. IR ($CHCl_3$) cm^{-1} 3528 (O-H), 1756 (C=O).

Anal. Calcd for $C_{35}H_{54}O_{11}$: C, 64.59; H, 8.36. Found: C, 64.71; H, 8.54.

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-ß-D-galactopyranosyl)-3-*n*-pentadecylcatechol (8b). White crystals, mp 66-67 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.87 (dd, 1H, $J_{4,6}$ = 2.1 Hz, $J_{4,5}$ = 7.2 Hz, H-4), 6.80 (dd, 1H, $J_{5,6}$ = 8.1 Hz, H-6), 6.72 (dd, 1H, H-5), 5.98 (s, 1H, OH), 5.46 (dd, 1H, $J_{2',3'}$ = 10.6 Hz, H-2'), 5.43 (dd, 1H, $J_{4',3'}$ = 3.4 Hz, $J_{5',4'}$ = 1.1 Hz, H-4'), 5.11 (dd, 1H, H-3'), 4.90 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.22 (dd, 1H, $J_{6'a,5'}$ = 7.8 Hz, $J_{6'a,6'b}$ = 11.6 Hz, H-6'a), 4.15 (dd, 1H, $J_{6'b,5'}$=5.7Hz, H-6'b), 4.04 (ddd, 1H, H-5'), 2.60 (m, 2H, CH_2-Ar), 2.21, 2.14, 2.06, 2.01 (4s, 12H, OAc), 1.58 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.25 (m, 24H, -CH_2-), 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.1 (4C), 145.1, 130.5, 125.5, 144 1. 119.3, 114.3, 101.9, 71.3, 70.5, 69.1, 66.8, 61.3, 31.9, 29.7 (12C), 29.4, 22.7, 20.8, 20.6 (2C), 14.1. IR ($CHCl_3$) cm^{-1} 3528 (O-H), 1752 (C=O).

Anal. Calcd for $C_{35}H_{54}O_{11}$: C, 64.59; H, 8.36. Found: C, 64.83; H, 8.52.

1-*O*-(2',3',4'-Tri-*O*-acetyl-ß-D-xylopyranosyl)-3-*n*-pentadecylcatechol (8c). White crystals, mp 57-58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.87 (dd, 1H, $J_{4,5}$ = 6.8 Hz, $J_{4,6}$ = 2.0 Hz, H-4), 6.76 (m, 2H, H-5, H-6), 5.92 (s, 1H, OH), 5.29 (dd, t like, 1H, $J_{3',4'}$ = 8.6 Hz, H-3'), 5.19 (dd, 1H, $J_{2',3'}$ = 8.0 Hz, $J_{1',2'}$ = 7.6 Hz, H-2'), 5.03 (ddd, 1H, H-4'), 5.01 (d, 1H, H-1'), 4.21 (dd, 1H, $J_{5'a,4'}$= 5.0 Hz, $J_{5'a,5'b}$ = 10.2 Hz, H-5'a), 3,49 (dd. 1H, $J_{5'b,4'}$ = 8.6 Hz, H-5'b), 2.61 (m, 2H, CH_2-Ar), 2.11, 2.08, 2.07 (3s, 9H, OAc), 1.58 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.25 (m, 24H, -CH_2-), 0.87 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 169.8, 169.7, 145.0, 143.5, 130.2, 125.2, 119.2, 114.1, 100.9, 70.9, 70.8, 68.5, 62.3, 29.6 (8C), 29.6, 29.5, 29.3, 22.6, 20.6, 31.9, 20.6, 29.8, 20.5, 14.0. IR ($CHCl_3$) cm^{-1} 3540 (O-H), 1756 (C=O).

Anal. Calcd for $C_{32}H_{50}O_9$: C, 66.41; H, 8.71. Found C, 66.61; H, 8.92.

1-*O*-(2',3',4',6'-Tetra-*O*-acetyl-α-D-mannopyranosyl)-3-*n*-pentadecylcatechol (8d). White crystals, mp 66-67 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.03 (dd, 1H, $J_{4,5}$ = 8.2 Hz, $J_{4,6}$ = 1.2 Hz, H-4), 6.85 (dd, 1H, $J_{5,6}$ = 7.8 Hz, H-6), 6.70 (dd, t like, 1H, H-5), 5.72 (s, 1H, Ar-OH), 5.50 (m, 3H, H-1', H-2', H-3'), 5.37 (ddd, 1H, $J_{4',3'}$ = 10.1 Hz, $J_{5',4'}$ = 9.8 Hz, $J_{4',6'a}$ = 1.1 Hz, H-4'), 4.30 (ddd, 1H, $J_{6'a,5'}$ = 5.6 Hz, $J_{6'a,6'b}$ = 12.1 Hz, H-6'a), 4.16 (ddd, 1H, H-5'), 4.12 (dd, 1H, $J_{6'b,5'}$ = 2.3 Hz, H-6'b), 2.62 (t, 2H, CH_2-Ar), 2.17, 2.07, 2.04 (3s, 12H, OAc), 1.61 (m, 2H, C<u>H</u>$_2$-CH_2-Ar), 1.25 (m, 24H, -CH_2-), 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.6, 170.1, 170.0, 169.7 145.8, 143.1, 130.4, 124.8, 119.5, 113.0, 97.3, 69.5, 69.2, 69.0, 65.9, 31.9, 29.9, 29.7, 29.6 (4C), 29.3, 29.3, 22.7 20.8, 62.1, 20.6 (3C), 14.1. IR ($CHCl_3$) cm^{-1} 3570, 3514 (O-H), 1752 (C=O).

Anal. Calcd for $C_{35}H_{54}O_{11}$: C, 64.59; H, 8.36. Found C, 64.62; H, 8.56.

1-*O*-[4-*O*-(2",3",4",6"-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2',3',6'-tri-*O*-acetyl-ß-D-glucopyranosyl]-3-*n*-pentadecylcatechol (8e). White crystals, mp 46-47 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.89 (dd, 1H, $J_{4,6}$ = 1.3 Hz, $J_{4,5}$ = 7.3 Hz, H-4), 6.80 (dd, 1H, $J_{5,6}$ = 8.1 Hz, H-6), 6.74 (dd, 1H, H-5), 5.91 (s, 1H, OH), 5.50 (d, 1H, $J_{1",2"}$ = 4.0Hz, H-1"), 5.36 (m, 2H, H-3', H-3"), 5.10 (dd, 1H, $J_{2',3'}$ = 9.3 Hz, $J_{2',1'}$ = 8.0 Hz, H-2'), 5.04 (dd, t like, 1H, $J_{3',4'}$ = 10.0 Hz, H-4'), 4.97 (d, 1H, H-1'), 4.83 (dd, 1H, $J_{2",3"}$ = 10.5 Hz, H-2"), 4.48 (dd, 1H, $J_{6'a,5'}$ = 2.6 Hz, $J_{6'a,6'b}$ = 12.1 Hz, H-6'a), 4.28 (dd, 1H, $J_{6'b,5'}$ = 5.4 Hz, H-6'b), 4.26 (dd, 1H, $J_{6'a,5'}$ = 4.2 Hz, $J_{6'a,6'b}$ = 12.7 Hz, H-6'a), 4.07 (m, 2H, H-4', H-6"b), 3.96 (ddd, 1H, $J_{5',4'}$ = 10.0 Hz, H-5"), 3.83 (ddd, 1H, $J_{5',4'}$ = 9.9 Hz, H-5'), 2.61 (t, 2H, CH_2-Ar), 2.13, 2.10, 2.08, 2.05, 2.04, 2.02, 2.00 (7s, 21H, OAc), 1.58 (m, 2H, C<u>H</u>$_2$-CH_2-Ar), 1.25 (m, 14H, -CH_2-), 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 170.3, 170.2, 170.0, 169.8, 169.7, 169.2, 145.2, 143.8, 130.5, 125.6, 119.3, 115.0, 100.9, 95.7, 74.8, 72.9, 72.5, 72.1, 70.0, 69.3, 68.6, 68.1, 62.6, 61.6, 31.8, 29.8, 29.6, 29.4, 29.2, 22.5, 20.7, 20.5, 20.4, 14.0. IR ($CHCl_3$) cm^{-1} 3522 (O-H), 1752 (C=O).

Anal. Calcd for $C_{47}H_{70}O_{19}$: C, 60.11; H, 7.51. Found: C, 60.47; H, 7.60.

General procedure for the deprotection of 1-(*O*-peracetylglycosyl)-3-alkylcatechols. To 1-(*O*-peracetylglycosyl)-3-alkylcatechol (5 mmol) in MeOH (50 mL) was added a solution of sodium methanolate (0.5 mmol) in MeOH (5 mL). The reaction was followed by TLC and methanol was removed under reduced pressure. The crude deprotected compound was crystallized from ethanol at 4 °C.

1-(*O*-ß-D-Glucopyranosyl)-3-methylcatechol (9a). White crystals, 98% yield, mp 187 °C. ^{1}H NMR (CD_3OD, 200 MHz) δ 7.00 (m, 1H, H-4), 6.81 (m, 1H, H-6), 6.64 (dd, 1H, $J_{5,6}$ = $J_{4,5}$ = 7.8Hz, H-5), 4.68 (d, 1H, $J_{1',2'}$= 7.4 Hz, H-1'), 3.88 (dd, 1H, $J_{6'a,5'}$ = 2.0 Hz, $J_{6'a,6'b}$ = 12.0 Hz, H-6'a), 3.71 (dd, 1H, $J_{6'b,5'}$ = 4.8 Hz, H-

6'b), 3.48-3.38 (m, 4H, H-2', H-3', H-4', H-5'), 2.18 (s, 3H, Me-Ar). ^{1}H NMR (C_5D_5N, 200 MHz) δ 9.93 (bs, 1H, Ar-OH), 8.65 (bs, 1H, OH), 7.43 (bs, 1H, OH), 7.40 (dd, 1H, H-6), 7.30 (bs, 1H, OH), 6.96 (d, 1H, $J_{4,5}$ = 6.6 Hz, H-4), 6.78 (dd, t like, 1H, $J_{5,6}$ = 8.0 Hz, H-5), 6.62 (bs, 1H, OH), 5.32 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1'), 4.47 (m, 2H, H-2', H-3'), 4.23 (m, 3H, H-4', H-6'a, H-6'b), 3.97 (m, 1H, H-5'), 2.41 (s, 3H, Me-Ar). ^{13}C NMR: (CD_3OD, 100 MHz) δ 146.8, 146.5, 116.7, 74.9, 126.5 (2C), 120.0, 105.0, 78.3, 71.3, 62.4, 77.7, 15.9. IR (KBr) cm^{-1} 3600-3100 (OH).

Anal. Calcd for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34. Found: C, 54.73; H, 6.48.

1-(*O*-ß-D-Galactopyranosyl)-3-methylcatechol (9b). White crystals, 96% yield, mp 175 °C. ^{1}H NMR (CD_3OD, 400 MHz) δ 7.01 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{5,6}$ = 8.0 Hz, H-6), 6.79 (dqn like, 1H, $J_{4,5}$ = 7.6 Hz, H-4), 6.64 (t like, 1H, H-5), 4.64 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 3.88 (dd, 1H, $J_{4',3'}$ = 4.0 Hz, $J_{5',4'}$ = 1.0 Hz, H-4'), 3.81 (dd, 1H, $J_{2',3'}$ = 10.0 Hz, H-2'), 3.88 (dd, 1H, $J_{6'a,5'}$ = 6.6 Hz, $J_{6'a,6'b}$ = 10.4 Hz, H-6'a), 3.85 (dd, 1H, $J_{6'b,5'}$ = 5.0 Hz, H-6'b), 3.56 (dd, 1H, H-3'), 3.61 (m, 1H, H-5'), 2.18 (s, 3H, CH_3-Ar). ^{13}C NMR (CD_3OD, 100 MHz) δ 147.0, 146.6, 126.5 (2C), 120.0, 117.0, 105.8, 77.1, 74.7, 72.5, 70.2, 62.4, 15.9. IR (KBr) cm^{-1} 3550-3100 (OH).

Anal. Calcd for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34. Found: C, 54.41; H, 6.44.

1-(*O*-ß-D-Xylopyranosyl)-3-methylcatechol (9c). White crystals, 88% yield, mp 84-86 °C. ^{1}H NMR (CD_3OD, 400 MHz) δ 6.92 (dd, 1H, $J_{5,6}$ = 7.8 Hz, $J_{4,6}$ = 0.8 Hz, H-6), 6.79 (dd, 1H, $J_{4,5}$ = 7.6 Hz, H-4). 6.64 (dd, t like, 1H, H-5), 4.61 (d, 1H, $J_{1',2'}$ = 7.4 Hz, H-1'). 3.93 (dd, 1H, $J_{5'a,4'}$ = 5.3 Hz, $J_{5'a,5'b}$ = 11.5 Hz, H-5'a), 3.57 (m, 2H, H-4', H-5'b), 3.46 (dd, 1H, $J_{2',3'}$ = 9.1 Hz, H-2'), 3.39 (dd, t like, 1H, $J_{3',4'}$ = 9.2 Hz, H-3'), 2.20 (s, 3H, CH_3). ^{13}C NMR (CD_3OD, 100 MHz) δ 145.0, 146.3, 126.6, 126.5, 119.9, 116.7, 105.5, 77.5, 74.7, 72.0, 67.0, 15.9. IR (KBr) cm^{-1} 3500-3175 (OH).

Anal. Calcd for $C_{12}H_{16}O_6$ + 1/2 H_2O: C, 54.33; H, 6.46. Found: C, 54.71; H, 6.42.

1-(*O*-α-D-Mannopyranosyl)-3-methylcatechol (9d). White crystals, 91% yield, mp 38-39 °C. ^{1}H NMR (CD_3OD, 200 MHz) δ 7.04 (dd, 1H, $J_{4,6}$ = 1.5 Hz, $J_{5,6}$ = 7.9 Hz, H-6), 6.74 (ddd, 1H, $J_{4,5}$ = 7.5 Hz, H-4), 6.63 (dd, t like, 1H, H-5), 5.38 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1'), 4.11 (dd, 1H, $J_{2',3'}$ = 3.4 Hz, H-2'), 4.01 (dd, 1H, $J_{3',4'}$ = 9.1 Hz, H-3'), 3.70 (m, 4H, H-4', H-5', H-6'a, H-6'b), 3.56 (dd, 1H, H-3'), 2.18 (s, 3H, CH_3-Ar). ^{13}C NMR (CD_3OD) δ 146.1, 145.7, 126.6, 125.6, 120.2, 115.4, 101.4, 75.3, 72.3, 71.8, 68.4, 62.6, 16.2. IR (KBr) cm^{-1} 3600-3200 (OH).

Anal. Calcd for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34. Found: C, 54.37; H, 6.54.

1-(*O*-ß-D-Glucopyranosyl)-3-*n*-pentylcatechol (10a). White crystals, 96 % yield, mp 120-121 °C. ^{1}H NMR ($CDCl_3/CD_3OD$, 400 MHz) δ 7.76 (s, 1H, OH), 6.93 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{5,6}$ = 8.0 Hz, H-6), 6.77 (dd, 1H, $J_{4,5}$ = 7.6 Hz, H-4), 6.50 (dd, t like, 1H, H-5), 4.68 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1'), 3.89 (dd, 1H, $J_{6'a,5'}$ = 2.5 Hz, $J_{6'a,6'b}$ = 12.1 Hz, H-6'a), 3.77 (dd, 1H, $J_{6'b,5'}$ = 5.0 Hz, H-6'b), 3.50 (m, 4H, H-2', H-3', H-4', H-5'), 2.60 (td, 2H, CH_2-Ar), 1.60 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.34 (m, 4H), 0.89 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3/CD_3OD$, 100 Mhz) δ 147.6 (2C), 132.3, 125.5, 117.1, 116.8, 105.3, 77.8, 77.5, 74.5, 71.0, 62.2, 32.8, 30.9, 30.5, 23.4, 14.4. IR (KBr) cm^{-1} 3600-3100 (OH).

Anal. Calcd for $C_{17}H_{26}O_7$ + 1 H_2O; C, 56.55; H, 7.76. Found: C, 56.16; H, 7.33.

1-(*O*-ß-D-Galactopyranosyl)-3-*n*-pentylcatechol (10b). White crystals, 97% yield, mp 90-92 °C. ^{1}H NMR (C_6D_6/CD_3OD, 400 MHz) δ 7.13 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{5,6}$ = 8.0 Hz, H-6), 6.83 (dd, 1H, $J_{4,5}$ = 7.6 Hz, H-4), 6.64 (dd, t like, 1H, H-5), 4.71 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.07 (dd, 1H, $J_{2',3'}$ = 9.8 Hz, H-2'), 4.01 (d, 1H, $J_{4',3'}$ = 3.2 Hz, $J_{5',4'}$ = 0.0 Hz, H-4'), 3.88 (dd. 1H, $J_{6'a,5'}$ = 5.7 Hz, $J_{6'a,6'b}$ = 12.1 Hz, H-6'a), 3.85 (dd, 1H, $J_{6'b,5'}$ = 5.7 Hz, H-6'b), 3.65 (dd, 1H, H-3'), 3.43 (dd, t like, 1H, H-5'), 2.73 (t, 2H, CH_2-Ar), 1.66 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.31 (m, 4H), 0.83 (t, 3H, CH_3). ^{13}C NMR (C_6D_6/CD_3OD, 100 MHz) δ 149.5, 146.9, 131.7, 125.3, 117.5 116.4, 105.2, 75.5, 73.8, 71.6, 69.6, 61.6, 32.3, 30.6, 30.1, 23.0, 14.1. IR (KBr) cm^{-1} 3600-3150 (OH).

Anal. Calcd for $C_{17}H_{26}O_7$ (+ 1/2 H_2O): C, 58.11; H, 7.75. Found: C, 58.12; H, 7.69.

1-(*O*-ß-D-Glucopyranosyl)-3-*n*-decylcatechol (11a). White crystals, 95 % yield, mp 102-104 °C. ^{1}H NMR (C_6D_6/CD_3OD, 200 MHz) δ 7.20 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{5,6}$ = 7.9 Hz, H-6), 6.88 (dd, 1H, $J_{4,5}$ = 7.6 Hz, H-4), 6.74 (dd, t like, 1H, H-5), 4.78 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1'), 3.90 (d, 2H, $J_{6'a,5'}$ = $J_{6'b,5'}$ = 3.7 Hz, H-6'a, H-6'b), 3.70 (m, 3H, H-2', H-3', H-4'), 3.30 (m, 1H, H-5'), 2.80 (td, 2H, CH_2-Ar), 1.70 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.22 (m, 14H, -CH_2-), 0.86 (m, 3H, CH_3). ^{13}C NMR (C_6D_6, 100 MHz, 340K) δ 146.87 (C1), 145.8, 131.9, 125.9, 119.7, 116.6, 104.2, 77.0, 76.6, 74.3, 70.3, 61.7, 32.3, 30.45, 30.2, 30.2, 30.1 (3 C), 29.8, 23.0, 14.2. IR (KBr) cm^{-1} 3500-3100 (OH).

Anal. Calcd for $C_{22}H_{36}O_7$ (+ 1/2 H_2O): C, 62.68; H, 8.85. Found: C, 62.70; H, 8.78.

1-(*O*-ß-D-Galactopyranosyl)-3-*n*-decylcatechol (11b). White crystals, 98% yield, mp 107-108 °C. ^{1}H NMR (C_6D_6/CD_3OD, 400 MHz) δ 7.13 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{5,6}$ = 8.0 Hz, H-6), 6.83 (dd, 1H, $J_{4,5}$ = 7.6 Hz, H-4), 6.64 (dd, t like, 1H, H-5), 4.68 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.03 (dd, 1H, $J_{2',3'}$ = 9.8Hz, H-2'), 3.97 (d, 1H,

$J_{4',3'}$ = 3.4 Hz, $J_{5',4'}$ = 0.0 Hz, H-4'), 3.86 (dd, 1H, $J_{6'a,5'}$ = 6.1 Hz, $J_{6'a,6'b}$ = 11.4 Hz, H-6'a), 3.83 (dd, 1H, $J_{6'b,5'}$ = 5.8 Hz, H-6'b), 3.60 (dd, 1H, H-3'), 3.42 (dd, t like, 1H, H-5'), 2.73 (t, 2H, CH_2-Ar), 1.67 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.23 (m, 14H), 0.83 (t, 3H, CH_3). ^{13}C NMR (C_6D_6/CD_3OD, 100 MHz) δ 149.0, 146.8, 131.6, 125.4, 117.8, 116.6, 105.3, 75.7, 73.9, 71.6, 69.5, 61.7, 32.3, 30.7, 30.4, 30.2, 30.1 (2C), 30.1, 29.8, 23.1, 14.1. IR (KBr) cm^{-1} 3500-3150 (OH).

Anal. Calcd for $C_{22}H_{36}O_7$: C, 64.05; H, 8.80. Found: C, 64.02; H, 8.95.

1-(*O*-ß-D-Glucopyranosyl)-3-*n*-pentadecylcatechol (12a). White crystals, 98% yield, mp 109-111 °C. ^1H NMR ($CDCl_3$ + CD_3OD, 400 MHz) δ 7.32 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{5,6}$ = 8.0 Hz, H-6), 6.99 (dd, 1H, $J_{4,5}$ = 8.0 Hz, H-4), 6.85 (t, 1H, H-5), 4.86 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.01 (dd, 1H, $J_{6'a,5'}$ = 2.7 Hz, $J_{6'a,6'b}$ = 12.1 Hz, H-6'a), 3.97 (dd, 1H, $J_{6'b,5'}$ = 4.4 Hz, H-6'b), 3.85 (dd, 1H, $J_{2',3'}$ = 9.3 Hz, H-2'), 3.80 (dd, t like, 1H, H-3'), 3.71 (dd, t like, 1H, $J_{4',3'}$ = 9.1 Hz, $J_{5',4'}$ = 9.1 Hz, H-4'), 3.43 (dd, t like, 1H, H-5'), 2.91 (t, 2H, CH_2-Ar), 1.80 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.48 (m, 2H, $C\underline{H}_2$-$(CH_2)_2$-Ar), 1.31 (m, 22H, -CH_2-), 0.97 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$ + CD_3OD, 100 MHz) δ 144. 7 (2C), 130.1, 124.6, 118.6, 115.3, 103.4, 76.2, 76.0, 73.0, 69.5, 61.0, 31.5, 29.5, 29.3, 29.2 (8C), 29.1, 28.9, 22.2, 13.4. IR (KBr) cm^{-1} 3550-3100 (OH).

Anal. Calcd for $C_{27}H_{46}O_7$: C, 67.19; H: 9.61. Found: C, 66.72; H: 9.59.

1-(*O*-ß-D-Galactopyranosyl)-3-*n*-pentadecylcatechol (12b). White crystals, 96% yield, mp 165 °C decomp. ^1H NMR (DMSO-d_6, 400 MHz, 320K) δ 9.00 (s, 1H, OH), 6.80 (dd, 1H, $J_{4,6}$ = 1.8 Hz, $J_{5,6}$ = 7.7 Hz, H-6), 6.65 (dd, 1H, $J_{4,5}$ = 7.4 Hz, H-4), 6.33 (t, 1H, H-5), 4.43 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1'), 3.68 (d, 1H, $J_{4',3'}$ = 3.2 Hz, $J_{5',4'}$ = 0.0 Hz, H-4'), 3.58 (dd, 1H, $J_{2',3'}$ = 9.5 Hz, H-2'), 4.25 (dd, 1H, $J_{6'a,5'}$ = 6.1 Hz, $J_{6'a,6'b}$ = 10.8 Hz, H-6'a), 3.83 (dd, 1H, $J_{6'b,5'}$ = 6.2 Hz, H-6'b), 3.44 (dd, t like, 1H, H-5'), 3.36 (dd, 1H, H-3') 2.48 (m, 2H, CH_2-Ar), 1.80 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.48 (m, 2H, $C\underline{H}_2$-$(CH_2)_2$-Ar), 1.23 (m, 22H, -CH_2-), 0.84 (t, 3H, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz, 320K) δ 146.3 (2C), 130.1, 123.8, 116.4, 114.0, 105.1, 75.6, 73.2, 70.7, 68.0, 60.4, 31.2, 29.9, 29.5, 29.4, 29.1, 29.0 (7C), 28.6, 22.0, 18.8. IR (KBr) cm^{-1} 3600-3100 (OH).

Anal. Calcd for $C_{27}H_{46}O_7 + H_2O$: C, 64.77; H, 9.66. Found: C, 64.89; H, 9.46

1-(*O*-ß-D-Xylopyranosyl)-3-*n*-pentadecylcatechol (12c). White crystals, 87% yield, mp 79-81 °C. ^1H NMR (C_6D_6/CD_3OD, 400 MHz) δ 7.19 (dd, 1H, $J_{5,6}$ = 8.0 Hz, $J_{4,6}$ = 1.5 Hz, H-6), 6.94 (dd, 1H, $J_{4,5}$ = 7.7 Hz, H-4). 6.69 (dd, t like, 1H, H-5), 4.72 (d, 1H, $J_{1',2'}$ = 7.4 Hz, H-1'). 5.29 (dd, t like, 1H, $J_{3',4'}$ = 8.6 Hz, H-3'), 5.19 (dd, 1H, $J_{2',3'}$ = 8.0 Hz, $J_{1',2'}$ = 7.6 Hz, H-2'), 5.03 (ddd, 1H, H-4'), 5.01 (d, 1H, H-1'), 4.21 (dd, 1H, $J_{4',5,a}$ = 5.0 Hz, $J_{5'a,5'b}$ = 10.2 Hz, H-5'a), 3,49 (dd, 1H, $J_{4',5'b}$ = 8.6

Hz, H-5'b), 2.61 (m, 2H, CH_2-Ar), 1.78 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.29 (m, 24H, -CH_2-), 0.89 (t, 3H, CH_3). ^{13}C NMR (C_6D_6/CD_3OD, 100 MHz) δ 149.3, 146.6, 131.7, 125.6, 117.7, 117.2, 105.3, 76.8, 73.8, 70.1, 66.4, 32.4, 30.8, 30.5, 30.2 (8C), 30.1, 29.8, 23.1, 14.3. IR (KBr) cm^{-1} 3400-3130 (OH).

Anal. Calcd for $C_{26}H_{41}O_6 + H_2O$: C, 66.78; H, 9.27. Found: C, 66.79; H, 9.66.

2-Methoxymethylene-3-*n*-pentadecylcatechol (14). To phenol **13** (2.0 g, 14.5 mmol) in ether (100 mL) were added at 0 °C TMEDA (5.5 mL, 31 mmol, 2.2 equiv) and *n*-BuLi (22 mL, 31 mmol, 2.2 equiv). The reaction mixture was stirred at room temperature for 1 h and bromopentadecane (11.7g, 40 mmol, 2.7 equiv) was added at 0 °C. After 24 h at room temperature the reaction was heated under reflux for an additional 24 h period. The reaction mixture was carefully hydrolyzed with a saturated solution of NH_4Cl (20 mL) and the organic layer washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (AcOEt 15%, hexane) to give 2.8 g (7.8 mmol, 54% yield) of **14** as a white solid, mp 39-40.5 °C. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.13 (s, 1H, OH), 6.65-6.53 (m, 3H), 4.87 (s, 2H, O-CH_2-O), 3.51 (s, 3H, OMe), 2.44 (t, 2H, CH_2-Ar), 1.42 (t, 2H, $C\underline{H}_2$-CH_2-Ar), 1.13 (m, 24H, -CH_2-), 0.75 (t, 3H, CH_2-$C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.9, 144.4, 136.2, 125.2, 121.0, 114.7, 100.0, 57.1, 31.9, 30.6, 30.2, 29.7, 29.5, 29.4, 22.7, 14.1. IR ($CHCl_3$) cm^{-1} 3367 (OH).

Anal. Calcd for $C_{23}H_{40}O_3$: C, 75.77; H, 11.05. Found C, 75.61; H, 11.05.

1-*O*-(2,3,4,6-Tetra-*O*-acetyl-ß-D-glucopyranosyl)-2-methoxymethyleneoxy-3-*n*-pentadecylcatechol (15). To phenol **14** (584 mg, 1.6 mmol) in $CHCl_3$ (10 mL) was added a solution of sodium hydroxide (8 mL, 1.25N, 10 mmol), acetobromoglucose (1.36 g, 3.3 mmol, 2 equiv) and tetrabutylammonium chloride (450 mg, 1.65 mmol, 1 equiv). The mixture was vigourously stirred at room temperature for 72 h and extracted with $CHCl_3$ (3 x 10 mL). The organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude adduct which was purified on column chromotography (AcOEt 25%, hexane) to give 467 mg (0.67 mmol, 42% yield) of **15** as white crystals, mp 49 °C. ^1H NMR (CD_2Cl_2, 200 MHz) δ 6.93 (m, 3H), 5.29 (m, 2H, H-2', H-3'), 5.12 (m, 1H, $J_{4',5'}$ = 10.0 Hz, $J_{4',3'}$ = 9.5 Hz, H-4'), 5.08 (m, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.98 (d, 1H, $J_{a,b}$ = 6.0 Hz, O-CH_2-O), 4.95 (d, 1H, O-CH_2-O), 4.26 (dd, 1H, $J_{6'a,5'}$ = 5.6 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6'), 4.15 (dd, 1H, $J_{6'b,5'}$ = 2.5 Hz, H-6'b), 3.87 (ddd, 1H, H-5'), 3.51 (s, 3H, OMe), 2.65 (m, 2H, Ar-CH_2), 2.05, 2.04, 2.02 , 2.00 (4s, 12H, OAc), 1.55 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.27 (m, 24 H, -CH_2-), 0.87 (t, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 170.5, 170.1, 169.3, 169.3, 149.5, 145.5, 137.8, 124.6, 123.8, 114.7, 99.7,

99.4, 72.7, 72.0, 71.1, 68.3, 61.9, 33.1, 31.7, 30.5, 30.2 29.6, 29.2, 20.6 (2C), 20.5 (2C), 14.0. IR ($CHCl_3$) cm^{-1} 1752 (C=O).

Anal. Calcd for $C_{37}H_{58}O_{12}$: C, 63.96; H, 8.41. Found C, 64.37; H, 8.63.

1-(*O*-ß-D-Glucopyranosyl)-2-methoxymethyleneoxy-3-*n*-pentadecylcatechol (16). Same procedure as for **9a**. White crystals, 96% yield, mp 100 °C. ^1H NMR ($CDCl_3/CD_3OD$, 400 MHz) δ 6.73 (m, 2H), 6.62 (dd, 1H), 4.91 (d, 1H, $J_{a,b}$ = 5.8 Hz, O-CH_2-O), 4.80 (d, 1H, O-CH_2-O), 4.62 (d, 1H, $J_{1',2'}$ = 7.0 Hz, H-1'), 3.59 (dd, 1H, $J_{6'a,5'}$ = 2.8 Hz, $J_{6'a,6'b}$ = 12.0 Hz, H-6'a), 3.49 (dd, 1H, $J_{6'b,5'}$ = 4.2 Hz, H-6'b), 3.35 (s, 3H, OMe), 3.25 (m, 4H, H-2', H-3', H-4', H-5'), 2.40 (t, 2H, CH_2-Ar), 1.80 (m, 2H, $C\underline{H}_2$-CH_2-Ar), 1.48 (m, 2H, $C\underline{H}_2$-$(CH_2)_2$-Ar), 1.31 (m, 22H, -CH_2-), 0.97 (t, 3H, CH_3). ^{13}C NMR (C_6D_6/CD_3OD, 100 MHz) δ 150.6, 145.5, 137.5, 124.6, 124.0, 114.9, 102.4, 99.8, 78.0, 77.6, 74.7, 71.4, 62.3, 60.1, 32.3, 31.1, 30.7, 30.5, 30.2 (6C), 30.1, 30.1, 29.8, 23.1, 14.2. IR ($CHCl_3$) cm^{-1} 3500-3300 (OH).

Anal. Calcd for $C_{29}H_{50}O_8$ (+ 2 H_2O): C, 61.90; H, 9.62. Found: C, 61.93, H, 9.21.

1-(*O*-ß-D-Glucopyranosyl)-3-*n*-pentadecylcatechol (12a). To glycoside **16** (70 mg, 0.13 mmol) in methanol (5.6 mL) was added HCl 5% (60 mL). The reaction mixture was stirred at 60 °C for 40 min, cooled down to 0 °C and neutralized with a saturated solution of $NaHCO_3$ (50 mL). Solvents were removed under reduced pressure, the residue dried under vacuum and crystallized from ethanol to give **12a** (44 mg, 0.09 mmol, 72% yield) as white crystals.

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