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1 **Synthesis and characterization of a small library of bisglucosides: influence of the**
2 **nature of the diol/diphenol used in O-glucosylation.**

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6

7 **Abstract:** In this paper, the synthesis of different bisglucosides is investigated through the
8 reaction of two acetylated glucose units with a diol (or diphenol) in order to develop a
9 versatile molecular platform for the future development of bio-based polymers. A panel of
10 five diols and one diphenol is initially used in order to examine the influence of their
11 chemical skeleton on the reaction yield and both nature and proportion of formed species.
12 Reaction products are identified using ^1H and ^{13}C NMR spectroscopies completed by
13 MALDI-TOF MS technique. The nucleophilicity of these dihydroxy compounds is identified
14 as being the main factor that governs the reaction characteristics. In particular, the best
15 selectivity is obtained with the use of hydroquinone. Inversely, by-products (oligomers,
16 deacetylated compounds) are observed with the diols defined by higher nucleophilicity
17 despite the choice of stereoselective pathway using acyl protecting groups.

18 **Keywords:** bisglucoside; diol; hydroquinone; biobased monomer; molecular spacer;
19 O-glycosylation; analytical techniques.

20

21 **1. Introduction**

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22 Over the last few decades, the development of biobased polymers arises a great interest
23 in both scientific and industrial communities [1, 2]. Different elements support researches in
24 this area such the reduced dependence on petroleum and the implementation of new
25 environmental and safety regulations. Then, the valorization of biobased (macro)molecules
26 appears as a possible solution for reducing the use of toxic precursor compounds [3]. A more
27 recent trend consists in creating innovative molecular building blocks to achieve the creation
28 of custom-made polymers by controlling the chemical structure in order to obtain precise
29 properties for specific use [4]. Among the different existing molecules, carbohydrates are
30 worth of interest because they combine a high degree of functionality with a non-toxic cyclic
31 structure [5]. The former characteristic offers a large range of possible reactions while the
32 latter insures higher physical properties than that observed with aliphatic sequences. As proof
33 of this, carbohydrate derivatives are already present into polymer formulations when high
34 glass transition temperature T_g is required. For instance, they are used to produce thermoset
35 polymeric formulations such as alkyd resins [6], polyurethanes [7] or epoxy resins [8].
36 Concerning this latter family, Pan et al. worked with commercial sucrose polyesters of fatty
37 acids (SPEFAs) named as Sefose® by Procter & Gamble (P&G) Chemicals [9]. Using a
38 classical peracetic pathway, these researchers produced epoxidized sucrose polyesters of
39 fatty acids (ESPEFAs) and reacted them with cyclic anhydrides [10]. The resulting materials
40 presented higher ultimate performances compared to that of materials derived from native
41 Epoxidized Soybean Oil (ESO) cured with same hardeners. This hierarchy was justified by
42 the presence of cyclic sucrose in ESPEFAs whereas ESO is made with aliphatic molecular

43 segments. Unfortunately, this study was limited to the only family of unsaturated SPEFAs
44 previously developed by P&G.

45 The boundaries of this concept are likely to be pushed back by the creation of other
46 cyclic molecular cores to achieve the emergence of new performances. Such approach could
47 be carried out through the prior synthesis of a little library of bisglucosides. We studied more
48 particularly the production of this class of molecules through the reaction of a dihydroxy
49 compound with two glucose units. This O-glycosylation process was investigated with
50 various aliphatic diols and a diphenol. Indeed, O-glycosylation is not easy to be performed in
51 organic chemistry because it is often accompanied by parasitic and complex mechanisms
52 [11]. For this reason, different strategies are described in literature involving the
53 pre-activation of the aglycone, Huisgen cycloaddition between alkynes and azides [12-15],
54 olefin cross-metathesis [16], and Sonogashira coupling [17]. The use of protective
55 participating groups (OAc) or non-participating groups (OBn) seems to be essential for
56 conducting selective O-glycosylation. For instance, β -D-glucose pentaacetate β -Glc(OAc)₅
57 can be easily synthesized through a simple acetylation. It is also suitable with a one-step
58 glycosylation that can be catalyzed by a Lewis-acid [18]. In literature, some works describe
59 the bisglycosylation reaction between glycosyl peracetates with various diols in
60 dichloromethane (CH₂Cl₂) as solvent and catalyzed by BF₃·OEt₂ [19, 20]. In fact, this
61 catalyst is frequently used for phenol O-glycosylation [21]. It efficiently promotes the
62 conversion of β -Glc(OAc)₅ into the corresponding aryl-O-glucosides with high yield and

63 β -stereoselectivity [22]. Other Lewis acids are also employed but they induce the formation
64 of complex mixtures [20] and even lead to lower reaction yield [23].

65 The nature of the solvent is another factor that has to be considered for performing
66 O-glycosylation reaction. For instance, Mabic *et al.* described the coupling reaction between
67 3-methylcatechol and β -Glc(OAc)₅ in the presence of BF₃·OEt₂ as an activator [24]. No
68 coupling is observed when participating solvents are used such as diethyl ether, acetonitrile
69 or tetrahydrofuran (THF). This result is probably the reason why CH₂Cl₂, a non-complexing
70 solvent, is preferred. The configuration of the anomeric center is also dependent on the
71 temperature used for the glucosylation. Temperatures lower than 30 °C favors β -glucoside
72 formation while both anomeric compounds coexist at higher temperatures [25].

73 Despite these numerous researches, it is important to note that the collection of bivalent
74 glycosides synthesized up to now remains rather limited. Most of the structures are derived
75 from linear diols such as long-chain alkyl “HO(CH₂)₁₂OH” [26], alkynes with
76 2-butyne-1,4-diol [27] and polyethoxy with HO(CH₂CH₂O)₅H [20]. Another researchers
77 investigated the use of phenols [28]. Reported reaction yields are comprised between 11 and
78 81%. Within this context, we decided to conduct a more global study by building with an
79 only pathway, a library of BisGlucosideX octaacetate with different spacers between two
80 glucose units. Each of them was represented as BGX(OAc)₈ in which X would correspond to
81 the diol or diphenol spacer (Figure 1). The synthesis results were carefully discussed and
82 interpreted on the basis of reliable molecular mechanisms.

83 2. Results and Discussion

84 2.1. Conditions retained for the synthesis of BisGlucosideX octaacetate BGX(OAc)₈

85 Considering the data already published in literature and summarized hereabove, the
86 synthesis of the BGX(OAc)₈ was conducted by reaction of β -Glc(OAc)₅ **1a** with a diol or a
87 diphenol (HO-X-OH) **2a-f** in anhydrous CH₂Cl₂ as solvent, catalyzed by BF₃·OEt₂ and at
88 room temperature (Figure 1). A molar ratio of the sugar donor/diol (or diphenol) acceptor
89 was set to 1:0.5 in order to promote the formation of BGX(OAc)₈.

90 *Insert Figure 1*

91 We chose to use different diols and one diphenol to investigate the effects and limitations
92 of the selected glycosylation conditions (Figure 2). The diols **2a-e** are based upon different
93 aliphatic skeletons and are likely to present discrepancies in terms of molecular mobility.
94 Indeed, compared to propane-1,3-diol (1,3-PD **2a**), diethylene glycol (DEG **2c**) is
95 characterized by a longer linear sequence including a flexible ether hinge. 2-butyne-1,4-diol
96 ByD (**2d**) and *cis*-2-butene-1,4-diol (BnD **2b**) have rigid unsaturations at the center of their
97 molecular structure. A cycloaliphatic spacer is represented by 1,4-cyclohexanediol (CHD **2e**)
98 while hydroquinone (HQ **2f**) is the only diphenol employed in this work section.

99 *Insert Figure 2*

100

101 2.2. Synthesis of BisGlucosidePropyl octaacetate BGP(OAc)₈

102 First experiments consisted in investigating the reaction kinetic of β -Glc(OAc)₅ **1a** with
103 commercial 1,3-PD **2a** in order to define the time necessary for obtaining the optimal
104 conversion rate of the chemicals used.

105 2.2.1. Kinetic study

106 The composition of the reaction mixture was followed over time by thin layer
107 chromatography (TLC) (supporting information Figure S1). These analyses show that the
108 glycosylation of the 1,3-PD leads to a mixture of compounds but can be roughly divided into
109 four fractions. To investigate their chemical composition, samples of the crude reaction
110 mixture were taken at different times t and analyzed by ^1H NMR spectroscopy. As depicted
111 in Figure 3, ^1H NMR spectroscopy can distinguish the starting ester leaving group of
112 $\beta\text{-Glc(OAc)}_5$ **1a** with the characteristic H_1 proton at 5.7 ppm. The formation of the final
113 product mixture is detected by the presence of different doublets between 4.4 and 4.7 ppm
114 that correspond to β -glucosidic links [29]. For information and in order to remove any form
115 of ambiguity, the peaks at 4.7 ppm are characteristic of β -glucosidic bonds of
116 homopolymerized glucose present in the F4 fraction.

117 *Insert Figure 3*

118 The conversion degree τ of the glycosylation can be evaluated by integration of these
119 different peaks. Indeed, it corresponds to the molar percentage of glucosides that can be
120 calculated at different times using the following formula (1):

$$121 \quad \tau = \frac{I_{\text{H1}\beta\text{G}} + I_{\text{H1}\alpha\text{G}}}{(I_{\text{H1}\beta\text{OAc}} + I_{\text{H1}\alpha\text{OAc}} + I_{\text{H1}\beta\text{G}} + I_{\text{H1}\alpha\text{G}})} * 100 \quad (1)$$

122 $I_{\text{H1}\alpha\text{OAc}}$ and $I_{\text{H1}\beta\text{OAc}}$ are the intensities of the ^1H NMR bands characteristic of the acetylated
123 glucoside under the α and β anomeric forms, respectively. $I_{\text{H1}\alpha\text{G}}$ and $I_{\text{H1}\beta\text{G}}$ define the
124 intensities of bands specific of the glucoside under the α and β anomeric forms,
125 respectively.

126 The exploitation of ^1H NMR spectra reveals a fast conversion of about 56% after 2 hours
127 and 77% after 8 hours. After, the evolution of τ is much reduced between 8 hours and 23
128 hours (+1%). In the same period, the anomerization from $\beta\text{-Glc(OAc)}_5$ **1a** to $\alpha\text{-Glc(OAc)}_5$ **1b**
129 is more noticeable and the α/β ratio reaches a final value of 3:1. In this same time interval, the
130 anomerization of residual Glc(OAc)_5 observed conjointly with the constancy of the
131 conversion rate ($\approx 78\%$) indicates that the consumption of 1,3-PD **2a** is total. As a result, an
132 average reaction time of 8 hours was considered as sufficient for achieving 1,3-PD
133 glucosylation.

134 The conversion of $\beta\text{-Glc(OAc)}_5$ **1a** and the composition of glucoside can be also
135 determined by the exploitation of the intensities of signals characteristic of anomeric carbons
136 in the ^{13}C NMR spectrum (supporting information Figure S2) as described by Sokolov [22].
137 In particular, ^{13}C NMR confirms in a clearer form the absence of α -glycosidic bonds that are
138 likely to have a chemical shift around 95 ppm in general [29].

139

140 2.2.2.Characterization and identification of the different species of the mixture

141 The different products resulting from 1,3-PD glucosylation were separated by silica gel
142 chromatography into four different fractions, F1, F2, F3 and F4. Then, the chemical
143 structures of the compounds present in each fraction were carefully investigated using
144 different analytical techniques.

145

146

147 • NMR analyses

148 The NMR coupling made it possible the identification of desired BisGlucosidePropyl
149 octaacetate BGP(OAc)₈ **3a** that is the only constituent of fraction F3. This compound is
150 produced in a low yield (21%) with essentially β-isomeric form (Figure 4). The fraction F2
151 contains a first by-product identified as MonoGlucosidePropyl pentaacetate (MGP(OAc)₅)
152 **4a** (24%; α/β ratio 0:1). F1 consists of residual Glc(OAc)₅ (22%) with both anomeric forms
153 (α/β ratio 3:1) **1a,b**. The last fraction F4 is in fact a mixture of different oligomers (33%; α/β
154 ratio 0:1), the nature of which will be defined later in our study by MALDI-TOF MS
155 techniques. Most formed products mainly have the β-configuration (supporting information
156 Figure S3). Such yield of BGP(OAc)₈ **3a** was comparable to those reported by Xue *et al.* for
157 the synthesis of 1,12-dodecyl bisgalactoside [20].

158 *Insert Figure 4*

159

160 • MALDI-TOF MS analysis

161 The efficiency of MALDI-TOF MS analyses was already shown in literature for the
162 identification of high mass compounds in product mixtures based on AlkylPolyGlycoside
163 (APG) models [30]. As regards our study, the MALDI-TOF MS spectrum characteristic of
164 the mixture after 23 hours of reaction is shown in Figure 5-a. Each ionized oligomer is
165 detected on the mass spectrum by a signal made of several peaks corresponding to the
166 mass-to-charge ratios *m/z* characteristic of various isotopic forms (Figure 5-b).

167 *Insert Figure 5*

168

169 The interest of the MALDI-TOF MS is given by comparing measured monoisotopic
170 $(m/z)_{\text{exp}}$ values for $[M_i + \text{Na}]^+$ ions with calculated values. Indeed, the mass spectrum of the
171 crude mixture (figure 5-a) contains five series of cationized adducts $[M_i + \text{Na}]^+$ separated by
172 $\Delta m/z = 288$ (hexose unit) corresponding to different degrees of glucose homopolymerization
173 (HD). The molar mass M_i of each oligomer can be calculated from the measured value
174 $(m/z)_{\text{exp}}$ according to the equation (2):

$$175 \quad M_i = \left(\frac{m}{z}\right)_{\text{exp}} \times z - m_{\text{cation}} \quad (2)$$

176 where m_{cation} is the molar mass of Na ($23 \text{ g}\cdot\text{mol}^{-1}$)

177 The adduct $[M_i + \text{Na}]^+ = 759.2$ is interpreted as being representative of the desired
178 bisglucoside BGP(OAc)₈ **3a** of molar mass $736.6 \text{ g}\cdot\text{mol}^{-1}$ (Figure 6). The adducts $[M_i + \text{Na}]^+$
179 registered at 413.3 and 471.3 are characteristic of residual Glc(OAc)₅ **1a,b** ($390.3 \text{ g}\cdot\text{mol}^{-1}$)
180 and MGP(OAc)₅ **4a** ($448.4 \text{ g}\cdot\text{mol}^{-1}$) respectively. The adducts $[M_i + \text{Na}]^+ = 717.2$ and 429.2
181 are attributed to the presence of mono- and BisGlucosideX but under deacetylated form. In
182 our work, all calculated $(m/z)_{\text{theo}}$ values for $[M_i + \text{Na}]^+$ ions including a possible 2-O
183 deprotection are gathered in supporting information (Table T1) to enable a further
184 comparison with the experimental data $(m/z)_{\text{exp}}$ obtained using MALDI-TOF MS. On the
185 basis of these calculations, two major populations, namely, B and C are suspected to be
186 formed during the O-glucosylation of 1,3-PD **2a**. Unfortunately, they cannot be distinguished
187 separately with MALDI-TOF MS experiments because their oligomers have equivalent m/z
188 values (Figures S3 and S4 in supporting information). The further exploitation of the
189 MALDI-TOF MS spectrum makes it possible the identification of the population **A** that

190 defines oligomers characterized by a sequence of peracetylated glucose units but without
191 1,3-PD building block in their structure (Figure 6).

192 *Insert Figure 6*

193 It is usually accepted that MALDI-TOF MS is a quantitative analysis of oligomers provided
194 that certain requirements are satisfied such as a polydispersity index PDI ($= M_w/M_n$) lower
195 than 1.3 [31, 32]. If these conditions are fulfilled, the intensity of the adducts detected in the
196 mass spectrum reflects the number of oligomers actually present in the sample. The crude
197 mixture of oligomers obtained in our research presents molecular weights lower than 2000
198 $\text{g}\cdot\text{mol}^{-1}$ and low degrees of oligomerization ranging from 1 to 6. In other words, they comply
199 with the criteria for the validity of this technique for quantitative evaluation. Then, the
200 BGP(OAc)₈ that is characterized by a peak at 759.2 with the greatest intensity, is the most
201 abundant chemical specie in the mixture by comparison with other oligomers. The relative
202 proportion of Glc(OAc)₅ **1a,b** and MGP(OAc)₅ **4a** cannot be accurately defined because their
203 corresponding peaks are located too close to the detection limit ($> 500 \text{ g}\cdot\text{mol}^{-1}$).

204

205 • Proposed mechanisms

206 The observation of MGP(OAc)₅ **4a** was coherent with results obtained by Murakami *et*
207 *al.*[29]. Indeed, these researchers reported the formation of bromoalkyl acetate as
208 side-product during the glucosylation of bromo-alkanols with the formation of 1,2-orthoester
209 intermediates. This latter topic is particularly well described in Kong's work [33]. By
210 analogy, MGP(OAc)₅ **4a** that was isolated is likely the result of the conversion of an

211 orthoester **1** into MGP(OAc)₃(OH)₂ **6a** and 3-hydroxy-propyl acetate **2'a** (not isolated). Such
212 mechanism is schematically drawn in Figure 7.

213 *Insert Figure 7*

214 Please note that 3-hydroxy-propyl acetate **2'a** can itself be potentially glycosylated to
215 give the MGP(OAc)₅ **4a** in accordance with the results of Banoub *et al.* and others [34, 35].
216 This mechanism suggests the formation of monoglucosides MGP(OAc)₃(OH)₂ **6a** and
217 MGP(OAc)₃(OH)(OR) **7a** that are deacetylated in position 2. It is very likely that these
218 intermediates are responsible of the formation of oligomers.

219

220 *2.3.Synthesis of the other BisGlucosideX derived from (cyclo)aliphatic diols*

221 Other bisglucosides were synthesized from the respective reaction of aliphatic diols
222 **2b-2e** (Figure 2) with β-Glc(OAc)₅ **1a** using the same chemical pathway as described
223 hereabove with 1,3-PD **2a**. The results issued from their chemical analyses (¹H, ¹³C NMR
224 and MALDI-TOF MS) are available in supporting information for preserving the clarity of
225 this paper. In all cases, the formation of by-products is observed in addition to the desired
226 bisglucoside production. The respective reaction yields of these compounds are summarized
227 in Table 1. Their proportion in the final mixture appear to be dependent on the nature of the
228 diol used for O-glucosylation. As concerns more particularly the bisglucoside BGX(OAc)₈
229 synthesis, the highest reaction yield value is observed with the use of 2-butyne-1,4-diol **2d**
230 (67%) whereas the reverse case is observed with propane-1,3-diol **2a** (21%). A first possible
231 hypothesis to explain the discrepancies observed between diols used is based on their

232 reactivity, i.e. in our study, their ability to react with peracetylated glucosidic units. This
 233 characteristic is directly related to the nucleophilicity of the hydroxyl groups, which is itself
 234 influenced by the nature of the chemical skeleton that bears them.

235 **Table 1.** BF₃·OEt₂ catalyzed glucosylation of diols (**2a-e**) with β-Glc(OAc)₅ (**1a**).

Entry	Diol	pKa ^a	Bisglucoside	Yield ^b	
				By-products	
				1 (22%)	
1	2a	15.1	3a (21%)	4a (24%)	A, B, C (33%)
				1 (15%)	
2	2b	14.5	3b (36%)	4b (13%)	A, B, C (36%)
				1 (22%)	
3	2c	14.4	3c (45%)	4c (15%)	A, B, C (18%)
				1 (9%)	
4	2d	12.5	3d (67%) ^c	4d (6%)	A, B, C (18%)
				1 (32%)	
5	2e	15	3e (25%)	4e (12%)	A, B, C (31%)

236 Experimental conditions: molar ratio 1:0.5:1 (β-Glc(OAc)₅ / HO-X-OH / BF₃·OEt₂) in
 237 CH₂Cl₂, r.t. - 23h.

238 ^a approximative pKa data

239 ^b Yields of products isolated after column chromatography based on crude reaction mixture.

240 ^c Reported yield: 34% [27].

241 In the present study in which we compare the reactivity of the same family of molecules,
242 (i.e. dihydroxy compounds), the nucleophilicity can be evaluated from the base strength with
243 approximate acid dissociation constant pKa [36-38]. The corresponding values range from
244 15.1 (for 1,3-PD **2a**) to 12.5 (for ByD **2d**). It is well known that a sp hybridized carbon as
245 found in (ByD **2d**) is less electron-donating than a sp² (BnD **2b**), which in turn is less
246 electron-donating than a sp³ carbon (1,3-PD **2a**). Such hierarchy is well illustrated by their
247 respective pKa values arranged in ascending order. DEG **2c** presents an oxygen atom in its
248 aliphatic sequence and that has an electron-withdrawing effect. This peculiarity decreases the
249 hydroxyl charge and affects the value of its corresponding pKa (14.4). CHD **2e** presents a
250 pKa value close to that of 1,3-PD **2a** (pKa ≈ 15) but both diols differ from each other with
251 their respective steric effects.

252 To summarize, the higher the pKa is, the higher diol reactivity is. But, considering our
253 own data, a high reactivity is not synonym of bisglucoside production with high yield. On the
254 contrary, a lower diol reactivity seems preferable for obtaining a better selectivity. When the
255 pKa value is low as encountered with ByD **2d**, the hydroxyl charge density is reduced. Then,
256 the hydroxyl units are involved into a direct nucleophilic attack on C-1 (Figure 7 - pathway
257 **I**), which favors the formation of MGX(OAc)₄(OH) (**5a-f**) and then BGX(OAc)₈ (**3a-f**).
258 Conversely, with a high pKa value as found with 1,3-PD **2a**, an increased charge density is
259 centered into hydroxyl units. Then, the attack of the carbonyl carbon present in the
260 acyloxonium ion (Figure 7 - pathway **II**) is privileged with the formation of intermediates
261 orthoesters.

262 With a pKa value similar to that of 1,3-PD **2a**, CHD **2e** led to the production of
263 BisGlucosideCyclohexyl octaacetate (BGC(OAc)₈) **3e** with a reaction yield close to that of
264 BGP(OAc)₈ **3a** (25% against 21%). Nevertheless, the low content of
265 MonoGlucosideCyclohexyl pentaacetate (MGC(OAc)₅) **4e** (12%) seems to indicate that
266 1,2-orthoesters pathway is not the only one to be involved in this reaction.

267 Among our results, it is interesting to note that, despite of its nucleophilicity value
268 comparable to that of BnD **2b**, DEG **2c** led to the production of bisglucoside **3c** with a higher
269 efficiency (yield of 45%) than that of BGBn(OAc)₈ **3b** (36%). This peculiarity is likely due to
270 the presence of an ether group in the chain (**2c**). This group is likely to have a better
271 interaction with BF₃ than an aliphatic diol bearing unsaturation such as found with **2b** or **2d**
272 diols.

273

274 *2.4.Synthesis of the BisGlucosideHydroquinone octaacetate (BGH(OAc)₈)*

275 The interest of hydroquinone was explored for the synthesis of diphenol-based
276 bisglucosides by following the same experimental procedure as that used previously with
277 (cyclo)aliphatic diols **2a-2e**. The products isolated from the glucosylation mixture were
278 analyzed by means of ¹H NMR and MALDI-TOF MS (see supporting information).

279 In strong contrast with the analyses previously registered with (cyclo)aliphatic diols,
280 MALDI-TOF MS analysis of the crude product obtained from O-glucosylation with
281 hydroquinone **2f** reveals the only presence of three *m/z* peaks. The first one can be assigned to
282 the residual Glc(OAc)₅ **1a,b** (390.3 g.mol⁻¹) being ionized by a sodium cation. The other two

283 peaks can be attributed to the monoglucoside $\text{MGH}(\text{OAc})_4(\text{OH})$ **5f** (440.4 g.mol^{-1}) and
284 desired bisglucoside $\text{BGH}(\text{OAc})_8$ **3f** (770.7 g.mol^{-1}). Both latter compounds result from
285 direct nucleophilic attack of **2f** on C-1.

286 The selectivity of the HQ **2f** glycosylation seems quite good without the parasitic
287 formation of orthoesters or 2-O-deacetylated by-products. Once more, this peculiarity can be
288 explained on the basis of nucleophilic considerations. Indeed, HQ presents two hydroxyl
289 groups directly linked to the aromatic ring in para position. The charge delocalization is
290 much reduced than that encountered with the dihydroxy compounds previously investigated.
291 In other words, HQ is less nucleophilic than (cyclo)aliphatic diols **2a-e** as shown by its pKa
292 value close to 10.2.

293 The extraction of each chemical specie from the mixture would make their respective
294 proportion in the mixture clear. In particular, the desired $\text{BGH}(\text{OAc})_8$ **3f** was produced in
295 moderate yield (53%; α/β ratio 0:1). The proportion of MonoGlucosideHydroquinone
296 ($\text{MGH}(\text{OAc})_4(\text{OH})$) **5f** was evaluated as being close to 22% (α/β ratio 0:1) while that of
297 residual $\text{Glc}(\text{OAc})_5$ **1a,b** was found close to 25% (α/β ratio 1:1). The yield obtained with
298 $\text{BGH}(\text{OAc})_8$ **3f** can appear weak but it remains in the same range of order of that observed by
299 Bergeron-Brlek [19] on the synthesis of a bisglucoside from bisphenol A BPA (49%). This
300 similarity is likely a consequence of the pKa values of these diphenols that are evaluated as
301 being rather close (10.2 for HQ against 9.6 for BPA).

302

303 *2.5.Overall hierarchy*

304 Considering our results and their interpretation, the different diols and phenol studied in this
305 research can be ranked in decreasing order considering the selectivity of their reactivity with
306 glucose via a direct attack on the anomeric carbon C-1 (previously defined as pathway I). The
307 corresponding hierarchy is built as following: aromatic > aliphatic (sp) > ethoxylated >
308 aliphatic (sp²) > cycloaliphatic > aliphatic (sp³) (figure 8).

309 *Insert Figure 8*

310 The influence of the nucleophilicity of the dihydroxy compounds upon the selectivity of their
311 reaction with glucose units seems now clear. In this present case, nucleophilicity can be
312 correlated to the base strength (pKa value). The best selectivity is obtained with the
313 compound (diphenol) characterized by the lowest pKa value, or in other words, lowest
314 nucleophilicity. This observation seems a direct consequence of its lowest reactivity due to
315 electronic charge delocalization that prevents the formation of by-products.

316

317 **3. Materials and methods**

318 *3.1. Materials*

319 β -glucose pentaacetate (β -Glc(OAc)₅), 1,3-propanediol (1,3-PD), hydroquinone (HQ),
320 diethylene glycol (DEG), 2-butyne-1,4-diol (ByD), *cis*-2-butene-1,4-diol (BnD),
321 1,4-cyclohexanediol (CHD), boron trifluoride diethyl etherate (BF₃·OEt₂; \geq 46.5% BF₃
322 basis) were purchased from Aldrich (France). Anhydrous dichloromethane (CH₂Cl₂), ethyl
323 acetate (EtOAc or EA) were purchased from Analytic Lab. Deuterated chloroform (CDCl₃)
324 were purchased from SDS. All these chemicals were used without further purification.

325 *3.2. Techniques*

326 Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance I 300
327 MHz or a Bruker Avance III 400 MHz spectrometers at room temperature with CDCl₃ as the
328 solvent. The chemical shifts measured in part per million (ppm) were referenced to the
329 CDCl₃ signal peak at 7.26 ppm (¹H) and 77.16 ppm (¹³C). Coupling constants (J) are reported
330 in Hz.

331 MALDI-TOF MS analyses were performed using a MALDI-TOF MS Bruker
332 Ultra-Flex III (2004) (Bremen, Germany) equipped with a nitrogen laser (337 nm, 30 ns)
333 and a detector. Peptide mixtures were used for external calibration. The ions were
334 accelerated with a potential of 25 kV. The measurements were performed in positive mode
335 POS. The spectra were obtained with
336 trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix
337 and NaI as ionizing salt.

338 High resolution electrospray ionization mass spectrometry (HRMS-ESI) analyses were
339 obtained using a Bruker MicroTOF QII mass spectrometer. The experiments were carried
340 out in positive ion mode at high resolution.

341 Thin layer chromatography analyses (TLC) of the reaction mixtures of BGX(OAc)₈
342 were carried out on silica gel plates with a mixture of CH₂Cl₂/EA (7/3; v/v) as eluent. The
343 various compounds were visualized by spraying the TLC plates with a solution of sulfuric
344 acid (10% by volume in ethanol), followed by charring at 150°C for a few minutes. Spots
345 were compared to standards.

346 Column chromatographic separations were carried out with a silica gel from VWR
347 (40-63 μm). The various products of the mixtures were isolated with the same eluent as the
348 TLC.

349 The thermo-oxidative stability of each bisglucoside was examined using a Q50
350 thermogravimetric analyzer (TGA) from TA Instruments® (New Castle, DE, USA). The
351 experiments consisted in registering the weight loss of the sample as a function of
352 temperature from ambient up to 600 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ under air flow
353 (25 $\text{mL}\cdot\text{min}^{-1}$). A relative weight loss (RWL) value of 5% was chosen as a reasonable
354 criterion to evaluate the thermal degradation temperature T_{deg} of each bisglucoside.

355 Differential scanning calorimetric experiment (DSC) were registered using a Mettler
356 Toledo DSC Star One (Greifensee, Switzerland), under air and with a heating rate of 5
357 $^{\circ}\text{C}\cdot\text{min}^{-1}$. Before analysis, the sample was cooled down from ambient to 0 $^{\circ}\text{C}$ with a ramp
358 of $-3^{\circ}\text{C}\cdot\text{min}^{-1}$ and maintained at this constant temperature during 15 min to insure thermal
359 equilibrium. The thermogram characteristic of each bisglucoside analysis presented an
360 endotherm. Then, the value of the corresponding melting temperature T_{m} was taken at the
361 inception of the endothermic peak.

362 3.3.Synthesis

363 3.3.1.Standard O-glucosylation protocol

364 $\beta\text{-Glc}(\text{OAc})_5$ **1a** (3.00 g, 7.68 mmol) and diol or diphenol (HO-X-OH) **2** (3.84 mmol) were
365 mixed in anhydrous CH_2Cl_2 (50 mL). Then $\text{BF}_3\cdot\text{OEt}_2$ (0.950 mL, 7.68 mmol) was added
366 dropwise. The molar ratio $\beta\text{-Glc}(\text{OAc})_5 / \text{HO-X-OH} / \text{BF}_3\cdot\text{OEt}_2$ is 1:0.5:1. The mixture was

367 stirred at room temperature for 23h under inert atmosphere (nitrogen), and then quenched by
368 saturated aq. NaHCO₃. The organic layer was separated, washed successively with aq.
369 NaHCO₃ and (once) with brine solution, dried over MgSO₄, and concentrated. BGX(OAc)₈
370 and other products are isolated by column chromatography (eluent CH₂Cl₂/EA, 7/3) or by
371 recrystallization (ethanol), depending on the nature of the BGX(OAc)₈.

372 **Remarks.** The glucosylation reactions were also carried out for different quantities up to
373 15g. The products were obtained in similar yields and selectivity.

374 3.3.2.β-BisGlucosidePropyl octaacetate (β-BGP(OAc)₈) (**3a**)

375 Compound (**3a**) 1,3-bis(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyloxy)propane

376 The reaction was carried out as described in the standard protocol using 0.292 g (3.84 mmol)

377 1,3-PD **2a**. The product **3a** was isolated after purification by column chromatography.

378 Yield: 0.594 g (21%).

379 R_f: 0.59 (CH₂Cl₂/EtOAc; 7/3)

380 DSC (5 °C.min⁻¹), T_m: 146 °C

381 TGA (10 °C.min⁻¹ – RWL = 5%), T_{deg}: 234 °C

382 ¹H NMR (CDCl₃, 400.1 MHz): δ (ppm) = 5.18 (t, J = 9.5, 2H, H-3'); 5.06 (t, J = 9.7, 2H,
383 H-4'); 4.96 (t, J = 9.6, 2H, H-2'); 4.45 (d, J = 7.9, 2H, H-1'β); 4.25 (dd, J = 4.8, 12.3, 2H,
384 H-6'b); 4.11 (dd, J = 2.3, 12.3, 2H, H-6'a); 3.86 (dt, J = 5.6, 10.0, 2H, H-1b); 3.68 (m, 2H,
385 H-5'); 3.58 (dt, J = 6.7, 9.7, 2H, H-1a); 1.99-2.07 (4s, 24H, CH₃CO); 1.83 (m, 2H, H-2).

386 ^{13}C NMR (CDCl_3 , 100.6 MHz): δ (ppm) = 170.60, 170.21, 169.38, 169.22 (O-C=O); 101.03
387 (C-1' β); 72.82 (C-3'); 71.84 (C-5'); 71.43 (C-2'); 68.47 (C-4'); 66.61 (C-1); 61.98 (C-6');
388 29.90 (C-2); 20.57-20.70 (CH_3CO).

389 HRMS (ESI): m/z calculated for $\text{C}_{31}\text{H}_{44}\text{O}_{20}$ $[\text{M}+\text{Na}]^+$: 759.2324; Found: 759.2315

390

391 3.3.3. β -BisGlucosideCyclohexane octaacetate (β -BGC(OAc) $_8$)

392 1,4-bis(2',3',4',6'-tetra-O-acetyl- β -D-glucopyranosyloxy)cyclohexane (mixture of *cis* and
393 *trans*) (**3e**)

394 The reaction was carried out as described in the standard protocol using 0.446 g (3.84 mmol)
395 CHD **2e**. The product **3e** was isolated after purification by column chromatography.

396 Yield: 0.746 g (25%).

397 R_f : 0.62 ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$; 7/3)

398 DSC (5 $^\circ\text{C}\cdot\text{min}^{-1}$), T_m : 180 $^\circ\text{C}$

399 TGA (10 $^\circ\text{C}\cdot\text{min}^{-1}$ – RWL = 5%), T_{deg} : 283 $^\circ\text{C}$

400 ^1H NMR (CDCl_3 , 400.1 MHz): δ (ppm) = 5.17 (t, J = 10.0, 2H, H-3'); 5.03 (t, J = 9.0, 2H,
401 H-4'); 4.93 (t, J = 9.3, 2H, H-2'); 4.53 (d, J = 9.3, 2H, H-1' β); 4.23 (dd, J = 4.0, 11.3, 2H,
402 H-6'b); 4.08 (dd, J = 12.2, 2H, H-6'a); 3.68 (m, 2H, H-1); 3.68 (m, 2H, H-5'); 1.30-1.94 (m,
403 8H, H-2); 1.98-2.05 (4s, 24H, CH_3CO).

404 ^{13}C NMR (CDCl_3 , 100.6 MHz): δ (ppm) = 170.72, 170.41, 169.50, 169.27 (O-C=O); 99.85,
405 98.32 (C-1' β); 76.50 (C-1); 72.96 (C-3'); 71.84 (C-5'); 71.64 (C-2'); 68.68 (C-4'); 62.21
406 (C-6'); 26.42, 27.34, 28.39, 28.87 (C-2); 20.73-20.84 (CH_3CO).

407 HRMS (ESI): m/z calculated for $C_{34}H_{48}O_{20}$ $[M+Na]^+$: 799.2637; Found: 799.2629
408
409 3.3.4. β -BisGlucosideButene octaacetate (β -BGBn(OAc)₈)
410 (Z)-1,4-bis(2',3',4',6'-tetra-O-acetyl- β -D-glucopyranosyloxy)-2-butene (**3b**)
411 The reaction was carried out as described in the standard protocol using 0.339 g (3.84 mmol)
412 BnD **2b**. The product **3b** was isolated after purification by column chromatography.
413 Yield: 1.036 g (36%).
414 R_f : 0.54 ($CH_2Cl_2/EtOAc$; 7/3)
415 DSC ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$), T_m : $127\text{ }^\circ\text{C}$
416 TGA ($10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ – RWL = 5%), T_{deg} : $221\text{ }^\circ\text{C}$
417 ^1H NMR ($CDCl_3$, 400.1 MHz): δ (ppm) = 5.66 (m, 2H, H-2); 5.19 (t, $J = 9.5$, 2H, H-3'); 5.06
418 (t, $J = 9.7$, 2H, H-4'); 4.95 (t, $J = 8.9$, 2H, H-2'); 4.49 (d, $J = 8.0$, 2H, H-1' β); 4.32 (m, 2H,
419 H-1b); 4.25 (dd, 2H, H-6'b); 4.18 (m, 2H, H-1a); 4.10 (dd, 2H, H-6'a); 3.68 (m, 2H, H-5');
420 1.97-2.06 (4s, 24H, CH_3CO).
421 ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) = 170.61, 170.21, 169.39, 169.28 (O-C=O); 128.71
422 (C-2); 99.43 (C-1' β); 72.76 (C-3'); 71.80 (C-5'); 71.20 (C-2'); 68.29 (C-4'); 64.47 (C-1);
423 61.79 (C-6'); 20.69 (CH_3CO).
424 HRMS (ESI): m/z calculated for $C_{32}H_{44}O_{20}$ $[M+Na]^+$: 771.2324; Found: 771.2311
425
426 3.3.5. β -BisGlucosideDiEthyleneGlycol octaacetate (β -BGDEG(OAc)₈)
427 1,5-bis(2',3',4',6'-tetra-O-acetyl- β -D-glucopyranosyloxy)-3-oxapentane (**3c**)

428 The reaction was carried out as described in the standard protocol using 0.408 g (3.84 mmol)
429 DEG **2c**. The product **3c** was isolated after purification by column chromatography.
430 Yield: 1.326 g (45%).
431 R_f: 0.30 (CH₂Cl₂/EtOAc; 7/3)
432 DSC (5 °C.min⁻¹), T_m: 117 °C
433 TGA (10 °C.min⁻¹ – RWL = 5%), T_{deg}: 267 °C
434 ¹H NMR (CDCl₃, 400.1 MHz): δ (ppm) = 5.18 (t, J = 9.5, 2H, H-3'); 5.05 (t, J = 9.7, 2H,
435 H-4'); 4.95 (t, J = 9.6, 2H, H-2'); 4.56 (d, J = 8.0, 2H, H-1'β); 4.23 (dd, J = 4.7, 12.3, 2H,
436 H-6'b); 4.11 (dd, J = 2.3, 12.3, 2H, H-6'a); 3.90 (dt, J = 4.2, 10.7, 2H, H-1b); 3.68 (m, 2H,
437 H-5'); 3.67 (m, 2H, H-1a); 3.59 (m, 4H, H-2); 1.97-2.05 (4s, 24H, CH₃CO).
438 ¹³C NMR (CDCl₃, 100.6 MHz): δ (ppm) = 170.74, 170.35, 169.51, 169.41 (O-C=O); 100.95
439 (C-1'β); 72.91 (C-3'); 71.91 (C-5'); 71.37 (C-2'); 70.46 (C-2); 69.23 (C-1); 68.51 (C-4');
440 62.05 (C-6'); 20.70-20.84 (CH₃CO).
441 HRMS (ESI): *m/z* calculated for C₃₂H₄₆O₂₁ [M+Na]⁺: 789.2429; Found: 789.2417
442
443 3.3.6.β-BisGlucosideButyne octaacetate (β-BGBy(OAc)₈)
444 1,4-bis(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyloxy)-2-butyne (**3d**)
445 The reaction was carried out as described in the standard protocol using 0.331 g (3.84 mmol)
446 ByD **2d**. The product **3d** was isolated after purification by column chromatography.
447 Yield: 1.922 g (67%).
448 R_f: 0.62 (CH₂Cl₂/EtOAc; 7/3)

449 DSC (5 °C.min⁻¹), T_m: 121 °C

450 TGA (10 °C.min⁻¹ – RWL = 5%), T_{deg}: 267 °C

451 ¹H NMR (CDCl₃, 400.1 MHz): δ (ppm) = 5.21 (t, J = 9.4, 2H, H-3'); 5.08 (t, J = 9.7, 2H,
452 H-4'); 4.97 (t, J = 9.5, 2H, H-2'); 4.70 (d, J = 7.9, 2H, H-1'β); 4.38 (m, 4H, H-1); 4.25 (dd, J
453 = 4.5, 12.4, 2H, H-6'b); 4.12 (dd, J = 2.3, 12.4, 2H, H-6'a); 3.72 (m, 2H, H-5'); 1.98-2.06 (4s,
454 24H, CH₃CO).

455 ¹³C NMR (CDCl₃, 100.6 MHz): δ (ppm) = 170.67, 170.27, 169.45, 169.42 (O-C=O); 98.39
456 (C-1'β); 81.84 (C-2); 72.76 (C-3'); 71.98 (C-5'); 71.15 (C-2'); 68.33 (C-4'); 61.83 (C-6');
457 56.22 (C-1); 20.66-20.80 (CH₃CO).

458 HRMS (ESI): *m/z* calculated for C₃₂H₄₂O₂₀ [M+Na]⁺: 769.2167; Found: 769.2150

459

460 3.3.7.β-BisGlucosideHydroquinone octaacetate (β-BGH(OAc)₈)

461 1,4-bis(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyloxy)benzene (**3f**)

462 The reaction was carried out as described in the standard protocol using 0.423 g (3.84 mmol)

463 HQ **2f**. The product **3f** was isolated after purification by column chromatography or by

464 recrystallization (ethanol).

465 Yield: 1.570 g (53%).

466 R_f: 0.64 (CH₂Cl₂/EtOAc; 7/3)

467 DSC (5 °C.min⁻¹), T_m: 185 °C

468 TGA (10 °C.min⁻¹ – RWL = 5%), T_{deg}: 311 °C

469 ¹H NMR (CDCl₃, 400.1 MHz): δ (ppm) = 6.92 (s, 4H, H-1); 5.27 (t, J = 9.2, 2H, H-3'); 5.23
470 (t, J = 9.3, 2H, H-2'); 5.15 (t, J = 9.3, 2H, H-4'); 4.98 (d, J = 7.5, 2H, H-1'β); 4.28 (dd, J = 5.1,

471 12.3, 2H, H-6'b); 4.16 (dd, J = 2.5, 12.3, 2H, H-6'a); 3.81 (m, 2H, H-5'); 2.02-2.07 (4s, 24H,
472 CH₃CO).

473 ¹³C NMR (CDCl₃, 100.6 MHz): δ (ppm) = 170.64, 170.34, 169.49, 169.38 (O-C=O); 152.97
474 (C-2); 118.57 (C-1); 99.96 (C-1'β); 72.82 (C-3'); 72.18 (C-5'); 71.34 (C-2'); 68.41 (C-4');
475 62.02 (C-6'); 20.73-20.82 (CH₃CO).

476 HRMS (ESI): *m/z* calculated for C₃₄H₄₂O₂₀ [M+Na]⁺: 793.2167; Found: 793.2153

477

478 **4. Conclusions**

479 This article demonstrates that the production of bisglucosides through O-glucosylation
480 of a dihydroxy compound is not a trivial topic at all. Indeed, depending on the nature of the
481 diol/diphenol used, different by-products can be formed in addition to the desired
482 bisglucoside. On the basis of our results, the nucleophilicity of the dihydroxy compound
483 related to the value of its pK_a seems an important factor to control the reaction yield and the
484 potential formation of side-products. Among the different molecules investigated, the
485 hydroquinone-based monomer is identified as the most promising compound for the
486 production of bisglucosides. Indeed, due to its low nucleophilicity, its reaction with
487 acetylated glucose units is characterized by a good selectivity without glucose
488 homopolymerization. Even if the reaction yield is limited, the purification process is easy to
489 perform and the overall production remains economical. Reminding that this research was
490 initially supported by the wish of producing biobased monomers, that based on hydroquinone
491 is undeniably promising. Indeed, β-BGH(OAc)₈ presents a high thermostability (T_{deg} > 300
492 °C) through the presence of an aromatic cycle set at the core of the bisglucoside chemical
493 skeleton. Moreover, this critical temperature is somewhat 120 °C higher than the melting

494 temperature. Thus, this temperature gap seems large enough to make the conduction of
495 further functionalization in the molten state possible i.e. without the use of any solvent.

496

497

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505 **Conflicts of Interest:** The authors declare no conflict of interest

506 **Abbreviations**

507 The following abbreviations are used in this manuscript:

508 BF₃·OEt₂: Boron trifluoride diethyl etherate

509 BGP(OAc)₈: BisGlucosidePropyl octaacetate

510 BGX: BisGlucosideX

511 BGX(OAc)₈: BisGlucosideX octaacetate

512 BnD: *cis*-2-butene-1,4-diol

513 BPA: Bisphenol A

514 ByD: 2-butyne-1,4-diol

515 CHD: Cyclohexanediol

516 DEG: Diethylene glycol

517 DSC: Differential Scanning Calorimetry

518 Glc(OAc)₅: Glucose pentaacetate (α or/and β)

- 519 HD: Homopolymerization Degree
- 520 HQ: Hydroquinone
- 521 HRMS (ESI): High Resolution Mass Spectrometry (ElectroSpray Ionization)
- 522 FT-IR: Fourier Transform InfraRed
- 523 MALDI-TOF MS: Matrix Assisted Laser Desorption/Ionization - Time of flight – Mass Spectrometry
- 524 Spectrometry
- 525 MGP(OAc)₅: MonoGlucosidePropyl pentaacetate
- 526 MGX(OAc)₅: MonoGlucosideX pentaacetate
- 527 NMR: Nuclear Magnetic Resonance
- 528 OAc: Acetate group –O(CO)CH₃
- 529 1,3-PD: 1,3-propanediol
- 530 PDI: PolyDispersity Index
- 531 pKa: Constant of acidity
- 532 RWL: Relative weight loss
- 533 T_{deg}: Degradation temperature
- 534 T_m: Melting temperature
- 535 TGA: ThermoGravimetric Analysis
- 536
- 537

538 **List of captions**

539 **Figure 1.** General glucosylation of diols/diphenol (**2a-f**) with β -Glc(OAc)₅ (**1a**) promoted by
540 BF₃·OEt₂ for the production of BisGlucosideX octaacetate (BGX(OAc)₈ with X = aromatic
541 chain, cycloaliphatic, aliphatic of variable length).

542 **Figure 2.** Panel of dihydroxy compounds (**2a-f**) used in this study for O-glucosylation.

543 **Figure 3.** ¹H NMR spectrum (400.1 MHz, CDCl₃) for the O-glucosylation of 1,3-PD **2a** (left)
544 and table of the calculated conversion rates at times from 2 to 23 hours (right).

545 **Figure 4.** ¹H NMR spectrum (CDCl₃) of the different fractions: F1: α,β -Glc(OAc)₅ (**1a,b**);
546 F2: MGP(OAc)₅ (**4a**); F3: BGP(OAc)₈ (**3a**) and F4: (A, B, C) mixture.

547 **Figure 5.** MALDI-TOF MS spectrum of the crude mixture obtained after 23 hours with
548 DCTB as matrix and NaI as cationizing agent (a). Zoom on the isotopic mass of the adduct
549 [M_i + Na]⁺ ($m/z = 759.2$) corresponding to BGP(OAc)₈ **3a** (736.6 g.mol⁻¹) (b).

550 **Figure 6.** Overview of the different products obtained by O-glucosylation of 1,3-PD **2a** with
551 β -Glc(OAc)₅ **1a** and identified according different techniques.

552 **Figure 7.** Intermediate products of the reaction involved in the formation of MGP(OAc)₅ **4a**

553 **Figure 8.** Influence of diol/diphenol nucleophilicity on O-glucosylation mechanisms.

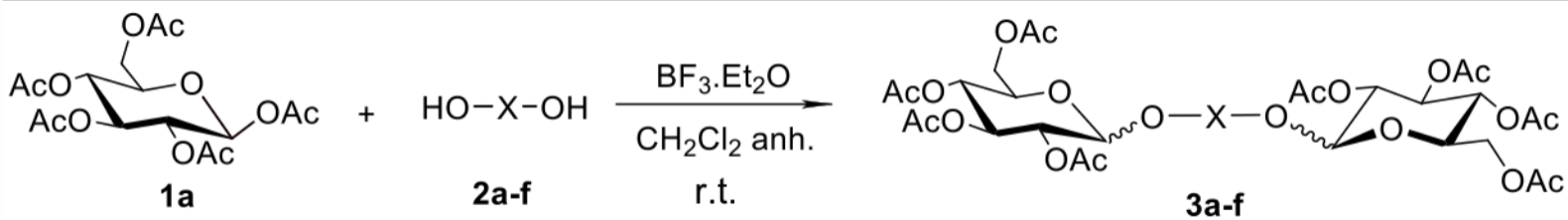
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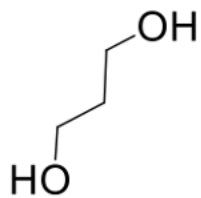
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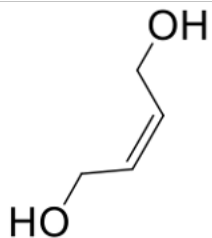
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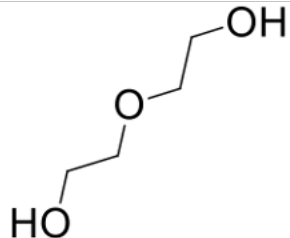




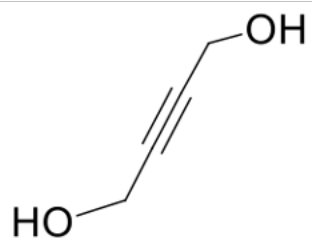
2a (1,3-PD)



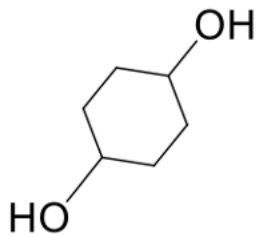
2b (BnD)



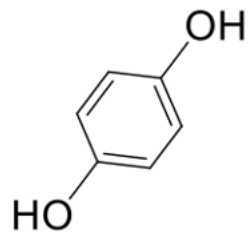
2c (DEG)



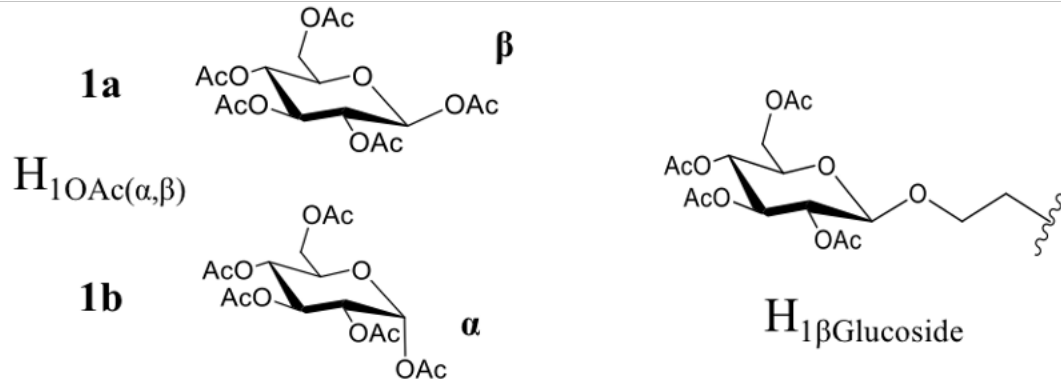
2d (ByD)



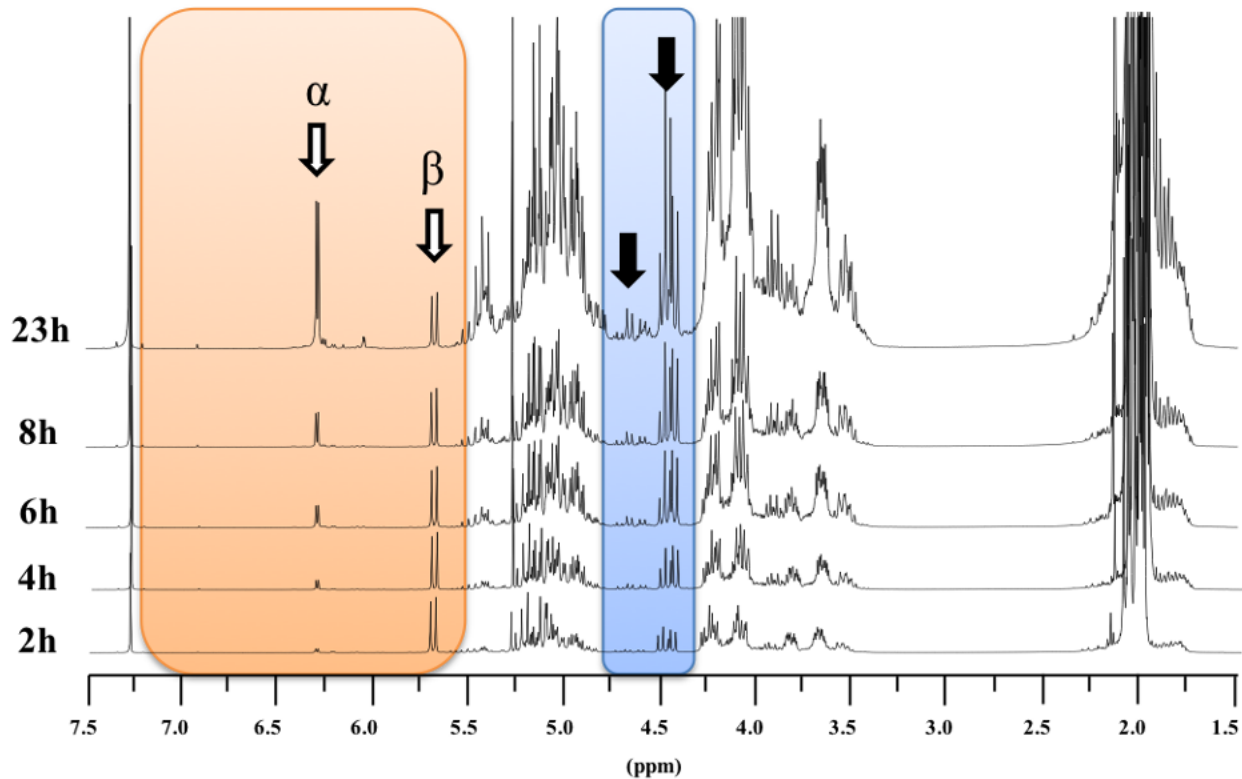
2e (CHD)



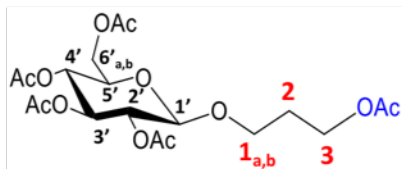
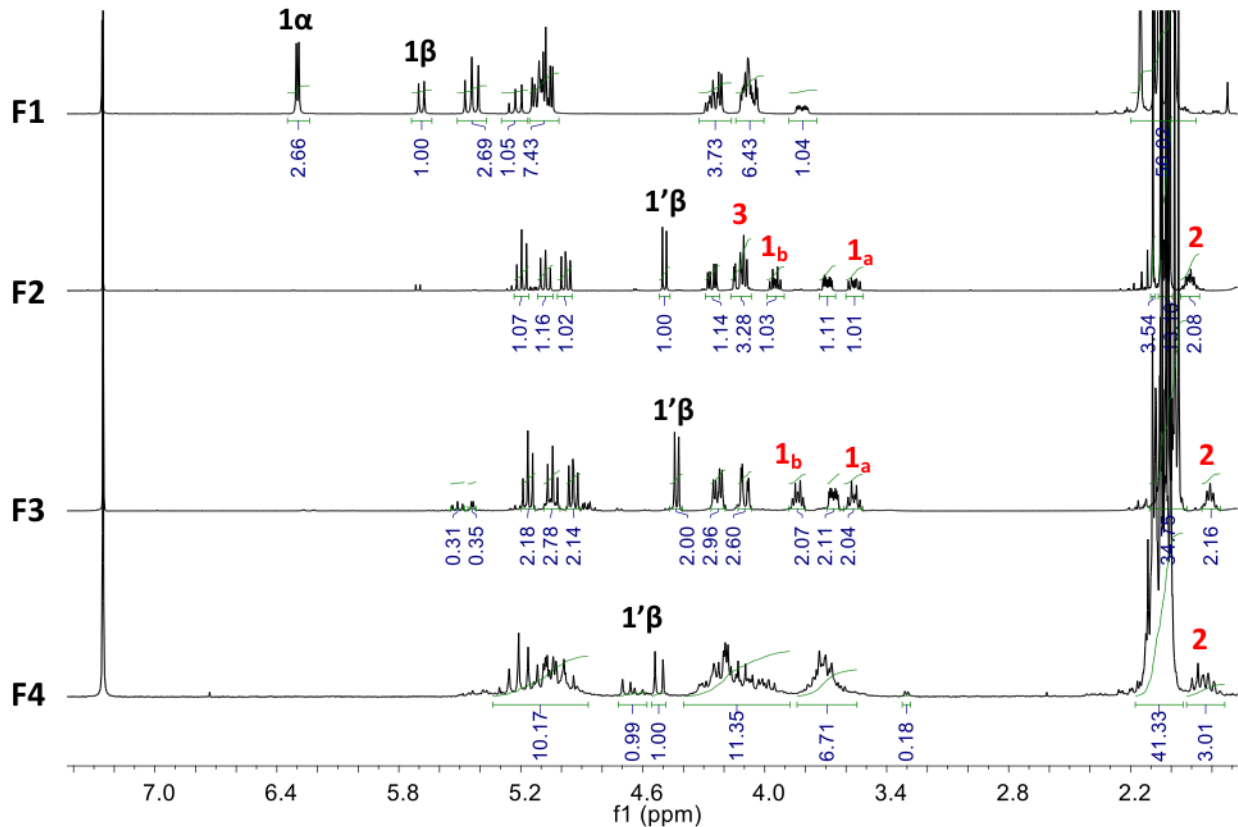
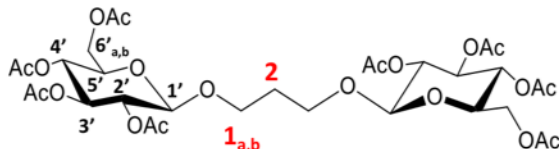
2f (HQ)



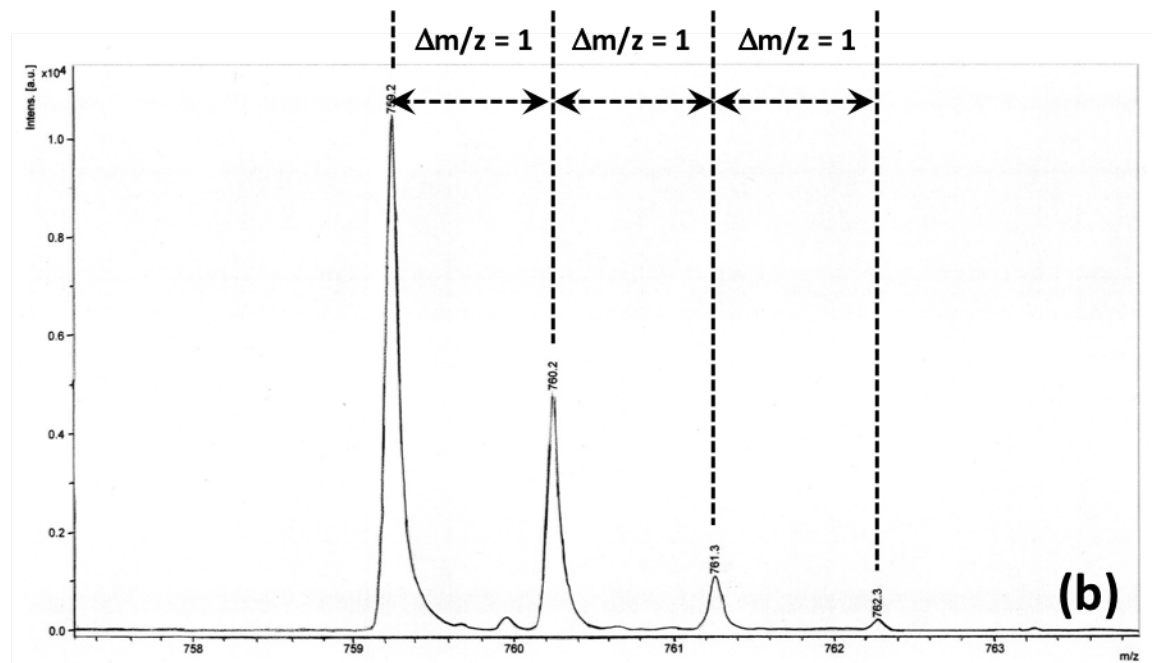
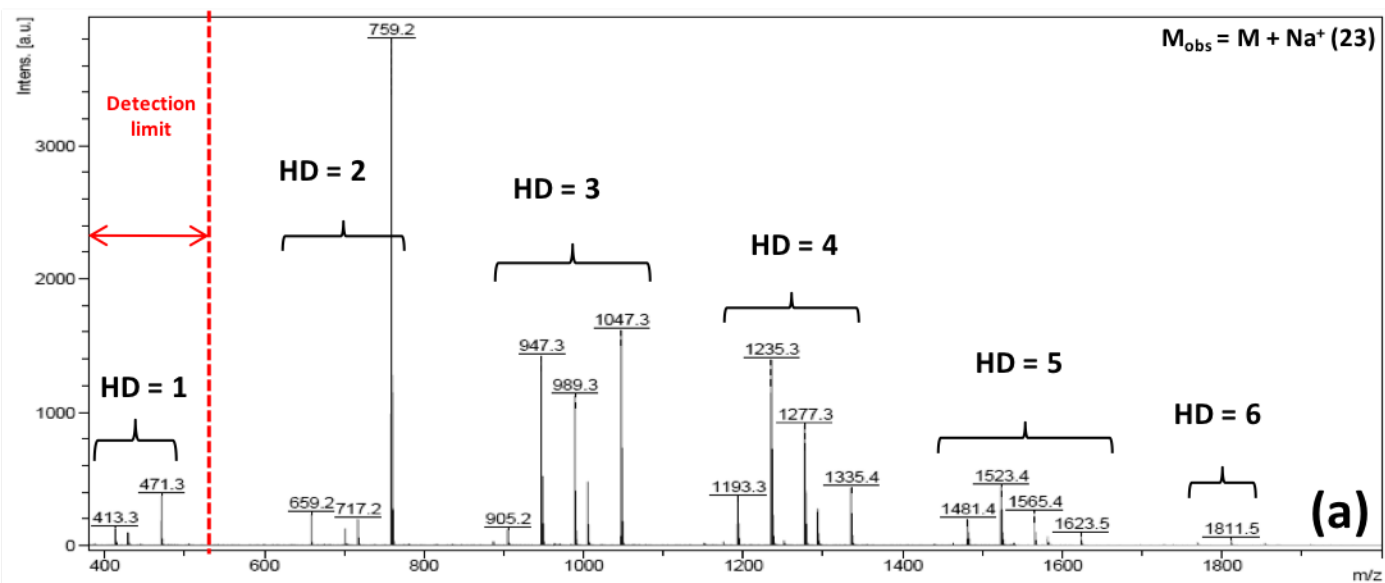
Anomerization **Glycosylation**

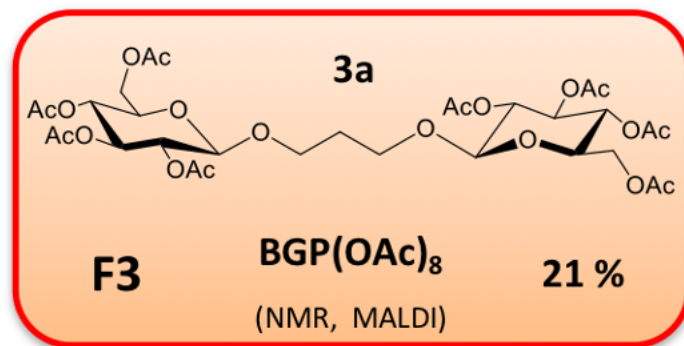
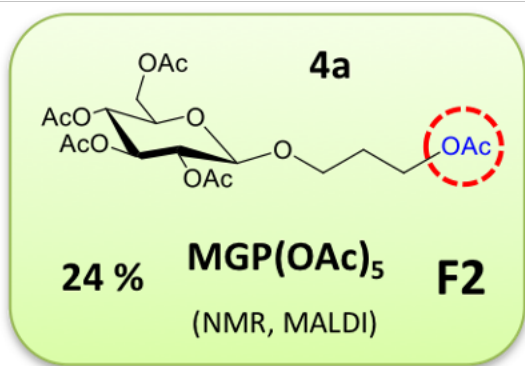


Time (h)	τ (%)	α/β ratio Glc(OAc) ₅
23	78	3:1
8	77	0.7:1
6	74	0.4:1
4	67	0.2:1
2	56	0.1:1

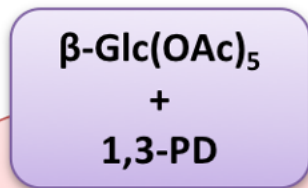
CDCl_3  MGP(OAc)_5  BGP(OAc)_8

$$M_{\text{obs}} = M + \text{Na}^+ (23)$$



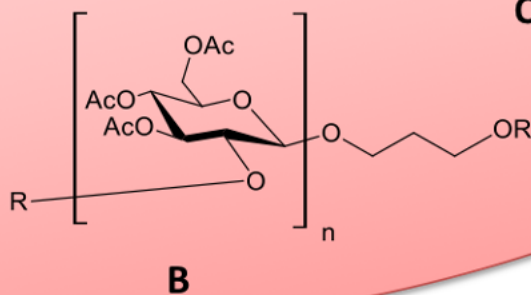
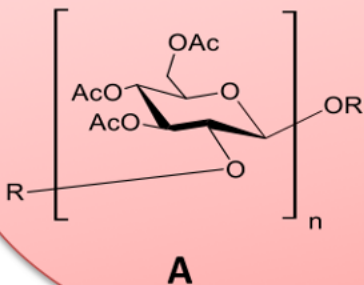
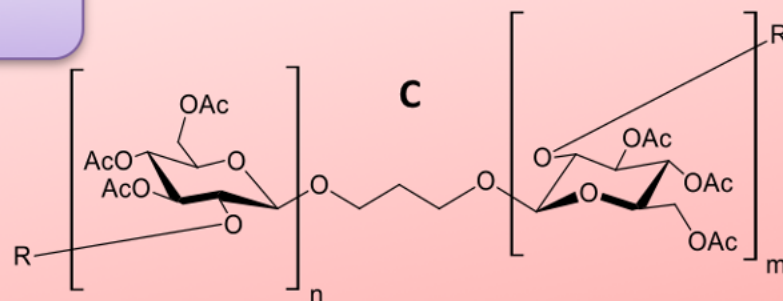


Non fonctionnalized
by-products
(NMR)

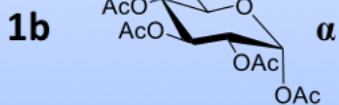


F4 33 %

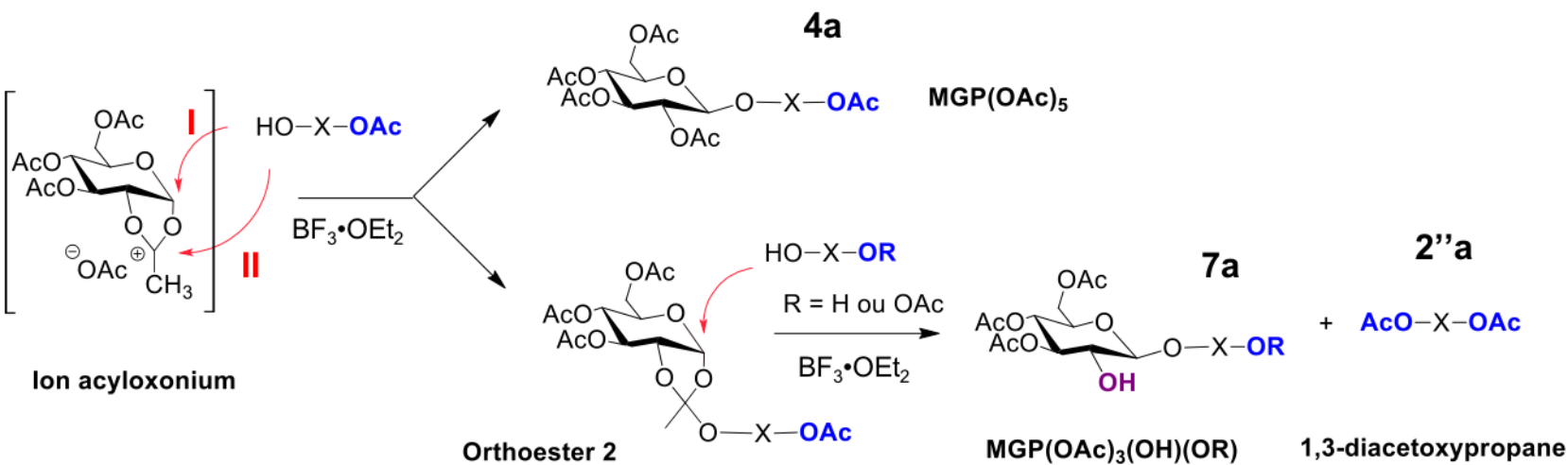
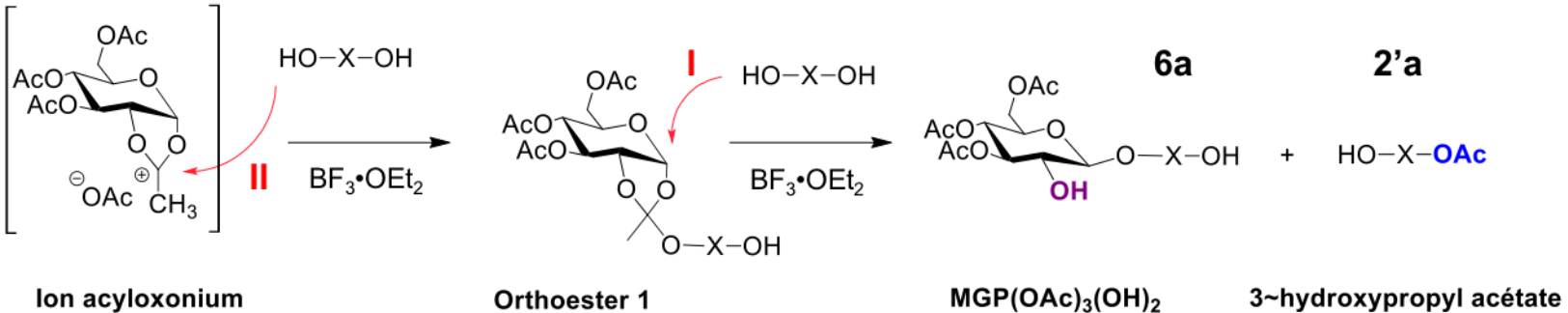
Homopolymerization
by-products
(MALDI)

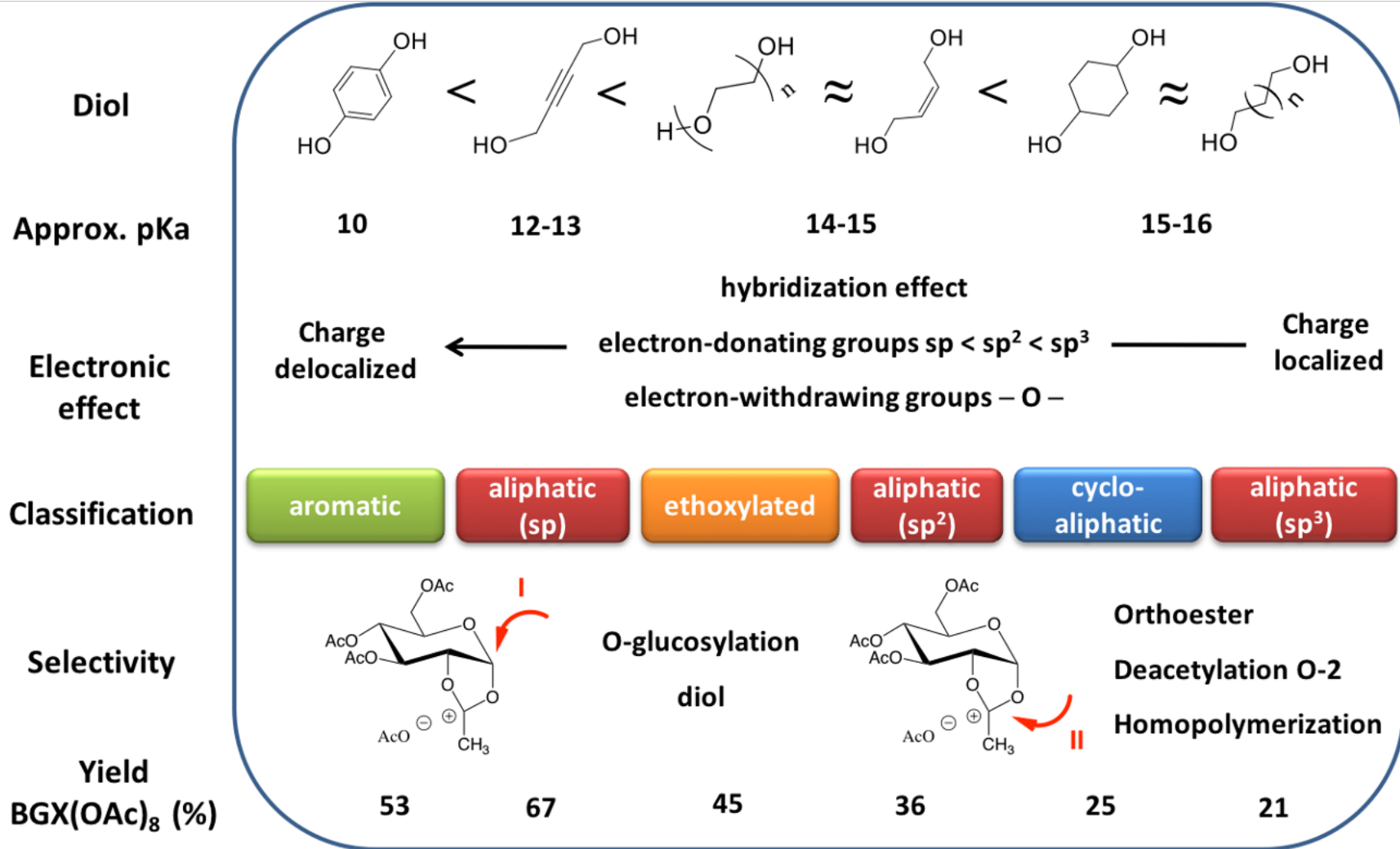


F1



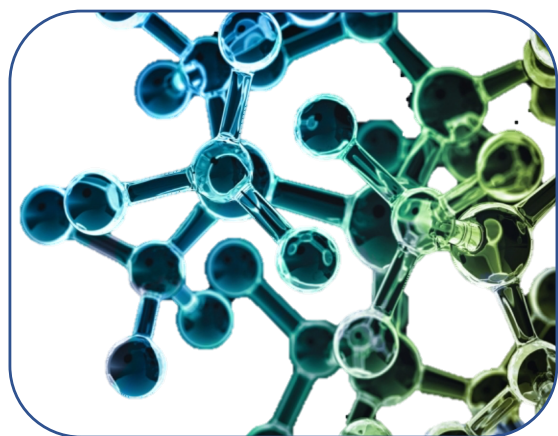
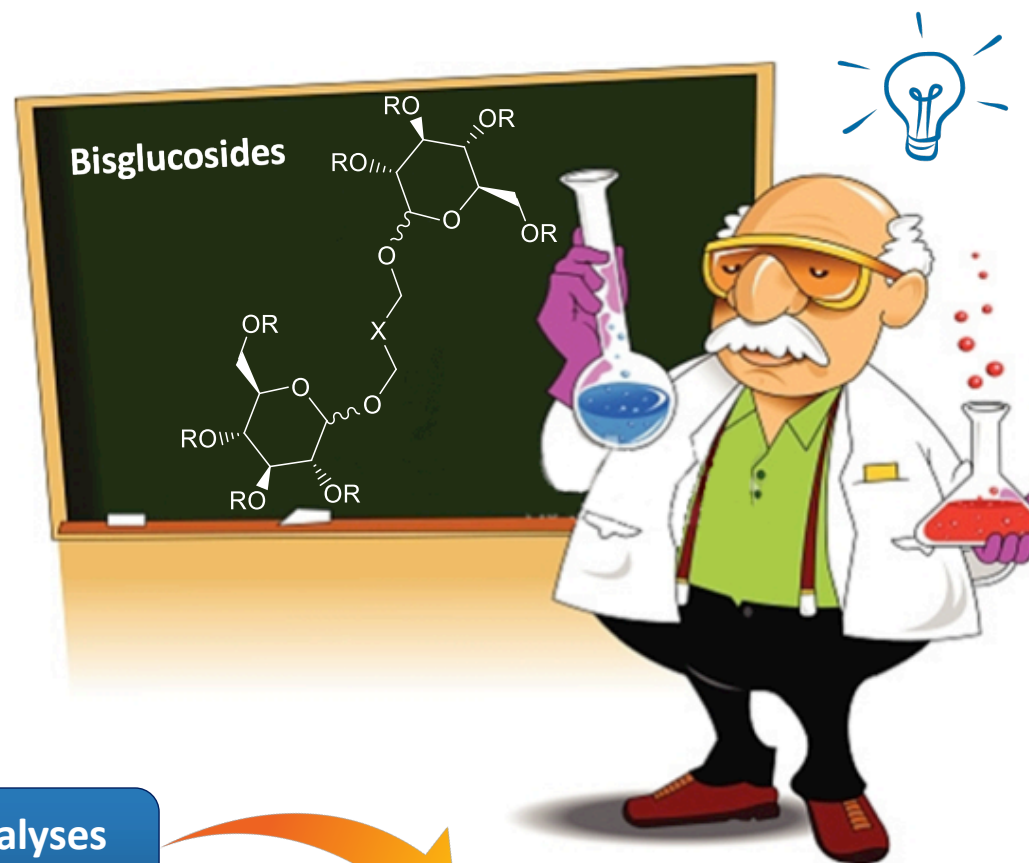
22 % Glc(OAc)₅





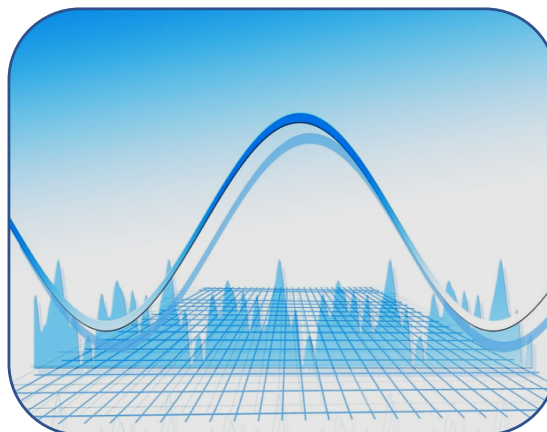
Experimental conditions: molar ratio 1:0.5:1 (β -Glc(OAc)₅ / HO-X-OH / BF₃•OEt₂) in CH₂Cl₂.

Greener
building blocks ?



Synthesis

Chemical analyses
(NMR, MALDI...)



Global discussion