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Permethacrylated carbohydrates: synthesis and reactivity in glycosidation reaction

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In the memory of Dr. C. Mioskowski

ABSTRACT

The synthesis of various permethacrylated mono- and disaccharides in acceptable yields is reported. The reactivity of these unusual polymerizable compounds has been investigated in diverse glycosidation reaction conditions. New original polymerizable donor sugars have been prepared successfully in good to excellent yields.

1. Introduction

As a part of our ongoing program devoted to the development of molecular imprinted polymers (MIP), functionalized polymerizable mono- and disaccharides (Fig. 1) were needed.[1] To date different approaches have been employed for the preparation of polymerizable carbohydrates. Of particular interest, is the strategy based on the use of styrilboronic esters described for monosaccharides by Wulff et al.[2] This approach, however, is limited to 1,2-*cis* diols and suffers from severe drawbacks such as their sensitivity toward aqueous hydrolysis, precluding their use in suspension, precipitation or emulsion polymerization techniques. Glucopyranoside-6-(mono)acrylate derivatives have been also synthesized, as the functional component for the preparation of diverse imprinted matrix.[3] The synthesis of cyclodextrin methacrylate monomers, cinnamic carbohydrates esters, as well perallylated sugars have also been mentioned in the literature.[4–6] However, efficient methods for the preparation mono- and disaccharides polyacrylates remain elusive, and have received only little attention.[7] The development of new approaches for the preparation of such molecules still stands as an important synthetic challenge. Such compounds not only represent fundamentally new molecular structures, but also offer the potential opportunity for creating novel functional polymers.

Herein we wish to report the development of new methodologies for the synthesis of permethacrylated carbohydrates (Fig. 1), and their reactivity toward direct glycosidation reactions.

Due to the potential propensity of permethacrylated sugars to polymerize, we envisioned first to use mild experimental conditions to guide our optimization strategy. Inspired by the profuse literature for sugar peracetylation reactions, we tested conditions that employ weak bases such as triethylamine/DMAP

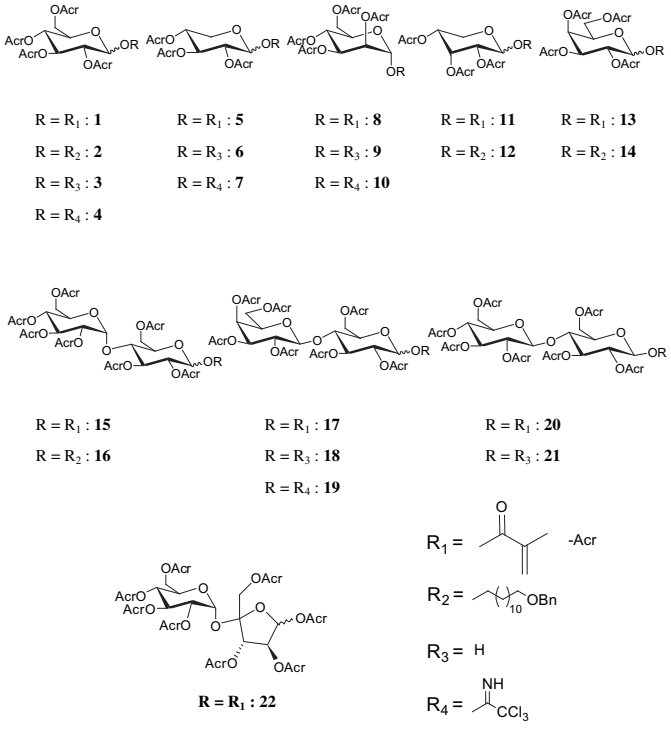

Figure 1. General structure of mono- and disaccharides targeted in this study (Acr=Methacryl).

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and sodium acetate in the presence of acrylic anhydride at room temperature.[8,9] The literature survey revealed also that peracetylation of sugar in solution, might afford two regioisomers, the pyranose and furanose forms by virtue of the existing mutarotation equilibrium. Moreover, the α/β ratio of the pyranose forms appears to depend on the nature of the base used for the peracetylation reactions.[10,11] The purpose of our optimization study, for the permethacrylation of sugars was directed to favor, at best, the formation of the β-pyranose anomer, which is, theoretically the most reactive for further envisioned direct glycosidation reactions.

2. Permethacrylation reactions: results and discussions

At first, the permethacrylation reaction was tested for glucose in different conditions. In Method 1, the reaction was performed at room temperature for 12 h, in the presence of Et_3N/DMAP as base and catalyst, and with methacrylic anhydride in DCM. The reaction was monitored by TLC, and a usual work up procedure was employed (see Experimental section). The crude product of the reaction was then simply purified by column chromatography using silica gel. In the second method (Method 2), the reaction, as well as the work up procedure, were carried out in the same conditions as Method 1, except for the temperature that has been fixed at −10 °C. Finally, two other conditions were also tested. In Methods 3 and 4, the reactions were performed in neat conditions, and in the presence of NaOAc as base, and with methacrylic anhydride. The reaction in Method 3 was performed at 110 °C for 30 min, while Method 4 was conducted at 140 °C for 5 min and under microwave conditions.[12] In the latter cases, no work up procedure was necessary and direct purification was effected.

In the case of glucose, the β/α ratio of the pyranose form was determined based on the ^{1}H NMR of the purified product by quantitative integration of the characteristic anomeric proton signals of permethacrylated glucose at 5.87 ppm for anomer β (J=8.0 Hz), and at 6.46 ppm for anomer α (J=4.0 Hz). As shown in Table 1, for glucose as substrate (Table 1, entry 1), we were pleased to observe that, all the four methods afforded the permethacrylated glucose as the pyranose isomer **1**, exclusively, in an acceptable isolated yields (40–59%). The undesired permethacrylated furanose regioisomer was not detected. The better β/α ratio of the pyranose form is obtained when Method 4 was used (β/α=5/1). The fact that the microwave influences the mutarotation equilibrium toward the formation of β-glucopyranoside is known, and is probably due to the increase of the temperature.[13] Identically, when the reaction is performed at 110 °C (Method 3) the β/α ratio of the pyranose form remains high (β/α=4/1), although it is slightly decreased. In sharp contrast, lower temperatures (−10 °C, Method 2) favored, as major anomer the α-pyranose **1** (β/α=1/4). The reaction carried out at room temperature was the less selective and a 1/1 (β/α) ratio of the pyranoside **1** was formed.

To extend the scope of the permethacrylation conditions to a wider set of saccharides, xylose, mannose, ribose, galactose, maltose, lactose, cellobiose, and saccharose were then tested (Table 1). As a general experimental observation, when the reactions afforded permethacrylated sugars, including the desired product, the initial heterogeneous suspension always became homogeneous, most likely due to the increased solubility of the products, suggesting total conversion of the starting materials. As mentioned previously for glucose, the furanose/pyranose ratio and the β/α ratio of the pyranose form, for all the new compounds, were determined based on the integration of the specific signals on the ^{1}H NMR of the purified products. For xylose, lactose, ribose, and saccharose, HSQC NMR analysis was necessary for the accurate identification of the anomeric proton signals.

For xylose (Table 1, entry 2), application of Method 1 afforded a mixture of β/α pyranose **5** as evidenced by analysis of the ^{13}C NMR spectrum, the α anomer **5** being the major product (undetermined ratio). No traces of the furanose regioisomer were detected. The permethacrylated xylose **5** was best obtained when Method 2 was used. In these conditions, the pure α-pyranose form is formed exclusively, with 71% of isolated yield. To reverse the α stereoselectivity toward the desired β-pyranose anomer, the permethacrylation of xylose was tested in more drastic conditions with Method 4. Unfortunately, a complex mixture of the pyranose/furanose forms was obtained, as identified upon analysis of the crude ^{13}C NMR spectrum of the reaction. Indeed, the signal at 98.6 ppm was identified and assigned, unambiguously, to the furanose anomeric carbon form (major isomer). Consequently, only Method 2 could be used for the efficient synthesis of permethacrylated xylose as the α-pyranoside **5**.

The treatment of mannose under Method 1 permethacrylation conditions gave selectively the pure α-pyranose form **8**, however, with a modest isolated yield of 23% (Table 1, entry 3). Because of the anomeric effect, the α-pyranose is largely preferred compared to the β-pyranose anomer. Furthermore, while the peracetylation of mannose is reported to be problematic and unselective at higher temperature (complex mixture of pyranose/furanose forms),[9a] we decided, however, to perform the permethacrylation reaction at 140 °C under microwave (Method 4). Unexpectedly, the reaction was highly regioselective in delivering the pyranoside form **8** exclusively, as the initially unwanted α-anomer (25% of yield). Even though the reaction did not afford the desired β-anomer, it is worthwhile to note the high stereoselectivity of the transformation.

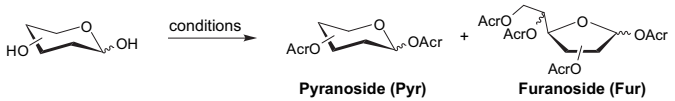
Ribose permethacrylation at room temperature using Method 1 afforded after 12 h of reaction a complex mixture containing both the pyranose and the furanose regioisomers (Table 1, entry 4). Even though the furanose form was the major compound (undetermined ratio) the product was contaminated with the α and β-pyranose anomers. The decrease of the temperature to −10 °C for 12 h by using Method 2, delivered cleanly and selectively the pyranose form of permethacrylated ribose **11**, with a favorable β/α ratio of 5/1, in 43% of isolated yield. The fact, that the pyranose is obtained exclusively, is ascribed to the temperature effect on the ribose mutarotation blockade, known to favor the pyranose form.[14] As a consequence, permethacrylation at higher temperature (Methods 4) was anticipated to be tedious. Expectedly, under microwave conditions at 140 °C for 5 min a complex mixture was obtained with the undesired furanoside as the major compound.

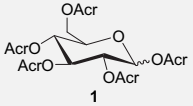
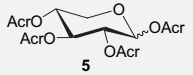
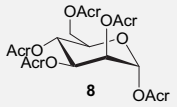
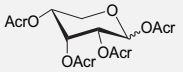
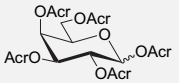
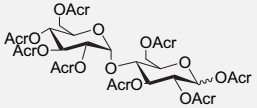
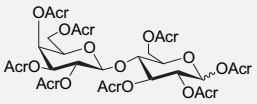
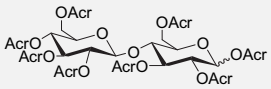
In the case of galactose the application of Method 1 afforded, with a disappointing selectivity, a 2/1 mixture of pyranose/furanose regioisomers **13** in 69% of yield. Indeed, the β/α ratio of the major pyranose form was unsatisfactory (β/α=2/1) (Table 1, entry 5). The decrease of the reaction temperature to −10 °C or the use of Method 3 at 110 °C, did not improve both, the pyranose/furanose selectivity and the chemical yields were decreased (Methods 2 and 3). In sharp contrast, increasing the temperature to 140 °C under microwave irradiation gave, albeit in modest yield (15%), as the major product, the desired β-galactopyranoside **13**, along with 5% of the furanose regioisomer and 20% of the α-galactopyranoside.

When maltose disaccharide was subjected to Method 1 permethacrylation conditions, the β-pyranose form **15** was successfully obtained as the predominant product with 42% of yield, and a good β/α ratio (5/1) (Table 1, entry 6). It is of paramount importance to point out that the α configuration of the $^4C_1$ linkage of the disaccharide was preserved during the reaction, and no isomerization of the anomeric stereocenter was observed in these conditions. Since the desired product was obtained in a satisfactory yield, and the preservation of the stereochemical integrity of $^4C_1$, the other three initially envisioned conditions were not tested.

The permethacrylation of lactose under Method 1 conditions was not total as could be observed by the heterogenic suspension of the reaction mixture even after 12 h of reaction (Table 1, entry 7).

Table 1
Permethacrylation of carbohydrates



Entry	SM[a]	Product	Method 1			Method 2			Method 3			Method 4		
			Yield (%)	Pyr/Fur	Pyr β/α	Yield (%)	Pyr/Fur	Pyr β/α	Yield (%)	Pyr/Fur	Pyr β/α	Yield (%)	Pyr/Fur	Pyr β/α
1	Glc	 **1**	59	1/0	1/1	40	1/0	1/4	40	1/0	4/1	**41**	**1/0**	**5/1**
2	Xylose	 **5**	—	1/0	α Major	**71**	**1/0**	**0/1**	Not tested			—	Furanoside major	—
3	Man	 **8**	**23**	**1/0**	**0/1**	Not tested			Not tested			25	1/0	0/1
4	Ribose	 **11**	—	Furanoside major	—	**43**	**1/0**	**5/1**	Not tested			—	Furanoside major	—
5	Gal	 **13**	69	2/1	7/4	25	2/1	1/1	28	2/1	1/1	15	95/5	5/1
6	Glc (α1→4) Glc	 **15**	**42**	**1/0**	**5/1**	Not tested			Not tested			Not tested		
7	Gal (β1→4) Glc	 **17**	**36**	**1/0**	**1/3**	Not tested			60	0/1	—	Not tested		
8	Glc (β1→4) Glc	 **20**	Traces			Not tested			Not tested			**32**	**1/0**	**1/0**

(*continued on next page*)

Table 1 (*continued*)

Entry	SM[a]	Product	Method 1			Method 2			Method 3			Method 4		
			Yield (%)	Pyr/Fur	Pyr β/α	Yield (%)	Pyr/Fur	Pyr β/α	Yield (%)	Pyr/Fur	Pyr β/α	Yield (%)	Pyr/Fur	Pyr β/α
9	Glc (α1→β2) Fru	**22**	No reaction			Not tested			5	0/1	0/1	**35**	**0/1**	**0/1**
10	**25**	**14**	35	0/1	1/0	Not tested			Not tested			Not tested		

Method 1: methacrylic anhydride (2 equiv/–OH); Et_3N (2 equiv/–OH); DMAP; DCM; rt; 12 h.
Method 2: methacrylic anhydride (2 equiv/–OH); Et_3N (2 equiv/–OH); DMAP; DCM; −10 °C; 12 h.
Method 3: methacrylic anhydride (2 equiv/–OH); NaOAc (0.5 equiv/–OH); 30 min; 110 °C.
Method 4: methacrylic anhydride (2 equiv/–OH); NaOAc (0.5 equiv/–OH); 5 min; 140 °C (for mono-); 180 °C (for disaccharide); microwave.
[a] SM = starting material.

The α-pyranose form **17** was isolated predominantly in 36% of yield (β/α=1/3). As observed for maltose, the stereochemistry of the anomeric stereocenter between both galactose and glucose units was preserved. To increase the proportion of β-pyranose anomer of **17**, the permethacrylation of lactose was envisioned at higher temperature with Method 3. Unfortunately, these drastic conditions did not allow the formation of the desired β-pyranose form. In contrast, we observed the exclusive formation of a β/α mixture of the furanose regioisomer in 60% of yield (undetermined β/α ratio). This somehow interesting result, but disappointing for our purposes, excluded Method 4 as a potential alternative for the formation of the β-pyranose form of the reducing sugar, due to the low selectivity induced by high temperatures.

While only traces of the desired product (**20**) was detected for the permethacrylation of cellobiose at room temperature, with Method 1 (Table 1, entry 8), the use of more drastic conditions (Method 4), afforded, selectively and unexpectedly, the β-pyranose form **20** in an acceptable yield of 32%. This lack of reactivity exhibited at room temperature for cellobiose was also noticed for saccharose (Table 1, entry 9), which was totally unreactive under Method 1 conditions. The use of higher temperature by using Method 3, and in neat conditions was not satisfactory, because only 5% of the α-furanose form of **22** was isolated, due to a partial polymerization of the crude mixture. In sharp contrast, the use of microwave at 140 °C was beneficial and the permethacrylation of saccharose with Method 4 was effective, and gave the permethacrylated product **22** with 35% of yield, selectively.

Analysis of the previous permethacrylation results for lactose (Method 1, Table 1, entry 7), that contains a galactose and a glucose unit, revealed that galactose sugar reacted with retention of the β-configuration of the glycosidic bond between the sugars ($^4C_1$). Consequently, we hypothesized that the permethacrylation of β-galactopyranoside, such as **25**, should yield to the selective formation of the corresponding permethacrylated β-galactopyranoside selectively, by virtue of the mutarotation blockade. Accordingly, the treatment of compound **25** with Method 1 conditions, gave the expected product **14** in reasonably good yield (35%), without any traces of the furanose isomer or the α-pyranose form either (entry 10).

As can be evaluated by the overall results reported in Table 1, it clearly appeared that each sugar (mono- or disaccharide) exhibits an intrinsic reactivity in the studied permethacrylation conditions. Therefore, based on our experimental data a general protocol cannot be ruled out and each sugar needs specific reaction conditions. The permethacrylation at room temperature, with Method 1, was the most effective for mannose, galactopyranoside **25**, maltose, and lactose. The α-pyranose form is obtained as the major product for mannose (Table 1, entry 3) and lactose (Table 1, entry 7) while the β-anomer is observed for galactopyranoside **25** (Table 1, entry 10), and maltose (Table 1, entry 6). Method 2 was advantageous for the permethacrylation of xylose and ribose (Table 1, entries 2 and 4). A quite high selectivity is observed for xylose since the α-pyranose form is isolated exclusively in high yield, while ribose afforded the β-pyranose as the major anomer. The use of Method 4 was effective for the preparation of permethacrylated β-glucoside **1** as the major anomer (Table 1, entry 1). Exclusive β permethacrylated cellobioside **20** could also be synthesized by this protocol (Table 1, entry 8).

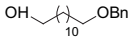
3. Reactivity of permethacrylated carbohydrates

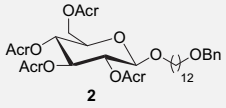
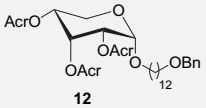
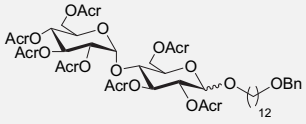
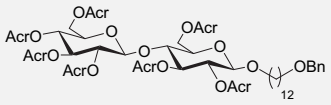
With the permethacrylated sugars in hands, we then investigated their chemical reactivity in diverse reactions conditions for the synthesis of our targeted intermediates (Fig. 1). We were surprised by the fact that the reactivity and the chemistry of such functionalized sugars are unknown. Therefore we decided to

investigate this field that would contribute in broadening the challenging chemistry of sugars.

Initially, it was anticipated that such polymerizable molecules would be sensitive and could probably be difficult to work with, without observing partial polymerization. The first attempts were to test classical selective reactions reported for the peracetylated sugars, such as direct glycosidation, halogenations, and hydrolysis of the anomeric position.[10] Direct glycosidation reactions were first performed on selected permethacrylated sugars, that have been obtained as major β-pyranoside isomers. Consequently, substrates **1**, **11**, **15**, and **20** were reacted with alcohol **23**[15] in the presence of $BF_3 \cdot Et_2O$ as activator in DCM, and at room temperature for 12 h. We observed that compounds **12**, **16**, and **21** (Table 2, entries 2–4) were obtained with reasonable yields (37–46%), while substrate **2** (Table 2, entry 1) was obtained with a poor isolated yield (15%). It is assumed that the moderate yields are ascribed to possible removal or loss of methacrylate(s) function(s) during the glycosidation reaction affording, eventually, more polar partially deprotected sugars. However, it is interesting to point out that the products **2** and **21** gave the β-anomer exclusively, probably due to the anchimeric assistance of the methacrylate group, while a 3/1 ratio of β/α is obtained for compound **16**.[16] In the case of **12**, the α-anomer was obtained selectively.

Table 2
Glycosidation reaction in the presence of $BF_3 \cdot Et_2O$ at room temperature in DCM for 12 h with alcohol **23**

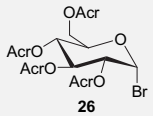
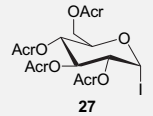
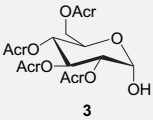
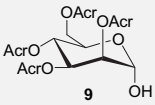
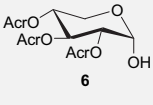
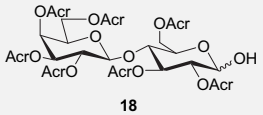
Compound **23**: 

Entry	Reagent	Product	Yield (%)	Ratio (β/α)
1	**1** β/α = 5/1	 **2**	15	1/0
2	**11** β/α = 5/1	 **12**	46	0/1
3	**15** β/α = 5/1	 **16**	37	3/1
4	**20** β/α = 1/0	 **21**	40	1/0

The direct glycosidation reaction was then attempted with permethacrylated α-pyranosides. When the substrate **8** was subjected to the same conditions as the one used for β-pyranosides (**1**, **11**, **15**, and **20**), the expected products were not obtained and the conversion of the starting material **8** was low, even after prolonged reaction time at 45 °C or the use of microwave irradiation. This lack of reactivity is reminiscent of the reactivity reported for α-peracetylated sugars in glycosidation conditions; the α-anomer remains kinetically unreactive.[17]

Consequently, prior to direct glycosylation reactions, the anomeric center of all permethacrylated α-anomers (glucose **1**, xylose **5**, mannose **8**, and lactose **17** derivatives) was first derivatized or activated. The offered alternatives were to explore the reactivity of these sugars toward halogenation conditions (Koenigs–Knorr reaction)[18,10b] and hydrolysis conditions.[19] While the halogenation reactions tested on permethacrylated α-glucopyranoside **1**, failed to give any traces of the desired products **26** and **27** (Table 3, entries 1 and 2), we were pleased to notice that the hydrolysis of substrates **1**, **5**, **8**, and **17** employing $BnNH_2$ afforded the expected compounds in acceptable yields, for such functionalized molecules. Except for substrate **5** (Table 3, entry 5), which was accompanied with small amount of the furanose form, the reagents were hydrolyzed smoothly without complication.

Table 3
Halogenation and hydrolysis reactions

Entry	Reagent	Product	Yield (%)	Ratio (β/α)
1	**1** β/α = 1/1	 **26**	0	—
2	**1** β/α = 1/1	 **27**	0	—
3	**1** β/α = 1/1	 **3**	48	0/1
4	**8** β/α = 0/1	 **9**	36	0/1
5	**5** β/α = 0	 **6**	38[a]	0/1
6	**17** β/α = 1/3	 **18**	54	1/3

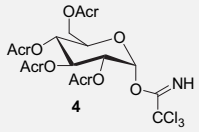
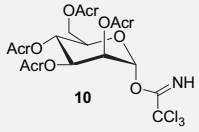
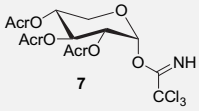
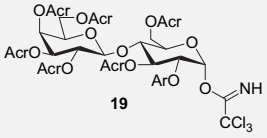
[a] ^{13}C NMR analysis revealed the presence of small amount of furanose form.

The intermediates **3**, **6**, **9**, and **18** were finally used for the preparation of Schmidt reagents, well known for their ability to be used in glycosidation reactions.[20] As expected good to excellent yields of the corresponding trichloroacetimidate α-anomer derivatives **4**, **7**, **10**, and **19** were isolated (Table 4), without observing epimerization of the anomeric center or detectable degradation of the disaccharide substrate.

It is worthwhile to mention that these functionalized glycosyl donors can be handled easily and are stable at room temperature. The uses of these new reagents for further transformations are underway in our laboratory and will be reported in due course.

In conclusion, each sugar behaved differently and requires specific reaction permethacrylation conditions. Three main problems were encountered: the presence of the furanose isomer form, the possibility of producing α and β pyranose form, and the lack of reactivity for some saccharides. In most cases, the control of the regioselectivity was achieved and the pyranose forms were obtained as the major products. The lack of reactivity could be

Table 4
Synthesis of trichloroacetimidate with trichloroacetonitrile, DBU at room temperature in DCM for 2 h

Entry	Reagent	Product	Yield (%)	Ratio (β/α)
1	**3** β/α = 0/1	 **4**	73	0/1
2	**9** β/α = 0/1	 **10**	66	0/1
3	**6** β/α = 0/1	 **7**	60	0/1
4	**18** β/α = 1/3	 **19**	55	0/1

circumvented in some instance, by modifying the reaction conditions. For instance, decreasing the reaction temperature to −10 °C, allowed the formation of permethacrylated ribose (Method 2), while permethacrylated galactose **16**, is obtained only from galactoside **25** and not from the free sugar. The use of microwave resolved the problem of reactivity for cellobiose and saccharose (Method 4). For all the permethacrylated carbohydrates obtained as β-anomer as the major product, direct glycosidation with $BF_3 \cdot Et_2O$ was possible and gave moderate yields of glycosylated products. All the carbohydrates where the α anomer was predominant the direct glycosidation was uneffective. Gratifyingly, two-step activations of the anomeric position by the preparation of the Schmidt reagent was possible in good to excellent yields. These activated building blocks are now investigated for diverse reactions that will be published elsewhere.

4. Experimental section

4.1. General procedure for the permethacrylation of glucose, xylose, mannose, maltose, lactose, and compound 14 at room temperature: Method 1

*4.1.1. Synthesis of permethacrylated glucose **1**.* Glucose (5.0 g, 27.70 mmol, 1 equiv) was suspended in dichloromethane (100 mL); methacrylic anhydride (40 mL, 268.4 mmol, 9.6 equiv), triethylamine (40 mL, 284.6 mmol, 10.3 equiv), and a catalytic amount of DMAP were added. The reaction mixture was stirred at rt overnight (12 h), then quenched with water (3×50 mL). The organic phase was separated, dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.63) to give a sticky solid (8.5 g, yield: 59%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 6.46 (d, *J*=3.6 Hz, 0.5H), 6.28–6.04 (m, 5H), 5.86 (d, *J*=8.0 Hz, 0.5H), 5.78–5.42 (m, 6H), 5.42–5.22 (m, 2H), 4.40–4.03 (m, 3H), 2.02–1.85 (m, 15H); ^{13}C NMR (APT) ($CDCl_3$, 50 MHz) δ (ppm): 167.0, 166.4, 165.8, 135.8–134.9, 128.3–126.5, 92.5, 89.8, 73.1, 72.7, 70.6, 70.4, 70.2, 70.0, 68.5, 68.3, 62.3, 62.2, 18.3; IR: ν (cm^{-1}) 2928, 1733, 1637, 1456, 1318, 1294, 1146, 1077; MM-ES: 543.3 $[M+Na]^+$, mp: 66–68 °C.

*4.1.2. Synthesis of permethacrylated mannose **8**.* From 4.0 g of mannose, 2.6 g of compound **8** as a colorless oil (yield: 23%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.56). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.24 (s, 1H), 6.22 (s, 1H), 6.21 (s, 1H), 6.13 (s, 1H), 6.05 (s, 1H), 5.73–5.42 (m, 8H), 4.30–4.21 (m, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H), 1.92 (s, 3H), 1.86 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (APT) ($CDCl_3$, 75 MHz) δ (ppm): 166.9, 166.1, 165.9, 165.8, 164.3, 135.9–135.2, 127.8–126.1, 91.1, 70.9, 69.6, 69.0, 65.7, 62.1, 18.2; IR: ν (cm^{-1}) 2980, 1728, 1637, 1458, 1319, 1294, 1147; MM-ES: 543.1 $[M+Na]^+$, 559.2 $[M+K]^+$.

*4.1.3. Synthesis of permethacrylated maltose **15**.* From 5.0 g of maltose, 10.4 g of compound **15** as a white solid (yield: 42%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.53). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.33 (d, *J*=3.7 Hz, 0.20H), 6.26–5.85 (m, 8.8H), 5.73 (d, 1H, *J*=7.5 Hz, Hanoβ), 5.68–5.42 (m, 12.8H), 5.30–5.13 (m, 2H), 5.10–4.90 (m, 1.2H), 4.55 (m, 1.1H), 4.40 (m, 1.1H), 4.26–4.01 (m, 5.5H), 1.98–1.80 (m, 31H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.1–165.4, 128.3–126.7, 136.0–135.3, 96.5, 92.2, 75.2, 73.6, 72.4, 71.2, 70.7, 69.9, 69.3, 68.6, 63.2, 62.3, 27.2, 18.4; IR: ν (cm^{-1}) 2978, 1731, 1638, 1454, 1319, 1295, 1154, 1082; API-ES. Pos: 909.4 $[M+Na]^+$; mp: 81–83 °C.

*4.1.4. Synthesis of permethacrylated lactose **17**.* From 2.0 g of compound lactose, 1.7 g of compound **17** as a colorless oil (yield: 34%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.60). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 6.35 (d, *J*=3.2 Hz, 1H), 6.25–5.93 (m, 15H), 5.81 (m, 0.5H), 5.77 (d, *J*=8.7 Hz, 0.5H), 5.72–5.48 (m, 18H), 5.30–5.25 (m, 2H), 5.16–5.08 (m, 2H), 4.64–4.41 (m, 3H), 4.24–3.90 (m, 8.5H), 2.10–1.76 (m, 24H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 172.9, 166.6–165.2, 135.1–134.9, 129.0–126.3, 100.9, 100.6, 92.5, 89.6, 75.4, 75.2, 73.7, 72.6, 71.6, 71.4, 71.1, 70.6, 70.2, 69.9, 69.7, 69.6, 67.3, 62.0, 61.8, 61.4, 61.2, 18.3–17.9; IR: ν (cm^{-1}) 2961, 1731, 1637, 1456, 1319, 1294, 1150, 1076; HRMS: *m*/*z*: calcd for $C_{44}H_{54}O_{19}Li$: 893.3419 $[M+Li]^+$; found: 893.3412.

*4.1.5. Synthesis of compound **14**.* From 446.7 mg of compound **25**, 248.7 mg of compound **14** as a colorless oil (yield: 35%) was recovered (SiO_2, cyclohexane/EtOAc=8/2, R_f=0.70). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.27 (m, 5H), 6.18 (s, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.92 (s, 1H), 5.60–5.44 (m, 5H), 5.29–5.17 (m, 2H), 4.53 (d, *J*=7.9 Hz, 1H,), 4, 49 (s, 2H), 4.33–4.28 (m, 1H), 4.12–3.98 (m, 2H), 3.80 (m, 1H), 3.40 (m, 3H), 1.91 (s, 3H), 1.86 (s, 3H), 1.83 (s, 3H), 1.75 (s, 3H), 1.53 (m, 4H), 1.17 (m, 17H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 166.9–166.0, 128.5–126.2, 101.5, 73.0, 71.5, 71.0, 70.7, 70.4, 69.6, 67.8, 61.7, 29.9–29.5, 26.3, 25.9, 18.4; IR: ν (cm^{-1}) 2927, 2854, 1730, 1457, 1320, 1154; HRMS: *m*/*z*: calcd for $C_{25}H_{42}O_7Li$: 733.4139 $[M+Li]^+$, found 733.4130.

4.2. General procedure for the permethacrylation of ribose at −10 °C: Method 2

*4.2.1. Synthesis of permethacrylated ribose **11**.* The procedure is identical as Method 1, except the temperature of the reaction was fixed at −10 °C. From 500.0 mg of ribose, 1.14 g of compound **11** as a white solid (yield: 70%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.67). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.26 (d, *J*=4.3 Hz, 0.2H), 6.19 (m, 1H), 6.16 (d, *J*=5.6 Hz, 1H), 6.12–6.05 (m, 3H), 5.70–5.58 (m, 5H), 5.31–5.25 (m, 2H), 4.17–4.00 (m, 2H), 1.97–1.92 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 166.0–164.6, 135.6–135.0, 127.2–125.6, 91.4(β), 88.7(α), 67.3(β), 67.1, 67.1(β), 66.5(β), 65.7, 62.5(β), 17.9–17.6; IR: ν (cm^{-1}) 2960, 1724, 1637, 1434,

1318, 1292, 1115, 1079; HRMS: *m*/*z*: calcd for $C_{21}H_{26}O_9Li_1$: 429.1737 $[M+Li]^+$; found 429.1732; mp: 100–102 °C.

4.2.2. Synthesis of permethacrylated xylose ***5***. From 500.0 mg of xylose, 1.12 g of compound **5** as a colorless oil (yield: 70%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.68). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.40 (d, *J*=3.7 Hz, 1H), 636–6.04 (m, 5H), 5.75–5.56 (m, 6H), 5.25–5.16 (m, 2H), 4.11–4.06 (m, 1H), 3.78 (t, *J*=9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 165.6–164.5, 135.5–135.3; 126.7–126.3, 89.4, 69.5, 69.3, 68.5, 60.6, 17.6–17.3; IR: ν (cm^{-1}) 2926, 1726, 1637, 1454, 1319, 1290, 1146, 1120; HRMS: *m*/*z*: calcd for $C_{21}H_{26}O_9Li_1$: 429.1737 $[M+Li]^+$; found 429.1732.

4.3. General procedure for the permethacrylation of cellobiose and saccharose under microwave irradiation: Method 4

4.3.1. Synthesis of permethacrylated cellobiose ***20***. Cellobiose (2.0 g, 5.55 mmol, 1 equiv) was charged in a vial containing methacrylic anhydride (10 mL, 67.1 mmol, 12.1 equiv), and sodium acetate (600.0 mg, 7.31 mmol, 1.3 equiv) was added. The reaction mixture was stirred at 140 °C for 5 min in the presence of microwave. The crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.48) to give a white solid (1.7 g, yield: 35%). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.17–6.00 (m, 7H), 5.77 (d, *J*=7.8 Hz, 1H), 5.25 (m, 8H), 5.35 (t, *J*=9.2 Hz, 1H), 5.18 (m, 2H), 4.64 (m, 1H), 4.52 (m, 1H), 4.20 (m, 2H), 4.13 (m, 2H), 3.85 (m, 1H), 3.75 (m, 1H), 2.00–1.80 (7s, 21H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 18.4, 62.3, 62.9, 68.8, 70.7, 71.6, 72.4, 73.6, 75.5, 92.3, 100.6, 126.7–129.1, 135.1; IR: ν (cm^{-1}) 2978, 1735, 1638, 1454, 1319, 1294, 1153, 1080; API-ES. Pos: 909.3 $[M+Na]^+$; temperature of degradation: 266 °C.

4.3.2. Synthesis of permethacrylated saccharose ***22***. From 100.0 mg of saccharose, 87.0 mg of compound **22** as a colorless oil (yield: 34%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.51). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.25–5.97 (m, 8H), 5.76 (d, *J*=5.8 Hz, 1H), 5.71–5.49 (m, 11H), 5.32 (t, *J*=8.0 Hz, 1H), 5.07–5.03 (m, 1H), 4.44–4.23 (m, 8H), 2.03–1.81 (m, 26H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.7–166.3, 135.8–135.4, 127.7–126.2, 104.2, 90.3, 79.1, 76.7, 75.9, 70.7, 70.0, 68.9, 68.5, 64.5, 64.0, 62.1, 18.4–18.2; IR: ν (cm^{-1}) 2961, 1727, 1637, 1453, 1319, 1296, 1151, 1016.

4.4. General procedure for direct glycosidation reaction

4.4.1. Synthesis of compound ***12***. Compound **11** (1.14 g, 2.69 mmol, 1 equiv) was dissolved in dichloromethane (40 mL) and monoprotected dodecane diol (946.0 mg, 3.23 mmol, 1.2 equiv) was added. The reaction mixture was cooled down to 0 °C then $BF_3{\cdot}EtO_2$ (1 mL 8.07 mmol, 3 equiv) was slowly added. The reaction mixture was stirred 5 min at 0 °C then allowed to warm up to room temperature and stirred overnight. The reaction mixture was then cooled down to 0 °C and quenched with a saturated $NaHCO_3$ solution (1×10 mL), the organic phase extracted, the aqueous phase extracted with dichloromethane (1×10 mL). The organic layers combined were dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc=8/2, R_f=0.57) to give a colorless oil (778.4 mg, yield: 46%). ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.27 (m, 5H), 6.09 (m, 3H), 5.53–5.46 (m, 4H), 5.20 (m, 1H), 5.08 (m, 1H), 4.81 (d, *J*=3.6 Hz, 1H), 3.81 (m, 1H), 3.83–3.66 (m, 2H), 3.40 (m, 3H), 1.87–1.82 (m, 9H), 1.53 (m, 4H), 1.21 (m, 16H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 166.8, 166.6, 165.8, 138.8, 136.1, 136.0, 135.9, 128.4, 127.7, 127.5, 126.4, 126.2, 126.1, 98.5, 72.9, 68.9, 68.7, 67.3, 66.3, 61.1; IR: ν (cm^{-1}) 2926, 1737, 1637, 1456, 1320, 1294, 1152, 1078; HRMS: *m*/*z*: calcd for $C_{36}H_{52}O_9Li$: 635.3771 $[M+Li]^+$; found 635.3755.

4.4.2. Synthesis of compound ***16***. From 617.8 mg of compound **15**, 332.7 mg of compound **16** as yellow oil (yield: 54%) was recovered (SiO_2, cyclohexane/EtOAc=8/2, R_f=0.62). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.27 (m, 5H), 6.06 (m, 7H), 5.52 (m, 10H), 5.32 (t, *J*=7.5 Hz, 1H), 5.20 (m, 1H), 4.95 (m, 1H), 4.52 (m, 1H), 4.44 (s, 2H), 4.32 (m, 1H), 4.10 (m, 4H), 4.70 (m, 2H), 3.40 (m, 3H), 1.93–1.74 (m, 21H), 1.52 (m, 4H), 1.20–1.16 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 166.9–165.7, 135.8–135.2, 128.5, 127.7, 127.5–126.5, 100.6, 96.1, 95.5, 75.1, 73.0, 72.4, 71.0, 70.7, 70.2, 69.6, 69.0, 68.5, 67.9, 63.3, 62.1, 29.9–29.4, 26.3, 21.1, 20.9, 18.4–18.1; IR: ν (cm^{-1}) 2928, 2855, 1732, 1638, 1454, 1319, 1295, 1159, 1043, 1019; MM-ES: 1089 [M−27].

4.4.3. Synthesis of compound ***21***. From 510.0 mg of compound **20**, 255.0 mg of compound **21** as yellow oil (yield: 40%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.63). ^1H ($CDCl_3$, 300 MHz) δ (ppm): 7.32 (m, 5H), 6.08 (m, 7H), 5.58 (m, 7H), 5.36 (m, 2H), 5.15 (m, 2H), 5.02 (m, 1H), 4.63 (m, 1H), 4.53 (m, 3H), 4.13 (m, 4H), 3.91 (m, 1H), 3.76 (m, 3H), 3.44 (m, 3H), 1.99–1.80 (7s, 21H), 1.52 (m, 4H), 1.26–1.22 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 136.1–135.2, 128.5, 127.7, 127.2–126.2, 100.9, 100.6, 76.1, 73.0, 72.9, 72.6, 72.4, 71.9, 71.8, 70.7, 70.3, 68.9, 62.9, 62.4, 29.9–29.5, 25.9, 18.4; IR: ν (cm^{-1}) 2927, 2854, 1730, 1637, 1456, 1320, 1295, 1151, 1068.

4.4.4. Synthesis of compound ***24***. Peracetylated galactose derivate: from 1.0 g of peracetylated galactose, 802.4 mg of compound **24** as a colorless oil (yield: 46%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.35). ^1H ($CDCl_3$, 300 MHz) δ (ppm): 7.27 (m, 5H), 5.33 (m, 1H), 5.13 (m, 1H), 4.96 (m, 1H), 4.40 (s, 2H), 4.38 (d, *J*=8.0 Hz, 1H), 4.10 (m, 2H), 3.84 (m, 2H), 3.40 (m, 3H), 2.08–1.92 (3s, 12H), 1.53 (m, 4H), 1.20 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 170.4–170.2, 138.8, 128.4, 127.6, 127.5, 101.4, 72.9, 71.0, 70.6, 70.5, 70.3, 69.0, 67.1, 61.3; IR: ν (cm^{-1}) 2926, 2854, 1733, 1454, 1319, 1295, 1150; HRMS: *m*/*z*: calcd for $C_{33}H_{50}O_{11}Li$: 629.3513 $[M+Li]^+$; found 629.3505.

4.5. General procedure for the hydrolysis of the anomeric position

4.5.1. Hydrolysis of compound ***1***. Compound **1** (1.0 g, 1.90 mmol, 1 equiv) was dissolved in tetrahydrofuran (20 mL) and benzylamine (250 μL, 2.30 mmol, 1.2 equiv) was added. The reaction mixture was stirred at rt for 24 h, then evaporated. The crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc=8/2, R_f=0.51) to give a yellow solid as compound **3** (365.0 mg, yield: 42%). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.18 (s, 1H), 6.12 (s, 1H), 6.07 (s, 1H), 6.01 (s, 1H), 5.78 (t, *J*=10.3 Hz, 1H), 5.55 (m, 5H), 5.29 (t, *J*=10.3 Hz, 1H), 4.96 (m, 1H), 4.37 (m, 2H), 4.19 (m, 1H), 1.96 (s, 3H), 1.89 (s, 3H), 1.87 (s, 3H), 1.84 (s, 3H); ^{13}C DEPT 135 NMR ($CDCl_3$, 50 MHz) δ (ppm): 127.4–126.5, 90.4, 71.9, 70.0, 69.0, 67.7, 62.6, 18.3; IR: ν (cm^{-1}) 3450, 2960, 1730, 1636, 1456, 1320, 1294, 1155; MM-ES: 435.1 $[M-OH]^+$; mp: 56–58 °C.

4.5.2. Hydrolysis of compound ***8***. From 2.6 g of compound **8**, 813.7 mg of compound **9** as yellow solid (yield: 36%) was recovered (SiO_2, cyclohexane/EtOAc=8/2, R_f=0.55). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.23–6.01 (m, 4H), 5.68–5.34 (m, 8H), 4.43–4.22 (m, 3H), 3.34 (m, 1H), 1.98 (s, 6H), 1.89 (s, 3H), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.4, 166.4–166.2, 136.0–135.4, 126.9–126.3, 92.3, 70.8, 69.6, 68.5, 66.5, 62.6, 18.3–18.1; IR: ν (cm^{-1}) 3470, 2980, 1732, 1637, 1456, 1295, 1152; MM-ES: 435.1 $[M-OH]^+$; mp: 89–92 °C.

4.5.3. Hydrolysis of compound ***5***. From 361.8 mg of compound **5**, 115.5 mg of compound **6** as a white solid (yield: 36%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.46). ^1H NMR ($CDCl_3$, 200 MHz)

δ (ppm): 6.09 (s, 1H), 6.04 (s, 1H), 6.02 (s, 1H), 5.73 (t, *J*=8.0 Hz, 1H), 5.56–5.44 (m, 4H), 5.06–4.87 (m, 2H), 1.84 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 166.7–166.3, 135.5–135.3, 127.2–126.4, 96.0 (α furanose), 90.4 (α pyranose), 73.4 (furanose), 71.8, 69.7, 69.5, 62.8 (furanose), 58.4, 18.2; IR: ν (cm^{-1}) 3467, 2960, 1724, 1637, 1455, 1322, 1293, 1151, 1054; HRMS: *m*/*z*: calcd for $C_{17}H_{22}O_8Li$: 361.1475 $[M+Li]^+$; found 361.1459; mp: 116–118 °C.

4.5.4. Hydrolysis of compound ***17***. From 1.5 g of compound **17**, 790.0 mg of compound **18** as a white solid (yield: 54%) was recovered (SiO_2, cyclohexane/EtOAc=6/4, R_f=0.40). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 6.22–5.96 (m, 5H), 5.72–5.47 (m, 7H), 5.29–5.22 (m, 0.5H), 5.12–5.08 (m, 0.5H), 4.82–4.92 (m, 0.5H), 4.65–4.60 (m, 0.5H), 4.53–4.45 (m, 1H), 4.26–4.15 (m, 2H), 4.06–3.89 (m, 2H), 2.02–1.79 (m, 21H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 166.8–165.5, 136.0–135.1, 129.9–125.9, 100.7, 95.7 (α furanose), 90.3 (α pyranose), 75.8, 71.9, 71.6, 71.1, 69.9, 69.7, 68.5, 67.3, 62.2, 61.4, 18.4; IR: ν (cm^{-1}) 3435, 2960, 1727, 1637, 1455, 1321, 1294, 1155, 1076; HRMS: *m*/*z*: calcd for $C_{40}H_{50}O_{18}Li$: 825.3157 $[M+Li]^+$; found 825.3131; mp: 100–102 °C.

4.6. General procedure for the synthesis of the Schmidt reagent

4.6.1. Preparation of compound ***4***. Compound **3** (440.0 mg, 0.97 mmol, 1 equiv) was dissolved in dichloromethane (20 mL) and trichloroacetonitrile (290 μL, 2.92 mmol, 3 equiv), followed by DBU (15 μL, 0.10 mmol, 0.1 equiv) were added. The reaction mixture was stirred at rt for 2 h, then evaporated. The crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc=6/4, R_f=0.72) to give a white solid (426.0 mg, yield: 73%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.68 (s, 1H), 6.63 (d, *J*=4.0 Hz, 1H), 6.15–6.04 (m, 12H), 5.81 (t, *J*=10.8 Hz, 1H), 5.55 (m, 5H), 5.34 (t, *J*=10.3 Hz, 1H), 5.27 (m, 1H), 4.35 (m, 2H), 4.24 (m, 1H), 1.84 (s, 3H), 1.82 (s, 3H), 1.75 (s, 3H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 166.9–165.8, 160.7, 135.2–135.0, 127.5–126.4, 93.1, 90.8, 70.6, 70.2, 70.1, 68.2, 62.2, 18.3; IR: ν (cm^{-1}) 3318, 2959, 1724, 1637, 1453, 1317, 1292, 1137, 1020; MM-ES: 622.0 $[M+Na]^+$, 435.1 $[M-CNHCCl_3]$; mp: 105–107 °C.

4.6.2. Preparation of compound ***10***. From 1.4 g of compound **9**, 1.2 g of compound **10** as a yellow solid (yield: 66%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.67). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.81 (s, 1H), 6.38 (s, 1H), 6.24 (s, 1H), 6.16 (s, 1H), 6.09 (s, 1H), 6.01 (s, 1H), 5.73–5.54 (m, 7H), 4.40–4.25 (m, 3H), 1.99 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H), 1.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 166.9, 166.1–165.9, 160.0, 136.0–135.3, 127.4–126.2, 94.7, 90.7, 71.5, 69.5, 68.6, 65.7, 62.3, 18.3; IR: ν (cm^{-1}) 3315, 2960, 1729, 1638, 1459, 1322, 1295, 1114, 1044; mp: 82–86 °C.

4.6.3. Preparation of compound ***7***. From 306.2 mg of compound **6**, 334.4 mg of compound **7** as a yellow oil (yield: 87%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.59). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.66 (s, 1H), 6.57 (d, *J*=4.0 Hz, 1H), 6.16 (s, 2H), 6.11 (s, 1H), 5.82 (t, *J*=4.0 Hz, 1H), 5.63–5.55 (m, 4H), 5.28–5.17 (m, 2H), 4.17–4.09 (m, 1H), 3.89 (m, 1H), 1.89 (m, 11H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 166.1–165.9, 160.7, 135.3–135.0, 127.3–126.5, 93.3, 90.7, 70.1, 69.5, 68.9, 61.1, 18.1; IR: ν (cm^{-1}) 3310, 2959, 1730, 1637, 1460, 1321, 1296, 1115, 1046; HRMS: *m*/*z*: calcd for $C_{19}H_{22}Cl_3O_8NLi$: 506.0542 $[M+Li]^+$; found 506.0529.

4.6.4. Preparation of compound ***19***. From 461.8 mg of compound **18**, 299.6 mg of compound **19** as a yellow oil (yield: 55%) was recovered (SiO_2, cyclohexane/EtOAc=7/3, R_f=0.55). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.38–5.97 (m, 8H), 5.77–5.48 (m, 9H), 5.35–5.29 (m, 1H), 5.17–5.11 (m, 1H), 4.65–4.59 (m, 1H), 4.47–4.27 (m, 1H), 4.28–4.13 (m, 2H), 4.09–3.89 (m, 4H), 1.99–1.80 (m, 22H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 166.6–165.2, 135.9–135.1, 128.0–126.1, 101.0, 89.6, 75.5, 71.6, 71.1, 70.2, 69.9, 69.7, 67.2, 61.7, 61.3; IR: ν (cm^{-1}) 3314, 2960, 1731, 1639, 1459, 1322, 1295, 1116, 1047.

4.7. General procedure for the hydrolysis of the acetate groups

Compound **24** was dissolved in MeOH (10 mL) and NaOMe (35.0 mg, 0.64 mmol, 0.5 equiv) was added. The reaction mixture was stirred at rt for 1 h then quenched with Dowex and filtered off on Celite to give compound **25** as a white solid (446.7 mg, yield: 77%). ^{1}H NMR (MeOD, 300 MHz) δ (ppm): 7.27 (m, 5H), 4.43 (m, 2H), 4.13 (d, *J*=7.9 Hz, 1H), 3.85–3.68 (m, 5H), 3.30–3.26 (m, 2H), 1.55 (m, 4H), 1.24 (m, 16H); ^{13}C NMR (MeOD, 75 MHz) δ (ppm): 129.3, 128.8, 128.6, 105.0, 76.5, 75.0, 73.8, 72.6, 71.4, 70.8, 62.4, 30.8–30.5, 27.2; IR: ν (cm^{-1}) 3384, 2927, 1597, 1454; HRMS: *m*/*z*: calcd for $C_{25}H_{42}O_7Li$: 4601.3091 $[M+Li]^+$; found 461.3086; mp: 68–70 °C.

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Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.08.083.

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